

Alicyclic Polyesters from a Bicyclic 1,3-dioxane-4-one

Supporting Information

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Materials and instruments

Commercial reagents were purchased from Acros Organics, Alfa Aesar, Fisher, Fluorochem, VWR or Sigma Aldrich and used as received unless otherwise stated. Benzyl alcohol and cyclopentyl-1,3-dioxane-4-one (cPeDOX) were purified by stirring over CaH₂, followed by distillation under an inert atmosphere. Toluene, THF, hexanes and diethyl ether were dried using an Innovative Technologies purification system consisting of alumina and copper catalyst. The solvents were degassed by three freeze-pump-thaw cycles prior to use. Salen-Al and β -Diiminate Zinc were synthesized according to the reported methods and the spectra matched reported literature values.¹⁻² All ¹H, ¹³C NMR spectra were obtained on Bruker Avance III 400 and 500 MHz spectrometers. All spectra were obtained at ambient temperature. The chemical shifts (δ) and coupling constants (J) were recorded in parts per million (ppm) and Hertz (Hz). Gel permeation chromatography (GPC) was carried out in THF at a flow rate of 1 mL min⁻¹ at 35 °C on an Agilent system with 2 mixed-bed styrene/DVB columns (300 × 7.5 mm). The molecular weight was calculated through a conventional method. Differential scanning calorimetry (DSC) was carried out on a DSC 2500 TA instrument using a heat (−10–220 °C) / cool (220–10 °C) / heat (−10–220 °C) cycle at a rate of 10 °C min⁻¹. Values of T_g and T_m were obtained from the second heating scan.

