5-Ethylidene-2-norbornene (ENB) and 5-Vinyl-2-norbornene (VNB) based Alicyclic Polyols for the Synthesis of Polyesters

Supplementary Information

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1. General considerations

Hydroformylation and hydrogenation reactions were performed in a 100 mL steel autoclave equipped with a glass inlay, magnetic stirring and oil bath heating under exclusion of water and oxygen. Additionally, for hydroformylation an atmosphere of a mixture of carbon monoxide 4.7 ($\geq$ 99.999 %, *Westfalen AG*) and hydrogen 5.0 ($\geq$ 99.999%, Westfalen AG), and for hydrogenation an atmosphere of hydrogen 5.0 ($\geq$ 99.999%, *Westfalen AG*). The big scale hydroformylation and hydrogenation reactions were performed in a 2 L Parr Bench Top reactor from *Parr Instrument Company* with a 4848 Reactor Controller. Unless otherwise stated, all other reactions with air and moisture-sensitive substances were carried out under argon atmosphere using standard Schlenk techniques or in a glovebox. Prior to use, all glassware was heat-dried under vacuum. Toluene, DCM and THF were dried over a solvent purification system (SPS) MB SPS-800 from *MBraun* and stored over 4 Å molecular sieves in 500 mL Schlenk flasks. Toluene was deoxygenated by bubbling argon through the solvent. 5-ethylidene-2-norbornene and 5-vinyl-2-norbornene were stored over 4 Å molecular sieves in 500 mL Schlenk flasks. All commercially available chemicals were purchased from *abcr GmbH*, *Acros Organics*, *Sigma Aldrich Chemie GmbH* and *Tokyo Chemical Industry Co* and used without further purification.

2. General analytical methods

Nuclear magnetic resonance spectroscopy (NMR). The ^{1}H and ^{13}C nuclear magnetic resonance spectra were measured on *Bruker* AV400, AV500 and AV500cryo at ambient temperature (298K). Chemical shifts are given in parts per million (ppm) and were referenced using the residual proton signal of $CDCl_3$ [δ (^{1}H) = 7.26 ppm, (^{13}C) = 77.2 ppm]. All coupling constants (*J*) are reported in Hertz (Hz). As abbreviation for the signal multiplicity the following abbreviations are used: s-singlet, bs-broad singlet, d-duplet, t-triplet, q-quartet, m-multiplet.

Gas chromatography mass spectrometry (GC MS). Gas chromatography mass spectrometry analytical measurements were performed with toluene, DCM and EtOAc solutions on an *Agilent* GC 7890B using a HP-5MS UI column (0.25 mm, 0.25 μm) and a single quadrupole mass detector MS 5977A, equipped with an G4514A autoinjector.

Gas chromatography flame ionization detector (GC FID). Gas chromatography mass spectrometry analytical measurements were performed on an *Agilent* GC 7890B using a HP-5 column (0.32 mm, 0.25 μm) and a flame ionization detector 7693A, equipped with an G4514A autoinjector.

Electron-Spray Ionization Mass Spectrometry (ESI MS). The purified sample was measured on a *Thermo Fisher Scientific* Exactive Plus Orbitrap in negative mode in HPLC acetonitrile.

Fourier-transform infrared spectroscopy (FT IR). The samples were prepared as a thin film by drop casting the sample on a silicon wafer and the spectra were obtained using a *Nicolet* 8700 FTIR in combination with a Nicolet Continuum FTIR microscope at ambient temperature (298 K).

Gel permeation chromatography (GPC). The polymer molar mass and distribution were assessed by gel permeation chromatography in THF as the eluent and poly(styrene) as the standard on a PL-GPC 50 Plus from *Polymer Laboratories* using PLgel 5 m MIXED-C (2 × 7.5 × 300 mm). Samples of 4 mg mL^{-1} were eluted at 40 °C.

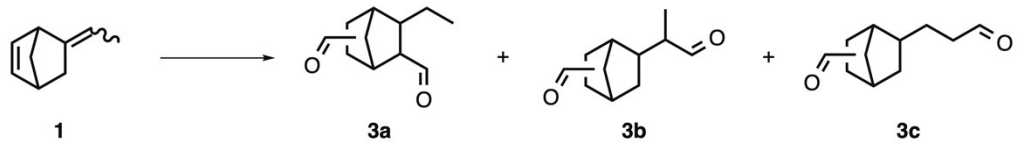
Thermogravimetric analysis (TGA). For thermogravimetric analysis a TGA Q5000 from *TA Instruments* is used. Generally, a heating rate of 10 K min^{-1} under argon is applied. All samples are in a mass range of 1 mg to 2 mg. Analysis of the mass loss in dependency of the time is performed using TA Universal software. The onset-point describes the initial temperature of the decomposition of the material.

Differential scanning calorimetry (DSC). Differential scanning calorimetry measurements were performed with a DSC Q2000 from *TA Instruments*. The samples of 5 mg to 10 mg were filled into an aluminum pan (T_{zero}) for non-hermetic measurements or a hermetic aluminum pan ($T_{zeroherm}$) for hermetic measurements. The samples were heated from −100 °C to 200 °C at a rate of 10 K min^{-1}. The reported values were determined with a TA Universal software from the third heating cycle.

3. Synthesis procedures

3.1 Monomer synthesis

Hydroformylation experiments



10.14 mg (24.96 μmol, 0.10 mol%) of $[Rh(COD)_2]BF_4$ and 50.06 mg (77.37 μmol, 0.31 mol%) of Alkanox® were dissolved in 25 mL toluene (1.00 M) in a snap-cap vial in an autoclave. To the solution 3.00 g (24.96 mmol, 1.00 eq.) of **1** were added. The autoclave was pressurized with 50 bar of syngas (CO/H_2 = 1/1) and the reaction mixture was stirred for 4 h at a reaction temperature of 100 °C. The resulting pale-yellow solution was cooled down to room temperature, the solvent was removed in vacuo and the product was purified by distillation (b.p.: 65-76 °C, p = 0.05 mbar) to yield 3.42 g (18.97 mmol, 76%) of **3** as a colorless liquid.

^{1}H NMR (500 MHz, $CDCl_3$, 298 K): δ (ppm) = 9.78-9.74 (m, 0.24 H, CHO), 9.67-9.53 (m, 1.76 H, CHO), 2.67-2.49 (m, 1 H), 2.49-2.38 (m, 1 H), 2.38-1.15 (m, 11 H), 1.14-0.99 (m, 3 H), 0.98-0.88 (m, 0.40 H), 0.88-0.63 (m, 0.40 H).

Due to the big overlap of the aliphatic proton signals in the ^{1}H NMR spectrum, only the resonances of the signals of the aldehyde protons could be assigned.

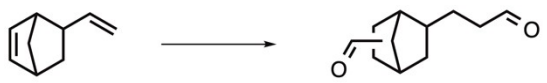
^{13}C NMR (101 MHz, $CDCl_3$, 298 K) δ (ppm) = 204.93 (CHO), 204.87 (CHO), 204.72 (CHO), 204.69 (CHO), 204.56 (CHO), 204.54 (CHO), 204.46 (CHO), 203.73 (CHO), 203.21 (CHO), 203.11 (CHO), 203.04 (CHO), 202.99 (CHO), 202.92 (CHO), 202.90 (CHO), 202.87 (CHO), 202.64 (CHO), 202.59 (CHO), 202.57 (CHO), 202.48 (CHO), 202.46 (CHO), 202.25 (CHO), 202.19 (CHO), 201.97 (CHO), 201.78 (CHO), 61.42 (CH), 61.09 (CH), 55.18 (CH), 55.13 (CH), 55.09 (CH), 54.82 (CH), 54.75 (CH), 53.93 (CH), 53.90 (CH), 53.80 (CH), 53.70 (CH), 51.60 (CH), 51.32 (CH), 51.15 (CH), 49.87 (CH), 49.74 (CH), 48.92 (CH), 48.87 (CH), 48.11 (CH), 47.76 (CH), 47.75 (CH), 47.66 (CH), 43.13 (CH_2), 43.10 (CH), 43.08 (CH_2), 43.04 (CH), 42.90 (CH), 42.84 (CH), 42.62 (CH), 42.50 (CH), 42.36 (CH_2), 41.93 (CH), 41.82 (CH), 41.67 (CH), 41.61 (CH), 41.53 (CH), 41.22 (CH), 41.07 (CH), 40.79 (CH), 40.77 (CH), 40.50 (CH), 40.39 (CH), 40.21 (CH), 39.79 (CH), 39.63 (CH), 39.53 (CH), 39.49 (CH), 39.47 (CH), 39.28 (CH), 39.11 (CH), 38.74 (CH), 38.65 (CH), 38.59 (CH), 38.56 (CH), 38.48 (CH), 38.41 (CH), 38.24 (CH), 38.22 (CH), 38.19 (CH), 38.01 (CH), 37.79 (CH_2), 37.70 (CH_2), 37.60 (CH_2), 37.54 (CH_2), 37.49 (CH_2), 37.48 (CH_2), 36.95 (CH_2), 36.88 (CH_2), 36.85 (CH), 36.76 (CH), 36.65 (CH), 36.55 (CH_2), 36.38 (CH_2), 36.36 (CH), 36.33 (CH_2), 36.28 (CH_2), 36.20 (CH), 36.09 (CH), 36.05 (CH_2), 35.44 (CH_2), 35.27 (CH_2), 35.14 (CH_2), 35.10 (CH_2), 35.03 (CH_2), 34.94 (CH_2), 33.80 (CH_2), 33.73 (CH_2), 33.70 (CH_2), 33.64 (CH_2), 33.28 (CH_2), 33.25 (CH_2), 30.84 (CH_2), 30.82 (CH_2), 30.76 (CH_2), 30.66 (CH_2), 30.60 (CH_2), 30.47 (CH_2), 29.85 (CH_2), 29.54 (CH_2), 29.47 (CH_2), 29.18 (CH_2), 28.55 (CH_2), 28.32 (CH_2), 25.09 (CH_2), 24.90 (CH_2),

24.87 (CH_2), 24.78 (CH_2), 23.65 (CH_2), 23.25 (CH_2), 22.98 (CH_2), 22.91 (CH_2), 13.59 (CH_3), 13.24 (CH_3), 13.14 (CH_3), 13.08 (CH_3), 12.95 (CH_3), 12.89 (CH_3), 11.73 (CH_3), 11.72 (CH_3).

GC MS: t_R = 8.0-8.8 min, *m*/*z* = 180.1 [M^+], 162.1 [$M\text{-}H_2O]^+$.

TGA: T_d = 107 °C.

DSC: T_g = −88 °C.



2 **3c**

10.14 mg (24.96 μmol, 0.10 mol%) of $[Rh(COD)_2]BF_4$ and 21.60 mg (27.46 μmol, 0.11 mol%) of Oxophos® were dissolved in 25 mL toluene (1.00 M) in a snap-cap vial in an autoclave. To the solution 3.00 g (24.96 mmol, 1.00 eq.) of **2** were added. The autoclave was pressurized with 50 bar of syngas (CO/H_2 = 3/1) and the reaction mixture was stirred for 4 h at a reaction temperature of 100 °C. The resulted pale-yellow solution was cooled down to room temperature, the solvent was removed in vacuo and the product was purified by distillation (b.p.: 74-76 °C, p = 0.05 mbar) to yield 1.80 g (9.98 mmol, 40%) of **3c** as a colorless liquid.

