Copolymerization of lactones and bioaromatics via concurrent ring-opening polymerization/polycondensation

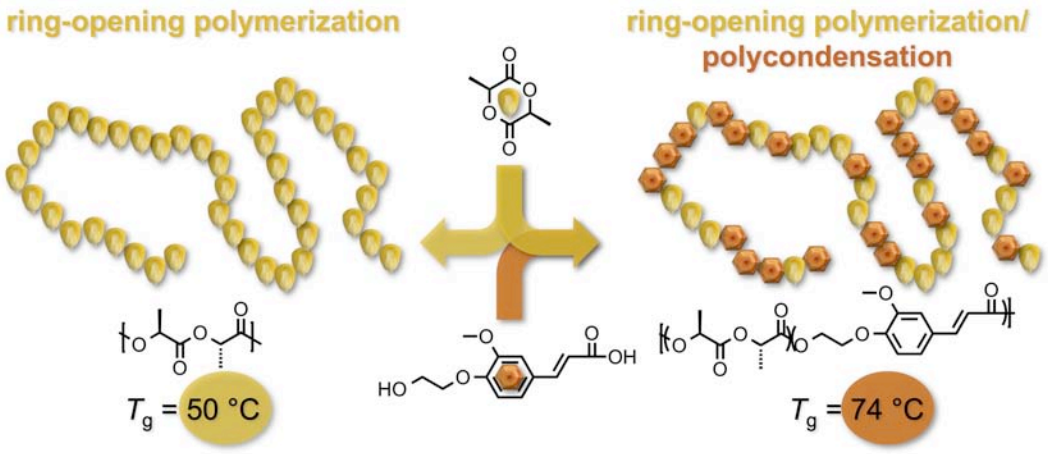
*Ha Thi Hoang Nguyen, Gabriel N. Short, Pengxu Qi and Stephen A. Miller**

The George and Josephine Butler Polymer Research Laboratory, Department of Chemistry, University of Florida Gainesville, Florida 32611-7200, United States

Supplementary Information

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

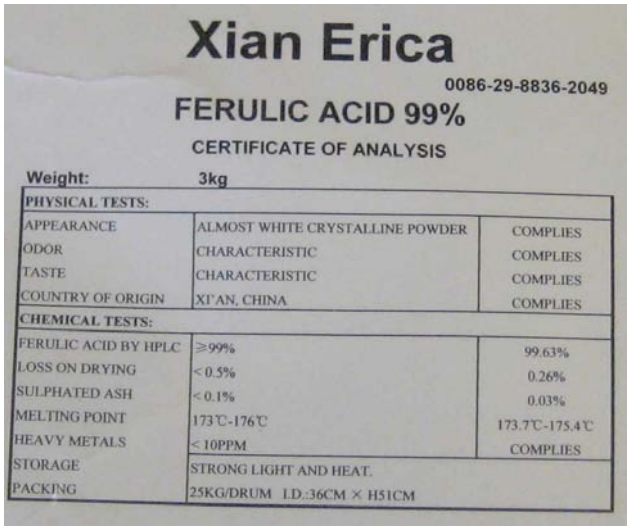
Table of Contents



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.



Xian Erica

0086-29-8836-2049

FERULIC ACID 99%

CERTIFICATE OF ANALYSIS

Weight: 3kg

PHYSICAL TESTS:		
APPEARANCE	ALMOST WHITE CRYSTALLINE POWDER	COMPLIES
ODOR	CHARACTERISTIC	COMPLIES
TASTE	CHARACTERISTIC	COMPLIES
COUNTRY OF ORIGIN	XI'AN, CHINA	COMPLIES
CHEMICAL TESTS:		
FERULIC ACID BY HPLC	≥99%	99.63%
LOSS ON DRYING	< 0.5%	0.26%
SULPHATED ASH	< 0.1%	0.03%
MELTING POINT	173℃-176℃	173.7℃-175.4℃
HEAVY METALS	< 10PPM	COMPLIES
STORAGE	STRONG LIGHT AND HEAT.	
PACKING	25KG/DRUM I.D:36CM × H51CM	

2-Chloroethanol was purchased from Acros Organics. Syringic acid was purchased from AK Scientific and vanillic acid was purchased from ICC Indofine. ε-Caprolactone was purchased from Acros Organics and distilled before use. L-lactide (PURASORB®) was purified by sublimation and stored in the glovebox before use. These were all utilized without further purification. NMR solvents, including deuterated 1,1,2,2-tetrachloroethane (TCE-d_2) deuterated chloroform ($CDCl_3$), deuterated dimethyl sulfoxide (DMSO-d_6), 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 (^{1}H 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, quintuplet; m, multiplet; br, broad.

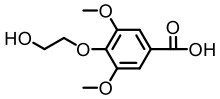
Differential scanning calorimetry (DSC) thermograms were obtained with a DSC Q1000 from TA instruments. About 3–5 mg of each sample were massed and added to a sealed pan that passed through a heat/cool/heat cycle at 10 °C/min. Reported data are from the second full cycle. The temperature typically ranged from –80 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 HFIP gel column (4.6 mm i.d., 250 mm length) using a solution of 0.1% potassium triflate (K(OTf)) in HPLC grade hexafluoroisopropanol (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.

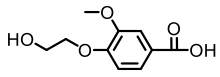
Monomer Preparation

Hydroxyethylsyringic acid



40.0 g (0.198 mol) of vanillic acid were dissolved in a mixture of 22.2g (0.554 mol) of sodium hydroxide and 5.14 g (0.034 mol) of sodium iodide in 350 mL of water. The mixture was stirred at room temperature until all solids had dissolved. At that point 19.3 mL (0.285 mol) of 2-chloroethanol were slowly added. After 30 minutes, 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 acidified with concentrated hydrochloric acid until the product crashed out. The product was isolated by gravity filtration, dried in air, and triturated in ethanol. 32.1 g of dry white powder were obtained in a 67.0% yield. ^{1}H NMR (DMSO-d_6): δ ppm 3.62 (t, J = 5.6 Hz, 2H), 3.82 (s, 6H), 3.94 (t, J = 5.6 Hz, 2H), 4.59 (s, 1H), 7.23 (d, J = 0.9 Hz, 2H), 12.91 (s, 1H). ^{13}C NMR (DMSO-d_6): δ ppm 56.0, 60.3, 74.2, 106.6, 125.8, 140.7, 152.7, 166.9.

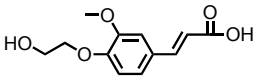
Hydroxyethylvanillic acid



30.0 g (0.178 mol) of vanillic acid were dissolved in a mixture of 16.3 g (0.408 mol) of sodium hydroxide and 4.59 g (0.030 mol) of sodium iodide in 366 mL of water. The mixture was stirred at room temperature until all solids had dissolved. At that point 17.3 mL (0.254 mol) of 2-chloroethanol were slowly added. After 30 minutes, 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 acidified with concentrated

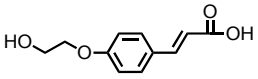
hydrochloric acid until the product crashed out. The product was isolated by gravity filtration, dried in air, and triturated in ethanol. 23.2 g of dry white powder were obtained in a 62.0% yield. ^{1}NMR (DMSO-d_6): δ ppm 3.74 (t, J = 5.1 Hz, 2H), 3.80 (s, 3H), 4.04 (t, J = 5.1 Hz, 2H), 4.88 (s, 1H), 7.04 (dd, J = 8.4, 0.9 Hz, 1H), 7.44 (dd, J = 2.0, 0.9 Hz, 1H), 7.54 (dd, J = 8.4, 2.0 Hz, 1H), 12.64 (s, 1H). ^{13}C NMR (DMSO-d_6): δ ppm 55.4, 59.4, 70.2, 111.9, 112.0, 122.9, 123.1, 148.4, 152.0, 167.1.

Hydroxyethylferulic acid



40.0 g (0.206 mol) of ferulic acid were dissolved in a mixture of 23.1 g (0.577 mol) of sodium hydroxide and 5.25 g (0.035 mol) of sodium iodide in 350 mL of water. The mixture was stirred at room temperature until all solids had dissolved. At that point 20.1 mL (0.297 mol) of 2-chloroethanol were slowly added. After 30 minutes, 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 acidified with concentrated hydrochloric acid until the product crashed out. The product was isolated by gravity filtration, dried in air, and triturated in ethanol. 38.9 g of dry white powder were obtained in a 79.3% yield. ^{1}H NMR (DMSO-d_6): δ ppm 3.72 (t, J = 4.9 Hz, 2H), 3.81 (s, 3H), 4.01 (t, J = 4.9 Hz, 2H), 4.90 (br. s., 1H), 6.44 (d, J = 15.9 Hz, 1H), 6.98 (d, J = 8.3 Hz, 1H), 7.17 (d, J = 8.3 Hz, 1H), 7.30 (s, 1H), 7.52 (d, J = 15.9 Hz, 1H), 12.20 (br. s., 1H). ^{13}C NMR (DMSO-d_6): 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.

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 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): δ ppm 3.60–3.83 (m, 2H), 4.03 (t, J = 4.9 Hz, 2H), 4.89 (br. s., 1H), 6.37 (d, J = 16.0 Hz, 1H), 6.97 (d, J = 8.7 Hz, 2H), 7.54 (d, J = 16.0 Hz, 1H), 7.62 (d, J = 8.7 Hz, 2H), 12.20 (br. s., 1H). ^{13}C NMR (DMSO-d_6): δ ppm 59.5, 69.7, 114.8, 116.4, 126.7, 129.9, 143.7, 160.4, 167.8.

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. Polymerizations were performed under ambient light, except the copolymer series with hydroxyethylferulic acid and hydroxyethylcoumaric acid, which were conducted in the dark by covering the apparatus in aluminum foil. See below.

General work-up procedure for polymerizations

The copolymers of hydroxyethylsyringic acid and ε-caprolactone were dissolved in 6 mL tetrachloroethane. These polymers were precipitated by pouring the polymer solution into 150 mL of cold methanol and cooling in the freezer overnight. These polymers were isolated by filtration and washed with methanol. The polymers were then dried under vacuum overnight. All other polymers were melted to remove them from the flask and used without further purification.

General NMR preparation

The copoly(caprolactone/hydroxyethylsyringic acid) series was prepared in TCE-d_2 and they were completely soluble. All other polymer samples were prepared in a combination of chloroform-*d* and trifluoroacetic acid-*d*. The insoluble samples were left overnight in the solvent and then heated, but were nonetheless only partially soluble.

Polyethylene ferulate (PEF)

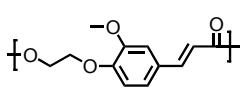


Table S2, Entry 31 and Table S3, Entry 17. A 50 mL round bottom flask was charged with 1.00 g (4.2 mmol) of hydroxyethylferulic acid and 12 mg (1 mol%) of

Sb_2O_3. The mixture was melted under an argon atmosphere gradually from 200 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 6 hours before cooling. Once cool, the aforementioned work-up procedure was applied to give the polymer in 89.6% yield (828 mg). ^{1}H NMR ($CDCl_3$/TFA-*d*): δ ppm 3.93 (m, 3H), 4.38 (m, 2H), 4.63 (m, 2H), 6.40 (d, *J* = 15.8 Hz, 1H), 6.95 (m, 1H), 7.12 (m, 2H), 7.70 (d, *J* = 15.8 Hz, 1H). ^{13}C NMR (DMSO-d_6/TFA-*d*): δ ppm 56.1, 59.2, 67.2, 111.2, 113.4, 115.9, 123.4, 127.8, 134.5, 145.5, 150.4, 166.9.

Polyethylene coumarate (PEC)

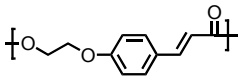


Table S2, Entry 35 and Table S3, Entry 23. A 50 mL round bottom flask was charged with 1.50 g (7.2 mmol) of hydroxyethylcoumaric acid and 21 mg (1 mol%) of Sb_2O_3. The mixture was melted under an argon atmosphere gradually from 200 to 250 ºC over a period of 4 hours. Afterwards the system was placed under dynamic vacuum to increase the degree of polymerization by removal of the volatile condensation product. The system was kept under vacuum for 6 hours before cooling. Once cool, the aforementioned work-up procedure was applied to give the polymer in 85.9% yield (1.18 g). ^{1}H NMR ($CDCl_3$/TFA-*d*): δ ppm 4.30 (br. s., 2H), 4.60 (br. s., 2H), 6.38 (d, *J* = 16.0 Hz, 1H), 6.95 (d, *J* = 8.1 Hz, 2H) 7.50 (d, *J* = 8.1Hz, 2H), 7.71 (d, *J* = 16.0 Hz, 1H). 4.30 (br. s., 2 H), 4.60 (br. s., 2 H), 6.38 (d, *J* = 16.0 Hz, 1 H), 6.95 (d, *J* = 8.1 Hz, 2 H) 7.50 (d, *J* = 8.1 Hz, 2 H), 7.71 (d, *J* = 16.0 Hz, 1 H). ^{13}C NMR ($CDCl_3$/TFA-*d*): δ ppm 63.3, 66.0, 114.4, 115.0, 127.2, 130.2, 146.4, 160.4, 168.8.

Polyethylene vanillate (PEV)

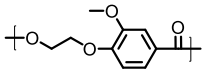


Table S2, Entry 21 and Table S3, Entry 11. A 50 mL round bottom flask connected to a bump trap containing 1 g of P_2O_5 was charged with 1.00 g (4.7 mmol) of hydroxyethylvanillic acid and 14 mg (1 mol%) of Sb_2O_3. The mixture was melted under an argon atmosphere gradually from 200 to 250 ºC over a period 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 3 hours before cooling. Once cool, the aforementioned work-up procedure was applied to give the polymer in 94.9% yield (868 mg); it is insoluble in various NMR solvents.

Polyethylene syringate (PES)

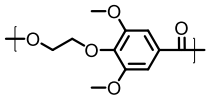


Table S2, Entry 11 and Table S3, Entry 6. A 50 mL round bottom flask connected to a bump trap containing 0.9 g of P_2O_5 was charged with 1.00 g (4.1 mmol) of hydroxyethylsyringic acid and 12 mg (1 mol%) of Sb_2O_3. The mixture was melted under an argon atmosphere gradually from 160 to 200 ºC over a 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 at 200 ºC for 4 hours then at 220 ºC for 4 hours before cooling. Once cool, the aforementioned work-up procedure was applied to give the polymer in 93.0% yield (861 mg). ^{1}H NMR ($Cl_2DCCDCl_2$): δ ppm 3.80 (s, 6H), 4.37–4.45 (m, 2H), 4.57–4.67 (m, 2H), 7.27 (s, 2H). ^{13}C NMR ($Cl_2DCCDCl_2$): δ ppm 56.3, 64.4, 70.9, 107.0, 125.4, 140.9, 153.0, 166.0.

Polycaprolactone (PCL)

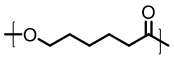


Table S1, Entry 1. A 50 mL round bottom flask was charged with 3.0 g (26.3 mmol) of ε-caprolactone and 107 mg (1 mol%) of $Sn(Oct)_2$. The mixture was melted under an argon atmosphere gradually from 80 to 170 ºC over a period of 3 hours. Afterwards the system was stirred for an additional 18 hours before cooling. Once cool, the aforementioned work-up procedure was applied to give the polymer in 90.0% yield (2.7 g). ^{1}H NMR ($Cl_2DCCDCl_2$): δ ppm 1.32 – 1.42 (m, 2H), 1.64 (quint, *J* = 7.7 Hz, 4H), 2.31 (t, *J* = 7.5 Hz, 2H), 4.05 (t, *J* = 6.7 Hz, 2H). ^{13}C NMR ($Cl_2DCCDCl_2$) δ ppm 24.4, 25.4, 28.2, 34.0, 64.0, 173.5.

Polylactic acid (PLA)

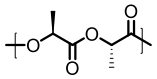
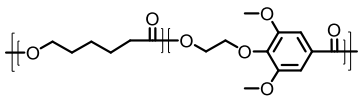


Table S3, Entry 1. In a glovebox, a 50 mL round bottom flask was charged with 1.0 g (6.9 mmol) of L-lactide and 28 mg (1 mol%) of $Sn(Oct)_2$. The mixture was melted under an argon atmosphere at 100 ºC for one hour, then gradually increased to 160 ºC over a period of 20 hours before cooling. The system was kept under vacuum for 8 hours before cooling. Once cool, the solid was dissolved in dichloromethane and then crashed out in cold MeOH. After drying on a Schlenk line, the white polymer was obtained in 86.1% yield (862 mg). ^{1}H NMR ($CDCl_3$/TFA-*d*): δ ppm 1.58 (d, *J* = 7.1 Hz, 3H), 5.16 (q, *J* = 7.1 Hz, 1H). ^{13}C NMR ($CDCl_3$): δ ppm: 16.6, 69.0, 169.5.

Copolymers of ε-caprolactone and hydroxyethylsyringic acid



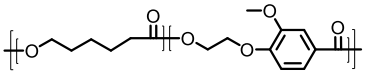
General polymerization procedure

A 50 mL round bottom flask connected to a bump trap containing 1.2 eq. of P_2O_5 was charged with hydroxyethylsyringic acid and ε-caprolactone with varying molar ratios and 1 mol% of Sb_2O_3. 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.

Copoly(caprolactone/ hydroxyethylsyringic acid) [50:50]

Table S2, Entry 6. 84.2% yield. ^{1}H NMR ($Cl_2DCCDCl_2$): δ ppm 1.30–1.53 (m, 2H), 1.57–1.83 (m, 4 H), 2.23–2.45 (m, 2H), 3.74–3.91 (m, 6 H), 4.04, 4.29 (m, m, 2H), 4.23, 4.34 (s, s, 2H), 4.39, 4,58 (s, s, 2H), 7.22–7.30 (m, 2H). ^{13}C NMR ($Cl_2DCCDCl_2$): δ ppm 24.5, 25.4, 28.2, 34.0, 56.2, 64.2, 65.0, 70.8, 106.8, 125.3, 140.7, 152.8, 165.9, 173.5.

Copolymers of ε-caprolactone and hydroxyethylvanillic acid



General polymerization procedure for Entries 12 to 20 in Table S2

A 50 mL round bottom flask connected to a bump trap containing 2 eq. of $MgSO_4$ was charged with hydroxyethylvanillic acid and *ε*-caprolactone utilizing varying molar ratios, and 1 mol% of Sb_2O_3. The mixture was melted under an argon atmosphere at 175 ºC for 16 hours, then at 195 ºC for 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.

Copoly(caprolactone/ hydroxyethylvanillic acid) [50:50]

Table S2, Entry 16. A 50 mL round bottom flask connected to a bump trap containing 1.1 g of $MgSO_4$ was charged with 1.01 g (4.8 mmol) of hydroxyethylvanillic acid, 543 mg (4.8 mmol) of caprolactone, and 28 mg (1 mol%) of Sb_2O_3. The mixture was melted under an argon atmosphere at 175 ºC for 14 hours, then at 220 ºC for 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 80.5% yield (1.18 g). ^{1}H NMR ($CDCl_3$/TFA-*d*): δ ppm 1.28–1.55 (m, 2H), 1.56–1.89 (m, 4H), 2.21–2.53 (m, 2H), 3.81–3.99 (m, 3H), 4.07, 4.30 (m, m, 2H), 4.30, 4.49 (s, s, 2H), 4.43, 4.71 (s, s, 2H), 6.85–7.02 (m, 1H), 7.46–7.59 (m, 1H), 7.60–7.73 (m, 1H). ^{13}C NMR ($CDCl_3$ /TFA-*d*): 24.4, 25.5, 28.2, 33.9, 56.1, 63.2, 64.6, 66.9, 112.1, 113.0, 122.8, 123.6, 149.0, 152.1, 166.6, 174.1.

Copoly(caprolactone/ hydroxyethylvanillic acid) [40:60]

Table S2, Entry 17. A 50 mL round bottom flask connected to a bump trap containing 1.3 g of $MgSO_4$ was charged with 1.25 g (5.9 mmol) of hydroxyethylvanillic acid, 448 mg (3.9 mmol) of caprolactone and 29 mg (1 mol%) of Sb_2O_3. The mixture was melted under an argon atmosphere at 180 ºC for 8.5 hours then at 220 ºC for 3 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 89.4% yield (1.42 g).

Copoly(caprolactone/ hydroxyethylvanillic acid) [30:70]

Table S2, Entry 18. A 50 mL round bottom flask connected to a bump trap containing 1.7 g of $MgSO_4$ was charged with 1.51 g (7.1 mmol) of hydroxyethylvanillic acid, 347 mg (3.0 mmol) of caprolactone and 30 mg (1 mol%) of Sb_2O_3. The mixture was melted under an argon atmosphere at 185 ºC for 4 hours then at 230 ºC for 3 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 90.7% yield (1.56 g).

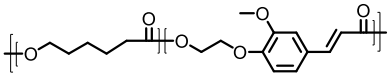
Copoly(caprolactone/ hydroxyethylvanillic acid) [20:80]

Table S2, Entry 19. A 50 mL round bottom flask connected to a bump trap containing 1.7 g of $MgSO_4$ was charged with 1.51 g (7.1 mmol) of hydroxyethylvanillic acid, 203 mg (1.8 mmol) of caprolactone and 26 mg (1 mol%) of Sb_2O_3. The mixture was melted under an argon atmosphere at 190 ºC for 4hours then at 230 ºC for 3 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 93.6% yield (1.48 g).

Copoly(caprolactone/ hydroxyethylvanillic acid) [10:90]

Table S2, Entry 20. A 50 mL round bottom flask connected to a bump trap containing 3.3 g of $MgSO_4$ was charged with 2.93 g (13.8 mmol) of hydroxyethylvanillic acid, 175 mg (1.5 mmol) of caprolactone and 46 mg (1 mol%) of Sb_2O_3. The mixture was melted under an argon atmosphere at 190 ºC for 3 hours then at 240 ºC for 3 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 93.8% yield (2.68 g).

Copolymers of ε-caprolactone and hydroxyethylferulic acid



General polymerization procedure for Entries 22 to 26 in Table S2

A 50 mL round bottom flask was charged with hydroxyethylferulic acid and ε-caprolactone with varying molar ratios, and 1 mol% of Sb_2O_3. The mixture was melted under an argon atmosphere at 175 ºC for 12 hours, then at 200 ºC for 3 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.

General polymerization procedure for Entries 27 to 30 in Table S2

A 50 mL round bottom flask was charged with hydroxyethylferulic acid and *ε*-caprolactone with varying molar ratios, and 1 mol% of Sb_2O_3. The mixture was melted under an argon atmosphere at 185 ºC for 12 hours, then at 220 ºC for 3 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.

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

Table S2, Entry 25. 84.6% yield ^{1}H NMR ($CDCl_3$ /TFA-*d*): δ ppm 1.31–1.54 (m, 2H), 1.57–1.84 (m, 4H), 2.24–2.49 (m, 2H), 3.84–3.94 (m, 3H), 4.07, 4.21 (m, m, 2H), 2.27, 4,48 (s, s, 2H), 4.35, 4.60 (s, s, 2H), 6.28–6.42 (m, 1H), 6.84–6.96 (m, 1H), 7.02–7.16 (m, 2H), 7.56–7.71 (m, 1H). ^{13}C NMR ($CDCl_3$/TFA-*d*): δ ppm 24.5, 25.4, 28.2, 33.9, 55.9, 62.3, 64.5, 67.0, 110.5, 113.3, 115.8, 122.5, 128.0, 145.1, 145.6, 150.0, 167.6, 174.0.

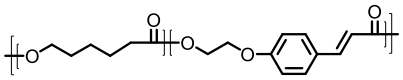
Copoly(caprolactone/ hydroxyethylferulic acid) [20:80]

Table S2, Entry 29. A 50 mL round bottom flask was charged with 1.67 g (7.0 mmol) of hydroxyethylferulic acid, 200 mg (1.7 mmol) of caprolactone and 26 mg (1 mol%) of Sb_2O_3. The mixture was melted under an argon atmosphere at 190 ºC for 6 hours then at 230 ºC for 3 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 (1.58 g).

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

Table S2, Entry 30. A 50 mL round bottom flask was charged with 3.23 g (13.6 mmol) of hydroxyethylferulic acid, 172 mg (1.5 mmol) of caprolactone and 45 mg (1 mol%) of Sb_2O_3. The mixture was melted under an argon atmosphere at 195 ºC for 4 hours then at 240 ºC for 2.5 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 hours before cooling. Once cool, the aforementioned work-up procedure was applied to give the polymer in 89.1% yield (2.82 g).

Copolymers of ε-caprolactone and hydroxyethylcoumaric acid



Copoly(caprolactone/ hydroxyethylcoumaric acid) [80:20]

Table S2, Entry 32. A 50 mL round bottom flask was charged with 997 mg (4.8 mmol) of hydroxyethylcoumaric acid, 2.19 g (19.2 mmol) of caprolactone and 71 mg (1 mol%) of Sb_2O_3. The mixture was melted under an argon atmosphere at 175 ºC for 17 hours then at 200 ºC for 3 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 88.1% yield (2.73 g).

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

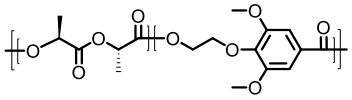
Table S2, Entry 33. A 50 mL round bottom flask was charged with 1.00 g (4.8 mmol) of hydroxyethylcoumaric acid, 548 mg (4.8 mmol) of caprolactone and 28 mg (1 mol%) of Sb_2O_3. The mixture was melted under an argon atmosphere at 180 ºC for 12 hours then at 220 ºC for 3 hours. Afterwards the system was 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 88.0% yield (1.29 g). ^{1}H NMR ($CDCl_3$/TFA-*d*): δ ppm 1.22–1.52 (m, 2H), 1.55–1.88 (m, 4H), 2.22–2.53 (m, 2H), 4.07, 4.21 (m, m, 2H), 4.21, 4.45 (s, s, 2H), 4.28, 4.57 (s, s, 2H), 6.26–6.48 (m, 1H), 6.84–7.02 (m, 2H), 7.40–7.57 (m, 2H), 7.60–7.74 (m, 1H). ^{13}C NMR ($CDCl_3$/TFA-*d*): δ ppm 24.5, 25.5, 28.3, 34.0, 62.6, 64.5, 65.9, 114.9, 115.5, 127.3, 130.0, 144.9, 145.5, 167.7, 173.9.

Copoly(caprolactone/ hydroxyethylcoumaric acid) [20:80]

Table S2, Entry 34. A 50 mL round bottom flask was charged with 1.7 g (8.2 mmol) of hydroxyethylcoumaric acid, 233 mg (2.0 mmol) of caprolactone and 30 mg (1 mol%) of Sb_2O_3. The mixture was melted under an argon atmosphere at 185 ºC for 9 hours then at 230 ºC for 3 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 85.1% yield (1.52 g).

Copolymers of L-lactide and hydroxyethylsyringic acid



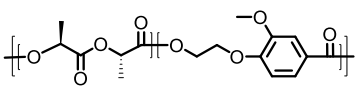
General polymerization procedure

A 50 mL round bottom flask connected to a bump trap containing 3 eq. of $MgSO_4$ was charged with hydroxyethylsyringic acid and L-lactide with varying molar ratios, and 1 mol% of Sb_2O_3. The mixture was melted under an argon atmosphere at 160 ºC for 10 hours then at 180 ºC for 30 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.

Copoly(L-lactide/hydroxyethylsyringic acid) [40:60]

Table S3, Entry 4. ^{1}H NMR ($CDCl_3$/TFA-*d*): δ ppm 1.33–1.79 (m, 6H), 3.58–4.06 (m, 6H), 4.16–4.44 (m, 2H), 4.44–4.70 (m, 2H), 5.09–5.47 (m, 2H), 7.10–7.42 (m, 2H). ^{13}C NMR ($CDCl_3$/TFA-*d*): δ ppm 16.9, 56.2, 64.4, 69.1, 70.8, 107.0, 125.4, 140.9, 152.9, 166.0, 170.6.

Copolymers of L-lactide and hydroxyethylvanillic acid



Copoly(L-lactide/hydroxyethylvanillic acid) [80:20]

Table S3, Entry 7. A 50 mL round bottom flask connected to a bump trap containing 876 mg of $MgSO_4$ was charged with 515 mg (2.4 mmol) of hydroxyethylvanillic acid, 1.4 g (9.7 mmol) of L-lactide, and 36 mg (1 mol%) of Sb_2O_3. The mixture was melted under an argon atmosphere at 160 ºC for 9 hours then at 180 ºC for 36 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 48.1% yield (900 mg). ^{1}H NMR ($CDCl_3$/TFA-*d*): δ ppm 1.14–1.98 (m, 6H), 3.65–4.07 (m, 3H), 4.12–4.45 (m, 2H), 4.45–4.77 (m, 2H), 4.97–4.52 (m, 2H), 6.72–7.06 (m, 1H), 7.46–7.60 (m, 1H), 7.60–7.91 (m, 1H). ^{13}C NMR ($CDCl_3$/TFA-*d*): δ ppm 16.7, 56.0, 63.3, 66.6, 69.0, 112.4, 112.9, 122.5, 123.8, 149.1, 152.2, 165.6, 170.8.

Copoly(L-lactide/hydroxyethylvanillic acid) [60:40]

Table S3, Entry 8. This polymer was synthesized using the same procedure as for copoly(L-lactide/ hydroxyethylvanillic acid) [80:20]. 1.18 g (5.6 mmol) of hydroxyethylvanillic acid, 1.2 g (8.3 mmol) of L-lactide and 41 mg (1 mol%) of Sb_2O_3 were used. The product was obtained in 63.8% yield (1.45 mg).

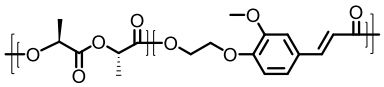
Copoly(L-lactide/hydroxyethylvanillic acid) [40:60]

Table S3, Entry 9. A 50 mL round bottom flask connected to a bump trap containing 2.2 g of $MgSO_4$ was charged with 1.3 g (6.1 mmol) of hydroxyethylvanillic acid, 589 mg (4.1 mmol) of L-lactide, and 30 mg (1 mol%) of Sb_2O_3. The mixture was melted under an argon atmosphere at 165 ºC for 9 hours, at 180 ºC for 27 hours, and then at 200 ºC for 3 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 79.0% yield (1.41 g).

Copoly(L-lactide/hydroxyethylvanillic acid) [20:80]

Table S3, Entry 10. A 50 mL round bottom flask connected to a bump trap containing 2.9 g of $MgSO_4$ was charged with 1.7 g (8.0 mmol) of hydroxyethylvanillic acid, 289 mg (2.0 mmol) of L-lactide, and 29 mg (1 mol%) of Sb_2O_3. The mixture was melted under an argon atmosphere at 165 ºC for 9 hours, at 180 ºC for 2 hours, and then at 200 ºC for 1 hour. 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 91.8% yield (1.69 g).

Copolymers of L-lactide and hydroxyethylferulic acid



General polymerization procedure for Entries 12 to 15 in Table S3

A 50 mL round bottom flask was charged with hydroxyethylferulic acid and *L*-lactide with varying molar ratios, and 1 mol% of Sb_2O_3. The mixture was melted under an argon atmosphere at 160 ºC for 10 hours then at 180 ºC for 30 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

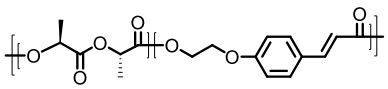
Copoly(L-lactide/hydroxyethylferulic acid) [60:40]

Table S3, Entry 15. ^{1}H NMR ($CDCl_3$/TFA-*d*): δ ppm 1.30–1.92 (m, 6H), 3.65–4.04 (m, 3H), 4.07–4.39 (m, 2H), 4.39–4.79 (m, 2H), 4.94–5.49 (m, 2H), 6.17–6.47 (m, 1H), 6.77–6.98 (m, 1H), 6.98–7.20 (m, 2H), 7.53–7.74 (m, 1H). ^{13}C NMR ($CDCl_3$ /TFA-*d*): δ ppm 16.9, 55.9, 63.5, 67.2, 68.9, 110.6, 113.6, 115.9, 122.9, 145.8, 146.2, 149.6, 159.0, 167.0, 171.3.

Copoly(L-lactide/hydroxyethylferulic acid) [20:80]

Table S3, Entry 16. A 50 mL round bottom flask connected to a bump trap was charged with 2.65 g (11.1 mmol) of hydroxyethylferulic acid, 0.4 g (2.8 mmol) of L-lactide, and 42 mg (1 mol%) of Sb_2O_3. The mixture was melted under an argon atmosphere at 180 ºC for 11 hours then at 210 ºC for 26 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 at 210 ºC then 2 more hours at 220 ºC before cooling. Once cool, the aforementioned work-up procedure was applied to give the polymer in 83.9% yield (2.39 g).

Copolymers of L-lactide and hydroxyethylcoumaric acid



General polymerization procedure for Entries 18 to 21 in Table S3

A 50 mL round bottom flask was charged with hydroxyethylcoumaric acid and L-lactide with varying molar ratios, and 1 mol% of Sb_2O_3. The mixture was melted under an argon atmosphere at 160 ºC for 10 hours then at 180 ºC for 30 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.

Copoly(L-lactide/hydroxyethylcoumaric acid) [60:40]

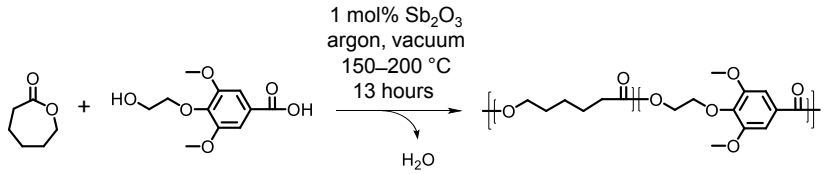
Table S3, Entry 21. ^{1}H NMR ($CDCl_3$/TFA-*d*): δ ppm 1.29–1.84 (m, 6H), 3.88–4.31 (m, 2H), 4.31–4.75 (m, 2H), 5.00–5.41 (m, 2H), 6.25–6.46 (m, 1H), 6.69–6.99 (m, 2H), 7.35–7.55 (m, 2H), 7.57–7.77 (m, 1H). ^{13}C NMR ($CDCl_3$ /TFA-*d*): δ ppm 16.9, 63.2, 66.1, 68.6, 114.6, 114.9, 127.4, 129.9, 145.5, 160.6, 167.0, 170.9.

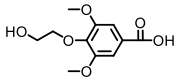
Copoly(L-lactide/hydroxyethylcoumaric acid) [20:80]

Table S3, Entry 22. This polymer was synthesized using the same procedure as for copoly(L-lactide/ hydroxyethylferulic acid) [20:80]. 2.31 g (11.1 mmol) of hydroxyethylcoumaric acid, 0.4 g (2.8 mmol) of lactide, and 42 mg (1 mol%) of Sb_2O_3 were used. The product was obtained in 84.4% yield (2.28 g).

Summary of Polymerization Data

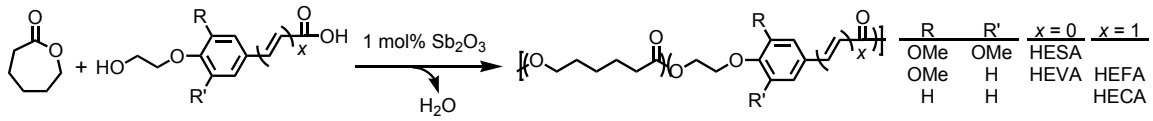
Table S1. ROP polycondensation optimization conditions for the copolymer of ε-caprolactone and hydroxyethylsyringic acid prepared with a 20:80 ratio of monomers, respectively.[a]



Entry			Catalyst	M_n [b] (Da)	M_w [b] (Da)	PDI [b]	T_g [c] (°C)	Yield (%)	Appearance
1	20	80	$Ti(OiPr)_4$	6,600	14,900	2.3	57	88.6	red
2	20	80	$Sn(Oct)_2$	5,500	9,500	1.7	56	69.8	white
3	20	80	TBD	3,200	5,200	1.6	44	72.5	white
4	20	80	Hydrotalcite 0.5%	2,500	4,300	1.7	40	40.5	white
5	20	80	Bu_2SnO	9,400	19,400	2.1	63	80.1	off-white
6	20	80	Sb_2O_3	12,200	21,300	1.7	53	97.0	white
7[d]	20	80	Sb_2O_3	13,100	23,200	1.8	60	85.2	white
8[e]	20	80	Sb_2O_3	17,800	31,500	1.8	60	91.2	white

[a]1 mol% catalyst except 0.5 mol% hydrotalcite; TBD = triazabicyclodecene; melted under argon for 5 hours with a temperature ramp from 150 to 200 °C; 8 hours dynamic vacuum at 200 °C. [b]GPC in hexafluoroisopropanol (HFIP) at 40 °C versus polymethyl methacrylate (PMMA) standards. [c]Determined by DSC. [d]4 hours dynamic vacuum at 200 °C then 4 hours at 220 °C. [e]Bump trap charged with 1.5 equivalents of P_2O_5.

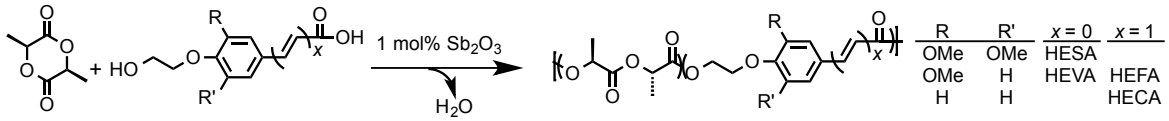
Table S2. Polymerization results and characterization of copolymers prepared from α-caprolactone and bioaromatics HESA, HEVA, HEFA, and HECA.[a]

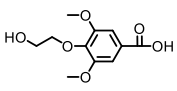


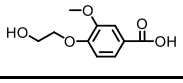
Entry[b]	Monomer feed %		Inc. HESA[e] (mol%)	Yield (%)	M_n[f] (Da)	M_w[f] (Da)	PDI[f]	T_g[g] (°C)	T_m[g] (°C)	$T_{95\%}$[h] (°C)
1	100	0	0	90.0	15,000	28,200	1.9	n.o.	53	255
2	90	10	11	93.3	29,700	60,400	2.0	-48	37	278
3	80	20	23	94.5	20,300	43,800	2.2	-35	n.o.	289
4	70	30	35	80.0	27,600	55,600	2.0	-18	n.o.	281
5	60	40	44	80.8	25,700	49,000	1.9	1	n.o.	293
6	50	50	57	84.2	25,700	49,200	1.9	20	n.o.	316
7	40	60	59	88.3	23,200	42,600	1.8	33	n.o.	316
8	30	70	78	89.7	21,100	37,800	1.8	47	126	316
9	20	80	85	91.2	17,800	31,500	1.8	60	156	316
10	10	90	95	95.6	14,900	27,900	1.9	67	171	300
11	0	100	100	93.0	10,600	18,500	1.7	76	183	318
Entry[c]	Monomer feed %		Inc. HEVA[e] (mol%)	Yield (%)	M_n[f] (Da)	M_w[f] (Da)	PDI[f]	T_g[g] (°C)	T_m[g] (°C)	$T_{95\%}$[h] (°C)
12	90	10	12	83.7	38,600	74,800	1.9	-42	36	314
13	80	20	23	85.6	32,800	64,100	2.0	-18	92	293
14	70	30	35	86.0	23,600	49,600	2.1	4	131	295
15	60	40	45	86.1	21,900	47,500	2.2	17	165	298
16	50	50	55	80.5	16,100	32,300	2.0	33	215	277
17	40	60	59	89.4	9,800	19,900	2.0	48	233	311
18	30	70	69	90.7	4,400	10,200	2.3	64	232	313
19	20	80	72	93.6	4,900	10,700	2.2	72	250	321
20	10	90	87	93.8	9,500	14,800	1.6	77	247	318
21	0	100	100	94.9	[g]	[g]	[g]	82	254	311
Entry[d]	Monomer feed %		Inc. HEFA[e] (mol%)	Yield (%)	M_n[f] (Da)	M_w[f] (Da)	PDI[f]	T_g[g] (°C)	T_m[g] (°C)	$T_{95\%}$[h] (°C)
22	90	10	11	92.1	60,700	179,100	3.0	-39	42	311
23	80	20	22	81.7	60,200	202.200	3.4	-12	n.o.	316
24	70	30	32	93.4	28,200	88,300	3.1	6	n.o.	310
25	60	40	49	84.6	22,900	45,100	2.0	35	n.o.	296
26	50	50	63	80.6	11,700	21,500	1.8	59	n.o.	302
27	40	60	74	82.2	6,300	13,800	2.2	70	n.o.	301
28	30	70	77	90.8	5,000	10,600	2.1	87	n.o.	307
29	20	80	86	90.5	4,200	9,000	2.1	93	n.o.	321
30	10	90	94	89.1	2,400	4,800	1.9	105	n.o.	331
31	0	100	100	89.6	1,600	2,500	1.6	113	n.o.	331
Entry[d]	Monomer feed %		Inc. HECA[e] (mol%)	Yield (%)	M_n[f] (Da)	M_w[f] (Da)	PDI[f]	T_g[g] (°C)	T_m[g] (°C)	$T_{95\%}$[h] (°C)
32	80	20	19	88.1	29,200	56,800	1.9	-25	39	320
33	50	50	54	88.0	14,600	36,800	2.5	35	n.o.	312
34	20	80	74	85.1	2,700	7,800	2.8	93	199	325
35	0	100	100	85.9	[i]	[i]	[i]	109	n.o.	343

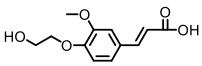
[a]1 mol% Sb_2O_3. [b]1.5 eq. of P_2O_5; melted under argon for 5 hours with a temperature ramp from 150 to 200 °C; 8 hours dynamic vacuum at 200 °C. [c]3.0 eq. of $MgSO_4$; melted under argon for 22 hours with a temperature ramp from 175 to 240 °C; 8 hours dynamic vacuum at 240 °C. [d]No drying agent; melted under argon for 20 hours with a temperature ramp from 165 to 240 °C; 6 hours dynamic vacuum at 240 °C. [e]Comonomer incorporation determined by ^{1}H NMR. [f]GPC in hexafluoroisopropanol (HFIP) at 40 °C versus polymethyl methacrylate (PMMA) standards. [g]Determined by DSC. [h]Determined by TGA; temperature at which 5% mass loss is observed under nitrogen. [i]Insolubility of the polymers prevented GPC analysis.

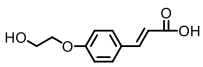
Table S3. Polymerization results and characterization of copolymers prepared from L-lactide and bioaromatics HESA, HEVA, HEFA, and HECA.[a]



Entry[b]	Monomer feed %		Inc. HESA[e] (mol%)	Yield (%)	M_n[f] (Da)	M_w[f] (Da)	PDI[f]	T_g[g] (°C)	T_m[g] (°C)	$T_{95\%}$[h] (°C)
										
1	100	0	0	86.1	21,800	49,300	2.3	50	161	207
2	80	20	44	47.4	7,800	16,000	2.0	62	n.o.	225
3	60	40	61	63.9	6,900	13,400	1.9	68	n.o.	239
4	40	60	75	82.1	4,900	9,000	1.9	70	n.o.	263
5	20	80	91	81.5	3,600	7,000	1.9	74	n.o.	301
6	0	100	100	93.0	10,600	18,500	1.7	76	183	318

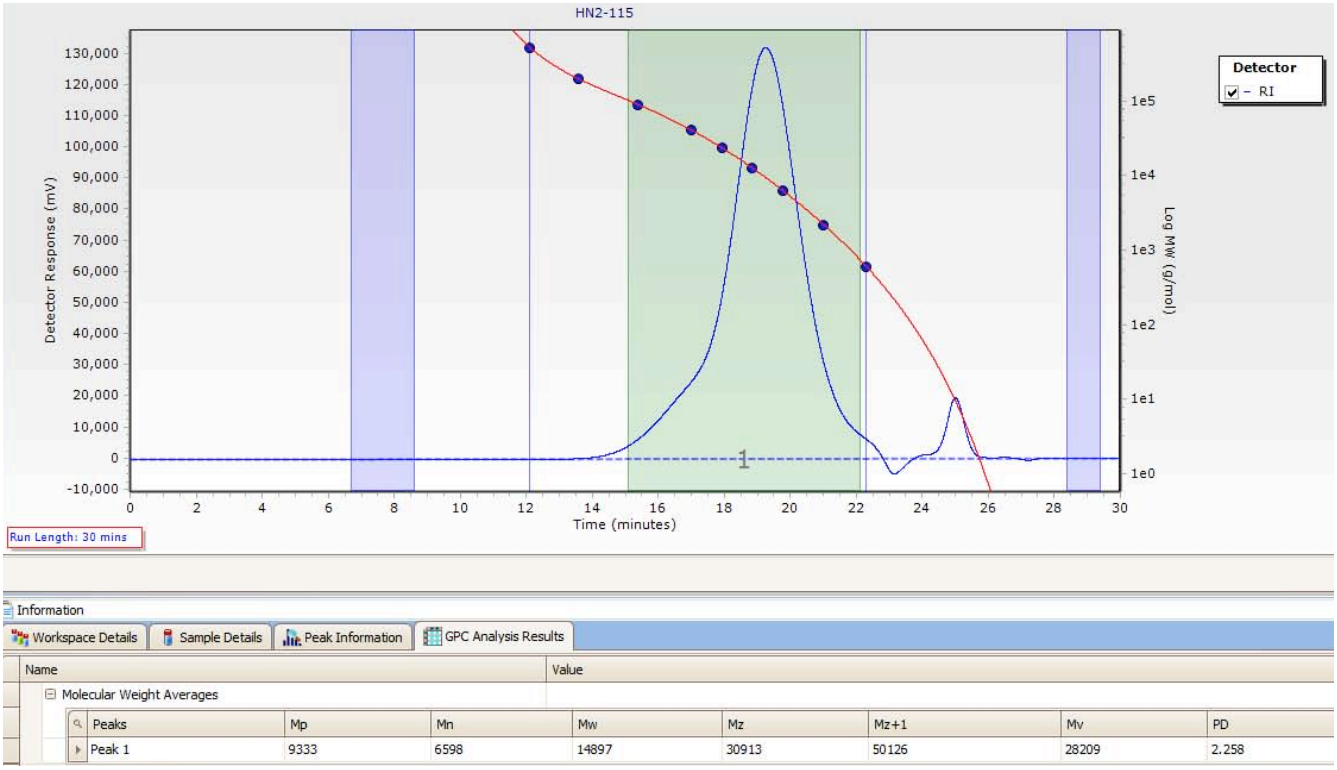
Entry[c]	Monomer feed %		Inc. HEVA[e] (mol%)	Yield (%)	M_n[f] (Da)	M_w[f] (Da)	PDI[f]	T_g[g] (°C)	T_m[g] (°C)	$T_{95\%}$[h] (°C)
										
7	80	20	41	48.1	10,500	21,900	2.1	66	n.o.	229
8	60	40	55	63.8	8,100	16,800	2.1	71	n.o.	233
9	40	60	72	79.0	5,200	10,900	2.1	77	178	271
10	20	80	77	91.8	4,800	8,500	1.8	79	240	281
11	0	100	100	94.9	[g]	[g]	[g]	82	254	311

Entry[d]	Monomer feed %		Inc. HEFA[e] (mol%)	Yield (%)	M_n[f] (Da)	M_w[f] (Da)	PDI[f]	T_g[g] (°C)	$T_{95\%}$[h] (°C)
									
12	90	10	26	32.0	16,300	65,200	4.0	64	220
13	80	20	38	46.5	10,900	27,600	2.5	69	229
14	70	30	50	47.9	10,100	38,500	3.8	74	244
15	60	40	59	66.3	6,900	19,000	2.7	82	249
16	20	80	89	83.9	1,500	2,700	1.9	107	323
17	0	100	100	89.6	1,600	2,500	1.6	113	331

Entry[d]	Monomer feed %		Inc. HECA[e] (mol%)	Yield (%)	M_n[f] (Da)	M_w[f] (Da)	PDI[f]	T_g[g] (°C)	$T_{95\%}$[h] (°C)
									
18	90	10	21	34.8	12,300	68,800	5.6	65	209
19	80	20	35	50.0	8,300	22,900	2.8	70	234
20	70	30	40	60.6	8,400	29,500	3.5	72	245
21	60	40	58	63.0	7,200	45,000	6.3	74	245
22	20	80	88	84.4	1,700	5,500	3.1	101	316
23	0	100	100	85.9	[i]	[i]	[i]	109	343

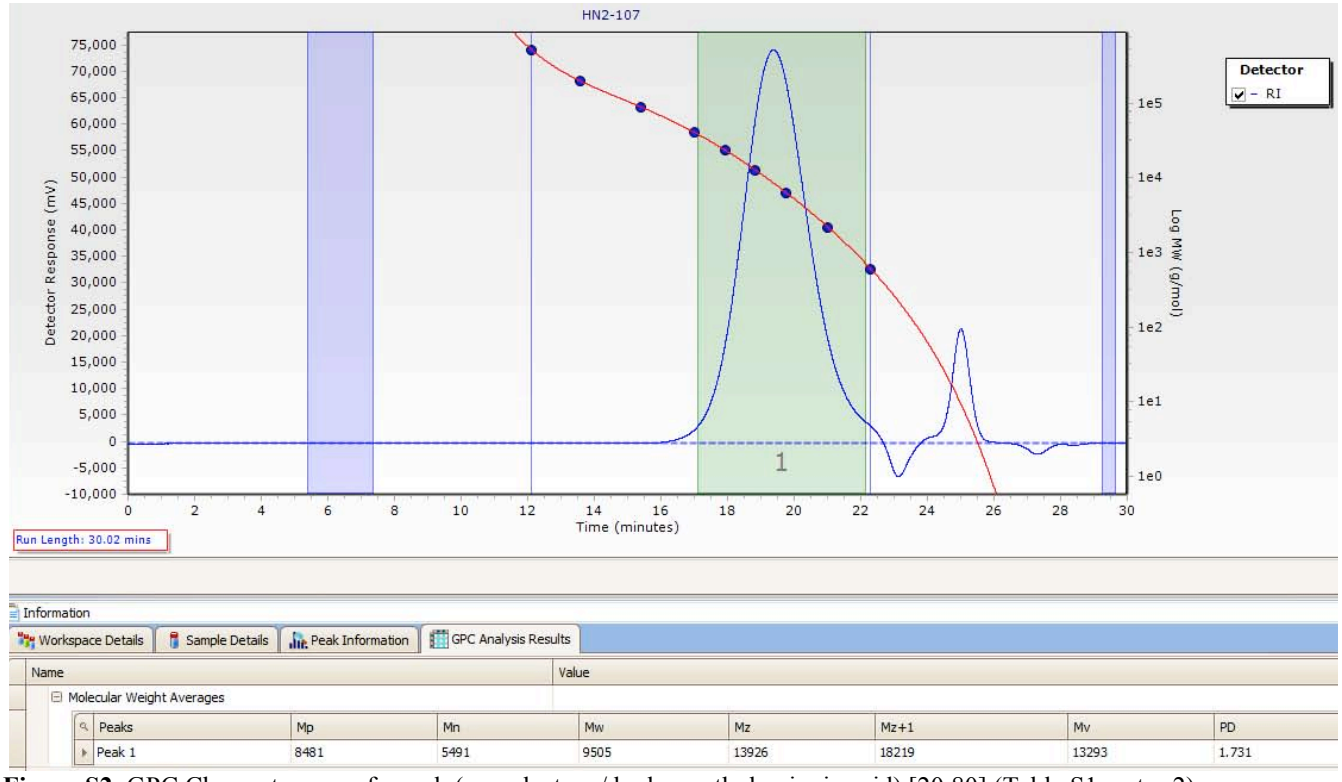
[a]1 mol% Sb_2O_3. [b]3.0 eq. of MgSO4; melted under argon for 40 hours with a temperature ramp from 160 to 180 °C; 8 hours dynamic vacuum at 180 °C. [c]3.0 eq. of $MgSO_4$; melted under argon for 40 hours with a temperature ramp from 160 to 200 °C; 8 hours dynamic vacuum at 200 °C. [d]No drying agent; melted under argon for 40 hours with a temperature ramp from 160 to 220 °C; 8 hours dynamic vacuum at 220 °C. [e]Comonomer incorporation determined by ^{1}H NMR. [f]GPC in hexafluoroisopropanol (HFIP) at 40 °C versus polymethyl methacrylate (PMMA) standards. [g]Determined by DSC. [h]Determined by TGA; temperature at which 5% mass loss is observed under nitrogen. [i]Insolubility of the polymers prevented GPC analysis.

Gel Permeation Chromatography (GPC) Data



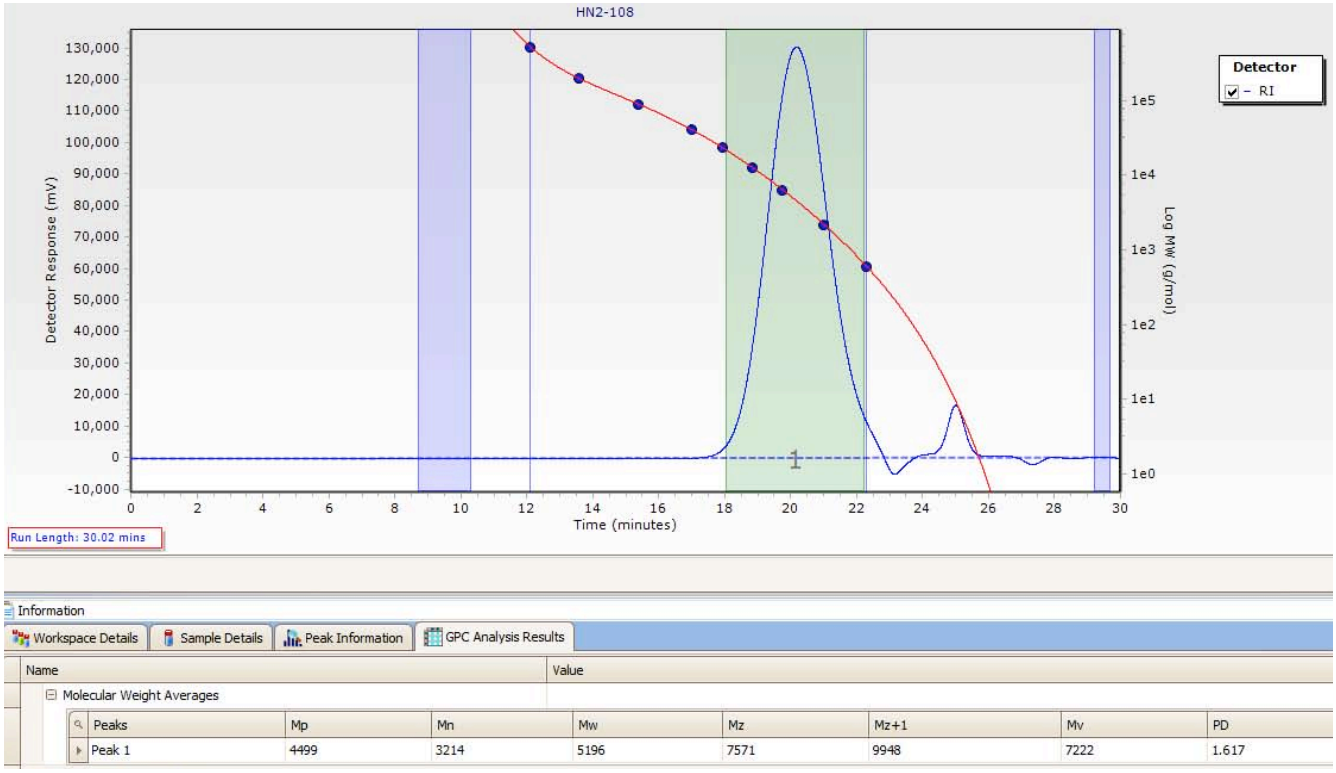
Peaks	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
Peak 1	9333	6598	14897	30913	50126	28209	2.258

Figure S1. GPC Chromatogram of copoly(caprolactone/ hydroxyethylsyringic acid) [20:80] (Table S1, entry 1).



Peaks	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
Peak 1	8481	5491	9505	13926	18219	13293	1.731

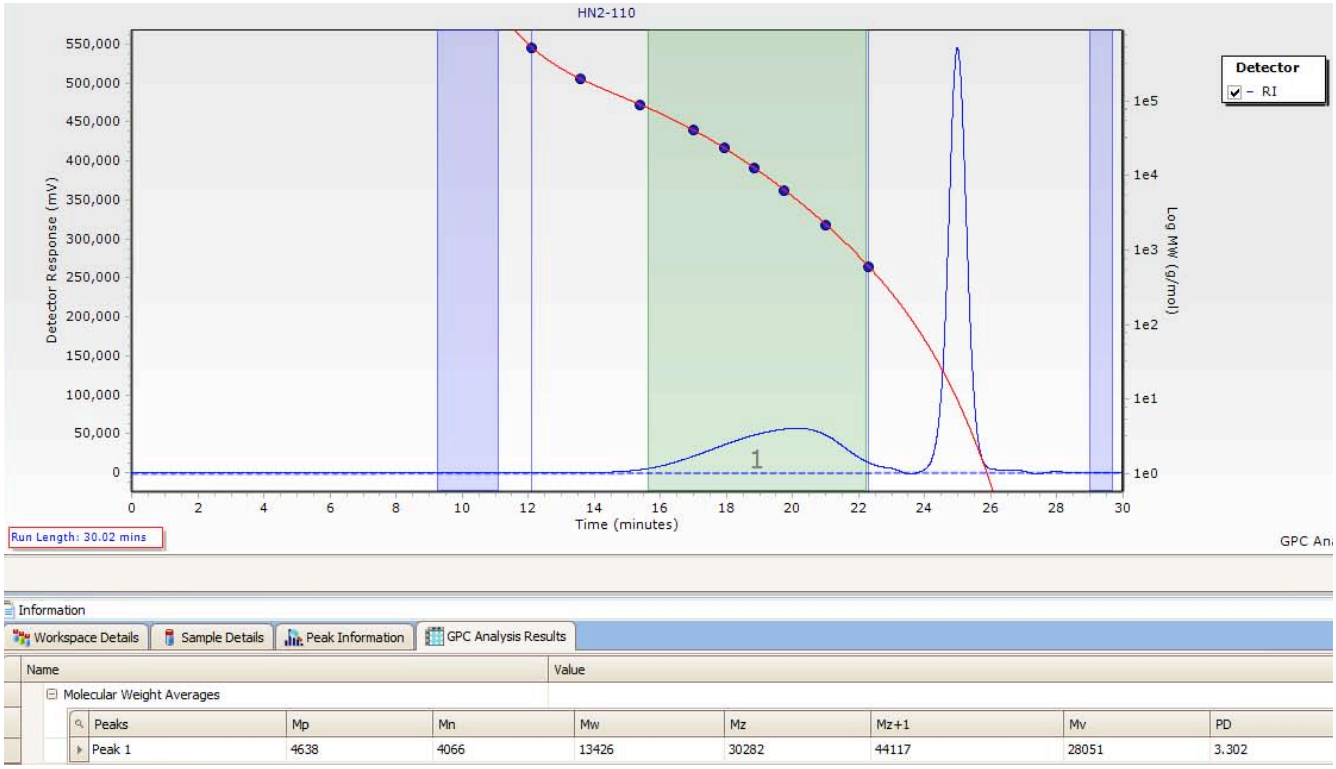
Figure S2. GPC Chromatogram of copoly(caprolactone/ hydroxyethylsyringic acid) [20:80] (Table S1, entry 2).



Name	Value
Molecular Weight Averages	

Peaks	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
Peak 1	4499	3214	5196	7571	9948	7222	1.617

Figure S3. GPC Chromatogram of copoly(caprolactone/ hydroxyethylsyringic acid) [20:80] (Table S1, entry 3).



Name	Value
Molecular Weight Averages	

Peaks	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
Peak 1	4638	4066	13426	30282	44117	28051	3.302

Figure S4. GPC Chromatogram of copoly(caprolactone/ hydroxyethylsyringic acid) [20:80] (Table S1, entry 4).

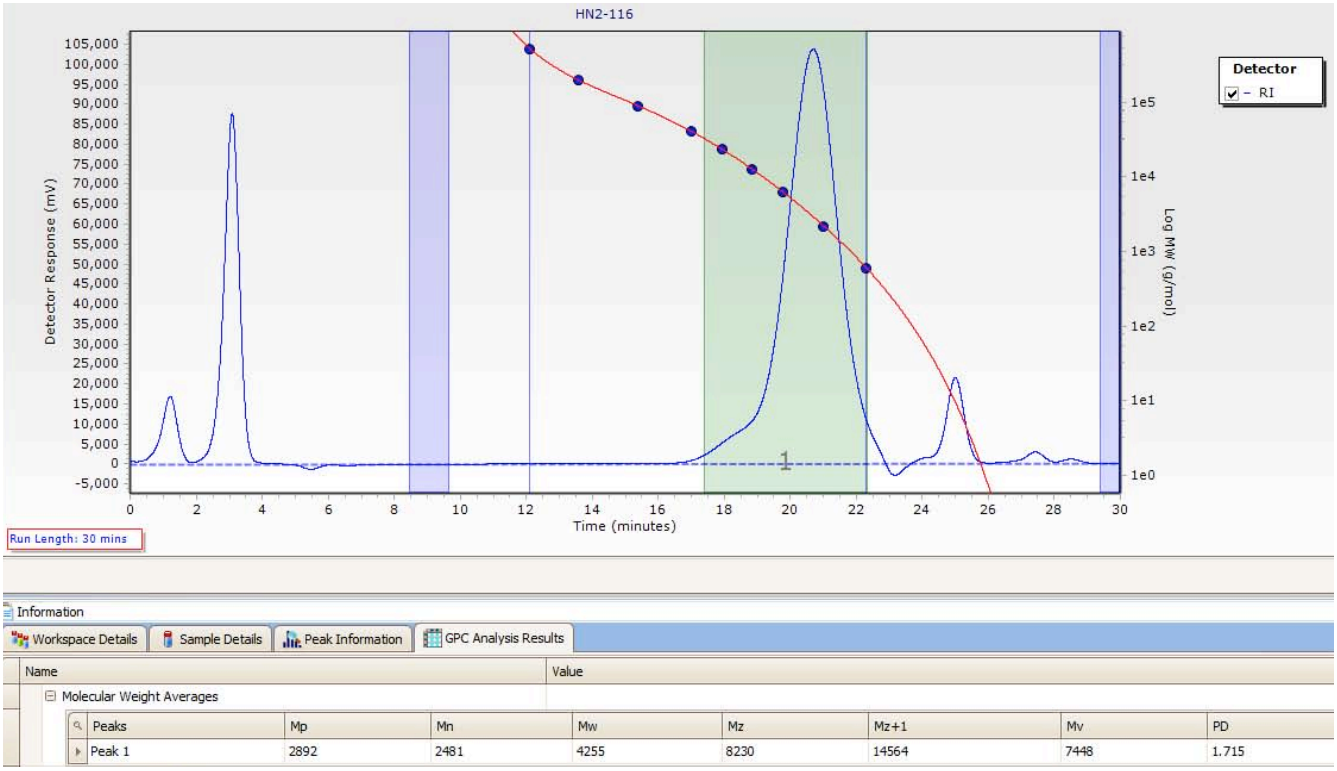


Figure S5. GPC Chromatogram of copoly(caprolactone/ hydroxyethylsyringic acid) [20:80] (Table S1, entry 5).

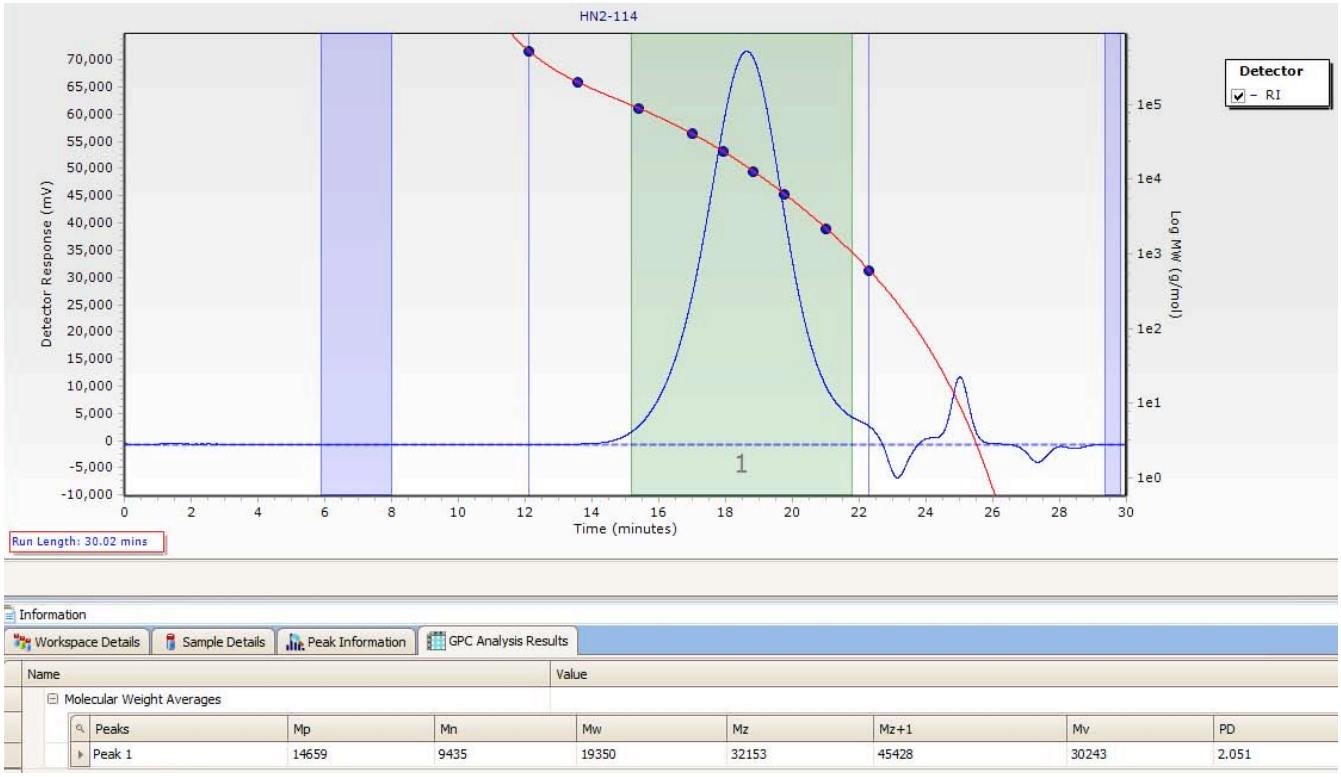


Figure S6. GPC Chromatogram of copoly(caprolactone/ hydroxyethylsyringic acid) [20:80] (Table S1, entry 6).

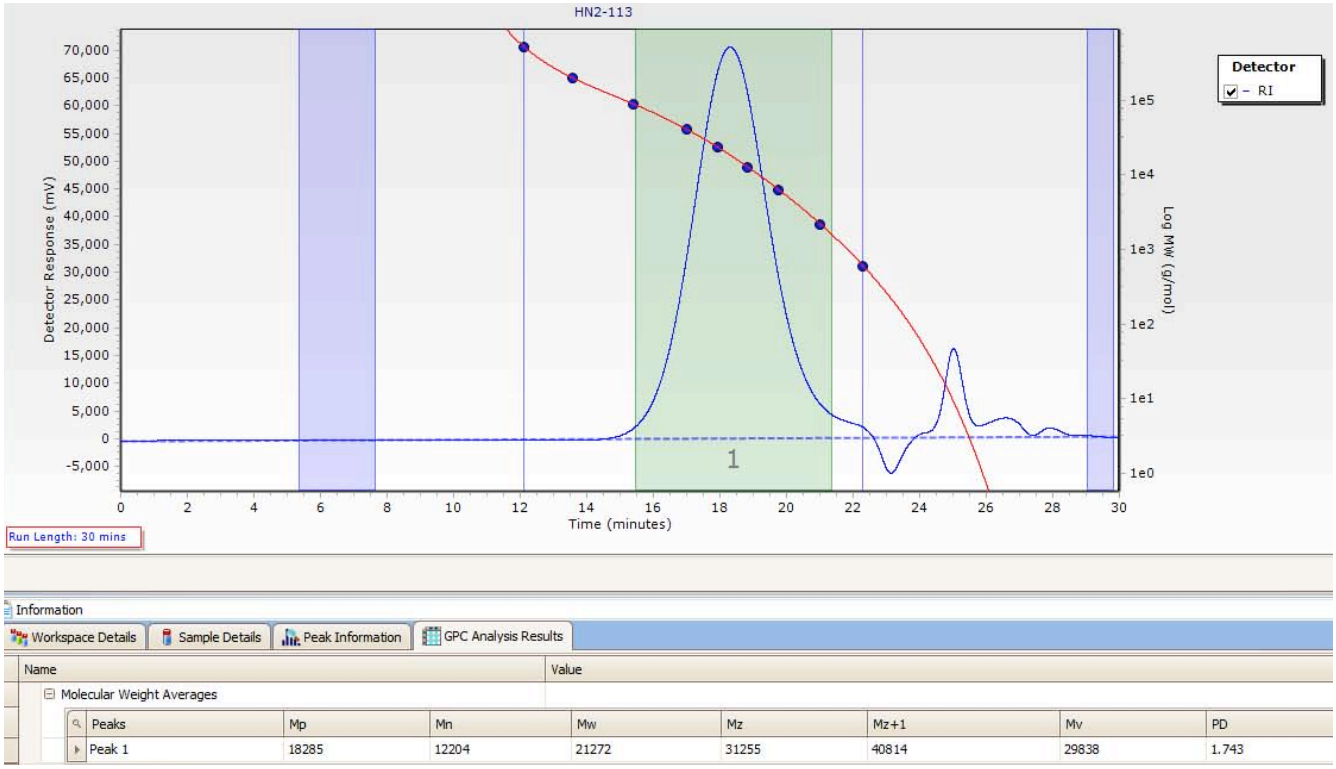


Figure S7. GPC Chromatogram of copoly(caprolactone/ hydroxyethylsyringic acid) [20:80] (Table S1, entry 7).

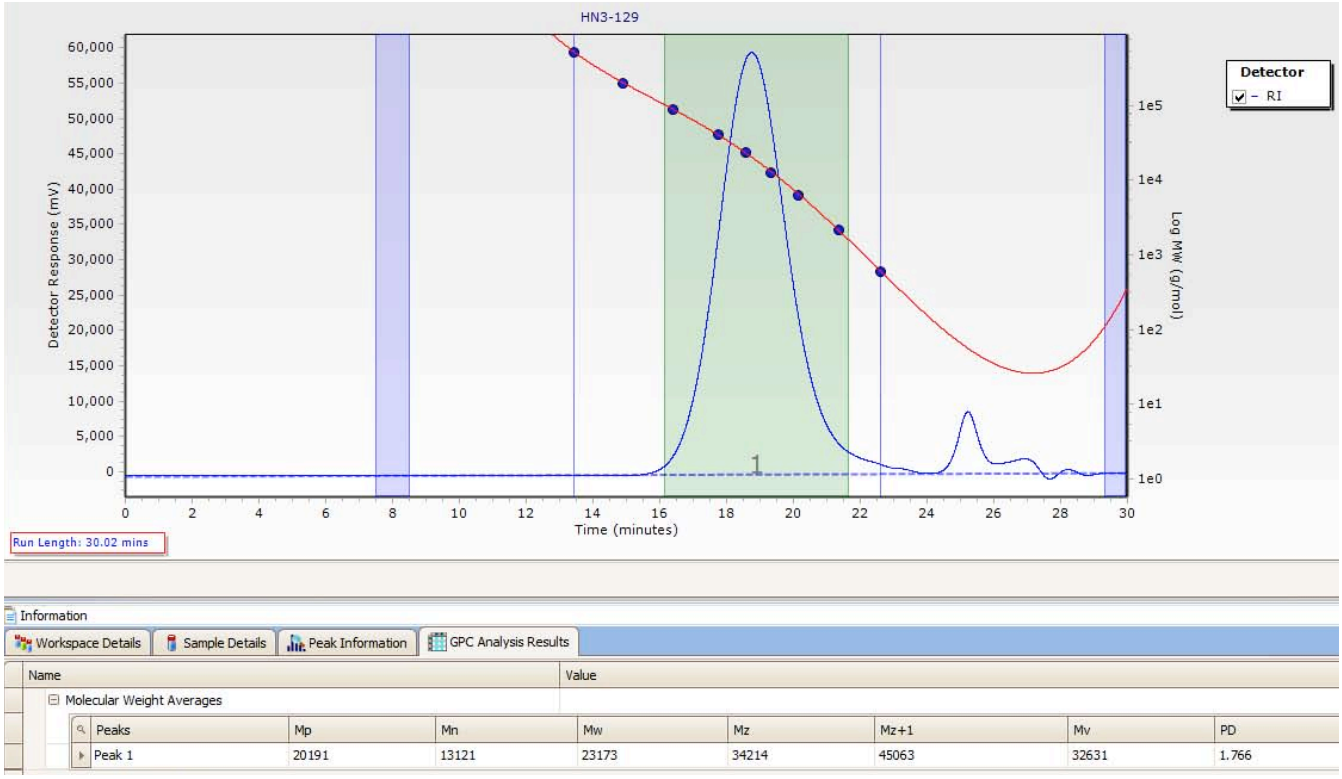


Figure S8. GPC Chromatogram of copoly(caprolactone/ hydroxyethylsyringic acid) [20:80] (Table S1, entry 8).

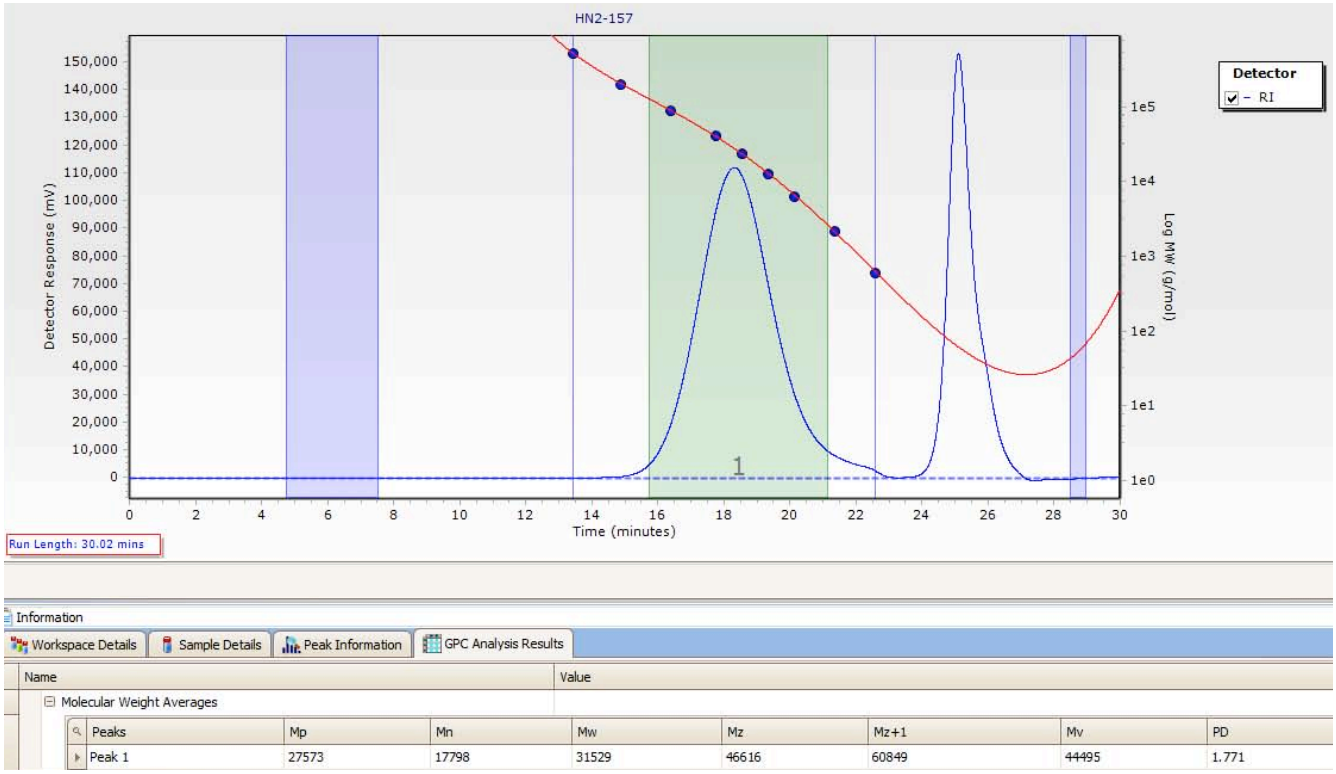


Figure S9. GPC Chromatogram of copoly(caprolactone/ hydroxyethylsyringic acid) [20:80] (Table S1, entry 8 and Table S2, entry 9).

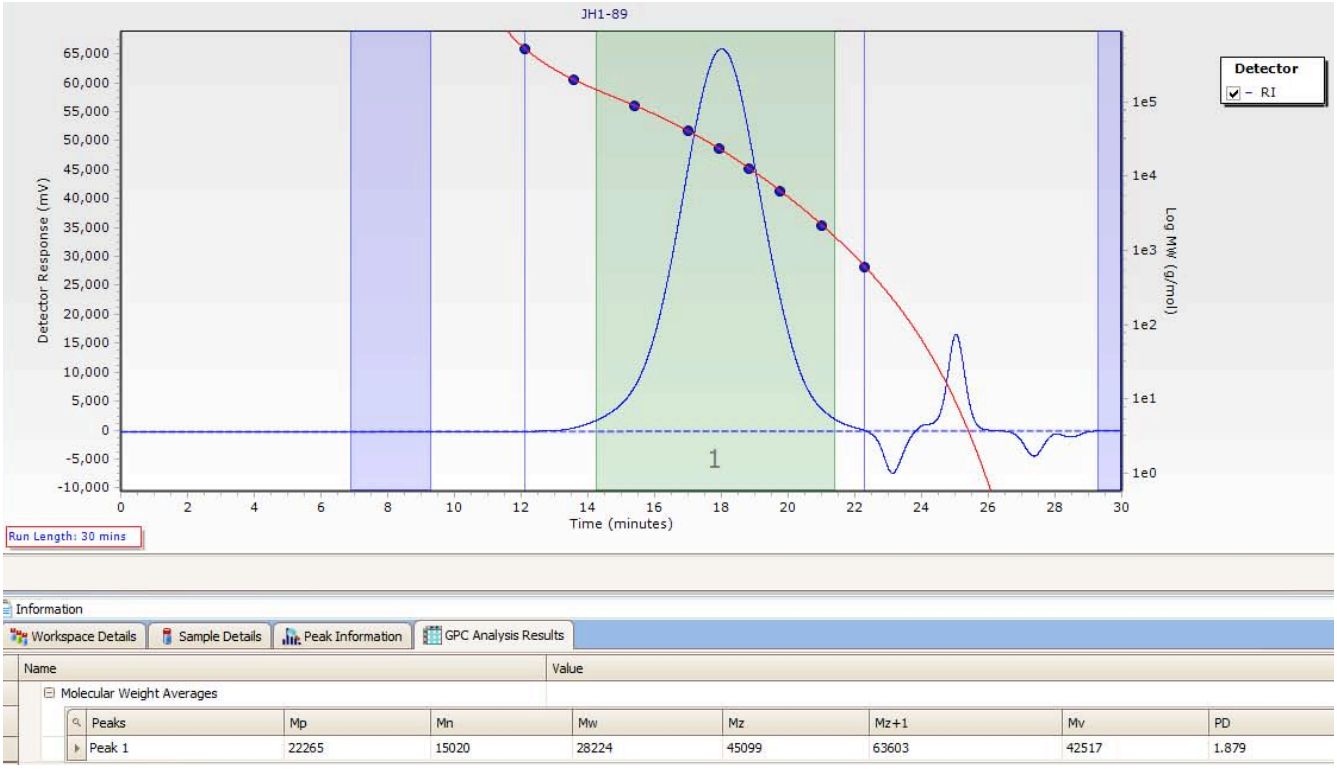


Figure S10. GPC Chromatogram of polycaprolactone (Table S2, entry 1).

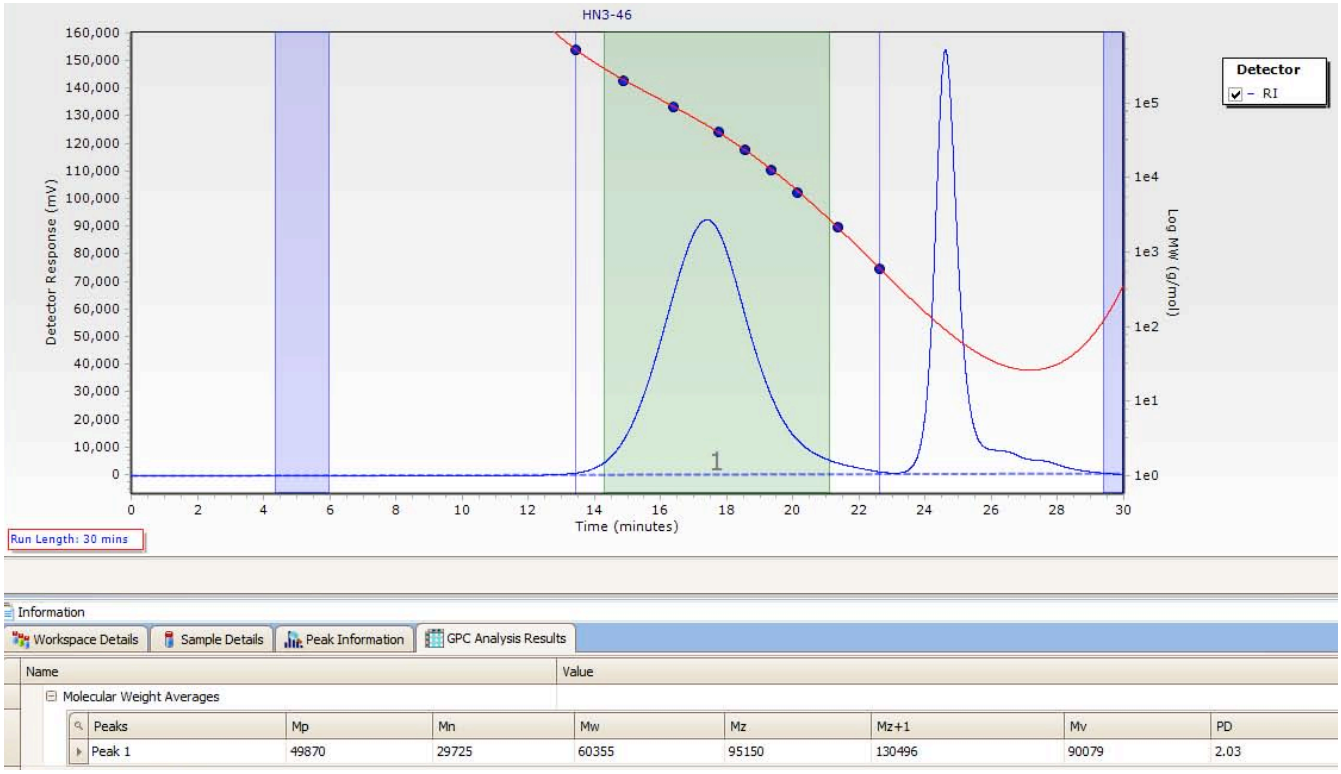


Figure S11. GPC Chromatogram of copoly(caprolactone/ hydroxyethylsyringic acid) [90:10] (Table S2, entry 2).

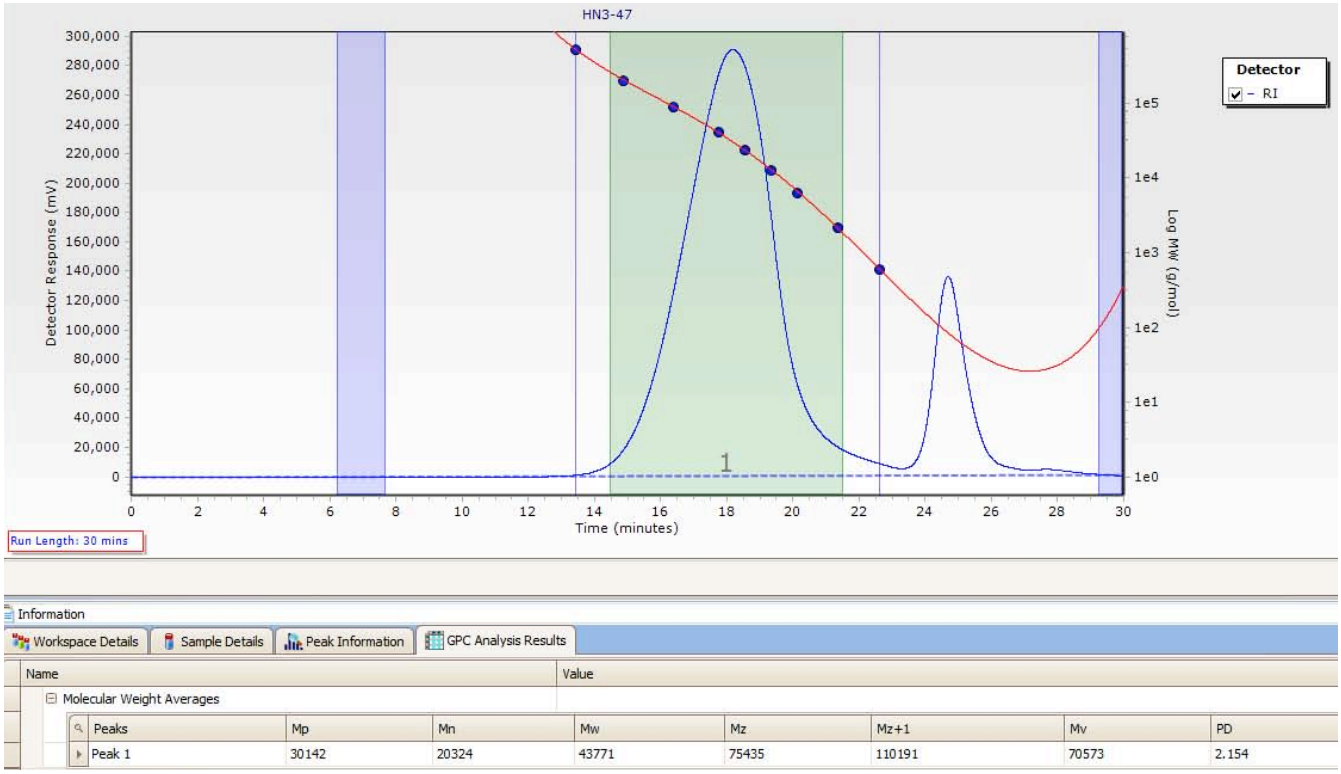


Figure S12. GPC Chromatogram of copoly(caprolactone/ hydroxyethylsyringic acid) [80:20] (Table S2, entry 3).

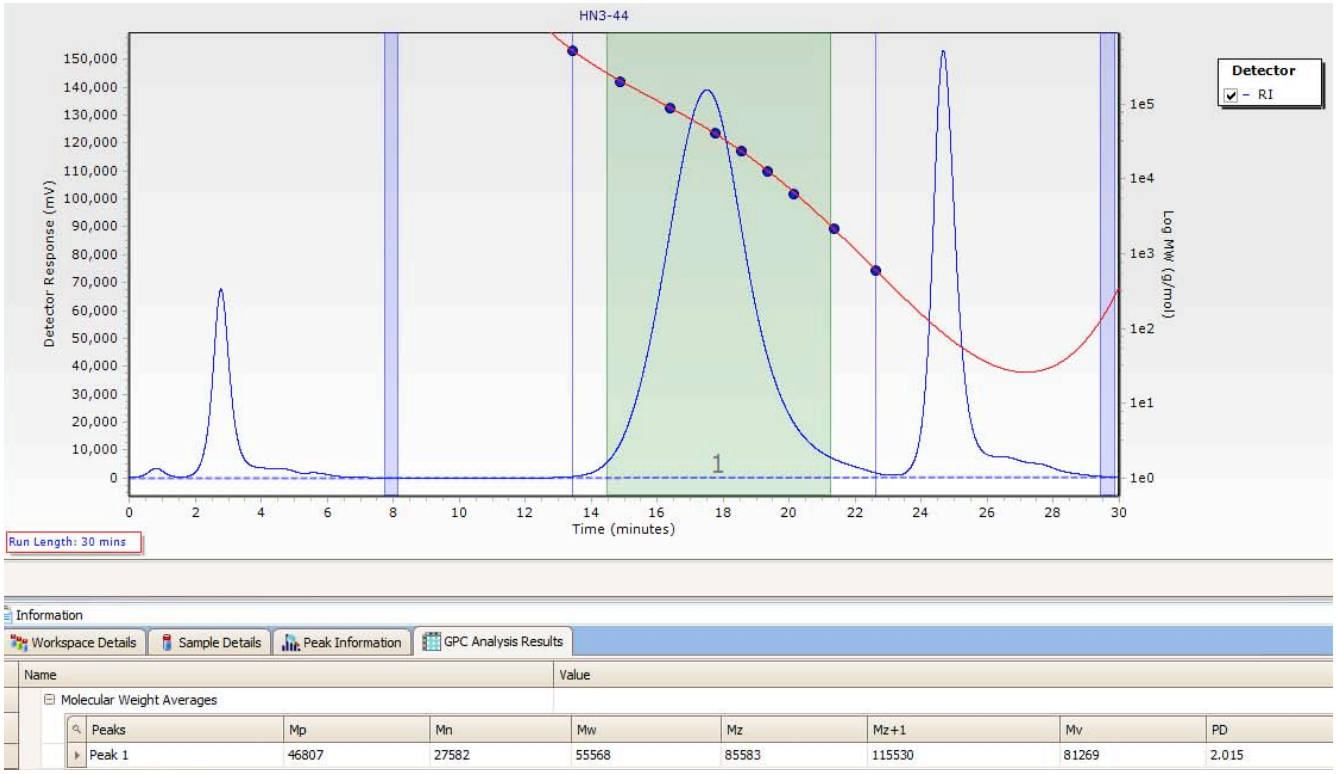


Figure S13. GPC Chromatogram of copoly(caprolactone/ hydroxyethylsyringic acid) [70:30] (Table S2, entry 4).

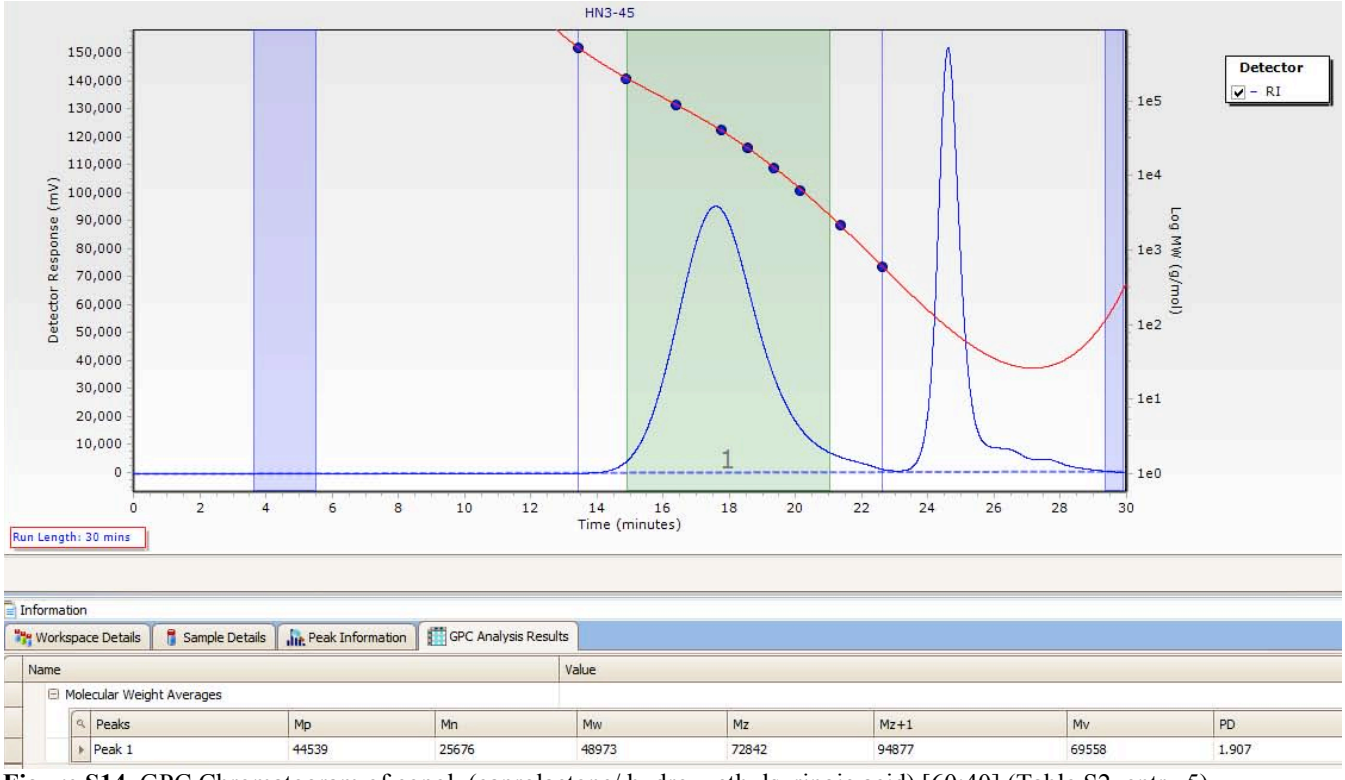
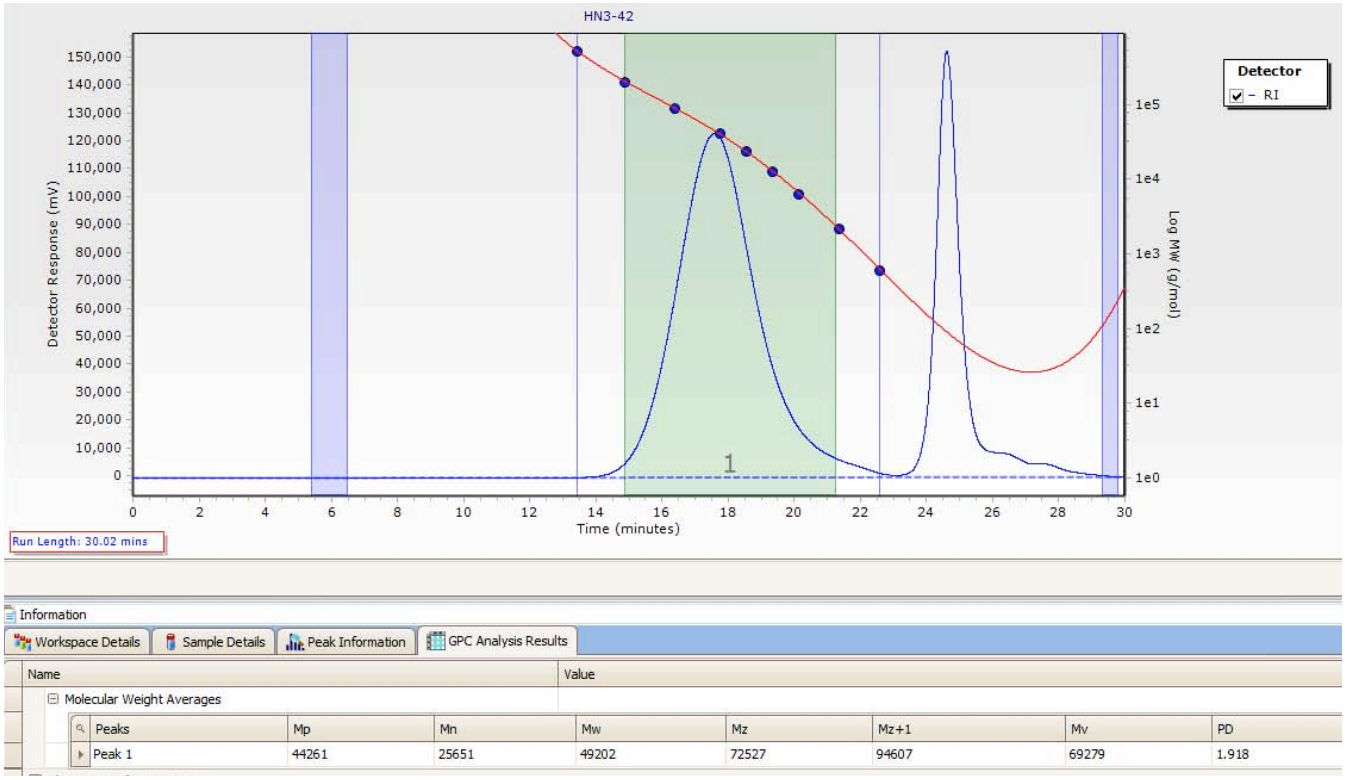
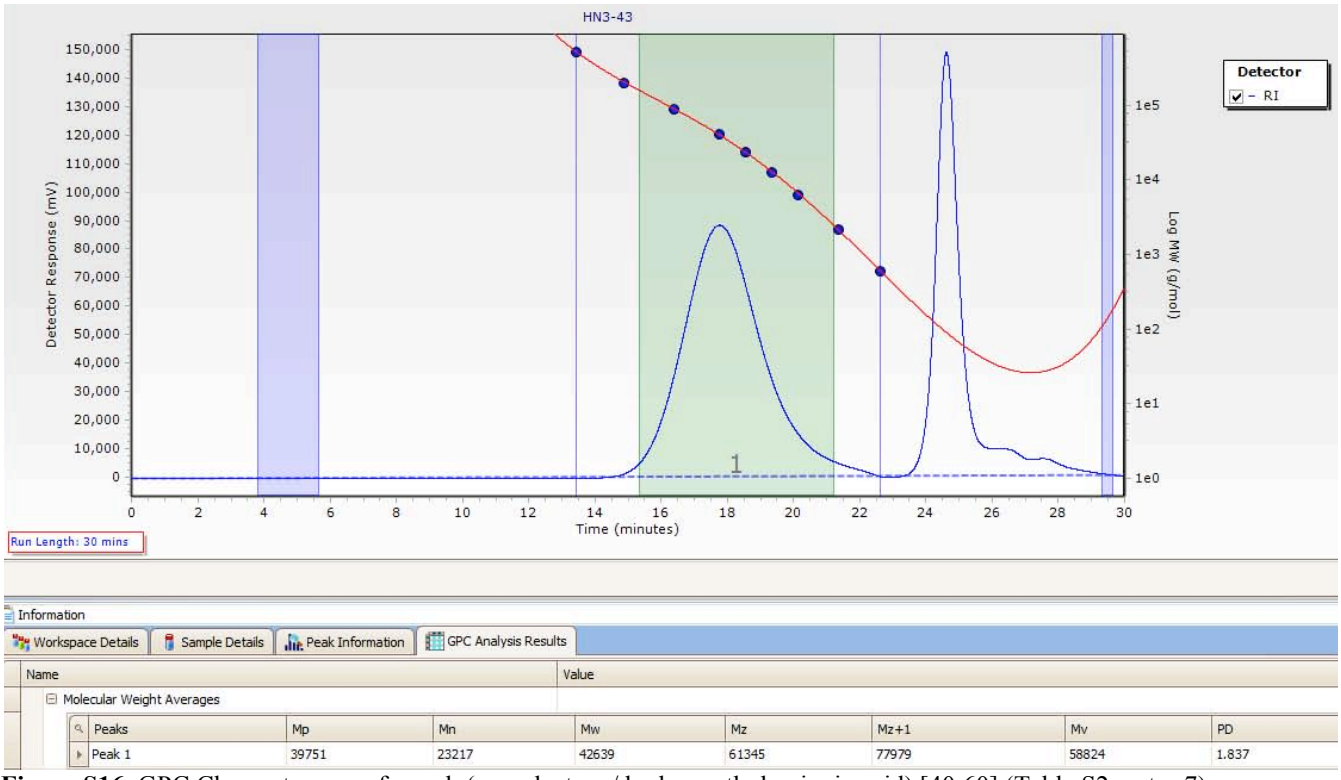


Figure S14. GPC Chromatogram of copoly(caprolactone/ hydroxyethylsyringic acid) [60:40] (Table S2, entry 5).



Peaks	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
Peak 1	44261	25651	49202	72527	94607	69279	1.918

Figure S15. GPC Chromatogram of copoly(caprolactone/ hydroxyethylsyringic acid) [50:50] (Table S2, entry 6).



Peaks	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
Peak 1	39751	23217	42639	61345	77979	58824	1.837

Figure S16. GPC Chromatogram of copoly(caprolactone/ hydroxyethylsyringic acid) [40:60] (Table S2, entry 7).

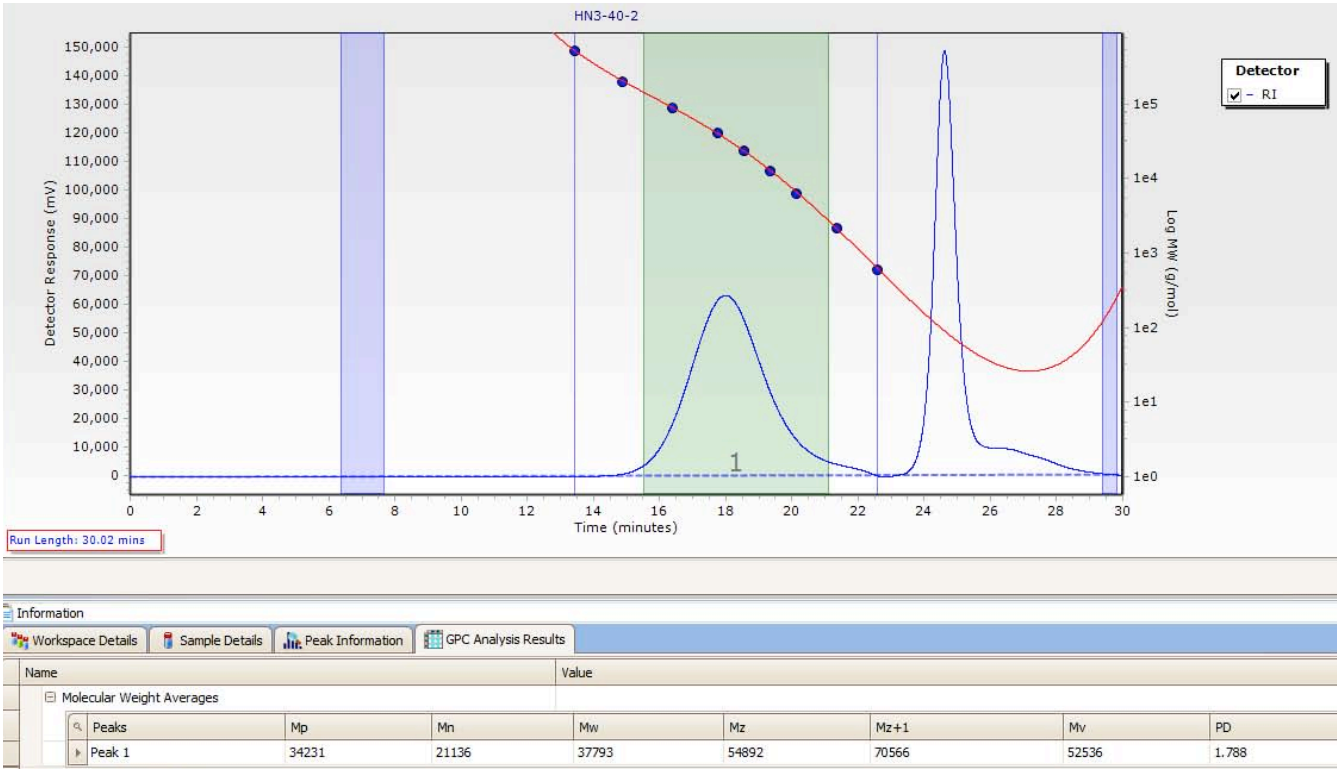


Figure S17. GPC Chromatogram of copoly(caprolactone/ hydroxyethylsyringic acid) [30:70] (Table S2, entry 8).

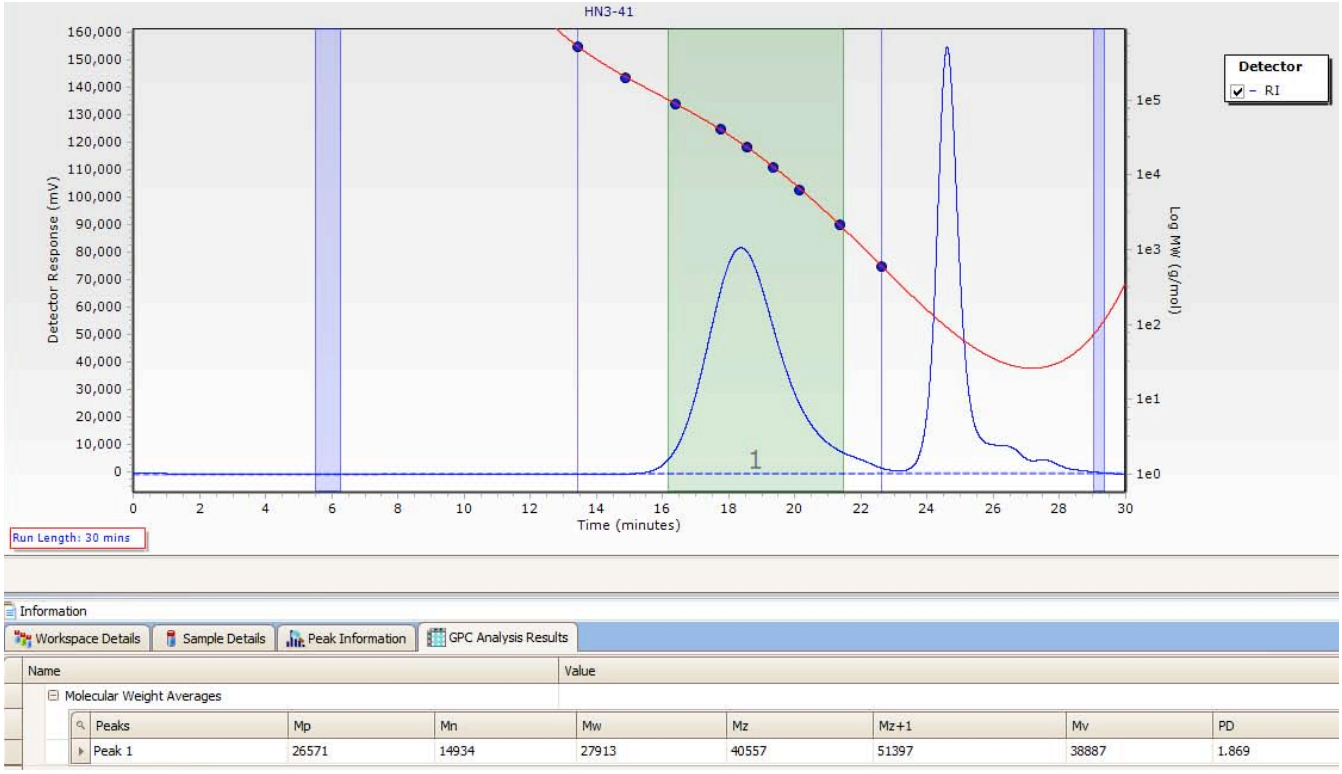


Figure S18. GPC Chromatogram of copoly(caprolactone/ hydroxyethylsyringic acid) [10:90] (Table S2, entry 10).

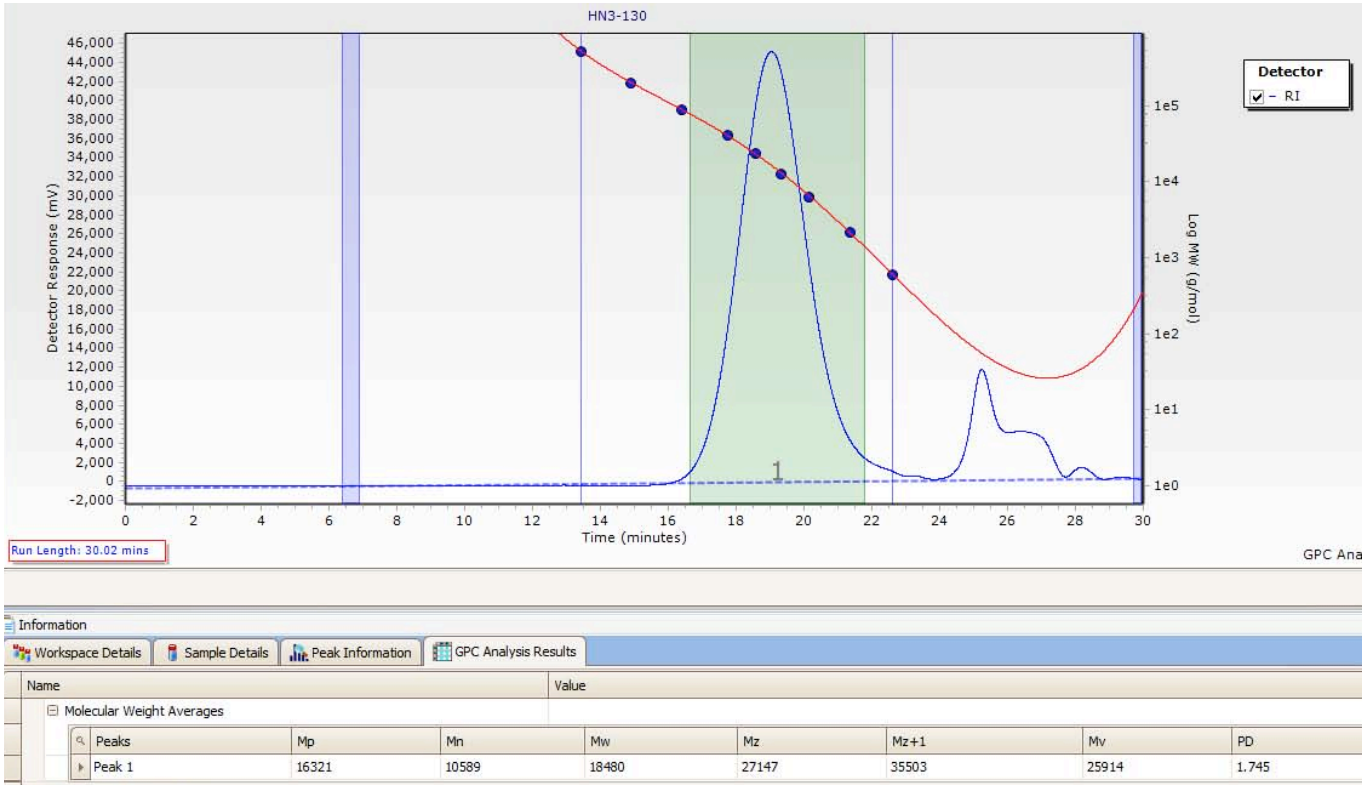


Figure S19. GPC Chromatogram of polyethylene syringate (Table S2, entry 21).

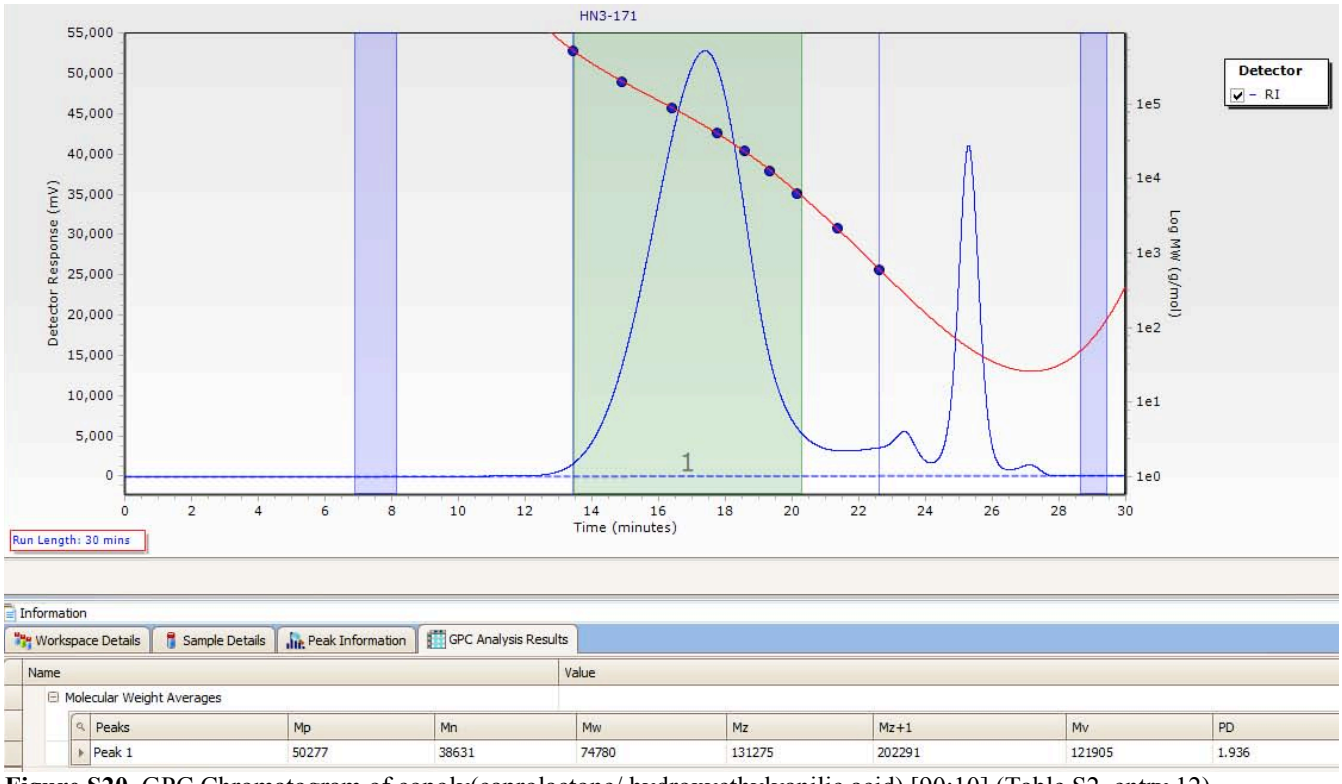
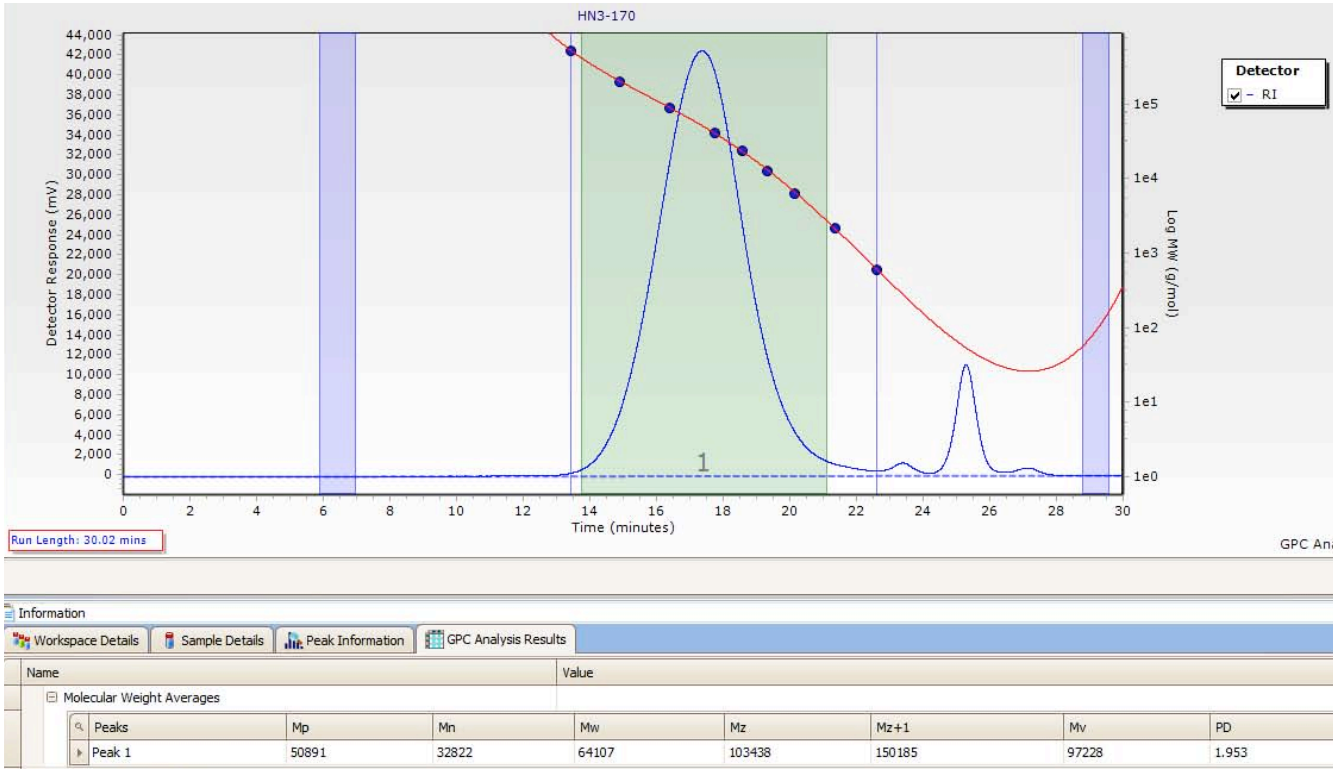
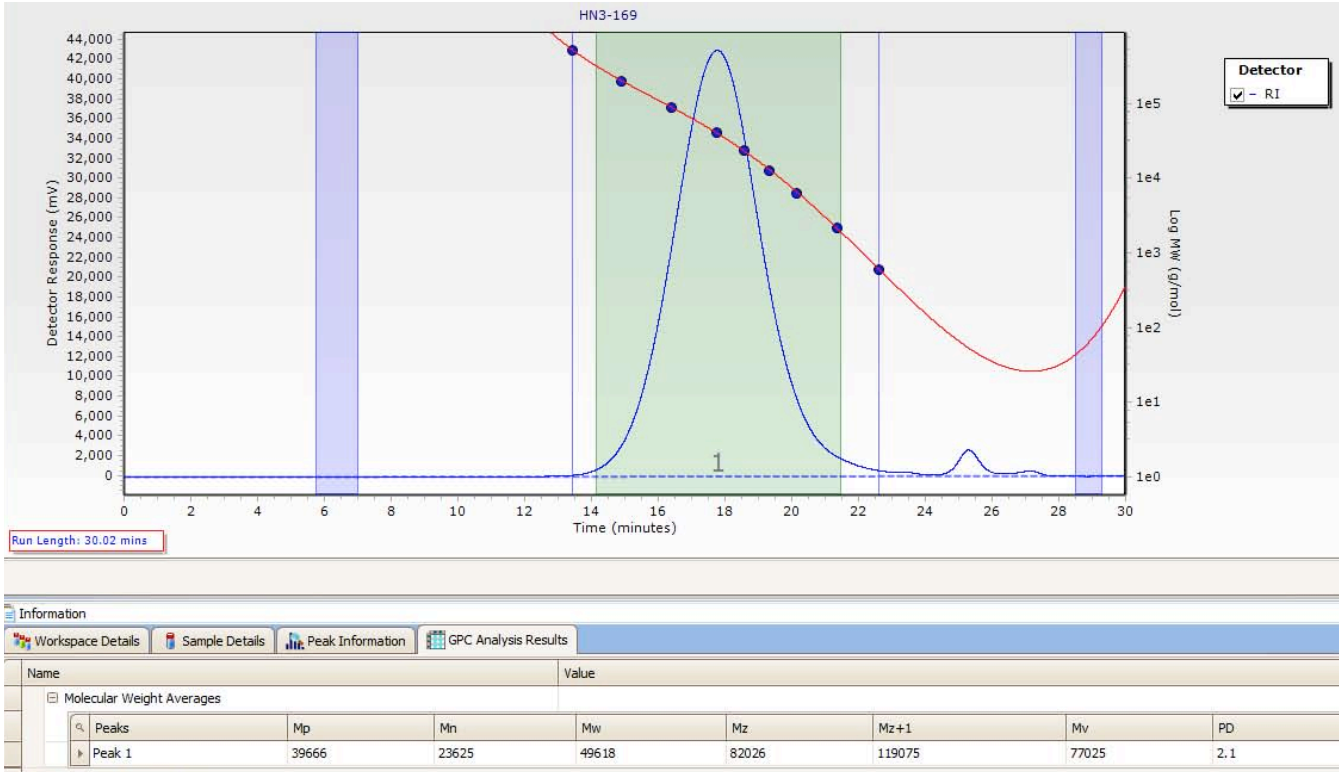


Figure S20. GPC Chromatogram of copoly(caprolactone/ hydroxyethylvanilic acid) [90:10] (Table S2, entry 12).



Peaks	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
Peak 1	50891	32822	64107	103438	150185	97228	1.953

Figure S21. GPC Chromatogram of copoly(caprolactone/ hydroxyethylvanilic acid) [80:20] (Table S2, entry 13).



Peaks	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
Peak 1	39666	23625	49618	82026	119075	77025	2.1

Figure S22. GPC Chromatogram of copoly(caprolactone/ hydroxyethylvanilic acid) [70:30] (Table 2, entry 14).

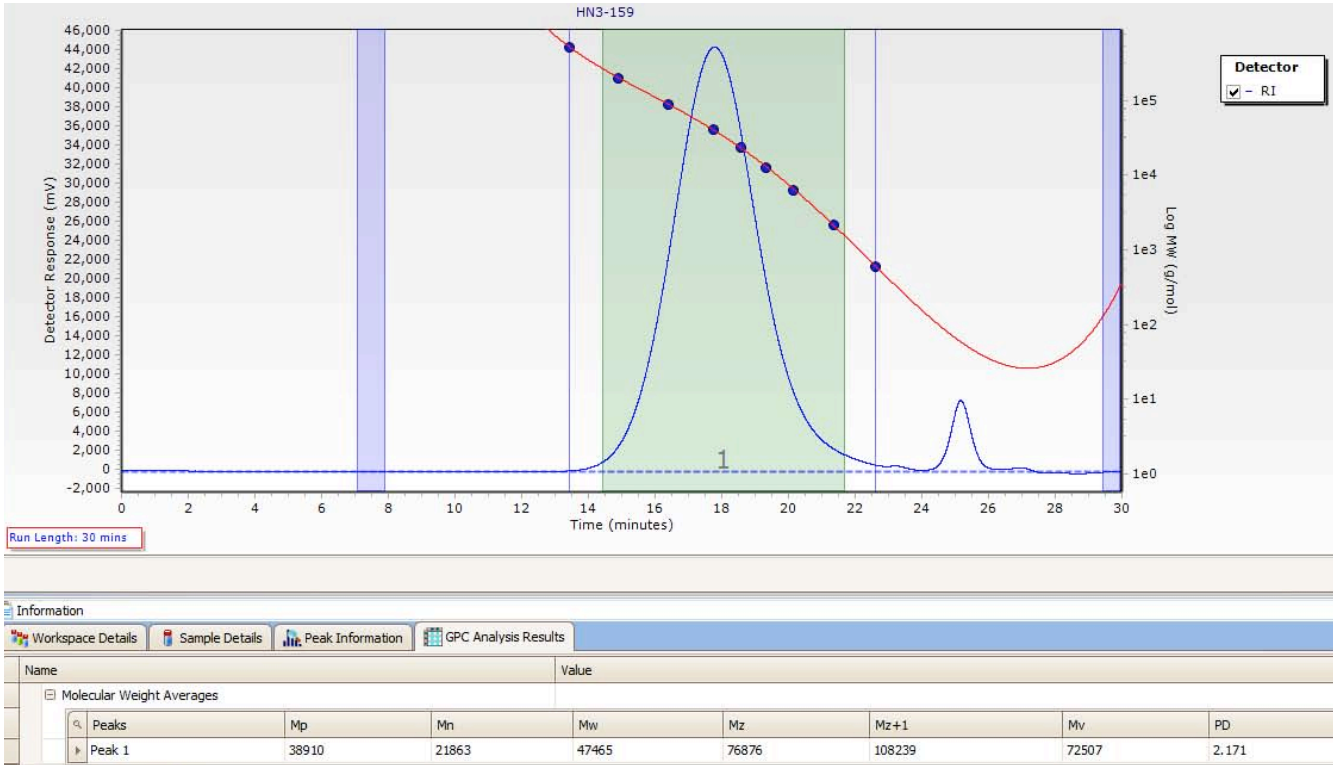


Figure S23. GPC Chromatogram of copoly(caprolactone/ hydroxyethylvanilic acid) [60:40] (Table S2, entry 15).

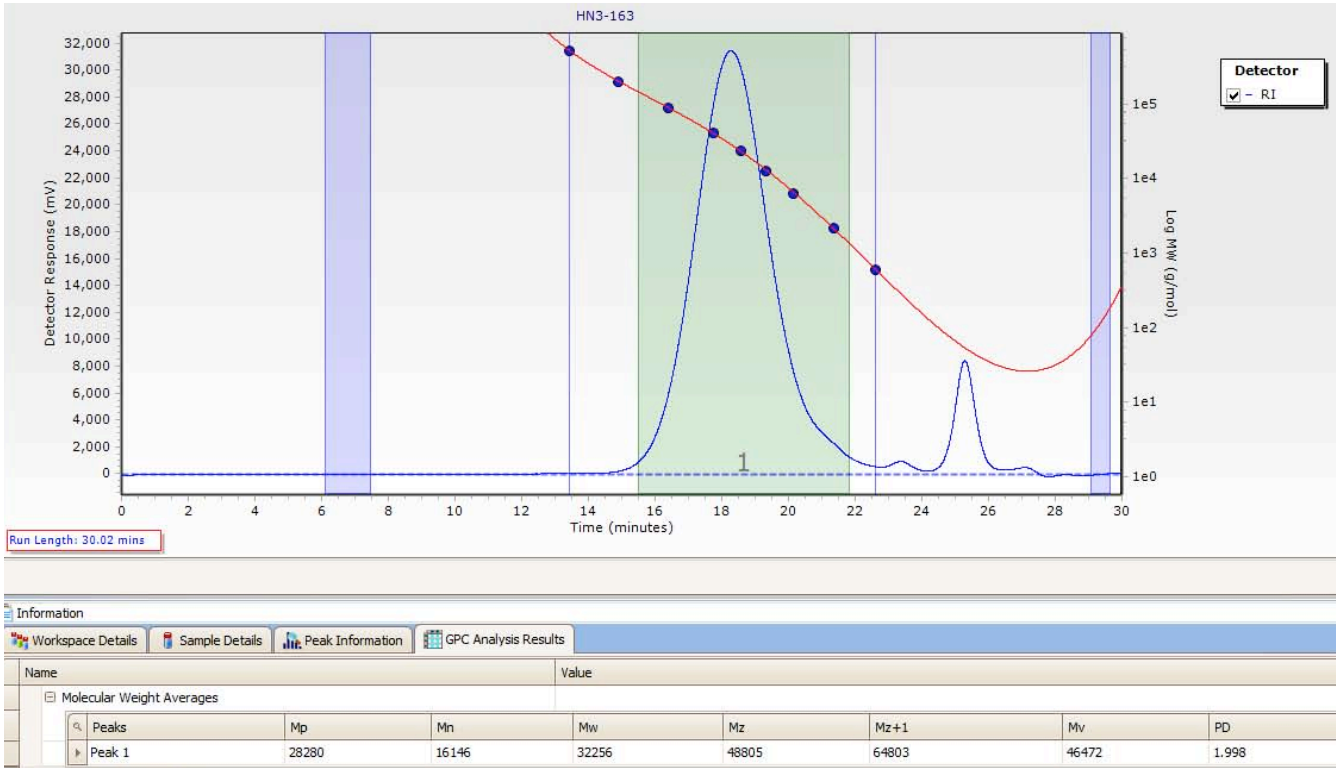


Figure S24. GPC Chromatogram of copoly(caprolactone/ hydroxyethylvanilic acid) [50:50] (Table S2, entry 16).

