# Dual Catalysis Systems for the Ring-Opening Polymerization of

## Lactones and 2,2-Dimethyltrimethylene Carbonate

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## EXPERIMENTAL SECTION

## Materials

All manipulations were carried out using standard Schlenk line under an inert atmosphere of argon. Solvents needed to be treated in the experiment were purified using standard methods. Toluene was dried with CaCl<sub>2</sub> before distilled over blue sodium-benzophenone. THF was distilled over blue sodium-benzophenone. Dichloromethane was distilled over CaH<sub>2</sub>. Benzyl alcohol (BnOH) was dried with CaH<sub>2</sub> for 48 h and distilled, then stored over 4Å molecular sieves.  $\gamma$ -Butyrolactone ( $\gamma$ -BL),  $\delta$ -valerolactone ( $\delta$ -VL),  $\epsilon$ -caprolactone ( $\epsilon$ -CL),  $\epsilon$ -decalactone ( $\epsilon$ -DL),  $\omega$ -pentadecalactone ( $\omega$ -PDL) (Alfa Aesar, 99%) were dried over fresh CaH<sub>2</sub> and followed by distillation under reduce pressure prior to use. 2,2-Dimethyltrimethylene carbonate was prepared as previous literature reports.<sup>1</sup> 2-Imidazolidinethione (CP) and 3,4,5,6-tetrahydro-2-Pyrimidinethiol (CP) were purchased from FLUORO CHEM Ltd. 1,2-Dibromoethane (AR) and 1,3-dibromo-propane (AR) were purchased from Tianjin Guangfu Fine Chemicals Ltd. MgCl<sub>2</sub> (Alfa Aesar, "ultra dry", 99.9%), MgBr<sub>2</sub> (Acros, anhydrous, 98%), Mgl<sub>2</sub> (Alfa Aesar, "ultra dry", 99.996%, ampouled under argon) were stored in dried vial bottles previously flamed and nitrogen-purged for several times. Methanol (AR) was used without further purification.

## Characterization

Nuclear magnetic resonance (NMR) spectra were recorded on a Bruker AV-600 MHz spectrometer in CDCl<sub>3</sub> with tetramethylsilane (TMS) as internal reference. The molecular weights and polydispersity indices of the polymers were measured by gel permeation chromatography (PL-GPC 220). THF was used as the eluent with a flow rate of 1.0 ml/min at 40 °C, and narrow PDI polystyrene was used as the calibration standard. IR spectra were determined with Varian 660-IR spectrometer using KBr pellets. The differential scanning calorimetry (DSC) analysis was performed on a DSC (NETZSCH DSC 200F3) instrument in the temperature range from -20 to 200 °C, with a heating rate of 10 °C/min under nitrogen using an aluminum capsule (typically 2~3 mg of polymer). Matrix-assisted laser desorption/ionization time-of-flight mass spectrometry (MALDI-ToF MS) of the obtained polymers was performed using a mass spectrometer (autoflexspeed; Bruker) equipped with a Smartbeam/ Smartbeam II modified Nd:YAG laser. Five hundred shots were accumulated for the spectra at a 25 kV acceleration voltage in the positive linear mode. The polymer sample was dissolved in THF at a concentration of 5 mg/mL and the matrix was trans-2-[3-(4-tert-butylphenyl)-2-methyl-2-propylidene]malonitrile (DCTB) dissolved in THF (20 mg/mL). The sample for MALDI-ToF MS was prepared by mixing the matrix solution, polymer solution and sodium trifluoroacetate (0.1 M in THF) with a volume ratio of 25:5:1. Then 0.5  $\mu$ L of which was spotted onto the MALDI-ToF sample plate before being air-dried.

High-Resolution mass spectral analyses were performed at Shanxi Normal University Analysis Center on a Impact II (Bruker) spectrometer using source type of electrospray ionization (ESI) and positive standard methods. All samples were dissolved in methanol to form 50 mg/L solutions and were infused directly into the ESI source at a flow rate of 5  $\mu$ L/min.

