

Supporting Information

Synthesis of a novel polyester building block from pentoses by tin-containing silicates

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Polymerization of Ethyl 6-Hydroxyhexanoate (E6-HH)

Ethyl 6-hydroxyhexanoate (E6-HH) (2.0 g, 12 mmol) and CAL-B (NZ435, 0.20 g) was transferred to a Schlenk tube. The suspension was then immersed in an oil bath at 80 °C under stirring and *va cuum* (200 mbar) for 18 h and terminated by cooling in a dry ice bath. The product was dissolved in THF and enzyme particles were filtered off by suction filtration (particle retention 5-13 μm). The residue was washed with THF several times. The filtrate was evaporated *in vacuo*, re-dissolved in THF and precipitated in cold methanol. The precipitate was filtered and the residue were dried under *va cuum* at room temperature overnight yielding 0.40 g polyester as a white solid. The procedure was repeated for 50, 60 and 70 °C respectively (results in Table S6) showing a linear increase in molecular weight as seen in the figure below. The yield of the polymerization was 20% after precipitation.

SEC: $M_n = 5421 \text{ g mol}^{-1}$, $M_w = 6878 \text{ g mol}^{-1}$, PDI = 1.27. DSC: $T_m = 51.82^\circ\text{C}$. IR: $\tilde{\nu} / \text{cm}^{-1} = 3425, 2944, 2864, 1721, 1167, 1043$. $^1\text{H NMR}$ (300 MHz, CDCl_3) δ 4.09 (m, 0.02H), 4.03 (t, $J = 6.7 \text{ Hz}$, 1H), 3.61 (t, $J = 6.4 \text{ Hz}$, 0.09H), 2.27 (t, $J = 7.5 \text{ Hz}$, 1H), 1.61 (m, 2H), 1.35 (qv, $J = 8.3 \text{ Hz}$, 1H), 1.22 (t, $J = 7.1 \text{ Hz}$, 0.08H). $^{13}\text{C NMR}$ (75 MHz, CDCl_3) δ 173.5, 64.0, 62.5, 60.2, 34.0, 28.3, 25.4, 24.5, 14.2.

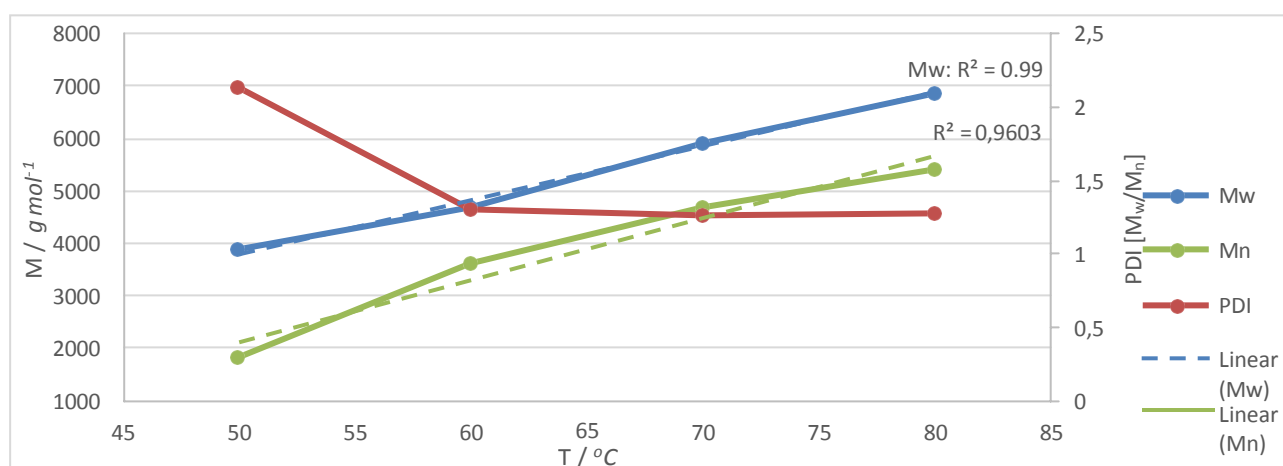


Figure S1. Polymerization Results. Influence of temperature on Mn, Mw and PDI for enzymatic polymerization of E6-HH.

