Electronic Supplementary Material (ESI) for RSC Sustainability.

Supporting Information:

Unexpected Performance of Iron(III)chloride in the Polymerization of Renewable 2,3-Butanediol and the Depolymerization of Poly(ethylene terephthalate)

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Contents

Purification of FDCA (1)

A mixture of water/methanol (3:5, v/v, 25 g) was prepared, followed by the addition of 1.00 g of unpurified FDCA and 0.30 g sodium hydrogen sulfite in a pressure vial. The mixture was heated to 90 °C for 30 minutes. Subsequently, water was added to dissolve unreacted sodium hydrogen sulfite, followed by cooling in an ice bath to 0 °C, which was maintained for 30 minutes. The precipitated product was filtered and dried under vacuum (<1 mbar). **1** was obtained as white powder.

^{1}H NMR (400 MHz, DMSO-d_6) δ / ppm = 7.26 (s, 2H, CH^1).

^{13}C NMR (101 MHz, DMSO-d_6) δ / ppm = 159.02, 147.29, 118.13.

IR (ATR) $\tilde{\nu}$ / cm^{-1} = 3151, 3124, 3065, 3055, 3046, 3011, 2999, 2989, 2978, 2970, 2941, 2915, 2884, 2874, 2859, 2797, 2789, 2557, 1680, 1674, 1571, 1522, 1417, 1273, 1228, 1187, 1162, 1041, 961, 845, 763, 525, 485.

HRMS (FAB) *m/z*: [M]$^+$ calc. for $C_8H_8O_5$, 156.0054, found 156.0053; Δ = 0.1 mmu.

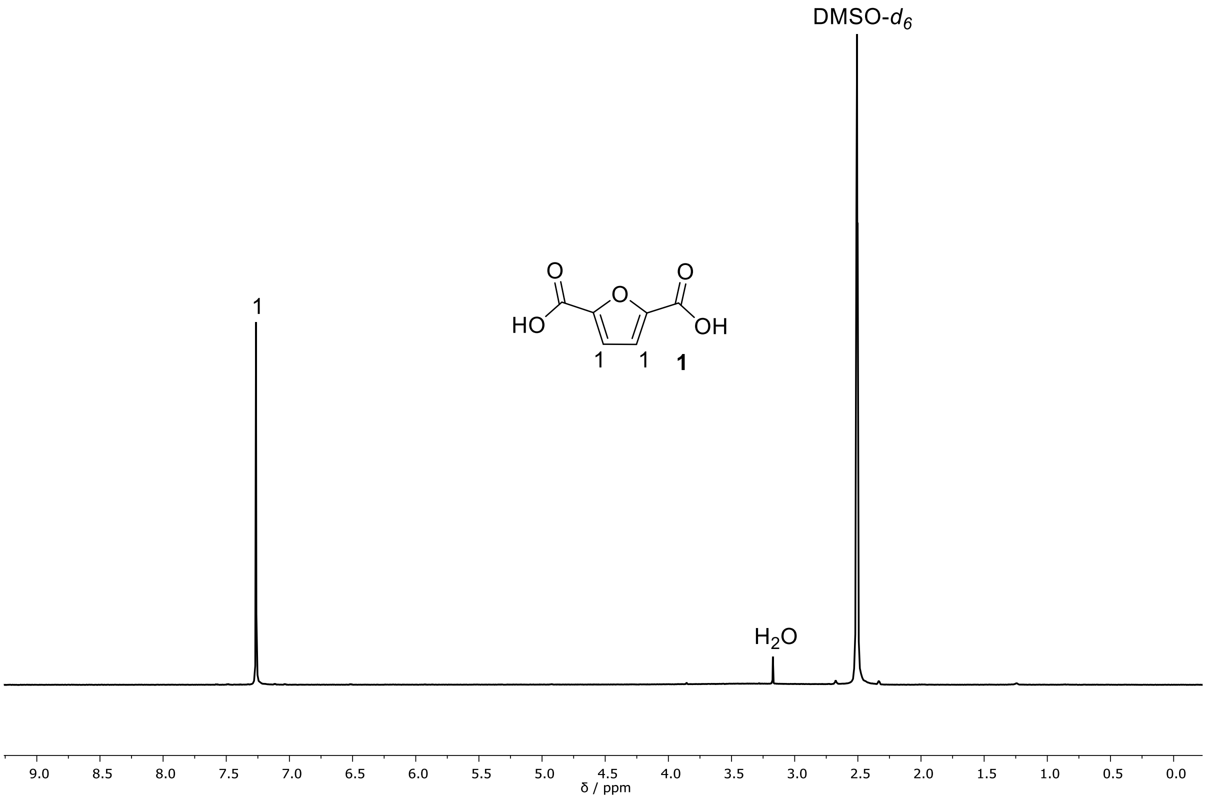

Figure S1. ^{1}H NMR spectrum of **1** in DMSO-d_6.

2,3-Furandicarboxylic acid dimethyl ester (2)

5.00 g FDCA (1.00 equiv., 32.0 mmol) were dissolved in 130 mL methanol (100 equiv. 103 g, 3.20 mol), followed by adding 85.4 µL sulfuric acid (0.05 equiv., 157 mg, 1.60 mmol). The mixture was stirred under reflux for 5 days. Reaction control was performed *via* ^{1}H NMR spectroscopy until full conversion was observed. The reaction mixture was concentrated under vacuum and the precipitated product was washed with water. A recrystallization from methanol was performed before drying the product under vacuum (<1 mbar) to obtain **2** as white powder.

^{1}H NMR (400 MHz, DMSO-d_6) δ / ppm = 7.43 (s, 2H, CH^2), 3.86 (s, 6H, CH$_3$^{1}).

^{13}C NMR (101 MHz, DMSO-d_6) δ / ppm = 157.83, 146.03, 119.03, 52.39.

IR (ATR): $\tilde{\nu}$ / cm^{-1} = 3116, 1718, 1602, 1584, 1514, 1432, 1378, 1308, 1271, 1236, 1191, 1160, 1131, 1028, 985, 921, 854, 835, 796, 765, 611, 481, 428.

HRMS (FAB) *m/z*: [M]$^+$ calc for $C_8H_8O_5$, 184.0367, found 184.0366; Δ = 0.1 mmu.

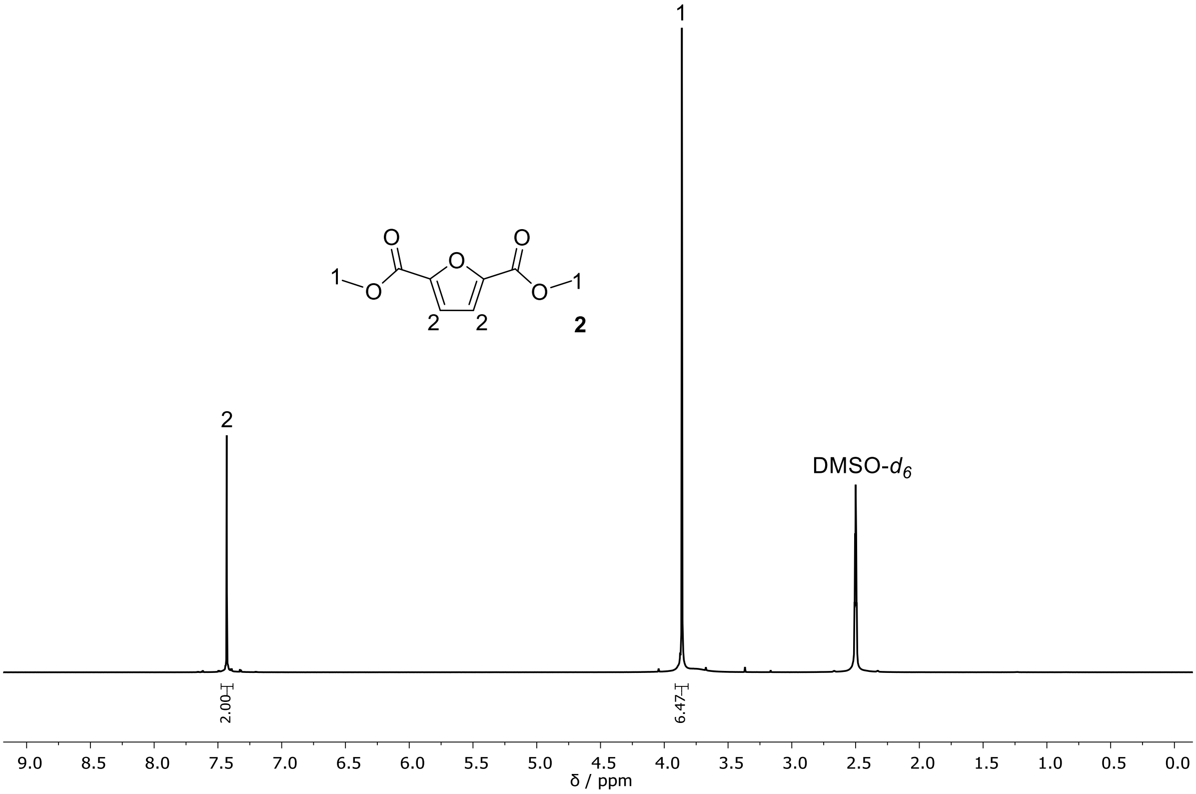

Figure S2. ^{1}H NMR spectrum of **2** in DMSO-d_6.

