

**Diphenyl Phosphate/Ethyl Diphenylphosphinite as an Efficient  
Organocatalytic System for Ring-opening Polymerization of  
 $\epsilon$ -Caprolactone and  $\delta$ -Valerolactone**

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## Experimental Section

**Materials.** Dichloromethane ( $\text{CH}_2\text{Cl}_2$ ,  $\geq 99.5\%$ ), toluene ( $>99.5\%$ ), methanol ( $\text{MeOH}$ ,  $>99.5\%$ ) and ethyl acetate ( $\geq 99.5\%$ ) were purchased from Titan Chemical Co., Ltd (Shanghai, China). Triethylamine ( $>99.0\%$ ) were purchased from Sinopharm Chemical Reagent Co., Ltd (Shanghai, China). Ethyl diphenylphosphinite (EDPP,  $>93.0\%$ ) and benzoic acid ( $\text{PhCO}_2\text{H}$ ,  $>99.0\%$ ) were purchased from TCI chemicals.  $\delta$ -Valerolactone ( $\delta$ -VL,  $\geq 98.5\%$ ) and diphenyl phosphate (DPP,  $\geq 99.7\%$ ) were purchased from J&K Scientific Co., Ltd. (Beijing, China). L-Lactide (L-LA,  $99.0\%$ ) and trimethylene carbonate (TMC,  $98\%$ ) were purchased from Rhawn reagent Co., Ltd. (Shanghai, China).  $\epsilon$ -Caprolactone ( $\epsilon$ -CL,  $99\%$ ), bis(trifluoromethane) sulfonamide ( $\text{HNTf}_2$ ,  $>97.0\%$ ), deuterated chloroform ( $\text{CDCl}_3$ ,  $99.8\%$ ), and calcium hydride ( $\text{CaH}_2$ ,  $95\%$ ) were purchased from Aladdin Biochemical Technology Co., Ltd. (Shanghai, China).  $\text{CH}_2\text{Cl}_2$ ,  $\epsilon$ -CL,  $\delta$ -VL, and DMF were distilled from  $\text{CaH}_2$  and degassed by three freeze-pump-thaw cycles under an argon atmosphere prior to use. Toluene was distilled over Na/benzophenone and degassed by three freeze-pump-thaw cycles under an argon atmosphere prior to use. L-LA was recrystallization in ethyl acetate and dried under vacuum before use. TMC was recrystallization in toluene at  $-20\text{ }^\circ\text{C}$  before use. Other chemical were used as received.

**Measurements.** The polymerizations were conducted in a MIKROUNA stainless steel glove-box full of argon gas equipped with a gas purification system under a dry argon atmosphere ( $\text{H}_2\text{O}$ ,  $\text{O}_2 < 0.01\text{ ppm}$ ). The moisture and oxygen contents in the glove box were monitored by an MB- MO-SE 1 and MB-OX-SE 1, respectively. The proton, carbon, and phosphorus nuclear magnetic resonance ( $^1\text{H}$ ,  $^{13}\text{C}$ , and  $^{31}\text{P}$  NMR) spectra were recorded by a

Bruker AVANCE III 400 Hz NMR spectrometer with superconducting magnet, Bruker Biospin GmbH Rheinstetten, Germany. The  $^{31}\text{P}$  NMR spectra were determined using  $\text{P}(\text{OnBu})_3$  as an internal standard (139.1 ppm) when there was no acid in the samples. The number-average molecular weights ( $M_{n,\text{SECS}}$ ) and dispersities ( $M_w/M_n$ s) were determined by HLC-8320 GPC at 40 °C in THF (0.35 mL min $^{-1}$ ) equipped with a refractive index detector (+, 0.5 s) and two TSKgel Super Multipore HZ-M columns (4.6 mm I.D.  $\times$  15 cm  $\times$  2), to which 10  $\mu\text{L}$  of sample is injected with the concentration of 0.2-0.3 wt% at once, calculated on the basis of a polystyrene calibration. Matrix-assisted laser desorption ionization-time of flight (MALDI-ToF) mass spectra were collected on a Bruker UltraFLEX MALDI-ToF in reflector mode with potassium trifluoroacetate as the cationic agent and 2,5-dihydroxybenzoic acid (DHB) as the matrix.

