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Supplementary Information for Manuscript Entitled

Stereoselective ring-opening polymerization of *rac*-lactide catalyzed by proton sponge bisphosphazene of 1,8-bis(hexamethyltriaminophosphazenyl)naphthalene

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Experimental Section

Materials.

Toluene and tetrahydrofuran (THF) were purified by purging with dry nitrogen, followed by passing through columns of activated alumina. *Rac*-LA was purchased from Macklin Inc. and recrystallized twice from toluene. Benzyl alcohol (BnOH), purchased from Shanghai Aladdin Biochemical Technology Co., Ltd, was stirred with CaH_2 at room temperature for 24 hours and distilled under reduced pressure prior to use. Other chemicals were purchased from commercial suppliers and used without further purification unless otherwise noted. HMPN,[1] U-1/U-2/U-3/U-4,[2, 3] and SQ-1/SQ-2[4] were synthesized according to the procedures reported before.

General Considerations.

All moisture/oxygen sensitive reactions/compounds were operated using standard

Schlenk technique or glovebox technique in an atmosphere of high-purity nitrogen. Nuclear magnetic resonance (NMR) spectra were recorded on a Bruker AVANCE NEO 400 MHz NMR spectrometer (400 MHz for ^{1}H NMR) at 298 K. Chemical shifts were reported in δ (ppm) and were referenced to tetramethylsilane (0.00 ppm). Gel permeation chromatography (GPC) experiments were performed on an Agilent HPLC system equipped with a model 1260 Hip degasser, a model 1260 Iso pump and a model 1260 differential refractometer detector with using THF as mobile phase at a flow rate of 1.0 mL/min at 40 °C. One PLgel5 μm guard column and three Mz-Gel SD_{plus} columns (10^3 Å, 10^4 Å, and 10^5 Å, linear range of M_w = 1000 - 2*10^6 Da) were connected in series. The molecular weight and dispersity were calculated using polystyrene standards with narrow molecular weight distribution as references. The sample concentration used for GPC analysis was about 5 mg/mL. Matrix-assisted laser desorption/ionization time-of-flight mass spectroscopy (MALDI-TOF MS) analyses were conducted on a Bruker Microflex MALDI-TOF MS spectrometer equipped with a 337 nm nitrogen laser. The polymer was dissolved in THF, and *trans*-2-[3-(4-*tert*-butylphenyl)-2-methyl-2-propenylidene]-malononitrile (DCTB) was used as the matrix and CF_3COONa as the ionization agent. Differential scanning calorimetry (DSC) was performed using a TA differential scanning calorimeter DSC 25 that was calibrated using high purity indium. 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.

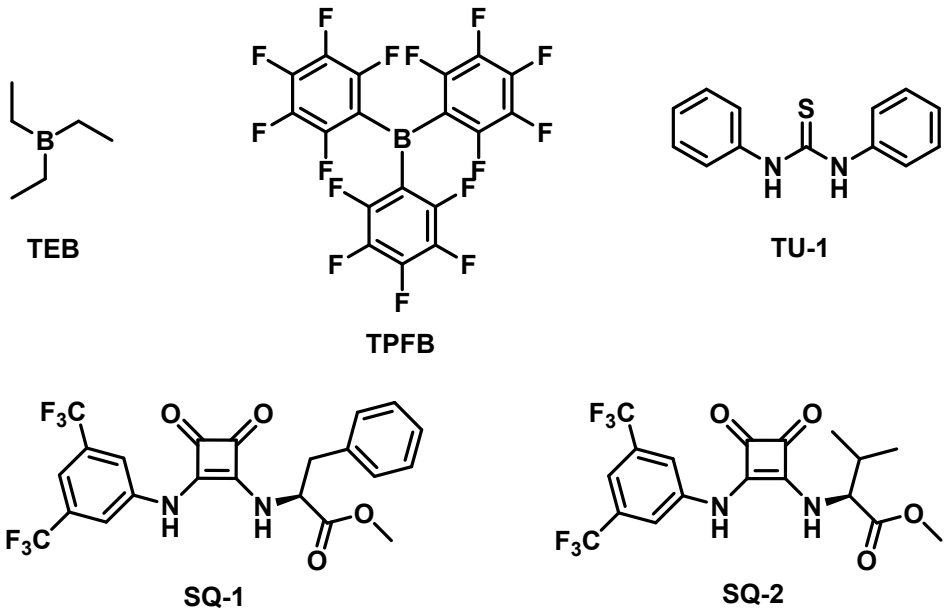
General procedure for ROP of *rac*-LA catalyzed by HMPN (Table 1, run 2).

In a glove-box, HMPN (4.2 mg, 0.01 mmol) and BnOH (1.0 μL, 0.01 mmol) were dissolved in 1 mL of toluene and stirred for 10 min in a Schlenk tube. Then *r*ac-LA (144 mg, 1.0 mmol) was added into the mixture to start the polymerization at room temperature (25 °C). After the desired polymerization time, acetic acid was added to quench the reaction and a small part of solution was taken and analyzed by ^{1}H NMR to determine the conversion. The conversion of rac-LA monomer was calculated based on the integration (I) ratio $I_{PLA}/[I_{PLA} + I_{rac\text{-}LA}]$ of the methine proton, which is at

5.18 ppm for PLA polymer and 4.87 ppm for *rac*-LA monomer. The other solution was poured into cold methanol (100 mL) to precipitate polymer, which was dried in a vacuum oven overnight.

General procedure for ROP of *rac*-LA catalyzed by HMPN/cocatalyst (Table 2, run 2).

