Supporting Information

Telechelic all-*cis* polycyclooctene via catalytic stereoretentive ROMP for the synthesis of polylactide-based ABA triblock copolymers

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Materials and Methods

General Reagent Information

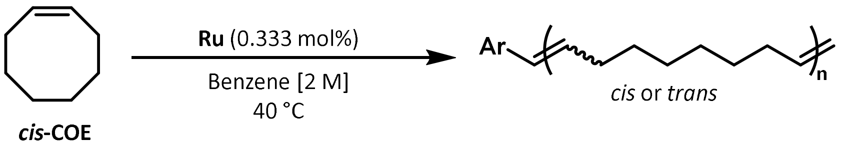
All polymerizations using ruthenium catalysts were set up in a nitrogen-filled glove box (SG1800/750TS-F, VIGOR) using dry solvents under anhydrous conditions. Dry dichloromethane (DCM) and toluene (PhMe) were obtained by passing the previously degassed solvents through activated alumina columns. Benzene was distilled over calcium hydride and degassed via "freeze-pump-thaw" before being brought into a nitrogen-filled glove box. Reagents were purchased at the highest commercial quality and used without further purification, unless otherwise stated. *cis*-cyclooctene, and *cis*-1,4-diacetoxy-2-butene were purchased from Acros Organics and distilled over calcium hydride before being brought into a nitrogen-filled glove box. TBD (97%) was purchased from Combi-blocks and used without further purification. DBU was distilled over calcium hydride and degassed via "freeze-pump-thaw" before bringing into a nitrogen-filled glove box. D,L-Lactide (97%) was purchased from Combi-blocks and recrystallized twice from ethyl acetate prior to use. Catalysts **Ru-1**, **Ru-2**, and **Ru-3a** were purchased from Sigma-Aldrich and used without further purification. Catalysts **Ru-3b**, **Ru-4a**, and **Ru-4b** were generously donated by Umicore. Polymers were isolated after precipitation with methanol using an Eppendorf 5804 centrifuge.

General Analytical Information

Polymer samples were analyzed using a Tosoh EcoSec HLC 8320GPC system with a TSKgel SuperHM-M column and a TSKgel SuperH-RC column at flow rates of 0.1 and 0.35 mL/min at 40 °C. THF stabilized with BHT was used as the eluent and all number-average molar masses (M_n), weight-average molar masses (M_w), and dispersities ($Đ$) for polymers were calculated from refractive index chromatograms against TSKgel polystyrene standards. NMR spectra were recorded on Bruker Avance Neo 400 or Bruker Avance 500 instruments and were calibrated using residual undeuterated solvent as an internal reference ($CHCl_3$ @ 7.26 ppm ^{1}H-NMR, 77.16 ppm ^{13}C-NMR). The following abbreviations were used to explain NMR peak multiplicities: s = singlet, d = doublet, dd = doublet of doublets, t = triplet, q = quartet, p = pentet, m = multiplet, br = broad. Due to the overlap between the *cis* and *trans* alkene signals in the ^{1}H NMR spectra of the polyalkenamers, the *cis*/*trans* contents were determined using an NMR deconvolution method described in the supporting information of a previous report from our group.[1] Thermogravimetric analysis (TGA) was performed on a TA Instruments TGA 5500 Thermogravimetric Analyzer. Samples were weighed onto a platinum sample pan and heated at 20 °C/min to 100 °C, followed by an isothermal period of 1 minute before heating at 10 °C/min to 600 °C under nitrogen. T_d was determined using the temperature at 5% decomposition. Differential scanning calorimetry (DSC) was performed using a TA instrument DSC 2500. Samples (3–5 mg) were heated to 200 °C at 10 °C/min, followed by an isothermal period of 5 min before cooling to –80 °C at 10 °C/min and another isothermal period of 5 min. A total of three scanning cycles were run for each sample, and thermograms were taken from the third heating/cooling cycle. Nanoindentation experiments were performed on a Hysitron TI 950 TriboIndenter equipped with a diamond Berkovich indenter tip. The tip shape was calibrated to a fused quartz standard using the Oliver and Pharr methodology prior to testing. Samples for nanoindentation experiments were prepared by drop-casting a solution of 30 mg of polymer in 0.4 mL DCM onto a 1 cm square glass plate. The samples were left at room temperature for 16 h then annealed at 80 °C under vacuum for 16 h, at room temperature under vacuum for 16 h, and then affixed onto steel pucks with epoxy. 5 x 5 Arrays of indentations with 20 µm spacing between neighboring indents were performed. All indents were load-controlled with a maximum applied load of 6000 µN, a loading and holding time of 10 s, and an unloading time of 2 s. The hardness (H) and reduced modulus (E_r) were then calculated from the unloading segments of the load-displacement curves using the standard Oliver and Pharr analysis.[2]

Polymer Synthesis

ROMP of *cis*-COE



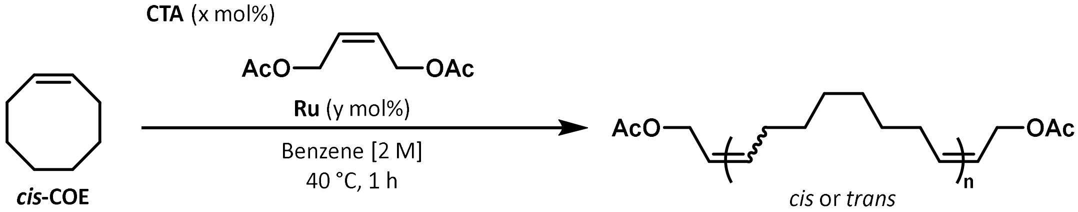
The synthesis of PCOE using **Ru-4b** is described here. **Ru-4b** (2.2 mg, 0.0025 mmol, 1 equiv) was weighed into a vial charged with a stir bar inside a nitrogen filled glovebox. *cis*-COE (83.2 mg, 0.75 mmol, 300 equiv) was measured into a separate vial and dissolved in 0.38 mL of benzene. The monomer solution was then quickly added to the reaction vial containing **Ru-4b** and left to stir at 400 rpm for 1 hour at 40 °C inside the glovebox. The reaction was cooled to 23 °C before quenching with 0.1 mL of EVE. The polymer was transferred to a centrifuge tube using a minimal amount of DCM, precipitated in MeOH, and centrifuged at 9500 rpm for 10 minutes. This purification process was repeated twice before drying under high vacuum for further analysis.

M_n^{theo} = 33.1 kg/mol, M_n^{exp} = 66.4 kg/mol, *Đ* = 1.54, % *cis* = 72%

The spectroscopic data for this compound were identical to those reported in the literature.[1, 3, 4]

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.42–5.29 (m, 2 H), 2.08–1.88 (m, 4 H), 1.41–1.20 (m, 8 H) ppm.

