Supporting Information for Manuscript Entitled with

Preparation of Biorenewable Poly(γ-butyrolactone)-*b*-poly(L-lactide) Diblock Copolyesters *via* One-pot Sequential Metal-free Ring-Opening Polymerization

Yong Shen, [a] Jinbo Zhang, [b] Na Zhao, [b] Fusheng Liu, [a] and Zhibo Li*, [b]

[a] College of Chemical Engineering, Qingdao University of Science and Technology, Qingdao 266042, China.
[b] Key Laboratory of Biobased Polymer Materials, Shandong Provincial Education Department; School of Polymer Science and Engineering, Qingdao University of Science and Technology, Qingdao 266042, China. E-mail: zbli@qust.edu.cn

Experimental Section

Materials.

Tetrahydrofuran (THF) and toluene were purified by purging with dry nitrogen, followed by passing through columns of activated alumina. γ-Butyrolactone (γBL) were obtained from Aladdin Reagent Co. Benzyl alcohol (BnOH) and L-lactide (L-LA) were purchased from TCI Chemical Co. γBL and BnOH were stirred with CaH_2 for 24 hours, then distilled under reduced pressure and stored over activated 4 Å molecular sieves in a glovebox. The cyclic trimeric phosphazene base (CTPB) was synthesized according to the procedure reported before.[1] All commercially obtained reagents were used as received without further purification unless otherwise noted.

Instruments.

Nuclear magnetic resonance (NMR) spectra were recorded on a Bruker DMX-500 FT-NMR spectrometer at 500 MHz for ^{1}H NMR and 125.7 MHz for ^{13}C NMR. Chemical shifts were reported in δ (ppm) and the residual deuterated solvent peak was used as reference. Matrix-assisted laser desorption/ionization time-of-flight mass spectroscopy (MALDI-TOF MS) analyses were conducted on a Bruker BIFLEX III MS spectrometer equipped with a 337 nm nitrogen laser. The sample was dissolved in THF and mixed with α-cyano-4-hydroxy cinnmaic acid/THF solution prior to dry. Size exclusion chromatography (SEC) spectra were performed on a Agilent HPLC system equipped with a model 1260 Hip degasser, a model 1260 Iso pump and a model 1260 differential refractometer detector. Three Mz-Gel SD_{plus} (10^3 Å, 10^4 Å, and 10^5Å) columns were connected in series. THF was used as mobile phase at a flow rate of 1.0 mL/min at 40 °C. The molecular weight and polydispersity were calculated using polystyrene standards with narrow molecular weight distribution as references. The sample concentration used for SEC analysis was about 10 mg/mL. Differential scanning calorimetry (DSC) measurements were performed on a TA instrument DSC 25. Temperature was calibrated with an indium standard. Measurements were performed under N_2 atmosphere with a flow rate of 50 mL/min. Each sample with a mass of 5-10 mg was used for the measurement. The typical procedures for the measurements of PγBL-*b*-PLLA samples were as follows: in the first heating scan, samples were heated from -85 °C to 190 °C at a heating rate of 10 °C/min and kept at 190 °C for 2 min to eliminate any thermal history. In the second heating scan, samples were cooled to -85 °C at 10 °C/min and then equilibrium at -85 °C for 2 min, and subsequently reheated to 190 °C at 10°C/min. The PγBL and PLLA homopolymer samples were measured at similar procedures except that the temperature range was from -85 °C to 100 °C for PγBL and from 0 °C to 200 °C for PLLA, respectively. Thermogravimetric analysis (TGA) measurements were preformed on a TA Q50 thermogravimetric analyzer. The samples were heated from 40 °C to 600 °C at a heating rate of 10 °C/min under N_2 atmosphere with a flow rate of 50 mL/min.

Table S1. Results of ROP of L-LA catalyzed by CTPB [a]

run	L-LA/C/I	Time (min)	C (L-LA) (%) [b]	M_n (kg/mol) [c]	PDI [c]
1	300/1/3	180	71.8	11.2	1.20
2	300/2/3	180	98.0	17.6	1.55
3	450/2/3	10	80.5	11.8	1.35
4	450/2/3	180	91.8	19.3	1.31

[a] Reaction conditions: CTPB was used as catalyst, BnOH (0.15mmol) was used as initiator. [L-LA] = 1 M in THF, reaction temperature was 25 °C. [b] Monomer conversions were determined by ^{1}H NMR spectra. [c] Number-average molecular weight and polydispersity (PDI) were determined by SEC in THF at 40 °C relative to polystyrene standards.

Table S2. Monomer conversion and molecular weight of PγBL-*b*-PLLA as a function of time. [a]

run	Time (min)	C (γBL) (%) [b]	C (L-LA) (%) [b]	M_n (kg/mol) [c]	PDI [c]
1	5	52.0	97.6	18.0	1.72
2	10	52.8	97.3	20.5	1.62
3	30	54.6	96.9	18.7	1.64
4	120	54.0	97.5	19.1	1.68
5	180	54.5	97.5	17.9	1.70

[a] Reaction conditions: [L-LA]/[γBL]/[C]/[I] = 300/300/2/3, CTPB = 0.1mmol was used as catalyst. The polymerization was conducted at [γBL] = 6 M in toluene for 2.5 h followed by addition of L-LA/THF solution (1 M) with temperature at -50 °C. The system temperature was then elevated to 25 °C. [b] Monomer conversions were determined by ^{1}H NMR spectra. [c] Number-average molecular weight and polydispersity (PDI) were determined by SEC in THF at 40 °C relative to polystyrene standards.

