Supporting Information:

Innovative Synthesis of PPC-P-co-PLA Multi-block copolymers via One-pot copolymerization and transesterification catalysed by Alkyl Boron and Diverse Lewis Bases

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Content

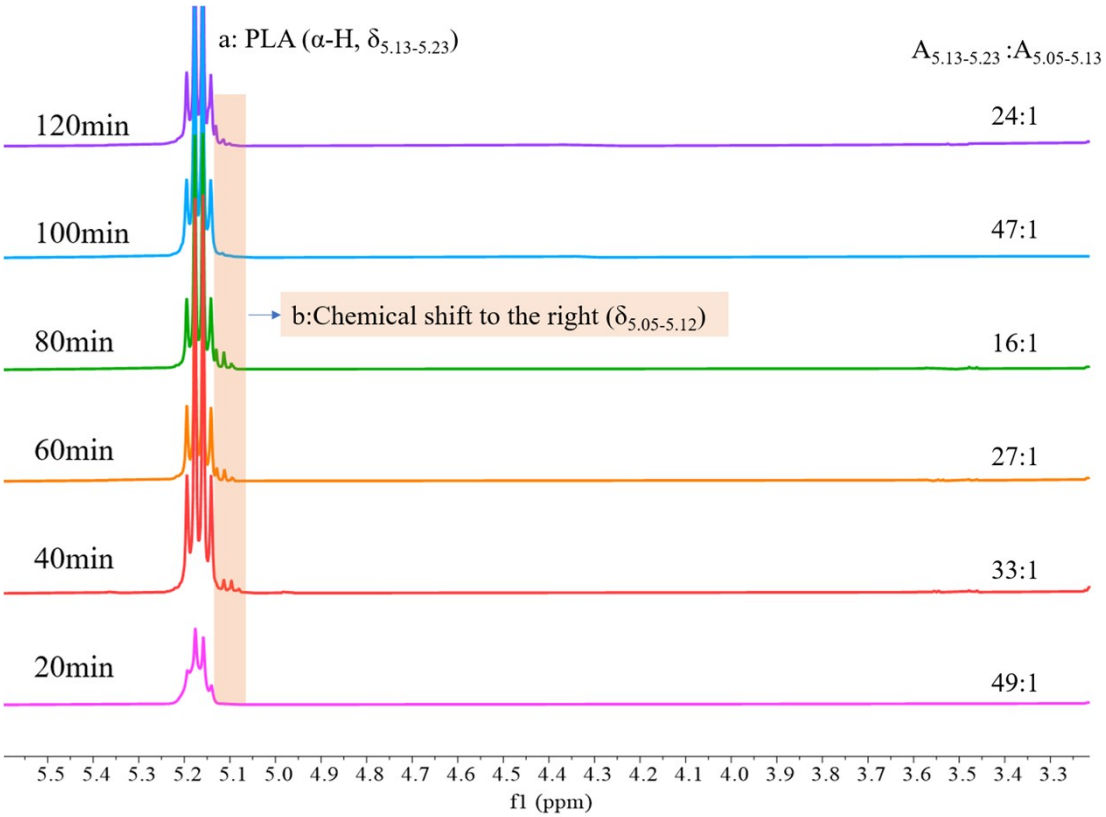

Figure S1. ^{1}H NMR spectra of 10PLA/1PPNCl sampled at different times.
$A_{5.13-5.23}$: $A_{5.05-5.13}$: Integral area ratio in hydrogen spectrum.

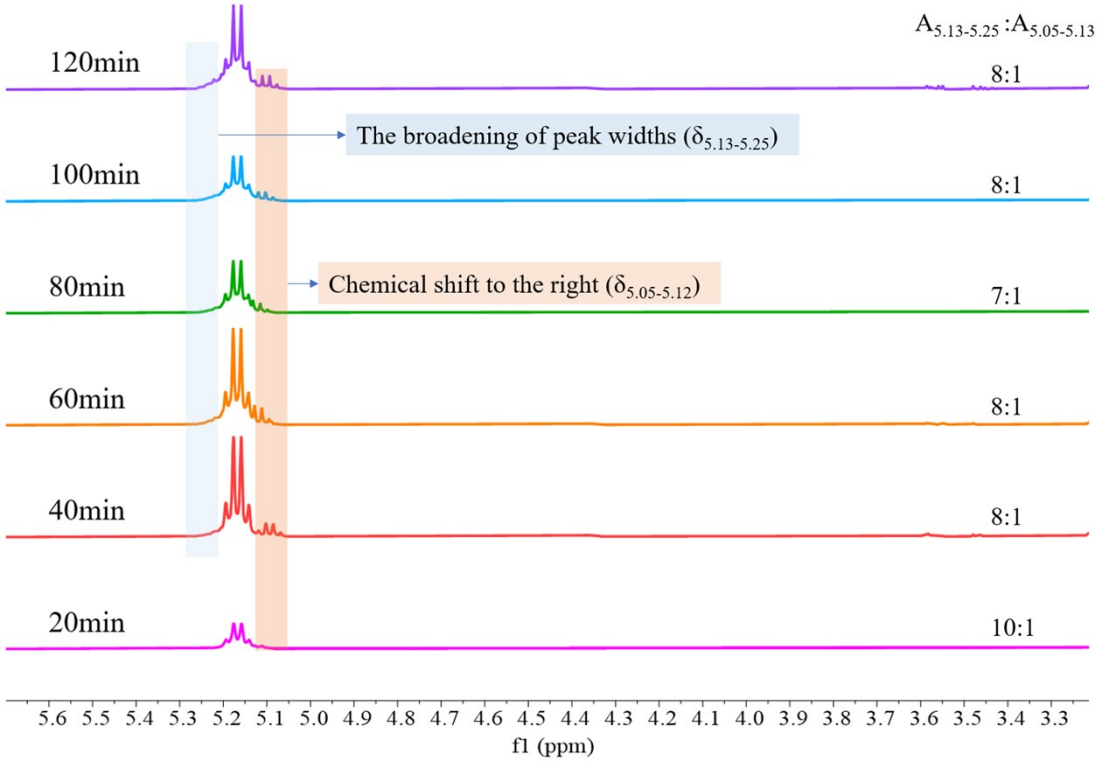

Figure S2. ^{1}H NMR spectra of 10PLA/4PPNCl sampled at different times.
$A_{5.13\text{-}5.25}$: $A_{5.05\text{-}5.13}$: Integral area ratio in hydrogen spectrum.

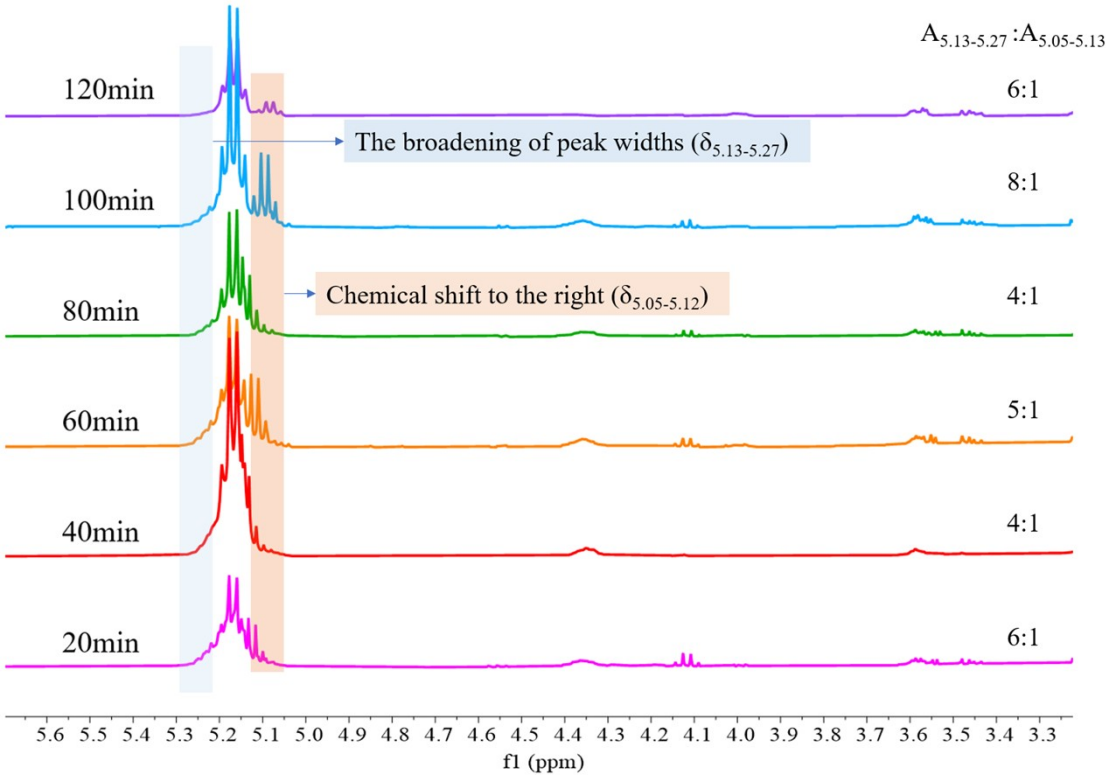

Figure S3. ^{1}H NMR spectra of 5PLA/4PPNCl sampled at different times.
$A_{5.13\text{-}5.27}$: $A_{5.05\text{-}5.13}$: Integral area ratio in hydrogen spectrum.

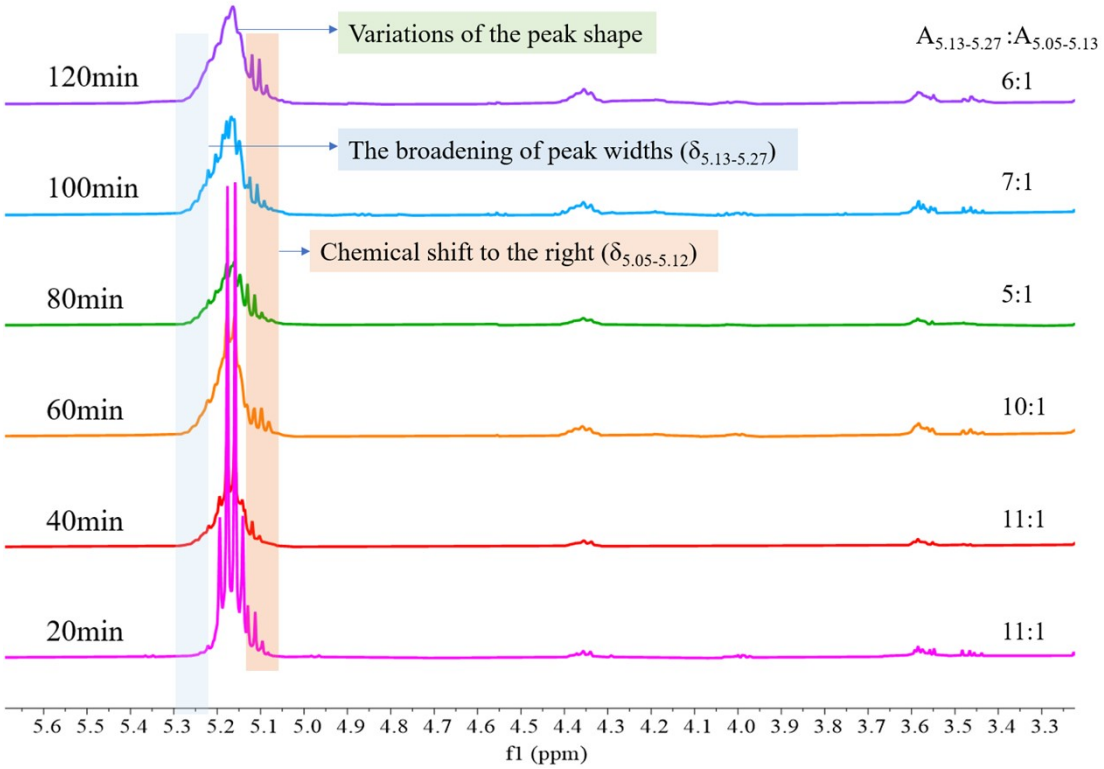

Figure S4. ^{1}H NMR spectra of 10PLA/8PPNCl sampled at different times.
$A_{5.13-5.27}$: $A_{5.05-5.13}$: Integral area ratio in hydrogen spectrum.

