Electronic Supplementary Material (ESI) for Green Chemistry.

Synthesis and characterization of biorenewable polyesters derived from natural camphoric acid

Olivier Nsengiyumva[‡] and Stephen A. Miller[‡,*]

[‡] *The George and Josephine Butler Laboratory for Polymer Research, Department of Chemistry, University of Florida Gainesville, Florida 32611-7200, USA*

Supporting Information

Supporting Information Available: Synthetic details, complete polymer characterization data, and polymer degradation data.

Table of Contents

General Considerations and Instrumentation S2

Polymerizations S3

Summary of Polymerization Data S11

Gel Permeation Chromatography (GPC) Chromatograms S13

Differential Scanning Calorimetry (DSC) Thermograms S24

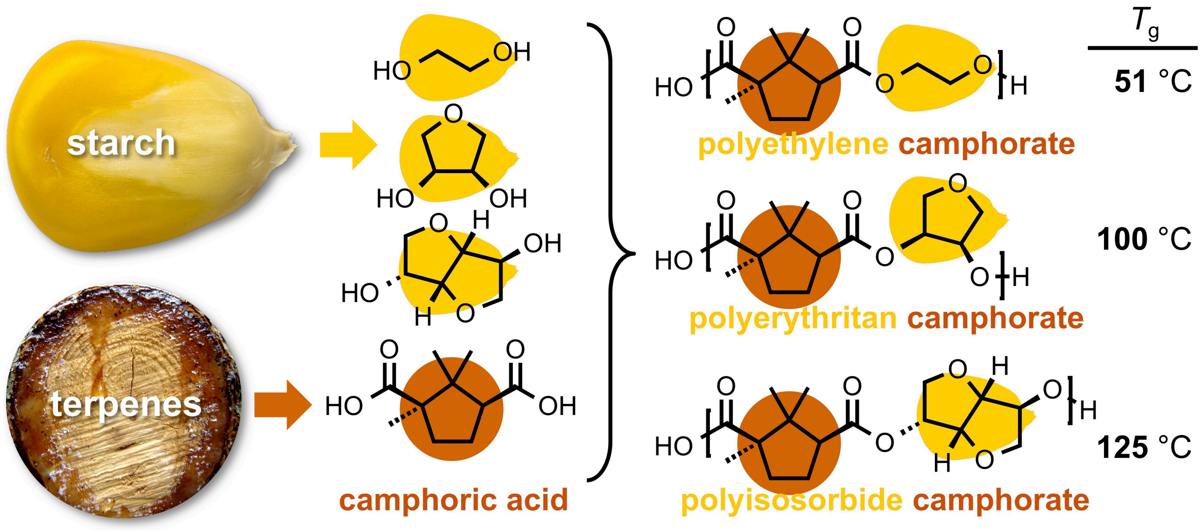
Thermogravimetric Analysis (TGA) Thermograms S34

^{1}H NMR Spectra S44

^{13}C NMR Spectra S55

Analysis of Copolymer Composition for Polyethylene (Camphorate/Terephthalate) S66

Degradation Studies S69



General Considerations and Instrumentation

Materials

(+)-Camphoric acid (99%) and ethylene glycol were purchased from Fisher Scientific and used without further purification. 1,3-propanediol (99.6+%), 1,4-butanediol (99%), 1,5-pentanediol (99%), 1,6-hexanediol (99%), bis(2-hydroxyethyl) terephthalate, and *para*-toluenesulfonic acid (*p*-TSA) monohydrate were purchased from Sigma-Aldrich and used as received. "Healthy Foods" erythritol (100% pure) was purchased from Amazon and isosorbide (98%) was purchased from Fisher and recrystallized from ethyl acetate. Antimony Oxide (Sb_2O_3, 99.5%), a catalyst for polymerization, was purchased from Acros and used as received. Deionized water and saturated aqueous HCl solution were purchased from Fisher Scientific. NMR solvents, including deuterated chloroform ($CDCl_3$) and deuterated trifluoroacetic acid (TFA-*d*), which do not contain tetramethylsilane (TMS), were purchased from Cambridge Isotope Laboratories. All other chemicals, unless expressly mentioned, were utilized as received.

Characterizations

Proton and carbon nuclear magnetic resonance (^1H and ^{13}C NMR) spectra were recorded using an Inova 500 MHz spectrometer. Chemical shifts are reported in parts per million (ppm) downfield relative to tetramethylsilane (TMS, 0.0 ppm) or residual proton and carbon in the specified solvent. Coupling constants (*J*) are reported in Hertz (Hz). Multiplicities are reported using the following abbreviations: s, singlet; d, doublet; t, triplet; q, quartet; quin, quintet; m, multiplet; br, broad.

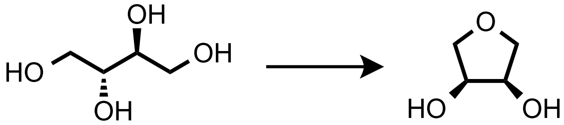
Differential scanning calorimetry (DSC) thermograms were obtained with a DSC Q1000 from TA instruments. About 3-5 mg of each sample were massed and added to a sealed pan that passed through a heat/cool/heat cycle at 10 °C/min. Reported data are from the second full cycle. The temperature ranged from –50 to 200 °C, depending on the samples.

Thermogravimetric analyses (TGA) were measured under nitrogen with a TGA Q5000 from TA Instruments. About 5-10 mg of each sample were heated at 20 °C/min from 25 to 600 °C.

Gel permeation chromatography (GPC) was performed at 40 °C using an Agilent Technologies 1260 Infinity Series liquid chromatography system with an internal differential refractive index detector, and a PL HFIP gel column (7.5 mm i.d., 300 mm length) using a solution of 0.1% potassium triflate (K(OTf)) in HPLC grade hexafluoroisopropanol (HFIP) as the mobile phase at a flow rate of 0.3 mL min-1. Calibration was performed with narrow dispersity polymethylmethacrylate (PMMA) standards.

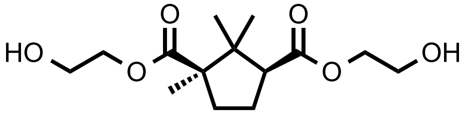
Monomer Preparation

Synthesis of *cis*-1,4-anhydroerythritol (erythritan)



24.4 g (200 mmol) of erythritol were added to a 250 mL round bottom flask equipped with a magnetic stir bar. The temperature was set to 135 °C until erythritol melted. Then 1.90 g (5 mol%) of *p*-toluene sulfonic acid were added and the mixture was stirred for 2.5 hours. After that time elapsed, the mixture was cooled to 90 °C and then stirred for 1 hour. After that it was cooled to room temperature and 3.36 g (2 mol%) of sodium bicarbonate were added along with 30 g of silica gel. 150 mL of ethyl acetate were added to the mixture and it was stirred for 1 hour. The solids were removed by filtration and washed with an additional 100 mL of ethyl acetate. The solution was then concentrated and a light yellow oil remained. The product was then purified by distillation a follows: a round bottom flask was fitted to a distillation apparatus containing a fractionating column, a reflux condenser, and a collecting flask. The system was heated to 175 °C under reduced pressure (0.5 torr) for 6 hours. After that time had elapsed, 20.0 g of *cis*-1,4-anhydroerythritol was collected (65% yield). ^{1}H NMR ($CDCl_3$): δ ppm 3.66 (dd, J = 9.6, 5.0 Hz, 2 H), 3.85 (dd, J = 9.5, 4.9 Hz, 2 H), 4.19 (br. s., 2 H), 4.23 (br. s., 2 H). ^{13}C NMR ($CDCl_3$): δ ppm 70.9, 72.3.

Synthesis of bis(2-hydroxyethyl) camphorate (BHEC)



In a 200 mL round bottom flask, 8.00 g (40 mmol) of camphoric and 50 mL of ethylene glycol (excess) were added. 12 mL of concentrated HCl were added and some solid particles formed. More ethylene glycol was added until the mixture became homogeneous. The reaction was heated at 90 °C overnight before neutralization by adding a saturated solution of NaOH in ethylene glycol until the pH of the solution was neutral. Then ethylene glycol was evaporated on a Schlenk line under reduced pressure at 120 °C. Acetone was added to the flask and the formed were removed by filtration. Acetone was evaporated and a light yellow liquid was obtained as the product (7.00 g, 61% yield). ^{1}H NMR ($CDCl_3$): δ 0.87 (s, 3 H), 1.24 (s, 3 H), 1.26 (s, 3 H), 1.53 (m, 1 H), 1.84 (m, 1 H), 2.17 (m, 1 H), 2.54 (m, 1 H), 2.85 (t, J = 9.4 Hz, 1 H), 3.83 (m, 2 H), 4.23 (m, 2 H), 4.32 (m, 2H), 4.39 (m, 2H), 4.82, (br s., 2H). ^{13}C NMR ($CDCl_3$): δ 21.5, 21.8, 22.8, 23.1, 31.1, 32.5, 47.0, 53.0, 56.5, 61.4, 64.4, 66.1, 174.6, 181.2.

Polymerizations

Polymerization apparatus

The polymerizations were conducted in a round bottom flask that was connected to a rotary evaporation bump trap affixed to a Schlenk line. With this apparatus, the by-product of condensation and volatiles (water primarily) were removed without changing the initial glassware configuration.

General work-up procedure for polymerizations

All polymers were melted to remove them from the flask and were characterized without further purification. Note: Regioirregularity is introduced because of the unsymmetrical nature of camphoric acid. This can result in additional ^{1}H and ^{13}C NMR peaks not prescribed by a regioregular structure.

Polyethylene camphorate (PEC), dual catalyst process

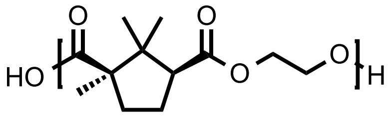


Table S1, Entry 1. 2.00 g (10 mmol) of (+)-camphoric acid was added to a 50 mL round bottom flask with a magnetic stir bar. 0.744 g (12.0 mmol) of ethylene glycol and 37 mg of zinc acetate ($Zn(OAc)_2$, 2 mol%) were added to the flask. The polymerization was conducted under melt conditions (no solvent) starting at 180 °C under nitrogen for 10 hours and then 29 mg of antimony oxide (Sb_2O_3, 1 mol%) was added. The mixture was stirred again under nitrogen for 11 hours. After that time had elapsed, the mixture was subjected to dynamic vacuum for 12 hours with a temperature gradient of 180-240 °C. A brown polymer was obtained and removed without further purification (1.70 g, 75 % yield). ^1H NMR ($CDCl_3$): δ ppm 0.79 (s, 3 H), 1.21 (s, 3 H), 1.24 (br. s., 3 H), 1.52 (m, 1 H), 1.83 (m, 1 H), 2.17 (m, 1 H), 2.55 (m, 1 H), 2.80 (m, 1 H), 4.30 (m, 4 H). ^{13}C NMR ($CDCl_3$): δ 21.3, 21.7, 22.6, 24.5, 32.5, 52.7, 53.9, 56.2, 61.3, 62.2, 173.6, 175.3.

Polyethylene camphorate (PEC)

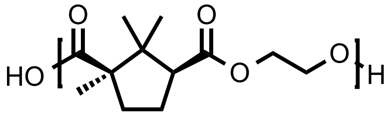


Table S1, Entry 2. 2.00 g (10 mmol) of (+)-camphoric acid were added to a 50 mL round bottom flask with a magnetic stir bar. 0.744 g (12.0 mmol) of ethylene glycol and 76 mg (4 mol%) of *p*-toluene sulfonic acid (*p*-TSA) were added to the flask. The polymerization was conducted under melt conditions (no solvent) starting at 180 °C under nitrogen for 17 hours and then subjected to dynamic vacuum for 14 hours with a temperature gradient of 180-230 °C. A light brown polymer was obtained and removed without further purification (1.90 g, 84 % yield). ^1H NMR ($CDCl_3$): δ ppm 0.79 (s, 3 H), 1.20 (s, 3 H), 1.24 (s, 3 H), 1.51 (m, 1 H), 1.83 (m, 1 H), 2.17 (m, 1 H), 2.55 (m, 1 H), 2.80 (t, J = 9.5, 1 H), 4.30 (m, 4 H). ^{13}C NMR ($CDCl_3$): δ ppm 21.0, 21.3, 22.2, 22.7, 32.2, 46.5, 54.2, 53.1, 61.5, 62.0, 173.3, 175.0.

Polypropylene camphorate

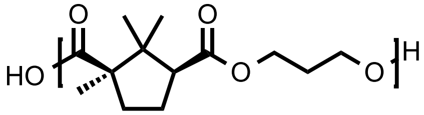


Table S1, Entry 3. 2.00 g (10 mmol) of (+)-camphoric acid were added to a 50 mL round bottom flask with a magnetic stir bar. 0.912 g (12.0 mmol) of 1,3-propanediol and 85 mg (5 mol%) of *p*-toluene sulfonic acid (*p*-TSA) were added to the flask. The polymerization was conducted under melt conditions (no solvent) starting at 180 °C under nitrogen for 17 hours and then subjected to dynamic vacuum for 14 hours with a temperature gradient of 180-230 °C. A light brown polymer was obtained and removed without further purification (1.80 g, 75 % yield). ^1H NMR ($CDCl_3$): δ 0.76 (s, 3 H), 1.19 (s, 3 H), 1.23 (m, 3 H), 1.50 (m, 1 H), 1.83 (m, 1 H), 1.99 (m, 2 H), 2.16 (m, 1 H), 2.55 (m, 1 H), 2.78 (t, J = 9.5 Hz, 1 H), 4.16 (m, 4 H). ^{13}C NMR ($CDCl_3$): δ 21.3, 21.6, 22.5, 23.0, 28.0, 32.4, 46.7, 52.8, 56.2, 60.8, 60.9, 173.8, 175.4.

Polybutylene camphorate

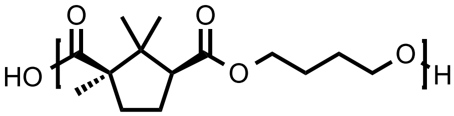


Table S1, Entry 4. 2.00 g (10 mmol) of (+)-camphoric acid were added to a 50 mL round bottom flask with a magnetic stir bar. 1.08 g (12.0 mmol) of 1,4-butanediol and 76 mg (4 mol%) of *p*-toluene sulfonic acid (*p*-TSA) were added to the flask. The polymerization was conducted under melt conditions (no solvent) starting at 180 °C under nitrogen for 17 hours and then subjected to dynamic vacuum for 14 hours with a temperature gradient of 180-230 °C. A light brown polymer was obtained and removed without further purification (1.80 g, 71 % yield). ^{1}H NMR (CDCl$_3$): δ 0.77 (s, 3 H), 1.20 (s, 3 H), 1.24 (s, 3 H), 1.50 (m, 1 H), 1.72 (br. s., 4 H), 1.83 (m, 1 H), 2.17 (m, 1 H), 2.56 (m, 1 H), 2.78 (t, *J* = 9.4 Hz, 1 H), 4.11 (m, 4 H). ^{13}C NMR (CDCl$_3$): δ 21.1, 21.4, 22.3, 22.7, 25.20, 25.22, 32.2, 46.5, 52.5, 55.9, 63.5, 173.6, 175.3.

Polypentylene camphorate

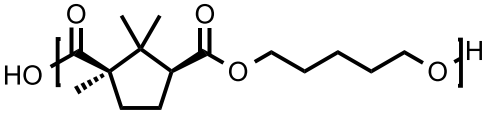


Table S1, Entry 5. 2.00 g (10 mmol) of (+)-camphoric acid were added to a 50 mL round bottom flask with a magnetic stir bar. 1.25 g (12.0 mmol) of 1,5-pentanediol and 76 mg (4 mol%) of *p*-toluene sulfonic acid (*p*-TSA) were added to the flask. The polymerization was conducted under melt conditions (no solvent) starting at 180 °C under nitrogen for 17 hours and then subjected to dynamic vacuum for 14 hours with a temperature gradient of 180-230 °C. A light brown polymer was obtained and removed without further purification (1.96 g, 73 % yield). ^{1}H NMR (CDCl$_3$): δ 0.74 (s, 3 H), 1.17 (br. s., 3 H), 1.21 (br. s., 3 H), 1.43 (m, 2H), 1.46 (m, 1 H), 1.65 (br. s., 4 H), 1.79 (m, 1 H), 2.15 (m, 1 H), 2.54 (m, 1 H), 2.75 (t, *J* = 9.5 Hz, 1 H), 4.05 (m, 4 H). ^{13}C NMR (CDCl$_3$): δ 21.2, 21.6, 22.4, 22.6, 22.9, 28.1, 28.2, 32.4, 46.6, 52.8, 56.1, 64.1, 173.9, 175.6.

Polyhexylene camphorate

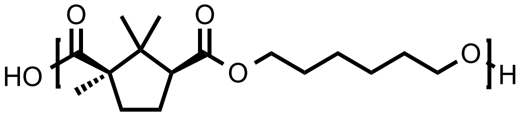


Table S1, Entry 6. 2.00 g (10 mmol) of (+)-camphoric acid were added to a 50 mL round bottom flask with a magnetic stir bar. 1.42 g (12.0 mmol) of 1,6-hexanediol and 76 mg (4 mol%) of *p*-toluene sulfonic acid (*p*-TSA) were added to the flask. The polymerization was conducted under melt conditions (no solvent) starting at 180 °C under nitrogen for 17 hours and then subjected to dynamic vacuum for 14 hours with a temperature gradient of 180-230 °C. A light brown polymer was obtained and removed without further purification (2.70 g, 96 % yield). ^{1}H NMR (CDCl$_3$): δ 0.78 (s, 3 H), 1.20 (s, 3 H), 1.25 (s, 3 H), 1.40 (m, 4 H), 1.50 (m, 1 H), 1.65 (m, 4 H), 1.83 (m, 1 H), 2.18 (m, 1 H), 2.56 (m, 1 H), 2.78 (t, *J* = 9.40 Hz, 1 H), 4.07 (m, 4 H). ^{13}C (CDCl$_3$): δ 21.3, 21.7, 22.6, 23.0, 25.7, 28.5, 32.5, 46.7, 52.9, 56.2, 64.3, 173.9, 175.7.

Polyerythritan camphorate

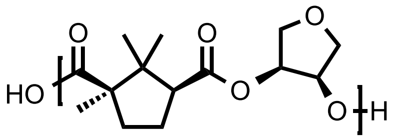


Table S1, Entry 7. 2.00 g (10 mmol) of (+)-camphoric acid were added to a 50 mL round bottom flask with a magnetic stir bar. 1.25 g (12.0 mmol) of *cis*-1,4-anhydroerythritol (Erythritan) and 37 mg of zinc acetate ($Zn(OAc)_2$, 2 mol%) were added to the flask. The polymerization was conducted under melt conditions (no solvent) starting at 180 °C under nitrogen for 10 hours and then 29 mg of antimony oxide (Sb_2O_3, 1 mol%) was added. The mixture was stirred again under nitrogen for 11 hours. After that time had elapsed, the mixture was subjected to dynamic vacuum for 12 hours with a temperature gradient of 180-240 °C. A brown polymer was obtained and removed without further purification (1.95 g, 73 % yield). ^1H NMR ($CDCl_3$): δ 0.82 (m, 3 H), 1.06 (m, 3 H), 1.21 (m, 3 H), 1.53 (m, 1 H), 1.65 (m, 1 H), 1.85 (m, 1 H), 2.17 (m, 1 H), 2.54 (m, 1 H), 2.82 (t, *J* = 9.3 Hz, 1 H), 3.82 (m, 2 H), 4.10 (m, 2 H), 5.17 (br. s., 2 H). ^{13}C NMR ($CDCl_3$): δ 18.7, 21.3, 22.8, 24.2, 24.6, 32.1, 33.9, 46.7, 47.2, 52.2, 53.5, 56.2, 71.6, 172.5, 174.2.

Polyisosorbide camphorate

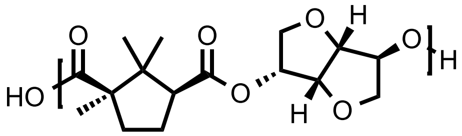
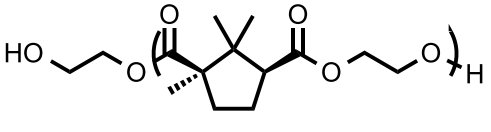


Table S1, Entry 8. 1.50 g (7.5 mmol) of (+)-camphoric acid were added to a 50 mL round bottom flask with a magnetic stir bar. 1.31 g (9.0 mmol) of isosorbide and 57 mg (4 mol%) of *p*-toluene sulfonic acid (*p*-TSA) were added to the flask. The polymerization was conducted under melt conditions (no solvent) starting at 180 °C under nitrogen for 17 hours and then subjected to dynamic vacuum for 14 hours with a temperature gradient of 180-240 °C. A light brown polymer was obtained and removed without further purification (2.29 g, 98 % yield). ^1H NMR ($CDCl_3$): δ 0.86 (m, 3H), 1.18 (m, 3 H), 1.23 (m, 3 H), 1.55 (m, 1 H), 1.84 (m, 1 H), 2.17 (m, 1 H), 2.56 (m, 1 H), 2.80 (m, 1 H), 3.78 (m, 1 H), 3.96 (m, 4 H), 4.49 (m, 1 H), 4.83 (m, 1 H), 5.15 (m, 1 H). ^{13}C NMR ($CDCl_3$): δ 19.3, 22.6, 25.0, 32.5, 34.4, 47.0, 47.7, 52.8, 56.5, 70.6, 73.4, 74.1, 78.2, 81.0, 86.2, 173.6, 175.1.

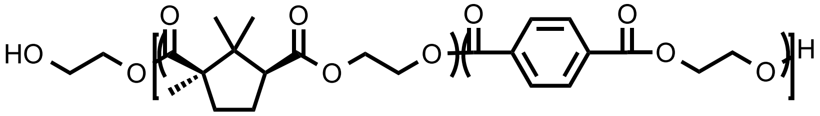
Copolymerization of bis(2-hydroxyethyl) camphorate (BHEC) and bis(2-hydroxyethyl) terephthalate (BHET)

Synthesis of polyethylene camphorate (PEC) (Table S2, Entry 1)



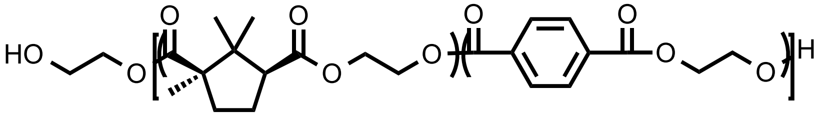
In a 50 mL round bottom flask, 1.00 g (3.47 mmol) of bis(2-hydroxyethyl) camphorate was added to 10 mg (1 mol%) of antimony oxide and a magnetic stir bar. The mixture was stirred from 175 to 240 °C under vacuum on a Schlenk line for 7 hours. After that time had elapsed, a viscous light brown polymer was obtained and removed without further purification (0.66 g, 84% yield). ^{1}H NMR (CDCl$_3$): δ 0.80 (s, 3 H), 1.22 (s, 3 H), 1.26 (s, 3 H), 1.55 (m, 1 H), 1.85 (m, 1 H), 2.18 (m, 1 H), 2.57 (m, 1 H), 2.81 (t, J = 9.5 Hz, 1 H), 4.31 (m, 4 H). ^{13}C NMR (CDCl$_3$): δ 21.0, 21.4, 22.3, 22.7, 24.3, 32.2, 46.5, 52.4, 55.9, 61.9, 173.3, 175.0.

Synthesis of poly[bis(2-hydroxyethyl) camphorate-*co*-bis(2-hydroxyethyl) terephthalate] 90% BHEC/10% BHET (Table S2, Entry 2)



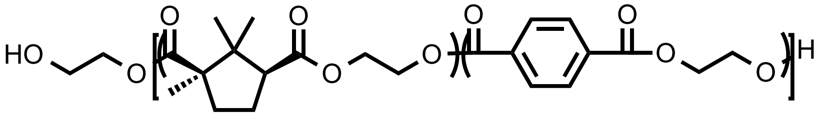
In a 50 mL round bottom flask, 765 mg (2.64 mmol) of bis(2-hydroxyethyl) camphorate were added to 75 mg (0.30 mmol) of bis(2-hydroxyethyl) terephthalate and 17 mg (2 mol%) of antimony oxide with a magnetic stir bar. The mixture was stirred from 200 to 240 °C under vacuum on a Schlenk line for 7 hours. After that time had elapsed, a viscous light brown polymer was obtained and removed without further purification (0.42 g, 64% yield). ^{1}H NMR (CDCl$_3$): δ 0.79 (s, 3 H), 1.21 (s, 3 H), 1.25 (s, 3 H), 1.52 (m, 1 H), 1.82 (m, 1 H), 2.17 (m, 1 H), 2.56 (m, 1 H), 2.80 (t, J = 9.3 Hz, 1 H), 4.30 (br. s., 4 H), 4.45 (br. s.), 4.57 (br. s.), 4.70 (br. s.), 8.10 (s). ^{13}C NMR (CDCl$_3$): δ 20.2, 21.3, 21.6, 22.5, 22.9, 24.5, 32.4, 34.2, 46.8, 47.2, 52.7, 53.8, 56.2, 56.5, 62.2, 129.6, 161.8, 163.2, 173.5, 175.2.

Synthesis of poly[bis(2-hydroxyethyl) camphorate-*co*-bis(2-hydroxyethyl) terephthalate] 80% BHEC/20% BHET (Table S2, Entry 3)



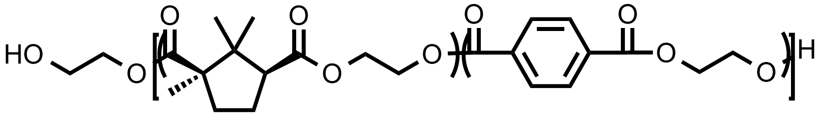
In a 50 mL round bottom flask, 1.13 g (3.93 mmol) of bis(2-hydroxyethyl) camphorate were added to 250 mg (0.983 mmol) of bis(2-hydroxyethyl) terephthalate and 28 mg (2 mol%) of antimony oxide with a magnetic stir bar. The mixture was stirred from 200 to 240 °C under vacuum on a Schlenk line for 7 hours. After that time had elapsed, a viscous light brown polymer was obtained and removed without further purification (0.80 g, 74% yield). ^{1}H NMR (CDCl$_3$): δ 0.88 (m, 3 H), 1.20 (m, 3 H), 1.24 (s, 3 H), 1.51 (m, 1 H), 1.82 (m, 1 H), 2.17 (m, 1 H), 2.56 (m, 1 H), 2.80 (m, 1 H), 4.30 (br. s., 4 H), 4.44 (br. s.), 4.56 (br. s.), 4.70 (br. s.), 8.09 (m). ^{13}C NMR (CDCl$_3$): δ 19.1, 20.2, 21.3, 21.6, 22.5, 22.9, 24.5, 32.4, 34.1, 46.8, 52.7, 53.8, 56.2, 61.9, 62.2, 63.0, 76.7, 77.3, 129.6, 133.7, 161.8, 162.5, 173.5, 175.2.

Synthesis of poly[bis(2-hydroxyethyl) camphorate-*co*-bis(2-hydroxyethyl) terephthalate] 70% BHEC/30% BHET (Table S2, Entry 4)



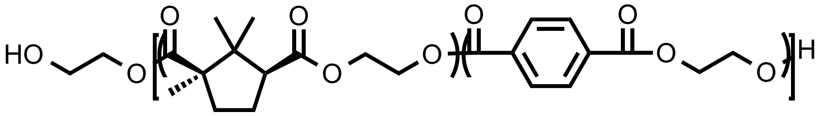
In a 50 mL round bottom flask, 1.06 g (3.67 mmol) of bis(2-hydroxyethyl) camphorate were added to 400 mg (1.57 mmol) of bis(2-hydroxyethyl) terephthalate and 15 mg (1 mol%) of antimony oxide with a magnetic stir bar. The mixture was stirred from 200 to 240 °C under vacuum on a Schlenk line for 7 hours. After that time had elapsed, a viscous light brown polymer was obtained and removed without further purification (0.97 g, 86% yield). ^{1}H NMR ($CDCl_3$): δ 0.78 (s, 3 H), 1.20 (s, 3 H), 1.24 (s, 3 H), 1.51 (m, 1 H), 1.82 (m, 1 H), 2.17 (m, 2 H), 2.56 (m, 1 H), 2.80 (m, 1 H), 4.30 (m, 4 H), 4.44 (br. s.), 4.56 (br. s.), 4.70 (br. s.), 8.09 (m). ^{13}C ($CDCl_3$): δ 20.2, 21.3, 21.6, 22.5, 22.9, 24.5, 32.4, 34.1, 46.8, 52.7, 53.8, 56.2, 61.9, 62.1, 63.0, 63.2, 129.6, 133.7, 142.1, 162.5, 165.4, 175.2, 176.7.

Synthesis of poly[bis(2-hydroxyethyl) camphorate-*co*-bis(2-hydroxyethyl) terephthalate] 60% BHEC/40% BHET (Table S2, Entry 5)



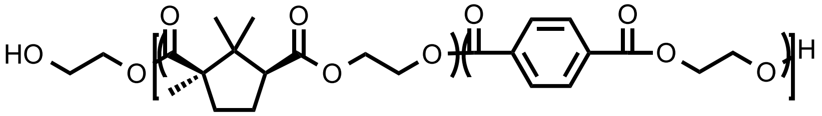
In a 50 mL round bottom flask, 700 mg (2.42 mmol) of bis(2-hydroxyethyl) camphorate were added to 412 mg (1.62 mmol) of bis(2-hydroxyethyl) terephthalate and 12 mg (1 mol%) of antimony oxide with a magnetic stir bar. The mixture was stirred from 200 to 240 °C under vacuum on a Schlenk line for 7 hours. After that time had elapsed, a viscous light brown polymer was obtained and removed without further purification (0.71 g, 83% yield). ^{1}H NMR ($CDCl_3$): δ 0.78 (s, 3 H), 1.20 (s, 3 H), 1.23 (s, 3 H), 1.51 (m, 1 H), 1.82 (m, 1 H), 2.17 (m, 1 H), 2.56 (m, 1 H), 2.83 (m, 1 H), 4.29 (br. s., 4 H), 4.44 (br. s.), 4.56 (br. s.), 4.70 (br. s.), 8.11 (s). ^{13}C NMR ($CDCl_3$): δ 19.2, 20.2, 21.3, 21.6, 22.8, 22.9, 24.5, 32.4, 34.2, 46.8, 52.7, 56.2, 61.9, 63.0,129.7, 133.7, 142.8, 143.5, 162.5, 165.4.

Synthesis of poly[bis(2-hydroxyethyl) camphorate-*co*-bis(2-hydroxyethyl) terephthalate] 50% BHEC/50% BHET (Table S2, Entry 6)



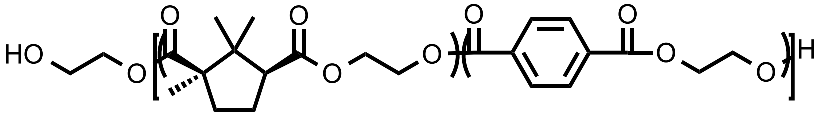
In a 50 mL round bottom flask, 1.50 g (5.2 mmol) of bis(2-hydroxyethyl) camphorate were added to 1.32 g (5.2 mmol) of bis(2-hydroxyethyl) terephthalate and 30 mg (2 mol%) of antimony oxide with a magnetic stir bar. The mixture was stirred from 200 to 240 °C under vacuum on a Schlenk line for 7 hours. After that time had elapsed, a viscous light brown polymer was obtained and removed without further purification (2.07 g, 95% yield). ^{1}H NMR ($CDCl_3$): δ 0.78 (br. s., 3 H), 1.20 (br. s., 3 H), 1.23 (br. s., 3 H), 1.51 (m, 1 H), 1.82 (m, 1 H), 2.17 (m, 1 H), 2.56 (m, 1 H), 2.82 (m, 1 H), 4.29 (br. s., 4 H), 4.43 (br. s.), 4.56 (m), 4.70 (br. s.), 8.11 (br. s.). ^{13}C NMR ($CDCl_3$): δ 18.8, 19.8, 21.0, 21.4, 22.2, 22.6, 24.3, 32.2, 33.9, 46.6, 52.4, 53.6, 56.0, 61.7, 62.8, 129.5, 133.4, 161.6, 162.3, 165.2, 175.0.

Synthesis of poly[bis(2-hydroxyethyl) camphorate-*co*-bis(2-hydroxyethyl) terephthalate] 40% BHEC/60% BHET (Table S2, Entry 7)



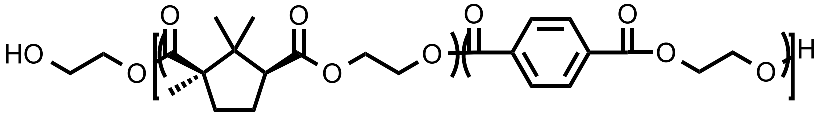
In a 50 mL round bottom flask, 1.00 g (3.47 mmol) of bis(2-hydroxyethyl) camphorate was added to 1.32 g (5.2 mmol) of bis(2-hydroxyethyl) terephthalate and 25 mg (2 mol%) of antimony oxide with a magnetic stir bar. The mixture was stirred from 200 to 240 °C under vacuum on a Schlenk line for 7 hours. After that time had elapsed, a viscous light brown polymer was obtained and removed without further purification (1.60 g, 90% isolated yield). ^{1}H NMR ($CDCl_3$): δ 0.77 (br. s., 3 H), 1.19 (br. s., 3 H), 1.23 (br. s., 3 H), 1.49 (m, 1 H), 1.80 (m, 1 H), 2.17 (m, 1 H), 2.57 (m, 1 H), 2.82 (m, 1 H), 4.28 (br. s., 4 H), 4.43 (m), 4.55 (br. s.), 4.69 (s), 8.10 (m). ^{13}C NMR ($CDCl_3$): δ 18.6, 19.9, 21.0, 21.3, 22.3, 22.6, 24.2, 32.2, 33.9, 46.6, 52.4, 53.6, 56.0, 61.7, 62.7, 129.5, 133.4, 162.4, 165.2.

Synthesis of poly[bis(2-hydroxyethyl) camphorate-*co*-bis(2-hydroxyethyl) terephthalate] 30% BHEC/70% BHET (Table S2, Entry 8)



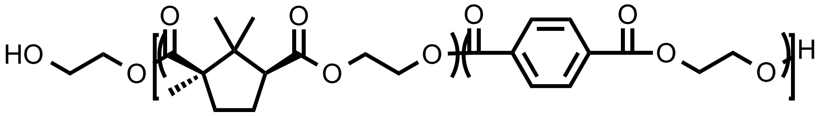
In a 50 mL round bottom flask, 750 mg (2.60 mmol) of bis(2-hydroxyethyl) camphorate were added to 1.54 g (6.06 mmol) of bis(2-hydroxyethyl) terephthalate and 25 mg (2 mol%) of antimony oxide with a magnetic stir bar. The mixture was stirred from 200 to 240 °C under vacuum on a Schlenk line for 7 hours. After that time had elapsed, a viscous light brown polymer was obtained and removed without further purification (1.70 g, 97% isolated yield). ^{1}H NMR ($CDCl_3$): δ 0.77 (br. s., 3 H), 1.19 (br. s., 3 H), 1.22 (br. s., 3 H), 1.50 (m, 1 H), 1.82 (m, 1 H), 2.17 (m, 1 H), 2.53 (m, 1 H), 2.80 (m, 1 H), 4.28 (m, 4 H), 4.42 (m), 4.55 (m), 4.69 (br. s.), 8.10 (m). ^{13}C NMR ($CDCl_3$ and TFA-*d*): δ 22.3, 23.6, 25.4, 33.4, 48.7, 49.2, 54.2, 57.8, 64.2, 65.0, 70.3, 131.2, 134.6, 168.7.

Synthesis of poly[bis(2-hydroxyethyl) camphorate-*co*-bis(2-hydroxyethyl) terephthalate] 20% BHEC/80% BHET (Table S2, Entry 9)



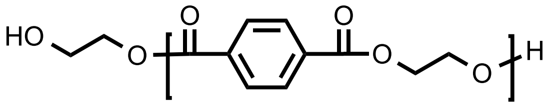
In a 50 mL round bottom flask, 750 mg (2.60 mmol) of bis(2-hydroxyethyl) camphorate were added to 2.65 g (10.43 mmol) of bis(2-hydroxyethyl) terephthalate and 38 mg (1 mol%) of antimony oxide with a magnetic stir bar. The mixture was stirred from 200 to 240 °C under vacuum on a Schlenk line for 7 hours. After that time had elapsed, a viscous light brown polymer was obtained and removed without further purification (2.59 g, 99% isolated yield). ^{1}H NMR ($CDCl_3$ and TFA-*d*): δ 0.77 (br. s., 3 H), 1.19 (s, 3 H), 1.22 (s, 3 H), 1.51 (m, 1 H), 1.81 (m, 1 H), 2.17 (m, 1 H), 2.55 (m, 1 H), 2.82 (m, 1 H), 4.28 (m, 4 H), 4.51 (m), 4.55 (m), 4.69 (br. s.), 8.10 (m). ^{13}C ($CDCl_3$ and TFA-*d*): δ 22.5, 23.7, 26.8, 31.2, 34.8, 66.5, 67.2, 71.7, 132.6, 132.7, 136.0, 170.2.

Synthesis of poly[bis(2-hydroxyethyl) camphorate-*co*-bis(2-hydroxyethyl) terephthalate] 10% BHEC/90% BHET (Table S2, Entry 10)



In a 50 mL round bottom flask, 400 mg (1.39 mmol) of bis(2-hydroxyethyl) camphorate were added to 3.17 g (12.48 mmol) of bis(2-hydroxyethyl) terephthalate and 40 mg (1 mol%) of antimony oxide with a magnetic stir bar. The mixture was stirred from 200 to 240 °C under vacuum on a Schlenk line for 7 hours. After that time had elapsed, a viscous light brown polymer was obtained and removed without further purification (2.83 g, 99% yield). ^{1}H NMR ($CDCl_3$ and TFA-*d*): δ 0.81 (s), 1.19 (s), 1.23 (s), 1.58 (m), 1.89 (m), 2.17 (m), 2.54 (m), 2.94 (m), 4.12 (s), 4.54 – 4.80 (m, 4 H), 8.13 (m, 4 H). ^{13}C NMR ($CDCl_3$ and TFA-*d*): δ 13.4, 43.9, 46.8, 51.9, 66.5, 67.2, 71.7, 132.6, 132.7, 136.0, 170.2.

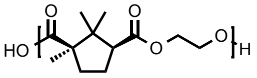
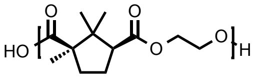
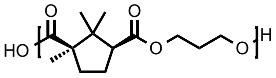
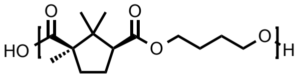
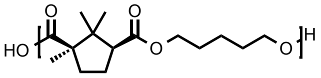
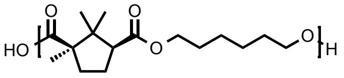
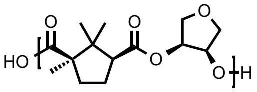
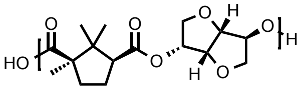
Synthesis of poly[bis(2-hydroxyethyl) terephthalate] (PET) (Table S2, Entry 11)



In a 50 mL round bottom flask, 2.00 g (7.87 mmol) of bis(2-hydroxyethyl) terephthalate, 23 mg (1 mol%) of antimony oxide, and a magnetic stir bar were combined. The mixture was stirred from 200 to 240 °C under vacuum on a Schlenk line for 7 hours. After that time had elapsed, a viscous light brown polymer was obtained and removed without further purification (1.73 g, 99% yield). ^{1}H NMR ($CDCl_3$ and TFA-*d*): δ 4.83 (s, 4 H), 8.17 (m, 4 H). ^{13}C NMR ($CDCl_3$ and TFA-*d*): δ 65.2, 131.3, 134.6, 169.3.

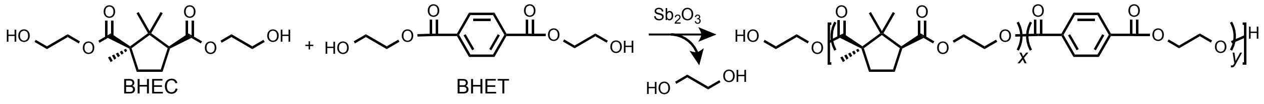
Summary of Polymerization Data

Table S1 Polymerization and characterization of polyalkylene camphorates from linear diols (entries 1–6) and camphorate polyesters derived from erythritan (Entry 7) and isosorbide (Entry 8)[a]

Entry	Polymer from camphoric acid + diol	Catalyst	Yield (%)	M_n[b] (Da)	M_w[b] (Da)	Đ[b]	T_g[c] (°C)	T_5[d] (°C)
1		$Zn(OAc)_2 + Sb_2O_3$	75	18,700	75,700	4.0	51	331
2		*p*-TSA	84	20,200	60,800	3.0	44	368
3		*p*-TSA	75	7,700	22,800	3.0	38	326
4		*p*-TSA	71	7,300	19,600	2.7	25	322
5		*p*-TSA	73	8,300	24,500	2.9	–1	352
6		*p*-TSA	96	8,000	35,800	4.4	–16	353
7		$Zn(OAc)_2 + Sb_2O_3$	73	9,000	25,000	2.8	100	304
8		*p*-TSA	98	6,900	42,000	6.1	125	355

[a] Polymerization conducted at 180 °C under nitrogen for 16 hours, followed by a temperature ramp over 12 hours to 230 °C under dynamic vacuum. [b] Gel permeation chromatography (GPC) in hexafluoroisopropanol (HFIP) at 40 °C *vs* polymethylmethacrylate standards. [c] Determined by DSC. [d] Temperature at which 5% mass loss was observed, determined by thermogravimetric analysis (TGA).