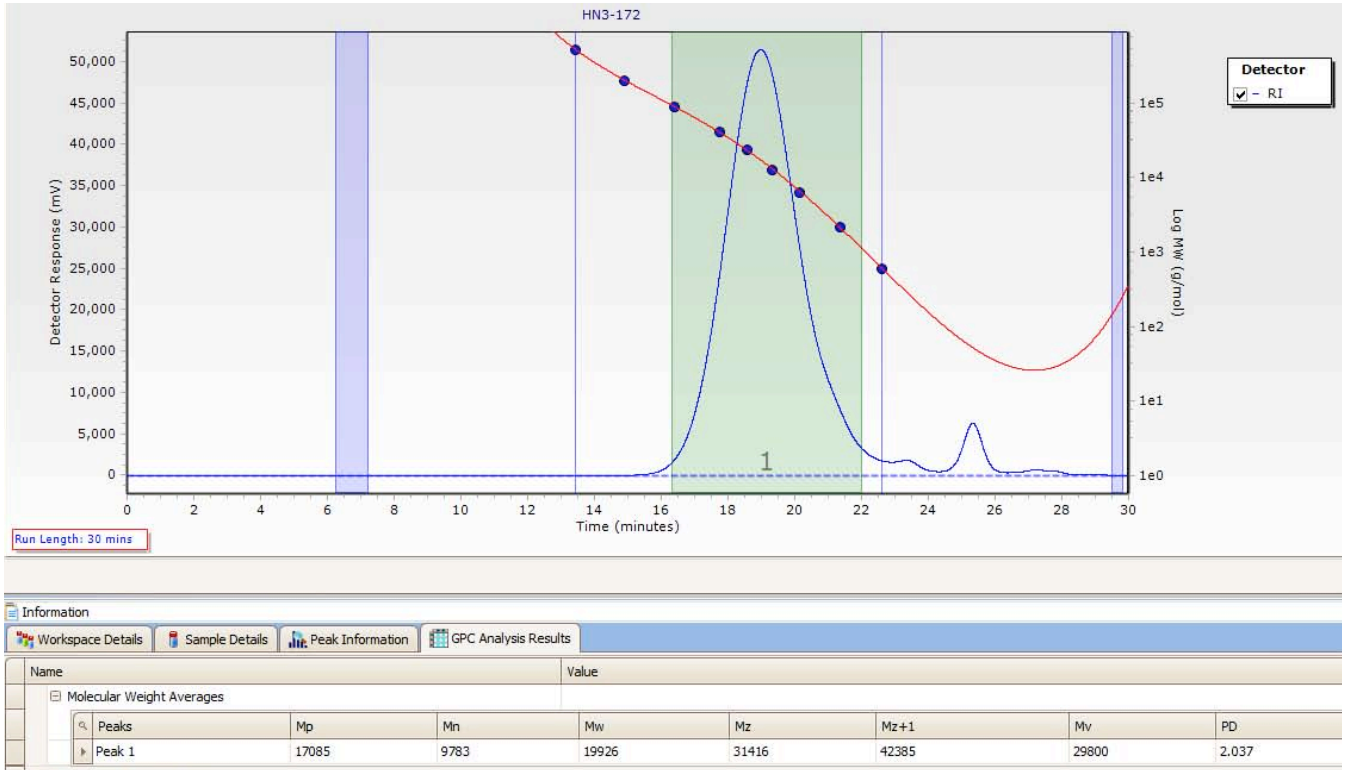


Figure S25. GPC Chromatogram of copoly(caprolactone/ hydroxyethylvanilic acid) [40:60] (Table S2, entry 17).

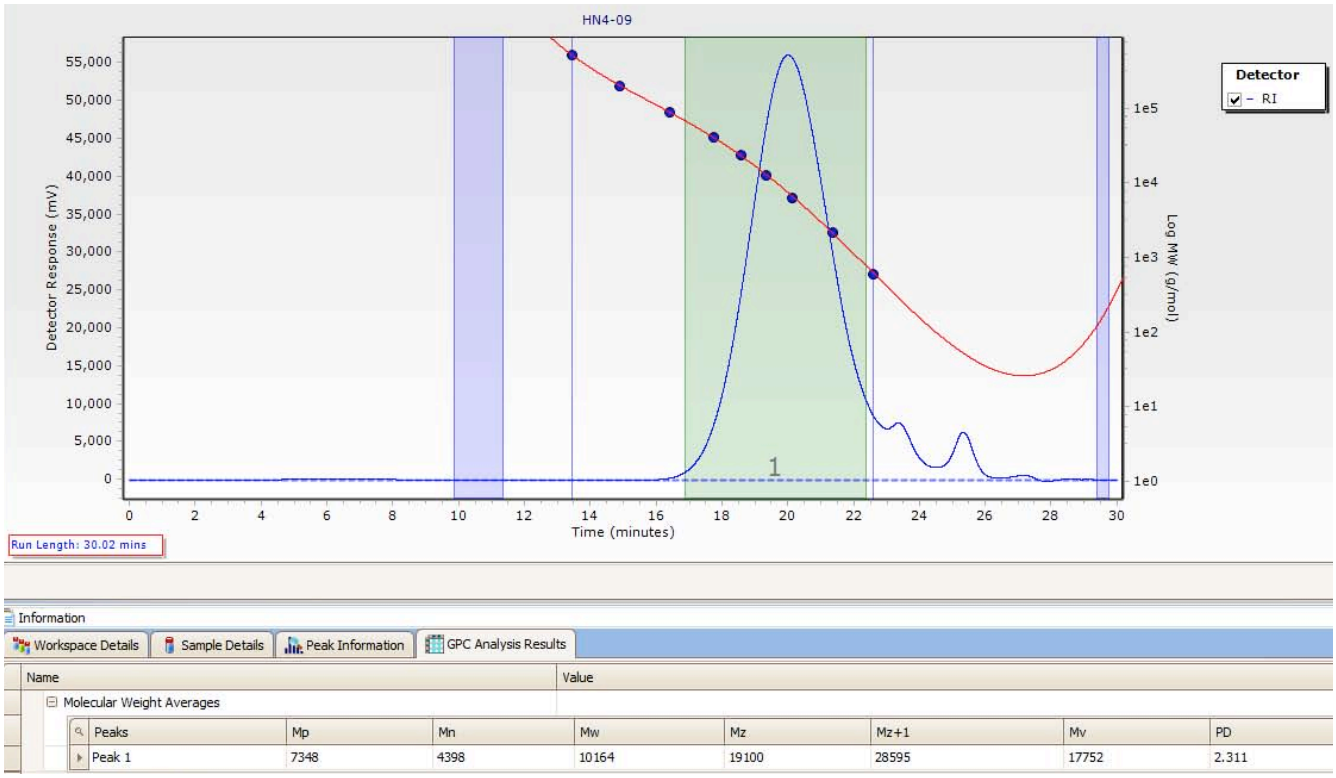


Figure S26. GPC Chromatogram of copoly(caprolactone/ hydroxyethylvanilic acid) [30:70] (Table S2, entry 18).

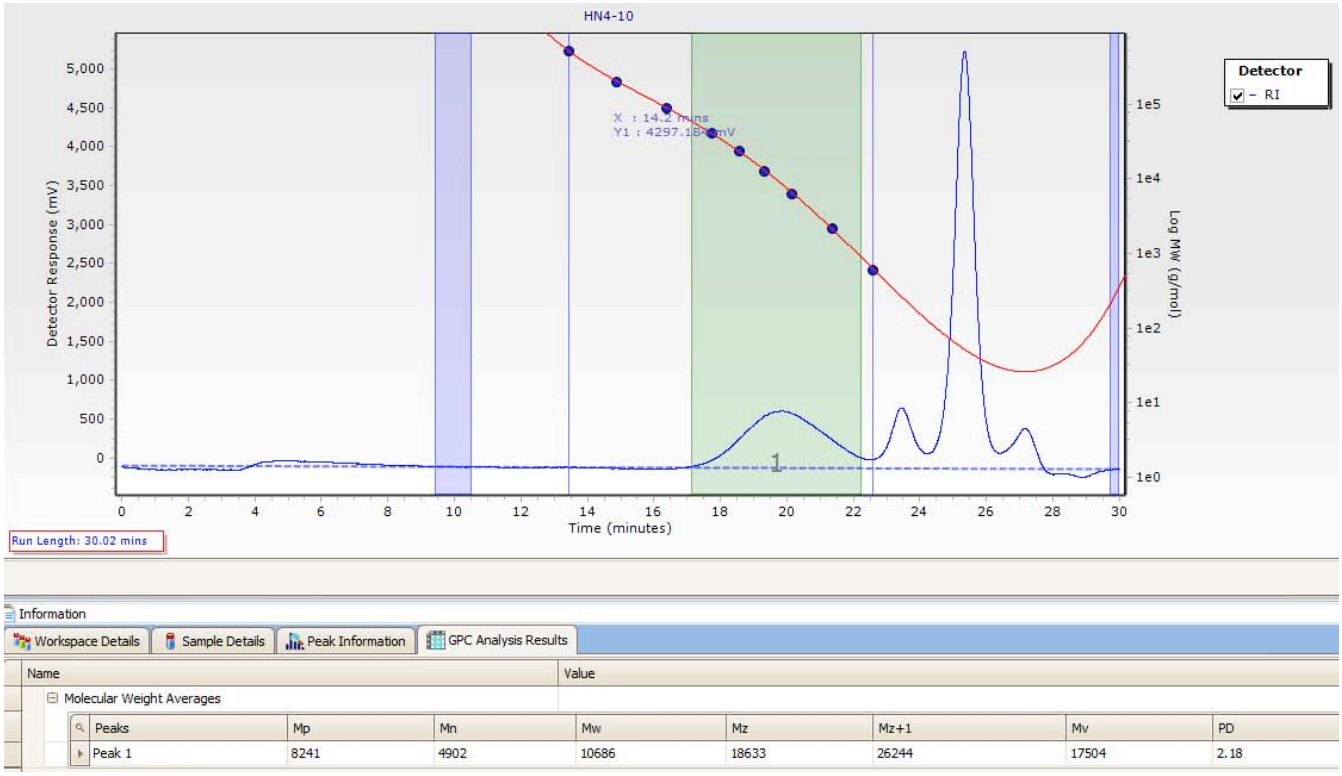


Figure S27. GPC Chromatogram of copoly(caprolactone/ hydroxyethylvanilic acid) [20:80] (Table S2, entry 19).

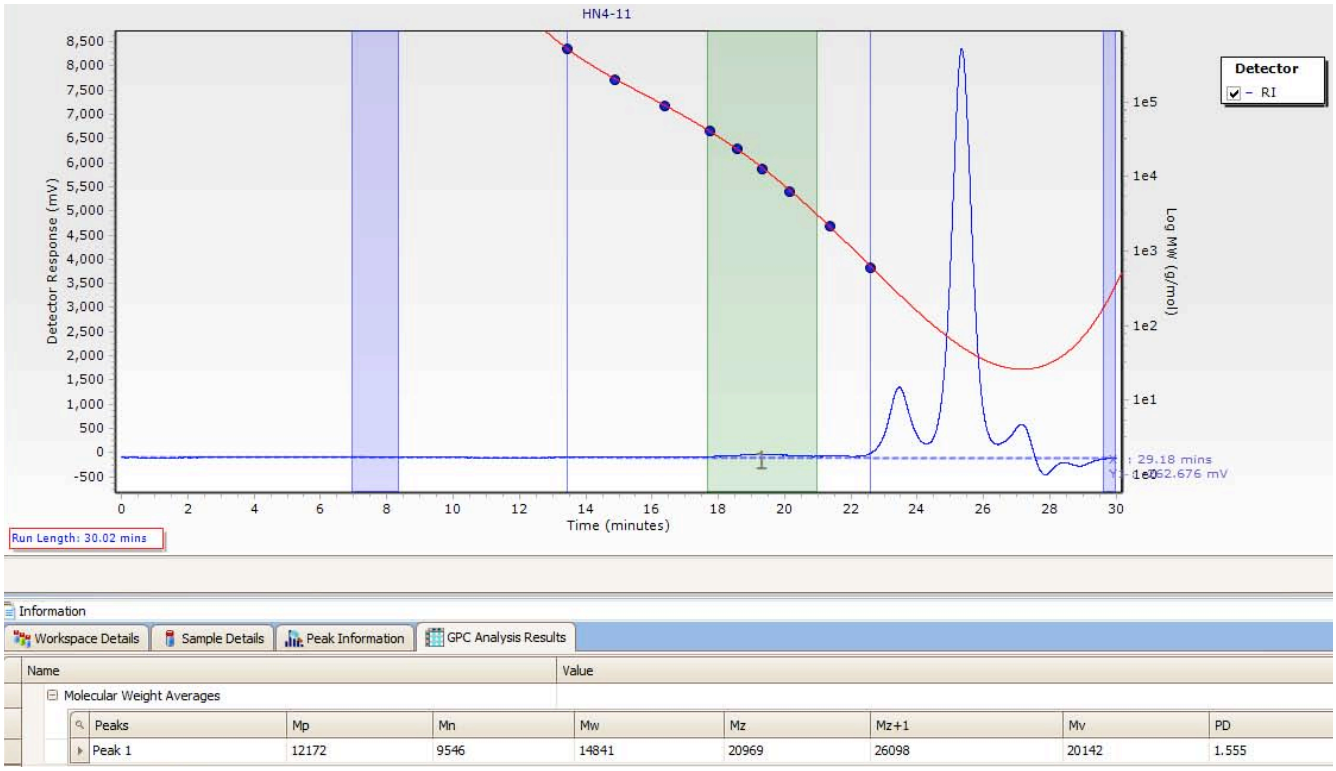
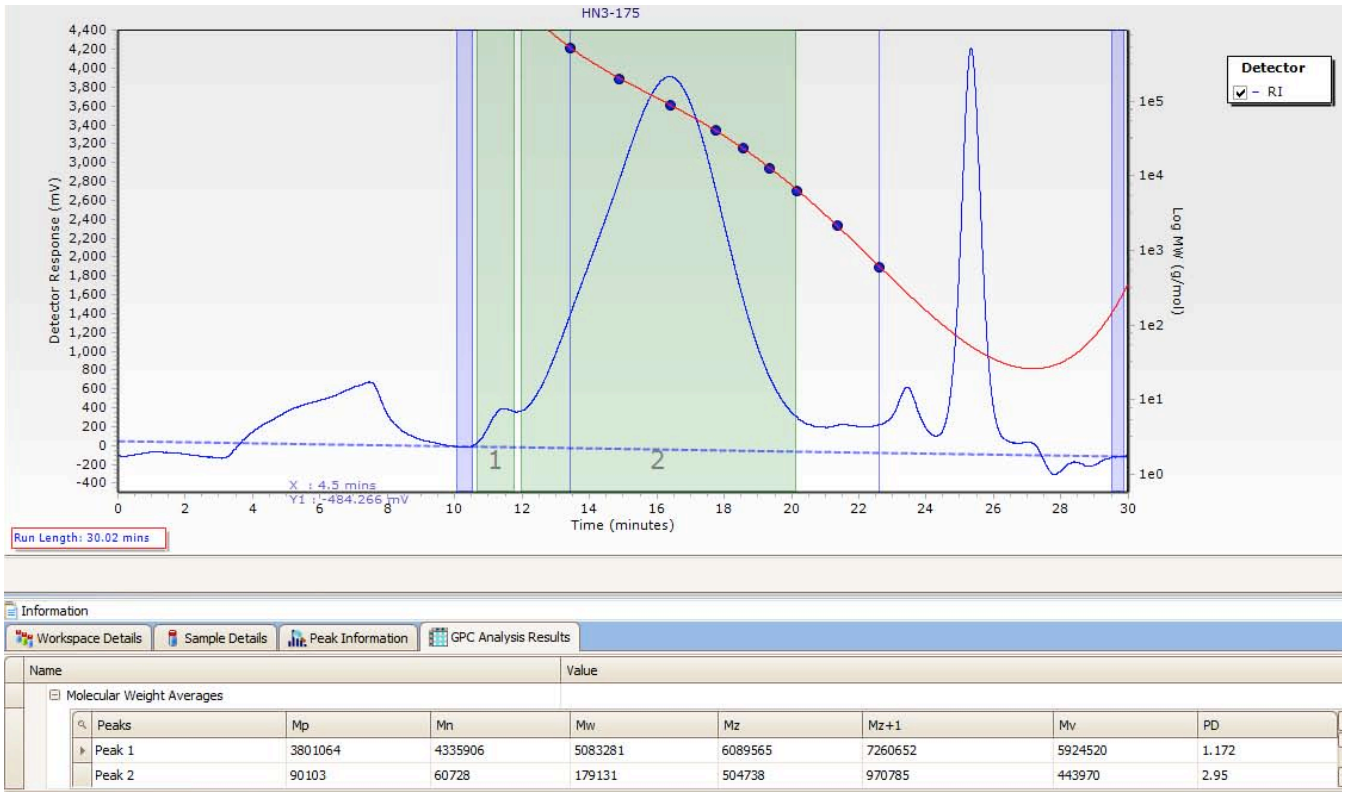
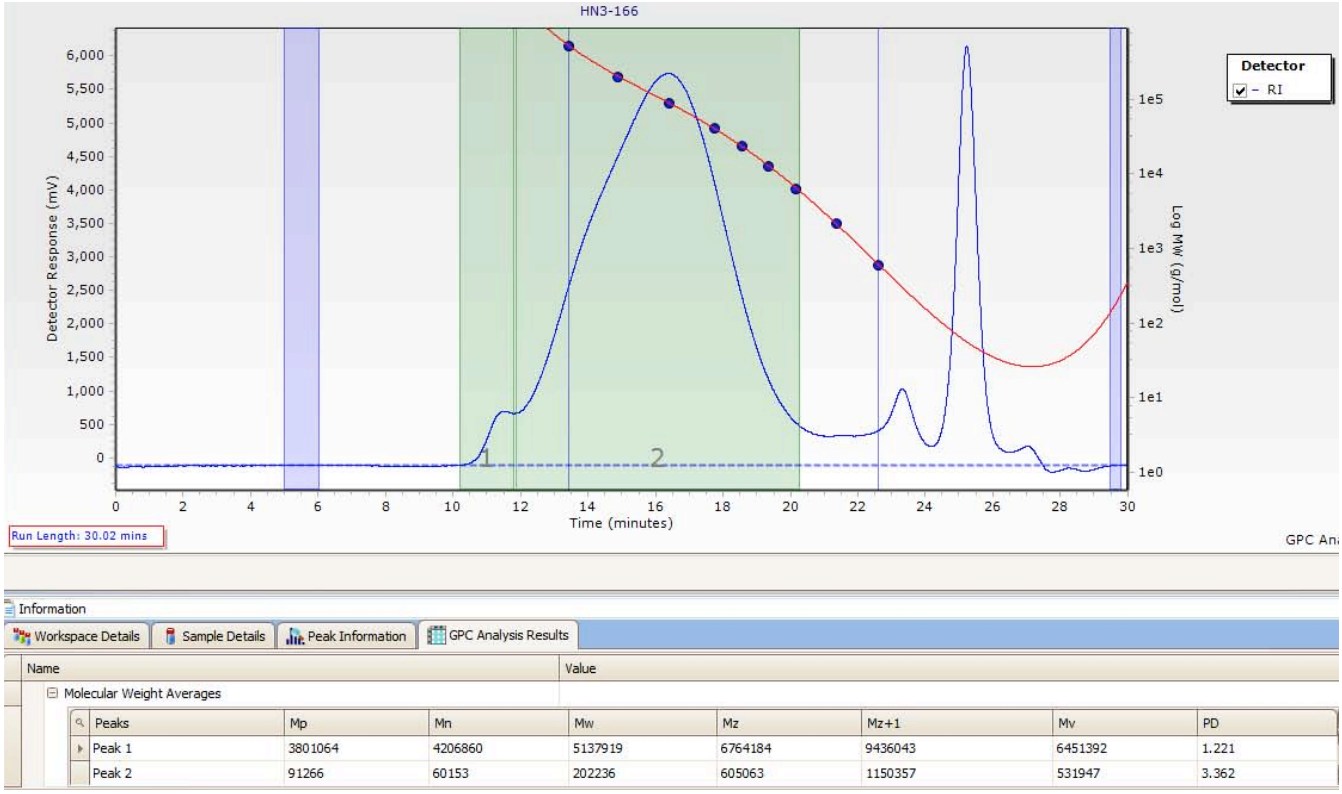


Figure S28. GPC Chromatogram of copoly(caprolactone/ hydroxyethylvanilic acid) [10:90] (Table S2, entry 20).



Peaks	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
Peak 1	3801064	4335906	5083281	6089565	7260652	5924520	1.172
Peak 2	90103	60728	179131	504738	970785	443970	2.95

Figure S29. GPC Chromatogram of copoly(caprolactone/ hydroxyethylferulic acid) [90:10] (Table S2, entry 22).



Peaks	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
Peak 1	3801064	4206860	5137919	6764184	9436043	6451392	1.221
Peak 2	91266	60153	202236	605063	1150357	531947	3.362

Figure S30. GPC Chromatogram of copoly(caprolactone/ hydroxyethylferulic acid) [80:20] (Table S2, entry 23).

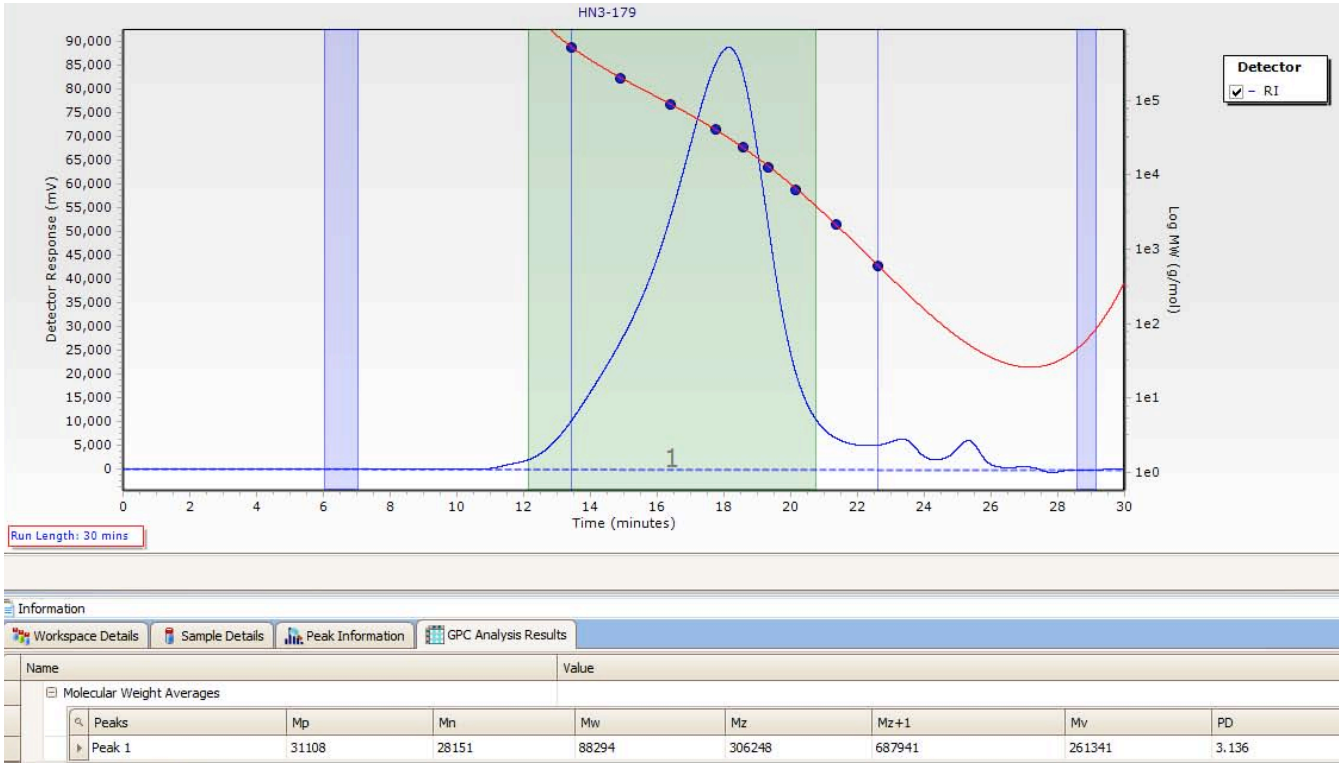


Figure S31. GPC Chromatogram of copoly(caprolactone/ hydroxyethylferulic acid) [70:30] (Table S2, entry 24).

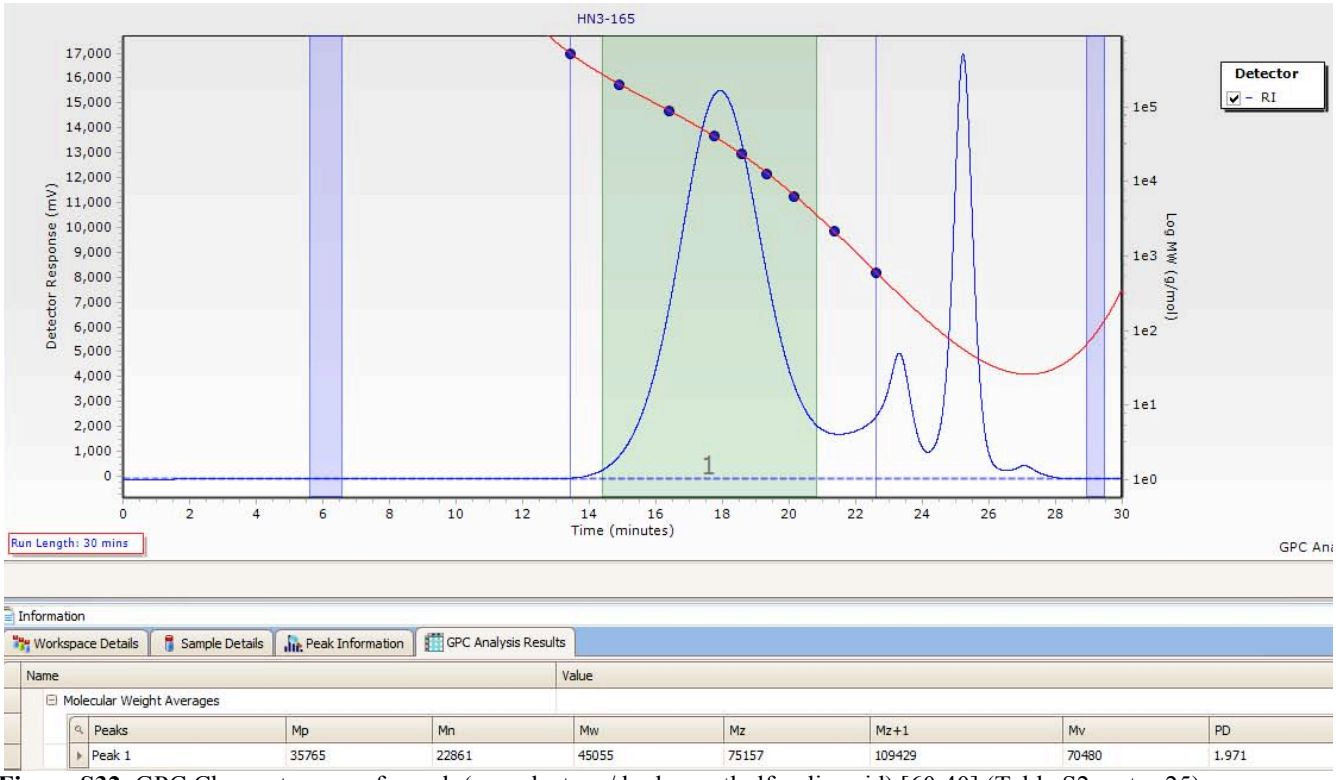


Figure S32. GPC Chromatogram of copoly(caprolactone/ hydroxyethylferulic acid) [60:40] (Table S2, entry 25).

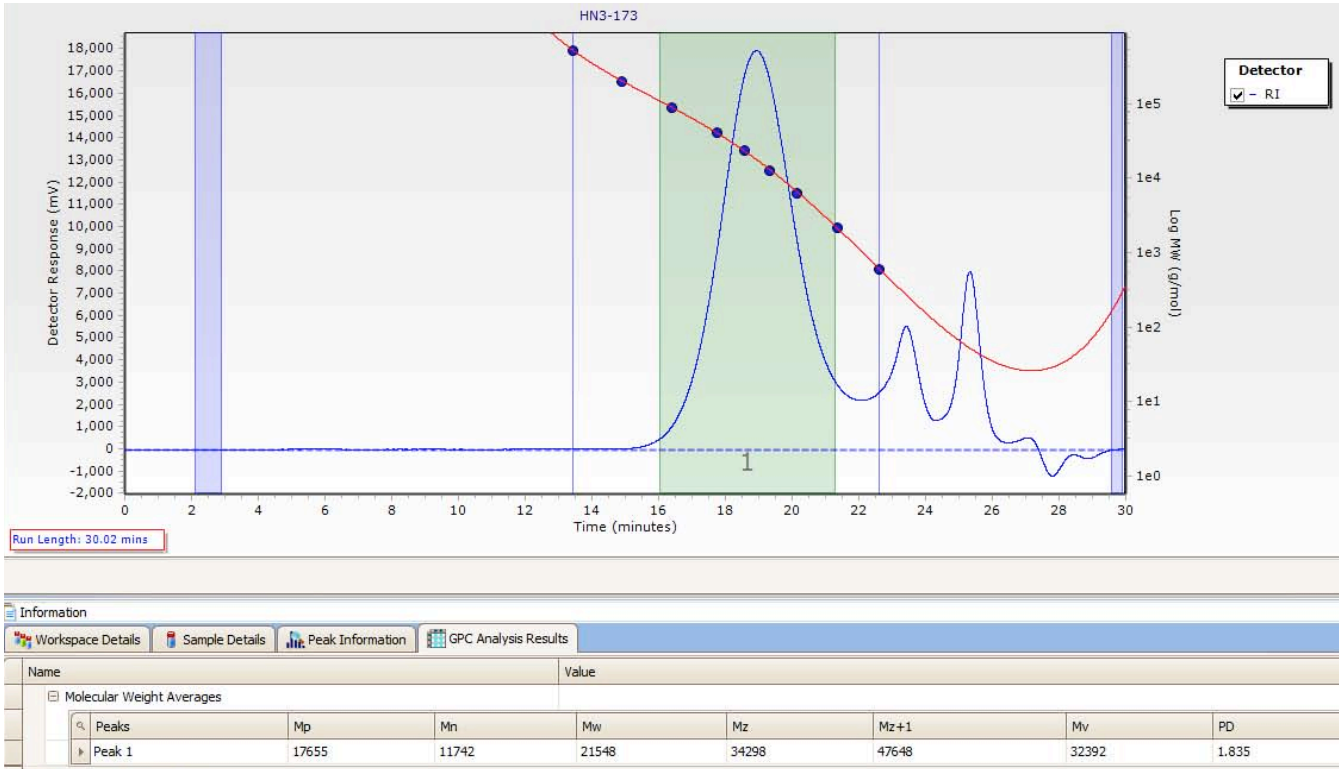


Figure S33. GPC Chromatogram of copoly(caprolactone/ hydroxyethylferulic acid) [50:50] (Table S2, entry 26).

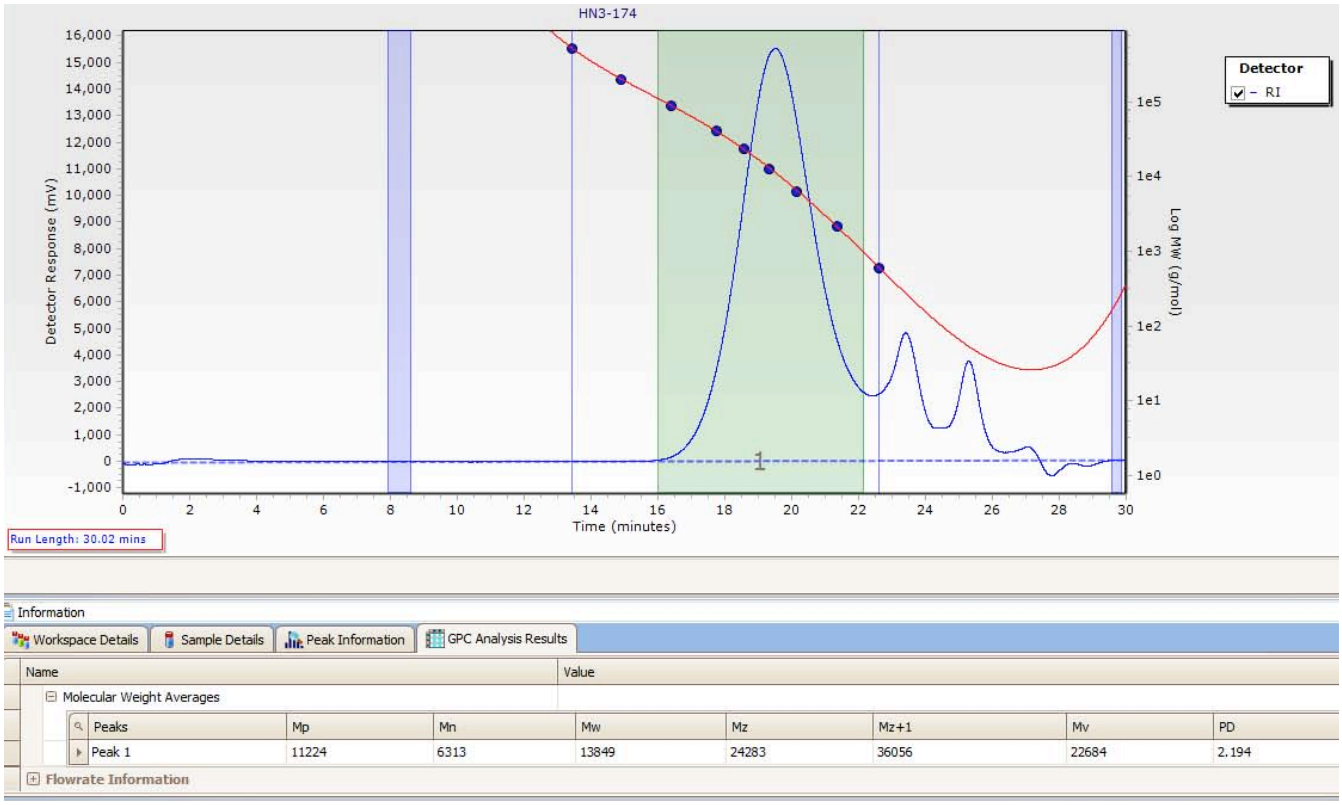
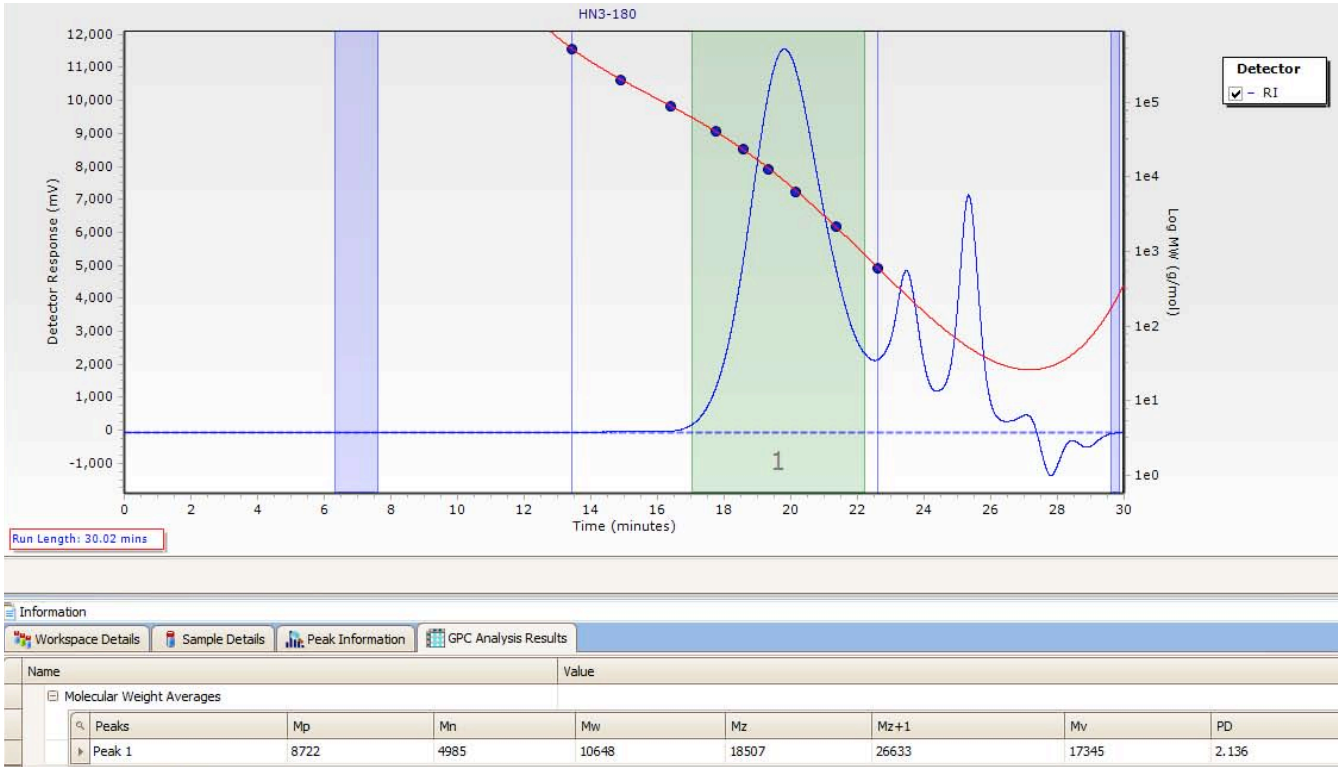
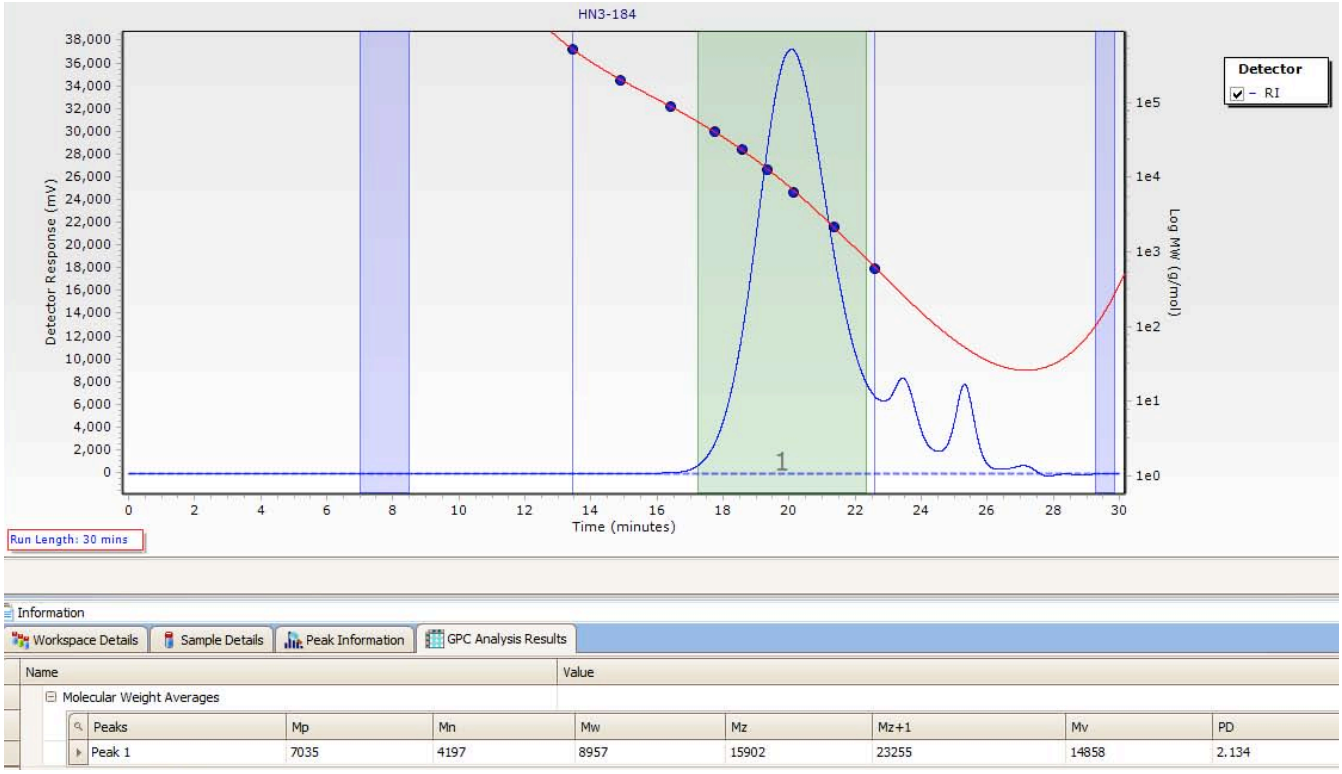


Figure S34. GPC Chromatogram of copoly(caprolactone/ hydroxyethylferulic acid) [40:60] (Table S2, entry 27).



Peaks	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
Peak 1	8722	4985	10648	18507	26633	17345	2.136

Figure S35. GPC Chromatogram of copoly(caprolactone/ hydroxyethylferulic acid) [30:70] (Table S2, entry 28).



Peaks	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
Peak 1	7035	4197	8957	15902	23255	14858	2.134

Figure S36. GPC Chromatogram of copoly(caprolactone/ hydroxyethylferulic acid) [20:80] (Table S2, entry 29).

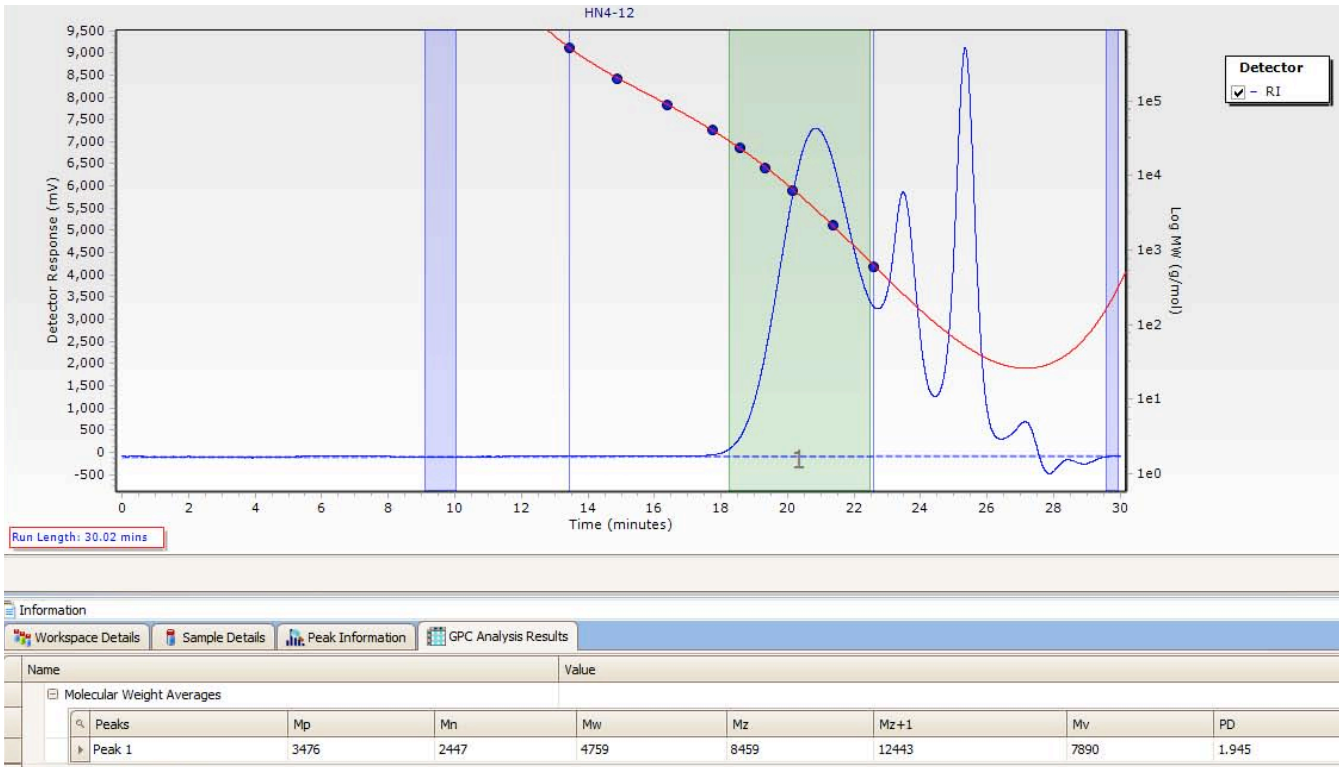


Figure S37. GPC Chromatogram of copoly(caprolactone/ hydroxyethylferulic acid) [10:90] (Table S2, entry 30).

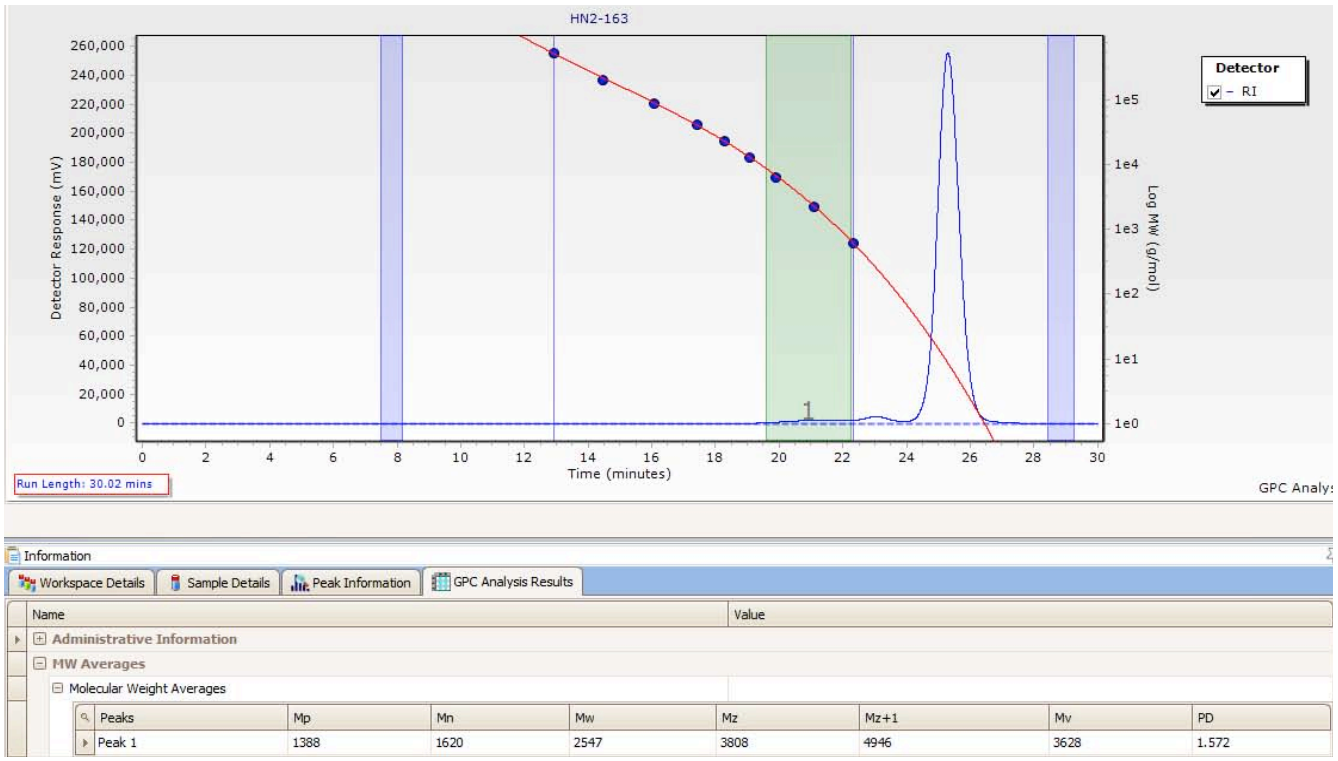


Figure S38. GPC Chromatogram of polyethylene ferulate(Table S2, entry 31).

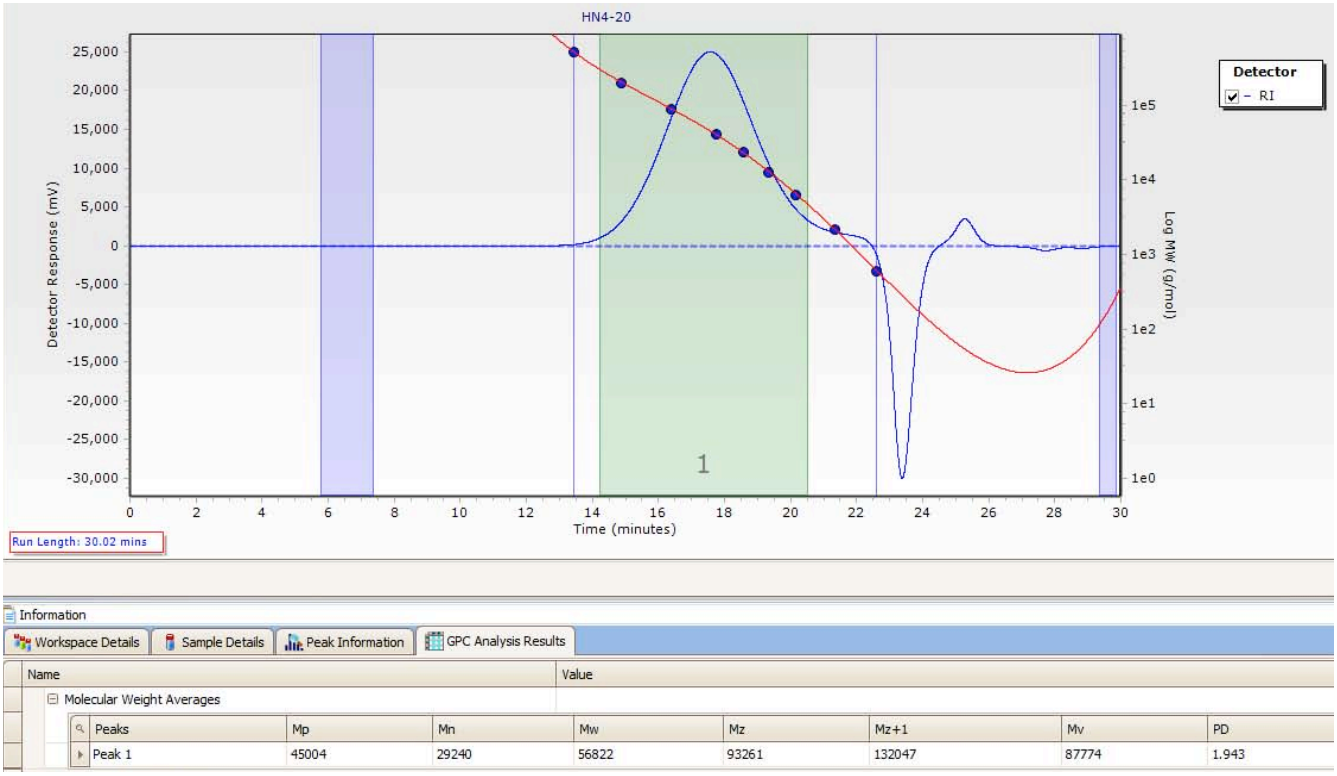


Figure S39. GPC Chromatogram of copoly(caprolactone/ hydroxyethylcoumaric acid) [80:20] (Table S2, entry 32).

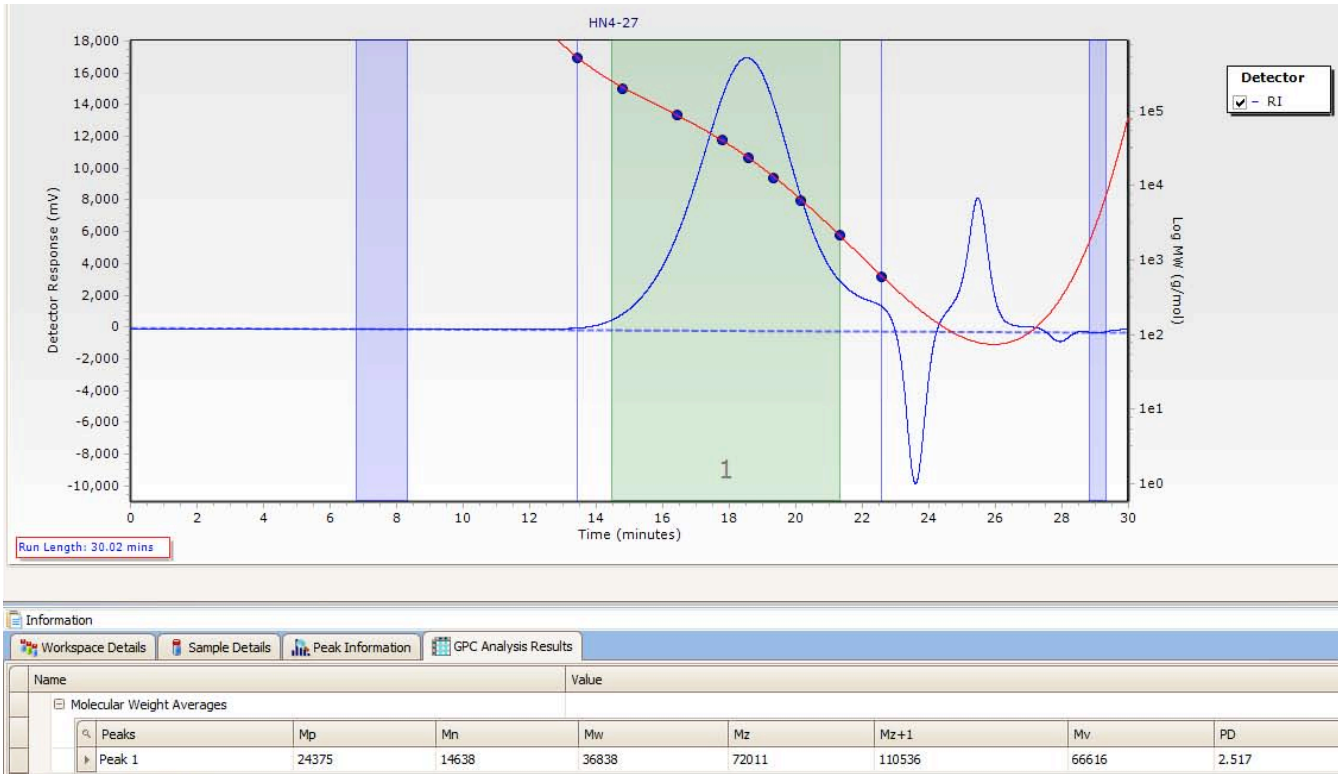


Figure S40. GPC Chromatogram of copoly(caprolactone/ hydroxyethylcoumaric acid) [50:50] (Table S2, entry 33).

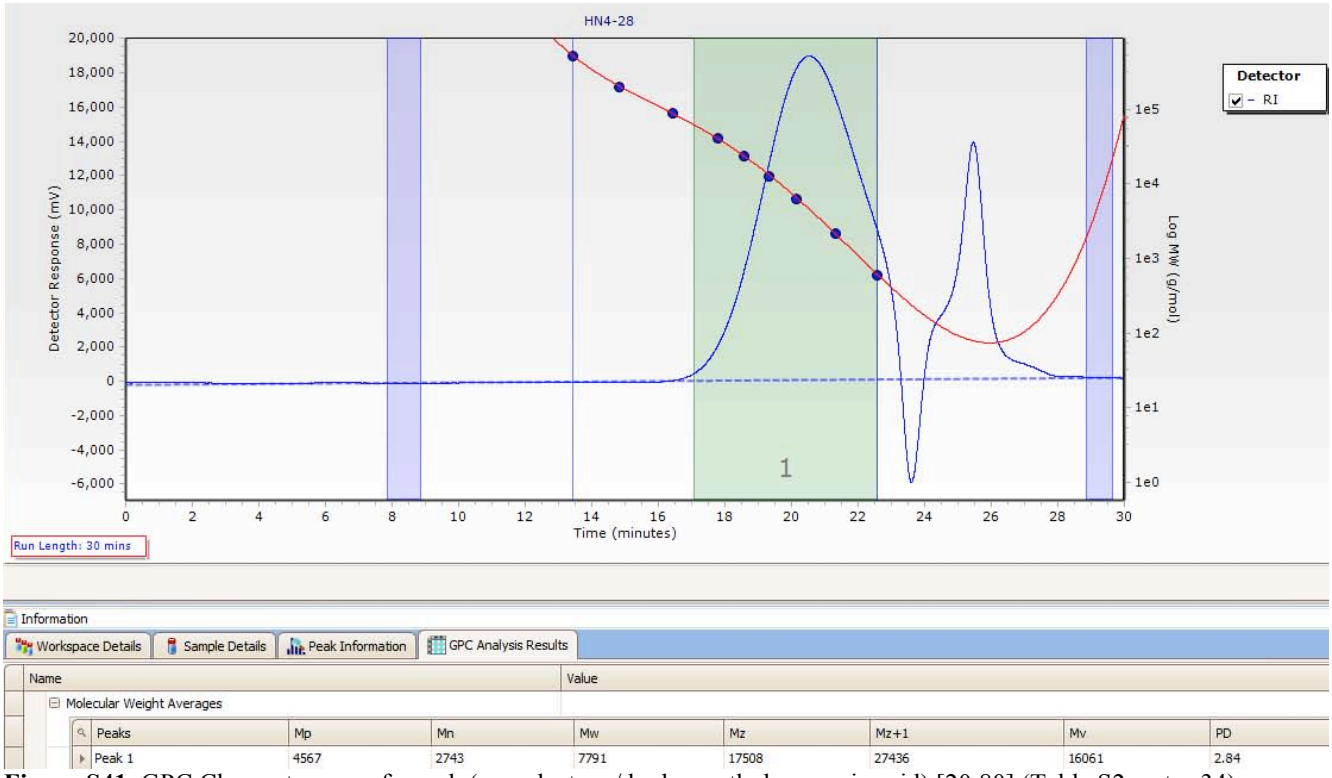


Figure S41. GPC Chromatogram of copoly(caprolactone/ hydroxyethylcoumaric acid) [20:80] (Table S2, entry 34).

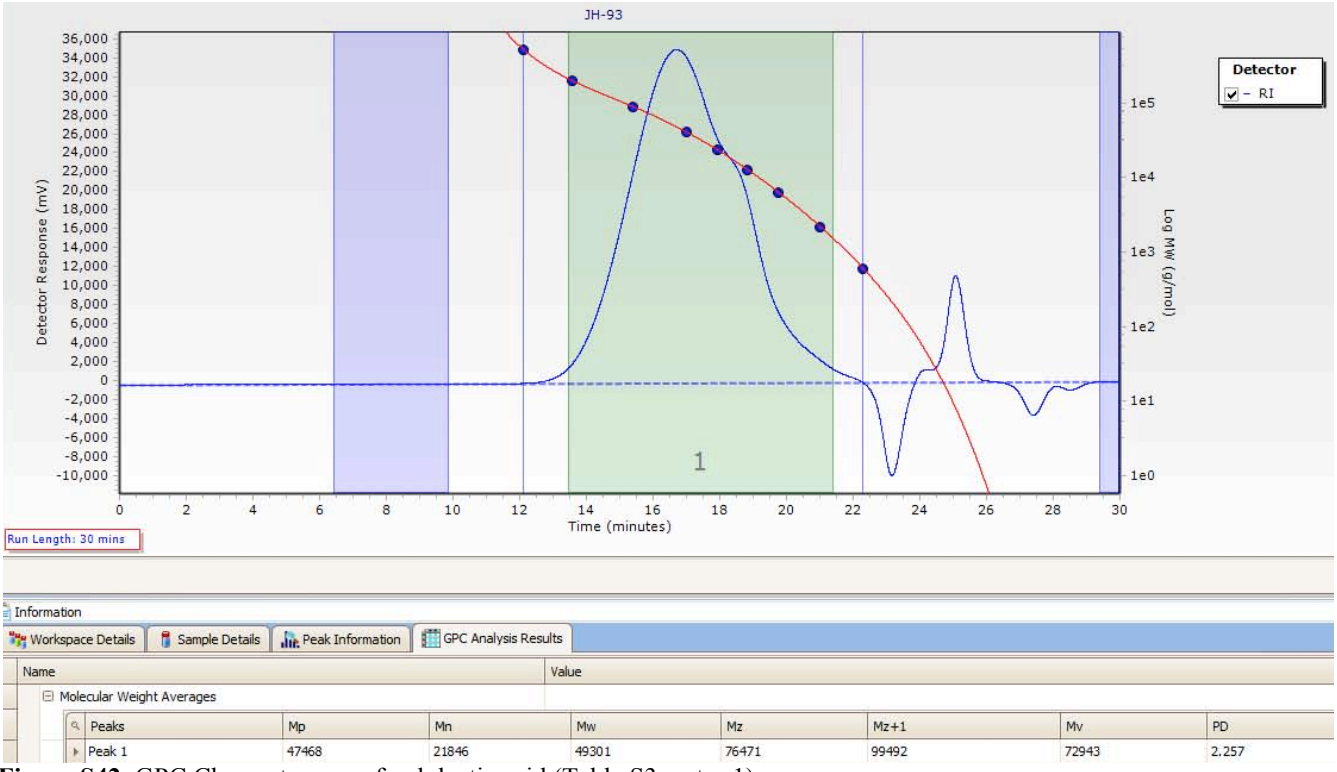


Figure S42. GPC Chromatogram of polylactic acid (Table S3, entry 1).

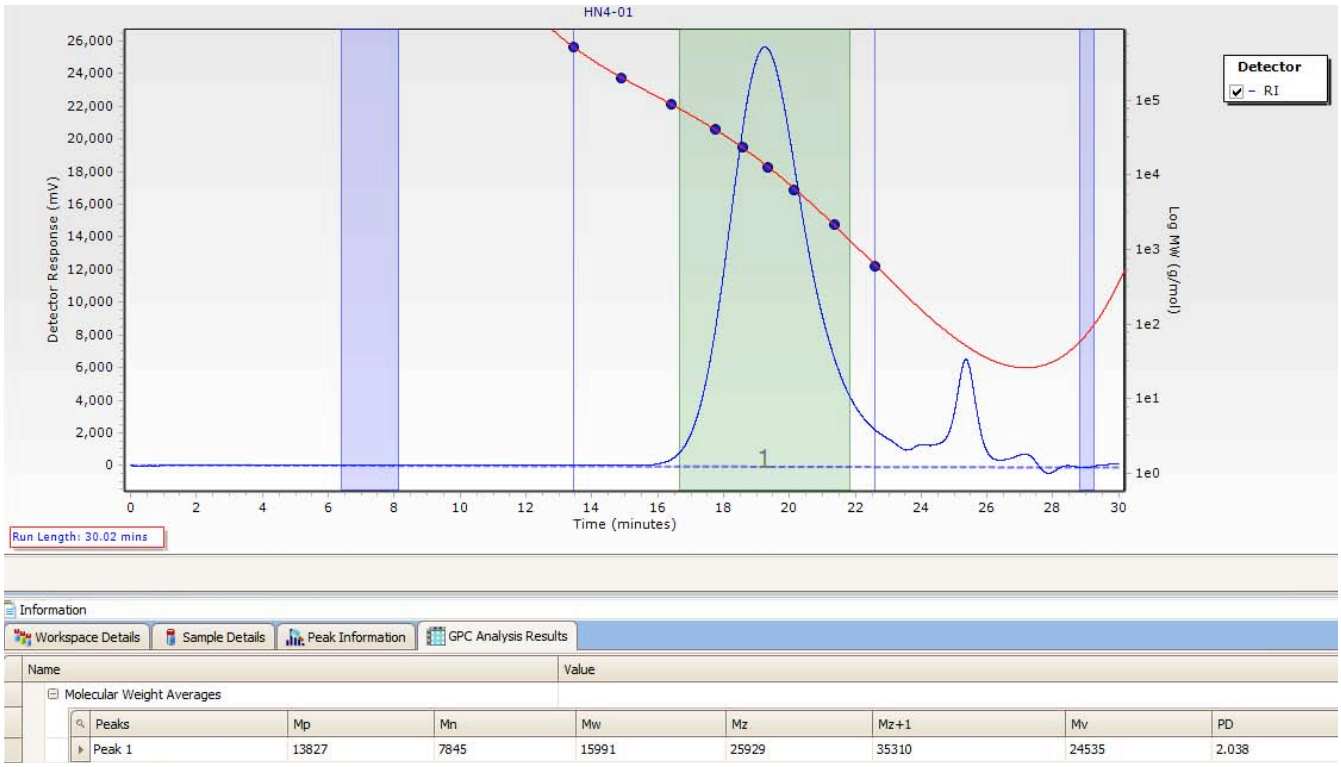


Figure S43. GPC Chromatogram of copoly(L-lactide/ hydroxyethylsyringic acid) [80:20] (Table S3, entry 2).

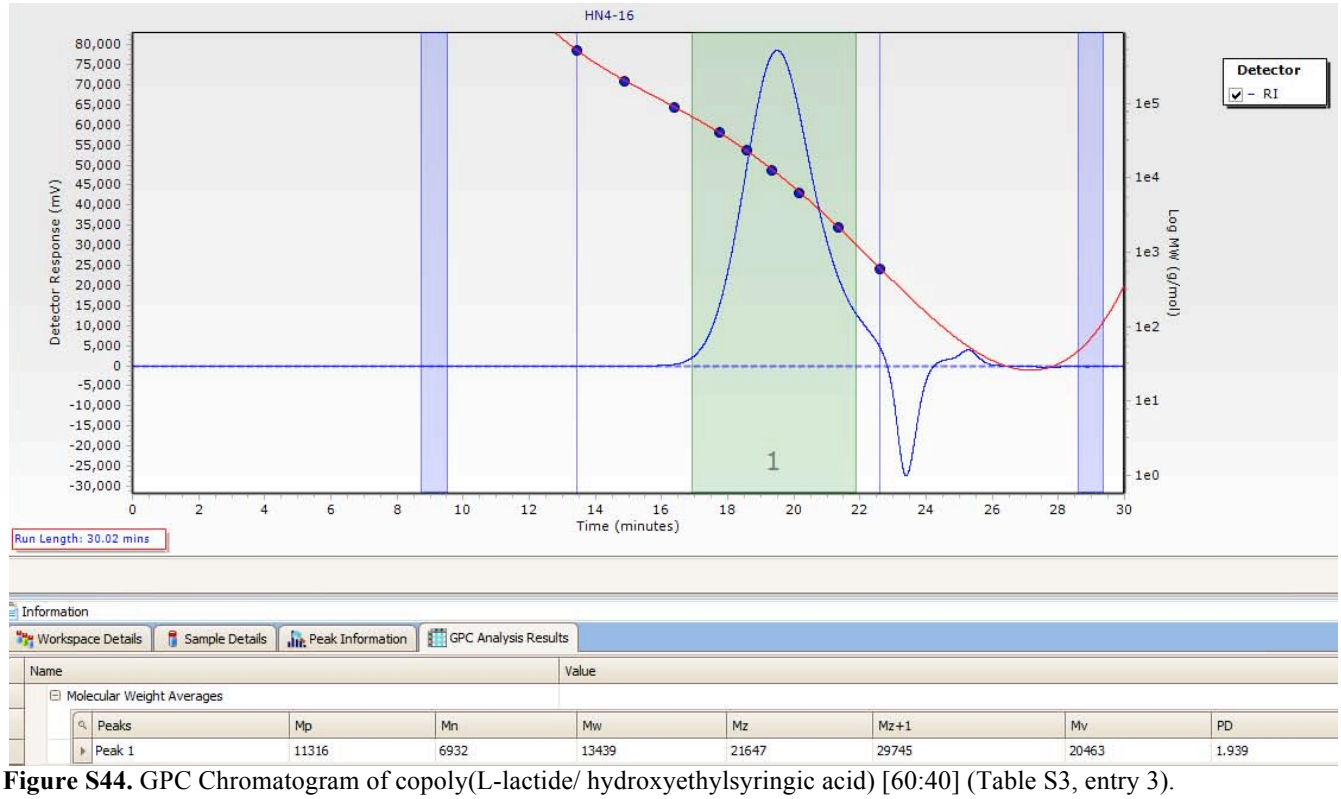
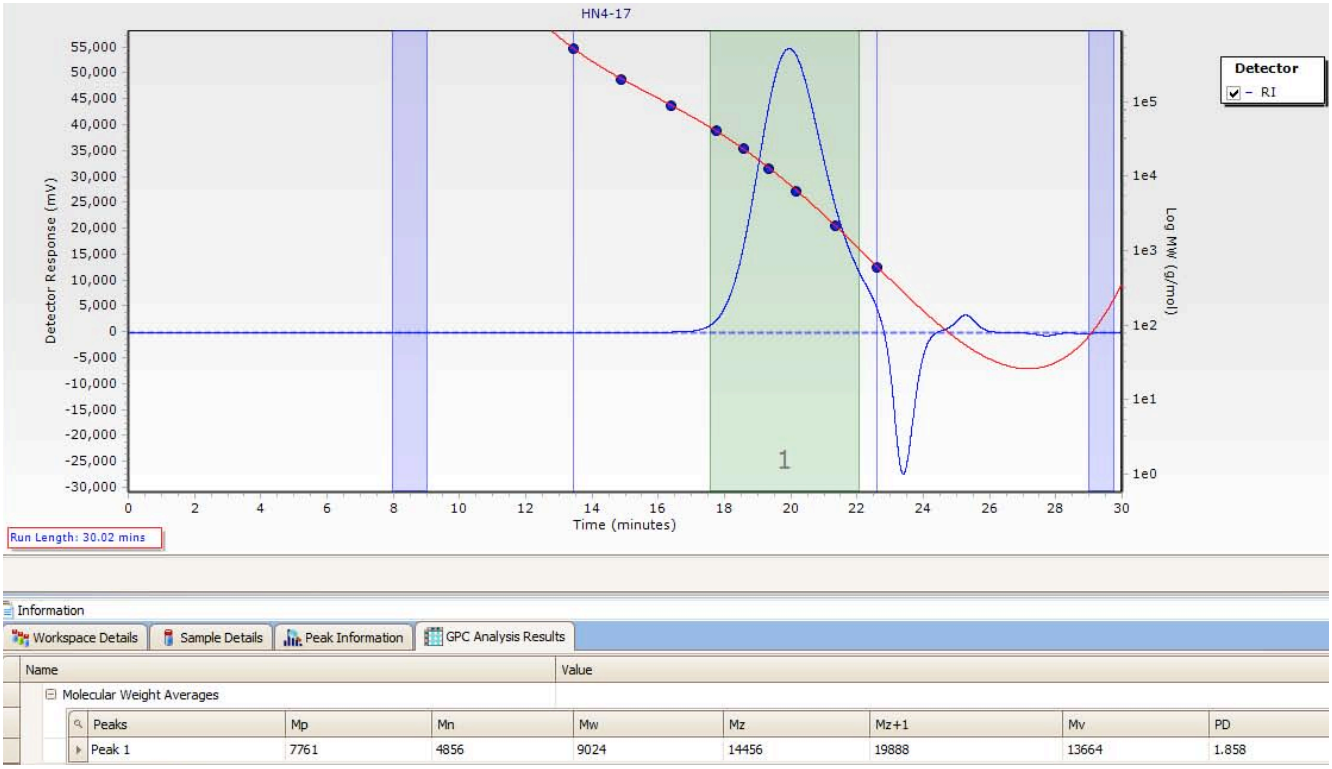
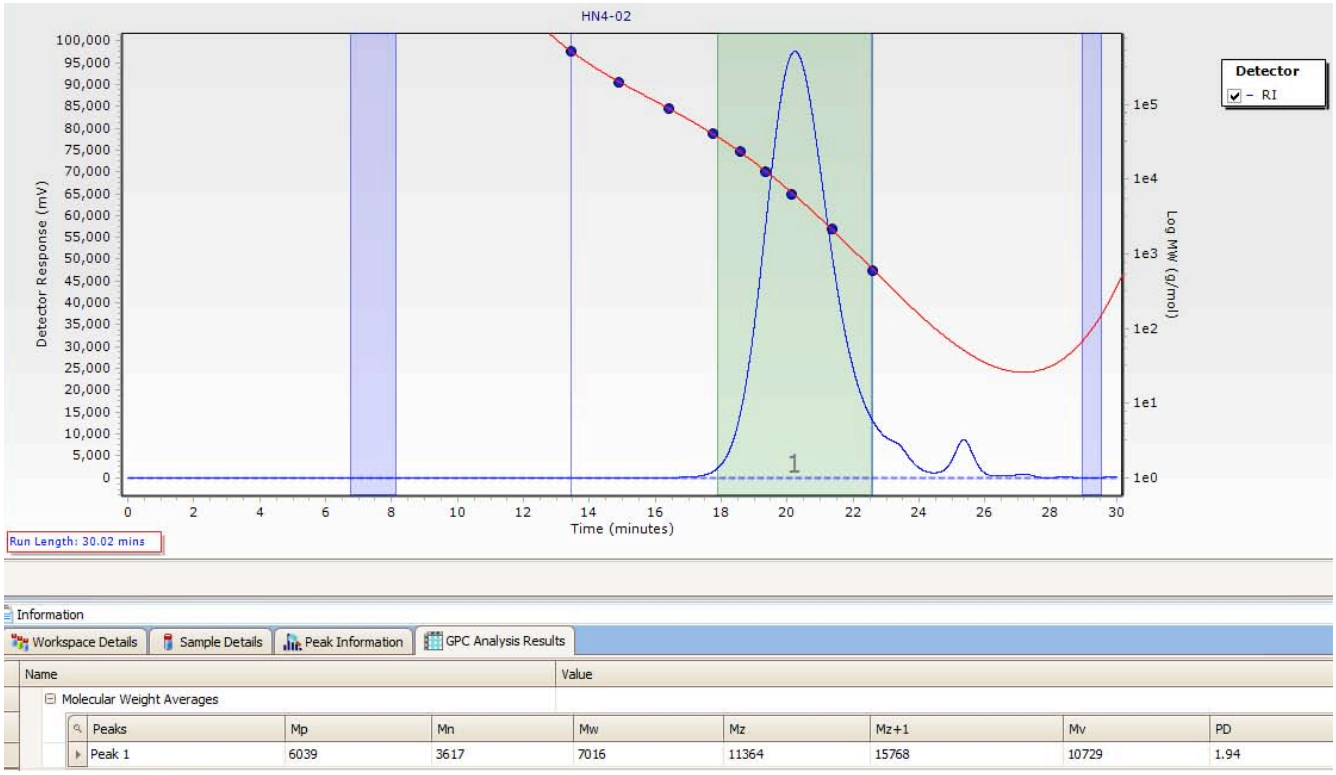


Figure S44. GPC Chromatogram of copoly(L-lactide/ hydroxyethylsyringic acid) [60:40] (Table S3, entry 3).



Peaks	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
Peak 1	7761	4856	9024	14456	19888	13664	1.858

Figure S45. GPC Chromatogram of copoly(L-lactide/ hydroxyethylsyringic acid) [40:60] (Table S3, entry 4).



Peaks	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
Peak 1	6039	3617	7016	11364	15768	10729	1.94

Figure S46. GPC Chromatogram of copoly(L-lactide/ hydroxyethylsyringic acid) [20:80] (Table S3, entry 5).

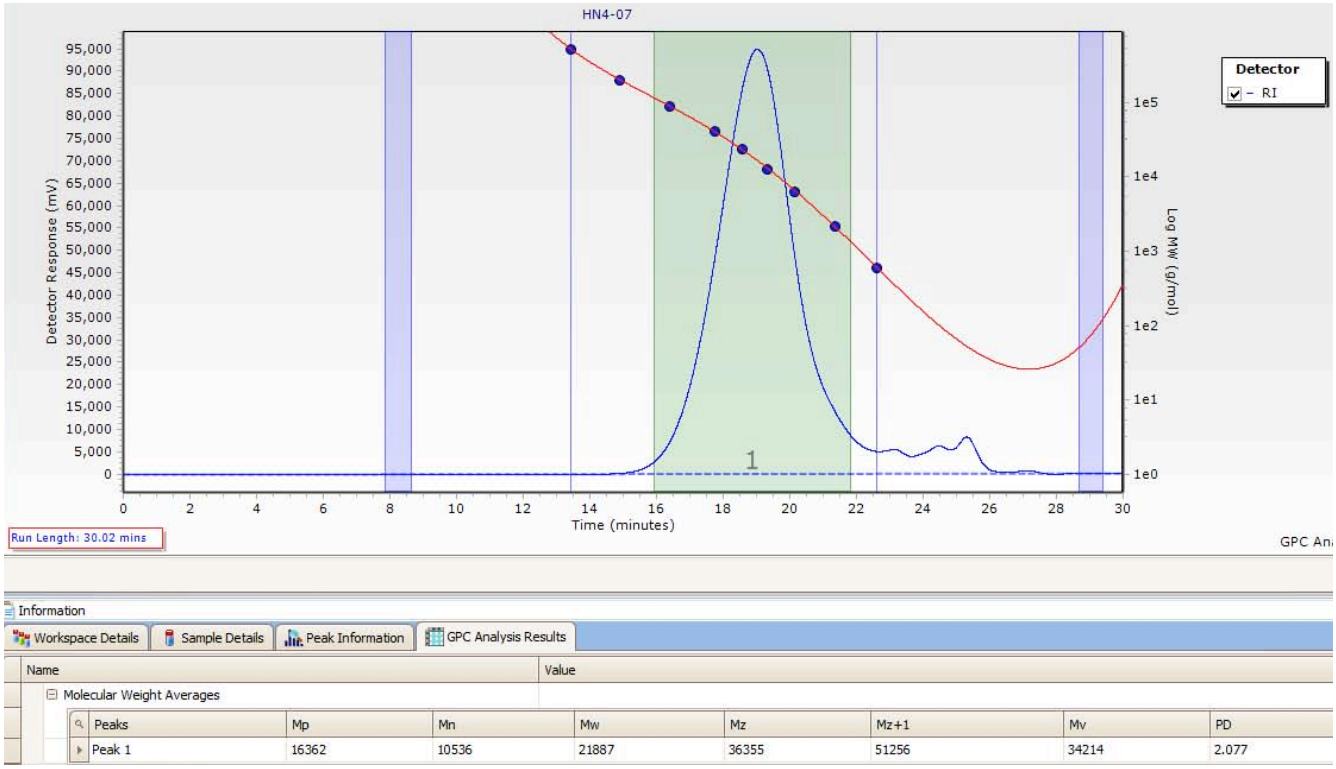


Figure S47. GPC Chromatogram of copoly(L-lactide/ hydroxyethylvanillic acid) [80:20] (Table S3, entry 7).

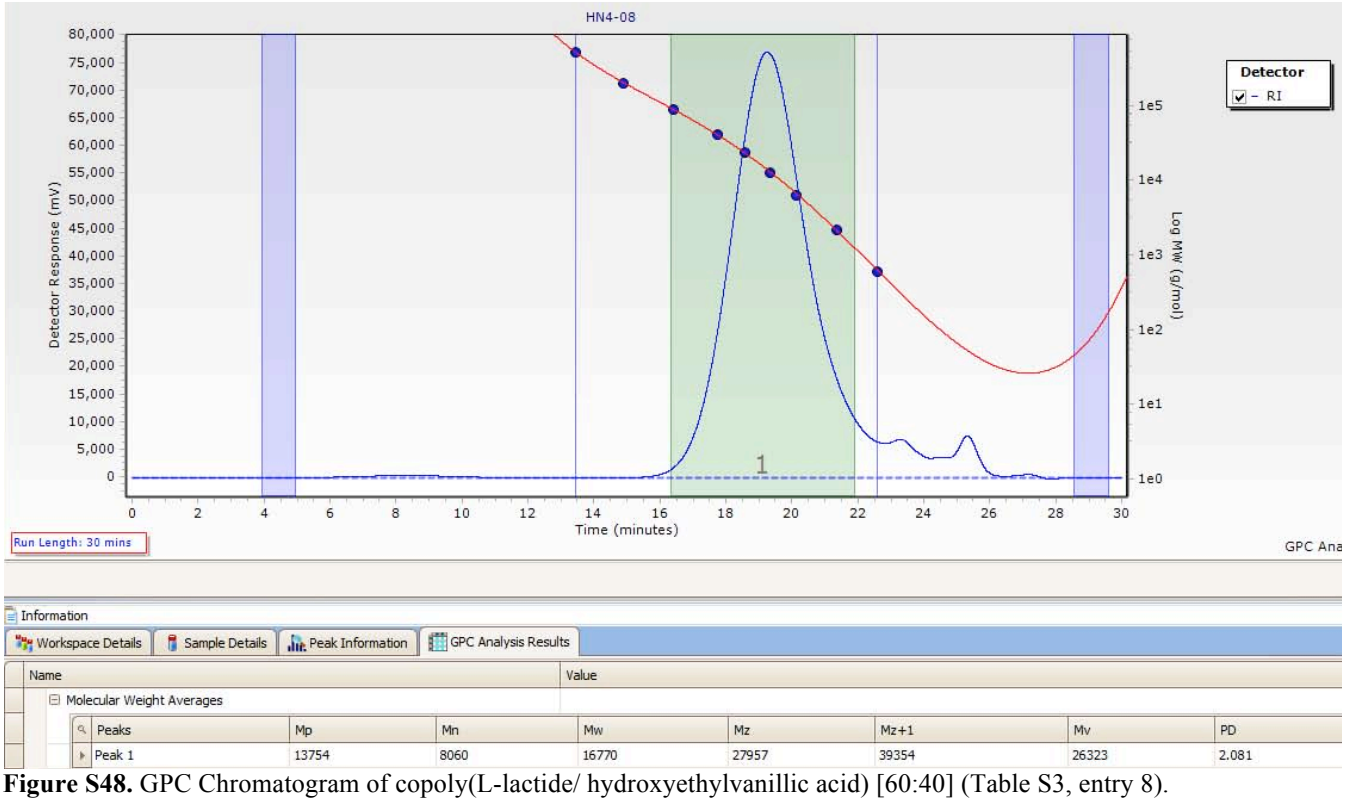
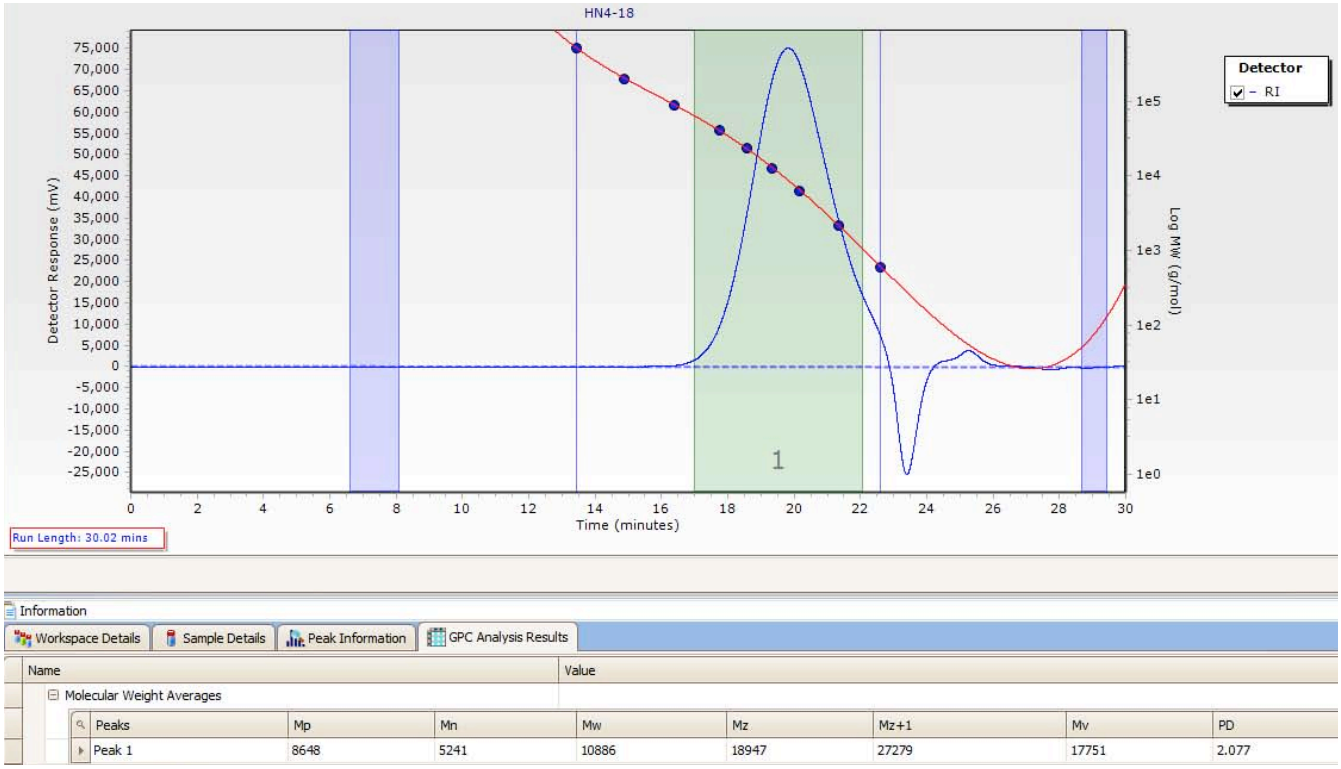


Figure S48. GPC Chromatogram of copoly(L-lactide/ hydroxyethylvanillic acid) [60:40] (Table S3, entry 8).



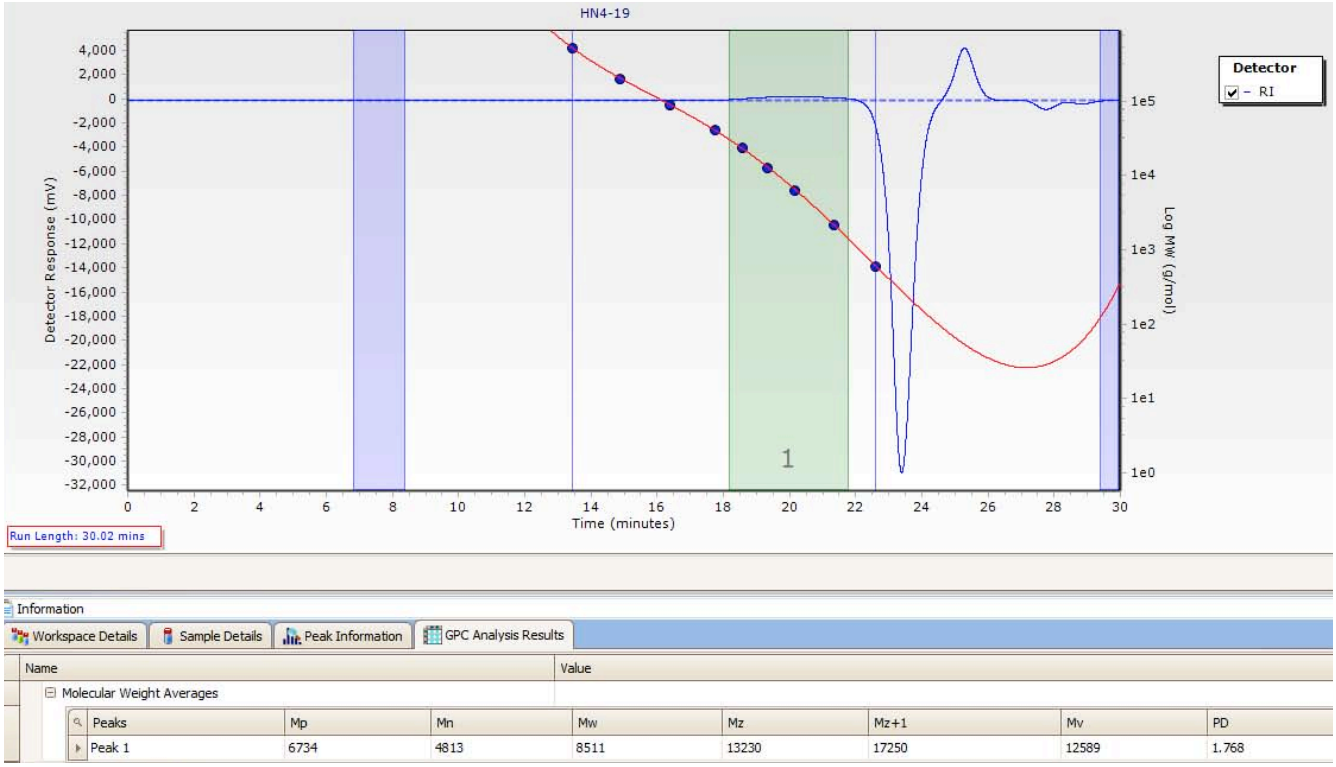
Information

Workspace Details | Sample Details | Peak Information | GPC Analysis Results

Name	Value
Molecular Weight Averages	

Peaks	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
Peak 1	8648	5241	10886	18947	27279	17751	2.077

Figure S49. GPC Chromatogram of copoly(L-lactide/ hydroxyethylvanillic acid) [40:60] (Table S3, entry 9).



Information

Workspace Details | Sample Details | Peak Information | GPC Analysis Results

Name	Value
Molecular Weight Averages	

Peaks	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
Peak 1	6734	4813	8511	13230	17250	12589	1.768

Figure S50. GPC Chromatogram of copoly(L-lactide/ hydroxyethylvanillic acid) [20:80] (Table S3, entry 10).

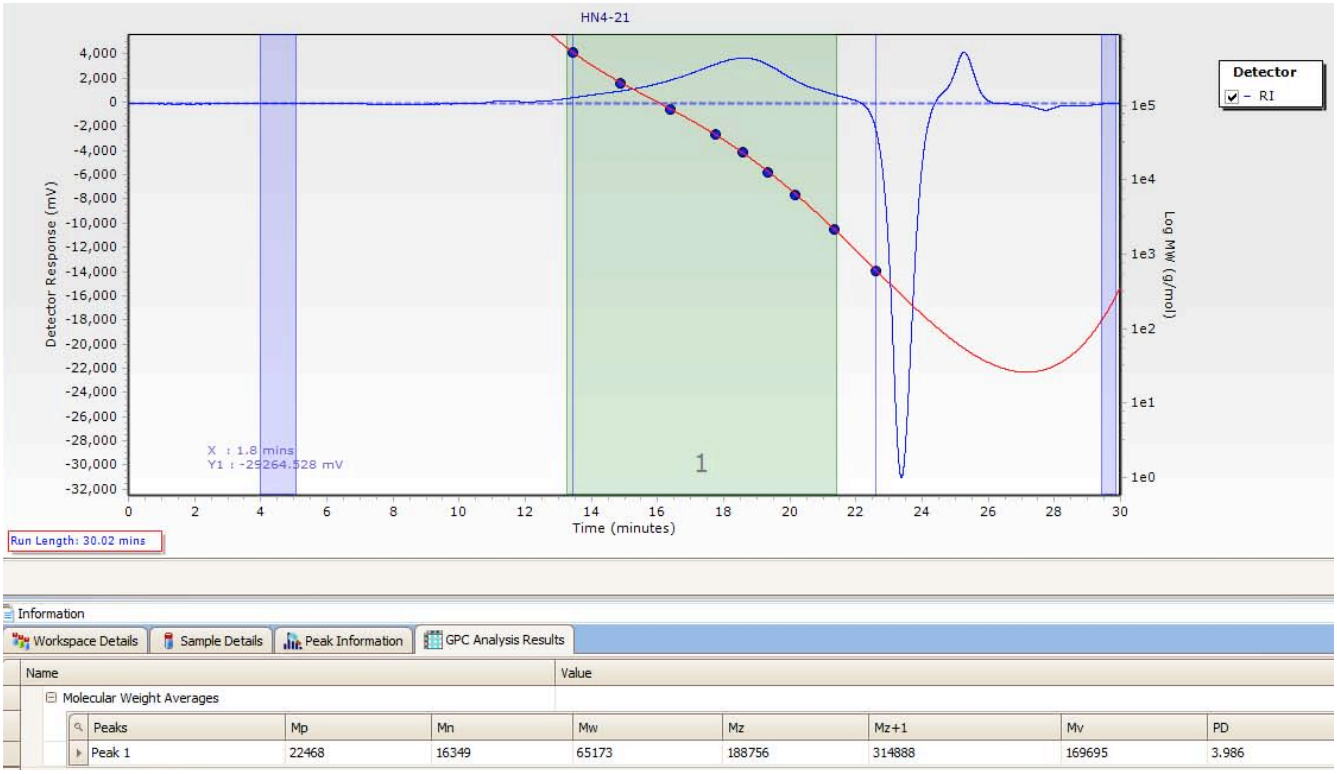


Figure S51. GPC Chromatogram of copoly(L-lactide/ hydroxyethylferulic acid) [90:10] (Table S3, entry 12).

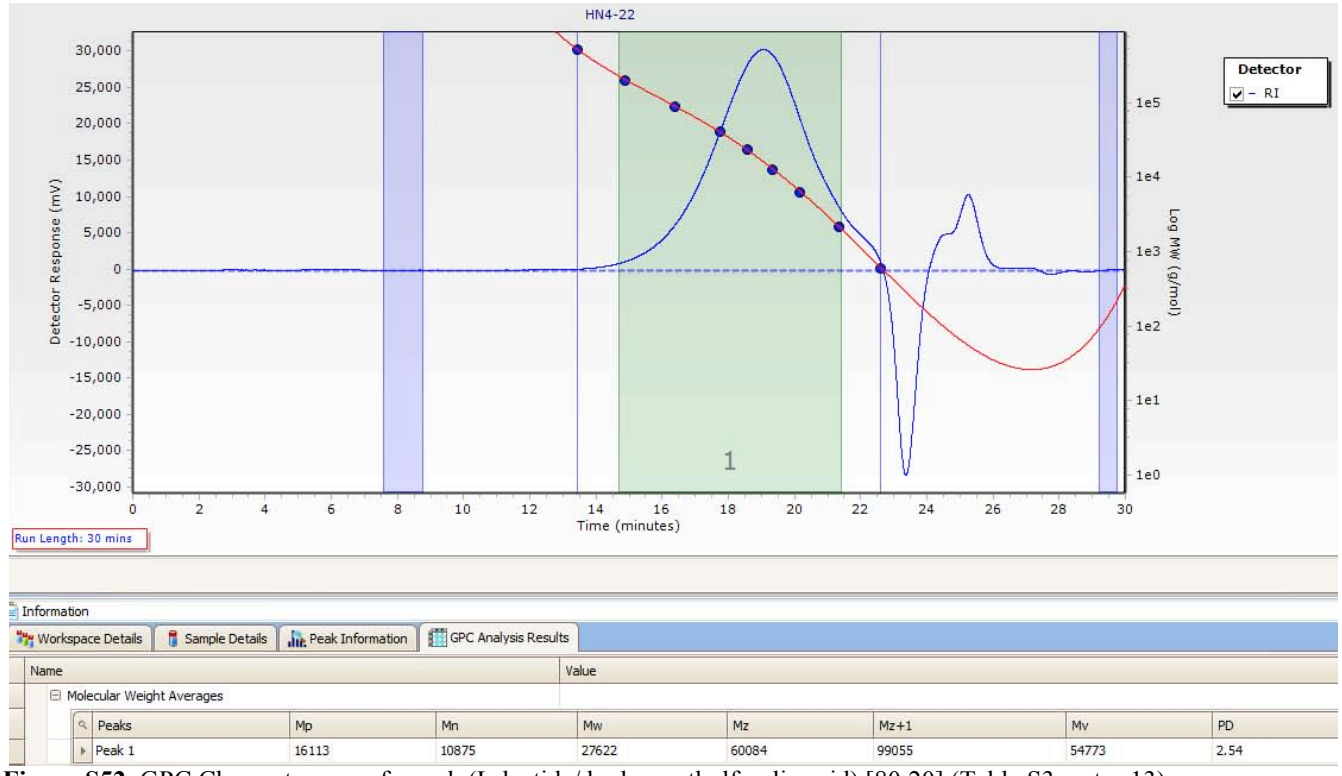


Figure S52. GPC Chromatogram of copoly(L-lactide/ hydroxyethylferulic acid) [80:20] (Table S3, entry 13).

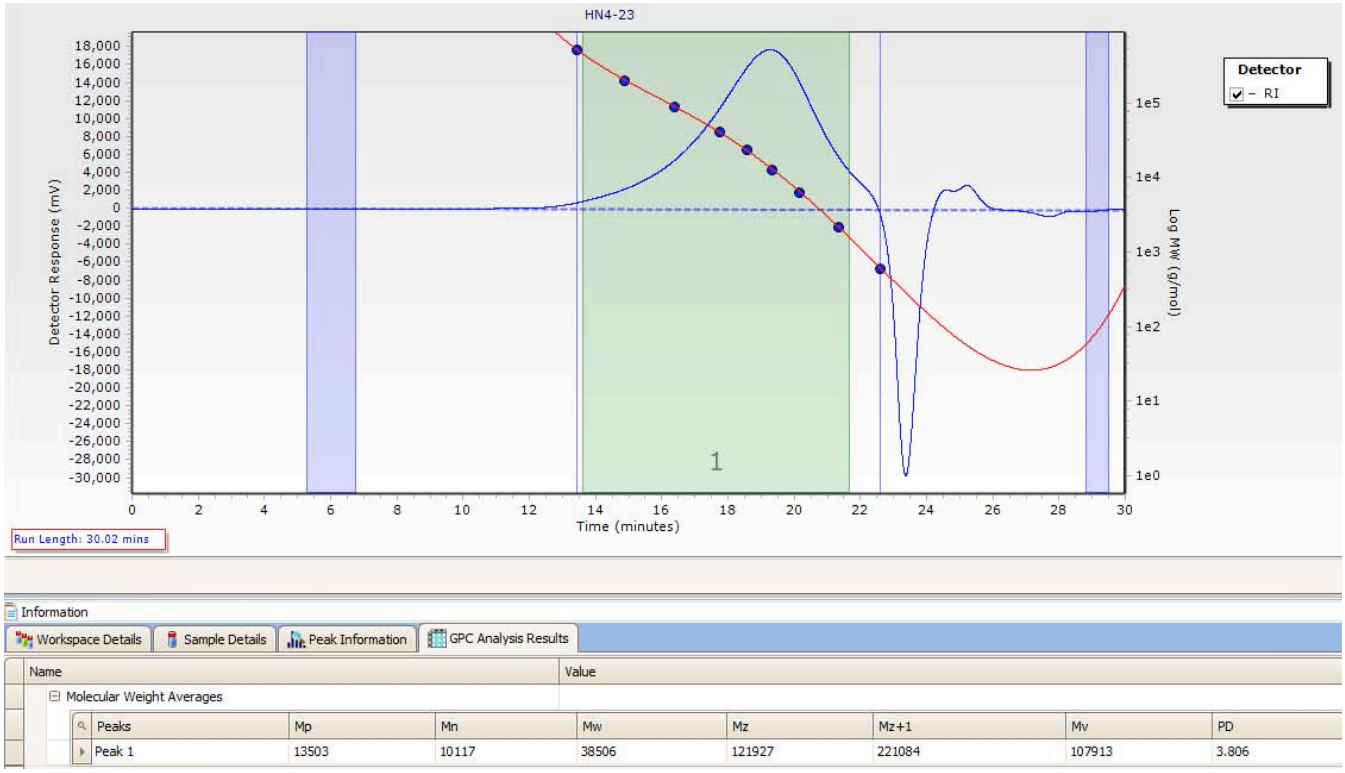


Figure S53. GPC Chromatogram of copoly(L-lactide/ hydroxyethylferulic acid) [70:30] (Table S3, entry 14).

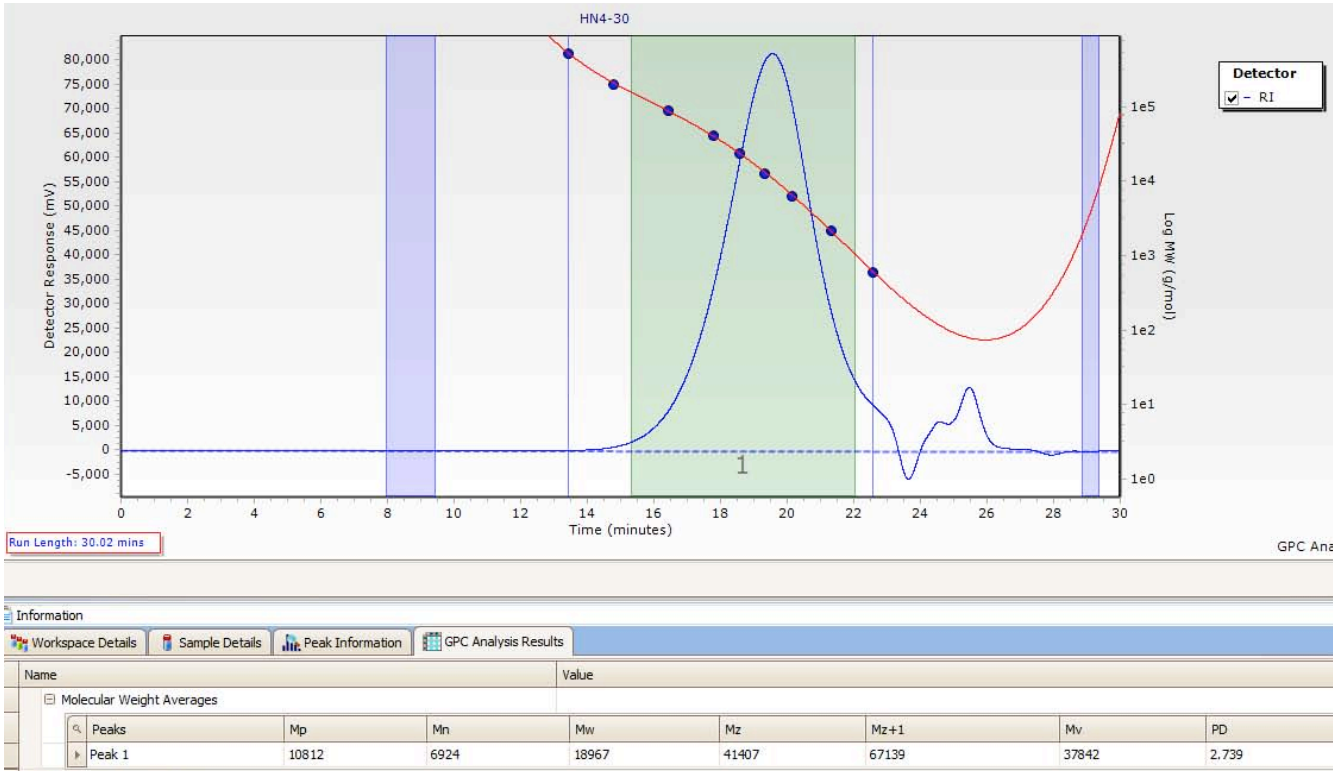
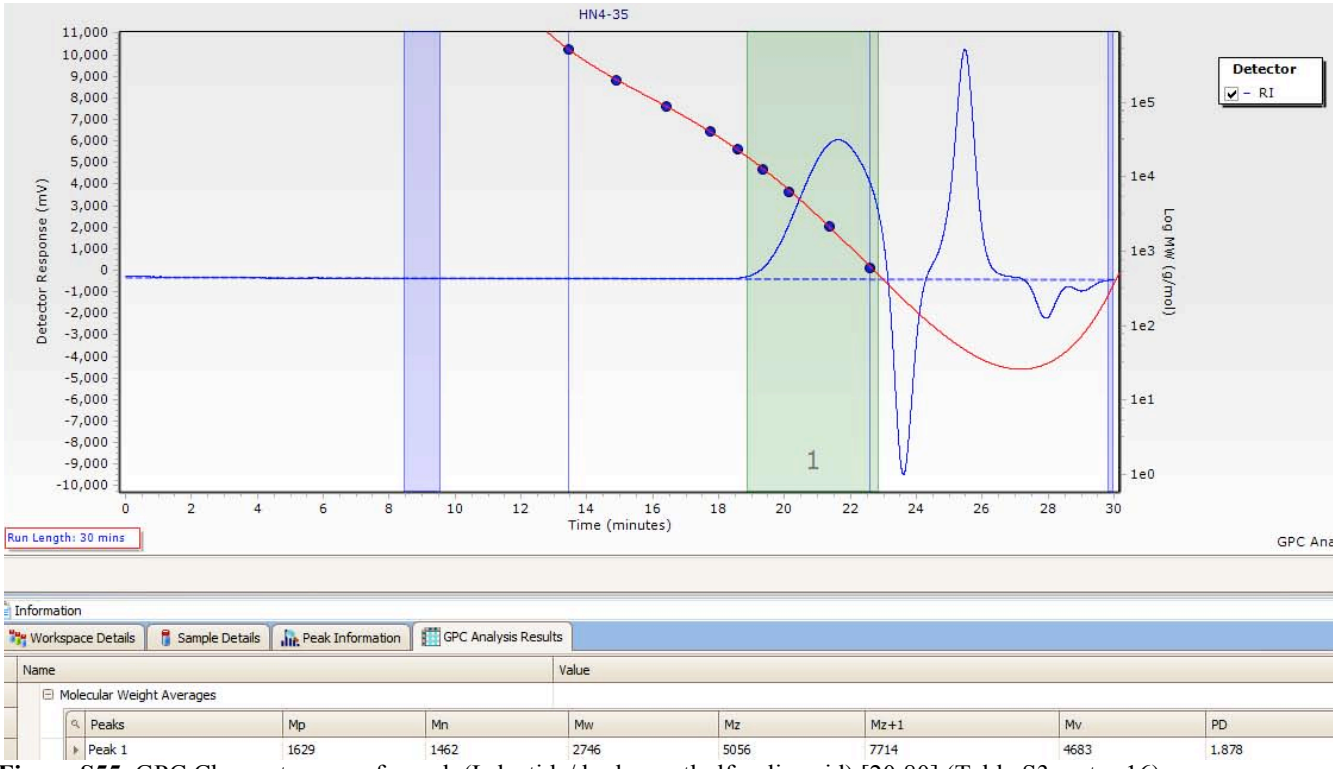


Figure S54. GPC Chromatogram of copoly(L-lactide/ hydroxyethylferulic acid) [60:40] (Table S3, entry 15).



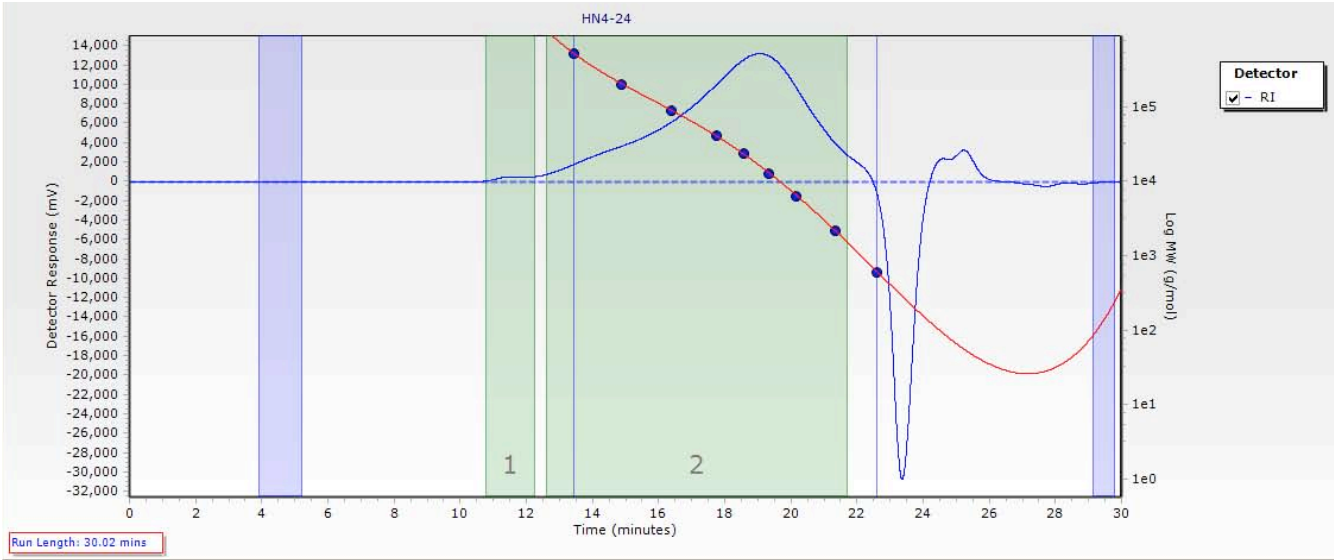
Information

Workspace Details | Sample Details | Peak Information | GPC Analysis Results

Name	Value
Molecular Weight Averages	

Peaks	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
Peak 1	1629	1462	2746	5056	7714	4683	1.878

Figure S55. GPC Chromatogram of copoly(L-lactide/ hydroxyethylferulic acid) [20:80] (Table S3, entry 16).



Information

Workspace Details | Sample Details | Peak Information | GPC Analysis Results

Name	Value
Molecular Weight Averages	

Peaks	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
Peak 1	1450417	2859331	3754139	4973842	6248672	4784574	1.313
Peak 2	15867	12291	68783	275236	510544	241341	5.596

Figure S56. GPC Chromatogram of copoly(L-lactide/ hydroxyethylcoumaric acid) [90:10] (Table S3, entry 18).

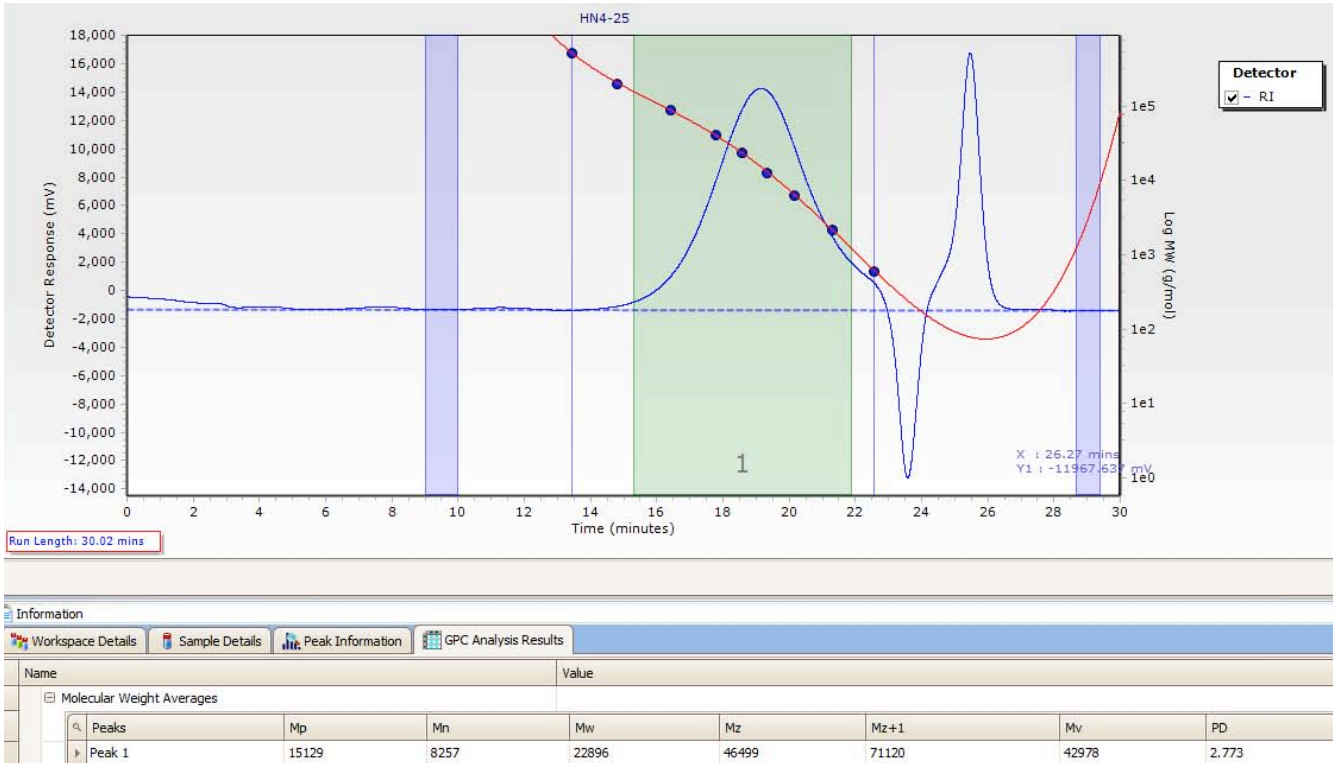


Figure S57. GPC Chromatogram of copoly(L-lactide/ hydroxyethylcoumaric acid) [80:20] (Table S3, entry 19).

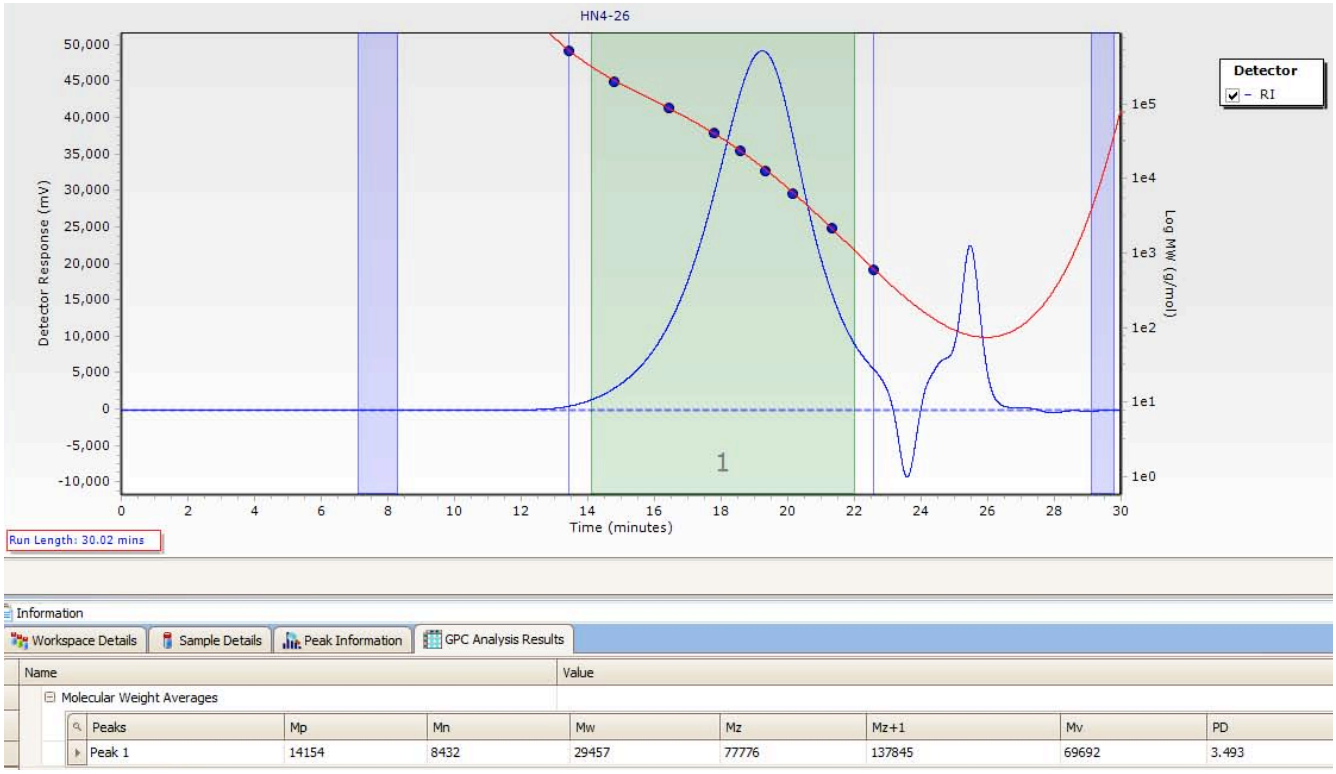


Figure S58. GPC Chromatogram of copoly(L-lactide/ hydroxyethylcoumaric acid) [70:30] (Table S3, entry 20).

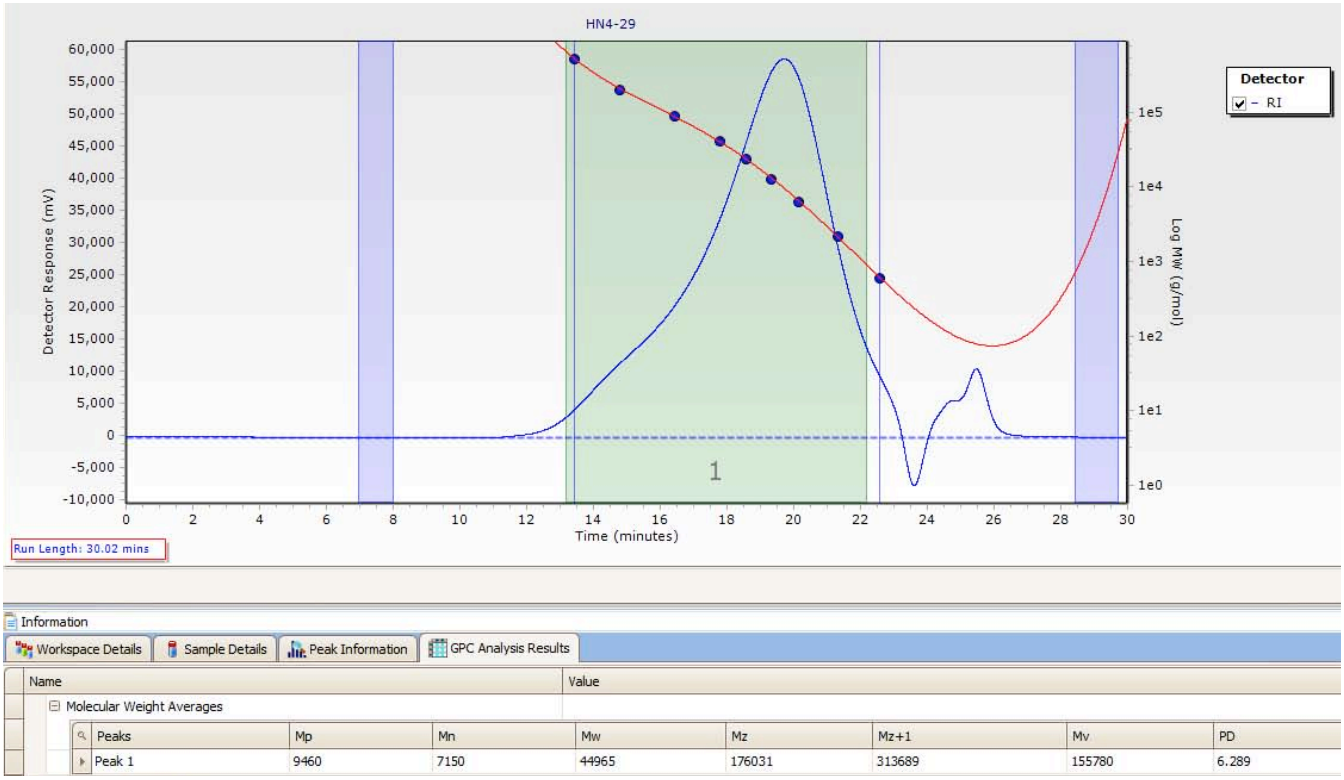


Figure S59. GPC Chromatogram of copoly(L-lactide/ hydroxyethylcoumaric acid) [60:40] (Table S3, entry 21).

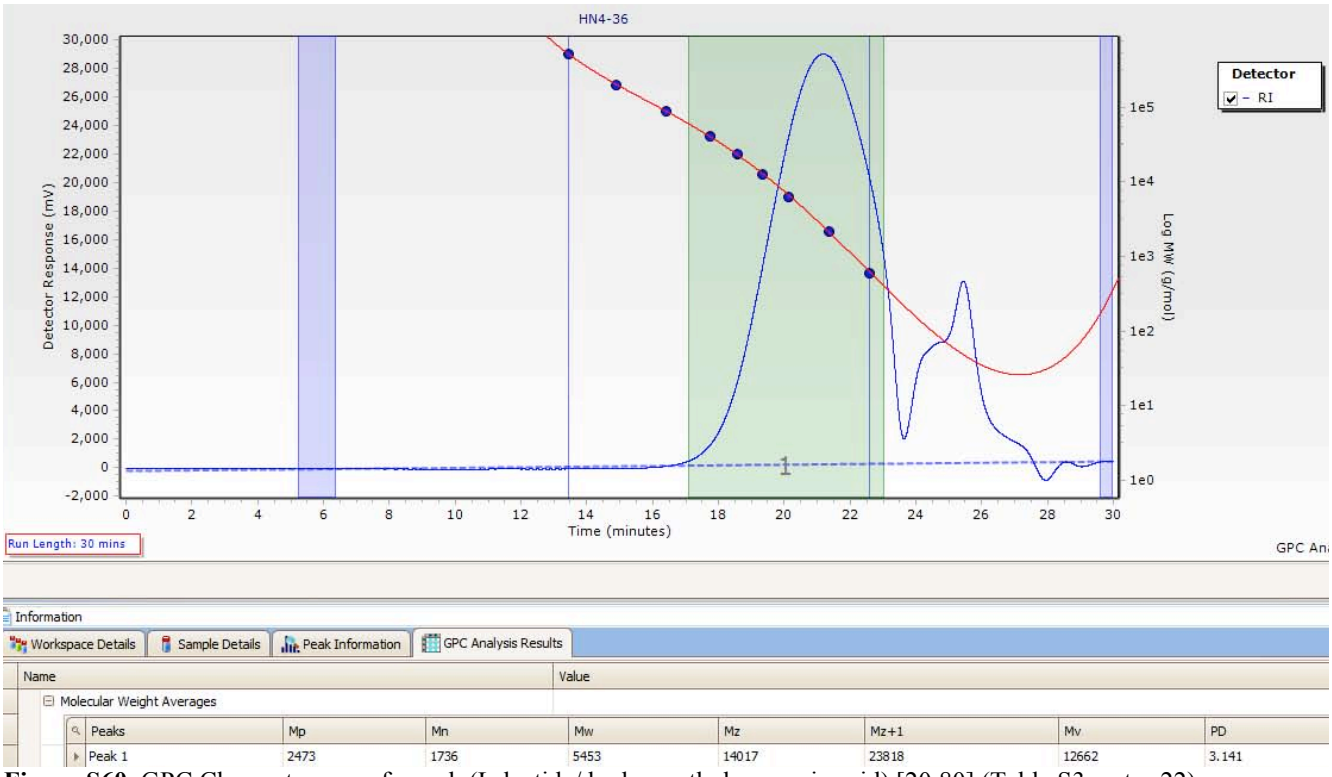
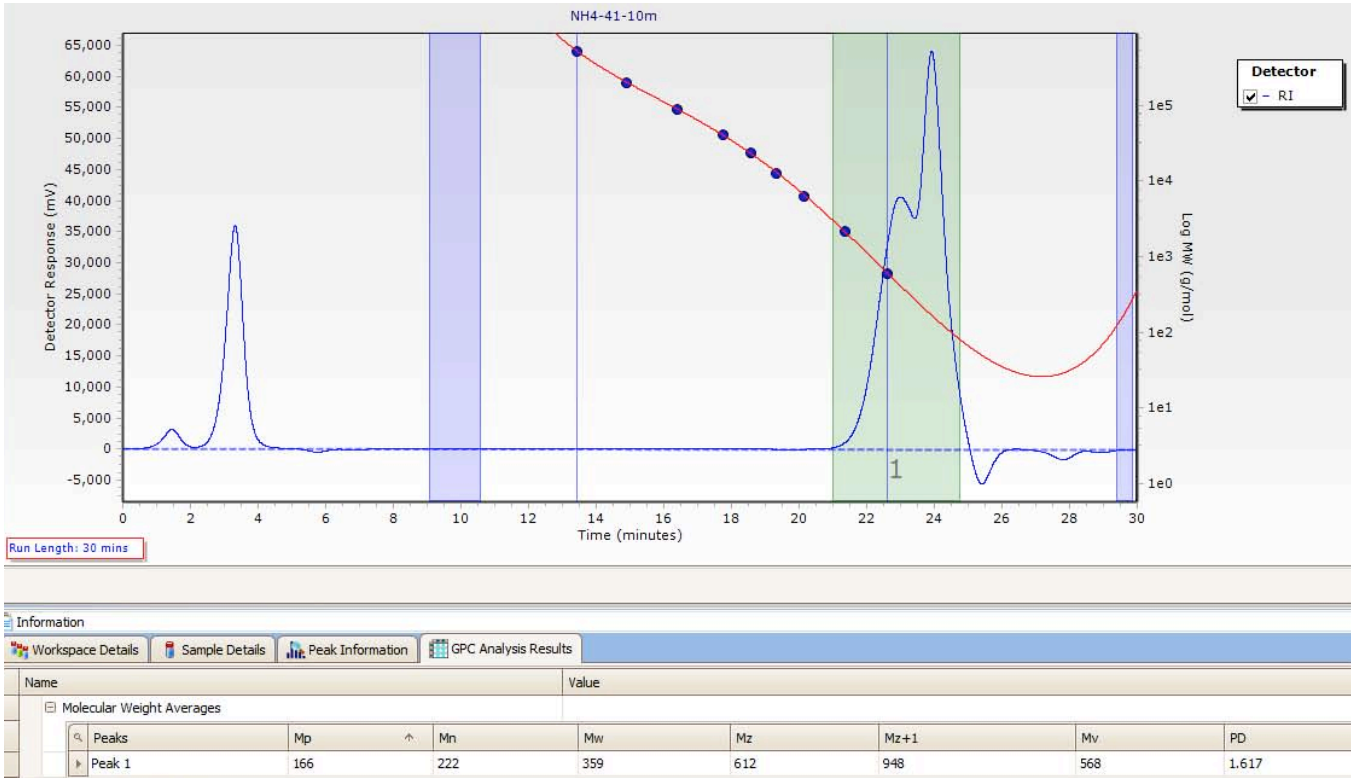


Figure S60. GPC Chromatogram of copoly(L-lactide/ hydroxyethylcoumaric acid) [20:80] (Table S3, entry 22).



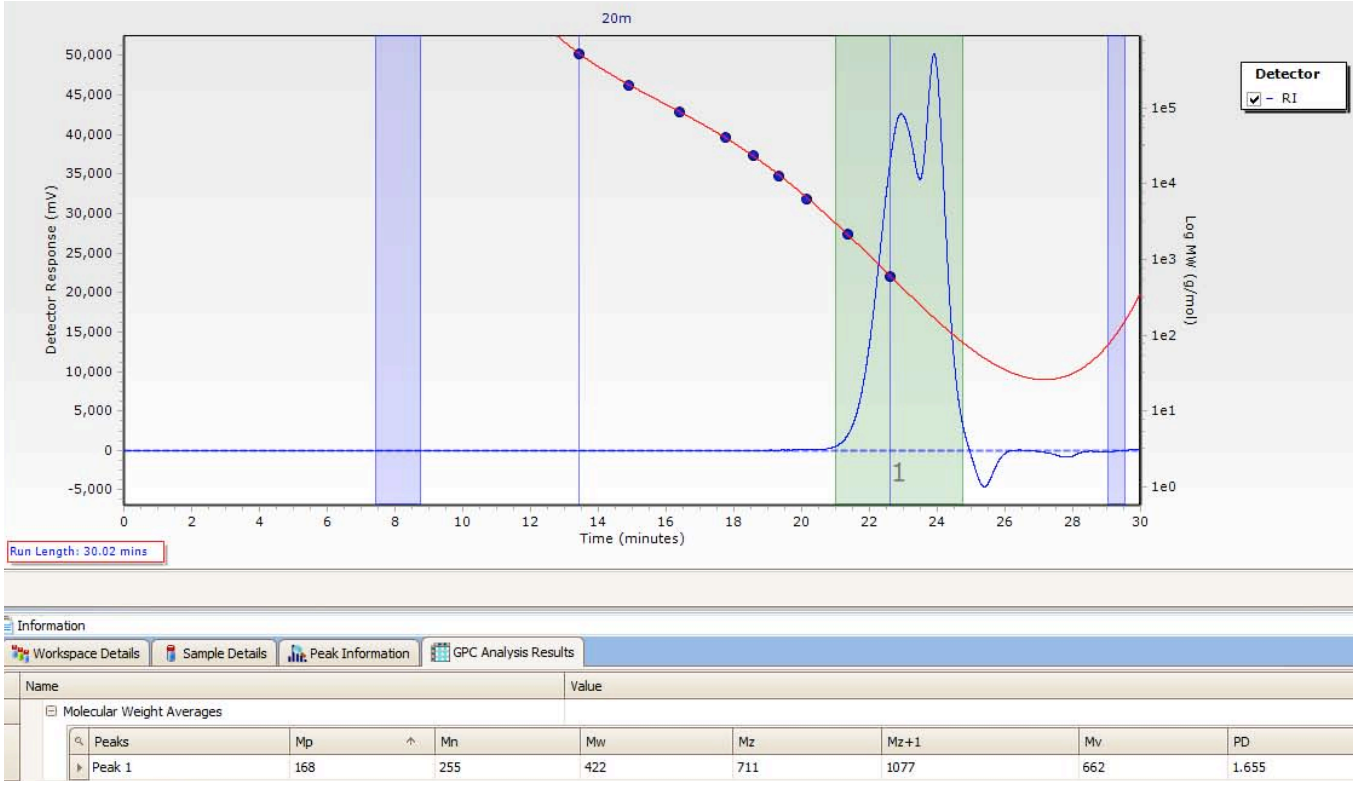
Information

Workspace Details | Sample Details | Peak Information | GPC Analysis Results

Name	Value
Molecular Weight Averages	

Peaks	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
Peak 1	166	222	359	612	948	568	1.617

Figure S61. GPC Chromatogram of copoly(caprolactone/ hydroxyethylsyringic acid) [50:50] at 10 min. (Table S4, entry 1).



