One–pot Copolymerization of Epoxides/Carbon Dioxide and Lactide by Ternary Catalyst System

Xiang Li, Chenyang Hu, Xuan Pang,* Ranlong Duan and Xuesi Chen

Supplementary Information
Contents

Table S1. Polymerization data of LLA using 1a and 1b.[a]

Entry	Catalyst Ratio[b]			LLA[b]	PO[b]	H_2O (%)[c]	Time (h)	Temp (°C)	Conversion (%)[d]
	1a	1b	PPNCl						
1[e]	-	1	-	250	2500	-	2	60	33
2[e]	1	-	-	250	2500	-	24	60	0
3[e]	-	-	1	250	2500	-	2	60	0
4[e]	1	-	1	250	2500	-	2	60	6
5[f], [g]	-	1	1	250	2500	-	2	60	66
6[f], [h]	-	1	-	250	2500	0.25	2	60	68
7	-	-	1	250	2500	0.25	2	60	5
8	1	-	1	250	2500	0.25	2	60	4
9[f], [i]	-	1	1	250	2500	0.25	2	60	92
10[f], [j]	-	1	-	250	2500	0.5	2	60	90
11	-	-	1	250	2500	0.5	2	60	17
12	1	-	1	250	2500	0.5	2	60	10
13	-	1	1	250	2500	0.5	2	60	92
14	-	1	-	250	2500	1.5	2	60	80
15	-	-	1	250	2500	1.5	2	60	7
16	1	-	1	250	2500	1.5	2	60	8
17	1	1	-	250	2500	1.5	2	60	29
18	-	1	1	250	2500	1.5	2	60	96

[a]: Using 2 mL PO as solvent. [b]: Feed ratio. [c]: By adding quantified H_2O into neat PO to achieve a suitable mass fraction. [d]: Measured by ^1H NMR, no polyether signal was found in both ^1H and ^{13}C NMR spectra. [e]: Using neat PO. [f] Determined by gel permeation chromatography calibrated with polystyrene, with a Waters 1515 GPC with tetrahydrofuran as the eluent (flow rate: 1 mLmin⁻¹, at 35 °C). [g] Mn = 4865, PDI = 1.15. [h] Mn = 5365, PDI = 1.16. [i] Mn = 3865, PDI = 1.26. [j] Mn = 4265, PDI = 1.32.

Table S2. Copolymerization data of PO and CO$_2$ using 1a and 1b.[a]

Entry	[1a][b]	[1b][b]	[PPNCl][b]	[PO][b]	Time (h)	Temp (°C)	Conversion (%)[c]	Selectivity (%)[c]
1	-	1	1	7500	8	60	95	98
2	1	-	1	2500	8	60	69.5	16.2
2	1	-	1	2500	20	60	81.2	0
4	1	1	1	7500	8	60	82	86

[a] The reactions were performed in 2 mL neat PO and 25 mL autoclave at 60 °C, 2 MPa, using PPNCl as cocatalyst. [b] Molar ratio. [c] Selectivity for polycarbonates over cyclic carbonate, determined by ^{1}H NMR spectroscopy.
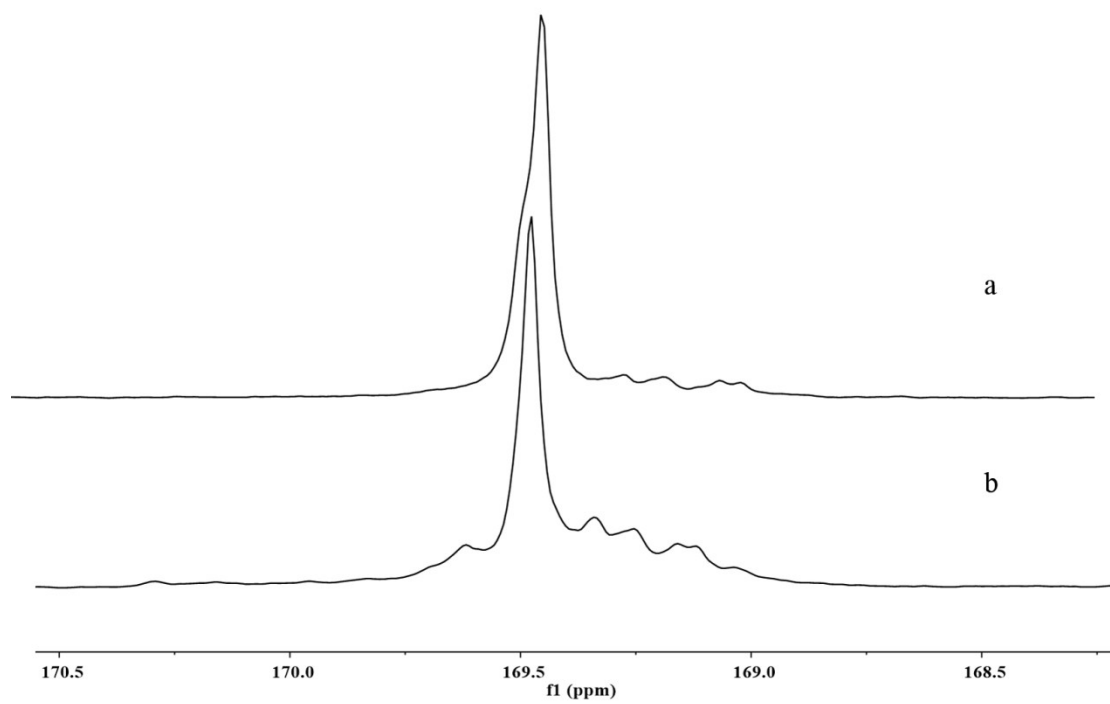
2

Figure S1. ¹³C NMR spectra of PLLAPC. **a**: Tg 52 °C (Table 1, Entry 5), **b**: Tg 38 °C (Table S4, Entry 2).
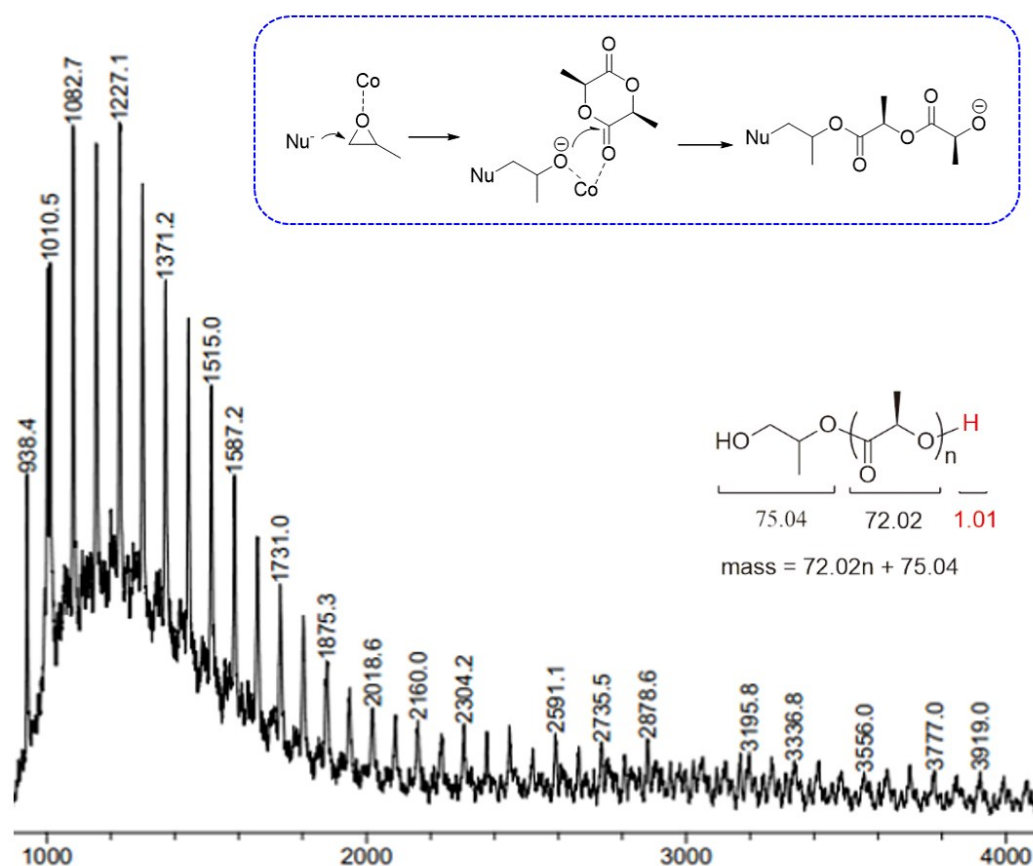
Figure S2. MALDI-TOF Mass spectrum of PLLA, [1b]:[LLA]:[PO]=1:250:2500, 60 ºC, 0.5h.

PO is ring-opened by trace amount of water first, and then initiates the following LLA ROP process, results in a PO-ended PLLA (the methine alkoxy end is supposed to be inactive due to the steric hindrance). In this process, PO is necessary as both solvent and initiator. The addition of PO or other epoxides are essential during this process. The peculiar end group is verified by MS and ^{1}H NMR spectrum (Figures S3). SalenCo[III] complexes are completely inactive in toluene or tetrahydrofuran (with or without isopropanol as initiator), which are widely used as solvent in LLA polymerization. Unlike SalenCo[III], SalenCo[II] is inactive in LLA polymerization unless with the aid of cocatalyst.
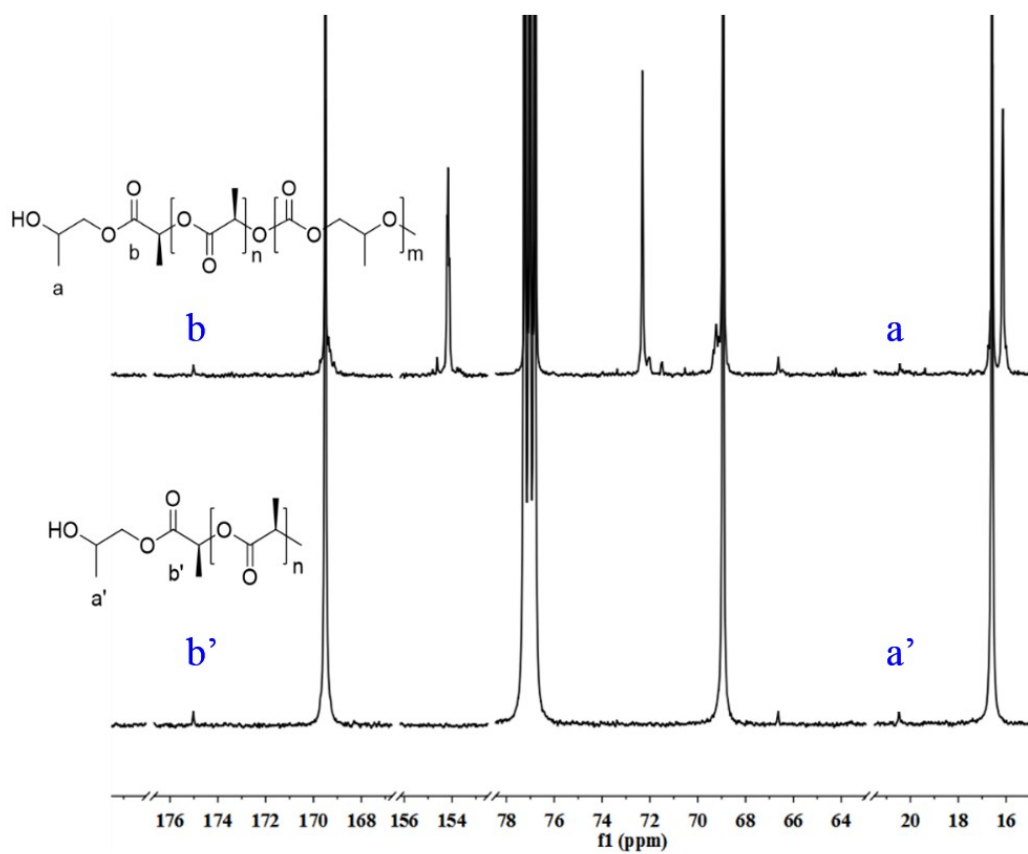
Figure S3. Assigned ^{13}C NMR spectra of PLLAPC and PLLA with similar end-groups (150 MHz). The analysis of both end-groups of PLLAPC are shown in Figure S5-S10.
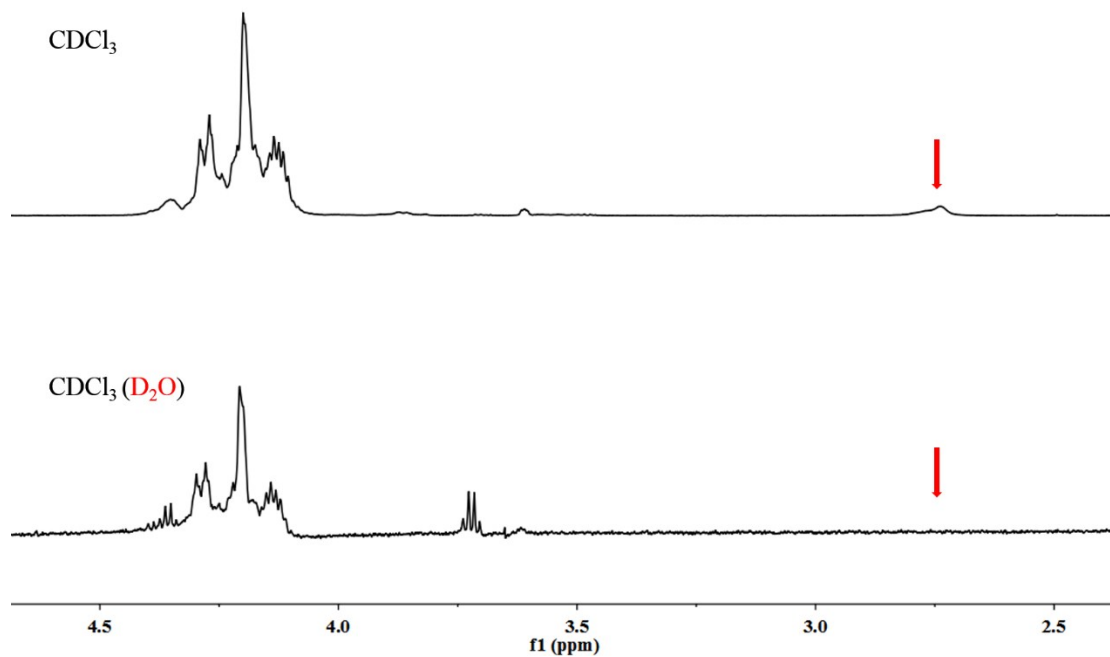
Figure S4. The ^{1}H NMR spectra of PLLAPC (Table 1, entry 3) (600 MHz).