Figures

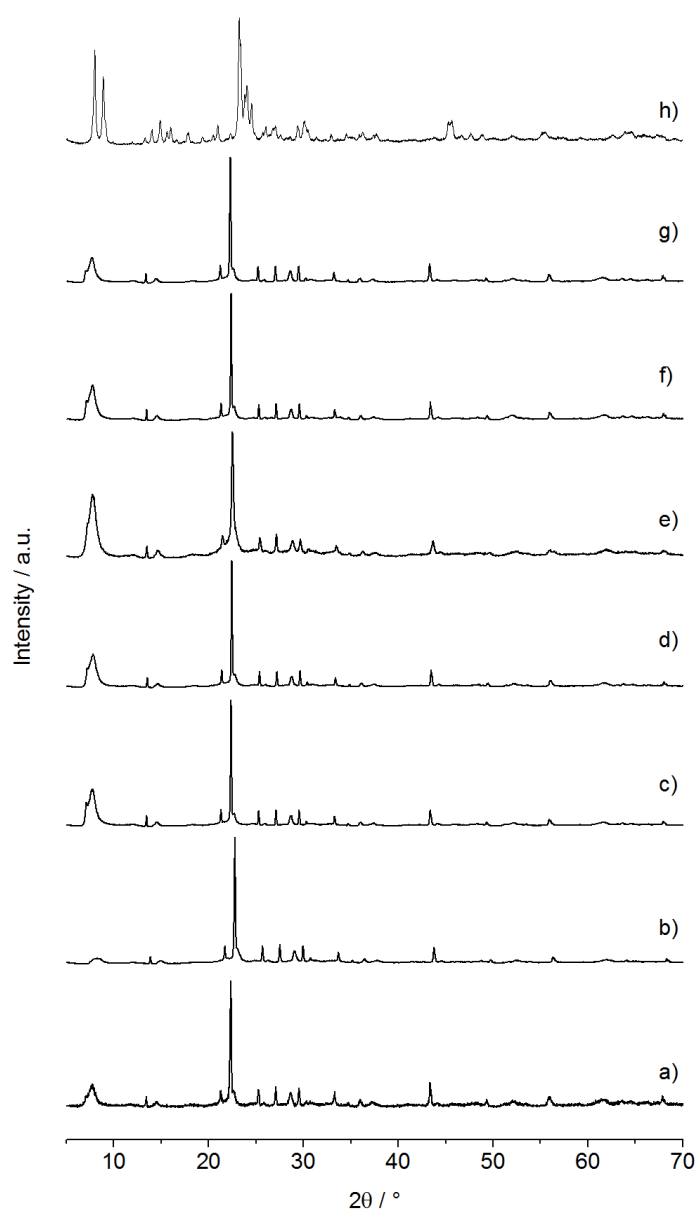


Figure S2. XRD Diff racto grams. XRD diffractograms of a) Sn-Beta (HT, Si/Sn = 150), b) Zr-Beta (HT, Si/Zr = 150), c) Ti-Beta (HT, Si/Ti = 150), d) Al-Beta (HT, Si/Al = 150), e) Sn-B eta (PT, Si/Sn = 125), f) SnO₂-Beta (HT, Si/Sn = 200), g) Si-Beta (HT), and h) Sn-MFI (OH⁻, Si/Sn = 100)

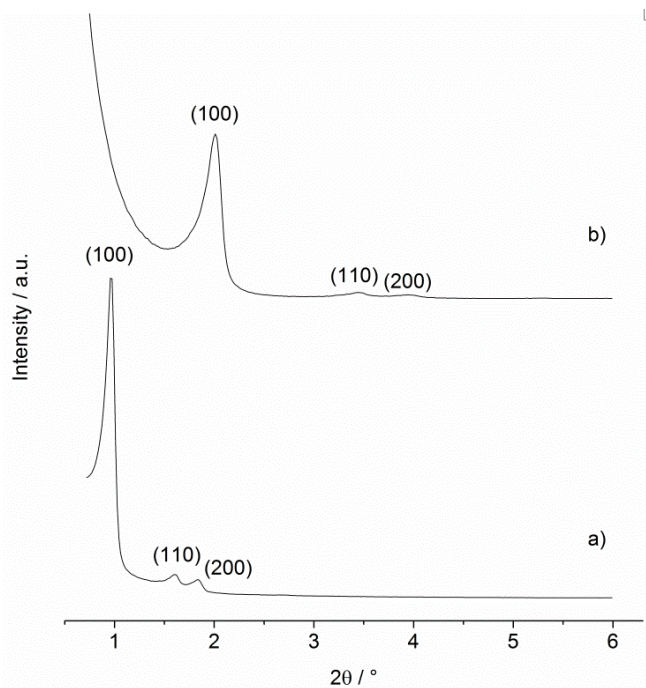


Figure S3. Low Angle XRD Diffractograms . Low angle XRD diffractograms of a) Sn-MCM-41 (Si/Sn = 200) and b) Sn-SBA-15 (Si/Sn = 200).

