SUPPORTING INFORMATION

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-Köhn[b] and Matthew D. Jones[b,*]

[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*

Characterisation and Preparation of ligands	2
Characterisation and Preparation of Complexes	3
Selected NMR Spectra	4-8
Selected MALDI-ToF Mass Spectra	9
Further Kinetic Plots	10-12
Selected Polymer NMR spectra	13-15
Selected GPC Data	15-16
Crystallographic Parameters	17
DFT details	18-19

Characterisation and Preparation of Ligands:

2H_2 Yield: 8.35 g, 23.3 mmol (67 %) ^{1}H NMR ($CDCl_3$): 1.43 (9H, s, C(CH_3)$_3$), 1.62 (9H, s, C(CH_3)$_3$), 7.22 (1H, dd, J = 7.3, 1.0 Hz, Ar-H), 7.36 (1H, d, J = 2.5 Hz, Ar-H), 7.51 - 7.56 (1H, m, Ar-H), 7.57 - 7.65 (3H, m, Ar-H), 7.81 (1H, d, J = 8.3 Hz, Ar-H), 7.90 - 7.95 (1H, m, Ar-H), 8.34 - 8.40 (1H, m, Ar-H), 8.78 (1H, s, N=CH), 13.78 (1H, br. s., OH). ^{13}C{^{1}H} NMR ($CDCl_3$): 29.5 (C(**C**H$_3$)$_3$), 31.5 (C(**C**H$_3$)$_3$), 34.2 (**C**(CH_3)$_3$), 35.2 (**C**(CH_3)$_3$), 114.0 (Ar-H), 118.6 (Ar), 123.4 (Ar-H), 125.9 (Ar-H), 126.3 (Ar), 126.6 (Ar-H), 126.9 (Ar-H), 127.8 (Ar-H), 128.2 (Ar-H), 128.3 (Ar), 134.0 (Ar), 138.0 (Ar-H), 140.7 (Ar-H), 146.5 (Ar-N), 158.4 (Ar-OH), 164.7 (CH=N). m/z [$C_{25}H_{29}NO$ + H]$^+$ Calc: 360.2327 gmol^{-1} Found: 360.2313 gmol^{-1}.

3H_2 Yield: 10.16 g, 32.3 mmol (93 %) ^{1}H NMR ($CDCl_3$): 7.21 (1H, dd, J = 7.4, 0.9 Hz, Ar-H), 7.35 (1H, d, J = 2.3 Hz, Ar-H), 7.48 - 7.54 (2H, m, Ar-H), 7.55 - 7.62 (2H, m, Ar-H), 7.84 (1H, d, J = 8.3 Hz, Ar-H), 7.87 - 7.93 (1H, m, Ar-H), 8.20 - 8.27 (1H, m, Ar-H), 8.64 (1H, s, N=CH), 14.35 (1H, br. s., OH). ^{13}C{^{1}H} NMR ($CDCl_3$): 114.1 (Ar-H), 120.5 (Ar-H), 122.9 (Ar-H), 123.6 (Ar-H), 125.8 (Ar-H), 126.9 (Ar-H), 128.0 (Ar-H), 128.0 (Ar), 129.8 (Ar), 132.9 (Ar-Cl), 134.0 (Ar-Cl), 144.6 (Ar-N), 155.9 (Ar-OH), 161.3 (CH=N). m/z [$C_{17}H_{12}Cl_2NO$ + H]$^+$ Calc: 316.0296 gmol^{-1} Found: 316.0260 gmol^{-1}.

4H_2 Yield: 0.55 g, 1.51 mmol (37 %) ^{1}H NMR ($CDCl_3$): 7.01 (2H, t, J = 7.5 Hz, Ar-H), 7.12 (2H, d, J = 7.9 Hz, Ar-H), 7.27 (2H, d, J = 7.2 Hz, Ar-H), 7.47 (4H, m, Ar-H), 7.58 (2H, t, J = 7.5 Hz, Ar-H), 8.23 (2H, d, J = 8.3 Hz, Ar-H), 8.74 (2H, s, N=CH), 13.33 (2H, br s, OH). ^{13}C{^{1}H} NMR ($CDCl_3$): 114.9 (Ar-H), 117.4 (Ar-H), 119.3 (Ar-H), 119.5 (Ar-H), 122.3 (Ar-H), 126.6 (Ar-H), 128.9 (Ar-H), 132.5 (Ar-H), 133.6 (Ar-H), 146.3 (Ar-H), 161.2 (N=CH), 163.9 (N=CH). m/z [$C_{24}H_{18}N_2O_2$ + H]$^+$ Calc: 367.1447 gmol^{-1} Found: 367.1456 gmol^{-1}.

5H_2 Yield: 0.91 g, 1.54 mmol, (72 %) ^{1}H NMR ($CDCl_3$): 1.28 (18H, s, C(CH_3)$_3$), 1.46 (18H, s, C(CH_3)$_3$), 7.16 (1H, s, Ar-H), 7.18 (1H, s, Ar-H), 7.23 (2H, d, J = 2.3 Hz, Ar-H) 7.44 (2H, d, J = 2.6 Hz, Ar-H), 7.50 (2H, dt, J = 1.1 Hz, Ar-H), 8.15 (2H, d, J = 8.3 Hz, Ar-H), 8.67 (2H, s, N=CH), 13.63 (2H, br s, OH). ^{13}C{^{1}H} NMR ($CDCl_3$): 29.5 (C(**C**H$_3$)$_3$), 31.5 (C(**C**H$_3$)$_3$), 34.3 (C(**C**H$_3$)$_3$), 35.2 (C(**C**H$_3$)$_3$), 114.9 (Ar-H), 118.7 (Ar-H), 122.1 (Ar-H), 126.5 (Ar-H), 127.0 (Ar-H), 128.4 (Ar-H), 128.9 (Ar-H), 137.1 (Ar-H), 140.8 (Ar-H), 146.5 (Ar-H), 158.4 (N=CH), 165.0 (N=CH). m/z [$C_{40}H_{50}N_2O_2$ + H]$^+$ Calc: 591.3945 gmol^{-1} Found: 591.4065 gmol^{-1}.

6H_2 Yield: 1.19 g, 2.37 mmol (90 %) Insoluble in organic solvents, no NMR or MS data could be obtained. Calc for $C_{24}H_{14}Cl_4N_2O_2$ C 57.17% H 2.80% N 5.56%; Found C 57.3% H 2.67% N 5.64%.

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 (0.268 g, 45%). ^{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(**C**H$_3$)$_3$, .31.5 (C(**C**H$_3$)$_3$), 34.1 147.0, (**C**(CH_3)$_3$), 34.7 (**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).

Characterisation and Preparation of Complexes:

Al(**2**)Me_2 Yield: 0.48 g, 1.16 mmol (21%) ^{1}H NMR (d_8-Tol): - 0.37 (6H, br s, Al-$(CH_3)_2$), 1.28 (9H, s, C$(CH_3)_3$) 1.62 (9H, s, C$(CH_3)_3$), 6.71 (1H, d, J = 2.6 Hz, Ar-H), 6.97 - 7.22 (4H, m, Ar-H), 7.47 (1H, d, J = 7.9 Hz, Ar-H), 7.51 (1H, s, N=CH), 7.54 (1H, dd, J = 8.5, 0.9 Hz, Ar-H), 7.66 (1H, d, J = 8.7 Hz, Ar-H), 7.74 (1H, d, J = 2.6 Hz, Ar-H). ^{13}C{^{1}H} NMR: - 9.1 (Al-$(CH_3)_2$), 29.6 (C(**C**$H_3)_3$), 31.4 (C(**C**$H_3)_3$), 34.2 (**C**$(CH_3)_3$), 35.7 (**C**$(CH_3)_3$), 118.9 (Ar), 120.8 (Ar-H), 123.3 (Ar-H), 126.9 (Ar-H), 127.2 (Ar-H), 128.0 (Ar-H), 128.4 (Ar-H), 129.7 (Ar-H), 133.3 (Ar-H), 134.9 (Ar-H), 139.3 (Ar), 141.3 (Ar), 143.4 (Ar-N), 163.3 (Ar-O), 174.5 (CH=N). Calc: C 78.04% H 8.25% N 3.76% Found: C 77.89% H 8.11% N 3.67%.

