Polyethylene ferulate (PEF) and congeners: Polystyrene mimics derived from biorenewable aromatics

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Supporting Information

Supporting Information Available: Synthetic details, complete polymer characterization data, and method to determine the copolymer composition.

Table of Contents

General Considerations and Instrumentation ................................................................................................................. S2
Monomer Preparation .......................................................................................................................................................... S2
Polymerizations .................................................................................................................................................................... S3
Summary of Polymerization Data ...................................................................................................................................... S8
Gel Permeation Chromatography (GPC) Data .................................................................................................................. S9
Differential Scanning Calorimetry (DSC) Thermograms ..................................................................................................... S21
Thermogravimetric Analysis (TGA) Thermograms ............................................................................................................. S35
$^1$H NMR Spectra ............................................................................................................................................................. S44
$^{13}$C NMR Spectra ............................................................................................................................................................ S52
$^1$H NMR Analysis for Copolymer Composition .............................................................................................................. S58

Ferulic acid and coumaric acid are abundantly available bioaromatics from megacrop agricultural waste (such as sugarcane bagasse) and are functional building blocks for polystyrene mimics.
General Considerations and Instrumentation

Materials

Via alibaba.com, ferulic acid (99%) was purchased from Xian Erica Botanical Products Co. or from Nanjing Zelang Medical Technology Co. and p-coumaric acid (99%) was purchased from Nanjing Zelang Medical Technology Co.

2-chloroethanol and 3-chloropropanol were purchased from Acros Organics. 6-chlorohexanol was purchased from Alfa Aesar. These were all utilized without further purification. NMR solvents, including deuterated chloroform (CDCl₃), deuterated dimethyl sulfoxide (DMSO-d₆), and deuterated trifluoroacetic acid (TFA-d) 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 ¹³C 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, quintuplet; 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 was 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 ~80 °C to 300 °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 HFIPgel column (4.6 mm i.d., 250 mm length) using a solution of 0.1% potassium triflate (KOTf) in HPLC grade hexafluorisopropanol (HFIP, purchased from SynQuest Laboratories, Alachua, Florida) as the mobile phase at a flow rate of 0.5 mL min. Calibration was performed with narrow polydispersity polymethyl methacrylate (PMMA) standards.

Monomer Preparation

Hydroxyethylferulic acid

\[
\text{HO-}O-\text{C-C-C-}O-\text{OH}
\]

25.0 g (0.129 mol) of ferulic acid were dissolved in a mixture of 11.9 g (0.297 mol) of sodium hydroxide and 3.35 g (0.022 mol) of sodium iodide in 268 mL of water. The mixture was refluxed at 85 °C until all solids had dissolved. At that point 12.6 mL (0.185 mol) of 2-chloroethanol were slowly added. After one hour the temperature was raised to 100 °C and the reaction was allowed to reflux for 4 days. The dark brown mixture was then hot vacuum filtered and let cool to room temperature. The filtrate was extracted with diethyl ether and acidified with concentrated hydrochloric acid until the product crashed out. The product was isolated by gravity filtration, dried in the air, and triturated in ethanol. 22.8 g of dry white powder were obtained in a yield of 74.5%. ¹H NMR (DMSO-d₆): δ ppm 3.72 (t, J=4.7 Hz, 2 H), 3.81 (s, 3 H), 4.01 (t, J=5.0 Hz, 2 H), 4.90 (br. s., 1 H), 6.44 (d, J=15.9 Hz, 1 H), 6.98 (d, J=8.4 Hz, 1 H), 7.17 (d, J=8.2 Hz, 1 H), 7.30 (s, 1 H), 7.52 (d, J=15.9 Hz, 1 H), 12.20 (br. s., 1 H). ¹³C NMR (DMSO-d₆): δ ppm 55.5, 59.4, 70.1, 110.5, 112.6, 116.7, 122.6, 127.1, 144.1, 149.1, 150.2, 167.9.

Hydroxyethylidihydroferulic acid

\[
\text{HO-}O-\text{C-C-C-}O-\text{OH}
\]

23.0 g (0.097 mol) of hydroxyethylferulic acid and 2.26 g (0.002 mol) of Pd/C (10 wt. % Pd) catalyst were mixed in 78 mL of methanol and 145 mL of THF. The mixture was hydrogenated at 60 psi for 4 hours. It was then vacuum filtered through a layer of Celite. The filtrate was dried by rotary evaporator and dissolved in THF. The product was then crashed out in cold hexane and isolated by gravity filtration. After drying under vacuum, 15.5 g of white solid were obtained in a yield of 66.9%. ¹H NMR (CDCl₃): δ ppm 2.67 (t, J=7.6 Hz, 2 H), 2.92 (t, J=7.6 Hz, 2 H), 3.83 (s, 3 H), 3.92 (t, J=4.6 Hz, 2 H), 4.12 (t, J=4.5 Hz, 2 H), 6.75 (d, J=7.7 Hz, 1 H), 6.76 (s, 1 H), 6.87 (d, J=7.8 Hz, 1 H). ¹³C NMR (DMSO-d₆): δ ppm 30.0, 35.6, 55.4, 59.6, 70.3, 112.4, 113.3, 112.0, 133.5, 146.4, 148.8, 173.9.
Hydroxyethylcoumaric acid

20.0 g (0.122 mol) of p-coumaric acid were dissolved in a mixture of 11.3 g (0.281 mol) of sodium hydroxide and 3.17 g (0.0207 mol) of sodium iodide in 250 mL of water. The mixture was refluxed at 85 °C until all solids had dissolved. At that point 11.9 mL (0.175 mol) of 2-chloroethanol were slowly added. After one hour the temperature was raised to 100 °C and the reaction was allowed to reflux for 64 hours. The dark brown mixture was then hot vacuum filtered and let cool to room temperature. The filtrate was extracted with diethyl ether and acidified with concentrated hydrochloric acid until the product crashed out. The product was isolated by gravity filtration, dried in the air, and triturated in ethanol. 15.6 g of dry white powder were obtained in a 61.8% yield. \(^1\)H NMR (DMSO-\(d_6\)): \(\delta\) ppm 3.60–3.83 (m, 2 H), 4.03 (t, \(J=4.9\) Hz, 2 H), 4.89 (br. s., 1 H), 6.37 (d, \(J=16.0\) Hz, 1 H), 6.97 (d, \(J=8.7\) Hz, 2 H), 7.54 (d, \(J=15.8\) Hz, 1 H), 7.62 (d, \(J=8.7\) Hz, 2 H), 12.20 (br. s., 1 H). \(^{13}\)C NMR (DMSO-\(d_6\)): \(\delta\) ppm 59.5, 69.7, 114.8, 116.4, 126.7, 129.9, 143.7, 160.4, 167.8.