**Ring-opening polymerization of  $\epsilon$ -caprolactone.** A typical procedure for polymerization of  $\epsilon$ -CL is described as follows:  $\epsilon$ -CL (2.0 mL, 2.0 mol L $^{-1}$  in  $\text{CH}_2\text{Cl}_2$ ), EDPP (160  $\mu\text{L}$ , 0.5 mol L $^{-1}$  in  $\text{CH}_2\text{Cl}_2$ ) and DPP (320  $\mu\text{L}$ , 0.5 mol L $^{-1}$  in  $\text{CH}_2\text{Cl}_2$ ) were added to a test tube in glove box. Aliquots were removed from the reaction mixture to determine the conversion based on  $^1\text{H}$  NMR spectrum. After stirring for 32 h, the polymerization was quenched by adding a small amount of triethylamine to the polymerization solution. The polymer product was purified by precipitation against methanol three times to give PCL as a white solid. Yield, 336.6 mg (75%); Conv. = 94.5%,  $M_{n,\text{theo.}} = 5,440 \text{ g mol}^{-1}$ ,  $M_{n,\text{NMR}} = 5,310 \text{ g mol}^{-1}$ ,  $M_{n,\text{SEC}} = 8,430 \text{ g mol}^{-1}$ ,  $M_w/M_n = 1.15$ .

## Derivation of polymerization rate equation

$$R_p = -\frac{d[M]}{dt} = k_p[M^*][I] \quad (1)$$

where  $[M^*]$  = [activated  $\varepsilon$ -CL],  $[I]$  is the concentration of active center, and  $k_p$  is the polymerization rate constant. Namely,

$$\frac{dC}{dt} = \frac{k_p[M^*][I]}{[M]_0} \quad (2)$$

$C$  is the monomer conversion and  $[M]_0$  is the initial monomer concentration. According to the proposed mechanism in Scheme S1(c), the following reactions can be known:



EDPP is the true active center and its protonated state (EDPP-DPP) is the dormant species. Thus, we can know  $[I] = [\text{EDPP}]$ . As discussed above, DPP acts as a dual-role catalyst and is divided into two parts. One role is to protonate the phosphinite species to establish an equilibrium reaction (equilibrium constant =  $K$ ), and the other is the residual DPP to activate  $\varepsilon$ -CL. Thus,  $[M^*] = [\text{DPP}] = [\text{DPP}]_0 - [\text{EDPP-DPP}]$  can be known. The following equations can be derived as:

$$[\text{EDPP}] + [\text{EDPP} - \text{DPP}] = [\text{EDPP}]_0 \quad (3)$$

$$[\text{DPP}] + [\text{EDPP} - \text{DPP}] = [\text{DPP}]_0 \quad (4)$$

$$[M^*] = [\text{DPP}] \quad (5)$$

$$K = \frac{[\text{EDPP-DPP}]}{[\text{EDPP}][\text{DPP}]} \quad (6)$$

eq. (7) can be obtained by combining (3)-(6),

$$K = \frac{[\text{EDPP}]_0 - [\text{EDPP}]}{[\text{EDPP}]([\text{DPP}]_0 + [\text{EDPP}] - [\text{EDPP}]_0)} \quad (7)$$

According to *eq. (7)*, [P] can be expressed by *K* as *eq. (8)*,

$$[\text{EDPP}] = \sqrt{K[\text{EDPP}]_0 + \left(\frac{1+K([\text{DPP}]_0 - [\text{EDPP}]_0)}{2}\right)^2} - \frac{1+K([\text{DPP}]_0 - [\text{EDPP}]_0)}{2} \quad (8)$$

