

Ring Opening Metathesis Polymerisation of a New Bio-derived Monomer from Itaconic Anhydride and Furfuryl Alcohol

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Supplementary Information

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The original raw data associated with this research is available at:

DOI: 10.15124ee9b6f2f-1409-4343-b855-bd5af8d97bc7

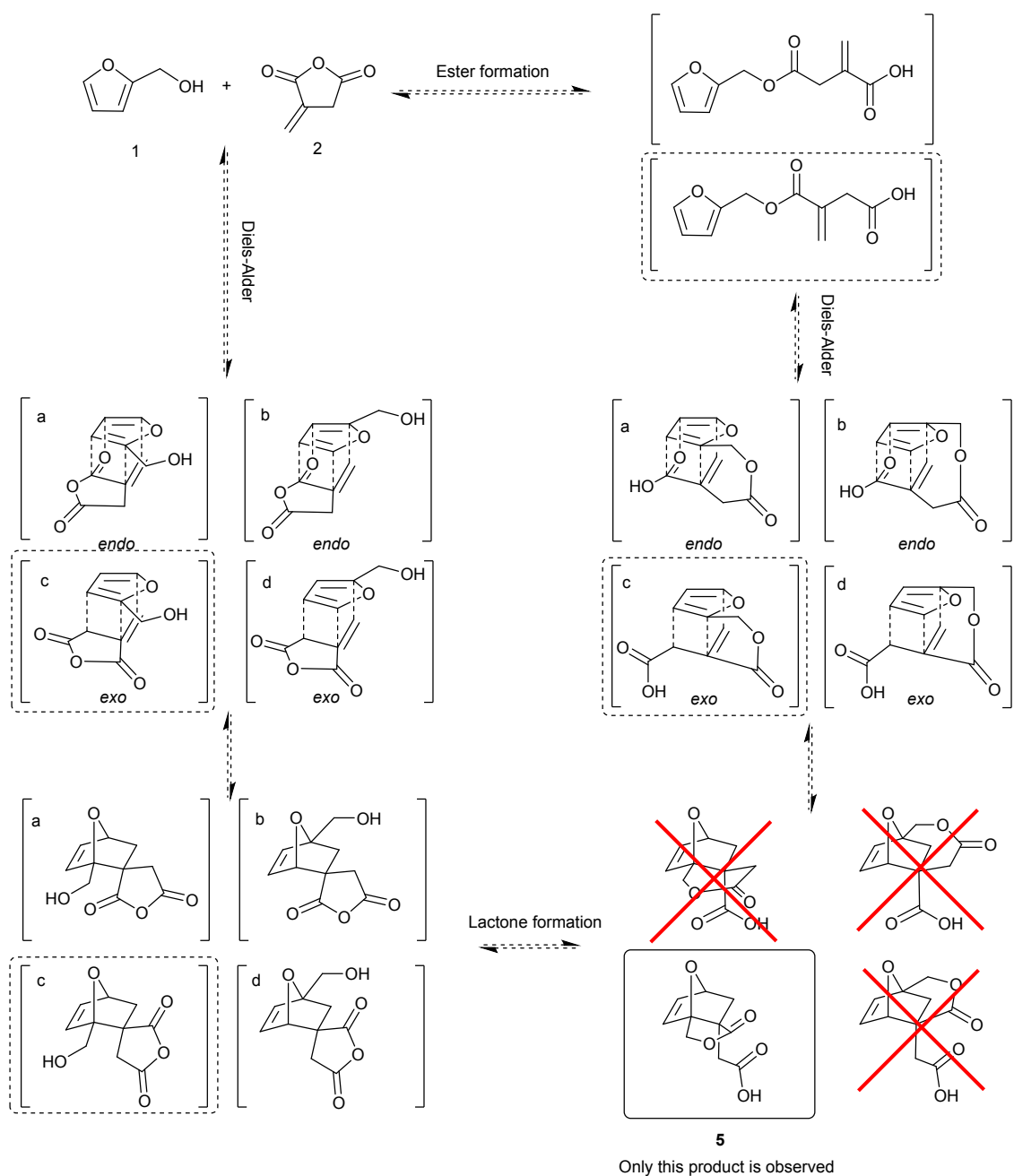


Figure S1: Expanded reaction scheme for tandem Diels-Alder addition and lactonisation of furfuryl alcohol (**1**) and itaconic anhydride (**2**) leading to compound **5** via the intermediates labelled **c**

Experimental Procedures:

Furfuryl alcohol (99+% Sigma-Aldrich) was distilled before use. Itaconic anhydride (99.0+%,Sigma-Aldrich), and all other chemicals, were used as received.