Information

Workspace Details | Sample Details | Peak Information | GPC Analysis Results

Name	Value
Molecular Weight Averages	

Peaks	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
Peak 1	168	255	422	711	1077	662	1.655

Figure S62. GPC Chromatogram of copoly(caprolactone/ hydroxyethylsyringic acid) [50:50] at 20 min. (Table S4, entry 2).

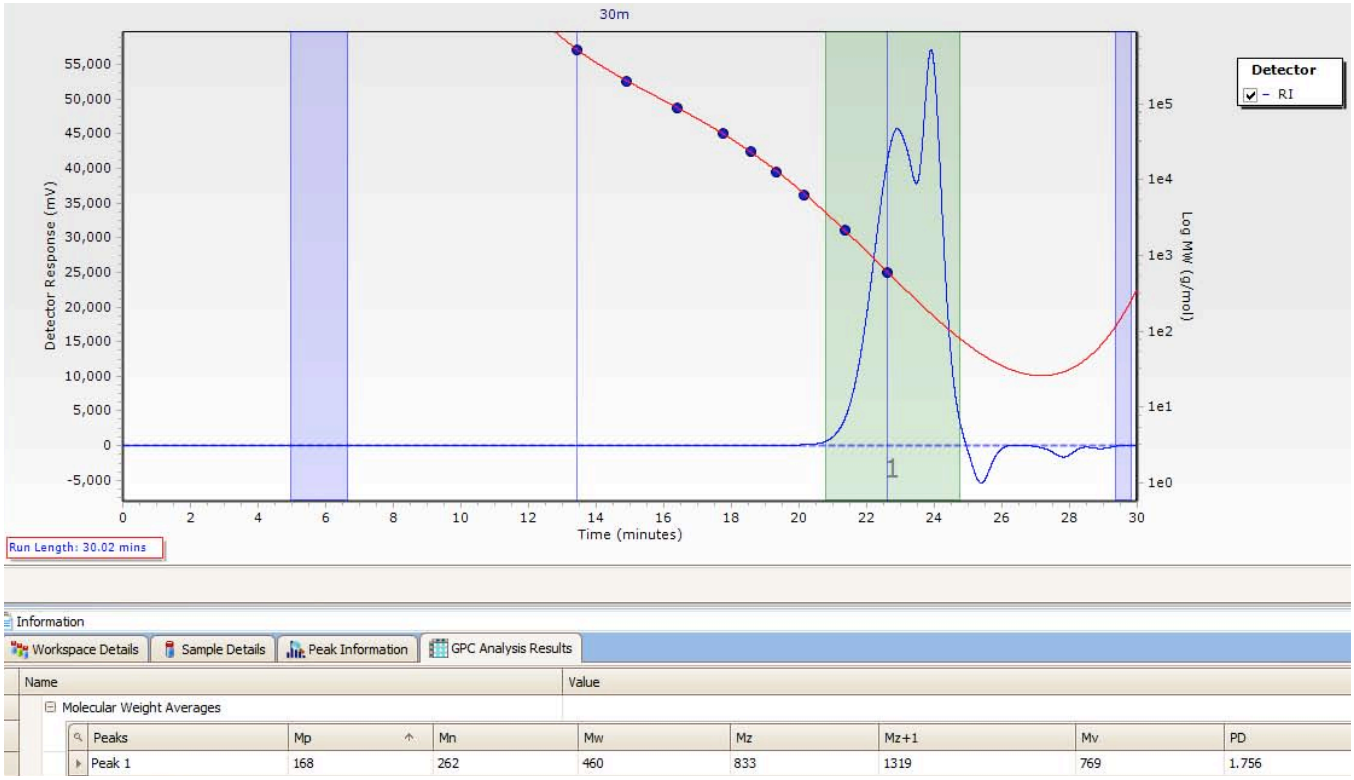


Figure S63. GPC Chromatogram of copoly(caprolactone/ hydroxyethylsyringic acid) [50:50] at 30 min. (Table S4, entry 3).

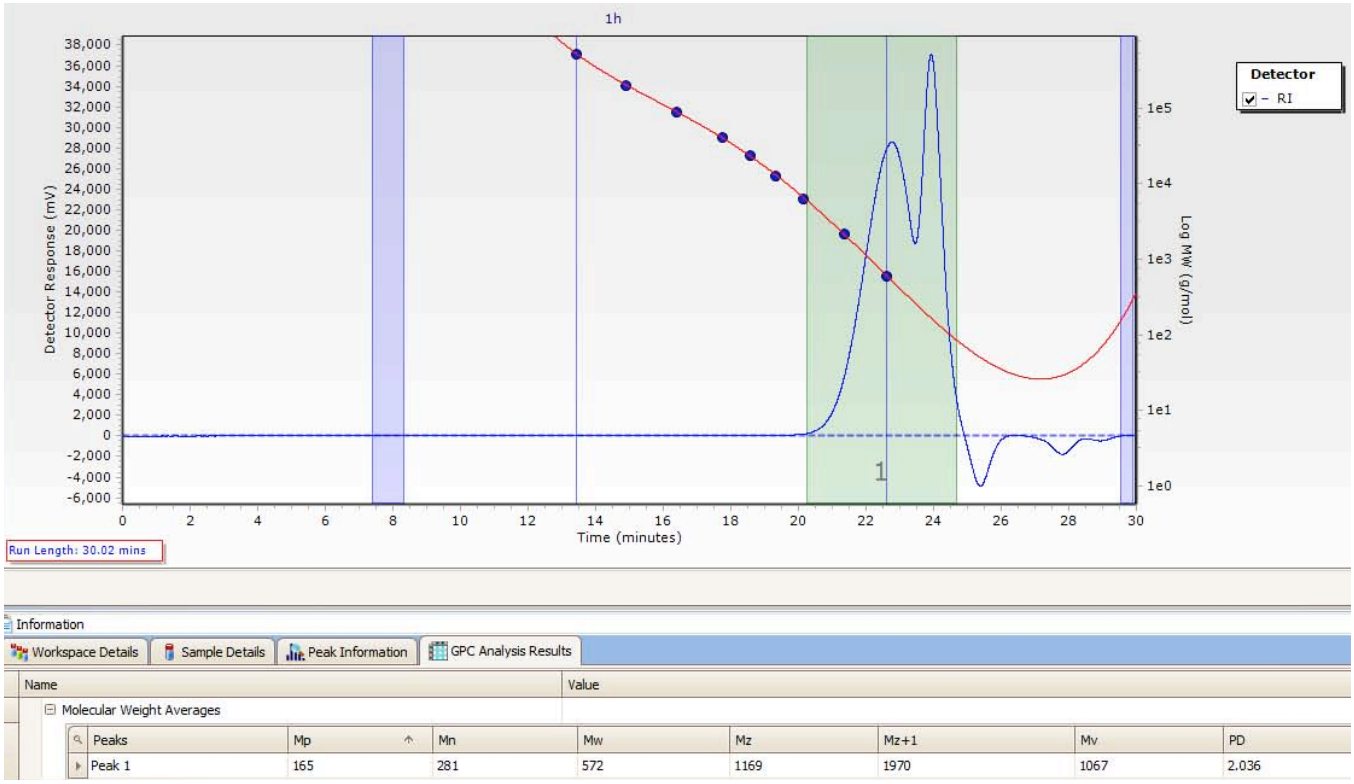


Figure S64. GPC Chromatogram of copoly(caprolactone/ hydroxyethylsyringic acid) [50:50] at 1 hour (Table S4, entry 4).

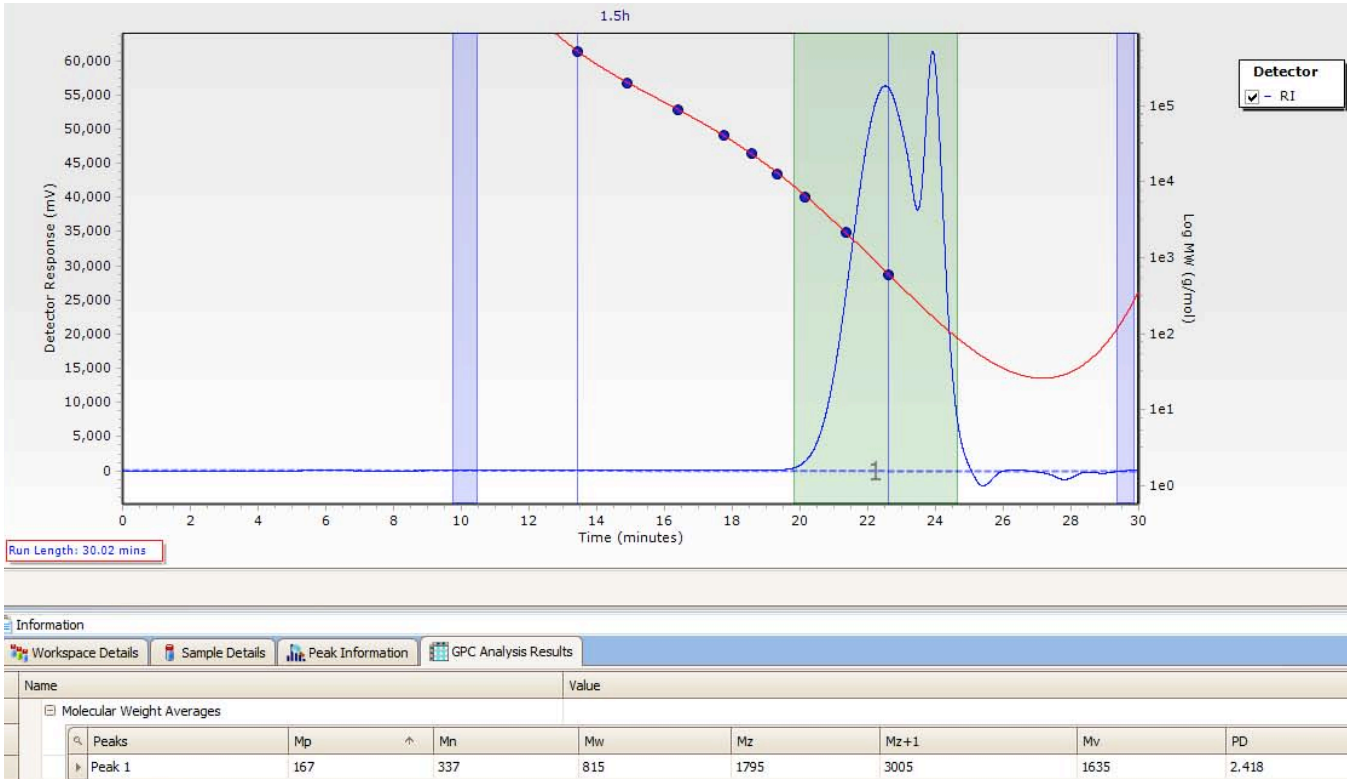


Figure S65. GPC Chromatogram of copoly(caprolactone/ hydroxyethylsyringic acid) [50:50] at 1.5 hours (Table S4, entry 5).

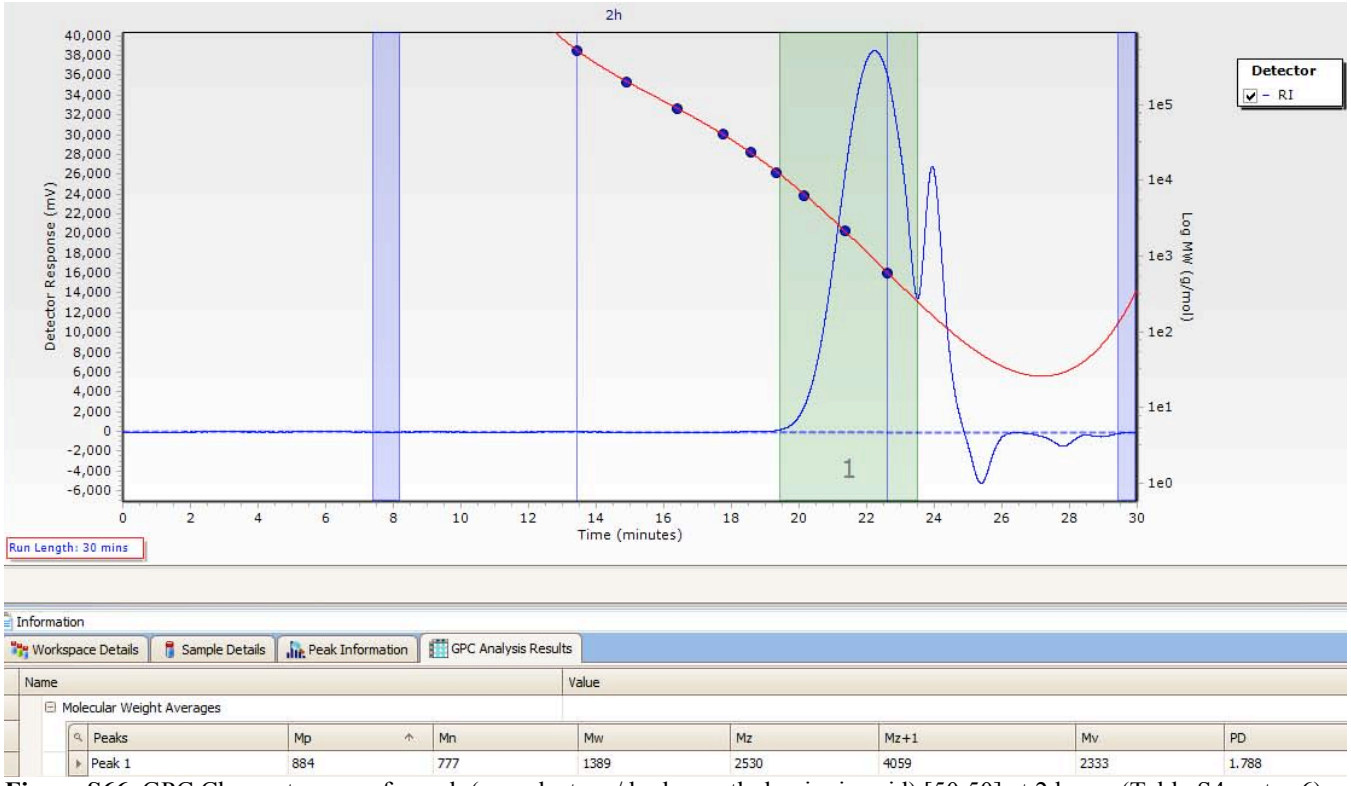


Figure S66. GPC Chromatogram of copoly(caprolactone/ hydroxyethylsyringic acid) [50:50] at 2 hours (Table S4, entry 6).

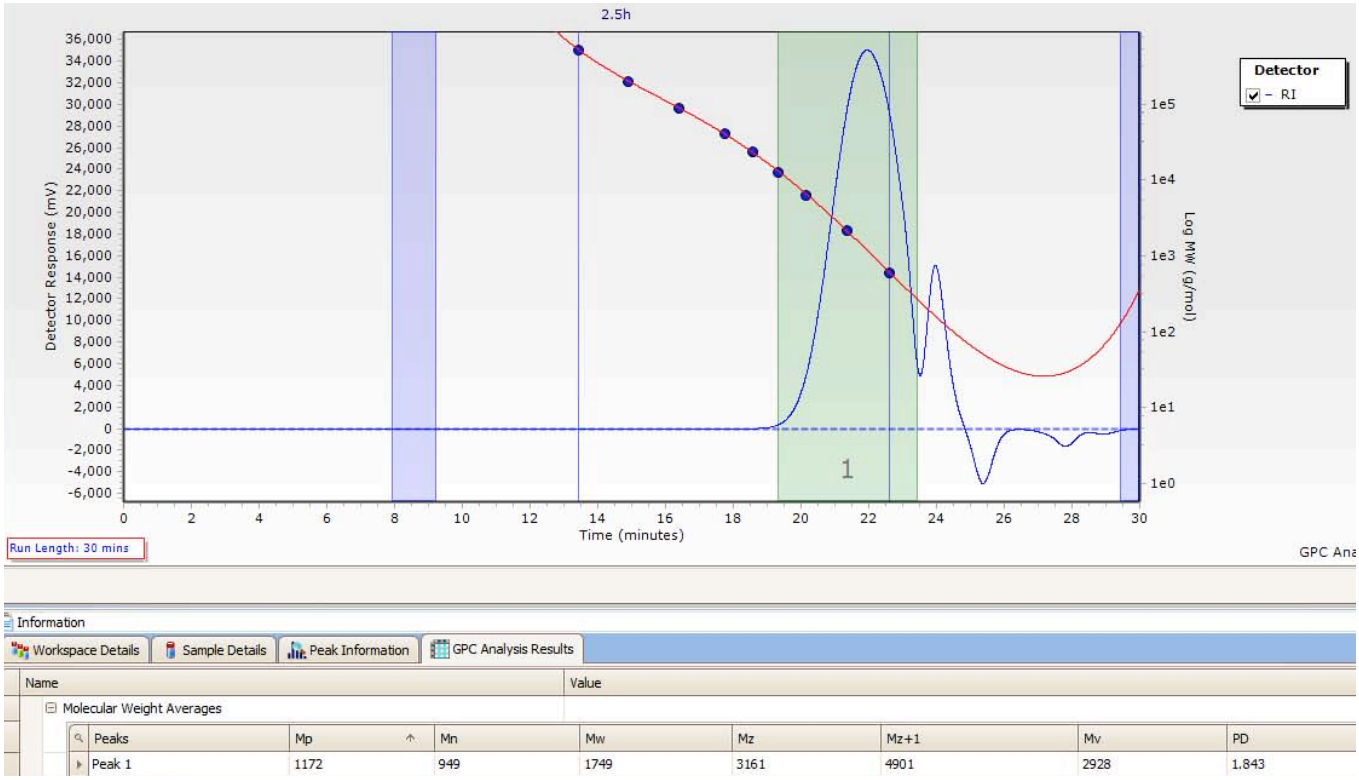


Figure S67. GPC Chromatogram of copoly(caprolactone/ hydroxyethylsyringic acid) [50:50] at 2.5 hours (Table S4, entry 7).

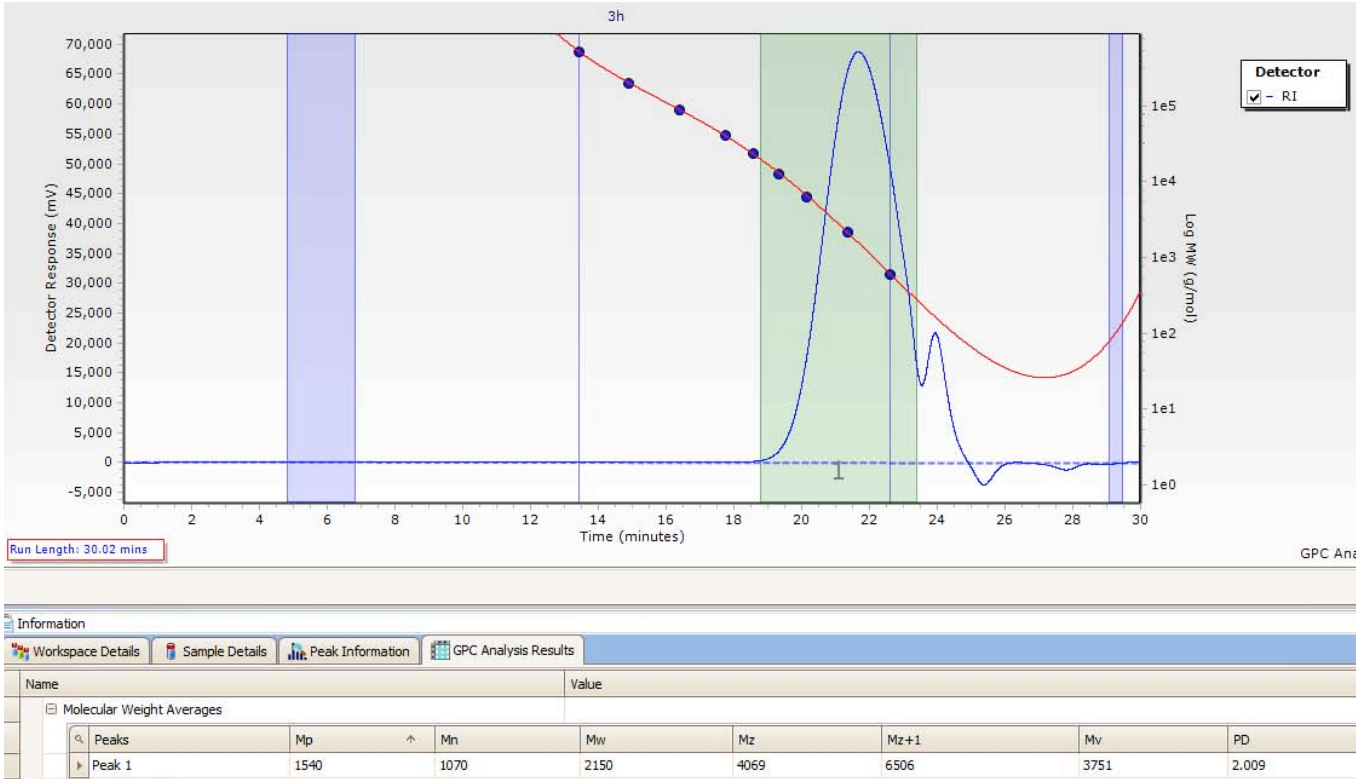


Figure S68. GPC Chromatogram of copoly(caprolactone/ hydroxyethylsyringic acid) [50:50] at 3 hours (Table S4, entry 8).

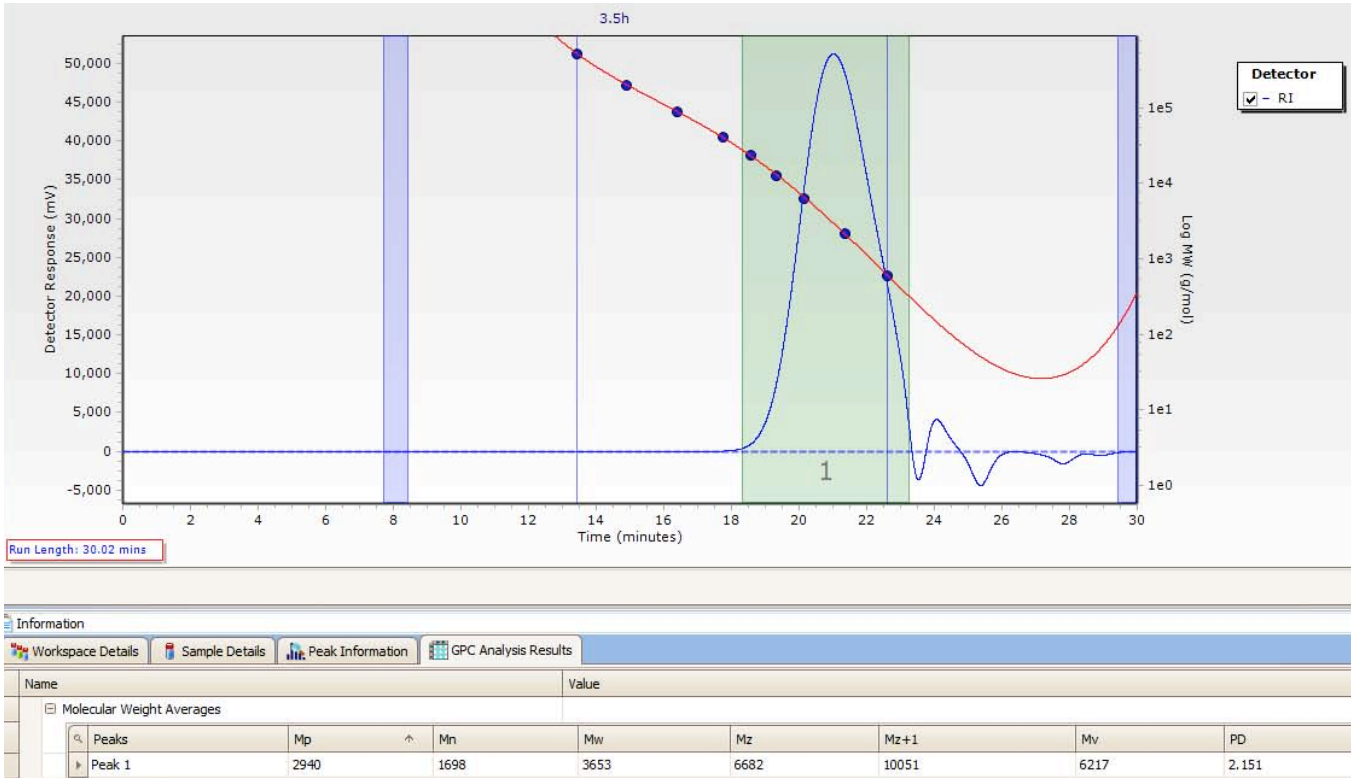


Figure S69. GPC Chromatogram of copoly(caprolactone/ hydroxyethylsyringic acid) [50:50] at 3.5 hours (Table S4, entry 9).

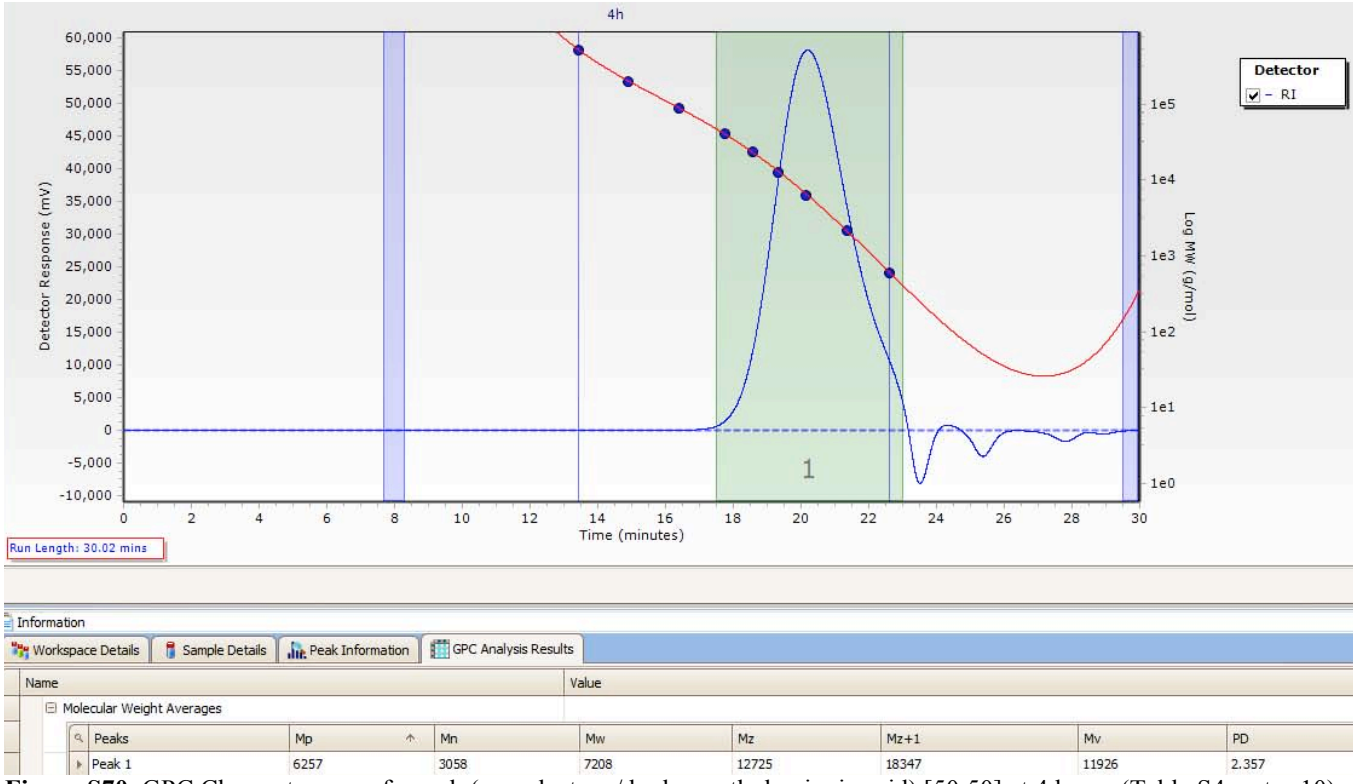
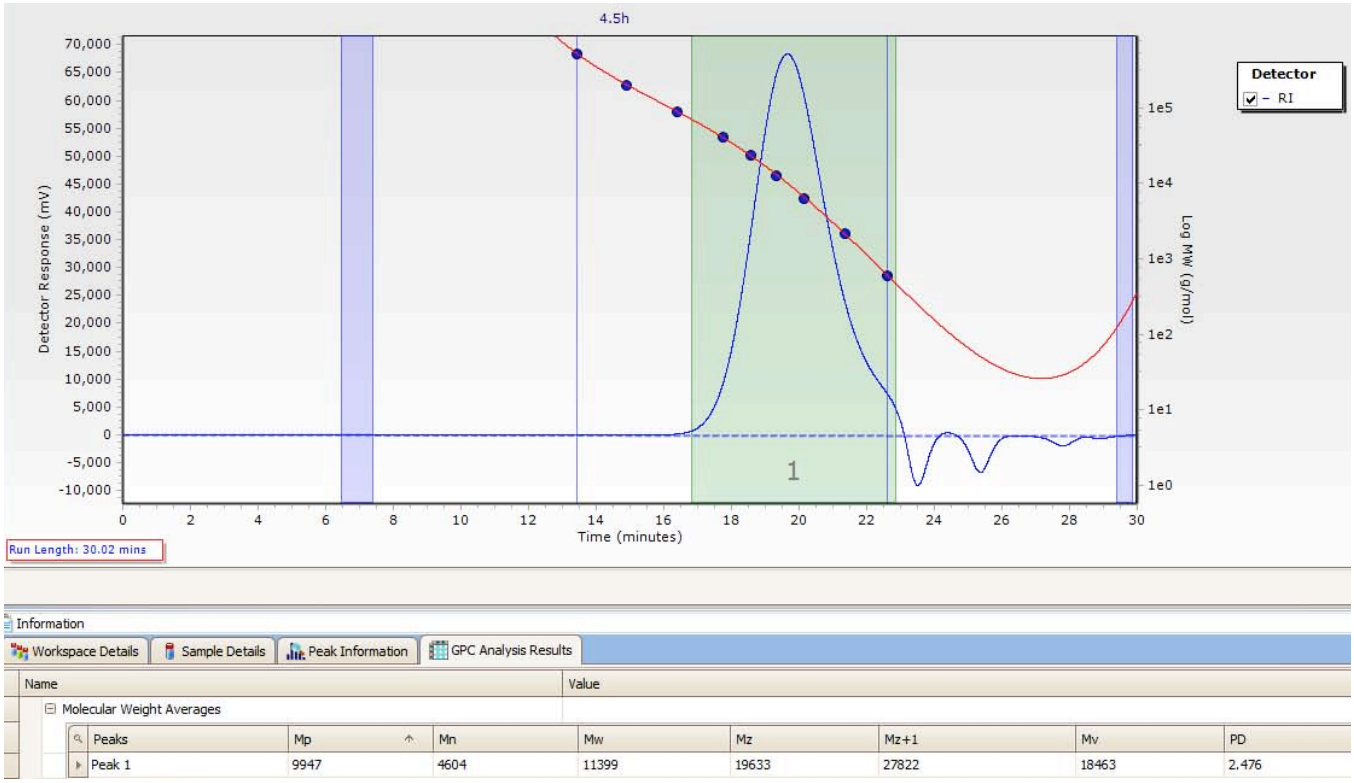


Figure S70. GPC Chromatogram of copoly(caprolactone/ hydroxyethylsyringic acid) [50:50] at 4 hours (Table S4, entry 10).



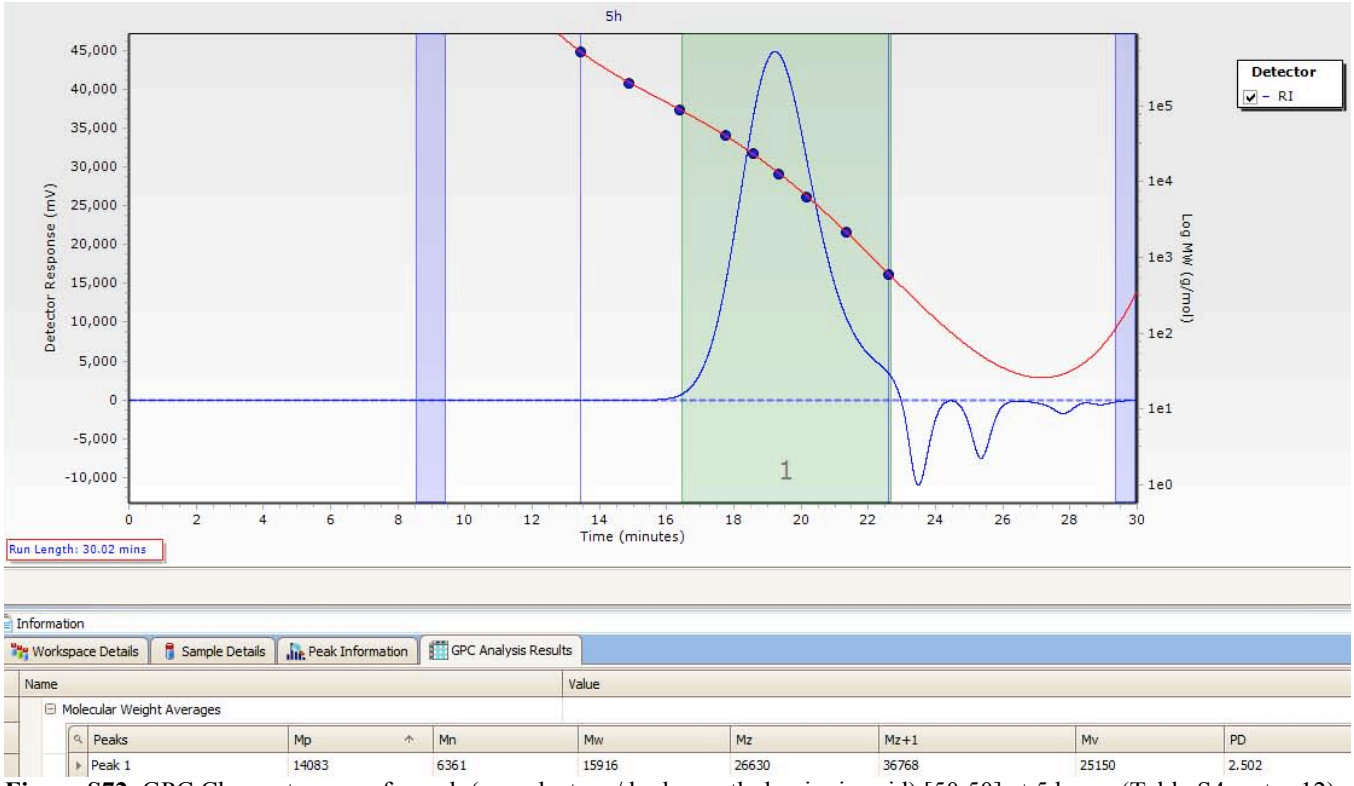
Information

Workspace Details | Sample Details | Peak Information | GPC Analysis Results

Name	Value
Molecular Weight Averages	

Peaks	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
Peak 1	9947	4604	11399	19633	27822	18463	2.476

Figure S71. GPC Chromatogram of copoly(caprolactone/ hydroxyethylsyringic acid) [50:50] at 4.5 hours (Table S4, entry 11).



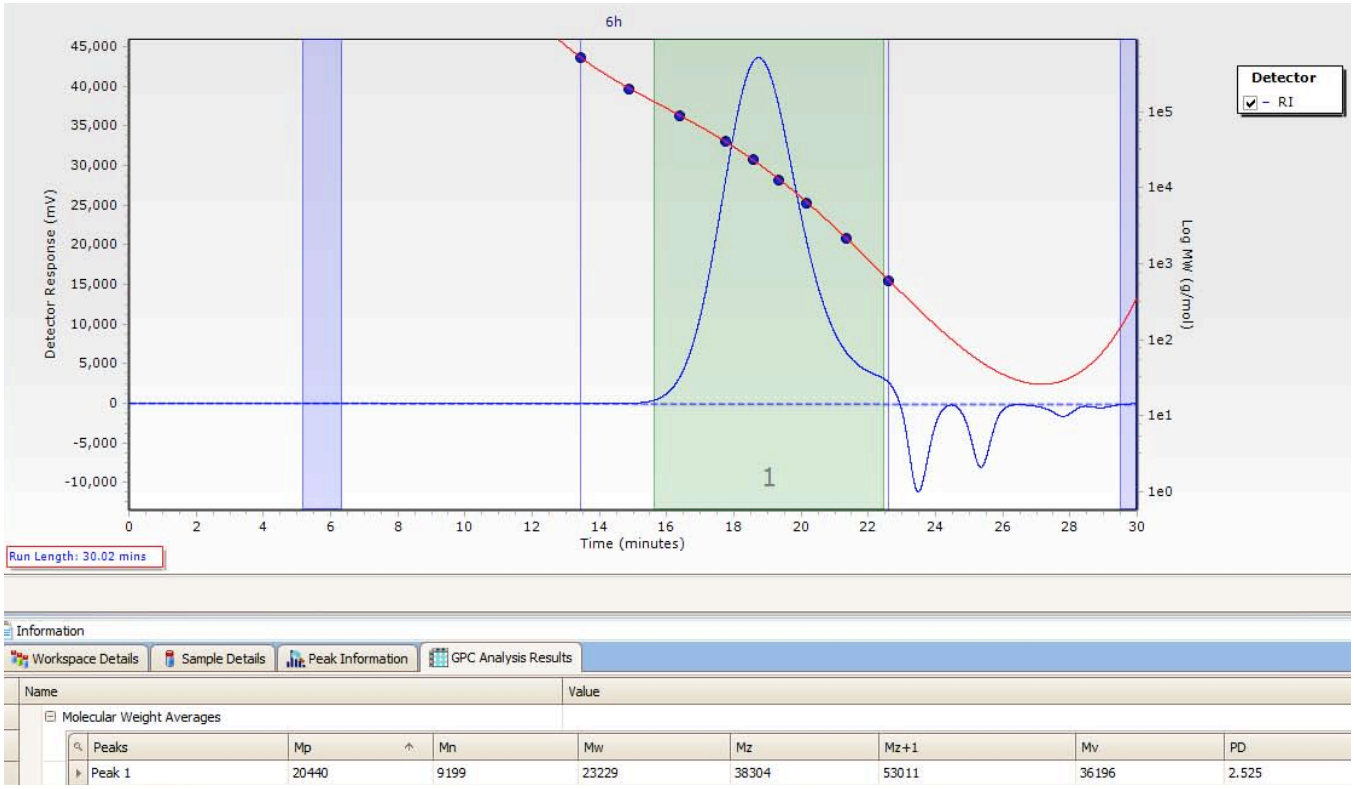
Information

Workspace Details | Sample Details | Peak Information | GPC Analysis Results

Name	Value
Molecular Weight Averages	

Peaks	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
Peak 1	14083	6361	15916	26630	36768	25150	2.502

Figure S72. GPC Chromatogram of copoly(caprolactone/ hydroxyethylsyringic acid) [50:50] at 5 hours (Table S4, entry 12).



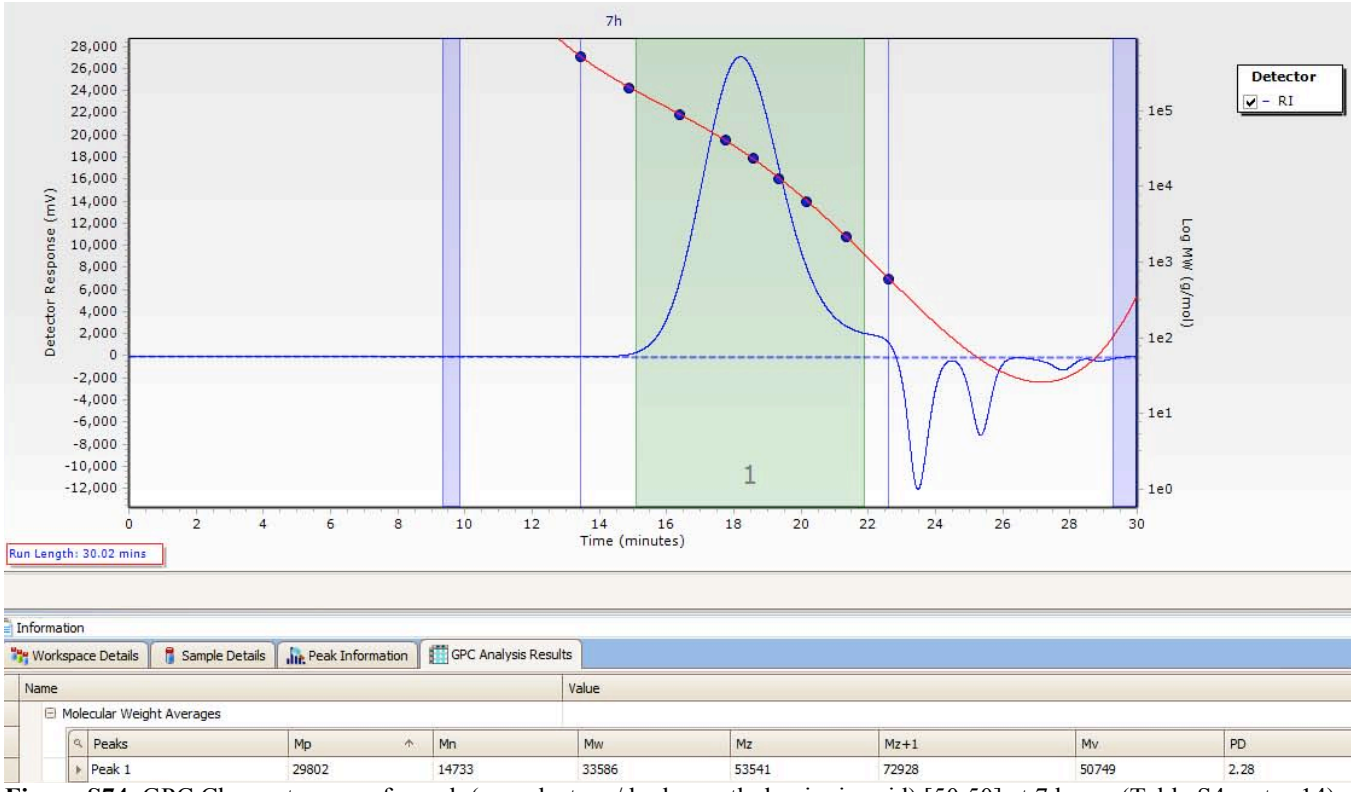
Information

Workspace Details | Sample Details | Peak Information | GPC Analysis Results

Name	Value
Molecular Weight Averages	

Peaks	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
Peak 1	20440	9199	23229	38304	53011	36196	2.525

Figure S73. GPC Chromatogram of copoly(caprolactone/ hydroxyethylsyringic acid) [50:50] at 6 hours (Table S4, entry 13).



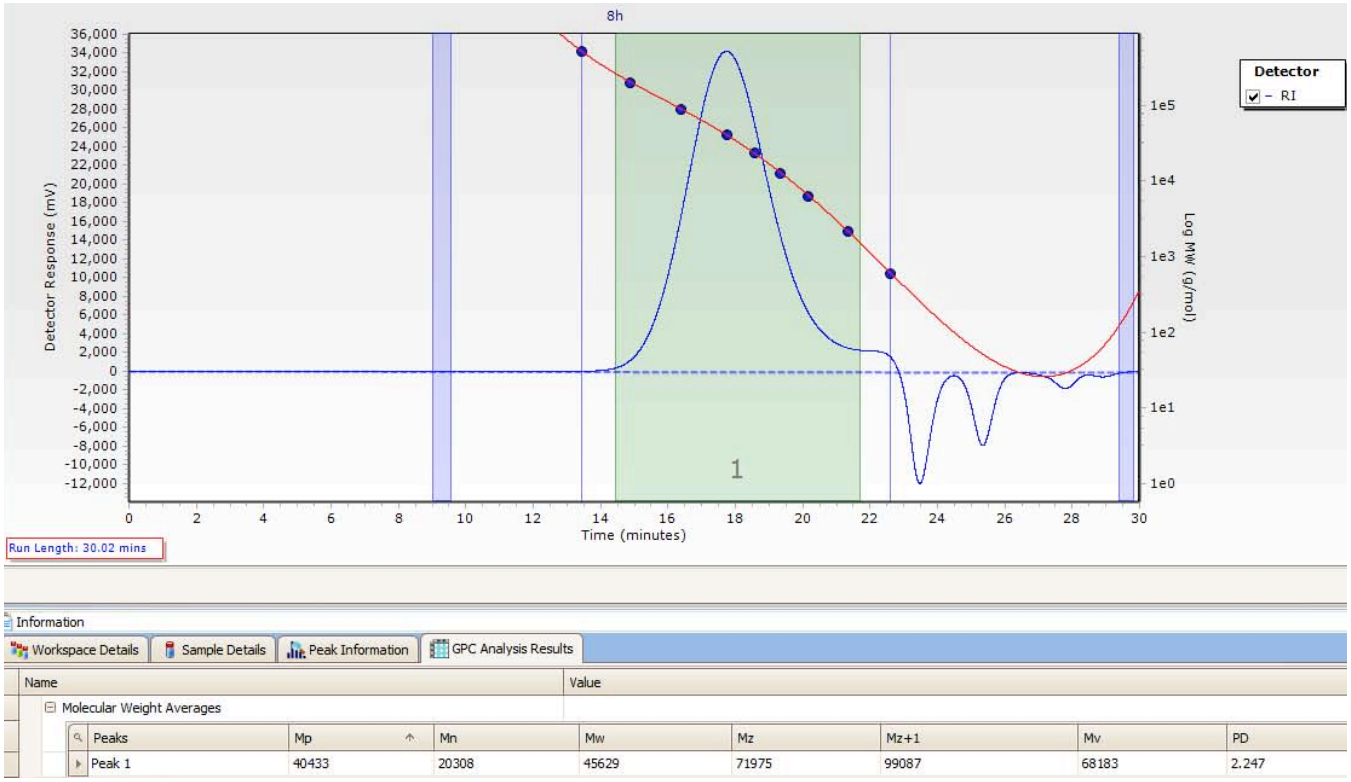
Information

Workspace Details | Sample Details | Peak Information | GPC Analysis Results

Name	Value
Molecular Weight Averages	

Peaks	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
Peak 1	29802	14733	33586	53541	72928	50749	2.28

Figure S74. GPC Chromatogram of copoly(caprolactone/ hydroxyethylsyringic acid) [50:50] at 7 hours (Table S4, entry 14).



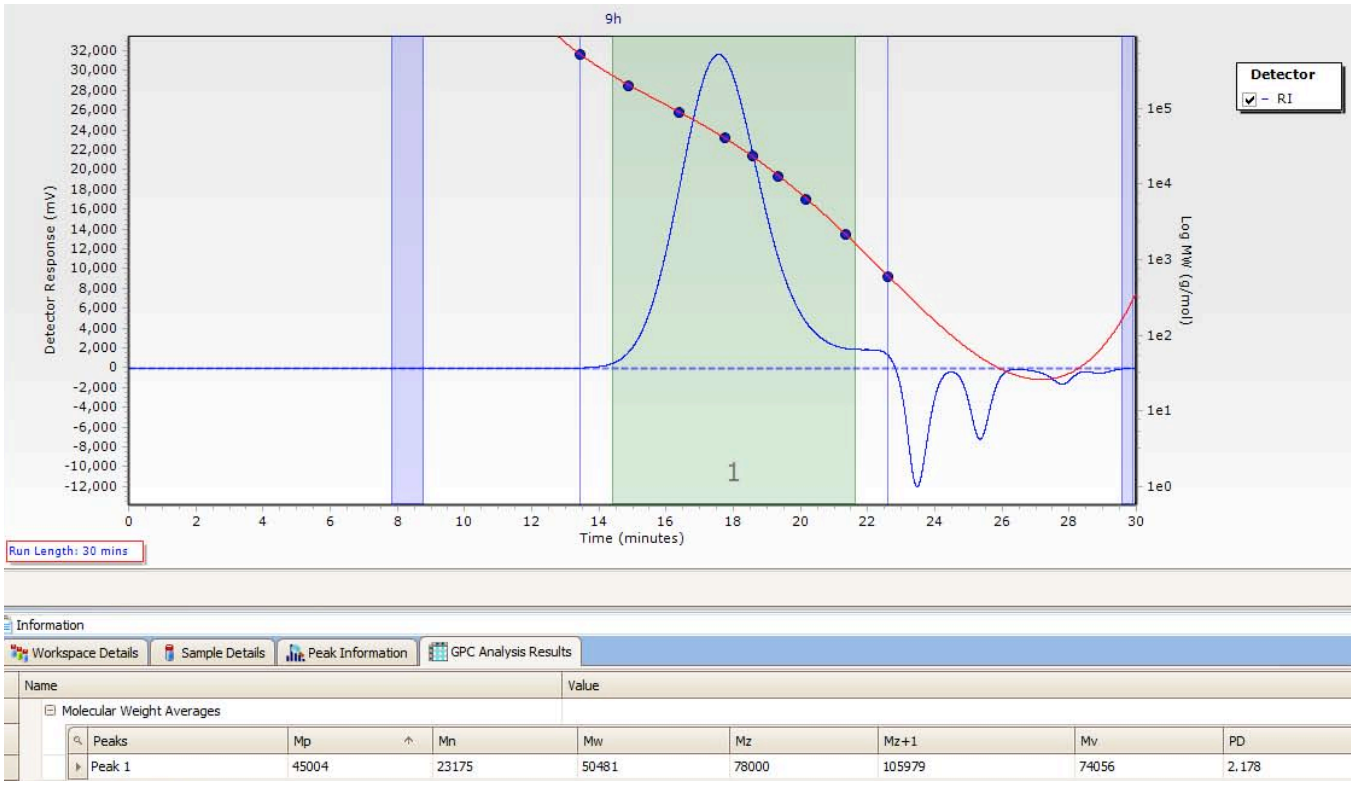
Information

Workspace Details | Sample Details | Peak Information | GPC Analysis Results

Name	Value
Molecular Weight Averages	

Peaks	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
Peak 1	40433	20308	45629	71975	99087	68183	2.247

Figure S75. GPC Chromatogram of copoly(caprolactone/ hydroxyethylsyringic acid) [50:50] at 8 hours (Table S4, entry 15).



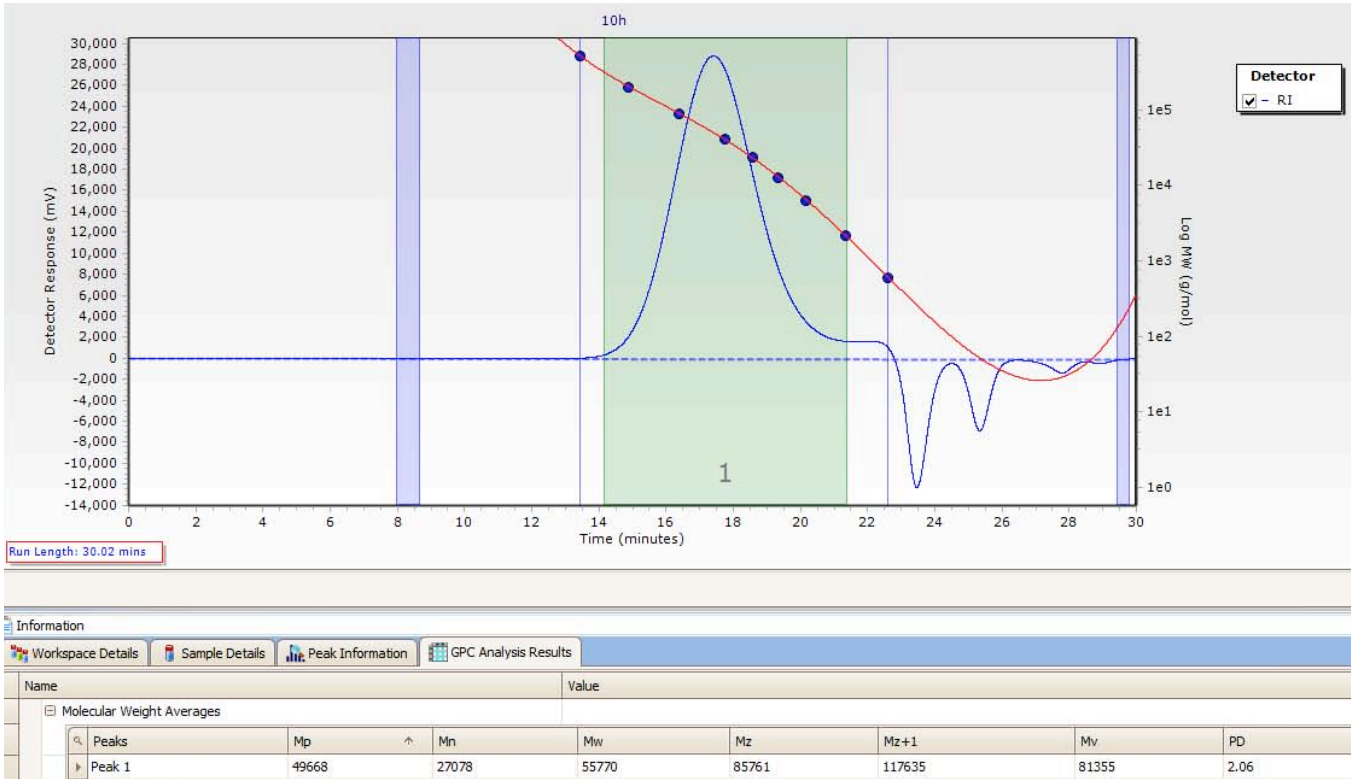
Information

Workspace Details | Sample Details | Peak Information | GPC Analysis Results

Name	Value
Molecular Weight Averages	

Peaks	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
Peak 1	45004	23175	50481	78000	105979	74056	2.178

Figure S76. GPC Chromatogram of copoly(caprolactone/ hydroxyethylsyringic acid) [50:50] at 9 hours (Table S4, entry 16).



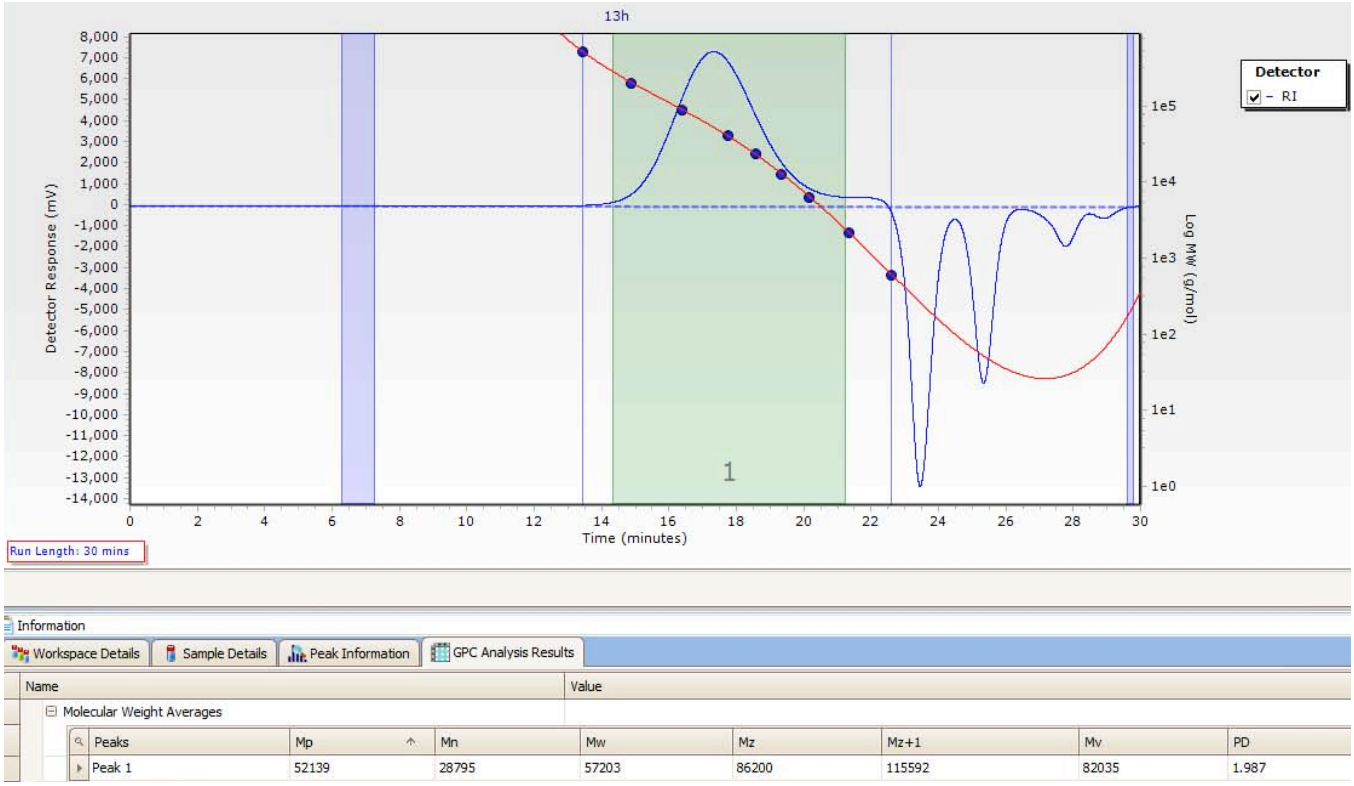
Information

Workspace Details | Sample Details | Peak Information | GPC Analysis Results

Name	Value
Molecular Weight Averages	

Peaks	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
Peak 1	49668	27078	55770	85761	117635	81355	2.06

Figure S77. GPC Chromatogram of copoly(caprolactone/ hydroxyethylsyringic acid) [50:50] at 10 hours (Table S4, entry 17).



Information

Workspace Details | Sample Details | Peak Information | GPC Analysis Results

Name	Value
Molecular Weight Averages	

Peaks	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
Peak 1	52139	28795	57203	86200	115592	82035	1.987

Figure S78. GPC Chromatogram of copoly(caprolactone/ hydroxyethylsyringic acid) [50:50] at 13 hours (Table S4, entry 18).

Differential Scanning Calorimetry (DSC) Thermograms

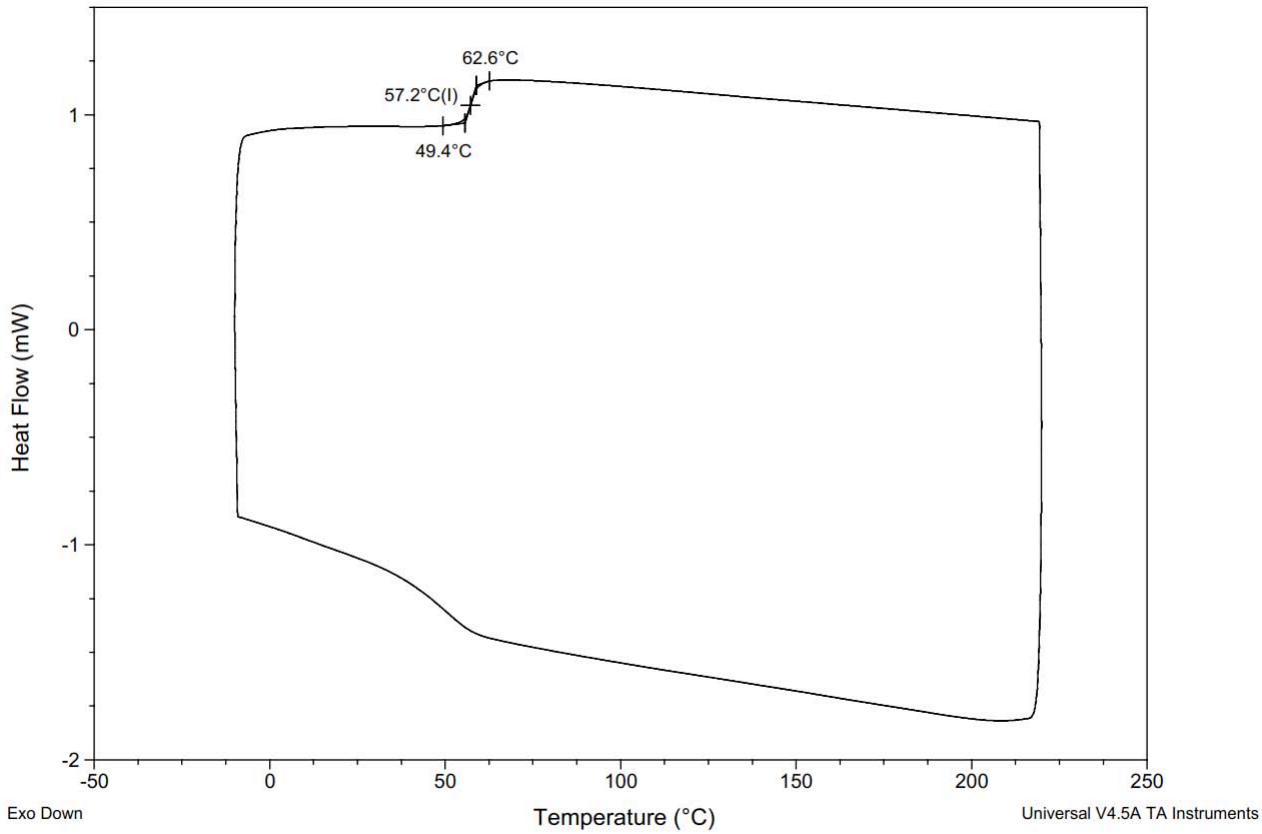


Figure S79. DSC Thermogram of copoly(caprolactone/ hydroxyethylsyringic acid) [20:80] (Table S1, entry 1).

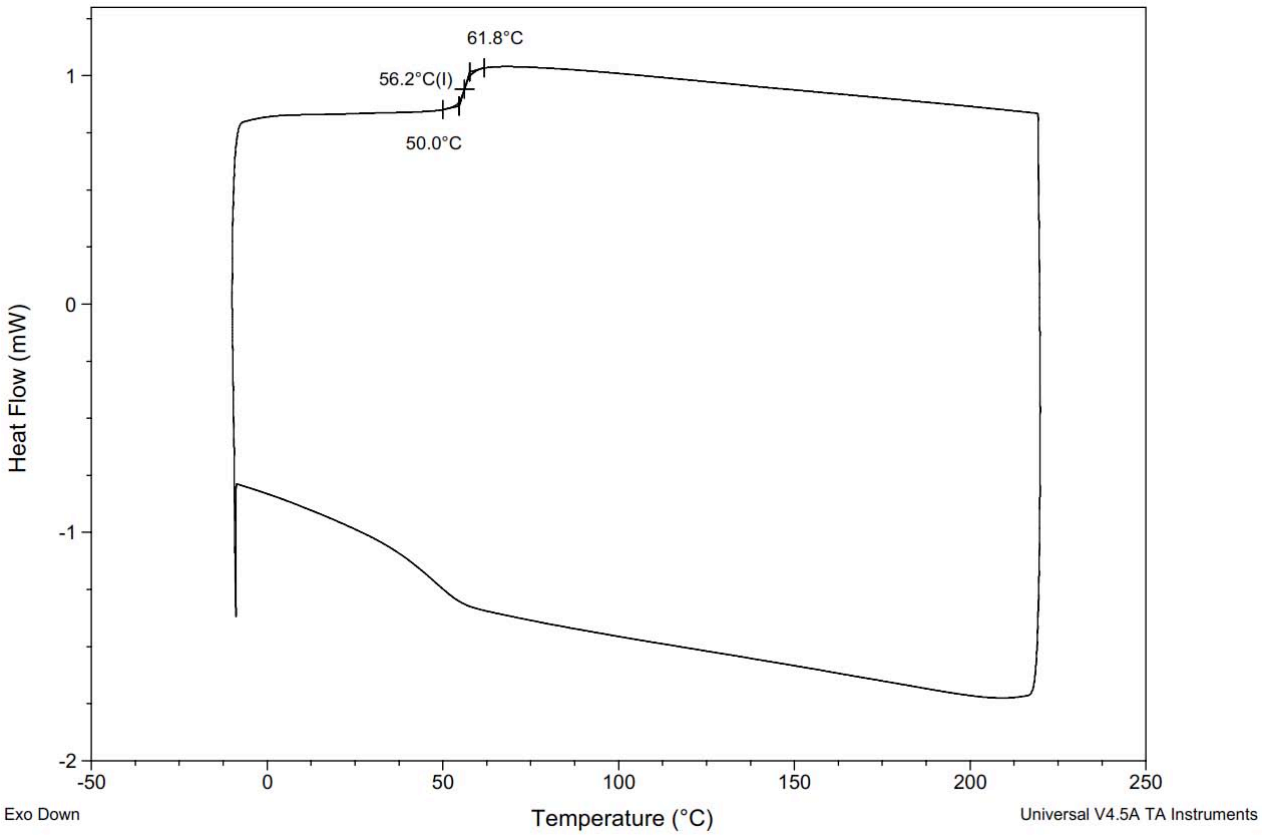


Figure S80. DSC Thermogram of copoly(caprolactone/ hydroxyethylsyringic acid) [20:80] (Table S1, entry 2).

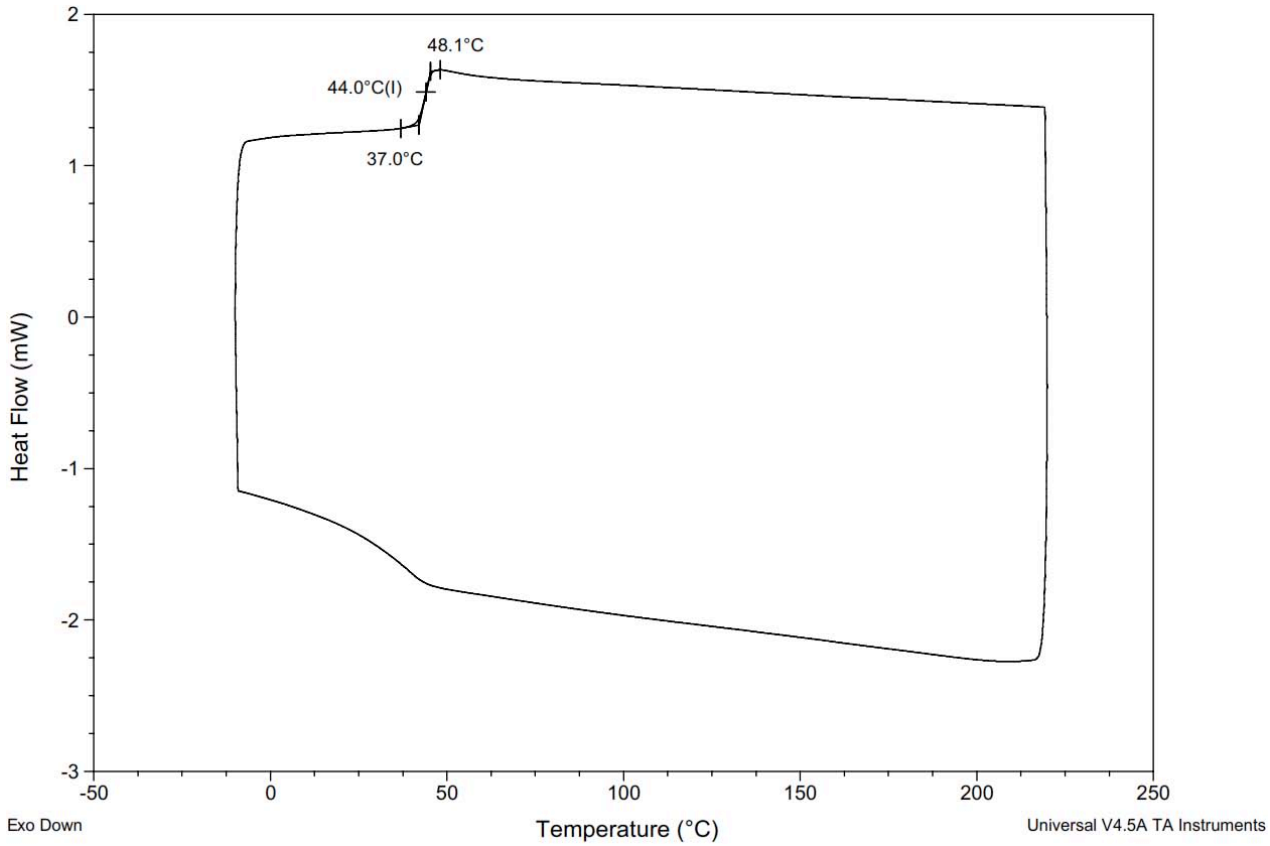


Figure S81. DSC Thermogram of copoly(caprolactone/ hydroxyethylsyringic acid) [20:80] (Table S1, entry 3).

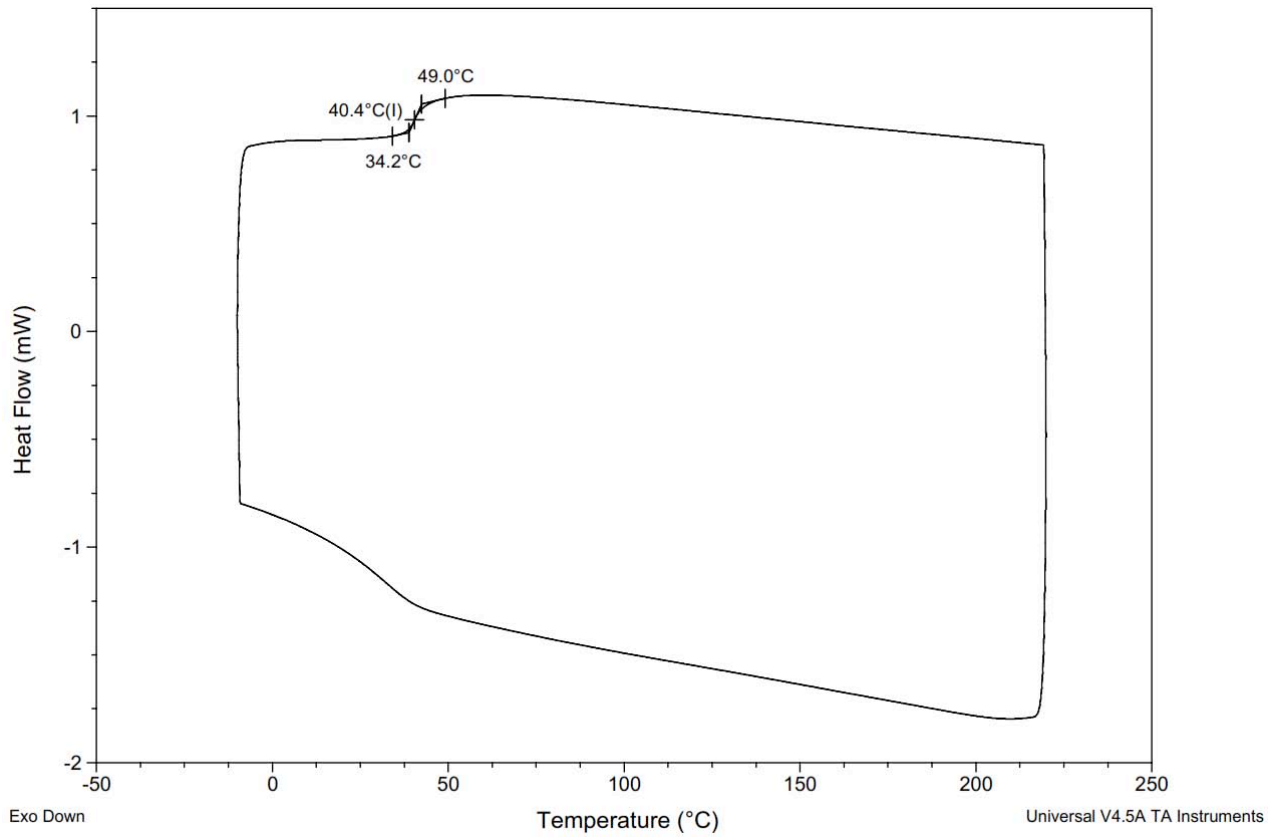


Figure S82. DSC Thermogram of copoly(caprolactone/ hydroxyethylsyringic acid) [20:80] (Table S1, entry 5).

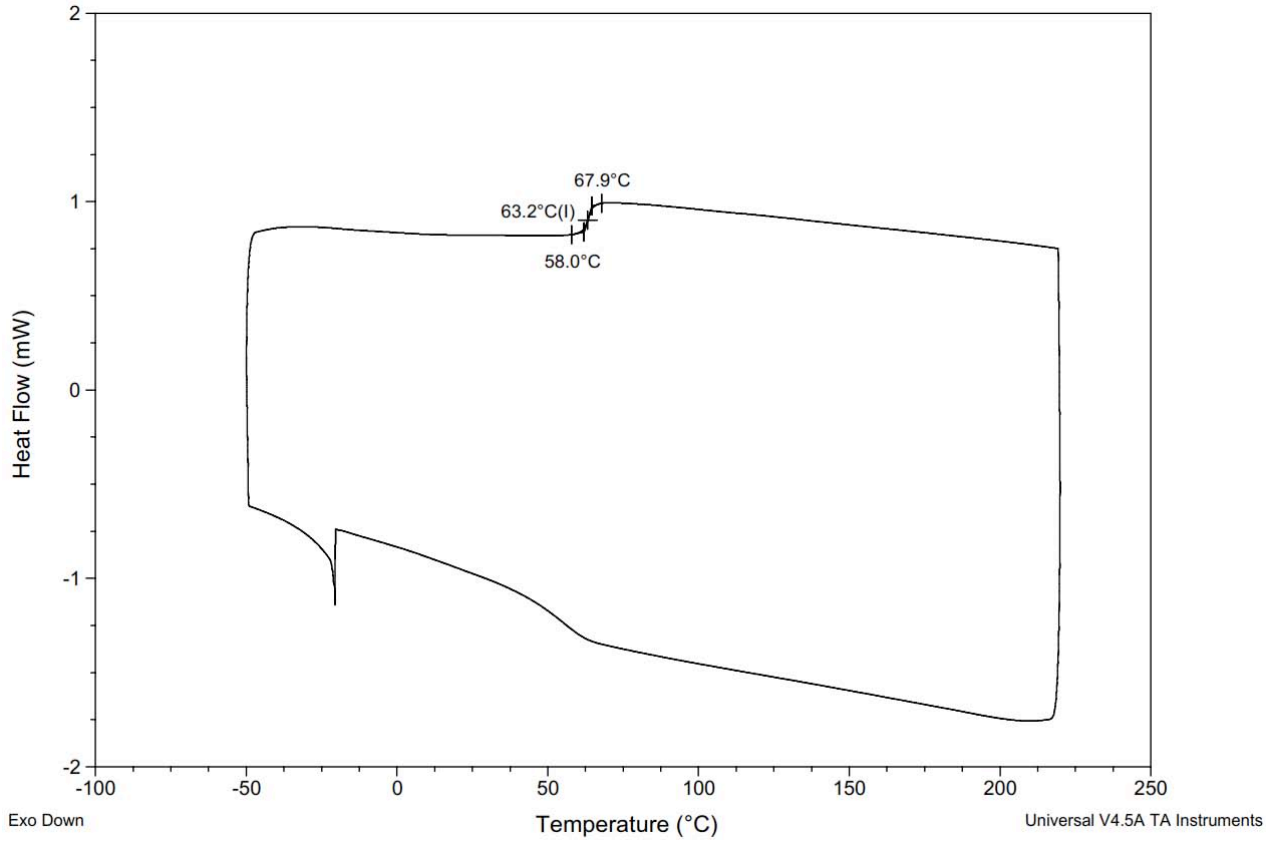


Figure S83. DSC Thermogram of copoly(caprolactone/ hydroxyethylsyringic acid) [20:80] (Table S1, entry 6).

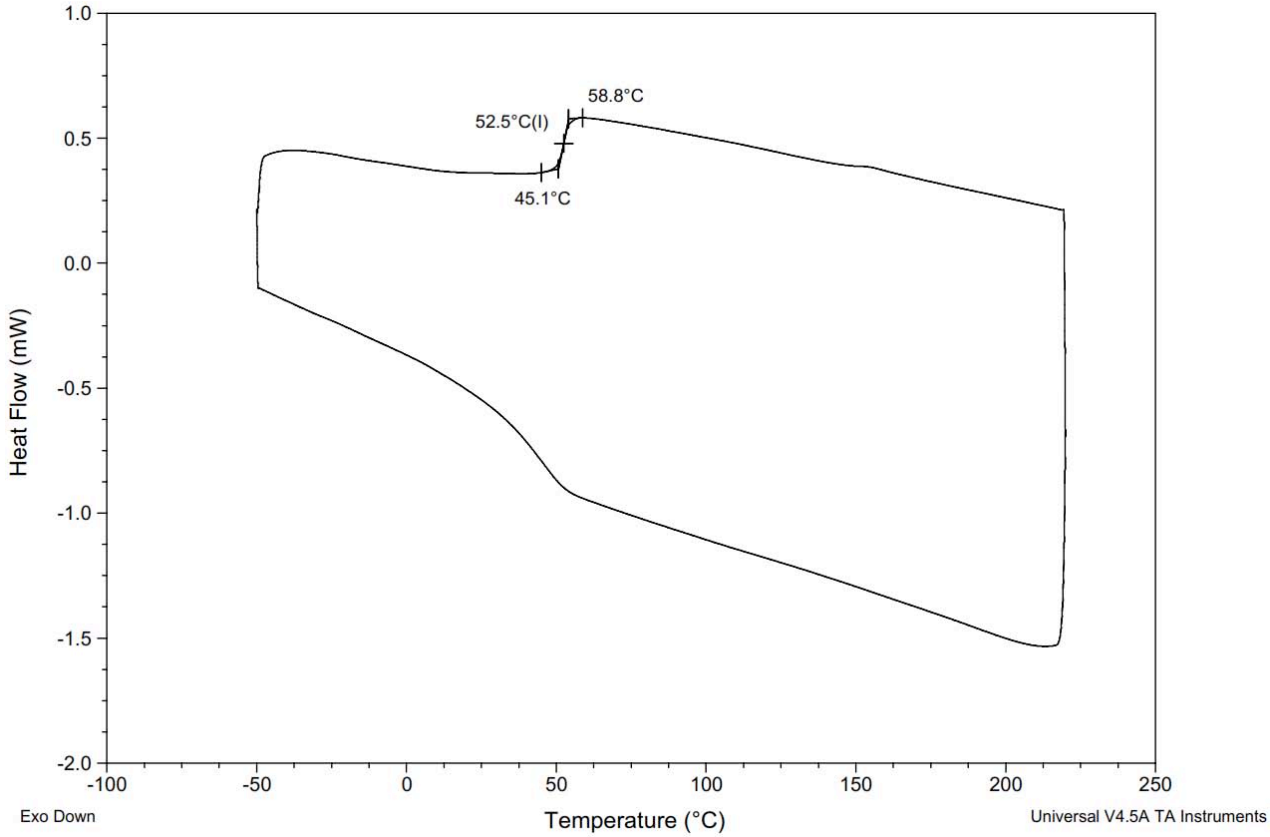


Figure S84. DSC Thermogram of copoly(caprolactone/ hydroxyethylsyringic acid) [20:80] (Table S1, entry 7).

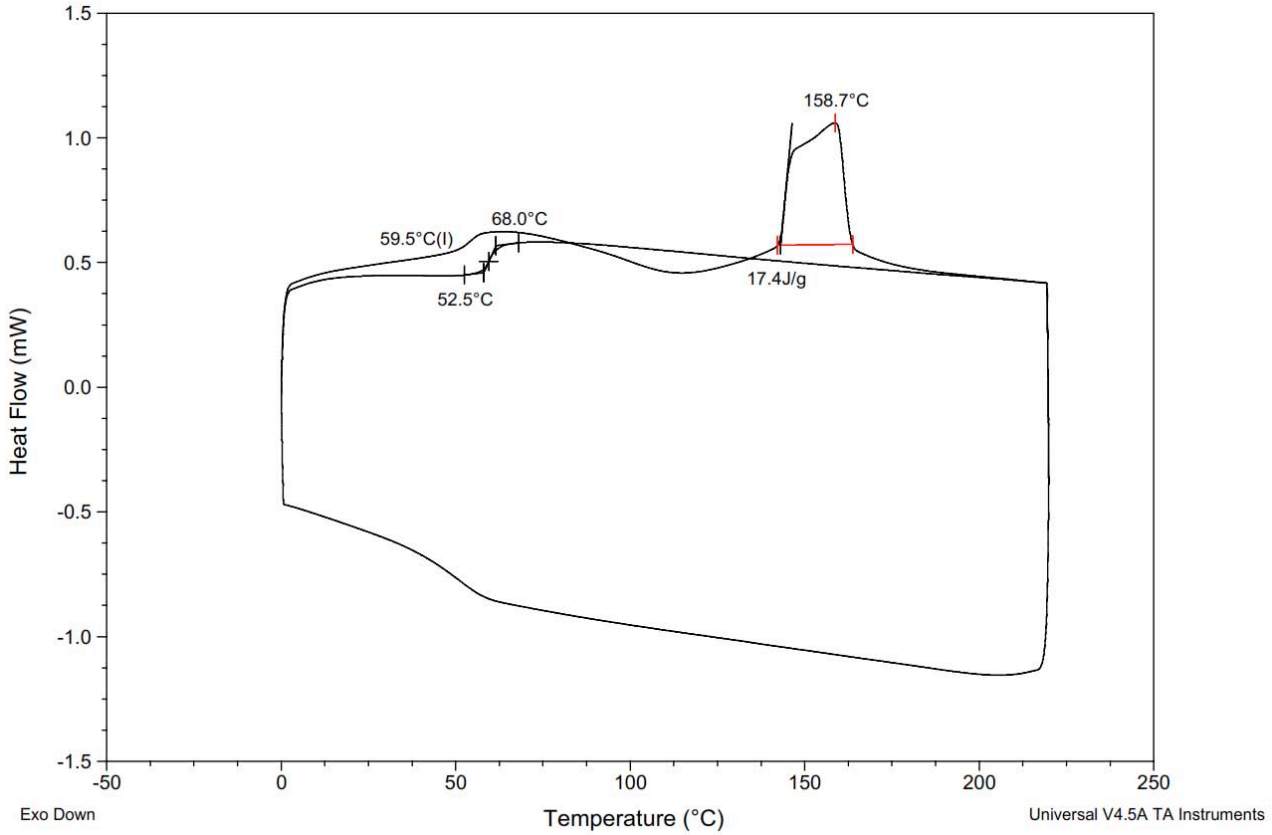


Figure S85. DSC Thermogram of copoly(caprolactone/ hydroxyethylsyringic acid) [20:80] (Table S1, entry 8).

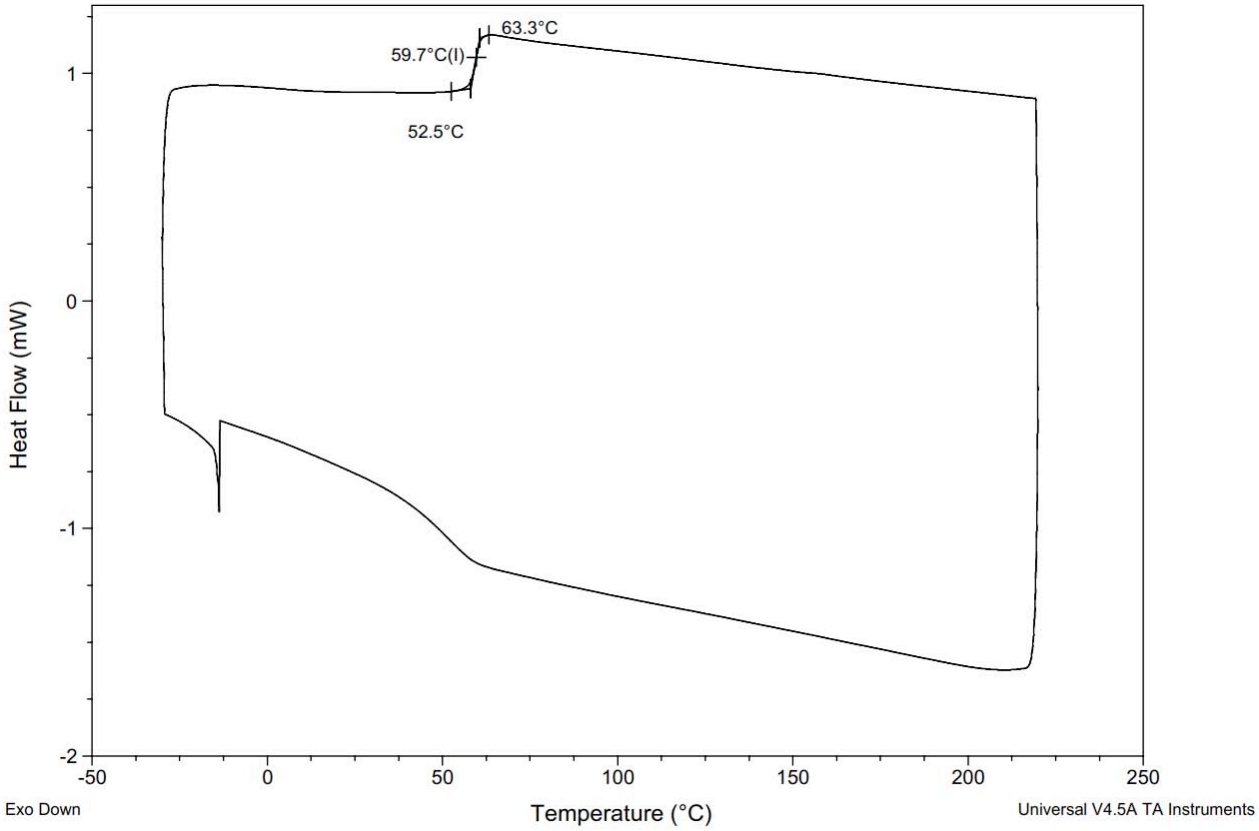


Figure S86. DSC Thermogram of copoly(caprolactone/ hydroxyethylsyringic acid) [20:80] (Table S1, entry 9 and Table S2, entry 9).

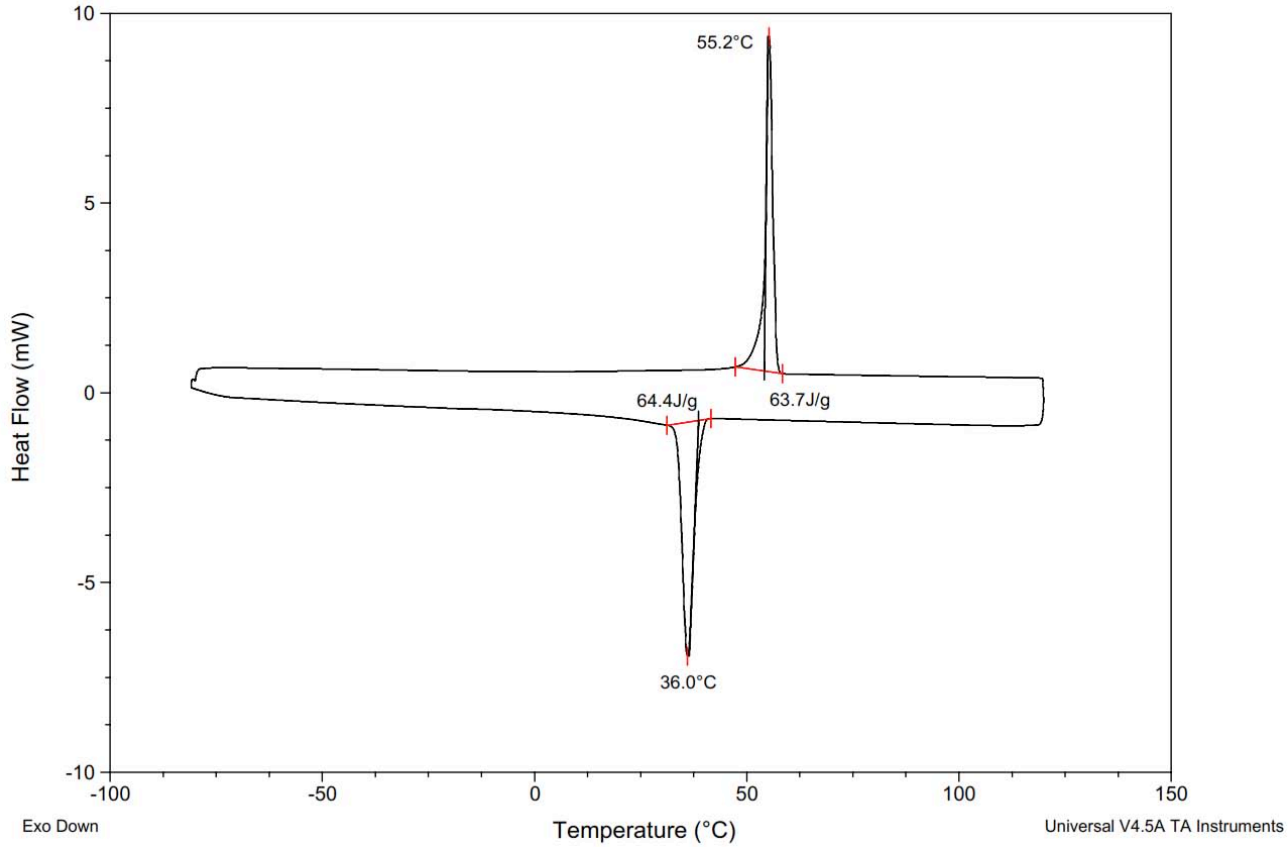


Figure S87. DSC Thermogram of polycaprolactone (Table S2, entry 1).

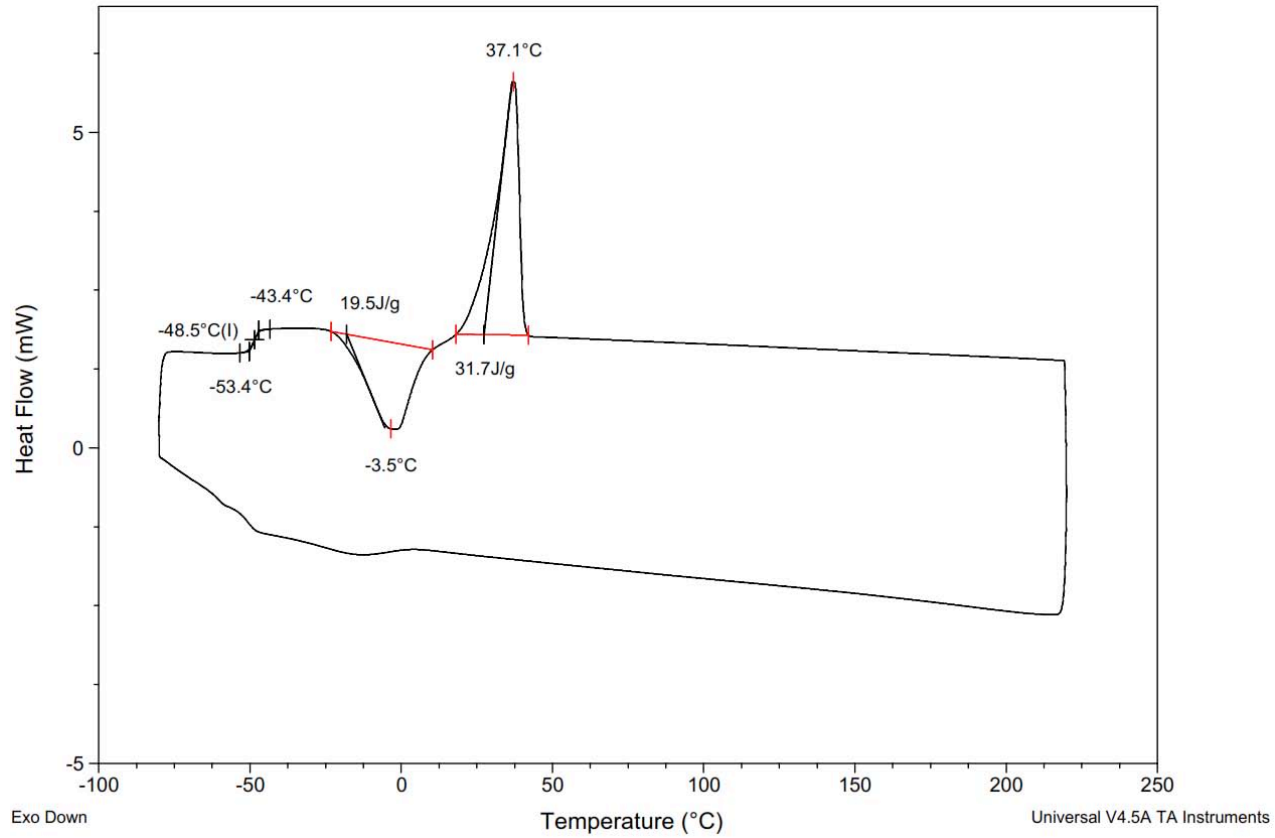


Figure S88. DSC Thermogram of copoly(caprolactone/ hydroxyethylsyringic acid) [90:10] (Table S2, entry 2).

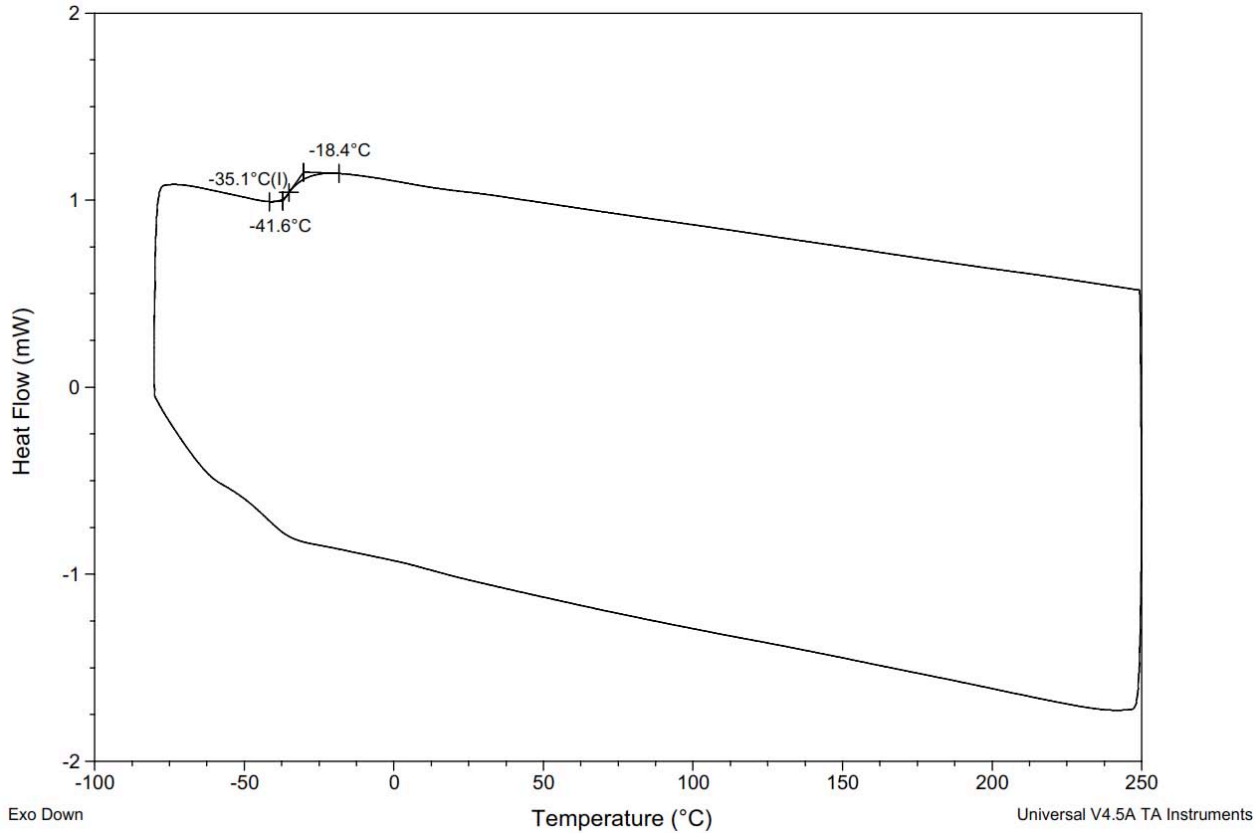


Figure S89. DSC Thermogram of copoly(caprolactone/ hydroxyethylsyringic acid) [80:20] (Table S2, entry 3).

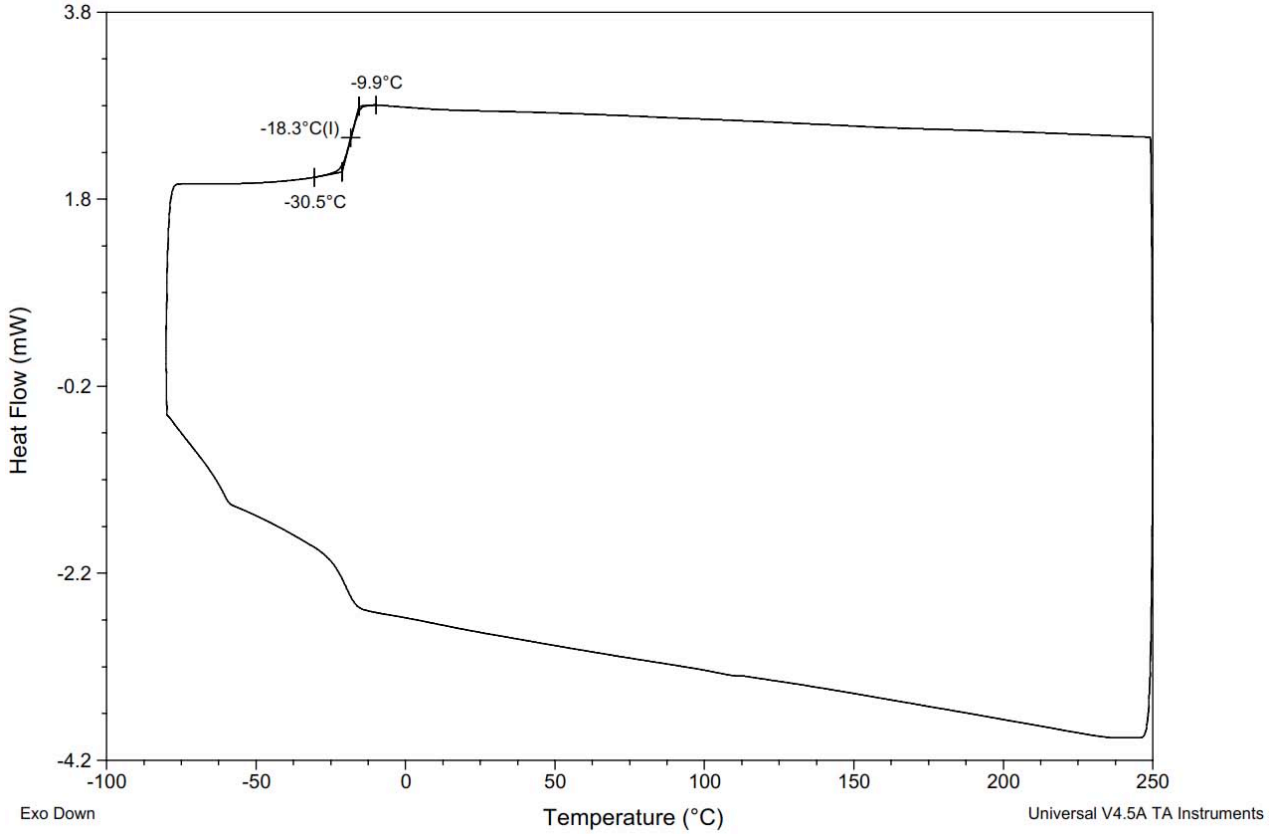


Figure S90. DSC Thermogram of copoly(caprolactone/ hydroxyethylsyringic acid) [70:30] (Table S2, entry 4).

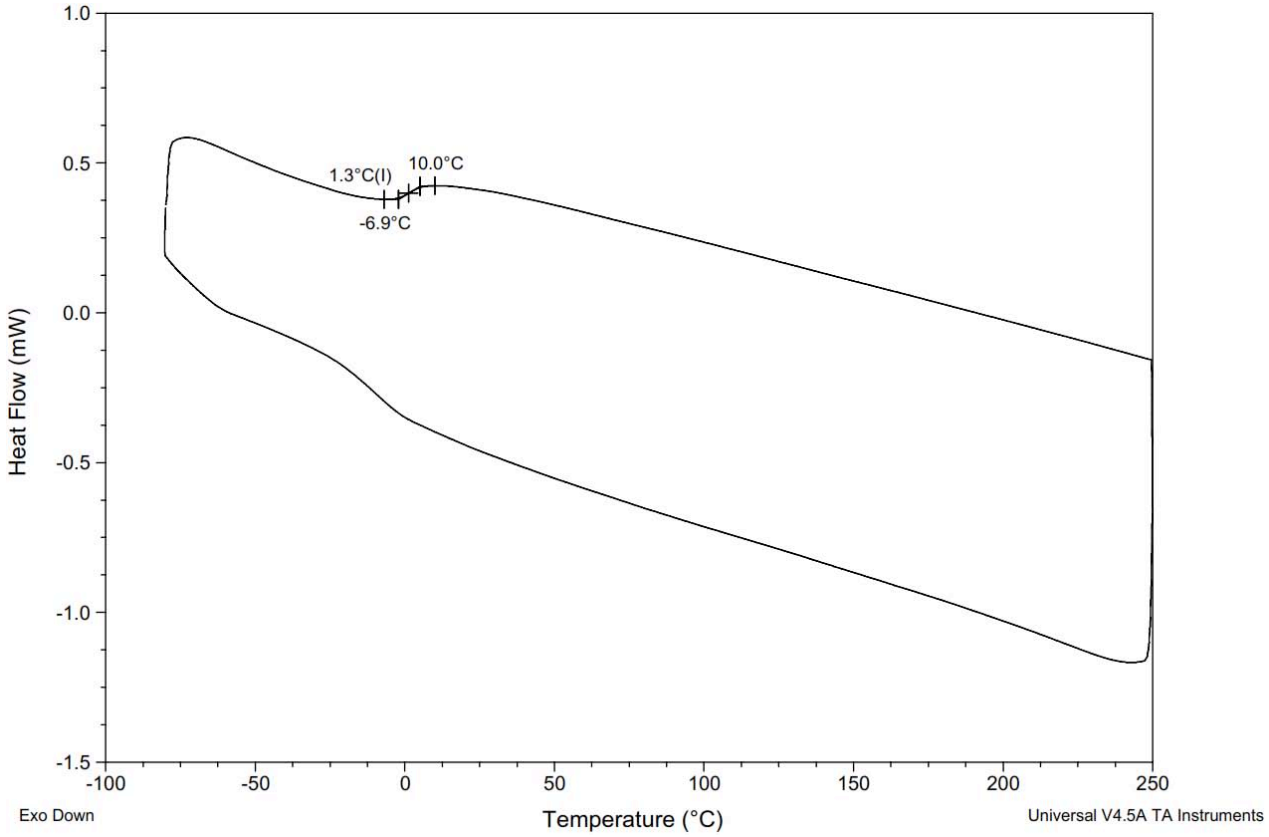


Figure S91. DSC Thermogram of copoly(caprolactone/ hydroxyethylsyringic acid) [60:40] (Table S2, entry 5).

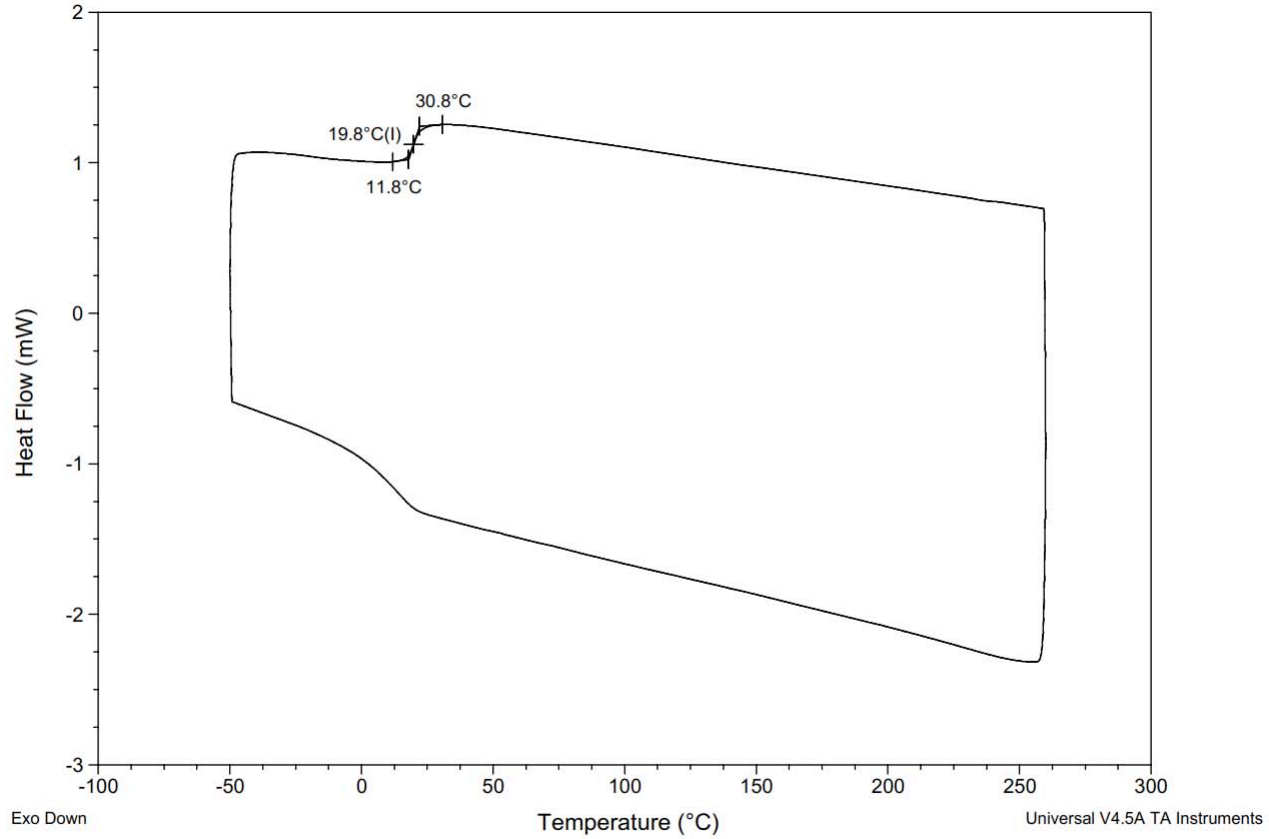


Figure S92. DSC Thermogram of copoly(caprolactone/ hydroxyethylsyringic acid) [50:50] (Table S2, entry 6).

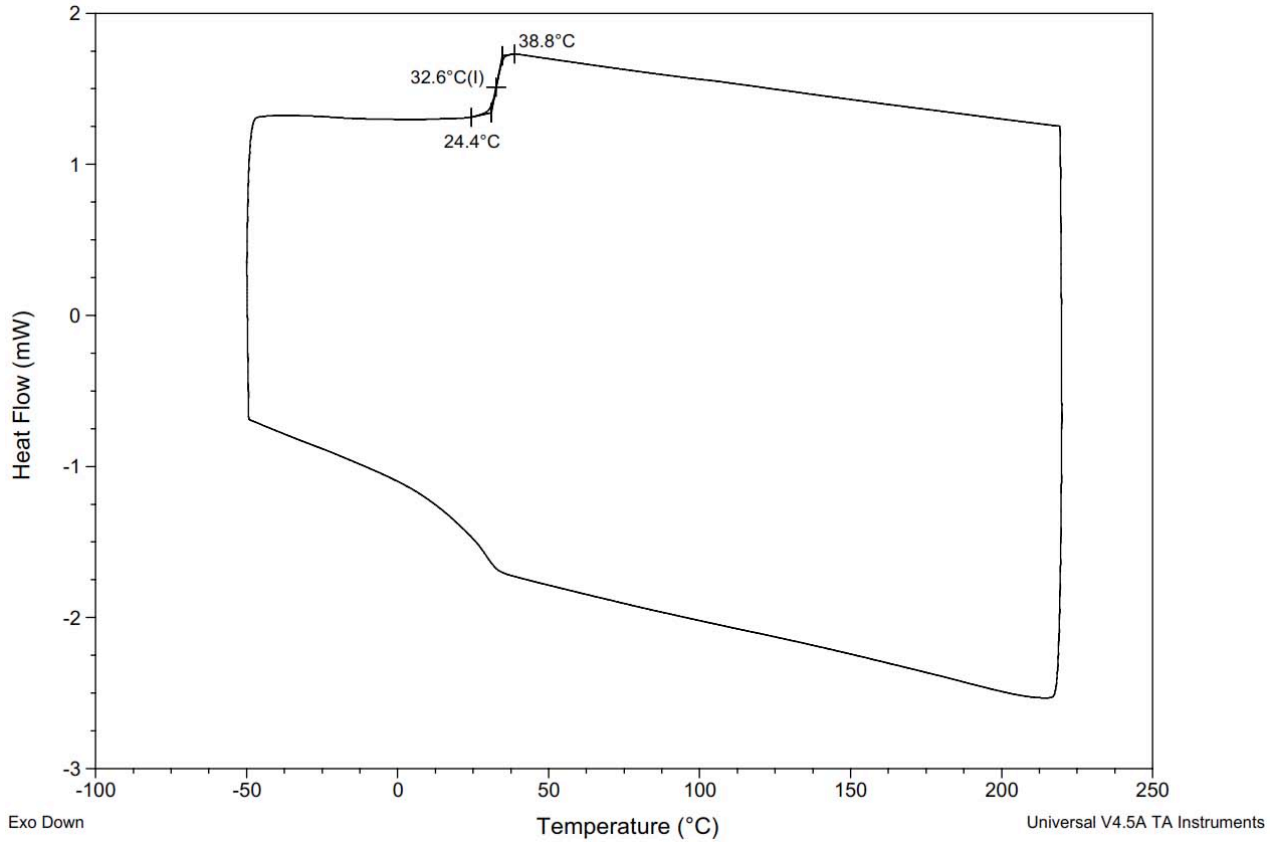


Figure S93. DSC Thermogram of copoly(caprolactone/ hydroxyethylsyringic acid) [40:60] (Table S2, entry 7).

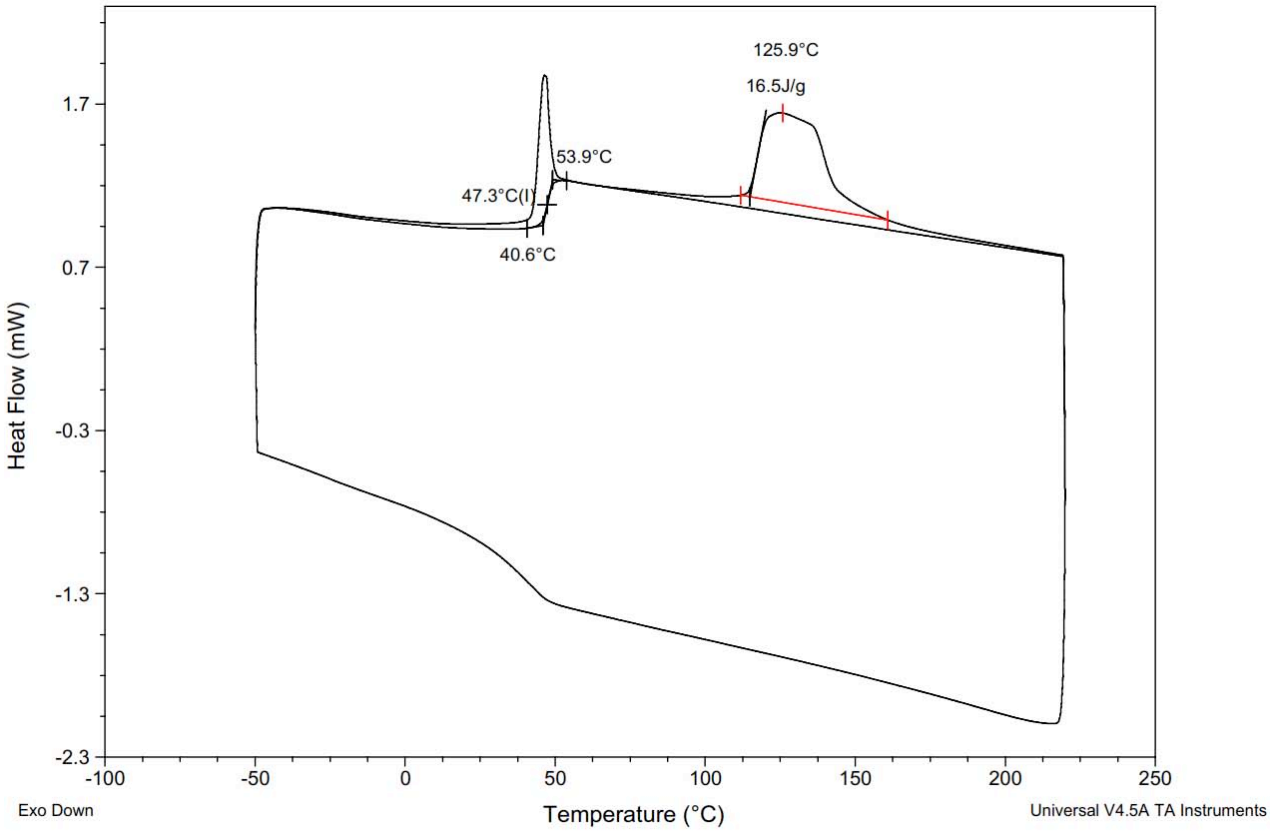


Figure S94. DSC Thermogram of copoly(caprolactone/ hydroxyethylsyringic acid) [30:70] (Table S2, entry 8).

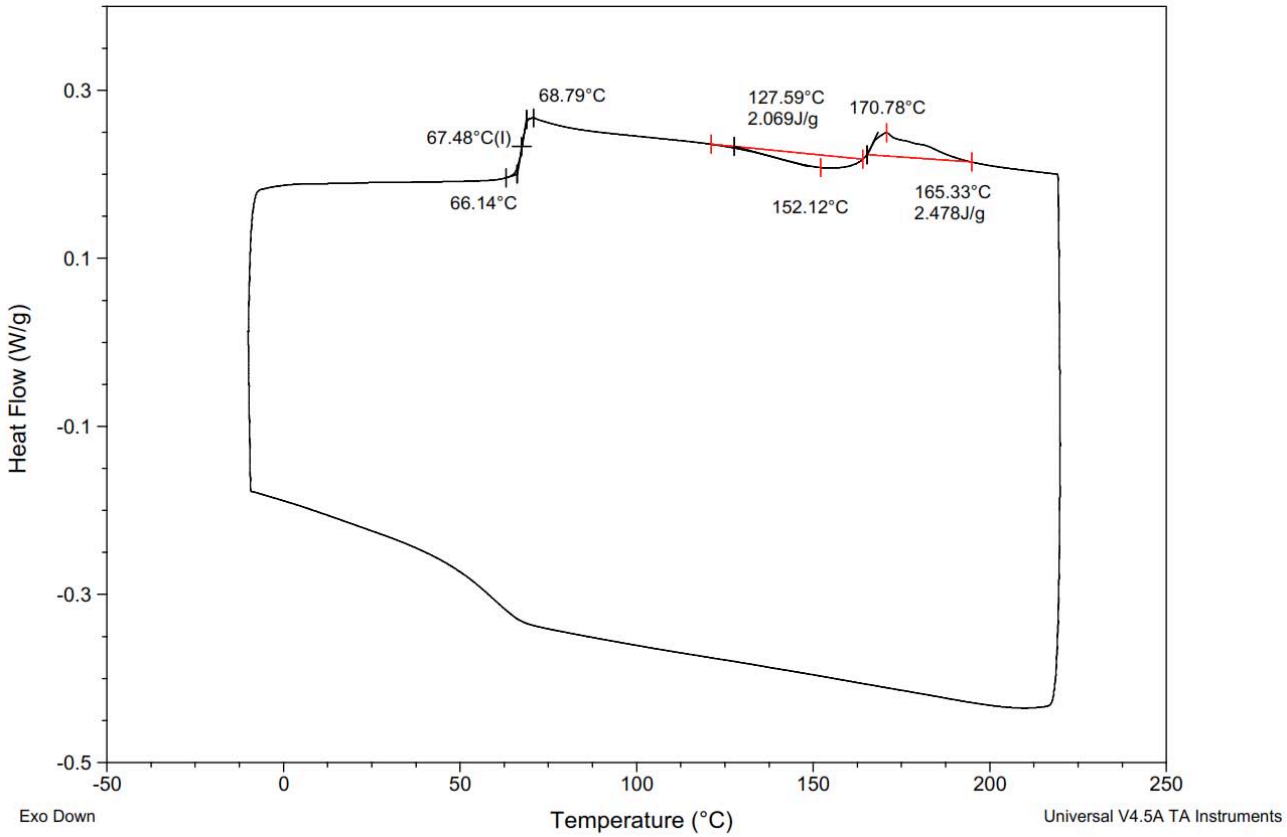


Figure S95. DSC Thermogram of copoly(caprolactone/ hydroxyethylsyringic acid) [10:90] (Table S2, entry 10).

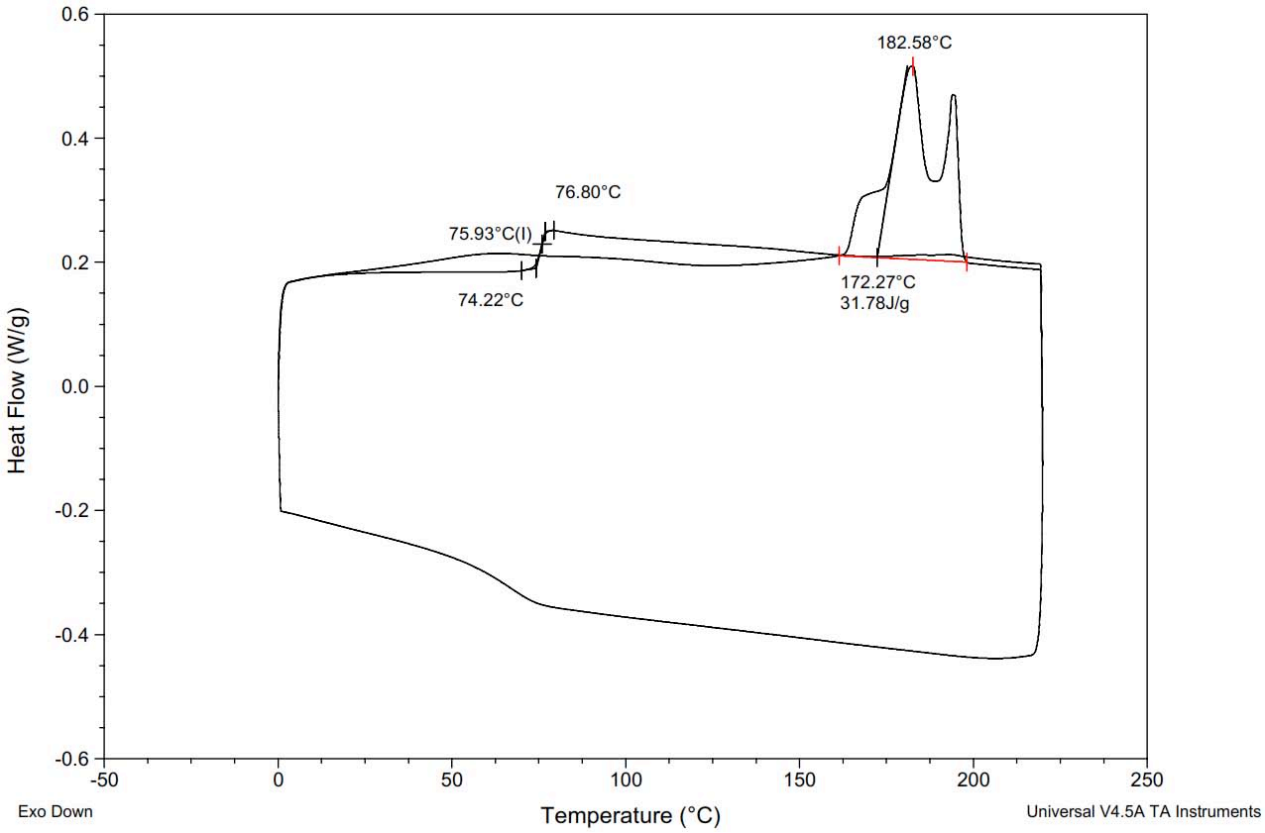


Figure S96. DSC Thermogram of polyethylene syringate (Table S2, entry 11).

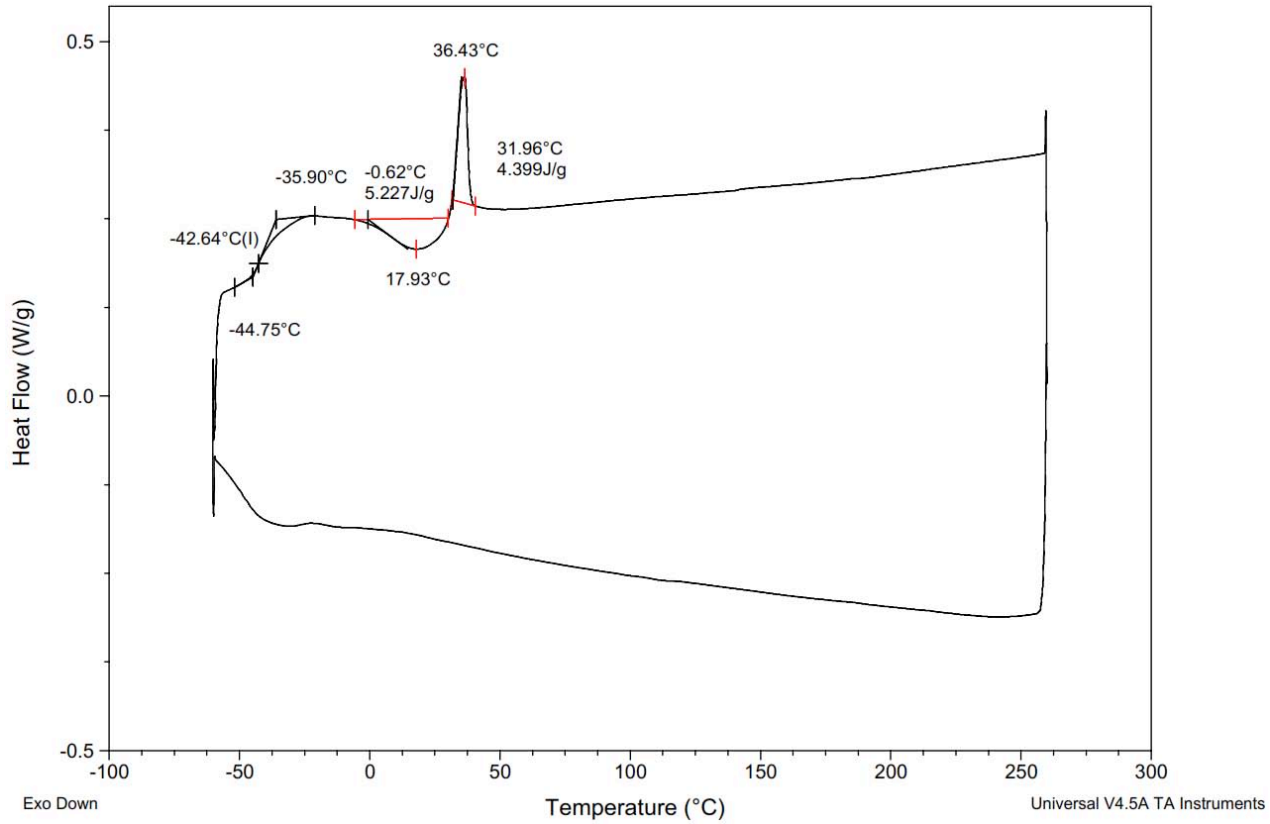


Figure S97. DSC Thermogram of copoly(caprolactone/ hydroxyethylvanillic acid) [90:10] (Table S2, entry 12).

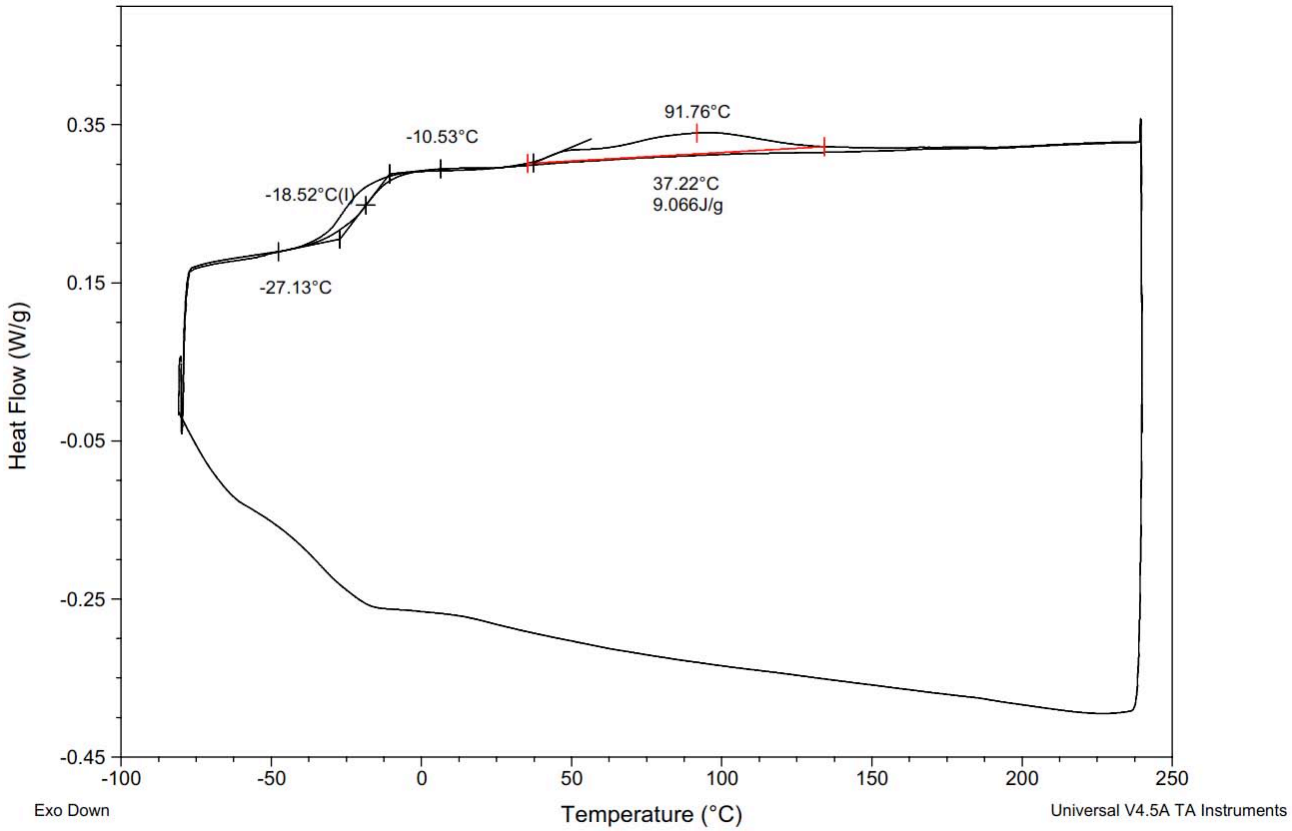


Figure S98. DSC Thermogram of copoly(caprolactone/ hydroxyethylvanillic acid) [80:20] (Table S2, entry 13).

