

# Supporting Information for

## **Metal-Free Living Cationic Ring-Opening**

## **Polymerization of Cyclic Esters Using Selenonium**

## **Salts as Lewis Acids**

Wenjing Shu,<sup>a</sup> Xiaoying Cheng,<sup>a</sup> Yihan Gao,<sup>a</sup> Xia Lin,<sup>a</sup> Xiangqiang Pan,<sup>a</sup>  
Jiajia Li<sup>a,\*</sup> and Jian Zhu<sup>a,\*</sup>

<sup>a</sup> State and Local Joint Engineering Laboratory for Novel Functional Polymeric Materials, Jiangsu Key Laboratory of Advanced Functional Polymer Design and Application, Department of Polymer Science and Engineering, College of Chemistry, Chemical Engineering and Materials Science, Soochow University, Suzhou 215123,

*E-mail:* chemzhujian@suda.edu.cn; chemjjli@suda.edu.cn

*Supporting Information Placeholder*

## Materials and General Methods

Phenylhydrazine (98%, Macklin), selenium dioxide (SeO<sub>2</sub>, 99%, Aladdin), 1-iodopropane (98%, J&K), sodium borohydride (NaBH<sub>4</sub>, 98%, Aladdin), silver hexafluoroantimonate (AgSbF<sub>6</sub>, 98%, J&K), silver hexafluorophosphate (AgPF<sub>6</sub>, 98%, Aladdin), silver tetrafluoroborate (AgBF<sub>4</sub>, 97%, Energy Chemical), iodomethane (MeI, 99%, Energy Chemical), calcium hydride (CaH<sub>2</sub>, Aladdin, 95%), ethyl acetate (EA, 99%, Qiangsheng), methanol (MeOH, 99%, Qiangsheng), ethanol (EtOH, 99%, Qiangsheng), tetrahydrofuran (THF, 99%, Qiangsheng), acetonitrile (ACN, 99%, Qiangsheng), ethyl ether (99%, Qiangsheng) and petroleum ether (PE, 99%, Qiangsheng) were used as received without further purification. E-caprolactone ( $\epsilon$ -CL, 99%, Aladdin),  $\delta$ -Valerolactone ( $\delta$ -VL, 98.5%, J&K) and benzyl alcohol (BnOH, 99.8%, Macklin) distilled twice on calcium hydride. EA is distilled once on calcium hydride. Toluene (TOL, 99%, Qiangsheng) is refluxed on sodium filaments and benzophenones for several hours, and when the color changes to blue or purple, atmospheric distillation is collected. Trimethylcarbonate (TMC, 98%, Meryer) and L-Lactide (L-LA, 98%, Adamas) was recrystallized twice using purified ethyl acetate and dried at 40 °C in a vacuum oven.

The number-average molecular weights ( $M_n$ ) and molecular weight distributions ( $\mathcal{D}$ ) of polymers were measured by TOSOH HLC-8320 Size Exclusion Chromatography (SEC) equipped with refractive index and UV detectors using two TSKgel SuperMultiporeHZ-N (4.6 × 150 mm) columns arranged in series. Tetrahydrofuran (THF) served as the eluent with a flow rate of 0.35 mL min<sup>-1</sup> at 40 °C. SEC samples were injected using a TOSOH HLC-8320 SEC plus autosampler. Data acquisition was performed using EcoSEC software, and molecular weights were calculated with polystyrene (PS) standards. The proton nuclear magnetic resonance (<sup>1</sup>H NMR) spectrum were measured on a Bruker 300 MHz spectrometer. The samples were dissolved with deuterated trichloromethane (CDCl<sub>3</sub>) using tetramethylsilane (TMS) as an internal standard. The matrix-assisted laser desorption/ionization time of flight mass spectrometry (MALDI-TOF MS) was measured using a Bruker Daltonics Ultraflex in the positive ion and reflection mode with a 337 nm nitrogen laser. Trans-2-[3-(4-

tert-butylphenyl)-2-methyl-2-propenylidene malononitrile (DCTB) was used as the matrix, and sodium trifluoroacetate (NaTFA) was used as the ionization agent. The concentration of the polymer solution is 10 mg mL<sup>-1</sup> in CHCl<sub>3</sub>.

#### **Synthesis of diphenyl selenide (DphSe).**

In a 250 mL single-mouth flask, dissolve phenylhydrazine (13 g, 0.12 mol) in 150 mL of acetonitrile, and then add selenium dioxide (20 g, 0.18 mol) several times in small amounts. The mixture was stirred vigorously for 1 h at 60 °C. The crude product was purified by column chromatography (petroleum ether) to provide diphenyl selenide as a yellow liquid; yield: 7.26 g (51.9%). <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>, 300 MHz; **Fig. S17**): δ 7.45 (m, 4H), 7.34 (m, 6H).

#### **Synthesis of phenyl(propyl)selane (4).**

Two neck 100 mL R B flask fitted with a reflux condenser, a rubber septum and a magnetic stir bar was charged with PhSeSePh (2.5 g, 8.0 mmol). Dry ethanol (50 mL) was introduced into the flask by syringe and allowed to stir for 10 min under dry nitrogen atmosphere. Septum was replaced with solid addition funnel containing NaBH<sub>4</sub> (0.61 g, 16 mmol) which was added to the contents slowly. Pale yellow solution was decolourized to a clear solution indicating the formation of phenyl selenyl anion. Solid addition funnel was replaced with septum again and 1-Iodopropane (1.75g, 16 mmol) was added dropwise to the reaction mixture. After the addition was completed, contents were refluxed for 3 h. Ethanol was removed under reduced pressure, quenched with 15% dil HCl to dissolve the solid concentrate and extracted with 2 x 50 mL of ether. The combined organic layer was washed with NaHCO<sub>3</sub>, H<sub>2</sub>O and brine solution respectively. Ether layer was separated out and dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. The crude product was purified by column chromatography (petroleum ether) to provide phenyl(propyl)selane as a yellow liquid; yield: 2.00 g (62.8%). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz; **Fig. S18**): δ 7.53-7.51 (m, 2H), 7.29-7.24 (m, 3H), 2.92 (t, 2H), 1.75 (h, 2H), 1.03 (t, 3H).