Gel Permeation Chromatography to determine polymer molecular weight was carried out using a set (PSS SDV High) of 3 analytical columns (300 x 8mm, particle diameter 5 μm) of 1000, 10^5 and 10^6 Å pore sizes, plus guard column, supplied by Polymer Standards Service GmbH (PSS) installed in a PSS SECcurity GPC system. Elution was with stabilised tetrahydrofuran at 1ml/min with a column temperature of 23 °C and detection by refractive index. 20 μL of a 1 mg/ml sample in THF was injected for each measurement and eluted for 40 minutes. Calibration was carried out in the molecular weight range 400 – 2×10^6 Da using ReadyCal polystyrene standards supplied by Sigma Aldrich.

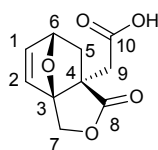
Modulated differential scanning calorimetry (MDSC) experiments were carried out on (DSC, TA Q2000, USA), under nitrogen atmosphere, at a heating rate of 10 °C/min up to a temperature of 200 °C, and using a sample mass of approximately 10 mg. the Tg values were reported from second heating scans.

Diffuse reflectance infrared Fourier transform (DRIFT) spectra were obtained using a Bruker Equinox 55 FT-IR instrument fitted with a Specac Graseby DRIFT accessory.

Diffraction data were collected at 110 K on an Oxford Diffraction SuperNova diffractometer with Cu-K α radiation (λ = 1.54184 Å) using an EOS CCD camera. The crystal was cooled with an Oxford Instruments Cryojet. Diffractometer control, data collection, initial unit cell determination, frame integration and unit-cell refinement was carried out with “CrysAlis”.^{S1} Face-indexed absorption corrections were applied using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm.^{S2} OLEX2^{S3} was used for overall structure solution, refinement and preparation of computer graphics and publication data. Within OLEX2, the algorithm used for structure solution was Superflip, charge-flipping.^{S4} Refinement by full-matrix least-squares used the SHELXL-97^{S5} algorithm within OLEX2.^{S3} All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed using a “riding model” and included in the refinement at calculated positions.

- S1 CrysAlisPro, Oxford Diffraction Ltd. Version 1.171.34.41
- S2 Empirical absorption correction using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm within CrysAlisPro software, Oxford Diffraction Ltd. Version 1.171.34.41
- S3 “Olex2” crystallography software, *J. Appl. Cryst.* 2009, **42**, 339–341.
- S4 SUPERFLIP - a computer program for the solution of crystal structures by charge flipping in arbitrary dimensions, L. Palatinus & G. J. Chapuis, *J. Appl. Cryst.* 2007, **40**, 786-790.
- S5 "SHELXL-97" - program for the Refinement of Crystal Structures. G.M. Sheldrick, *Acta Cryst.* 2008, **A64**, 112-122.

1-oxo-6,7-dihydro-3a,6-epoxy-2-benzofuran-7a(1H,3H)-yl) aceticacid (5)



(5)

Acetonitrile reaction solvent:

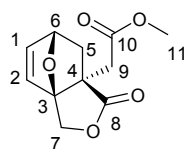
Furfuryl alcohol (8.8 g, 90 mmol) and itaconic anhydride (10 g, 90 mmol) were stirred at 25 °C in acetonitrile (5 ml) for 24 h. The white solid formed was filtered, recrystallized from ethanol and dried under reduced pressure to give acid **5** (11.4 g, 61%). Crystals suitable for X-ray analysis were obtained by recrystallization from acetone (chloroform or ethanol could also be used).

No reaction solvent:

Furfuryl alcohol (8.8 g, 90 mmol) and itaconic anhydride (10 g, 90 mmol) were stirred together at 25 °C for 24 h. Following the reaction the solidified mixture was recrystallized from ethanol to give the desired product **(5)** as white crystals (12.8 g, 68%).

¹H NMR: (MeOD, 400 MHz) δ 6.59 (1H, dd, J=1.6, 5.8, (1)), 6.55 (1H, d, J=5.8, (2)), 5.01 (1H, dd, J=1.6, 4.7, (6)), 4.92 (1H, d, J=10.8, (7)), overlaps water in solvent), 4.54 (1H, d, J = 10.8, (7)), 2.40 (3H, m, (5) & (9)), 1.55 (1H, d, J = 12.2, (5)); ¹³C NMR (δ MeOD, 100 MHz): δ 180.28 (10), 173.25 (8), 139.5 (1), 131.76 (2), 95.85 (4), 80.28 (6), 70.24 (7), 53.52 (3), 40.97 (9), 37.97 (5); FTIR (neat, ATR) ν_{\max} 2956, 1774, 1707; HRMS (ESI) m/z: [M+Na]⁺Calcd for C₁₀H₁₀NaO₅ 233.0420, Found 233.0425; Anal. Calcd for C₁₀H₁₀O₅: C, 57.14; H, 4.80; N, 0.00, Found: C, 57.18; H, 4.76; N, 0.00; Mpt = 132 °C

