

Supporting Information

One-Step Approach Towards Polycarbonate-*b*-Polyester Block Copolymers *via* Chemoselective Polymerization Catalyzed by One-Component Phosponium Borane Lewis Pair

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1 Chemicals

Unless otherwise stated, all chemicals are used without further purification. Propylene oxide (PO), Cyclohexeneoxide (CHO), 9-borabicyclo[3.3.1]nonane (9-BBN), 4-Bromo-1-butene, 4-Phenyl-1-butene were purchased from Sinopharm Chemical Reagent Co., Ltd. L-LA were purchased from Macklin Co., Ltd. Dichloromethane(CH₂Cl₂), Tetrahydrofuran (THF) were purchased as Super-dry solvent from Energy Chemical Co. Ltd. CDCl₃, PO and CHO were dried over CaH₂ for 48 h, distilled and stored under nitrogen atmosphere. L-LA was used after recrystallization from toluene twice. PBB-Br was synthesized according to the literature.¹

2 Characterization and Analysis

NMR

Nuclear Magnetic Resonance (NMR) spectra were recorded on a Bruker AVANCE NEO 400 MHz NMR spectrometer (¹H NMR 400 MHz, ¹³C{¹H} NMR 100 MHz, 128 MHz ¹¹B{¹H} NMR, 162 MHz ³¹P NMR) at 298 K. ¹H and ¹³C{¹H} NMR Chemical shifts were reported in δ (ppm) with the residual deuterated solvent peak as reference [¹H: TMS in CDCl₃ = 0 ppm; ¹³C{¹H}: CDCl₃ = 77.16 ppm; ¹¹B{¹H}: BF₃.Et₂O (external standard) = 0 ppm, ³¹P{¹H}: 85% H₃PO₄ (external standards) = 0 ppm]. Data are reported as follows: Chemical shift in ppm, multiplicity (s =singlet, d = doublet, t = triplet, q = quartet, m = multiplet, dd = doublet of doublets, br = broad signals, etc.), coupling constant *J* in Hz, integration, and (where applicable) interpretation. The substitution pattern of phenyl group and assignments of phenyl carbon in ¹³C{¹H} NMR were named as follows: ortho- (*o*-Ph), meta- (*m*-Ph), para- (*p*-Ph) and ipso- (*i*-Ph).

MALDI-TOF-MS

Matrix-assisted laser desorption/ionization time-of-flight mass spectroscopy (MALDI-TOF-MS) analyses were conducted on a Bruker Microflex LRF MS spectrometer equipped with a 337 nm nitrogen laser operating at a positive ion, linear mode (modified according to experiments). The polymer samples (10 mg mL⁻¹), trans -2[3-(4-tert-

butylphenyl)-2-methyl-2-propenylidene] malononitrile (DCTB, 25 mg mL⁻¹) and CF₃COONa (5 mg mL⁻¹) were dissolved in THF and mixed in a volume ratio of 20:5:5 (Sample concentration, matrix type, ionic salt and volume ratio are modified according to experimental conditions).

GPC

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⁻¹ at 40 °C. One PLgel 5 μm guard column and three Mz-Gel SDplus columns (10³Å, 10⁴Å and 10⁵Å, linear range of $M_w = 1000 - 2 \times 10^6$ Da) were connected in series. The molecular weight and dispersity were calculated using 6 commercially available PS as standards with narrow molecular weight distribution as references. The sample concentration used for GPC analyses was 5-10 mg mL⁻¹.

3 General Procedure for the Syntheses of Polymers

Ring-opening copolymerization of CHO and CO₂

In a glovebox, a 10 mL autoclave (Anhui Kemi Machinery Technology Co., Ltd.) equipped with magnetic stirrer was added catalyst, CHO. The sealed autoclave was charged with CO₂ to reach a pressure of 20 bar and placed in an oil bath at a preset temperature. The reaction mixture was allowed to stir for a fixed time.