#### **General procedure for the synthesis of selenium salts (Se-X).**

AgX (2.0 mmol) and the **DphSe** (2.0 mmol) were dissolved and stirred in acetonitrile (6 mL) under argon atmosphere. Then methyl iodide (4.0 mmol) was added via syringe to the stirred solution and stirred overnight in the dark at room temperature. The mixture was filtered to remove AgI, and the filtrate was evaporated under reduced pressure at 40 °C.

Methyldiphenylselenonium tetrafluoroborate (**Se-1**): **Se-1** was obtained as a white solid at a yield of 57.4%. A white solid. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz; **Fig. S19**) δ 7.57- 7.71 (m, 10H), 3.40 (s, 3H).

Methyldiphenylselenonium hexafluorophosphate (**Se-2**): **Se-2** was obtained as a white solid at a yield of 51.0%. A white solid. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz; **Fig. S20**) δ 7.59-7.69 (m, 10H), 3.43 (s, 3H).

Methyldiphenylselenonium hexafluoroantimonate (**Se-3**): **Se-3** was obtained as a white solid at a yield of 67.8%. A white solid. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz; **Fig. S21**) δ 7.61-7.74 (m, 10H), 3.45 (s, 3H).

Methylphenyl(propyl)selenonium hexafluoroantimonate (**Se-4**): **Se-4** was obtained as a white solid at a yield of 48.6%. A white solid. <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>, 300 MHz; **Fig. S22**) δ 7.91-8.00 (m, 2H), 7.60-7.75 (m, 3H), 3.42-3.58 (m, 2H), 3.07 (s, 3H), 1.45-1.76 (m, 2H), 0.95 (t, 3H).

### Polymerization Procedures

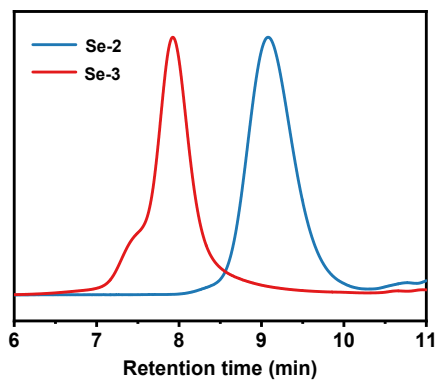
Polymerization of ε-CL: The polymerization of ε-CL was described as the typical example. A mixture of ε-CL (0.5 mL, 4.68 mmol), BnOH (5.1 mg, 0.047 mmol), **Se-3** (22.7 mg, 0.047 mmol) and TOL (0.5 mL) was added in a 4 mL vial in a glovebox with nitrogen atmosphere with the molar ratio of [ε-CL]<sub>0</sub>/[BnOH]<sub>0</sub>/[**Se-3**]<sub>0</sub> = 100:1:1. Then the vial was stirred in an oil bath at 50 °C. After a predetermined time, the product was diluted and terminated by triethylamine/tetrahydrofuran mixture (10% V/V). The polymer was dissolved with tetrahydrofuran and precipitated in a large amount of methanol. The purification process was repeated three times before being dried in a

vacuum at 40 °C. Monomer conversion was calculated by  $^1\text{H}$  NMR. Molecular weight and molecular weight distribution were determined by SEC.

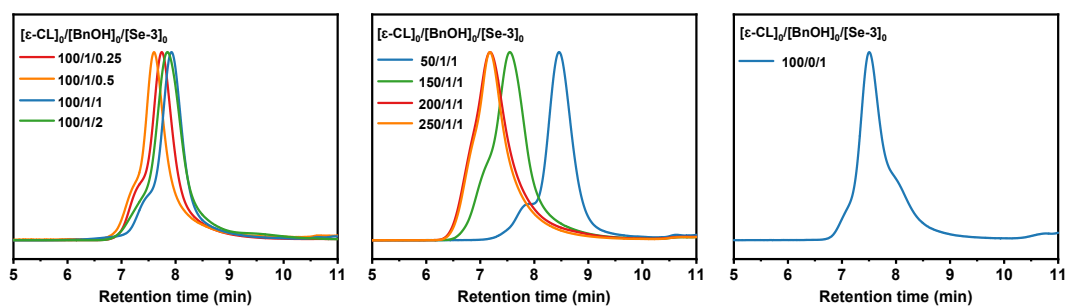
Polymerization of L-LA: Cationic polymerization of L-LA using **Se-3** as a Lewis acid catalyst as a typical example: A mixture of L-LA (675.1 mg, 4.68 mmol), BnOH (5.1 mg, 0.047 mmol), **Se-3** (22.7 mg, 0.047 mmol) and TOL (1 mL) was added in a 4 mL vial in a glovebox with nitrogen atmosphere with the molar ratio of  $[\text{L-LA}]_0/[\text{BnOH}]_0/[\text{Se-3}]_0 = 100:1:1$ . Then the vial was stirred in an oil bath at 110 °C. After a predetermined time, the product was diluted and terminated by triethylamine/tetrahydrofuran mixture (10% V/V). Monomer conversion was calculated by  $^1\text{H}$  NMR. Molecular weight and molecular weight distribution were determined by SEC.

