SUPPORTING INFORMATION

Make or Break: Mg(II)- and Zn(II)-Catalen Complexes for PLA Production and Recycling of Commodity Polyesters

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Contents

1. General Experimental Methods:

The synthesis and characterisation of all metal-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. Commercial PLA samples were purchased (Vegware™; R600Y-VW). PET coke bottles were sourced from a local grocery store (Fresh, University of Bath), rinsed with acetone and air-dried prior to use. PET thin-films represent waste from the manufacturing sector. All dry solvents used in handling all metal complexes were obtained *via* SPS (solvent purification system). ^{1}H and ^{13}C{^{1}H} NMR spectra were obtained on either a Bruker 400 or 500 MHz spectrometer and referenced to residual solvent resonances.[1] HSQC experiments were run on a Bruker 500 MHz spectrometer. Coupling constants (*J*) are provided in Hertz (Hz) to the nearest integer. CDCl$_3$ was dried over CaH$_2$ prior to use with all metal complexes. C$_6$D$_6$ was degassed and stored over molecular sieves for use with all metal 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.

Single crystal X-ray data was collected on an EOS SuperNova diffractometer with Cu Kα radiation (λ = 1.54184 Å) at 150(2) K unless otherwise stated. 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 of *rac*-LA

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, 6.94 mmol) to which the required amount of metal complex and benzyl alcohol (BnOH) co-initiator were loaded in a glovebox (2.4 μL, 0.023 mmol) {[*rac*-LA]:[M]:[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 resulted in significant slowing of the stirrer bar. Mass-transfer limitations resulted in a conversion plateau between 60 – 70% (Table 1). 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, maintaining a constant [*rac*-LA]:[BnOH] ratio {[*rac*-LA]:[M]:[BnOH] = 3000:1:10}. For solution polymerisations, *rac*-LA (0.5 g, 3.47 mmol) was dissolved in anhydrous toluene (5 mL) with the required amount of metal complex and BnOH (3.6 μL, 0.035 mmol). The flask was then placed in a preheated oil bath (80 °C) and stirred for the required amount of time. 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. *N.B.* [Zn(**1-3**)]$_2$ and [Mg(**1,3**)]$_2$ were treated as monomeric to ensure one -OBn moiety per metal centre.

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.*[2] 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.

1.1.1. Polymerisation Kinetics

Kinetic analysis was performed as described for the solution polymerisation procedure in section 1.1. {toluene, 80 °C, [*rac*-LA]:[M]:[BnOH] = 100:1:1}. Aliquots were taken under a dynamic flow of Ar in equal intervals across the total reaction time. Plotting ln([LA]$_0$/[LA]$_t$) against time afforded a straight line fit with the gradient equivalent to the pseudo-first-order rate constant (k_{app}).

1.2. PLA Degradation

Degradation reactions were performed in a Young's ampoule under argon. The flask was loaded with metal complex (4 - 8 wt%, 0.01 – 0.02 g) in a Glovebox to which PLA (0.25 g, Vegware^{TM}, PLLA cup, M_n = 45,510 g mol^{-1}) was added under a flow of argon. The polymer was then dissolved in THF (4 mL) with heating and stirring assisting dissolution. The flask was then submerged in a preheated oil bath (80 °C) to which MeOH (1 mL) was added. Aliquots were taken for ^{1}H NMR (CDCl$_3$) analysis of the methine region. After the reaction, the solvent was removed *in vacuo* and the residual methyl lactate (Me-La) was analysed further. This procedure was repeated for degradation reactions conducted in dry toluene (4 mL).

1.2.1. Degradation Kinetics

Reaction kinetic analysis was performed as described for the degradation procedure in section 1.2. [Mg(**1**)]$_2$ was tested at 4 and 8 wt% respectively (0.01 – 0.02 g, 0.29 – 0.57 mol% relative to ester linkages) in THF, whilst [Zn(**1**)]$_2$ was investigated at the latter (8 wt%, 0.02 g, 0.53 mol% relative to ester linkages) in dry toluene. Aliquots were taken to obtain a minimum of 5 data points across the total reaction time. The pseudo-first-order constant (k_{app}) was determined by plotting ln([Int]$_0$/[Int]$_t$) against time.

1.3. PET Degradation

Degradation reactions were performed in a Young's ampoule under argon. The flask was charged with metal complex (8 wt%, 0.02 g) and PET (0.25 g, Coke bottle, The Coca-Cola Company, M_n ~ 40,000 g mol^{-1}) in a Glovebox. The flask was evacuated for 30 minutes *in vacuo* and purged with three argon-vacuum cycles. EG (2 mL, 27.5 equivalents) was added under a flow of argon before submerging the flask in a preheated oil bath at 180 °C and stirred for the desired amount of time or until complete dissolution of PET was observed. Following this the flask was removed and allowed to cool for a few minutes after which deionised H$_2$O

(5 mL) was added, the flask vigorously shaken and rapidly filtered. The flask was rinsed with an additional portion of deionised H_2O (5 mL), which was used to stir the filter cake. The filtrate was retained and refrigerated (*ca.* 4 °C) for 18 h. White needle-like crystals were isolated by filtration, washed with deionised H_2O (2 x 1 mL) and dried *in vacuo* at 90 °C for 3 h. This method was repeated for PET thin-films (waste from manufacturing sector).

2. Synthesis and Characterisation:

2.1. Ligand Precursor

A^{TD}:
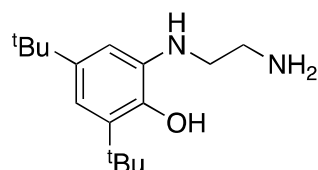
To a solution of 3,5-di-tert-butylcatechol (3.0 g, 13.5 mmol) in CH_3CN (20 mL), ethylenediamine (0.9 mL, 13.5 mmol) in MeCN (2 mL) was added dropwise with stirring and then refluxed at 100 °C for 1 h. The solution was allowed to cool to room temperature slowly and then stirred for 3 h to afford a light blue precipitate, which was isolated by filtration, washed with MeCN (10 mL) and air-dried.
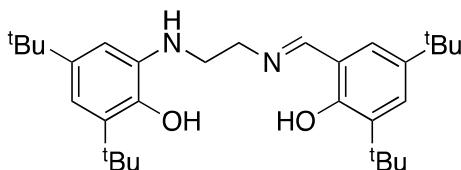
^{1}H NMR ($CDCl_3$, 400 MHz): δ = 6.97 (s, 1H; ArH), 6.86 (s, 1H; ArH), 3.13 (t, J = 5 Hz, 2H; CH_2), 2.86 (t, J = 6 Hz, 2H; CH_2), 1.42 (s, 9H; $C(CH_3)_3$) and 1.28 (s, 9H; $C(CH_3)_3$).

^{13}C$\{^1$H$\}$ NMR ($CDCl_3$, 100 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 **A**^{TD} (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$_3$)$_3$). *N.B.* Relative peak area of -OH lower than expected owing to peak broadening, resulting in lower signal intensity.

^{13}C{^{1}H} NMR (CDCl$_3$, 100 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, 29.6 (CH$_3$).

Yield = 0.78 g, 86%
ESI-MS (+ve, MeCN): Calculated m/z [C$_{31}$H$_{49}$N$_2$O$_2$]$^+$ = 481.3794; found m/z = 481.3927

2H$_2$:
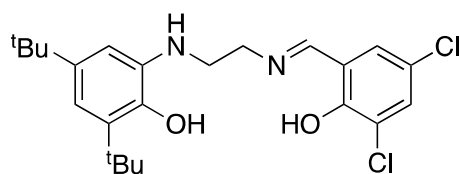
To a solution of **A**^{TD} (0.67 g, 2.53 mmol) dissolved in MeCN (20 mL), 3,5-dicholoro-2-hydroxybenzaldehyde (0.48 g, 2.53 mmol) was added portion wise and the solution stirred for 30 minutes at RT. The solvent was removed *in vacuo*, replaced with *n*-hexane (10 mL) and stirred for 1 hour. A yellow 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$_3$)$_3$). *N.B.* Relative peak area of -OH lower than expected owing to peak broadening, resulting in lower signal intensity.

^{13}C{^{1}H} NMR (C$_6$D$_6$, 125 MHz): δ = 164.8 (ArCHN), 157.3, 142.2 132.5, 129.3, 123.4, 122.6, 119.7, 118.6, 115.9 (Ar), 58.2, 47.6 (CH$_2$), 35.1, 34.6 (C(CH$_3$)$_3$), 32.0, 30.0 (CH$_3$). *N.B.* Unaccounted for Ar resonances indicative of fluxionality on the ^{13}C{^{1}H} timescale, resulting in poor signal intensity.

Yield = 0.70 g, 63%
ESI-MS (+ve, MeCN): Calculated m/z [C$_{23}$H$_{31}$Cl$_2$N$_2$O$_2$]$^+$ = 438.1796; found m/z = 438.1786

3H$_2$:
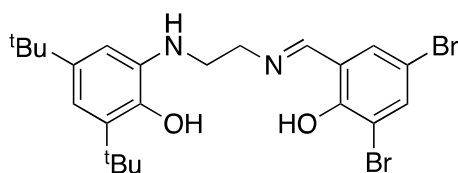
To a solution of $\mathbf{A}^{TD}$ (0.67 g, 2.53 mmol) dissolved in MeCN (20 mL), 3,5-dibromo-2-hydroxybenzaldehyde (0.71 g, 2.53 mmol) was added portion wise and the solution stirred for 30 minutes at RT. The solvent was removed *in vacuo*, replaced with *n*-hexane (10 mL) and stirred for 1 hour. A 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$_3$)$_3$). *N.B.* Relative peak area of -OH lower than expected owing to peak broadening, resulting in lower signal intensity.

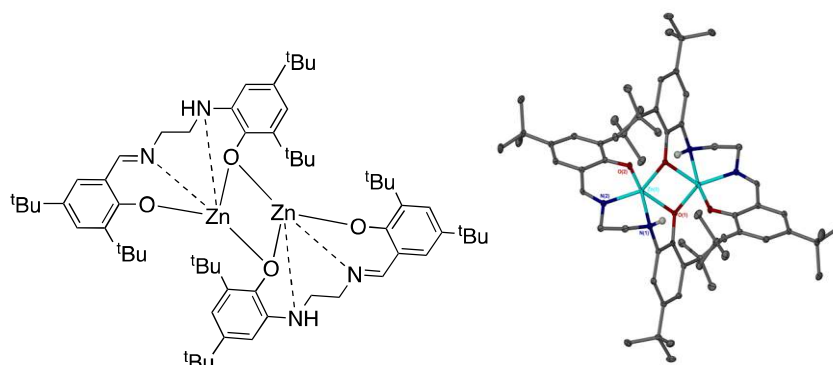^{13}C{^{1}H} NMR (CDCl$_3$, 100 MHz): δ = 164.9 (ArCHN), 145.3, 142.4, 138.0, 133.0, 114.6, 112.9, 109.4 (Ar), 47.3 (CH$_2$), 36.5, 34.8 (C(CH$_3$)$_3$), 31.8, 29.9 (CH$_3$). *N.B.* Unaccounted for CH$_2$ and Ar resonances indicative of fluxionality on the ^{13}C{^{1}H} timescale, resulting in poor signal intensity.

