

Supporting Information for Manuscript

Synthesis of well-defined and recyclable polyester from ring opening polymerization of 1,5-dioxepan-2-one catalyzed by Lewis acid-base pair

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Experimental Section

Materials

Moisture-sensitive compounds were handled in a glovebox or by using standard Schlenk techniques. 3-Chloroperbenzoic acid (mCPBA) and Tetrahydro-4H-pyran-4-one were purchased from Energy Chemical Co. 4-Dimethylaminopyridine (DMAP) was obtained from Macklin Co. 1,8-Diazabicyclo[5.4.0]undec-7-ene (DBU) was

obtained from J&K Scientific Co. Diethyl Zinc (ZnEt_2) and 1,5,7-Triazabicyclo[4.4.0]dec-5-ene (TBD) were purchased from Aladdin Co. Tetrahydrofuran (THF) and toluene (Tol) were obtained from Tianjin Fuyu Chemical Reagent Co. and were stirred with sodium for 4 h, then distilled under reduced pressure and stored in a glove box. N,N-dimethylformamide (DMF) was obtained from Tianjin Fuyu Chemical Reagent Co. was refluxed with CaH_2 for 4 h and then distilled under reduced pressure. Benzyl alcohol (BnOH) was obtained from Alfa Aesar Co. and stirred with CaH_2 for 24 h then distilled under reduced pressure. All commercially obtained reagents were used as received without further purification unless otherwise noted.

Instruments

Nuclear magnetic resonance (NMR) spectra were recorded on a Bruker AVNEO400ASCEND FT-NMR spectrometer at 400 MHz for ^1H NMR and 100 MHz for ^{13}C NMR.

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, linear mode. The sample solutions (10 mg/mL in THF), trans-2-[3-(4-tert-butylphenyl)-2-methyl-2-propenylidene] malononitrile (DCTB) solution (50 mg/mL in THF) and sodium trifluoroacetate aqueous solution (5 mg/mL in THF) were mixed in a volume ratio of 4:1:1, 1 μL of which was then deposited on the target plate and dried before measurement.

Size exclusion chromatography (SEC) experiments were performed on an Agilent HPLC system equipped with a model 1260 Hip degasser, a model 1260 Iso pump and a model 1260 differential refractometer detector with using THF as mobile phase at a flow rate of 1.0 mL min^{-1} at $40 \text{ }^\circ\text{C}$. The sample concentration used for SEC analyses was 5-8 mg/mL.

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. Each sample with a mass of 4-5 mg was used for the measurement. The typical procedures for the measurements of PDXO samples were as follow: in the first heating scan, samples were heated from -80 to $200 \text{ }^\circ\text{C}$ at a heating rate of $10 \text{ }^\circ\text{C/min}$. In the second heating scan, samples were cooled to $-80 \text{ }^\circ\text{C}$ at $10 \text{ }^\circ\text{C min}^{-1}$ and subsequently reheated to $180 \text{ }^\circ\text{C}$ at $10 \text{ }^\circ\text{C/min}$. In the third heating scan, samples were recooled to $-80 \text{ }^\circ\text{C}$ at $10 \text{ }^\circ\text{C/min}$ and subsequently reheated to $200 \text{ }^\circ\text{C}$ at $10 \text{ }^\circ\text{C min}^{-1}$.

Infrared (IR) spectroscopy tests were carried out on a JASCO FT-IR-4700 spectrometer recorded from 4000 to 400 cm^{-1} . The solution was dropped on a KBr plate, and the solvent evaporated before performing the measurements.

The various block copolymer samples were completely dissolved in chloroform (CHCl_3) to form homogeneous solutions, which were subsequently poured into flat molds. Following slow solvent evaporation at room temperature, the resulting solvent-cast copolymer films (with a thickness of 0.3-0.5 mm) were cut into standard dogbone-shaped specimen bars with an overall length of 4.7 cm, a gauge length of 2.0 cm and a

width of 0.4 cm using a die cutter.

All tensile tests were carried out at room temperature on an Instron 5900 universal testing machine equipped with a pair of hydraulic grips. For uniaxial tensile experiments, a constant stretching rate of $50 \text{ mm} \cdot \text{min}^{-1}$ was applied until the ultimate failure of the specimens. At least three replicates were tested for each sample to ensure consistency, and the derived values for Young's modulus (E), tensile strength at break (σ_b), and elongation at break (ε_b) were averaged. For cyclic tensile experiments, the specimens were subjected to 10 cycles of loading and unloading ($50 \text{ mm} \cdot \text{min}^{-1}$) at a fixed maximum strain of 100%. The elastic recovery rate (ER) was calculated using the equation: $\text{ER} (\%) = [(\varepsilon_m - \varepsilon_r) / \varepsilon_m] \cdot 100\%$, where ε_m represents the maximum applied strain (100%) and ε_r is the residual strain at zero stress after the unloading cycle.

2. EXPERIMENTAL SECTION

2.1 Preparation of 1,5-Dioxepan-2-one (DXO)

The DXO was prepared according to the reported procedure.^{1, 2} A Schlenk flask was charged with 600 mL dichloromethane (DCM) and 94 g 3-chloroperbenzoic acid (mCPBA), and the mixture was stirred to obtain a homogeneous solution. The solution was cooled down to 0 °C in an ice bath, then 30 g tetrahydro-4H-pyran-4-one was added dropwise using a dropping funnel within 30 min. The solution was stirred at RT for 16 hr to obtain white turbid solution. After the complete oxidation, the solution was filtered to remove the acids. The filtrate was washed with solution of sodium bisulfite, sodium bicarbonate and saturated sodium chloride to eliminate acid. Then, the organic phase was dried with anhydrous MgSO₄ and concentrated to obtain a yellow liquid, which was recrystallized in ether twice to give white crystals (80% yield). ¹H NMR (400 MHz, Chloroform-d) δ 4.35-4.29 (m, 2H), 3.95-3.88 (m, 2H), 3.88-3.81 (m, 2H), 2.95-2.88 (m, 2H). ¹³C NMR (100 MHz, Chloroform-d) δ 174.06, 70.63, 70.22, 64.62, 39.17.

2.2 Ring opening polymerization (ROP) of DXO

A typical polymerization procedure (Table 1, Run 9) is described as follows. In a glovebox, a flame-dried Schlenk tube was charged with 34 μL of ZnEt₂ (0.03 mmol, 1.0 mol/L in hexane), 3.7 mg of DMAP (0.03 mmol), and 1150 μL of toluene (Tol). Subsequently, 4 μL of benzyl alcohol (BnOH) (0.03 mmol) and 0.4 g of DXO (3.44 mmol) were sequentially added to the tube. The polymerization was conducted at room temperature (RT). An aliquot of the reaction mixture was withdrawn under nitrogen via

a syringe for gel permeation chromatography (GPC) and ^1H NMR characterizations. The remaining mixture was quenched with acetic acid, precipitated into excess cold methanol three times, and dried under vacuum to obtain PDXO as a transparent syrup. ^1H NMR (400 MHz, Chloroform- d) δ 4.26-4.19 (m, 2H), 3.76 (t, 2H), 3.72-3.63 (m, 2H), 2.62 (t, 2H). ^{13}C NMR (100 MHz, Chloroform- d) δ 171.34, 68.82, 66.46, 63.56, 34.87.

2.3 Ring-Opening Copolymerization (ROCP) of DXO with L-Lactide (LLA)

A typical copolymerization procedure (Table 1, Run 9) is described as follows. In a glovebox, a flame-dried Schlenk tube was charged with 26 μL of ZnEt_2 (0.023 mmol), 2.8 mg of DMAP (0.023 mmol), and 1150 μL of toluene (Tol). Then, 3.2 mg of 1,4-benzenedimethanol (BDM) (0.023 mmol) and 0.4 g of DXO (3.44 mmol) were sequentially added to the tube. The polymerization was conducted at room temperature (RT). An aliquot of the reaction mixture was withdrawn under nitrogen via a syringe for gel permeation chromatography (GPC) and ^1H NMR characterizations. After that, a predetermined amount of L-lactide (LLA) was added to the system, and the reaction was allowed to proceed at 40 $^\circ\text{C}$ for an additional period. The remaining mixture was quenched with acetic acid, precipitated into excess cold methanol three times, and dried under vacuum to obtain the PDXO-based block copolymer as a transparent syrup. The molecular weight of the final block copolymer was determined by GPC.

2.4 Depolymerization of PDXO

A single-neck flask was charged with 300 mg PDXO, 100 mg PEG_{2k} and 42 μL SnOct_2 (5 mol % relative to the repeating units of polymer). A water-cooled cold-finger was

connected to the Schlenk and the reaction mixture was heated to 160 °C with magnetic stirring *in vacuo*. After 5 h, the product was collected which was determined by ^1H NMR.

Table S1. Results of ROP of DXO with different catalysts.^[a]

Run	Base	T (°C)	Time (h)	Conv. ^[b] (%)	$M_{n, \text{theo}}$ (kDa) ^[c]	$M_{n, \text{GPC}}$ (kDa) ^[d]	\bar{D} ^[d]
1	DBU	RT	10	-	-	n.a.	n.a.
2	DBU	RT	24	-	-	n.a.	n.a.
3	DMAP	RT	10	-	-	n.a.	n.a.
4	DMAP	RT	24	-	-	n.a.	n.a.
5	CTPB	RT	8	53	6.3	1.7	2.41
6	CTPB	RT	10	51	6.0	1.4	2.34
7	CTPB	-30	10	66	7.8	3.2	1.22
8	CTPB	0	10	50	5.9	2.8	1.18
9	CTPB	60	10	-	-	n.a.	n.a.
10	TBD	RT	1	97	11.3	9.0	1.99
11	TBD	RT	2	97	11.3	8.1	1.78

[a] Conditions: The polymerization was performed at RT with BnOH as initiator. $[M]:[\text{base}]:[I] = 100:1:1$, $[M]_0 = 3.0$ M in toluene. n.a. = not available (no polymer precipitation occurred); [b] Determined by ¹H NMR; [c] The theoretical molecular weight was calculated as $M_{n, \text{theo}} = ([M]_0:[I]_0) \times \text{Conv.}\% \times (\text{molecular weight of DXO}) + (\text{molecular weight of BnOH})$. [d] Determined by GPC in THF relative to PS standards.