Hydroxyethylidihydrocoumaric acid

6.5 g (0.031 mol) of hydroxyethylcoumaric acid and 1.8 g (0.00016 mol) of Pd/C (10 wt. % Pd) catalyst was mixed in 25 mL of MeOH and 47 mL of THF. The mixture was hydrogenated at 60 psi for 14 hours. It was then vacuum filtered through a layer of Celite. A rotary evaporator was then used to remove a majority of the solvent, and the filtrate was allowed to cool down slowly to crystallize overnight. The crystals were then gravity filtered and washed with cold hexanes. After drying under vacuum, 6.3 g of colorless to white crystals were obtained in a 96.3% yield. \(^1\)H NMR (CDCl\(_3\)): \(\delta\) ppm 1.41–1.56 (m, 4 H), 1.62 (quin, \(J=7.0\) Hz, 2 H), 1.89 (quin, \(J=7.0\) Hz, 2 H), 3.68 (d, \(J=6.5\) Hz, 2 H), 3.91 (s, 3 H), 4.07 (d, \(J=6.7\) Hz, 2 H), 6.32 (d, \(J=15.8\) Hz, 1 H), 6.88 (d, \(J=8.2\) Hz, 1 H), 7.08 (d, \(J=1.7\) Hz, 1 H), 7.12 (dd, \(J=8.4\) Hz, \(J=1.9\) Hz, 1 H), 7.73 (d, \(J=15.9\) Hz, 1 H). \(^{13}\)C NMR (CDCl\(_3\)): \(\delta\) ppm 25.2, 25.4, 28.7, 32.5, 55.6, 60.6, 68.1, 110.5, 112.5, 116.6, 122.6, 126.9, 144.1, 149.1, 150.2, 167.9.

Hydroxypropylferulic acid

15.0 g (0.077 mol) of ferulic acid were dissolved in a mixture of 7.14 g (0.174 mol) of sodium hydroxide and 2.01 g (0.0131 mol) of sodium iodide in 158 mL of water. The mixture was refluxed at 85 °C until all solids had dissolved. At that point 9.5 mL (0.111 mol) of 3-chloropropanol were slowly added. After one hour the temperature was raised to 100 °C and the reaction was allowed to reflux for 67 hours. The dark brown mixture was then hot vacuum filtered and let cool to room temperature. The filtrate was extracted with diethyl ether and acidified with concentrated hydrochloric acid until the product crashed out. The product was isolated by gravity filtration, dried in the air, and triturated in ethanol. 13.0 g of dry white powder were obtained in a 71.6% yield. \(^1\)H NMR (DMSO-\(d_6\)): \(\delta\) ppm 1.86 (quin, \(J=6.2\) Hz, 2 H), 3.55 (t, \(J=6.0\) Hz, 2 H), 3.80 (s, 3 H), 4.05 (t, \(J=6.3\) Hz, 2 H), 4.56 (br. s., 1 H), 6.43 (d, \(J=16.0\) Hz, 1 H), 6.96 (d, \(J=8.4\) Hz, 1 H), 7.18 (d, \(J=8.4\) Hz, 1 H), 7.30 (s, 1 H), 7.52 (d, \(J=16.0\) Hz, 1 H), 12.21 (br. s., 1 H). \(^{13}\)C NMR (DMSO-\(d_6\)): \(\delta\) ppm 32.1, 55.6, 57.3, 65.3, 110.5, 112.4, 116.6, 122.7, 127.0, 144.2, 149.1, 150.2, 168.0.

Hydroxyhexylferulic acid

20.0 g (0.103 mol) of ferulic acid were dissolved in a mixture of 9.52g (0.238 mol) of sodium hydroxide and 2.68 g (0.018 mol) of sodium iodide in 214 mL of water. The mixture was refluxed at 85 °C until all solids had dissolved. At that point 20.5 mL (0.148 mol) of 6-chlorohexanol were slowly added. After one hour the temperature was raised to 100 °C and the reaction was allowed to reflux for 3 days. The dark brown mixture was then hot vacuum filtered and let cool to room temperature. The filtrate was extracted with diethyl ether and acidified with concentrated hydrochloric acid until the product crashed out. The product was isolated by gravity filtration, dried in the air, then recrystallized in ethanol. 19.2 g of dry white powder were obtained in a 63.4% yield. \(^1\)H NMR (CDCl\(_3\)): \(\delta\) ppm 1.41–1.56 (m, 4 H), 1.62 (quin, \(J=7.0\) Hz, 2 H), 1.89 (quin, \(J=7.0\) Hz, 2 H), 3.68 (d, \(J=6.5\) Hz, 2 H), 3.91 (s, 3 H), 4.07 (d, \(J=6.7\) Hz, 2 H), 6.32 (d, \(J=15.8\) Hz, 1 H), 6.88 (d, \(J=8.2\) Hz, 1 H), 7.08 (d, \(J=1.7\) Hz, 1 H), 7.12 (dd, \(J=8.4\) Hz, \(J=1.9\) Hz, 1 H), 7.73 (d, \(J=15.9\) Hz, 1 H). \(^{13}\)C NMR (CDCl\(_3\)): \(\delta\) ppm 25.2, 25.4, 28.7, 32.5, 55.6, 60.6, 68.1, 110.5, 112.5, 116.6, 122.6, 126.9, 144.1, 149.1, 150.2, 167.9.

Polymerizations

Polymerization apparatus

The polymerizations were typically conducted in a round bottom flask, connected to a rotary evaporation bump trap, connected to a vacuum line. With this apparatus, the by-product of condensation could be collected and seen in the bump trap. At the same time, all volatiles could be removed without changing the initial glassware configuration. All polymerizations were performed in the dark by covering the outside of the apparatus in aluminum foil. See below.
General work-up procedure for polymerizations

Polyethylene dihydrocoumarate and polyethylene dihydroferulate were dissolved in a mixture of 3 mL tetrachloroethane and 7 mL chloroform. The polymer was crashed out of solution by pouring the polymer solution into 170 mL of cold methanol. The polymer was isolated by filtration and the polymer was washed with methanol. The polymer was dried under vacuum overnight. All other polymers were melted to remove them from the flask and used without further purification.

General NMR preparation

Polyethylene dihydroferulate and polyethylene dihydrocoumarate were prepared in chloroform-d. Polyethylene ferulate was prepared in DMSO-d6 for 13C NMR and in chloroform-d for 1H NMR. All other polymer samples were prepared in a combination of chloroform-d and trifluoroacetic acid-d. Even after heating and sonication, the polymers were only partially soluble in the NMR solvents.

Polyethylene ferulate (PEF)

Table S1, Entry 2 and Table S2, Entry 1. A 50 mL round bottom flask was charged with 1.00 g (4.2 mmol) of hydroxyethylferulic acid and 12 mg (1 mol%) of Sb2O3. The mixture was melted under an argon atmosphere gradually from 150 to 200 °C over a period of 4 hours. Afterwards the system was placed under dynamic vacuum to increase the degree of polymerization by removal of the volatile condensation product. The system was kept under vacuum for 8 hours before cooling. Once cool, the aforementioned work-up procedure was applied to give the polymer in 87.1% yield (806 mg). 1H NMR (CDCl3): δ ppm 2.65 (t, J=7.8, 2 H), 2.90 (t, J=7.8, 2 H), 3.83 (3, s, 3 H), 4.18 (t, J=4.8, 2 H), 4.42 (t, J=4.7, 2 H), 6.72 (dd, J=8.1 Hz, J=1.8 Hz, 1 H), 6.75 (d, J=1.7 Hz, 1 H), 6.80 (d, J=8.1 Hz, 1 H). 13C NMR (CDCl3): δ ppm 30.5, 35.9, 55.9, 62.9, 67.4, 112.4, 114.7, 120.2, 134.4, 146.3, 149.7, 172.8.

