Electronic Supporting Information (ESI) for

Tuning Thermal Properties and Microphase Separation in Aliphatic Polyester ABA Copolymers

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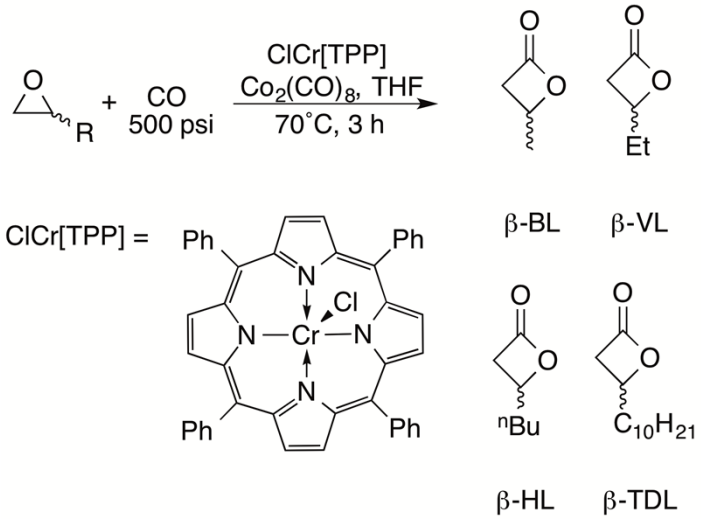
Table of Contents

Table S1 Carbonylation of terminal epoxyalkanes using ClCr[TPP]



R	[epoxide]/[catalyst]	mass epoxide (g)	Conversion (%)
Et	4000	5.8	> 99
^{n}Bu	2000	4.0	> 99
$C_{10}H_{21}$	1000	3.1	> 99

Table S2 Homopolymerisation of alkyl-substituted β-lactones at 120˚C

Monomer	Time (h)	Conversion (%)[b]	$M_{n,th}$[c]	M_n[d]	Đ[d]
β-VL	6	> 99	10120	9410	1.11
β-HL	6	> 99	12920	10760	1.07
β-TDL	12	> 99	21340	17430	1.05

[a] Polymerisation conducted in toluene at 120˚C with $[Al]_0/[M]_0:[BnOH]_0$ = 1:100:1. [b]

Conversion determined by ^{1}H NMR spectroscopy. [c] $M_{n,th}$ = conversion × MW monomer + MW endgroup. [d] M_n and Đ determined by GPC.

Table S3 Homopolymerisation of alkyl – substituted β-lactones using 3[a]

Monomer	Temperature (˚C)	Time (h)	Conversion (%)[b]	$M_{n,th}$[c]	M_n[d]	Đ[d]
β-VL	22	48	-	-	-	-
	85	18	>99	10120	8300	1.05
	120	6	>99	10120	9530	1.08
β-HL	22	48	-	-	-	-
	85	18	>99	12920	10250	1.04
	120	6	96	12410	9860	1.07

[a] Polymerisation conducted in toluene with $[Al]_0/[M]_0:[BnOH]_0$ = 1:100:1. [b] Conversion determined by ^{1}H NMR spectroscopy. [c] $M_{n,th}$ = conversion × MW monomer + MW endgroup. [d] M_n and Đ determined by GPC.