Ring-opening polymerization of L-LA in the presence of CHO

In a glovebox, to a 15 mL in a teflon sealed pressure tube equipped with magnetic stirrer, catalyst, L-LA, solvent and CHO were added. The teflon sealed pressure tube was immediately taken out of glovebox and immersed in an oil bath with preset temperature. The reaction mixture was allowed to stir for a fixed time.

Ring-opening terpolymerization of CHO, CO₂ and L-LA

In a glovebox, a 10 mL autoclave (Anhui Kemi Machinery Technology Co., Ltd.) equipped with magnetic stirrer was added catalyst, L-LA, solvent and CHO. The sealed autoclave was charged with CO₂ to reach a pressure of 20 bar and placed in an oil bath at a preset temperature. The reaction mixture was allowed to stir for a fixed time.

4 Representative Tables and Figures

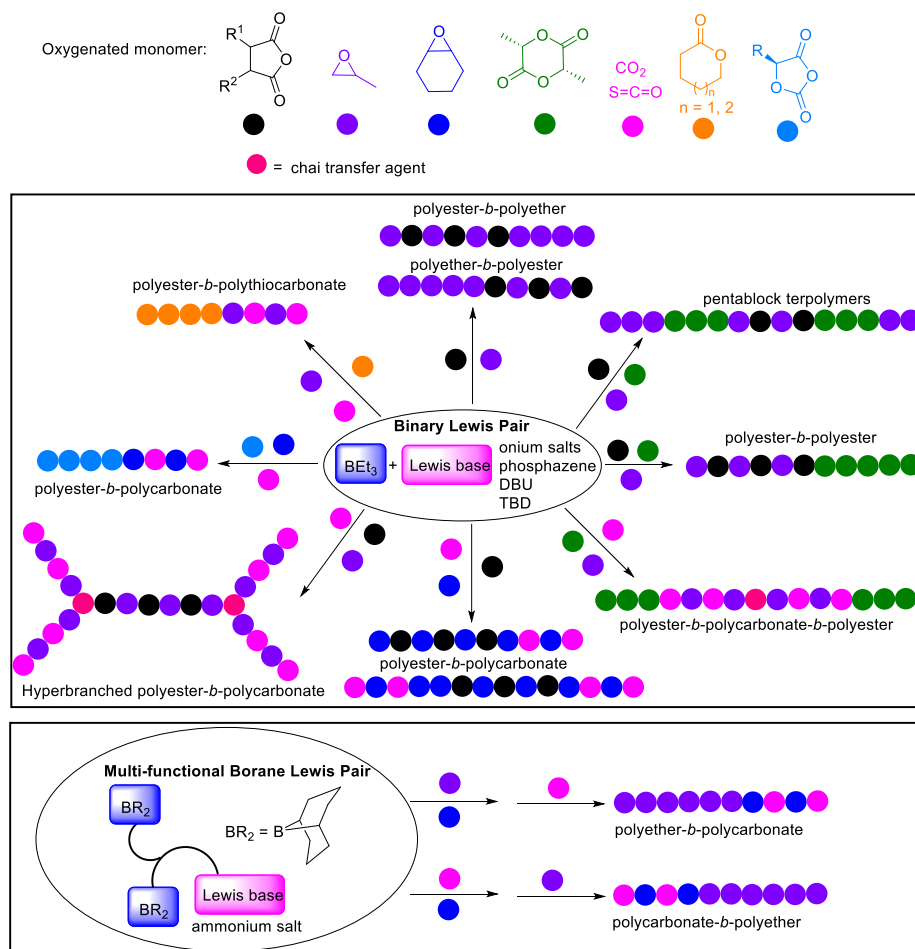


Figure S1. Borane-based Lewis pairs in the preparation of low carbon block copolymers