Al(**3**)Me_2 Yield: 1.35 g, 3.63 mmol (57%) ^{1}H NMR (d_8-Tol): - 0.48 (6H, br. s., Al$(CH_3)_2$), 6.31 (1H, d, J = 2.5 Hz, Ar-H), 6.98 (1H, dd, J = 7.4, 1.4 Hz Ar-H), 7.01 (1H, s, N=CH), 7.10 (2H, t, J = 7.8 Hz, Ar-H), 7.17 - 7.26 (3H, m, Ar-H), 7.45 (1H, d, J = 8.3 Hz, Ar-H), 7.48 - 7.56 (2H, m, Ar-H). ^{13}C{^{1}H} NMR (d_8-Tol): - 9.2 (Al-$(CH_3)_2$), 119.7 (Ar), 120.5 (Ar-H), 121.4 (Ar-H), 122.8 (Ar-H), 125.3 (Ar-H), 127.2 (Ar-H), 127.4 (Ar-H), 127.8 (Ar-H), 127.9 (Ar-H), 128.6 (Ar-H), 128.7 (Ar-H), 132.7 (Ar), 134.8 (Ar-Cl), 137.0 (Ar-Cl), 142.5 (Ar-N), 159.4 (Ar-O), 172.6 (CH=N). Calc: C 61.31% H 4.33% N 3.76% Found: C 61.40% H 4.27% N 3.84%.

Al_2(**5**)Me_4 Yield: 0.14 g, 0.20 mmol (25 %) ^{1}H NMR (C_6D_6): - 0.33 (6H, br s., Al$(CH_3)_2$), - 0.23 (6H, br s., Al$(CH_3)_2$), 1.31 (18H, s, C$(CH_3)_3$), 1.65 (18H, s, C$(CH_3)_3$), 6.74 (2H, d, J = 2.6 Hz, Ar-H), 6.98 - 7.09 (6H, m, Ar-H) 7.55 - 7.63 (2H, m, Ar-H), 7.79 (2H, d, J = 2.6 Hz, N=CH). ^{13}C{^{1}H} NMR (d_8-tol): - 8.9 (Al$(CH_3)_2$), 29.6 (C(**C**$H_3)_3$), 31.4 (C(**C**$H_3)_3$), 34.3 (**C**$(CH_3)_3$), 35.7 (**C**$(CH_3)_3$), 118.9 (Ar), 122.1 (Ar-H), 123.3 (Ar-H), 126.7 (Ar-H), 129.6 (Ar-H), 129.9 (Ar-H), 133.7 (Ar), 137.8 (Ar) 139.6 (Ar), 141.3 (Ar), 143.8 (Ar-N), 163.4 (Ar-O), 174.8 (N=CH). Calc: C 75.18% H 8.60% N 3.99% Found: C 75.00% H 8.62% N 3.91%

Al_2(**6**)Me_4 Yield: 0.13 g, 0.21 mmol (5 %) ^{1}H NMR (C_6D_6): - 0.49 (6H, br s., Al$(CH_3)_2$), - 0.35 (6H, br s., Al$(CH_3)_2$), 6.94 (2H, d, J = 7.16 Hz, Ar-H) 6.99 - 7.01 (2H, m, Ar-H), 7.03 – 7.09 (4H, m, Ar-H), 7.30 (2H, d, J = 2.64 Hz, Ar-H) 7.45 (1H, s, N=CH) 7.48 (1H, s, N=CH). ^{13}C{^{1}H} NMR (C_6D_6): - 8.9 (Al$(CH_3)_2$), 119.9 (Ar), 122.1 (Ar-H), 122.3 (Ar-H), 123.7 (Ar-H), 127.2 (Ar-H), 129.1 (Ar-H), 133.2 (Ar-Cl), 137.9 (Ar-Cl), 143.2 (Ar-N), 159.9 (Ar-O), 173.3 (N=CH). Calc: C 54.57% H 3.93% N 4.55% Found: C 54.36% H 3.93% N 4.43%.

Selected NMR Spectra:

