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SUPPORTING INFORMATION

Novel Hybrid Aluminium(III)-Complexes as Highly Active Initiators for Lactide Polymerisation: Towards Industrial Relevance

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Contents

1. General experimental methods:

The synthesis and characterisation of all Al(III)-catalen complexes was performed under an inert atmosphere of argon using standard Schlenk or Glovebox techniques. All chemicals used were purchased from Sigma-Aldrich and used as received, with the exception of *rac*-lactide (*rac*-LA), which was recrystallised once from anhydrous toluene prior to use. All dry solvents used in handling Al(III)-complexes were obtained *via* SPS (solvent purification system). ^{1}H and ^{13}C{^{1}H} NMR spectra were obtained on a Bruker 400 MHz spectrometer and referenced to residual solvent resonances.[1] Coupling constants (*J*) are provided in Hertz (Hz) to the nearest integer. $CDCl_3$ was dried over CaH_2 prior to use with Al(III)-complexes. C_6D_6 was degassed and stored over molecular sieves for use with Al(III)-complexes. All ligands were prepared *via* novel synthetic procedures and characterised *via* electron-spray ionisation-mass spectrometry (ESI-MS) in positive mode. CHN microanalysis was performed by Elemental Microanalysis under an inert atmosphere. Diffusional ordered spectroscopy (DOSY) NMR analysis was carried out on a Bruker 500 MHz instrument.[2] The standard Bruker pulse sequence ledsp2s used was with 8 scans recorded per gradient level. A gradient strength between 1600 to 1750 µs was used with a diffusion time of 0.05 seconds. Eight gradient strengths were used between 10 to 90 %. Data was processed using DOSY methods.

Single crystal X-ray data was collected on an EOS SuperNova diffractometer with Cu Kα radiation ($\lambda = 1.54184$ Å) at 150(2) K. All structures were solved by direct methods and refined on all F^2 data using the SHELXL-2014 or 2017 suite of programs. All hydrogen atoms were included in idealised positions and refined using the riding model, all refinement details are given in the .cif file.

1.1 Polymerisation

Polymerisations were conducted in a Young's ampoule under argon. All melt polymerisations were performed in the absence of solvent. Initial melt polymerisations were performed with *rac*-LA (1.0 g, 0.69 mmol) to which the required amount of Al(**1,3**)Me and benzyl alcohol (BnOH) co-initiator were loaded in a glovebox (2.4 µL, 0.023 mmol) {[*rac*-LA]:[Al]:[BnOH] = 300:1:1}. The ampoule was then submerged in a preheated oil bath (130 °C) and the polymerisation start time commenced on melting of the monomer. The reaction was deemed finished once a polymer melt of sufficient viscosity stopped the stirrer bar. The reaction was then quenched in air and the product dissolved in DCM (20 mL) with stirring. The solvent was then removed *in vacuo* and a crude ^{1}H NMR spectrum of the polymer was obtained. The polymer was then washed with copious amounts of MeOH (80 mL) to remove initiator and any unreacted monomer, dried *in vacuo* and retained for materials characterisation. This procedure was repeated for melt polymerisations at 180 °C, which maintained a constant [*rac*-LA]:[BnOH] ratio {[*rac*-LA]:[Al]:[BnOH] = 3000:1:10}. For solution polymerisations, *rac*-LA (0.5 g, 0.35 mmol) was dissolved in anhydrous toluene (5 mL) with the required amount of Al(**1,3**)Me and BnOH (3.6 µL, 0.035 mmol). The flask was then placed in a preheated oil bath (80 °C) and stirred for 30 minutes. The reaction was then quenched in air, the solvent removed *in vacuo* and a crude ^{1}H NMR spectrum of the polymer was obtained. The polymer was then purified as described for melt polymerisations. This method was repeated for solution polymerisations performed at room temperature (RT). *N.B.* For polymerisations using [Al(**1-3**){OBn}]$_2$, the initiator was treated as monomeric such that there is one -OBn moiety associated per Al centre, thus no additional BnOH was required for {[*rac*-LA]:[Al]:[BnOH] = 300:1:1 or 100:1:1}. For{[*rac*-LA]:[Al]:[BnOH] = 3000:1:10}, treating [Al(**3**){OBn}]$_2$ as monomeric required the addition of 9 equivalents of BnOH (2.2 µL, 0.022 mmol).

All polymer molecular weights were characterised by gel permeation chromatography (GPC), which was performed with a 1 mL min^{-1} flow rate at 35 °C with a THF eluent using a PLgel 5 μm MIXED-D 300 x 7.5 mm column. The system was referenced against 11 narrow molecular weight polystyrene standards with detection *via* refractive index response. Polymer tacticity was determined *via* homonuclear decoupled ^{1}H NMR ($CDCl_3$) spectroscopy analysis of the methine region in accordance to relationships described by Coates *et al*.[3] MALDI-ToF mass spectra were determined on a Bruker Autoflex speed instrument using DCTB (trans-2- [3-(4-tert-Butylphenyl)-2-methyl-2-propenylidene]malononitrile) as the matrix and ionised using NaTFA.

Materials characterisation (GPC, ESI-MS and MALDI-ToF) facilities were provided by the Material and Chemical Characterisation Facility (MC^2) at the University of Bath.

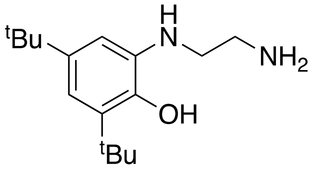
1.2 Reaction kinetics

1.2.1. Polymerisation

Kinetic analysis was performed as described for the solution polymerisation procedure in section 1.1 (toluene, 80 °C, [LA]:[I]:[BnOH] = 100:1:1). Aliquots were taken every 5 minutes over 30 minutes for [Al(**1-3**){OBn}]$_2$ totalling six data points. Plotting ln([LA]$_0$/[LA]$_t$) against time afforded a straight line fit with the gradient equivalent to the pseudo first-order rate constant.

2. Synthesis and characterisation:

2.1 Ligand precursor - *2-((2-aminoethyl)amino)-4,6-di-tert-butylphenol*



To a solution of 3,5-di-tert-butylcatechol (3.0 g, 13.5 mmol) in CH_3CN (15 mL), ethylenediamine (0.9 mL, 13.5 mmol) in MeCN (2 mL) was added dropwise with stirring and then refluxed at 100 °C for 1 h. The solution was allowed to cool to room temperature slowly and then stirred for 3 h to afford a light blue precipitate, which was isolated by filtration, washed with MeCN (10 mL) and air-dried.

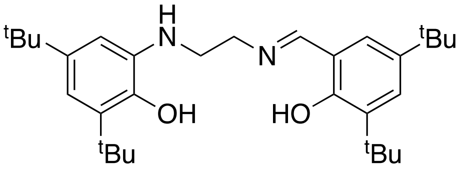
^{1}H NMR ($CDCl_3$, 400 MHz): δ = 6.97 (s, 1H; ArH), 6.86 (s, 1H; ArH), 3.13 (t, J = 5 Hz, 2H; CH_2), 2.86 (t, J = 6 Hz, 2H; CH_2), 1.42 (s, 9H; $C(CH_3)_3$) and 1.28 (s, 9H; $C(CH_3)_3$).

$^{13}C\{^1H\}$ NMR ($CDCl_3$, 400 MHz): δ = 145.9, 142.1, 135.8, 117.6, 115.5, 110.6 (Ar), 50.4, 41.3 (CH_2), 35.0, 34.4 ($C(CH_3)_3$), 31.8, 30.0 (CH_3).

Yield = 2.50 g, 69%

2.2 Catalen ligands

1H_2:



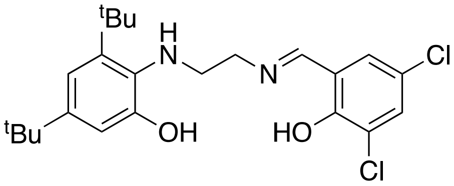
To a solution of 2-((2-aminoethyl)amino)-4,6-di-*tert*-butylphenol (0.50 g, 1.89 mmol) dissolved in MeCN (20 mL), 3,5-di-*tert*-butyl-2-hydroxybenzaldehyde (0.44 g, 1.89 mmol) was added and the solution stirred at 0 °C for 30 minutes. The solvent was removed *in vacuo* to afford a green oil from which a green solid was isolated upon drying *in vacuo*

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 13.59 (s, 1H; OH), 8.40 (s, 1H; ArCHN), 7.40 (d, J = 3 Hz, 1H; ArH), 7.10 (d, J = 3 Hz, 1H; ArH), 6.99 (d, J = 2 Hz, 1H; ArH), 6.91 (d, J = 2 Hz, 1H; ArH), 3.80 (t, J = 6 Hz, 2H; CH_2), 3.40 (t, J = 6 Hz, 2H; CH_2), 1.45 (s, 9H; $C(CH_3)_3$), 1.41 (s, 9H; $C(CH_3)_3$), 1.31 (s, 9H; $C(CH_3)_3$), 1.29 (s, 9H; $C(CH_3)_3$).

$^{13}C\{^1H\}$ NMR ($CDCl_3$, 400 MHz): δ = 167.7 (ArCHN), 158.2, 140.4, 140.2, 137.0, 136.8, 127.3, 127.2, 126.2, 126.2, 118.0, 116.1, 110.6 (Ar), 59.8, 59.4 (CH_2), 35.2, 35.2, 34.3, 34.3 ($C(CH_3)_3$), 31.7, 31.6, 29.6 (CH_3).

Yield = 0.78 g, 86%
ESI-MS (+ve, MeCN): Calculated m/z $[C_{31}H_{49}N_2O_2]^+$ = 481.3794; found m/z = 481.3927.