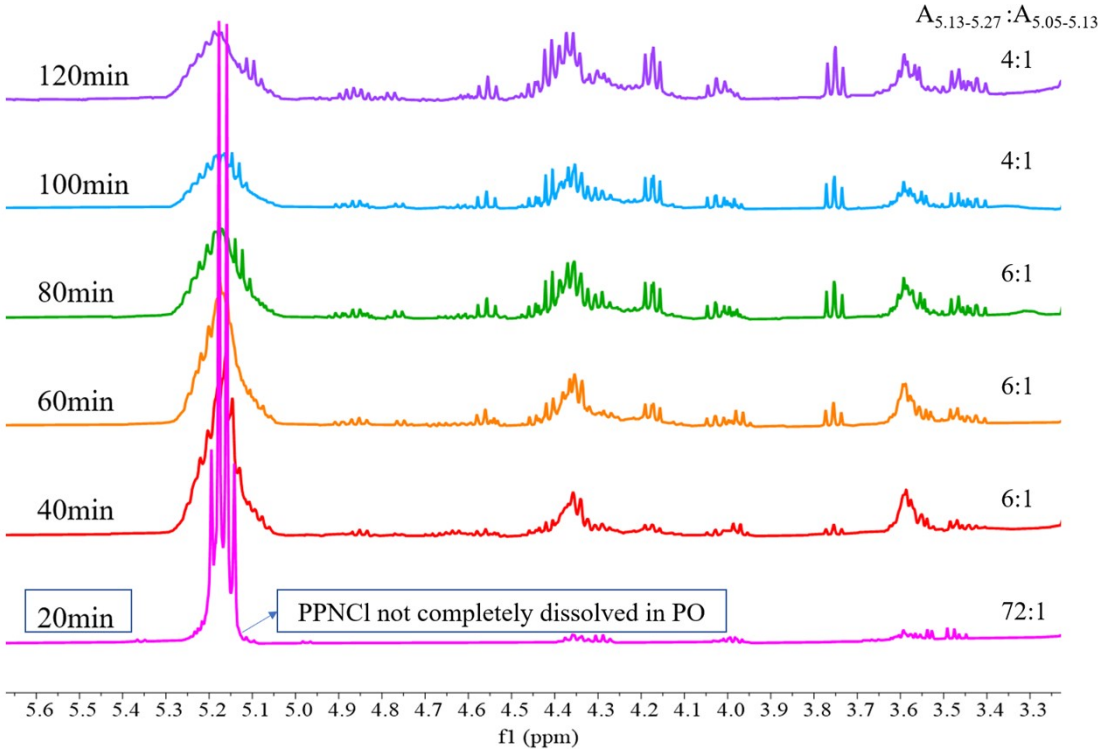

Figure S5. ^{1}H NMR spectra of 10PLA/20PPNCl sampled at different times.
The peak undergoing the rightward chemical shift gradually converges with the product peak subsequent to the depolymerization of PLA.
$A_{5.13-5.27}$: $A_{5.05-5.13}$: Integral area ratio in hydrogen spectrum.

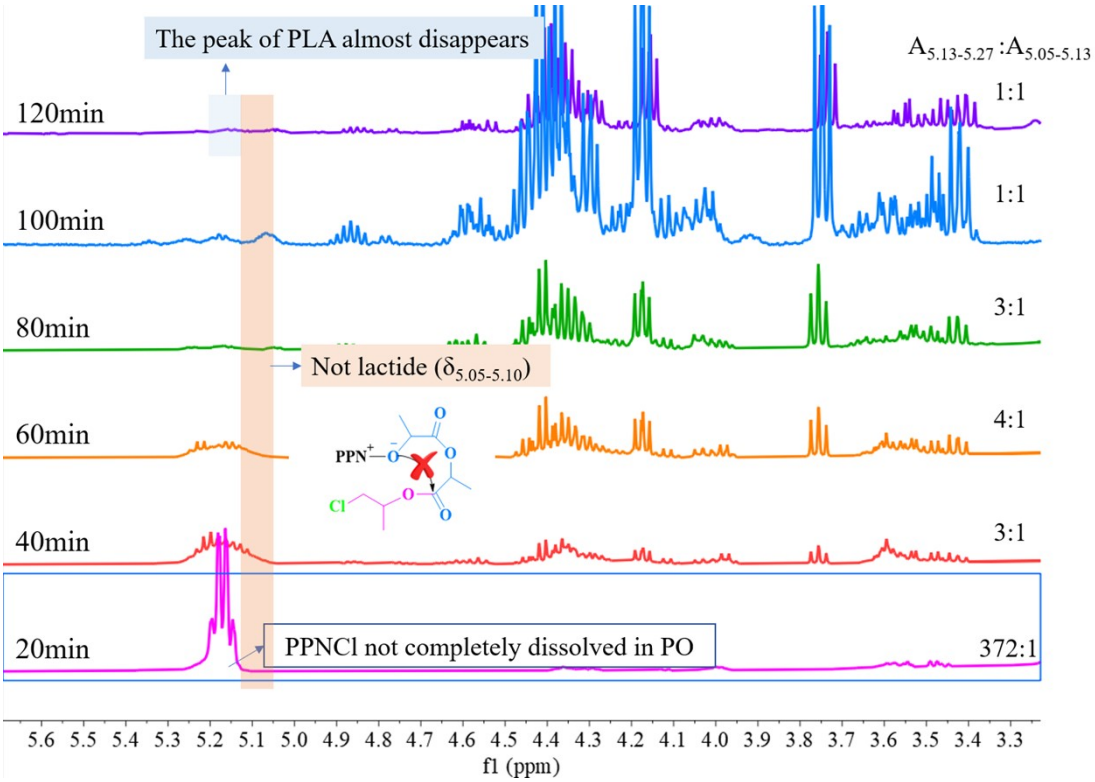

Figure S6. ^{1}H NMR spectra of 5PLA/20PPNCl sampled at different times.
$A_{5.13-5.27}$: $A_{5.05-5.13}$: Integral area ratio in hydrogen spectrum.

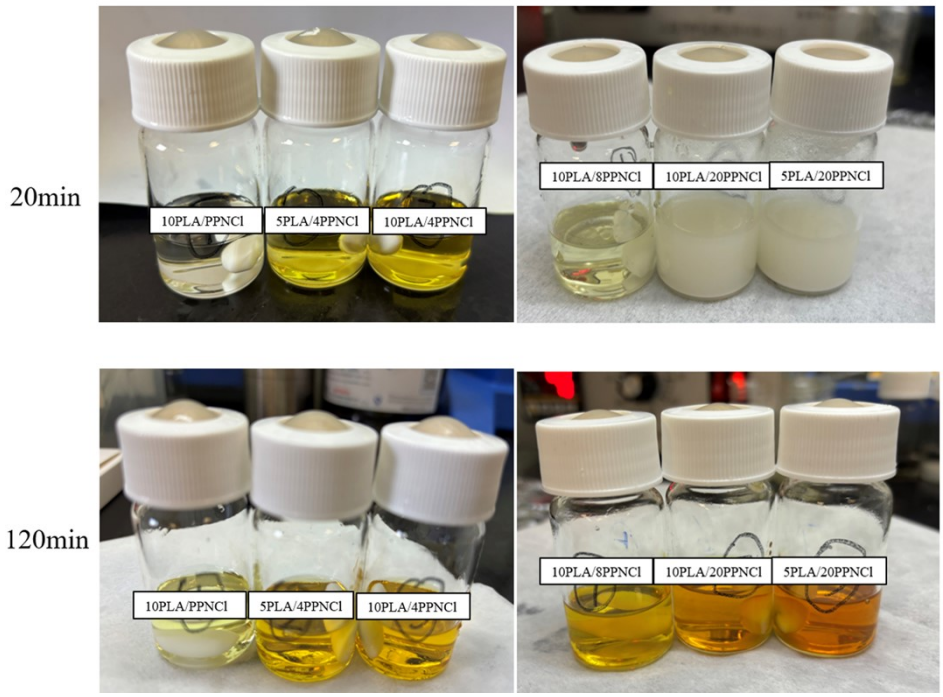

Figure S7. Photos of the color and solubility of the sample at 20 and 120 minutes.
At 20 minutes, when the initiator content is high, the dissolution of the sample and initiator is inhibited. As the concentration of the initiator reaction increases, the color

of the sample becomes more pronounced.

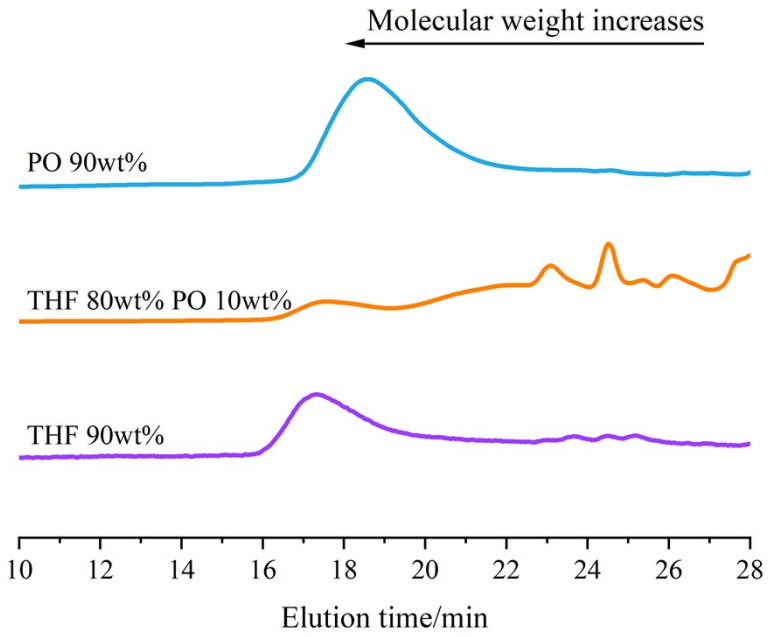

Figure S8. GPC curves of PO: PPNCl 4000:1, PLA 10wt% with different concentrations of solvents at 70 °C for 2 hours.

Upon addition of THF as the sole solvent, a minor peak emerges during the elution time range of 22-26 min, attributed to PLA depolymerization (Purple line). Incorporating a small quantity of PO into the THF solvent results in an intensified peak profile within the 19-28 min, suggesting an acceleration of PLA depolymerization (Orange line). Exclusive use of PO as the solvent leads to a reduction in molecular weight, accompanied by an overall shift of the peak towards longer elution times (Blue line).