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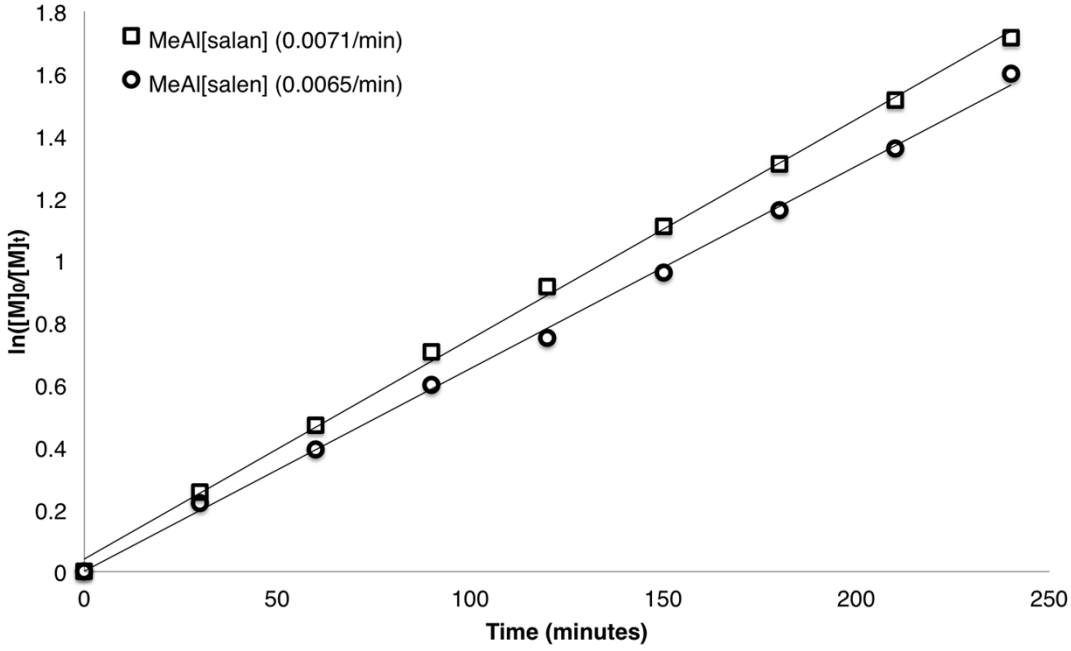

Figure S1 Kinetic plot of β-VL using **1** (○□ and **3** (□).

Table S4 Higher molecular weight P(3HP) and P(3HH) using 1[a]

Monomer	$[M]_0/[Al]_0$	Temperature (˚C)	Time (h)	Conv. (%)[b]	$M_{n,th}$[c]	M_n[d]	Đ[d]
β-VL	200	85	40	95	19130	13020	1.10
	500	85	72	> 99	50170	27890	1.13
		120	48	> 99	50170	26680	1.21
β-HL	200	85	40	> 99	25740	19380	1.08
	500	85	72	78	50010	27600	1.08
		120	48	89	56820	23870	1.10

[a] Polymerisation conducted in toluene. [b] Conversion determined by ^{1}H NMR spectroscopy. [c] $M_{n,th}$ = conversion × MW monomer + MW endgroup. [d] M_n and Đ determined by GPC.