Deconvolution Method for polycondensation reactions

BDO (3.00 equiv., 2.70 g, 30.0 mmol) and FDCA (1.00 equiv., 1.56 g, 10.0 mmol) were used in a polycondensation reaction performed as follows: The catalyst loading per batch was 1.00 mol%. In the first batch, 16 different Lewis acids were tested, i.e., $AlCl_3$, $MgCl_2$ $6H_2O$, TTIP, $In(Otf)_3$, $InCl_3$, CuCl, $SnCl_2$, $ZnBr_2$, $Zn(Otf)_2$, $Yb(Otf)_3$, BF_3 $O(C_2H_5)_2$, $Sc(Otf)_3$, $FeCl_3$, $Bi(Otf)_3$, Ag(Otf), LiBr. The reaction flask was heated to 140 °C, followed by increasing the temperature to 180 °C within 4 hours. The temperature of 180 °C was kept for another 19 hours before vacuum (< 1 mbar) was applied to the system. The temperature was further increased to 190 °C and kept at this temperature for 1 hour. Then, the mixture was stirred at 200 °C under continuous vacuum (<1 mbar) for another 23 hours. The obtained polyester **3** was dissolved in HFIP, precipitated into methanol, then dried at 80 °C under vacuum (<1 mbar) for 6 hours, before SEC-HFIP was performed.

With batches **B1** to **B4** the desired polyesters were obtained and are listed with M_n and $Đ$ determined by SEC-HFIP in Tab. S1. For catalyst CuCl, no SEC-HFIP measurement was performed, as no precipitation to a desired polyester could be carried out.

Table S1. M_n and *Đ* determined by SEC-HFIP of the respective polyesters listed with the used catalyst during the Deconvolution Method.

Batch/Catalyst Number	**Catalyst(s)**	***M*** M_n **/ kDa**	***Đ***
B1	$AlCl_3$, $MgCl_2$ * $6H_2O$, $InCl_3$, CuCl	9	1.47
B2	$Zn(Otf)_2$, $Yb(Otf)_3$, $In(Otf)_3$, $Bi(Otf)_3$	-	-
B3	TTIP, $FeCl_3$, $SnCl_2$, $ZnBr_2$	9	1.93
B4	$BF_3{\cdot}O(C_2H_5)_2$, $Sc(Otf)_3$, Ag(Otf), LiBr	-	-
B5	$AlCl_3$, $MgCl_2$ * $6H_2O$	12	1.57
B6	$InCl_3$, CuCl	10	1.47
B7	$FeCl_3$, TTIP	16	2.22
B8	$SnCl_2$, $ZnBr_2$	10	1.82
	$AlCl_3$	15	1.65
	$MgCl_2$ * 6 H_2O	11	1.19
	$InCl_3$	9	1.86
	CuCl	-	-
	TTIP	14	1.95
	$FeCl_3$	18	1.55
	$SnCl_2$	11	1.23
	$ZnBr_2$	10	2.26
	*TTIP	10	2.22
	*$FeCl_3$	17	1.53
	$Ti(OBu)_4$	15	1.96

*__2__ was used instead of unpurified FDCA

Polycondensation reactions of a dicarboxylic acid with BDO

2.70 g of BDO (3.00 equiv., 30.0 mmol) were mixed with the respective dicarboxylic acid (1.00 equiv., 10.0 mmol) and $FeCl_3$ (1.25 mol%., 20.0 mg, 0.120 mmol) as catalyst. The reaction mixture was heated to 160 °C for 17 hours. Then, the temperature was increased to 215 °C for another 7 hours and vacuum (<1 mbar) was applied to the system. The reaction mixture was cooled to room temperature and dissolved in THF, then precipitated in a 1:1 (v/v) mixture of water and ethanol. The precipitated polymer was dried under vacuum (<1 mbar) at room temperature. However, some polyesters still showed solvent leftovers in their NMR spectra, also visible in TGA measurements. Thus, TGA is depicted at two different weight losses.

For polyester **3**, FDCA (1.56 g) was used as second monomer with 2.70 g BDO. The polyester was isolated as brownish solid.

^{1}H NMR (400 MHz, DMSO-d_6) δ / ppm = 7.43 – 7.19 (m, 2H, CH^3), 5.33 – 5.11 (m, 2H, CH^2), 1.49 – 1.10 (m, 6H, CH$_3$^{1}).

^{13}C NMR (101 MHz, DMSO-d_6) δ / ppm = 157.09, 147.56, 145.40, 119.65, 72.96, 16.17, 14.90.

IR (ATR) $\tilde{\nu}$ / cm^{-1} = 1718, 1578, 1382, 1267, 1224, 1135, 1107, 1080, 1018, 996, 965, 825, 763, 618.

$T_{\mathrm{d,5\%}}$ = 303 °C (TGA), $T_{\mathrm{d,15\%}}$ = 325 °C (TGA), M_{n} = 6 kDa and $Đ$ = 1.80 (SEC-THF), M_{n} = 18 kDa and $Đ$ = 1.55 (SEC-HFIP), T_{g} = 106 °C (DSC).

ICP-OES measurements were performed with the antisolvents after a threefold precipitation of polyester **3**. In the first precipitation step, 6 to 10 wt% of FeCl$_3$ were washed out. In precipitation step 2, less than an additional 0.20 wt% were removed and in the third precipitation step less than 0.01 wt% were removed.

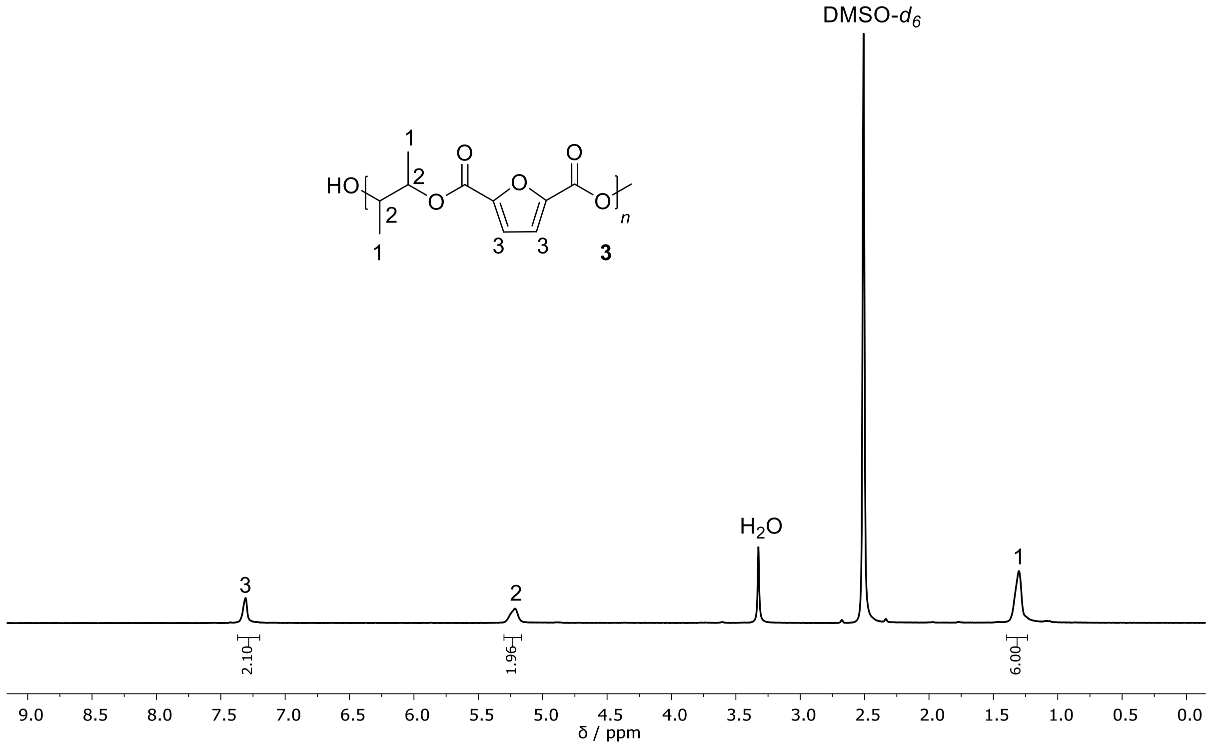

Figure S3. ^{1}H NMR spectrum of **3** in DMSO-d_6.

For polyester **4**, **1** (1.56 g) was used as dicarboxylic acid with 2.70 g BDO. The polyester was isolated as brownish solid.

^{1}H NMR (400 MHz, DMSO-d_6) δ / ppm = 7.41 – 7.25 (m, 2H, CH^3), 5.36 – 5.10 (m, 2H, CH^2), 1.39 – 1.24 (m, 6H, CH$_3$^{1}).