Catalytic Stereoretentive ROMP of *cis*-COE



The synthesis of telechelic all-*cis* PCOE using **Ru-4b** is described here. 2.2 mg of **Ru-4b** was weighed into a vial inside a nitrogen filled glovebox and dissolved in 1 mL of benzene (C = 0.0025 mol/L). Next, 4.3 mg of *cis*-1,4-diacetoxy-2-butene (*cis*-DAB) was dissolved in 1 mL of benzene (C = 0.025 mol/L). 0.4 mL (0.001 mmol, 0.05 equiv) of the catalyst stock was then mixed with 0.8 mL (0.02 mmol, 1 equiv) of the *cis*-DAB stock into a vial equipped with a stir bar and stirred at 400 rpm for 5 minutes at 40 °C inside the glovebox before quickly adding a solution of *cis*-COE (332.8 mg, 3.0 mmol, 150 equiv) dissolved in 0.3 mL of benzene. The reaction was left to stir at 400 rpm for 1 hour at 40 °C inside the glovebox. The reaction was cooled to 23 °C before quenching with 0.1 mL of EVE. The polymer was transferred to a centrifuge tube using a minimal amount of DCM, precipitated in MeOH, and centrifuged at 9500 rpm for 10 minutes. This purification process was repeated twice before drying under high vacuum for further analysis.

M_n^{theo} = 16.8 kg/mol, M_n^{exp} = 28.7 kg/mol, *Đ* = 1.62, % *cis* = >99%

^{1}H NMR including chain-end analysis (400 MHz, $CDCl_3$) δ 5.42–5.29 (m, 271 H), 4.64–4.60 (d, *J* = 6.8 Hz, 4 H), 2.08–1.88 (m, 556 H), 1.41–1.20 (m, 1106 H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ 130.0, 29.9, 29.4, 27.4 ppm.

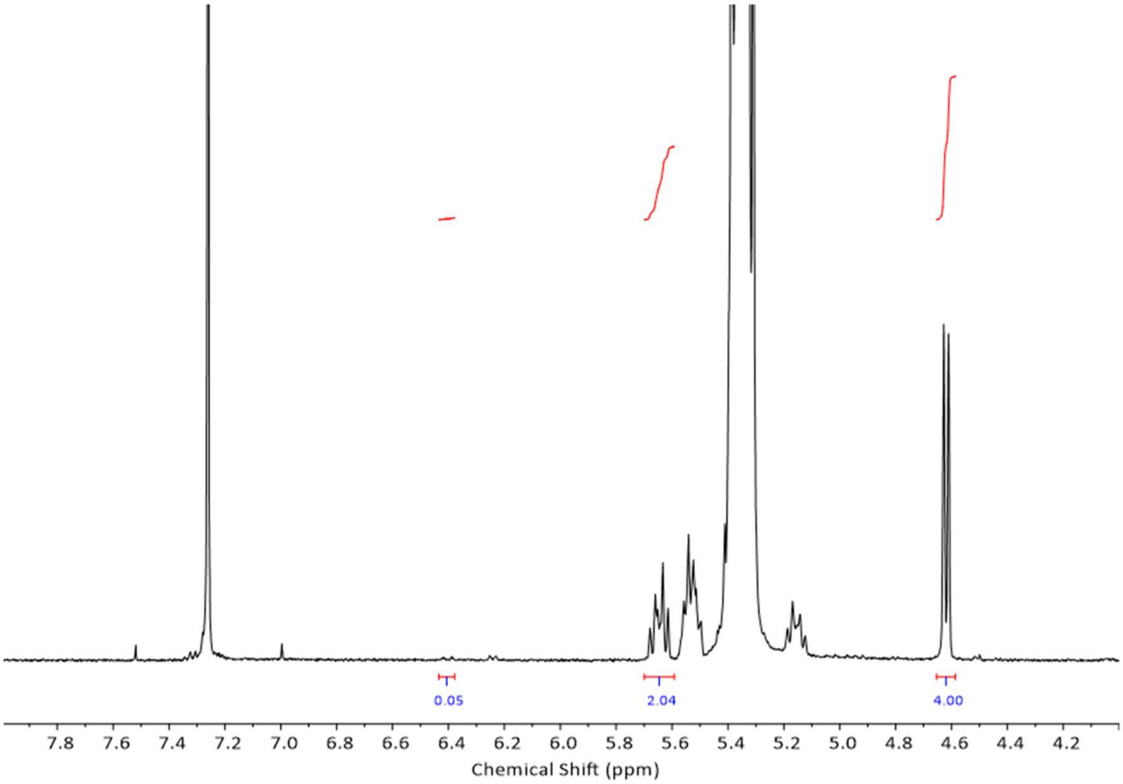
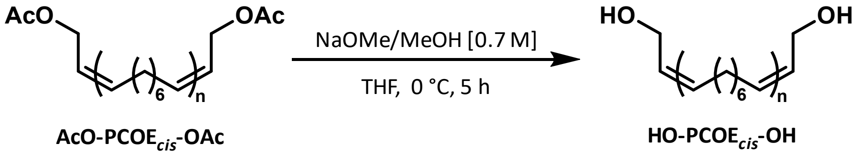


Figure S1. Chain-end analysis of **AcO-PCOE*cis*-OAc** showing ≥ 95% chain-end functionalization.

Synthesis of **HO-PCOE*cis*-OH**



Synthesis adapted from a literature procedure.[5] To a reaction tube charged with a stir bar, 97.0 mg of **AcO-PCOE*cis*-OAc** (M_n^{exp} = 28.7 kg/mol, *Đ* = 1.62) was measured and dissolved in 2 mL of THF before cooling to 0 °C. A solution of NaOMe in MeOH (C = 0.7 mol/L, 0.53 mL) was added to the polymer solution and the mixture was stirred at 0 °C for 5 hours. After completion, HCl (C = 12 mol/L, 0.05 mL) was added dropwise to the reaction at 23 °C and stirred at 400 rpm while a white precipitate was observed. The polymer was transferred to a centrifuge tube, further precipitated in MeOH, and centrifuged at 9500 rpm for 10 minutes. This purification process was repeated twice before drying under high vacuum for further analysis.

M_n^{exp} = 28.8 kg/mol, *Đ* = 1.52, % *cis* = >99%

^{1}H NMR including chain-end analysis (400 MHz, $CDCl_3$) δ 5.42–5.29 (m, 273 H), 4.22–4.17 (t, *J* = 5.8 Hz, 4 H), 2.08–1.88 (m, 555 H), 1.41–1.20 (m, 1121 H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ 130.0, 29.9, 29.4, 27.4 ppm.