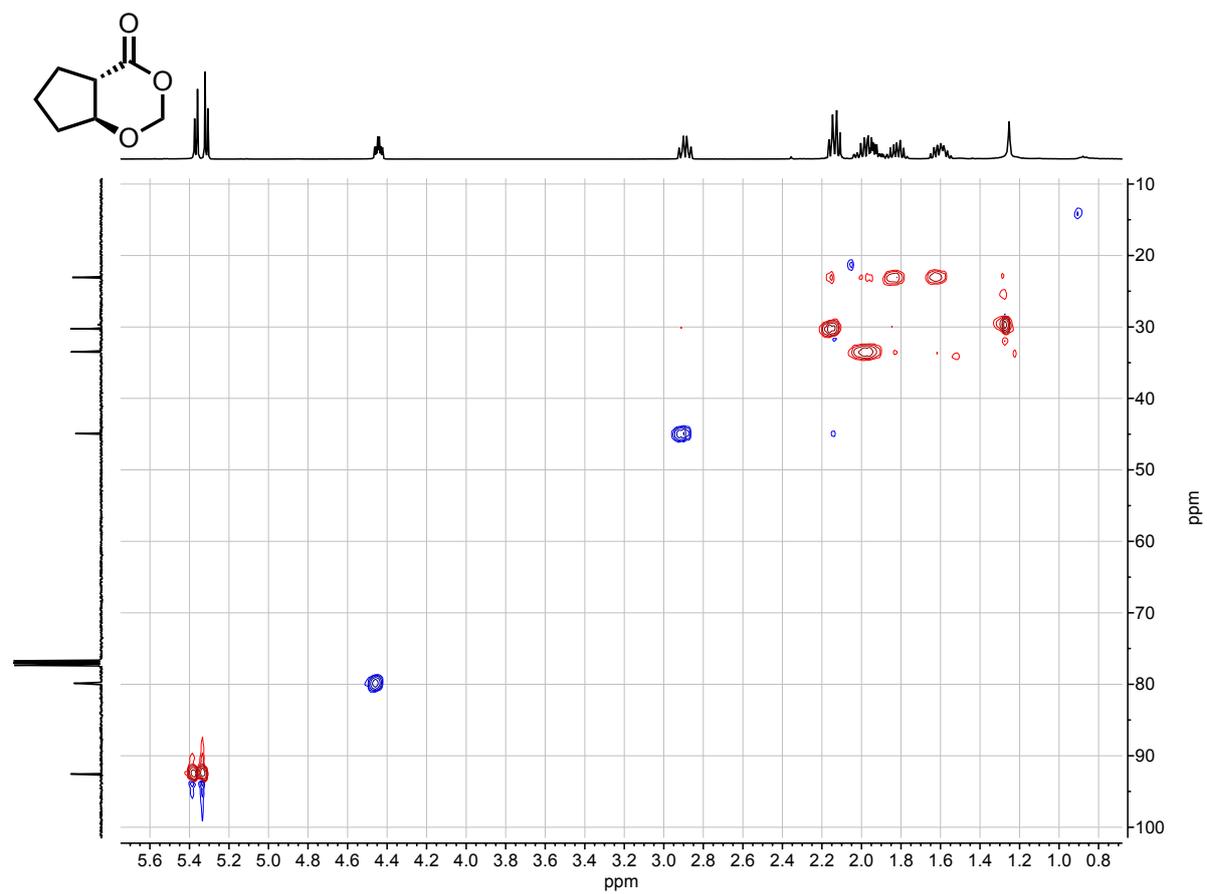


Figure S01 HSQC NMR spectrum of cPeDOX

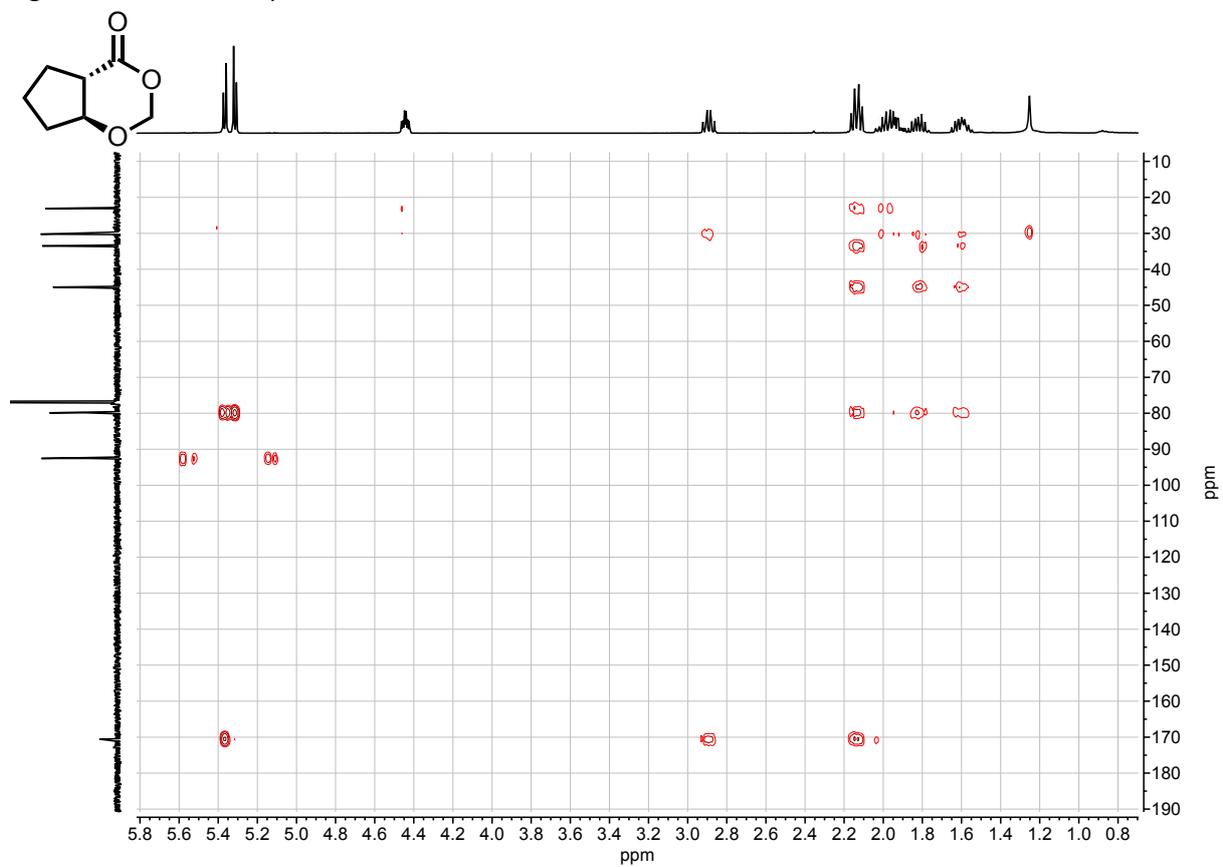


Figure S02 HMBC NMR spectrum of cPeDOX

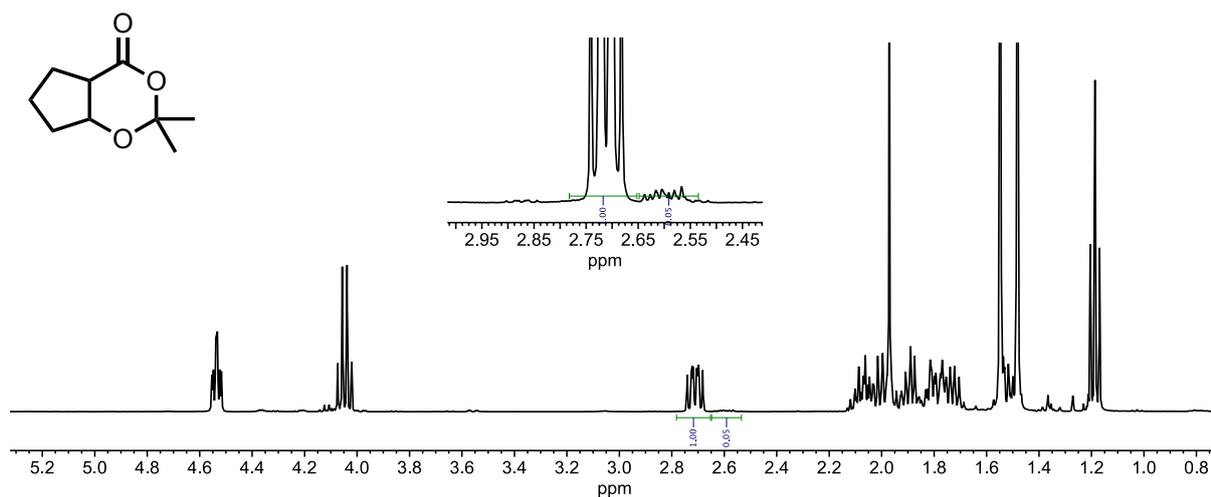


Figure S03 Acetone used as a ring-closing partner

