Electronic Supplementary Material (ESI) for Green Chemistry.

Supporting Information

Organocatalysis for versatile polymer degradation

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Contents

General considerations

All chemicals were purchased from Sigma Aldrich and used as received with the following exceptions; lactide (*rac*- and *L*-) was recrystallised from anhydrous toluene and stored under and inert atmosphere; the majority of solvents (MeOH, EtOH, Acetone, THF, EtOAc, ACN, Toluene) were purchased from VWR (HPLC grade) and used as received. Toluene was degassed and dried using a solvent-purification system prior to use. The remaining solvents and reagents (DMC, 2-MeTHF) were purchased from Sigma Aldrich (anhydrous). NMR solvents were purchased from Sigma Aldrich, d_6-DMSO (anhydrous) was stored under an inert atmosphere. NMR spectra were recorded on either a 400 MHz or 500 MHz Bruker spectrometer and referenced to residual solvent resonances.

Various grades of polymer samples were commercially sourced. PLA was represented by a plastic cup (M_n = 45,150 g mol^{-1}, $Đ$ = 2.08; T_m = 149 °C, T_g =60°C) and cut into 0.1 × 0.1 cm^2 pieces before degradation; PCL pellets (Sigma Aldrich; M_n = 45,000, $Đ$ = 1.53) and used as received; PC pellets (Sigma Aldrich; M_w ~ 45,000) and used as received; PET bottle (M_n ~ 40,000 g mol^{-1})[1] washed thoroughly with acetone, dried and cut into 0.1 × 0.1 cm^2 pieces before degradation.

GPC was performed on an Agilent 1260 Infinity instrument fitted with detection by refractive index, calibrated by 11 narrow polystyrene standards. Samples were prepared in THF (GPC grade) and analysed with a flow rate of 1 mL min^{-1} and an oven temperature of 35 °C. A correction factor of 0.58 has been applied to weight values.[2] MALDI-ToF was performed on a Bruker Autoflex MALDI-ToF/ToF instrument. Samples were prepared with DCTB (matrix, 50 µL, 10 mg mL^{-1}), NaTFA (ion source, 2 µL, 1 M) and poymer sample (10 µL, 5 mg mL^{-1}), all in THF. After centrifugation, samples were spotted onto a polished steel plate and data was collected in reflector positive mode.

Differential scanning calorimetry (DSC) analyses were conducted with TA-instruments Q20 differential scanning calorimeter. All runs were performed under nitrogen atmosphere, with a constant flow rate of 18 mL min^{-1}. 4-6 mg of sample was weighed into the DSC pan. The sample was first equilibrated at 40 °C and then heated to 280 °C at a heating rate of 20 °C min^{-1} to construct the first heating curve. The sample was held at 280 °C isothermally for 1 min before starting the cooling scan. In the cooling scan, sample was cooled at 10 °C min^{-1} rate from 280 °C to 40 °C and maintained there for 1 minute. Finally, in the second heating scan, temperature was increased from 40 to 280 °C using a 10 °C min^{-1} heating rate. The glass transition temperature (T_g), melting peak (T_m) and melting enthalpy (ΔH_m) were recorded from analysis of the second heating scan.

Catalysts synthesis

1 was prepared in accordance with literature methods.[3] The reaction was also scaled up from the reported 2.5 mmol scale to 21 mmol: tetramethylammonium hydroxide (10 mL, 25 wt % solution in methanol, 22 mmol) was added to dimethyl carbonate under an argon atmosphere. The reaction was stirred for 16 h before solvent was removed *in vacuo* to yield a white solid, **1** (3.20 g, 99 % yield, 21 mmol).

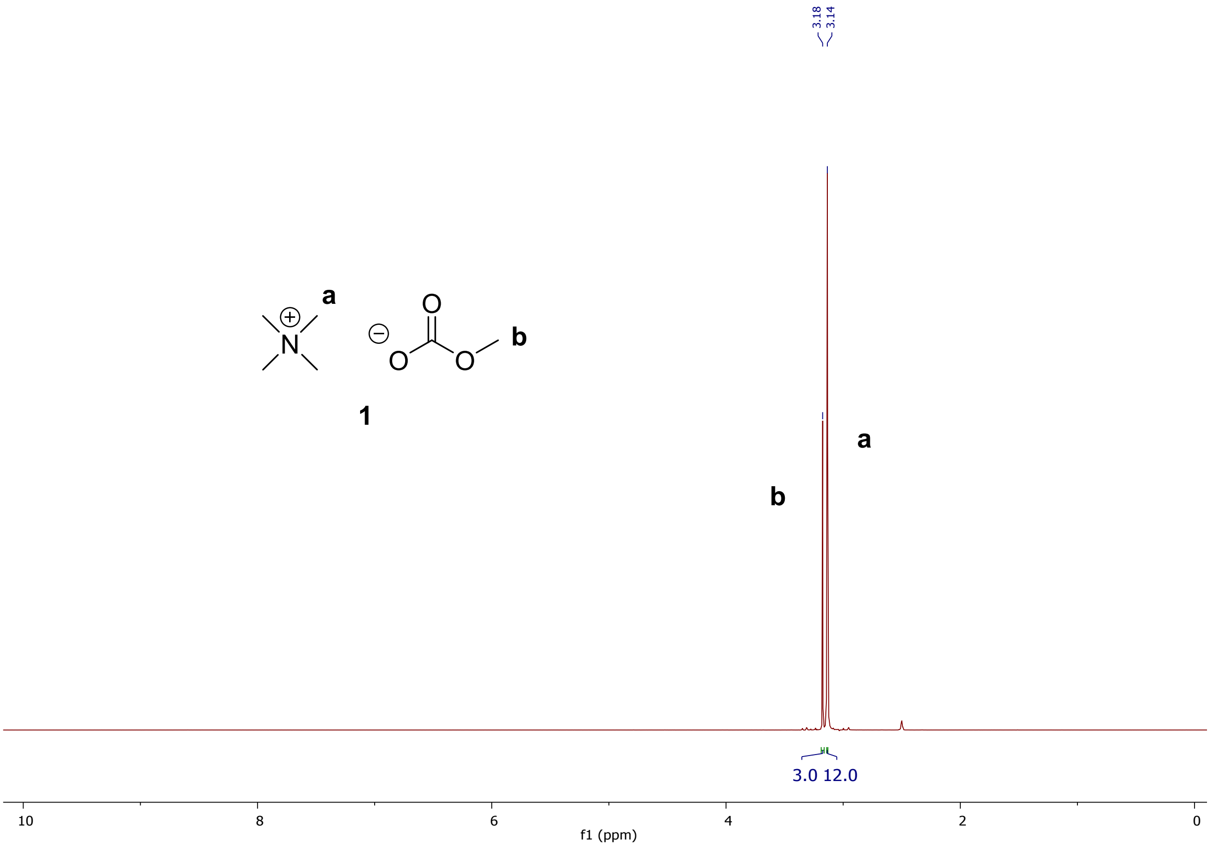


Figure S1: ^{1}H NMR spectrum (d_6-DMSO, 400 MHz, 298 K) of **1**.