In a glove-box, *rac*-LA (144 mg, 1.0 mmol) was dissolved in toluene (0.5 mL) in a Schlenk tube. In a second tube, HMPN (4.2 mg, 0.01 mmol), BnOH (1.0 μL, 0.01 mmol), U-2 (6.5 mg, 0.03 mmol) were mixed in toluene (0.5 mL) and stirred for 2 min. The latter mixture was then added into *rac*-LA solution to start the polymerization at room temperature (25 °C). After the desired polymerization time, acetic acid was added to quench the reaction and a small part of solution was taken and analysed by ^{1}H NMR to determine the conversion.



Scheme S1. Chemical structures of the cocatalysts

Table S1. ROP of *rac*-LA catalyzed by binary catalytic system[a]

run	M/B/I/C[b]	Cocatalyst	Solvent	Time (min)	Conv.[c] (%)	M_n[d] (kg/mol)	$Đ$[d]	P_m[e]
1	100/1/1/2	TEB	Toluene	60	95	3.1	1.26	0.66
2	100/1/1/1	TPFB	Toluene	720	0	n.d.	n.d.	n.d.
3	100/1/1/3	SQ-1	THF	20	8	21.6	1.36	0.67
4	100/1/1/3	SQ-2	THF	20	5	22.0	1.33	0.68
5	100/1/1/3	TU-1	toluene	10	88	21.2	1.09	0.76

[a]Conditions: $[rac\text{-LA}]_0$ = 1.0 mol/L, the polymerizations were carried out ar room temperature using HMPN as catalyst. [b]M/B/I/C indicates the mole ratio of $[rac\text{-LA}]_0/[\text{HMPN}]_0/[\text{BnOH}]_0/[\text{cocatalyst}]_0$. [c]Determined by ^{1}H-NMR. [d]Determined by GPC at 40 ℃ in THF using standard polystyrene as a reference. [e]Determined by homonuclear decoupled ^{1}H NMR spectroscopy of purified polymers.

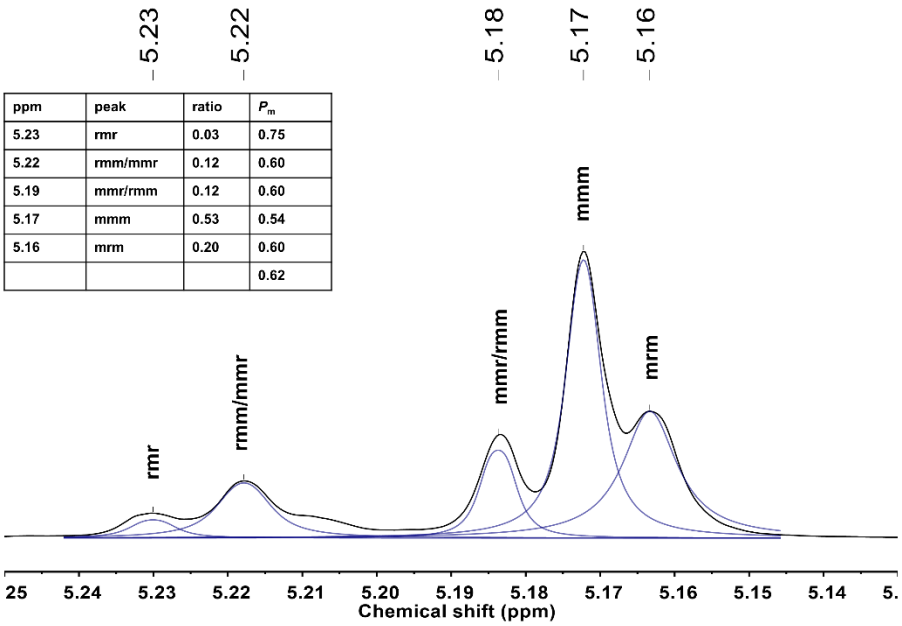
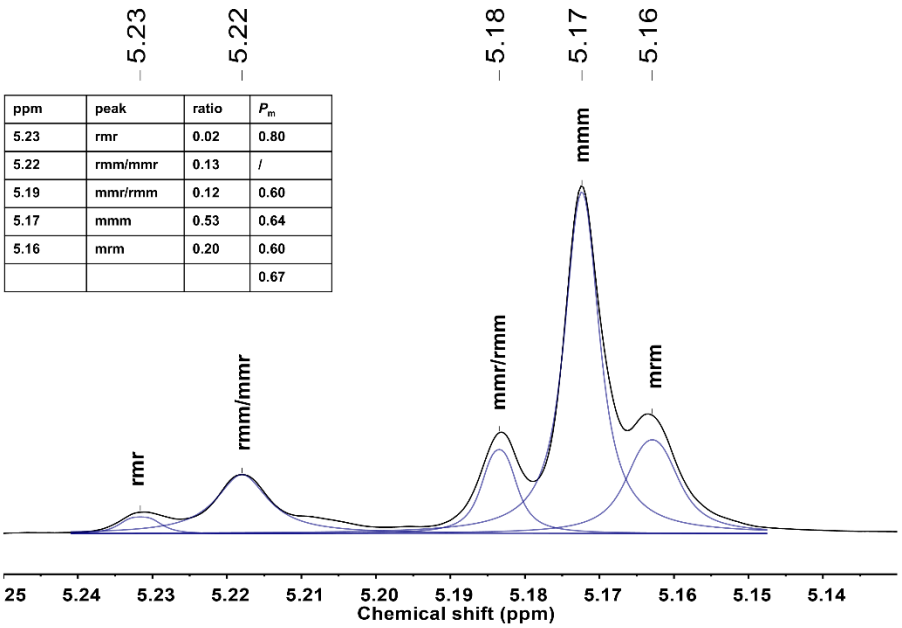
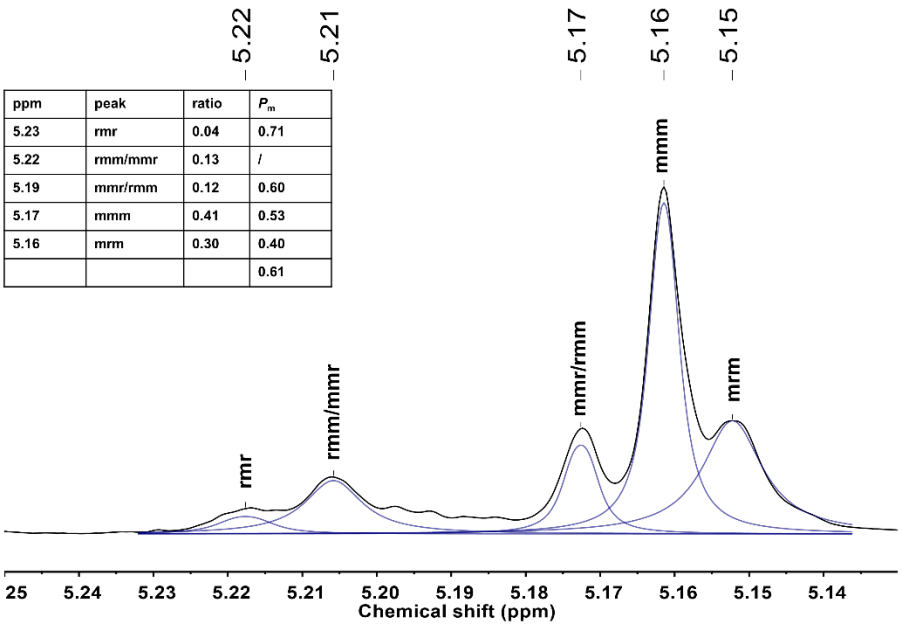


