Supporting Information for

Cis-Fused Cyclohexane Promoted the Chemical Recycling of Polycarbonate to Monomer

Si-Yi Shan,[a] Wei Zhang,[b] Qing Cao,[a] Yun-Cong Ye,[a] Zhongzheng Cai,*[a] Jian-Bo Zhu*[a]

[a]National Engineering Laboratory of Eco-Friendly Polymeric Materials (Sichuan), College of Chemistry, Sichuan University, Chengdu, 610064, P. R. China
[b]Tianjin Key Laboratory of Brine Chemical Engineering and Resource Eco-utilization, College of Chemical Engineering and Materials Science, Tianjin University of Science and Technology, Tianjin 300457, China

Materials and Methods

NMR. ^{1}H and ^{13}C NMR spectra were recorded on an Agilent 400-MR DD2 or a Brüker Advance 400 spectrometer (^{1}H: 400 MHz, ^{13}C: 100 MHz). Chemical shifts (δ) for ^{1}H and ^{13}C NMR spectra are given in ppm relative to TMS. The residual solvent signals were used as references for ^{1}H and ^{13}C NMR spectra and the chemical shifts converted to the TMS scale ($CDCl_3$: δH = 7.26 ppm, δC = 77.16 ppm. The following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet.

Size Exclusion Chromatography (SEC). Measurements of polymer weight-average molecular weight (M_w), number average molecular weight (M_n), and molecular weight distributions or dispersity indices ($Đ = M_w/M_n$) were performed via size exclusion chromatography (SEC). The SEC instrument consisted of an Agilent LC system equipped with one guard column and two PL gel 5 µm mixed-C gel permeation columns and coupled with an Agilent G7162A 1260 Infinity II RI detector; The analysis was performed at 40 °C using THF as the eluent at a flow rate of 1.0 mL/min. The instrument was calibrated with nine polystyrene standards, and chromatograms were processed with Agilent OpenLab CDS Acquisition 2.5 molecular weight characterization software.

Differential scanning calorimetry (DSC). Melting-transition temperature (T_m) and glass-transition temperature (T_g) of purified and thoroughly dried polymer samples were measured by differential scanning calorimetry (DSC) on a TRIOS DSC25, TA Instrument. All T_g values were obtained from a second scan after the thermal history was removed from the first scan. The first heating rate was 10 °C/min and cooling rate was 10 °C/min and the second heating rate was 10 °C/min.

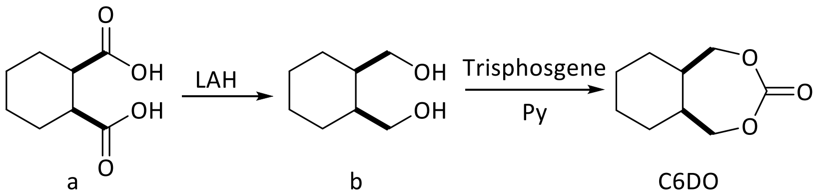
Thermo-gravimetric analysis (TGA). Decomposition onset temperatures (T_{onset}) and maximum rate decomposition temperatures (T_{max}) of the polymers were measured by thermal gravimetric analysis (TGA) on a TGA55 Analyzer, TA Instrument. Polymer samples were heated from ambient temperature to 600 °C at a heating rate of 10 °C/min. Values of T_{max} were obtained from derivative (wt%/°C) vs. temperature (°C) plots and defined by the peak values, while T_{onset} values were obtained from wt% vs. temperature (°C) plots and defined by the temperature of 5% weight loss.

Matrix-assisted laser desorption/ionization time-of-flight mass spectroscopy (MALDI-TOF MS). An AXIMA Performance instrument was used in reflection mode with anthralin as the matrix. A thin layer of a 1% NaI solution was first deposited on the target plate, followed by the solutions of matrix (0.4 µL, 5 mg/mL in tetrahydrofuran) and polymer (2 µL, 5 mg/mL in tetrahydrofuran) were mixed together. The mixed solution was spotted on the MALDI sample plate and air-dried. The raw data was processed in the Shimadzu Biotech MALDI-MS software.

Mechanical Analysis. Tensile stress/strain testing was performed by an Instron 34SC-1 universal testing system. Samples were made by melt press in a steel mold ($50 \times 4 \times 0.4$ mm^3) and were stretched at a strain rate of 10 mm/min at ambient temperature until break. The measurements were performed 4 times for each test, and the values reported are averaged from the measured data.

X-Ray Crystallographic Analysis. X-Ray single-crystal diffraction data were collected on an Agilent Technologies Gemini plus single crystal diffraction.

General Monomer Preparations



Scheme S1. Synthesis of C6DO.

To a suspension of $LiAlH_4$ (15.2 g, 400 mmol, 4 equiv.) in anhydrous THF (300 mL) was added *cis*-cyclohexane-1,2-dicarboxylic acid (17.2 g, 100 mmol, 1 equiv.) in portions at 0 °C. The mixture was stirred at room temperature overnight and then heated at 60 °C for 5 h. The reaction mixture was cooled to 0 °C by adding 15.2 mL of H_2O, 15.2 mL of 15% aq NaOH and 45.6 mL of H_2O. The reaction mixture was diluted with Et_2O, filtered and concentrated under reduced pressure to yield crude b, (*cis*-cyclohexane-1,2-diyl) dimethanol.

In a 1000 mL round bottom flask, b (12.0 g, 83.2 mmol, 1.0 equiv.) was added to a solution of pyridine (39.5 g, 499.2 mmol, 6.0 equiv.) in 50 mL THF. The reaction mixture was chilled to 0 °C. A solution of triphosgene (12.4 g, 41.6 mmol, 0.5 equiv.) in THF (50 mL) was added dropwise over 1 h at this temperature. The reaction mixture was subsequently warmed up to ambient conditions and stirred for another 2 h. The reaction was quenched with the addition of saturated NH_4Cl and washed by saturated aqueous $NaHCO_3$ and saturated aqueous NaCl. Then the organic layer was separated and evaporated to yield crude product. The residue was purified by flash column chromatography on silica gel to afford product as a white solid (85% yield). ^1H NMR (400 MHz, $CDCl_3$) δ 4.23 (m, 7.3 Hz, 2H), 4.08 (dd, *J* = 12.2, 2.8 Hz, 2H), 2.05 (s, 2H), 1.73 – 1.64 (m, 2H), 1.62 – 1.54 (m, 2H), 1.51 – 1.31 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.6, 72.3, 37.3, 25.8, 23.5.

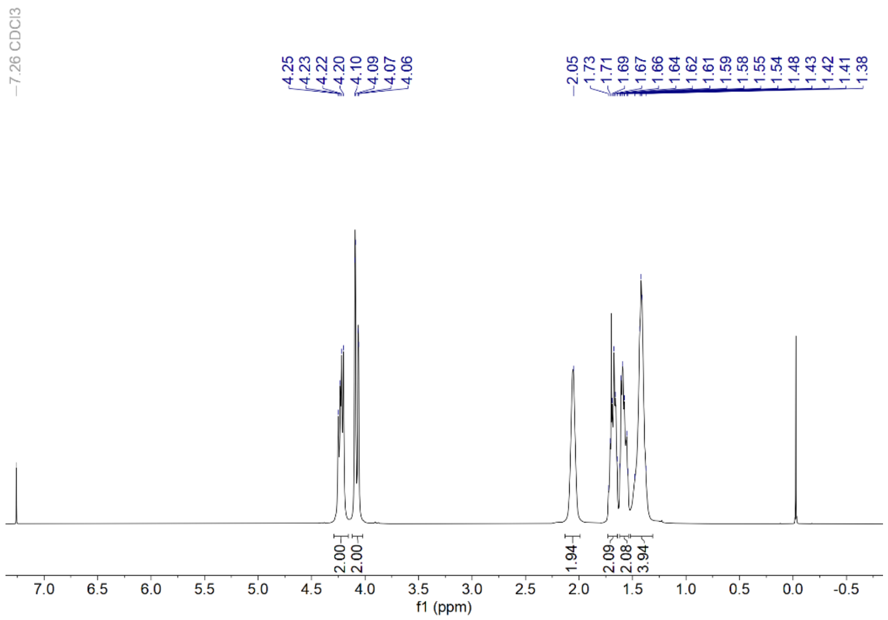


Fig. S1. ^1H NMR ($CDCl_3$, 25 °C) spectrum of C6DO.

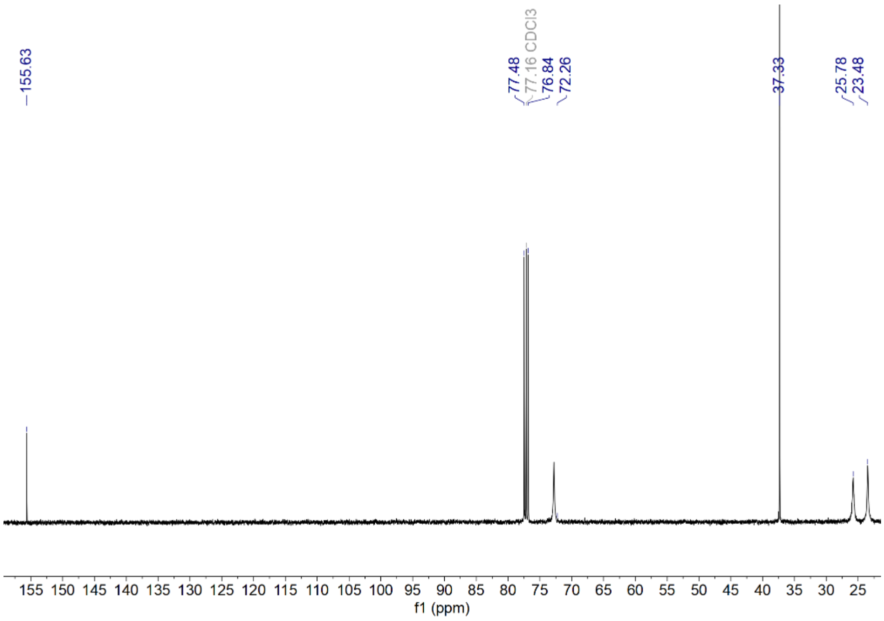


Fig. S2. ^{13}C NMR (CDCl$_3$, 25 °C) spectrum of C6DO.

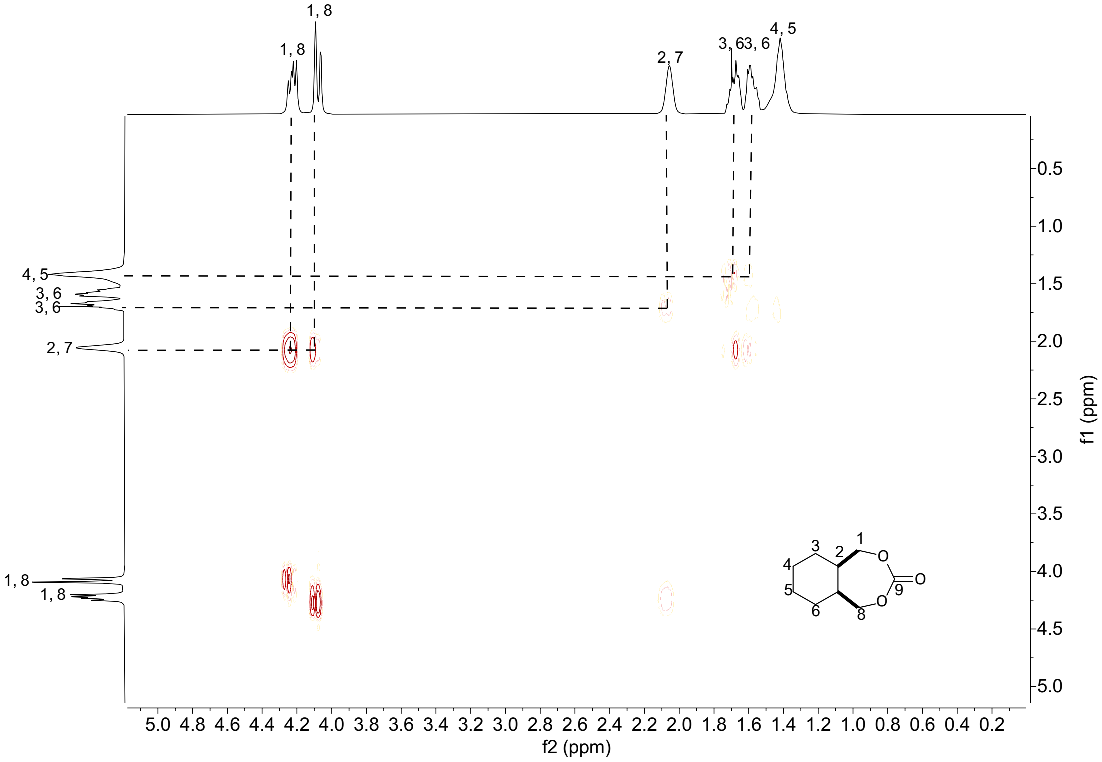


Fig. S3. COSY (CDCl$_3$, 25 °C) spectrum of C6DO.