Table S3. Results of sequential ROP of γBL with ε-CL or δ-VL. [a]

run	M/γBL/C/I	M	Temp [b] (°C)	Time [b] (min)	C (γBL)[c] (%)	C (M)[c] (%)	M_n[d] (kg/mol)	PDI[d]
1	300/300/1/3	ε-CL	25	10	35.5	17.5	6.5	2.35
2	300/300/1/3	δ-VL	25	10	28.7	50.8	9.5	1.68

[a] Reaction conditions: CTPB was used as catalyst, BnOH (0.15mmol) was used as initiator. The polymerization was conducted at [γBL] = 6 M in toluene for 2.5 h followed by addition of ε-CL/THF or δ-VL/THF solution (1M) with temperature at -50 °C. [b] Temperature and time of the ROP of second monomer. [c] Determined by ^{1}H NMR spectra. [d] Determined by SEC in THF at 40 °C relative to polystyrene standards.

Table S4. TGA results of PγBL, PLLA and PγBL$_x$-*b*-PLLA$_y$. [a]

sample	$T_{d,\,5\%}$ (°C)	$T_{d,\,max}$ (°C)
PγBL	240	288, 349
PLLA	337	370
PγBL$_{50}$-*b*-PLLA$_{29}$	284	252, 384
PγBL$_{44}$-*b*-PLLA$_{49}$	331	369
PγBL$_{50}$-*b*-PLLA$_{77}$	330	368
PγBL$_{53}$-*b*-PLLA$_{97}$	326	368

[a] PγBL$_x$-*b*-PLLA$_y$,where x = [γBL]/[BnOH] * C (γBL), y = [L-LA]/[BnOH] * C (L-LA). Samples were obtained from conditions as followed: PγBL, Table 1, run 7; PLLA, Table S1, run 2; PγBL$_{50}$-*b*-PLLA$_{29}$, Table 1, run 10; PγBL$_{44}$-*b*-PLLA$_{49}$, Table 1, run 11; PγBL$_{50}$-*b*-PLLA$_{77}$, Table 1, run 12; PγBL$_{53}$-*b*-PLLA$_{97}$, Table 1, run 9.

Table S5. DSC results of PγBL$_x$-*b*-PLLA$_y$. [a]

Sample	First heating scan				Cooling scan			Second heating scan			
	T_{m1} (°C)	ΔH_{m1} (J/g)	T_{m2} (°C)	ΔH_{m2} (J/g)	T_c (°C)	ΔH_c (J/g)	T_g (°C)	T_{m1} (°C)	ΔH_{m1} (J/g)	T_{m2} (°C)	ΔH_{m2} (J/g)
PγBL$_{50}$-*b*-PLLA$_{29}$	43.6	23.1	153.8	6.9	N.A.	N.A.	-26.5	53.7	11.3	152.5	15.4
PγBL$_{44}$-*b*-PLLA$_{49}$	44.1	11.4	164.4	38.1	87.7	26.4	-38.4	56.4	1.0	163.3	37.8
PγBL$_{50}$-*b*-PLLA$_{77}$	45.4	1.5	165.5	48.3	89.1	31.1	-37.9	N.A.	N.A.	165.8	51.6
PγBL$_{53}$-*b*-PLLA$_{97}$	60.2	3.6	166.4	47.5	93.1	34.3	-44.2	N.A.	N.A.	165.8	49.5

[a] PγBL$_x$-*b*-PLLA$_y$, where x = [γBL]/[BnOH] * C (γBL), y = [L-LA]/[BnOH] * C (L-LA). Samples were obtained from conditions as followed: PγBL$_{50}$-*b*-PLLA$_{29}$, Table 1, run 10; PγBL$_{44}$-*b*-PLLA$_{49}$, Table 1, run 11; PγBL$_{50}$-*b*-PLLA$_{77}$, Table 1, run 12; PγBL$_{53}$-*b*-PLLA$_{97}$, Table 1, run 9.

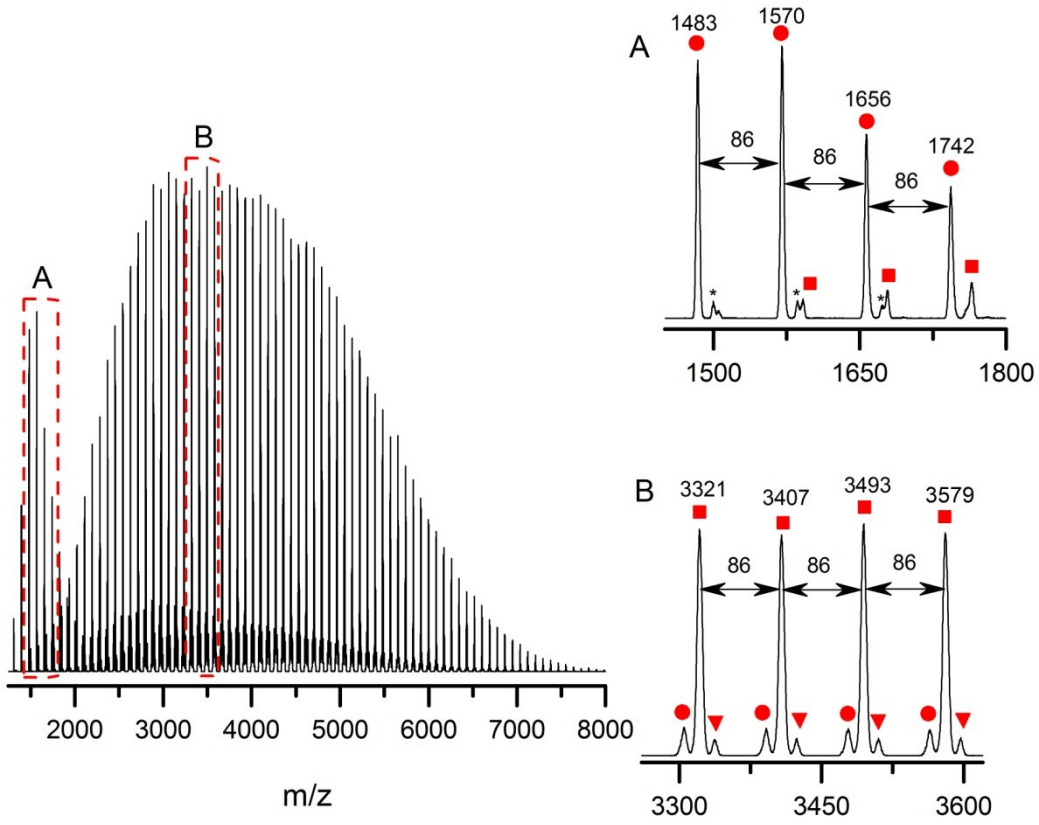

Figure S1. MALDI-TOF spectrum of PγBL polymerized at [γBL]/[CTPB]/[BnOH] = 300/1/3 at -50°C for 2.5 h (Table 1, run 1). Distribution A is assigned as cyclic PγBL structure whereas distribution B is assigned as linear PγBL structure terminated with BnO/H. ●indicate cyclic PγBL+Na^+, ■indicate linear BnO-PγBL-H+Na^+, * indicate cyclic PγBL+K^+, ▼indicate linear BnO-PγBL-H+K^+.