Geometry optimizations and vibrational frequency analyses of ITU 1, ITU 2 as well as ITU 3 have been

implemented using the GAUSSIAN09 package<sup>2</sup> based on density functional theory. The exchange-correlation functional B3LYP and an effective basis set 6-311G were used for all of the computations.

## Synthesis of 2,2-Dimethyltrimethylene carbonate (DTC)

A mixture of neopentyl glycol (124.8 g, 1.20 mol), diethyl carbonate (180.0 mL, 1.52 mol) and dry sodium methoxide (1.4 g, 0.026 mol) was placed in a round bottom flask. The mixture was heated gradually and the resultant of reaction-ethanol was distilled at 75-85  $^{\circ}$ C. At the end, excess of diethyl carbonate was removed by distillation at reduced pressure. When the residue was cooled, an opaque, glassy and tough material was obtained. Then the product was dissolved in benzene, washed with water three times. The organic extract was dried over CaCl<sub>2</sub>, filtered and steamed out of benzene under atmospheric pressure. Finally, the crude product was obtained by distillation at reduced pressure. The pure product was recrystallized from benzene three times and dried under vacuum 48 h before use.

#### Synthesis of Catalysts

## Preparation of 2,3,5,6-Tetrahydroimidazo[2,1-b]thiazole (ITU 1)

Prepared according to the modified procedure. 2 A solution of absolute ethanol (50.0 mL) and 1,2dibromoethane (4.5 mL, 52.0 mmol) was added to a stirred mixture of 2-imidazolidinethione (5.1 g, 50.0 mmol) and Na<sub>2</sub>CO<sub>3</sub> (6.0 g, 56.6 mmol) under N<sub>2</sub> taking care at 25 °C. The mixture was refluxed for 24 h, and monitored by TLC. The solvent was removed completely under vacuum, and the residue was basified with 20 % NaOH to pH = 14. The resulting mixture was extracted three times with CH<sub>2</sub>Cl<sub>2</sub>, dried over Na<sub>2</sub>SO<sub>4</sub>. Then the mixture was filtered and evaporated in a vacuum rotary evaporator. Flash chromatography (50 % EtOAc, 5 % Et<sub>3</sub>N, 45 % Hexane) afforded 4.01 g of the title compound (63 % yield). <sup>1</sup>**H NMR** (600 MHz, CDCl<sub>3</sub>) spectrum matched the previously reported values<sup>3</sup> :  $\delta$  = 4.03 ppm (t, 2H), 3.52 ppm (t, 2H), 3.16 ppm (t, 2H), 3.13 ppm (t, 2H), (Fig. S15). <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>) :  $\delta$  = 173.47 ppm, 60.75 ppm, 49.81 ppm, 48.01 ppm, 33.35 ppm, (Fig. S16).

## Preparation of 2,3,6,7-Tetrahydro-5H-thiazolo[3, 2-a]pyrimidine (ITU 2)

3,4,5,6-Tetrahydro-2-pyrimidinethiol (5.7 g, 50.0 mmol), Na<sub>2</sub>CO<sub>3</sub> (6.0 g, 56.6 mmol), absolute ethanol (50.0 ml) and 1,2-dibromoethane (4.5 ml, 50.0 mmol) were added to a round bottom flask under N<sub>2</sub> taking care at 25 °C. The reaction was finished after stirring for 15 h at 70 °C, monitored by TLC. The resulting mixture was concentrated under vacuum. The residue was basified with 20 % NaOH to pH = 14, extracted three times with CH<sub>2</sub>Cl<sub>2</sub>, dried over Na<sub>2</sub>SO<sub>4</sub>, filtered, and concentrated in vacuo to give a pale yellow oil. The crude product was treated with column chromatography (5 % MeOH, 5 % Et<sub>3</sub>N and 90 % CH<sub>2</sub>Cl<sub>2</sub>) to yield the product (69 %) as a clear oil product. <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) spectrum matched the previously reported values<sup>3</sup> :  $\delta$  = 3.51 ppm (t, 2H), 3.38 ppm (t, 2H), 3.23 ppm (t, 2H), 3.11 ppm (t, 2H), 1.85 ppm (m, 2H), (Fig. S17). <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>) :  $\delta$  = 160.41 ppm, 53.67 ppm, 44.74 ppm, 44.36 ppm, 25.95 ppm, 20.39 ppm, (Fig. S18). IR (cm<sup>-1</sup>): 1616, 1350, 1287 (Fig. S23); MS: HRMS (ESI) calculated for C<sub>6</sub>H<sub>11</sub>N<sub>2</sub>S (M+H<sup>+</sup>) *m/z*: 143.0643, found: 143.0642, mSigma: 4.1 (Fig. S21).