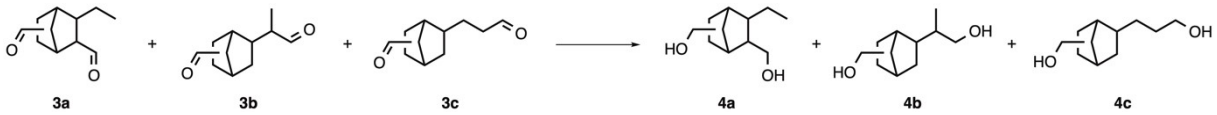
^{1}H NMR (500 MHz, $CDCl_3$, 298 K): δ (ppm) = 9.76-9.71 (m, 1H, CHO), 9.62-9.57 (m, 1 H, CHO), 2.58-2.51 (m, 0.50 H), 2.49 (d, $^3J_{H,H}$ = 4.8 Hz, 0.50 H), 2.45-2.37 (m, 2 H), 2.31-2.18 (m, 2.50 H), 2.05 (d, $^3J_{H,H}$ = 4.2 Hz, 0.15 H), 1.82-1.70 (m, 1.50 H), 1.69-1.54 (m, 2.50 H), 1.54-1.39 (m, 1 H), 1.32-1.13 (m, 2.50 H), 1.13-1.07 (m, 0.30 H), 1.07-0.98 (m, 0.60 H), 0.72 (ddd, $^3J_{H,H}$ = 4.8 Hz, 0.40 H), 0.65 (ddd, $^3J_{H,H}$ = 5.1 Hz, 0.30 H).

Due to the big overlap of the aliphatic proton signals in the ^{1}H NMR spectrum, only the resonances of the signals of the aldehyde protons can be assigned.

^{13}C NMR (101 MHz, $CDCl_3$, 298 K) δ (ppm) = 203.70 (CHO), 203.18 (CHO), 202.96 (CHO), 202.89 (CHO), 202.57 (CHO), 202.47 (CHO), 202.44 (CHO), 202.23 (CHO), 55.06 (CH), 54.79 (CH), 53.86 (CH), 47.63 (CH), 43.10 (CH_2), 43.04 (CH_2), 42.46 (CH), 42.32 (CH_2), 41.63 (CH), 41.58 (CH), 41.50 (CH), 40.76 (CH), 39.46 (CH), 39.43 (CH), 39.08 (CH), 38.70 (CH), 38.37 (CH), 37.67 (CH_2), 37.56 (CH_2), 37.50 (CH_2), 37.45 (CH_2), 36.82 (CH), 36.52 (CH_2), 36.33 (CH), 36.30 (CH_2), 33.24 (CH_2), 33.22 (CH_2), 30.62 (CH_2), 30.56 (CH_2), 29.44 (CH_2), 28.52 (CH_2), 28.29 (CH_2), 24.87 (CH_2), 24.74 (CH_2), 22.88 (CH_2).

GC MS: t_R = 8.6-8.8 min, *m/z* = 180.1 [M^+], 162.1 [$M-H_2O$]$^+$.

Hydrogenation experiments



7.18 g (4.00 wt%) of Raney nickel, 35.9 g (20.0 wt%) of H_2O and 149 mL toluene (1.00 M) together with 30.9 g (171 mmol, 1.00 eq.) of **3** were added to a snap-cap vial in an autoclave. The autoclave was subsequently flushed 3 times with 50 bar of argon and H_2 to exchange the atmosphere and then pressurized with 50 bars of H_2. The reaction mixture was stirred for 16 hours at a temperature of 140 °C. The autoclave was cooled down and depressurized. The reaction mixture was dissolved in EtOAc and filtered through glass wool. The solvent was removed in vacuo and the product was purified by distillation (b.p.: 105-120 °C, p = 0.05 mbar) to yield 25.3 g (140 mmol, 82%) of **4** as a colorless viscous liquid.

^{1}H NMR (500 MHz, $CDCl_3$, 298 K): δ (ppm) = 3.70-3.56 (m, 1.47 H, CH_2OH), 3.47-3.28 (m, 2.53 H, CH_2OH), 2.23-2.08 (m, 1.80 H), 1.97-1.92 (m, 0.40 H), 1.86-1.72 (m, 0.60 H), 1.70-1.47 (m, 2 H), 1.46-1.11 (m, 6 H), 1.11-0.86 (m, 3 H), 0.85-0.57 (m, 0.50 H).

Due to the big overlap of the aliphatic proton signals in the ^{1}H NMR spectrum, only the resonances of the signals of the CH_2 groups next to the hydroxyl groups could be assigned.

^{13}C NMR (101 MHz, $CDCl_3$, 298 K): δ (ppm) = 67.93 (CH_2OH), 67.86 (CH_2OH), 67.82 (CH_2OH), 67.33 (CH_2OH), 67.30 (CH_2OH), 67.10 (CH_2OH), 66.92 (CH_2OH), 66.87 (CH_2OH), 66.83 (CH_2OH), 66.78 (CH_2OH), 66.65 (CH_2OH), 66.61 (CH_2OH), 66.55 (CH_2OH), 66.53 (CH_2OH), 66.49 (CH_2OH), 66.44 (CH_2OH), 66.38 (CH_2OH), 66.36 (CH_2OH), 66.31 (CH_2OH), 66.18 (CH_2OH), 63.20 (CH_2OH), 63.15 (CH_2OH), 63.12 (CH_2OH), 63.08 (CH_2OH), 52.86 (CH), 52.00 (CH) , 46.14 (CH), 46.00 (CH), 45.61 (CH), 45.59 (CH), 45.58 (CH), 45.54 (CH), 45.53 (CH), 45.47 (CH), 45.28 (CH), 45.25 (CH), 45.21 (CH), 45.15 (CH), 44.60 (CH), 44.53 (CH), 44.29 (CH), 44.08 (CH), 43.05 (CH), 43.00 (CH), 42.98 (CH), 42.49 (CH), 42.24 (CH), 41.68 (CH), 41.47 (CH), 41.43 (CH), 41.10 (CH), 41.05 (CH), 40.87 (CH), 40.77 (CH), 40.71 (CH), 40.64 (CH), 40.41 (CH), 40.16 (CH), 40.06 (CH), 39.65 (CH), 39.27 (CH), 39.11 (CH), 38.98 (CH), 38.95 (CH), 38.93 (CH), 38.67 (CH), 38.65 (CH), 38.56 (CH), 38.54 (CH), 38.52 (CH), 38.46 (CH), 38.44 (CH), 38.38 (CH), 38.30 (CH_2), 38.03 (CH), 37.65 (CH_2), 37.53 (CH_2), 37.47 (CH_2), 37.07 (CH) , 37.04 (CH), 36.95 (CH), 36.92 (CH), 36.88 (CH_2), 36.86 (CH_2), 36.82 (CH_2), 36.63 (CH_2), 36.61 (CH), 36.57 (CH_2), 36.55 (CH), 36.52 (CH), 36.45 (CH_2), 36.37 (CH), 36.32 (CH), 36.30 (CH_2), 36.29 (CH), 36.20 (CH_2), 36.16 (CH_2), 36.09 (CH_2), 35.59 (CH_2), 35.40 (CH_2), 34.88 (CH_2), 34.87 (CH_2), 34.85 (CH_2), 34.71 (CH_2), 34.42 (CH_2), 34.39 (CH_2), 33.93 (CH_2), 33.74 (CH_2), 33.24 (CH_2), 33.15 (CH_2), 33.01 (CH_2), 32.89 (CH_2), 32.87 (CH_2), 32.67 (CH_2), 32.57 (CH_2), 32.51 (CH_2), 32.49 (CH_2), 32.28 (CH_2), 32.24 (CH_2), 32.04 (CH_2), 31.85 (CH_2), 31.74 (CH_2), 31.24 (CH_2), 31.16 (CH_2), 28.90 (CH_2), 28.26 (CH_2), 27.42 (CH_2), 27.15 (CH_2), 27.11 (CH_2), 26.65 (CH_2), 24.83 (CH_2), 24.15 (CH_2), 16.82 (CH_3), 16.54 (CH_3), 16.40 (CH_3), 16.29 (CH_3), 16.19 (CH_3), 16.17 (CH_3), 15.01 (CH_3), 14.67 (CH_3), 13.24 (CH_3), 13.22 (CH_3).

GC MS: t_R = 9.2-9.8 min, *m*/*z* = 184.1 [M^+], 166.1 [$M\text{-}H_2O]^+$.

TGA: T_d = 163 °C.

DSC: T_g = −28 °C.

3c **4c**

6.50 g (4.00 wt%) of Raney nickel, 32.5 g (20.0 wt%) of H_2O and 135 mL toluene (1.00 M) together with 28.0 g (155 mmol, 1.00 eq.) of **3c** were added to a snap-cap vial in an autoclave. The autoclave was subsequently flushed three times with argon and H_2 to remove air and then pressurized with 50 bars of H_2. The reaction mixture was stirred for 16 hours at a temperature of 90 °C. The autoclave was cooled down and depressurized. The reaction mixture was dissolved in EtOAc and filtered through glass wool. The solvent was then removed in vacuo and the product was purified by distillation (b.p.: 130 °C, p = 0.05 mbar) to yield 16.8 g (93 mmol, 60%) of **4c** as a colorless viscous liquid.

^{1}H NMR (500 MHz, $CDCl_3$, 298 K): δ (ppm) = 3.61 (q, ^3J = 6.5 Hz, 2 H, CH_2OH), 3.38-3.30 (m, 2 H), 2.19-2.07 (m, 2 H), 1.95-1.92 (m, 0.75 H), 1.85-1.75 (m, 2 H), 1.67 (ddd, $^3J_{H,H}$ = 8.5 Hz, 0.50 H), 1.57-1.49 (m, 4 H), 1.24-1.17 (m, 1.40 H), 1.16-1.10 (m, 1 H), 1.07-1.01 (m, 0.50 H), 1.01-0.95 (m, 0.50 H), 0.89-0.80 (m, 1 H), 0.65-0.61 (m, 0.30 H), 0.59-0.55 (m, 0.20 H).

Due to the big overlap of the aliphatic proton signals in the ^{1}H NMR spectrum, only the resonances of the signals of the CH_2 groups next to the hydroxyl groups can be assigned.

^{13}C NMR (101 MHz, $CDCl_3$, 298 K): δ (ppm) = 66.92 (CH_2OH), 66.88 (CH_2OH), 66.79 (CH_2OH), 66.61 (CH_2OH), 63.20 (CH_2OH), 63.15 (CH_2OH), 63.13 (CH_2OH), 63.08 (CH_2OH), 45.60 (CH), 45.29 (CH), 44.30 (CH), 42.99 (CH), 41.68 (CH), 41.47 (CH), 41.10 (CH), 40.25 (CH), 40.24 (CH), 40.07 (CH), 39.65 (CH), 38.98 (CH), 38.51 (CH), 38.29 (CH_2), 37.52 (CH_2), 37.46 (CH_2), 36.92 (CH), 36.88 (CH_2), 36.83 (CH_2), 36.62 (CH_2), 36.55 (CH), 36.37 (CH), 34.71 (CH_2), 34.41 (CH_2), 33.24 (CH_2), 32.87 (CH_2), 32.66 (CH_2), 32.28 (CH_2), 32.24 (CH_2), 32.05 (CH_2), 31.88 (CH_2), 31.25 (CH_2), 31.17 (CH_2), 28.89 (CH_2), 28.25 (CH_2), 27.09 (CH_2).

GC MS: t_R = 9.6-9.9 min, *m/z* = 184.1 [M^+], 166.1 [$M-H_2O]^+$.

TGA: T_d = 156 °C.

DSC: T_g = −44 °C.