Upon the addition of D_2O, signal at 2.7 ppm disappeared due to the hydrogen exchange. This indicated that signal in 2.7 ppm belonged to an hydroxyl: the ROH end group of PLLAPC.[1]
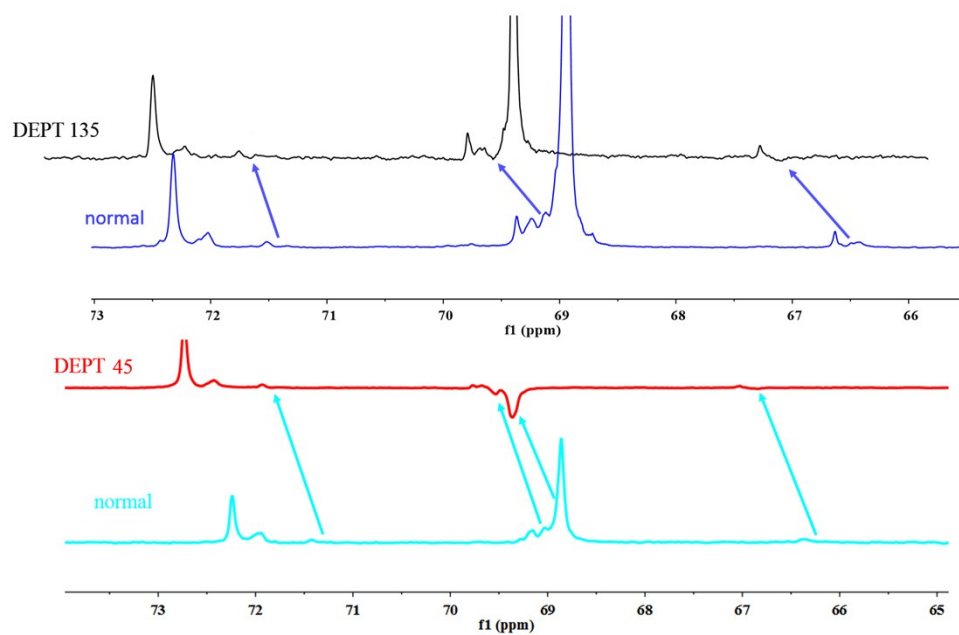
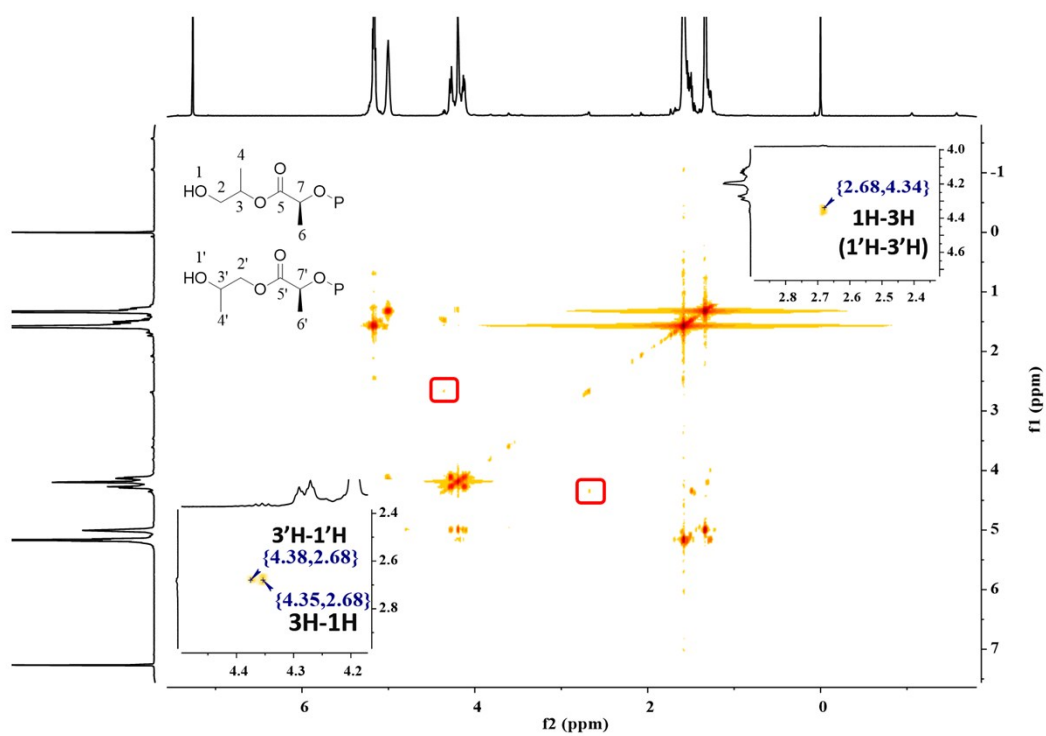Figure S5. The normal, DEPT 45, and DEPT 135 ^{13}C NMR spectra of PLLAPC (150 MHz).

Figure S6. Assigned HHCOSY NMR spectrum of PLLAPC (^{1}H 600 MHz, ^{13}C 150 MHz).

The signals of end-group are weak, and the correlation spectroscopy between 1H and 3H (1'H and 3'H) are visible only after magnification.
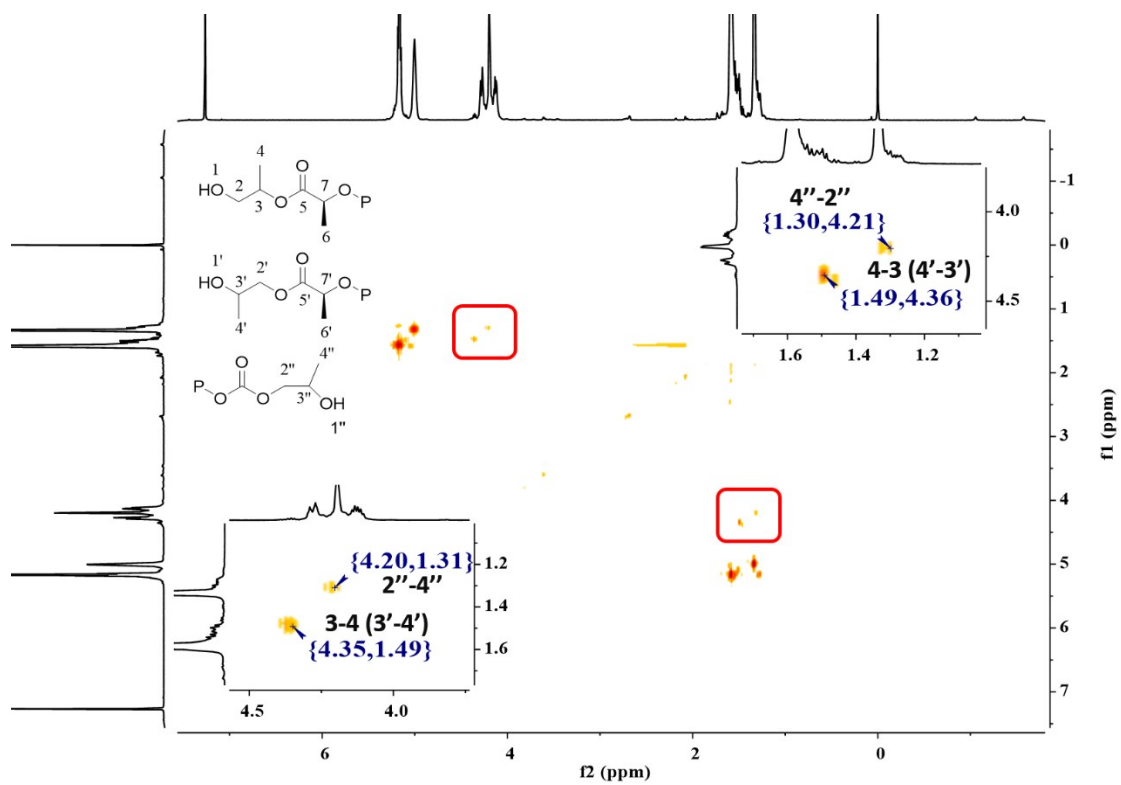
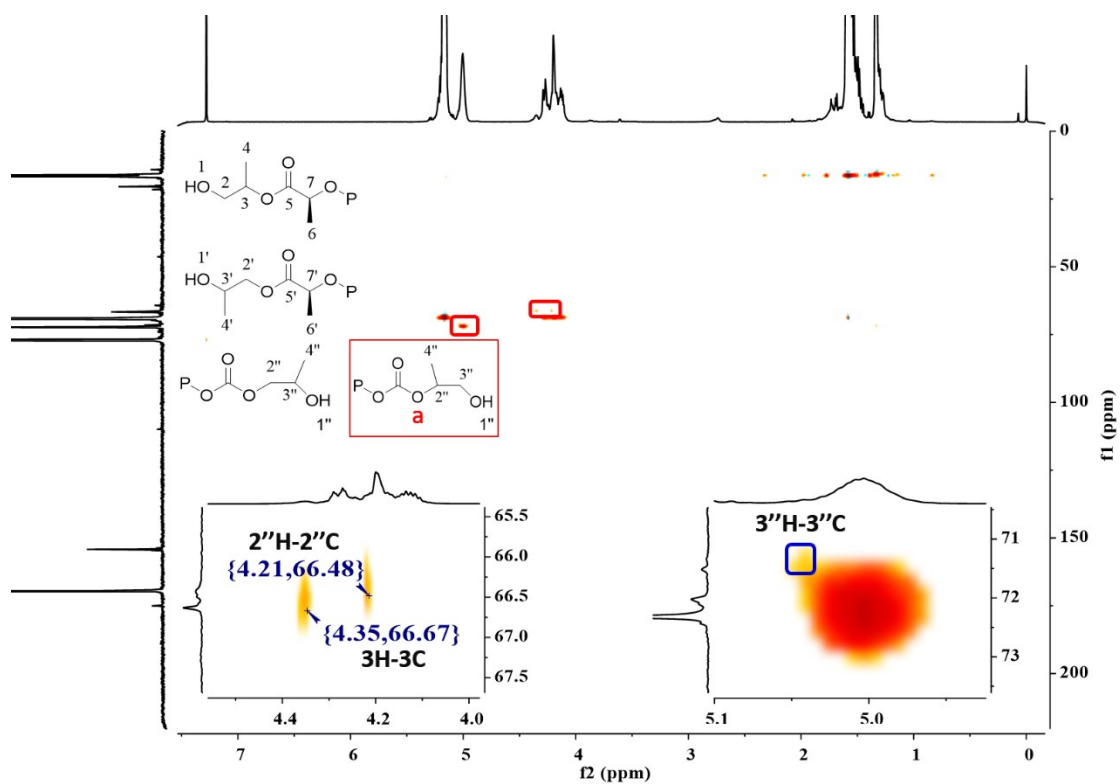Figure S7. Assigned HHCOSY NMR spectrum of PLLAPC (^{1}H 600 MHz, ^{13}C 150 MHz).