Table S2. Results of ROP of DXO catalyzed by metal catalysts.^[a]

Run	Catalyst	$[M]_0:[C]_0:[I]_0$	T (°C)	t (h)	Conv. (%) ^[b]	$M_{n, \text{theo}}$ (kDa) ^[c]	$M_{n, \text{GPC}}$ (kDa) ^[d]	\bar{D} ^[d]
1	Sn(Oct) ₂	500:1:0	RT	10	0	0.1	n.a.	n.a.
2 ^[e]	Sn(Oct) ₂	500:1:0	110	10	>99	34.6	77.0	1.95
3	Al(O ⁱ Pr) ₃	300:1:0	-30	10	0	0.1	n.a.	n.a.
4	Al(O ⁱ Pr) ₃	300:1:0	RT	10	95	33.2	26.8	1.16
5	CH ₃ OK	300:1:0	-30	10	30	10.6	2.5	1.16
6	CH ₃ OK	300:1:0	RT	10	0	0.1	n.a.	n.a.
7	La[N(SiMe ₃) ₂] ₃	300:1:0	-30	10	55	19.3	8.2	1.51

8	La[N(SiMe ₃) ₂] ₃	300:1:0	RT	10	83	29.0	10.0	2.11
9	La[N(SiMe ₃) ₂] ₃	300:1:0	100	10	77	26.9	5.6	2.11
10 ^[f]	La[N(SiMe ₃) ₂] ₃	300:1:1	RT	10	86	30.0	8.4	1.38
11 ^[f]	La[N(SiMe ₃) ₂] ₃	300:1:1	RT	12	90	31.4	8.1	1.37
12 ^[f]	TsOH	100:1:1	RT	12	41	4.9	6.6	1.31
13 ^[f]	TfOH	100:1:1	RT	12	>99	13.1	6.7	1.42
14 ^[f]	ZnEt ₂	100:1:1	RT	16	98	11.5	12.7	1.30
15 ^[f]	ZnEt ₂	100:1:1	RT	20	98	11.5	12.7	1.31

[a] Conditions: The polymerization was performed at $[M]_0 = 5.0$ M in toluene. n.a. = not available (no polymer precipitation occurred). [b] Determined by ¹H NMR. [c] The theoretical molecular weight was calculated as $M_{n, \text{theo}} = ([M]_0:[I]_0 \text{ or } [M]_0:[C]_0) \times \text{Conv.}\% \times (\text{molecular weight of DXO}) + (\text{molecular weight of BnOH})$. [d] Determined by GPC in THF relative to PS standards. [e] The polymerization was performed in bulk. [f] The polymerization was performed using BnOH as initiator.

Table S3. Results of ROP of DXO with DBU/ZnEt₂ as catalyst.^[a]

Run	[M]:[ZnEt ₂]: [DBU]:[I]	Temp. (°C)	t (h)	Conv. ^[b] 1 (%)	$M_{n, \text{theo}}$ (kDa) ^[c]	$M_{n, \text{GPC}}$ (kDa) ^[d]	\bar{D} ^[d]
1	100:1:1:1	RT	6	96	11.1	11.7	1.52
2	100:1:1:1	50	6	82	9.5	9.1	1.50
3	100:1:1:1	100	6	69	8.0	1.5	1.61
4	100:1:1:2	RT	6	93	5.4	5.6	1.68
5	200:2:2:1	RT	6	86	20.0	12.7	1.59
6	400:4:4:1	RT	12	96	44.5	20.6	1.67
7	800:8:8:1	RT	12	55	25.5	2.0	2.38

[a] Conditions: The polymerization was performed at RT with BnOH as initiator. $[M]_0 = 3.0$ M in toluene.; [b] Determined by ¹H NMR; [c] The theoretical molecular weight was calculated as $M_{n, \text{theo}} = ([M]_0:[I]_0) \times \text{Conv.}\% \times (\text{molecular weight of DXO}) + (\text{molecular weight of BnOH})$. [d] Determined by GPC in THF relative to PS standards.

Table S4. Results of ROP of DXO with ZnEt₂ as catalyst.^[a]

Run	t (h)	Conv. ^[b] (%)	$M_{n, GPC}$ (kDa) ^[c]	\mathcal{D} ^[c]
1	40	3	-	-
2	60	8	-	-
3	120	19	3.2	1.17
4	240	42	6.5	1.24
5	360	60	9.1	1.22
6	480	78	10.9	1.27
7	600	87	11.4	1.28
8	720	93	12.5	1.29
9	960	98	12.7	1.3
10	1200	98	12.7	1.31
11	1440	98	12.8	1.32

[a] Conditions: The polymerization was performed at RT with BnOH as initiator. $[M]_0:[ZnEt_2]_0:[I]_0 = 100:1:1$, $[M]_0 = 3.0$ M in toluene.; [b] Determined by 1H NMR; [c] Determined by GPC in THF relative to PS standards.

Table S5. Results of ROP of DXO with DMAP/ $ZnEt_2$ as catalyst.^[a]

Run	t (h)	Conv. ^[b] (%)	$M_{n, GPC}$ (kDa) ^[c]	\mathcal{D} ^[c]
1	5	20	3.1	1.1
2	10	41	6.7	1.1
3	20	57	9.6	1.2
4	40	81	12.4	1.4
5	60	90	13.4	1.43
6	120	94	13.6	1.43

[a] Conditions: The polymerization was performed at RT with BnOH as initiator. $[M]_0:[DMAP]_0:[ZnEt_2]_0:[I]_0 = 100:1:1:1$, $[M]_0 = 3.0$ M in toluene.; [b] Determined by 1H NMR; [c] Determined by GPC in THF relative to PS standards.

Table S6. Results of ROP of DXO with DBU/ZnEt₂ as catalyst.^[a]

Run	t (h)	Conv. ^[b]]	<i>M</i> _{n, GPC} (kDa) ^[c]	<i>D</i> ^[c]
		(%)		
1	5	25	3.5	1.15
2	10	49	7.2	1.17
3	20	67	9.5	1.35
4	40	72	10	1.45
5	60	76	10.2	1.41
6	120	81	10.7	1.43
7	360	96	11.7	1.52

[a] Conditions: The polymerization was performed at RT with BnOH as initiator. [M]₀: [DBU]₀: [ZnEt₂]₀: [I]₀ = 100:1:1:1, [M]₀ = 3.0 M in toluene.; [b] Determined by ¹H NMR; [c] Determined by GPC in THF relative to PS standards.

Table S7. Results of ROP of DXO with DBU/ZnEt₂ as catalyst.^[a]

Run	PEG	[M]:[ZnEt ₂]: [DBU]:[PEG]	Temp .	t (h)	Conv. ^[b]]	<i>M</i> _{n, GPC} (kDa) ^[c]	<i>D</i> ^[c]
			(°C)		(%)		
1	PEG _{2k}	100:1:1:1	RT	6	92	9.2	1.14
2	PEG _{2w}	200:2:2:1	RT	6	95	24.6	1.27

[a] Conditions: The polymerization was performed at RT with PEG-OH as initiator. [M]₀ = 3.0 M in toluene.; [b] Determined by ¹H NMR; [c] Determined by GPC in THF relative to PS standards.

Table S8. Results of ROP of DXO with DMAP/ZnEt₂ as catalyst.^[a]

Run	M	[DXO]:[M]:[ZnEt ₂]: [DBU]:[I]	Conv. _{DXO} ^[b] (%)	Conv. _M ^[b] (%)	$M_{n, \text{theo}}$ (kDa) ^[c]	$M_{n, \text{GPC}}$ (kDa) ^[d]	\mathcal{D} ^[d]
1	δ -VL	40:160:1:1:1	52	>99	20.6	63.3	1.30
2	δ -VL	80:120:1:1:1	92	>99	21.3	24.6	1.23
3	δ -VL	100:100:1:1:1	85	>99	21.6	27.4	1.31
4	δ -VL	120:60:1:1:1	81	>99	21.9	23.4	1.70
5	δ -VL	160:40:1:1:1	>99	>99	22.6	37.1	1.95
6	L-LA	150:30:1:1:1	99	99	21.7	20.8	1.51
7	L-LA	150:60:1:1:1	99	99	26.0	25.2	1.48
8	L-LA	150:90:1:1:1	99	99	30.4	27.0	1.40
9	L-LA	50:200:1:1:1	99	99	34.6	31.1	1.67

[a] Conditions: The block copolymerizations of DXO and δ -VL were performed at RT with BnOH as initiator. The block copolymerizations of DXO and L-LA were performed at RT with 1,4-benzenedimethanol as initiator.; [b] Determined by ¹H NMR; [c] The theoretical molecular weight was calculated as $M_{n, \text{theo}} = ([M]_0:[I]_0) \times \text{Conv.}\% \times (\text{molecular weight of DXO}) + ([M]_0:[I]_0) \times \text{Conv.}\% \times (\text{molecular weight of M}) + (\text{molecular weight of BnOH})$. [d] Determined by GPC in THF relative to PS standards.

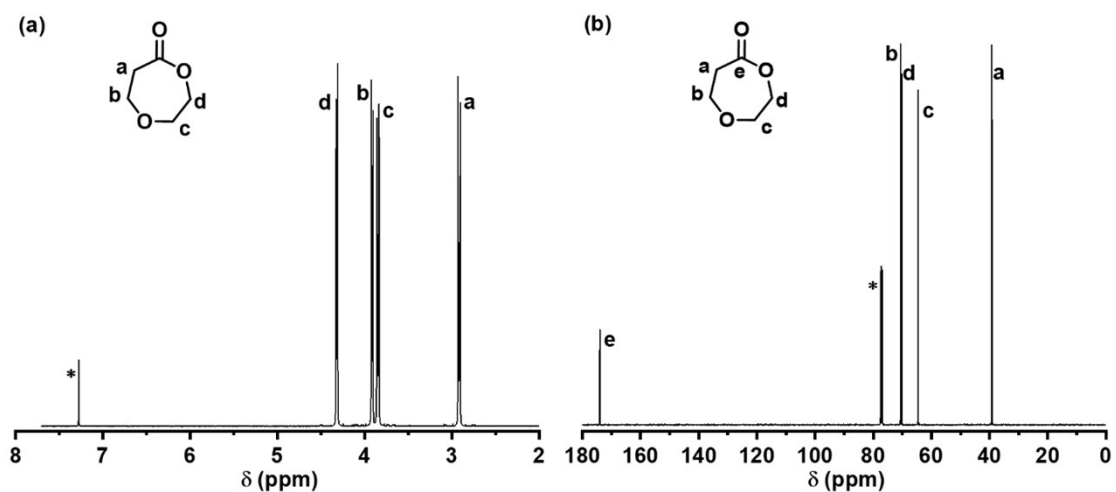


Figure S1. (a) ^1H NMR spectrum and (b) ^{13}C NMR spectrum of DXO. (residual undeuterated solvent peak marked as *) Solvent: CDCl_3

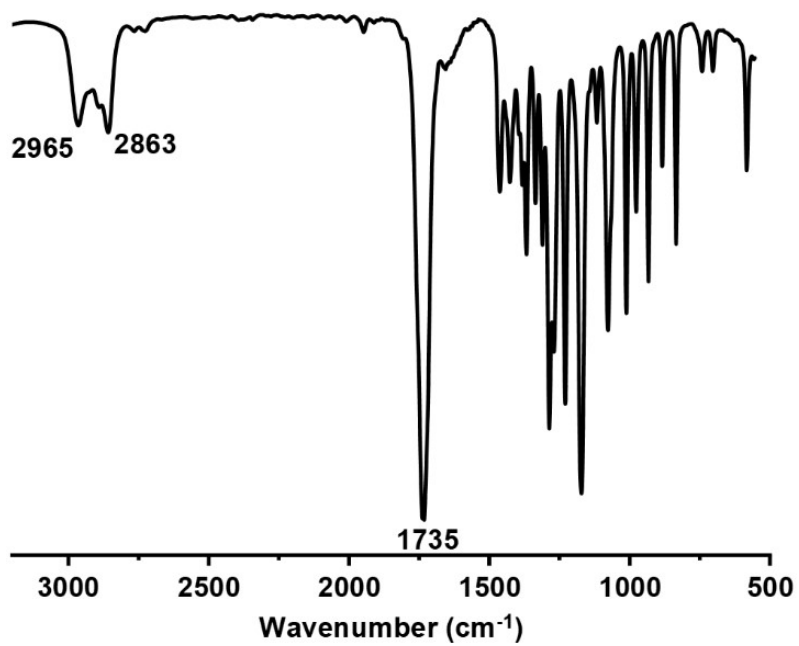


Figure S2. FT-IR spectrum of DXO.