General up-scaling procedure for hydroformylation and hydrogenation

Hydroformylation. The pre-catalyst $[Rh(COD)_2]BF_4$, the ligand, the diene and toluene (1.00 M) as solvent were added to a 500 mL Schlenk flask. The 2 L Parr Bench Top reactor was flushed with five cycles of 50 bar of argon to exchange the atmosphere at room temperature. The reaction mixture was transferred via a canula into the reactor, equipped with a glass inlay, the autoclave was pressurized with 50 bar of syngas and the mixture was heated to the corresponding reaction temperatures. The pale-yellow solution was cooled down to room temperature and the reactor was depressurized. The excess solvent of the crude mixture was removed in vacuo and the product was purified by distillation to yield colorless, odorous liquids. Due to their high reactivity at ambient atmosphere, the resulting dialdehydes were immediately used for the hydrogenation in the next step.

Hydrogenation. A mixture of dialdehydes, Raney nickel, water and toluene (1.00 M) was placed into an inlay and transferred into the 2 L Parr Bench Top reactor. The reaction mixture and the reactor were flushed with five cycles of 50 bar of argon and three cycles of 60 bar of H_2 to exchange the atmosphere at room temperature. The reactor was pressurized with 50 bar H_2 and the mixture was stirred at the corresponding reaction temperature. The mixture was cooled down to room temperature and the reactor was depressurized. The remaining Raney nickel was filtered carefully and quenched immediately with 1 N HCl. The resulted solution was reduced by removing most of the solvent in vacuo and the crude product was purified by distillation to yield the diols as colorless viscous liquids, respectively.

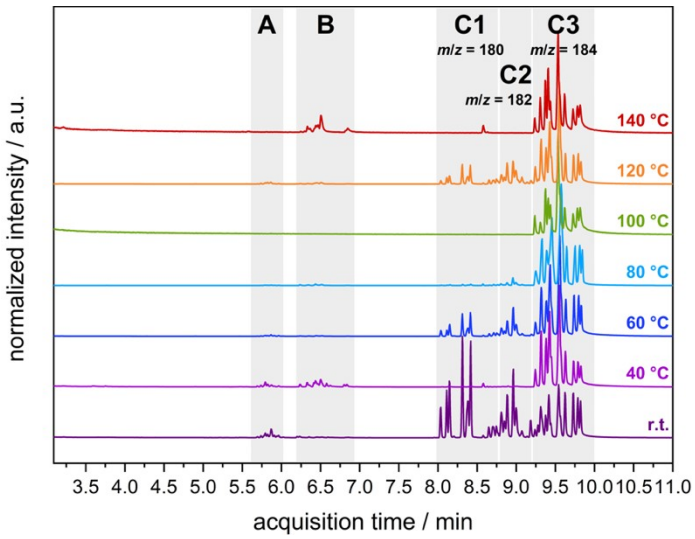
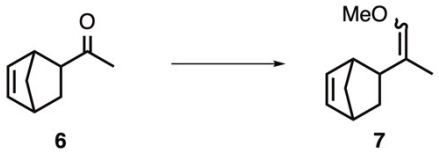


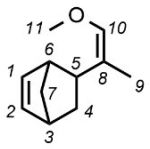
Figure S1. Stacked GC chromatograms from hydrogenation reactions of crude dialdehydes **3** at different temperatures using Raney nickel as the catalyst in toluene/H_2O solution. Reaction conditions: 24.96 mmol **3**, 2 wt% Raney nickel, 10 wt% H_2O, 50 bar H_2.

Synthesis of *branched* diols 4b



6 **7**

To a suspension of 2.52 g (7.34 mmol, 2.00 eq.) $[PPh_3PCH_2OCH_3]Cl$ in 12 mL THF (0.61 M), 865 mg (7.71 mmol, 2.20 eq.) of potassium-*tert*-butanolate (KO*t*Bu) was added in portions at a temperature of 0 °C. The deep red reaction mixture was stirred at 0 °C for 45 min and subsequently, 500 mg (3.67 mmol, 1.00 eq.) of 5-acetyl-2-norbornene (**6**) in 30 mL THF (0.12 M) was added dropwise via a syringe. The reaction mixture was warmed to ambient temperature for 2 h. To the orange suspension 50 mL distilled water was added and the organic phase was extracted with *n*-pentane (3 × 50 mL). The combined organic phases were washed with water (50 mL), dried over Na_2SO_4, filtered and the solvent was removed in vacuo. The crude product was purified via silica gel column chromatography (*n*-pentane/Et_2O = 50/1) to yield 513 mg (3.12 mmol, 92%) of **7** as a colorless liquid.

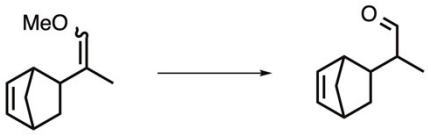


^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ (ppm) = 6.22-5.82 (m, 2H, H1/H2), 5.83-5.60 (m, 1 H, H10), 3.54 (t, $^3J_{H,H}$ = 9.4, 7.9 Hz, 3 H, H11), 3.22 (dtd, $^3J_{H,H}$ = 8.6 Hz, 0.10 H), 2.96-2.62 (m, 2 H, H3/H6), 2.61-2.50 (m, 0.40 H),1.90-1.71 (m, 1 H), 1.88 (dd, $^3J_{H,H}$ = 8.5 Hz, 0.60 H), 1.83 (dd, $^3J_{H,H}$ = 3.8 Hz, 0.05 H), 1.80 (d, $^3J_{H,H}$ = 3.8 Hz, 0.05 H), 1.75 (ddd, $^3J_{H,H}$ = 11.4, 9.9, 3.8 Hz, 0.30 H), 1.57-1.52 (m, 1 H), 1.47-1.36 (m, 2 H), 1.35-1.18 (m, 3 H), 1.08-1.02 (m, 0.10 H), 0.90 (ddd, $^3J_{H,H}$ = 11.3, 4.9, 2.3 Hz, 0.30 H).

Due to the big overlap of the aliphatic proton signals in the ^{1}H NMR spectrum, only the resonances of the signals of the double bonds and the methoxy group could be assigned.

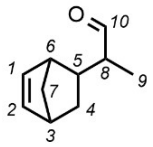
^{13}C NMR (101 MHz, $CDCl_3$, 298 K) δ (ppm) = 142.71 (C10), 142.34 (C10), 142.16 (C10), 141.54 (C10), 138.12 (C1/C2), 137.49 (C1/C2), 136.80 (C1/C2), 136.37 (C1/C2), 136.23 (C1/C2), 59.42 (C11), 59.39 (C11), 50.42, 49.64, 47.84, 47.13, 46.68, 46.44, 46.22, 45.58, 42.88, 42.70, 42.57, 42.22, 42.20, 41.97, 36.70, 30.74, 30.29, 29.45, 29.20, 16.87, 16.02, 13.77 (C9), 13.50 (C9).

GC MS: t_R = 6.0-6.2 min, *m*/*z* = 164.1 $[M^+]$, 131.1 $[M\text{-}CH_3O]^+$.



7 **8**

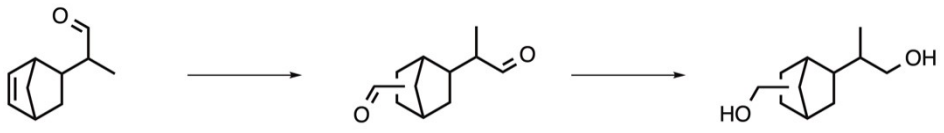
315 mg (1.92 mmol, 1.00 eq.) of **7** was dissolved in toluene (3.84 mL) and water (0.35 mL, 10.0 eq.) was added. The solution was cooled to 0 °C and 73.0 mg (0.38 mmol, 0.20 eq.) of *p*-toluene sulfonic acid monohydrate (*p*-TsOH × H_2O) was added in portions. The reaction mixture was refluxed for 1 h and after cooling to ambient temperature, saturated $NaHCO_3$ solution was added. The organic phase was extracted with Et_2O (3 × 50 mL), dried over Na_2SO_4, filtered and the solvent was removed in vacuo. The product was purified via silica gel column chromatography (*n*-pentane/Et_2O = 10/1) to yield 242 mg (1.61 mmol, 84%) of **8** as a colorless liquid.



^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ (ppm) = 9.62 (d, $^3J_{H,H}$ = 3.7 Hz, 0.50 H, H10), 9.59 (d, $^3J_{H,H}$ = 3.2 Hz, 0.50 H, H10), 6.07 (dtd, $^3J_{H,H}$ = 8.6, 5.3, 2.9 Hz, 2 H, H1/H2), 2.89-2.82 (m, 1 H, H3/H6), 2.77-2.56 (m, 1 H, H3/H6), 2.18 (dpd, $^3J_{H,H}$ = 17.5, 6.9, 3.4 Hz, 1 H, H8), 1.56-1.49 (m, 0.50 H, H7), 1.48-1.41 (m, 0.50 H, H7), 1.40-1.22 (m, 4 H, H4/H5), 1.16 (d, $^3J_{H,H}$ = 6.8 Hz, 1.50 H, H9), 1.11 (d, $^3J_{H,H}$ = 6.9 Hz, 1.50 H, H9).

^{13}C NMR (101 MHz, $CDCl_3$, 298 K): δ (ppm) = 205.40 (C10), 205.08 (C10), 137.18 (C1/C2), 136.74 (C1/C2), 136.71 (C1/C2), 136.18 (C1/C2), 52.08 (C8), 51.73 (C8), 45.57 (C4/C5), 45.39 (C4/C5), 44.81 (C3/C6), 43.61 (C3/C6), 42.37 (C3/C6), 41.82 (C3/C6), 40.37 (C7), 40.15 (C7), 31.43 (C4/C5), 30.69 (C4/C5), 13.54 (C9), 13.48 (C9).

GC MS: t_R = 5.5-5.6 min, *m*/*z* = 150.1 [M^+], 132.1 [M-H_2O]$^+$.



8 **3b** **4b**

4.05 mg (9.99 μmol, 0.10 mol%) of $[Rh(COD)_2]BF_4$ and 32.3 mg (49.9 μmol, 0.50 mol%) of Alkanox® were dissolved in toluene (2.70 mL), and 1.50 g (9.99 mmol, 1.00 eq.) of **8** was added to the suspension. The reaction mixture was pressurized with 50 bar of syngas (CO/H_2 = 1/1) and stirred for 2 h at 60 °C. The yellowish reaction mixture was cooled to ambient temperature, **3b** was redissolved in 45 mL MeOH, and 1.02 g (27.1 mmol, 3.00 eq.) of $NaBH_4$ was added in portions at a temperature of 0 °C. The reaction mixture was stirred for 16 h at ambient temperature. The reaction mixture was concentrated in vacuo, and 50 mL of distilled water was added. Subsequently, 50 mL of 1 N HCl was added, and the organic phase was extracted with Et_2O (3 × 100 mL). The collected organic phase was dried over Na_2SO_4, filtered and the solvent was removed in vacuo. The product was purified by silica gel chromatography (Et_2O) to yield 1.07 g (5.81 mmol, 64%) of **4b** as a colorless viscous liquid.

3b: ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ (ppm) = 9.66 (dd, $^3J_{H,H}$ = 3.5 Hz, 0.70 H), 9.64-9.62 (m, 0.50 H), 9.60 (d, $^3J_{H,H}$ = 3.4 Hz, 0.30 H), 9.57 (dd, $^3J_{H,H}$ = 4.1 Hz, 0.50 H), 2.61 (d, $^3J_{H,H}$ = 4.1 Hz, 0.60 H), 2.58-2.42 (m, 0.70 H), 2.21-2.18 (m, 0.50 H), 2.18-2.05 (m, 1.10 H), 2.03-1.88 (m, 1.30 H), 1.76-1.50 (m, 2.80 H), 1.45-1.32 (m, 2.10 H), 1.32-1.22 (m, 2.80 H), 1.16 (d, $^3J_{H,H}$ = 6.9 Hz, 1 H), 1.14 (d, $^3J_{H,H}$ = 6.9 Hz, 1 H).

