Supplementary Information for Manuscript Entitled with

A Polycondensation–Depolymerization Strategy Enables Closed-Loop Recyclable Polyoxalates via Ring-Opening Polymerization of Six-Membered Cyclic Oxalates

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Experimental Section

Materials

Dimethyl oxalate (DMO), ethylene glycol (98%), 1,2-propanediol (99%), 1,2 -butanediol (95%), 1,2-hexanediol (98%) , stannous octoate ($Sn(Oct)_2$, 95%) and tetrabutyl titanate (TBT, 98%) were purchased from Aladdin Reagent Co. Sodium glycollate (98%), zinc chloride (ZnCl, 98%), p-toluenesulfonic acid (TsOH, 99%), sodium acetate (NaAc, 99%), trimethylaluminium ($AlMe_3$), diethylzinc solution ($ZnEt_2$) were obtained from Macklin Reagent Co. 1-Tert-butyl-2,2,4,4,4 -pentakis(dimethylamino)-2λ^5, 4λ^5-catenadi-(phosphazene) (*t*Bu-P_2, ~ 2.0 M in THF) and *N*-[tert-butylimino-bis(dimethylamino)-λ^5-phosphanyl]-*N*-methylmethanamine (*t*Bu-P_1) and tris[*N,N*-bis(trimethylsilyl)amide]lanthanum(III) was purchased from Sigma-Aldrich. Potassium hydroxide (KOH) were obtained from Sinopharm Chemical Reagent Co. 1, 8-Diazabicyclo[5.4.0]undec-7-ene (DBU) was purchased from Alfa Aesear. Superdry benzyl alcohol (BnOH), N-methylpyrrolidone (NMP, 98%) and tetrahydrofuran (THF, 99.9%) was purchased from J&K Scientific Co. All commercially obtained reagents were used as received without further purification unless otherwise noted.

Instruments

NMR: Nuclear magnetic resonance (NMR) spectra were recorded on a Bruker AVNEO400ASCEND FT-NMR spectrometer at 400 MHz for ^{1}H NMR and 100 MHz for ^{13}C NMR. Chemical shifts were reported in δ (ppm) relative to the residual deuterated solvent peak.

ESI-MS: The positive ion electrospray ionization mass spectroscopy (ESI-MS) measurements were conducted with an Impact II of Bruker.

MALDI-TOF MS: Matrix-assisted laser desorption/ionization time-of-flight mass spectroscopy (MALDI-TOF MS) analyses were conducted on a Bruker Microflex LRF MS spectrometer equipped with a 337 nm nitrogen laser operating in a positive ion, reflectron mode. The sample solutions (10 mg/mL in THF), *trans*-2-[3-(4-*tert*-butylphenyl)-2-methyl-2-propenylidene] malononitrile (DCTB) solution (40 mg/mL in THF) and sodium trifluoroacetate aqueous solution (5 mg/mL) were mixed in a volume ratio of 4:4:1, 1 μL of which was then deposited on the target plate and dried before measurement.

SEC: Size exclusion chromatography (SEC) experiments were performed on an Agilent HPLC system equipped with a model 1260 Hip degasser, a model 1260 Iso pump a model 1260 differential refractometer detector using THF as mobile phase at a flow rate of 1.0 mL/min at 40 ºC. One PLgel 5 μm guard column and three Mz-Gel SDplus columns (10^3 Å, 10^4 Å and 10^5 Å, linear range of MW = 1000 - 2*10^6 Da) were connected in series. The molecular weights and dispersities were calculated using 10 polystyrene standards with narrow molecular weight distribution as references. The sample concentration used for SEC analyses was 5-10 mg mL^{-1}.

DSC: Differential scanning calorimetry (DSC) measurements were performed on a TA instrument DSC 25. Temperature was calibrated with an indium standard. Measurements were performed under N_2 atmosphere with a flow rate of 50 mL min^{-1}. Each sample with a 5 ~ 10 mg mass was used for the measurement. The typical procedures were described as follows: in the first heating scan, samples were heated

from -80 to 200 ºC at a heating rate of 10 ºC min^{-1} and kept at 200 ºC for 2 min to eliminate any thermal history. In the second heating scan, samples were cooled to -80 ºC at 10 ºC min^{-1}, then equilibrium at -80 ºC for 2 min then reheated to 200 ºC at 10 ºC min^{-1}.

TGA: Thermogravimetric analysis (TGA) measurements were performed on a STA 8000 thermogravimetric analyzer. The samples were heated from 40 to 400 °C at a heating rate of 10 °C min^{-1} under N_2 atmosphere with a flow rate of 20 mL min^{-1}.

Uniaxial tensile testing: The uniaxial tensile tests were performed on an Instron 5943 tensile testing machine at room temperature at an extension rate of 50 mm min^{-1}. The polymer thin films for the tensile tests were prepared by hot-press molding at 200 °C (PEOx) or 100 °C (PPOx) for 5 min and then cold-press at room temperature for 10 min. The films were then cut into dumbbell-shaped specimens with dimensions of 15 mm in length, 2 mm in neck width and 1.5 mm in thickness. The elongation at break (ε_b) and tensile strength (σ_b) were reported as average values with standard deviations, obtained from at least 3 specimens.

Synthesis of POx

Dimethyl oxalate (60 g, 0.508 mol), 1,2-propanediol (46 g, 0.610 mol), and tetrabutyl titanate (0.018 g) were added to a 250 mL round-bottomed flask equipped with a magnetic stirrer and reflux condenser. The reaction was first carried out at 80 °C for 1 hour under nitrogen atmosphere. The reaction was then carried out at 110 °C for 1 hour, 140 °C for 2 hours, and 150 °C for 1 hour. Finally, at 150 °C, the pressure was gradually reduced to 50 Pa and maintained for 2 hours to remove methanol and excess 1,2-propanediol to obtain low molecular weight polymers.

Under nitrogen protection, 1 wt% sodium glycolate was added as a depolymerization catalyst. The system was evacuated to 50 Pa and reacted at 180 °C for 2 hours to afford a crude product of POx, which was then purified by rectification. Subsequently, The obtained POx was stirred with CaH_2 for 48 hours, then distilled under reduced pressure and stored in a glove box. The BOx and HOx were prepared in a similar method of POx.

5-methyl-1,4-dioxane-2,3-dione **POx** (colorless oil, 80% yield): ^{1}H NMR (400 MHz, Chloroform-d) δ (ppm) 5.03 - 4.90 (m, 1H), 4.59 - 4.39 (m, 2H), 1.50 (d, *J* = 6.5 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-d) δ (ppm) 153.07, 153.04, 74.30, 70.77, 15.85. ESI-MS: Calculated for ($C_5H_6O_4H^+$) 131.0344 and ($C_5H_6O_4Na^+$) 153.0164; found: 131.03381 and 153.01564.

5-ethyl-1,4-dioxane-2,3-dione **BOx** (colorless oil, 83% yield): ^{1}H NMR (400 MHz, Chloroform-d) δ (ppm) 4.72 (dddd, *J* = 8.5, 7.6, 5.7, 2.6 Hz, 1H), 4.59 - 4.43 (m, 2H), 1.94 - 1.68 (m, 2H), 1.09 (t, *J* = 7.5 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-d) δ (ppm) 153.33, 153.28, 78.98, 69.59, 23.51, 9.03. ESI-MS: Calculated for ($C_6H_8O_4H^+$) 145.0502 and ($C_6H_8O_4Na^+$) 167.0321; found: 145.04961 and 167.03146.

5-butyl-1,4-dioxane-2,3-dione **HOx** (colorless oil, 83% yield): ^{1}H NMR (400 MHz, Chloroform-d) δ (ppm) 4.77 (tdd, *J* = 8.2, 5.3, 2.8 Hz, 1H), 4.57 - 4.41 (m, 2H), 1.88 - 1.59 (m, 2H), 1.55 - 1.24 (m, 4H), 0.88 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-d) δ (ppm) 153.24, 153.22, 77.85, 69.82, 29.82, 26.58, 22.36, 22.19, 13.71. ESI-MS: Calculated for ($C_8H_{12}O_4H^+$) 173.0815 and ($C_8H_{12}O_4Na^+$) 195.0634;

found: 173.08085 and 195.06519.

Synthesis of EOx

The synthetic route for low MW PEOx is analogous to that of PPOx, but the depolymerization of PEOx was conducted in a sublimation apparatus in the presence of sodium glycolate as the catalyst at 210 °C and 50 Pa. The obtained EOx was further purified by recrystallization using THF (Yield: 48%).

1,4-dioxane-2,3-dione **EOx** (white powder, 48% yield): ^{1}H NMR (400 MHz, DMSO) δ (ppm) 4.66 (s, 1H). ^{13}C NMR (101 MHz, DMSO) δ (ppm) 154.39, 66.67.

ESI-MS: Calculated for ($C_4H_4O_4H^+$) 117.0189 and ($C_4H_4O_4Na^+$) 139.0008; found: 117.01686 and 139.00431.

Preparation of organoaluminum complexes

The organoaluminum complexes were prepared according to previously reported roceduces.[1, 2] The obtained organoaluminum complexes were dried under vacuum and stored in a glove box.

General polymerization procedure

A typical polymerization procedure was described as follows. A flame-dried Schlenk tube was charged with (0.02 mmol, 2.2 mg) BnOH and (6 mmol, 780 mg) POx in a glove box. The Schlenk tube was then taken out of the glove box and immersed into an oil bath set at 130 °C. After equilibrium at set temperature for 2 minutes, (0.02 mmol, 8.1 mg) $Sn(Oct)_2$ was then added into the Schlenk tube *via* a pipettor to start

the polymerization. The polymerization was conducted at 130 °C for 20 minutes. The reaction was quenched by rapid cooling. Two aliquots were withdrawn and diluted using $CDCl_3$ or THF. The POx conversion was determined by ^1H NMR measurement. The molar mass M_n and dispersity $Đ$ were determined by SEC. The remaining solution was precipitated into excess cold methanol. The obtained precipitate was washed with cold methanol once more and then dried under vacuum at room temperature to give PPOx as a white powder with 69% yield.

General depolymerization procedure

A distillation device was charged with polyoxalates (~ 20 g) and depolymerization catalyst (1 wt%). The monomers were then recovered by simple distillation at 180 ° C, 50 Pa. The monomer purity was determined by ^1H NMR.

General procedure for the kinetic study

The polymerization was conducted at a feeding molar ratio of $[M]_0/[BnOH]/[Sn(Oct)_2]$ = 300/1/1. The monomer conversions and the molecular weights M_ns of resultant polyoxalates was monitored by withdrawing aliquots of polymerization mixtures at certain time intervals and measured with ^1H NMR and SEC, respectively.

