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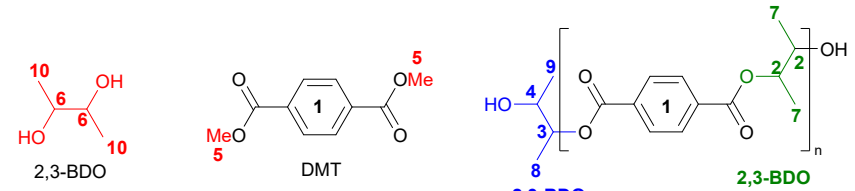
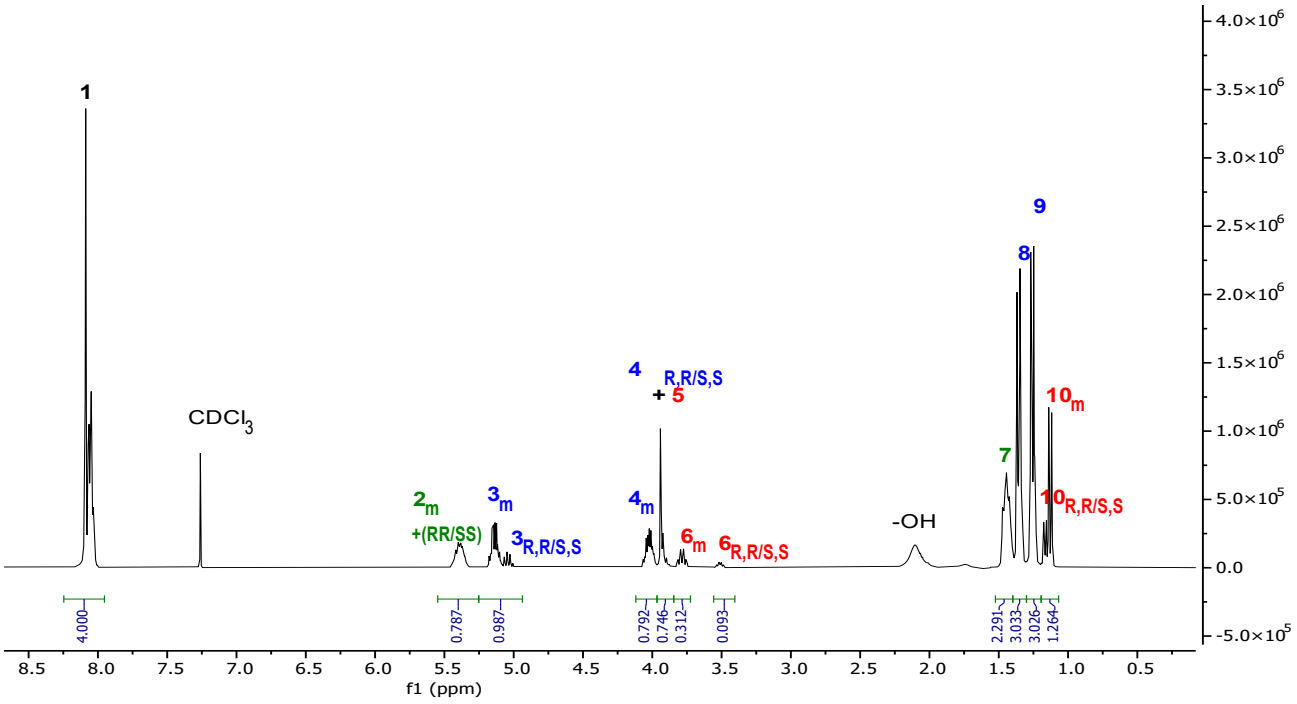
NMR spectra and calculations

I. Interpretation of NMR for transesterification of DMT with 2,3-BDO to P23BT (example)

For the polymerization experiments (P23BT synthesis), the progress of the transesterification reaction was monitored over time, and the final polyester was confirmed by ^{1}H-NMR analysis. Below, we provide an example of a representative spectrum recorded during the transesterification step, along with its interpretation. This interpretation is universally applicable to all P23BT syntheses and, together with the detailed calculation procedure described thereafter, forms the basis for the data presented in the main text (Figures 4 and 5).



Three stereoisomers exist
m: meso-2,3-BDO
R,R: R,R-2,3-BDO
S,S: S,S-2,3-BDO
R,R/S,S, because: S,S is the mirror image of R,R; they have the same NMR shifts and cannot be distinguished.



Before calculation, normalize integral at ~8.1 ppm to 4.000

Calculation:

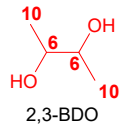
1. % 2,3-BDO ester = ("OL C**H**: signal **2**" + "End1Meso+R,R/S,S C**H**: signal $\mathbf{3_m}$+ $\mathbf{3_{R,R/S,S}}$")/2*100%
2. "Total 2,3-BDO free and bound"= ("OL C**H**: signal **2**" + "End1Meso+R,R/S,S C**H**: signal $\mathbf{3_m}$+ $\mathbf{3_{R,R/S,S}}$"**x2** + "Free1=$\mathbf{6_m}$" + "Free2: $\mathbf{6_{R,R/S,S}}$")**/2**
3. Methyl ester signal (CH3 & two per DMT) = "Integral **5** + **4** (due to overlap)" – "**3**"

Explanation:

- Normalized on protons of terephthalate “T” (4H), so 4 = 1 equivalent of terephthalate.
- Both “OL C**H**: signal **2**” + “End1meso+R,R/S,S C**H**: signal **3_m**+ **$3_{R,R/S,S}$**” belong to -C**H-** (1H) next to a 2,3-BDO ester group
- Divided by 2, since each terephthalate has two ester groups
- Both **4** and **3** should have same integral, belonging to the two different CH groups of an 2,3-BDO endgroup

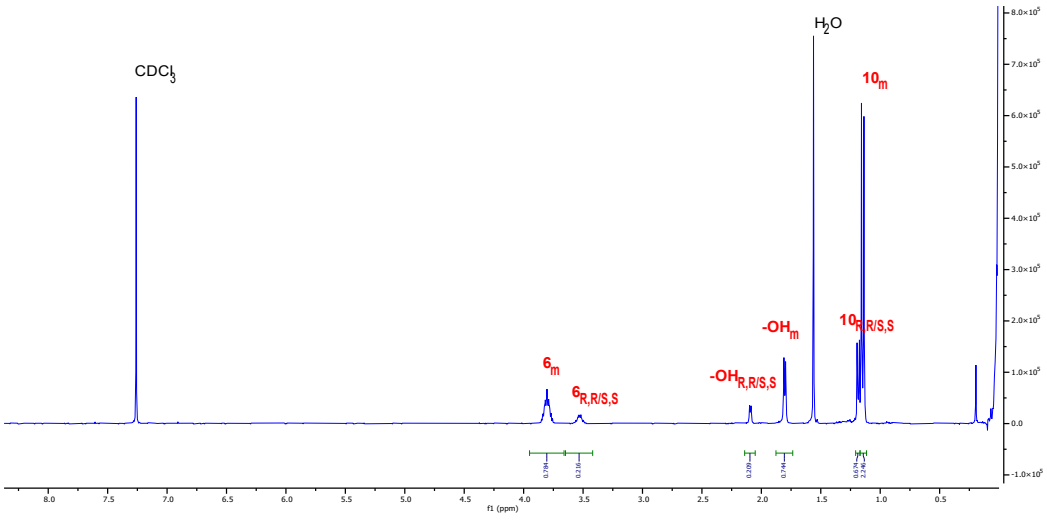
II. 2,3-BDO 78% used for La & Zn polymerization experiments

In the experimental section, we report using “2,3-BDO (98%, Sigma-Aldrich, meso:R,R ratio of 78:22 based on ^{1}H-NMR spectrum)” for the synthesis of P23BT with either La or Zn as catalyst. Below, we provide the ^{1}H-NMR spectrum and the corresponding interpretation used to determine the meso:R,R ratio of 78:22.



2,3-BDO

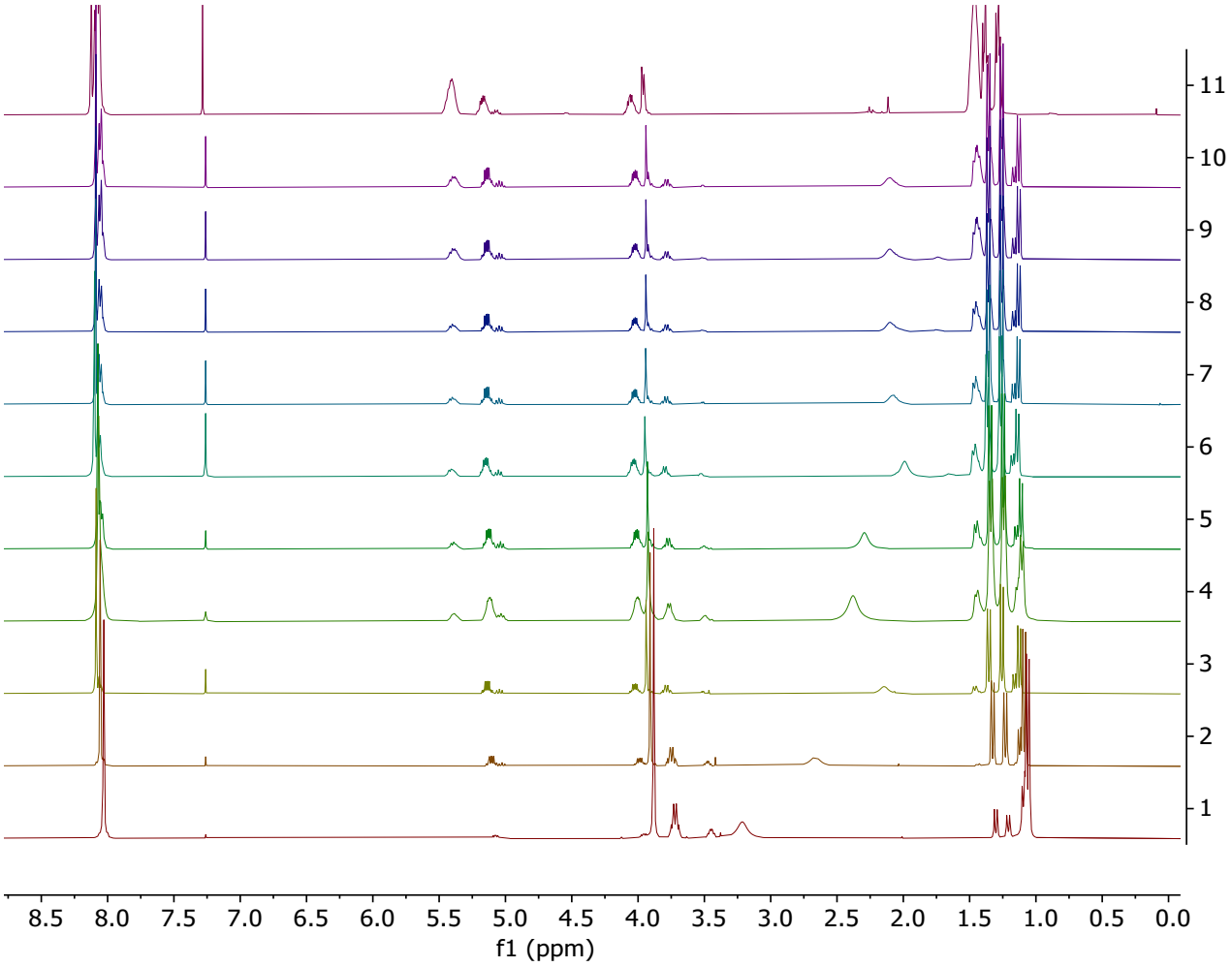
Three stereoisomers exist
m: meso-2,3-BDO
R,R: R,R-2,3-BDO
S,S: S,S-2,3-BDO
R,R/S,S, because: S,S is the mirror image of R,R; they have the same NMR shifts and cannot be distinguished.



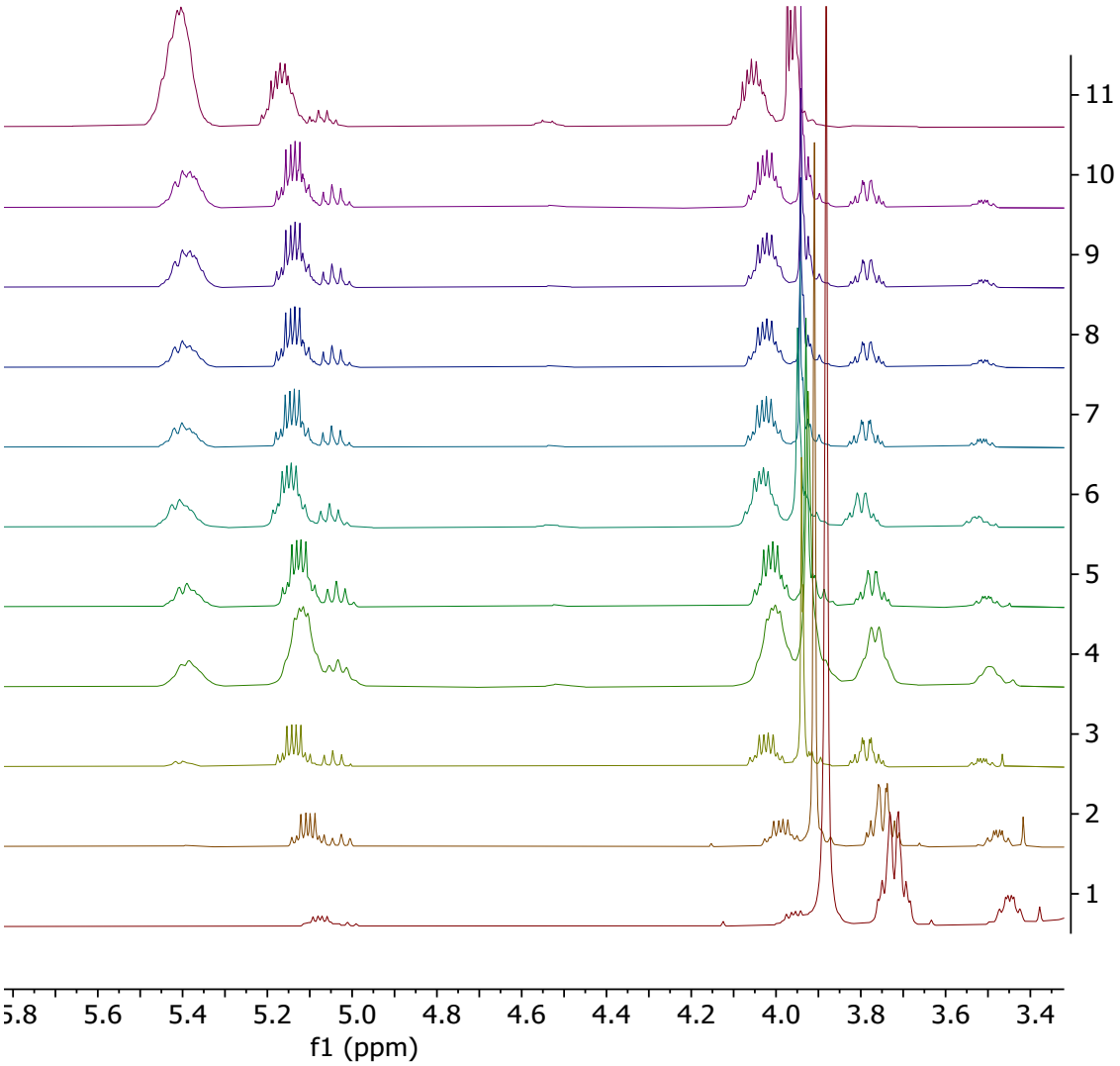
III. DMT, 2,3-BDO & La(acac)$_3$ catalyst for P23BT synthesis: 1H NMR over time

In the first section of the supplementary information we discussed the interpretation of an exemplary spectrum for the synthesis of P23BT. In addition, the relevant calculations are also shared in this first section. Now in this section, we firstly share all the complete spectra used to generate the red diamond datapoints in figure 4 in the main text, "Transesterification over time for DMT and commercial 2,3-BDO catalysed by 0.3 mol% La(acac)3". However, since most relevant changes are clearly visible ~5.8-3.4 ppm, a zoomed in version of the spectra below is showed immediately hereafter. The spectra are named #1-#11 (and in the later discussed table fig #1-11) and represent a time point, thus #1 is taken at 0.5h and #2 at 1.5 h etc. Of course the spectra are integrated and this data is summarized in a table directly after the zoomed in spectrum (area5.8-3.4ppm). These integrations are used to calculate (using calculations and abbreviations as discussed in the first section) for the transesterification over time.