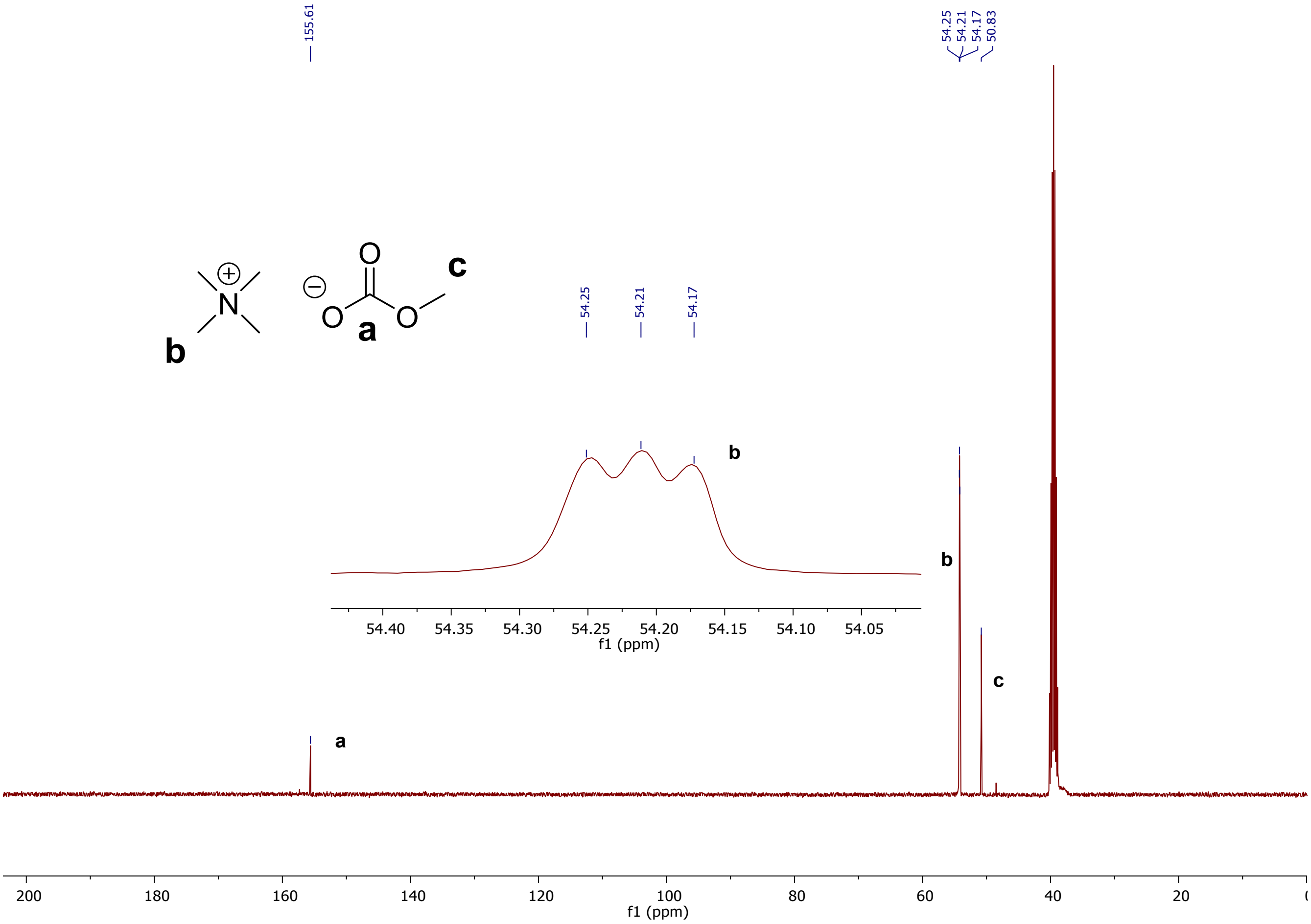


Figure S2: $^{13}C\{^{1}H\}$ NMR spectrum (d_6-DMSO, 400 MHz, 298 K) of **1**. Tetramethyl ammonium, b, resonance presents as a 1:1:1 triplet due to coupling to ^{14}N nuclei.

PLA Degradation

General solvent procedure: **1** (2.6 mg, 1 wt %) was added to a J Young's flask containing PLA pieces (0.25 g, 0.1 × 0.1 cm^2) in a glove box filled with argon. This flask was sealed, and charged with solvent (e.g. THF, 4 mL) on a Schlenk line. The flask was submerged in a pre-heated oil bath (eg 50 °C) and polymer dissolution carried out for 10 min prior to the addition of alcohol (e.g. MeOH, 1 mL) and the start of the degradation reaction time. Sample aliquots were taken under a flow of argon and analysed by ^{1}H NMR spectroscopy.

General solvent-free procedure: **1** (2.6 mg, 1 wt %) was added to a J Young's flask containing PLA pieces (0.25 g, 0.1 × 0.1 cm^2) in a glove box filled with argon. This flask was sealed, and charged with alcohol (e.g. MeOH, 2 mL) and the pressure of the flask reduced. The flask was submerged in a pre-heated oil bath (100 °C) signifying the start of the degradation reaction time. The reaction was monitored until all the polymer had dissolved after which time the flask was removed from the oil bath and cooled under a flow of cold water before ^{1}H NMR analysis. To ensure a representative sample, $CHCl_3$ (1 mL) was added prior to analysis.

Conversion in internal methine groups (X_{Int}), selectivity of alkyl lactate (S_{A-La}) and yield of alkyl lactate (Y_{A-La}) where calculated from the following equations:

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

$$S_{A-La} = \frac{[A-La]}{[Int]_0 - [Int]}$$

$$Y_{A-La} = X_{Int} S_{A-La}$$

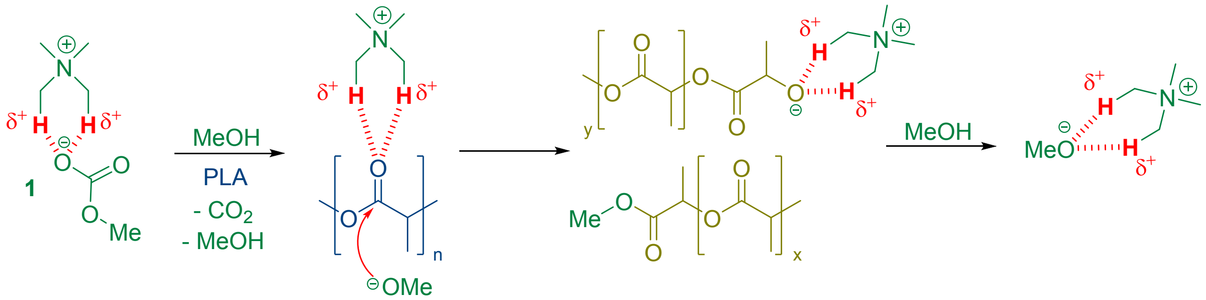
where $[Int]_0$ is the initial concentration of internal methine groups.

The formation of Me-La takes place through a consecutive irreversible reaction where Int methine groups degrade first into chain end (CE) groups from which the product is then formed (Scheme S2). The concentration of Int, CE and $Me-La$ at any time (t) can be calculated from the following equations:

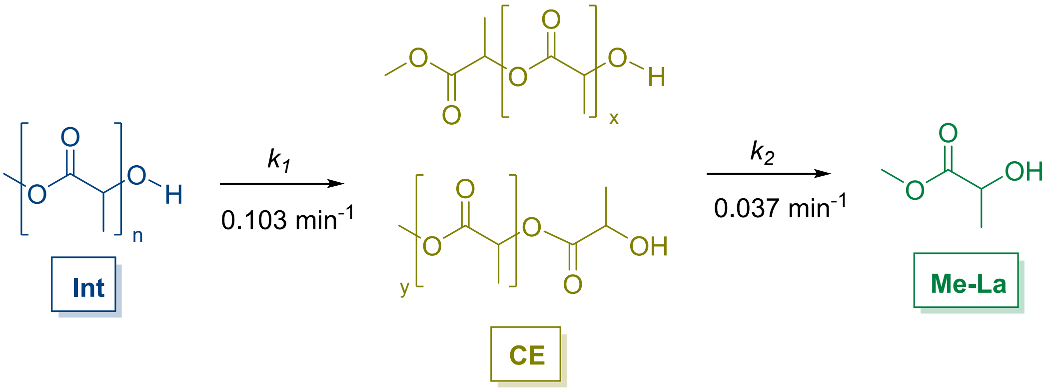
$$[Int] = 100e^{-k_1 t}$$

$$[CE] = \frac{100k_1}{k_2 - k_1}\left(e^{-k_1 t} - e^{-k_2 t}\right)$$

$$[Me-La] = 100\left(1 + \frac{k_1 e^{-k_2 t} - k_2 e^{-k_1 t}}{k_2 - k_1}\right)$$



Scheme S1: Mechanism of transesterifcation by **1** for PLA. Hydrogen bonding interaction based on literature examples.[3,4]



Scheme S2: PLA degradation with **1**. Kinetic parameters based on consecutive reaction steps (k_1 = 0.103 ± 0.008 min^{-1}, k_2 = 0.037 ± 0.002 min^{-1}) (MeOH/THF, 50°C). (See also Figure 2).

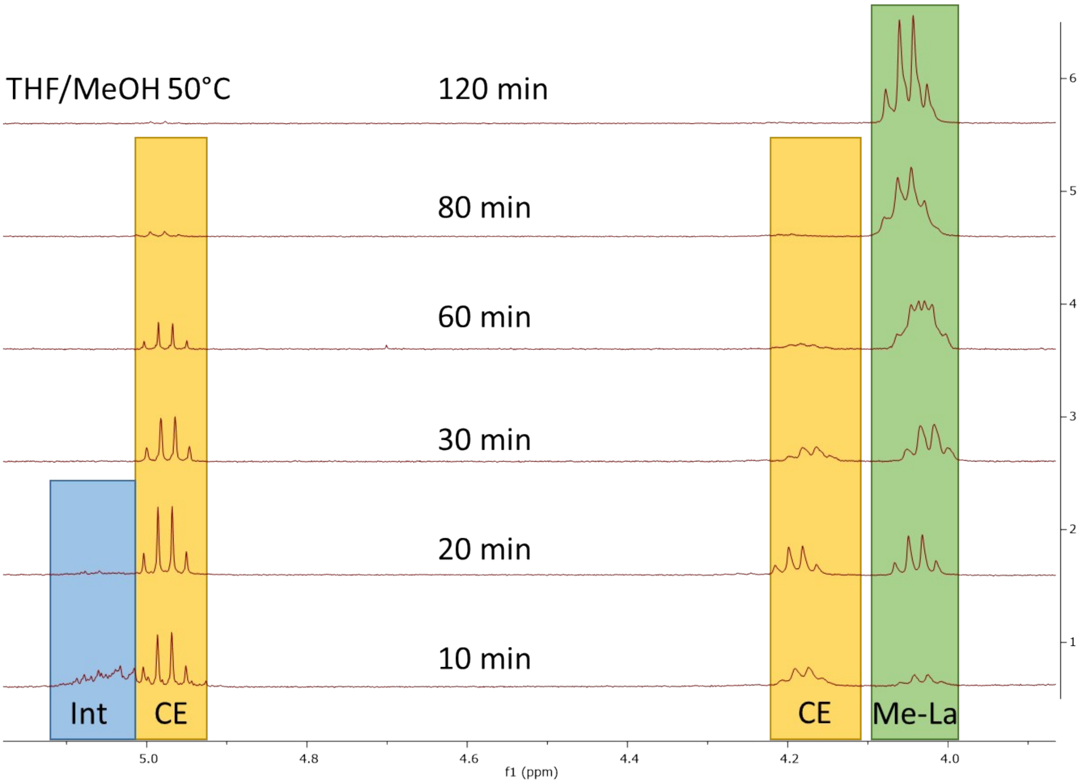


Figure S3: ^{1}H NMR spectra (C_6D_6, 400 MHz, 298 K) of PLA degradation over time by **1** in THF/MeOH (50 °C).