2H$_2$:



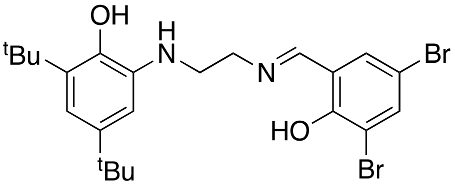
To a solution of 2-((2-aminoethyl)amino)-4,6-di-*tert*-butylphenol (0.67 g, 2.53 mmol) dissolved in MeCN (20 mL), 3,5-dicholoro-2-hydroxybenzaldehyde (0.48 g, 2.53 mmol) was added portion wise and the solution stirred for 30 minutes at RT. The solvent was removed *in vacuo*, replaced with *n*-hexane (10 mL) and stirred for 1 hour. A yellow solid was isolated by filtration and dried *in vacuo*.

^{1}H NMR (CDCl$_3$, 400 MHz): δ = 14.28 (s, 1H; OH)), 8.24 (s, 1H; ArCHN) , 7.40 (s, 1H; ArH), 7.11 (s, 1H; ArH), 6.98 (s, 1H; ArH), 6.89 (s, 1H; ArH), 3.86 (t, *J* = 5 Hz, 2H; CH$_2$), 3.46 (t, *J* = 5 Hz, 2H; CH$_2$), 1.40 (s, 9H; C(CH$_3$)$_3$), 1.28 (s, 9H; C(CH$_3$)$_3$).

^{13}C{^{1}H} NMR (CDCl$_3$, 400 MHz): δ = 165.1 (ArCHN), 146.5, 143.0, 136.6, 133.1, 132.6, 130.2, 129.2, 124.5, 124.2, 116.4, 112.7 (Ar), 47.3 (CH$_2$), 35.3, 34.9, 34.8, 34.6 (C(CH$_3$)$_3$), 31.8, 31.7, 29.9, 29.6 (CH$_3$). *N.B.* Unaccounted for peaks indicative of fluxionality on the ^{13}C{^{1}H} timescale, resulting in poor peak intensity. Additional C(CH$_3$)$_3$ and CH$_3$ peaks observed indicating inequivalence, liking arising from structural fluxionality.

ESI-MS (+ve, MeCN): Calculated m/z [$C_{23}H_{31}Cl_2N_2O_2$]$^+$ = 438.1796; found m/z = 438.1786
Yield = 0.7 g, 63%

3H$_2$:



To a solution of 2-((2-aminoethyl)amino)-4,6-di-*tert*-butylphenol (0.67 g, 2.53 mmol) dissolved in MeCN (20 mL), 3,5-dibromo-2-hydroxybenzaldehyde (0.71 g, 2.53 mmol) was added portion wise and the solution stirred for 30 minutes at RT. The solvent was removed *in vacuo*, replaced with *n*-hexane (10 mL) and stirred for 1 hour. A yellow solid was isolated by filtration and dried *in vacuo*.

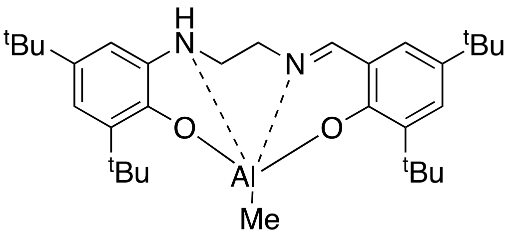
^{1}H NMR (CDCl$_3$, 400 MHz): δ = 14.45 (s, 1H; OH), 8.20 (s, 1H; ArCHN), 7.69 (d, *J* = 2 Hz, 1H; ArH), 7.29 (d, *J* = 2 Hz, 1H; ArH), 6.98 (d, *J* = 2 Hz, 1H; ArH), 6.89 (d, *J* = 2 Hz, 1H; ArH), 3.85 (t, *J* = 6 Hz, 2H; CH$_2$), 3.46 (t, *J* = 6 Hz, 2H; CH$_2$), 1.40 (s, 9H; C(CH$_3$)$_3$), 1.28 (s, 9H; C(CH$_3$)$_3$).

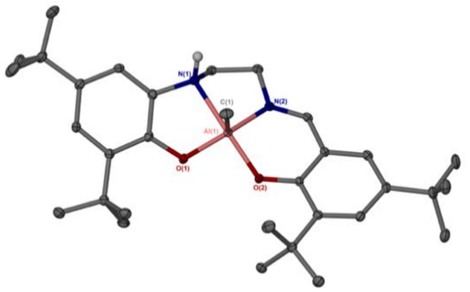
^{13}C{^{1}H} NMR (CDCl$_3$, 400 MHz): δ = 164.9 (ArCHN), 145.3, 142.4, 138.0, 133.0, 114.6, 112.9, 109.4 (Ar), 47.3 (CH$_2$), 36.5, 34.8 (C(CH$_3$)$_3$), 31.8, 29.9 (CH$_3$). *N.B.* Unaccounted for peaks indicative of fluxionality on the ^{13}C{^{1}H} timescale, resulting in poor peak intensity.

ESI-MS (+ve, MeCN): Calculated m/z [$C_{23}H_{31}Br_2N_2O_2$]$^+$ = 527.0732; found m/z = 527.0869
Yield = 0.92 g, 69%

2.3 Al(III)-catalen initiators

Al(**1**)Me:





To a pre-stirred solution of **1**H_2 (0.48 g, 1 mmol) in dry toluene (10 mL) at 0 °C for 5 minutes, $AlMe_3$ (2M, hexane, 0.5 mL, 1 mmol) was added dropwise and the solution gradually warmed from 0 °C to room temperature where it was stirred for 2 hours. The solvent was then removed *in vacuo*, replaced with *n*-hexane (5 mL) and stirred for 5 minutes to afford a yellow solid, which was isolated by cannula filtration and dried *in vacuo*.

^1H NMR (C_6D_6, 400 MHz): δ = 7.75 (s, 1H; ArCHN), 7.48 (s, 1H; ArH), 7.23 (s, 1H; ArH), 6.79 (s, 1H; ArH), 6.77 (s, 1H; ArH), 2.71 (t, *J* = 12 Hz, 1H; CH_2), 2.41 (d, *J* = 7 Hz, 1H; CH_2), 2.31 (t, *J* = 9 Hz, 1H; CH_2), 2.21 (d, *J* = 14 Hz, 1H; CH_2), 1.81 (s, 9H; $C(CH_3)_3$), 1.75 (s, 9H; $C(CH_3)_3$), 1.45 (s, 9H; $C(CH_3)_3$), 1.37 (s, 9H; $C(CH_3)_3$), -0.38 (s, 3H; CH_3).

$^{13}C\{^1H\}$ NMR (C_6D_6, 400 MHz): δ = 171.7 (ArCHN), 165.2, 156.0, 141.5, 138.4, 137.6, 137.2, 131.9, 131.6, 122.9, 118.0, 117.6 (Ar), 55.6, 49.9 (CH_2), 35.8, 35.8, 34.5, 34.2 ($C(CH_3)_3$), 32.2, 31.7, 29.9, 29.7 (CH_3). *N.B.* Al-Me unaccounted for indicative of structural fluxionality.

Elemental analysis: Calculated for: $C_{32}H_{49}AlN_2O_2$: C; 73.81 %; H; 9.49 %; N; 5.38 %. Found: C; 69.50 %; H; 9.66 %; N; 4.78%, consistent with hydrolysed product (Calculated for $C_{31}H_{47}AlN_2O_3$: C; 71.23 % H; 9.06 %; N; 5.36 %).

Yield = 0.20 g, 38%

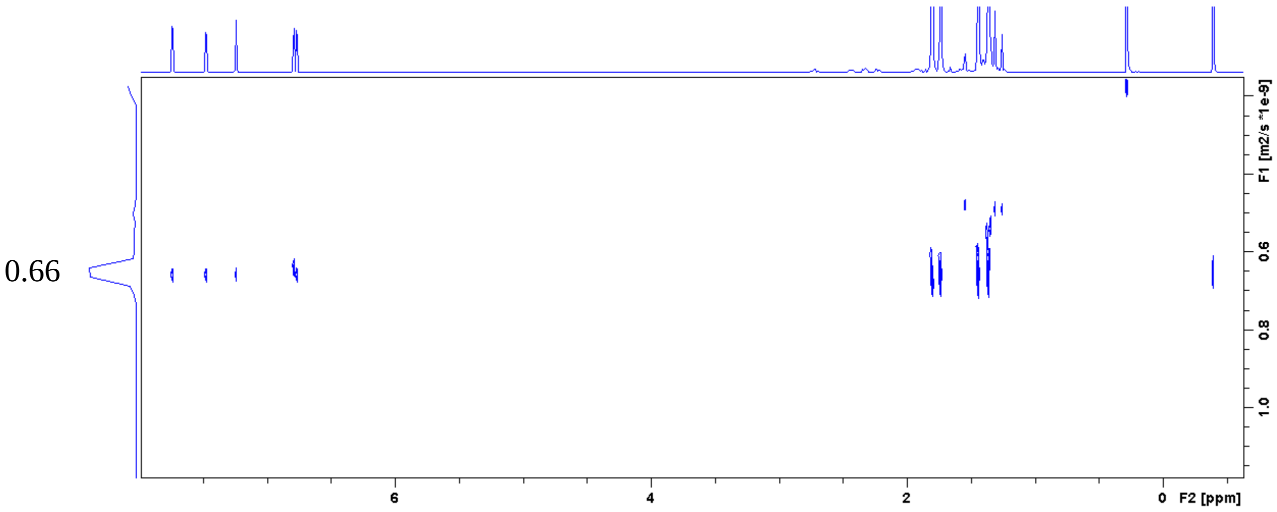


Figure 1. DOSY NMR spectrum (C_6D_6, 500 MHz) of Al(**1**)Me, indicating only one species present in solution, with a diffusion constant of 0.66 x 10^{-9} m^2 s^{-1}.

