Supporting Information

For

Epoxide-Modulated Ring-Opening Polymerization of *β*-Butyrolactone

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General methods

All manipulations involving air- and/or water-sensitive compounds were carried out in a glove box or with the standard Schlenk techniques under dry nitrogen. Carbon monoxide (99.95%) was purchased from Dalian Institute of Special Gases and used as received. *R*-propylene epoxide (*R*-PO), *S*-propylene epoxide (*S*-PO), phenyl glycidyl ether (PGE), cyclohexene oxide (CHO), 4-vinylcyclohexene oxide (VCHO), cyclopentene oxide (CPO), 3,4-epoxytetrahydrofuran (COPO) and styrene oxide (SO), *rac*-*β*-butyrolactone (*rac*-BL) were purchased from Acros and dried over calcium hydride. *R*-*β*-butyrolactone (*R*-BL, 97.5 *ee*%) and *S*-*β*-butyrolactone (*S*-BL, 97.5 *ee*%) were synthesized according to literature report.[1] All lactones were distilled over calcium hydride under dry nitrogen. Dichloromethane (DCM) was distilled from calcium hydride under nitrogen. Toluene was distilled from sodium/benzophenone under nitrogen. All other chemicals and reagents were purchased from commercial sources and used as received.

NMR Experiments. ^{1}H and ^{13}C NMR spectra were recorded on Bruker 600 MHz and Vaian DLG400 spectrometer. Their peak frequencies were referenced versus an internal standard (TMS) shift at 0 ppm for ^{1}H NMR and against the solvent, chloroform-*d* at 77.0 ppm for ^{13}C NMR, respectively.

Mass Spectrometry. All high-resolution mass spectrums (HRMS) were measured on a Time-of-flight mass spectrometer (Agilent, USA) equipped with the Dual spray ESI/APCI ion source.

Matrix-assisted LASER Desorption/ionization-time Of Flight Spectroscopy (MALDI-TOF) were performed on Ultraflextreme MALDI TOF mass spectrometer (Bruker Daltonik GmbH, Bremen, Germany) equipped with a 355 nm solid state laser. An accelerating voltage of 20 kV was applied.

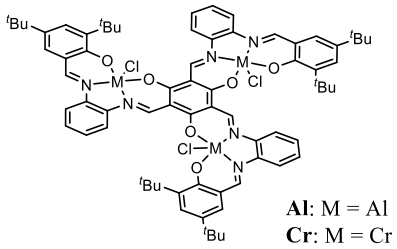
Size exclusion chromatography (SEC). Molecular weights and molecular weight distributions of polymers were measured on an Agilent 1260 instrument coupled with an Agilent RI detector and equipped with two PL gel columns (5μm MIXED-C 300 × 7.5 mm). The analysis was performed at 30 ºC and a flow rate of 1.0 mL/min, with THF as the eluent according to the solubility of the polymer. The sample concentration was about 0.1%, and the injection volume was 100 μL. The curve was calibrated using monodisperse polystyrene standards covering the molecular weight range from 580 to 460000 Da.

High Performance Liquid Chromatography (HPLC). HPLC was performed on

Agilent 1260 Infinity II Quaternary LC system. Enantiomeric excesses (*ee*) were determined by chiral HPLC (*Regis*, (*R,R*)-Whelk-01, hexane/^{i}PrOH = 95/5, 1.0 mL/min, 22 ºC, 254 nm, t_r = 16 min for (*R*)-enantiomer and 19 min for (*S*)-enantiomer). The chromatograms were processed with Agilent OpenLab CDS software.

Experimental procedures

Catalysts preparation



The Catalysts **Al** and **Cr** were prepared by the previously reported method.[2]

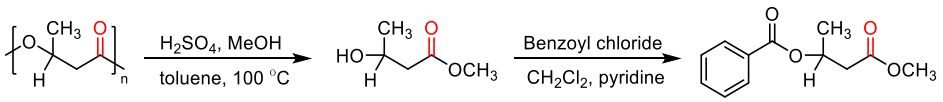
General procedure for polymerization performed with complexes

In an argon-filled glovebox, polymerization was performed in a 10 mL Schlenk flask. Catalyst **Al/Cr** (0.01 mmol, 1.0 equiv) and CHO (2.94 mg, 0.03 mmol, 3.0 equiv) were dissolved in 0.5 mL of dry toluene. The mixture was stirred at the specified temperature for a designated period to form the catalytic system. Subsequently, 0.5 mL of a toluene solution containing *rac*-BL (176 mg, 2 mmol, 200 equiv) was added to the system. The reaction was then transferred to an 80 °C oil bath and allowed to proceed for the indicated time. After cooling to room temperature, a 20 μL aliquot of the reaction mixture was taken, and the monomer conversion was determined by ^{1}H NMR analysis.

Procedures for polymer purification

The crude product dissolved in 5 mL of dichloromethane, then 5 mL 30% H_2O_2 was added, and stirred at room temperature for 12 h. Then organic phase was separated, and precipitated with MeOH.

Procedure for the Alcoholysis and Derivatization of P3HB

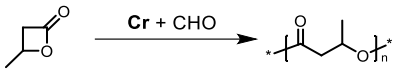


P3HB methanolysis[3]: Under a nitrogen atmosphere, a P3HB sample (100 mg) was dissolved in dry toluene (15 mL) in a flask. To this solution was added 15 mL of a H_2SO_4- methanol solution (3% v/v). The mixture was heated at 100 °C in an oil bath for 12 h. After cooling, saturated aqueous NaCl solution (3 mL) and diethyl ether (15 mL) were introduced, and the mixture was transferred to a separatory funnel. The layers were separated, and the aqueous layer was extracted with diethyl ether. The combined organic phase was washed sequentially with saturated aqueous $NaHCO_3$ and saturated

aqueous NaCl, dried over Na_2SO_4, and concentrated under reduced pressure to afford methyl 3-hydroxybutyrate.

Hydroxyester benzoylation[4]: At room temperature, a solution of methyl 3-hydroxybutanoate in CH_2Cl_2 (0.2 M) was treated successively with pyridine (5.0 equiv.) and benzoyl chloride (2.0 equiv.). The reaction mixture was stirred until thin-layer chromatography (TLC) analysis indicated complete consumption of the starting material (ca. 16 h). The mixture was then washed sequentially with aqueous NaOH (5%, 2 × 5 mL) and aqueous HCl (1 M, 2 × 5 mL). The organic layer was dried over Na_2SO_4, and the solvent was removed under reduced pressure. Purification of the crude product by flash chromatography (silica gel, 2.5 × 16 cm; PE/EtOAc = 10:1, v/v) afforded methyl 3-benzoyloxybutyrate.

Table S1. ROP of BL at various chromium and CHO reaction conditions[a]



Entry	Pre-reaction time (min)	Pre-reaction Temperature (°C)	M_n (kg/mol)[b]	$Đ$[b]
1[c]	---	----	5.7	1.35
2	0	25	22.3	1.88
3	5	25	23.4	1.76
4	15	25	26.2	1.78
5	30	25	24.2	1.63
6	5	80	26.0	1.71
7	15	80	31.1	1.86
8	30	80	32.3	2.11

[a]Reactions performed in *rac*-BL (2 mmol) catalyzed by trimetallic Cr complex in 2.0 M toluene at 80 °C in 25 min in a 10 mL bar bottle, and **Cr** and CHO were reacted prior to the addition of *rac*-BL. Molar ratio of BL/CHO/ **Cr** was 200/3/1. All lactones conversion were >99% based on ^{1}H NMR spectroscopy. [b]Determined by using size exclusion chromatography in THF, calibrated with polystyrene. [c]Molar ratio of BL/CHO/**Cr** was 200/0/1.

Table S2. ROP of BL at various CHO loading and treatment method[a]

Entry	BL/CHO/**Cr**[b]	Time	Conv.[c] (%)	TOF[d] (h^{-1})	M_n[e] (kg/mol)	$Đ$[e]
1	400/0/1	60 min	57	228	---[h]	---[h]
		4 h	>99	100	8.6	1.32
2	400/3/1	30 min	>99	800	36.8	1.67
3	400/5/1	30 min	90	720	35.9	1.78
4	400/10/1	30 min	55	440	---[h]	---[h]
		6 h	>99	67	29.4	1.63
5	400/20/1	30 min	19	152	---[h]	---[h]
		6 h	>99	67	18.7	1.76
6[f]	400/10/1	30 min	74	592	---[h]	---[h]
		2 h	>99	200	33.7	1.37
7[f]	400/20/1	30 min	70	560	---[h]	---[h]
		2 h	>99	200	35.9	1.54
8[g]	400/10/1	30 min	91	728	42.8	1.28
		1 h	>99	400	47.6	1.26
9[g]	400/20/1	30 min	89	712	---[h]	---[h]
		2 h	>99	200	41.2	1.38
10[g]	200/10/1	30 min	>99	400	26.5	1.23
11[g]	800/10/1	1 h	47	376	---[h]	---[h]
		4 h	>99	200	53.2	1.29

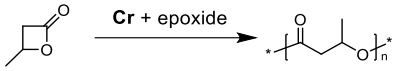
[a]Reactions performed in *rac*-BL (2 mmol) catalyzed by **Cr** in 2.0 M toluene at 80 °C in a 10 mL bar bottle, and **Cr** and CHO were reacted at 80 °C for 15 min prior to the addition of *rac*-BL. [b]Molar ratio. [c]Determined by ^{1}H NMR spectroscopy of the crude reaction mixture. [d]TOF = ([BL]/[**Cr**] × conversion (%))/time (h). [e]Determined by using size exclusion chromatography in THF, calibrated with polystyrene. [f]**Cr** and CHO were reacted in 80 °C for 15 min, and vacuumed at 80 °C for 15 min to remove residual CHO, prior to the addition of *rac*-BL. [g]**Cr** and CHO were reacted in 80 °C for 30 min, and vacuumed at 80 °C for 30 min to remove residual CHO, prior to the addition of *rac*-BL. [h]Not applicable.

Table S3. ROP of *rac*-BL at different reaction times[a]

Entry	Time (min)	Conv.[b] (%)	M_n[c] (kg/mol)	$Đ$[c]
1	10	30	11.3	1.26
2	20	50	26.8	1.19
3	30	91	42.8	1.28
4	60	>99	47.6	1.26

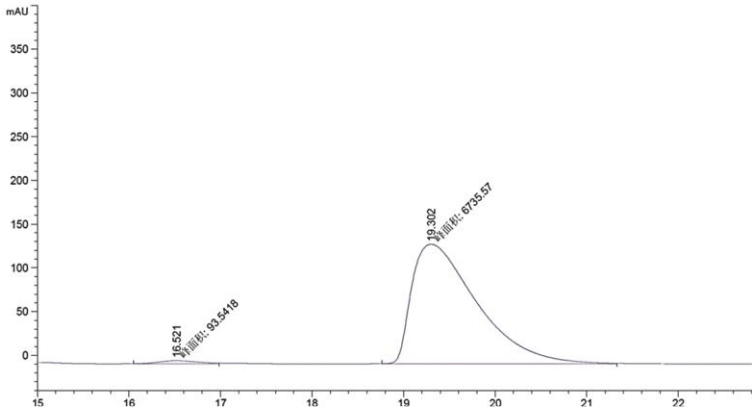
[a]Reactions performed in *rac*-BL (2 mmol) catalyzed by **Cr** in 2.0 M toluene at 80 °C in a 10 mL bar bottle, and **Cr** and CHO were reacted at 80 °C for 30 min, and vacuumed at 80 °C for 30 min to remove residual epoxides, prior to the addition of *rac*-BL. Molar ratio of BL/CHO/**Cr** was 400/10/1. [b]Determined by ^{1}H NMR spectroscopy of the crude reaction mixture. [c]Determined by using size exclusion chromatography in THF, calibrated with polystyrene.