IR (ATR) $\tilde{\nu}$ / cm^{-1} = 1718, 1578, 1382, 1267, 1224, 1135, 1107, 1080, 1018, 996, 965, 825, 763, 617.

$T_{d,5\%}$ = 251 °C (TGA), $T_{d,15\%}$ = 343 °C (TGA), M_n = 6 kDa and Đ = 2.27 (SEC-THF), T_g = 95 °C (DSC).

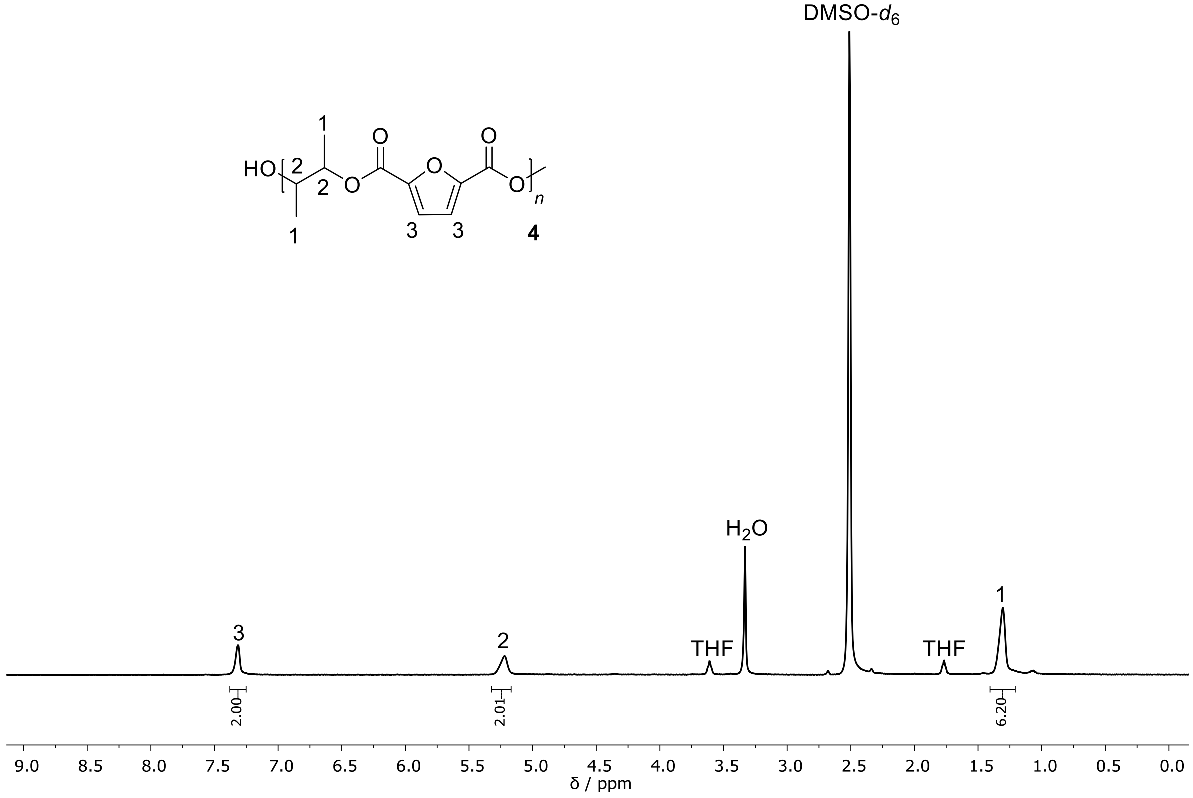

Figure S4. ^{1}H NMR spectrum of **4** in DMSO-d_6.

For polyester **5**, **2** (1.84 g) was used with 2.70 g BDO. The polyester was isolated as brownish solid.

^{1}H NMR (400 MHz, DMSO-d_6) δ / ppm = 8.12 – 7.96 (m, side-product), 7.48 – 7.17 (m, 2H, CH^3), 5.31 – 5.08 (m, 2H, CH_2^2), 1.40 – 1.12 (m, 6H, CH_3^1).

IR (ATR) $\tilde{\nu}$ / cm^{-1} = 2989, 1715, 1578, 1448, 1380, 1265, 1220, 1129, 1098, 1076, 1018, 998, 963, 905, 893, 868, 825, 761, 734, 685, 617.

$T_{d,5\%}$ = 172 °C (TGA), $T_{d,15\%}$ = 329 °C (TGA), M_n = 8 kDa and $Đ$ = 2.32 (SEC-THF), T_g = 90 °C (DSC).

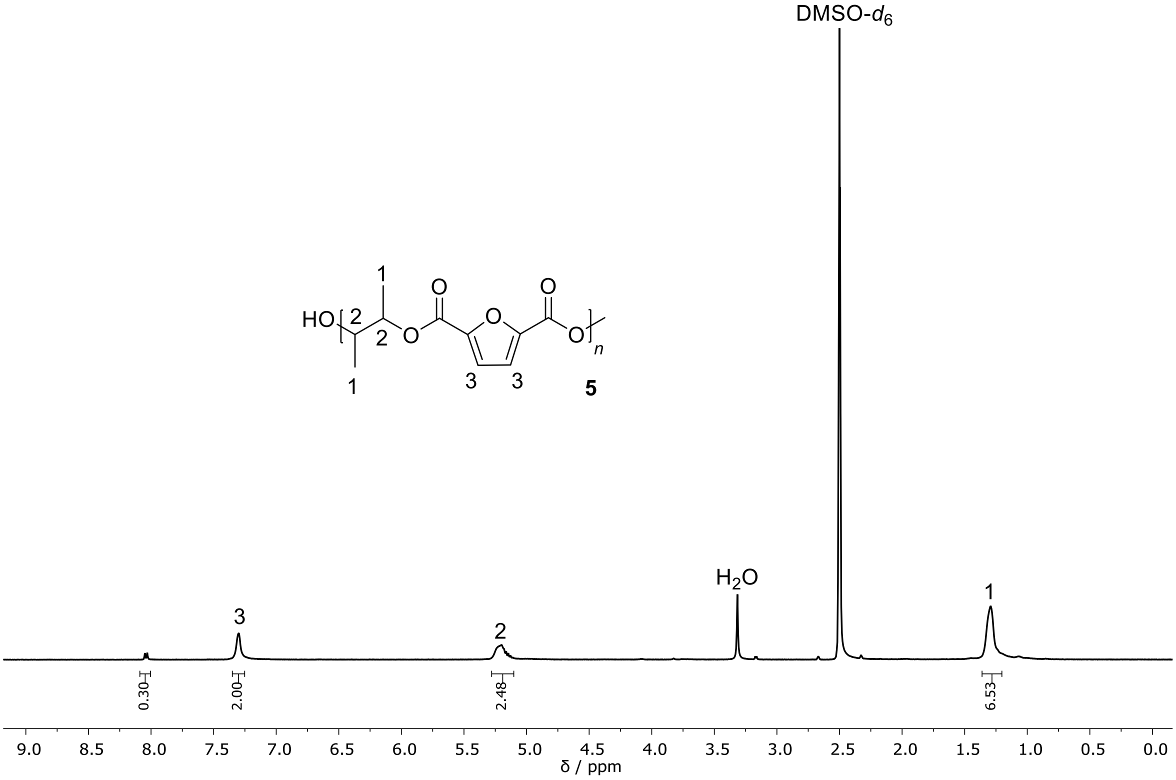

Figure S5. ^{1}H NMR spectrum of **5** in DMSO-d_6.

For polyester **6** the dicarboxylic acid succinic acid (SA, 1.18 g) was used with 2.70 g BDO. The product was isolated as brownish highly viscous liquid.

^{1}H NMR (400 MHz, $CDCl_3$) δ / ppm = 5.09 – 4.87 (m, 2H, CH^2), 2.71 – 2.49 (m, 4H, $CH_2{}^3$), 1.34 – 1.07 (m, 6H, $CH_3{}^1$).

IR (ATR) $\tilde{\nu}$ / cm^{-1} = 2987, 2941, 1726, 1537, 1446, 1413, 1376, 1349, 1316, 1261, 1240, 1209, 1152, 1100, 1082, 1035, 1020, 1000, 965, 921, 860, 802, 570.

$T_{\mathrm{d,5\%}}$ = 280 °C (TGA), $T_{\mathrm{d,15\%}}$ = 336 °C (TGA), M_n = 5 kDa and $Đ$ = 1.47 (SEC-THF).

