Supplementary Information

Enzymatic Polymerization of Various Biobased and Biodegradable BHMTHF-Based (Co)Polyesters

Cornelis Post[1,2], George Karchilakis[1,2], Dina Maniar[1], Vincent S.D. Voet[2], Rudy Folkersma[2], Katja Loos[*1]
[*]Corresponding author, Email. k.u.loos@rug.nl.

[1]Macromolecular Chemistry & New Polymeric Materials, Zernike Institute for Advanced Materials, University of Groningen, Nijenborgh 3, 9747 AG Groningen, the Netherlands
[2]Circular Plastics, Academy Tech & Design, NHL Stenden University of Applied Sciences, Van Schaikweg 94, 7811 KL Emmen, the Netherlands

^{1}H-NMR data of the BHMTHF-based (co)polyesters

Poly(tetrahydrofurandimethylene succinate) (PTSuc) was obtained in a 63% yield and appeared as a viscous colorless liquid. ^{1}H-NMR (600 MHz, DMSO-d6), δ (ppm): 4.58 (t, 1H, **OH** end group), 4.04 + 3.94 (m, 6H, **CH**-THF ring + **CH_2**-THF ester group), 3.85 (m, 1H, **CH**-THF ring end group), 3.59 (s, 3H, DMSuc ester-**CH_3** end group), 3,32 (m, **CH_2**-THF end group), (2.58 (t, 4H, ester-**CH_2**-**CH_2**-ester), 1.92 + 1.63 (m, 4H, **CH_2**-THF ring).

Poly(tetrahydrofurandimethylene glutarate) (PTGlu) was obtained in a 78% yield and appeared as a viscous colorless liquid. ^{1}H-NMR (600 MHz, DMSO-d6), δ (ppm): 4.57 (t, 1H, **OH** end group), 4.04 + 3.94 (m, 6H, **CH**-THF ring + **CH_2**-THF ester group), 3.84 (m, 1H, **CH**-THF ring end group), 3.58 (s, 3H, DM ester-**CH_3** end group), 3,32 (m, **CH_2**-THF end group), 2.36 (t, 4H, ester-**CH_2**-CH_2-**CH_2**-ester), 1.92 + 1.63 (m, 4H, **CH_2**-THF ring), 1.76 (m, 2H, ester-CH_2-**CH_2**-CH_2-ester).

Poly(tetrahydrofurandimethylene adipate) (PTAd, PTAd-TF_00, PTAd-FAd_00) was obtained in a 74% yield and appeared as a viscous colorless liquid. ^{1}H-NMR (600 MHz, DMSO-d6), δ (ppm): 4.58 (t, 1H, **OH** end group), 4.04 + 3.93 (m, 6H, **CH**-THF ring + **CH_2**-THF ester group), 3.84 (m, 1H, **CH**-THF ring end group), 3.57 (s, 3H, DM ester-**CH_3** end group), 3,32 (m, **CH_2**-THF end group), 2.32 (t, 4H, ester-**CH_2**-CH_2-CH_2-**CH_2**-ester), 1.92 + 1.63 (m, 4H, **CH_2**-THF ring), 1.54 (m, 4H, ester-CH_2-**CH_2**-**CH_2**-CH_2-ester).

Poly(tetrahydrofurandimethylene pimelate) (PTPim) was obtained in a 63% yield and appeared as a viscous colorless liquid. ^{1}H-NMR (600 MHz, DMSO-d6), δ (ppm): 4.58 (t, 1H, **OH** end group), 4.04 + 3.92 (m, 6H, **CH**-THF ring + **CH_2**-THF ester group), 3.84 (m, 1H, **CH**-THF ring end group), 3.57 (s, 3H, DM ester-**CH_3** end group), 3,32 (m, **CH_2**-THF end group), 2.29 (t, 4H, ester-**CH_2**-CH_2-CH_2-CH_2-**CH_2**-ester), 1.92 + 1.62 (m, 4H, **CH_2**-THF ring), 1.52 (m, 4H, ester-CH_2-**CH_2**-CH_2-**CH_2**-CH_2-ester), 1.27 (m, 2H, ester-CH_2-CH_2-**CH_2**-CH_2-CH_2-ester).

Poly(tetrahydrofurandimethylene suberate) (PTSub) was obtained in a 70% yield and appeared as a viscous colorless liquid. ^{1}H-NMR (600 MHz, DMSO-d6), δ (ppm): 4.57 (t, 1H, **OH** end group), 4.04 + 3.92 (m, 6H, **CH**-THF ring + **CH_2**-THF ester group), 3.84 (m, 1H, **CH**-THF ring end group), 3.57 (s, 3H, DM ester-**CH_3** end group), 3,31 (m, **CH_2**-THF end group), 2.28 (t, 4H, ester-**CH_2**-CH_2-CH_2-CH_2-CH_2-**CH_2**-ester), 1.92 + 1.62 (m, 4H, **CH_2**-THF ring), 1.50 (m, 4H, ester-CH_2-**CH_2**-CH_2-CH_2-**CH_2**-CH_2-ester), 1.26 (m, 4H, ester-CH_2-CH_2-**CH_2**-**CH_2**-CH_2-CH_2-ester).

Poly(tetrahydrofurandimethylene azelate) (PTAze) was obtained in a 61% yield and appeared as a viscous colorless liquid. ^{1}H-NMR (600 MHz, DMSO-d6), δ (ppm): 4.58 (t, 1H, **OH** end group), 4.04 + 3.92 (m, 6H, **CH**-THF ring + **CH_2**-THF ester group), 3.84 (m, 1H, **CH**-THF ring end group), 3.57 (s, 3H, DM ester-**CH_3** end group), 3,32 (m, **CH_2**-THF end group), 2.28 (t, 4H, ester-**CH_2**-CH_2-CH_2-CH_2-CH_2-CH_2-**CH_2**-ester), 1.92 + 1.62 (m, 4H, **CH_2**-THF ring), 1.50 (m, 4H, ester-CH_2-**CH_2**-CH_2-CH_2-CH_2-**CH_2**-CH_2-ester), 1.25 (m, 6H, ester-CH_2-CH_2-**CH_2**-**CH_2**-**CH_2**-CH_2-CH_2-ester).

Poly(tetrahydrofurandimethylene sebacate) (PTSeb) was obtained in a 67% yield and appeared as a viscous colorless liquid. ^{1}H-NMR (600 MHz, DMSO-d6), δ (ppm): 4.58 (t, 1H, **OH** end group), 4.04 + 3.92 (m, 6H, **CH**-THF ring + **CH_2**-THF ester group), 3.84 (m, 1H, **CH**-THF ring end group), 3.57 (s, 3H, DM ester-**CH_3** end group), 3,32 (m, **CH_2**-THF end group), 2.29 (t, 4H, ester-**CH_2**-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-**CH_2**-ester), 1.91 + 1.62 (m, 4H, **CH_2**-THF ring), 1.50 (m, 4H, ester-CH_2-**CH_2**-CH_2-CH_2-CH_2-CH_2-**CH_2**-CH_2-ester), 1.24 (m, 8H, ester-CH_2-CH_2-**CH_2**-**CH_2**-**CH_2**-**CH_2**-CH_2-CH_2-ester).

Poly(2,5-furandimethylene adipate) (PTAd-FAd_100) (PFAd) was obtained in a 71% yield and appeared as a solid. ^{1}H-NMR (600 MHz, DMSO-d_6), δ (ppm): 6.47 (s, 2H, furan), 5.01 (s, 4H, ester-**CH_2**-furan), 4.36 (m, 2H, OH-**CH_2**-furan end group), 3.56 (s, 3H, ester-**CH_3**, end group DMAd), 2.31 (t, 4H, ester-**CH_2**-CH_2-CH_2-**CH_2**-ester), 1.51 (m, 4H, ester-CH_2-**CH_2**-**CH_2**-CH_2-ester).

