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Journal Name

ARTICLE

Monomeric and dimeric Al(III) Complexes for the production of polylactide

Sarah M. Kirk[a,b], Helena C. Quilter[a,b], Antoine Buchard,[b] Lynne H. Thomas[b], Gabriele Kociok-Kohn[b] and Matthew D. Jones[b,*]

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A series of monometallic and bimetallic Al(III) complexes with substituted naphthyl based Schiff base ligands have been prepared and characterised. When 1-aminonaphthalene based ligands were reacted with $AlMe_3$ monometallic complexes were isolated, however, with 1,5 and 1,8- diaminonaphthalene based ligands bimetallic complexes were formed. In all cases 4-coordinate tetrahedral Al(III) centres were observed in the solid state and in solution. There was little difference in rate of polymerisation of *rac*-lactide between the monometallic and bimetallic complexes based on 1,5-diaminonaphthalene. However, for the 1,8-diaminonaphthalene the complex was an order of magnitude faster than the monometallic and the analogous 1,5-system. Moreover, this complex was active at room temperature, which is rare for aluminium initiators, and PLA with a high degree (P_m = 0.82) of isotacticity was observed.

Introduction

Polylactide has been extensively researched in recent years. This is due to the fact that it is biodegradable, renewable and biocompatible.[1] It has found many uses from high value biomedical applications (sutures and drug delivery vesicles) to commodity packaging materials. Polylactide (PLA) is prepared *via* ring opening polymerisation of the cyclic ester lactide (LA), the monomer is available in various stereoforms – meso, racemic or chirally pure.[2] When *rac*-lactide (*rac*-LA) is polymerised either atactic, heterotactic or isotactic PLA can be prepared.[3] The physical properties (melting temperature, *Tg*, rate of degradation) are intrinsically linked to the polymers microstructure.[3] In the literature there are complexes based on group 4,[4] zinc[5], indium[6], aluminium[7], rare earth metals[8] and groups 1-3[5a, 9] that are capable of imparting selectivity during the polymerisation. It is fair to say that aluminium initiators are amongst some of the successful in the literature, since the early work of Spassky[7e], Chisholm[7a], Feijen[7g, 7h], Coates and Gibson[7c, 10] there have been a multitude of aluminium complexes with salan, salen and salalen ancillary ligands reported.[7] Moreover it is also fair to say that there is still a significant degree of serendipity in choice of ligand-metal in terms of rate of polymerisation and stereocontrol observed in the resultant PLA. Currently, there has been interest in the preparation of multimetallic catalysts, with the hope there will be beneficial cooperativity between the metal centres and enhancement in the catalytic properties. There are only a limited number of dinuclear complexes for the polymerisation of cyclic esters.[6c, 11] For example, Carpentier has shown that for dinuclear aluminium systems based on biphenyl ligands the rate of polymerisation is almost an order of magnitude faster than the monometallic complex.[12] This is believed to be due to the fact that in these examples the aluminium centres can potentially be close enough to cooperate (within 3.0 Å) and this potentially may facilitate a dual activation mechanisms. Further evidence for the existence of cooperation between aluminium centres has be demonstrated by Yao and co-workers.[13] They prepared a series of Al-alkyl complexes of piperazidine ligands and observed a 2 – 8 times rate enhancement in polymerisation activity. Redshaw suggests that cooperative effects are present in aluminium complexes as long as they are not linked in an aluminoxane [Al-O-Al] and they suggest a favourable Al-Al distance of around 6 Å for ε-caprolactone polymerisation.[14] Chen has pioneered the use of bimetallic Al(III) complexes for the ROP of lactide and ε-caprolactone.[15] Importantly they have shown that it is possible to induce stereoselectivity with such complexes.[15a] Very recently Mazzeo has highlighted the importance of cooperativity in the polymerisation of *rac*-LA initiated with Al(III) salen complexes with Al…Al distance the key parameter. They propose that this is due to synergic interactions during the alcoholysis and polymer growth steps.[16] In this paper we have prepared a series of dinuclear Al(III) complexes based on naphthyl derived ligands (varying the substitution) and compared these to mononuclear complexes in terms of their ability to control the polymerisation and kinetics.

