Electronic Supplementary Material (ESI) for Chemical Science.

Supporting Information

for

Highly Efficient One-pot/one-step Synthesis of Multiblock Copolymers from Three-Component Polymerization of Carbon Dioxide, Epoxide and Lactone

Yang Li, Jiali Hong, Renjian Wei, Yingying Zhang, Zaizai Tong, Xinghong Zhang*, Binyang Du, Junting Xu, Zhiqiang Fan

MOE Key Laboratory of Macromolecular Synthesis and Functionalization, Department of Polymer Science and Engineering, Zhejiang University, Hangzhou, 310027, China

CORRESPONDING AUTHOR: Associate Prof. Dr. Xing-Hong Zhang

Tel and Fax: +86-571 87953732; E-mail: xhzhang@zju.edu.cn

OUTLINE

1 Materials.
2 Preparation of nanolamellar Zn-Co(III) DMCC catalyst.
3 Typical terpolymerization of CHO, CO_2 and ε-CL.
4 Copolymerization of CHO/CO_2.
5 Ring opening polymerization of ε-CL.
6 Control experiments.
  6.1 Testing of two catalysts under various reaction conditions
  6.2 Zn-Co(III) DMCC-catalyzed CHO/CO_2 copolymerization in the presence of HO-PCL-OH.
  6.3 $Sn(Oct)_2$-catalyzed ring-opening polymerization of ε-CL in the presence of HO-PCHC-OH.
7 The blending of PCL and PCHC.
8 Characterization.
9 Schemes and Figures.

1 Materials.

$K_3Co(CN)_6$ (Yixing City Lianyang Chemical Co., Ltd, China, 99%) was recrystallized from deionized water and dried in vacuum before use. Cyclohexene oxide (CHO) (Aladdin, 98%) was distilled over calcium hydride, in which trace amounts of cyclohexanediol was completely removed. ε-Caprolactone (ε-CL) was distilled under reduced pressure over calcium hydride. Benzyl alcohol (BnOH) was distilled under reduced pressure over magnesium sulfate and stored in vacuum over 4 Å molecular sieves. Stannous octoate (Sigma, Aldrich) was distilled at 140^{o}C for 1h, then added dried THF, the concentration of $Sn(OCt_2)$ in THF was 47.5 mg/mL. Carbon dioxide (99.995%) was used without purification. CH_2Cl_2, methanol, $ZnCl_2$ and *t*-BuOH were all analytical grade and used as received.

2 Preparation of nanolamellar Zn-Co(III) DMCC catalyst

The nanolamellar Zn-Co(III) DMCC catalyst was synthesized according to our previous report. The procedure is described as follows: $ZnCl_2$ (8.0 g) was dissolved into the mixed de-ionized water (10 mL) and *tert*-BuOH (10 mL). $K_3Co(CN)_6$ (6.6 g) was dissolved into 10 ml de-ionized water was added dropwisely into $ZnCl_2$ solution over 30 min at room temperature under vigorous stirring. The precipitation reaction was then heated to 75 °C and agitated greatly for 3 h. The resulting white precipitate was separated by pressure filtration and reslurried in a mixture of *tert*-BuOH and water (v/v = 1/1) with vigorous stirring over 2 h. Once again the precipitation was isolated and reslurried in a mixture of alcohol and water. With increasing proportion of alcohol over water, the precipitate was washed several times to remove potassium ion. Finally the deposition was reslurried in neat *tert*-BuOH, separated and dried at 70 °C under vacuum to a constant weight.

Table S1. BET results of Zn-Co(III) DMCC catalyst.

Cat.	BET surface area (m^2/g)	t-Plot Micropore Area (m^2/g)	t-Plot External Surface Area (m^2/g)	Average Pore Size (nm)
Zn-Co(III) DMCC	653.4	363.6	289.8	2.9

Table S2. Elemental analysis results of Zn-Co(III) DMCC catalyst.

Catalyst	Co (wt%)	Zn (wt%)	C (wt%)	N (wt%)	Cl (wt%)	H (wt%)
Zn-Co(III) DMCC	12.48	27.29	23.34	16.57	9.50	2.27

Zn and Co were determined by ICP method (ICP-AES instrument, Leeman Labs), and 37wt% HCl used for dissolving the catalyst. C, N and H were determined by VARIO MACRO CHN (Elemetar analysis). X-ray fluorescence (XRF) was used to determine the weight percentage content of Cl in the catalyst based on the standard curves, which is depicted from the concentration of each element *vs.* its XRF intensity. The standard sample for XRF test was the mixture of dried $Zn_3[Co(CN)_6]$ and $ZnCl_2$ with various weight rations.

3 Typical terpolymerization of CHO, CO_2 and ε-CL

The terpolymerization was conducted in a Büchi autoclave, which had been pre-dried at 80 °C under vacuum for 2 h. Desired amounts of Zn-Co(III) DMCC, $Sn(Oct)_2$ (in dried THF), BnOH, CHO and ε-CL were transferred into the autoclave equipped with a mechanical stirrer (500 rpm) and a pressure gauge, CO_2 was then pressurized to the target pressure. The autoclave was heated by a cyclic oil heating bath with designed temperature (e.g., 100 °C) and kept stirring for a certain time (e.g., 4 h). After reaction, the autoclave was cooled down to room temperature and CO_2 was slowly vented. A small amount of the crude product was removed for ^1H NMR spectroscopy. The remaining sample was dissolved in the CH_2Cl_2 and precipitated from methanol. This process was repeated for 3 times to give the purified polymers.

4 CHO/CO_2 Copolymerization (run-1 in Table 1)

The copolymerization was conducted in a Büchi autoclave which had been pre-dried. 70 mg Zn-Co(III) DMCC catalyst, and 60 mL CHO were added into the autoclave equipped with a mechanical stirrer and a pressure gauge, CO_2 was then pressurized to the target pressure. The autoclave was heated to 100 °C by a cyclic oil heating bath. Keep stirring for 4 h. After reaction, the autoclave was cooled down to room temperature and the excess CO_2 was slowly released. A small amount of the crude product was removed for ^{1}H NMR spectroscopy. The remaining sample was dissolved in the CH_2Cl_2 and precipitated from methanol. This process was repeated for 3 times to afford purified polymers.

A specific PCHC diol (HO-PCHC-OH) with number average molecular weight (M_n) of 700 (GPC, THF) and F_{CO2} of 59% was also prepared. The polymerization was conducted in a 100 mL autoclave which had been pre-dried at 80 °C for 2 h. Zn-Co(III) DMCC catalyst (20 mg), CHO (20 mL), de-ionized water (180 μL) and THF (20 mL) were added into the autoclave, CO_2 was then pressurized to 4.0 MPa while the temperature was increased to 75 °C. After stirring for 6 h, the autoclave was cooled down to room temperature and the excess CO_2 was slowly released. PCHC diol was precipitated from hexane.

5 Ring-opening polymerization (ROP) of ε-CL (run-2 in Table 1)

The polymerization reaction was conducted in a 25 mL flask, which had been flame dried. 12.0 mL ε-CL, 78 μL BnOH and 3.04 mL $Sn(Oct)_2$/THF solution were added into the autoclave equipped with magnetic stirrer. The flask was put in an oil bath, which had been heated to 100 °C. After reaction, the autoclave was cooled down to room temperature. A small amount of rude product was removed for ^{1}H-NMR spectroscopy. The remaining product was dissolved in CH_2Cl_2 and precipitated from methanol. This process was repeated for 3 times to afford purified PCL.

A specific PCL diol (HO-PCL-OH) with a M_n of 1700 (GPC, THF) using glycol as the initiator was prepared. The polymerization reaction was conducted in a pre-dried 25 mL Schlenk flask. 10 mL ε-CL, 0.52 mL ethylene glycol ($C_2H_6O_2$), 5 mL $Sn(Oct)_2$/THF solution were added into the flask with a magnetic stirrer. The flask was put in an oil bath, which had been heated to 110 °C. After reaction for 4 h, the flask was cooled down to room temperature. The product was precipitated from hexane.

6 Control experiments

6.1 Testing of two catalysts under various reaction conditions

Table S3. The summary of reaction conditions and results of the control experiments.[a]

Run	Zn-Co(III) DMCC (mg)	$Sn(Oct)_2$/THF (mL)	CHO (mL)	CO_2 (MPa)	ε-CL (mL)	Conv.% CHO/ε-CL
S1	3.0	0	0	0	2.0	-
S2	3.0	0	0	5.0	2.0	-
S3	3.0	0	2.0	4.0	2.0	55 / -
S4	0	0.8	2.0	5.0	0	-
S5	0	0.8	2.0	0	0	-
S6	0	0.8	2.0	0	2.0	-/ 74
S7	0	0.8	2.0	3.5	2.0	- / 80
S8	3.0	0.8	2.0	5.0	0	95 / -
S9	3.0	0.8	0	0	2.0	- / 86
S10[b]	12.0	0	10.0	4.0	0	>99 / -
S11[c]	0	4.0	0	5.0	0.5	- / 64

[a] 100 °C, 4 h, 20 μL BnOH; runs S1-S3: 1.0 mL dried THF; runs S9-S10: no BnOH; $Sn(Oct)_2$/THF solution: 47.5 mg/mL; [b] 7.0 g HO-PCL-OH with a M_n of 1700 (PDI: 1.4) was used; [c] 0.25 g HO-PCHC-OH with a M_n of 700 (PDI: 1.6) was used, [OH]/[ε-CL] = 1/10.