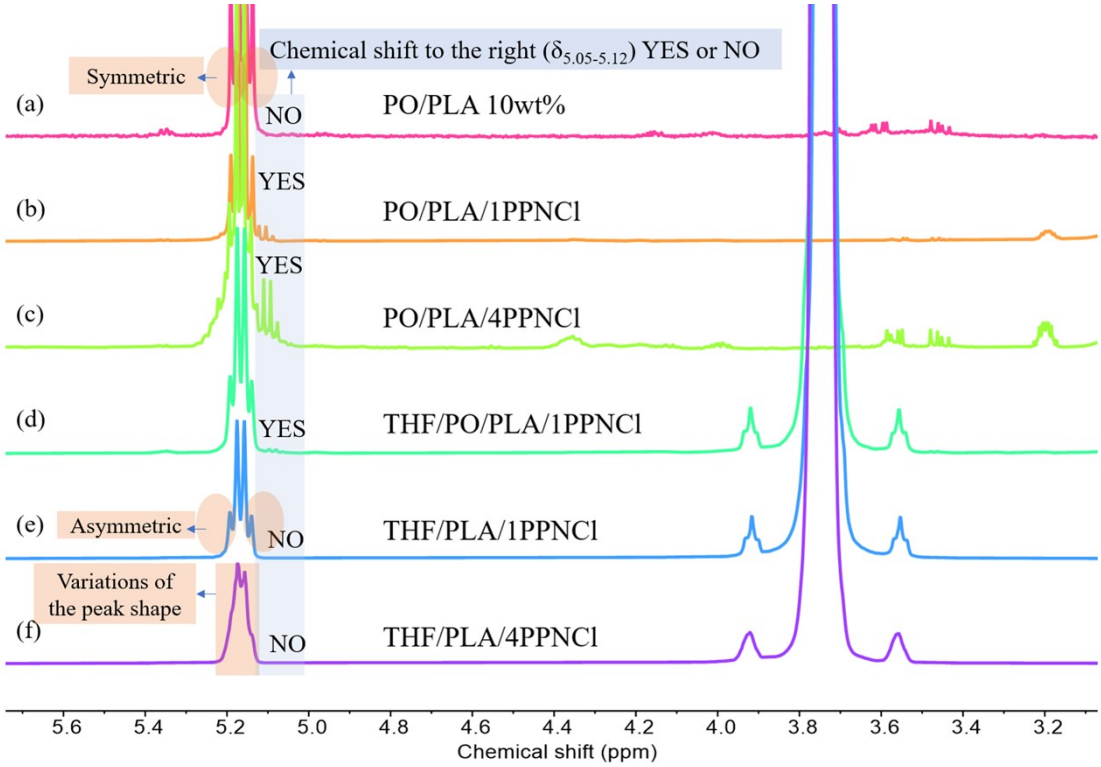

Figure S9. ^{1}H NMR spectra of the interaction between PLA and PPNCl using PO as solvent and THF as solvent.

Naming rules: The amount of PO or THF added is fixed; The value before PLA is the mass fraction of PLA; n PPNCl represents PO: PPNCl = 4000: n. When PO is used as a solvent, the impact of changes in PLA peak of α-H: (a) The absence of PPNCl and the lack of chemical shift changes were observed. (b) The addition of a minute quantity of PPNCl elicits a discernible change in chemical shift. (c) An increase in the concentration of PPNCl results in an augmentation of the kurtosis of the rightward shift. When THF is used as a solvent, the impact of changes in PLA peak of α-H: (d) The presence of a a minimal amount of PO triggers a chemical shift to the right. (e) In the absence of PPNCl, the peak shape of α-H in PLA exhibited asymmetry. (f) Increasing the concentration of PPNCl results in alterations to the peak shape.

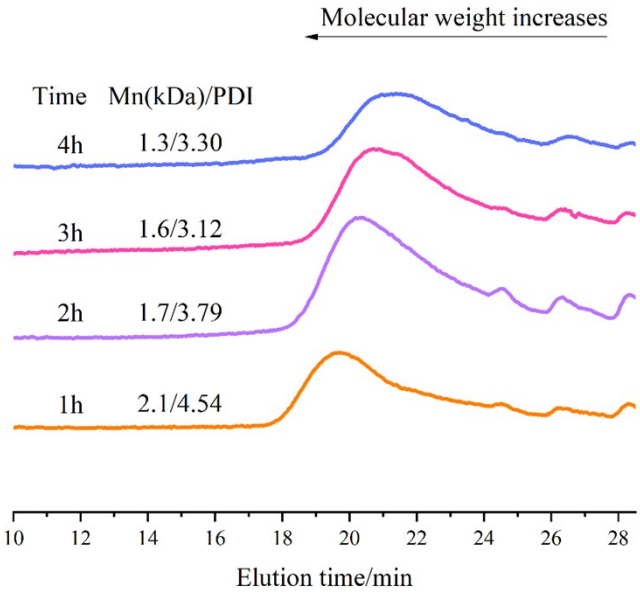

Figure S10. GPC curves of 10PLA/4PPNCl sampled at different times.

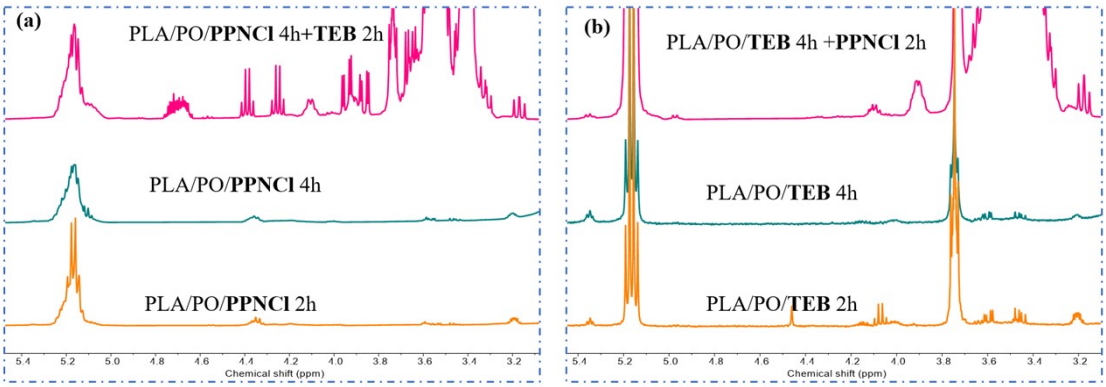

Figure S11. ^{1}H NMR spectra of the binding between PLA, PPNCl and TEB using PO as solvent.

(a) PLA, PO, and PPNCl were combined and allowed to react for 2 hours (orange line) and subsequently for 4 hours (green line) for sampling purposes. Notably, the characteristic peak of PLA exhibited a broadening, suggestive of structural alterations within PLA. Nonetheless, no formation of PPO was detected. Following the addition of TEB for 2 hours (red line), a substantial chemical shift to the right was observed in the characteristic peak of PLA, transforming it into a bulge. This shift coincided with a significant production of PPO and the detection of PPO-*co*-PLA copolymer. (b) PLA, PO, and TEB were reacted together for 2 hours (orange line) followed by an additional 2 hours (green line) for sampling. The characteristic peak of PLA remained largely stable, with minimal PPO formation observed. Subsequently, upon adding PPNCl and allowing for 2 hours of reaction (red line), the characteristic peak of PLA remained largely stable, while a substantial amount of PPO was produced, with minimal formation of PPO-*co*-PLA copolymer.

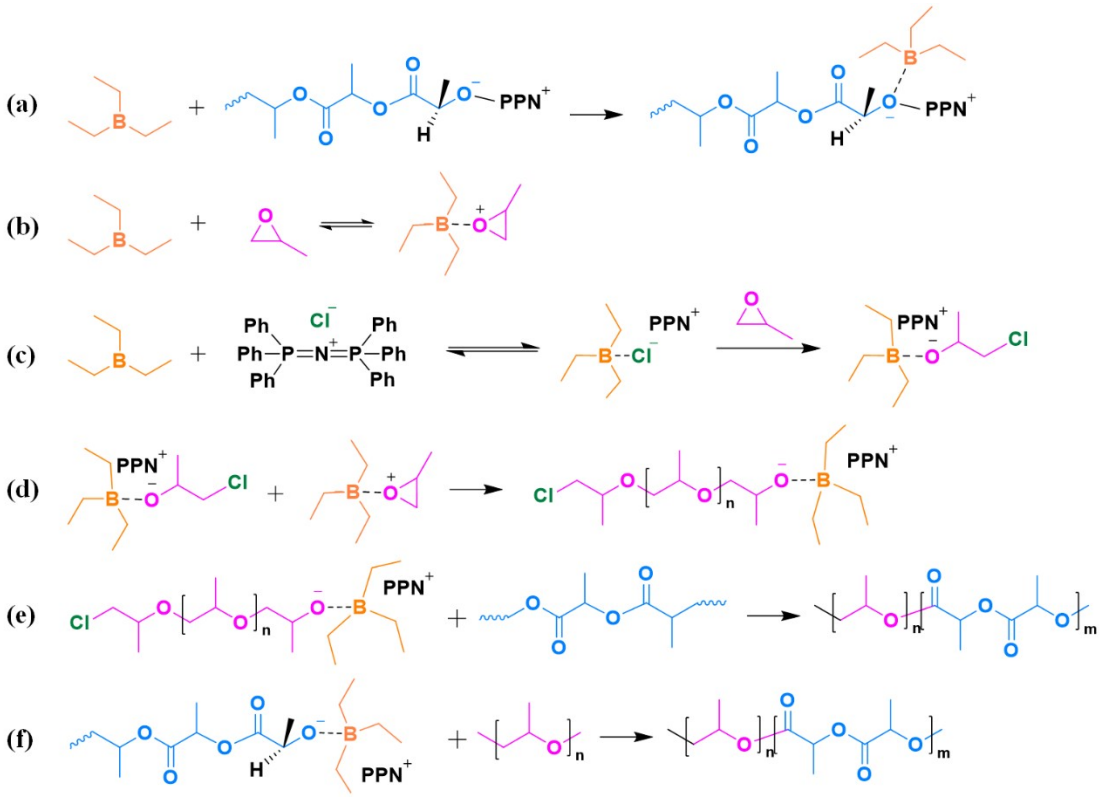

Figure S12. Proposed mechanism upon the addition of TEB into PO/PLA/PPNCl and PO/PLA/TEB/PPNCl.

TEB preferentially binds to (a) PLA segments that have undergone depolymerization, (b) PO, and (c) PPNCl. (d) Activated PO undergoes ring-opening polymerization, resulting in the formation of PPO [1]. (e) and (f) Subsequently, PPO and PLA undergo ester exchange, leading to the formation of copolymers.

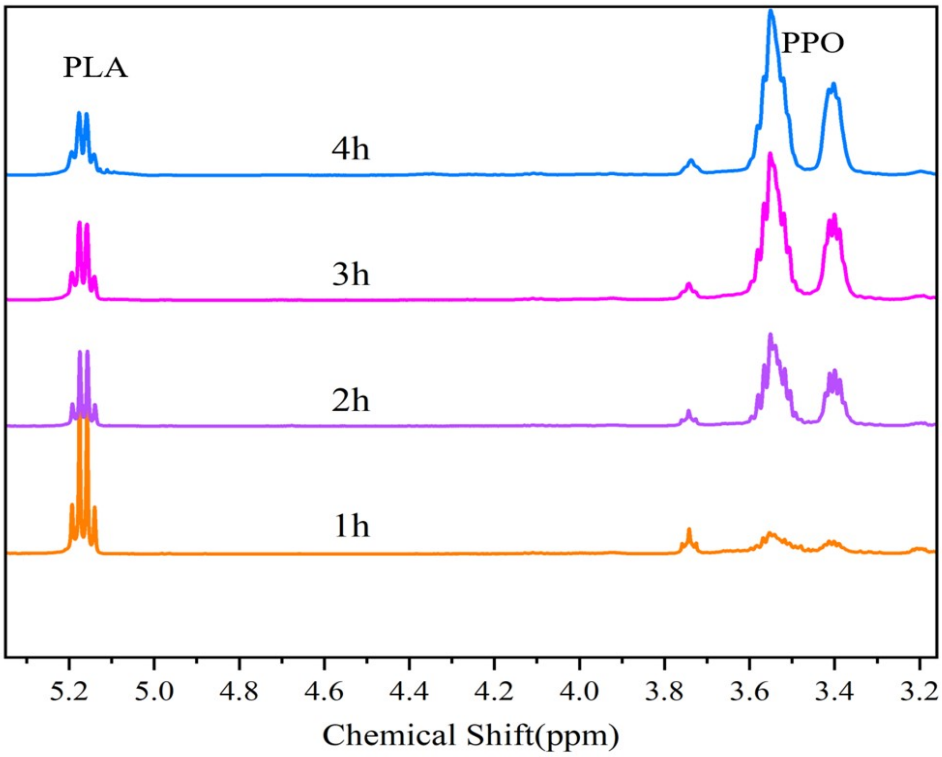

Figure S13. ^{1}H NMR spectra of PO: TEB: PPNCl 4000:2:1, PLA 10 wt% at 70 ℃ with different times.