Yield = 0.83 g, 84%
ESI-MS (+ve, MeCN): Calculated m/z [C$_{23}$H$_{31}$Br$_2$N$_2$O$_2$]$^+$ = 527.0732; found m/z = 527.0869

2.3. Zn(II)-Catalen Complexes

[Zn(**1**)]$_2$:

To a precooled solution of **1**H$_2$ (0.48 g, 1 mmol) in dry toluene (10 mL) at 0 °C, ZnEt$_2$ (1 mL, 1 mmol, 1.0 M in hexane) was added dropwise with stirring. The solution was allowed to gradually warm to room temperature, resulting in a green precipitate. The precipitate was redissolved upon gentle heating and the solution stirred for a further 30 minutes at room temperature. Pale green crystals were isolated by cannula filtration and dried *in vacuo* at 80 °C for 4 hours.

^{1}H NMR (CDCl$_3$, 500 MHz): δ = 8.17 (s, 1H; ArCHN), 7.24 (d, *J* = 2 Hz, 1H; ArH), 7.00 (s, 1H; ArH), 6.95 (s, 1H; ArH), 6.73 (d, *J* = 2 Hz, 1H; ArH), 4.44 (s, 1H; NH), 4.07 (m, 1H; CH), 3.87 (m, 1H; CH), 3.66 (m, 2H; CH$_2$), 1.36 (s, 9H; C(CH$_3$)$_3$), 1.24 (s, 9H; C(CH$_3$)$_3$), 1.22 (s, 9H; C(CH$_3$)$_3$), 1.20 (s, 9H; C(CH$_3$)$_3$).

^{13}C{^{1}H} NMR (CDCl$_3$, 100 MHz): δ = 170.9 (ArCHN), 169.0, 155.9, 140.6, 138.5, 137.8, 134.2, 132.7, 129.6, 129.0, 120.3, 117.4, 116.7 (Ar), 53.1, 44.6 (CH$_2$), 35.3, 35.1, 34.4, 33.8 (C(CH$_3$))$_3$, 31.8, 31.5, 30.3, 29.8 (CH$_3$).

Elemental analysis: Calculated for C$_{62}$H$_{92}$N$_4$O$_4$Zn$_2$: C; 68.43 %; H; 8.52 %; N; 5.15 %. Found: C; 67.34 %; H, 8.32 %; N, 5.18 %

Yield = 0.45 g, 83%

[Zn(**2**)]₂:
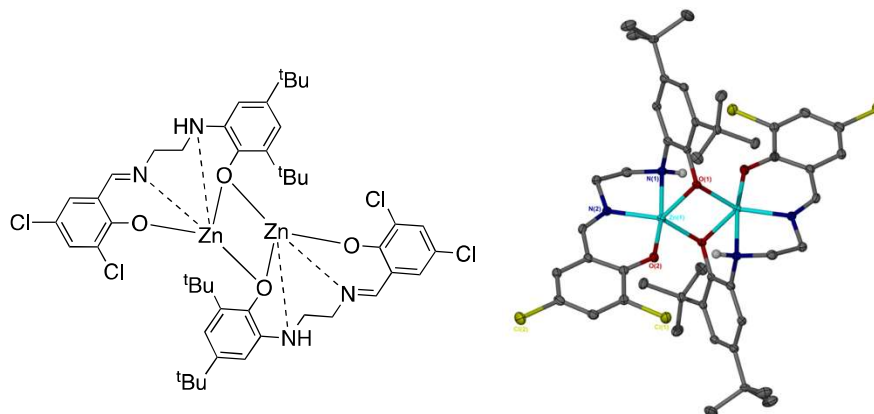
To a solution of **2**H₂ (0.44 g, 1 mmol) in dry toluene (10 mL), ZnEt₂ (1 mL, 1 mmol, 1.0 M in hexane) was added dropwise at room temperature and the resulting solution stirred for 30 minutes. A pale-yellow solid precipitated, which was then redissolved upon heating prior to isolation by cannula filtration and dried *in vacuo* at 80 °C for 4 hours.

^{1}H NMR (CDCl₃, 500 MHz): δ = 8.09 (s, 1H; ArCHN), 7.18 (s, 1H; ArH), 7.16 (d, *J* = 3 Hz, 1H; ArH), 7.00 (d, *J* = 2 Hz, 1H; ArH), 6.80 (d, *J* = 3 Hz, 1H; ArH), 4.75 (s, 1H; NH), 3.82 (m, 1H; CH), 3.73 (m, 2H; CH₂), 3.56 (m, 1H; CH), 1.31 (s, 9H; C(CH₃)₃), 1.27 (s, 9H; C(CH₃)₃).

^{13}C{^{1}H} NMR (CDCl₃, 125 MHz): δ = 168.4 (ArCHN), 164.6, 156.1, 139.1, 137.6, 132.8, 131.9, 131.9 128.0, 120.8, 118.5, 117.0, 115.8 (Ar), 52.9, 44.6 (CH₂), 35.3, 34.5 (C(CH₃)₃), 31.9, 29.9 (CH₃).

Elemental analysis: Calculated for C₄₆H₅₆Cl₄N₄O₄Zn₂: C; 55.17 %; H; 5.64 %; N; 5.59 %. Found: C; 53.50 %; H, 5.42 %; N, 5.51 %

Yield = 0.40 g, 80%

[Zn(**3**)]₂:
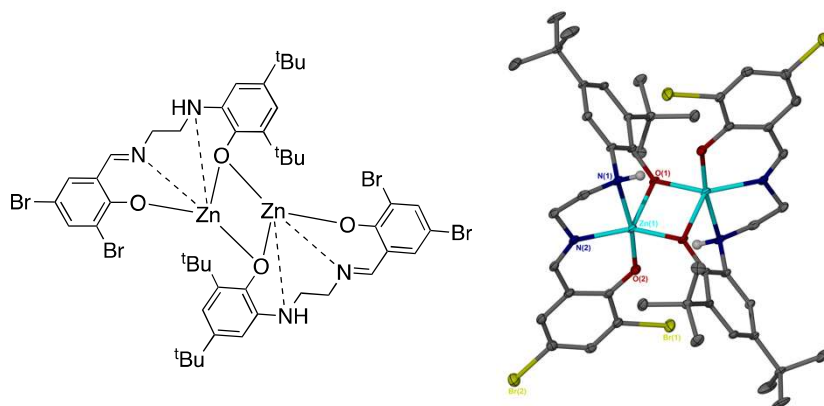
To a solution of **3**H₂ (0.53 g, 1 mmol) in dry toluene (10 mL), ZnEt₂ (1 mL, 1 mmol, 1.0 M in hexane) was added dropwise with stirring and then stirred at 90 °C for 45 minutes. A yellow solid was isolated by cannula filtration and dried *in vacuo* at 80 °C for 4 hours.

^{1}H NMR (CDCl₃, 500 MHz): δ = 8.06 (s, 1H; ArCHN), 7.46 (s, 1H; ArH), 7.17 (s, 1H; ArH), 7.01 (s, 1H; ArH), 6.98 (s, 1H; ArH), 4.80 (s, 1H; NH), 3.86 (m, 3H; CH₂, CH), 3.65 (m, 1H; CH), 1.31 (s, 9H; C(CH₃)₃), 1.28 (s, 9H; C(CH₃)₃).
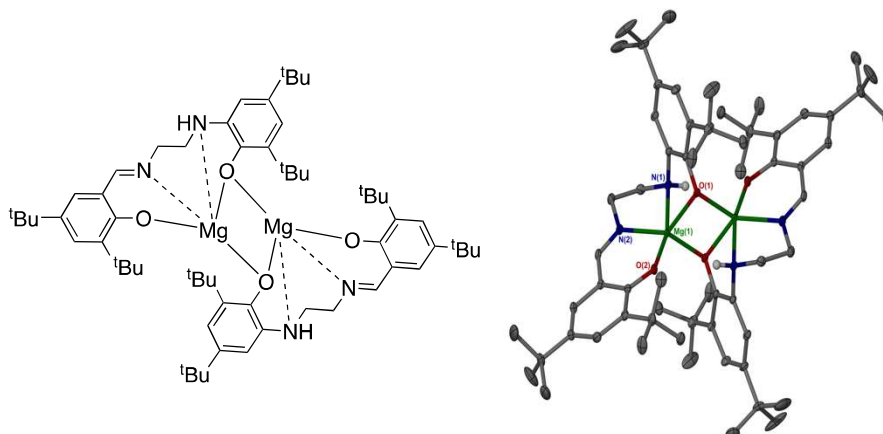
^{13}C{^{1}H} NMR (CDCl₃, 100 MHz): δ = 168.37 (ArCHN), 165.4, 156.1, 139.1, 138.3, 137.7, 135.9, 131.8, 120.8, 119.4, 119.2, 117.2, 102.6 (Ar), 52.8, 44.5 (CH₂), 35.3, 34.5 (C(CH₃)₃), 31.9, 29.9 (CH₃).

Elemental analysis: Calculated for C₄₆H₅₆Br₄N₄O₄Zn₂: C; 46.85 %; H; 4.79 %; N; 4.75 %. Found: C; 44.66 %; H, 4.40 %; N, 4.68 %

Yield = 0.52 g, 88%

2.4. Mg(II)-Catalen Complexes

[Mg(**1**)]₂:

To a precooled solution of **1**H₂ (0.48 g, 1 mmol) in dry toluene (10 mL) at 0 °C, Mg(^{n}Bu)₂ (1 mmol, 1 mL, 1.0 M in *n*-heptane) was added dropwise with stirring. The solution was gradually warmed to room temperature and stirred for 30 minutes. Yellow crystals were isolated after 3 days at -20 °C. Following XRD analysis, the solvent volume was reduced by two thirds and stored at -20 °C for 18 hours to enhance yield. A yellow solid was isolated by cannula filtration and dried *in vacuo* at 80 °C for 3 hours.