6.2 Zn-Co(III) DMCC-catalyzed CO_2/CHO copolymerization in the presence of HO-PCL-OH (Run-S10 in Table S3)

The Zn-Co(III) DMCC-catalyzed CO_2/CHO copolymerization in the presence of HO-PCL-OH was conducted in a 100 mL autoclave, which had been pre-dried at 80 °C under vacuum for 2 h. 12 mg Zn-Co(III) DMCC catalyst, 10 mL of CHO and 7.0 g HO-PCL-OH with M_n of 1700 were added into the autoclave equipped with a mechanical stirrer and a pressure gauge, CO_2 was then pressurized to 4.0 MPa. The autoclave was heated to 100 °C. Keep stirring for 4 h. After reaction, the autoclave was cooled down to room temperature and the excess CO_2 was slowly released. A small amount of the crude product was removed for ^{1}H NMR test directly. The remaining sample was dissolved in the CH_2Cl_2 and precipitated from hexane. This process was repeated twice to remove small molecules. M_n and PDI of the resultant product were 5700 and 2.1, respectively (see Figure S6).

6.3 $Sn(Oct)_2$-catalyzed ring-opening polymerization of ε-CL in the presence of HO-PCHC-OH (Run-S11 in Table S3)

The $Sn(Oct)_2$-catalyzed ring-opening polymerization of ε-CL in the presence of HO-PCHC-OH was conducted in a 10 mL autoclave which had been pre-dried at 100 °C in oven for 2 h. 0.5 mL ε-CL, 4.0 mL $Sn(Oct)_2$/THF solution (47.5 mg/mL), 0.25 g HO-PCHC-OH (M_n: 700) were added into the autoclave equipped with magnetic stirring. CO_2 was introduced and the pressure kept at 5.0 MPa. The autoclave was put in an oil bath, which had been heated to 100 °C. Keep stirring for 4 h. After reaction, the autoclave was cooled down to the room temperature. A small amount of the crude product was removed for ^1H NMR spectroscopy. The remaining sample was dissolved in the CH_2Cl_2 and precipitated from hexane. M_n and PDI of the resultant product were 1500 and 1.6, respectively(see Figure S6).

7 The blending of PCL and PCHC

A certain amount of PCL (M_n = 22.7 kg/mol, PDI = 1.7, run-2 in Table 1) and PCHC (M_n = 37.4 kg/mol, PDI = 2.2, synthesized at 70 °C as the same procedure as section **4**, F_{CO2} = 95.2%) with weight ratio of 1/1 were dissolved in 20 mL CH_2Cl_2 and stirred for 2 h in order to prepare PCL/PCHC blends. Afterwards, rotary evaporation was applied to remove the CH_2Cl_2 and the obtained blends were further dried under vacuum at 50 °C for 24 h. This sample was used for testing the mechanical property.

For excluding the possible transesterification between PCHC and PCL in the presence of two catalysts, another blend of PCHC (M_n = 37.4 kg/mol) and PCL (M_n = 22.7 kg/mol) was carried out in the presence of two catalysts, THF and CO_2 in the autoclave at 100 °C for 4 h. This reaction was conducted in a 10 mL autoclave, which was pre-dried at 100 °C in oven for 2 h. Then 1.0 mg Zn-Co(III) DMCC, 0.57 g PCHC, 0.57 g PCL, 0.15 mL $Sn(Oct)_2$/THF solution and 5.0 mL dried THF were added into the cooled autoclave with a magnetic stirrer. After reaction at 100 °C and CO_2 pressure of 4.0 MPa for 4 h, the autoclave was cooled down to room temperature and the excess CO_2 was slowly released. A small amount of the crude product was removed for ^1H NMR test directly. The remaining sample was dissolved in CH_2Cl_2 and precipitated from hexane. This process was repeated for 3 times to remove small molecules. The M_n and PDI of the blend was 26.4 kg/mol and 2.4, respectively.

8 Characterization

Gel permeation chromatography (GPC) was performed in a PL-GPC220 equipped with an HP 1100 pump from Agilent Technologies to determine the number-average molecular weight (M_n) and polydispersity (PDI). The GPC columns were eluted with THF at 1.0 mL/min at 40 °C. The concentration of sample was ca. 3 wt.% and the injection volume was 50 μL. Calibration was performed using monodispersed polystyrene standards covering the molecular weight ranging from 580 to 460000 Da.

Fourier transform infrared spectroscopy (FT-IR) spectra were recorded in a Bruker Vector 22 FTIR spectrometer. Typically, 32 scans were signal-averaged to reduce spectral noise.

^{1}H NMR,^{13}C NMR and ^{1}H–^{13}C HMQC spectra of the products were obtained on a Bruker Advance DMX 400, 500 and 600 MHz spectrometer using $CDCl_3$ as solvent and TMS as internal reference.

Differential scanning calorimetry (DSC) was taken on a DSCQ200 quipped with a liquid nitrogen cooling system. 3~5 mg of samples were placed in aluminum pans. The cooling and heating rates were 10 or 20 °C /min. For the observation of T_gs, ca. 10 mg of samples and the cooling and heating rate of 20 °C /min were used.

Scanning electron microscopy (SEM): The morphology of the catalysts was observed by scanning electron microscopy (SEM) (JEOL JSM 840A instrument) under vacuum after sputter-coated with gold at 10 mA for 1 min.

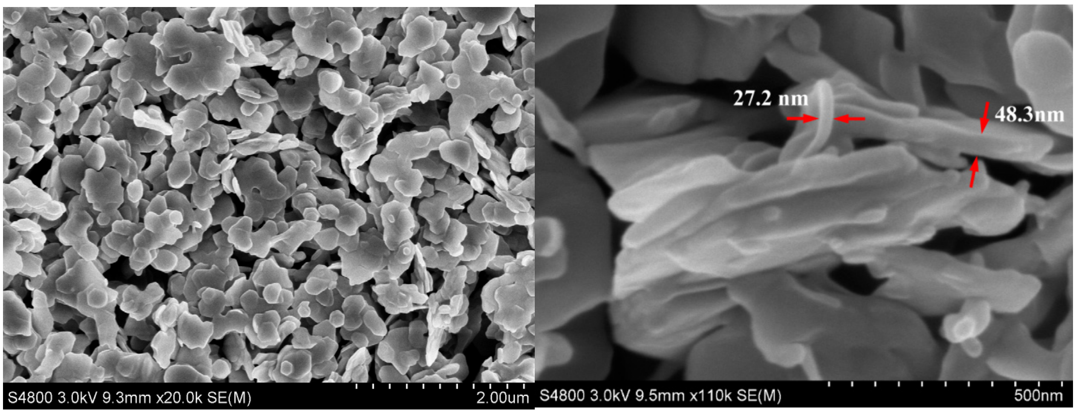
N_2 adsorption isotherms: The specific surface area was tested using the BET method (Quantachrome automated gas sorption system, AUTOSORB-1-C) and was determined by N_2 adsorption isotherms (at liquid nitrogen temperature). The pore size distribution was calculated by analyzing the adsorption/desorption branches of the isotherm using the Barrett-Joyner-Halenda (BJH) method.

Small-Angle X-ray Scattering. Small-angle X-ray scattering (SAXS) experiments were performed at

BL16B1 beamline in Shanghai Synchrotron Radiation Facility (SSRF) in China. The wavelength of X-ray was 1.24 Å, and the sample-to-detector distance was set as 5100 mm. Two-dimensional (2D) SAXS patterns at room temperatures were recorded. The average exposure time was 300 s for each scan. Bull tendon was used as standard material for calibrating the scattering vector. The 2D SAXS patterns were converted into one-dimensional (1D) SAXS profiles using Fit2D software.

Mechanical Behavior. The stress−strain behavior of two MBCs under uniaxial tension was performed on a CMT 4204 instrument. The tensile specimens were cut from the compression-molded films with the thickness of 2.0 mm. The distance of two grips was 30 mm, and the specimen width was 13.0 mm. A strain rate of 10 mm/min, i.e., 100% per min, was applied to uniaxial tension.