Poly(tetrahydrofurandimethylene adipate-co-2,5-furandimethylene adipate) (PTAd-FAd) copolyesters were obtained in a 61 – 71% yield, and appeared all as yellowish viscous liquids. ^{1}H-NMR (600 MHz, DMSO-d_6), δ (ppm): 6.47 (s, 2H, furan), 5.01 (s, 4H, ester-**CH_2**-furan), 4.36 (m, 2H, OH-**CH_2**-furan end group), 4.04 + 3.92 (m, 6H, **CH**-THF ring + **CH_2**-THF ester group), 3.57 (s, 3H, DMAd ester-**CH_3** end group), 2.32 (t, 4H, ester-**CH_2**-CH_2-CH_2-**CH_2**-ester), 1.91 + 1.62 (m, 4H, **CH_2**-THF ring), 1.52 (m, 4H, ester-CH_2-**CH_2**-**CH_2**-CH_2-ester).

Poly(tetrahydrofurandimethylene adipate-co-tetrahydrofurandimethylene 2,5-furandicarboxylate) (PTAd-TF) copolyesters were obtained in a 64 – 75% yield, and appeared all as colorless viscous liquids. ^{1}H-NMR (600 MHz, DMSO-d_6), δ (ppm): 7.42+ 7.39 + 7.36 (s, 2H, furan), 4.33 + 4.19 (m, 6H, **CH**-THF ring + **CH_2**-THF ester group (furan)), 4.04 + 3.92 (m, 6H, **CH**-THF ring + **CH_2**-THF ester group (DMAd)), 3.57 (s, 3H, DMAd ester-**CH_3** end group), 2.31 (t, 4H, ester-**CH_2**-CH_2-CH_2-**CH_2**-ester), 1.97 + 1.69 (m, 4H, **CH_2**-THF ring (furan)), 1.91 + 1.62 (m, 4H, **CH_2**-THF ring (DMAd)), 1.53 (m, 4H, ester-CH_2-**CH_2**-**CH_2**-CH_2-ester).

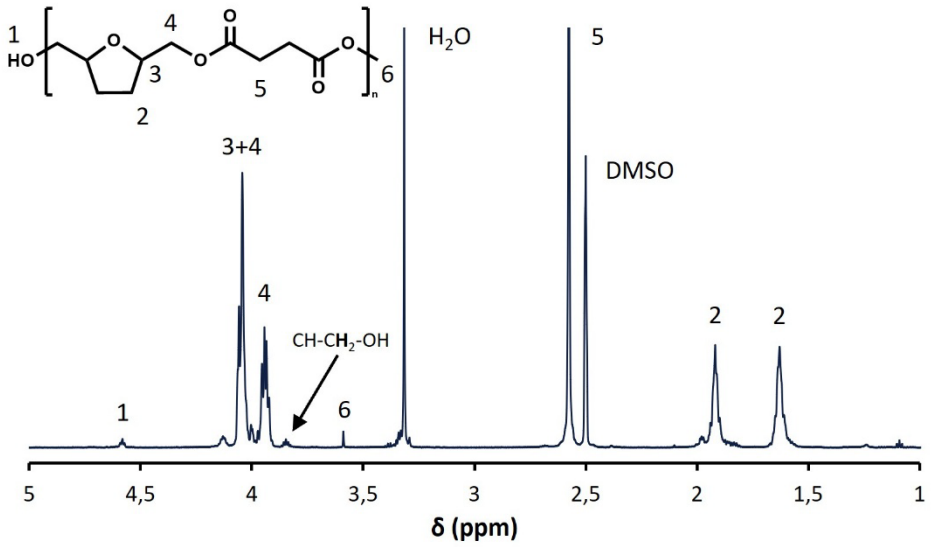

Figure S1: ^{1}H-NMR spectrum of poly(tetrahydrofurandimethylene succinate) (PTSuc) in DMSO-d_6.

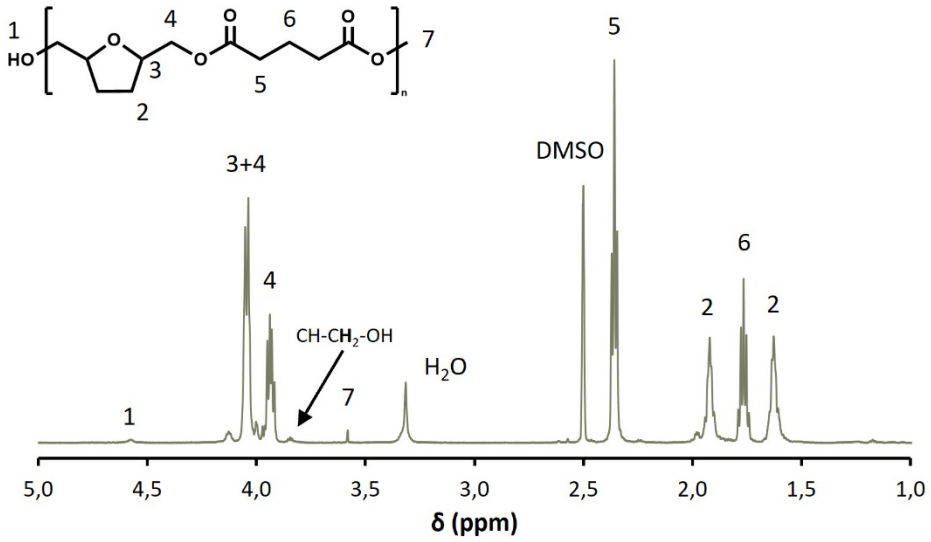

Figure S2: ^{1}H-NMR spectrum of poly(tetrahydrofurandimethylene glutarate) (PTGlu) in DMSO-d_6.

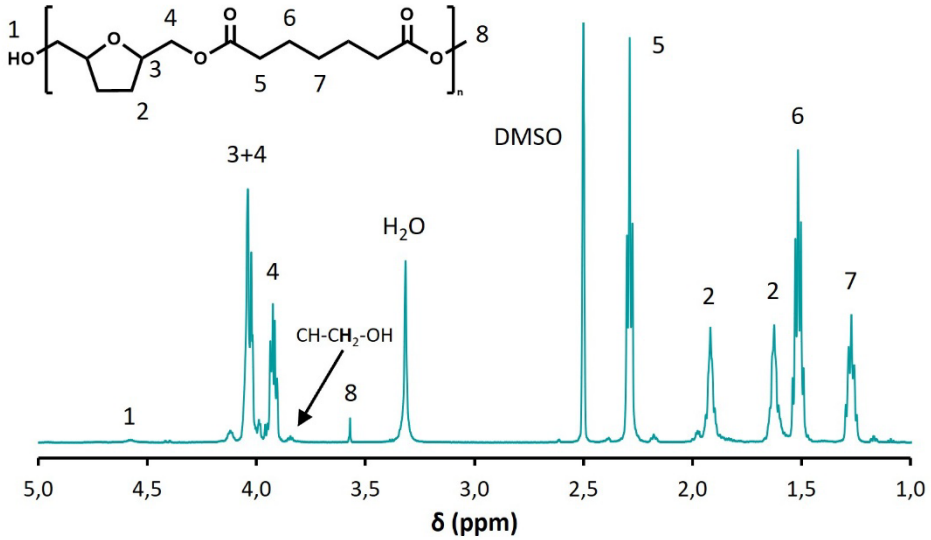

Figure S3: ^{1}H-NMR spectrum of poly(tetrahydrofurandimethylene pimelate) (PTPim) in DMSO-d_6.

