

Supporting Information for

A recyclable process between monomer and polyester with a natural catalyst

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Experimental Procedures

Materials

L-lactide (L-LA), ϵ -caprolactone (ϵ -CL), δ -valerolactone (δ -VL), β -butyrolactone (β -BL), L-ascorbic acid (**VC**), sodium L-ascorbate (**VCNa**), mesitylene, CH_2Cl_2 , EtOAc, MeOH, EtOH, and CDCl_3 were purchased from Energy Chemical. L-LA was recrystallized from EtOAc and dried *in vacuo*. ϵ -CL, δ -VL, and β -BL were dried over CaH_2 before distillation. PLA resins R190 and R290 were purchased from Zhejiang Hisun Biomaterials, and 4032D was purchased from NatureWorks.

Instrument

^1H NMR spectra were recorded with a 300 MHz Bruker NMR spectrometer at 23 °C. ^{13}C NMR and DOSY NMR spectra were recorded with a 500 MHz Bruker NMR spectrometer at 23 °C. Size-exclusion chromatography (SEC) was conducted with a Waters 515 SEC with CH_2Cl_2 as the eluent (flow rate: 1 mL min^{-1} at 30 °C). The molecular weights were calibrated against linear polystyrene (PS) standards. *In situ* ATR-IR was monitored using a Mettler-Toledo ReactIR 15 spectrometer equipped with a MCT detector and a silver halide DiComp probe.

General procedure of ROP

A model reaction using **VCNa** as the catalyst for ROP of L-LA to PLA was described herein. ROP reactions were carried out in a glove box in argon atmosphere. An ampule vial with a stir bar was dried at 130 °C overnight before quickly transferred to a glove box. **VCNa** (0.05 mmol), L-LA (5 mmol), and mesitylene (0.2 mL) were added to the ampule vial and sealed with a rubber stopper. The ampule vial was taken out of the glovebox and put in an oil bath at 170 °C for 24 h reaction. After the reaction, the ampule vial was cooled to room temperature. Then, 10 mL CH_2Cl_2 was added to the sticky product in order to dissolve the product for calculating the conversion by ^1H NMR. The product in CH_2Cl_2 was transferred in a glass vial and CH_2Cl_2 was removed *in vacuo*. The product was washed with EtOH for three times and dried *in vacuo*. M_n and D for the polymer products were determined by SEC.

For the ROP reactions with initiator, the procedure was like ROP reactions mentioned above.

For the ROP reactions in air, the procedure was like ROP reactions in dry condition. However, the ampule vials were not dried on purpose. The monomer and catalyst were exposed in air for 1 h before the reaction.

General procedure of alcoholysis of PLA

PLA resin R190 (4 mmol lactidyl unit), **VCNa** (0.04 mmol), MeOH (100 mmol) were added in a thick wall pressure tube. The reaction mixture was heated at 120 °C for 1 h. A small aliquot was taken out for determination of conversion by ^1H NMR.

General procedure of the reaction from MLA to of lactide

MLA (31.2 g, 0.3 mol) and **VCNa** (2.97 g, 0.015 mol) were added in 100 mL round bottom flask. The reaction mixture was heated at 130 °C for 48 h. A small aliquot was taken out for determination of conversion by ¹H NMR. The unreacted MLA was removed *in vacuo*, and the mixture was heated at 200 °C for 6 h with a distillation setup *in vacuo*. White solid was collected, and ¹H NMR illustrated that the product was lactide.

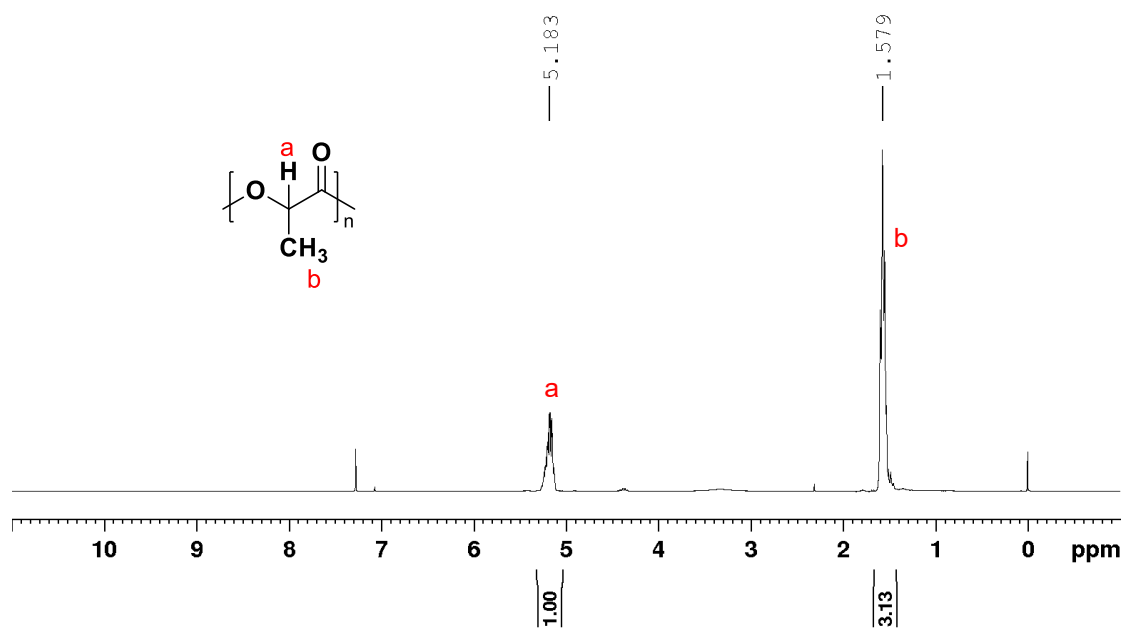


Figure S1. ^1H NMR of PLA (300 MHz, CDCl_3).