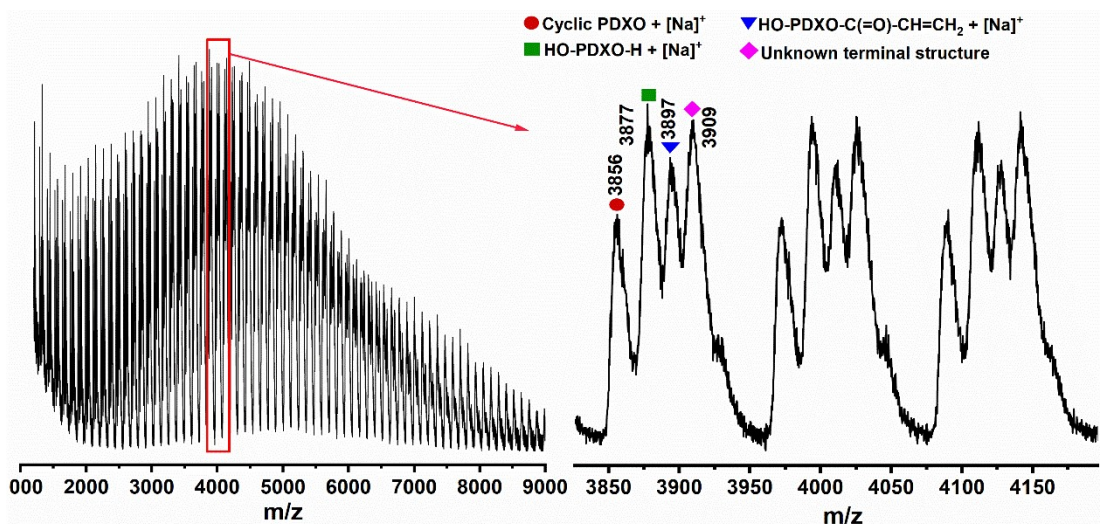


Figure S3. MALDI-TOF MS spectra of the PDXO produced by $\text{Sn}(\text{Oct})_2$ -catalyzed ROP of DXO.

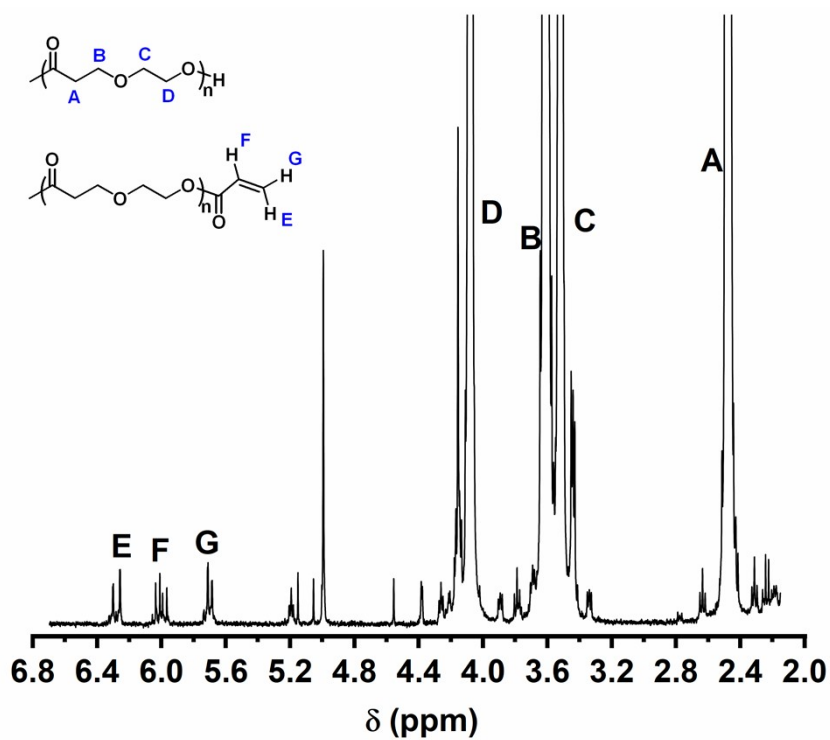


Figure S4. ^1H NMR spectrum of PDXO from ROP of DXO catalyzed by $\text{Sn}(\text{Oct})_2$.

Solvent: CDCl_3

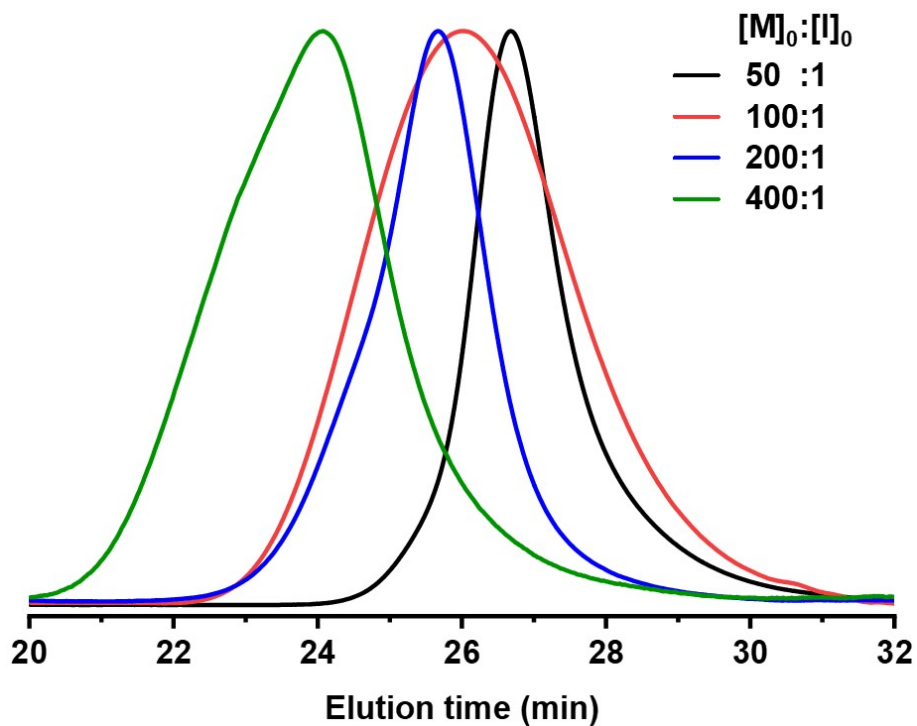


Figure S5. GPC curves of PDXOs prepared through ROP catalyzed by $ZnEt_2$ ($[M]_0:[I]_0 = 50\sim 400:1$).

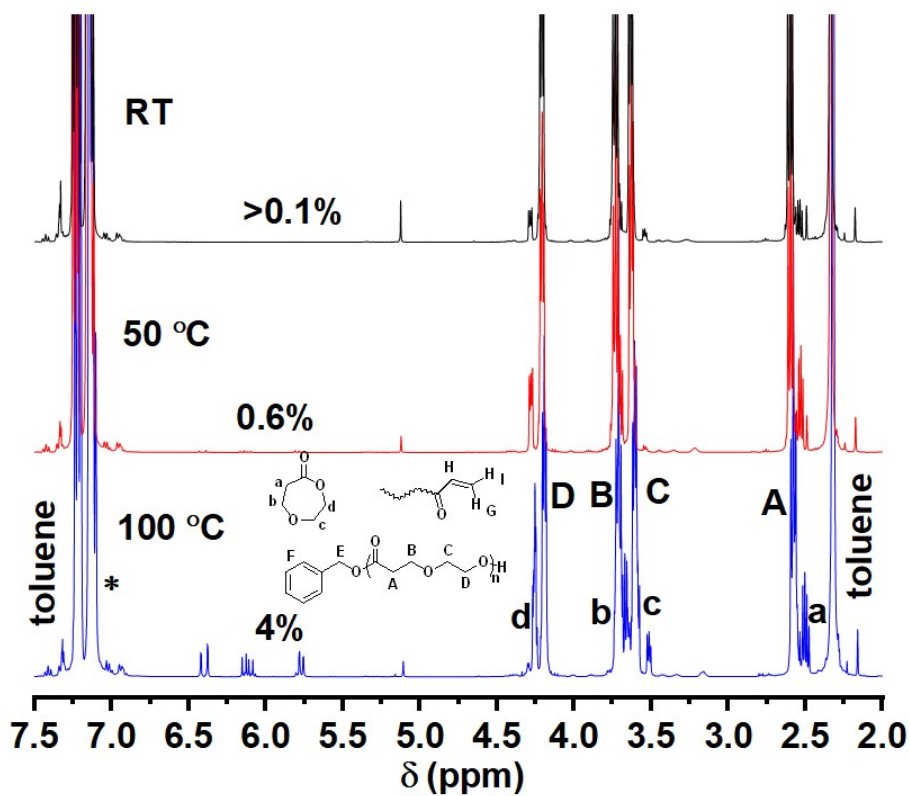


Figure S6. 1H NMR spectra *in situ* of mixture from ROP of DXO catalyzed by $DBU/ZnEt_2$ at different temperatures. Solvent: $CDCl_3$