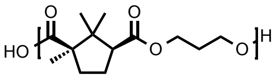
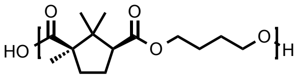
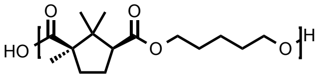
Table S2 Copolymerization of bis(hydroxyethyl) camphorate (BHEC, from camphoric acid) and bis(hydroxyethyl) terephthalate (BHET, from terephthalic acid) [a]



Entry	BHEC % Feed	BHEC % Incorporation [b]	Yield (%)	M_n[c] (Da)	M_w[c] (Da)	Đ[c]	T_g[d] (°C)	T_m[d] (°C)	T_5[e] (°C)
1	100	100.0	84	23,800	54,400	2.3	41	n.o.	343
2	90	82.9	64	13,300	34,100	2.6	42	n.o.	335
3	80	65.8	74	14,600	42,700	2.9	50	n.o.	344
4	70	52.7	86	17,300	56,600	3.3	46	n.o.	344
5	60	34.0	83	19,500	54,600	2.8	52	n.o.	342
6	50	31.6	95	21,300	59,200	2.7	54	n.o.	345
7	40	22.2	90	14,800	38,300	2.6	54	n.o.	351
8	30	19.8	97	13,700	33,100	2.4	59	180	352
9	20	12.3	99	16,800	42,200	2.5	64	193	348
10	10	7.6	99	22,300	55,900	2.5	66	209	361
11	0	0.0	99	19,800	55,100	2.8	71	229	371

[a] Polymerization conducted from 190 to 230 °C under dynamic vacuum with antimony oxide as a catalyst (Sb_2O_3, 1–2 mol%). [b] BHEC and BHET % incorporation determined by ^{1}H NMR by integrating the 1-methyl group of the camphoric acid ring (0.77 ppm) versus the aromatic protons (near 8.1 ppm). [c] Gel Permeation Chromatography (GPC) in hexafluoroisopropanol (HFIP) at 40 °C *vs* polymethylmethacrylate standards. [d] Determined by DSC; n.o. = not observed. [e] Temperature at which 5% mass loss was observed under nitrogen, determined by TGA.

Table S3 Summary of GPC results for polyalkylene camphorates with longer diols (*n* = 3,4,5) made via the dual catalyst technique [a]

Entry	Polymers	Catalysts	M_n [b] (Da)	M_w [b] (Da)	*Đ* [b]
1		$Zn(OAC)_2$ Sb_2O_3	4,200	13,600	3.2
2		$Zn(OAC)_2$ Sb_2O_3	4,600	16,700	3.6
3		$Zn(OAC)_2$ Sb_2O_3	2,800	7,200	2.6

[a] Polymerizations conducted at 180 °C under nitrogen for 16 hours, followed by a temperature ramp over 12 hours to 230 °C under dynamic vacuum. Catalysts: $Zn(OAC)_2$ (2 mol%) and Sb_2O_3 (1 mol%, added after first stage) for each entry. [b] Gel Permeation Chromatography (GPC) in hexafluoroisopropanol (HFIP) at 40 °C *vs* polymethylmethacrylate standards.

Gel Permeation Chromatography (GPC) Chromatograms

Molecular Weight Averages

Peak	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
Peak 1	33423	18734	75686	2595587	43207013	1178641	4.04

Peak information

	Start (mins)	End (mins)
Baseline region 1	6.36	7.95
Baseline region 2	32.68	34.77
Peak 1	10.77	21.54

Peak	Trace	Peak Max RT (mins)	Peak Area (mV.s)	Peak Height (mV)
Peak 1	RI	17.88	5571988.311	24698.669

Chromatogram

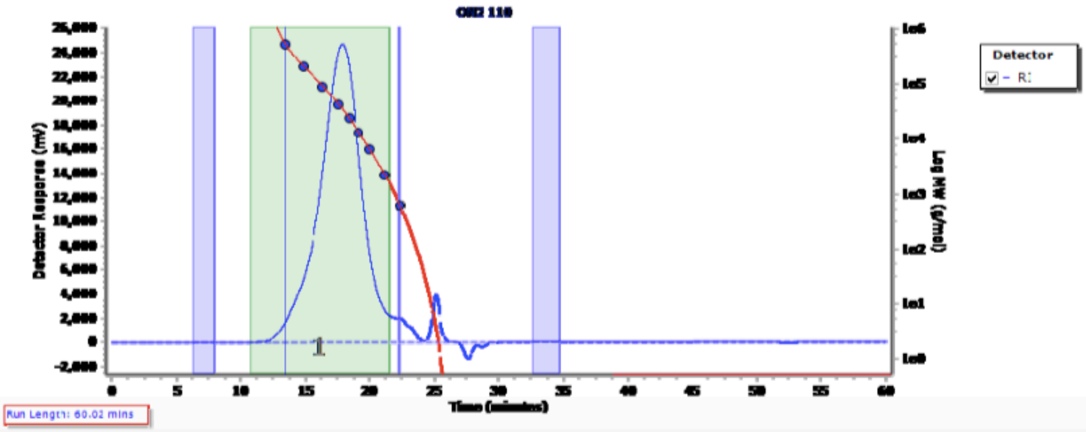


Figure S1. GPC chromatogram for polyethylene camphorate (Table S1, Entry 1)

Molecular Weight Averages

Peak	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
Peak 1	34549	20182	60835	141591	238487	128204	3.014

Peak information

	Start (mins)	End (mins)
Baseline region 1	2.89	5.71
Baseline region 2	31.52	34.99
Peak 1	13.52	21.33

Peak	Trace	Peak Max RT (mins)	Peak Area (mV.s)	Peak Height (mV)
Peak 1	RI	17.83	8914449.939	41052.699

Chromatogram

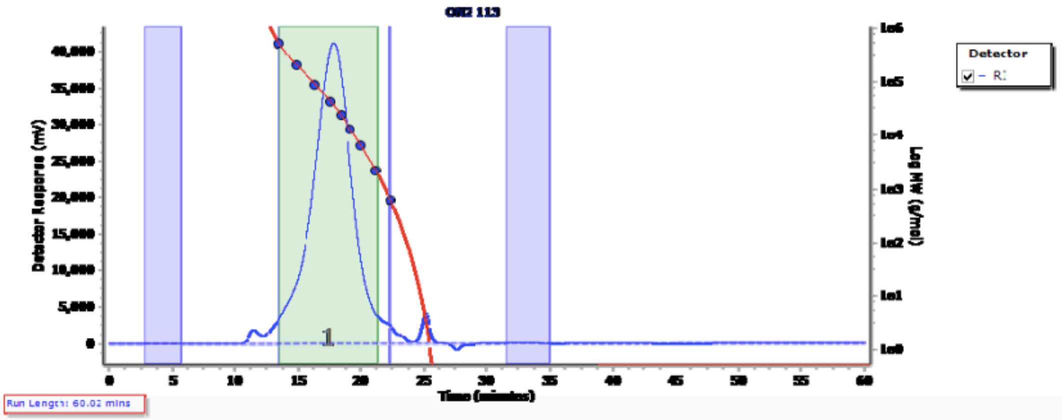


Figure S2. GPC chromatogram for polyethylene camphorate [dual catalyst] (Table S1, Entry 2)

Molecular Weight Averages

Peak	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
Peak 1	15303	7672	22836	45614	68942	42202	2.977

Peak information

	Start (mins)	End (mins)
Baseline region 1	2.53	4.84
Baseline region 2	39.54	42.94
Peak 1	15.62	22.84

Peak	Trace	Peak Max RT (mins)	Peak Area (mV.s)	Peak Height (mV)
Peak 1	RI	18.91	9565854.948	51966.887

Chromatogram

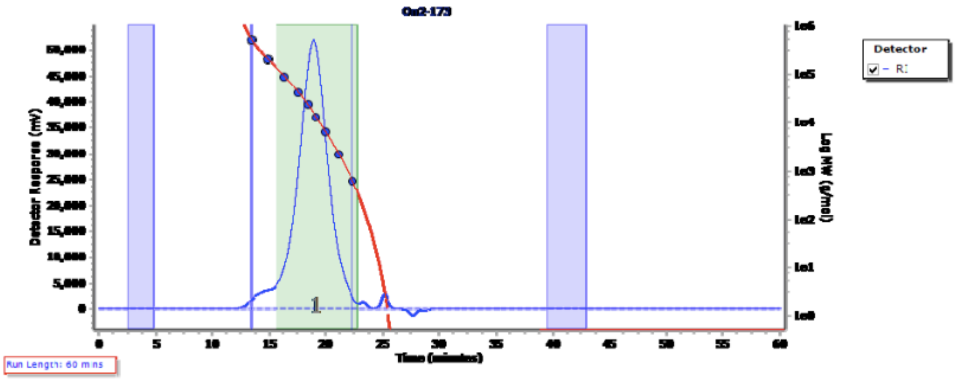


Figure S3. GPC chromatogram for polypropylene camphorate (Table S1, Entry 3)

Molecular Weight Averages

Peak	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
Peak 1	15966	7276	19591	36942	61369	34049	2.693

Peak information

	Start (mins)	End (mins)
Baseline region 1	7.01	9.83
Baseline region 2	40.78	44.61
Peak 1	14.75	22.56

Peak	Trace	Peak Max RT (mins)	Peak Area (mV.s)	Peak Height (mV)
Peak 1	RI	18.86	3800695.504	22274.507

Chromatogram

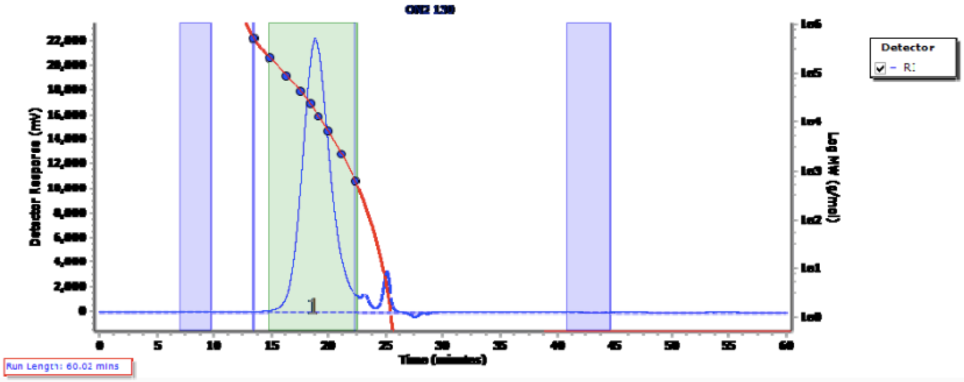


Figure S4. GPC chromatogram for polybutylene camphorate (Table S1, Entry 4)

Molecular Weight Averages

Peak	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
Peak 1	337533	394744	549997	895012	1417430	828174	1.393
Peak 2	19625	8322	24481	43854	62744	41102	2.942

Peak information

	Start (mins)	End (mins)
Baseline region 1	3.61	5.78
Baseline region 2	39.19	43.02
Peak 1	12.07	14.75
Peak 2	15.62	22.70

Peak	Trace	Peak Max RT (mins)	Peak Area (mV.s)	Peak Height (mV)
Peak 1	RI	14.02	132513.496	1220.053
Peak 2	RI	18.60	5805399.642	32114.002

Chromatogram

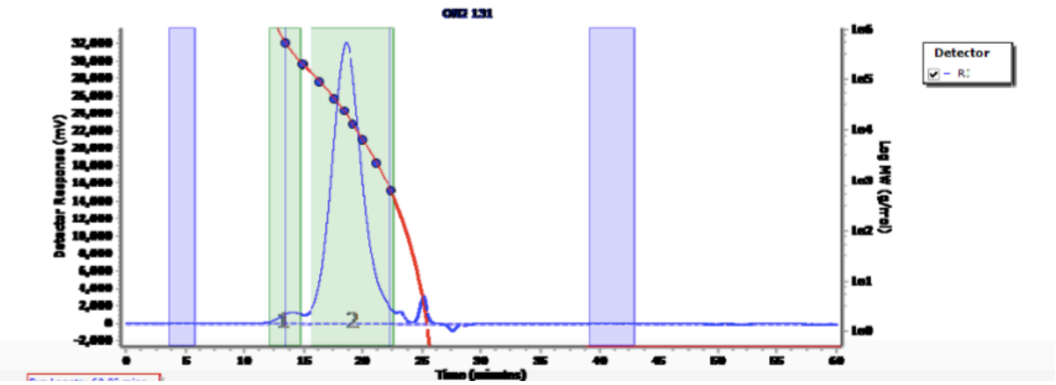


Figure S5. GPC chromatogram for polypentylene camphorate (Table S1, Entry 5)

Molecular Weight Averages

Peak	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
Peak 1	18300	8039	35839	127228	312759	107375	4.458

Peak information

	Start (mins)	End (mins)
Baseline region 1	2.82	5.64
Baseline region 2	41.21	45.04
Peak 1	12.87	22.85

Peak	Trace	Peak Max RT (mins)	Peak Area (mV.s)	Peak Height (mV)
Peak 1	RI	18.69	12027287.363	60340.880

Chromatogram

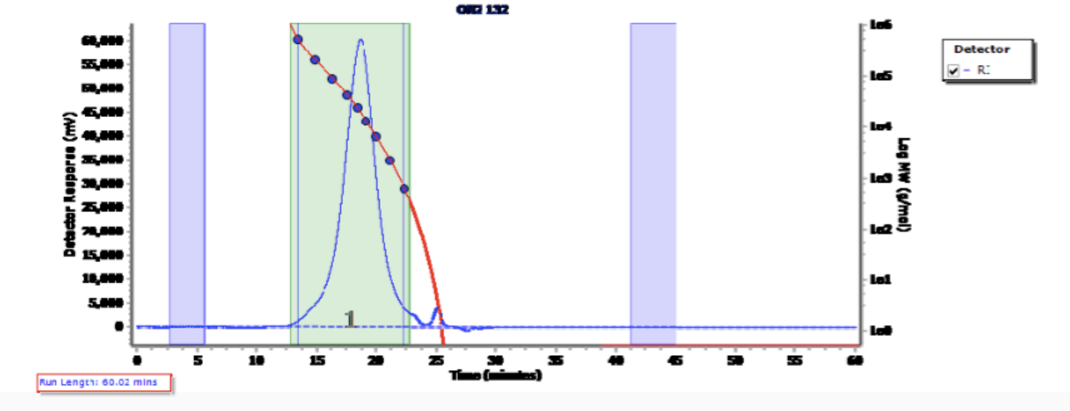


Figure S6. GPC chromatogram for polyhexylene camphorate (Table S1, Entry 6)

Molecular Weight Averages

Peak	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
Peak 1	11281	8955	24980	61234	100475	55561	2.79

Peak information

	Start (mins)	End (mins)
Baseline region 1	10.63	10.96
Baseline region 2	24.37	25.32
Peak 1	11.07	16.78

Peak	Trace	Peak Max RT (mins)	Peak Area (mV.s)	Peak Height (mV)
Peak 1	RI	14.49	872567.737	4674.660

Chromatogram

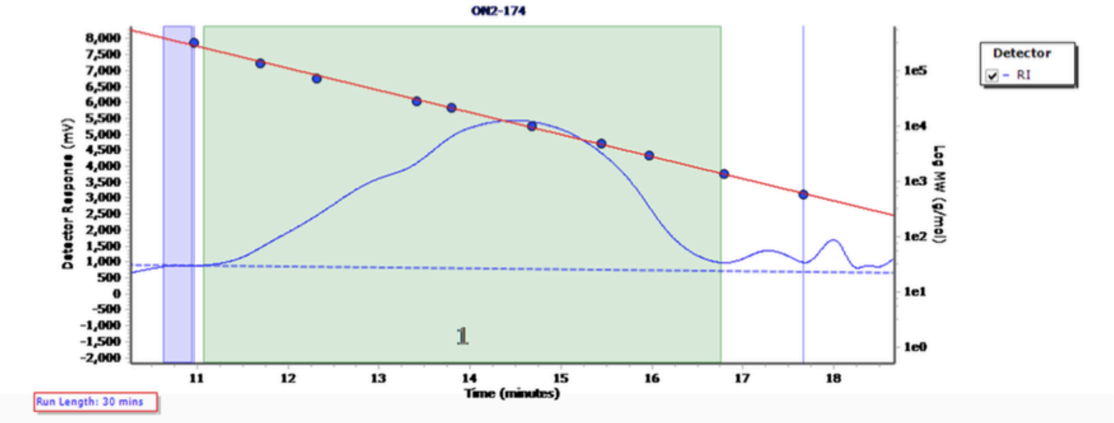


Figure S7. GPC chromatogram for polyerythritan camphorate (Table S1, Entry 7)

Molecular Weight Averages

Peak	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
Peak 1	0	0	0	0	0	1294691009	0
Peak 2	12820	6895	41985	284184	792958	225902	6.089

Peak information

	Start (mins)	End (mins)
Baseline region 1	2.46	4.89
Baseline region 2	29.36	29.90
Peak 1	10.82	12.40
Peak 2	12.90	22.90

Peak	Trace	Peak Max RT (mins)	Peak Area (mV.s)	Peak Height (mV)
Peak 1	RI	11.47	94872.818	1590.176
Peak 2	RI	19.27	5906724.619	25914.309

Chromatogram

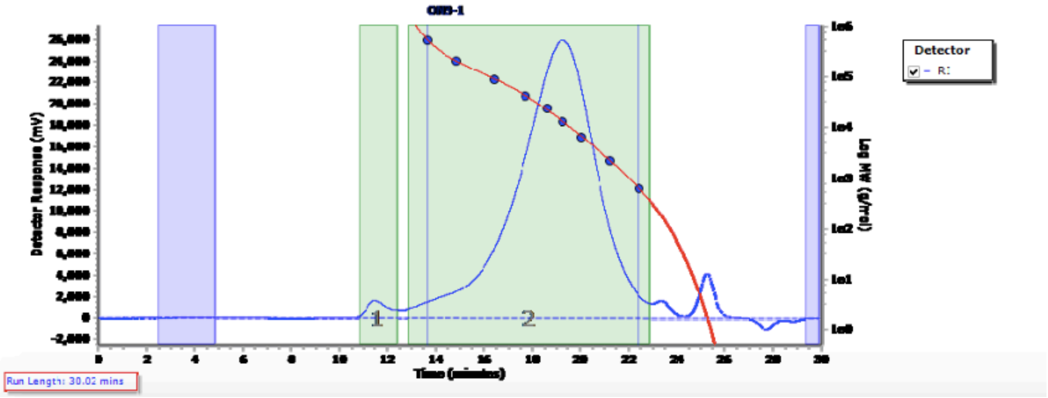


Figure S8. GPC chromatogram for polyisosorbide camphorate (Table S1, Entry 8)

Molecular Weight Averages

Peak	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
Peak 1	43026	23774	54425	95970	152313	89186	2.289

Peak information

	Start (mins)	End (mins)
Baseline region 1	1.66	6.94
Baseline region 2	38.61	43.09
Peak 1	13.16	21.18

Peak	Trace	Peak Max RT (mins)	Peak Area (mV.s)	Peak Height (mV)
Peak 1	RI	17.52	6922030.894	36419.349

Chromatogram

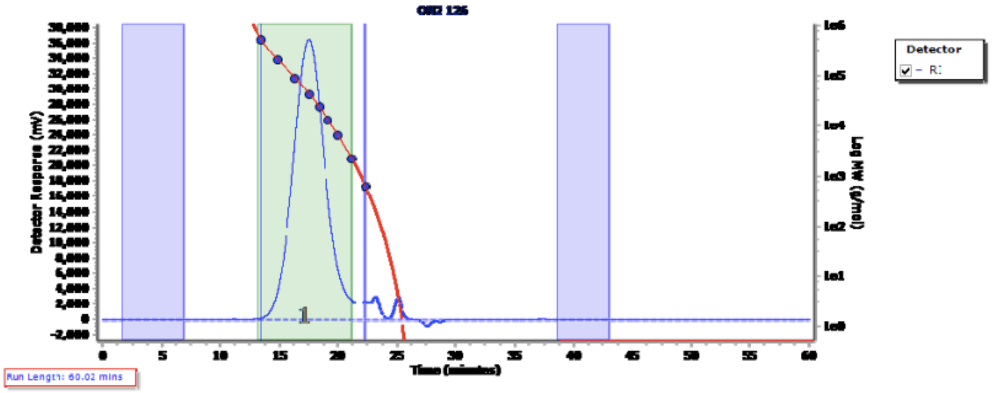


Figure S9. GPC chromatogram for polyBHEC (Table S2, Entry 1)

Molecular Weight Averages

Peak	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
Peak 1	27845	13291	34087	57652	81274	54303	2.565

Peak information

	Start (mins)	End (mins)
Baseline region 1	1.37	3.13
Baseline region 2	28.13	29.79
Peak 1	14.70	22.08

Peak	Trace	Peak Max RT (mins)	Peak Area (mV.s)	Peak Height (mV)
Peak 1	RI	18.30	10117318.130	56556.364

Chromatogram

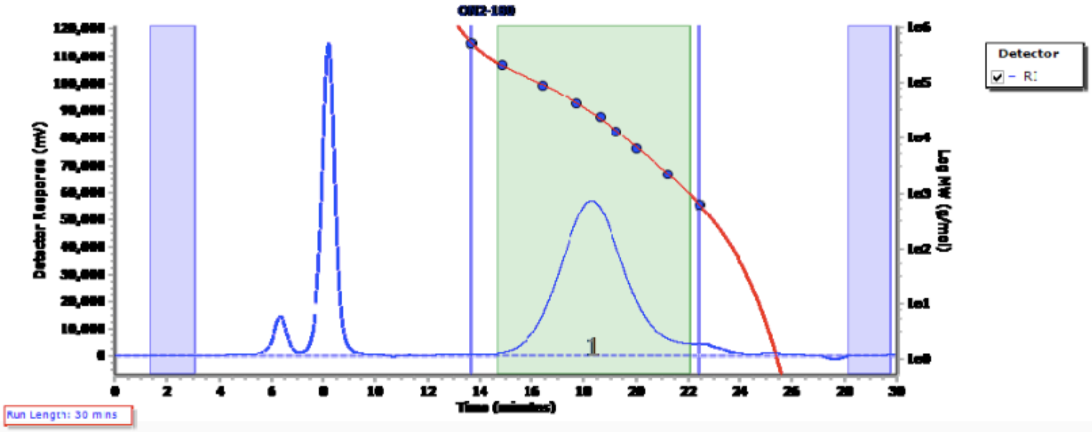


Figure S10. GPC chromatogram for poly(BHEC/BHET) with 90% BHEC (Table S2, Entry 2)

Molecular Weight Averages

Peak	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
Peak 1	30227	14578	42709	99183	240605	87116	2.93

Peak information

	Start (mins)	End (mins)
Baseline region 1	1.01	2.75
Baseline region 2	39.76	43.52
Peak 1	12.65	21.98

Peak	Trace	Peak Max RT (mins)	Peak Area (mV.s)	Peak Height (mV)
Peak 1	RI	18.02	4895734.712	25004.820

Chromatogram

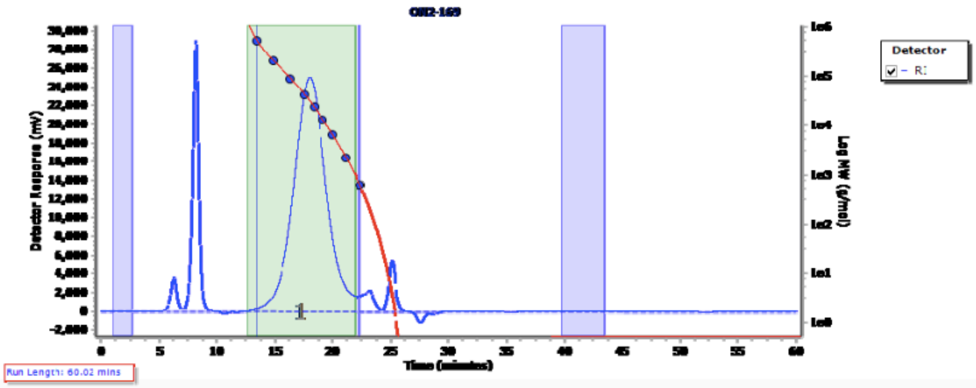


Figure S11. GPC chromatogram for poly(BHEC/BHET) with 80% BHEC (Table S2, Entry 3)

Molecular Weight Averages

Peak	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
Peak 1	34876	17297	56613	146491	377238	126820	3.273

Peak information

	Start (mins)	End (mins)
Baseline region 1	2.67	7.16
Baseline region 2	42.08	54.51
Peak 1	12.36	21.98

Peak	Trace	Peak Max RT (mins)	Peak Area (mV.s)	Peak Height (mV)
Peak 1	RI	17.82	7595873.842	36140.531

Chromatogram

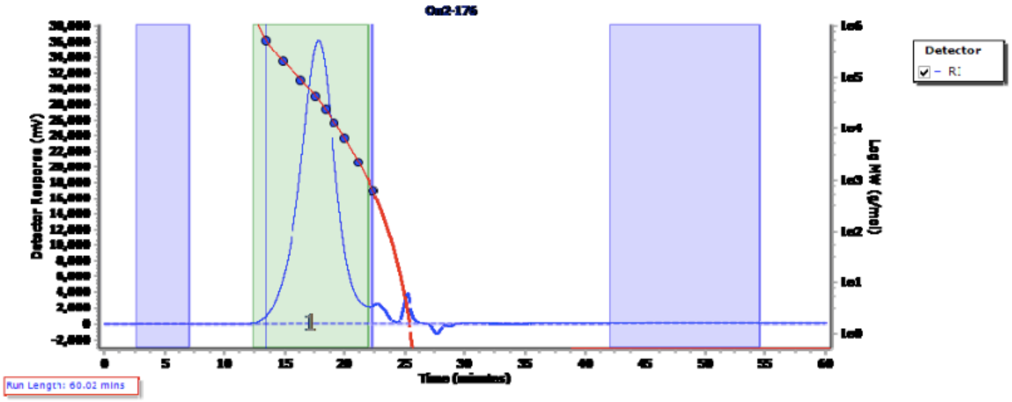


Figure S12. GPC chromatogram for poly(BHEC/BHET) with 70% BHEC (Table S2, Entry 4)

Molecular Weight Averages

Peak	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
Peak 1	43319	19537	54576	100190	161121	92795	2.793

Peak information

	Start (mins)	End (mins)
Baseline region 1	3.04	6.65
Baseline region 2	38.03	49.16
Peak 1	13.23	21.98

Peak	Trace	Peak Max RT (mins)	Peak Area (mV.s)	Peak Height (mV)
Peak 1	RI	17.50	3557078.626	17832.677

Chromatogram

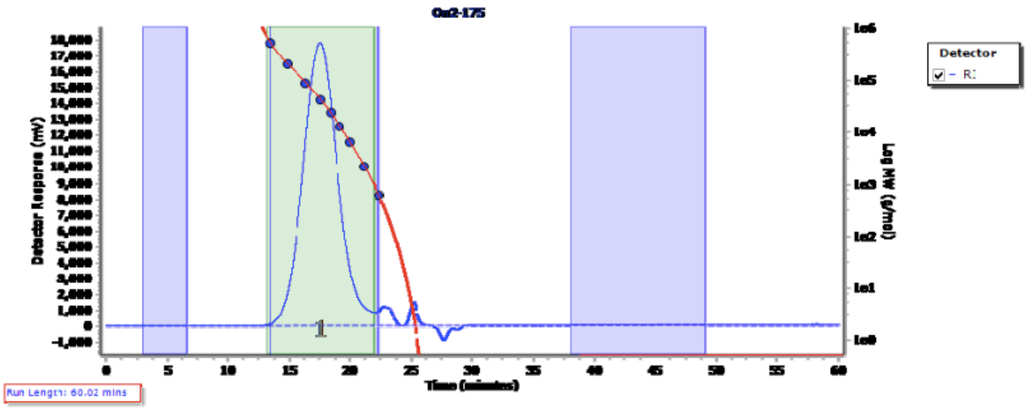


Figure S13. GPC chromatogram for poly(BHEC/BHET) with 60% BHEC (Table S2, Entry 5)

Molecular Weight Averages

Peak	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
Peak 1	44206	21356	59178	115033	205251	105161	2.771

Peak information

	Start (mins)	End (mins)
Baseline region 1	2.24	5.78
Baseline region 2	41.35	52.92
Peak 1	12.87	21.83

Peak	Trace	Peak Max RT (mins)	Peak Area (mV.s)	Peak Height (mV)
Peak 1	RI	17.47	5897785.799	29334.630

Chromatogram

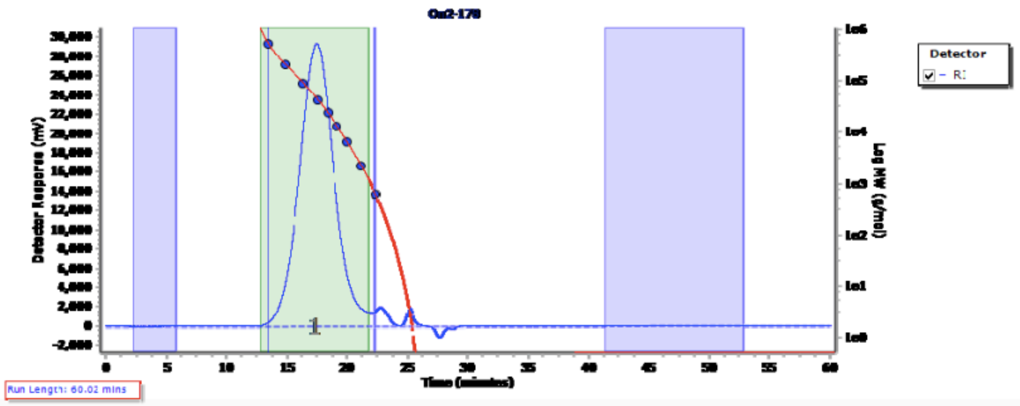


Figure S14. GPC chromatogram for poly(BHEC/BHET) with 50% BHEC (Table S2, Entry 6)

Molecular Weight Averages

Peak	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
Peak 1	30300	14830	38318	67857	103649	63264	2.584

Peak information

	Start (mins)	End (mins)
Baseline region 1	4.27	8.10
Baseline region 2	39.19	47.14
Peak 1	13.59	22.05

Peak	Trace	Peak Max RT (mins)	Peak Area (mV.s)	Peak Height (mV)
Peak 1	RI	18.02	8337394.187	45599.149

Chromatogram

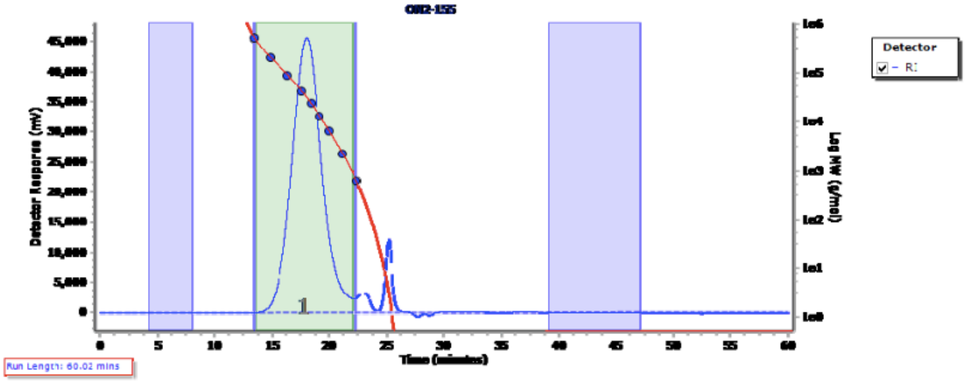


Figure S15. GPC chromatogram for poly(BHEC/BHET) with 40% BHEC (Table S2, Entry 7)

Molecular Weight Averages

Peak	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
Peak 1	25090	13713	33142	59650	93066	55415	2.417

Peak information

	Start (mins)	End (mins)
Baseline region 1	3.69	7.09
Baseline region 2	36.94	48.22
Peak 1	13.66	21.91

Peak	Trace	Peak Max RT (mins)	Peak Area (mV.s)	Peak Height (mV)
Peak 1	RI	18.27	12231059.784	69204.853

Chromatogram

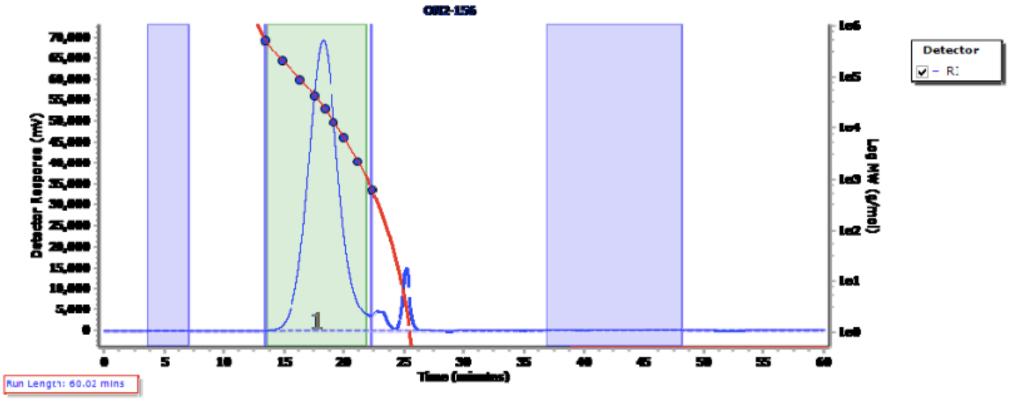


Figure S16. GPC chromatogram for poly(BHEC/BHET) with 30% BHEC (Table S2, Entry 8)

Molecular Weight Averages

Peak	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
Peak 1	33423	16838	42191	73445	110317	68629	2.506

Peak information

	Start (mins)	End (mins)
Baseline region 1	4.70	9.18
Baseline region 2	42.44	50.68
Peak 1	13.74	21.98

Peak	Trace	Peak Max RT (mins)	Peak Area (mV.s)	Peak Height (mV)
Peak 1	RI	17.88	8484466.411	46280.031

Chromatogram

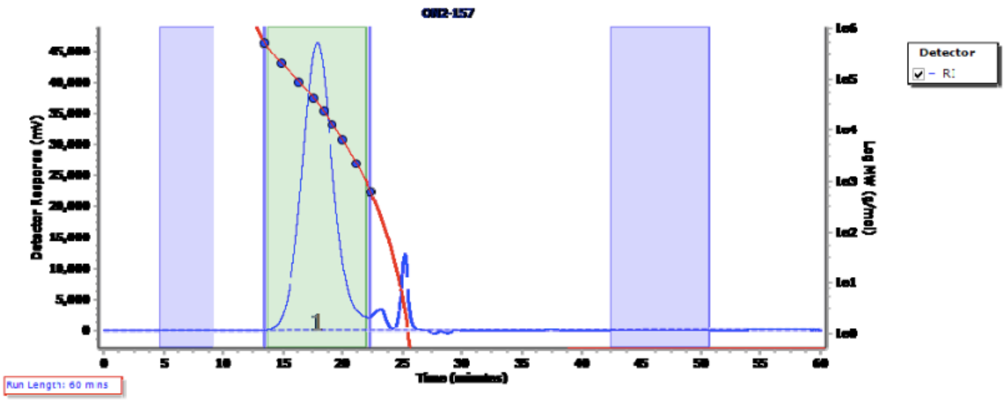


Figure S17. GPC chromatogram for poly(BHEC/BHET) with 20% BHEC (Table S2, Entry 9)

Molecular Weight Averages

Peak	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
Peak 1	41776	22298	55952	101992	168149	94243	2.509

Peak information

	Start (mins)	End (mins)
Baseline region 1	2.24	5.64
Baseline region 2	36.65	42.66
Peak 1	13.09	21.83

Peak	Trace	Peak Max RT (mins)	Peak Area (mV.s)	Peak Height (mV)
Peak 1	RI	17.56	9689316.564	50632.024

Chromatogram

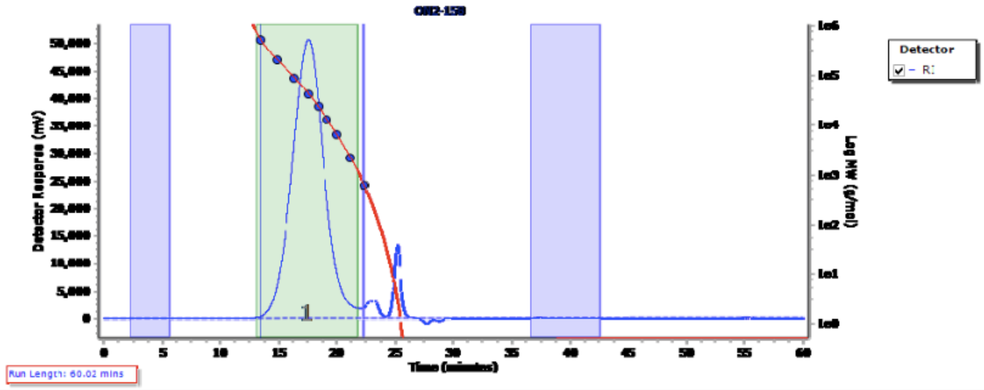


Figure S18. GPC chromatogram for poly(BHEC/BHET) with 10% BHEC (Table S2, Entry 10)

Molecular Weight Averages

Peak	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
Peak 1	44531	19765	55145	100546	174037	92724	2.79

Peak information

	Start (mins)	End (mins)
Baseline region 1	2.71	6.47
Baseline region 2	28.79	29.86
Peak 1	13.36	22.08

Peak	Trace	Peak Max RT (mins)	Peak Area (mV.s)	Peak Height (mV)
Peak 1	RI	17.63	7109421.929	35459.524

Chromatogram

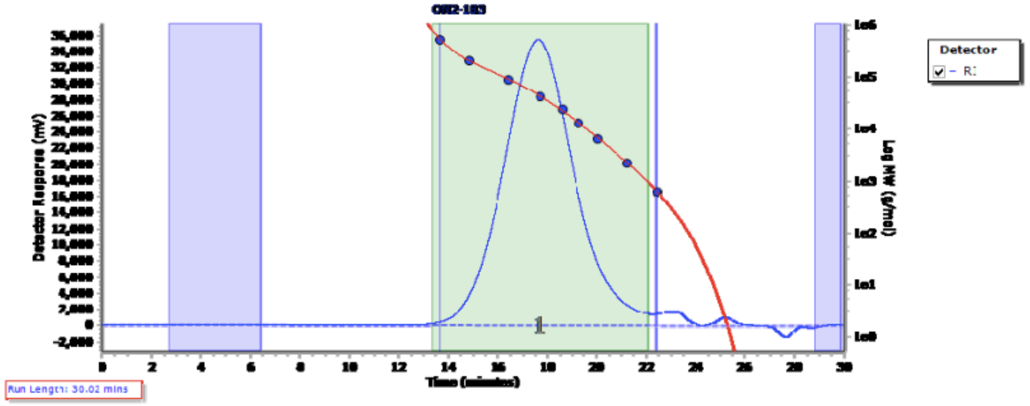


Figure S19. GPC chromatogram for polyBHET (Table S2, Entry 11)

Molecular Weight Averages

Peak	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
Peak 1	9979	4245	13608	28968	49339	26415	3.206

Peak information

	Start (mins)	End (mins)
Baseline region 1	1.59	2.75
Baseline region 2	33.47	40.05
Peak 1	15.04	22.92

Peak	Trace	Peak Max RT (mins)	Peak Area (mV.s)	Peak Height (mV)
Peak 1	RI	19.43	6137230.888	34443.734

Chromatogram

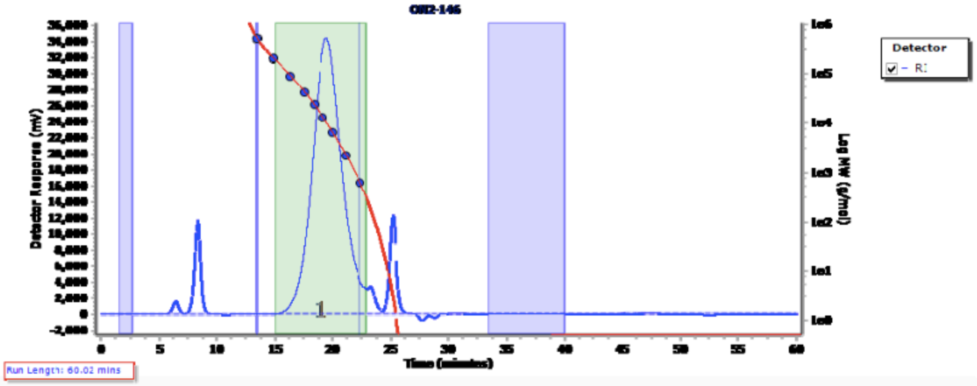


Figure S20. GPC chromatogram for polypropylene camphorate [dual catalyst] (Table S3, Entry 1)