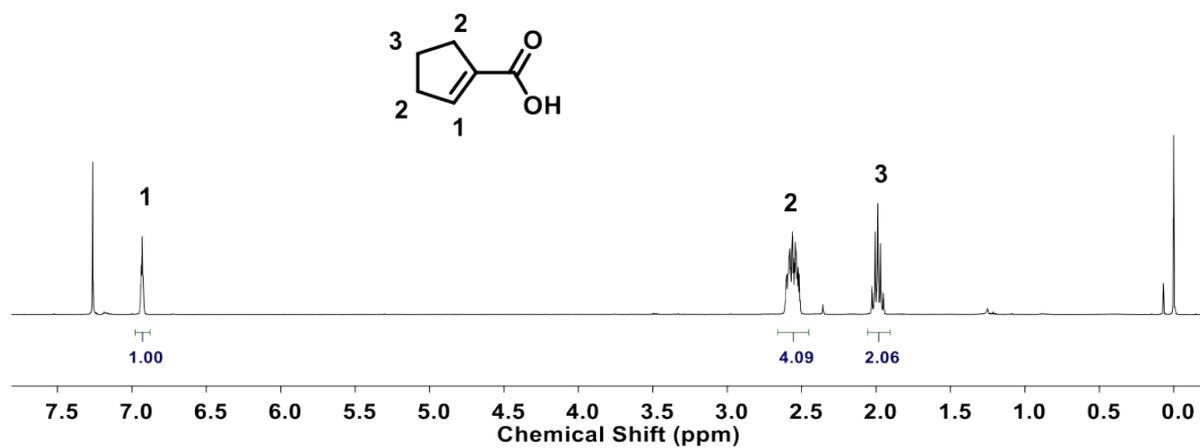


Figure S04 Formation of 1-cyclopentene carboxylic acid, isolable through recrystallisation from cold toluene

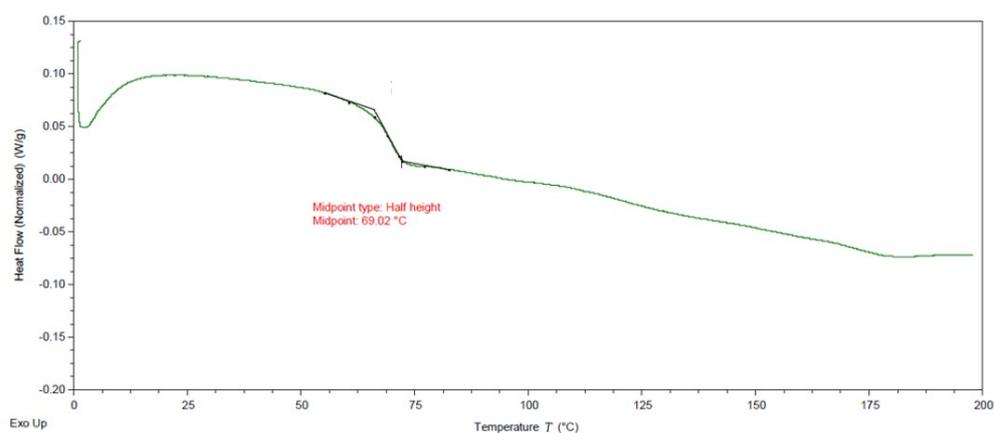


Figure S05 DSC profile of p(cPeDOX)

