Supporting Information

Metal-free Lewis Pair Catalysts for a One-pot Terpolymerization of Propylene Oxide, L-Lactide and CO_2

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This Supporting Information contains:

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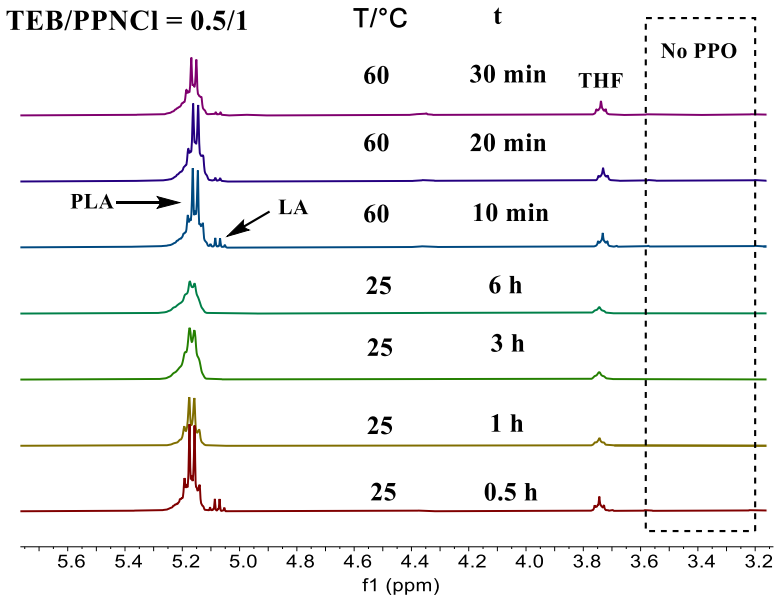


Fig. S1. ^{1}H NMR spectra of LA ROP at different times and temperatures (PO/LA/TEB/PPNCl = 500/100/0.5/1).

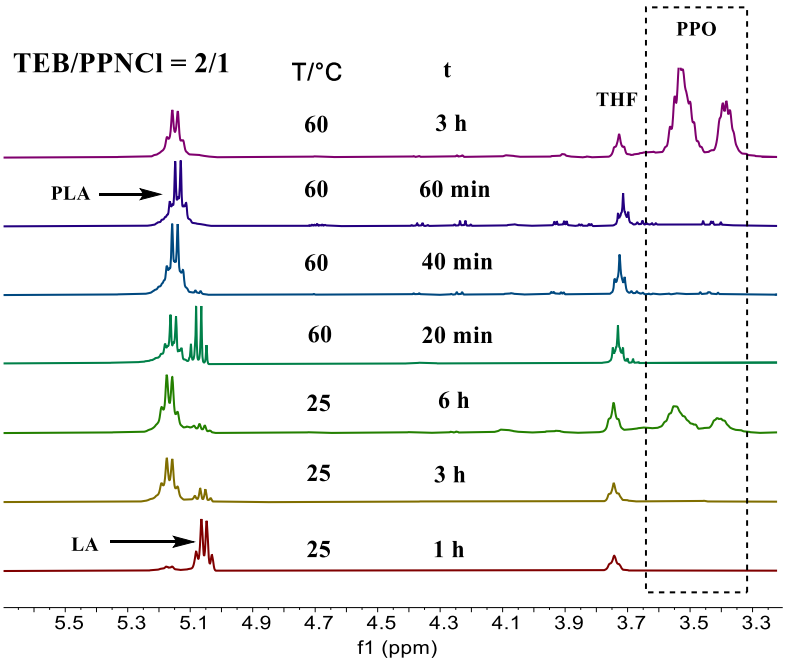


Fig. S2. ^{1}H NMR spectra of LA ROP at different times and temperatures (PO/LA/TEB/PPNCl = 500/100/2/1).