#### Preparation of 3,4,7,8-Tetrahydro-2H,6H-pyrimido[2,1-b][1,3]thiazine (ITU 3)

To a stirred mixture of 3,4,5,6-tetrahydro-2-pyrimidinethiol (5.8 g, 50.0 mmol), Na<sub>2</sub>CO<sub>3</sub> (6.0 g, 6.6 mmol) in absolute ethanol (50.0 mL) was added in 1,3-dibromopropane (5.35 mL, 55.0 mmol) under N<sub>2</sub> taking care at 25 °C. Then the mixture was refluxed at 60-70 °C for 24 h and filtered through Celite, and concentrated under vacuum. The crude residue was basified with 20 % NaOH to pH = 14 and immediately extracted with CH<sub>2</sub>Cl<sub>2</sub>. The crude product was treated with column chromatography (5 % MeOH, 5 % Et<sub>3</sub>N and 90 % CH<sub>2</sub>Cl<sub>2</sub>). Evaporation of the solvent gave a clear oil product (86 % yield). <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) spectrum matched the previously reported values<sup>3</sup> :  $\delta$  = 3.30 ppm (t, 2H), 3.13 ppm (t, 2H), 3.09 ppm (t, 2H), 2.85 ppm (t, 2H), 2.07 ppm (m, 2H), 1.84 ppm (m, 2H), (Fig. S17). <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>) :  $\delta$  = 155.30 ppm, 50.37 ppm, 49.65 ppm, 45.77 ppm, 28.27ppm, 24.98ppm, 21.27 ppm (Fig. S18). **IR** (cm<sup>-1</sup>): 1617, 1450, 1313 (Fig. S24); **MS:** HRMS (ESI) calculated for

#### C<sub>7</sub>H<sub>12</sub>N<sub>2</sub>S (M+H<sup>+</sup>) *m/z*: 157.0799, found: 157.0789, mSigma: 7.5 (Fig. S21).

## General Procedure for Polymerization of $\epsilon$ -CL

All the polymerizations were performed in 20 ml ampoules under argon atmosphere free of moisture and oxygen. For a typical polymerization experiment,  $\epsilon$ -CL (1 g, 8.76 mmol) in DCM ([M] = 2.0 mol/L) was combined with MgI<sub>2</sub> (0.0876 mmol), BnOH (0.0876 mmol) and ITUs (0.0876 mmol) under argon atmosphere in an ampoule, which was submerged in a preheated water bath (25 °C). After the desired reaction time, the polymerization was quenched by addition of excess MeOH. The resulting polymer was isolated and washed by MeOH for several times and dried at 40 °C in vacuum to a constant weight.

The chemical shifts of PCL in <sup>1</sup>H NMR were found to be as follows: 7.43 ppm, 7.36 ppm (s, 5H,  $C_6H_5$ ), 5.12 ppm (s, 2H,  $C_6H_5CH_2$ ), 2.31 ppm (t, 2H,  $CH_2CO-O$ ), 1.63 ppm (m, 4H,  $CH_2CH_2CH_2CH_2CO-O$ ), 1.38 ppm (m, 2H,  $CH_2CH_2CH_2CO-O$ ), 4.05 ppm (t, 2H,  $CH_2O-CO$ ), 3.65 ppm (t, 2H,  $CH_2O-O$ ), (Fig. S2).

