

## Supporting Information for

# An aromatic/aliphatic polyester prepared *via* ring-opening polymerisation and its remarkably selective and cyclable depolymerisation to monomer

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## Table of Contents

Table S1 Polymerisation of 2,3-DHB using Sn(oct) <sub>2</sub>	S2
Table S2 Polymerisation of 2,3-DHB using MeAl[salen]	S2
Table S3 Polymerisation of 2,3-DHB using organocatalysts	S2
Table S4 Rate of 2,3-DHB polymerisation	S3
Figure S1 Catalysts attempted for 2,3-DHB polymerisation	S3
Figure S2 <sup>1</sup> H (bottom) and <sup>13</sup> C{ <sup>1</sup> H} (top) NMR spectra of P2HEB	S3
Effect of temperature on polymer-monomer equilibrium	S4
Table S5 Polymerisation of P(L-LA <sub>n</sub> - <i>b</i> -2HEB <sub>m</sub> )	S4
Table S6 Polymerisation of P(L-LA <sub>n</sub> - <i>b</i> -2HEB <sub>m</sub> -L-LA <sub>n</sub> )	S4
Figure S3 P(L-LA) methine region for P(L-LA <sub>n</sub> - <i>b</i> -3HES <sub>m</sub> - <i>b</i> -L-LA <sub>n</sub> ) where n = 100, m = 40 (top left); n = 100, m = 200 (top right); and n = 20, m = 200 (bottom). • = residual lactide, * = residual CH <sub>2</sub> Cl <sub>2</sub>	S5
Table S7 Thermal decomposition on P2HEB and copolymers	S5
Figure S4 TGA traces for P2HEB and copolymers with L-lactide	S6
Depolymerisation of P2HEB with MeAl[salen]	S6
Figure S5 <sup>1</sup> H NMR spectra for depolymerisation of P2HEB at 60°C at 0h, 2h, 6h and 1h.	S7
Table S8 Depolymerisation of P2HEB catalysed by MeAl[salen] at 60°C	S7
Concentration dependent reversible polymerisation of 2,3-DHB	S7
Figure S6 Expanded GPC chromatograms (15 and 30 minutes) for concentration dependent reversible polymerisation shown in Figure 1	S8
Depolymerisation of P(3HB- <i>b</i> -2HEB) with MeAl[salen]	S8
Figure S7 <sup>1</sup> H NMR spectra of crude samples for synthesis of P3HB (bottom), P(3HB- <i>b</i> -2HEB) (middle) and depolymerisation of copolymer (top) in CDCl <sub>3</sub> , * = residual solvent	S9
Table S9 Determination of [2,3-DHB] <sub>eq</sub> by ROP with MeAl[salen] at 60°C in toluene	S9
Table S10 Determination of [2,3-DHB] <sub>eq</sub> by depolymerisation of P2HEB with MeAl[salen] at 60°C in C <sub>6</sub> D <sub>6</sub>	S9
Table S11 Thermal properties of P2HEB and P(l-LA- <i>b</i> -2HEB- <i>b</i> -l-LA)	S10
References	S10

**Table S1** Polymerisation of 2,3-DHB using Sn(oct)<sub>2</sub><sup>a</sup>

Temperature (°C)	Time (h)	Conversion <sup>b</sup> (%)	M <sub>n,th</sub> <sup>c</sup>	M <sub>n</sub> <sup>b</sup>	Đ <sup>d</sup>
70	3	0	-	-	-
120	3	58	9060	8300	1.23
120	6	61	10100	11400	1.44

<sup>a</sup> Polymerisation of 2,3-DHB in toluene with [2,3-DHB]<sub>0</sub>: [Sn]<sub>0</sub>: [BnOH]<sub>0</sub> = 100:0.5:1. <sup>b</sup> Determined by <sup>1</sup>H NMR spectroscopy. <sup>c</sup> M<sub>n,th</sub> = ([2,3-DHB]<sub>0</sub>/[BnOH]<sub>0</sub>) × % conversion × MW<sub>2,3-DHB</sub>. <sup>d</sup> Determined by gel permeation chromatography.