1-oxo-6,7-dihydro-3a,6-epoxy-2-benzofuran-7a(1H,3H)-yl) methyl ester, 6



(6)

5 (4 g) was dissolved in an excess of methanol (40 ml) and heated for 7 hours at reflux with a catalytic quantity of sulfuric acid (one drop) with added molecular sieves (0.5 g) to remove water. In order to evaluate the utility of different work up conditions the reaction mixture was divided into four equal portions. Each portion was filtered to remove the molecular sieves, neutralised with 5% aqueous sodium bicarbonate solution (10 ml), and the methanol removed *in vacuo*. Three of the portions were extracted with dichloromethane, 2-methyl

tetrahydrofuran or ethyl acetate (20ml) respectively, the crude solid was recovered from the fourth portion by simple filtration and washing with deionised water. Cyclopentyl methyl ether (CPME) was considered, but tests showed that the authentic product was not soluble in this solvent.

Work up/solvent	DCM	2-MeTHF	EtOAc	Filtration	CPME
Crude Mass (g)	0.82	0.48	0.66	0.62	Product insoluble
Crude Yield (%)	77	45	62	58	-

Following this, the reaction was carried out again on the same scale, substituting the use of molecular sieves for Dean-Stark apparatus with continuous removal of methanol/water from the Dean-Stark trap and addition of clean methanol to the reaction to maintain an approximately constant volume of solvent. Otherwise, reaction conditions were as described above. This was divided equally into two portions. In each case, as above, the mixture was neutralised with aqueous sodium bicarbonate solution and the methanol removed *in vacuo*. For one portion the crude material was recovered by simple filtration and washing with deionised water (1.11g, 52%). For the other portion, the material was extracted with ethyl acetate (30 ml), washed with deionised water (2 x 20ml) and concentrated *in vacuo* to give the crude material (1.35g) which was then recrystallized from methanol (1.039g, 49%).

¹H NMR (CDCl₃, 400 MHz,) δ 6.55 (1H, dd, J = 5.8, 1.7, (1)), 6.48 (1H, d, J = 5.8, (2)), 5.04 (1H, dd, J = 4.7, 1.6, (6)), 4.79 (1H, d, J = 10.8, (7)), 4.61 (1H, d, J = 10.8, (7)), 3.69 (3H, s, (11)), 2.53 (2H, m, (5) & (9)), 2.31 (1H, d, J = 14.6, (9)), 1.49 (1H, d, J = 12.2, (5)). ¹³C NMR (CDCl₃, 100 MHz) δ 177.2 (10), 170.0 (8), 138.1 (1), 130.7 (2), 94.1 (4), 78.8 (6), 68.8 (7), 52.3 (11), 52.1 (3), 39.9 (9), 36.7 (5); FTIR (neat, ATR) ν_{\max} 3020, 2960, 1768, 1724; HRMS (ESI) m/z: [M+Na]⁺ Calcd for C₁₁H₁₂NaO₅ 247.0577; Found 247.0582; Mpt = 96 °C

ROMP General Method

At ambient temperature, the appropriate amount of the synthesized monomer **6** was dissolved in 1,2-dichloroethane (DCE) and the solution was degassed by three freeze-thaw cycles. A degassed solution of Grubbs 2nd gen in DCE was added to the monomer solution with constant stirring under an argon atmosphere. The reaction was terminated after specified time by the addition of ethyl vinyl ether followed by stirring for additional 30 min. After filtration through short column of silica gel, the polymer was precipitated into hexane, the hexane decanted and the polymer dried under reduced pressure. The copolymer of **6** and **8** was prepared by the same method. In later experiments, DCE was substituted with dimethylcarbonate, diethylcarbonate, tetrahydrofuran and ethyl acetate but otherwise the methodology for these reactions was the same.

Spectroscopic data:

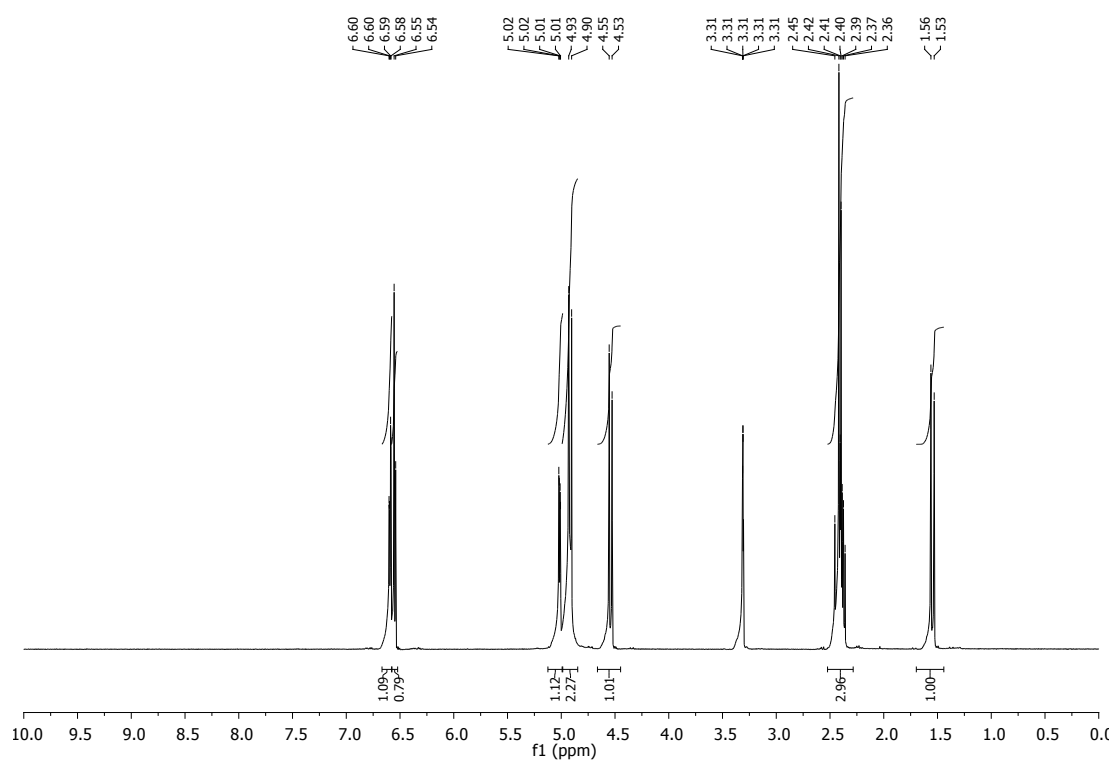


Figure S2: ¹H NMR spectrum of acid **5** in CD₃OD – for full assignment see synthetic procedure above

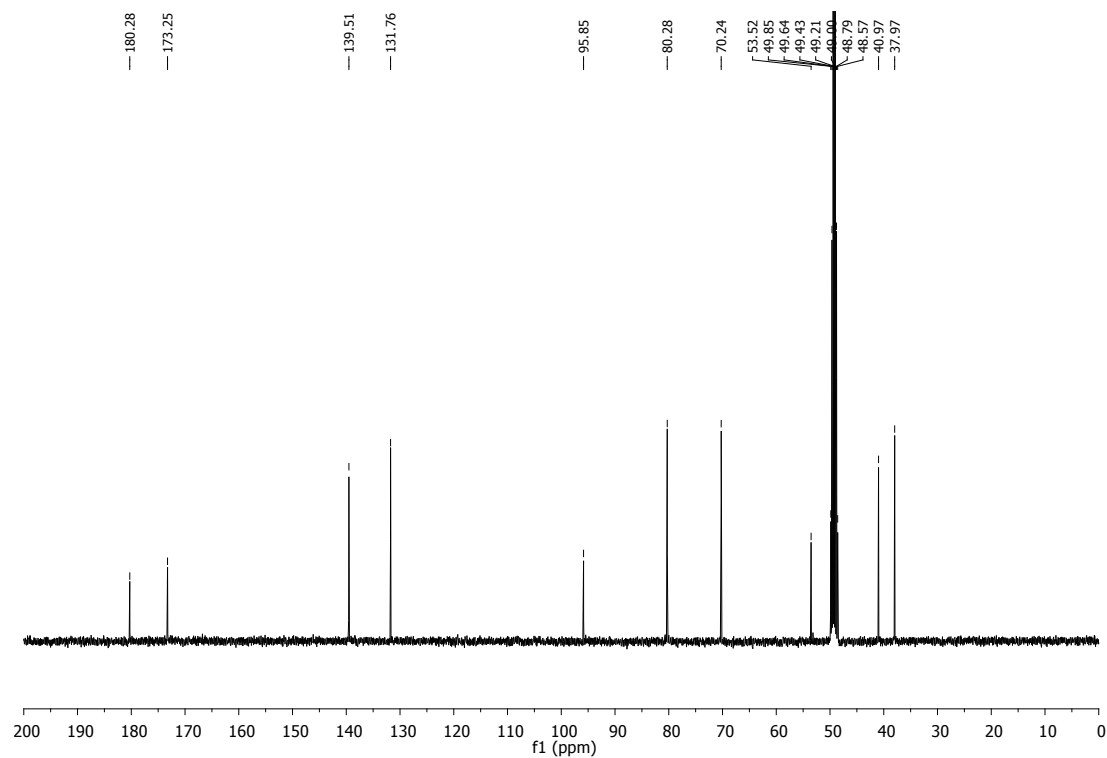


Figure S3: ¹³C NMR spectrum of acid **5** in CD₃OD – for full assignment see synthetic procedure above