*In situ* chain expansion: **(A)** At 50 °C, a mixture of  $\epsilon$ -CL (1 mL, 9.37 mmol), BnOH (20.3 mg, 0.187 mmol), **Se-3** (90.7 mg, 0.187 mmol) and TOL (1 mL) was added in a 4 mL vial in a glovebox with nitrogen atmosphere with the molar ratio of  $[\epsilon\text{-CL}]_0/[\text{BnOH}]_0/[\text{Se-3}]_0 = 50:1:1$ . After 24 h, 0.05 mL of the reaction solution was taken out and dissolved in 0.6 mL of  $\text{CDCl}_3$  containing excess triethylamine (Sample A). Then, 1 mL of  $\epsilon$ -CL and 1 mL of TOL were added with the 4 mL vial to continue the reaction. After 14 h, another 0.05 mL solution was taken out and dissolved in  $\text{CDCl}_3$  containing excess triethylamine (Sample B). The conversion rate of two samples was calculated by  $^1\text{H}$  NMR. Molecular weight and molecular weight distribution were determined by SEC. **(B)** At 50 °C, a mixture of  $\epsilon$ -CL (1 mL, 9.37 mmol), BnOH (20.3 mg, 0.187 mmol), **Se-3** (90.7 mg, 0.187 mmol) and TOL (1 mL) was added in a 4 mL vial in a glovebox with nitrogen atmosphere with the molar ratio of  $[\epsilon\text{-CL}]_0/[\text{BnOH}]_0/[\text{Se-3}]_0 = 50:1:1$ . After 24 h, 0.05 mL of the reaction solution was taken out and dissolved in 0.6 mL of  $\text{CDCl}_3$  containing excess triethylamine (Sample C). Then, 1 mL of  $\delta$ -VL and 1 mL of TOL were added with the 4 mL vial to continue the reaction. After 9 h, another 0.05 mL solution was taken out and dissolved in  $\text{CDCl}_3$  containing excess triethylamine (Sample D). The conversion rate of two samples was calculated by  $^1\text{H}$  NMR. Molecular weight and molecular weight distribution were determined by SEC.

## Additional Results



**Figure S1.** SEC traces of PCL obtained from **Table 1 (Entry 2 and 3)**.

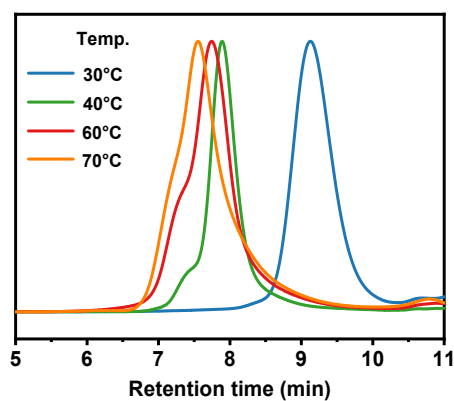


**Figure S2.** SEC traces of PCL obtained from **Table 2**.

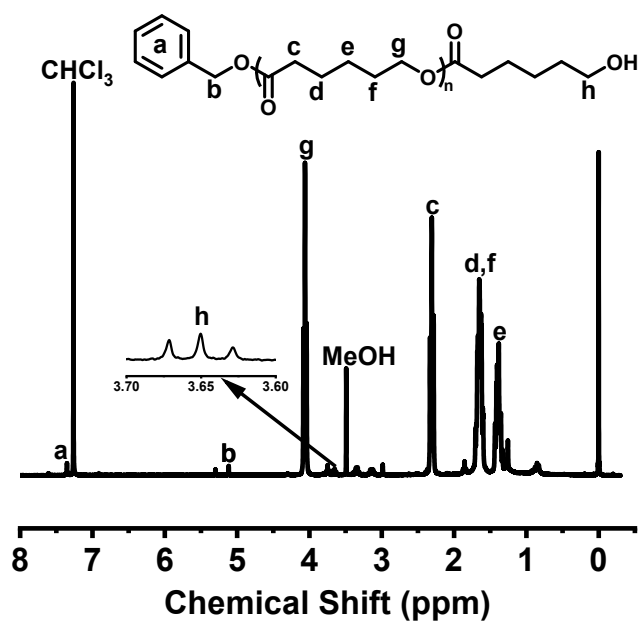
**Table S1** Polymerization of  $\epsilon$ -CL in TOL using **Se-3** as a Lewis acid with a molar ratio of  $[\epsilon\text{-CL}]_0/[\text{BnOH}]_0/[\text{Se-3}]_0 = 100:1:1$  at different temperatures,  $V_{\epsilon\text{-CL}} = 0.5$  mL and  $V_{\text{TOL}} = 0.5$  mL

Entry	Temp. (°C)	Time (h)	Conv. <sup>a</sup> (%)	$M_{n,\text{th}}^b$ (g mol <sup>-1</sup> )	$M_{n,\text{SEC}}^c$ (g mol <sup>-1</sup> )	$\bar{D}$
1	30	161	22.5	2700	2500	1.19
2	40	78	89.9	10400	9400	1.10
3	60	16	90.7	10500	11500	1.14
4	70	6	90.6	10400	11400	1.27

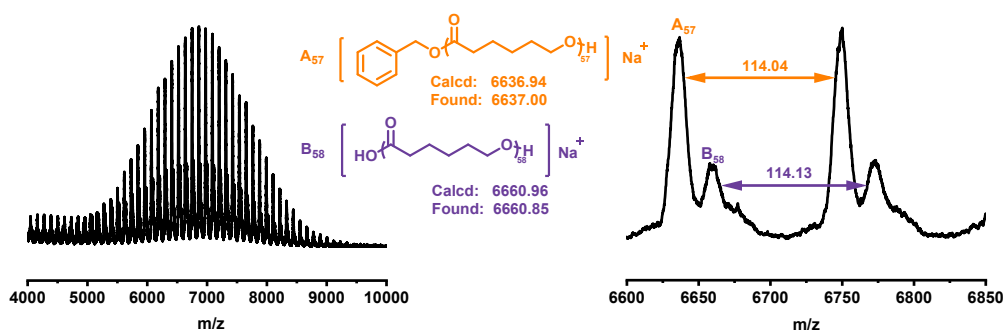
<sup>a</sup>Monomer conversion was calculated by <sup>1</sup>H NMR. <sup>b</sup>Calculated based on conversion ( $M_{n,\text{th}} = [\epsilon\text{-CL}]_0/[\text{BnOH}]_0 \times M_{\epsilon\text{-CL}} \times \text{conversion} + M_{\text{BnOH}}$ ). <sup>c</sup>Determined by SEC using polystyrene (PS) as a standard in tetrahydrofuran (THF) multiplied by a correction factor of 0.67.