**Table S2** Polymerisation of 2,3-DHB using MeAl[salen]<sup>a</sup>

Temperature (°C)	Solvent	Time (h)	Conversion <sup>b</sup> (%)	M <sub>n,th</sub> <sup>c</sup>	M <sub>n</sub> <sup>b</sup>	Đ <sup>d</sup>
120	neat	3	66	10960	11000	1.60
120	toluene	3	56	9230	9310	1.76
70	neat	1	64	10580	10760	1.13
70	toluene	3	75	12370	12510	1.16
70	toluene	3	75	12370	14240	1.17

<sup>a</sup> Polymerisation of 2,3-DHB with [2,3-DHB]<sub>0</sub>: [Al]<sub>0</sub>: [BnOH]<sub>0</sub> = 100:1:1. <sup>b</sup> Determined by <sup>1</sup>H NMR spectroscopy. <sup>c</sup> M<sub>n,th</sub> = ([2,3-DHB]<sub>0</sub>/[BnOH]<sub>0</sub>) × % conversion × MW<sub>2,3-DHB</sub>. <sup>d</sup> Determined by gel permeation chromatography.

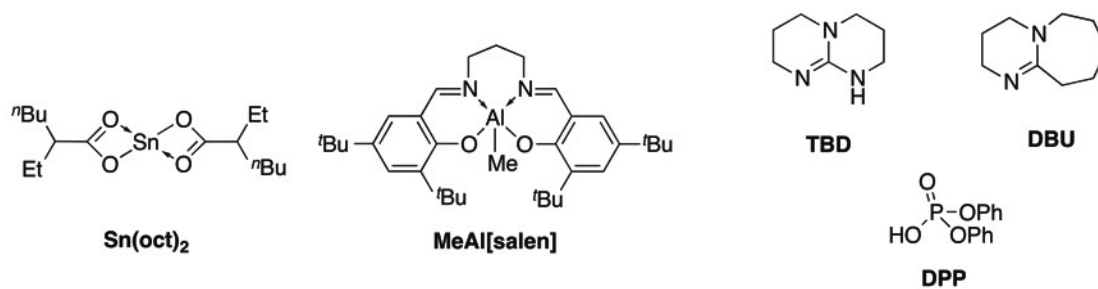
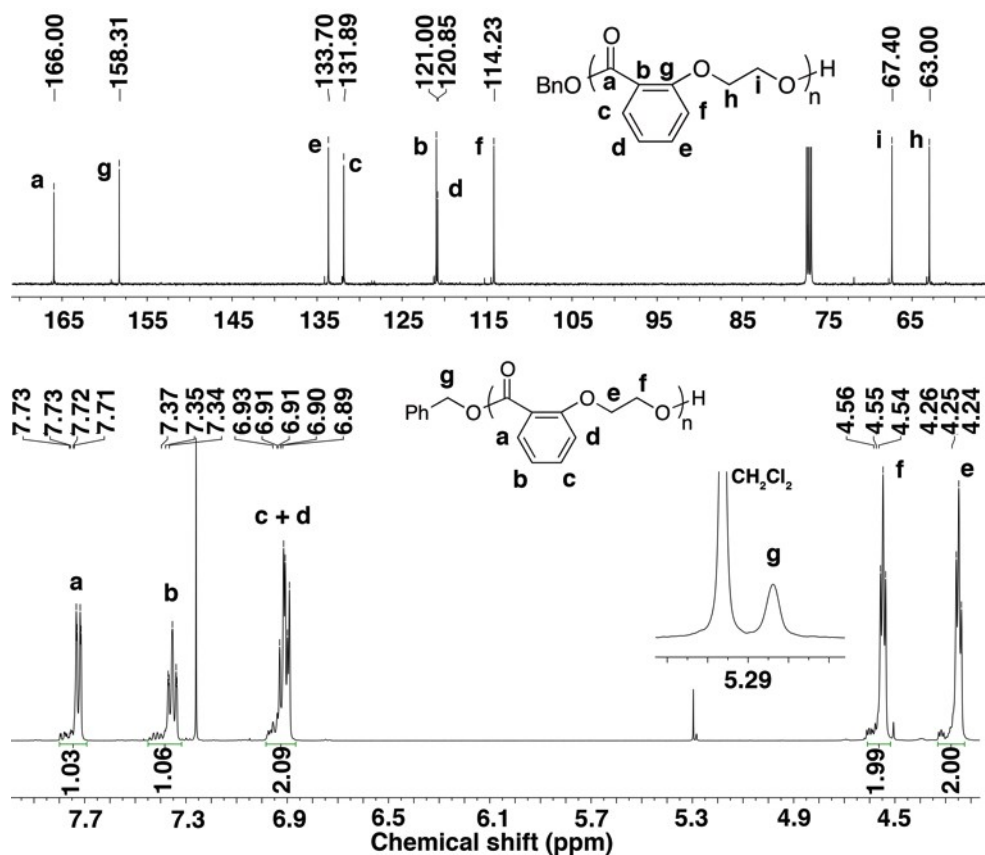
**Table S3** Polymerisation of 2,3-DHB using organocatalysts