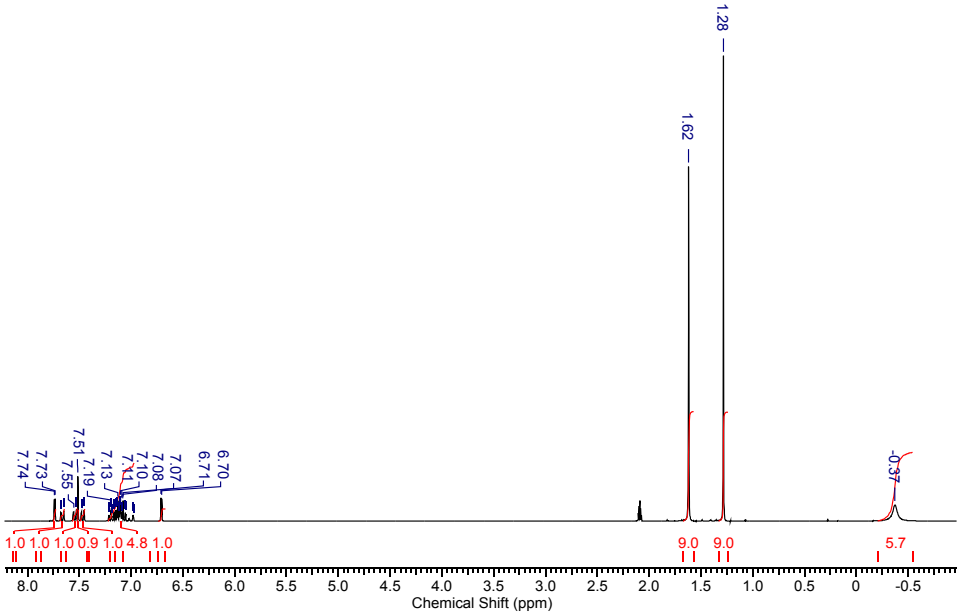


Figure SI1: ^{1}H NMR Al(**2**)Me_2

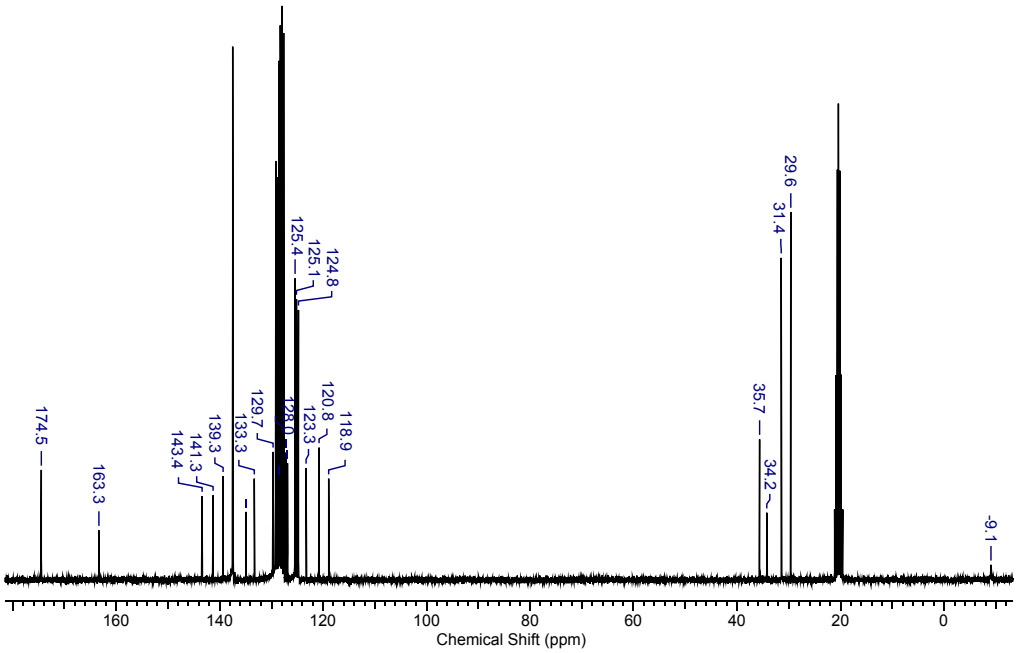


Figure SI2: $^{13}C\{^{1}H\}$ NMR Al(**2**)Me_2

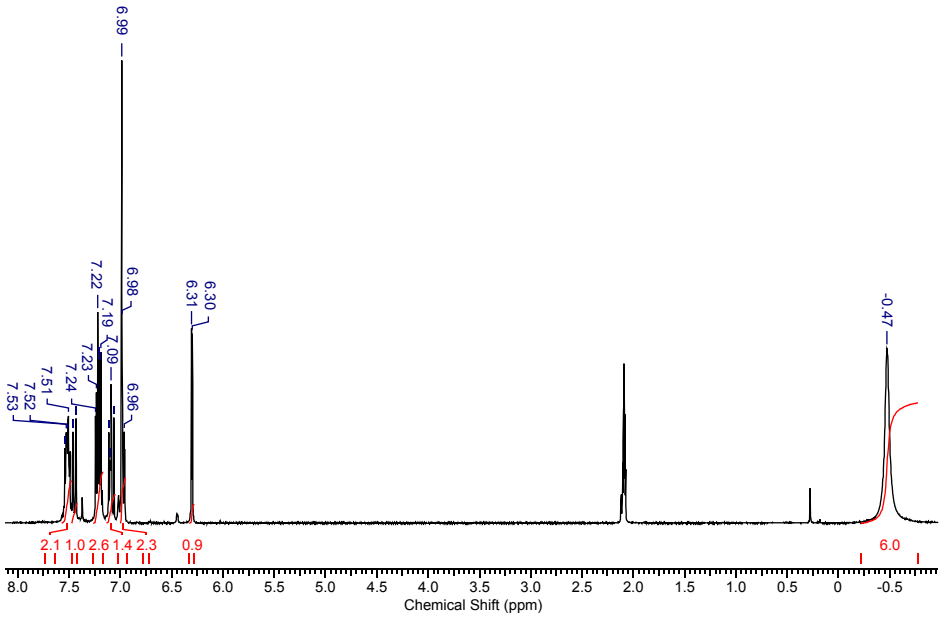


Figure SI3: ^{1}H NMR Al(**3**)Me_2

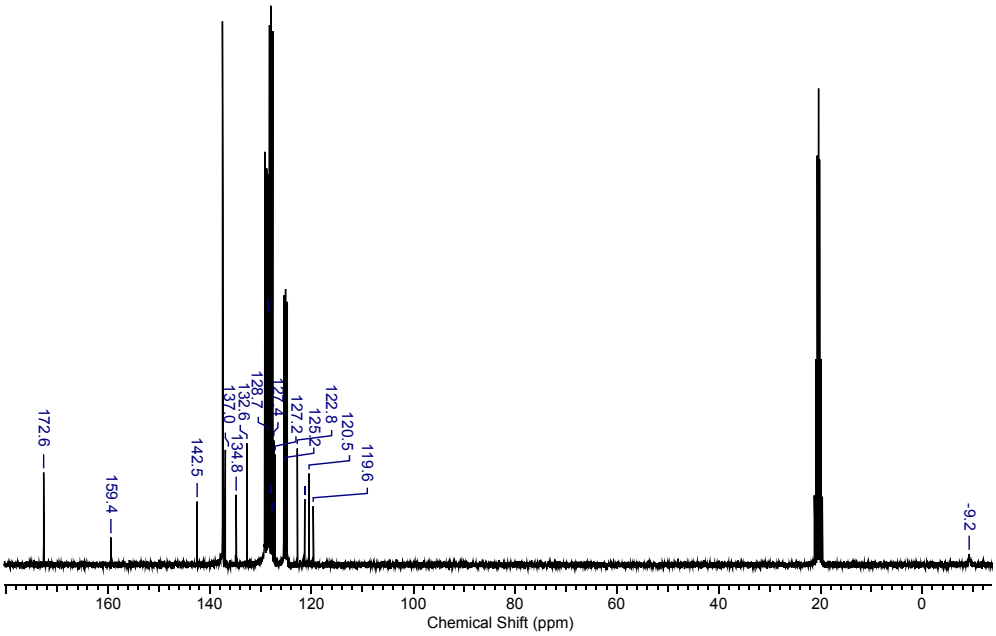


Figure SI4: $^{13}C\{^{1}H\}$ NMR Al(**3**)Me_2

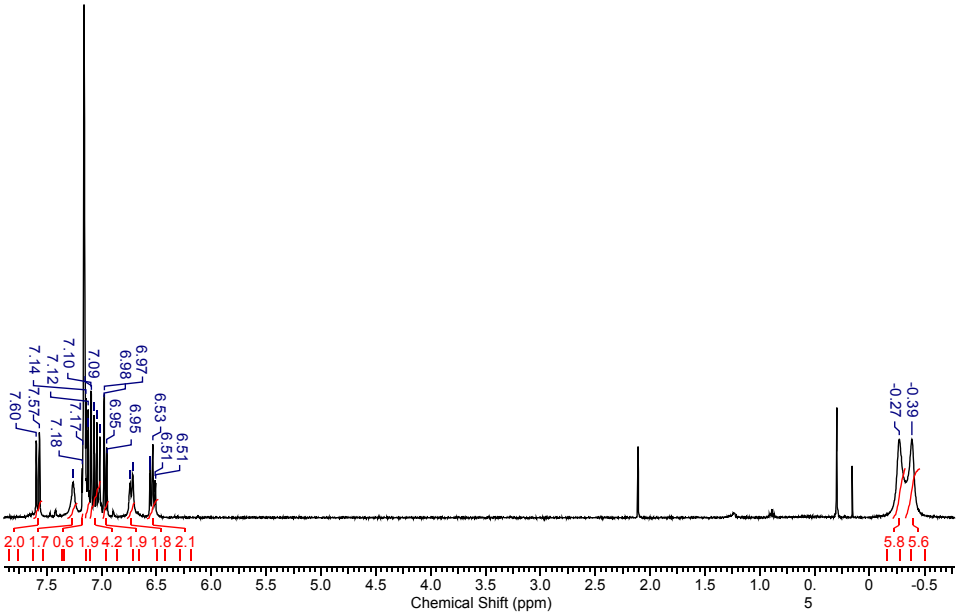


Figure SI5: ^{1}H NMR Al_2(**4**)Me_4

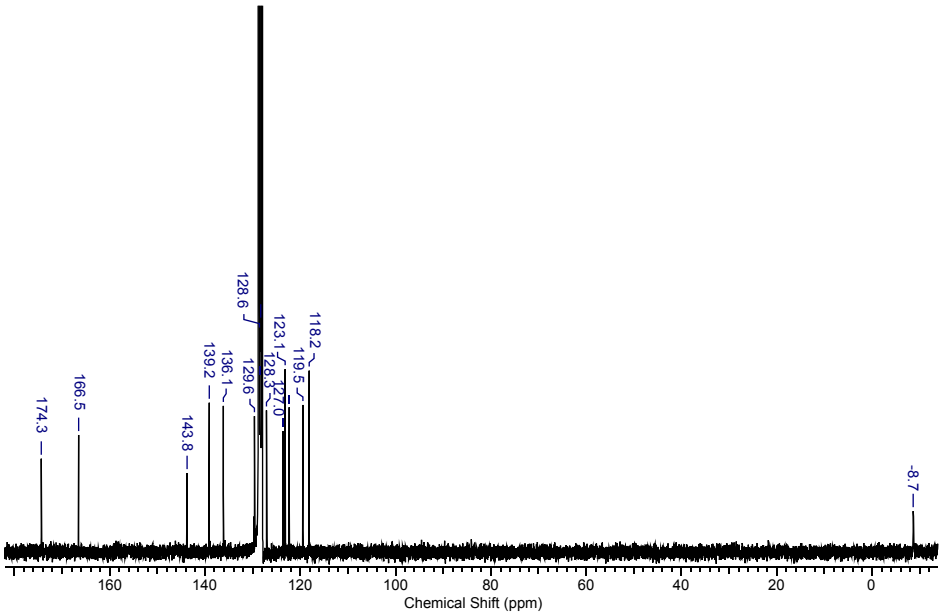


Figure SI6: $^{13}C\{^{1}H\}$ NMR Al_2(**4**)Me_4

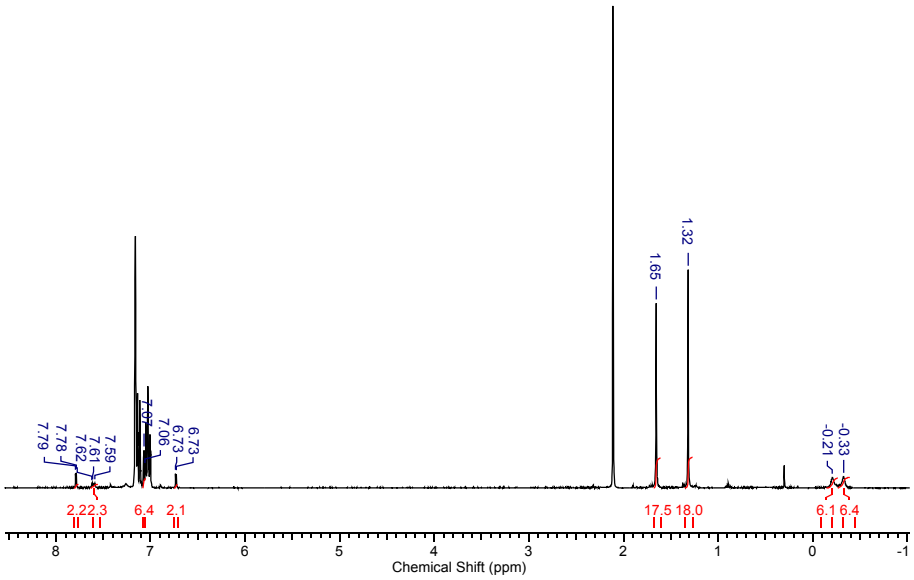