9 Schemes and Figures



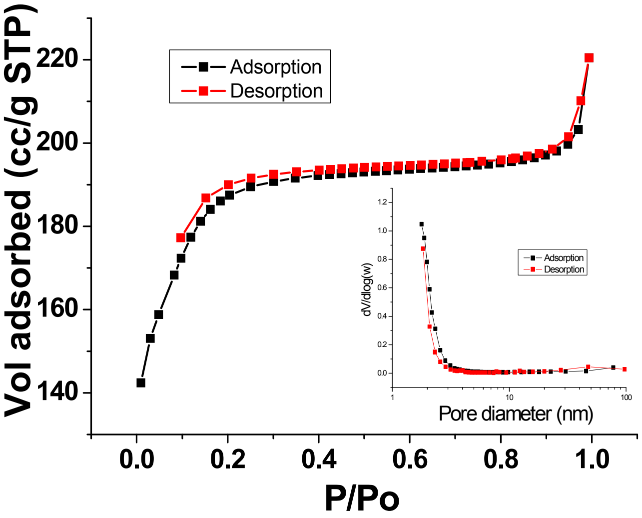
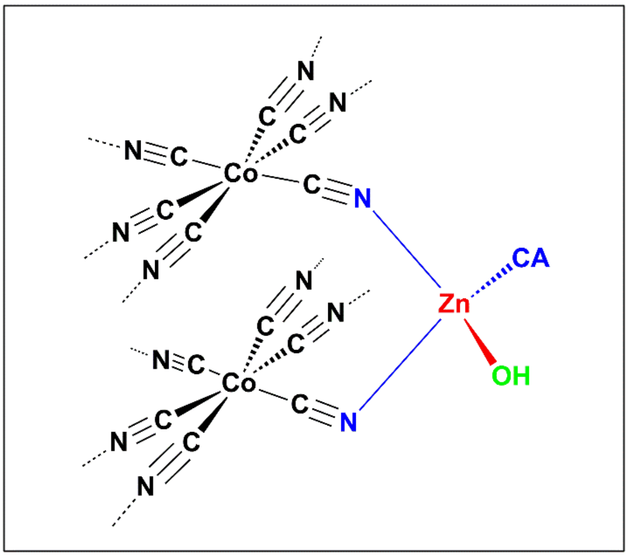
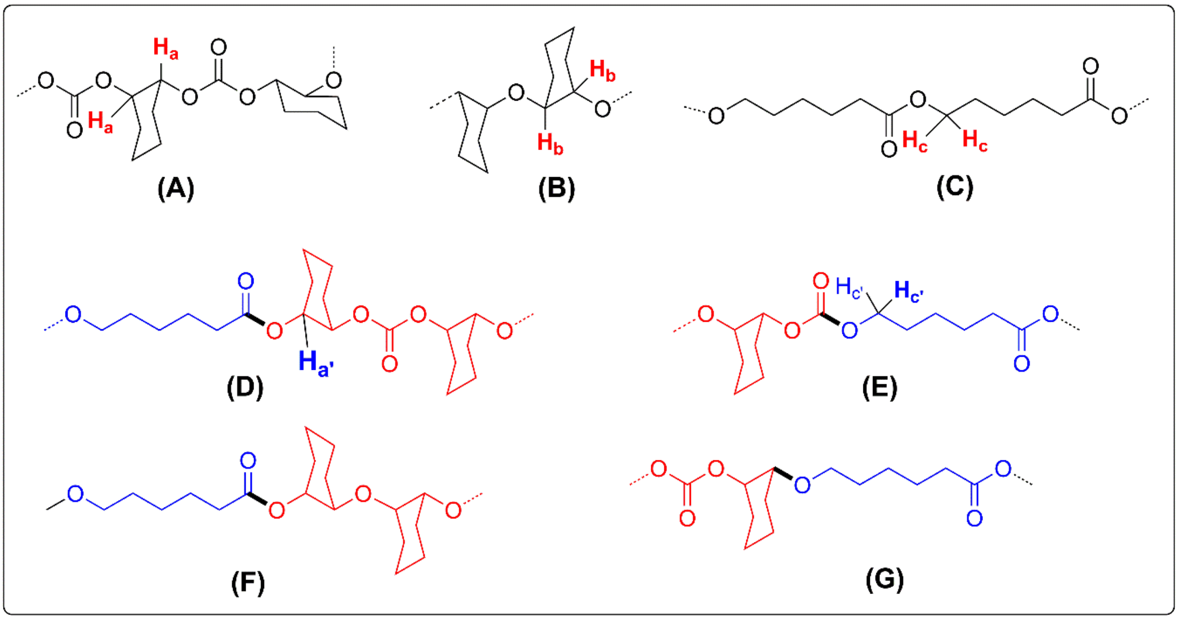


Figure S1. SEM images and N_2 absorption and desorption curves of nanolamellar Zn-Co(III) DMCC catalyst.



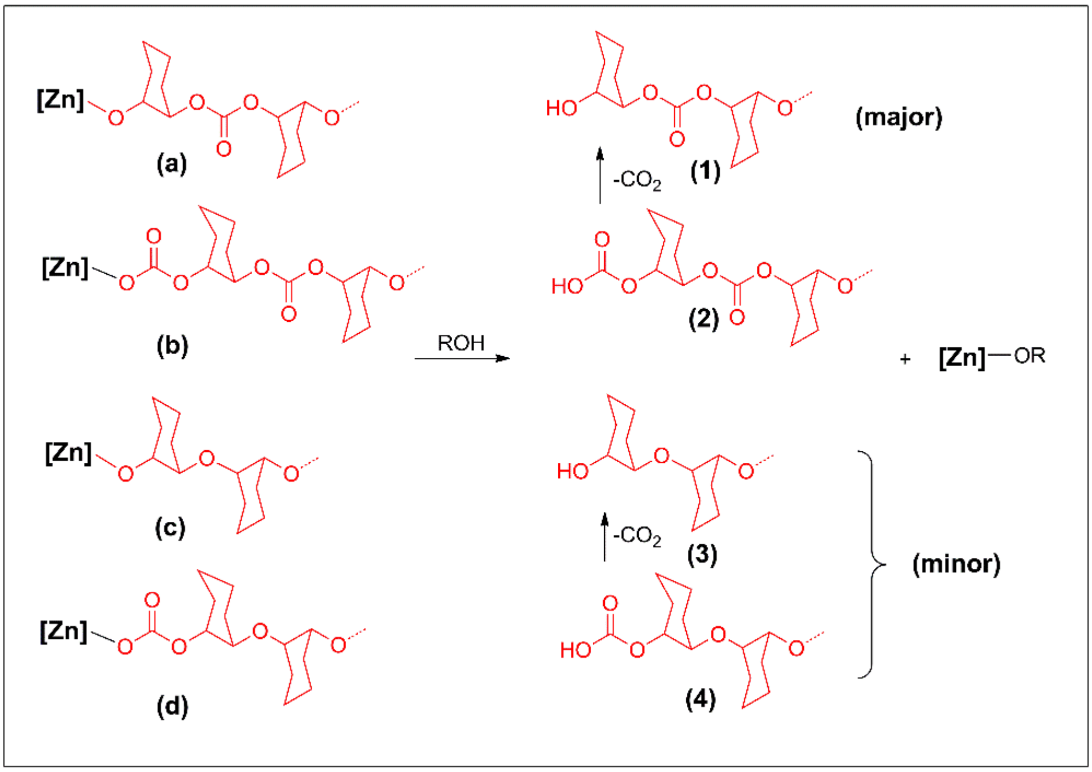
Scheme S1. The proposed ground-state structure of the active site of Zn-Co(III) DMCC catalyst. In this structure, two CN^- are linked by Zn^{2+} and Co^{3+} ions and are calculated as one negative charge in one Zn^{2+} structure, which meets the principle of electroneutrality due to the presence of OH^- (or Cl^-) based on the elemental results. Herein, CA is complexing agent, generally H_2O and *t*-BuOH when *t*-BuOH was used.



Scheme S2. All predicted junction units and corresponding protons.

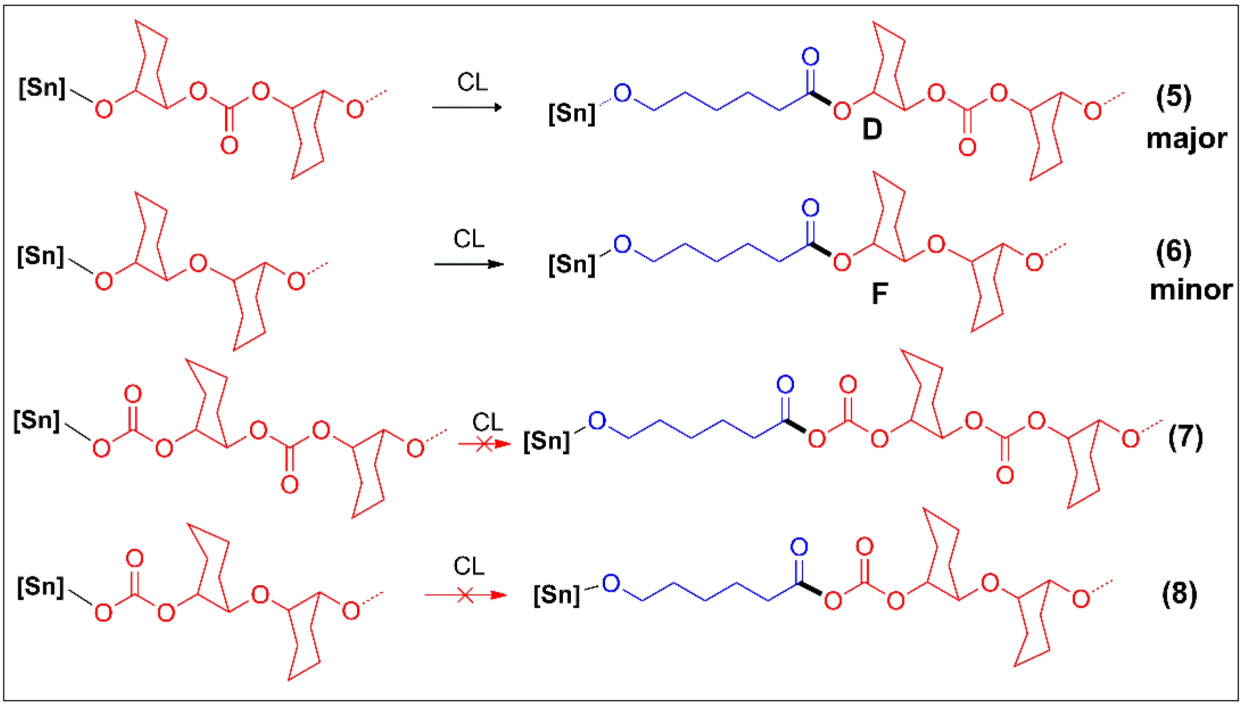
The analysis of the production of all possible junction units (D)-(G) in Scheme 2:

(i) All possible chain transfer reactions at Zn site:



Description: R-OH could be BnOH (the initiator for ring-opening polymerization of ε-CL), H_2O and dormant polymer chain with at least one –OH end group. When R is a dormant polymer chain, chain exchange reaction would occur. Because the ether content in PCHC was relative small and insertion of CHO into PCL-O-Zn was rather slow, **(1)** and **(2)** were the major dormant PCHC chain, while **(3)** and **(4)** were minor. Thereof, (**2**) and (**4**) could possibly exist in the presence of CO_2, which was captured by ESI-MS in our previous report [X.-K. Sun, X.-H. Zhang, R.-J. Wei, B.-Y. Du, Q. Wang, Z.-Q. Fan, G.-R. Qi, J. Polym. Sci., Part A: Polym. Chem., 2012, 50, 2924-2934]. When **(1)-(4)** were attached to the Sn center via chain transfer reaction, four kinds of propagating species would generate, as shown as follows.