Figure S1. Homonuclear decoupled ^{1}H NMR spectrum of PLA sample (Table 1, run 1).



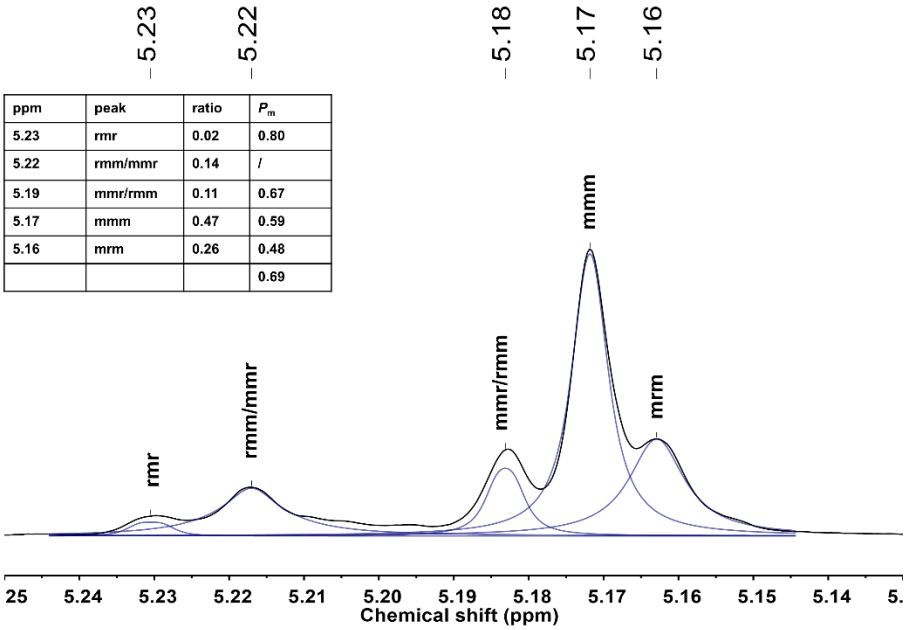
ppm	peak	ratio	P_m
5.23	rmr	0.02	0.80
5.22	rmm/mmr	0.13	/
5.19	mmr/rmm	0.12	0.60
5.17	mmm	0.53	0.64
5.16	mrm	0.20	0.60
			0.67

Figure S2. Homonuclear decoupled ^{1}H NMR spectrum of PLA sample (Table 1, run 2).



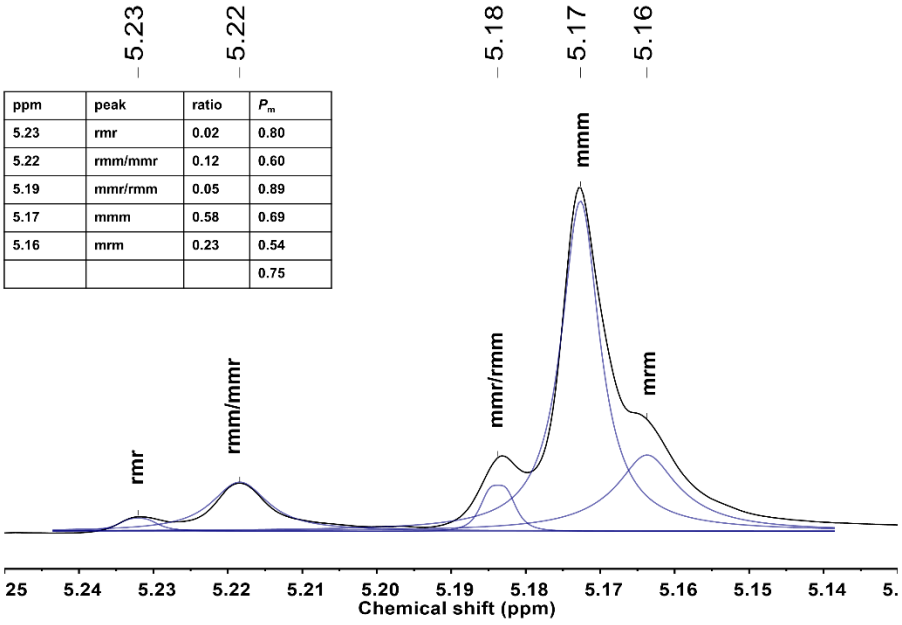
ppm	peak	ratio	P_m
5.23	rmr	0.04	0.71
5.22	rmm/mmr	0.13	/
5.19	mmr/rmm	0.12	0.60
5.17	mmm	0.41	0.53
5.16	mrm	0.30	0.40
			0.61

Figure S3. Homonuclear decoupled ^{1}H NMR spectrum of PLA sample (Table 1, run 3).