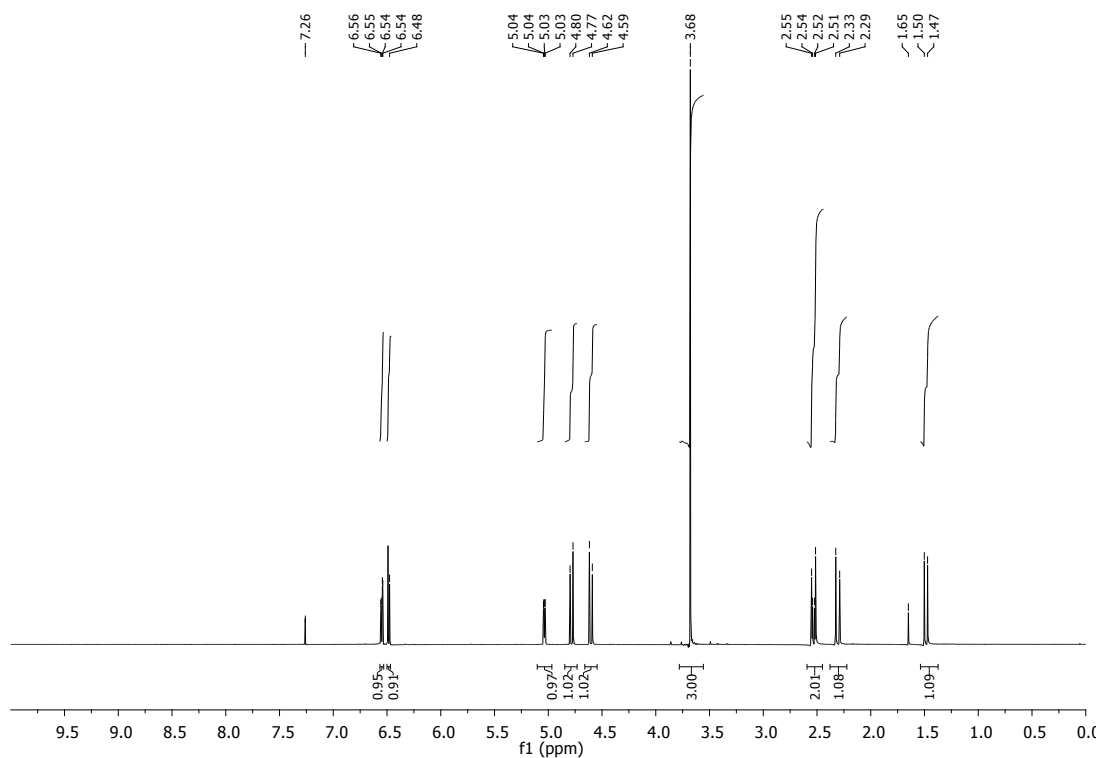


Figure S4: ^1H NMR spectrum of methylester **6** in CD_3OD – for full assignment see synthetic procedure above