Figure S8. Assigned HSQC NMR spectrum of PLLAPC ([1]H 600 MHz, [13]C 150 MHz), a small quantity of structure "**a**" also existed.
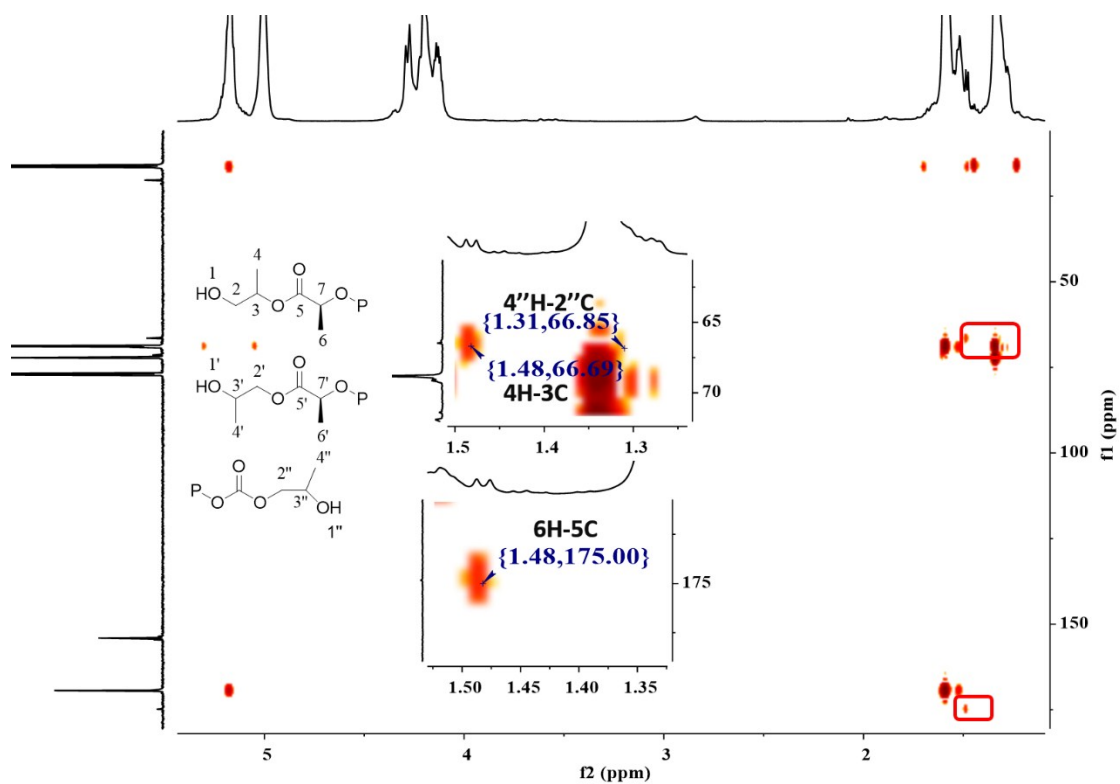
Figure S9. Assigned gHMBCAD NMR spectrum of PLLAPC (^{1}H 600 MHz, ^{13}C 150 MHz).
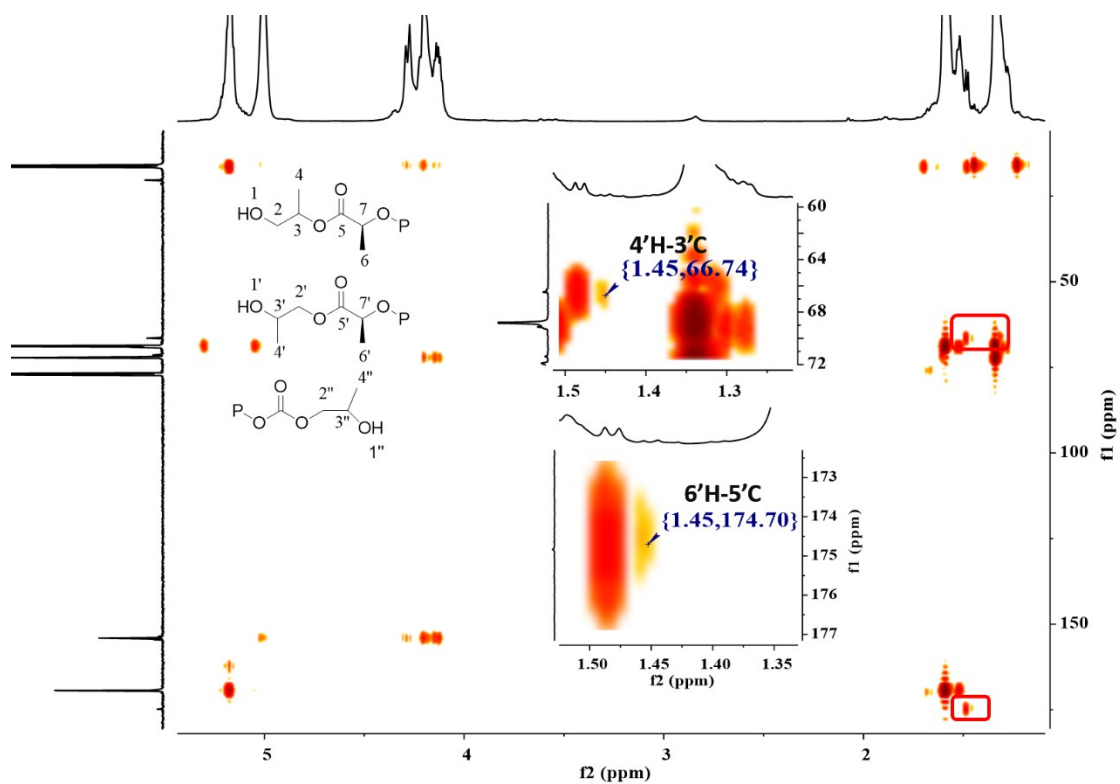
Figure S10. Assigned gHMBCAD NMR spectrum of PLLAPC (^{1}H 600 MHz, ^{13}C 150 MHz).
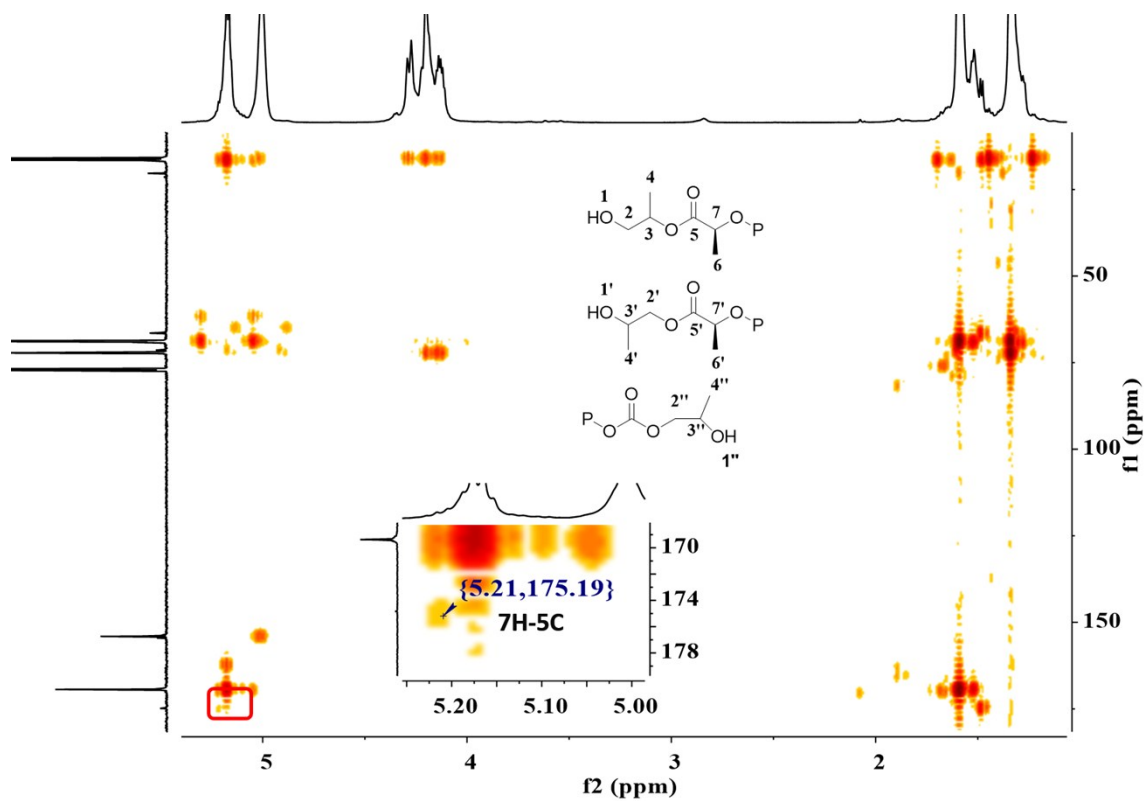
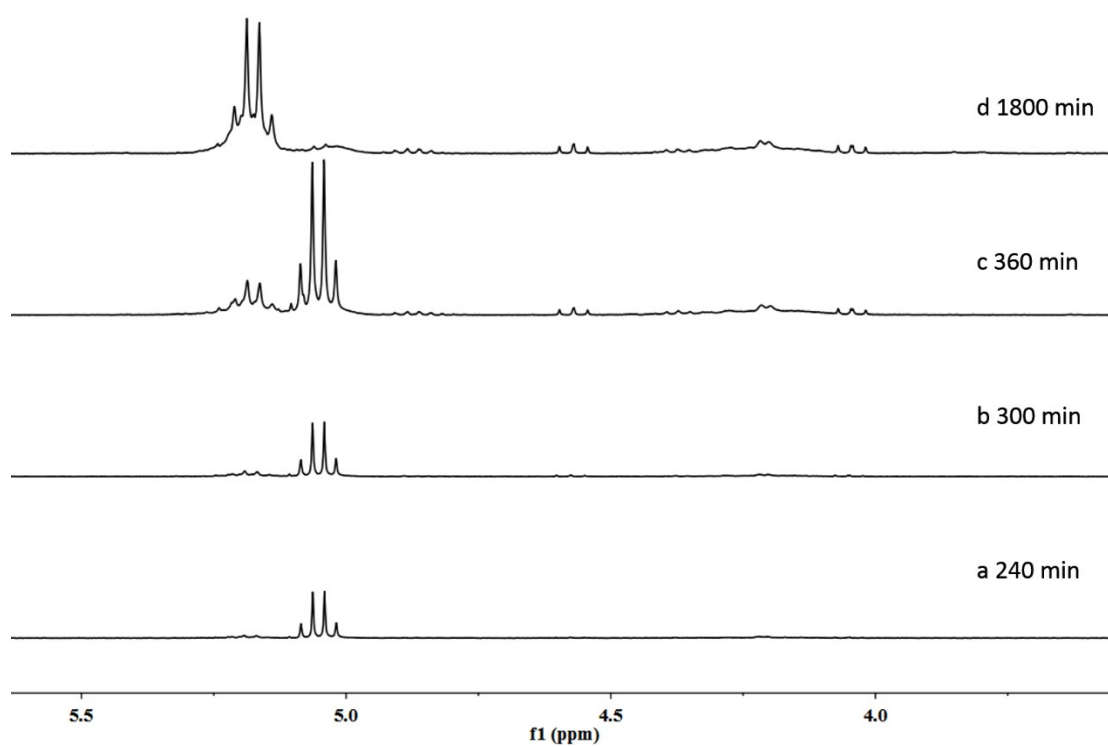Figure S11. Assigned gHMBCAD NMR spectrum of PLLAPC (^{1}H 600 MHz, ^{13}C 150 MHz).

Figure S12. The ¹H NMR spectra of the rough copolymerization product of LLA, PO and CO_2 with different reaction time, [1a]:[1b]:[coCat]:[PO]:[LLA]=1:1:1:2500:500, 60 ℃, 2MPa. The conversions of LA (%): 20.9 (a), 25.8 (b), 31.1 (c), 87.7 (d). The conversions of PO into chain polymer (%): - (a), 10 (b), 15 (c), 22 (d).
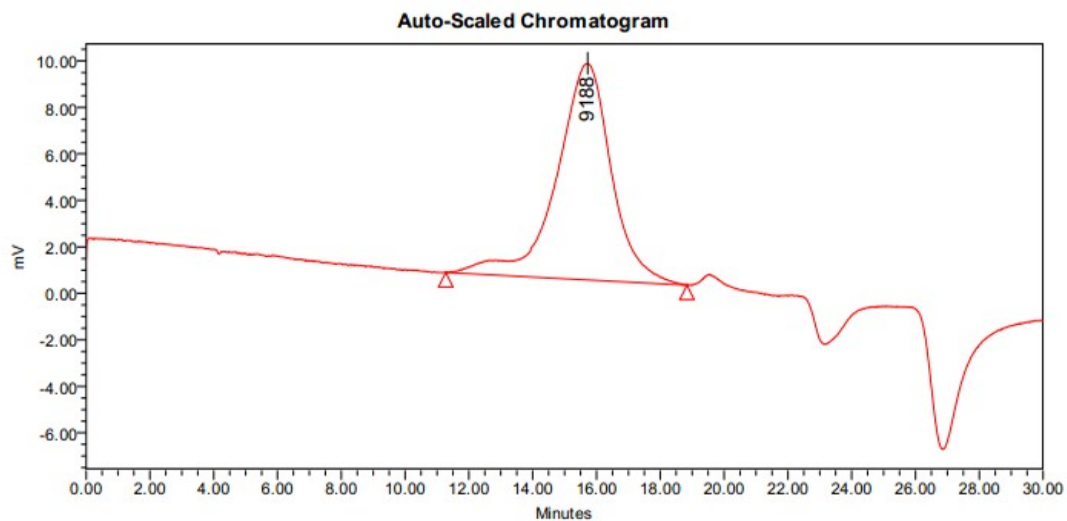
Auto-Scaled Chromatogram

Figure S13. The GPC trace of PLLACHC (M_n=8600, PDI=1.60).