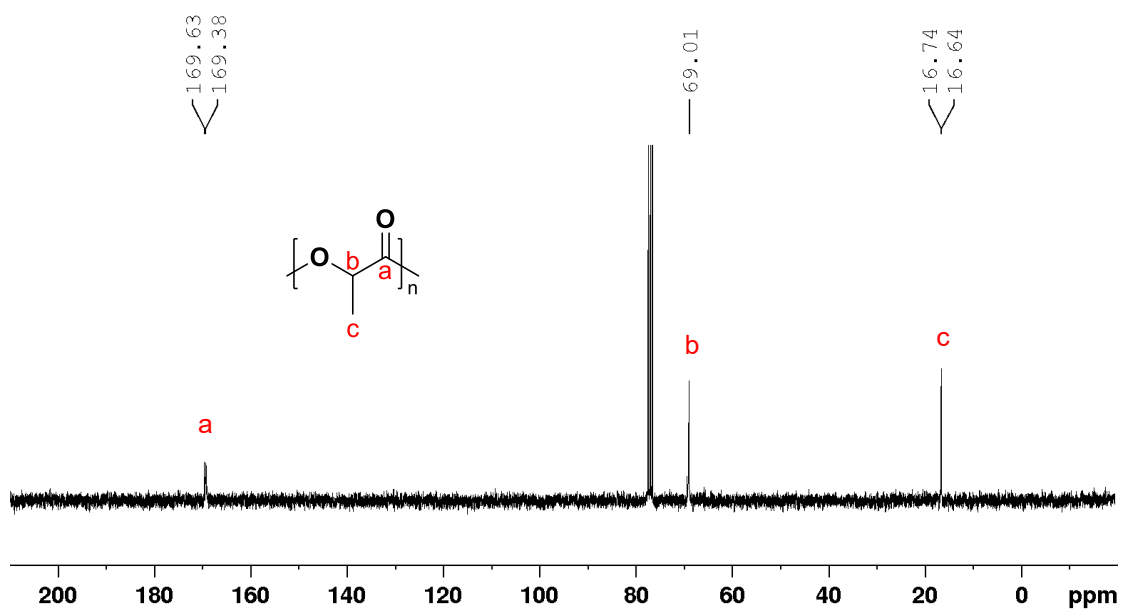


Figure S2. $^{13}\text{C}\{^1\text{H}\}$ NMR of PLA (75 MHz, CDCl_3).

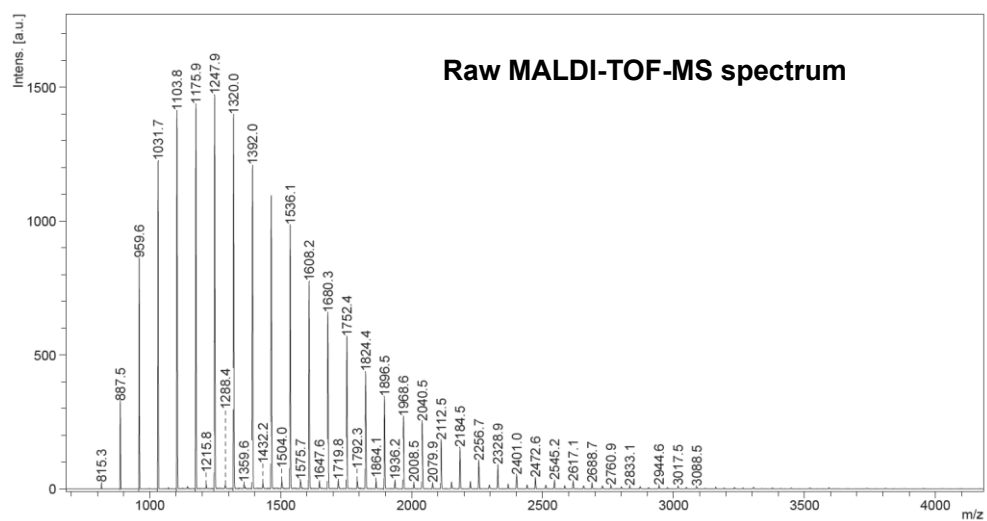
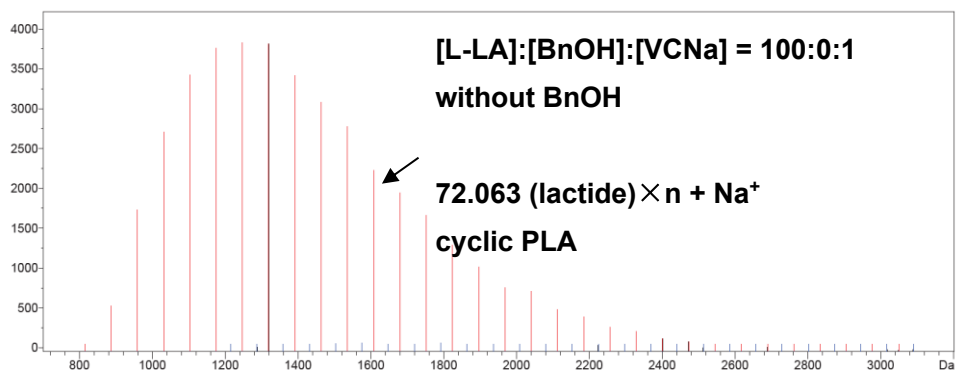


Figure S3. MALDI-TOF-MS for PLA catalyzed by VCNa without initiator.