General procedure for thermodynamic study

The polymerization was conducted at an initial monomer concentration of $[M]_0$ = 4 M followed the general polymerization procedure. Typically, a flame-dried Schlenk tube was charged with (0.12 mmol, 13.0 mg) BnOH, (0.12 mmol, 48.6 mg) $Sn(Oct)_2$, (900 μL) NMP and (6 mmol, 780 mg) POx in a glove box. The Schlenk tube was then

taken out of the glove box and immersed into an oil bath set at different temperatures (90, 110, 130, 150 or 170 °C). The polymerization was allowed to proceed at least one hour. An aliquot of solution was withdrawn at different time intervals and then quenched by rapidly cooling. The polymerization was considered to reach equilibrium when the monomer conversion measured by ^{1}H NMR remained constant for 30 min.

Calculation of the ceiling temperature (T_c) and the equilibrium monomer conversion

The equilibrium monomer conversions at different temperatures were determined according to the above procedures. The equilibrium monomer concentration ($[M]_{eq}$) was then calculated from the monomer conversion using Equation 1-1, where $[M]_0$ was the initial monomer concentration and conv. was the equilibrium monomer conversion.

$$[M]eq = [M]_0 \times (1 - conv.) \quad (1\text{-}1)$$

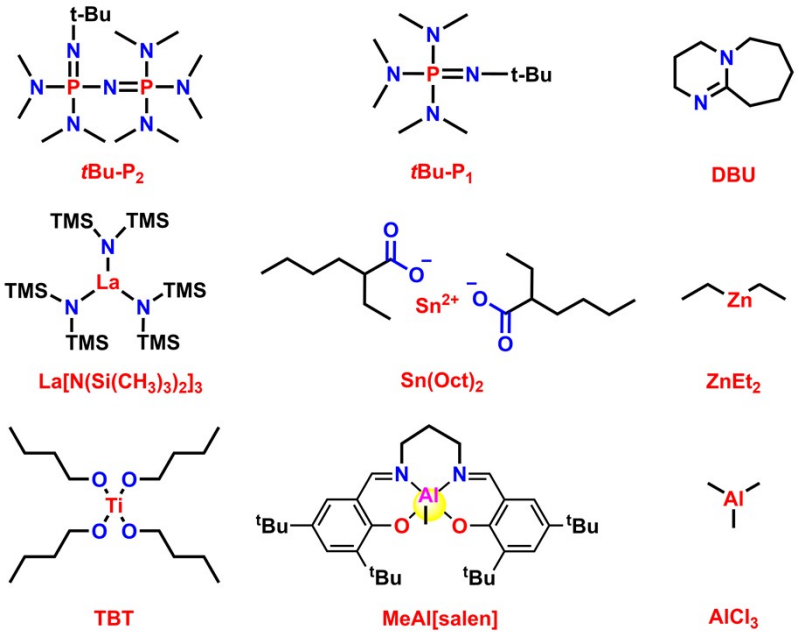
The thermodynamic parameters can be then calculated from the Van't Hoff plot (Equation 1-2). The enthalpy change ($^{\Delta H_p^\theta}$) and the entropy change ($^{\Delta S_P^\theta}$) can be calculated from the slope and the intercept, respectively, according to the linear regression analysis. $[M]_{ss}$ is a standard state monomer concentration (1.0 mol L^{-1}). R is the gas constant, R = 8.314 J·mol^{-1}·K^{-1} and T is the absolute temperature.

$$ln\left(\frac{[M]_{eq}}{[M]_{ss}}\right) = \frac{\Delta H_p^\theta}{TR} - \frac{\Delta S_P^\theta}{R} \quad (1\text{-}2)$$

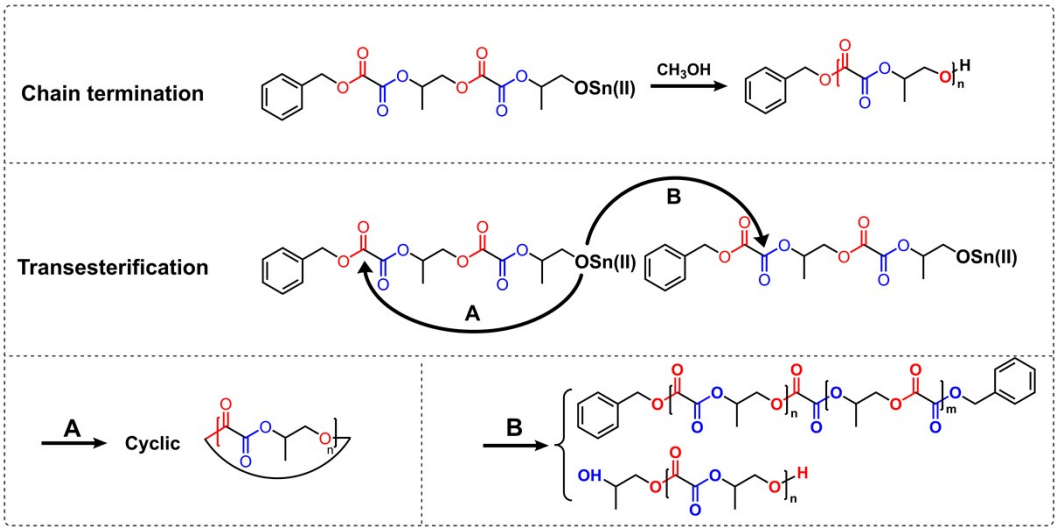
The ceiling temperature (T_c) at a specified monomer concentration could then be calculated using Equations 1-3.

$$T_c = \frac{\Delta H_p^\theta}{\Delta S_p^\theta + Rln[M]} \quad (1\text{-}3)$$

On the other hand, if the thermodynamic parameters (ΔH_p^θ and ΔS_P^θ) are known, the equilibrium monomer concentration ($[M]_{eq}$) can be calculated according to Equation 1-2. The equilibrium monomer conversion can be then calculated using Equation 1-1.



Scheme S1. The chemical structures of the catalysts used in this study.



Scheme S2. Proposed mechanism for the formation of PPOx with various terminal groups due to inter- or intra-transesterification.

Figure S1. The photo of apparatus used for polycondensation.

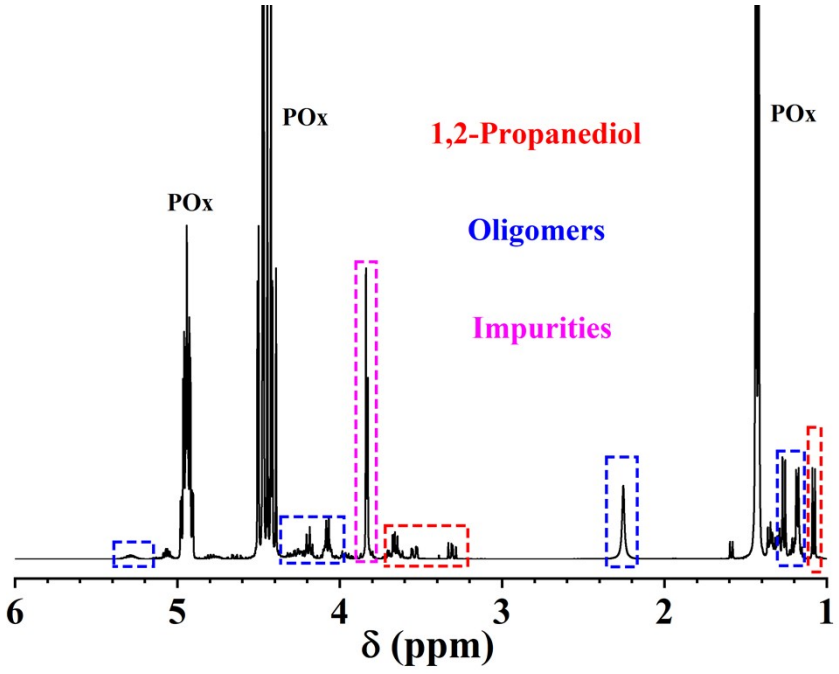


Figure S2. ^{1}H NMR spectrum of crude product of POx measured in $CDCl_3$.

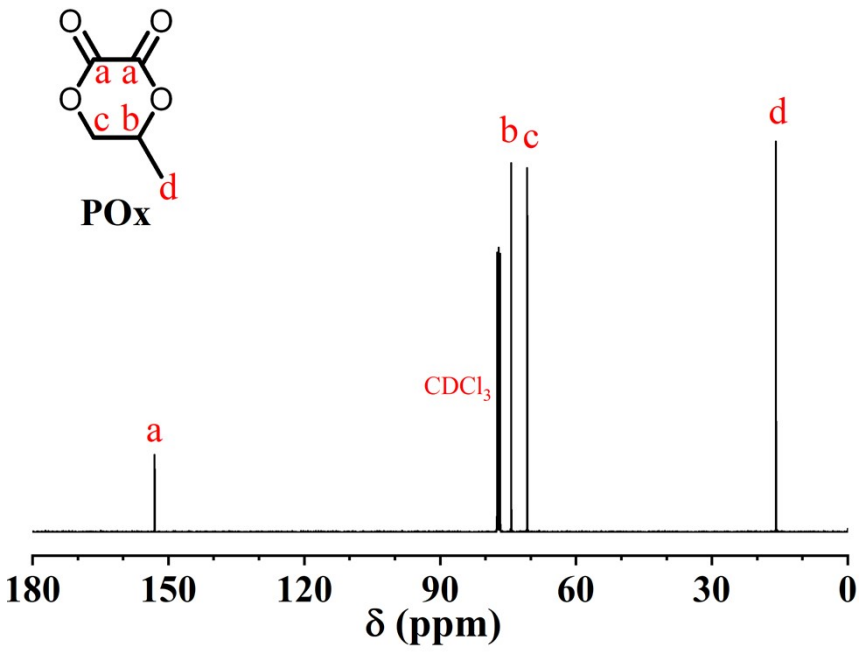


Figure S3. ^{13}C NMR spectrum of POx measured in $CDCl_3$.