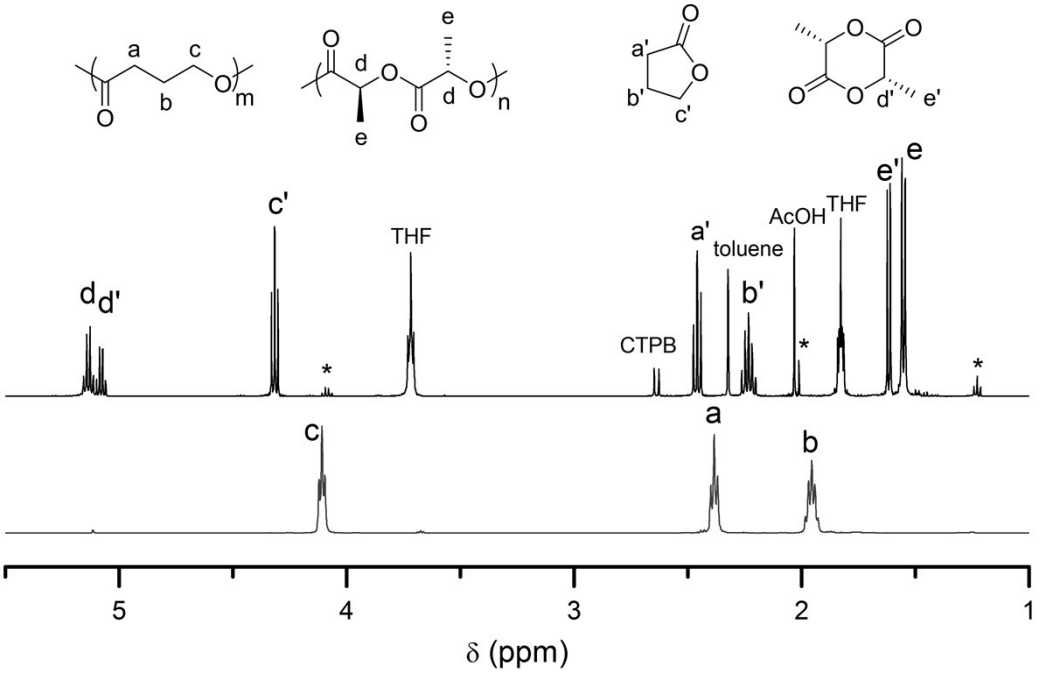

Figure S2. Stacked ^{1}H NMR spectra of the reaction mixtures of copolymerization of γBL with L-LA (top) and PγBL homopolymer (bottom). Deuterated chloroform was used as solvent. (Reaction conditions: [L-LA]/[γBL]/[Cat.]/[I] = 300/300/1/3, CTPB was used as catalyst, BnOH (0.15mmol) was used as initiator. [γBL] = [L-LA] = 1 M in THF were first mixed, then added into the mixture of CTPB and BnOH. The polymerization was conducted under N_2 at -50 °C for 3h. *indicates ethyl acetate. The polymerization conducted at 25 °C gave similar ^{1}H NMR spectrum).

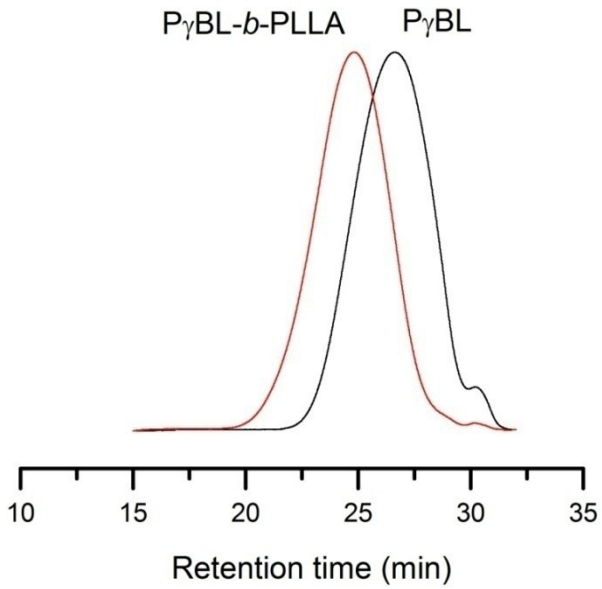

Figure S3. SEC traces of PγBL (Table 1, run 16) and PγBL-*b*-PLLA (Table 1, run 17) obtained at [Cat.]/[I] = 3/3.