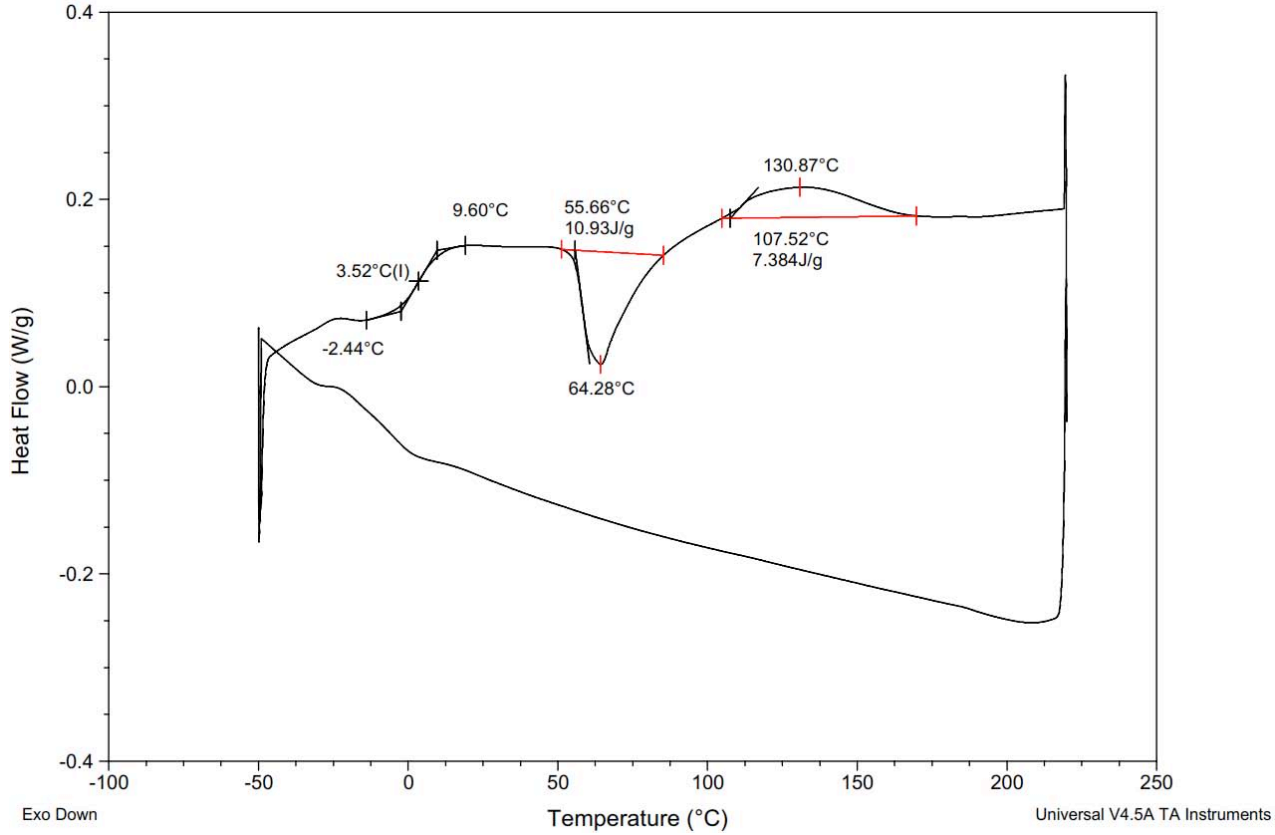


Figure S99. DSC Thermogram of copoly(caprolactone/ hydroxyethylvanillic acid) [70:30] (Table S2, entry 14).

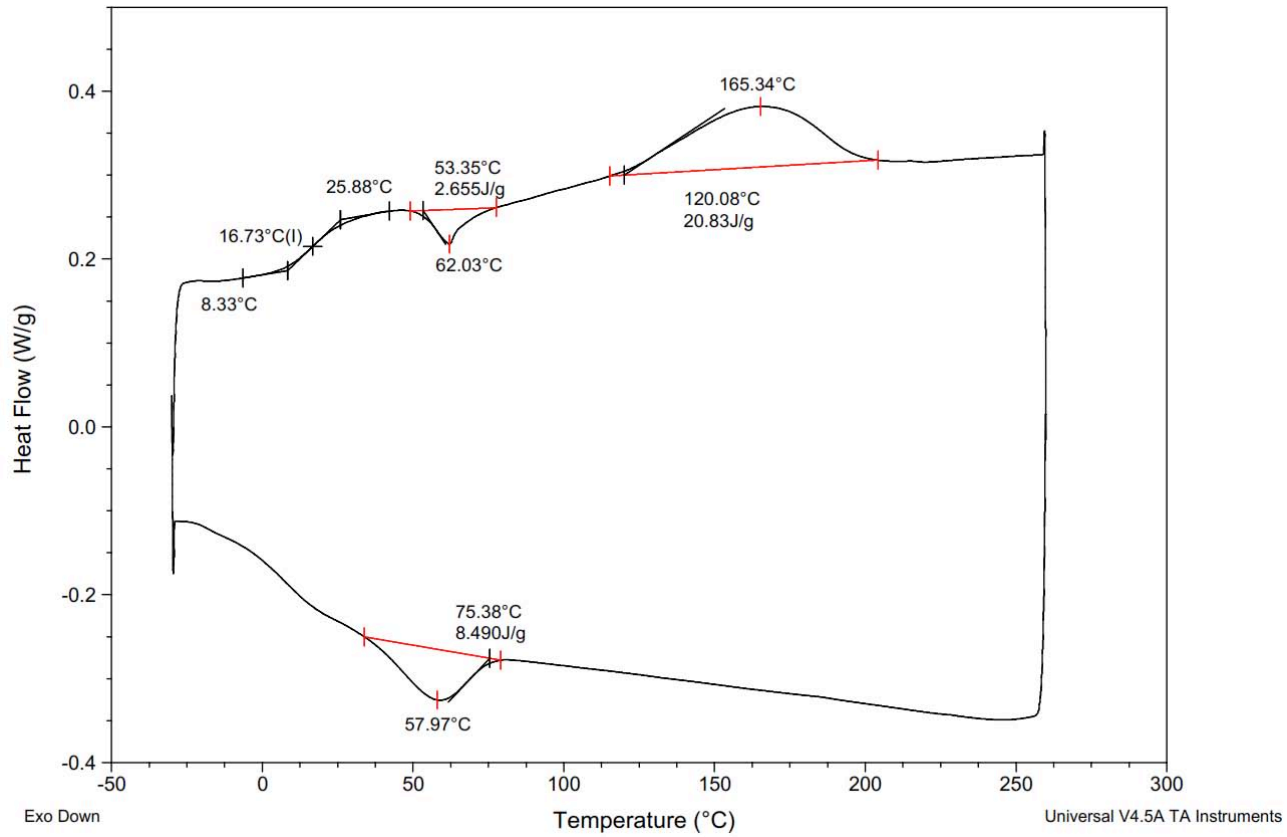


Figure S100. DSC Thermogram of copoly(caprolactone/ hydroxyethylvanillic acid) [60:40] (Table S2, entry 15).

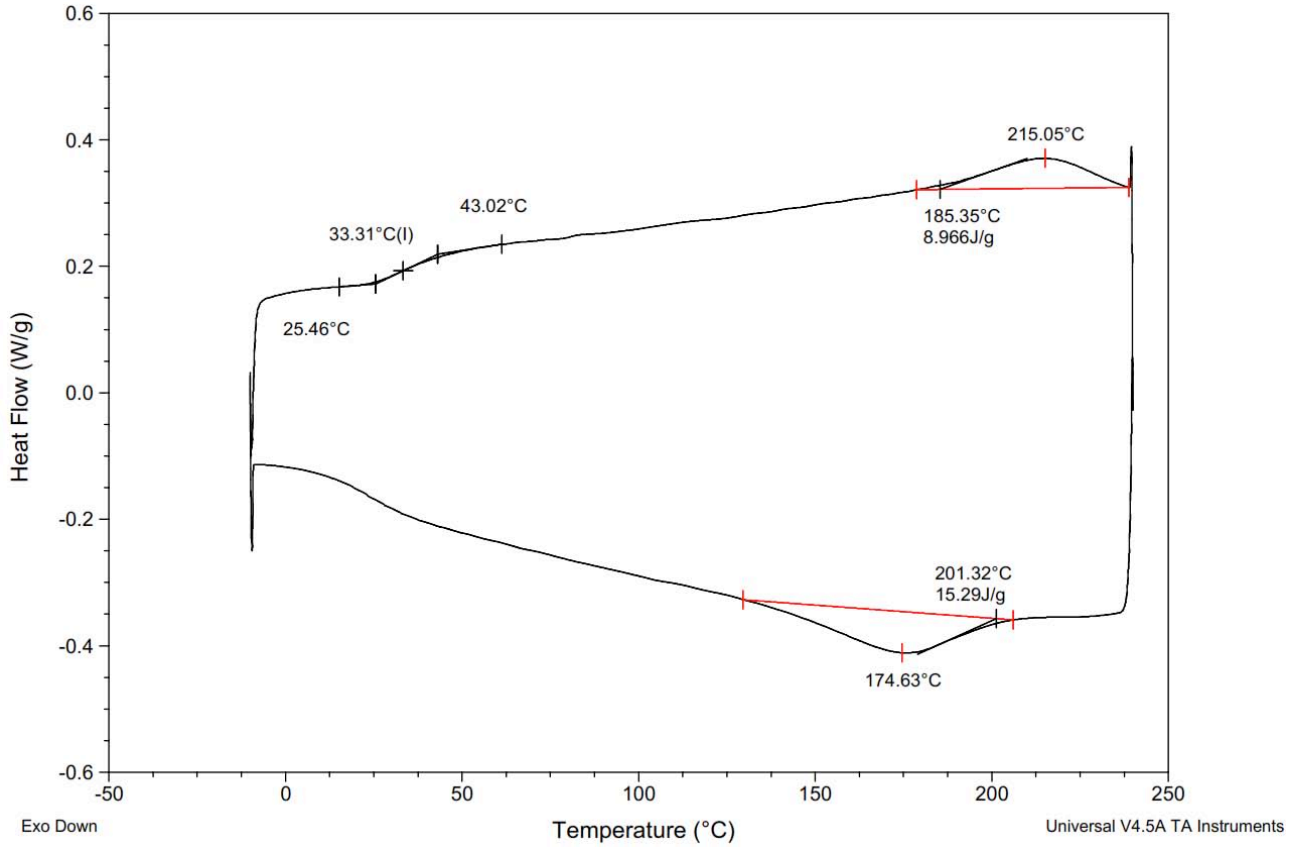


Figure S101. DSC Thermogram of copoly(caprolactone/ hydroxyethylvanillic acid) [50:50] (Table S2, entry 16).

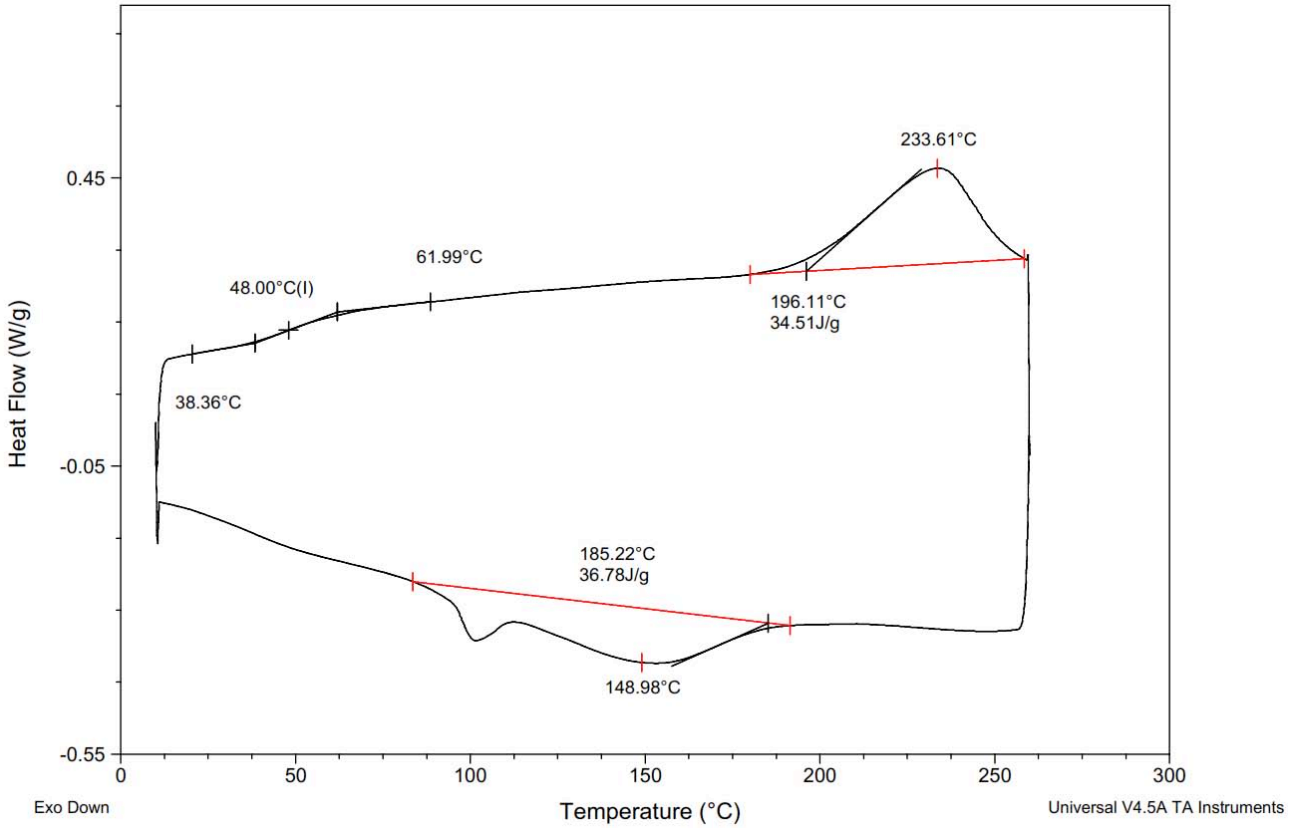


Figure S102. DSC Thermogram of copoly(caprolactone/ hydroxyethylvanillic acid) [40:60] (Table S2, entry 17).

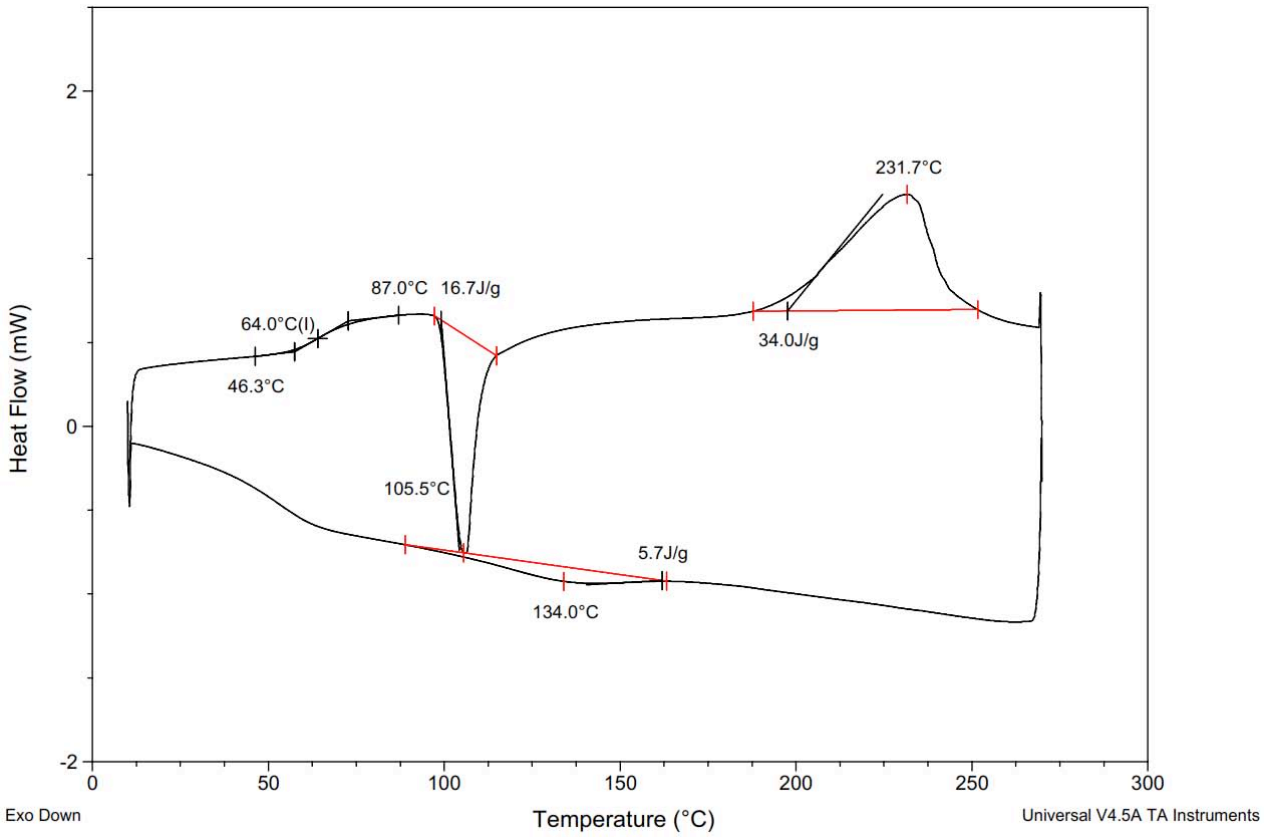


Figure S103. DSC Thermogram of copoly(caprolactone/ hydroxyethylvanillic acid) [30:70] (Table S2, entry 18).

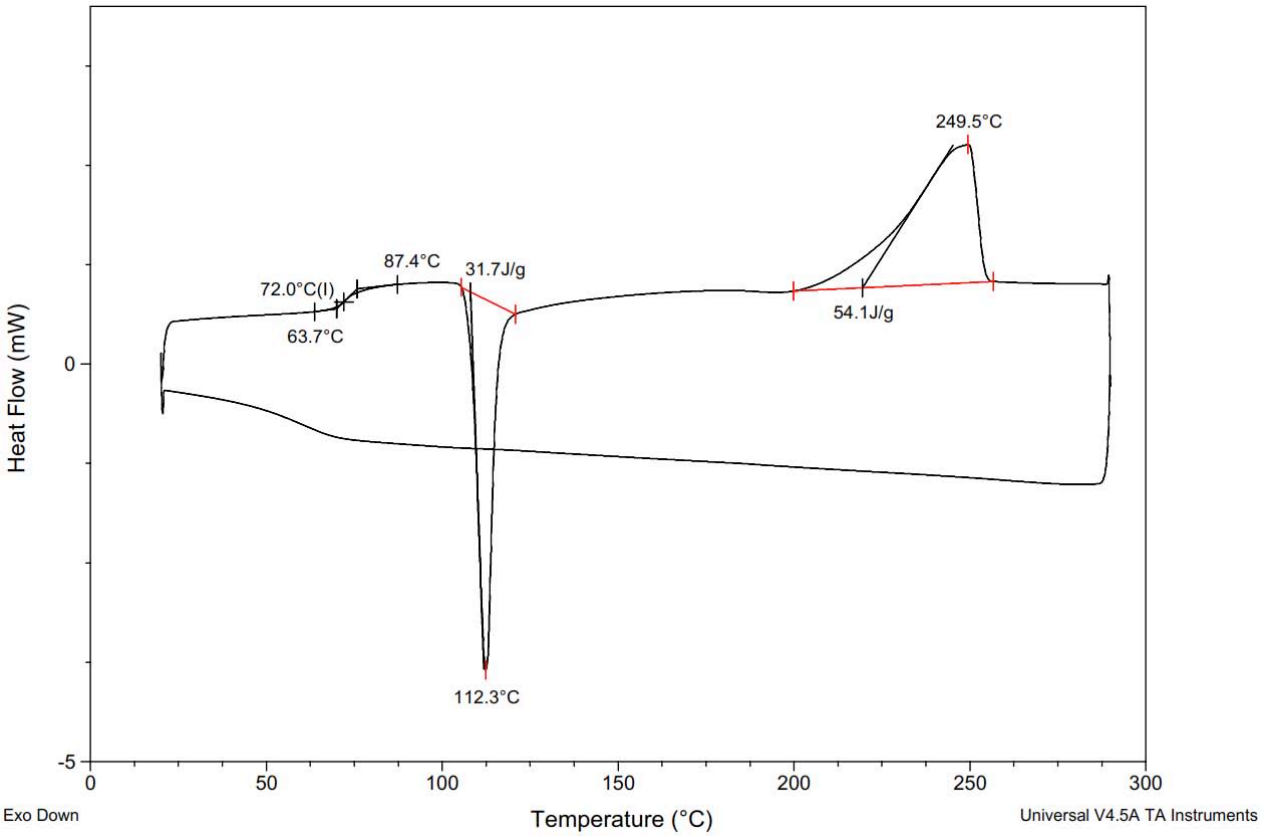


Figure S104. DSC Thermogram of copoly(caprolactone/ hydroxyethylvanillic acid) [20:80] (Table S2, entry 19).

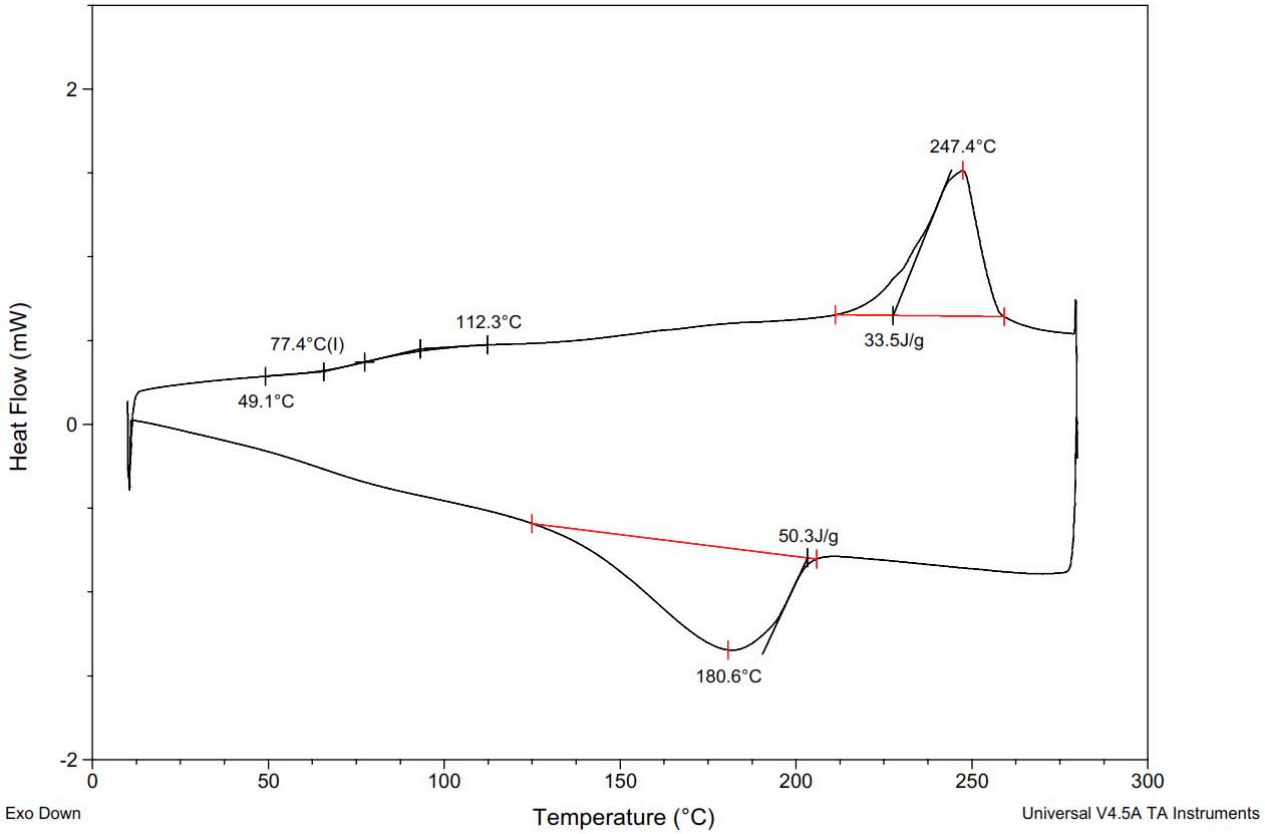


Figure S105. DSC Thermogram of copoly(caprolactone/ hydroxyethylvanillic acid) [10:90] (Table S2, entry 20).

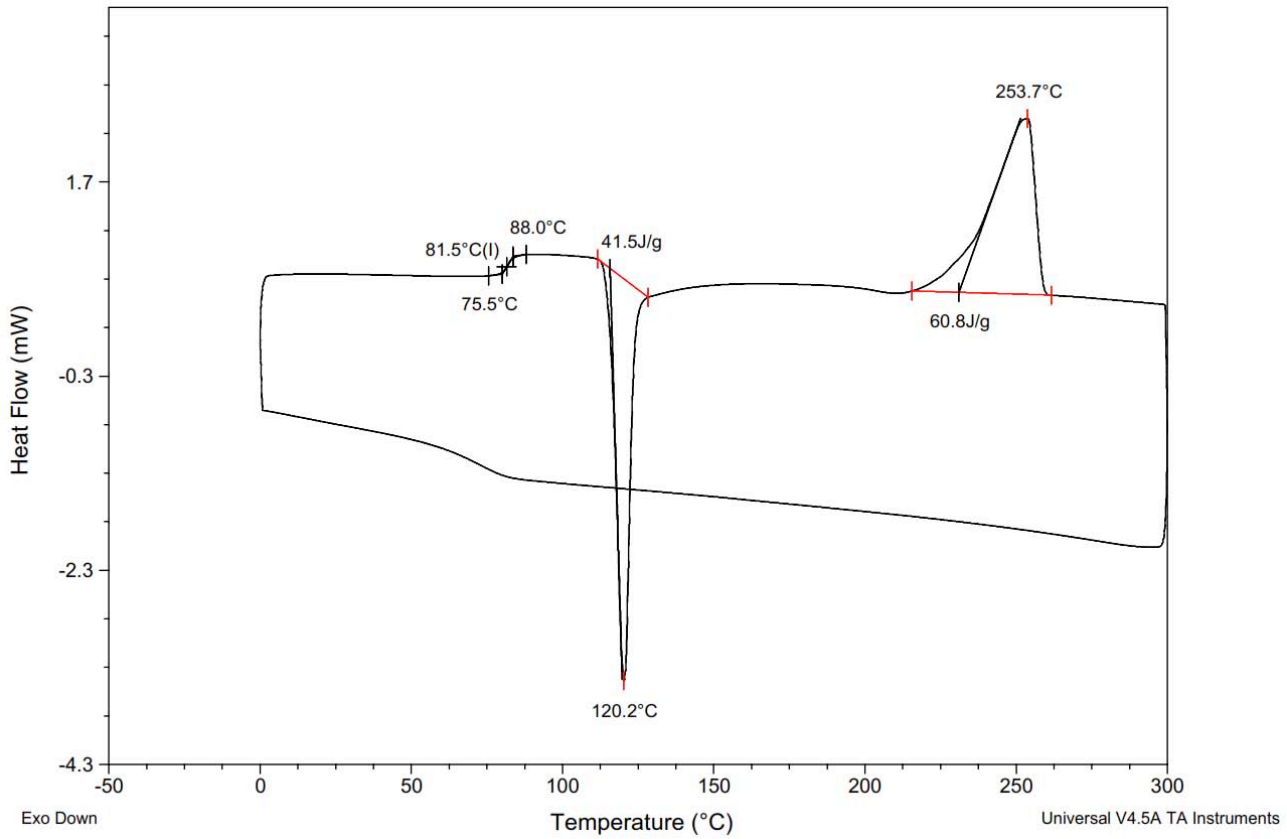


Figure S106. DSC Thermogram of polyethylene vanillate (Table S2, entry 21).

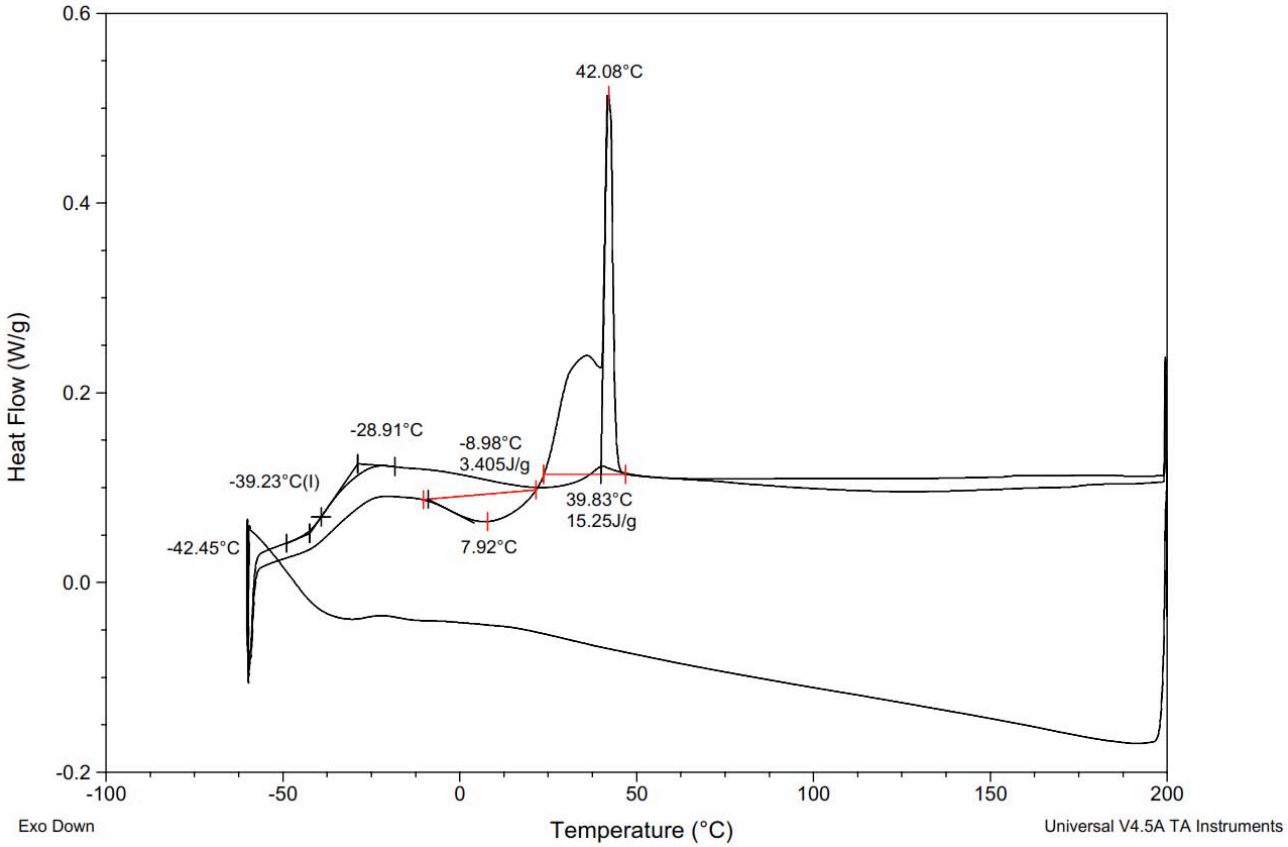


Figure S107. DSC Thermogram of copoly(caprolactone/ hydroxyethylferulic acid) [90:10] (Table S2, entry 22).

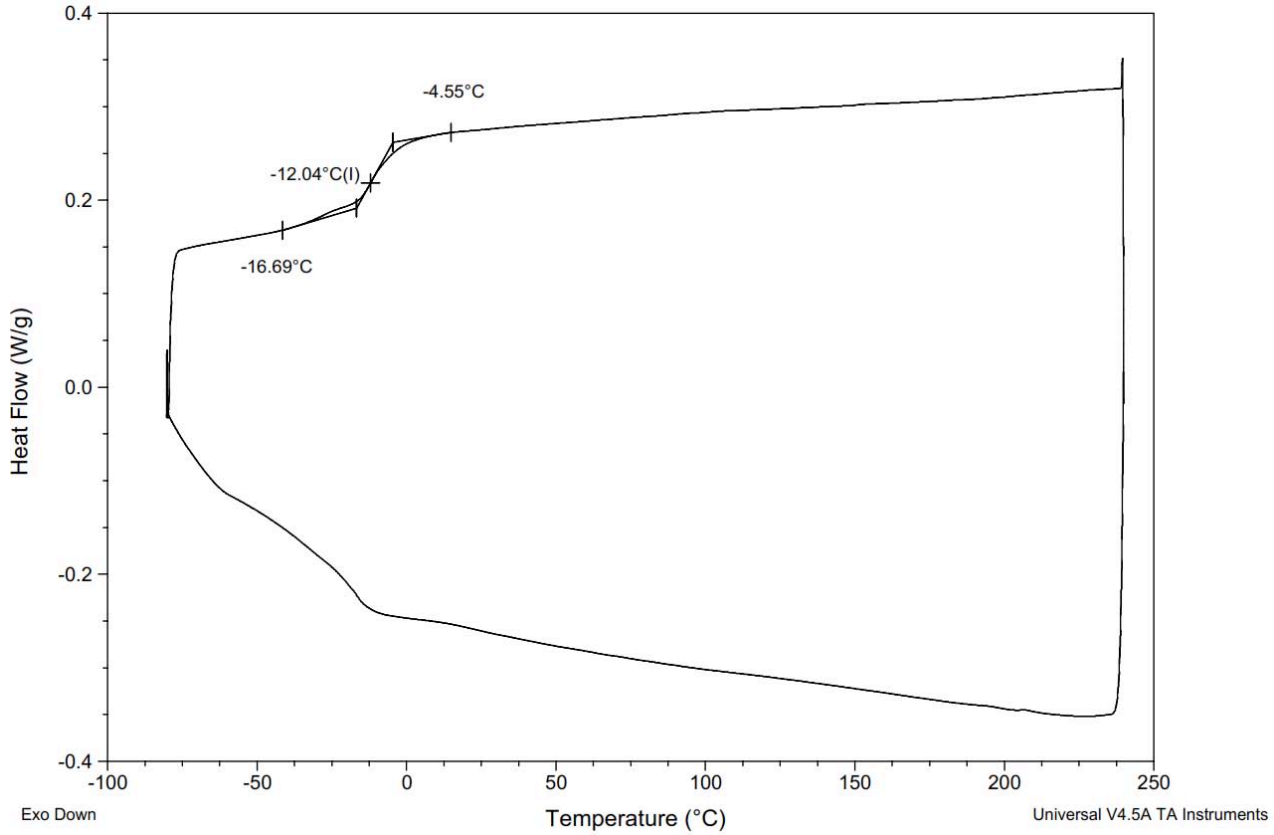


Figure S108. DSC Thermogram of copoly(caprolactone/ hydroxyethylferulic acid) [80:20] (Table S2, entry 23).

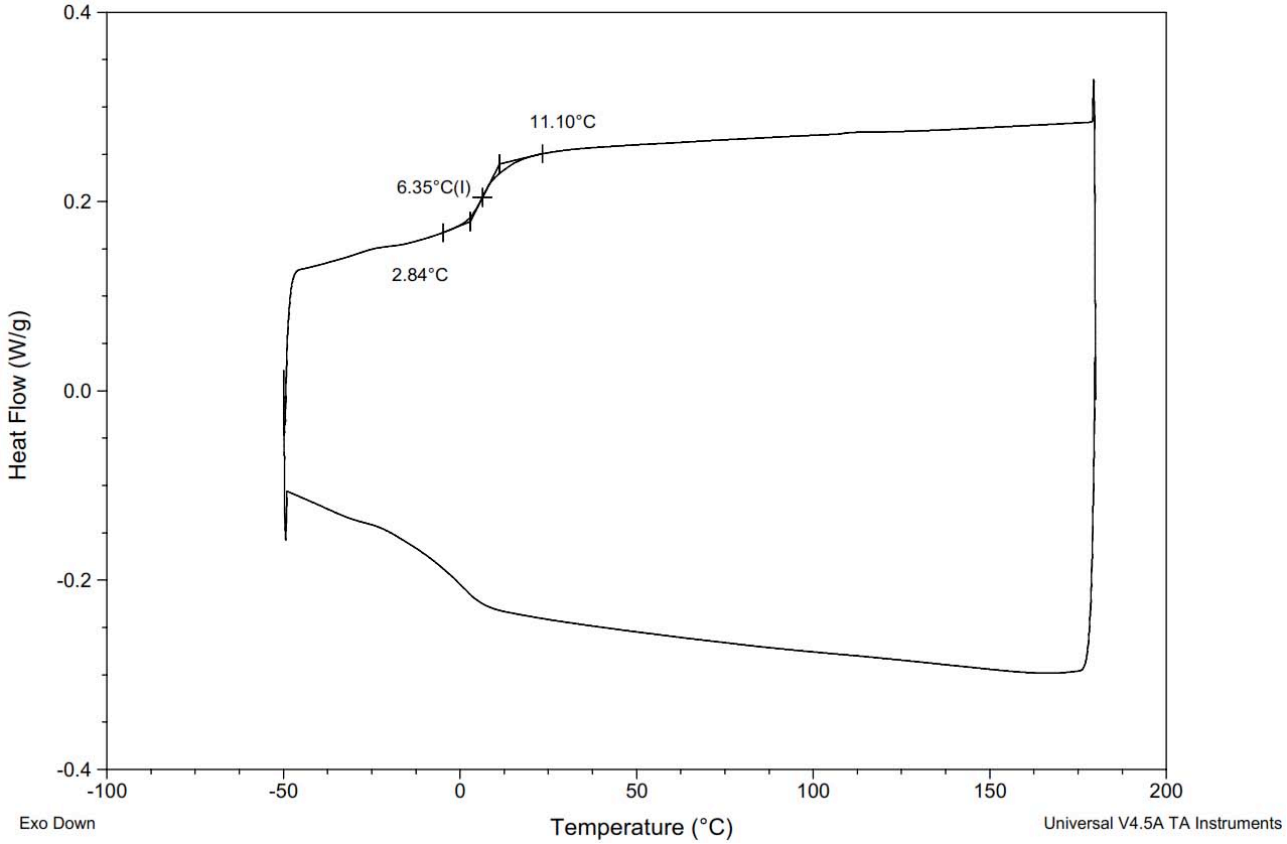


Figure S109. DSC Thermogram of copoly(caprolactone/ hydroxyethylferulic acid) [70:30] (Table S2, entry 24).

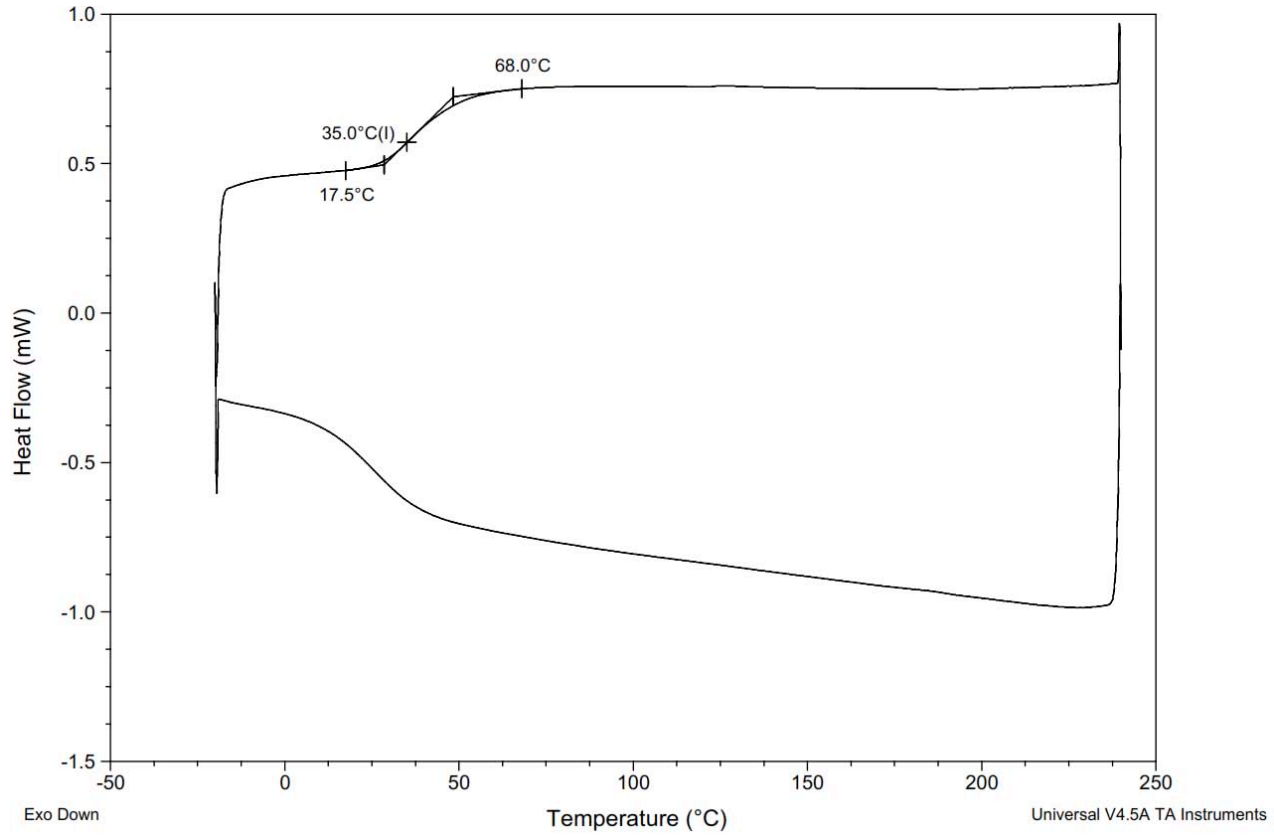


Figure S110. DSC Thermogram of copoly(caprolactone/ hydroxyethylferulic acid) [60:40] (Table S2, entry 25).

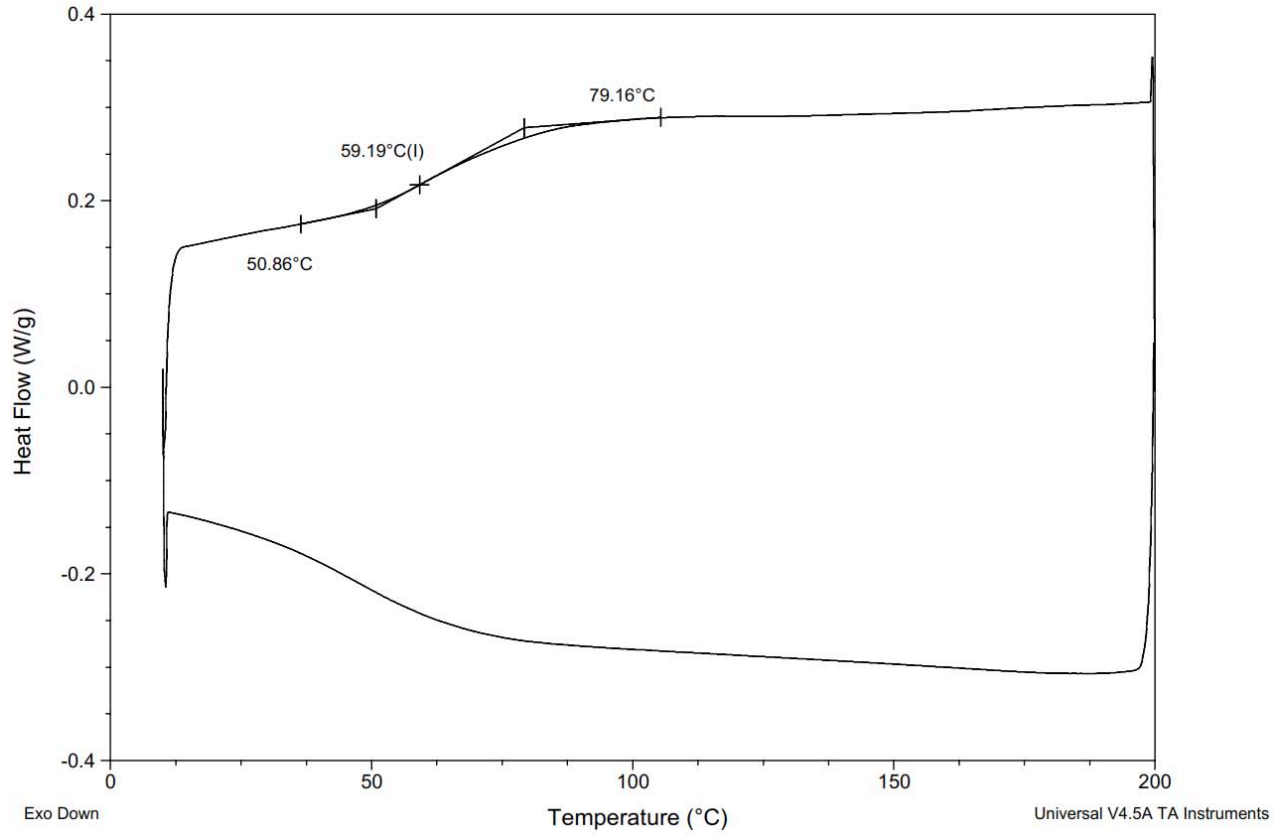


Figure S111. DSC Thermogram of copoly(caprolactone/ hydroxyethylferulic acid) [50:50] (Table S2, entry 26).

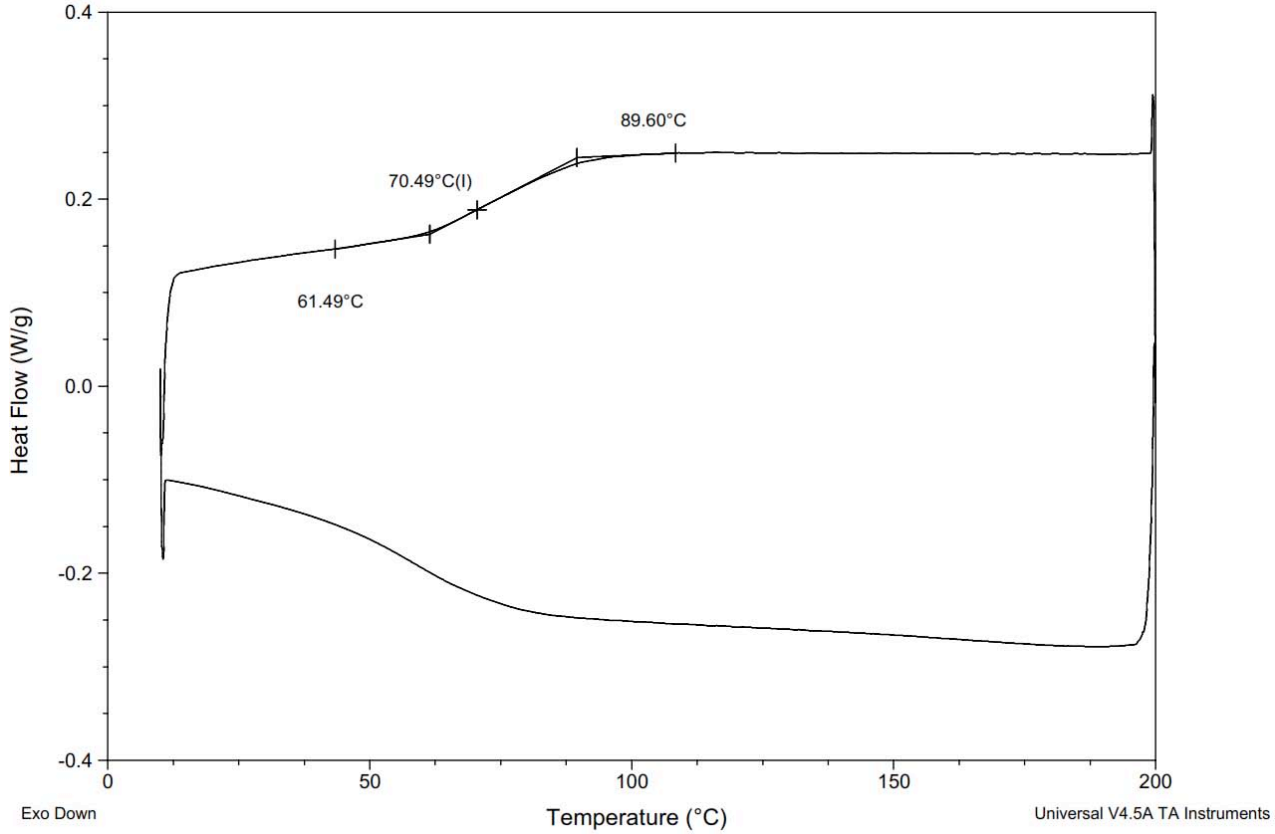


Figure S112. DSC Thermogram of copoly(caprolactone/ hydroxyethylferulic acid) [40:60] (Table S2, entry 27).

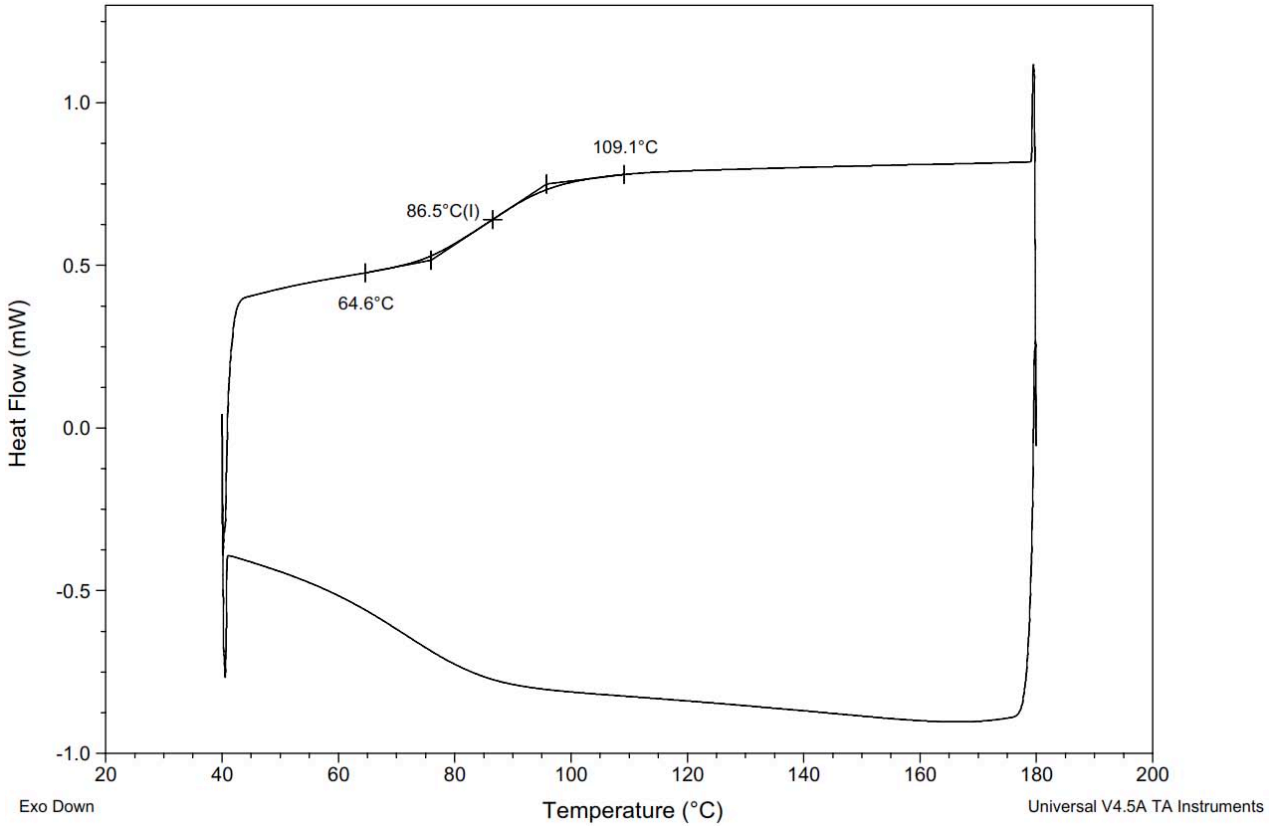


Figure S113. DSC Thermogram of copoly(caprolactone/ hydroxyethylferulic acid) [30:70] (Table S2, entry 28).

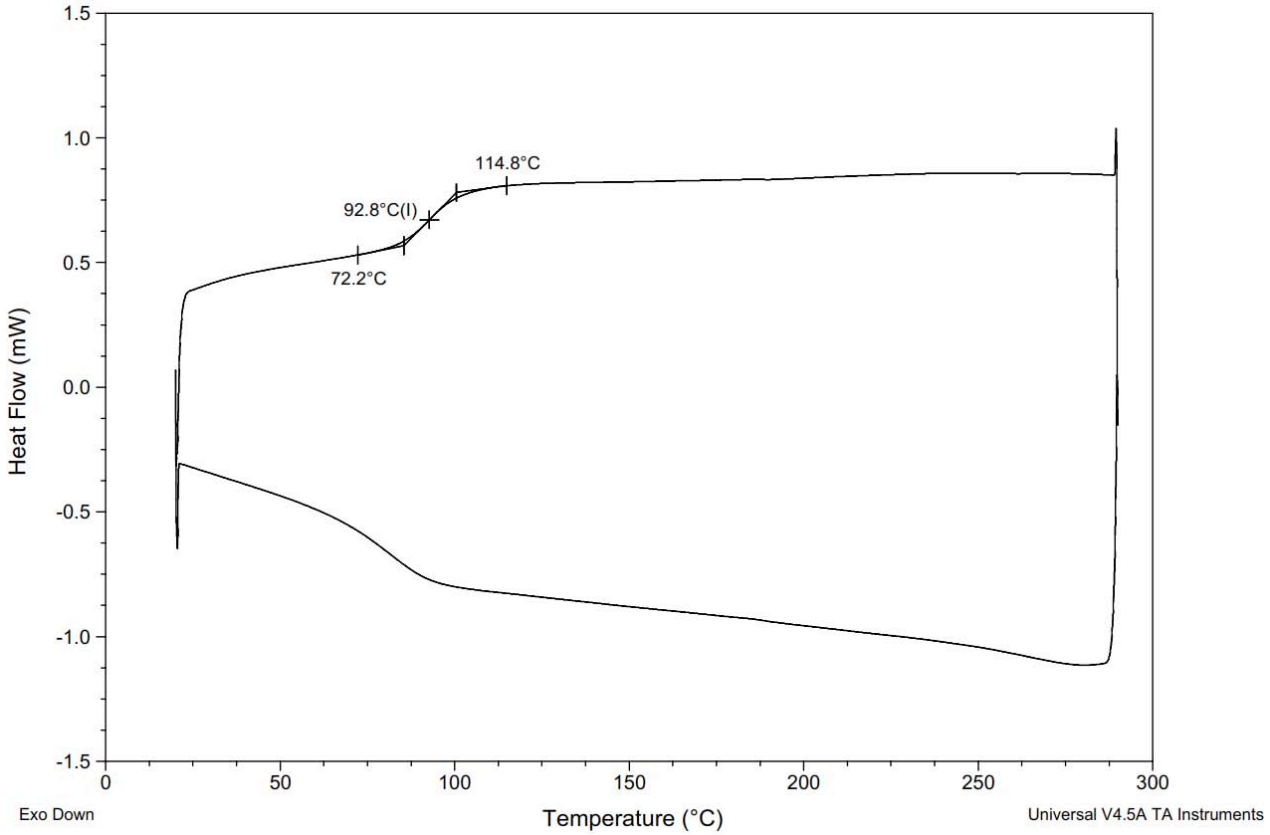


Figure S114. DSC Thermogram of copoly(caprolactone/ hydroxyethylferulic acid) [20:80] (Table S2, entry 29).

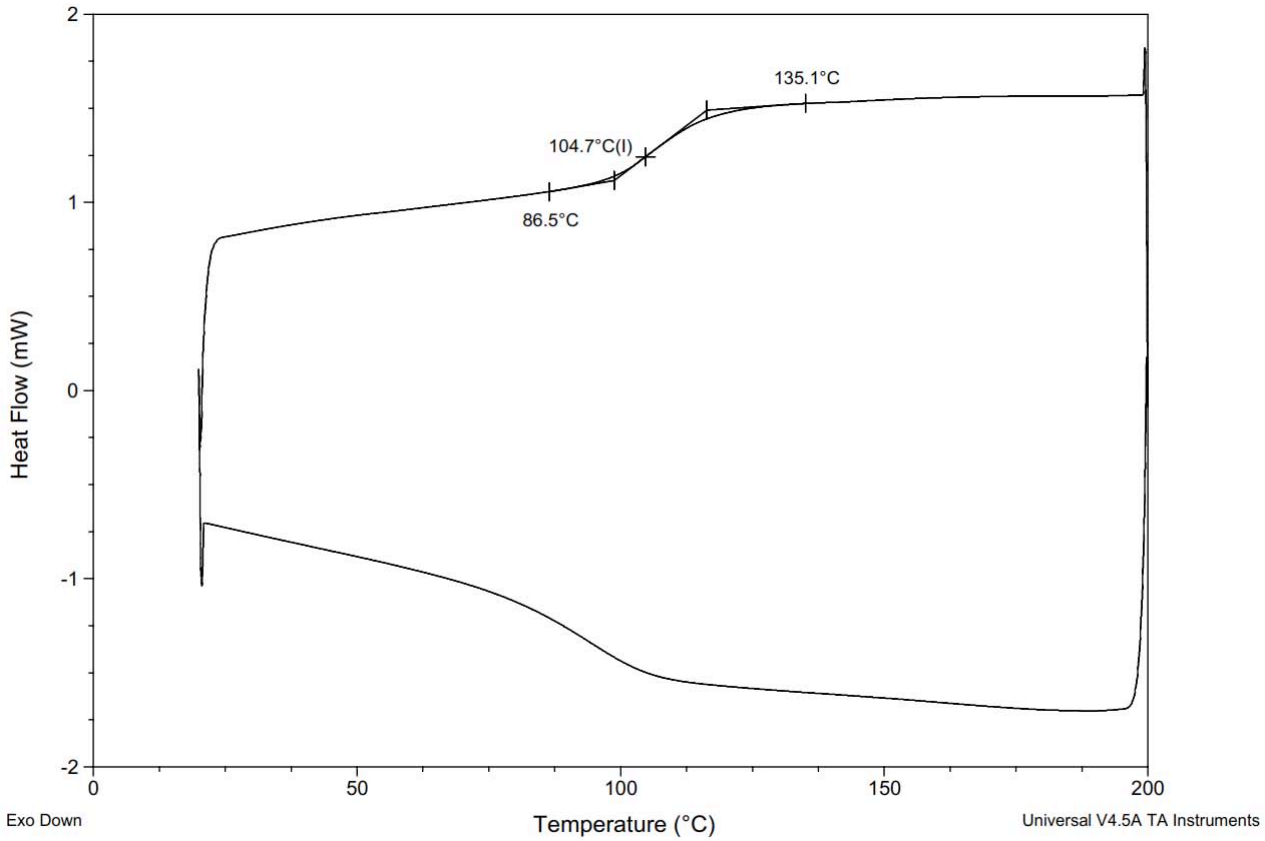


Figure S115. DSC Thermogram of copoly(caprolactone/ hydroxyethylferulic acid) [10:90] (Table S2, entry 30).

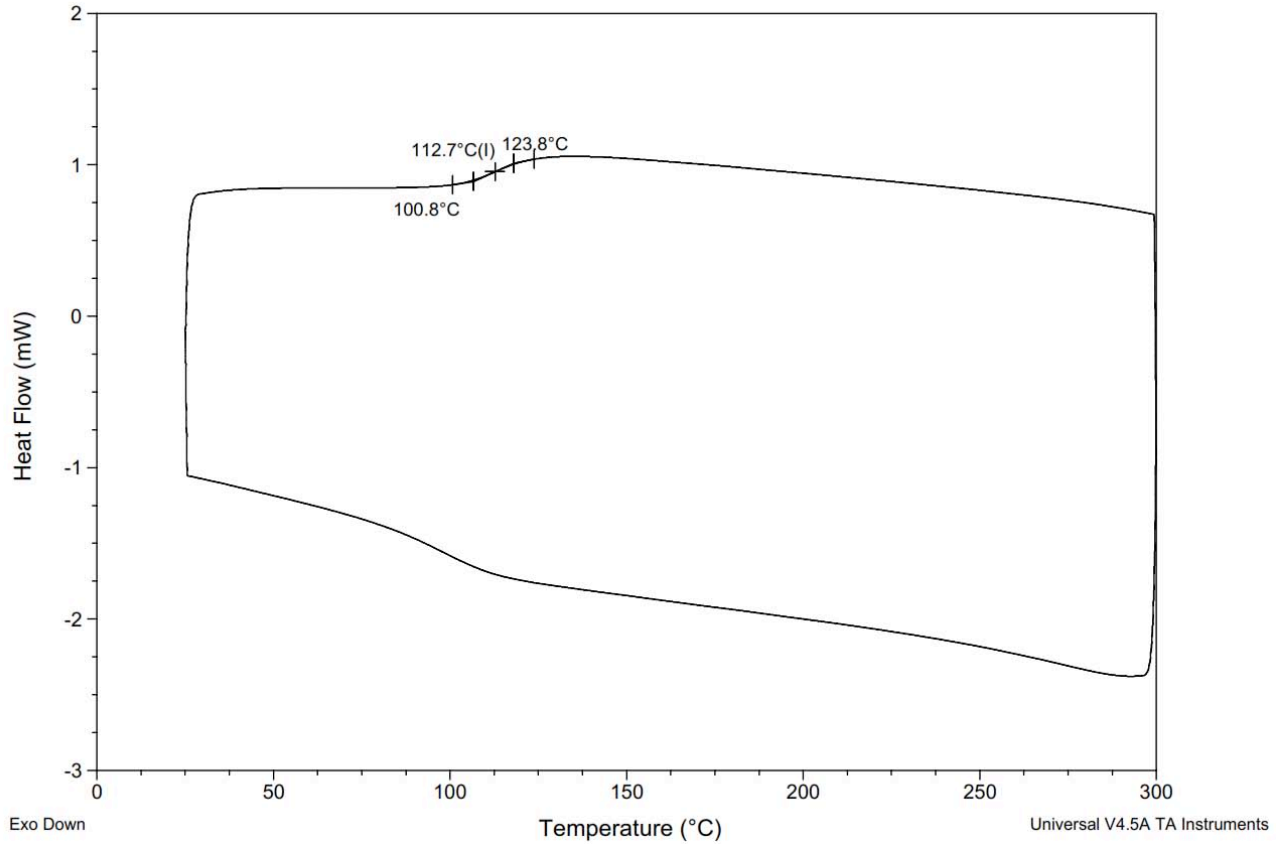


Figure S116. DSC Thermogram of polyethylene ferulate(Table S2, entry 31).

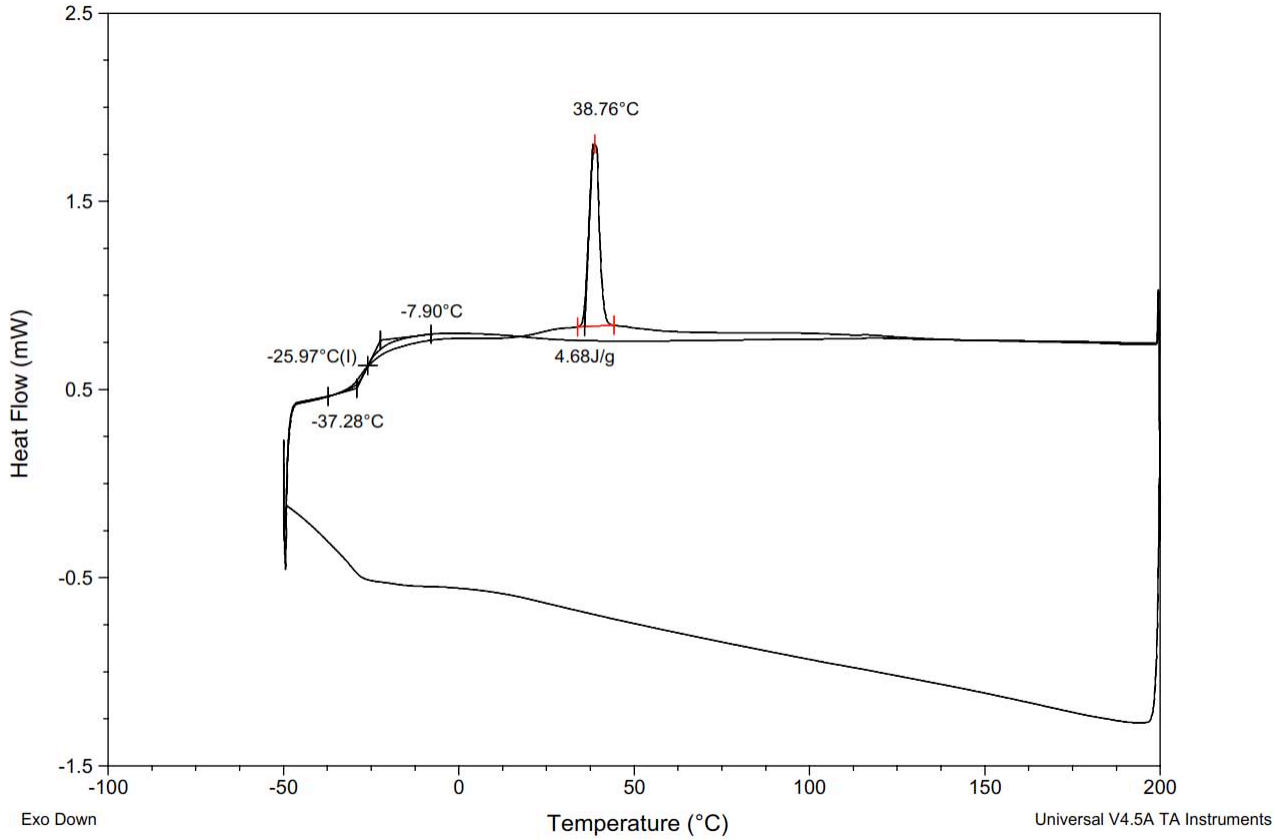


Figure S117. DSC Thermogram of copoly(caprolactone/ hydroxyethylcoumaric acid) [80:20] (Table S2, entry 32).

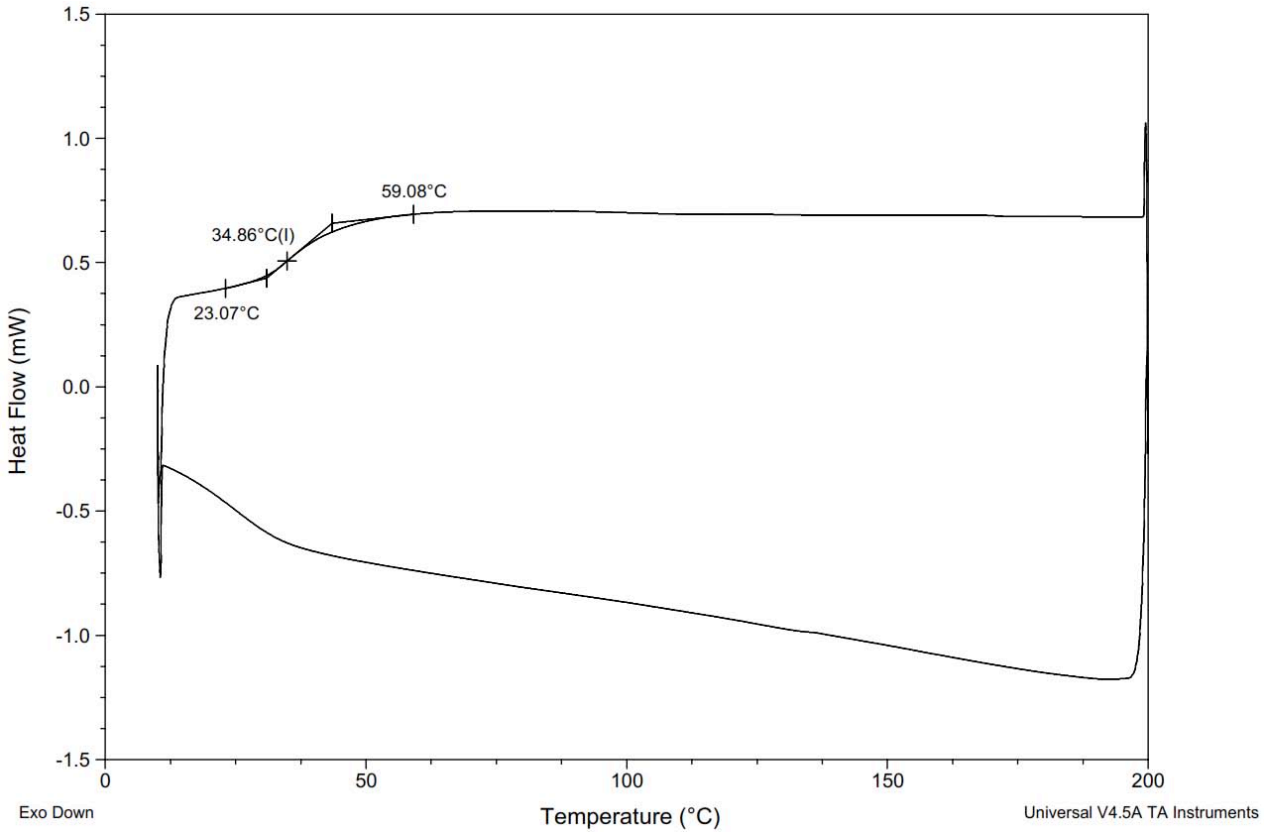


Figure S118. DSC Thermogram of copoly(caprolactone/ hydroxyethylcoumaric acid) [50:50] (Table S2, entry 33).

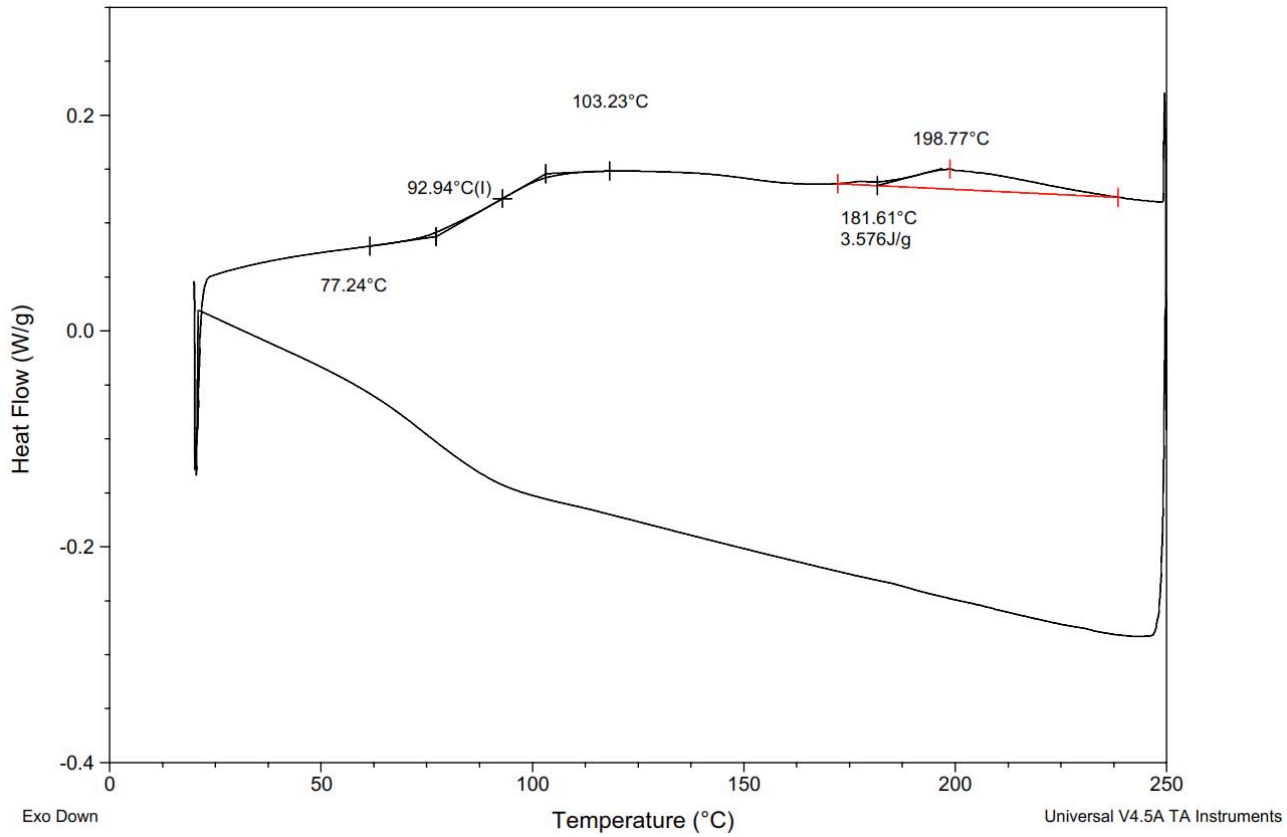


Figure S119. DSC Thermogram of copoly(caprolactone/ hydroxyethylcoumaric acid) [20:80] (Table S2, entry 34).

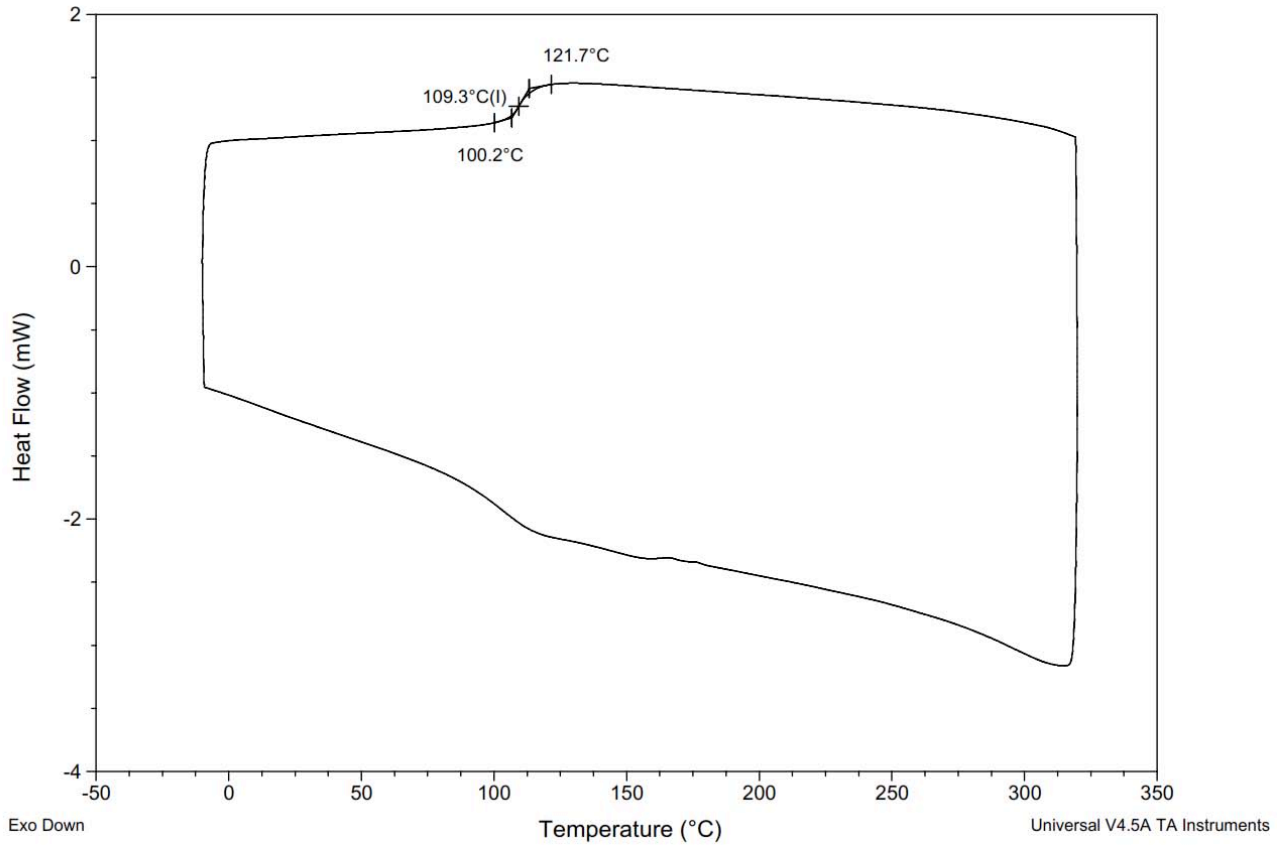


Figure S120. DSC Thermogram of polyethylene coumarate (Table S2, entry 35).

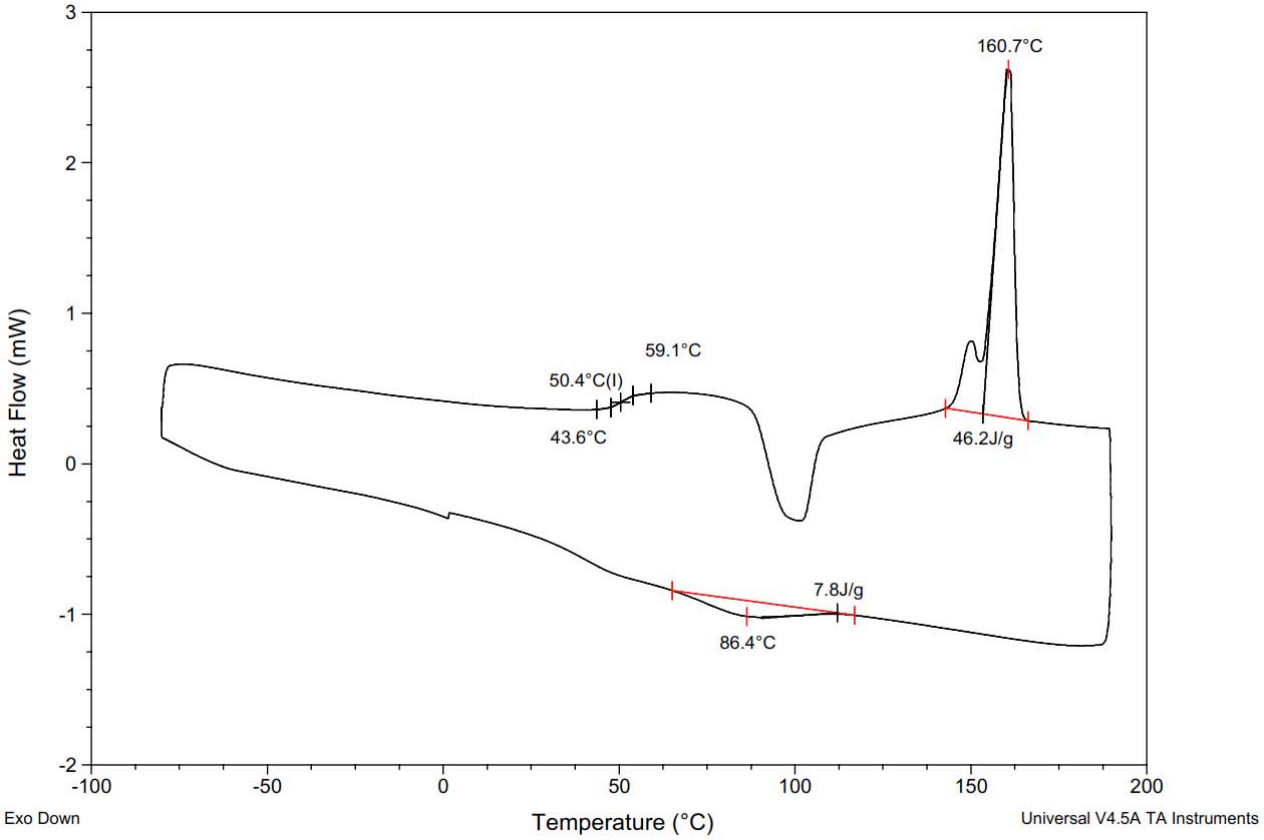


Figure S121. DSC Thermogram of polylactic acid (Table S3, entry 1).

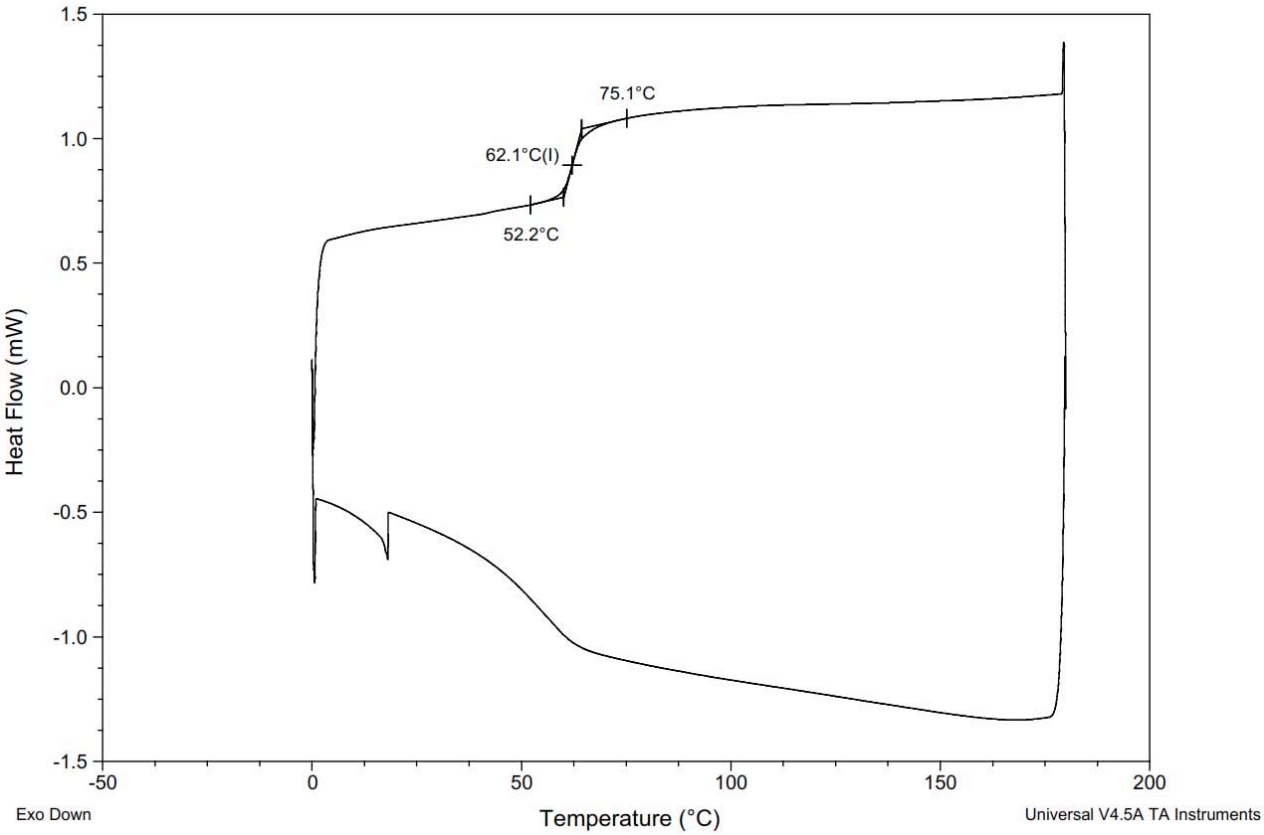


Figure S122. DSC Thermogram of copoly(L-lactide/ hydroxyethylsyringic acid) [80:20] (Table S3, entry 2).

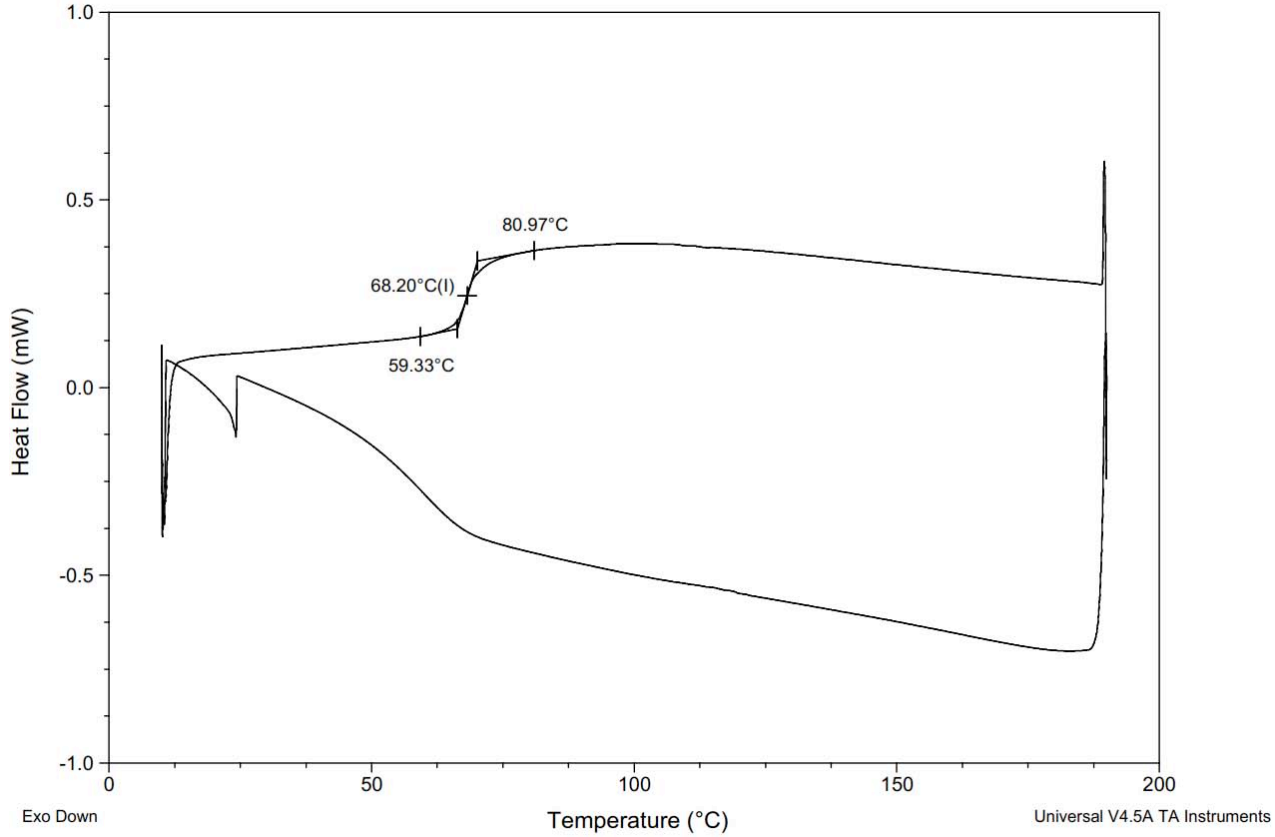


Figure S123. DSC Thermogram of copoly(L-lactide/ hydroxyethylsyringic acid) [60:40] (Table S3, entry 3).

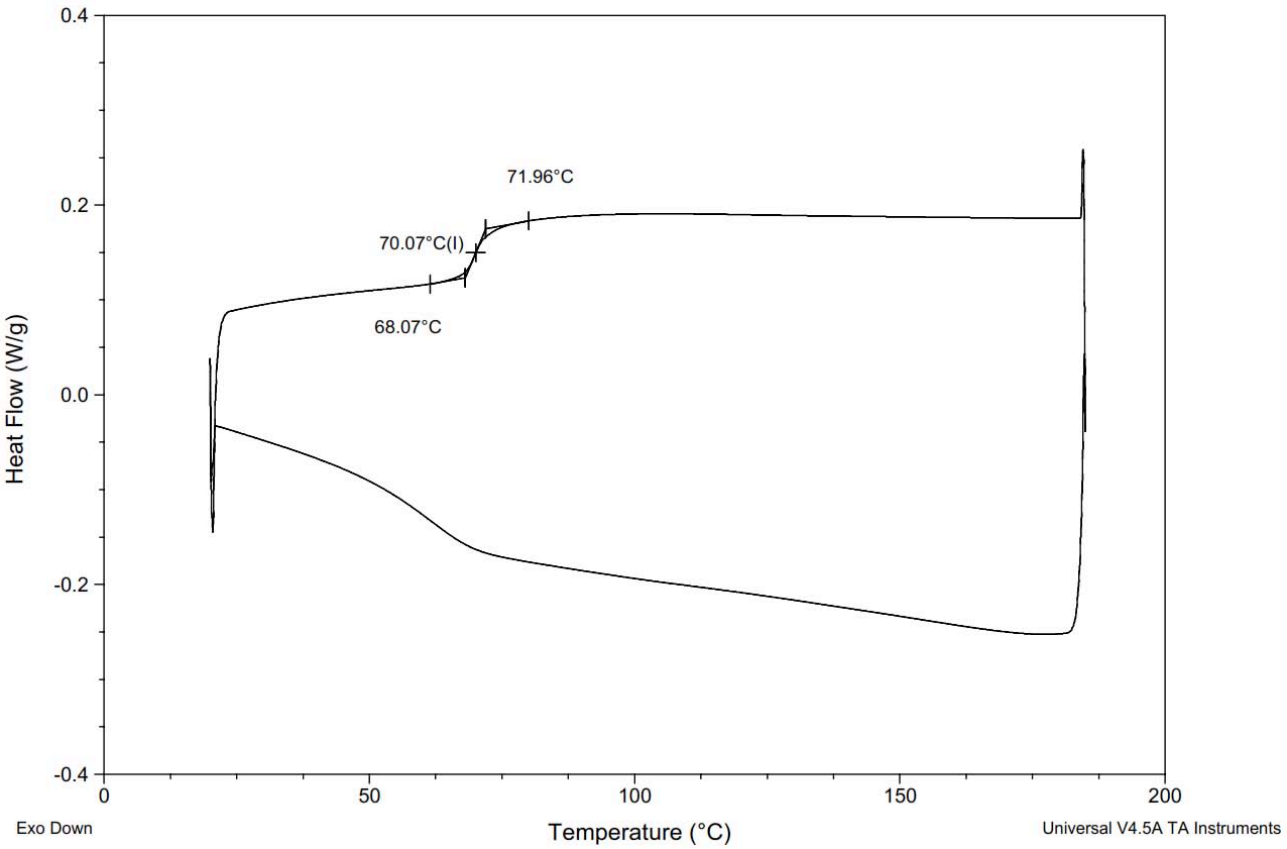


Figure S124. DSC Thermogram of copoly(L-lactide/ hydroxyethylsyringic acid) [40:60] (Table S3, entry 4).

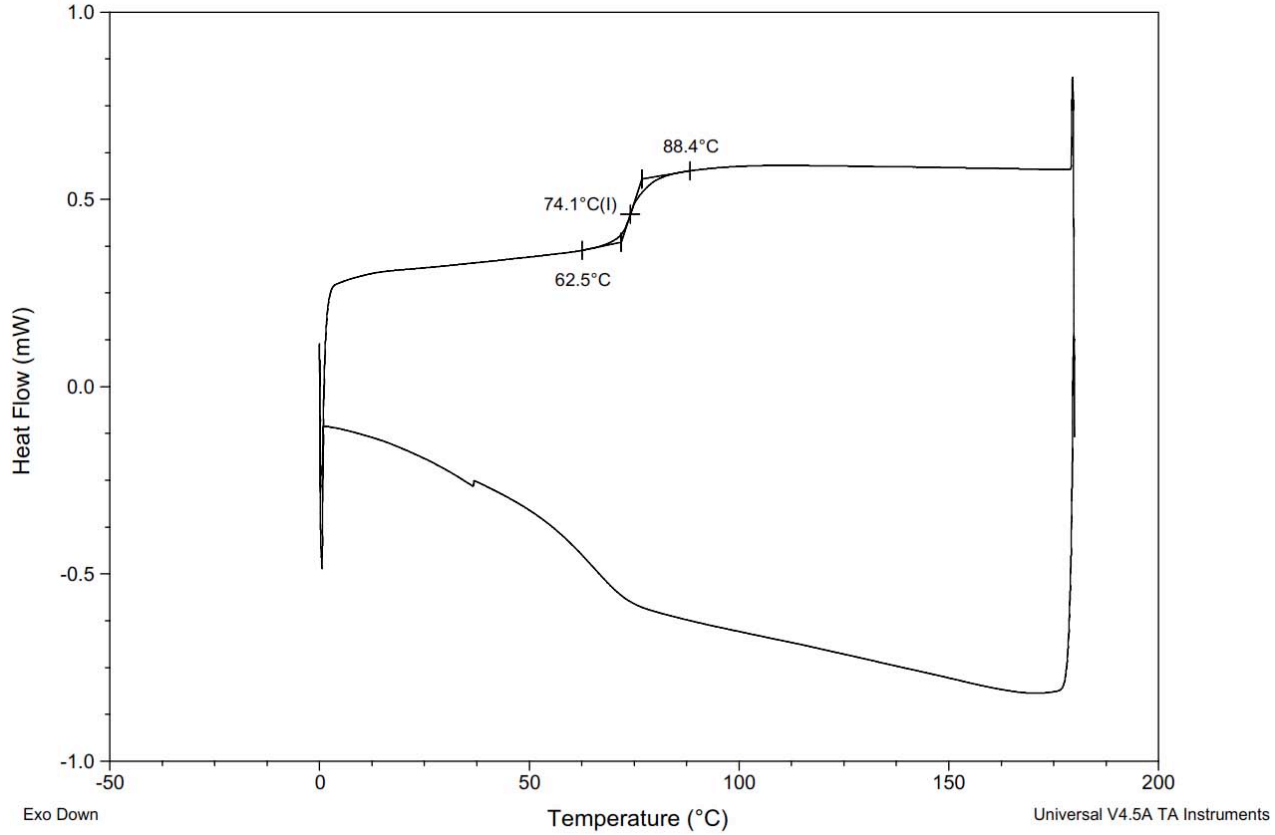


Figure S125. DSC Thermogram of copoly(L-lactide/ hydroxyethylsyringic acid) [20:80] (Table S3, entry 5).

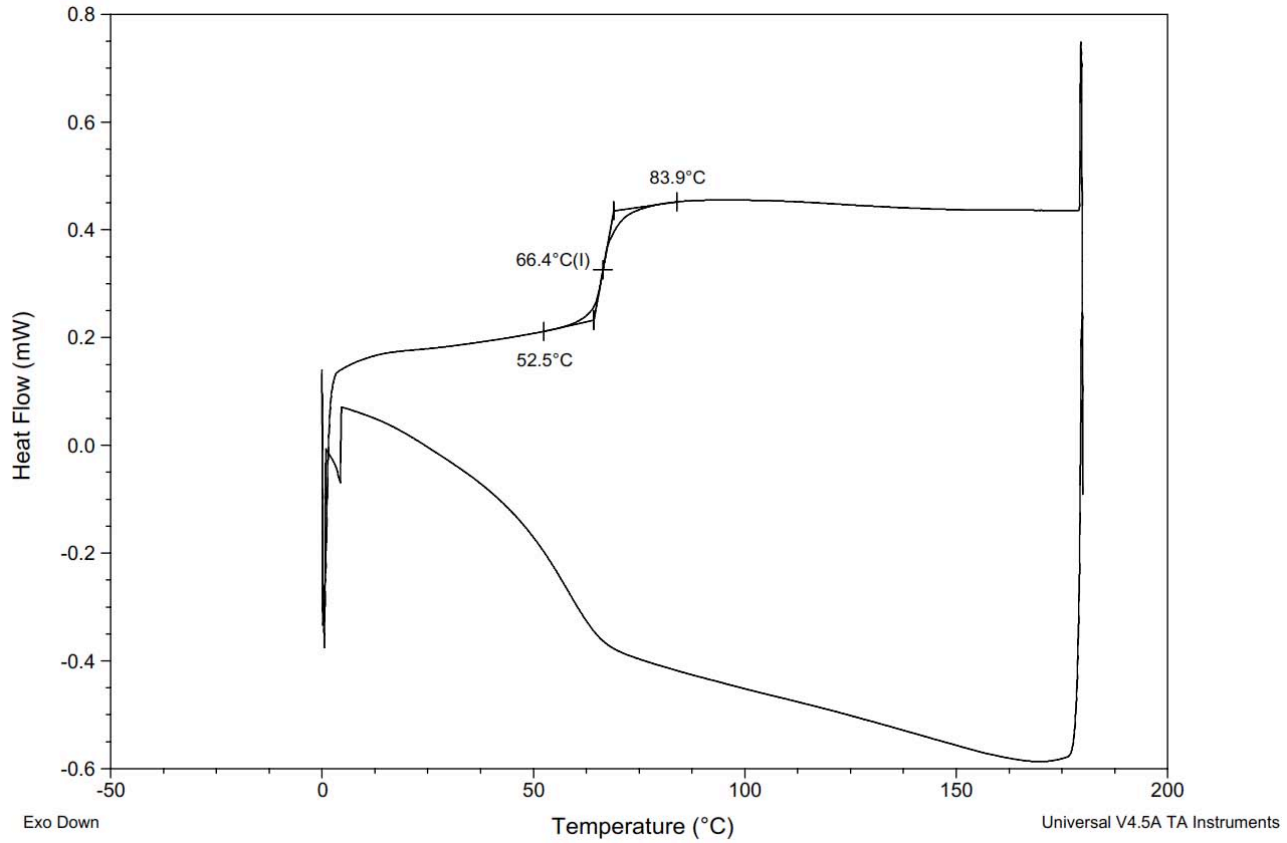


Figure S126. DSC Thermogram of copoly(L-lactide/ hydroxyethylvanillic acid) [80:20] (Table S3, entry 7).

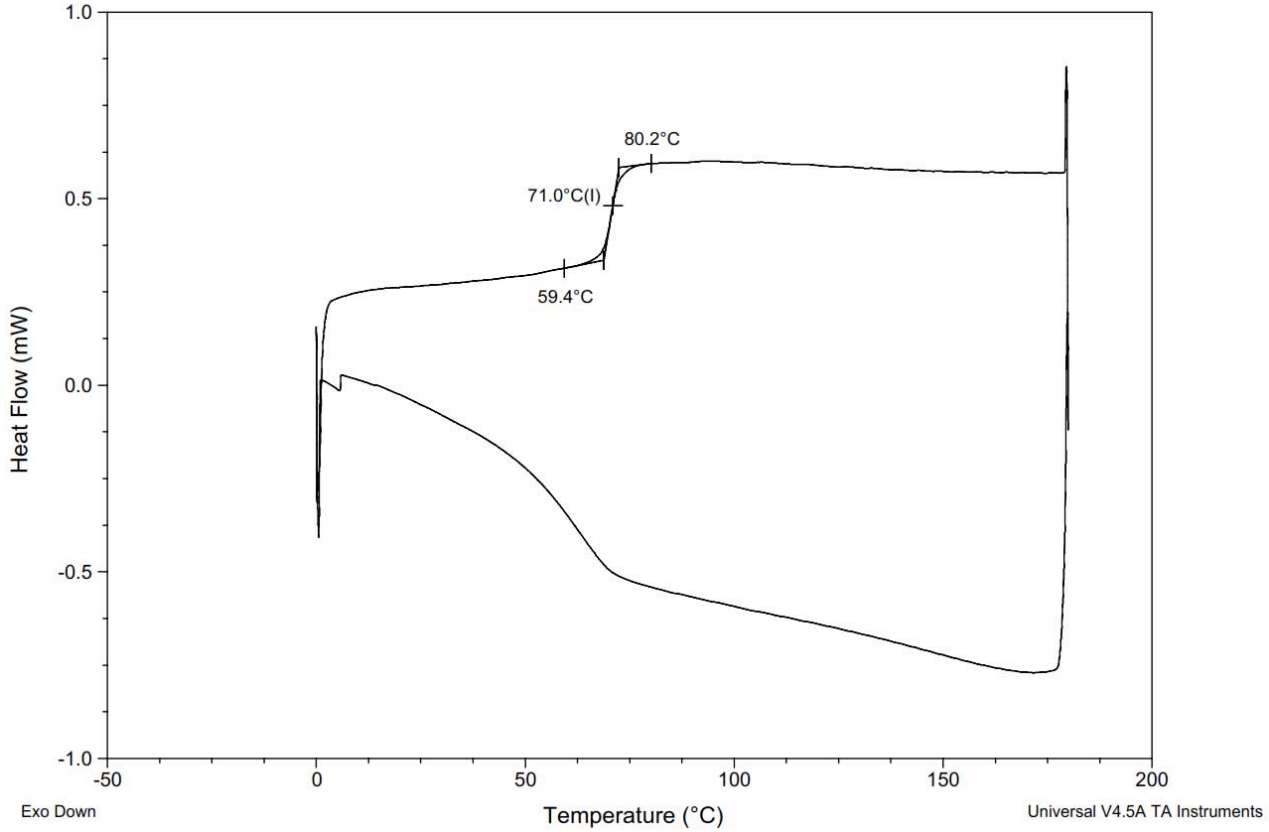


Figure S127. DSC Thermogram of copoly(L-lactide/ hydroxyethylvanillic acid) [60:40] (Table S3, entry 8).

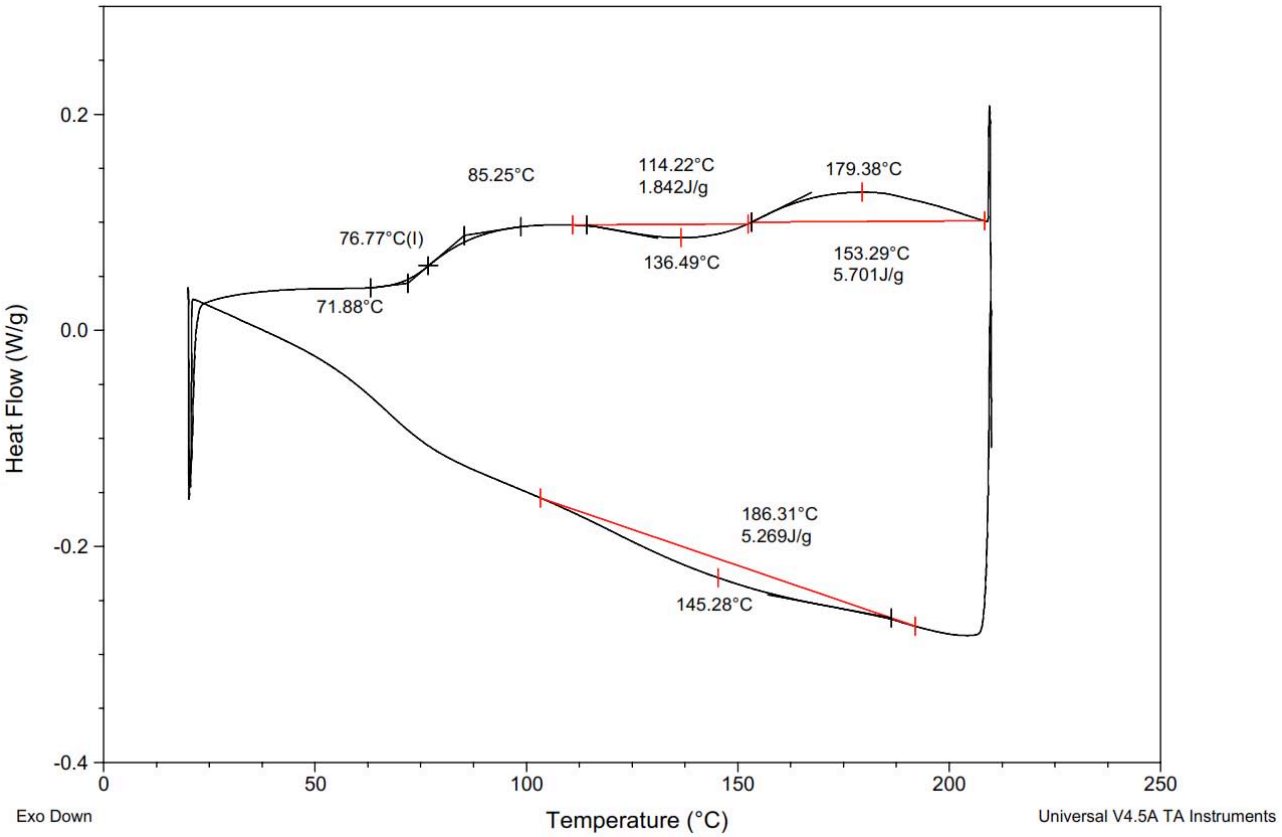


Figure S128. DSC Thermogram of copoly(L-lactide/ hydroxyethylvanillic acid) [40:60] (Table S3, entry 9).

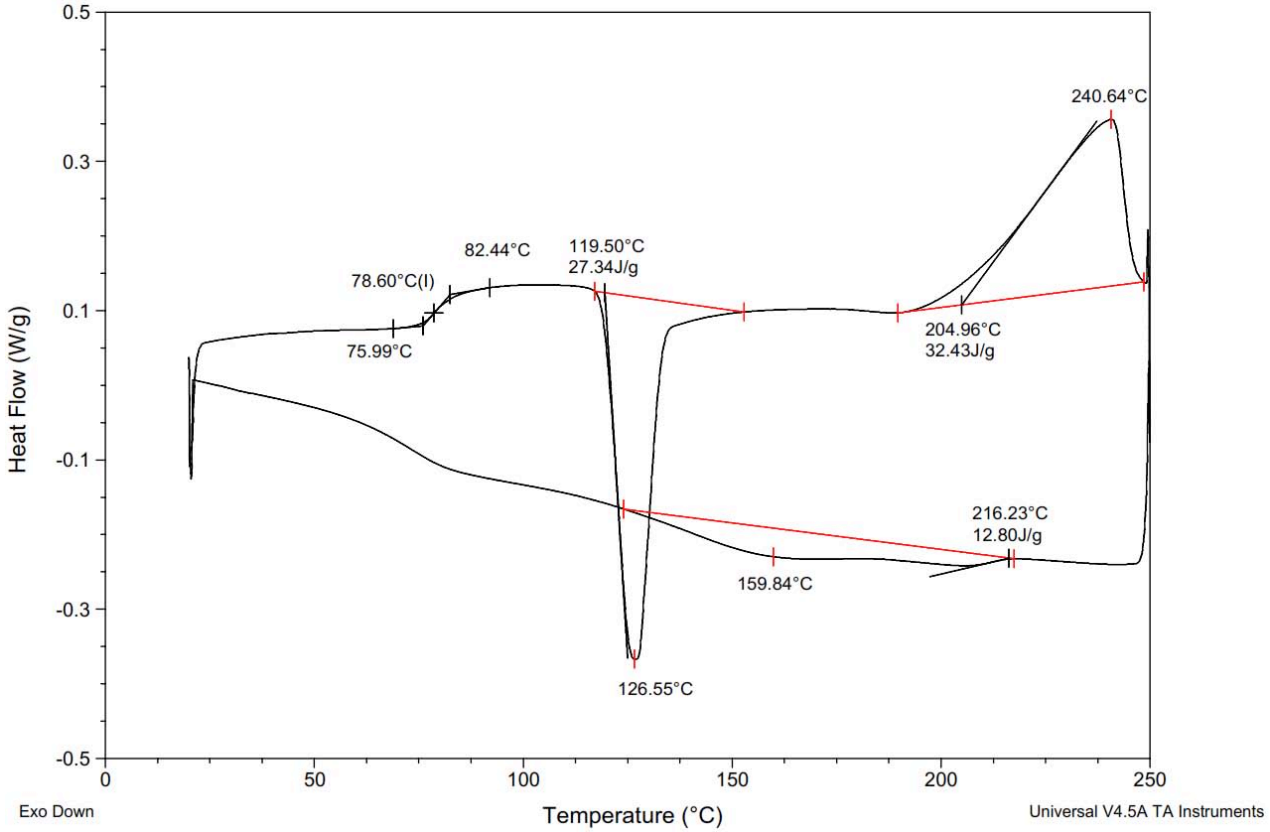


Figure S129. DSC Thermogram of copoly(L-lactide/ hydroxyethylvanillic acid) [20:80] (Table S3, entry 9).

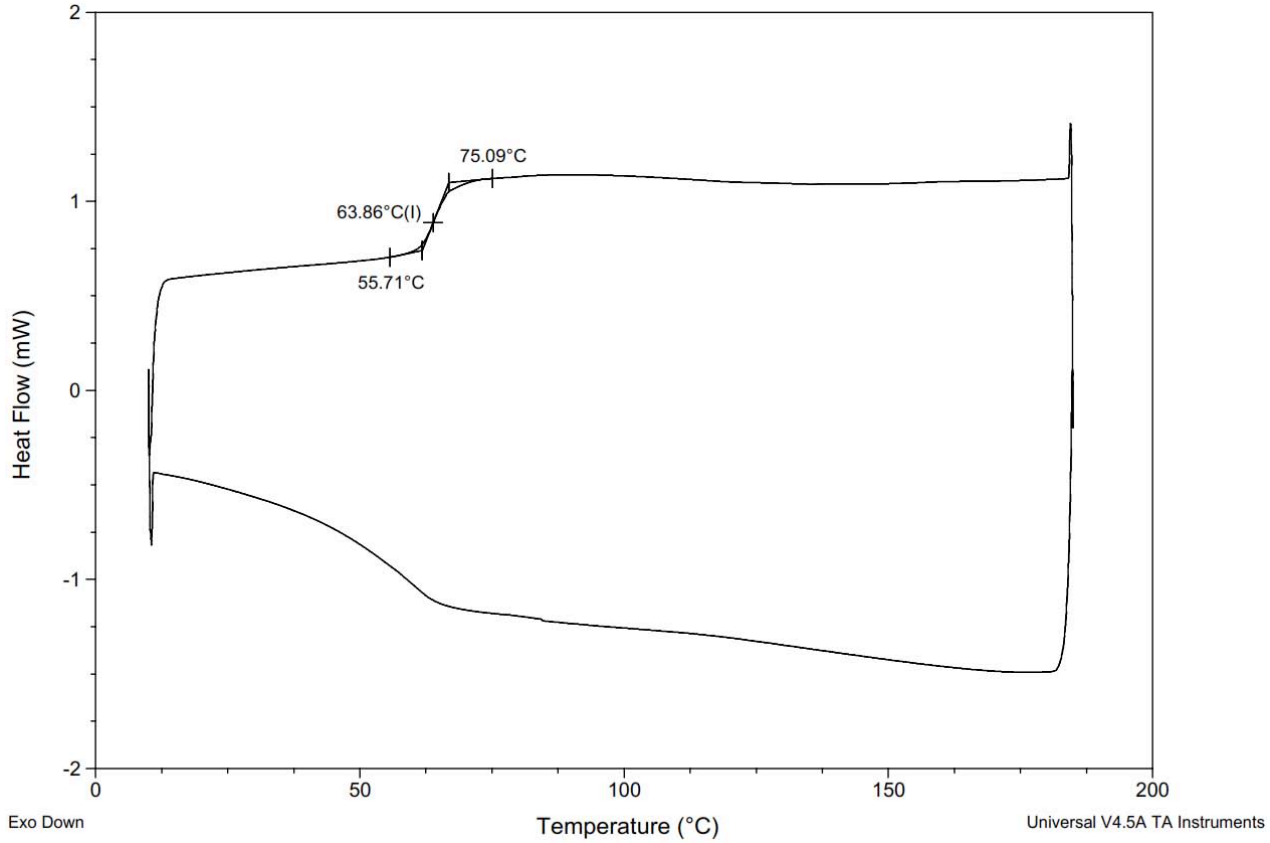


Figure S130. DSC Thermogram of copoly(L-lactide/ hydroxyethylferulic acid) [90:10] (Table S3, entry 12).

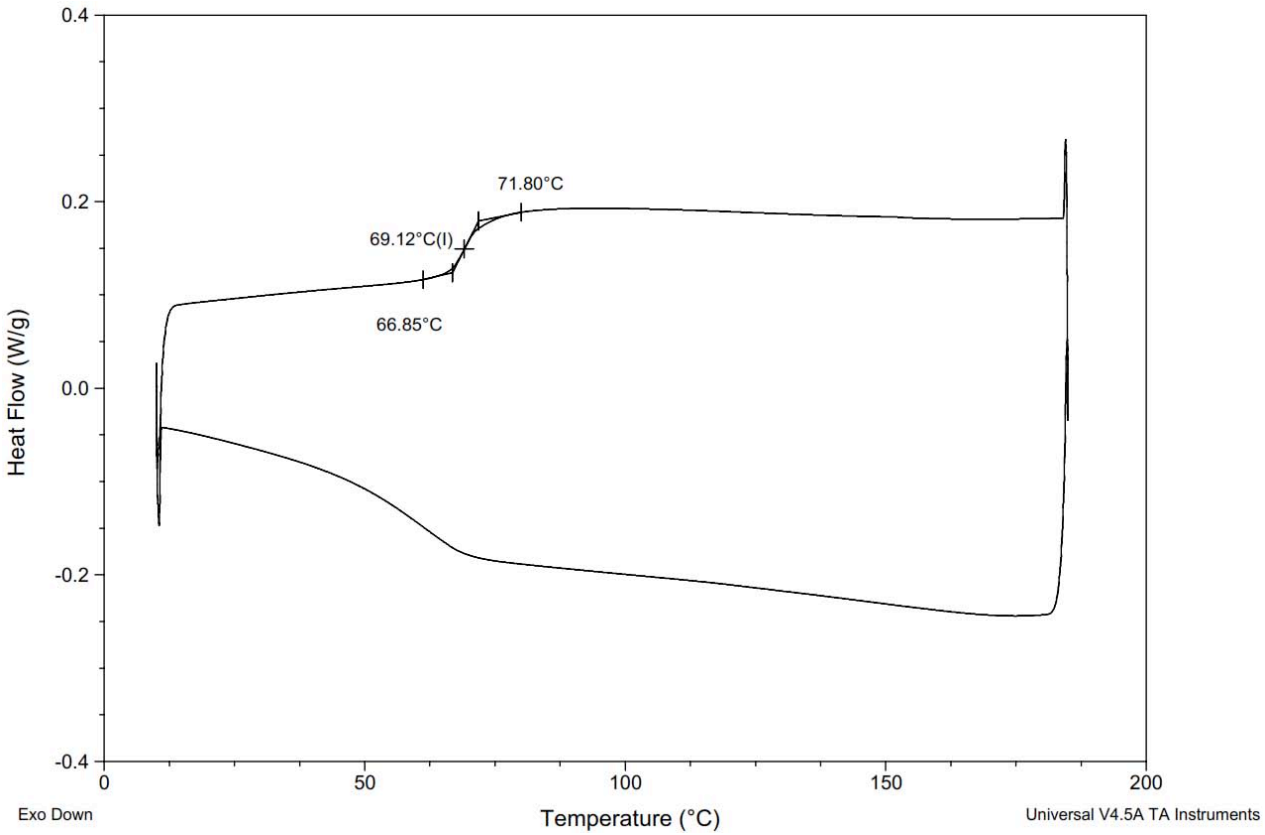


Figure S131. DSC Thermogram of copoly(L-lactide/ hydroxyethylferulic acid) [80:20] (Table S3, entry 13).

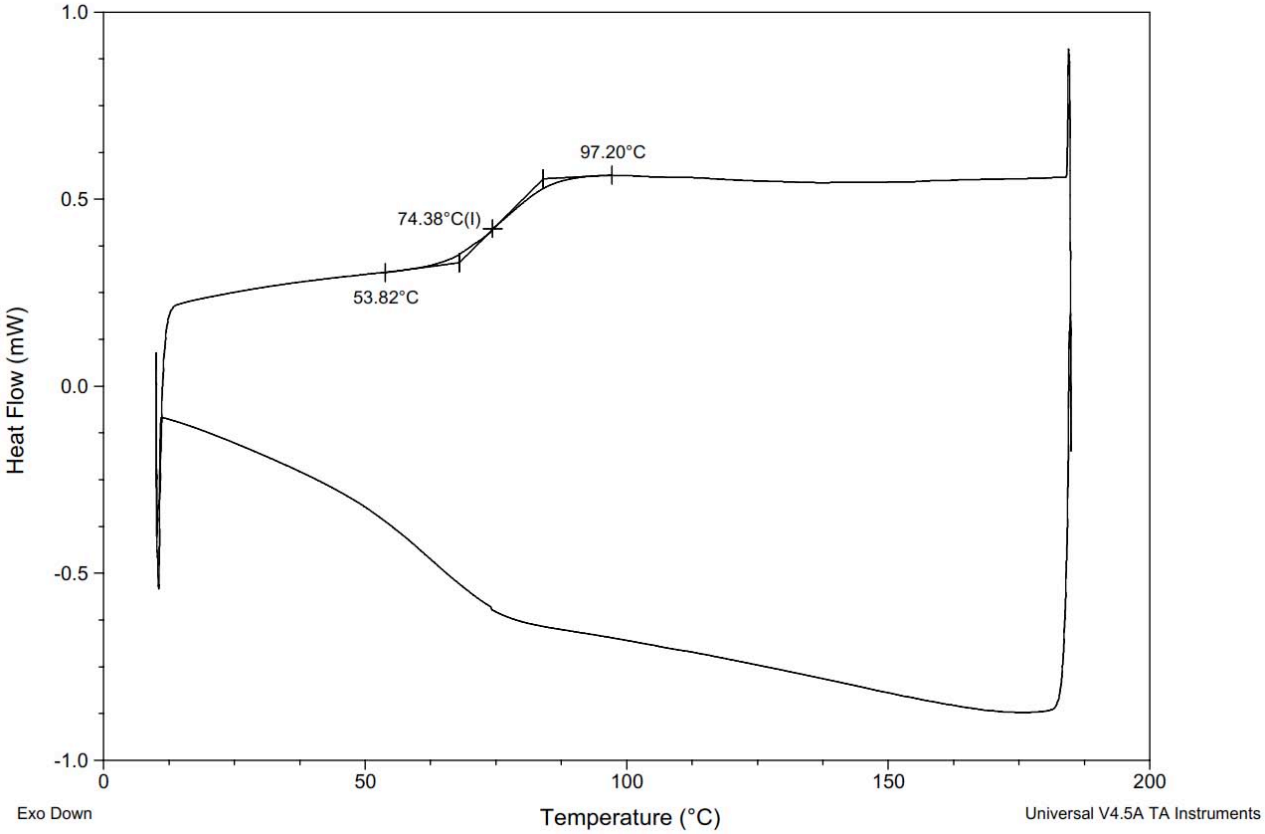


Figure S132. DSC Thermogram of copoly(L-lactide/ hydroxyethylferulic acid) [70:30] (Table S3, entry 14).

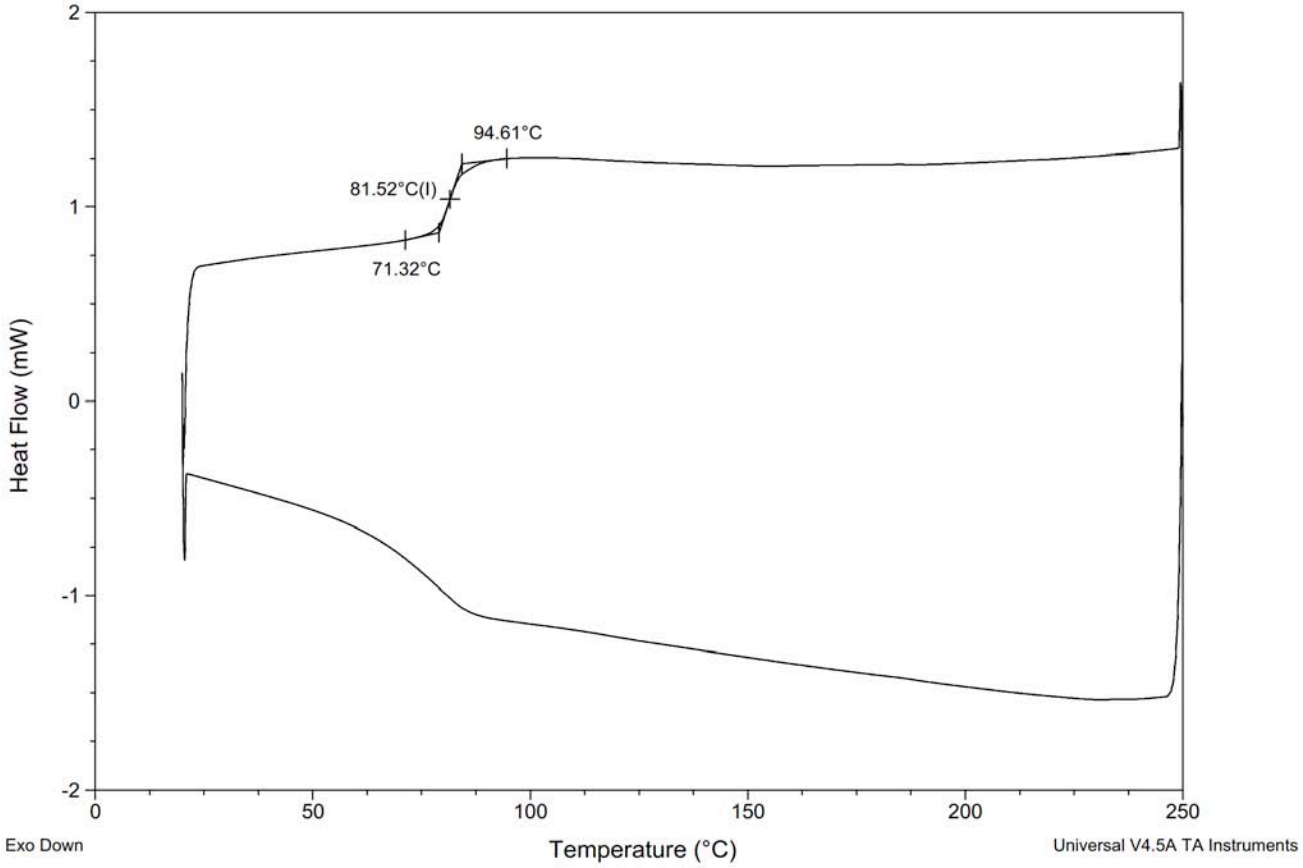


Figure S133. DSC Thermogram of copoly(L-lactide/ hydroxyethylferulic acid) [60:40] (Table S3, entry 15).

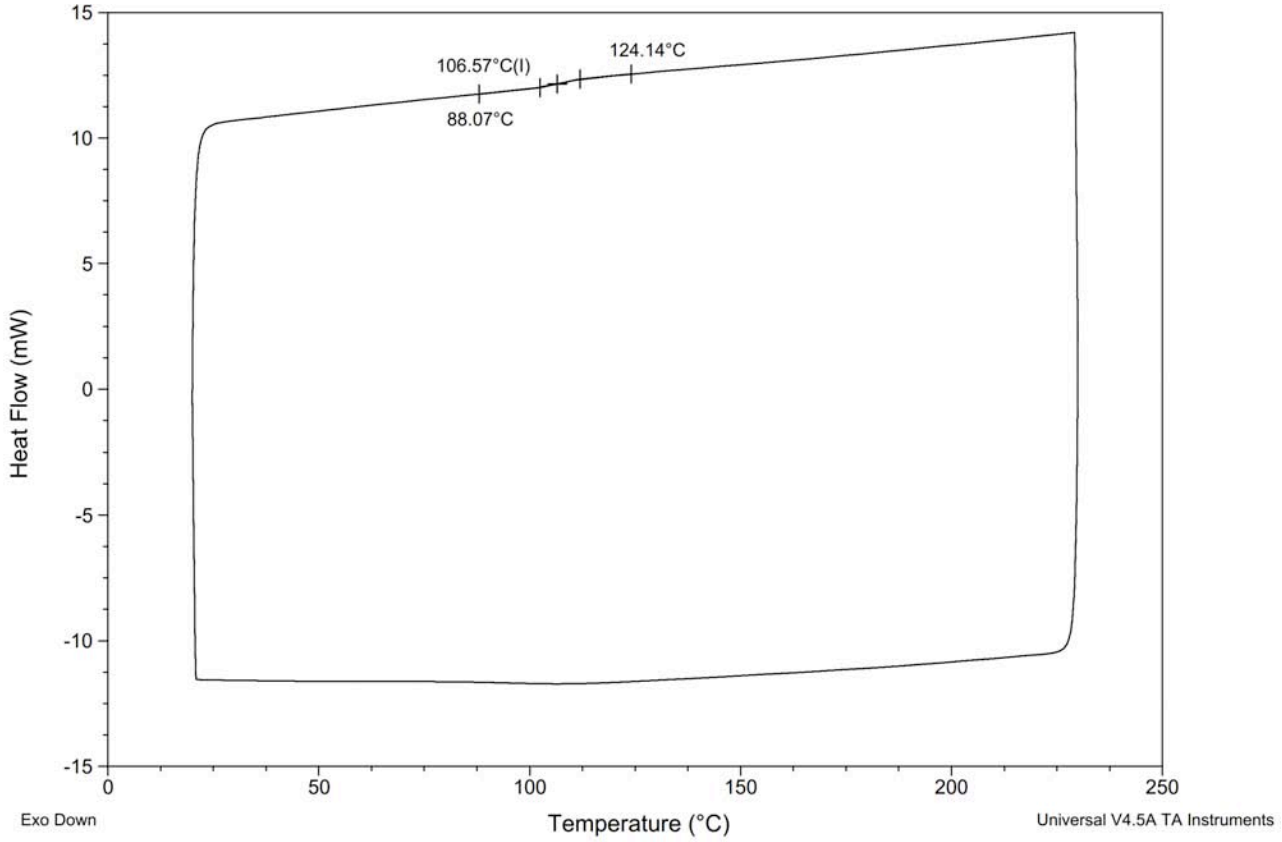


Figure S134. DSC Thermogram of copoly(L-lactide/ hydroxyethylferulic acid) [20:80] (Table S3, entry 16).

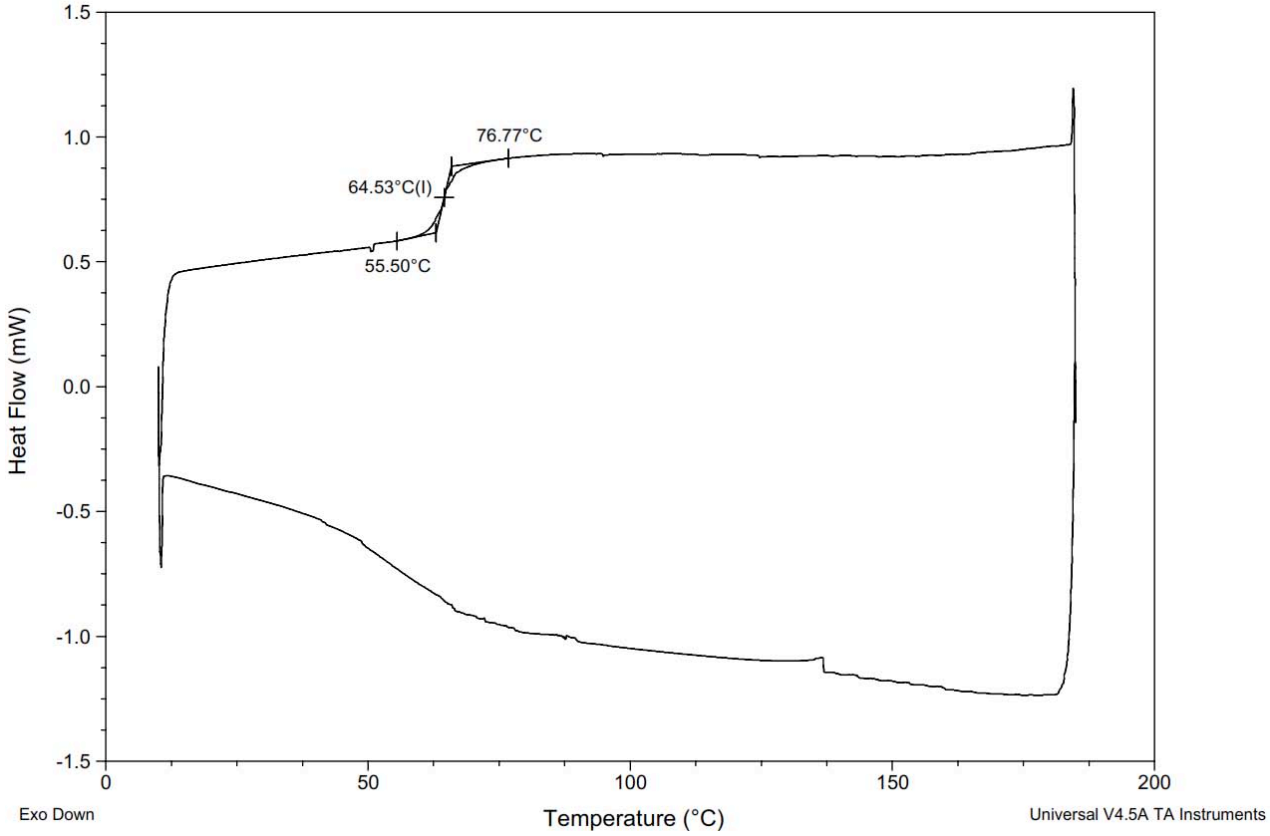


Figure S135. DSC Thermogram of copoly(L-lactide/ hydroxyethylcoumaric acid) [90:10] (Table S3, entry 18).