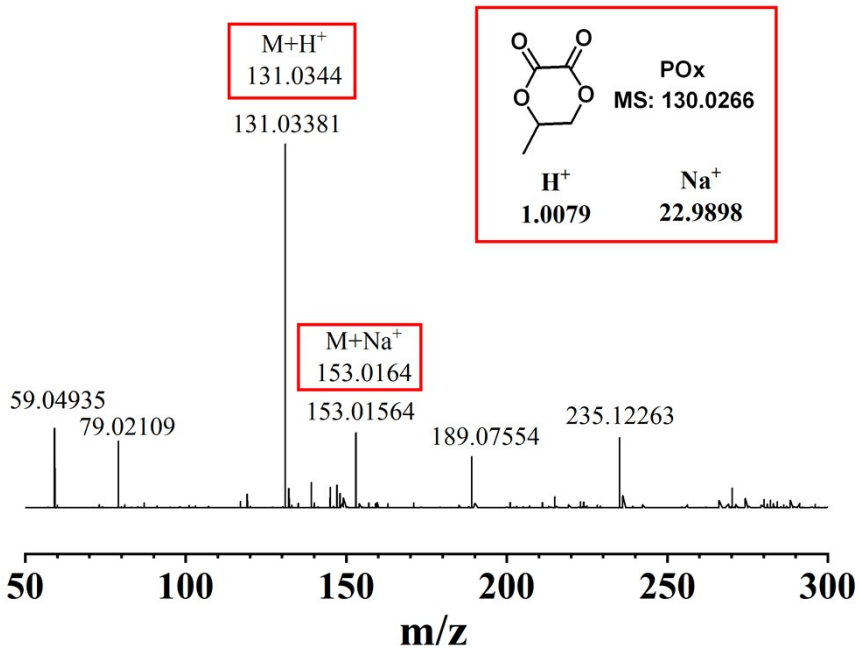


Figure S4. ESI-MS spectrum of POx measured in DCM.

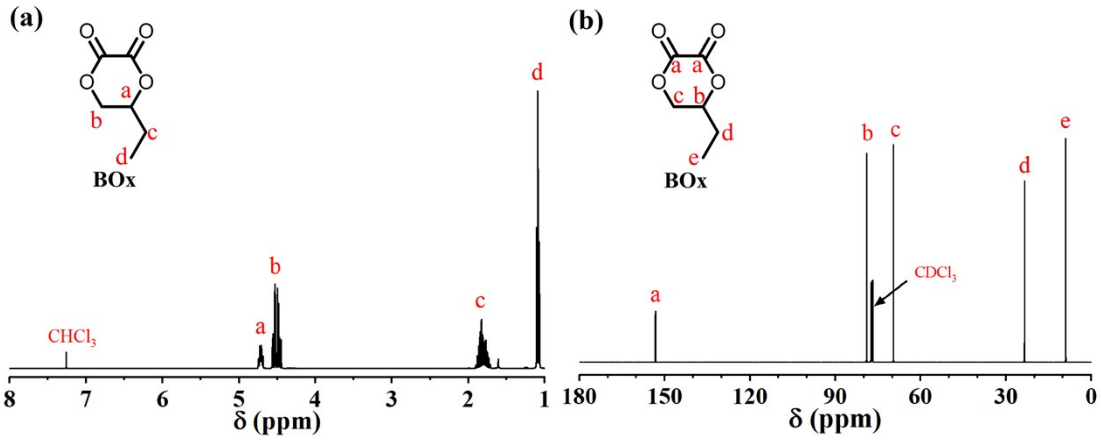


Figure S5. (a) ^{1}H NMR and (b) ^{13}C NMR spectra of BOx measured in $CDCl_3$.

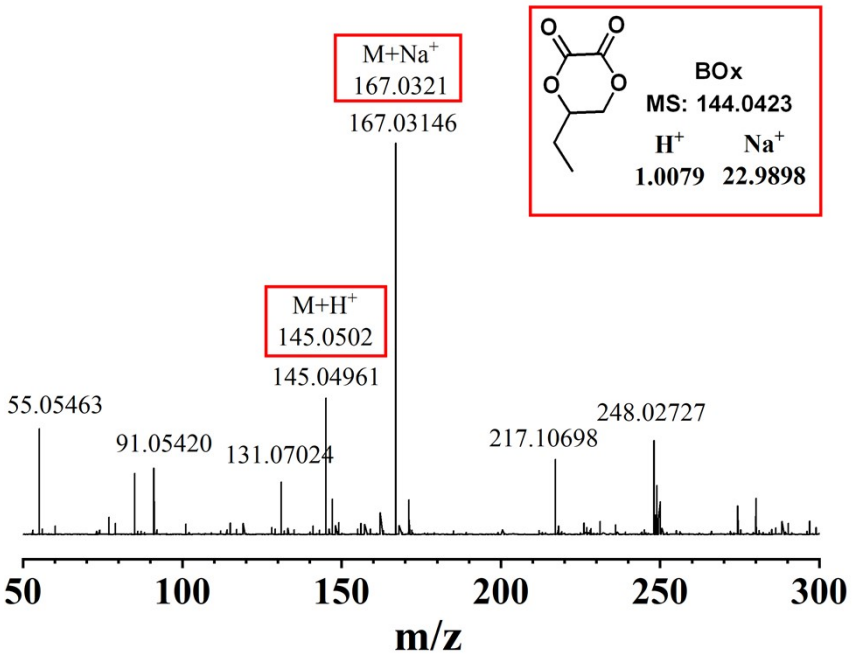


Figure S6. ESI-MS spectrum of BOx measured in DCM.

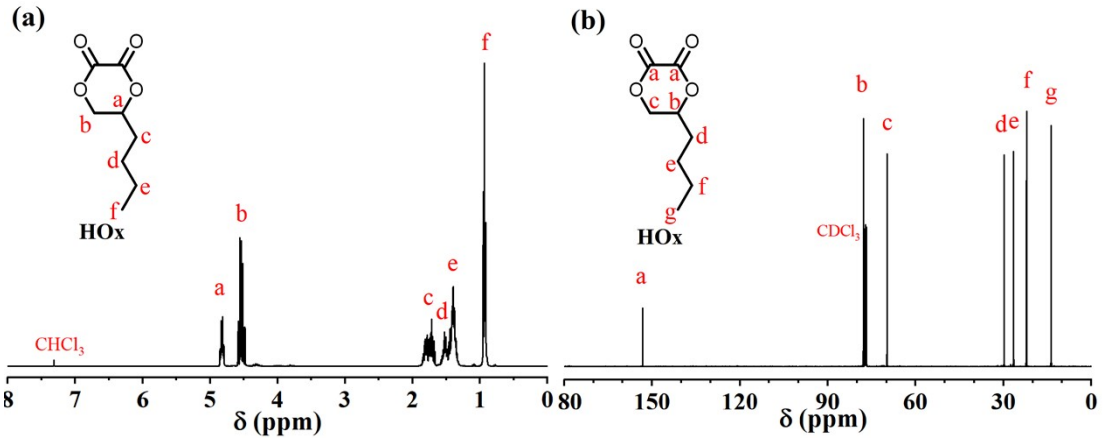


Figure S7. (a) ^{1}H NMR and (b) ^{13}C NMR spectra of HOx measured in $CDCl_3$.

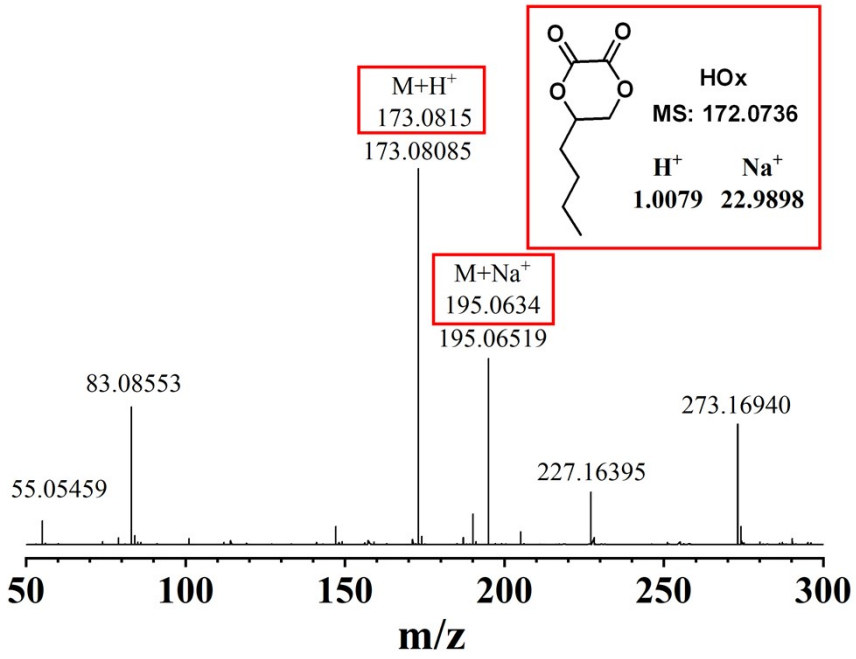


Figure S8. ESI-MS spectrum of HOx measured in DCM.

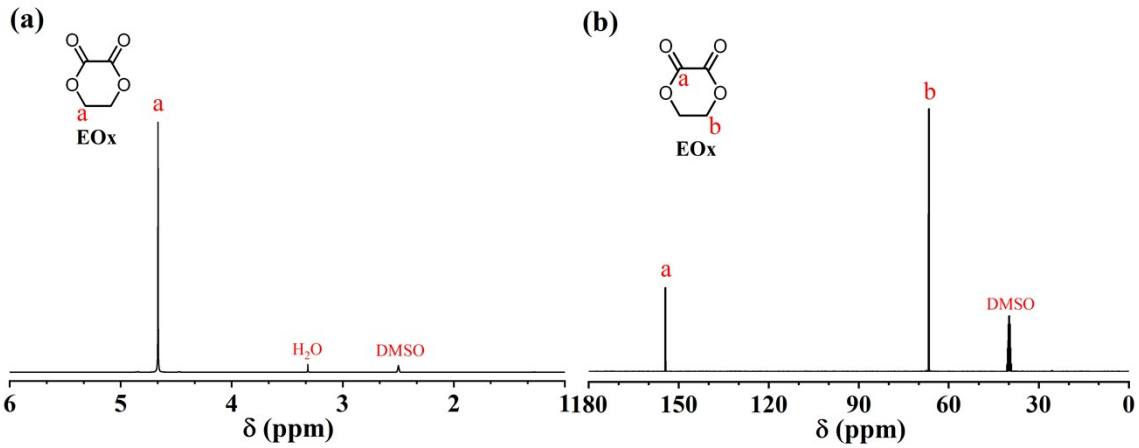


Figure S9. (a) ^{1}H NMR and (b) ^{13}C NMR spectra of EOx measured in DMSO.