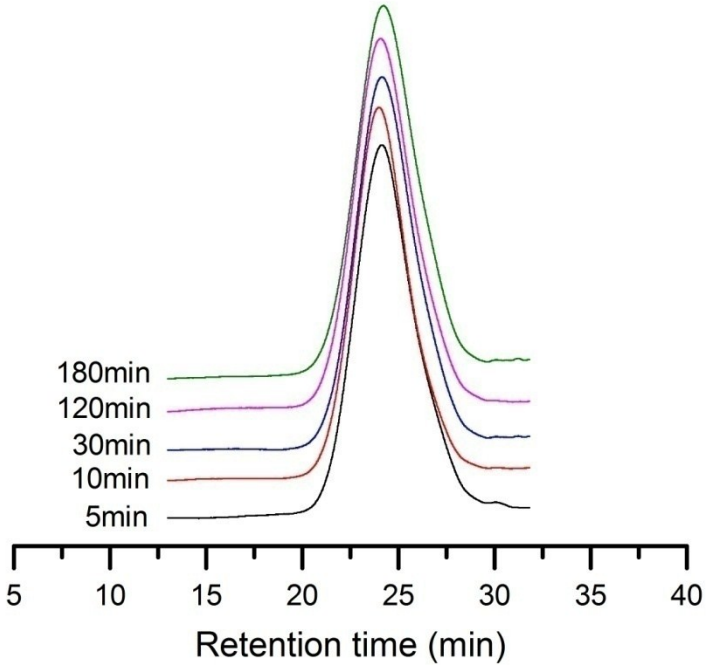

Figure S4. SEC traces of the aliquots withdrawn from the reaction mixtures at different time intervals (Table S2, run 1 to run 5).

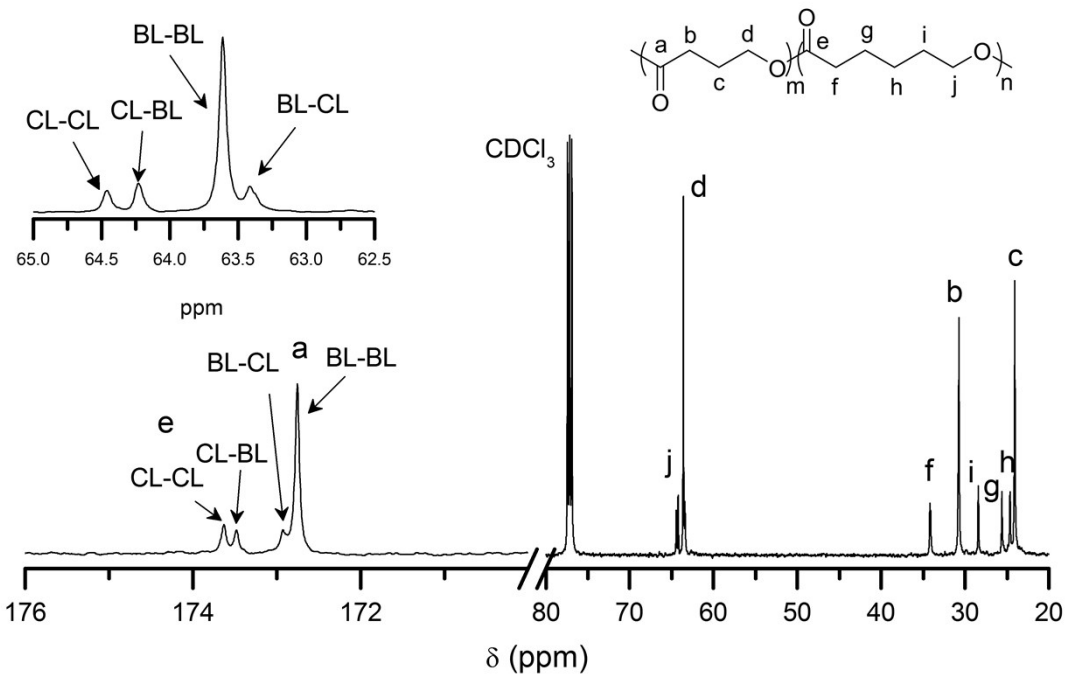

Figure S5. ^{13}C NMR spectrum of PγBL-*co*-PCL (Table S3, run 1). Deuterated chloroform was used as solvent.

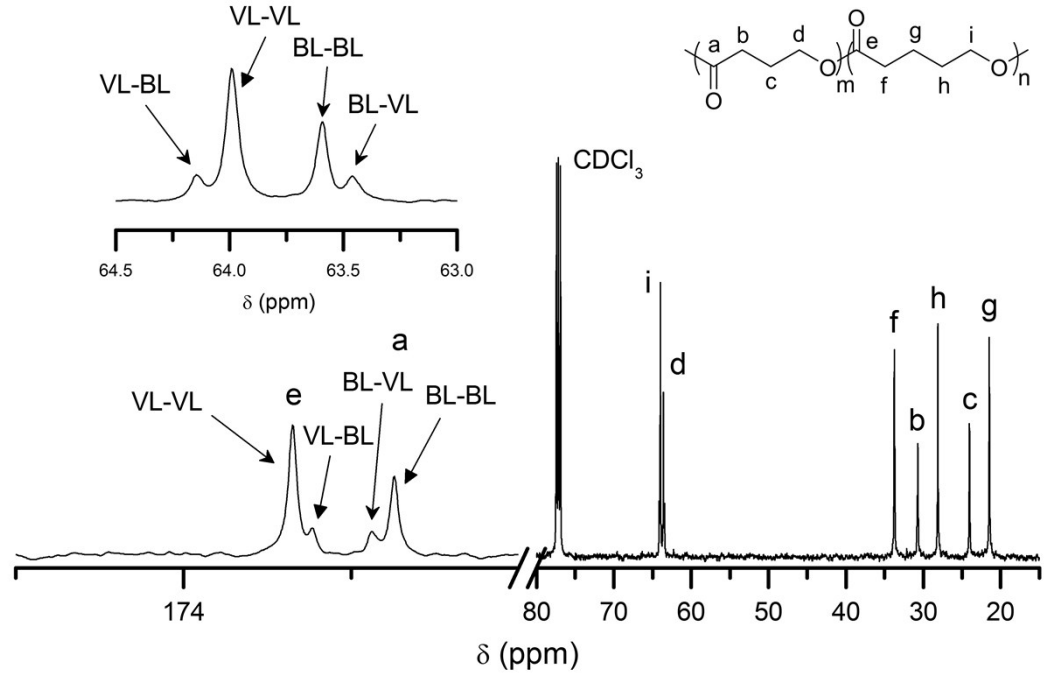

Figure S6. ^{13}C NMR spectrum of PγBL-*co*-PVL (Table S3, run 2). Deuterated chloroform was used as solvent.