Experimental

General Considerations

[a] *Doctoral Training Centre in Sustainable Chemical Technologies, University of Bath, Bath BA2 7AY, UK*

[b] *Department of Chemistry, University of Bath, Bath BA2 7AY, UK. E-mail mj205@bath.ac.uk*

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The preparation and characterisation of all metal complexes was carried out under inert argon atmosphere using standard Schlenk or glovebox techniques. All chemicals used were purchased from Aldrich and used as received except for *rac*-LA which was recrystallised from dry toluene and doubly sublimed prior to use. Caprolactone was dried by distilling over CaH_2. Dry solvents used in handling metal complexes were obtained *via* SPS (solvent purification system). ^{1}H and ^{13}C{^{1}H} NMR spectra were recorded on a Bruker 400 or 500 MHz instrument and referenced to residual solvent peaks. $CDCl_3$/C_6D_6 were dried over CaH_2 prior to use with metal complexes. Coupling constants are given in Hertz. CHN microanalysis was performed by Mr. Stephen Boyer of London Metropolitan University or Elemental microanalysis, Oakhampton UK.

Synthesis of ligands

In a typical experiment **1**H_2 was prepared by addition of salicylaldehyde (4.263 g, 34.9 mmol) to 1-aminonaphthalene (5 g, 34.9 mmol) dissolved in methanol (30 ml). After stirring for 1 hour, the precipitate was filtered, washed with cold methanol (3 × 10 ml) and dried to yield an orange solid (3.42 g, 13.8 mmol, 40 %). **1**H_2 ^{1}H NMR ($CDCl_3$): 7.01 (1H, td, J = 7.5, 1.0 Hz, CH), 7.14 (1H, dd, J = 8.8, 0.5 Hz, CH), 7.20 (1H, dd, J = 7.3, 1.0 Hz, CH), 7.42 - 7.49 (2H, m, CH), 7.52 (1H, dd, J = 8.3, 7.3 Hz, CH), 7.58 (2H, dt, J = 9.5, 3.3 Hz, CH), 7.81 (1H, d, J = 8.3 Hz, CH), 7.91 (1H, dt, J = 9.5, 3.5 Hz, CH), 8.25 - 8.35 (1H, m, CH), 8.71 (1H, s, N-CH) 13.44 (br. s., 1H, OH). ^{13}C{^{1}H} NMR ($CDCl_3$): 114.0 (Ar-H), 117.3 (Ar-H), 119.2 (Ar-H), 119.5 (Ar), 123.2 (Ar-H), 125.9 (Ar-H), 126.5 (Ar-H), 126.7 (Ar-H), 126.9 (Ar-H), 127.9 (Ar-H), 128.2 (Ar), 132.4 (Ar-H), 133.4 (Ar-H), 133.9 (Ar), 146.2 (Ar-N), 161.2 (Ar-OH), 163.6 (CH=N). m/z $[C_{17}H_{13}NO + H]^+$ Calc: 248.1031 gmol^{-1} Found: 248.1063 gmol^{-1}.

7H_2 A solution of 1,8-diaminonapthalene (1.08 g, 6.85 mmol), 3,5-di-tert-butyl-2-hydroxybenzaldehyde (3.85 g, 2.4 eq.) and formic acid (5 drops) in EtOH was heated to reflux for 48 h. On cooling to RT a yellow precipitate formed which was isolated by vacuum filtration and washed with cold EtOH. The product was taken up in $CHCl_3$, dried over $MgSO_4$ to remove traces of H_2O and dried *in vacuo* to yield **7**H_2 as a deep yellow powder (0.96 g, 1.62 mmol, 24%). ^{1}H NMR ($CDCl_3$): 1.01 ppm (18H, s, $C(CH_3)_3$), 1.32 (18H, s, $C(CH_3)_3$), 6.98 (2H, dd, *J* = 7.3, 1.0 Hz, Ar), 7.29 (4H, s, Ar), 7.51 (2H, dd, *J* = 8.2, 7.3 Hz, Ar), 7.77 (2H, dd, *J* = 8.3, 1.0 Hz, Ar), 8.66 (2H, s, N=CH), 13.25 (2H, s, OH). m/z calculated for $[C_{40}H_{50}N_2O_2 + H]^+$: 591.9651, found 591.3950. ^{13}C{^{1}H} NMR ($CDCl_3$): 29.1 ppm ($C(\mathbf{C}H_3)_3$, .31.5 ($C(\mathbf{C}H_3)_3$), 34.1 147.0, ($\mathbf{C}(CH_3)_3$), 34.7 ($\mathbf{C}(CH_3)_3$), 117.2 (Ar), 119.0, 126.5, 126.7, 126.8, 127.9, 136.4, 140.1, 158.6 (Ar-OH), 161.7 (CH=N).