Table S4. ROP of BL with various epoxides[a]



Entry	Epoxide	Time (h)	TOF[b] (h^{-1})	M_n[c] (kg/mol)	$Đ$[c]
1	---	4	100	8.6	1.32
2	CHO	1	400	47.6	1.26
3	VCHO	1	400	42.1	1.31
4	PGE	1	400	44.8	1.32
5	CPO	1	400	34.7	1.21
6	COPO	1	400	36.2	1.21
7	SO	4	100	8.9	1.32

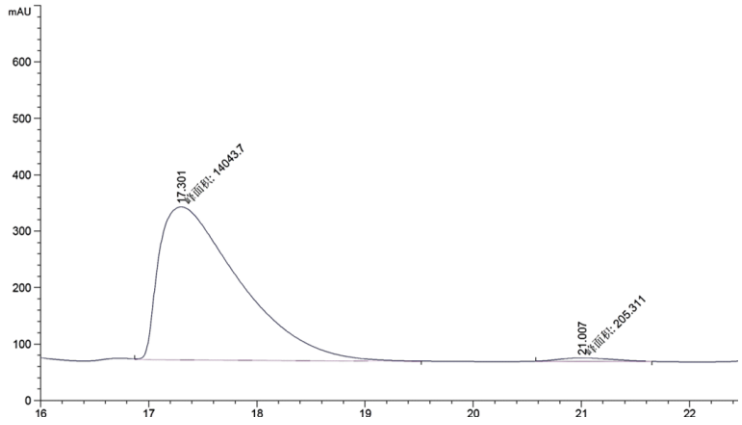
[a]Reactions performed in *rac*-BL (2 mmol) catalyzed by **Cr** in 2.0 M toluene at 80 °C in a 10 mL bar bottle, and **Cr** and epoxides were reacted at 80 °C for 30 min, and vacuumed at 80 °C for 30 min to remove residual epoxides, prior to the addition of *rac*-BL. Molar ratio of BL/epoxide/**Cr** was 400/10/1. All lactones conversion were >99% based on ^{1}H NMR spectroscopy. [b]TOF = ([BL]/[**Cr**] × conversion (%))/time (h). [c]Determined by using size exclusion chromatography in THF, calibrated with polystyrene.



Peak #	RT [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	16.521	MM	0.4670	93.54182	3.33853	1.3698
2	19.302	MM	0.8225	6735.56689	136.48955	98.6302

Figure S1. HPLC of (*S*)-methyl 3-(benzoyloxy)butanoate with 97.3% *ee* (P3HB by alcoholysis and benzoylation).

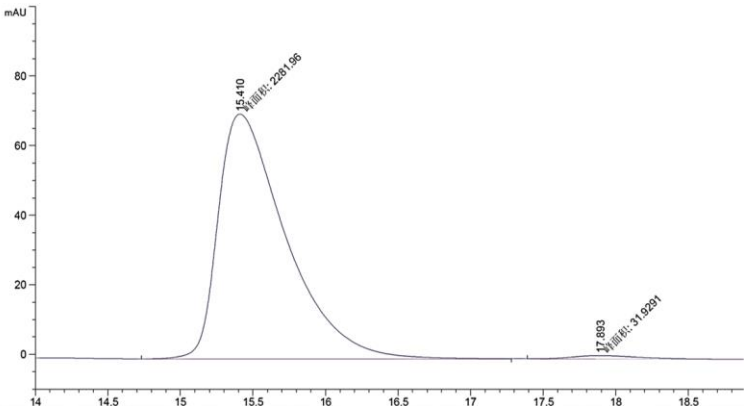
Note: P3HB from Table 1, entry 1 with *R*-BL.



Peak #	RT [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	17.301	MM	0.8626	1.40437e4	271.35291	98.5591
2	21.007	MM	0.5590	205.31133	6.12173	1.4409

Figure S2. HPLC of (*R*)-methyl 3-(benzoyloxy)butanoate with 97.1% *ee* (P3HB by alcoholysis and benzoylation).

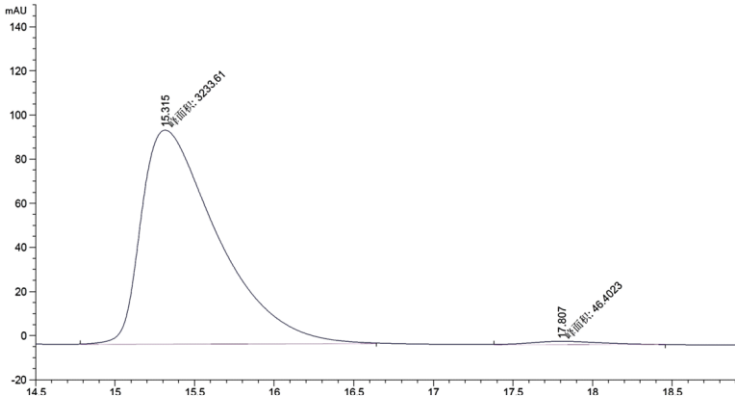
Note: P3HB from Table 1, entry 2 with *R*-BL.



Peak #	RT [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	15.410	MM	0.5403	2281.95728	70.39028	98.6201
2	17.893	MM	0.5387	31.92913	9.87795e-1	1.3799

Figure S3. HPLC of (*R*)-methyl 3-(benzoyloxy)butanoate with 97.3% *ee* (P3HB by alcoholysis and benzoylation).

Note: P3HB from Table 1, entry 3 with *S*-BL.



Peak #	RT [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	15.315	MM	0.5556	3233.60986	96.99677	98.5853
2	17.807	MM	0.5081	46.40228	1.52217	1.4147

Figure S4. HPLC of (*R*)-methyl 3-(benzoyloxy)butanoate with 97.1% *ee* (P3HB by alcoholysis and benzoylation).

Note: P3HB was produced by [*S*-BL]/[**Cr**]/[CHO] = 50/1/3 (30 min, 99% conversion) in toluene.

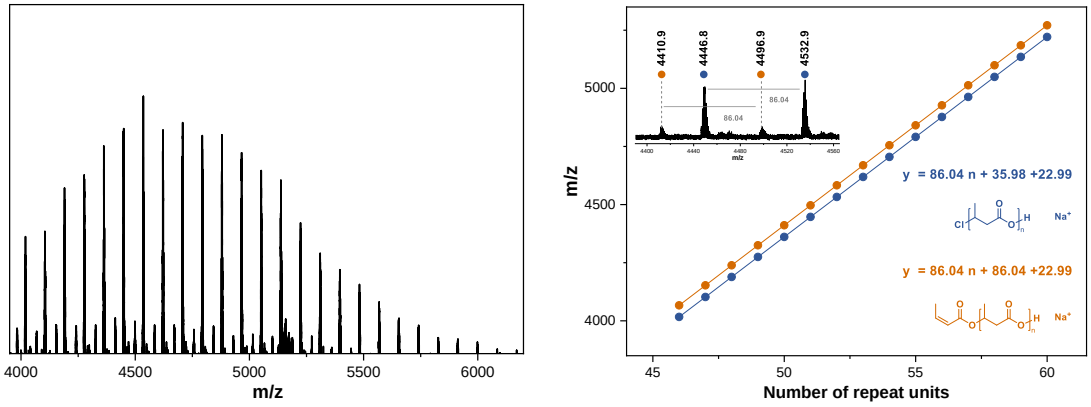


Figure S5. MALDI-TOF MS spectrum of the P3HB from Table 1, entry 1 with *R*-BL and the linear plots of *m/z* values (y) vs the number of BL repeat units (x).

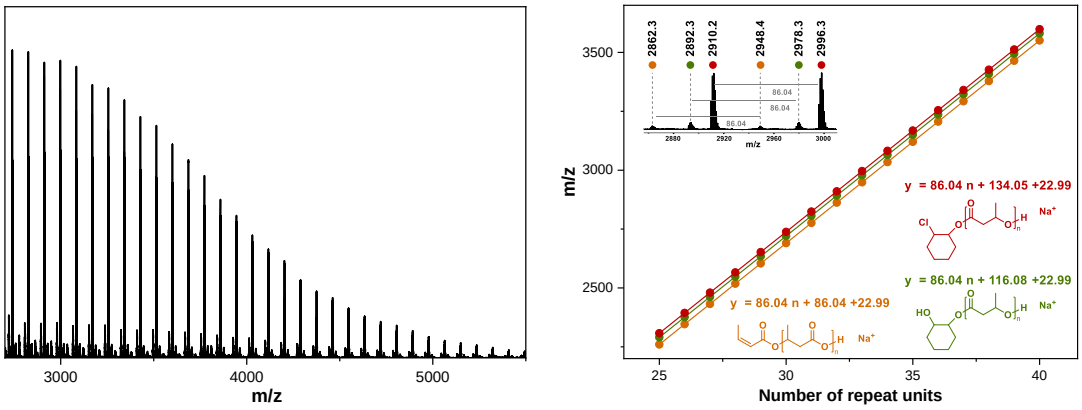


Figure S6. MALDI-TOF MS spectrum of the P3HB from Table 1, entry 2 with *R*-BL and the linear plots of *m/z* values (y) vs the number of BL repeat units (x).

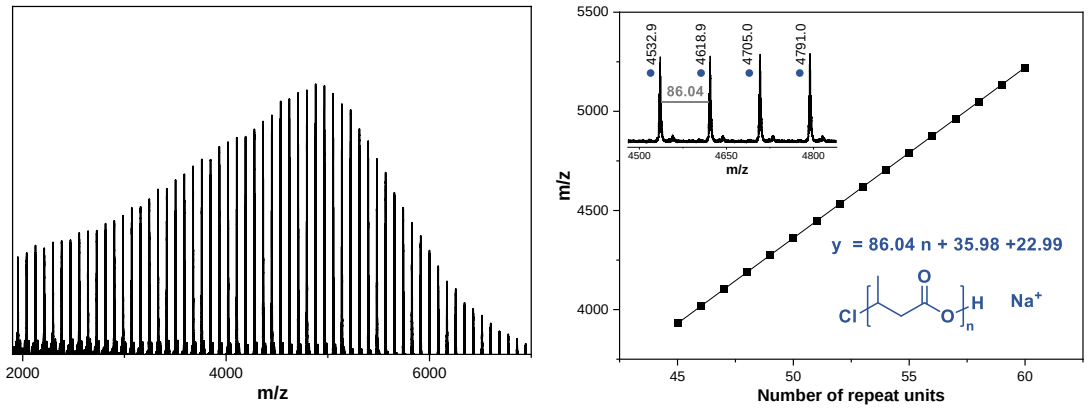


Figure S7. MALDI-TOF MS spectrum of the P3HB from Table 1, entry 3 with *S*-BL and the linear plots of *m/z* values (y) vs the number of BL repeat units (x).

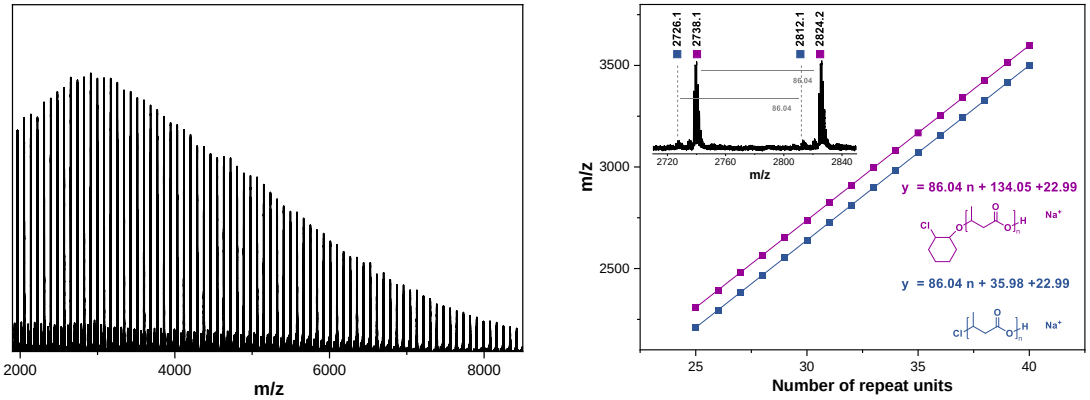


Figure S8. MALDI-TOF MS spectrum of a P3HB sample. P3HB was produced by [*S*-BL]/[**Cr**]/[CHO] = 50/1/3 (30 min, 99% conversion) in toluene and the linear plots of *m/z* values (y) vs the number of BL repeat units (x).