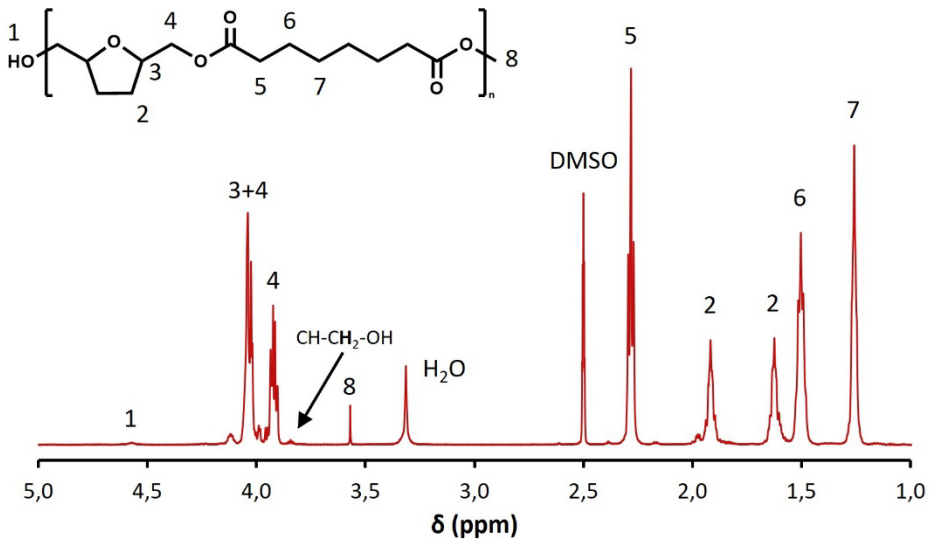

Figure S4: ^{1}H-NMR spectrum of poly(tetrahydrofurandimethylene suberate) (PTSub) in DMSO-d_6.

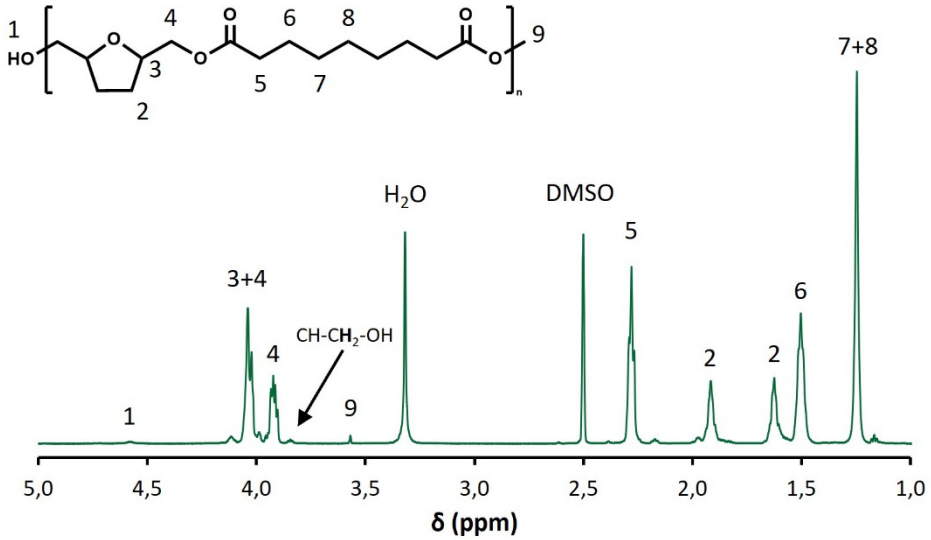

Figure S5: ^{1}H-NMR spectrum of poly(tetrahydrofurandimethylene azelate) (PTAze) in DMSO-d_6.

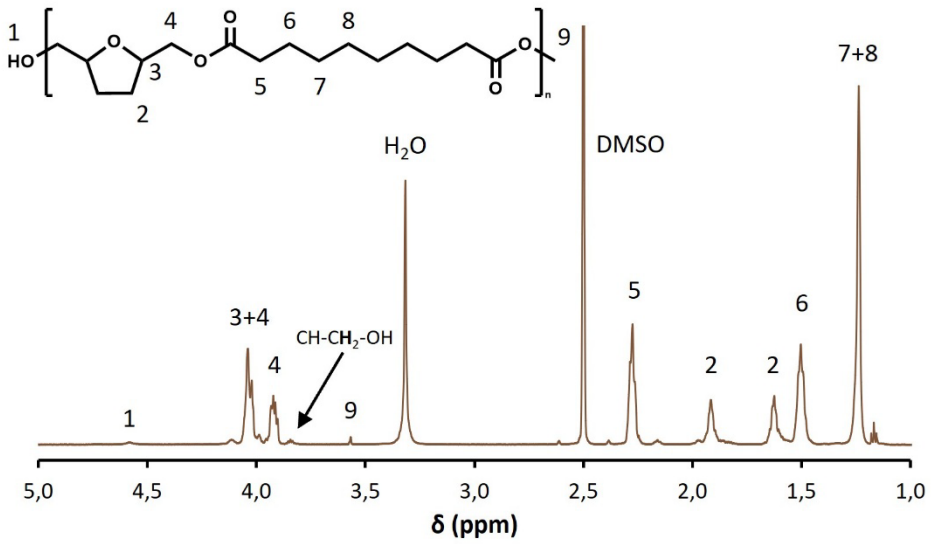

Figure S6: [1]H-NMR spectrum of poly(tetrahydrofurandimethylene sebacate) (PTSeb) in DMSO-d_6.

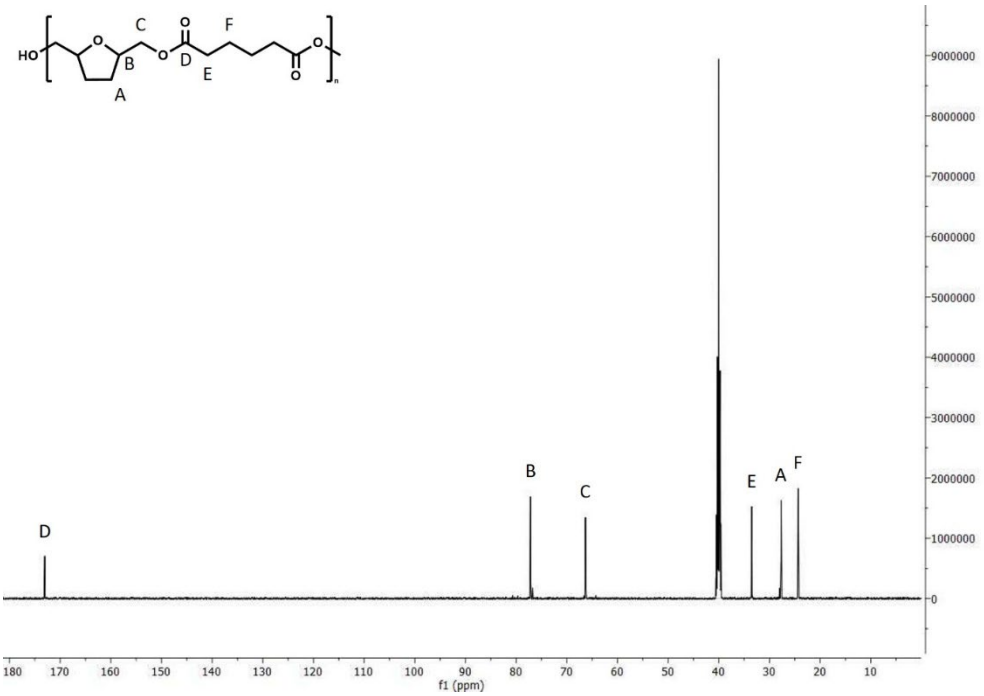

Figure S7: [13]C-NMR spectrum of poly(tetrahydrofurandimethylene adipate) (PTAd, PTAd-TF_00, PTAd-FAd_00) in DMSO-d_6.