3b: ^{13}C NMR (101 MHz, $CDCl_3$, 298 K): δ (ppm) = 204.80, 204.67, 204.66, 204.48, 202.85, 202.83, 202.58, 202.41, 55.18, 55.13, 53.79, 53.70, 51.78, 51.59, 51.31, 51.14, 43.10, 43.04, 42.90, 42.84, 41.06, 39.78, 39.53, 38.58, 38.23, 38.18, 36.64, 36.38, 36.28, 36.19, 35.13, 35.09, 33.79, 33.72, 33.68, 33.62, 30.83, 30.81, 29.53, 29.17, 13.23, 11.73, 11.71.

4b: ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ (ppm) = 3.72-3.67 (m, 0.30 H), 3.66-3.62 (m, 0.40 H), 3.60 (dd, $^3J_{H,H}$ = 3.6 Hz, 0.30 H), 3.56 (dd, $^3J_{H,H}$ = 5.7 Hz, 0.25 H), 3.47-3.39 (m, 0.50 H), 3.39-3.30 (m, 2.25 H), 2.24-2.18 (m, 0.70 H), 1.67-1.63 (m, 0.80 H), 1.45-1.11 (m, 8.30 H), 1.01 (dd, $^3J_{H,H}$ = 6.5 Hz, 2 H), 0.88 (dd, $^3J_{H,H}$ = 6.5 Hz, 1.50 H).

3b: GC MS: t_R = 8.4-8.6 min, *m/z* = 180.1 $[M^+]$, 162.1 $[M\text{-}CHO]^+$.

4b: GC MS: t_R = 9.5-9.7 min, *m/z* = 184.1 $[M^+]$, 166.1 $[M\text{-}H_2O]^+$.

3.2 Stability studies of dialdehydes 3

To evaluate the stability of a mixture of dialdehydes **3**, three samples were collected, transferred into vials, and stored under different conditions The first vial was placed in an oxygen- and moisture-free glove box at room temperature, the second one was stored in a freezer at −30 °C, and the third one was kept under ambient laboratory conditions at room temperature. Over a period of four weeks, *Fourier*-transformed infrared spectroscopy (FT IR) and electrospray ionization (ESI) measurements were performed to monitor structural changes.

The most visible structural alterations within one month were observed in the sample stored at −30°C (Figure S2). In addition to the characteristic transmittance bands of carbonyl H-C=O oscillations (**A** and **B**), the FT IR data revealed significant changes in the fingerprint region , particularly at ν = 1058 cm^{-1} (**C**). Within the spectral range of 1000-1250 cm^{-1}, transmittance increased with a prolonged storage time. Additionally, these samples exhibited increased viscosity compared to their freshly distilled counterparts. A similar transformation was observed in the sample stored at room temperature under ambient conditions, although at a slower rate than the sample at −30°C.

In contrast, the sample stored in the glove box at room temperature showed no changes, as confirmed by FT IR and NMR measurements. This suggests that dialdehydes **3** underwent a reaction leading to the formation of a new product, specifically affecting the fingerprint region in the IR spectra. The fingerprint region between 1300 and 1020 cm^{-1} is typically associated with acetal oscillations, implying potential acetalization. To verify this hypothesis, ESI MS measurements were conducted (Table S1). The observed mass to charge ratio (*m*/*z*) of the product was 563, significantly higher than the characteristic *m*/*z* = 180 of dialdehydes **3**. This increases in molecular mass indicates a reaction between dialdehydes **3**, likely resulting in a cyclic acetalization process that yields a trimer (**9**, Figure S3), in which one carbonyl group of each dialdehyde remains unreacted.

Table S1. Result of the ESI measurement.

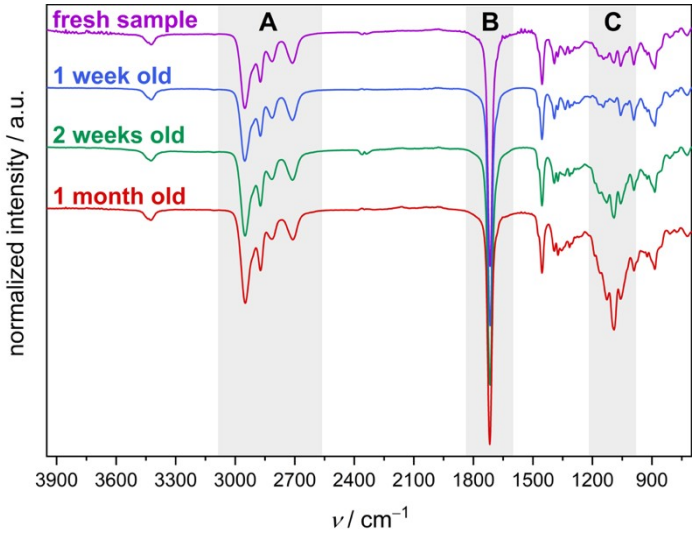


Figure S2. Stacked FT IR spectra of a sample of **3** stored under –30 °C.

	ESI MS
found	563.3323 $[M + Na^+]^+$
calculated	563.3342 $[M + Na^+]^+$

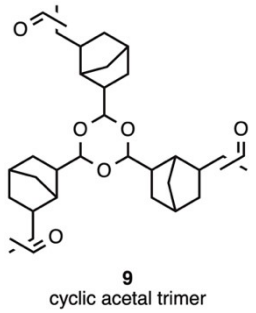


Figure S3. Proposed structure of cyclic acetal **9**.

3.3 Polyester synthesis

General polycondensation procedure

Polyester samples were synthesized via a two-step melt polycondensation reaction in a 100 mL three-necked flask, equipped with a heating block, a KPG stirrer, a distillation column and a Schlenk apparatus. Initially, in the first step, the diester and the diols (diol:diester = 2:1) were combined along with $Ti(O\textit{n}Bu)_{4,}$ and the system was rendered inert three to five moderate cycles of vacuum and argon to eliminate oxygen at room temperature. Subsequently, the reaction mixture was heated from 160 °C to 220 °C under ambient pressure with consistent stirring (500 rpm). Esterification conversion was estimated when no further evolution of methanol occurred, typically after approximately 6 h. In the second step, the pressure is reduced to 0.05 mbar and the temperature raised to 240 °C for 2 to 3 h to remove the excess diols via distillation. The resulting polymer melt was dissolved in DCM or THF, precipitated from cold methanol, subjected to three methanol washes, and dried overnight at 70 °C in vacuo. The resulted colorless to pale-yellow polyester samples were then analyzed using $^{1}H/^{13}C$/DOSY NMR, GPC, TGA and DSC techniques.

Table S2. Polycondensation series of diols **4**, **4b** and **4c** with DMT (diol:diester = 2:1)at 220-240 °C yielding the respective polyesters P**4**T, P**4b**T and P**4c**T.

polyester	$M_{n,rel}$ [kg mol^{-1}]	$M_{w,rel}$ [kg mol^{-1}]	$Đ$ [–]	T_d [°C]	T_g [°C]
P**4**T1	7.89	13.0	1.65	361	87
P**4**T2	15.7	47.5	3.03	381	92
P**4**T3	17.3	82.2	4.74	369	99
P**4**T4	19.2	60.8	3.17	364	100
P**4b**T1	9.39	23.4	2.50	387	96
P**4b**T2	11.4	23.7	2.10	382	98
P**4b**T3	15.0	30.9	2.10	384	100
P**4b**T4	23.8	63.3	2.70	379	103
P**4c**T	12.8	57.3	4.48	371	75

4. Additional analytical data

4.1 NMR analysis of P4T polyesters

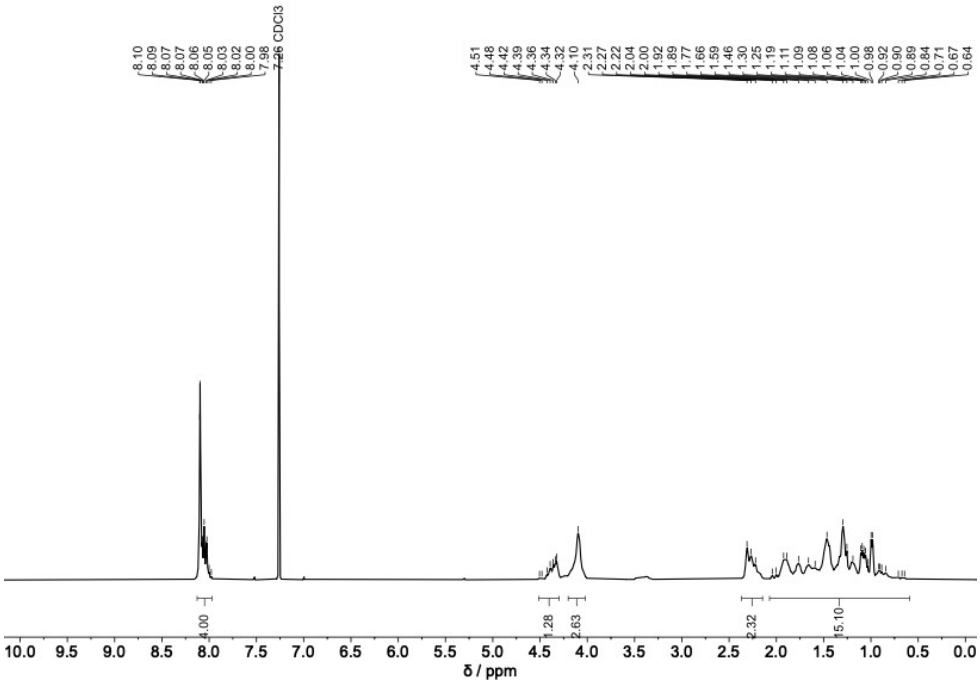


Figure S4. ^{1}H NMR of polyester P**4**T1.

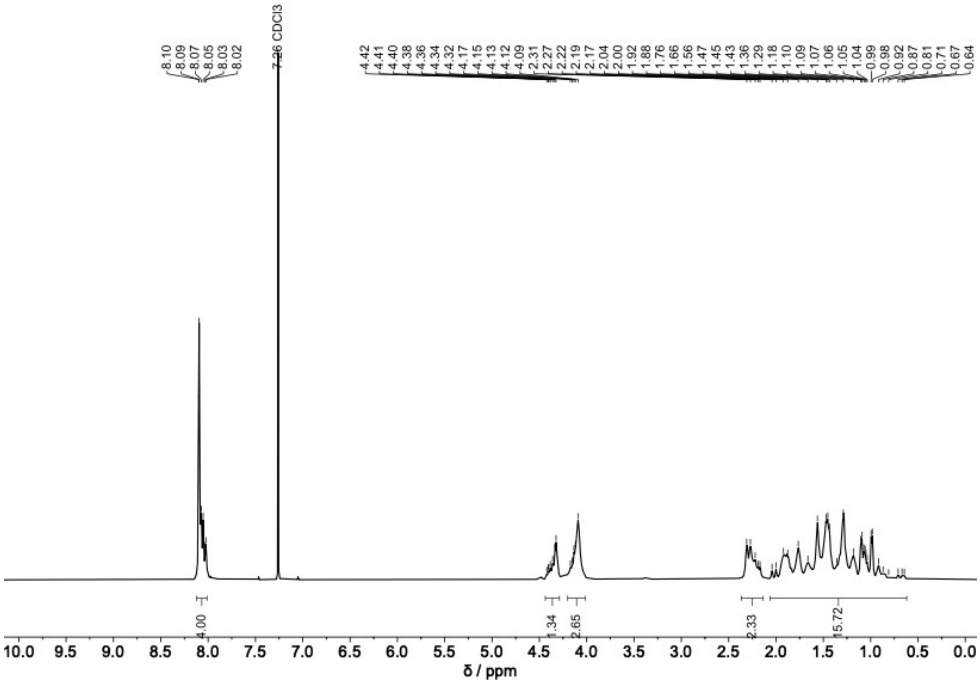


Figure S5. ^{1}H NMR of polyester P**4**T2.