Synthesis of Complexes

In a typical experiment Al(**1**)Me_2 was prepared by the slow addition of trimethylaluminium solution (4.0 ml, 2M in hexane, 8.0 mmol) to a solution of **1**H_2 (2 g, 8.09 mmol) in hexane (50 ml). The solution was left to stand at room temperature overnight to yield a crop of yellow crystals. The resulting crystals were filtered and dried under vacuum to yield a yellow solid (1.20 g, 3.94 mmol, 49%). Al(**1**)Me_2 ^{1}H NMR (400 MHz, C_6D_6) δ ppm -0.33 (6H, br. s., Al-$(CH_3)_2$), 6.48 - 6.53 (1H, m, Ar-H), 6.66 (1H, dd, J = 7.9, 1.9 Hz, Ar-H), 7.01 (1H, dd, *J*=6.00, 1.00 Hz, Ar-H), 7.05 - 7.10 (1H, m, Ar-H), 7.12 - 7.22 (2H, m, Ar-H), 7.43 (1H, s, CH=N), 7.46 (1H, d, J = 8.3 Hz, Ar-H), 7.52 - 7.56 (1H, m, Ar-H), 7.58 (2H, d, J = 8.5 Hz, Ar-H), 7.64 (1H, dd, J = 8.3, 1.3 Hz, Ar-H). ^{13}C{^{1}H} NMR (d_8-Tol): - 9.1 (Al-$(CH_3)_2$), 117.5 (Ar-H), 119.1 (Ar), 120.7 (Ar-H), 122.6 (Ar-H), 123.1 (Ar-H), 125.3 (Ar-H), 127.0 (Ar-H), 127.2 (Ar-H), 128.1 (Ar-H), 128.6 (Ar-H), 134.8 (Ar-H), 135.6 (Ar-H), 138.3 (Ar), 143.1 (Ar), 165.0 (Ar-N), 166.1 (Ar-O), 173.7 (CH=N). Calc: C 75.23% H 5.98% N 4.62% Found: C 75.36% H 5.88% N 4.80%.

Al_2(**4**)Me_4 Yield: 0.33 g, 0.69 mmol (46 %) ^{1}H NMR (C_6D_6): - 0.39 (6H, br s, Al$(CH_3)_2$), - 0.27 (6H, br s, Al$(CH_3)_2$), 6.53 (2H, m, Ar-H), 6.73 (2H, d, J = 7.2 Hz, Ar-H), 6.96 (2H, dd, J = 6.0 Hz, 1 Hz, Ar-H), 7.01 - 7.10 (4H, m, Ar-H), 7.11 - 7.18 (2H, m, Ar-H), 7.26 (2H, br. s., Ar-H), 7.57 (1H, s, N=CH), 7.60 (1H, s, N=CH). ^{13}C{^{1}H} NMR (C_6D_6): - 8.7 (Al$(CH_3)_2$), 118.2 (Ar-H), 119.5 (Ar), 122.3 (Ar-H), 123.1 (Ar-H), 123.6 (Ar-H), 127.0 (Ar-H), 128.2 (Ar-H) 128.3 (Ar-H), 128.5 (Ar-H), 128.6 (Ar-H), 129.6 (Ar-H), 136.1 (Ar), 139.2 (Ar), 143.8 (Ar-N), 166.5 (Ar-O), 174.3 (N=CH). Calc: C 70.28% H 5.90% N 5.85% Found: C 70.14% H 5.78% N 5.69%.

Al_2(**7**)Me_4 In this case 0.5 g of ligand was utilised. Yield: 0.27 g, 0.38 mmol (45%) ^{1}H NMR (C_6D_6): - 0.34 ppm (s, 6 H, Al-CH_3), - 0.29 (6H, s, Al-CH_3), 1.31 (18H, br. s., $C(CCH_3)_3$), 1.32 (18H, s, $C(CCH_3)_3$), 6.92 (2H, d, *J* = 2.6 Hz, Ar-H), 7.03 - 7.11 (2H, m, Ar-H), 7.44 (2H, s, CH=N), 7.49 (2H, d, *J* = 8.0 Hz, Ar-H), 7.57 (2H, d, *J* = 2.0 Hz, Ar-H), 7.74 (2H, d, *J* = 7.5 Hz, Ar-H). ^{13}C{^{1}H} NMR (C_6D_6): - 9.2 ppm (Al-CH_3), - 6.9 (Al-CH_3), 30.2 ($C(CH_3)_3$), 31.9 ($C(CH_3)_3$), 34.7 ($C(CH_3)_3$), 35.6 ($C(CH_3)_3$), 119.7, 124.9, 126.0, 126.5, 128.9, 129.7, 131.2, 134.5, 139.5, 140.8, 142.0, 163.6(Ar-O), 175.4 (CH=N). Calc: C 75.18% H 8.60% N 3.99% Found: C 74.78% H 8.49% N 3.65%.