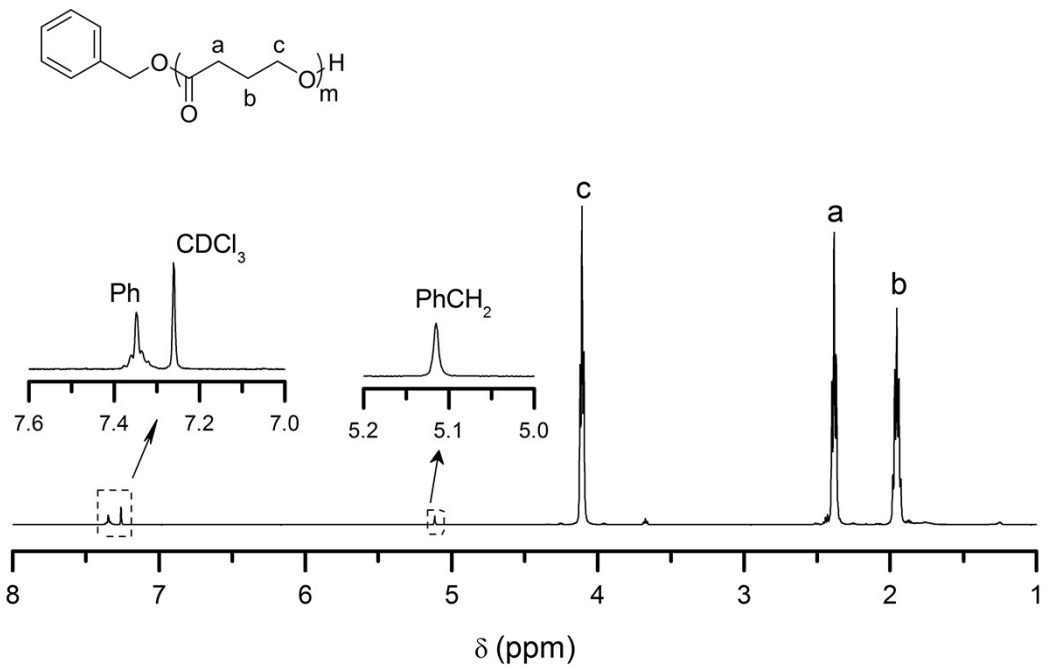

Figure S7. Representative ^{1}H NMR spectrum of PγBL. Deuterated chloroform was used as solvent.

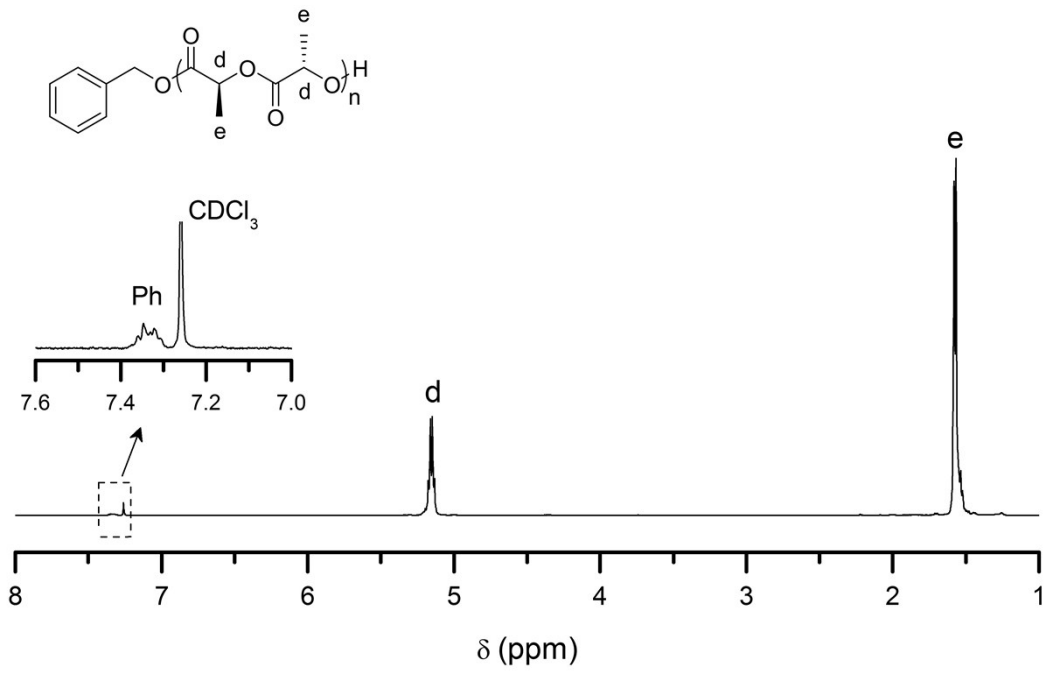

Figure S8. Representative ^{1}H NMR spectrum of PLLA. Deuterated chloroform was used as solvent.