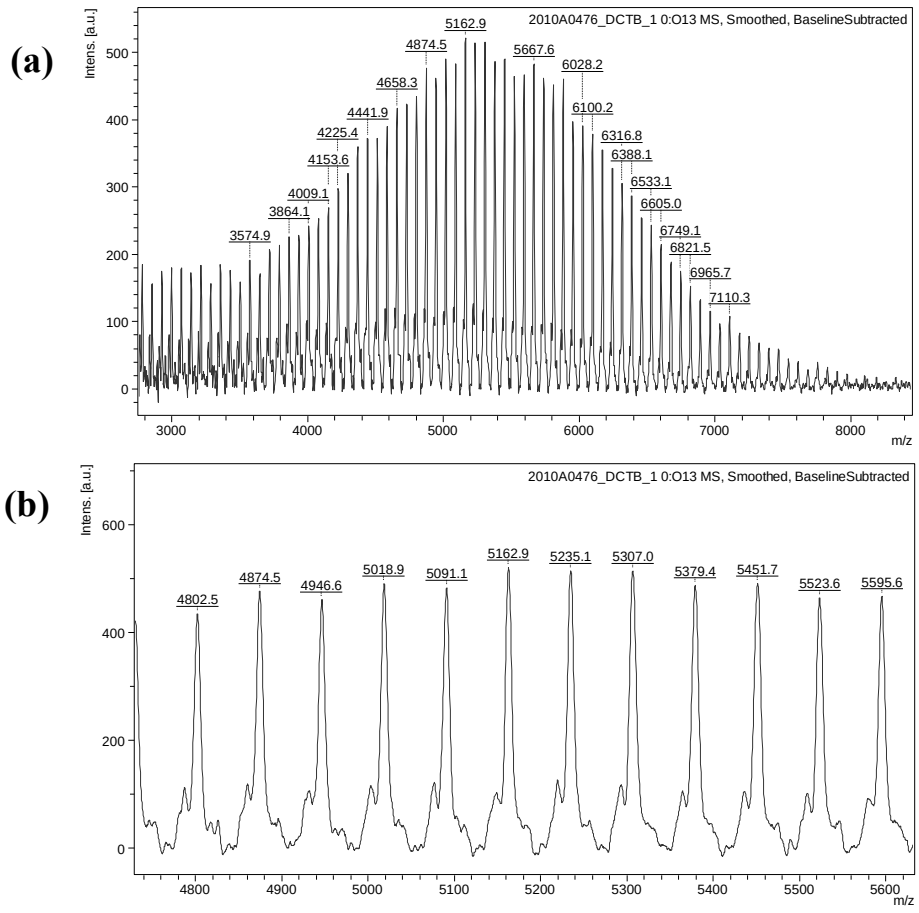
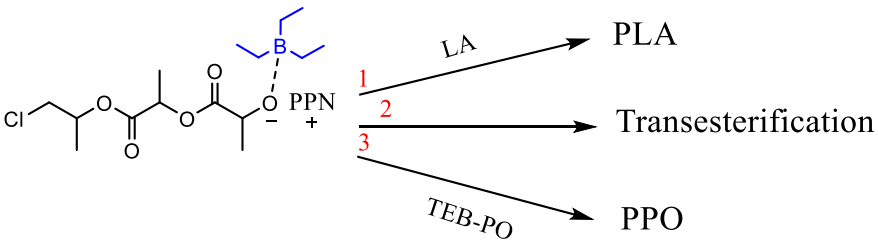


Fig. S3. MALDI spectra of PLA obtained from the ROP of LA catalyzed by TEB/PPNCl = 1/1 at 25 °C for 60 minutes: (a) initial spectrum; (b) the magnified part. The major series of the oligomers can be assigned as An = $(1/2LA)_nPOClNa^+$ with 72.02 interval



Scheme S1. Three kinds of reactions in the synthesis of PLA with PO as solvent.

Table S1. Synthesis of PPCLA at different temperatures [a]

entry	temp. (°C)	select. (%) [b]	composition (mol%) [c]			M_n (kg·mol^{-1})/PDI [d]
			PLA	PPC	PPO	
1	60	90	19	78	3	9.5/1.60
2	70	82	16	76	8	9.2/2.26
3	80	66	17	73	9	10.9/2.30

[a] All polymerizations were conducted under a PO/LA/TEB/PPNCl molar ratio of 920/80/2/1 at 1 MPa CO_2 for 12 h. [b] Calculated by ^{1}H NMR, linear vs cyclic selectivity. [c] Calculated by ^{1}H NMR. [d] Determined by GPC in chloroform with polystyrene standard.