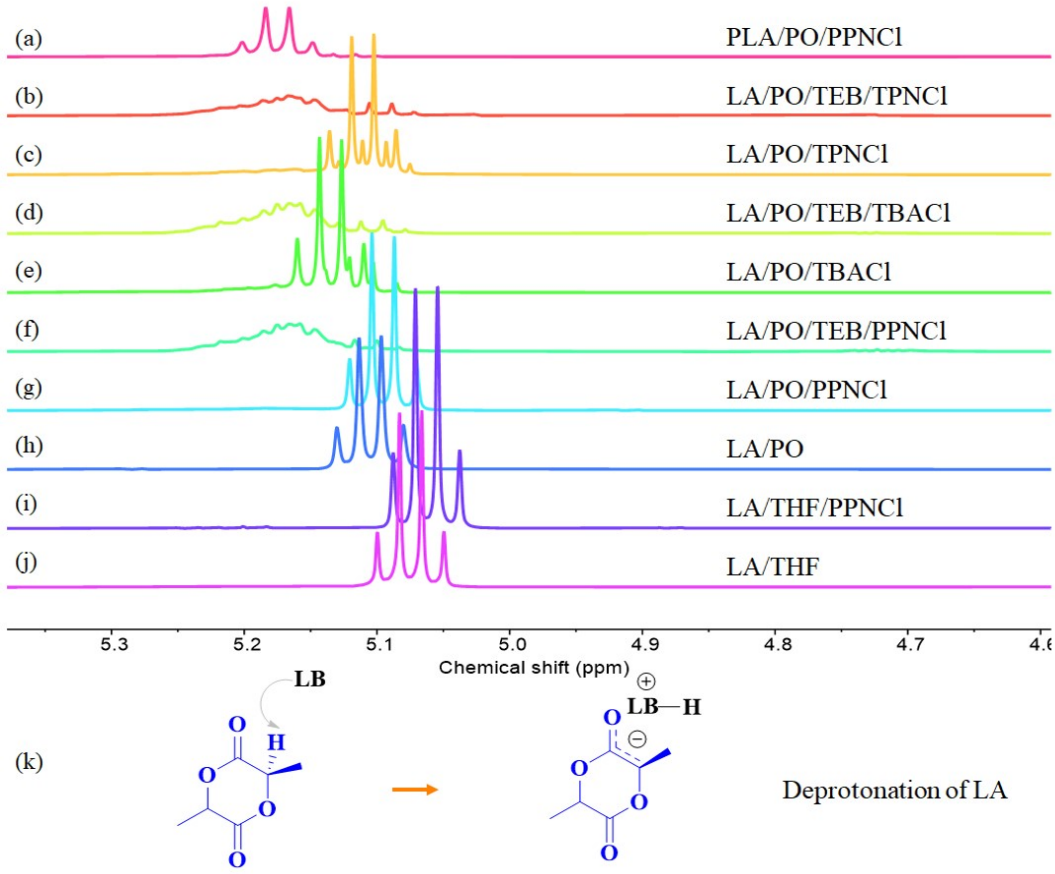

Figure S14. ^{1}H NMR spectra of the effect of different initiators and solvents on the α-H of lactide（LA）.

Upon comparing spectra (a) and (g), it was observed that the peak position of PLA, exhibiting a rightward chemical shift, did not align precisely with the position of lactide LA. The addition of TEB in spectra (b), (d) and (f) compared to (c), (e) and (g) resulted in the formation of oligomers. Upon analyzing spectra (g), (h), (i), and (j), it became evident that the solvation effect was more significant for LA. The influence of various initiators on the chemical shift of α-H exhibits diverse patterns. The addition of PPNCl specifically induces a rightward shift in the α-H of all lactide (g). The addition of TBACl leads to a notable leftward shift of α-H, with certain instances demonstrating a left-shifted α-H followed by a rightward shift (e). The addition of TPNCl results in a slight leftward shift of α-H, with some instances exhibiting subsequent rightward shifts in the previously left-shifted hydrogen (c). (k) Anions of Lewis bases deprotonate the α-H of PLA to form an enolate intermediates[2].

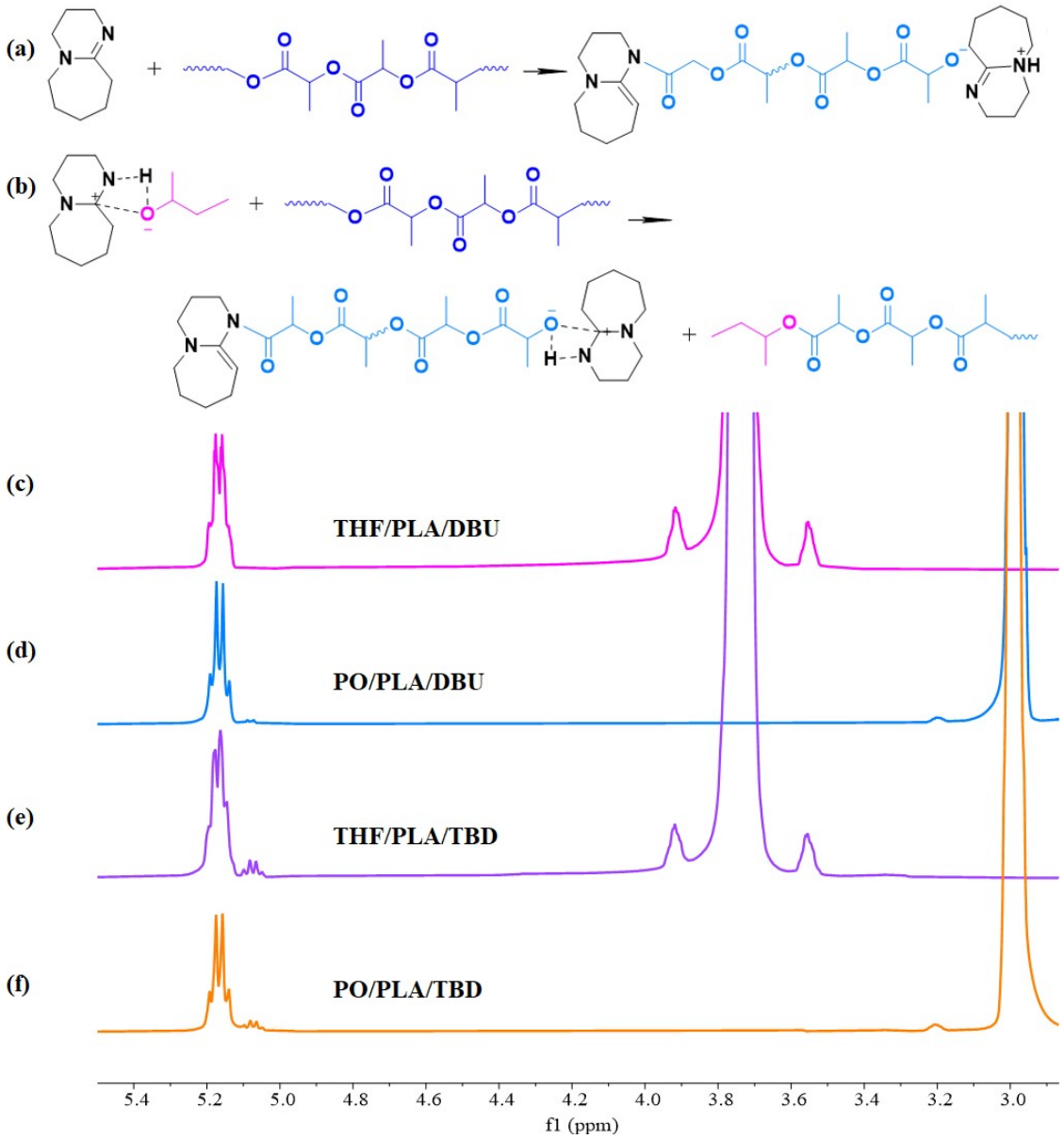

Figure S15. Possible mechanism of PLA depolymerization induced by non-ionic initiator DBU.

(a) DBU interacts with both oxygen negative ions and carbonyl groups of PLA *via* alcohol activation pathway and nucleophilic attack pathway [3]; (b) In the presence of PO as a solvent, DBU first interacts with oxygen anions of PO and subsequently binds to PLA [4]; So compared to using THF as a solvent (c), the peak shape of α-H in PLA using PO (d) as a solvent does not change as much in ^{1}H NMR spectra. (c)-(f) ^{1}H NMR spectra of PLA 10wt% with DBU and TBD as initiator at 70 ℃ for 4 hours.

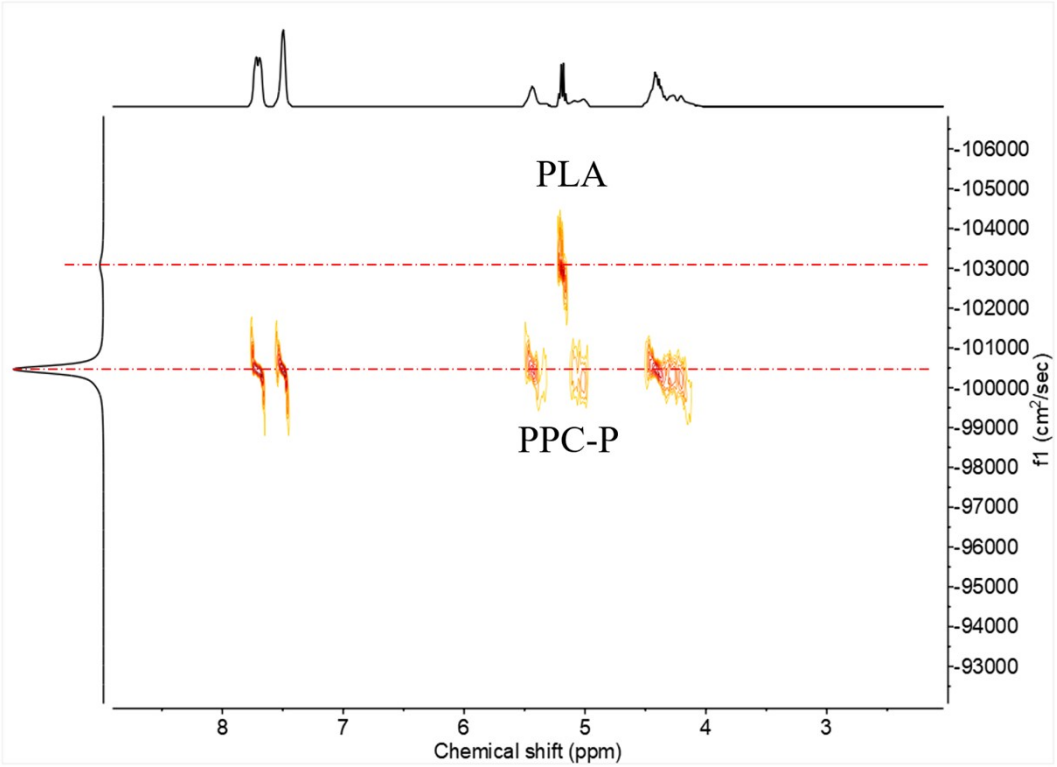

Figure S16. DOSY spectrum of products prepared with TEA/BnOH as the initiator.