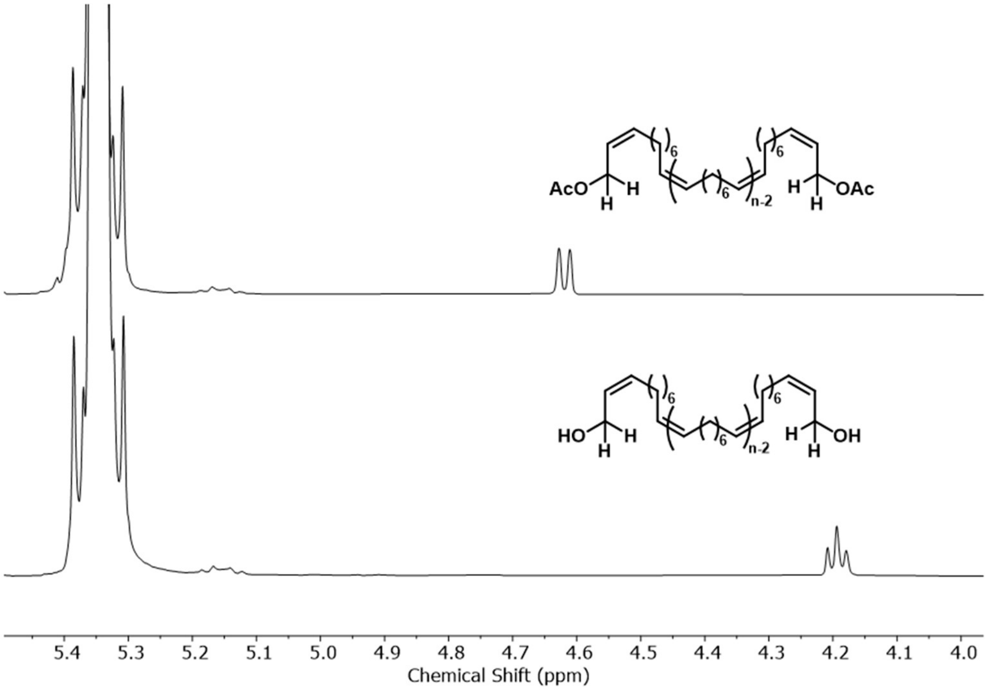
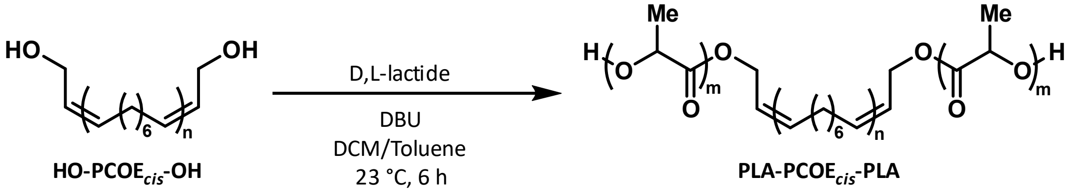


Figure S2. ^{1}H NMR analysis of the chain-end hydrolysis.

ABA Triblock Copolymer Synthesis



The synthesis of ABA triblock copolymer using DBU is described here. 2.0 mg of DBU was dissolved in 2.0 mL of toluene inside the glovebox (C = 0.013 mol/L). 0.1 mL (0.6569 µmol, 1.9 equiv) of the DBU stock solution was then added into a vial containing vacuum-dried **HO-PCOE$_{cis}$-OH** (M_n^{exp} = 28.8 kg/mol, *Đ* = 1.52) and a stir bar. An additional 0.1 mL of toluene was added, and the solution was mixed well before leaving to stir on a stir plate inside the glovebox at 400 rpm for 5 minutes at 23 °C. Next, D,L-lactide (50.0 mg, 0.342 mmol, 1000 equiv.) was dissolved in 0.2 mL of DCM and quickly transferred to the polymer solution. The polymerization was left to stir at 400 rpm at 23 °C for 6 hours. The reaction was quenched using 0.1 mL of acetic acid outside the glovebox. The polymer was transferred to a centrifuge tube using a minimal amount of DCM, precipitated in MeOH, and centrifuged at 9500 rpm for 10 minutes. This purification process was repeated twice before drying under high vacuum for further analysis. The final polymer was dried in a vacuum oven at 70 °C for 12 hours prior to obtaining thermal data.

M_n^{theo} = 172.9 kg/mol, M_n^{exp} = 91.9 kg/mol, *Đ* = 1.30, % *cis* = >99%

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.42–5.29 (m, 2 H), 5.25–5.07 (m, 7 H), 2.08–1.88 (m, 4 H), 1.68–1.46 (m, 23 H), 1.41–1.20 (m, 8 H) ppm.

^{13}C NMR (126 MHz, $CDCl_3$) δ 169.8, 130.0, 69.2, 29.9, 29.4, 27.4, 16.8 ppm.

Thermal Characterization

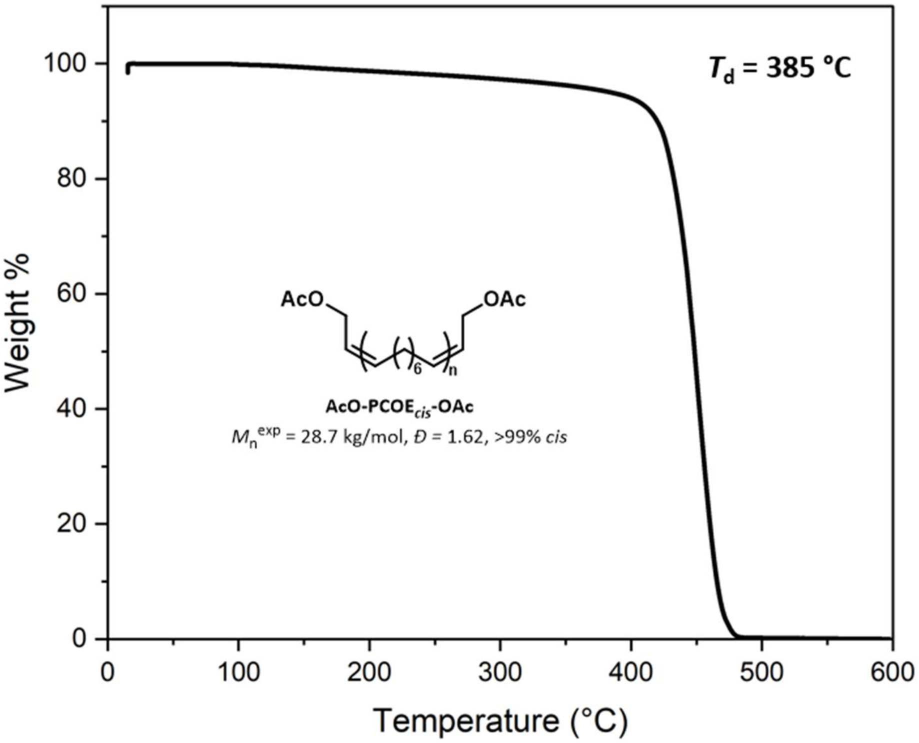


Figure S3. TGA thermogram of **AcO-PCOE$_{cis}$-OAc**.