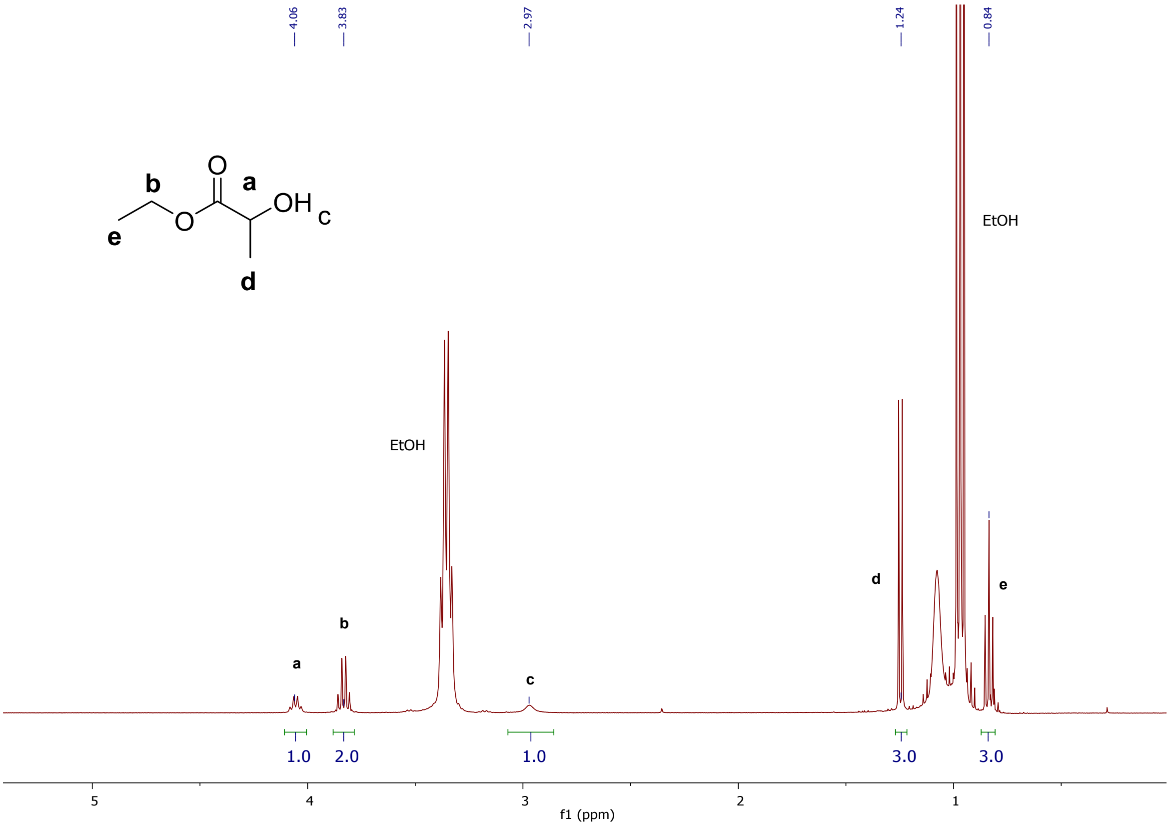


Figure S4: ^{1}H NMR spectrum (C_6D_6, 400 MHz, 298 K) of ethyl lactate produced by solvent free degradation of PLA with **1** and EtOH (100 °C).

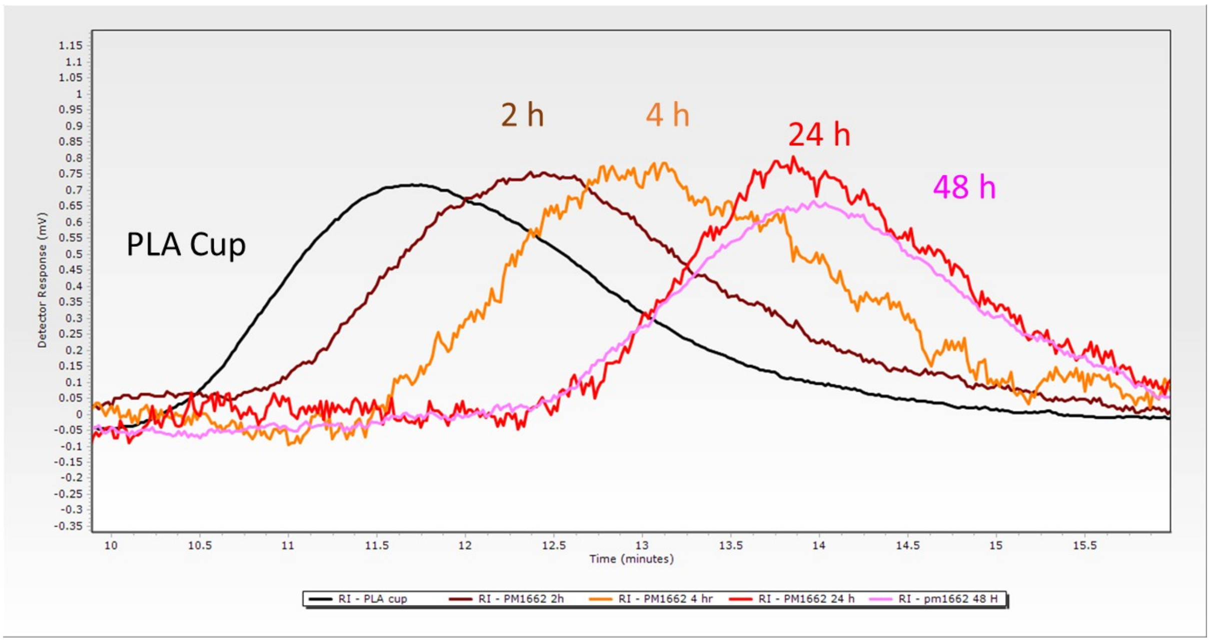


Figure S5: GPC traces of controlled PLA degradation. PLA Cup, M_n = 45,150 g mol^{-1}, after 48 h, M_n = 8450 g mol^{-1}.

LA Polymerisation

General procedure: LA (*rac*- or *L-,* 1.0 g, 6.9 mmol), **1** (10.4 mg, [LA]:[**1**] = 100), BnOH ([**1**]:[BnOH] = 1) and toluene (10 mL) were charged into a J Young's ampoule under an inert atmosphere. This ampoule was then placed in a pre-heated oil bath (80°C) for 2 h after which the solution was cooled and solvent removed *in vacuo.* Crude ^{1}H NMR spectrum was recorded for calculation of conversion. The polymer was further analysed by decoupled ^{1}H NMR spectroscopy, GPC and MALDI-ToF analysis.