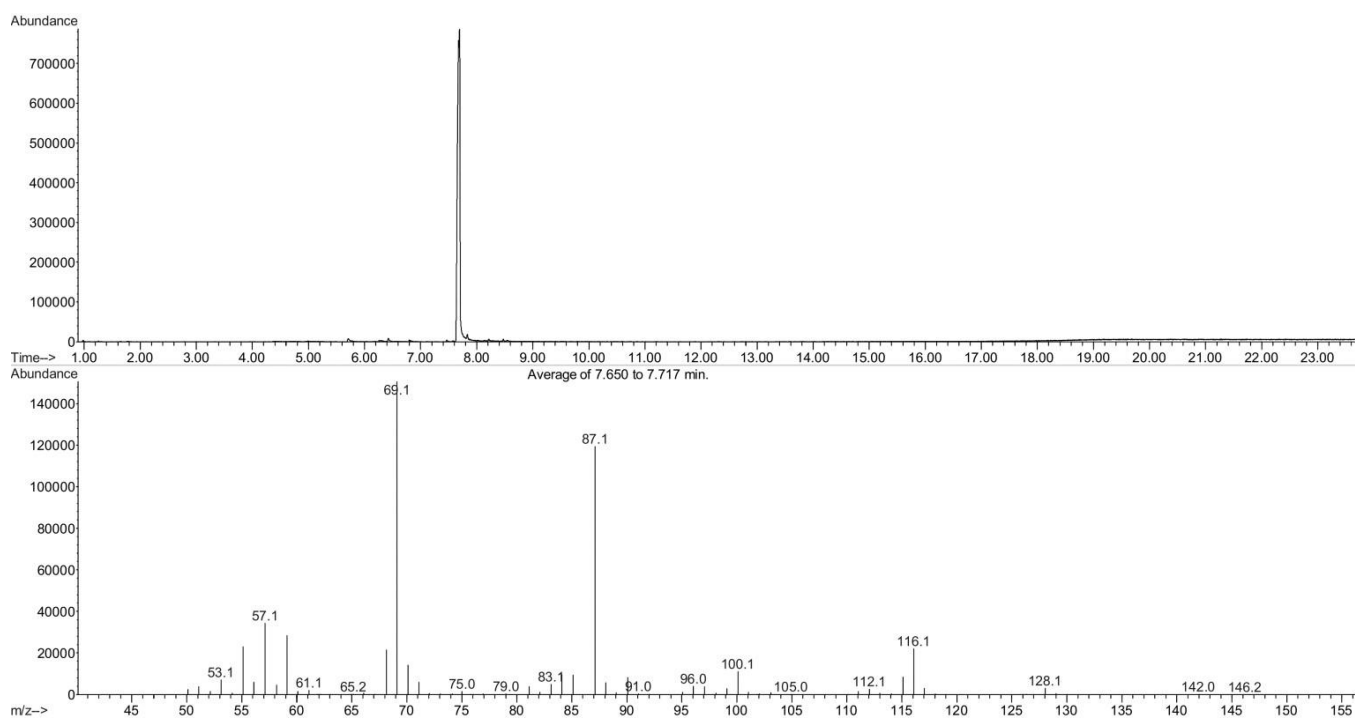


Figure S4. DPM GC-MS Spectrum m. GC-MS spectrum of purified trans-2,5-dihydroxy-3-pentenoic acid methyl ester (DPM), analysed on an Agilent 6890 with a Phenomenex Zebron ZB-5 column.