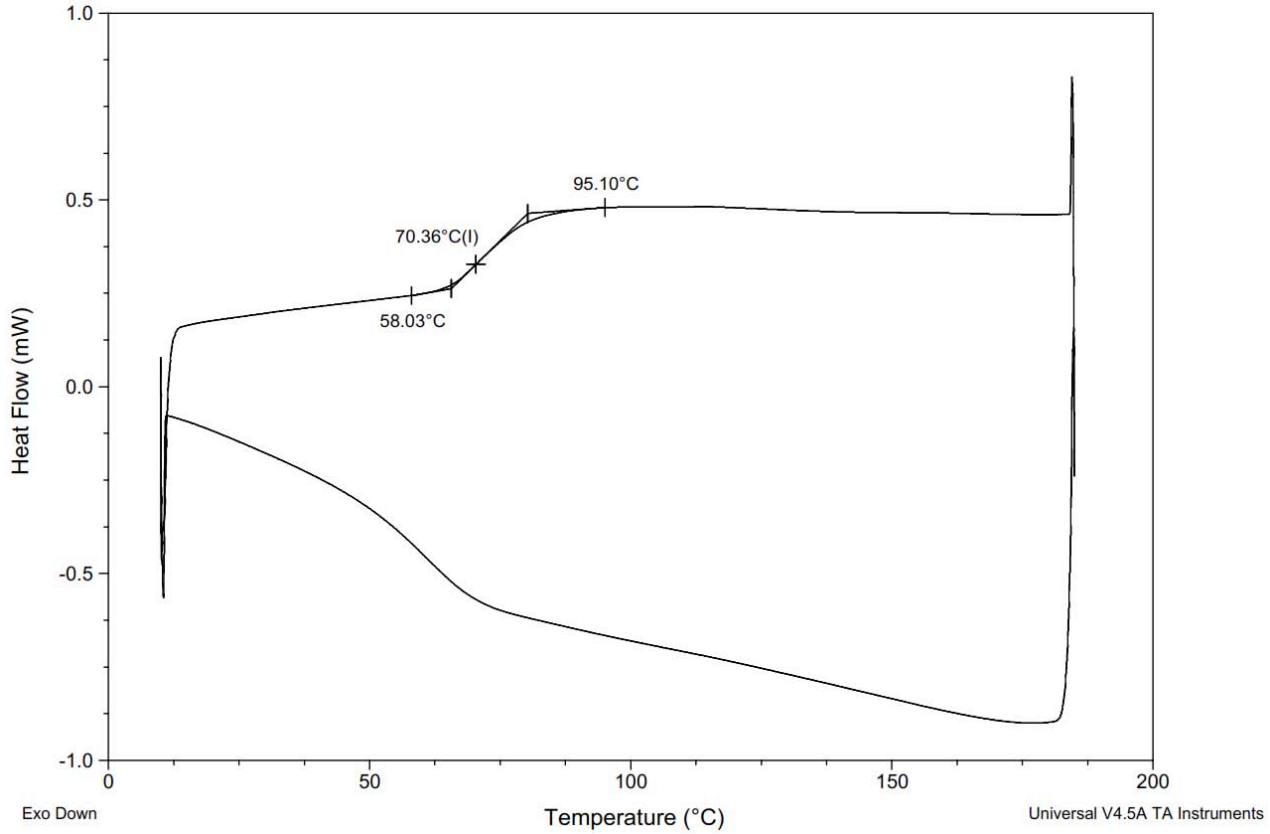


Figure S136. DSC Thermogram of copoly(L-lactide/ hydroxyethylcoumaric acid) [80:20] (Table S3, entry 19).

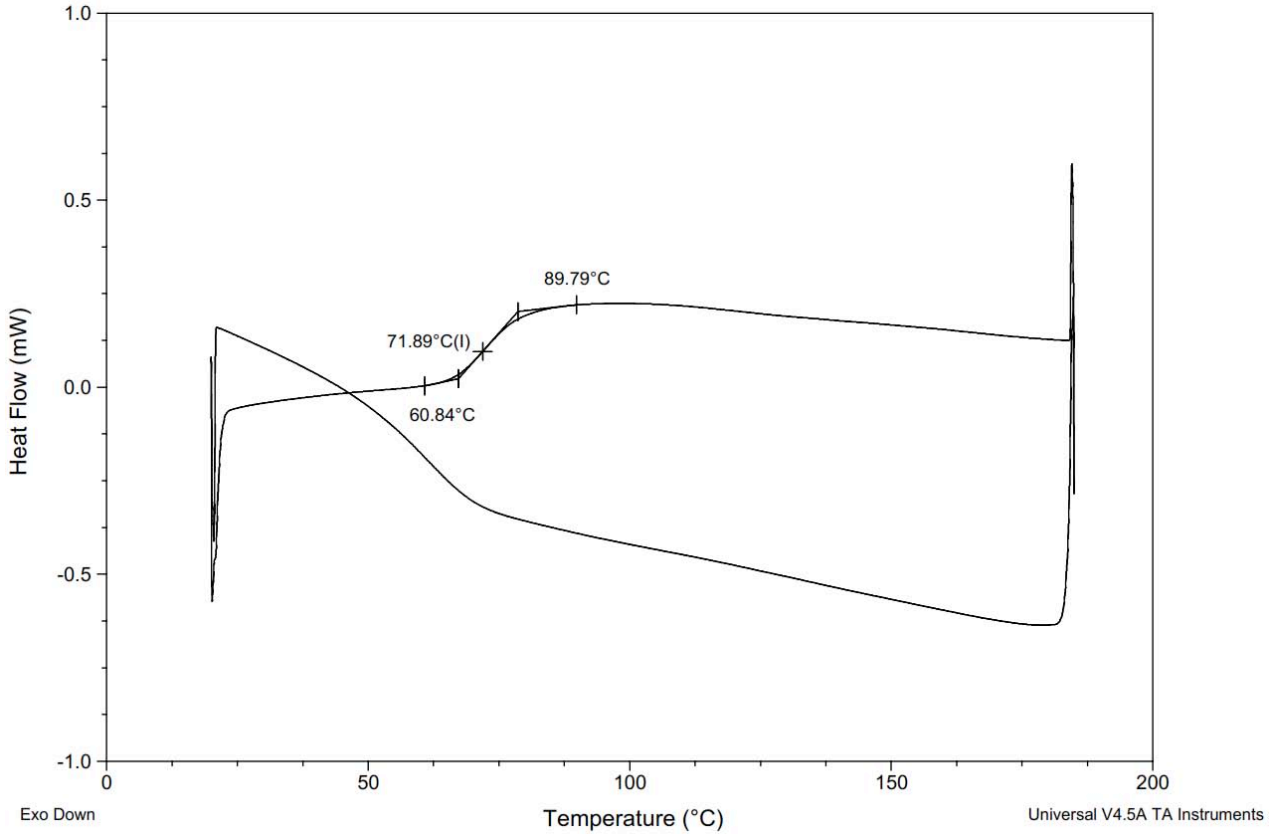


Figure S137. DSC Thermogram of copoly(L-lactide/ hydroxyethylcoumaric acid) [70:30] (Table S3, entry 20).

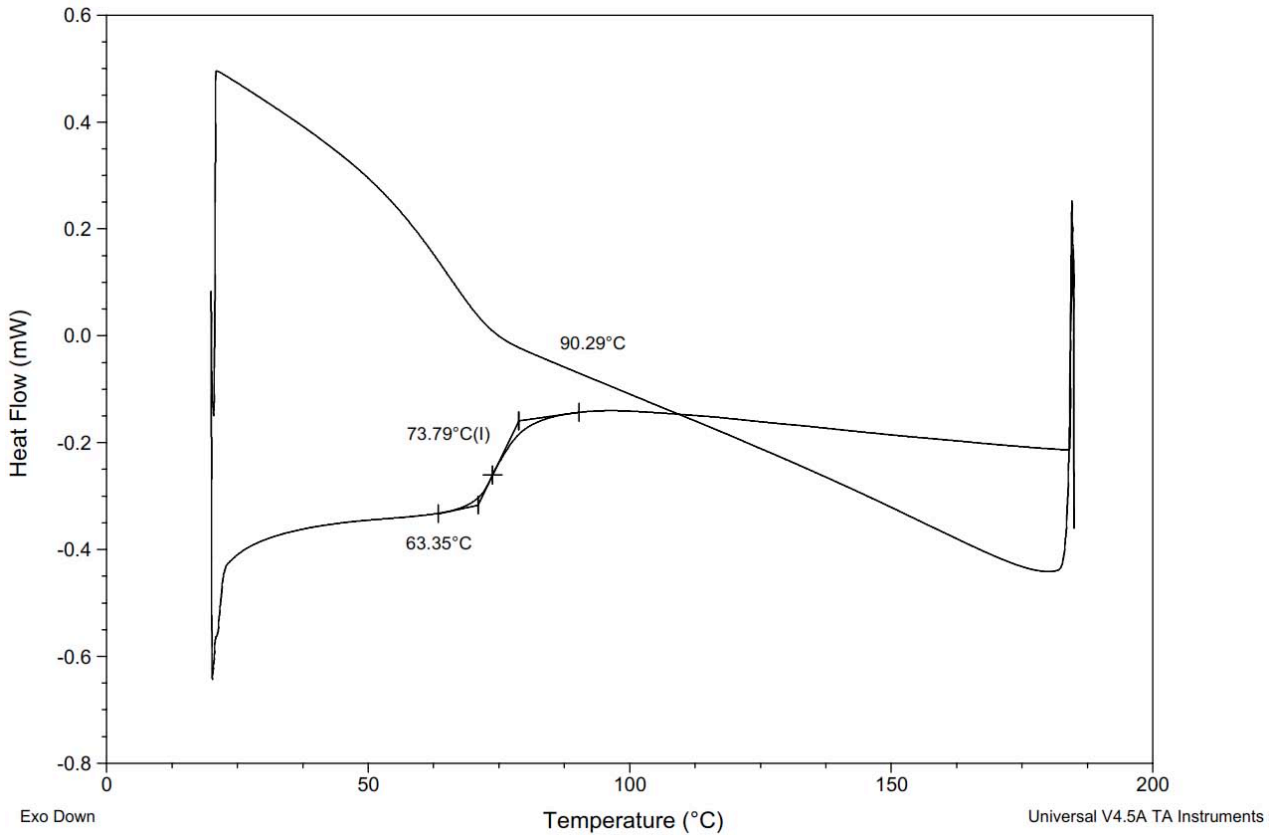


Figure S138. DSC Thermogram of copoly(L-lactide/ hydroxyethylcoumaric acid) [60:40] (Table S3, entry 21).

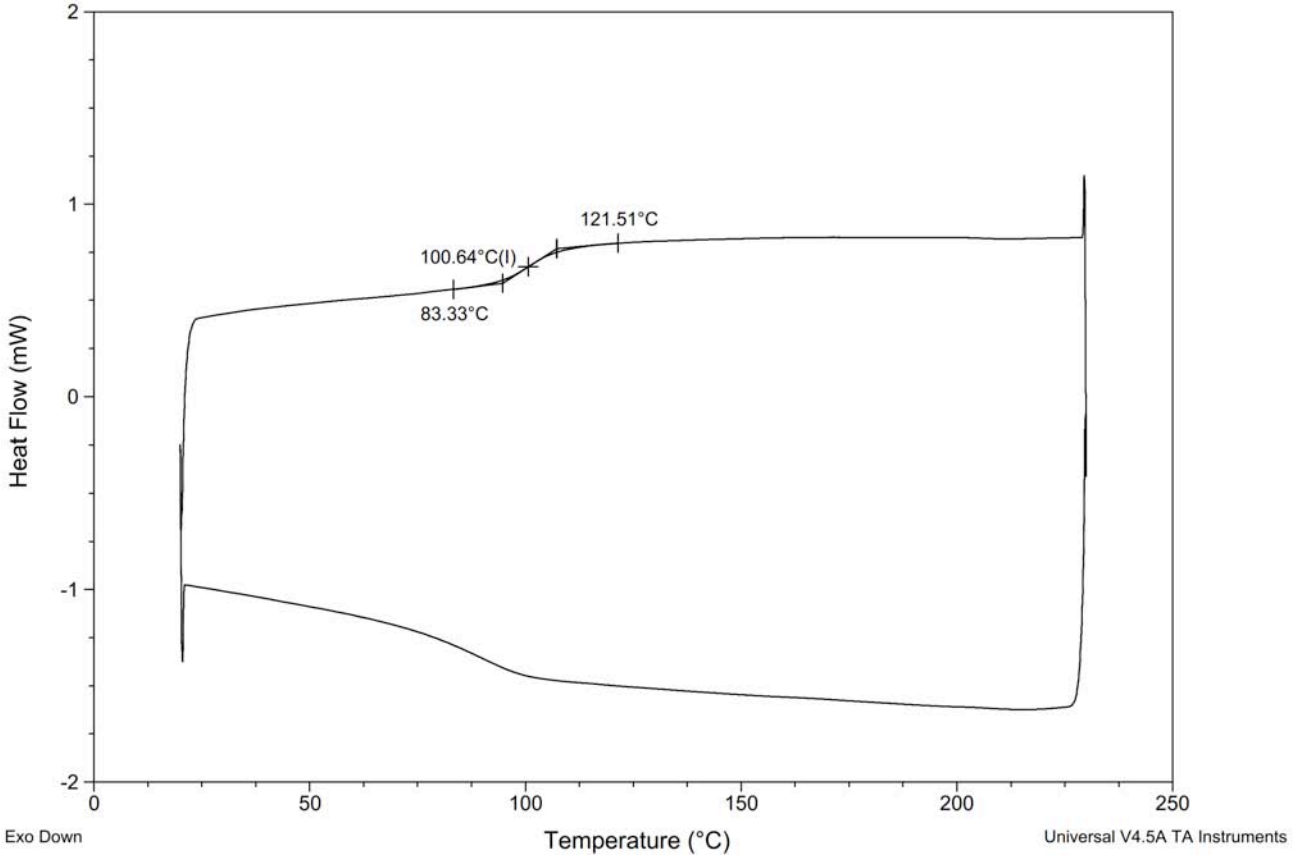


Figure S139. DSC Thermogram of copoly(L-lactide/ hydroxyethylcoumaric acid) [20:80] (Table S3, entry 22).

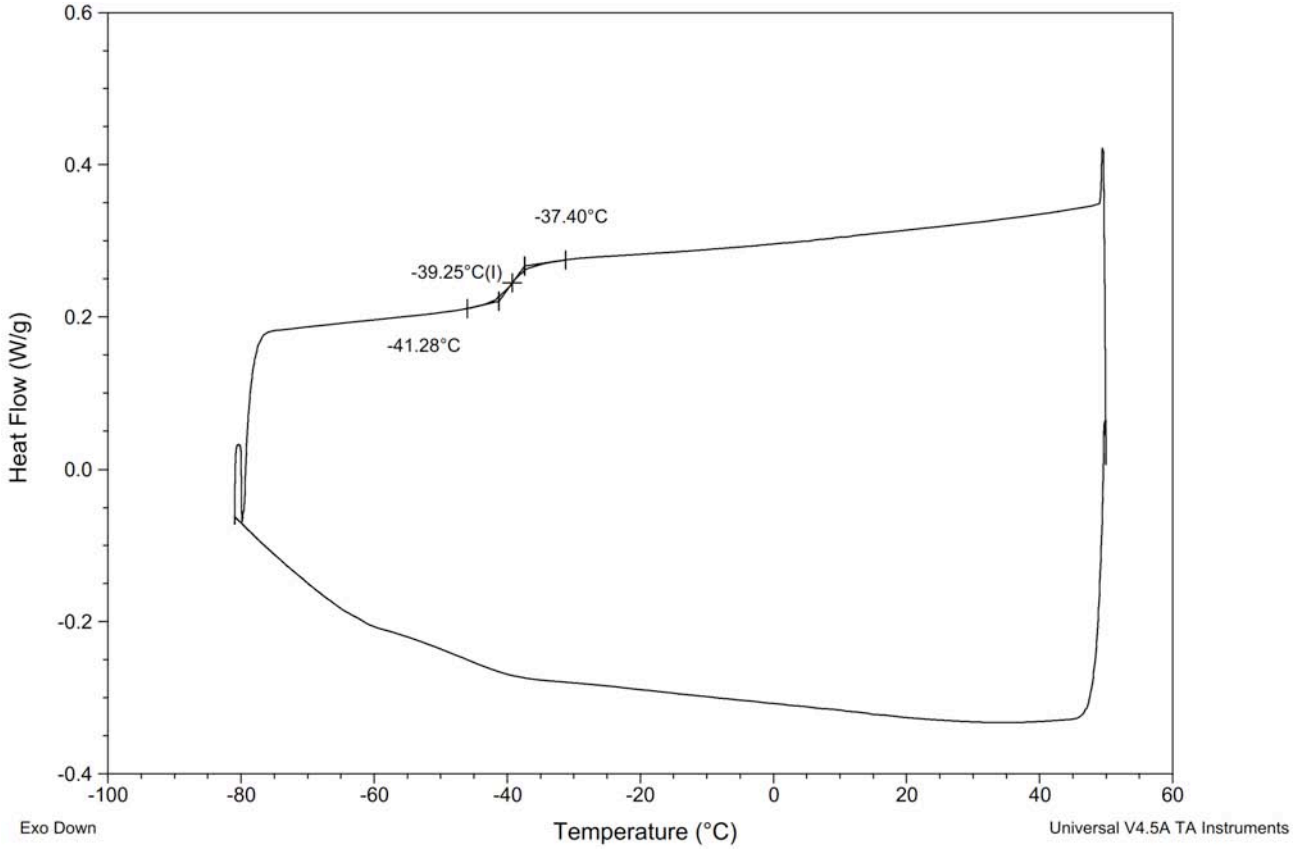


Figure S140. DSC Thermogram of copoly(caprolactone/ hydroxyethylsyringic acid) [50:50] at 10 min. (Table S4, entry 1).

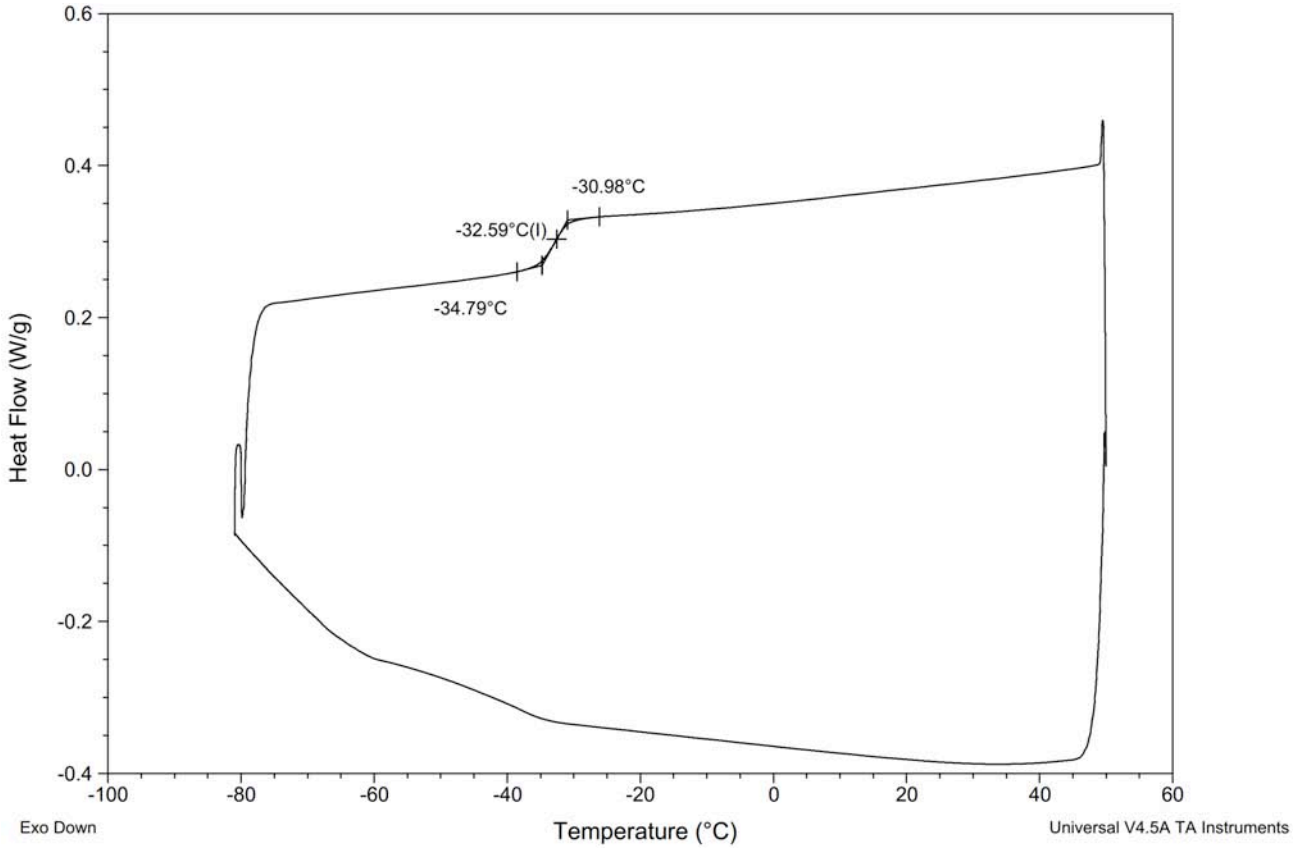


Figure S141. DSC Thermogram of copoly(caprolactone/ hydroxyethylsyringic acid) [50:50] at 20 min. (Table S4, entry 2).

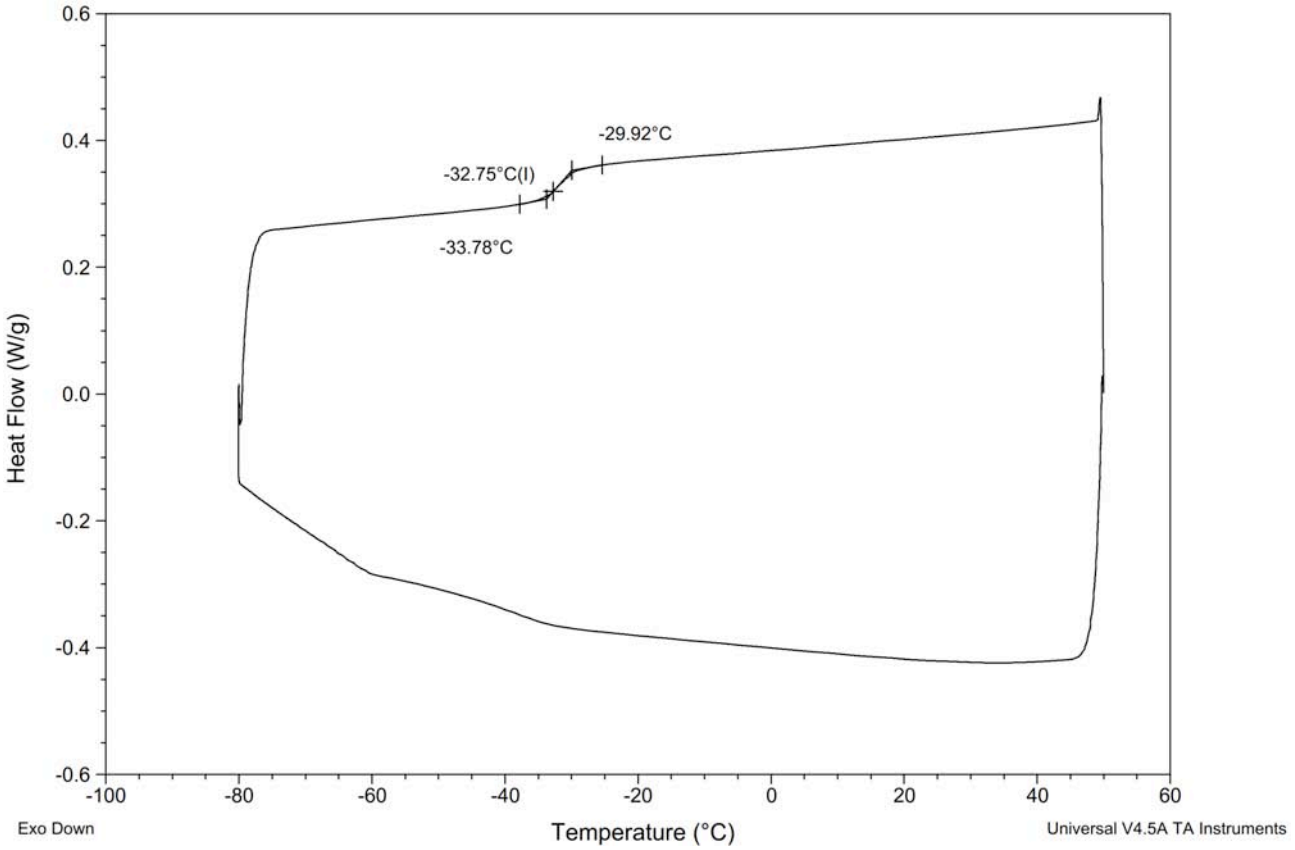


Figure S142. DSC Thermogram of copoly(caprolactone/ hydroxyethylsyringic acid) [50:50] at 30 min. (Table S4, entry 3).

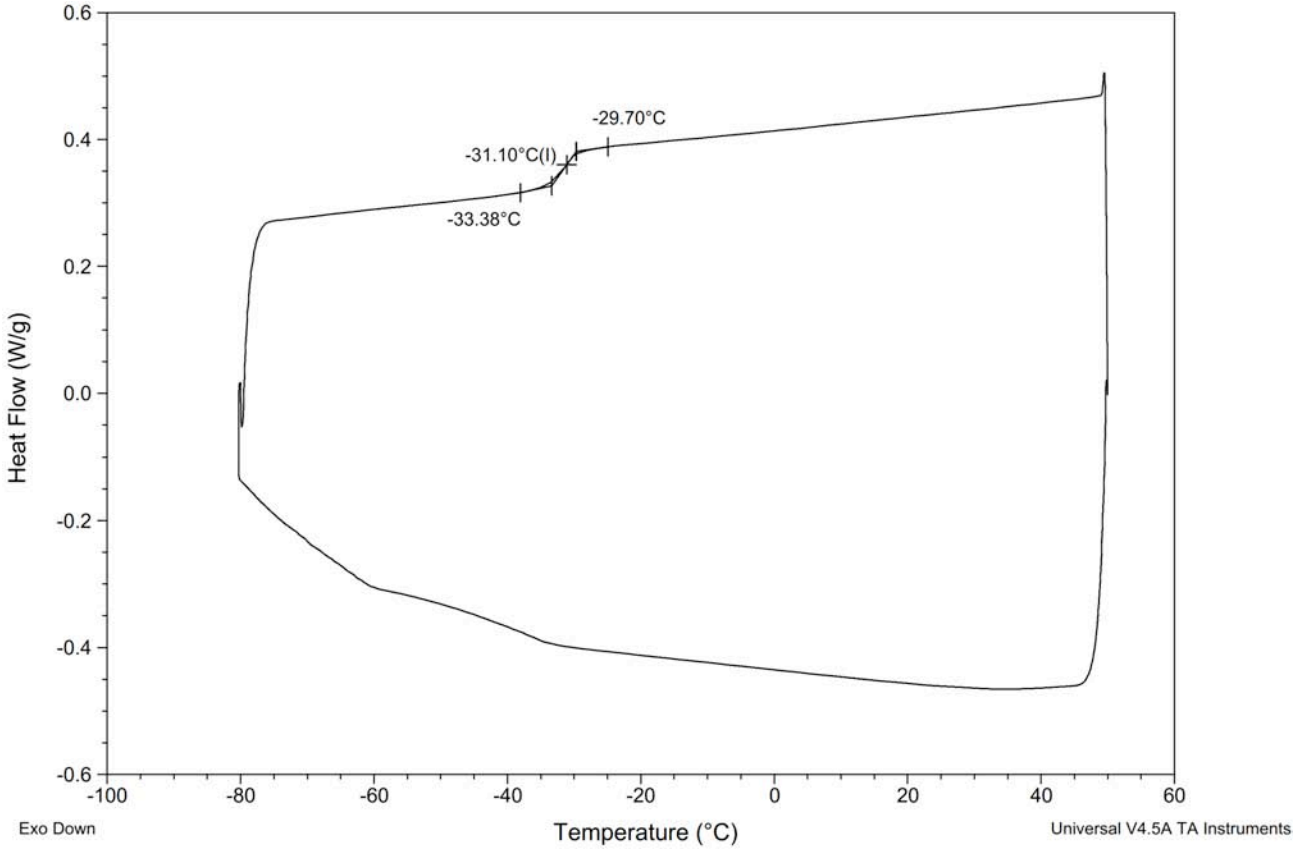


Figure S143. DSC Thermogram of copoly(caprolactone/ hydroxyethylsyringic acid) [50:50] at 1 hour (Table S4, entry 4).

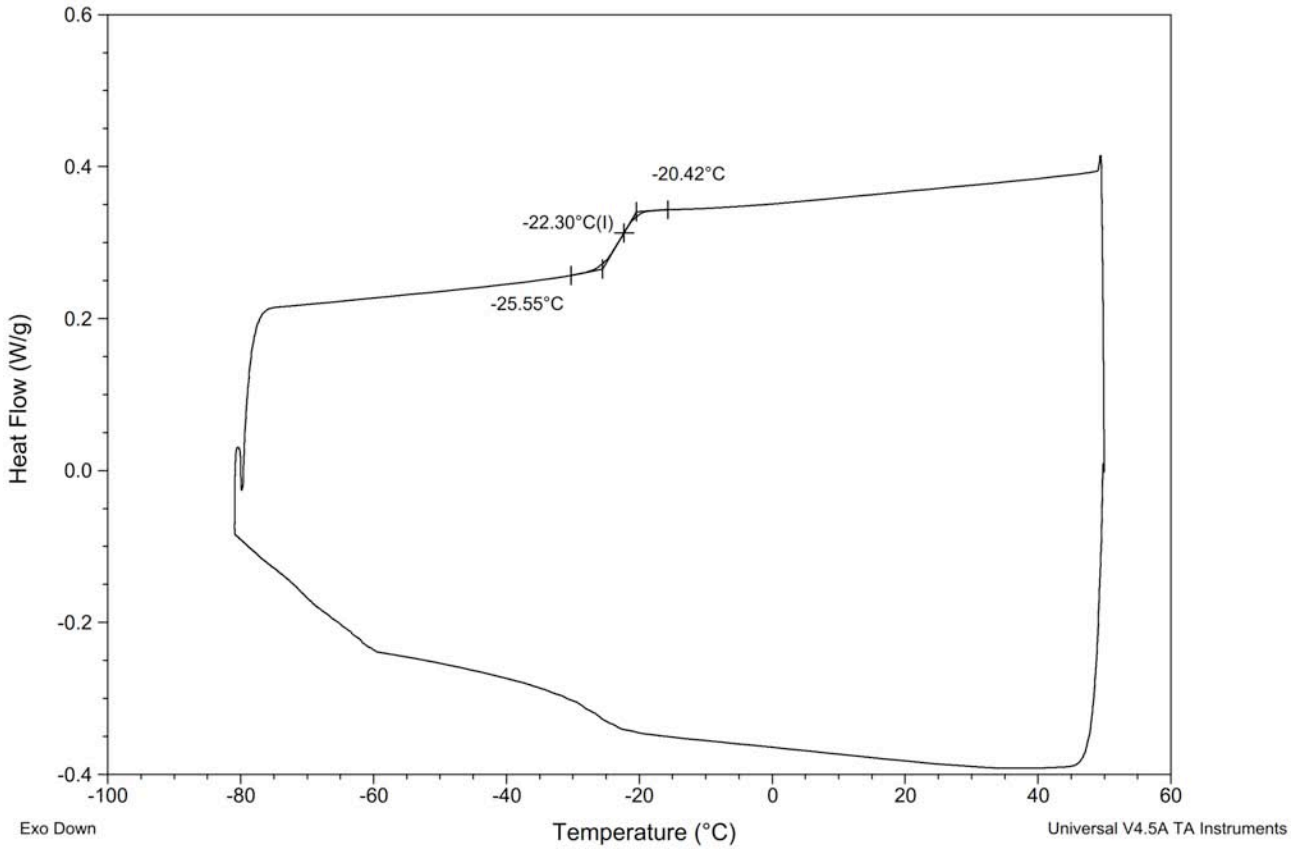


Figure S144. DSC Thermogram of copoly(caprolactone/ hydroxyethylsyringic acid) [50:50] at 1.5 hours (Table S4, entry 5).

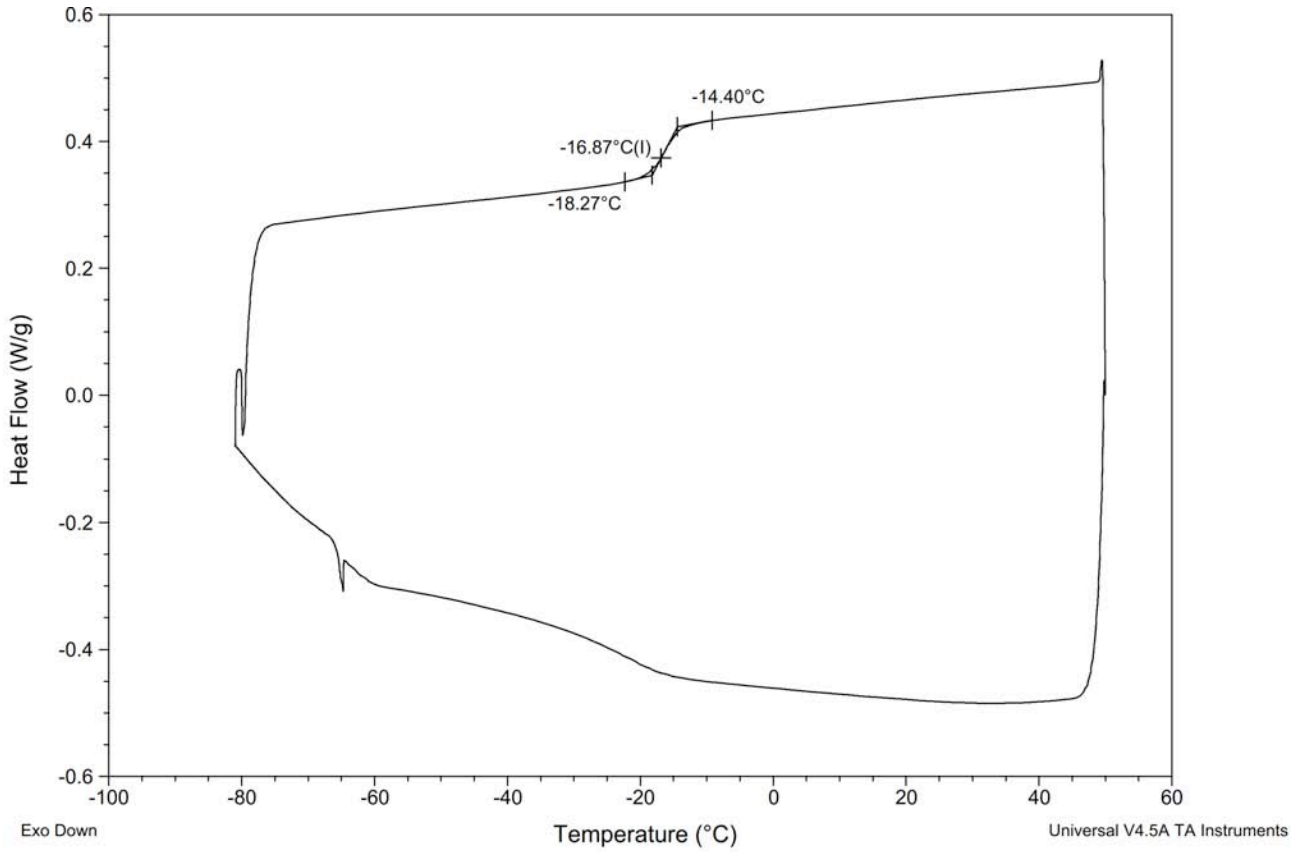


Figure S145. DSC Thermogram of copoly(caprolactone/ hydroxyethylsyringic acid) [50:50] at 2 hours (Table S4, entry 6).

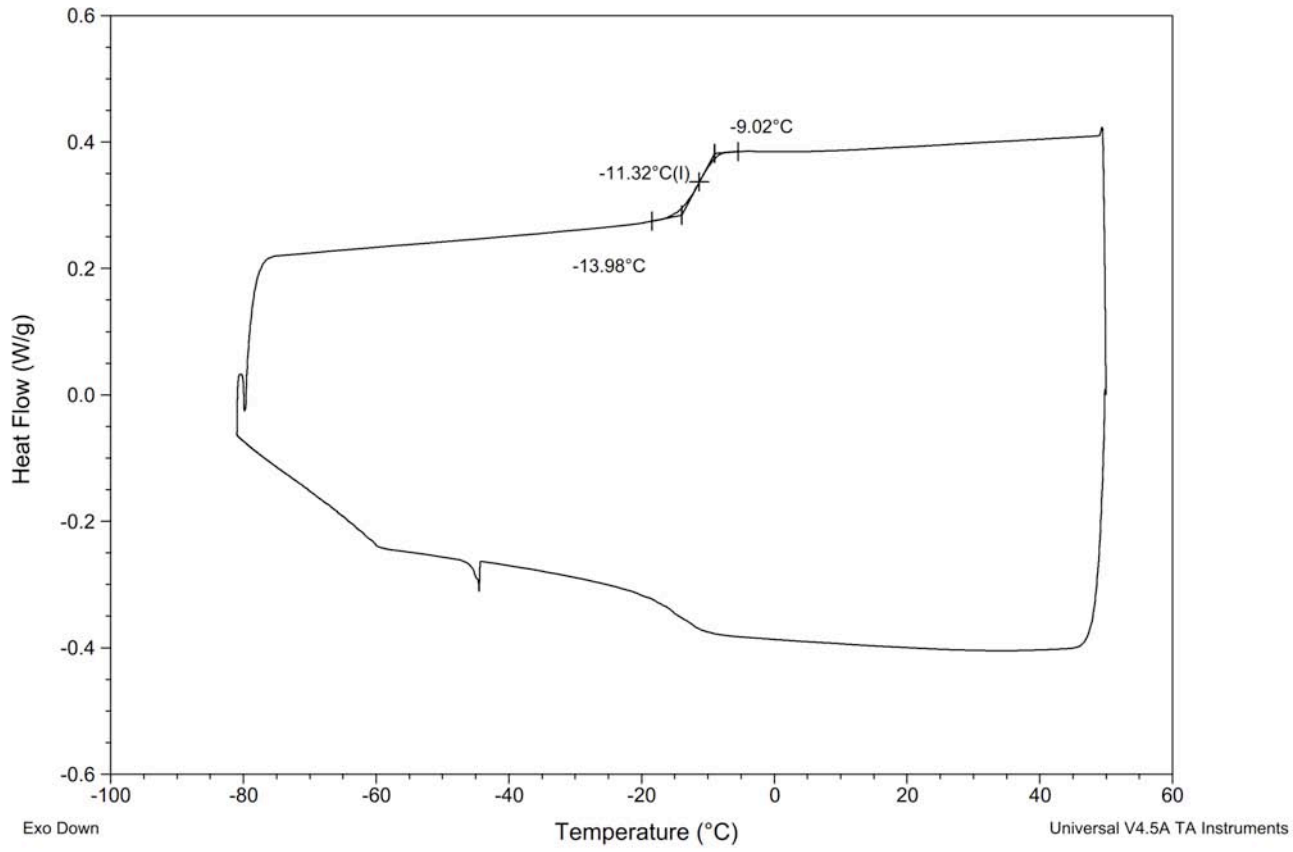


Figure S146. DSC Thermogram of copoly(caprolactone/ hydroxyethylsyringic acid) [50:50] at 2.5 hours (Table S4, entry 7).

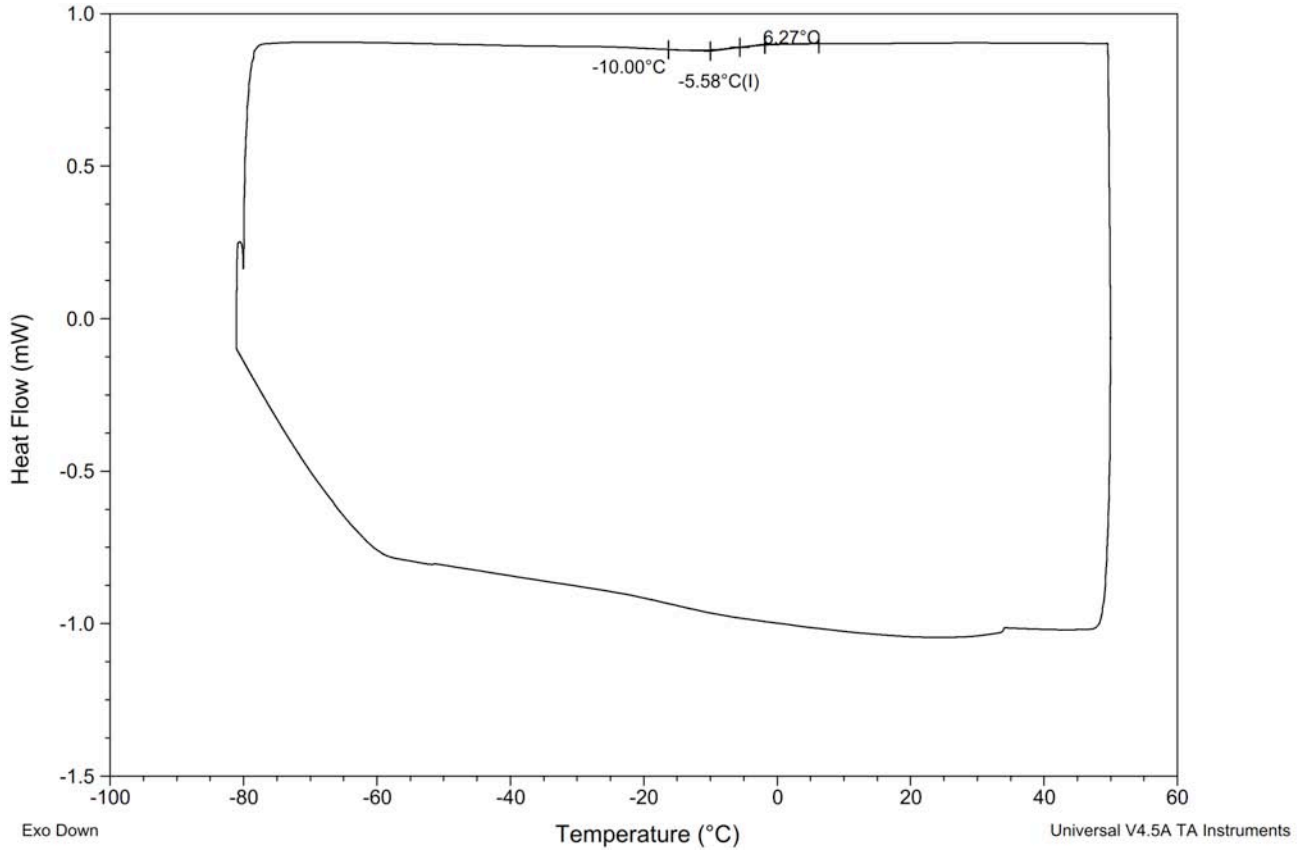


Figure S147. DSC Thermogram of copoly(caprolactone/ hydroxyethylsyringic acid) [50:50] at 3 hours (Table S4, entry 8).

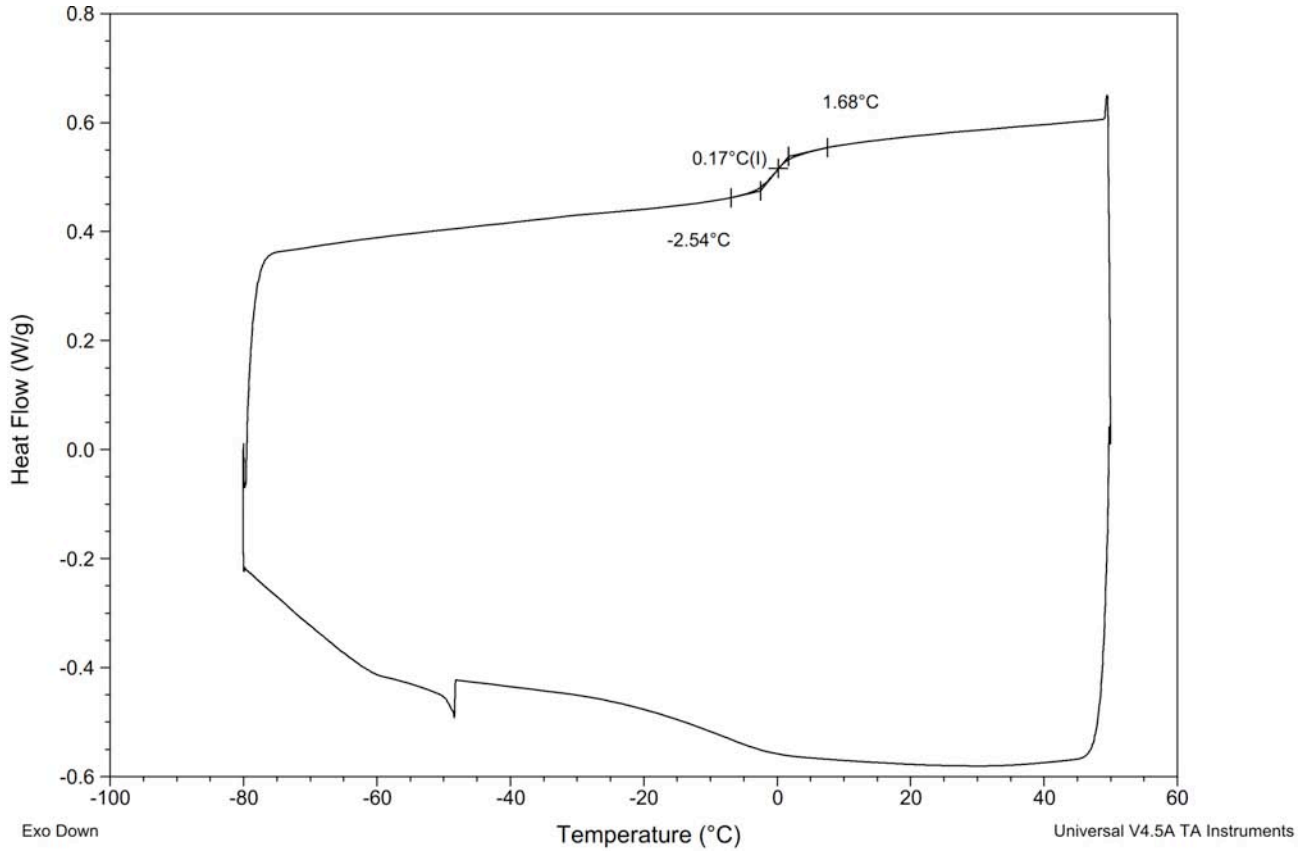


Figure S148. DSC Thermogram of copoly(caprolactone/ hydroxyethylsyringic acid) [50:50] at 3.5 hours (Table S4, entry 9).

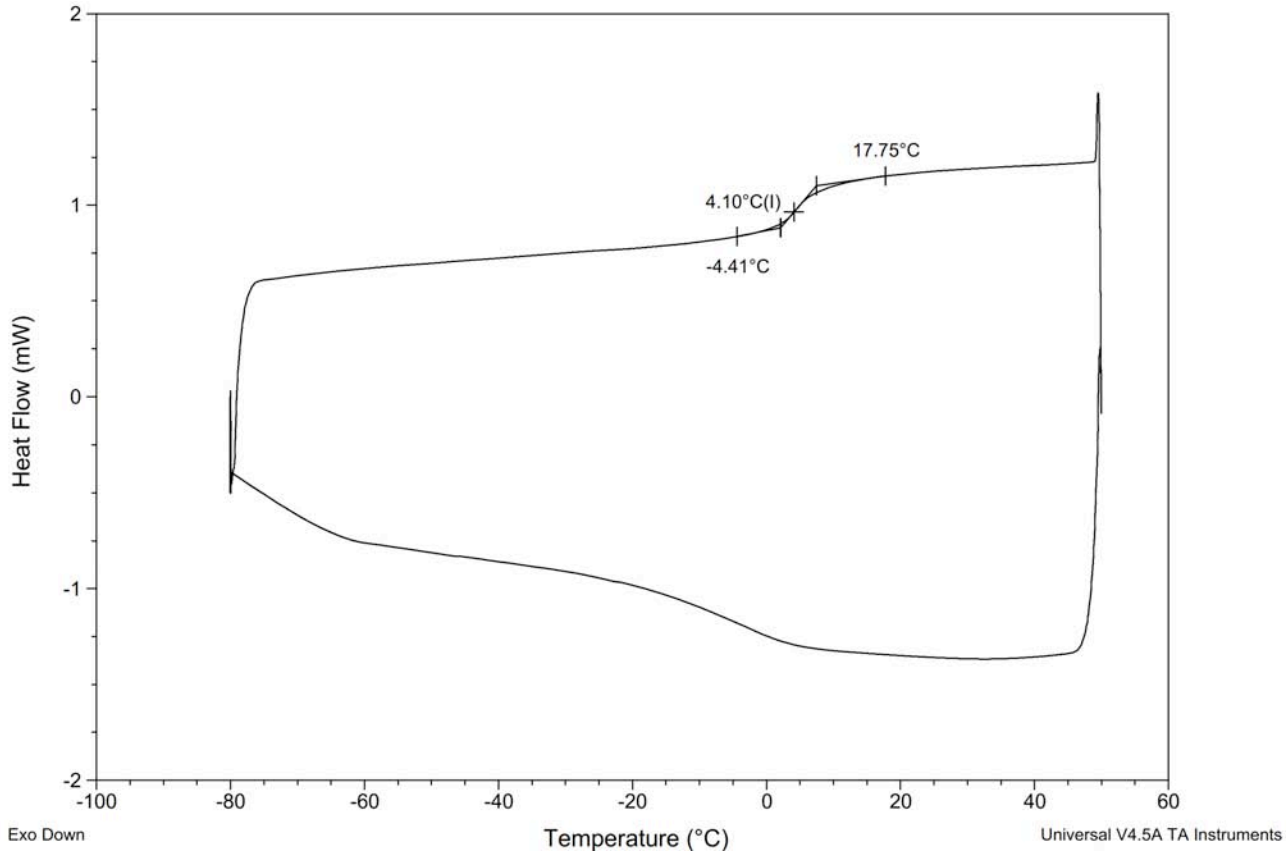


Figure S149. DSC Thermogram of copoly(caprolactone/ hydroxyethylsyringic acid) [50:50] at 4 hours (Table S4, entry 10).

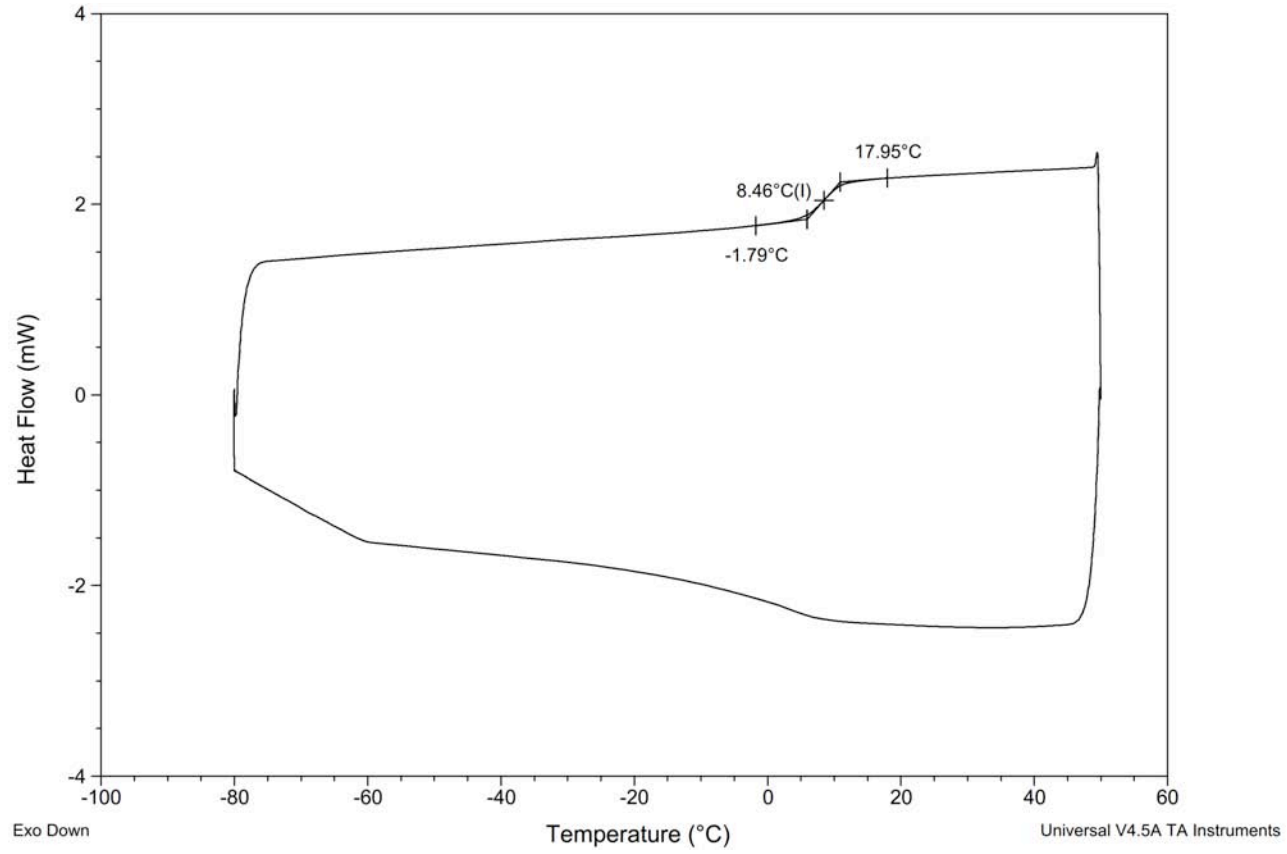


Figure S150. DSC Thermogram of copoly(caprolactone/ hydroxyethylsyringic acid) [50:50] at 4.5 hours (Table S4, entry 11).

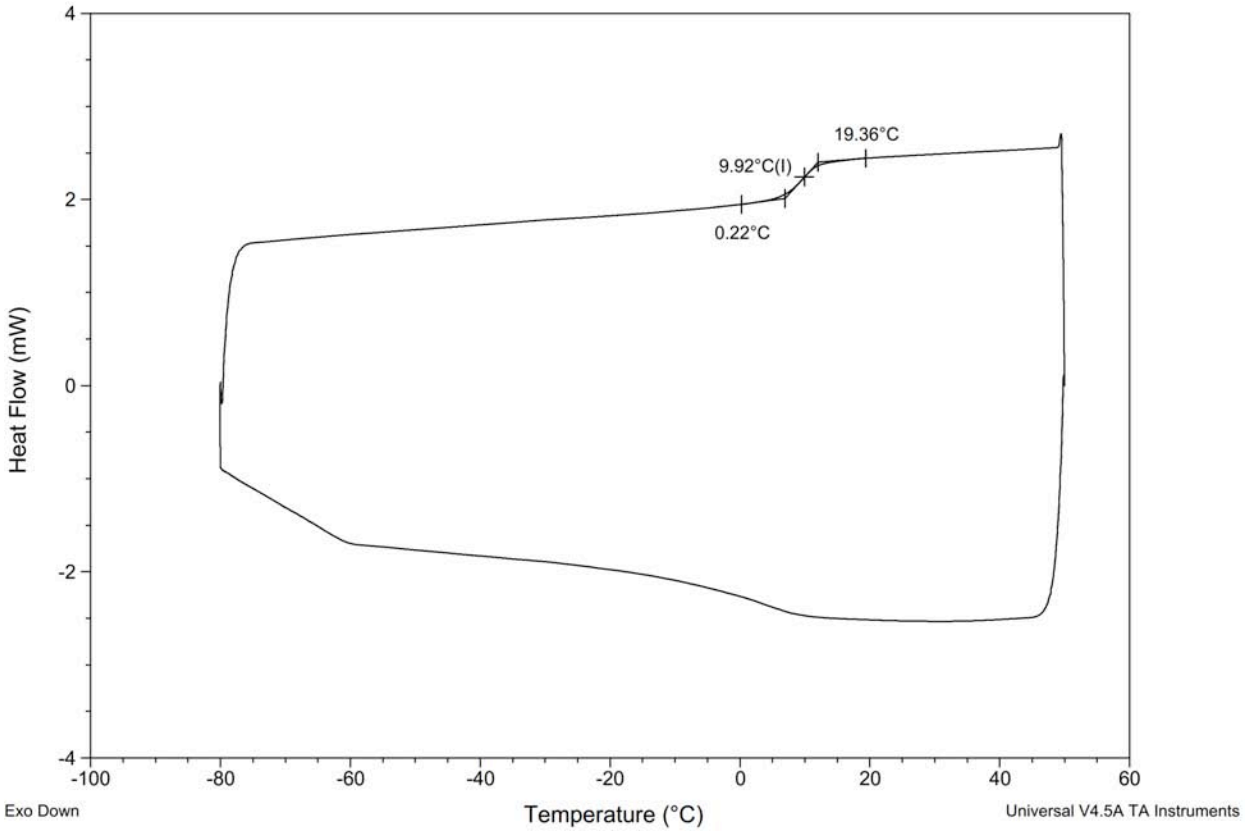


Figure S151. DSC Thermogram of copoly(caprolactone/ hydroxyethylsyringic acid) [50:50] at 5 hours (Table S4, entry 12).

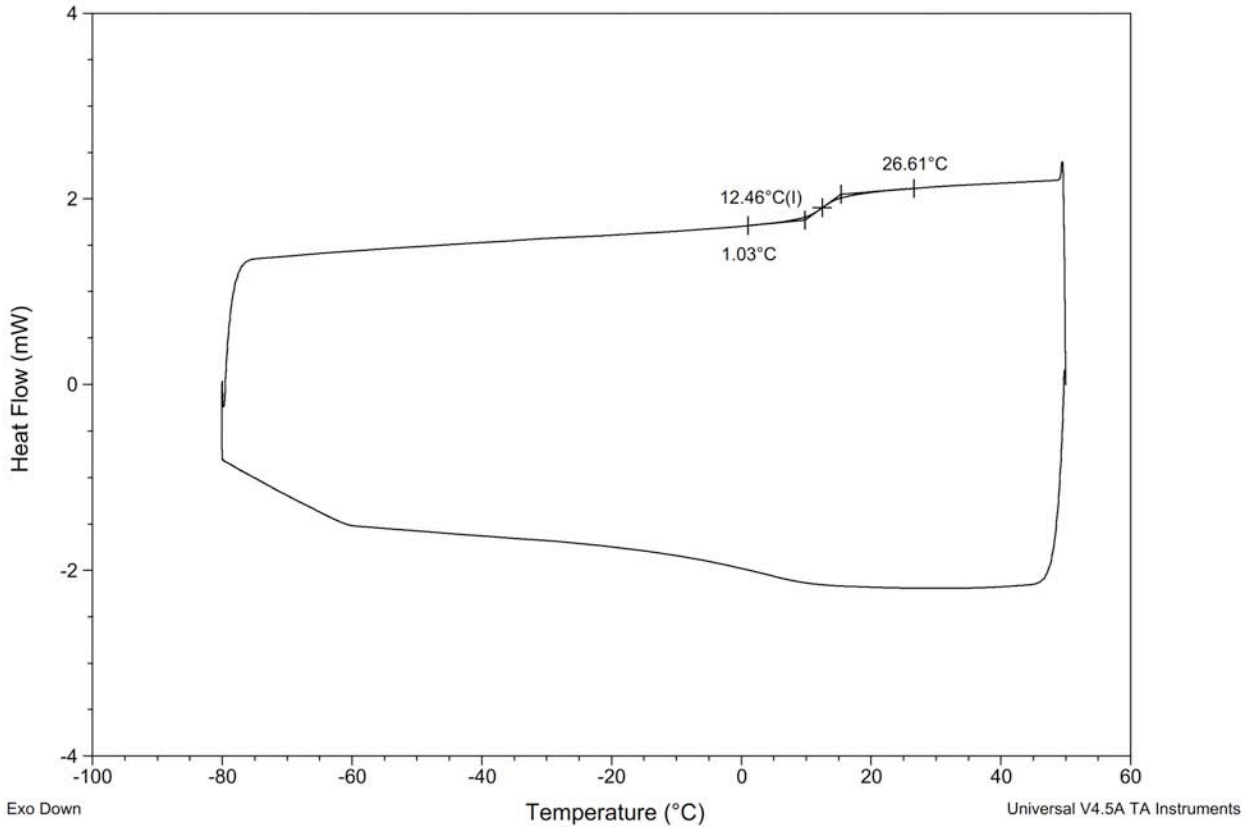


Figure S152. DSC Thermogram of copoly(caprolactone/ hydroxyethylsyringic acid) [50:50] at 6 hours (Table S4, entry 13).

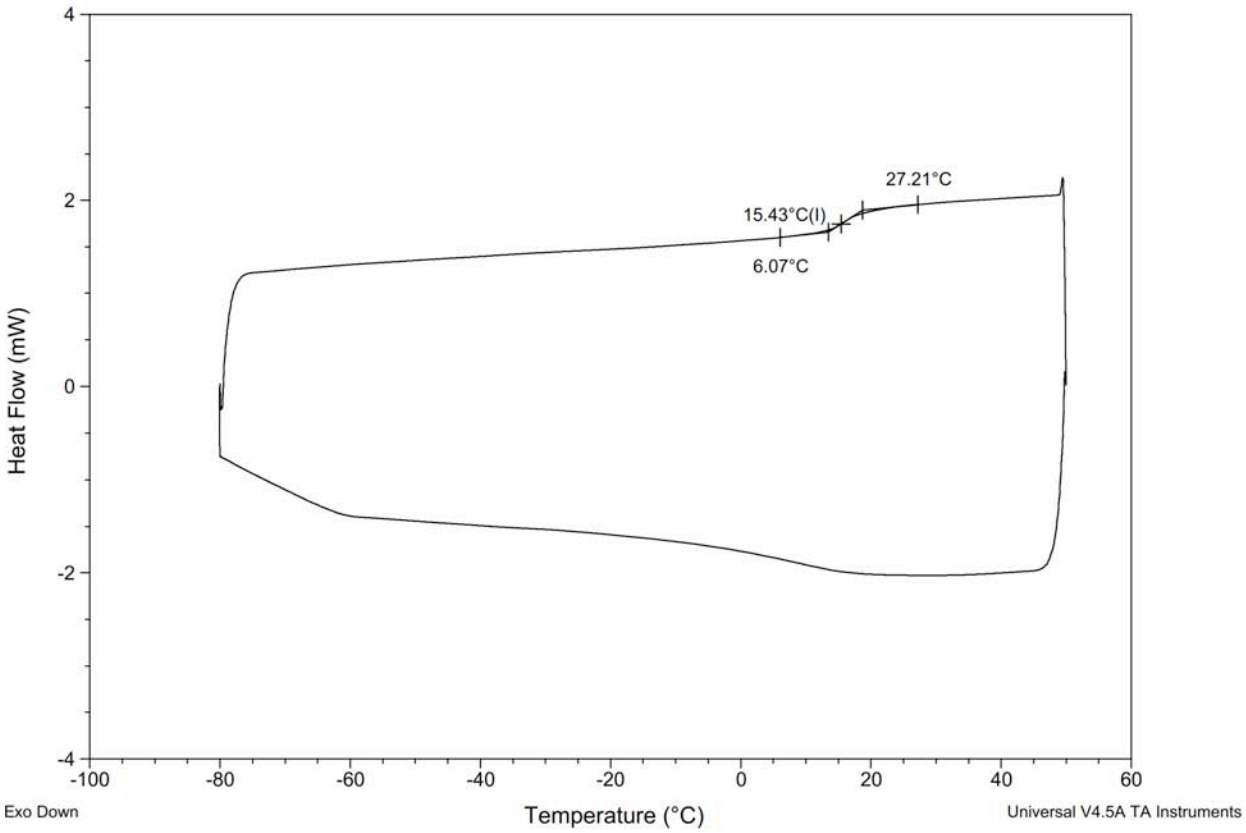


Figure S153. DSC Thermogram of copoly(caprolactone/ hydroxyethylsyringic acid) [50:50] at 7 hours (Table S4, entry 14).

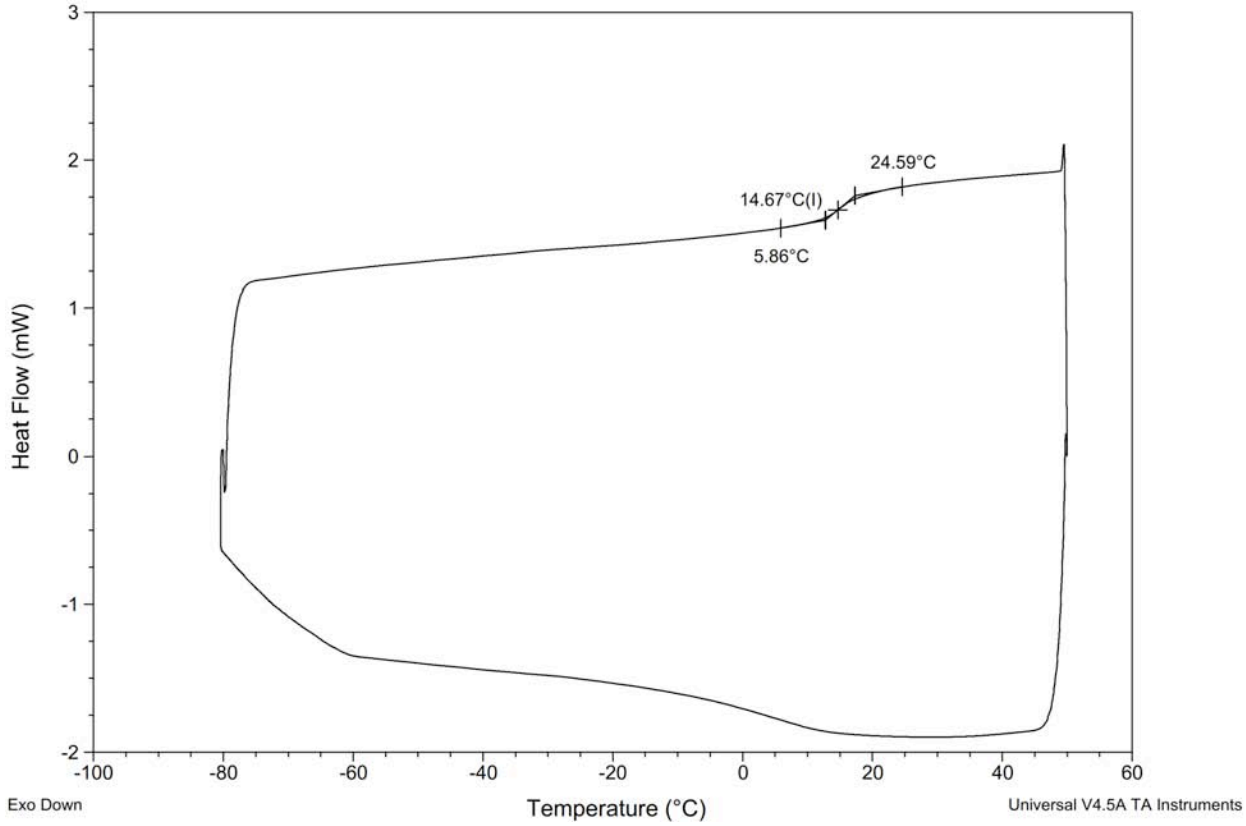


Figure S154. DSC Thermogram of copoly(caprolactone/ hydroxyethylsyringic acid) [50:50] at 8 hours (Table S4, entry 15).

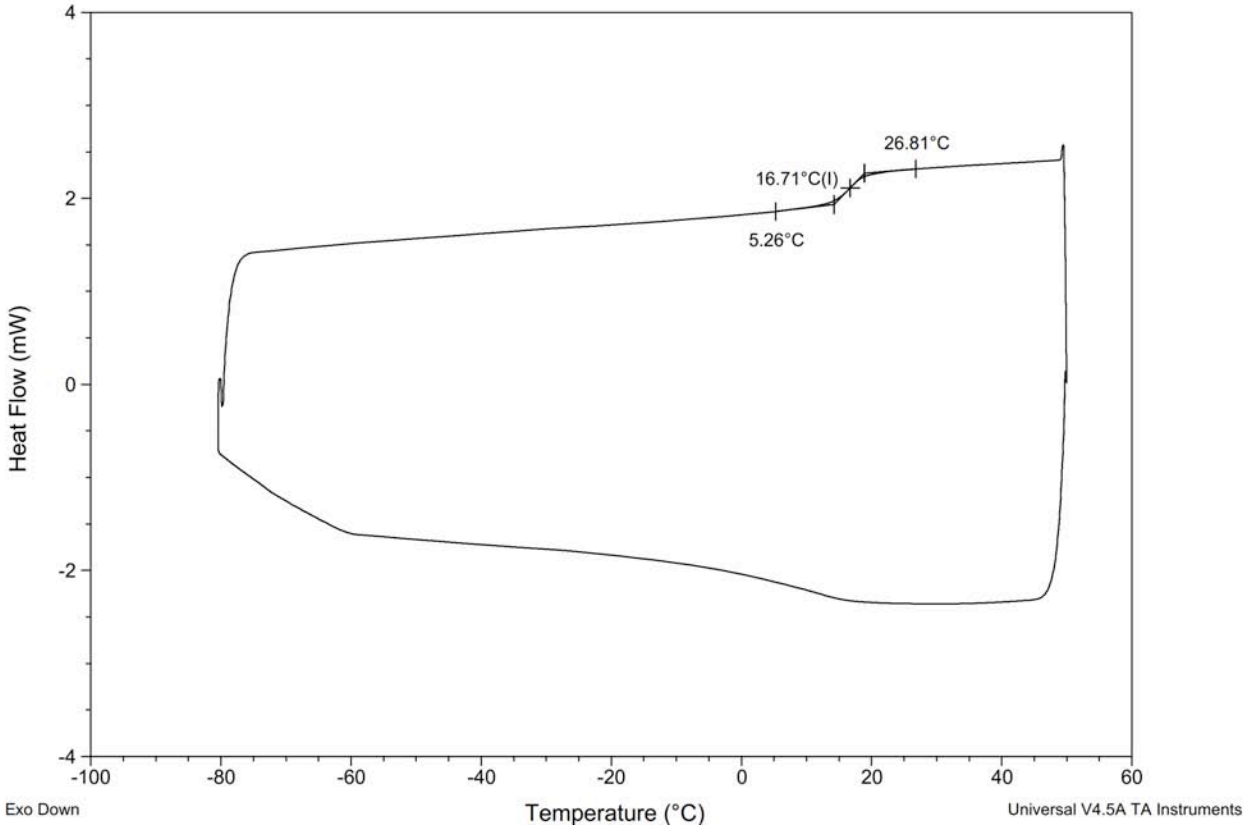


Figure S155. DSC Thermogram of copoly(caprolactone/ hydroxyethylsyringic acid) [50:50] at 9 hours (Table S4, entry 16).

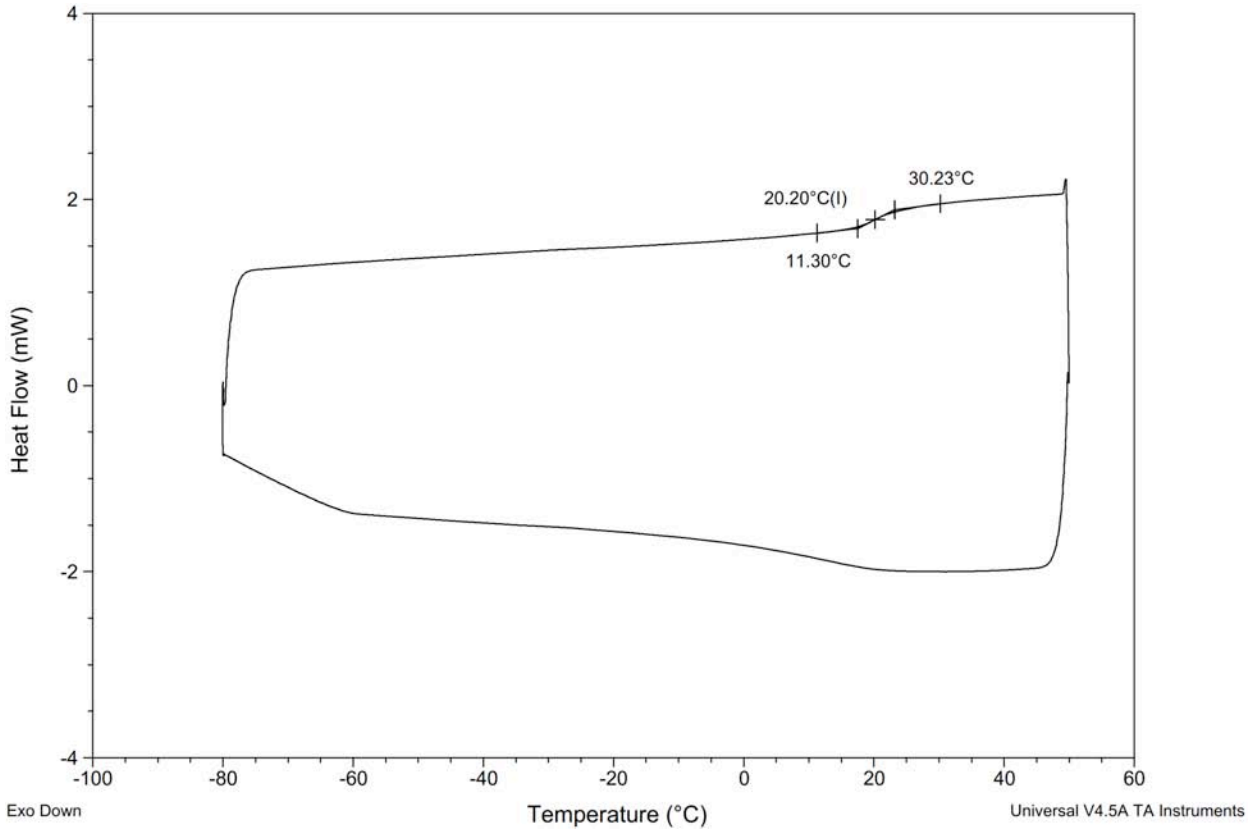


Figure S156. DSC Thermogram of copoly(caprolactone/ hydroxyethylsyringic acid) [50:50] at 10 hours (Table S4, entry 17).

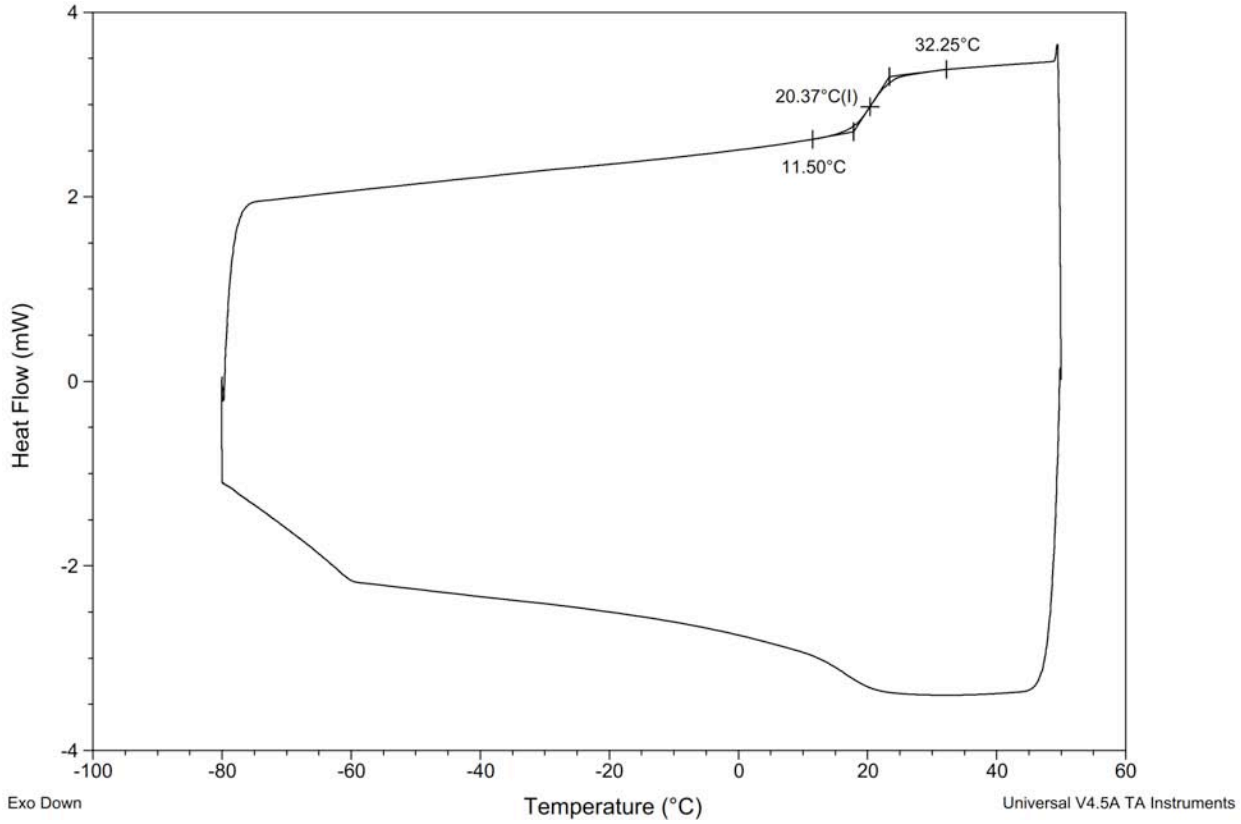


Figure S157. DSC Thermogram of copoly(caprolactone/ hydroxyethylsyringic acid) [50:50] at 13 hours (Table S4, entry 18).

Thermogravimetric Analysis (TGA) Thermograms

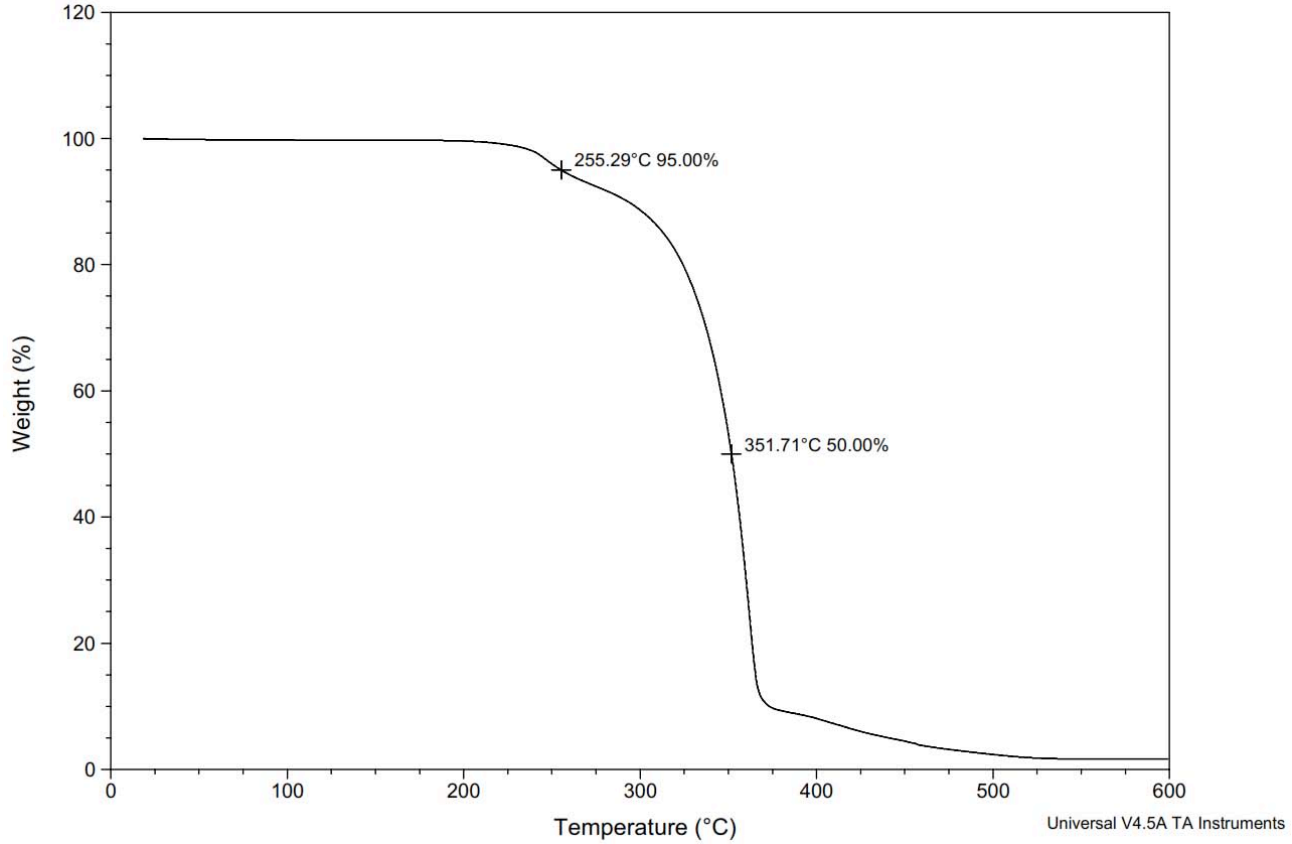


Figure S158. TGA Thermogram of polycaprolactone (Table S2, entry 1).

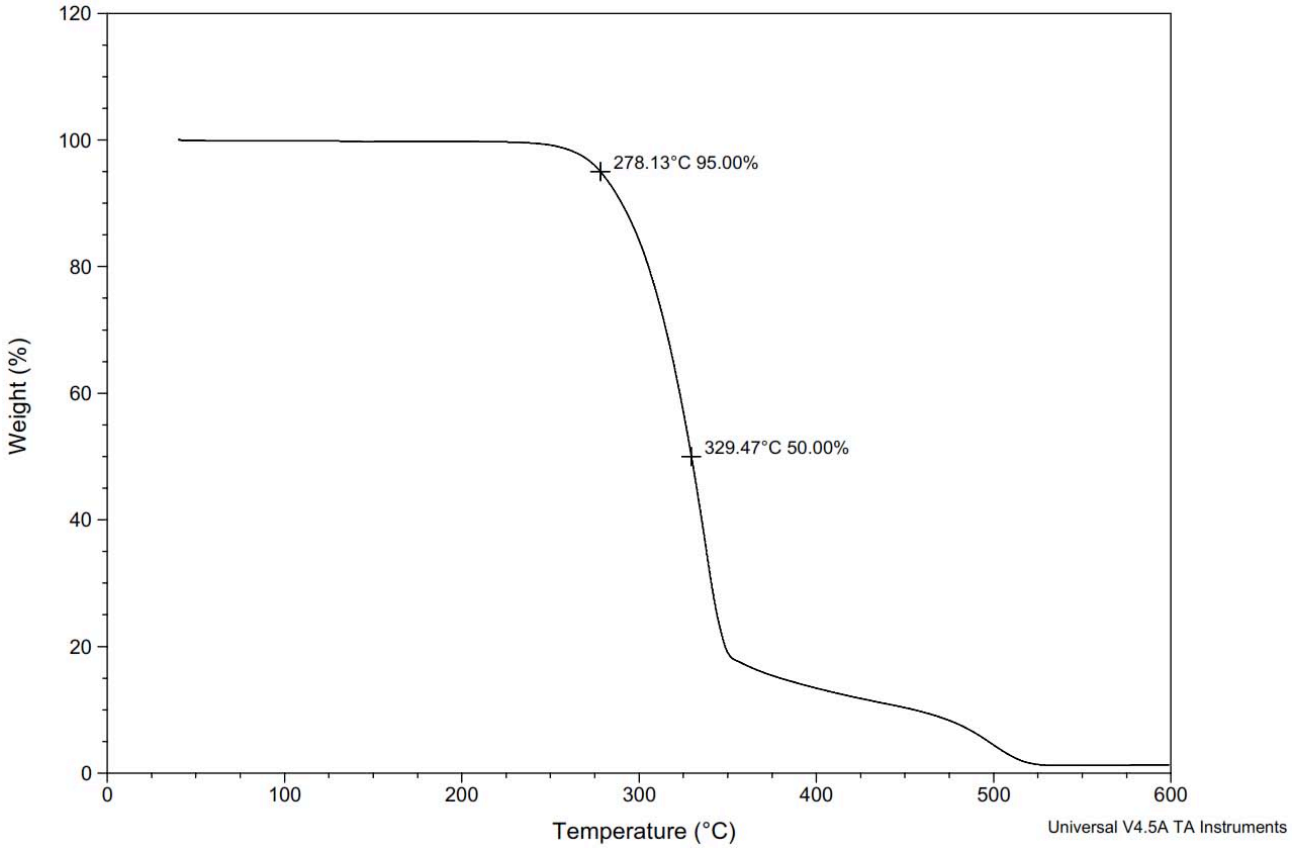


Figure S159. TGA Thermogram of copoly(caprolactone/ hydroxyethylsyringic acid) [90:10] (Table S2, entry 2).

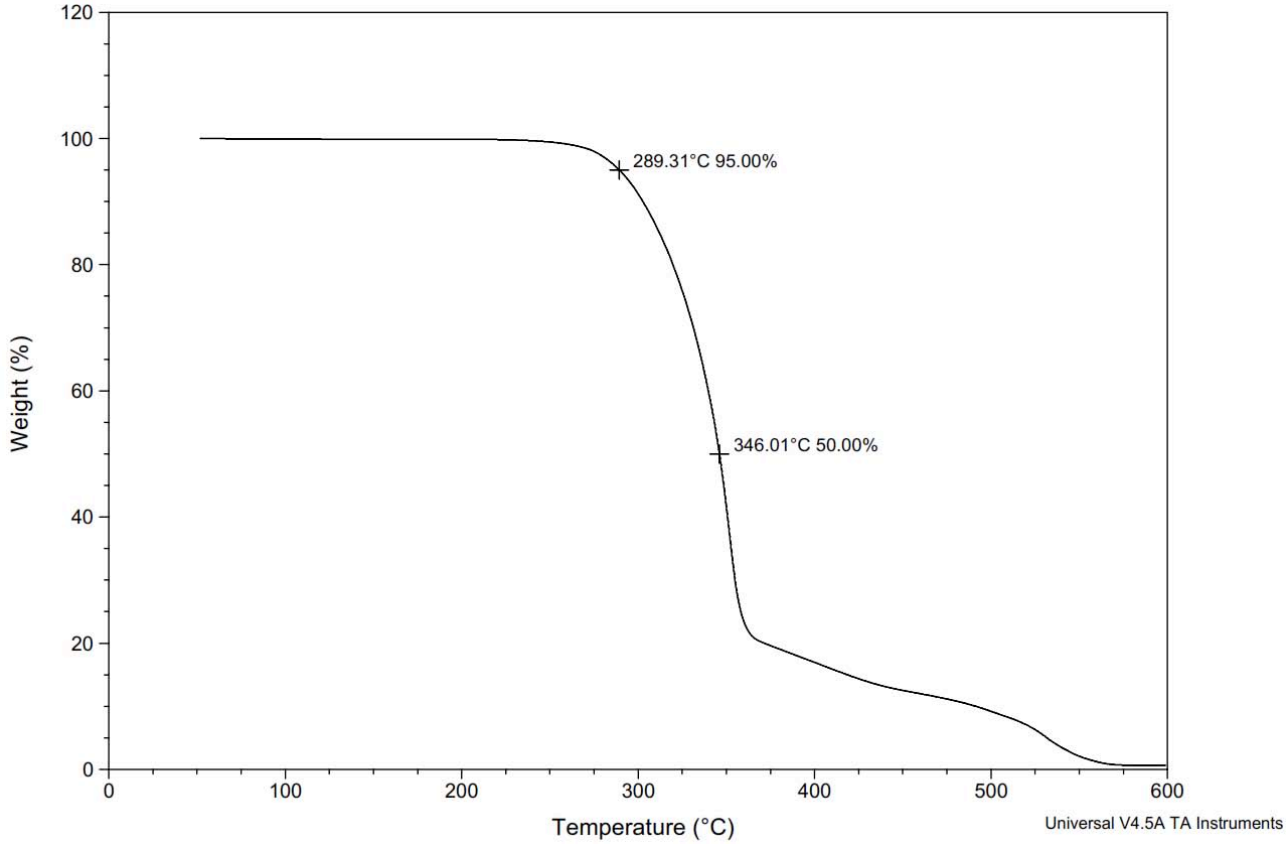


Figure S160. TGA Thermogram of copoly(caprolactone/ hydroxyethylsyringic acid) [80:20] (Table S2, entry 3).

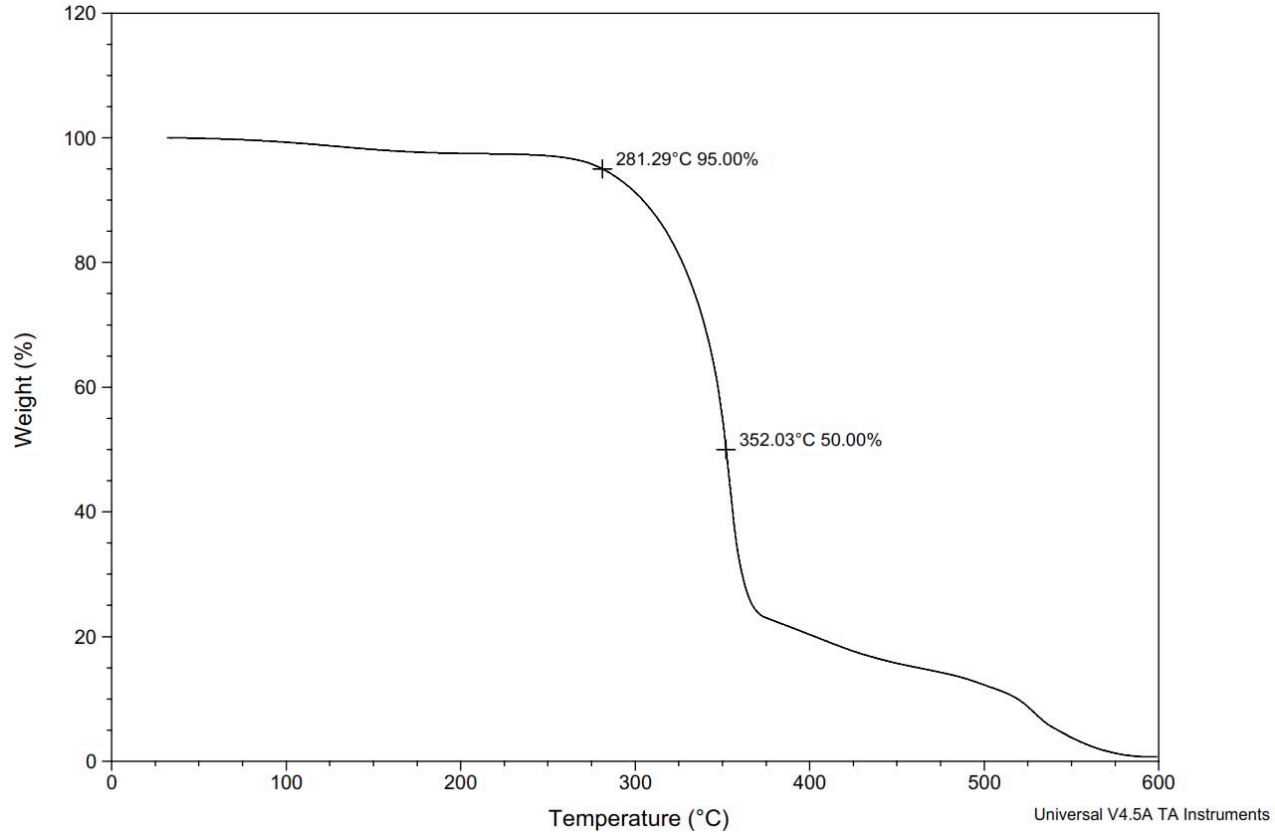


Figure S161. TGA Thermogram of copoly(caprolactone/ hydroxyethylsyringic acid) [70:30] (Table S2, entry 4).

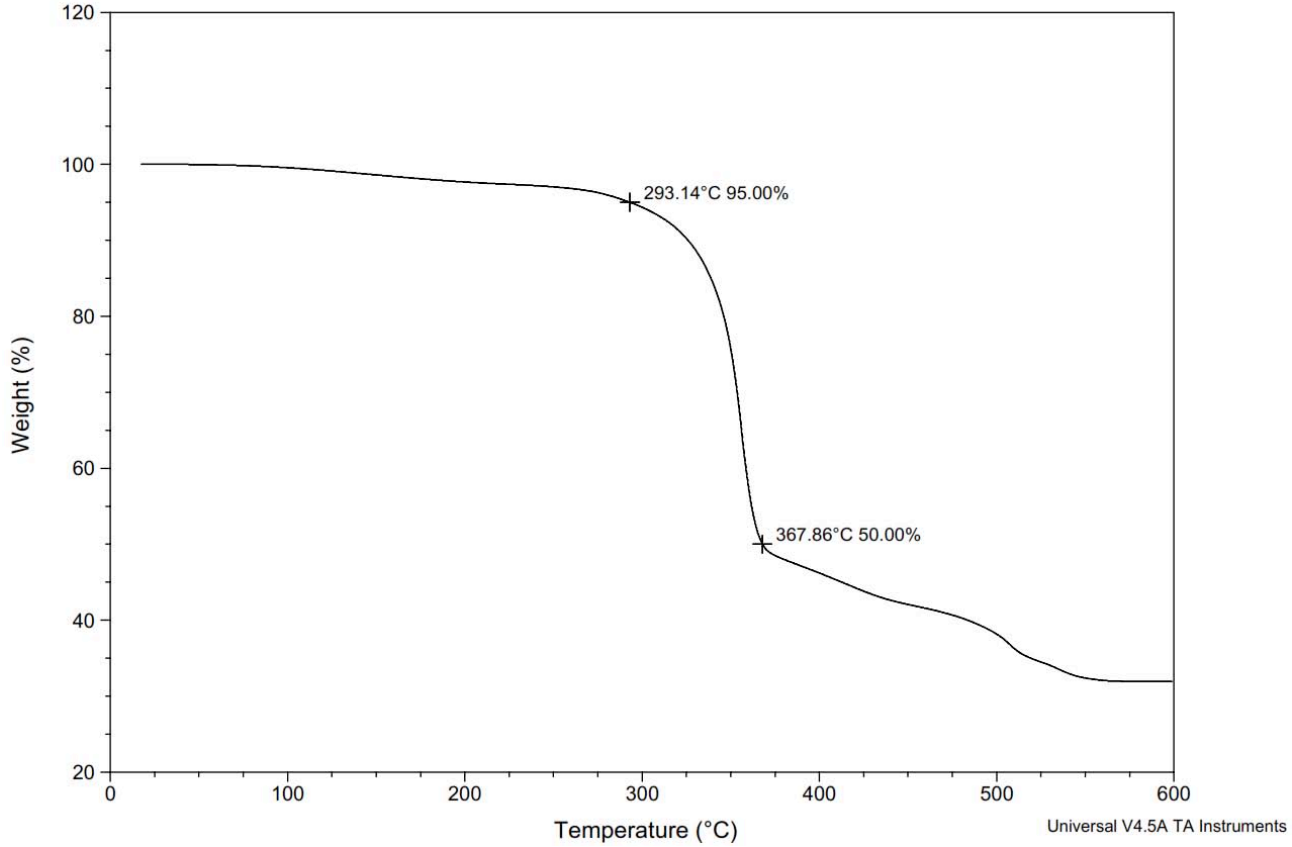


Figure S162. TGA Thermogram of copoly(caprolactone/ hydroxyethylsyringic acid) [60:40] (Table S2, entry 5).

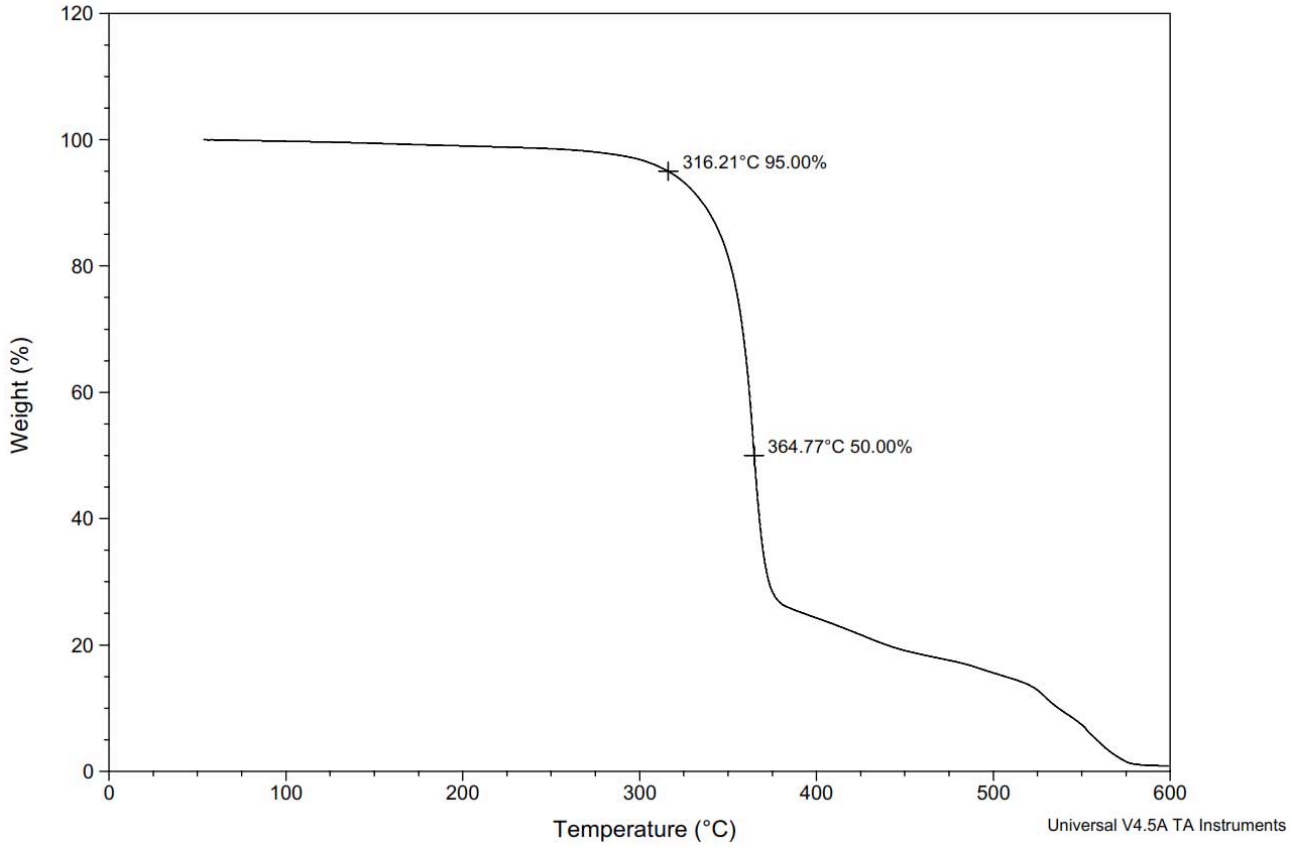


Figure S163. TGA Thermogram of copoly(caprolactone/ hydroxyethylsyringic acid) [50:50] (Table S2, entry 6).

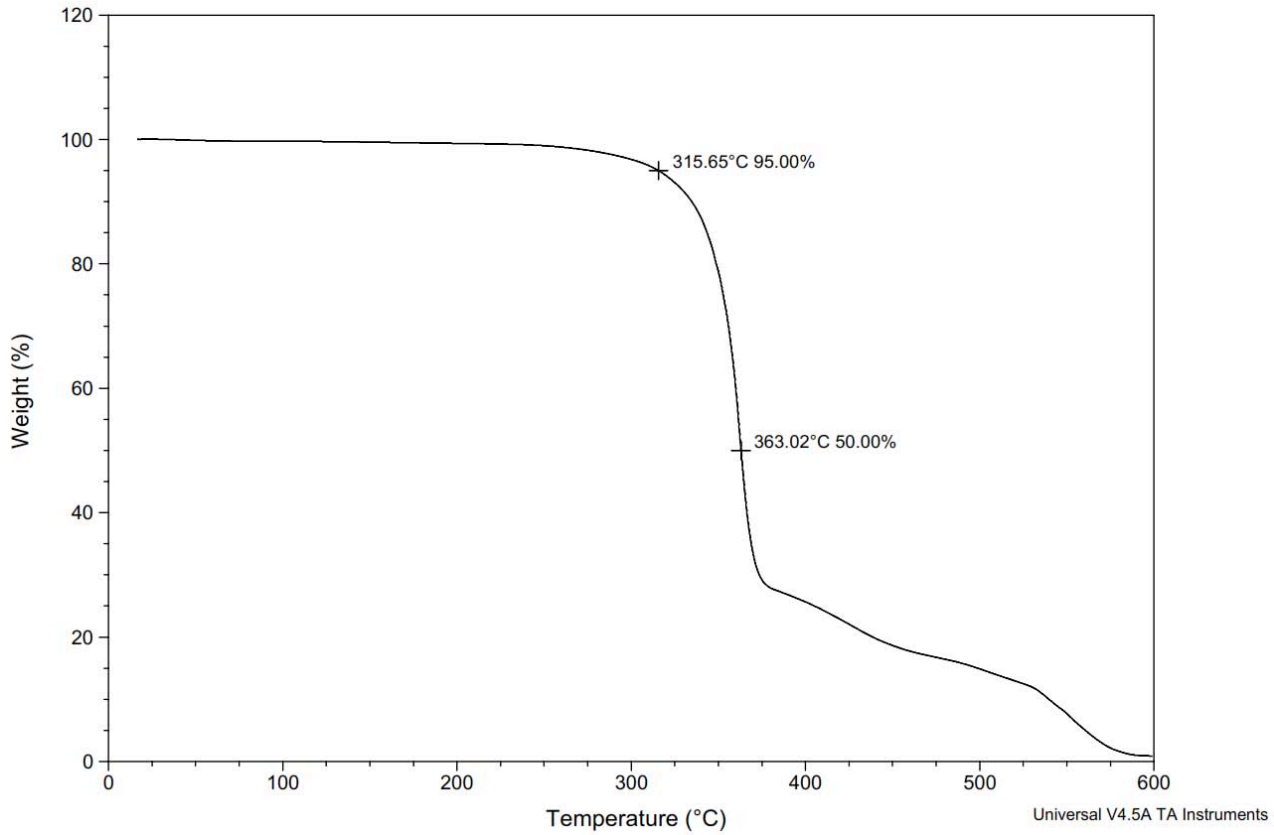


Figure S164. TGA Thermogram of copoly(caprolactone/ hydroxyethylsyringic acid) [40:60] (Table S2, entry 7).

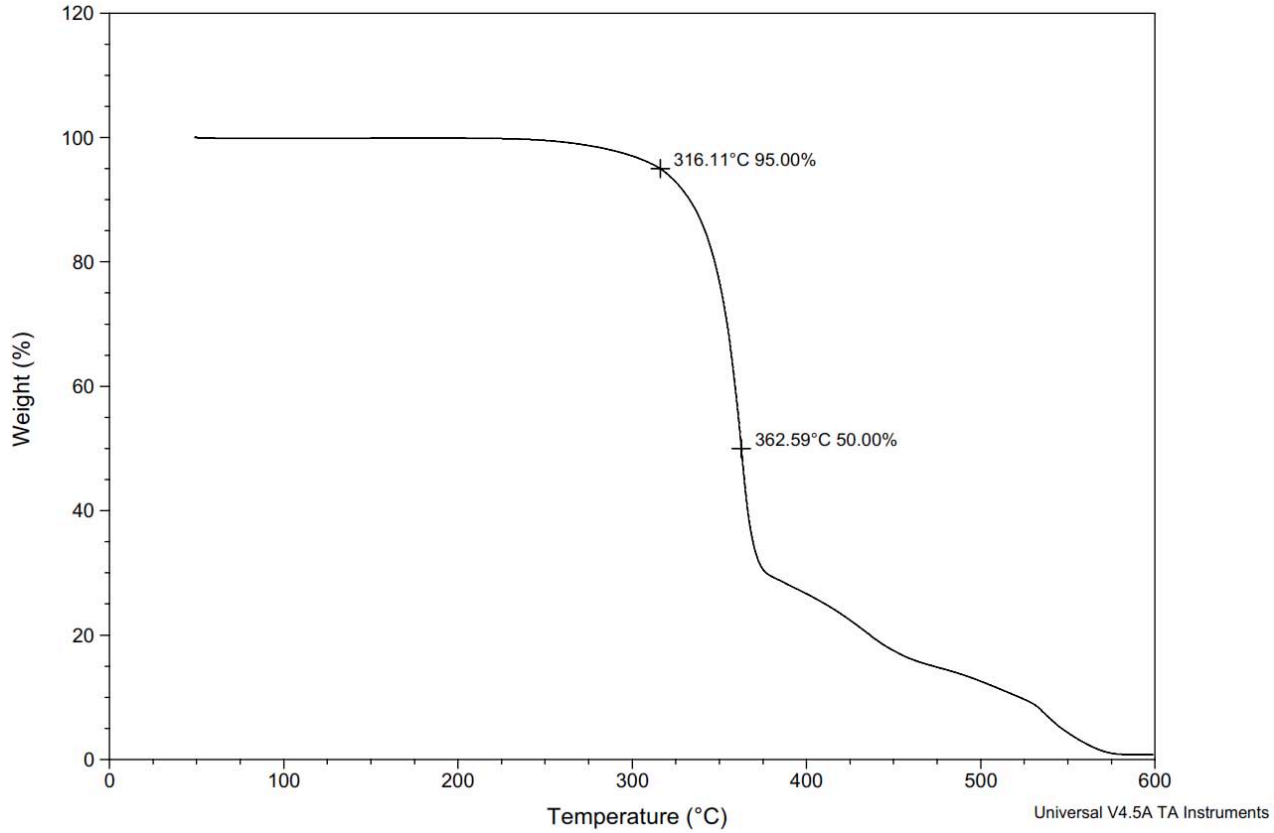


Figure S165. TGA Thermogram of copoly(caprolactone/ hydroxyethylsyringic acid) [30:70] (Table S2, entry 8).

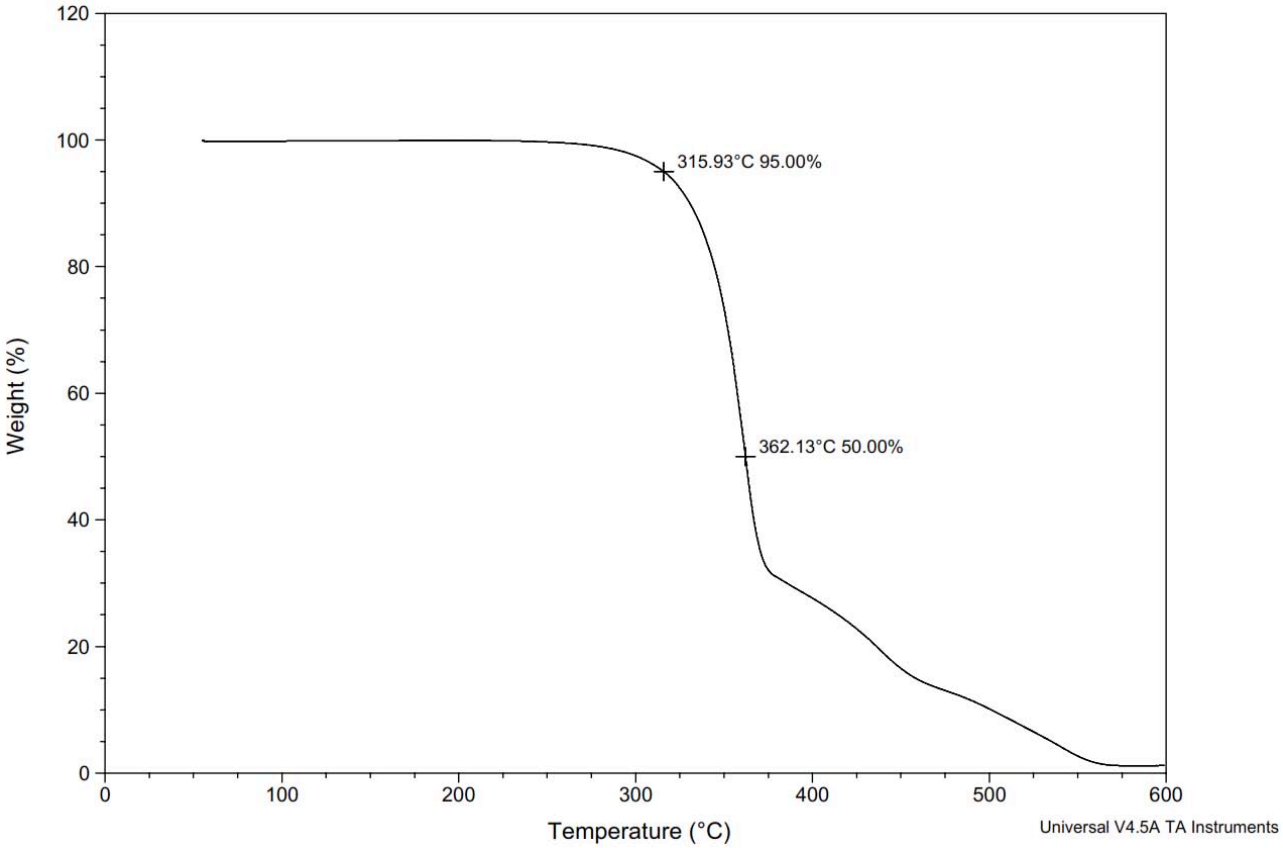


Figure S166. TGA Thermogram of copoly(caprolactone/ hydroxyethylsyringic acid) [20:80] (Table S2, entry 9).

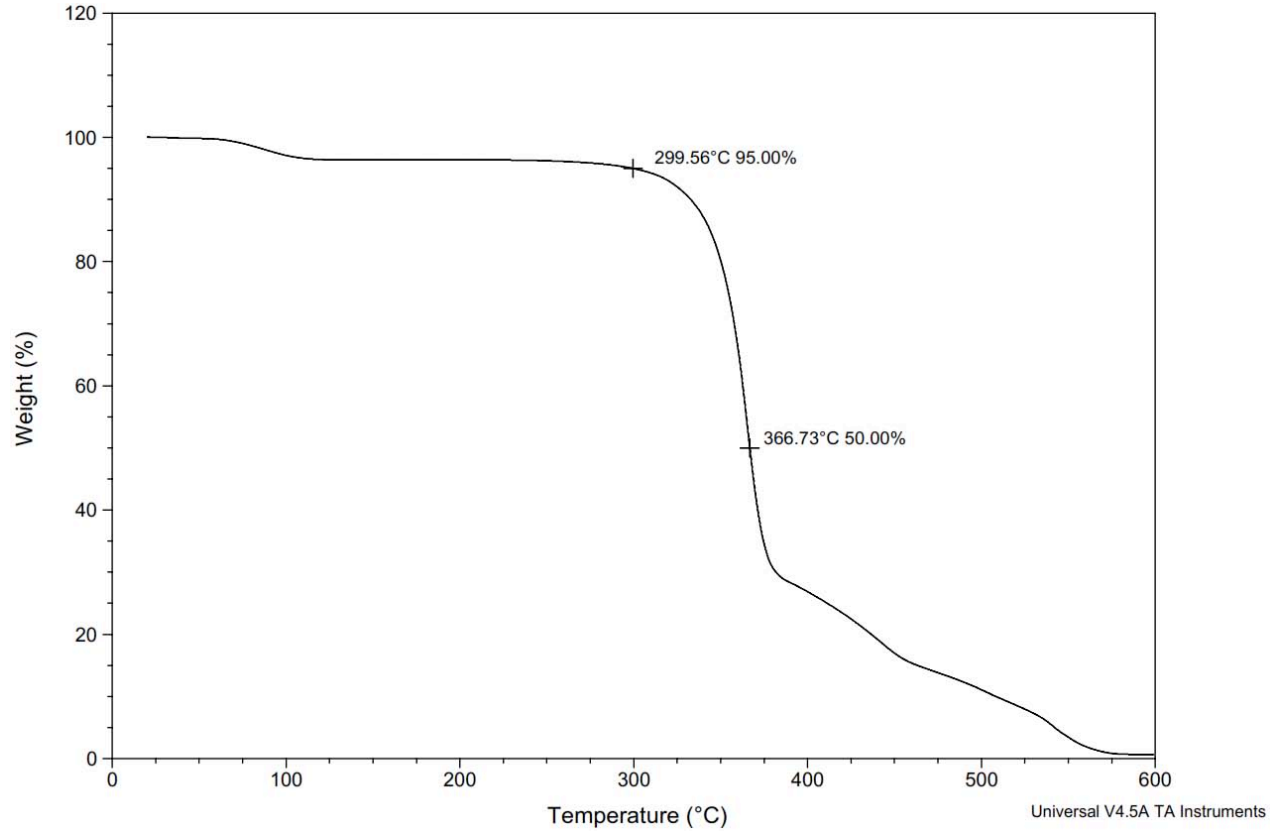


Figure S167. TGA Thermogram of copoly(caprolactone/ hydroxyethylsyringic acid) [10:90] (Table S2, entry 10).

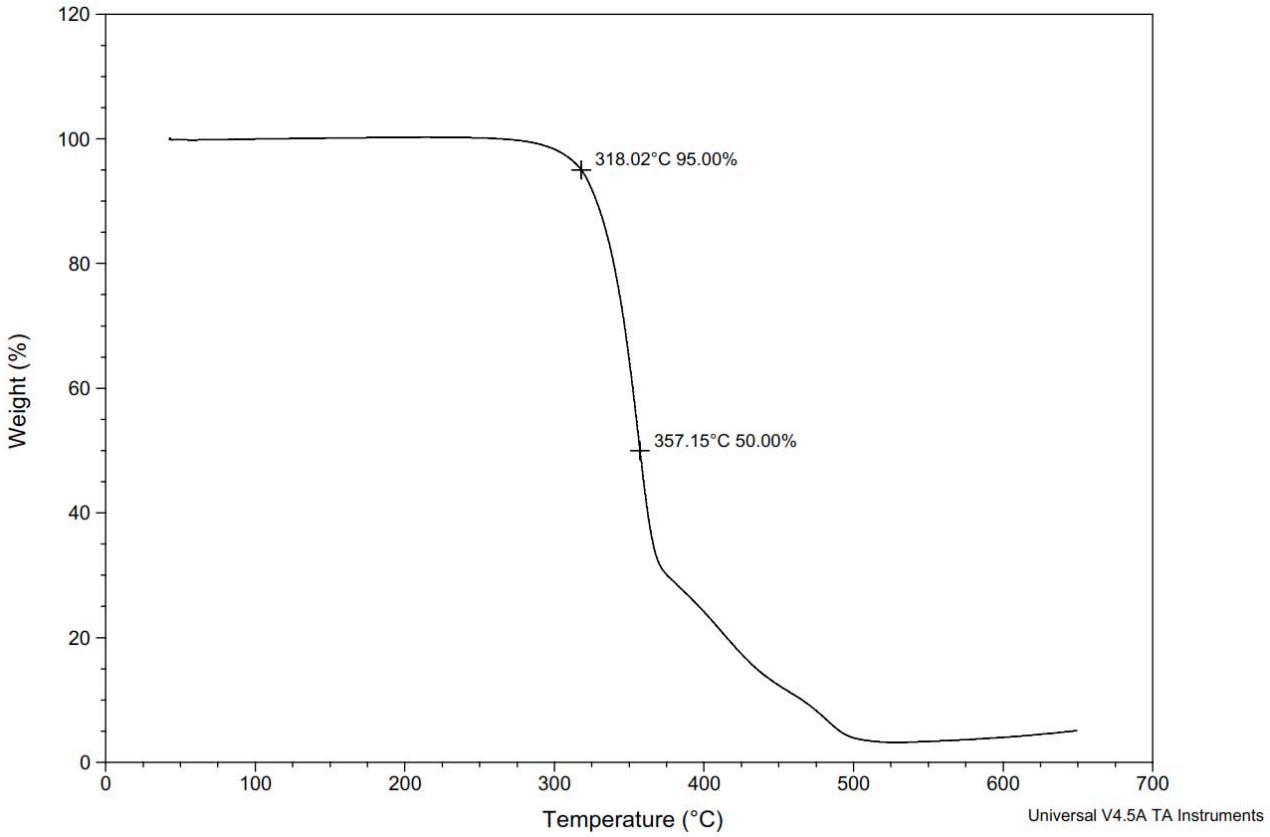


Figure S168. TGA Thermogram of polyethylene synringate (Table S2, entry 11).

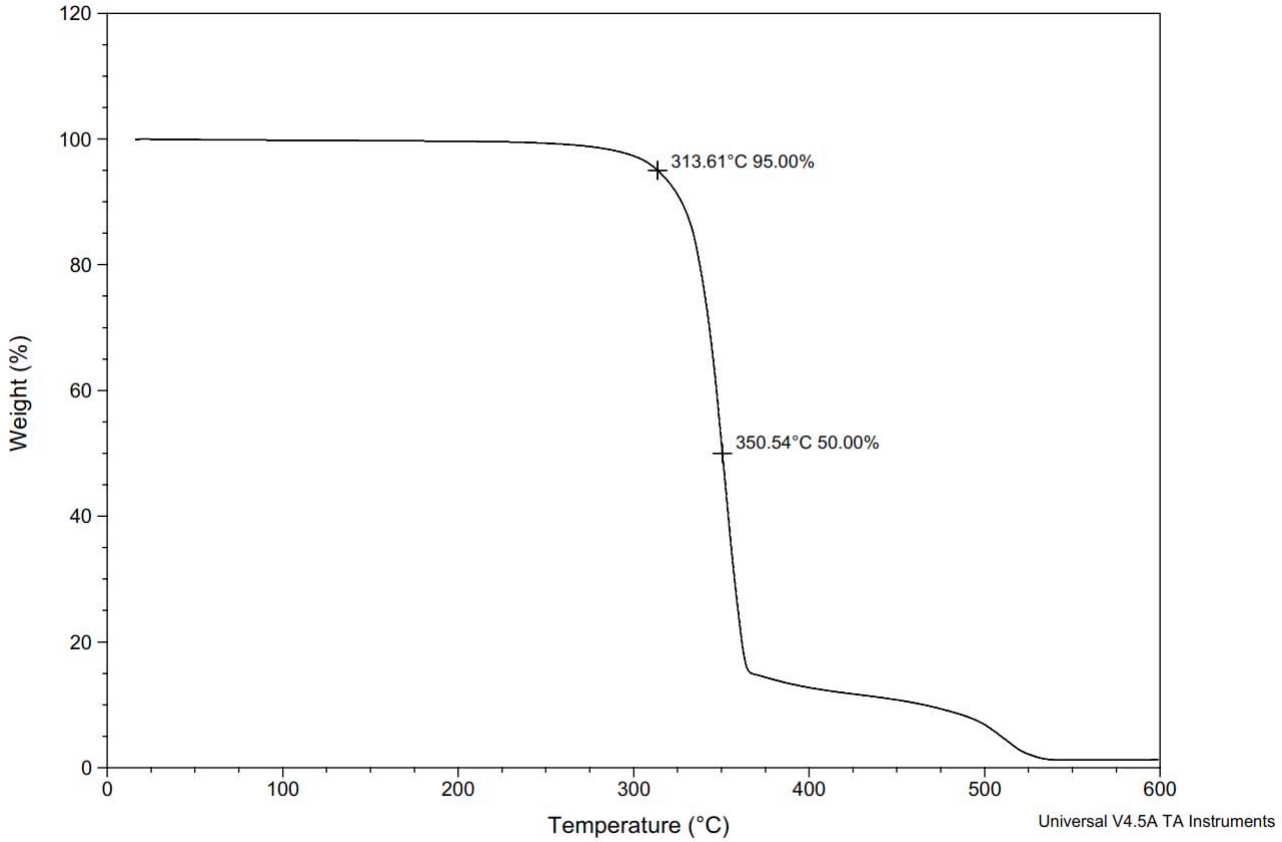


Figure S169. TGA Thermogram of copoly(caprolactone/ hydroxyethylvanillic acid) [90:10] (Table S2, entry 12).

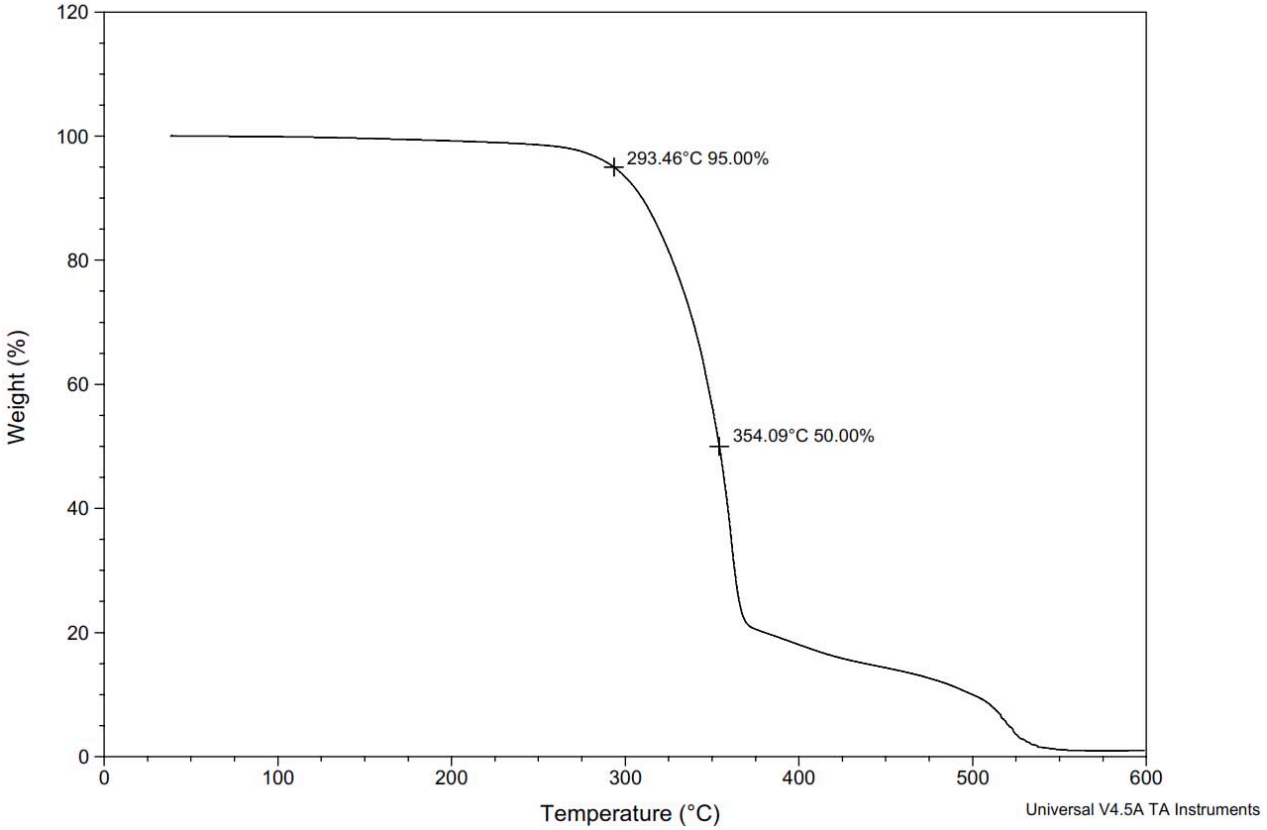


Figure S170. TGA Thermogram of copoly(caprolactone/ hydroxyethylvanillic acid) [80:20] (Table S2, entry 13).

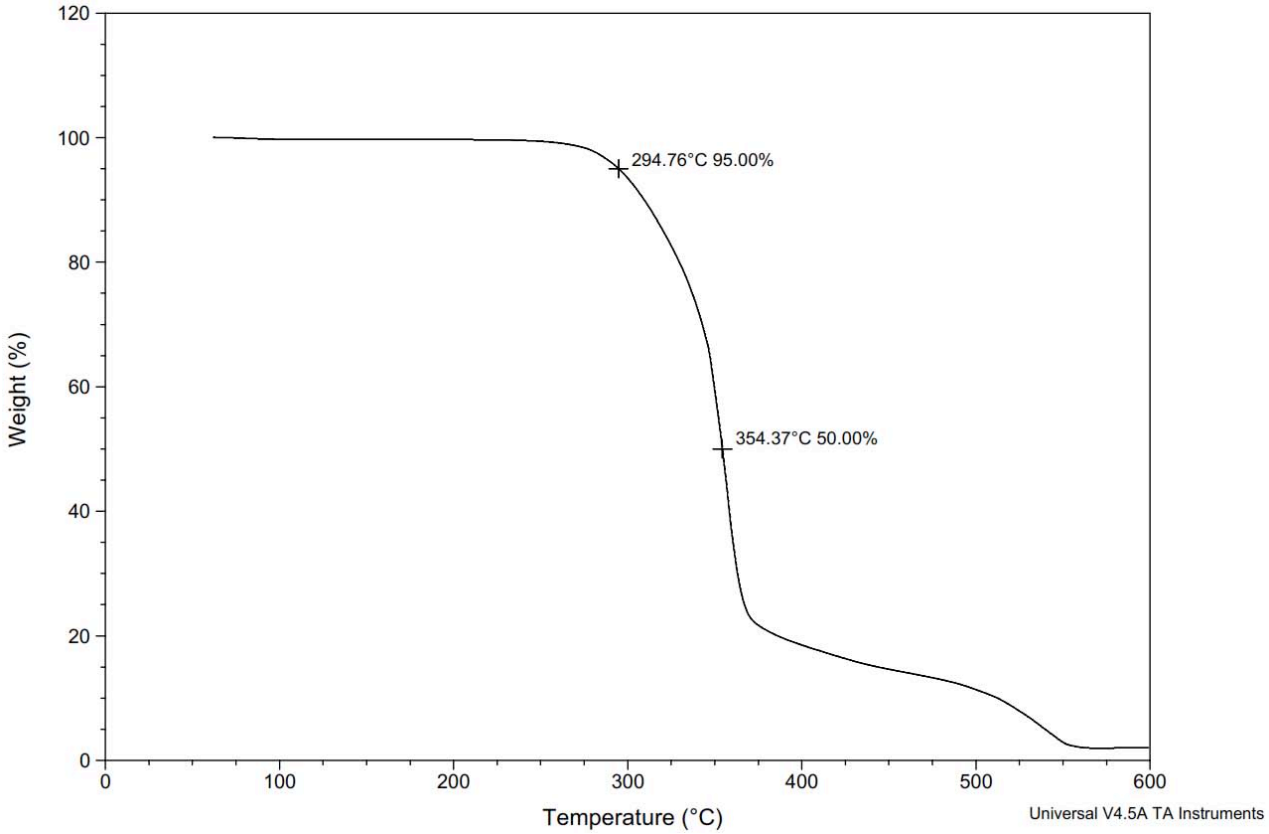


Figure S171. TGA Thermogram of copoly(caprolactone/ hydroxyethylvanillic acid) [70:30] (Table S2, entry 14).