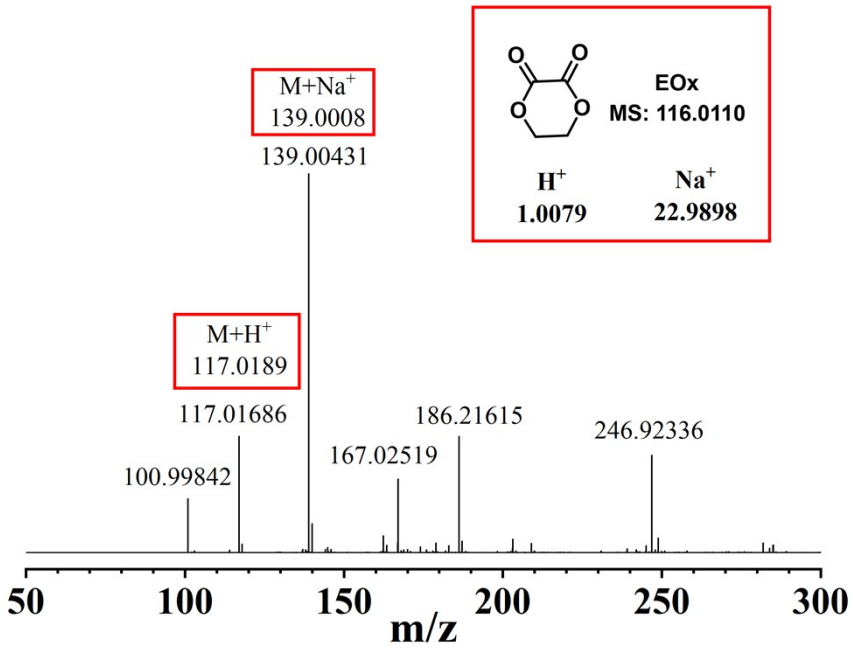


Figure S10. ESI-MS spectrum of EOx measured in Acetone.

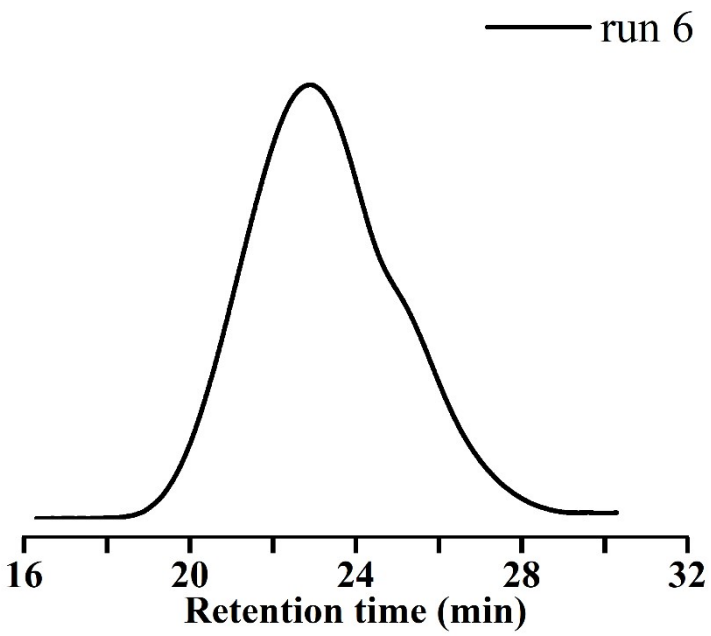


Figure S11. SEC curve of PPOx catalyzed by $La[N(Si(CH_3)_3)_2]_3$ (data shown in Table S3, run 6)

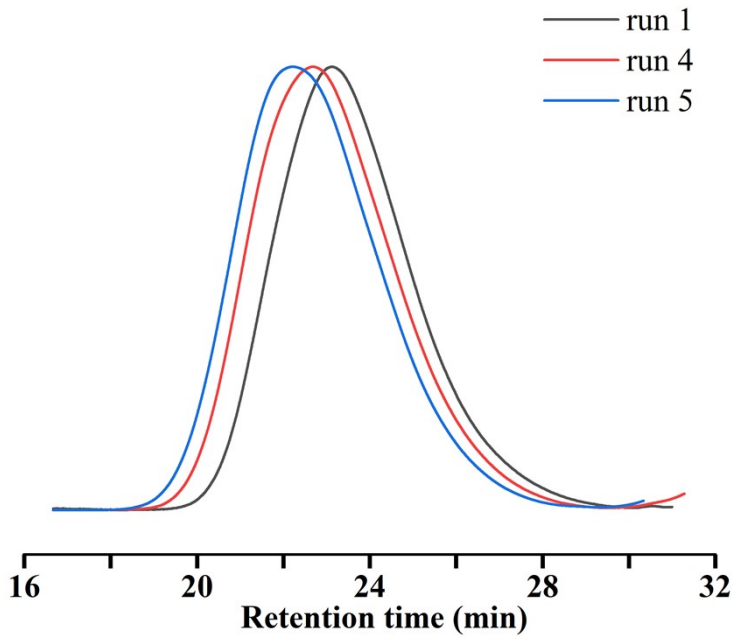


Figure S12. SEC curves of PPOx, PBOx and PHOx (data shown in Table 1, runs 1, 4 and 5) ($[M]_0/[Sn(Oct)_2]/[BnOH]$ = 300/1/1)

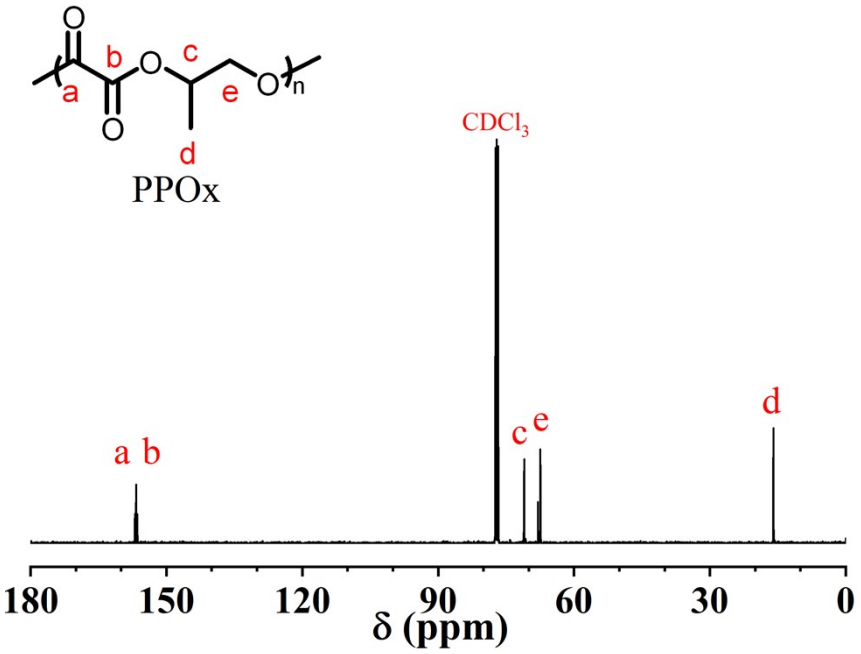


Figure S13. ^{13}C NMR spectrum of PPOx measured in $CDCl_3$. [POx]/[$Sn(Oct)_2$]/[BnOH] = 100/1/1)

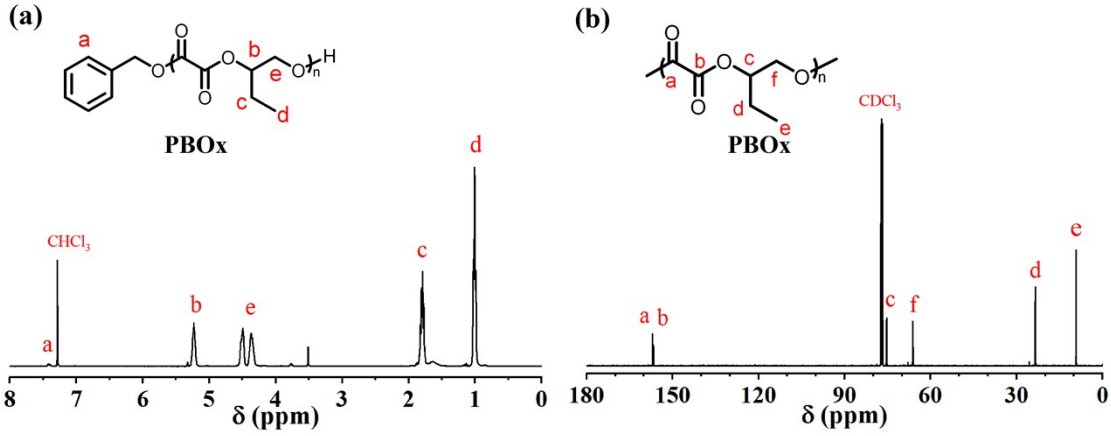


Figure S14. (a) ^{1}H NMR and (b) ^{13}C NMR spectra of PBOx measured in $CDCl_3$. ([BOx]/[$Sn(Oct)_2$]/[BnOH] = 100/1/1)

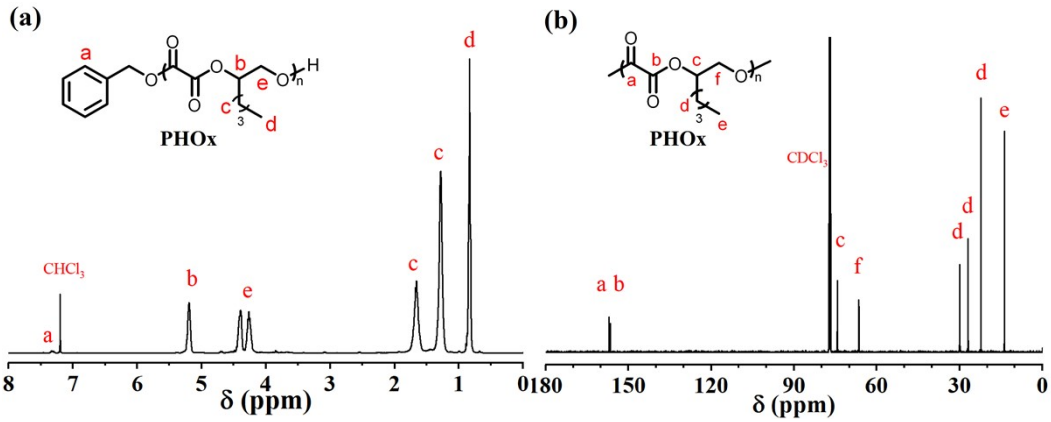


Figure S15. (a) ^{1}H NMR and (b) ^{13}C NMR spectra of PHOx measured in $CDCl_3$.