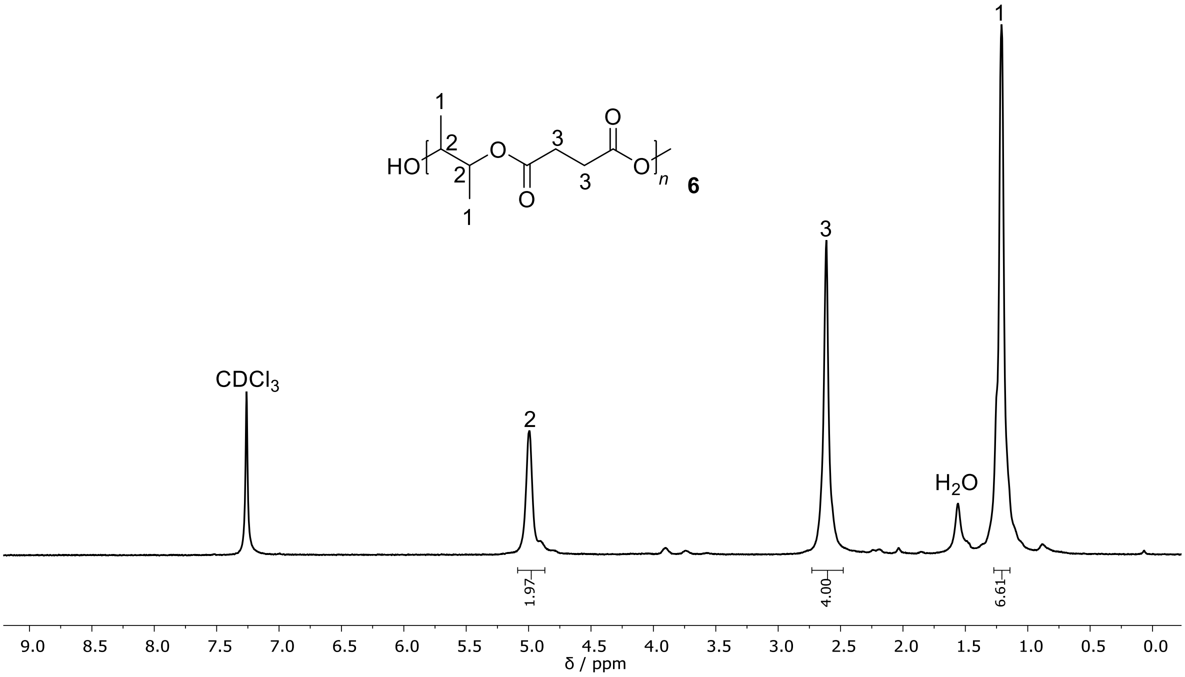

Figure S6. ^{1}H NMR spectrum of **6** in $CDCl_3$.

For polyester **7**, the dicarboxylic acid adipic acid (AA, 1.46 g) was used with 2.70 g BDO. The product was isolated as brownish highly viscous liquid.

^{1}H NMR (400 MHz, DMSO-d_6) δ / ppm = 4.98 – 4.80 (m, 2H, CH^2), 4.33 (d, J = 5.3 Hz, 1H, OH^7), 3.44 (t, J = 6.6 Hz, 2H, CH^6), 2.36 – 2.19 (m, 4H, CH_2^{3}), 1.60 – 1.46 (m, 4H, CH_2^{4}), 1.18 – 1.07 (m, 6H, CH_3^{1}), 1.07 (s, 3H, CH_3^{5}).

IR (ATR) $\tilde{\nu}$ / cm^{-1} = 2985, 2941, 1728, 1528, 1448, 1419, 1378, 1312, 1286, 1240, 1216, 1166, 1137, 1100, 1080, 1043, 1022, 1002, 946.

$T_{d,5\%}$ = 326 °C (TGA), $T_{d,15\%}$ = 350 °C (TGA), M_n = 8 kDa and $Đ$ = 1.44 (SEC-HFIP).

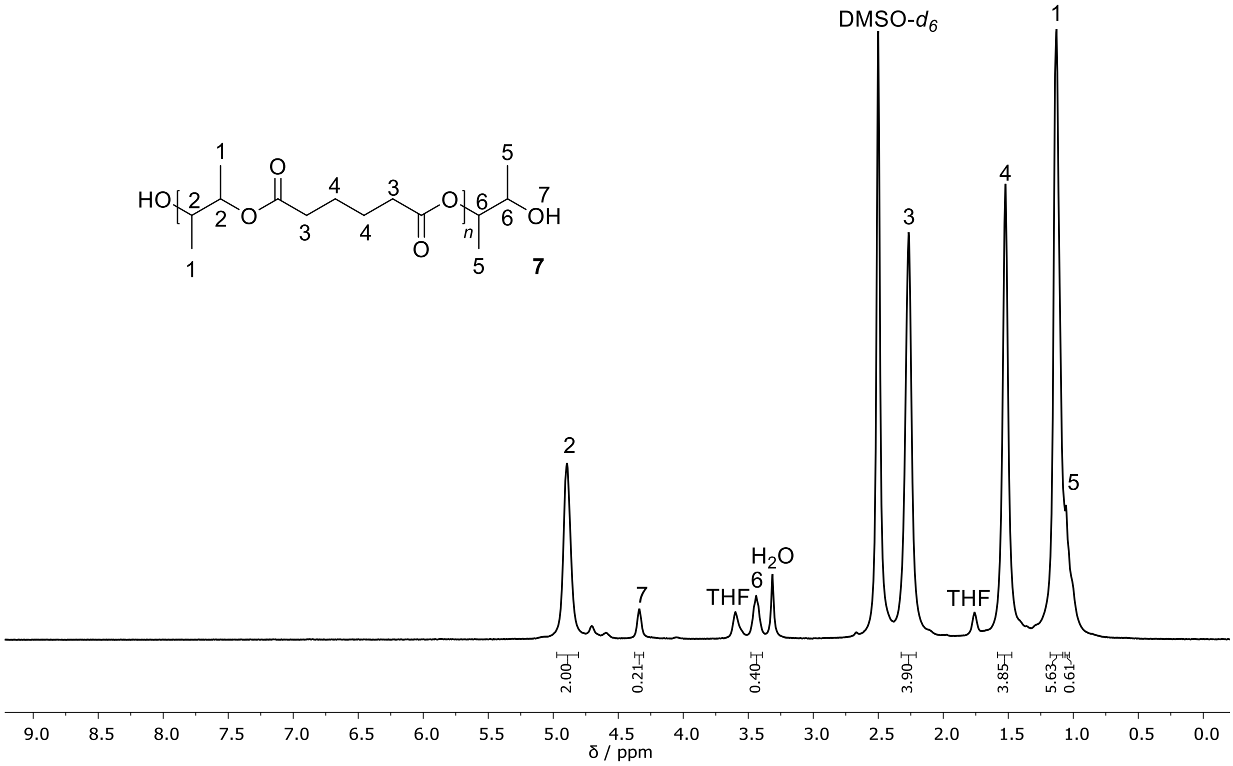

Figure S7. ^{1}H NMR spectrum of **7** in DMSO-d_6.

For polyester **8**, the dicarboxylic acid sebacic acid (SBA, 2.02 g) was used with 2.70 g BDO. The product was isolated as brownish highly viscous liquid.

^{1}H NMR (400 MHz, DMSO-d_6) δ / = 4.96 – 4.82 (m, 2H, CH^2), 2.28 – 2.17 (m, 4H, CH_2^3), 1.54 – 1.45 (m, 4H, CH_2^4), 1.28 – 1.20 (m, 8H, CH_2^5), 1.16 – 0.98 (m, 6H, CH_3^1).

IR (ATR) $\tilde{\nu}$ / cm^{-1} = 2983, 2931, 2855, 1732, 1450, 1419, 1378, 1349, 1316, 1300, 1242, 1166, 1131, 1100, 1082, 1035, 1004, 944, 868, 726.

$T_{\mathrm{d,\,5\%}}$ = 358 °C (TGA), M_n = 10 kDa and $Đ$ = 1.47 (SEC-HFIP).