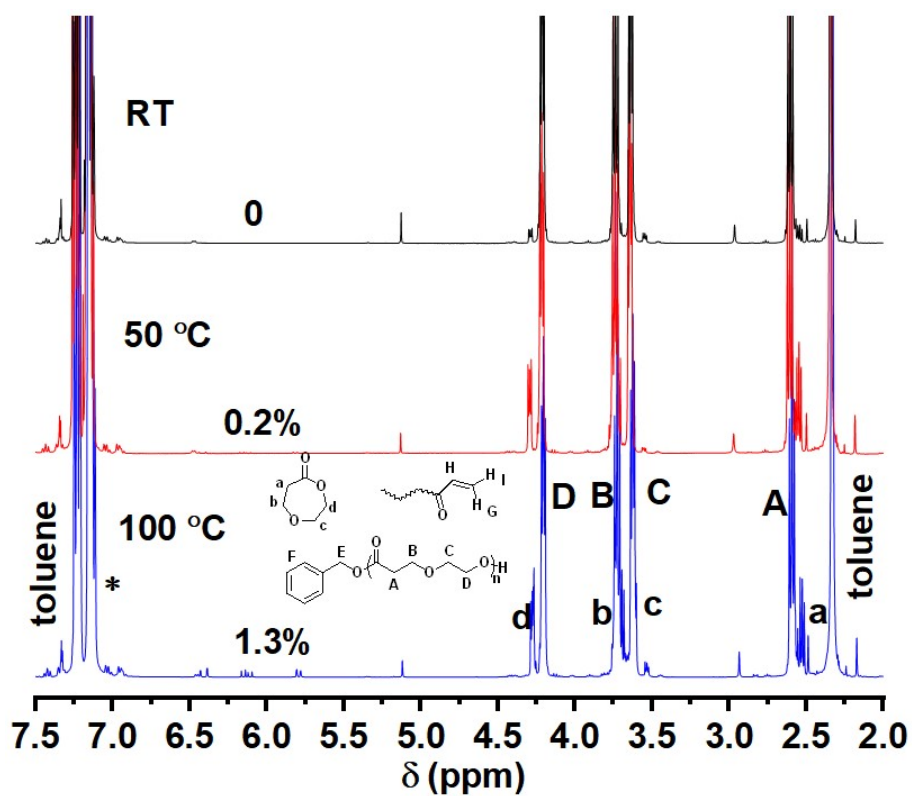


Figure S7. In-situ ^1H NMR spectra of mixture from ROP of DXO catalyzed by DMAP/ ZnEt_2 at different temperatures. Solvent: CDCl_3 .

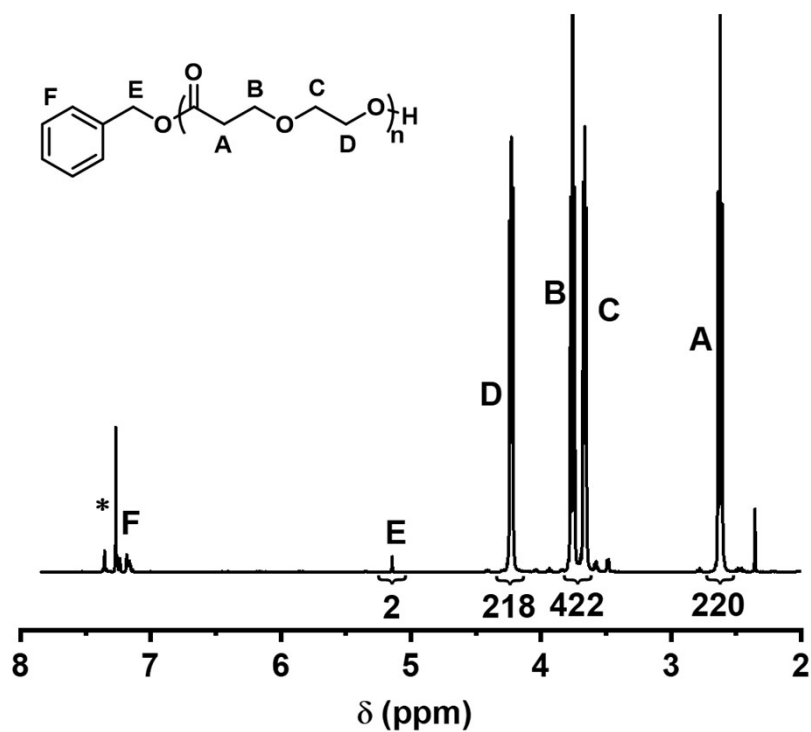


Figure S8. ^1H NMR spectrum of PDXO from ROP of DXO catalyzed by DMAP/ ZnEt_2 .

Solvent: CDCl_3 .

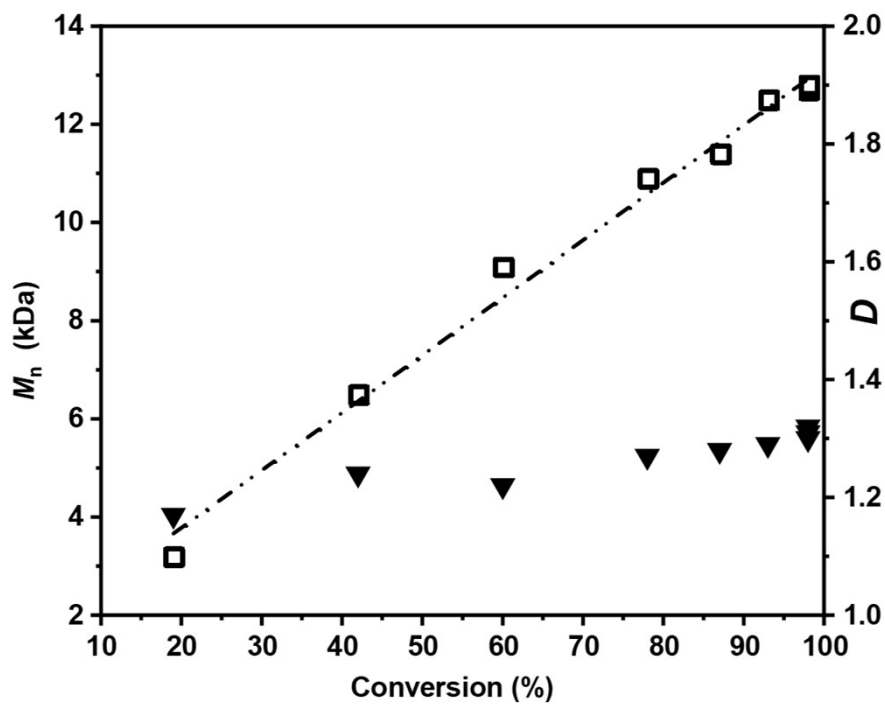


Figure S9. M_n (square) and \bar{D} (triangle) versus monomer conversion (Conditions: ZnEt_2 , RT, 3.0 M in toluene, data shown in Table S5)

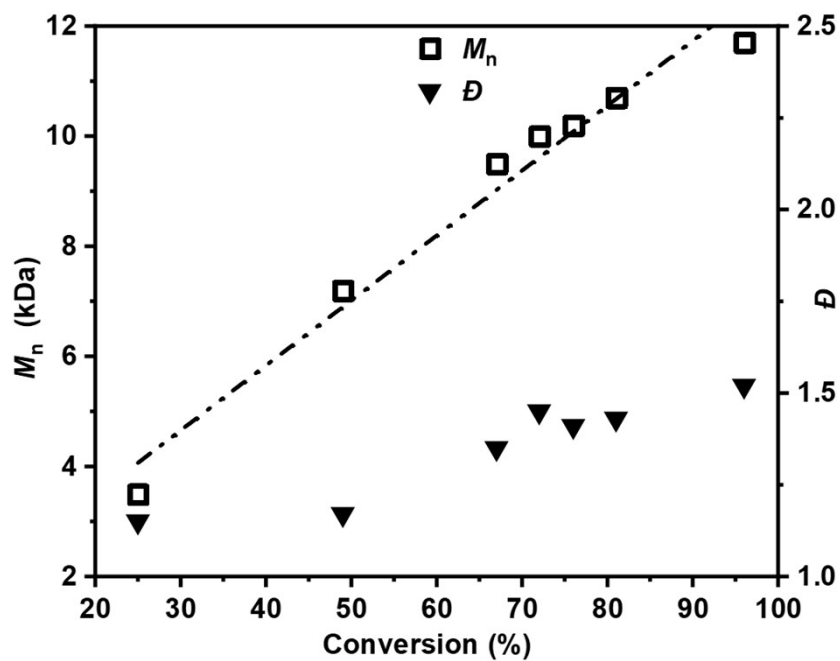


Figure S10. (a) M_n (square) and \bar{D} (triangle) versus monomer conversion (data shown in Table S7). (Conditions: ZnEt_2/DBU , RT, 3.0 M in toluene)

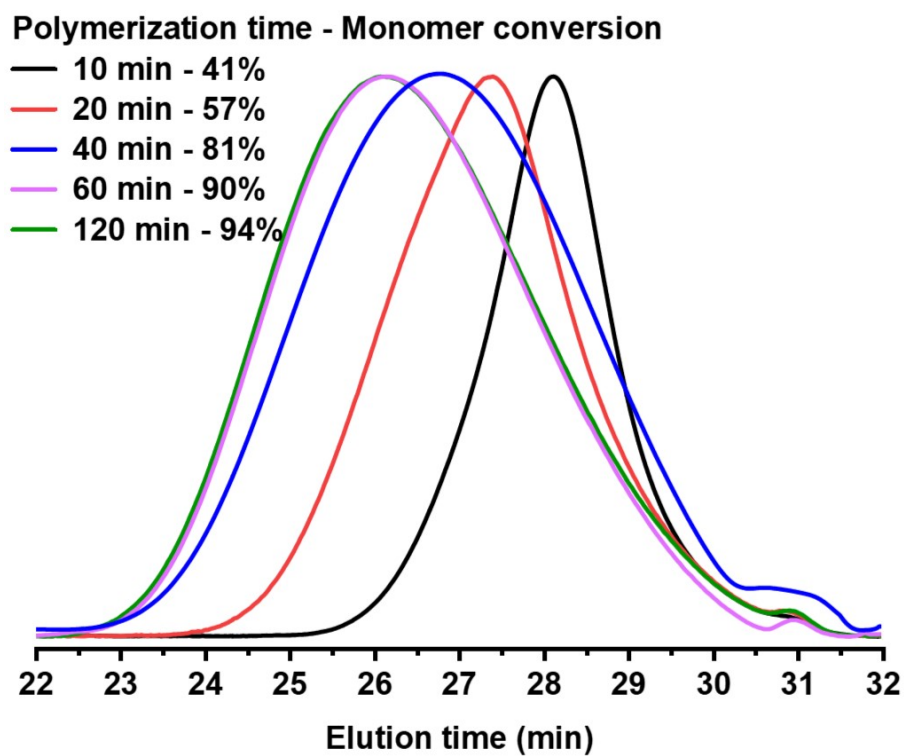


Figure S11. Overlay of GPC curves at different times. (Conditions: $\text{ZnEt}_2/\text{DMAP}$, RT, 3.0 M in toluene, data shown in Table S6)