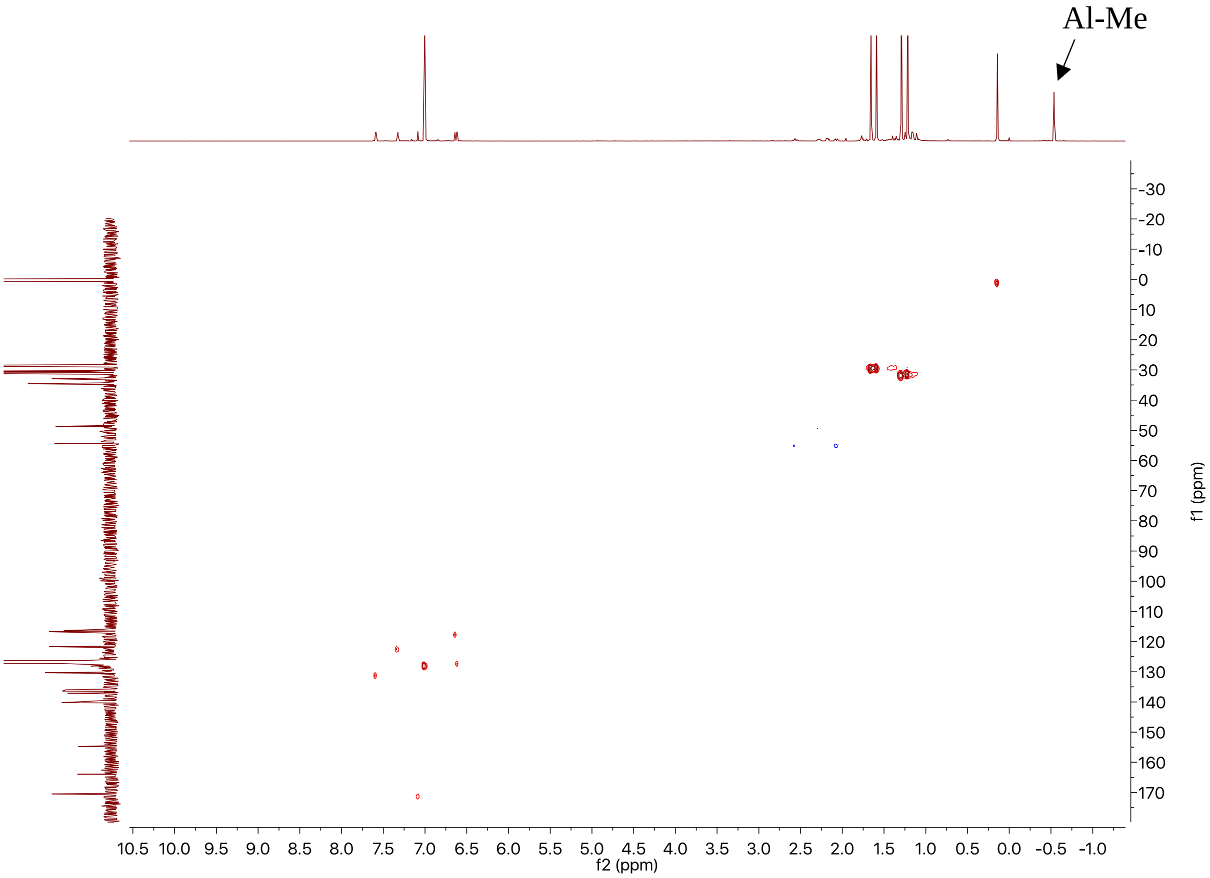
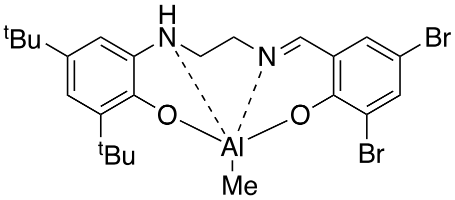


Figure 2. HSQC NMR spectrum (C_6D_6, 500 MHz) of Al(**1**)Me with Al-Me resonance absent, indicative of structural fluxionality.

Al(**3**)Me:



To a solution of $AlMe_3$ (0.5 mL,1 mmol) in dry toluene (10 mL), **3**H_2 (0.53 g, 1 mmol) was added portion wise over 5 minutes under a dynamic flow of argon with stirring. The resulting solution was stirred at room temperature for 1 hour. The solvent was then removed *in vacuo*, replaced with *n*-hexane (10 mL) and stirred for 3 days from which a light brown solid was isolated by cannula filtration and dried *in vacuo*.

^{1}H NMR (C_6D_6, 400 MHz): δ = 7.68 (s, 1H; ArCHN), 7.46 (s, 1H; ArH), 6.74 (s, 2H; ArH), 6.67 (s, 1H; ArH), 2.52 (t, *J* = 11 Hz, 1H; CH_2), 2.31 (t, *J* = 11 Hz, 2H; CH_2), 2.12 (d, *J* = 9 Hz, 1H; CH_2), 1.73 (s, 9H; $C(CH_3)_3$), 1.43 (s, 9H; $C(CH_3)_3$), -0.47 (s, 3H; CH_3).

^{13}C{^{1}H} NMR (C_6D_6, 400 MHz): δ = 169.5 (ArCHN), 162.3, 155.8, 141.2, 138.7, 138.1, 134.7, 131.2, 129.3, 128.6, 125.7, 123.1, 119.0, 118.5, 117.6, 106.0 (Ar), 55.4, 49.0 (CH_2), 34.5, 34.2 ($C(CH_3)_3$), 32.2, 31.7 (CH_3). *N.B.* Additional Ar peaks observed due to the presence of residual solvent (toluene), indicative of structural fluxionality. Al-Me resonance identified by HSQC.

Elemental analysis: Calculated for $C_{24}H_{31}AlBr_2N_2O_2$: C; 50.90 %; H; 5.52 %; N; 4.95 %. Found: C; 47.08 %; H, 5.26 %; N, 4.52 %, consistent with hydrolysed product (Calculated for $C_{23}H_{29}AlBr_2N_2O_3$: C; 48.61 % H; 5.14 %; N; 4.93 %).

Yield = 0.25 g, 45%

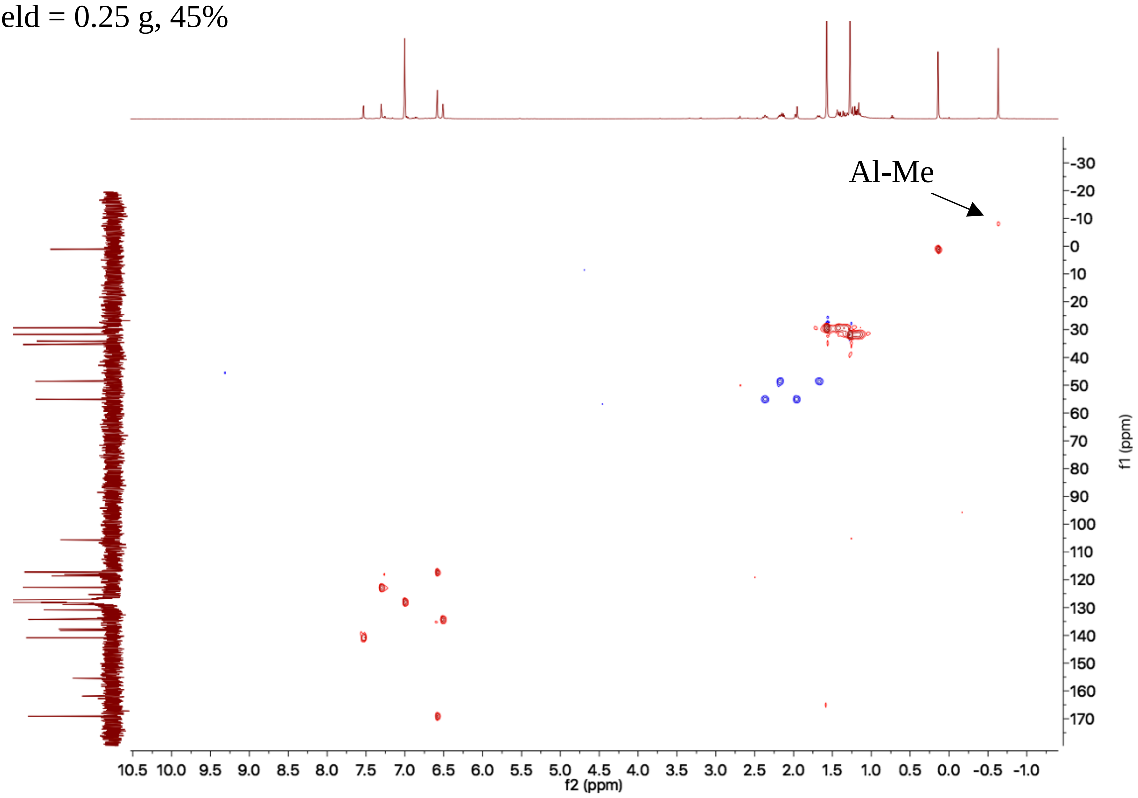
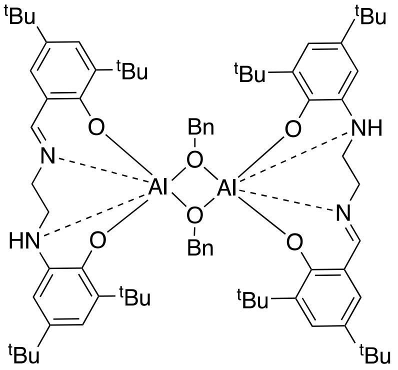
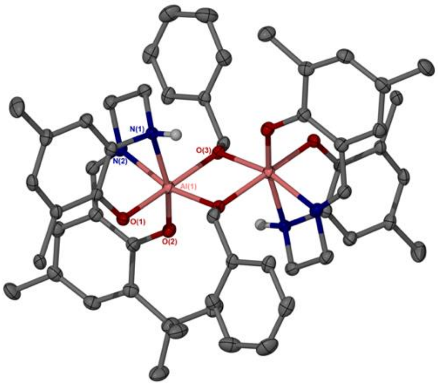


Figure 3. HSQC NMR spectrum (C_6D_6, 500 MHz) of Al(**3**)Me with Al-Me peak present at *ca.* δ = -8 ppm.