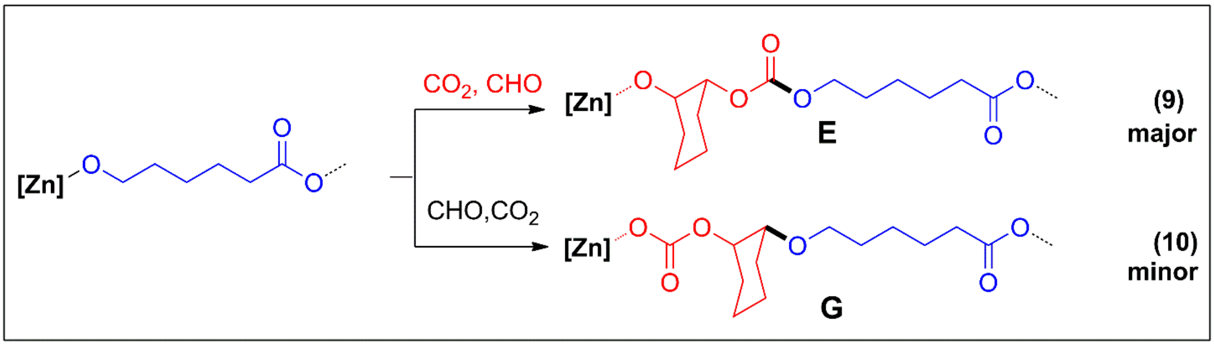
(ii) Four possible propagating species generated by the insertion and ring-opening polymerization of ε-CL:



Description: After the insertion of ε-CL and followed ROP, the propagating species **(5)-(8)** would form. (**5**) and (**6**) could be formed because the Sn-alkoxide was highly active to ring-opening polymerization of ε-CL, however, because the end –OCOOH group was unstable (releasing CO_2) and had relative strong acidity and was hard to initiate ring-opening polymerization of ε-CL (the nucleophilic attack of –OCOO-Sn was pretty weak), the equation of **(7)** and **(8)** were inhibited in the system.

As a result, (**D**) was the main junction unit, and (**F**) could be neglected when the ether content in the final polymers was low.

(iii) the possible formation of **(E)** and **(G)** from Zn-O-PCL:



When PCL-OH was attached to the zinc center of Zn-Co(III) DMCC catalyst, two kinds of propagating species **(9)** and **(10)** coexisted in the system, the junction unit of (**E**) would be mainly generated because CO_2 insertion was a fast step. Even if (**G**) were formed, the chemical shifts of the corresponding protons might be covered by ether units, while the ether content in MBC was pretty small in Table 1.

Scheme S3. The analysis of the production of the junction units (**D**)-(**G**).

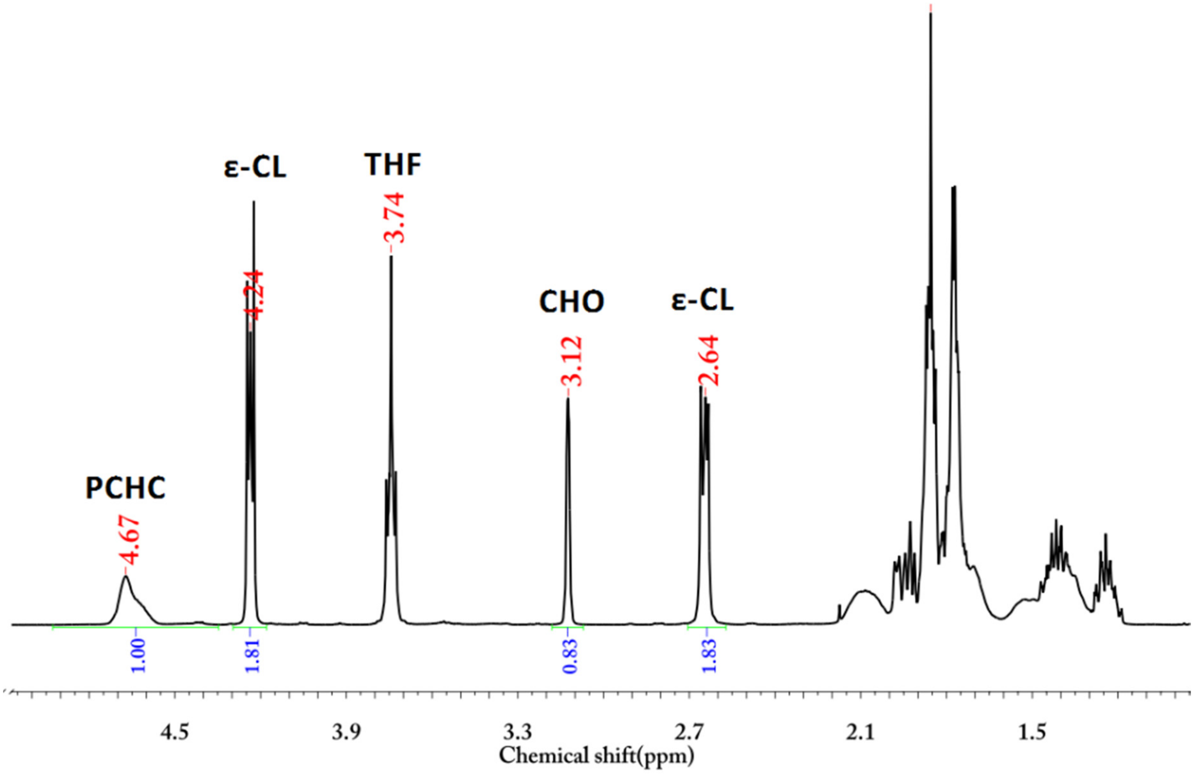
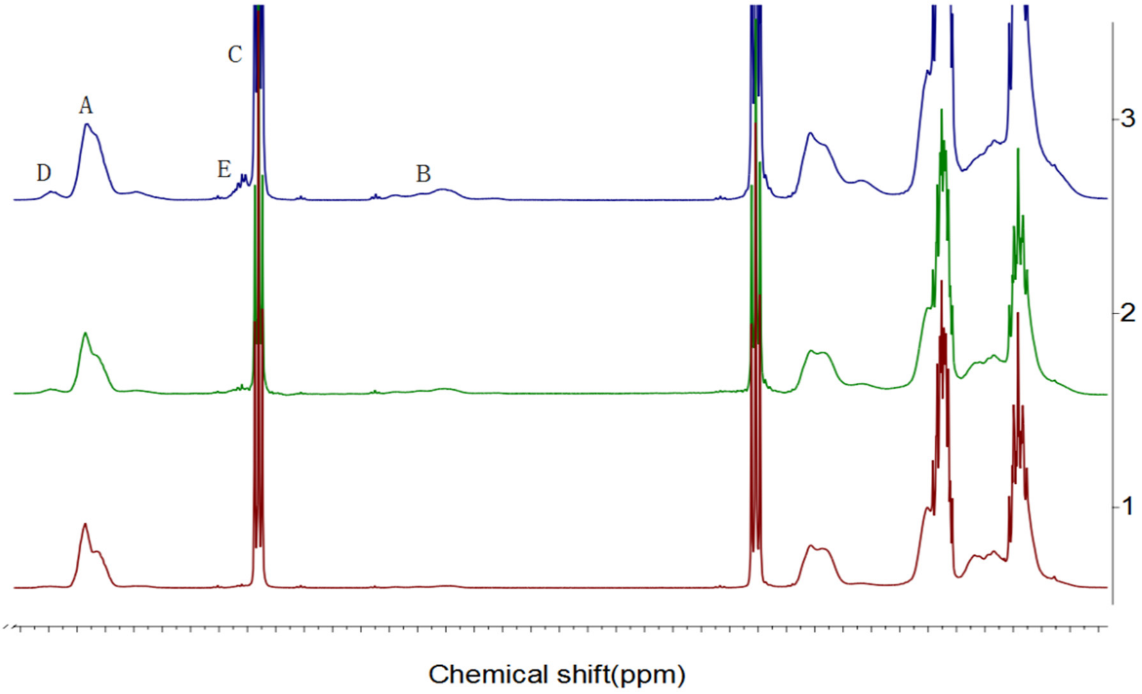
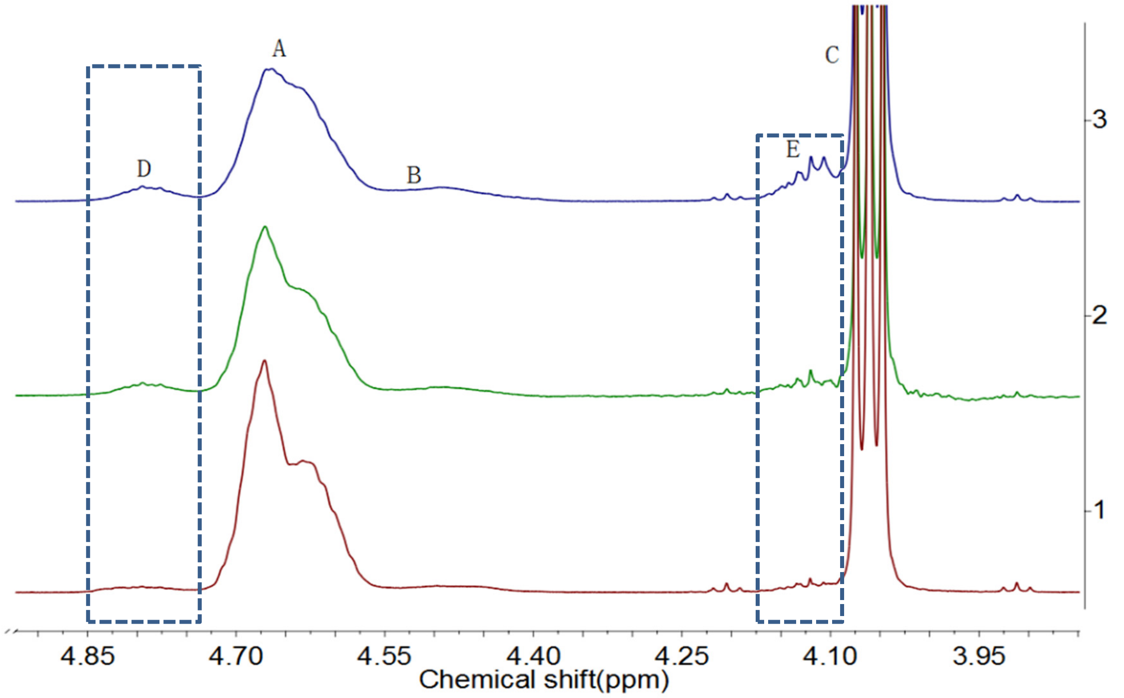