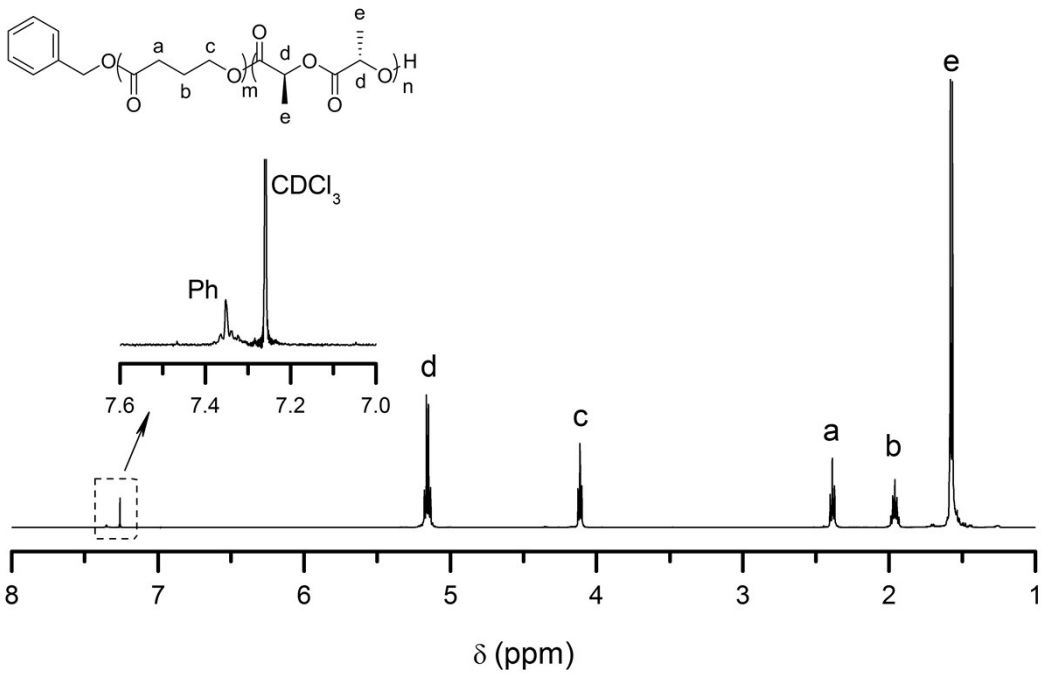

Figure S9. Representative ^{1}H NMR spectrum of PγBL-*b*-PLLA. Deuterated chloroform was used as solvent.

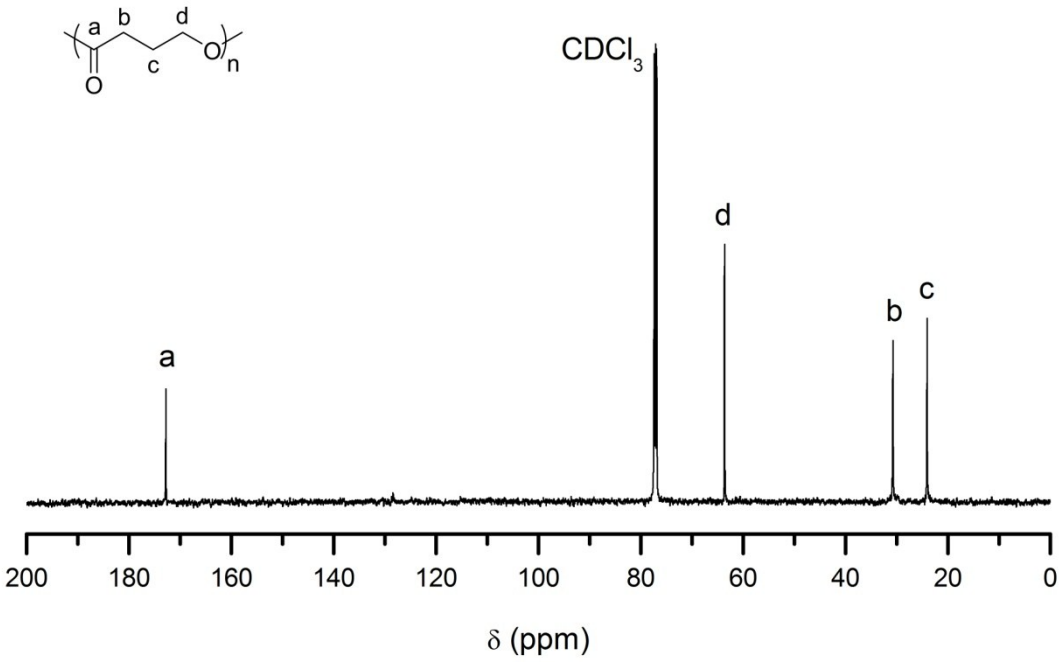

Figure S10. Representative ^{13}C NMR spectrum of PγBL. Deuterated chloroform was used as solvent.

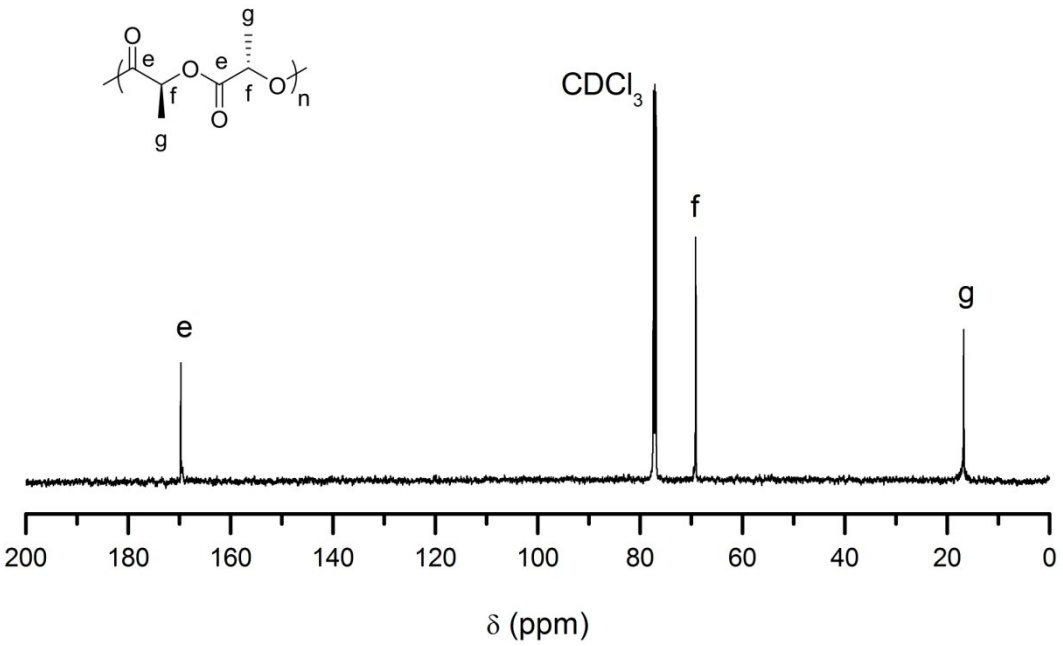

Figure S11. Representative ^{13}C NMR spectrum of PLLA. Deuterated chloroform was used as solvent.