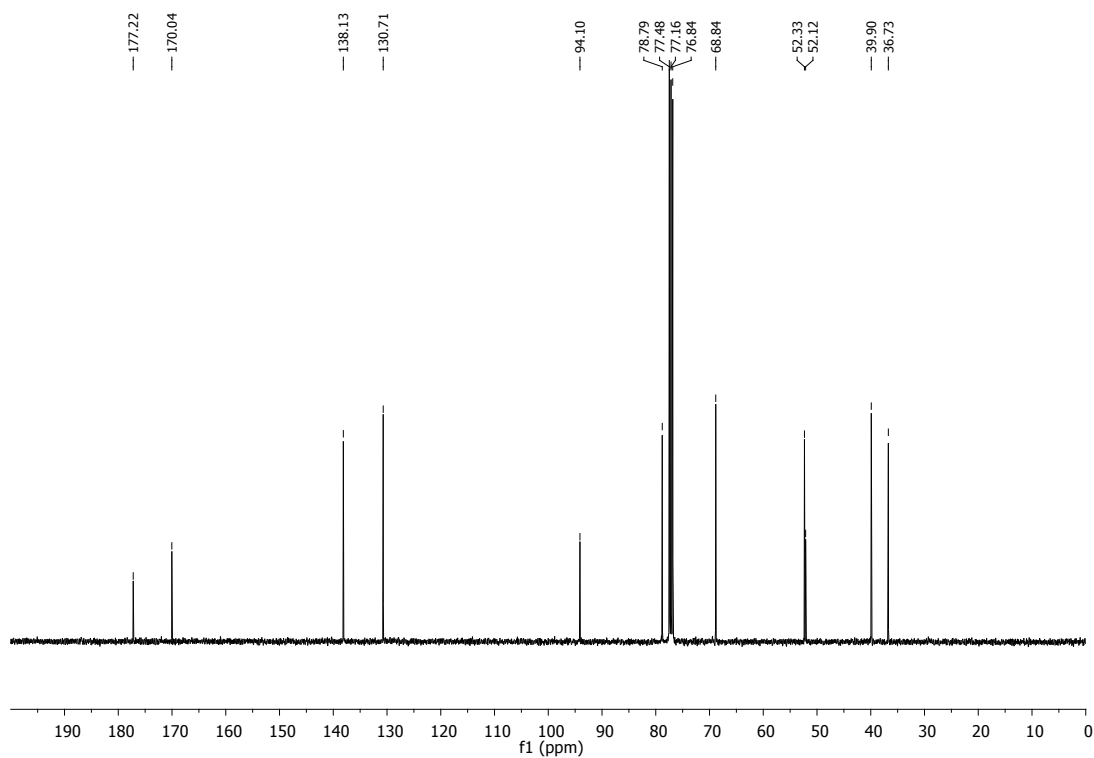


Figure S5: ^{13}C NMR spectrum of methylester **6** in CD_3OD – for full assignment see synthetic procedure above

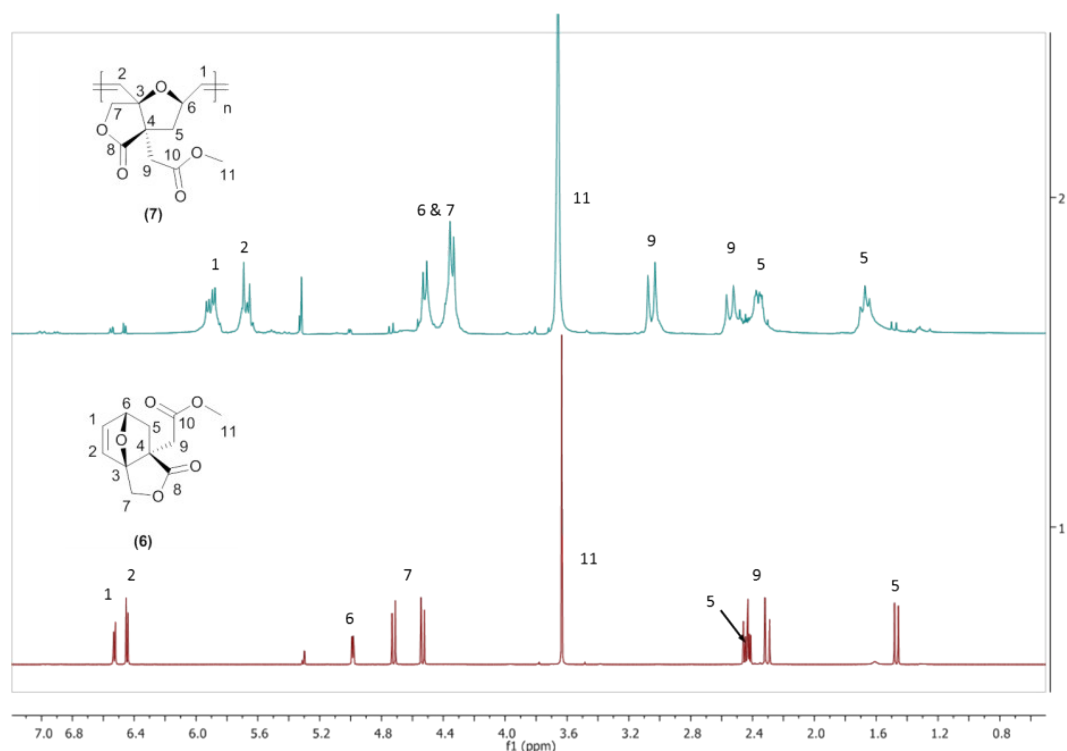


Figure S6: ^1H NMR ((400 MHz/ CD_2Cl_2) of the monomer **6** and the corresponding polymer, spectrum obtained *in situ* before quenching with ethyl vinyl ether, after which this homopolymer becomes insoluble.