Catalyst	Solvent	[M] <sub>0</sub>	[M] <sub>0</sub> / [Al] <sub>0</sub>	Temp. (°C)	Time (min)	Conv. <sup>a</sup> (%)	M <sub>n,th</sub> <sup>b</sup>	M <sub>n</sub> <sup>a</sup>	Đ <sup>c</sup>
DBU	toluene	0.52	100	22	180	0	-	-	-
	toluene	1.30	100	22	180	0	-	-	-
DPP	toluene	1.30	100	22	360	0	-	-	-
	toluene	1.30	100	50	360	0	-	-	-
TBD	toluene	0.52	100	22	190	51	7990	6370	1.14
	toluene	1.30	100	22	60	80	13240	13130	1.14
	toluene	2.38	100	22	30	89	14720	14660	1.19
	toluene	1.30	200	22	240	78	24080	22450	1.15
	toluene	1.30	500	22	360	29	23620	14390	1.42
	toluene	1.30	100	50	60	46	7660	8710	1.11
	CH <sub>2</sub> Cl <sub>2</sub>	1.30	100	22	120	60	9960	9760	1.14

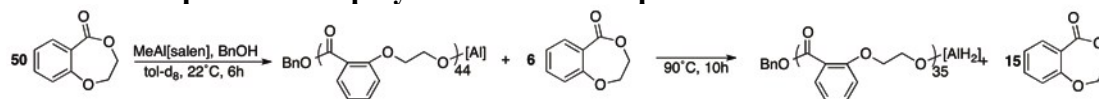
<sup>a</sup> Determined by <sup>1</sup>H NMR spectroscopy. <sup>b</sup> M<sub>n,th</sub> = ([2,3-DHB]<sub>0</sub>/[BnOH]<sub>0</sub>) × % conversion × MW<sub>2,3-DHB</sub>. <sup>c</sup> Determined by gel permeation chromatography.

**Table S4** Rate of 2,3-DHB polymerisation

Catalyst	Temperature (°C)	Concentration (M)	Rate (min <sup>-1</sup> )
MeAl[salen]	60	5.3	0.010
	50	5.3	0.007
	22	5.3	0.005
TBD	22	2.4	0.045
	22	1.4	0.016
	22	0.5	0.003

**Figure S1** Catalysts attempted for 2,3-DHB polymerisation**Figure S2** <sup>1</sup>H (bottom) and <sup>13</sup>C{<sup>1</sup>H} (top) NMR spectra of P2HEB in CDCl<sub>3</sub>

### Effect of temperature on polymer-monomer equilibrium



In a glovebox, MeAl[salen] (9.3 mg, 0.02 mmol), 2,3-DHB (140 mg, 0.85 mmol), benzyl alcohol (1.8  $\mu$ L, 0.02 mmol) and toluene- $d_8$  (300 mg) were added to a Young's tap NMR tube. The NMR tube was then left at room temperature for six hours.  $^1\text{H}$  NMR spectroscopy revealed that the polymerisation had reached 88% conversion ( $n = 44$ ). The NMR tube was then heated to  $90^\circ\text{C}$  for 10 hours.  $^1\text{H}$  NMR spectroscopy revealed that polymer conversion had decreased to 70% ( $n = 35$ ). Conversion could be increased by leaving the reaction to cool.