^{1}H NMR (CDCl₃, 500 MHz): δ = 8.13 (s, 1H; ArCHN), 7.24 (d, J = 2 Hz, 1H; ArH), 7.00 (s, 1H; ArH), 6.96 (d, J = 2 Hz, 1H; ArH), 6.81 (d, J = 2 Hz, 1H; ArH), 4.22 (s, 1H; NH), 3.95 (m, 1H; CH), 3.84 (m, 1H; CH), 3.70 (m, 1H; CH), 3.54 (m, 1H; CH), 1.33 (s, 9H; C(CH₃)₃), 1.22 (s, 9H; C(CH₃)₃), 1.21 (s, 18H; C(CH₃)₃).
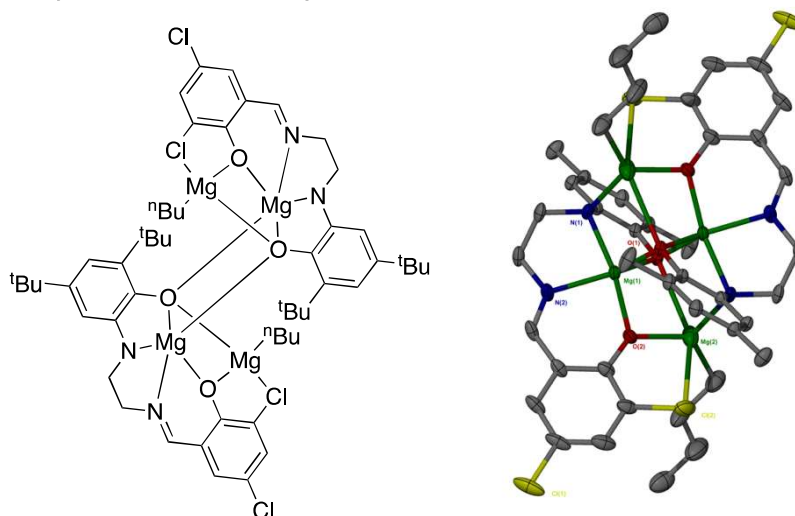
^{13}C{^{1}H} NMR (CDCl₃, 125 MHz): δ = 171.2 (ArCHN), 167.5, 155.0, 139.9, 138.8, 138.0, 133.9, 132.3, 129.2, 128.8, 121.0, 119.5, 116.9 (Ar), 54.6, 45.6 (CH₂), 35.1, 35.1, 34.4, 33.8 (C(CH₃)₃), 31.8, 31.6, 30.4, 29.6 (CH₃).

Calculated for $C_{62}H_{92}N_4O_4Mg_2$: C; 74.02 %; H; 9.22 %; N; 5.57 %. Found: C; 72.06 %; H, 9.22 %; N, 5.05 %
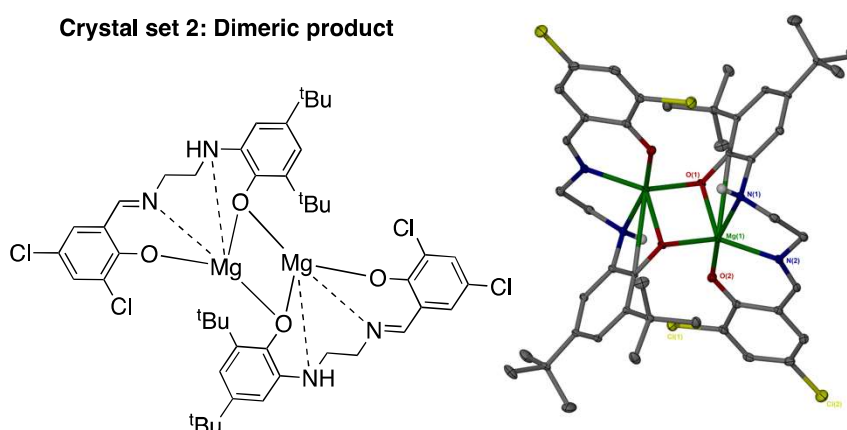
Yield = 0.12 g, 24%

[Mg(**2**)]₂:

Crystal set 1: Tetrameric product

Crystal set 2: Dimeric product

To a solution of **2**H₂ (0.44 g, 1 mmol) in dry toluene (10 mL), Mg(ⁿBu)₂ (1 mL, 1 mmol, 1.0 M in *n*-heptane) was added dropwise with stirring at room temperature and the resulting solution stirred for 30 minutes. Crystal set 1 was observed after 10 days at RT. The solution was concentrated *in vacou* with stirring to *ca.* 5 mL. Crystal set 2 was observed after 3 hours at RT. Crystal set 2 was isolated by cannula filtration and dried *in vacou* at 80 °C for 3 hours to afford a light-yellow solid.
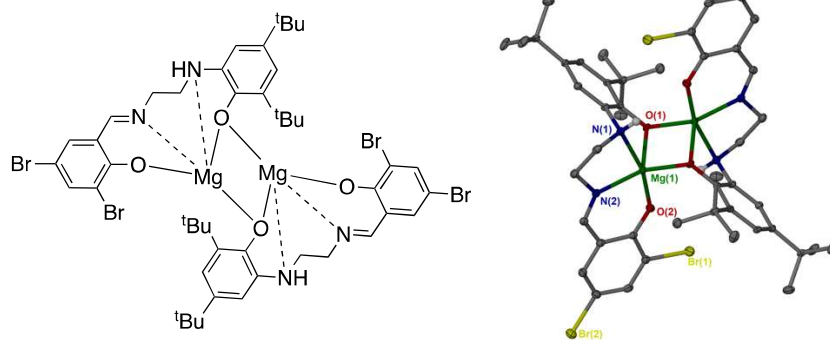
^{1}H NMR (CDCl₃, 500 MHz): δ = 8.06 (s, 1H; ArCHN), 7.20 (s, 1H; ArH), 7.14 (s, 1H; ArH), 7.02 (s, 1H; ArH), 6.87 (s, 1H; ArH), 4.59 (s, 1H; NH), 3.79 (m, 4H; CH₂), 1.29 (s, 9H; (C(CH₃)₃), 1.27 (s, 9H; C(CH₃)₃).

^{13}C{^{1}H} NMR (CDCl₃, 125 MHz): δ = 168.7 (ArCHN), 163.3, 160.1, 155.3, 139.4, 137.9, 132.8, 131.7, 131.7, 121.3, 120.6, 117.0, 115.7 (ArH), 54.4, 45.4 (CH₂), 35.1, 34.5 (C(CH₃)₃), 31.9, 30.2 (CH₃).

Calculated for C₄₆H₅₆Cl₄Mg₂N₄O₄: C; 60.09 %; H; 6.14 %; N; 6.09 %. Found: C; 44.70 %; H, 4.43 %; N, 3.40 %.%. Elemental analysis is consistently low on carbon, potentially indicative of the complex being air- and moisture sensitivity.

Yield = 0.065 g, 14%

[Mg(**3**)]₂:

To a solution of **3**H₂ (0.53 g, 1 mmol) in dry toluene (10 mL), Mg(^{n}Bu)₂ (1 mL, 1 mmol, 1.0 M in *n*-heptane) was added dropwise with stirring at room temperature and then stirred at 90 °C for 45 minutes. A yellow solid was isolated by cannula filtration and dried *in vacou* at 80 °C for 3 hours.

^{1}H NMR (CDCl₃, 500 MHz): δ = 8.04 (s, 1H; ArCHN), 7.48 (s, 1H; ArH), 7.15 (s, 1H; ArH), 7.04 (s, 1H; ArH), 7.03 (s, 1H; ArH), 4.59 (s, 1H; NH), 3.79 (m, 4H; CH₂), 1.29 (s, 9H; C(CH₃)₃), 1.27 (s, 9H; C(CH₃)₃).

^{13}C{^{1}H} NMR (CDCl₃, 125 MHz): δ = 168.7 (ArCHN), 164.0, 155.3, 139.3, 138.2, 137.9, 135.6, 131.5, 121.3, 121.1, 118.9, 117.1, 102.4 (Ar), 54.1, 45.2 (CH₂), 35.1, 34.5 (C(CH₃)₃), 31.9, 30.1 (CH₃).

Yield = 0.15 g, 27%

Calculated for C₄₆H₅₆Br₄Mg₂N₄O₄: C; 50.36 %; H; 5.14 %; N; 5.11 %. Found: C; 45.66 %; H, 4.54 %; N, 4.41 %. Elemental analysis is consistently low on carbon, this is potentially due to the hydroscopic nature of the complexes and incorporation of water.
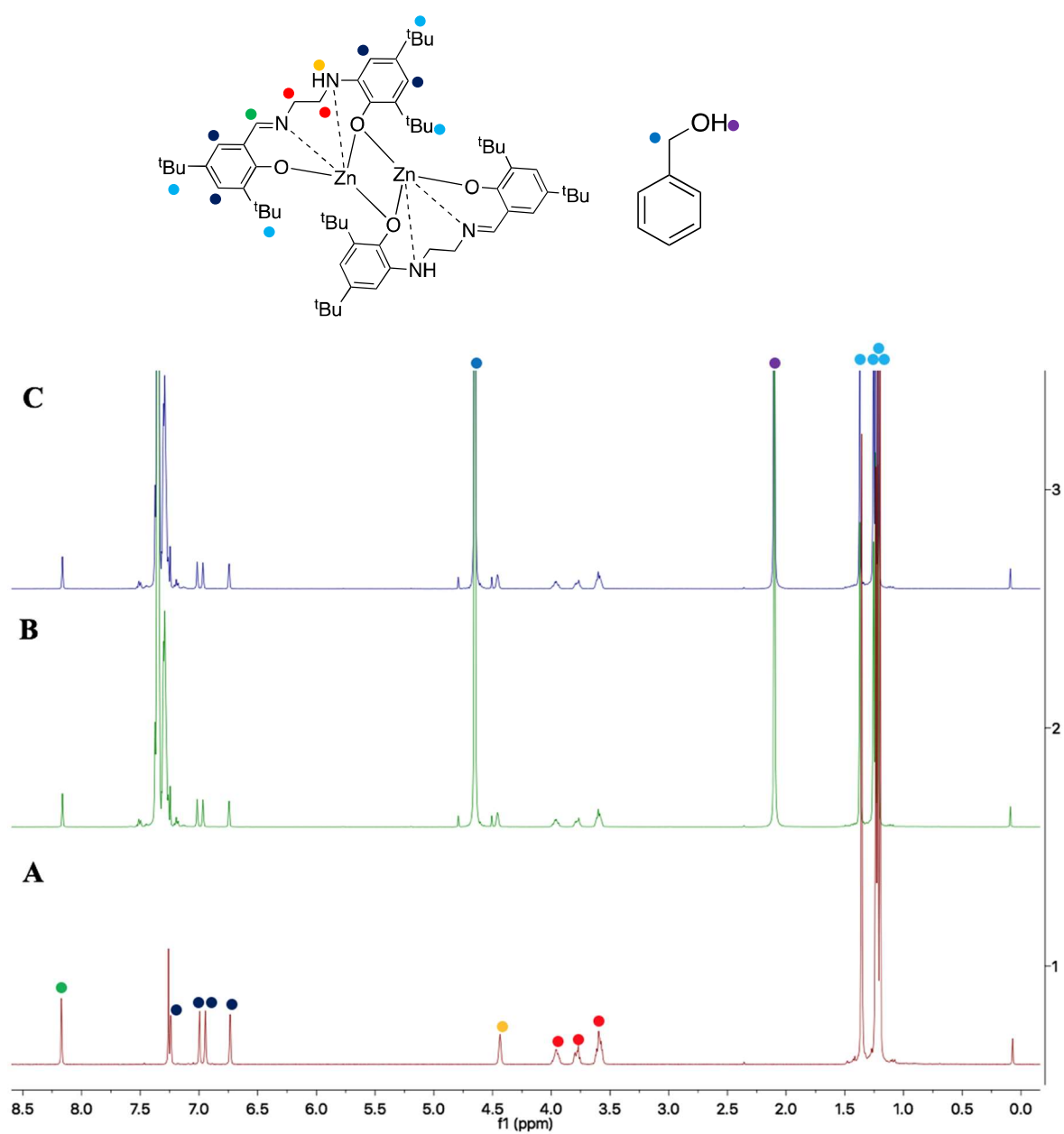
2.5. Catalyst Stability Testing