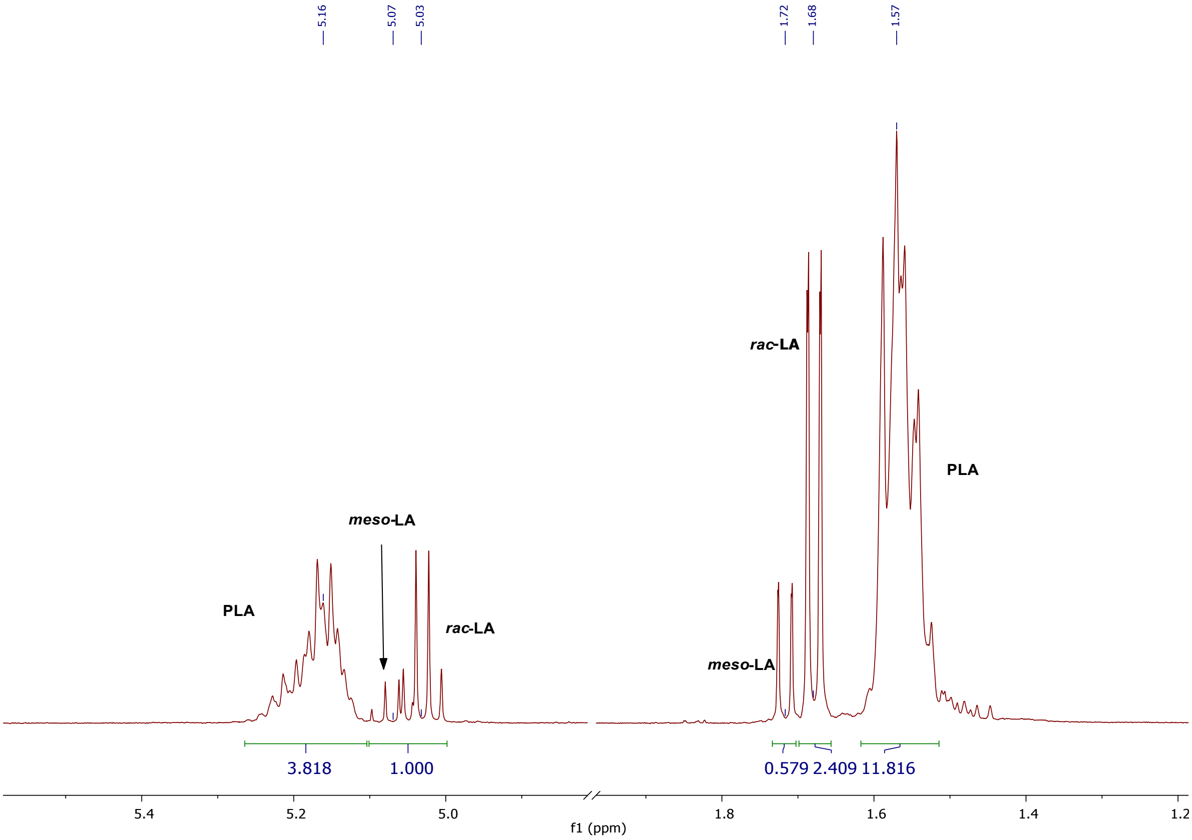


Figure S6: ^{1}H NMR spectrum ($CDCl_3$, 400 MHz, 298 K) of crude PLA sample prepared with **1** and *rac*-LA.

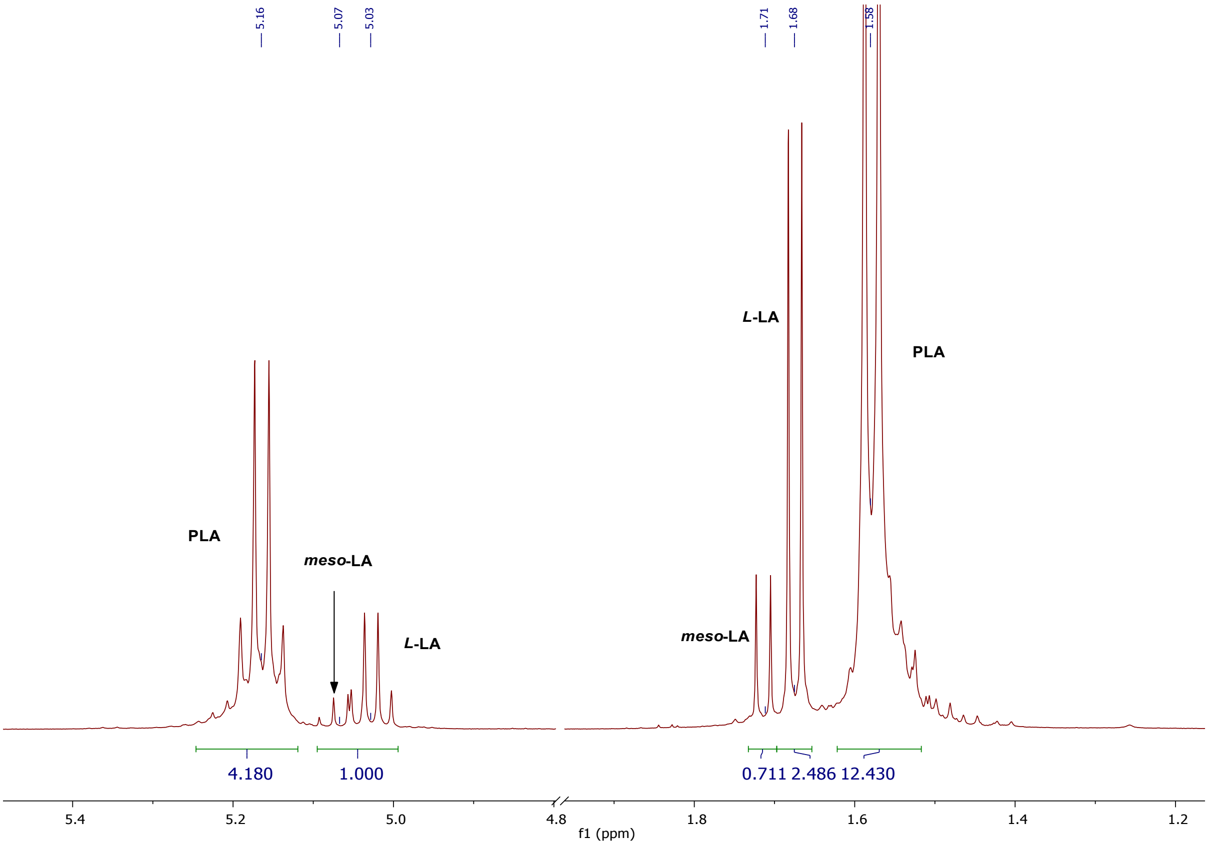


Figure S7: ^{1}H NMR spectrum (CDCl$_3$, 400 MHz, 298 K) of crude PLA sample prepared with **1** and *L*-LA.

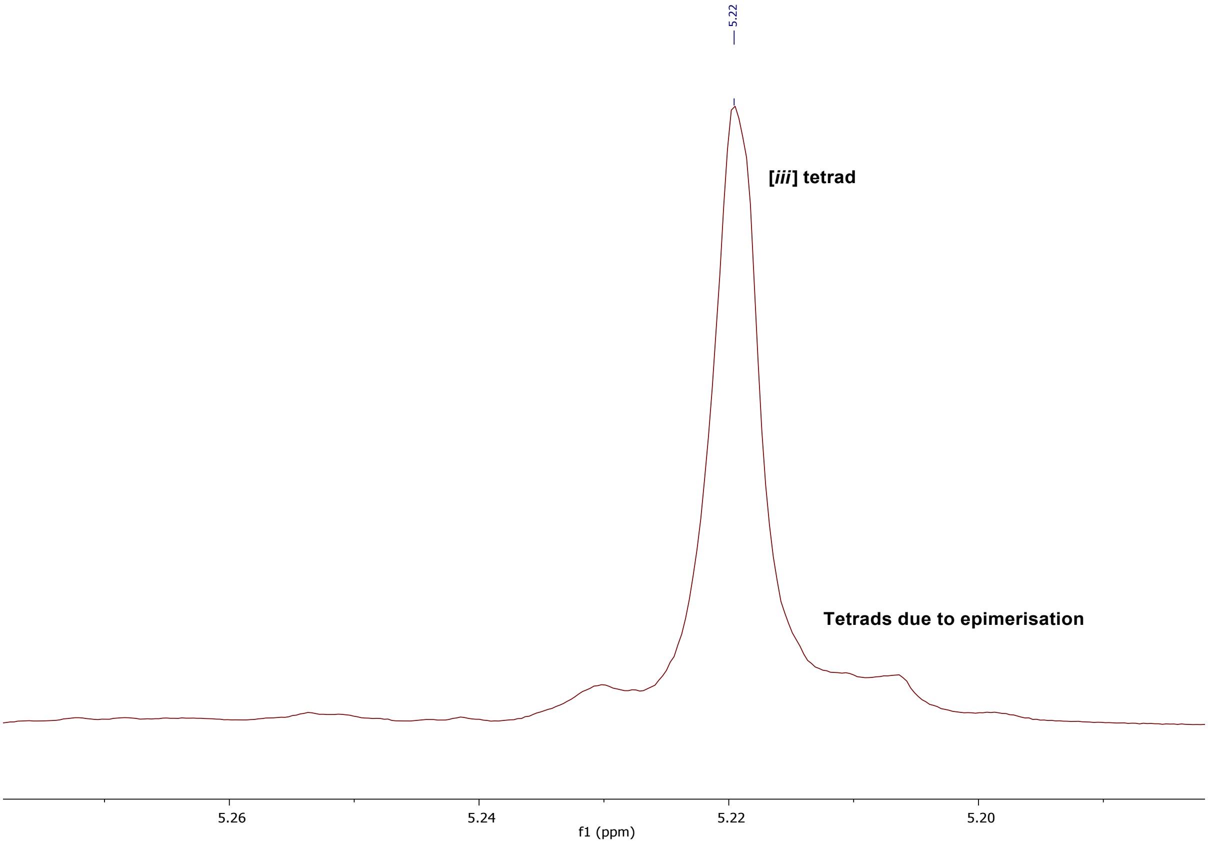


Figure S8: ^{1}H homonuclear decoupled NMR spectrum (CDCl$_3$, 400 MHz, 298 K) of PLA sample prepared with **1** and *L*-LA.