According to *eq. (2)*, (5), (6) and [I] = [EDPP],

$$\frac{dC}{dt} = \frac{k_p[\text{M}^*][\text{I}]}{[\text{M}]_0} = \frac{k_p}{[\text{M}]_0} [\text{DPP}][\text{EDPP}] = \frac{k_p}{[\text{M}]_0} \frac{[\text{EDPP}]_0 - [\text{EDPP}]}{K} \quad (9)$$

Thus, the final equation can be expressed as *eq. (10)* after (8) is input to (9),

$$\frac{dC}{dt} = \frac{k_p}{[\text{M}]_0} \frac{K[\text{EDPP}]_0 - \left\{ \sqrt{K[\text{EDPP}]_0 + \left(\frac{1+K([\text{DPP}]_0 - [\text{EDPP}]_0)}{2}\right)^2} - \frac{1+K([\text{DPP}]_0 - [\text{EDPP}]_0)}{2} \right\}}{K^2} \quad (10)$$

Namely,

$$C = \frac{k_p}{[\text{M}]_0} \frac{K[\text{EDPP}]_0 - \left\{ \sqrt{K[\text{EDPP}]_0 + \left(\frac{1+K([\text{DPP}]_0 - [\text{EDPP}]_0)}{2}\right)^2} - \frac{1+K([\text{DPP}]_0 - [\text{EDPP}]_0)}{2} \right\}}{K^2} t \quad (11)$$

**Table S1.** Ring-opening polymerization (ROP) of  $\epsilon$ -caprolactone ( $\epsilon$ -CL) using an organocatalytic system composed of ethyl diphenylphosphinite (EDPP) and an organic acid in  $\text{CH}_2\text{Cl}_2$  <sup>a</sup>

run	Organic acid (C)	$[\text{C}]_0/[\text{EDPP}]_0$	Conv. <sup>b</sup> (%)	$M_{n,\text{theo.}}$ <sup>c</sup> ( $\text{g mol}^{-1}$ )	$M_{n,\text{SEC}}$ <sup>d</sup> ( $\text{g mol}^{-1}$ )	$M_w/M_n$ <sup>d</sup>
S1	PhCO <sub>2</sub> H	1:1	0	--	n.d. <sup>h</sup>	n.d.
S2	PhCO <sub>2</sub> H	2:1	0	--	n.d.	n.d.
S3	HNTf <sub>2</sub>	1:1	0	--	n.d.	n.d.
S4	HNTf <sub>2</sub>	2:1	58.8	6,760	16,100	1.40
S5	DPP	1:1	39.9	4,600	5,840	1.17
S6	DPP	2:1	80.3	9,210	11,800	1.15
S7 <sup>e</sup>	DPP	2:1	99.2	11,400	19,300	1.34
S8	none	0:1	0	--	n.d.	n.d.
S9 <sup>f</sup>	none	0:1	0	--	n.d.	n.d.
S10 <sup>g</sup>	DPP	2:0	62.1	--	54,400	1.15

<sup>a</sup>  $[\epsilon\text{-CL}]_0, 2.0 \text{ mol L}^{-1}$ ;  $[\epsilon\text{-CL}]_0/[\text{EDPP}]_0 = 100$ , time = 24 h; temperature, r.t. <sup>b</sup> Determined by <sup>1</sup>H NMR in CDCl<sub>3</sub>. <sup>c</sup> Calculated from  $([\epsilon\text{-CL}]_0/[\text{EDPP}]_0) \times \text{Conv.} \times (\text{M.W. of } \epsilon\text{-CL}) + (\text{M.W. of EDPP residue})$ . <sup>d</sup> Determined by SEC equipped with an RI detector using THF as eluent at 40 °C and the flow rate of 0.35 mL min<sup>-1</sup>. <sup>e</sup> Polymerization was carried out in toluene. <sup>f</sup> The monomer was L-lactide (LLA). <sup>g</sup>  $[\epsilon\text{-CL}]_0/[\text{DPP}]_0 = 100:2$ . <sup>h</sup> Not determined.