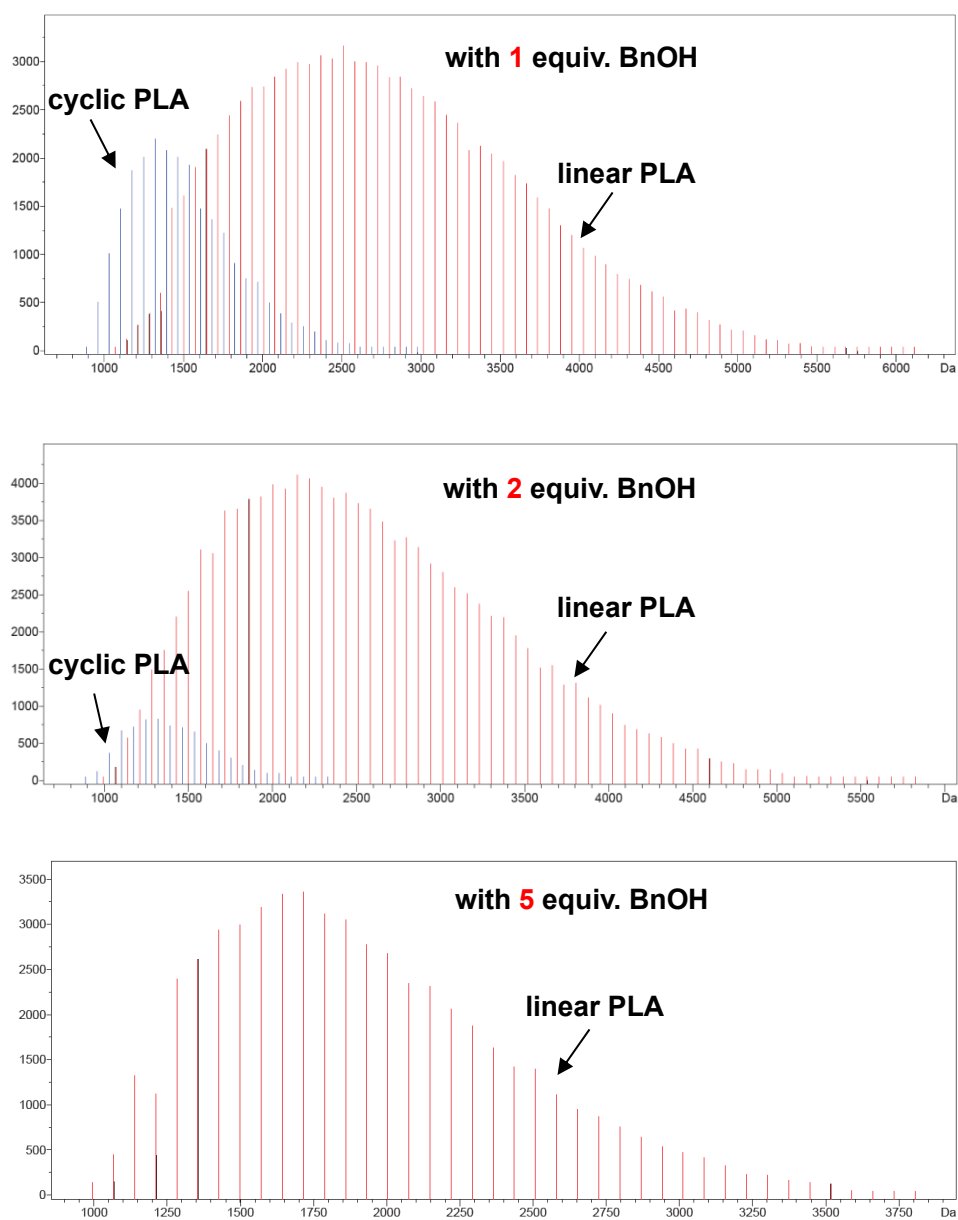
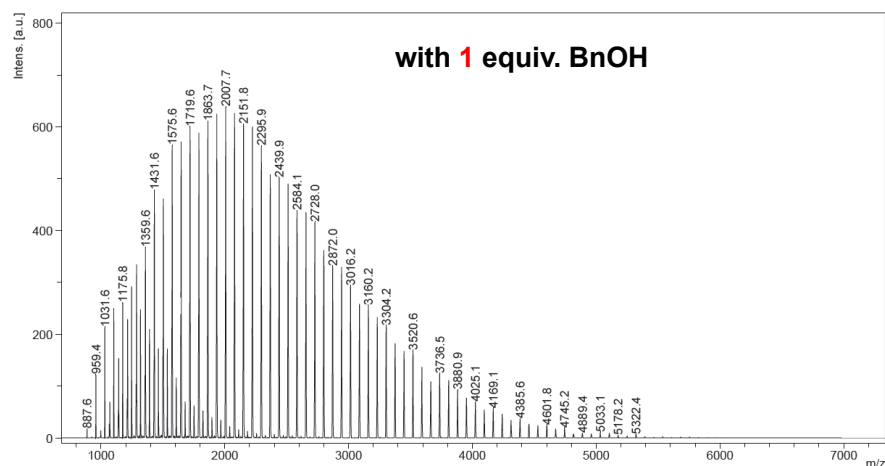
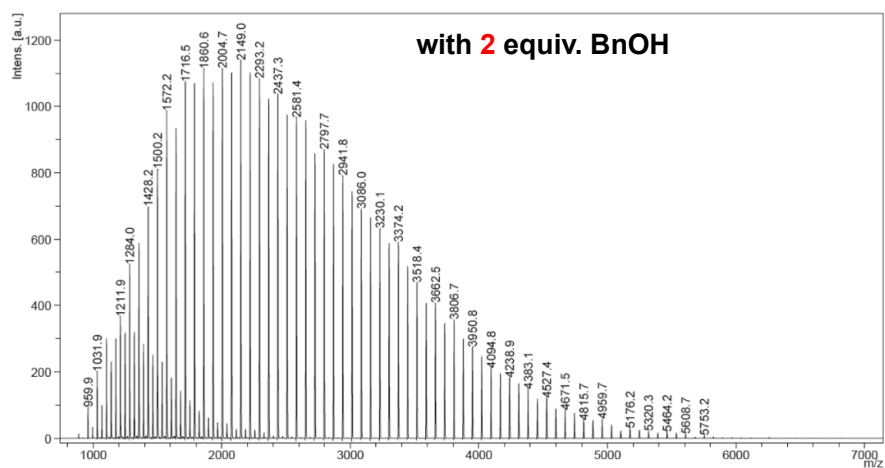


Figure S4. MALDI-TOF-MS for PLA catalyzed by VCNa with various amount of initiator. $[L-LA]:[BnOH]:[VCNa] = 100:n:1$ ($n = 1, 2, \text{ or } 5$)

(A) [L-LA]:[BnOH]:[VCNa] = 100:1:1



(B) [L-LA]:[BnOH]:[VCNa] = 100:2:1



(C) [L-LA]:[BnOH]:[VCNa] = 100:5:1

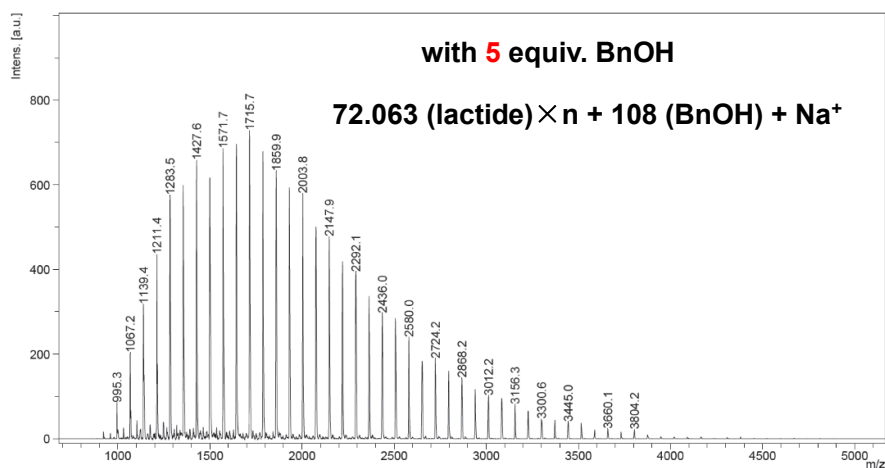


Figure S5. Raw MALDI-TOF-MS spectra for PLA catalyzed by VCNa with various amount of initiator attached to Figure S4.