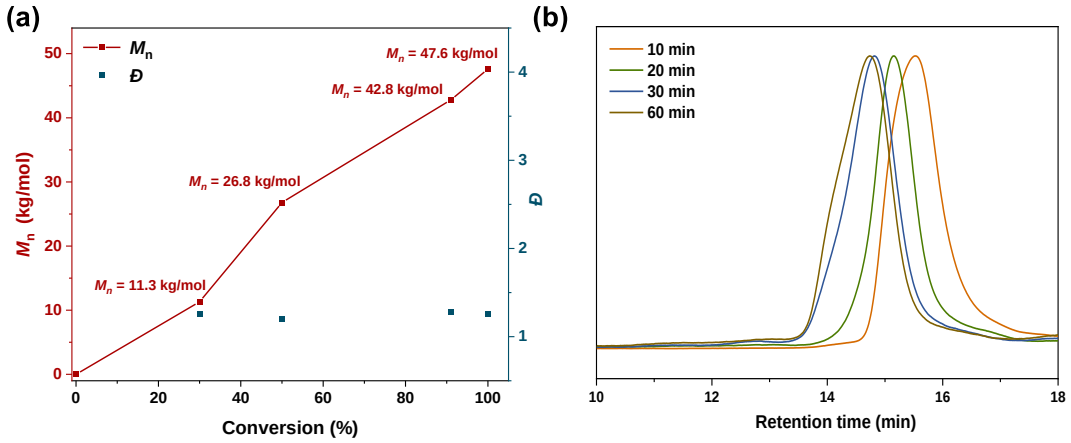


Figure S9. (a). Kinetic study for ROP of *rac*-BL. Conversion-M_n and Conversion-$Đ$ plots of BL, 2.0 M in toluene, at 80 °C, [BL]/[**Cr**]/[CHO] = 400/1/10. (b). The inset is an overlay of SEC curves at different time.

Note: The minimal shoulder peak observed in the SEC curves of Figure S9 is attributed to the presence of two kinetically distinct active species (Cr-Cl and Cr-OR). Although the asynchronous initiation issue was resolved by removing unreacted CHO under vacuum, the inherent difference in chain growth rates between these two species persists, leading to a shoulder on the high molecular weight side.

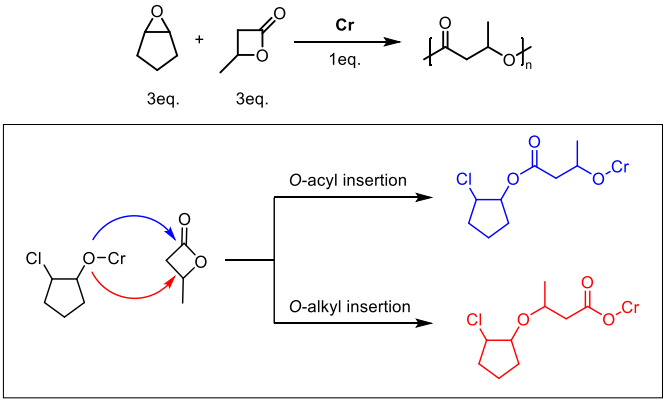


Figure S10. Different attack pathways of metal alkoxide species.

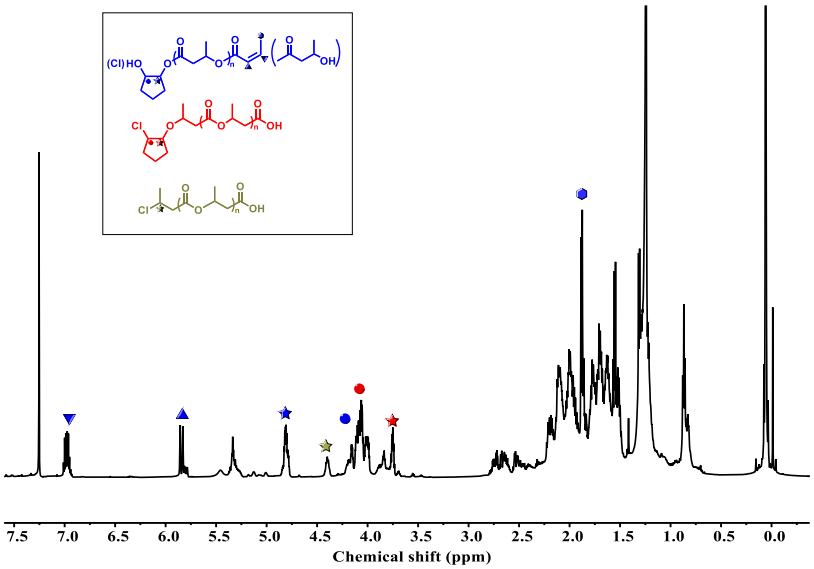


Figure S11. ^{1}H NMR spectra of the products from BL/CPO/**Cr** = 3/3/1 experiment. Spectrums of the products from BL/CPO/**Cr** = 3/3/1 experiment (30 min, 99% conversion) in toluene at 80 °C.

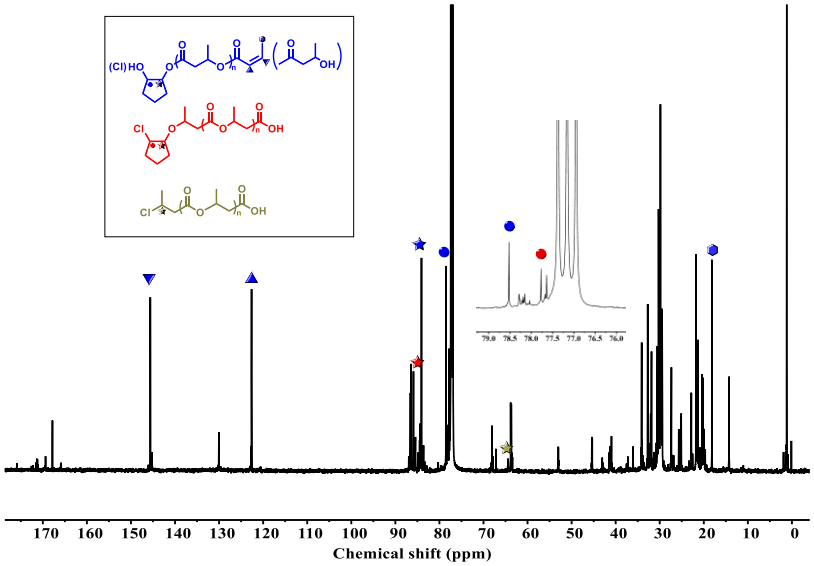


Figure S12. ^{13}C NMR spectra of the products from BL/CPO/**2** = 3/3/1 experiment. Spectrums of the products from BL/CPO/**Cr** = 3/3/1 experiment (30 min, 99% conversion) in toluene at 80 °C.