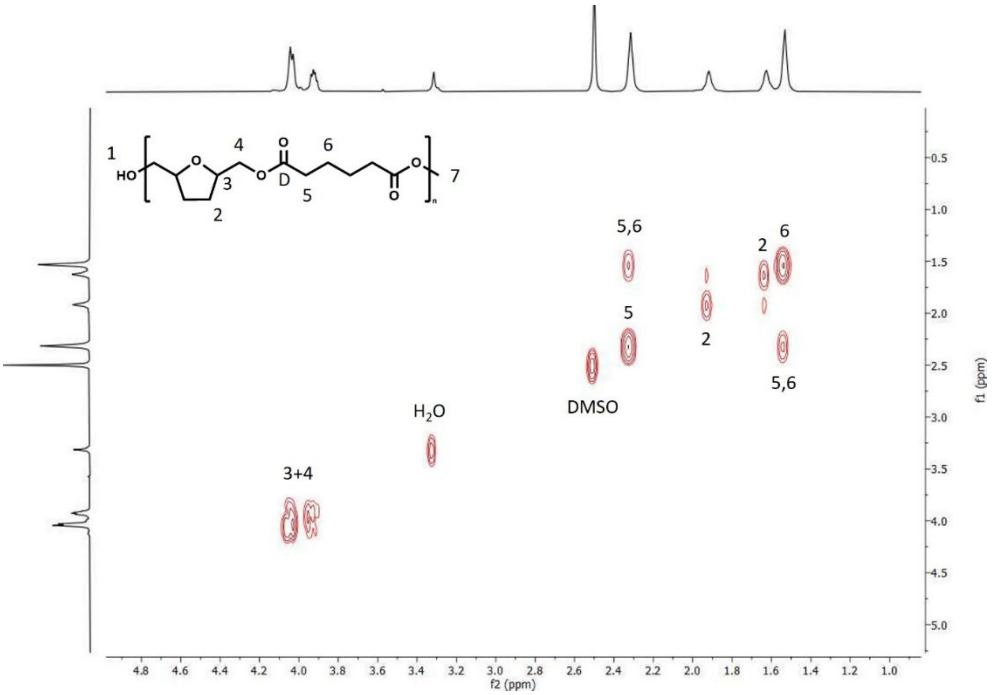

Figure S8: Correlated Spectroscopy (COSY) spectrum of poly(tetrahydrofurandimethylene adipate) (PTAd, PTAd-TF_00, PTAd-FAd_00) in DMSO-d_6.

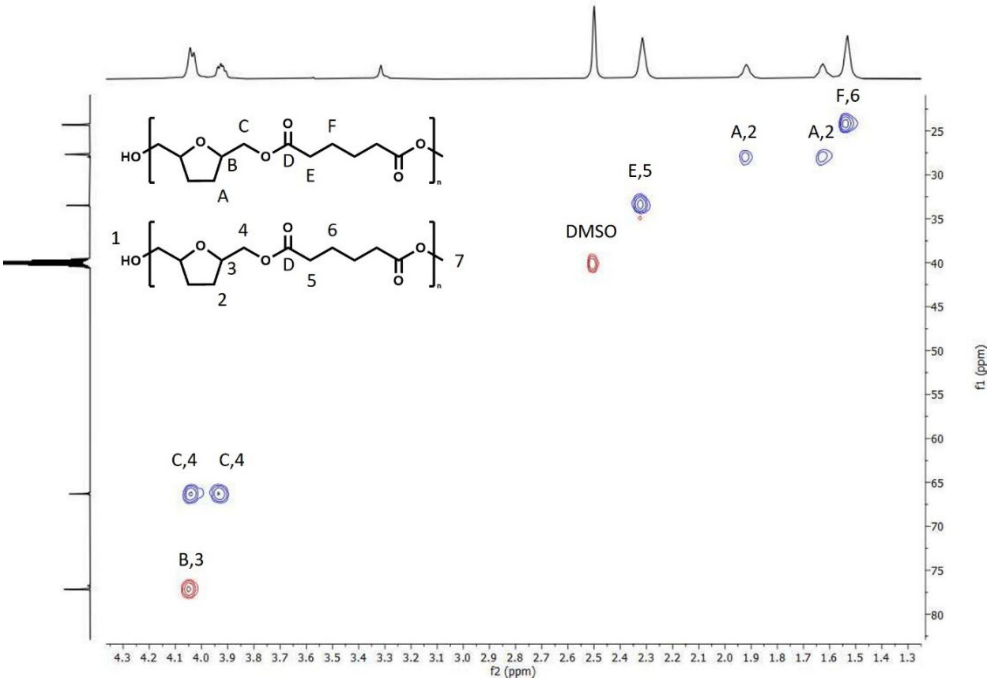

Figure S9: Heteronuclear Single Quantum Coherence (HSQC) spectrum of poly(tetrahydrofurandimethylene adipate) (PTAd, PTAd-TF_00, PTAd-FAd_00) in DMSO-d_6, a blue spot refers to a CH_2 group and a red spot to either a CH or CH_3 group.

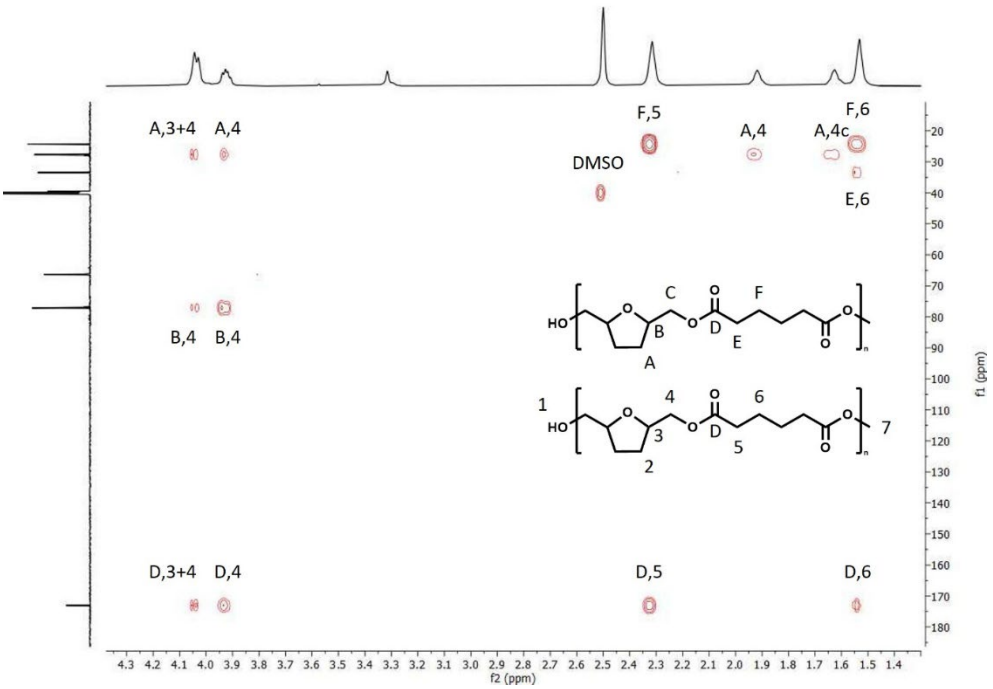

Figure S10: Heteronuclear Multiple Bond Correlation (HMBC) spectrum of poly(tetrahydrofurandimethylene adipate) (PTAd, PTAd-TF_00, PTAd-FAd_00) in DMSO-d_6.

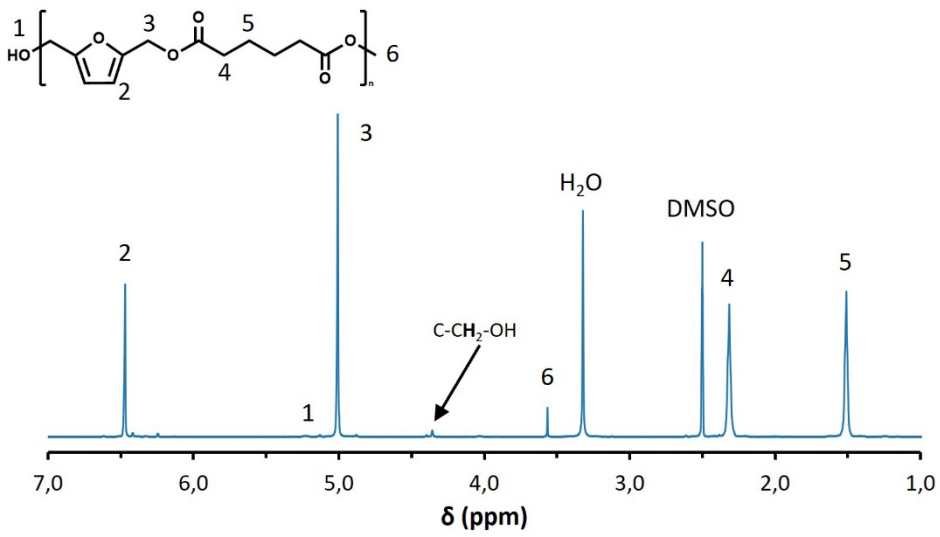

Figure S11: ^{1}H-NMR spectrum of the polyester poly(2,5-furandimethylene adipate) (PTAd-FAd_100) (PFAd) in DMSO-d_6.