Table S1. M_n and D of PLA samples.

PLA resin sample	source	M_n (kg mol ⁻¹) ^a	D ^a
Revode190 (R190)	Zhejiang Hisun Biomaterials	98.1	1.66
Revode290 (R290)	Zhejiang Hisun Biomaterials	87.8	1.46
4032D	NatureWorks	111.0	1.56

^a Determined by SEC using CH₂Cl₂ as the solvent.

Table S2. PLA methanolysis without catalyst. ^a

entry	PLA resin sample	<i>T</i> (°C)	time (h)	conv. (%) ^b
1	R190	120	1	0
2	R290	120	1	0
3	4032D	120	1	0

^a Reaction conditions: PLA resin (4 mmol lactidyl repeating unit), methanol (100 mmol). ^b Determined by ¹H NMR (300 MHz, CDCl₃).

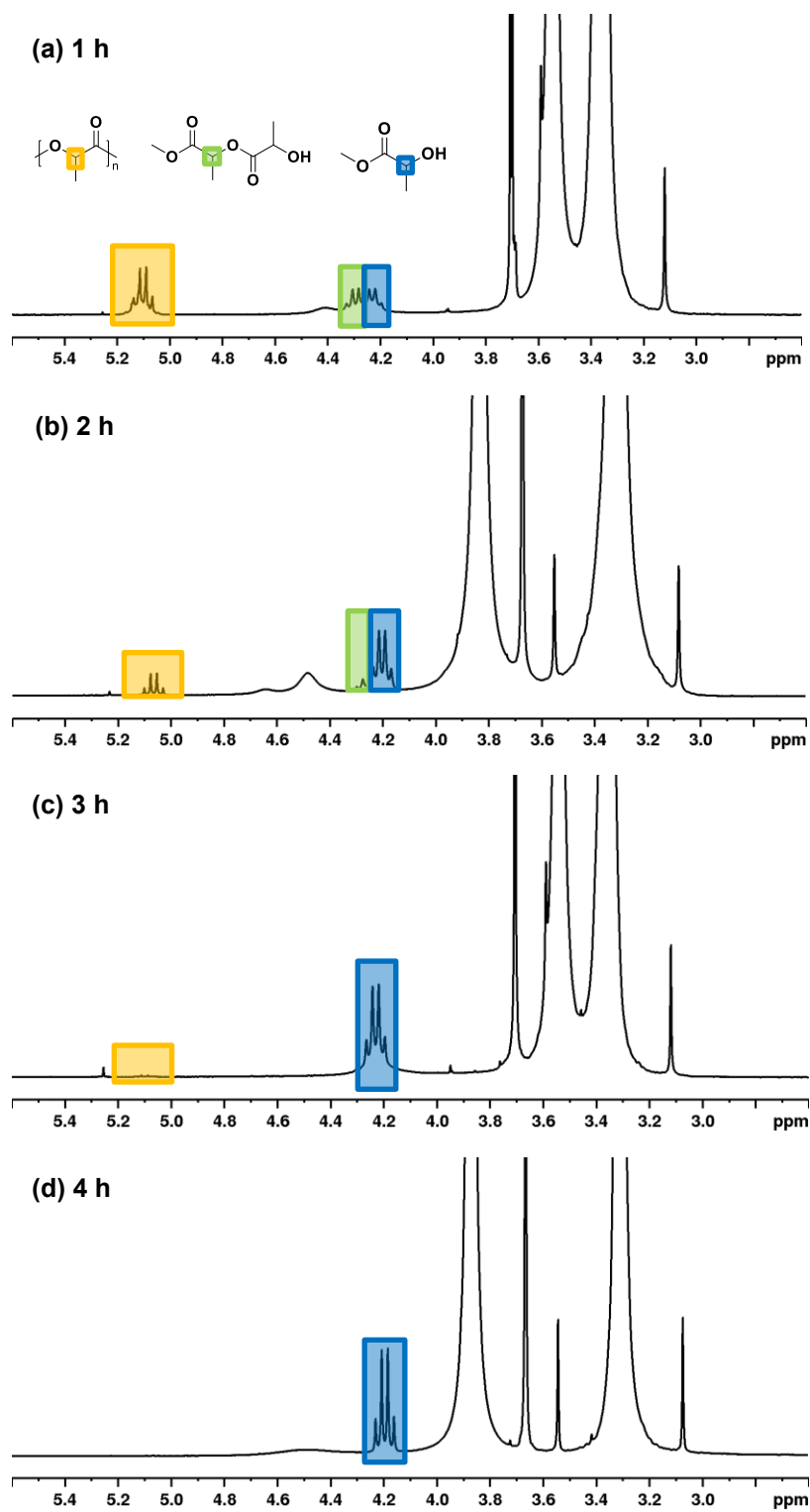


Figure S6. ^1H NMR analysis (300 MHz, CDCl_3) of methanolysis of PLA (4032D) catalyzed by **VCNa** corresponding to Table 2 entry 3.