The terpolymerization was performed in 2 mL neat CHO in 25 mL autoclave at 60 °C, 2 MPa, 24h. Feed ratio: [1a]:[1b]:[PPNCl]:[LLA]:[CHO]=1:1:1:200:1000, retractive index detector (Waters 1515-2414).
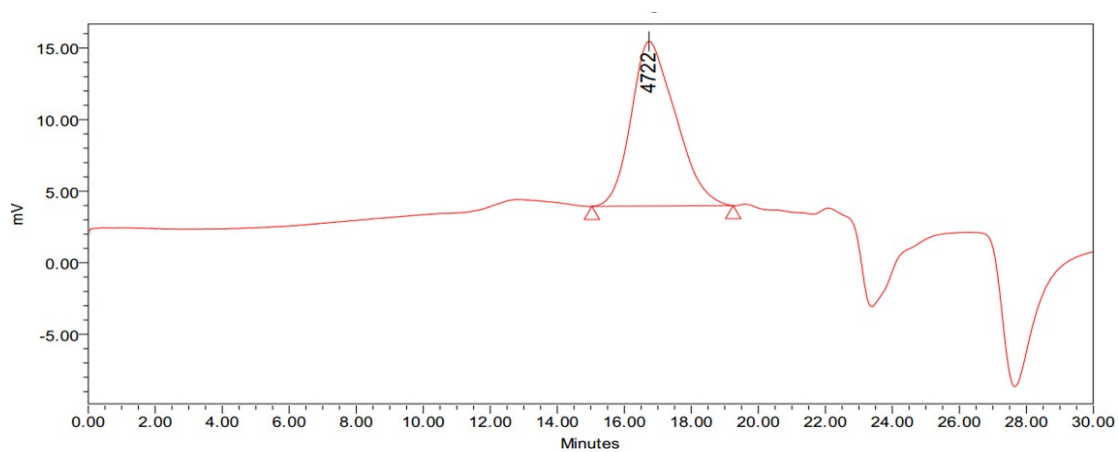
Figure S14. The GPC trace of PLLASC (*M*n=3700, PDI=1.20).

The terpolymerization was performed in 2 mL neat SO in 25 mL autoclave at 60 °C, 2 MPa, 24h. Feed ratio: [1a]:[1b]:[PPNCl]:[LLA]:[SO]=1:1:0.5:100:500, retractive index detector (Waters 1515-2414).
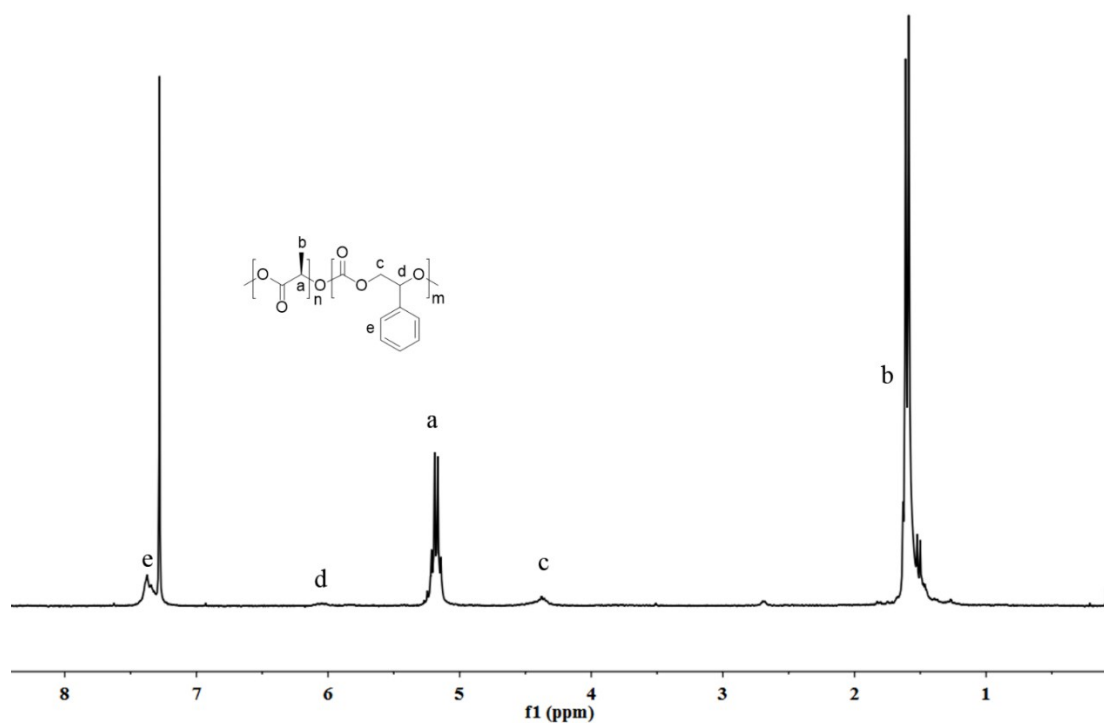
Figure S15. Assigned ¹H NMR spectrum of PLLASC (300 MHz).

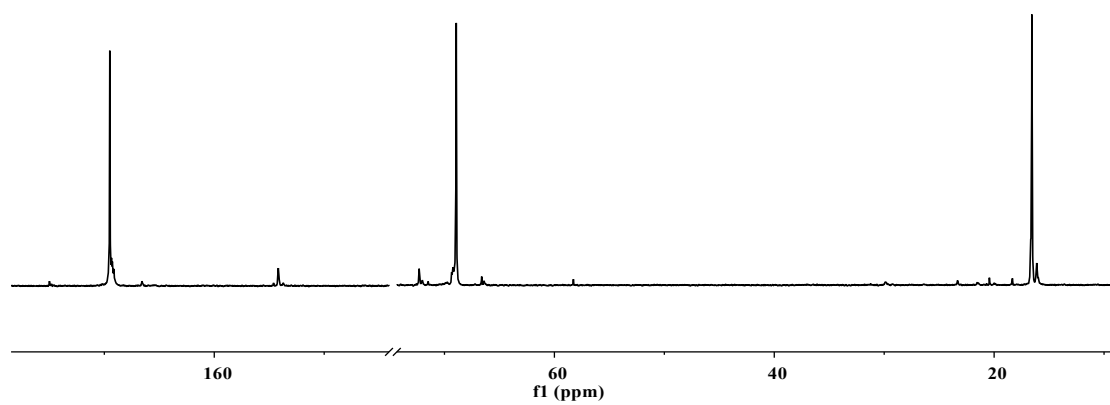Figure S16. The ^{13}C NMR spectrum of PDLAPC (150 MHz).