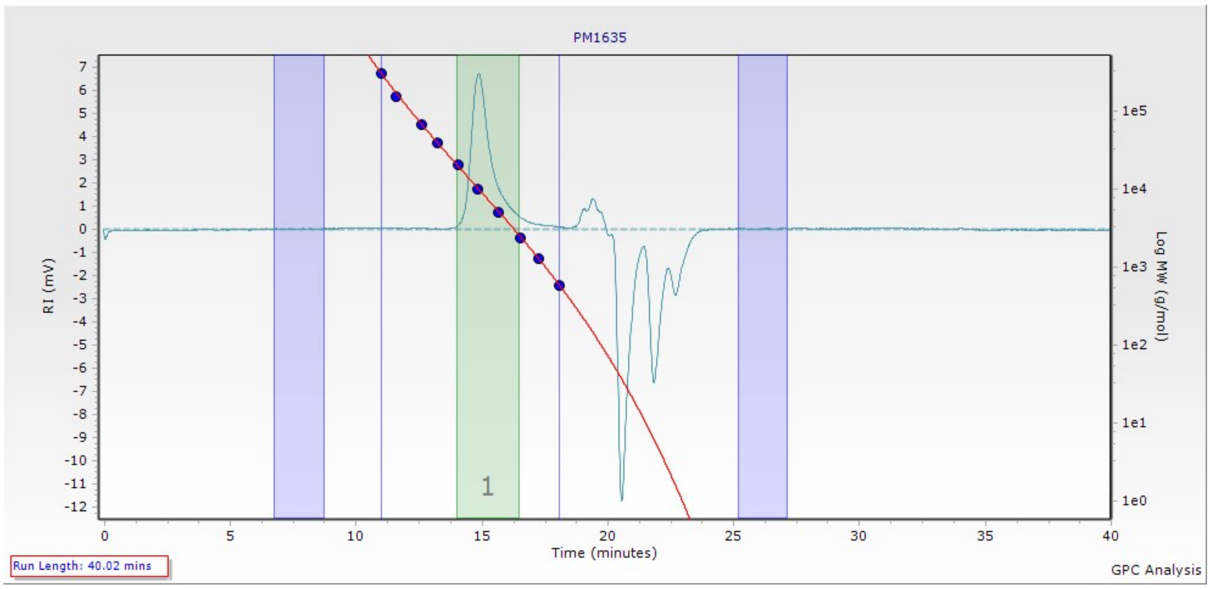


Figure S9: GPC trace of PLA derived from **1** and *rac*-LA.

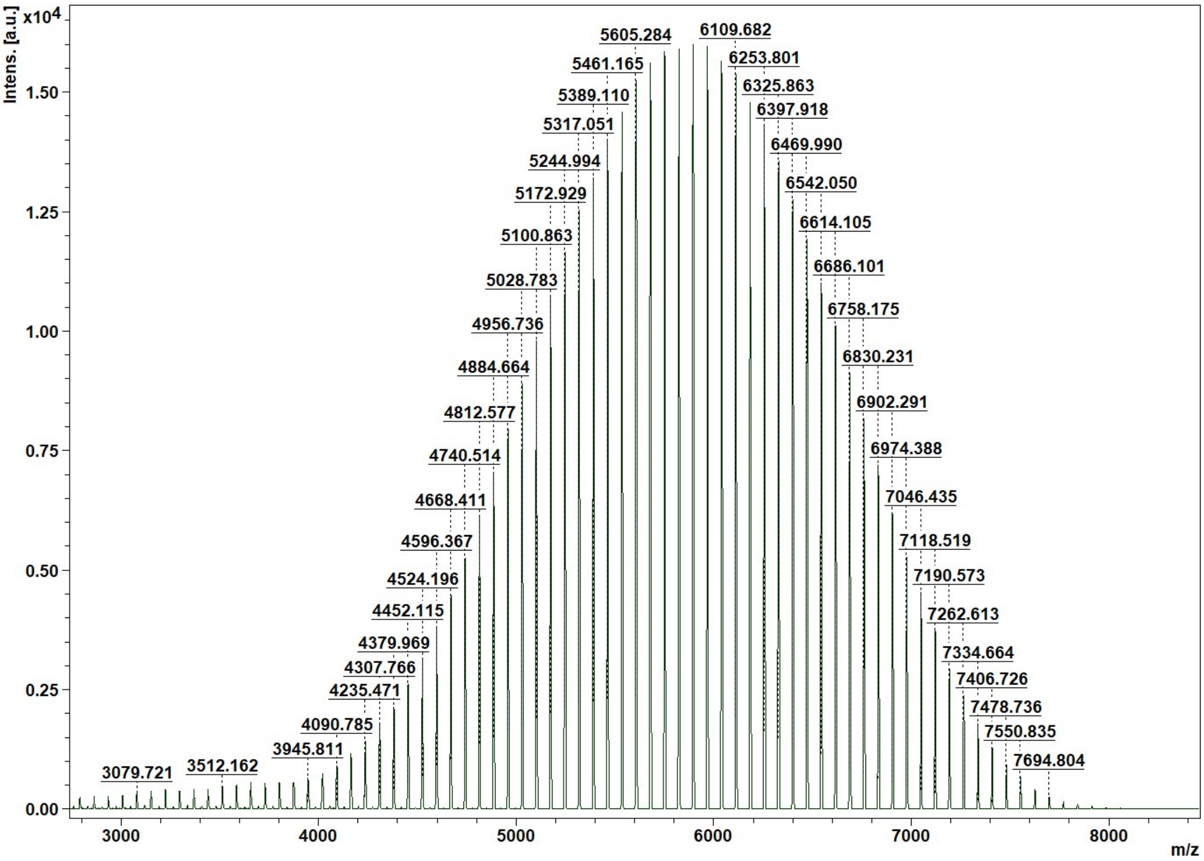


Figure S10: MALDI-ToF spectrum of PLA derived from **1** and *rac*-LA. (For 6109.682 m/z, n = 41.48, (BnOH end group), 42.01 (MeOH end group); For 5605.284 m/z, n = 37.98 (BnOH end group), 38.51 (MeOH end group).

PCL Degradation

General procedure: **1** (10.4 mg, 4 wt %) was added to a J Young's flask containing PCL pieces (0.25 g, M_n = 45,000 g mol^{-1}) in a glove box filled with argon. Toluene (4 mL) and MeOH (1 mL) was added and the flask was submerged in a pre-heated oil bath (100 °C). PCL dissolution occurring within the first 10 min of reaction. Sample aliquots were taken under a flow of argon and analysed by ^{1}H NMR spectroscopy. ^{1}H NMR assignments of methyl 6-hydroxyhexanoate based on literature example.[5]

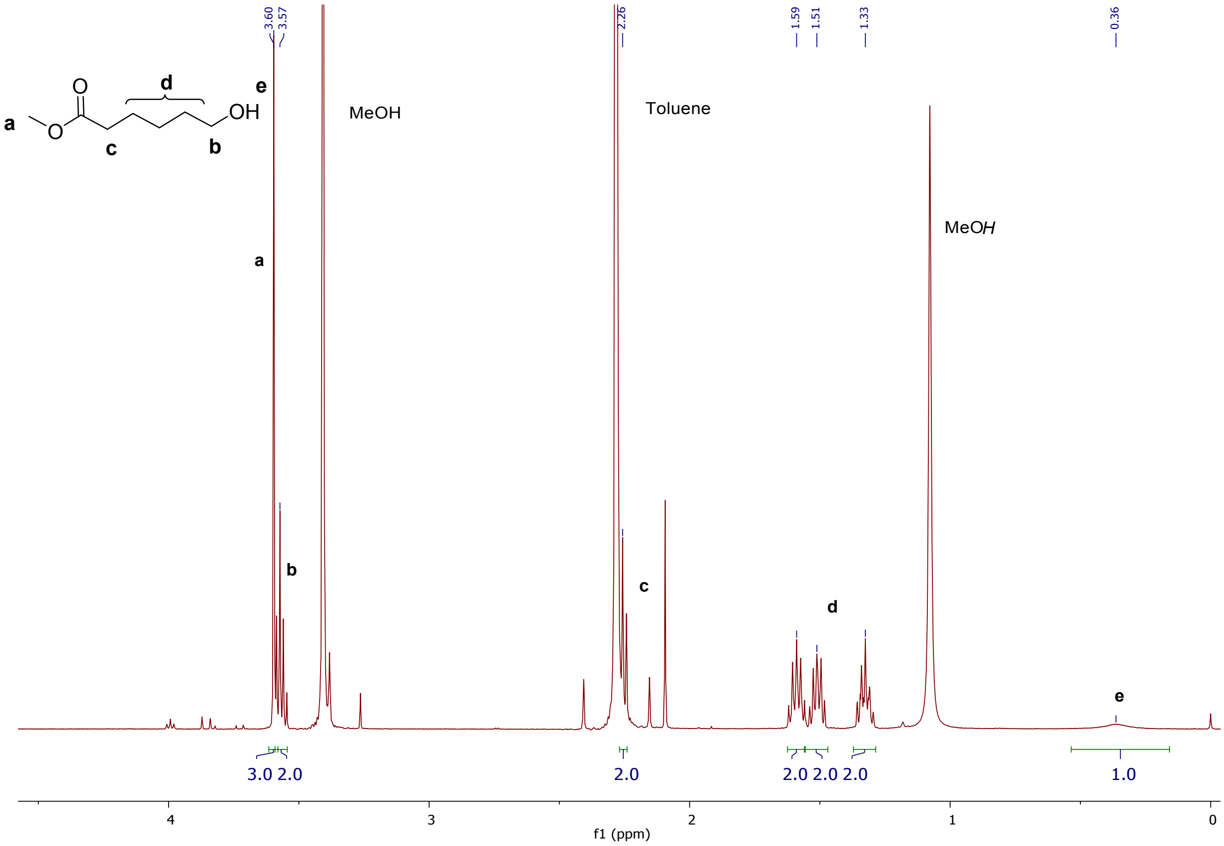


Figure S11: ^{1}H NMR spectrum ($CDCl_3$, 400 MHz, 298 K) of PCL degradation reaction aliquot.