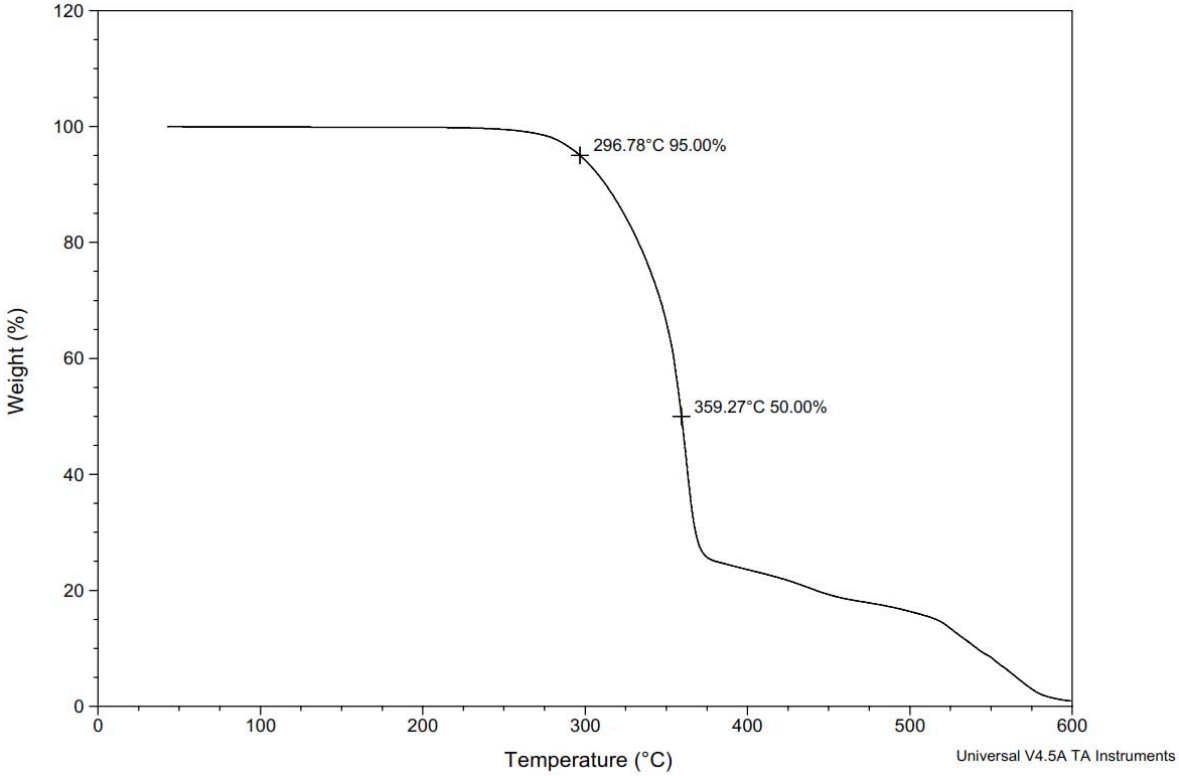


Figure S172. TGA Thermogram of copoly(caprolactone/ hydroxyethylvanillic acid) [60:40] (Table S2, entry 15).

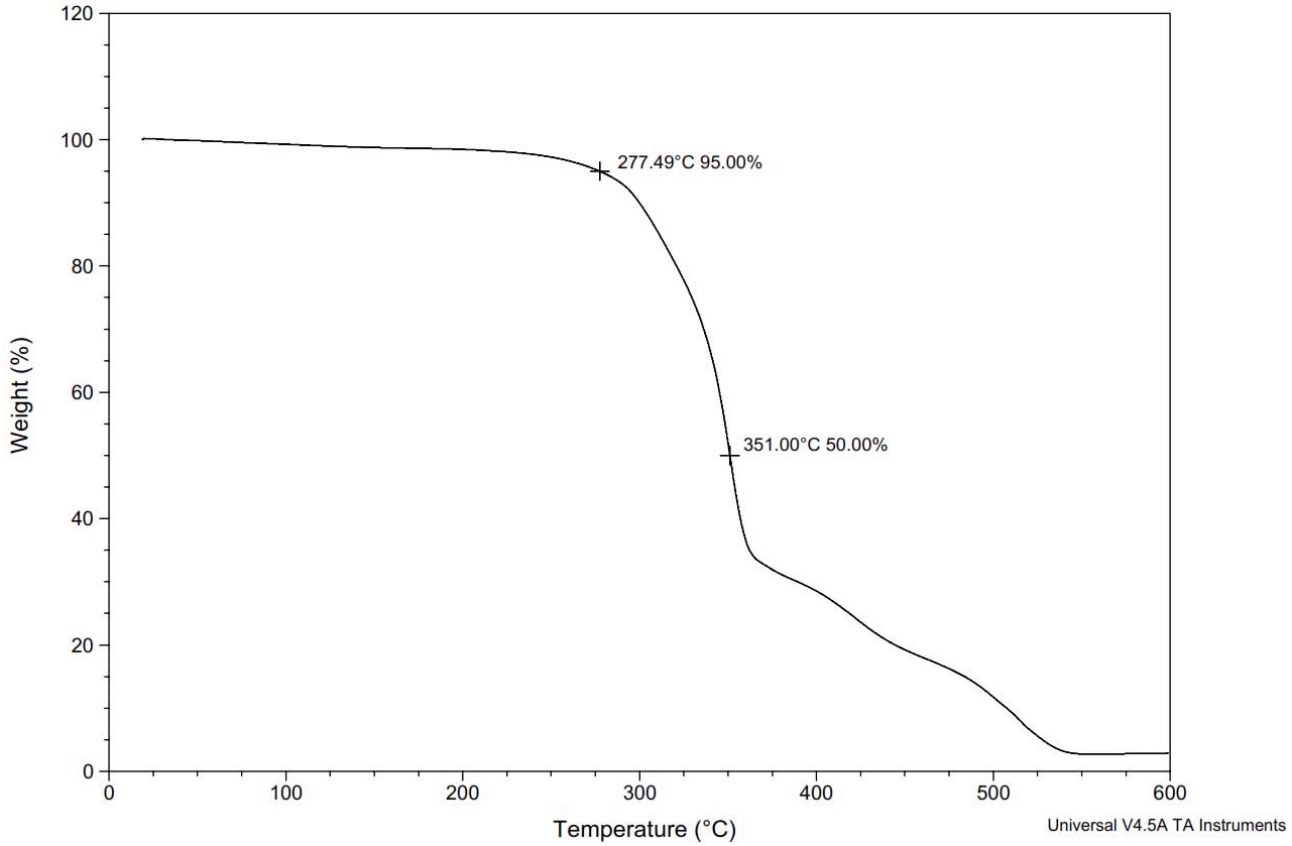


Figure S173. TGA Thermogram of copoly(caprolactone/ hydroxyethylvanillic acid) [50:50] (Table S2, entry 16).

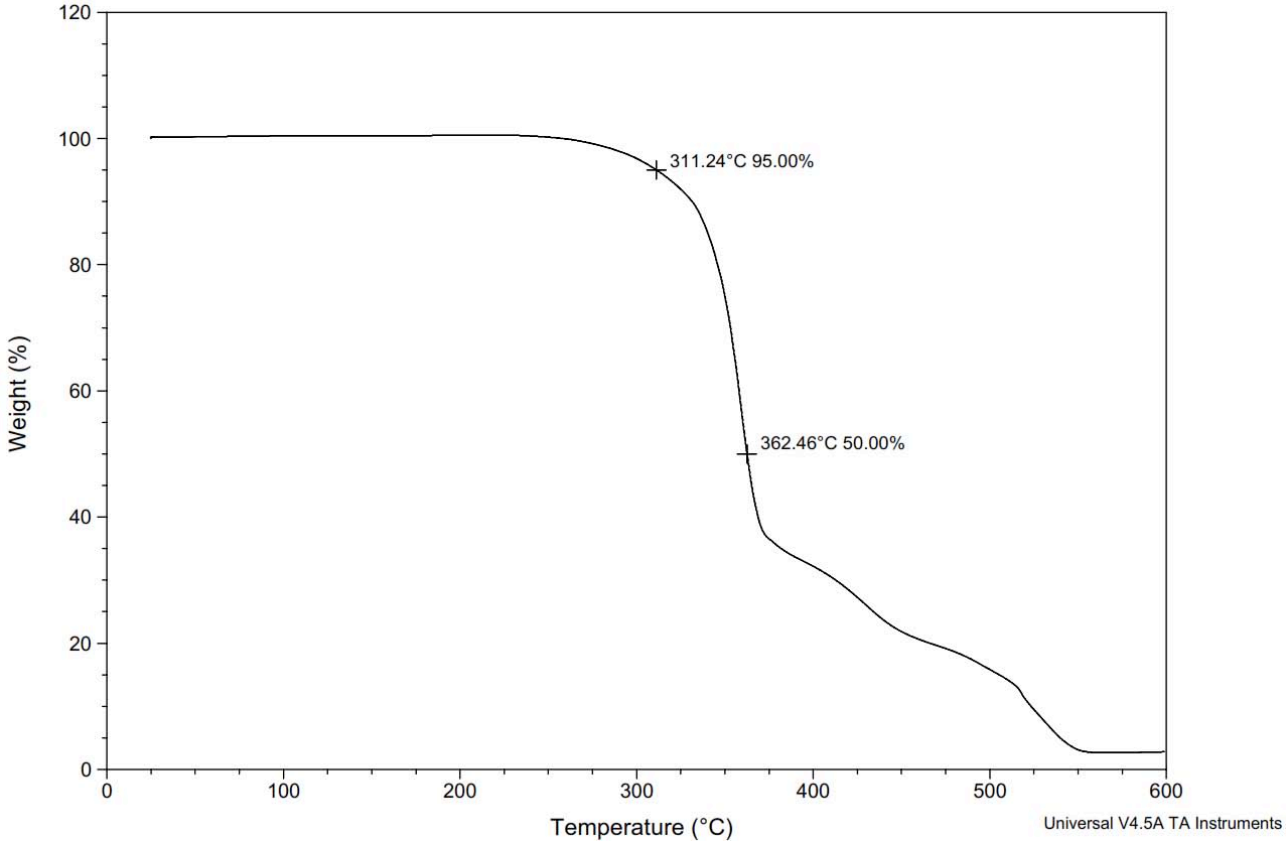


Figure S174. TGA Thermogram of copoly(caprolactone/ hydroxyethylvanillic acid) [40:60] (Table S2, entry 17).

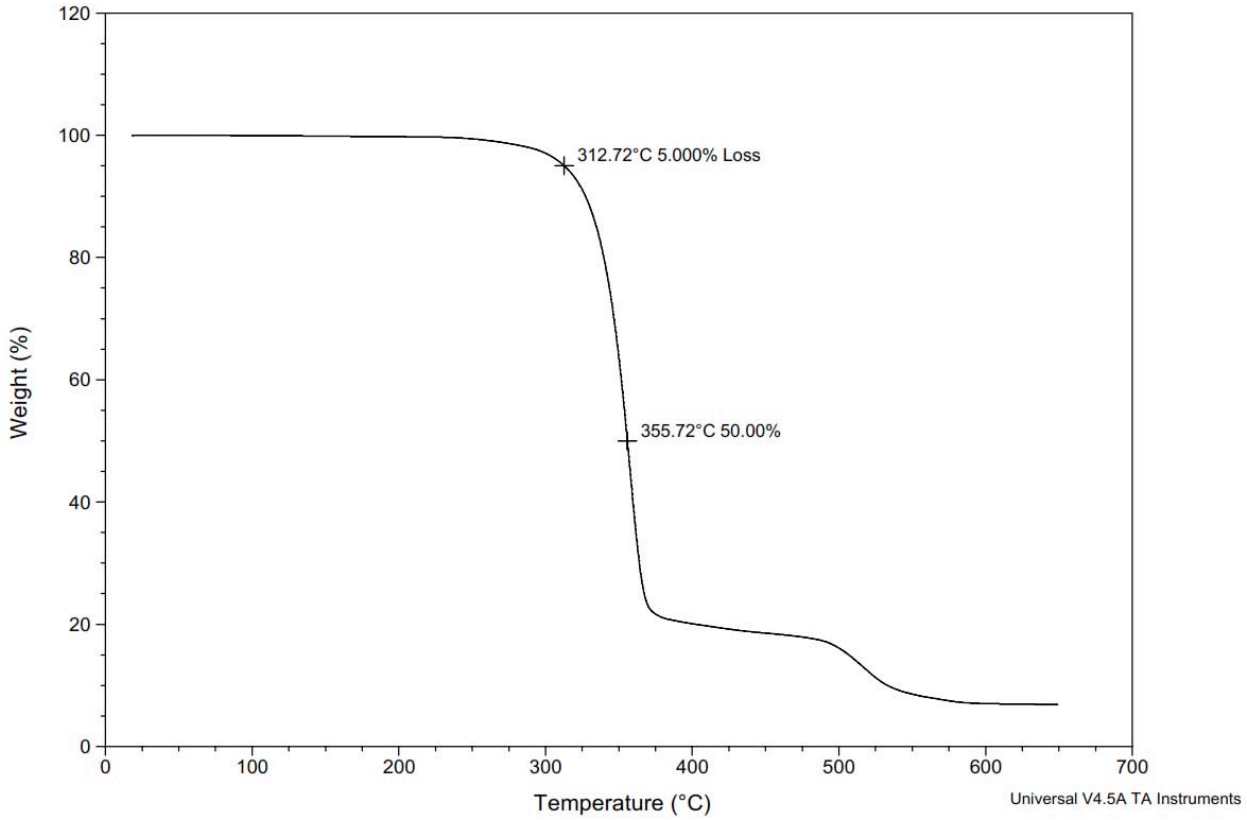


Figure S175. TGA Thermogram of copoly(caprolactone/ hydroxyethylvanillic acid) [30:70] (Table S2, entry 18).

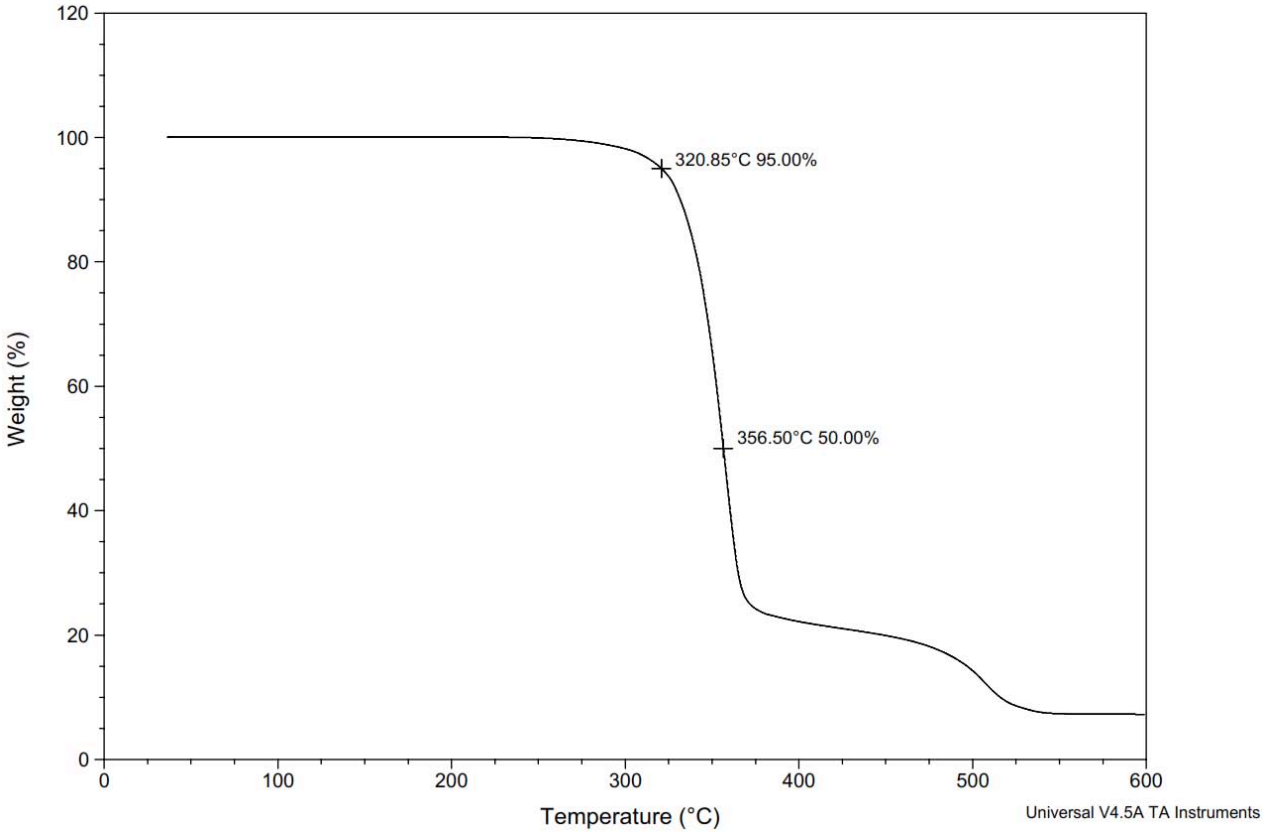


Figure S176. TGA Thermogram of copoly(caprolactone/ hydroxyethylvanillic acid) [20:80] (Table S2, entry 19).

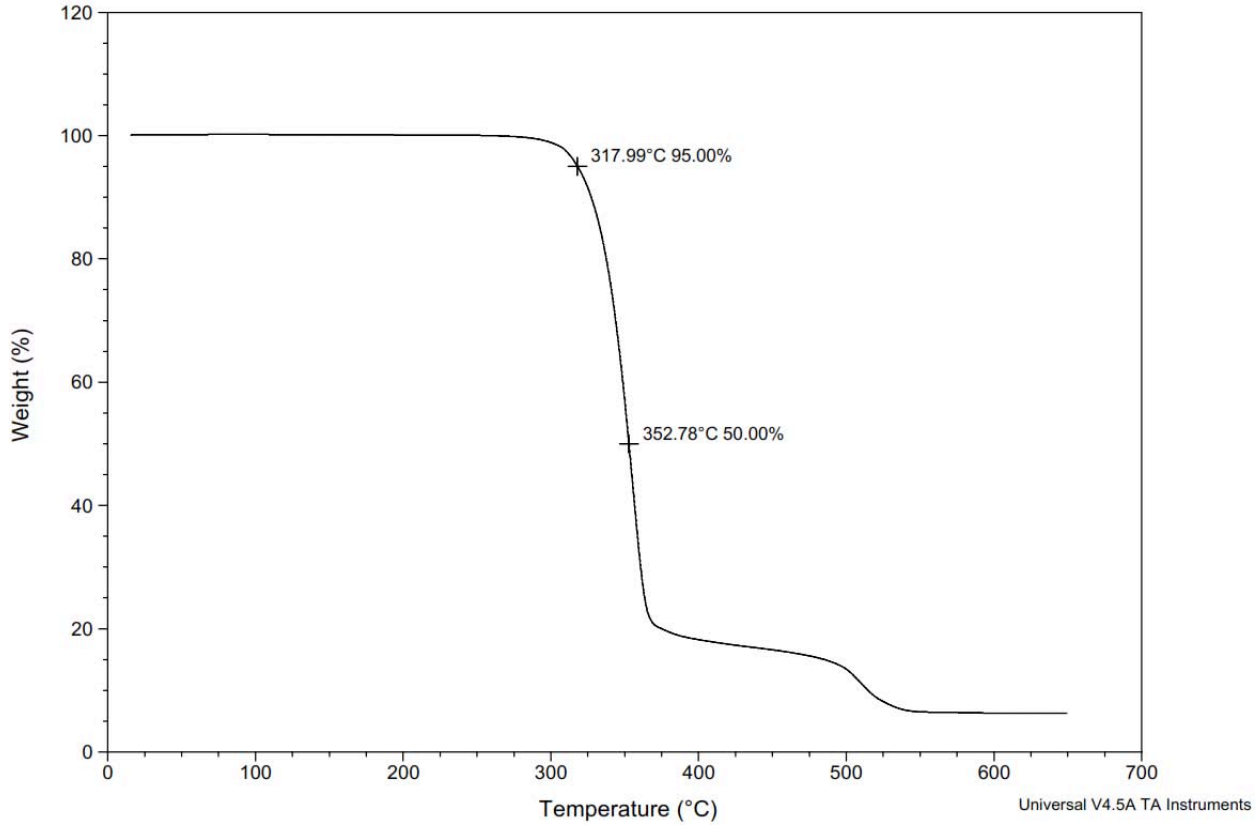


Figure S177. TGA Thermogram of copoly(caprolactone/ hydroxyethylvanillic acid) [10:90] (Table S2, entry 20).

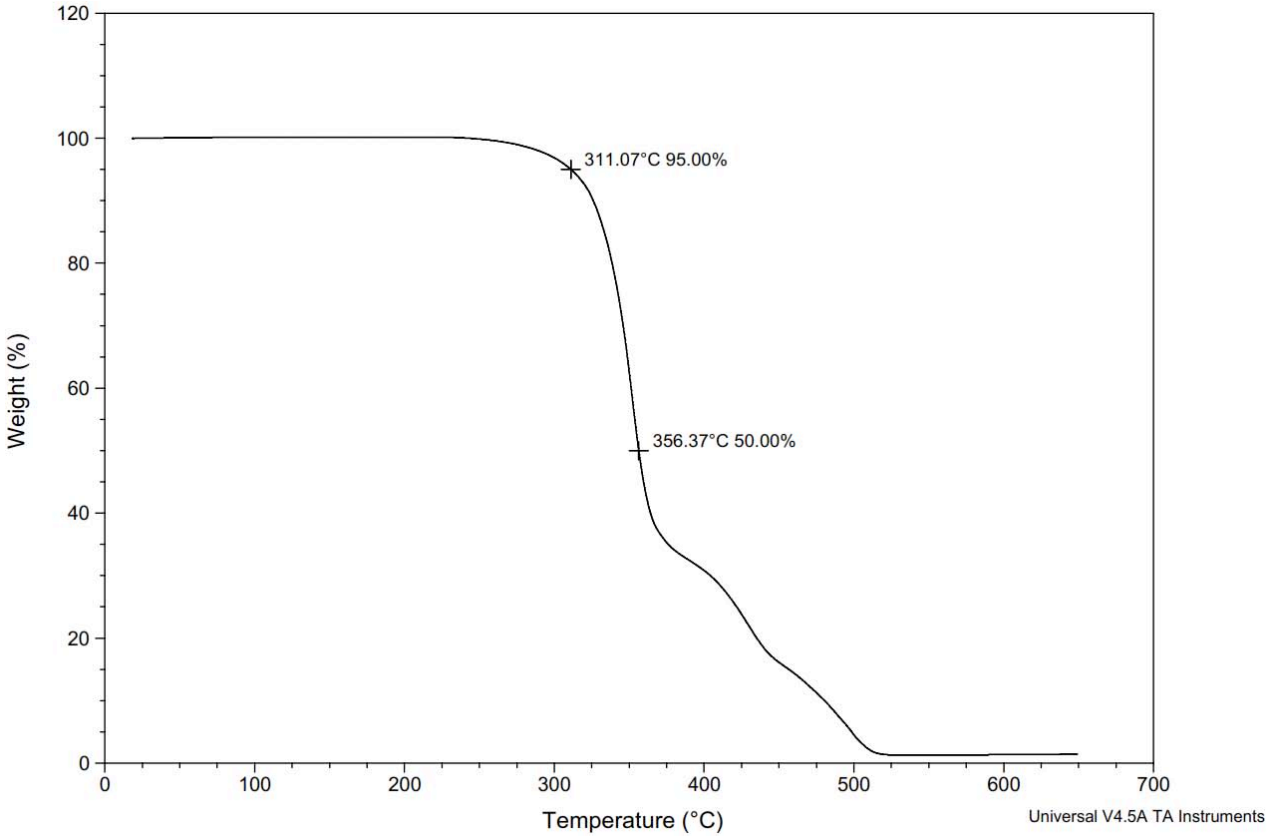


Figure S178. TGA Thermogram of polyethylene vanillate (Table S2, entry 21).

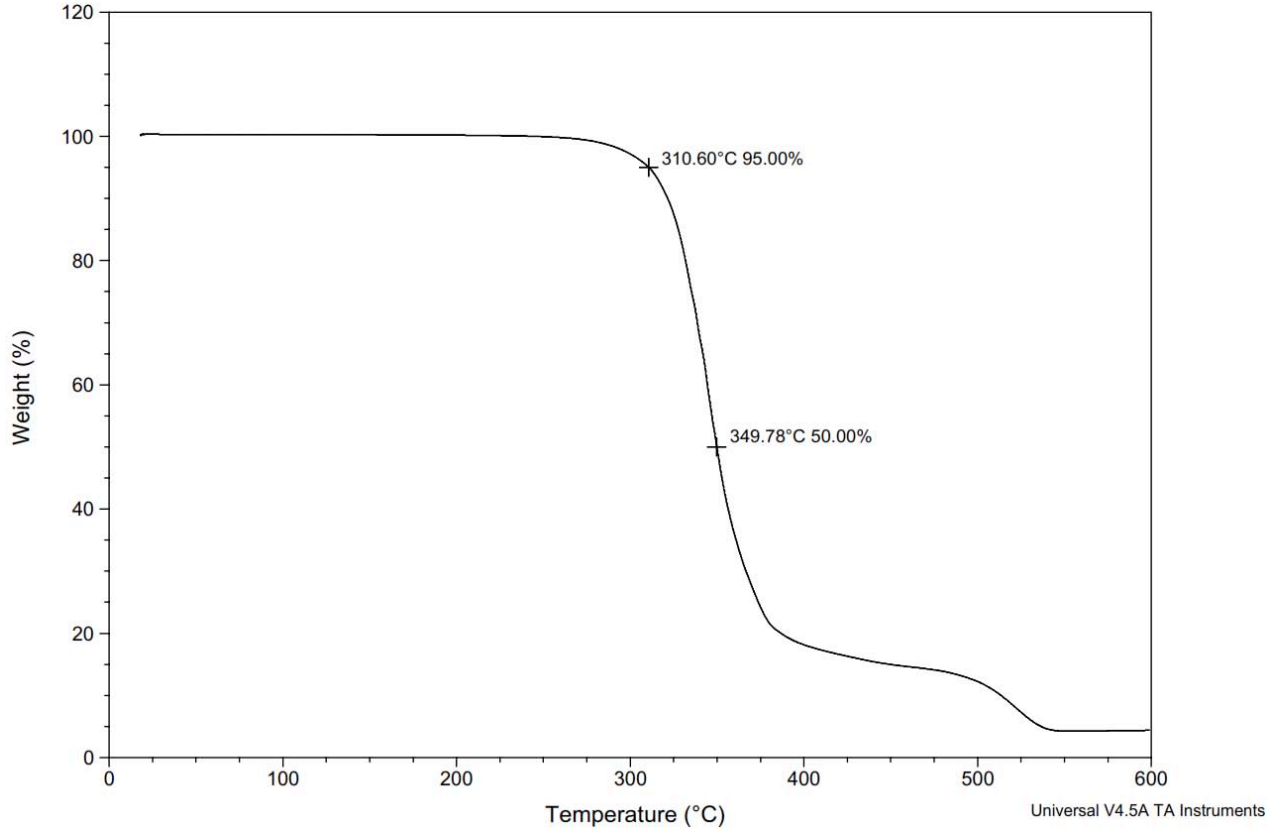


Figure S179. TGA Thermogram of copoly(caprolactone/ hydroxyethylferulic acid) [90:10] (Table S2, entry 22).

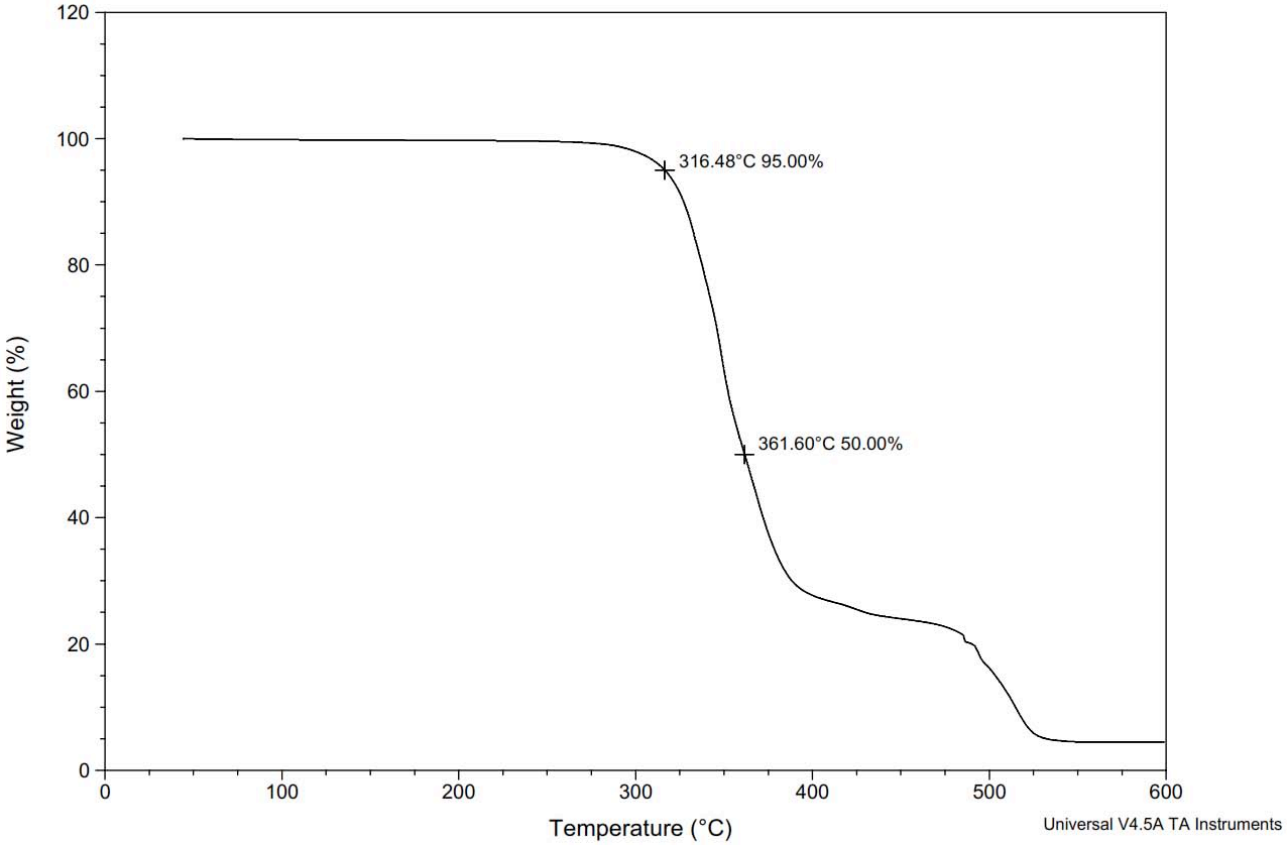


Figure S180. TGA Thermogram of copoly(caprolactone/ hydroxyethylferulic acid) [80:20] (Table S2, entry 23).

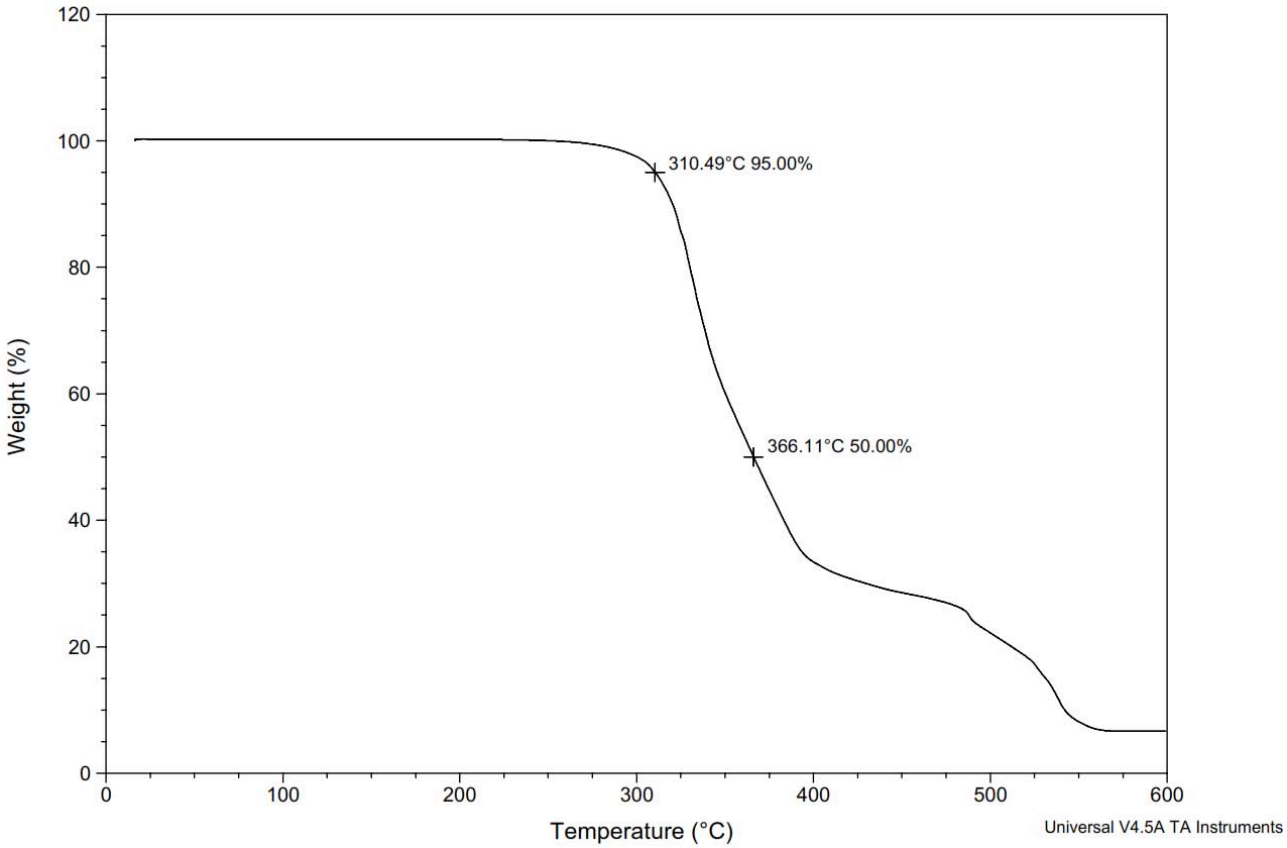


Figure S181. TGA Thermogram of copoly(caprolactone/ hydroxyethylferulic acid) [70:30] (Table S2, entry 24).

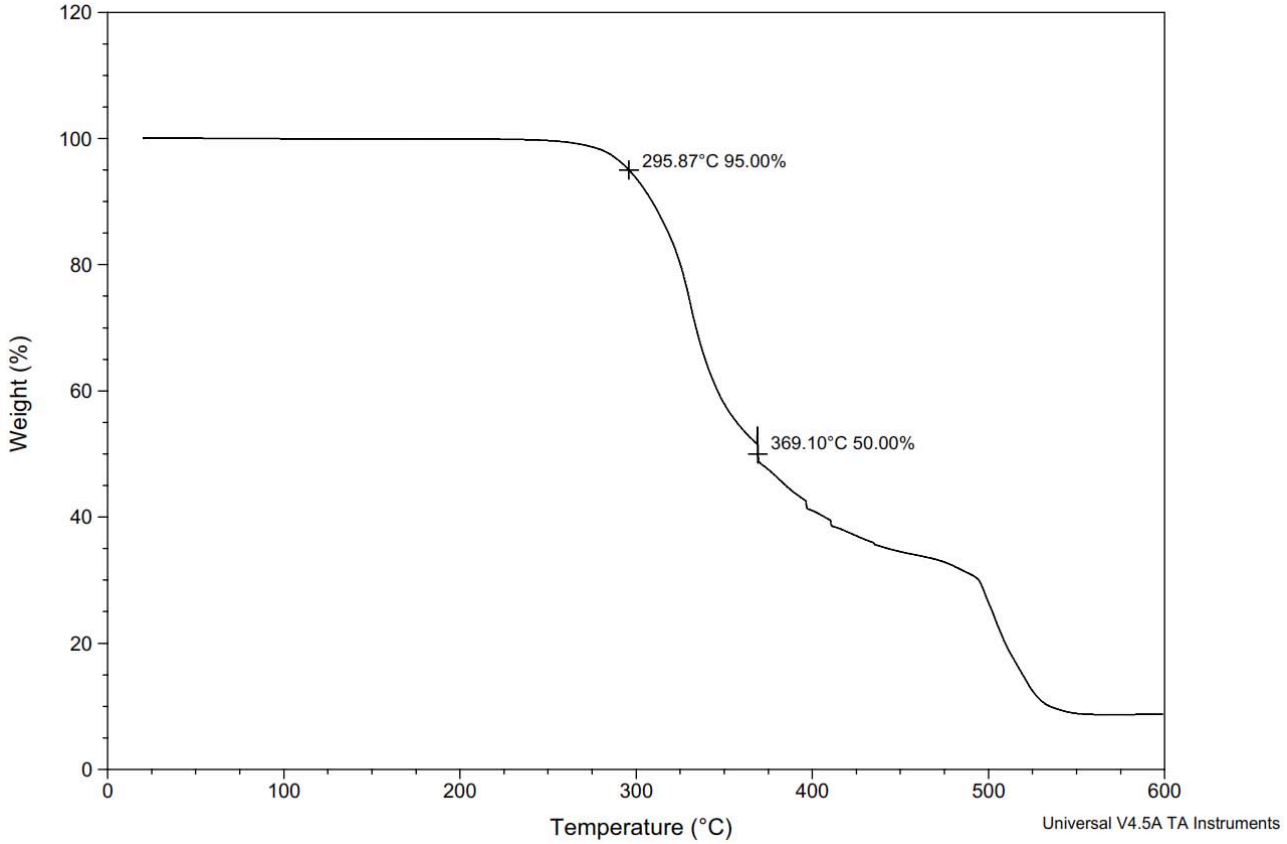


Figure S182. TGA Thermogram of copoly(caprolactone/ hydroxyethylferulic acid) [60:40] (Table S2, entry 25).

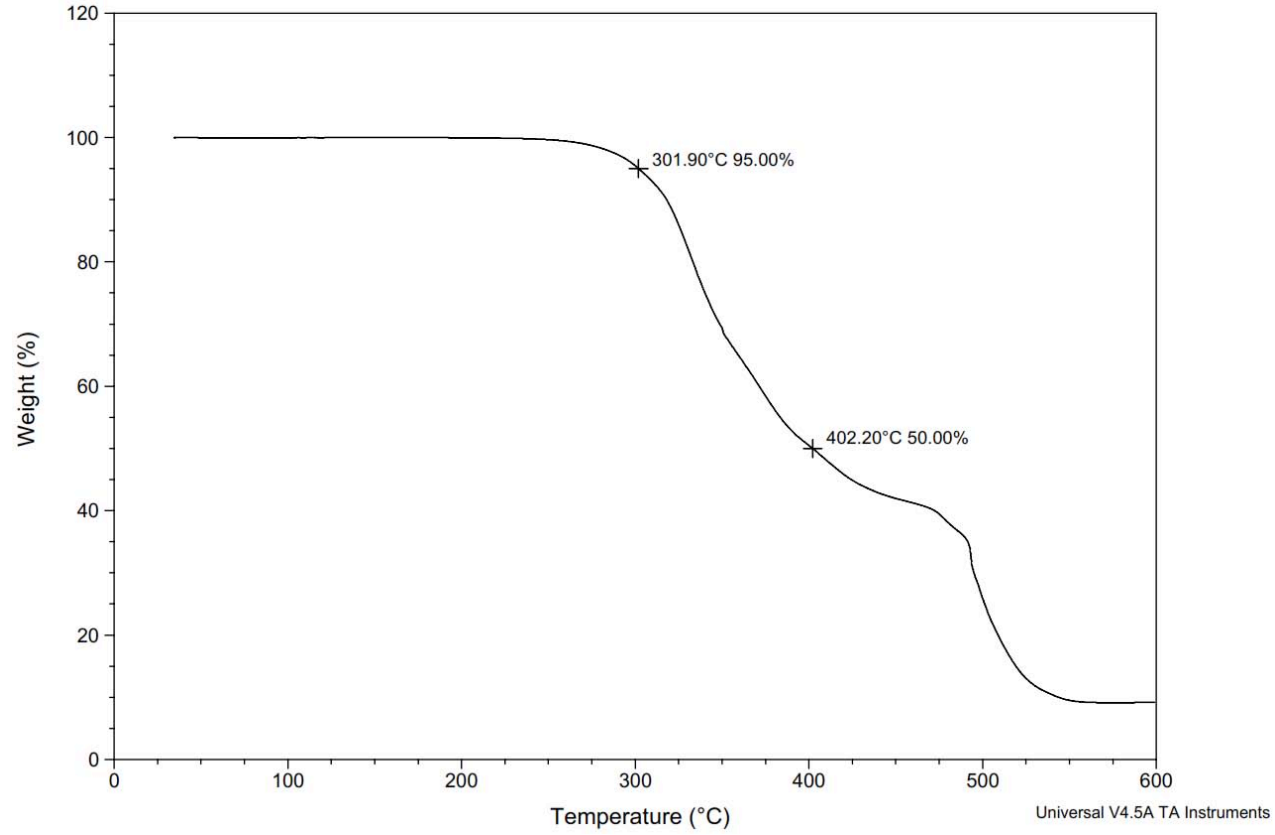


Figure S183. TGA Thermogram of copoly(caprolactone/ hydroxyethylferulic acid) [50:50] (Table S2, entry 26).

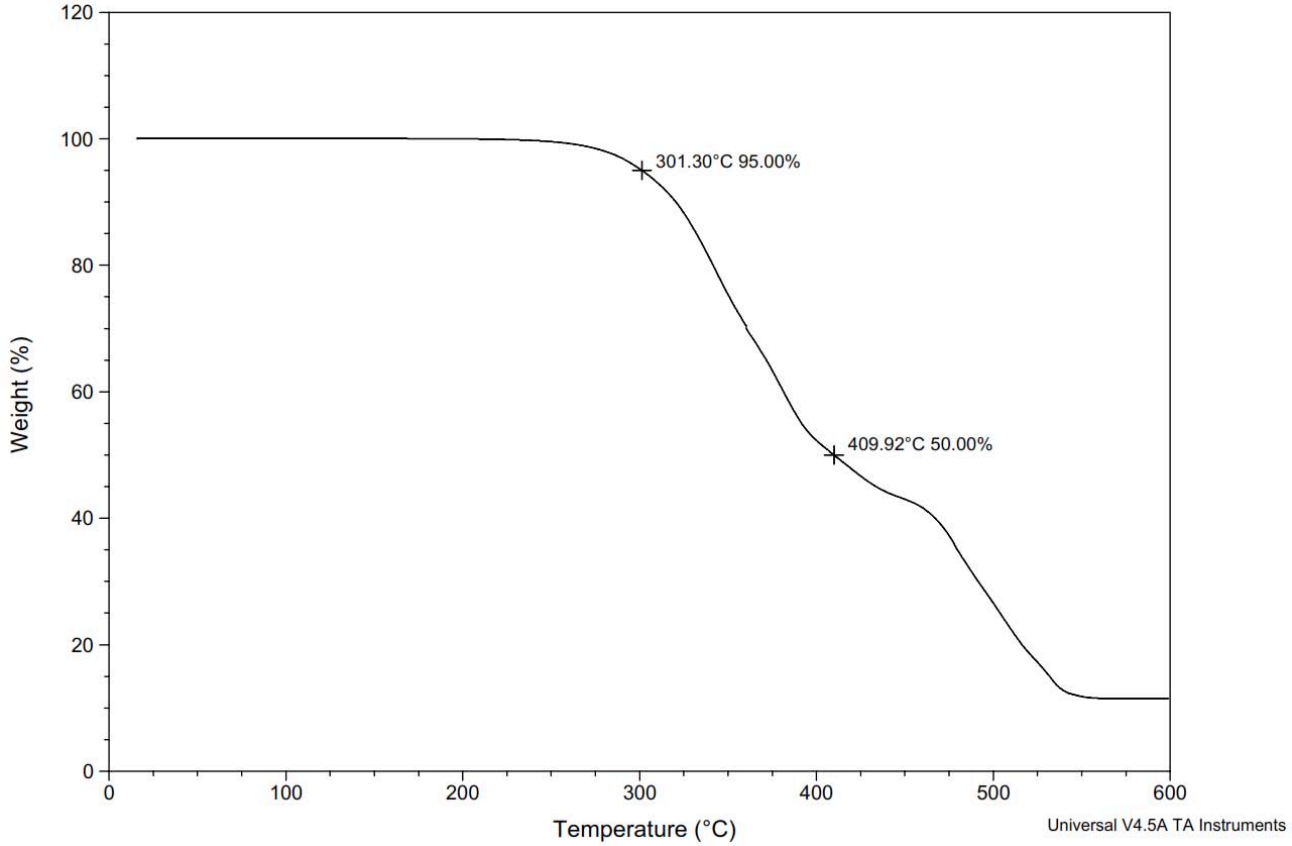


Figure S184. TGA Thermogram of copoly(caprolactone/ hydroxyethylferulic acid) [40:60] (Table S3, entry 37).

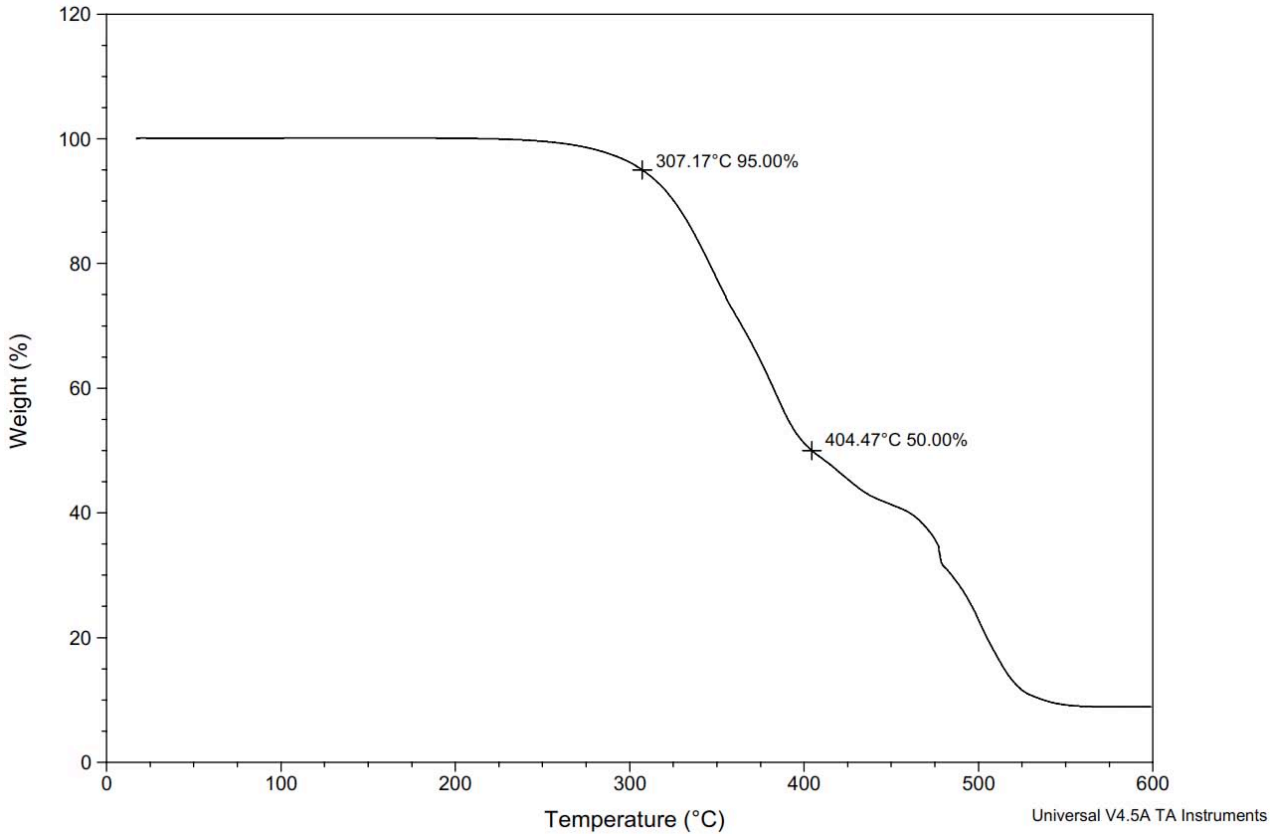


Figure S185. TGA Thermogram of copoly(caprolactone/ hydroxyethylferulic acid) [30:70] (Table S2, entry 28).

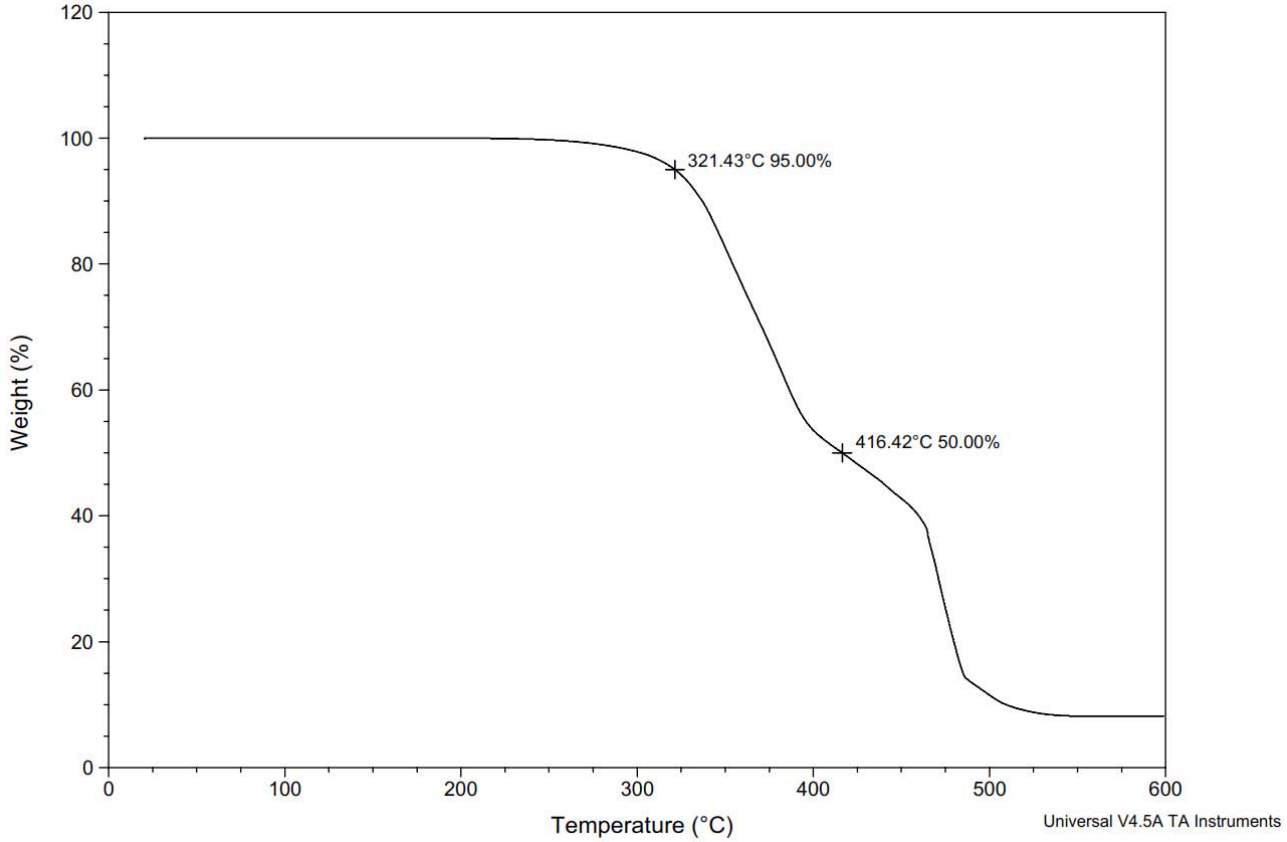


Figure S186. TGA Thermogram of copoly(caprolactone/ hydroxyethylferulic acid) [20:80] (Table S2, entry 29).

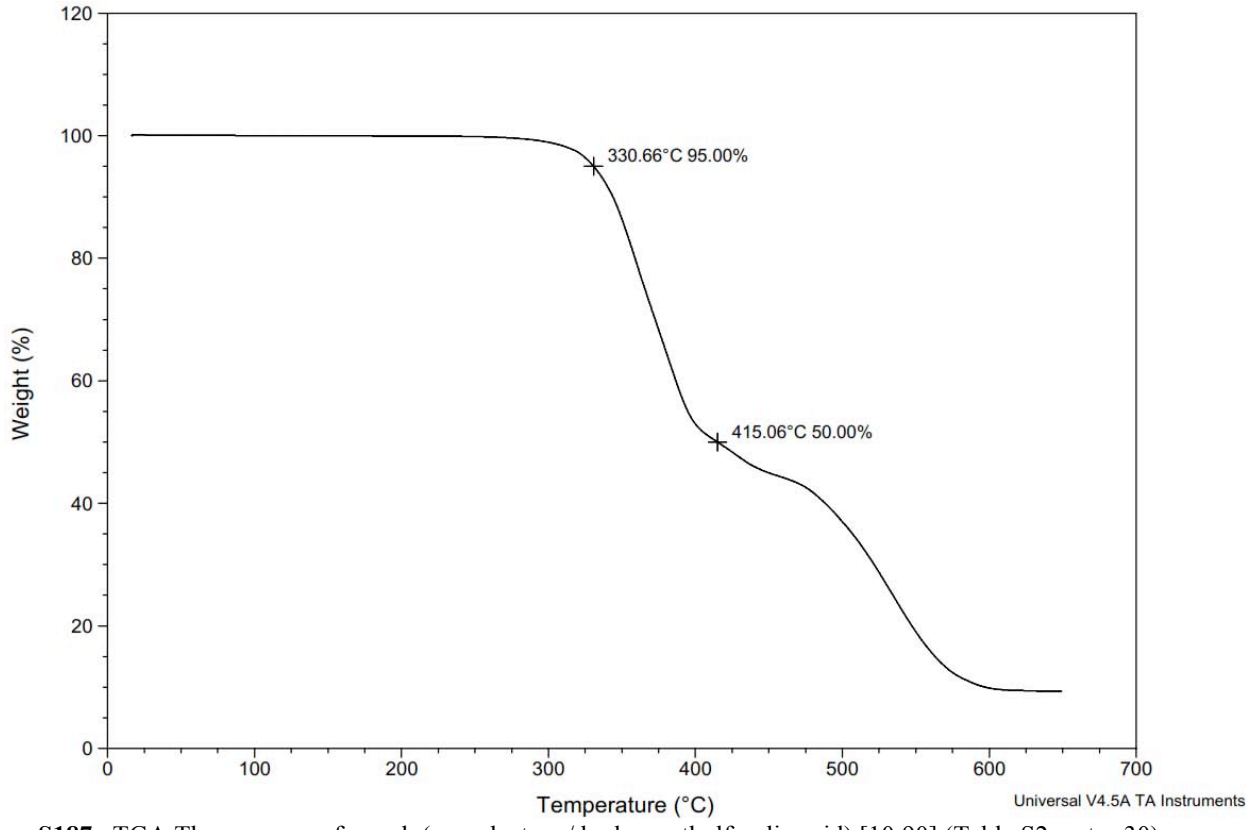


Figure S187. TGA Thermogram of copoly(caprolactone/ hydroxyethylferulic acid) [10:90] (Table S2, entry 30).

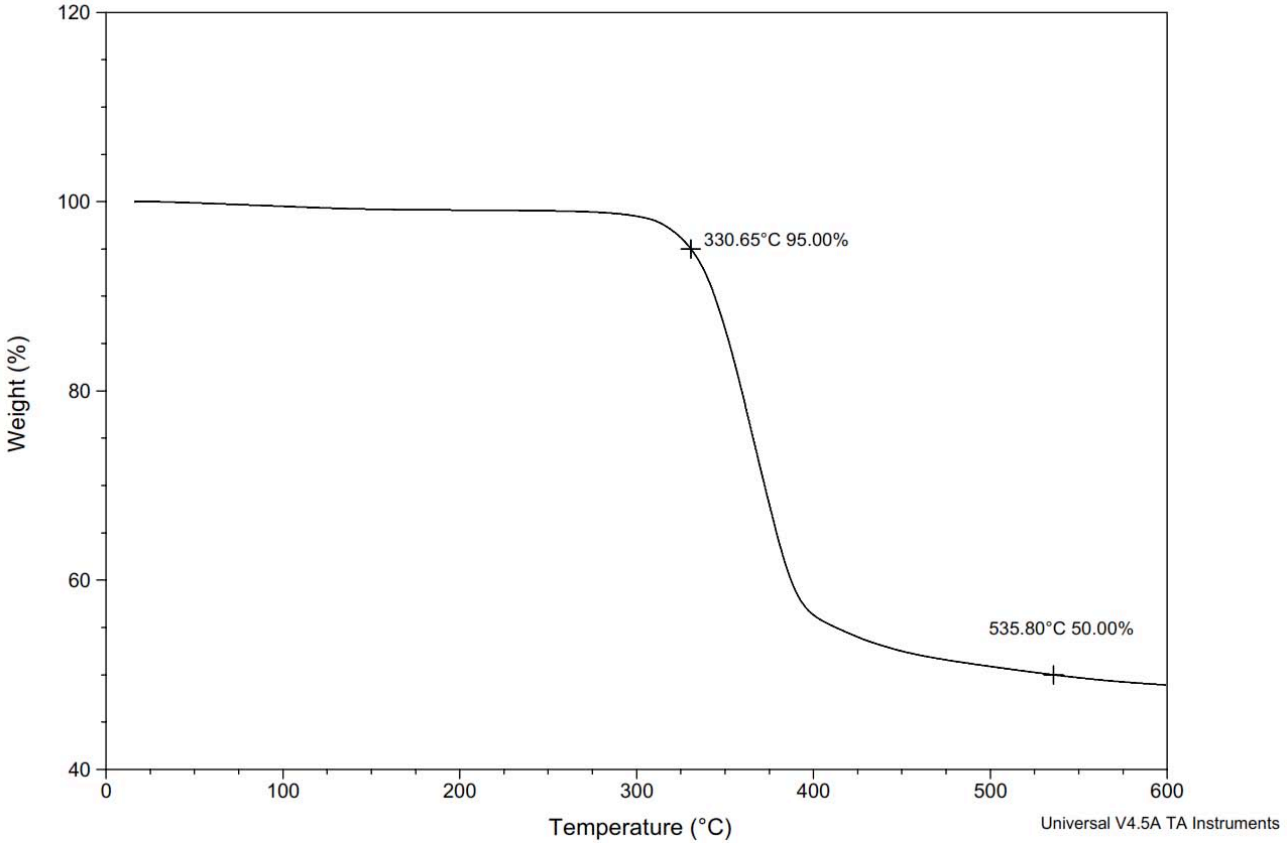


Figure S188. TGA Thermogram of polyethylene ferulate (Table S2, entry 31).

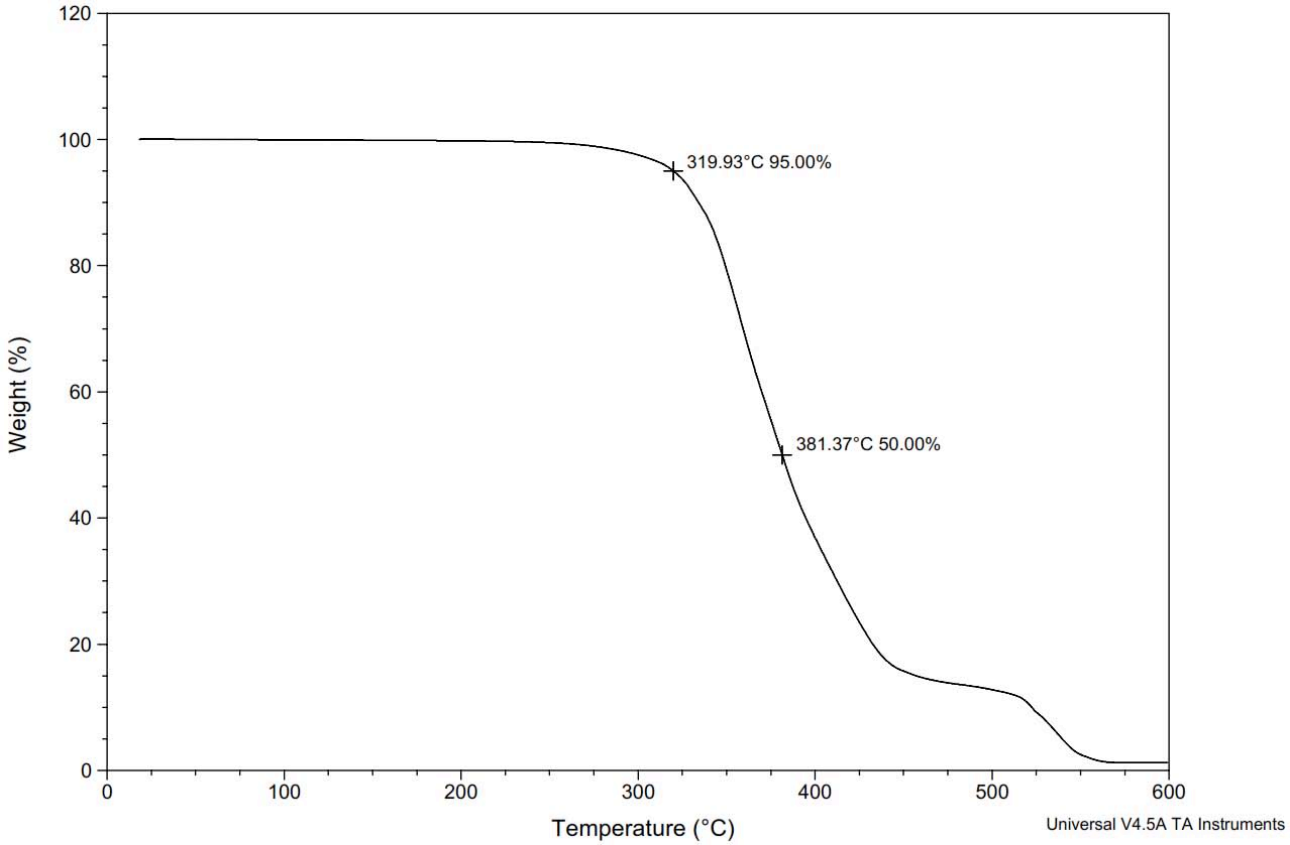


Figure S189. TGA Thermogram of copoly(caprolactone/ hydroxyethylcoumaric acid) [80:20] (Table S2, entry 32).

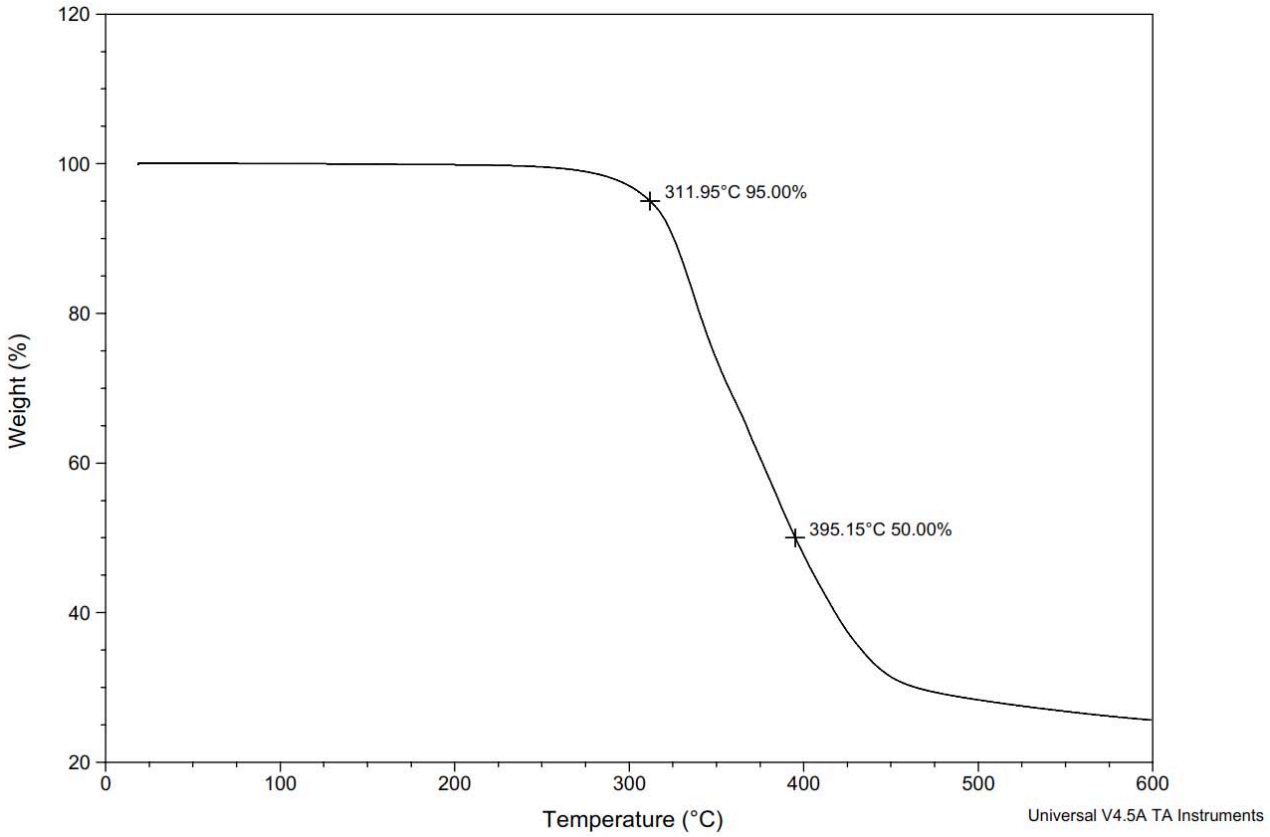


Figure S190. TGA Thermogram of copoly(caprolactone/ hydroxyethylcoumaric acid) [50:50] (Table S2, entry 33).

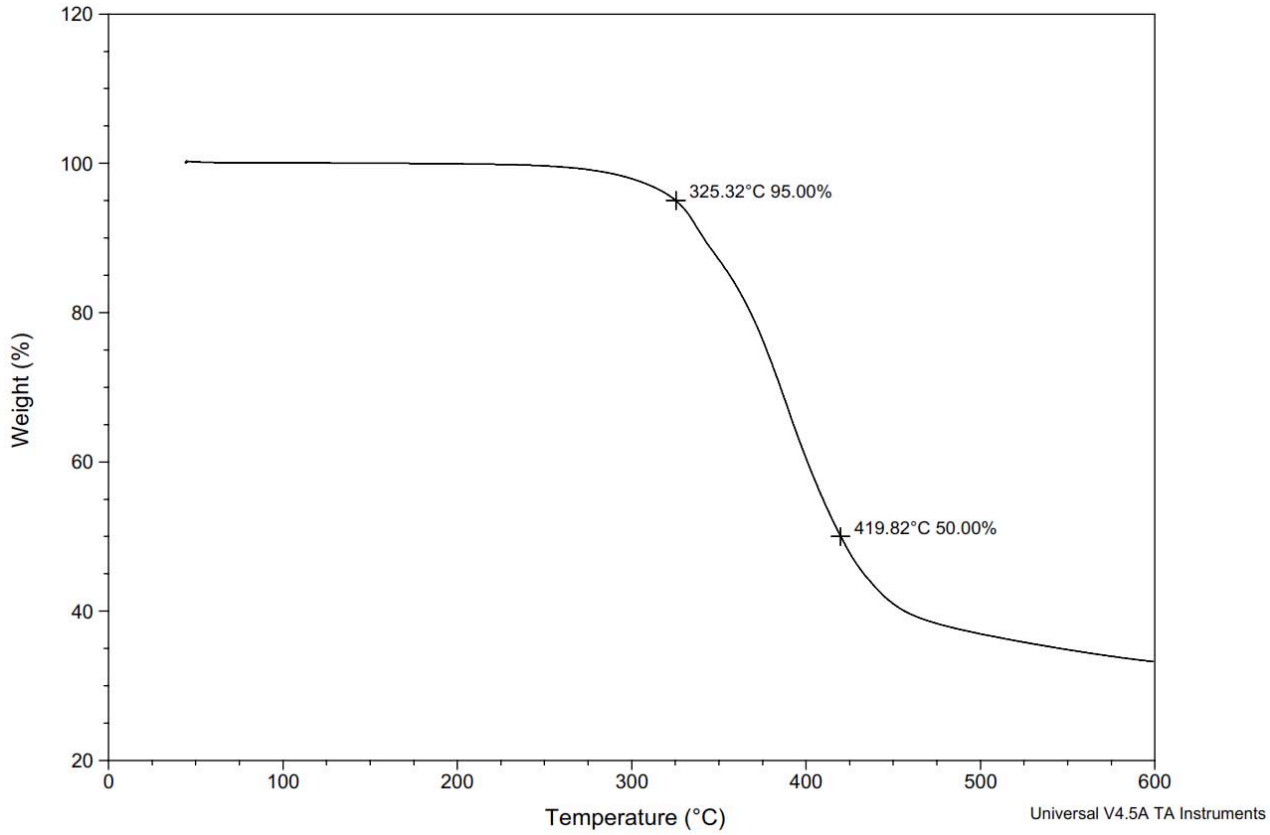


Figure S191. TGA Thermogram of copoly(caprolactone/ hydroxyethylcoumaric acid) [20:80] (Table S2, entry 34).

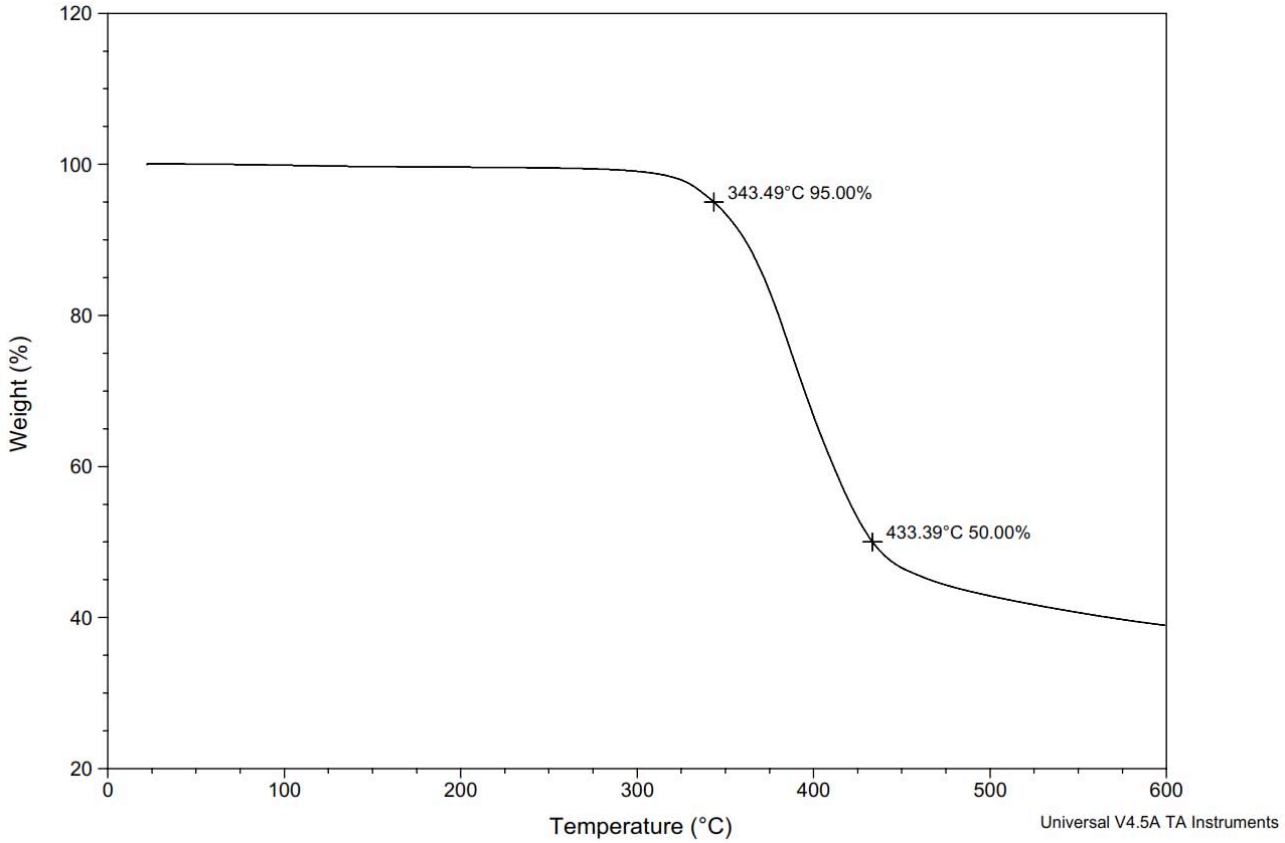


Figure S192. TGA Thermogram of polyethylene coumarate (Table S2, entry 35).

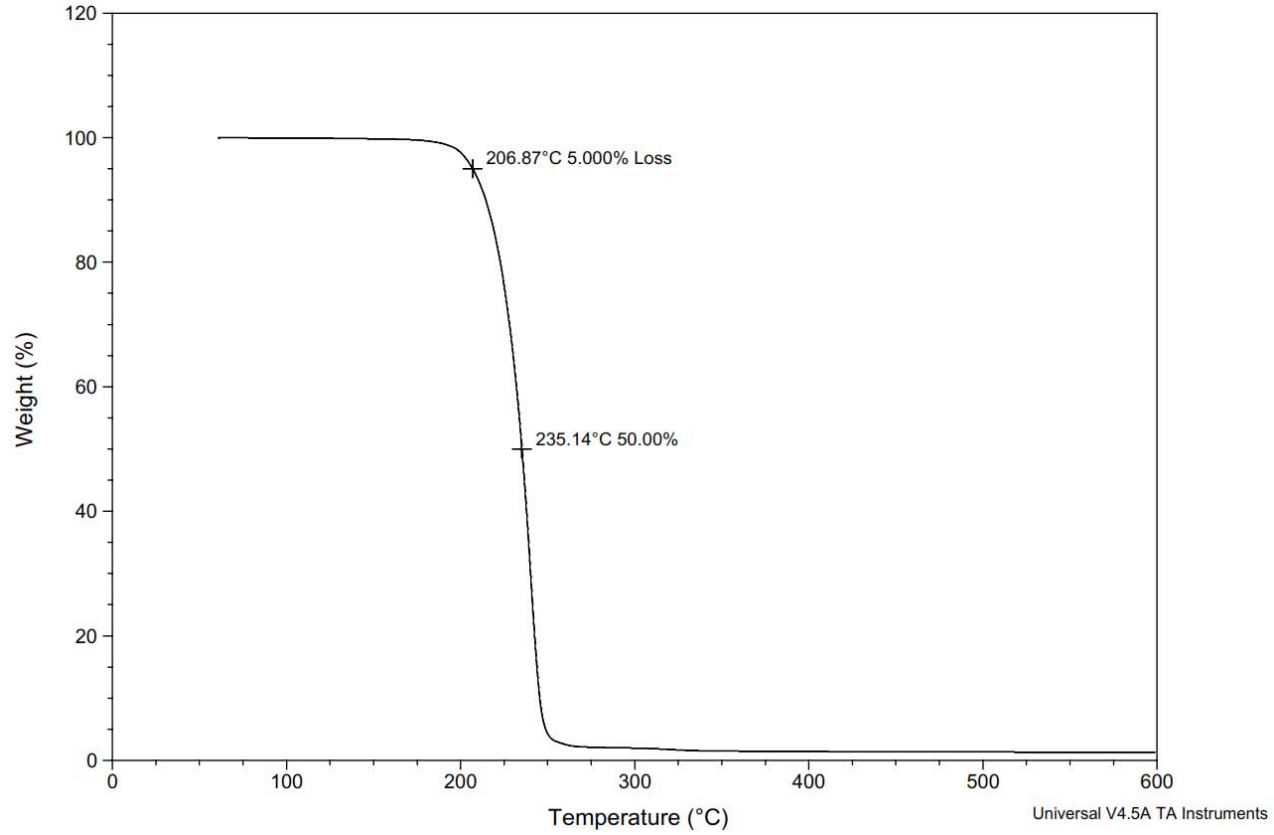


Figure S193. TGA Thermogram of polylactic acid (Table S3, entry 1).

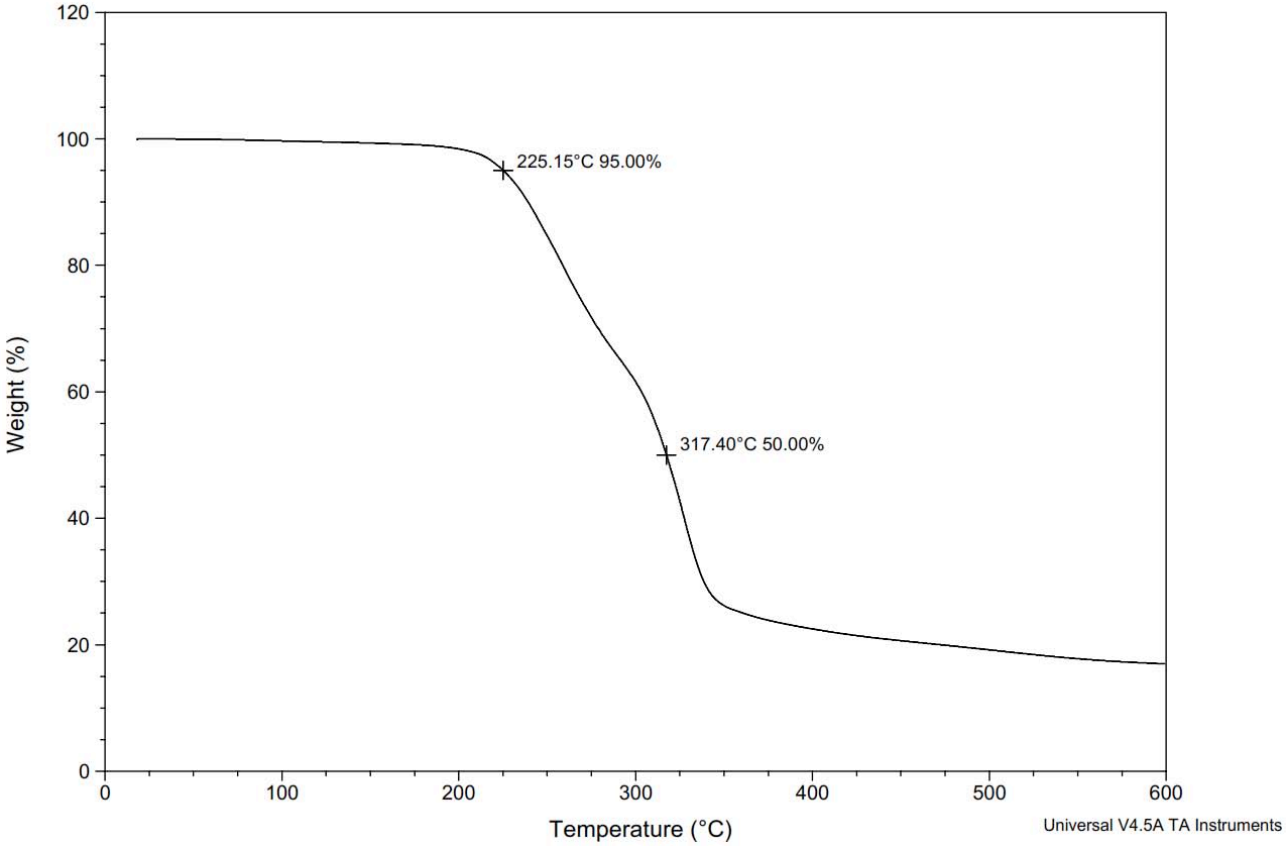


Figure S194. TGA Thermogram of copoly(L-lactide/ hydroxyethylsyringic acid) [80:20] (Table S3, entry 2).

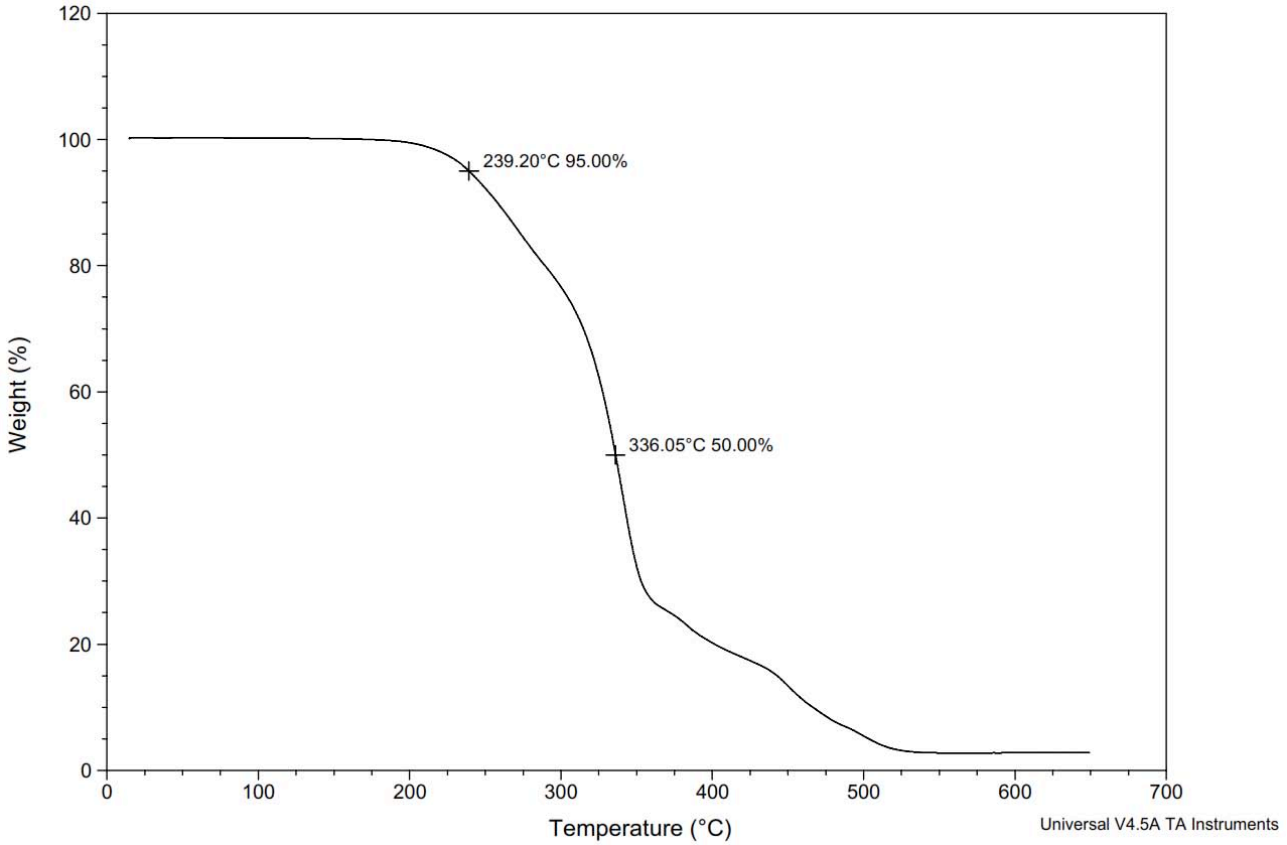


Figure S195. TGA Thermogram of copoly(L-lactide/ hydroxyethylsyringic acid) [60:40] (Table S3, entry 3).

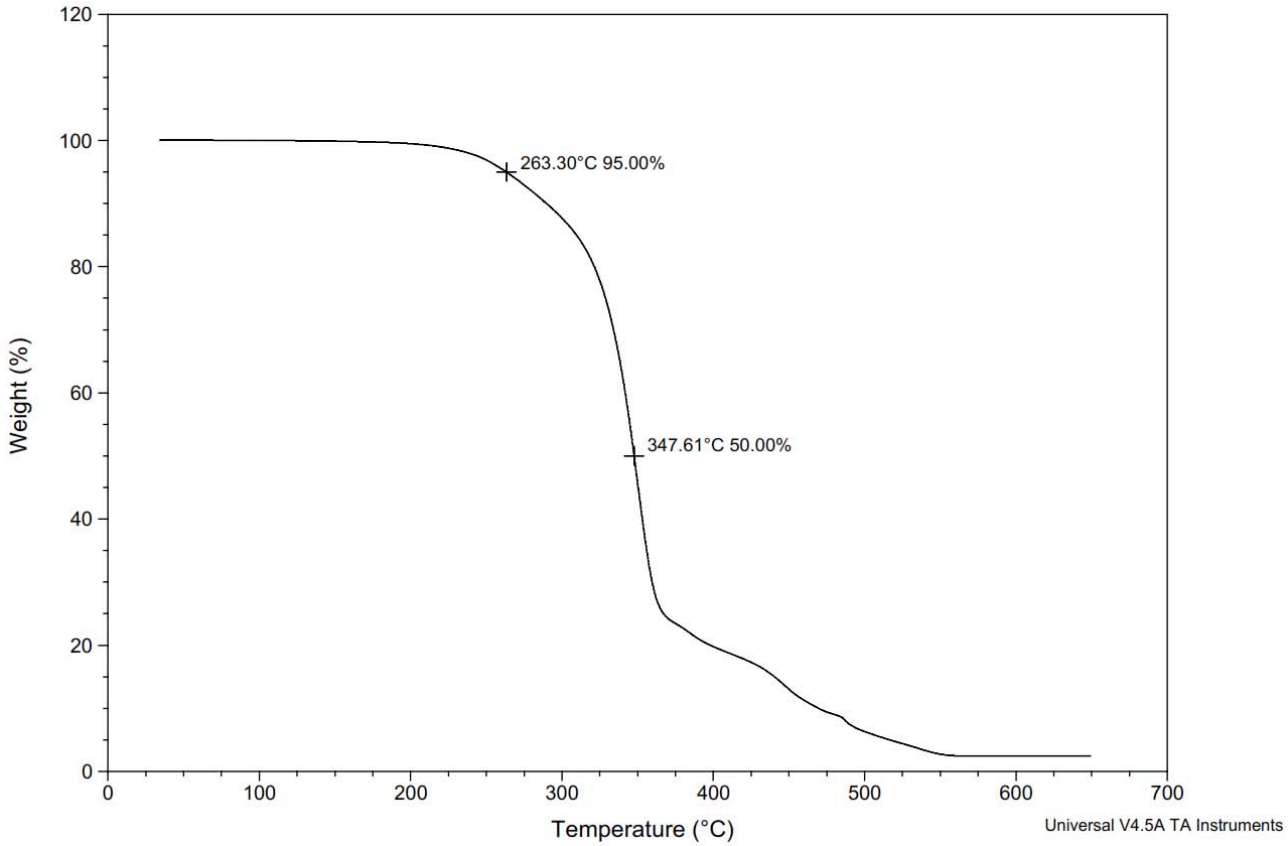


Figure S196. TGA Thermogram of copoly(L-lactide/ hydroxyethylsyringic acid) [40:60] (Table S3, entry 4).

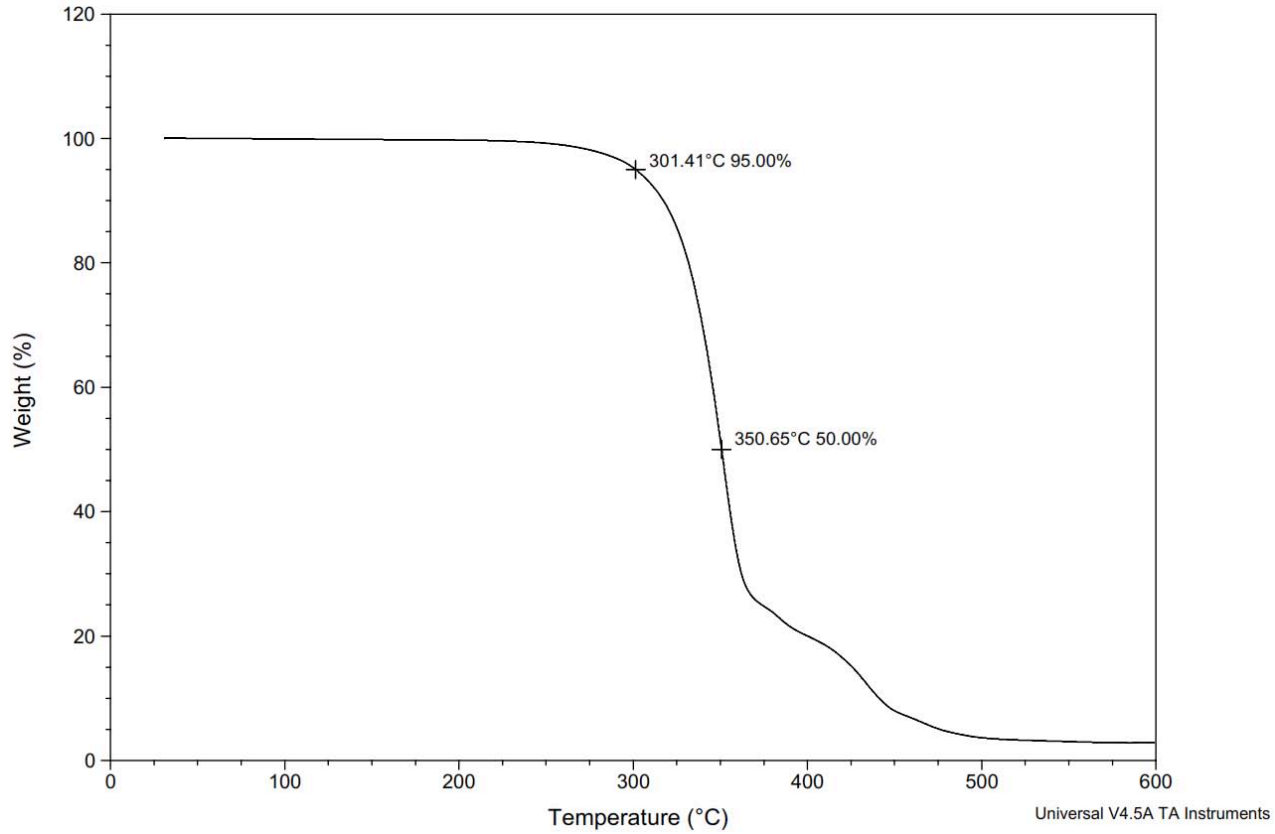


Figure S197. TGA Thermogram of copoly(L-lactide/ hydroxyethylsyringic acid) [20:80] (Table S3, entry 5).

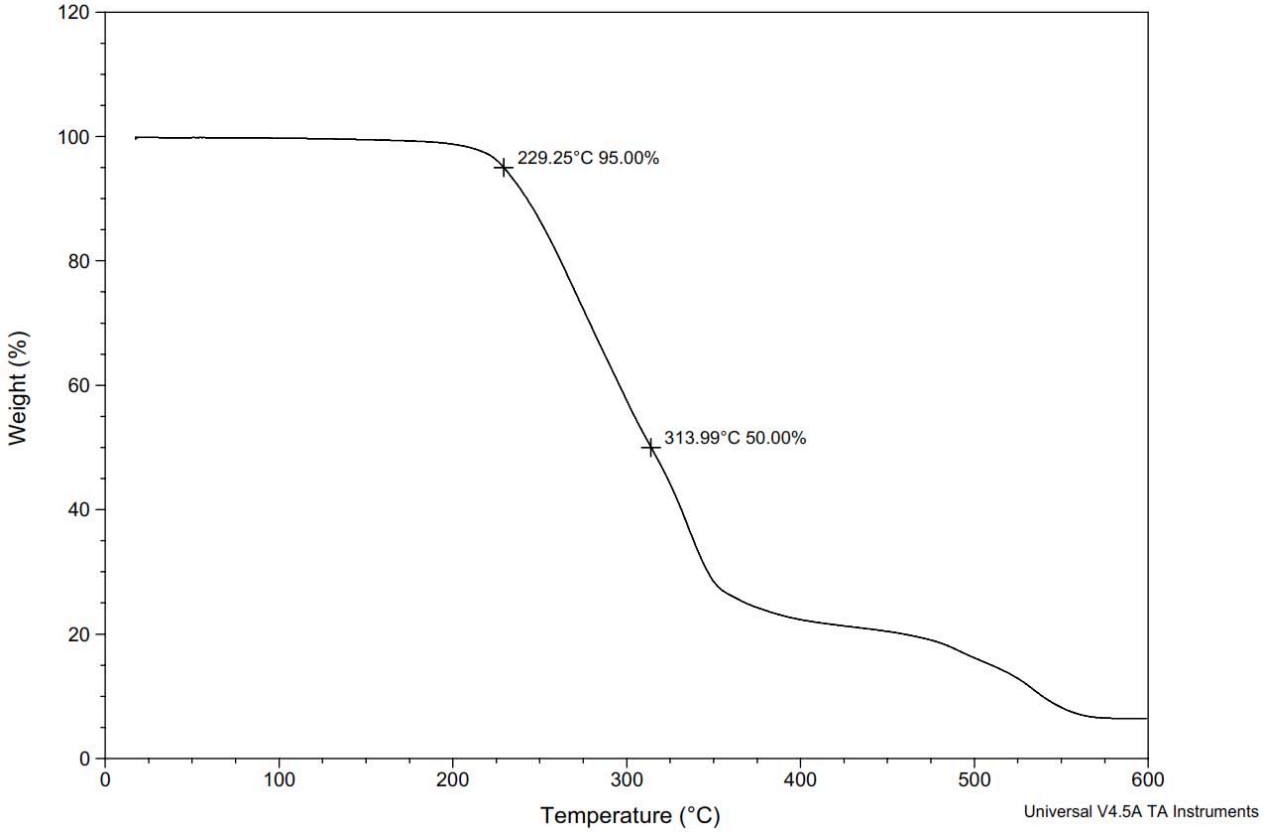


Figure S198. TGA Thermogram of copoly(L-lactide/ hydroxyethylvanillic acid) [80:20] (Table S3, entry 7).

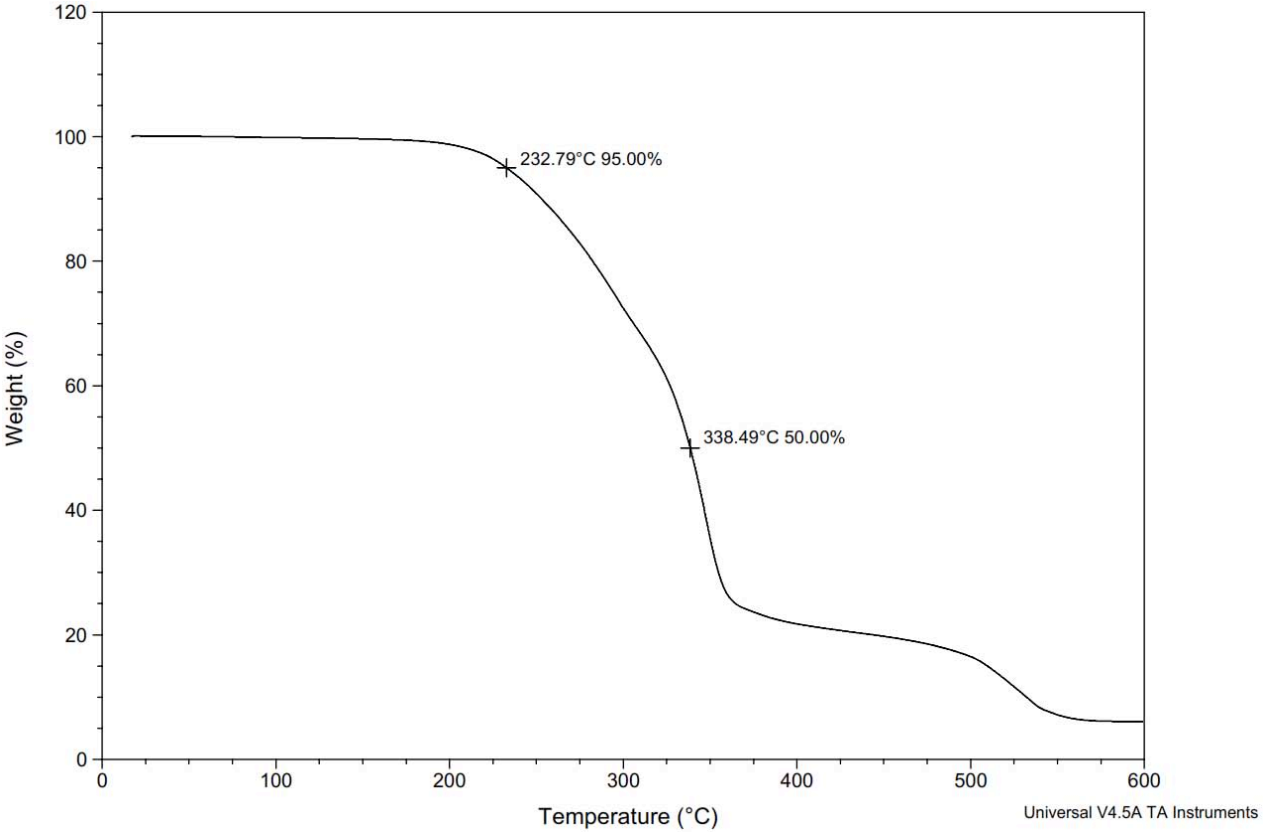


Figure S199. TGA Thermogram of copoly(L-lactide/ hydroxyethylvanillic acid) [60:40] (Table S3, entry 8).

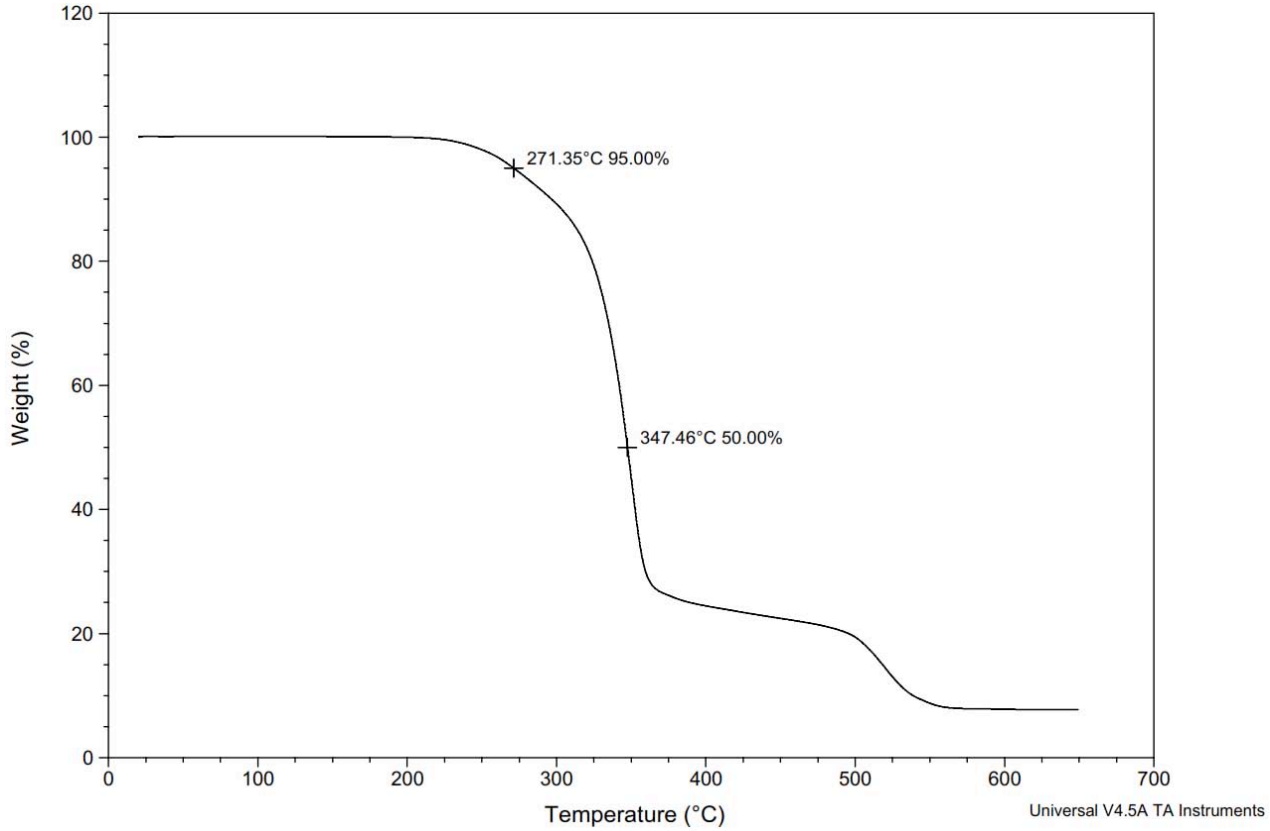


Figure S200. TGA Thermogram of copoly(L-lactide/ hydroxyethylvanillic acid) [40:60] (Table S3, entry 9).

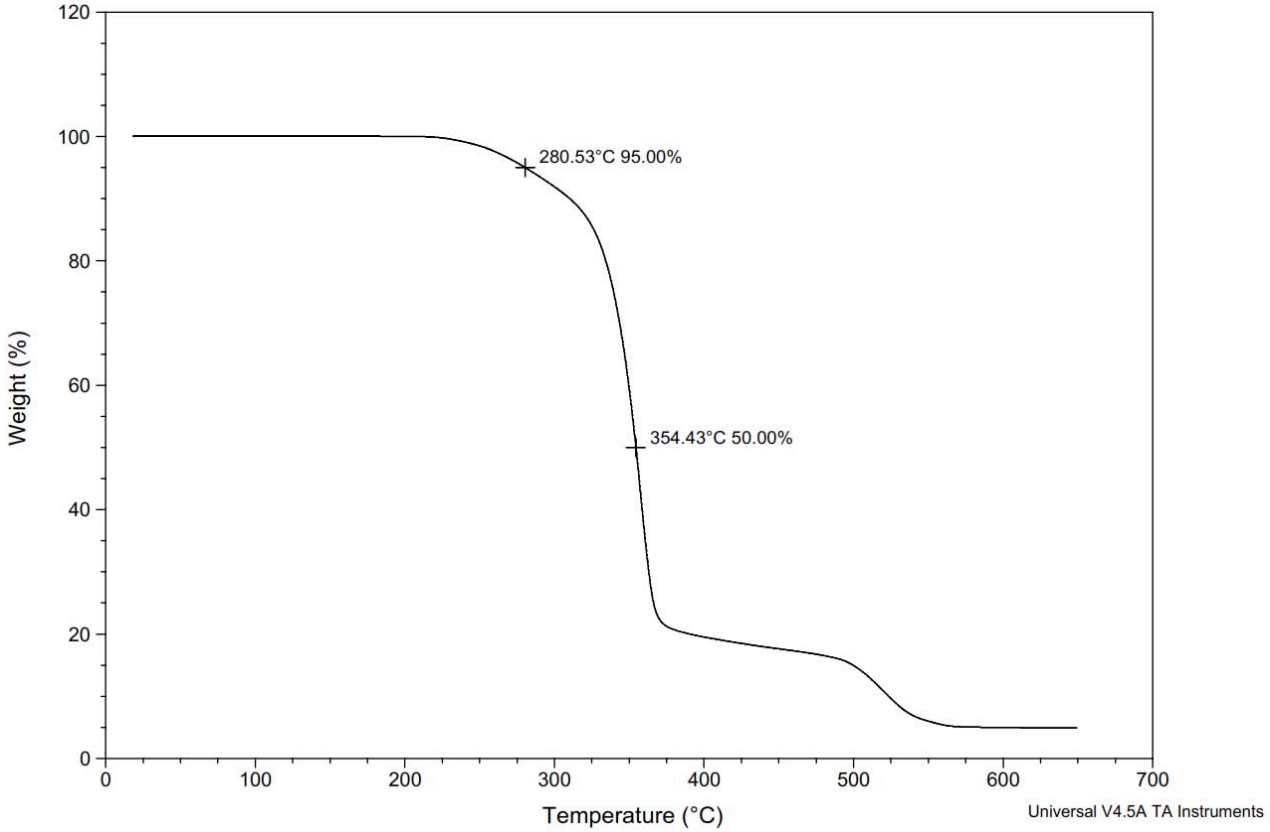


Figure S201. TGA Thermogram of copoly(L-lactide/ hydroxyethylvanillic acid) [20:80] (Table S3, entry 10).

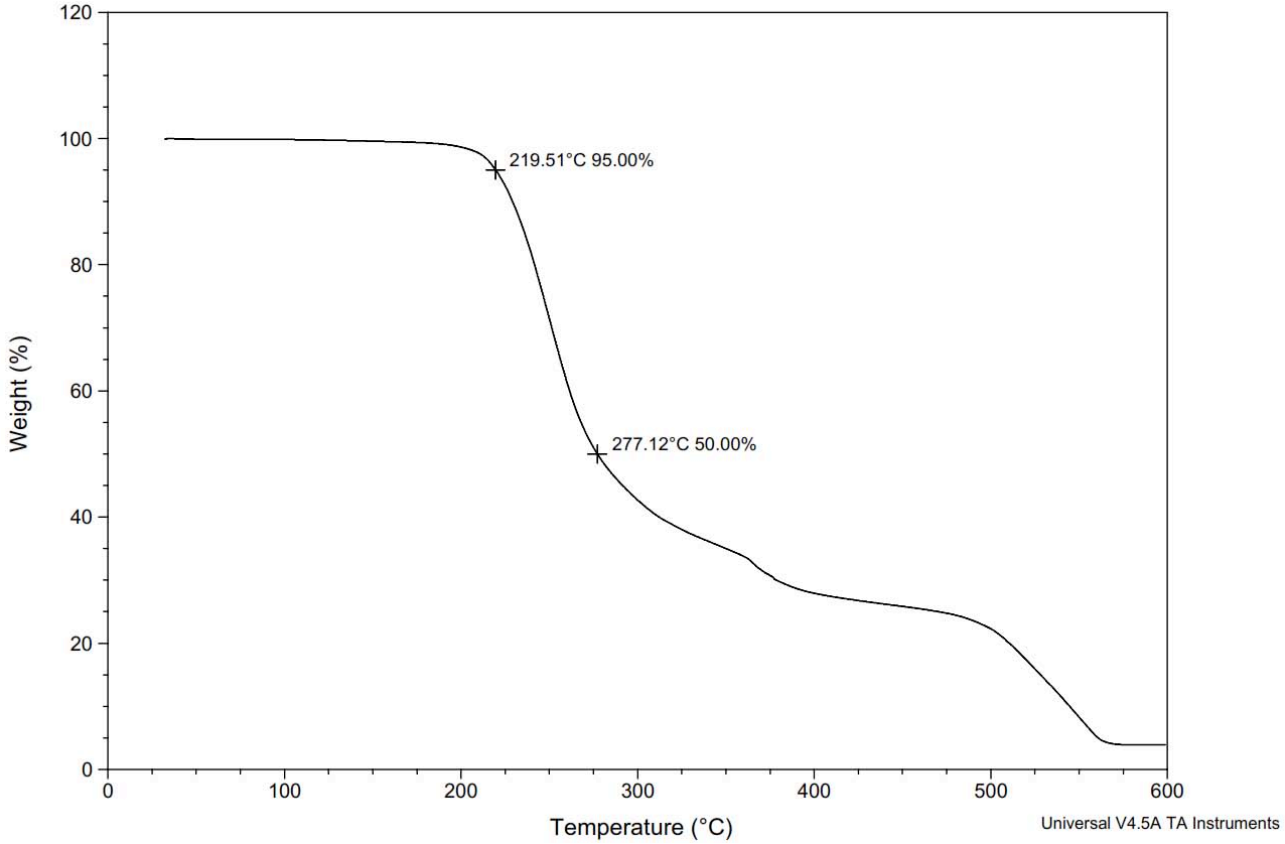


Figure S202. TGA Thermogram of copoly(L-lactide/ hydroxyethylferulic acid) [90:10] (Table S3, entry 12).

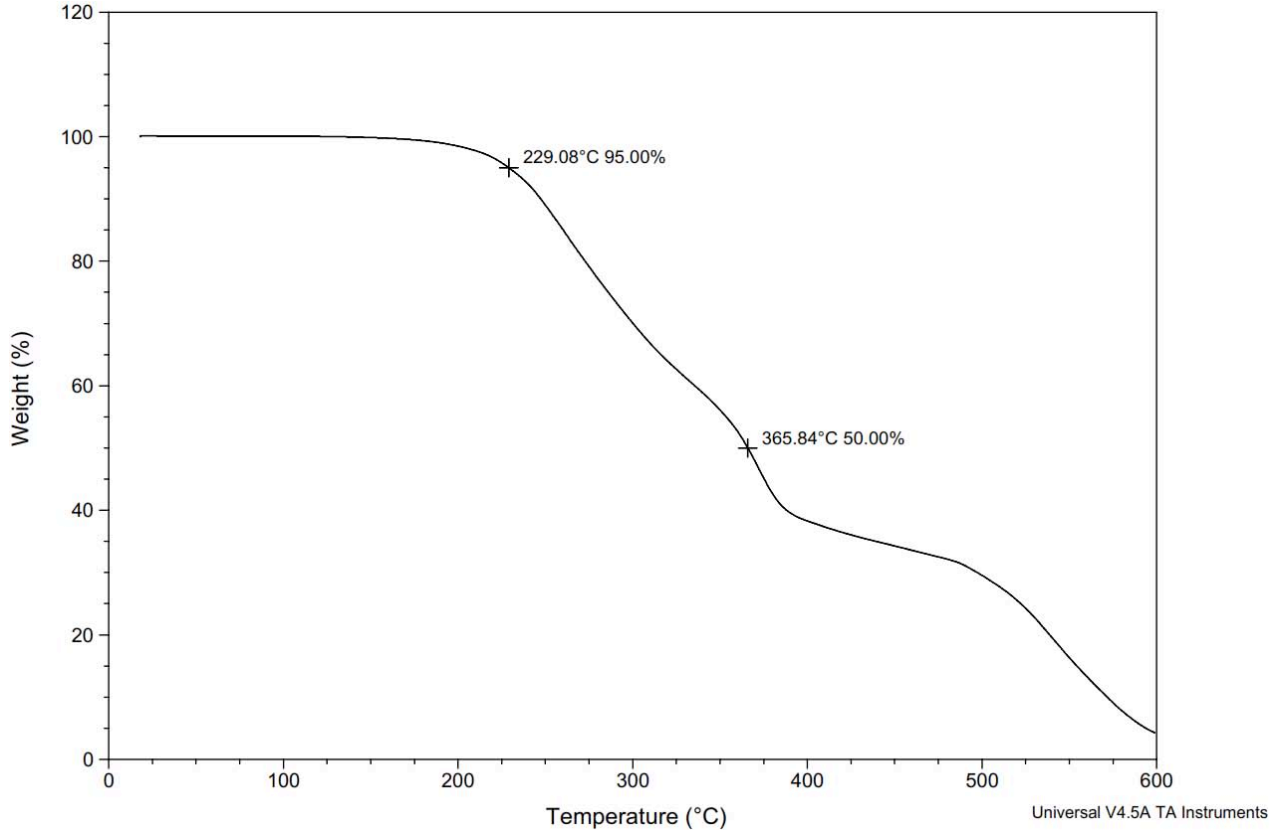


Figure S203. TGA Thermogram of copoly(L-lactide/ hydroxyethylferulic acid) [80:20] (Table S3, entry 13).

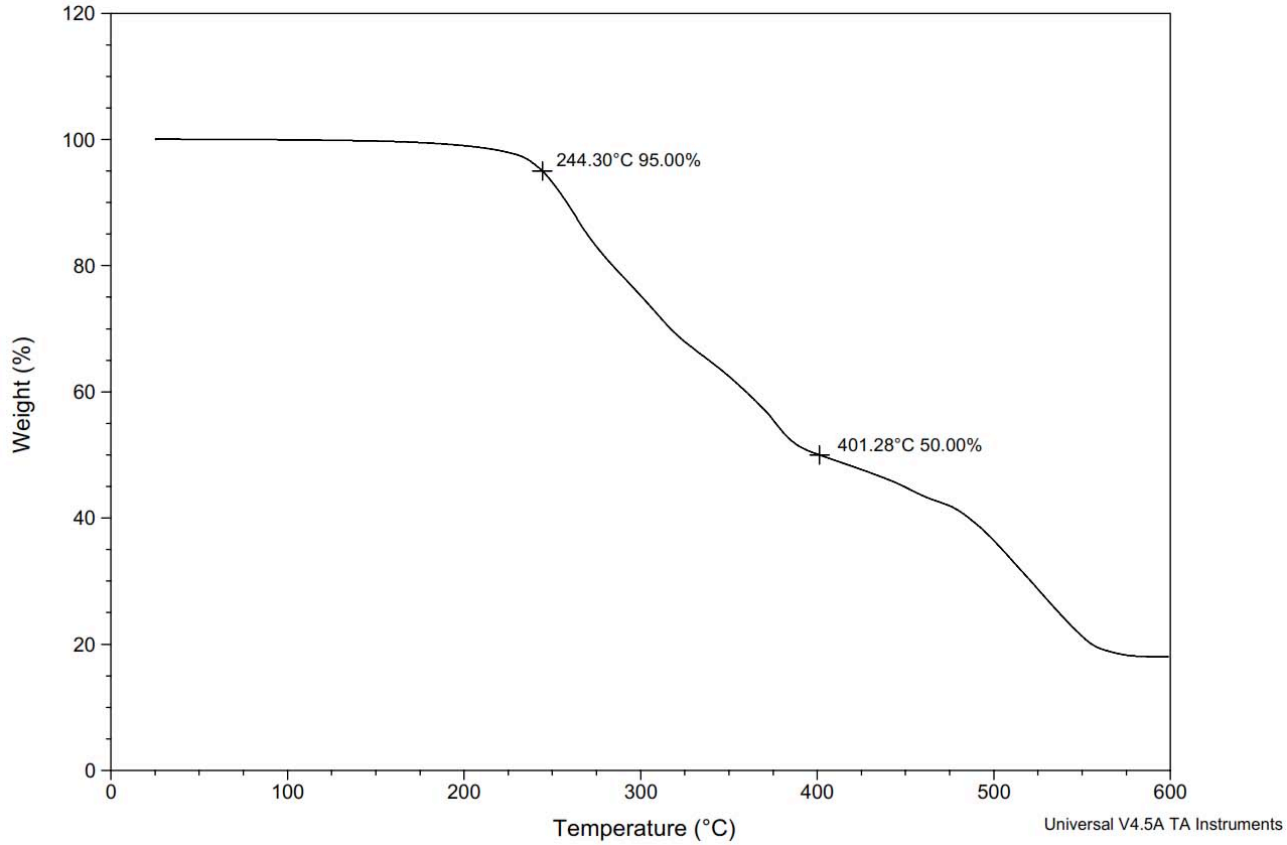


Figure S204. TGA Thermogram of copoly(L-lactide/ hydroxyethylferulic acid) [70:30] (Table S3, entry 14).

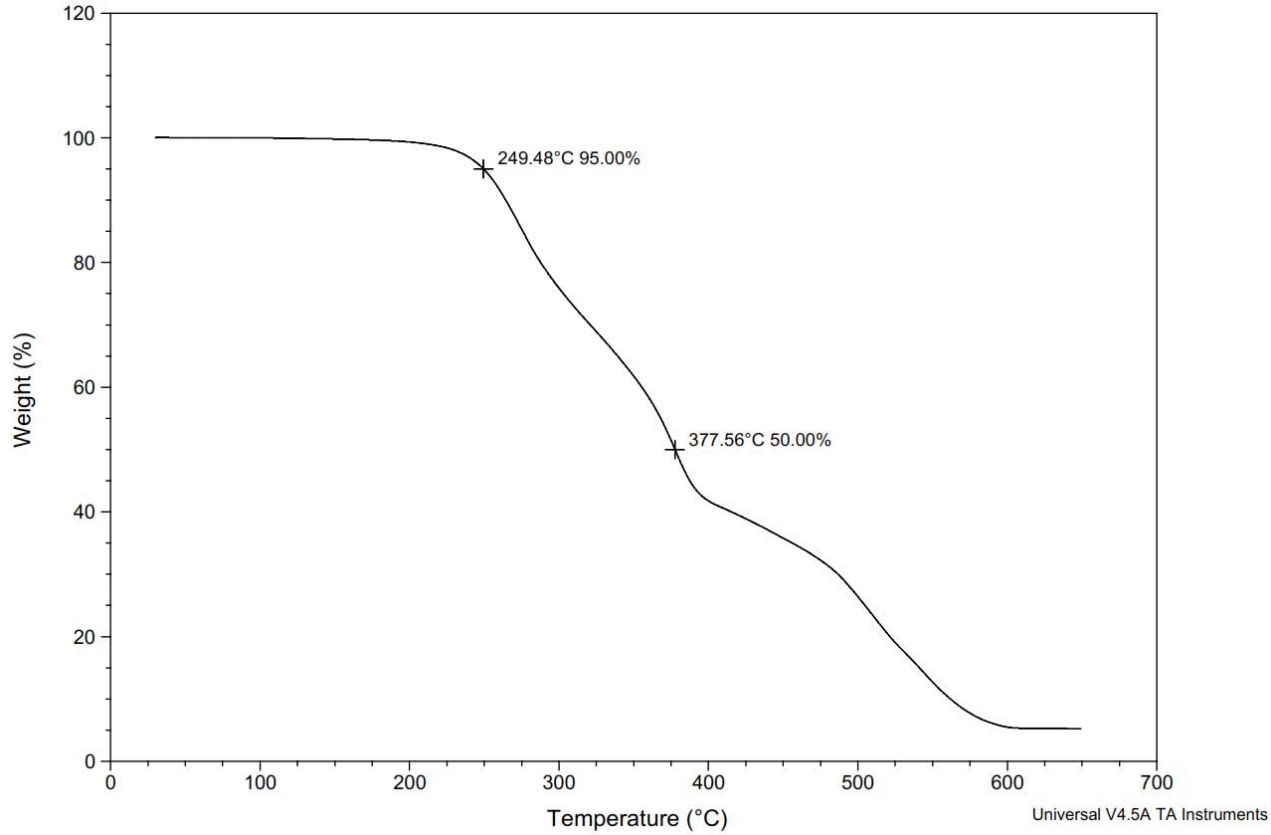


Figure S205. TGA Thermogram of copoly(L-lactide/ hydroxyethylferulic acid) [60:40] (Table S3, entry 15).

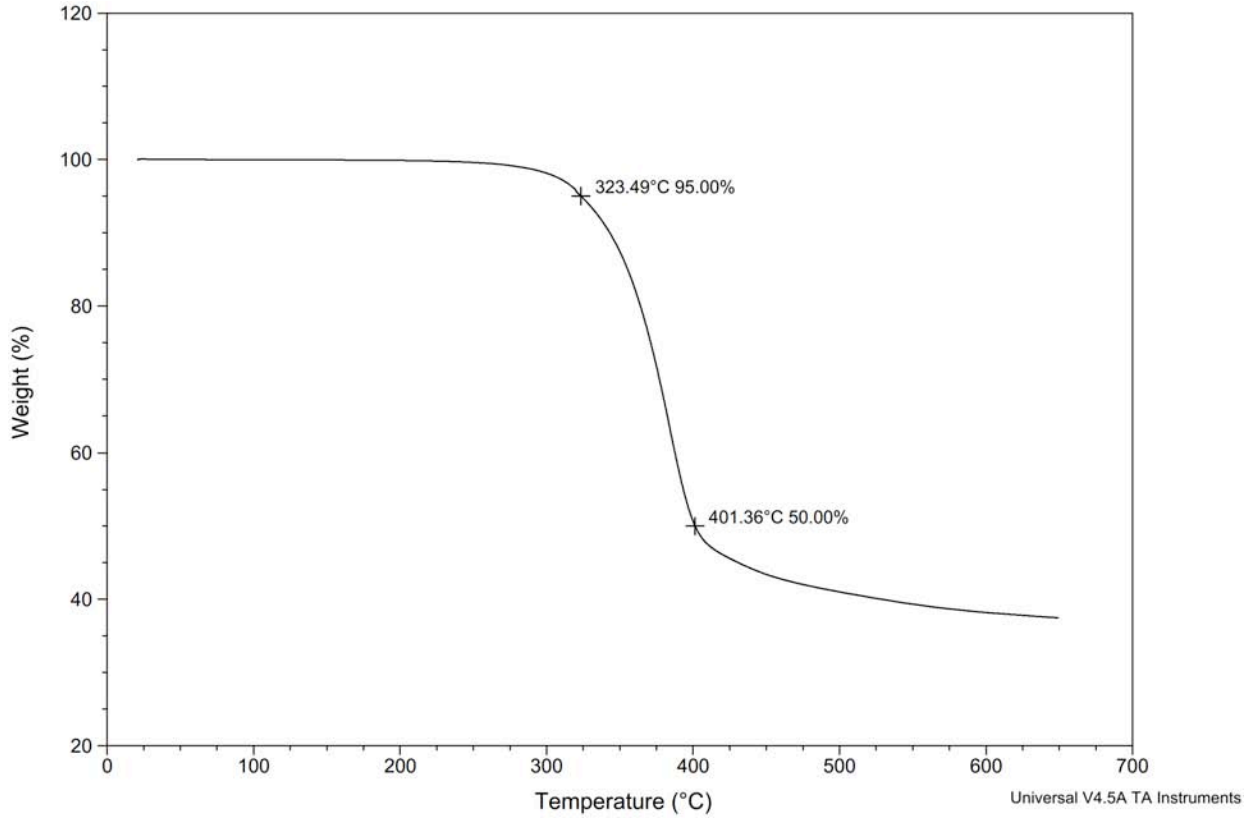


Figure S206. TGA Thermogram of copoly(L-lactide/ hydroxyethylferulic acid) [20:80] (Table S3, entry 16).

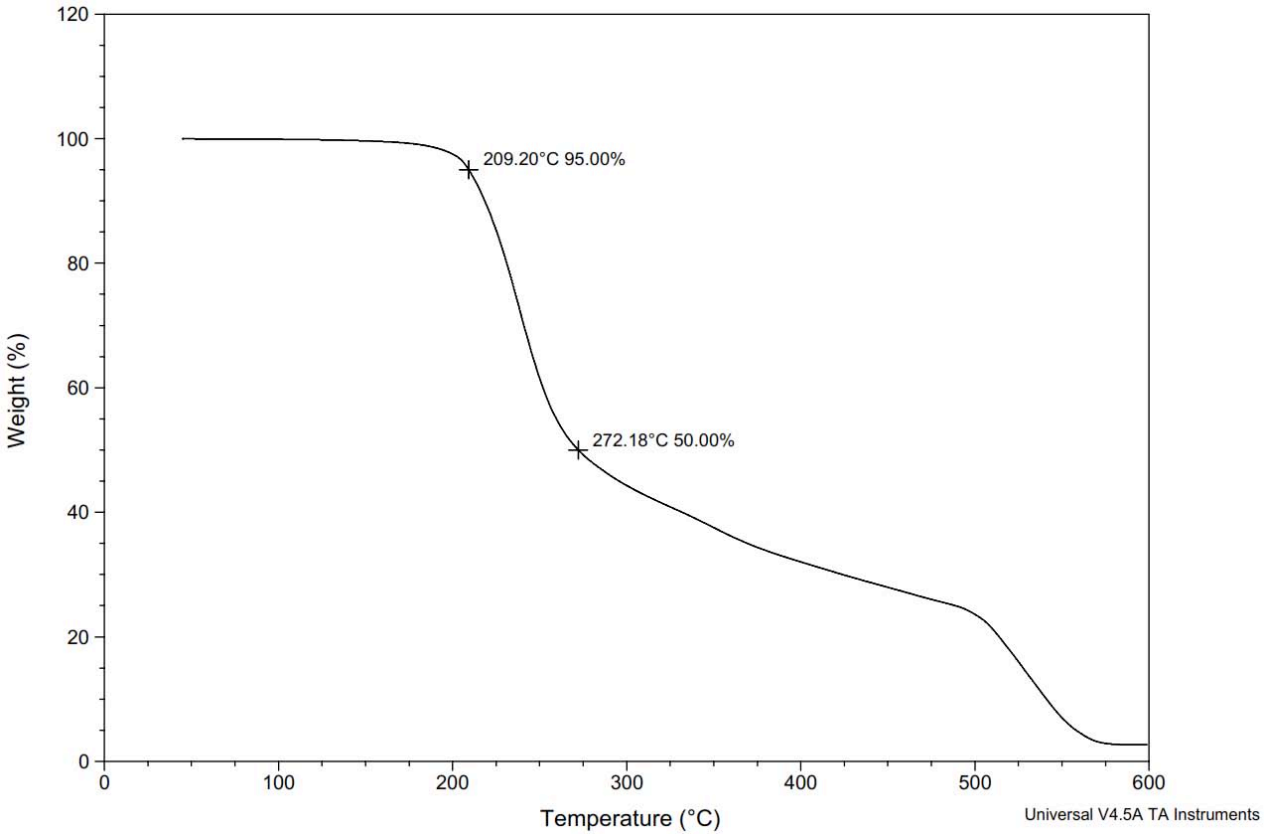


Figure S207. TGA Thermogram of copoly(L-lactide/ hydroxyethylcoumaric acid) [90:10] (Table S3, entry 18).

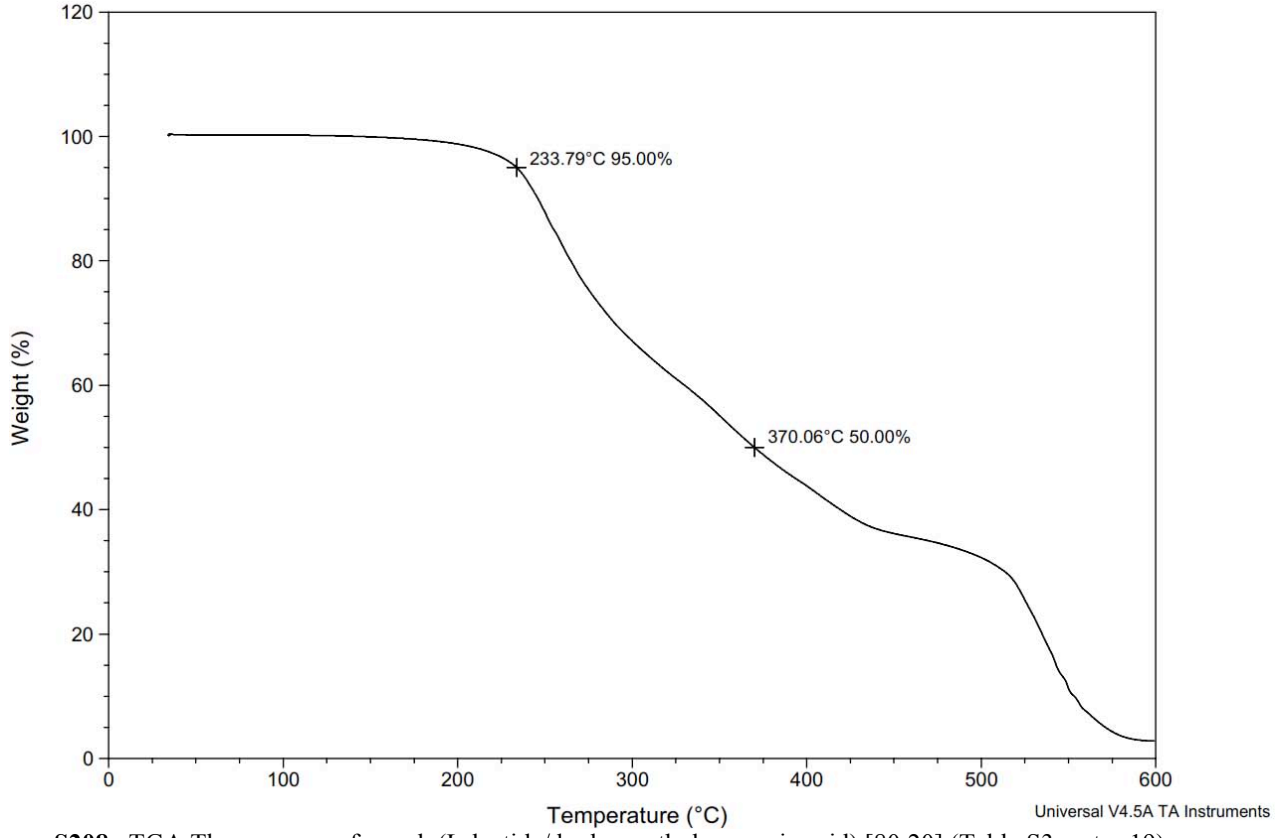


Figure S208. TGA Thermogram of copoly(L-lactide/ hydroxyethylcoumaric acid) [80:20] (Table S3, entry 19).