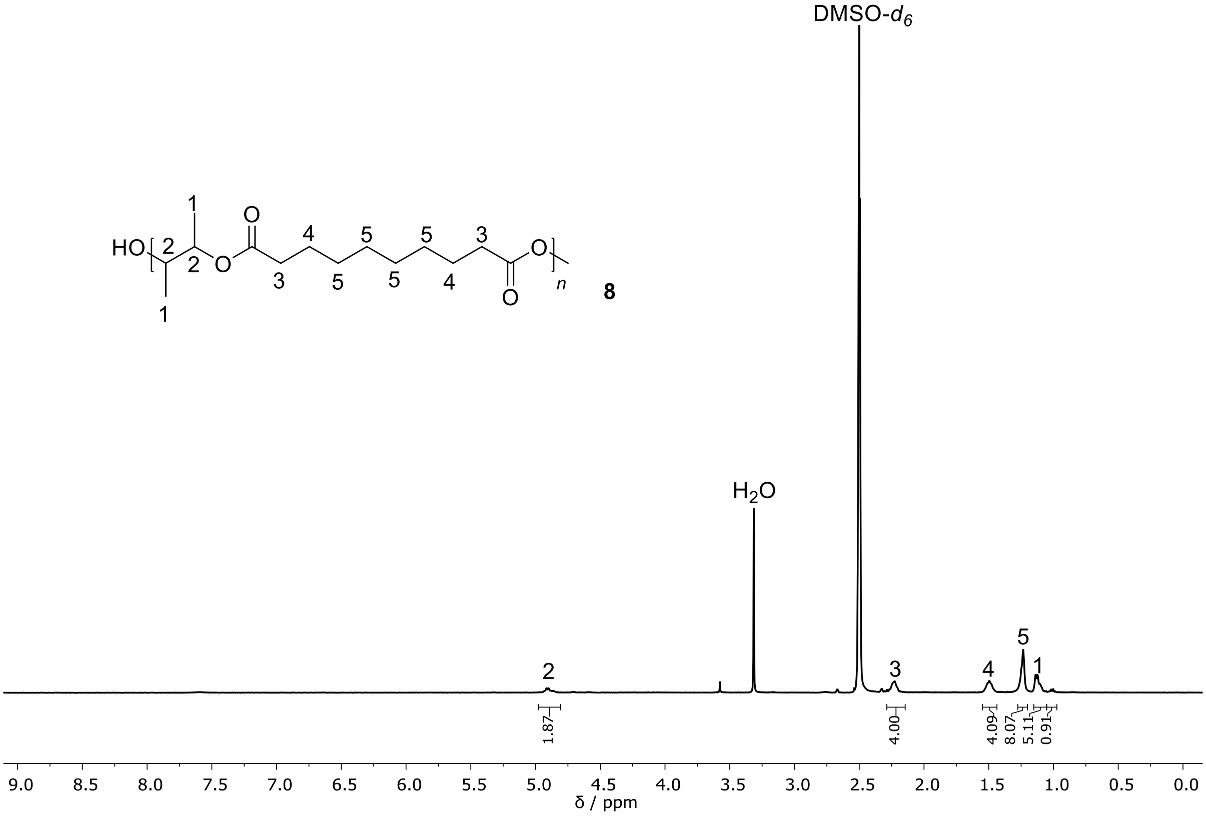

Figure S8. ^{1}H NMR spectrum of **8** in DMSO-d_6.

Copolymerization reactions of two dicarboxylic acids with BDO

2.70 g of BDO (3.00 equiv., 30.0 mmol) were added to 1 equiv. (1 mmol) of a mixture of two dicarboxylic acids (FDCA and AA) and $FeCl_3$ (1.25 mol%., 20.0 mg, 0.120 mmol) as catalyst. The mixture was stirred at 160 °C for 17 hours. Then, the temperature was increased to 215 °C and vacuum (<1 mbar) was applied. The mixture was cooled to room temperature, dissolved in THF, and precipitated in a mixture of 1:1 (v/v) water and ethanol. The isolated copolyester was dried under vacuum (<1mbar) at room temperature. However, some polyesters still showed solvent leftovers in their NMR spectra, also visible in TGA measurements. Thus, TGA is depicted at two different weight losses.

For copolyester **9**, a mixture of 94% FDCA (9.40 mmol, 1.46 g) and 6% AA (0.60 mmol, 88.0 mg) was used. The copolyester was isolated as brownish solid.

^{1}H NMR (400 MHz, DMSO-d_6) δ / ppm = 7.43 – 7.20 (m, 2H, CH^1), 5.30 – 4.89 (m, 4H, CH^2), 2.30 – 2.11 (m, 4H, CH$_2$^{4}), 1.48 – 1.36 (m, 4H, CH$_2$^{5}), 1.36 – 1.08 (m, 12H, CH$_3$^{3}).

IR (ATR) $\tilde{\nu}$ / cm^{-1} = 2987, 1715, 1578, 1506, 1448, 1380, 1265, 1220, 1131, 1107, 1078, 1016, 996, 963, 905, 866, 825, 784, 761, 720, 617.

$T_{d,5\%}$ = 310 °C (TGA), $T_{d,15\%}$ = 340 °C (TGA), M_n = 15 kDa and *Đ* = 1.62 (SEC-HFIP), T_g = 84 °C (DSC).

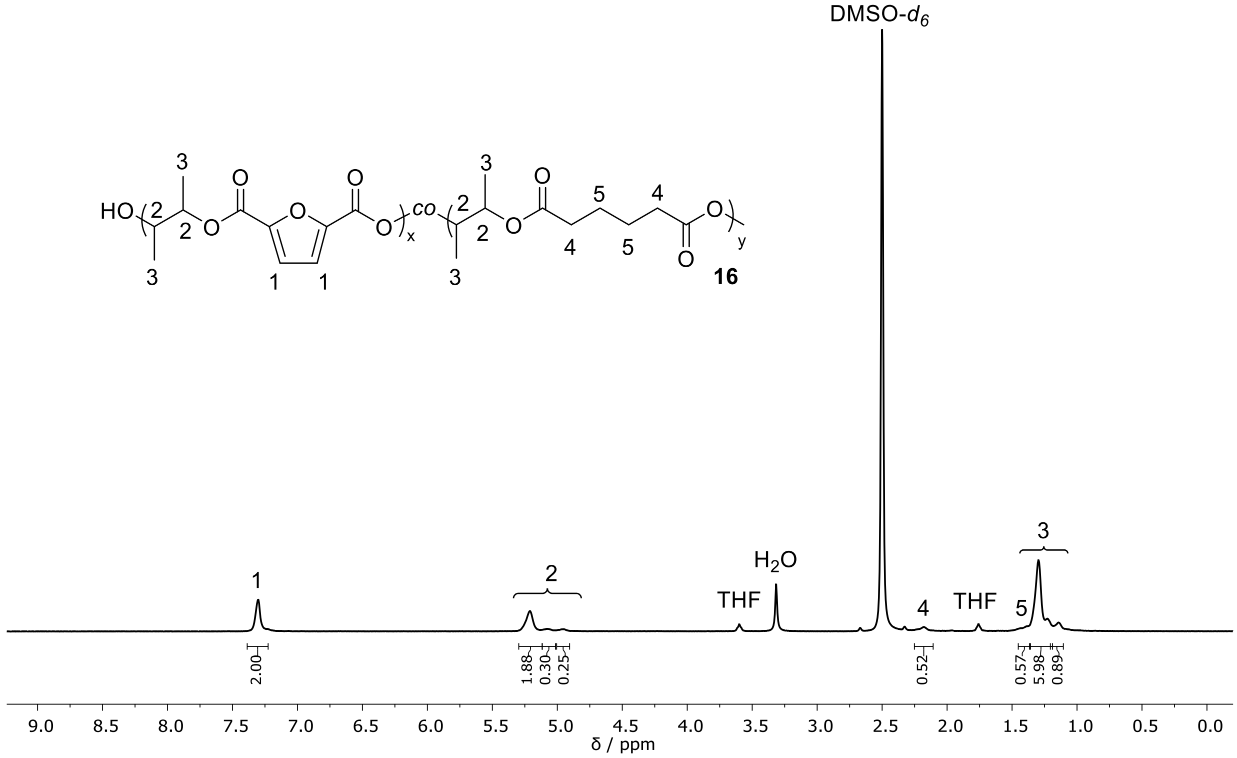

Figure S9. ^{1}H NMR spectrum of **16** in DMSO-d_6.

For copolyester **10**, a mixture of 88% FDCA (8.80 mmol, 1.37 g) and 12% AA (1.20 mmol, 175 mg) was used. The copolyester was isolated as brownish solid.

^{1}H NMR (400 MHz, DMSO-d_6) δ / ppm = 7.40 – 7.23 (m, 2H, CH^1), 5.34 – 4.90 (m, 4H, CH^2), 2.22 – 2.11 (m, 4H, CH$_2$^{4}), 1.50 – 1.36 (m, 4H, CH$_2$^{5}), 1.36 – 1.10 (m, 12H, CH$_3$^{3}).

IR (ATR) $\tilde{\nu}$ / cm^{-1} = 2989, 1715, 1580, 1448, 1380, 1265, 1220, 1131, 1107, 1078, 1016, 996, 963, 905, 866, 825, 763, 617.

$T_{d,5\%}$ = 324 °C (TGA), $T_{d,15\%}$ = 343 °C (TGA), M_n = 21 kDa and $Đ$ = 1.80 (SEC-HFIP), T_g = 81 °C (DSC).