The spectrum is similar to PLLAPC (Figure S17), and DLA showed the same activity and selectivity as LLA during the copolymerization.
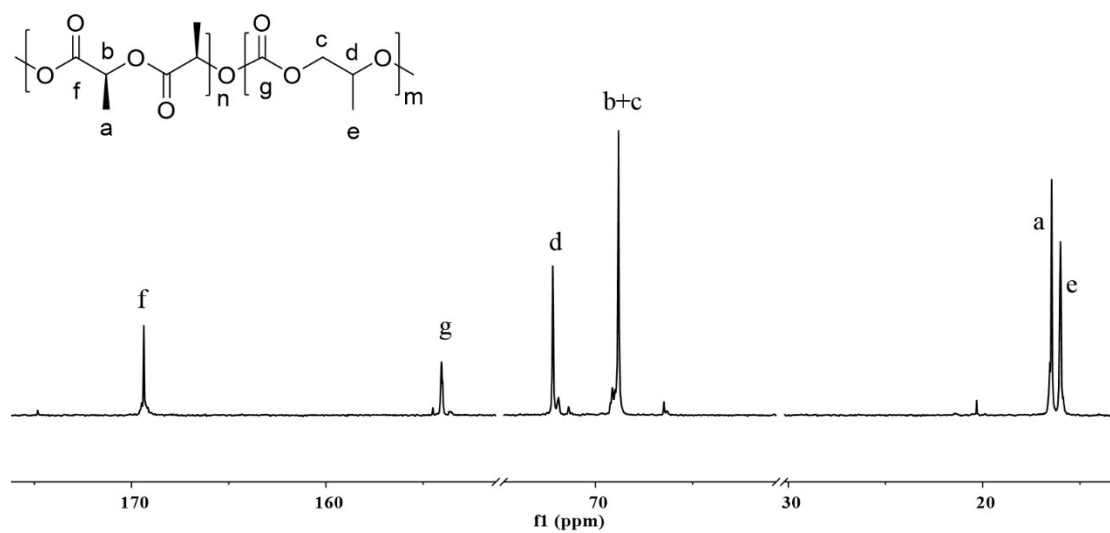
Figure S17. Assigned ¹³C NMR spectrum of PLLAPC (150 MHz).
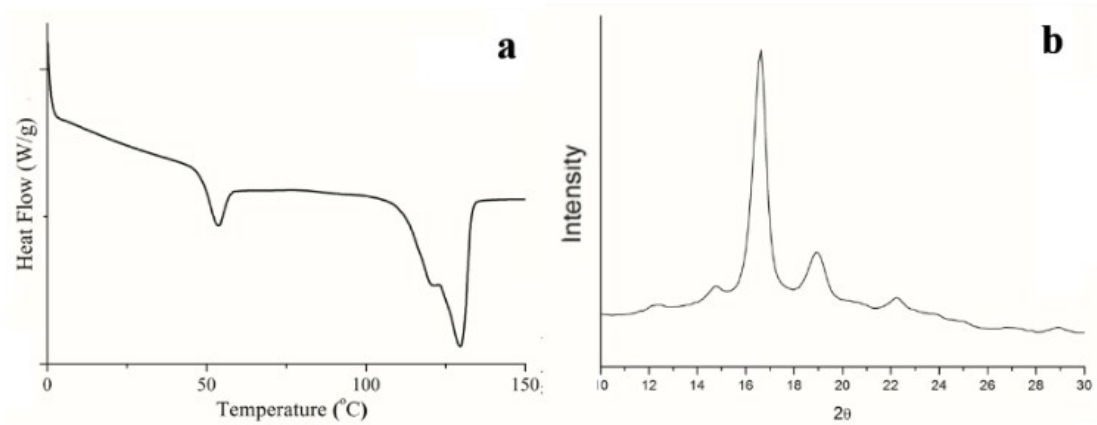
Figure S18. (a) Differential scanning calorimetry (DSC) and (b) WAXD spectra of crystallizable PLLAPC (Table 1, Entry 5)
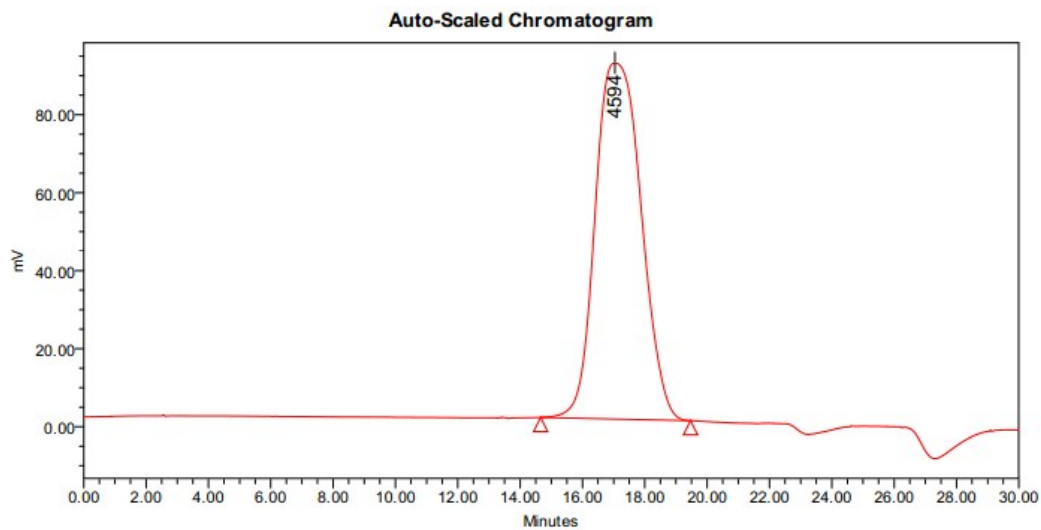
Figure S19. The GPC trace of PLLAPC (Table 1, Entry 1), retractive index detector (Waters 1515-2414).
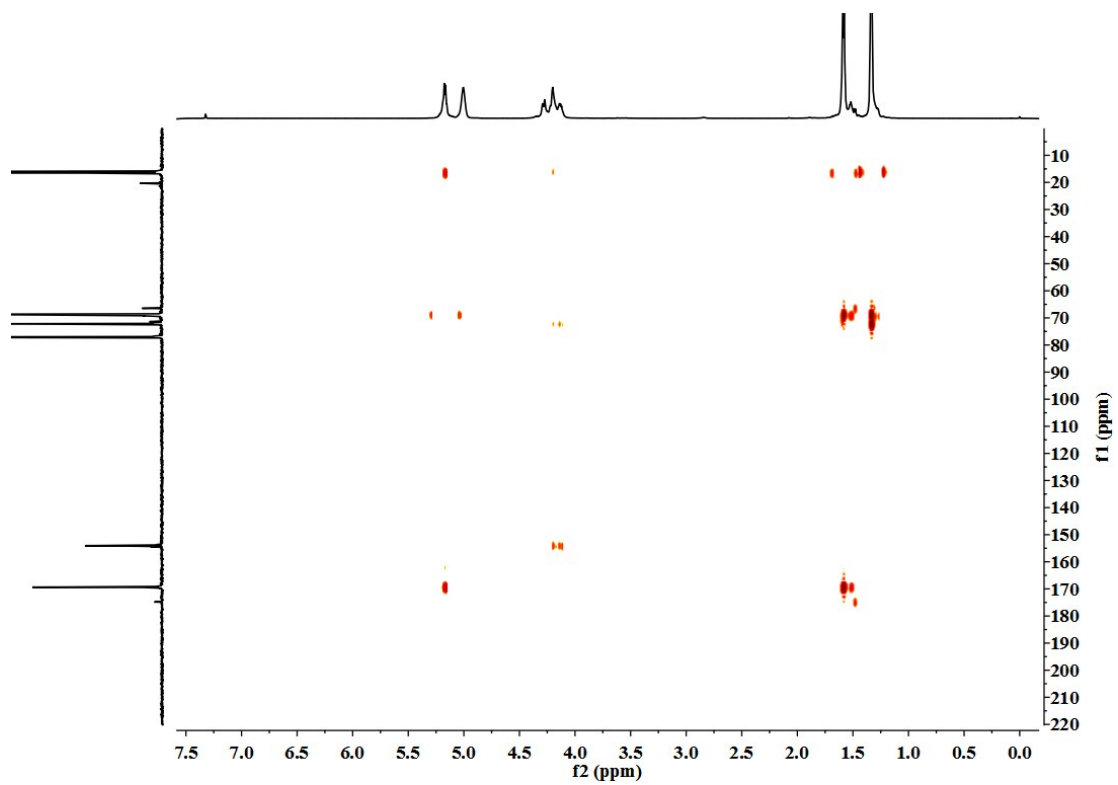
Figure S20. The gHMBCAD NMR spectrum of PLLAPC (^{1}H 600 MHz, ^{13}C 150 MHz).
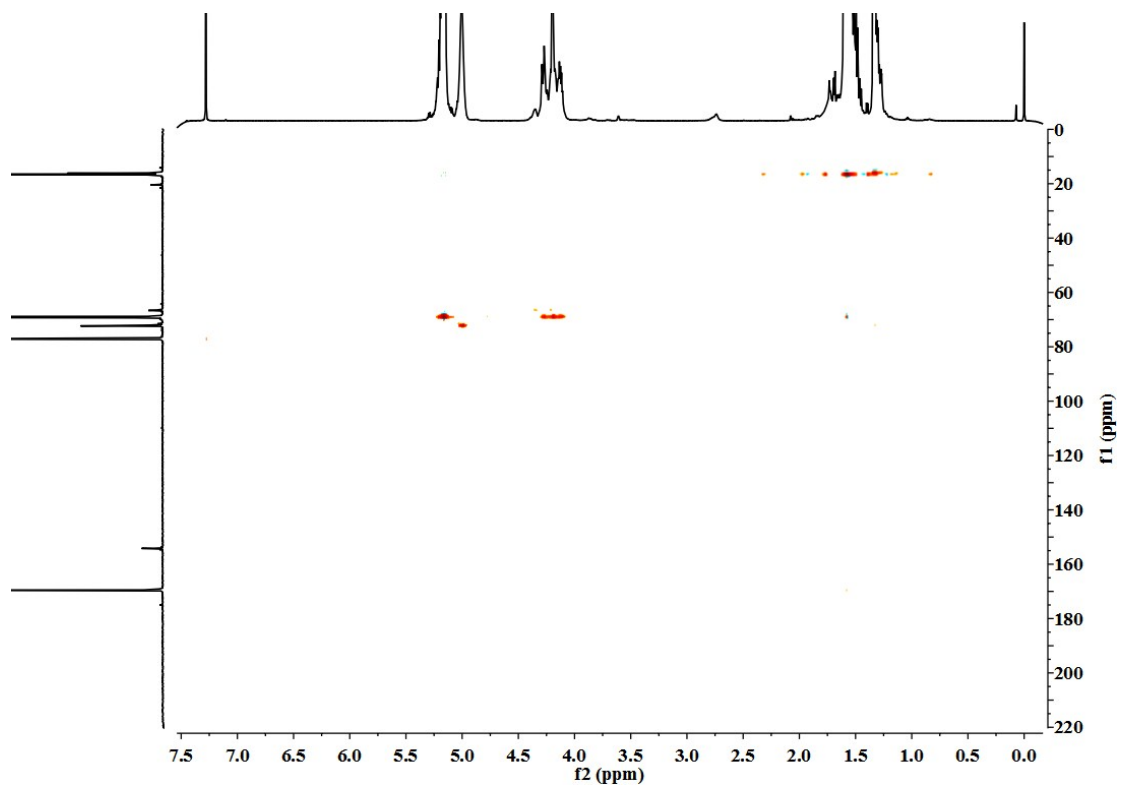
Figure S21. The HSQC NMR spectrum of PLLAPC (^{1}H 600 MHz, ^{13}C 150 MHz).
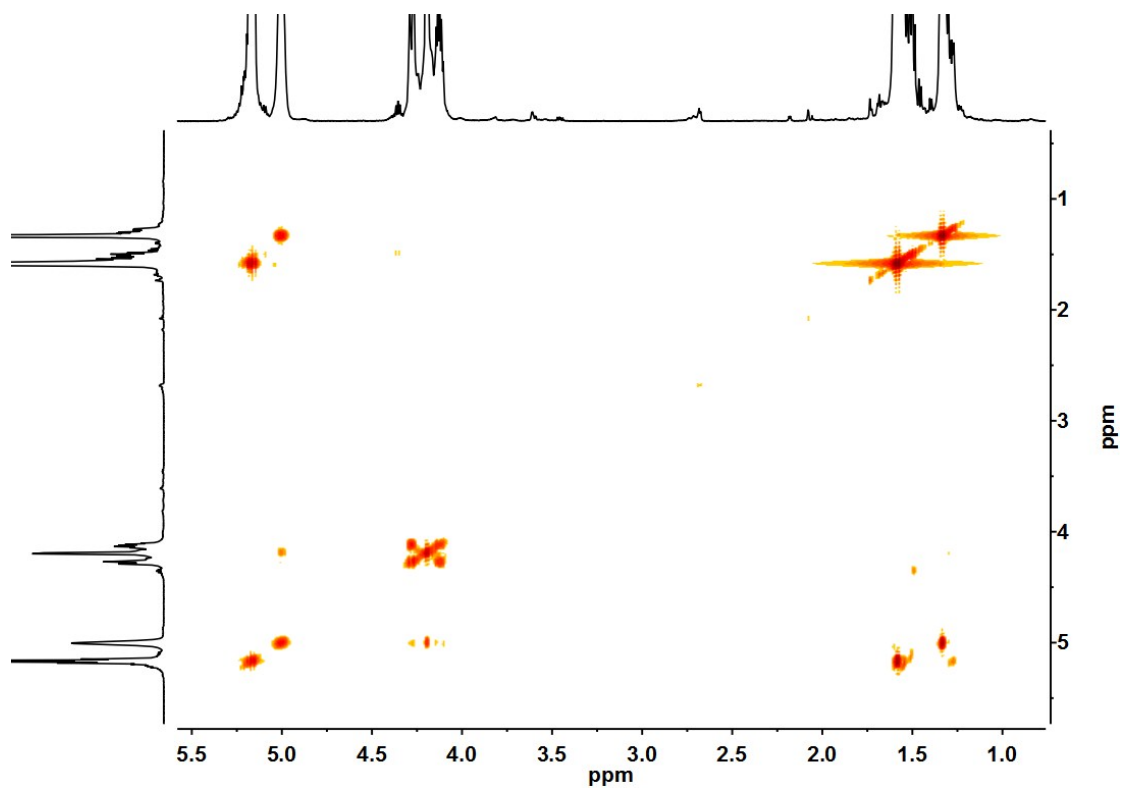
Figure S22. The HH COSY NMR spectrum of PLLAPC (^{1}H 600 MHz).
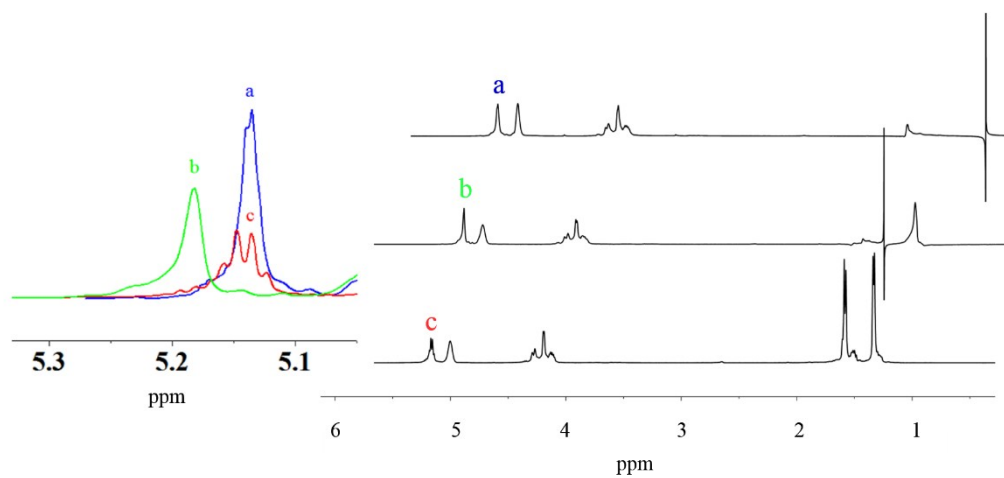
Figure S23. The ¹H homonuclear decoupled ¹H NMR spectrum of PLLAPC (400 MHz).

Homonuclear decoupled ¹H NMR spectra of PLLAPC in the methyl reigon (a: 1.33 ppm; b: 1.58 ppm) and the ¹H NMR spectrum of PLLAPC (c) were showed above (in the magnified image (left), curve b was shifted 0.05 ppm for clear comparison).

The "PO-LLA" and "LLA-CO_2-PO" are discrepant with normal PLLA and PPC units and they shows special signals in ^{1}H, ^{13}C NMR and 2-D NMR spectra. For the "PO-LLA" linkage, it is like the end group of PO-LLA in PLLAPC (Figure S2-S11). The methine and methyl of LLA in "PO-LLA" linkage show clear and individual related signals in HHCOSY. And the methine and methyl of PO in "PO-LLA" linkage also show individual signals (Figure S23). These signals are clear evidence of the existence of "PO-LLA" linkages. For the "LLA-CO_2-PO" linkage, the methine of LLA shows individual related signals with neighboring atoms in 2-D spectra (Figure S26, 27).

For PLLACHC, there are conjunctional structures of "CHO-LLA" and "LLA-CO_2-CHO", similar as "PO-LLA" and "LLA-CO_2-PO" linkages. The methyl of "CHO-LLA" linkage shows specific chemical shift in ^{1}H NMR spectrum compared with the methyl of PLLA units, more detailed investigation are in Figure S28 and S29. By contrast, PLLASHC which derives from LLA, styrene oxide (SO) and CO_2, shows no individual and significative peak in ^{1}H and ^{13}C NMR spectra.