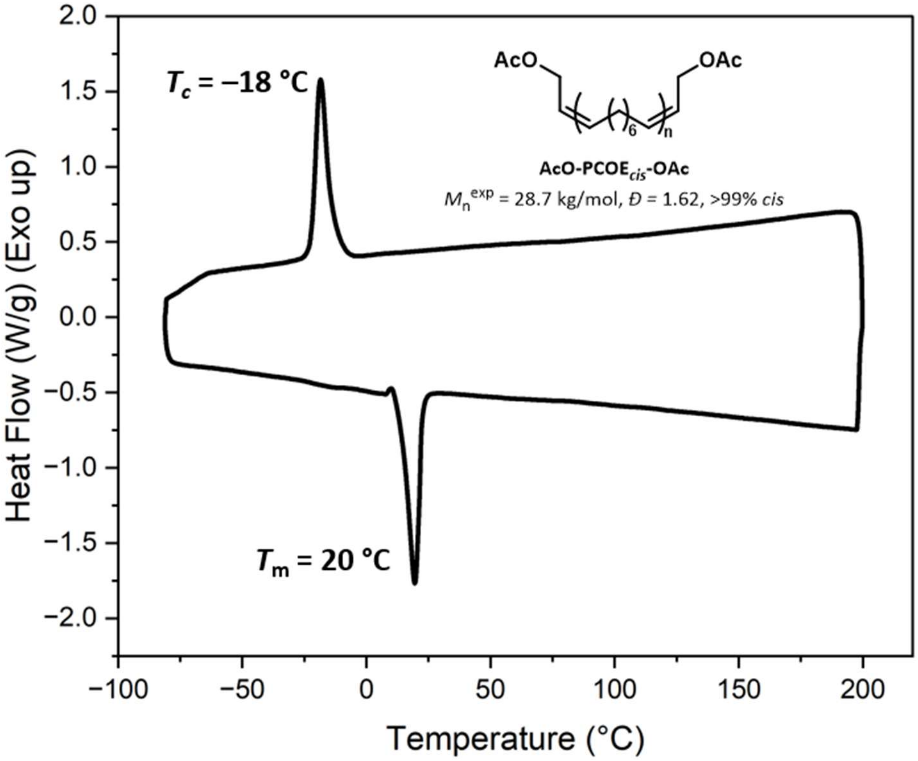


Figure S4. DSC thermogram of **AcO-PCOE$_{cis}$-OAc**.

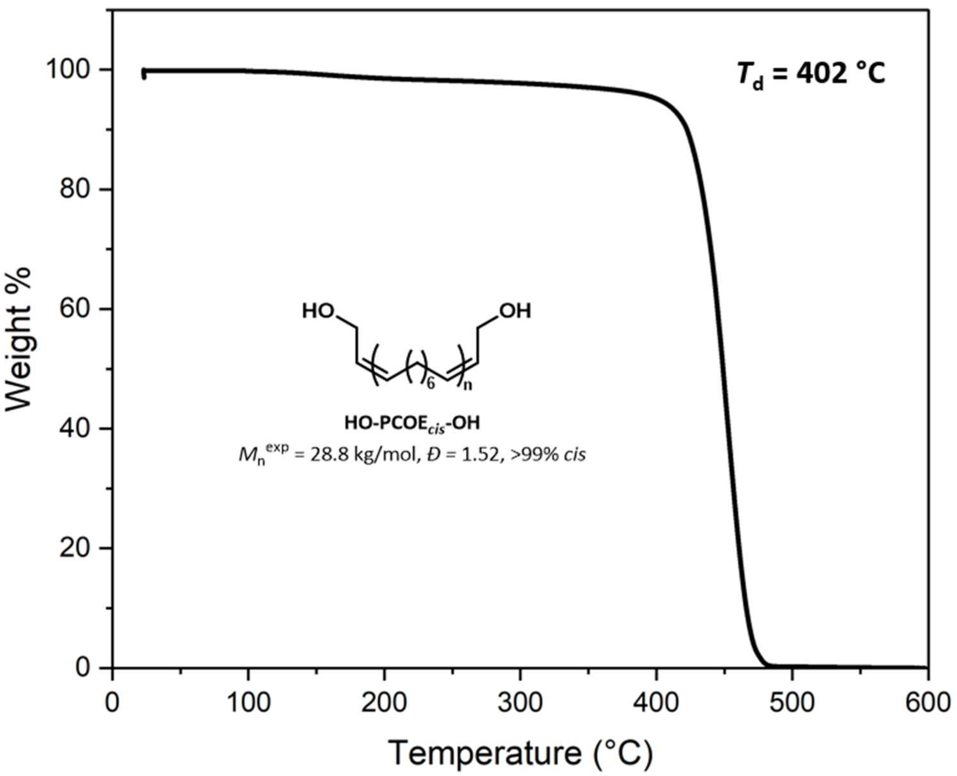


Figure S5. TGA thermogram of **HO-PCOE$_{cis}$-OH**.

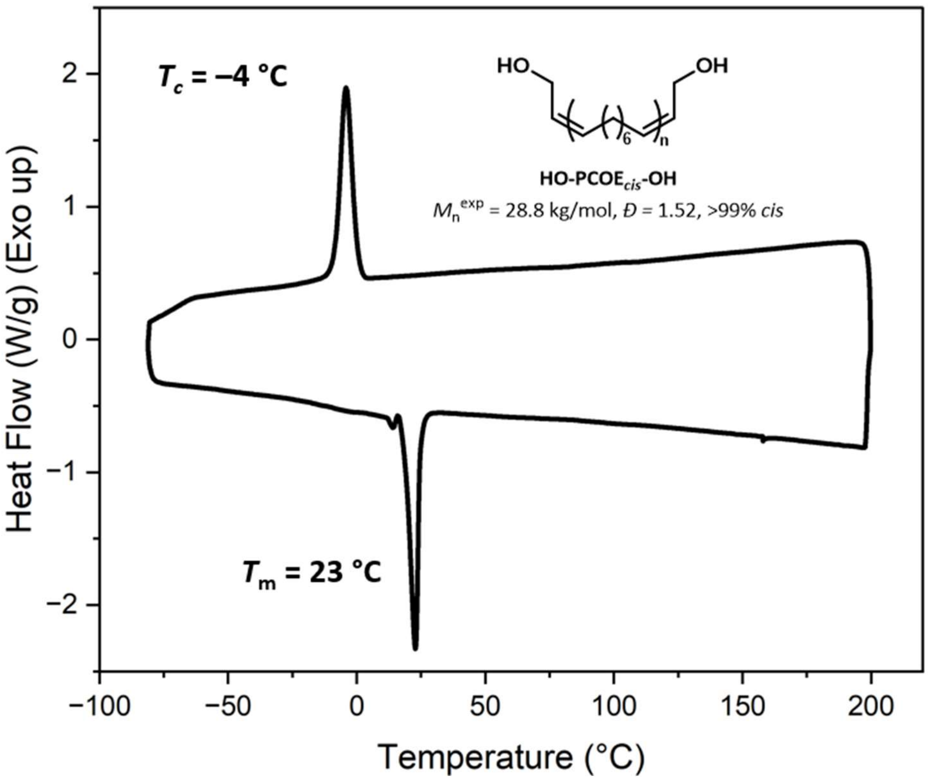


Figure S6. DSC thermogram of **HO-PCOE$_{cis}$-OH**.