**Table S5** Polymerisation of P(L-LA $_n$ -*b*-2HEB $_m$ )

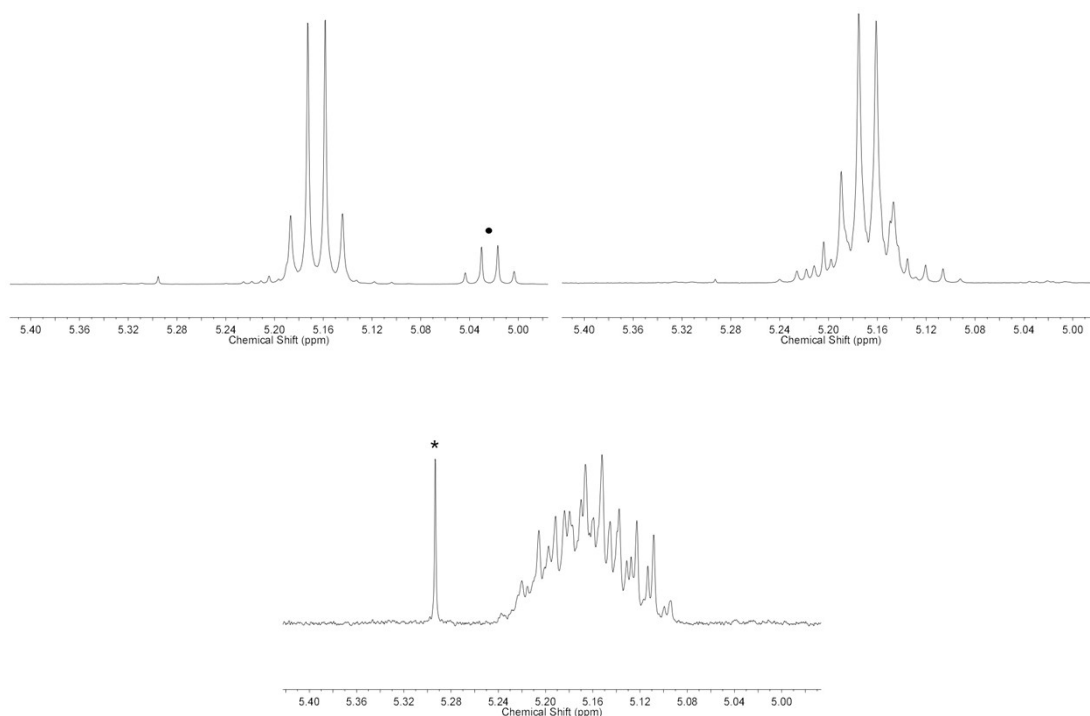
Target		Experimental <sup>a</sup>		$M_{n,th}$ <sup>b</sup>	$M_n$ <sup>a</sup>	$\bar{D}$ <sup>c</sup>
n	m	n	m			
100	20	100	18	10030	10990	1.10
100	100	100	93	20830	12380	1.13
20	100	20	100	15390	10630	1.15

<sup>a</sup> Determined by  $^1\text{H}$  NMR spectroscopy. <sup>b</sup>  $M_{n,th} = (n \times \% \text{ conv.}_{LA} \times 144.13) + (m \times \% \text{ conv.}_{2,3\text{-DHB}} \times 164.16) + 108.14$ . <sup>c</sup> Determined by gel permeation chromatography.