PC Degradation

General procedure: **1** (2.6 mg, 1 wt %) was added to a J Young's flask containing PC pellets (0.25 g, M_n = 45,000 g mol^{-1}) in a glove box filled with argon. 2-MeTHF or DMC (4 mL) and MeOH (1 mL) were added to the flask under a flow of argon and the flask submerged in a pre-heated oil bath (75 °C) Sample aliquots were taken under a flow of argon and analysed by ^{1}H NMR spectroscopy. ^{1}H NMR assignments of degradation products based on literature example.[6]

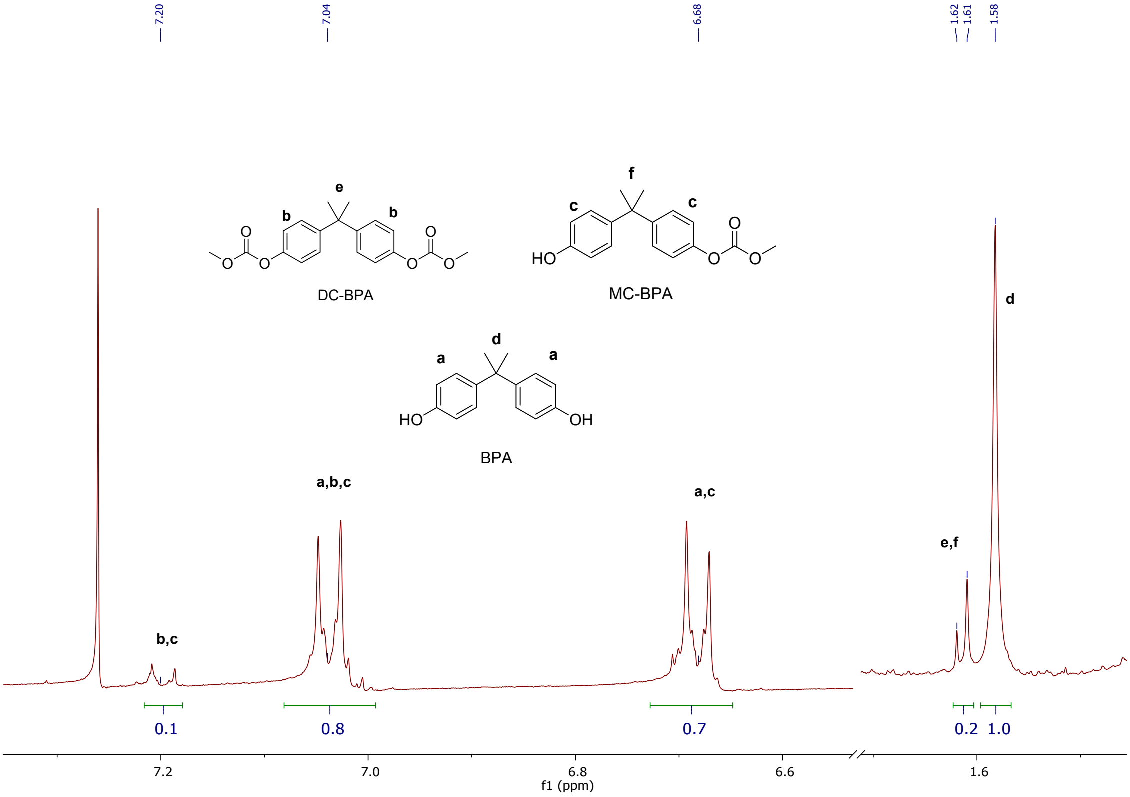


Figure S12: ^{1}H NMR spectrum ($CDCl_3$, 400 MHz, 298 K) of PC degradation in 2-MeTHF after 3 h (75 °C). Selectivity calculated based on methyl region at 1.60 ppm. Signals from carbonates (MC-BPA and DC-BPA) overlap with solvent resonances.

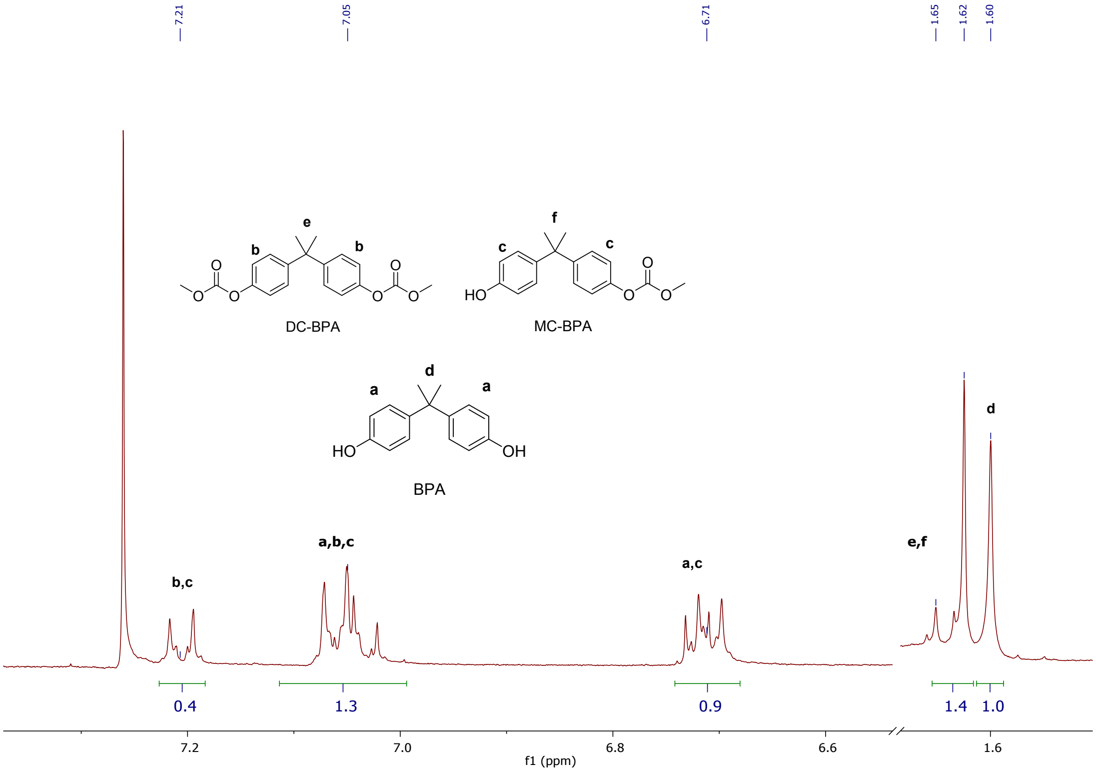


Figure S13: ^{1}H NMR spectrum ($CDCl_3$, 400 MHz, 298 K) of PC degradation in DMC after 3 h (75 °C). Selectivity calculated based on methyl region at 1.60 ppm. Signals from carbonates (DMC, MC-BPA and DC-BPA) overlap with solvent resonances.