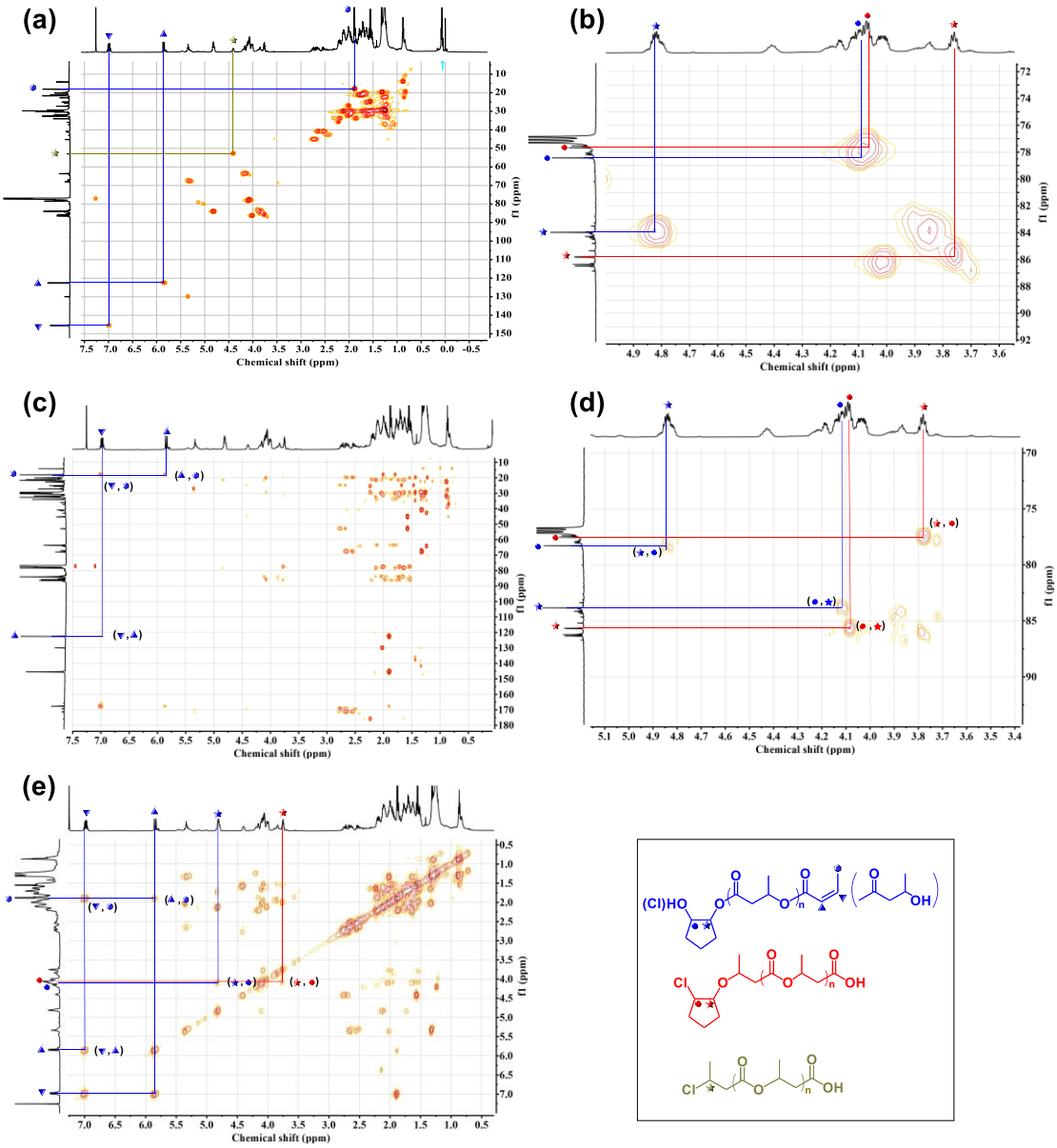


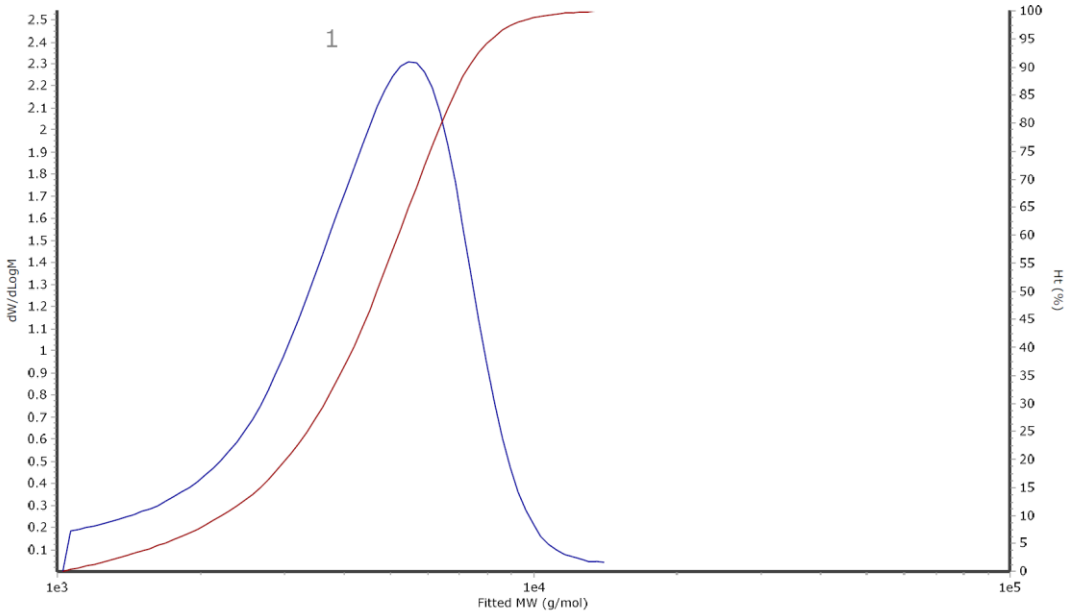
Figure S13. HSQC, HMBC and COSY spectra of the products from BL/CPO/**Cr** = 3/3/1 experiment. (a, b). HSQC; (c, d). HMBC; (e). COSY. Spectrums of the products from BL/CPO/**Cr** = 3/3/1 experiment (30 min, 99% conversion) in toluene at 80 °C.

Note:

The specific structures of series A and C were unambiguously assigned by NMR analysis. Generally, if the initial ring-opening occurs at the *O*-acyl bond, the proton signal adjacent to the ester group is expected to appear downfield, typically in the range of δ 4.5-5.0 ppm[5]. Conversely, if ring-opening takes place at the *O*-alkyl bond, the proton linked to the ether group usually resonates upfield, generally at or below δ 4.0 ppm[5].

Therefore, the resonance at δ 4.8 ppm was assigned to the proton adjacent to the ester group(-C*H*OC=O-) (Figure 3b and S11). HSQC NMR correlated this proton with a carbon at δ 84.0 ppm (Figure S12 and 13a,b). COSY NMR indicated that this proton signal is coupled to signals at δ 4.1 ppm and in the δ 1.5-2.5 ppm region (Figure S13e), where the δ 4.1 ppm signal was assigned to the neighboring methine proton on the ring, and the δ 1.5-2.5 ppm signals were assigned to the neighboring methylene protons on the ring. The signal at δ 4.1 ppm was correlated *via* HSQC NMR to a carbon at δ 78.4 ppm. HMBC NMR correlations observed between the proton at δ 4.8 ppm and the carbon at δ 78.4 ppm, as well as between the proton at δ 4.1 ppm and the carbon at δ 84.0 ppm, further confirmed their adjacency (Figure S13c,d). Thus, this moiety was unambiguously established as the product of *O*-acyl bond cleavage. The resonance at δ 3.8 ppm was assigned to the proton adjacent to the ether group (-C*H*OCH(CH_3)-) (Figure 3b and S11). HSQC NMR correlated this proton with a carbon at δ 85.7 ppm (Figure S12 and 13a,b). COSY NMR revealed correlations between this proton signal and the signals at δ 4.1 ppm and in the region of δ 1.5-2.1 ppm (Figure S13e). The signal at δ 4.1 ppm was again assigned to the adjacent ring methine proton, and the signals in the region of δ 1.5-2.1 ppm were assigned to the adjacent ring methylene protons. HSQC NMR correlated the δ 4.1 ppm signal to a carbon at δ 77.5 ppm. HMBC correlations observed between the proton at δ 3.8 ppm and the carbon at δ 77.5 ppm, as well as between the proton at δ 4.1 ppm and the carbon at δ 85.7 ppm (Figure S13c,d), confirmed their connectivity. Thus, this moiety was established as the product of *O*-alkyl bond cleavage (series C in the MS data). The resonances in the region of δ 5.5-7.0 ppm were assigned to terminal olefinic protons. HSQC NMR correlated these protons to carbons at δ 122.4 and 140.1 ppm, and HMBC/COSY data verified their adjacency. Notably, the terminal olefin structure can only arise from β-OH elimination of the structure derived from the *O*-acyl bond cleavage pathway (β-OH elimination of the structure derived from the *O*-alkyl bond cleavage pathway would yield an endocyclic olefin). This observation further confirms the occurrence of the *O*-acyl bond cleavage pathway and is consistent with series A observed in the MS data. Additionally, the signal at δ 4.33 ppm matches the expected chemical shift for the proton adjacent to chlorine in the -Cl-initiated species (ClC*H*(CH_3)-), corresponding to series B. The proton resonances ranging from 5.25-5.47 and 2.40-2.82 ppm should result from methine and methylene motif in the repeated units. Collectively, these data demonstrate that the initial ring-opening proceeds *via* concurrent *O*-acyl and *O*-alkyl bond cleavage, with both mechanisms operating simultaneously in the model reaction.

Distribution Plot



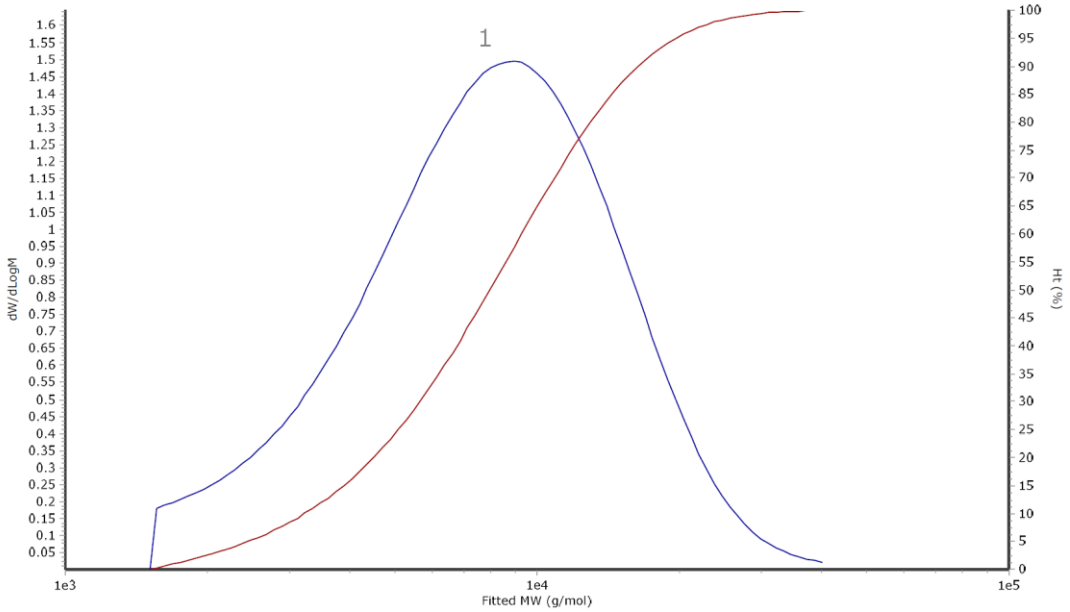
Molecular Weight Averages

Peak	Mp (g/mol)	Mn (g/mol)	Mw (g/mol)	Mz (g/mol)	Mz+1 (g/mol)	Mv (g/mol)
Peak 1	5473	3872	4842	5687	6438	4711

PD
1.251

Figure S14. SEC trace of P3HB: M_n = 3.9 kg/mol, $Đ$ = 1.25 (determined by SEC using THF as eluent, calibrated with polystyrene standard) (Table 1, entry 1).

Distribution Plot



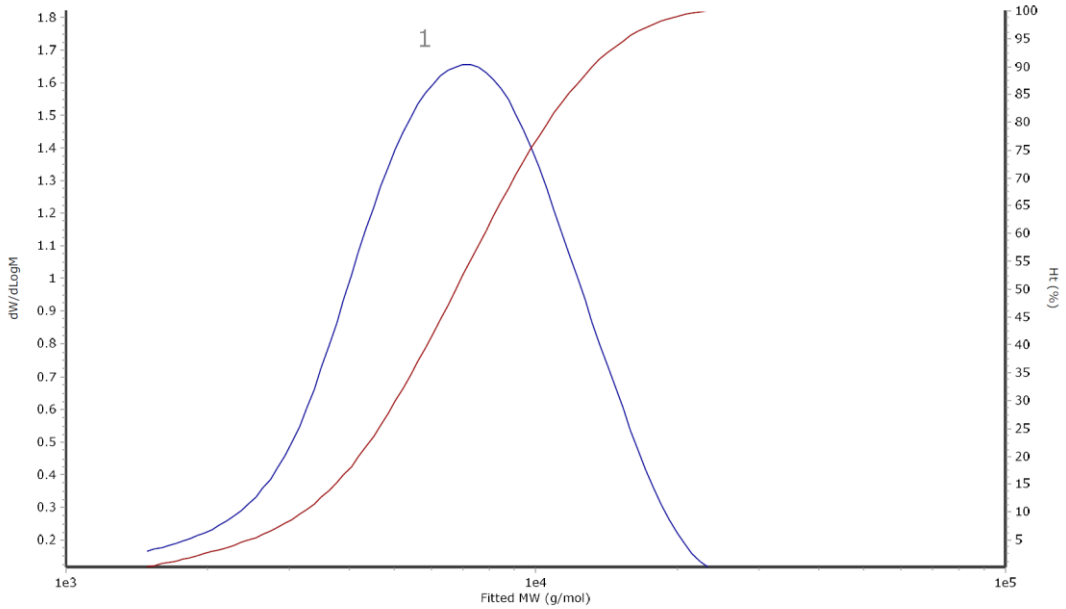
Molecular Weight Averages

Peak	Mp (g/mol)	Mn (g/mol)	Mw (g/mol)	Mz (g/mol)	Mz+1 (g/mol)	Mv (g/mol)
Peak 1	8767	6275	9186	12555	16108	8725

PD
1.464

Figure S15. SEC trace of P3HB: M_n = 6.3 kg/mol, $Đ$ = 1.46 (determined by SEC using THF as eluent, calibrated with polystyrene standard) (Table 1, entry 2).