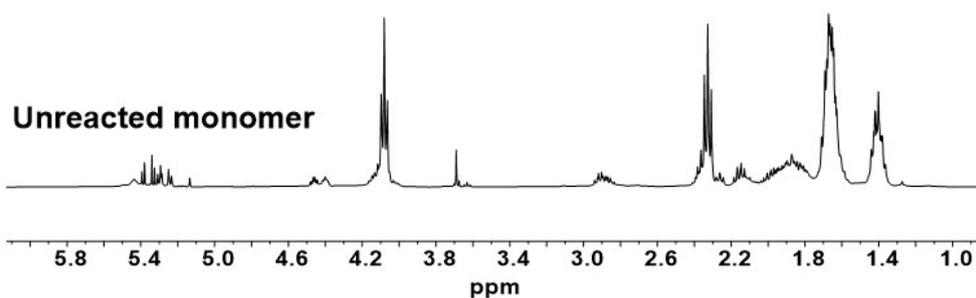


Figure S06 ^1H NMR of purified copolymer of cPeDOX and $\epsilon\text{-CL}$

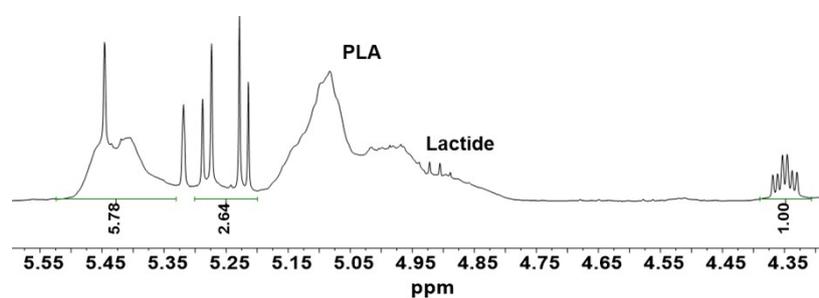


Figure S07 Overlapped peaks of PLA and lactide

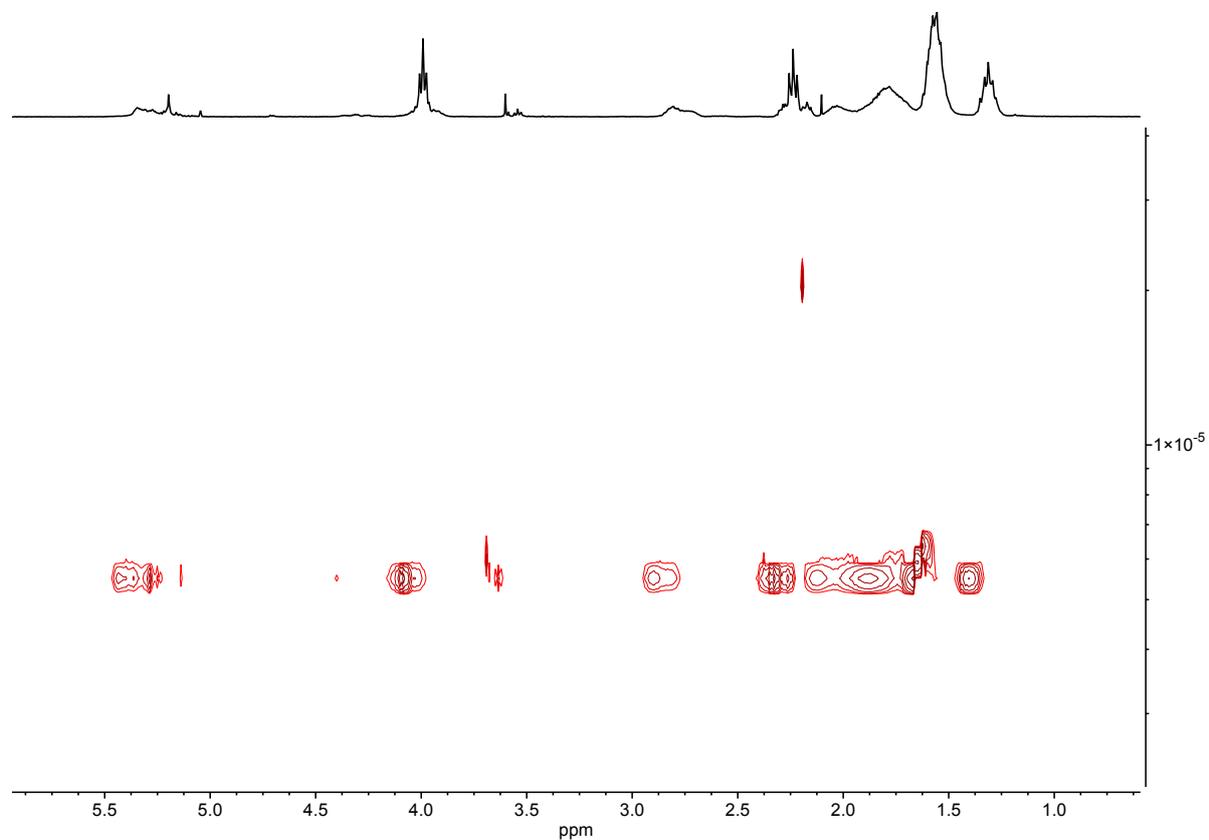


Figure S08 DOSY NMR of cPeDOX/ $\epsilon\text{-CL}$ copolymer

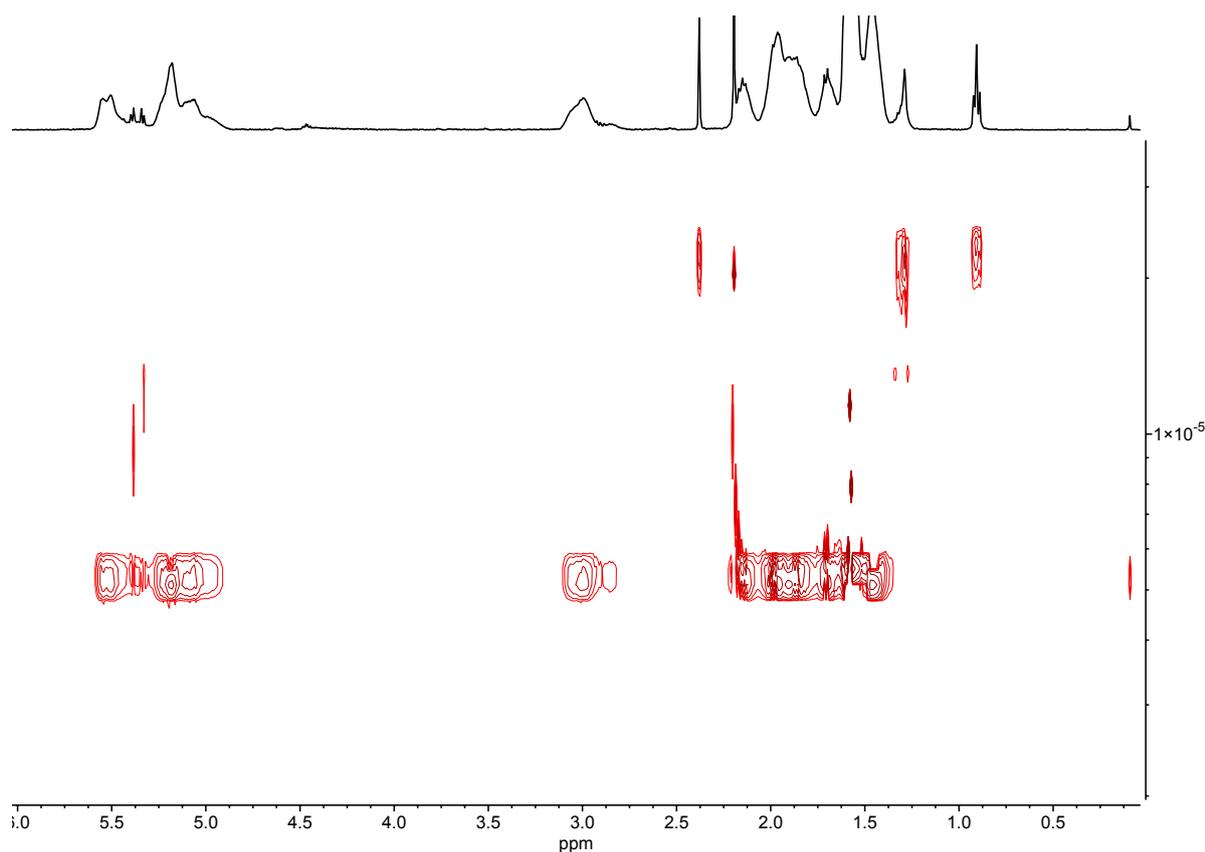


Figure S09 DOSY NMR of cPeDOX/*rac*-LA copolymer

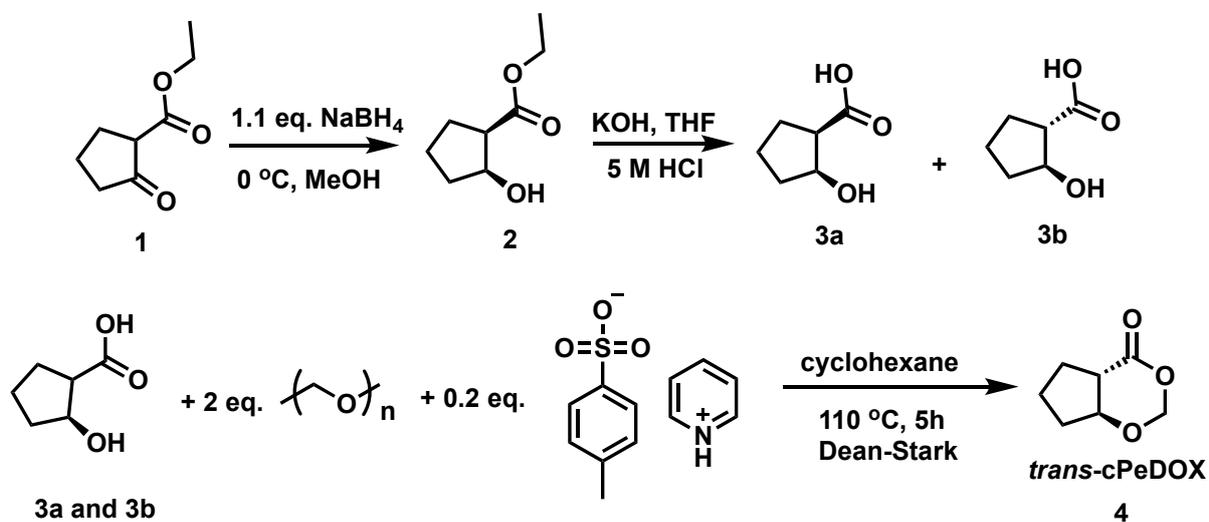


Figure S10 Synthesis of monomer cPeDOX

Synthesis of compound **2**: NaBH_4 was added slowly to a MeOH solution containing compound **1** (50 g compound **1** in 800 mL MeOH) at 0 °C. After the addition of NaBH_4 , the reaction was stirred at r.t. for 4 h. The crude reaction mixture was neutralised (pH = 7) with 5 M HCl. The resulting mixture was concentrated *in vacuo* followed by extraction with ethyl acetate and saturated aqueous NaHCO_3 solution/aqueous NaCl (saturated) solution. The organic phase was collected and dried with Na_2SO_4 . The mixture was dried *in vacuo* and distilled at 110 °C to obtain compound **2**.

Synthesis of compound **3**: Compound **2** (25 g) was dissolved in THF (400 mL). An aqueous KOH solution (2 eq.) was added and the mixture was stirred for 4 h at r.t. The aqueous phase containing compound

3 was washed with THF twice, followed by acidification with a 5 M HCl solution to a pH of *ca.* 2. The mixture was then stirred for 2 h and extracted with diethyl ether. The organic phase was collected and dried with Na₂SO₄. 1D NMR spectra of compounds **2** and **3** match reported literature values.³⁻⁷

Synthesis of compound **4**: Compound **3** (10 g), paraformaldehyde (2 eq.) and pyridinium *p*-toluenesulfonate (0.2 eq.) were dissolved in cyclohexane (400 mL). The mixture was heated under reflux for 5 h and water was removed *via* azeotropic distillation using a Dean-Stark apparatus. The reaction was cooled to r.t. and ethyl acetate (200 mL) was added. The resulting solution was then washed with saturated aqueous NaHCO₃ solution/deionised water/aqueous NaCl (saturated) solution. The organic phase was collected and dried with Na₂SO₄. The filtrate was dried *in vacuo* and the crude mixture was dried over CaH₂ and distilled under vacuum to afford **4**.