**Figure S3.** SEC traces of PCL obtained from **Table S1**.



**Figure S4.** <sup>1</sup>H NMR data of PCL ( $M_{n,SEC} = 7300$ ,  $\mathcal{D} = 1.07$ , conversion = 57.4%), obtained from polymerization of  $\epsilon$ -CL with a molar ratio of  $[\epsilon\text{-CL}]_0/[\text{BnOH}]_0/[\text{Se-3}]_0 = 100:1:1$  at 50 °C,  $V_{\epsilon\text{-CL}} = 0.5$  mL and  $V_{\text{TOL}} = 0.5$  mL.



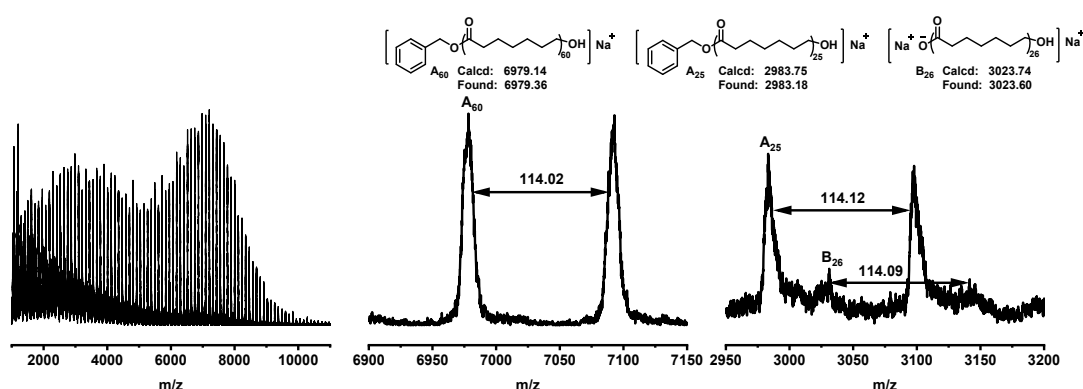
**Figure S5.** MALDI-TOF data of PCL ( $M_{n,SEC} = 7300$ ,  $\mathcal{D} = 1.07$ , conversion = 57.4%), obtained from polymerization of  $\epsilon$ -CL with a molar ratio of  $[\epsilon\text{-CL}]_0/[\text{BnOH}]_0/[\text{Se-3}]_0 = 100:1:1$  at 50 °C,  $V_{\epsilon\text{-CL}} = 0.5$  mL and  $V_{\text{TOL}} = 0.5$  mL.



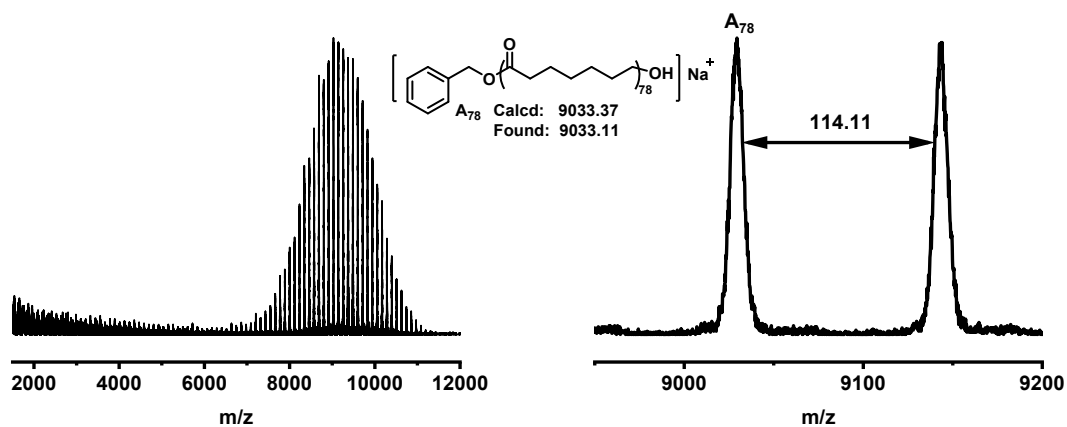
**Table S2** Polymerization of  $\epsilon$ -CL in TOL using different catalysts with a molar ratio of  $[\epsilon\text{-CL}]_0/[\text{BnOH}]_0/[\text{Catalyst}]_0 = 100:1:1$ ,  $V_{\epsilon\text{-CL}} = 0.5$  mL and  $V_{\text{TOL}} = 0.5$  mL

Entry	Temp.(°C)	Time	Conv. <sup>a</sup> (%)	$M_{n,\text{th}}^b(\text{g mol}^{-1})$	$M_{n,\text{SEC}}^c(\text{g mol}^{-1})$	$\mathcal{D}$
TBD	25	60min	97.9	11300	9200	1.21
DPP	50	160min	94.8	10900	10100	1.06

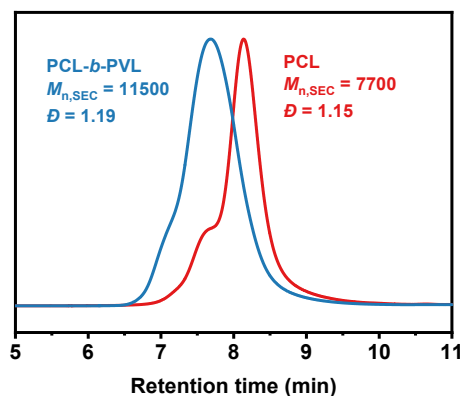
<sup>a</sup>Monomer conversion was calculated by <sup>1</sup>H NMR. <sup>b</sup>Calculated based on conversion ( $M_{n,\text{th}} = [\epsilon\text{-CL}]_0/[\text{BnOH}]_0 \times M_{\epsilon\text{-CL}} \times \text{conversion} + M_{\text{BnOH}}$ ). <sup>c</sup>Determined by SEC using polystyrene (PS) as a standard in tetrahydrofuran (THF) multiplied by a correction factor of 0.67.