Crystallography

All data were collected on a SuperNova, EOS detector diffractometer using radiation CuKα (*λ*= 1.54184 Å) or Mo-Kα (*λ*= 0.71073 Å) or a Nonius kappa diffractometer using Mo-Kα (λ= 0.71073 Å) all recorded at 150(2) K. All structures were solved by direct methods and refined on all F^2 data using the SHELXL-2014 suite of programs. All hydrogen atoms were included in idealized positions and refined using the riding model, all refinement details are given in the .cif file. Data was straightforward except the following: For Al(**3**)Me_2 it was necessary to account for twinning in the crystal by a 2-fold rotation about the reciprocal c axis ca. 44%; Al_2(**4**)Me_4 contains half a molecule of toluene in the asymmetric unit; Al_2(**5**)Me_4 contains a molecule of toluene in the asymmetric unit; Al_2(**7**)Me_4 contains a molecule of toluene in the asymmetric unit and is twinned about the 1 -1 0 lattice direction at ca. 43%.

Ring-opening polymerisation (ROP) studies

For polymerisations the required monomer:Initiator:BnOH ratio was dissolved in toluene at 80 °C (10 ml), in all cases 1.0 g of *rac*-LA were used. For co-polymerisations ε-caprolactone and *rac*-LA were added together in toluene at the appropriate ratio. After the reaction time the vessel was opened to air and methanol (1-2 drops) was added to quench the reaction and the resulting solid was dissolved in dichloromethane. The solvents were removed in vacuo and washed with copious amount of methanol to remove unreacted monomer. ^{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

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produced; P_m (the probability of isotactic linkages) were determined by analysis of the methine region of the homonuclear decoupled ^{1}H NMR spectra.[5a] GPC were recorded on a polymer labs GPC-50 instrument and referenced to polystyrene standards. Kinetic studies were carried out using a stock solution of initiator (3.47×10^{-5} mol Initiator and 3.47×10^{-5} mol BnOH) were dissolved in 1.0 ml d_8 toluene. For 100:1:1: to a solution of lactide (50 mg, 3.47×10^{-4} mol in 0.5 ml d_8 toluene) in a Young's NMR tube, stock solution (0.1 ml) was added and heated to 353 K inside a Bruker 400 MHz NMR instrument. For experiments which deviated from 100:1:1 appropriate stock solutions were prepared in all cases the overall volume of solvent was 0.6 ml. ^{1}H NMR spectra were taken at regular intervals. The k_{app} was determined using a pseudo-first order rate kinetic plot. Some graphs have a y-intercept due to time between first sample acquired and sample preparation coupled with temperature equilibration in the NMR spectrometer.

Results and Discussion

The ligands were prepared in methanol/ethanol as shown in Figure 1 by the simple addition on the amine and substituted salicylaldehyde derivate. Typically the product precipitated from the solution and was isolated by vacuum filtration. Ligand **7**H_2 required the addition of a small amount of formic acid as a catalyst to facilitate its preparation.[17] The ligands were characterised *via* ^{1}H, ^{13}C{^{1}H} and HR-ESI mass spectrometry and used without further purification. Ligand **6**H_2 was insoluble in common organic solvents and precluded the acquisition of meaningful analytical data, although the purity was confirmed by elemental analysis. These ligands all have a naphthyl backbone with either mono imino, 1,5- or 1,8- di-imino functionality. The Al(III) complexes were prepared by reacting 1eq of $AlMe_3$ with ligands **1**H_2-**3**H_2, however for **4**H_2-**7**H_2 2eq. of $AlMe_3$ were used. Complexes Al(**1/3**)Me_2 and Al_2(**4/5/7**)Me_4 were further characterised in the solid state by X-ray crystallography, Figure 2 for Al(**1**)Me_2 and Al_2(**4/7**)Me_4. Surprisingly, for **7**H_2 a bimetallic complex was isolated regardless of the stoichiometry of the reaction. In all cases the aluminium centres are in a tetrahedral environment and coordinated to the phenolate, imine and two alkyl moieties. The metric data for all complexes are in agreement with literature precedent of tetrahedral aluminium Schiff base complexes.[18] A noteworthy observation of Al_2(**7**)Me_4 is if we look down the plane formed by the aromatic naphthyl rings then the aluminium centres orient themselves on opposite sides of this plane, this gives an Al(1)-Al(2) distance of ca. 5.4 Å. This is presumably necessary to minimise steric clashes between the tBu groups. For Al_2(**4**)Me_4 the corresponding Al…Al distance is 9.0 Å. If there were free rotation around the $N_{imine}C$-C_{naphth} sp^3 hybridised bond then these distance reduce to ca. 3.5 Å for Al_2(**7**)Me_4 and 7.0 Å Al_2(**4**)Me_4 respectively. However, for Al_2(**7**)Me_4 DFT analysis indicates that it is unlikely that the Al…Al will ever get this short, with a minimum accessible distance of 4 Å under the polymerisation conditions, still significantly shorter that Al_2(**4**)Me_4. This allows for a comparison between the Al…Al distance and any potential cooperativity between metal centres to be investigated. The 1,5-substituted system is compared to the monometallic complexes and the 1,8-substituted system. Given the simplicity of the ligands it is surprising how few crystallographically characterised examples exist with these ligand motifs in the literature. It is apparent from analysis of the ^{1}H NMR spectra for the complexes that the solid state structures are maintained in solution, with discrete resonances observed for the imine and Al-Me moieties.