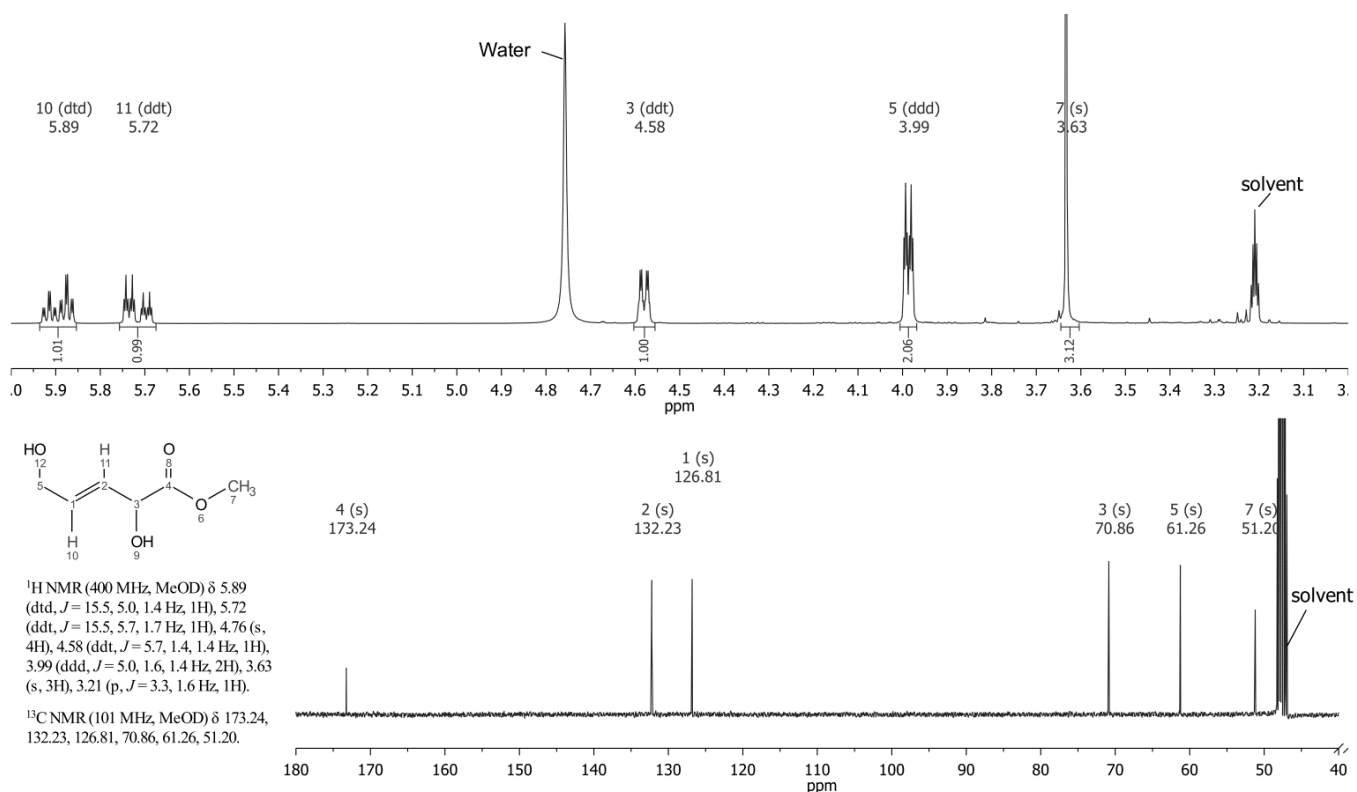


Figure S5. DPM NMR Spectra. Spectra and assignment of ^1H NMR (400 MHz) and ^{13}C NMR (100 MHz) signals in trans-2,5-dihydroxy-3-pentenoic acid methyl ester (DPM). NMR spectra were recorded on a Bruker Ascend 400 spectrometer, ^1H NMR was recorded at 400 MHz and ^{13}C NMR was recorded at 100 MHz. The chemical shifts are given in ppm relative to the residual solvent signals and the chemical shifts are reported downfield to TMS.

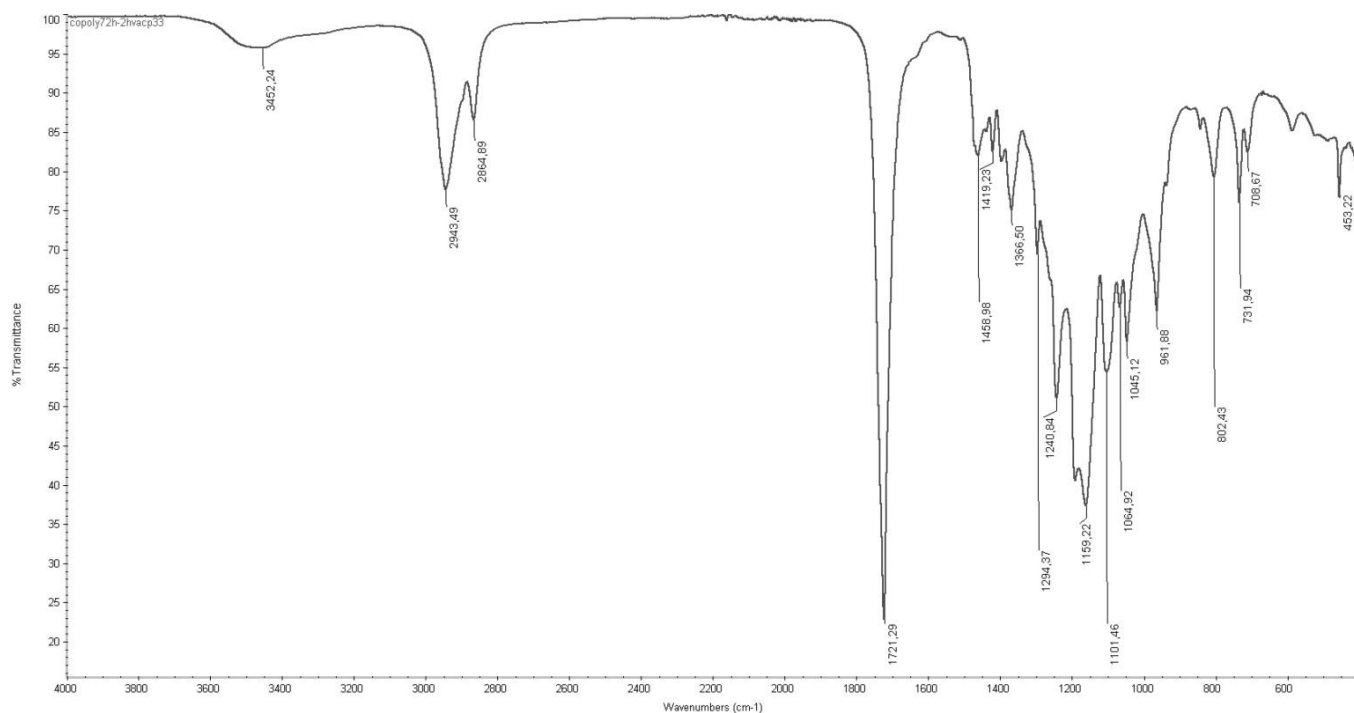


Figure S6. FT-IR of poly(E6-HH-co-DPM). FT-IR spectrum of poly(E6-HH-co-DPM) showing a broad signal at 3496 cm^{-1} arising from the O-H stretch as well as a characteristic C=O stretch at 1721 cm^{-1} and C-O stretch at 1159 cm^{-1} and 1045 cm^{-1} from the ester functionality. A weak signal from the C=C stretch is visible on the shoulder of the C=O stretch and a strong C=C out-of-plane bend signal is visible at 961 cm^{-1} .