<sup>13</sup>C NMR spectra (Fig. S3) was found to be as follows: 173.5 ppm (**C**O), 64.1 ppm (**C**H<sub>2</sub>-O), 34.1 ppm (CO**C**H<sub>2</sub>), 28.4 ppm (**C**H<sub>2</sub>CH<sub>2</sub>-O), 25.5 ppm (COCH<sub>2</sub>**C**H<sub>2</sub>CH<sub>2</sub>), 24.6 ppm (COCH<sub>2</sub>CH<sub>2</sub>-**C**H<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>O).

## General Procedure for Polymerization of ε-DL

Polymerization is similar to the procedure described for  $\varepsilon$ -CL homopolymerization.  $\varepsilon$ -DL (1 g, 5.87 mmol), Mgl<sub>2</sub> (0.0587 mmol) and BnOH (0.0587 mmol) was dissolved in TOL ([M] = 2.0 mol/L) in a ampoule, and then ITU 2 (0.0587 mmol) was added under argon atmosphere. The ampoule was placed in a preheated water bath (50 °C). After the desired reaction time, the polymerization was quenched by addition of excess MeOH. The resulting polymer was isolated and washed by MeOH. Then the polymer was dried at 40 °C under vacuum to a constant weight.

The chemical shifts of PDL in <sup>1</sup>H NMR were found to be as follows: 7.36 ppm, 7.35 ppm (s, 5H, C<sub>6</sub>H<sub>5</sub>), 5.11 ppm (s, 2H, C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub>), 2.28 ppm (t, 2H, CH<sub>2</sub>CO-O), 1.63 ppm (m, 2H, CH<sub>2</sub>CH<sub>2</sub>CO-O), 1.31 ppm (m, 6H, CH<sub>2</sub> CH<sub>2</sub>CH(CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>O-CO), 1.53 ppm (m, 4H, CH<sub>2</sub>CH(C<sub>3</sub>H<sub>7</sub>CH<sub>2</sub>)O-CO), 4.86 ppm (m, 1H, CH<sub>2</sub>CH(C<sub>4</sub>H<sub>9</sub>)-O-CO), 0.89 ppm (t, 3H, CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH(CH<sub>2</sub>)- O-CO), 3.59 ppm (m, 1H, CH<sub>2</sub>CH(C<sub>4</sub>H<sub>9</sub>)OH) (Fig. S5).

<sup>13</sup>C NMR spectra (Fig. S6) was found to be as follows: 173.31 ppm (**C**0), 73.88 ppm (CH<sub>2</sub>**C**H(C<sub>4</sub>H<sub>9</sub>)-O), 34.50 ppm (**C**H<sub>2</sub>CH(C<sub>4</sub>H<sub>9</sub>)-O), 33.81 ppm (CO**C**H<sub>2</sub>), 27.46 ppm ((C<sub>2</sub>H<sub>5</sub>)**C**H<sub>2</sub>CH<sub>2</sub>CH(CH<sub>2</sub>)-O), 24.96 ppm (COCH<sub>2</sub>**C**H<sub>2</sub>**C**H<sub>2</sub>**C**H<sub>2</sub>), 22.58 ppm (CH<sub>3</sub>**C**H<sub>2</sub>), 14.01 ppm (**C**H<sub>3</sub>**C**H<sub>2</sub>).

## General Procedure for Polymerization of $\delta\text{-VL}$

All the polymerizations were similar to the procedure described for  $\varepsilon$ -CL homopolymerization. The differences lie in the reaction time and temperature.  $\delta$ -VL (0.5 g, 4.99 mmol) and MgI<sub>2</sub> (0.0499 mmol) mixed in TOL ([M] = 2.0 mol/L), then BnOH (0.0499 mmol) and ITU 2 (0.0499 mmol) was added in sequence. The ampoule was submerged in a preheated oil bath (70 °C). After the desired reaction time, the polymerization was quenched by addition of excess MeOH. The resulting polymer was isolated and washed by MeOH. Then the polymer was dried at 40 °C under vacuum to a constant weight.