Figure SI7: ^{1}H NMR Al_2(**5**)Me_4

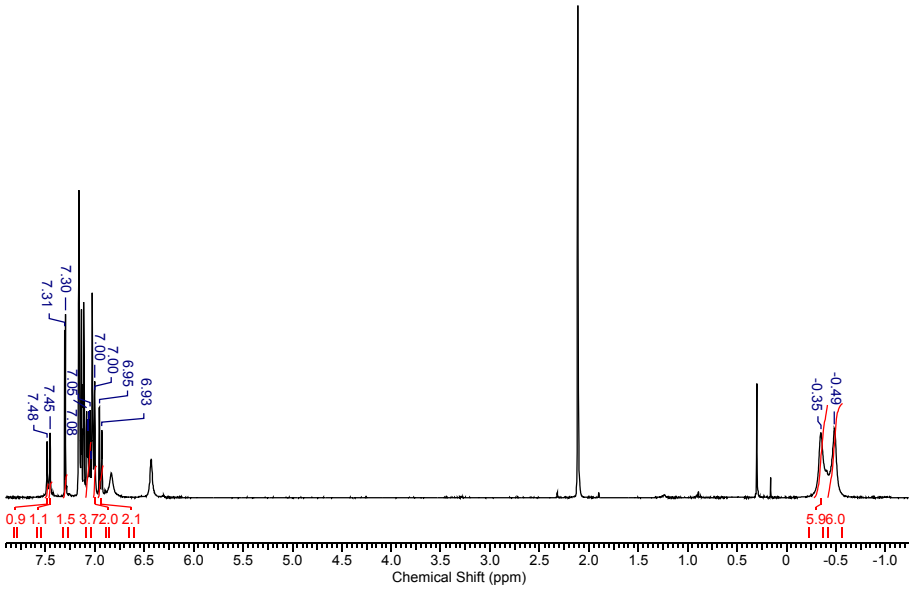


Figure SI8: ^{1}H NMR Al_2(**6**)Me_4

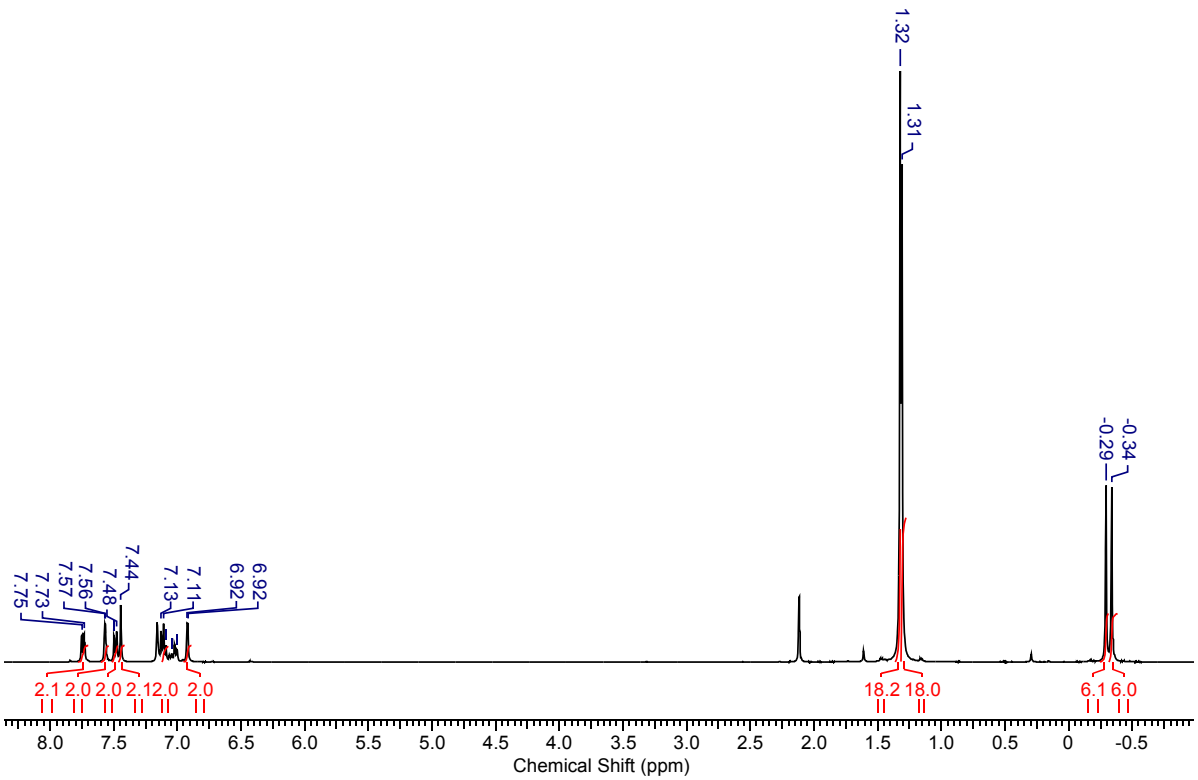


Figure SI9: ^{1}H NMR Al_2(**7**)Me_4

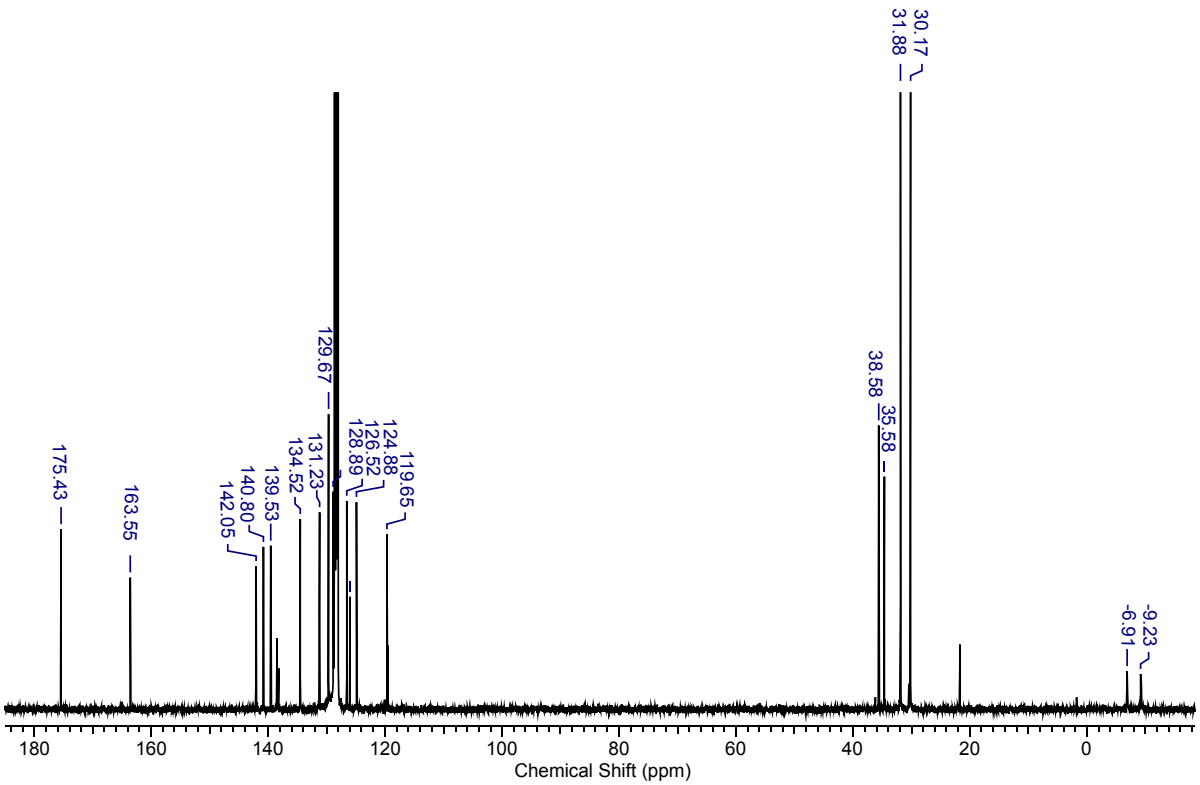


Figure SI10: $^{13}C\{^{1}H\}$ NMR Al_2(**7**)Me_4

Selected MALDI-ToF Mass Spectra

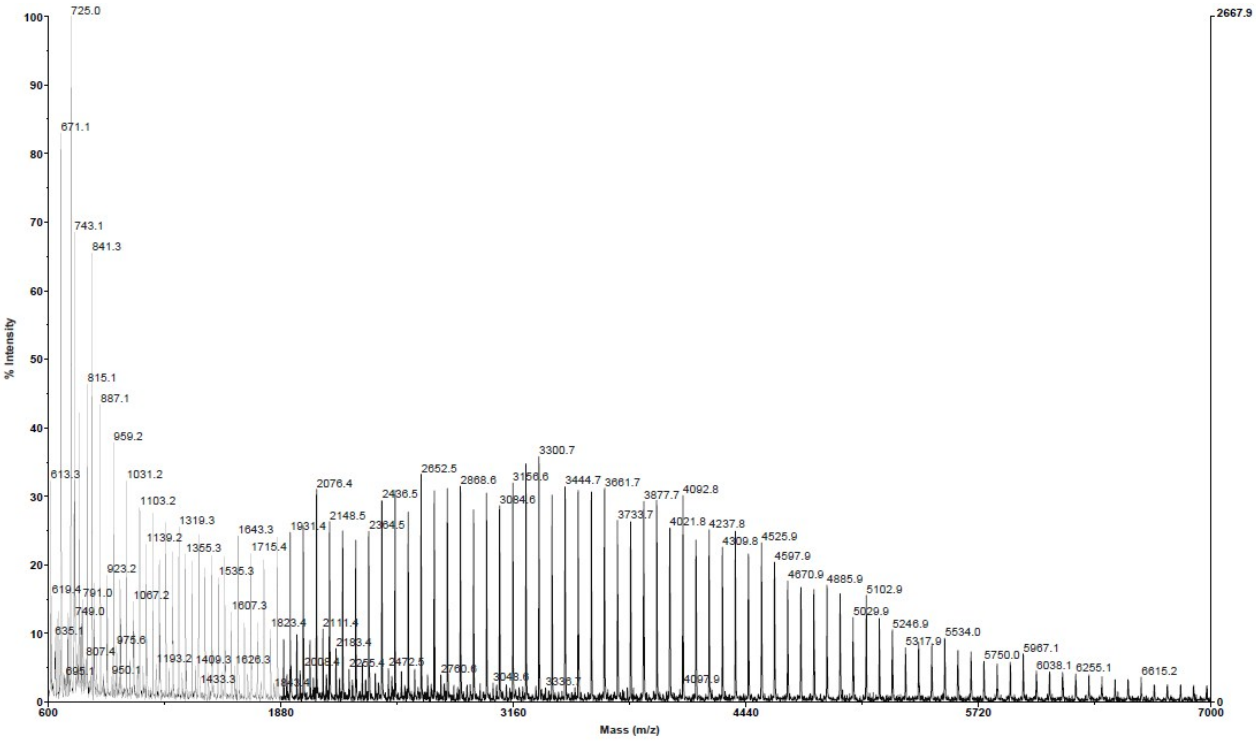


Figure SI11: MALDI-ToF MS data for PLA, Table 1 entry 19

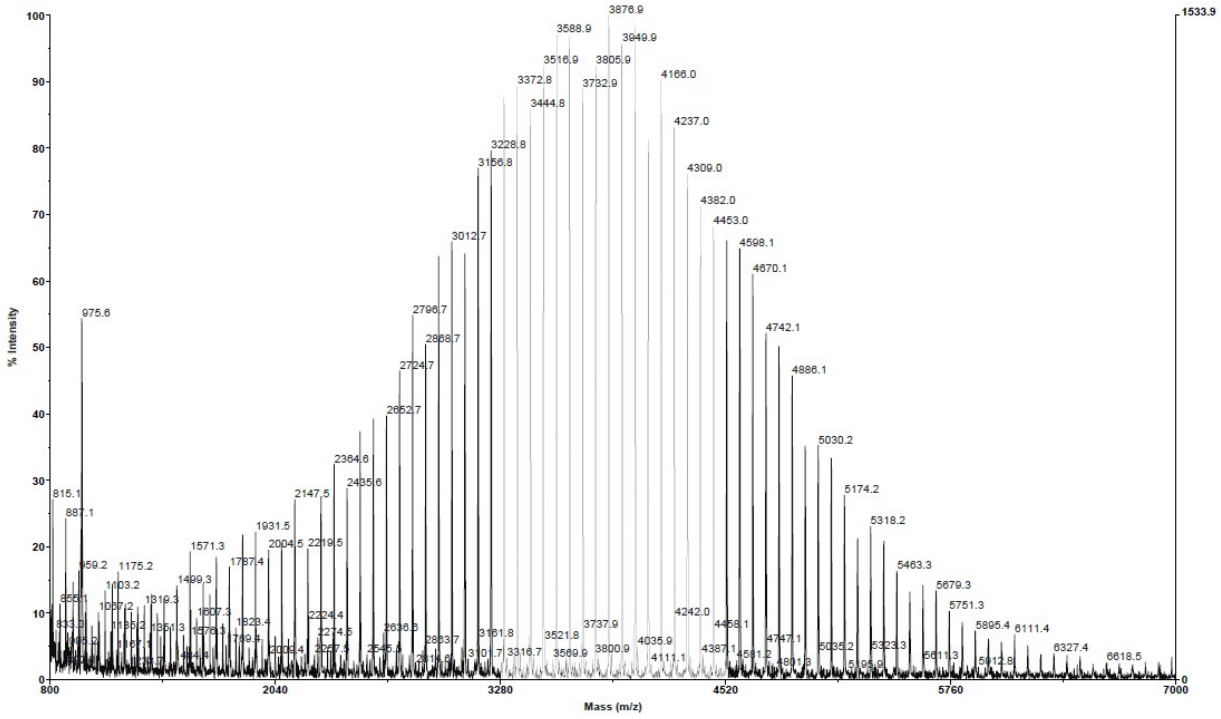