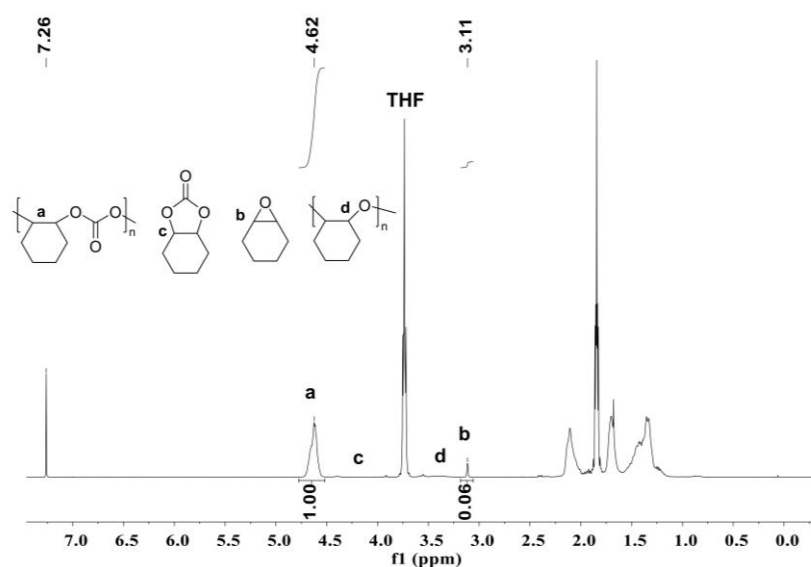


Figure S2. ^1H NMR (400 MHz, CDCl_3 , 298 K) of the obtained polymer from Table1, run 1

Table S1 Polymerization of CHO and CO₂ catalyzed by **PBB-Br**

Run ^a	Temp. (°C)	Time (min)	Pressure (bar)	Conv. (%) ^b	$M_n^{Theo.}$ (kg/mol) ^c	M_n^{GPC} (kg/mol) ^d	\bar{D}^d
1	45	25	20	37	4.7	2.2	1.25
2	45	45	20	62	7.9	3.9	1.21
3	45	65	20	82	10.5	5.2	1.24
4	45	1440	1	0	-	-	-

a. The polymerizations were conducted at 45 °C in an equal volume of THF with feed ratios of CHO/**PBB-Br** = 100/1. The polymerizations were performed using **PBB-Br** as catalyst (18.6 μmol, 11 mg) b. Conv.(%) is the conversion of the CHO, which was determined by ¹H NMR spectroscopy. c. $M_n^{Theo.}=142.15 \times [CHO+CO_2] \times Conv.\%$. d. Determined by GPC in THF, calibrated with standard polystyrene.

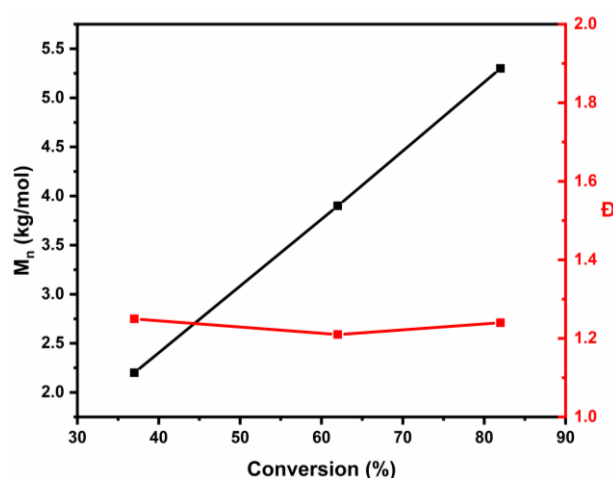


Figure S3. The controlled polymerization behavior for **PBB-Br** initiated ROCOP of CHO and CO₂. The polymerization was performed at 45 °C under 20 bar CO₂ with equal volume of THF under [CHO]₀/[**PBB-Br**]₀=100/1 molar ratio. Linear increase of M_n s with CHO conversion, together with narrow dispersity.