DMT, commercial mix of 2,3-BDO & La(acac)$_3$ catalyst for P23BT synthesis: Proton NMR over time: Full spectra



DMT, commercial mix of 2,3-BDO & $La(acac)_3$ catalyst for P23BT synthesis: Proton NMR over time: area 5.8-3.4 ppm

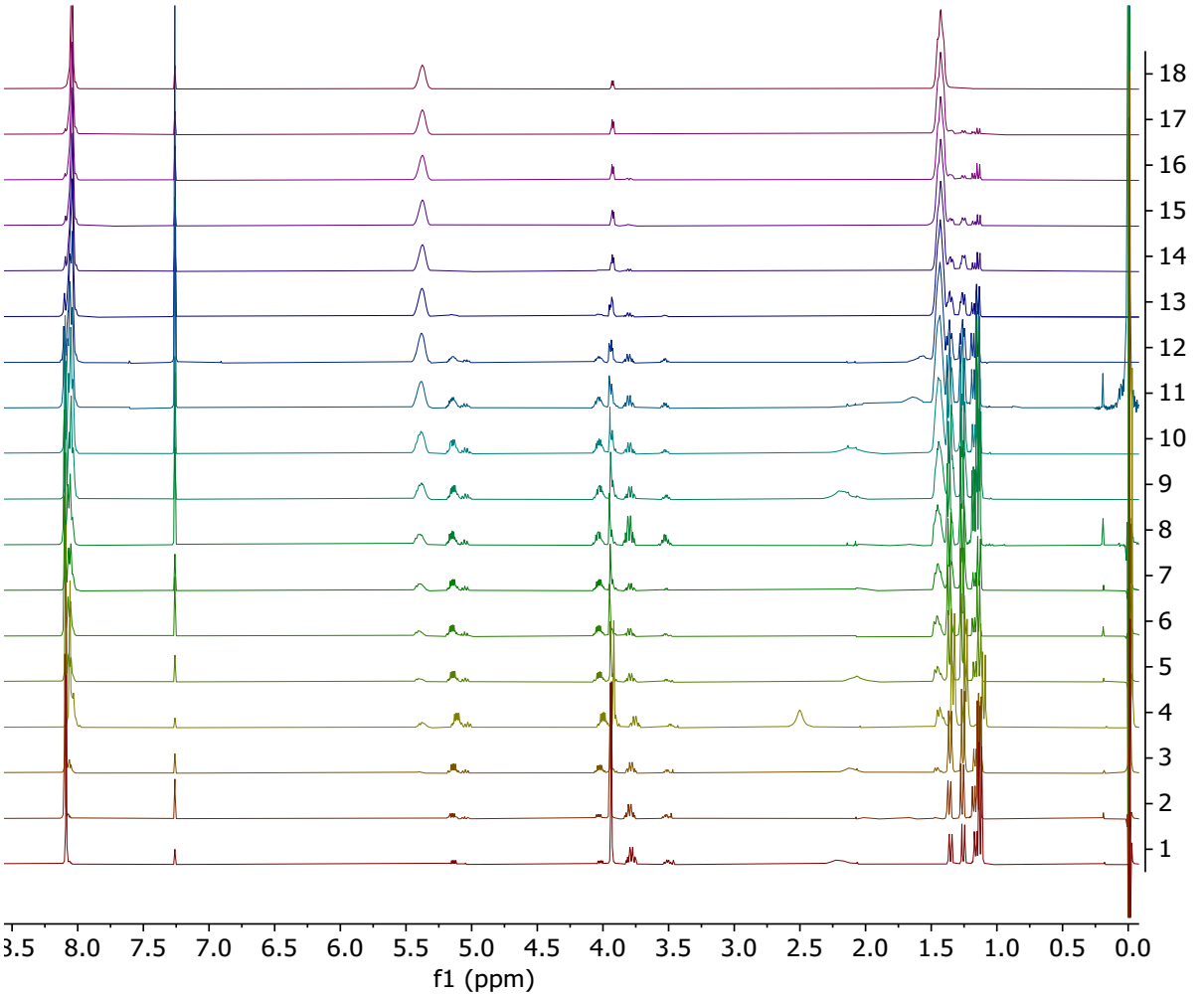


Time (h) /integral	T	Ol CH	End1meso+RR CH	End2meso+RR CH+ MeR	Free1	Free2	Fig.#
0.5	4	0.004	0.305	5.382	2.395	0.755	1
1.5	4	0.057	0.865	4.018	1.376	0.393	2
3	4	0.226	1.209	2.832	0.704	0.252	3
4.5	4	0.353	1.230	2.365	0.674	0.239	4
6	4	0.441	1.218	2.133	0.477	0.165	5
7.5	4	0.520	1.166	0.954+0.969	0.456	0.156	6
9.5	4	0.608	1.148	1.772	0.411	0.140	7
11.5	4	0.654	1.145	1.755	0.408	0.138	8
27	4	0.782	0.990	1.538	0.327	0.100	9
27.5	4	0.787	0.987	0.792+0.746	0.312	0.093	10
End PC	4	1.214	0.573	0.988			11

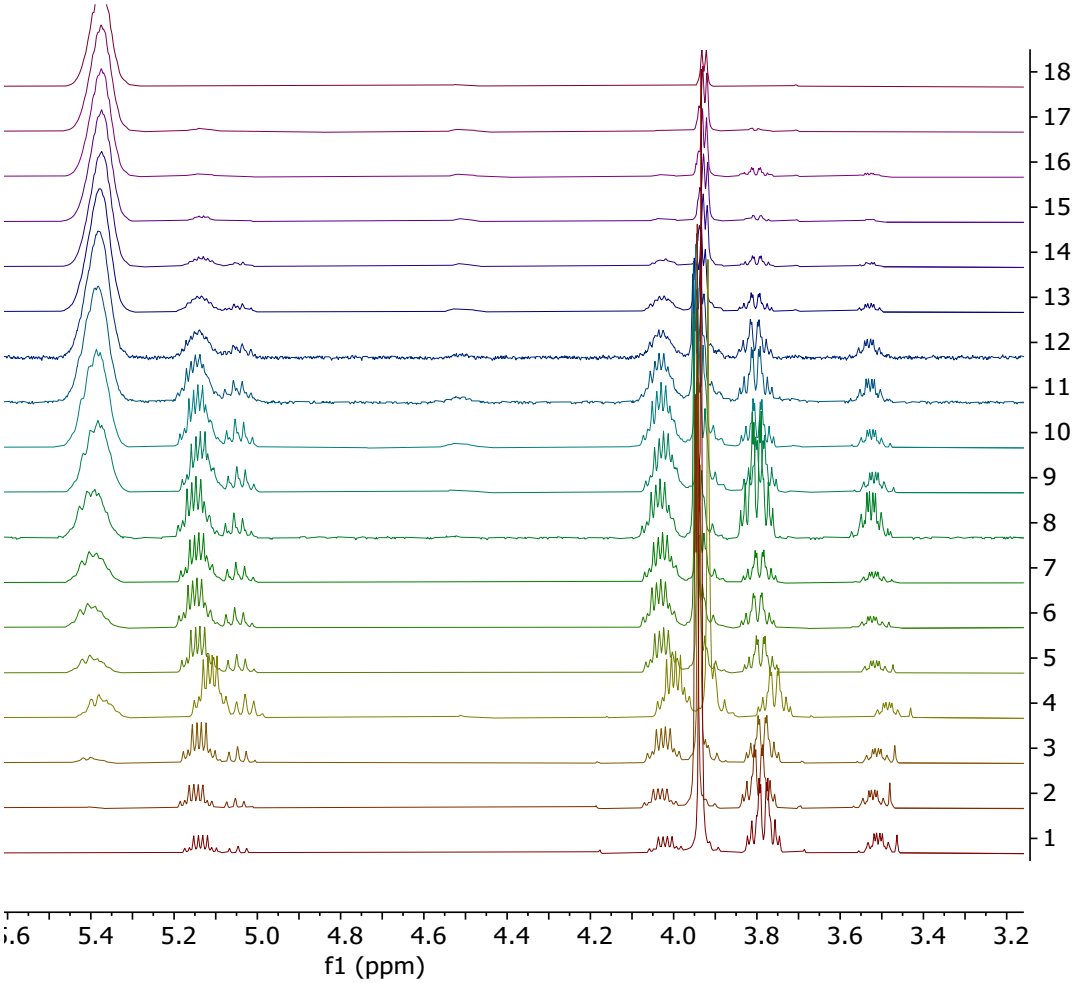
IV. DMT, 2,3-BDO & $Zn(OAc)_2•2H_2O$ catalyst for P23BT synthesis: 1H NMR over time

In the first section of the supplementary information we discussed the interpretation of an exemplary spectrum for the synthesis of P23BT. In addition, the relevant calculations are also shared in this first section. Now in this section, we firstly share all the complete spectra used to generate the purple diamond (◊) datapoints in figure 4 in the main text, "Transesterification over time for DMT and commercial 2,3-BDO catalysed by 0.3 mol% $Zn(OAc)_2$". However, since most relevant changes are clearly visible ~5.8-3.4 ppm, a zoomed in version of the spectra below is showed immediately hereafter. The spectra are named #1-#18 (and in the later discussed table fig #1-#18) and represent a time point, thus #1 is taken at 0.5h and #2 at 1.0 h etc. Of course the spectra are integrated and this data is summarized in a table directly after the zoomed in spectrum (area5.8-3.4ppm). These integrations are used to calculate (using calculations as discussed in the first section) for the transesterification over time.

DMT, commercial mix of 2,3-BDO & Zn(OAc)2•2H2O catalyst for P23BT synthesis, Proton NMR over time: full spectra



DMT, commercial mix of 2,3-BDO & $Zn(OAc)_2 \cdot 2H_2O$ catalyst for P23BT synthesis: Proton NMR over time: area 5.8-3.2 ppm

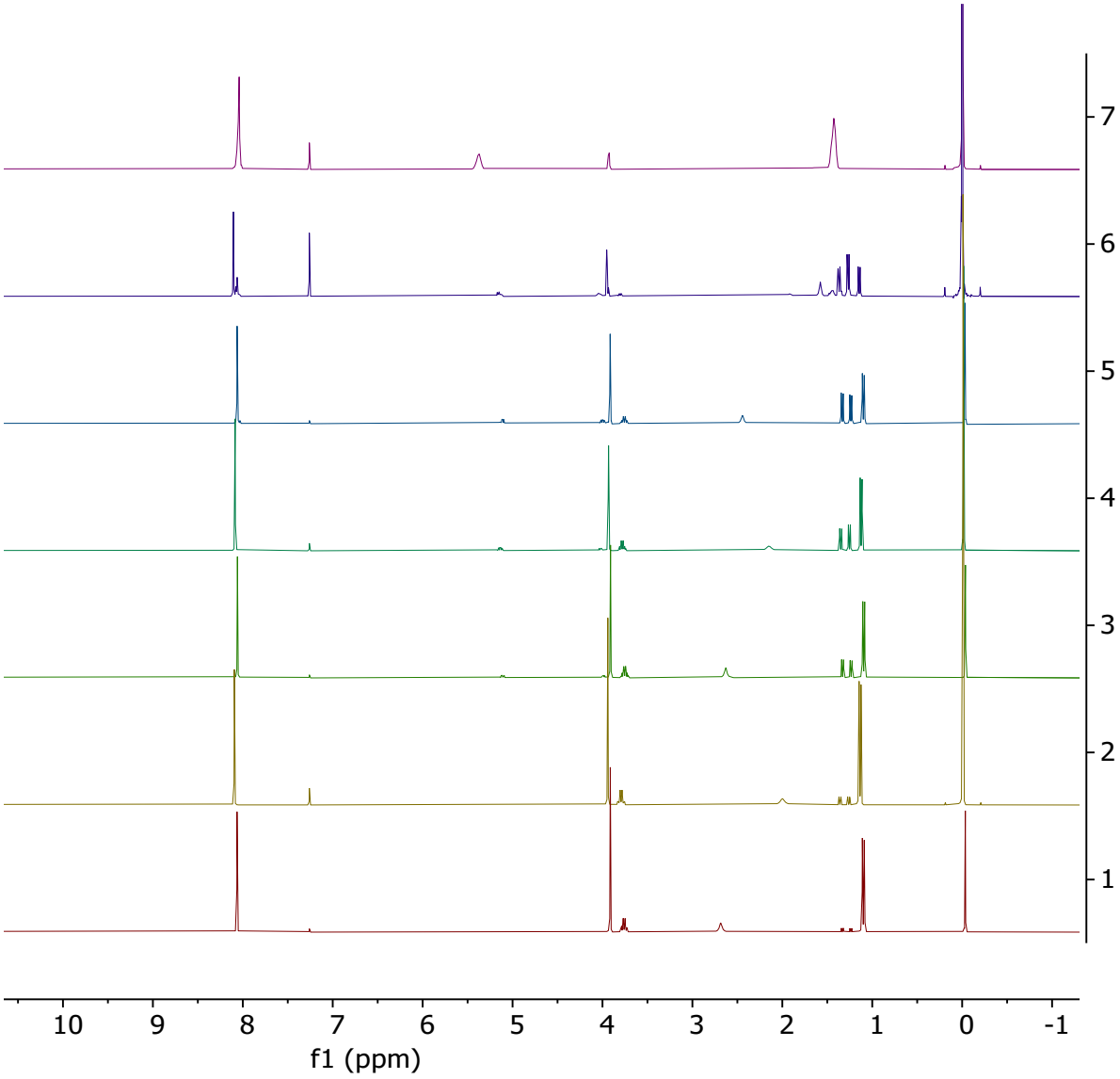


Time(h)/integral	T	Ol CH	End1meso+RR CH	End2meso+RR CH+ MeR	Free1	Free2	Fig.#
0.5	4	0.015	0.55	4.76	1.863	0.598	1
1	4	0.034	0.772	4.095	1.545	0.573	2
2	4	0.192	1.055	3.111	0.94	0.305	3
4	4	0.444	1.094	2.316	0.584	0.192	4
4.5	4	0.498	1.066	2.139	0.565	0.219	5
6	4	0.609	1.026	1.897	0.458	0.16	6
7.5	4	0.746	0.947	1.641	0.374	0.135	7
9	4	0.872	0.809	1.326	0.987	0.397	8
11	4	1.017	0.737	1.247	0.383	0.151	9
12.5	4	1.119	0.642	1.105	0.263	0.11	10
14.5	4	1.295	0.547	0.938	0.328	0.138	11
17.5	4	1.442	0.357	0.687	0.22	0.109	12
19.5	4	1.535	0.248	0.583	0.133	0.06	13
21.75	4	1.666	0.186	0.487	0.097	0.043	14
24.75	4	1.728	0.117	0.42	0.072	0.029	15
27	4	1.764	0.094	0.38	0.096	0.04	16
27.5	4	1.775	0.09	0.372	0.051	0.018	17
End PC	4	1.866	0.035	0.188			18

V. DMT, Meso 2,3-BDO & $Zr(OBu)_4$ catalyst for P23BT synthesis: 1H NMR Spectra of samples over time

Similar to the pervious sections III and IV, the relevant ^{1}H-NMR spectra are shared, firstly the full spectra then one zoomed in for the relevant area, followed by integrations used to calculate the conversion. These are used for the datapoints in figure 5, left side blue diamonds (◊).