Polyethylene coumarate (PEC)

Table S1, Entry 1 and Table S2, Entry 11. A 50 mL round bottom flask was charged with 1.00 g (4.2 mmol) of hydroxyethylcoumaric acid and 12 mg (1 mol%) of Sb2O3. The mixture was melted under an argon atmosphere gradually from 150 to 200 °C over a period of 4 hours. Afterwards the system was placed under dynamic vacuum to increase the degree of polymerization by removal of the volatile condensation product. The system was kept under vacuum for 6 hours before cooling. Once cool, the aforementioned work-up procedure was applied to give the polymer in 85.9% yield (1.18 g). 1H NMR (CDCl3/TFA-d): δ ppm 4.30 (br. s., 2 H), 4.60 (br. s., 2 H), 6.38 (d, J=16.2 Hz, 1 H), 6.95 (d, J=8.0 Hz, 2 H) 7.50 (d, J=8.2 Hz, 2 H), 7.71 (d, J=15.9 Hz, 1 H). 13C NMR (CDCl3/TFA-d): δ ppm 63.3, 66.0, 114.4, 115.0, 127.2, 130.2, 146.4, 160.4, 168.8.

Polyethylene dihydrocoumarate

Table S1, Entry 3 and Table S2, Entry 16. A 50 mL round bottom flask was charged with 1.50 g (7.2 mmol) of hydroxyethylcoumaric acid and 21 mg (1 mol%) of Sb2O3. The mixture was melted under an argon atmosphere gradually from 200 to 250 °C over a period of 4 hours. Afterwards the system was placed under dynamic vacuum to increase the degree of polymerization by removal of the volatile condensation product. The system was kept under vacuum for 6 hours before cooling. Once cool, the aforementioned work-up procedure was applied to give the polymer in 90.5% yield (1.24 g). 1H NMR (CDCl3) δ ppm 2.06 (t, J=7.8, 2 H), 2.90 (t, J=7.8, 2 H), 4.09 (t, J=4.7, 2 H), 4.40 (t, J=4.7, 2 H), 6.80 (d, J=8.7 Hz, 2 H), 7.11 (d, J=8.5 Hz, 2 H). 13C NMR (DMSO-d6/TFA-d): δ ppm 30.1, 35.2, 55.9, 62.9, 67.4, 112.4, 114.7, 120.2, 134.4, 146.3, 149.7, 172.8.
NMR (CDCl₃): δ ppm 30.0, 36.0, 62.8, 65.9, 114.6, 129.3, 133.0, 156.9, 172.8.

**Polypropylene ferulate**

**Table S1, Entry 5.** A 50 mL round bottom flask was charged with 1.50 g (5.9 mmol) of hydroxypropylferulic acid and 17 mg (1 mol%) of Sb₂O₅. The mixture was melted under an argon atmosphere gradually from 180 to 220 °C over a period of 5 hours. Afterwards the system was placed under dynamic vacuum to increase the degree of polymerization by removal of the volatile condensation product. The system was kept under vacuum for 8 hours before cooling. Once cool, the aforementioned work-up procedure was applied to give the polymer in 92.7% yield (1.3 g). ¹H NMR (CDCl₃/TFA-d): δ ppm 2.28 (quin, J=6.2 Hz, 2 H), 3.92 (s, 3 H), 4.22 (t, J=6.0 Hz, 2 H), 4.46 (t, J=6.2 Hz, 2 H), 6.37 (d, J=15.9 Hz, 1 H), 6.92 (d, J=8.4 Hz, 1 H), 7.10 (m, 1 H), 7.14 (d, J=8.1 Hz, 1 H), 7.68 (d, J=15.9 Hz, 1 H). ¹³C NMR (CDCl₃/TFA-d): δ ppm: 28.4, 56.0, 62.1, 65.5, 110.5, 112.6, 114.9, 123.2, 127.4, 146.2, 149.3, 150.5, 169.0.

**Polyhexalene ferulate**

**Table S1, Entry 6.** A 50 mL round bottom flask was charged with 1.50 g (5.1 mmol) of hydroxyhexylferulic acid and 13 mg (1 mol%) of Sb₂O₅. The mixture was melted under an argon atmosphere gradually from 155 to 200 °C over a period of 5 hours. Afterwards the system was placed under dynamic vacuum to increase the degree of polymerization by removal of the volatile condensation product. The system was kept under vacuum for 8 hours before cooling. Once cool, the aforementioned work-up procedure was applied to give the polymer in 92.7% yield (1.31 g). ¹H NMR (CDCl₃/TFA-d): δ ppm 1.40–163 (m, 4 H), 1.77 (quin, J=6.9 Hz, 2 H), 1.88 (quin, J=6.7 Hz, 2 H), 3.93 (s, 3 H), 4.09 (t, J=6.7 Hz, 2 H), 4.27 (t, J=6.7 Hz, 2 H), 6.37 (d, J=15.9 Hz, 1 H), 6.89 (d, J=8.5 Hz, 1 H), 7.10 (s, 1 H), 7.14 (d, J=8.2 Hz, 1 H), 7.68 (d, J=15.9 Hz, 1 H). ¹³C NMR (CDCl₃/TFA-d): δ ppm 25.57, 25.64, 28.4, 28.7, 56.1, 65.8, 69.0, 110.6, 112.4, 115.5, 123.5, 127.0, 146.5, 148.8, 150.7, 170.0.

**Copolymers of hydroxyethylidihydroferulic acid and hydroxyethylferulic acid**

Copoly(hydroxyethylidihydroferulic acid/ hydroxyethylferulic acid) [90:10]

**Table S2, Entry 2.** A 50 mL round bottom flask was charged with 908 g (3.8 mmol) of hydroxyethylidihydroferulic acid, 100 mg (0.4 mmol) of hydroxyethylferulic acid and 12 mg (1 mol%) of Sb₂O₅. The mixture was melted under an argon atmosphere gradually from 160 to 200 °C over a period of 4 hours. Afterwards the system was placed under dynamic vacuum to increase the degree of polymerization by removal of the volatile condensation product. The system was kept under vacuum for 8 hours before cooling. Once cool, the aforementioned work-up procedure was applied to give Copoly(hydroxyethylidihydroferulic acid/ hydroxyethylferulic acid) [80:20]

**Table S1, Entry 3.** This polymer was synthesized using the same procedure as for copoly(hydroxyethylidihydroferulic acid/ hydroxyethylferulic acid) [90:10], 807 mg (3.4 mmol) of hydroxyethylidihydroferulic acid, 200 mg (0.8 mmol) of hydroxyethylferulic acid and 12 mg (1 mol%) of Sb₂O₅ were used. The product was obtained in 88.4% yield (823 mg). ¹³C NMR (CDCl₃/TFA-d): δ ppm major peaks: 30.4, 36.0, 55.85, 63.3, 67.3, 112.5, 114.3, 120.6, 134.3, 145.9, 149.1, 174.3; minor peaks: 55.91, 63.1, 66.9, 110.6, 113.2, 114.4, 123.0, 128.0, 134.2, 146.2, 149.4, 174.2.