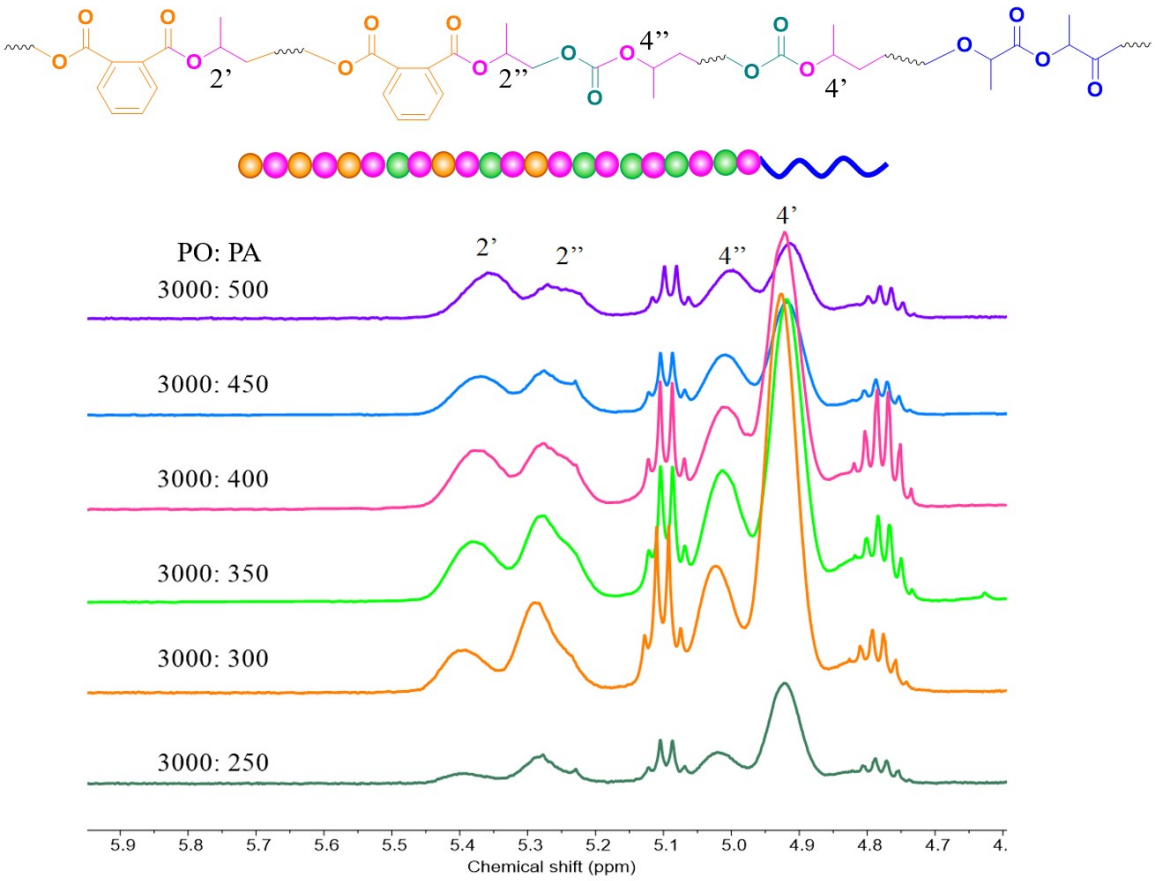

Figure S17. ^{1}H NMR spectra of PPC-P-co-PLA copolymers with different ratio of PO: PA.

The peaks observed between 5.20 and 5.45 ppm correspond to the characteristic peaks of the -OCH(Me)- group in the PO/PA fragment. Meanwhile, the peaks between 4.85 and 5.05 ppm are indicative of the characteristic peaks of the -OCH(Me)- group in the PO/CO_2 fragment. An increase in PA content results in a continuous augmentation of the proportion of 2', along with a corresponding continuous decrease in the proportion of 4'. [5]

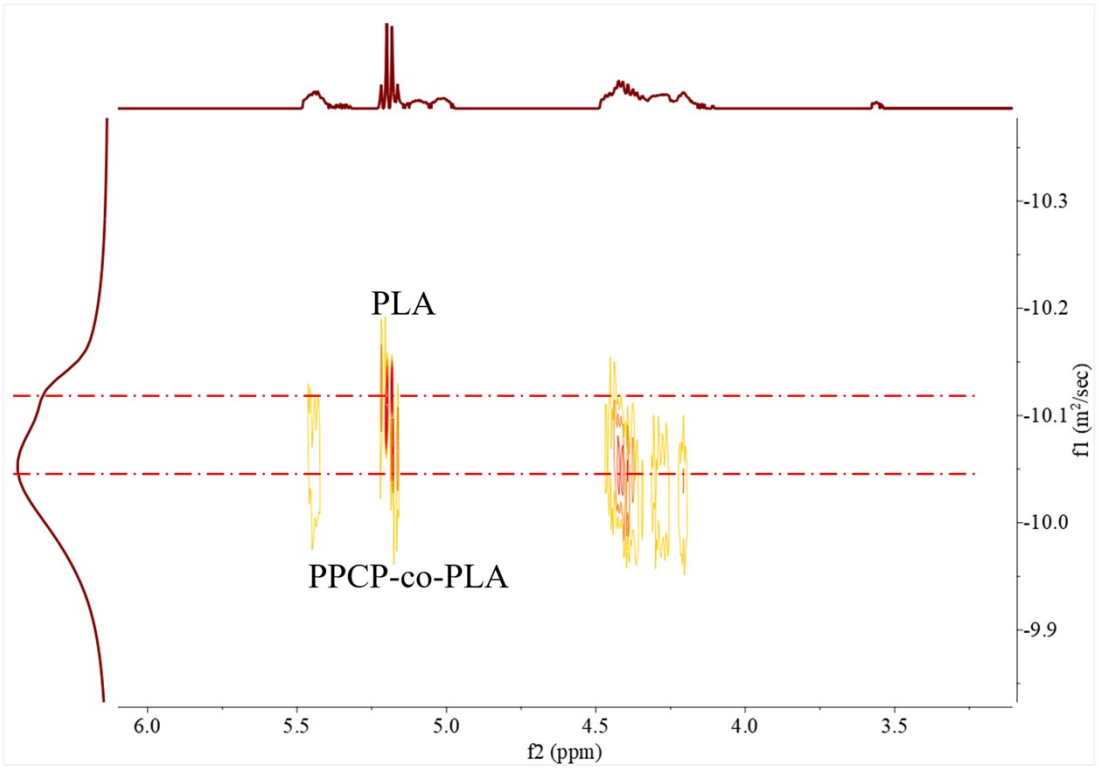

Figure S18. DOSY spectrum of products with 16wt% PLA.

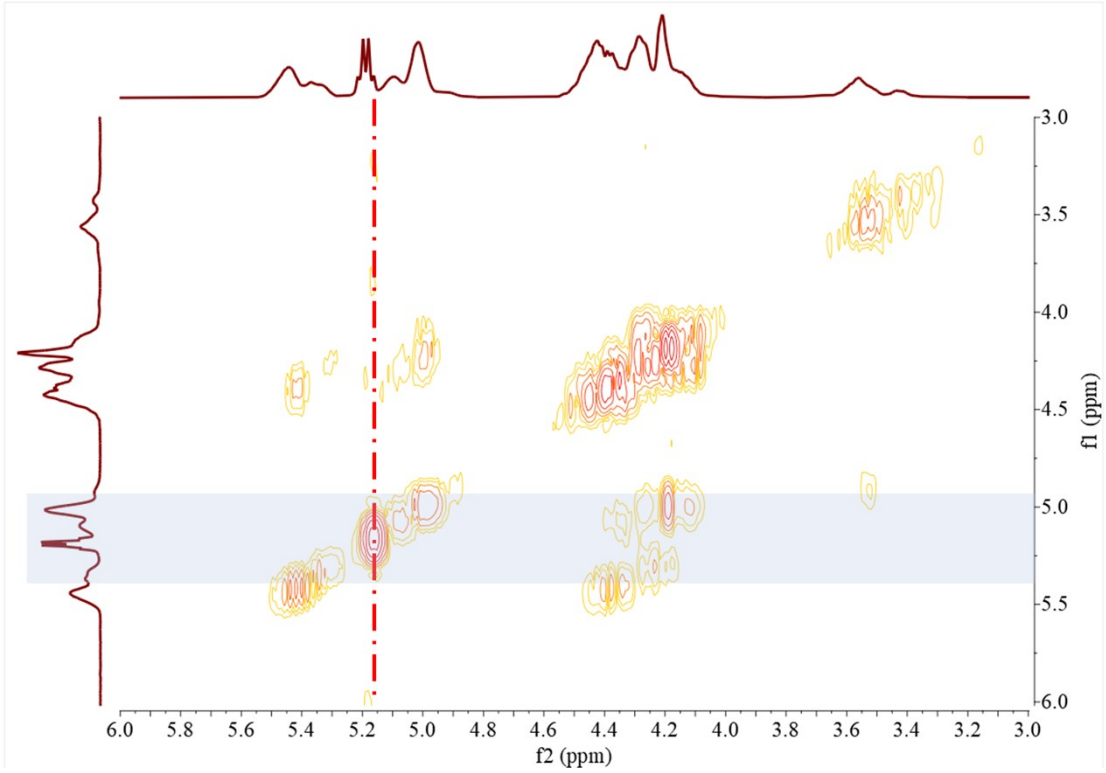

Figure S19. COSY spectrum of products with 12wt% PLA.

Table S1. PO, PA, CO_2 copolymerization and PLA transesterification by different times.

Entry	Time (h)	$PA^{Conv.}$ [a] (%)	PE [a] (%)	PPC [a] (%)	PPO [a] (%)	PLA [a] (%)	CC [a] (%)	PLA [a] (wt%)	M_n [b] (kg/mol)	PDI [b]
1	2	86.4	43.2	32.1	2.0	22.6	4.5	11.7	28.3	1.44
2	4	100	38.3	36.4	7.4	17.9	5.8	9.7	46.0	1.40
3	6	100	35.8	38.1	9.4	16.7	10.1	9.2	48.4	1.40
4	8	100	34.9	42.1	9.5	13.5	11.0	7.5	48.9	1.44

[a]: Calculated by ^{1}H NMR;

$PA^{Conv.}\% = A_{7.8\text{-}8.2ppm} / (A_{7.8\text{-}8.2ppm} + A_1) * 100$;

$PE\% = A_1/4 / (A_1/4 + A_4 + (A_{6,7})/3 + A_8) * 100$;

$PPC\% = A_4 / (A_1/4 + A_4 + (A_{6,7})/3 + A_8) * 100$;

$PPO\% = (A_{6,7})/3 / (A_1/4 + A_4 + (A_{6,7})/3 + A_8) * 100$;

$PLA\% = A_8 / (A_1/4 + A_4 + (A_{6,7})/3 + A_8 + A_c) * 100$;

$PLAwt\% = 72 * PLA\% / (72*PLA\% + 206*PE\% + 102*PPC\% + 58*PPO\%) * 100$.

[b]: Determined by GPC in Tetrahydrofuran (THF).

Table S2. Thermal properties and transmittance of PPC-P-*co*-PLA copolymers.

Entry	PLA (ωt%)	$T_{5\%}$ [c] (℃)	T_g [d] (℃)	T_m [d] (℃)	T_m [e] (℃)	$\triangle H_c$ [e] (J/g)	$\triangle H_m$ [e] (J/g)	χ_c [f] (%)	Transmittance [g] (%)
1	0	235.1	42.5	-	-	-	-	-	93.1
2	3.7	253.8	47.9	-	160.4	-	0.28	8.1	93.3
3	8.2	267.5	48.9	156.6	161.7	-6.14	4.27	24.4	90.9
4	12.1	280.4	49.2	160.8	164.6	-0.16	7.29	63.0	85.9
5	16.0	264.5	49.6	157.7	159.0	-0.58	11.2	66.4	83.8
6 [h]	100	329.1	61.0	173.0	173.5	-	93.1	99.5	94.1

[c]: Determined by TGA, $T_{5\%}$:5% weight loss temperature;

[d]: From second heating run at 10 °C/min by DSC;

[e]: From first heating run at 10 °C/min by DSC;

[f]: The enthalpy of PLA in 100% crystalline form ΔH_m^0 is 93.6 J/g.

$$X_c = \frac{(\Delta H_m - \Delta H_c)}{\omega_{PLA} \times \Delta H_m^0} \times 100\%$$

[g]: Transmittance by WGT-S Transmittance/haze tester.