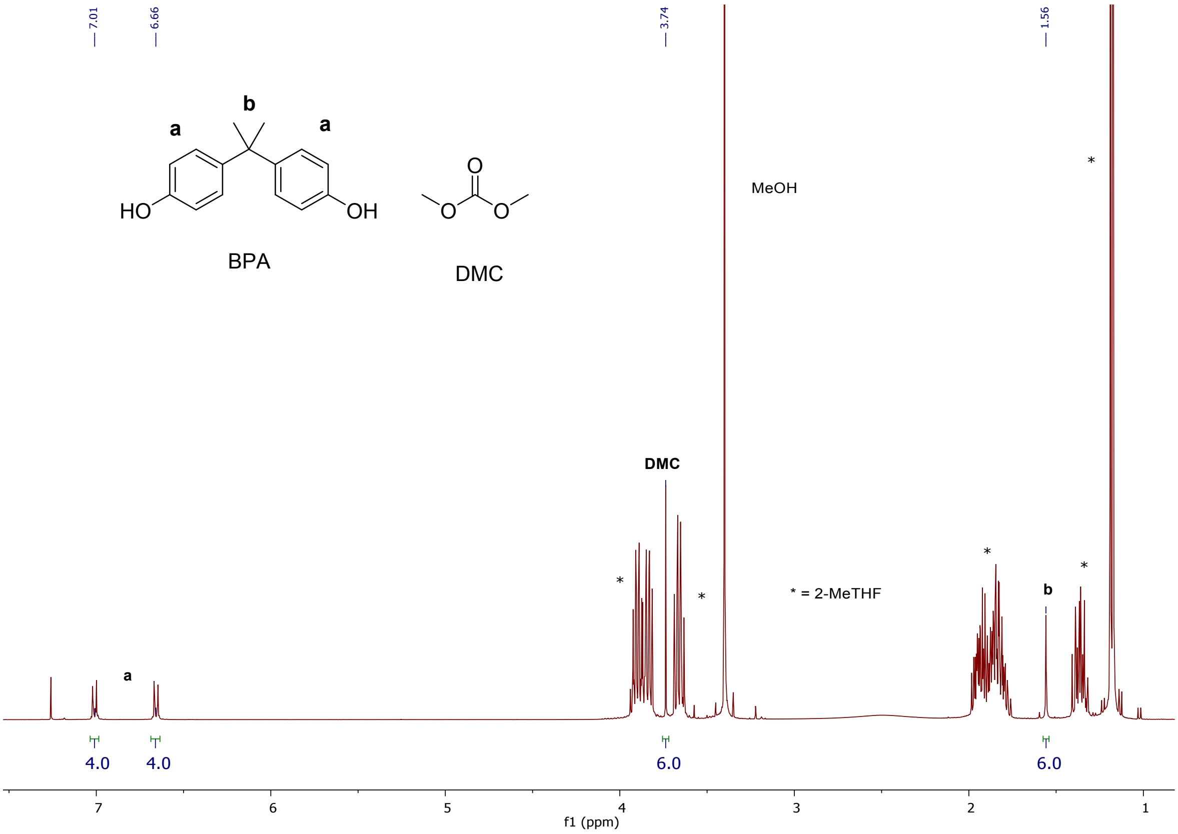


Figure S14: ^{1}H NMR spectrum (CDCl$_3$, 400 MHz, 298 K) of PC degradation in 2-MeTHF after 20 h (75 °C).

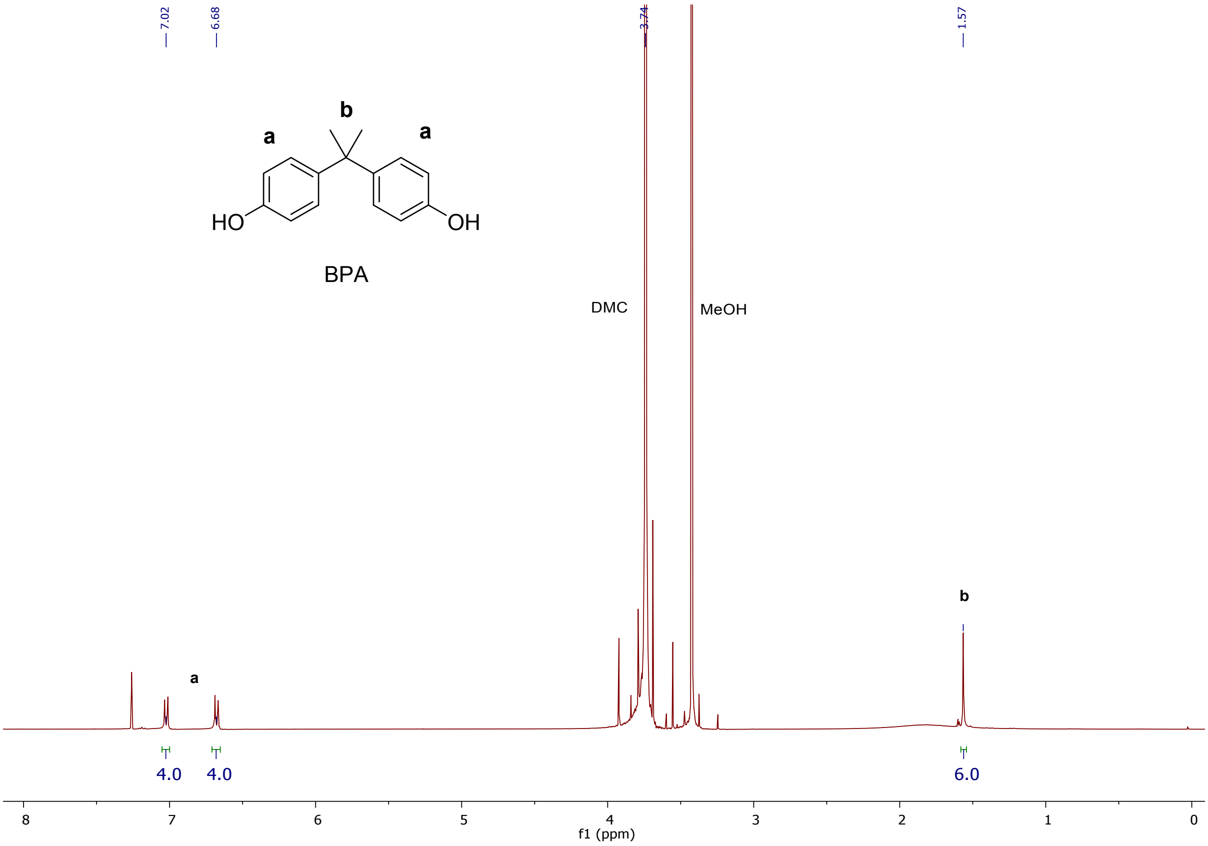


Figure S15: ^{1}H NMR spectrum (CDCl$_3$, 400 MHz, 298 K) of PC degradation in DMC after 20 h (75 °C).

PET Degradation

General degradation procedure: **1** (20.8 mg, 4 wt %) was added to a J Young's flask containing PET pieces (0.50 g, M_n ~ 40,000 g mol^{-1}) in a glove box filled with argon. Toluene (8 mL) and MeOH (2 mL) were added and the flask was submerged in a pre-heated oil bath (100 °C). After reaction, signified by PET dissolution (~16 h), solvent was removed *in vacuo* and the white residue washed with cold MeOH (5 × 5 mL) to give DMT (white powder, 0.36 g, 72 %).

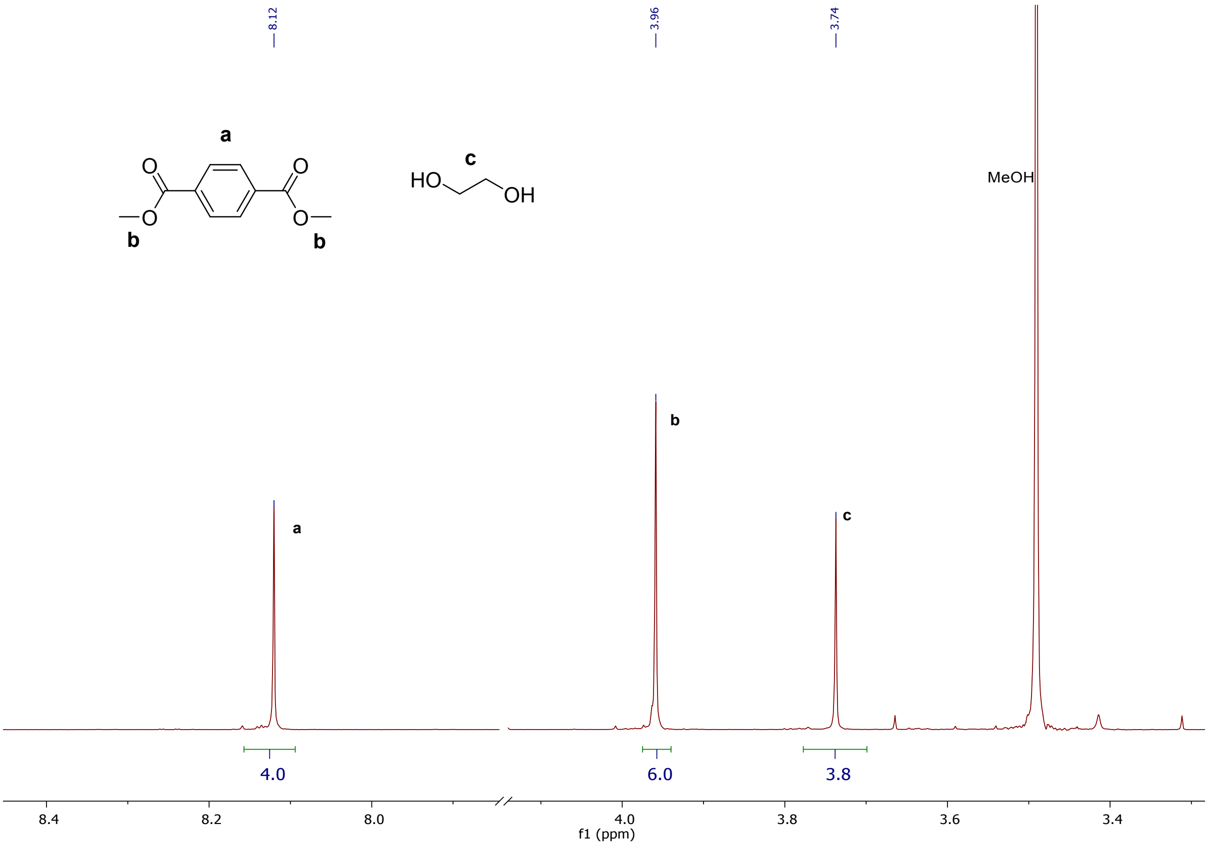


Figure S16: ^{1}H NMR spectrum (CDCl$_3$, 400 MHz, 298 K) of PET degradation with **1** (100 °C).