Figure SI12: MALDI-ToF MS for PLA, Table 1 entry 10. Take peak at 3876.9, (Na + ($C_6H_8O_4$) x 26 + 1 + C_7H_7O)

Further Kinetic Plots

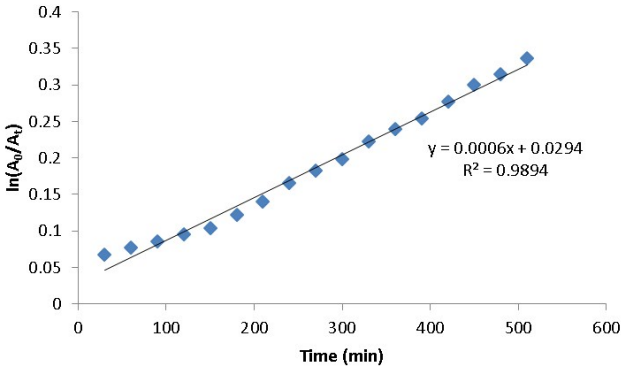


Figure SI13: Pseudo first order plot for the polymerisation of *rac*-LA using Al(**2**)Me_2 Table 1 entry 8.

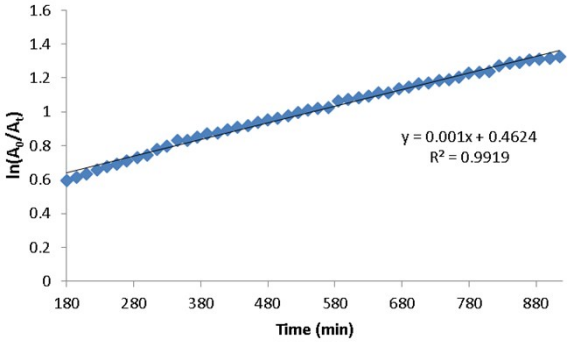


Figure SI14: Pseudo first order plot for the polymerisation of *rac*-LA using Al_2(**5**)Me_4 Table 1 entry 19.

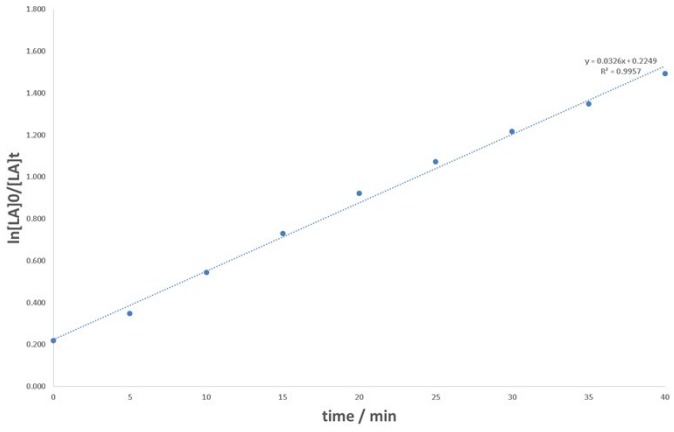


Figure SI15: Pseudo first order plot for the polymerisation of *rac*-LA using Al_2(**7**)Me_4 Table 1 entry 21.