([HOx]/[$Sn(Oct)_2$]/[BnOH] = 100/1/1)

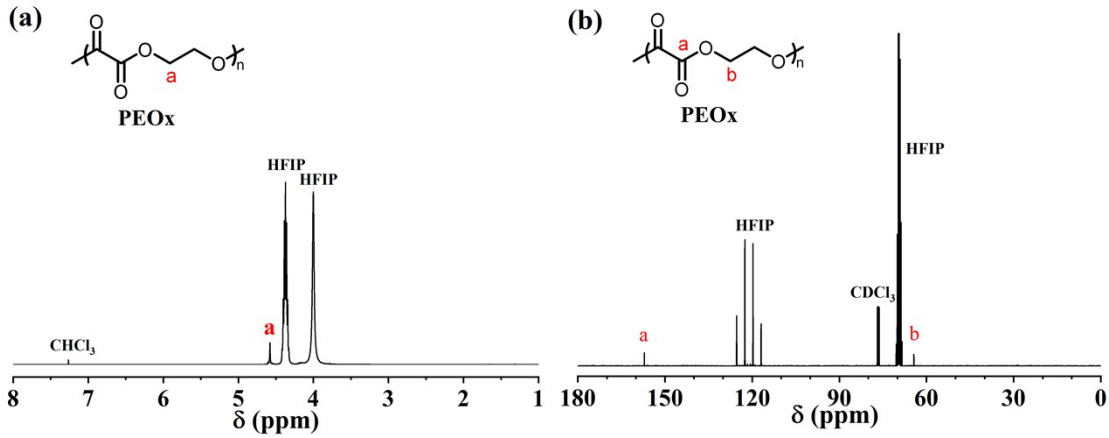


Figure S16. (a) ^{1}H NMR and (b) ^{13}C NMR spectra of PEOx measured in a mixture of HFIP and $CDCl_3$.

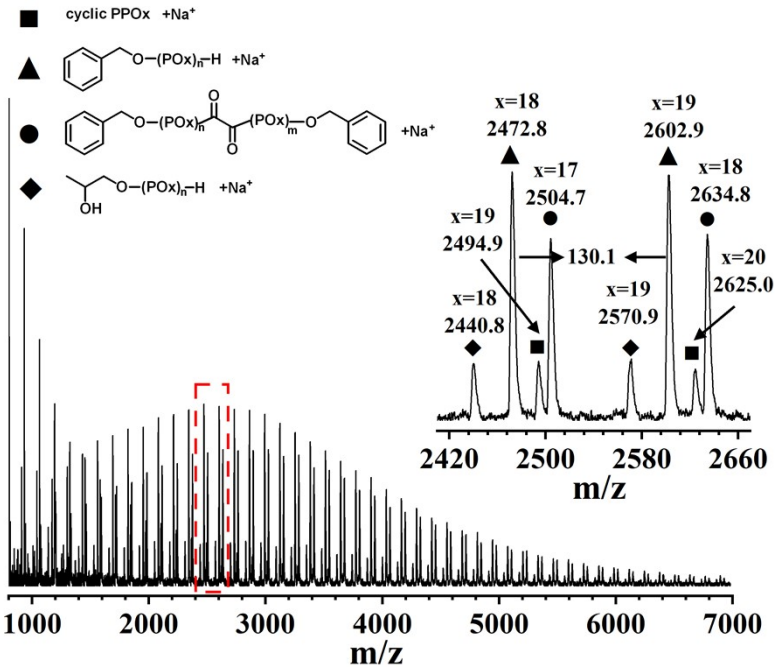


Figure S17. MALDI-TOF mass spectrum of PPOx obtained using $Sn(Oct)_2$ as catalyst. ($[POx]_0/[BnOH]/[Sn(Oct)_2]$ = 300:6:1, Conv. = 95%, M_n = 7.1 kDa, $Đ$ = 1.57)

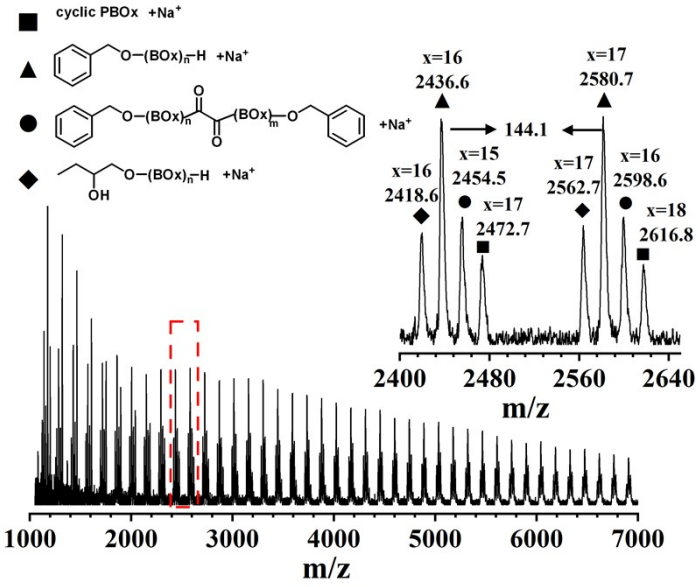


Figure S18. MALDI-TOF mass spectrum of PBOx obtained using $Sn(Oct)_2$ as catalyst. ($[BOx]_0/[BnOH]/[Sn(Oct)_2]$ = 300:6:1, Conv. = 95%, M_n = 7.8 kDa, $Đ$ = 1.59)

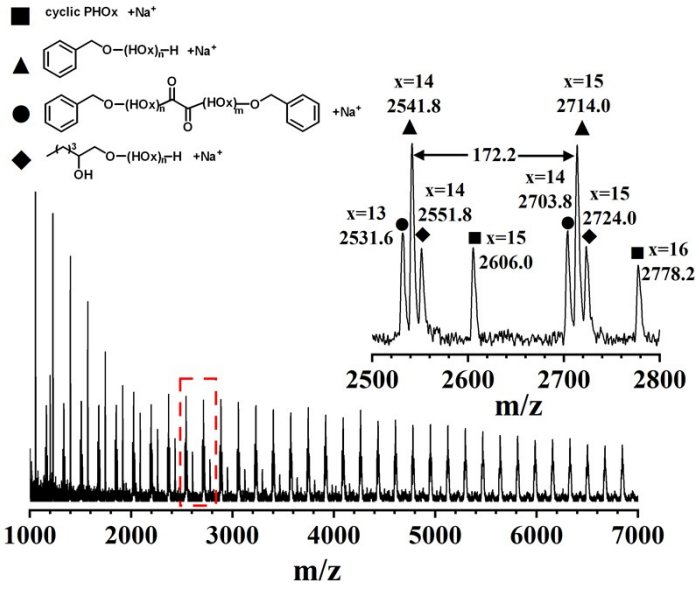


Figure S19. MALDI-TOF mass spectrum of PHOx obtained using $Sn(Oct)_2$ as catalyst. ($[HOx]_0/[BnOH]/[Sn(Oct)_2]$ = 300:6:1, Conv. = 95%, M_n = 8.0 kDa, $Đ$ = 1.66)

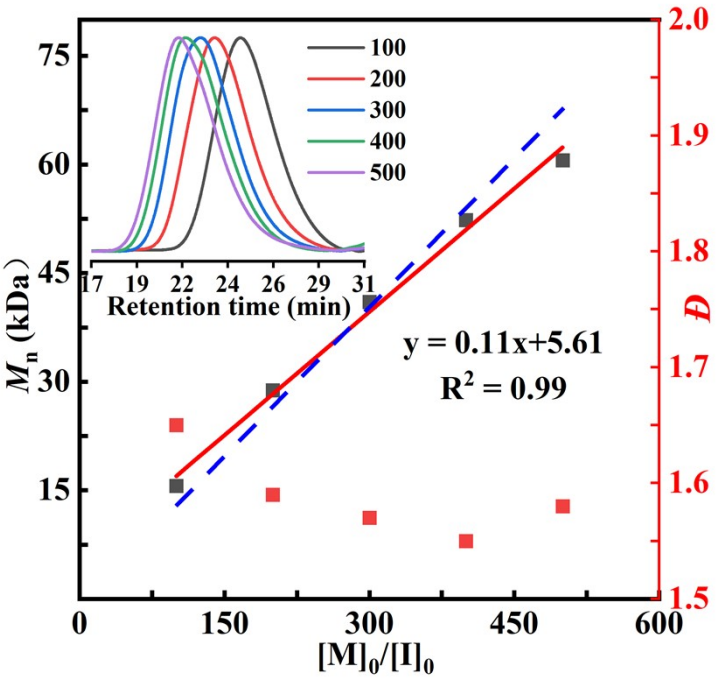


Figure S20. Evolution of M_n and $Đ$ as a function of monomer conversion at $[BOx]_0/[BnOH]$ ratio. Inset: Overlay of SEC curves at different $[BOx]_0/[BnOH]$ ratios ($[BnOH]/[Sn(Oct)_2]$ = 1:1 data shown in Table S9). The dashed lines indicate the evolution of theoretical molar mass.

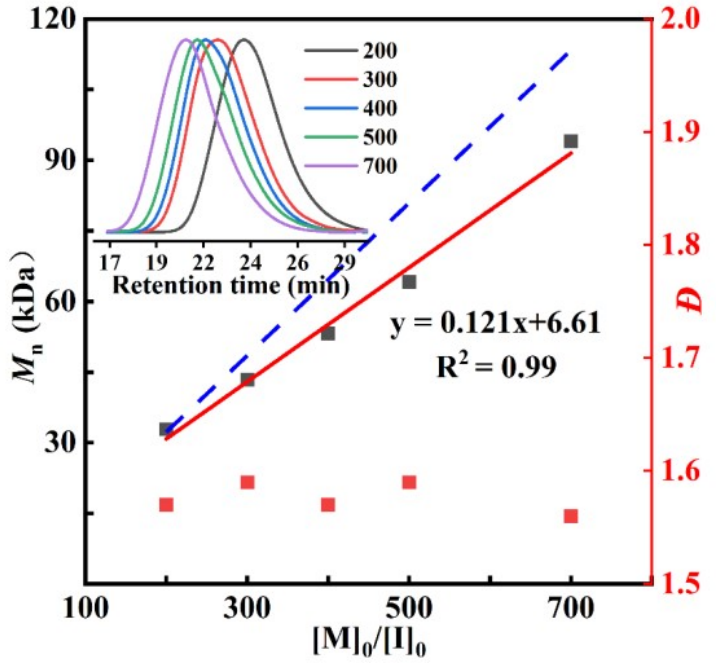


Figure S21. Evolution of M_n and $Đ$ as a function of monomer conversion at $[HOx]_0/[BnOH]$ ratio. Inset: Overlay of SEC curves at different $[HOx]_0/[BnOH]$

ratios ([BnOH]/[Sn(Oct)$_2$] = 1:1 data shown in Table S10). The dashed lines indicate the evolution of theoretical molar mass.