The chemical shifts of PVL in <sup>1</sup>H NMR were found to be as follows: 7.43 ppm, 7.36 ppm (s, 5H,  $C_6H_5$ ), 5.12 ppm (s, 2H,  $C_6H_5CH_2$ ), 2.35 ppm (t, 2H,  $CH_2CO-O$ ), 1.70 ppm (m, 4H,  $CH_2CH_2CH_2CO-O$ ), 4.09 ppm (t, 2H,  $CH_2O-CO$ ), 3.66 ppm (t, 2H,  $CH_2OH$ ) (Fig. S7).

<sup>13</sup>C NMR spectra (Fig. S8) was found to be as follows: 173.28 ppm (CO), 63.93 ppm (CH<sub>2</sub>-O), 33.71 ppm (COCH<sub>2</sub>),
28.10 ppm (COCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>-O), 21.44 ppm (COCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>O).

## General Procedure for Polymerization of γ-BL

All the polymerizations were similar to the procedure described for  $\varepsilon$ -CL homopolymerization.  $\gamma$ -BL (0.5 g, 5.81 mmol) in TOL ([M] = 2.0 mol/L) was combined with MgI<sub>2</sub> (0.0581 mmol), BnOH (0.0581 mmol) and ITU 2 (0.0581 mmol) under argon atmosphere in a ampoule, which was submerged in oil bath with different temperature (25-110 °C). After the desired reaction time, the polymerization was quenched by addition of excess MeOH and no

#### polymer was obtained.

## General Procedure for Polymerization of ω-PDL

All the polymerizations were performed in 20 ml ampoules under argon atmosphere free of moisture and oxygen. In the typical producer for  $\omega$ -PDL polymerization,  $\omega$ -PDL (1.0 g, 4.2 mmol) in TOL ([C] = 1.0 mol/L) was combined with MgI<sub>2</sub> (0.021 mmol), BnOH (0.042 mmol), ITU 2 (0.021 mmol) under argon atmosphere in an ampoule, which was submerged in a preheated water bath (70 °C). After the indicated reaction time, the reaction was quenched by addition of excess MeOH. The produced polymer was isolated and washed by MeOH. Then the polymer was dried to constant weight in vacuo at 40 °C.

The chemical shifts of PPDL in <sup>1</sup>H NMR were found to be as follows: 7.44 ppm, 7.36 ppm (s, 5H,  $C_6H_5$ ), 5.11 ppm (s, 2H,  $C_6H_5CH_2$ ), 2.30 ppm (t, 2H,  $CH_2CO-O$ ), 1.62 ppm (m, 2H,  $CH_2CH_2CH_2CO-O$ ), 4.06 ppm (t, 2H,  $CH_2O-CO$ ), 3.64 ppm (t, 2H,  $CH_2OH$ ) (Fig. S10).

<sup>13</sup>C NMR spectra (Fig. S11) was found to be as follows: 174.02 ppm (**C**O), 64.41 ppm (**C**H<sub>2</sub>-O), 34.42 ppm (CO**C**H<sub>2</sub>), 29.66 ppm, 29.63 ppm, 29.61 ppm, 29.56 ppm, 29.50 ppm, 29.31 ppm, 29.29 ppm, 29.20 ppm, 28.68 ppm, 25.96 ppm, 25.04 ppm (the peaks from 29.66 ppm to 25.04 ppm belong to the other carbons of PPDL).