**Table S2.** ROP of cyclic esters using EDPP/DPP as an organocatalytic system in CH<sub>2</sub>Cl<sub>2</sub> <sup>a</sup>

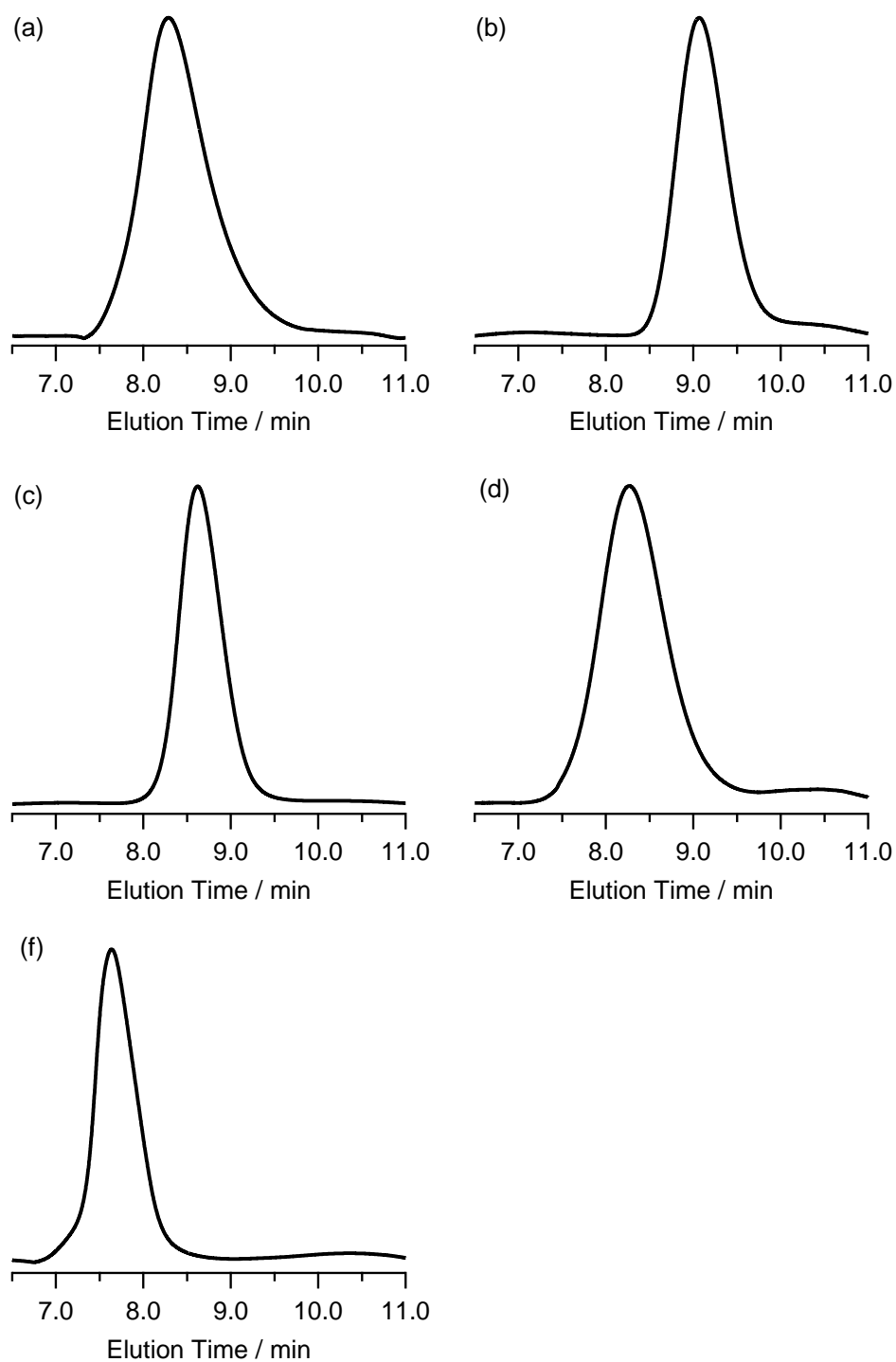
run	Monomer (M)	Time	Conv. <sup>b</sup> (%)	$M_{n,theo.}$ <sup>c</sup> (g mol <sup>-1</sup> )	$M_{n,SEC}$ <sup>d</sup> (g mol <sup>-1</sup> )	$M_w/M_n$ <sup>d</sup>
S6	$\epsilon$ -CL	24	80.3	9,210	11,800	1.15
S11	$\delta$ -VL	4.5	85.1	8,600	11,600	1.31
S12	TMC	5.5	5.0	560	n.d.	n.d.
S13	LLA	3	0	n.d. <sup>e</sup>	n.d.	n.d.