**Copoly(hydroxyethylidihydroferulic acid/ hydroxyethylferulic acid) [70:30]**

**Table S1, Entry 4.** This polymer was synthesized using the same procedure as for copoly(hydroxyethylidihydroferulic acid/ hydroxyethylferulic acid) [90:10], 706 mg (2.9 mmol) of hydroxyethylidihydroferulic acid, 300 mg (1.3 mmol) of hydroxyethylferulic acid and 12 mg (1 mol%) of Sb₂O₅ were used. The product was obtained in 89.5% yield (832 mg). ¹³C NMR (CDCl₃/TFA-d): δ ppm major peaks: 30.3, 36.0, 55.9, 63.6, 67.3, 112.6, 114.1, 120.9, 134.2, 145.7, 148.7, 175.4; minor peaks: 56.0, 63.3, 66.9, 110.8, 113.02, 114.9, 123.3, 128.0, 134.7, 146.7, 149.9, 175.1.

**Copoly(hydroxyethylidihydroferulic acid/ hydroxyethylferulic acid) [60:40]**

**Table S1, Entry 5.** This polymer was synthesized using the same procedure as for copoly(hydroxyethylidihydroferulic acid/ hydroxyethylferulic acid) [90:10], 605 mg (2.5 mmol) of hydroxyethylidihydroferulic acid, 400 mg (1.7 mmol) of hydroxyethylferulic acid and 12 mg (1 mol%) of Sb₂O₅ were used. The product was obtained in 90.9% yield (844 mg).

**Copoly(hydroxyethylidihydroferulic acid/ hydroxyethylferulic acid) [50:50]**

**Table S1, Entry 6.** A 50 mL round bottom flask was charged with 530 mg (2.2 mmol) of hydroxyethylidihydroferulic acid, 526 mg (2.2 mmol) of hydroxyethylferulic acid and 13 mg (1 mol%) of Sb₂O₅. The mixture was melted under an argon atmosphere gradually from 170 to 230 ºC over a period of 4 hours. Afterwards the system was placed under dynamic vacuum to increase the degree of polymerization by removal of the volatile condensation product. The system was kept under vacuum for 8 hours before cooling. Once cool, the aforementioned work-up procedure was applied to give
the polymer in 90.9% yield (888 mg). 1H NMR (CDCl3 /TFA-d): δ ppm 2.60–2.75 (m, 2 H), 2.81–3.01 (m, 2 H), 3.67–3.86 (m, 3 H), 3.87–4.03 (m, 3 H), 4.08–4.88 (m, 8 H), 6.38 (d, J=16.0 Hz, 1 H), 6.50–7.21 (m, 6 H), 7.66 (d, J=15.7 Hz, 1 H).

Copoly(hydroxyethylhydroferulic acid/ hydroxyethylferulic acid) [40:60]

Table S1, Entry 7. This polymer was synthesized using the same procedure as for copoly(hydroxyethyl-dihydroferulic acid/ hydroxyethylferulic acid) [50:50]. 400 mg (1.7 mmol) of hydroxyethylhydroferulic acid, 595 mg (2.5 mmol) of hydroxyethylferulic acid and 12 mg (1 mol%) of Sb2O3 were used. The product was obtained in 76.4% yield (703 mg).

Copoly(hydroxyethylhydroferulic acid/ hydroxyethylferulic acid) [30:70]

Table S1, Entry 8. A 50 mL round bottom flask was charged with 300 mg (1.2 mmol) of hydroxyethylhydroferulic acid, 694 mg (2.9 mmol) of hydroxyethylferulic acid and 12 mg (1 mol%) of Sb2O3. The mixture was melted under an argon atmosphere gradually from 180 to 240 ºC over a period of 4 hours. Afterwards the system was placed under dynamic vacuum to increase the degree of polymerization by removal of the volatile condensation product. The system was kept under vacuum for 6.5 hours before cooling. Once cool, the aforementioned work-up procedure was applied to give the polymer in 82.5% yield (758 mg).

Copoly(hydroxyethylhydroferulic acid/ hydroxyethylferulic acid) [20:80]

Table S1, Entry 9. A 50 mL round bottom flask was charged with 250 mg (1.04 mmol) of hydroxyethylhydroferulic acid, 992 mg (4.2 mmol) of hydroxyethylferulic acid and 15 mg (1 mol%) of Sb2O3. The mixture was melted under an argon atmosphere gradually from 190 to 240 ºC over a period of 3.5 hours. Afterwards the system was placed under dynamic vacuum to increase the degree of polymerization by removal of the volatile condensation product. The system was kept under vacuum for 6.5 hours before cooling. Once cool, the aforementioned work-up procedure was applied to give the polymer in 89.9% yield (1.03 g).

Copoly(hydroxyethylhydroferulic acid/ hydroxyethylferulic acid) [10:90]

Table S1, Entry 10. A 50 mL round bottom flask was charged with 120 mg (0.5 mmol) of hydroxyethyl-dihydroferulic acid, 1.07 g (4.5 mmol) of hydroxyethylferulic acid and 15 mg (1 mol%) of Sb2O3. The mixture was melted under an argon atmosphere gradually from 200 to 250 ºC over a period of 3.5 hours. Afterwards the system was placed under dynamic vacuum to increase the degree of polymerization by removal of the volatile condensation product. The system was kept under vacuum for 6.5 hours before cooling. Once cool, the aforementioned work-up procedure was applied to give the polymer in 90.6% yield (998 mg).

Copolymers of hydroxyethylhydrocoumaric acid and hydroxyethylcoumaric acid

Copoly(hydroxyethylhydrocoumaric acid/ hydroxyethylcoumaric acid) [90:10]

Table S2, Entry 13. A 50 mL round bottom flask was charged with 909 mg (4.3 mmol) of hydroxyethylhydrocoumaric acid, 100 mg (0.5 mmol) of hydroxyethylcoumaric acid and 14 mg (1 mol%) of Sb2O3. The mixture was melted under an argon atmosphere gradually from 150 to 200 ºC over a period of 5 hours. Afterwards the system was placed under dynamic vacuum to increase the degree of polymerization by removal of the volatile condensation product. The system was kept under vacuum for 8 hours before cooling. Once cool, the aforementioned work-up procedure was applied to give the polymer in 92.2% yield (851 mg). 13C NMR (CDCl3 /TFA-d): δ ppm major peaks: 30.0, 36.2, 63.8, 65.9, 114.9, 129.4, 132.8, 156.7, 175.5; minor peaks: 63.6, 66.1, 114.3, 115.0, 127.2, 130.3, 146.8, 160.6, 175.4.

Copoly(hydroxyethylhydrocoumaric acid/ hydroxyethylcoumaric acid) [50:50]

Table S2, Entry 14. A 50 mL round bottom flask was charged with 606 mg (2.9 mmol) of hydroxyethylhydrocoumaric acid, 600 mg (2.9 mmol) of hydroxyethylcoumaric acid and 17 mg (1 mol%) of Sb2O3. The mixture was melted under an argon atmosphere gradually from 160 to 220 ºC over a period of 5 hours. Afterwards the system was placed under dynamic vacuum to increase the degree of polymerization by removal of the volatile condensation product. The system was kept under vacuum for 7 hours before cooling. Once cool, the aforementioned work-up procedure was applied to give the polymer in 94.1% yield (1.04 g). 1H NMR (CDCl3 /TFA-d): 2.64–2.77 (m, 2 H), 2.83–2.99 (m, 2 H), 3.99–4.72 (m, 8 H), 6.39 (d, J=16.0 Hz, 1 H), 6.73–6.87 (m, 2 H), 6.87–7.01 (m, 2 H), 7.04–7.18 (m, 2 H), 7.44–7.57 (m, 2 H), 7.72 (d, J=15.9 Hz, 1 H).