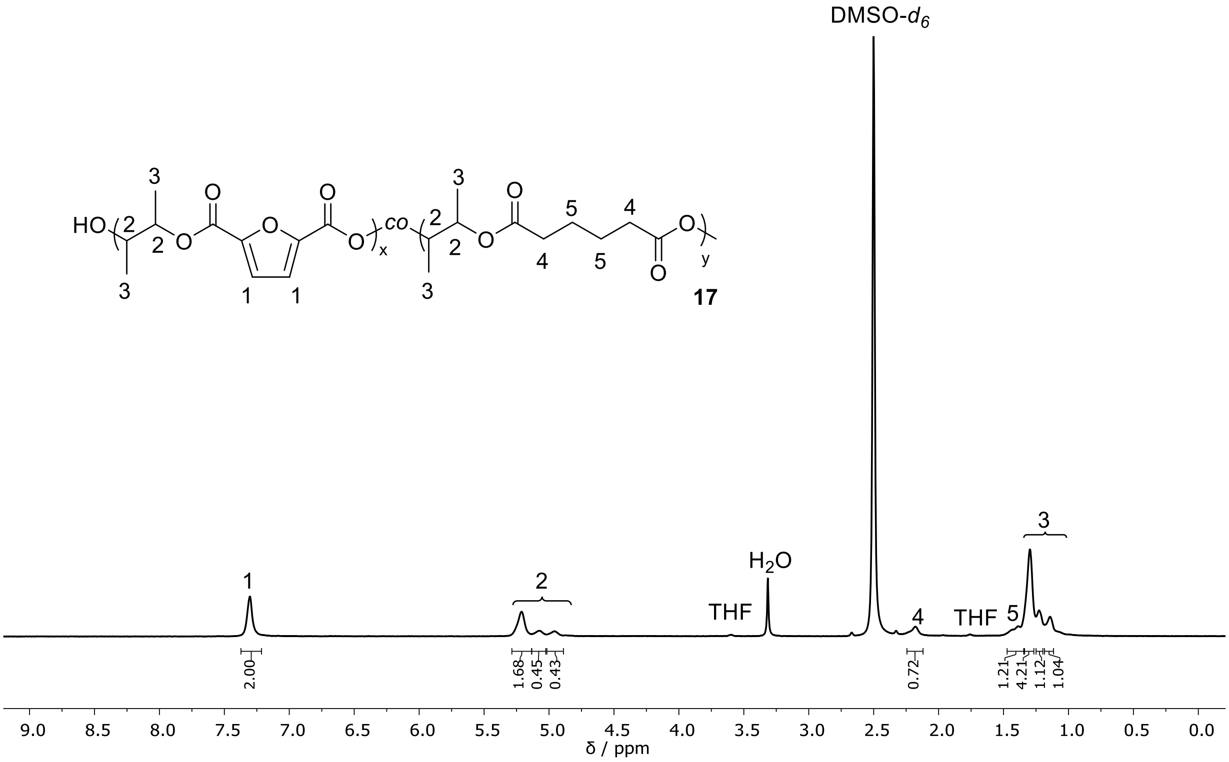

Figure S10. ^{1}H NMR spectrum of **17** in DMSO-d_6.

For copolyester **11**, a mixture of 82% FDCA (8.20 mmol, 1.28 g) and 18% AA (1.80 mmol, 263 mg) was used. The copolyester was isolated as brownish solid.

^{1}H NMR (400 MHz, DMSO-d_6) δ / ppm = 7.49 – 7.13 (m, 2H, CH^1), 5.37 – 4.89 (m, 4H, CH^2), 2.30 – 2.06 (m, 4H, CH$_2^4$), 1.47 – 1.38 (m, 4H, CH$_2^5$), 1.35 – 0.84 (m, 12H, CH$_3^3$).

IR (ATR) $\tilde{\nu}$ / cm^{-1} = 2987, 2934, 1715, 1578, 1448, 1380, 1347, 1335, 1265, 1220, 1131, 1107, 1078, 1016, 996, 963, 905, 866, 825, 792, 763, 617.

$T_{\mathrm{d,5\%}}$ = 149 °C (TGA), $T_{\mathrm{d,15\%}}$ = 337 °C (TGA), M_n = 16 kDa and $Đ$ = 1.84 (SEC-HFIP), T_g = 62 °C (DSC).

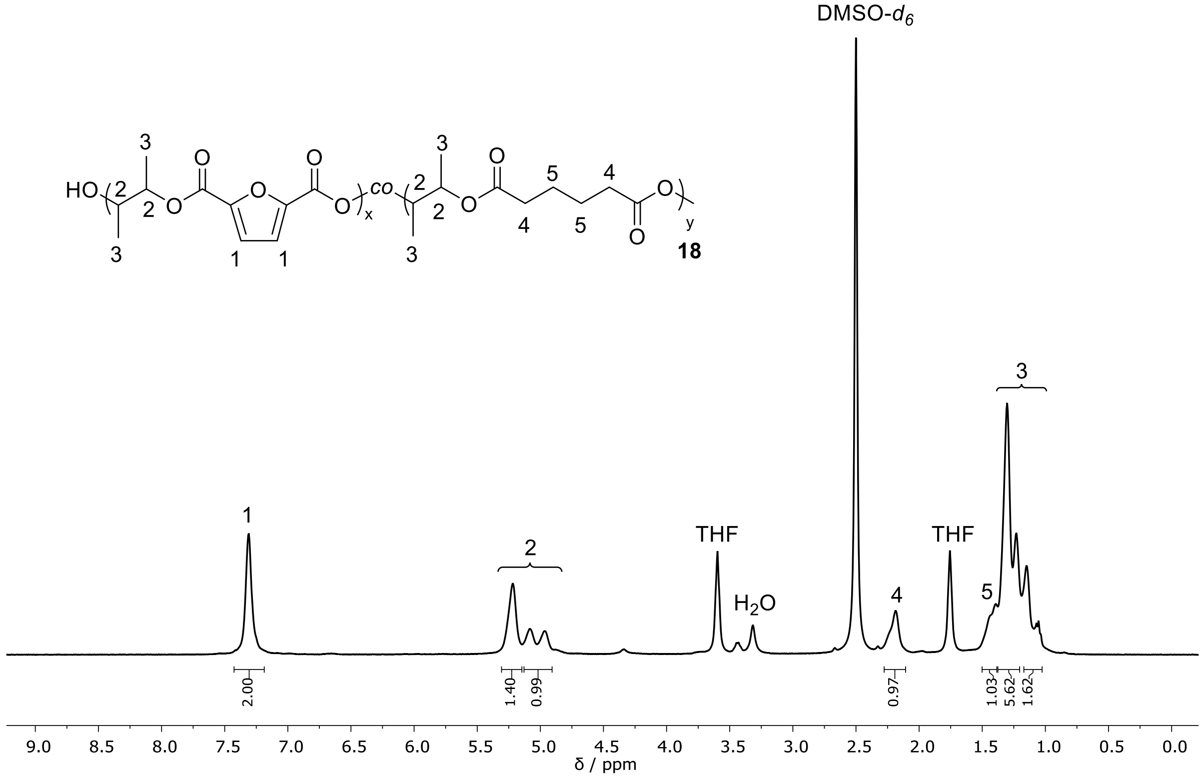

Figure S11. ^{1}H NMR spectrum of **18** in DMSO-d_6.

For copolyester **12**, a mixture of 76% FDCA (7.60 mmol, 1.18 g) and 24% AA (2.40 mmol, 351 mg) was used. The copolyester was isolated as brownish solid.

^{1}H NMR (400 MHz, DMSO-d_6) δ / ppm = 7.51 – 7.12 (m, 2H, CH^1), 5.42 – 4.78 (m, 4H, CH^2), 2.33 – 2.04 (m, 4H, CH$_2$^{4}), 1.55 – 1.34 (m, 4H, CH$_2$^{5}), 1.36 – 1.02 (m, 12H, CH$_3$^{3}).

IR (ATR) $\tilde{\nu}$ / cm^{-1} = 2985, 2941, 1715, 1580, 1448, 1380, 1339, 1267, 1222, 1133, 1107, 1078, 1016, 963, 905, 866, 827, 763, 617.

$T_{d,5\%}$ = 145 °C (TGA), $T_{d,15\%}$ = 338 °C (TGA), M_n = 14 kDa and $Đ$ = 1.68 (SEC-HFIP), T_g = 58 °C (DSC).