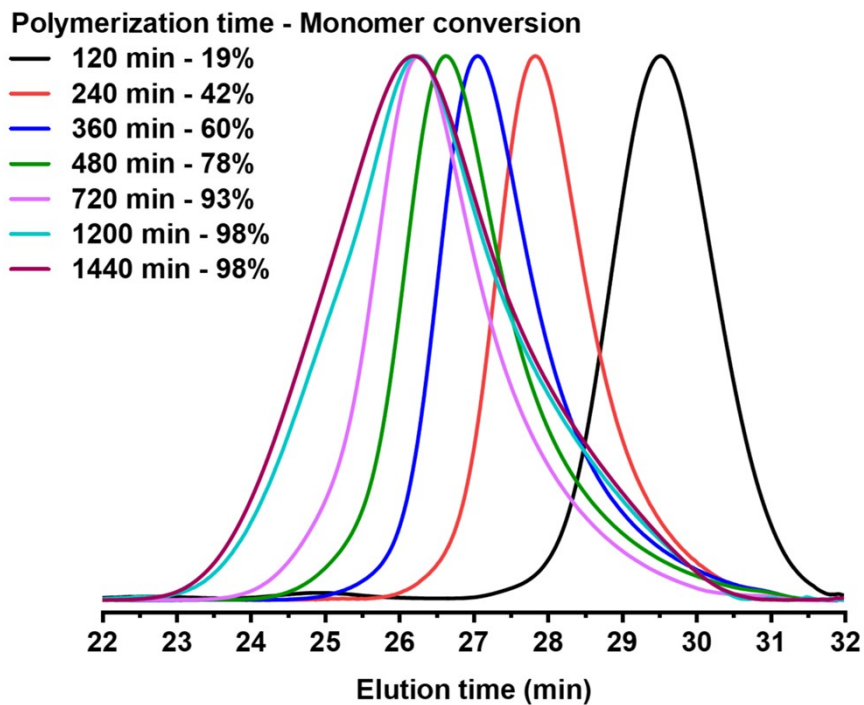


Figure S12. Overlay of GPC curves at different times. (Conditions: ZnEt_2 , RT, 3.0 M in toluene, data shown in Table S5)

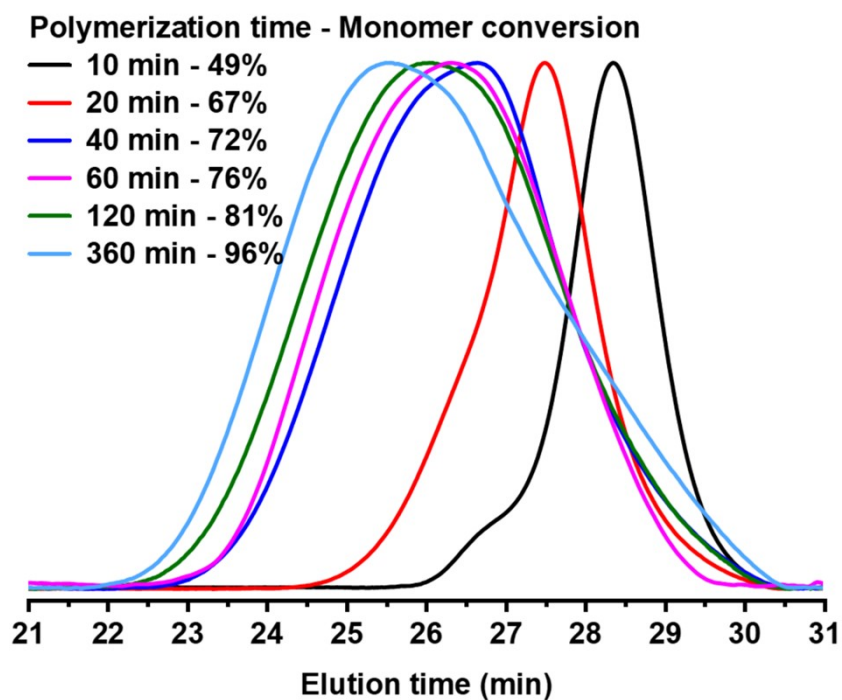


Figure S13. Overlay of GPC curves at different times. (Conditions: ZnEt_2/DBU , RT, 3.0 M in toluene, data shown in Table S7)

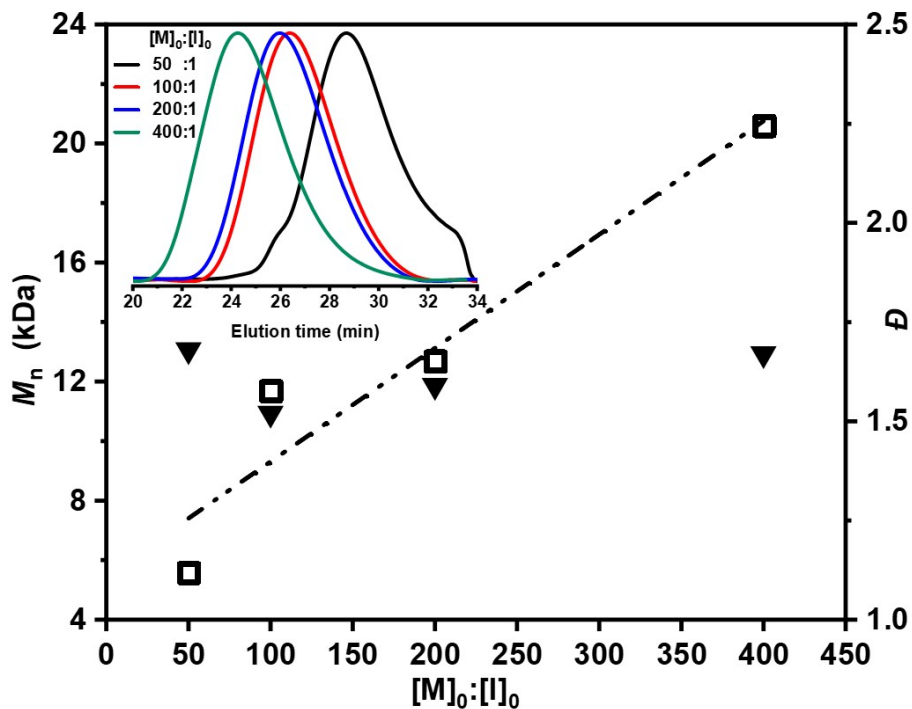


Figure S14. M_n (square) and D (triangle) versus $[\text{M}]_0:[\text{I}]_0$ ratio. Inset: Overlay of GPC curves versus $[\text{M}]_0:[\text{I}]$ ratios. (Conditions: ZnEt_2/DBU , RT, 3.0 M in toluene)

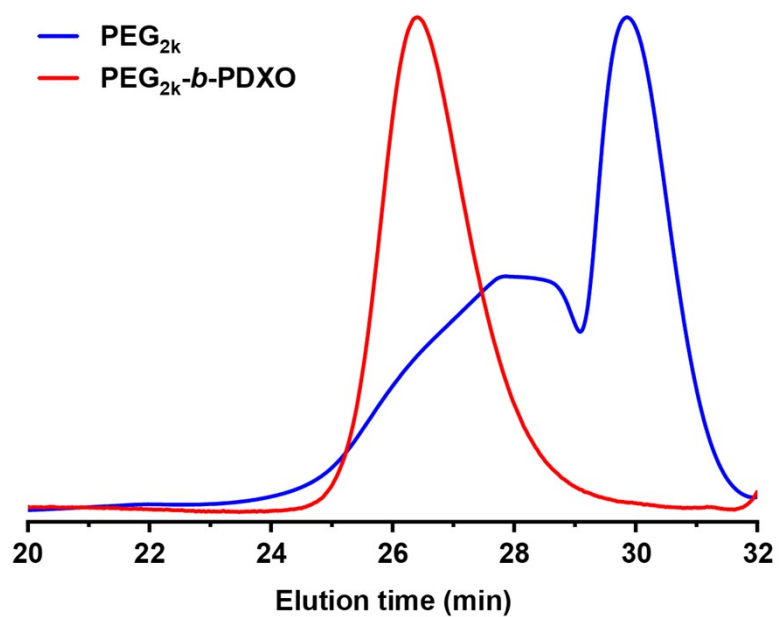


Figure S15. GPC curves of PEG_{2k}-OH and PEG_{2k}-*b*-PDXO.

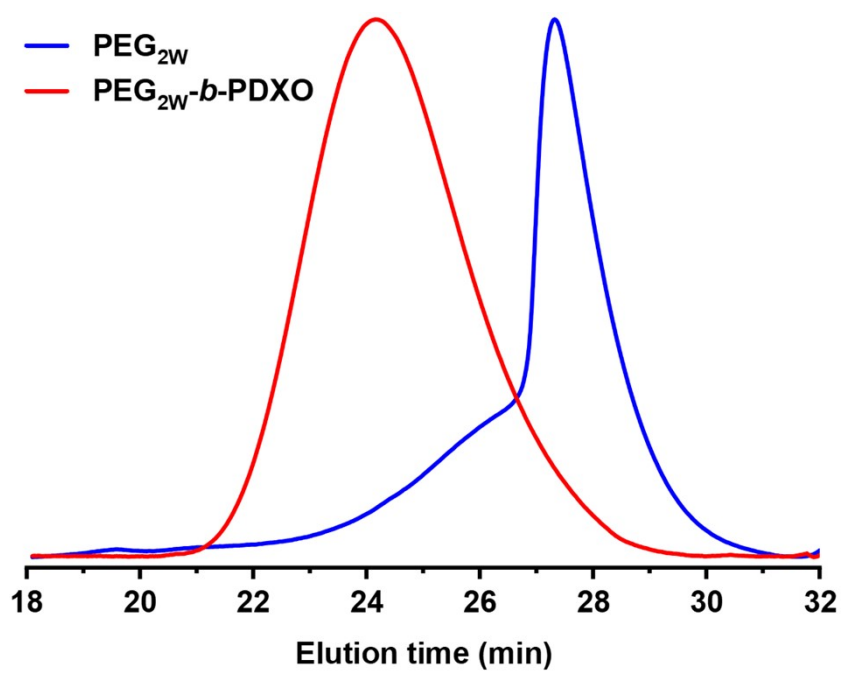


Figure S16. GPC curves of PEG_{2w}-OH and PEG_{2w}-*b*-PDXO.

