Supporting Information

Ring-Opening Polymerization of ε-Caprolactone Mediated by Di-Zinc Complex Bearing Macrocyclic Thioether-phenolate [OSSO]-type Ligand

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Experimental Section

Materials and methods

Unless otherwise stated, all reagents were purchased from commercial suppliers and used without further purification. All manipulations involving air- and/or watersensitive compounds were carried out with the standard Schlenk and vacuum line techniques under argon atmosphere. Propylene oxide (PO), styrene oxide (SO), epichlorohydrin (ECH), ethylene carbonate (EC), and cyclohexene oxide (CHO) were refluxed over CaH₂ and distilled under nitrogen. Tetrabutylammonium bromide (TBAB), tetrabutylammonium iodide (TBAI), tetrabutylammonium chloride (TBACl) and bis-(triphenylphosphine)-iminium chloride (PPNCl) were recrystallized from ether and acetone. ϵ -CL, acetic acid and ZnBr₂ were purchased from J&K Scientific (Beijing, China) and used directly.

All ¹H NMR spectra were recorded on a Bruker-400 spectrometer at frequencies of 400 MHz. The molecular weight of polymer was determined by using gel permeation chromatography (GPC) on a PL-GPC 220 instrument with a refractive index detector, calibrated with polystyrene standards. The columns used were MIXED-B 300 × 7.5 mm columns held at 40 °C using THF as eluents at a flow rate of 1.0 mL/min. ESI-MS experiments were carried out using a Bruker Q-TOF mass spectrometer. Samples were inserted into the electrospray interface at a flow rate of 2 mL/min and the source temperature was kept at 200 °C. Mass spectra were acquired over the range of m/z 50-3000 in positive ion mode.

Synthetic Process

Complexes 1-2 were synthesized according to the report.^{S1}

General Method for epoxides (PO, ECH, CHO and SO) ring-opening reaction with acetic acid catalysed by complex 1/TBAB^{S2}

0.015 mmol complex **1** and 0.15 mmol TBAB were added to a 25 mL tube fitted with a three-way stopcock equipped with a magnetic stirrer containing 0.75 mmol epoxides (PO, ECH, CHO and SO), the reaction was stirred for 300 min at 30 °C, add 0.75 mmol acetic acid, and the products were examined by ¹H NMR and GC-MS.

General Method for ECH ring-opening reaction with acetic acid catalysed by complex 1/cocatalyst^{S2}

0.015 mmol complex 1 and 0.15 mmol cocatalyst (PPNCl, TBACl, TBAB, TBAI) were added to a 25 mL tube fitted with a three-way stopcock equipped with a magnetic stirrer containing 0.75 mmol ECH, the reaction was stirred for 300 min at 30 °C, add 0.75 mmol acetic acid, and the products were examined by ¹H NMR and GC-MS.

EC ring-opening reaction with acetic acid catalysed by complex 1/TBAB

0.015 mmol complex **1** and 0.15 mmol TBAB were added to a 25 mL tube fitted with a three-way stopcock equipped with a magnetic stirrer containing 0.75 mmol EC, the reaction was stirred for 40 min at 170 °C, add 0.75 mmol acetic acid, and the products were examined by ¹H NMR and GC-MS.

General Method of batch feeding for the polymerization of *ε*-CL.

0.015 mmol complex **1** and 0.15 mmol cocatalyst were added to a 250 mL tube fitted with a three-way stopcock equipped with a magnetic stirrer containing 0.75 mmol epoxides, the reaction was stirred to the set temperature and reacted for a

predetermined time, add ε -CL and epoxides to make it reach ε -CL/epoxides/complex 1(Zn)/cocatalyst = 40000/1500/1/5. Then the mixture is reacted at 170 °C for 40 minute and the products were examined by ¹H NMR.

References

S1. J. W. Chen, X. M. Wu, H. N. Ding, N. Liu, B. Y. Liu, L. R. He, *ACS Sustain*. *Chem. Eng.*, 2021, **9**, 16210-16219. DOI: 10.1039/D0GC00469C.

S2. D. H. Nicole, Y. Li, H. C. Malcolm, *Macromolecules*, 2013, 46, 692-698.
DOI: 10.1021/ma302492p.

Entry	[&-CL]/[Zn]/[TBAB]/[ECH]	T (°C)	time (h)	yield $^{b}(\%)$
1	1000/1/0/0	110	9	none
2	1000/1/0/10	110	2	none
3	1000/0/2/10	110	2	none
4	1000/1/2/10	110	2	53.8
5	1000/0/2/0	110	2	none
6	1000/0/0/10	110	9	none
7	1000/1/2/0	110	2	none

Table S1 ROP of *E*-CL under complex 1/TBAB/ECH^{*a*}

^a Complex 1: 0.0017 g (0.00375 mmol Zn), 110 °C; ^b According to isolated mass.