Molecular Weight Averages

Peak	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
Peak 1	11491	4631	16739	39241	72781	35276	3.615

Peak information

	Start (mins)	End (mins)
Baseline region 1	5.13	7.30
Baseline region 2	36.29	44.97
Peak 1	14.31	22.92

Peak	Trace	Peak Max RT (mins)	Peak Area (mV.s)	Peak Height (mV)
Peak 1	RI	19.26	6144430.639	32802.061

Chromatogram

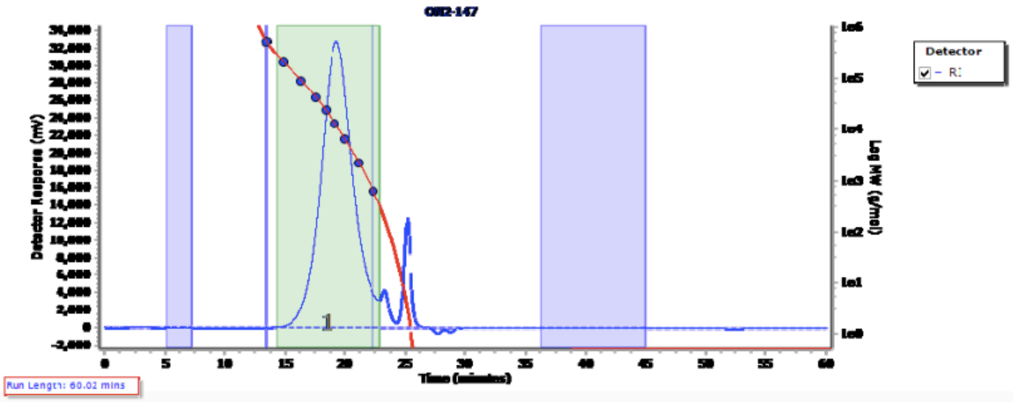


Figure S21. GPC chromatogram for polybutylene camphorate [dual catalyst] (Table S3, Entry 2)

Molecular Weight Averages

Peak	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
Peak 1	5933	2808	7240	13713	21009	12725	2.578

Peak information

	Start (mins)	End (mins)
Baseline region 1	4.12	7.52
Baseline region 2	36.51	42.65
Peak 1	16.99	22.77

Peak	Trace	Peak Max RT (mins)	Peak Area (mV.s)	Peak Height (mV)
Peak 1	RI	20.04	5640827.040	34344.683

Chromatogram

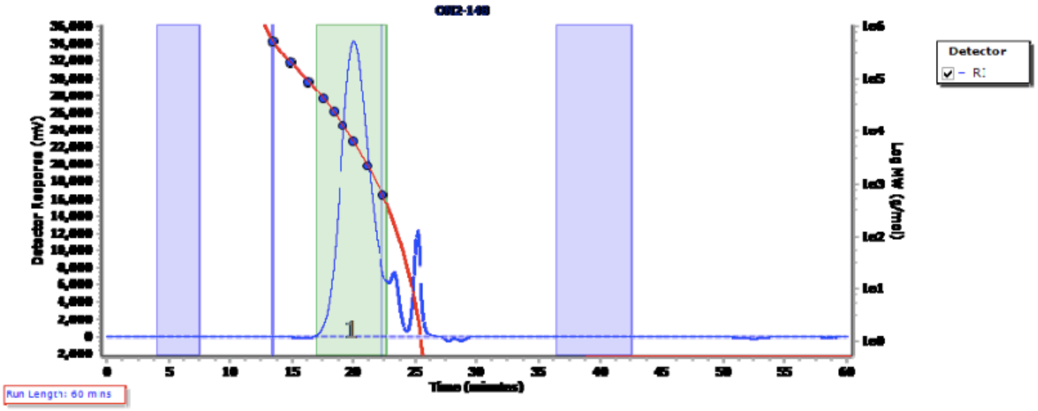


Figure S22. GPC chromatogram for polypentylene camphorate [dual catalyst] (Table S3, Entry 3)

Differential Scanning Calorimetry (DSC) Thermograms

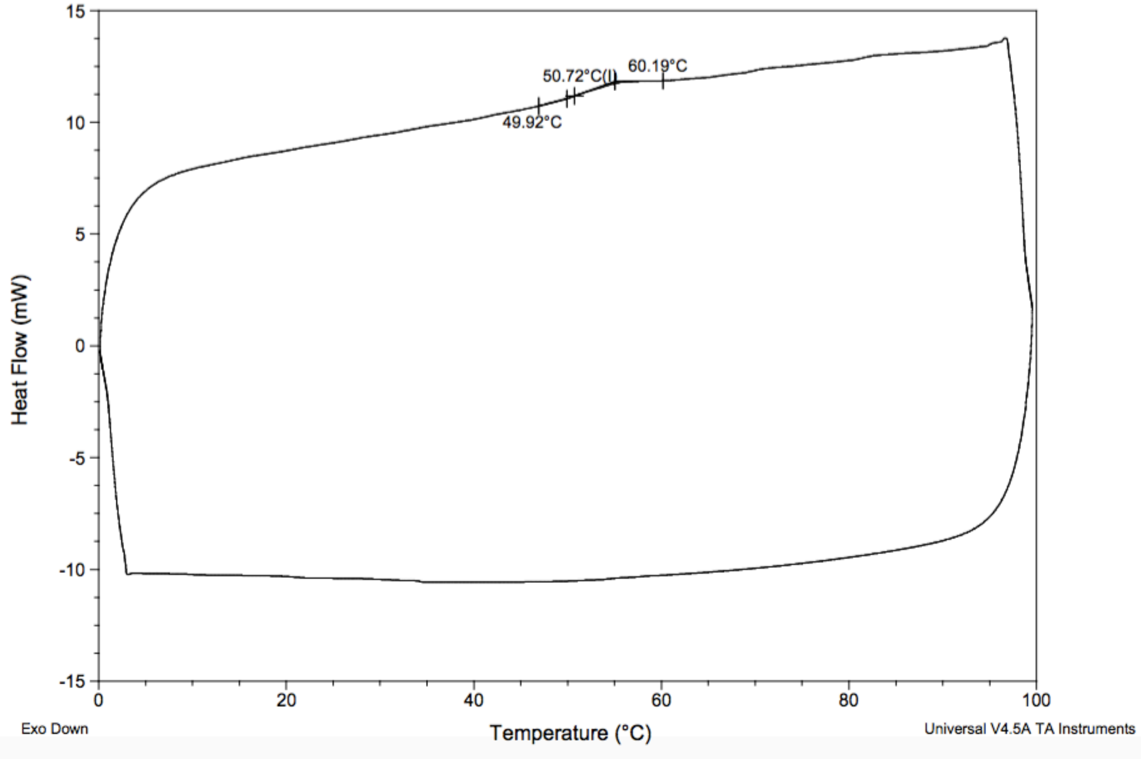


Figure S23. DSC thermogram for polyethylene camphorate (Table S1, Entry 1)

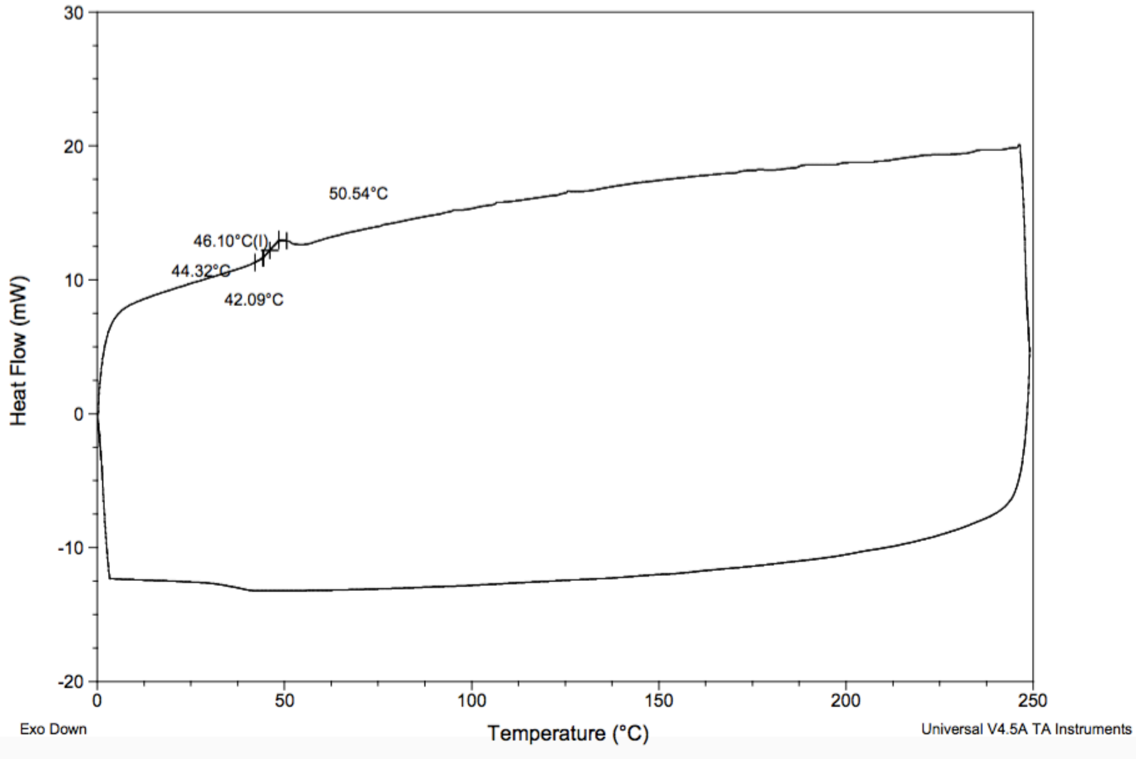


Figure S24. DSC thermogram for polyethylene camphorate [dual catalyst] (Table S1, Entry 2)

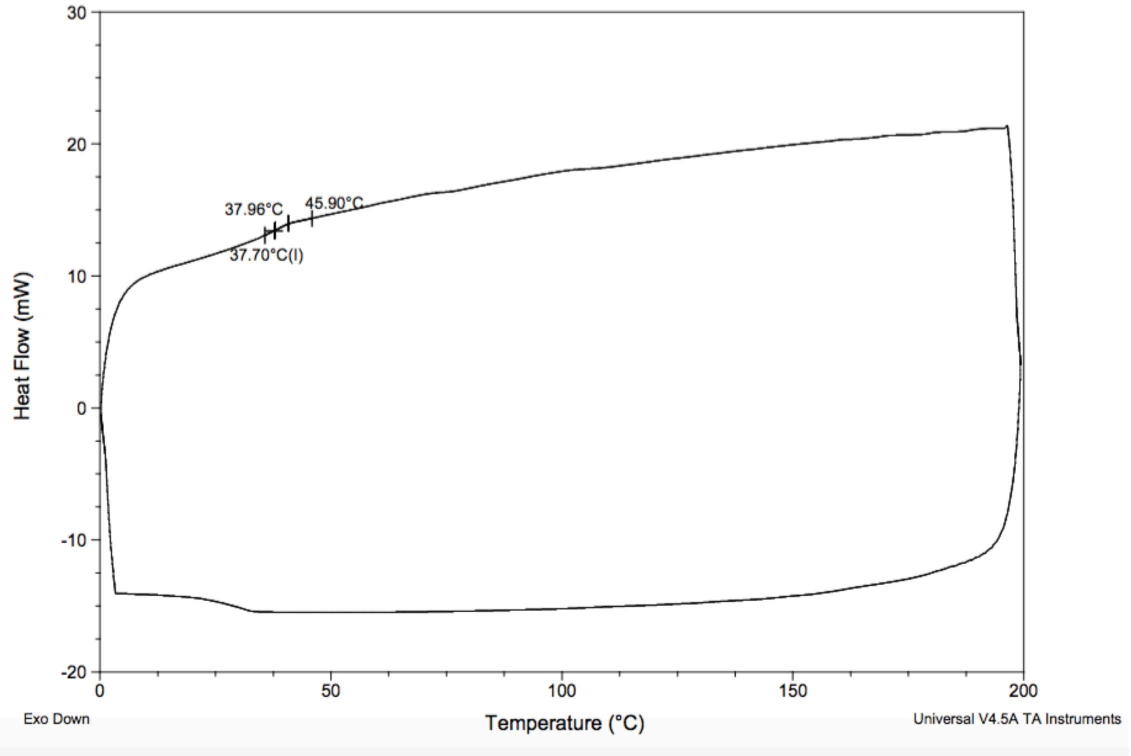


Figure S25. DSC thermogram for polypropylene camphorate (Table S1, Entry 3)

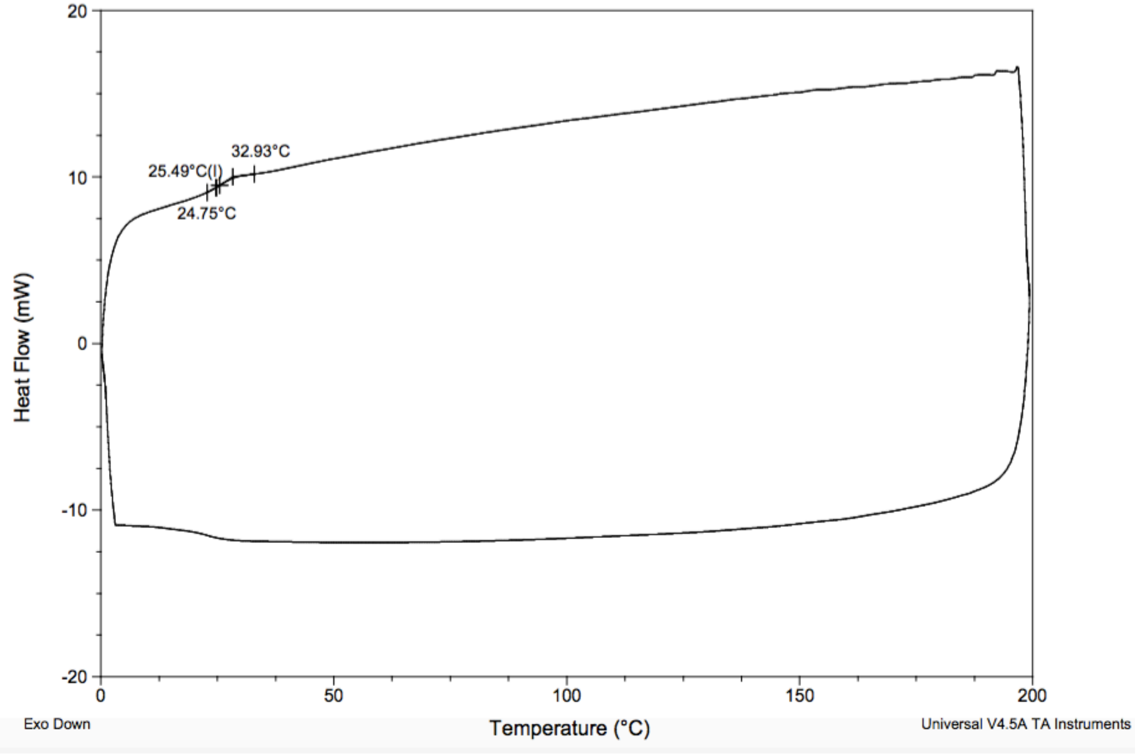


Figure S26. DSC thermogram for polybutylene camphorate (Table S1, Entry 4)

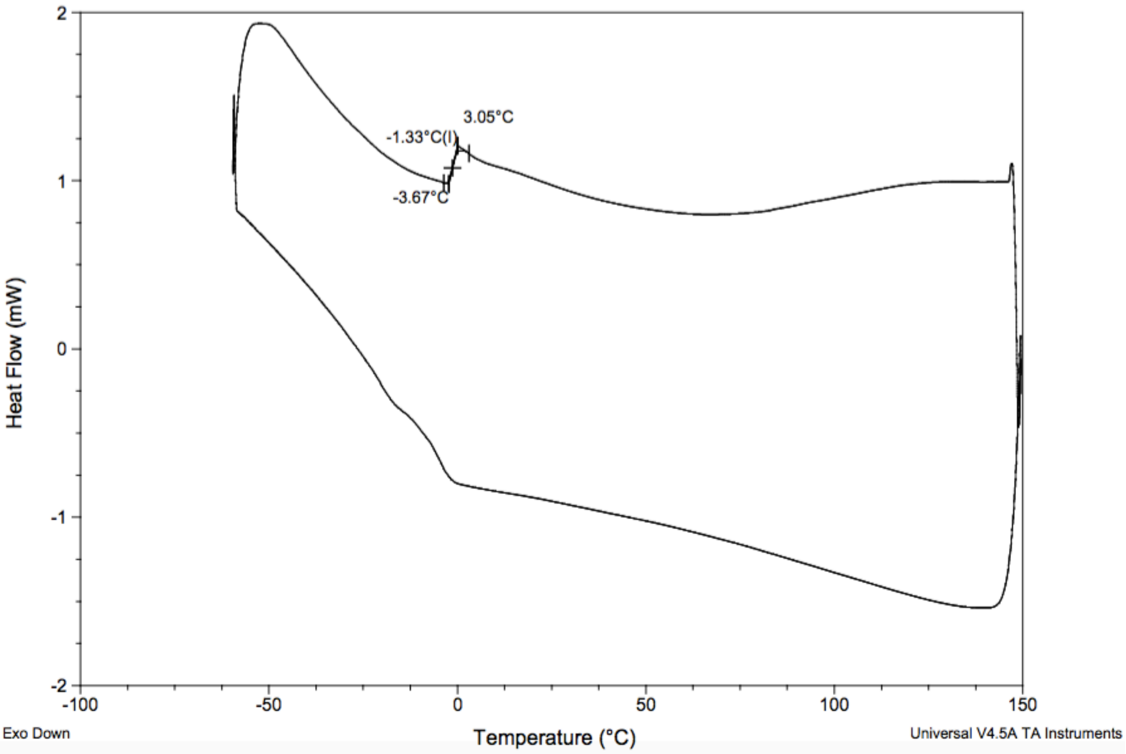


Figure S27. DSC thermogram for polypentylene camphorate (Table S1, Entry 5)

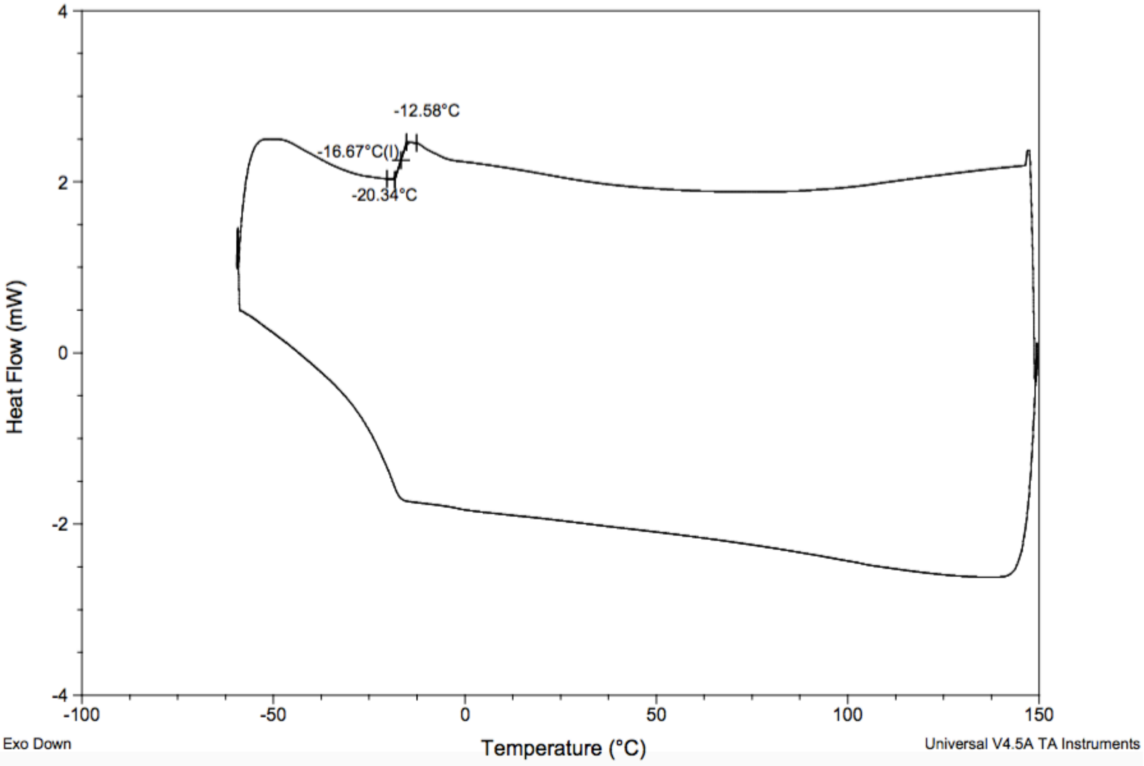


Figure S28. DSC thermogram for polyhexylene camphorate (Table S1, Entry 6)

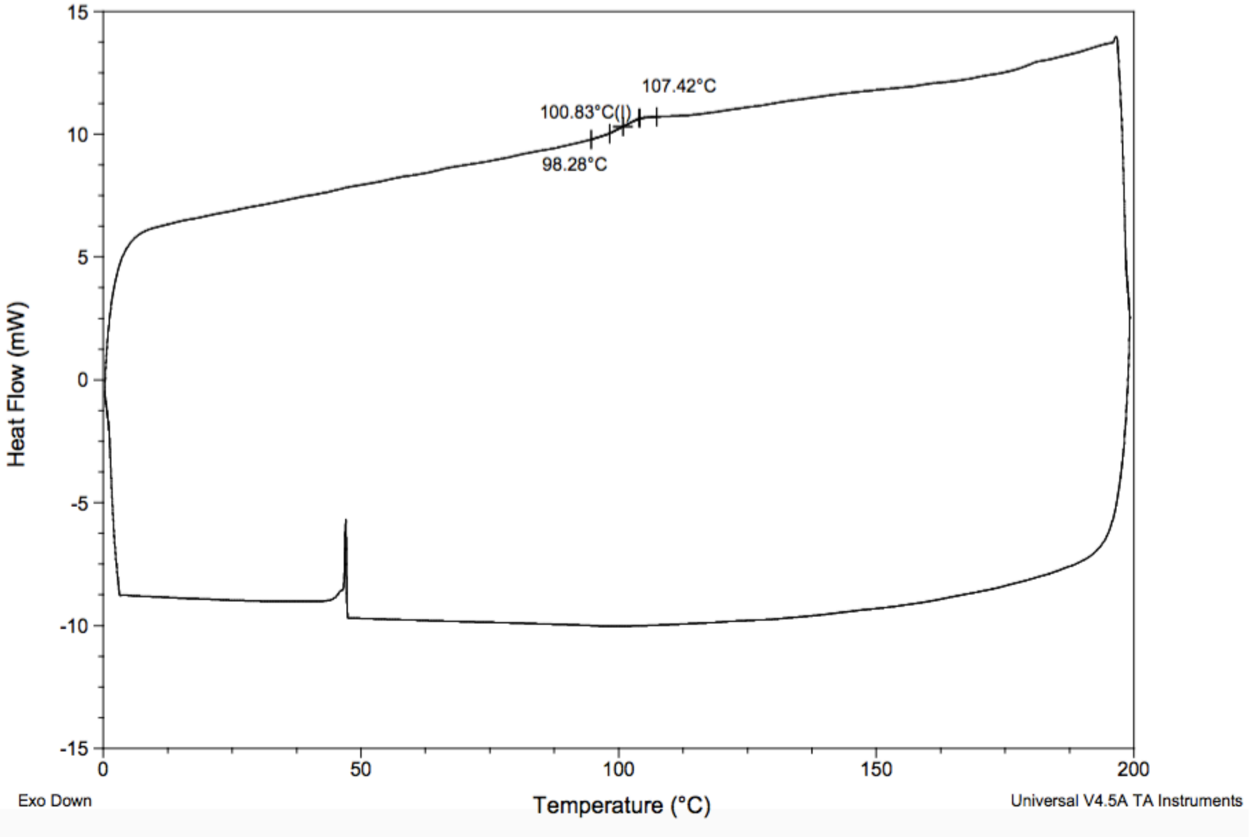


Figure S29. DSC thermogram for polyerythritan camphorate (Table S1, Entry 7)

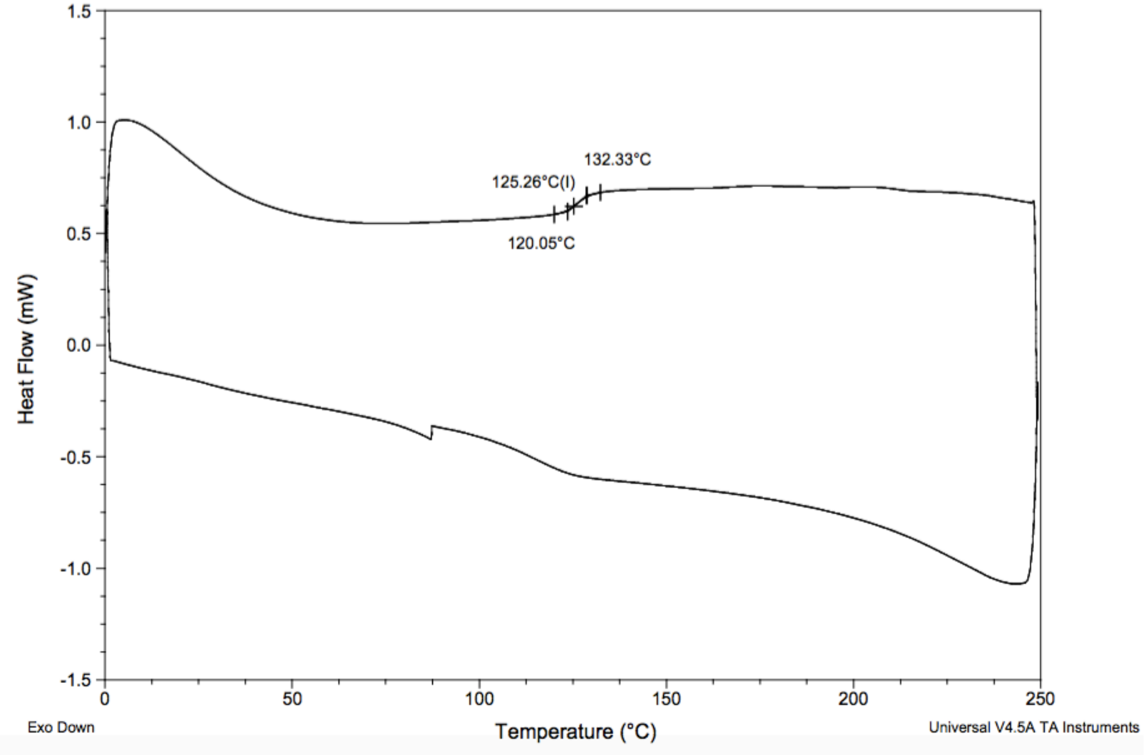


Figure S30. DSC thermogram for polyisosorbide camphorate (Table S1, Entry 8)

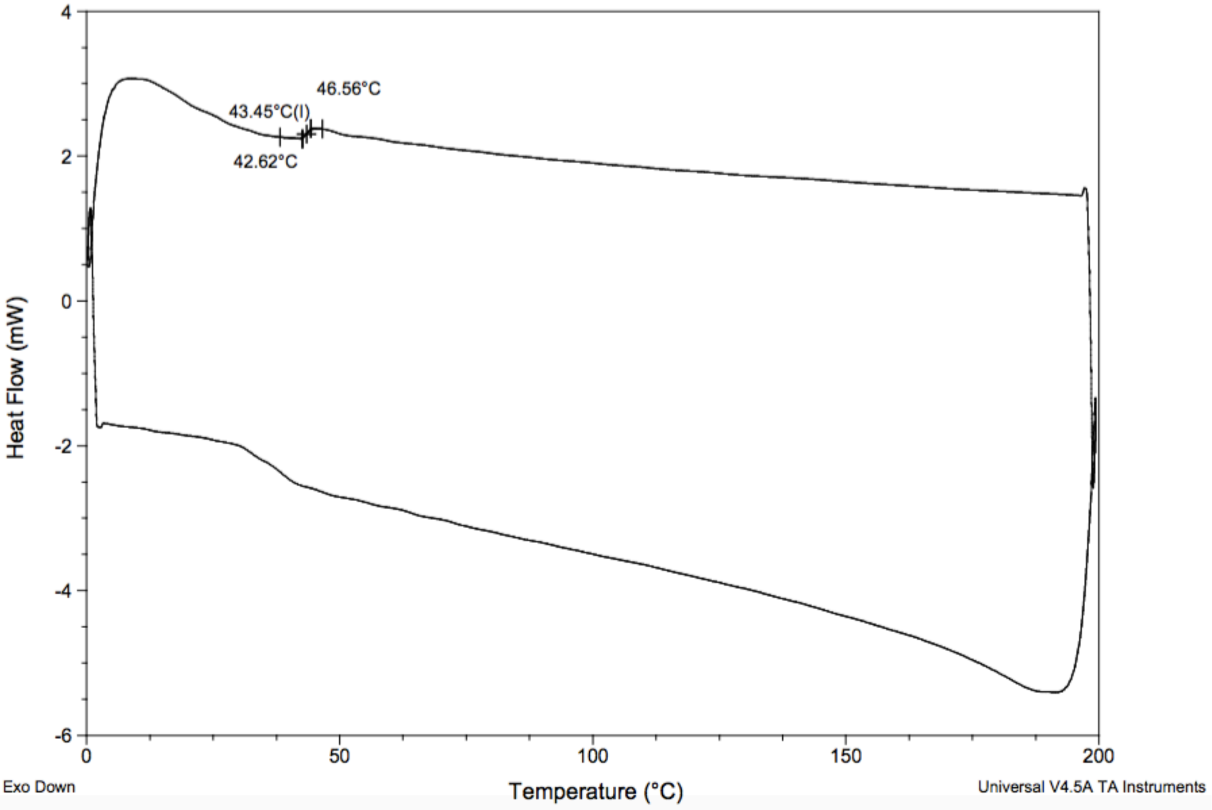


Figure S31. DSC thermogram for polyBHEC/BHET (Table S2, Entry 1)

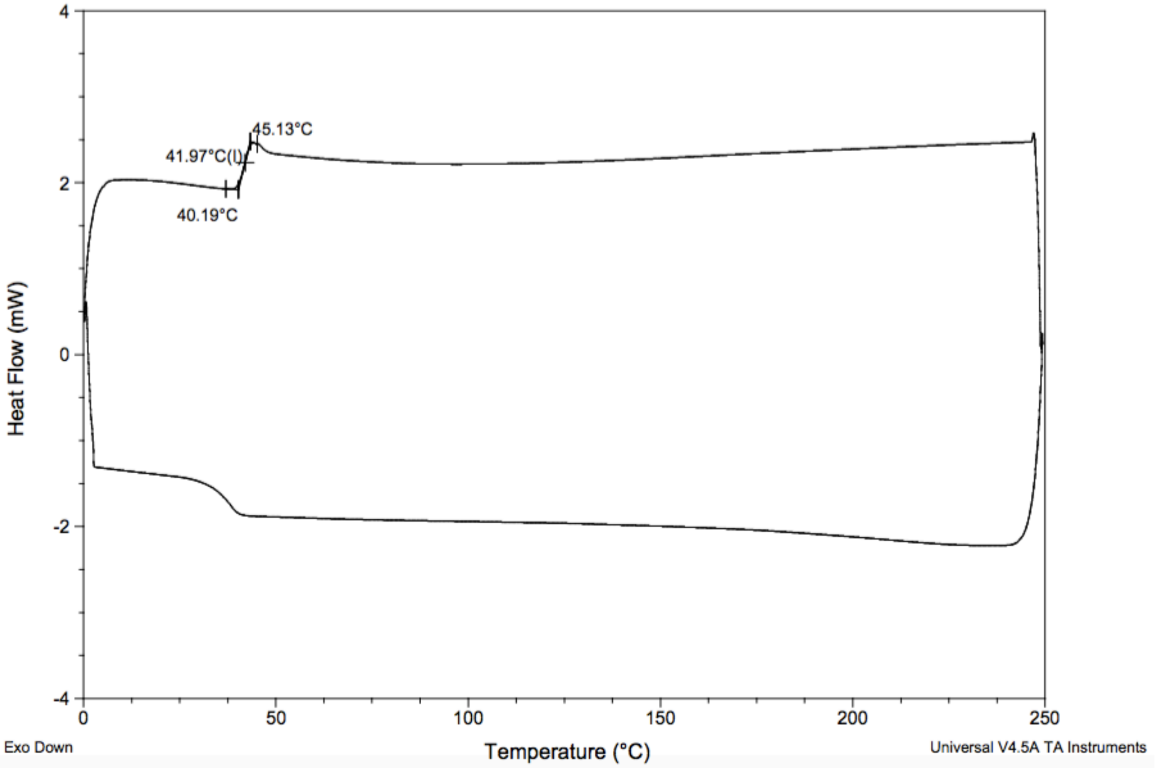


Figure S32. DSC thermogram for poly(BHEC/BHET) with 90% BHEC (Table S2, Entry 2)

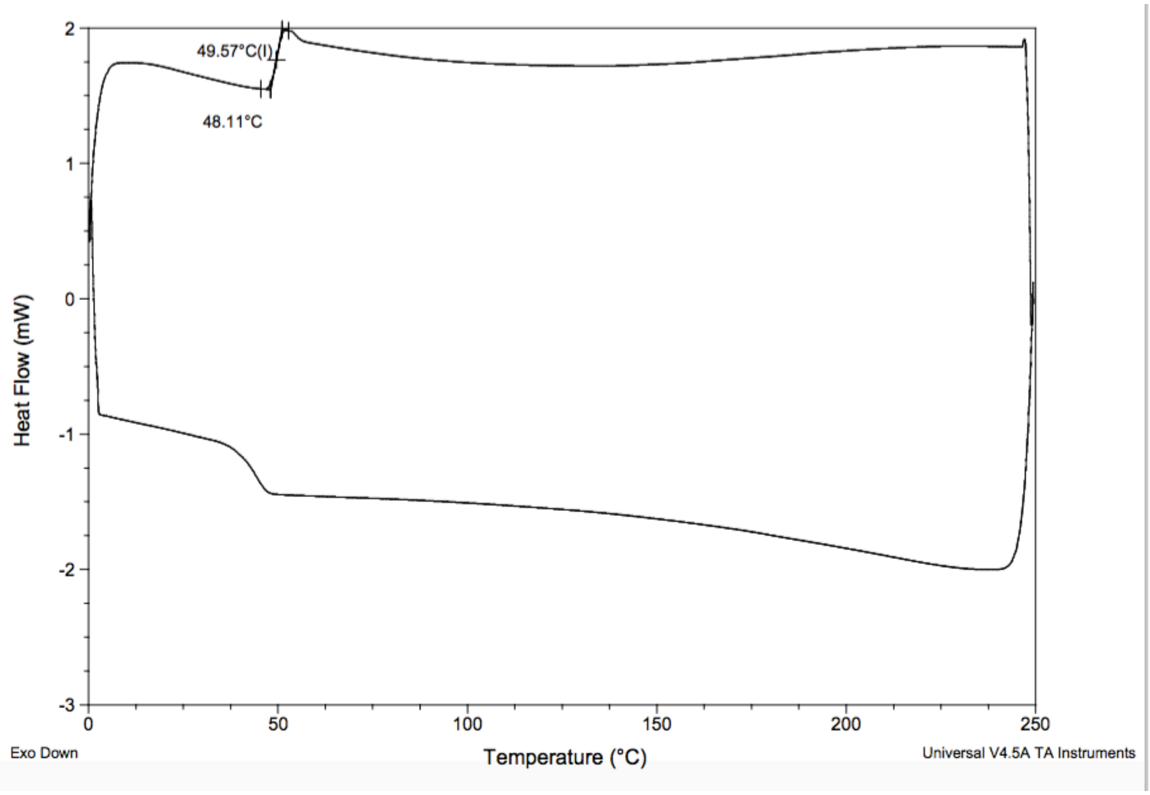


Figure S33. DSC thermogram for poly(BHEC/BHET) with 80% BHEC (Table S2, Entry 3)

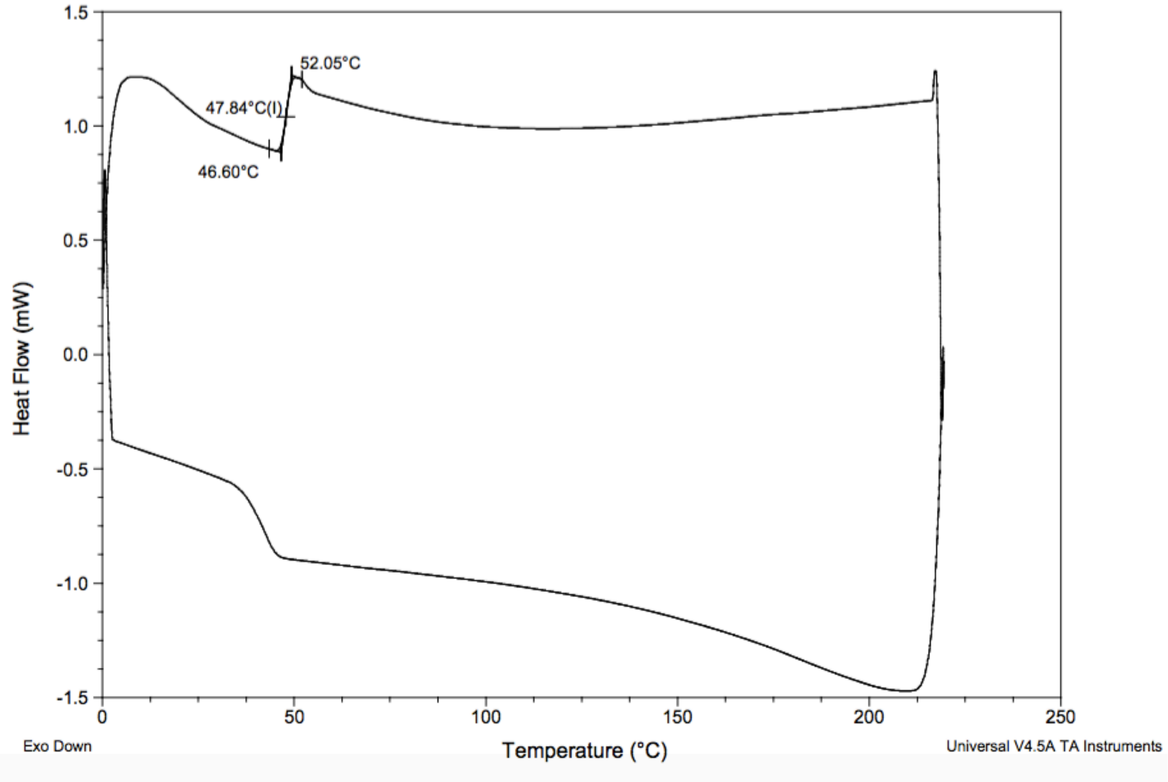


Figure S34. DSC thermogram for poly(BHEC/BHET) with 70% BHEC (Table S2, Entry 4)

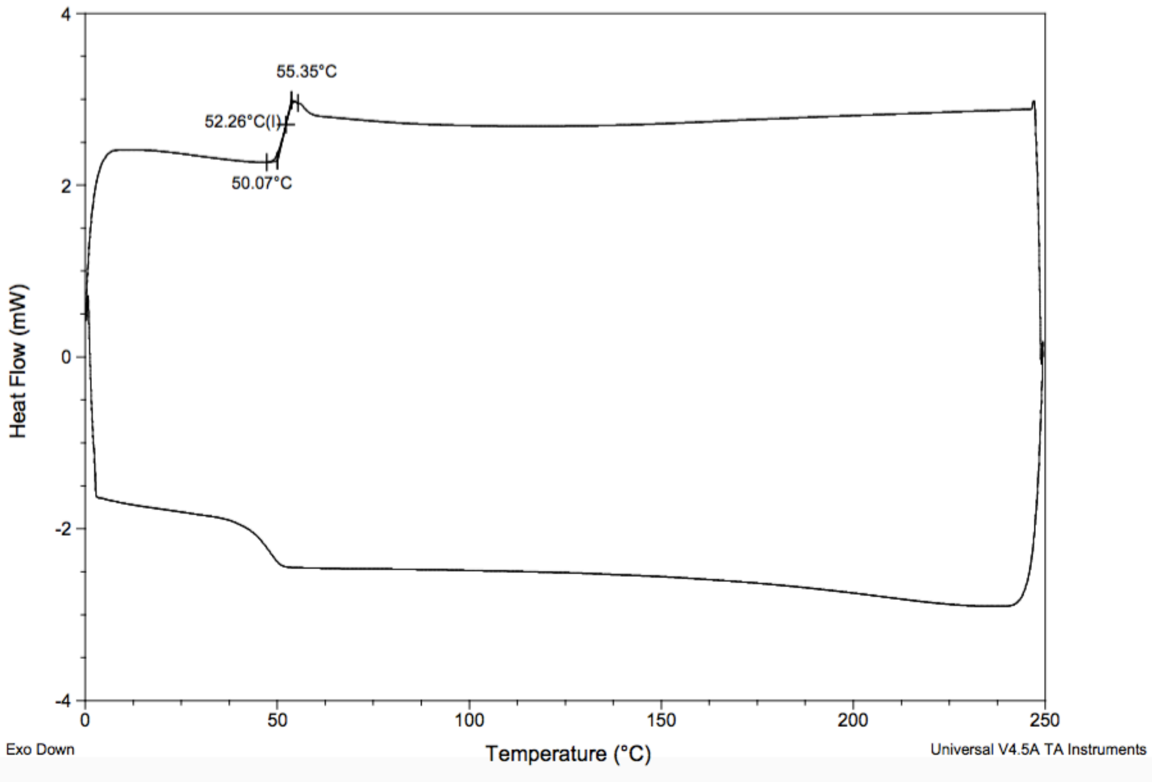


Figure S35. DSC thermogram for poly(BHEC/BHET) with 60% BHEC (Table S2, Entry 5)