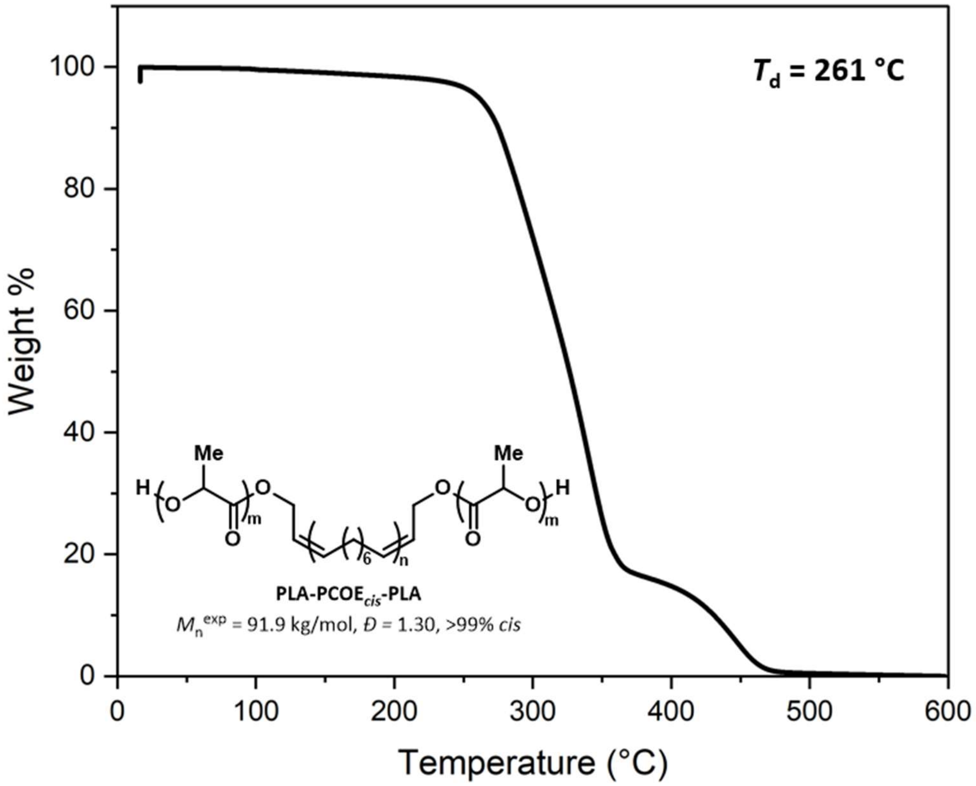


Figure S7. TGA thermogram of **PLA-PCOE$_{cis}$-PLA**.

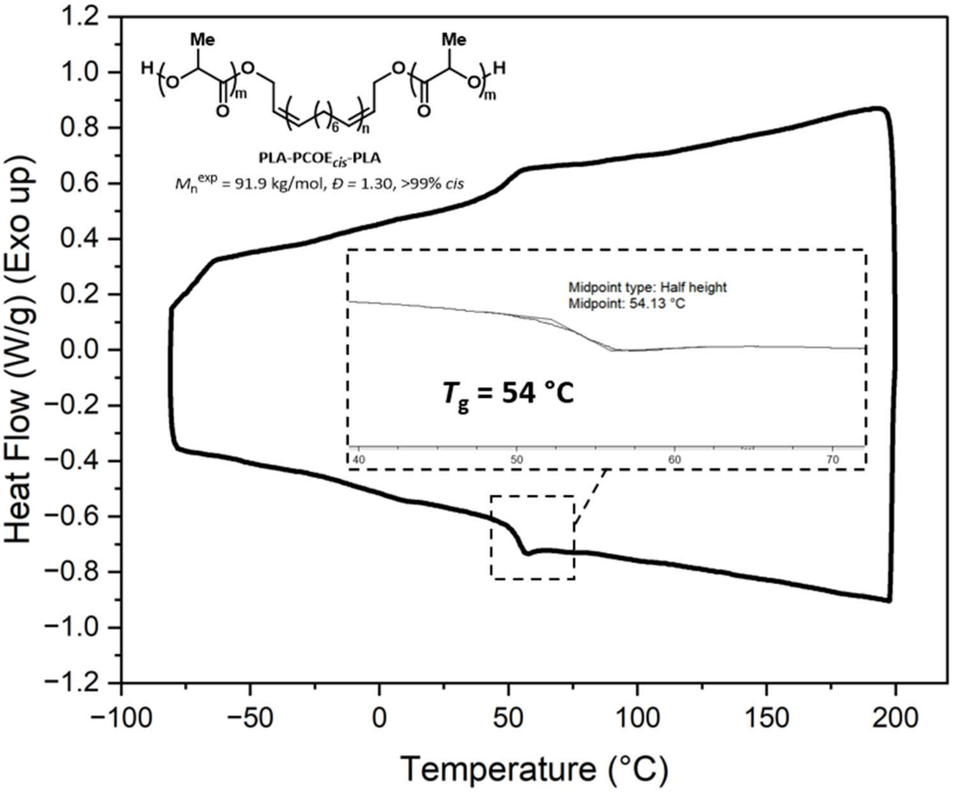


Figure S8. DSC thermogram of **PLA-PCOE$_{cis}$-PLA**.