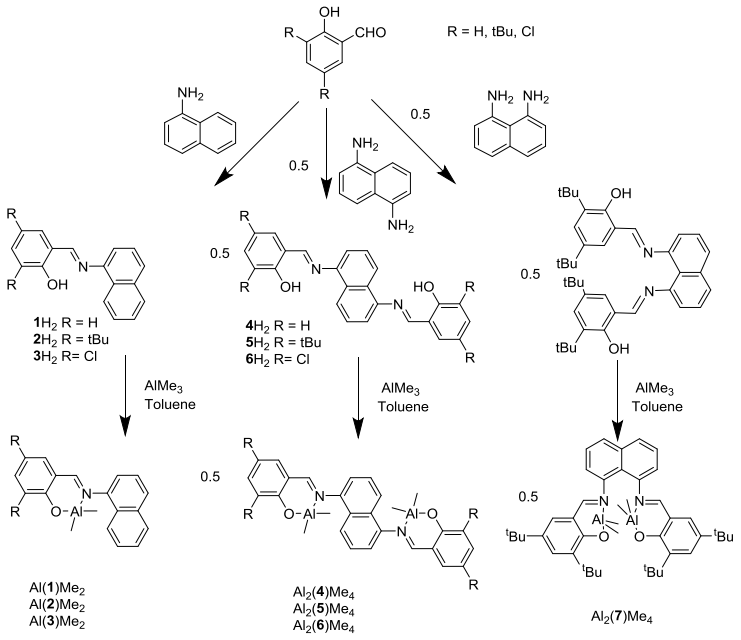

Figure 1: Preparation of the ligands and complexes used in this study.

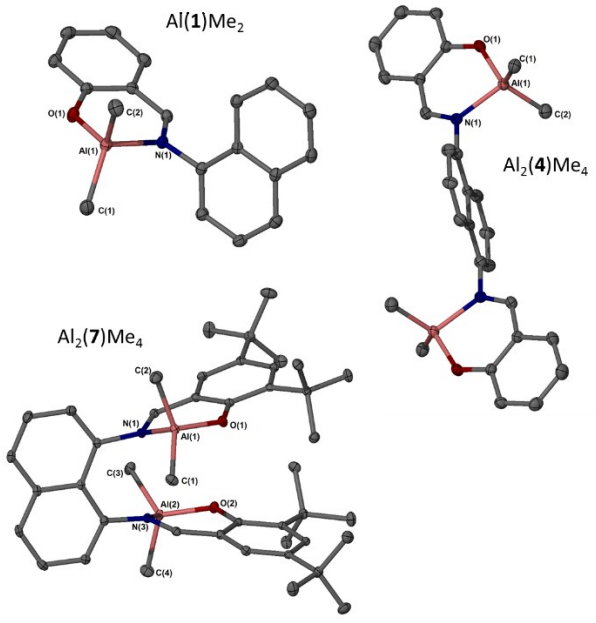

Figure 2: Solid state structure of Al(**1**)Me_2, Al_2(**4**)Me_4 and Al_2(**7**)Me_4 ellipsoids are shown at the 30% probability level. All hydrogen atoms have been removed for clarity.

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Al(**1**)Me_2 was able to polymerise *rac*-LA in solution with the addition of BnOH co-initiator. MALDI-ToF analysis of the resulting polymer indicated that the BnO- and H- endgroups were present, which is expected from the coordination insertion mechanism. The repeat unit was 72 g/mol implying a degree of intermolecular transesterification. For Al(**1**)Me_2 there was excellent control of the molecular weight on varying the addition of benzyl alcohol, indicative of a highly controlled system. The kinetics for Al(**1**)Me_2 was studied at a fixed concentration of *rac*-LA of 0.58 moldm^{-3} (Table 1 entries 1-3 and 5 and Figure 3), as expected as the concentration of catalyst and initiator reduce the apparent first order rate constant reduces. In all cases, as indicated by analysis of the ^{1}H homonuclear decoupled NMR spectrum, atactic PLA was formed. Regardless of the ortho substituents screened atactic PLA was produced. Complex Al(**2**)Me_2 was slower than Al(**1**)Me_2, which is presumably related to the increased steric hindrance around the metal centre (entry 2 vs 8). Utilising the 1,5-diaminonaphthyl bridged complexes Al_2(**4-6**)Me_4 the molecular weight was also controlled by the addition of BnOH and atactic PLA was again observed (entries 10-20). The importance of the addition of BnOH can be seen by comparison of entries 16-18 with 13-15, with unpredictable molecular weight and low conversions achieved without the addition of BnOH.