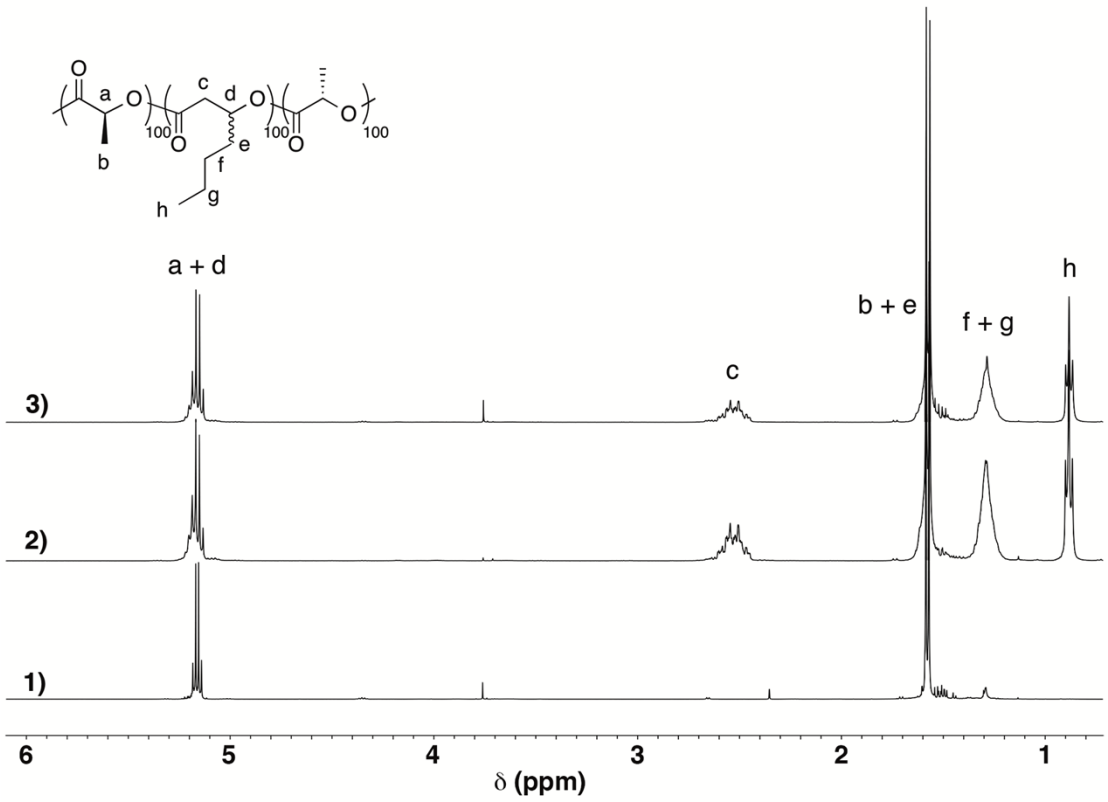

Figure S2 ^{1}H NMR spectra of 1) P(L-LA$_{100}$), 2) P(L-LA$_{100}$-*b*-3HH$_{100}$) and 3) P(L-LA$_{100}$-*b*-3HH$_{100}$-*b*- L-LA$_{100}$).

Table S5 Effect of Temperature of Monomer Addition and Polymer Dispersites[a]

Sample	Monomer addition temperature	
	25[b]	85[c]
P(L-LA$_{200}$)	1.09	1.09
P(L-LA$_{200}$-*b*-3HH$_{20}$)	1.10	1.10
P(L-LA$_{200}$-*b*-3HH$_{20}$-*b*-L-LA$_{200}$)	1.30	1.14

[a] Sequential addition block copolymerisation. [b] Monomer added in glovebox at room temperature. [c] Monomer added in toluene at 85˚C.

Table S6 DSC analysis of P(L-LA$_n$-*b*-3HB$_m$-*b*-L-LA$_n$)

n	m	T_g (˚C)	T_m (˚C)	T_c (˚C)
10	100	0.7	-	-
20	100	9.9	-	-
50	100	21.9	138.8	108.6
75	100	23.3	155.6	99.2
100	100	28.9	152.2	101.6
100	75	34.8	153.6	103.0
100	50	43.9	157.7	104.4
100	20	51.4	159.6	111.9
100	10	52.4	162.4	104.4