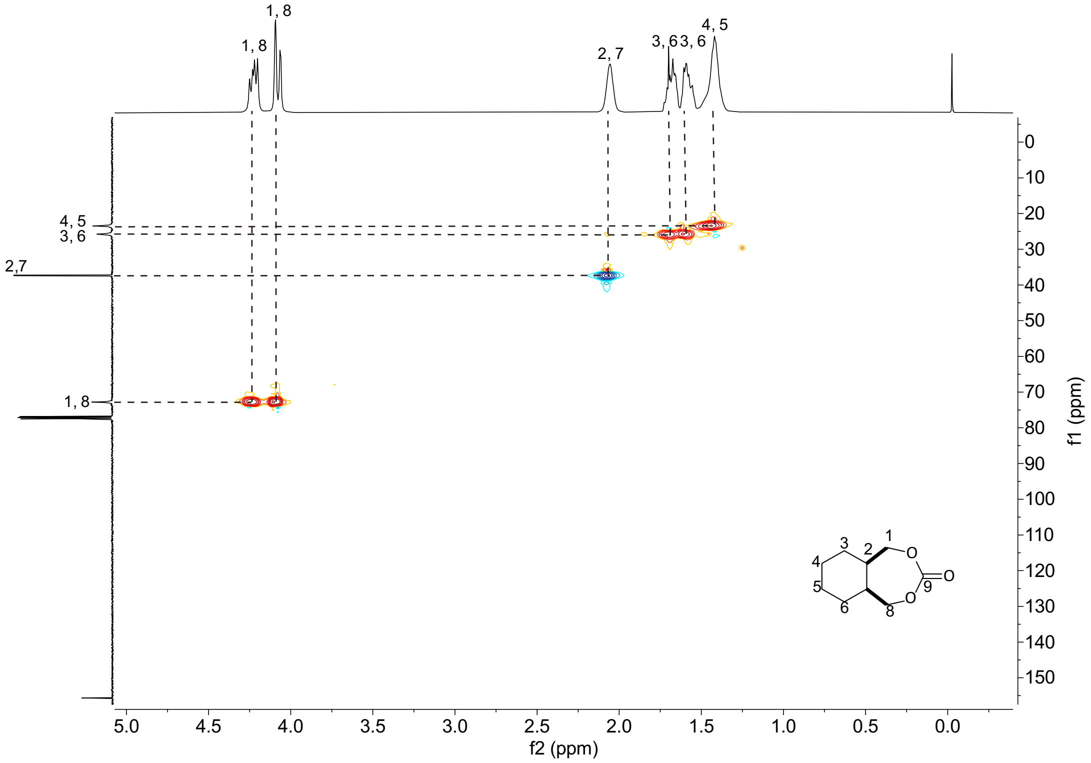


Fig. S4. HSQC (CDCl$_3$, 25 °C) spectrum of C6DO.

X-Ray Single-Crystal Structures

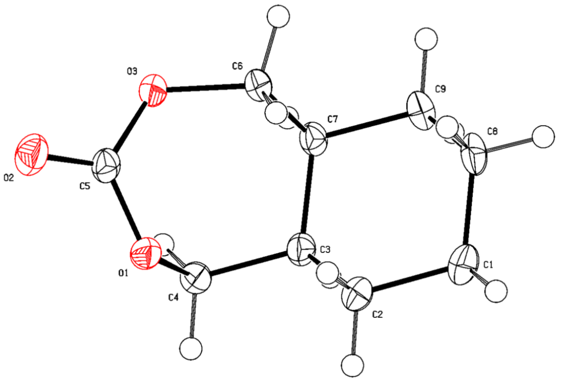


Fig. S5. X-ray structure of C6DO.

Compound	C6DO
CCDC number	2301341
Empirical formula	$C_9H_{14}O_3$
Formula weight	170.20
Temperature (K)	150.0
Crystal system	orthorhombic
Space group	$P2_12_12_1$
A (Å)	5.3341(11)
B (Å)	7.7048(16)
C (Å)	20.413(4)
α (°)	90
β (°)	90
γ (°)	90
Volume (Å^3)	838.9(3)
Z	4
Calc. ρ (g/cm^3)	1.348
μ (mm^{-1}	0.825
F (000)	368.0
Crystal size (mm^3)	0.5 × 0.45 × 0.23
Radiation	CuKα (λ = 1.54178)
2θ range for data collection (°)	8.664 to 137.212
Index ranges	$-6 \le h \le 6$, $-9 \le k \le 9$, $-24 \le l \le 24$
Reflections collected	17245
Independent reflections	1555 [R_{int} = 0.0712, R_{sigma} = 0.0318]
Data/restraints/parameters	1555/0/109
Goodness-of-fit on F^2	1.096
Final R indexes [I>=2σ (I)]	R_1 = 0.0310, wR_2 = 0.0774
Final R indexes [all data]	R_1 = 0.0312, wR_2 = 0.0775

General Polymerization Procedures

Procedures for the homopolymerization of C6DO.

Note: Prior to polymerization, C6DO was further purified via recrystallization from a mixture of petroleum ether and ethyl acetate ($v_{(\text{petroleum ether})}$: $v_{(\text{ethyl acetate})}$ = 3:1), sublimation at 80 °C, and recrystallization from toluene inside glovebox.

Polymerizations were performed in 4 mL vials at room temperature inside the glovebox. The solution of catalyst **Zn1** in toluene was added to the vigorously stirred prepared monomer and initiator (benzyl alcohol) solution (toluene). After a desired period of time, the polymerization was quenched by addition of 1 mL of benzoic acid/wet chloroform (10 mg mL^{-1}) and a 20 µL of aliquot was taken from the reaction mixture and prepared for ^1H NMR analysis to obtain the percentage of monomer conversion. The quenched mixture was diluted in DCM and precipitated into 100 mL of cold methanol, filtrated, and washed with cold methanol. Finally, the polymer product was dried in a vacuum oven at 60 °C to a constant weight.

Procedures for the copolymerization of C6DO and L-LA.

Copolymerizations were performed in 4 mL vials at room temperature inside the glovebox. The solution of **Zn1** in toluene was added to the vigorously stirred prepared monomers (C6DO and L-LA) and initiator (benzyl alcohol) solution(toluene). After a desired period of time, the polymerization was quenched by addition of 1 mL of benzoic acid/wet chloroform (10 mg mL^{-1}) and a 20 µL of aliquot was taken from the reaction mixture and prepared for ^1H NMR analysis to obtain the percentages of each monomer conversion. The quenched mixture was diluted in DCM and precipitated into 100 mL of cold methanol, filtrated, and washed with cold methanol. This procedure was repeated twice to ensure any catalyst residue or unreacted monomer was removed. Finally, the polymer product was dried in a vacuum oven at 60 °C to a constant weight.

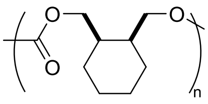
Table S1. Screen of various catalysts for copolymerization of C6DO and L-LA.[a]

Entry	Catalyst	Time /h	Conv.[b]/%		$M_{n,\text{SEC}}$[c]/kDa	$Đ$[c]
			L-LA	C6DO		
1	**Zn1**	1.5	94	88	208	1.11
2	DBU	3	88	85	255	1.45
3	TBD	2	95	0	181	1.55
4	DPP	3	0	0	-	-

[a]Reaction conditions: initiator (I) = benzyl alcohol (BnOH), toluene, [M] = 1 M, room temperature. [b]Monomer conversion measured by ^1H NMR of the quenched solution. [c]Number-average molecular weight (M_n) and dispersity index ($Đ = M_w/M_n$), determined by size exclusion chromatography (SEC) at 40 °C in THF.

Polymer Characterizations

NMR spectra of polymers



PC6DO

^{1}H NMR (400 MHz, $CDCl_3$) δ 4.11 (d, J = 7.3 Hz, 4H), 2.16 – 2.06 (m, 2H), 1.57 – 1.46 (m, 6H), 1.44 – 1.36 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.4, 68.3, 36.6, 26.2, 23.3.

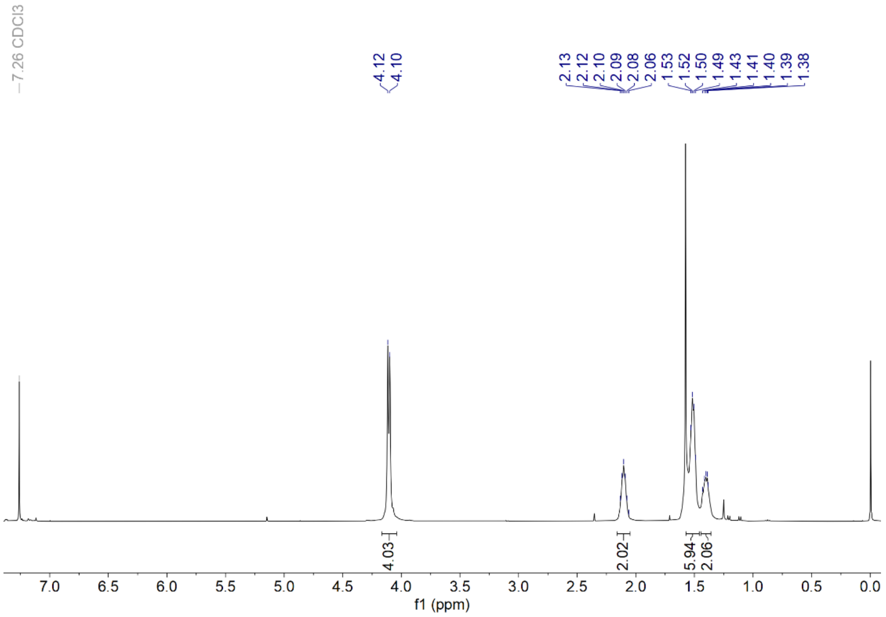


Fig. S6. ^{1}H NMR ($CDCl_3$, 25 °C) spectrum of P(C6DO) produced by [C6DO]/[**Zn1**]/[BnOH] = 100/1/1 in toluene.