Table S2. Synthesis of PPCLA catalyzed by different TEB/PPNCl ratios [a]

entry	TEB/PPNCl	select. (%) [b]	composition (mol%) [c]			M_n(kg·mol^{-1})/PDI [d]
			PLA	PPC	PPO	
1	0.5	78	69	31	0	5.9/2.40
2	1	82	48	52	< 1	8.7/2.08
3	1.5	87	38	61	1	9.3/1.84
4	2	93	33	65	2	10.1/1.58
5	3	92	32	66	2	10.6/2.16
6	5	90	31	66	3	9.1/2.35
7 [e]	0.5	80	75	25	0	6.3/2.45
8 [f]	0.5	0	-	-	-	No polymer

[a] All polymerizations were conducted under a PO/LA/PPNCl molar ratio of 500/100/1 at 1 MPa CO_2, 60 °C for 4 h or under conditions otherwise mentioned. [b] Calculated by ^{1}H NMR, linear vs cyclic selectivity. [c] Calculated by ^{1}H NMR. [d] Determined by GPC in chloroform with polystyrene standard. [e] The reaction was conducted at 25 °C for 1 h first and then charged with 1 MPa CO_2 to react at 60 °C for 3 h. [f] No addition of LA; only propylene carbonate was formed.

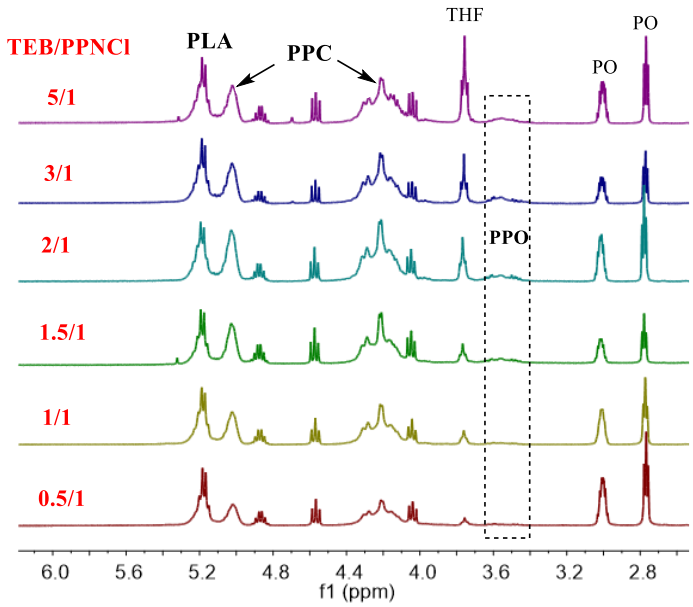
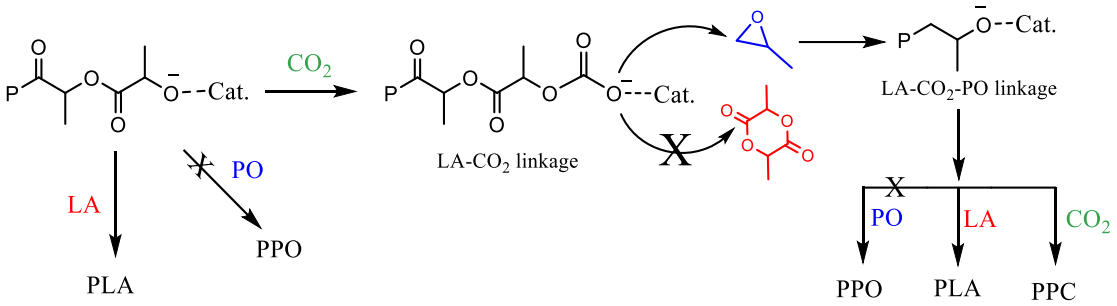


Fig. S4. ^{1}H NMR spectra of PPCLA at different TEB/PPNCl ratios (Table S2).



No long-chain PPC can be formed because of faster backbiting rate than chain growth

Scheme S2. Proposed chain propagation process at TEB/PPNCl = 0.5/1.