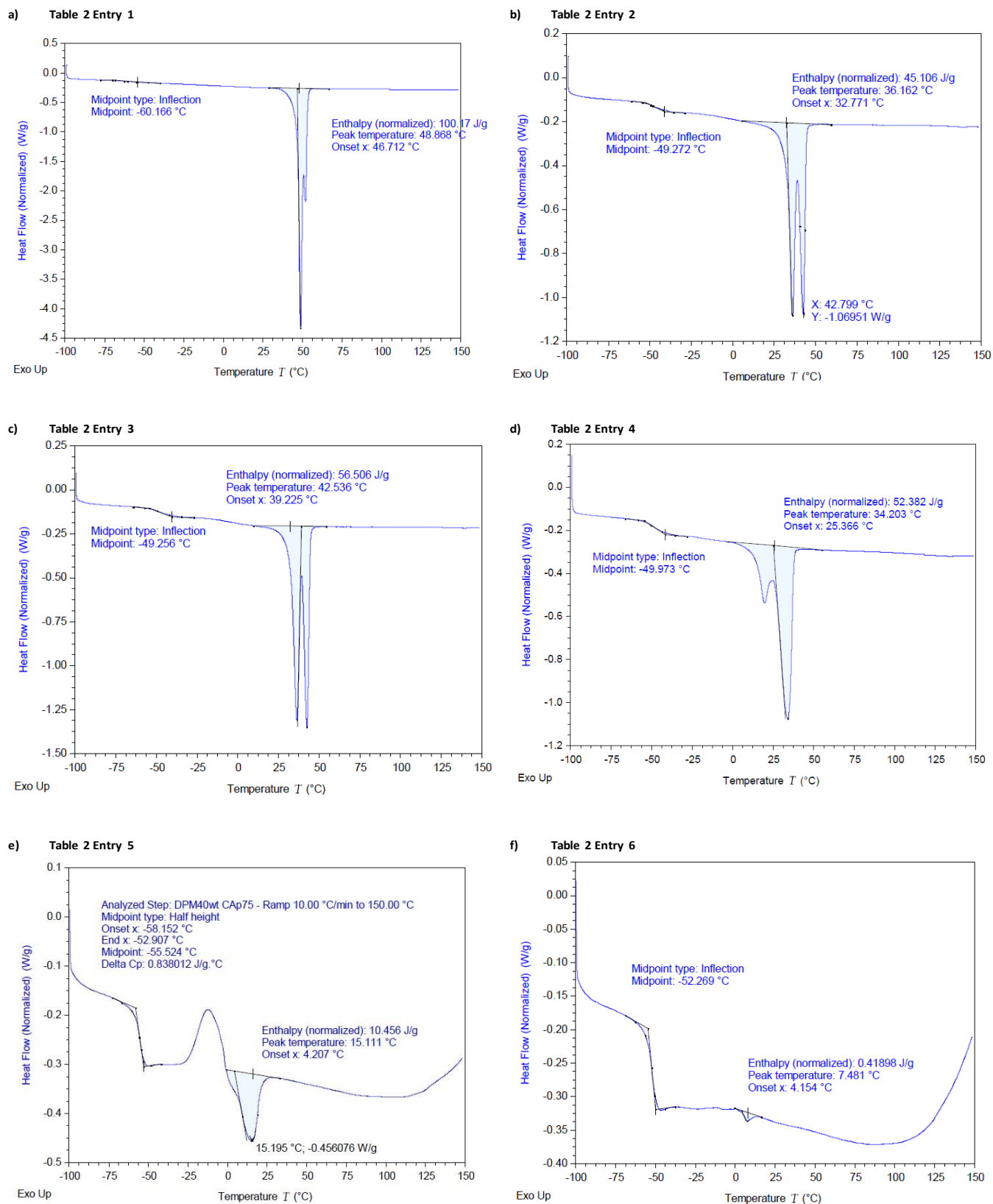


Figure S7. DSC of poly(E6-HH-co-DPM). DSC spectra of different poly(E6-HH-co-DPM) synthesis. a) table 2 entry 1, 18 hours reaction time, 100% E6 -HH. b) table 2 entry 2, 18 hours reaction time, 0.22 DPM/E6-HH. c) table 2 entry 3, 42 hours reaction time, 0.22 DPM/E6 -HH. d) table 2 entry 4, 72 hours reaction time, 0.22 DPM/E6-HH. e) table 2 entry 5, 72 hours reaction time, 0.44 DPM/E6-HH. f) table 2 entry 6, 72 hours reaction time, 0.66 DPM/E6 -HH.