Entry	Т	time	activity	yield ^b	Mn ^c	Đ¢
	(°C)	(min)	(Kg PCL/g complex 1)	(%)	(g/mol)	
1	130	40	0.73	7.3	7100	1.21
2	150	40	3.39	33.7	27200	1.39
3	170	40	7.17	71.3	48900	1.52
4^d	170	40	8.94	89.9	55600	1.64
5^d	150	40	7.06	70.2	42200	1.44
6^d	130	40	3.76	37.4	25900	1.31
7	150	100	7.59	75.5	47100	1.46
8	170	120	9.73	96.7	70600	1.68

Table S2 ROP of *ε*-CL at different temperature and time ^{*a*}

^{*a*} Entries 1-3, 7-8 were one feeding, [ε -CL]/[ECH]/[Zn]/[TBAB]=40000/1500/1/5, complex 1: 1.7 mg (0.00375 mmol Zn); ^{*b*} According to isolated mass; ^{*c*} Determined by GPC; ^{*d*} Entries 4-6: ECH first reacts with complex 1/TBAB at 50 °C for 350 min ([ECH]/[Zn]/[TBAB] = 25/1/5), and then ε -CL and the remaining ECH is added to reach [ε -CL]/[ECH]/[Zn]/[TBAB] = 40000/1500/1/5, react at different temperature for 40 min. Complex 1: 0.0136 g (0.03 mmol Zn).



Fig. S1 GC-MS spectrum of the crude mixture of the reaction of ECH under complex 1/TBAB (Conditions: [ECH]/[Zn]/[TBAB] = 25/1/5, 30 °C, 300 min, complex 1: 13.6 mg (0.03 mmol Zn)).



Fig. S2 ¹H NMR of different epoxides ring-opening products under complex 1/TBAB. (Conditions: [epoxides]/[Zn]/[TBAB] = 25/1/5, 30 °C, 300 min. Complex 1: 13.6 mg (0.03 mmol Zn). The conv. of epoxides = the ring-opened product (mol)/TBAB (mol). A: CHO ring-opening product; B: SO ring-opening product; C: PO ring-opening product)



Fig. S3 GC-MS spectrum of the crude mixture of the reaction of CHO under complex 1/TBAB (Conditions: [CHO]/[Zn]/[TBAB] = 25/1/5, 30 °C, 300 min, complex 1: 13.6 mg (0.03 mmol Zn)).



Fig. S4 GC-MS spectrum of the crude mixture of the reaction of SO under complex 1/TBAB (Conditions: [SO]/[Zn]/[TBAB] = 25/1/5, 30 °C, 300 min, complex 1: 13.6 mg (0.03 mmol Zn)).



Fig. S5 ¹H NMR of EC ring-opening products under complex 1/TBAB (Conditions: [EC]/[Zn]/[TBAB] = 25/1/5, 170 °C, 40 min, complex 1: 13.6 mg (0.03 mmol Zn)).



Fig. S6 GC-MS of EC ring-opening products under complex 1/TBAB (Conditions: [EC]/[Zn]/[TBAB] = 25/1/5, 170 °C, 40 min, complex 1: 13.6 mg (0.03 mmol Zn)).



Fig. S7 GC-MS spectrum of the crude mixture of the reaction of ECH under complex 1/PPNC1 (Conditions: [ECH]/[Zn]/[PPNC1] = 25/1/5, 30 °C, 300 min, complex 1: 13.6 mg (0.03 mmol Zn)).



Fig. S8 GC-MS spectrum of the crude mixture of the reaction of ECH under complex 1/TBAC1 (Conditions: [ECH]/[Zn]/[TBAC1] = 25/1/5, 30 °C, 300 min, complex 1: 13.6 mg (0.03 mmol Zn)).



Fig. S9 GC-MS spectrum of the crude mixture of the reaction of ECH under complex 1/TBAI (Conditions: [ECH]/[Zn]/[TBAI] = 25/1/5, 30 °C, 300 min, complex 1: 13.6 mg (0.03 mmol Zn)).



Fig. S10 ε-CL conversion versus time. (Conditions: [ε-CL]/[ECH]/[Zn]/[TBAB] = 40000/1500/1/5, 170 °C, complex 1: 1.7 mg (0.00375 mmol Zn))



Fig. S11A ¹H NMR of ECH ring-opening products at 30 °C (Conditions: [ECH]/[Zn]/[TBAB] = 25/1/5. Complex 1: 13.6 mg (0.03 mmol Zn). The conv. of ECH = the ring-opened product (mol)/TBAB (mol)).



Fig. S11B ¹H NMR of ECH ring-opening products at 50 °C (Conditions: [ECH]/[Zn]/[TBAB] = 25/1/5. Complex 1: 13.6 mg (0.03 mmol Zn). The conv. of ECH = the ring-opened product (mol)/TBAB (mol)).



Fig. S11C ¹H NMR of ECH ring-opening products at 70 °C (Conditions: [ECH]/[Zn]/[TBAB] = 25/1/5. Complex 1: 13.6 mg (0.03 mmol Zn). The conv. of ECH = the ring-opened product (mol)/TBAB (mol)).



Fig. S12 Arrhenius plots for the ECH ring-opening. The inset in the bottom left is activation energies, and the upper right corner is the linear fitting equation.



Fig. S13 ¹H NMR of ECH ring-opening products under complex 1/TBAI. (Conditions: [ECH]/[Zn]/[TBAI] = 25/1/5, 70 °C, 12 h. Complex 1:13.6 mg (0.03 mmol Zn). The conv. of ECH = the ring-opened product (mol)/TBAI (mol)).