Table S3. Terpolymerization of PO, LA and CO_2 catalyzed by TEB/PPNCl (2/1) [a]

entry	time (h)	LA conv. (%)[b]	select. (%) [c]	composition (mol%) [b]			M_n(kg·mol^{-1})/PDI [d]
				PLA	PPC	PPO	
1	2	61	84	78	22	0	5.8/1.47
2	4	100	89	33	65	2	10.1/1.58
3	6	100	93	30	66	4	11.4/1.80
4	8	100	93	26	69	5	12.8/1.88
5	10	100	94	24	69	7	13.6/2.23

[a] All polymerizations were conducted under a PO/LA/PPNCl molar ratio of 500/100/1 at 1 MPa CO_2, 60 °C. [b] Calculated by ^{1}H NMR. [c] Calculated by ^{1}H NMR, linear vs cyclic selectivity. [d] Determined by GPC in chloroform with polystyrene standard.

Table S4. Terpolymerization of PO, LA and CO_2 catalyzed by TEB/DBU/BDM (2/1/0.5) [a]

entry	time (h)	LA conv. (%) [b]	select. (%) [c]	composition (mol%) [b]			M_n(kg·mol^{-1})/PDI [d]
				PLA	PPC	PPO	
1	1	50	84	79	21	0	2.8/1.51
2	2	83	86	59	41	0	4.3/1.51
3	4	100	88	38	60	2	8.7/1.44
4	6	100	90	30	66	4	9.2/1.64
5	8	100	88	24	67	9	12.6/2.06
6	10	100	86	24	65	10	13.2/2.32

[a] All polymerizations were conducted under a PO/LA/DBU molar ratio of 500/100/1 at 1 MPa CO_2, 60 °C. [b] Calculated by ^{1}H NMR. [c] Calculated by ^{1}H NMR, linear vs cyclic selectivity. [d] Determined by GPC in chloroform with polystyrene standard.

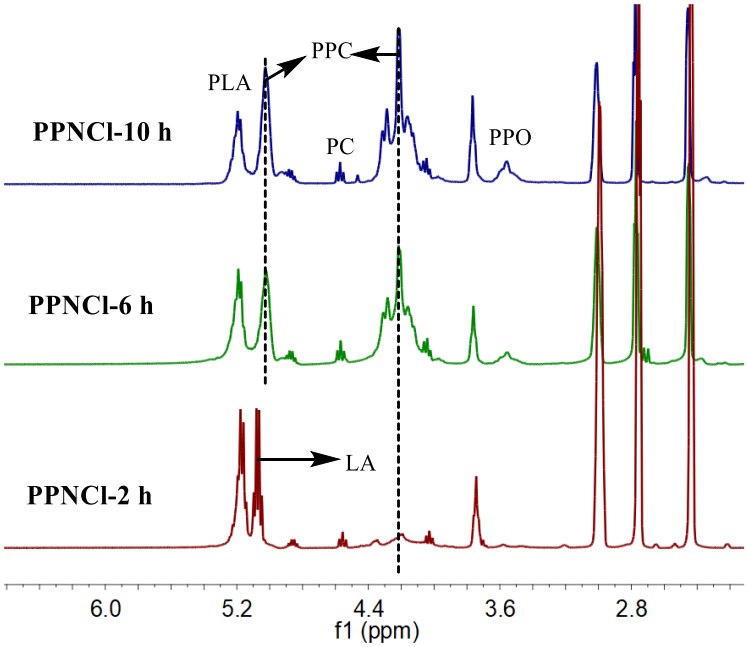


Fig. S5. ^{1}H NMR spectra of PPCLA catalyzed by TEB/PPNCl at different time (Table S3).

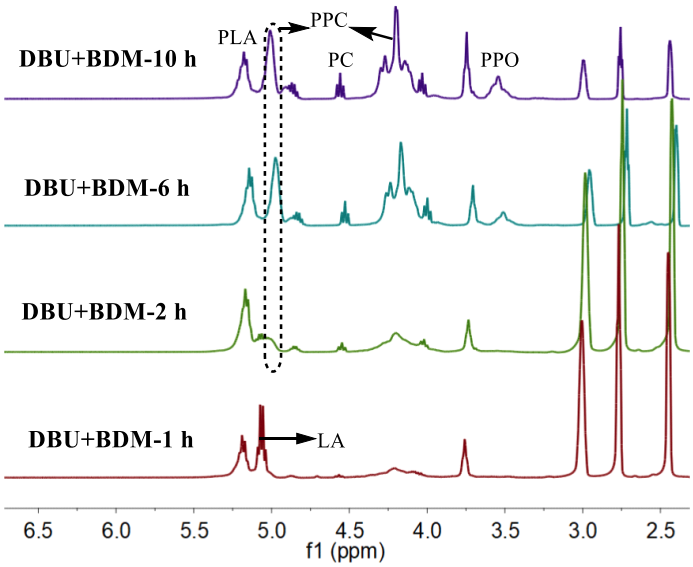


Fig. S6. ^{1}H NMR spectra of PPCLA catalyzed by TEB/DBU/BDM at different time (Table S4).