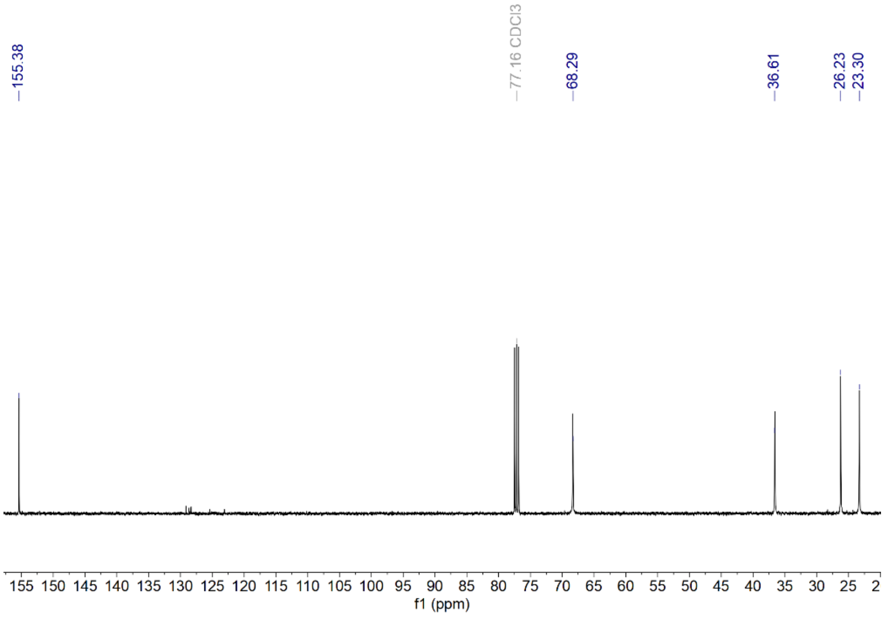


Fig. S7. ^{13}C NMR ($CDCl_3$, 25 °C) spectrum of P(C6DO) produced by [C6DO]/[**Zn1**]/[BnOH] = 100/1/1 in toluene.

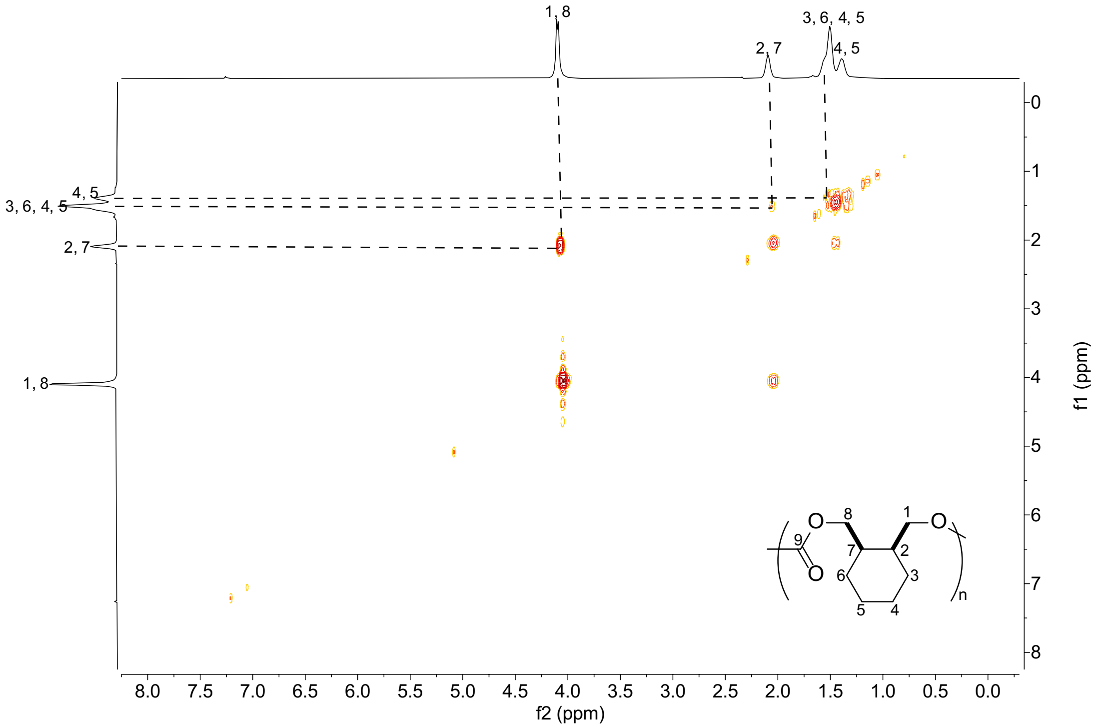


Fig. S8. COSY ($CDCl_3$, 25 °C) spectrum of P(C6DO).

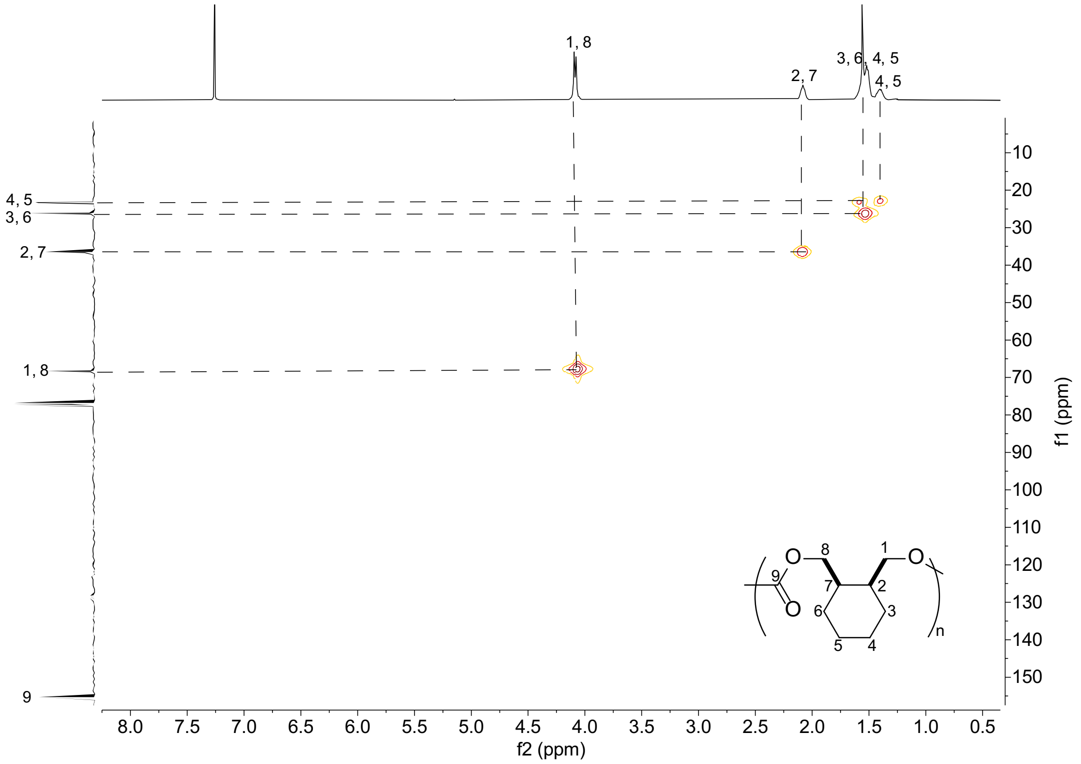
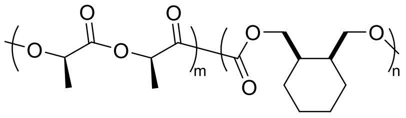


Fig. S9. HSQC ($CDCl_3$, 25 °C) spectrum of P(C6DO).



P[(C6DO)$_n$-*co*-(L-LA)$_m$]

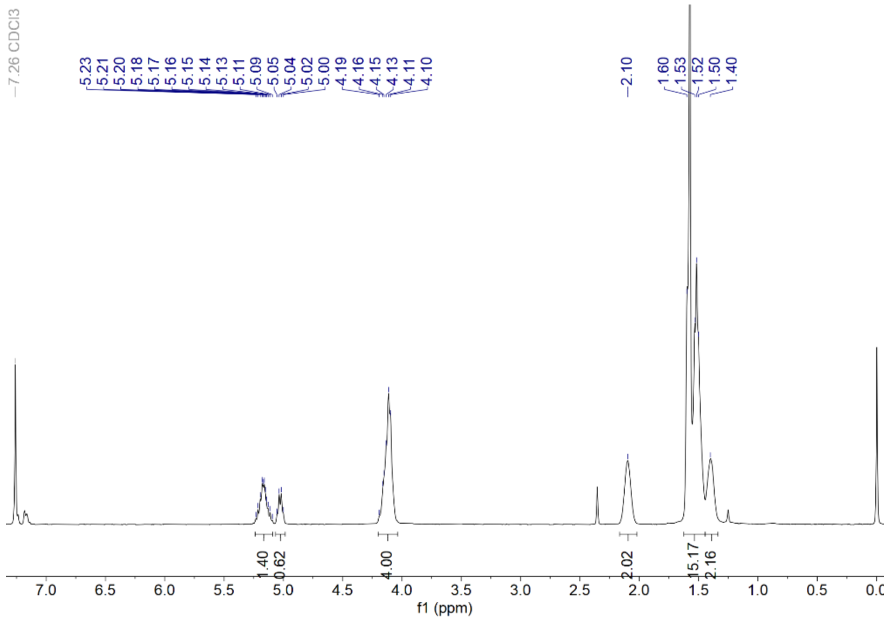


Fig. S10 ^{1}H NMR ($CDCl_3$, 25 °C) spectrum of P[(C6DO)$_{500}$-*co*-(L-LA)$_{500}$] obtained by [C6DO]/[L-LA]/[**Zn1**]/[I] = 500/500/1/1.

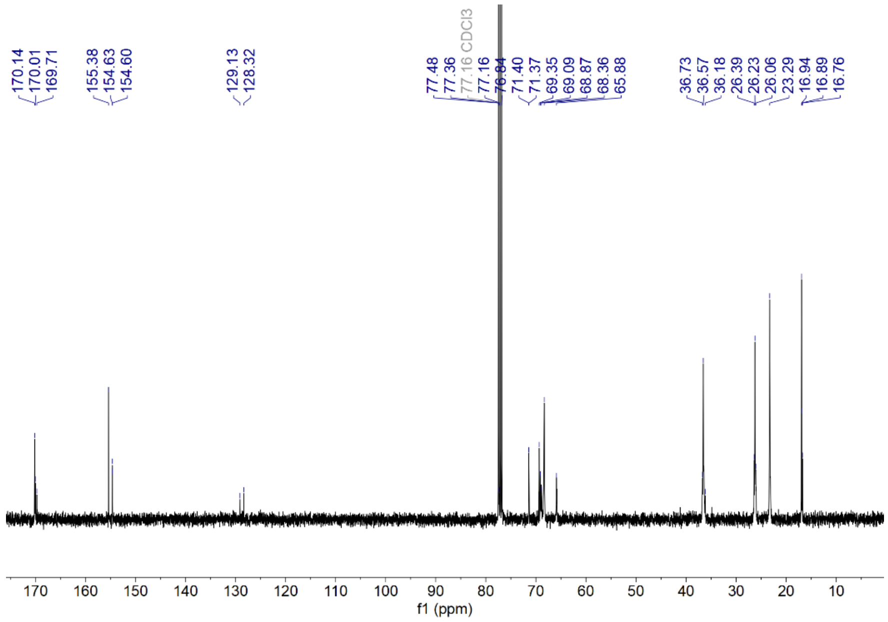


Fig. S11. ^{13}C NMR ($CDCl_3$, 25 °C) spectrum of P[(C6DO)$_{667}$-*co*-(L-LA)$_{333}$] obtained by [C6DO]/[L-LA]/[**Zn1**]/[I] = 667/333/1/1.