Copoly(hydroxyethylhydrocoumaric acid/ hydroxyethylcoumaric acid) [10:90]

Table S2, Entry 15. A 50 mL round bottom flask was charged with 110 mg (0.5 mmol) of hydroxyethylhydrocoumaric acid, 982 mg (4.7 mmol) of hydroxyethylcoumaric acid and 15 mg (1 mol%) of Sb2O3. The mixture was melted under an argon atmosphere gradually from 195 to 250 ºC over a period of 4 hours. Afterwards the system was placed under dynamic vacuum to increase the degree of polymerization by removal of the volatile condensation product. The system was kept under vacuum for 7 hours before cooling. Once cool, the aforementioned work-up procedure was applied to give the polymer in 87.3% yield (871 mg).
Copolymer GPC and $T_g$ analysis as a function of time

A 50 mL round bottom flask was charged with 1.00 g (4.2 mmol) of hydroxyethylidihydroferulic acid, 2.31 g (9.7 mmol) of hydroxyethylferulic acid, and 41 mg (1 mol%) of Sb$_2$O$_3$. This corresponds to a 30:70 ratio of the monomers. The mixture was melted under an argon atmosphere gradually from 180 to 240 °C over a period of 4 hours. Afterwards the system was placed under dynamic vacuum for 7 hours at a constant temperature of 240 °C. A polymer aliquot was removed from the flask (at hot temperature) at $T_p = 1, 2, 3, 4, 5, 6, 8$, and 11 hours. Table S3 summarizes the results.
### Summary of Polymerization Data

**Table S1.** Polymerization results and characterization of polyalkylene hydroxycinnamates and polyalkylene dihydroxycinnamates.\(^a\)

<table>
<thead>
<tr>
<th>Entry</th>
<th>Polymers</th>
<th>Yield (%)</th>
<th>(M_n^a) (Da)</th>
<th>(M_w^b) (Da)</th>
<th>PDI(^b)</th>
<th>(T_g^c) (°C)</th>
<th>(T_m^c) (°C)</th>
<th>(T_{np}^c) (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td><img src="image1.png" alt="Polymer" /></td>
<td>89.6</td>
<td>1,600</td>
<td>2,500</td>
<td>1.6</td>
<td>113</td>
<td>n.o.</td>
<td>536</td>
</tr>
<tr>
<td>2</td>
<td><img src="image2.png" alt="Polymer" /></td>
<td>87.1</td>
<td>22,100</td>
<td>79,400</td>
<td>3.6</td>
<td>32</td>
<td>n.o.</td>
<td>394</td>
</tr>
<tr>
<td>3</td>
<td><img src="image3.png" alt="Polymer" /></td>
<td>85.9</td>
<td>e</td>
<td>e</td>
<td>e</td>
<td>109</td>
<td>n.o.</td>
<td>433</td>
</tr>
<tr>
<td>4</td>
<td><img src="image4.png" alt="Polymer" /></td>
<td>90.5</td>
<td>22,900</td>
<td>63,400</td>
<td>2.8</td>
<td>24</td>
<td>123</td>
<td>415</td>
</tr>
<tr>
<td>5</td>
<td><img src="image5.png" alt="Polymer" /></td>
<td>93.1</td>
<td>7,700</td>
<td>13,700</td>
<td>1.8</td>
<td>82</td>
<td>n.o.</td>
<td>405</td>
</tr>
<tr>
<td>6</td>
<td><img src="image6.png" alt="Polymer" /></td>
<td>92.7</td>
<td>10,000</td>
<td>26,600</td>
<td>2.6</td>
<td>51</td>
<td>n.o.</td>
<td>397</td>
</tr>
</tbody>
</table>

\(^a\)1 mol% \(\text{Sb}_2\text{O}_3\); mixtures were typically melted under argon during a 4 hour temperature ramp from 150 to 250 °C; 8 hours of dynamic vacuum at 250 °C; see above text for exact temperature profile. \(^b\)Obtained by GPC in hexafluoroisopropanol (HFIP) at 40 °C versus polymethyl methacrylate (PMMA) standards. 
\(^c\)Determined by DSC. n.o. = not observed. 
\(^d\)Temperature at which 50% mass loss is observed under nitrogen. 
\(^e\)Insolubility of the polymer prevented GPC analysis.

**Table S2.** Polymerization results and characterization of copolymers prepared according to Scheme 2.\(^a\)

<table>
<thead>
<tr>
<th>Monomer feed %</th>
<th>Inc. FA (^b) (mol%)</th>
<th>Yield (%)</th>
<th>(M_n^c) (Da)</th>
<th>(M_w^c) (Da)</th>
<th>PDI(^c)</th>
<th>(T_g^c) (°C)</th>
<th>(T_m^c) (°C)</th>
<th>(T_{np}^c) (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>100</td>
<td>0</td>
<td>0</td>
<td>87.1</td>
<td>22,100</td>
<td>79,400</td>
<td>3.6</td>
<td>32</td>
</tr>
<tr>
<td>2</td>
<td>90</td>
<td>10</td>
<td>12</td>
<td>91.7</td>
<td>39,000</td>
<td>228,700</td>
<td>5.9</td>
<td>37</td>
</tr>
<tr>
<td>3</td>
<td>80</td>
<td>20</td>
<td>19</td>
<td>88.4</td>
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<td>81,100</td>
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<td>41</td>
</tr>
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<td>4</td>
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<td>2.7</td>
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<td>53</td>
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</tr>
<tr>
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<td>60</td>
<td>56</td>
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<td>1.9</td>
<td>66</td>
</tr>
<tr>
<td>8</td>
<td>30</td>
<td>70</td>
<td>66</td>
<td>82.5</td>
<td>3,400</td>
<td>6,400</td>
<td>1.9</td>
<td>77</td>
</tr>
<tr>
<td>9</td>
<td>20</td>
<td>80</td>
<td>74</td>
<td>89.9</td>
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<td>100</td>
<td>89.6</td>
<td>1,600</td>
<td>2,500</td>
<td>1.6</td>
<td>113</td>
</tr>
</tbody>
</table>

\(^a\)1 mol% \(\text{Sb}_2\text{O}_3\); mixtures were typically melted under argon during a 4 hour temperature ramp from 150 to 250 °C; 8 hours of dynamic vacuum at 250 °C; see above text for exact temperature profile. 
\(^b\)Incorporation of hydroxystyrylferulic acid (hydroxystyryl FA) and hydroxyethylcoumaric acid (hydroxystyryl CA) in the copolymers determined by \(^1\)H NMR. 
\(^c\)Obtained by GPC in hexafluoroisopropanol (HFIP) at 40 °C versus polymethyl methacrylate (PMMA) standards. 
\(^d\)Determined by DSC. 
\(^e\)Temperature at which 50% mass loss is observed under nitrogen. 
\(^f\)Insolubility of the polymers prevented GPC analysis.