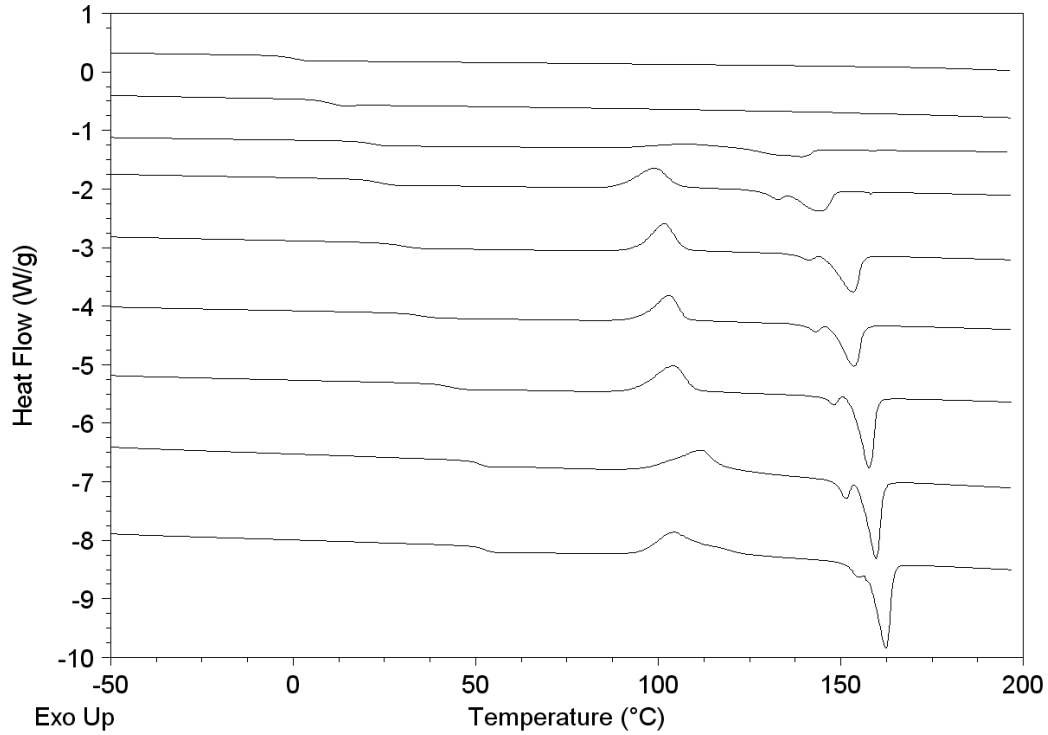

Figure S3 DSC thermograms for P(L-LA$_n$-*b*-3HB$_m$-*b*-L-LA$_n$) (increasing PLA% top to bottom). Heating rate = 10˚C min^{-1}.

Table S7 DSC analysis of P(L-LA$_n$-*b*-3HP$_m$-*b*-L-LA$_n$)

n	m	T_g (˚C)	T_m (˚C)	T_c (˚C)
10	100	-14.8	-	-
20	100	-6.3	-	-
50	100	1.5	130.7	81.0
75	100	19.0	145.0	86.5
100	100	19.0	152.0	88.0
100	75	27.0	153.5	88.2
100	50	31.5	154.9	82.5
100	20	46.3	155.4	105.5
100	10	53.5	160.1	106.5