TGA curves of polymers

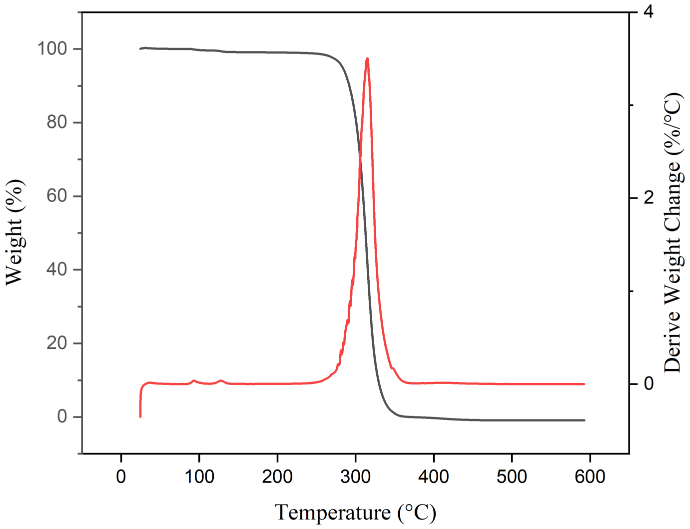


Fig. S12. TGA and DTG curves for P(C6DO) obtained by [C6DO]/[**Zn1**]/[I] = 100/1/1, $T_{\text{d, 5\%}}$ = 283 °C, T_{max} = 316 °C.

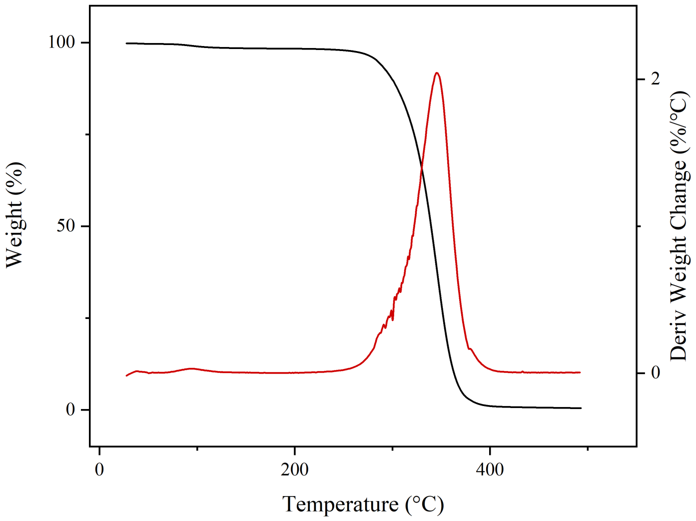


Fig. S13. TGA and DTG curves for P[(C6DO)$_{500}$-*co*-(L-LA)$_{500}$] obtained by [C6DO]/[L-LA]/[**Zn1**]/[I] = 500/500/1/1, $T_{\text{d, 5\%}}$ = 284 °C, T_{max} = 345 °C.

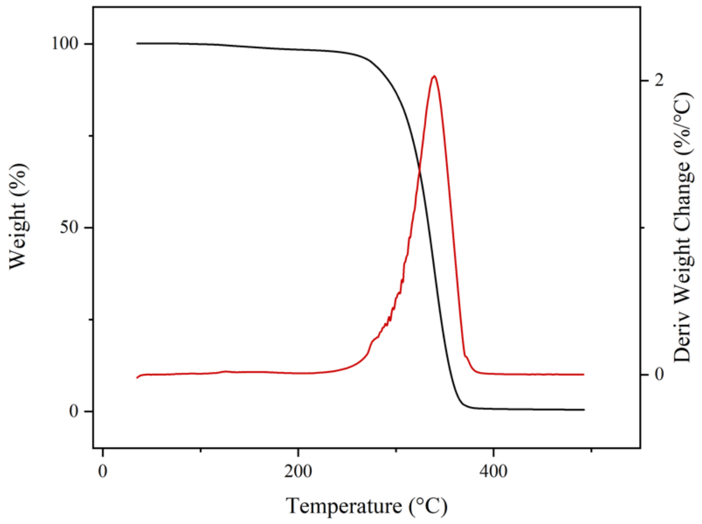


Fig. S14. TGA and DTG curves for P[(C6DO)$_{667}$-*co*-(L-LA)$_{333}$] obtained by [C6DO]/[L-LA]/[**Zn1**]/[I] = 667/333/1/1, $T_{d, 5\%}$ = 275 °C, T_{max} = 339 °C.

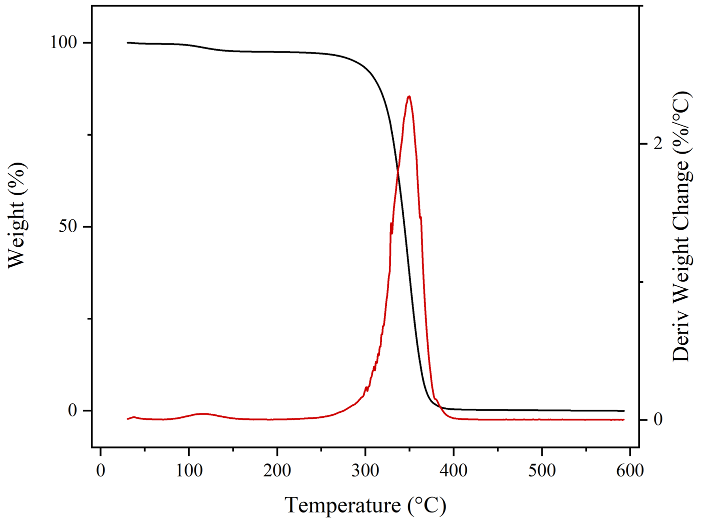


Fig. S15. TGA and DTG curves for P[(C6DO)$_{800}$-*co*-(L-LA)$_{200}$] obtained by [C6DO]/[L-LA]/[**Zn1**]/[I] = 800/200/1/1, $T_{d, 5\%}$ = 287 °C, T_{max} = 350 °C.

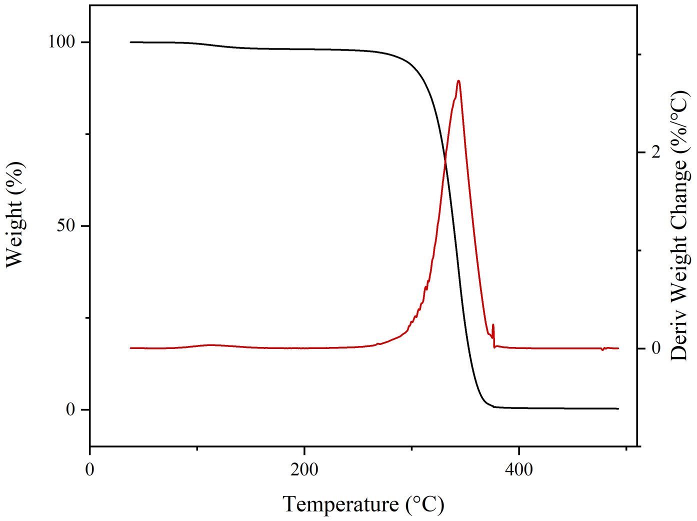


Fig. S16. TGA and DTG curves for P[(C6DO)$_{900}$-*co*-(L-LA)$_{100}$] obtained by [C6DO]/[L-LA]/[**Zn1**]/[I] = 900/100/1/1, $T_{d, 5\%}$ = 294 °C, T_{max} = 344 °C.

DSC curves of polymers

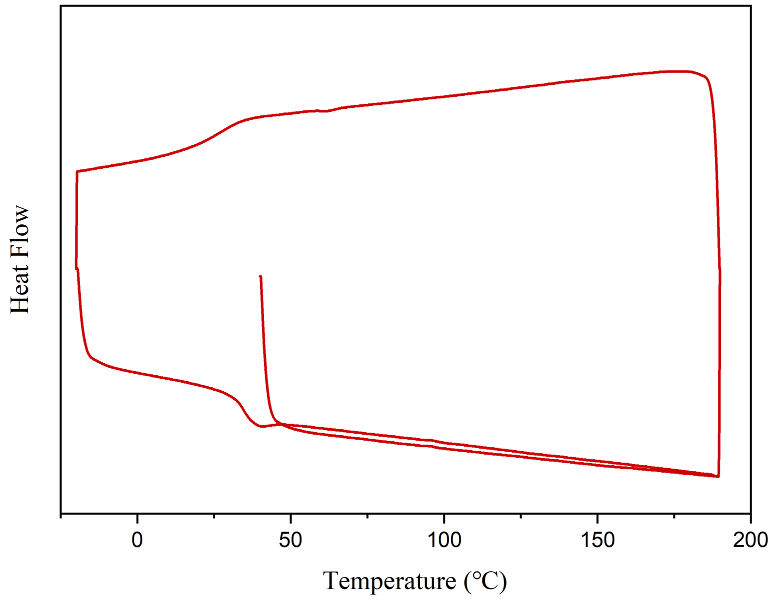


Fig. S17 DSC curves for P(C6DO) obtained by [C6DO]/[**Zn1**]/[I] = 100/1/1, T_g = 35 °C.

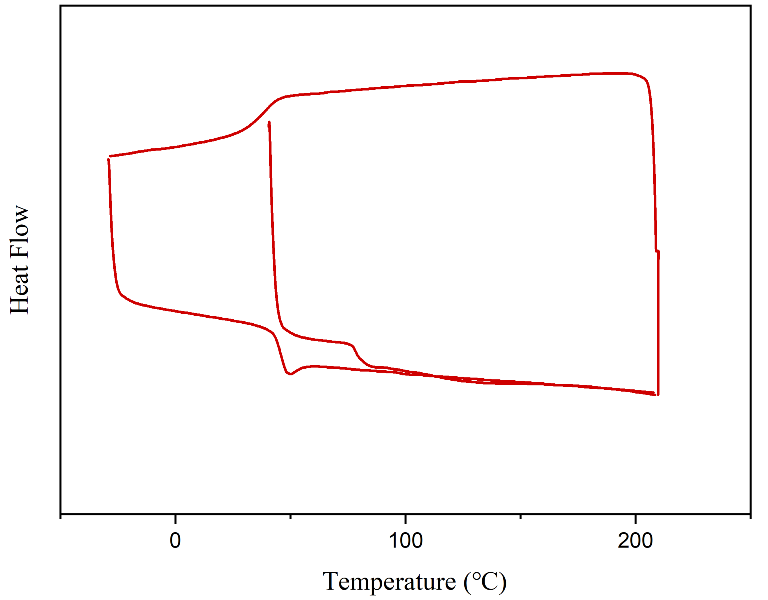


Fig. S18. DSC curves for P[(C6DO)$_{500}$-*co*-(L-LA)$_{500}$] obtained by [C6DO]/[L-LA]/[**Zn1**]/[I] = 500/500/1/1, T_g = 46 °C.

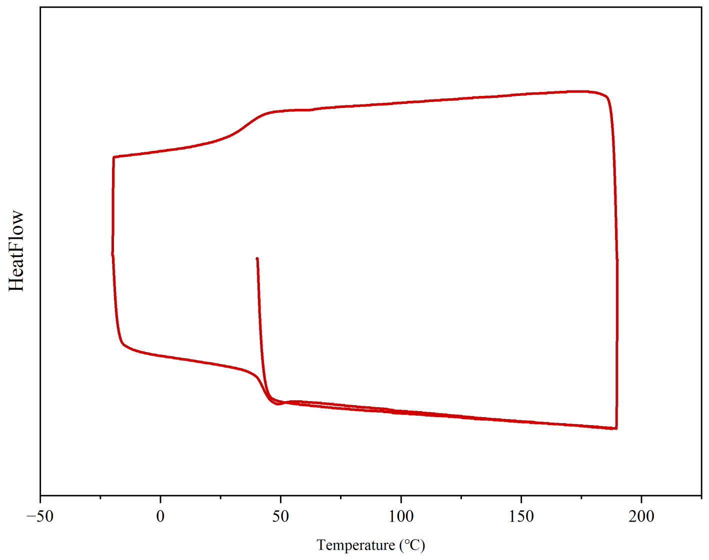


Fig. S19. DSC curves for P[$(C6DO)_{667}$-*co*-$(\text{L-LA})_{333}$] obtained by [C6DO]/[L-LA]/[**Zn1**]/[I] = 667/333/1/1, T_g = 43 °C.