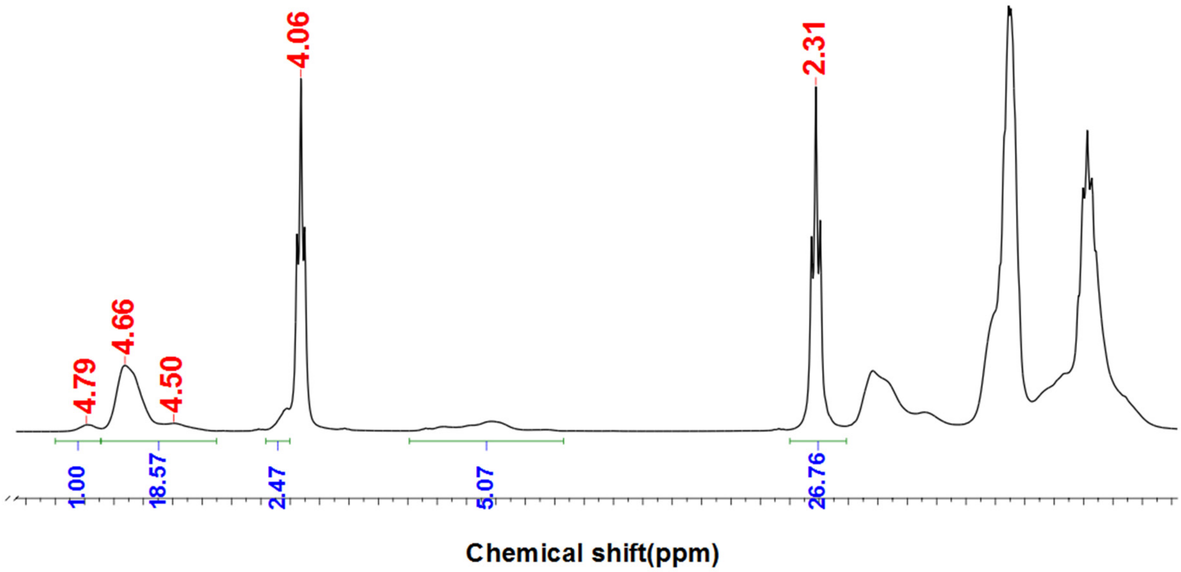
Figure S2. ^{1}H NMR spectra of the crude product of run-S3 in Table S3 (400 MHz, $CDCl_3$ as a solvent).



(A) ^{1}H NMR spectra of run-5 (Spectra 1), run-4 (Spectra 2) and run-3 (Spectra 3) obtained with rotating the NMR tube during testing in a 500 MHz NMR instrument (CDCl$_3$) (Table 1). The sample concentration: 10-15 mg/mL CDCl$_3$.



(B) The magnified region of Spectra 1, 2 and 3 (3.9-4.9 ppm) of **(A)**.



(C) An example (run-3 MBC in Table 1 without rotating the NMR tube during test, the sample concentration: ca. 100 mg/mL $CDCl_3$) for the calculation of carbonate, ester, ether units in MBC and the rate percentage of two CCERs to two propagations (*N*).

The calculation method:

C% (polyester) = $A_{2.31}/(A_{4.67}+A_{3.2\text{-}3.5}+A_{2.31})$ *100%;

A% (polycarbonate) = $A_{4.67}/(A_{4.67}+A_{3.2\text{-}3.5}+A_{2.31})$ *100%;

B% (polyether) = $A_{3.2\text{-}3.5}/(A_{4.67}+A_{3.2\text{-}3.5}+A_{2.31})$ *100%;

N% = $(2*A_{4.79}+A_{4.13})/(A_{4.79}+A_{4.67}+A_{4.50}+A_{3.2\text{-}3.5}+A_{2.31})$ *100%;

Tr_A% = $2*A_{4.79}/(A_{4.79}+A_{4.67}+A_{4.50}+A_{3.2\text{-}3.5})$ *100%;

Tr_B% = $A_{4.13}/A_{2.31}$ *100%.

Herein, T_{rA} and T_{rB} were defined as the ratio of the integral area of **D** and **E** to the carbonate and ester units, respectively. T_{rA} and T_{rB} could represent the rate ratios of CCERs at Sn and Zn sites to the polycarbonate and polyester formation, respectively. In most cases, T_{rA} and T_{rB} are approximately equal, as the following calculation from Table 1 in the text. The similar result can be seen in Table S6.

^{1}H NMR test without rotating the NMR tube:

Run in Table 1	Tr$_A$ (%)	Tr$_B$ (%)	*N* (%)
3	**11**	**9**	**9**
4	**8**	**7**	**7**
5	**6**	**4**	**5**
6	**10**	**10**	**10**

^{1}H NMR test with rotating the NMR tube:

Run in Table 1	Tr$_A$ (%)	Tr$_B$ (%)	*N* (%)
3	**11**	**10**	**10**
4	**11**	**7**	**9**
5	**4**	**2**	**3**

Figure S3. The ^{1}H NMR spectra of MBCs under different testing conditions and the calculation results of the carbonate, ester, and ether units in MBC and *N* values.

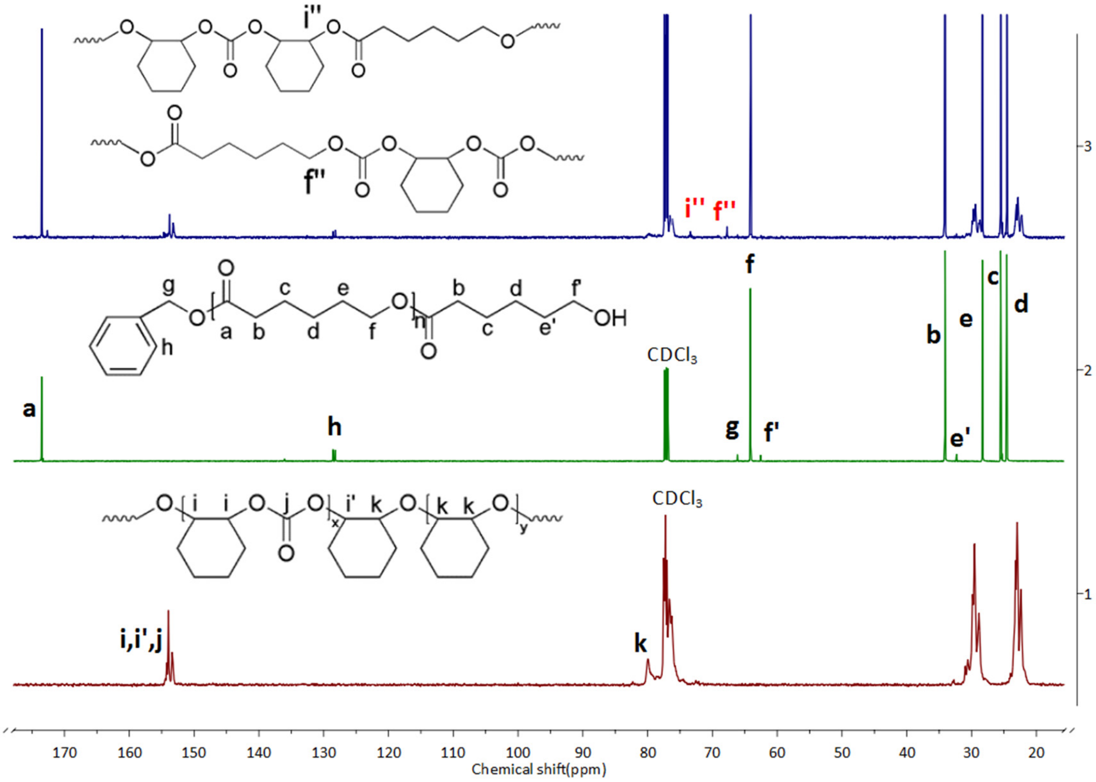


Figure S4. ^{13}C NMR spectra of the purified PCL, PCHC and the run-3 terpolymer in Table 1 (Spectra 1, 2 and 3 respectively), (with 600 MHz NMR instrument, CDCl$_3$ as a solvent).