Nanoindentation

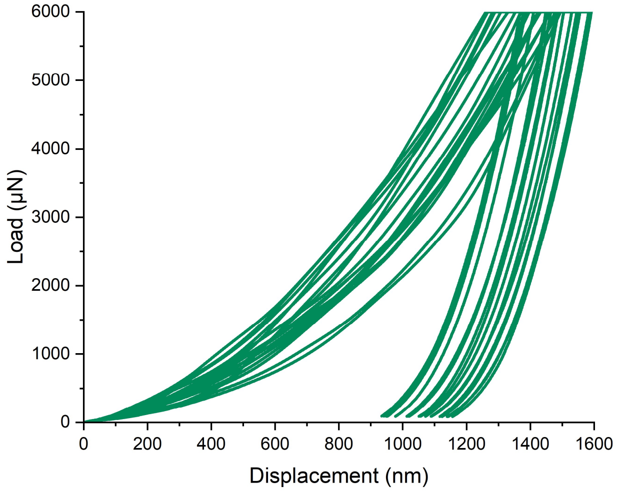


Figure S9. Load-displacement curves for **PLA-PCOE$_{cis}$-PLA** (M_n^{exp}= 105.0 kg/mol, $Đ$ = 1.28, H = 0.137 ± 0.016, E_r = 3.55 ± 0.21).

Solvent Casting

A plastic thin film was created by casting 150 mg of **PLA-PCOE$_{cis}$-PLA** (M_n^{exp}= 105.0 kg/mol, $Đ$ = 1.28) dissolved in 20 mL of DCM into a beaker (5 cm diameter) and letting evaporate over the course of 5 days under a fume hood.

^{1}H and ^{13}C NMR Data

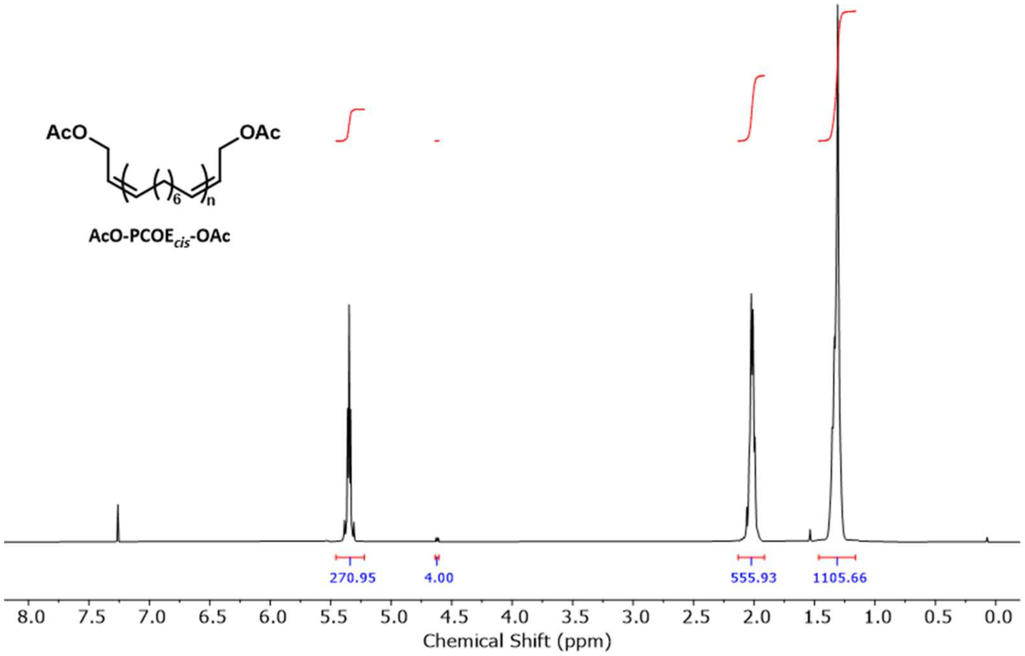


Figure S10. ^{1}H NMR (400 MHz, CDCl$_3$) spectrum of **AcO-PCOE$_{cis}$-OAc** including chain-end analysis.

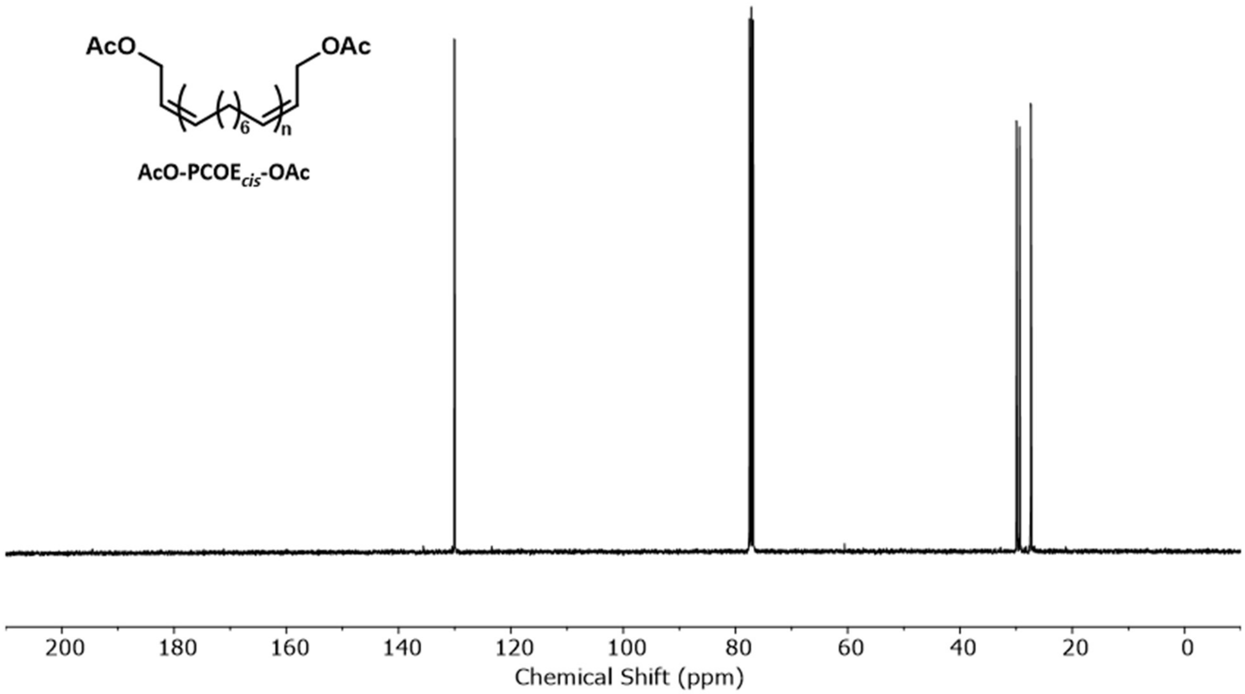


Figure S11. ^{13}C NMR (101 MHz, CDCl$_3$) spectrum of **AcO-PCOE$_{cis}$-OAc**.