<sup>a</sup> [M]<sub>0</sub>, 2.0 mol L<sup>-1</sup>; [M]<sub>0</sub>/[DPP]<sub>0</sub>/[EDPP]<sub>0</sub> = 100/2/1; temperature, r.t. <sup>b</sup> Determined by <sup>1</sup>H NMR in CDCl<sub>3</sub>. <sup>c</sup> Calculated from ([ $\epsilon$ -CL]<sub>0</sub>/[EDPP]<sub>0</sub>) × Conv. × (M.W. of  $\epsilon$ -CL) + (M.W. of EDPP residue). <sup>d</sup> Determined by SEC equipped with an RI detector using THF as eluent at 40 °C and the flow rate of 0.35 mL min<sup>-1</sup>. <sup>e</sup> Not determined.

**Table S3.** Block copolymerization of  $\delta$ -VL and  $\epsilon$ -CL using EDPP/DPP as an organocatalytic system in CH<sub>2</sub>Cl<sub>2</sub> by sequential monomer addition method <sup>a</sup>

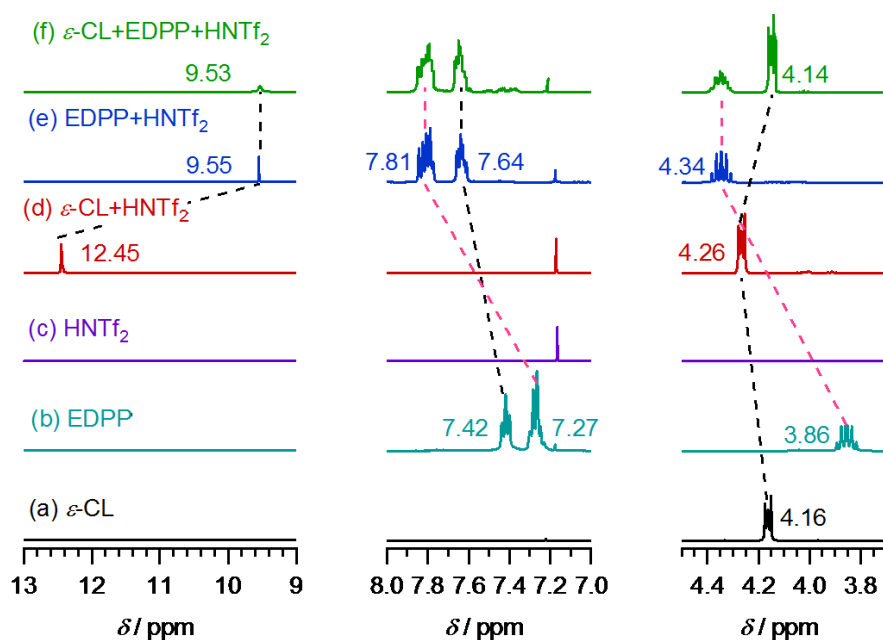
Polymer	$[\delta\text{-VL}+\epsilon\text{-CL}]_0$ /[EDPP] <sub>0</sub>	time (h)	Conv. ( $\delta$ -VL) <sup>b</sup> (%)	Conv. ( $\epsilon$ -CL) <sup>b</sup> (%)	$M_{n,theo.}$ <sup>c</sup> (g mol <sup>-1</sup> )	$M_{n,NMR}$ <sup>b</sup> (g mol <sup>-1</sup> )	$M_{n,SEC}$ <sup>d</sup> (g mol <sup>-1</sup> )	$M_w/M_n$ <sup>d</sup>
PVL- <i>b</i> -poly (VL- <i>co</i> -CL)	(50+0)/1	3	78.0	0	3,950	4,720	5,960	1.25
PCL- <i>b</i> -poly (CL- <i>co</i> -VL)	(0+50)/1	32	97.3	82.2	9,610	8,940	17,100	1.21
PCL- <i>b</i> -poly (CL- <i>co</i> -VL)	(0+50)/1	32	0	84.7	4,880	5,380	7,200	1.14
PCL- <i>b</i> -poly (CL- <i>co</i> -VL)	(50+0)/1	5	71.5	88.0	8,650	8,130	12,400	1.25