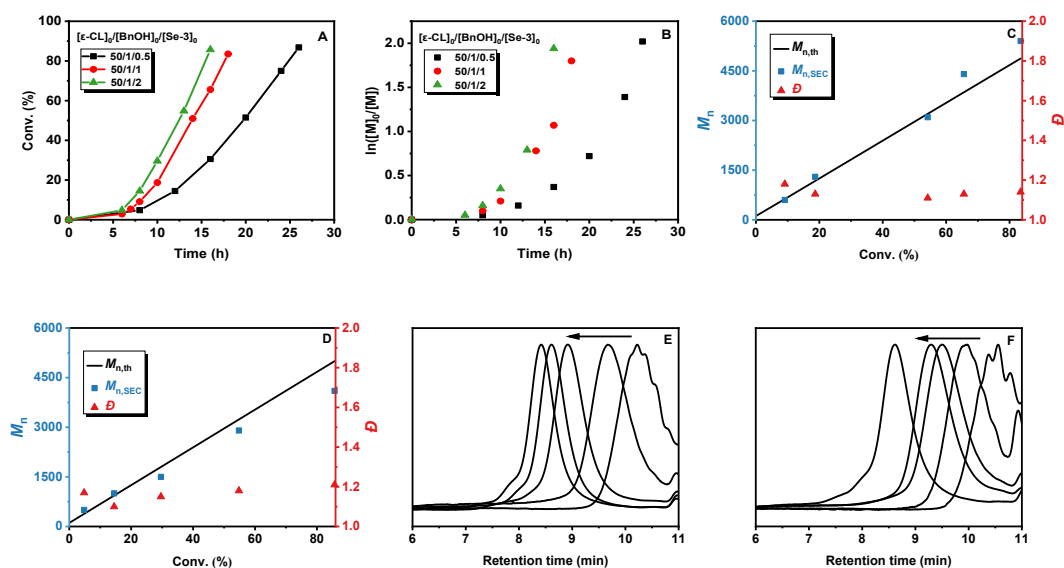
**Figure S6.** MALDI-TOF data of PCL ( $M_{n,\text{SEC}} = 9200$ ,  $\mathcal{D} = 1.21$ , conversion = 97.9%), obtained from polymerization of  $\epsilon$ -CL with a molar ratio of  $[\epsilon\text{-CL}]_0/[\text{BnOH}]_0/[\text{TBD}]_0 = 100:1:1$  at 25 °C,  $V_{\epsilon\text{-CL}} = 0.5$  mL and  $V_{\text{TOL}} = 0.5$  mL.



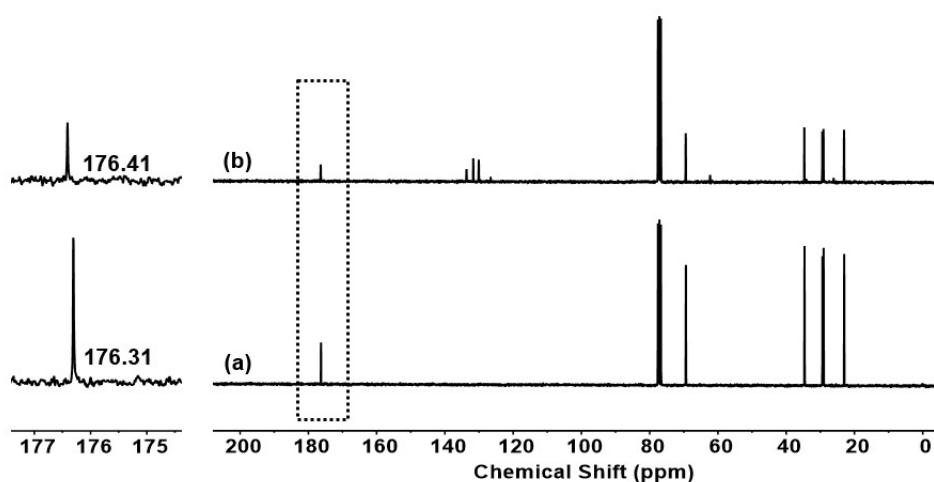
**Figure S7.** MALDI-TOF data of PCL ( $M_{n,SEC} = 10100$ ,  $\mathcal{D} = 1.06$ , conversion = 94.8%), obtained from polymerization of  $\epsilon$ -CL with a molar ratio of  $[\epsilon\text{-CL}]_0/[\text{BnOH}]_0/[\text{DPP}]_0 = 100:1:1$  at 50 °C,  $V_{\epsilon\text{-CL}} = 0.5$  mL and  $V_{\text{TOL}} = 0.5$  mL.



**Figure S8.** SEC traces of PCL before and after *in situ* chain extension using  $\delta$ -VL.



**Figure S9.** Cationic polymerization results for  $\epsilon$ -CL with molar ratios of  $[\epsilon\text{-CL}]_0/[\text{BnOH}]_0/[\text{Se-3}]_0 = 50:1:0.5$ ,  $[\epsilon\text{-CL}]_0/[\text{BnOH}]_0/[\text{Se-3}]_0 = 50:1:1$  and  $[\epsilon\text{-CL}]_0/[\text{BnOH}]_0/[\text{Se-3}]_0 = 50:1:2$  at  $50^\circ\text{C}$ : (A) Conversion rate versus time; (B)  $\ln([M]_0/[M])$  versus time; (C) molecular weight ( $M_n$ ) and molecular weight distribution ( $\mathcal{D}$ ) versus conversion of 50:1:1; (D) molecular weight ( $M_n$ ) and molecular weight distribution ( $\mathcal{D}$ ) versus conversion of 50:1:2; (E) SEC trace of 50:1:1; and (F) SEC trace of 50:1:2.



**Figure S10.**  $^{13}\text{C}$  NMR spectra of (a)  $\epsilon$ -CL and (b) the 1:1 mixture of **Se-3** and  $\epsilon$ -CL in  $\text{CDCl}_3$ .

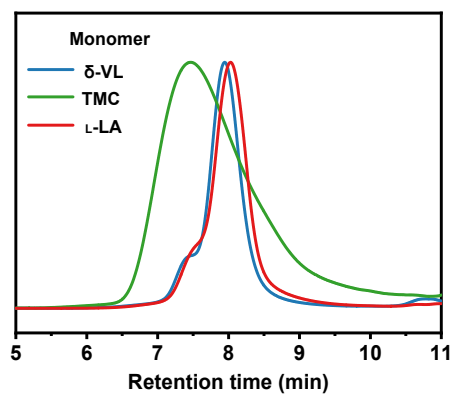


Figure S11. SEC traces of PCL obtained from Table 3.