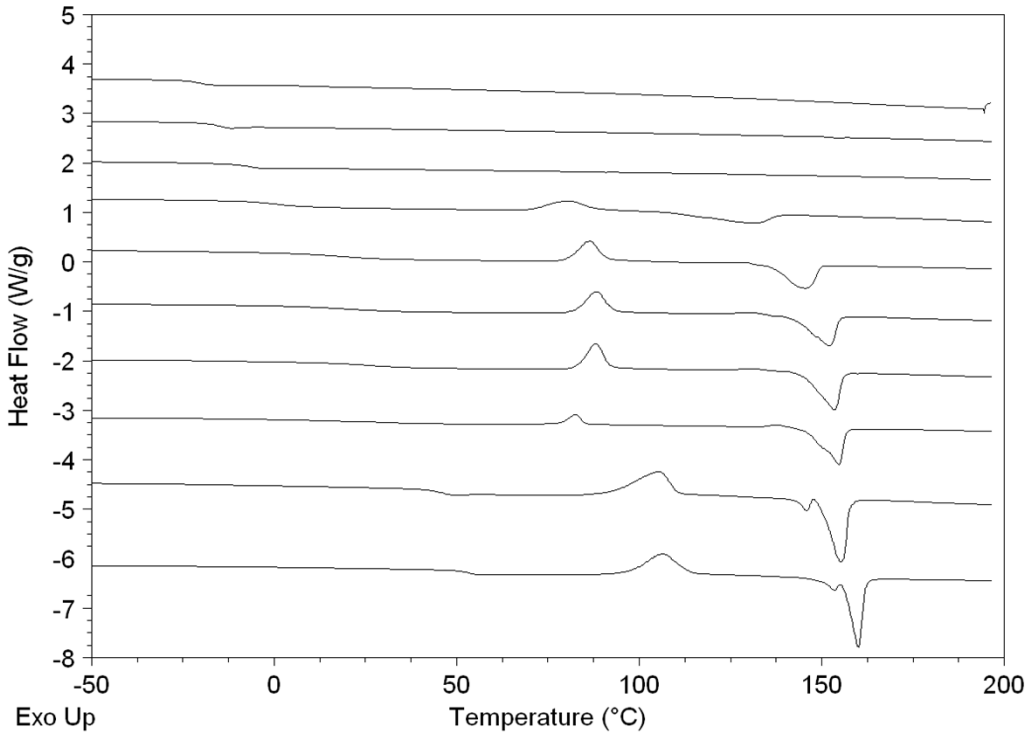

Figure S4 DSC thermograms for P(L-LA$_n$-*b*-3HP$_m$-*b*-L-LA$_n$) (increasing PLA% top to bottom). Heating rate = 10˚C min^{-1}.

Table S8 DSC analysis of P(L-LA$_n$-*b*-3HH$_m$-*b*-L-LA$_n$)

n	m	T_g (˚C)	T_m (˚C)	T_c (˚C)
10	100	-25.7	-	-
20	100	-21.1	-	-
50	100	-23.5	130.2	64.2
75	100	-25.1	141.0	73.0
100	100	-24.4 45.9	152.0	82.5
100	75	-21.4 40.5	153.2	94.2
100	50	40	156.5	89.3
100	20	46.9	157.0	93.5
100	10	47.4	157.0	95.2

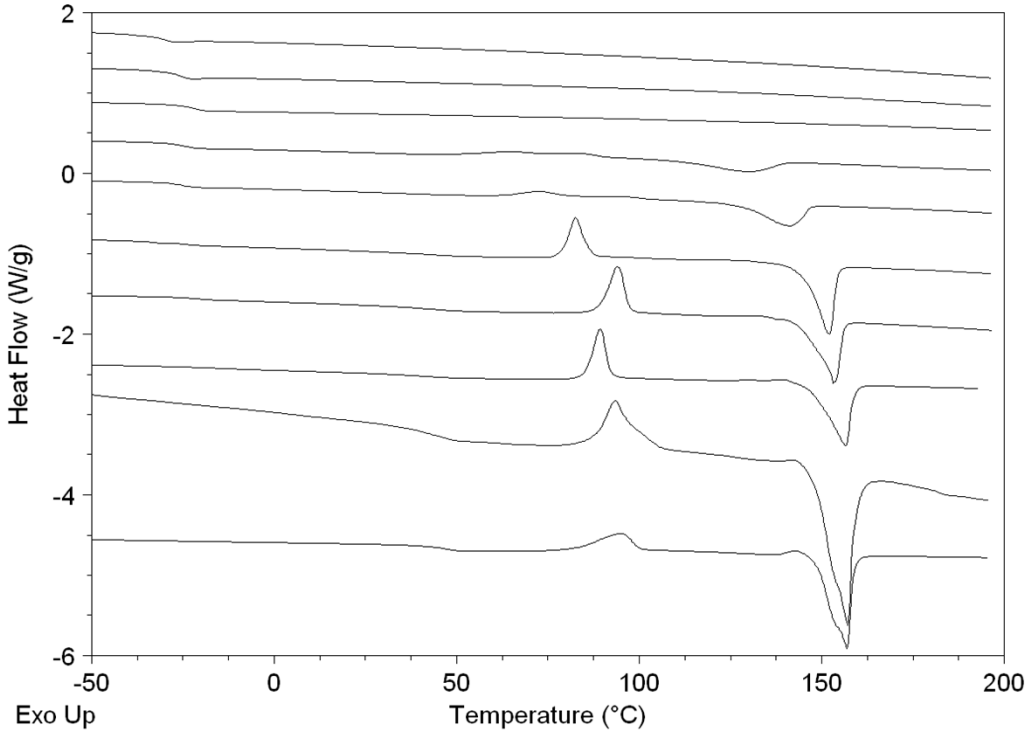

Figure S5 DSC thermograms for P(L-LA$_n$-*b*-3HH$_m$-*b*-L-LA$_n$) (increasing PLA% top to bottom). Heating rate = 10˚C min^{-1}.