[Al(**1**){OBn}]$_2$:





To a pre-stirred solution of **1**H_2 (0.48 g, 1 mmol) in dry toluene (10 mL) at 0 °C for 5 minutes, $AlMe_3$ (0.5 mL, 1 mmol) was added dropwise at room temperature and the resulting solution stirred for 1 hour. BnOH (0.10 mL, 1 mmol) was then added dropwise and the solution stirred for a further hour. A pale-yellow solid was isolated by cannula filtration and dried *in vacuo*.

^{1}H NMR (C_6D_6, 400 MHz): δ = 7.86 (s, 1H; ArCHN), 7.41 (s, 1H; ArH), 7.35 (s, 2H; ArH), 7.29 (s, 1H; ArH), 7.06 (s, 1H; ArH), 7.00 (s, 3H; ArH), 6.95 (s, 1H; ArH), 4.90 (s, 1H; NH), 4.76 (d, *J* = 12 Hz, 1H; Ph-CH_2), 4.38 (d, *J* = 13 Hz, 1H; Ph-CH_2), 3.71 (d, *J* = 4 Hz, 1H; CH_2), 2.62 (t, *J* = 14 Hz, 1H; CH_2), 2.51 (d, *J* = 8 Hz, 1H; CH_2), 1.87 (s, 1H; CH_2), 2.02 (s, 9H; $C(CH_3)_3$), 1.42 (s, 9H; $C(CH_3)_3$), 1.38 (s, 9H; $C(CH_3)_3$), 1.30 (s, 9H; $C(CH_3)_3$).

^{13}C{^{1}H} NMR ($CDCl_3$, 400 MHz): δ = 157.7, 135.9, 130.2, 130.0, 129.0, 128.7, 128.4, 127.84, 127.4, 127.2, 126.8, 122.1, 120.5, 117.5 (Ar), 67.2, 65.6, 49.4, 47.1 (CH_2), 35.6, 34.9, 34.1, 34.0 ($C(CH_3)_3$), 31.9, 31.6, 30.8, 29.4 (CH_3). *N.B.* Unaccounted for resonances indicative of fluxionality on the ^{13}C{^{1}H} timescale, resulting in poor peak intensity.

Elemental analysis: Calculated for: $C_{76}H_{106}Al_2N_4O_6$: C; 74.48 %; H; 8.72 %; N; 4.57 %. Found: C; 71.64 %; H, 8.21 %; N, 4.64%. Elemental analysis is consistently low on carbon, this is potentially due to the hydroscopic nature of the complexes and incorporation of water.

Yield = 0.20 g, 33%

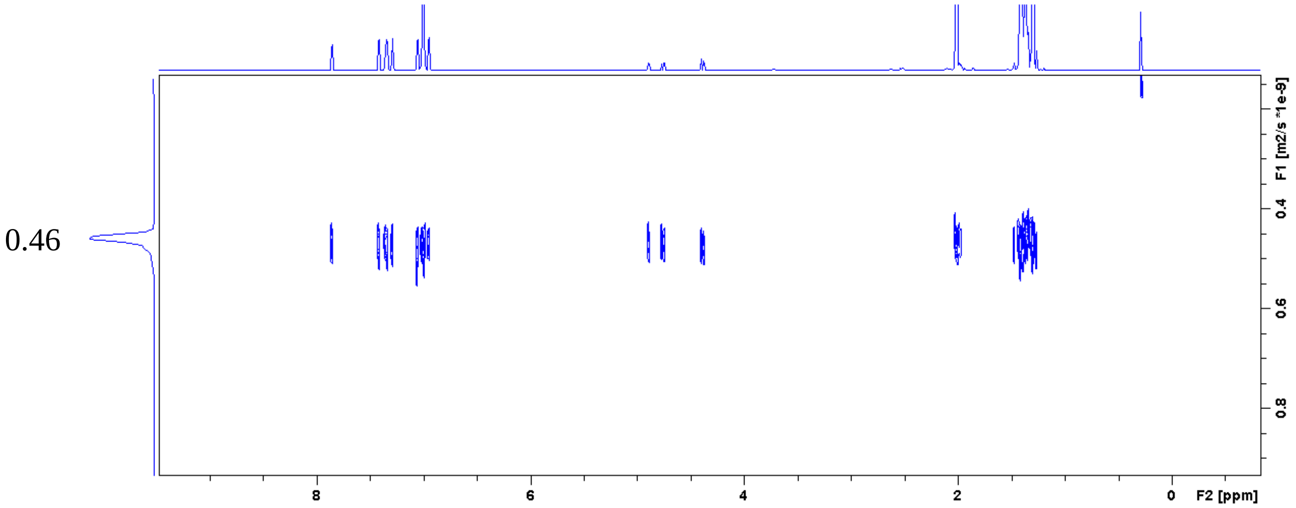
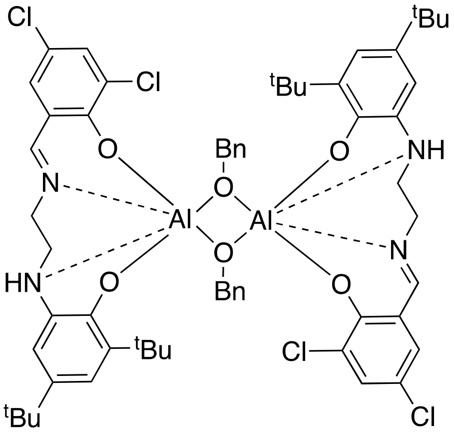
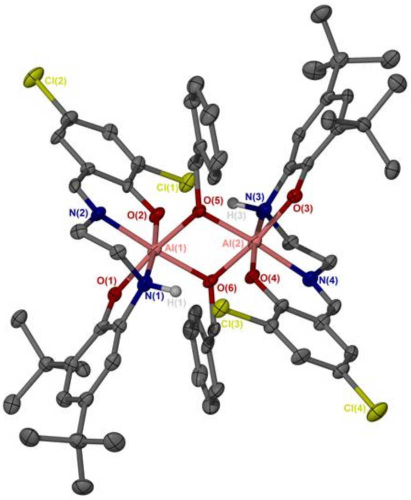


Figure 4. DOSY NMR spectrum (C_6D_6, 500 MHz) of [Al(**1**){OBn}]$_2$, indicating only one species present in solution, with a diffusion constant of 0.46 x 10^{-9} m^2 s^{-1}.

[Al(**2**){OBn}]$_2$:





To a solution of **2**H$_2$ (0.44 g, 1 mmol) in dry toluene (10 mL), AlMe$_3$ (0.5 mL, 1 mmol) was added dropwise at room temperature and the resulting solution stirred for 30 minutes. BnOH (0.10 mL, 1 mmol) was then added dropwise and the solution stirred for a further hour. A yellow solid was isolated by cannula filtration and dried *in vacuo* at 80 °C for 4 hours.

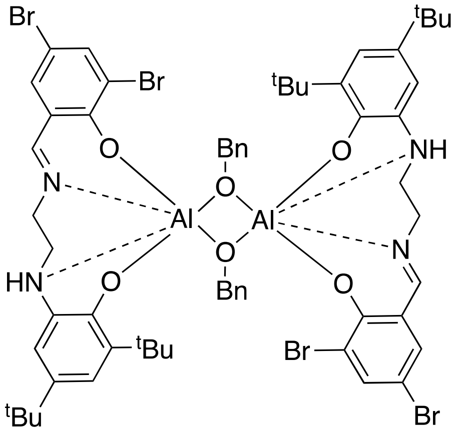
^{1}H NMR (C$_6$D$_6$, 400 MHz): δ = 7.41 (s, 3H; ArCHN; ArH), 7.29 (s, 4H; ArH), 6.94 (s, 1H; ArH), 6.58 (s, 1H; ArH), 5.62 (s, 1H; NH), 4.63 (d, *J* = 14 Hz, 1H; Ph-CH$_2$), 3.70 (d, *J* = 13 Hz, 1H; Ph-CH$_2$), 3.12 (s, 1H; CH$_2$), 2.85 (d, *J* = 17 Hz, 1H; CH$_2$), 2.27 (s, 1H; CH$_2$), 2.15 (d, *J* = 23 Hz, 1H; CH$_2$), 1.34 (s, 9H; C(CH$_3$)$_3$), 1.26 (s, 9H; C(CH$_3$)$_3$). *N.B.* Peak broadening observed in the aromatic region, indicative of fluxionality at the ^{1}H NMR timescale.