#### **General Procedure for Polymerization of DTC**

All the polymerizations were performed in 20 ml ampoules under argon atmosphere free of moisture and oxygen. In the typical producer for DTC polymerization, DTC (1.0 g, 7.68 mmol) in TOL ([C] = 1.0 mol/L) was combined with MgI<sub>2</sub> (0.0768 mmol), BnOH (0.0256 mmol) and ITU (0.0768 mmol) under argon atmosphere in an ampoule, which was submerged in a preheated water bath (70  $^{\circ}$ C). After the indicated reaction time, the reaction was quenched by addition of excess MeOH. The produced polymer was isolated and washed by MeOH. Then the polymer was dried to constant weight in vacuo at 40  $^{\circ}$ C.

The chemical shifts of PDTC in <sup>1</sup>H NMR were found to be as follows: 7.43 ppm, 7.38 ppm (s, 5H,  $C_6H_5$ ), 5.16 ppm (s, 2H,  $C_6H_5CH_2$ ), 3.97 ppm (s, 4H, (CH<sub>3</sub>)<sub>2</sub>C(CH<sub>2</sub>O-CO)<sub>2</sub>), 1.00 ppm (s, 6H, (CH<sub>3</sub>)<sub>2</sub>), 3.36 ppm (s, 2H, CH<sub>2</sub>OH) (Fig. S12). <sup>13</sup>C NMR spectra (Fig. S13) was found to be as follows: 154.29 ppm (CO), 71.42 ppm (CH<sub>2</sub>O-CO), 34.13 ppm ((CH<sub>3</sub>)<sub>2</sub>C(CH<sub>2</sub>O-CO)<sub>2</sub>), 20.36 ppm (CH<sub>3</sub>)<sub>2</sub>.

Entry	MgX <sub>2</sub>	ITUs /	CL / ITU 2	Time (h)	Conv <sup>b</sup> (%)	<i>M</i> n, th <sup>c</sup>	$oldsymbol{M}_{n,\mathrm{GPC}}^{\mathrm{d}}$	PDI <sup>d</sup>
		MgX <sub>2</sub>				(g/mol)	(g/mol)	
1	$MgI_2$	1:1	80	2	96	11100	22900	1.22
2	$MgI_2$	1:1	80	4	95	10900	26100	1.31
3	$MgBr_2$	1:1	80	4	71	8100	16000	1.21
4	$MgI_2$	1:1	120	4	90	10300	22500	1.15
5	$MgI_2$	1:0.5	100	8	91	10500	27400	1.39
6	$MgI_2$	1:0.75	100	8	92	10600	28300	1.36
7	$MgI_2$	1:1	100	6	99	11400	25500	1.14
8	$MgI_2$	1:1	100	8	98	11300	24700	1.17
9	$MgI_2$	1:1	100	14	93	10700	21000	1.54
10	$MgI_2$	1:1	100	24	91	10500	19300	2.31
11	$MgI_2$	1:2	100	6	64	7450	13100	1.11
12	$MgI_2$	1:3	100	6	45	5190	9200	1.12
13	Mgl <sub>2</sub>	1:5	100	6	26	3100	-	-

## Table S1 Polymerization of $\epsilon$ -CL Using ITU 2 with MgX2 Cocatalysts <sup>a</sup>

<sup>a</sup> Conditions: [BnOH]/[CL] = 1:100,  $[M]_0 = 2.0$  M in DCM, room temperature. <sup>b</sup> Monomer conversion determined by <sup>1</sup>H NMR spectroscopy; <sup>c</sup> Theoretical M<sub>n</sub> calculated by MW<sub>mon</sub> ×  $[M]_0/[I]_0 \times \text{conv.} + MW_{end group}$  (MW<sub>mon</sub> = 114.14 for CL, MW<sub>end group</sub> = 108 when the initiator is BnOH); <sup>d</sup> M<sub>n</sub> and PDI obtained by gel permeation chromatography (GPC) in THF using polystyrene standard.