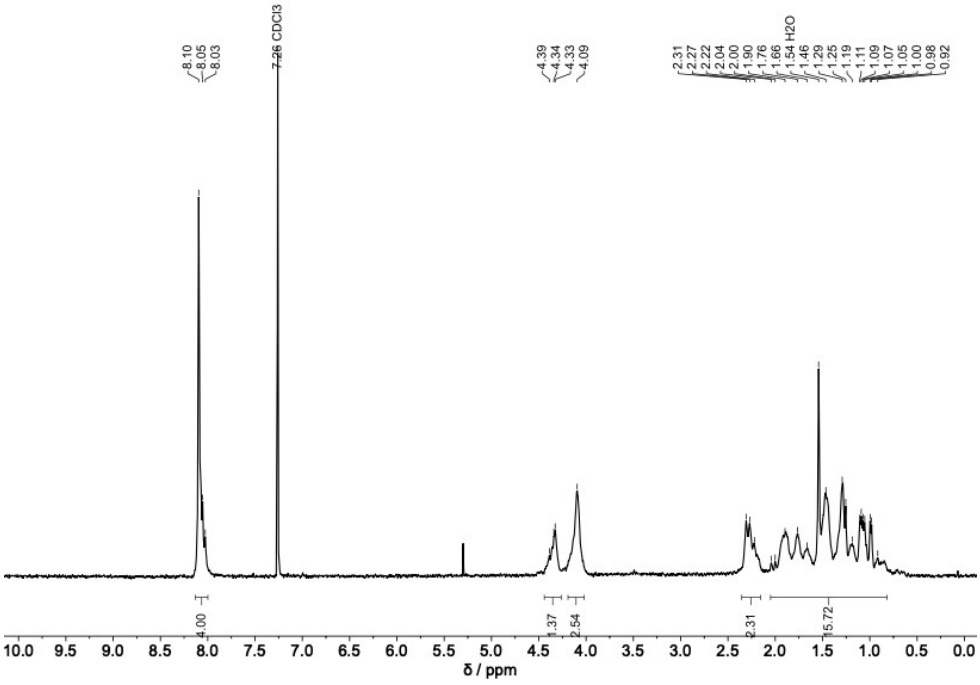


Figure S6. ^{1}H NMR of polyester P**4**T3.

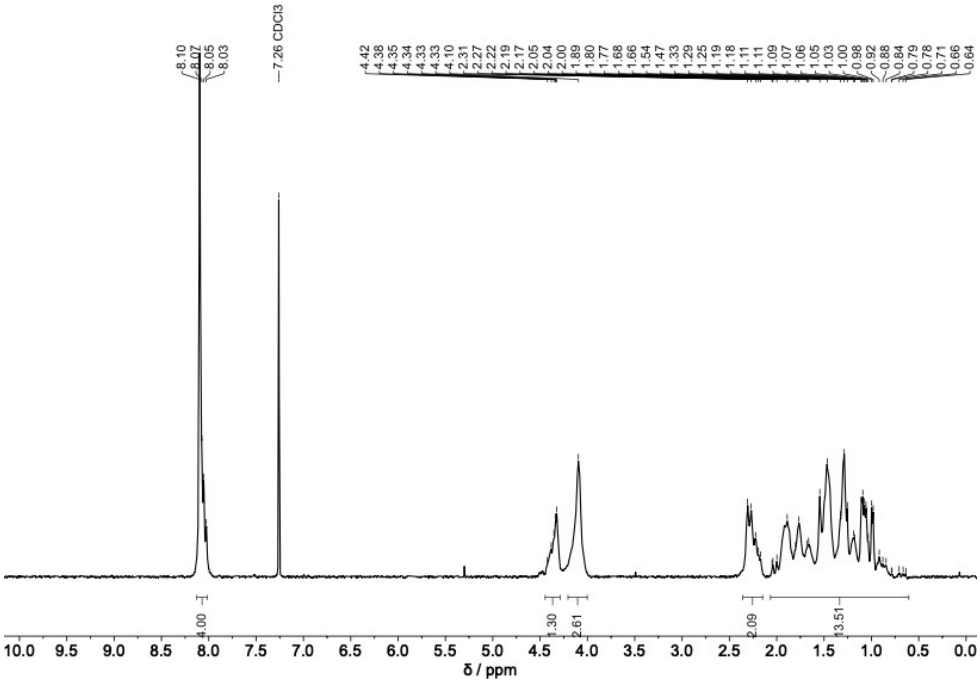


Figure S7. ^{1}H NMR of polyester P**4**T4.

4.2 NMR analysis of P4bT polyesters

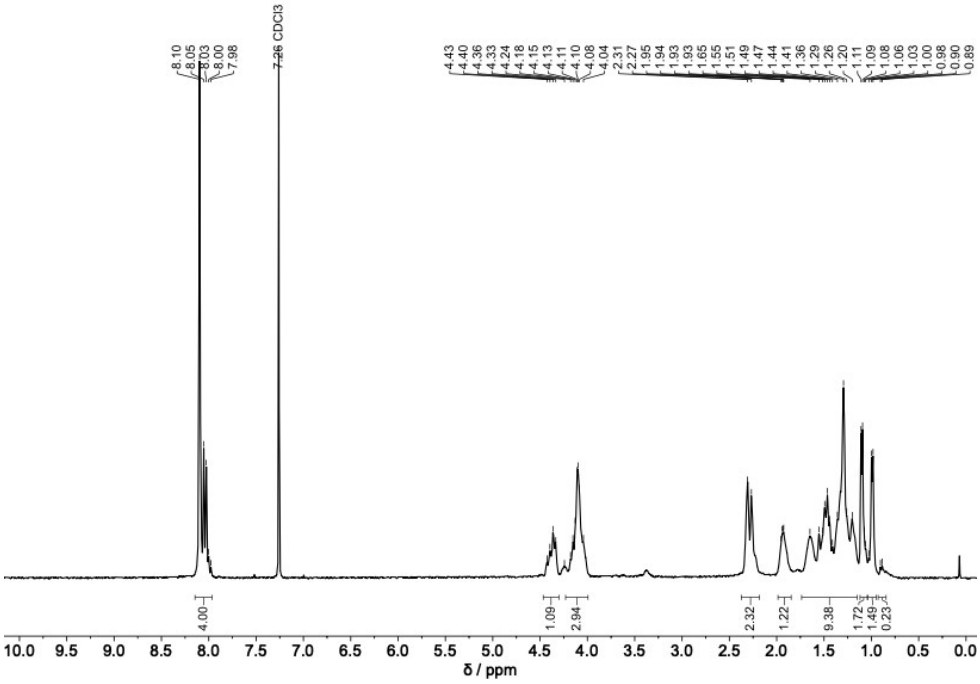


Figure S8. ^{1}H NMR of polyester P**4b**T1.

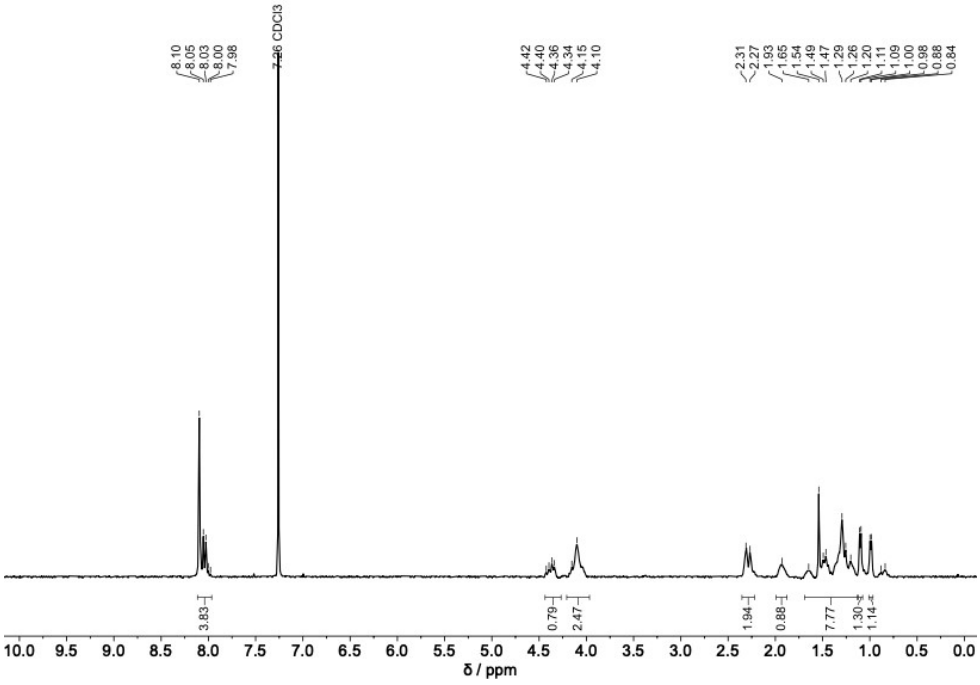


Figure S9. ^{1}H NMR of polyester P**4b**T2.

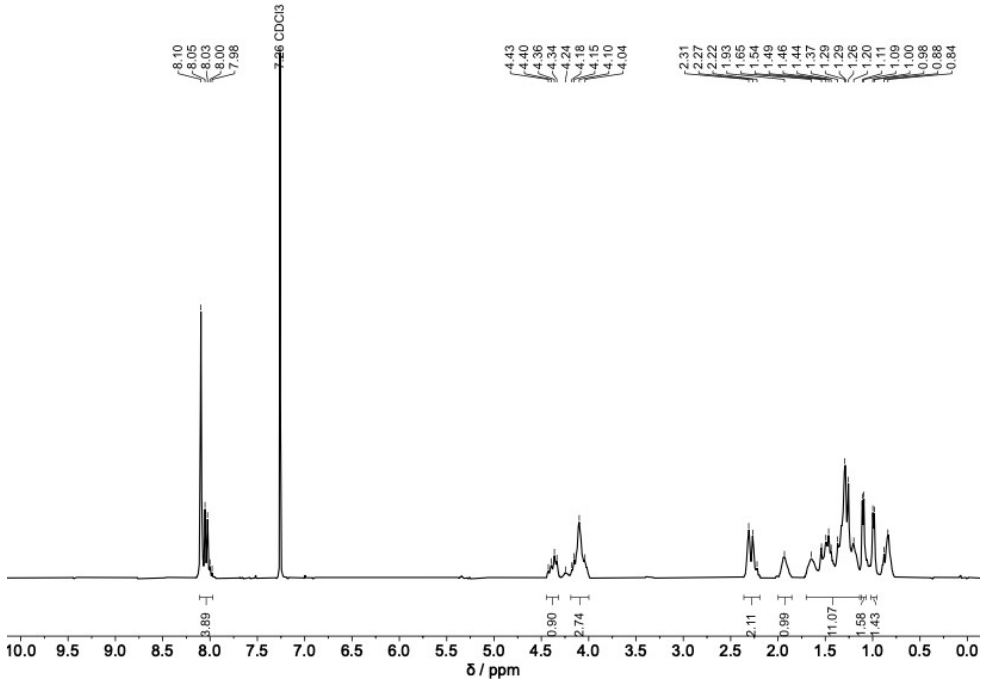


Figure S10. ^{1}H NMR of polyester P**4b**T3.