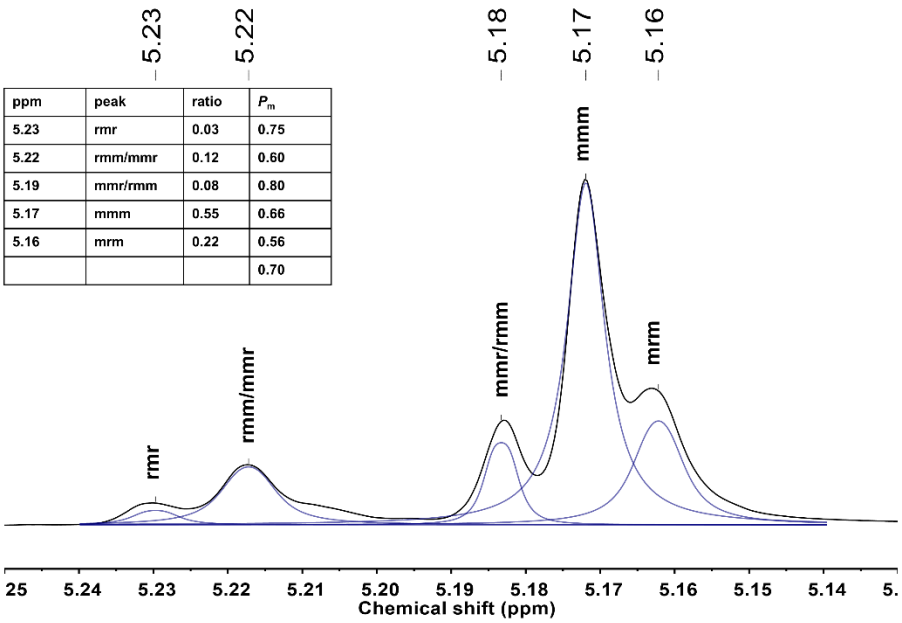
ppm	peak	ratio	P_m
5.23	rmr	0.02	0.80
5.22	rmm/mmr	0.14	/
5.19	mmr/rmm	0.11	0.67
5.17	mmm	0.47	0.59
5.16	mrm	0.26	0.48
			0.69

Figure S4. Homonuclear decoupled ^{1}H NMR spectrum of PLA sample (Table 1, run 4).



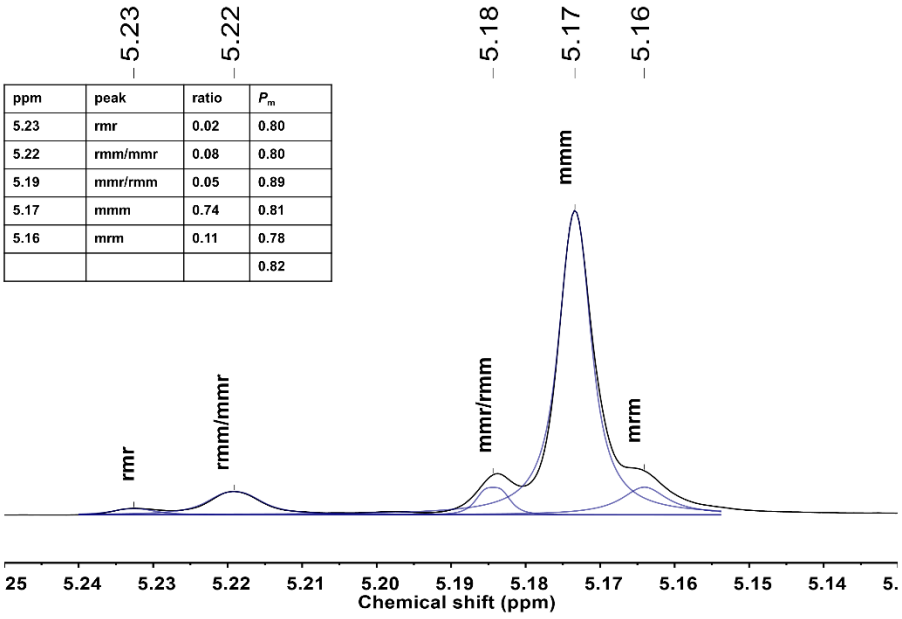
ppm	peak	ratio	P_m
5.23	rmr	0.02	0.80
5.22	rmm/mmr	0.12	0.60
5.19	mmr/rmm	0.05	0.89
5.17	mmm	0.58	0.69
5.16	mrm	0.23	0.54
			0.75

Figure S5. Homonuclear decoupled ^{1}H NMR spectrum of PLA sample (Table 1, run 5).