Entry	ITUs	Time (h)	Solvent	Conv <sup>b</sup> (%)	<b>М</b> <sub>п, th</sub> <sup>с</sup>	$M_{n, GPC}^{d}$	PDI <sup>d</sup>
					(g/mol)	(g/mol)	
1	ITU 1	72	DCM	0	-	-	-
2	ITU 2	6	DCM	99	11400	25500	1.14
3	ITU 3	72	DCM	38	4500	12200	1.29
4	ITU 2	0.25	DCM	7	900	-	-
5	ITU 2	1	DCM	39	4500	9200	1.11
6	ITU 2	4	DCM	96	11000	24800	1.17
7	ITU 2	4	THF	100	11500	28700	1.63
8	ITU 2	4	TOL	93	10700	22800	1.18

Table S2 Polymerization of  $\epsilon$ -CL Using ITUs with MgI<sub>2</sub> Cocatalysts <sup>a</sup>

<sup>a</sup> Conditions:  $[ITUS]/[MgI_2]/[BnOH]/[CL] = 1:1:1:100, [M]_0 = 2.0 M, room temperature. <sup>b</sup> Monomer conversion determined by <sup>1</sup>H NMR spectroscopy; <sup>c</sup> Theoretical M<sub>n</sub> calculated by MW<sub>mon</sub> × [M]_0/[I]_0 × conv. + MW<sub>end group</sub> (MW<sub>mon</sub> = 114.14 for CL, MW<sub>end group</sub> = 108 when the initiator is BnOH); <sup>d</sup> M<sub>n</sub> and PDI obtained by gel permeation chromatography (GPC) in THF using polystyrene standard.$ 



**Fig. S1:** MALDI-ToF MS analysis of PCL synthesized by ITU 2/Mgl<sub>2</sub> cocatalyst with the [ $\epsilon$ -CL]<sub>0</sub>/[BnOH]<sub>0</sub> of 100:1 (Table 1, entry **5**). The spectrum was recorded with sodium trifluoroacetate as an ionization salt. Mass = [Initiator] + [Monomer] × n + [Na<sup>+</sup>]. a) full spectrum; b) detail including experimentally found masses; c) tabular comparison of a series of experimental values and their calculated counterparts ( $\delta$  : the relative error); d) the plot of the molar mass (m/z) vs the number of monomer repeat units (n).





Fig. S4: The DSC curve of PCL (Table 1, entry 7).





Fig. S7: <sup>1</sup>H NMR spectrum of PVL (Table 2, entry 6).



Fig. S8: <sup>13</sup>C NMR spectrum of PVL (Table 2, entry 6).



**Fig. S9:** MALDI-ToF MS analysis of PVL synthesized by ITU 2/Mgl<sub>2</sub> cocatalyst with the  $[\delta$ -VL]<sub>0</sub>/[BnOH]<sub>0</sub> of 100:1 (Table 2, entry 6). The spectrum was recorded with sodium trifluoroacetate as an ionization salt. Mass = [Initiator] + [Monomer] × n + [Na<sup>+</sup>]. a) full spectrum; b) detail including experimentally found masses; c) tabular comparison of a series of experimental values and their calculated counterparts ( $\delta$  : the relative error); d) the plot of the molar mass (m/z) vs the number of monomer repeat units (n).



Fig. S10: <sup>1</sup>H NMR spectrum of PPDL (Table 2, entry 13).







Fig. S12: <sup>1</sup>H NMR spectrum of PDTC (Table 2, entry 16).



Fig. S13: <sup>13</sup>C NMR spectrum of PDTC (Table 2, entry 16).



Fig. S14: IR spectra of PCL (Table 1, entry 7), PVL (Table 2, entry 6) and PDL (Table 2, entry 1).



Fig. S15: <sup>1</sup>H NMR spectrum of ITU 1.



Fig. S18: <sup>13</sup>C NMR spectrum of ITU 2.



Fig. S20: <sup>13</sup>C NMR spectrum of ITU 3.



Fig. S21: HRMS (ESI) spectrum of ITU 2.



Fig. S22: HRMS (ESI) spectrum of ITU 3.



Fig. S24: IR spectrum of ITU 3.

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