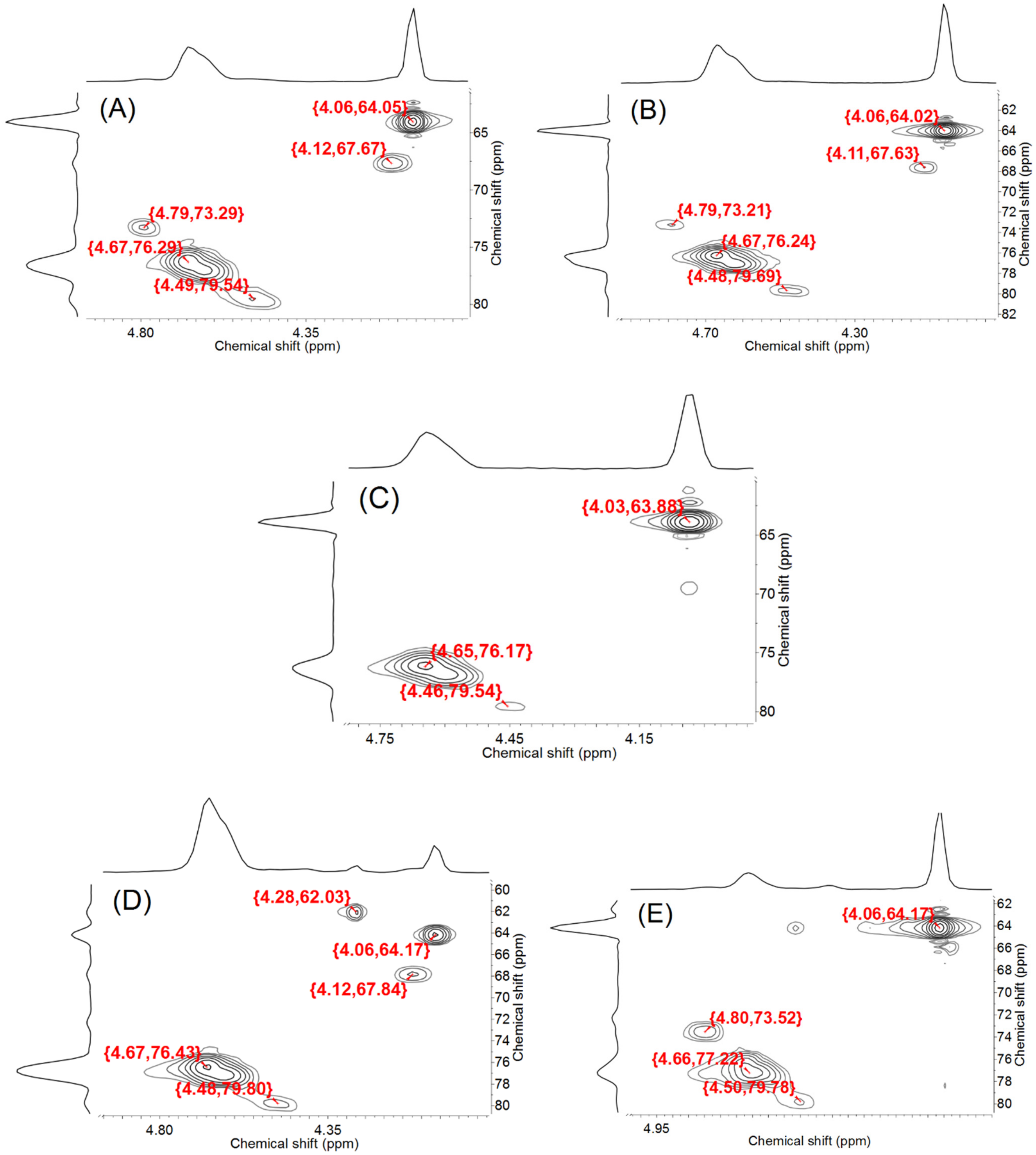


Figure S5. ^{1}H-^{13}C HSQC spectra from a 500 MHz NMR instrument ($CDCl_3$ as a solvent): (A) Run-4 terpolymer in Table 1 ([BnOH]/[ε-CL] = 1/150); (B) Run-5 terpolymer in Table 1 ([BnOH]/[ε-CL] = 0). (C) PCL (run-2 in Table 1)/PCHC (F_{CO2}: 95.2%, synthesized at 70 ºC) blend; (D) The product from **1**-catalyzed CO_2/CHO copolymerization in the presence of HO-PCL-OH (M_n = 1700); and (E) The product from **2**-catalyzed ring-opening polymerization of ε-CL in the presence of HO-PCHC-OH (M_n = 700) under 5.0 MPa CO_2.

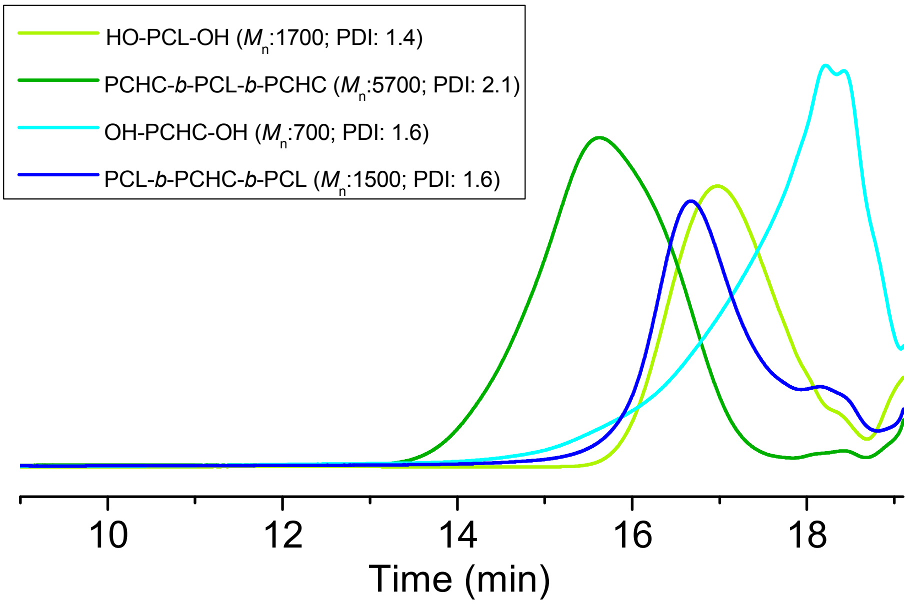


Figure S6. GPC traces of the control experiments of runs S10-11 in Table S3.

Table S4. Effect of reaction time on CHO/CO_2/ε-CL terpolymerization by two catalysts.[a]

Run	Time (min)	M_n (g/mol)	PDI	Composition (%)			Conv. (%)		Tr_A (%)	Tr_B (%)	N^b (%)
				C	**A**	**B**	CHO	ε-CL			
S12	10	/	/	/	/	/	<1	<1	/	/	/
S13	15	700	1.25	20.5	7.4	72.1	8.8	2.3	/	/	/
S14	30	2900	1.67	30.6	47.8	21.6	53	25	9	13	11
S15	40	3900	1.69	32.4	52.2	15.4	58	29	10	13	11
S16	60	6100	1.89	37.8	47.7	14.6	90	60	9	12	11
S17	75	6600	1.98	39.9	50.1	10.0	95	68	13	15	14
S18	120	7500	2.01	43.1	51.0	5.9	99	77	13	13	13

[a]Polymerization conditions: 75.0 mg of Zn-Co(III) DMCC catalyst, 1.25 mL BnOH, 625.0 mg $Sn(Oct)_2$, 50.0 mL CHO, 50.0 mL ε-CL, the system was up to ca. 98 °C within 15 min, then kept at 101±2 °C from ca. 20-120 min, mechanical stirring; [b]The ratio of the integral area of the junction units **(D+E)** to the total units of MBC in ^{1}H NMR spectra, 4.0 MPa CO_2 pressure.

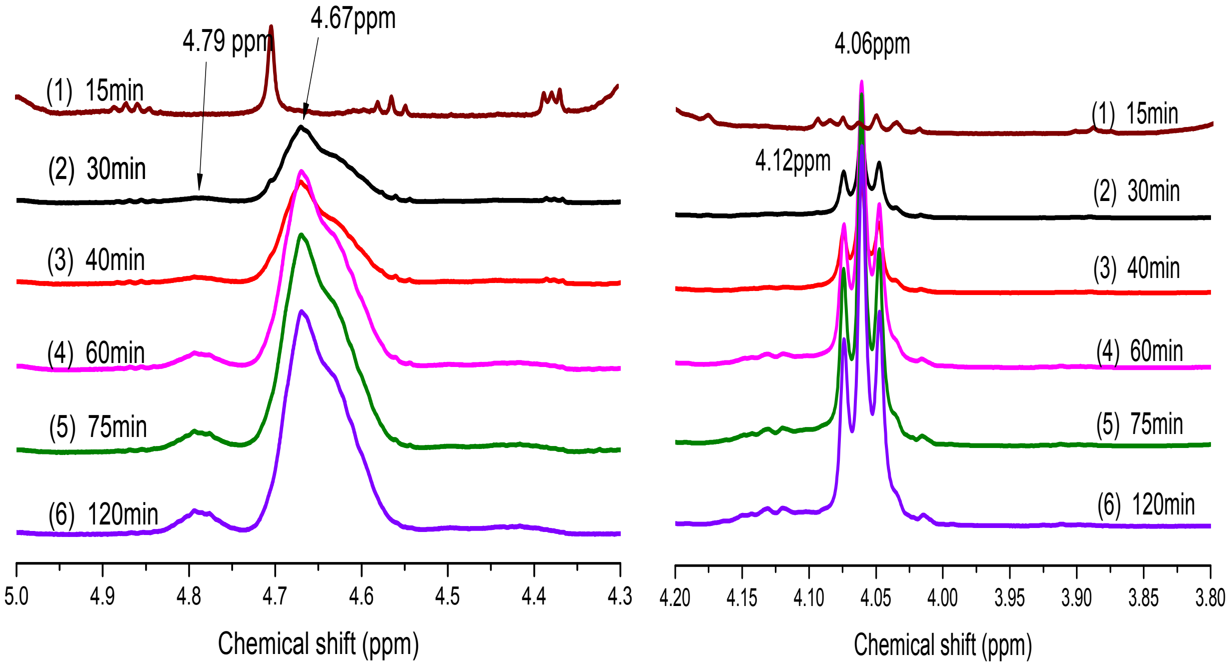


Figure S7. ^{1}H NMR spectra (500 MHz, $CDCl_3$) of the crude terpolymers sampled at different times (Table S4).