<sup>a</sup> [ $\epsilon$ -CL]<sub>0</sub>, 2.0 mol L<sup>-1</sup>; [EDPP]<sub>0</sub>, 0.5 mol L<sup>-1</sup>; [DPP]<sub>0</sub>, 0.5 mol L<sup>-1</sup>; temperature, r.t. <sup>b</sup> Determined by <sup>1</sup>H NMR in CDCl<sub>3</sub>. <sup>c</sup> Calculated from ([ $\epsilon$ -CL]<sub>0</sub>/[EDPP]<sub>0</sub>) × Conv. × (M.W. of  $\epsilon$ -CL) + (M.W. of EDPP residue). <sup>d</sup> Determined by SEC equipped with an RI detector using THF as eluent at 40 °C and the flow rate of 0.35 mL min<sup>-1</sup>. <sup>e</sup> not determined.

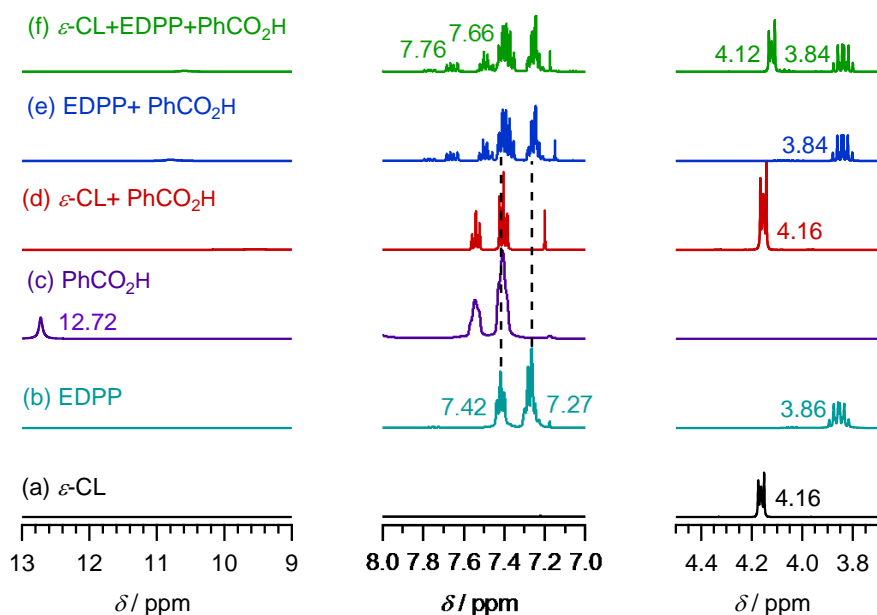


**Figure S1.** SEC traces of (a) run 4, (b) run 5, (c) run 6, (d) run 7, and run 9 determined by a SEC equipped with an RI detector using THF as eluent at 40 °C and the flow rate of 0.35 mL min<sup>-1</sup>.