**Table S6** Polymerisation of P(L-LA $_n$ -*b*-2HEB $_m$ -*b*-L-LA $_n$ )

Target		Experimental <sup>a</sup>		$M_{n,th}$ <sup>b</sup>	$M_n$ <sup>a</sup>	$\bar{D}$ <sup>c</sup>
n	m	n	m			
100	20	89	17	15690	17900	1.08
100	100	100	85	28440	22400	1.13
20	100	20	86	16750	13460	1.16

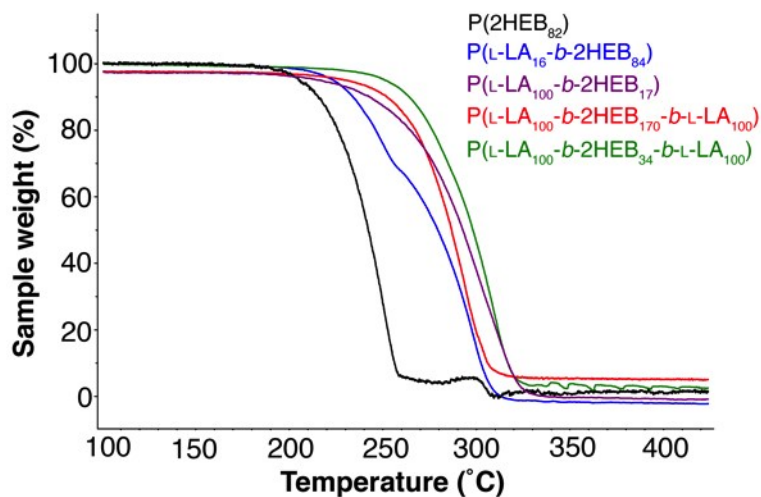
<sup>a</sup> Determined by  $^1\text{H}$  NMR spectroscopy. <sup>b</sup>  $M_{n,th} = (n \times \% \text{ conv.}_{LA} \times 144.13) + (m \times \% \text{ conv.}_{2,3\text{-DHB}} \times 164.16) + 76.09$ . <sup>c</sup> Determined by gel permeation chromatography.



**Figure S3** P(L-LA) methine region for P(L-LA<sub>n</sub>-*b*-3HEB<sub>m</sub>-*b*-L-LA<sub>n</sub>) where n = 100, m = 40 (top left); n = 100, m = 200 (top right); and n = 20, m = 200 (bottom). • = residual lactide, \* = residual CH<sub>2</sub>Cl<sub>2</sub>.

**Table S7** Thermal decomposition on P2HEB and copolymers

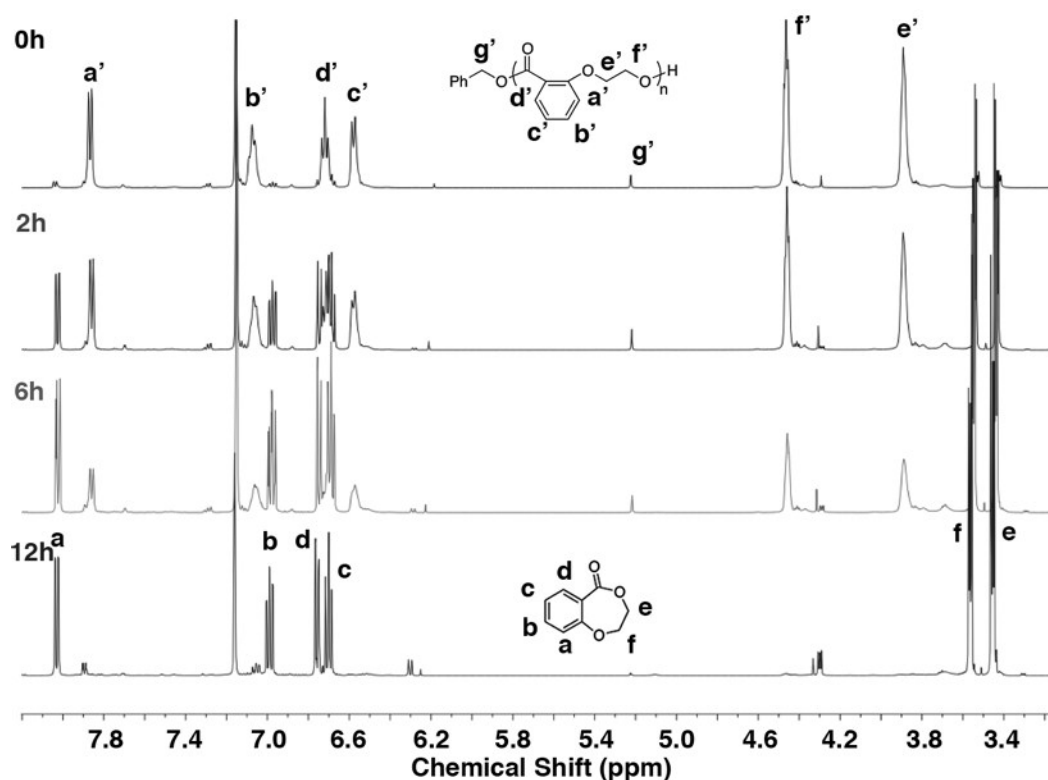
Polymer	$T_{d,onset}$ (°C)	$T_{d,endpoint}$ (°C)
P2HEB <sub>82</sub>	219.3	262.8
P(L-LA <sub>100</sub> - <i>b</i> -2HEB <sub>170</sub> - <i>b</i> - L-LA <sub>100</sub> )	251.2	310.7
P(L-LA <sub>100</sub> - <i>b</i> -2HEB <sub>34</sub> - <i>b</i> - L-LA <sub>100</sub> )	278.7	319.3
P(L-LA <sub>100</sub> - <i>b</i> -2HEB <sub>17</sub> )	273.3	321.2
P(L-LA <sub>16</sub> - <i>b</i> -2HEB <sub>84</sub> )	263.1	307.8
P(3HB <sub>50</sub> - <i>b</i> -2HEB <sub>50</sub> )	244.1	338.0