Figure 1. ^{1}H NMR (CDCl$_3$, 500 MHz) spectra assessing the stability of [Zn(**1**)]$_2$ with excess BnOH: (**A**) [Zn(**1**)]$_2$, (**B**) [Zn(**1**)]$_2$ + BnOH at RT, and; (**C**) [Zn(**1**)]$_2$ + BnOH at 80 °C for 1h.

3. Polymer Characterisation

3.1. Representative ^{1}H NMR spectra:

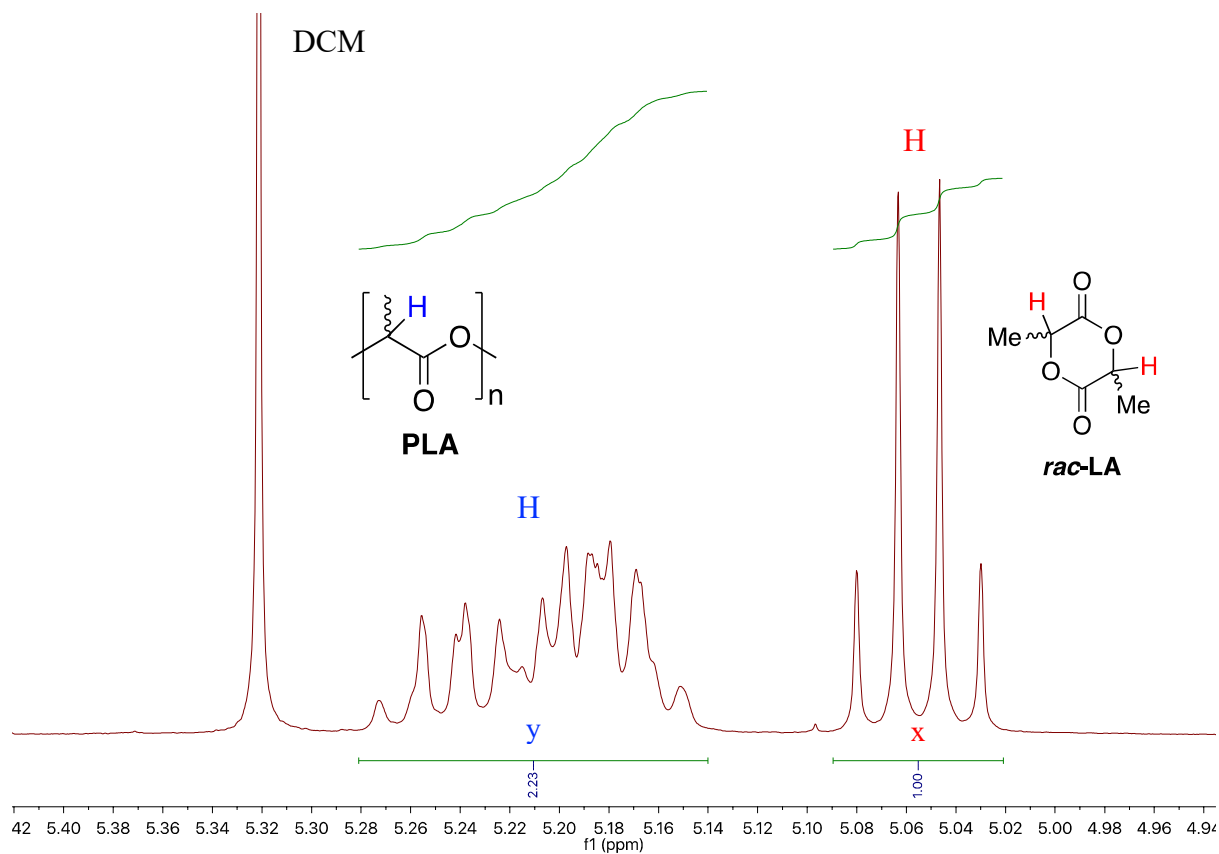**Figure 2.** ^{1}H NMR (CDCl$_3$, 400 MHz) spectrum of crude PLA product from the melt polymerisation of *rac*-LA at 130 °C using [Zn(**1**)]$_2$ {[*rac*-LA]:[M]:[BnOH] = 300:1:1} (Table 1, Entry 1). PLA conversion = [y/(x+y)] x 100%.

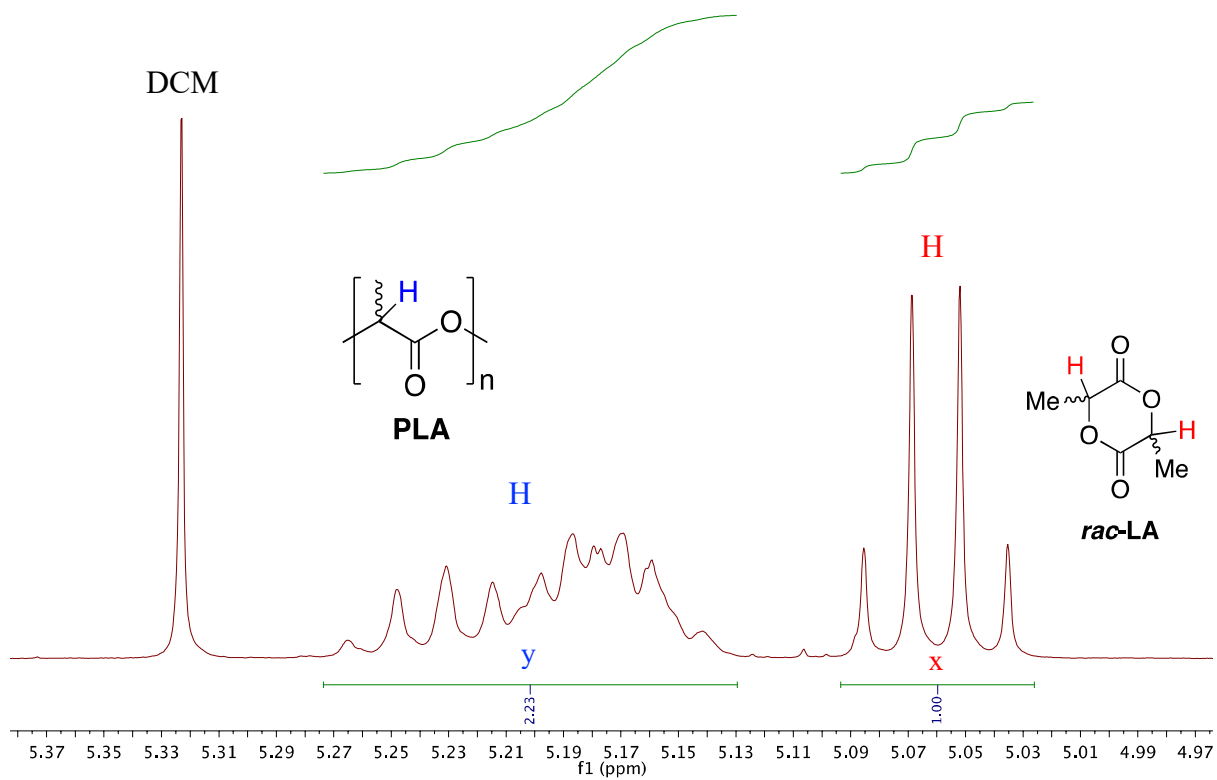**Figure 3.** ^{1}H NMR (CDCl$_3$, 400 MHz) spectrum of crude PLA product from the melt polymerisation of *rac*-LA at 130 °C using [Mg(**1**)]$_2$ {[*rac*-LA]:[M]:[BnOH] = 300:1:1} (Table 1, Entry 7). PLA conversion = [y/(x+y)] x 100%.
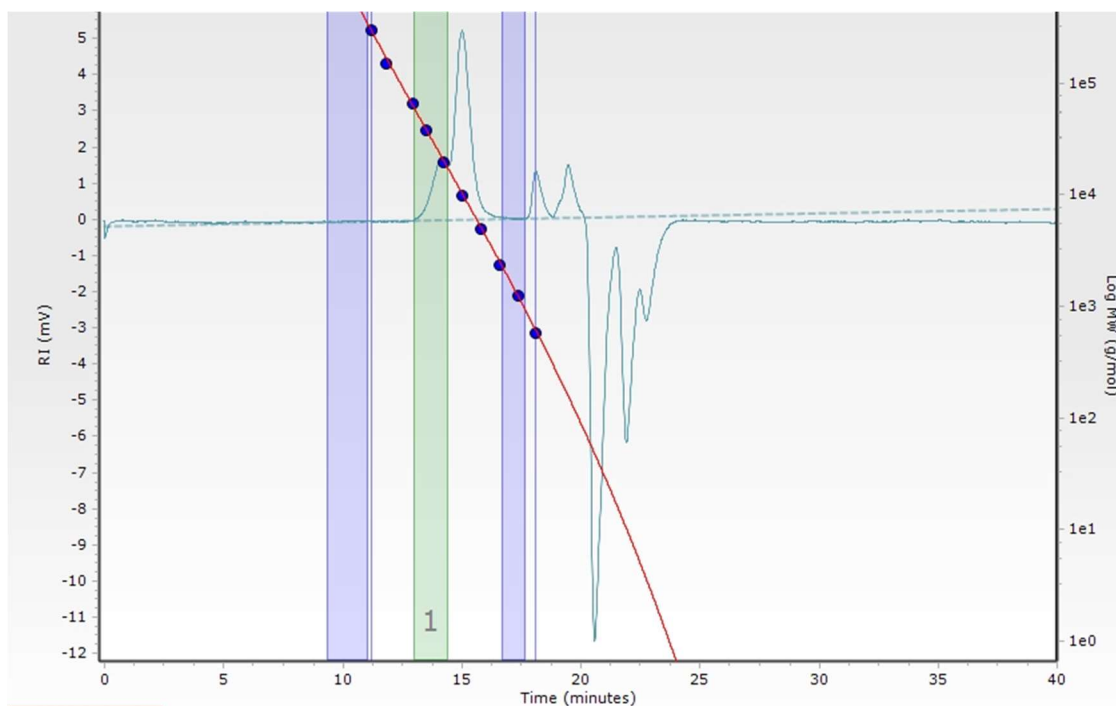
3.2. Representative GPC Spectra:

Figure 4. Bimodal GPC spectrum of purified PLA product from the solution polymerisation of *rac*-LA at 80 °C for 8 h using [Zn(**1**)]$_2$ {[*rac*-LA]:[M]:[BnOH] = 100:1:1} (Table 2, Entry 1).
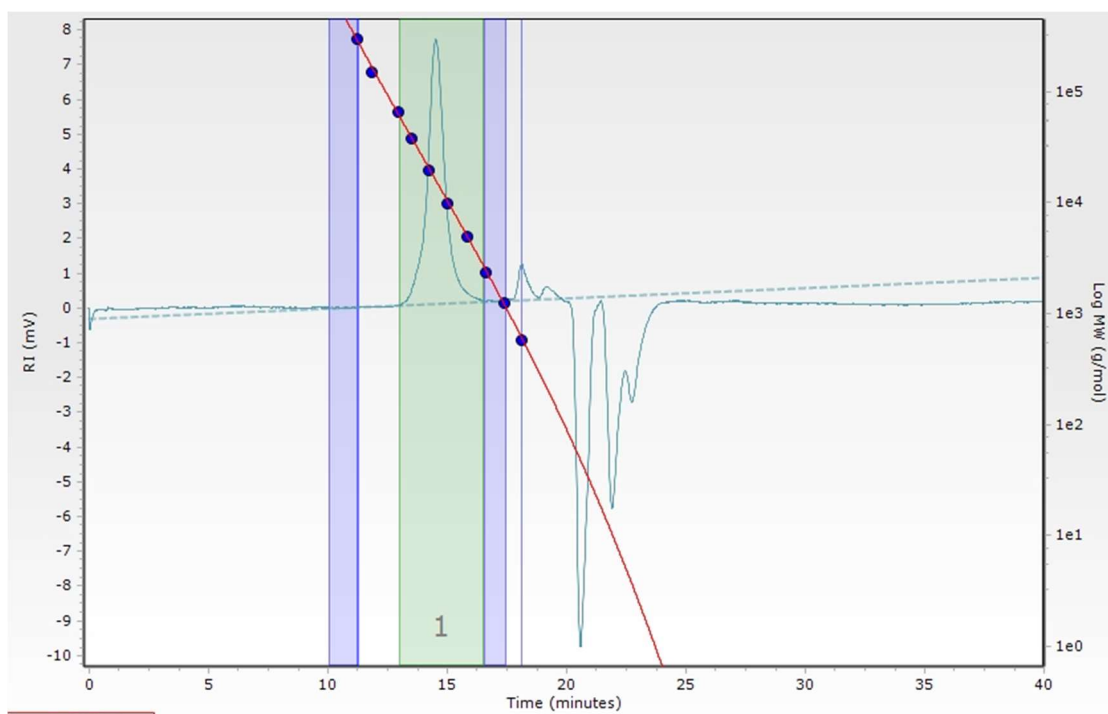

Figure 5. Monomodal GPC spectrum of purified PLA product from the solution polymerisation of *rac*-LA at 80 °C for 1.5 h using [Mg(**1**)]$_2$ {[*rac*-LA]:[M]:[BnOH] = 100:1:1} (Table 2, Entry 4).

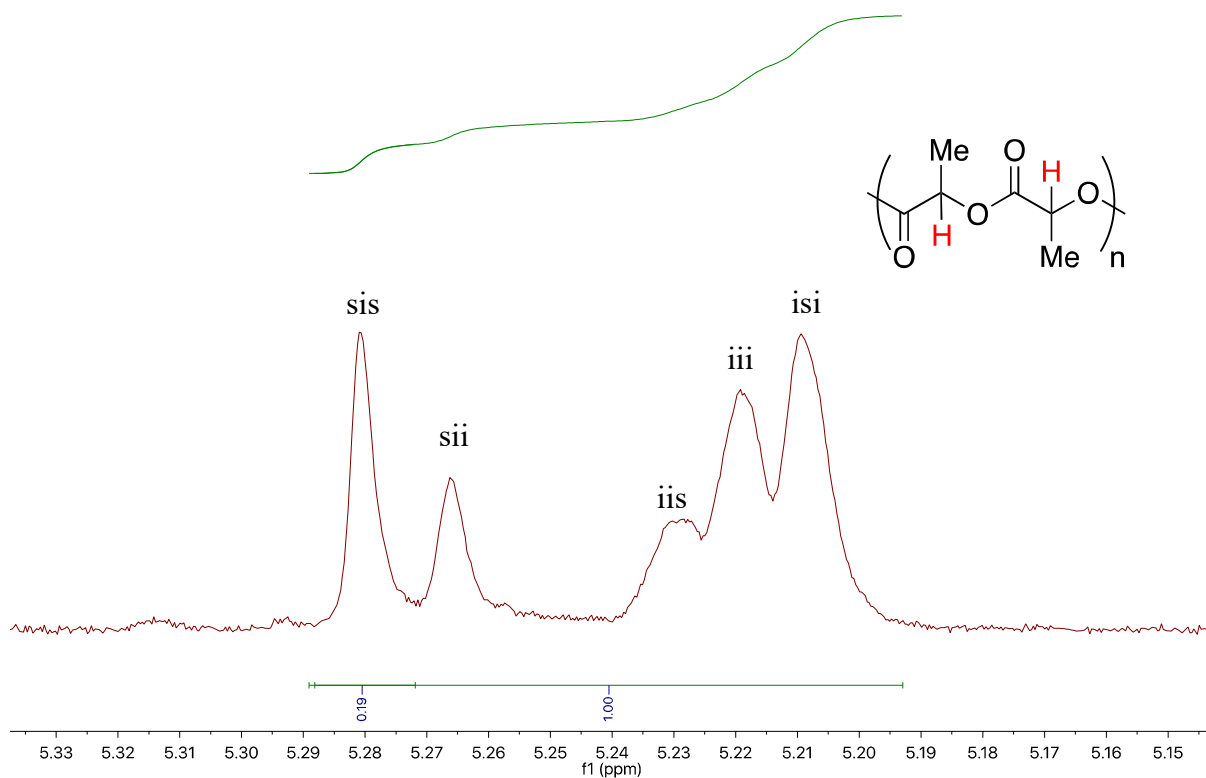## 3.3. Representative Homonuclear Decoupled ^{1}H NMR Spectra:

Figure 6. Homonuclear decoupled ^{1}H NMR (CDCl$_3$, 400 MHz) spectrum of purified PLA product with a slight heterotactic bias ($P_r = 0.61$) from the solution polymerisation of *rac*-LA at 80 °C for 8 h using [Zn(**1**)]$_2$ {[*rac*-LA]:[M]:[BnOH] = 100:1:1} (Table 2, Entry 1), displaying the five tetrad possibilities in the methine region (red).[2]
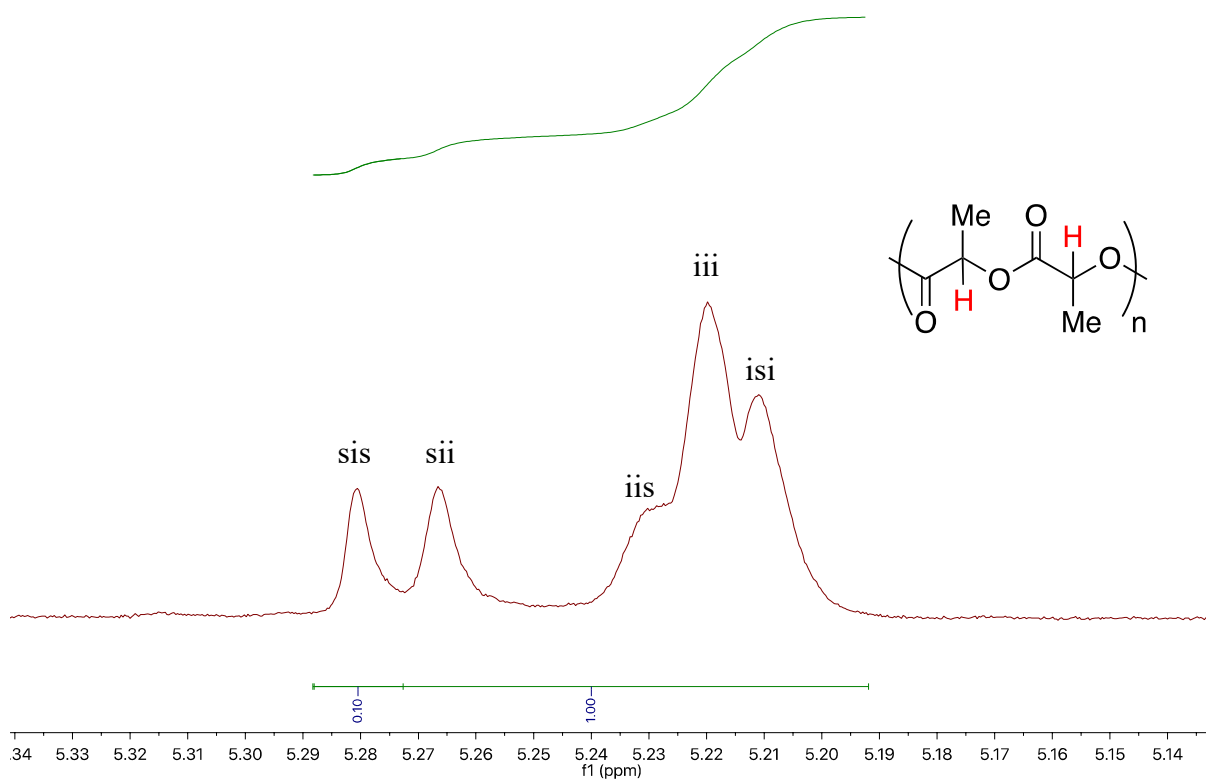
Figure 7. Homonuclear decoupled ^1H NMR (CDCl$_3$, 400 MHz) spectrum of purified atactic PLA product (P_r = 0.46) from the solution polymerisation of *rac*-LA at 80 °C for 1.5 h using [Mg(**1**)]$_2$ {[*rac*-LA]:[M]:[BnOH] = 100:1:1} (Table 2, Entry 4), displaying the five tetrad possibilities in the methine region (red).[2]