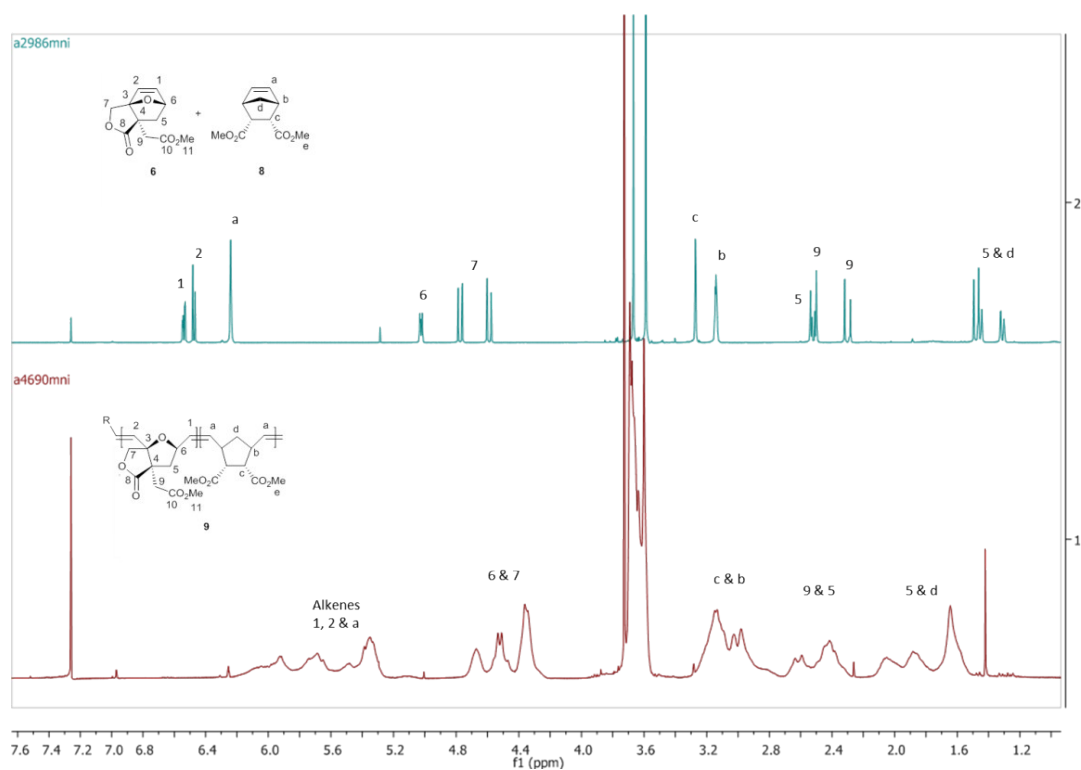


Figure S7: ^1H NMR (400 MHz/ CDCl_3) of a mixture of the monomers **6** and **8** and the corresponding equimolar copolymer

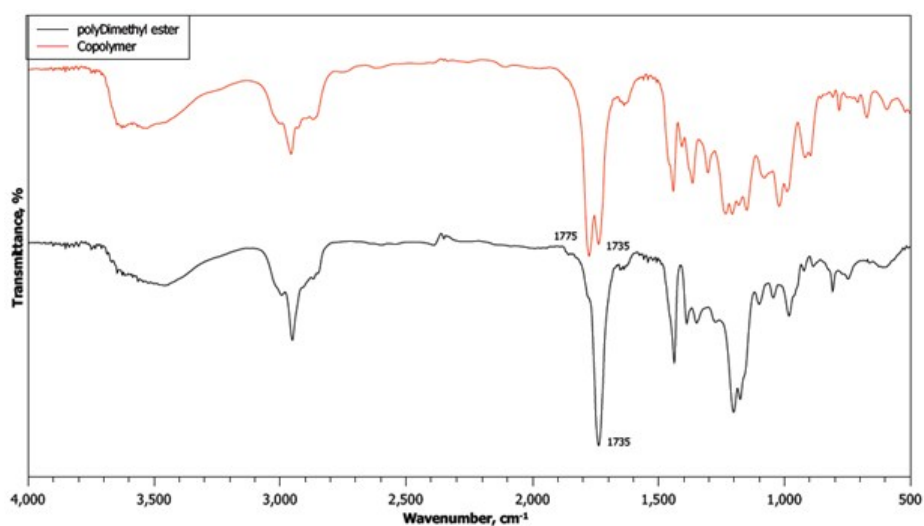


Figure S8: DRIFT spectra of the homopolymer of **8** and the copolymer **9**.