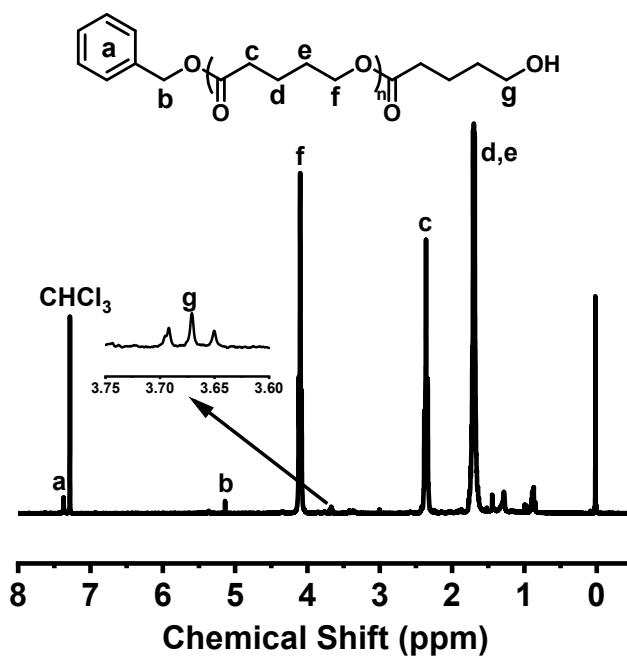
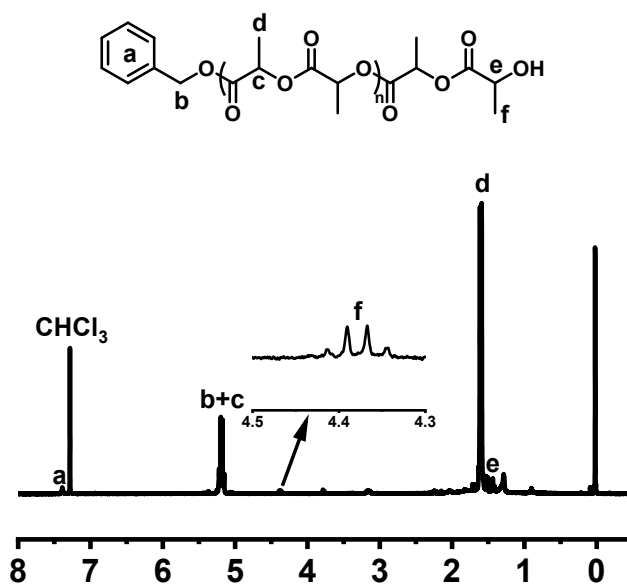
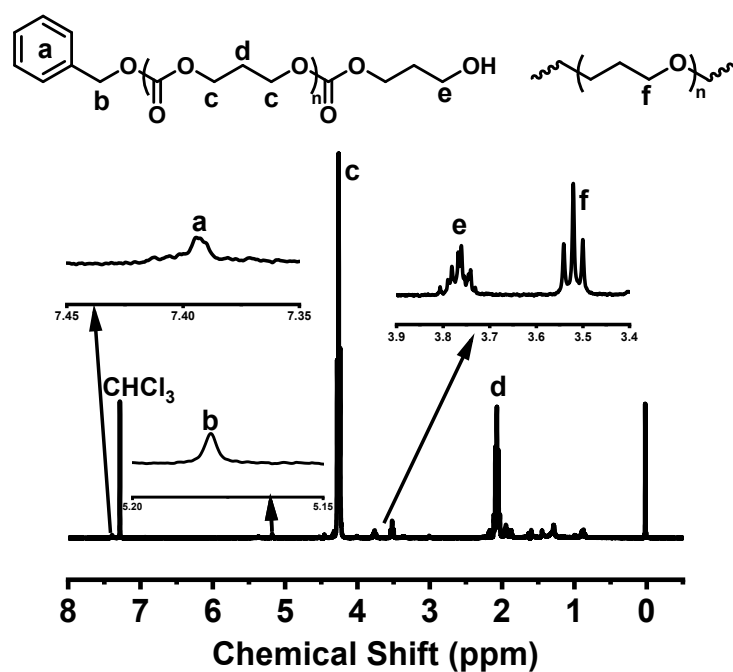


Figure S12.  $^1\text{H}$  NMR spectrum of PVL in  $\text{CDCl}_3$  ( $M_{n,\text{SEC}} = 10100$ ,  $D = 1.20$ ).



**Figure S13.**  $^1\text{H}$  NMR spectrum of PLLA in  $\text{CDCl}_3$  ( $M_{n,\text{SEC}} = 6700$ ,  $D = 1.16$ ).

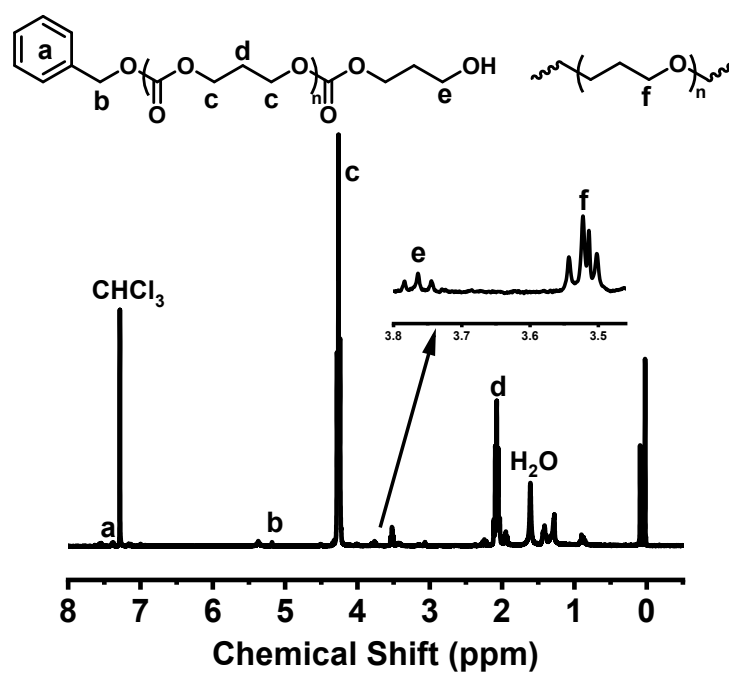


**Figure S14.**  $^1\text{H}$  NMR spectrum of PTMC obtained by **Se-3** in  $\text{CDCl}_3$  ( $M_{n,\text{SEC}} = 10200$ ,  $D = 1.38$ ).