DMT, Meso 2,3-BDO & $Zr(OBu)_4$ catalyst for P23BT synthesis, Proton NMR Spectra of samples over time: full spectra



DMT, Meso 2,3-BDO & $Zr(OBu)_4$ catalyst for P23BT synthesis: Proton NMR Spectra of samples over time (ZOOMED IN 6.1-3.35 ppm)

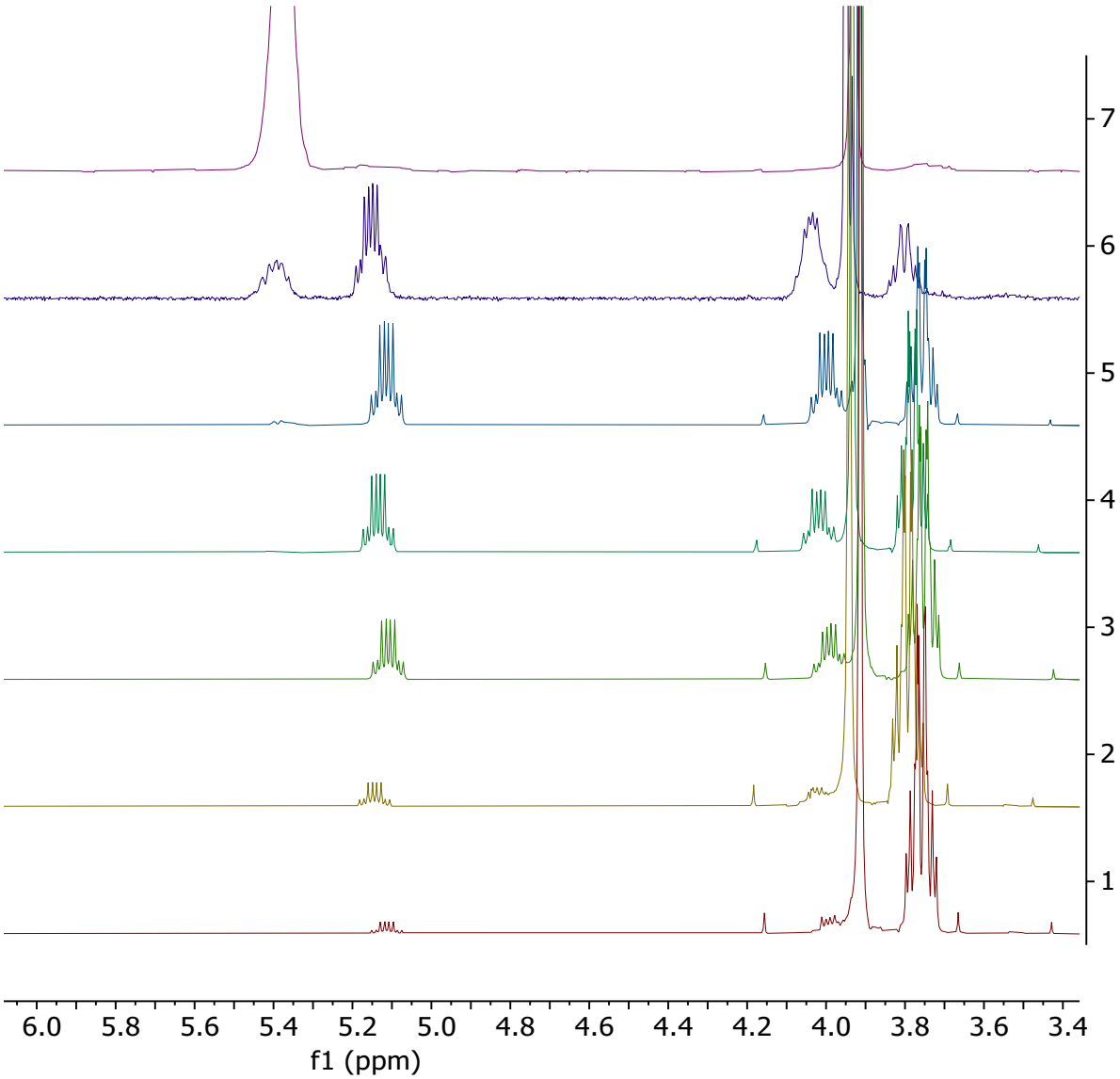


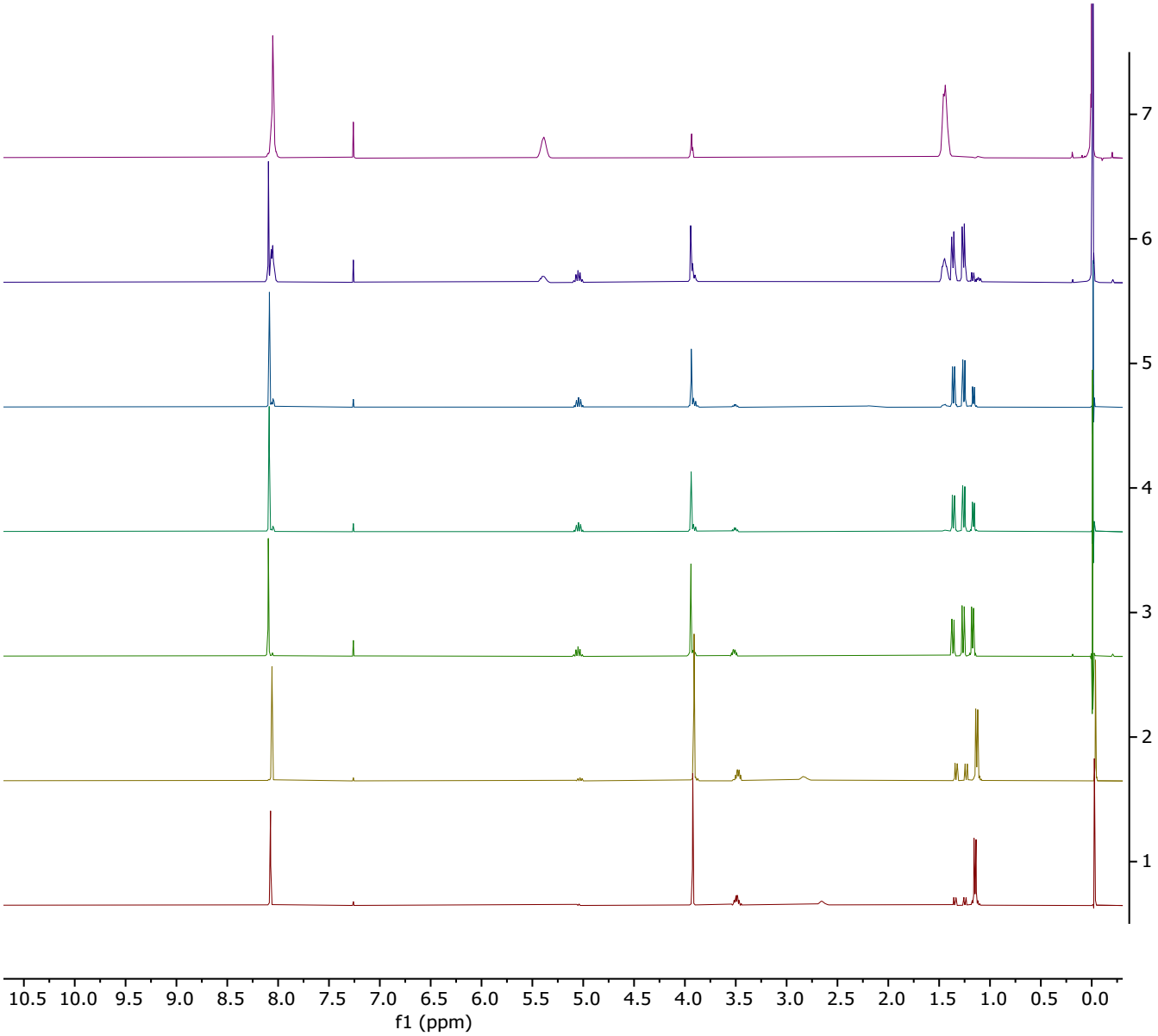
Table of integrals based on spectra above

Time(h)/integral	T	Ol CH	End1 CH	End2 CH+ MeOR	Fig.#
0.5	4	0	0.097	5.830	1
1	4	0	0.173	5.736	2
3	4	0.013	0.431	5.122	3
5	4	0.035	0.608	4.711	4
7	4	0.061	0.738	4.345	5
23.5	4	0.445	0.893	2.818	6
End PC	4	1.745	0.064	0.564	7

VI. DMT, R,R-2,3-BDO & $Zr(OBu)_4$ catalyst for P23BT synthesis: ^1H NMR Spectra of samples over time

Similar to the pervious sections III and IV, the relevant ^1H-NMR spectra are shared, firstly the full spectra then one zoomed in for the relevant area, followed by integrations used to calculate the conversion. These are used for the datapoints in figure 5, left side green diamonds (◊).

DMT, R,R-2,3-BDO & $Zr(OBu)_4$ catalyst for P23BT synthesis, Proton NMR Spectra of samples over time: full spectra



DMT, R,R-2,3-BDO & $Zr(OBu)_4$ catalyst for P23BT synthesis: Proton NMR Spectra of samples over time (ZOOMED IN 5.85-3.05 ppm)

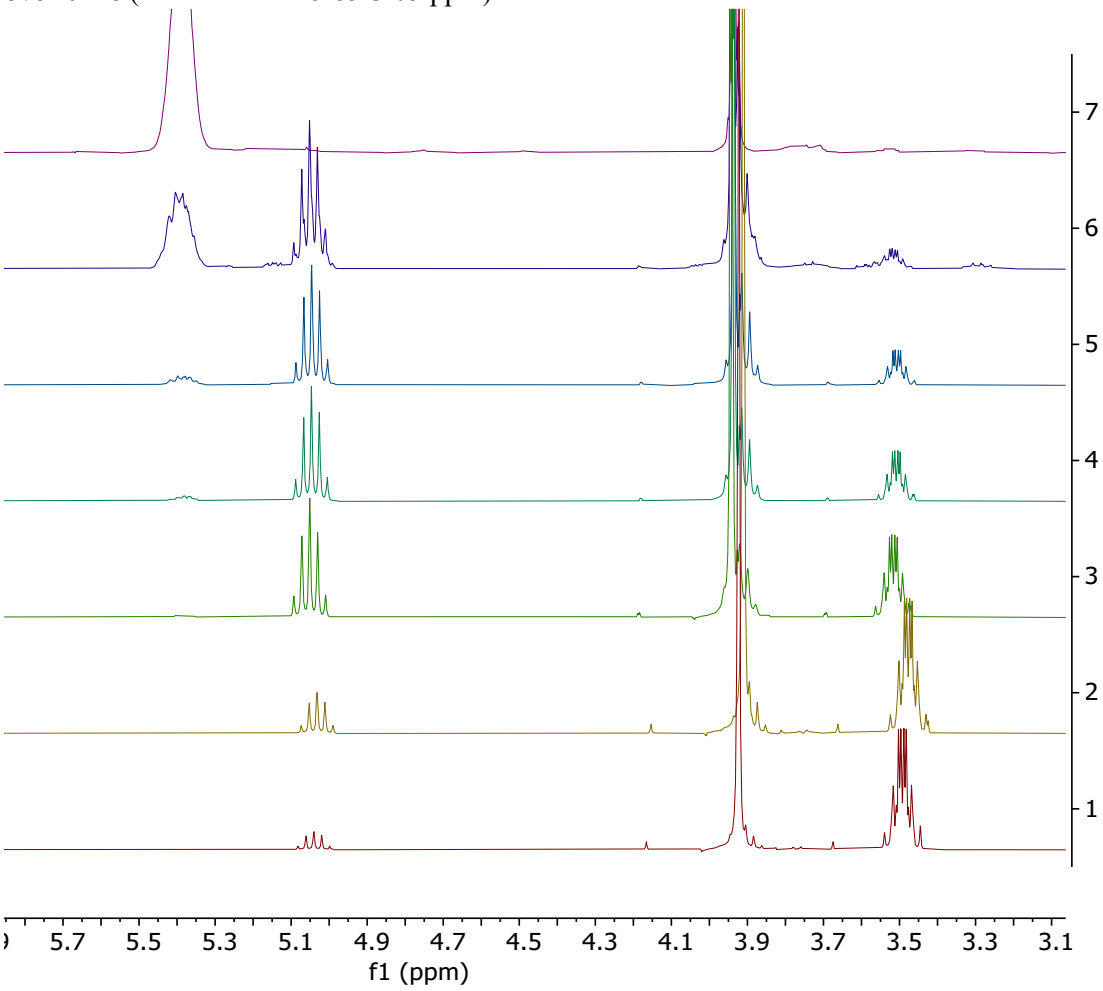


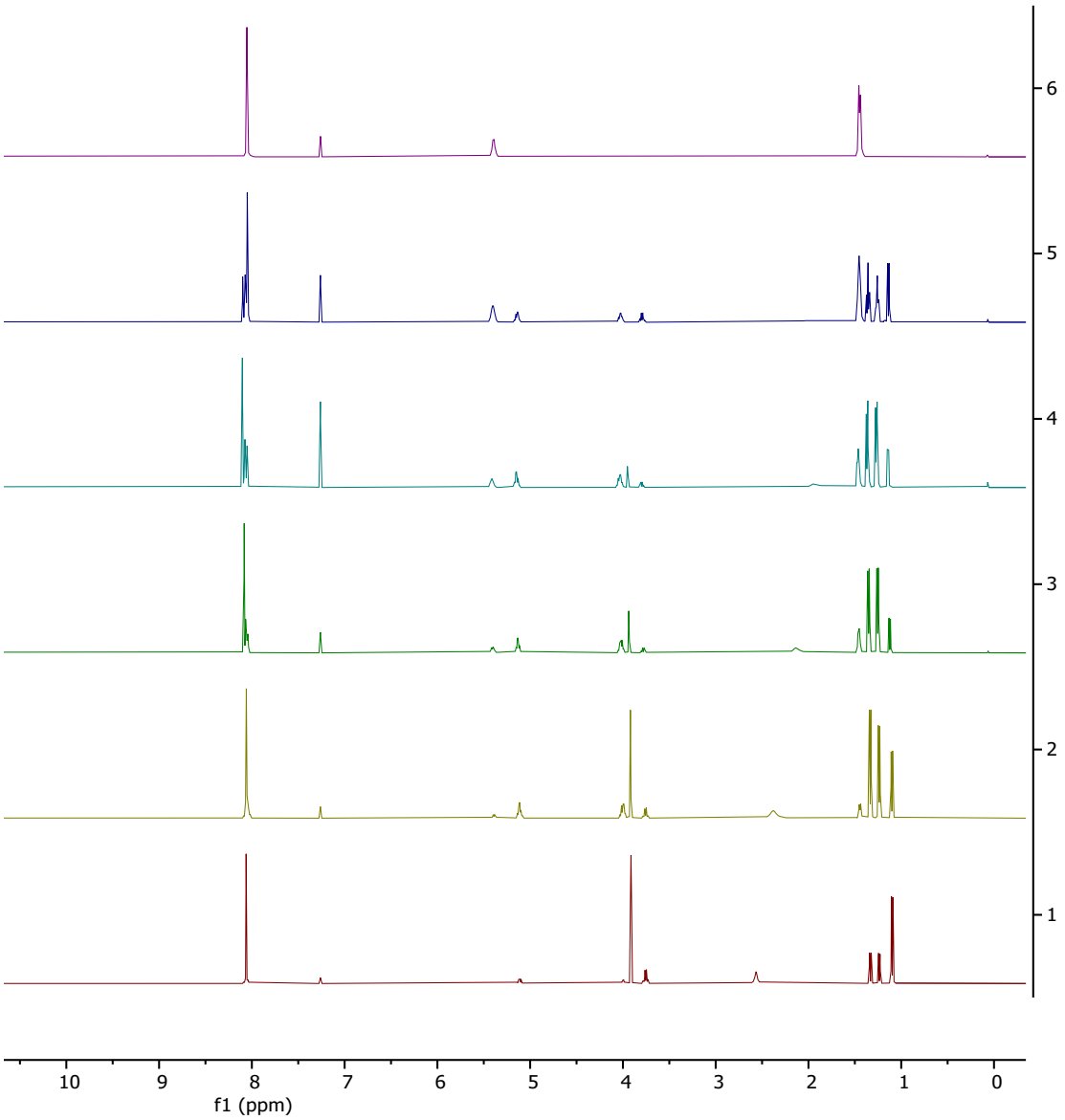
Table of integrals based on spectra above

Time(h)/integral	T	Ol CH	End1 CH	End2 CH+ MeOR	Fig.#
0.5	4	0	0.232	5.526	1
1	4	0	0.399	5.199	2
3	4	0.043	0.859	4.048	3
5	4	0.131	1.029	3.481	4
7	4	0.221	1.049	3.192	5
23.5	4	0.820	0.691	1.913	6
End PC	4	1.716	0.098	0.513	7

VII. DMT, Meso 2,3-BDO & $Ti(OBu)_4$ catalyst for P23BT synthesis: ^1H NMR Spectra of samples over time

Similar to the pervious sections III and IV, the relevant ^{1}H-NMR spectra are shared, firstly the full spectra then one zoomed in for the relevant area, followed by integrations used to calculate the conversion. These are used for the datapoint in figure 5, right side blue diamonds (◊).