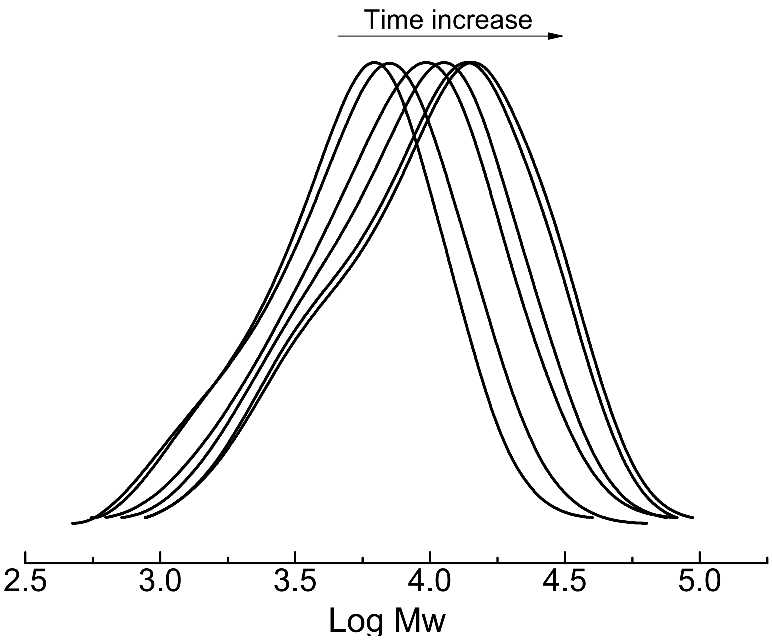


Figure S8. GPC traces of the crude terpolymers picked out at different reaction times (Table S4).

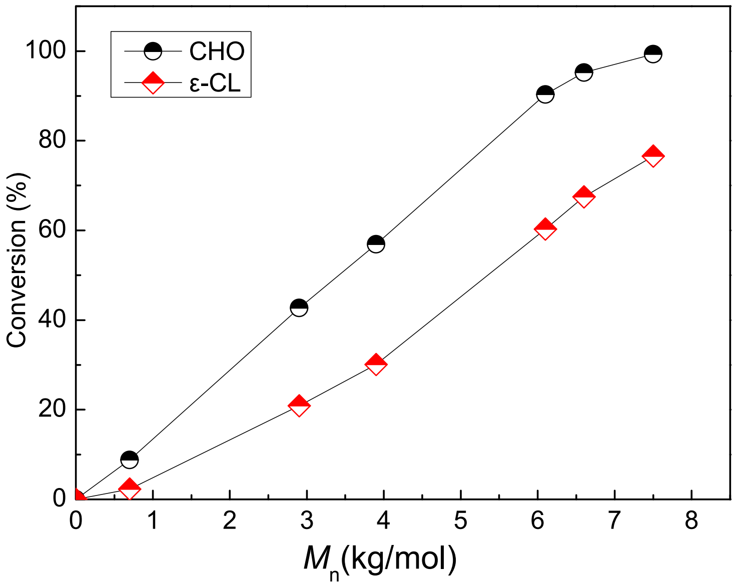


Figure S9. The conversion rate of CHO and ε-CL versus M_n of terpolymers (Table S4).

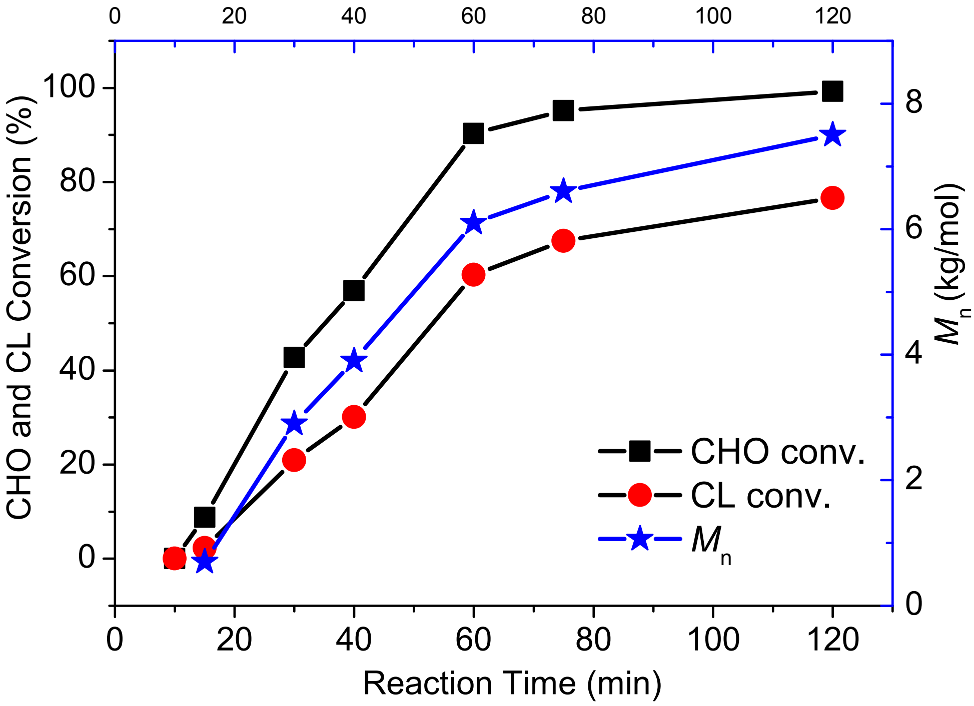


Figure S10. The conversion of CHO, ε-CL and M_n of the resultant product versus polymerization time (Table S4).

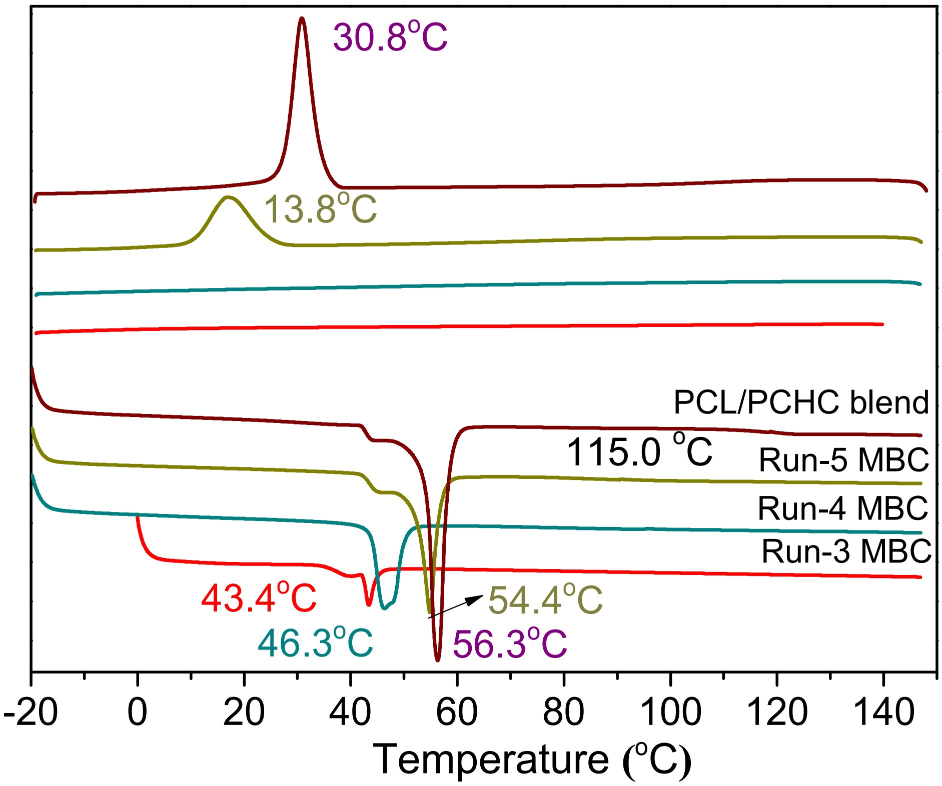


Figure S11. DSC curves of MBCs (ca. 3.0-5.0 mg) from runs 3-5 and PCL/PCHC blend (M_n: 26.4 kg/mol), 10 °C/min, N_2 atmosphere. Because small amounts of samples were used and relative slow heating and cooling rates, T_gs of MBCs herein were not clearly observed.

Table S5. Melting and crystallization behaviors of MBCs and PCHC/PCL blend (10 °C/min).