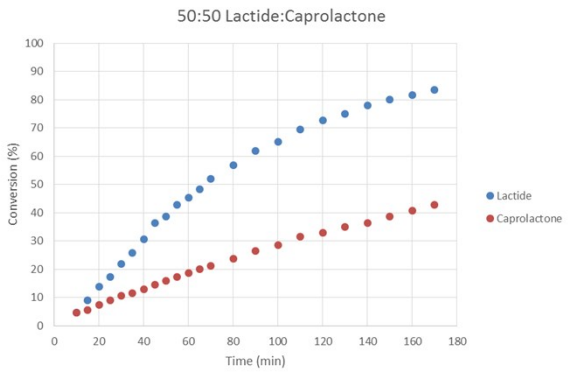


Figure SI16: Graph of conversion vs time for the 50:50 copolymerisation LA:CL with Al_2(**4**)Me_4 100:1:2. k_{app} LA = 0.011 $mins^{-1}$, k_{app} CL = 0.0032 $mins^{-1}$.

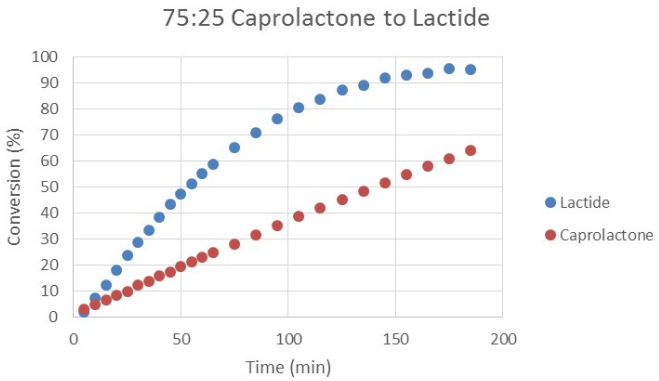


Figure SI17: Graph of conversion vs time for the 25:75 copolymerisation LA:CL with Al_2(**4**)Me_4 100:1:2. k_{app} LA = 0.015 $mins^{-1}$, k_{app} CL = 0.0044 $mins^{-1}$.

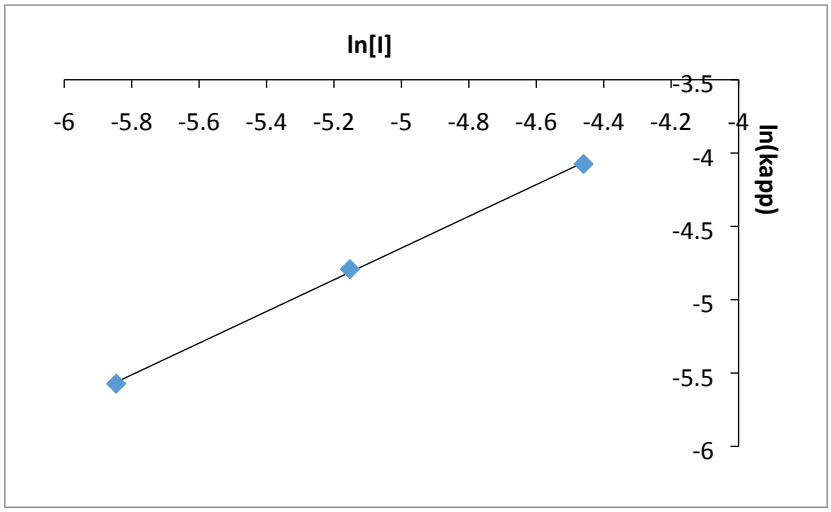


Figure SI18: Plot of ln(k_{app}) vs ln[I] for Al_2(**4**)Me_4 100:1:1

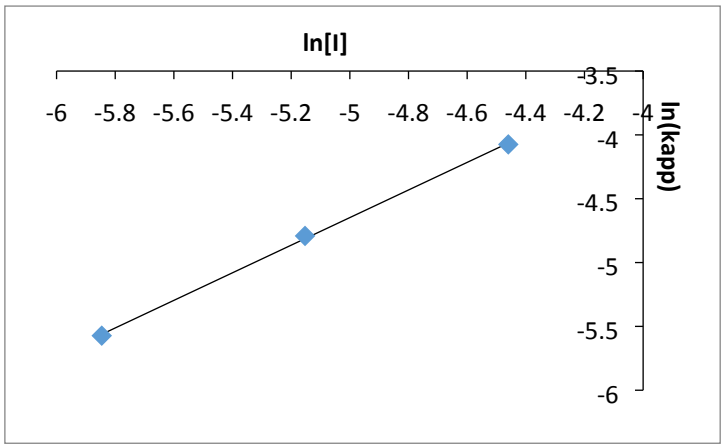


Figure SI19: Plot of ln(k_{app}) vs ln[I] for Al_2(**4**)Me_4 100:1:2

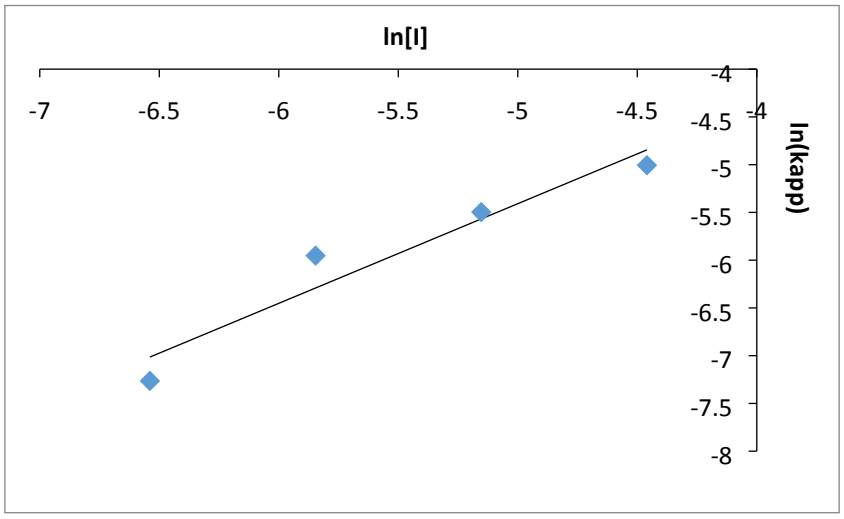


Figure SI20: Plot of ln(k_{app}) vs ln[I] for Al(**1**)Me_2 100:1:1

Selected Polymer NMR spectra

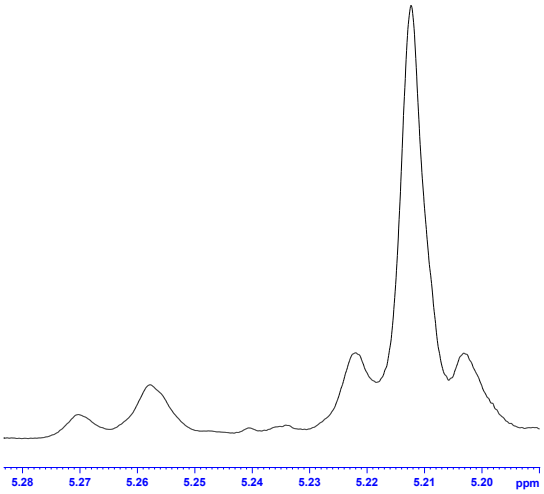


Figure SI21: ^{1}H homonuclear decoupled NMR of PLA prepared from Al_2(**7**)Me_4. Table 1 entry 21.

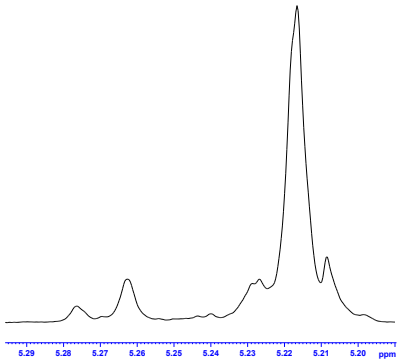


Figure SI22: ^{1}H homonuclear decoupled NMR of PLA prepared from Al_2(**7**)Me_4. Table 1 entry 22.