Table S3. PLA methanolysis catalyzed by 5 mol% **VCNa**^a

entry	PLA resin sample	<i>T</i> (°C)	time (h)	conv. (%) ^b	MLA:dimer ^b
1	R190	120	0.5	99	99:1
2	R190	120	1	100	100:0
3	R190	80	1	N/A ^c	N/A
4	R290	120	1	97	100:0
5	4032D	120	1	95	85:15
6	4032D	120	2	97	100:0

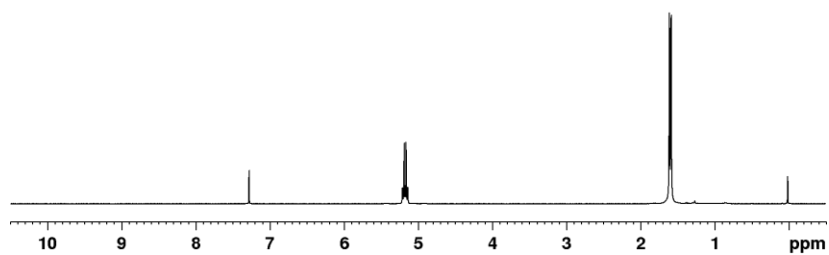
^a Reaction condition: PLA resin (4 mmol lactidyl repeating unit), **VCNa** (0.2 mmol, 5 mol%), MeOH (100 mmol). ^b Determined by ¹H NMR (300 MHz CDCl₃). ^c Most of the PLA samples remained resin type at 80 °C.

Table S4. PLA ethanolysis catalyzed by 5 mol% **VCNa**^a

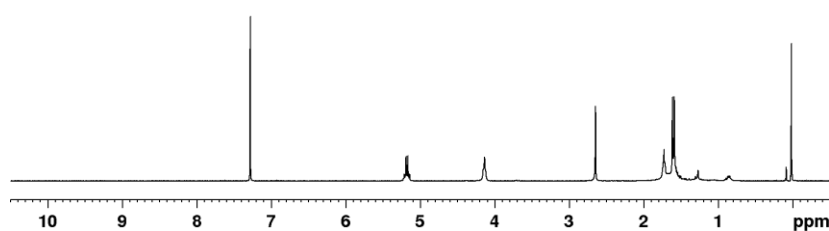
entry	PLA resin sample	time (h)	conv. (%) ^b	ELA:dimer ^b
1	R190	3	75	80:20
		18	97	95:5
2	R290	3	79	79:21
		18	98	96:4
3	4032D	3	74	78:22
		18	97	95:5

^a Reaction condition: PLA resin (4 mmol lactidyl repeating unit), **VCNa** (0.2 mmol, 5 mol%), EtOH (100 mmol), 120 °C. ^b Determined by ¹H NMR (300 MHz CDCl₃).

(A) 3D printing material



(B) ballpoint pen



(C) space bottle

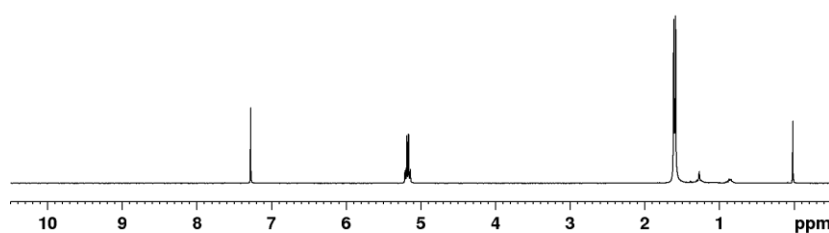


Figure S7. ^1H NMR (300 MHz, CDCl_3) of PLA based commercial products.

Table S5. M_n and D of PLA based commercial products.

sample	M_n (kg mol^{-1}) ^a	D ^a
3D printing material	125.8	1.52
ballpoint pen	202.0	1.25
space bottle	134.0	1.45

^a Determined by SEC using CH_2Cl_2 as the solvent.

Table S6. Reaction from MLA to PLA oligomer without / with catalyst ^a

entry	reactant	product	catalyst	<i>T</i> (°C)	time (h)	conv. (%) ^b
1	MLA	PLA oligomer	N/A	130	24	1.2
2	MLA	PLA oligomer	VCNa	130	48	48

^a Reaction condition: MLA (0.3 mol), **VCNa** (5 mol% for entry 2). ^b Determined by ¹H NMR (300 MHz CDCl₃).

Table S7. Reaction from PLA oligomer to lactide without / with catalyst during a short time in order to test the efficiency of the catalyst ^a

entry	reactant	product	catalyst	<i>T</i> (°C)	yield (g)
1	PLA oligomer ^b	lactide	N/A	200	2.35
2	PLA oligomer ^b	lactide	VCNa	200	5.13

^a Reaction condition: PLA oligomer (21.5 g), **VCNa** (for entry 2), 1.5 h. ^b from the previous step in Table S5.

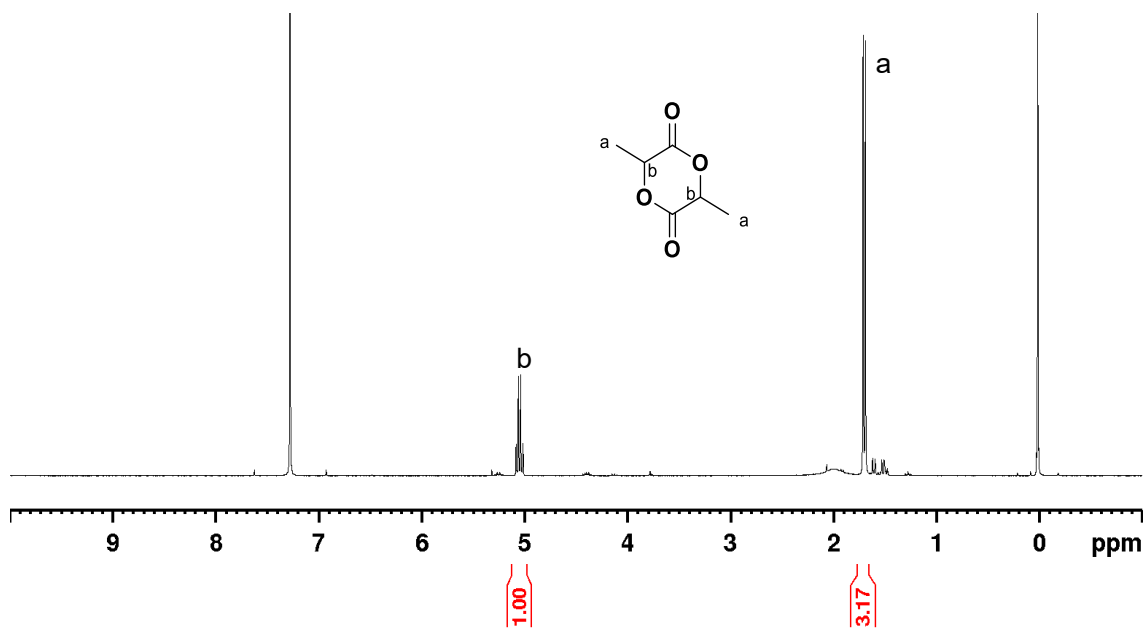


Figure S8. ¹H NMR (300 MHz, CDCl₃) of lactide synthesized from MLA.