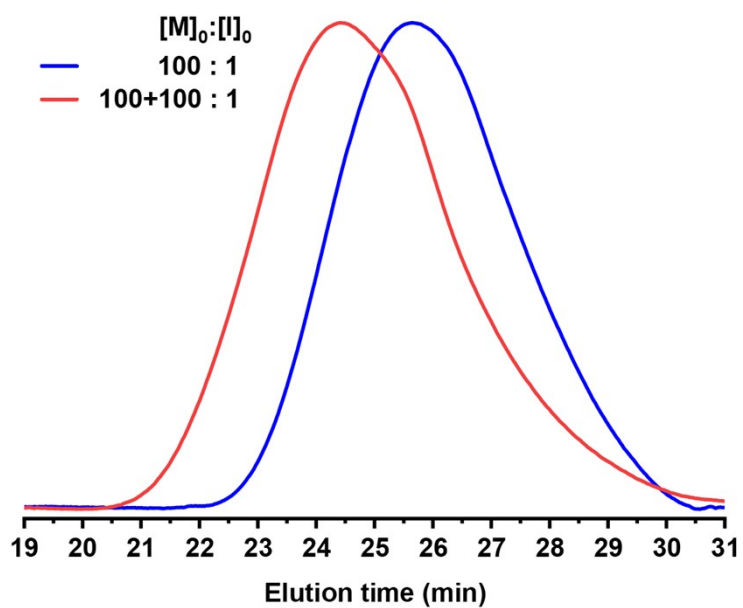


Figure S17. GPC curves of PDXOs obtained by sequential addition of two batches of DXOs (data shown in Table 2).

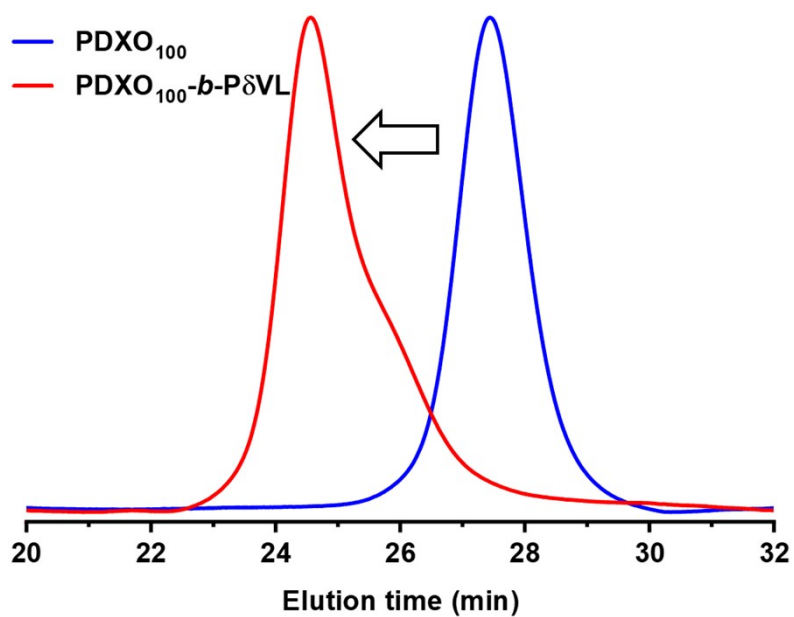


Figure S18. GPC curves of PDXO and PDXO-*b*-PδVL obtained by sequential addition of DXO and valerolactone (δ -VL) (data shown in Table S8).

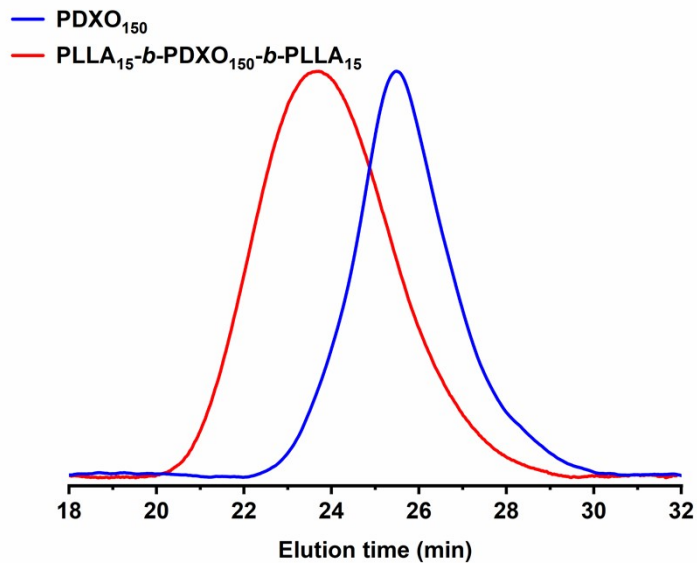


Figure S19. GPC curves of PDXO and PLLA₁₅-b-PDXO₁₅₀-b-PLLA₁₅ obtained by sequential addition of DXO and L-lactide (LLA) (data shown in Table S8).

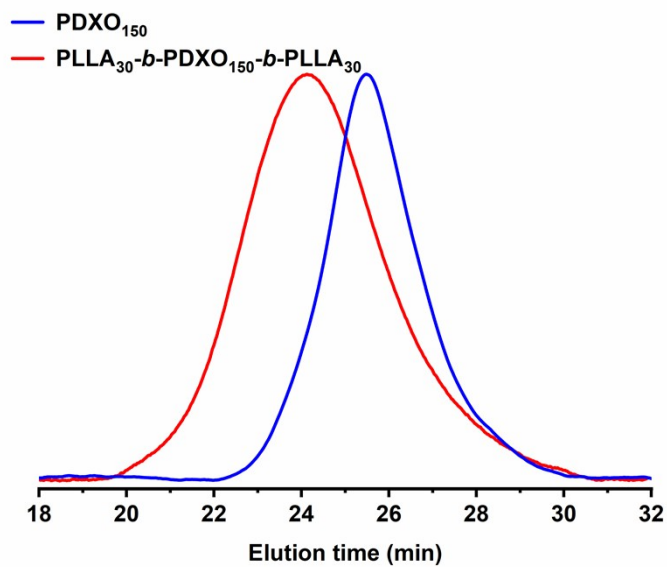


Figure S20. GPC curves of PDXO and PLLA₃₀-b-PDXO₁₅₀-b-PLLA₃₀ obtained by sequential addition of DXO and L-lactide (LLA) (data shown in Table S8).

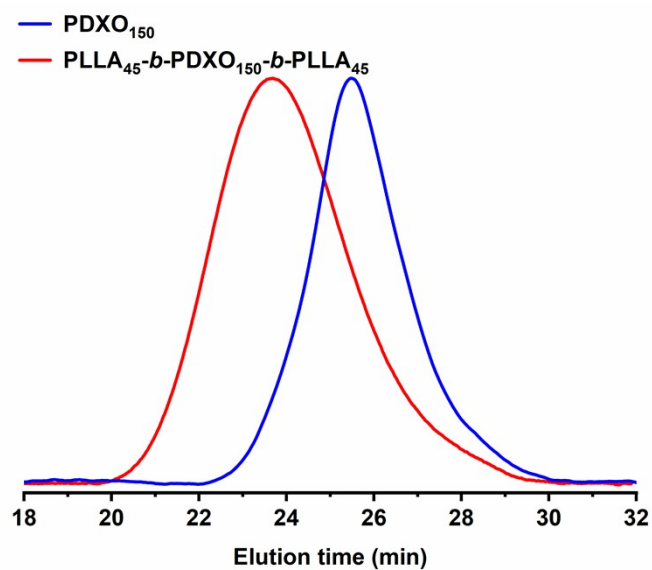


Figure S21. GPC curves of PDXO and PLLA₄₅-b-PDXO₁₅₀-b-PLLA₄₅ obtained by sequential addition of DXO and L-lactide (LLA) (data shown in Table S8).

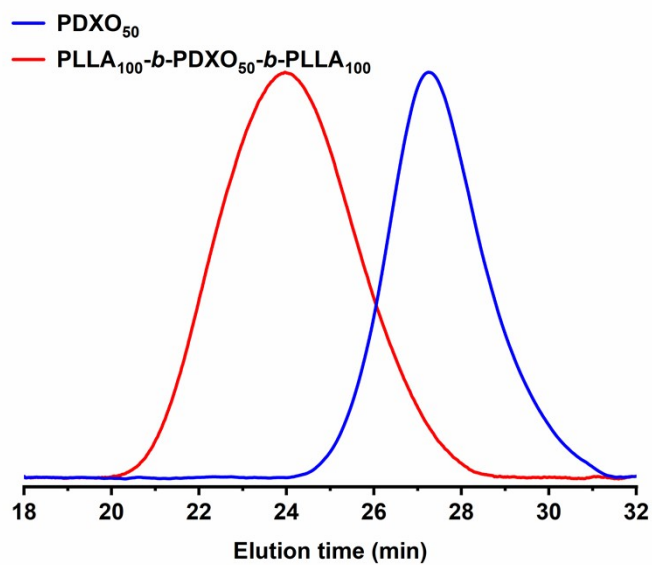


Figure S22. GPC curves of PDXO and PLLA₁₀₀-b-PDXO₅₀-b-PLLA₁₀₀ obtained by sequential addition of DXO and L-lactide (LLA) (data shown in Table S8).

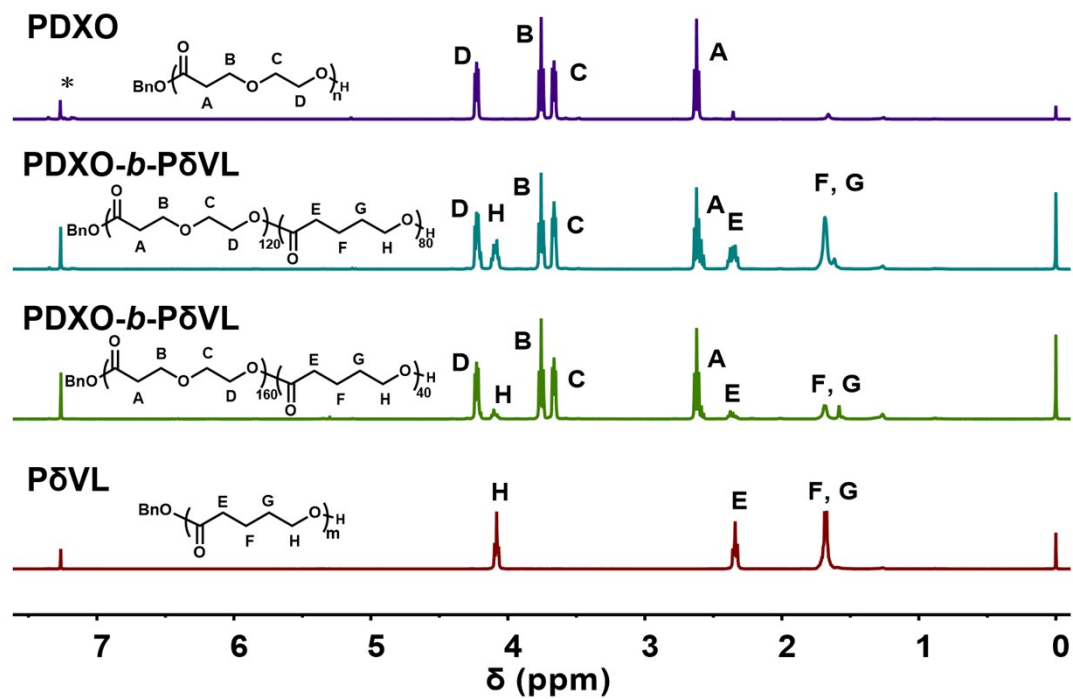


Figure S23. ^1H NMR spectra of PDXO-*b*-P δ VL. Solvent: CDCl_3 .