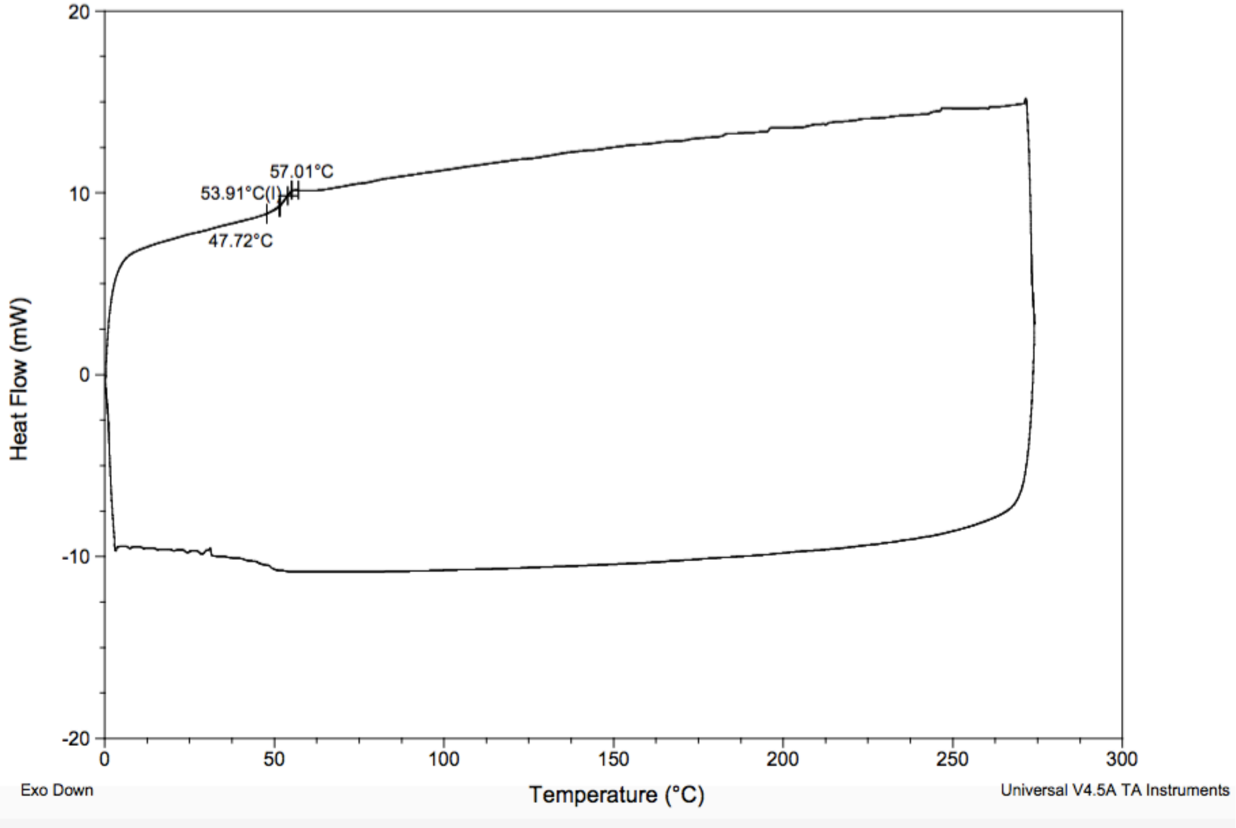


Figure S36. DSC thermogram for poly(BHEC/BHET) with 50% BHEC (Table S2, Entry 6)

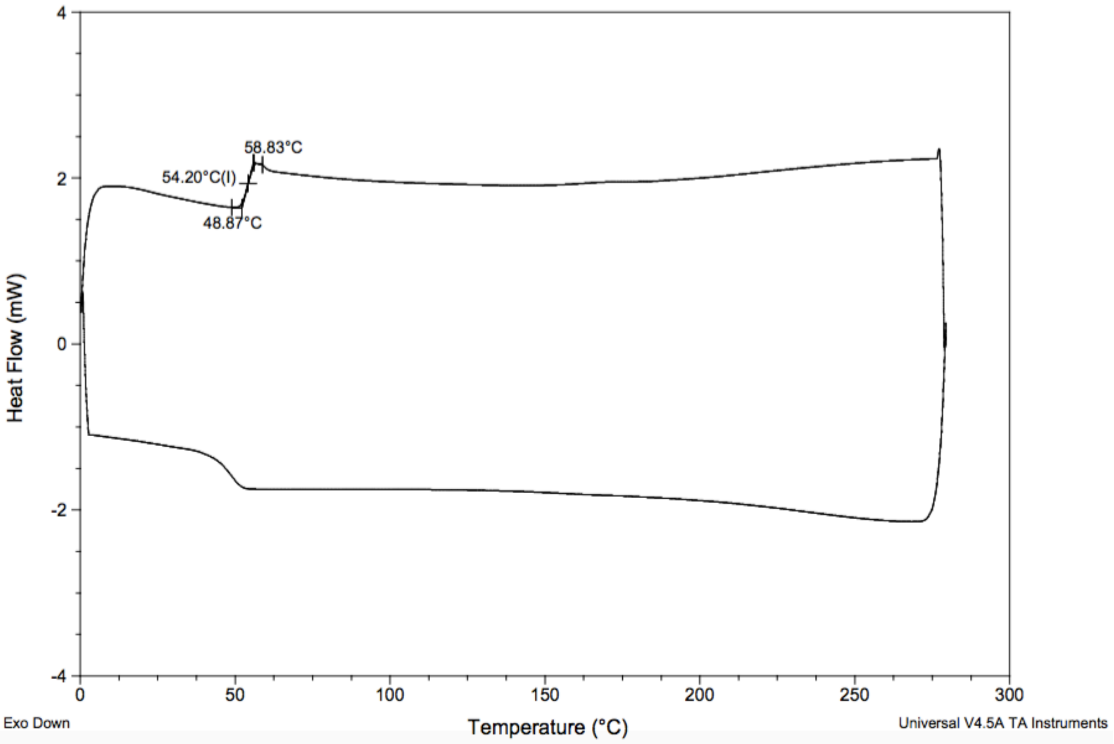


Figure S37. DSC thermogram for poly(BHEC/BHET) with 40% BHEC (Table S2, Entry 7)

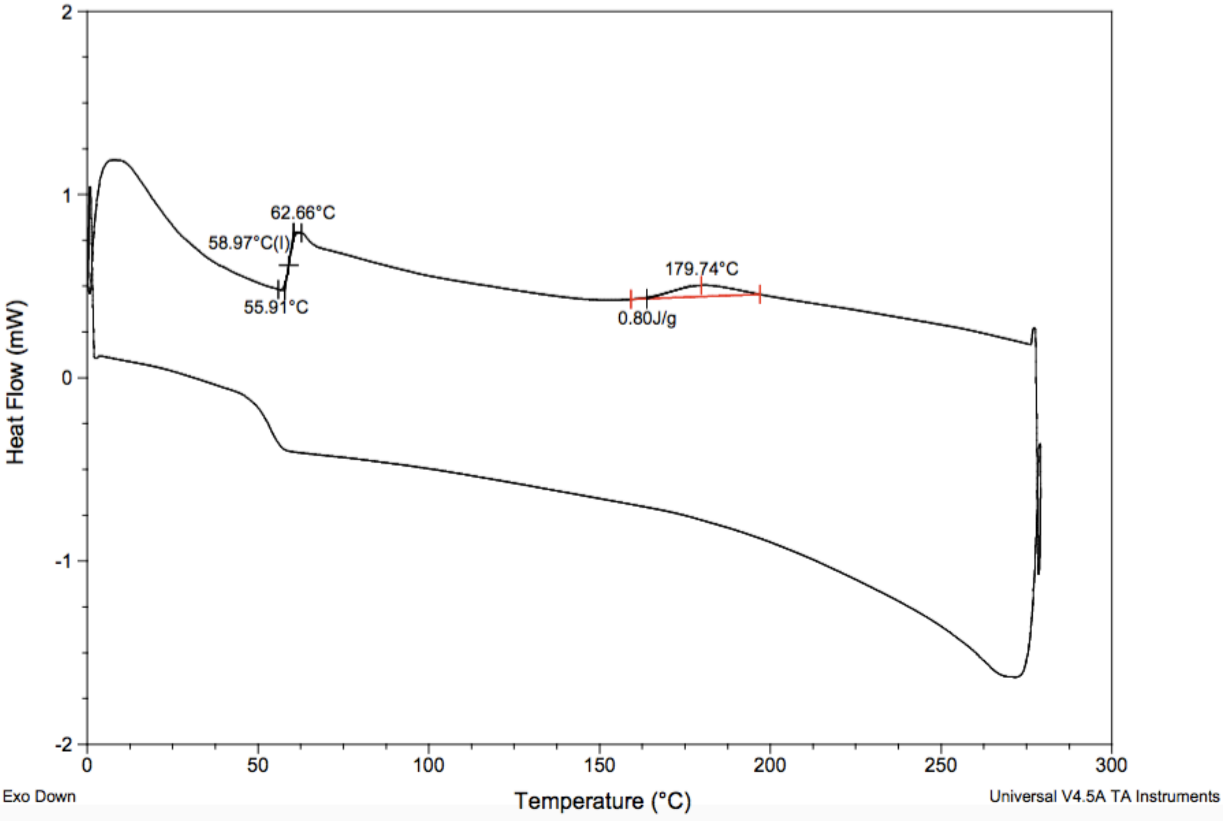


Figure S38. DSC thermogram for poly(BHEC/BHET) with 30% BHEC (Table S2, Entry 8)

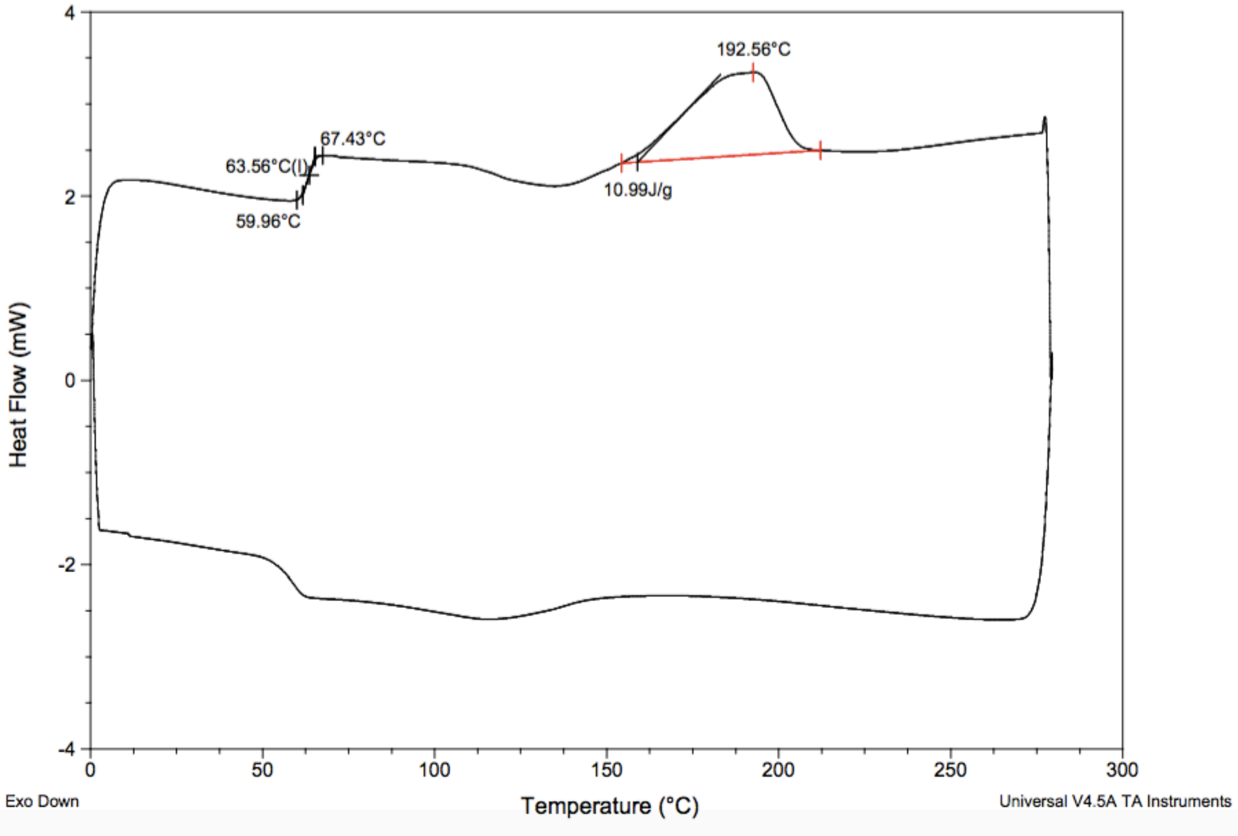


Figure S39. DSC thermogram for poly(BHEC/BHET) with 20% BHEC (Table S2, Entry 9)

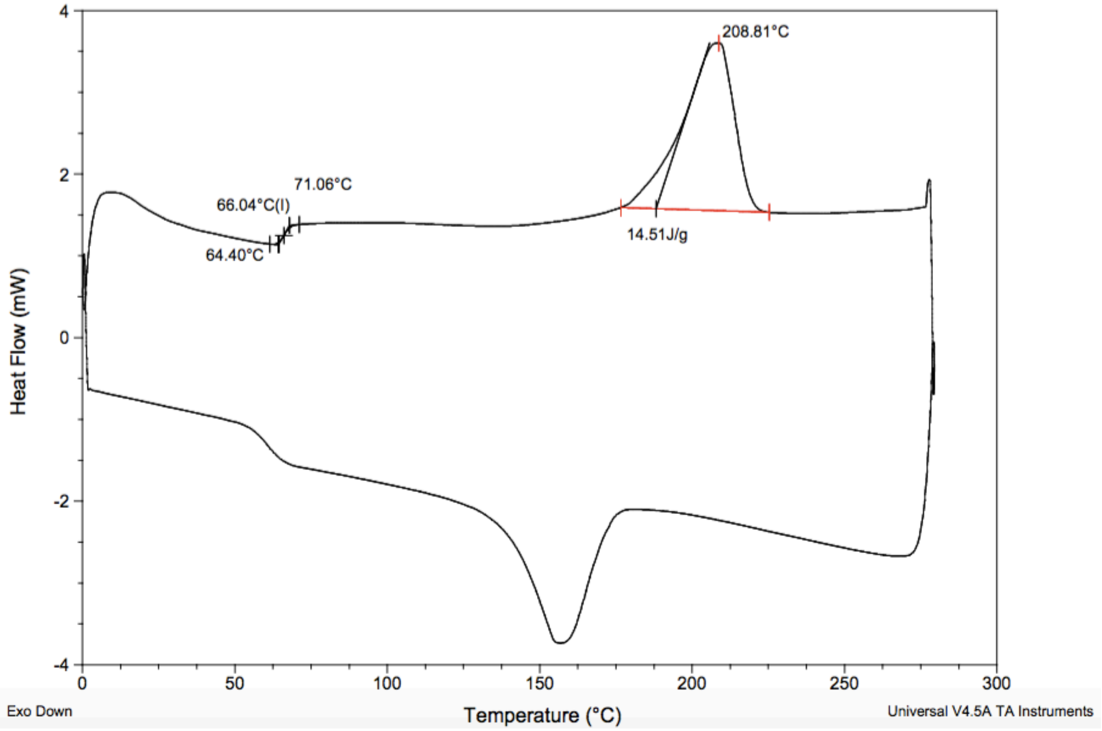


Figure S40. DSC thermogram for poly(BHEC/BHET) with 10% BHEC (Table S2, Entry 10)

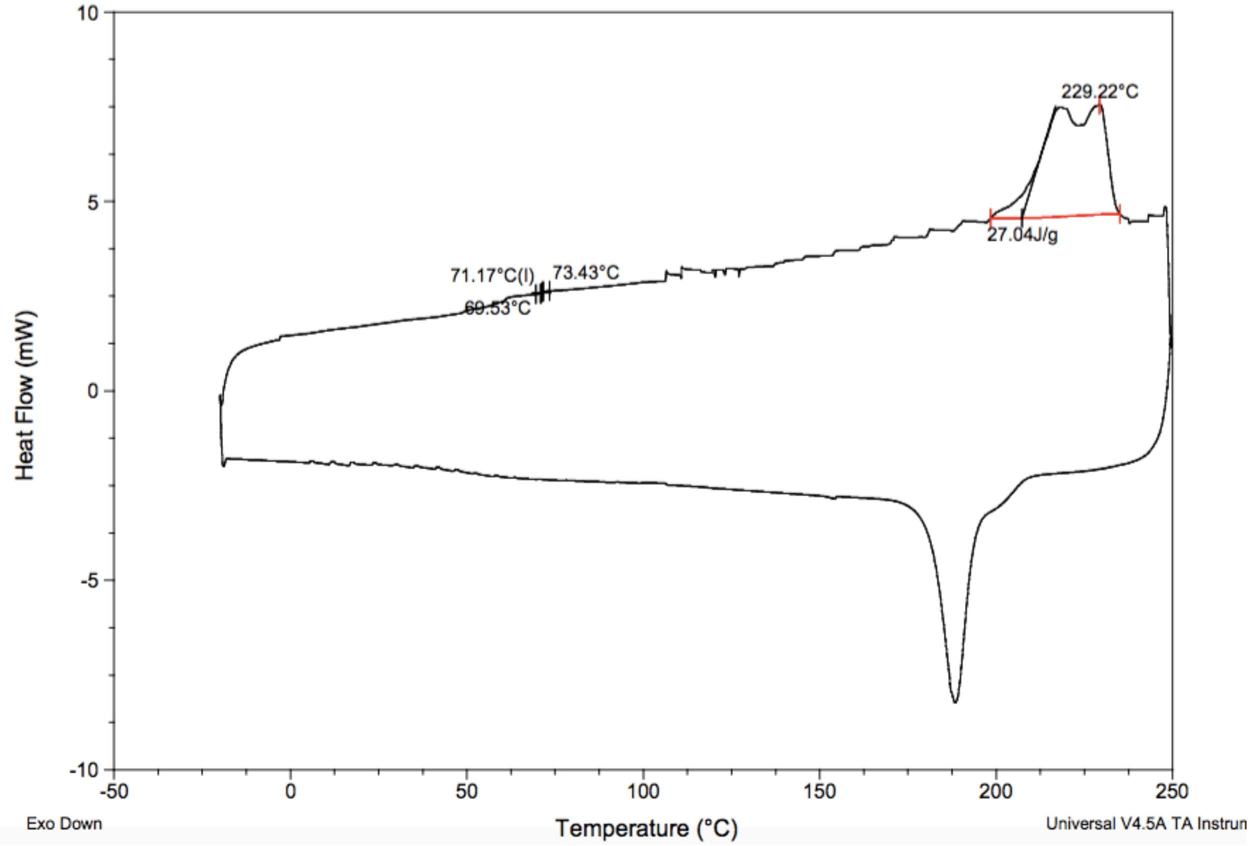


Figure S41. DSC thermogram for polyBHET (Table S2, Entry 11)

Thermogravimetric Analysis (TGA) Thermograms

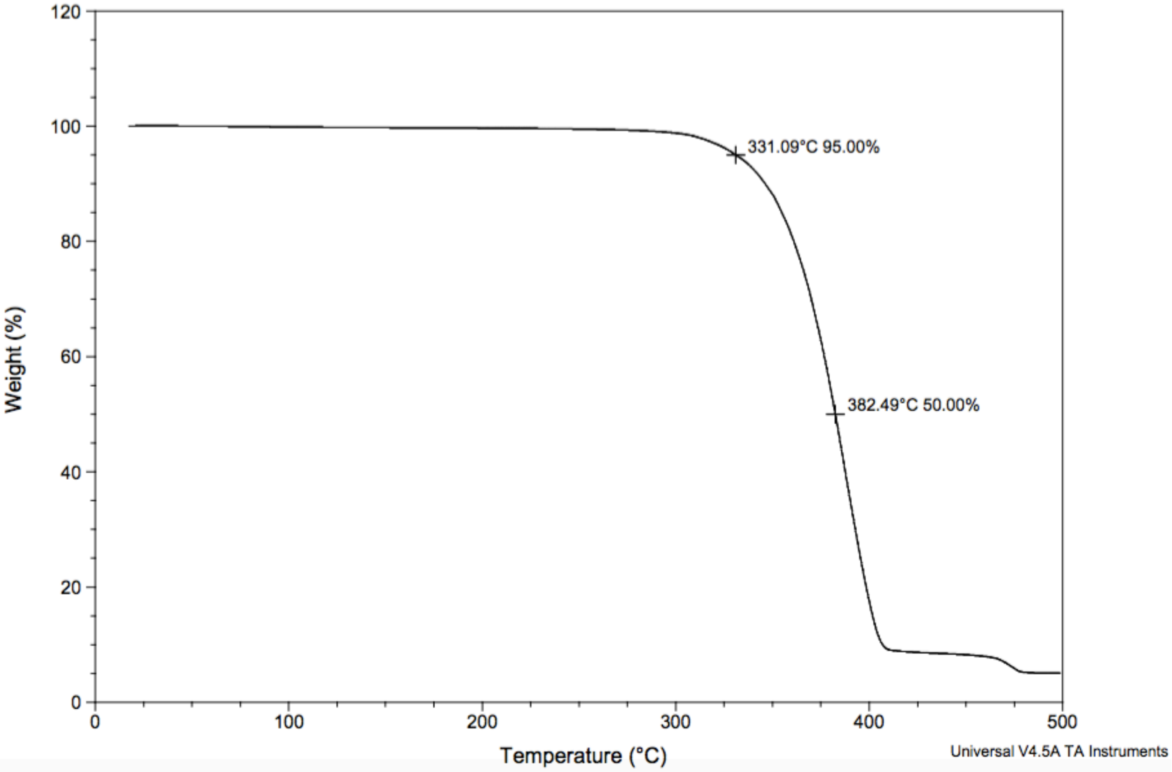


Figure S42. TGA thermogram for polyethylene camphorate (Table S1, Entry 1)

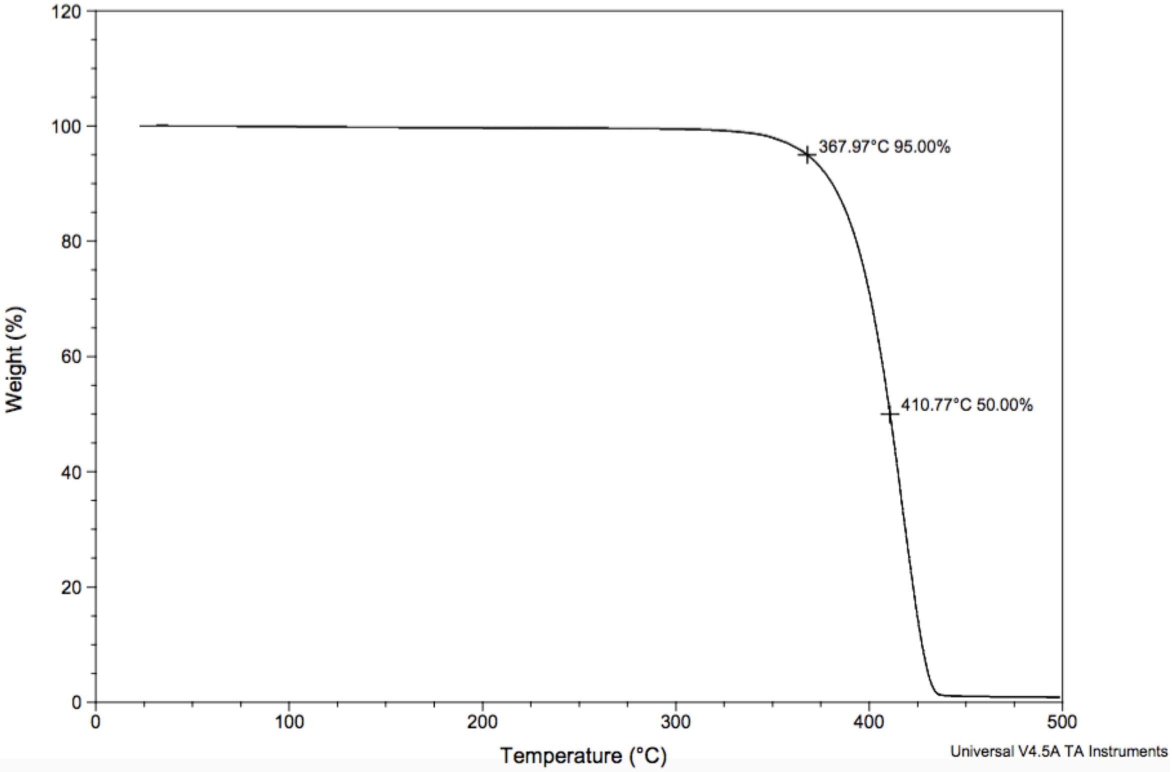


Figure S43. TGA thermogram for polyethylene camphorate [dual catalyst] (Table S1, Entry 2)

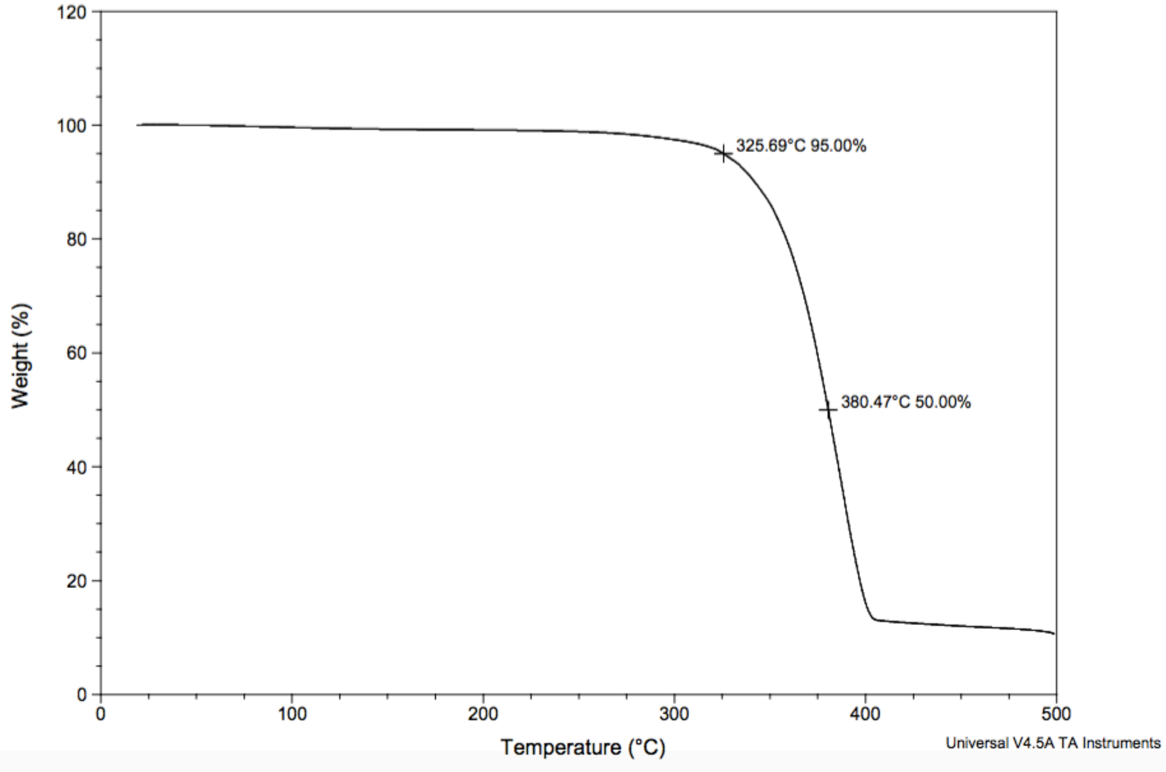


Figure S44. TGA thermogram for polypropylene camphorate (Table S1, Entry 3)

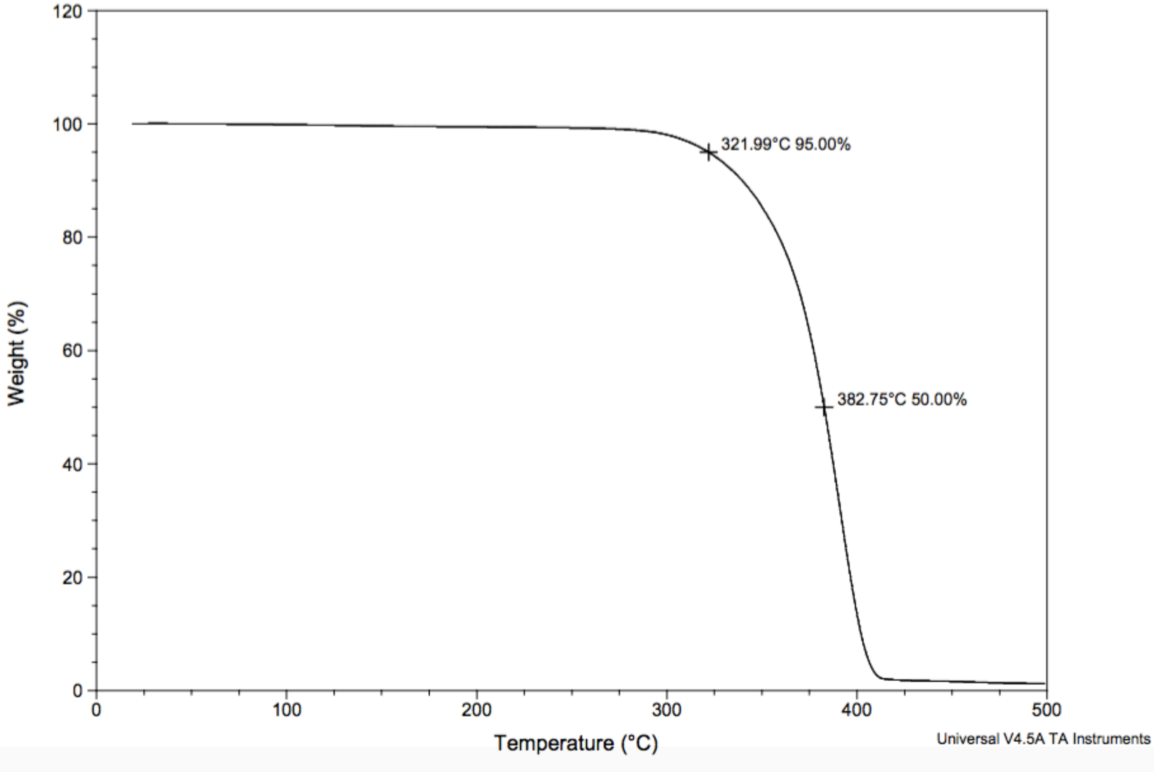


Figure S45. TGA thermogram for polybutylene camphorate (Table S1, Entry 4)

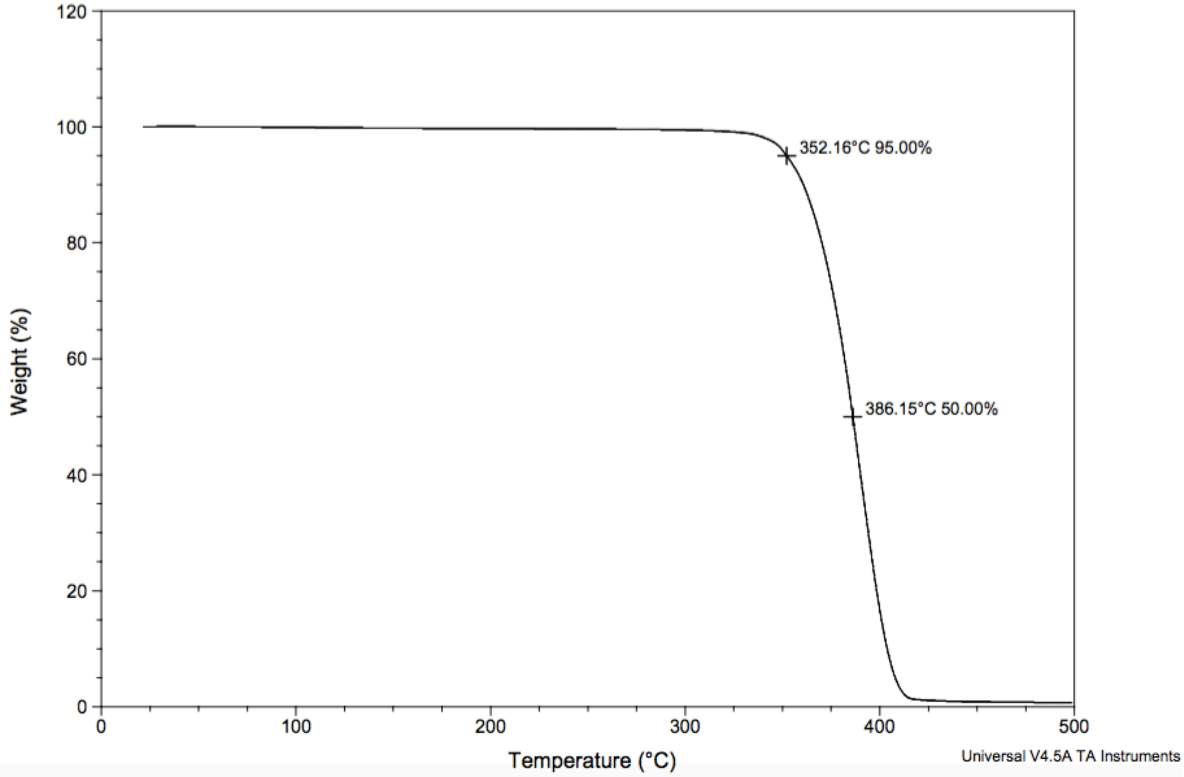


Figure S46. TGA thermogram for polypentylene camphorate (Table S1, Entry 5)

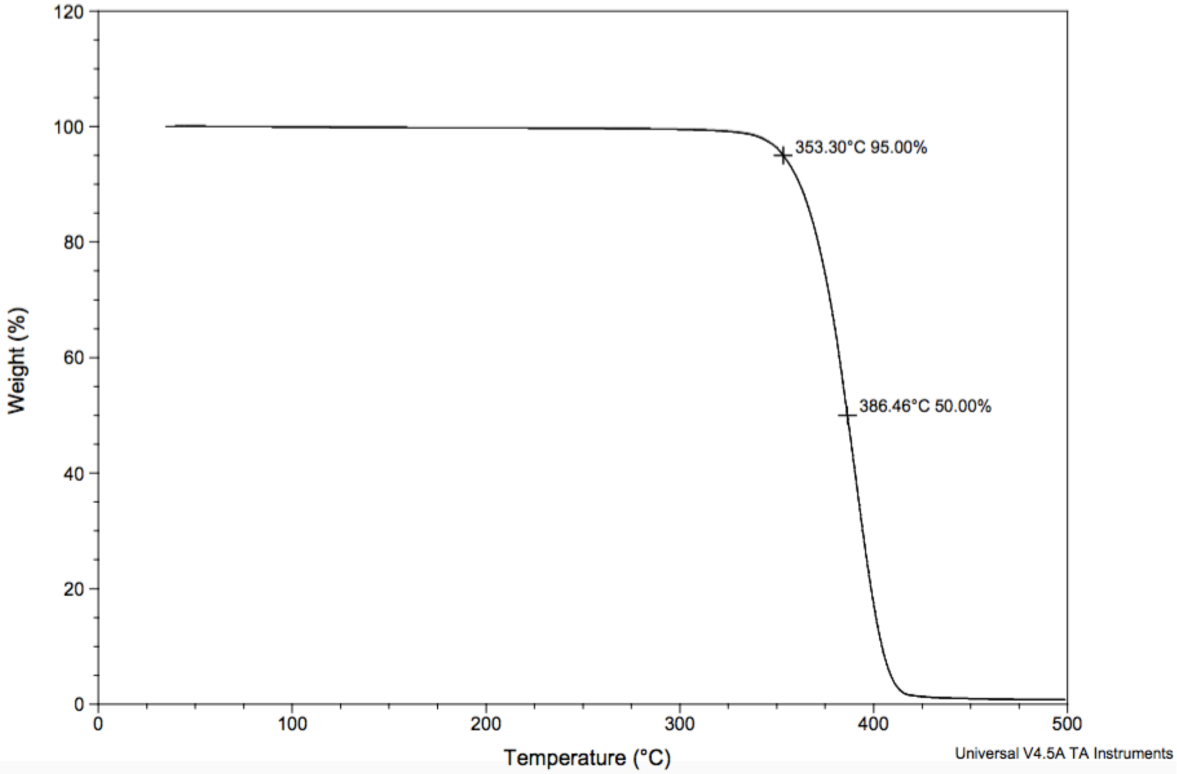


Figure S47. TGA thermogram for polyhexylene camphorate (Table S1, Entry 6)

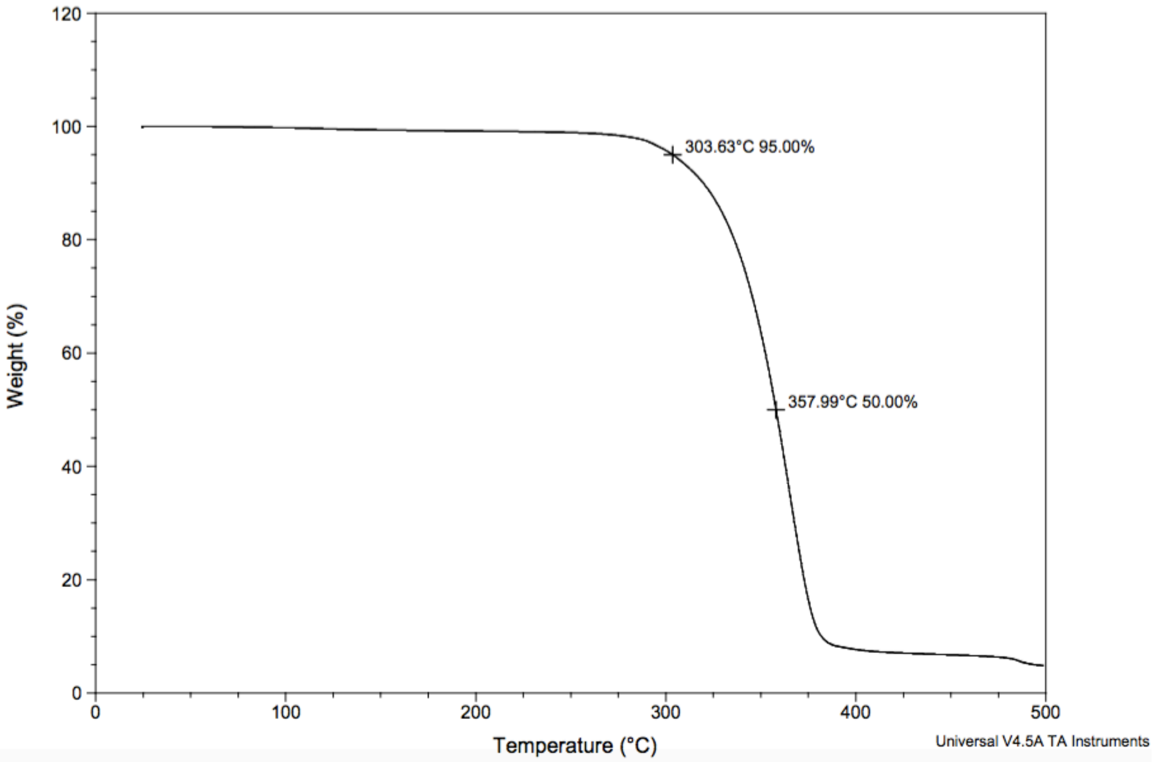


Figure S48. TGA thermogram for polyerythritan camphorate (Table S1, Entry 7)