[h]: Sample dried for 96 hours.

-: not observed;

Data S1. M06-2X/6-21G optimized geometries of PLA (R, S) segments.

C	-1.57217100	0.58397100	0.18463100
H	-1.47984900	0.26311900	1.22790600
C	-0.23320500	0.33077000	-0.48323100
C	2.02409200	0.92860700	-0.40386600
H	2.06225800	0.81514700	-1.49073200
C	2.48094200	-0.38596800	0.21938800
C	4.18981500	-1.97144700	0.24192300
H	3.49839300	-2.79252600	0.04848100
H	5.13622300	-2.13530800	-0.26727200
H	4.33992200	-1.88170700	1.31880800
O	1.88322000	-0.99436300	1.06687300
O	3.66426300	-0.75179900	-0.28838100
O	0.68991300	1.18523400	0.01170700
O	0.00466400	-0.50117800	-1.31443100
C	2.88388300	2.08924300	0.06811600
H	2.82597400	2.17979700	1.15453600
H	3.92115600	1.92206000	-0.22320200
H	2.53013000	3.01772700	-0.38109000
C	-2.00122500	2.04439100	0.12820100
H	-2.11984500	2.36130100	-0.91006000
H	-2.95221900	2.15405100	0.65002200
H	-1.25489900	2.67489600	0.61093900
C	-3.59519300	-0.60916200	0.23558800
C	-4.49637600	-1.50035000	-0.57317000
H	-5.35896900	-1.78020700	0.02624100
H	-4.81351900	-0.97497700	-1.47557000
H	-3.94283000	-2.38696700	-0.88627900
O	-2.51354700	-0.24712500	-0.48505900
O	-3.78792600	-0.25286000	1.37076500

Data S2. M06-2X/6-21G optimized geometries of PLA (R, S) segments with TBACl.

C	3.61985900	-0.82833600	-0.47206100
H	4.21120900	-1.74088500	-0.59380200
C	2.16445500	-1.22279700	-0.32790600
C	0.36365700	-2.14213700	-1.47797900
H	-0.14378700	-1.18285600	-1.34254800

C	-0.06623700	-3.10987100	-0.39233800
C	-1.90986400	-3.84734500	0.84977700
H	-1.43960200	-3.67547600	1.82000900
H	-2.97873100	-3.64518300	0.89811700
H	-1.72792400	-4.87984200	0.54872200
O	0.61747700	-3.94014500	0.14147100
O	-1.38263000	-2.94321100	-0.12057900
O	1.76791400	-1.92259900	-1.39395300
O	1.45036700	-0.96181300	0.61117000
C	0.07899300	-2.67696600	-2.86914600
H	0.64652200	-3.59169400	-3.05148700
H	-0.98773100	-2.88656900	-2.97608900
H	0.36526400	-1.90666800	-3.58729600
C	3.83533900	0.10296300	-1.65787800
H	3.24777200	1.01415800	-1.53457000
H	4.89861100	0.33358700	-1.73684600
H	3.49422100	-0.37994000	-2.57373800
N	-1.99035100	1.57223600	0.56033200
C	-3.05850900	1.32860100	1.60441900
H	-2.87457600	2.03643300	2.41639400
H	-4.00517200	1.61289000	1.13414700
C	-3.14833900	-0.07545300	2.19274300
H	-2.24746100	-0.29289900	2.77582800
H	-3.21104500	-0.83463400	1.40993200
C	-4.37490700	-0.18279000	3.10077600
H	-5.27942200	0.01548700	2.51406400
H	-4.32951100	0.59432800	3.87270300
C	-4.47578400	-1.55654300	3.75685800
H	-3.59202800	-1.76444900	4.36570500
H	-5.35291800	-1.62545400	4.40240700
H	-4.55268000	-2.34341700	3.00152100
C	-2.50123400	1.25179100	-0.83312300
H	-1.63715700	1.38539500	-1.49395600
H	-3.25725300	2.01223200	-1.05386600
C	-3.06936500	-0.14280900	-1.04398600
H	-4.05477500	-0.24853300	-0.57122500
H	-2.41574700	-0.90731200	-0.61492300
C	-3.17729500	-0.42795500	-2.54449500
H	-3.78166200	0.34595600	-3.03253000
H	-2.17162000	-0.35769700	-2.97726700
C	-3.78321300	-1.80464900	-2.79943600
H	-4.81843600	-1.85264400	-2.44827100

H	-3.77808800	-2.05357000	-3.86236600
H	-3.21778000	-2.57533600	-2.26547200
C	-1.66867900	3.05701000	0.60666000
H	-1.29060800	3.22865700	1.61566900
H	-2.63534800	3.56559000	0.52158800
C	-0.67799900	3.58294100	-0.43246600
H	-0.14477800	4.40601200	0.05855100
H	0.07739900	2.82891700	-0.67879400
C	-1.27028200	4.12039500	-1.73771600
H	-1.74253900	3.31531200	-2.30514300
H	-2.04656200	4.86360300	-1.51189600
C	-0.17369300	4.73220000	-2.60456100
H	0.55601700	3.96025400	-2.86275800
H	-0.58405800	5.14008800	-3.53038200
H	0.34058100	5.54202600	-2.07771400
C	-0.74441000	0.74089600	0.81187100
H	-1.07030800	-0.29761700	0.80035100
H	-0.11026800	0.87654600	-0.06825900
C	0.00969100	1.05975300	2.10413700
H	0.34688600	0.10029200	2.50446200
H	-0.65064300	1.49449700	2.86722000
C	1.24899800	1.93784700	1.90326400
H	0.96434400	2.98115700	1.72500600
H	1.77313700	1.59030300	1.00647400
C	2.19120000	1.84553700	3.09776900
H	3.04239800	2.52100800	2.98833700
H	1.68269500	2.09823000	4.03371600
H	2.57489100	0.82467000	3.18046400
Cl	0.50072200	1.00598300	-2.46121800
C	5.30429600	-0.22789200	1.05294200
C	5.58397500	0.49971300	2.34003300
H	6.64783300	0.44531800	2.55756100
H	5.26806500	1.54010300	2.24541300
H	5.00624000	0.05113100	3.15001700
O	3.99037300	-0.19010000	0.75310300
O	6.13179800	-0.77632000	0.36956900

Data S3. M06-2X/6-21G optimized geometries of PLA (R, S) segments with TBACl *via* the SMD implicit solvation model.

C	3.73842000	-1.10288400	-0.43413300
H	4.21896100	-2.03818300	-0.12802300
C	2.24028900	-1.31535400	-0.32651400
C	0.33815000	-2.13880100	-1.40142000
H	-0.09121200	-1.13636500	-1.30425800
C	-0.13512200	-3.00544100	-0.24745900
C	-2.02024700	-3.64437500	1.00149600
H	-1.62376400	-3.30693000	1.96084400
H	-3.09224500	-3.47056800	0.94683800
H	-1.79599300	-4.70143000	0.85601300
O	0.56903800	-3.74672000	0.40190000
O	-1.44647900	-2.86639900	-0.06239300
O	1.76393000	-2.02502700	-1.35379200
O	1.56179800	-0.94129200	0.60243500
C	-0.02154500	-2.74840600	-2.74283900
H	0.43725800	-3.73330900	-2.85240200
H	-1.10553200	-2.84771300	-2.82387400
H	0.33433800	-2.09118500	-3.53803600
C	4.19876000	-0.69015400	-1.82106600
H	3.66870500	0.21061100	-2.13656800
H	5.27430400	-0.50920000	-1.80285400
H	3.99220500	-1.49022300	-2.53279500
N	-2.04687200	1.52532200	0.53032000
C	-3.17562800	1.17150000	1.48495100
H	-3.05144100	1.81218000	2.36021300
H	-4.09473700	1.47784700	0.97820500
C	-3.26009300	-0.27794300	1.94705500
H	-2.37698000	-0.53779000	2.54095800
H	-3.29762700	-0.97241700	1.10409700
C	-4.50823900	-0.46759200	2.80965600
H	-5.39619600	-0.19420600	2.22879600
H	-4.46734100	0.21949900	3.66224500
C	-4.63564500	-1.90409400	3.30431100
H	-3.74809800	-2.20271400	3.87027500
H	-5.50527700	-2.02528000	3.95412400
H	-4.74512500	-2.59717300	2.46515900
C	-2.45684100	1.31179800	-0.91241000
H	-1.55614300	1.50908900	-1.50196700
H	-3.20421900	2.08024100	-1.12536700

C	-3.00947400	-0.05962300	-1.26542900
H	-4.01197700	-0.18702700	-0.84203500
H	-2.37944000	-0.85982200	-0.86825600
C	-3.07081100	-0.21728100	-2.78552900
H	-3.57874500	0.64562900	-3.23168600
H	-2.04664400	-0.21630800	-3.17978400
C	-3.78720900	-1.50367500	-3.18080100
H	-4.84076700	-1.46632400	-2.88937600
H	-3.74160200	-1.67515000	-4.25858300
H	-3.33913100	-2.36822300	-2.68025800
C	-1.78034700	3.00845800	0.71944400
H	-1.46969600	3.11413300	1.75852100
H	-2.75571800	3.49166900	0.61352200
C	-0.75215700	3.63880200	-0.22085500
H	-0.22128000	4.39170800	0.37236900
H	0.00467900	2.90878400	-0.53043200
C	-1.32055400	4.33607300	-1.45924600
H	-1.80990500	3.61501900	-2.12038000
H	-2.09202600	5.04947000	-1.14727300
C	-0.22125200	5.05792500	-2.23154600
H	0.54087400	4.34663800	-2.56428300
H	-0.61880900	5.56487700	-3.11380200
H	0.27044300	5.80790000	-1.60473500
C	-0.80358800	0.70715500	0.79900300
H	-1.10623800	-0.33441000	0.70037100
H	-0.11768200	0.91855900	-0.02422900
C	-0.13451000	0.95270400	2.15268000
H	0.19504500	-0.02447400	2.51726200
H	-0.85331700	1.32091400	2.89392500
C	1.08691600	1.87789300	2.08871100
H	0.77367200	2.92548800	2.02479200
H	1.64762800	1.66110200	1.17128500
C	2.00083900	1.67988500	3.29282800
H	2.83983400	2.37982100	3.28137000
H	1.45629100	1.82398000	4.23111500
H	2.40668100	0.66278300	3.29405400
Cl	1.02046400	1.13039400	-2.34518200
C	5.28662200	-0.07517800	1.02865100
C	5.47079300	1.02342300	2.02767400
H	6.53243200	1.16933200	2.21484600
H	5.01035200	1.94321700	1.66566400
H	4.97253500	0.73539200	2.95711500

O	4.03745600	-0.08435700	0.52799200
O	6.13097300	-0.88399300	0.70509000

Data S4. M06-2X/6-21G optimized geometries of PLA (S, S) segments.