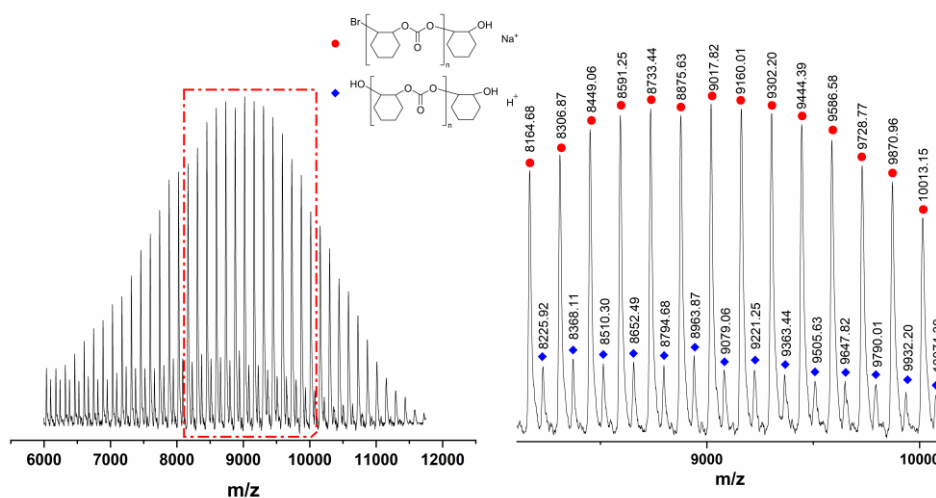


Figure S4. MALDI-TOF-MS of the generated PCHC obtained from [CHO]₀/[**PBB-Br**]₀=100/1 under 20 bar CO₂ for 2 h at 45 °C

Table S2 ROP of L-LA using **PBB-Br**

Run	[L-LA]/ [Cat.]	Temp (°C)	Time (h)	Conv. (%) ^b	$M_n^{Theo.}$ (kg/mol) ^c	M_n^{GPC} (kg/mol) ^d	\bar{D}^d
1 ^a	100/1	45	24	-	-	-	-

a. The polymerizations were performed using **PBB-Br** as catalyst (18.6 μmol , 11 mg) 200 μL THF was added as solvent. b. Conv.(%) is the conversion of the L-LA, which was determined by ^1H NMR spectroscopy. c. $M_n^{Theo.}=144 \times [\text{L-LA}] \times \text{Conv.}\%$ d. Determined by GPC in THF, calibrated with standard polystyrene.

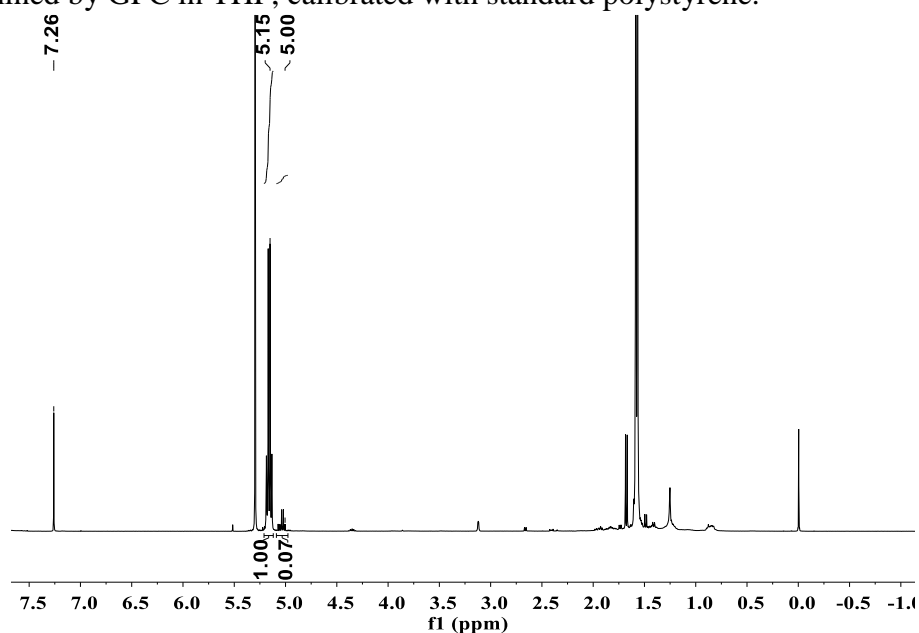


Figure S5. ^1H NMR (400 MHz, CDCl_3 , 298 K) of crude product obtained from ROP of L-LA using **PBB-Br** with 5% CHO under $[\text{CHO}]_0/[\text{L-LA}]_0/[\text{PBB-Br}]_0 = 5/100/1$ at 45 °C for 24 h.