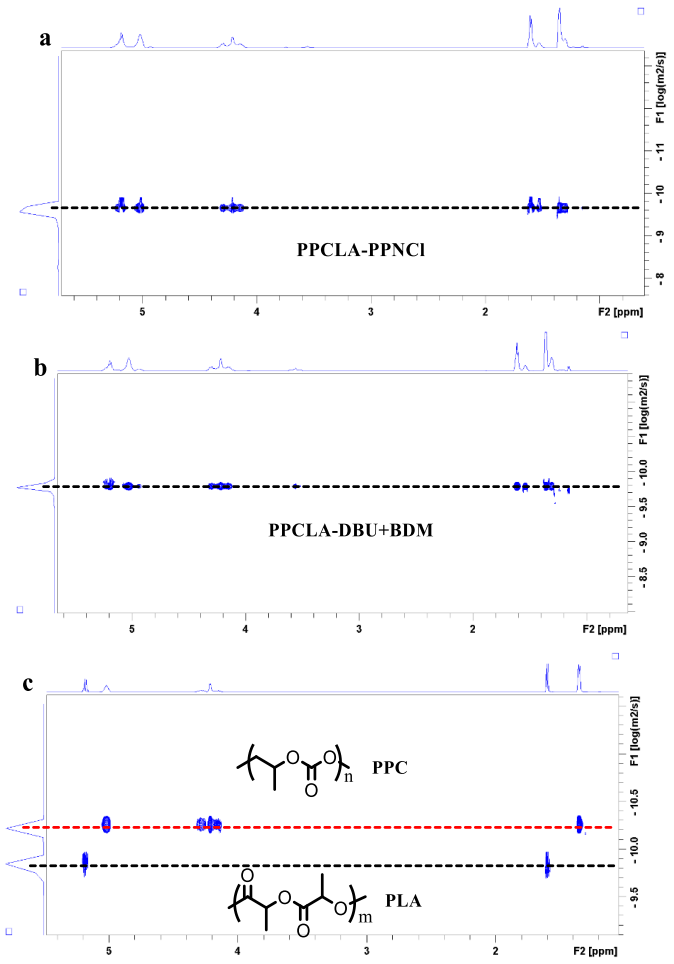
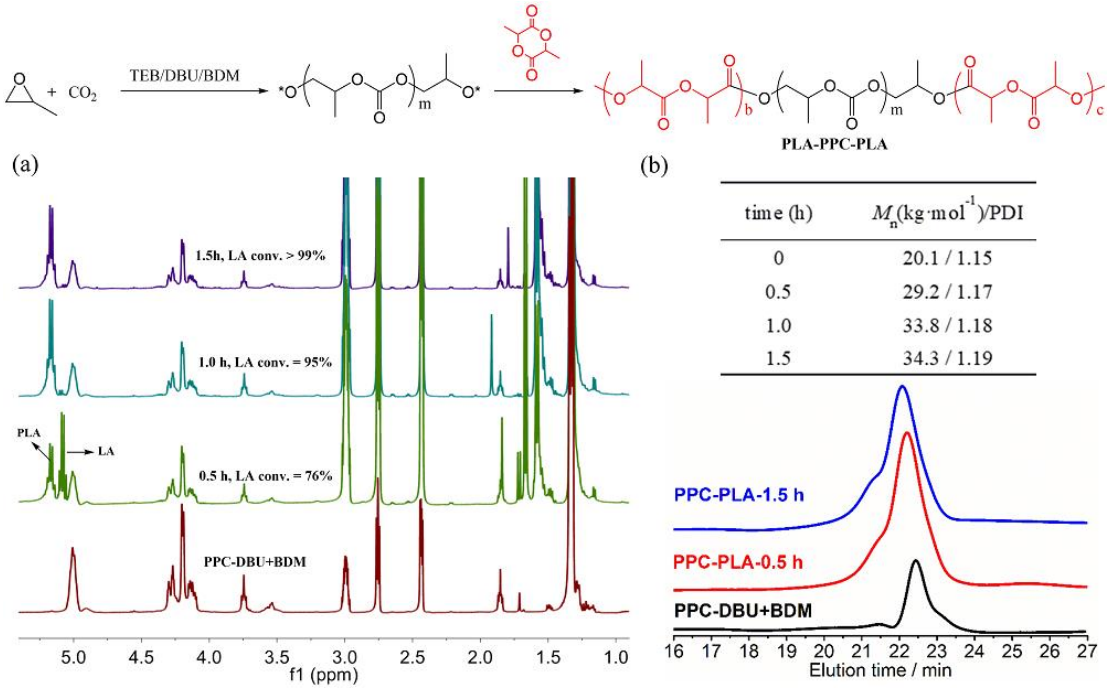