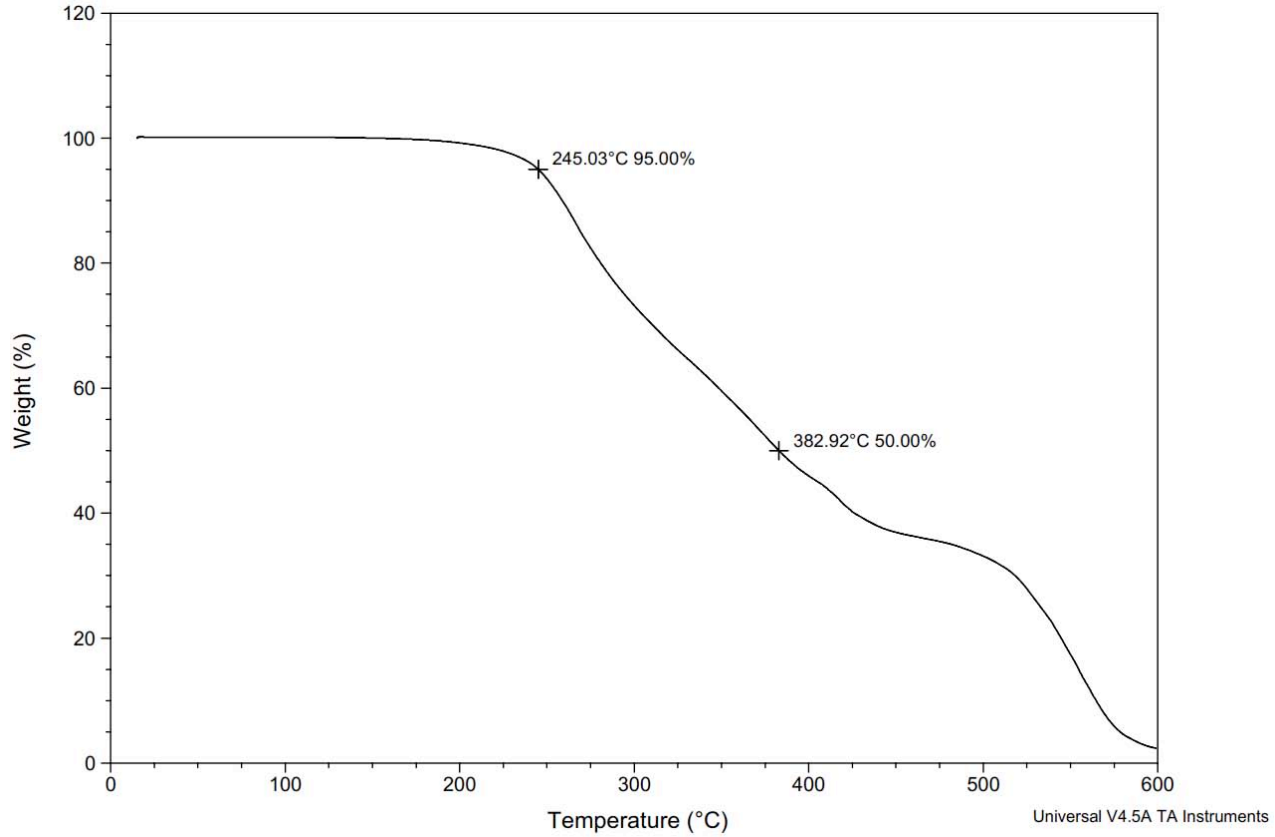


Figure S209. TGA Thermogram of copoly(L-lactide/ hydroxyethylcoumaric acid) [70:30] (Table S3, entry 20).

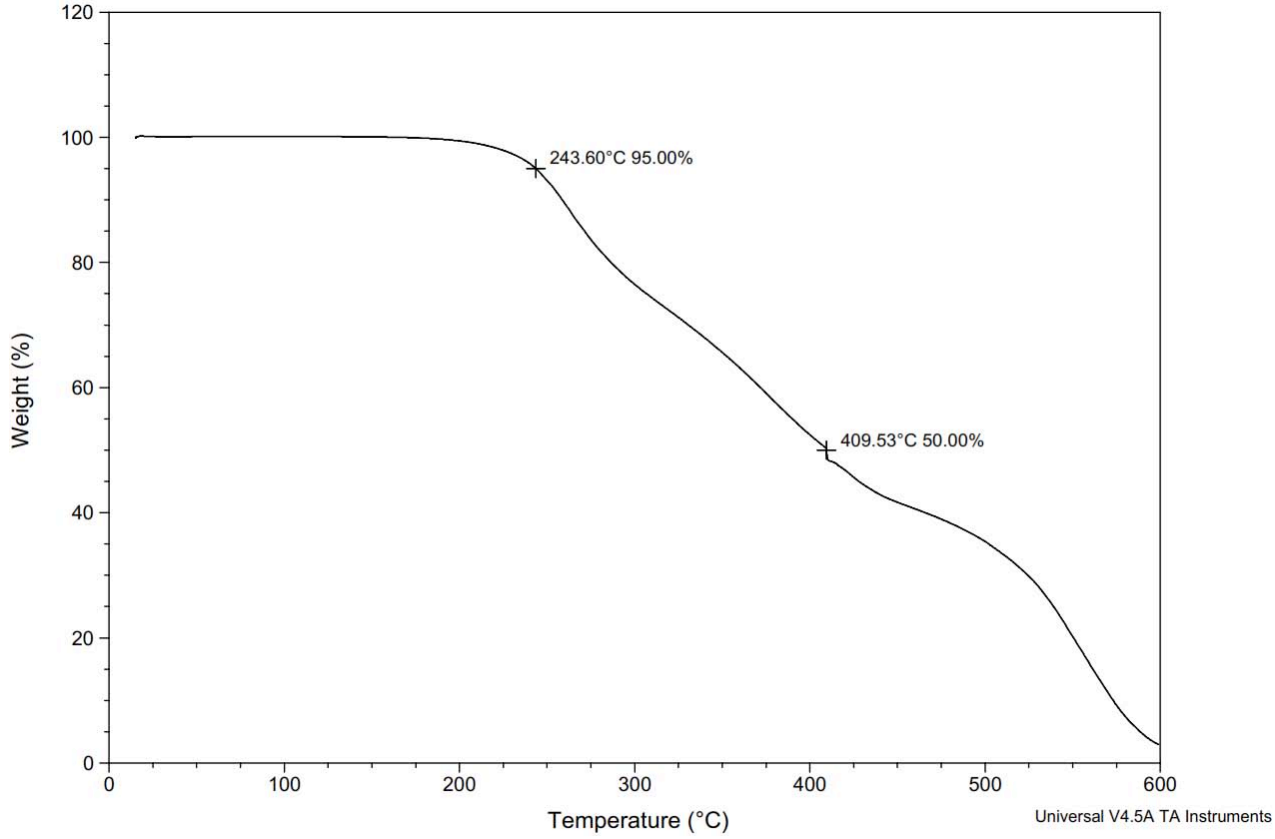


Figure S210. TGA Thermogram of copoly(L-lactide/ hydroxyethylcoumaric acid) [60:40] (Table S3, entry 21).

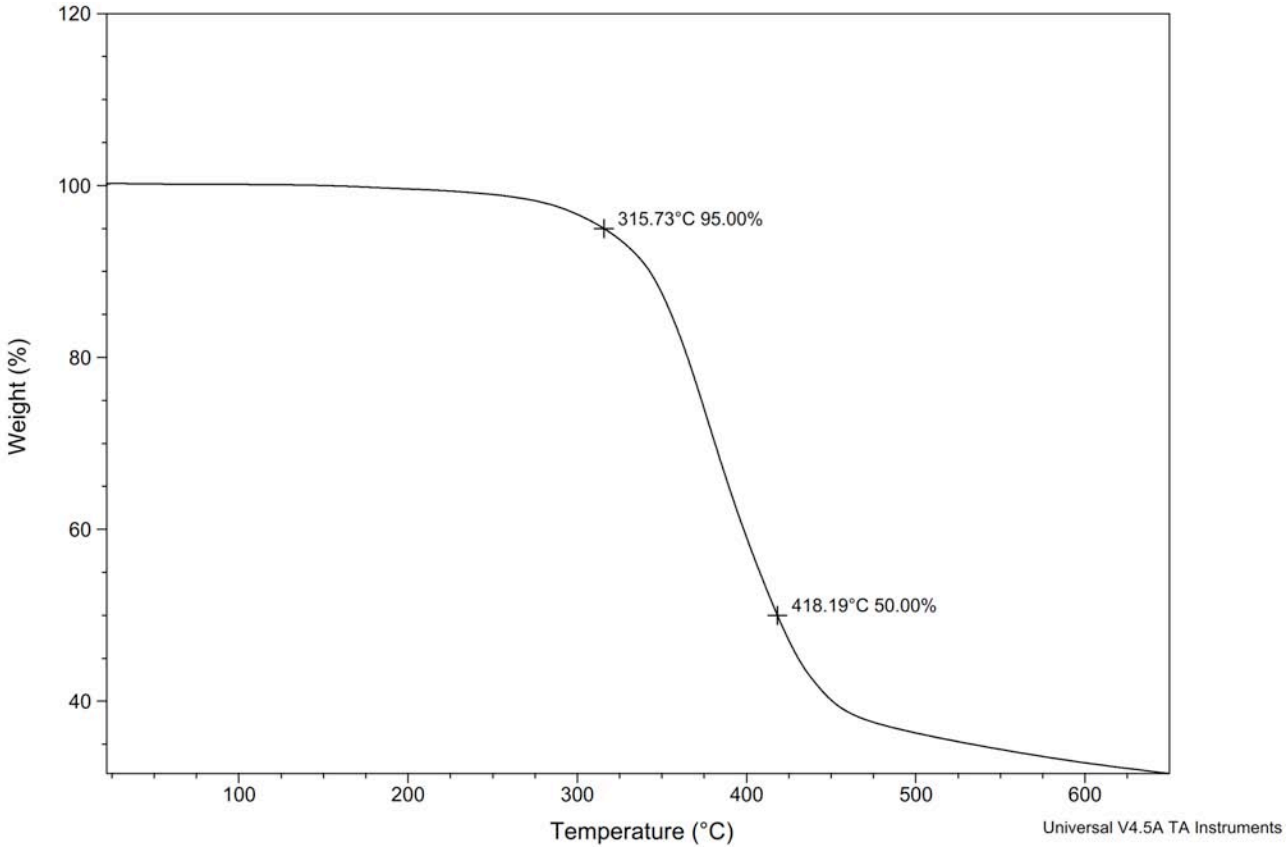


Figure S211. TGA Thermogram of copoly(L-lactide/ hydroxyethylcoumaric acid) [20:80] (Table S3, entry 22).

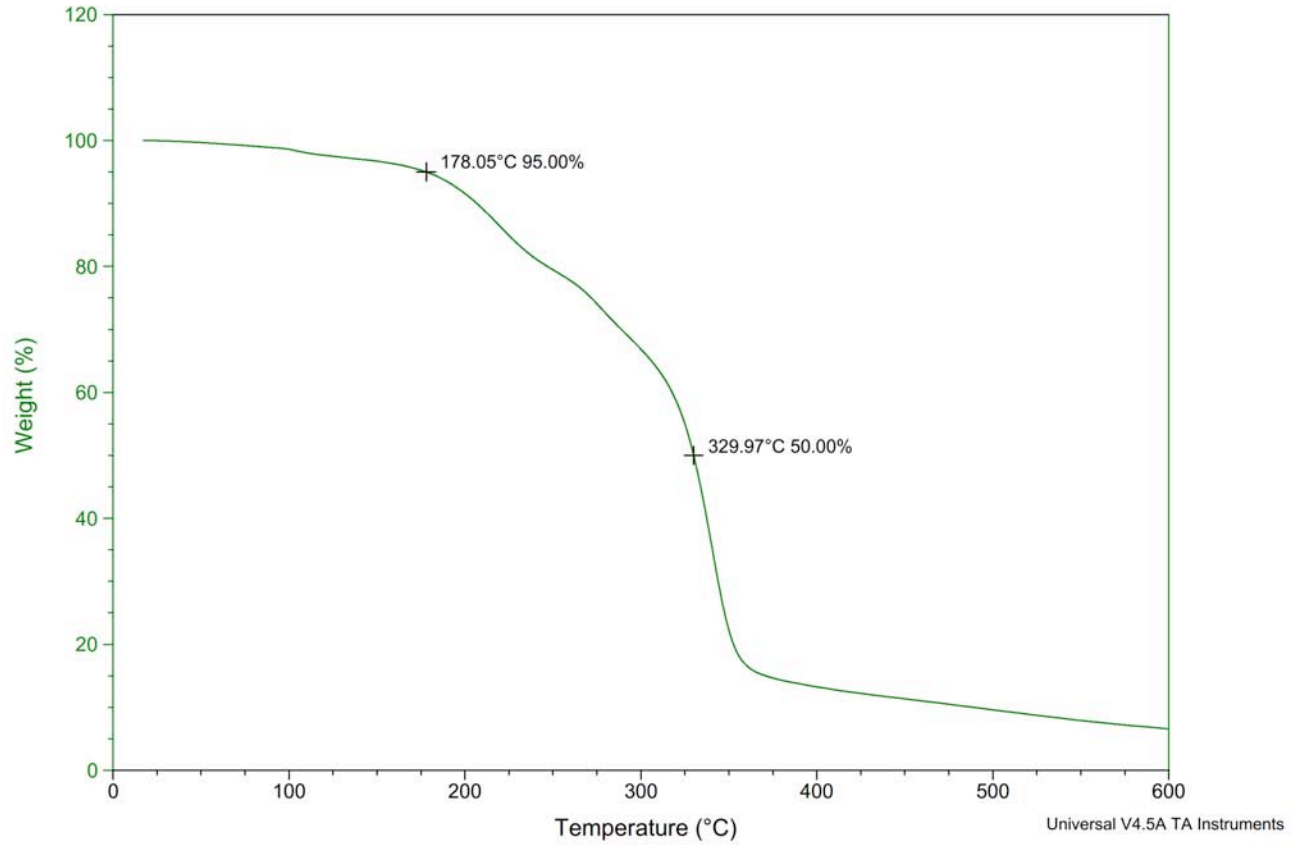


Figure S212. TGA Thermogram of copoly(caprolactone/ hydroxyethylsyringic acid) [50:50] at 10 min. (Table S4, entry 1).

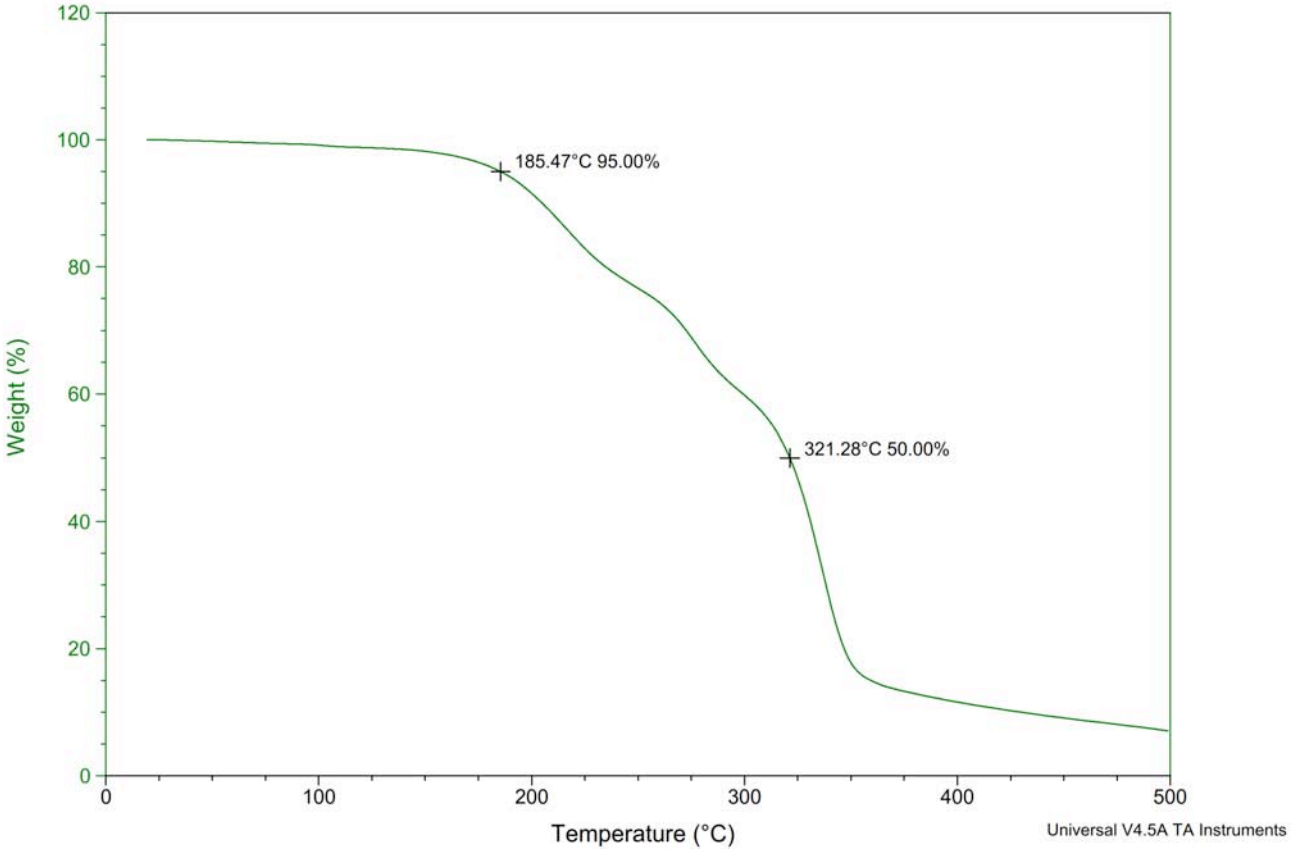


Figure S213. TGA Thermogram of copoly(caprolactone/ hydroxyethylsyringic acid) [50:50] at 20 min. (Table S4, entry 2).

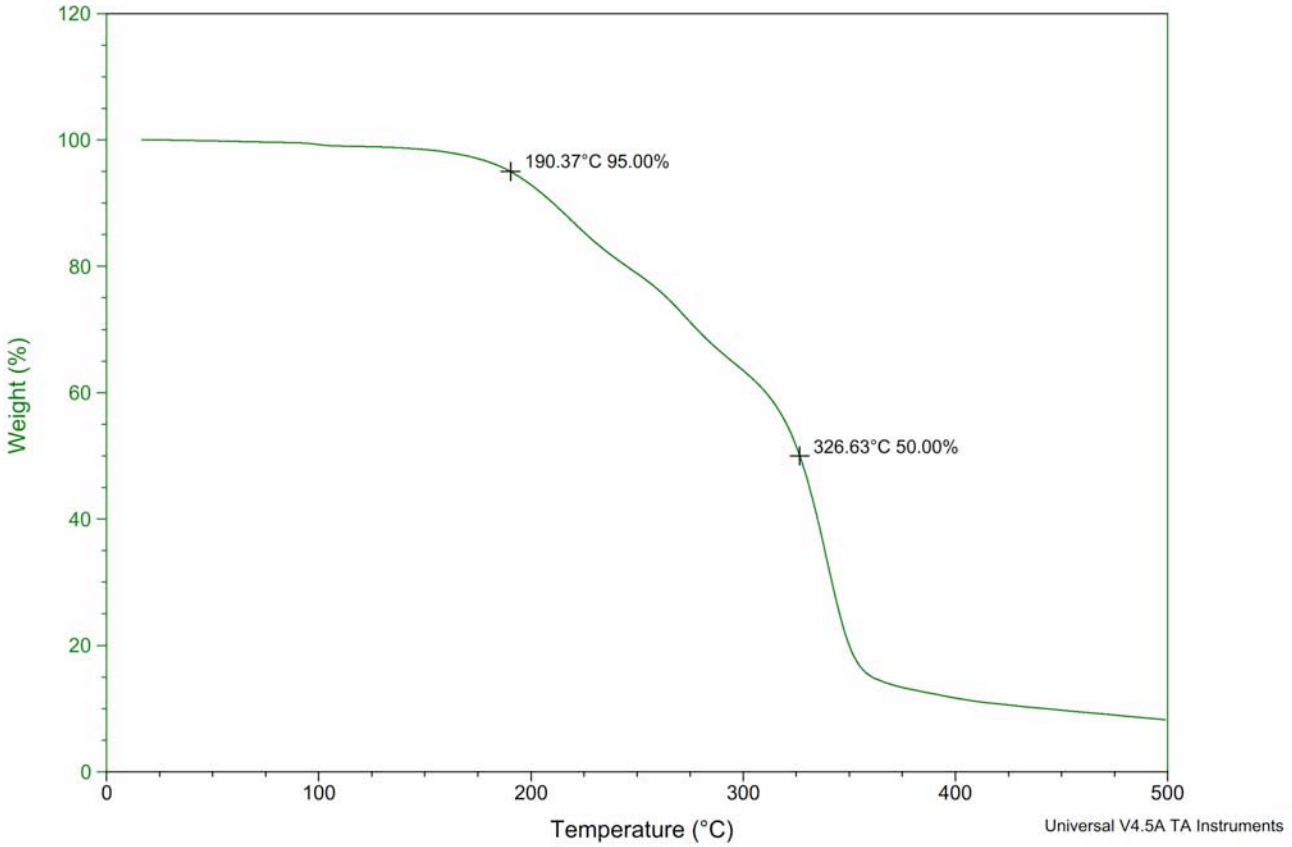


Figure S214. TGA Thermogram of copoly(caprolactone/ hydroxyethylsyringic acid) [50:50] at 30 min. (Table S4, entry 3).

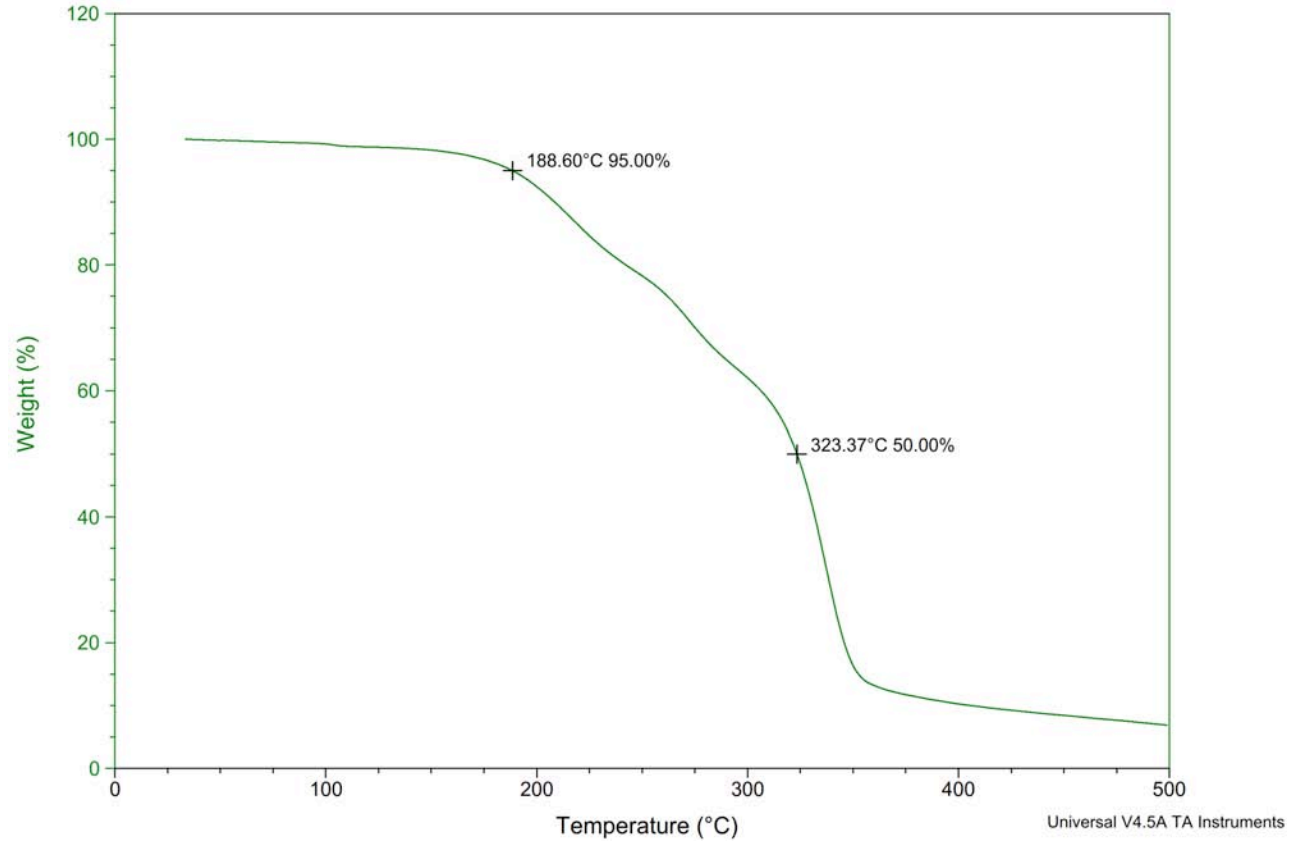


Figure S215. TGA Thermogram of copoly(caprolactone/ hydroxyethylsyringic acid) [50:50] at 1 hour (Table S4, entry 4).

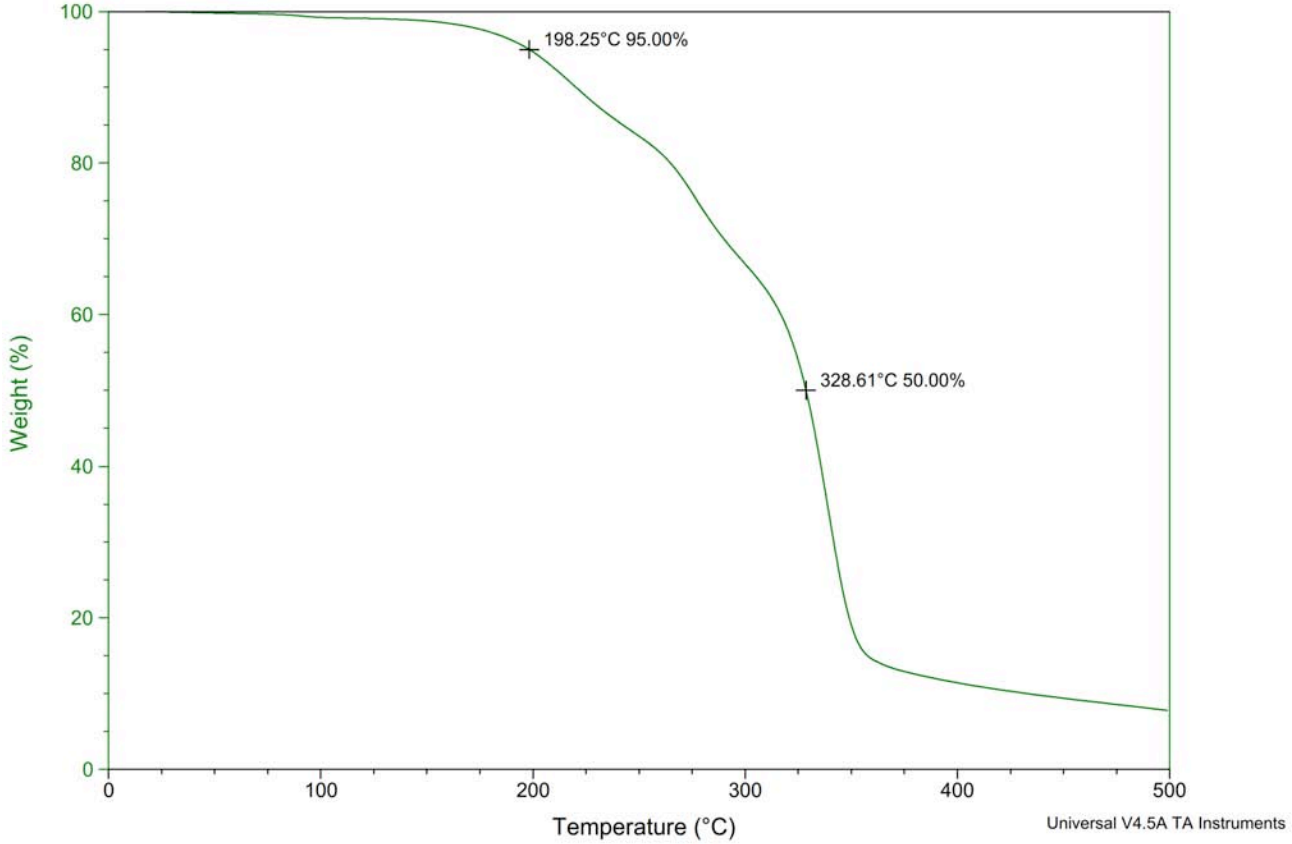


Figure S216. TGA Thermogram of copoly(caprolactone/ hydroxyethylsyringic acid) [50:50] at 1.5 hours (Table S4, entry 5).

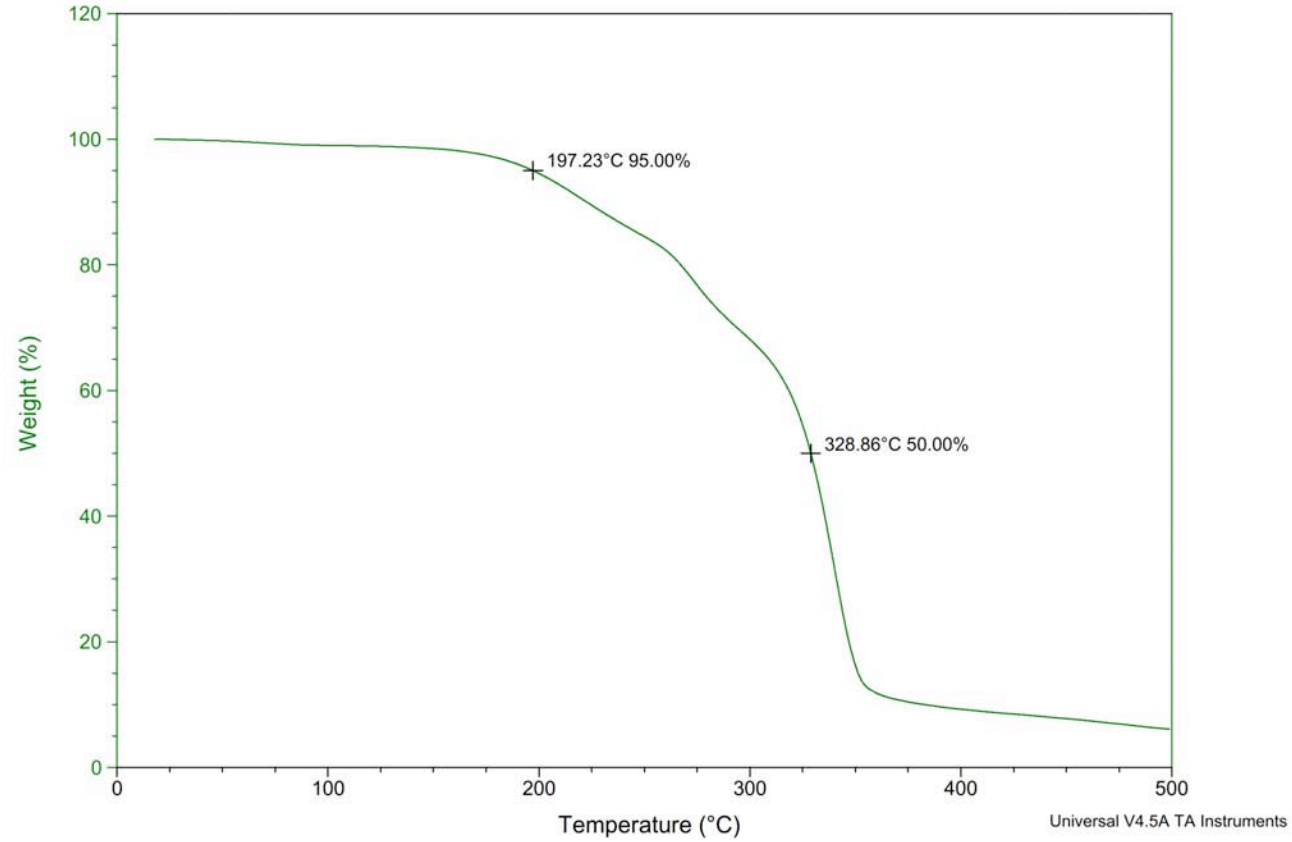


Figure S217. TGA Thermogram of copoly(caprolactone/ hydroxyethylsyringic acid) [50:50] at 2 hours (Table S4, entry 6).

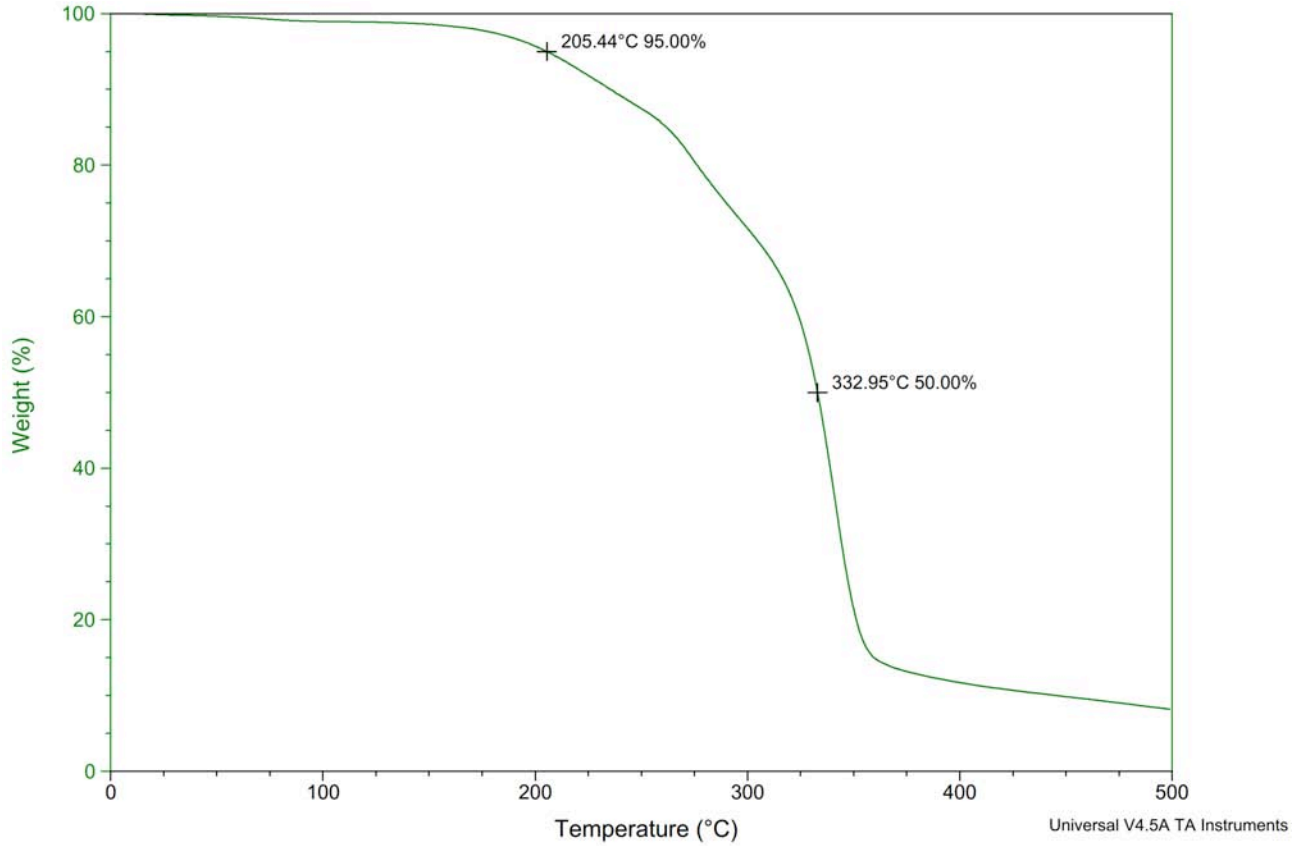


Figure S218. TGA Thermogram of copoly(caprolactone/ hydroxyethylsyringic acid) [50:50] at 2.5 hours (Table S4, entry 7).

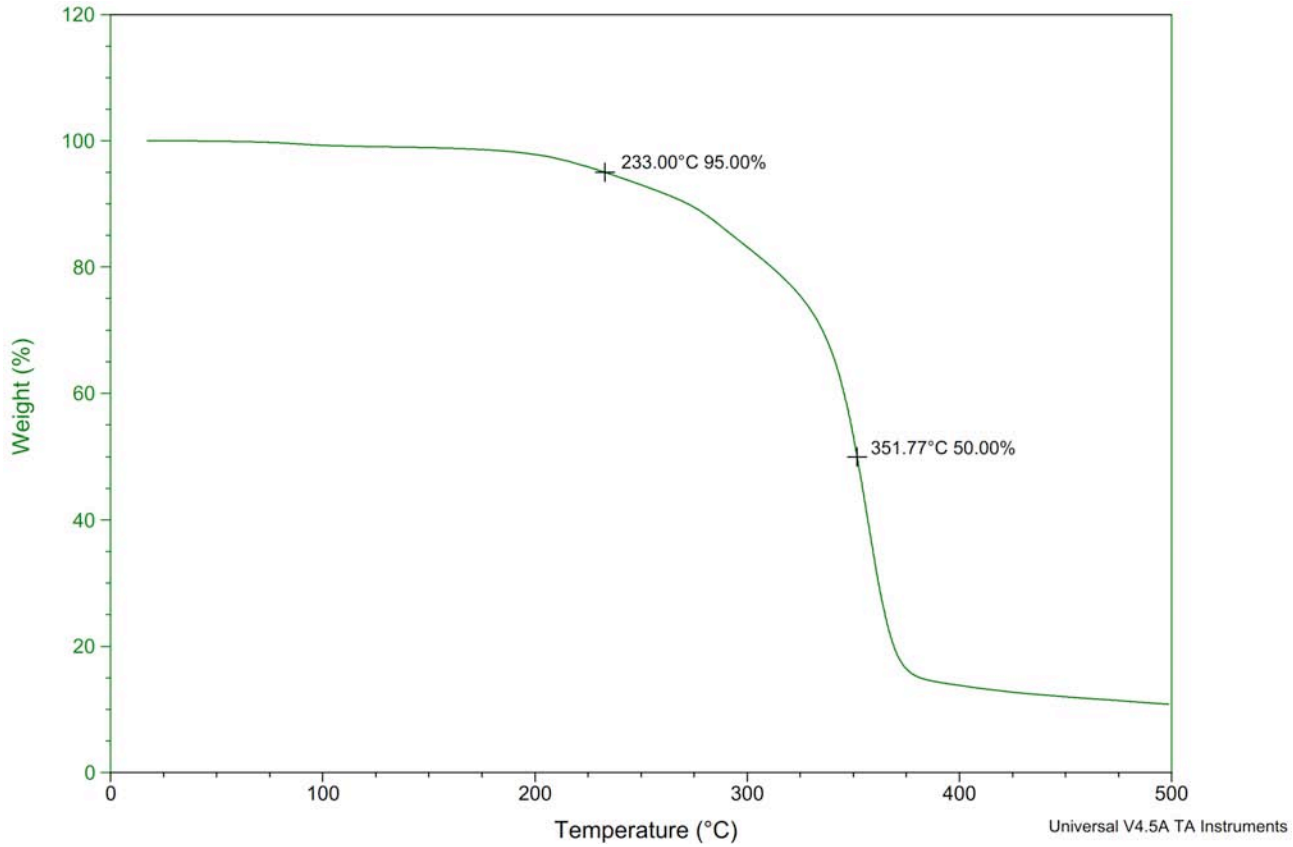


Figure S219. TGA Thermogram of copoly(caprolactone/ hydroxyethylsyringic acid) [50:50] at 3 hours (Table S4, entry 8).

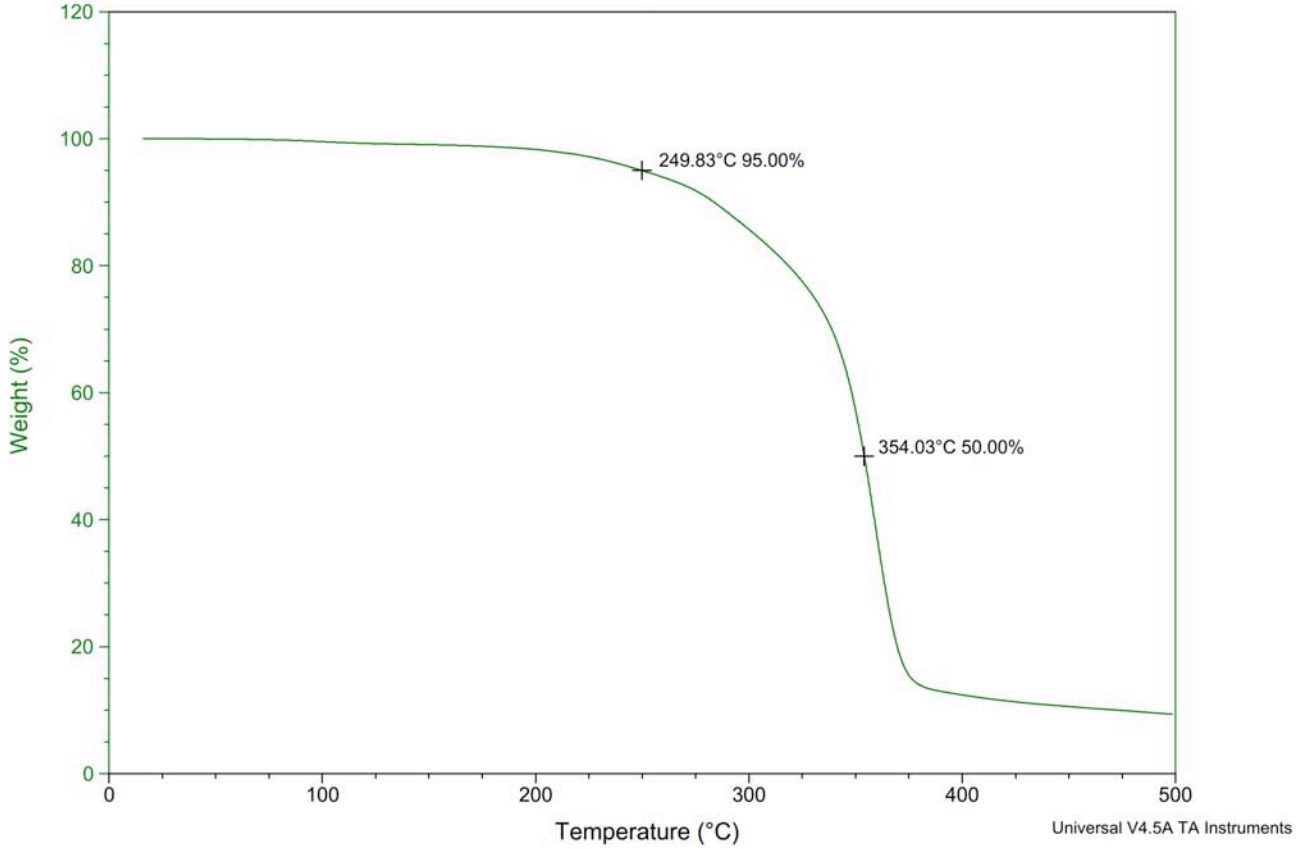


Figure S220. TGA Thermogram of copoly(caprolactone/ hydroxyethylsyringic acid) [50:50] at 3.5 hours (Table S4, entry 9).

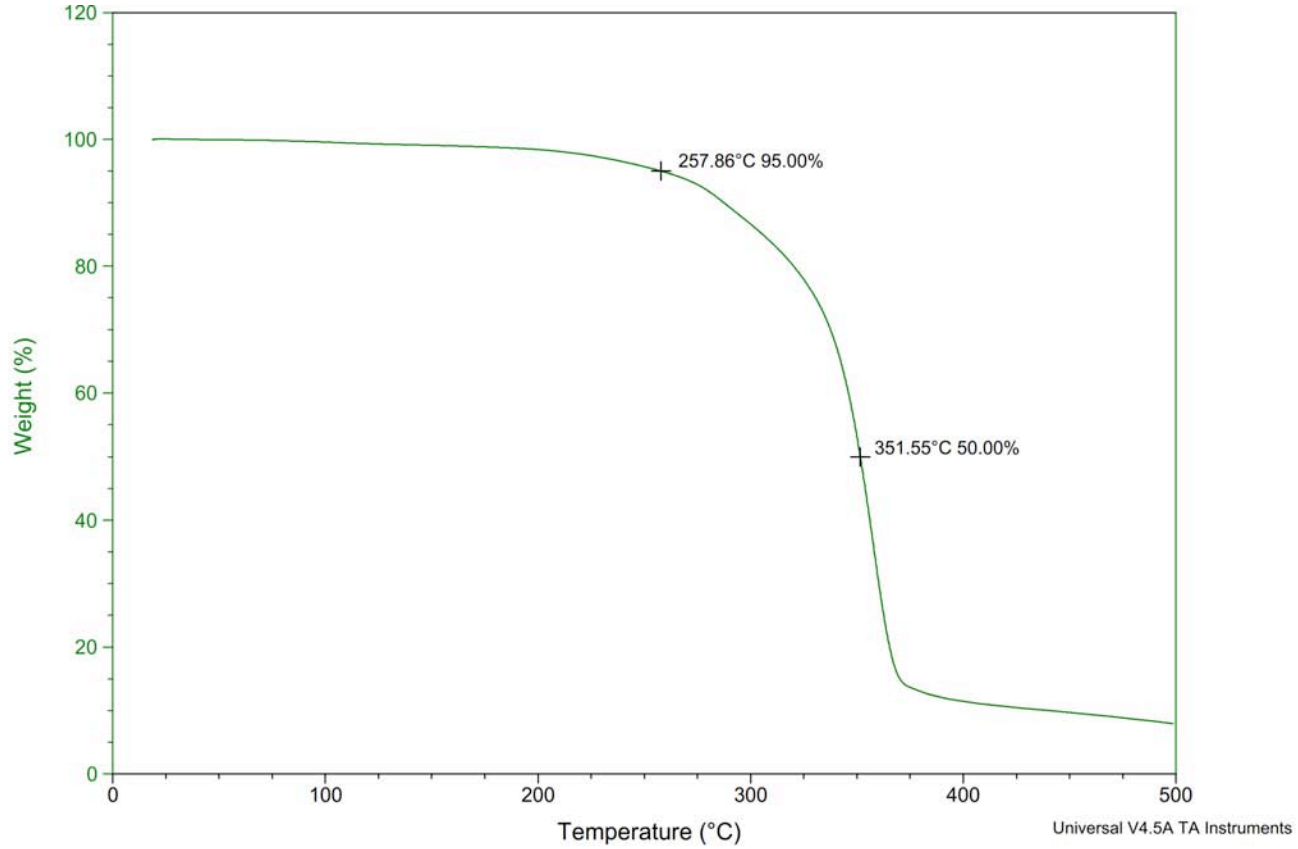


Figure S221. TGA Thermogram of copoly(caprolactone/ hydroxyethylsyringic acid) [50:50] at 4 hours (Table S4, entry 10).

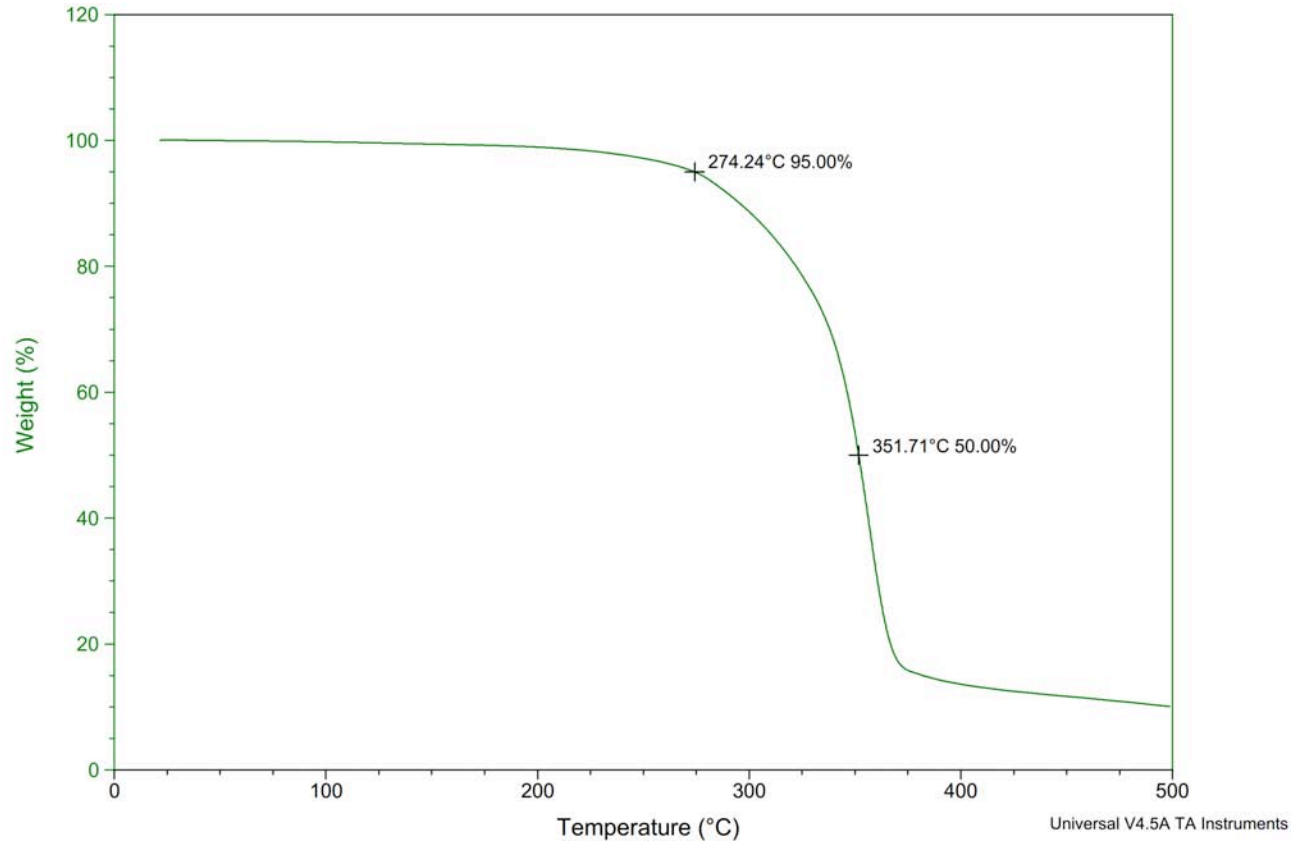


Figure S222. TGA Thermogram of copoly(caprolactone/ hydroxyethylsyringic acid) [50:50] at 4.5 hours (Table S4, entry 11).

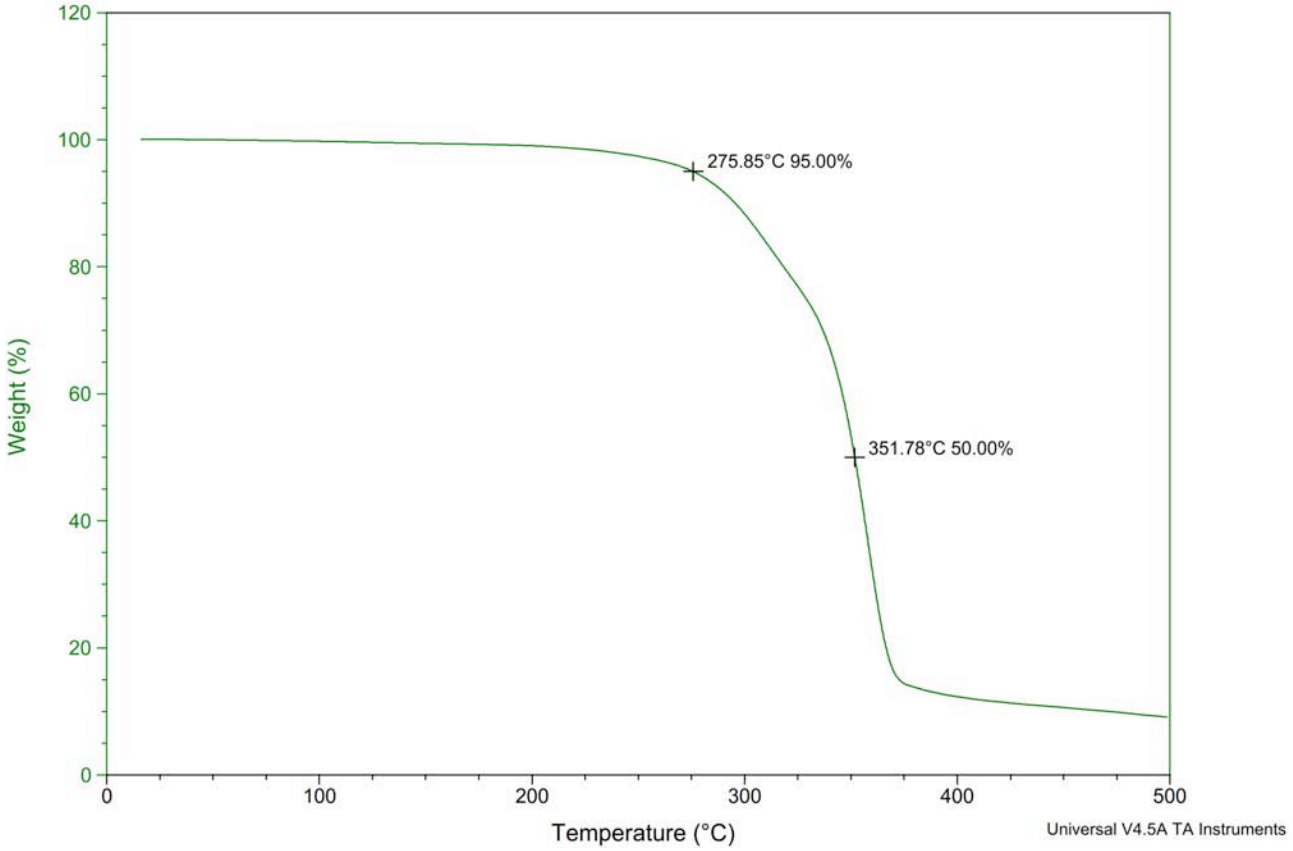


Figure S223. TGA Thermogram of copoly(caprolactone/ hydroxyethylsyringic acid) [50:50] at 5 hours (Table S4, entry 12).

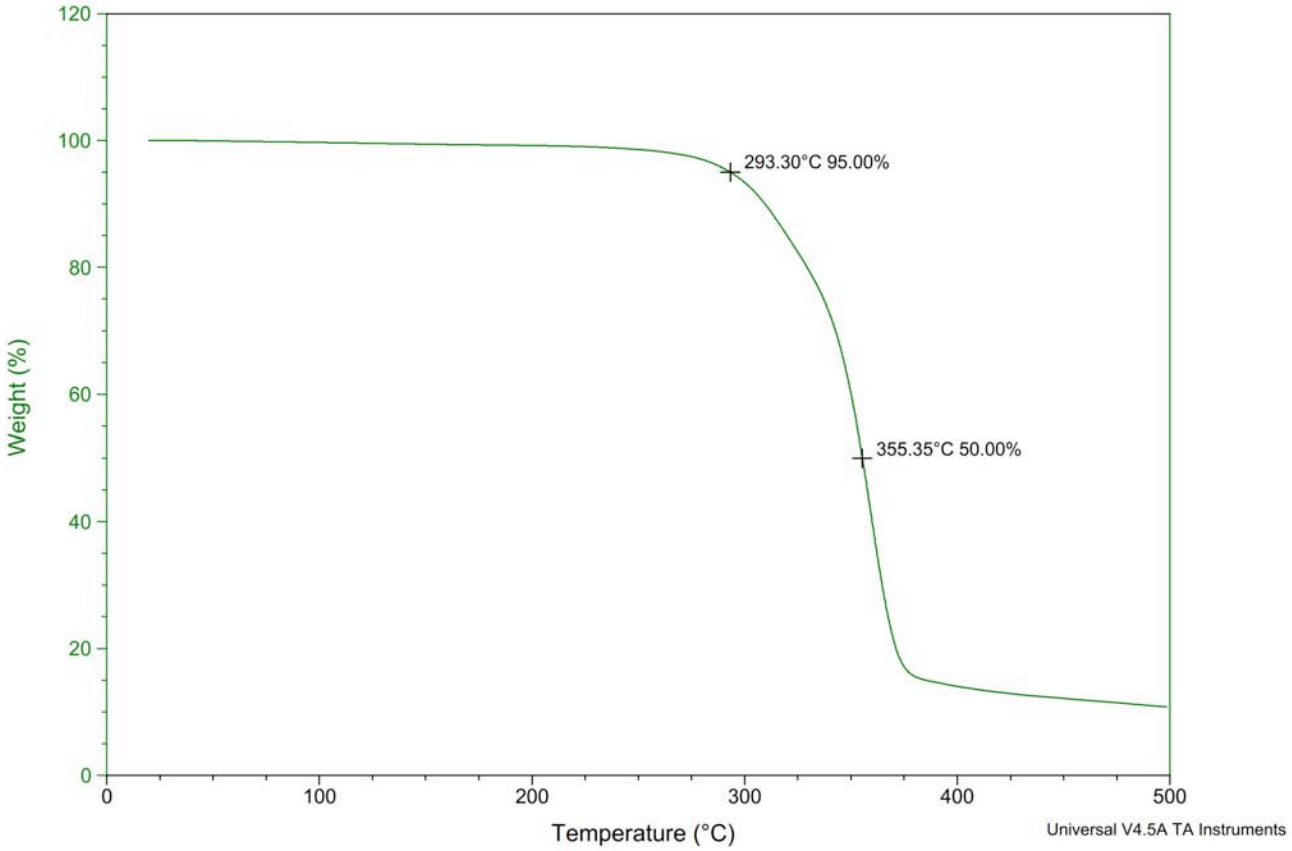


Figure S224. TGA Thermogram of copoly(caprolactone/ hydroxyethylsyringic acid) [50:50] at 6 hours (Table S4, entry 13).

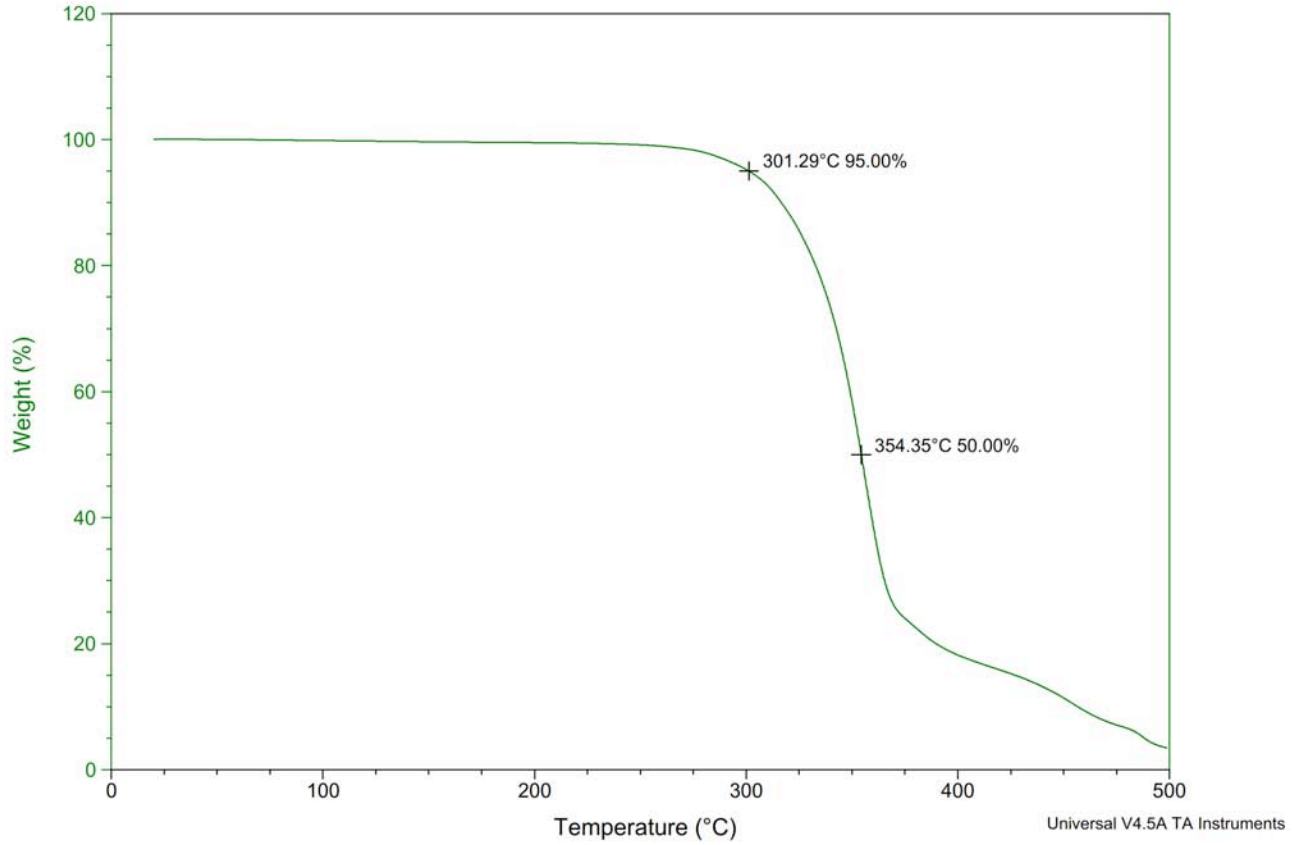


Figure S225. TGA Thermogram of copoly(caprolactone/ hydroxyethylsyringic acid) [50:50] at 7 hours (Table S4, entry 14).

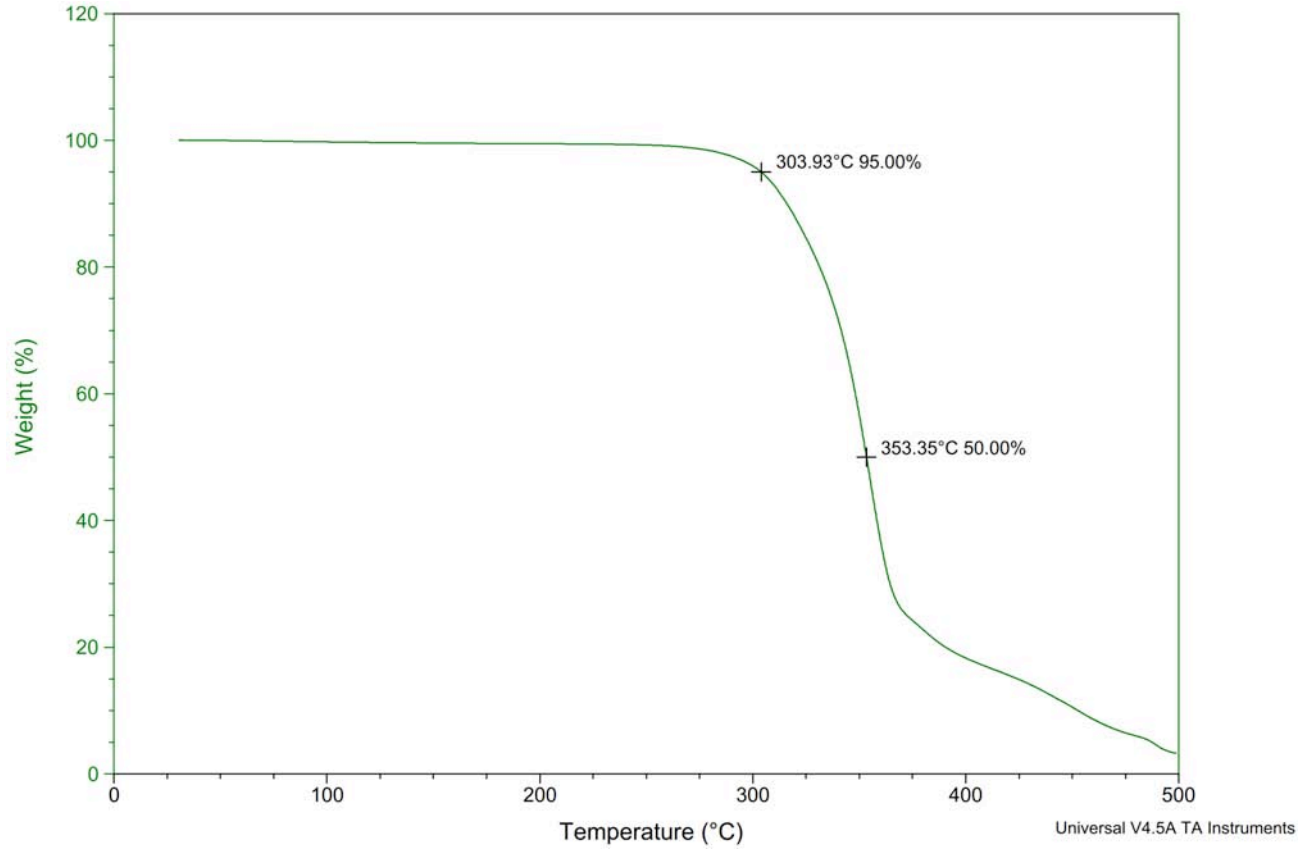


Figure S226. TGA Thermogram of copoly(caprolactone/ hydroxyethylsyringic acid) [50:50] at 8 hours (Table S4, entry 15).

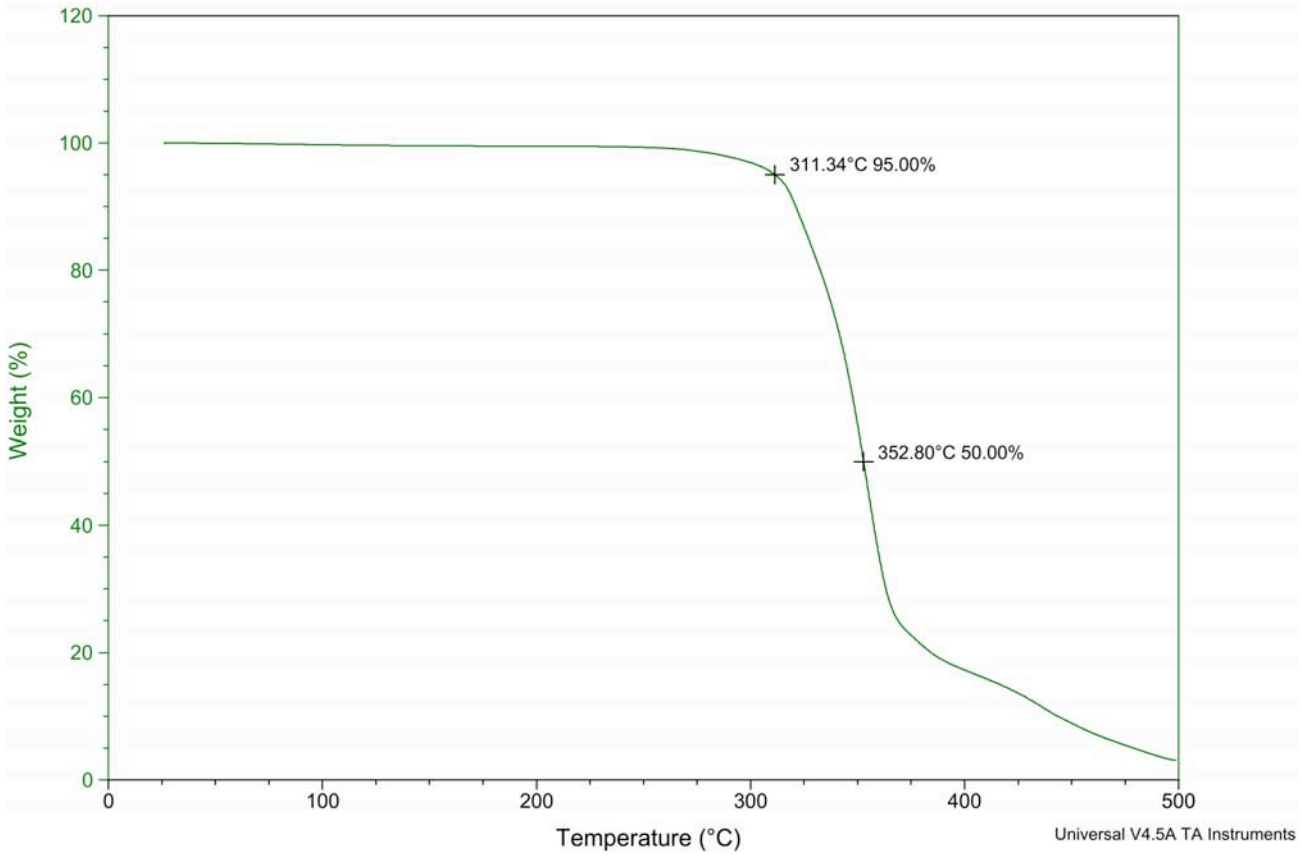


Figure S227. TGA Thermogram of copoly(caprolactone/ hydroxyethylsyringic acid) [50:50] at 9 hours (Table S4, entry 16).

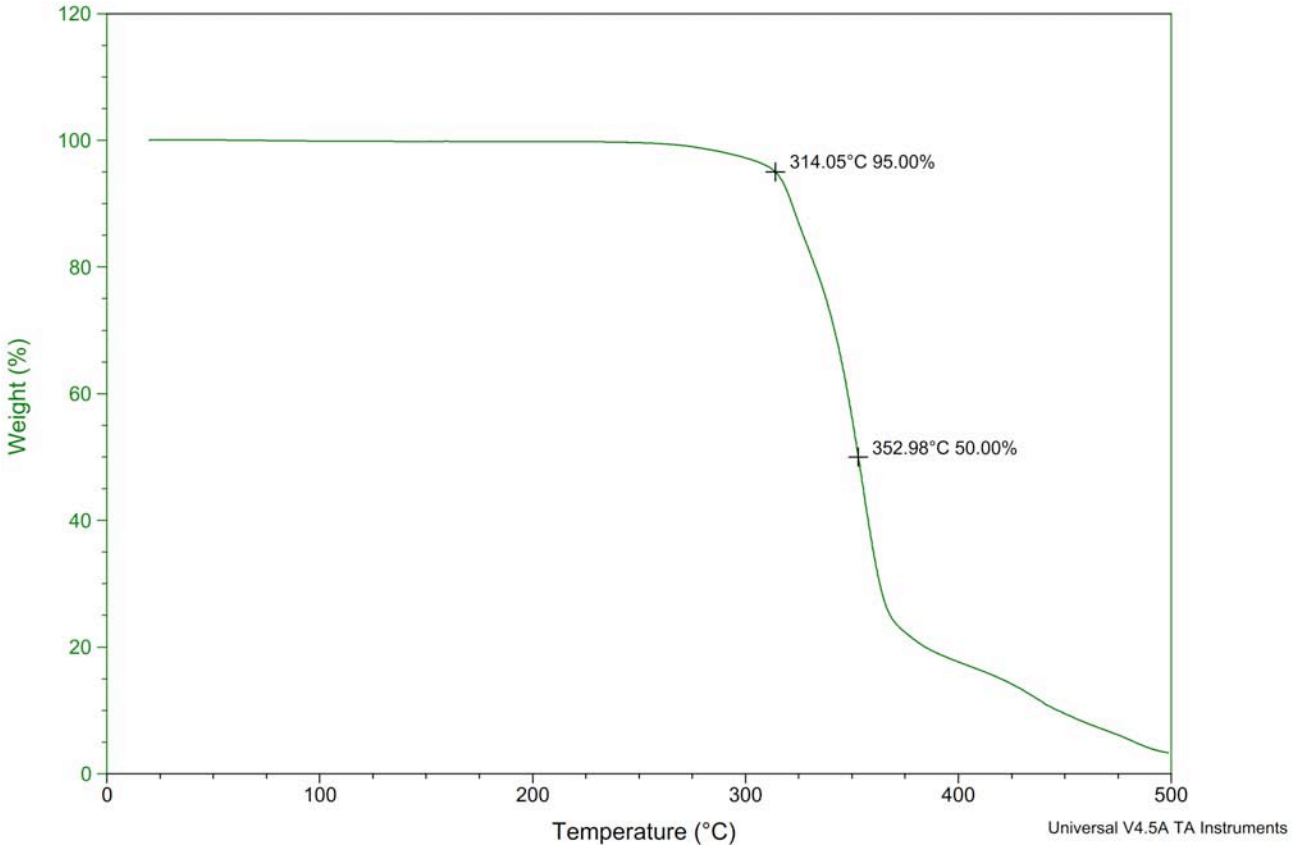


Figure S228. TGA Thermogram of copoly(caprolactone/ hydroxyethylsyringic acid) [50:50] at 10 hours (Table S4, entry 17).

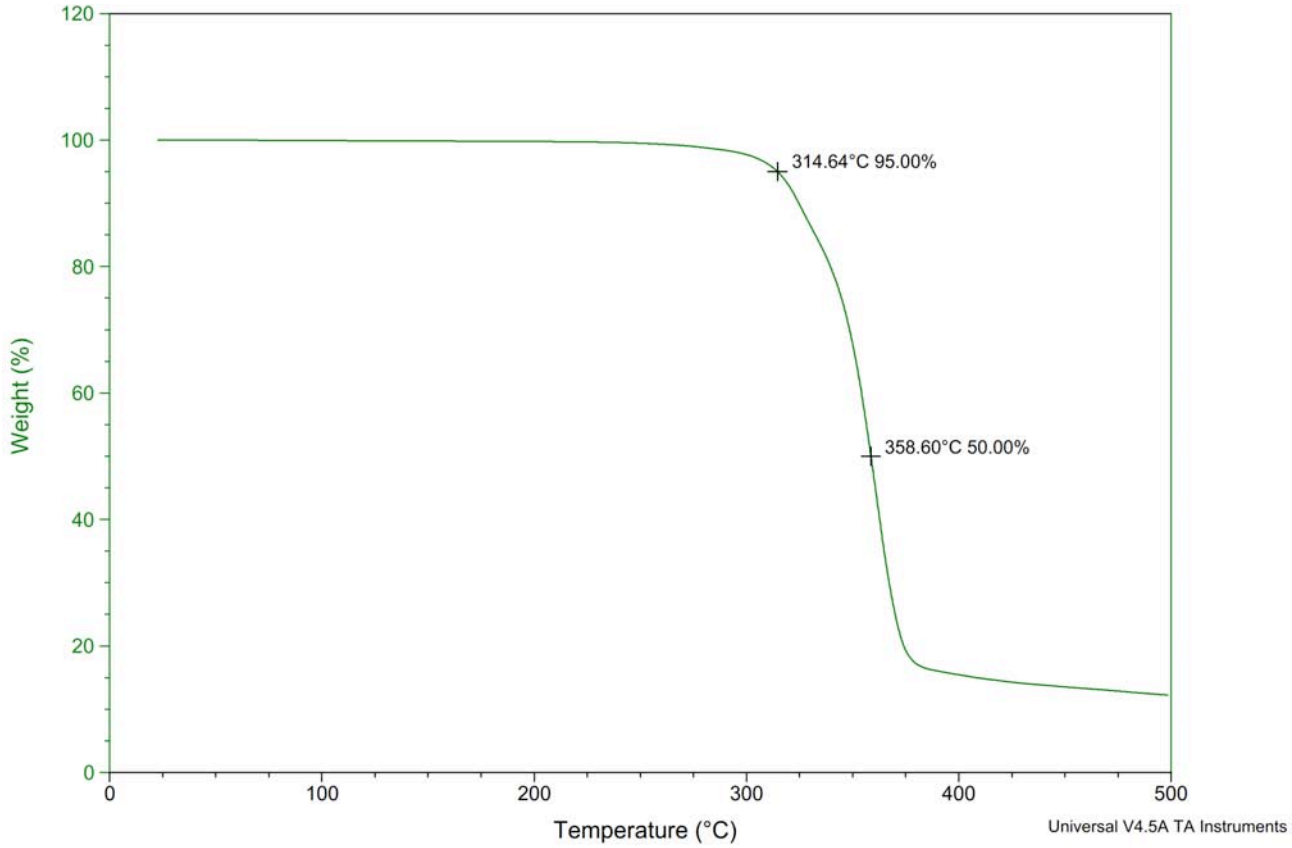


Figure S229. TGA Thermogram of copoly(caprolactone/ hydroxyethylsyringic acid) [50:50] at 13 hours (Table S4, entry 18).

^{1}H NMR Spectra

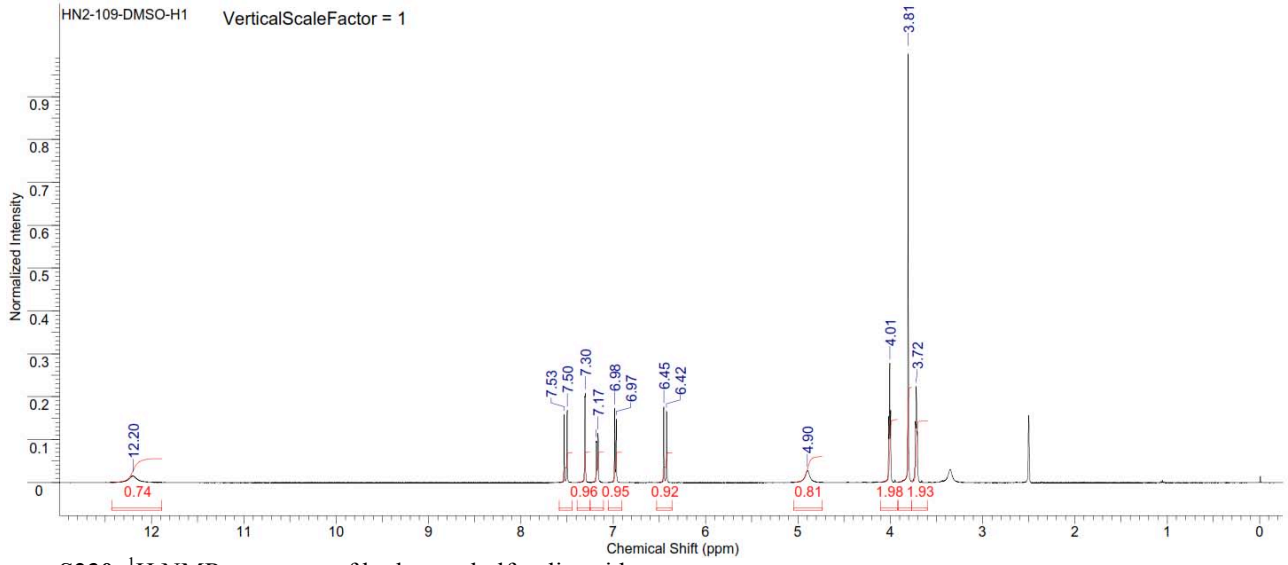


Figure S230. ^{1}H NMR spectrum of hydroxyethylferulic acid.

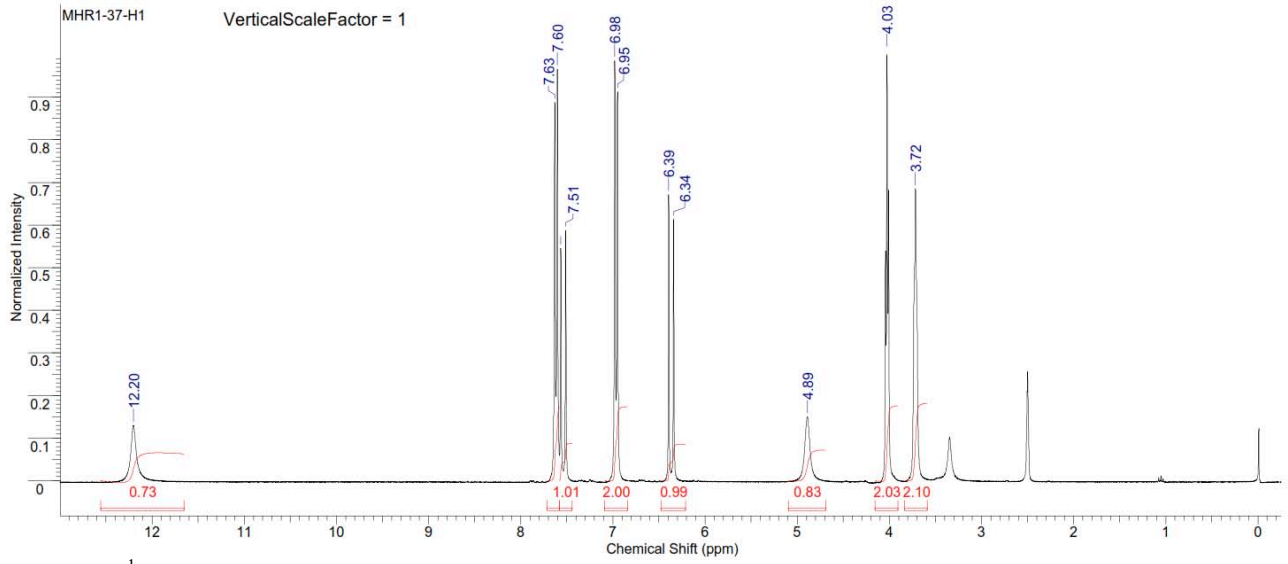


Figure S231. ^{1}H NMR spectrum of hydroxyethylcoumaric acid.

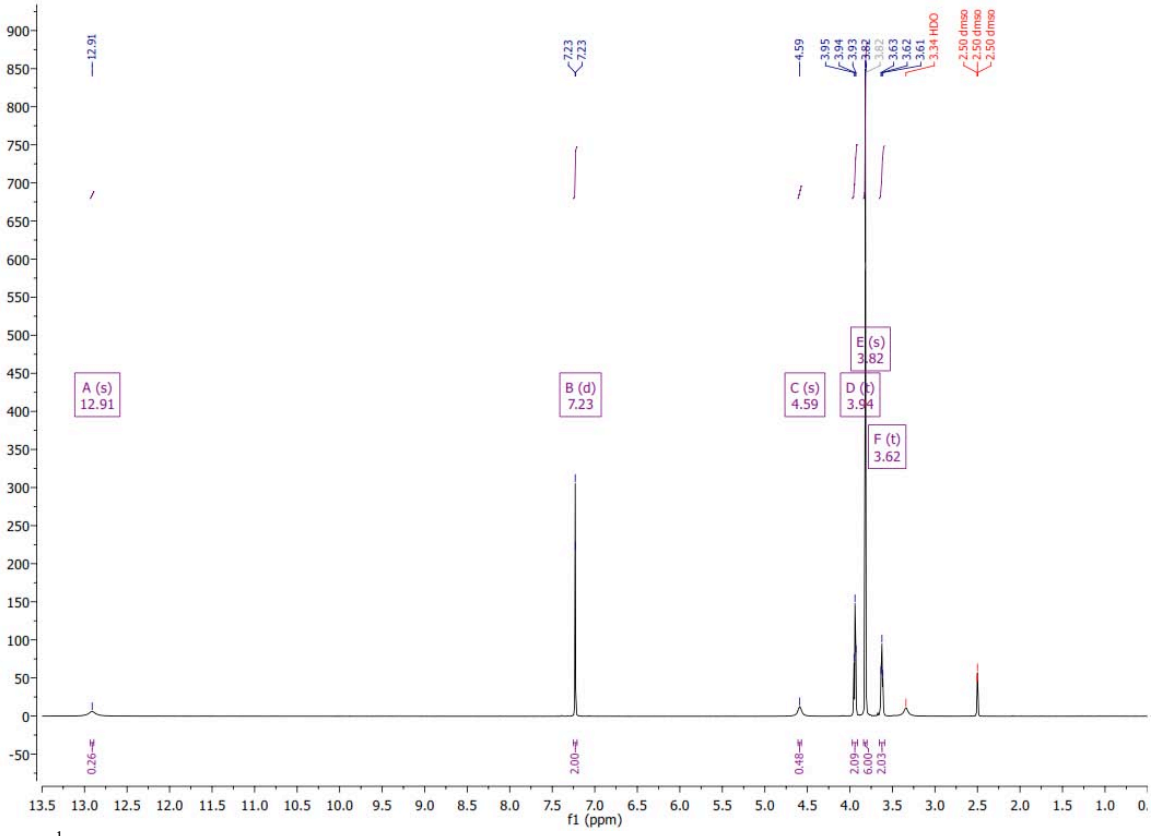


Figure S232. [1]H NMR spectrum of hydroxyethylsyringic acid.

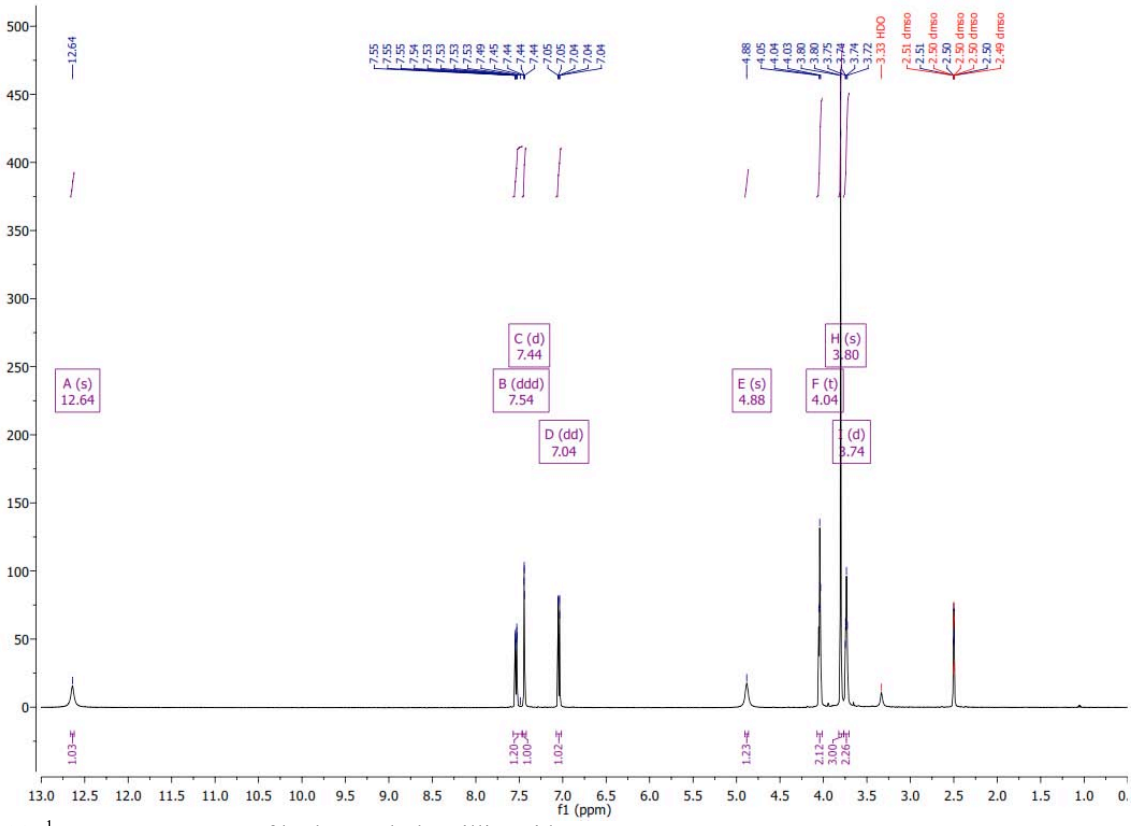


Figure S233. [1]H NMR spectrum of hydroxyethylvanillic acid.

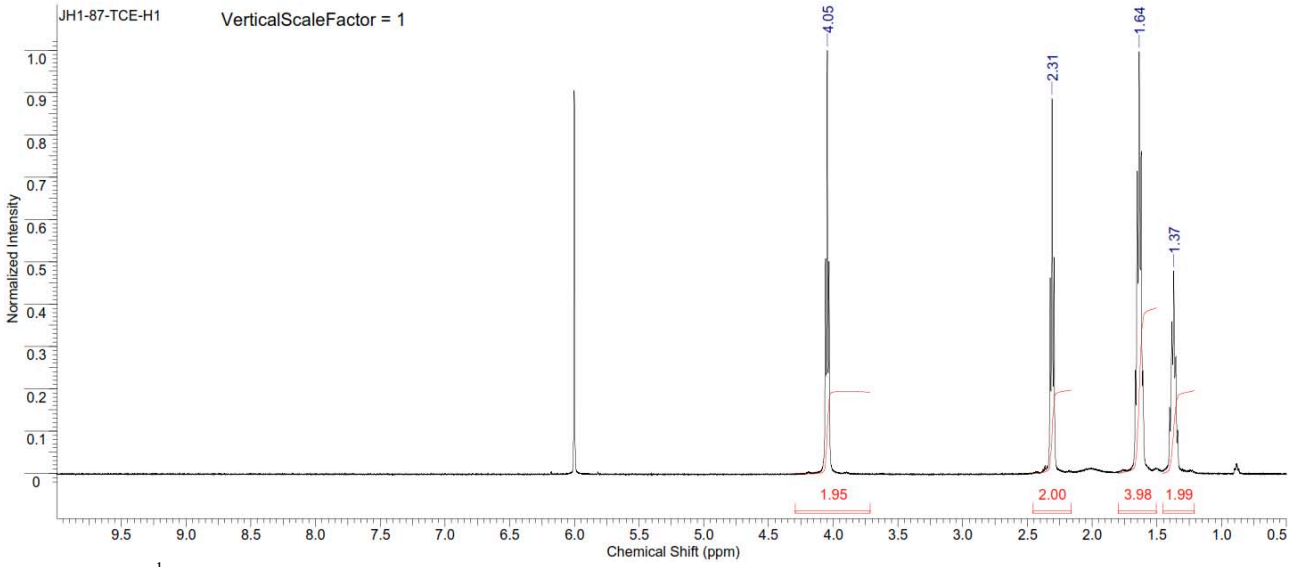


Figure S234. [1]H NMR spectrum of polycaprolactone (Table S2, entry 1).

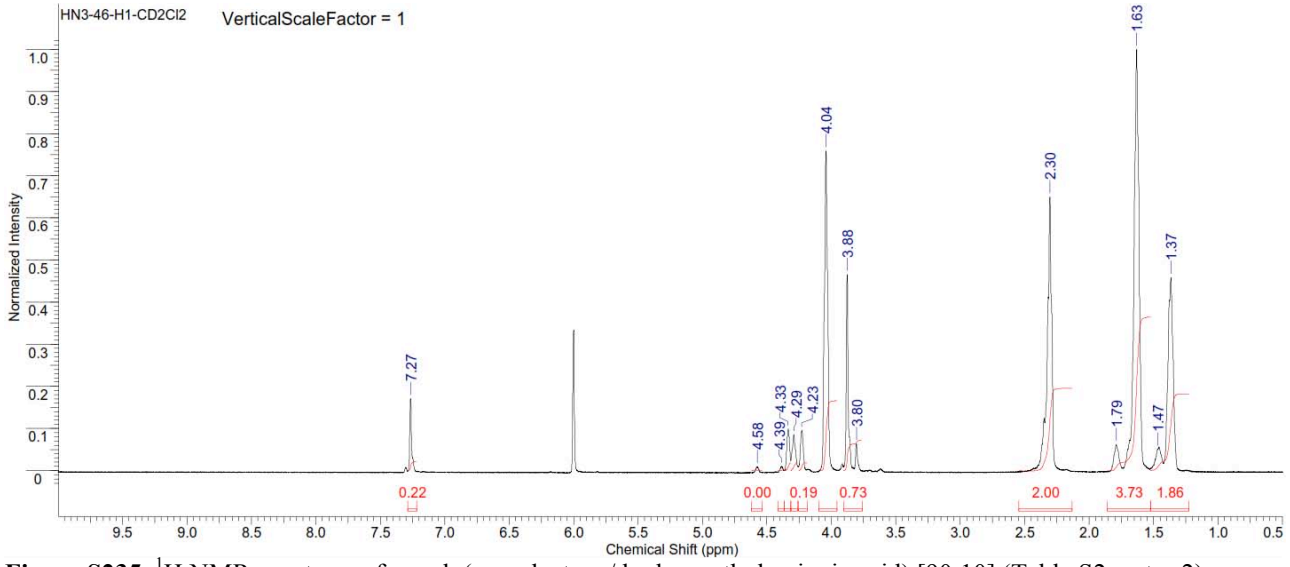


Figure S235. [1]H NMR spectrum of copoly(caprolactone/ hydroxyethylsyringic acid) [90:10] (Table S2, entry 2).

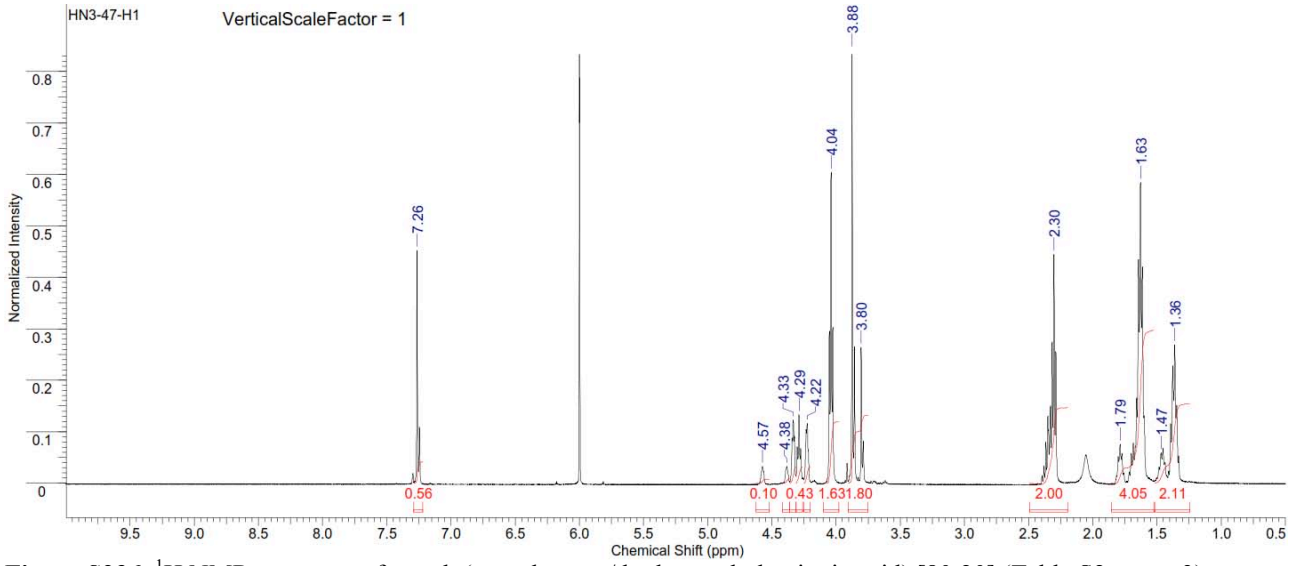


Figure S236. [1]H NMR spectrum of copoly(caprolactone/ hydroxyethylsyringic acid) [80:20] (Table S2, entry 3).

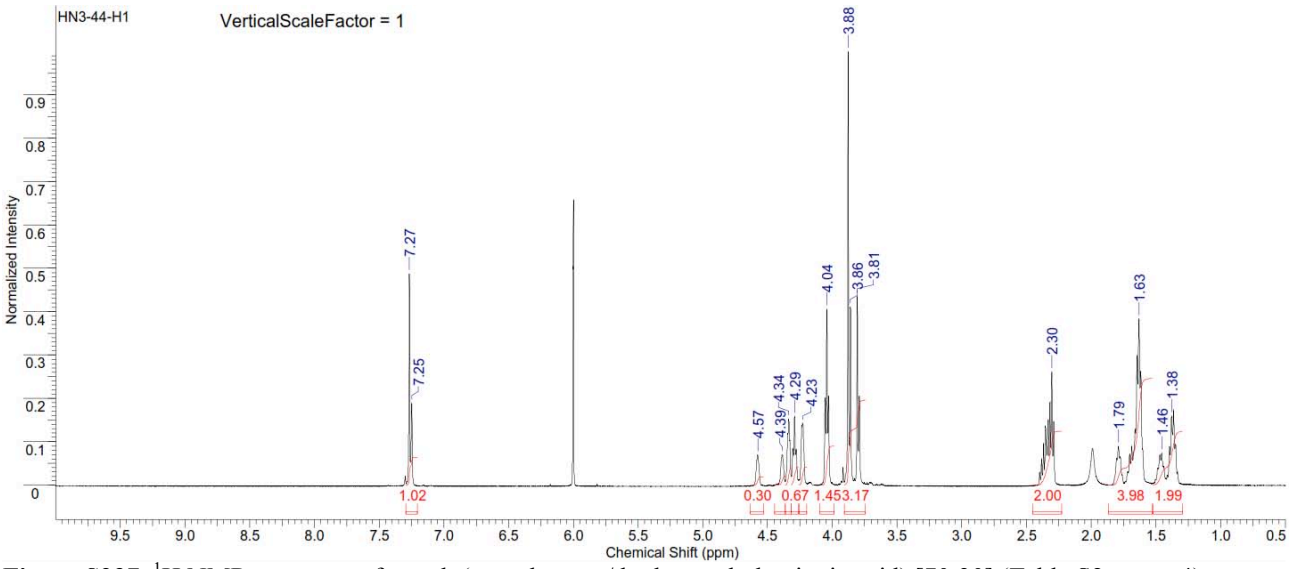


Figure S237. ^{1}H NMR spectrum of copoly(caprolactone/ hydroxyethylsyringic acid) [70:30] (Table S2, entry 4).

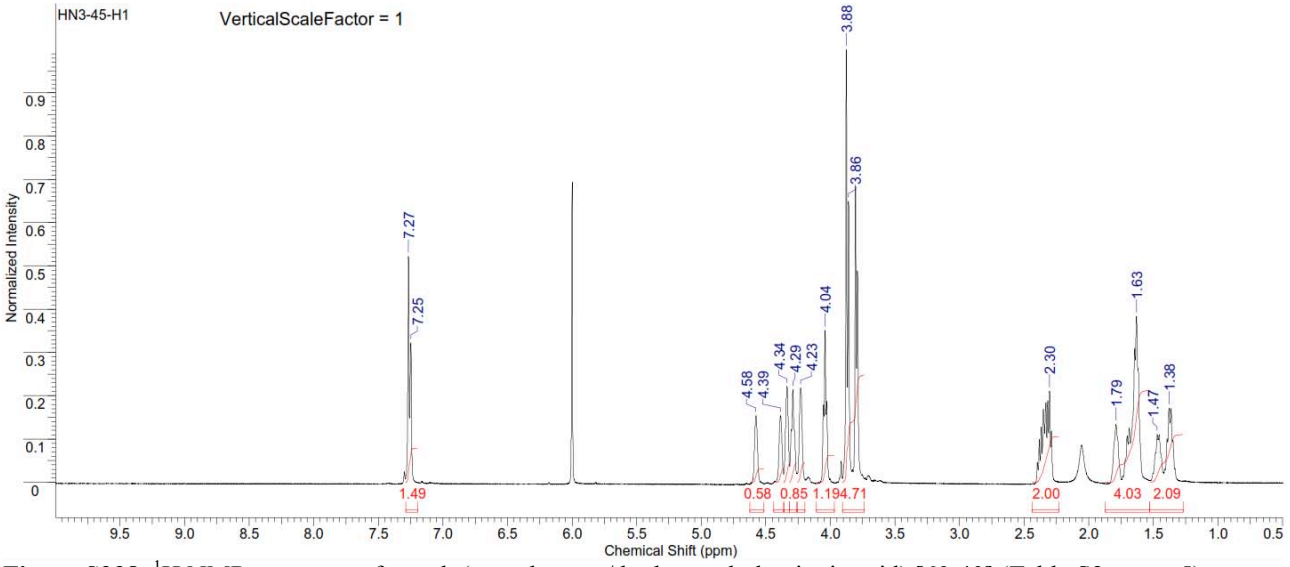


Figure S238. ^{1}H NMR spectrum of copoly(caprolactone/ hydroxyethylsyringic acid) [60:40] (Table S2, entry 5).

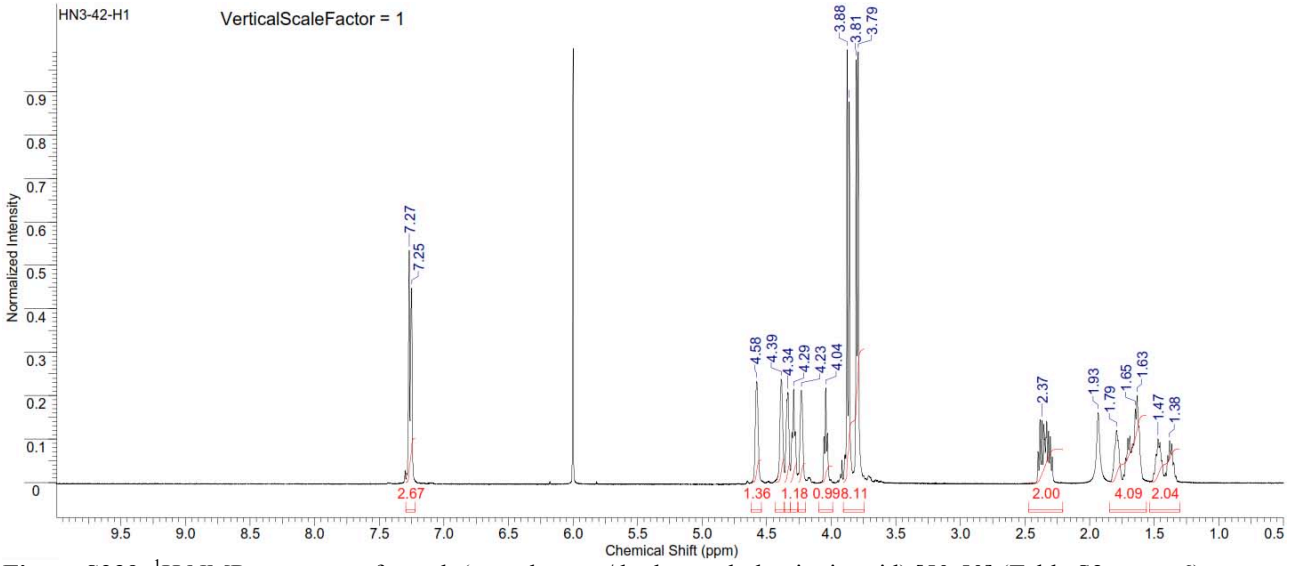


Figure S239. ^{1}H NMR spectrum of copoly(caprolactone/ hydroxyethylsyringic acid) [50:50] (Table S2, entry 6).

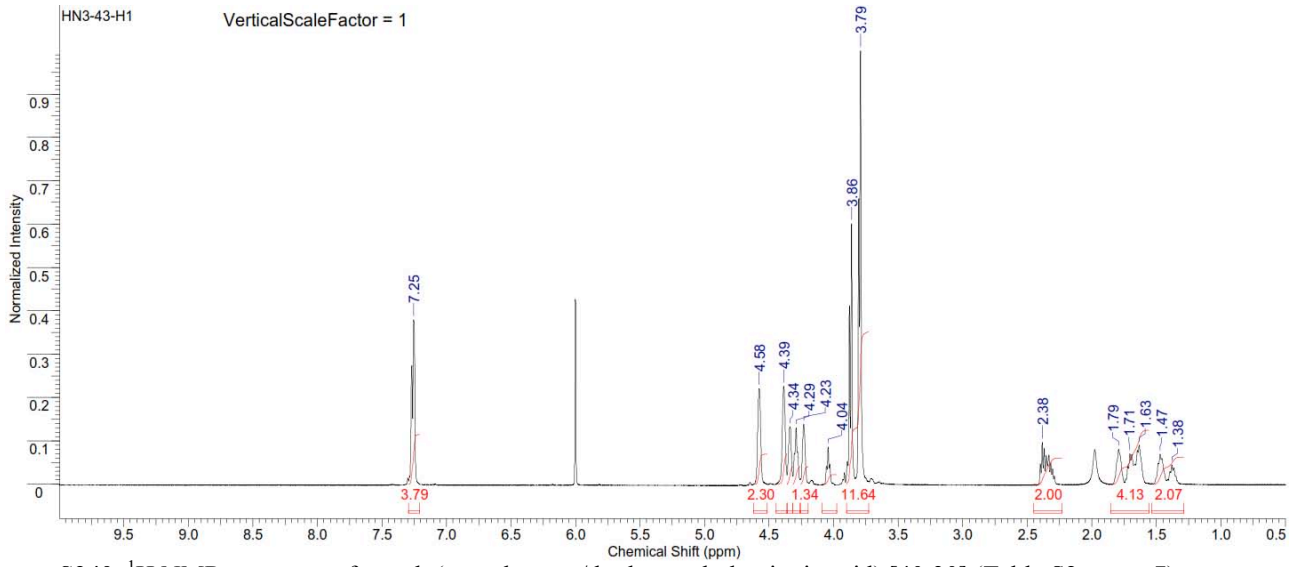


Figure S240. [1]H NMR spectrum of copoly(caprolactone/ hydroxyethylsyringic acid) [40:30] (Table S2, entry 7).

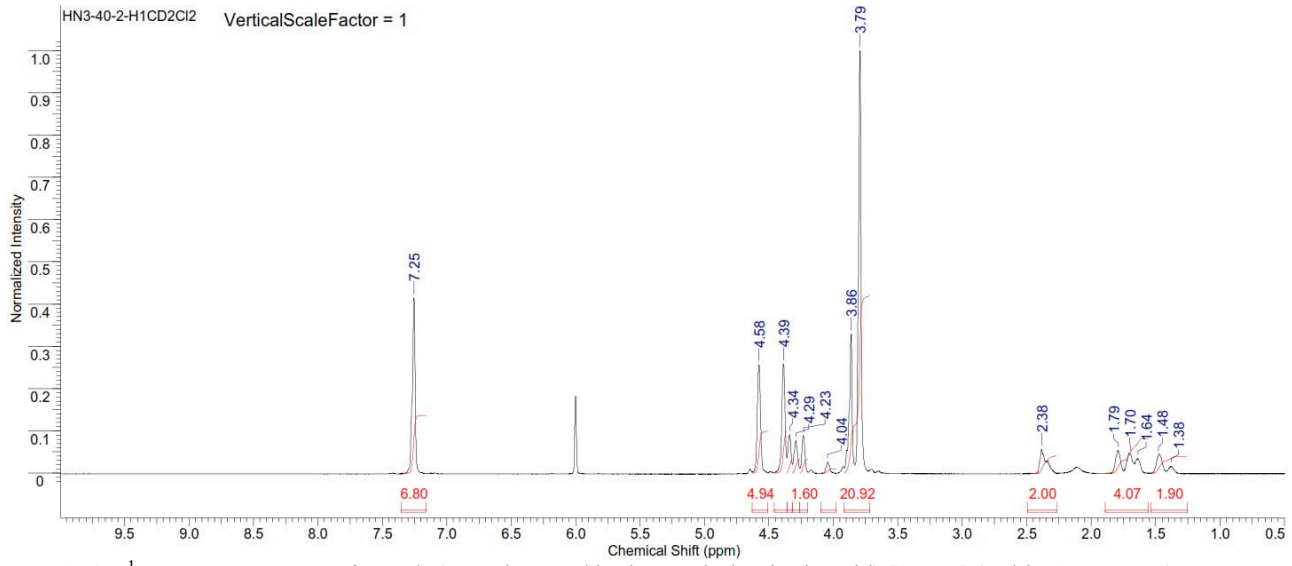


Figure S241. [1]H NMR spectrum of copoly(caprolactone/ hydroxyethylsyringic acid) [30:70] (Table S2, entry 8).

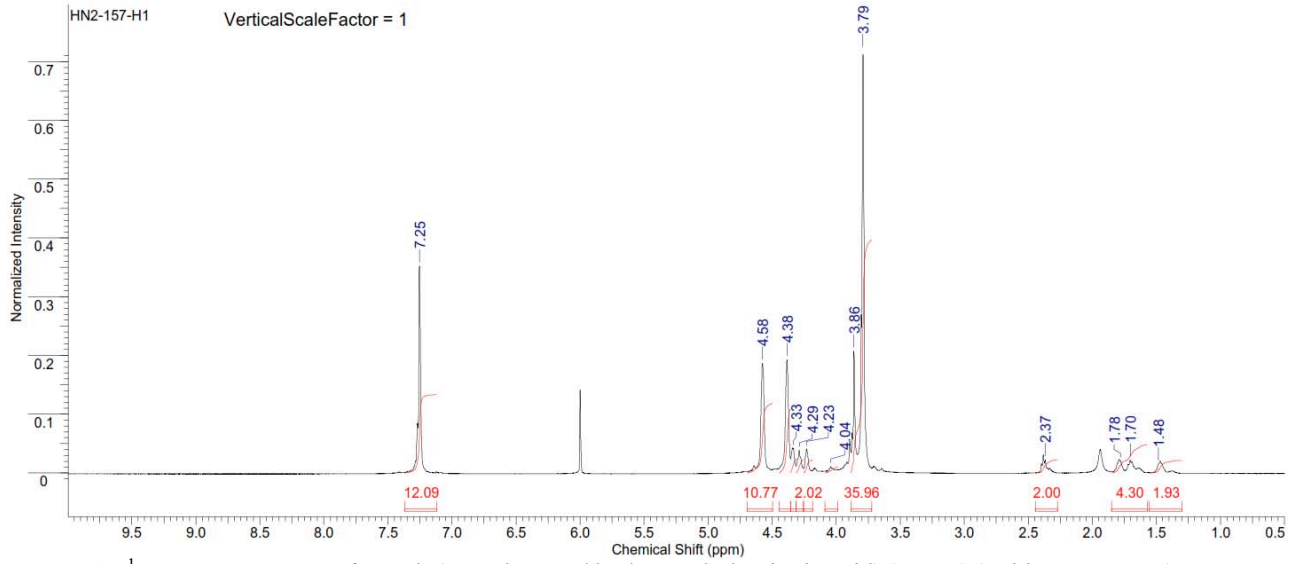


Figure S242. [1]H NMR spectrum of copoly(caprolactone/ hydroxyethylsyringic acid) [20:80] (Table S2, entry 9).

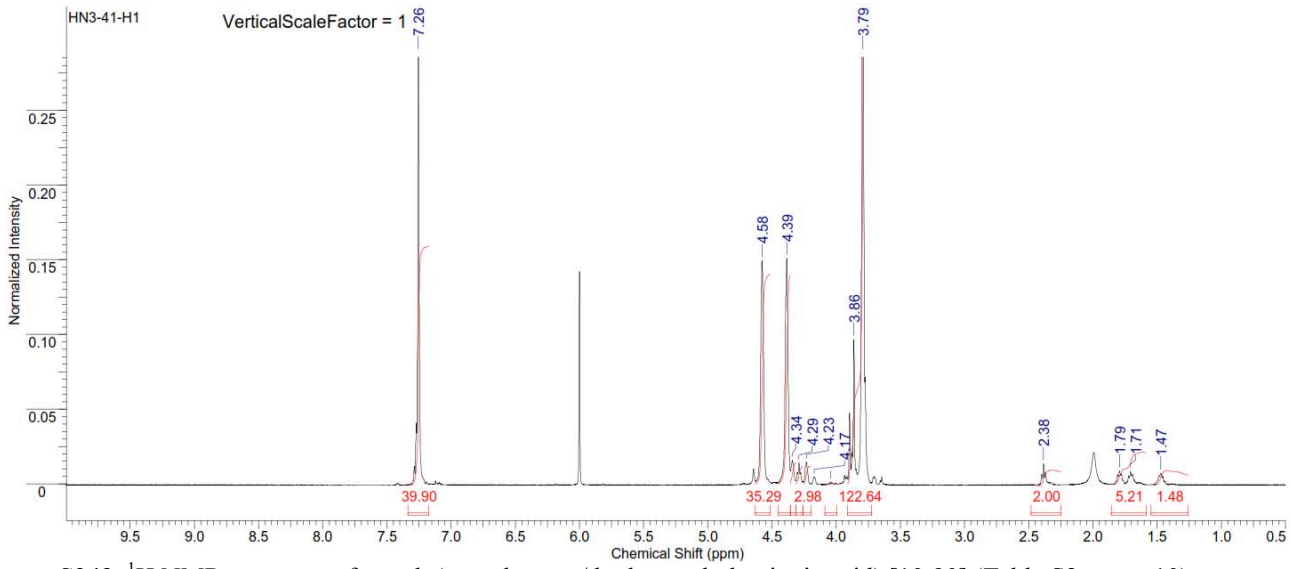


Figure S243. [1]H NMR spectrum of copoly(caprolactone/ hydroxyethylsyringic acid) [10:90] (Table S2, entry 10).

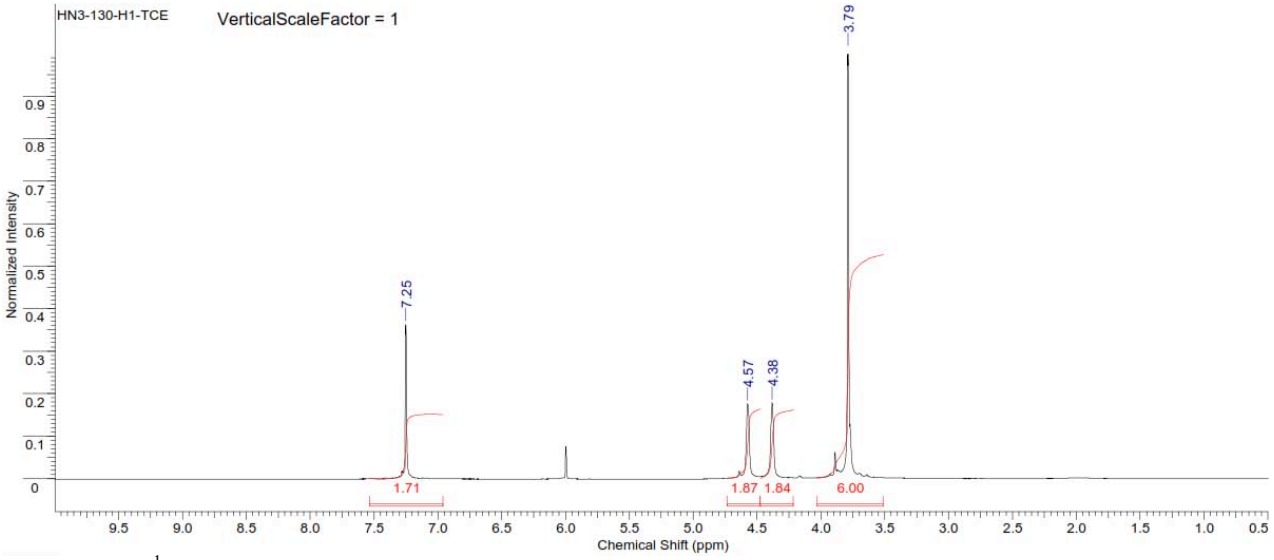


Figure S244. [1]H NMR spectrum of polyethylene syringate (Table S2, entry 11).

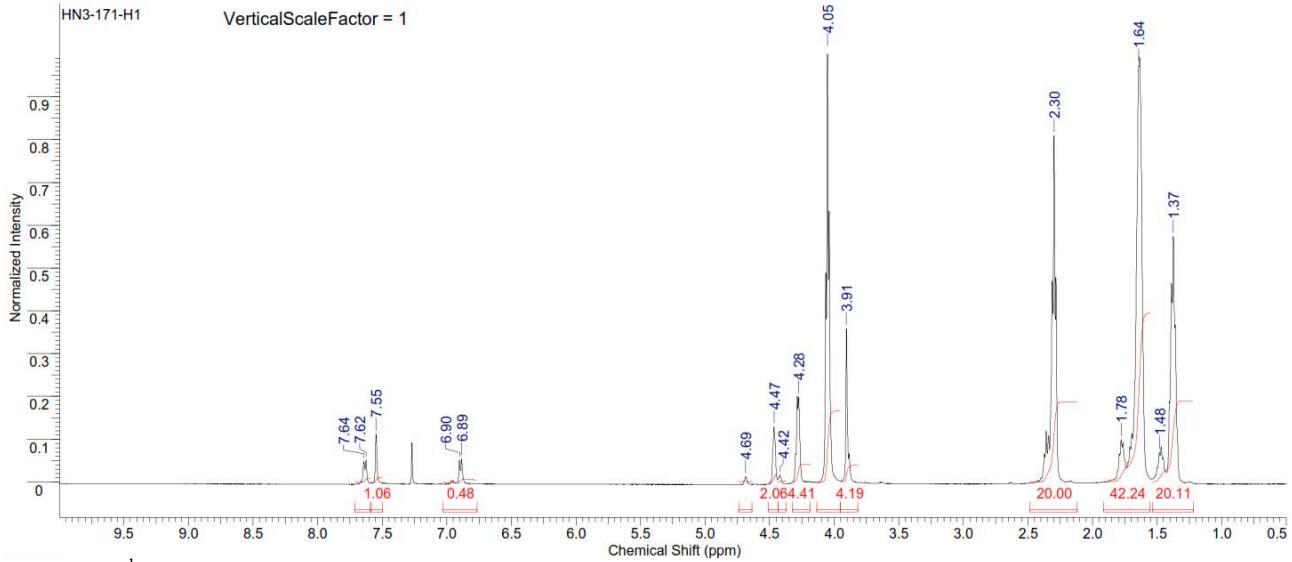


Figure S245. [1]H NMR spectrum of copoly(caprolactone/ hydroxyethylvanillic acid) [90:10] (Table S2, entry 12).

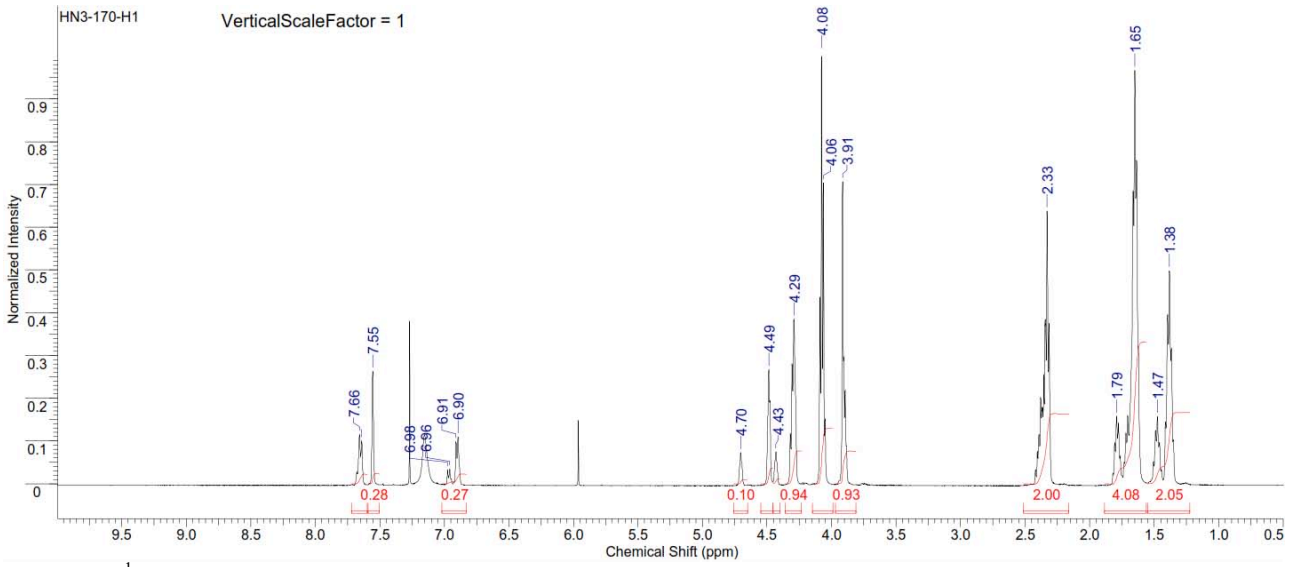


Figure S246. [1]H NMR spectrum of copoly(caprolactone/ hydroxyethylvanillic acid) [80:20] (Table S2, entry 13).

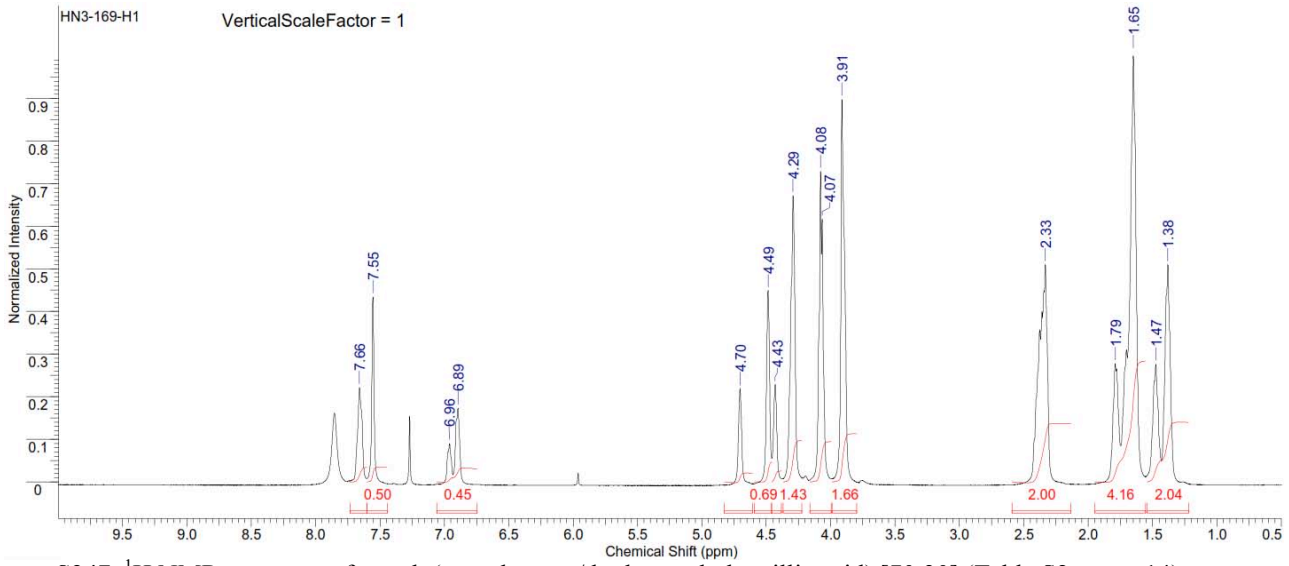


Figure S247. [1]H NMR spectrum of copoly(caprolactone/ hydroxyethylvanillic acid) [70:30] (Table S2, entry 14).

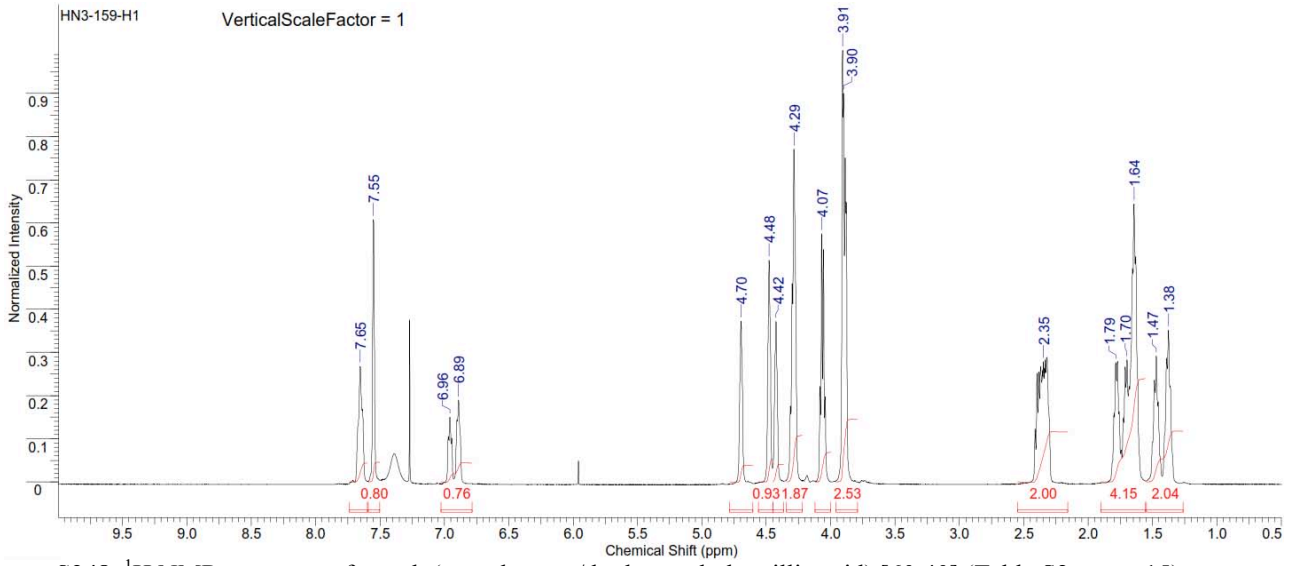


Figure S248. [1]H NMR spectrum of copoly(caprolactone/ hydroxyethylvanillic acid) [60:40] (Table S2, entry 15).

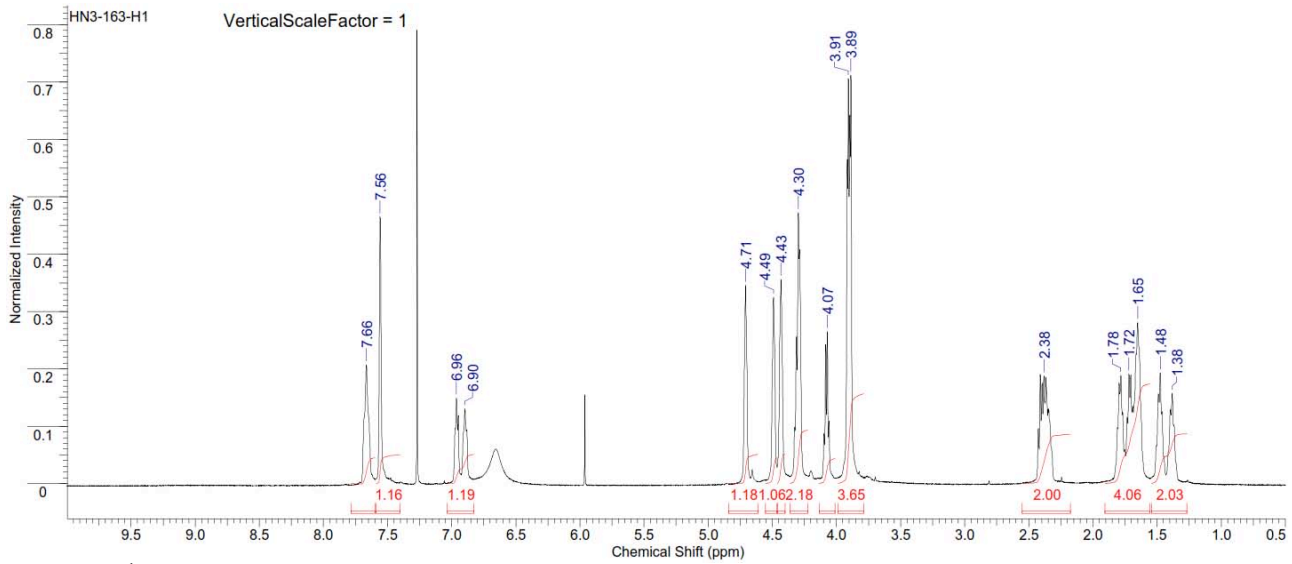


Figure S249. [1]H NMR spectrum of copoly(caprolactone/ hydroxyethylvanillic acid) [50:50] (Table S2, entry 16).