**Table S3.** Copolymerization study of hydroxystyrylhydroferulic acid and hydroxyethylferulic acid in a 30:70 ratio.\(^a\)

<table>
<thead>
<tr>
<th>Entry</th>
<th>Reaction time (hours)</th>
<th>Reaction temperature (°C)</th>
<th>(T_g^b) (°C)</th>
<th>(M_n^c) (Da)</th>
<th>(T_m^c) (°C)</th>
<th>(M_w^c) (Da)</th>
<th>PDI(^c)</th>
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<td>1</td>
<td>180</td>
<td>42</td>
<td>460</td>
<td>870</td>
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</tr>
<tr>
<td>2</td>
<td>2</td>
<td>ramp</td>
<td>63</td>
<td>1,800</td>
<td>10,000</td>
<td>5.5</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>3</td>
<td>ramp</td>
<td>66</td>
<td>3,200</td>
<td>65,500</td>
<td>20.6</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>4</td>
<td>240</td>
<td>69</td>
<td>5,000</td>
<td>18,300</td>
<td>3.7</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>5</td>
<td>240</td>
<td>72</td>
<td>5,900</td>
<td>13,600</td>
<td>2.3</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>6</td>
<td>240</td>
<td>73</td>
<td>4,700</td>
<td>11,800</td>
<td>2.5</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>7</td>
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<td>74</td>
<td>5,000</td>
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<td>77</td>
<td>3,600</td>
<td>7,900</td>
<td>2.2</td>
<td></td>
</tr>
</tbody>
</table>

\(^a\)1 mol% \(\text{Sb}_2\text{O}_3\); mixture was typically melted under argon during a 4 hour temperature ramp from 180 to 240 °C; 7 hours of dynamic vacuum at 240 °C. 
\(^b\)Determined by DSC. 
\(^c\)Obtained by GPC in hexafluoroisopropanol (HFIP) at 40 °C versus polymethyl methacrylate (PMMA) standards. All samples are only partially dissolved in HFIP solvent.
Gel Permeation Chromatography (GPC) Data

Figure S1. GPC Chromatogram of polyethylene ferulate (Table S1, entry 1 and Table S2, entry 11).

Figure S2. GPC Chromatogram of polyethylene dihydroferulate (Table S1, entry 2 and Table S2, entry 1).
Figure S3. GPC Chromatogram of polyethylene dihydrocoumarate (Table S1, entry 4 and Table S2, entry 12).

Figure S4. GPC Chromatogram of polypropylene ferulate (Table S1, entry 5).
Figure S5. GPC Chromatogram of polyhexalene ferulate (Table S1, entry 6).

Figure S6. GPC Chromatogram of copoly(hydroxyethylidihydroferulic acid/ hydroxyethylferulic acid) [90:10] (Table S2, entry 2).
Figure S7. GPC Chromatogram of copoly(hydroxyethylidihydroferulic acid/ hydroxyethylferulic acid) [80:20] (Table S2, entry 3).

Figure S8. GPC Chromatogram of copoly(hydroxyethylidihydroferulic acid/ hydroxyethylferulic acid) [70:30] (Table S2, entry 4).
Figure S9. GPC Chromatogram of copoly(hydroxyethylidihydroferulic acid/ hydroxyethylferulic acid) [60:40] (Table S2, entry 5).

Figure S10. GPC Chromatogram of copoly(hydroxyethylidihydroferulic acid/ hydroxyethylferulic acid) [50:50] (Table S2, entry 6).
Figure S11. GPC Chromatogram of copoly(hydroxyethylidihydroferulic acid/ hydroxyethylferulic acid) [40:60] (Table S2, entry 7).

Figure S12. GPC Chromatogram of copoly(hydroxyethylidihydroferulic acid/ hydroxyethylferulic acid) [30:70] (Table S2, entry 8).
Figure S13. GPC Chromatogram of copoly(hydroxyethylidihydroferulic acid/ hydroxyethylferulic acid) [20:80] (Table S2, entry 9).

Figure S14. GPC Chromatogram of copoly(hydroxyethylidihydroferulic acid/ hydroxyethylferulic acid) [10:90] (Table S2, entry 10).
Figure S15. GPC Chromatogram of copoly(hydroxyethylidihydrocoumaric acid/ hydroxyethylcoumaric acid) [90:10] (Table S2, entry 13).

Figure S16. GPC Chromatogram of copoly(hydroxyethylidihydrocoumaric acid/ hydroxyethylcoumaric acid) [50:50] (Table S2, entry 14).
Figure S17. GPC Chromatogram of copoly(hydroxyethyldihydrocoumaric acid/ hydroxyethylcoumaric acid) [30:70] (Table S3, entry 1).

Figure S18. GPC Chromatogram of copoly(hydroxyethyldihydrocoumaric acid/ hydroxyethylcoumaric acid) [30:70] (Table S3, entry 2).
Figure S19. GPC Chromatogram of copoly(hydroxyethyldehydrocoumaric acid/ hydroxyethylcoumaric acid) [30:70] (Table S3, entry 3).

Figure S20. GPC Chromatogram of copoly(hydroxyethyldehydrocoumaric acid/ hydroxyethylcoumaric acid) [30:70] (Table S3, entry 4).
Figure S21. GPC Chromatogram of copoly(hydroxyethylidihydrocoumaric acid/ hydroxyethylcoumaric acid) [30:70] (Table S3, entry 5).

Figure S22. GPC Chromatogram of copoly(hydroxyethylidihydrocoumaric acid/ hydroxyethylcoumaric acid) [30:70] (Table S3, entry 6).
Figure S23. GPC Chromatogram of copoly(hydroxyethyldihydrocoumaric acid/ hydroxyethylcoumaric acid) [30:70] (Table S3, entry 7).

Figure S24. GPC Chromatogram of copoly(hydroxyethyldihydrocoumaric acid/ hydroxyethylcoumaric acid) [30:70] (Table S3, entry 8).
Differential Scanning Calorimetry (DSC) Thermograms

Figure S25. DSC Thermogram of polyethylene ferulate (Table S1, entry 1 and Table S2, entry 11).

Figure S26. DSC Thermogram of polyethylene dihydroferulate (Table S1, entry 2 and Table S2, entry 1).
Figure S27. DSC Thermogram of polyethylene coumarate (Table S1, entry 3 and Table S2, entry 16).

Figure S28. DSC Thermogram of full first cycle of polyethylene dihydrocoumarate (Table S1, entry 4 and Table S2, entry 12).
Figure S29. DSC Thermogram of full second cycle of polyethylene dihydrocoumarate (Table S1, entry 4 and Table S2, entry 12).

Figure S30. DSC Thermogram of polypropylene ferulate (Table S1, entry 5).
Figure S31. DSC Thermogram of polyhexalene ferulate (Table S1, entry 6).

Figure S32. DSC Thermogram of copoly(hydroxyethylidihydroferulic acid/ hydroxyethylferulic acid) [90:10] (Table S2, entry 2).
Figure S33. DSC Thermogram of copoly(hydroxyethylidihydroferulic acid/ hydroxyethylferulic acid) [80:20] (Table S2, entry 3).

Figure S34. DSC Thermogram of copoly(hydroxyethylidihydroferulic acid/ hydroxyethylferulic acid) [70:30] (Table S2, entry 4).
Figure S35. DSC Thermogram of copoly(hydroxyethylidihydroferulic acid/hydroxyethylferulic acid) [60:40] (Table S2, entry 5).

Figure S36. DSC Thermogram of copoly(hydroxyethylidihydroferulic acid/hydroxyethylferulic acid) [50:50] (Table S2, entry 6).
Figure S37. DSC Thermogram of copoly(hydroxyethylidihydroferulic acid/ hydroxyethylferulic acid) [40:60] (Table S2, entry 7).