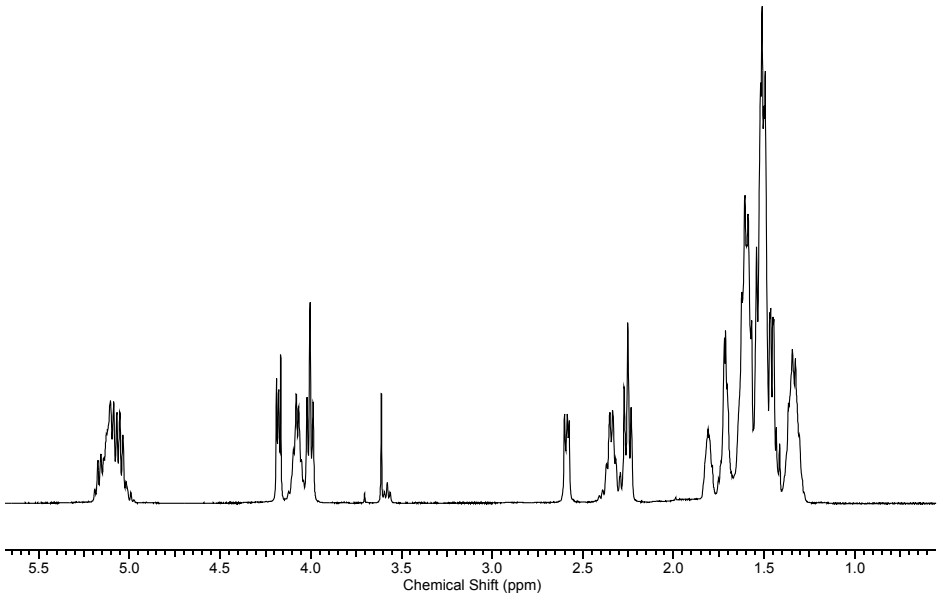


Figure SI23: ^{1}H NMR of the PLA-PCL co-polymer prepared with Al_2(**4**)Me_4. Table 2 entry 7.

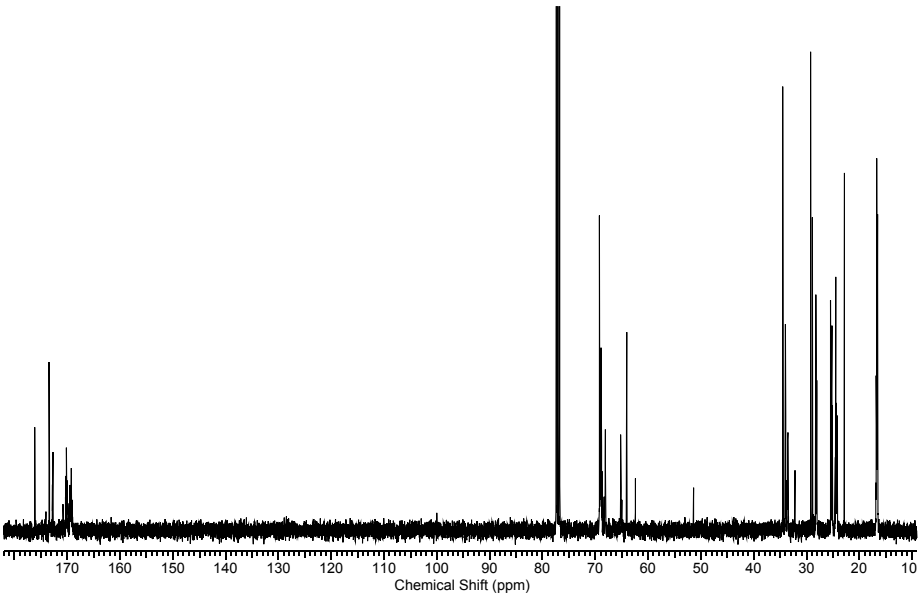


Figure SI24: $^{13}C\{^{1}H\}$ NMR of the PLA-PCL co-polymer prepared with Al_2(**4**)Me_4. Table 2 entry 7.

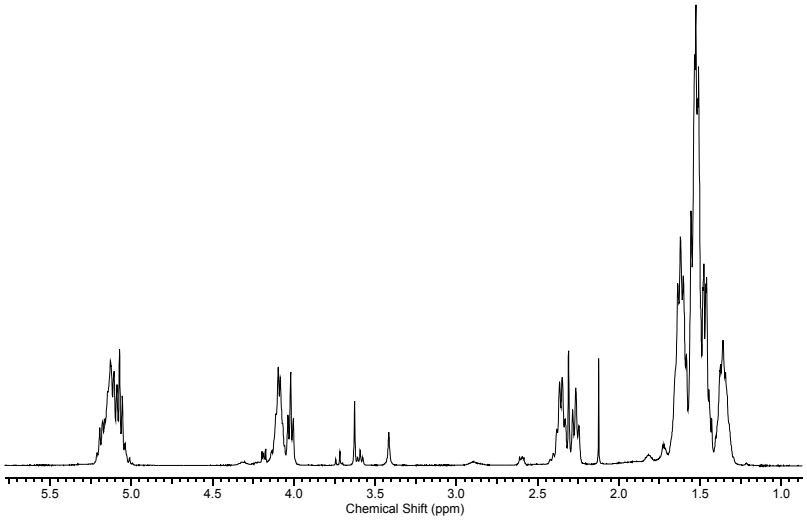


Figure SI25: ^{1}H NMR of the PLA-PCL co-polymer prepared with Al_2(**4**)Me_4. Table 2 entry 3.

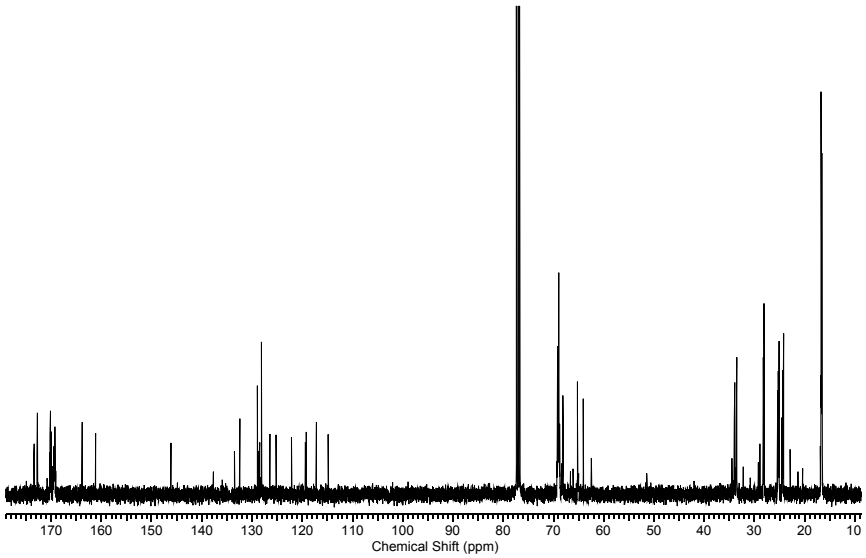


Figure SI26: $^{13}C\{^{1}H\}$ NMR of the PLA-PCL co-polymer prepared with Al_2(**4**)Me_4. Table 2 entry 3.