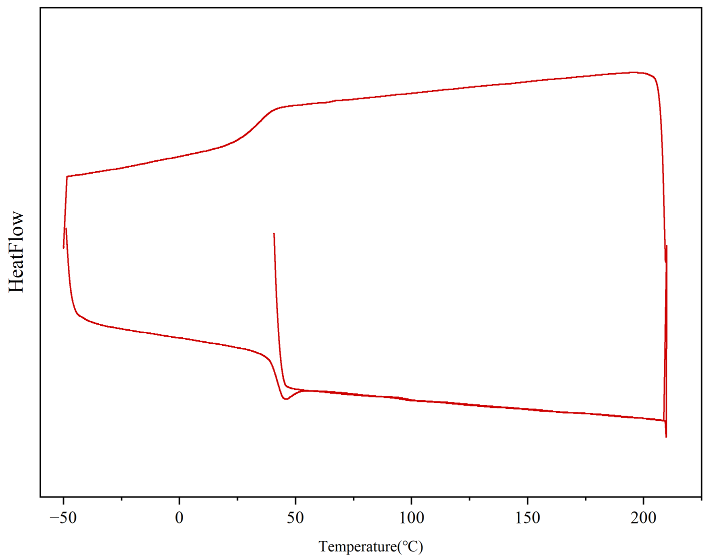


Fig. S20. DSC curves for P[$(C6DO)_{800}$-*co*-$(\text{L-LA})_{200}$] obtained by [C6DO]/[L-LA]/[**Zn1**]/[I] = 800/200/1/1, T_g = 42 °C.

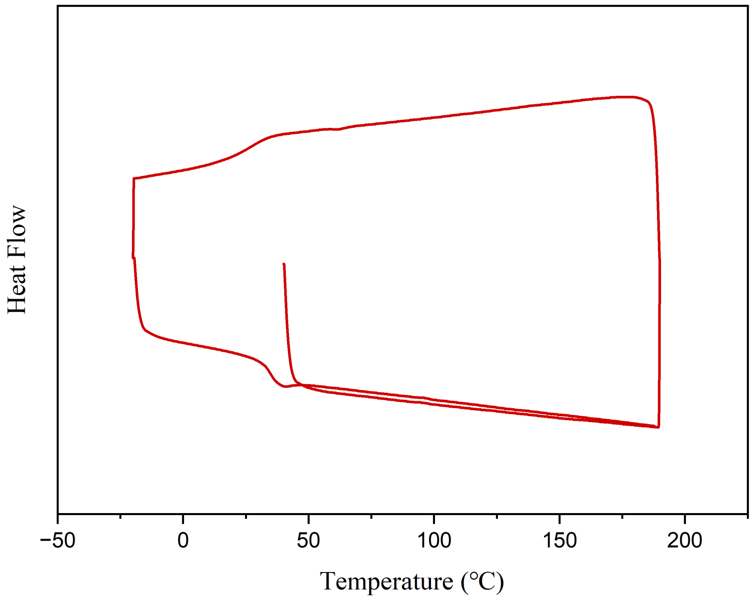
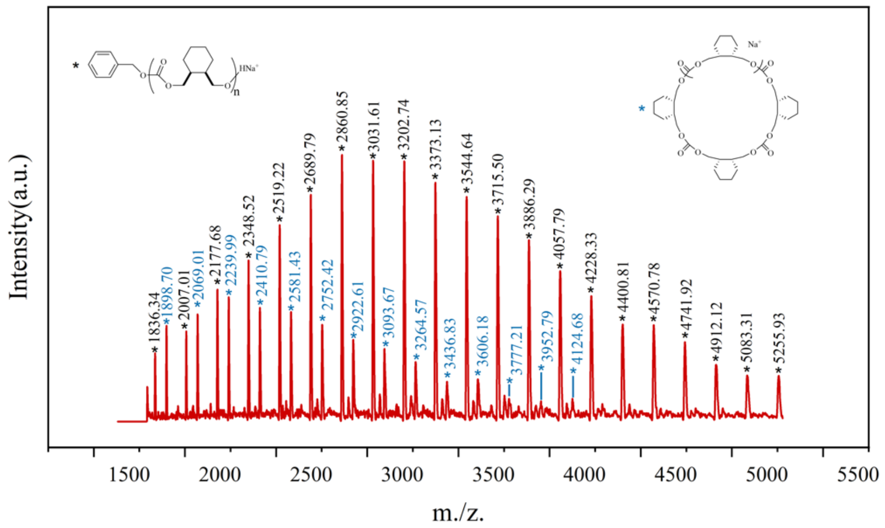


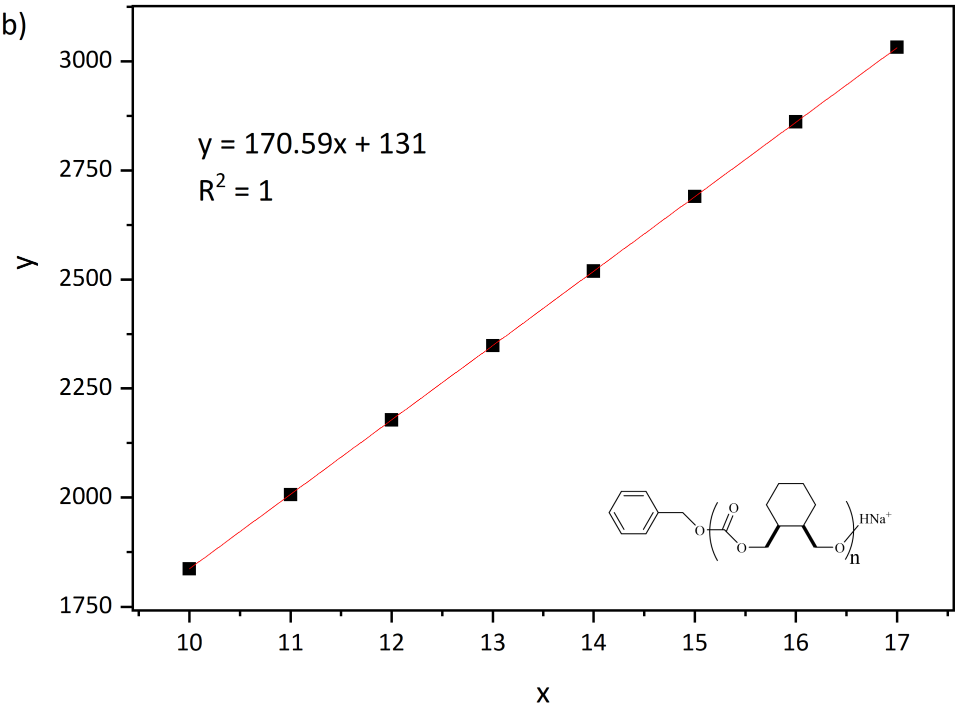
Fig. S21. DSC curves for P[(C6DO)$_{900}$-*co*-(L-LA)$_{100}$] obtained by [C6DO]/[L-LA]/[**Zn1**]/[I] = 900/100/1/1, T_g = 42 °C.

MALDI-TOF MS Spectrum (Top) of The Low-Molecular-Weight P(C6DO)

a)



b)



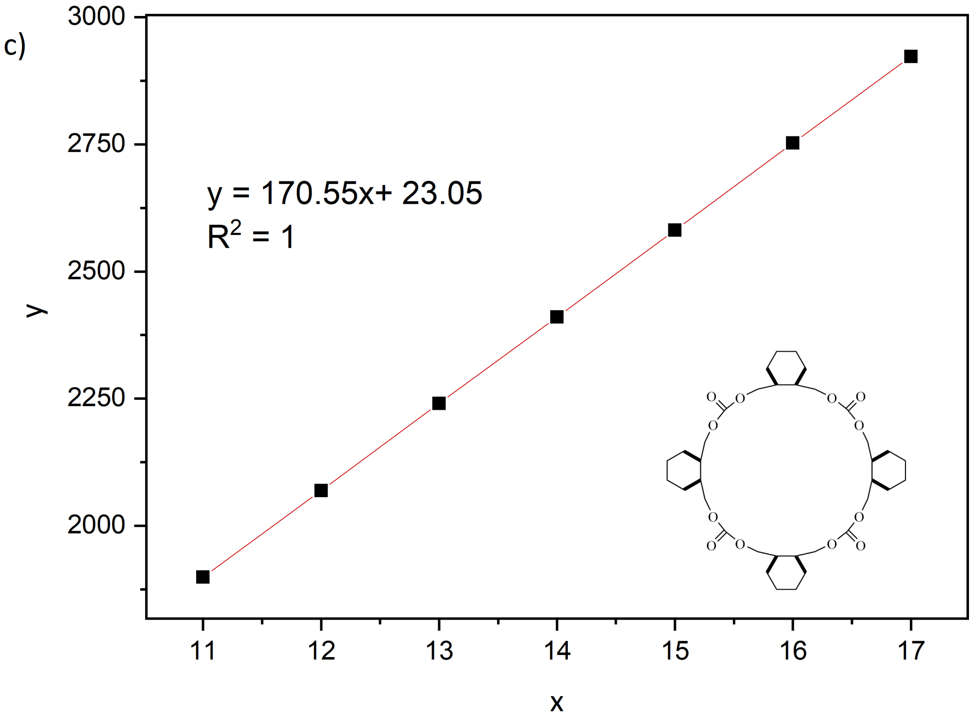


Fig. S22. a) MALDI-TOF MS spectrum of P(C6DO) produced by [C6DO]/[**Zn1**]/[I] = 50/1/1. b) linear plot of m/z values (y) *vs* the number of C6DO repeat units (x). c) cyclic plot of m/z values (y) vs the number of C6DO repeat units (x).

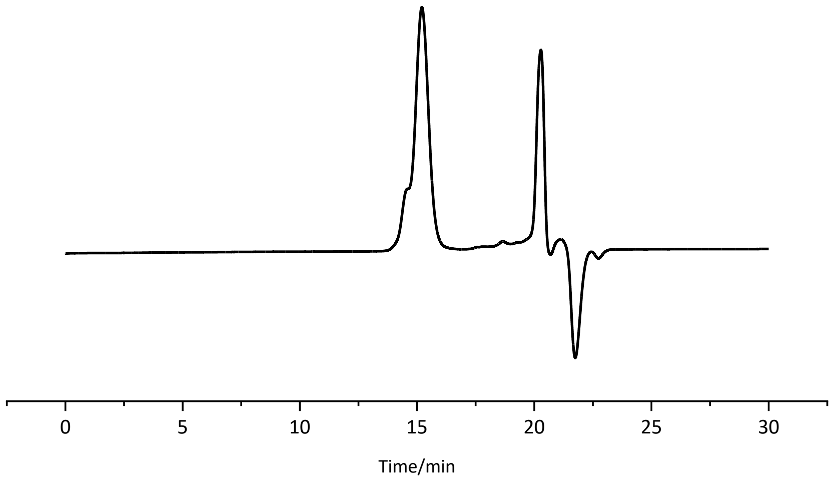


Fig. S23. SEC trace of P(C6DO) obtained by [C6DO]/[**Zn1**]/[I] = 100/1/1, M_n = 20.1 kg mol^{-1}, $Đ$ = 1.17.