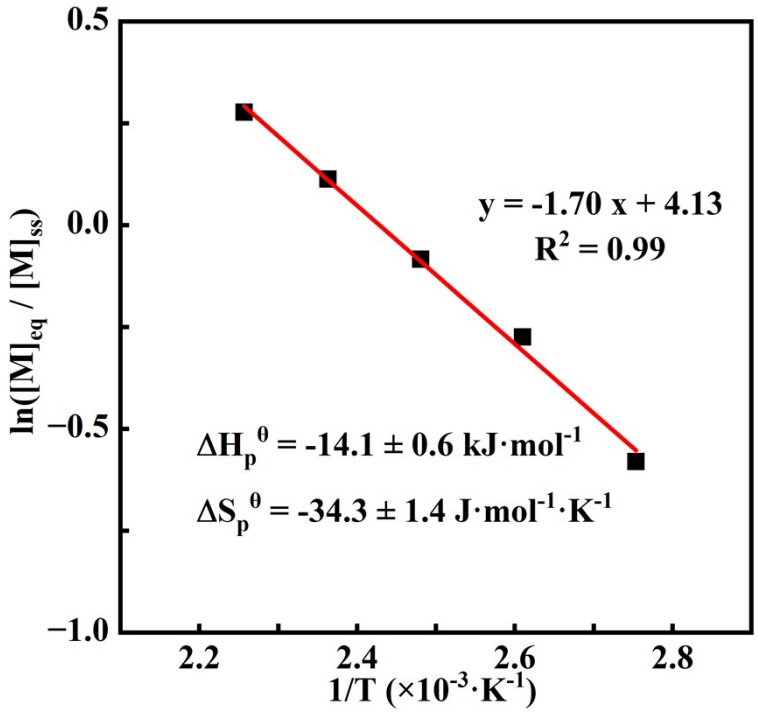


Figure S22. The Van't Hoff plot of the ROP of POx (data shown in Table S11).

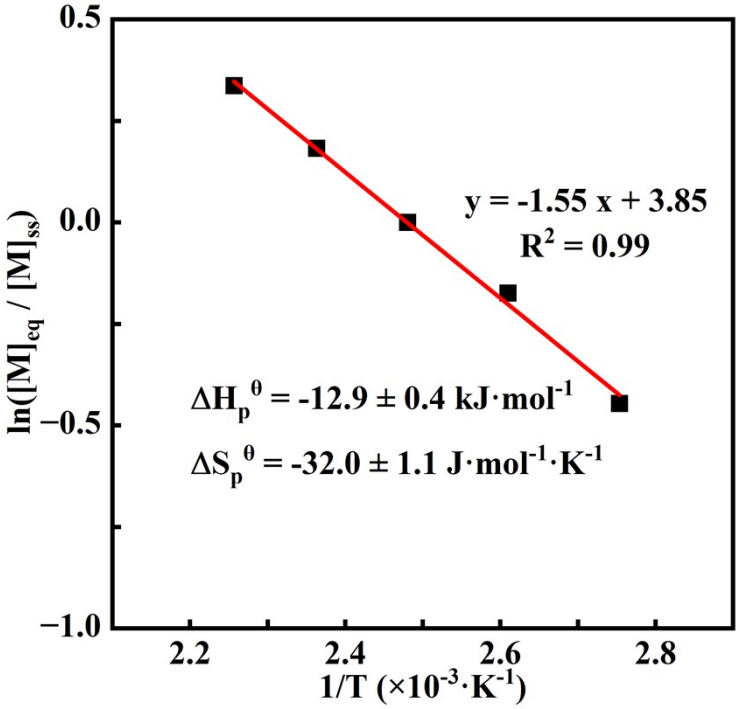


Figure S23. The Van't Hoff plot of the ROP of BOx (data shown in Table S12).

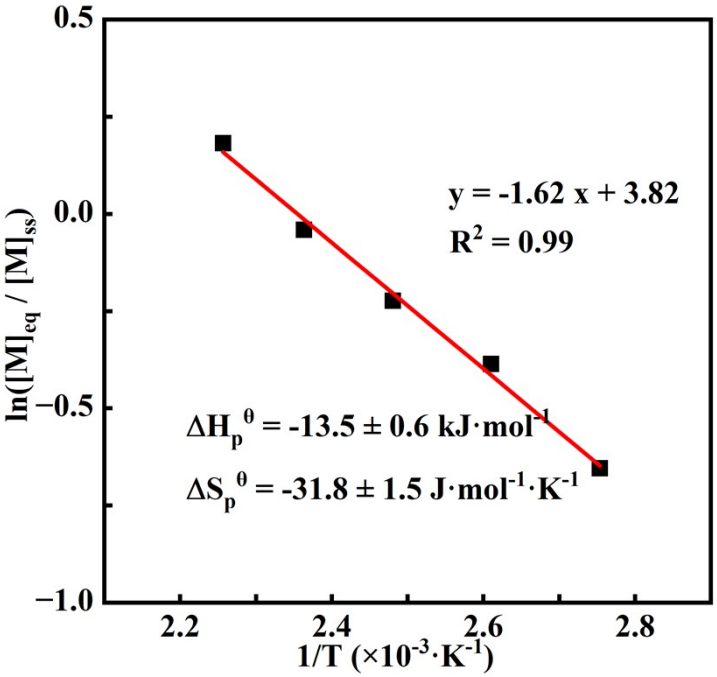


Figure S24. The Van't Hoff plot of the ROP of HOx (data shown in Table S13).

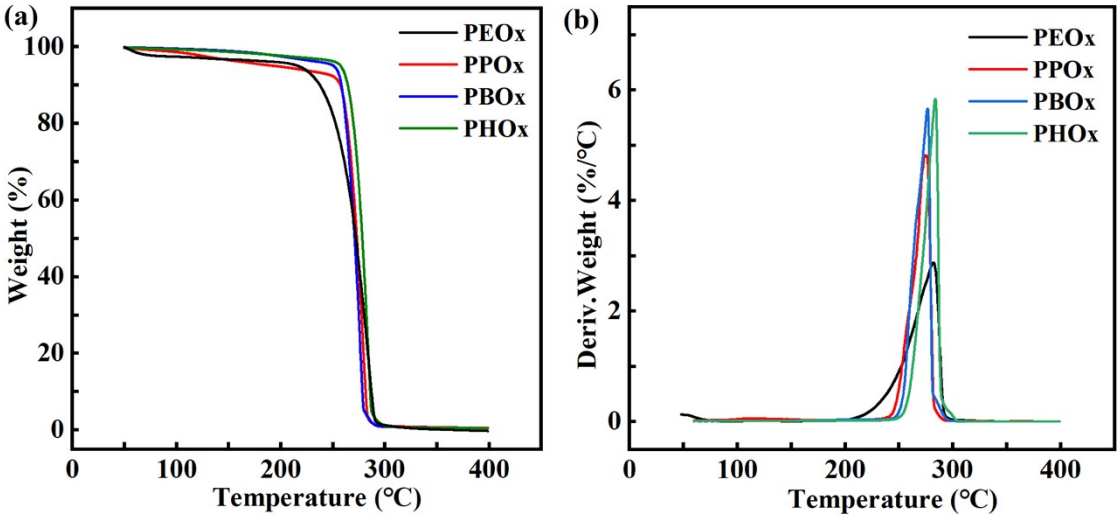


Figure S25. (a) TGA and (b) DTG curves of PEOx, PPOx, PBOx and PHOx (data shown in Table S14).

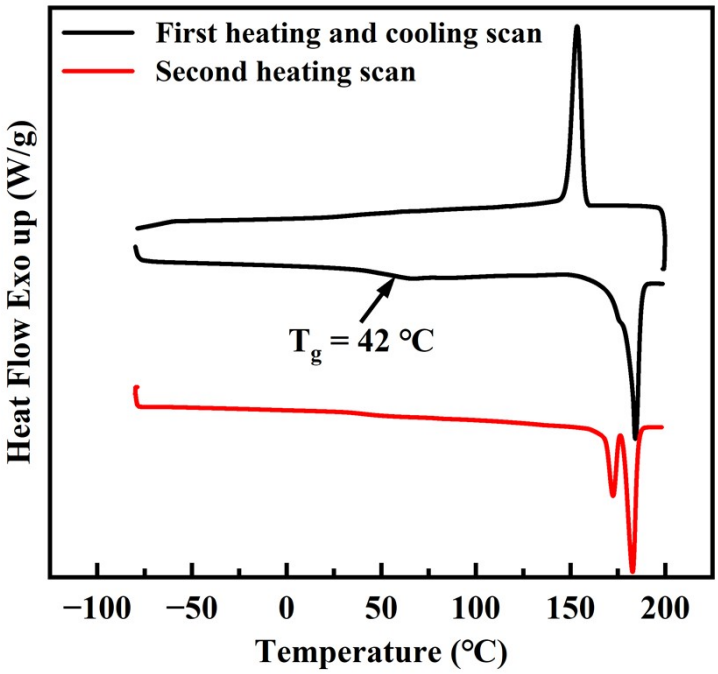


Figure S26. DSC curves of PEOx sample with a targeted DP of 300.

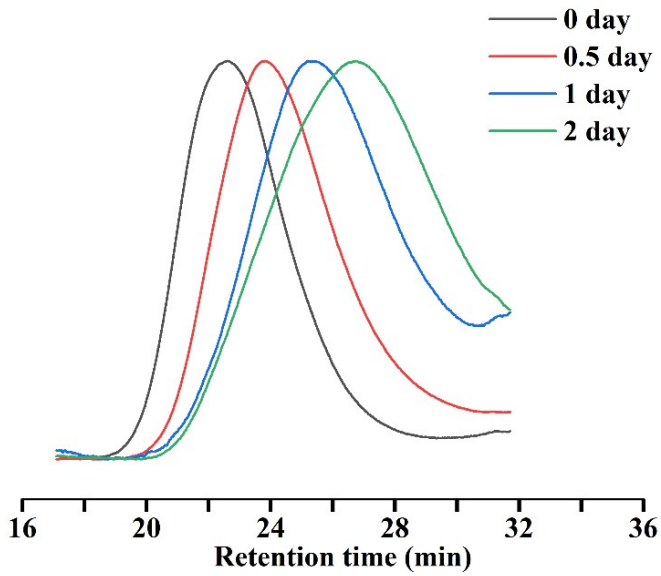


Figure S27. SEC curves of the remaining polymer during the degradation of PPOx in artificial seawater.