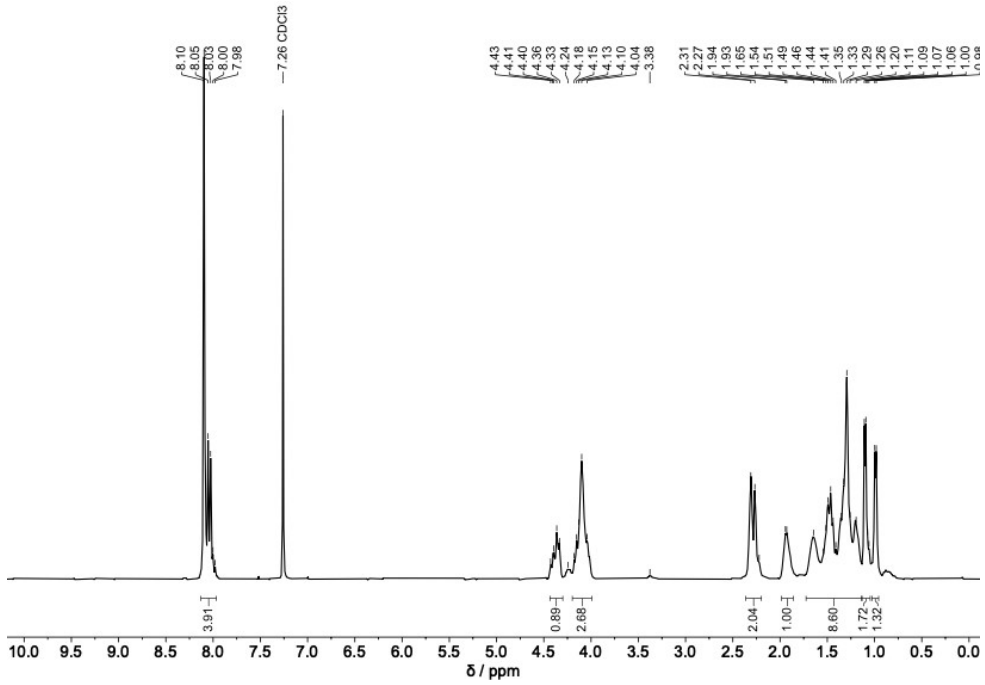


Figure S11. ^{1}H NMR of polyester P**4b**T4.

4.3 NMR analysis of P4cT polyester

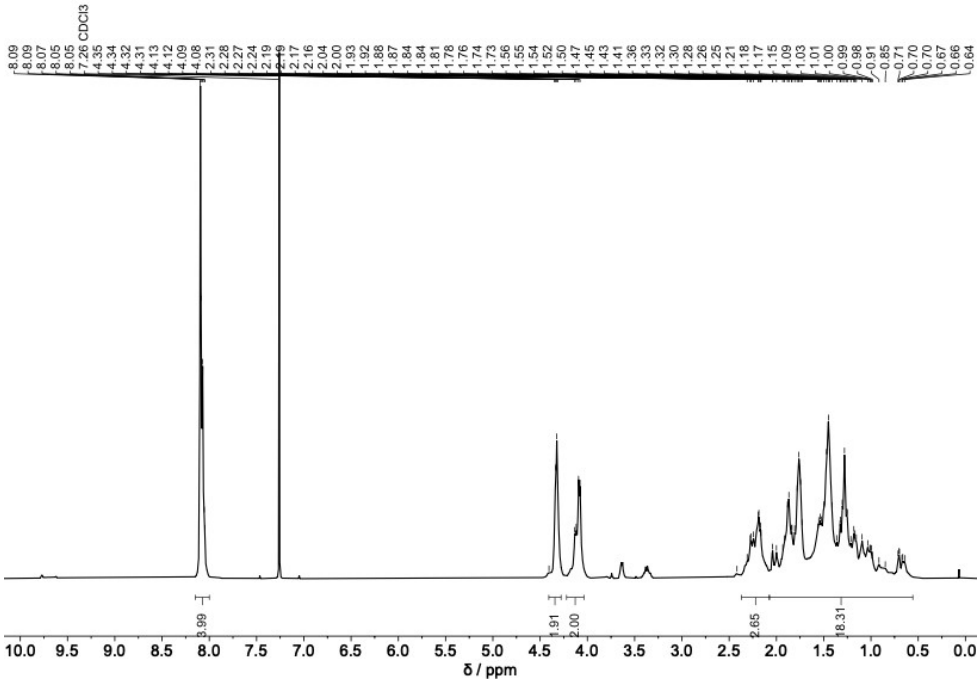


Figure S12. ^{1}H NMR of polyester P**4c**T.

4.4 NMR analysis of copolyesters P4*co*IST, P4c*co*IST and P4*co*ISF

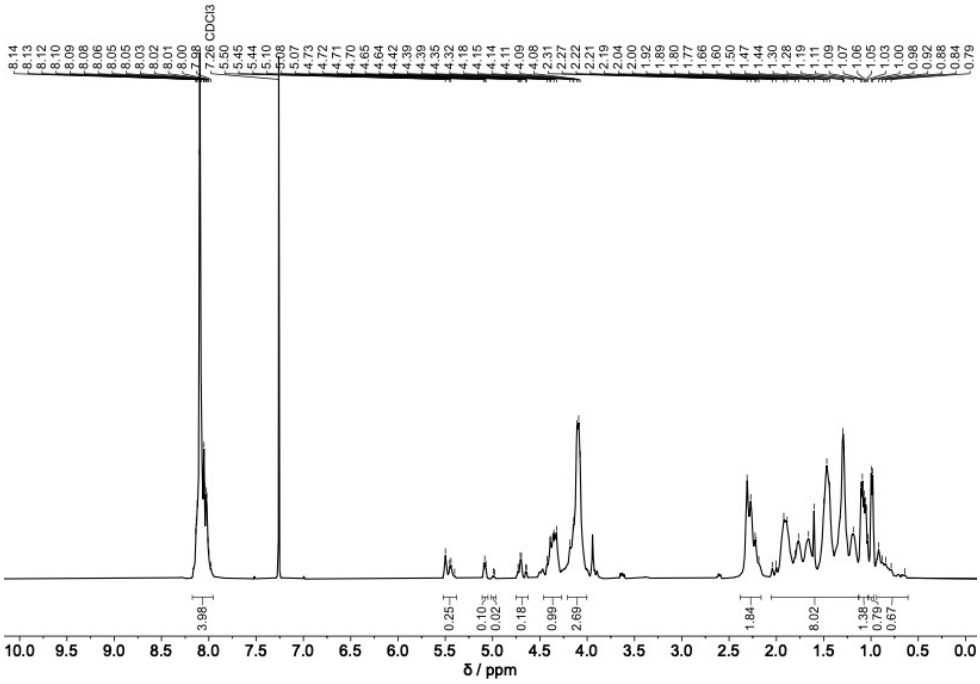


Figure S13. ^{1}H NMR of copolyester P**4***co*IST.

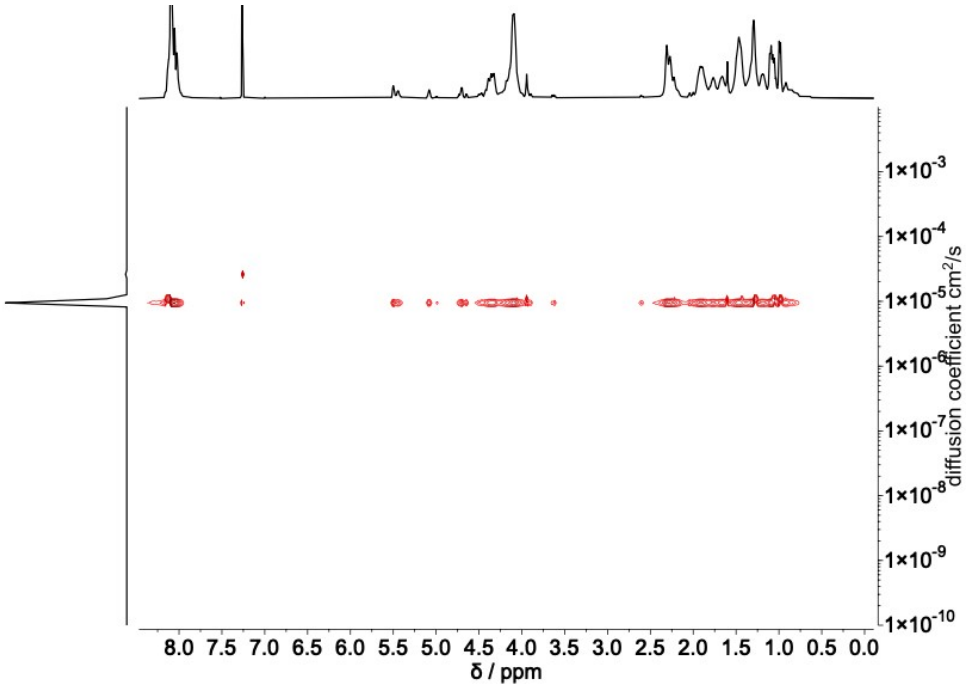


Figure S14. DOSY NMR of copolyester P**4***co*IST.

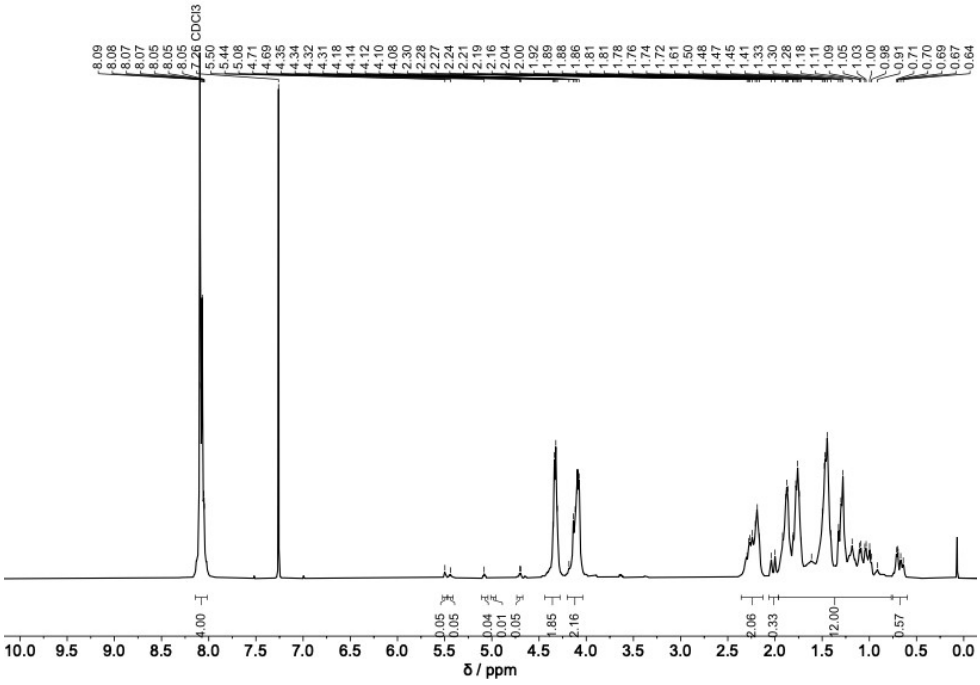


Figure S15. ^{1}H NMR of copolyester P**4c***co*IST.