3.4. MALDI-ToF Spectra:

Figure 8. MALDI-ToF spectrum of purified PLA product from the solution polymerisation of *rac*-LA at 80 °C for 1.5 h using [Mg(**1**)]$_2$ {[*rac*-LA]:[M]:[BnOH] = 100:1:1} (Table 2, Entry 4). Magnified version of main series provided to assist in identifying the repeat unit and end group determination.
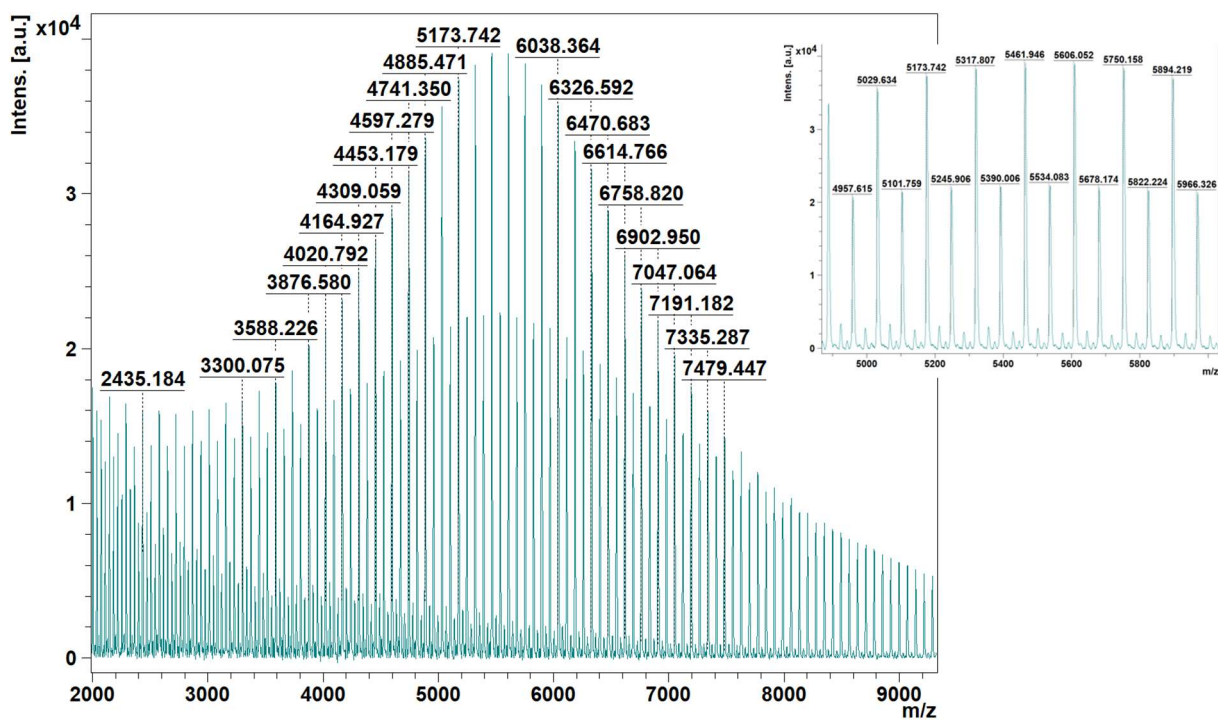
Figure 9. MALDI-ToF spectrum of purified PLA product from the melt polymerisation of *rac*-LA at 180 °C using [Mg(**1**)]$_2$ {[*rac*-LA]:[M]:[BnOH] = 3000:1:10} (Table 1, Entry 8). Magnified version of main series provided to assist in identifying the repeat unit and end group determination.
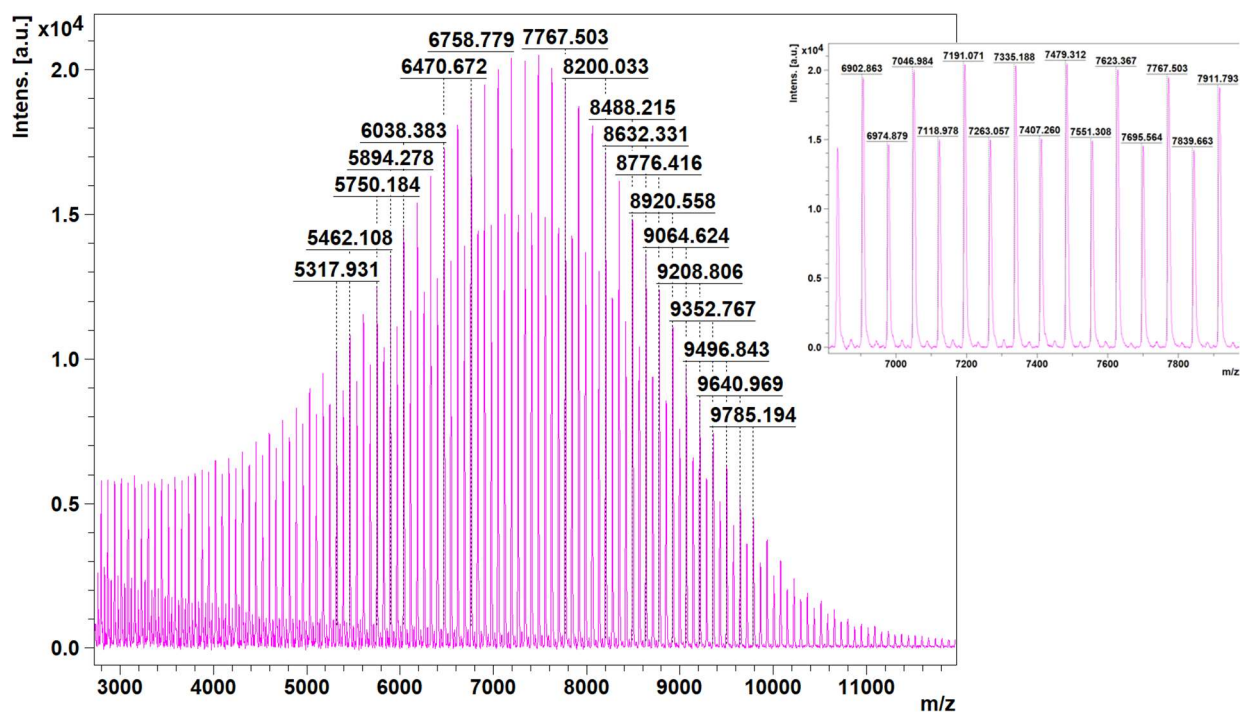

Figure 10. MALDI-ToF spectrum of purified PLA product from the solution polymerisation of *rac*-LA at 80 °C for 8 h using [Mg(**3**)]$_2$ {[*rac*-LA]:[M]:[BnOH] = 100:1:1} (Table 2, Entry 5). Magnified version of main series provided to assist in identifying the repeat unit and end group determination.
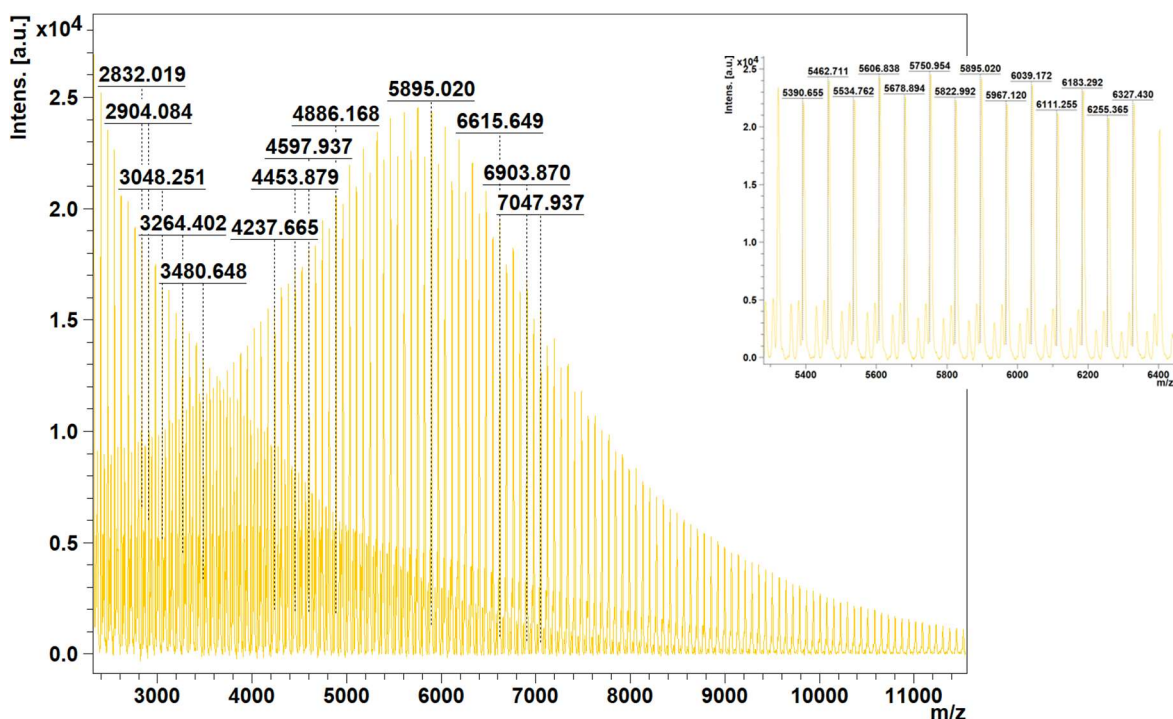
4. Degradation Characterisation