DMT, Meso 2,3-BDO & Ti(OBu)4 catalyst for P23BT synthesis, Proton NMR Spectra of samples over time: full spectra



DMT, Meso 2,3-BDO & $Ti(OBu)_4$ catalyst for P23BT synthesis: Proton NMR Spectra of samples over time (ZOOMED IN 5.85-3.3ppm)

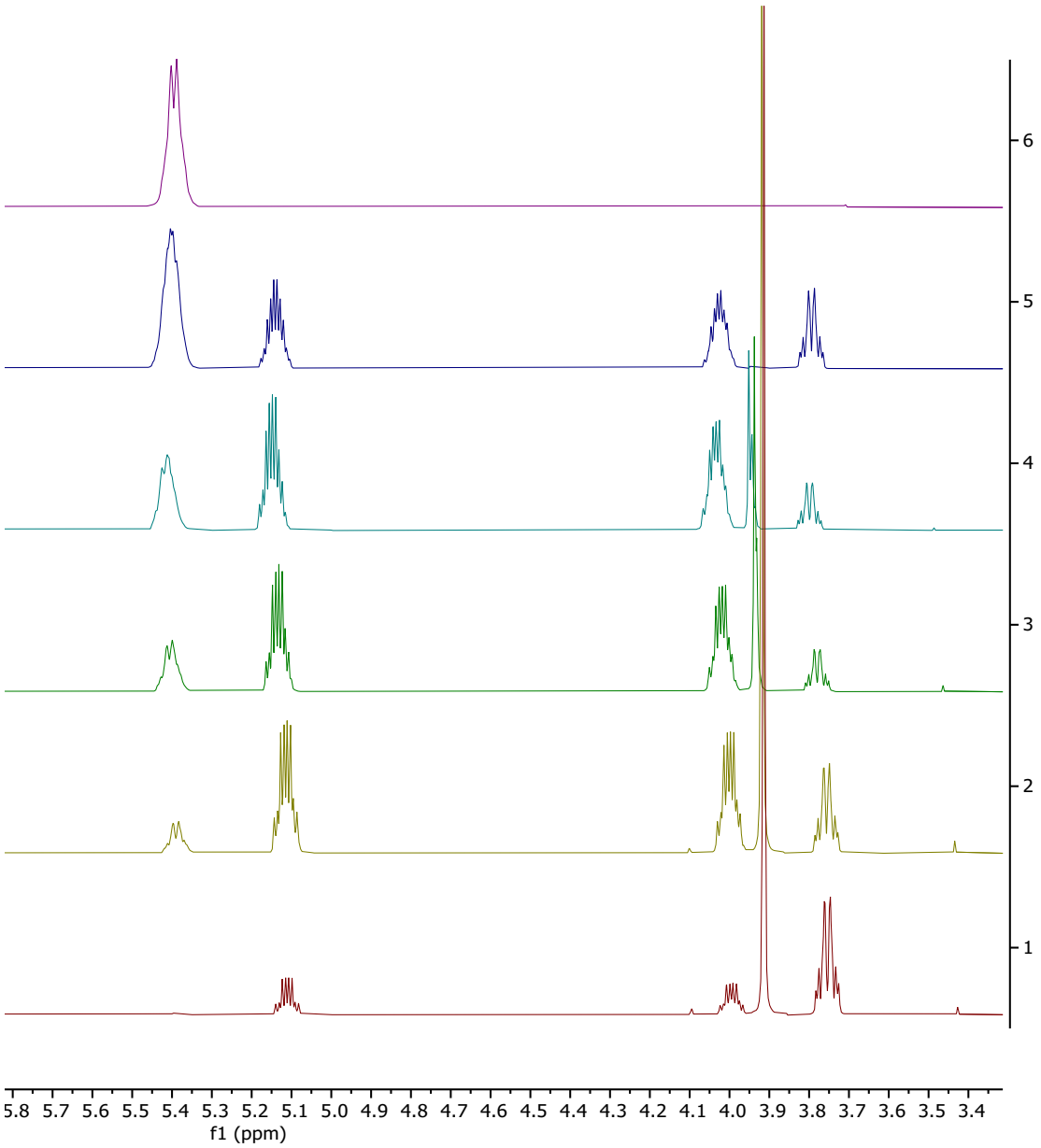


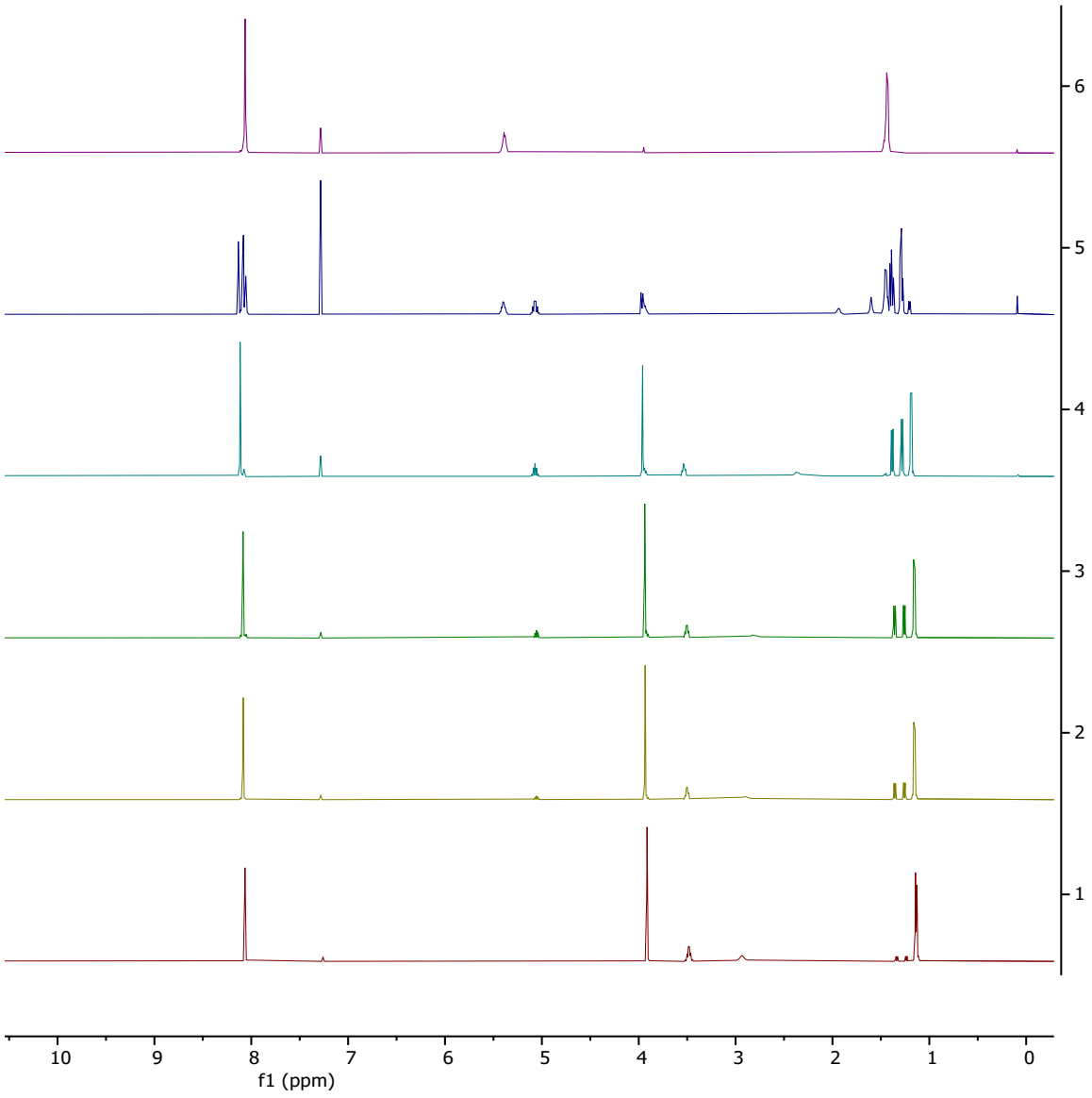
Table of integrals based on spectra above

Time(h)/integral	T	Ol CH	End1 CH	End2 CH+ MeOR	Fig.#
1	4	0.036	0.595	4.749	1
3	4	0.302	1.105	2.889	2
5	4	0.602	1.112	1.968	3
7	4	0.813	1.024	1.031	4
23.5	4	1.376	0.607	0.607 /0.6	5
End PC	4	1.971	0.013	0.007	6

VIII. DMT, R,R-2,3-BDO & $Ti(OBu)_4$ catalyst for P23BT synthesis: ^1H NMR Spectra of samples over time

Similar to the pervious sections III and IV, the relevant ^1H-NMR spectra are shared, firstly the full spectra then one zoomed in for the relevant area, followed by integrations used to calculate the conversion. These are used for the datapoint in figure 5, right side green diamonds (◊).

DMT, R,R-2,3-BDO & $Ti(OBu)_4$ catalyst for P23BT synthesis, Proton NMR Spectra of samples over time: full spectra



DMT, R,R-2,3-BDO & $Ti(OBu)_4$ catalyst for P23BT synthesis: Proton NMR Spectra of samples over time (ZOOMED IN)

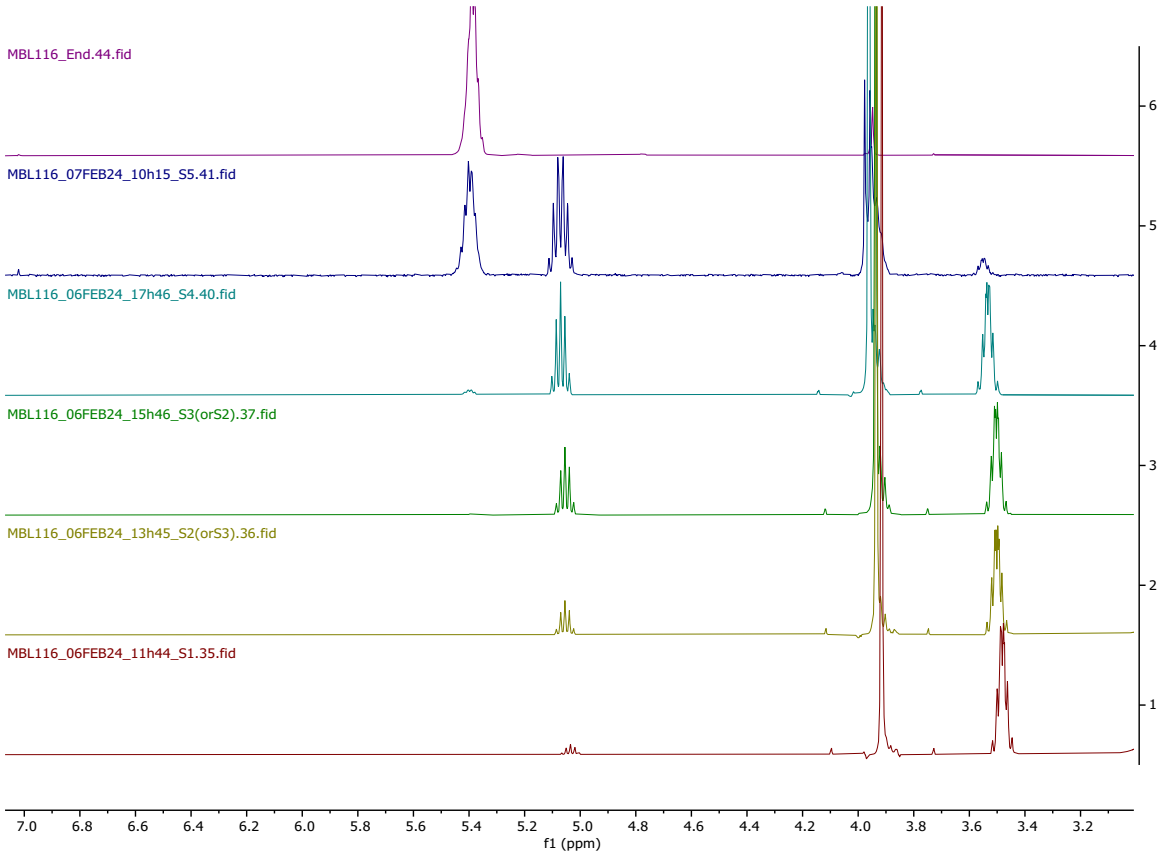


Table of integrals based on spectra above

Time(h)/integral	T	Ol CH	End1 CH	End2 CH+ MeOR	Fig.#
1	4	0	0.147	5.774	1
3	4	0	0.386	5.252	2
5	4	0.036	0.627	4.688	3
7	4	0.082	0.831	4.144	4
23.5	4	1.005	0.828	1.335	5
End PC	4	1.927	0.006	0.126	6

IX. Converted integrals for data conversion graph

In sections V-VIII, the integrals are shared that form the basis of the points in figure 5. In the table below these integrals are converted into percentages, written as "% $E_{2,3\text{-BDO}}$" which are shown in this figure using the previously discussed calculations. The colors are the same color as of the diamonds (◊) used in the figure.

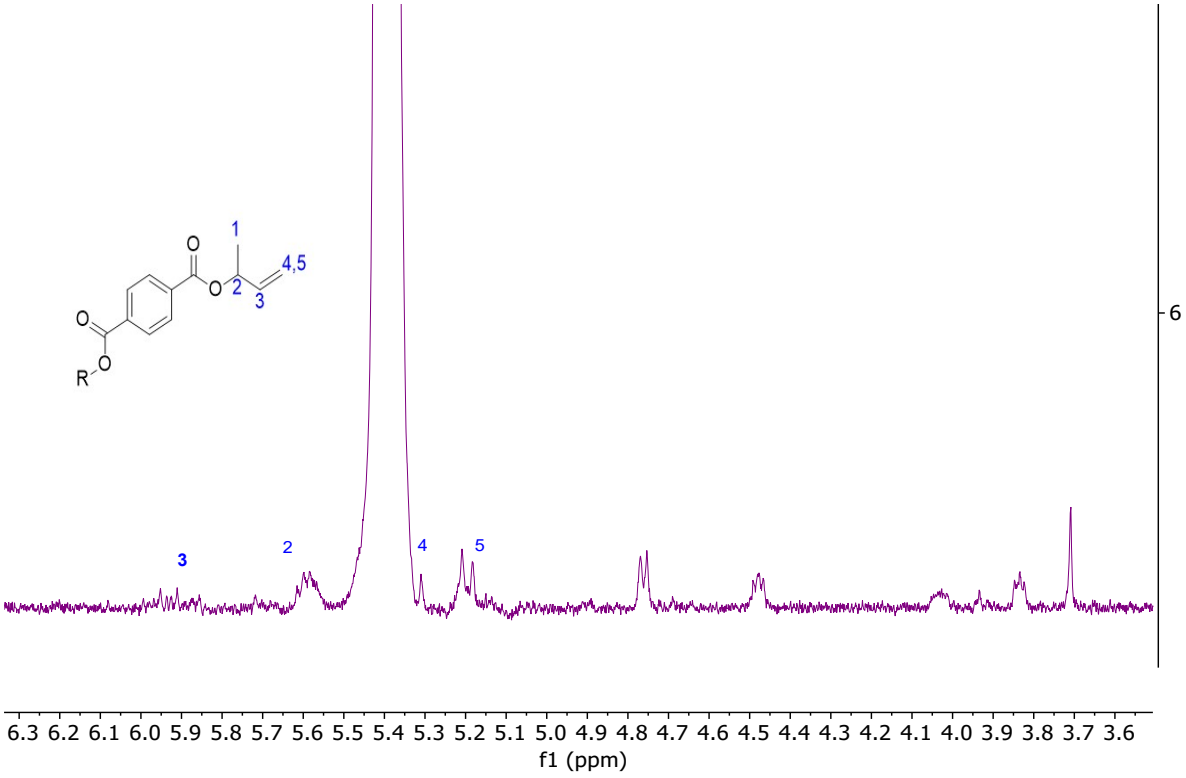
Time	Zr Meso		Zr RR		Ti Meso		Ti RR	
(h)	% $E_{2,3\text{-BDO}}$	% $E_{2,3\text{-BDO\_ol}}$	% $E_{2,3\text{-BDO}}$	% $E_{2,3\text{-BDO\_ol}}$	% $E_{2,3\text{-BDO}}$	% $E_{2,3\text{-BDO\_ol}}$	% $E_{2,3\text{-BDO}}$	% $E_{2,3\text{-BDO\_ol}}$
0.5	4.9	0	11.6	0	-	-	-	-
1	8.7	0	20.0	0	31.55	1.8	7.35	0.0
3	22.2	0.7	45.1	2.2	70.35	15.1	19.3	0.0
5	32.2	1.8	58.0	6.6	85.7	30.1	33.15	1.8