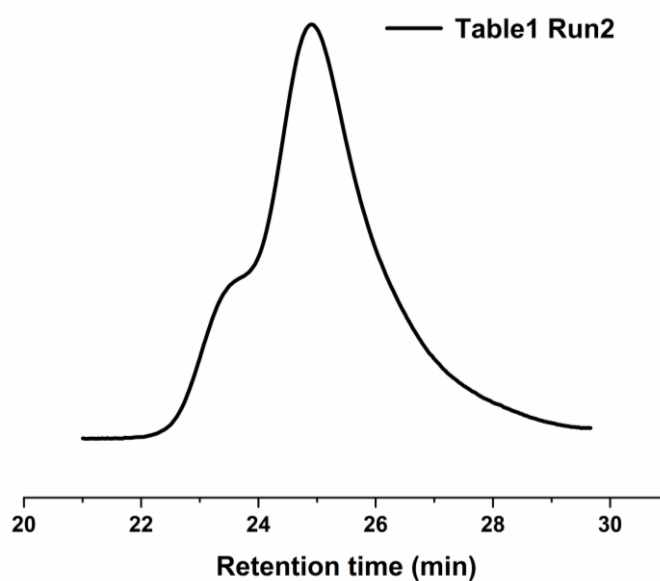


Figure S6. GPC curve of obtained PL-LA from Table 1, run 2

Table S3 ROP of L-LA using **PBB-Br**

Run ^a	[L-LA]/[BnOH] /[KOME]/[Cat.]	Temp (°C)	Time (h)	Conv. (%) ^b	$M_n^{Theo.}$ (kg/mol) ^c	M_n^{GPC} (kg/mol) ^d	\bar{D}^d
1	50/-/1/1	45	12	85.4	6.2	6.5	1.40
2	50/5/0.5/1	45	24	65.4	-	1.0	1.20
3	50/5/0.1/1	45	24	0	-	-	-

a. The polymerizations were performed using **PBB-Br** as catalyst (18.6 μmol , 11 mg) 200 μL THF was added as solvent. b. Conv.(%) is the conversion of the L-LA, which was determined by ^1H NMR spectroscopy. c. $M_n^{Theo.}=144 \times [\text{L-LA}] \times \text{Conv.}\%$ d. Determined by GPC in THF, calibrated with standard polystyrene.

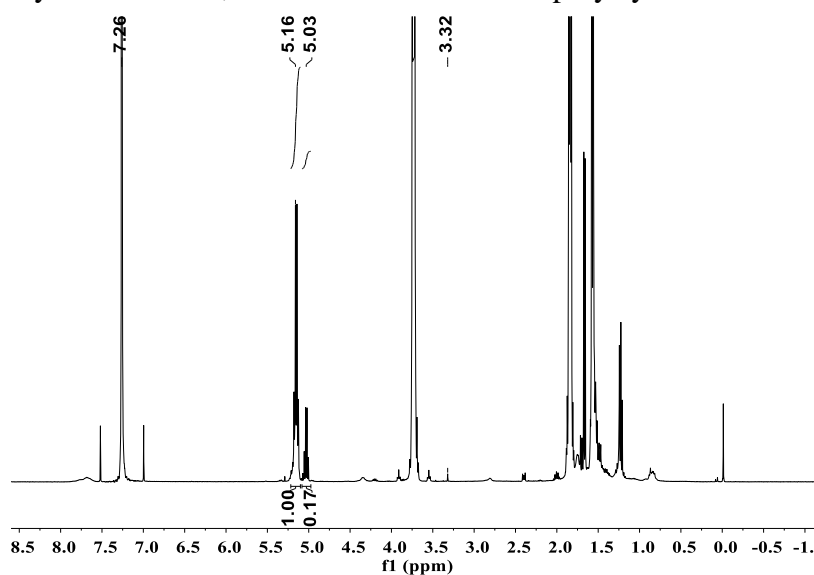


Figure S7. ^1H NMR (400 MHz, CDCl_3 , 298 K) of the obtained polymer from Table S3, run 1