**Figure S4** TGA traces for P2HEB and copolymers with L-lactide

#### **Depolymerisation of P2HEB with MeAl[salen]**

In a glovebox, P2HEB (41 mg, 0.005 mmol) and MeAl[salen] (2.7 mg, 0.005 mmol) in C<sub>6</sub>D<sub>6</sub> (0.4 mL) were added to a J. Young NMR tube. The NMR tube was sealed and heated at 70°C for 12h. After 12h, the NMR tube was cooled to room temperature and <sup>1</sup>H NMR analysis indicated the solution contained a mixture of 2,3-DHB:P2HEB = 92:8.



**Figure S5**  $^1\text{H}$  NMR spectra for depolymerisation of P2HEB at  $60^\circ\text{C}$  at 0h, 2h, 6h and 12h.

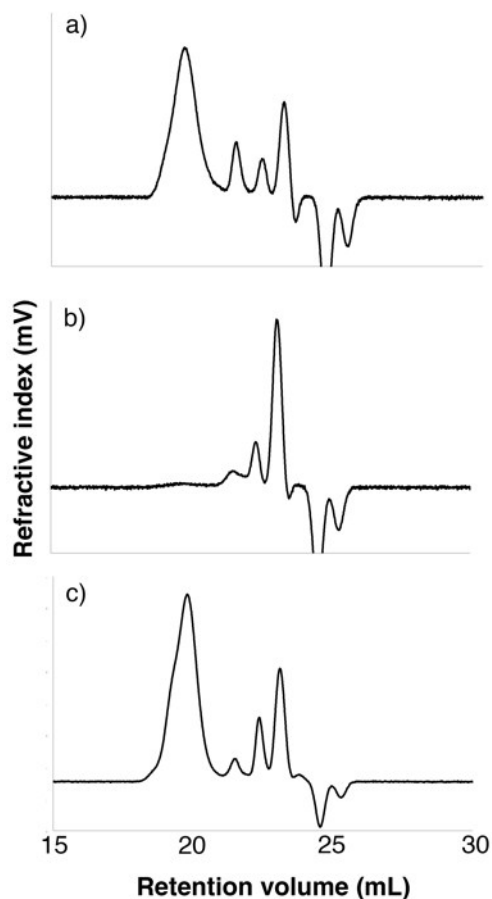
**Table S8** Depolymerisation of P2HEB catalysed by  $\text{MeAl}[\text{salen}]$  at  $60^\circ\text{C}$ <sup>a</sup>

Time (h)	Conversion (%) <sup>b</sup>
2	39
4	59
12	92

<sup>a</sup> Depolymerisation of P2HEB with  $\text{MeAl}[\text{salen}]$  with  $[\text{M}]_0 = 0.17\text{M}$  at  $60^\circ\text{C}$  in toluene.  $[\text{M}]_0 = (\text{mass polymer} / \text{MW}_{2,3\text{-DHB}}) / \text{volume toluene}$ . <sup>b</sup> Determined by  $^1\text{H}$  NMR spectroscopy.