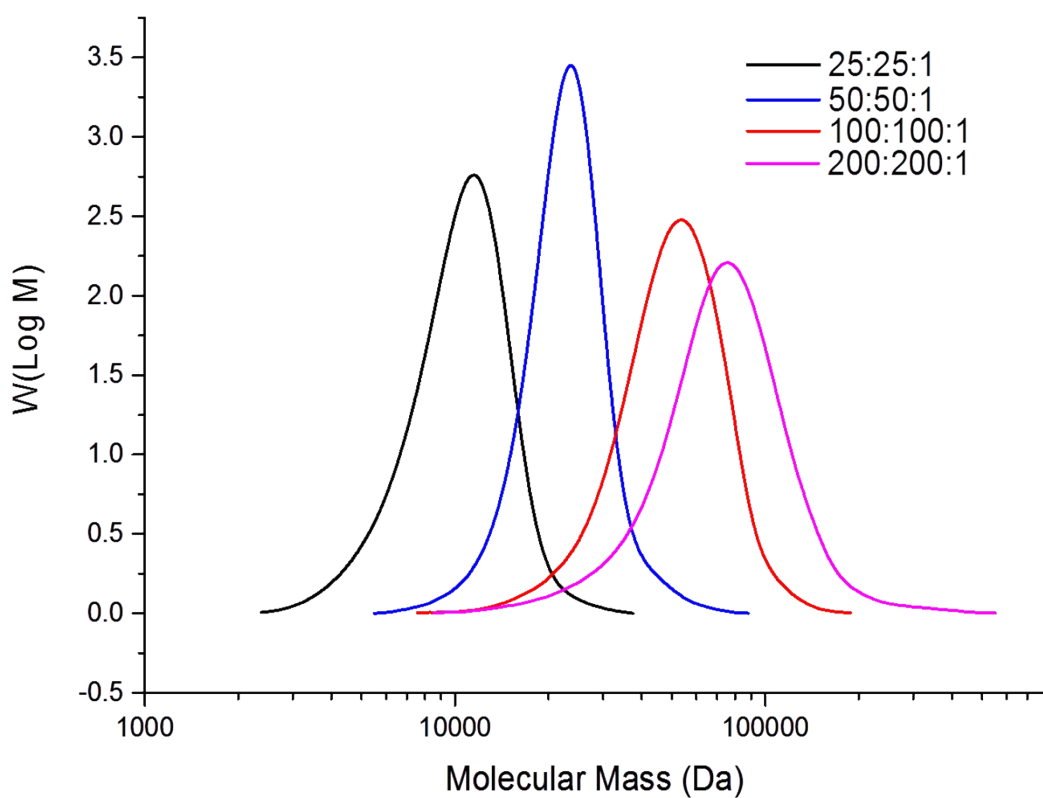


Figure S9: GPC Molecular mass data of 1:1 copolymers **9** at increasing monomer: catalyst ratios.

Thermal Stability Data:

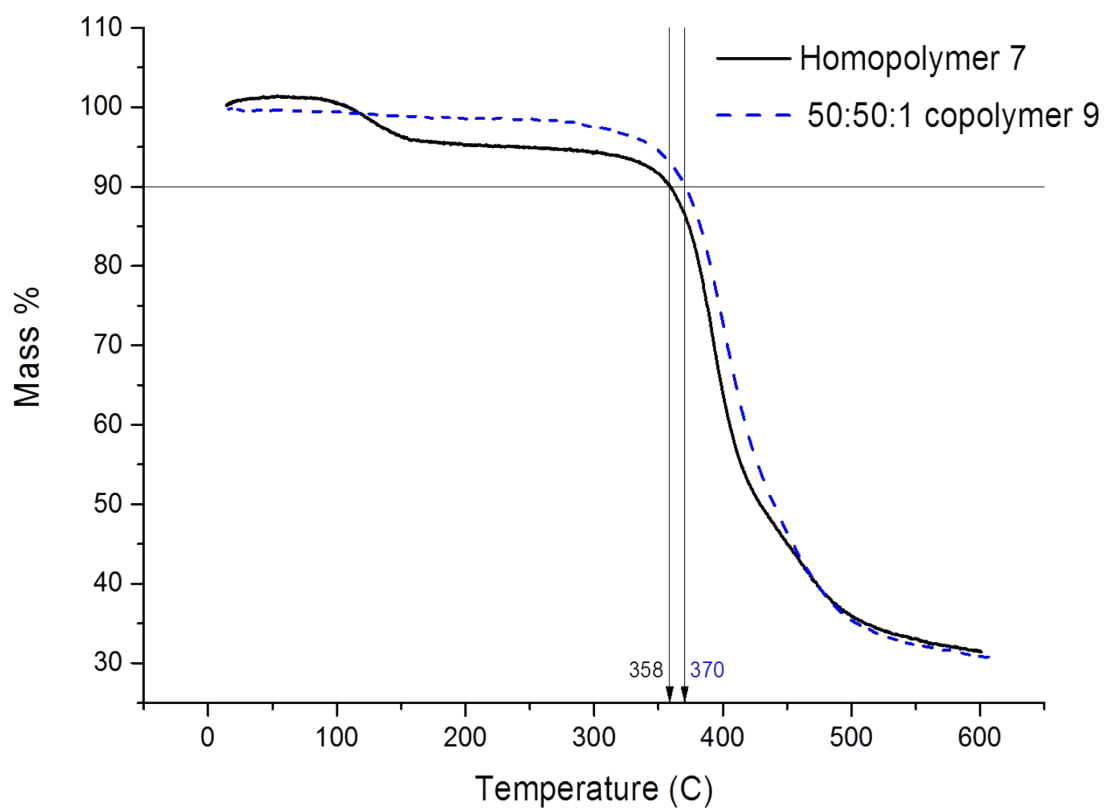


Figure S10: Thermogravimetric analysis showing stability of homopolymer **7** and copolymer **9**, with the temperature of 10% decomposition mass loss (TD₁₀) highlighted.