Figure S24. Assigned HHCOSY NMR spectrum of PLLAPC (^{1}H 600 MHz, ^{13}C 150 MHz).
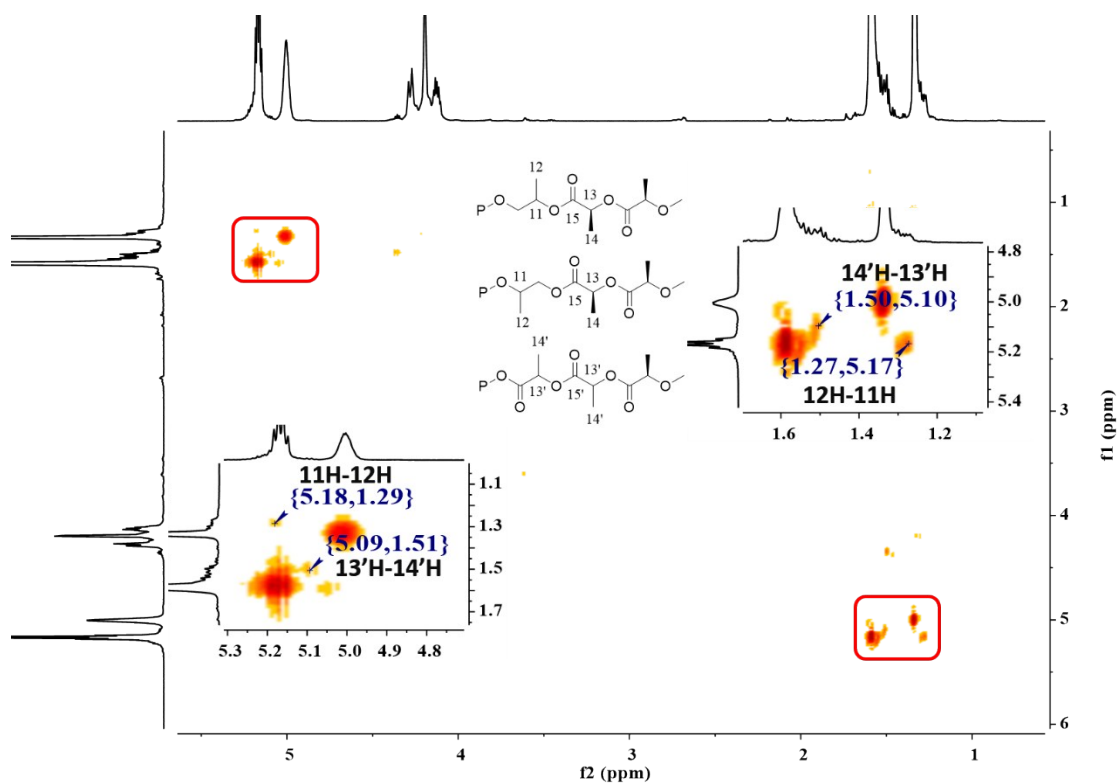
Figure S25. Assigned HSQC NMR spectrum of PLLAPC (^{1}H 600 MHz, ^{13}C 150 MHz).

Figure S26. Assigned gHMBCAD NMR spectrum of PLLAPC (^{1}H 600 MHz, ^{13}C 150 MHz).

The signals of 6H-7C and 14H-13C are very close due to their similar microstructures.
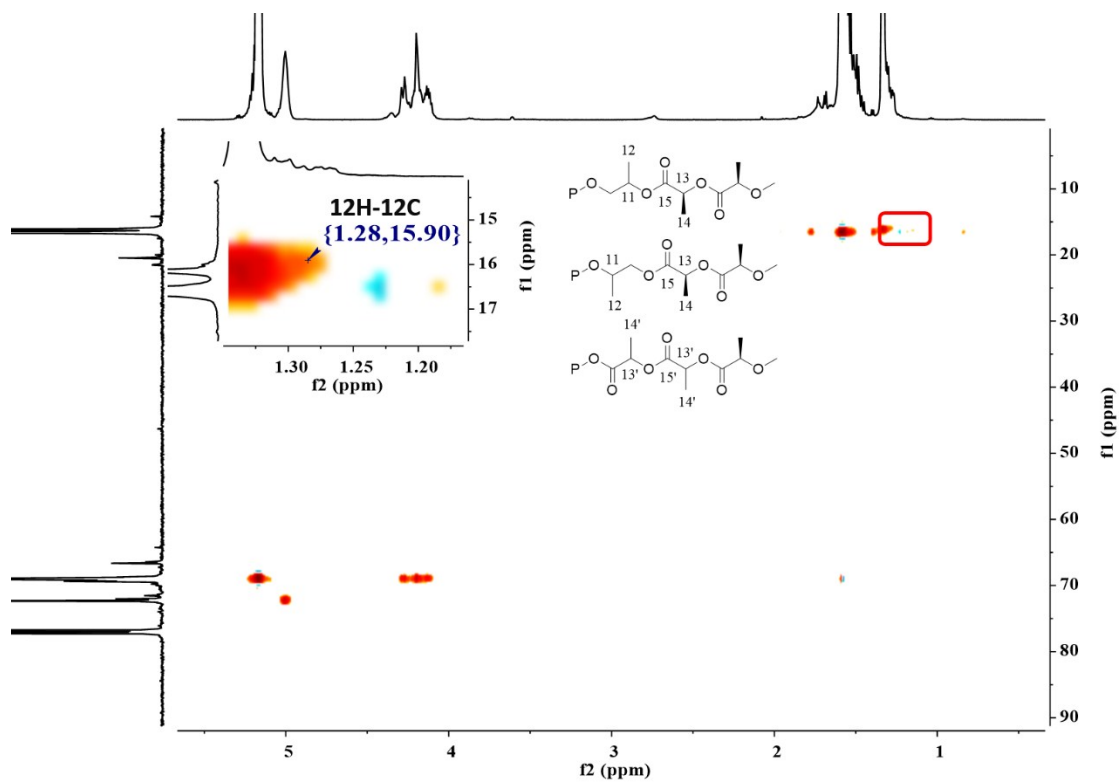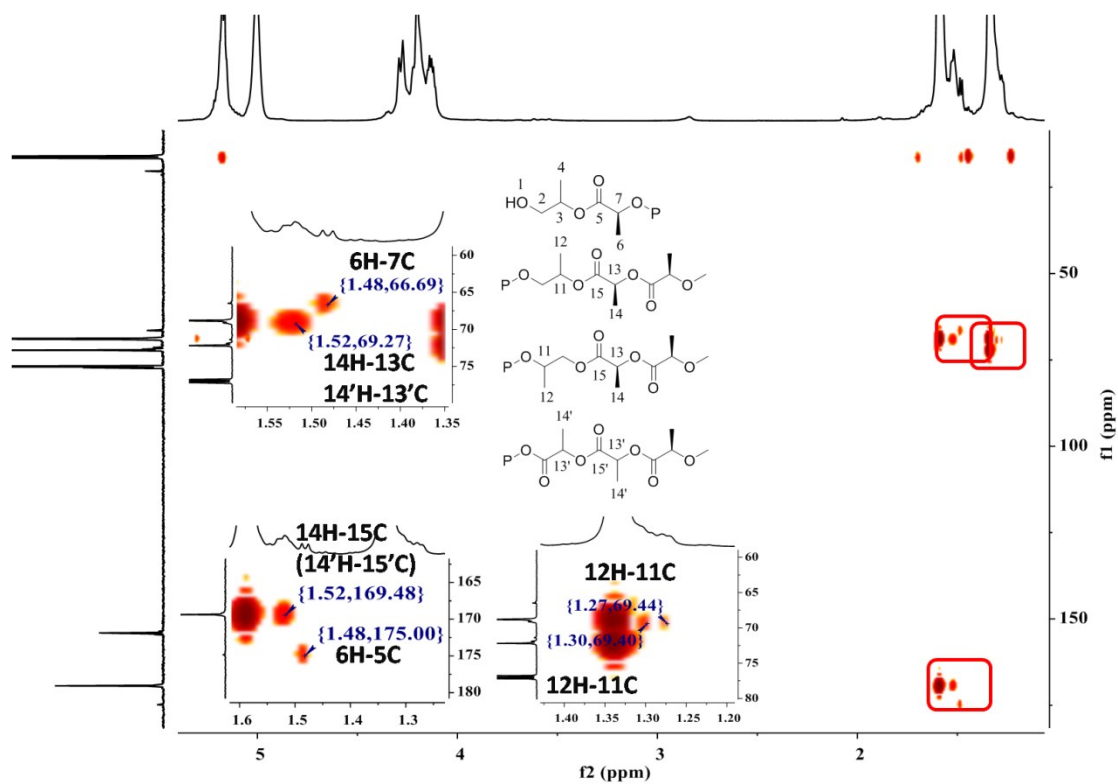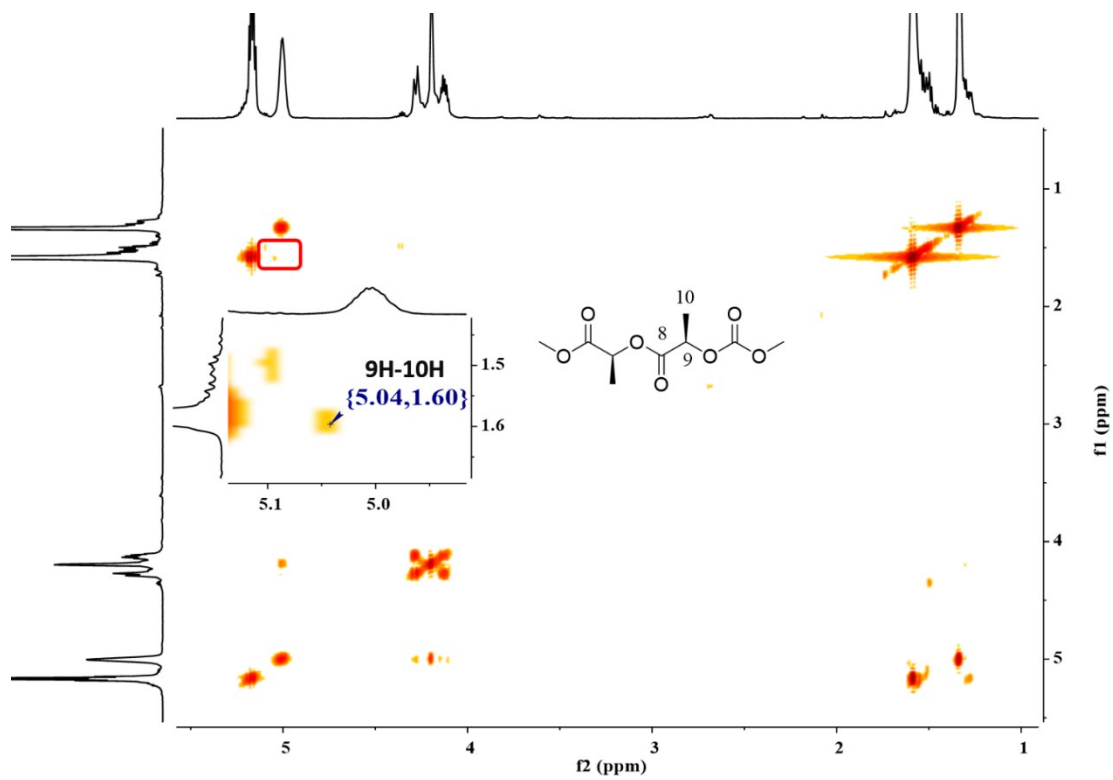
Figure S27. Assigned COSY NMR spectrum of PLLAPC (^{1}H 600 MHz, ^{13}C 150 MHz).

Figure S28. Assigned gHMBCAD NMR spectrum of PLLAPC (^{1}H 600 MHz, ^{13}C 150 MHz).