Figure S38. DSC Thermogram of copoly(hydroxyethylidihydroferulic acid/ hydroxyethylferulic acid) [30:70] (Table S2, entry 8).
Figure S39. DSC Thermogram of copoly(hydroxyethylidihydroferulic acid/ hydroxyethylferulic acid) [20:80] (Table S2, entry 9).

Figure S40. DSC Thermogram of copoly(hydroxyethylidihydroferulic acid/ hydroxyethylferulic acid) [10:90] (Table S2, entry 10).
Figure S41. DSC Thermogram of copoly(hydroxyethyldihydrocoumaric acid/ hydroxyethylcoumaric acid) [90:10] (Table S2, entry 13).

Figure S42. DSC Thermogram of copoly(hydroxyethyldihydrocoumaric acid/ hydroxyethylcoumaric acid) [50:50] (Table S2, entry 14).
Figure S43. DSC Thermogram of copoly(hydroxyethylidihydrocoumaric acid/ hydroxyethylcoumaric acid) [10:90] (Table S2, entry 15).

Figure S44. DSC Thermogram of copoly(hydroxyethylidihydrocoumaric acid/ hydroxyethylcoumaric acid) [30:70] (Table S3, entry 1).
Figure S45. DSC Thermogram of copoly(hydroxyethylidihydrocoumaric acid/ hydroxyethylcoumaric acid) [30:70] (Table S3, entry 2).

Figure S46. DSC Thermogram of copoly(hydroxyethylidihydrocoumaric acid/ hydroxyethylcoumaric acid) [30:70] (Table S3, entry 3).
Figure S47. DSC Thermogram of copoly(hydroxyethylidihydrocoumaric acid/ hydroxyethylcoumaric acid) [30:70] (Table S3, entry 4).

Figure S48. DSC Thermogram of copoly(hydroxyethylidihydrocoumaric acid/ hydroxyethylcoumaric acid) [30:70] (Table S3, entry 5).
Figure S49. DSC Thermogram of copoly(hydroxyethyldihydrocoumaric acid/ hydroxyethylcoumaric acid) [30:70] (Table S3, entry 6).

Figure S50. DSC Thermogram of copoly(hydroxyethyldihydrocoumaric acid/ hydroxyethylcoumaric acid) [30:70] (Table S3, entry 7).
Figure S51. DSC Thermogram of copoly(hydroxyethylidihydrocoumaric acid/ hydroxyethylcoumaric acid) [30:70] (Table S3, entry 8).
Thermogravimetric Analysis (TGA) Thermograms

Figure S52. TGA Thermogram of polyethylene ferulate (Table S1, entry 1 and Table S2, entry 11).

Figure S53. TGA Thermogram of polyethylene dihydroferulate (Table S1, entry 2 and Table S2, entry 1).
Figure S54. TGA Thermogram of polyethylene coumarate (Table S1, entry 3 and Table S2, entry 16).

Figure S55. TGA Thermogram of polyethylene dihydrocoumarate (Table S1, entry 4 and Table S2, entry 12).
Figure S56. TGA Thermogram of polypropylene ferulate (Table S1, entry 5).

Figure S57. TGA Thermogram of polyhexalene ferulate (Table S1, entry 6).
Figure S58. TGA Thermogram of copoly(hydroxyethyldihydroferulic acid/hydroxyethylferulic acid) [90:10] (Table S2, entry 2).

Figure S59. TGA Thermogram of copoly(hydroxyethyldihydroferulic acid/hydroxyethylferulic acid) [80:20] (Table S2, entry 3).
Figure S60. TGA Thermogram of copoly(hydroxyethylidihydroferulic acid/ hydroxyethylferulic acid) [70:30] (Table S2, entry 4).

Figure S61. TGA Thermogram of copoly(hydroxyethylidihydroferulic acid/ hydroxyethylferulic acid) [60:40] (Table S2, entry 5).
Figure S62. TGA Thermogram of copoly(hydroxyethylidinehydroferulic acid/ hydroxyethylferulic acid) [50:50] (Table S2, entry 6).

Figure S63. TGA Thermogram of copoly(hydroxyethylidinehydroferulic acid/ hydroxyethylferulic acid) [40:60] (Table S2, entry 7).
Figure S63. TGA Thermogram of copoly(hydroxyethylhydroferulic acid/ hydroxyethylferulic acid) [30:70] (Table S2, entry 8).

Figure S65. TGA Thermogram of copoly(hydroxyethylhydroferulic acid/ hydroxyethylferulic acid) [20:80] (Table S2, entry 9).
Figure S66. TGA Thermogram of copoly(hydroxyethyldihydroferulic acid/ hydroxyethylferulic acid) [10:90] (Table S2, entry 10).

Figure S67. TGA Thermogram of copoly(hydroxyethyldihydrocoumaric acid/ hydroxyethylcoumaric acid) [90:10] (Table S2, entry 13).
Figure S68. TGA Thermogram of copoly(hydroxyethyldihydrocoumaric acid/ hydroxyethylcoumaric acid) [50:50] (Table S2, entry 14).

Figure S69. TGA Thermogram of copoly(hydroxyethyldihydrocoumaric acid/ hydroxyethylcoumaric acid) [10:90] (Table S2, entry 15).
**1H NMR Spectra**

Figure S70. 1H NMR spectrum of hydroxyethylferulic acid.

Figure S71. 1H NMR spectrum of hydroxyethyl dihydroferulic acid.

Figure S72. 1H NMR spectrum of hydroxyethyl coumaric acid.
Figure S73. $^1$H NMR spectrum of hydroxyethyldihydrocoumaric acid.

Figure S74. $^1$H NMR spectrum of hydroxypropylferulic acid.

Figure S75. $^1$H NMR spectrum of hydroxyhexylferulic acid.
Figure S76. $^1$H NMR spectrum of polyethylene ferulate (Table S1, entry 1 and Table S2, entry 11).

Figure S77. $^1$H NMR spectrum of polyethylene dihydroferulate (Table S1, entry 2 and Table S2, entry 1).

Figure S78. $^1$H NMR spectrum of polyethylene coumarate (Table S1, entry 3 and Table S2, entry 16).
Figure S79. $^1$H NMR spectrum of polyethylene dihydrocoumarate (Table S1, entry 4 and Table S2, entry 12).

Figure S80. $^1$H NMR spectrum of polypropylene ferulate (Table S1, entry 5).

Figure S81. $^1$H NMR spectrum of polyhexalene ferulate (Table S1, entry 6).
Figure S82. $^1$H NMR spectrum of copoly(hydroxyethylhydroferulic acid/ hydroxyethylferulic acid) [90:10] (Table S2, entry 2).

Figure S83. $^1$H NMR spectrum of copoly(hydroxyethylhydroferulic acid/ hydroxyethylferulic acid) [80:20] (Table S2, entry 3).

Figure S84. $^1$H NMR spectrum of copoly(hydroxyethylhydroferulic acid/ hydroxyethylferulic acid) [70:30] (Table S2, entry 4).
Figure S85. $^1$H NMR spectrum of copoly(hydroxyethyldihydroferulic acid/ hydroxyethylferulic acid) [60:40] (Table S2, entry 5).

Figure S86. $^1$H NMR spectrum of copoly(hydroxyethyldihydroferulic acid/ hydroxyethylferulic acid) [50:50] (Table S2, entry 6).