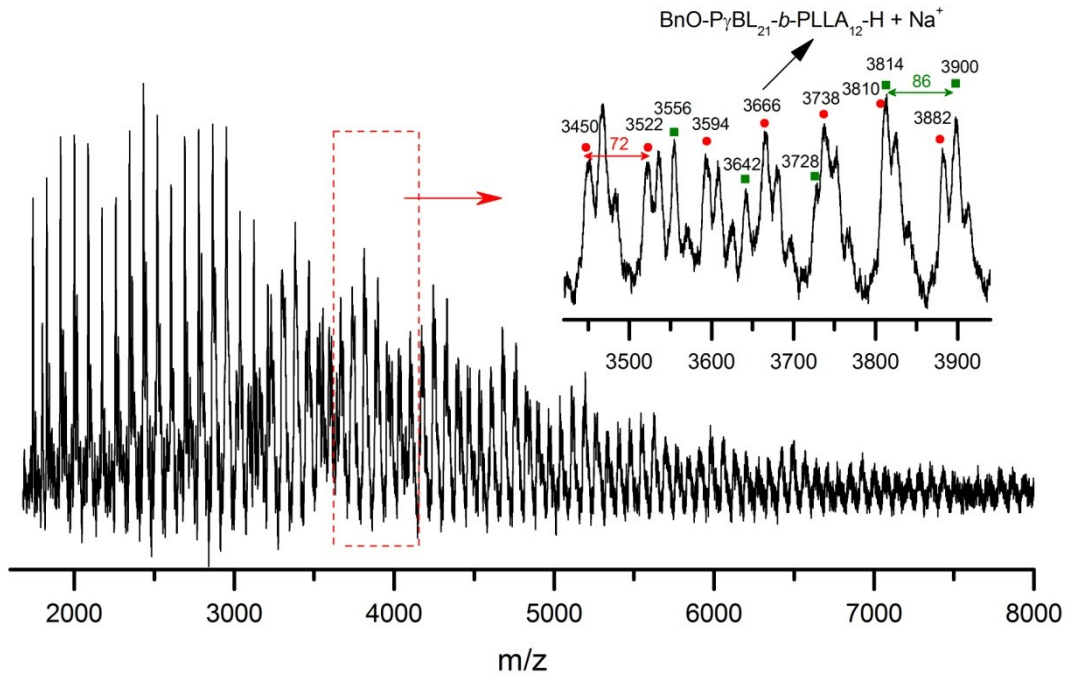

Figure S12. MALDI-TOF spectrum of PγBL-*b*-PLLA (Table 1, run 15). One possible structure for peak 3666 is BnO-PγBL_{21}-*b*-$PLLA_{12}$-H + Na^+.