Selected GPC Data

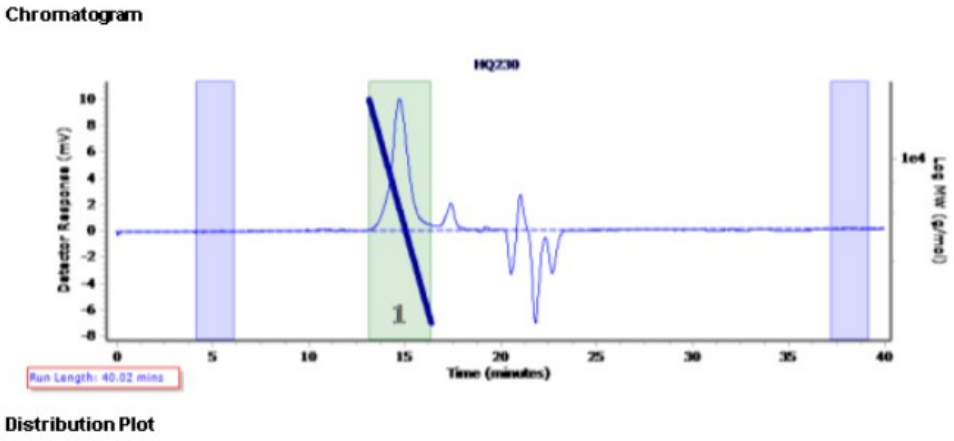


Figure SI27: GPC entry 21 Table 1

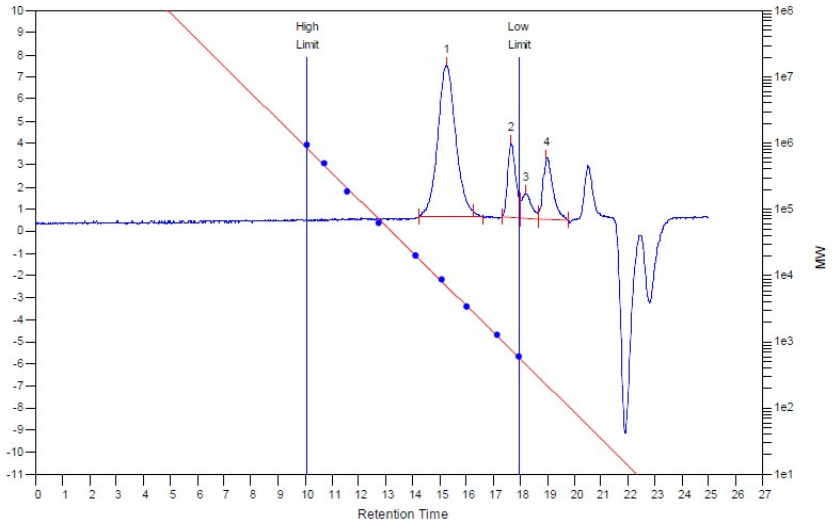


Figure SI28: GPC for PLA with Al_2(**4**)Me_4 entry 10 Table 1

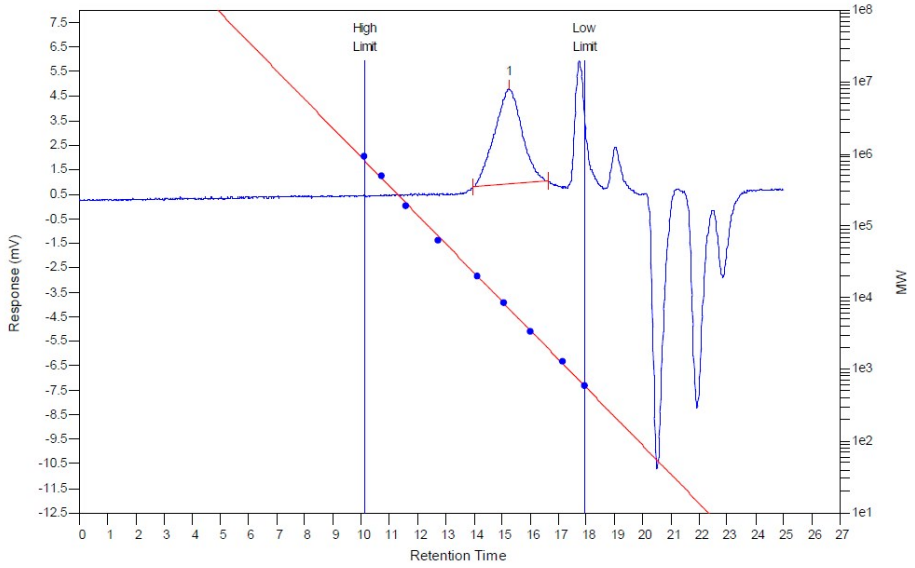


Figure SI29: GPC for PLA with Al_2(**5**)Me_4 entry 19 Table 1

Table 1 Crystallographic parameters

Compound reference	Al(**1**)Me_2	Al(**3**)Me_2	Al_2(**4**)Me_4	Al_2(**5**)Me_4	Al_2(**7**)Me_4
Chemical formula	$C_{19}H_{18}AlNO$	$C_{19}H_{16}AlCl_2NO$	$C_{35}H_{36}Al_2N_2O_2$	$C_{58}H_{76}Al_2N_2O_2$	$C_{51}H_{68}Al_2N_2O_2$
Formula Mass	303.32	372.21	570.62	887.17	795.03
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Triclinic
a/Å	14.2070(2)	7.14900(10)	9.0890(3)	14.1650(3)	12.6028(6)
b/Å	7.01600(10)	22.3190(3)	19.1017(7)	13.0700(3)	12.7588(6)
c/Å	32.8480(6)	22.6950(4)	9.1614(3)	14.7260(4)	16.5415(5)
α/°	90	90	90	90	109.990(4)
β/°	97.5650(10)	97.6340(10)	93.941(2)	101.7450(10)	107.578(4)
γ/°	90	90	90	90	90.572(4)
Unit cell volume/Å^3	3245.67(9)	3589.09(9)	1586.80(9)	2669.24(11)	2363.75(19)
Temperature/K	150(2)	150(2)	150(2)	150(2)	150(2)
Space group	*C*2/*c*	*P*2$_1$/*n*	*P*2$_1$/*c*	*P*2$_1$/*a*	***P*Error!**
No. of formula units per unit cell, *Z*	8	8	2	2	2
No. of reflections measured	22280	6294	16164	23401	16144
No. of independent reflections	3673	6294	2803	4696	16144
R_{int}	0.0583	-	0.0820	0.0746	-
Final R_1 values ($I > 2\sigma(I)$)	0.0430	0.1410	0.0622	0.0562	0.0542
Final $wR(F^2)$ values ($I > 2\sigma(I)$)	0.0969	0.3471	0.1401	0.1340	0.1698
Final R_1 values (all data)	0.0709	0.1613	0.0969	0.0869	0.0722
Final $wR(F^2)$ values (all data)	0.1103	0.3559	0.1595	0.1518	0.1885

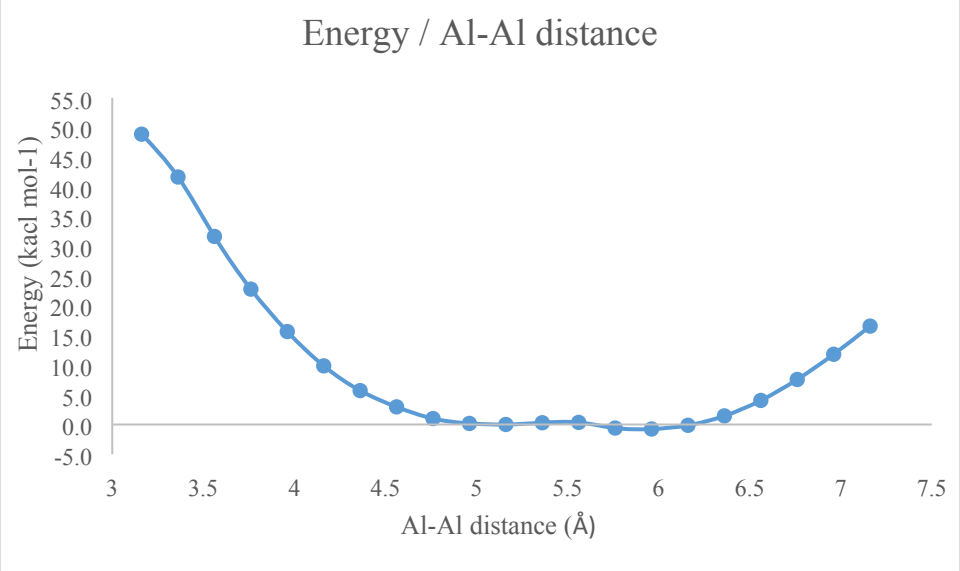
Comparison X-day structure/ DFT calculated

model: M06
6-311+g(d)[N,O,Al]/6-31+g(d) [C,H]
scrf(cpcm,solvent=toluene)
T=298.15K

distances in Å, angles in °	**X-ray**	**DFT Calculated**
Al1-Al2	5.358	5.16118
Al1-N1	1.972	1.98704
Al1-O1	1.774	1.80542
Al1-C1	1.962	1.96913
Al1-C2	1.958	1.96626
Al2-N2	1.974	1.98745
Al2-O2	1.775	1.80558
Al2-C3	1.960	1.96592
Al2-C4	1.963	1.96937
N1-C20-C26-N2	12.64	19.29533
C20-C19-N1-Al1	158.38	156.38442
C26-C30-N2-Al2	157.35	155.55865
C26-C20-N1-C19	-101.50	-113.42292
C20-C26-N2-C30	-102.11	-113.75044

Energy versus Al-Al distance

model: M06
6-31+g(d)
scrf(cpcm,solvent=toluene)
T=298.15K



Al1-Al2 distance (Å)	Energy (Hartree)	Energy (kcal mol^{-1})
7.161176	-2456.364622	16.6
6.961176	-2456.372181	11.8
6.761176	-2456.378939	7.6
6.561176	-2456.384568	4.1
6.361176	-2456.388717	1.4
6.161176	-2456.391248	-0.1
5.961176	-2456.392241	-0.8
5.761176	-2456.391986	-0.6
5.561176	-2456.390472	0.3
5.361176	-2456.390559	0.3
5.161176	-2456.391027	0.0
4.961176	-2456.390746	0.2
4.761176	-2456.389441	1.0
4.561176	-2456.3863	3.0
4.361177	-2456.381934	5.7
4.161176	-2456.37529	9.9
3.961177	-2456.366087	15.6
3.761177	-2456.354699	22.8
3.561177	-2456.340551	31.7
3.361177	-2456.324596	41.7
3.161177	-2456.313104	48.9