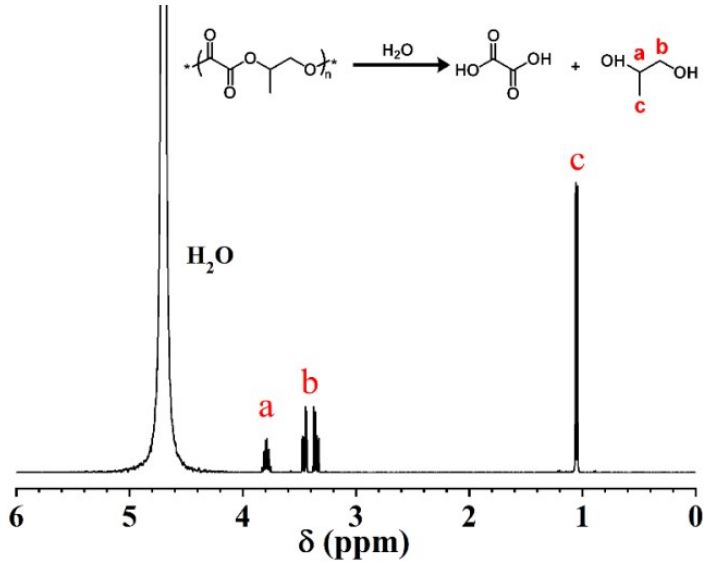


Figure S28. [1] H NMR spectrum of the hydrolytic degradation product of PPOx in artificial seawater.

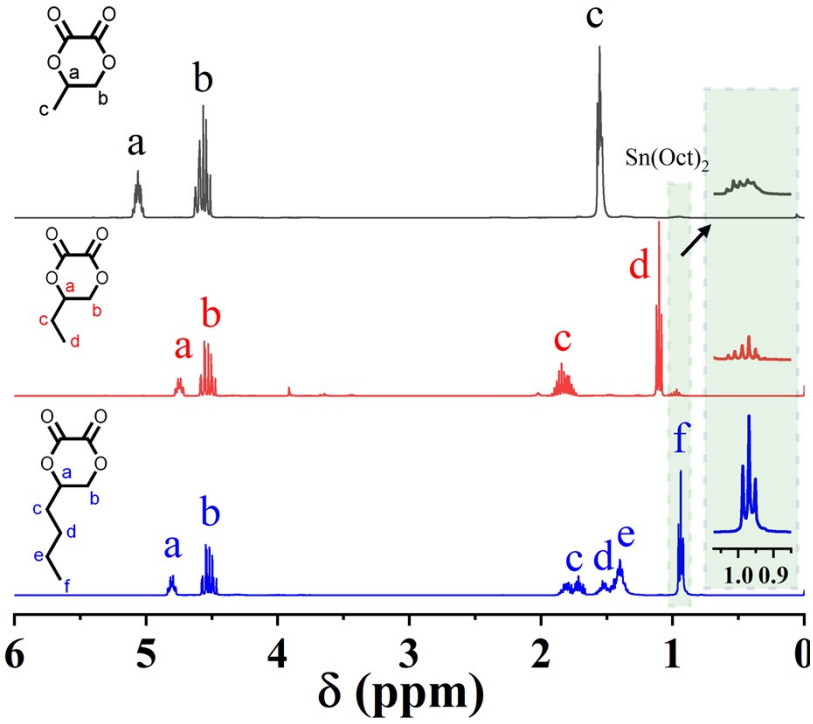


Figure S29. [1]H NMR spectra of recovered POx, BOx and HOx using $Sn(Oct)_2$ as the catalyst for depolymerization.

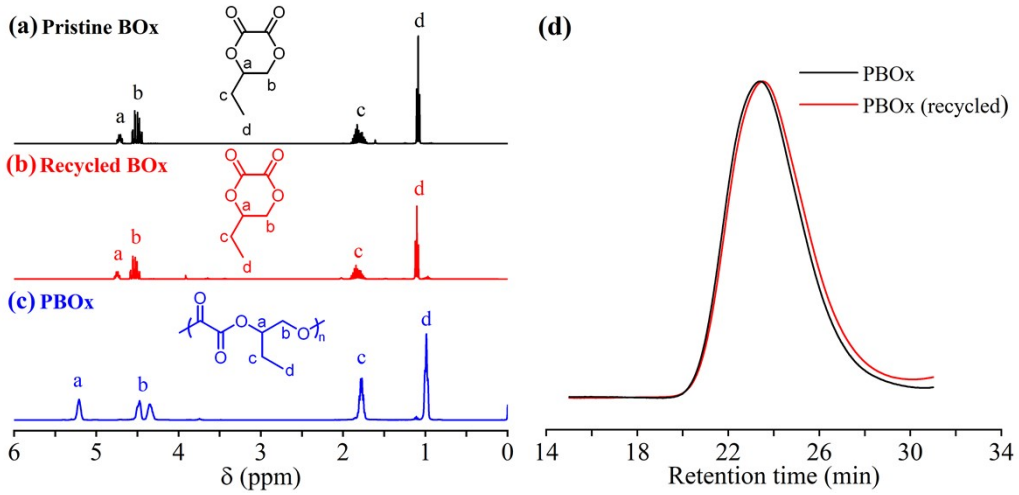


Figure S30. Overlay of ^{1}H NMR spectra measured in $CDCl_3$ of (a) pristine BOx as comparison, (b) recycled BOx by distillation and (c) PBOx obtained using recycled monomer. (d) SEC traces of PBOx prepared from pristine monomer (black line, M_n = 41.0 kDa, $Đ$ = 1.57) and PBOx prepared from recycled monomer (red line, M_n = 40.8 kDa, $Đ$ = 1.56).

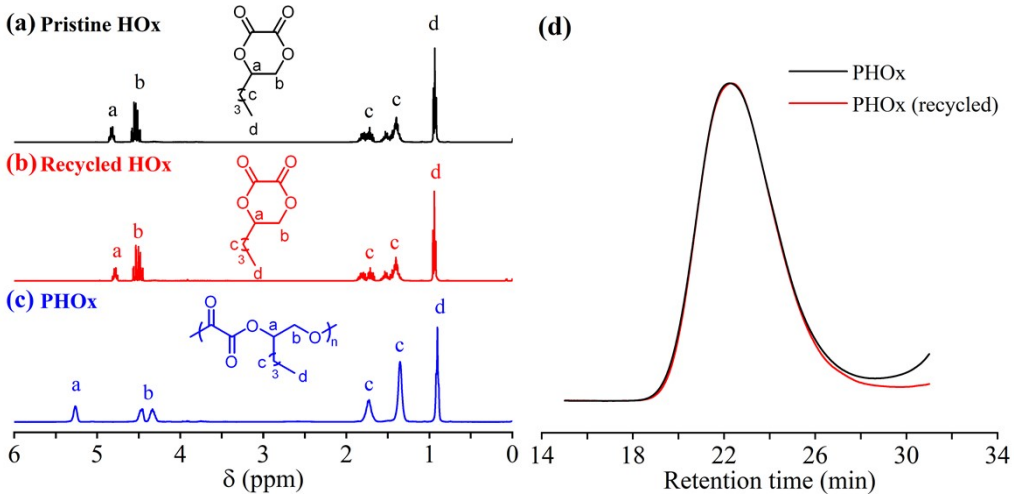


Figure S31. Overlay of ^{1}H NMR spectra measured in $CDCl_3$ of (a) pristine HOx as comparison, (b) recycled HOx by distillation and (c) PHOx obtained using recycled monomer. (d) SEC traces of PHOx prepared from pristine monomer (black line, M_n = 45.2 kDa, $Đ$ = 1.58) and PHOx prepared from recycled monomer (red line, M_n = 45.1 kDa, $Đ$ = 1.59).

Table S1. Results of depolymerization of PPOx in the presence of different catalysts [a]

Run	Catalyst	Time (h)	Yield (%)	Purity (POx, %)
1	$Sn(Oct)_2$	1	63.4	82.9
2	ZnCl	2	59.5	71.4
3	TsOH	2	40.3	82.7
4	NaAc	1.5	83.5	86.2
5	Sodium glycolate	1	87.4	90.7
6	KOH	1	90.2	93.0
7	DBU	2	34.6	21.5

[a] Conditions: The mass of polymer sample used for depolymerization is 20-21g; Depolymerization was carried out at 180 °C, 50 Pa in the presence of 1 wt% catalyst relative to the prepolymer.

Table S2. Results of depolymerization of poly(1, 2-oxalate)s in the presence of different catalysts and conditions [a]

Run	poly(1, 2-oxalate)s	Depolymerization Catalyst	Temp. (°C)	Time (h)	Yield (%)	Purity (%)
1	PBOx	KOH	180	1	92.5	93.0
2	PHOx	KOH	180	1	93.4	93.0
3	PEOx	KOH	210	6	n.d.	n.d.
4	PEOx	Sodium glycolate	210	6	60.5	85.7

[a] Conditions: The mass of polymer sample used for depolymerization is 20-21g; Depolymerization was carried out at 50 Pa in the presence of 1 wt% catalyst relative to the prepolymer. n.d. = not determined since no product was collected.

Table S3. Results of ROP of POx conducted at [M]/[C]/[I] = 300/1/1 in solution [a]

Run	Catalyst	Temp. (°C)	Sol.	Time (min)	Conv. (%) [b]	$M_{n,theo}$ (kDa) [c]	$M_{n,SEC}$ (kDa) [d]	Đ [d]
1	tBu-P_2	25	THF	2	97	37.9	23.4	1.54
2	tBu-P_1	25	THF	5	96	35.9	29.2	1.72
3	DBU	25	THF	5	97	37.9	26.1	1.52
4	$AlMe_3$	25	THF	1440	30	11.8	9.8	1.20
5	TBT	25	THF	1440	31	12.1	9.9	1.19
6	$La[N(Si(CH_3)_3)_2]_3$	25	THF	1	96	37.5	29.6	1.70
7	$ZnEt_2$	25	THF	90	94	36.7	29.8	1.60
8	MeAl[salen]	25	THF	120	95	37.1	32.9	1.59

[a] Conditions: The polymerizations were conducted at $[M]_0$ = 4 M in the presence of 0.02 mmol benzyl alcohol (BnOH) as the initiator. [b] Determined by ^1H NMR spectra. [c] Theoretical molecular weight was calculated from the feeding molar ratio and monomer conversion as $M_{n,\ theo}$ = [M]/[I] * conv.(M) * MW(M) + MW(Initiator). [d] Determined by SEC in THF relative to PS standards.