4.1. Representative ^{1}H NMR spectrum of PLA Degradation into Me-LA

Int conversion (X_{Int}), Me-La selectivity (S_{Me-La}) and Me-La yield (Y_{Me-La}) were calculated using Equations 1 to 3 below:[3-4]

$$X_{int} = 1 - \frac{[Int]}{[Int]_0} \tag{1}$$

$$S_{Me\text{-}LA} = \frac{[Me-LA]}{[Int]_0 - [Int]} \tag{2}$$

$$Y_{Me\text{-}LA} = X_{int}\, S_{Me\text{-}LA} \tag{3}$$

Figure 11. ^{1}H NMR (CDCl$_3$, 400 MHz) spectrum of PLA Vegware cup degradation into methyl lactate (Me-LA) using [Mg(**1**)]$_2$ (4 wt% - 0.29 mol% relative to ester linkages) at 80 °C for 8 h in THF (Table 4, Entry 1).
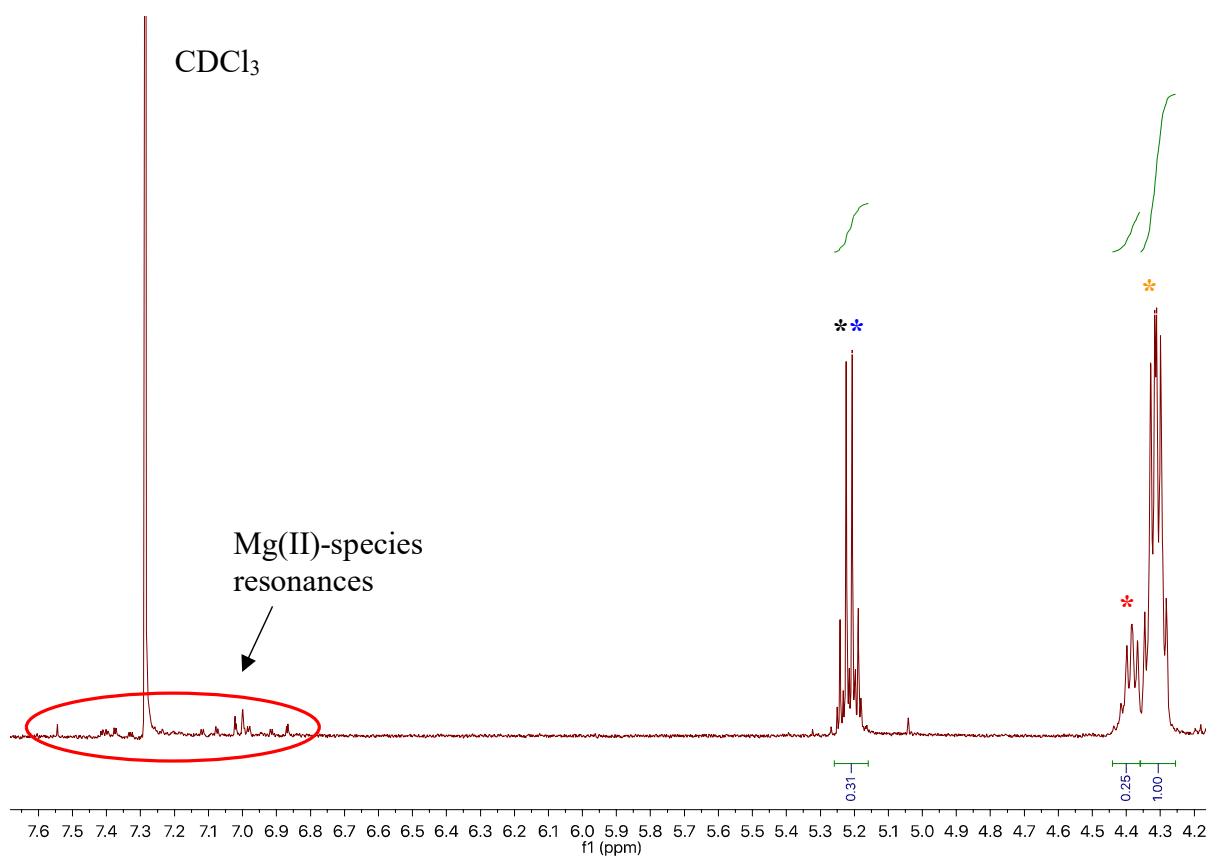
Figure 12. ^{1}H NMR (CDCl$_3$, 400 MHz) spectrum of PLA Vegware cup degradation into methyl lactate (Me-LA) using [Mg(**1**)]$_2$ (4 wt% - 0.29 mol% relative to ester linkages) at 80 °C for 8 h in THF (solvent removed). Aromatic resonances can be attributed to the presence of Mg(II)-species in the sample (Table 3, Entry 12).

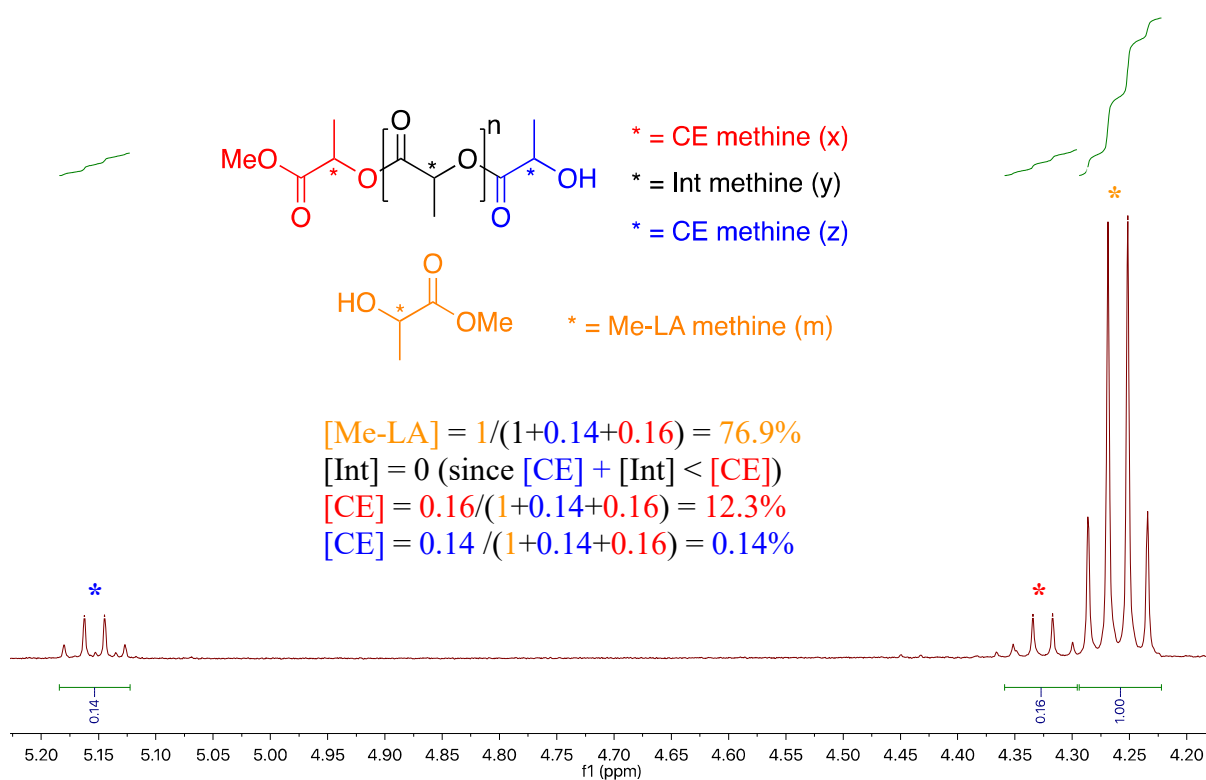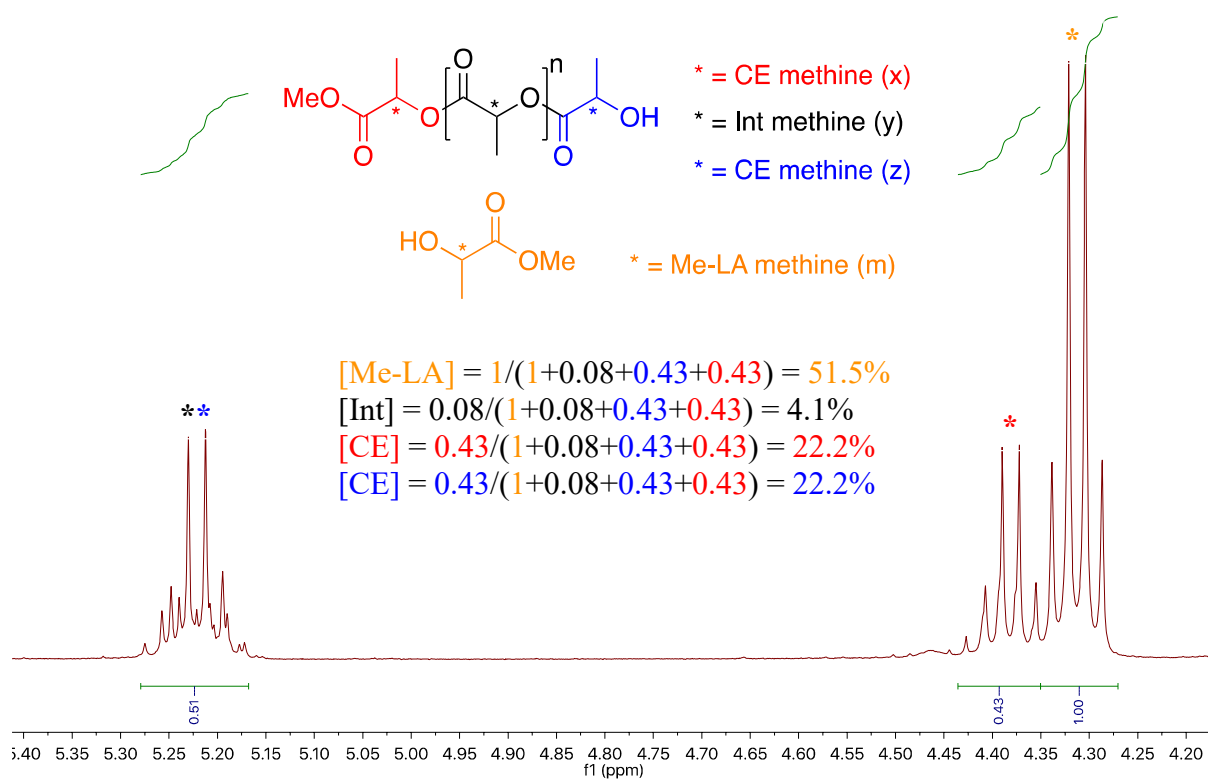**Figure 13.** ^{1}H NMR (CDCl₃, 400 MHz) spectrum of PLA Vegware cup degradation into methyl lactate (Me-LA) using [Zn(**1**)]₂ (8 wt% - 0.53 mol% relative to ester linkages) at 80 °C for 8 h in dry toluene (solvent removed) (Table 3, Entry 3).