7	40.0	3.1	63.5	11.1	91.85	40.65	45.65	4.1
23.5	66.9	22.3	75.6	41.0	99.15	68.8	91.65	50.3

X. Side products

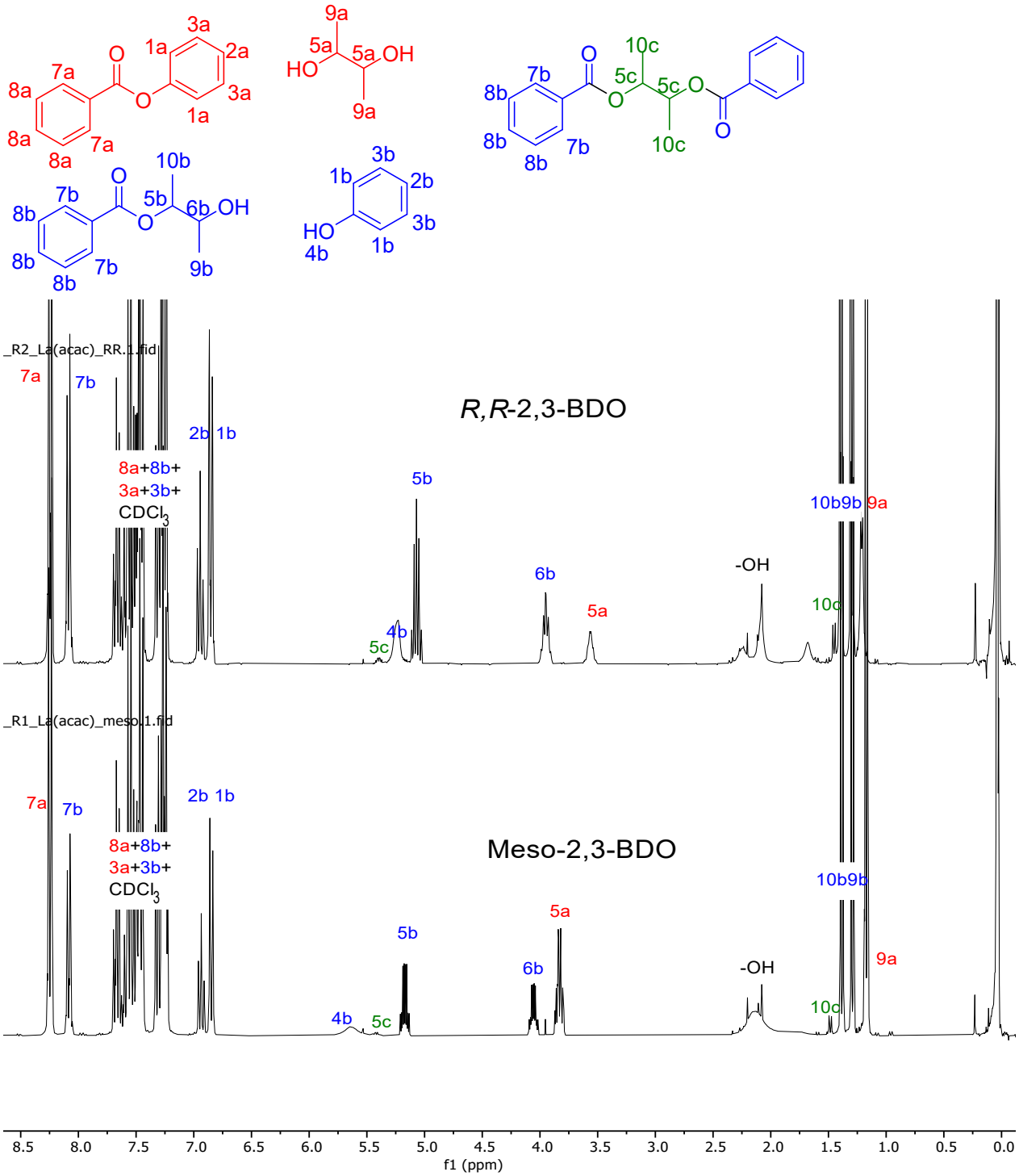
In the main text side products in P23BT polyester synthesis is discussed, below the relevant spectra that shows side products besides the main polyester peak. This is for the synthesis of P23BT using meso-2,3-BDO and titanium catalyst besides DMT. The allyl dehydration product of 2,3-BDO is shown as an end group and interpreted in the NMR above. Other peaks remain unknown, some could be ethers of 2,3-BDO or other side products.

Ti Meso final polymer zoomed in to show side products in NMR



XI. Interpretation spectra of catalyst study using phenylbenzoate and meso- or *R,R*-2,3-BDO.

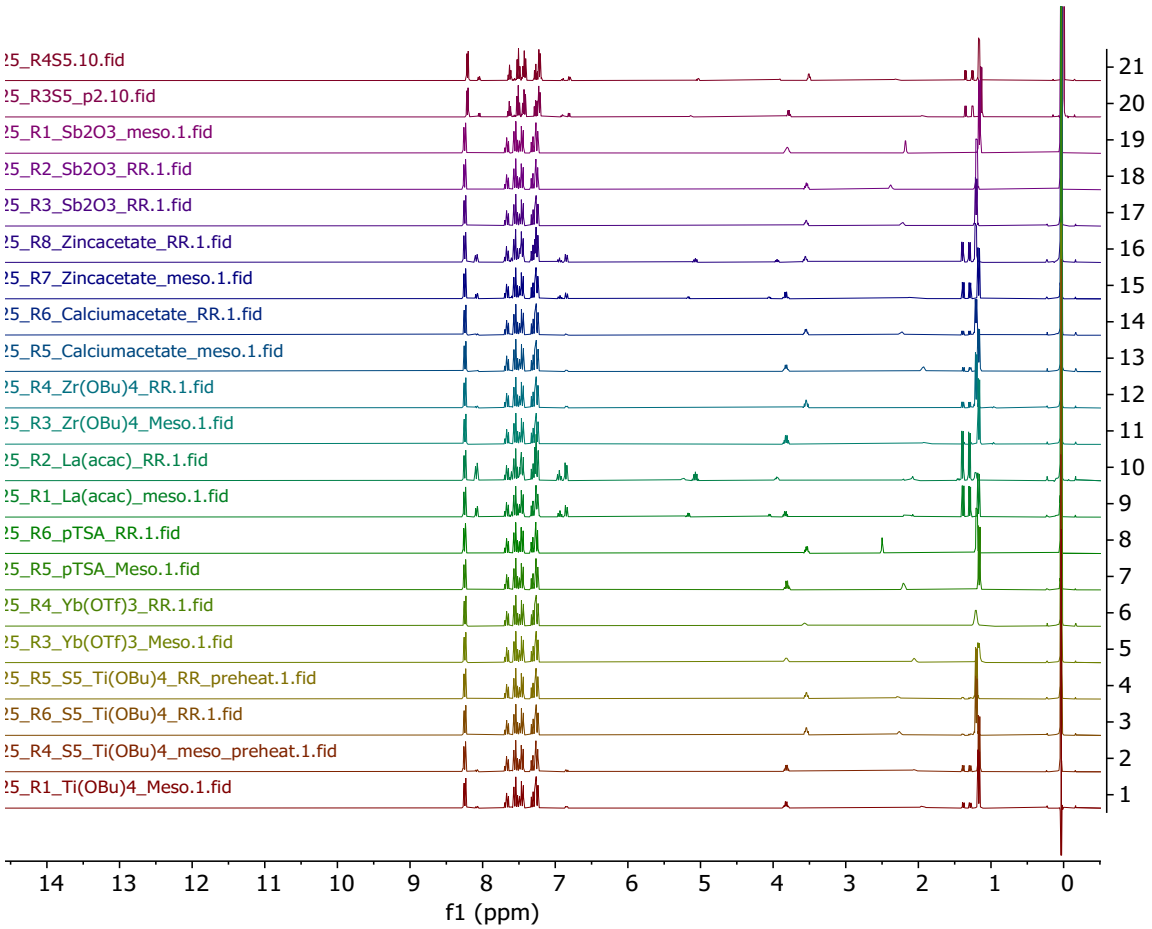
Below results of phenylbenzoate transesterification using $La(acac)_3$ catalyst with either R,R- (top) or Meso-2,3-BDO (below). Interpretation shown: start materials in red & main products in blue. Since this was one of the most active catalyst, thus (exceptionally) also another transesterification product was visible in the spectra in a very small quantities: the diester of 2,3-BDO, indicated in green.



XII. Spectra of catalyst study using phenylbenzoate and meso or R,R-2,3-BDO, various catalysts

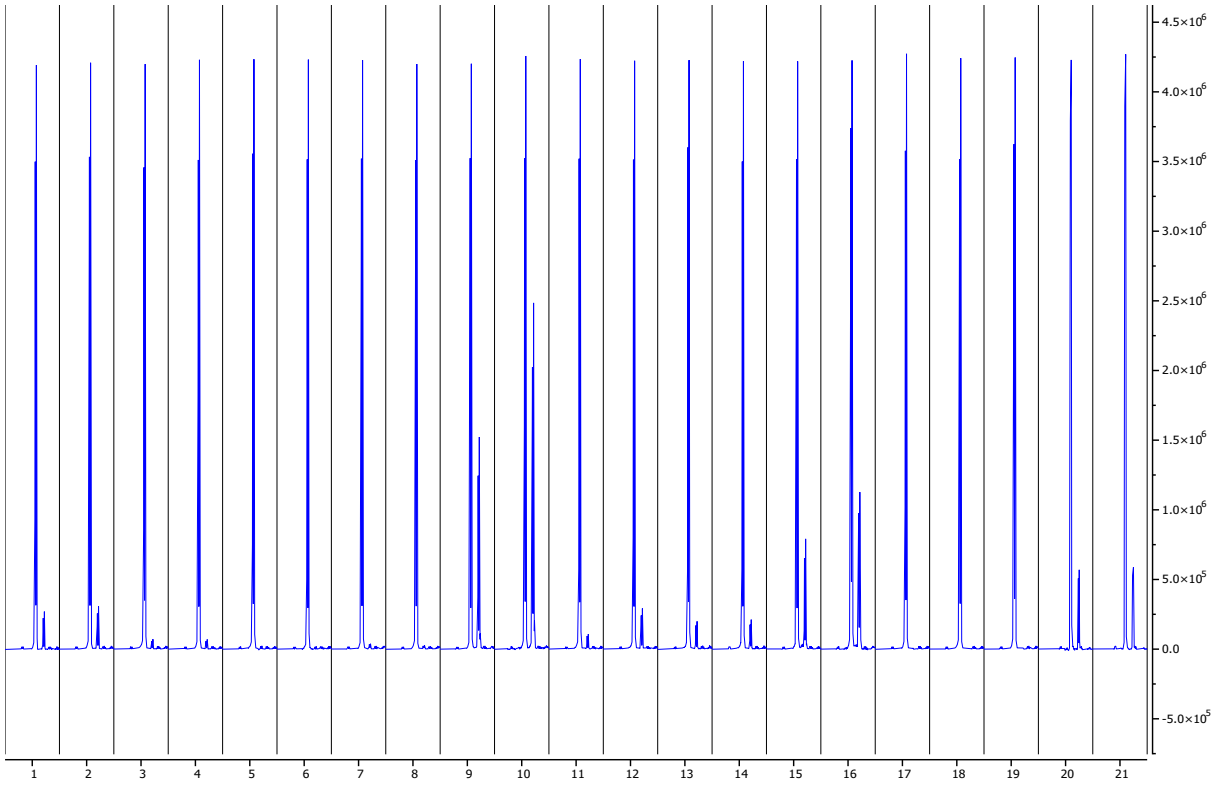
First set of spectra is the full range (stacked horizontal) and the second set of spectra is zoomed in on the aromatic part (~8.5-8.0 ppm) used to quantify the conversion of the benzoate ester. This aromatic area of the spectra is stacked vertically (so peaks of benzoate of each film reactor experiment is next to each other by experiment number). The spectrum/experiment number is related to an experiment specified in the table below the set of spectra. The "*" stands for an experiment of which the mixture was preheated before catalyst addition.

set of spectra for model reaction (phenylbenzoate TE): the full range (stacked horizontal)



Set of spectra for model reaction (phenylbenzoate TE): area ~8.5-8.0ppm (stacked vertically)

#1 stands for the most left spectrum, which is a zoomed in version of the same " spectra #1" in the previous figure (Ti(OBu)4_meso in maroon color), this continues in a similar fashion and is also the same order as used to describe the results in the table below.



#	1	2*	3	4*	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21
Cat	Ti	Ti	Ti	Ti	Yb	Yb	TSA	TSA	La	La	Zr	Zr	Ca	Ca	Zn	Zn	Sb2O3	Sb2O3	Sb2O3	Tin	Tin
2,3	M	M	RR	RR	M	RR	M	RR	M	RR	M	RR	M	RR	M	RR	RR	RR	M	M	RR
Min.	**58**	55	55	55	**58**	**58**	**58**	**58**	55	55	55	55	55	55	55	55	55	55	55	55	55
Int.1	0.941	0.931	0.983	0.983	0.994	0.995	0.986	0.989	0.725	0.615	0.973	0.934	0.952	0.949	0.838	0.786	0.998	0.997	0.997	0.881	0.878
Int.2	0.059	0.069	0.017	0.017	0.006	0.005	0.014	0.011	0.275	0.385	0.027	0.066	0.048	0.051	0.162	0.214	0.002	0.003	0.003	0.119	0.122

Table with experimental information, specific catalyst, isomer used (M=meso-, RR=*R,R*-2,3-BDO) and reaction time. In addition the integration of the benzoate peaks belonging to spectra above are shown which are used to calculate yields ("Int.1" stands for the starting material , Phenyl Benzoate, numbers need to be multiplied by 100 for percentages used for graph in main text of paper).