Figure S87. $^1$H NMR spectrum of copoly(hydroxyethyldihydroferulic acid/ hydroxyethylferulic acid) [40:60] (Table S2, entry 7).
Figure S88. $^1$H NMR spectrum of copoly(hydroxyethyldihydroferulic acid/ hydroxyethylferulic acid) [30:70] (Table S2, entry 9).

Figure S89. $^1$H NMR spectrum of copoly(hydroxyethyldihydroferulic acid/ hydroxyethylferulic acid) [20:80] (Table S2, entry 9).

Figure S90. $^1$H NMR spectrum of copoly(hydroxyethyldihydroferulic acid/ hydroxyethylferulic acid) [10:90] (Table S2, entry 10).
Figure S91. $^1$H NMR spectrum of copoly(hydroxyethyldihydrocoumaric acid/ hydroxyethylcoumaric acid) [90:10] (Table S2, entry 13).

Figure S92. $^1$H NMR spectrum of copoly(hydroxyethyldihydrocoumaric acid/ hydroxyethylcoumaric acid) [50:50] (Table S2, entry 14).

Figure S93. $^1$H NMR spectrum of copoly(hydroxyethyldihydrocoumaric acid/ hydroxyethylcoumaric acid) [10:90] (Table S2, entry 15).
\textbf{\(^{13}\text{C NMR Spectra}\)}

![Figure S94. \(^{13}\text{C NMR spectrum of hydroxyethylferulic acid.}\)](image1)

![Figure S95. \(^{13}\text{C NMR spectrum of hydroxyethyldihydroferulic acid.}\)](image2)

![Figure S96. \(^{13}\text{C NMR spectrum of hydroxyethylcoumaric acid.}\)](image3)
Figure S97. $^{13}$C NMR spectrum of hydroxyethylhydrocoumaric acid.

Figure S98. $^{13}$C NMR spectrum of hydroxypropylferulic acid.

Figure S99. $^{13}$C NMR spectrum of hydroxyhexylferulic acid.
Figure S100. $^{13}$C NMR spectrum of polyethylene ferulate (Table S1, entry 1 and Table S2, entry 11).

Figure S101. $^{13}$C NMR spectrum of polyethylene dihydroferulate (Table S1, entry 2 and Table S2, entry 1).
Figure S102. $^{13}$C NMR spectrum of polyethylene coumarate (Table S1, entry 3 and Table S2, entry 16).

Figure S103. $^{13}$C NMR spectrum of polyethylene dihydrocoumarate (Table S1, entry 4 and Table S2, entry 12).

Figure S104. $^{13}$C NMR spectrum of polypropylene ferulate (Table S1, entry 5).
Figure S105. $^{13}$C NMR spectrum of polyhexalene ferulate (Table S1, entry 6).

Figure S106. $^{13}$C NMR spectrum of copoly(hydroxyethyldihydroferulic acid/ hydroxyethylferulic acid) [90:10] (Table S2, entry 2).

Figure S107. $^{13}$C NMR spectrum of copoly(hydroxyethyldihydroferulic acid/ hydroxyethylferulic acid) [80:20] (Table S2, entry 3).
**Figure S108.** $^{13}$C NMR spectrum of copoly(hydroxyethyldihydroferulic acid/hydroxyethylferulic acid) [70:30] (Table S2, entry 4).

**Figure S109.** $^{13}$C NMR spectrum of copoly(hydroxyethyldihydrocoumaric acid/hydroxyethylcoumaric acid) [90:10] (Table S2, entry 13).
**1H NMR Analysis for Copolymer Composition**

**For copoly(hydroxyethyldihydroferulic acid/hydroxyethylferulic acid) series:**

Figure S110 depicts exemplary 1H NMR spectra for the homopolymers and copolymer with hydroxyethylferulic acid (HEFA) feed fractions of 0%, 40%, and 100%. Of particular use are the peaks attributed to the methoxy hydrogens of both hydroxyethylferulic acid (HEFA) and hydroxyethyldihydroferulic acid (HEHFA) repeat units (3.8 and 3.9 ppm, respectively) and the methylene hydrogens of the HEHFA repeat units (2.6 and 2.9 ppm). Relative integration provided the incorporation values reported in Table 2.

- the polyethylene dihydroferulate (from Table S2, Entry 1),
- the 60:40 (feed ratio, HEHFA:HEFA) copolymer (from Table S2, Entry 5),
- and the polyethylene ferulate (PEF) (from Table S2, Entry 11).

Integration of the peaks for the 60:40 HEHFA:HEFA copolymer spectrum gives an area of 30.00 corresponding to the 4 methylene protons for the HEHFA repeat unit at 2.6 and 2.9 ppm and an area of 35.65 corresponding to the 3 methoxy protons for both repeat units at 3.8 and 3.9 ppm. Thus we have:

\[
\left(\frac{30.00}{4}\right) / \left(\frac{35.65}{3}\right) \times 100 = 63\% \text{ HEHFA monomers present in the copolymer.}
\]

This computes to 100 – 63 = 37% HEFA monomers present in the copolymer.

This is in close agreement with the 60:40 feed ratio of HEHFA:HEFA monomers employed. All the other compositions (from Table S2) displayed a similar agreement between the feed ratio and the measured incorporation ratio.

**For copoly(hydroxyethyldihydrocoumaric acid/hydroxyethylcoumaric acid) series:**

Figure S111 depicts exemplary 1H NMR spectra for the homopolymers and copolymer with hydroxyethylcoumaric acid (HECA) feed fractions of 0%, 10%, and 100%. Of particular use are the peaks attributed to the methylene hydrogens in the ethereal positions of both hydroxyethylcoumaric acid (HECA) and hydroxyethyldihydrocoumaric acid (HEHCA) repeat units (4.1, 4.4 and 4.3, 4.6 ppm) and the methylene hydrogens between the aromatic ring and the carbonyl group of the HEHCA repeat units (2.6 and 2.9 ppm). Relative integration provided the incorporation values reported in Table 3.

- the polyethylene dihydrocoumarate (from Table S2, Entry 12),
- the 90:10 (feed ratio, HEHCA:HECA) copolymer (from Table S2, Entry 13),
- and the polyethylene coumarate (PEC) (from Table S2, Entry 16).

Integration of the peaks for the 90:10 EHCA:ECA copolymer spectrum gives an area of 300.0 corresponding to the 4 methylene protons for the HEHCA repeat unit at 2.6 and 2.9 ppm and an area of 333.6 corresponding to the 4 methylene protons for both repeat units at 4.1, 4.3, 4.5 and 4.6 ppm. Thus we have

\[
\left(\frac{300.0}{4}\right) / \left(\frac{333.6}{4}\right) \times 100 = 90\% \text{ HEHCA monomers present in the copolymer.}
\]

This computes to 100 – 90 = 10% HECA monomers present in the copolymer.

This is in agreement with the 90:10 feed ratio of HEHCA:HECA monomers employed. All the other compositions (from Table S3) displayed a similar agreement between the feed ratio and the measured incorporation ratio.
Figure S110. $^1$H NMR spectra of copoly(hydroxyethyl)dihydroferulic acid/hydroxyethylferulic acid) with hydroxyethylferulic acid (HEFA) feed fractions of 0%, 40%, and 100%.
Figure S111. $^1$H NMR spectra of copoly(hydroxyethylidihydrocoumaric acid/hydroxyethylcoumaric acid) with hydroxyethylcoumaric acid (HECA) feed fractions of 0%, 10%, and 100%.