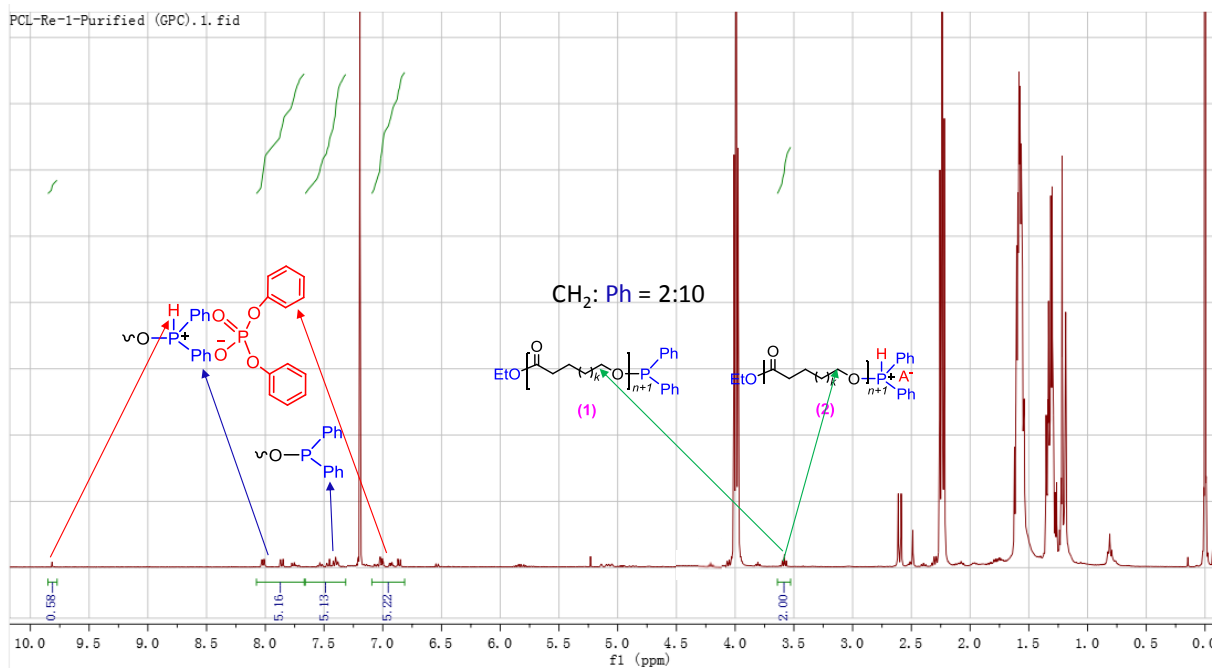




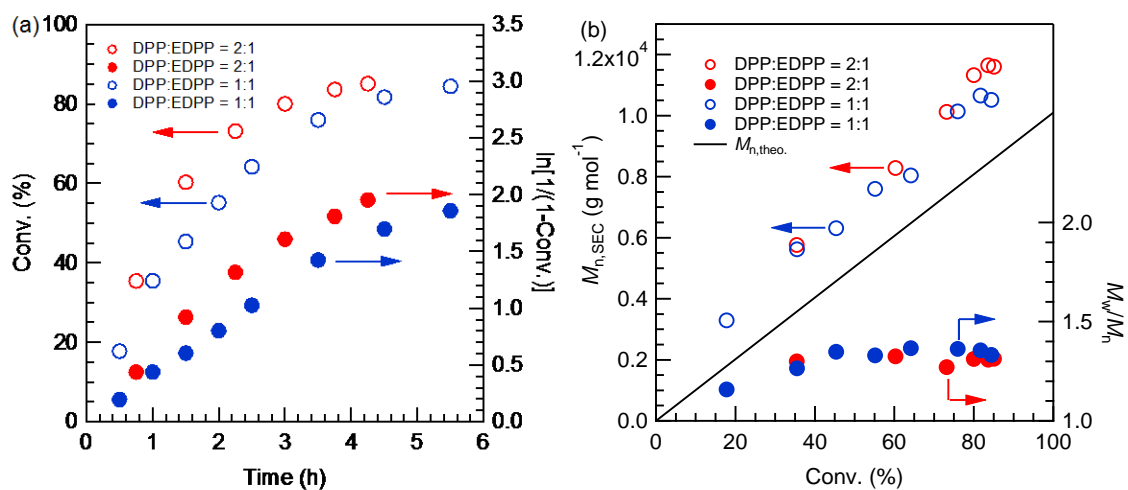
**Figure S2.**  $^1\text{H}$  NMR spectra of (a)  $\epsilon\text{-CL}$ , (b) EDPP, (c) HNTf<sub>2</sub> (d)  $\epsilon\text{-CL}$  + HNTf<sub>2</sub> (molar ratio, 1:1, the same for the following mixtures), (e) EDPP + HNTf<sub>2</sub>, and (f)  $\epsilon\text{-CL}$  + EDPP + HNTf<sub>2</sub> determined in CDCl<sub>3</sub>.