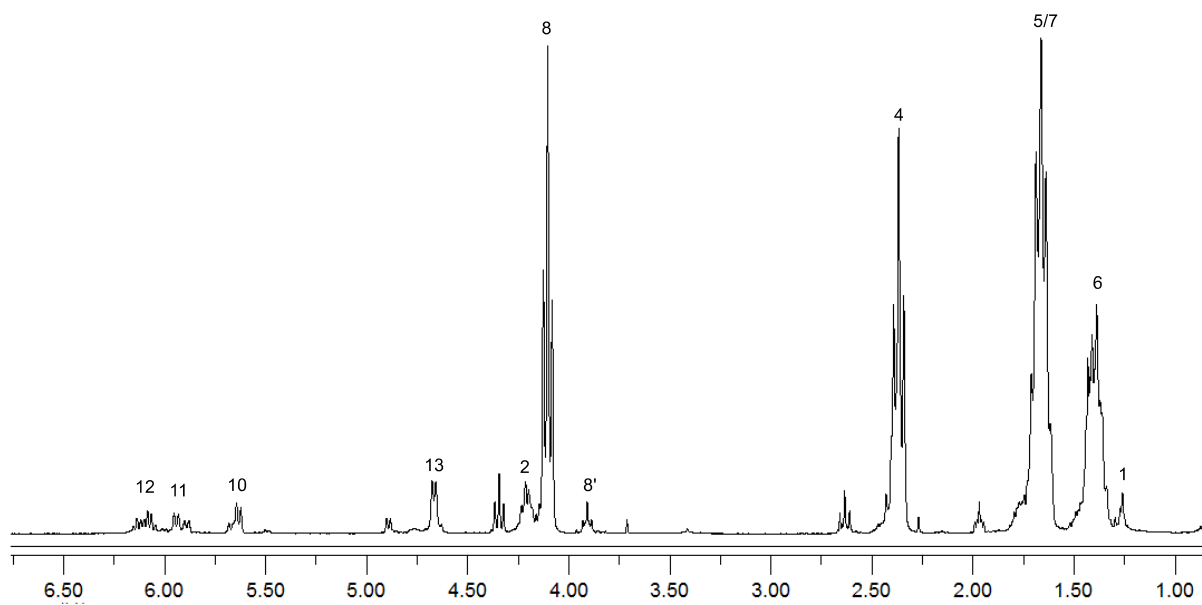
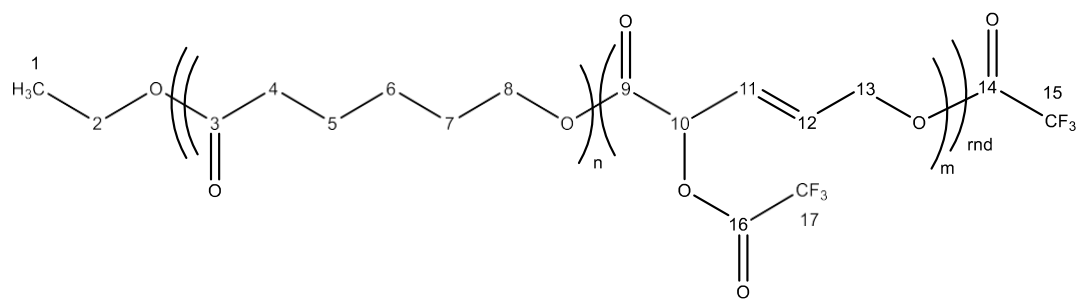


Figure S8. $^1\text{H-NMR}$ of Polymer II. ^1H NMR assignment of TFA modified poly(E6-HH-co-DPM).

Tables

Table S1. Physical properties of the various catalysts used in the study measured using N₂-adsorption/desorption and from XRD diffraction.

Entry	Catalyst	Elemental Analysis	X-ray diffraction	N ₂ -adsorption			
				S _{BET}	S _{micropore} ^[a]	V _{total}	V _{micropore} ^[a]
1	Sn-Beta (HT, 150)	186	*BEA	486	362	0.33	0.19
2	Sn-Beta (PT, 125)	113	*BEA	557	373	0.37	0.19
3	Sn-MFI (100)	82	MFI	404	273	0.25	0.14
4	Sn-MCM-41 (200)	252	-	962	-	1.00	-
5	Sn-SBA-15 (200)	271	-	918	111	1.09	0.06
6	SnO ₂ -Beta (200)	303	*BEA	457	365	0.27	0.19
7	Ti-Beta (HT, 150)	245	*BEA	460	372	0.27	0.19
8	Zr-Beta (HT, 150)	167	*BEA	470	374	0.27	0.19
9	Al-Beta (HT, 150)	142	*BEA	472	366	0.27	0.19
10	Si-Beta	-	*BEA	465	378	0.27	0.20

n.a. = not available

[a] Determined using the t-plot method.

Table S2. Conversion of xylose using a variety of catalysts.

Entry	Catalyst	XYL	MG	Retro-Aldol					Dehydration					
				%	GA-DMA	ML	MVG	MMHB	Total	DPL	TPM/DMPM ^[a]	FUR ^[b]	DPM	Total
1	Sn-Beta (HT)	n.d.	4 (1)	1.81 (7)	14 (1)	2.1 (6)	0.6 (3)	19	10.3 (5)	13 (1)	11 (1)	33 (3)	68	
2	Sn-Beta (PT)	n.d.	23 (1)	3.18 (2)	10.8 (3)	0.63 (4)	0.8 (8)	15	5.7 (9)	9 (1)	17.4 (6)	23 (1)	55	
3	Sn-MFI	0.9 (9)	30 (4)	6.0 (2)	16.9 (4)	1.29 (6)	0.36 (3)	24	3.0 (2)	3.0 (2)	10.1 (5)	11 (1)	27	
4	Sn-MCM-41	n.d.	23 (5)	4.0 (8)	12.5 (7)	0.40 (6)	0.8 (2)	18	6 (1)	14 (1)	20.5 (7)	16 (1)	57	
5	Sn-SBA-15	0.3 (2)	32 (6)	6.0 (1)	10.9 (3)	0.30 (2)	0.6 (3)	18	3.3 (1)	9.5 (3)	17.7 (8)	12 (1)	42	
6	SnO ₂ -Beta ^[c]	53 (5)	42 (5)	2.3 (2)	0.45 (4)	0.39 (4)	0.1 (1)	3	1.281 (3)	2.3 (6)	1.4 (2)	0.42 (2)	6	
7	Ti-Beta	0.46 (4)	48	7.4 (1)	11.2 (8)	2.81 (5)	0.34 (1)	22	3.8 (2)	6.7 (2)	4.8 (3)	0.83 (2)	16	
8	Zr-Beta	0.3 (2)	39	12.0 (2)	10.3 (1)	2.0 (1)	0.54 (2)	25	2.5 (3)	2.1 (1)	3.9 (3)	0.65 (7)	9	
9	Al-Beta	6 (1)	81.9 (5)	n.d.	n.d.	n.d.	n.d.	0	n.d.	n.d.	1.2 (2)	n.d.	1	
10	Si-Beta	13	42	5.1 (2)	2.01 (6)	0.37 (6)	0.321 (4)	8	1.61 (5)	3.1 (3)	3.4 (6)	0.2 (2)	8	
11	Blank	87.7 (6)	6.2 (3)	0.28 (7)	0.2 (3)	0.6 (1)	0.1 (1)	1	n.d.	n.d.	0.3 (2)	n.d.	1	