Table S8. VC or VCNa catalyzed ring-opening polymerizations of ϵ -CL.^a

entry	catalyst	[M]:[cat.]	<i>T</i> (°C)	time (h)	conv. (%) ^b	<i>M</i> _n (kg mol ⁻¹) ^c	<i>D</i> ^c
1	VC	100:1	170	24	96	15.8	1.63
2	VCNa	100:1	170	24	99	14.1	1.58
3	VC	100:1	120	24	6	N/A	N/A
4	VCNa	100:1	120	24	11	N/A	N/A
5	VC	200:1	170	48	93	29.3	1.79
6	VC	400:1	170	96	43	14.9	1.26
7	VCNa	400:1	170	96	97	36.1	1.71
8	VCNa	1000:1	170	96	46	N/A	N/A
9	N/A	N/A	170	24	0	N/A	N/A

^a Reaction conditions: catalyst (0.05 mmol), the amount of ϵ -CL was determined by [M]:[cat.] ratio. ^b Determined by ¹H NMR (300 MHz, CDCl₃). ^c Determined by SEC using CH₂Cl₂ as the solvent.

Table S9. VC or VCNa catalyzed ring-opening polymerizations of δ -VL.^a

entry	catalyst	[M]:[cat.]	<i>T</i> (°C)	time (h)	conv. (%) ^b	<i>M_n</i> (kg mol ⁻¹) ^c	<i>D</i> ^c
1	VC	100:1	170	24	73	11.8	1.49
2	VCNa	100:1	170	24	74	11.6	1.68
3	VC	100:1	120	24	40	N/A	N/A
4	VCNa	100:1	120	24	24	N/A	N/A
5	VC	200:1	170	48	81	14.9	1.49
6	VCNa	200:1	170	48	86	18.3	1.64
7	VC	400:1	170	48	75	25.1	1.73
8	VCNa	400:1	170	48	79	22.5	1.70
9	N/A	N/A	170	24	0	N/A	N/A

^a Reaction conditions: catalyst (0.05 mmol), the amount of δ -VL was determined by [M]:[cat.] ratio. ^b Determined by ¹H NMR (300 MHz, CDCl₃). ^c Determined by SEC using CH₂Cl₂ as the solvent.

Table S10. VC or VCNa catalyzed ring-opening polymerizations of β -BL.^a

entry	catalyst	[M]:[cat.]	<i>T</i> (°C)	time (h)	conv. (%) ^b	<i>M_n</i> (kg mol ⁻¹) ^c	<i>D</i> ^c
1	VC	100:1	70	24	7	N/A	N/A
2	VCNa	100:1	70	24	16	N/A	N/A
3	VC	100:1	120	24	45	N/A	N/A
4	VCNa	100:1	120	24	98	3.7	1.38
5	VCNa	200:1	120	24	97	9.7	1.35
6	VCNa	400:1	120	48	82	16.9	1.12
7	N/A	N/A	120	24	27	N/A	N/A

^a Reaction conditions: catalyst (0.05 mmol), the amount of β -BL was determined by [M]:[cat.] ratio. Reactions were carried out in thick wall pressure glass tubes. ^b Determined by ¹H NMR (300 MHz, CDCl₃). ^c Determined by SEC using CH₂Cl₂ as the solvent.

Table S11. Ring-opening polymerizations of cyclic esters initiated by BnOH.^a

entry	monomer	catalyst	<i>T</i> (°C)	time (h)	conv. (%) ^b	<i>M_n</i> (kg mol ⁻¹) ^c	<i>D</i> ^c
1	ε-CL	VC	170	24	88	8.8	1.69
2	ε-CL	VCNa	170	24	93	10.6	1.50
3	δ-VL	VC	170	24	87	5.7	1.64
4	δ-VL	VCNa	170	24	89	4.7	1.54
5	β-BL	VCNa	120	24	90	3.1	1.51

^a Reaction conditions: monomer (20 mmol), catalyst (0.2 mmol), BnOH (0.2 mmol), [monomer]:[catalyst]:[BnOH] = 100:1:1. ^b Determined by ¹H NMR (300 MHz, CDCl₃). ^c Determined by SEC using CH₂Cl₂ as the solvent.

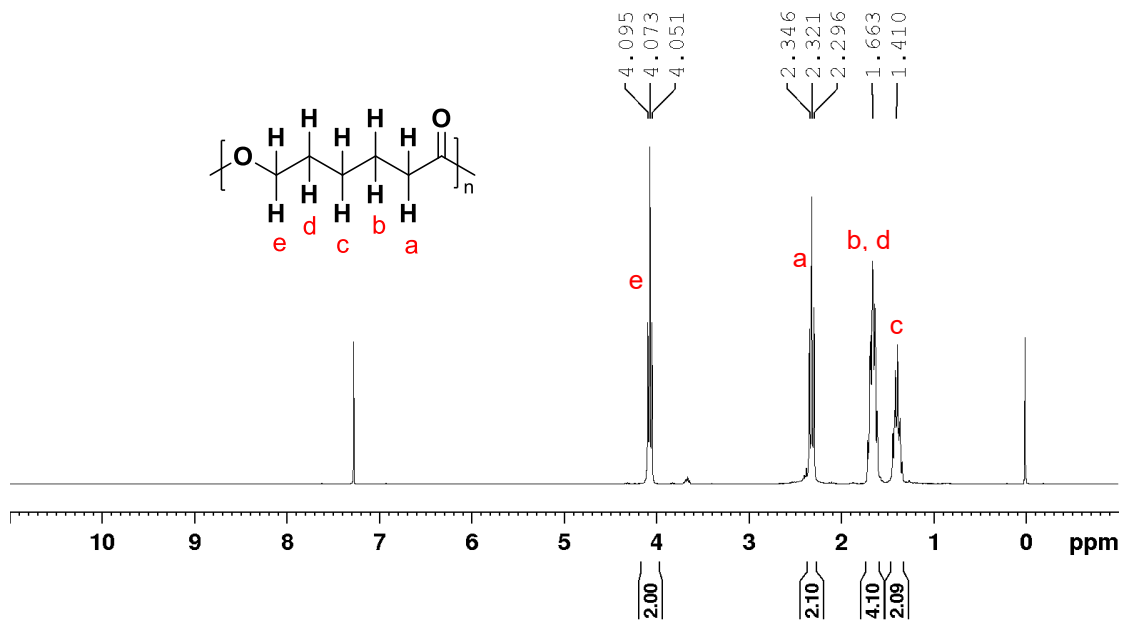


Figure S9. ^1H NMR of PCL (300 MHz, CDCl_3).