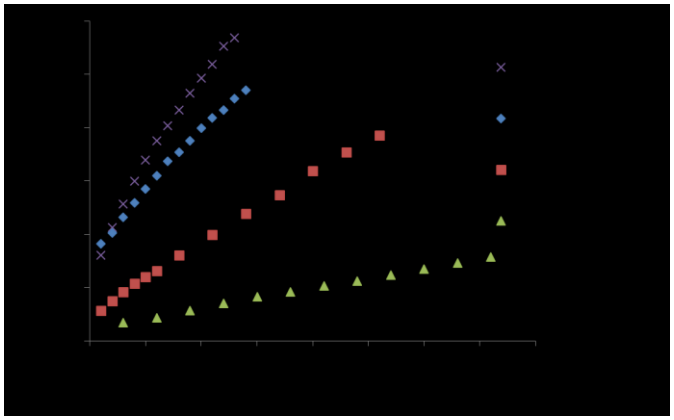

Figure 3: Kinetic plots at various [LA]:[Init]:[BnOH] ratios all at 80 °C, init = Al(**1**)Me_2. Equations of lines of best-fit (50:1:1) y = 0.0067x + 0.31 (R^2 = 0.986); (100:1:1) y = 0.0041x + 0.36 (R^2 = 0.9867); (200:1:1) y = 0.0026x + 0.104 (R^2 = 0.999); (400:1:1) y = 0.00075x + 0.04 (R^2 = 0.998).

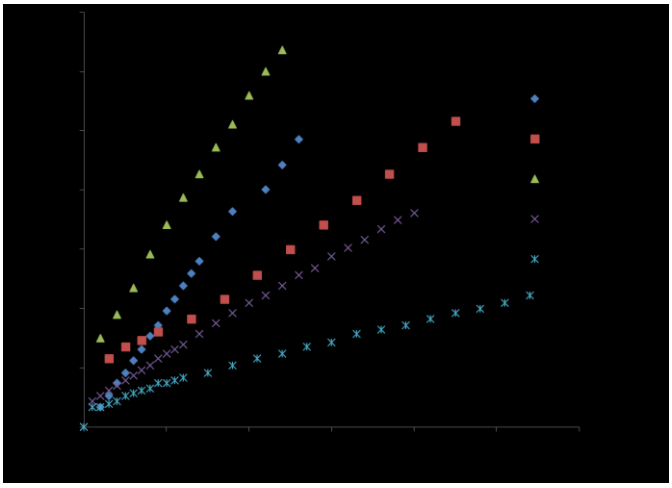

Figure 4: Kinetic plots at various [LA]:[Init]:[BnOH] ratios all at 80 °C, init = Al_2(**4**)Me_4. Equations of lines of best-fit (100:1:2) y = 0.0076x + 0.059 (R^2 = 0.994); (200:1:2) y = 0.0038x + 0.144 (R^2 = 0.991); (100:1:1) y = 0.0090x + 0.210 (R^2 = 0.998); (200:1:1) y = 0.0034x + 0.07 (R^2 = 0.994); (200:1:1) y = 0.0014x + 0.06 (R^2 = 0.983).

The rates of polymerisation of *rac*-LA were similar for complexes Al(**1**)Me_2 and Al_2(**4**)Me_4, with little difference in the apparent rate constant for the polymerisation. For example, comparing the 50:1:1 (entry 1) with 100:1:2 (entry 10) {in this scenario there is the same concentration of Al-OBn initiating species} rate constants of 6.7 $\times$ 10^{-3} mins^{-1} vs. 8.3 $\times$ 10^{-3} mins^{-1} were achieved. This is further exemplified if 100:1:1 (entry 2) for Al(**1**)Me_2 is compared to 200:1:2 (entry 11) for Al_2(**4**)Me_4. Therefore, it is evident that there is no cooperative effect comparing the monometallic to the bimetallic derived from the 1,5-naphthlene system, with the long Al…Al distance. The order of reaction with respect to catalyst has been studied for Al(**1**)Me_2 and Al_2(**4**)Me_4 (see ESI figures 18-20) the polymerisation was observed to be first order with respect to catalyst. For the 1,8-naphthlene system only ligand **7**H_2 could be prepared in pure form for complexation. When reacted with $AlMe_3$ the bimetallic complex was formed in high yield. Interestingly, this is in contrast to work of Gibson and co-workers[10] who report the preparation of a monometallic complex under analogous conditions, with this complex having a slight isotactic bias (P_m = 0.72). In our hands the bimetallic complex produced PLA with a higher isotactic enchainment with $P_m \approx$ 0.8 (entries 21 and 22). Al_2(**7**)Me_4 is significantly more active than the complexes based on 1,5-naphthlene backbone (entry 19 vs 21) and this complex is active at room temperature (entry 22) which is relatively unusual for aluminium complexes. Analysis of the microstructure of the PLA 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 to the PLA.[19] It is also interesting to note that L-AlMe_2 systems rarely afford PLA with any significant degree of tacticity.[4f, 12, 18, 20] When the order with respect to Al_2(**7**)Me_4 was investigated at 100(200 or 400):1:2 (at constant [LA]) the order was observed to be less than 1 with respect to initiator. Such non-integer orders are rare but not uncommon.[21] Moreover, to our surprise the rate was slower with 50:1:2 (ca. 12 $\times$ 10^{-3} min^{-}