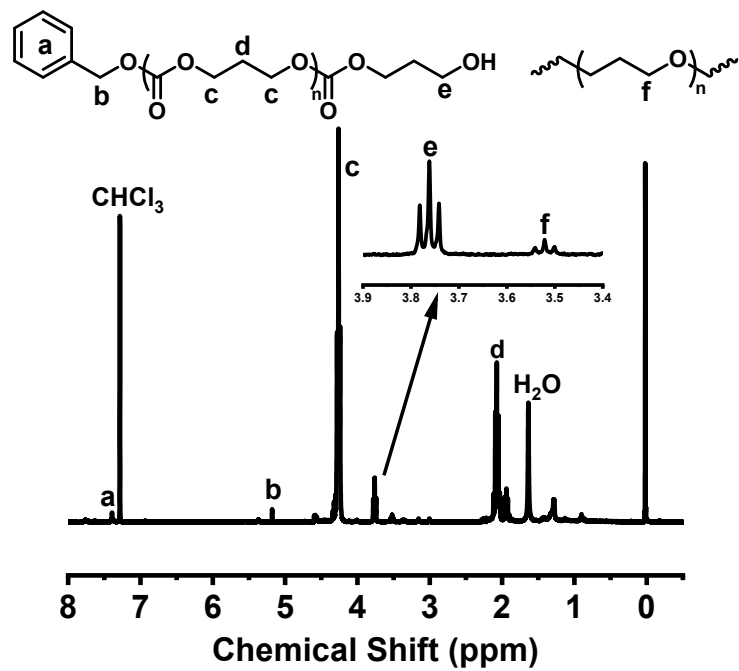
**Table S3** Polymerization of TMC using different catalysts in TOL with a molar ratio of  $[\text{TMC}]_0/[\text{BnOH}]_0/[\text{Catalyst}]_0 = 100:1:1$  and  $[\text{TMC}]_0 = 4.68 \text{ M}$ ,  $V_{\varepsilon\text{-CL}} = 0.5 \text{ mL}$  and  $V_{\text{TOL}} = 0.5 \text{ mL}$ .

Catalyst	Temp. (°C)	Time (h)	Conv. <sup>a</sup> (%)	$M_{n,\text{th}}^b$ (g mol <sup>-1</sup> )	$M_{n,\text{SEC}}^c$ (g mol <sup>-1</sup> )	$\mathcal{D}$
<b>Se-1</b>	70	48	51.9	5400	5400	1.43
<b>Se-4</b>	70	156	51.7	5400	4900	1.24

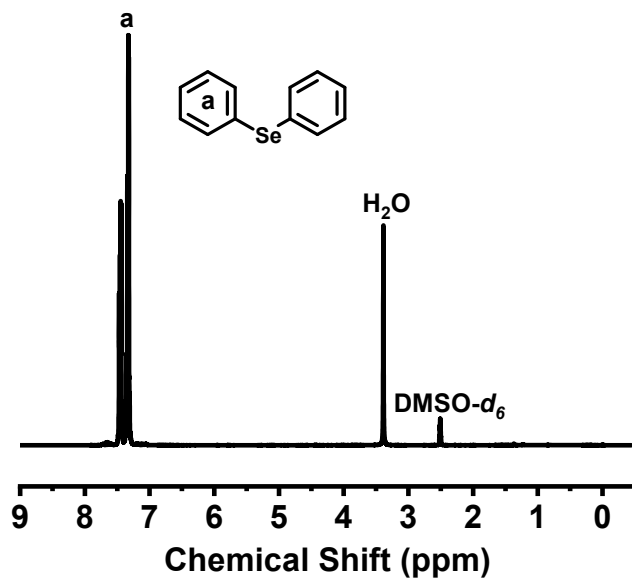
<sup>a</sup>Monomer conversion was calculated by <sup>1</sup>H NMR. <sup>b</sup>Calculated based on conversion ( $M_{n,\text{th}} = [\text{TMC}]_0/[\text{BnOH}]_0 \times M_{\text{TMC}} \times \text{conversion} + M_{\text{BnOH}}$ ). <sup>c</sup>Determined by SEC using polystyrene (PS) as a standard in tetrahydrofuran (THF) multiplied by a correction factor of 0.67.



**Figure S15.** <sup>1</sup>H NMR spectrum of PTMC by **Se-1** in CDCl<sub>3</sub> ( $M_{n,\text{SEC}} = 5400$ ,  $\mathcal{D} = 1.43$ ).



**Figure S16.**  $^1\text{H}$  NMR spectrum of PTMC by **Se-4** in  $\text{CDCl}_3$  ( $M_{n,\text{SEC}} = 4900$ ,  $\bar{D} = 1.24$ ).



**Figure S17.**  $^1\text{H}$  NMR spectrum of **DphSe** in  $\text{DMSO-}d_6$ .

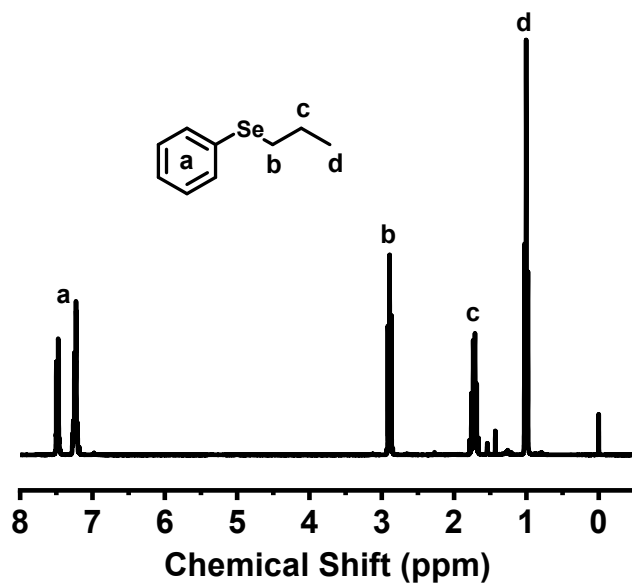


Figure S18.  $^1\text{H}$  NMR spectrum of **4** in  $\text{CDCl}_3$ .