Reactions were performed in triplicate and employed the standard reaction conditions: 360 mg xylose (8.3 wt%), 4 g methanol, 180 mg catalyst, 2 h, 160 °C, 600 rpm stirring. Standard deviations of the last digit are given in parenthesis. Compound abbreviations: 2,5-dihydroxy-4-methoxy-pentanoic acid methyl ester (DMPM), 3-deoxypentanolactone (DPL), *trans*-2,5-dihydroxy-3-pentenoic acid methyl ester (DPM), furanics (FUR), glycolaldehyde dimethyl acetal (GA-DMA), methyl glycosides (MG), methyl lactate (ML), methyl 4-methoxy-2-hydroxybutanoate (MMHB), methyl vinyl glycolate (MVG), 2,4,5-trihydroxy-3-pentanoic acid methyl ester (TPM) and xylose (XYL). n.d. = not detected.

[a] Combined yields (carbon%) of 2,4,5-trihydroxy-3-pentanoic acid methyl ester and 2,5-dihydroxy-4-methoxy-pentanoic acid methyl ester.

[b] Combined yields (carbon%) of furfural and furfural dimethyl acetal.

[c] Dispersed SnO₂ nanoparticles on Si-Beta.

Table S3. Reaction yields from the conversion of pentoses with varying substrates and concentrations.

Entry	Substrate	Substrate	PENT	MG	Retro-Aldol					Dehydration					
					%	GA-DMA	ML	MVG	MMHB	Total	DPL	TPM/DMPM ^[a]	FUR ^[b]	DPM	Total
1	Ribose	8.3	n.d.	3 (2)	2.0 (1)	12 (2)	2.0 (7)	0.5 (2)	17	10.37 (3)	10.1 (3)	12 (2)	30 (2)	63	
2	Lyxose	8.3	n.d.	2.6 (6)	2.1 (1)	15 (3)	2 (1)	0.5 (3)	20	11.6 (2)	12.6 (1)	11 (3)	31 (2)	66	
3	Xylose	8.3	n.d.	4 (1)	1.81 (7)	14 (1)	2.1 (6)	0.6 (3)	19	10.3 (5)	13 (1)	11 (1)	33 (3)	68	
4	Xylose	15	0.06 (9)	6 (1)	0.3 (1)	14 (1)	1.9 (4)	0.3 (1)	17	11.37 (4)	13 (1)	8.7 (9)	34 (4)	68	
5	Xylose	23	n.d.	6 (1)	2 (2)	13 (1)	1.7 (4)	0.3 (2)	17	11.1 (5)	13 (2)	11 (2)	32 (2)	67	

Reactions were performed in triplicate and employed the reaction conditions: 180 -1200 mg pentose (4.3-23 wt%), 4 g methanol, 180 mg Sn-Beta (HT, 150), 2 h, 160 °C, 600 rpm stirring. Standard deviations of the last digit are given in parenthesis. Compound abbreviations: 2,5-dihydroxy-4-methoxy-pentanoic acid methyl ester (DMPM), 3-deoxypentanolactone (DPL), *trans*-2,5-dihydroxy-3-pentenoic acid methyl ester (DPM), furanics (FUR), glycolaldehyde dimethyl acetal (GA-DMA), methyl glycosides (MG), methyl lactate (ML), methyl 4-methoxy-2-hydroxybutanoate (MMHB), methyl vinyl glycolate (MVG), reactant pentose (PENT) and 2,4,5-trihydroxy-3-pentanoic acid methyl ester (TPM). n.d. = not detected.

[a] Combined yields (carbon%) of 2,4,5-trihydroxy-3-pentanoic acid methyl ester and 2,5-dihydroxy-4-methoxy-pentanoic acid methyl ester.

[b] Combined yields (carbon%) of furfural and furfural dimethyl acetal.

Table S4. Reaction yields from the conversion of xylose, varying catalyst to substrate ratio and temperature.