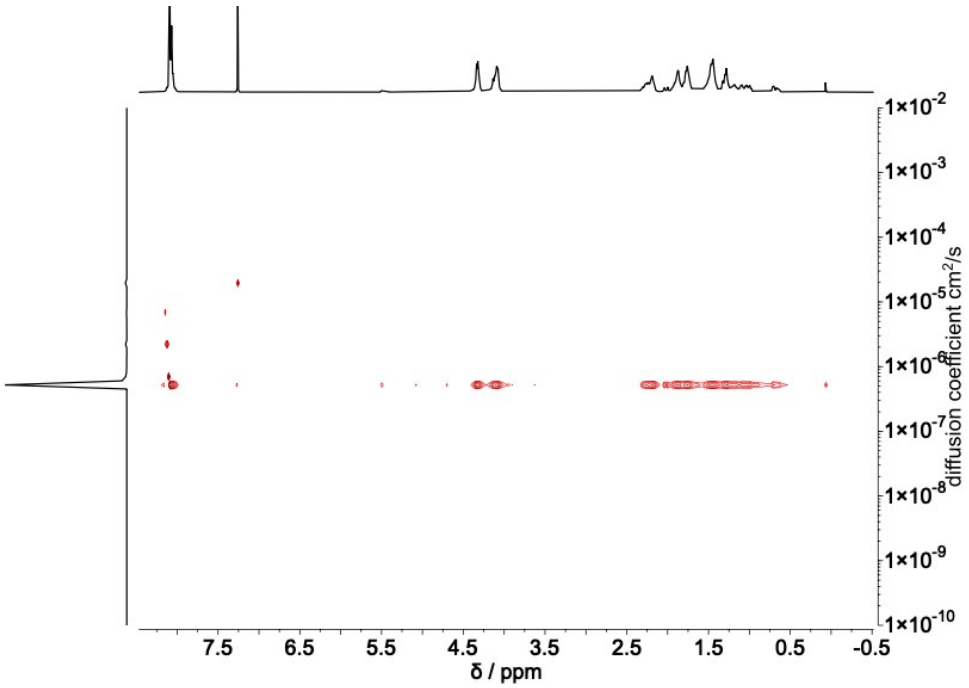


Figure S16. DOSY NMR of copolyester P**4c***co*IST.

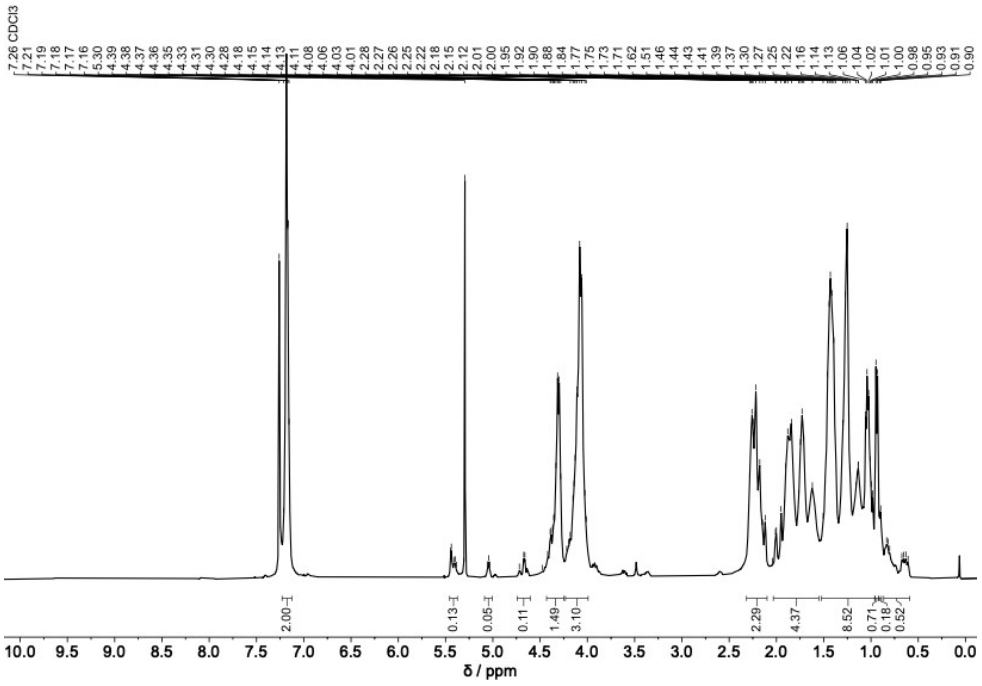


Figure S17. ^{1}H NMR of copolyester P**4***co*ISF.

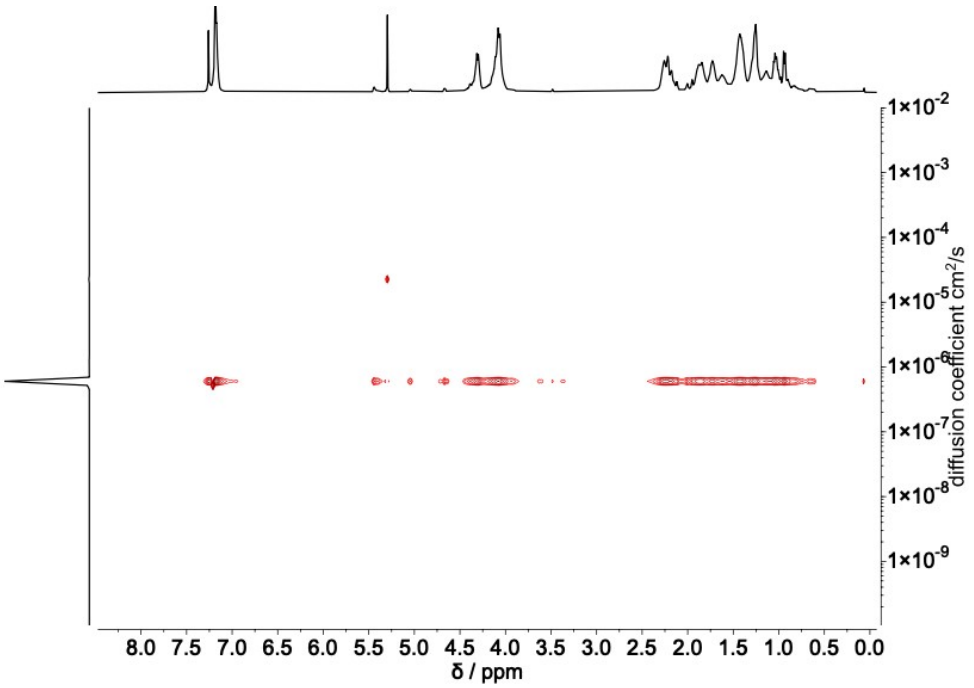


Figure S18. DOSY NMR of copolyester P**4***co*ISF.

4.4 GPC analysis of P4T polyester

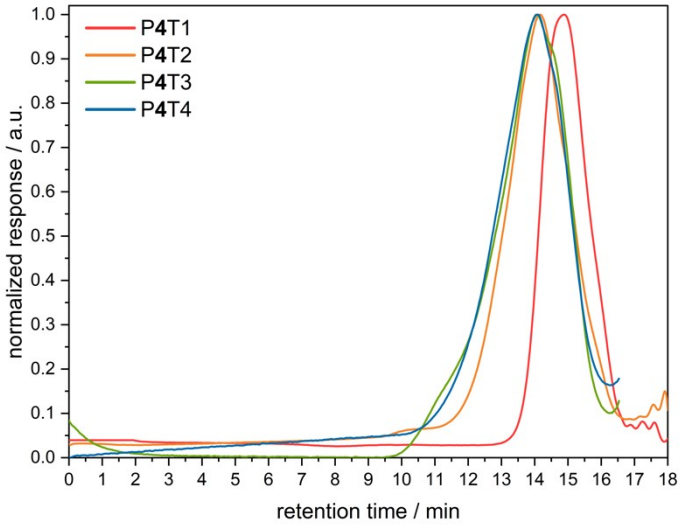


Figure S19. Molecular weight distributions of P**4**T polyesters determined via GPC in THF at 40 °C using RI as detection.

4.5 GPC analysis of P4bT polyester

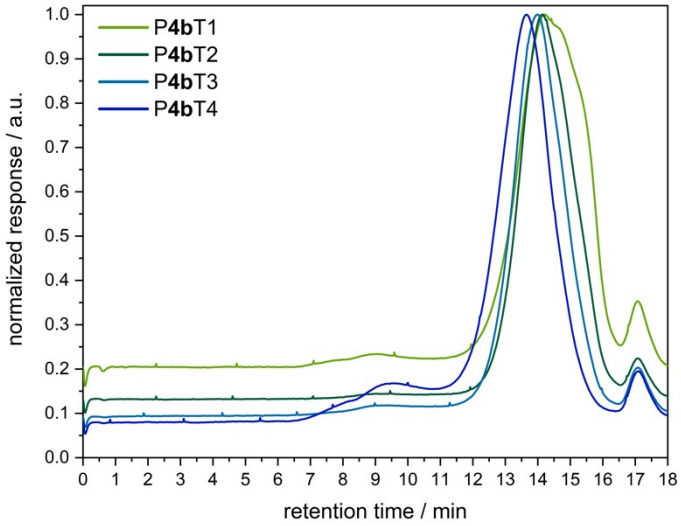


Figure S20. Molecular weight distributions of P**4b**T polyesters determined via GPC in THF at 40 °C using RI as detection.

4.6 GPC analysis of polyester P4cT and copolyester P4c*co*IST

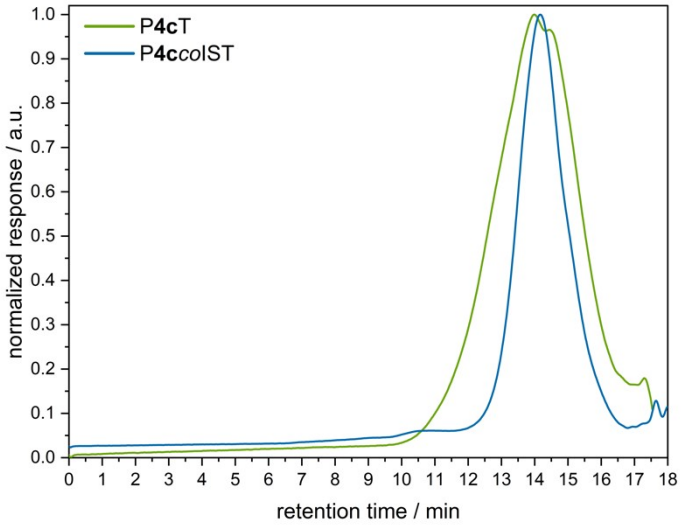


Figure S21. Molecular weight distributions of polyester P**4c**T and copolyester **P4c***co*IST determined via GPC in THF at 40 °C using RI as detection.