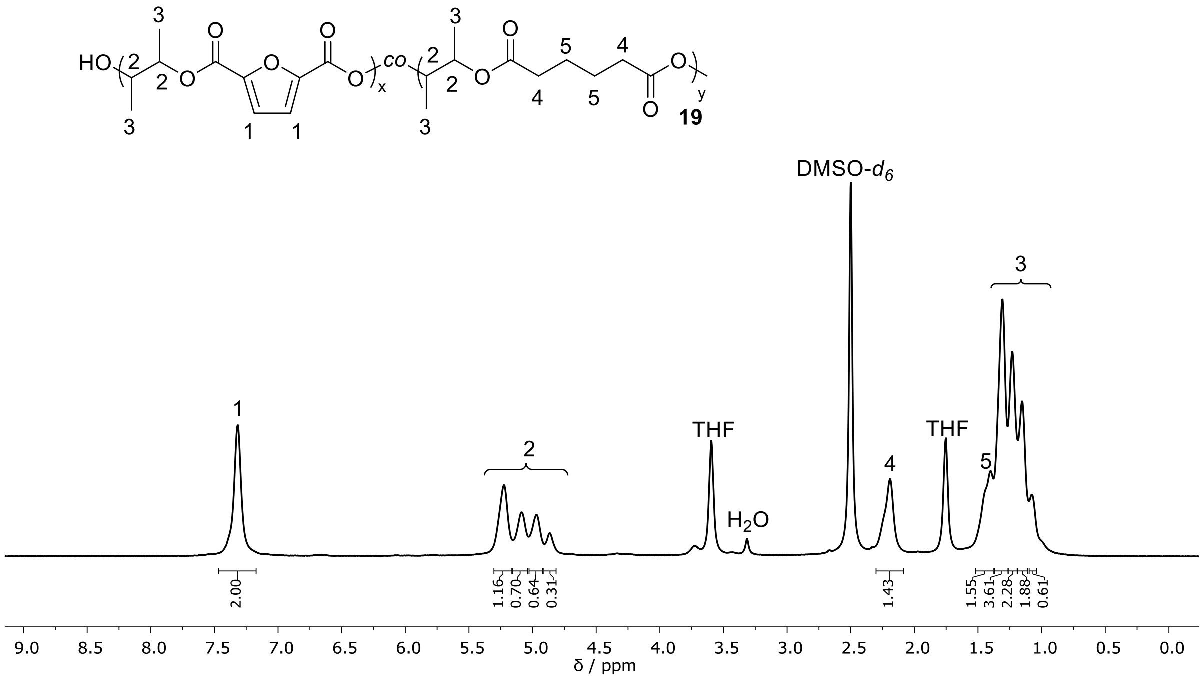

Figure S12. ^{1}H NMR spectrum of **19** in DMSO-d_6.

For copolyester **13**, a mixture of 70% FDCA (7.00 mmol, 1.09 g) and 30% AA (3.00 mmol, 483 mg) was used. The copolyester was isolated as brownish solid.

^{1}H NMR (400 MHz, DMSO-d_6) δ / ppm = 7.47 – 7.19 (m, 2H, CH^1), 5.34 – 4.78 (m, 4H, CH^2), 2.28 – 2.13 (m, 4H, CH$_2$^{4}), 1.54 – 1.36 (m, 4H, CH$_2$^{5}), 1.37 – 1.02 (m, 12H, CH$_3$^{3}).

IR (ATR) $\tilde{\nu}$ / cm^{-1} = 2985, 2941, 1715, 1580, 1448, 1380, 1341, 1267, 1222, 1160, 1133, 1105, 1078, 1037, 1016, 963, 903, 866, 827, 763, 617.

$T_{\mathrm{d,5\%}}$ = 245 °C (TGA), $T_{\mathrm{d,15\%}}$ = 338 °C (TGA), M_{n} = 10 kDa and $Đ$ = 1.73 (SEC-HFIP), T_{g} = 40 °C (DSC).

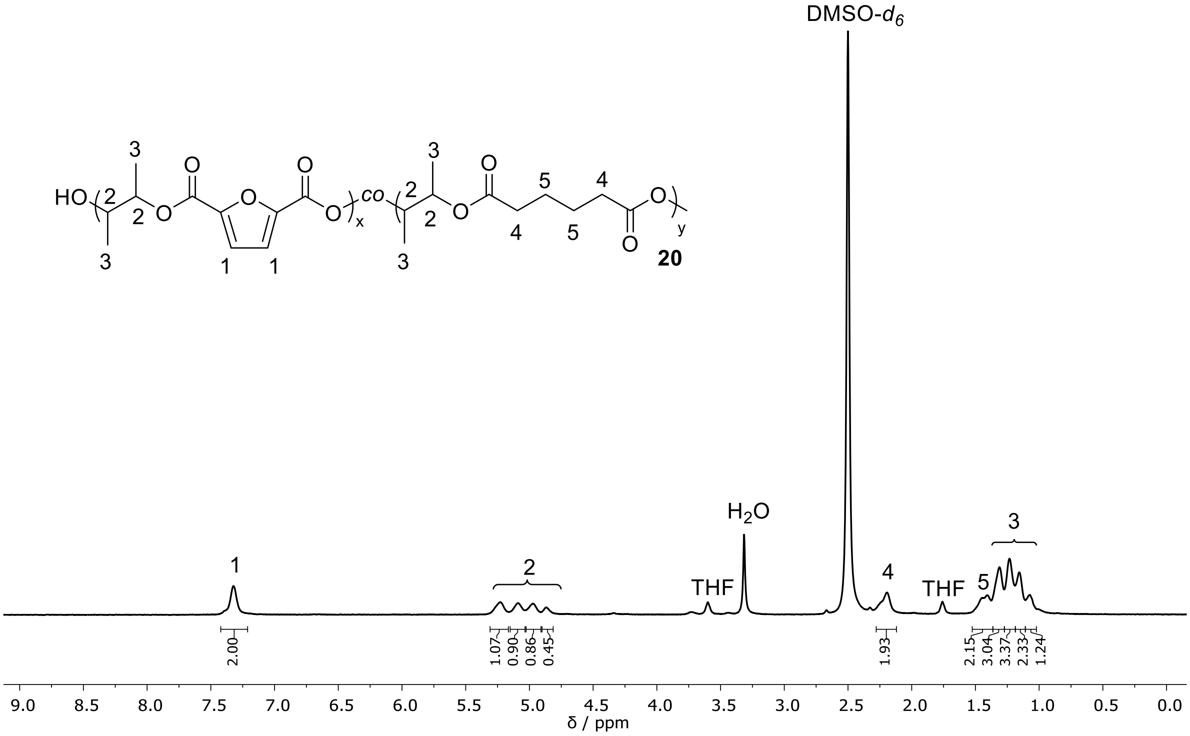

Figure S13. ^{1}H NMR spectrum of **20** in DMSO-d_6.

For copolyester **14**, a mixture of 60% FDCA (6.00 mmol, 937 mg) and 40% AA (4.00 mmol, 585 mg) was used. The copolyester was isolated as brownish viscous liquid.

^{1}H NMR (400 MHz, DMSO-d_6) δ / ppm = 7.43 – 7.23 (m, 2H, CH^1), 5.35 – 4.78 (m, 4H, CH^2), 2.31 – 2.10 (m, 4H, CH$_2$^{4}), 1.61 – 1.39 (m, 4H, CH$_2$^{5}), 1.36 – 1.01 (m, 12H, CH$_3$^{3}).

IR (ATR) $\tilde{\nu}$ / cm^{-1} = 2987, 2941, 1715, 1580, 1448, 1417, 1380, 1345, 1267, 1222, 1162, 1133, 1109, 1078, 1037, 1018, 899, 866, 827, 784, 763, 617.

$T_{d,5\%}$ = 243 °C (TGA), $T_{d,15\%}$ = 337 °C (TGA), M_n = 12 kDa and $Đ$ = 1.67 (SEC-HFIP).

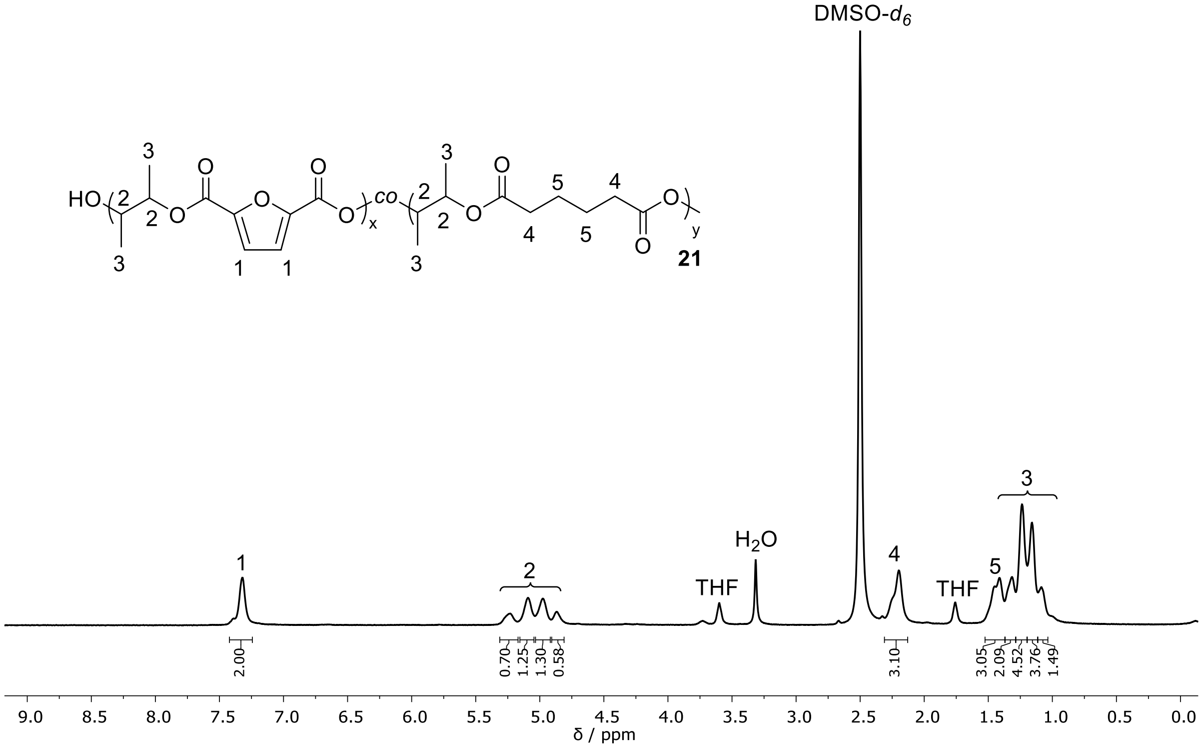

Figure S14. ^{1}H NMR spectrum of **21** in DMSO-d_6.