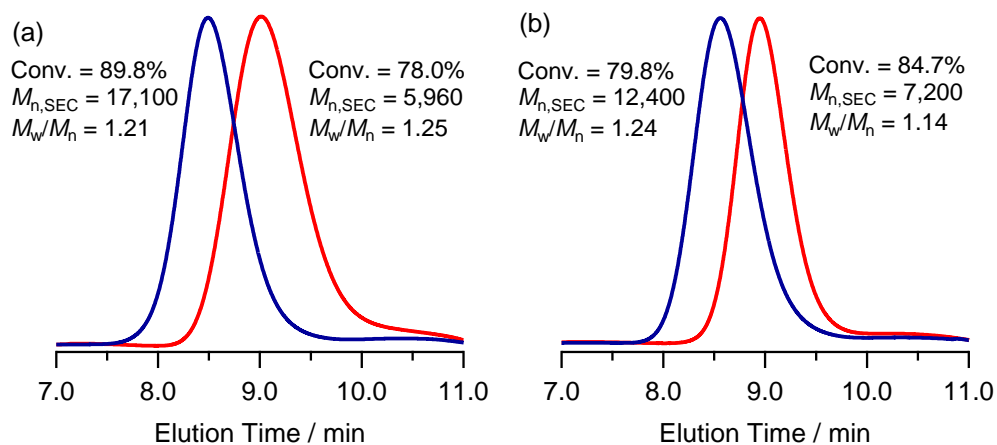
**Figure S3.**  $^1\text{H}$  NMR spectra of (A): (a)  $\epsilon\text{-CL}$ , (b) EDPP, (c) PhCO<sub>2</sub>H, (d)  $\epsilon\text{-CL}$  + PhCO<sub>2</sub>H (molar ratio, 1:1, the same for the following mixtures), (e) PhCO<sub>2</sub>H + EDPP, and (f)  $\epsilon\text{-CL}$  + PhCO<sub>2</sub>H + EDPP determined in CDCl<sub>3</sub>.



**Figure S4.** <sup>1</sup>H NMR spectrum of a PCL (theoretically 25-mer) purified after reprecipitation from hexane for three times and then preparative SEC in CH<sub>2</sub>Cl<sub>2</sub>, determined in CDCl<sub>3</sub>.



**Figure S5.** (a) Conv. vs time and  $\ln[1/(1-\text{Conv.})]$  vs time plots, and (b) the dependence of  $M_{n,SEC}$  and  $M_w/M_n$  on Conv. of the ROP of  $\delta$ -VL carried out at r.t. in CH<sub>2</sub>Cl<sub>2</sub> under various  $[\delta\text{-VL}]_0/[\text{EDPP}]_0/[\text{DPP}]_0$  ratios of 100/2/1 (○) and 100/1/1 (○) ( $[\delta\text{-VL}]_0 = 2.0 \text{ mol L}^{-1}$ ).



**Figure S6.** SEC traces of copolymerization of  $\delta$ -VL and  $\varepsilon$ -CL by sequential monomer addition method: (a) PVL in first polymerization (red line) and PVL-*b*-poly(VL-*co*-CL) (blue line) in the following copolymerization and (b) PCL in first polymerization (red line) and PCL-*b*-poly(CL-*co*-VL) (blue line) in the following copolymerization determined by a SEC equipped with an RI detector using THF as eluent at 40 °C and the flow rate of 0.35 mL min<sup>-1</sup>.