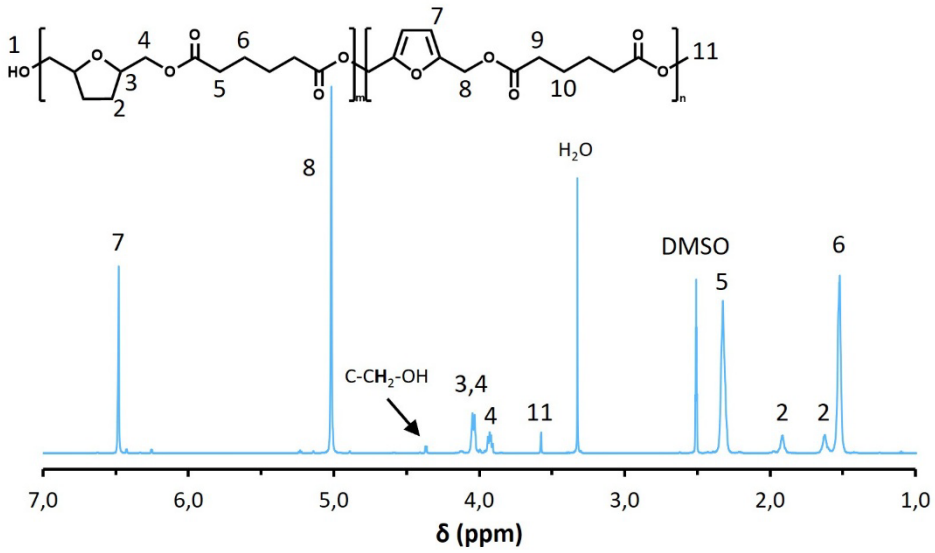

Figure S12: ^{1}H-NMR spectrum of the copolyester poly(tetrahydrofurandimethylene adipate-co-2,5-furandimethylene adipate) (PTAd-FAd_75) in DMSO-d_6.

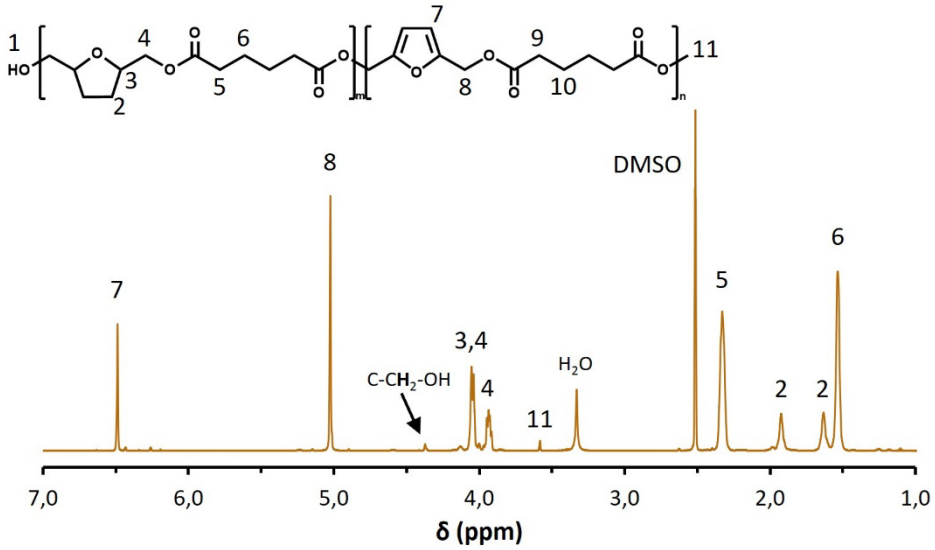

Figure S13: ^{1}H-NMR spectrum of the copolyester poly(tetrahydrofurandimethylene adipate-co-2,5-furandimethylene adipate) (PTAd-FAd_50) in DMSO-d_6.

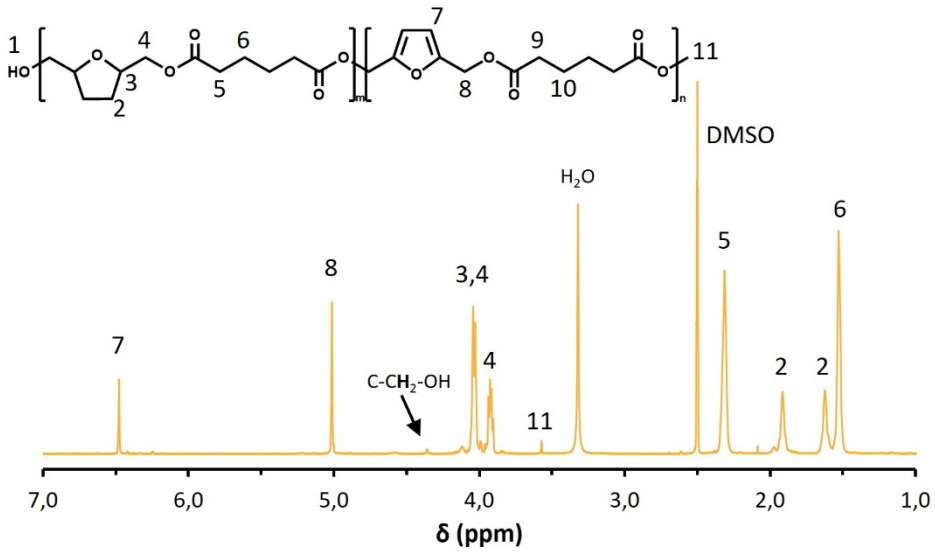

Figure S14: ^{1}H-NMR spectrum of the copolyester poly(tetrahydrofurandimethylene adipate-co-2,5-furandimethylene adipate) (PTAd-FAd_25) in DMSO-d_6.

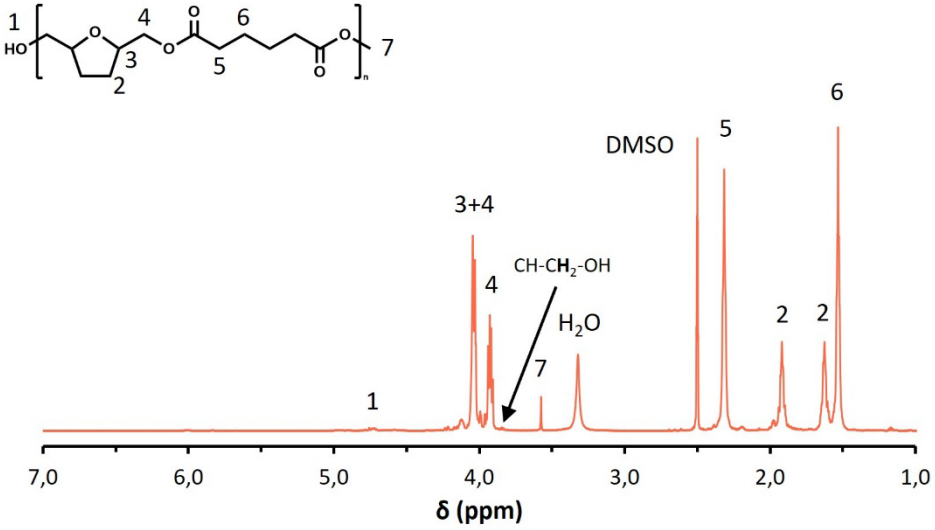

Figure S15: ^{1}H-NMR spectrum of the copolyester poly(tetrahydrofurandimethylene adipate) (PTAd-FAd_00) (PTAd) in DMSO-d_6.