Cyclopentyl-1,3-dioxane-4-one (cPeDOX): white solid, 45% yield. ¹H NMR (400 MHz, CDCl₃) δ 5.37-5.29 (dd, 2H, OCH₂O), 4.46-4.41 (ddd, 1H, OCHC), 2.92-2.84 (ddd, 1H, OCCHC), 2.17-1.53 (m, 6H, CHCH₂CH₂CH₂CH). ¹³C NMR (100 MHz, CDCl₃) δ 170.50, 92.57, 79.88, 44.95, 33.53, 30.26, 23.09.

Polymerisation Procedure

In the glovebox, the catalyst and monomer of interest (cPeDOX 1 mmol, 142 mg) were mixed together and added to an ampoule. The sealed ampoule was removed from the glovebox and placed in a pre-heated oil bath. After a predetermined time, the reaction was removed from the oil bath, cooled, and quenched in air or by adding 3-4 drops of methanol. A crude sample was then taken for conducting ¹H NMR spectroscopy analysis (CDCl₃). The polymer was then precipitated from hexane. The precipitate was collected, dried under vacuum to constant weight before GPC analysis.

Copolymerisation Procedure

In the glovebox, the catalyst and the two monomers were mixed together in an ampoule. The sealed sample was removed from the glovebox and placed in a pre-heated oil bath. After a predetermined time, the reaction was removed from the oil bath, cooled, and quenched by adding 3-4 drops of methanol. A crude sample was taken for conduction ¹H NMR analysis. The polymer was then precipitated from hexane. The precipitate was collected and dried under vacuum to constant weight before GPC analysis.

Kinetic Study Procedure

Four homopolymerisation reactions (M:C:I = 200:1:2) were set up in parallel as previously described under identical reaction conditions (5 M in toluene, BnOH as initiator, 120 °C). The reactions were quenched after 1, 2, 3 and 4 hours. The conversion of each reaction was determined by ¹H NMR spectroscopic analysis (CDCl₃) of the crude sample. The polymers were then precipitated from hexane, collected and dried under vacuum to constant weight before GPC analysis.

Computational Details

All the calculations were performed on the full structures of the reported compounds. Calculations were performed with the GAUSSIAN 09 suite of programs.⁸ The stationary points were characterized as minima by full vibration frequencies calculations (no imaginary frequency, positive values). All geometry optimizations were carried out without any symmetry constraints. The energies were then refined by single point calculations to include solvent effects using the SMD solvation model⁹ with the experimental solvent at the B3LYP/6-31+G** level of theory. All optimised structures along with their

associated free enthalpy (H) and Gibbs (G) free energies as well as their cartesian coordinates are fully detailed below.

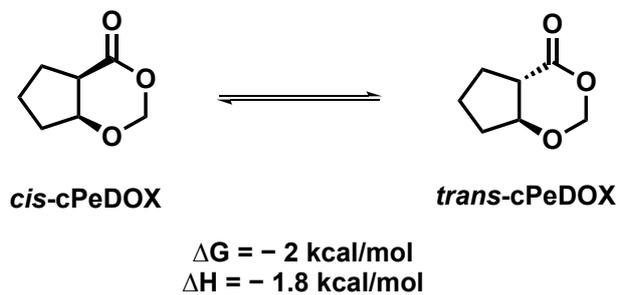


Figure S11 *cis-trans* isomerisation of cPeDOX along with associated free enthalpy (ΔH) and Gibbs free energy (ΔG)