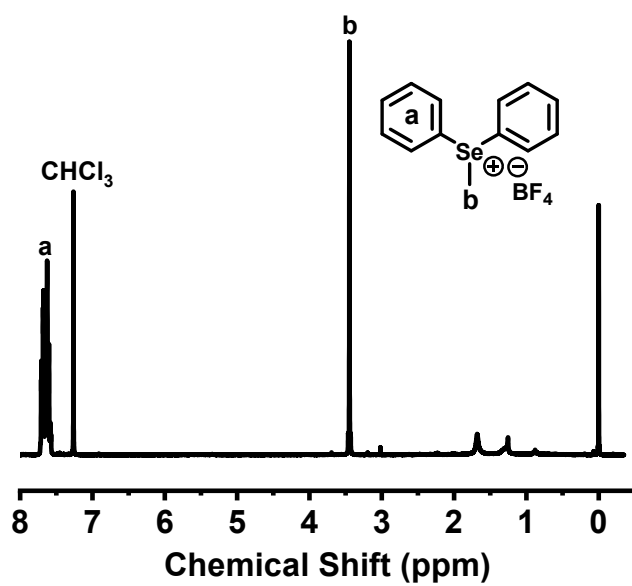


Figure S19.  $^1\text{H}$  NMR spectrum of **Se-1** in  $\text{CDCl}_3$ .



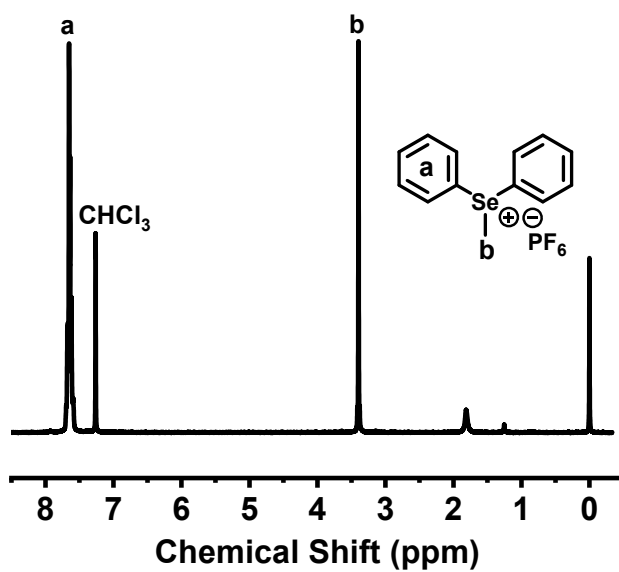


Figure S20.  $^1\text{H}$  NMR spectrum of **Se-2** in  $\text{CDCl}_3$ .

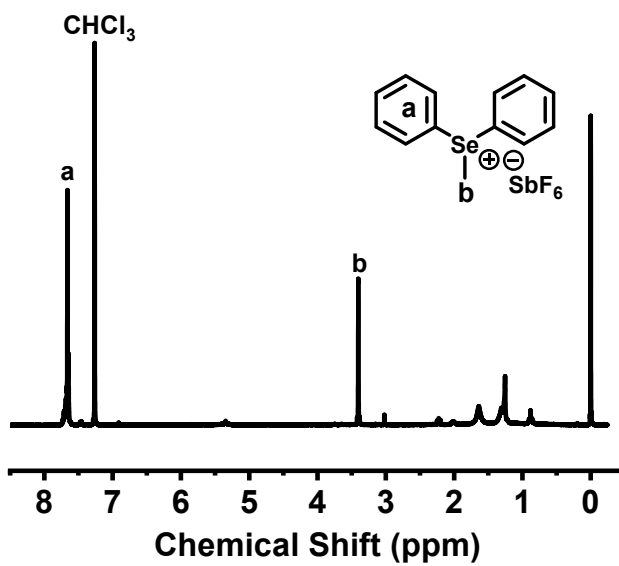


Figure S21.  $^1\text{H}$  NMR spectrum of **Se-3** in  $\text{CDCl}_3$ .

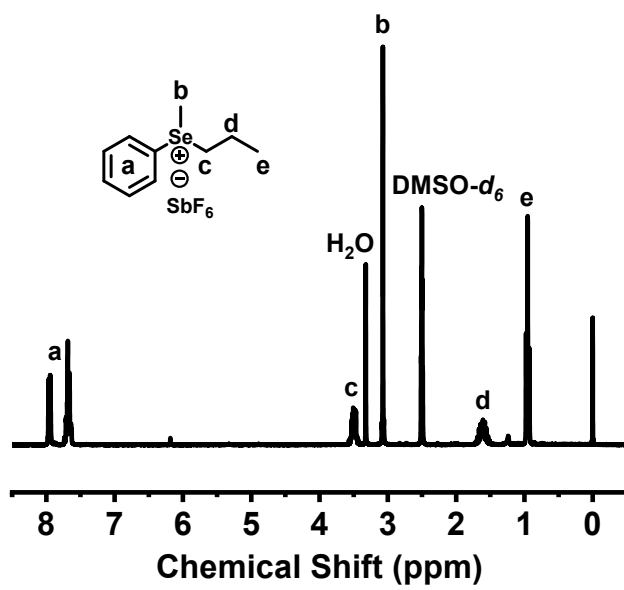


Figure S22.  $^1\text{H}$  NMR spectrum of **Se-4** in  $\text{DMSO-}d_6$ .