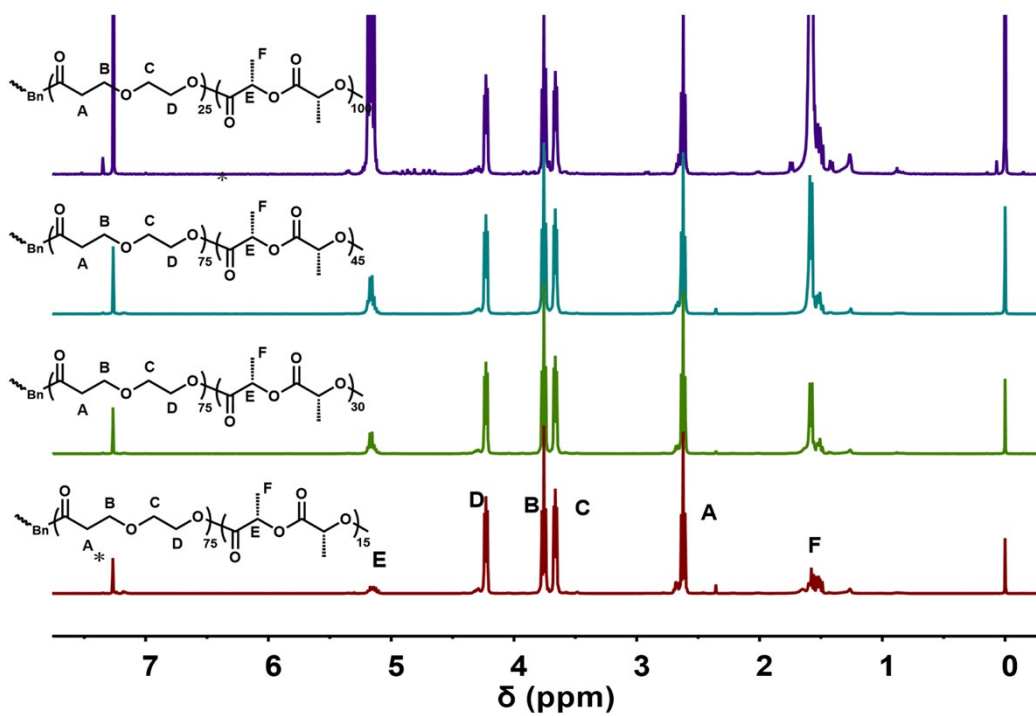


Figure S24. ^1H NMR spectra of PDXO-*b*-PLLA. Solvent: CDCl_3 .

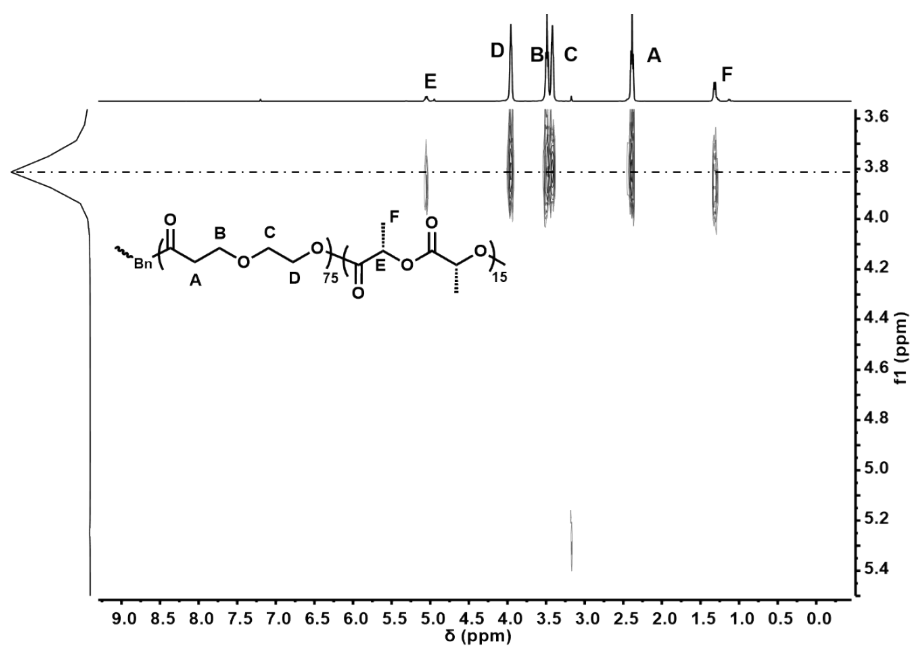


Figure S25. DOSY spectrum of PLLA₁₅-*b*-PDXO₁₅₀-*b*-PLLA₁₅. Solvent: DMSO-d₆.

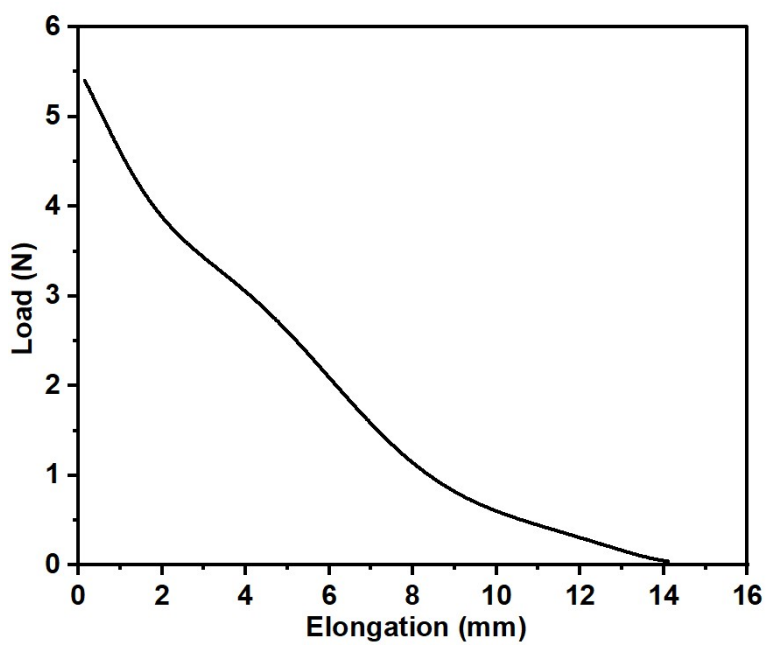


Figure S26. Shear tensile testing on bonding PMMA.

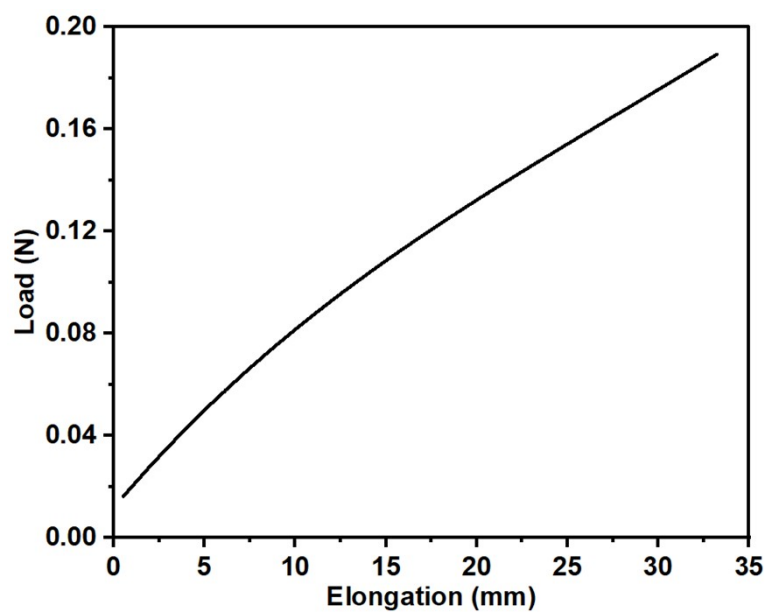


Figure S27. peeling strength testing on bonding PMMA.

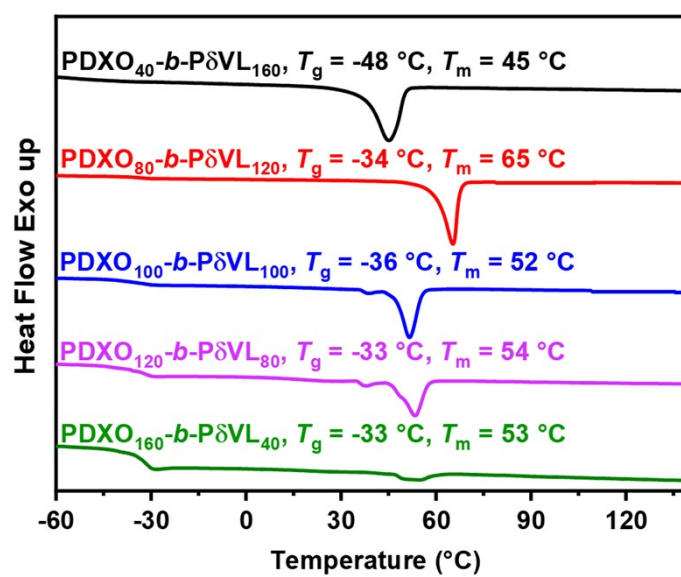


Figure S28. Second DSC curves of PDXO-*b*-PδVLs.

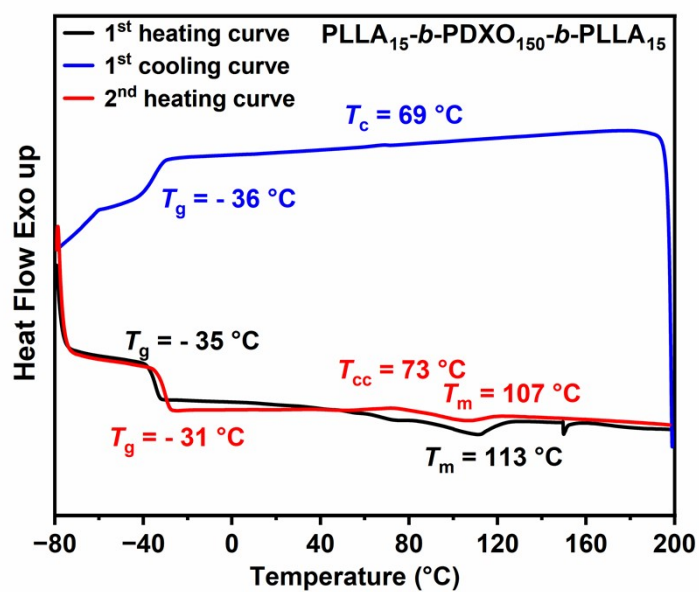


Figure S29. DSC curves of PLLA₁₅-*b*-PDXO₁₅₀-*b*-PLLA₁₅.