Mechanical Property

Table S2. Summary of mechanical properties of polymers.[a]

Polymer	M_n/kDa	E/GPa	σ_Y/MPa	σ_B/MPa	Elongation/%
P(C6DO)	84	1.08±0.04	18.60±1.30	14.36±1.34	423.41±39.22
P[(C6DO)$_{500}$-*co*-(L-LA)$_{500}$]	163	0.85±0.57	40.15±4.01	38.46±3.81	4.24±1.26
P[(C6DO)$_{667}$-*co*-(L-LA)$_{333}$]	159	1.24±0.15	39.48±2.62	21.91±1.82	122.02±28.04
P[(C6DO)$_{800}$-*co*-(L-LA)$_{200}$]	144	1.10±0.05	16.04±1.41	10.88±1.08	336.78±46.13
P[(C6DO)$_{900}$-*co*-(L-LA)$_{100}$]	143	1.28±0.10	21.17±2.12	14.49±0.91	246.96±20.01

[a] Condition: tested by uniaxial tensile tests. Strain rate of 5 mm/min, E: Tensile modulus, σ_Y: yield strength, σ_B: break strength.

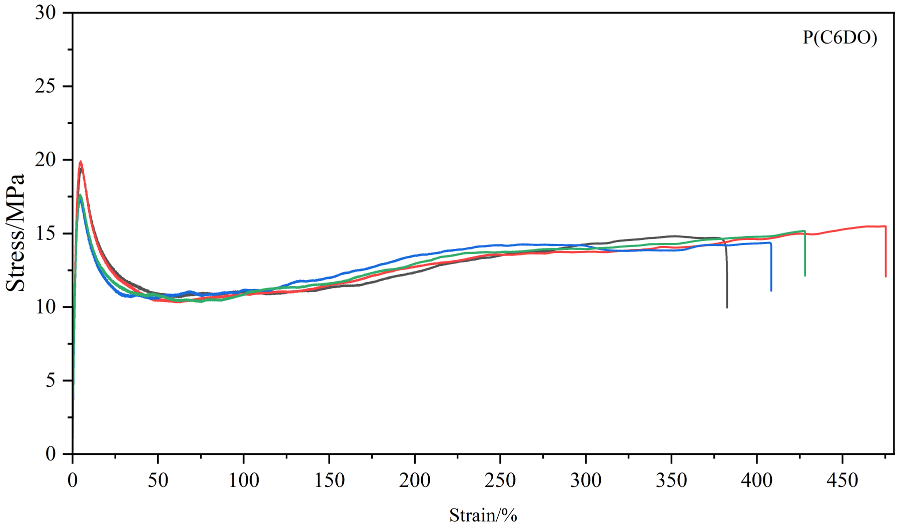


Fig. S24. Stress-strain curves of P(C6DO).

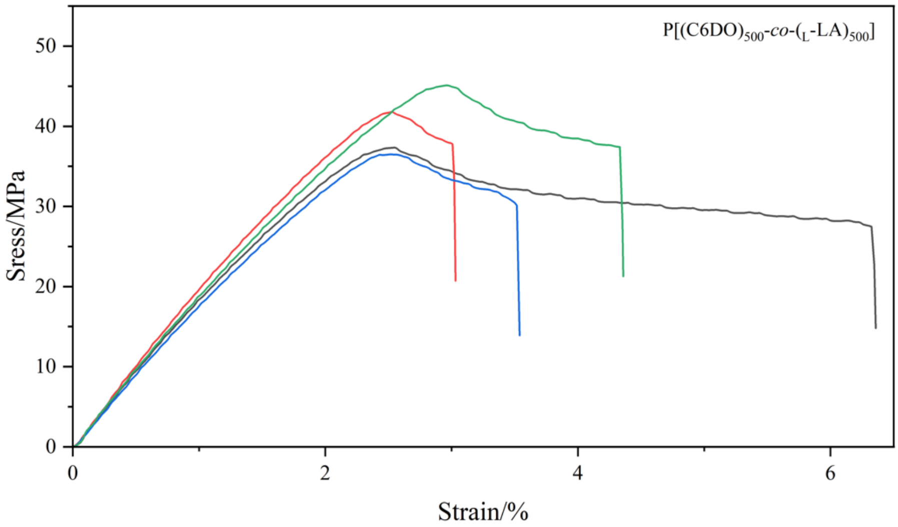


Fig. S25. Stress-strain curves of P[(C6DO)$_{500}$-*co*-(L-LA)$_{500}$].

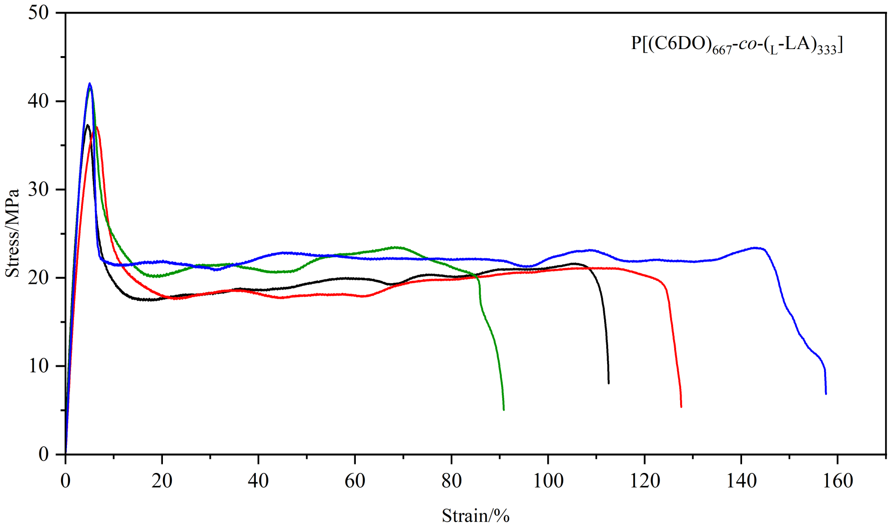


Fig. S26. Stress-strain curves of P[(C6DO)$_{667}$-*co*-($_{L}$-LA)$_{333}$].

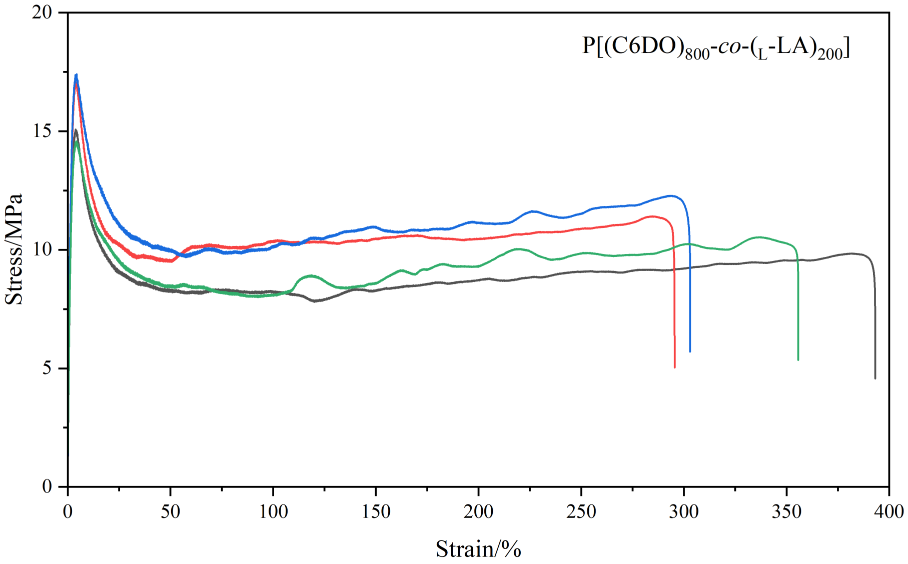


Fig. S27. Stress-strain curves of P[(C6DO)$_{800}$-*co*-($_{L}$-LA)$_{200}$].

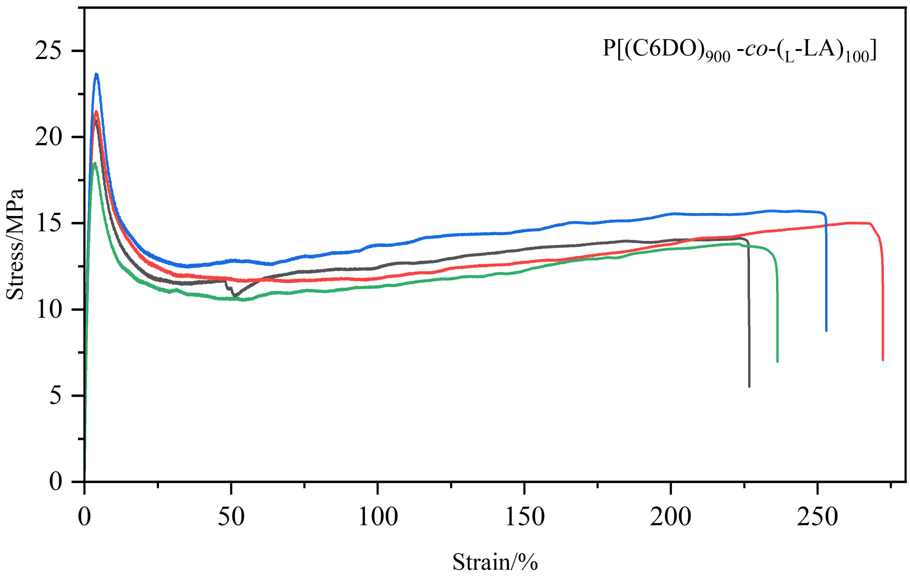
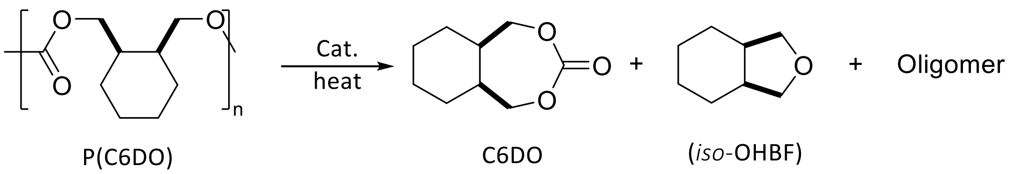


Fig. S28. Stress-strain curves of P[(C6DO)$_{900}$-*co*-($_{\text{L}}$-LA)$_{100}$].

Chemical Recycling to Monomer (CRM)



General procedures for the CRM of polymers under thermal bulk condition.

Without catalyst: In an argon-filled glovebox, 150 mg P(C6DO) was added into a 25 mL reaction tube with cold-finger condenser. The reaction tube was heated at 320 °C in vacuo (80 Pa) for a certain time, while the cold-finger condenser was filled with coolant liquid (EtOH, -20 °C). After the reaction was stopped, the sublimate was collected as white solid (127.4 mg, 85%), weighted, and characterized by ^{1}H NMR spectroscopy.

With catalyst: In an argon-filled glovebox, a reaction tube was charged with 150 mg P(C6DO) and desired catalyst (10 mol%) and heated at desired temperature in vacuo for 4h. After the reaction was stopped, both the sublimate and the product at the bottom of the reaction tube were collected (*iso*-OHBF cannot be sublimated to the cold finger condenser), weighted, and characterized by ^{1}H NMR spectroscopy.