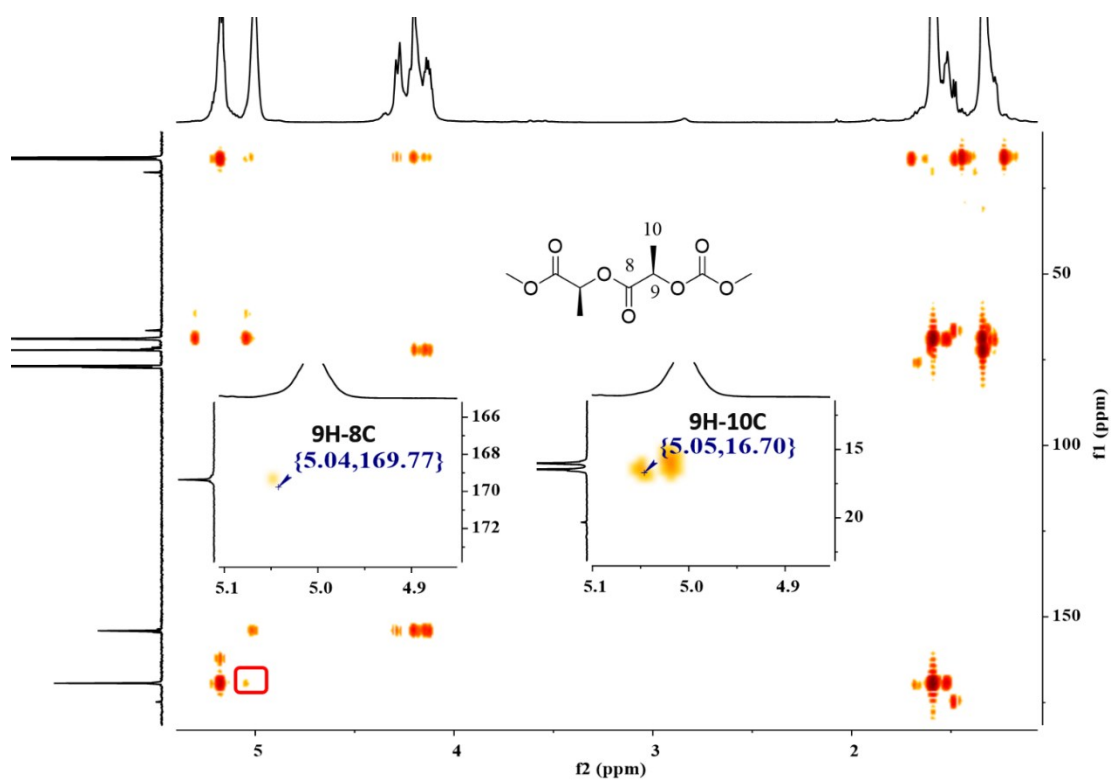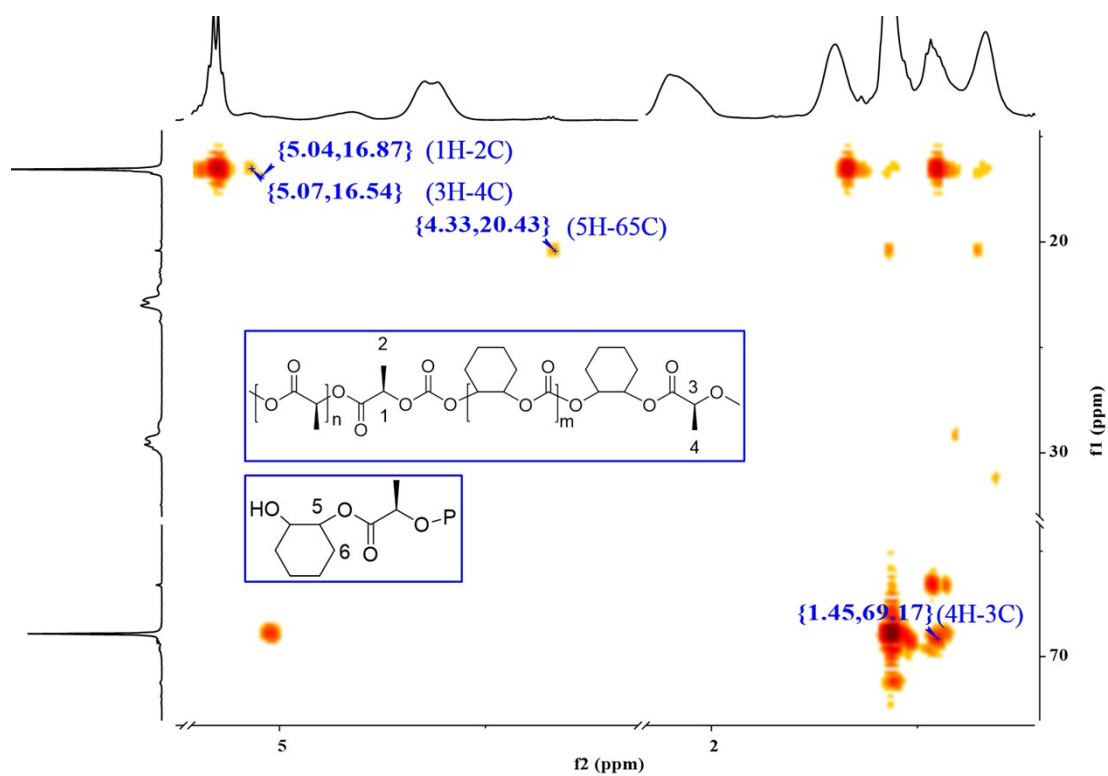Figure S29. Assigned gHMBCAD NMR spectrum of PLLACHC (¹H 600 MHz, ¹³C 150 MHz).
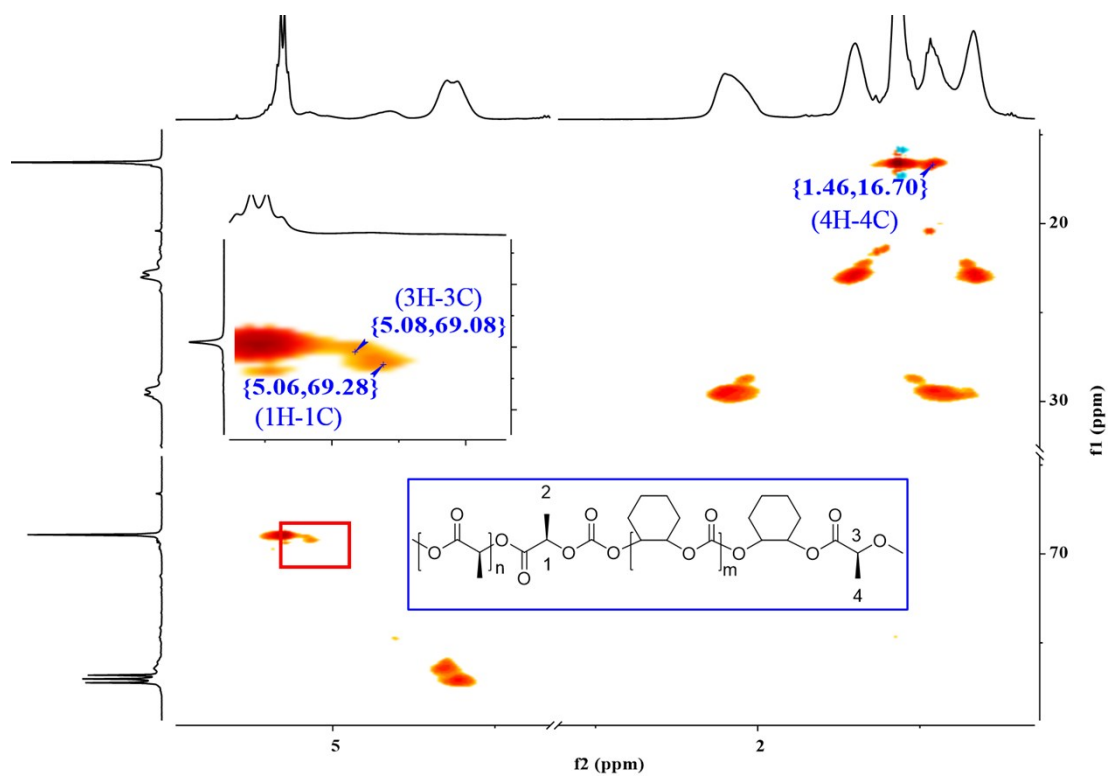
Figure S30. Assigned HSQC NMR spectrum of PLLACHC (^{1}H 600 MHz, ^{13}C 150 MHz).
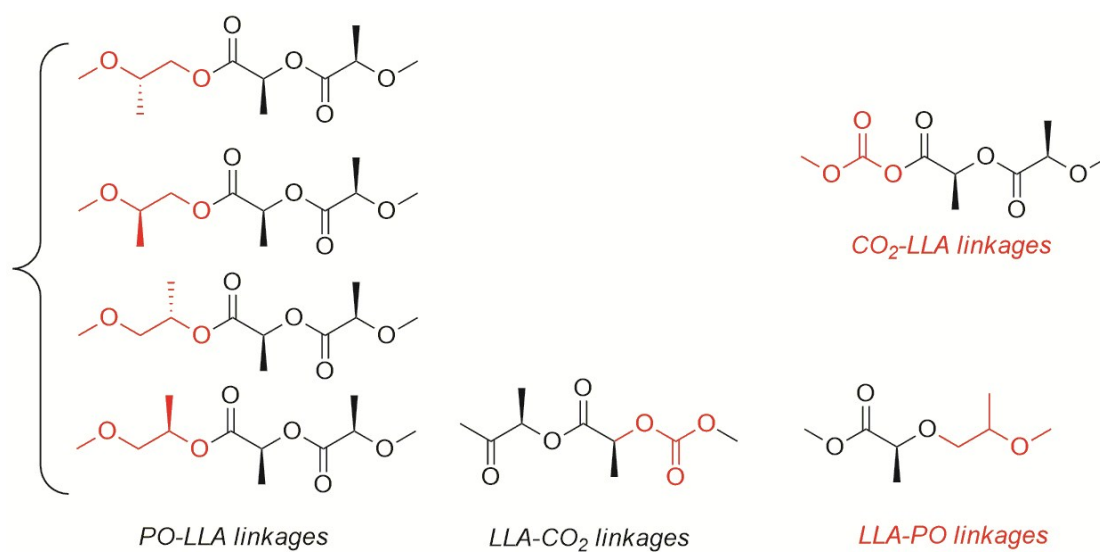
Figure S31. The *PO-LLA* and *LLA-CO₂-PO* linkages.

As there were no signals of polyether in ¹H NMR spectrum and no signals of consecutive carbonyl in ¹³C NMR spectrum, we supposed that *LLA-PO* linkages and *CO₂-LLA* linkages did not exist.

Figure S32. The signals of the new linkages ("PO-LLA" and "LLA-CO_2-PO") in ^1H NMR and ^{13}C NMR spectra, and these signals were hard to be calculated precisely.