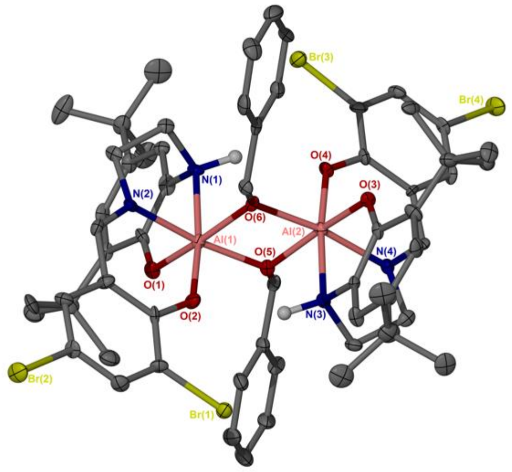
^{13}C{^{1}H} NMR (CDCl$_3$, 400 MHz): δ = 134.2, 131.3, 128.7, 128.4, 127.7, 122.3, 119.1, 117.8 (Ar), 34.9 (C(CH$_3$)$_3$), 31.9, 29.5 (CH$_3$). *N.B.* Unaccounted for peaks indicative of fluxionality at the ^{13}C{^{1}H} NMR timescale, confounded by poor catalyst solubility, resulting in low signal intensity.

Elemental analysis: Calculated for $C_{60}H_{70}Al_2Cl_4N_4O_6$: C; 63.27 %; H; 6.19 %; N; 4.92 %. Found: C; 60.25 %; H, 5.78 %; N, 4.65 %. Elemental analysis is consistently low on carbon, this is potentially due to the hydroscopic nature of the complexes and incorporation of water.

Yield = 0.21 g, 37%

[Al(**3**){OBn}]$_2$:





To a pre-stirred solution of **3**H$_2$ (0.53 g, 1 mmol) in dry toluene (10 mL) at 0 °C for 5 minutes, AlMe$_3$ (0.5 mL, 1 mmol) was added dropwise at room temperature and the resulting solution stirred for 30 minutes. BnOH (0.10 mL, 1 mmol) was then added dropwise and the solution stirred for a further hour. A yellow solid was isolated by cannula filtration and dried *in vacuo* at 80 ^{o}C for 4 hours.

^{1}H NMR (C$_6$D$_6$, 400 MHz): δ = 7.71 (s, 1H; ArCHN), 7.39 (s, 2H; ArH), 7.31 (s, 4H; ArH), 7.01 (d, *J* = 5 Hz, 1H; ArH), 6.88 (s, 1H; ArH), 6.73 (s, 1H; ArH), 5.65 (s, 1H; NH), 4.61 (d, *J* = 17 Hz, 1H; Ph-CH$_2$), 3.64 (d, *J* = 17 Hz, 1H; Ph-CH$_2$), 3.16 (s, 1H; CH$_2$), 2.81 (t, *J* = 14, 12.4 Hz, 1H; CH$_2$), 2.35 (m, 2H; CH$_2$), 1.33 (s, 9H; C(CH$_3$)$_3$), 1.26 (s, 9H; C(CH$_3$)$_3$).

^{13}C{^{1}H} NMR (CDCl$_3$, 400 MHz): δ = 142.1, 139.7, 138.0, 136.9, 135.3, 129.2, 128.9, 128.4, 127.8, 126.8, 125.5, 122.3, 121.0, 117.7 (Ar), 48.0 (CH$_2$), 34.9, 34.2 (C(CH$_3$)$_3$, 31.9, 29.5 (CH$_3$). *N.B.* Unaccounted for resonances indicative of fluxionality at the ^{13}C{^{1}H} NMR timescale, confounded by poor catalyst solubility, resulting in low signal intensity.

Elemental analysis: Calculated for C$_{60}$H$_{70}$Al$_2$Br$_4$N$_4$O$_6$: C; 54.73 %; H; 5.36 %; N; 4.25 %. Found: C; 54.94 %; H, 5.40 %; N, 3.92 %
Yield = 0.50 g, 76%

2.2 Catalyst stability testing:

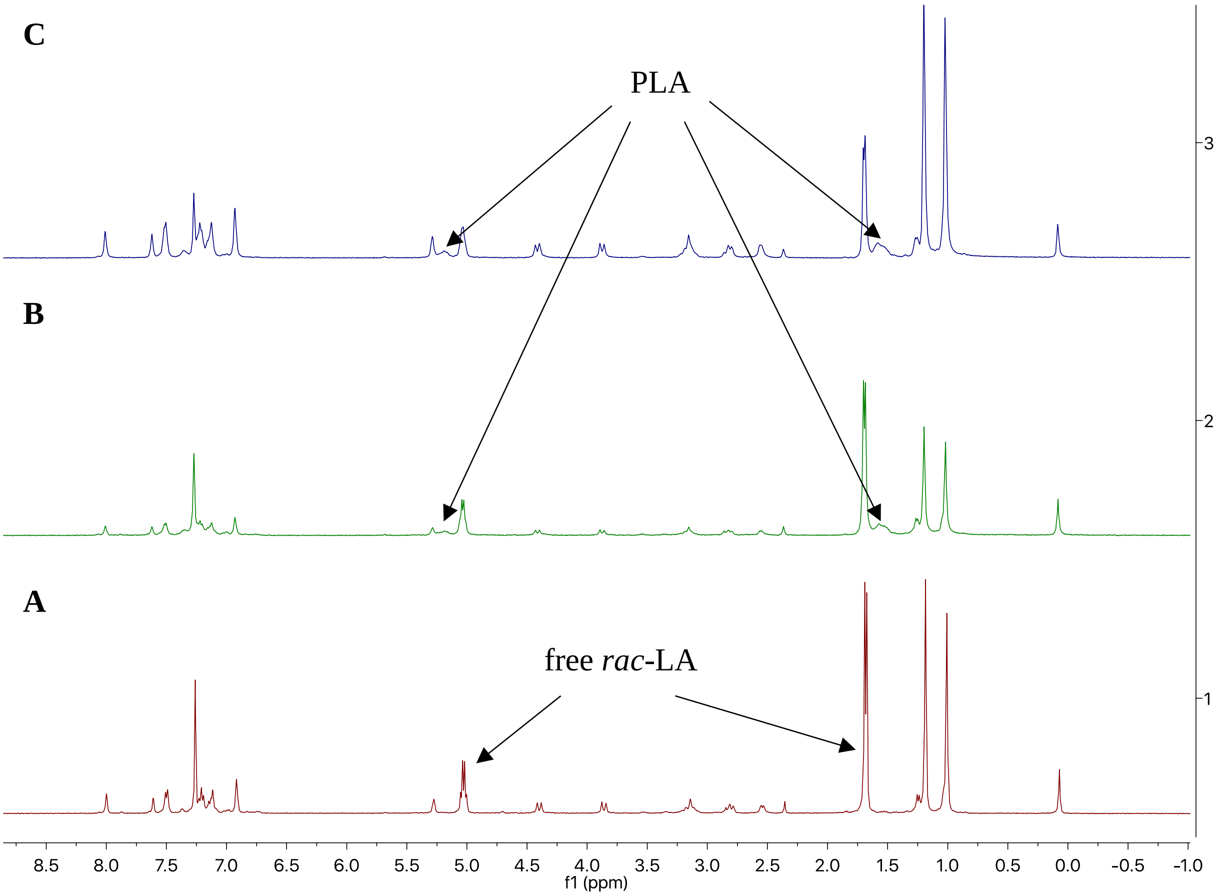


Figure 5. ^{1}H NMR ($CDCl_3$, 400 MHz) spectra assessing the stability of [Al(**2**){OBn}]$_2$ with *rac*-LA ([Al(**2**){OBn}]$_2$:[*rac*-LA] = 1:1): (**A**) 10 minutes at RT; (**B**) 24 hours at RT, and; (**C**) 1 hour at 80 °C.