### Concentration dependent reversible polymerisation of 2,3-DHB

In a glovebox, 2,3-DHB (116 mg, 0.71 mmol),  $\text{MeAl}[\text{salen}]$  (3.8 mg, 0.01 mmol),  $\text{BnOH}$  ( $0.7 \mu\text{L}$ , 0.01 mmol) and toluene (150 mg) were added to an ampoule. The ampoule was sealed and heated to  $60^\circ\text{C}$  for 6h. A sample was removed *via* syringe under nitrogen. GPC and  $^1\text{H}$  NMR spectroscopy analysis of the crude sample indicated 82% conversion to polymer. Dry toluene (3 mL) was then added to the ampoule and the reaction was stirred at  $60^\circ\text{C}$  for 16h. A sample was removed *via* syringe under nitrogen. GPC and  $^1\text{H}$  NMR spectroscopy analysis of the crude sample indicated conversion of 2,3-DHB to polymer had decreased to 6%. The reaction was then concentrated under reduced pressure and toluene ( $120 \mu\text{L}$ ) was then added. The reaction was stirred at  $60^\circ\text{C}$  for 6h. A sample was removed *via* syringe under nitrogen. GPC and  $^1\text{H}$  NMR spectroscopy analysis of the crude sample indicated 84% conversion to polymer.

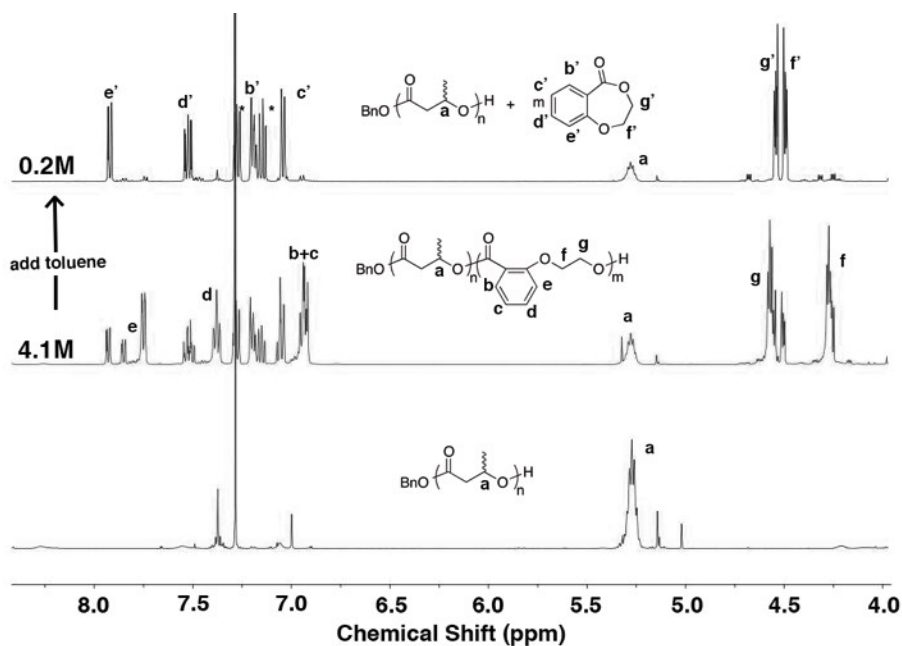


**Figure S6** Expanded GPC chromatograms (15 and 30 minutes) for concentration dependent reversible polymerisation shown in Figure 1

**Depolymerisation of P(3HB-*b*-2HEB) with MeAl[salen]**

P(3HB-*b*-2HEB) was prepared as described previously. In place of quenching, after two hours of 2,3-DHB polymerisation, toluene was added so that apparent  $[2,3\text{-DHB}]_0 = 0.2\text{M}$  and stirred at  $60^\circ\text{C}$  for 12 hours. After 12h, several drops of MeOH were added to the reaction and volatiles were removed under reduced pressure.  $^1\text{H}$  NMR spectroscopy indicated that P2HEB:2,3-DHB = 0.91:0.09. Analysis by gel permeation showed a decrease in polymer molecular weight, consistent with depolymerisation.