Distribution Plot



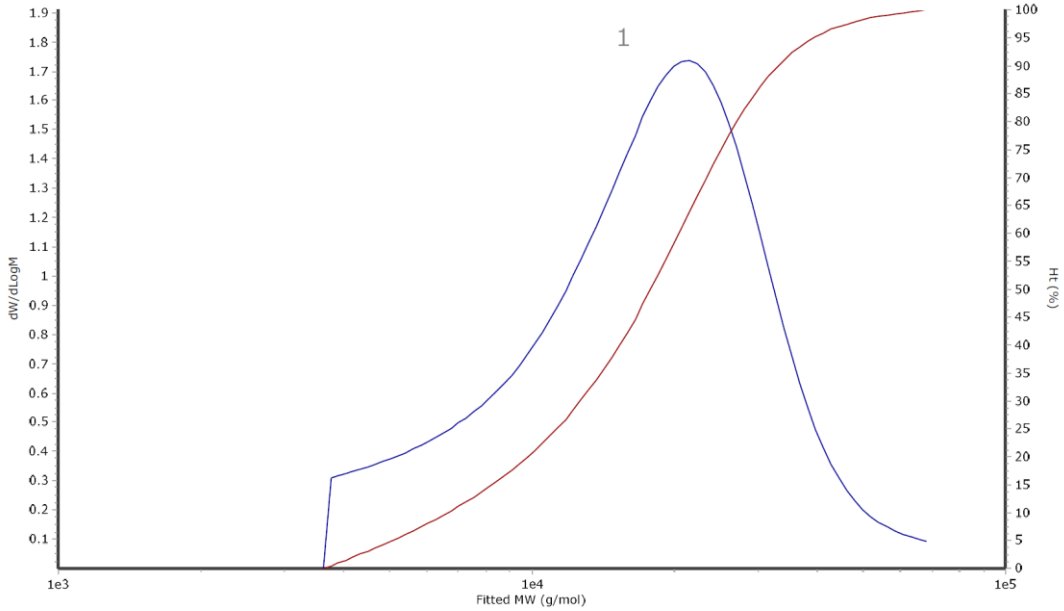
Molecular Weight Averages

Peak	Mp (g/mol)	Mn (g/mol)	Mw (g/mol)	Mz (g/mol)	Mz+1 (g/mol)	Mv (g/mol)
Peak 1	7137	5690	7665	9820	11941	7360

PD
1.347

Figure S16. SEC trace of P3HB: M_n = 5.7 kg/mol, $Đ$ = 1.35 (determined by SEC using THF as eluent, calibrated with polystyrene standard) (Table 1, entry 3).

Distribution Plot



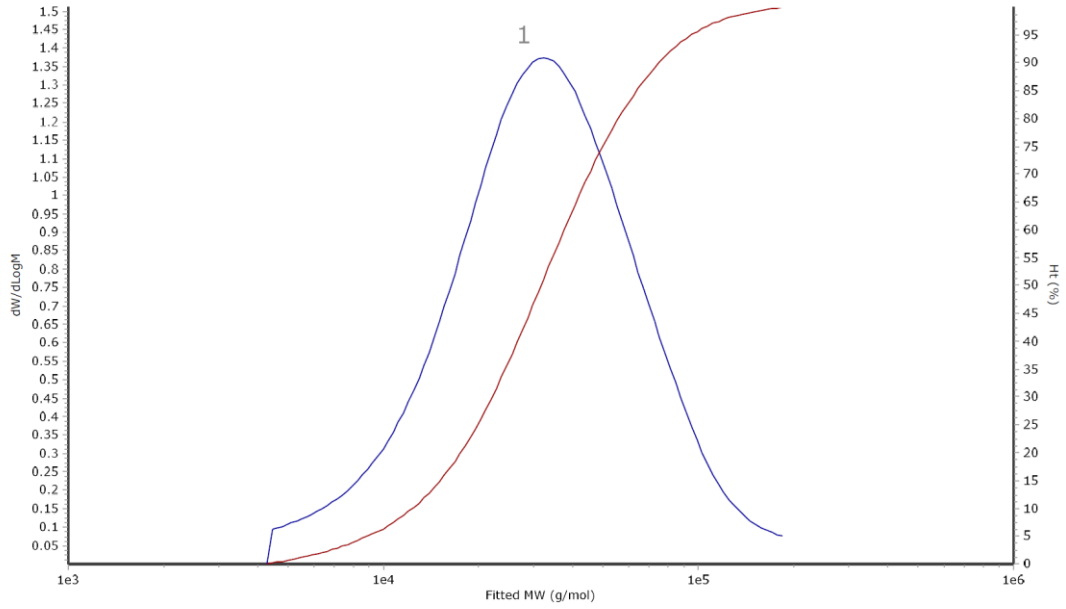
Molecular Weight Averages

Peak	Mp (g/mol)	Mn (g/mol)	Mw (g/mol)	Mz (g/mol)	Mz+1 (g/mol)	Mv (g/mol)
Peak 1	21147	13612	19543	25710	31805	18656

PD
1.436

Figure S17. SEC trace of P3HB: M_n = 13.6 kg/mol, $Đ$ = 1.44 (determined by SEC using THF as eluent, calibrated with polystyrene standard) (Table 1, entry 4).

Distribution Plot



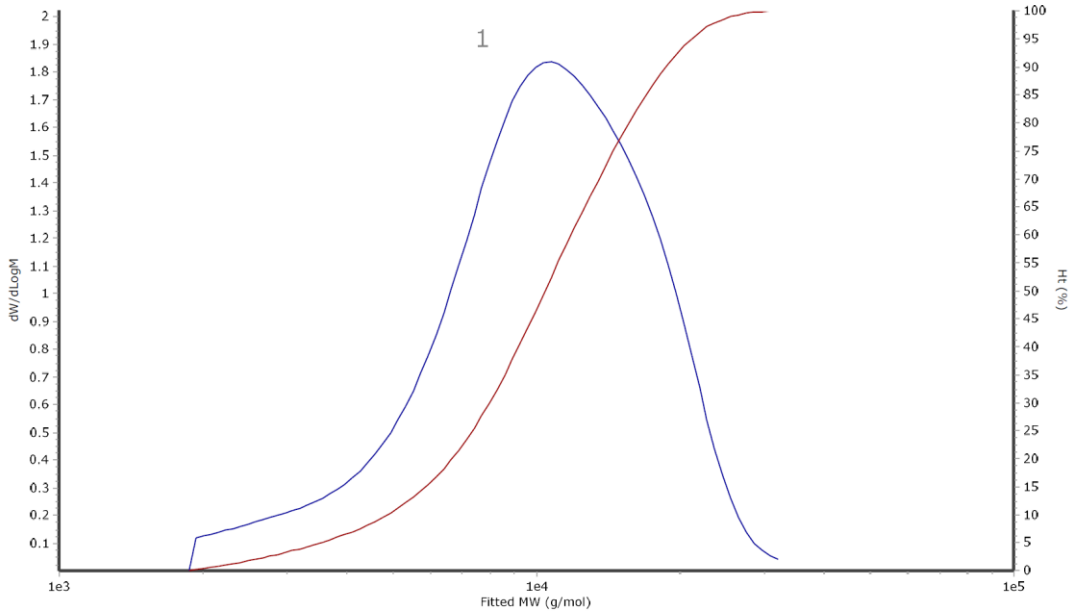
Molecular Weight Averages

Peak	Mp (g/mol)	Mn (g/mol)	Mw (g/mol)	Mz (g/mol)	Mz+1 (g/mol)	Mv (g/mol)
Peak 1	31555	24200	39366	59620	83087	36809

PD
1.627

Figure S18. SEC trace of P3HB: M_n = 24.2 kg/mol, $Đ$ = 1.63 (determined by SEC using THF as eluent, calibrated with polystyrene standard) (Table 1, entry 5).

Distribution Plot



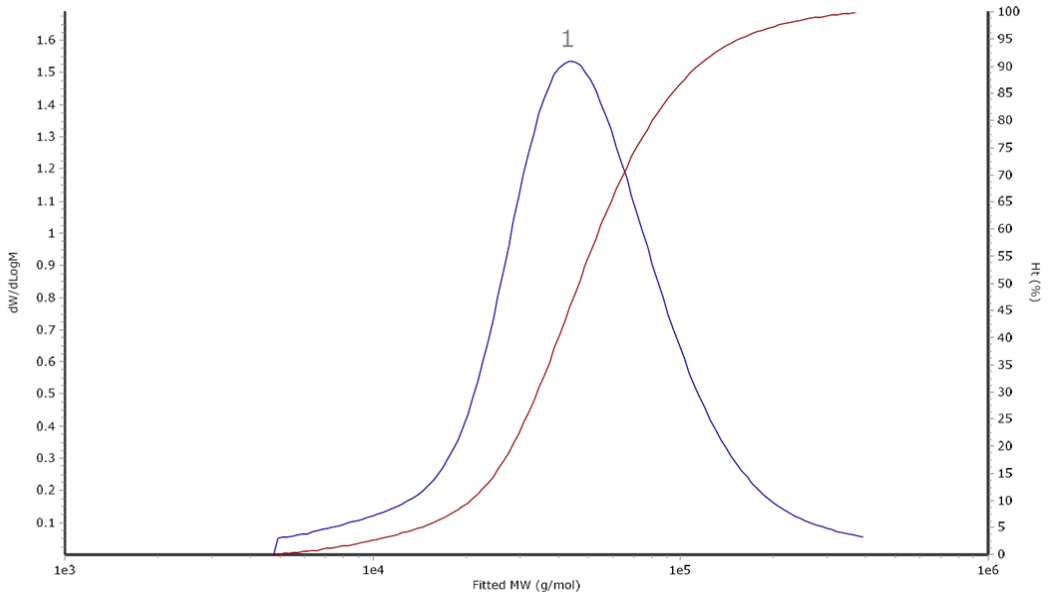
Molecular Weight Averages

Peak	Mp (g/mol)	Mn (g/mol)	Mw (g/mol)	Mz (g/mol)	Mz+1 (g/mol)	Mv (g/mol)
Peak 1	10540	8559	11336	13887	16151	10949

PD
1.324

Figure S19. SEC trace of P3HB: M_n = 8.6 kg/mol, $Đ$ = 1.32 (determined by SEC using THF as eluent, calibrated with polystyrene standard) (Table 1, entry 6).

Distribution Plot



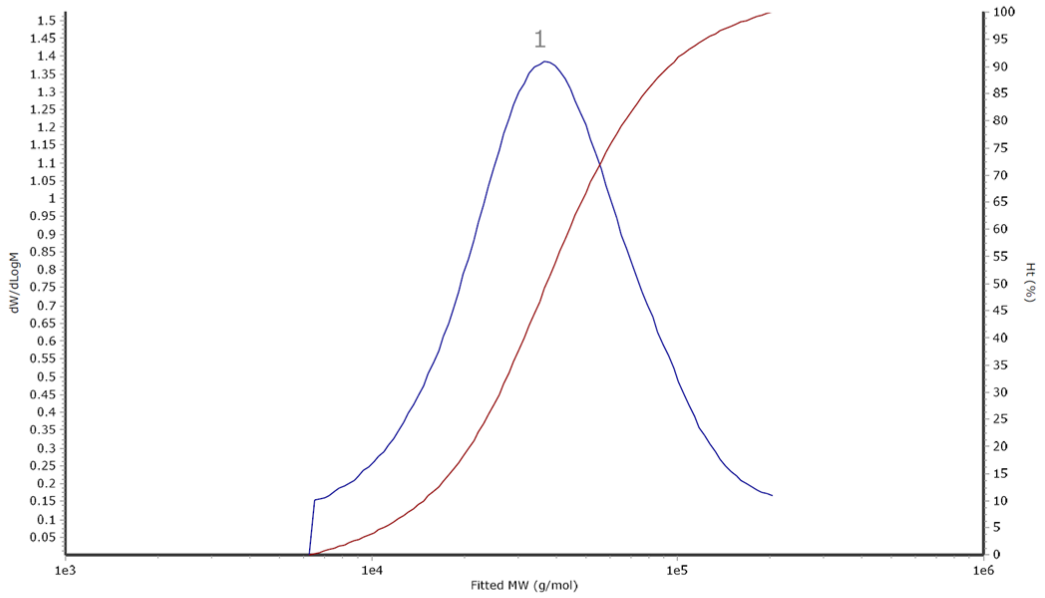
Molecular Weight Averages

Peak	Mp (g/mol)	Mn (g/mol)	Mw (g/mol)	Mz (g/mol)	Mz+1 (g/mol)	Mv (g/mol)
Peak 1	43738	36795	61440	103346	167007	56934

PD
1.67

Figure S20. SEC trace of P3HB: M_n = 36.8 kg/mol, $Đ$ = 1.67 (determined by SEC using THF as eluent, calibrated with polystyrene standard) (Table 1, entry 7).