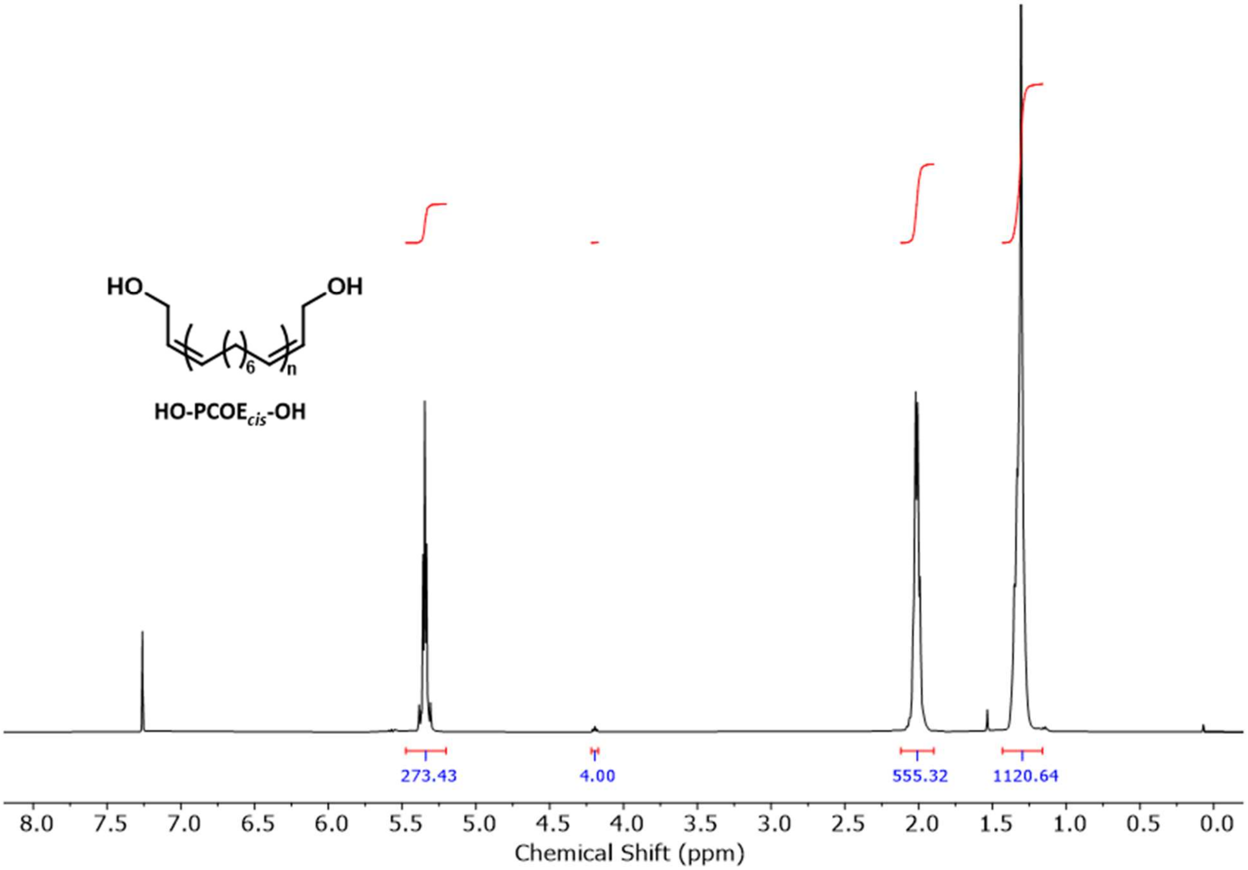


Figure S12. ^{1}H NMR (400 MHz, CDCl$_3$) spectrum of **HO-PCOE$_{cis}$-OH** including chain-end analysis.

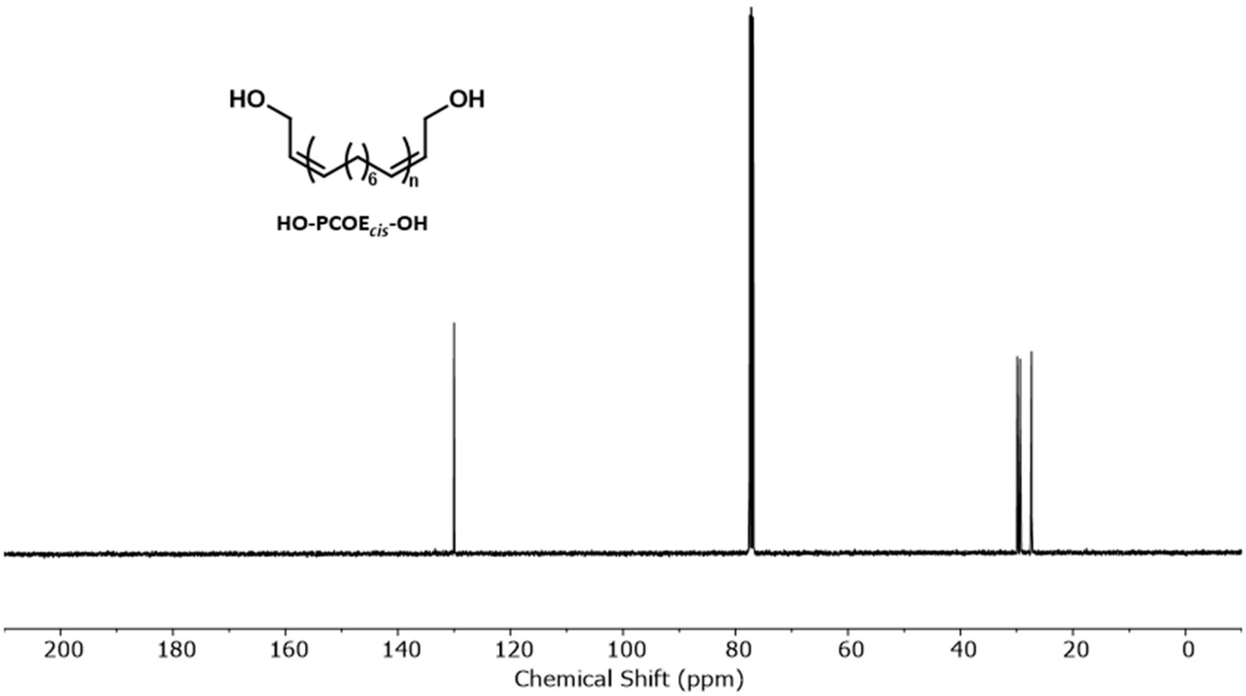


Figure S13. ^{13}C NMR (101 MHz, CDCl$_3$) spectrum of **HO-PCOE$_{cis}$-OH**.