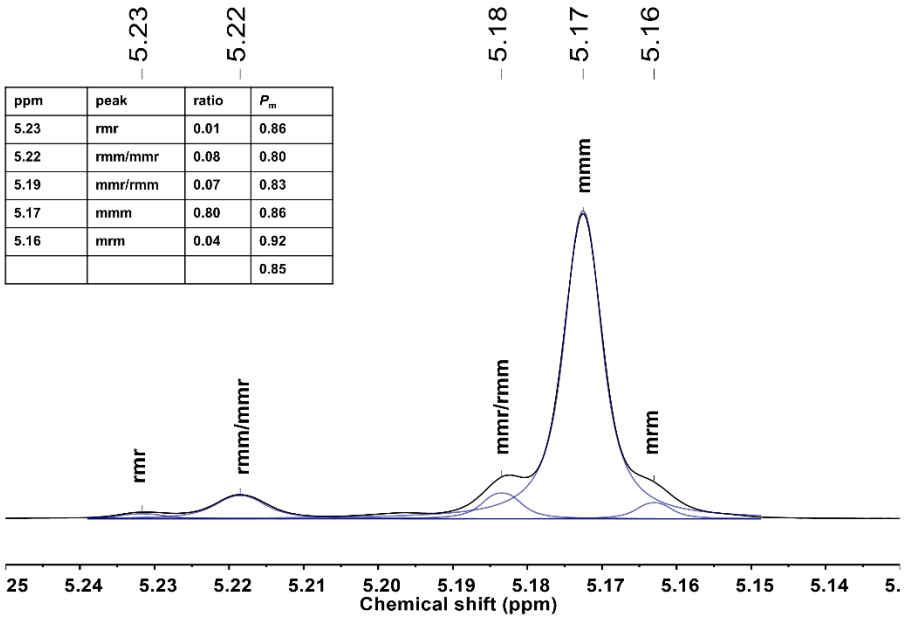
ppm	peak	ratio	P_m
5.23	rmr	0.03	0.75
5.22	rmm/mmr	0.12	0.60
5.19	mmr/rmm	0.08	0.80
5.17	mmm	0.55	0.66
5.16	mrm	0.22	0.56
			0.70

Figure S6. Homonuclear decoupled ^{1}H NMR spectrum of PLA sample (Table 1, run 7).



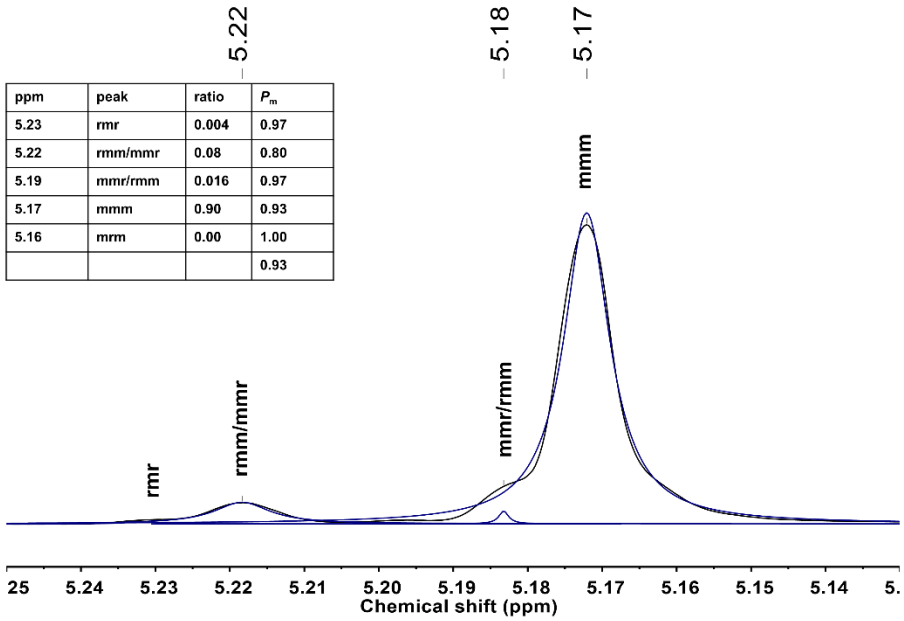
ppm	peak	ratio	P_m
5.23	rmr	0.02	0.80
5.22	rmm/mmr	0.08	0.80
5.19	mmr/rmm	0.05	0.89
5.17	mmm	0.74	0.81
5.16	mrm	0.11	0.78
			0.82

Figure S7. Homonuclear decoupled ^{1}H NMR spectrum of PLA sample (Table 1, run 8).



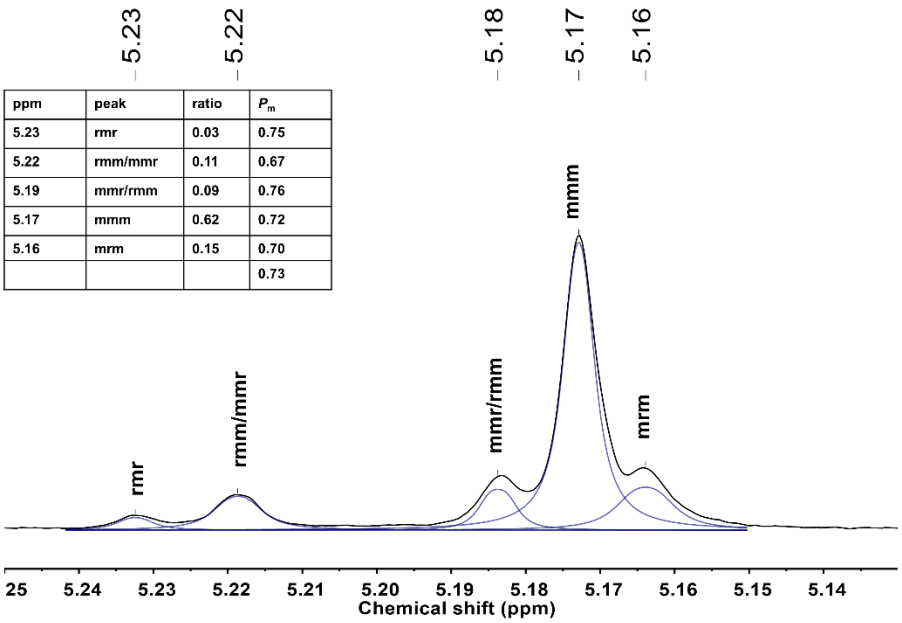
ppm	peak	ratio	P_m
5.23	rmr	0.01	0.86
5.22	rmm/mmr	0.08	0.80
5.19	mmr/rmm	0.07	0.83
5.17	mmm	0.80	0.86
5.16	mrm	0.04	0.92
			0.85

Figure S8. Homonuclear decoupled ^{1}H NMR spectrum of PLA sample (Table 1, run 9).