Distribution Plot



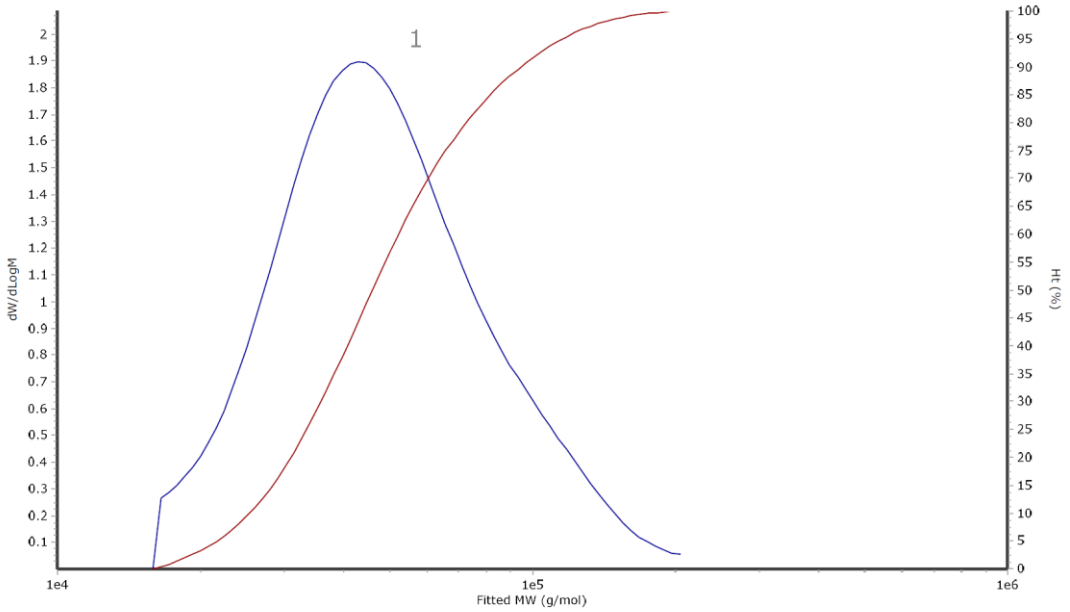
Molecular Weight Averages

Peak	Mp (g/mol)	Mn (g/mol)	Mw (g/mol)	Mz (g/mol)	Mz+1 (g/mol)	Mv (g/mol)
Peak 1	36786	29397	47918	74354	104127	44644

PD
1.63

Figure S21. SEC trace of P3HB: M_n = 29.4 kg/mol, $Đ$ = 1.63 (determined by SEC using THF as eluent, calibrated with polystyrene standard) (Table 1, entry 8).

Distribution Plot

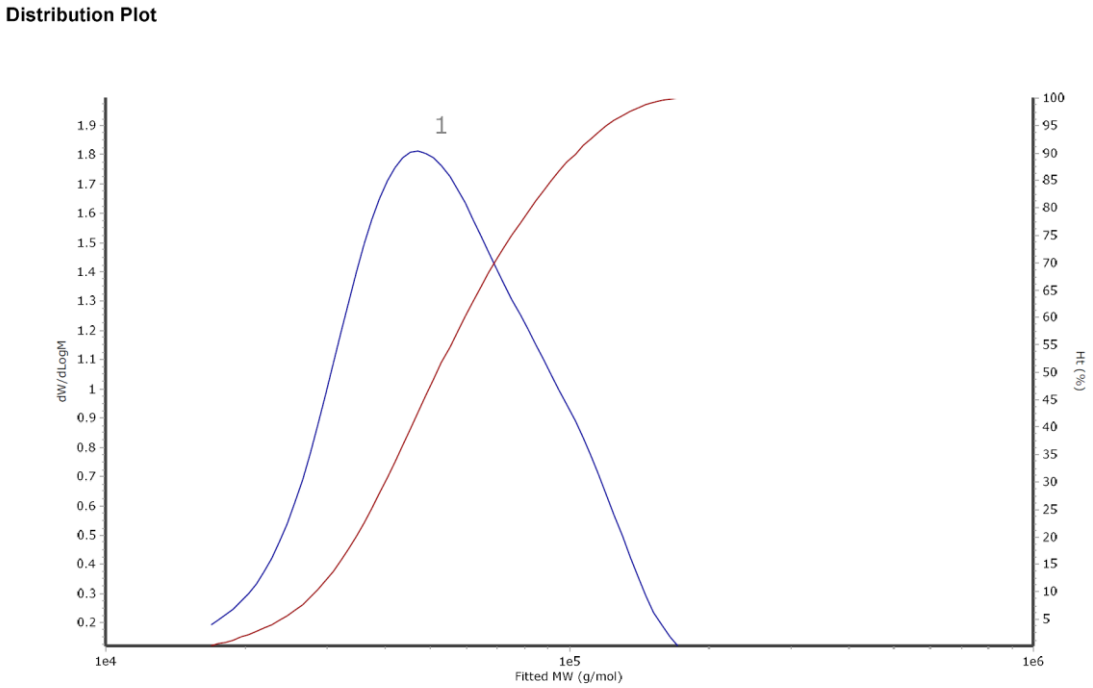


Molecular Weight Averages

Peak	Mp (g/mol)	Mn (g/mol)	Mw (g/mol)	Mz (g/mol)	Mz+1 (g/mol)	Mv (g/mol)
Peak 1	42904	42759	54624	71114	91041	52525

PD
1.277

Figure S22. SEC trace of P3HB: M_n = 42.8 kg/mol, $Đ$ = 1.28 (determined by SEC using THF as eluent, calibrated with polystyrene standard) (Table 1, entry 9).



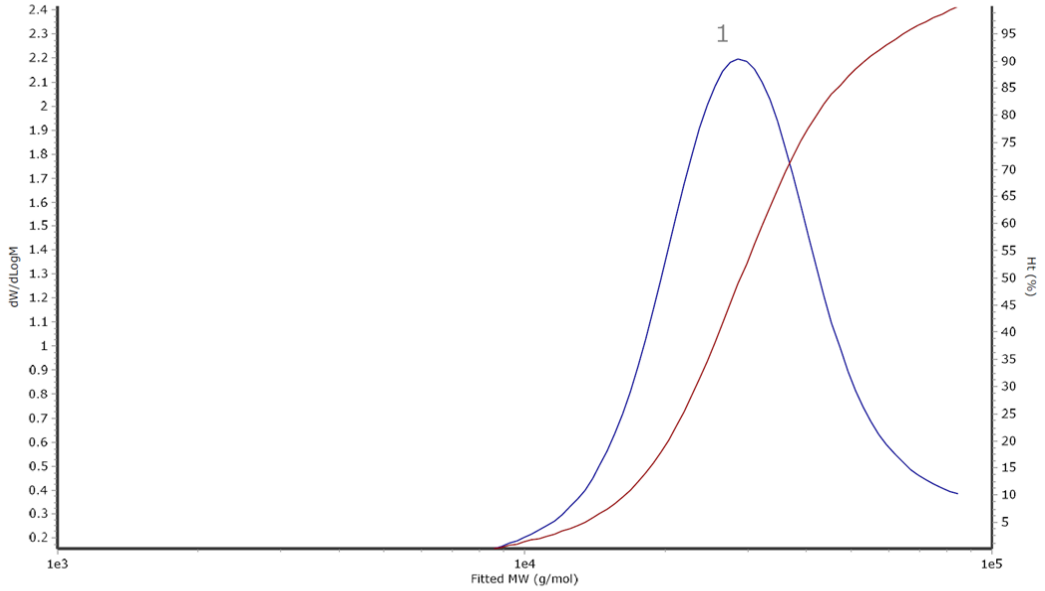
Molecular Weight Averages

Peak	Mp (g/mol)	Mn (g/mol)	Mw (g/mol)	Mz (g/mol)	Mz+1 (g/mol)	Mv (g/mol)
Peak 1	47245	47610	60112	75183	90743	58043

PD
1.263

Figure S23. SEC trace of P3HB: M_n = 47.6 kg/mol, $Đ$ = 1.26 (determined by SEC using THF as eluent, calibrated with polystyrene standard) (Table 1, entry 10).

Distribution Plot



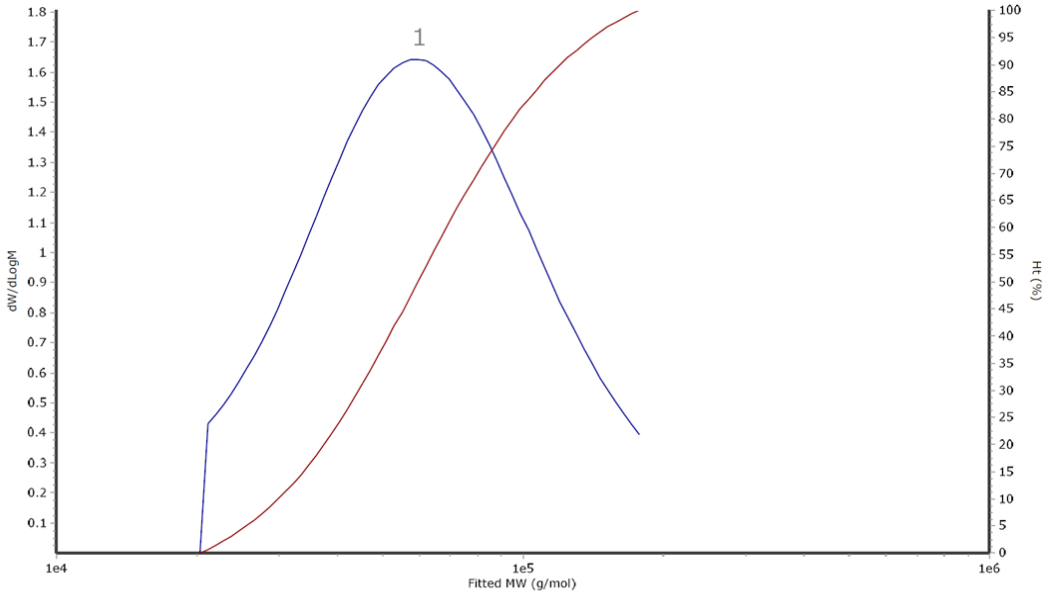
Molecular Weight Averages

Peak	Mp (g/mol)	Mn (g/mol)	Mw (g/mol)	Mz (g/mol)	Mz+1 (g/mol)	Mv (g/mol)
Peak 1	28678	26526	32577	39685	47404	31603

PD
1.228

Figure S24. SEC trace of P3HB: M_n = 26.5 kg/mol, $Đ$ = 1.23 (determined by SEC using THF as eluent, calibrated with polystyrene standard) (Table S2, entry 10).

Distribution Plot



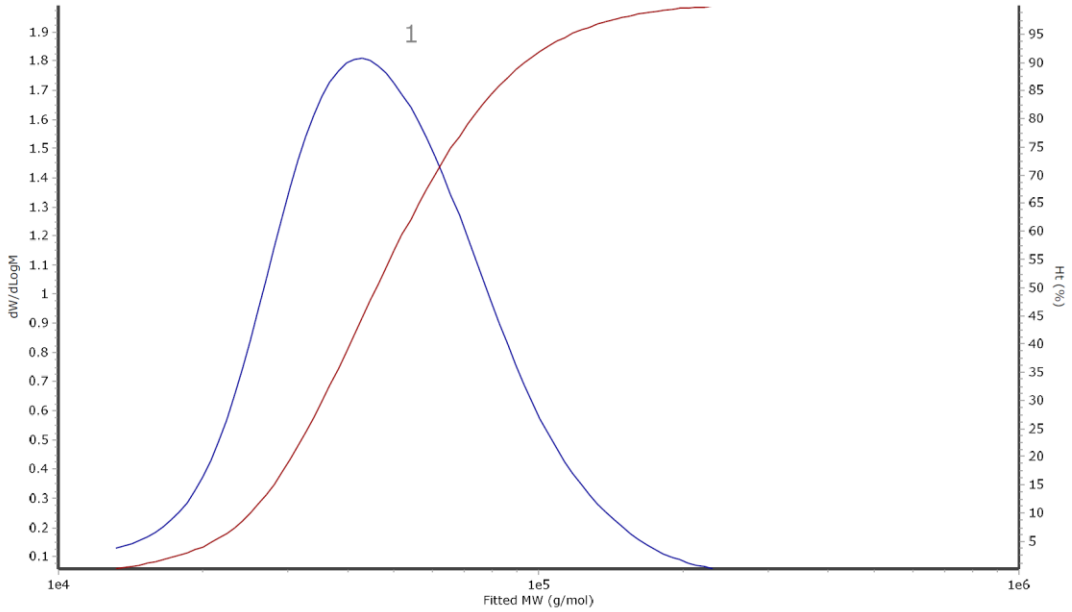
Molecular Weight Averages

Peak	Mp (g/mol)	Mn (g/mol)	Mw (g/mol)	Mz (g/mol)	Mz+1 (g/mol)	Mv (g/mol)
Peak 1	59586	53173	68634	86895	104753	66089

PD
1.291

Figure S25. SEC trace of P3HB: M_n = 53.2 kg/mol, $Đ$ = 1.29 (determined by SEC using THF as eluent, calibrated with polystyrene standard) (Table S2, entry 11).