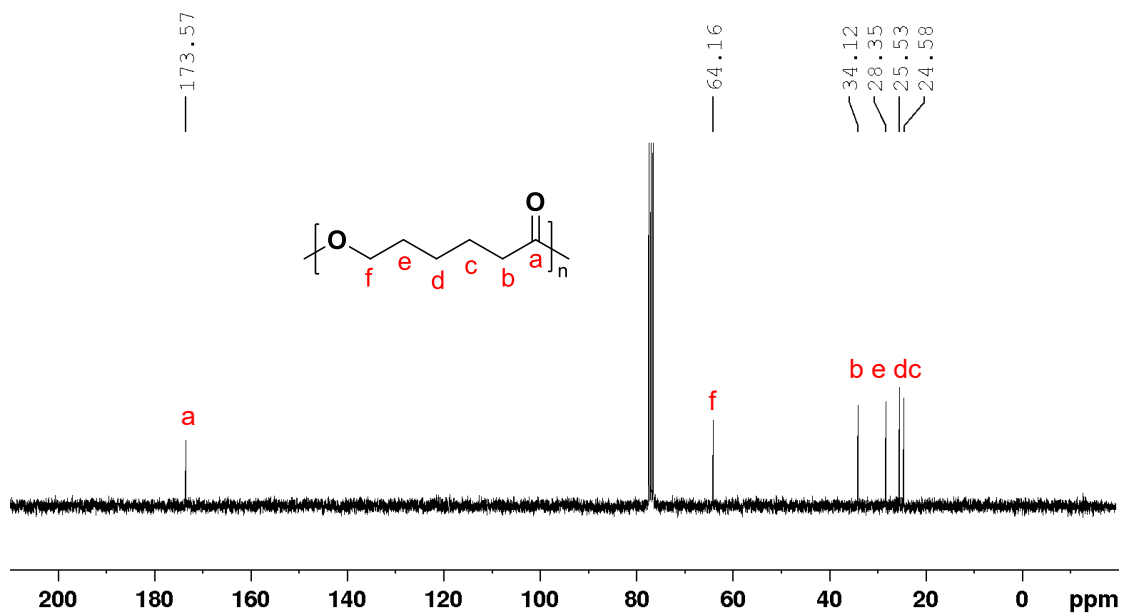


Figure S10. $^{13}\text{C}\{^1\text{H}\}$ NMR of PCL (75 MHz, CDCl_3).

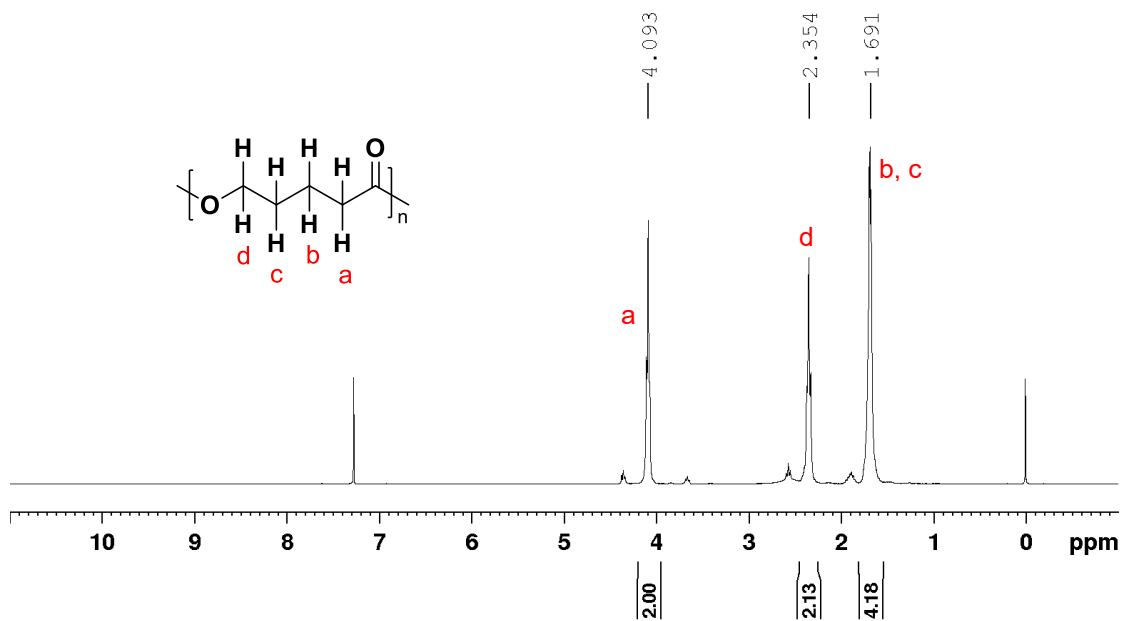


Figure S11. ^1H NMR of PVL (300 MHz, CDCl_3).