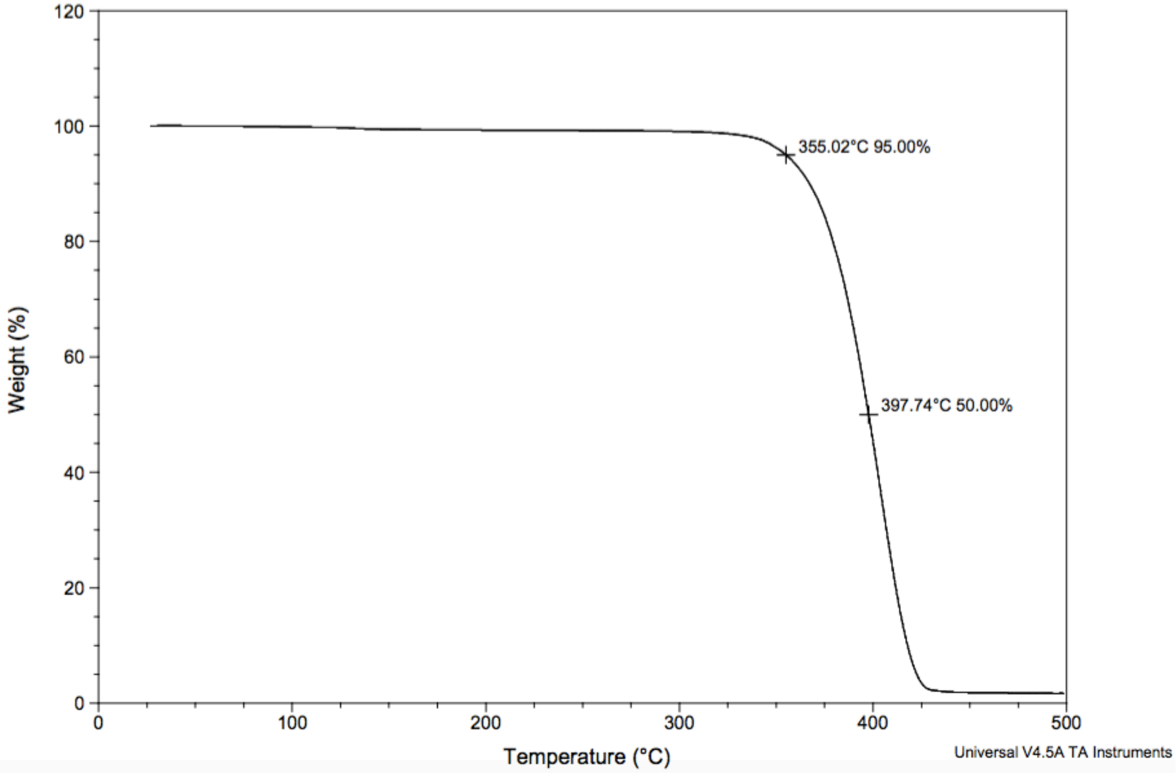


Figure S49. TGA thermogram for polyisosorbide camphorate (Table S1, Entry 8)

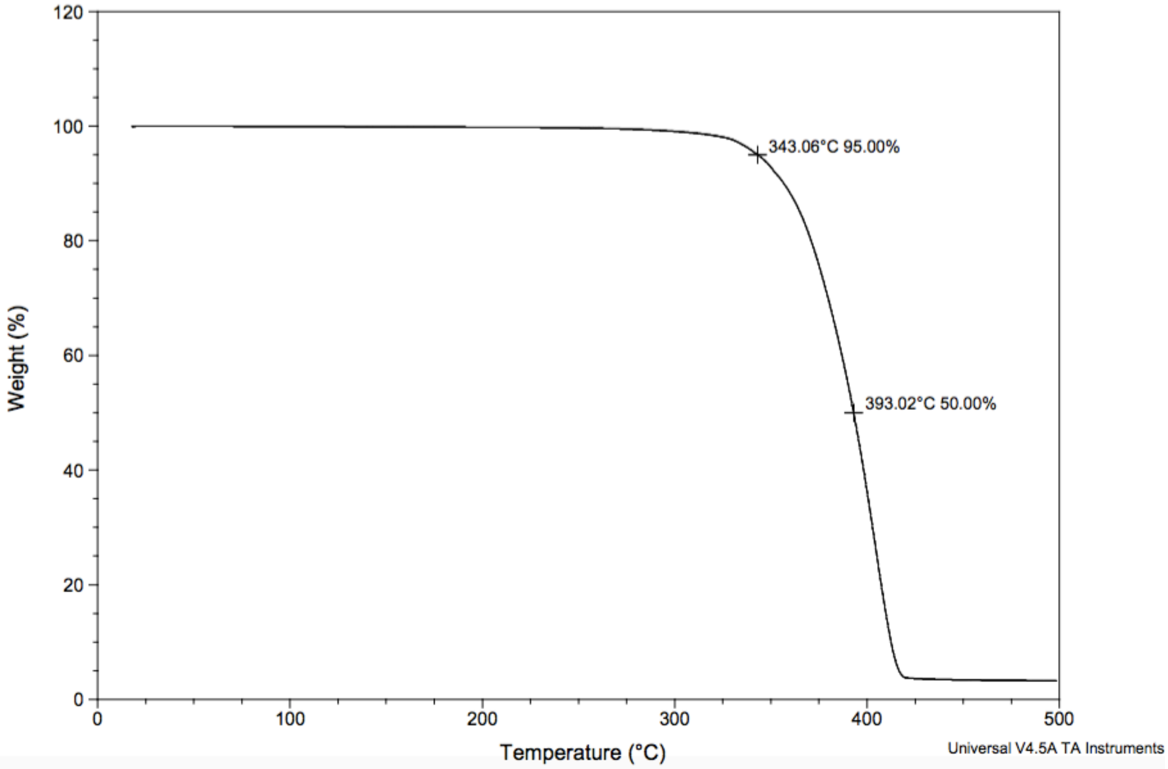


Figure S50. TGA thermogram for polyBHEC (Table S2, Entry 1)

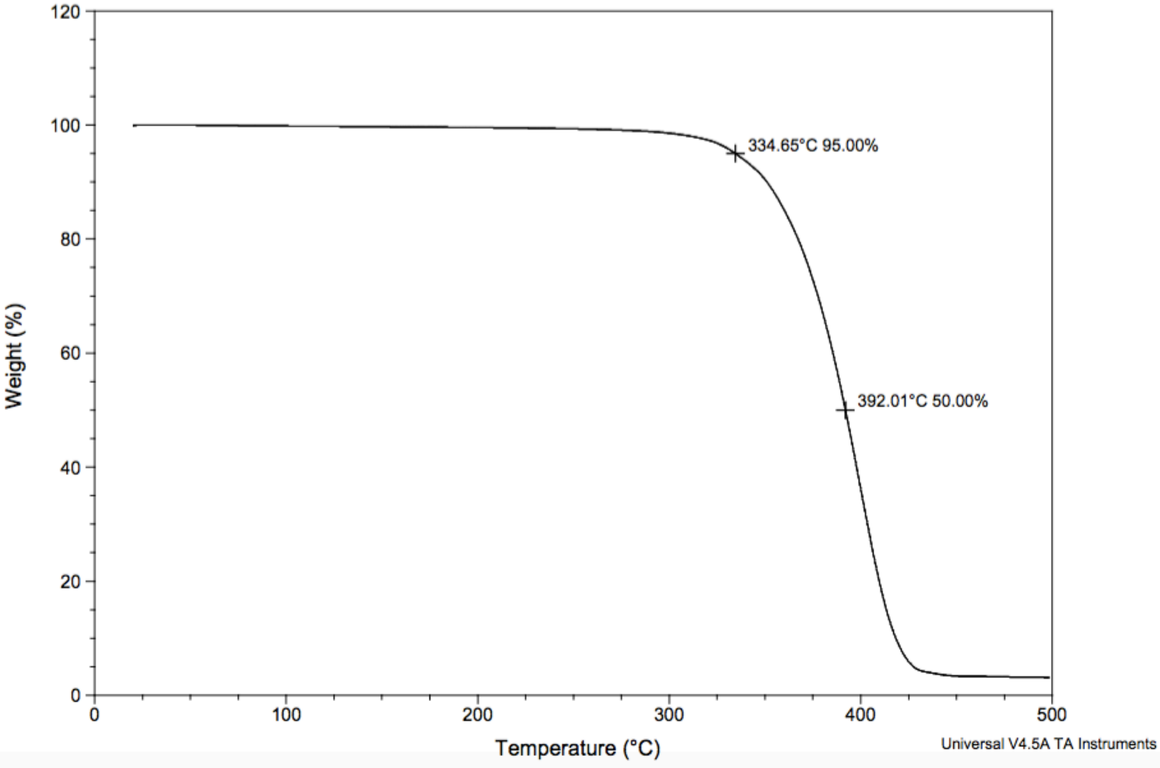


Figure S51. TGA thermogram for poly(BHEC/BHET) with 90% BHEC (Table S2, Entry 2)

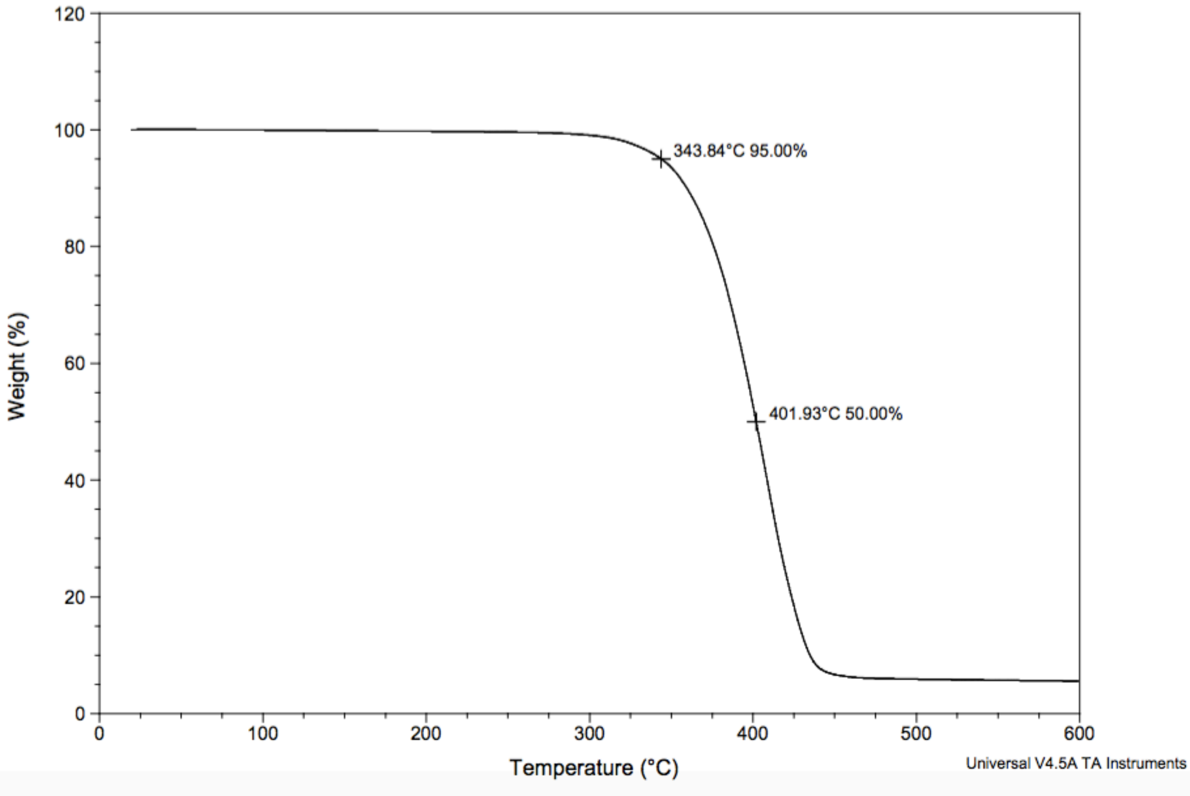


Figure S52. TGA thermogram for poly(BHEC/BHET) with 80% BHEC (Table S2, Entry 3)

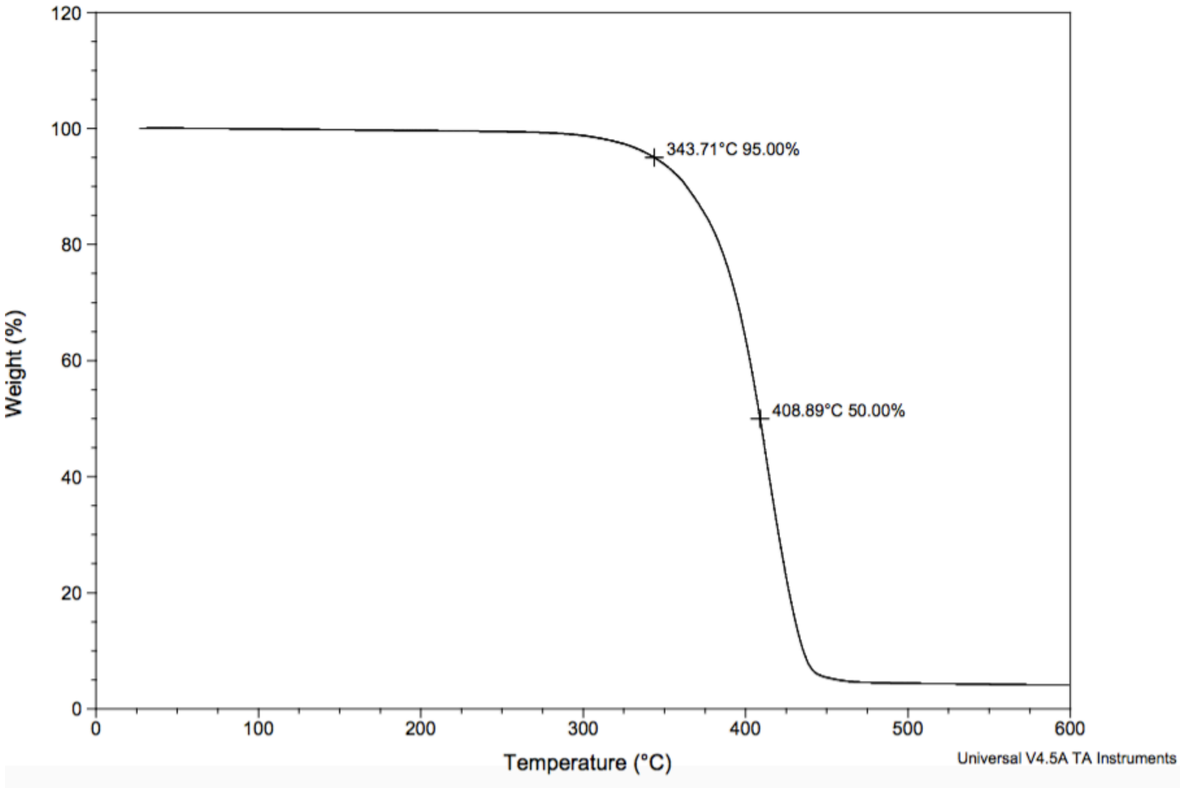


Figure S53. TGA thermogram for poly(BHEC/BHET) with 70% BHEC (Table S2, Entry 4)

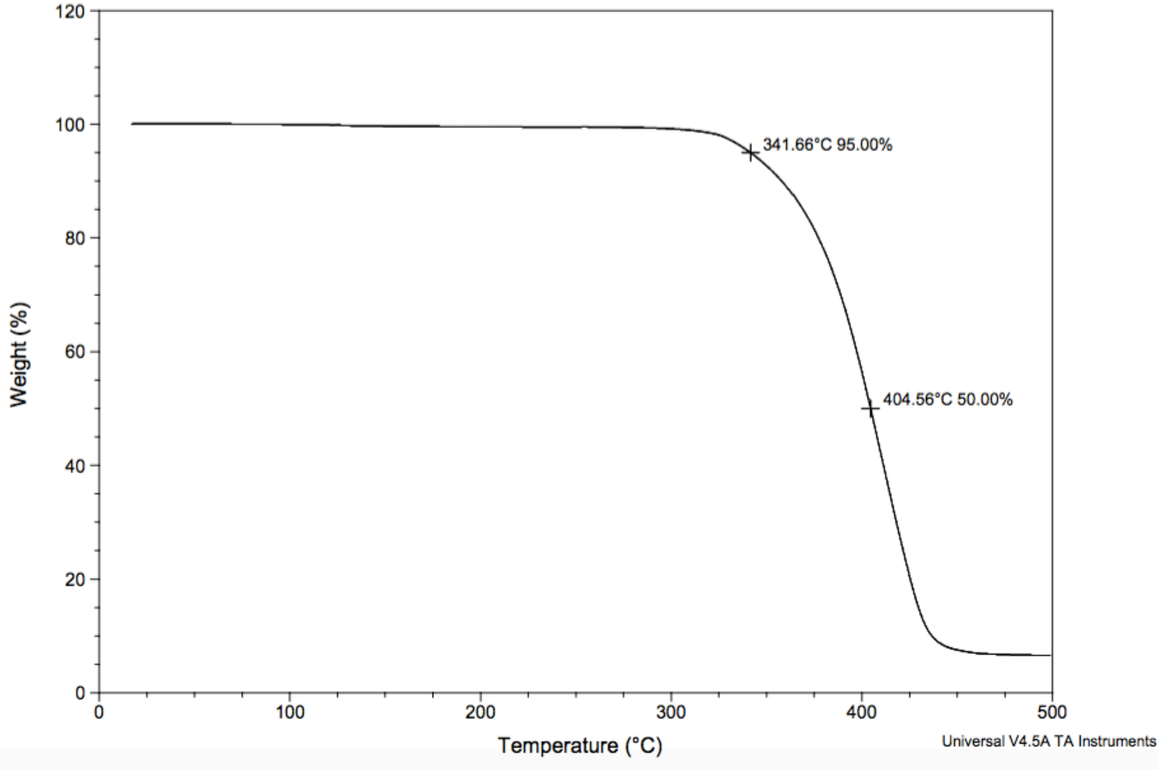


Figure S54. TGA thermogram for poly(BHEC/BHET) with 60% BHEC (Table S2, Entry 5)

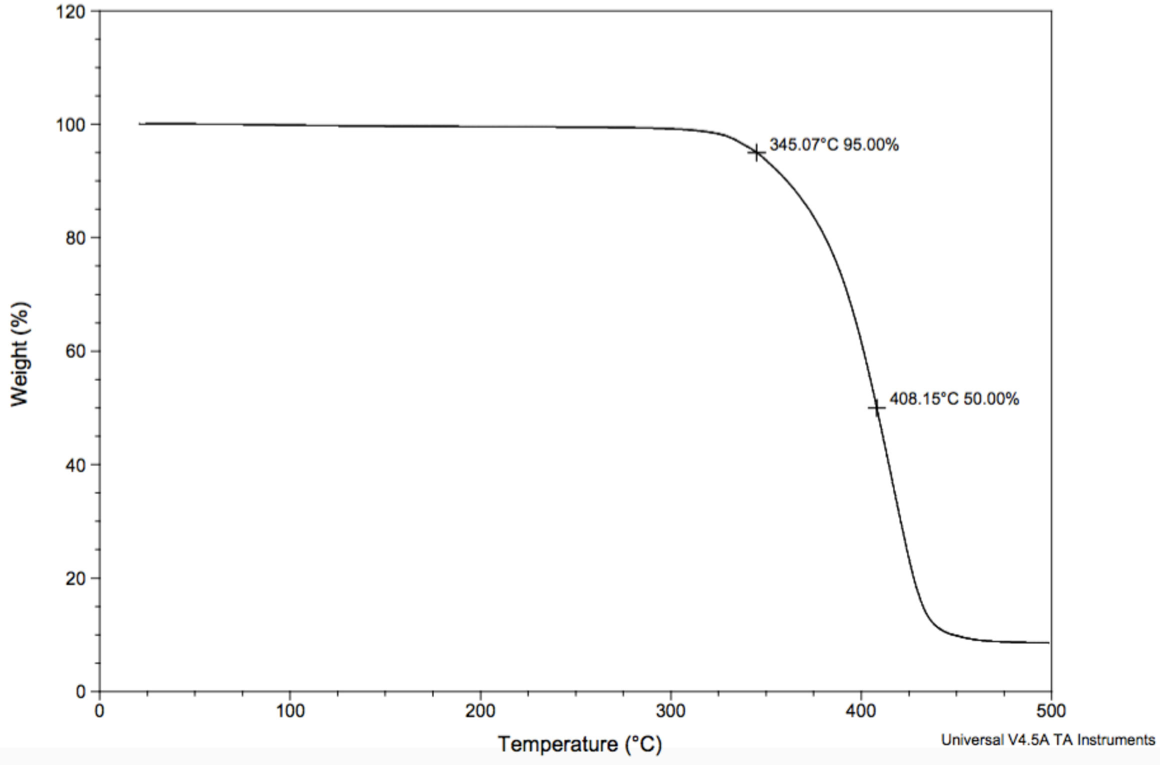


Figure S55. TGA thermogram for poly(BHEC/BHET) with 50% BHEC (Table S2, Entry 6)

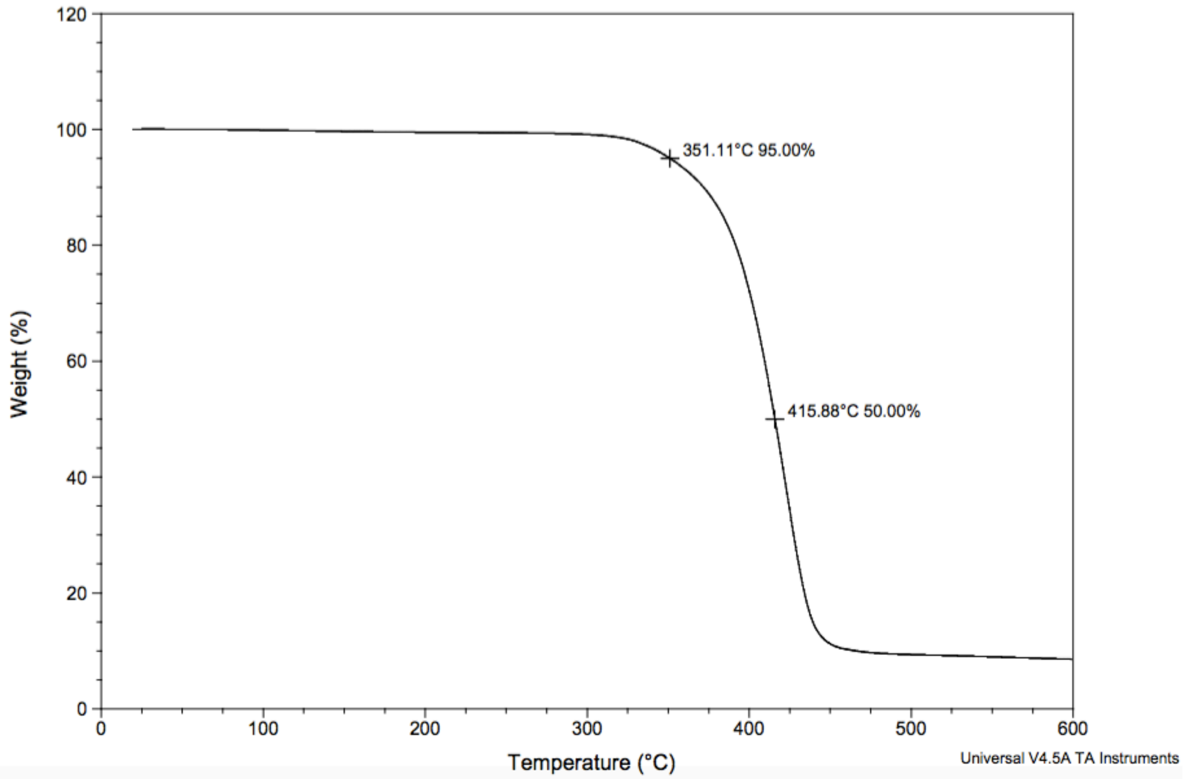


Figure S56. TGA thermogram for poly(BHEC/BHET) with 40% BHEC (Table S2, Entry 7)

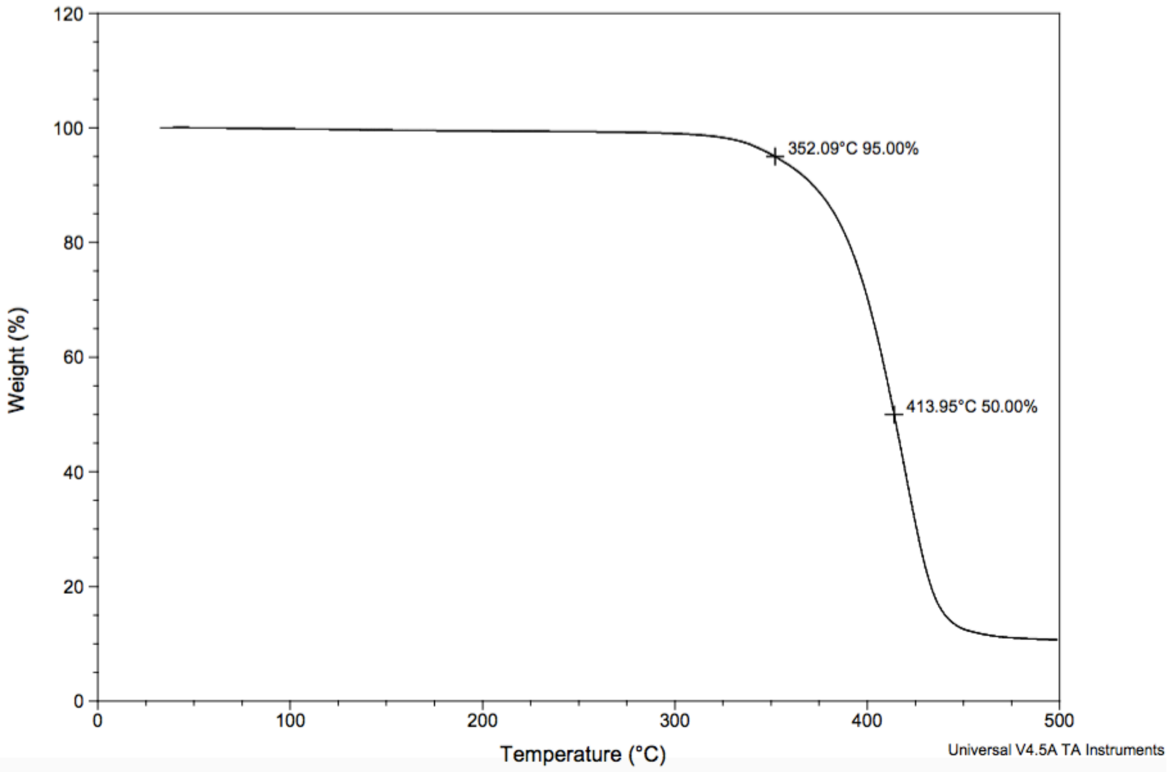


Figure S57. TGA thermogram for poly(BHEC/BHET) with 30% BHEC (Table S2, Entry 8)

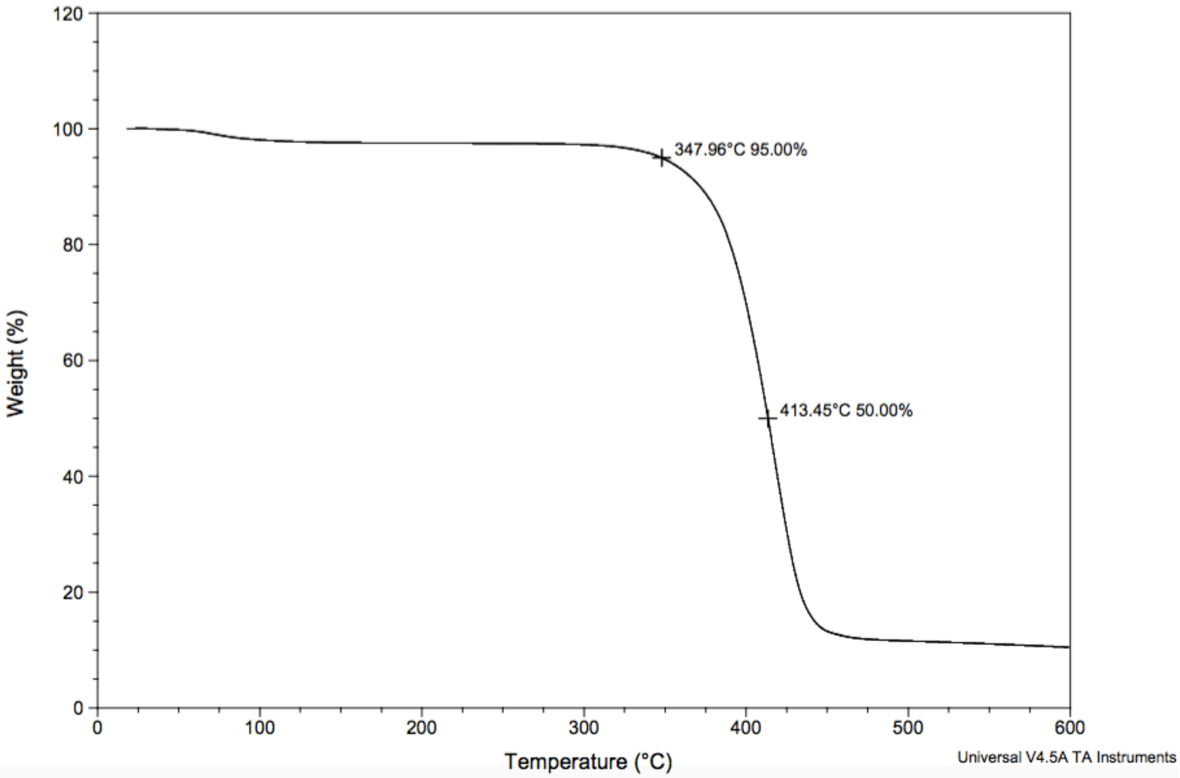


Figure S58. TGA thermogram for poly(BHEC/BHET) with 20% BHEC (Table S2, Entry 9)

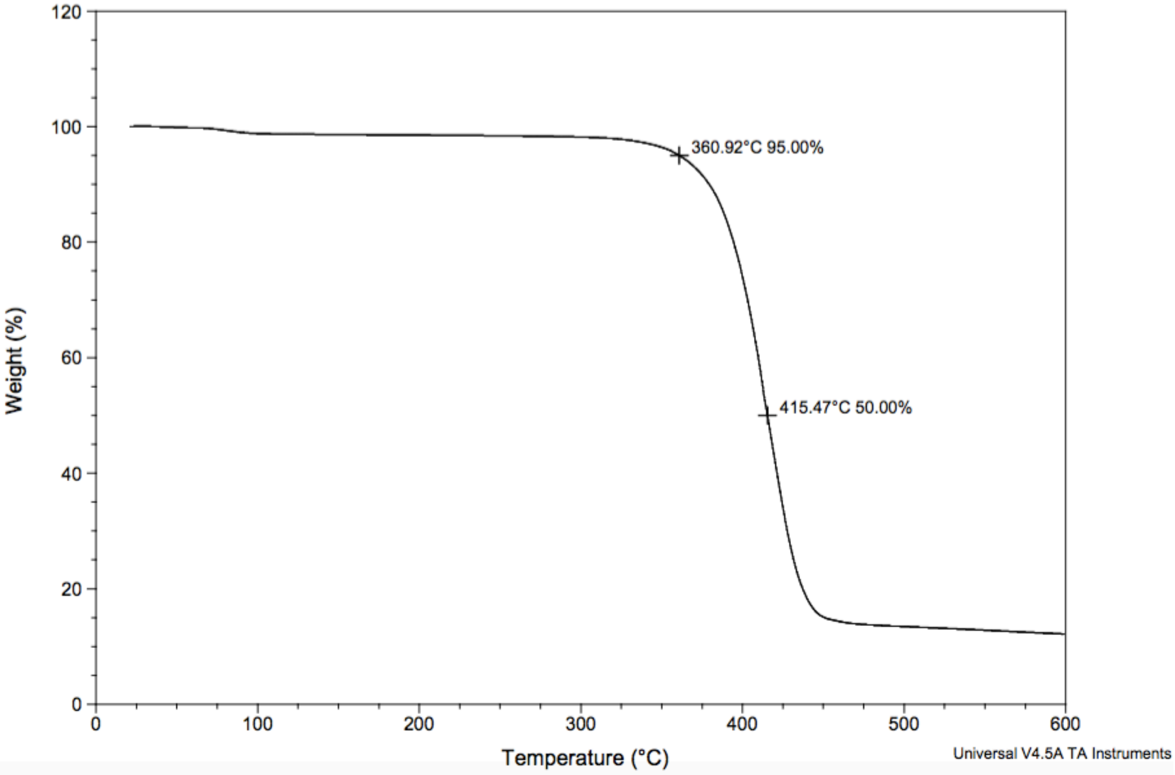


Figure S59. TGA thermogram for poly(BHEC/BHET) with 10% BHEC (Table S2, Entry 10)

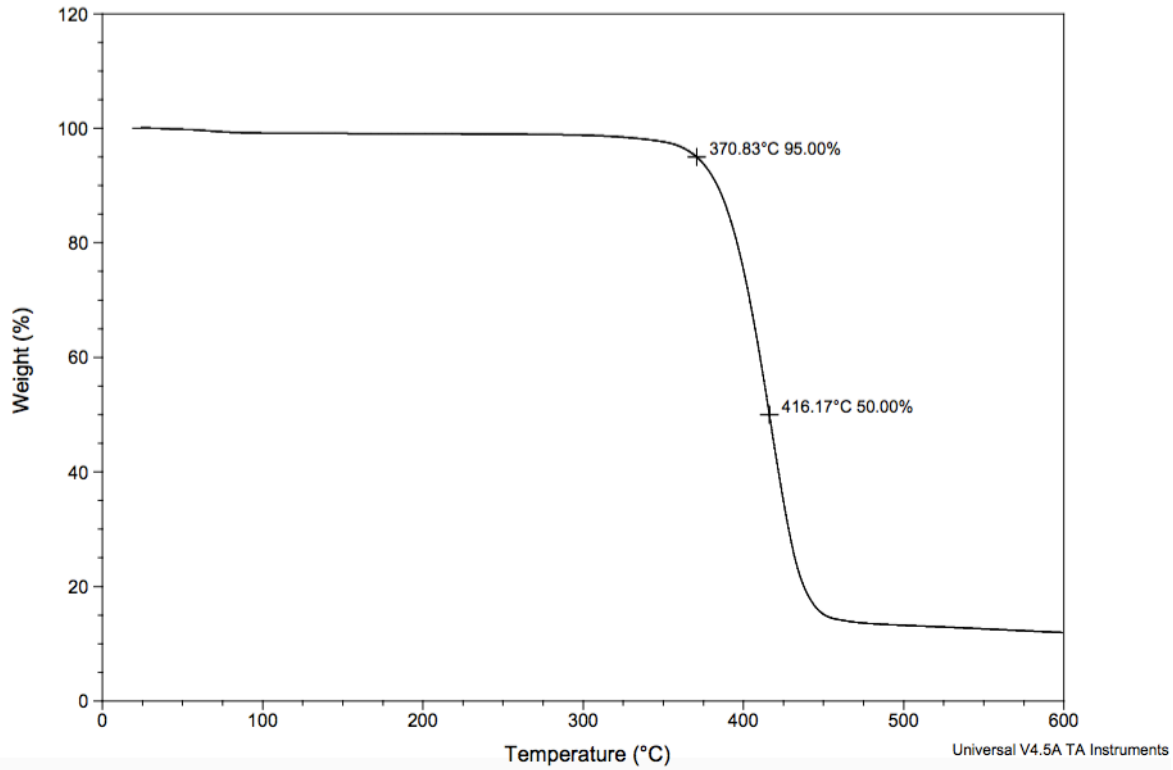


Figure S60. TGA thermogram polyBHET (Table S2, Entry 11)

^{1}H NMR Data

Monomers:

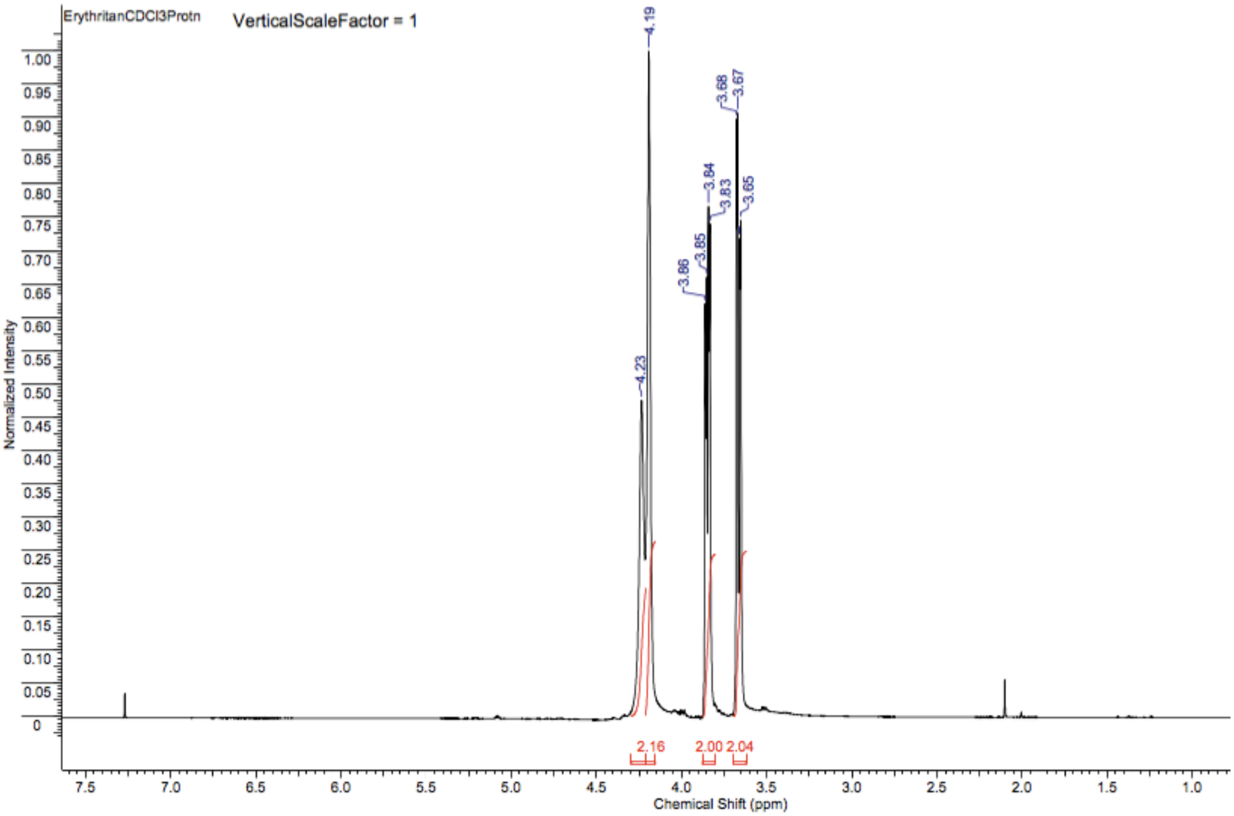


Figure S61. ^{1}H NMR of erythritan monomer

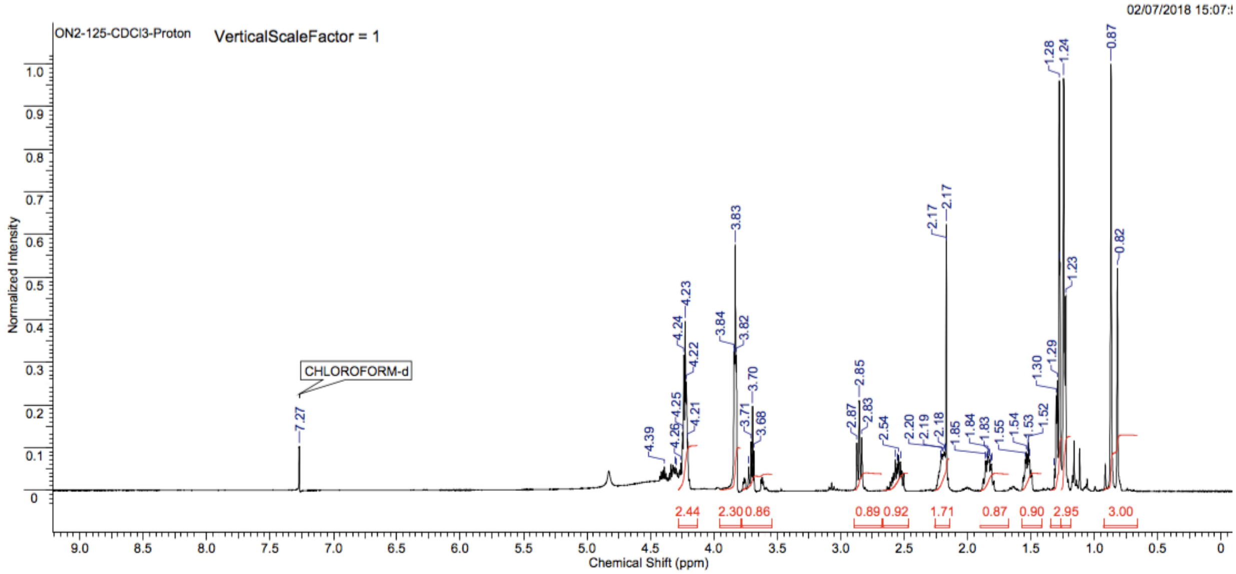


Figure S62. ^{1}H NMR of bis(2-hydroxyethyl) camphorate (BHEC) monomer

Polymers:

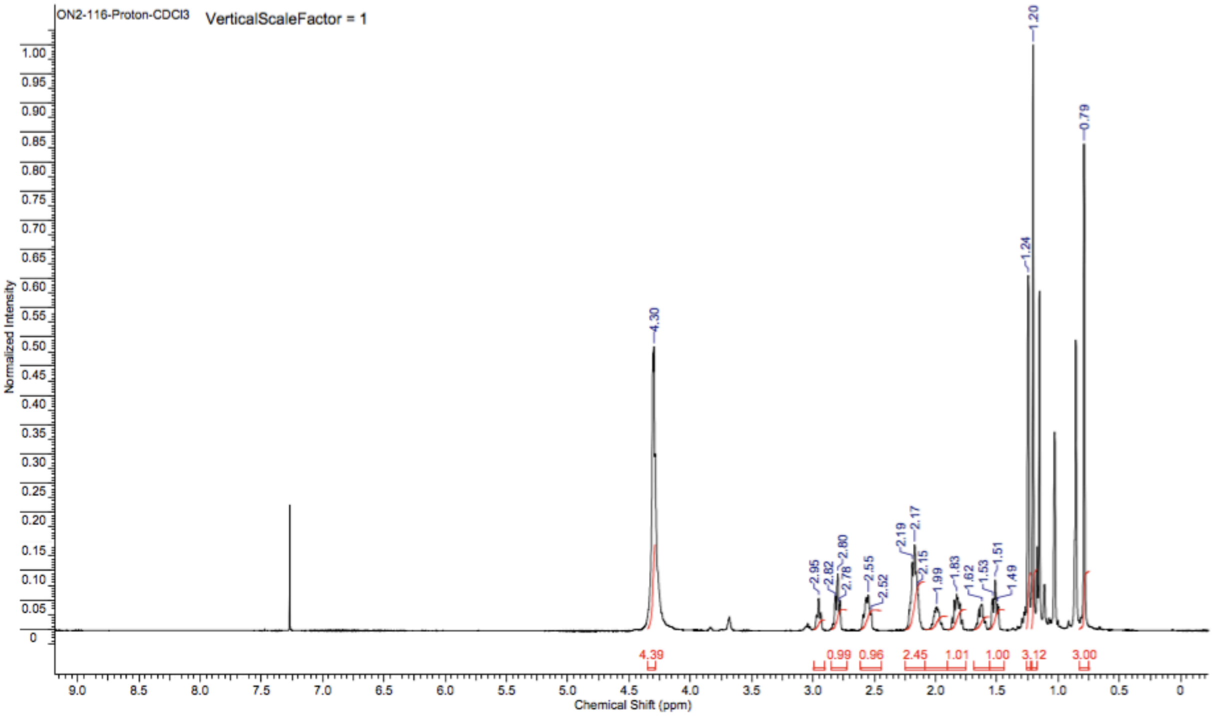


Figure S63. ^{1}H NMR of polyethylene camphorate (Table S1, Entry 1)

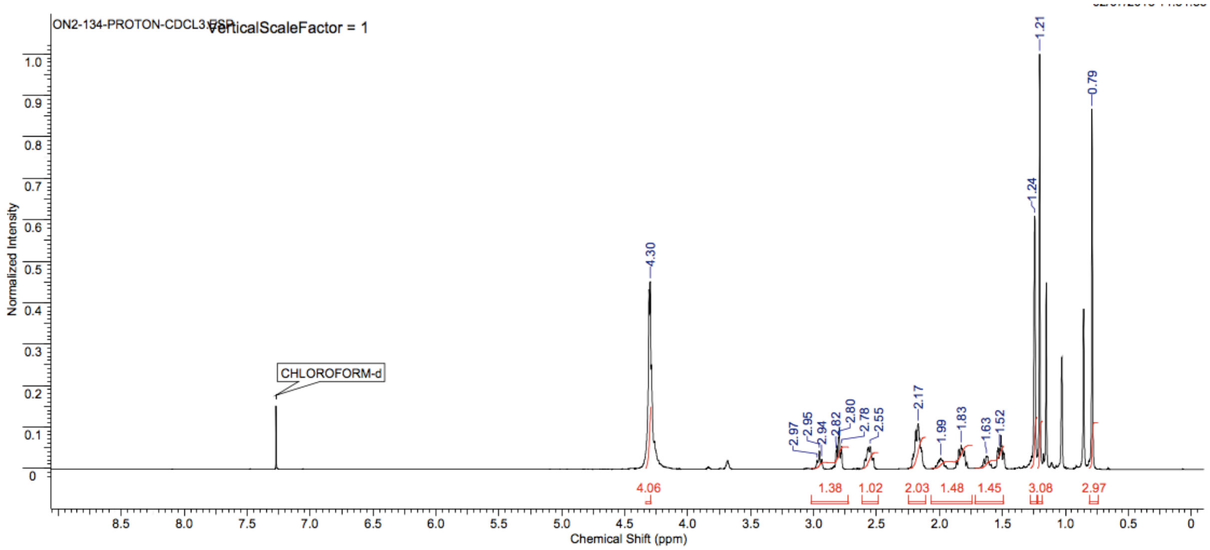


Figure S64. ^{1}H NMR of polyethylene camphorate [dual catalyst] (Table S1, Entry 2)

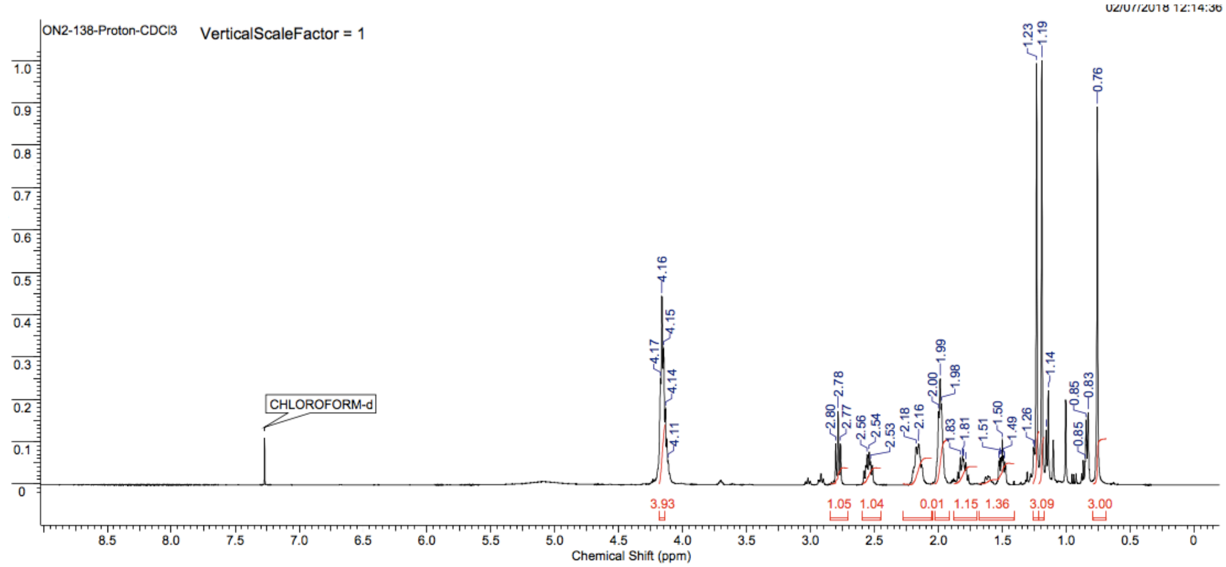


Figure S65. ^{1}H NMR of polypropylene camphorate (Table S1, Entry 3)

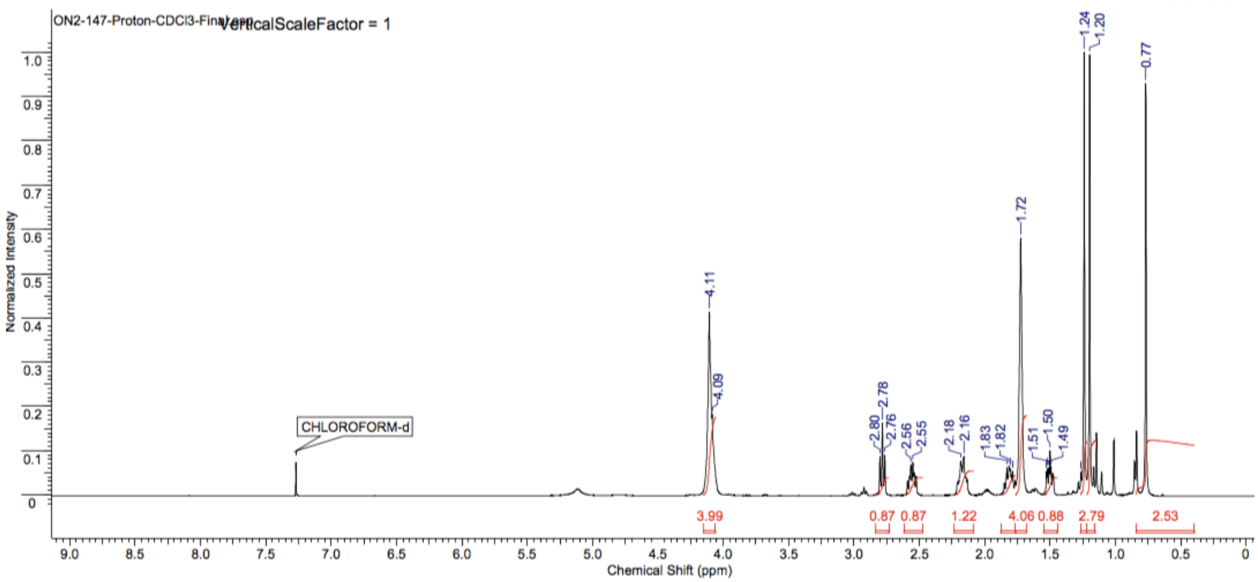


Figure S66. ^{1}H NMR of polybutylene camphorate (Table S1, Entry 4)

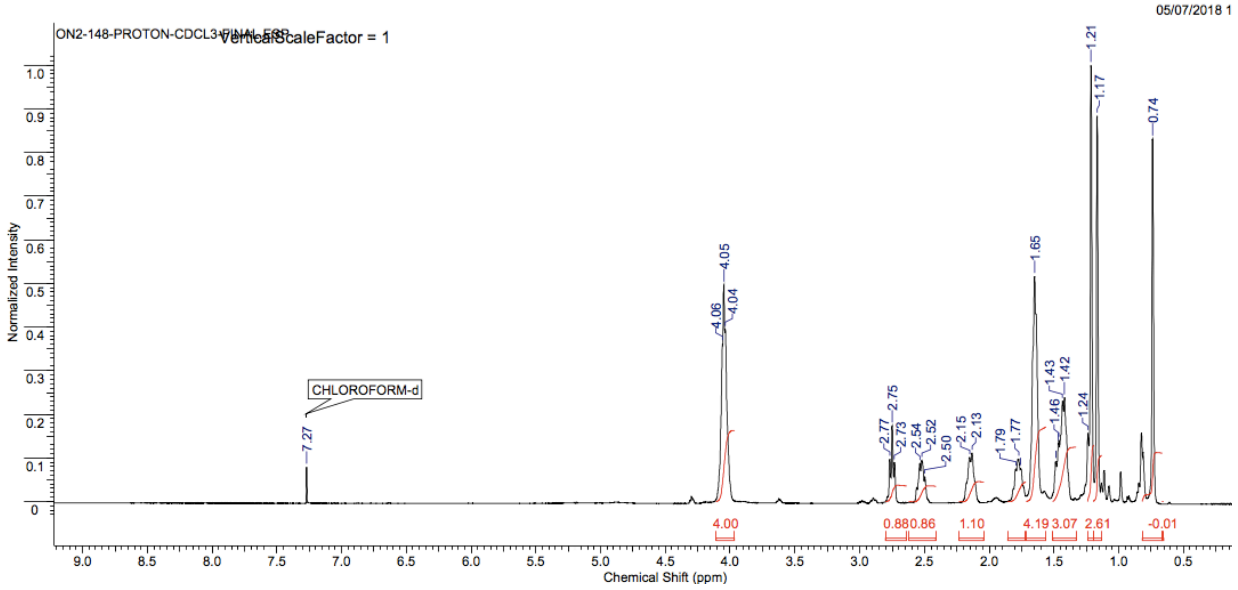


Figure S67. ^{1}H NMR of polypentylene camphorate (Table S1, Entry 5)

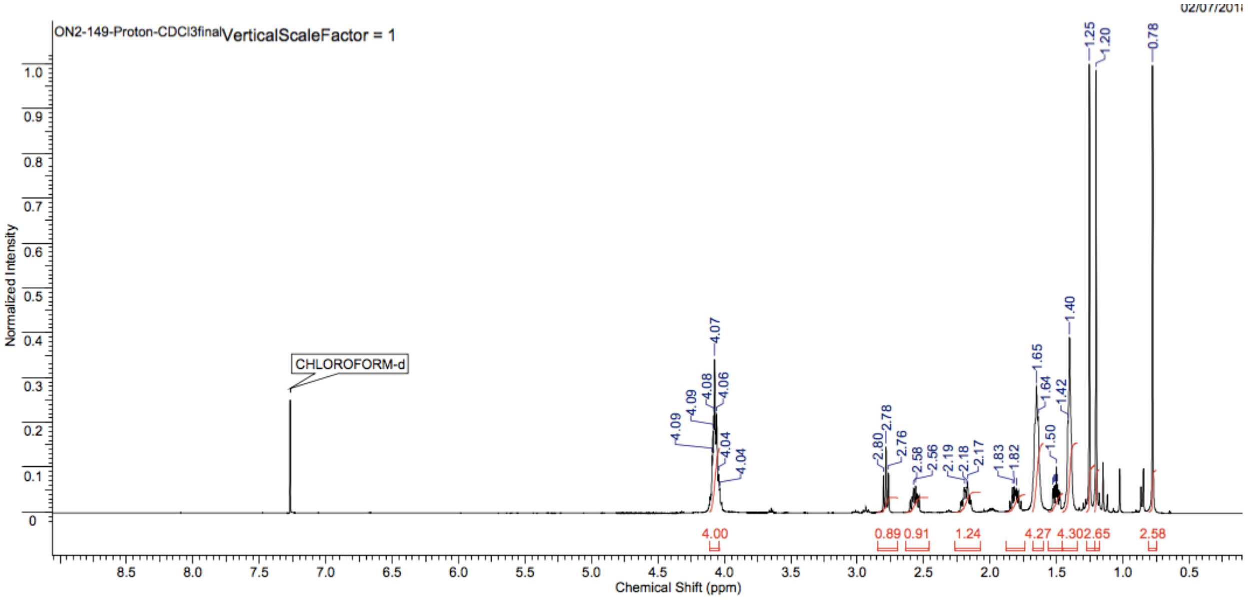


Figure S68. ^{1}H NMR of polyhexylene camphorate (Table S1, Entry 6)

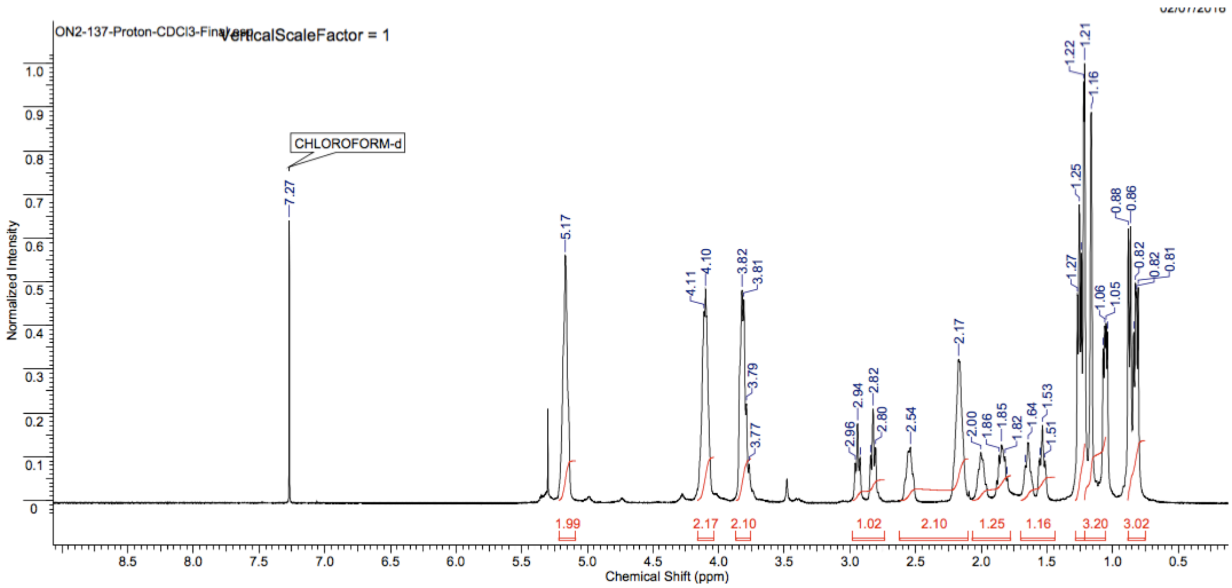


Figure S69. ^{1}H NMR of polyerythritan camphorate (Table S1, Entry 7)

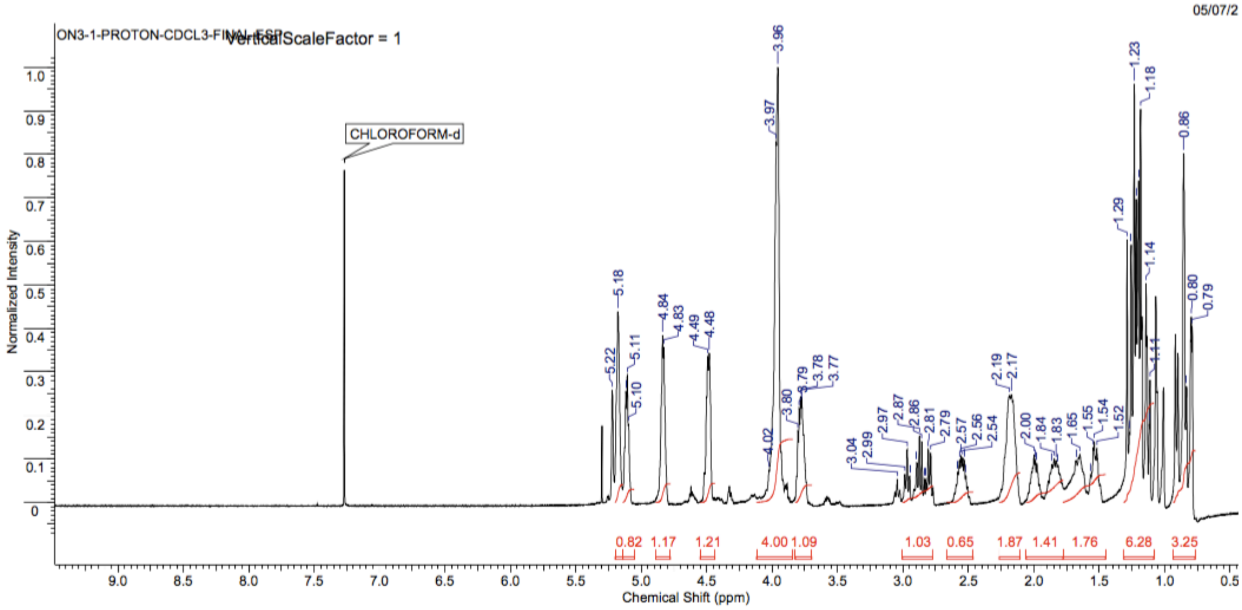


Figure S70. ^{1}H NMR of polyisosorbide camphorate (Table S1, Entry 8)

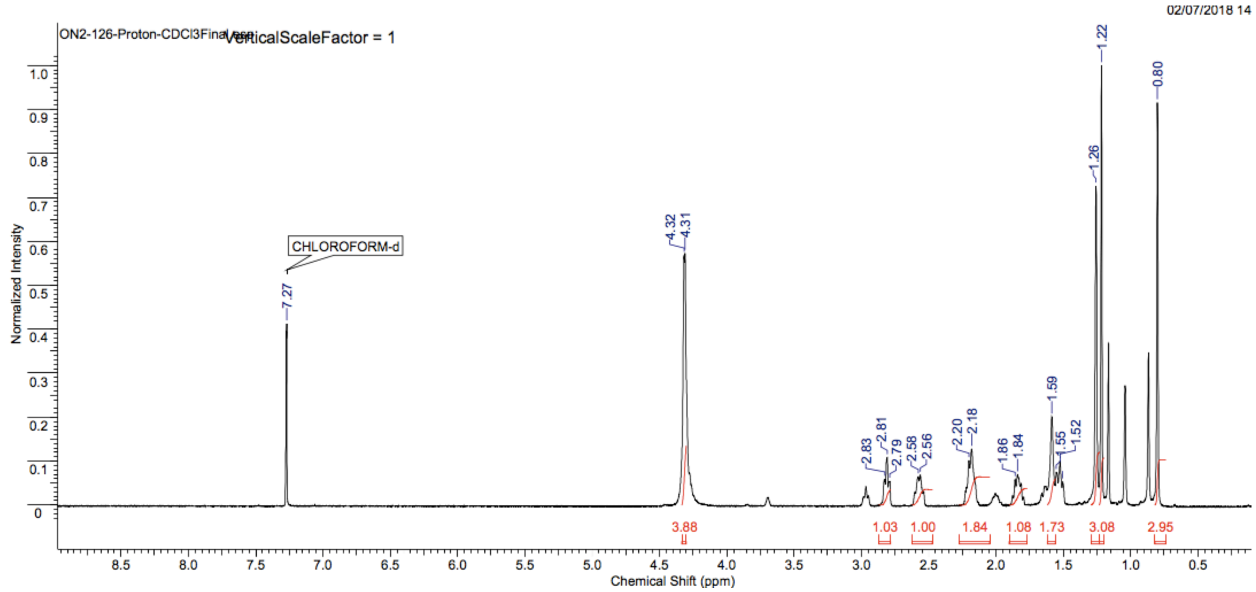


Figure S71. ^{1}H NMR of polyBHEC (Table S2, Entry 1)

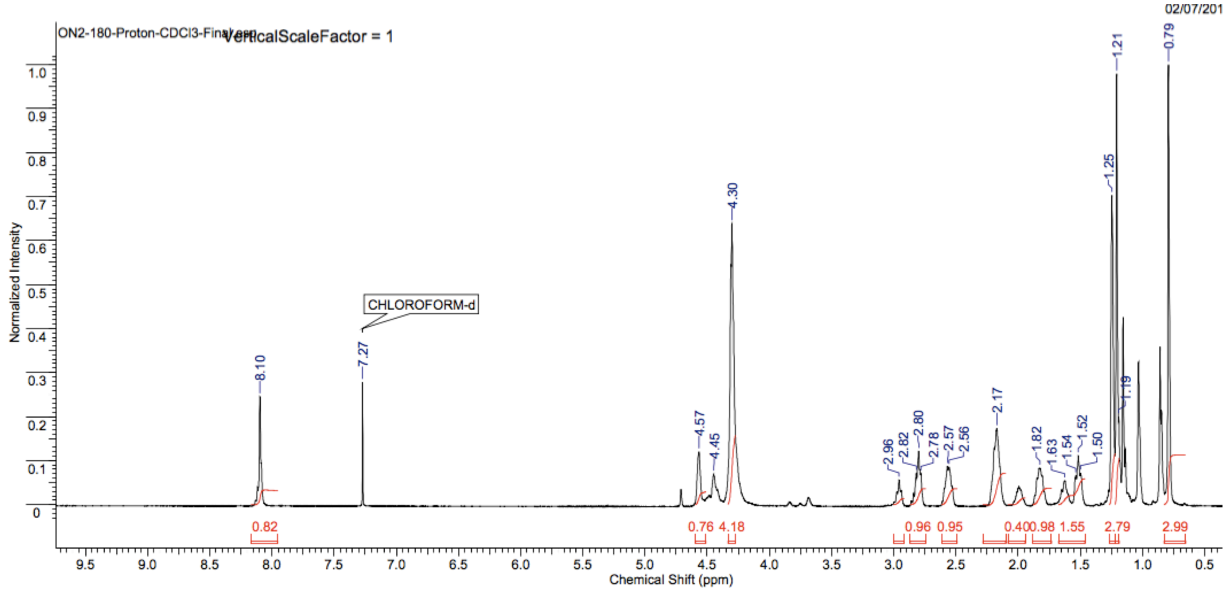


Figure S72. ^{1}H NMR of poly(BHEC/BHET) with 90% BHEC (Table S2, Entry 2)

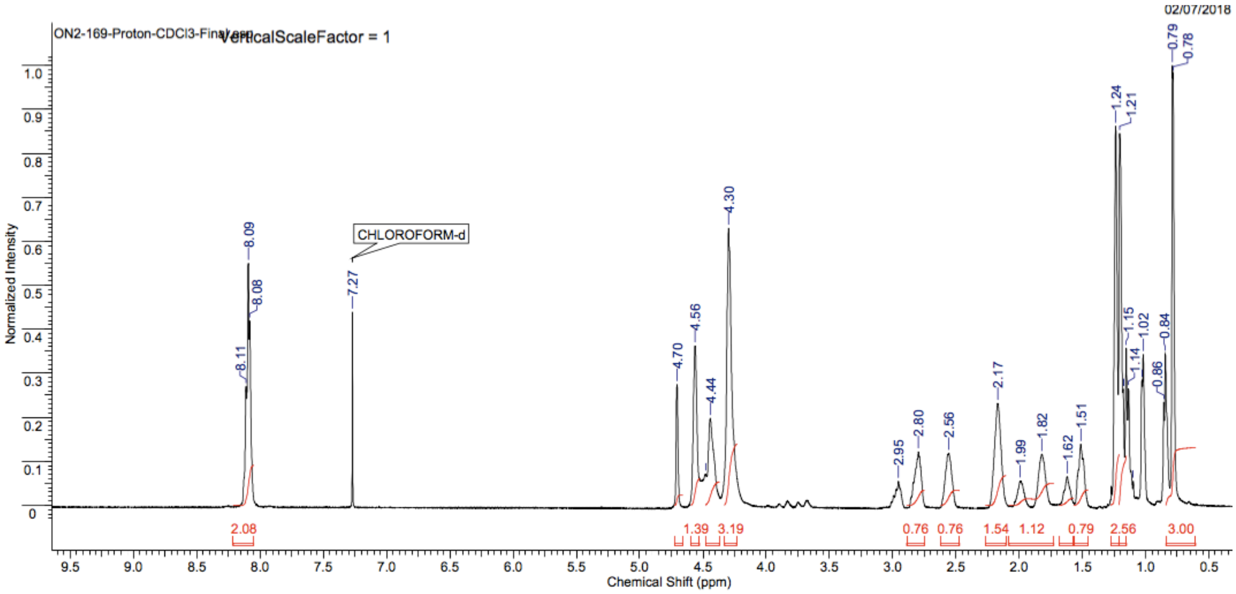


Figure S73. ^{1}H NMR of poly(BHEC/BHET) with 80% BHEC (Table S2, Entry 3)

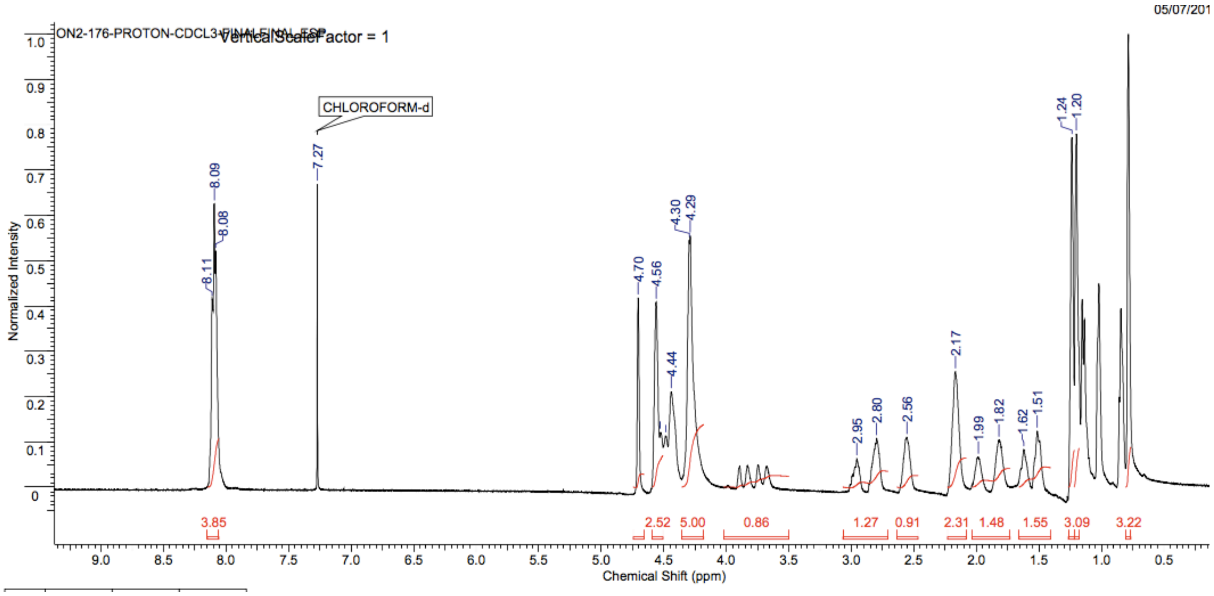


Figure S74. ^{1}H NMR of poly(BHEC/BHET) with 70% BHEC Table (S2, Entry 4)

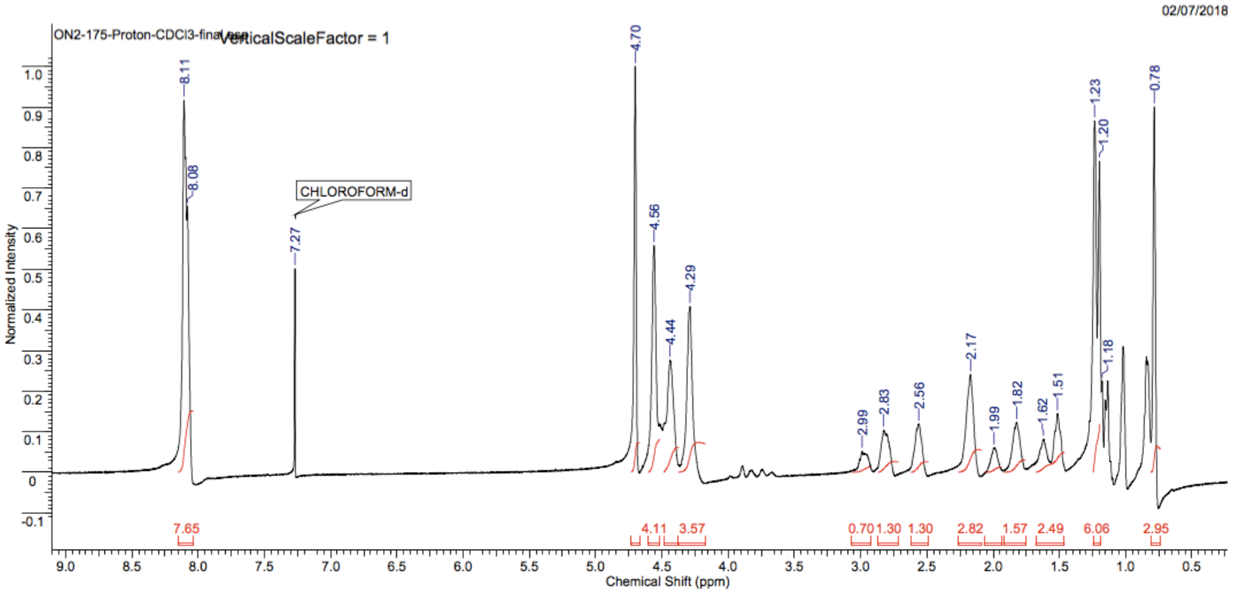


Figure S75. ^{1}H NMR of poly(BHEC/BHET) with 60% BHEC (Table S2, Entry 5)

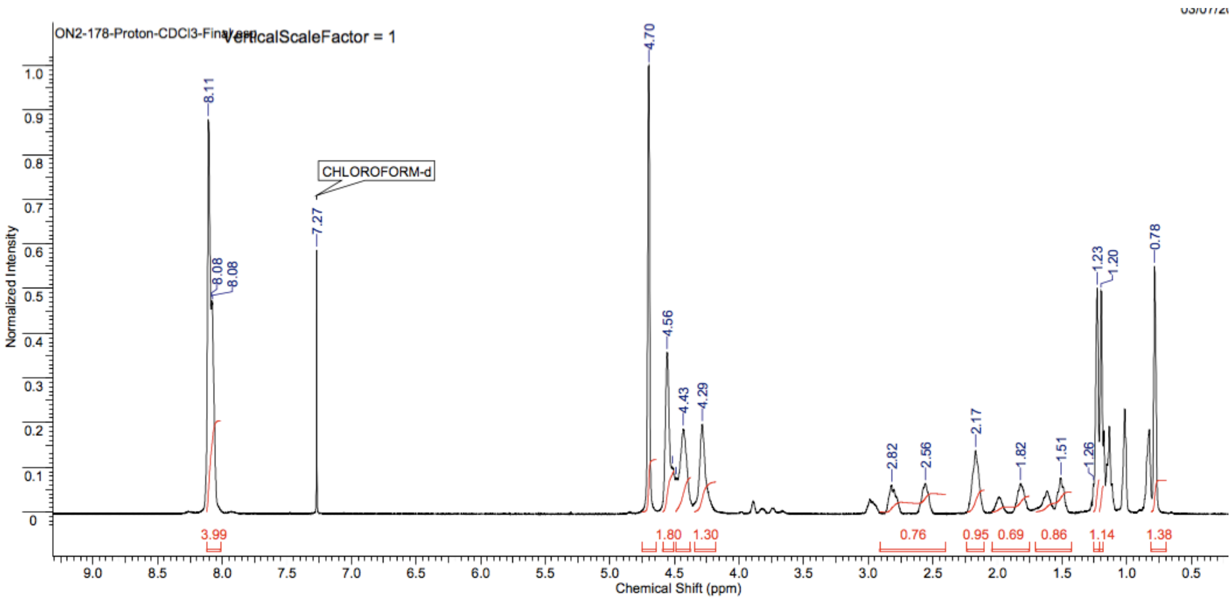


Figure S76. ^{1}H NMR of poly(BHEC/BHET) with 50% BHEC (Table S2, Entry 6)

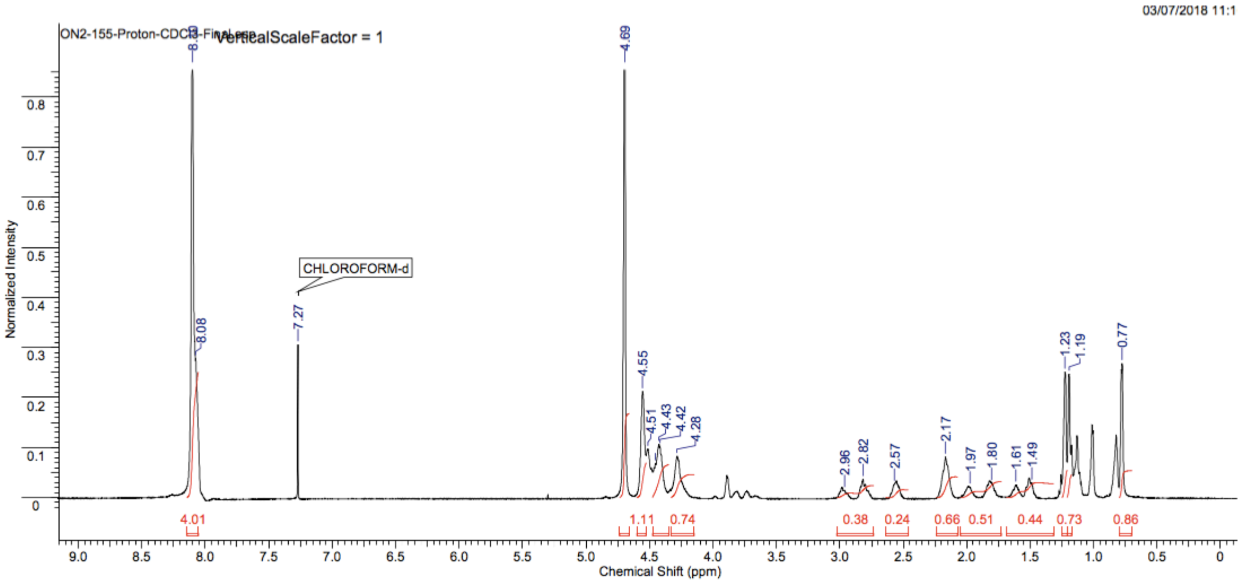


Figure S77. ^{1}H NMR of poly(BHEC/BHET) with 40% BHEC (Table S2, Entry 7)

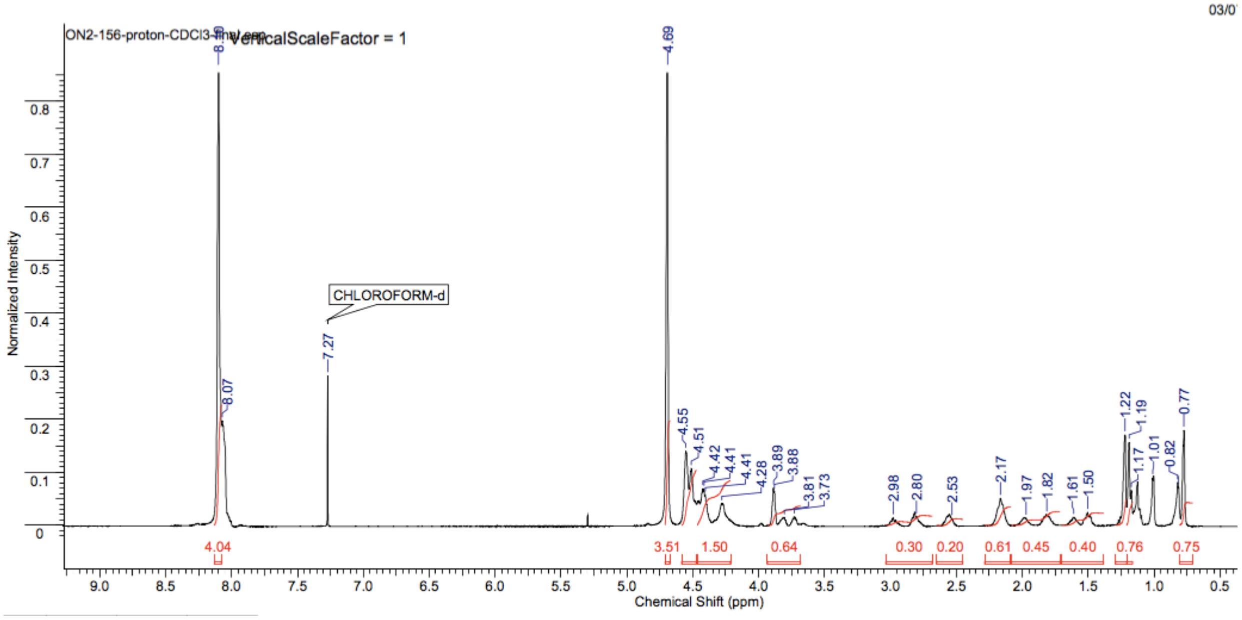


Figure S78. ^{1}H NMR of poly(BHEC/BHET) with 30% BHEC (Table S2, Entry 8)