Fig. S7. DOSY spectra of (a) PPCLA-PPNCl; (b) PPCLA-DBU+BDM; (c) the mixture of PPC and PLA.



time (h)	M_n(kg·mol^{-1})/PDI
0	20.1 / 1.15
0.5	29.2 / 1.17
1.0	33.8 / 1.18
1.5	34.3 / 1.19

Fig. S8. Synthesis of PPC-PLA block copolymers catalyzed by TEB/DBU/BDM: (a) Evolution of ^{1}H NMR spectra of LA ROP with reaction time; (b) Evolution of GPC traces and MWs.

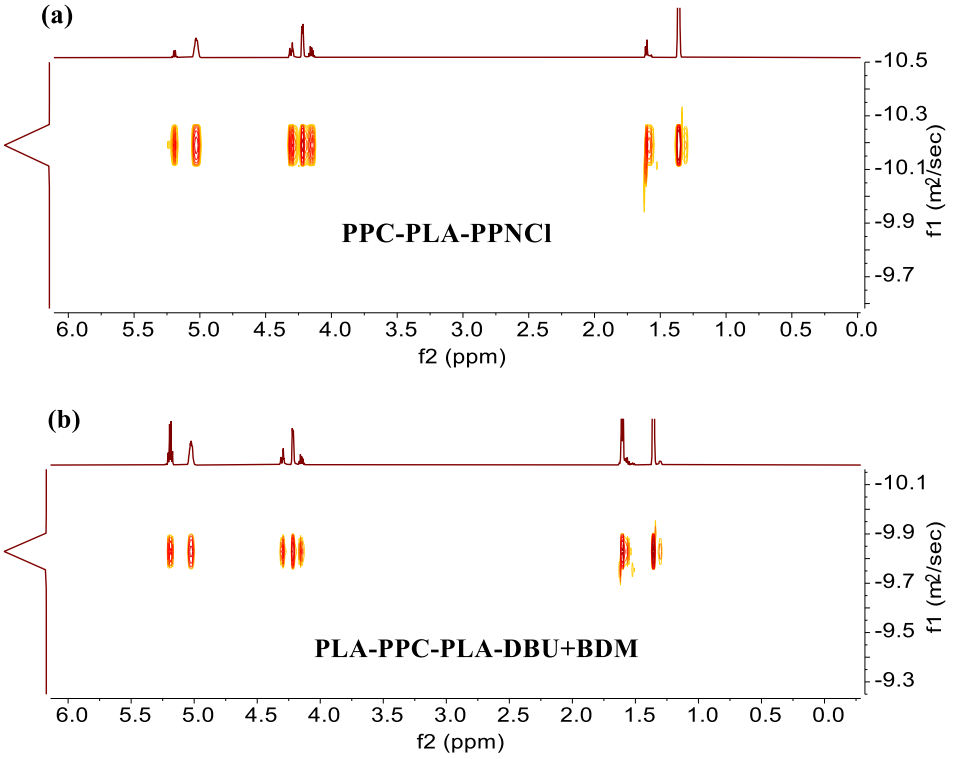


Fig. S9. DOSY spectra of (a) PPC-PLA-PPNCl; (b) PLA-PPC-PLA-DBU+BDM