3. Polymer characterisation:

3.1 Representative ^{1}H NMR spectra

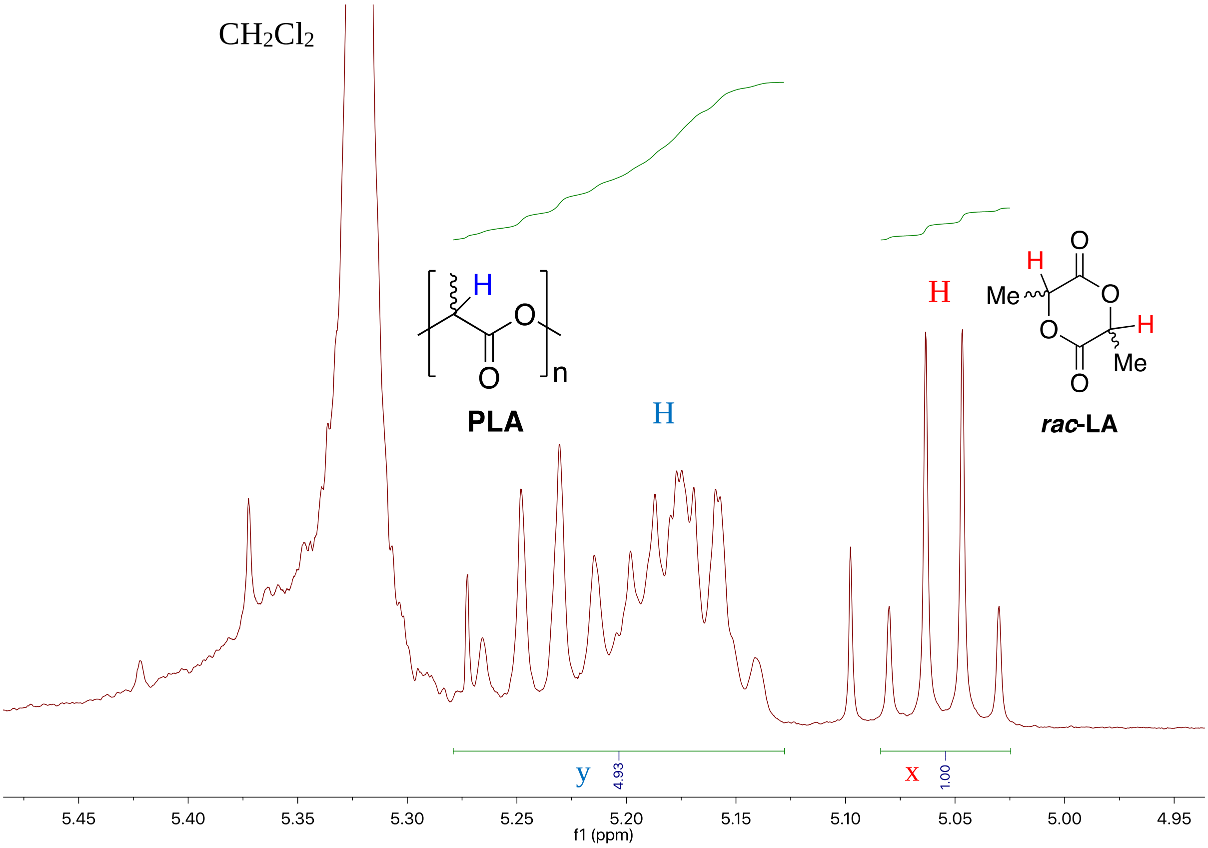


Figure 6. ^{1}H NMR ($CDCl_3$, 400 MHz) spectrum of crude PLA product from the melt polymerisation of *rac*-LA at 130 °C using Al(**3**)Me {[*rac*-LA]:[Init]:[BnOH] = 300:1:1} (Table 1, Entry 3). PLA conversion = [y/(x+y)] x 100%.

3.2 Representative GPC spectra:

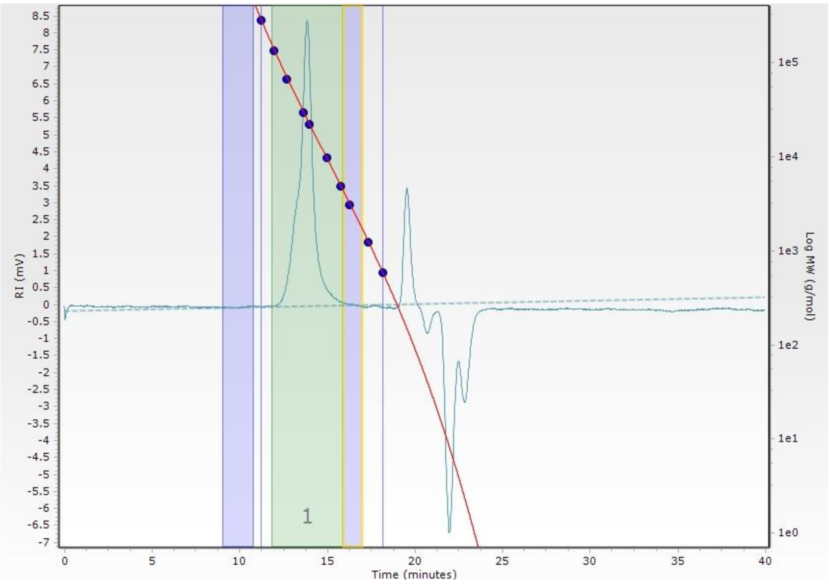


Figure 7. GPC spectrum of purified PLA product from the melt polymerisation of *rac*-LA at 180 °C using [Al(**3**){OBn}]$_2$ {[*rac*-LA]:[Init]:[BnOH] = 3000:1:10} (Table 1, Entry 8).

3.3. Representative homonuclear decoupled ^{1}H NMR spectra:

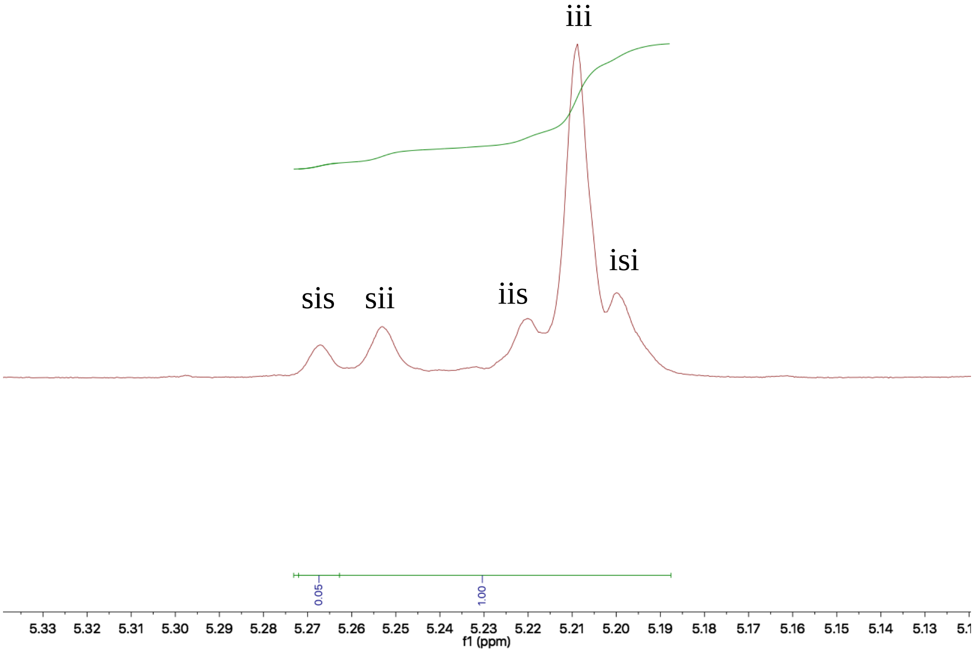


Figure 8. Homonuclear decoupled ^{1}H NMR (CDCl$_3$, 400 MHz) spectra of purified isotactic PLA (P_r = 0.31) from the solution polymerisation of *rac*-LA using [Al(**1**){OBn}]$_2$ at RT in DCM (Table 2, Entry 6) displaying the five tetrad possibilities in the methine region (red). [3]

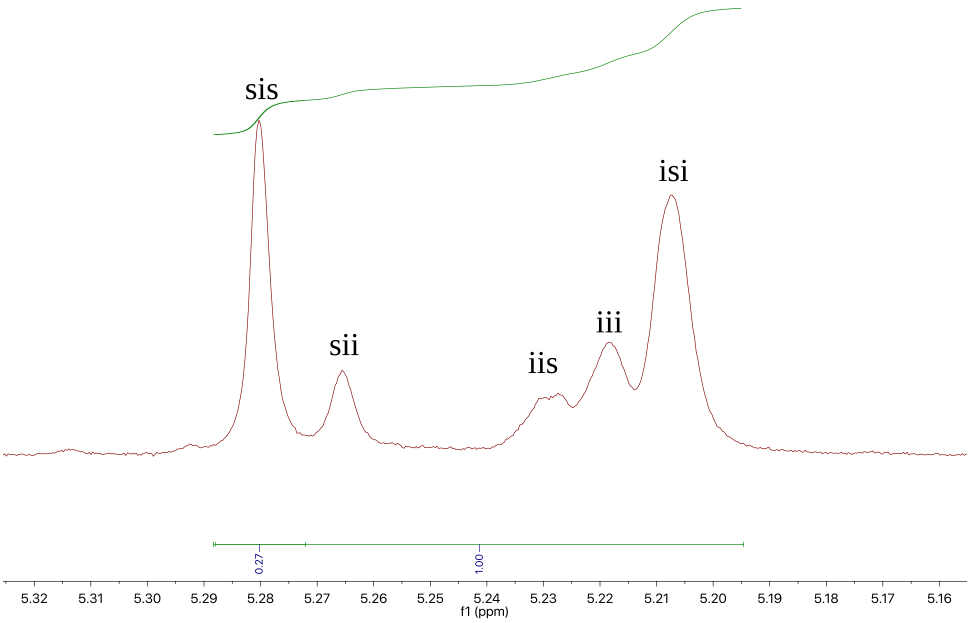


Figure 9. Homonuclear decoupled ^{1}H NMR ($CDCl_3$, 400 MHz) spectra of purified heterotactic PLA (P_r = 0.72) from the solution polymerisation of *rac*-LA using Al(**3**)Me at RT in DCM (Table 2, Entry 4), displaying the five tetrad possibilities in the methine region (red). [3]

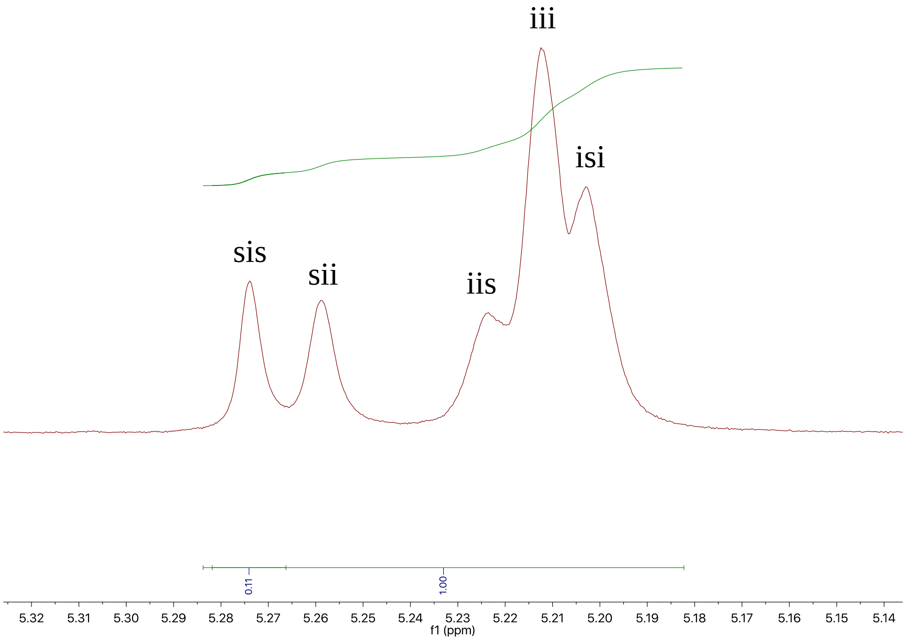


Figure 10. Homonuclear decoupled ^{1}H NMR ($CDCl_3$, 400 MHz) spectra of purified atactic PLA (P_r = 0.46) from the melt polymerisation of *rac*-LA using Al(**1**)Me at 130 °C (Table 1, Entry 1) displaying the five tetrad possibilities in the methine region (red). [3]