C	-0.26320500	0.24207500	-0.49262700
C	1.94489600	1.00112900	-0.55750600
H	1.94712900	0.82873000	-1.63730700
C	2.50836400	-0.24565200	0.11690500
C	4.32220800	-1.70944000	0.17620600
H	3.68668600	-2.58447700	0.03467200
H	5.26848300	-1.83094100	-0.34486700
H	4.48477600	-1.55867700	1.24439200
O	1.96977200	-0.85285700	1.00567300
O	3.70308000	-0.55510000	-0.39818000
O	0.61609200	1.19071900	-0.09502100
O	-0.02520600	-0.58377000	-1.32981100
C	2.74469800	2.23909100	-0.18780900
H	2.72614300	2.38784600	0.89361000
H	3.77774600	2.12321100	-0.51656000
H	2.31039900	3.11549900	-0.66956800
C	-1.53504300	0.37028200	0.31880500
H	-1.84753900	1.41771200	0.34420700
C	-3.80388900	-0.09688700	-0.06902100
C	-4.74517200	-0.99671700	-0.82119300
H	-5.77050400	-0.70981800	-0.60186500
H	-4.54579300	-0.92167300	-1.89122200
H	-4.56874200	-2.03253200	-0.52623300
C	-1.29181700	-0.14475000	1.73434000
H	-2.20004500	-0.01801900	2.32398400
H	-1.01389900	-1.19950500	1.69535700
H	-0.47379600	0.40998000	2.19470300
O	-2.52214600	-0.41004700	-0.34792500
O	-4.12500200	0.78828900	0.68377800

Data S5. M06-2X/6-21G optimized geometries of PLA (S, S) segments with TBACl.

C	1.86354600	-1.68965000	0.07065500
C	0.01643300	-2.49990800	-1.07162700

H	-0.29925800	-1.45777000	-1.18514100
C	-0.65703300	-3.12156900	0.13898800
C	-2.56157800	-3.08522400	1.48978400
H	-1.98226100	-2.95294900	2.40568400
H	-3.50376900	-2.54273900	1.54972600
H	-2.74007700	-4.15062700	1.33792600
O	-0.23721700	-4.04589100	0.78039800
O	-1.85356700	-2.53301800	0.37922200
O	1.42781100	-2.50726100	-0.89653900
O	1.15105400	-1.25036200	0.94229000
C	-0.27469600	-3.28983900	-2.33350700
H	0.10394900	-4.30893200	-2.23387700
H	-1.35096400	-3.32378300	-2.51608000
H	0.21624500	-2.79376300	-3.17196200
N	-1.66617400	1.83879700	0.17077100
C	-2.95751000	1.91562400	0.95409700
H	-2.79100000	2.62437200	1.76915300
H	-3.69104700	2.36553200	0.27743500
C	-3.49360200	0.61409100	1.54092600
H	-2.80277000	0.23432300	2.30140600
H	-3.58086900	-0.16245600	0.77761400
C	-4.86213400	0.85725900	2.18021300
H	-5.55140600	1.25529900	1.42649900
H	-4.77210400	1.62712200	2.95533900
C	-5.44239800	-0.41831600	2.78337100
H	-4.76510200	-0.84095800	3.53084600
H	-6.40145100	-0.22910700	3.26853600
H	-5.60388300	-1.17487000	2.01023300
C	-1.92432900	1.51115000	-1.28855200
H	-0.93089400	1.39010400	-1.73574700
H	-2.41388000	2.39552400	-1.70901000
C	-2.74881600	0.26601300	-1.57891900
H	-3.80931600	0.42815100	-1.34597600
H	-2.40984900	-0.58620400	-0.98158000
C	-2.59168500	-0.10243300	-3.05704900
H	-2.82198500	0.76710700	-3.68427700
H	-1.53717800	-0.34361600	-3.23862500
C	-3.49496100	-1.27030200	-3.43955600
H	-4.55098000	-0.99617900	-3.35872900
H	-3.31059600	-1.59952400	-4.46371000
H	-3.32713700	-2.12328100	-2.77481700
C	-1.03971300	3.22180300	0.23019700

H	-0.86251600	3.40057800	1.29186000
H	-1.82535300	3.91147500	-0.09763900
C	0.24576200	3.43192700	-0.57078200
H	0.82859700	4.16892400	-0.00491800
H	0.84868800	2.51789500	-0.60067500
C	0.08995000	3.95572600	-2.00077700
H	-0.41398900	3.21664900	-2.62759700
H	-0.53029300	4.86195500	-1.99657500
C	1.45875700	4.24102400	-2.61179200
H	2.03592800	3.31368100	-2.65665800
H	1.36388400	4.63517300	-3.62544700
H	2.01270300	4.97301900	-2.01580300
C	-0.71860400	0.79095700	0.72836100
H	-1.25786100	-0.15359500	0.67913200
H	0.10240400	0.71769900	0.01114000
C	-0.20624100	1.04834000	2.14582400
H	-0.13936300	0.06517700	2.62057300
H	-0.92511000	1.62689300	2.74295300
C	1.18586800	1.68584900	2.21473700
H	1.14192200	2.75176900	1.96257100
H	1.81782700	1.19803600	1.46409600
C	1.80766200	1.50338900	3.59579700
H	2.75527800	2.03893700	3.68455000
H	1.14484000	1.87018100	4.38615500
H	2.00048400	0.44254900	3.77872500
Cl	1.22486600	0.46836600	-2.14950100
C	3.34730000	-1.44118900	-0.08247600
H	3.49238000	-1.00894200	-1.07725700
C	4.80935400	0.23740300	0.67120200
C	4.99068400	1.30898600	1.71269900
H	5.97765900	1.75263900	1.60551000
H	4.22310800	2.07372100	1.56833000
H	4.85929300	0.88797400	2.71046000
C	4.15364100	-2.72240100	0.09137400
H	5.20926600	-2.50761300	-0.07264900
H	4.01311100	-3.12104600	1.09851900
H	3.82266300	-3.46669000	-0.63369600
O	3.68860100	-0.47234600	0.91011800
O	5.54814100	0.03464400	-0.25792800

Data S6. M06-2X/6-21G optimized geometries of PLA (R, S) segments with TPACl.

C	3.51802400	0.42524600	0.29992400
H	4.21246200	1.21310700	-0.01284600
C	2.10775900	0.94706700	0.10142800
C	0.42511600	2.24145700	1.02207300
H	-0.16676300	1.32422800	1.08403500
C	0.10224200	2.99519000	-0.25555200
C	-1.59069800	3.53914500	-1.77049700
H	-1.02138500	3.19479500	-2.63586800
H	-2.65315100	3.34173400	-1.90476700
H	-1.41357600	4.60706100	-1.63635300
O	0.85571300	3.70078100	-0.86917300
O	-1.19529500	2.81678600	-0.60352000
O	1.79994300	1.87037400	1.01711800
O	1.36302300	0.62141500	-0.79324900
C	0.19050800	3.09634400	2.25250700
H	0.83239800	3.97920000	2.23292800
H	-0.85509500	3.41162800	2.28854800
H	0.41283800	2.49275200	3.13376400
C	3.80637300	0.00371500	1.73251500
H	3.09557600	-0.76249200	2.04663400
H	4.83258200	-0.36256600	1.78993900
H	3.69488600	0.86140000	2.39615300
N	-2.36897000	-1.37584900	-0.31312600
C	-3.49510900	-1.05000500	-1.26756400
H	-3.48972300	-1.81821300	-2.04512300
H	-4.41868600	-1.17577600	-0.69341500
C	-3.45550600	0.32415200	-1.92937300
H	-2.61102800	0.37421600	-2.62286200
H	-3.30199800	1.11153600	-1.18978900
C	-4.76172100	0.56344100	-2.68500700
H	-5.61491300	0.57975000	-2.00156200
H	-4.94093900	-0.21835300	-3.42812600
C	-2.69400300	-0.90832100	1.09363600
H	-1.78584200	-1.09844600	1.67596400
H	-3.50353400	-1.55943100	1.44071200
C	-3.08173200	0.55174000	1.27627400
H	-4.07097400	0.75808600	0.85103700
H	-2.36677300	1.21408100	0.78075200
C	-3.07378100	0.85097800	2.77730800
H	-3.77550300	0.20517600	3.31330900

H	-2.07190200	0.67728700	3.18187500
C	-2.25103300	-2.88799300	-0.26900600
H	-1.97053500	-3.17844200	-1.28263400
H	-3.26677400	-3.25505200	-0.08617300
C	-1.27059600	-3.47896600	0.74842200
H	-0.93152300	-4.41715100	0.29651600
H	-0.38371800	-2.84569500	0.85814200
C	-1.83513400	-3.78161700	2.13831500
H	-1.88402600	-2.88899200	2.76215000
H	-2.82863200	-4.23891400	2.07928500
C	-1.05384900	-0.74767700	-0.74688800
H	-1.23080100	0.32641800	-0.76766100
H	-0.34786000	-0.92939900	0.06768500
C	-0.51595000	-1.24035300	-2.09470700
H	-0.10823600	-0.36310700	-2.60214700
H	-1.32631300	-1.61454400	-2.73344000
C	0.60060700	-2.27742600	-1.96886900
H	0.26119800	-3.20424200	-1.49875000
H	1.41297500	-1.86283100	-1.36600800
Cl	0.39427800	-0.80430200	2.41981100
C	4.88565200	-0.95712700	-1.03282400
C	4.86845100	-2.15806700	-1.94013700
H	5.87668000	-2.35918800	-2.29361100
H	4.47736300	-3.01850000	-1.39411900
H	4.19882000	-1.96823900	-2.78093800
O	3.64363800	-0.68226100	-0.59352700
O	5.86194100	-0.31769000	-0.73185500
H	-1.17564100	-4.48366000	2.65069400
H	-4.73404900	1.51979000	-3.20939700
H	-3.36094100	1.88674700	2.96668600
H	0.99769300	-2.53245000	-2.95435200

Data S7. M06-2X/6-21G optimized geometries of PLA (R, S) segments with TPNCl.

C	3.66938300	-1.00729800	-1.07300400
H	4.13209400	-1.67997600	-1.79994000
C	2.17171700	-1.22937500	-1.10580800
C	0.30759100	-1.14401600	-2.49541500
H	-0.08271700	-0.35200200	-1.85051800

C	-0.27291300	-2.48167400	-2.07812000
C	-2.23045900	-3.53080800	-1.33122300
H	-1.75866100	-3.98527800	-0.45792300
H	-3.25873800	-3.24721600	-1.11068200
H	-2.19763500	-4.24101100	-2.15857500
O	0.27802100	-3.54790000	-2.11861100
O	-1.55786100	-2.32240000	-1.68269600
O	1.72561300	-1.17707400	-2.36231300
O	1.46540200	-1.42622800	-0.14501900
C	0.00457600	-0.81556300	-3.94525400
H	0.46032900	-1.55370100	-4.60819700
H	-1.07592000	-0.80436800	-4.10585800
H	0.40609700	0.17789200	-4.15187800
C	4.02585400	0.43788700	-1.39402400
H	3.59235900	1.11077700	-0.65166400
H	5.11237300	0.53742800	-1.41026400
H	3.60888700	0.71862000	-2.36173900
N	-1.55649100	1.21599600	1.32339300
C	-2.64173900	0.60790300	2.18587000
H	-2.35980900	0.79211400	3.22541800
H	-3.54462800	1.19335400	1.98560200
C	-2.91410800	-0.88263100	2.01192900
H	-2.05215300	-1.45989900	2.36214400
H	-3.06544600	-1.14284200	0.96199500
C	-4.15269300	-1.28344000	2.81399300
H	-5.02347300	-0.72458800	2.44696000
H	-4.02408900	-0.99777400	3.86618400
C	-4.44078900	-2.78086800	2.72856300
H	-3.57028400	-3.33596300	3.09614300
H	-4.56261600	-3.06222200	1.67579600
C	-2.11322400	1.69555000	-0.00545200
H	-1.24043600	2.03020300	-0.57702900
H	-2.75011300	2.55421900	0.23092600
C	-2.88160500	0.67135800	-0.82558100
H	-3.85571200	0.45771400	-0.37008600
H	-2.33250200	-0.27220800	-0.89669800
C	-3.06035700	1.20038500	-2.25220200
H	-3.61855600	2.14595100	-2.23452700
H	-2.06509700	1.42818000	-2.65462400
C	-3.77671100	0.19871000	-3.16015800
H	-3.75502200	0.57706200	-4.18689900
H	-3.21280900	-0.74228600	-3.15991700