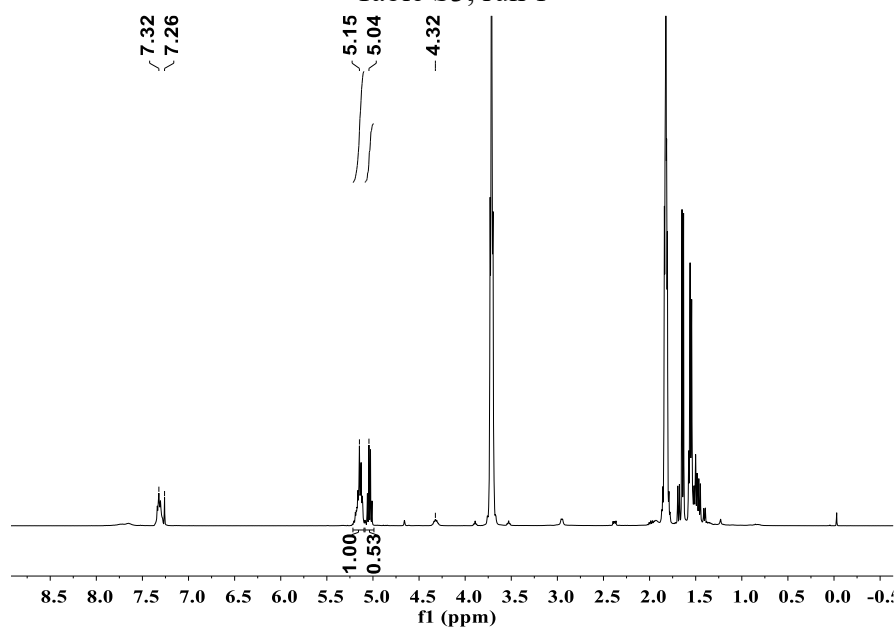


Figure S8. ^1H NMR (400 MHz, CDCl_3 , 298 K) of the obtained polymer from Table S3, run 2

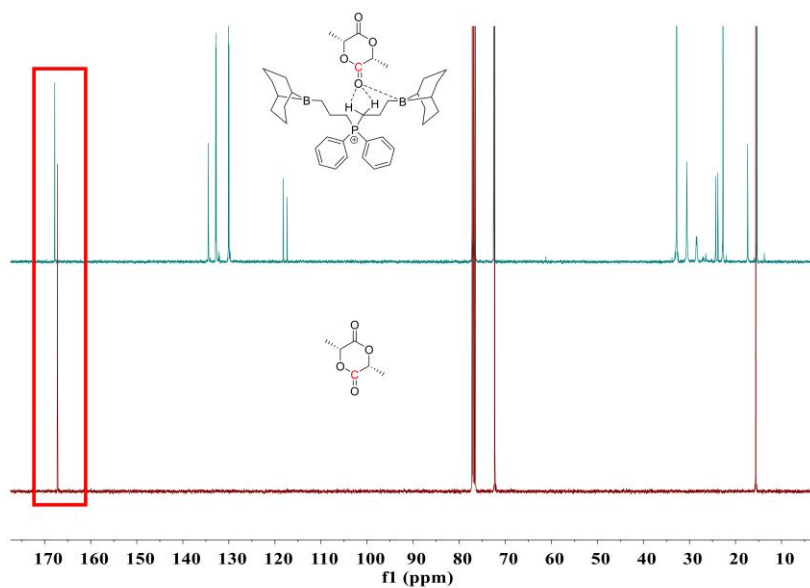


Figure S9. *In situ* $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (100 MHz, CDCl_3 , 298 K) of equal molar amount of **PBB-Br** and L-LA