Table S3. Screen of various catalysts for depolymerization of P(C6DO) under thermal bulk condition.[a]

Entry	Cat.	Catalyst loading/mol%	Temp./°C	Time/h	Conv.[b]/%	product
1	**Zn1**	10	260	1.5	74	*iso*-OHBF
2	$ZnCl_2$	10	170	2	>99	*iso*-OHBF
3	^{t}BuOK	10	170	11	>99	*iso*-OHBF
4	$Sn(Oct)_2$	10	260	4	89	*iso*-OHBF + oligomer
5	NaOH	10	170	4	44	C6DO+ *iso*-OHBF
6	-	-	320	0.75	85	C6DO

[a] Reaction conditions: All reactions were in vacuum (80 Pa). P(C6DO) obtained by [C6DO]/[**Zn1**]/[I] = 100/1/1. [b] Conversions measured by the amount of the residue in the reaction tube (*iso*-OHBF cannot be sublimated to the cold finger condenser) and the products determined by ^{1}H NMR of the spectroscopy.

Table S4. Screen of various temperature for depolymerization of P(C6DO) under thermal bulk condition.[a]

Entry	Temp./°C	Time/h	C6DO yield[b]/ %
1	180	5	3
2	200	5	11
3	220	1.5	46
4	240	2	43
5	260	40 min	41
6	280	55 min	47
7	300	50 min	66
8	320	45 min	85

[a] Reaction conditions: All reactions were in vacuum (80 Pa). P(C6DO) obtained by [C6DO]/[**Zn1**]/[I] = 100/1/1. [b] The C6DO yield determined by the amount of the sublimate and the purity of recycled monomer determined by ^{1}H NMR spectroscopy.

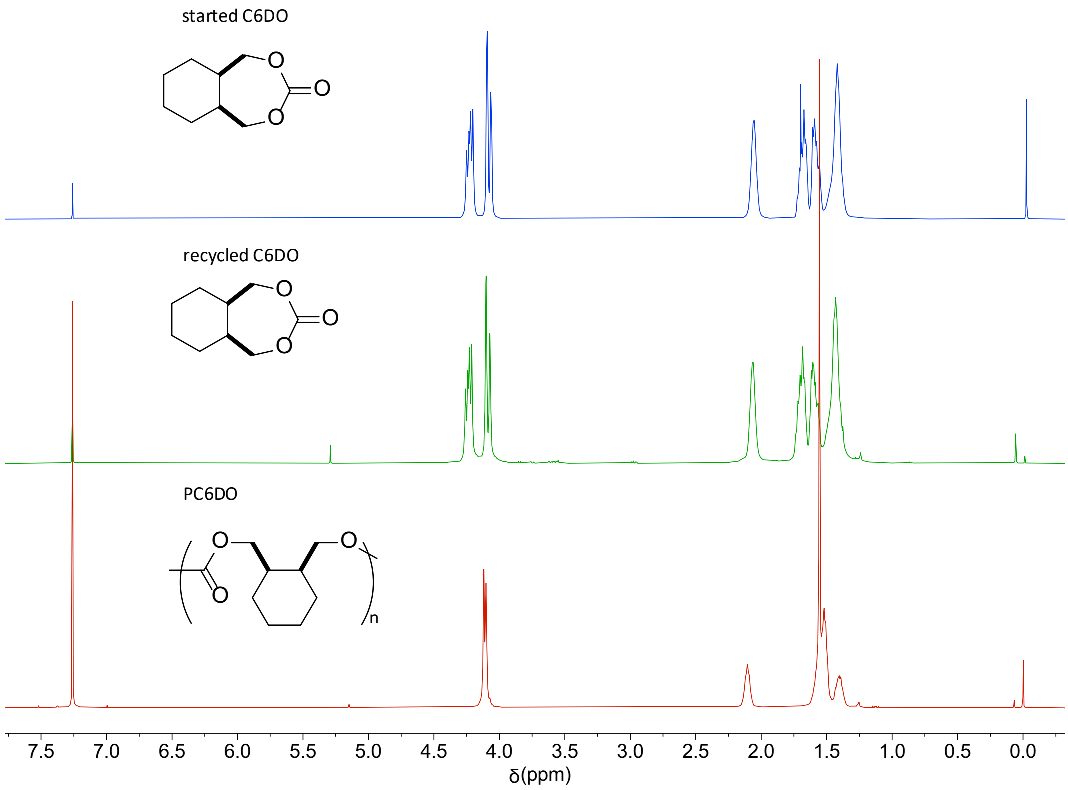


Fig. S29. ^{1}H NMR spectra of P(C6DO) prepared by [C6DO]/[**Zn1**]/[I] = 100/1/1 (bottom), recycled C6DO after depolymerization (middle) and clean started C6DO for comparison (top).

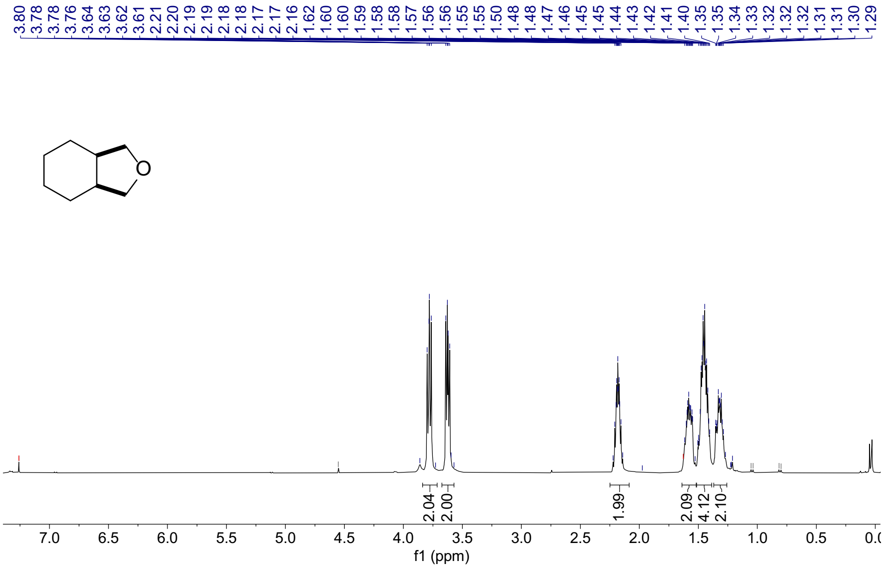


Fig. S30. ^{1}H NMR spectrum of *iso*-OHBF depolymerized from PC6DO under 260 °C with 10 mol% Sn(Oct)$_2$.

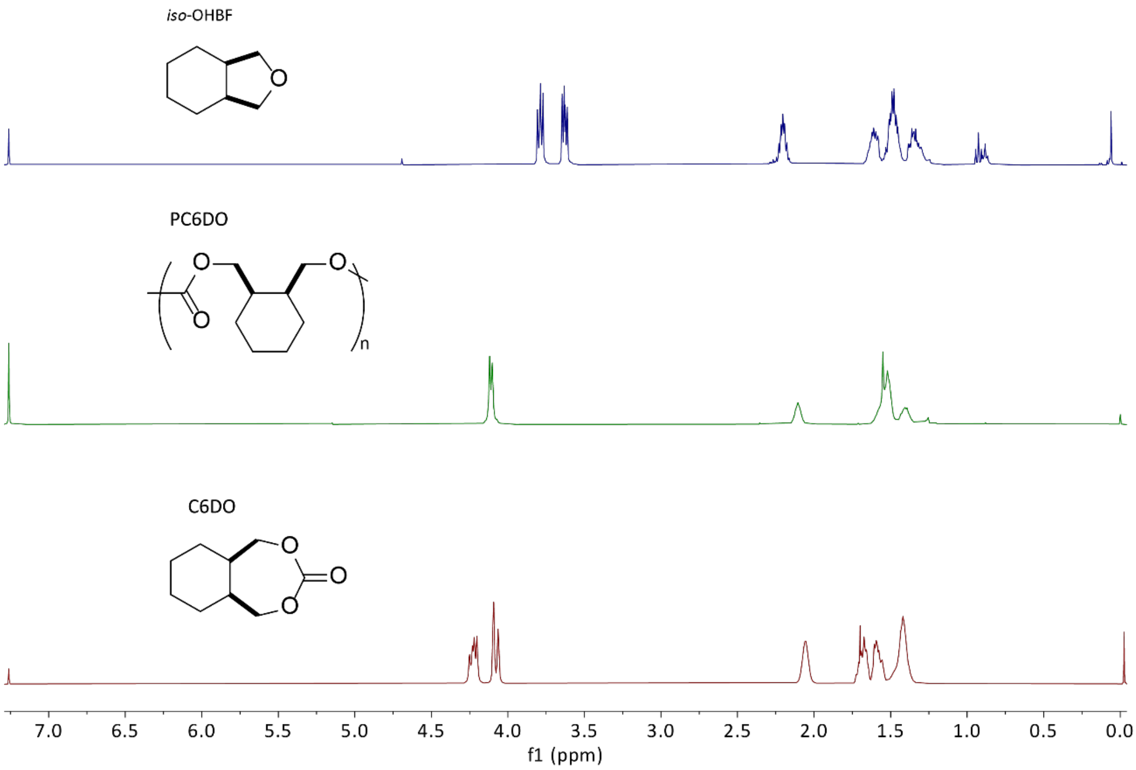
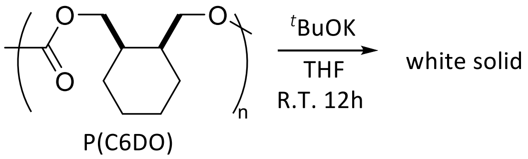


Fig. S31. ^{1}H NMR spectra of clean starting C6DO for comparison (bottom), P(C6DO) prepared by [C6DO]/[**Zn1**]/[I] = 100/1/1(middle), *iso*-OHBF after depolymerization at 260 °C (top).

General procedures for the CRM of PC6DO in solution.

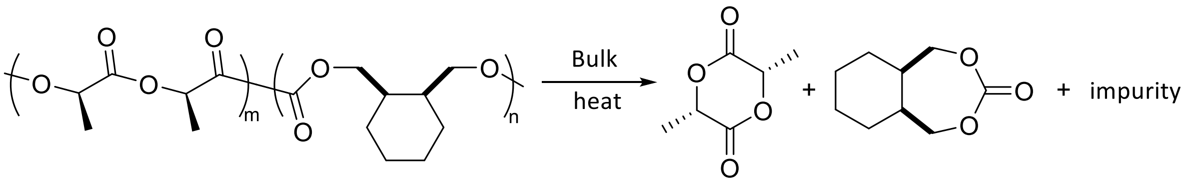


In a 50 mL glass reactor, P(C6DO) (120 mg) was added to a solution of ^{t}BuOK (5 mol%) and in THF (4 mL). The mixture was stirred at room temperature for 12 h. After the reaction was completed, the reaction mixture was filtrated and washed with appropriate amount of THF to yield a white solid (78 mg, 65%). This white solid was completely insoluble in common organic solvents and could not be characterized by NMR spectroscopy or mass spectroscopy.

Depolymerization of copolymers

General procedures for the depolymerization of copolymers under thermal bulk condition.

A reaction tube was charged with 100 mg P[(C6DO)$_n$-*co*-($_L$-LA)$_m$] and heated at desired temperature in vacuo for 4 h. After the reaction was stopped, the product cannot sublimate to the cold-finger condenser and it was collected from the bottom of the reaction tube as yellow solid and characterized by ^{1}H NMR spectroscopy. The yield of each component can not be calculated accurately because of the messy spectra. All possible products have been marked.