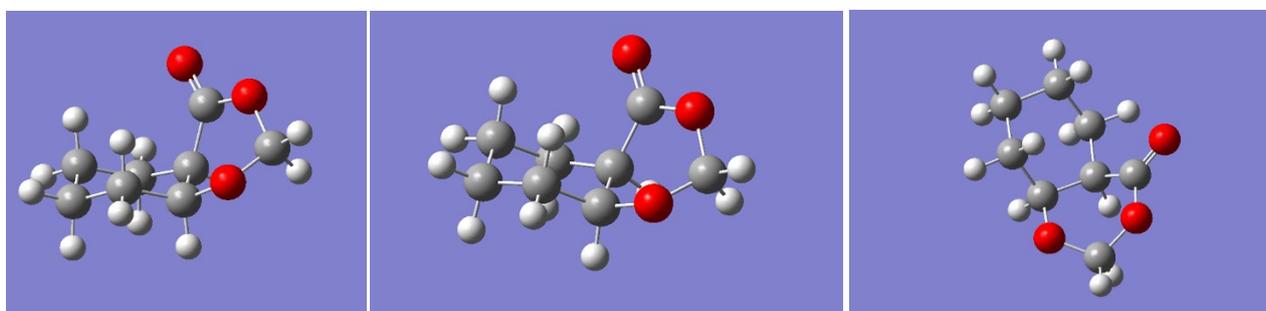


Figure S12 Optimised structure for *cis*-cPeDOX

cis-cPeDOX

Sum of electronic and thermal Enthalpies (Hartree) = - 537.581274

Sum of electronic and thermal Free Energies (Hartree)= -537.625403

0 1

C	2.31998600	0.66082800	-0.15644200
C	1.36199100	0.98926100	0.99779000
C	-0.04366800	0.38956900	0.81248800
C	0.00433900	-1.11627100	0.44071000
C	0.97965900	-1.40944400	-0.70094800
C	2.38085100	-0.85172500	-0.41284700
H	-0.57622800	0.47676700	1.77096800
H	1.77651200	0.59072600	1.93378500
H	1.26751700	2.07182800	1.12295800
H	1.98483700	1.17625000	-1.06469600
H	3.31730400	1.05020400	0.07903100
H	0.30511200	-1.68019600	1.33505500

H	1.00586600	-2.49223400	-0.86640200
H	0.58243600	-0.95866600	-1.61975400
H	2.81099200	-1.35890800	0.46337800
H	3.04477800	-1.07254100	-1.25621100
O	-1.29633700	-1.59934800	0.03154400
C	-0.91007500	1.14912200	-0.18699200
O	-2.10673400	0.54706300	-0.44911100
O	-0.63127700	2.19745300	-0.71809400
C	-2.34128100	-0.70184700	0.22734200
H	-3.23280900	-1.12700300	-0.23169300
H	-2.52235300	-0.49453700	1.29226000

***trans*-cPeDOX**

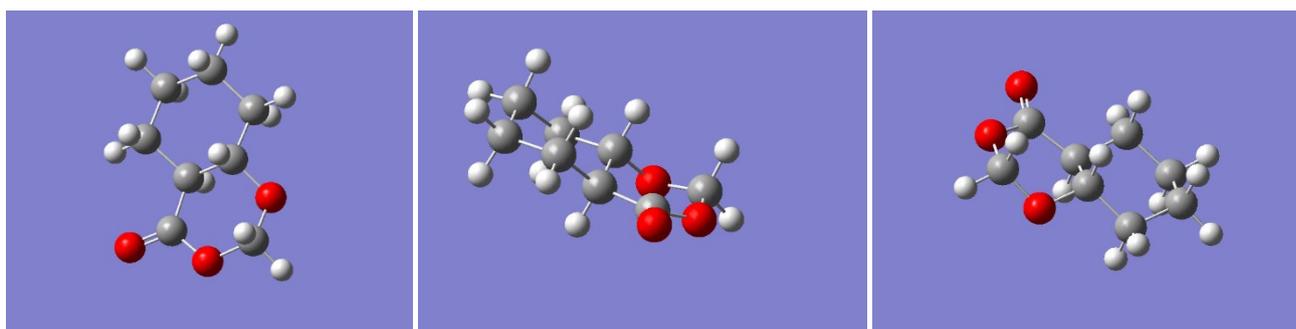


Figure S13 Optimised structure for *trans*-cPeDOX

Sum of electronic and thermal Enthalpies (Hartree) = -537.584273
Sum of electronic and thermal Free Energies (Hartree)= - 537.628688

0 1

C	2.45485800	0.99168900	-0.17510100
C	1.05482200	1.49690300	0.21328700
C	-0.01423200	0.52549800	-0.30718900
C	0.22863300	-0.89640300	0.21393200
C	1.59567800	-1.41587200	-0.20841400
C	2.69766200	-0.45837800	0.28315800
H	0.97426000	1.57715800	1.30603500
H	0.86955100	2.49759700	-0.18588800
H	2.56678000	1.04971000	-1.26719300

H	3.22000500	1.65090600	0.25088700
H	0.16461100	-0.89892500	1.31688200
H	1.74619100	-2.42507800	0.19063600
H	1.61697900	-1.49347500	-1.30347900
H	2.73713600	-0.48848900	1.38137200
H	3.67387300	-0.80915600	-0.07023100
H	0.06661100	0.47167800	-1.40489200
C	-1.44677600	0.98306900	-0.06017700
O	-0.80974900	-1.74426900	-0.29672100
C	-2.04009200	-1.37273500	0.23159800
H	-2.81207600	-1.97154800	-0.25089000
H	-2.05945500	-1.51085500	1.32320500
O	-1.78478200	2.14123700	0.01059900
O	-2.39894200	0.00651300	-0.01800500

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