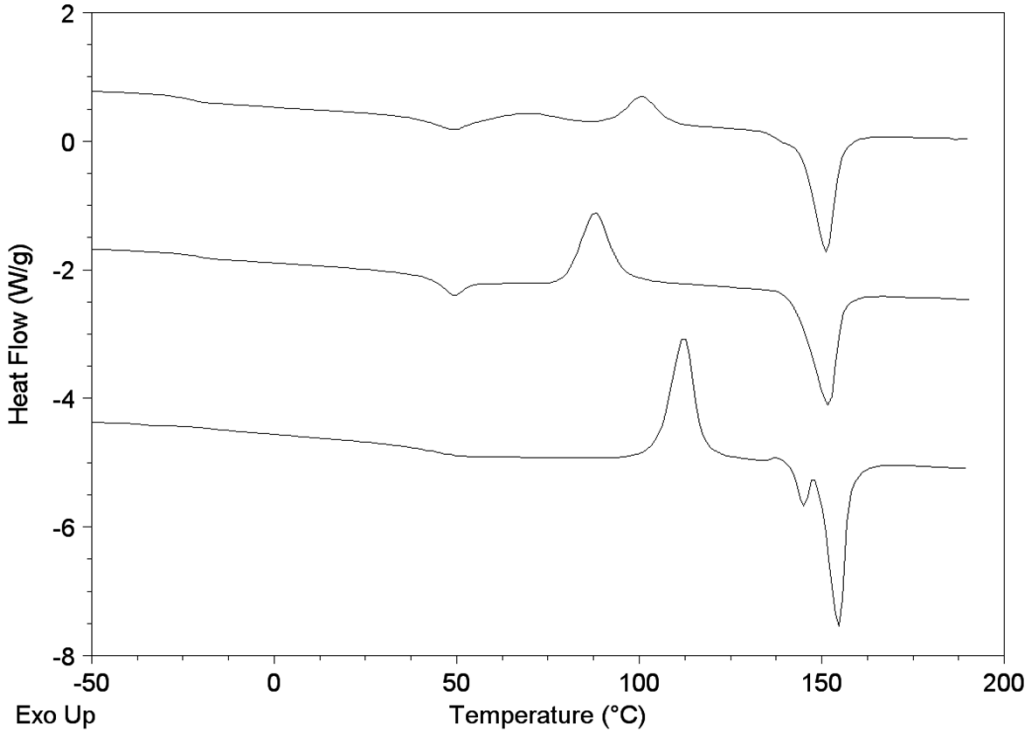

Figure S6 DSC thermograms for P(L -LA_{100}-*b*-3HH_{100}-*b*-L-LA_{100}) (top), P(L -LA_{100}-*b*-3HH_{75}-*b*-L-LA_{100}) and P(L -LA_{100}-*b*-3HH_{50}-*b*-L-LA_{100}) (bottom). Heating rate = 30˚C min^{-1}.

Table S9 Homopolymerisation of β-BL with 1[a]

T (˚C)	Time (h)	Conv. (%)[b]	$M_{n,th}$[c]	M_n[d]	Đ[d]
70	6	92	7900	6400	1.03
85	6	>99	8720	7570	1.04

[a] Polymerisation conducted in toluene with $[Al]_0/[M]_0:[BnOH]_0$ = 1:100:1. [b] Conversion determined by ^1H NMR spectroscopy. [c] $M_{n,th}$ = conversion × MW monomer + MW endgroup. [d] M_n and Đ determined by GPC.

GPC Details: In some cases, solubility became an issue, particularly polymer samples with higher amounts of semi-crystalline PLA. While all homopolymer samples as well as AB block copolymers were dissolved in THF alone, several ABA block copolymer samples would not fully dissolve. ABA block copolymers where n < 100 were dissolved in THF while samples where n = 100 were dissolved in $CHCl_3$ and run with THF as an eluent.