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[1] at the same concentration of monomer). This illustrates a clear difference between the two sets of bimetallic complexes.

Complexes Al_2(**4**/**7**)Me_4 were also trialled for the ROP of ε-caprolactone with a Monomer:Init:BnOH ratio of 100:1:2 at 80 °C in toluene 20 mins was sufficient to achieve high conversion {Al_2(**4**)Me_4 99%, M_n = 8,800, PDI = 1.25 Al_2(**7**)Me_4 99%, M_n = 11,000, PDI = 1.64). Al_2(**4**)Me_4 was also active at 40 °C ($C_6D_5CD_3$)}One at the same ratio the apparent-first order rate constant was 0.025 min^{-1}, an order of magnitude faster than the for the ROP of *rac*-LA. Due to the efficiency of Al_2(**4**)Me_4 for the ROP of both monomers attempts were made to copolymerise *rac*-LA with ε-caprolactone, Table 2.

TABLE 2 HERE (DOUBLE COLUMN)
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From ^{1}H NMR analysis it is evident that when LA and CL are co-polymerised Al_2(**4**)Me_4 has preference for LA over CL, even though the homopolymerisation is significantly faster for CL than LA. One possible explanation might be that the rate of insertion of a CL unit into a growing LA-chain is slower than a LA into a growing CL-chain and the rate of initiation is faster for LA than CL, which may be related to the fact that LA has two coordinating ester groups whereas CL only has one. To investigate this further the co-polymerisation (50:50 and 75:25 CL:LA) has been monitored via NMR spectroscopy, see ESI figures SI16 and SI17, using Al_2(**4**)Me_4 at 100:1:2 (monomer:catalyst:BnOH). In both cases LA was polymerised faster than CL, even at the higher CL ratio, indicating a preference for LA over CL when both are present. For the 50:50 isolated copolymers it is evident from analysis of the ^{1}H NMR spectra there is a high level of hetero-binding in the polymers, indicating that they are not mixtures of homopolymers or block copolymers. It has been shown that it is possible to probe the microstructure of copolymers and to determine the average block length of each monomer by NMR spectroscopic methods.[22] If a 50:50 ratio of each monomer was utilised then the average block length for each unit is ca. 2-3. This is indicative of random copolymers being produced, as an average block length of 2 is indicative of random copolymers.[22-23] An explanation for this could be related to high levels of transesterification randomising monomers with the polymer. This is further exemplified by 90:10 LA:CL copolymerisation, which has a low level of CL-CL linkages. The same is seen for LA-LA linkages when the ratio is reversed.

Conclusions

In conclusion a series of Al(III) complexes have been prepared and fully characterised. A comparison between mononuclear and dinuclear complexes has shown that when the 1,8-naphthlene system was utilised isotactic PLA was achieved and dramatic enhancement in the rate of polymerisation of *rac*-LA was achieved. This is potentially related to the beneficial cooperativity between the two metal centres, which are significantly closer in this case. Work in on going (computational, further ligand variation) to probe the exact reason for this enhancement and the kinetic behaviour of Al_2(**7**)Me_4. Further, Al_2(**4**)Me_4 was utilised for the production of PLA-PCL copolymers with random co-polymers being produced as a consequence of intermolecular transesterification.

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Notes and references

‡ Crystallographic data for compounds have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication 1491894-1491898. Representative NMR spectra, GPCs and homonuclear decoupled NMR spectra are given in the ESI.

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Table 1 Polymerisation data using complexes derived from ligands **1-7**H_2.