Distribution Plot



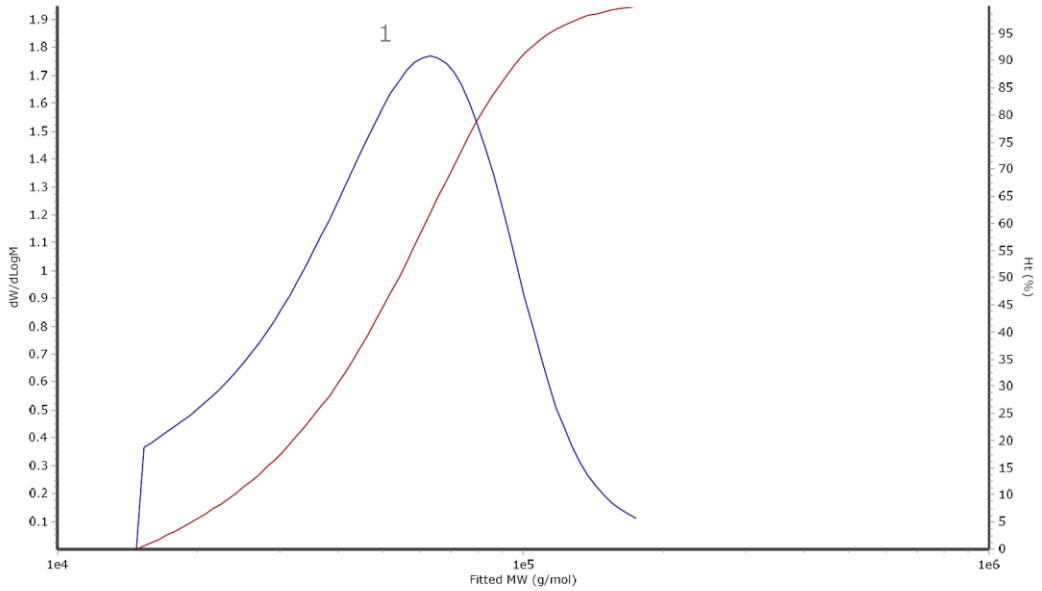
Molecular Weight Averages

Peak	Mp (g/mol)	Mn (g/mol)	Mw (g/mol)	Mz (g/mol)	Mz+1 (g/mol)	Mv (g/mol)
Peak 1	42086	42052	54870	73438	97697	52582

PD
1.305

Figure S26. SEC trace of P3HB: M_n = 42.1 kg/mol, $Đ$ = 1.31 (determined by SEC using THF as eluent, calibrated with polystyrene standard) (Table S4, entry 3).

Distribution Plot



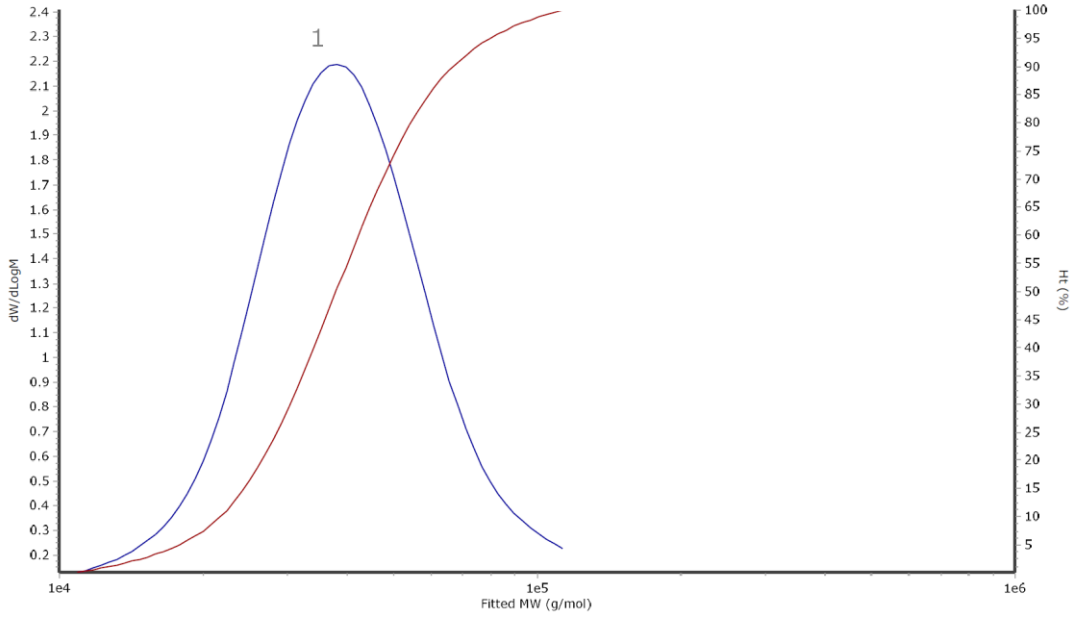
Molecular Weight Averages

Peak	Mp (g/mol)	Mn (g/mol)	Mw (g/mol)	Mz (g/mol)	Mz+1 (g/mol)	Mv (g/mol)
Peak 1	63155	44802	58927	73864	88164	56764

PD
1.315

Figure S27. SEC trace of P3HB: M_n = 44.8 kg/mol, $Đ$ = 1.32 (determined by SEC using THF as eluent, calibrated with polystyrene standard) (Table S4, entry 4).

Distribution Plot



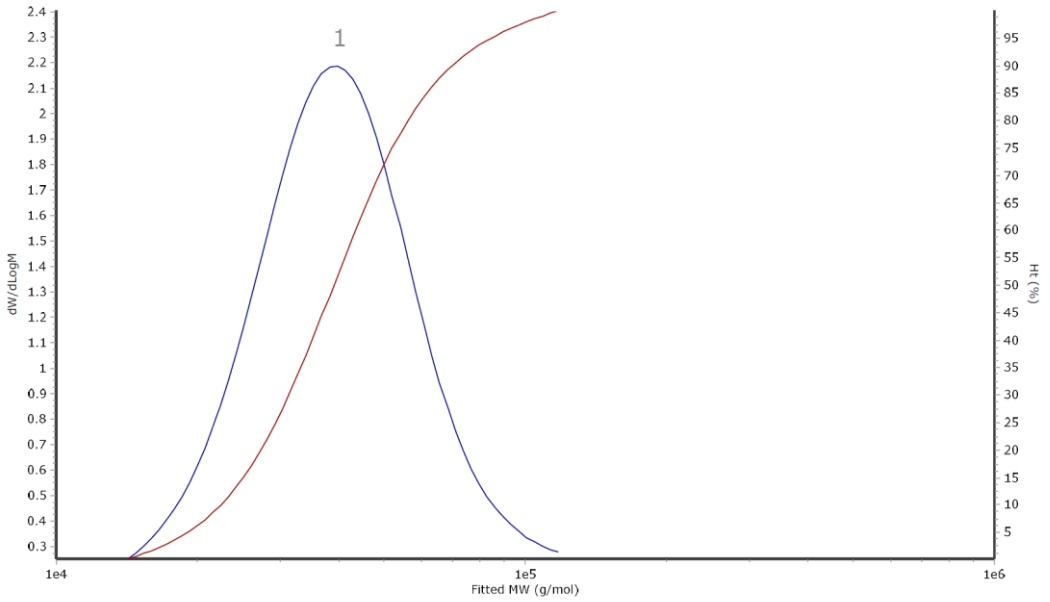
Molecular Weight Averages

Peak	Mp (g/mol)	Mn (g/mol)	Mw (g/mol)	Mz (g/mol)	Mz+1 (g/mol)	Mv (g/mol)
Peak 1	38227	34704	42122	50632	59931	40946

PD
1.214

Figure S28. SEC trace of P3HB: M_n = 34.7 kg/mol, $Đ$ = 1.21 (determined by SEC using THF as eluent, calibrated with polystyrene standard) (Table S4, entry 5).

Distribution Plot



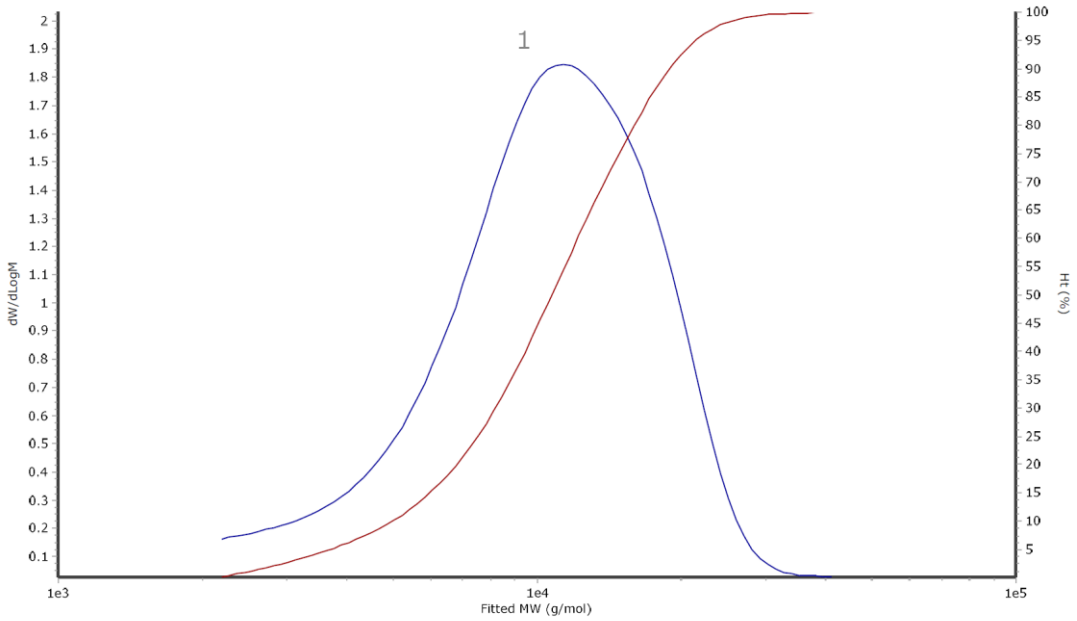
Molecular Weight Averages

Peak	Mp (g/mol)	Mn (g/mol)	Mw (g/mol)	Mz (g/mol)	Mz+1 (g/mol)	Mv (g/mol)
Peak 1	38969	36223	43663	52747	62974	42435

PD
1.205

Figure S29. SEC trace of P3HB: M_n = 36.2 kg/mol, $Đ$ = 1.21 (determined by SEC using THF as eluent, calibrated with polystyrene standard) (Table S4, entry 6).