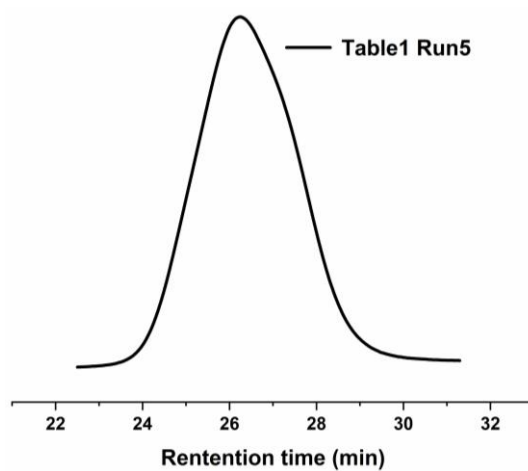


Figure S10. GPC curve of PCHC-*b*-PL-LA obtained from Table 1, run 5

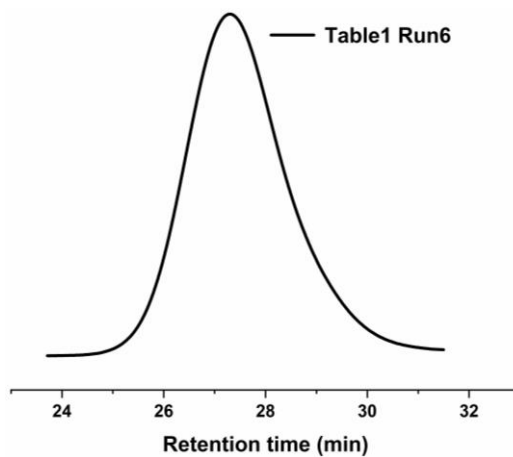


Figure S11. GPC curve of PCHC- *b*-PL-LA obtained from Table 1, run 6

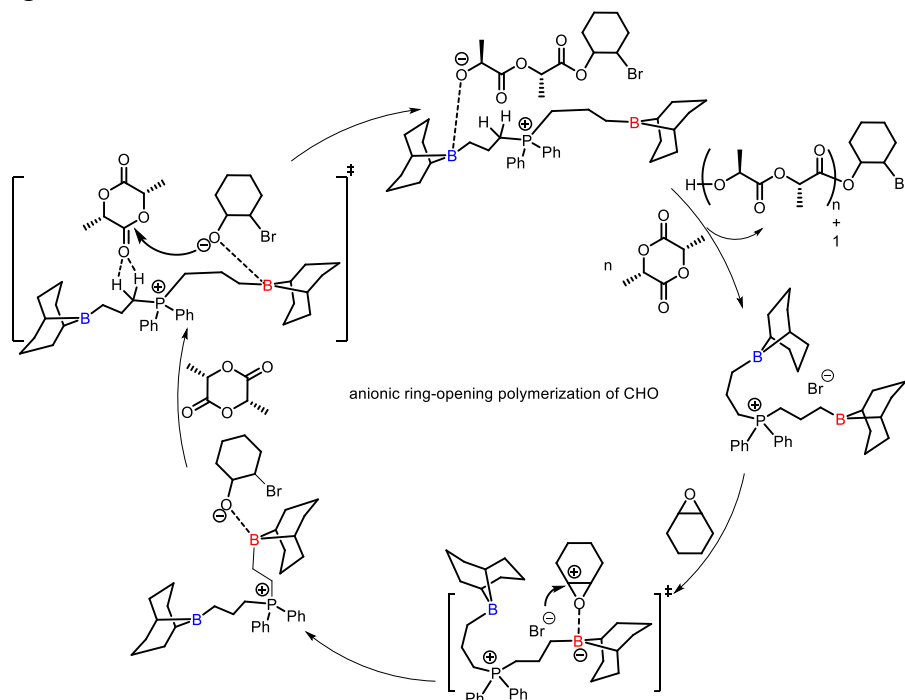


Figure S12. Mechanism diagram of anionic polymerization of L-LA in the presence of CHO

5 References

1. Wang, X.; Hui, J.; Shi, M.; Kou, X.; Li, X.; Zhong, R.; Li, Z., Exploration of the Synergistic Effect in a One-Component Lewis Pair System: Serving as a Dual Initiator and Catalyst in the Ring-Opening Polymerization of Epoxides. *ACS Catal.* **2022**, *12* (14), 8434-8443.