Table S4. Results of ROP of POx conducted at [M]/[C]/[I] = 300/1/1 in bulk [a]

Run	Catalyst	Time (min)	Conv. (%) [b]	$M_{n,theo}$ (kDa) [c]	$M_{n,SEC}$ (kDa) [d]	Đ [d]
1	tBu-P_2	2	98	38.3	25.6	1.71
2	tBu-P_1	2	97	37.9	29.7	1.71
3	DBU	2	98	38.3	27.5	1.66
4	TBT	240	89	34.8	13.2	1.50
5	$ZnEt_2$	10	95	37.1	33.5	1.68
6	MeAl[salen]	10	93	36.3	32.9	1.70

[a] Conditions: The polymerizations were conducted at 130 °C in the presence of 0.02 mmol benzyl alcohol (BnOH) as the initiator. [b] Determined by ^{1}H NMR spectra. [c] Theoretical molecular weight was calculated from the feeding molar ratio and monomer conversion as $M_{n,\ theo}$ = [M]/[I] * conv.(M) * MW(M) + MW(Initiator). [d] Determined by SEC in THF relative to PS standards.

Table S5. Kinetic data of ROP of POx obtained at $[M]_0/[Sn(Oct)_2]/[BnOH]$ = 300/1/1 [a]

Run	Time (min)	Conv. (%) [b]	$M_{n,\ SEC}$ (kDa) [c]	$Đ$ [c]
1	1	25	7.4	1.50
2	2	50	16.2	1.50
3	3	70	22.2	1.52
4	4	83	28.3	1.51
5	6	90	30.1	1.53
6	10	94	32.1	1.54

[a] Conditions: The bulk polymerization was conducted at 130 °C using 0.02 mmol BnOH as the initiator. [b] Determined by ^{1}H NMR. [c] Determined by SEC in THF relative to PS standards.

Table S6. Kinetic data of ROP of BOx obtained at $[M]_0/[Sn(Oct)_2]/[BnOH] = 300/1/1$ [a]

Run	Time (min)	Conv. (%) [b]	$M_{n,\,SEC}$ (kDa) [c]	$Đ$ [c]
1	1	25	8.0	1.52
2	2	53	19.8	1.62
3	3	69	28.0	1.60
4	4	81	33.0	1.59
5	6	88	36.0	1.55
6	10	93	37.1	1.56

[a] Conditions: The bulk polymerization was conducted at 130 °C using 0.02 mmol BnOH as the initiator. [b] Determined by ^{1}H NMR. [c] Determined by SEC in THF relative to PS standards.

Table S7. Kinetic data of ROP of HOx obtained at $[M]_0/[Sn(Oct)_2]/[BnOH] = 300/1/1$ [a]

Run	Time (min)	Conv. (%) [b]	$M_{n,\,SEC}$ (kDa) [c]	$Đ$ [c]
1	1	30	12.5	1.50
2	2	59	27.4	1.57
3	3	76	36.6	1.55
4	4	86	39.7	1.58
5	6	91	42.1	1.58
6	10	94	44.3	1.56

[a] Conditions: The bulk polymerization was conducted at 130 °C using 0.02 mmol BnOH as the initiator. [b] Determined by ^{1}H NMR. [c] Determined by SEC in THF relative to PS standards.

Table S8. Results of ROP of POx obtained at varied $[M]_0/[BnOH]$ ratios. [a]

Run	$[M]_0/[I]$	Time (min)	Conv. (%) [b]	$M_{n,\,theo}$ (kDa) [c]	$M_{n,\,SEC}$ (kDa) [d]	$Đ$ [d]
1	100/1/1	10	95	12.4	13.2	1.61
2	150/1/1	13	94	18.5	17.4	1.56
3	200/1/1	15	95	24.7	24.3	1.55
4	250/1/1	18	94	30.8	28.3	1.55
5	300/1/1	20	95	37.2	32.2	1.54

[a] Conditions: The bulk polymerization was conducted at 130 °C at $[Sn(Oct)_2]/[BnOH]=1/1$ using 0.02 mmol BnOH as the initiator. [b] Monomer conversions were determined by ^1H NMR. [c] Theoretical molecular weight was calculated from the feeding molar ratio and monomer conversion as $M_{n,\,theo}$ = [M]/[I] * Conv.(M) * MW(M) + MW(Initiator). [d] Determined by SEC in THF relative to PS standards.

Table S9. Results of ROP of BOx obtained at varied $[M]_0/[BnOH]$ ratios. [a]

Run	$[M]_0/[I]$	Time (min)	Conv. (%) [b]	$M_{n,\,theo}$ (kDa) [c]	$M_{n,\,SEC}$ (kDa) [d]	$Đ$ [d]
1	100/1/1	10	93	13.5	15.6	1.65
2	200/1/1	15	92	26.7	28.8	1.59
3	300/1/1	20	94	40.5	41.0	1.57
4	400/1/1	25	94	54.0	52.3	1.55
5	500/1/1	30	94	67.8	60.6	1.58

[a] Conditions: The bulk polymerization was conducted at 130 °C at $[Sn(Oct)_2]/[BnOH]=1/1$ using 0.02 mmol BnOH as the initiator. [b] Monomer conversions were determined by ^1H NMR. [c] Theoretical molecular weight was calculated from the feeding molar ratio and monomer conversion as $M_{n,\,theo}$ = [M]/[I] * Conv.(M) * MW(M) + MW(Initiator). [d] Determined by SEC in THF relative to PS standards.

Table S10. Results of ROP of HOx obtained at varied $[M]_0/[BnOH]$ ratios. [a]

Run	$[M]_0/[I]$	Time (min)	Conv. (%) [b]	$M_{n,\,theo}$ (kDa) [c]	$M_{n,\,SEC}$ (kDa) [d]	$Đ$ [d]
1	200/1/1	15	94	32.4	32.9	1.57
2	300/1/1	20	93	48.3	43.4	1.59
3	400/1/1	25	93	63.8	53.2	1.57
4	500/1/1	30	94	81.0	64.2	1.59
5	700/1/1	40	94	113.3	94.0	1.56

[a] Conditions: The bulk polymerization was conducted at 130 °C at $[Sn(Oct)_2]/[BnOH]=1/1$ using 0.02 mmol BnOH as the initiator. [b] Monomer conversions were determined by ^1H NMR. [c] Theoretical molecular weight was calculated from the feeding molar ratio and monomer conversion as $M_{n,\,theo}$ = [M]/[I] * Conv.(M) * MW(M) + MW(Initiator). [d] Determined by SEC in THF relative to PS standards.

Table S11. Equilibrium monomer concentration of POx measured at various temperatures [a]

Run	Temp. (°C)	Temp. (K)	Time (min)	Conv. (%) [b]	$[M]_{eq.}$ ($mol \cdot L^{-1}$)
1	90	363.15	60	86	0.56
2	90	363.15	90	86	0.56
3	110	383.15	60	81	0.76
4	110	383.15	90	81	0.76
5	130	403.15	60	77	0.92
6	130	403.15	90	77	0.92
7	150	423.15	60	72	1.12
8	150	423.15	90	72	1.12
9	170	443.15	60	67	1.32
10	170	443.15	90	67	1.32

[a] Conditions: The polymerizations were conducted at an initial monomer concentration of $[POx]_0$ = 4 M in *N*-methyl pyrrolidone with a feeding molar ratio of $[M]_0/[Sn(Oct)_2]/[BnOH]$ = 50/1/1 using 0.12 mmol BnOH as the initiator. [b] Monomer conversions were determined by ^1H NMR.

Table S12. Equilibrium monomer concentration of BOx measured at various temperatures [a]

Run	Temp. (°C)	Temp. (K)	Time (min)	Conv. (%) [b]	$[M]_{eq.}$ ($mol \cdot L^{-1}$)
1	90	363.15	60	84	0.64
2	90	363.15	90	84	0.64
3	110	383.15	60	79	0.84
4	110	383.15	90	79	0.84
5	130	403.15	60	75	1.00
6	130	403.15	90	75	1.00
7	150	423.15	60	70	1.20
8	150	423.15	90	70	1.20
9	170	443.15	60	68	1.28
10	170	443.15	90	68	1.28

[a] Conditions: The polymerizations were conducted at an initial monomer concentration of $[POx]_0$ = 4 M in *N*-methyl pyrrolidone with a feeding molar ratio of $[M]_0/[Sn(Oct)_2]/[BnOH]$ = 50/1/1 using 0.12 mmol BnOH as the initiator. [b] Monomer conversions were determined by ^1H NMR.

Table S13. Equilibrium monomer concentration of HOx measured at various temperatures [a]

Run	Temp. (°C)	Temp. (K)	Time (min)	Conv. (%) [b]	$[M]_{eq.}$ ($mol \cdot L^{-1}$)
1	90	363.15	60	87	0.52
2	90	363.15	90	87	0.52
3	110	383.15	60	83	0.68
4	110	383.15	90	83	0.68
5	130	403.15	60	80	0.80
6	130	403.15	90	80	0.80
7	150	423.15	60	76	0.96
8	150	423.15	90	76	0.96
9	170	443.15	60	70	1.20
10	170	443.15	90	70	1.20

[a] Conditions: The polymerizations were conducted at an initial monomer concentration of $[POx]_0$ = 4 M in *N*-methyl pyrrolidone with a feeding molar ratio of $[M]_0/[Sn(Oct)_2]/[BnOH]$ = 50/1/1 using 0.12 mmol BnOH as the initiator. [b] Monomer conversions were determined by ^1H NMR.

Table S14. Thermal properties of PEOx, PPOx, PBOx and PHOx sample. [a]

Run	Sample	M_n (kDa)	$Đ$	T_g (°C)	$T_{d,5\%}$ (°C)	$T_{d,max}$ (°C)
1	PEOx	-	-	42	203	282
2	PPOx	32.2	1.54	29.3	193	274
3	PBOx	41.0	1.57	6.4	250	276
4	PHOx	43.3	1.59	-5.8	257	283

[a] Glass transition temperature determined using DSC.

Table S15. Degradation results of PPOx in artificial seawater [a]

Run	Time (day)	Residual weight (%)	$M_{n,SEC}$ (kDa) [d]	$Đ$ [d]
1	0	100	37.2	1.60
2	0.5	100	20.3	1.90
3	1	100	9.3	2.20
4	2	94.5	4.5	3.63
5	3	46.4	n.d.	n.d.
6	4	2.1	n.d.	n.d.
7	5	0	n.d.	n.d.

n.d.= The molecular weight was too low to be measured.

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