4.2. Representative ^{1}H NMR spectrum of PET Degradation into BHET

Figure 14. ^{1}H NMR (D$_6$-DMSO, 400 MHz) spectrum of recrystallised BHET from PET Coke bottle degradation using [Mg($\mathbf{1}$)]$_2$ (8 wt% - 1.5 mol% relative to ester linkages) in 27.5 equivalents (2 mL) of EG at 180 °C for 3h (Table 5, Entry 5).

5. Crystallographic Data

Special refinement details include:

[Zn(**1**)]$_2$: One solvent molecule of toluene is disordered over a centre of inversion and was refined with 50% occupation.

[Zn(**3**)]$_2$: Half the structure is generated by symmetry. One tBu group (C14) disordered over two positions in a ratio of 50:50.

[Mg(**1**)]$_2$: Three partial molecules of toluene contained in the unit cell with bond lengths subject to constraints. One tBu group (C23) disordered over two sites in a ratio of 78:22.
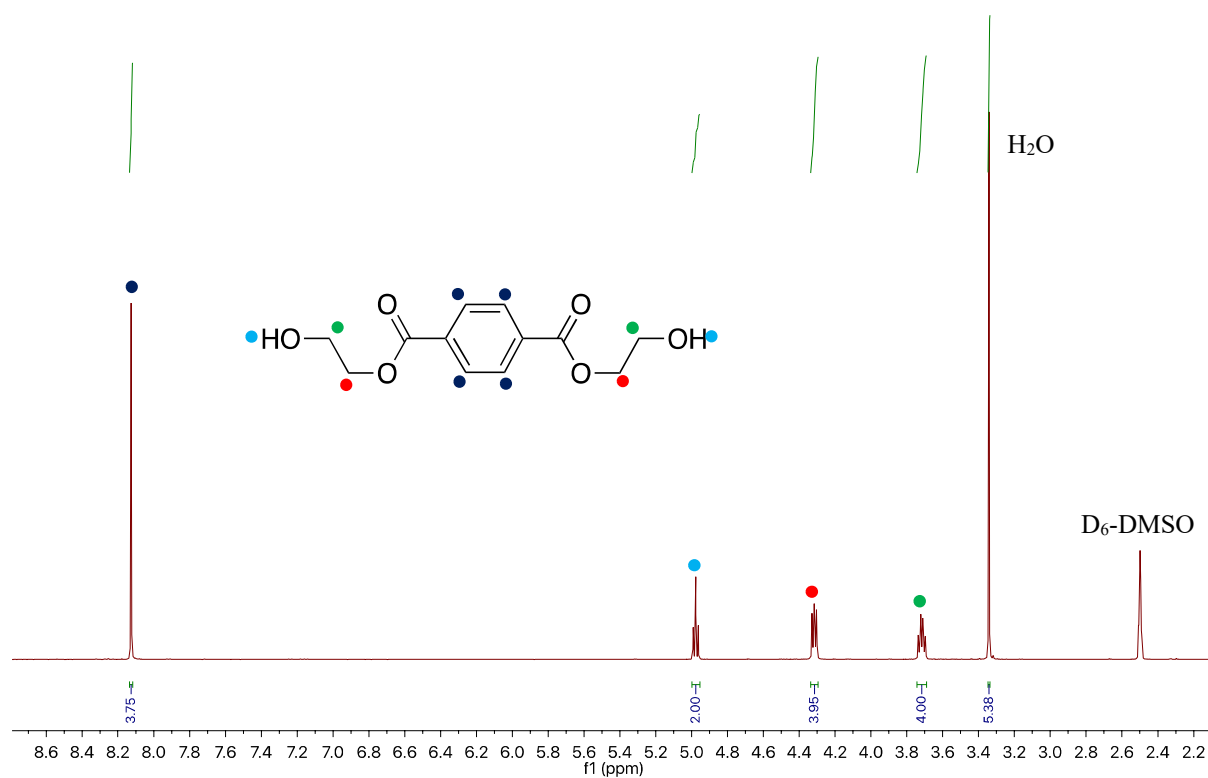
Table 1. Crystallographic data of [Zn(**1-3**)]$_2$.

Compound reference	[Zn(**1**)]$_2$	[Zn(**2**)]$_2$	[Zn(**3**)]$_2$
Empirical formula	$C_{83}H_{116}N_4O_4Zn_2$	$C_{30}H_{36}Cl_2N_2O_2Zn$	$C_{30}H_{36}Br_2N_2O_2Zn$
Formula Mass	1364.53	592.88	681.80
Crystal system	Triclinic	Monoclinic	Monoclinic
a/Å	9.5822(2)	9.8683(8)	10.0556(3)
b/Å	13.6635(3)	14.2238(12)	14.2825(3)
c/Å	15.4413(3)	20.5519(9)	20.6880(4)
α/°	98.426(2)	90	90
β/°	105.508	94.567(5)	95.646(2)
γ/°	99.504	90	90
Unit cell volume/Å^3	1882.26(7)	2875.6(4)	2956.78(12)
Temperature/K	150.0(3)	150(2)	150.01(10)
Space group	P-1	P 2$_1$/c	P 2$_1$/c
No. of formula units per unit cell, Z	1	4	4
Radiation type	Mo Kα	Cu Kα	Cu Kα
No. of reflections measured	45742	10029	15599
No. of independent reflections	8588	5054	5840
R_{int}	0.0391	0.0539	0.0181
Final R_1 values ($I > 2\sigma(I)$)	0.0363	0.0563	0.0408
Final $wR(F^2)$ values ($I > 2\sigma(I)$)	0.0848	0.1353	0.1003
Final R_1 values (all data)	0.0539	0.0721	0.0426
Final $wR(F^2)$ values (all data)	0.0939	0.1474	0.1019

Table 2. Crystallographic data of [Mg(**1-3**)]$_2$. *N.B.* DP refers to deprotonated amine as observed in the tetrameric analogue of [Mg(**2**)]$_2$, namely (Mg(**2^{DP}**)-tetramer).

Compound reference	[Mg(**1**)]$_2$	[Mg(**2**)]$_2$	Mg(**2^{DP}**)-tetramer	[Mg(**3**)]$_2$
Empirical formula	$C_{84}H_{118}Mg_2N_4O_4$	$C_{30}H_{36}Cl_2MgN_2O_2$	$C_{27}H_{36}Cl_2Mg_2N_2O_2$	$C_{30}H_{36}Br_2MgN_2O_2$
Formula Mass	1296.44	551.82	540.10	640.74
Crystal system	Monoclinic	Monoclinic	Triclinic	Monoclinic
a/Å	9.7766(3)	9.9229(4)	10.8720(12)	10.0761(5)
b/Å	31.3712(9)	14.2743(5)	11.0298(10)	14.3226(7)
c/Å	25.4191(5)	20.5348(5)	13.0224(12)	20.665(4)
α/°	90	90	112.876(9)	90
β/°	96.789(2)	95.319(3)	100.644(8)	96.011(10)
γ/°	90	90	93.112(8)	90
Unit cell volume/Å^3	7741.5(4)	2896.07(17)	1400.2(3)	2965.9(5)
Temperature/K	150.00(10)	150(2)	150.01(10)	150(2)
Space group	C 2/c	P 2$_1$/c	P-1	P 2$_1$/c
No. of formula units per unit cell, Z	4	4	2	4
Radiation type	Cu Kα	Mo Kα	Cu Kα	Cu Kα
No. of reflections measured	41029	20024	8571	11526
No. of independent reflections	7085	6390	5278	5538
R_{int}	0.0652	0.0489	0.0528	0.0451
Final R_1 values ($I > 2\sigma(I)$)	0.0725	0.0524	0.0768	0.0495
Final $wR(F^2)$ values ($I > 2\sigma(I)$)	0.1852	0.1352	0.1801	0.1346
Final R_1 values (all data)	0.1026	0.0709	0.1275	0.0550
Final $wR(F^2)$ values (all data)	0.2051	0.1483	0.2117	0.1409

Selected bond lengths and angles:

Table 3. Selected bond lengths for [Zn(**1-3**)]$_2$ and [Mg(**1-3**)]$_2$.

Init.	Bond	Bond length / Å
[Zn(**1**)]$_2$	Zn(1)-N(1) {amine}, Zn(1)-N(2) {imine}	2.2326(15), 2.0124(15)
[Zn(**2**)]$_2$		2.204(3), 2.026(3)
[Zn(**3**)]$_2$		2.212(2), 2.026(3)
[Mg(**1**)]$_2$	Mg(1)-N(1) {amine}, Mg(1)-N(2) {imine}	2.236(2), 2.088(3)
[Mg(**2**)]$_2$		2.2181(19), 2.0994(18)
[Mg(**3**)]$_2$		2.221(3), 2.105(3)

Table 4. Selected bond angles for [Zn(**1-3**)]$_2$ and [Mg(**1-3**)]$_2$ with calculated τ_5 values. Ideal square pyramidal geometry corresponds to $\tau_5 = 0$.

Init.	Bond	Bond angle / °	τ_5
[Zn(**1**)]$_2$	N(2)-Zn(1)-O(1), O(2)-Zn(1)-N(1)	133.43(5), 168.78(6)	0.59
[Zn(**2**)]$_2$		126.55(10), 171.33(10)	0.75
[Zn(**3**)]$_2$		126.22(9), 170.68(9)	0.74
[Mg(**1**)]$_2$	O(1)-Mg(1)-N(2), O(2)-Mg(1)-N(1)	132.05(10), 164.11(9)	0.53
[Mg(**2**)]$_2$		125.22(7), 166.45(7)	0.69
[Mg(**3**)]$_2$		124.85(10), 165.92(11)	0.68

References:

1. G. R. Fulmer, A. J. M. Miller, N. H. Sherden, H. E. Gottlieb, A. Nudelman, B. M. Stoltz, J. E. Bercaw and K. I. Goldberg, *Organometallics*, **9**, 2010, 2176-2179.
2. B. M. Chamberlain, M. Cheng, D. R. Moore, T. M. Ovitt, E. B. Lobkovsky and G. W. Coates, *J. Am. Chem. Soc.*, 2001, **123**, 3229-3238.
3. L. A. Román-Ramírez, P. Mckeown, M. D. Jones and J. Wood**,** *ACS Catal.,* 2019, **9**, 409-416.
4. P. McKeown, L. A. Román-Ramírez, S. Bates, J. Wood and M. D. Jones, *ChemSusChem*, 2019, **12**, 5233–5238.