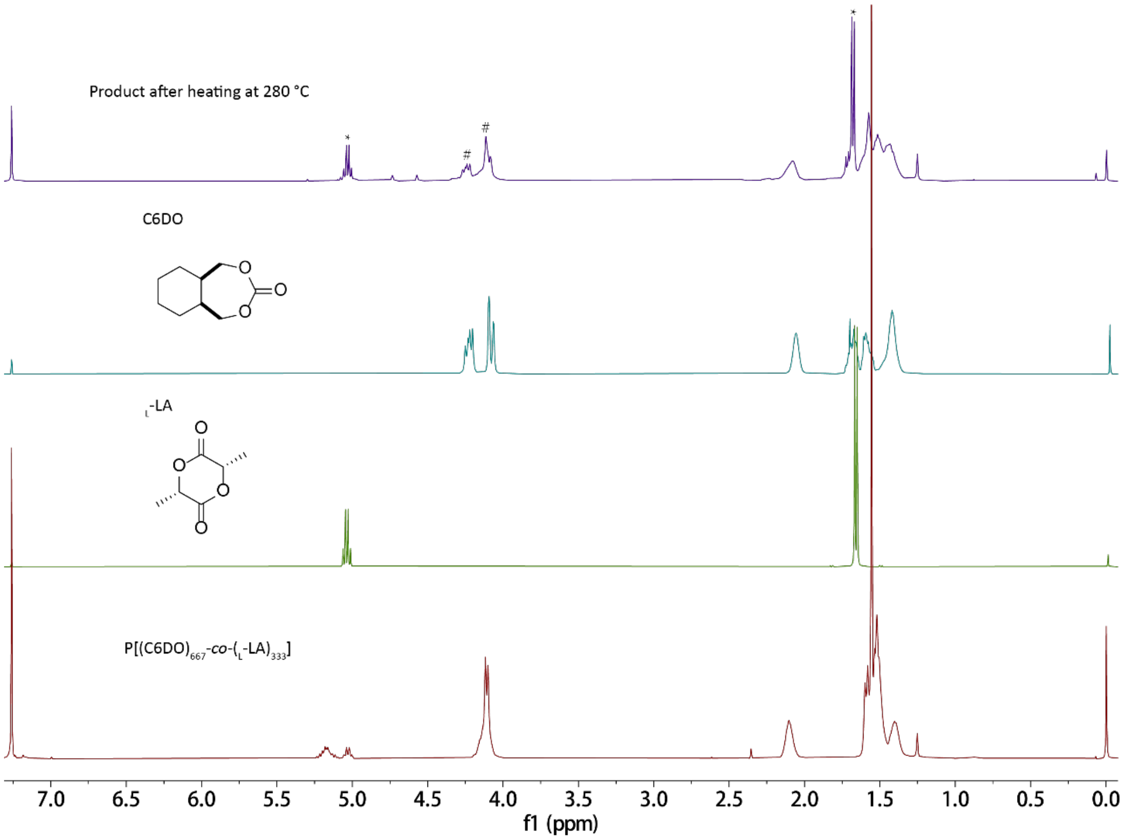
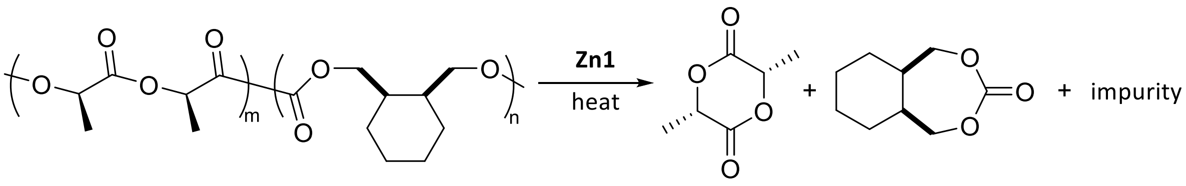


Fig. S32. ^{1}H NMR spectra of product after heating at 280 °C (include $_L$-LA, C6DO and impurity); Cleaning C6DO for comparison; Cleaning $_L$-LA for comparison; Starting copolymer for comparison. (# Recycled C6DO, *Recycled $_L$-LA)

General procedures for the thermal depolymerization of copolymers.

A reaction tube was charged with 100 mg P[(C6DO)$_n$-*co*-(L-LA)$_m$] and heated at desired temperature in vacuo for 4 h. After the reaction was stopped, the product cannot sublimate to the cold-finger condenser and it was collected from the bottom of the reaction tube as yellow solid and characterized by ^{1}H NMR spectroscopy. The yield of each component cannot be calculated accurately because of the messy spectra. All possible products have been marked.



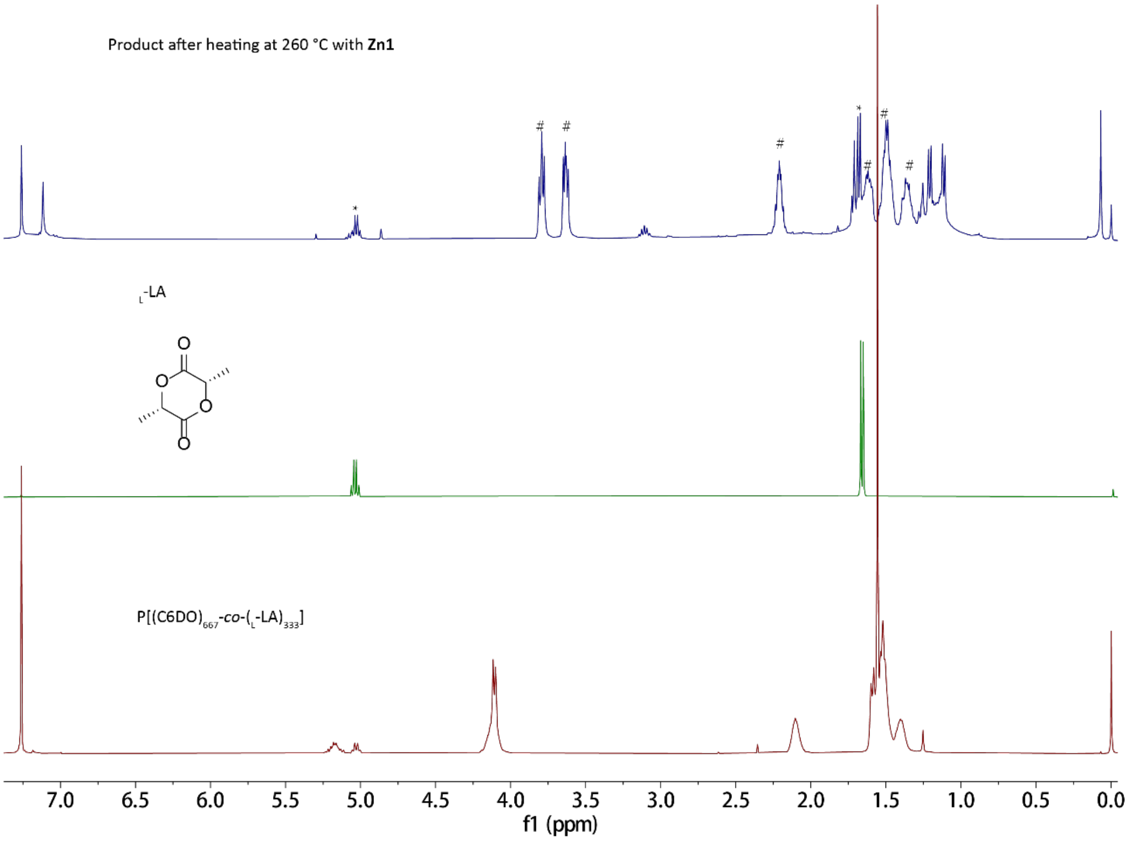
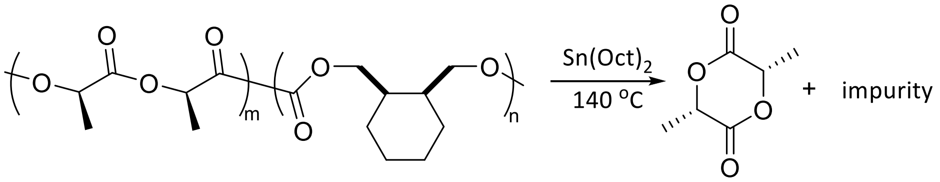


Fig. S33. ^{1}H NMR spectra of product after heating at 260 °C with catalyst **Zn1** (include L-LA, *iso*-OHBF and impurity); Cleaning L-LA for comparison; Starting copolymer for comparison. (# *iso*-OHBF, *Recycled L-LA)

General procedures for the depolymerization of copolymers in dilute solution.

A reaction tube was charged with 100 mg P[(C6DO)$_n$-*co*-($_L$-LA)$_m$] and desired catalyst heated at desired temperature in vacuo for 4h. After the reaction was stopped, the product was collected as yellow solid and characterized by ^{1}H NMR spectroscopy. A mixture of product was obtained.



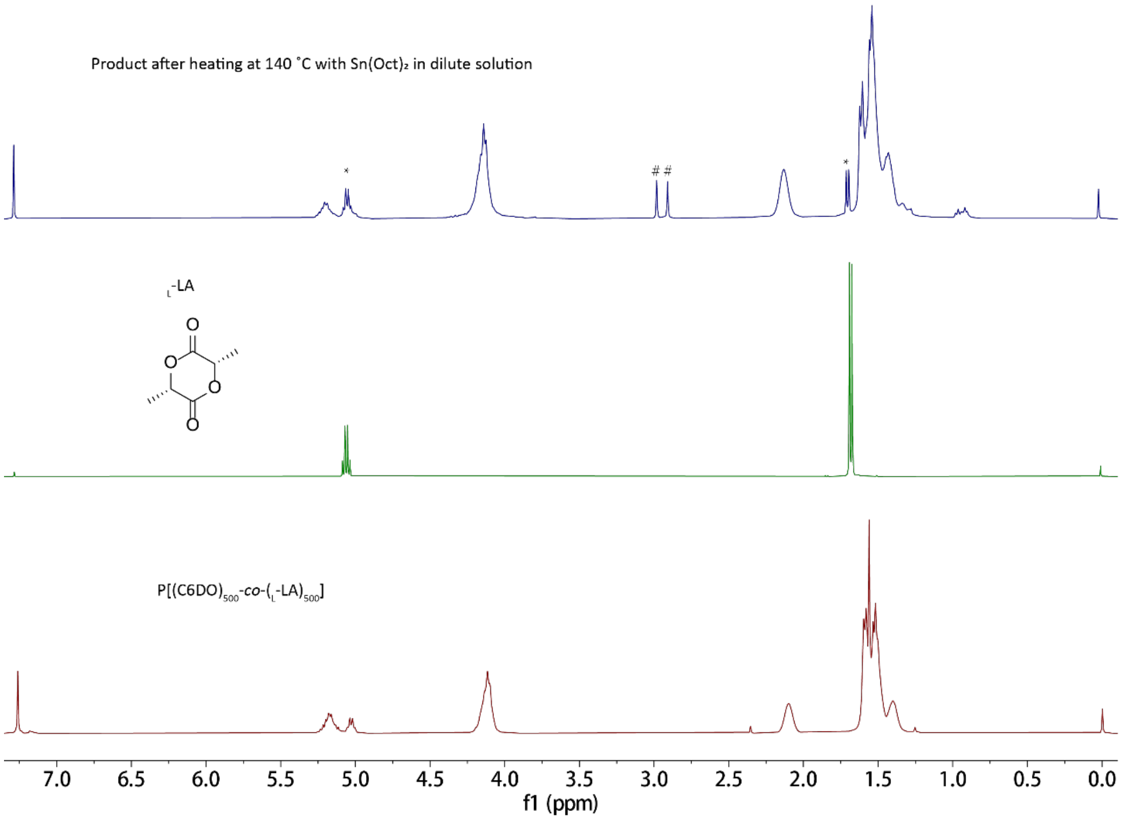


Fig. S34. ^{1}H NMR spectra of product after heating at 140 °C with Sn(Oct)$_2$ in dilute solution; Cleaning $_L$-LA for comparison; Starting copolymer for comparison.(#solvent DMF impurity, *Recycled $_L$-LA)