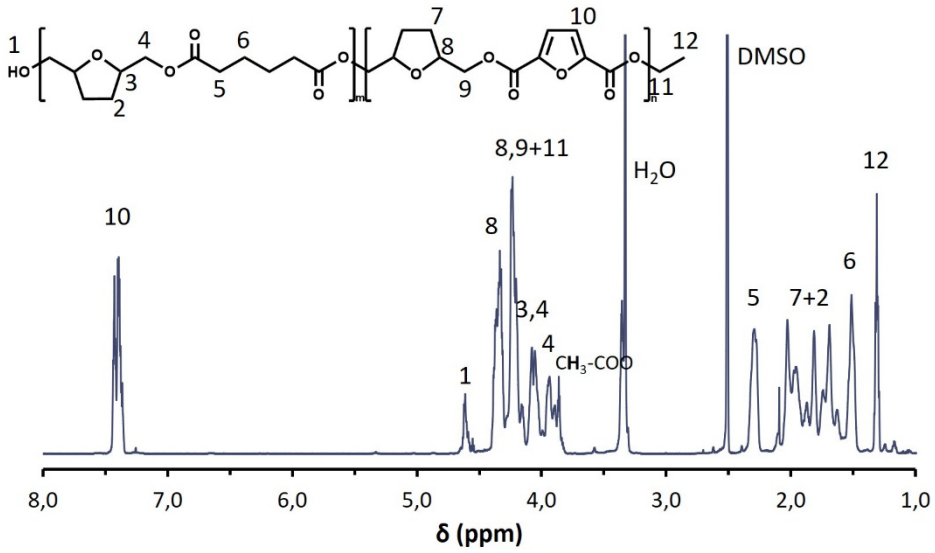

Figure S16: ^{1}H-NMR spectrum of the copolyester poly(tetrahydrofurandimethylene adipate-co-tetrahydrofurandimethylene 2,5-furandicarboxylate) (PTAd-TF_75) in DMSO-d_6.

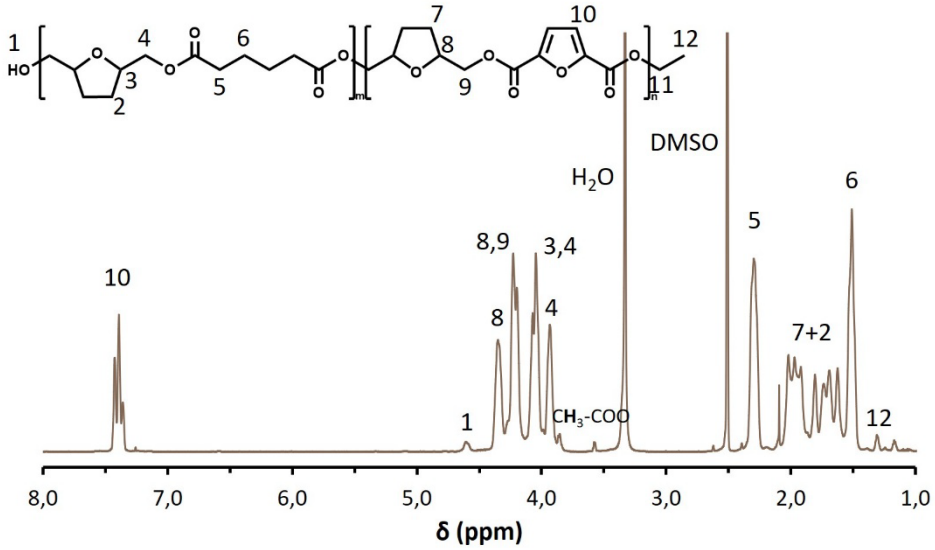

Figure S17: ^{1}H-NMR spectrum of the copolyester poly(tetrahydrofurandimethylene adipate-co-tetrahydrofurandimethylene 2,5-furandicarboxylate) (PTAd-TF_50) in DMSO-d_6.

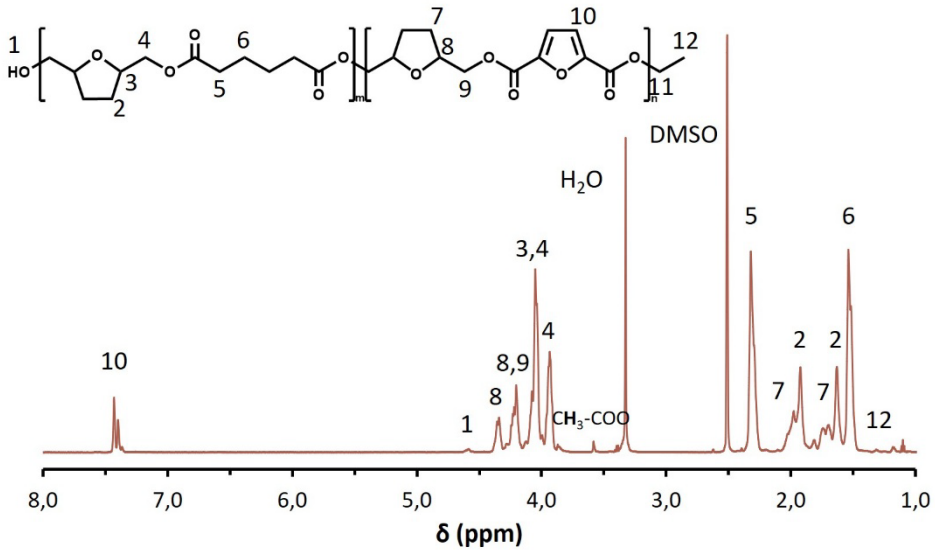

Figure S18: ^{1}H-NMR spectrum of the copolyester poly(tetrahydrofurandimethylene adipate-co-tetrahydrofurandimethylene 2,5-furandicarboxylate) (PTAd-TF_25) in DMSO-d_6.

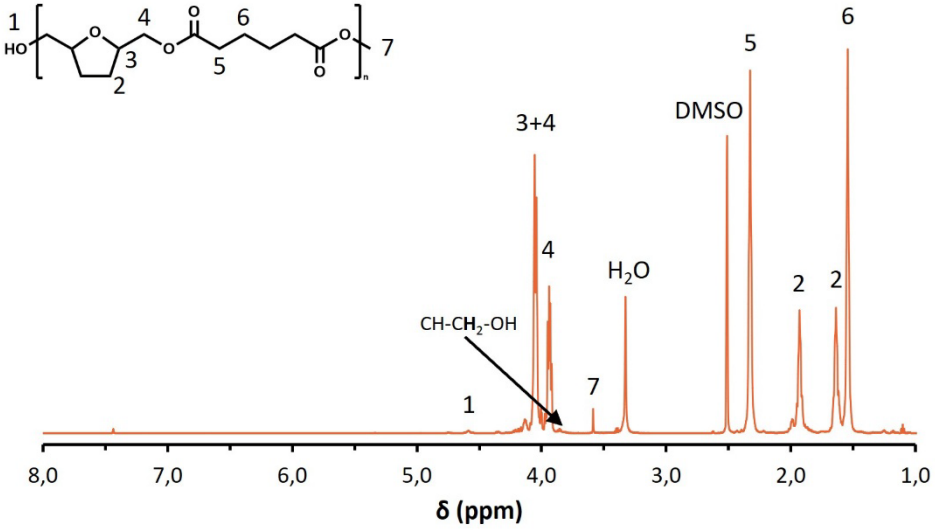

Figure S19: ^{1}H-NMR spectrum of the copolyester poly(tetrahydrofurandimethylene adipate-co-tetrahydrofurandimethylene 2,5-furandicarboxylate) (PTAd-TF_00) (PTAd) in DMSO-d_6.