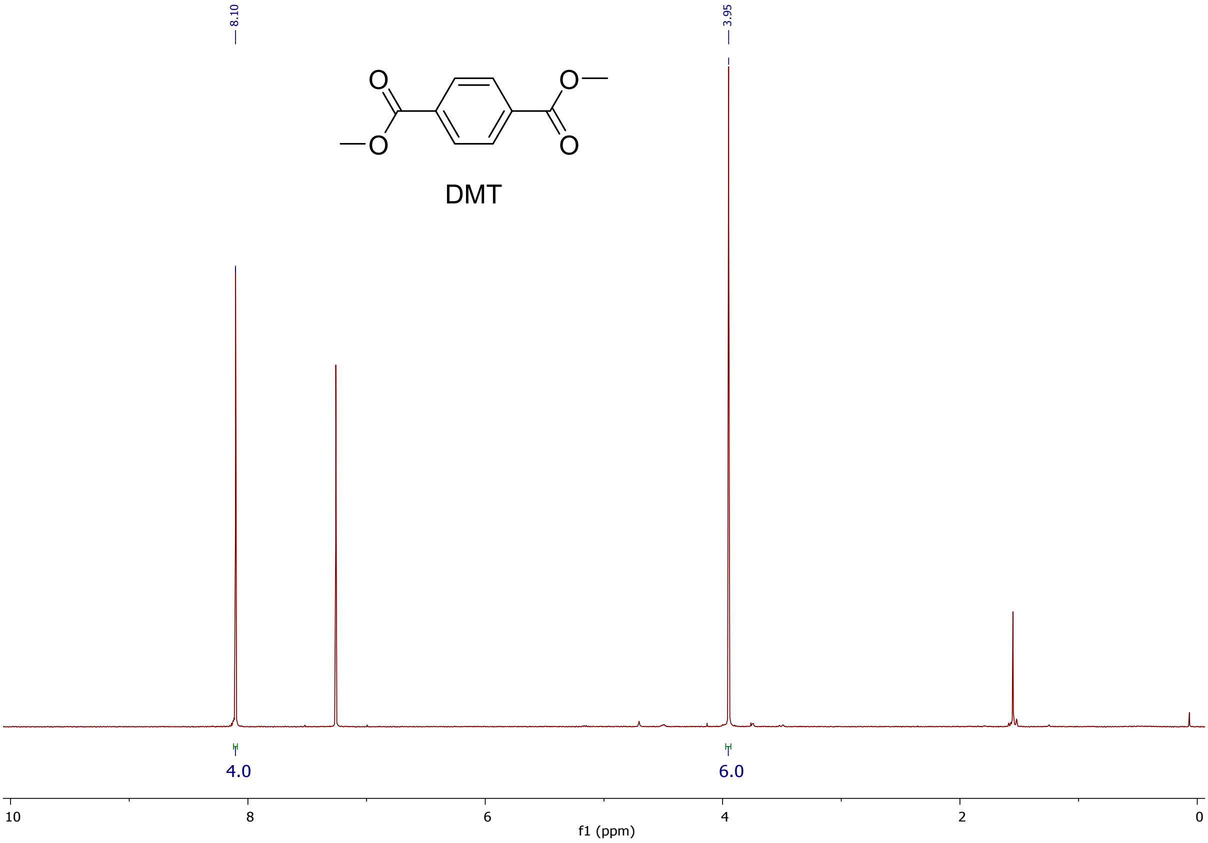


Figure S17: ^{1}H NMR spectrum ($CDCl_3$, 400 MHz, 298 K) of isolated DMT.

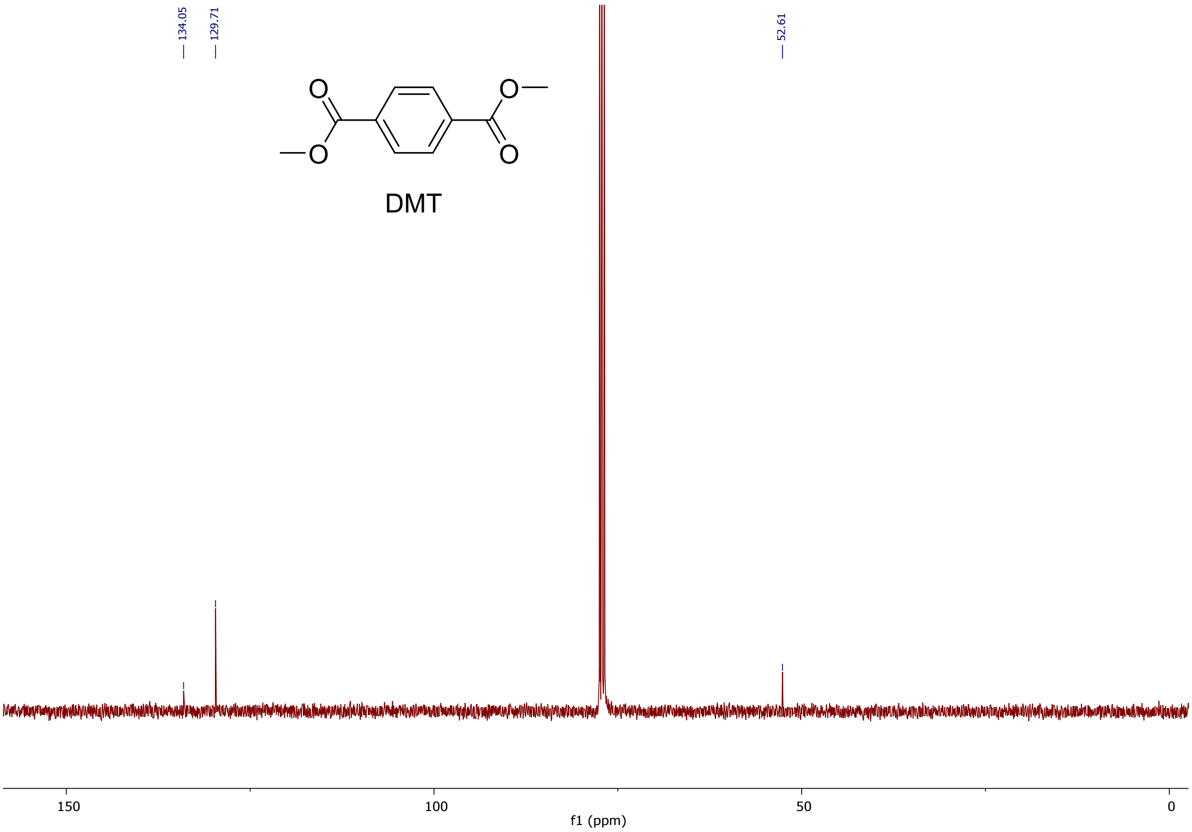
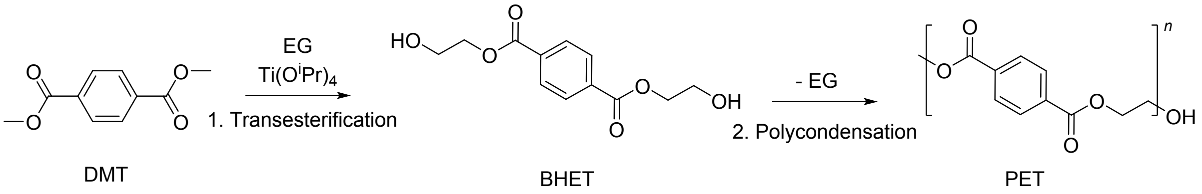


Figure S18: $^{13}C\{^{1}H\}$ NMR spectrum ($CDCl_3$, 100 MHz, 298 K) of isolated DMT.



Scheme 3: DMT polymerisation to PET by transesterification followed by polycondensation.

DMT polymerisation procedure: DMT (125 mg, 0.64 mmol) EG (110.7 mg ,1.78 mmol) were charged into a glass vial with a magnetic stirrer bar. Ti(O^{i}Pr)$_4$ catalyst (400 ppm, stock solution 20 µl mL^{-1} in toluene) was then added. Vials were sealed, evacuated and purged with argon three times. A two-step polymerisation process was performed:

Transesterification stage: performed at 200 ˚C for 4 h under argon. The samples were then dried *in vacuo* at 60 °C for at least 3 h to remove the MeOH formed before the next stage.

Polycondensation stage: reaction vials were placed in a heating block fitted with a distillation assembly. The contents were again subjected to vacuum and argon cycles to remove any oxygen before starting the heating process under argon. Stirring was started once temperature had reached to 200 °C and was further increased to 230 °C at which point vacuum was slowly applied through the distillation assembly. After reaching a pressure of < 1 mbar, temperature was raised to 260 °C and reaction was allowed to take place for 1.5 h followed by 1.5 h at 275 °C and finally 1 h at 280 °C. After this time, the heating was stopped and vacuum removed with introduction of argon and samples were allowed to cool down before analysis with DSC.

References

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