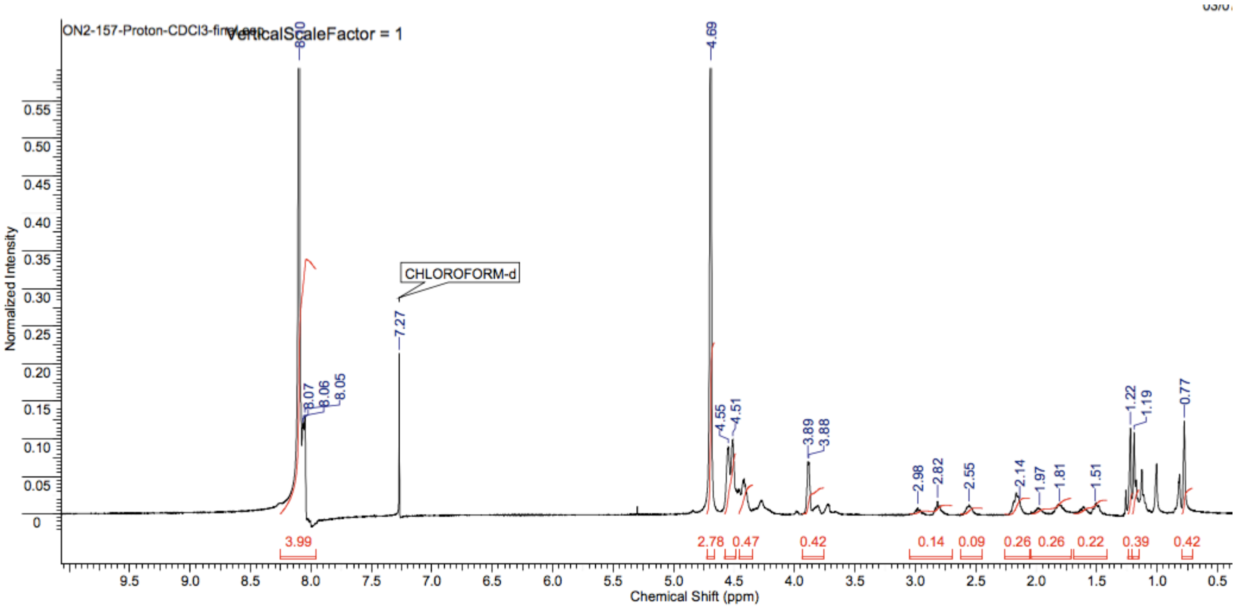


Figure S79. ^{1}H NMR of poly(BHEC/BHET) with 20% BHEC (Table S2, Entry 9)

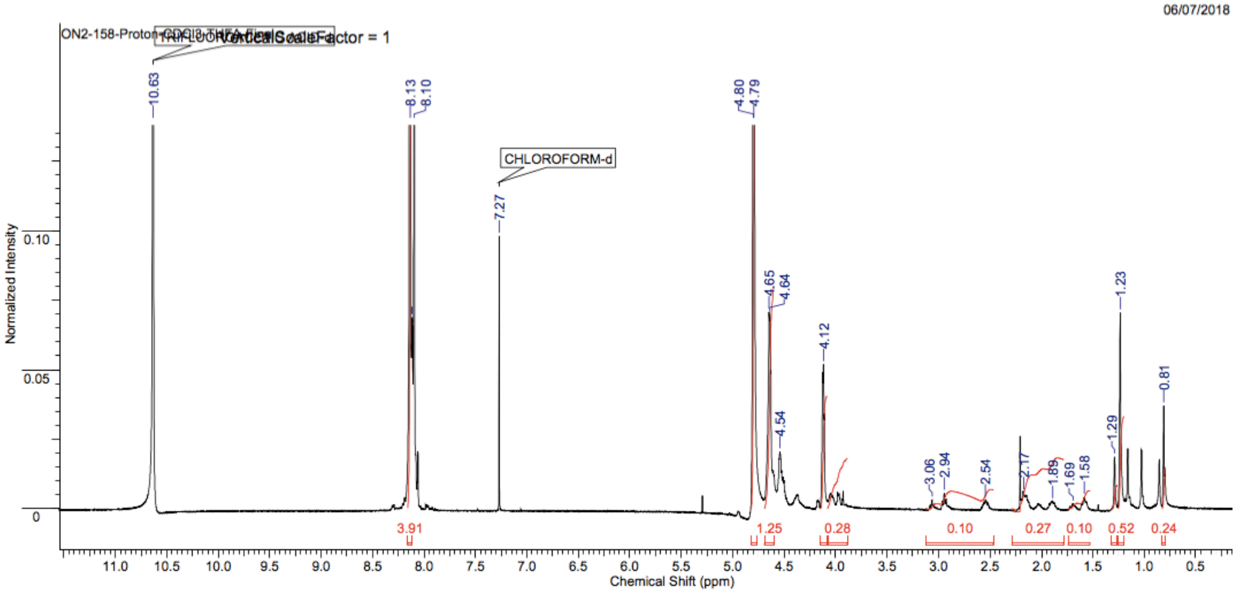


Figure S80. ^{1}H NMR of poly(BHEC/BHET) with 10% BHEC (Table S2, Entry 10)

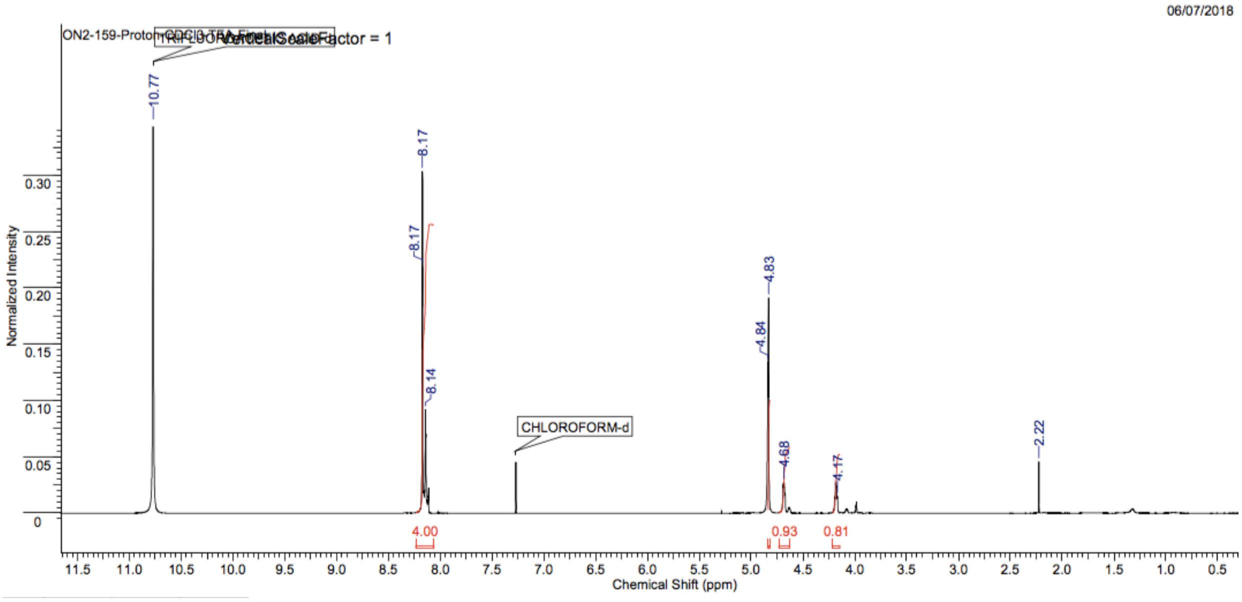


Figure S81. ^{1}H NMR of polyBHET (Table S2, Entry 11)

^{13}C NMR Data

Monomers:

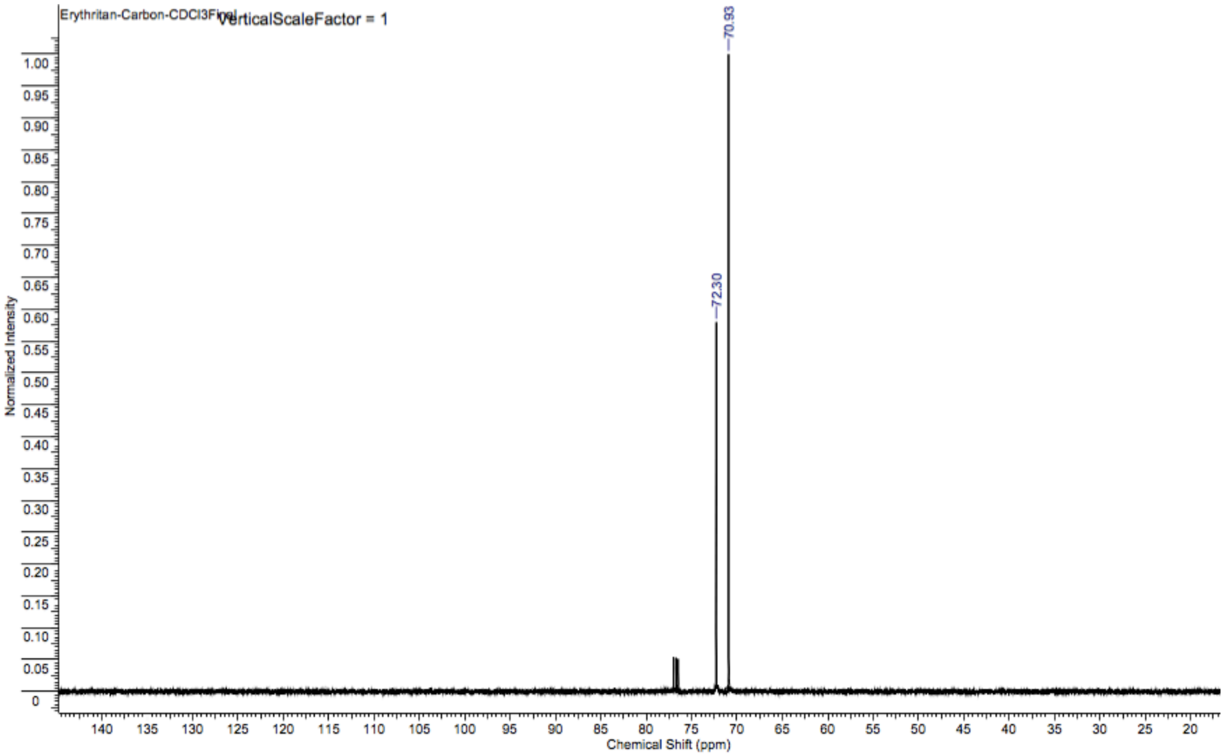


Figure S82. ^{13}C NMR of erythritan monomer

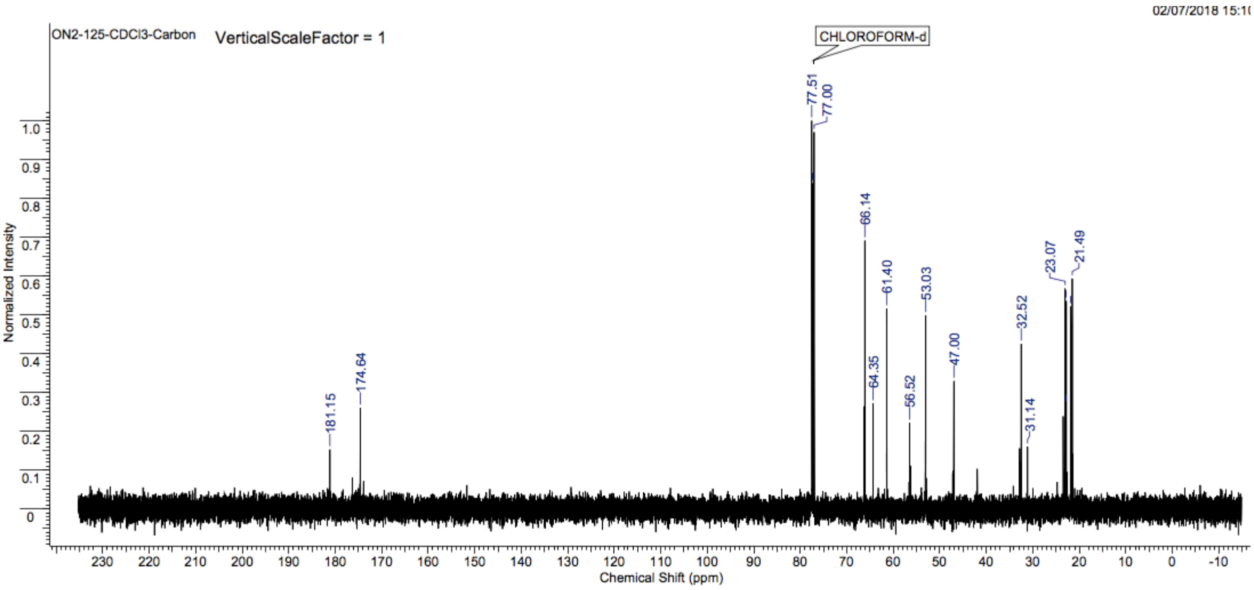


Figure S83. ^{13}C NMR of bis(2-hydroxyethyl) camphorate (BHEC) monomer

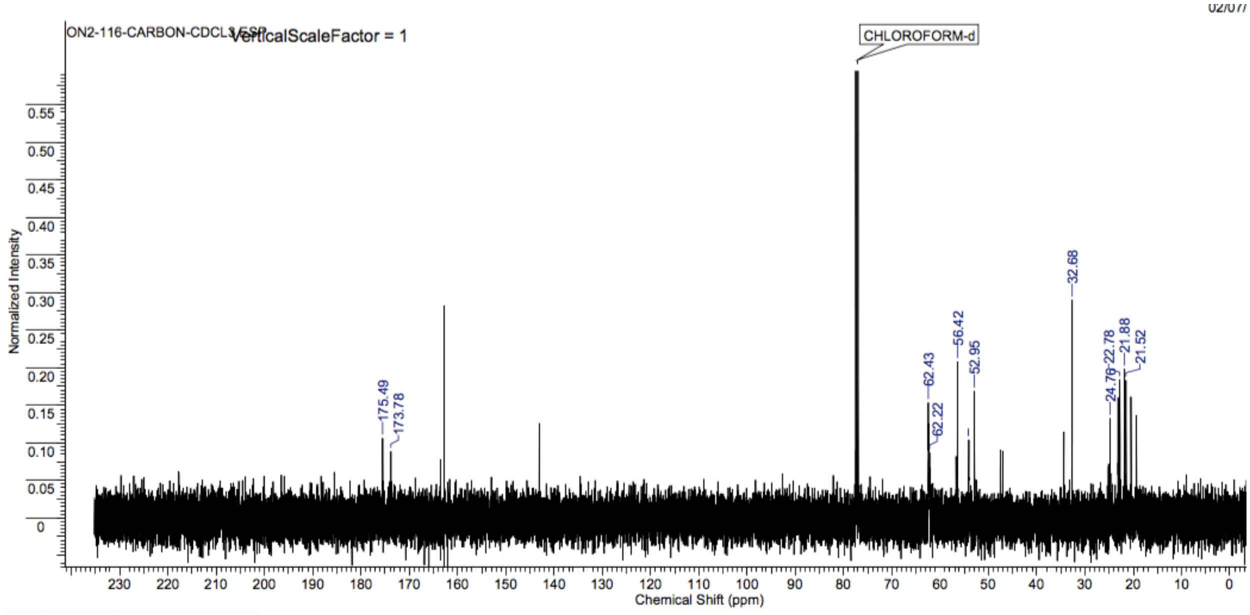


Figure S84. ^{13}C NMR of polyethylene camphorate (Table S1, Entry 1)

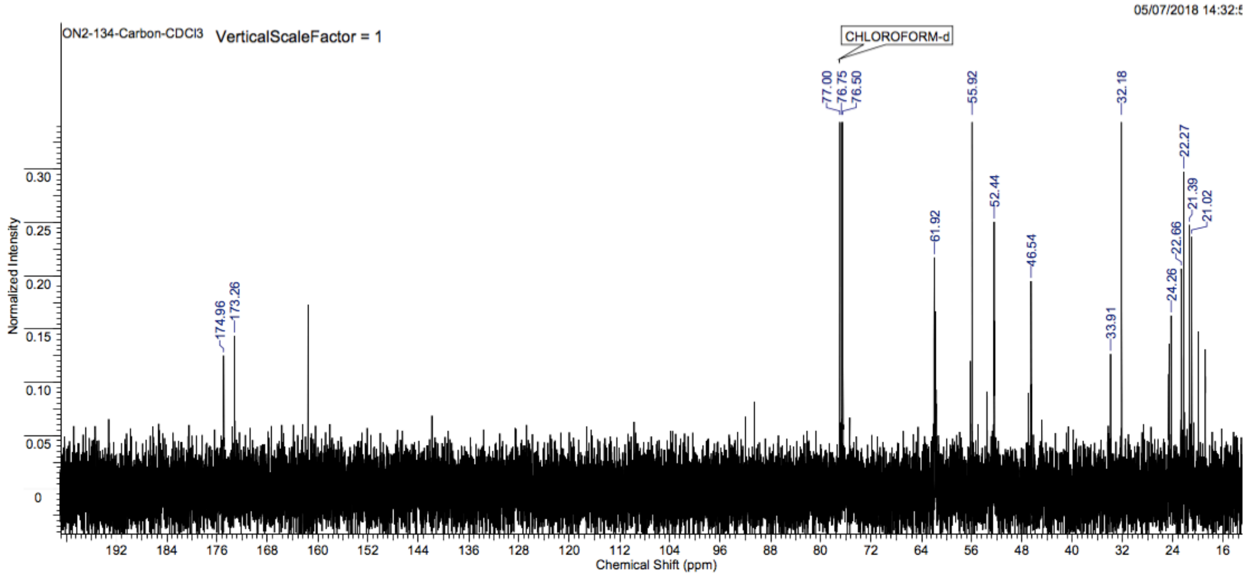


Figure S85. ^{13}C NMR of polyethylene camphorate [dual catalyst] (Table S1, Entry 2)

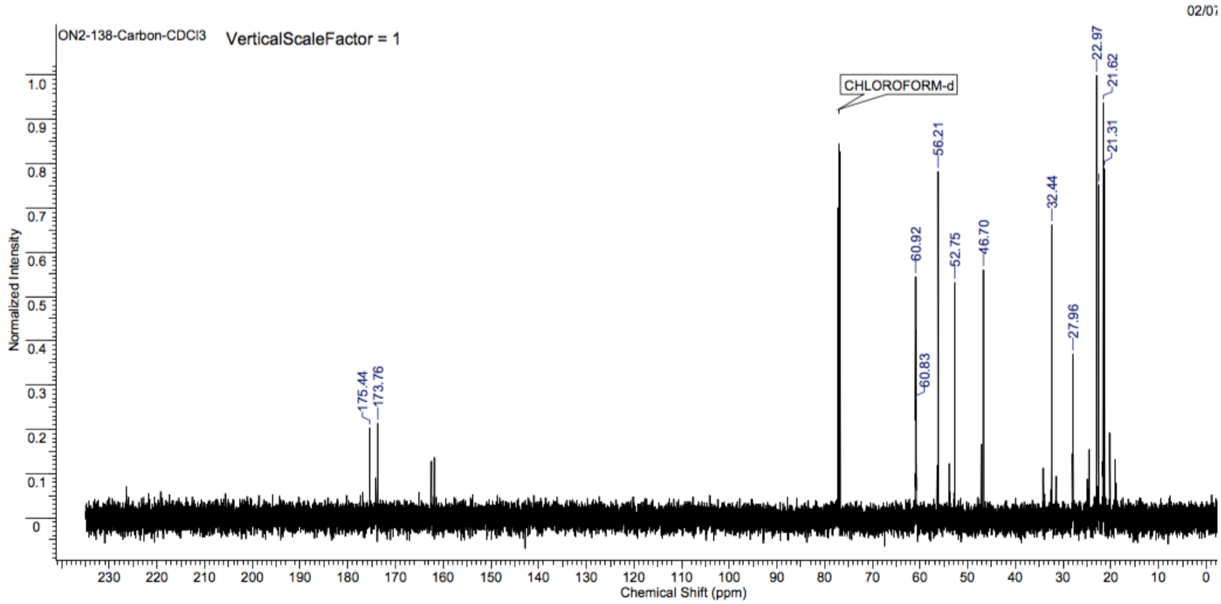


Figure S86. ^{13}C NMR of polypropylene camphorate (Table S1, Entry 3)

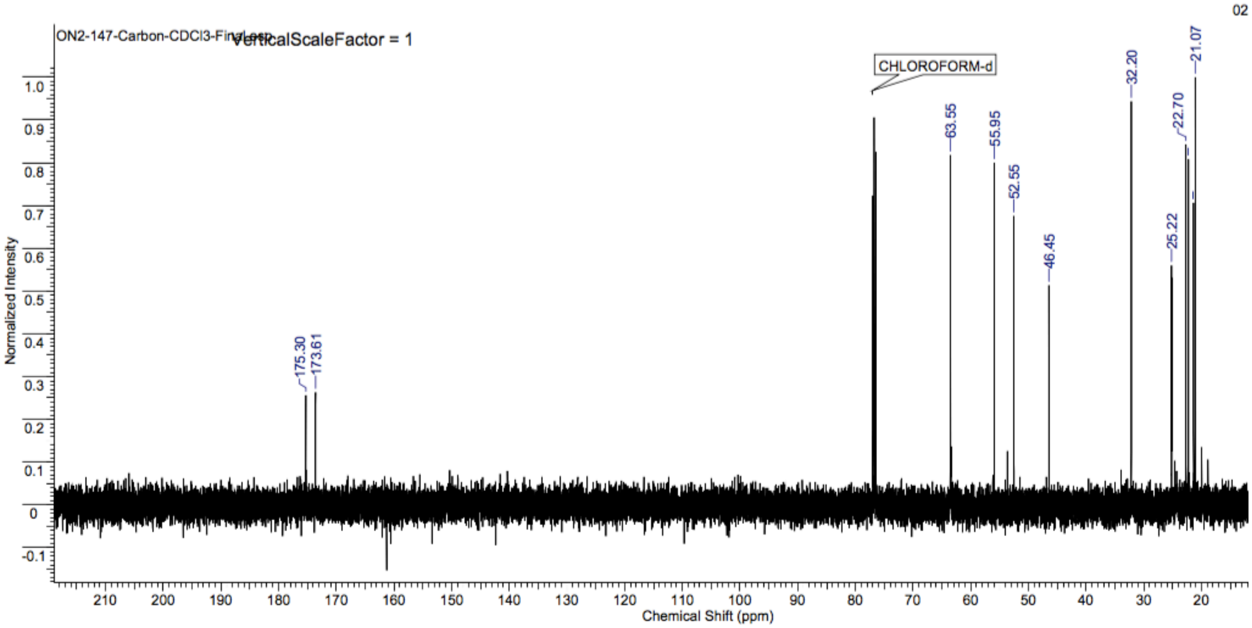


Figure S87. ^{13}C NMR of polybutylene camphorate (Table S1, Entry 4)

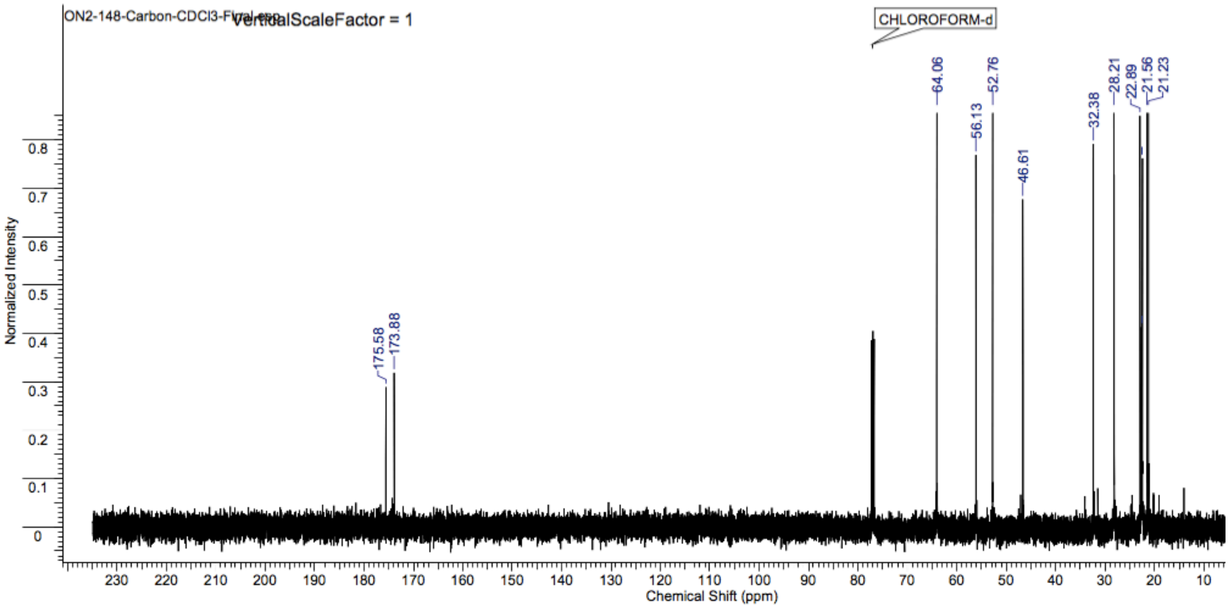


Figure S88. ^{13}C NMR of polypentylene camphorate (Table S1, Entry 5)

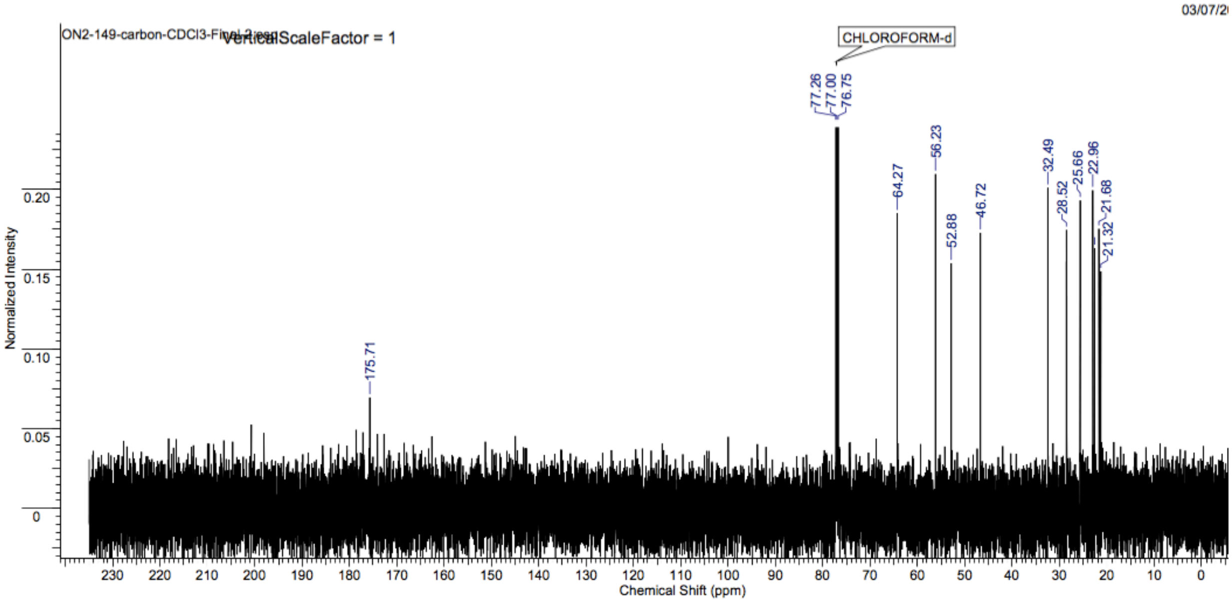


Figure S89. ^{13}C NMR of polyhexylene camphorate (Table S1, Entry 6)

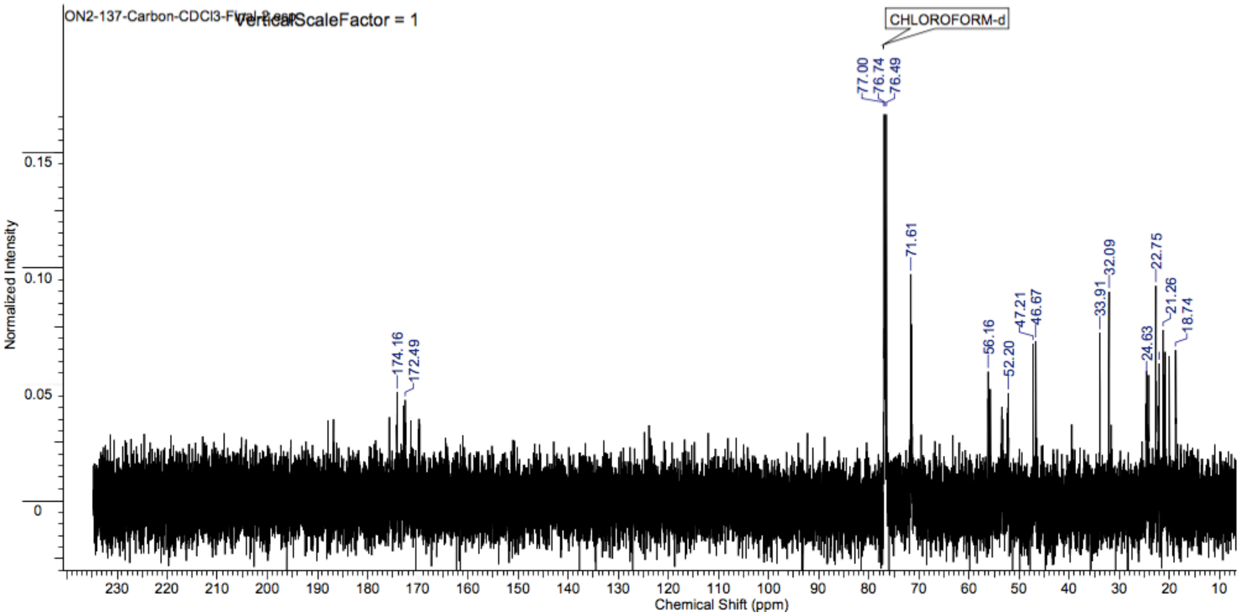


Figure S90. ^{13}C NMR of polyerythritan camphorate (Table S1, Entry 7)

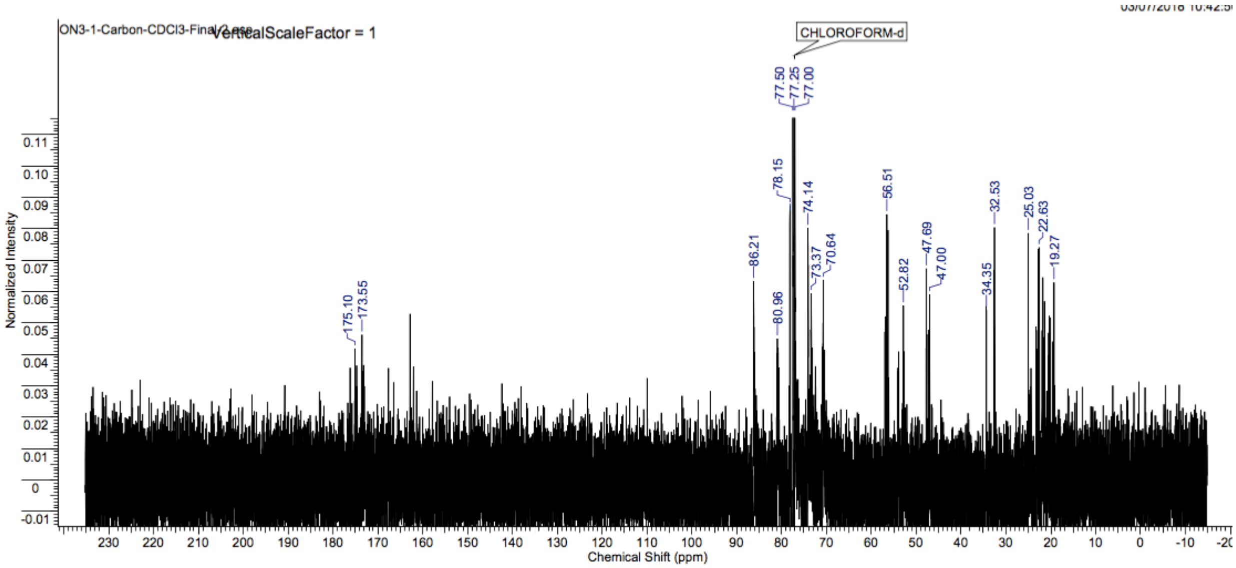


Figure S91. ^{13}C NMR of polyisosorbide camphorate (Table S1, Entry 8)

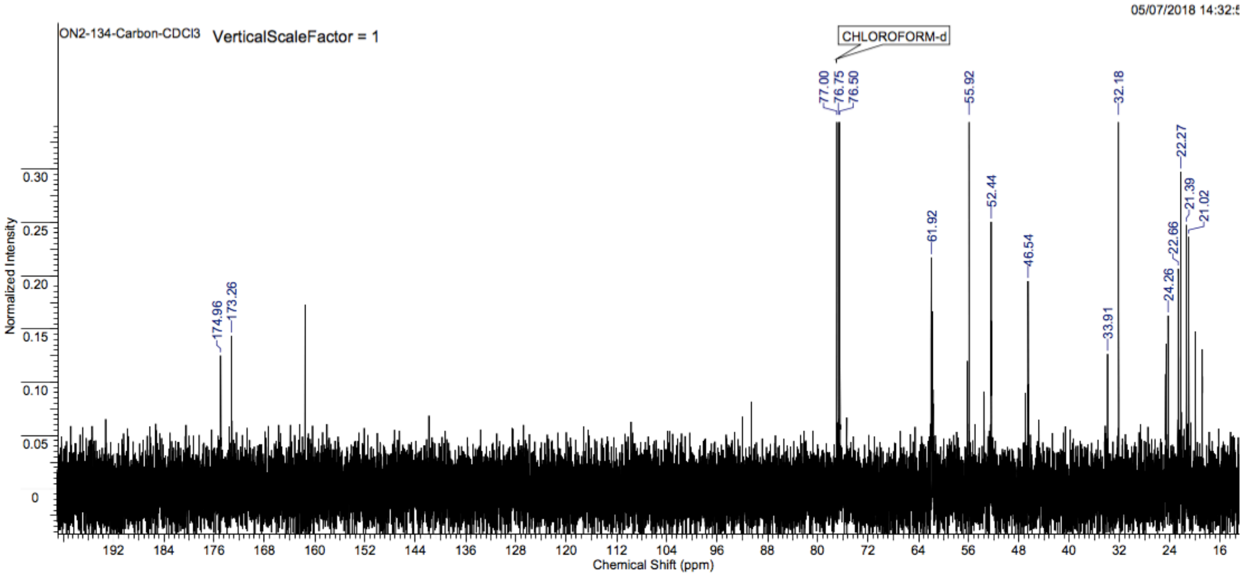


Figure S92. ^{13}C NMR for polyBHEC (Table S2, Entry 1)

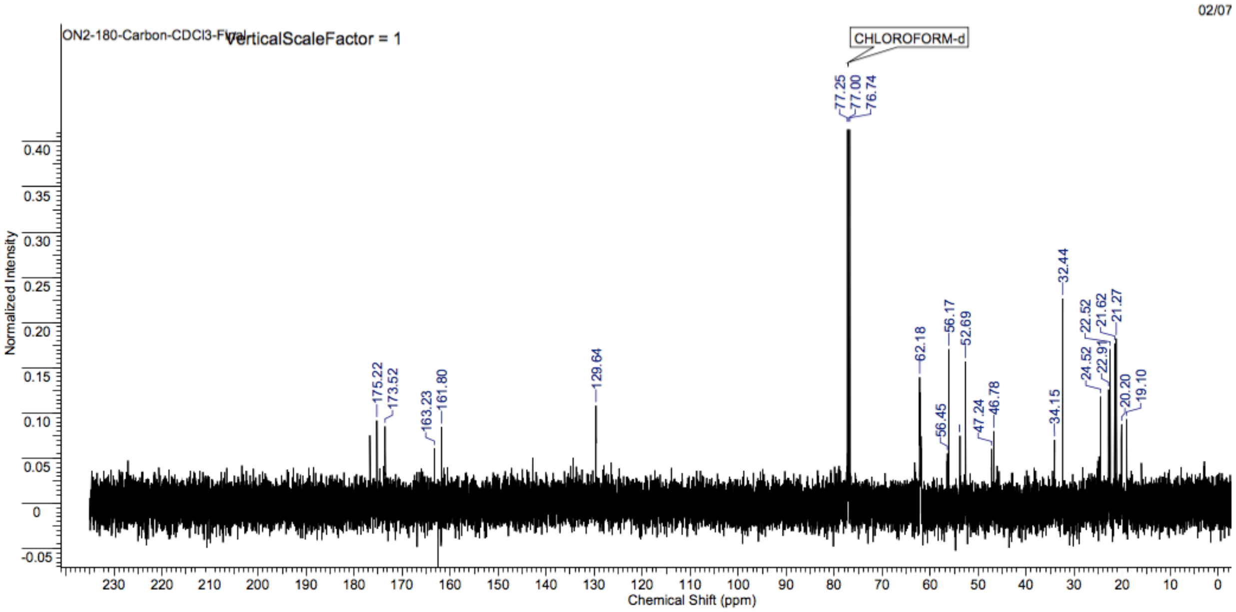


Figure S93. ^{13}C NMR for poly(BHEC/BHET) with 90% BHEC (Table S2, Entry 2)

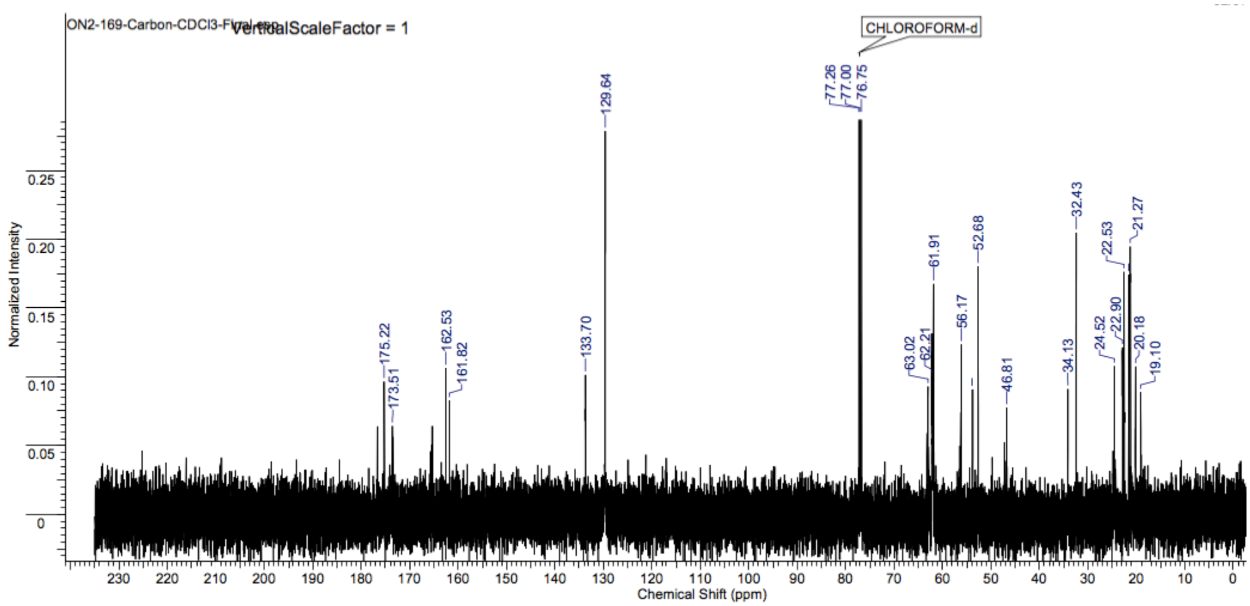


Figure S94. ^{13}C NMR for poly(BHEC/BHET) with 80% BHEC (Table S2, Entry 3)

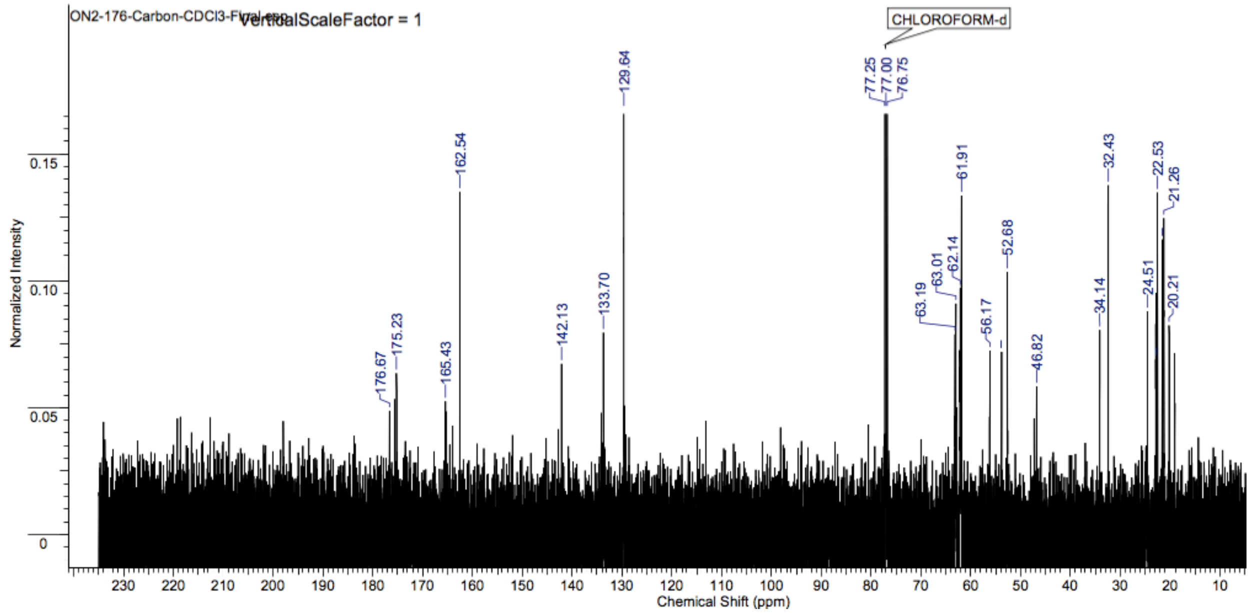


Figure S95. ^{13}C NMR for poly(BHEC/BHET) with 70% BHEC (Table S2, Entry 4)