Experimental: exact weight of starting materials in vials

	Catalyst					**PhOBz**			**2,3-BDO**					
NMR spectra number	Catalyst	mg of catalyst solution	mg of catalyst	mw	mmol	mg	mw	mmol	stereoisomer	mg	mw	mmol	Cat. loading %	Ratio 2,3-BDO
20	BTHOH		3.32	*208.83*	0.016	1189.31	198.22	5.99995	Meso	270.27	90.12	2.999001	0.26	2.00
21	BTHOH		3.35	*208.83*	0.016	1192.72	198.22	6.017153	R,R	268.57	90.12	2.980138	0.27	2.02
19	Sb2O3		4.92	291.52	0.017	1187.03	198.22	5.988447	Meso	267.92	90.12	2.972925	0.28	2.01
18	Sb2O3		5.34	291.52	0.018	1190.81	198.22	6.007517	R,R	278.90	90.12	3.094763	0.30	1.94
17	Sb2O3		5.04	291.52	0.017	1192.11	198.22	6.014075	R,R	270.03	90.12	2.996338	0.29	2.01
2	Ti(Obu)4*		6.9	340.32	0.020	1188.37	198.22	5.995207	Meso	273.83	90.12	3.038504	0.34	1.97

4	Ti(Obu)4*		6.9	340.32	0.020	1187.94	198.22	5.993038	R,R	266.41	90.12	2.95617	0.34	2.03
3	Ti(Obu)4		6.89	340.32	0.020	1189.38	198.22	6.000303	R,R	270.04	90.12	2.996449	0.34	2.00
1	Ti(Obu)4		6.87	340.32	0.020	1188.73	198.22	5.997024	Meso	274.39	90.12	3.044718	0.34	1.97
5	Yb(Otf)3		11.18	620.25	0.018	1190.45	198.22	6.005701	Meso	270.36	90.12	3	0.30	2.00
6	Yb(Otf)3		11.36	620.25	0.018	1187.33	198.22	5.989961	R,R	271.74	90.12	3.015313	0.31	1.99
7	p-TSA		3.10	190.213	0.016	1188.45	198.22	5.995611	Meso	269.61	90.12	2.991678	0.27	2.00
8	p-TSA		2.90	190.213	0.015	1191.02	198.22	6.008576	R,R	272.7	90.12	3.025965	0.25	1.99
9	La(acac)3		7.61	440.952	0.017	1189.87	198.22	6.002775	Meso	271.07	90.12	3.007878	0.29	2.00
10	La(acac)3		7.79	440.952	0.018	1192.29	198.22	6.014983	R,R	264.79	90.12	2.938194	0.29	2.05
12	Zr(Obu)4	9.53	(7.62)	383.68	0.020	1187.88	198.22	5.992735	Meso	270.37	90.12	3.000111	0.33	2.00
11	Zr(Obu)4	9.22	(7.38)	383.68	0.019	1190.56	198.22	6.006256	R,R	278.33	90.12	3.088438	0.32	1.94
13	Calciumacetate		3.29	176.18	0.019	1188.17	198.22	5.994198	Meso	268.57	90.12	2.980138	0.31	2.01
14	Calciumacetate		3.29	176.18	0.019	1189.41	198.22	6.000454	R,R	269.8	90.12	2.993786	0.31	2.00
15	Zinc acetate		4.26	219.5	0.019	1188.58	198.22	5.996267	Meso	269.24	90.12	2.987572	0.32	2.01
16	Zinc acetate		4.37	219.5	0.020	1196.59	198.22	6.036676	R,R	271.48	90.12	3.012428	0.33	2.00

Experimental: exact weight of starting materials polyester synthesis

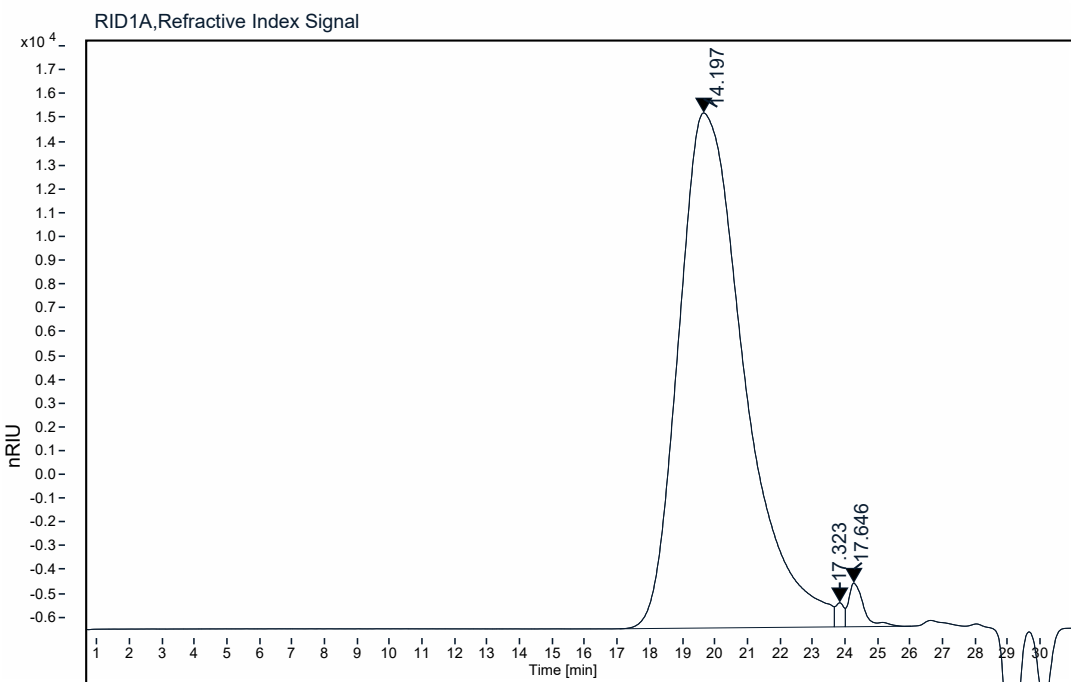
DMT	2,3-BDO		$Zr(OBu)_4$ 80% in butanol (% based on DMT)
5.24 g 0.027 mol **1 eq.**	Meso	4.50 g 0.050 mol **1.85 eq.**	9.7 µL, 10.379 mg corrected 80wt% 8.3032 mg, 0.021641mmol, **0.08 mol%**
5.24 g 0.027 mol **1 eq.**	*R,R*	4.50 g 0.050 mol **1.85 eq.**	9.7 µL, 10.379 mg corrected 80wt% 8.3032 mg, 0.021641mmol, **0.08 mol%**
DMT	2,3-BDO		$Ti(OBu)_4$ (% based on DMT)
5.84 g 0.030 mol **1 eq.**	Meso	4.979 g 0.055 mol **1.84 eq.**	15 µL **0.15 mol%**
5.71 g 0.029 mol **1 eq.**	*R,R*	4.834 g 0.054 mol **1.82 eq.**	15 µL **0.15 mol%**

GPC

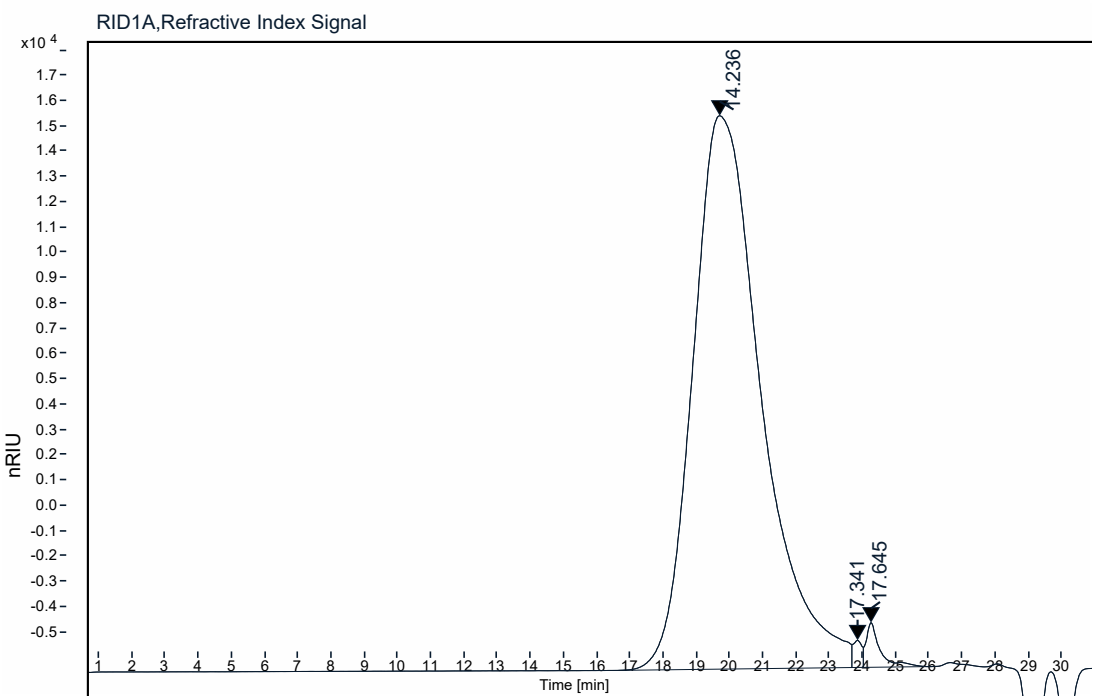
Below a section of GPC spectra, integrated and the summary of the integrated peaks, including <Mn>, <Mw> and dispersity index obtained from the software. These are all measurements of the final polyesters of P23BT. First the results of the section on " Meso- and R,R-2,3-BDO-based P23BT: Zr and Ti butoxide" are shown of which the titanium catalyzed P23BT experiments had been measured in duplicate, which are the first 4 spectra shown, followed by the Zr-catalyzed 2,3-BDO (only measured once, thus one spectra per P23BT.) The average of the duplicates and the single measurements for Zr-catalyzed results are all summarized in the main text table 2. The last two spectra shown in this section belong to experiments performed as described in the section "P23BT synthesis using a mixture of 2,3-BDO and La or Zn catalyst" and the GPC results are used for table 1 in the main text.

XIII. P23BT using $Ti(OBu)_4$ & Meso-2,3-BDO, 2 measurements

Peak #	RT (min)	Mn (g/mol)	Mw (g/mol)	PD	Mp (g/mol)
1	14.197	16331	36310	2.22	37731
2	17.323	1216	1221	1	1212
3	17.646	793	827	1.04	901

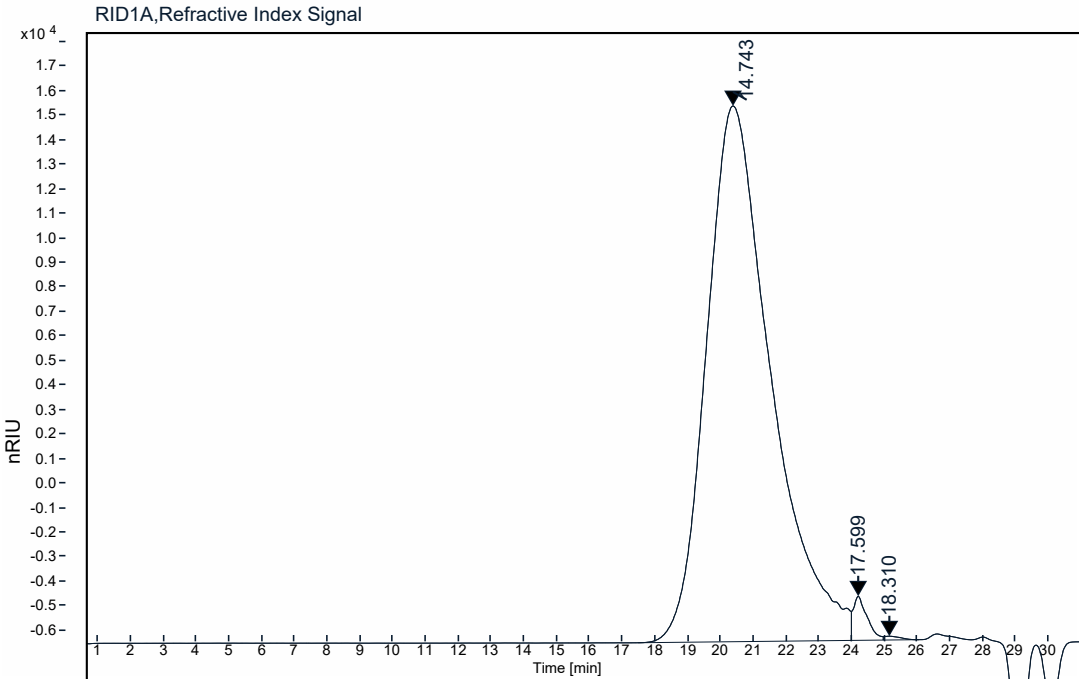


Peak #	RT (min)	Mn (g/mol)	Mw (g/mol)	PD	Mp (g/mol)
1	14.236	15844	36380	2.3	36190
2	17.341	1196	1202	1.01	1196
3	17.645	766	812	1.06	901

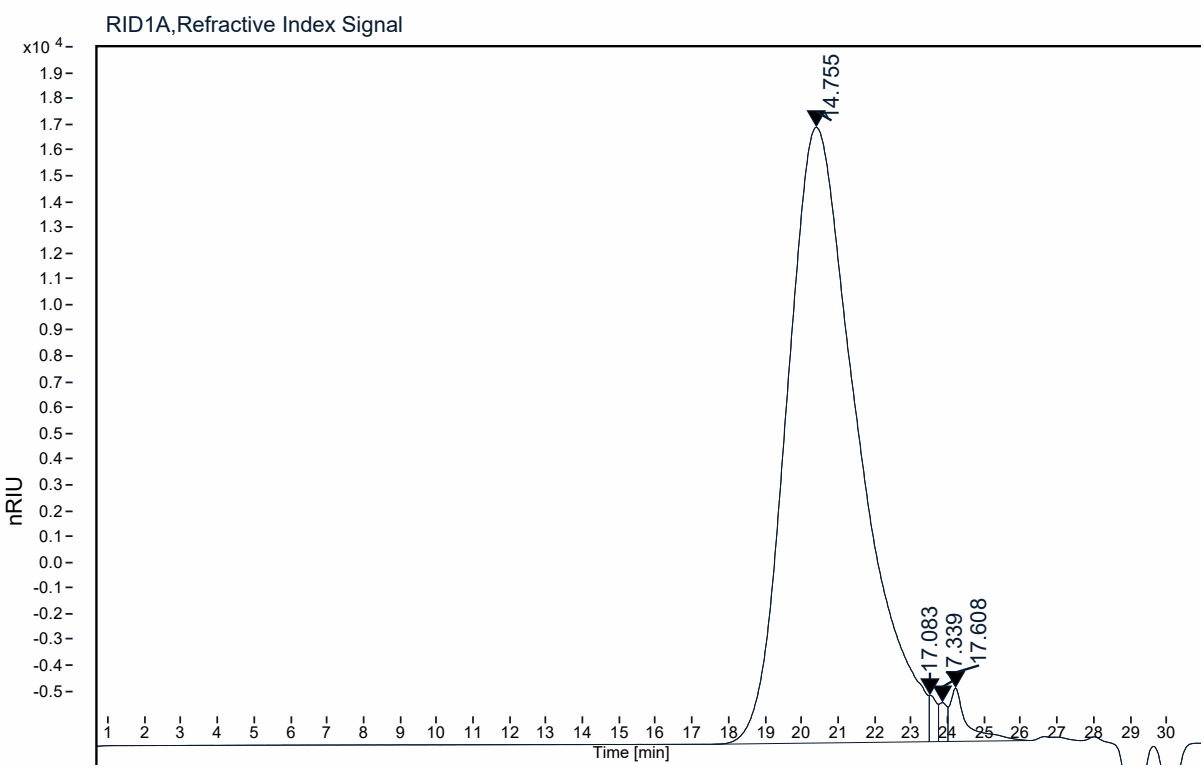


XIV. P23BT using $Ti(OBu)_4$ & R,R-2,3-BDO, 2 measurements

Peak #	RT (min)	Mn (g/mol)	Mw (g/mol)	PD	Mp (g/mol)
1	14.743	9694	20646	2.13	19978
2	17.599	859	877	1.02	938
3	18.31	449	458	1.02	497