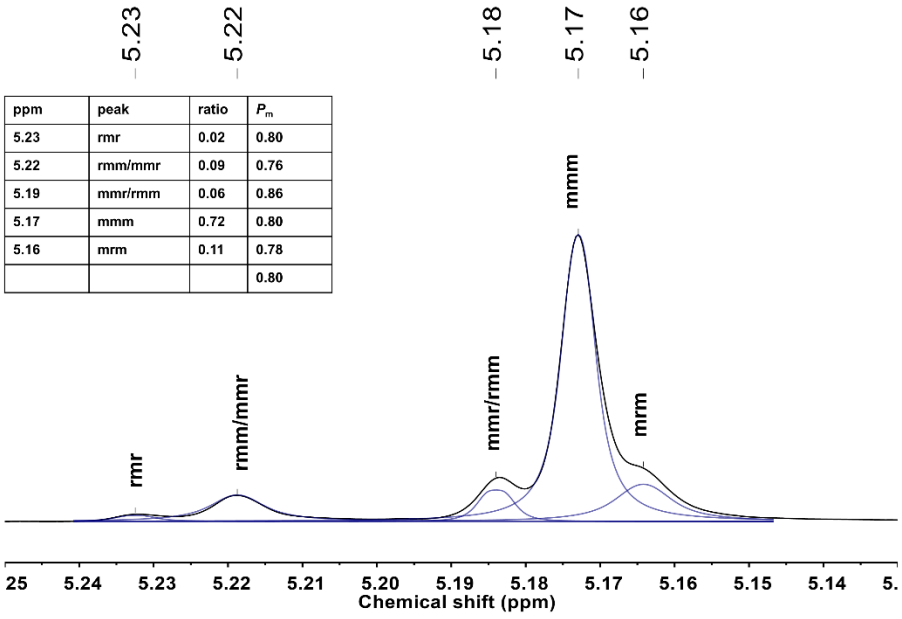
ppm	peak	ratio	P_m
5.23	rmr	0.004	0.97
5.22	rmm/mmr	0.08	0.80
5.19	mmr/rmm	0.016	0.97
5.17	mmm	0.90	0.93
5.16	mrm	0.00	1.00
			0.93

Figure S9. Homonuclear decoupled ^{1}H NMR spectrum of PLA sample (Table 1, run 10).



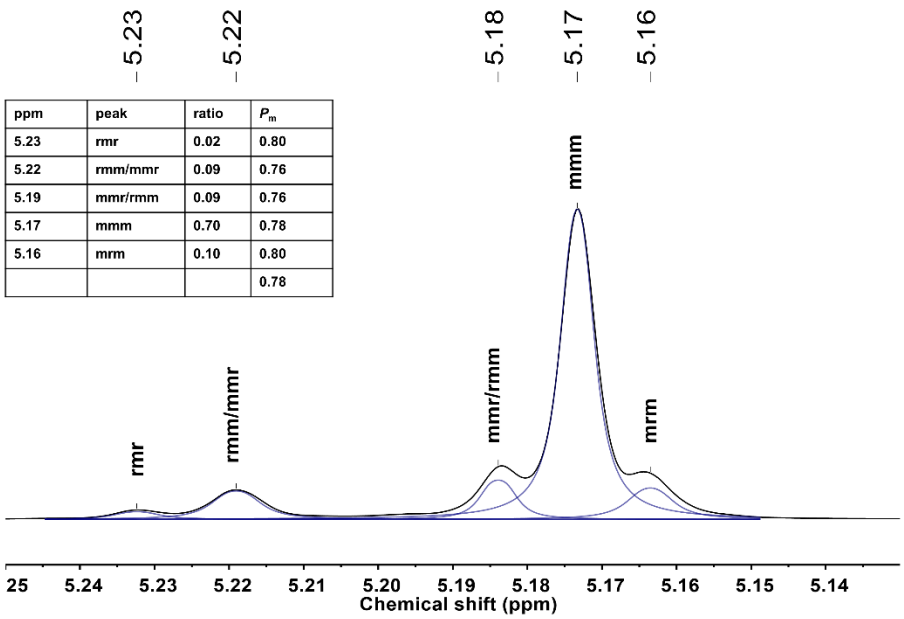
ppm	peak	ratio	P_m
5.23	rmr	0.03	0.75
5.22	rmm/mmr	0.11	0.67
5.19	mmr/rmm	0.09	0.76
5.17	mmm	0.62	0.72
5.16	mrm	0.15	0.70
			0.73

Figure S10. Homonuclear decoupled ^{1}H NMR spectrum of PLA sample (Table 2, run 1).