Distribution Plot



Molecular Weight Averages

Peak	Mp (g/mol)	Mn (g/mol)	Mw (g/mol)	Mz (g/mol)	Mz+1 (g/mol)	Mv (g/mol)
Peak 1	11357	8855	11645	14330	16898	11247

PD
1.315

Figure S30. SEC trace of P3HB: M_n = 8.9 kg/mol, $Đ$ = 1.32 (determined by SEC using THF as eluent, calibrated with polystyrene standard) (Table S4, entry 7).

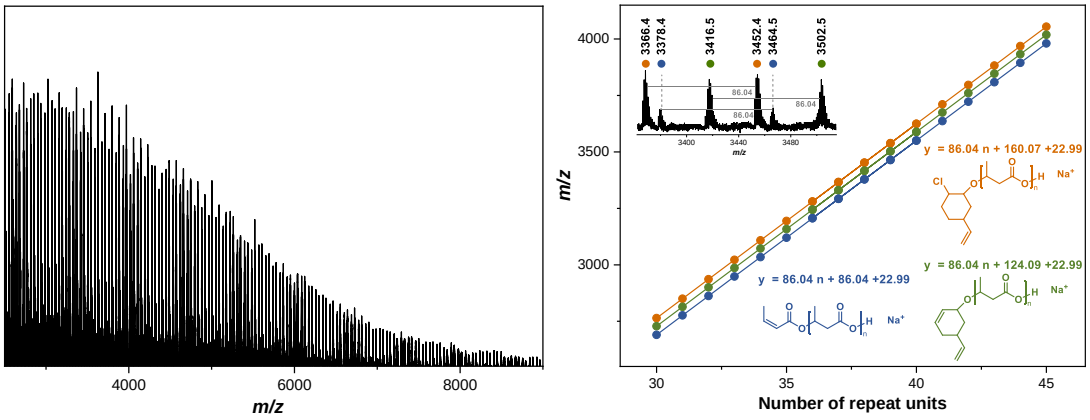


Figure S31. MALDI-TOF MS spectrum of the P3HB from Table S4, entry 3 and the linear plots of *m/z* values (y) vs the number of BL repeat units (x).

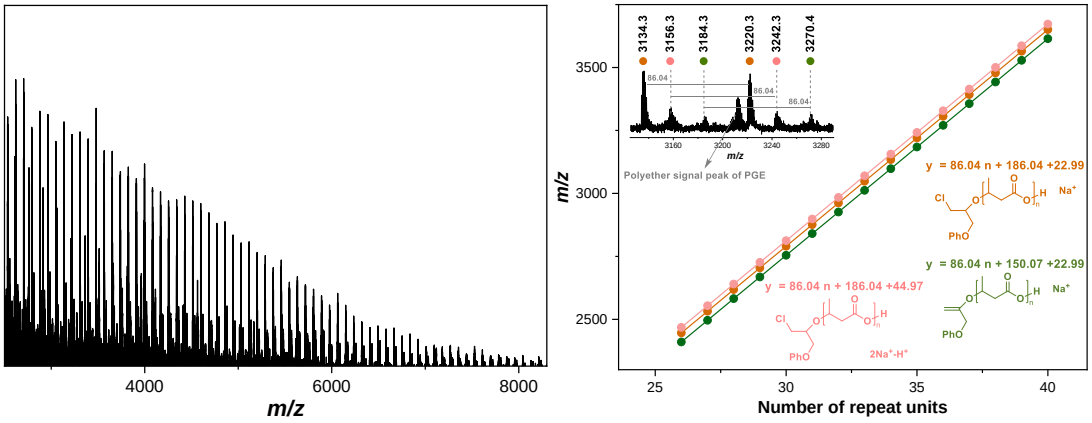


Figure S32. MALDI-TOF MS spectrum of the P3HB from Table S4, entry 4 and the linear plots of *m/z* values (y) vs the number of BL repeat units (x).

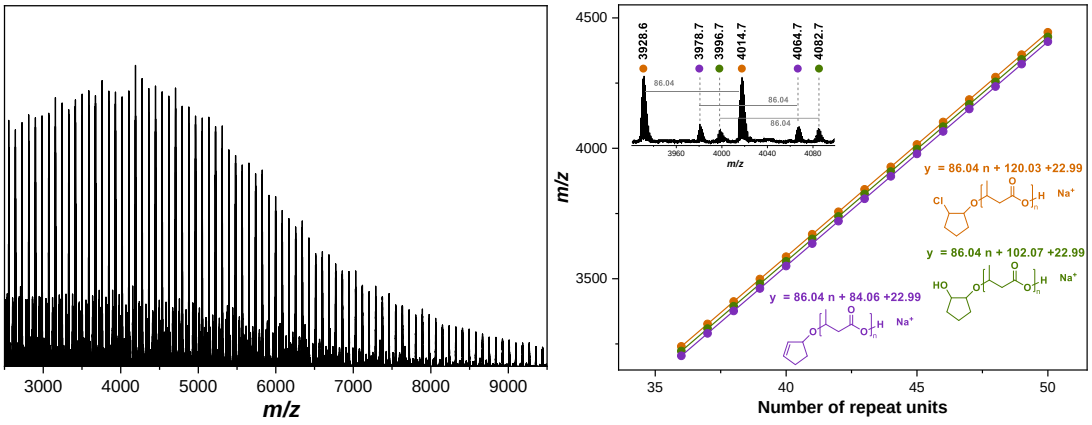


Figure S33. MALDI-TOF MS spectrum of the P3HB from Table S4, entry 5 and the linear plots of *m/z* values (y) vs the number of BL repeat units (x).

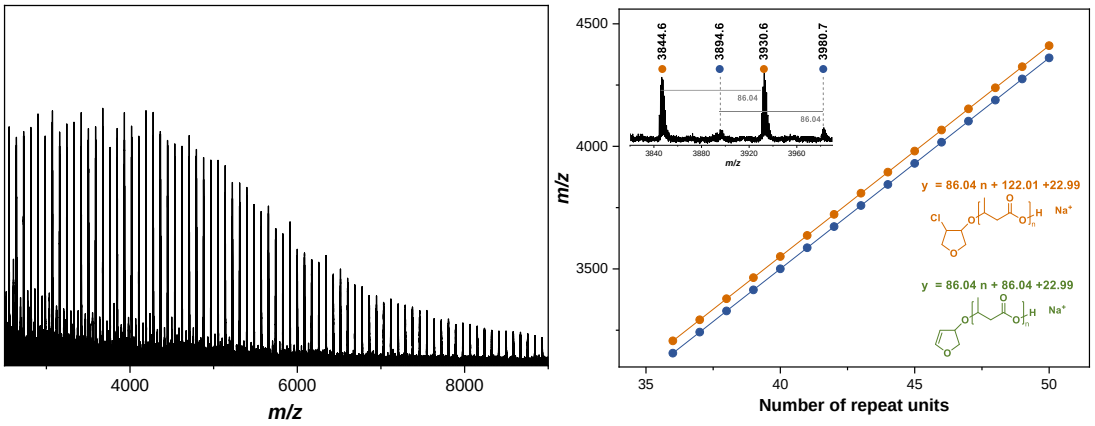


Figure S34. MALDI-TOF MS spectrum of the P3HB from Table S4, entry 6 and the linear plots of *m/z* values (y) vs the number of BL repeat units (x).

Note: Since the *m/z* value is identical to that of P3HB obtained by chlorine initiation, ^{1}H NMR was used for further characterization.

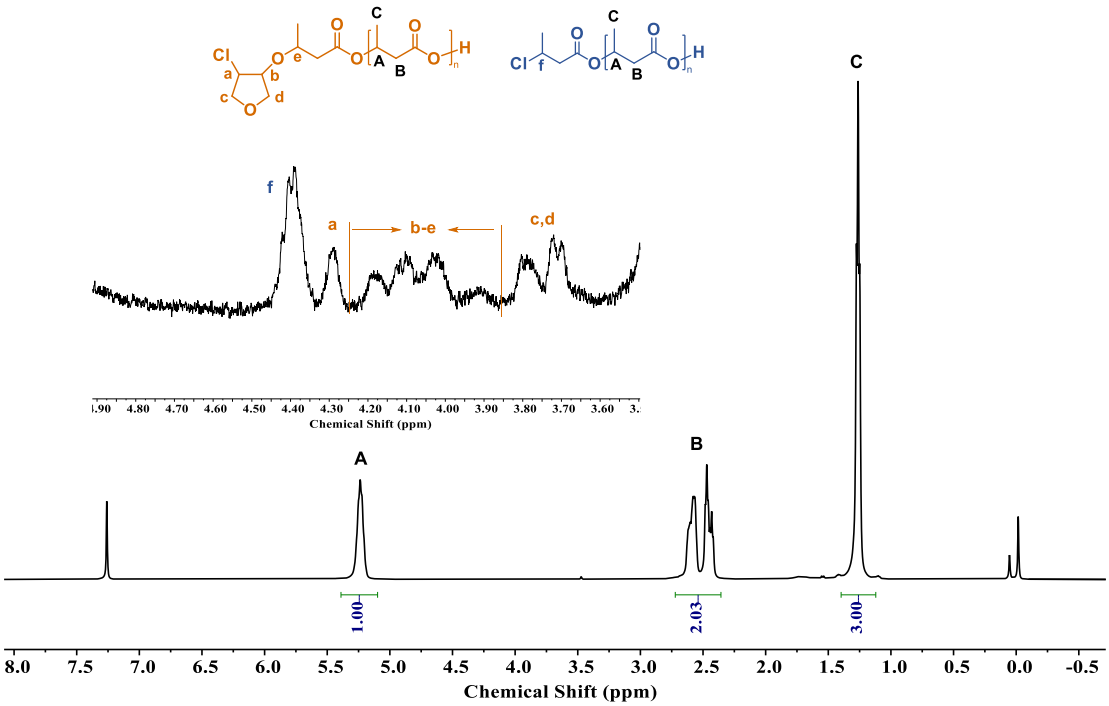


Figure S35. ^{1}H NMR spectrum of the P3HB from Table S4, entry 6.

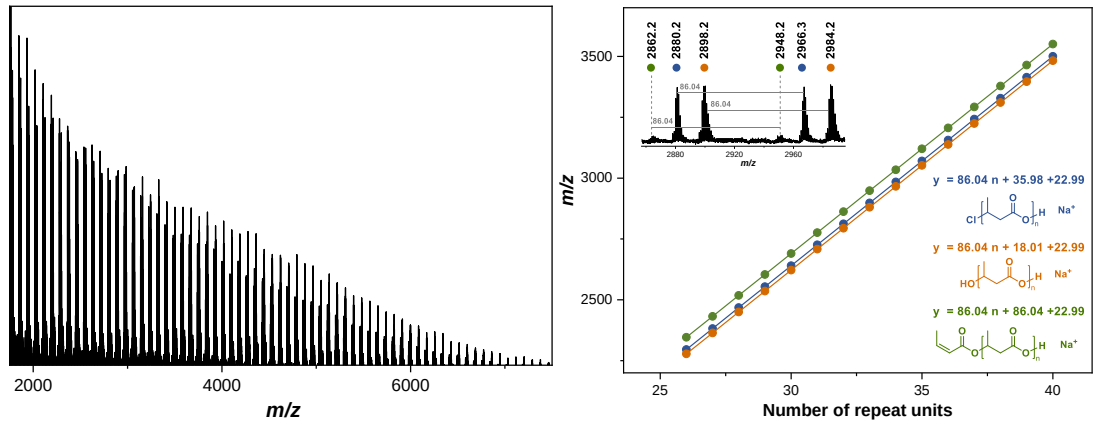


Figure S36. MALDI-TOF MS spectrum of the P3HB from Table S4, entry 7 and the linear plots of *m/z* values (y) vs the number of BL repeat units (x).

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