**Figure S7**  $^1\text{H}$  NMR spectra of crude samples for synthesis of P3HB (bottom), P(3HB-*b*-2HEB) (middle) and depolymerisation of copolymer (top) in  $\text{CDCl}_3$ , \* = residual solvent

**Table S9** Determination of  $[\text{2,3-DHB}]_{\text{eq}}$  by ROP with  $\text{MeAl}[\text{salen}]$  at  $60^\circ\text{C}$  in toluene<sup>a</sup>

$[\text{2,3-DHB}]_0$ (M)	Composition <sup>b</sup> (%)		$[\text{2,3-DHB}]_{\text{eq}}$ (M)
	2,3-DHB	P2HEB	
3.6	10	90	0.36
3.9	9	91	0.35
4.5	8	92	0.36

<sup>a</sup> Depolymerisation of P2HEB in toluene at  $60^\circ\text{C}$  for six hours with  $[\text{2,3-DHB}]_0:[\mathbf{58}]_0:[\text{BnOH}]_0 = 50:1:1$ . <sup>b</sup> Determined by  $^1\text{H}$  NMR spectroscopy. <sup>c</sup>  $[\text{2,3-DHB}]_{\text{eq}} = (100 - \% \text{ conv.})/100 \times [\text{2,3-DHB}]_0$ .

**Table S10** Determination of  $[\text{2,3-DHB}]_{\text{eq}}$  by depolymerisation of P2HEB with  $\text{MeAl}[\text{salen}]$  at  $60^\circ\text{C}$  in  $\text{C}_6\text{D}_6$ <sup>a</sup>

$[\text{2,3-DHB}]_0$ <sup>b</sup> (M)	Composition <sup>c</sup> (%)		$[\text{2,3-DHB}]_{\text{eq}}$ <sup>d</sup> (M)
	2,3-DHB	P2HEB	
1.88	19	81	0.358
1.37	26	74	0.355
0.99	34	66	0.355

<sup>a</sup> Depolymerisation of P2HEB in  $\text{C}_6\text{D}_6$  at  $60^\circ\text{C}$  for 12 hours with  $\text{MeAl}[\text{salen}]$ . <sup>b</sup>  $[\text{2,3-DHB}]_0 = (\text{mass P2HEB}/164.16)/\text{volume C}_6\text{D}_6$ . <sup>c</sup> Determined by  $^1\text{H}$  NMR spectroscopy. <sup>d</sup>  $[\text{2,3-DHB}]_{\text{eq}} = [(\% \text{ conv.}/100) \times (\text{mass P2HEB}/164.16)]/\text{volume toluene}$ .

**Table S11** Thermal properties of P2HEB and P(l-LA<sub>100</sub>-b-2HEB<sub>170</sub>-b-l-LA<sub>100</sub>)

Polymer	$T_g$ (°C)	$T_m$ (°C)	$T_{d,onset}$ (°C)	$T_{d,endpoint}$ (°C)
P(l-LA <sub>100</sub> -b-2HEB <sub>170</sub> -b-l-LA <sub>100</sub> )	51.3	124.8	251.2	310.7
P2HEB <sub>82</sub>	-	78.2	219.3	262.8

<sup>a</sup> DSC samples were heated at 10°C min<sup>-1</sup> to 150°C and held for 10 minutes to remove residual solvent and cooled to room temperature at 10°C min<sup>-1</sup>.  $T_g$  and  $T_m$  were obtained on the second heating cycle.

## References

1. D. A. Atwood, M. S. Hill, J. A. Jegier and D. Rutherford, *Organometallics*, 1997, **16**, 2659-2664.
2. P. Hornnirun, E. L. Marshall, V. C. Gibson, R. I. Pugh and A. J. P. White, *Proc. Natl. Acad. Sci. U. S. A.*, 2006, **103**, 15343-15348.