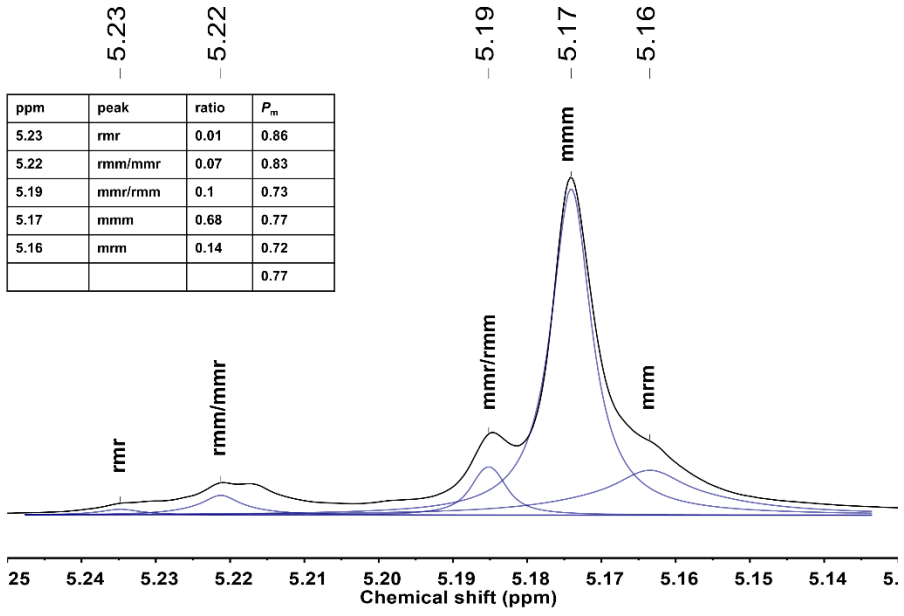
ppm	peak	ratio	P_m
5.23	rmr	0.02	0.80
5.22	rmm/mmr	0.09	0.76
5.19	mmr/rmm	0.06	0.86
5.17	mmm	0.72	0.80
5.16	mrm	0.11	0.78
			0.80

Figure S11. Homonuclear decoupled ^{1}H NMR spectrum of PLA sample (Table 2, run 2).



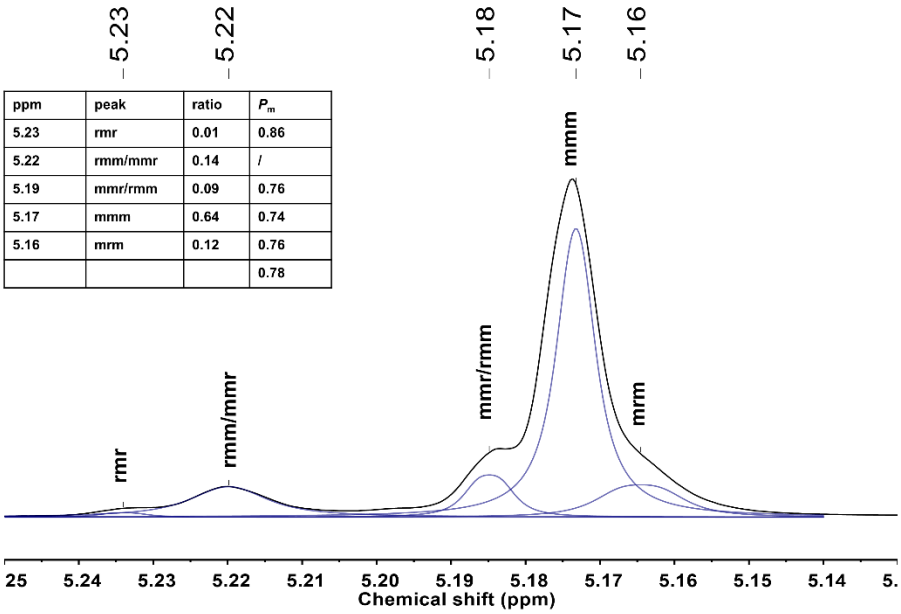
ppm	peak	ratio	P_m
5.23	rmr	0.02	0.80
5.22	rmm/mmr	0.09	0.76
5.19	mmr/rmm	0.09	0.76
5.17	mmm	0.70	0.78
5.16	mrm	0.10	0.80
			0.78

Figure S12. Homonuclear decoupled ^{1}H NMR spectrum of PLA sample (Table 2, run 3).



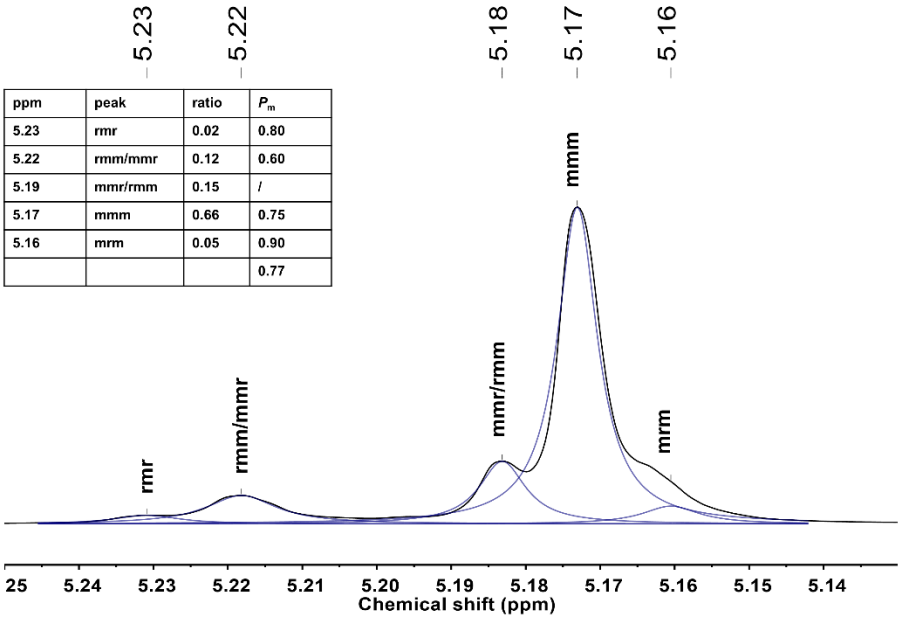
ppm	peak	ratio	P_m
5.23	rmr	0.01	0.86
5.22	rmm/mmr	0.07	0.83
5.19	mmr/rmm	0.1	0.73
5.17	mmm	0.68	0.77
5.16	mrm	0.14	0.72
			0.77

Figure S13. Homonuclear decoupled ^{1}H NMR spectrum of PLA sample (Table 2, run 4).