A two-step method was tried to obtain PPC-PLLA diblock copolymer. At the first step, PPC was prepared from PO and CO_2 by SalenCo^{III} and PPNCl. Then, CO_2 was released and LLA was added at the second step. Unfortunately, the PPC chain was unable to act as LLA 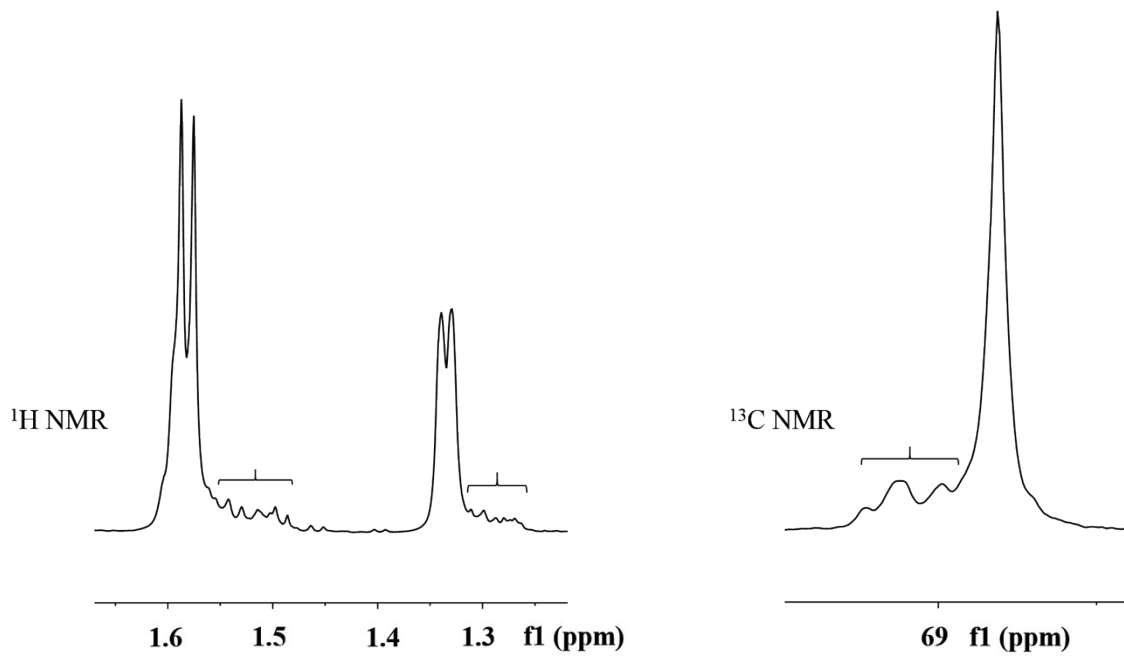macroinitiator with SalenCo^{III} alone. Instead of PPC-PLLA diblock copolymers, only PLLA homopolymer was obtained, and PPC degraded into cPC at the same time. PPC-PLLA diblock copolymer was successfully prepared when SalenCo^{II} was added at the second step (M_n = 21 Kg/mol, PDI = 1.69). The absence of signal at 4.35 ppm in Figure S32 indicating the formation of PPC-PLLA diblock copolymer (homopolymer PLLA initiated by PO had obvious end group signal at 4.35 ppm).
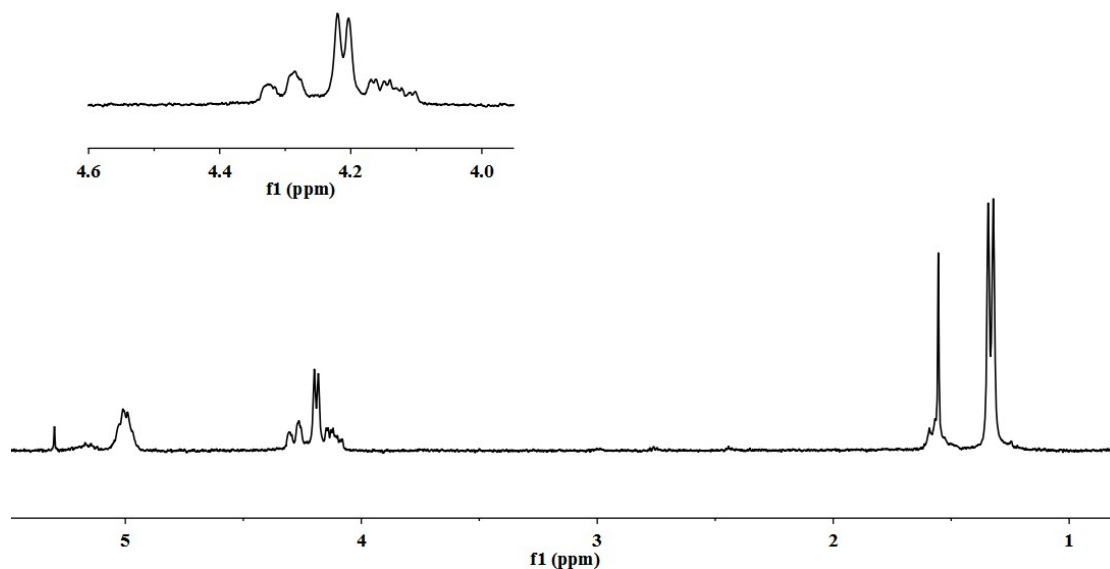
Figure S33. The ^{1}H NMR spectrum of the diblock PPC-PLLA copolymer (300 MHz).
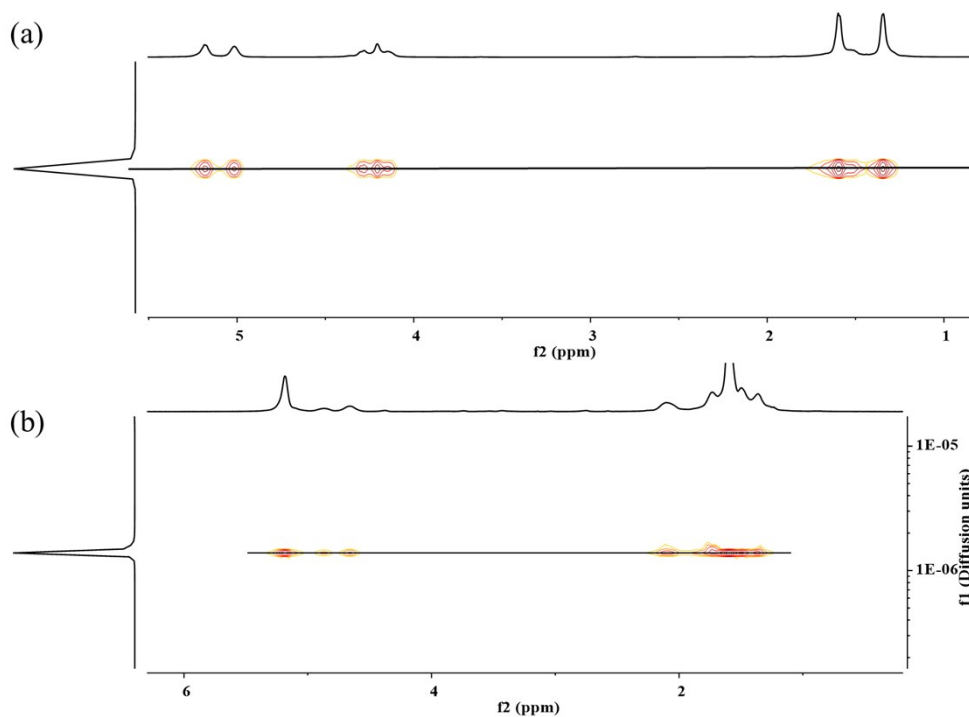
Figure S34. The DOSY spectra of the PLLAPC (a) and the PLLACHC (b).

Diffusion-ordered NMR spectroscopy (DOSY) enabled an estimation of polymer diffusion rates. In the case of a block copolymer, a single diffusion coefficient was expected, with all blocks expected to diffuse at the same rate and the mixtures of homopolymers showed two coefficients. Therefore, as shown in Figure S34, the result indicated the polymer obtained from copolymerization of monomer mixtures was a block copolymer.

Table S3. Copolymerization data of PO, CO₂ and LLA with different loadings of SalenCo^{II}.[a]

Entry	Catalyst[b]			Monomer[b]		Time (h)	Mn (Kg/mol)[c]	PDI[c]
	1a	1b	PPNCl	PO	LLA			
1	1	1	1	2500	250	20	10.2	1.35
2	0.5	1	1	2500	250	20	8.8	2.95
3	2	1	1	2500	250	20	9.7	1.21

[a]: the copolymerization was performed at 60 ºC. [b]: molar ratio. [c]: Determined by gel permeation chromatography, calibrated with polystyrene.

Table S4. Copolymerization data of PO, CO$_2$ and LLA by typical SalenCo complexes.[a]

Entry	Catalyst systems[b]			Monomer[b]		Time (h)	[PLA] (%)	Mn (Kg/mol)[c]	PDI[c]
	SalenCo^{III}	SalenCo^{II}	PPNCl	[PO]: [SalenCo^{III}]	[LLA]: [SalenCo^{III}]				
1	1 (2b)	1 (2a)	1	1000	100	24	37	6.7	1.6
2	1 (3b)	1 (3a)	1	1000	100	20	35	5.4	1.9
3	1 (1b)	2 (2a)	1	2500	250	24	36	8.9	1.5
4	1 (1b)	2 (3a)	1	2500	250	24	35	6.3	1.9
5	1 (2b)	0.5 (1a)	1	1000	100	20	40	2.4	1.8
6	1 (3b)	0.5 (1a)	1	1000	100	20	42	2.8	1.8

[a]: the copolymerization was performed at 60 °C. [b]: molar ratio. [c]: Determined by gel permeation chromatography, calibrated with polystyrene.
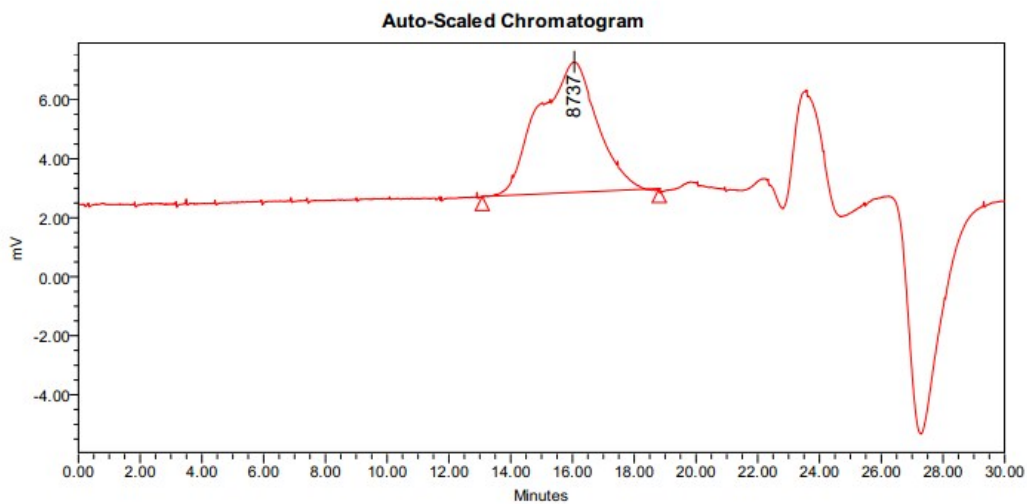
Auto-Scaled Chromatogram
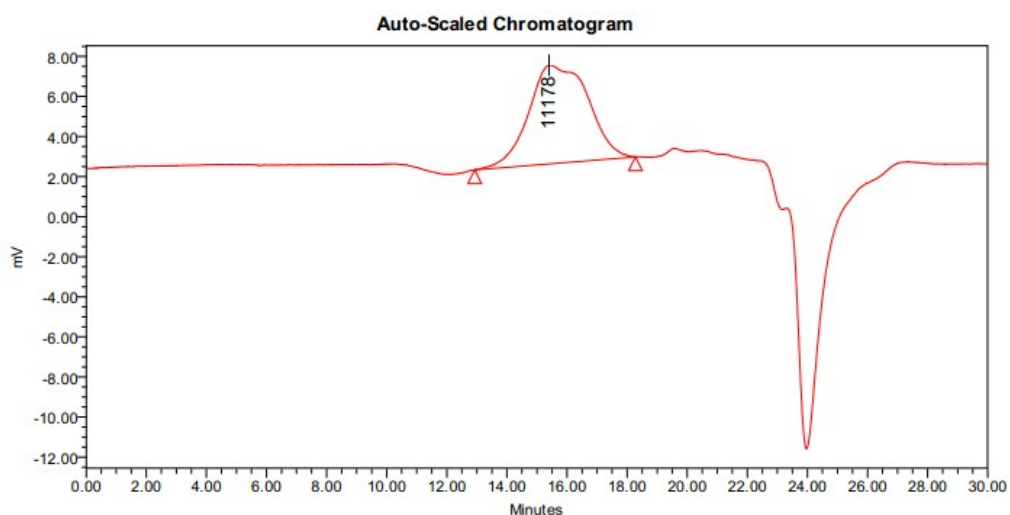
GPC Results

	Dist Name	Mn	Mw	Mv	MP	Mz	Mz+1	Poly dispersity	K	alpha
1		7581	10112		11178	13086	16501	1.333967		

Figure S35. GPC trace of PLLAPC. Experiment condition: [PO]:[LLA]:[1a]:[1b]:[PPNCl]=2500:300:1:1:1, 2 Mpa CO_2, 14 h, 60 ^{o}C, retractive index detector (Waters 1515-2414).

Auto-Scaled Chromatogram

GPC Results

	Dist Name	Mn	Mw	MP	Mz	Mz+1	Mv	Poly dispersity	MW Marker 1	MW Marker 2
1		8607	11544	8737	14853	18151		1.341315		

Figure S36. GPC trace of PLLAPC. Experiment condition: [PO]:[LLA]:[1a]:[1b]:[PPNCl]=2500:250:1:1:1, 2 Mpa CO_2, 16 h, 60 °C, retractive index detector (Waters 1515-2414).

S A M P L E   I N F O R M A T I O N

Sample Name:	lix-574-160620	Acquired By:	System
Sample Type:	Broad Unknown	Sample Set Name:	
Vial:	1	Acq. Method Set:	bio
Injection #:	3	Processing Method:	chcl3160513
Injection Volume:	100.00 ul	Channel Name:	eSATIN-Ch2
Run Time:	30.0 Minutes	Proc. Chnl. Descr.:	Channel 2
Date Acquired:	2016-6-20 16:45:43 CST		
Date Processed:	2016-6-20 18:57:19 CST		

Auto-Scaled Chromatogram
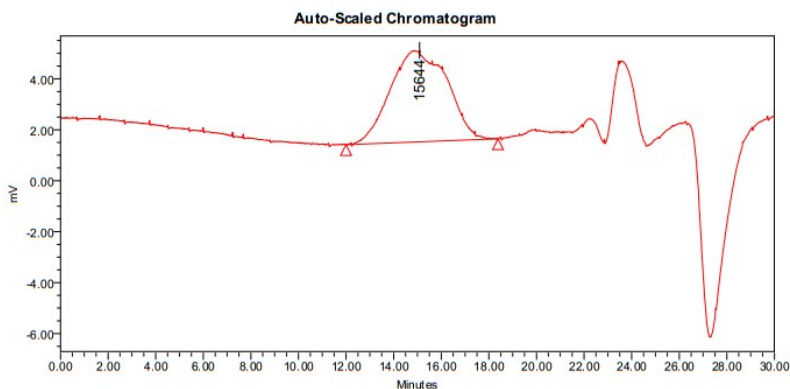
GPC Results

	Dist Name	Mn	Mw	MP	Mz	Mz+1	Mv	Poly dispersity	MW Marker 1	MW Marker 2
1		12873	18971	15644	27414	37695		1.473691		

Reported by User: System
Report Method: Default Individual Report
Report Method ID: :39272
Page: 1 of 2

Project Name: bio
Date Printed:
2016-6-20
18:58:40 Asia/Harbin

Figure S37. GPC trace of PLLAPC (Table 1, Entry 5), retractive index detector (Waters 1515-2414).

REFERENCES

1. Xue, M.; Kitahara, R.; Yoshimura, Y.; Mulder, F. A. A., *Biochem. Biophys. Res. Commun.* **2016,** *478*, 1185.