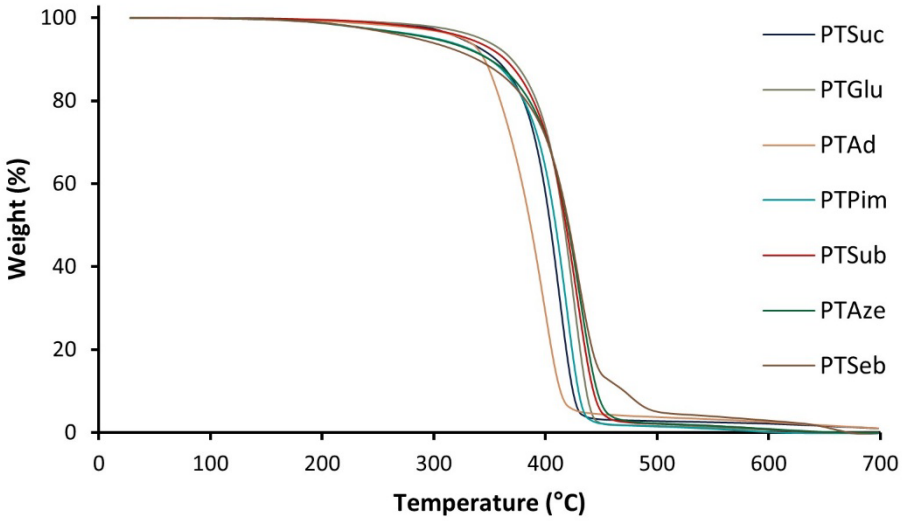

Figure S20: Thermogravimetric analysis curves of BHMTHF-based polyesters containing different numbers of methylene units in the comonomer segment.

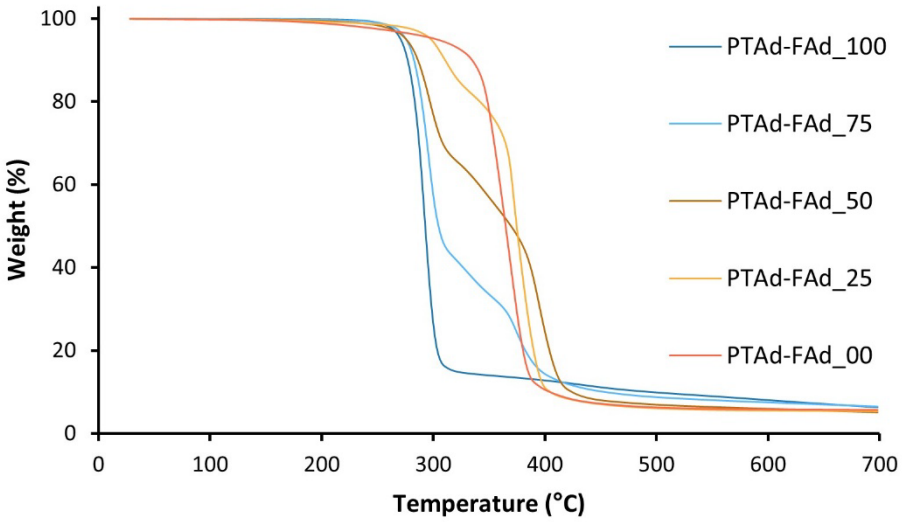

Figure S21: Thermogravimetric analysis curves of the copolyesters poly(tetrahydrofurandimethylene adipate-co-2,5-furandimethylene adipate) (PTAd-FAd_X) with varying BHMF content (X).

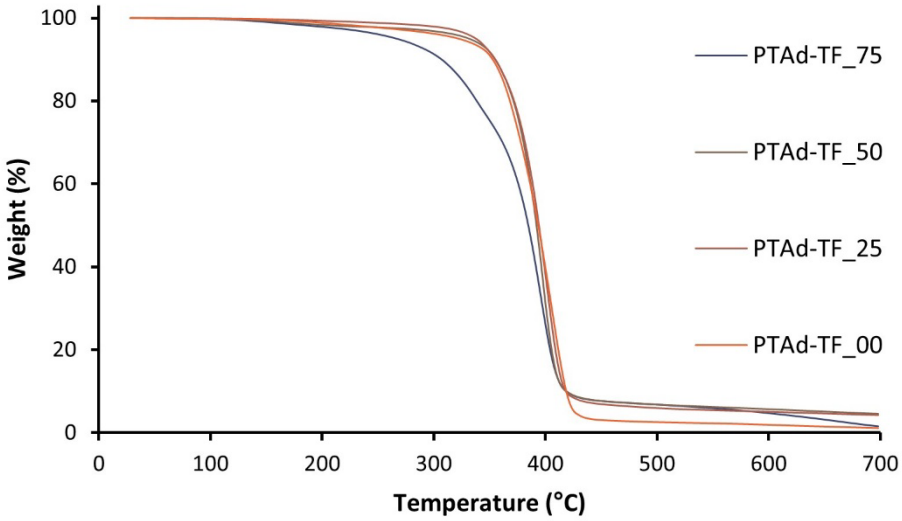

Figure S22: Thermogravimetric analysis curves of the copolyesters poly(tetrahydrofurandimethylene adipate-co-tetrahydrofurandimethylene 2,5-furandicarboxylate) (PTAd-TF_Y) with varying FDCA content (Y).

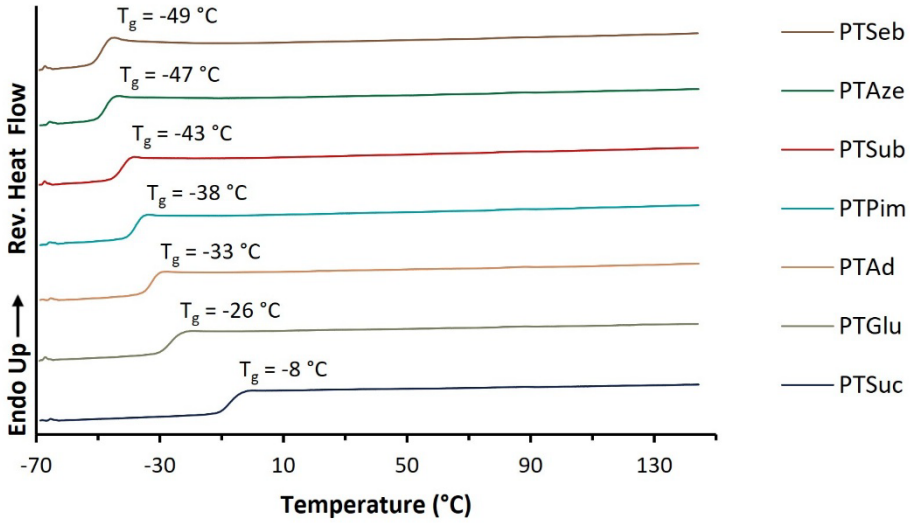

Figure S23: Modulated DSC curves of the second reversing heating ramp of BHMTHF-based polyesters containing different numbers of methylene units in the comonomer segment.

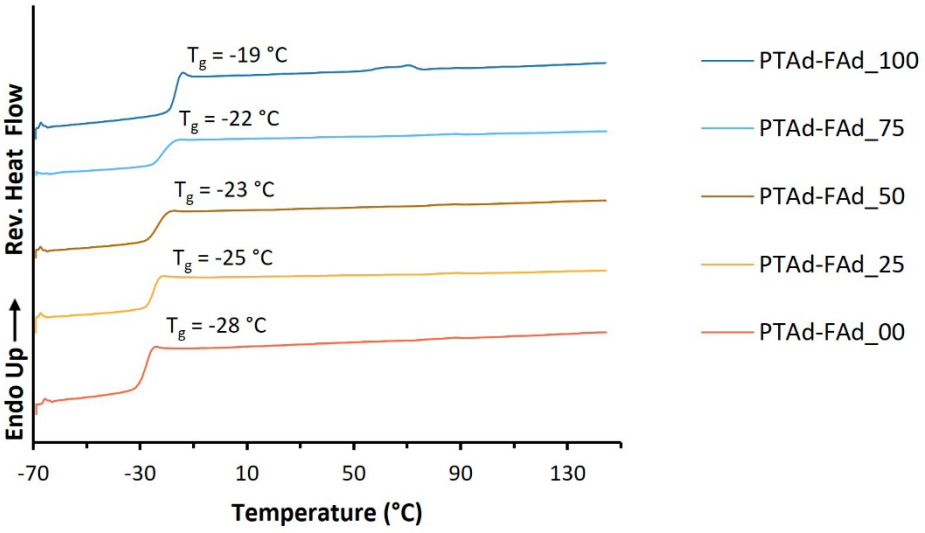

Figure S24: Modulated DSC curves of the second reversing heating ramp of the copolyesters (PTAd-FAd_X) with varying BHMF content (X).