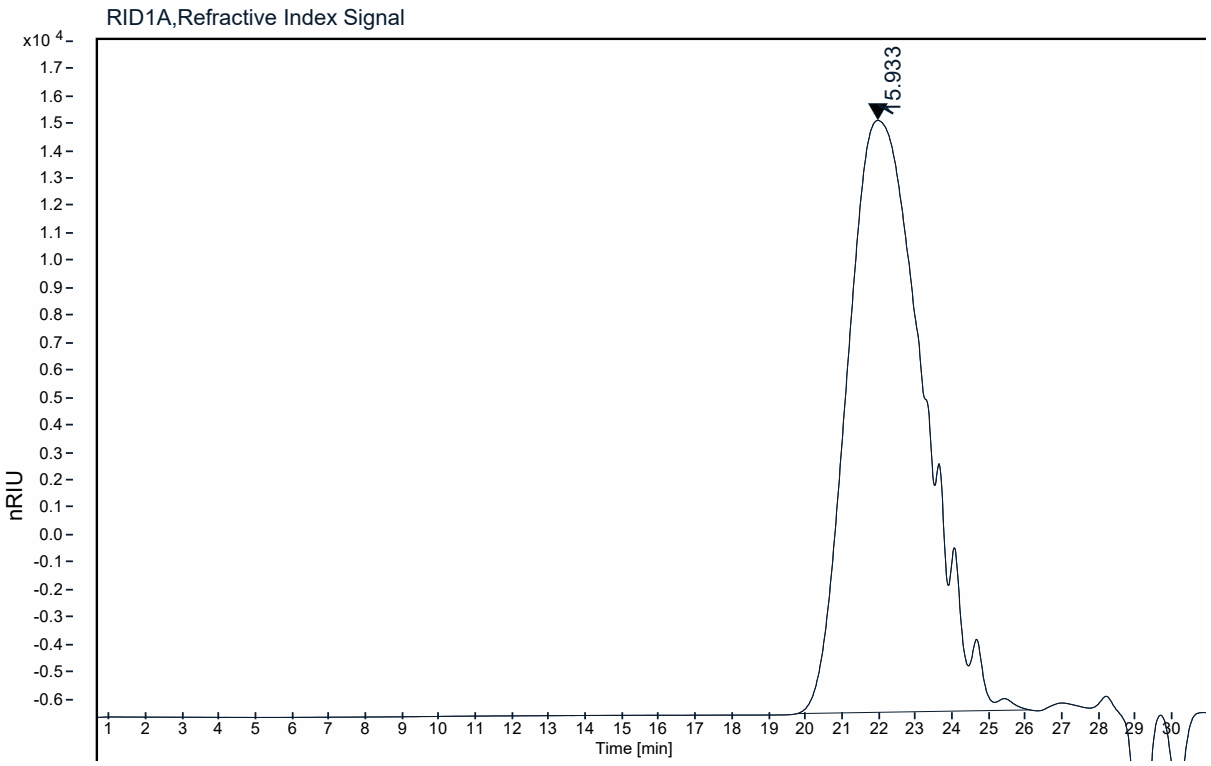


Peak #	RT (min)	Mn (g/mol)	Mw (g/mol)	PD	Mp (g/mol)
1	14.755	10475	20508	1.96	19812
2	17.083	1421	1425	1	1547
3	17.339	1180	1183	1	1204
4	17.608	733	801	1.09	931



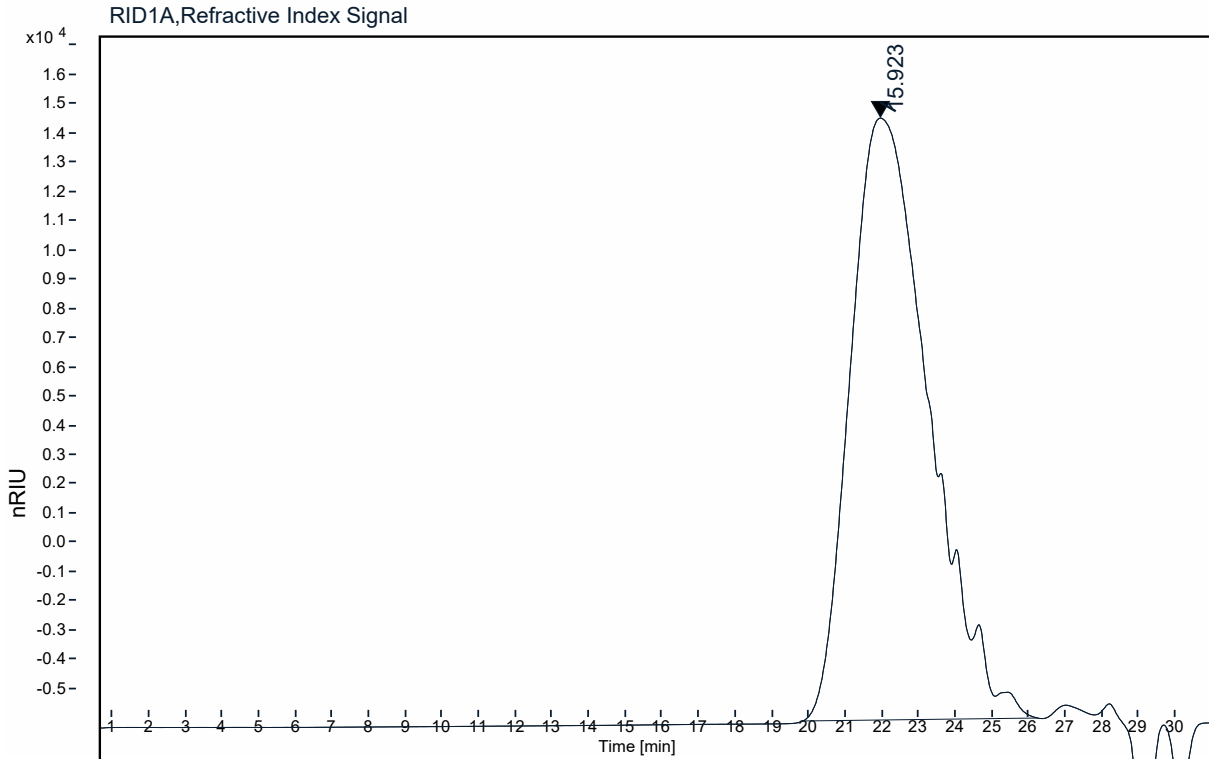
XV. P23BT using $Zr(OBu)_4$ & Meso-2,3-BDO

Peak #	RT (min)	Mn (g/mol)	Mw (g/mol)	PD	Mp (g/mol)
1	15.933	2918	5159	1.77	5135



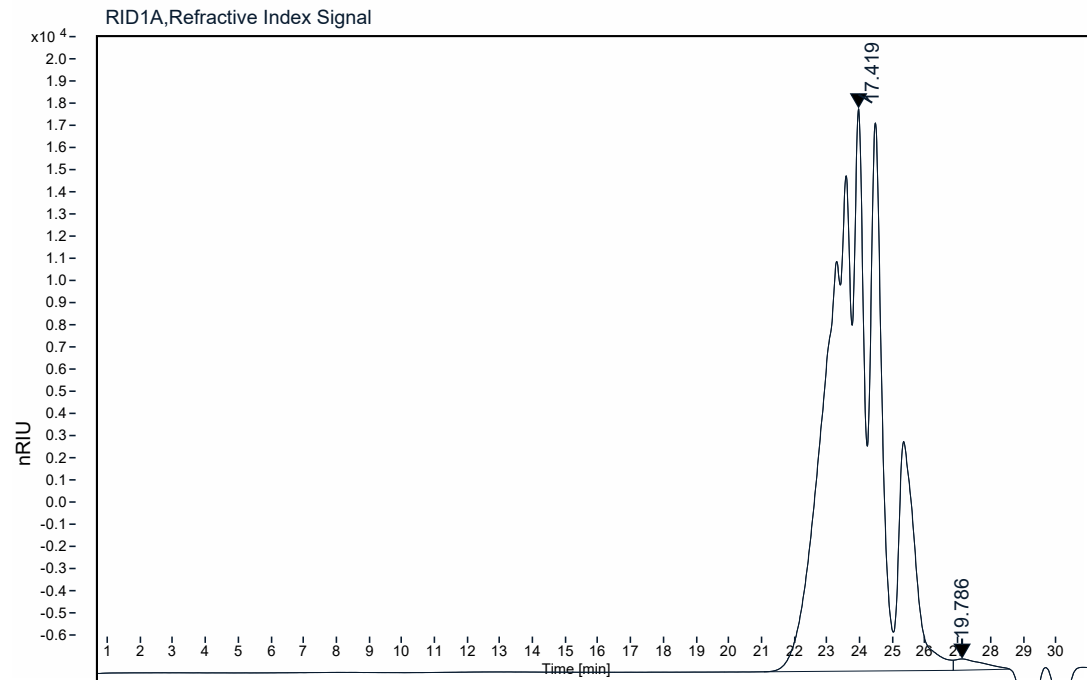
XVI. P23BT using $Zr(OBu)_4$ & R,R-2,3-BDO

Peak #	RT (min)	Mn (g/mol)	Mw (g/mol)	PD	Mp (g/mol)
1	15.923	2686	5065	1.89	5176



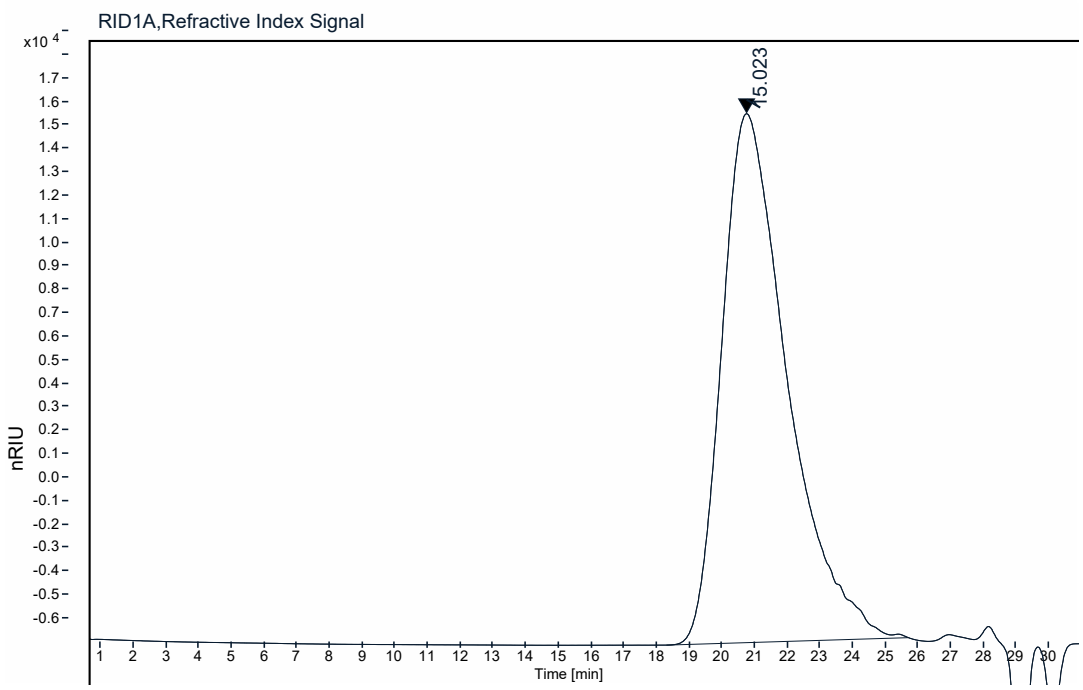
XVII. P23BT using $La(acac)_3$

Peak #	RT (min)	Mn (g/mol)	Mw (g/mol)	PD	Mp (g/mol)
1	17.419	939	1420	1.51	1117
2	19.786	83	96	1.16	124



XVIII. P23BT using $Zn(OAc)_2.H_2O$

Peak #	RT (min)	Mn (g/mol)	Mw (g/mol)	PD	Mp (g/mol)
1	15.023	6318	13632	2.16	14417



DSC

XIX. DSC curves P23BT polyesters synthesized using either $Zr(OBu)_4$ or $Ti(OBu)_4$

Catalyst	*2,3-BDO*	T_g (°C)	T_m
$Zr(OBu)_4$	*meso*	81	-
$Zr(OBu)_4$	R,R	76	-
$Ti(OBu)_4$	*meso*	120	-
$Ti(OBu)_4$	R,R	115	-

Below a table of the four P23BT polyesters synthesized using either $Zr(OBu)_4$ or $Ti(OBu)_4$, with the relevant DSC results (which are shown in the main text in table 2).

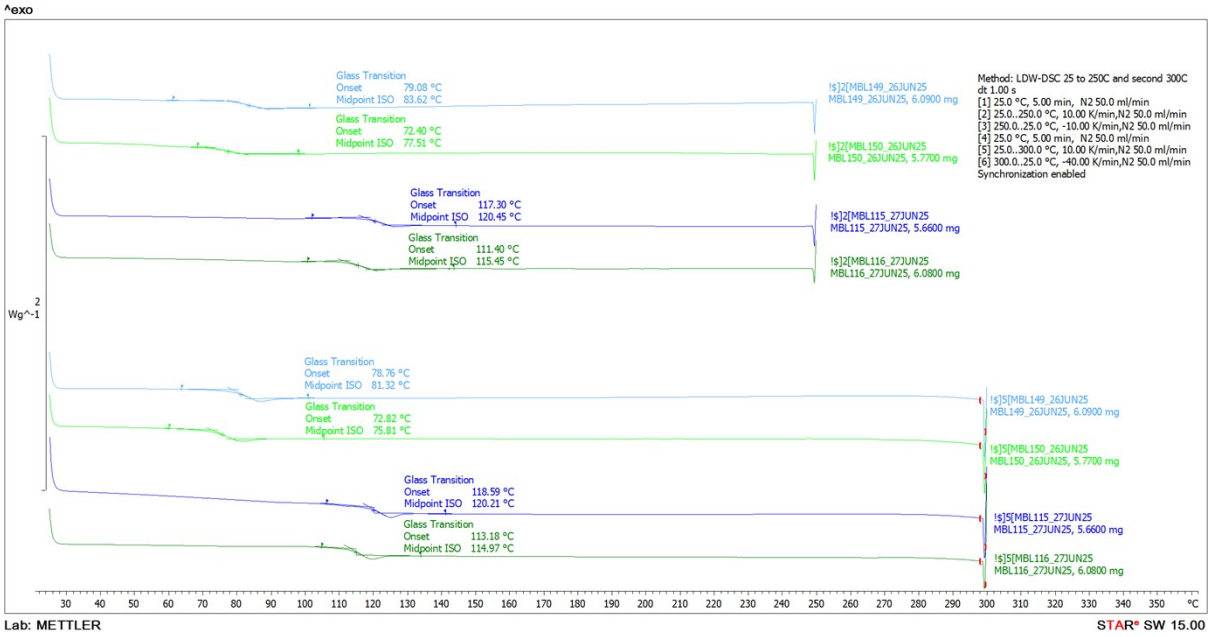
These results were based on the second cycle of the regular DSC program, the relevant curves shown in the figure below:

Method (full program: N_2 50 ml/min)
[1] 25 °C, 5 min
[2] 25 → 250 °C: 10 °C/min
[3] 250 → 25 °C: -10 °C/min
[4] 25 °C, 5 min
[5] 25 → 300 °C: 10 °C/min
[6] 300 → 25 °C: -40 °C/min

Curves in order of top to bottom:

1st cycle: P23BT: $Zr(OBu)_4$ & meso-2,3-BDO
1st cycle: P23BT: $Zr(OBu)_4$ & *R,R*-2,3-BDO
1st cycle: P23BT: $Ti(OBu)_4$ & meso-2,3-BDO
1st cycle: P23BT: $Ti(OBu)_4$ & *R,R*-2,3-BDO

2st cycle: P23BT: $Zr(OBu)_4$ & meso-2,3-BDO: T_g midpoint ISO: 81.32 °C
2st cycle: P23BT: $Zr(OBu)_4$ & *R,R*-2,3-BDO: T_g midpoint ISO: 75.81 °C
2st cycle: P23BT: $Ti(OBu)_4$ & *meso*-2,3-BDO: T_g midpoint ISO: 120.97 °C
2st cycle: P23BT: $Ti(OBu)_4$ & *R,R*-2,3-BDO: T_g midpoint ISO: 114.97 °C



XX. Annealing "P23BT synthesized using Ti(OBu)4 & R,R-2,3-BDO"

Annealing programmes were applied using the same DSC set-up, below the figure showing the curves obtained using the annealing programmes applied on "P23BT synthesized using Ti(OBu)4 & R,R-2,3-BDO".