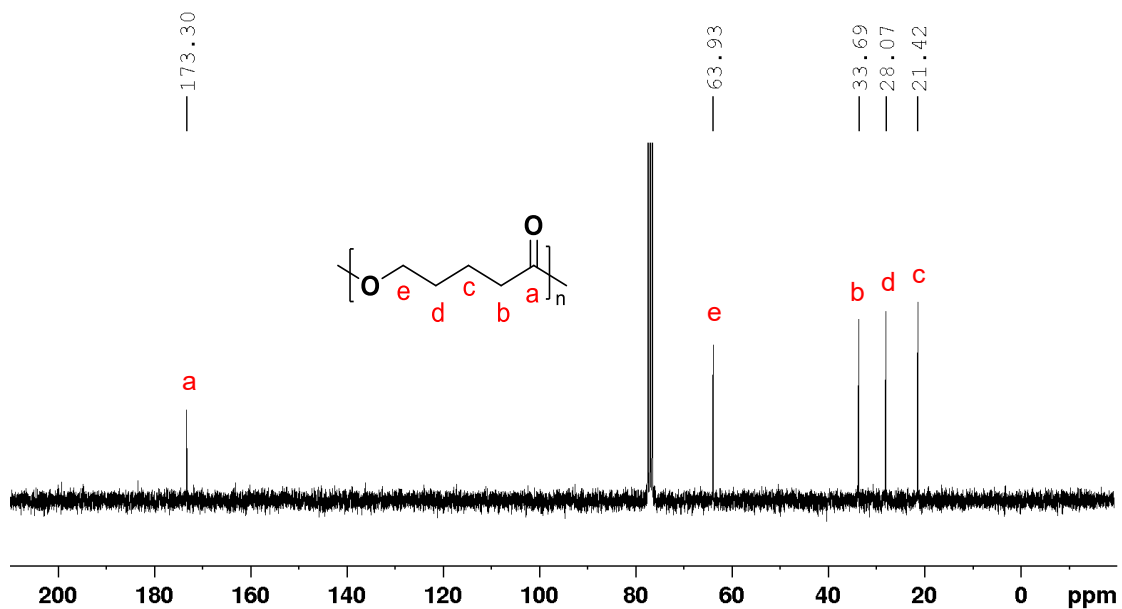


Figure S12. $^{13}\text{C}\{^1\text{H}\}$ NMR of PVL (75 MHz, CDCl_3).

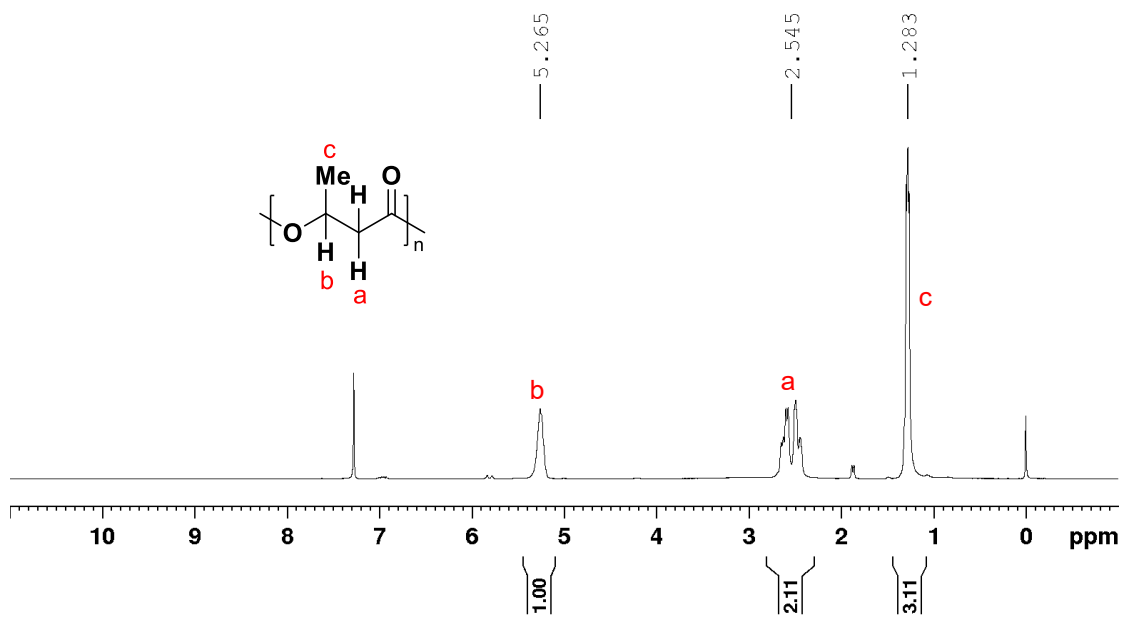


Figure S13. ^1H NMR of PHB (300 MHz, CDCl_3).

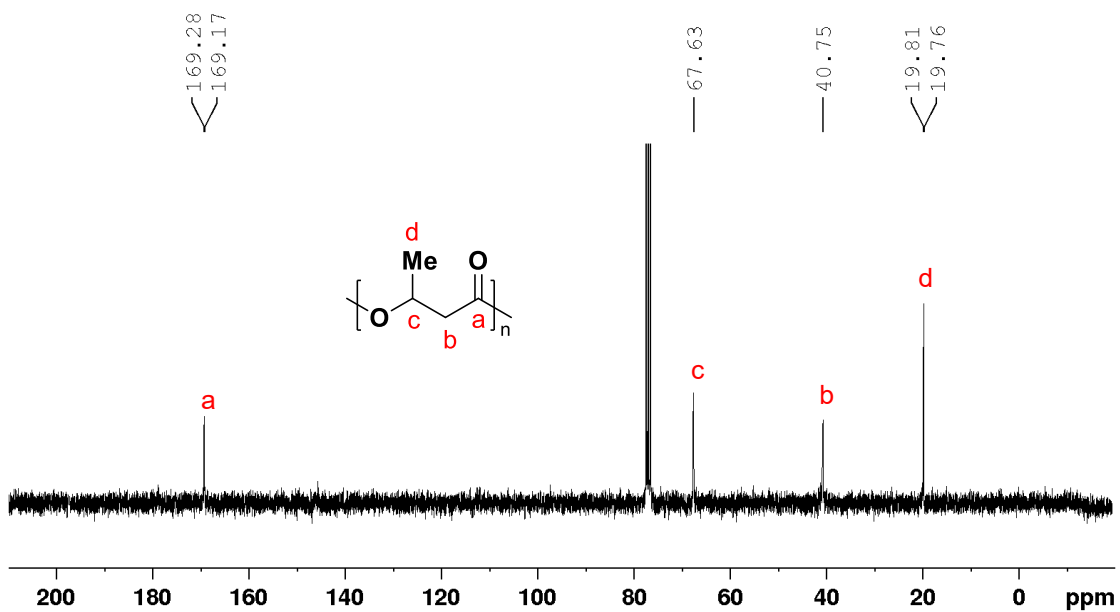


Figure S14. $^{13}\text{C}\{^1\text{H}\}$ NMR of PHB (75 MHz, CDCl_3).