For copolyester **15**, a mixture of 40% FDCA (4.00 mmol, 624 mg) and 60% AA (6.00 mmol, 877 mg) was used. The copolyester was isolated as brownish viscous liquid.

^{1}H NMR (400 MHz, DMSO-d_6) δ / ppm = 7.40 – 7.27 (m, 2H, CH^1), 5.34 – 4.78 (m, 4H, CH^2), 2.35 – 2.10 (m, 4H, CH$_2^4$), 1.58 – 1.38 (m, 4H, CH$_2^5$), 1.33 – 0.49 (m, 12H, CH$_3^3$).

IR (ATR) $\tilde{\nu}$ / cm^{-1} = 2987, 2941, 1722, 1580, 1448, 1419, 1380, 1271, 1222, 1164, 1135, 1100, 1080, 1039, 1018, 1002, 965, 897, 866, 829, 765, 617.

$T_{d,5\%}$ = 274 °C (TGA), $T_{d,15\%}$ = 343 °C (TGA), M_n = 6 kDa and $Đ$ = 1.48 (SEC-HFIP).

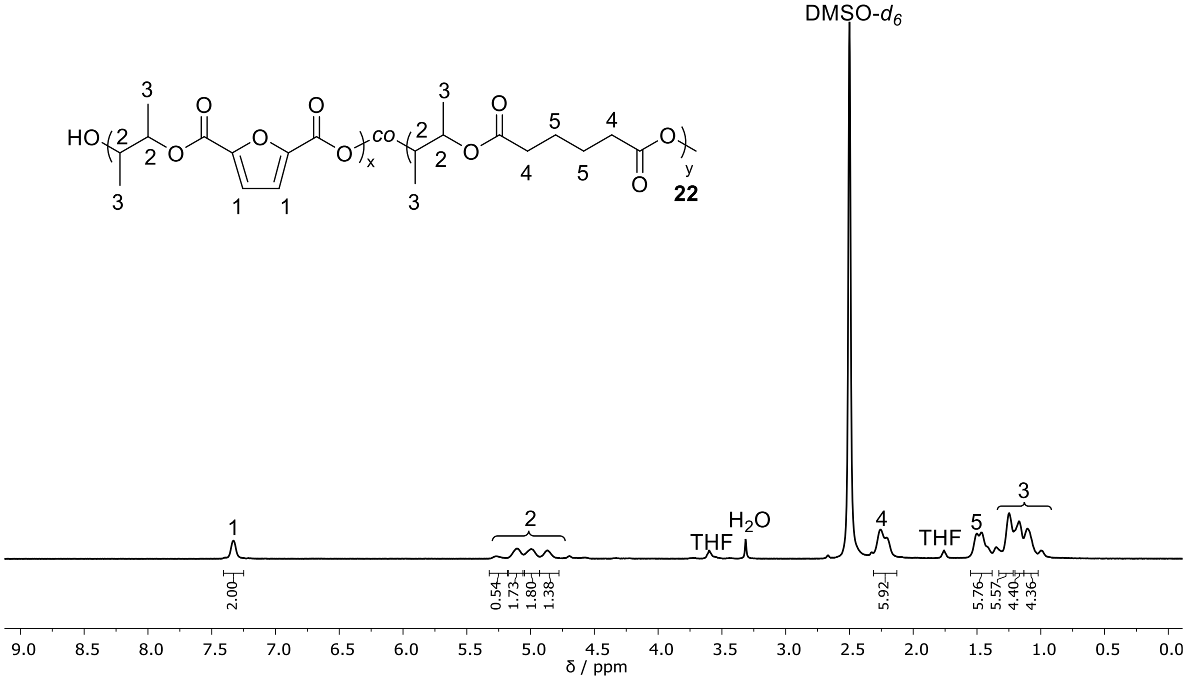

Figure S15. ^{1}H NMR spectrum of **22** in DMSO-d_6.

Depolymerization of Poly(ethylene terephthalate)

Commercially available PET materials (1.00 equiv., 500 mg, 2.60 mmol) were cut into flakes and polyester solid **3** (powder) was used for optimization. Per batch, the chosen material was mixed with ethylene glycol (15.48 equiv., 2.50 g, 2.25 mL) and $FeCl_3$ (1.25 mol%, 100 mg, 0.062 mmol). The mixture was heated in a carousel reactor to 190 °C for 3 h. Then, the mixture was cooled to room temperature followed by adding 15.0 mL distilled water and heating up to 70 °C for 30 min. Subsequently, the solid fraction was filtered off and the remaining liquid fraction put into a fridge at 8 °C, for 16 h. The precipitated BHET was filtered off, dried, and obtained as white crystals as final product.

^{1}H NMR (400 MHz, DMSO-d_6) δ / ppm = 8.13 (s, 4H, CH_{Ar}^1), 4.96 (t, J = 5.7 Hz, 2H, OH^2), 4.33 (t, J = 9.8 Hz, 4H, CH_2^3), 3.73 (q, J = 5.5 Hz, 4H, CH_2^4).

^{13}C NMR (101 MHz, DMSO-d_6) δ / ppm = 165.63, 134.22, 129.99, 67.50, 59.45.

HRMS (ESI) *m/z*: $[M]^+$ calc for $C_{12}H_{14}O_6$, 254.0790, found 255.0862.

T_m = 108 °C (DSC).

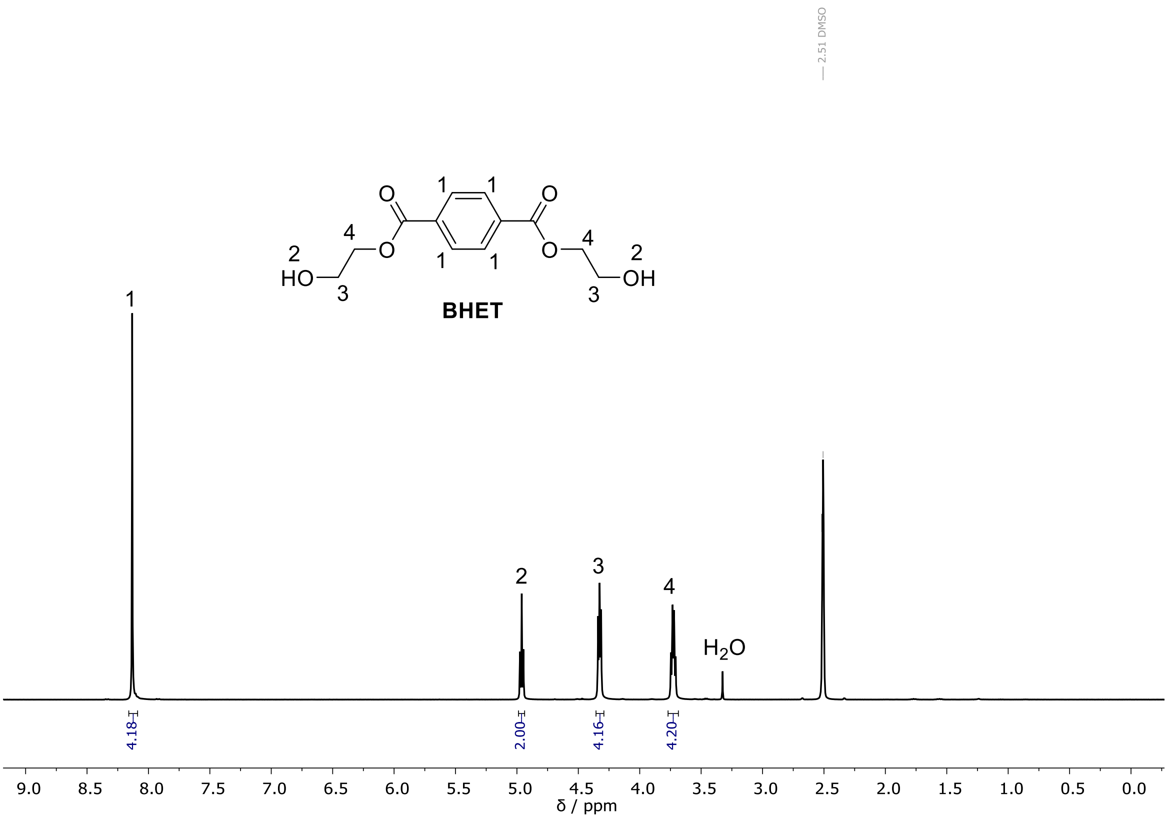

Figure S16. ^{1}H NMR spectrum of **BHET** in DMSO-d_6.