Sample	$T_{c,PCL}$ (°C)[a]	$T_{m,PCL}$ (°C)[b]	$\Delta H_{m,PCL}$ (J/g)[c]	$X_{c,PCL}$ (%)[d]
Run-3 MBC (Table 1, [BnOH]/[ε-CL] = 1/40)	-	43.42	9.65	7.1
Run-4 MBC (Table 1, [BnOH]/[ε-CL] = 1/150)	-	46.34	41.14	30.2
Run-5 MBC (Table 1, no BnOH)	13.76	52.72	62.44	45.9
PCHC/PCL blend	30.80	56.34	74.82	55.0

[a] $T_{c,PCL}$ denotes the crystallization temperature of PCL segments in the cooling run, respectively;

[b] $T_{m,PCL}$ is the melting temperature of PCL segments in the second heating run, respectively;

[c] $\Delta H_{m,PCL}$ denotes the fusion enthalpy of PCL segments in the second heating run, respectively, $\Delta H_{m,PCL} = \Delta H_{m,sample}$/PCL (weight percentage in MBC);

[d] $X_{c,PCL} = \Delta H_{m,PCL}/\Delta H^0_{m,PCL}$, where $\Delta H^0_{m,PCL}$ is 136.1 J/g.

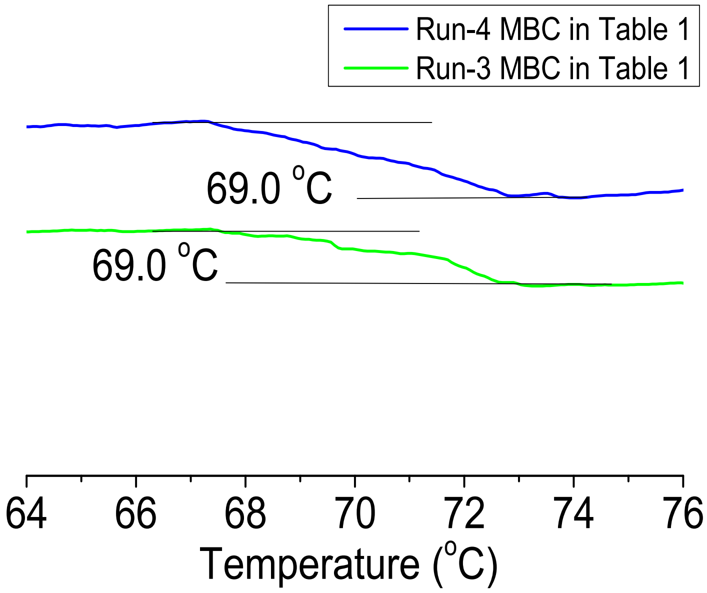


Figure S12. Magnified DSC traces of Figure 5-B with subtracting the base lines for runs 3-4 MBCs.

Table S6. The effect of the reaction temperatures, pressure and [OH]/[ε-CL] molar ratios on the structure of the synthesized MBCs.[a]

Run	T/°C	Pre. (MPa)	[BnOH]/ [ε-CL]	M_n[b](kg/ mol)	PDI[b]	Composition (%)[c]			Tr_A[d] (%)	Tr_B[d] (%)	*N*[e] (%)	Conv. (%)[f]	
						C	**A**	**B**				CHO	ε-CL
S19	110	2.0	1:40	9.3	2.5	51.7	38.0	10.3	12	9	10	100	95
S20	110	2.0	1:150	15.9	2.3	48.9	44.2	6.9	7	6	7	97	94
S21	110	1.0	1:40	7.2	2.0	50.2	22.3	27.5	9	8	8	99	99
S22	100	2.0	1:40	8.9	2.8	45.8	43.9	10.3	11	10	11	99	87
S23	100	2.0	1:100	11.7	2.7	47.8	44.3	7.9	8	7	7	99	82
S24	90	2.0	1:40	8.4	2.8	45.5	49.2	5.3	9	8	9	78	61

[a]Polymerization conditions: 35.0 mg of Zn-Co(III) DMCC, [ε-CL]/[$Sn(Oct)_2$] = 300, 4.0 h, 30.0 mL CHO, 30.0 mL ε-CL, 20.0 mL THF; [b]Determined by GPC of the purified product using THF as a solvent; [c]**C** (polyester) = $A_{2.31}/(A_{4.67}+A_{3.2\text{-}3.5}+A_{2.31})$, **A** (polycarbonate) = $A_{4.67}/(A_{4.67}+A_{3.2\text{-}3.5}+A_{2.31})$, **B** (polyether) = $A_{3.2\text{-}3.5}/(A_{4.67}+A_{3.2\text{-}3.5}+A_{2.31})$ from ^{1}H NMR spectra; [d]$Tr_A = 2*A_{4.79}/(A_{4.79}+A_{4.67}+A_{4.50}+A_{3.2\text{-}3.5})$, $Tr_B = A_{4.13}/A_{2.31}$; [e]*N*, the ratio of the integral area of the junction units **(D+E)** to the total units of MBC in ^{1}H NMR spectra, $N = (2*A_{4.79}+A_{4.13})/(A_{4.79}+A_{4.67}+A_{4.50}+A_{3.2\text{-}3.5}+A_{2.31})$; [f]Based on ^{1}H NMR spectra of the crude products.

Table S7. Results of CHO/CO_2/ε-CL terpolymerization under different CHO/ε-CL feeding ratios[a]

Run	CHO/ε-CL	M_n[b]	PDI[b]	Composition (%)[c]			Tr_A[d]	Tr_B[d]	N[e]	Conv. (%)[f]	
	(mL/mL)	(kg/mol)		**C**	**A**	**B**	(%)	(%)	(%)	CHO	ε-CL
S25	48/12	26.9	1.9	86.3	12.0	1.7	14	3	5	95	99
S26	12/48	9.3	2.2	17.5	64.6	17.9	5	14	6	96	90

[a]Reaction conditions: 100 °C, 4.0 MPa, 35.0 mg of Zn-Co(III) DMCC, 4.0 h, 30.0 mL CHO, 30.0 mL ε-CL, 20.0 mL THF, no BnOH was used; [b]Determined by GPC of the purified product using THF as a solvent, [c]**C** (polyester) = $A_{2.31}/(A_{4.67}+A_{3.2\text{-}3.5}+A_{2.31})$, **A** (polycarbonate) = $A_{4.67}/(A_{4.67}+A_{3.2\text{-}3.5}+A_{2.31})$, **B** (polyether) = $A_{3.2\text{-}3.5}/(A_{4.67}+A_{3.2\text{-}3.5}+A_{2.31})$ from ^{1}H NMR spectra; [d]Tr_A = $2*A_{4.79}/(A_{4.79}+A_{4.67}+A_{4.50}+A_{3.2\text{-}3.5})$, Tr_B = $A_{4.13}/A_{2.31}$, [e]N, the ratio of the integral area of the junction units **(D+E)** to the total units of MBC in ^{1}H NMR spectra, $N = (2*A_{4.79}+A_{4.13})/(A_{4.79}+A_{4.67}+A_{4.50}+A_{3.2\text{-}3.5}+A_{2.31})$; [f]Based on the ^{1}H NMR spectra.

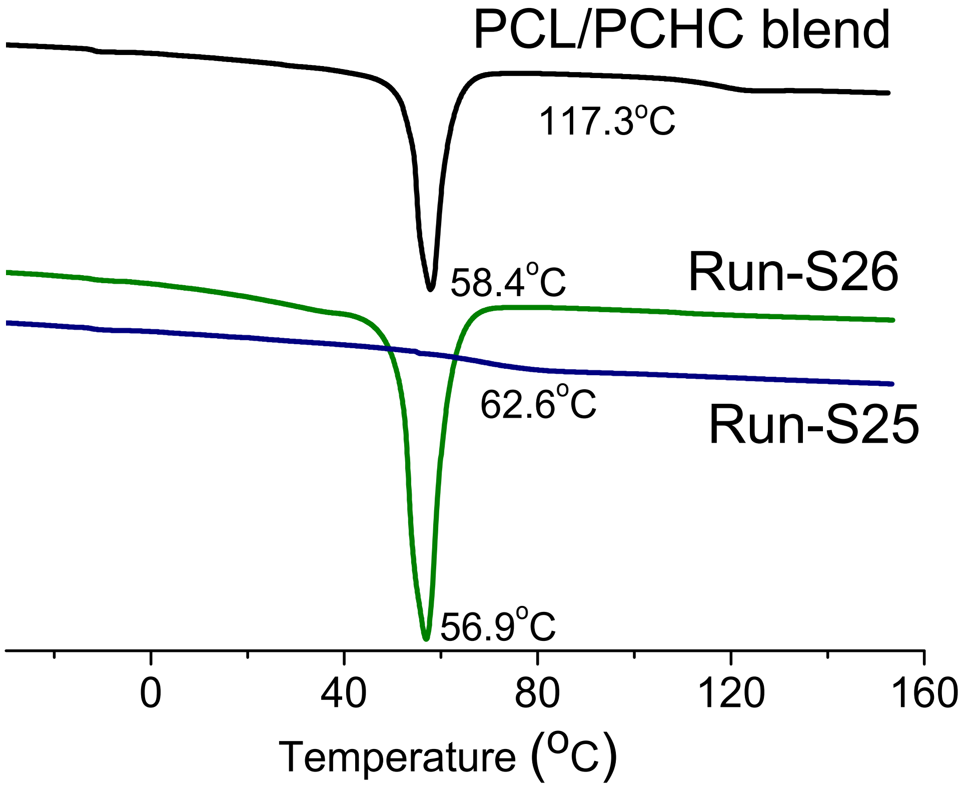


Figure S13. DSC traces of MBCs from run-S25 and run-S26 in Table S7 and the PCL/PCHC blend (M_n: 26.4 kg/mol) obtained with the heating rate of 20 °C/min in N_2 atmosphere, ca. 10 mg sample was used. Samples were kept at 160 °C for 10 min, then were cooled to -20 °C and heated to 160 °C again. For run-S25, just a T_g at 62.6 °C was observed because this MBC had 17.5% PCL blocks.