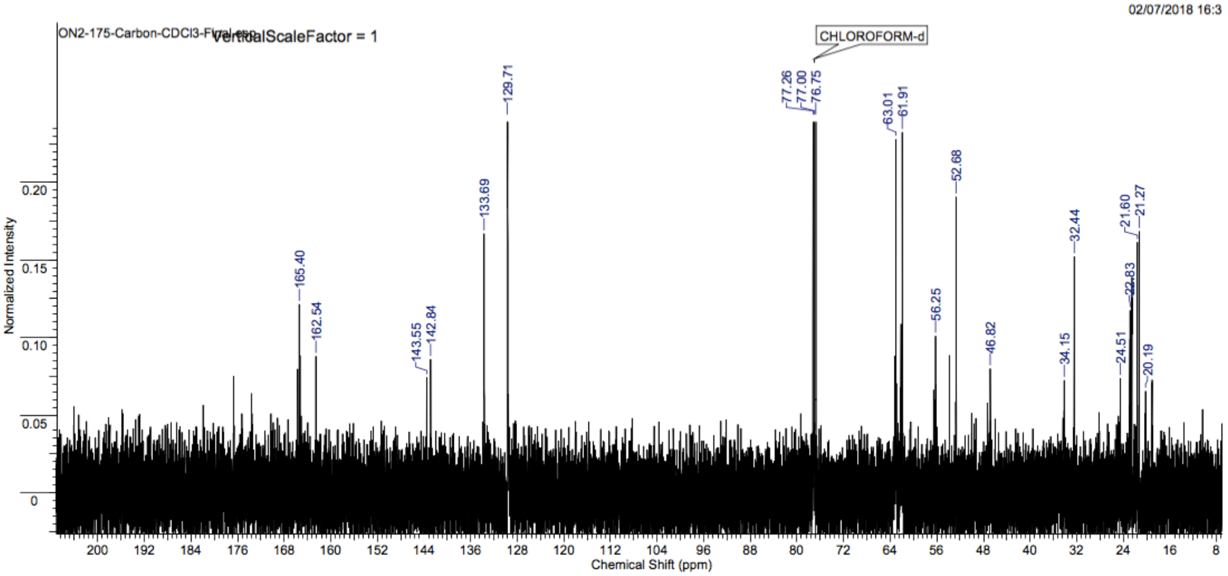


Figure S96. ^{13}C NMR for poly(BHEC/BHET) with 60% BHEC (Table S2, Entry 5)

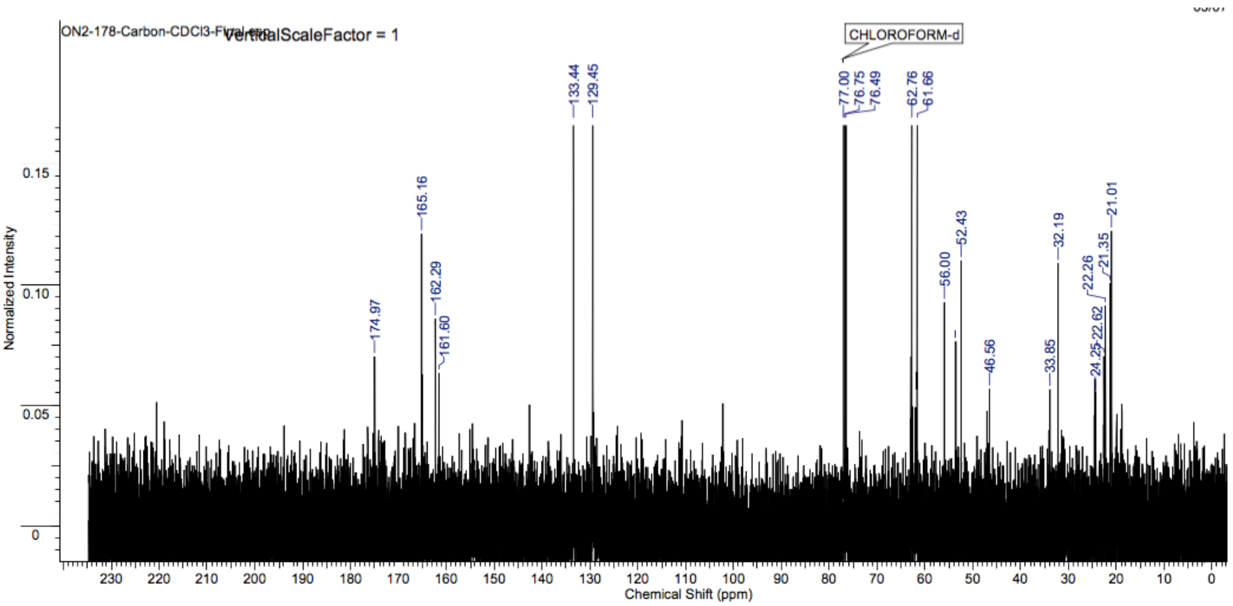


Figure S97. ^{13}C NMR for poly(BHEC/BHET) with 50% BHEC (Table S2, Entry 6)

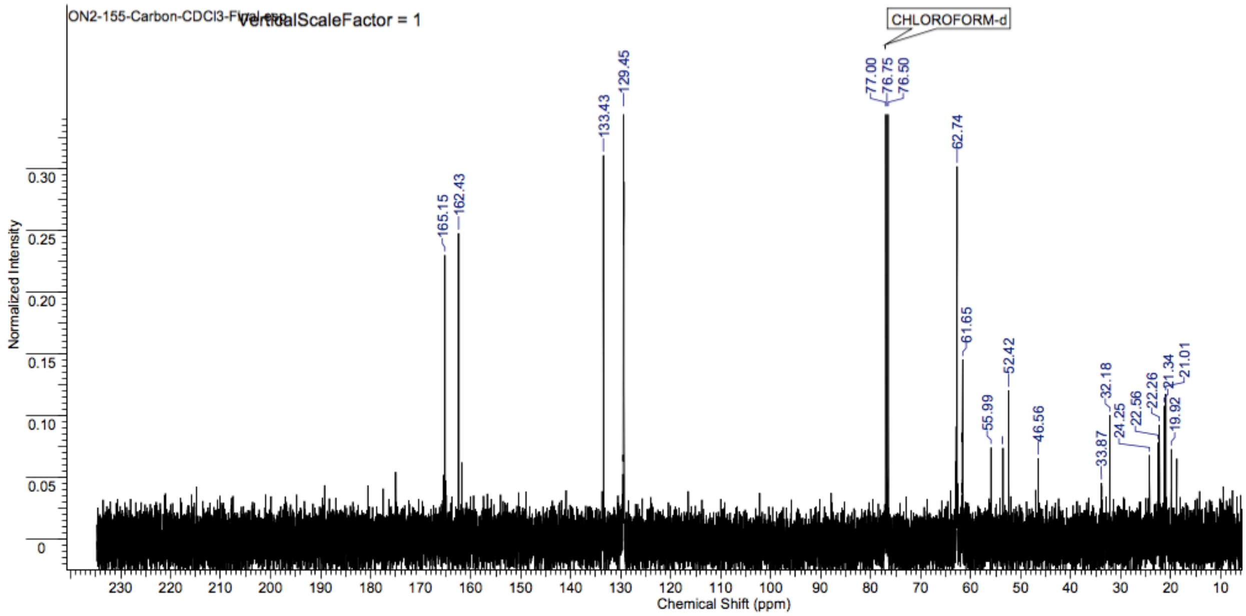


Figure S98. ^{13}C NMR for poly(BHEC/BHET) with 40% BHEC (Table S2, Entry 7)

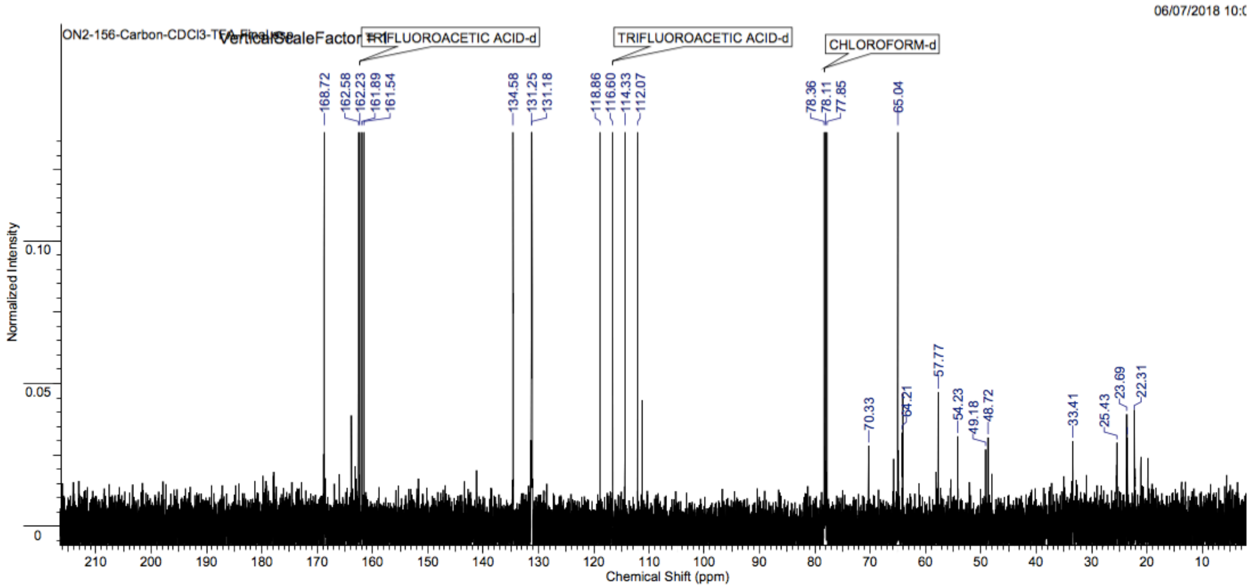


Figure S99. ^{13}C NMR for poly(BHEC/BHET) with 30% BHEC (Table S2, Entry 8)

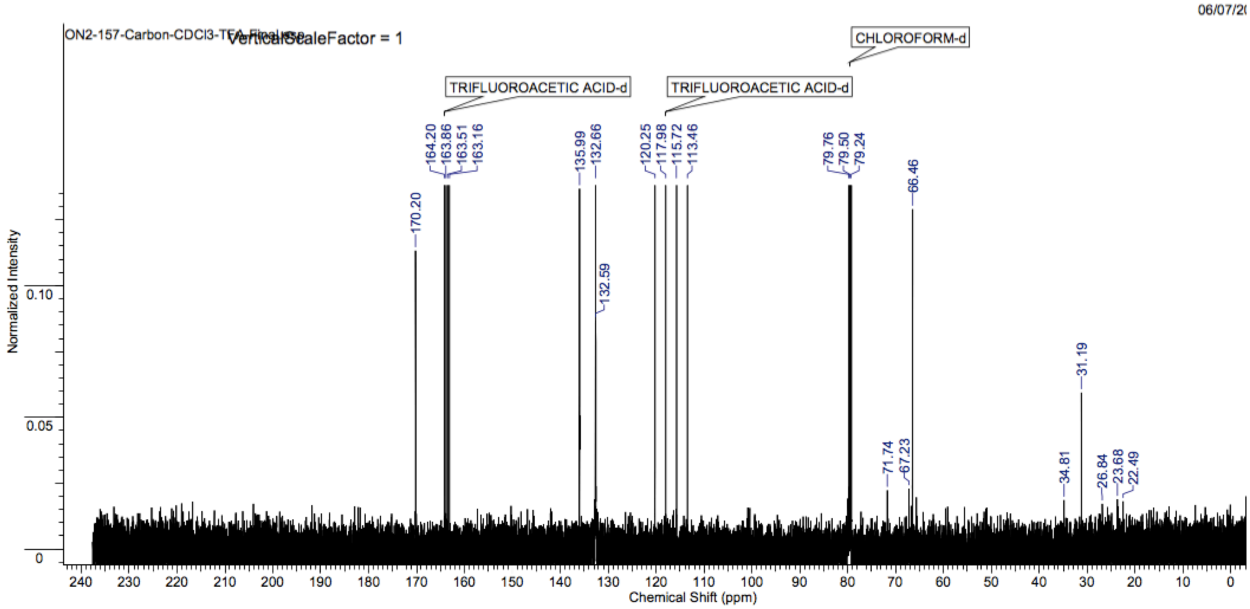


Figure S100. ^{13}C NMR for poly(BHEC/BHET) with 20% BHEC (Table S2, Entry 9)

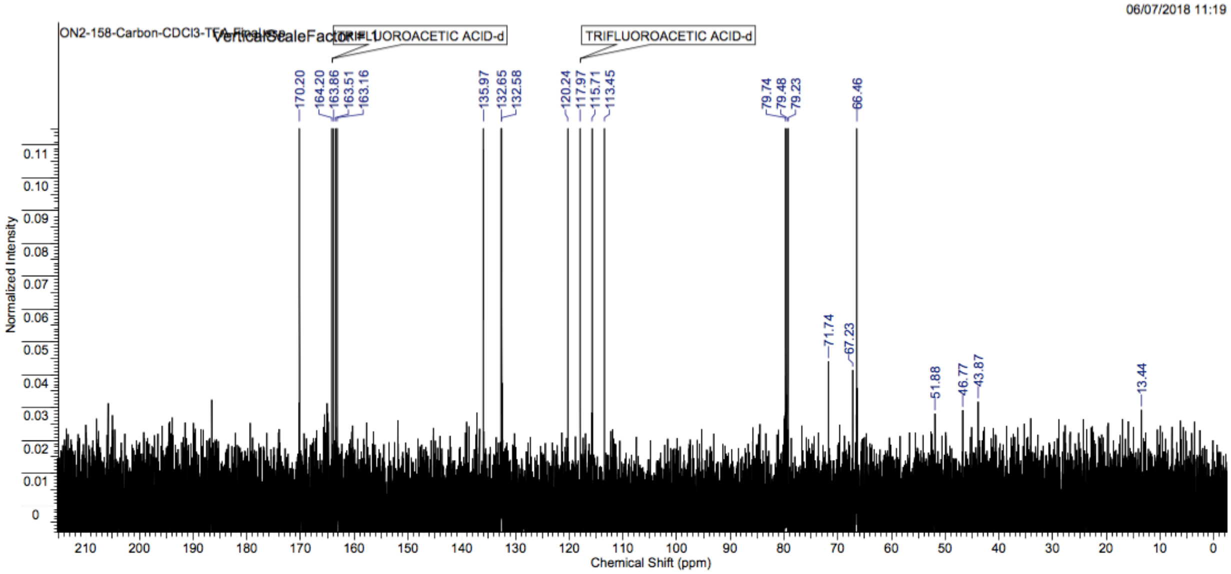


Figure S101. ^{13}C NMR for poly(BHEC/BHET) with 10% BHEC Table (S2, Entry 10)

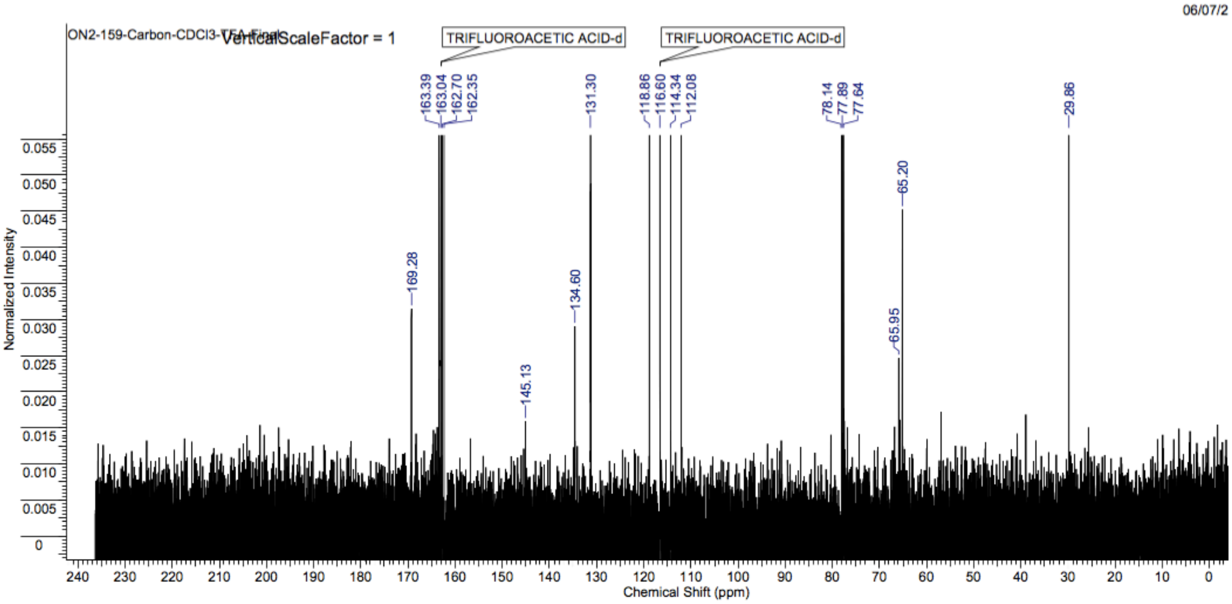
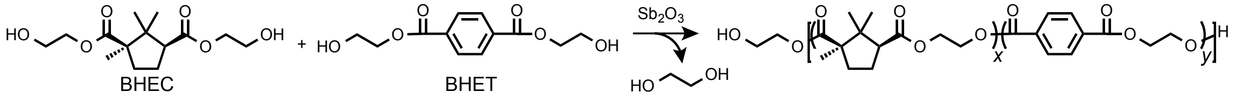


Figure S102. ^{13}C NMR for polyBHET (Table S2, Entry 11)

Analysis of Copolymer Composition for Polyethylene (Camphorate/Terephthalate)

For the copolymers of Table S2, the BHEC incorporation percentage was determined by ^{1}H NMR by integrating the 1-methyl group of the camphoric acid ring (near 0.77 ppm) versus the aromatic protons of the terephthalate ring (near 8.1 ppm). The integration values, taken from the spectra in **Figures S71–S81**, are given below in Table S4.

Table S4 Incorporation fraction of bis(hydroxyethyl) camphorate (BHEC, from camphoric acid) and bis(hydroxyethyl) terephthalate (BHET, from terephthalic acid) for polyethylene (camphorate/terephthalate) copolymers as described in Table S2.



Entry	BHEC % Feed	BHEC methyl integration (^{1}H NMR)	BHET Ar-H integration (^{1}H NMR)	BHEC % Incorporation (^{1}H NMR)	BHET % Incorporation (^{1}H NMR)	BHEC % for $r_{\mathrm{BHEC}} = 0.47$ $r_{\mathrm{BHET}} = 2.26$
1	100	2.95	0.00	100.0	0.0	100.0
2	90	2.99	0.82	82.9	17.1	80.8
3	80	3.00	2.08	65.8	34.2	64.9
4	70	3.22	3.85	52.7	47.3	51.7
5	60	2.95	7.65	34.0	66.0	40.6
6	50	1.38	3.99	31.6	68.4	31.1
7	40	0.86	4.01	22.2	77.8	23.1
8	30	0.75	4.04	19.8	80.2	16.1
9	20	0.42	3.99	12.3	87.7	10.0
10	10	0.24	3.91	7.6	92.4	4.7
11	0	0.00	4.00	0.0	100.0	0.0

Since the methyl group bears 3 hydrogens and the aromatic phenylene component bears 4 hydrogens, the molar percent of BHEC in the copolymer is calculated according to

$$\text{BHEC \% Incorporation} = \frac{[(\text{BHEC integration}) / 3]}{[(\text{BHEC integration}) / 3] + [(\text{BHET integration}) / 4]}$$

The reactivity ratios reported in Figure S103 below were calculated with an excel spreadsheet (Table S5) according to the copolymer molar composition equation, usually applied to chain-growth copolymerization, but mathematically applicable to step-growth copolymerization as well:

$$F_C = \frac{r_C f_C^2 + f_C f_T}{r_C f_C^2 + 2 f_C f_T + r_T f_T^2}$$

where

$r_C = r_{\mathrm{BHEC}}$ = the reactivity ratio of bis(hydroxyethyl) camphorate, BHEC
$r_T = r_{\mathrm{BHET}}$ = the reactivity ratio of bis(hydroxyethyl) terephthalate, BHET

f_C = the feed fraction of bis(hydroxyethyl) camphorate, BHEC
f_T = the feed fraction of bis(hydroxyethyl) terephthalate, BHET

$F_C = 1 - F_T$ = the composition fraction of bis(hydroxyethyl) camphorate, BHEC
F_T = the composition fraction of bis(hydroxyethyl) terephthalate, BHET

Note in this copolymerization,

$r_C = r_{BHEC} = k_{CC} / k_{CT}$ and
$r_T = r_{BHET} = k_{TT} / k_{TC}$

But, the chain end for BHEC and BHET are nearly identical, with both ending in $C(O)OCH_2CH_2OH$. So the following approximation applies:

$r_C = r_{BHEC} \sim k_C / k_T$ and
$r_T = r_{BHET} \sim k_T / k_C$

where k_C is the reaction rate constant of *any* chain end with BHEC
and k_T is the reaction rate constant of *any* chain end with BHET.

This suggests that r_C and r_T should bear a reciprocal relationship, which is essentially true:

$r_C = 0.47$
$1 / 0.47 = 2.12$

$r_T = 2.26$
$1 / 2.26 = 0.44$

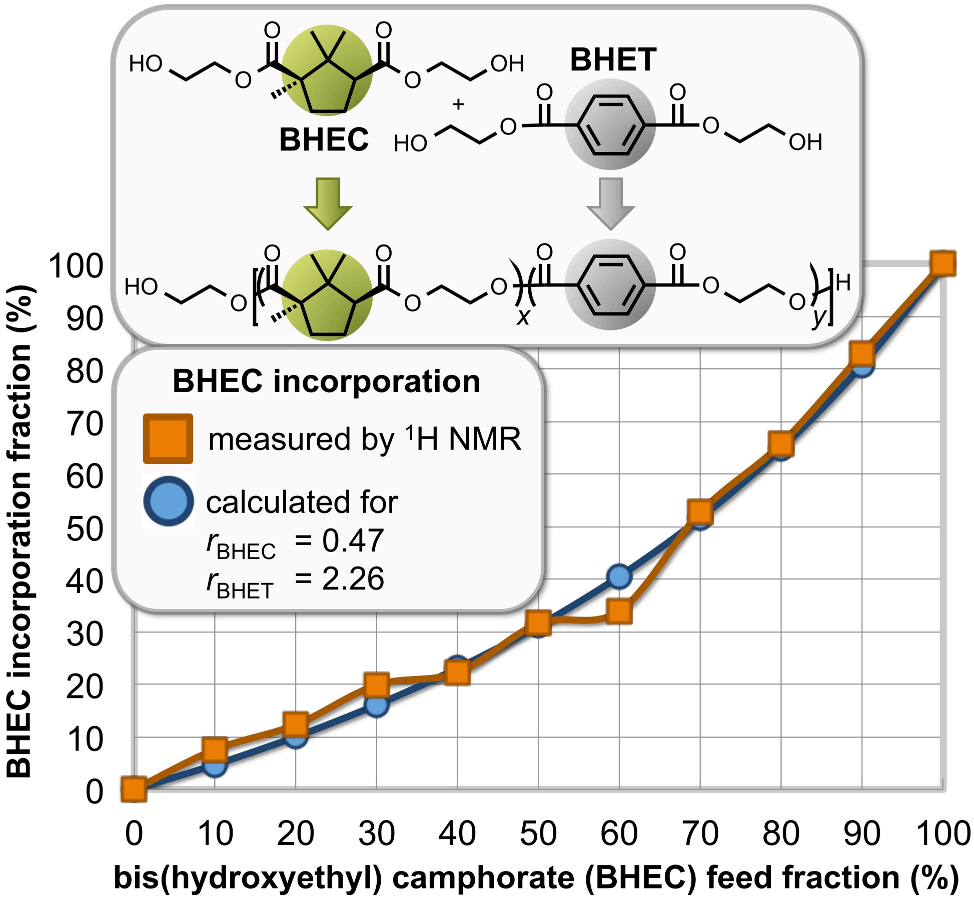


Figure S103. BHEC incorporation fraction (%) as a function of the BHEC feed fraction (%) as determined experimentally (squares, by ^1H NMR) and calculated with $r_{BHEC} = 0.47$ and $r_{BHET} = 2.26$ (circles). RMS error = 2.67.

Table S5 Excel spreadsheet showing calculations for the determination of reactivity ratios r_{BHEC}, r_{BHET}, and the RMS (root mean square) error.

		BHEC	r1	0.47			
		BHET	r2	2.26			
BHEC feed	NMR BHEC incorp.	f1	f2	F1 calc	F1 * 100	diff	square
100	100.00	1	0	1.000	100.0	0.000000	0.000000
90	82.94	0.9	0.1	0.808	80.8	2.174197	4.727134
80	65.79	0.8	0.2	0.649	64.9	0.909059	0.826388
70	52.72	0.7	0.3	0.517	51.7	1.062679	1.129288
60	33.96	0.6	0.4	0.406	40.6	-6.596201	43.509861
50	31.56	0.5	0.5	0.311	31.1	0.428387	0.183515
40	22.24	0.4	0.6	0.231	23.1	-0.829923	0.688773
30	19.84	0.3	0.7	0.161	16.1	3.742346	14.005151
20	12.31	0.2	0.8	0.100	10.0	2.277095	5.185162
10	7.57	0.1	0.9	0.047	4.7	2.859575	8.177168
0	0.00	0	1	0.000	0.0	0.000000	0.000000
						AVE	7.130221713
						RMS error	2.6702475

Degradation Studies

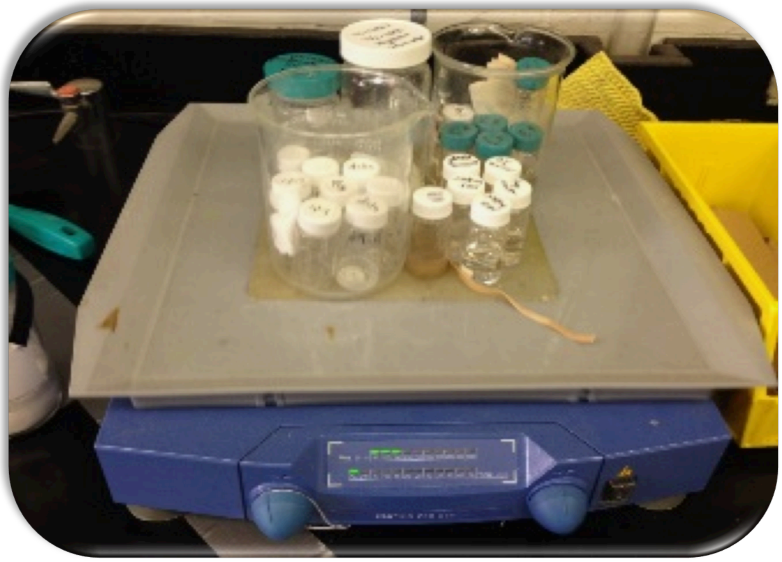


Figure S104. Polymers were left on an orbital shaker for 14 days.

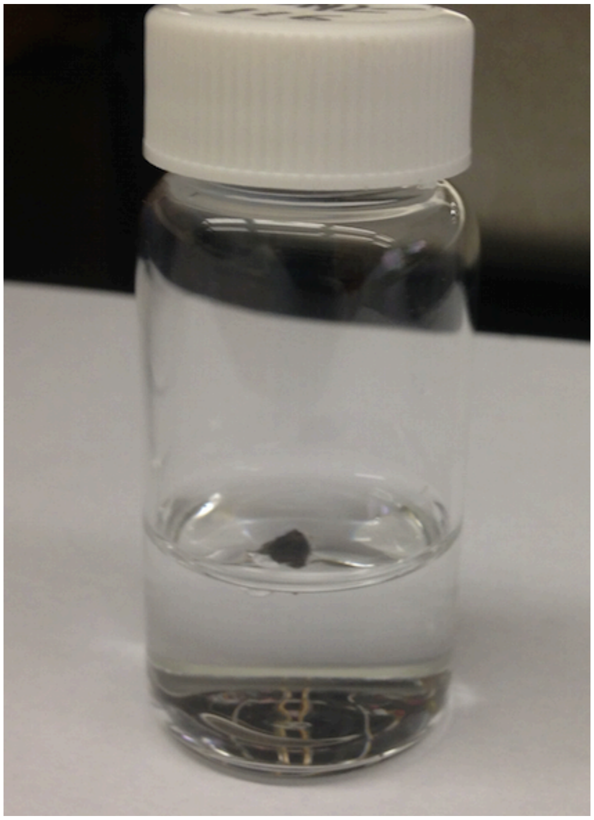


Figure S105. On Day 1, this polyethylene camphorate has not undergone significant gelation or degradation.

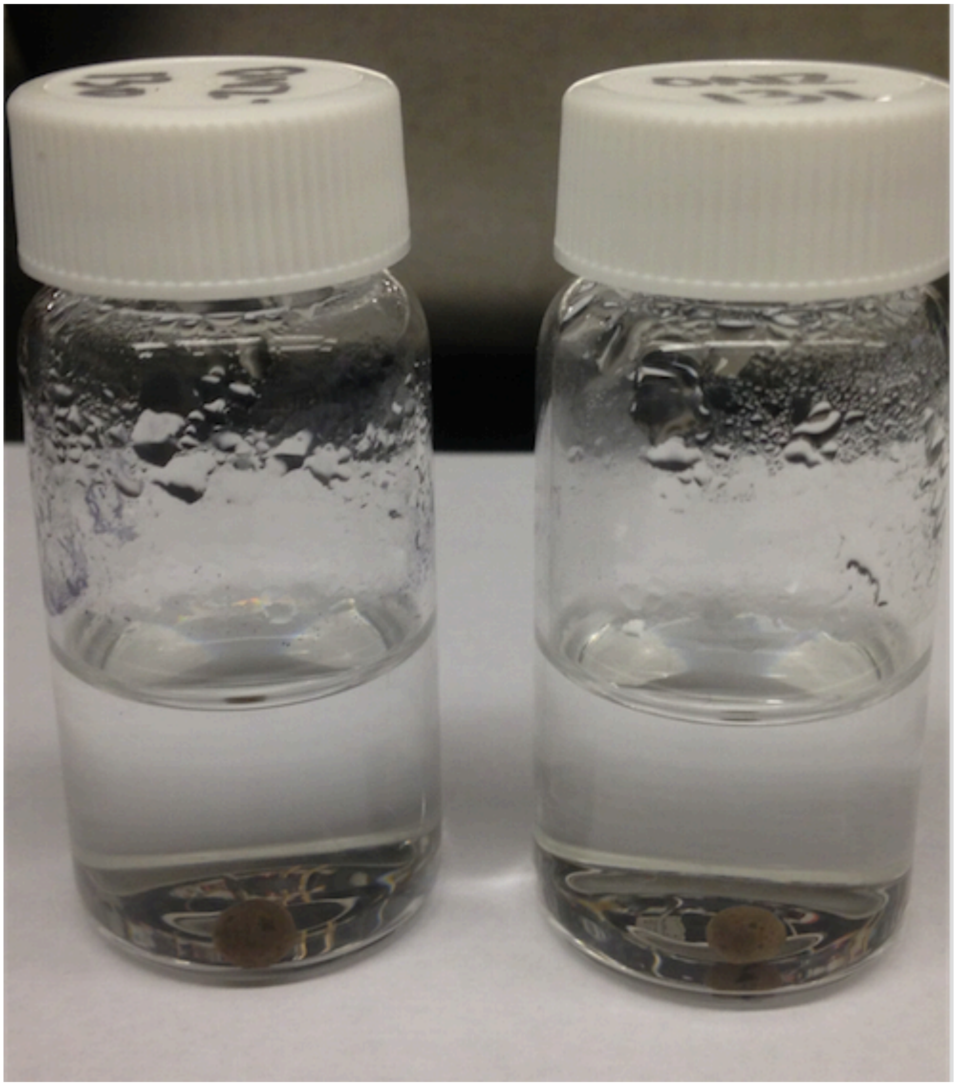
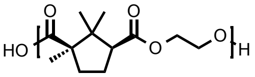
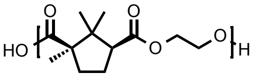
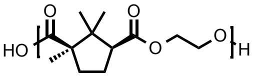


Figure S106. After 14 days, the polyethylene camphorate (at bottom) shows obvious signs of swelling (gelation), having assumed a spherical shape.

Table S6 Molecular weight data for the aqueous degradation study of polyethylene camphorate (from Table S1, Entry 2)[a]

Entry	Polymer	Initial		M_n (Da) After 14 days		
		M_n (Da)	M_w (Da)	pH = 1 buffer	pH = 2 buffer	deionized water
1		20,200	60,800	< 600		
2		20,200	60,800		< 600	
3		20,200	60,800			< 600

[a] Gel permeation chromatography (GPC) in hexafluoroisopropanol (HFIP) at 40 °C *vs* polymethylmethacrylate standards.

GPC data for the degradation studies

Molecular Weight Averages

Peak	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
Peak 1	0	0	0	0	0	32780	0

Peak information

	Start (mins)	End (mins)
Baseline region 1	4.91	10.18
Baseline region 2	29.68	30.00
Peak 1	15.46	26.91

Peak	Trace	Peak Max RT (mins)	Peak Area (mV.s)	Peak Height (mV)
Peak 1	RI	22.79	11217559.518	40848.608

Chromatogram

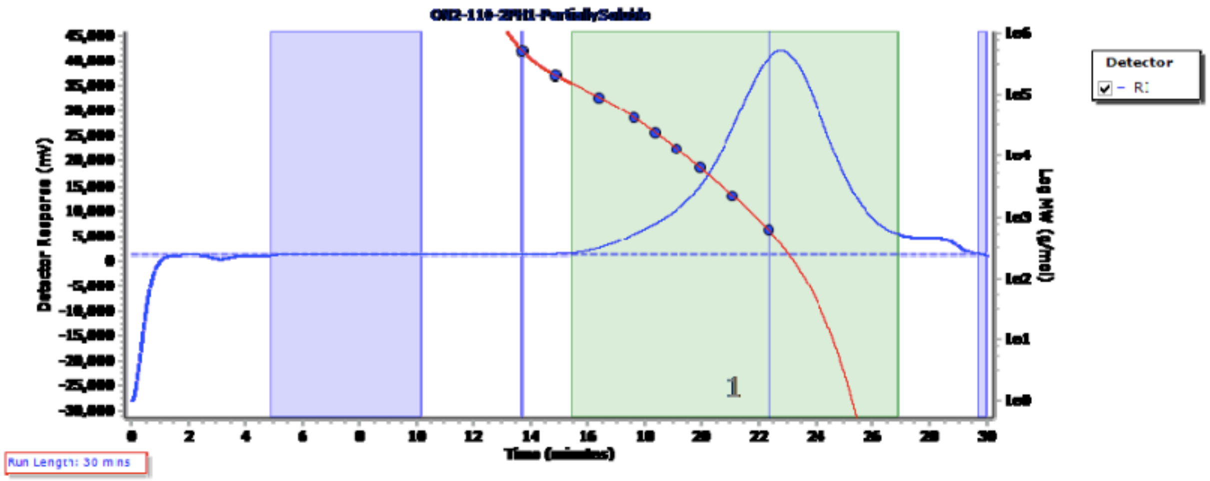


Figure S107. GPC chromatogram for polyethylene camphorate in **aqueous pH = 1** buffer after 14 days. The peak max (22.79 minutes) appears after the lowest molecular weight PMMA standard (22.4 minutes, 600 Da).

Molecular Weight Averages

Peak	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
Peak 1	0	0	0	0	0	40152	0

Peak information

	Start (mins)	End (mins)
Baseline region 1	2.47	6.80
Baseline region 2	29.60	29.97
Peak 1	14.69	27.17

Peak	Trace	Peak Max RT (mins)	Peak Area (mV.s)	Peak Height (mV)
Peak 1	RI	22.69	8769469.371	31070.980

Chromatogram

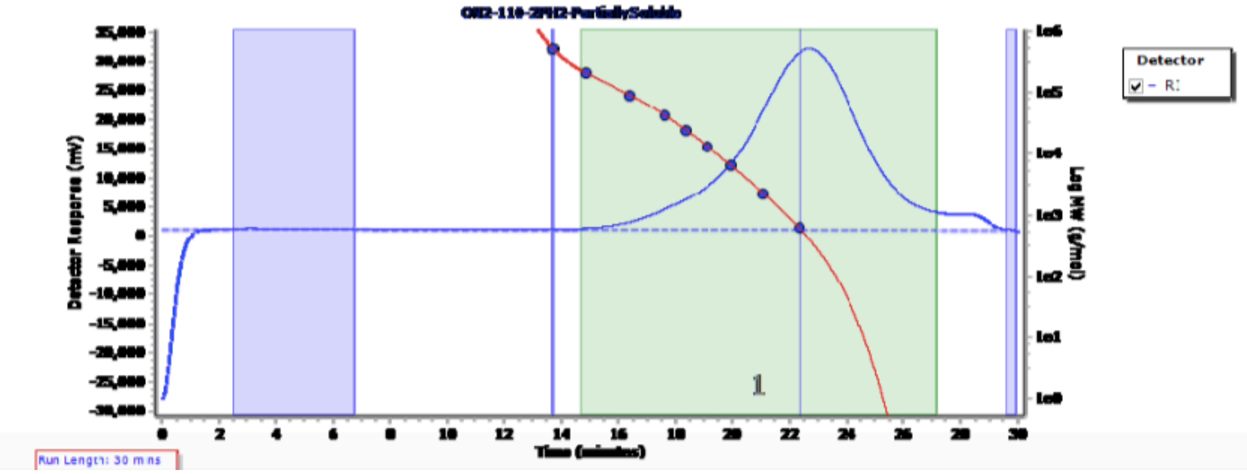


Figure S108. GPC chromatogram for polyethylene camphorate in **aqueous pH = 2** buffer after 14 days. The peak max (22.69 minutes) appears after the lowest molecular weight PMMA standard (22.4 minutes, 600 Da).

Molecular Weight Averages

Peak	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
Peak 1	267341	240218	260528	283755	308491	280139	1.085
Peak 2	0	0	0	0	0	32006	0

Peak information

	Start (mins)	End (mins)
Baseline region 1	6.07	8.23
Baseline region 2	29.43	29.72
Peak 1	13.73	15.34
Peak 2	15.78	27.35

Peak	Trace	Peak Max RT (mins)	Peak Area (mV.s)	Peak Height (mV)
Peak 1	RI	14.43	74359.822	1026.219
Peak 2	RI	23.07	9328555.287	35433.566

Chromatogram

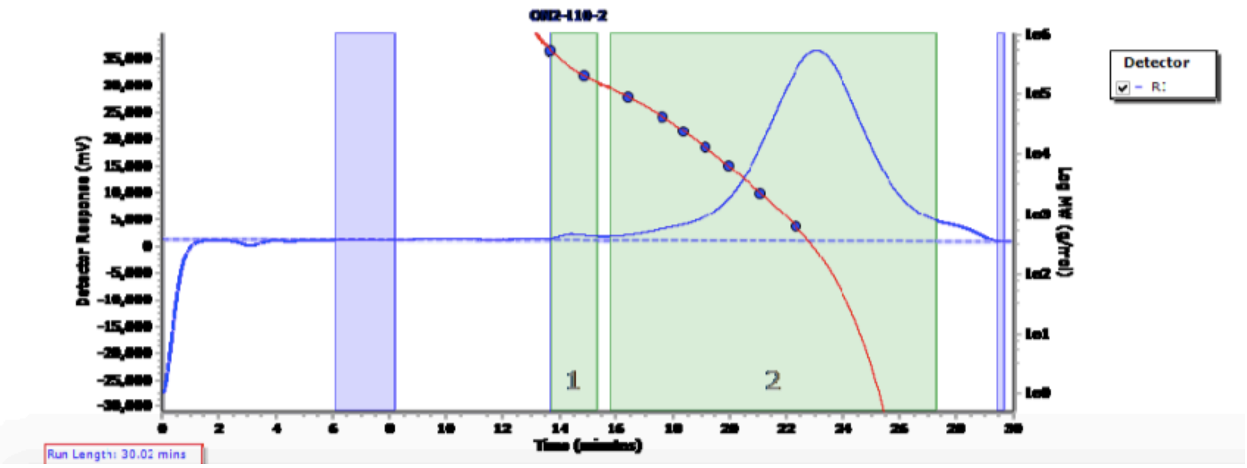


Figure S109. GPC chromatogram for polyethylene camphorate in **deionized water** after 14 days. The peak max (23.07 minutes) appears after the lowest molecular weight PMMA standard (22.4 minutes, 600 Da).