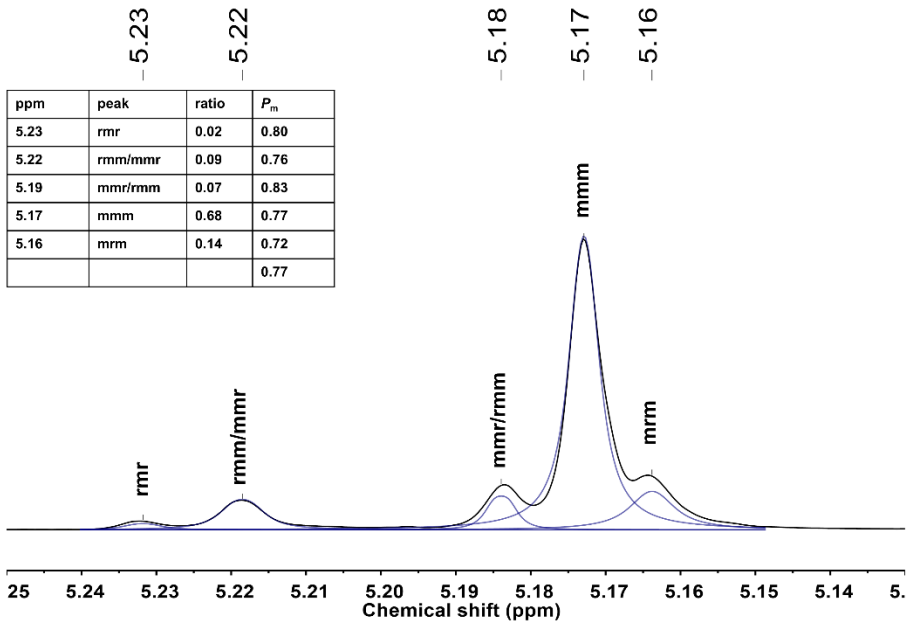
ppm	peak	ratio	P_m
5.23	rmr	0.01	0.86
5.22	rmm/mmr	0.14	/
5.19	mmr/rmm	0.09	0.76
5.17	mmm	0.64	0.74
5.16	mrm	0.12	0.76
			0.78

Figure S14. Homonuclear decoupled ^{1}H NMR spectrum of PLA sample (Table 2, run 5).



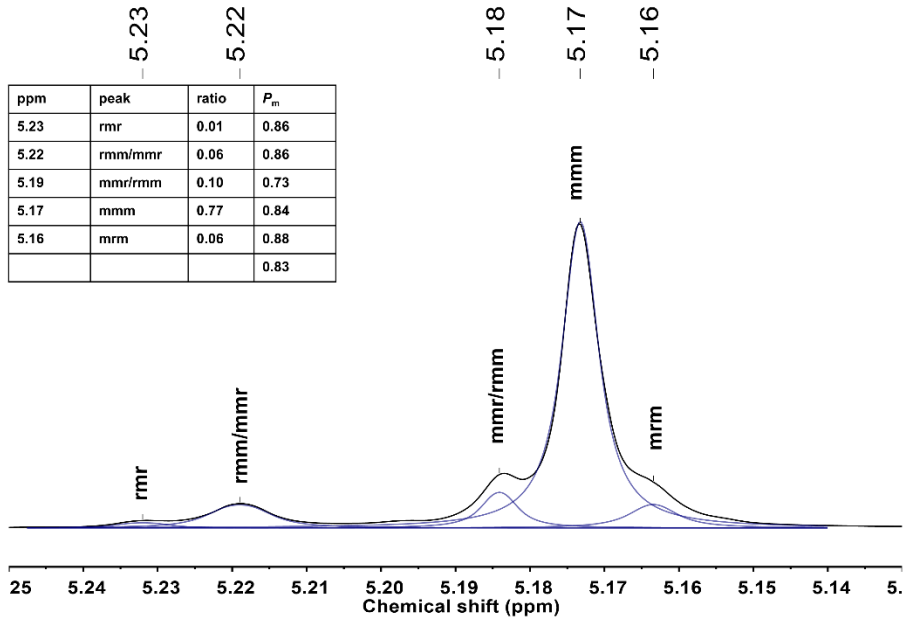
ppm	peak	ratio	P_m
5.23	rmr	0.02	0.80
5.22	rmm/mmr	0.12	0.60
5.19	mmr/rmm	0.15	/
5.17	mmm	0.66	0.75
5.16	mrm	0.05	0.90
			0.77

Figure S15. Homonuclear decoupled ^{1}H NMR spectrum of PLA sample (Table 2, run 6).



ppm	peak	ratio	P_m
5.23	rmr	0.02	0.80
5.22	rmm/mmr	0.09	0.76
5.19	mmr/rmm	0.07	0.83
5.17	mmm	0.68	0.77
5.16	mrm	0.14	0.72
			0.77

Figure S16. Homonuclear decoupled ^{1}H NMR spectrum of PLA sample (Table 2, run 7).



ppm	peak	ratio	P_m
5.23	rmr	0.01	0.86
5.22	rmm/mmr	0.06	0.86
5.19	mmr/rmm	0.10	0.73
5.17	mmm	0.77	0.84
5.16	mrm	0.06	0.88
			0.83

Figure S17. Homonuclear decoupled ^{1}H NMR spectrum of PLA sample (Table 2, run 8).

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