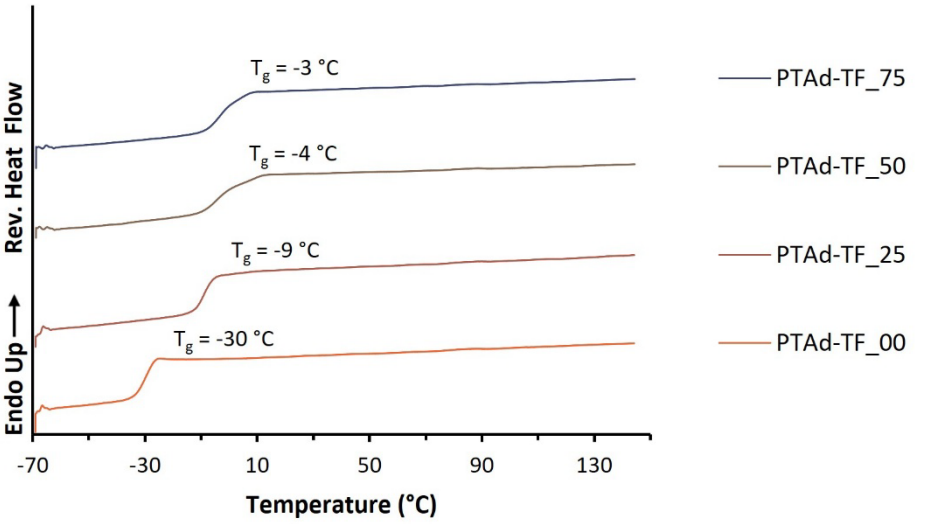

Figure S25: Modulated DSC curves of the second reversing heating ramp of the copolyesters (PTAd-TF_Y) with varying FDCA content (Y).

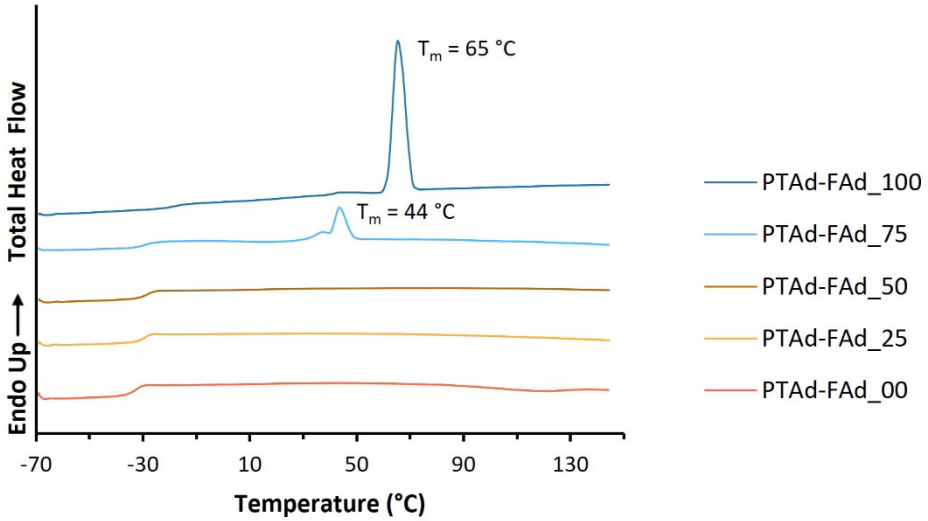

Figure S26: Modulated DSC curves of the first total heating ramp of the copolyesters (PTAd-FAd_X) with varying BHMF content (X).

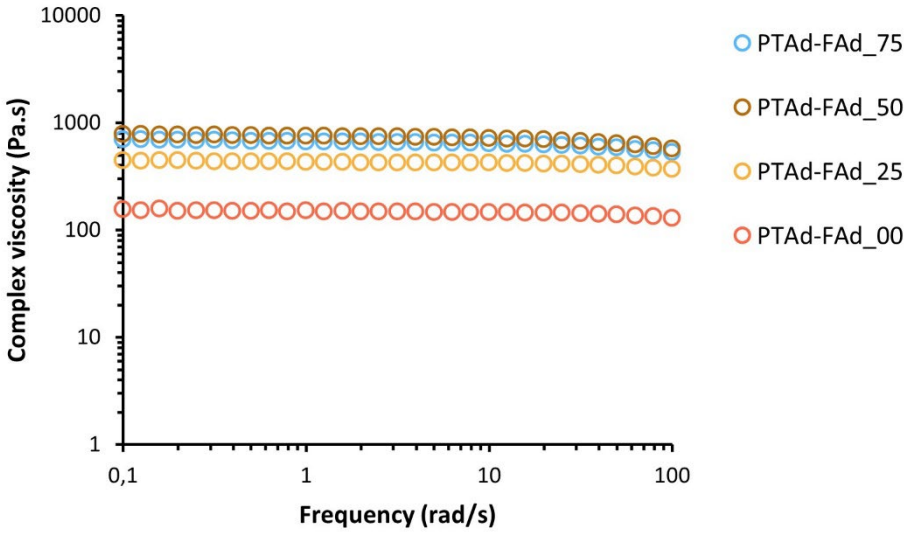

Figure S27: Complex viscosity versus angular frequency of the copolyesters (PTAd-FAd_X) with varying BHMF content (X), measured at a constant temperature of 40 °C.

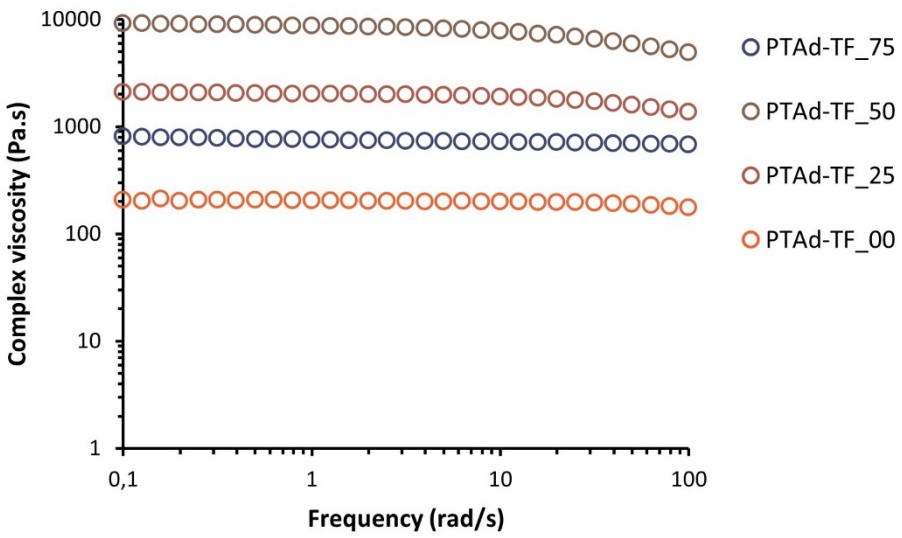

Figure S28: Complex viscosity versus angular frequency of the copolyesters (PTAd-TF_Y) with varying FDCA content (Y), measured at a constant temperature of 40 °C.