3.4 MALDI-ToF spectrum:

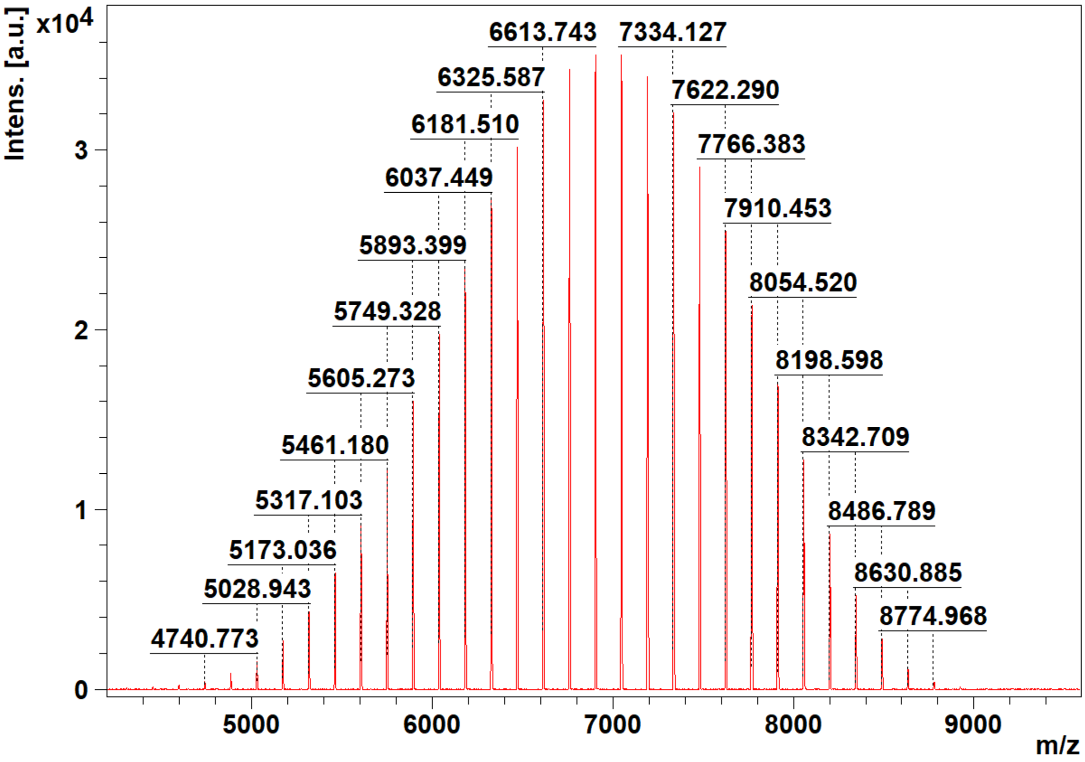


Figure 11. MALDI-ToF spectra of PLA produced using [Al(**1**){OBn}]$_2$ at RT (DCM, {[*rac*-LA]:[Init]:[BnOH] = 100:1:1}) (Table 2, Entry 6).

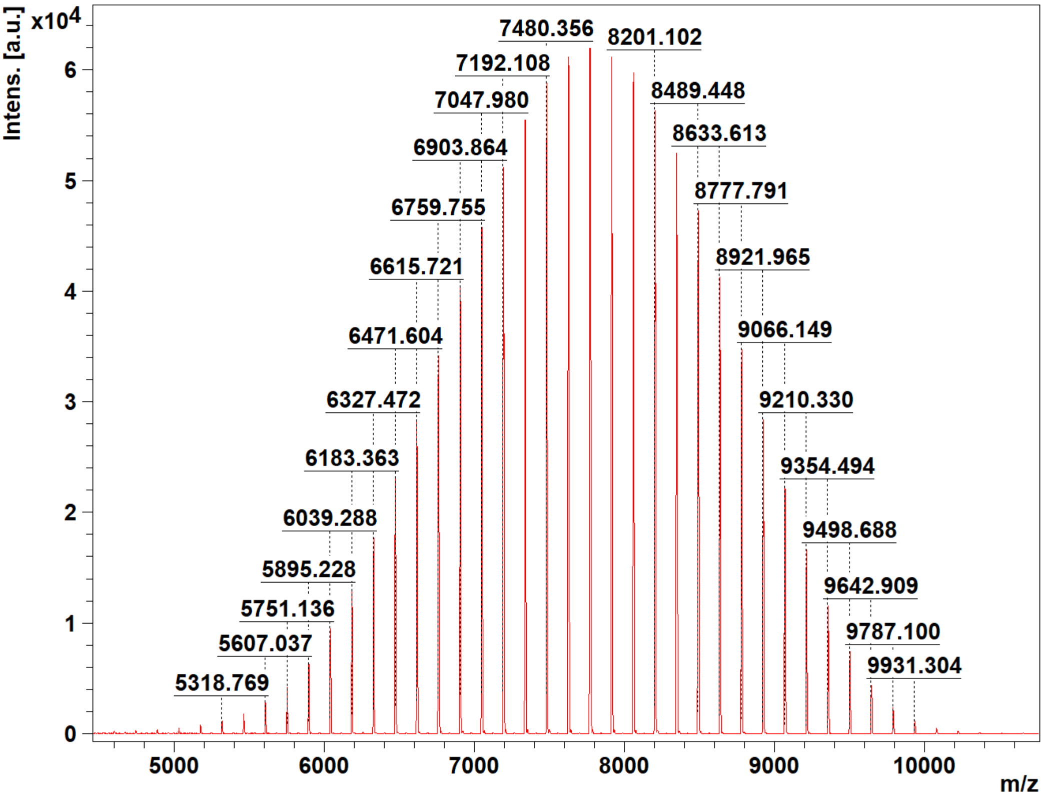


Figure 12. MALDI-ToF spectra of PLA produced using [Al(**2**){OBn}]$_2$ with the addition of 1 equivalent of BnOH at 80 °C in toluene (Table 2, Entry 8).

4. Crystallographic data

Special refinement details include:
Al(**1**)Me: Crystal was weakly diffracting, achieving a completeness of 95.6 % (66.601°). The structure is nevertheless unambiguous and a testament to modern diffractometers.

[Al(**1**)OBn]$_2$: The NH hydrogen atom has been located in the difference Fourier map and was refined with bond length restraint. One of the t-Bu groups in the dimeric complex shows rotational disorder in the ratio 40:60.
Atoms within this disorder have been refined using ADP restraints. The cavity in the unit cell contains 1.75 solvent molecules of toluene or 0.875 per asymmetric unit, distributed over three sites. Every solvent molecule is sitting on a centre of inversion. One solvent molecule was refined with 50% occupation, the second one with 25% and the third one with 12.5% occupation. The methyl group of the lowest occupied toluenes has been refined with bond length restraints and all atoms in the lowest occupied toluenes have been refined with ADP restraints.

[Al(**1**)OMe]$_2$: Methyl groups of one ^{t}Bu (C24) groups disordered over two positions (55:45), minor component treated isotropically.

[Al(**3**)OBn]$_2$: ISOR restraints applied to carbon atoms (C22,45) directly attached to bromine groups.

Table 1. Crystallographic data of Al(**1**)Me,[Al(**1-3**){OBn}]$_2$ and [Al(**1**){OMe}]$_2$.

Compound reference	Al(**1**)Me	[Al(**1**){OBn}]$_2$	[Al(**1**){OMe}]$_2$	[Al(**2**){OBn}]$_2$	[Al(**3**){OBn}]$_2$
Chemical formula	$C_{32}H_{49}AlN_2O_2$	$C_{88.25}H_{120}Al_2N_4O_6$	$C_{32}H_{49}AlN_2O_3$	$C_{81}H_{94}Al_2Cl_4N_4O_6$	$C_{81}H_{94}Al_2Br_4N_4O_6$
Formula Mass	520.71	1386.84	536.71	1415.36	1593.20
Crystal system	Triclinic	Triclinic	Monoclinic	Monoclinic	Monoclinic
a/Å	9.6309(7)	10.1019(6)	12.4849(9)	9.8297(11)	9.8437(7)
b/Å	11.5396(8)	14.8501(12)	14.4299(9)	29.388(8)	29.300(4)
c/Å	15.2779(10)	15.5646(11)	18.0897(11)	25.847(2)	26.1541(19)
α/°	103.549(6)	111.216(7)	90	90	90
β/°	102.775(6)	103.321(6)	91.719(6)	94.656(9)	94.073(7)
γ/°	98.081(6)	97.899(6)	90	90	90
Unit cell volume/Å^3	1576.3(2)	2054.4(3)	3257.5(4)	7442(2)	7524.2(13)
Temperature/K	150(2)	150(2)	150(2)	150(2)	150(2)
Space group	$P\bar{1}$	$P\bar{1}$	$P2_1/c$	$P2_1/n$	$P2_1/n$
No. of formula units per unit cell, Z	2	1	4	4	4
Radiation type	Cu Kα	Cu Kα	Cu Kα	Cu Kα	Cu Kα
No. of reflections measured	9363	13154	10718	48475	24315
No. of independent reflections	5330	7395	5621	13140	12986
R_{int}	0.0397	0.0672	0.0626	0.2112	0.1514
Final R_1 values ($I > 2\sigma(I)$)	0.0503	0.0669	0.0925	0.1028	0.0991
Final $wR(F^2)$ values ($I > 2\sigma(I)$)	0.1299	0.1486	0.2158	0.2049	0.1696
Final R_1 values (all data)	0.0629	0.1144	0.1502	0.2233	0.2207
Final $wR(F^2)$ values (all data)	0.1403	0.1784	0.2491	0.2770	0.2342

Selected bond lengths and angles:

Table 2. Selected bond lengths for Al(**1**)Me and [Al(**1-3**){OBn}]$_2$.