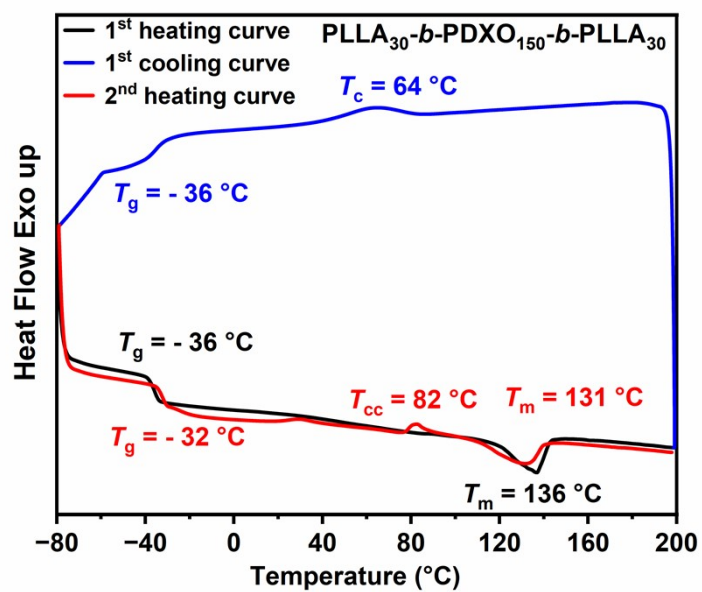


Figure S30. DSC curves of PLLA₃₀-*b*-PDXO₁₅₀-*b*-PLLA₃₀.

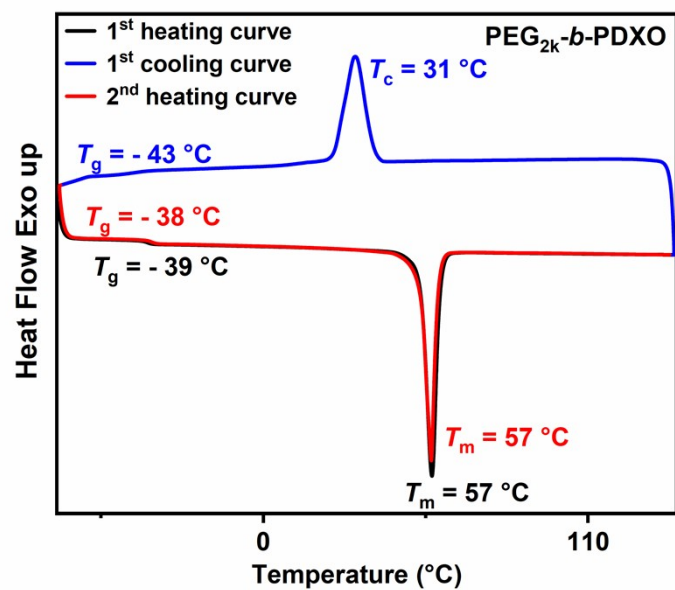


Figure S31. DSC curves of PEG_{2k}-*b*-PDXOs.

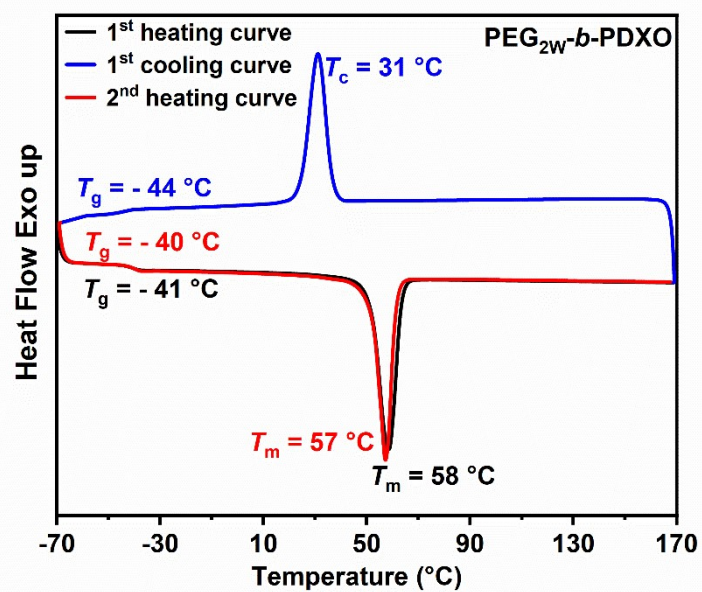


Figure S32. DSC curves of PEG_{2w}-*b*-PDXOs.

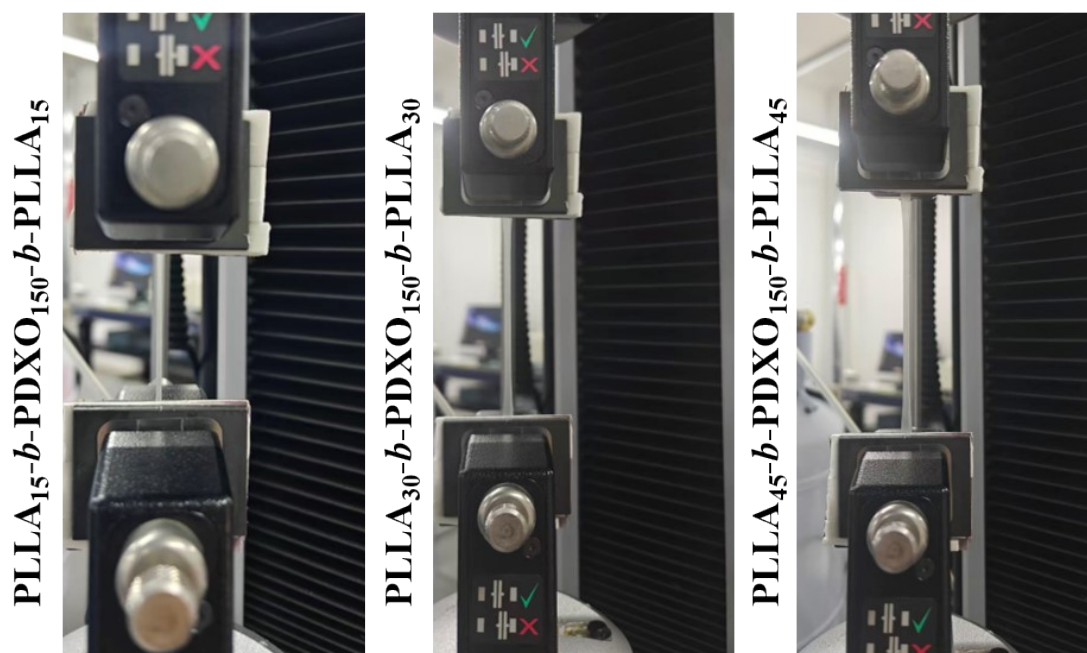


Figure S33. Oriented stretching images of different PLLA-*b*-PDXO-*b*-PLLA triblock polymers.

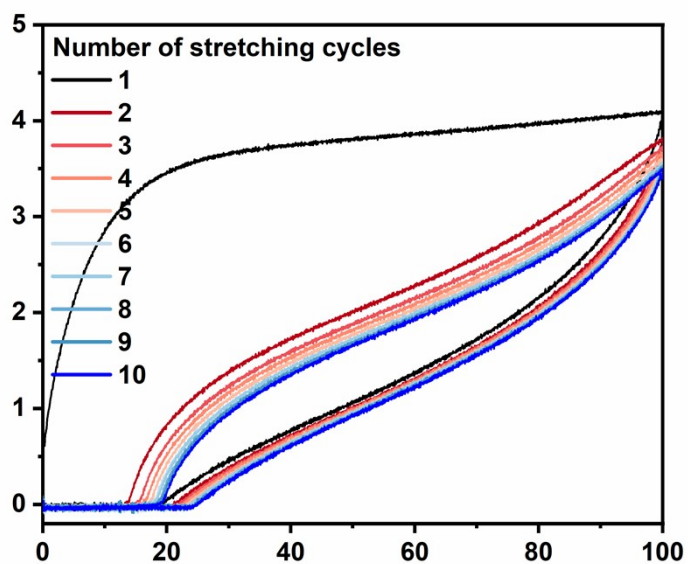


Figure S34. Representative loading-unloading curves of the PLLA₄₅-*b*-PDXO₁₅₀-*b*-PLLA₄₅ elastomer in cyclic tensile measurements with the fixed maximum strain of 100%.

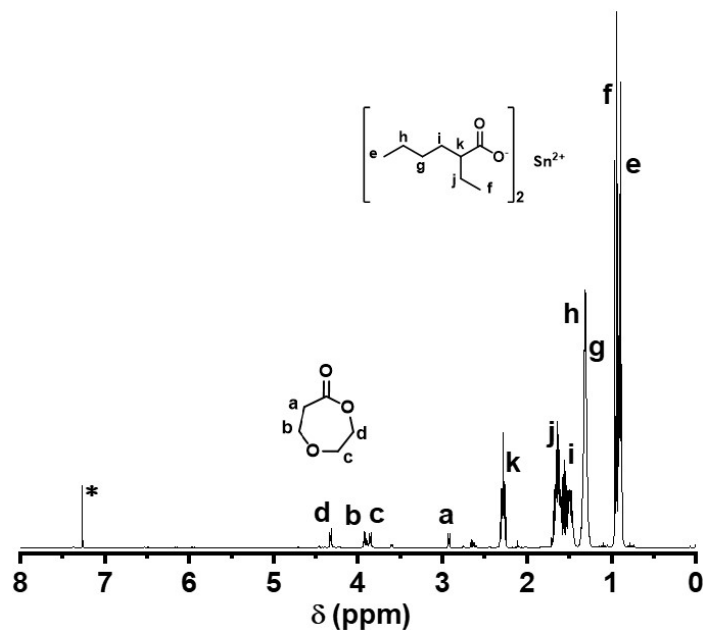


Figure S35. ^1H NMR spectrum of recovered DXO *via* $\text{Sn}(\text{Oct})_2$ -catalyzed pyrolysis.

Solvent: CDCl_3 .

References:

1. Mathisen, T.; Masus, K.; Albertsson, A. C. Polymerization of 1, 5-dioxepan-2-one. II. Polymerization of 1, 5-dioxepan-2-one and its cyclic dimer, including a new procedure for the synthesis of 1, 5-dioxepan-2-one. *Macromolecules* **1989**, *22* (10), 3842-3846.
2. Mathisen, T.; Albertsson, A. C. Polymerization of 1,5-dioxepan-2-one. I. Synthesis and characterization of the monomer 1,5-dioxepan-2-one and its cyclic dimer 1,5,8,12-tetraoxacyclotetradecane-2,9-dione. *Macromolecules* **1989**, *22* (10), 3838-3842.