Entry	Initiator	[LA]:[I]:BnOH	Time/h	Con./%[a]	M_n[b]	PDI[b]	P_m[b]	k_{app} ($\times 10^{-3}$) $mins^{-1}$ [c]
1	Al(**1**)Me_2	50:1:1	3	94	9600	1.26	0.50	6.7
2	Al(**1**)Me_2	100:1:1	6	97	18650	1.19	0.50	4.1
3	Al(**1**)Me_2	200:1:1	22	96	37350	1.61	0.52	2.6
4	Al(**1**)Me_2	300:1:1	24	79	40500	1.21	0.50	-
5	Al(**1**)Me_2	400:1:1	48	97	90950	1.44	0.50	0.7
6	Al(**1**)Me_2	200:1:2	20	95	23650	1.37	0.52	-
7	Al(**1**)Me_2	200:1:4	20	95	12350	1.33	0.52	-
8	Al(**2**)Me_2	100:1:1	24	92	16800	1.48	0.56	0.6
9	Al(**3**)Me_2	100:1:1	24	98	18700	1.94	0.55	-
10	Al_2(**4**)Me_4	100:1:2	2	97	6450	1.1	0.50	8.3
11	Al_2(**4**)Me_4	200:1:2	24	98	11700	1.07	0.50	3.8
12	Al_2(**4**)Me_4	400:1:2	24	25	5100	1.05	-	-
13	Al_2(**4**)Me_4	100:1:1	2	57	9100	1.08	0.53	9.0
14	Al_2(**4**)Me_4	200:1:1	6	79	34350	1.15	0.49	3.3
15	Al_2(**4**)Me_4	400:1:1	22	93	94750	1.45	0.49	1.4
16	Al_2(**4**)Me_4	100:1:0	24	32	27600	1.20	0.53	-
17	Al_2(**4**)Me_4	200:1:0	24	29	57100	1.12	0.51	-
18	Al_2(**4**)Me_4	400:1:0	24	21	39650	1.16	0.53	-
19	Al_2(**5**)Me_4	100:1:2	18	91	6550	1.2	0.50	1.0
20	Al_2(**6**)Me_4	100:1:2	18	98	6500	1.25	0.50	-
21	Al_2(**7**)Me_4	100:1:2	2	99	5250	1.16	0.75	33
22	Al_2(**7**)Me_4[e]	100:1:2	24	86	7000	1.01	0.82	-

All polymerisations have been conducted in toluene at 80 °C. [a] Determined from analysis of the ^{1}H NMR spectrum. [b] As determined by GPC (THF), using polystyrene standards. [c] As determined from $^1H\{^1H\}$ NMR. [d] first order rate constant. [e] Polymerisation performed at 25 °C. It is possible to apply a correction factor of 0.58 for the M_n values due to the use of polystyrene references. The calculated molecular weight can be determined by the following equation: $(144 \times LA_{eq})/BnOH_{eq} + 108$.

Table 2: Co-polymerisation data using Al_2(**4**)Me_2.

M:I:BnOH	LA:CL	Time	Con.% LA[a]	Con.% CL[a]	M_n[b]	Ratio in Polymer[a]	PDI[b]	Ratio of linkages in co-polymer[a]			
						[PLA]:PCL]		LA-LA	CL-CL	LA-CL	CL-LA
100:1:1	50:50	2	100	85	19450	0.52:0.48	1.37	0.29	0.21	0.25	0.25
100:1:2	50:50	2	96	60	7200	0.58:0.42	1.11	0.40	0.21	0.25	0.22
100:1:2	50:50	3	100	69	8800	0.60:0.40	1.13	0.41	0.21	0.25	0.13
100:1:2	50:50	4	100	75	9200	0.57:0.43	1.11	0.38	0.21	0.25	0.16
200:1:2	100:100	5	90	49	16150	0.62:0.38	1.19	0.37	0.13	0.26	0.23
400:1:2	200:200	24	100	89	23500	0.52:0.48	2.21	0.30	0.23	0.23	0.24
800:1:2	400:400	24	100	77	55200	0.53:0.47	1.79	0.31	0.24	0.23	0.22
100:1:2	75:25	2	87	46	6850	0.82:0.18	1.10	0.65	0.02	0.21	0.12
100:1:2	25:75	2	100	88	8200	0.38:0.62	1.16	0.12	0.37	0.25	0.26
100:1:2	90:10	4	99	68	8950	0.92:0.08	1.26	0.86	0.01	0.06	0.06
100:1:2	10:90	4	100	98	9500	0.11:0.89	1.67	0	0.76	0.12	0.12

All polymerisations have been conducted in toluene at 80 °C for the given time. [a] Determined from analysis of the ^{1}H NMR spectrum. [b] As determined by GPC (THF), using polystyrene standards.

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