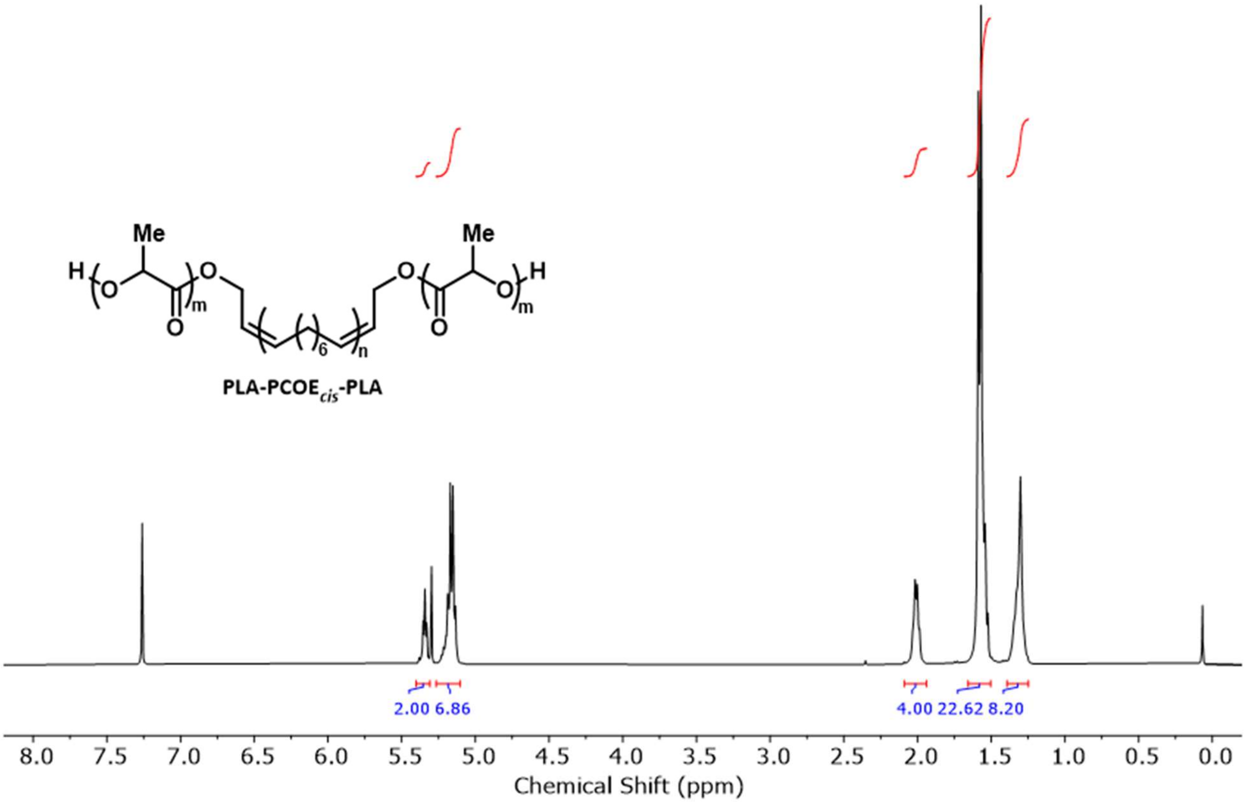


Figure S14. ^{1}H NMR (400 MHz, CDCl$_3$) spectrum of **PLA-PCOE$_{cis}$-PLA**.

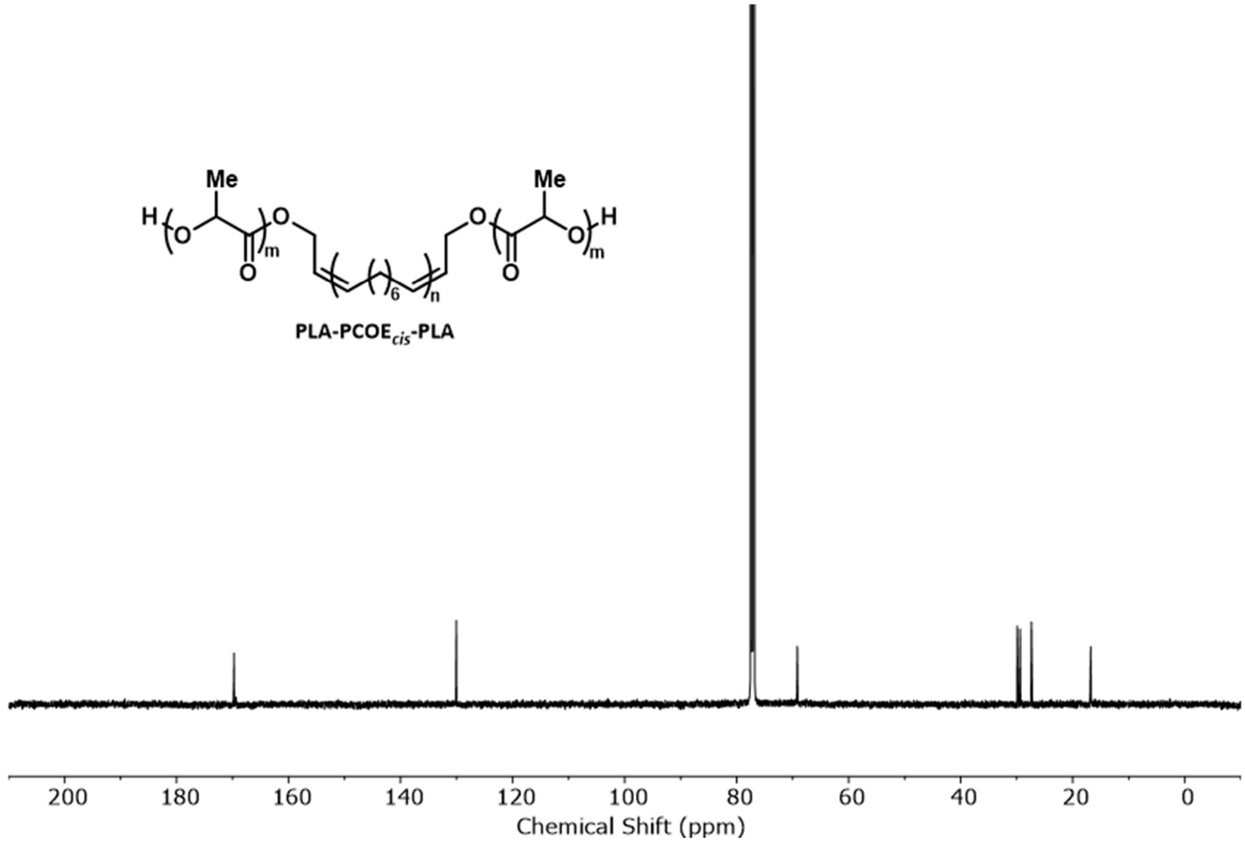


Figure S15. ^{13}C NMR (126 MHz, CDCl$_3$) spectrum of **PLA-PCOE$_{cis}$-PLA**.

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