Init.	Bond	Bond length / Å
Al(**1**)Me	Al(1)-N(1) {imine}, Al(1)-N(2) {amine}	2.1603(17), 1.9827(19)
[Al(**1**){OBn}]$_2$		2.122(3), 2.027(3)
[Al(**2**){OBn}]$_2$		2.088(7), 2.020(6)
[Al(**3**){OBn}]$_2$		2.072(9), 2.014(10)

Table 3. Selected bond angles for Al(**1**)Me and [Al(**1-3**){OBn}]$_2$ with calculated $\boldsymbol{\tau}_5$ value for the former. Ideal square pyramidal geometry corresponds to $\boldsymbol{\tau}_5 = 0$.

Init.	Bond	Bond angle / °	$\boldsymbol{\tau}_5$
Al(**1**)Me	O(1)-Al(1)-N(2), O(2)-Al(1)-N(1)	124.13(7), 161.30(7)	0.62
[Al(**1**){OBn}]$_2$	O(1)-Al(1)-N(2), O(2)-Al(1)-N(1)	92.09(11), 166.54	-
[Al(**2**){OBn}]$_2$		88.2(3), 172.2(3)	-
[Al(**3**){OBn}]$_2$		89.0(4), 171.6(4)	-

5. Polymerisation Data

Table 4 and Table 5 below include M_n values with a correction factor of 0.58.[4]

Table 4. Melt polymerisation of *rac*-LA using Al(III)-complexes.

Init.	Time / min	[*rac*-LA] : [Al] : [BnOX]	Conv.[a] / %	$M_{n,theo}$[b] / g mol^{-1}	M_n[c] / g mol^{-1}	Đ[c]	P_r[d]
Al(**1**)Me / BnOH	2	300 : 1 : 1	94	40700	46250 (26800)	1.35	0.46
	19	3000 : 1 : 10	83	35950	25400 (14700)	1.35	0.46
Al(**3**)Me / BnOH	0.33	300 : 1 : 1	83	35950	206700 (119900)	1.81	0.64
	11	3000 : 1 : 10	90	39000	24050 (13950)	1.28	0.60
[Al(**1**){OBn}]$_2$	2	300 : 1 : 1	88	38100	70500 (40900)	1.42	0.46
[Al(**2**){OBn}]$_2$	5	300 : 1 : 1	76	32950	252100 (146200)	1.52	0.64
[Al(**3**){OBn}]$_2$	8	300 : 1 : 1	74	32100	160500 (93100)	1.39	0.65
	32[e]	3000 : 1 : 10	82	35550	23600 (13700)	1.24	0.62

Conditions: *rac*-LA (1.0 g), solvent free (130 °C) [a] Determined *via* ^{1}H NMR spectroscopy. [b] Theoretical average number molecular weight (M_n) dependent on conversion and co-initiator added {($M_{r,LA}$ x 3 x $\%_{conv}$) + $M_{n,BnOH}$}. [c] Determined *via* GPC analysis (in THF). [d] Determined *via* homonuclear decoupled NMR spectroscopy. [e] 9 equivalents of BnOH added to achieve {[Al] : [BnOH] = 1:10}. A correction factor of 0.58 has been applied corresponding to bracketed M_n values.[4]

Table 5. Solution polymerisation of *rac*-LA using Al(III)-complexes.

Init.	Time / h	[*rac*-LA] : [Al] : [BnOX]	Conv.[a] / %	$M_{n,theo}$[b] / g mol^{-1}	M_n[c] / g mol^{-1}	Đ[c]	P_r[d]
Al(**1**)Me / BnOH	0.5	100 : 1 : 1	97	14100	15850 (9200)	1.33	0.36
	8[e]	100 : 1 : 1	62	9050	9050 (6050)	1.06	0.30
Al(**3**)Me / BnOH	0.5	100 : 1 : 1	97	14100	16150 (9350)	1.33	0.64
	8[e]	100 : 1 : 1	81	11750	13550 (7850)	1.08	0.72
[Al(**1**){OBn}]$_2$	0.5	100 : 1 : 1	96	13950	19300 (11200)	1.64	0.38
	8[e]	100 : 1 : 1	62	9050	12000 (6950)	1.06	0.31
[Al(**2**){OBn}]$_2$	0.5	100 : 1 : 1	94	13650	146900 (85200)	1.56	0.64
	0.5[f]	100 : 1 : 2	91	6900	12250 (7100)	1.10	0.67
	8[e]	100 : 1 : 1	<10	-	-	-	-
	8[g]	100 : 1 : 1	0	-	-	-	-
[Al(**3**){OBn}]$_2$	0.5	100 : 1 : 1	97	14100	99500 (57700)	1.97	0.65
	8[e]	100 : 1 : 1	<10	-	-	-	-
	8[g]	100 : 1 : 1	0	-	-	-	-

Conditions: *rac*-LA (0.5 g), solvent (toluene, 80 °C). [a] Determined *via* ^{1}H NMR spectroscopy. [b] Theoretical average number molecular weight (M_n) dependent on conversion and co-initiator added {($M_{r,LA}$ x $\%_{conv}$) + $M_{n,BnOH}$}. [c] Determined *via* GPC analysis (in THF). [d] Determined *via* homonuclear decoupled NMR spectroscopy. [e] RT (25 °C) in DCM. [f] 1 equiv. of BnOH added to achieve {[Al] : [BnOH] = 1:2}. [g] RT (25 °C) in THF. M_n, *Đ* and P_r values for [Al(**2-3**){OBn}]$_2$ at RT in DCM could not be determined due to insufficient polymeric material being isolated. A correction factor of 0.58 has been applied corresponding to bracketed M_n values.[4]

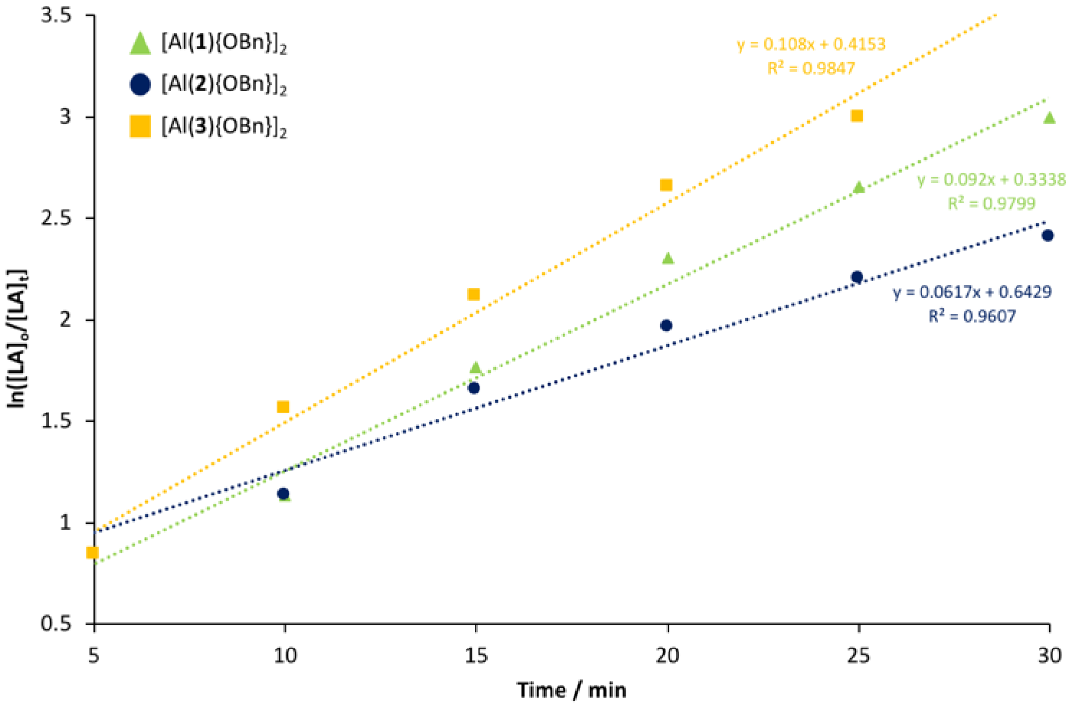


Figure 13. First-order logarithmic plot for the polymerisation of *rac*-LA at 80 °C in toluene {[*rac*-LA]:[Al][BnOH] = 100:1:1} using [Al(**1-3**){OBn}]$_2$ **.** Note [LA]$_o$ = 0.69 mol dm^{-3}. Data points at 5 and 30 minutes have been omitted for [Al(**1-2**){OBn}]$_2$ and [Al(**3**){OBn}]$_2$ respectively to achieve R^2 values > 0.96.

References:

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