Entry	Catalyst/ Substrate	Temp. °C	XYL %	MG	Retro-Aldol					Dehydration				
					GA-DMA	ML	MVG %	MMHB	Total	DPL	TPM/DMPM ^[a]	FUR ^[b] %	DPM	Total
1	0.00 ^[c]	160	87.7 (6)	6.2 (3)	0.28 (7)	0.2 (3)	0.6 (1)	0.1 (1)	1	n.d.	n.d.	0.3 (2)	n.d.	1
2	0.125	160	n.d.	3.8 (3)	3 (2)	23 (1)	4.3 (2)	1.0 (6)	32	9.0 (5)	11.19 (6)	14.3 (4)	19 (3)	53
3	0.25	160	n.d.	3.7 (1)	2.5 (9)	21 (2)	3 (1)	0.8 (5)	28	8.8 (5)	13 (1)	11 (1)	28 (3)	60
4	0.50	160	n.d.	4 (1)	1.81 (7)	14 (1)	2.1 (6)	0.6 (3)	19	10.3 (5)	13 (1)	11 (1)	33 (3)	68
5	0.75	160	n.d.	3.02 (7)	1.00 (7)	13.2 (9)	1.9 (2)	0.5 (1)	17	10.1 (2)	11.8 (2)	9.9 (4)	34 (3)	67
6	1.00	160	n.d.	3.5 (4)	0.61 (7)	11 (2)	1.2 (5)	1.5 (7)	15	12.4 (6)	12.7 (5)	10 (2)	34 (3)	70
7	0.5	140	n.d.	4.4 (4)	2.5 (1)	11 (3)	1.0 (7)	0.5 (1)	16	9.7 (1)	13.6 (9)	17 (2)	31 (3)	72
8	0.5	150	n.d.	3.3 (6)	2.1 (4)	15 (4)	2 (1)	0.5 (3)	19	10 (1)	12 (2)	13.4 (7)	32 (3)	68
9	0.5	170	n.d.	3.0 (3)	1.31 (4)	18 (4)	4 (1)	1.3 (5)	25	10 (1)	9.7 (3)	9 (1)	34 (3)	63
10	0.5	180	n.d.	3.4 (7)	0.8 (4)	18 (3)	3.9 (9)	1.2 (3)	24	10 (1)	9 (0)	7.7 (4)	32 (3)	59

Reactions were performed in triplicate and employed the reaction conditions: 360 mg xylose (8.3 wt%), 4 g methanol, 0-360 mg Sn-Beta (HT, 150), 2 h, 600 rpm stirring. Standard deviations of the last digit are given in parenthesis. Compound abbreviations: 2,5-dihydroxy-4-methoxy-pentanoic acid methyl ester (DMPM), 3-deoxypentanolactone (DPL), *trans*-2,5-dihydroxy-3-pentenoic acid methyl ester (DPM), furanics (FUR), glycolaldehyde dimethyl acetal (GA-DMA), methyl glycosides (MG), methyl lactate (ML), methyl 4-methoxy-2-hydroxybutanoate (MMHB), methyl vinyl glycolate (MVG), 2,4,5-trihydroxy-3-pentanoic acid methyl ester (TPM) and xylose (XYL). n.d. = not detected.

[a] Combined yields (carbon%) of 2,4,5-trihydroxy-3-pentanoic acid methyl ester and 2,5-dihydroxy-4-methoxy-pentanoic acid methyl ester.

[b] Combined yields (carbon%) of furfural and furfural dimethyl acetal.

[c] Blank sample; contains no catalyst.

Table S5. Reaction yields from the conversion of xylose using Sn-Beta with addition of K₂CO₃.

Entry	K ₂ CO ₃ mM	XYL %	MG	Retro-Aldol					Dehydration		
				GA-DMA	ML	MVG %	MMHB	Total	FUR ^[a]	DPM	Total
1	0.00	n.d.	6	2	14	2	<1	19	11	33	54
2	0.05	n.d.	1	2	27	7	2	38	9	21	30
3	0.10	n.d.	1	2	34	13	2	51	4	14	28
4	0.15	n.d.	1	2	34	14	2	52	6	11	17
5	0.25	n.d.	2	2	35	14	3	54	4	8	12
6	0.50	n.d.	5	1	29	13	2	45	2	4	6
7	0.75	n.d.	6	1	23	12	2	38	2	2	4
8	1.00	n.d.	5	1	16	9	2	28	1	2	3

All reactions employed the reaction conditions: 360 mg xylose (8.3 wt%), 4 g methanol, 180 mg Sn-Beta (HT, 150), 2 h, 160 °C, 600 rpm stirring. Compound abbreviations: *trans*-2,5-dihydroxy-3-pentenoic acid methyl ester (DPM), furanics (FUR), glycolaldehyde dimethyl acetal (GA-DMA), methyl glycosides (MG), methyl lactate (ML), methyl 4-methoxy-2-hydroxybutanoate (MMHB), methyl vinyl glycolate (MVG) and xylose (XYL). n.d. = not detected, n.a. = not available.

[a] Combined yields (carbon%) of furfural and furfural dimethyl acetal.

Table S6. Enzymatic polymerization of E6-HH

Polymer ^[a]	Temperature °C	M _n ^[b] g mol ⁻¹	M _w ^[b] g mol ⁻¹	PDI ^[b]
I-1	50	1816	3874	2.1
I-2	60	3616	4701	1.3
I-3	70	4688	5905	1.3
I-4	80	5421	6878	1.3

[a] All reactions were conducted at 200 mbar for 18 h.

[b] Determined by SEC in THF.