C	-1.03602300	2.43043800	2.07544600
H	-0.63080100	2.02875300	3.00550500
H	-1.92604500	3.01820000	2.32560100
C	0.01052500	3.29194500	1.36962700
H	0.62385200	3.71754100	2.17350700
H	0.68179800	2.67780500	0.76034300
C	-0.50146900	4.44662200	0.50695500
H	-1.01740700	4.06797600	-0.37922600
H	-1.22095200	5.05386400	1.07543400
C	0.65827700	5.31684500	0.02694900
H	1.36482000	4.66836700	-0.50230200
H	1.18303200	5.73883900	0.89337100
C	-0.43664900	0.23181000	1.03478200
H	-0.90450800	-0.61943800	0.54403200
H	0.19724100	0.71360000	0.28546800
C	0.37945400	-0.21659500	2.24936000
H	0.58019500	-1.28128300	2.10780700
H	-0.19380800	-0.13287500	3.18269700
C	1.72697700	0.50027000	2.37253500
H	1.59765400	1.51718100	2.76495000
H	2.15207200	0.60250100	1.36634400
C	2.72221400	-0.25989000	3.24203000
H	2.28774200	-0.45469700	4.23067900
H	2.90540300	-1.23356100	2.77225600
Cl	0.85249200	2.00352100	-1.72711500
C	5.37198300	-1.83121100	0.32393000
C	5.71978800	-2.21126400	1.73760100
H	6.63362600	-2.80093200	1.73093700
H	5.87675800	-1.30337300	2.32357200
H	4.90046200	-2.76826600	2.19308800
O	4.10798600	-1.36560900	0.24102500
O	6.11598500	-1.91697300	-0.62016500
C	-5.68290000	-3.18203900	3.51824100
H	-5.87266900	-4.25443900	3.44580300
H	-5.56965300	-2.93248800	4.57674300
H	-6.56815900	-2.65882700	3.14664900
C	0.19417300	6.43489400	-0.90038200
H	1.02989800	7.05975000	-1.22197500
H	-0.27263900	6.01617800	-1.79593200
H	-0.53879700	7.08227600	-0.40860000
C	-5.22385800	-0.07774100	-2.75458400
H	-5.72198300	-0.72242700	-3.48175900

H	-5.28461000	-0.57651700	-1.78308200
H	-5.79531800	0.85301300	-2.68623100
C	4.03655100	0.49962700	3.38820800
H	3.87633200	1.48041600	3.84536000
H	4.75228900	-0.04312500	4.01069300
H	4.48898000	0.66247700	2.40469200

Data S8. M06-2X/6-21G optimized geometries of PLA (R, S) segments with TBPC.

C	3.75308000	-0.88260600	-0.32816600
H	4.39163400	-1.77122300	-0.35754000
C	2.31240800	-1.33457500	-0.19368500
C	0.55047700	-2.31965600	-1.35120300
H	0.02037800	-1.36485800	-1.29184000
C	0.11449100	-3.22490500	-0.21487800
C	-1.70552500	-3.82066800	1.13066100
H	-1.15854400	-3.66398800	2.06200600
H	-2.75036100	-3.53590200	1.24388300
H	-1.62233000	-4.87057500	0.84603300
O	0.77592600	-4.07684600	0.31336200
O	-1.17832300	-2.98094300	0.10389300
O	1.94907300	-2.06149800	-1.25445200
O	1.58309600	-1.09323400	0.73825500
C	0.31509500	-2.96216400	-2.70510300
H	0.90992300	-3.87256200	-2.80178200
H	-0.74268800	-3.20938700	-2.82227900
H	0.60090900	-2.24355700	-3.47510800
C	3.96901700	-0.03320400	-1.57343000
H	3.32317800	0.84631300	-1.54762300
H	5.01954000	0.25617200	-1.62563900
H	3.70369400	-0.60668000	-2.46165500
C	-3.35435400	1.46282900	1.54644600
H	-3.17524600	2.22472700	2.31359500
H	-4.29801100	1.72493700	1.05352600
C	-3.44270400	0.07556700	2.19357600
H	-2.50479600	-0.14134500	2.71839900
H	-3.54887100	-0.69488100	1.42155900
C	-4.60842300	-0.02547700	3.17591100
H	-5.54393000	0.20127000	2.65178500
H	-4.49412300	0.74145200	3.95064700

C	-4.69592200	-1.40603600	3.81959200
H	-3.77449800	-1.64560100	4.35723600
H	-5.52316400	-1.46354800	4.52914500
H	-4.85056800	-2.17962200	3.06219700
C	-2.60944500	1.01158300	-1.30903700
H	-1.72151300	1.10083100	-1.95573300
H	-3.39016900	1.68768100	-1.67424900
C	-3.07615600	-0.45005100	-1.29237600
H	-4.08512100	-0.52694600	-0.86653700
H	-2.41677800	-1.05863500	-0.66197400
C	-3.05127800	-1.05042500	-2.69793400
H	-3.67183400	-0.44661500	-3.37012600
H	-2.02390600	-0.98140500	-3.07672900
C	-3.53082500	-2.49857600	-2.69503000
H	-4.58026000	-2.56596300	-2.39272800
H	-3.43803600	-2.95375300	-3.68334800
H	-2.94396600	-3.09437500	-1.98832600
C	-1.61565700	3.39416100	0.22067200
H	-1.29792500	3.63576400	1.24223700
H	-2.55183800	3.93837300	0.04408700
C	-0.53759100	3.78872700	-0.80442800
H	-0.05068800	4.69808000	-0.43393700
H	0.23349000	3.01272800	-0.87347300
C	-1.07838400	4.05264700	-2.20854800
H	-1.56163700	3.15008600	-2.59410100
H	-1.84314300	4.83925800	-2.16371400
C	0.04547100	4.44423700	-3.16233500
H	0.75561400	3.61755300	-3.24471500
H	-0.34165000	4.66532700	-4.15902400
H	0.57428800	5.33206800	-2.80180200
C	-0.60291000	0.65287300	0.80600200
H	-0.94110700	-0.38787400	0.85748400
H	0.08954500	0.69676700	-0.04627400
C	0.07697300	1.09218900	2.11290700
H	0.43394500	0.18744600	2.61208100
H	-0.63296500	1.57147600	2.80463600
C	1.27629600	2.00940700	1.87330800
H	0.95258700	2.94609700	1.40391000
H	1.94348800	1.51078900	1.16171200
C	2.02969700	2.30671000	3.16501200
H	2.86947000	2.98306700	2.99111700
H	1.37819700	2.77111500	3.91208500

H	2.42495300	1.38192400	3.59493900
Cl	0.59557600	0.83948000	-2.41145300
C	5.34169300	-0.07479800	1.21003700
C	5.51446200	0.76304700	2.44812400
H	6.56900800	0.80840200	2.70861300
H	5.12286800	1.76548400	2.26596100
H	4.93852000	0.32718300	3.26640600
O	4.04357800	-0.13609100	0.85541400
O	6.22867500	-0.62482300	0.60742400
P	-2.03043100	1.62321500	0.29212900

Data S9. M06-2X/6-21G optimized geometries of PLA (R, S) segments with TBAB.

C	3.54489700	-0.81953000	-0.34763300
H	4.15347000	-1.67413900	-0.65677700
C	2.09569700	-1.25965300	-0.30908500
C	0.35158000	-2.02531300	-1.64644900
H	-0.17785600	-1.11403000	-1.35581900
C	-0.10405600	-3.16848800	-0.76293300
C	-1.98721200	-4.11972300	0.25189900
H	-1.54487400	-4.12573600	1.24989700
H	-3.05706200	-3.92533800	0.30505200
H	-1.79566000	-5.08333300	-0.22233700
O	0.57099000	-4.06725000	-0.34029700
O	-1.43323100	-3.06023000	-0.52716400
O	1.74859100	-1.80908800	-1.47552800
O	1.34779400	-1.14850800	0.63346100
C	0.12310400	-2.28667500	-3.12330900
H	0.71670700	-3.13845500	-3.46064400
H	-0.93478400	-2.48456400	-3.30897100
H	0.41781100	-1.38028800	-3.65694600
C	3.75735400	0.34923900	-1.30099600
H	3.16014600	1.20735200	-0.98815100
H	4.81957400	0.59696800	-1.32238700
H	3.41457300	0.08091300	-2.30104100
N	-2.02550600	1.43800000	0.91956600
C	-3.11892100	1.07537300	1.90112500
H	-2.93224500	1.65027300	2.81147900
H	-4.04854700	1.45231800	1.46318300
C	-3.25656000	-0.39735000	2.27167800
H	-2.37894600	-0.72095600	2.84089200

H	-3.31029900	-1.03012700	1.38293900
C	-4.51332800	-0.60728700	3.11838500
H	-5.39462000	-0.30763400	2.53943900
H	-4.48005300	0.05031600	3.99495000
C	-4.65891600	-2.05823900	3.56717400
H	-3.80199100	-2.36802900	4.17091000
H	-5.56069100	-2.20060600	4.16496600
H	-4.71839900	-2.72790100	2.70485200
C	-2.52138100	1.33056300	-0.51092900
H	-1.65381700	1.56903500	-1.13323800
H	-3.28199400	2.11025200	-0.62058000
C	-3.06571400	-0.01850200	-0.95530000
H	-4.06286100	-0.20855800	-0.53725200
H	-2.41400700	-0.83727100	-0.63528300
C	-3.11997700	-0.05209000	-2.48637800
H	-3.72564700	0.78375200	-2.85710600
H	-2.10096700	0.10895100	-2.86103700
C	-3.69104700	-1.37413100	-2.98865700
H	-4.73750600	-1.49200000	-2.69110200
H	-3.64247800	-1.44215600	-4.07720400
H	-3.13157400	-2.21603700	-2.56847500
C	-1.67233200	2.89410200	1.17803400
H	-1.32346800	2.91595800	2.21162500
H	-2.62406400	3.43511800	1.13593600
C	-0.63557700	3.53400400	0.25281200
H	-0.11181900	4.27539600	0.86842500
H	0.12074100	2.80716800	-0.06207800
C	-1.16550200	4.25187600	-0.99166700
H	-1.64661600	3.54391100	-1.67016300
H	-1.92186000	4.99061400	-0.69523400
C	-0.01956700	4.92083800	-1.74593300
H	0.66629800	4.14957400	-2.10672100
H	-0.38944300	5.48212200	-2.60628400
H	0.52850200	5.61429500	-1.10050200
C	-0.80325000	0.54958900	1.07354100
H	-1.15272900	-0.46910200	0.91930600
H	-0.14883100	0.78153600	0.22947100
C	-0.06559600	0.67076600	2.40789700
H	0.25287800	-0.34130800	2.67034100
H	-0.73285500	1.00066500	3.21617700
C	1.18873800	1.54859600	2.35499300
H	0.92312600	2.61119700	2.32173600

H	1.72538800	1.32192300	1.42715100
C	2.10634100	1.27448800	3.54067900
H	2.96638000	1.94772200	3.54288600
H	1.58229500	1.39987500	4.49360000
H	2.47772300	0.24732800	3.48563800
C	5.20475600	-0.54940400	1.29460000
C	5.46027100	-0.12964400	2.71689000
H	6.52050800	-0.23222400	2.93471400
H	5.14305600	0.90555100	2.85389000
H	4.87036500	-0.74894300	3.39486000
O	3.89430800	-0.45552400	0.99139800
O	6.04701000	-0.92355800	0.51803000
Br	0.53288800	1.24787100	-2.20679400

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