4.7 GPC analysis of copolyesters P4*co*IST and P4*co*ISF

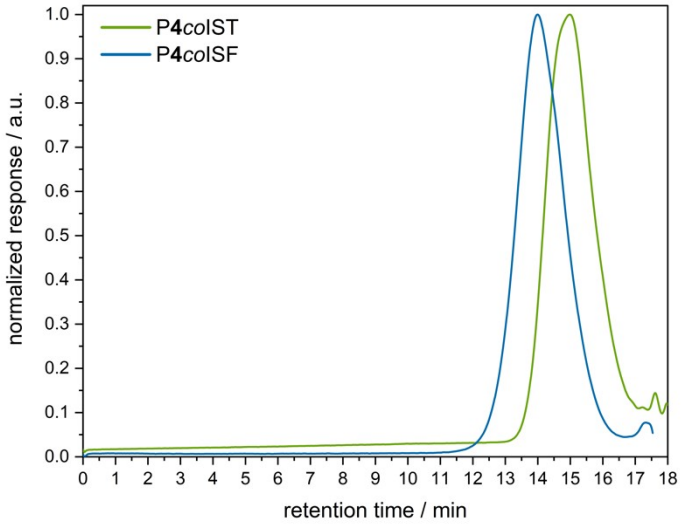


Figure S22. Molecular weight distributions of P**4***co*IST, P**4c***co*IST and copolyester **P4***co*ISF determined via GPC in THF at 40 °C using RI as detection.

4.8 TGA and DSC analysis of P4T polyester

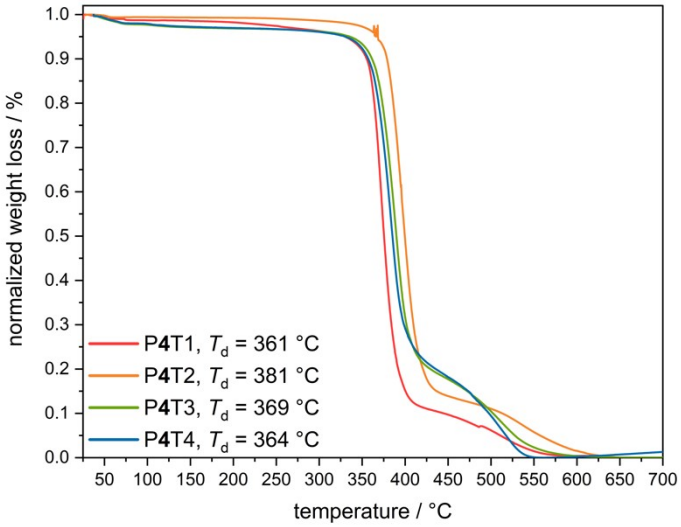


Figure S23. TGA analysis of P**4**T polyesters measured in a temperature range from 25 to 700 °C.

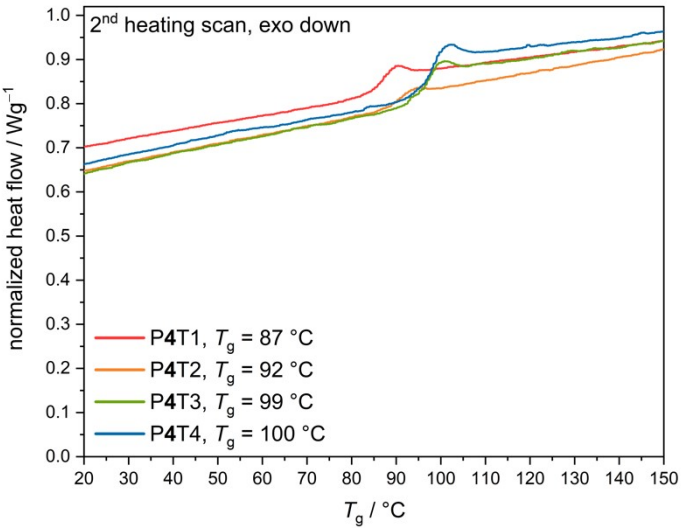


Figure S24. Extract from DSC analysis of P**4**T polyesters measured in a temperature range from –100°C to 200 °C.

4.9 TGA and DSC analysis of P4bT polyester

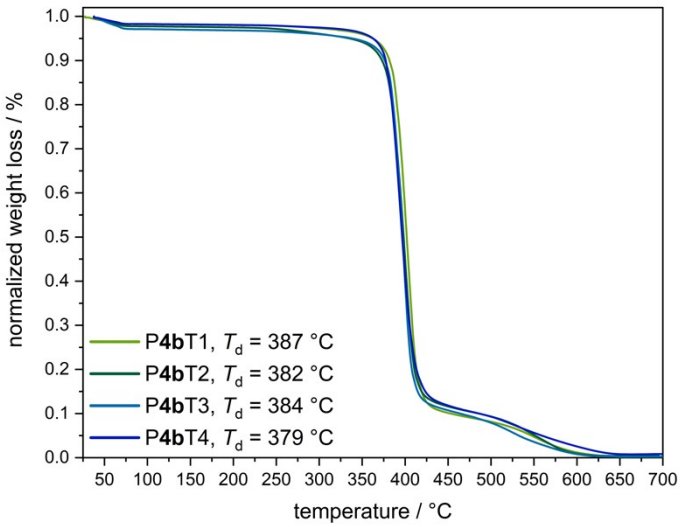


Figure S25. TGA analysis of P**4b**T polyesters measured in a temperature range from 25 to 700 °C.

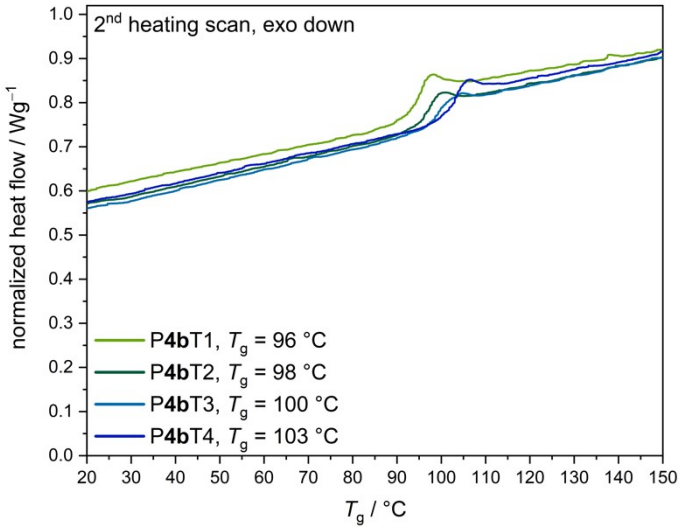


Figure S26. Extract from DSC analysis of P**4b**T polyesters measured in a temperature range from −100°C to 200 °C.

4.10 TGA and DSC analysis of polyester P4cT and copolyester P4c*co*IST

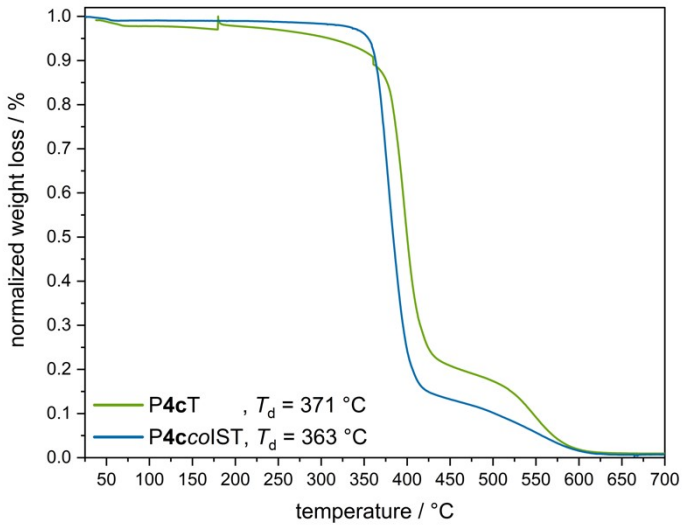


Figure S27. TGA analysis of polyester P**4c**T and copolyester P**4c***co*IST measured in a temperature range from 25 to 700 °C.

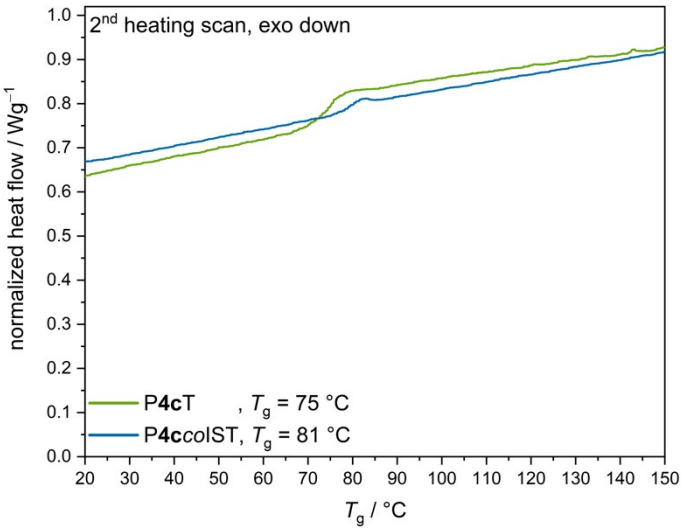


Figure S28. Extract from DSC analysis of polyester P**4c**T and copolyester P**4c***co*IST measured in a temperature range from – 100°C to 200 °C.

4.11 TGA and DSC analysis of copolyesters P4*co*IST and P4*co*ISF

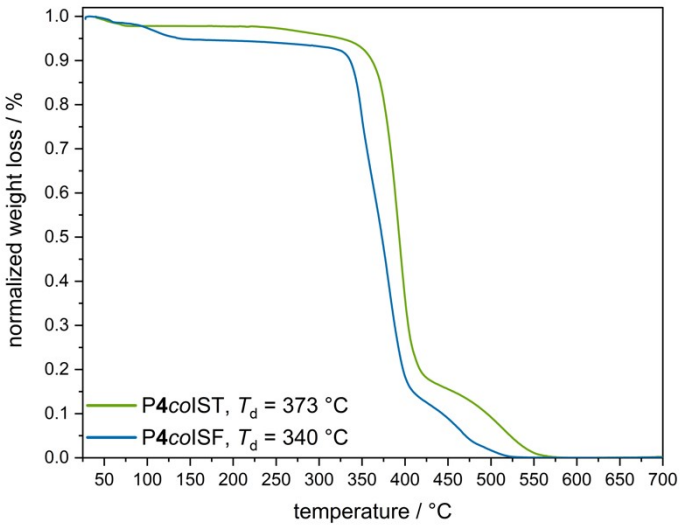


Figure S29. TGA analysis of P**4***co*IST and P**4***co*ISF copolyesters measured in a temperature range from 25 to 700 °C.

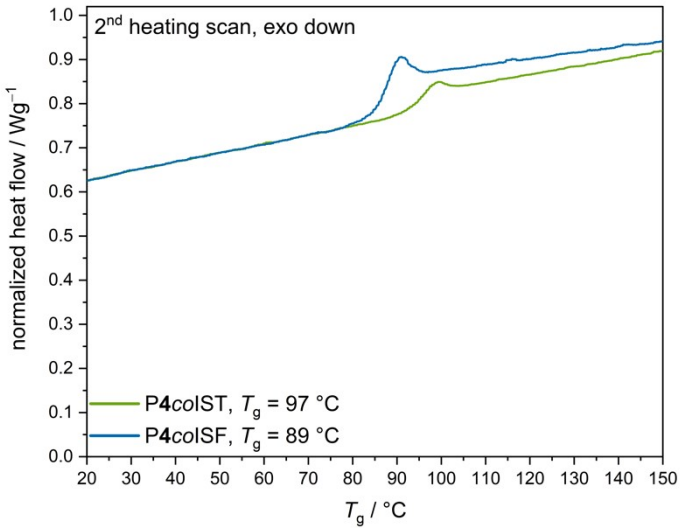


Figure S30. Extract from DSC analysis of P**4***co*IST and P**4***co*ISF copolyesters measured in a temperature range from –100°C to 200 °C.