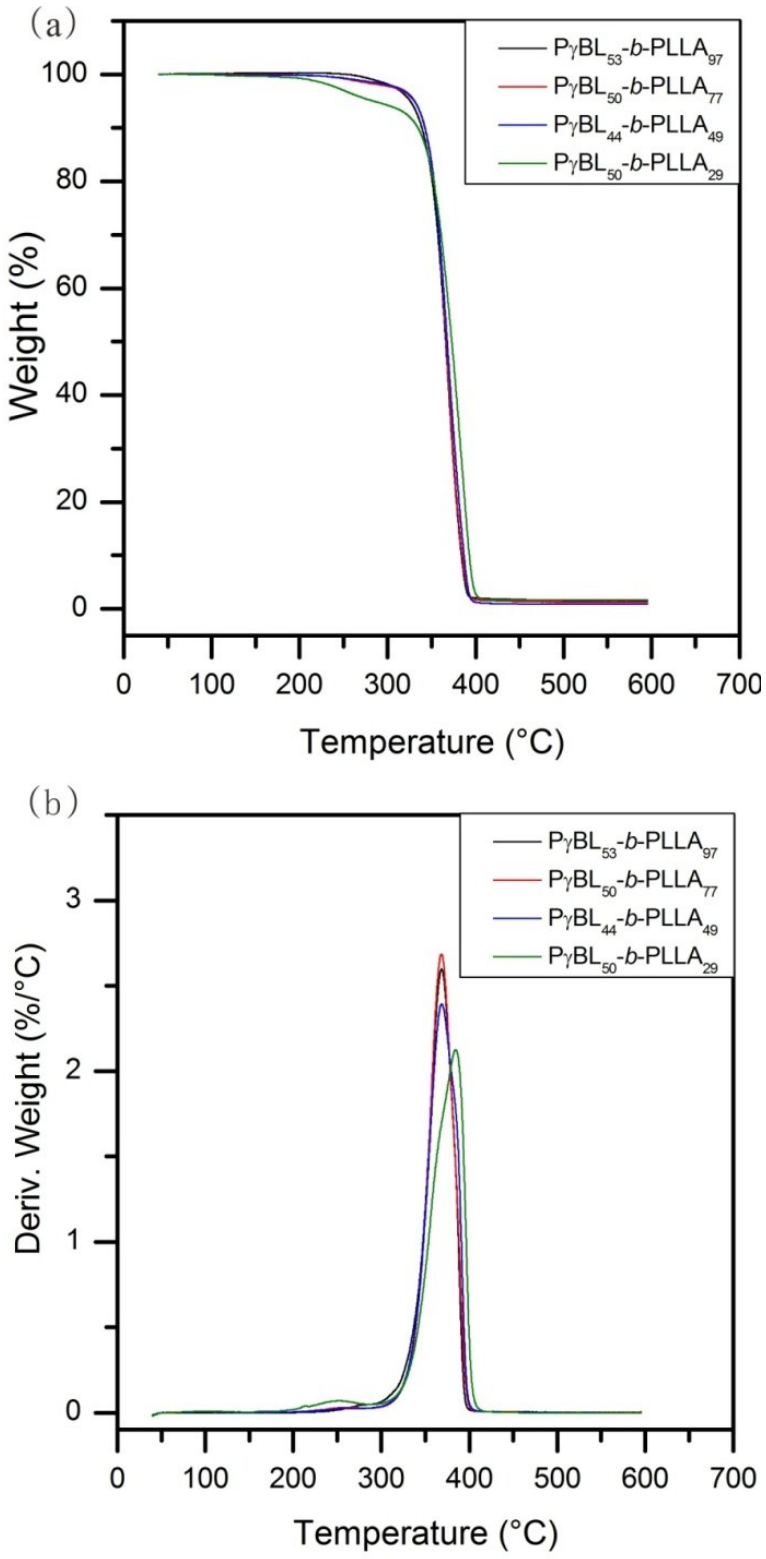

Figure S13. Representative (a) TGA and (b) DTG curves of PγBL$_x$-*b*-PLLA$_y$. The samples used were the same with Table S4.

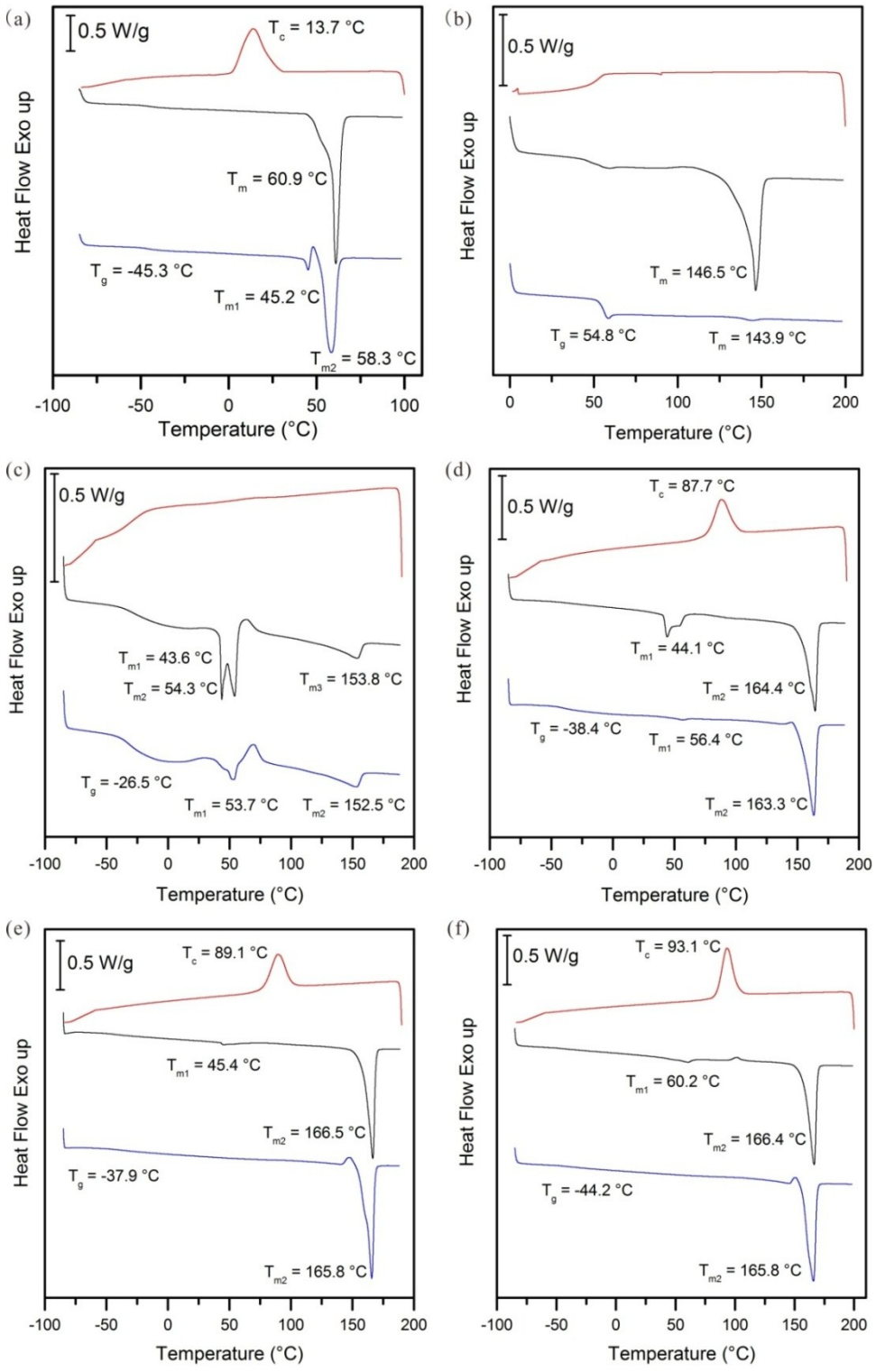

Figure S14. DSC curves (black lines: first heating scans; red lines: cooling scans; blue lines: second heating scans) of (a) PγBL (Table 1, run 7), (b) PLLA (Table S1, run 2), (c) PγBL_{50}-*b*-$PLLA_{29}$ (Table 1, run 10), (d) PγBL_{44}-*b*-$PLLA_{49}$ (Table1, run 11), (e) PγBL_{50}-*b*-$PLLA_{77}$ (Table 1, run 12) and (f) PγBL_{53}-*b*-$PLLA_{97}$ (Table 1, run 9).

References

1. N. Zhao, C. Ren, H. Li, Y. Li, S. Liu and Z. Li, *Angew. Chem. Int. Ed.*, 2017, **56**, 12987-12990.