Curves and method in order from top to bottom:

Method in red (N_2 50 ml/min for full program, steps in brackets [])
[1] 25 °C, 3 min;[2] 25 °C, 3 min;[3] 25 → 250 °C, 5 °C/min;[4] 250 → 140 °C, -1 °C/min;[5] 140 °C, 480 min;[6] 140 → 25 °C, -5 °C/min;[7] 25 → 260 °C, 5 °C/min;[8] 260 → 25 °C, -50 °C/min

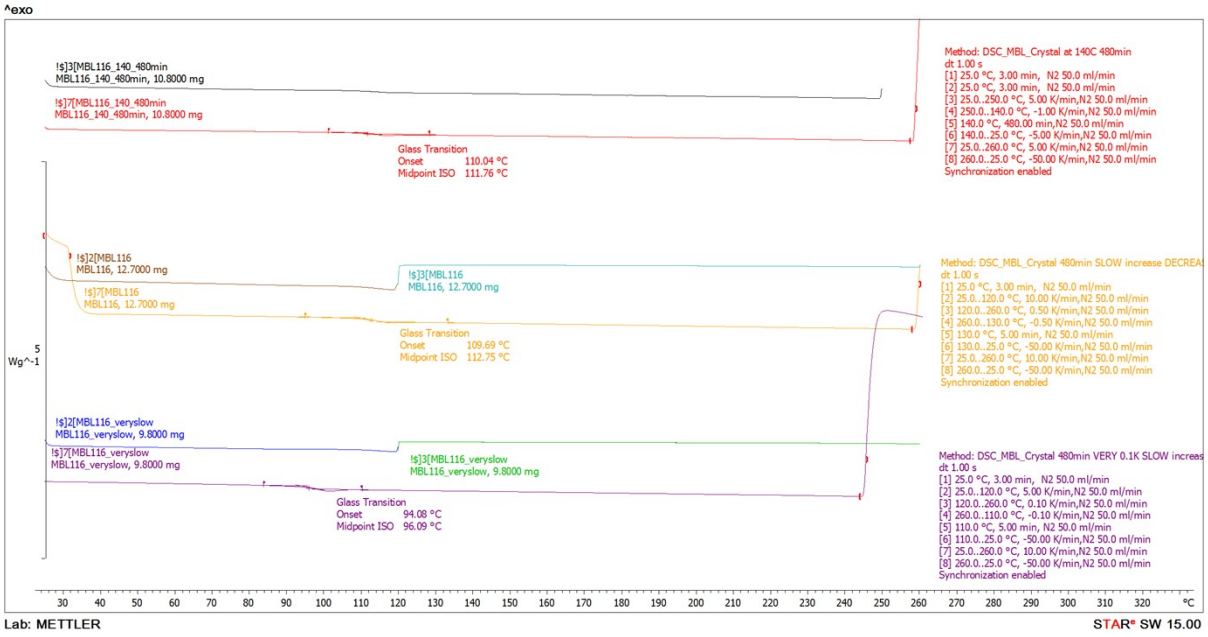
1. 1st cycle "red method" for P23BT synthesized using Ti(OBu)4 & R,R-2,3-BDO
2. 2nd cycle "red method" for P23BT synthesized using Ti(OBu)4 & R,R-2,3-BDO

Method in orange (N_2 50 ml/min for full program)
[1] 25°C, 3 min;[2] 25→120 °C, 10 °C/min;[3]120→260 °C, 0.5 °C/min;[4] 260→130 °C, -0.5°C/min;[5]130 °C, 5 min;[6]130 → 25 °C, -50 °C/min;[7]25 →260 °C, 10 °C/min;[8]260→ 25 °C, -50 °C/min

3. 1st cycle "orange method" for P23BT synthesized using Ti(OBu)4 & R,R-2,3-BDO
4. 2nd cycle "orange method" for P23BT synthesized using Ti(OBu)4 & R,R-2,3-BDO

Method in purple (N_2 50 ml/min for full program)
[1] 25 °C, 3 min;[2] 25 → 120 °C, 5 °C/min;[3] 120 → 260 °C, 0.1 °C/min;[4] 260 → 110 °C, -0.1 °C/min;[5]110 °C, 5 min;[6] 110 °C → 25 °C, -50 °C/min;[7] 25 → 260 °C, 10 °C/min;[8] 260 → 25 °C, -50 °C/min

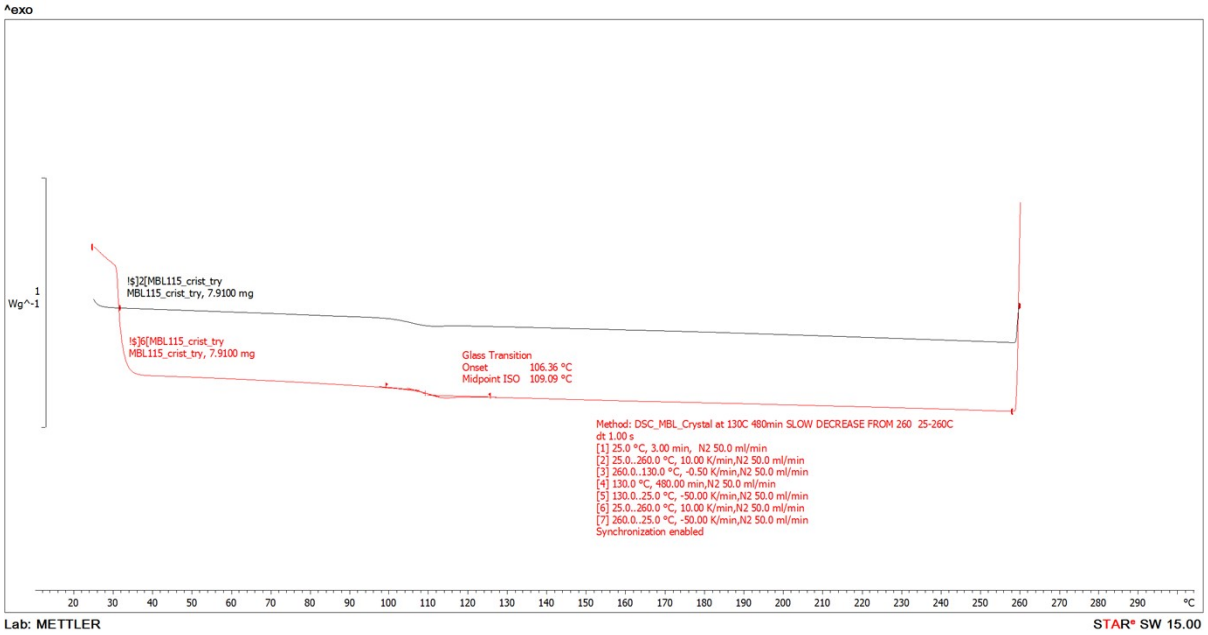
5. 1st cycle "orange method" for P23BT synthesized using Ti(OBu)4 & R,R-2,3-BDO
6. 2nd cycle "orange method" for P23BT synthesized using Ti(OBu)4 & R,R-2,3-BDO



Besides the "P23BT synthesized using Ti(OBu)4 & R,R-2,3-BDO", an annealing program was also applied on the analogous polyester with meso-2,3-BDO instead of R,R-2,3-BDO, thus "P23BT synthesized using Ti(OBu)4 & meso-2,3-BDO", this is shown in the figure below.

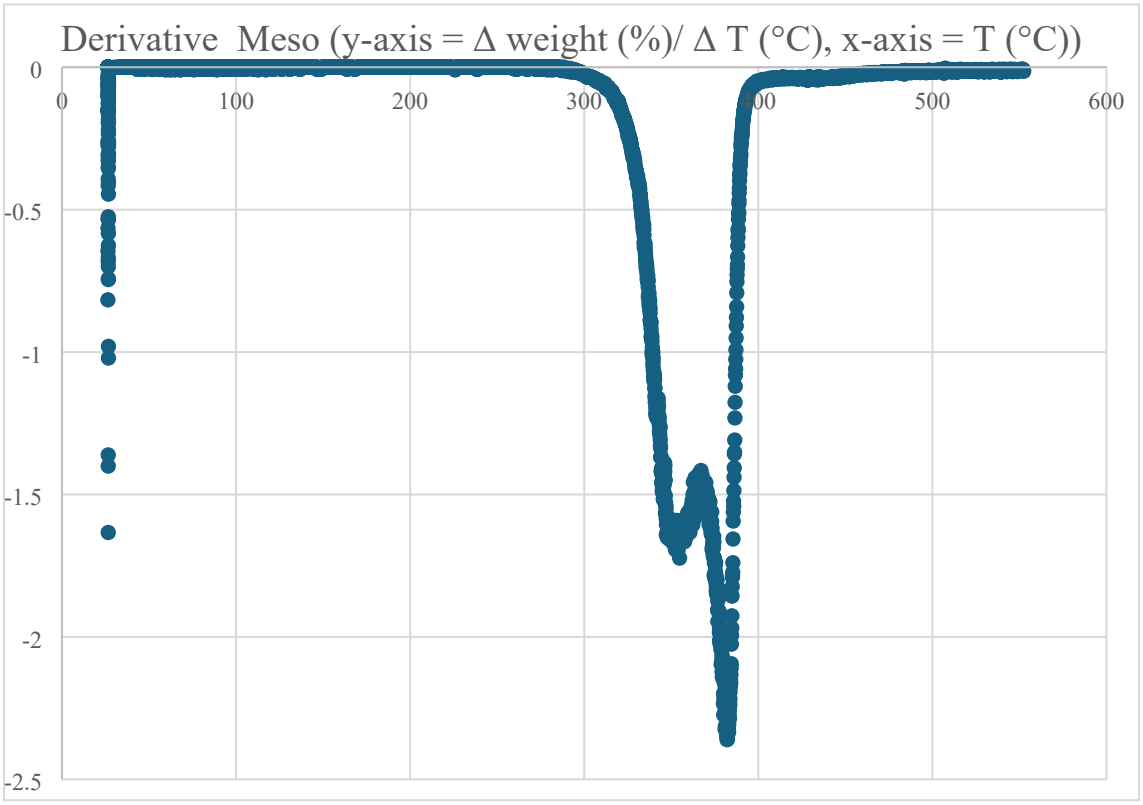
XXI. Annealing "P23BT synthesized using Ti(OBu)4 & meso-2,3-BDO"

Method(N_2 50 ml/min for full program)
[1] 25 °C, 3 min;[2] 25 → 260 °C, 10 °C/min;[3] 260 → 130 °C, -0.5 °C/min;[4] 130 °C, 480 min;[5] 230 → 25 °C, -50 °C/min [6] 25 → 260 °C, 10 °C/min;[7] 260 → 25 °C, -50 °C/min

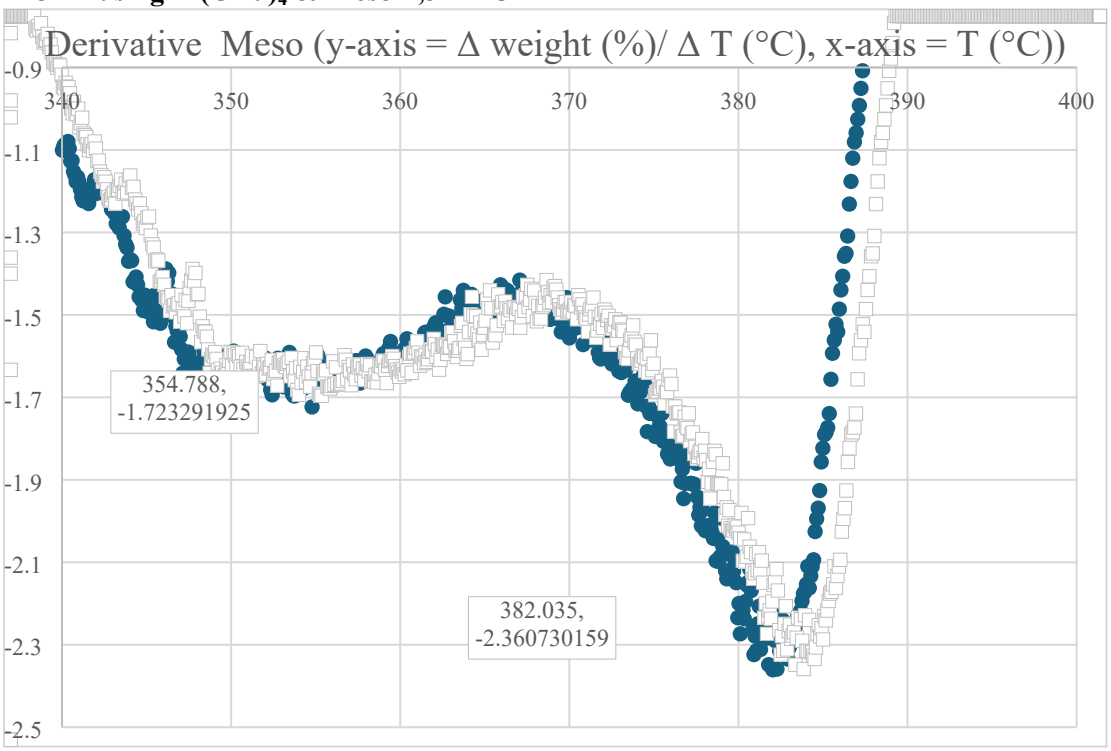


TGA (original curve in paper)

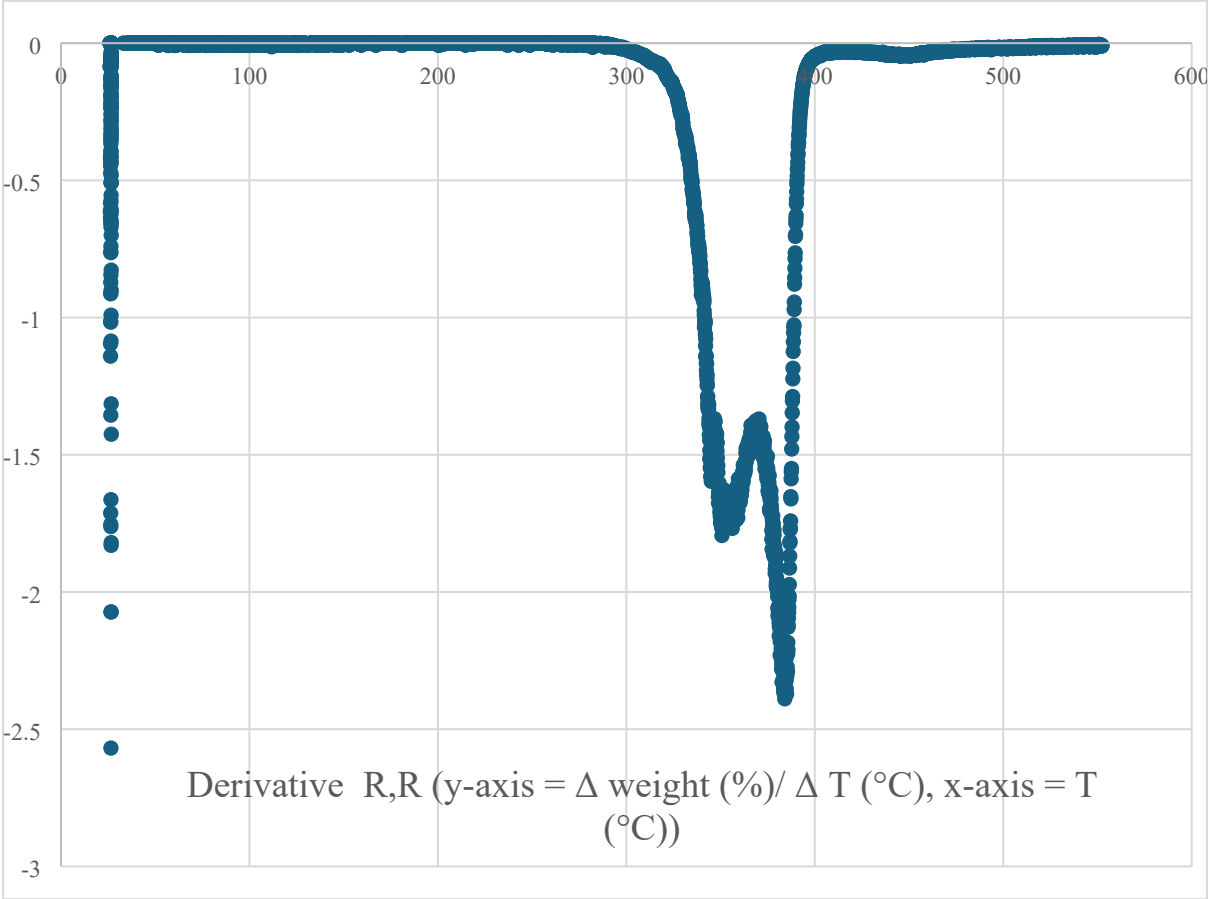
P23BT using $Ti(OBu)_4$ & meso-2,3-BDO: derivative of TGA



P23BT using $Ti(OBu)_4$ & Meso-2,3-BDO: derivative of TGA ZOOM



P23BT using $Ti(OBu)_4$ & R,R-2,3-BDO: derivative of TGA



P23BT using $Ti(OBu)_4$ & R,R-2,3-BDO: derivative of TGA ZOOM