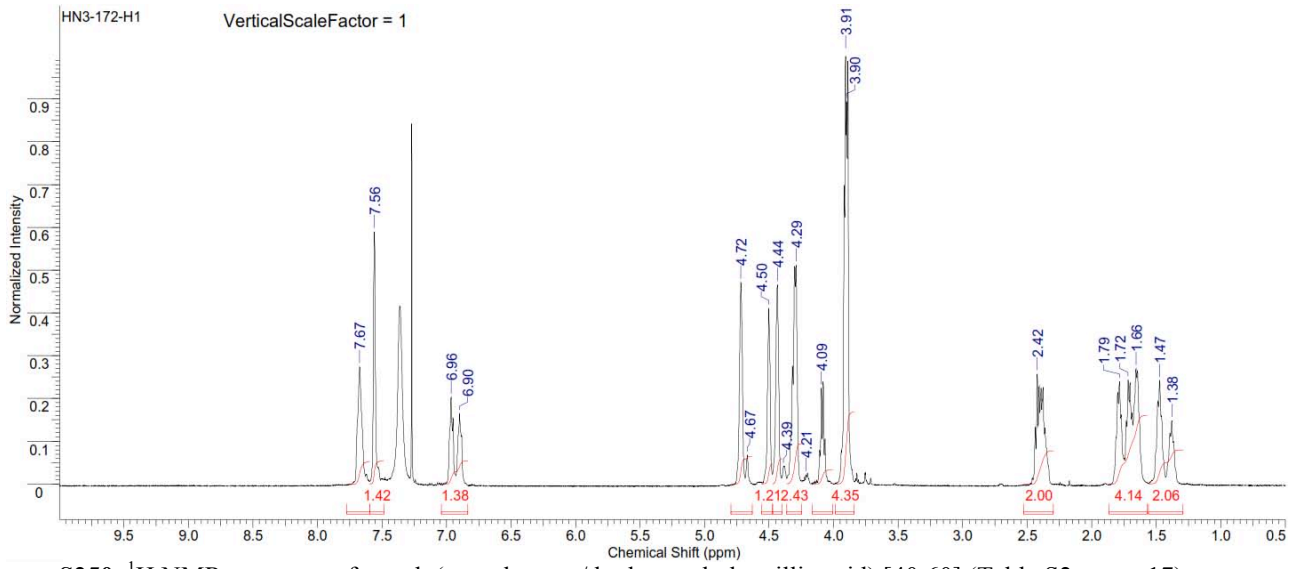


Figure S250. [1]H NMR spectrum of copoly(caprolactone/ hydroxyethylvanillic acid) [40:60] (Table S2, entry 17).

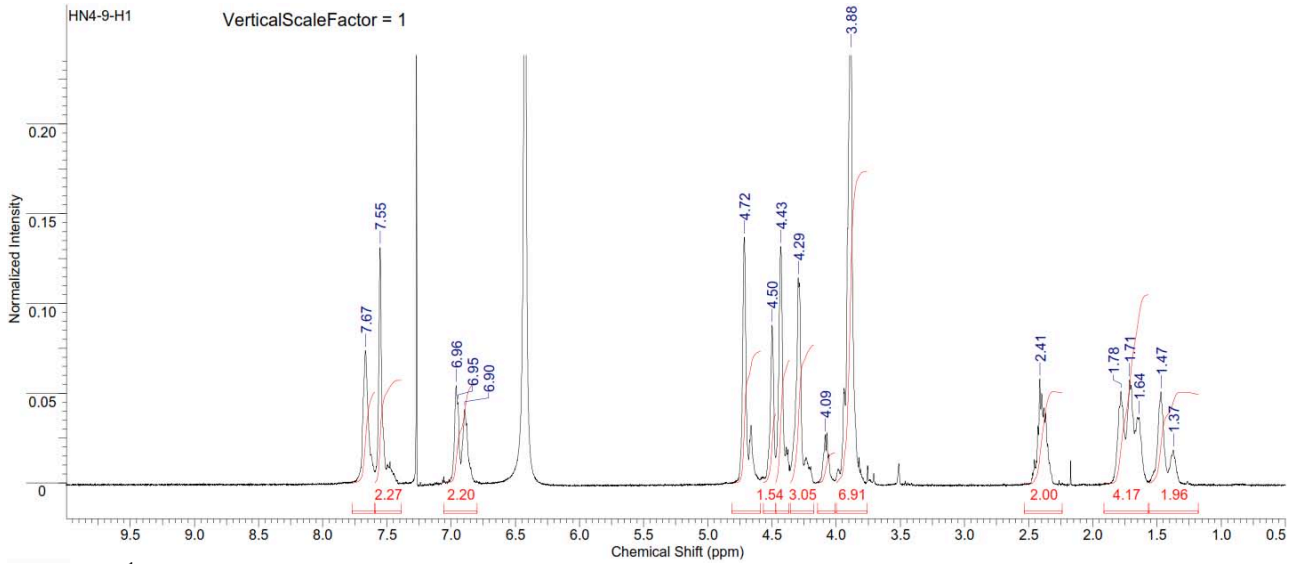


Figure S251. [1]H NMR spectrum of copoly(caprolactone/ hydroxyethylvanillic acid) [30:70] (Table S2, entry 18).

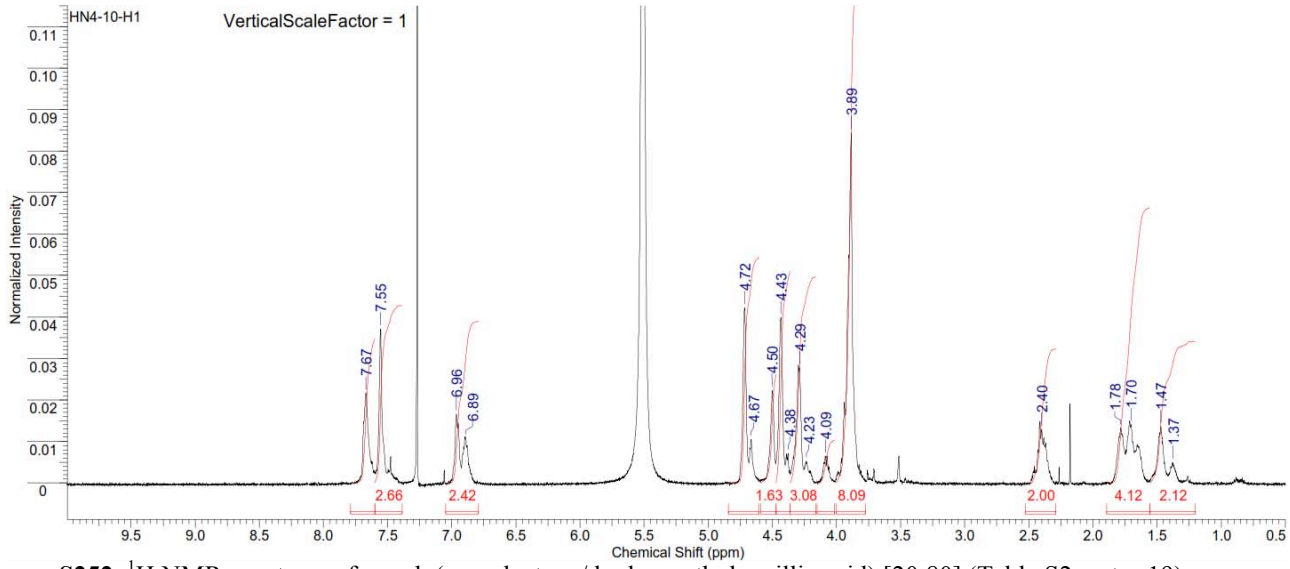


Figure S252. [1]H NMR spectrum of copoly(caprolactone/ hydroxyethylvanillic acid) [20:80] (Table S2, entry 19).

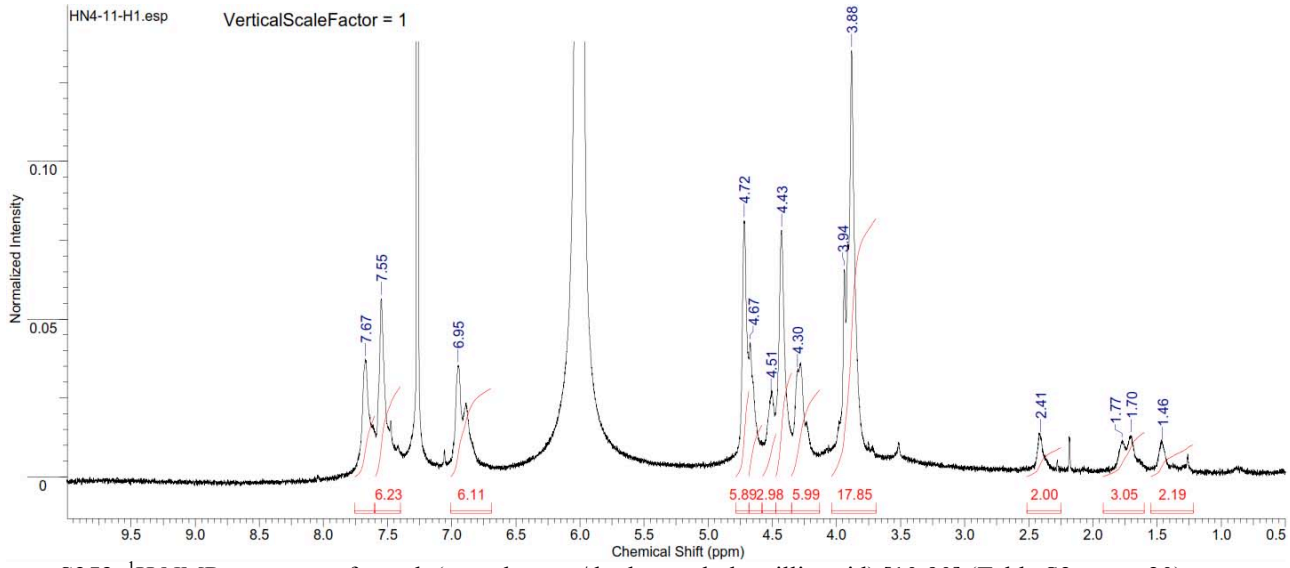


Figure S253. [1]H NMR spectrum of copoly(caprolactone/ hydroxyethylvanillic acid) [10:90] (Table S2, entry 20).

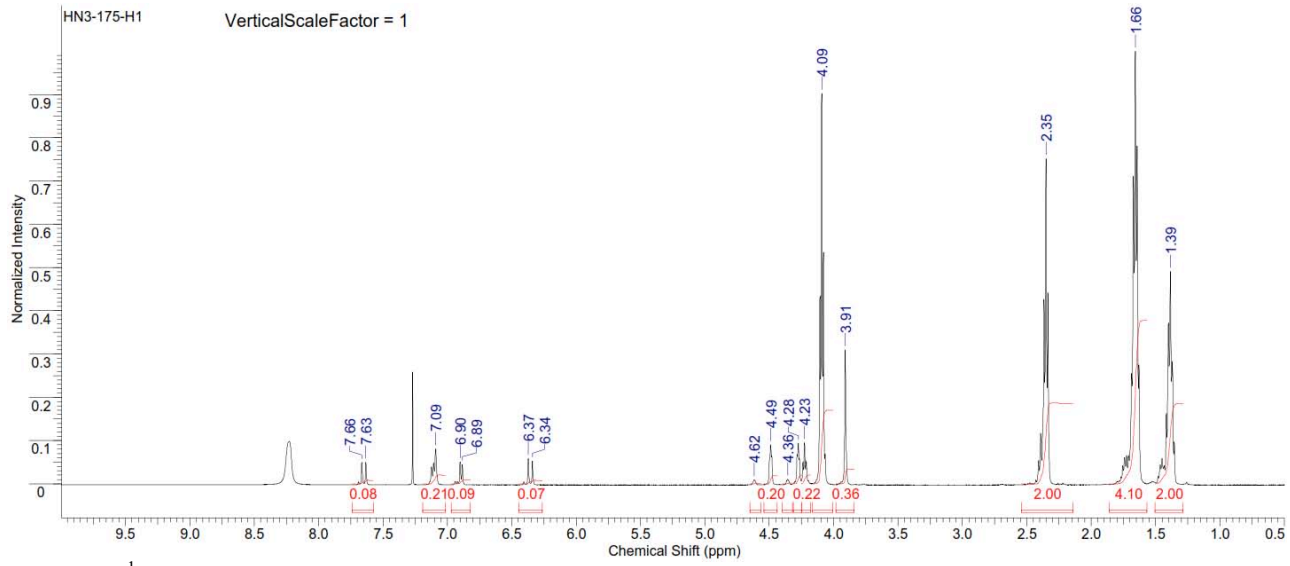


Figure S254. [1]H NMR spectrum of copoly(caprolactone/ hydroxyethylferulic acid) [90:10] (Table S2, entry 22).

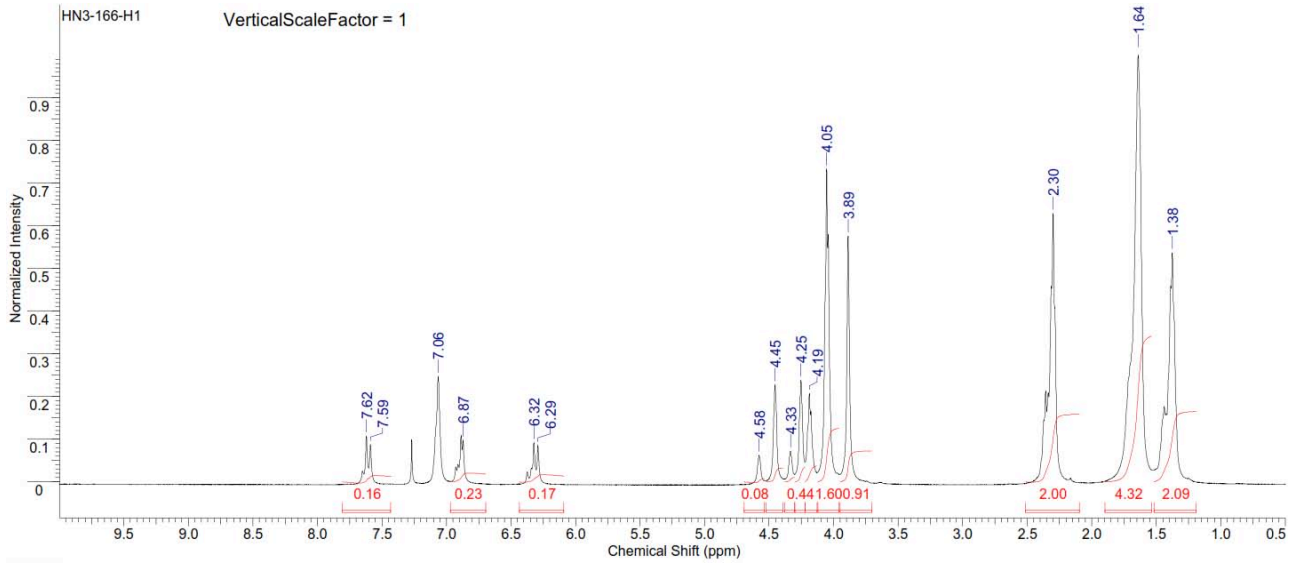


Figure S255. [1]H NMR spectrum of copoly(caprolactone/ hydroxyethylferulic acid) [80:20] (Table S2, entry 23).

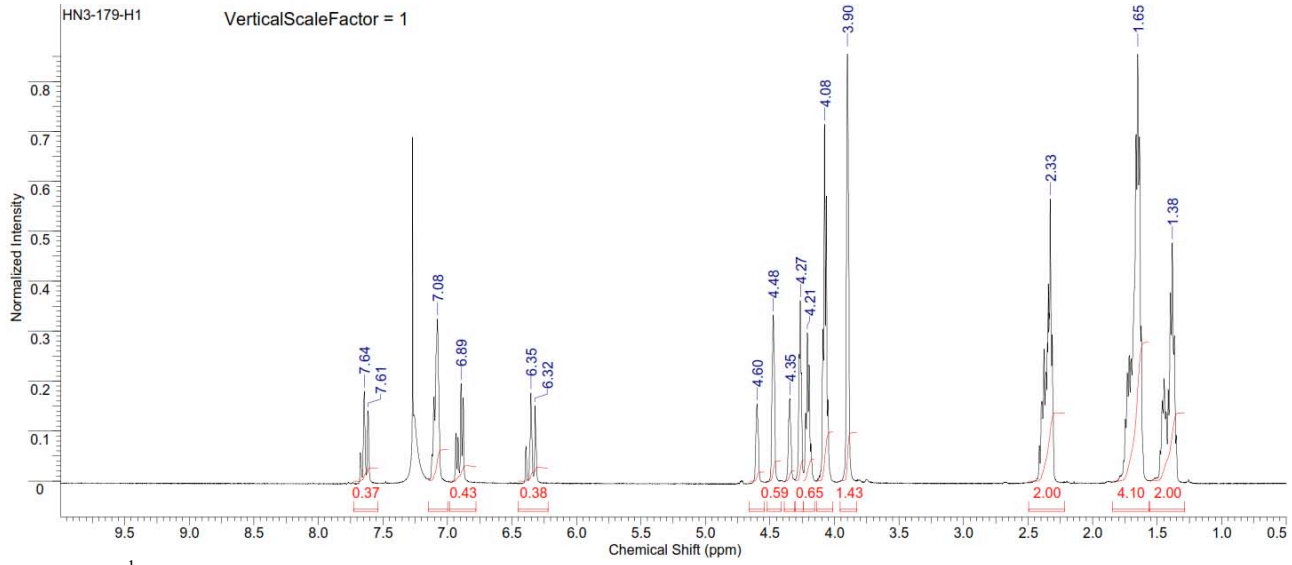


Figure S256. [1]H NMR spectrum of copoly(caprolactone/ hydroxyethylferulic acid) [70:30] (Table S2, entry 24).

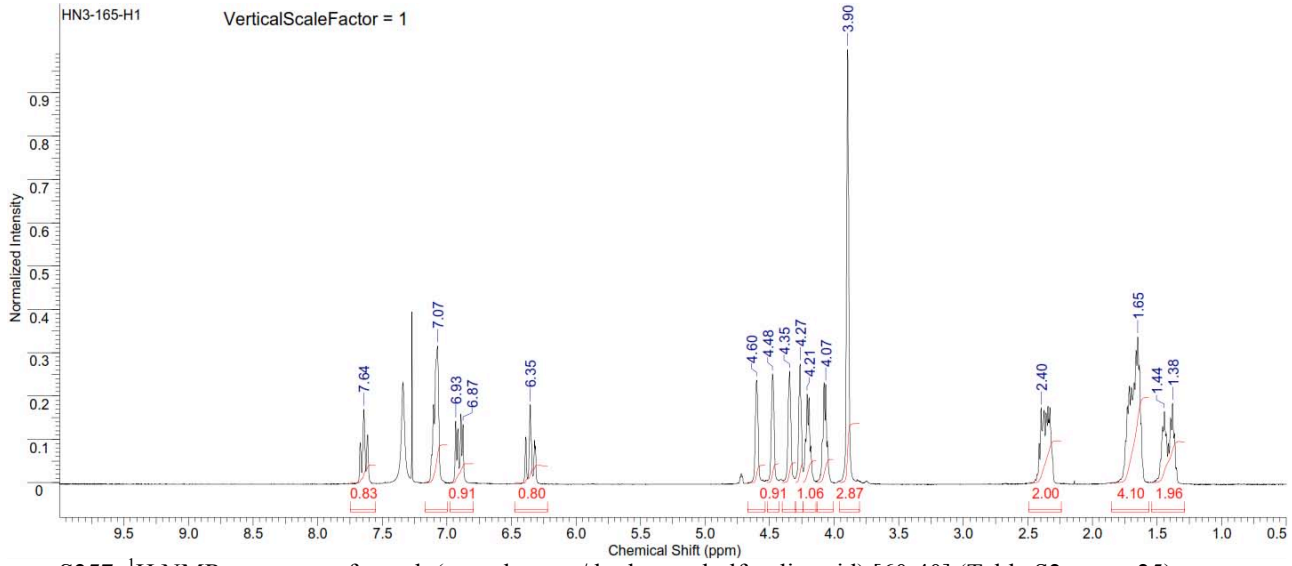


Figure S257. [1]H NMR spectrum of copoly(caprolactone/ hydroxyethylferulic acid) [60:40] (Table S2, entry 25).

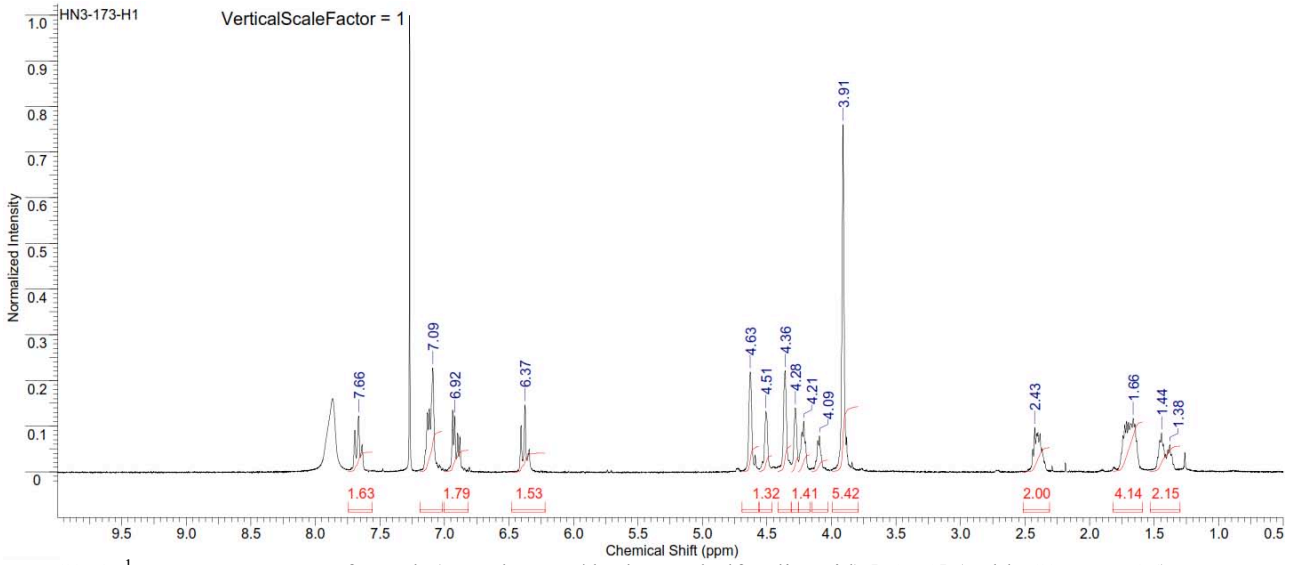


Figure S258. [1]H NMR spectrum of copoly(caprolactone/ hydroxyethylferulic acid) [50:50] (Table S2, entry 26).

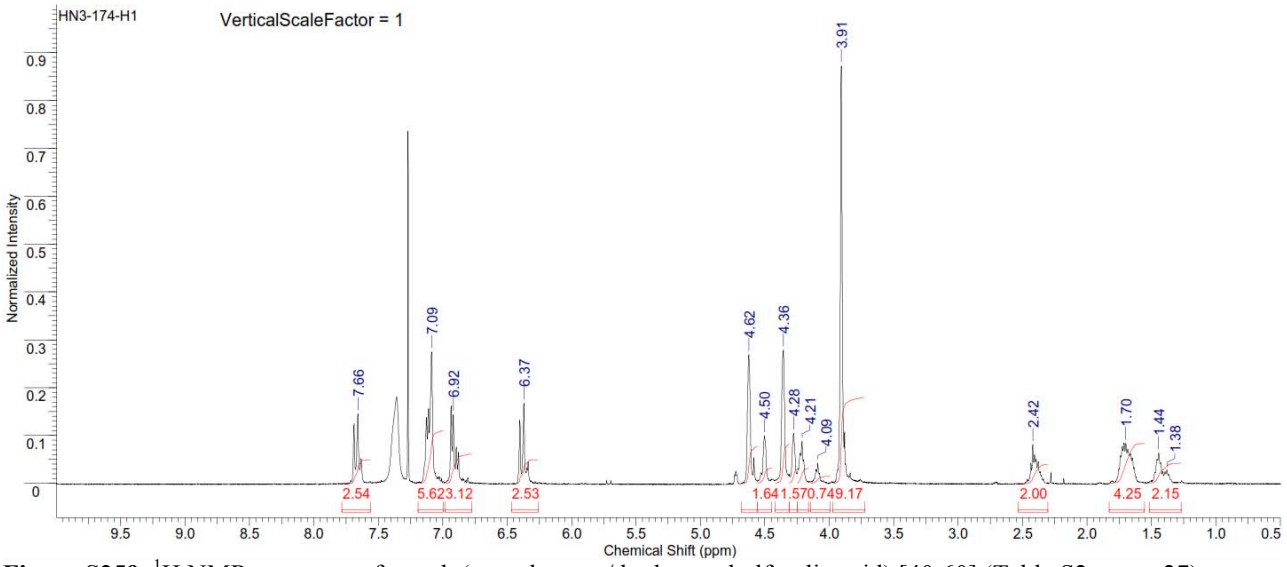


Figure S259. [1]H NMR spectrum of copoly(caprolactone/ hydroxyethylferulic acid) [40:60] (Table S2, entry 27).

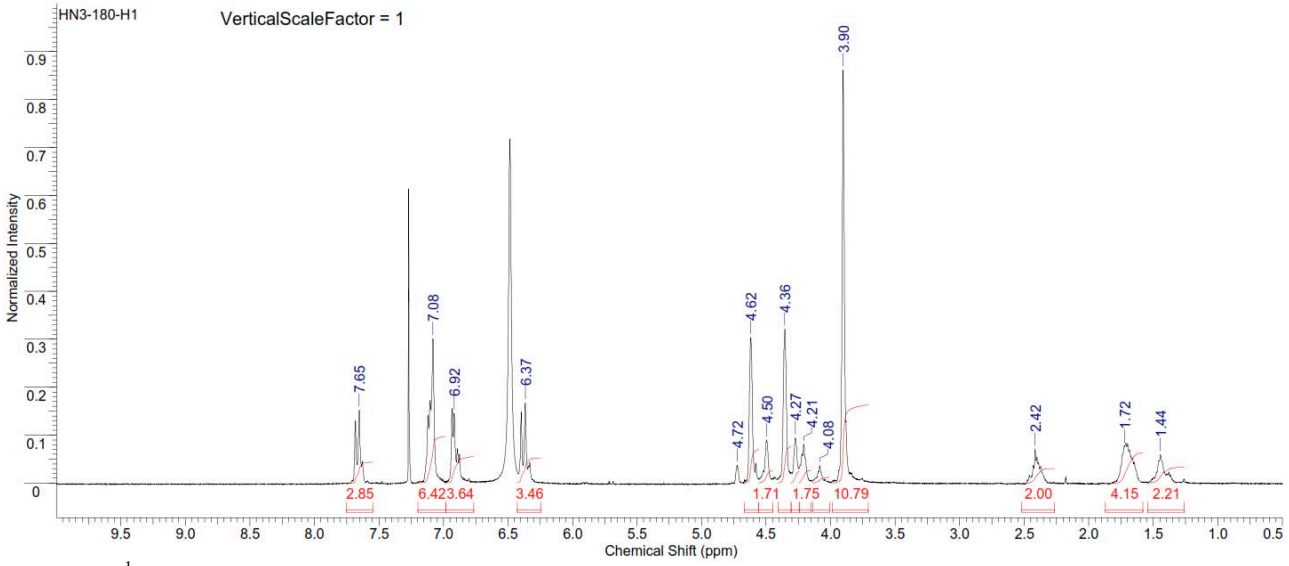


Figure S260. [1]H NMR spectrum of copoly(caprolactone/ hydroxyethylferulic acid) [30:70] (Table S2, entry 28).

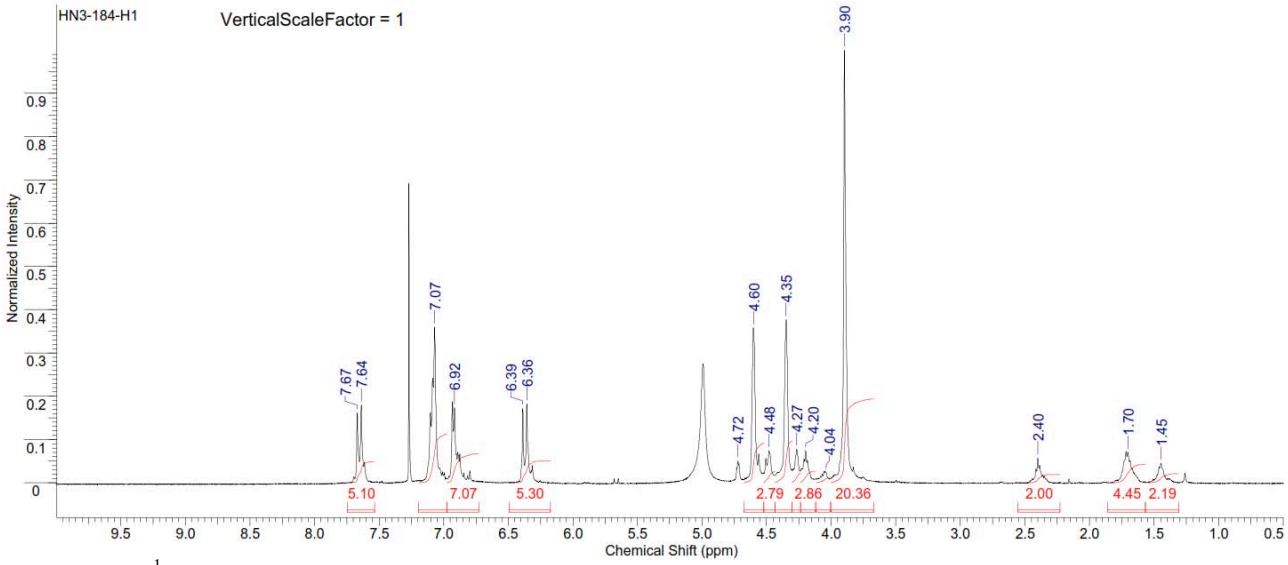


Figure S261. [1]H NMR spectrum of copoly(caprolactone/ hydroxyethylferulic acid) [20:80] (Table S2, entry 29).

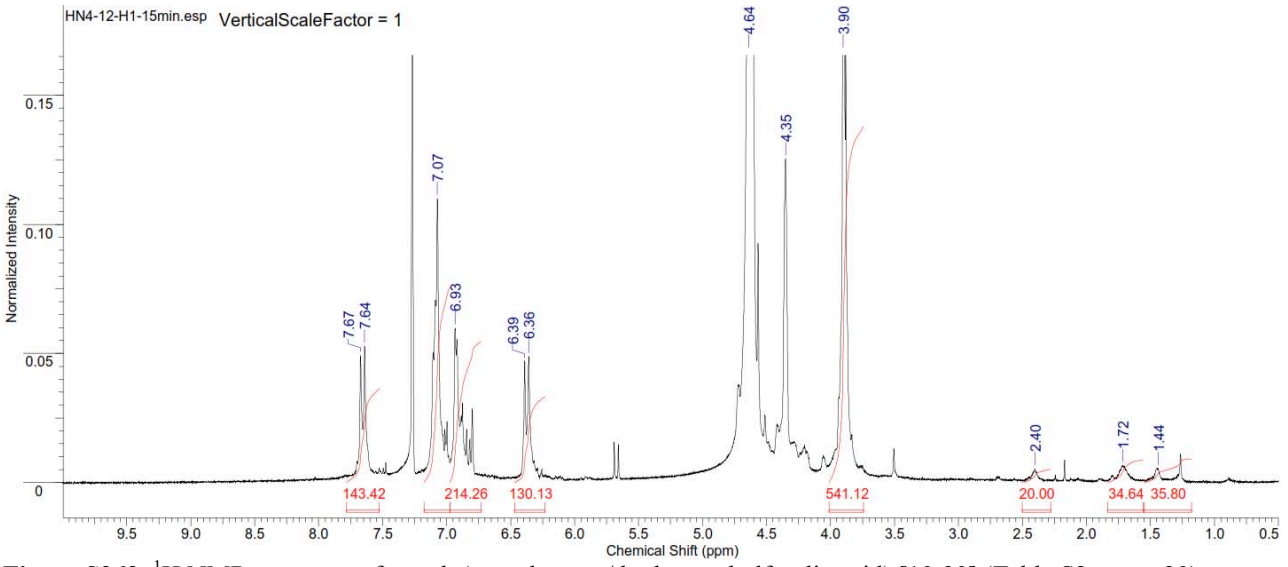


Figure S262. [1]H NMR spectrum of copoly(caprolactone/ hydroxyethylferulic acid) [10:90] (Table S2, entry 30).

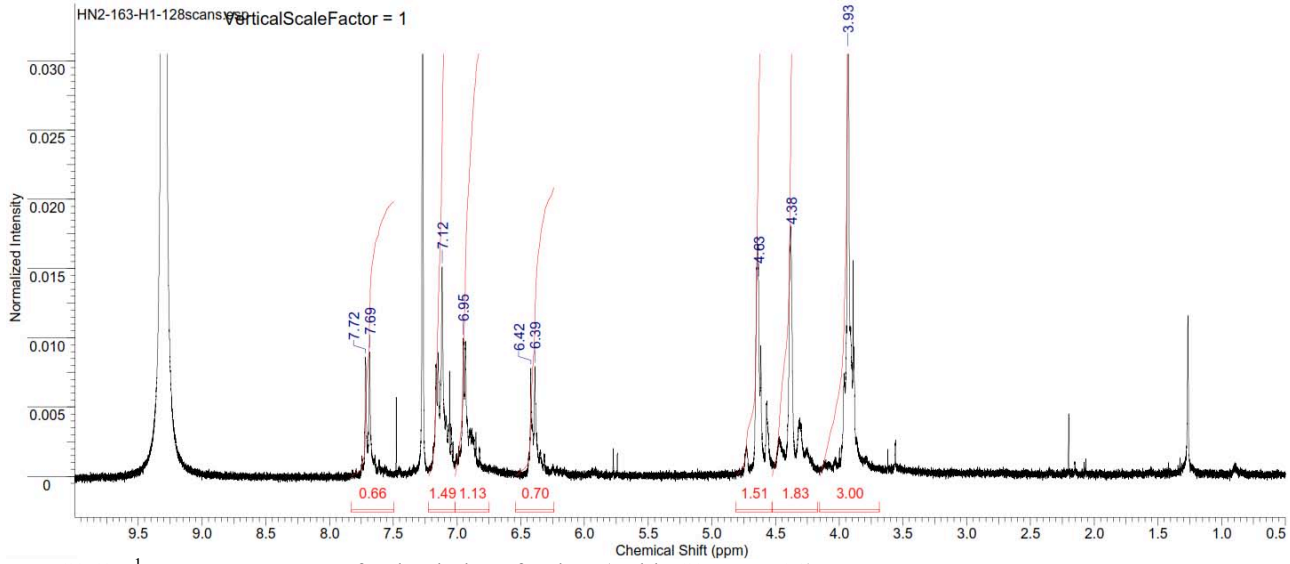


Figure S263. [1]H NMR spectrum of polyethylene ferulate (Table S2, entry 31).

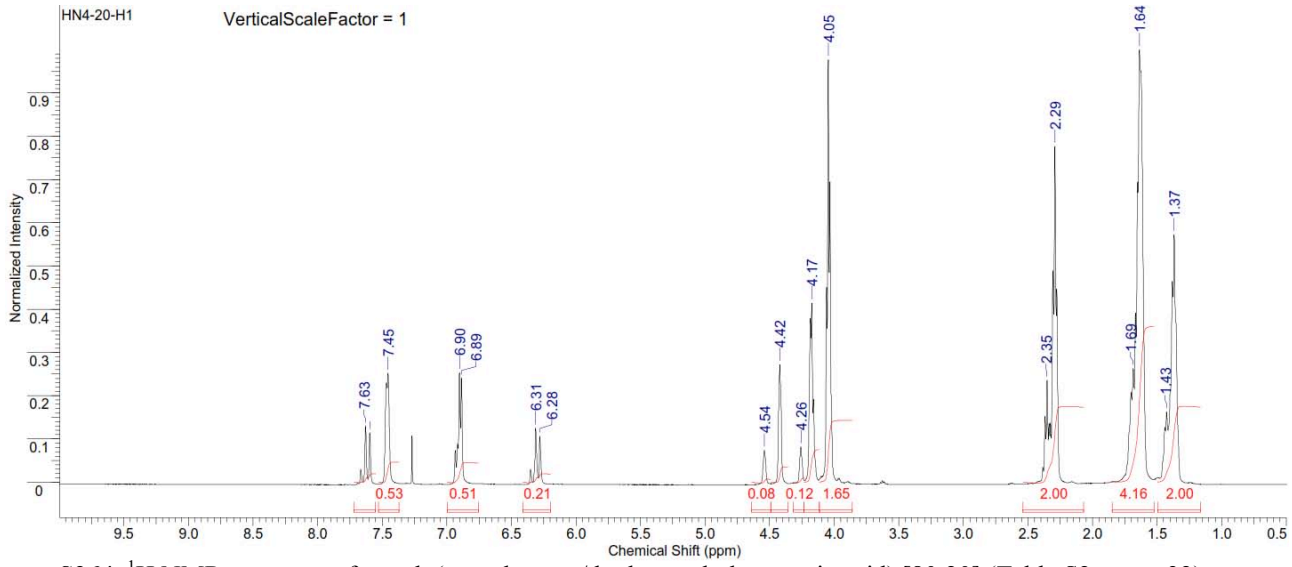


Figure S264. [1]H NMR spectrum of copoly(caprolactone/ hydroxyethylcoumaric acid) [80:20] (Table S2, entry 32).

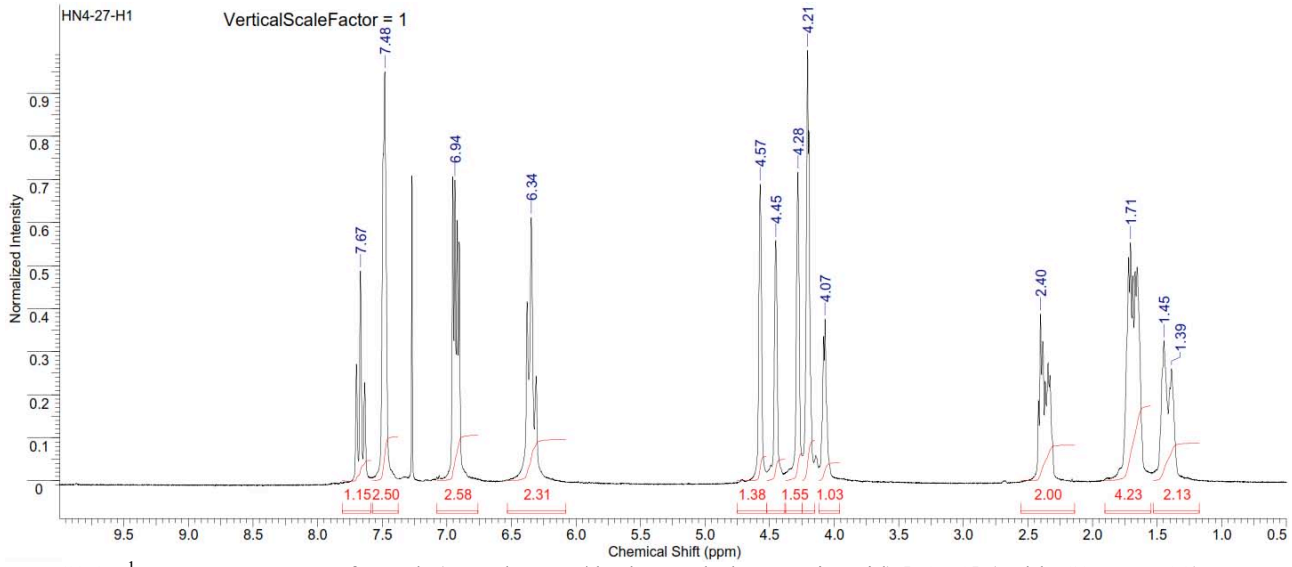


Figure S265. [1]H NMR spectrum of copoly(caprolactone/ hydroxyethylcoumaric acid) [50:50] (Table S2, entry 33).

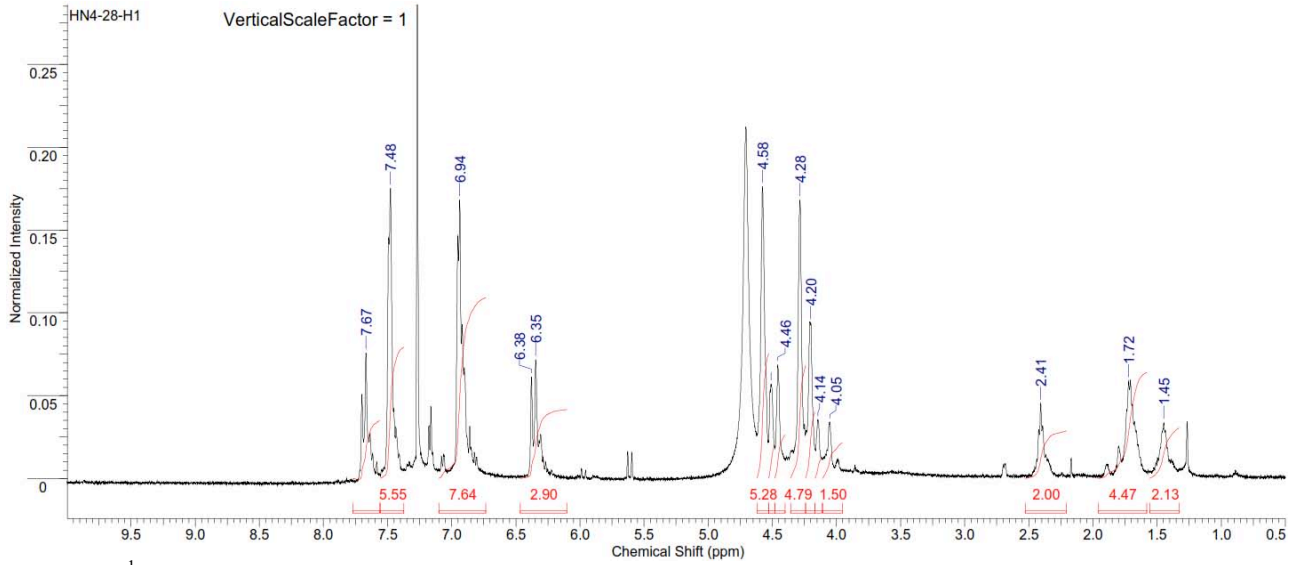


Figure S266. [1]H NMR spectrum of copoly(caprolactone/ hydroxyethylcoumaric acid) [20:80] (Table S2, entry 34).

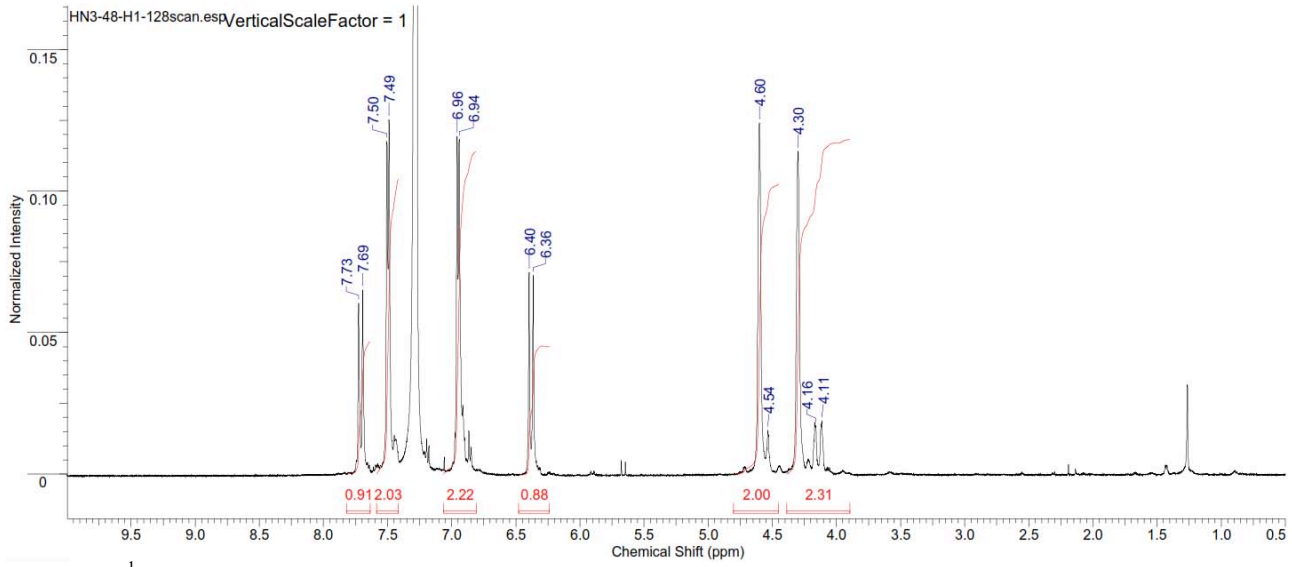


Figure S267. [1]H NMR spectrum of polyethylene coumarate (Table S2, entry 35).

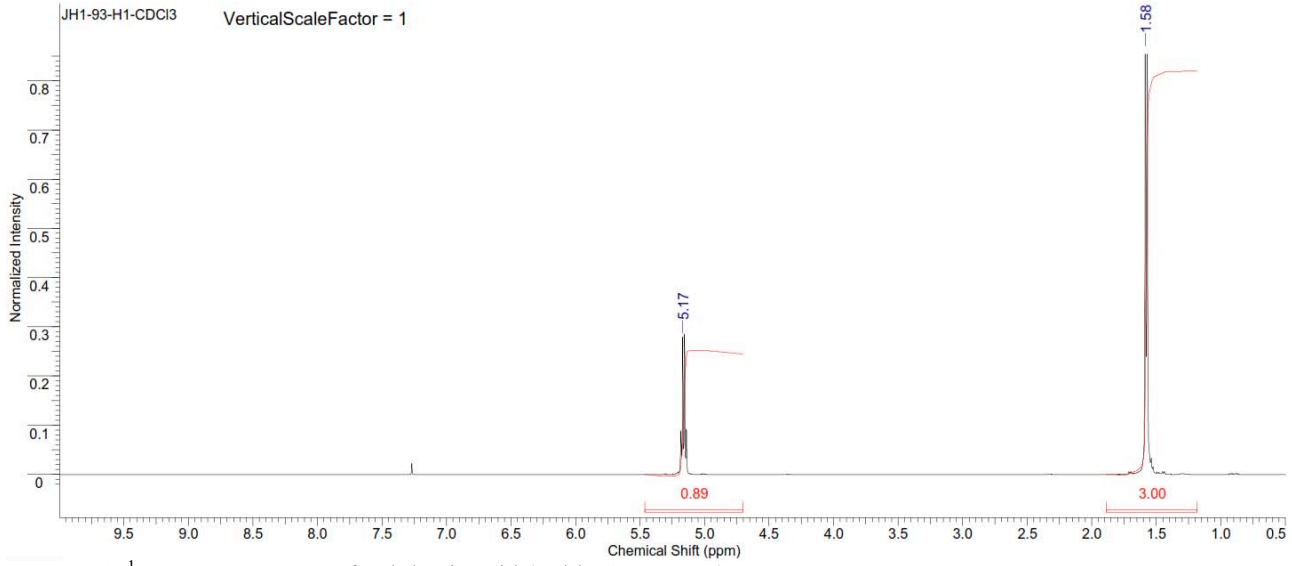


Figure S268. [1]H NMR spectrum of polylactic acid (Table S3, entry 1).

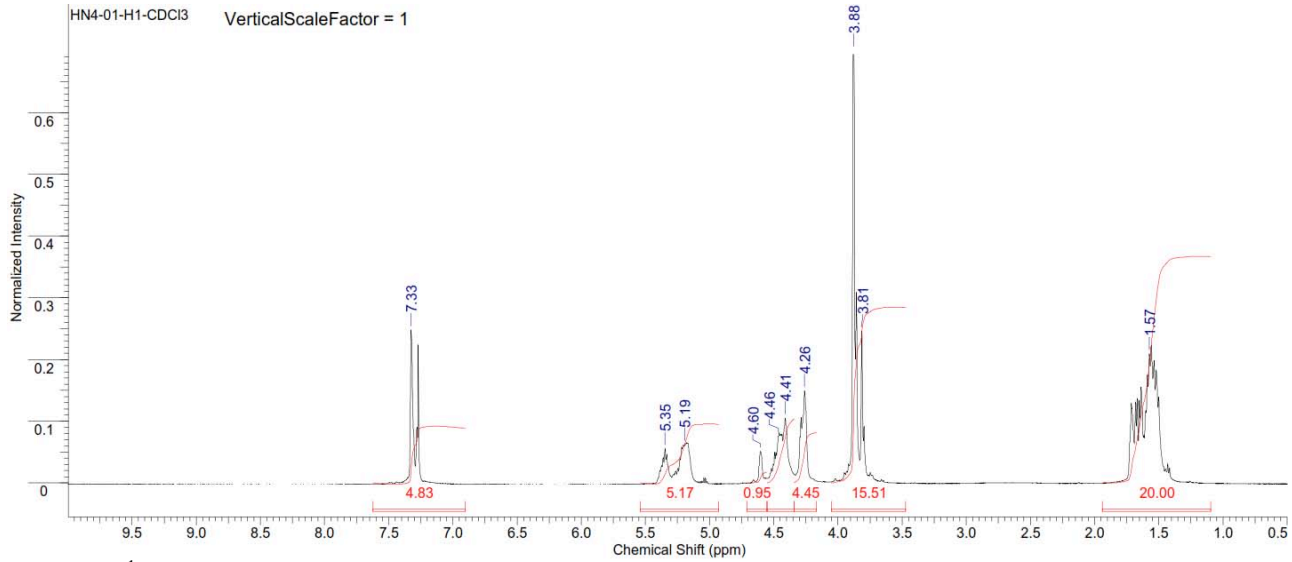


Figure S269. [1]H NMR spectrum of copoly(L-lactide/ hydroxyethylsyringic acid) [80:20] (Table S3, entry 2).

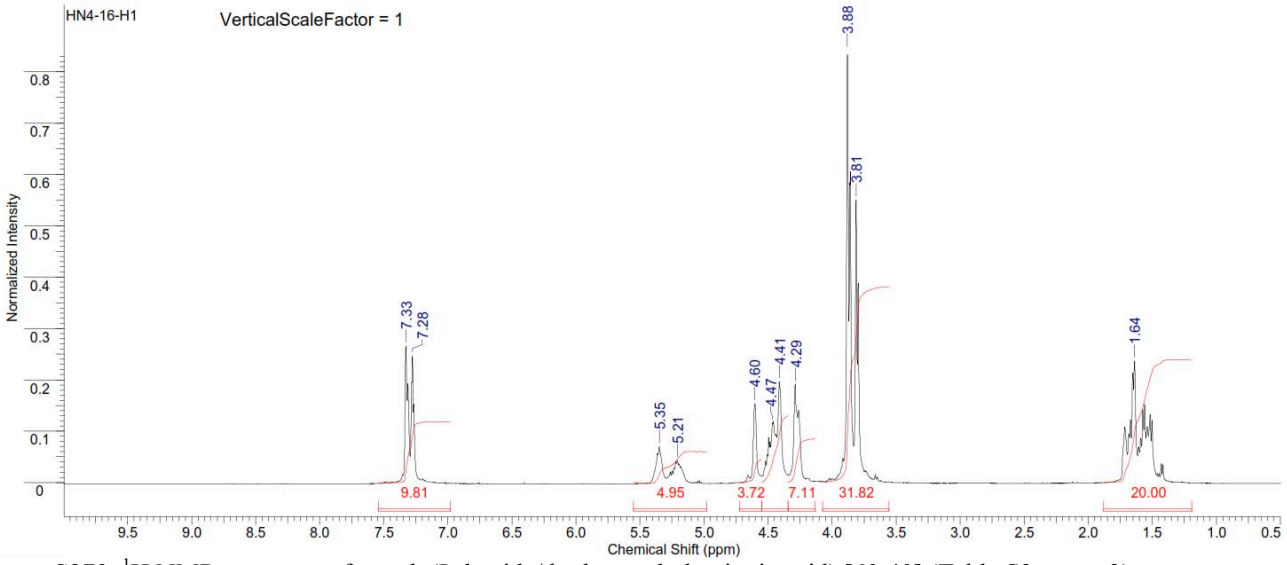


Figure S270. [1]H NMR spectrum of copoly(L-lactide/ hydroxyethylsyringic acid) [60:40] (Table S3, entry 3).

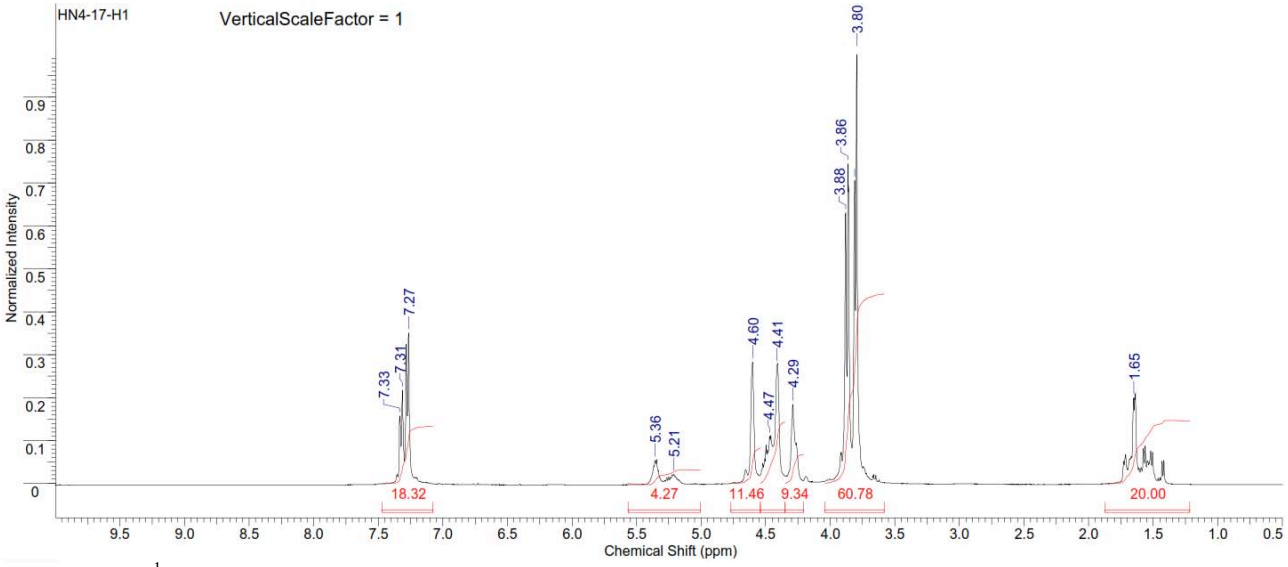


Figure S271. [1]H NMR spectrum of copoly(L-lactide/ hydroxyethylsyringic acid) [40:60] (Table S3, entry 4).

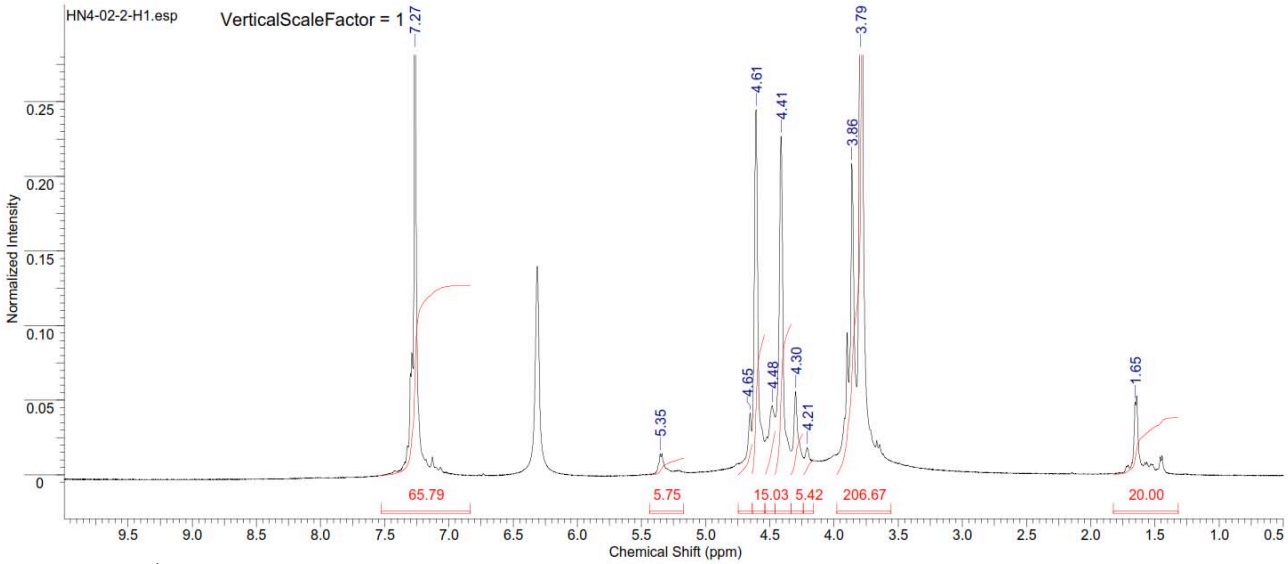


Figure S272. [1]H NMR spectrum of copoly(L-lactide/ hydroxyethylsyringic acid) [20:80] (Table S3, entry 5).

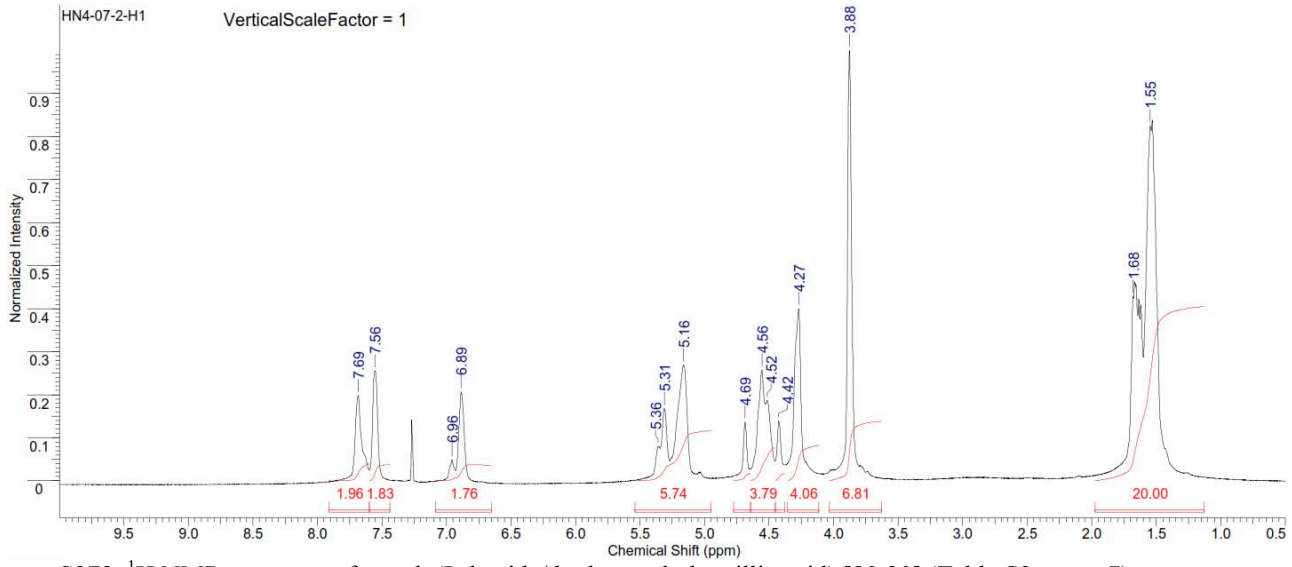


Figure S273. ^{1}H NMR spectrum of copoly(L-lactide/ hydroxyethylvanillic acid) [80:20] (Table S3, entry 7).

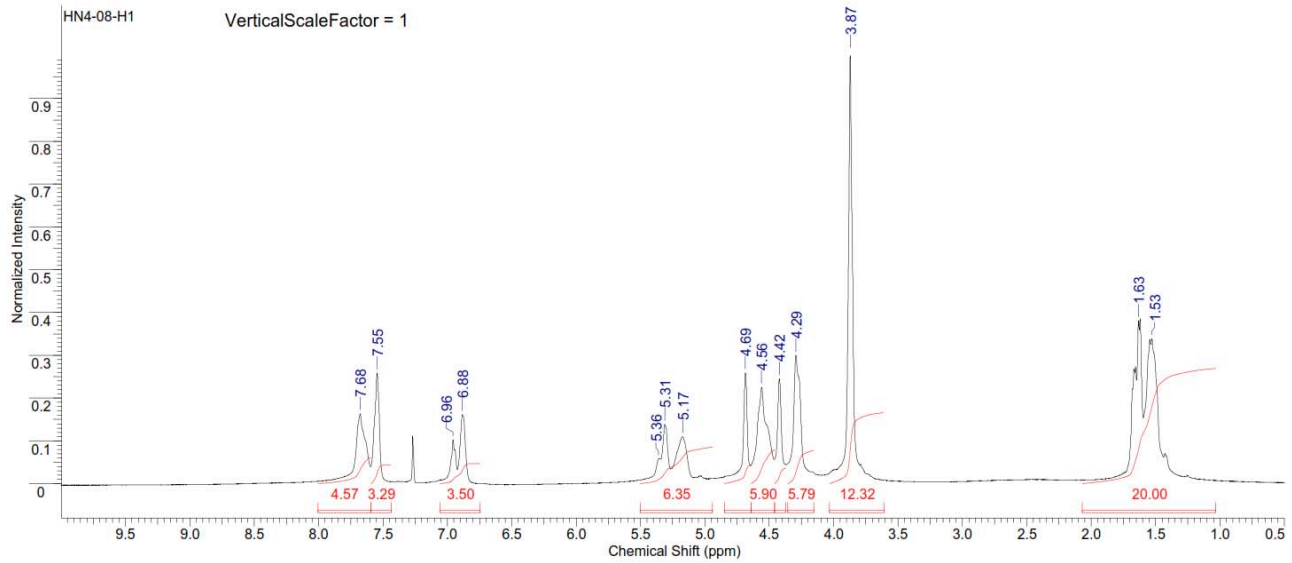


Figure S274. ^{1}H NMR spectrum of copoly(L-lactide/ hydroxyethylvanillic acid) [60:40] (Table S3, entry 8).

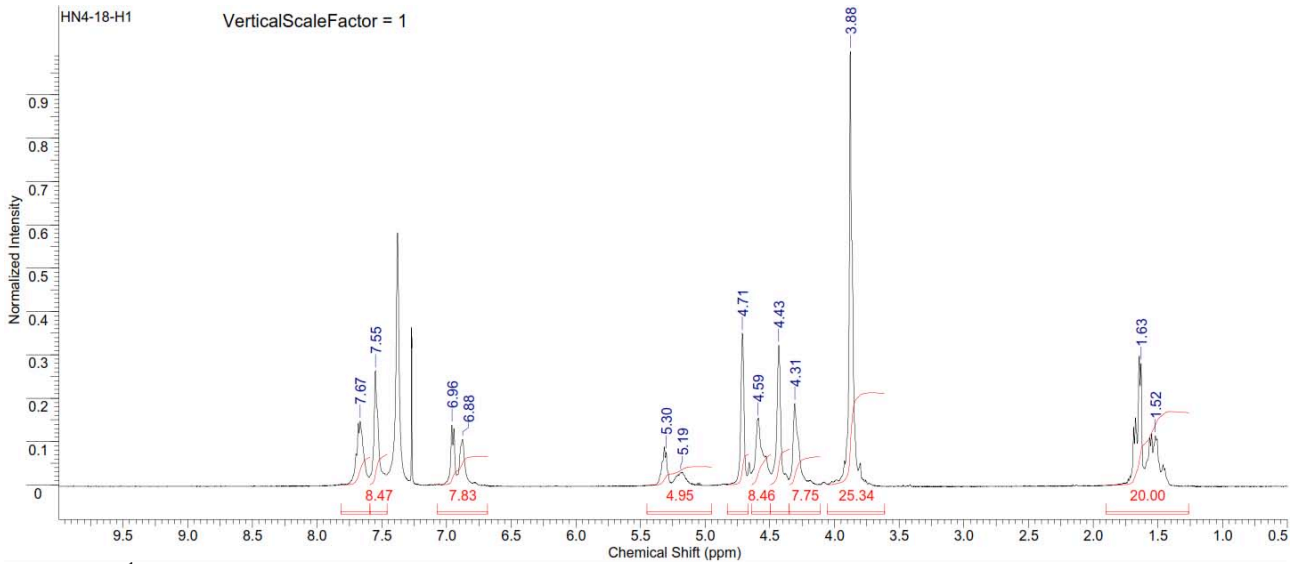


Figure S275. ^{1}H NMR spectrum of copoly(L-lactide/ hydroxyethylvanillic acid) [40:60] (Table S3, entry 9).

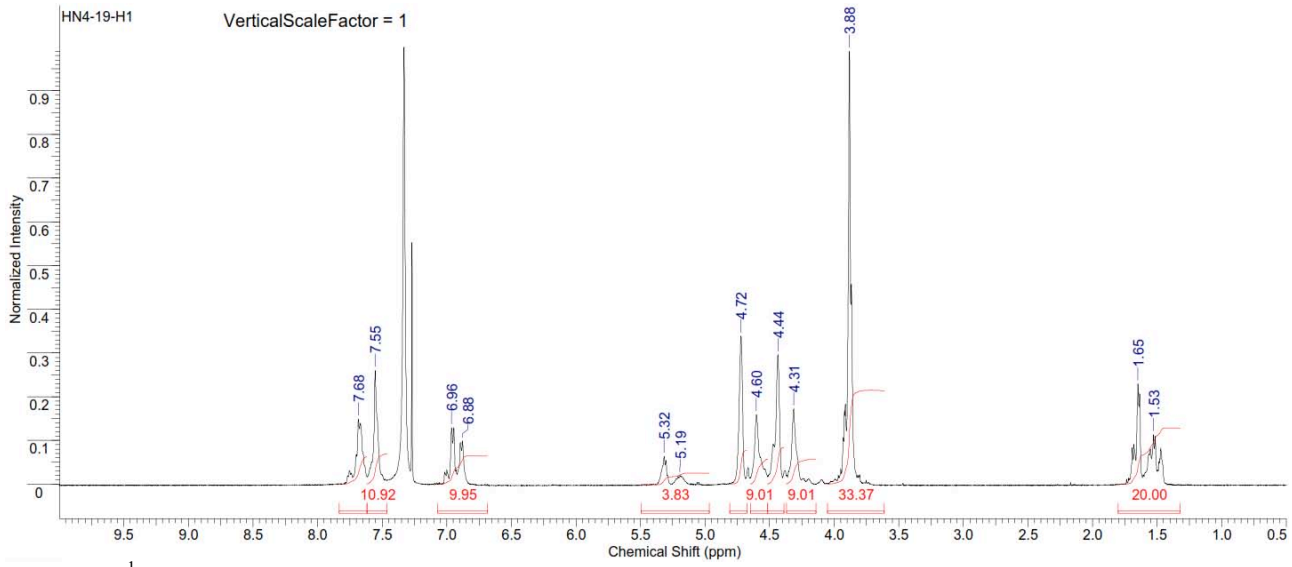


Figure S276. [1]H NMR spectrum of copoly(L-lactide/ hydroxyethylvanillic acid) [20:80] (Table S3, entry 10).

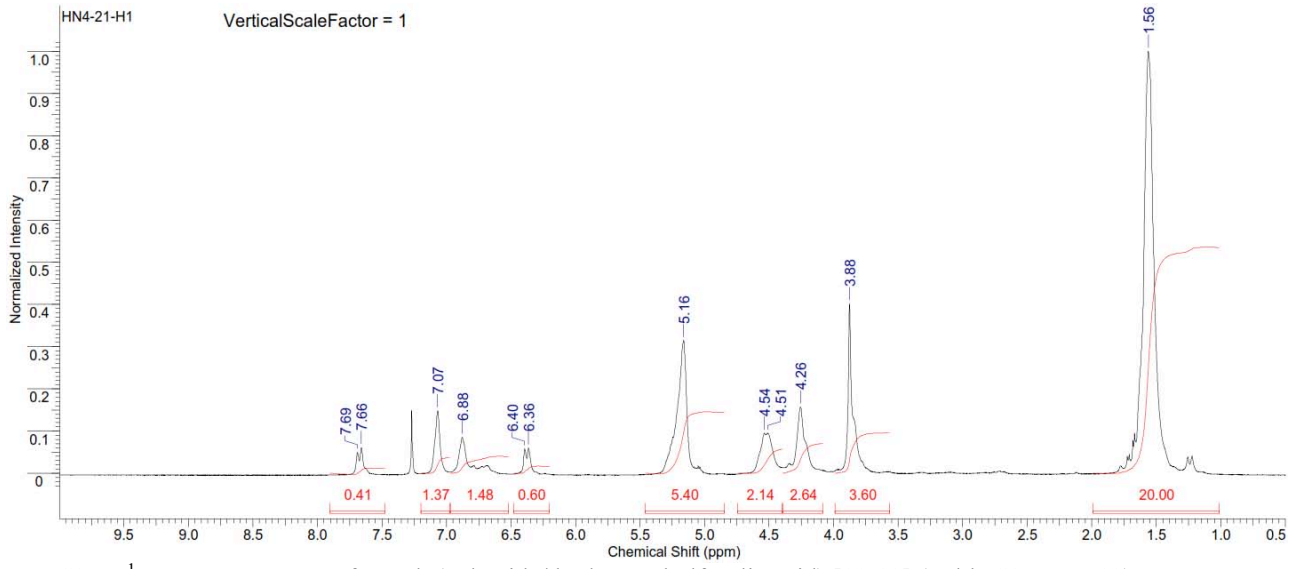


Figure S277. [1]H NMR spectrum of copoly(L-lactide/ hydroxyethylferulic acid) [90:10] (Table S3, entry 12).

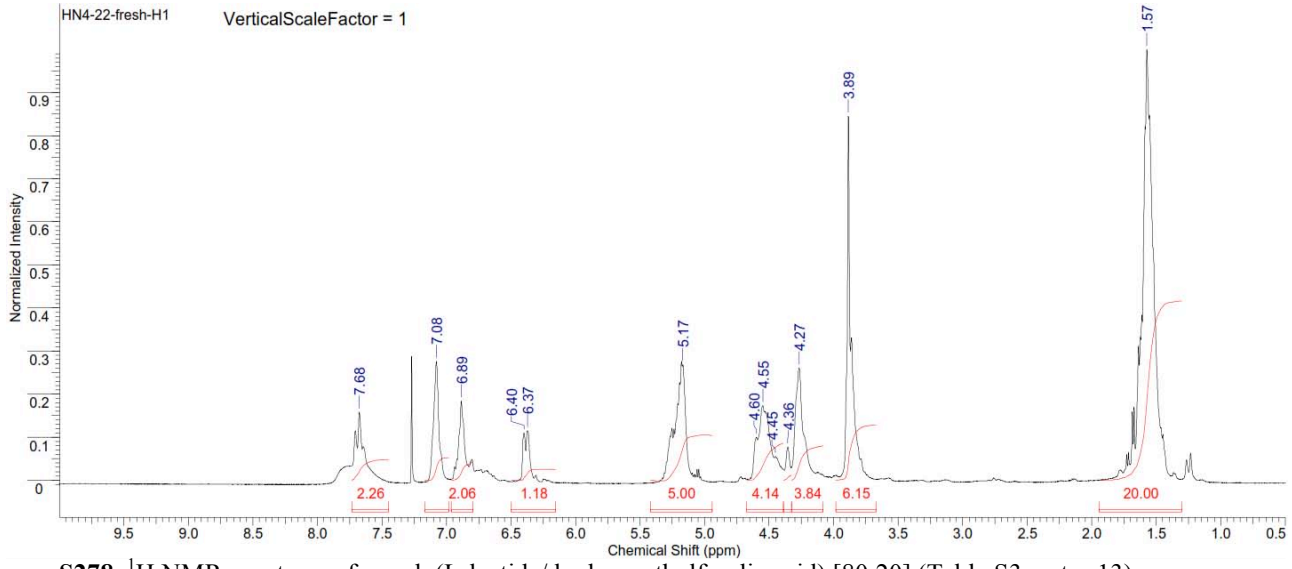


Figure S278. [1]H NMR spectrum of copoly(L-lactide/ hydroxyethylferulic acid) [80:20] (Table S3, entry 13).

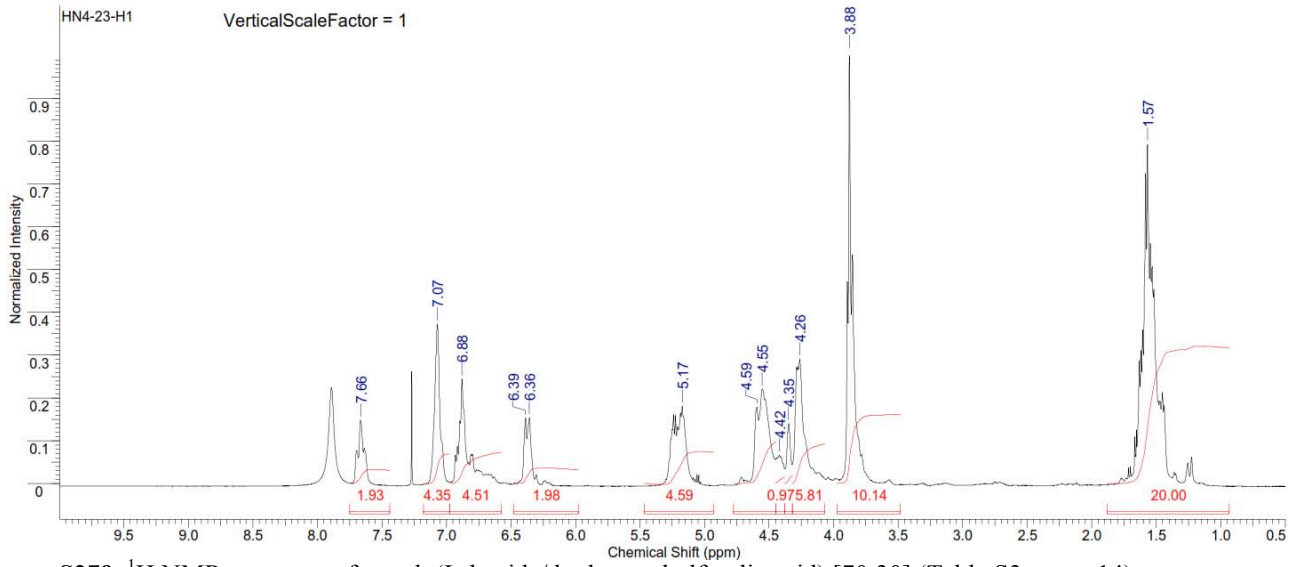


Figure S279. [1]H NMR spectrum of copoly(L-lactide/ hydroxyethylferulic acid) [70:30] (Table S3, entry 14).

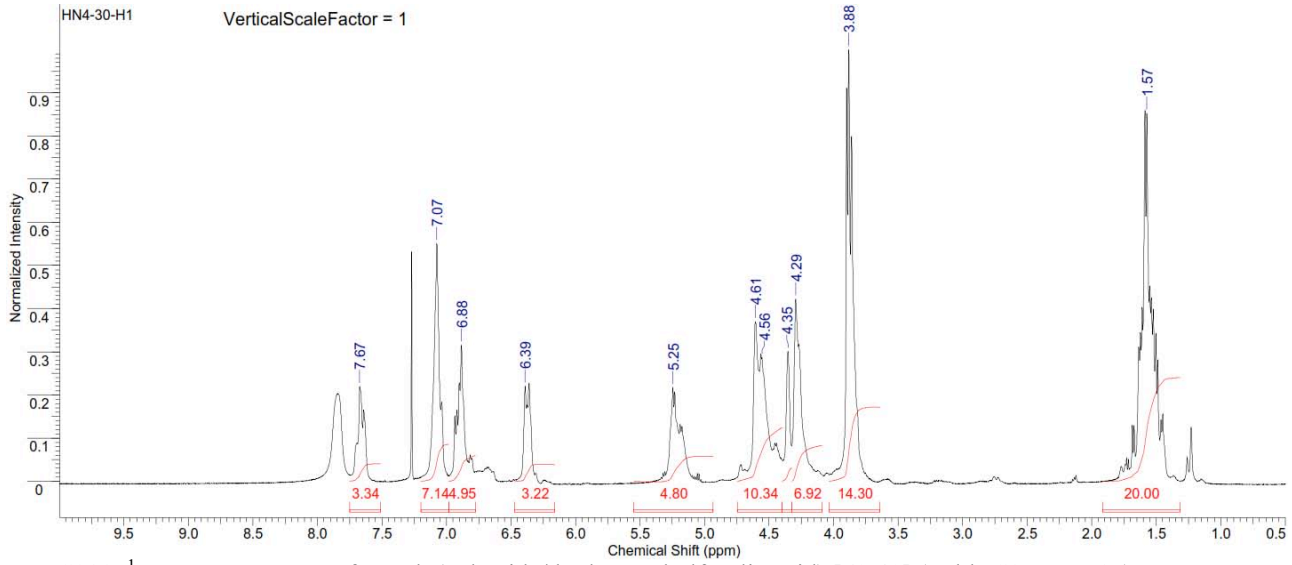


Figure S280. [1]H NMR spectrum of copoly(L-lactide/ hydroxyethylferulic acid) [60:40] (Table S3, entry 15).

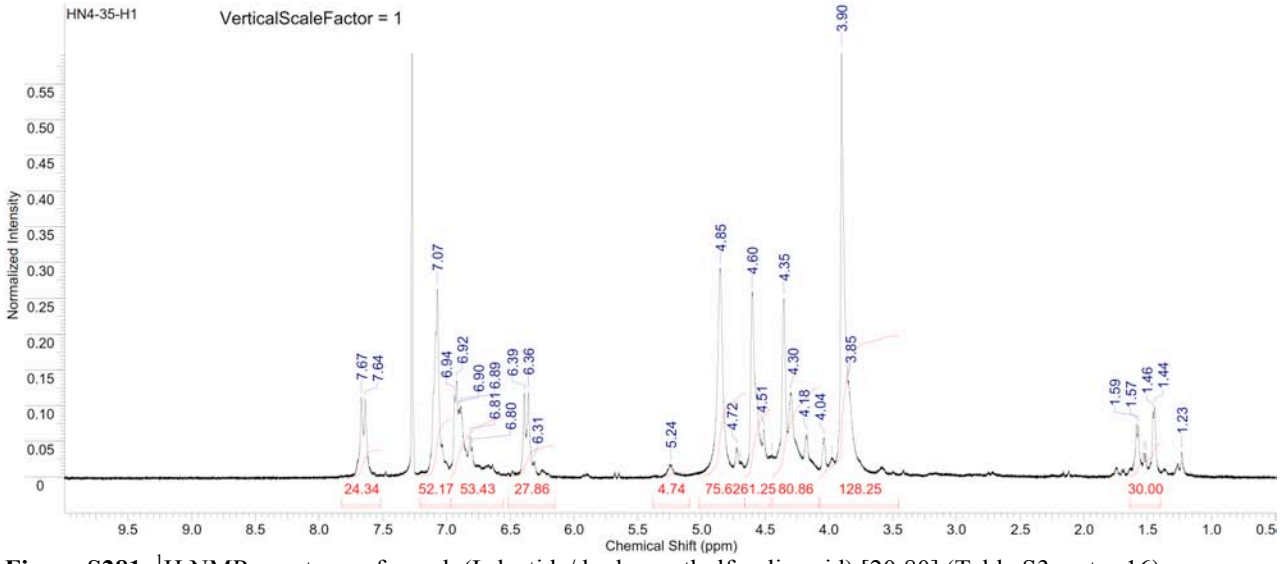


Figure S281. [1]H NMR spectrum of copoly(L-lactide/ hydroxyethylferulic acid) [20:80] (Table S3, entry 16).

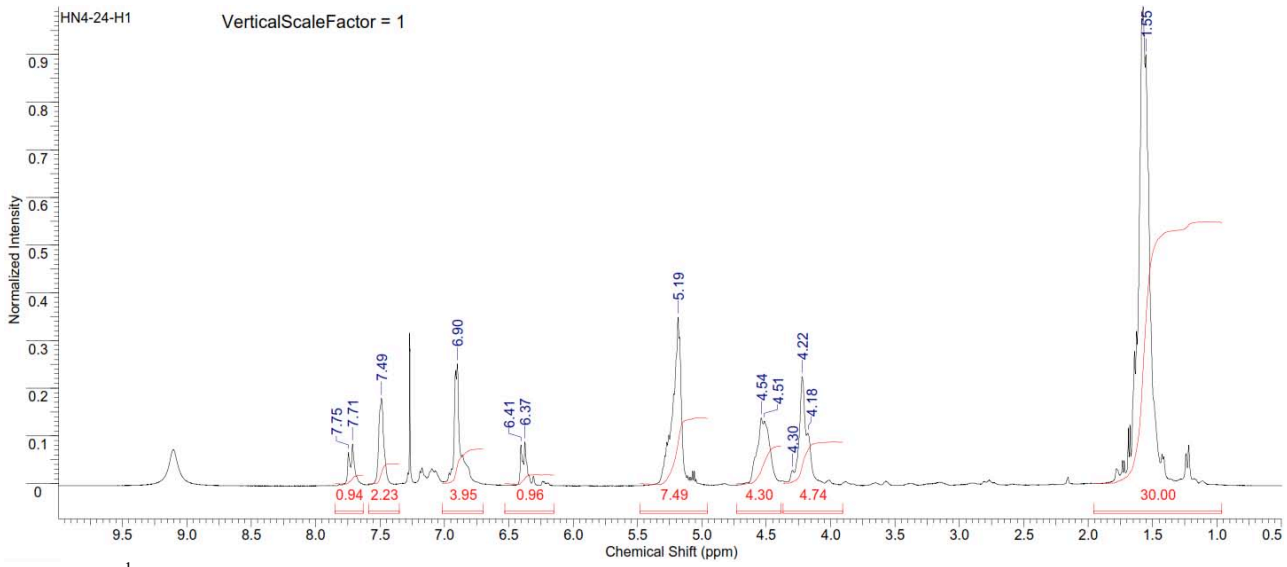


Figure S282. [1]H NMR spectrum of copoly(L-lactide/ hydroxyethylcoumaric acid) [90:10] (Table S3, entry 18).

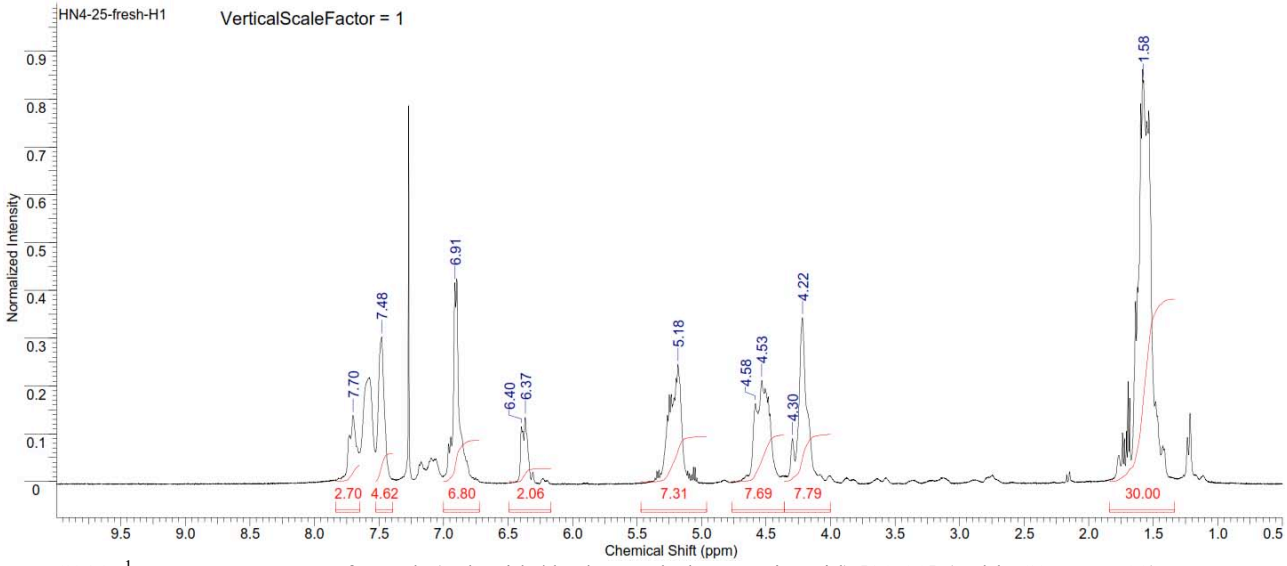


Figure S283. [1]H NMR spectrum of copoly(L-lactide/ hydroxyethylcoumaric acid) [80:20] (Table S3, entry 19).

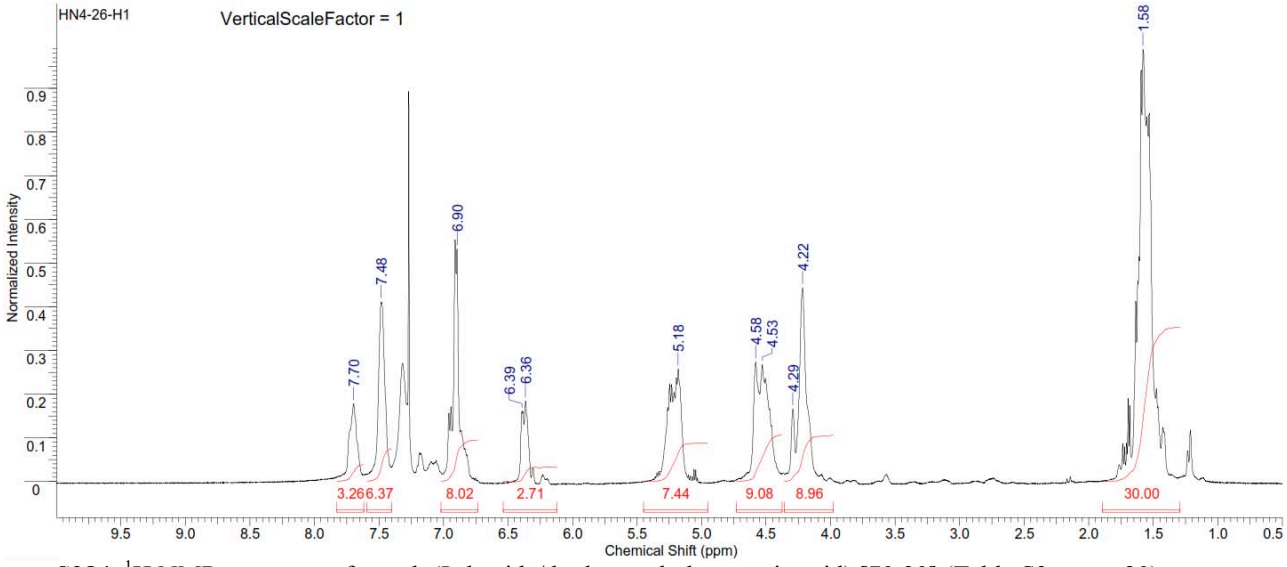


Figure S284. [1]H NMR spectrum of copoly(L-lactide/ hydroxyethylcoumaric acid) [70:30] (Table S3, entry 20).

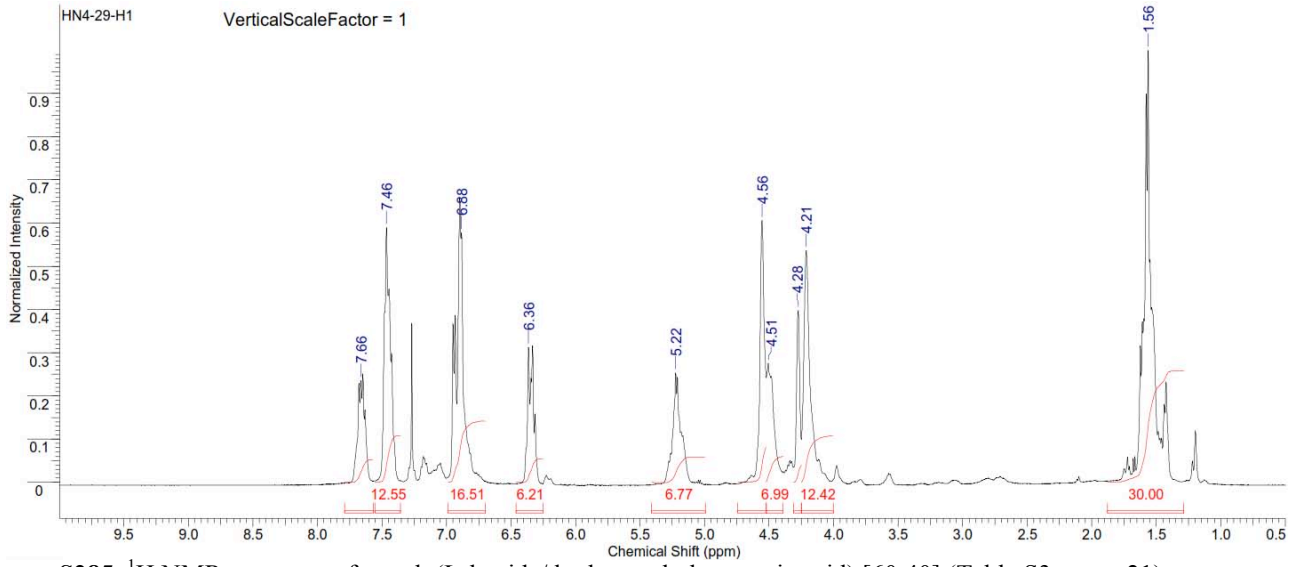


Figure S285. [1]H NMR spectrum of copoly(L-lactide/ hydroxyethylcoumaric acid) [60:40] (Table S3, entry 21).

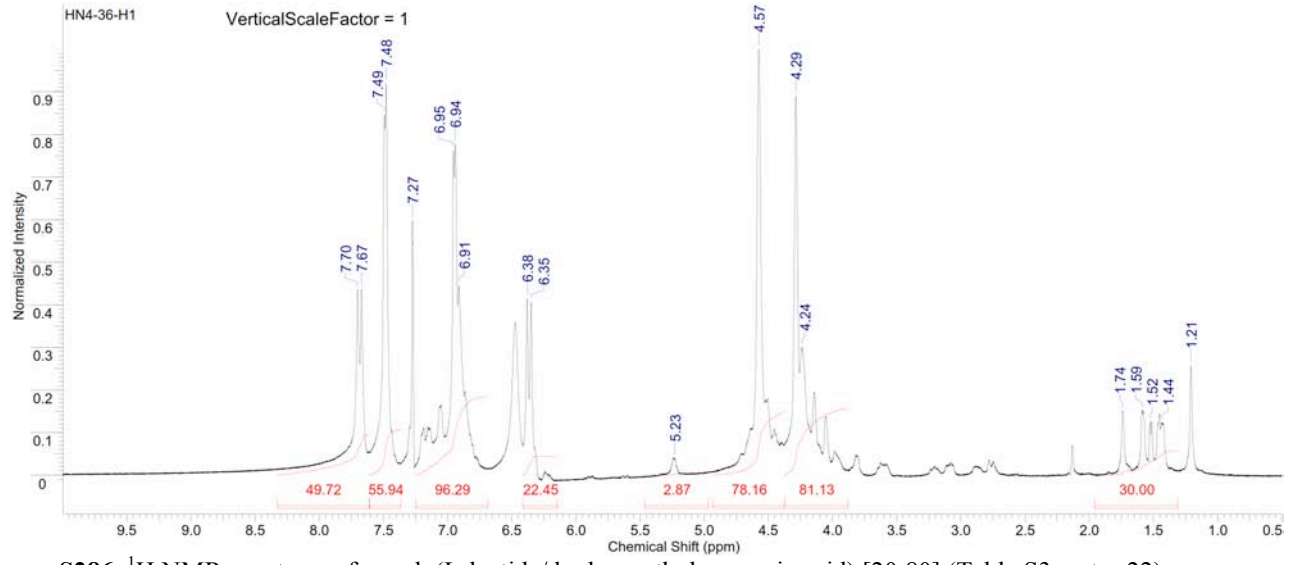


Figure S286. [1]H NMR spectrum of copoly(L-lactide/ hydroxyethylcoumaric acid) [20:80] (Table S3, entry 22).

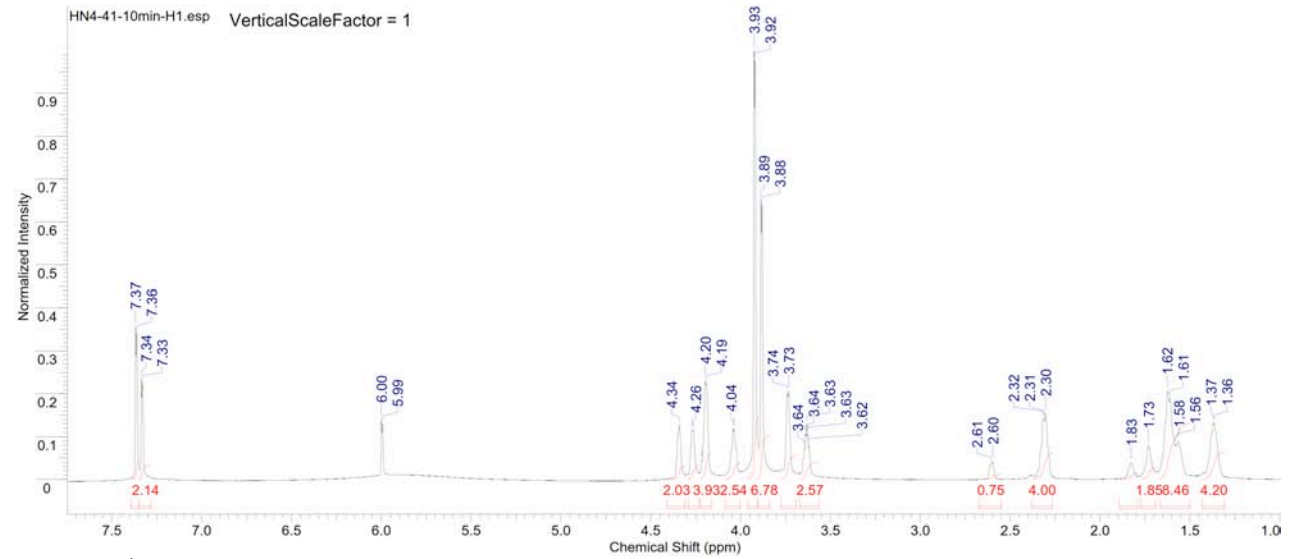


Figure S287. [1]H NMR spectrum of copoly(caprolactone/ hydroxyethylsyringic acid) [50:50] at 10 min. (Table S4, entry 1).

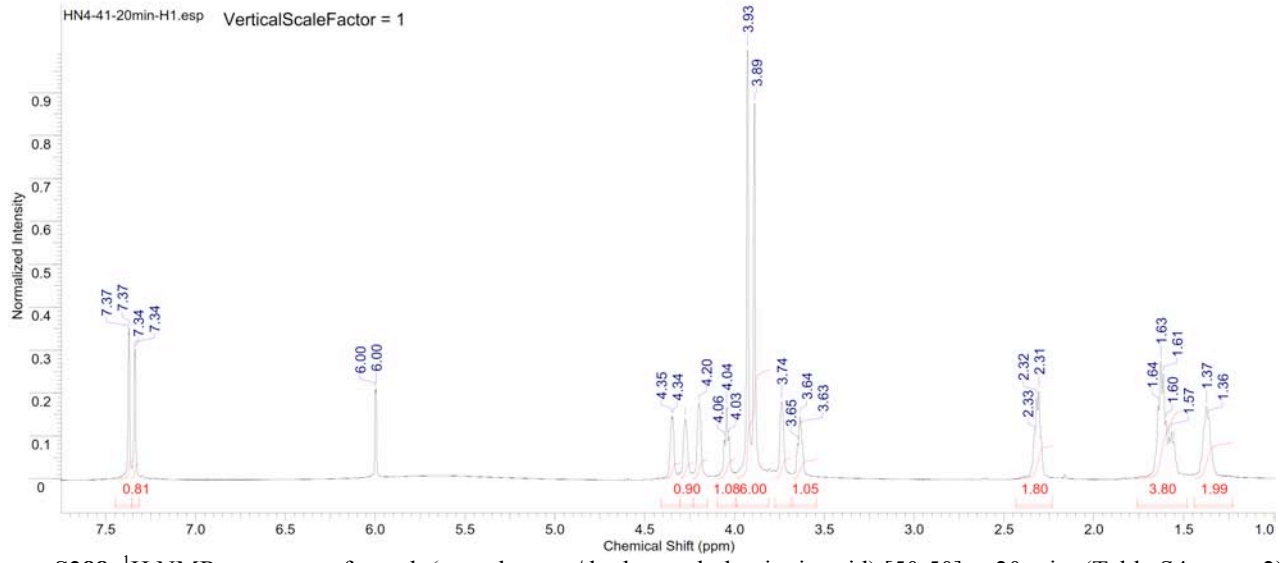


Figure S288. [1]H NMR spectrum of copoly(caprolactone/ hydroxyethylsyringic acid) [50:50] at 20 min. (Table S4, entry 2).

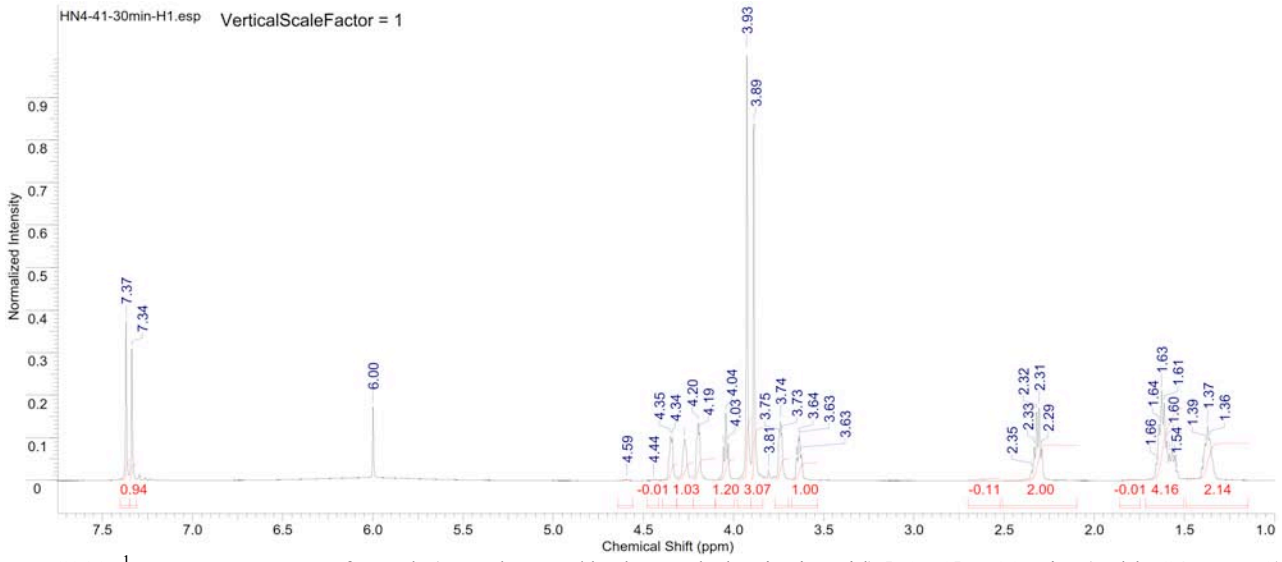


Figure S289. [1]H NMR spectrum of copoly(caprolactone/ hydroxyethylsyringic acid) [50:50] at 30 min. (Table S4, entry 3).

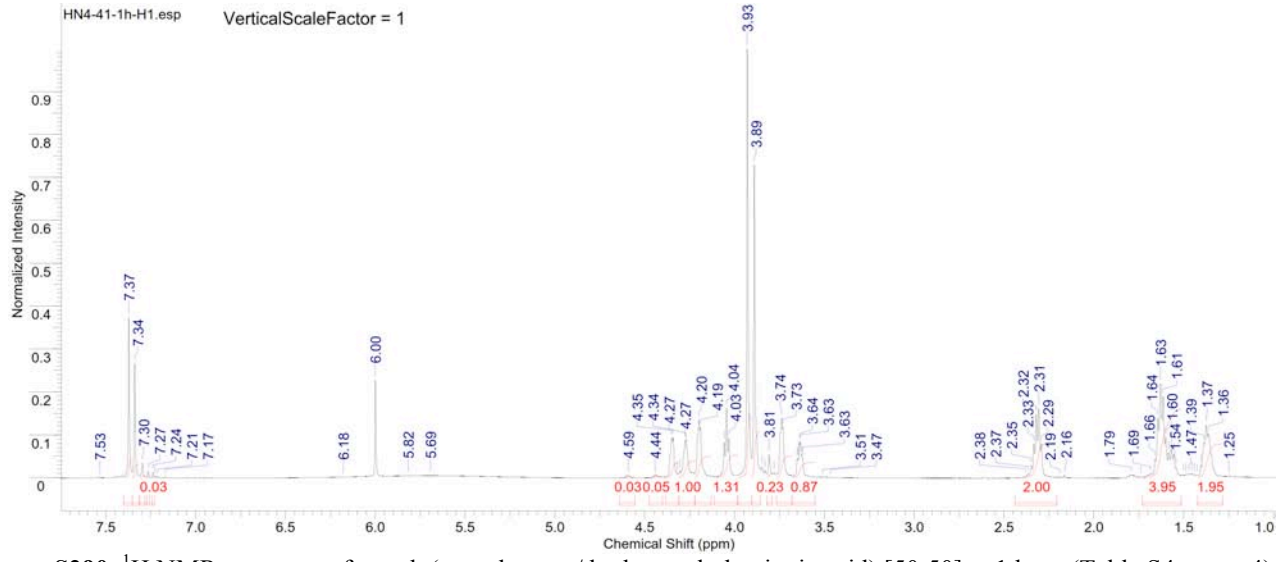


Figure S290. [1]H NMR spectrum of copoly(caprolactone/ hydroxyethylsyringic acid) [50:50] at 1 hour (Table S4, entry 4).

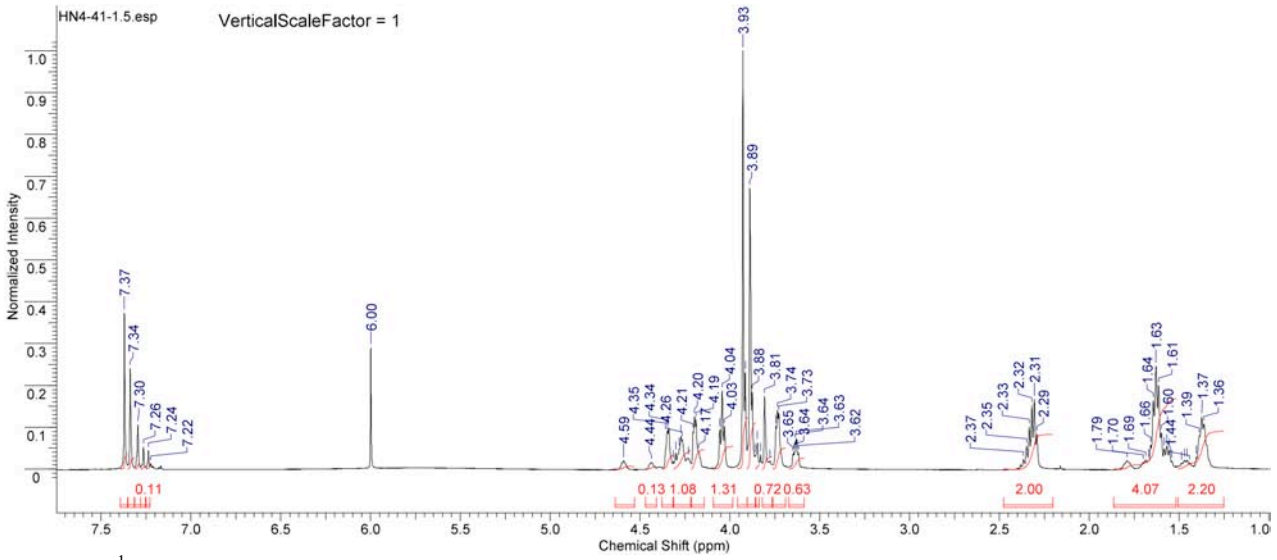


Figure S291. [1]H NMR spectrum of copoly(caprolactone/ hydroxyethylsyringic acid) [50:50] at 1.5 hours (Table S4, entry 5).

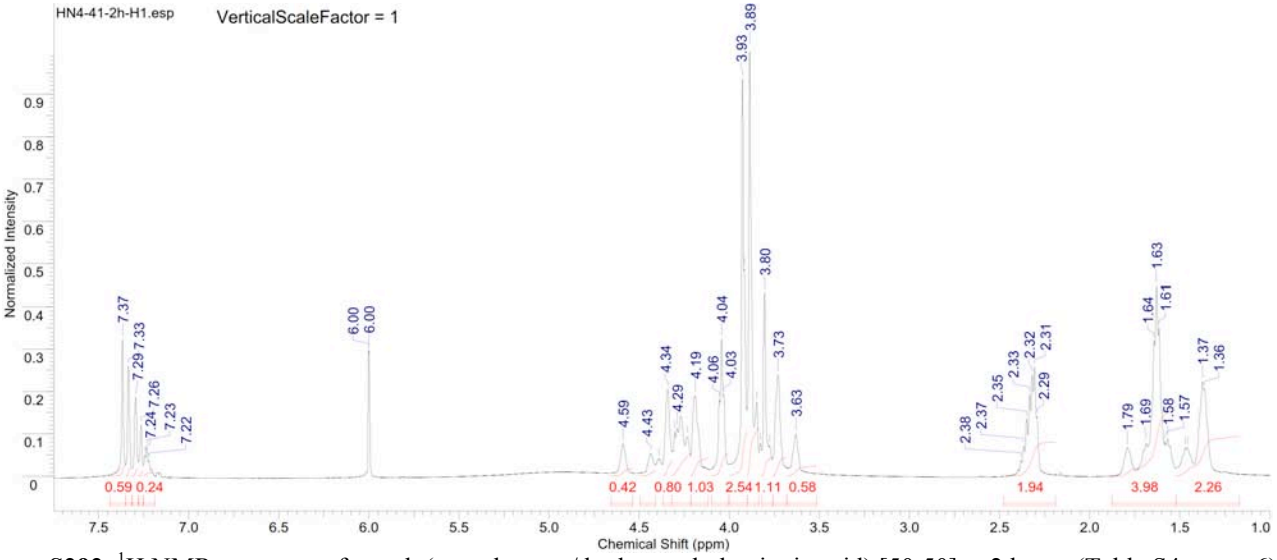


Figure S292. [1]H NMR spectrum of copoly(caprolactone/ hydroxyethylsyringic acid) [50:50] at 2 hours (Table S4, entry 6).

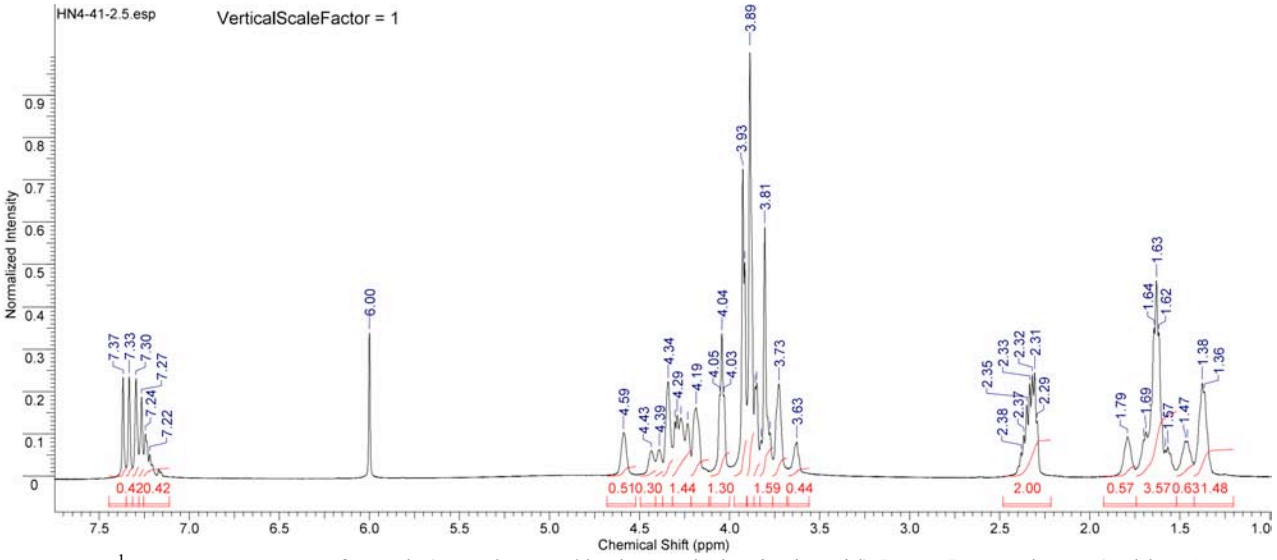


Figure S293. [1]H NMR spectrum of copoly(caprolactone/ hydroxyethylsyringic acid) [50:50] at 2.5 hours (Table S4, entry 7).

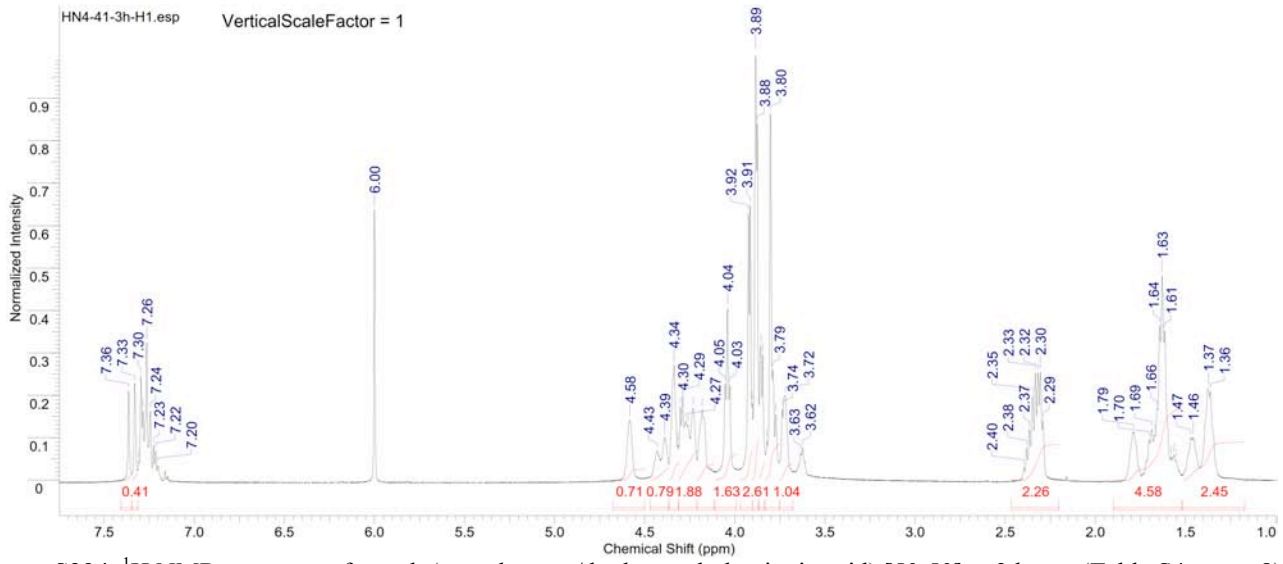


Figure S294. [1]H NMR spectrum of copoly(caprolactone/ hydroxyethylsyringic acid) [50:50] at 3 hours (Table S4, entry 8).

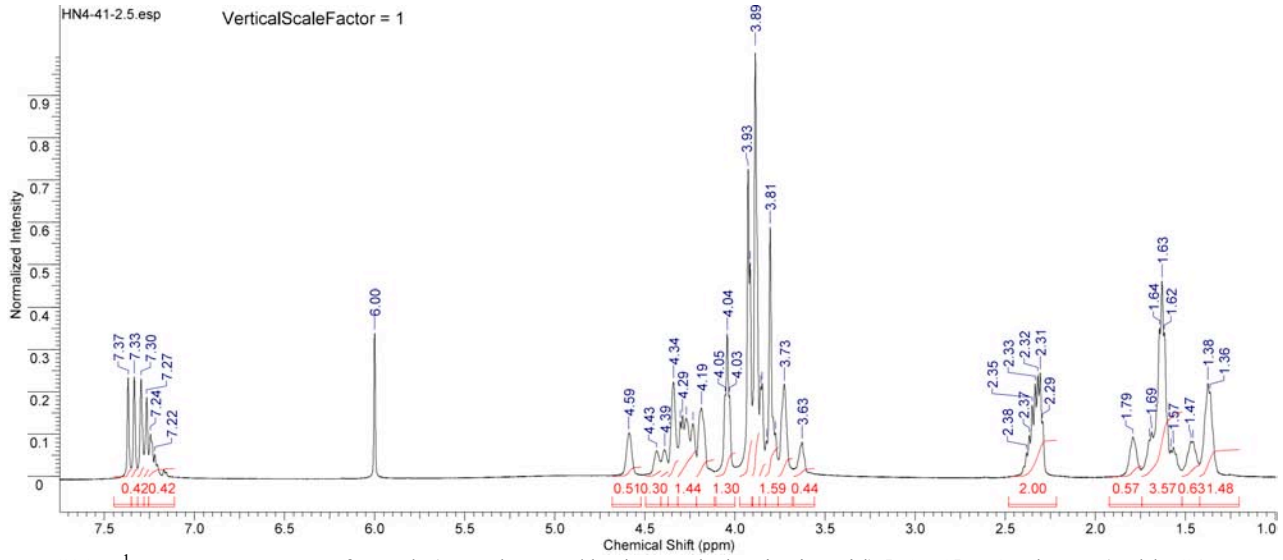


Figure S295. [1]H NMR spectrum of copoly(caprolactone/ hydroxyethylsyringic acid) [50:50] at 3.5 hours (Table S4, entry 9).

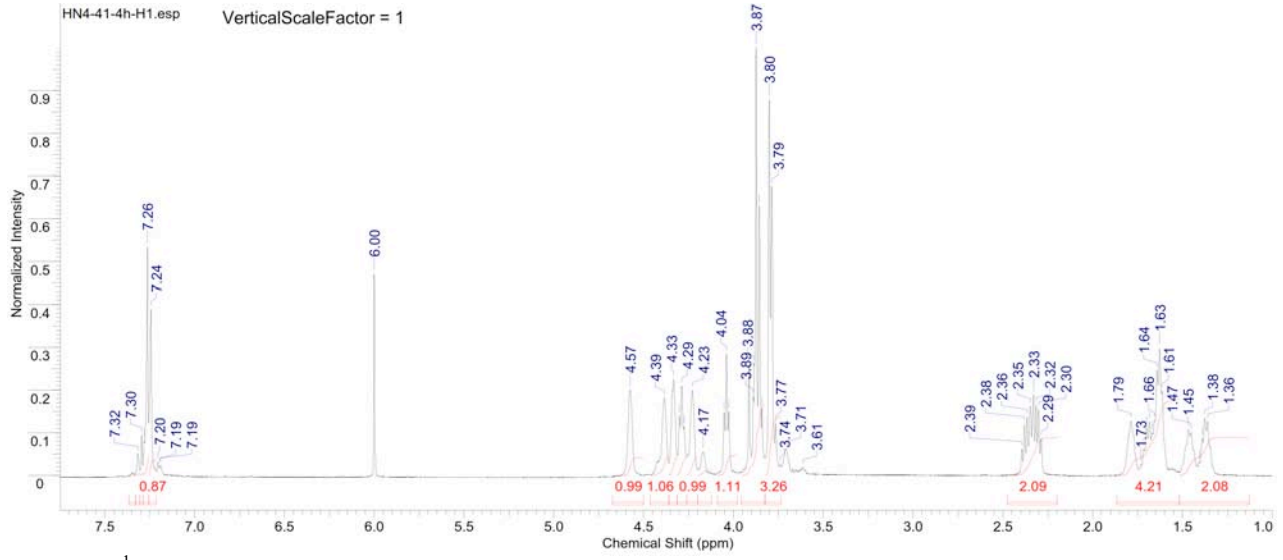


Figure S296. [1]H NMR spectrum of copoly(caprolactone/ hydroxyethylsyringic acid) [50:50] at 4 hours (Table S4, entry 10).

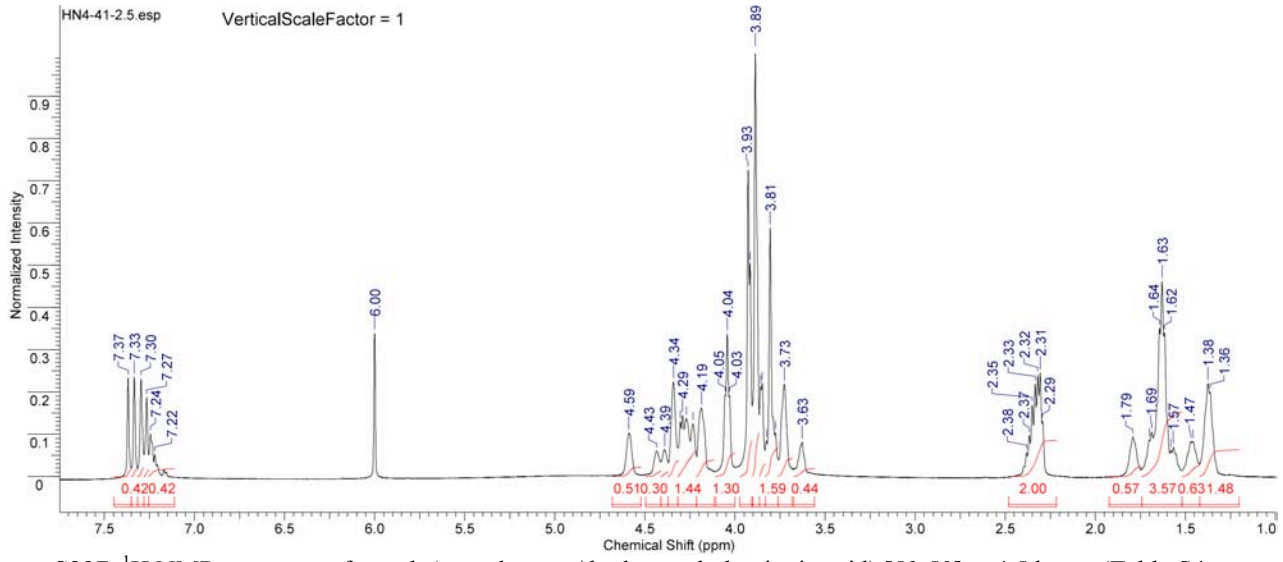


Figure S297. [1]H NMR spectrum of copoly(caprolactone/ hydroxyethylsyringic acid) [50:50] at 4.5 hours (Table S4, entry 11).

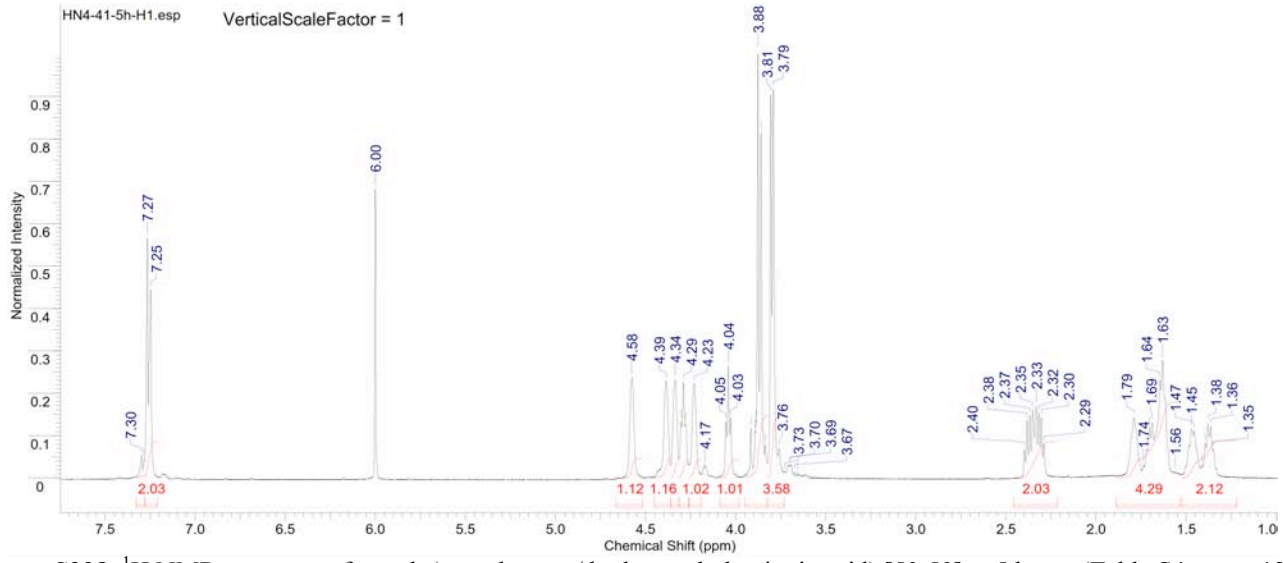


Figure S298. [1]H NMR spectrum of copoly(caprolactone/ hydroxyethylsyringic acid) [50:50] at 5 hours (Table S4, entry 12).

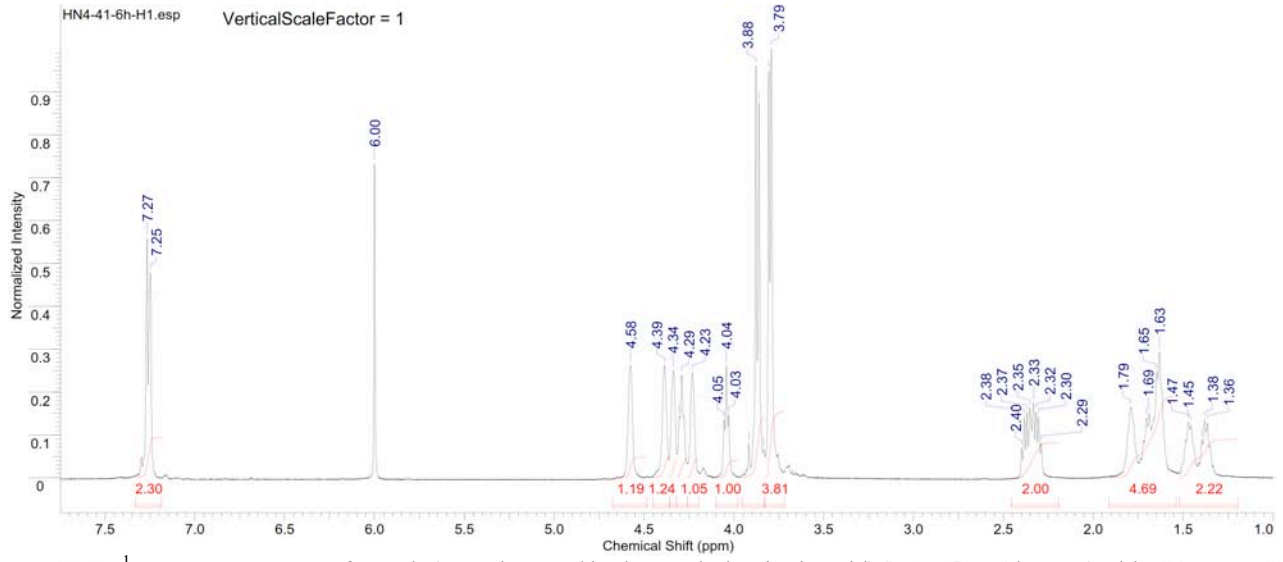


Figure S299. [1]H NMR spectrum of copoly(caprolactone/ hydroxyethylsyringic acid) [50:50] at 6 hours (Table S4, entry 13).

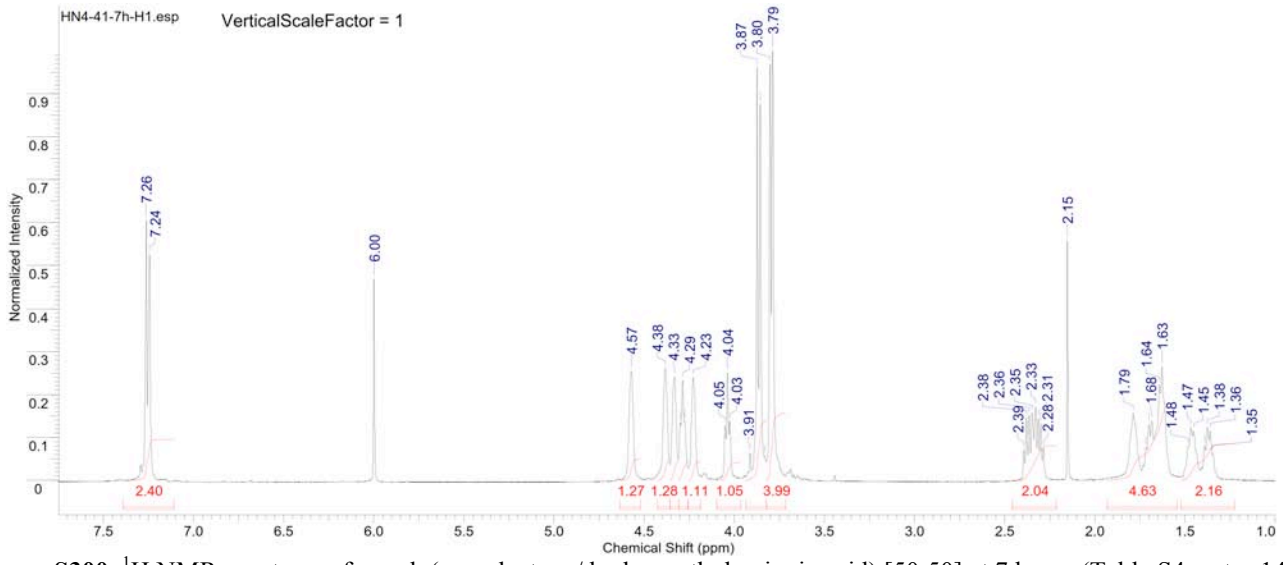


Figure S300. [1]H NMR spectrum of copoly(caprolactone/ hydroxyethylsyringic acid) [50:50] at 7 hours (Table S4, entry 14).

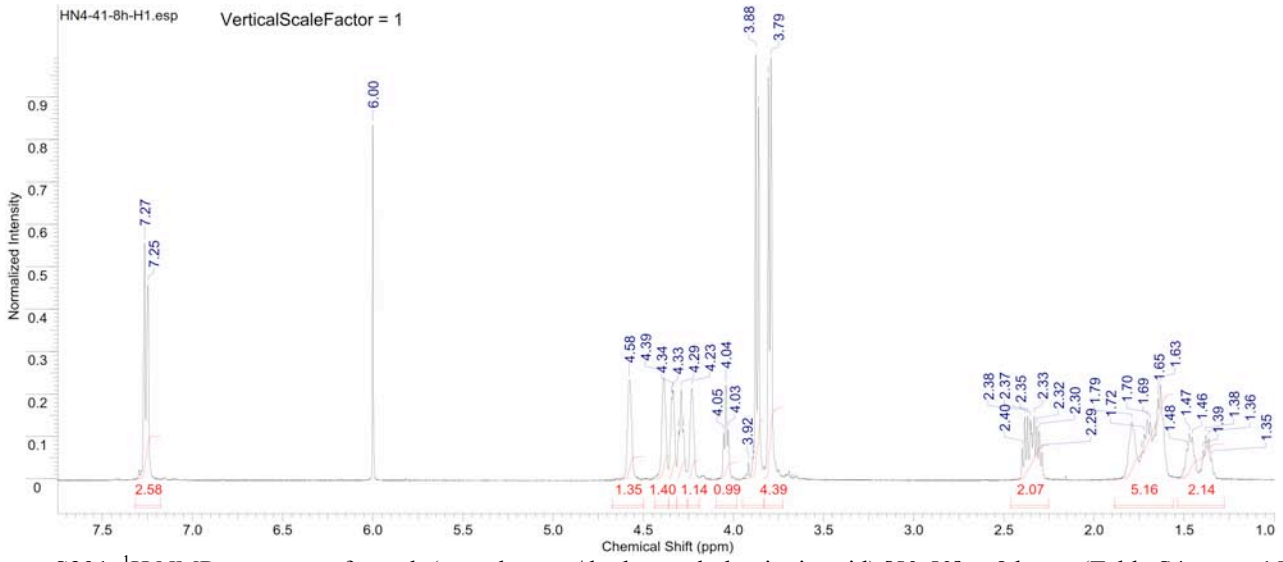


Figure S301. [1]H NMR spectrum of copoly(caprolactone/ hydroxyethylsyringic acid) [50:50] at 8 hours (Table S4, entry 15).

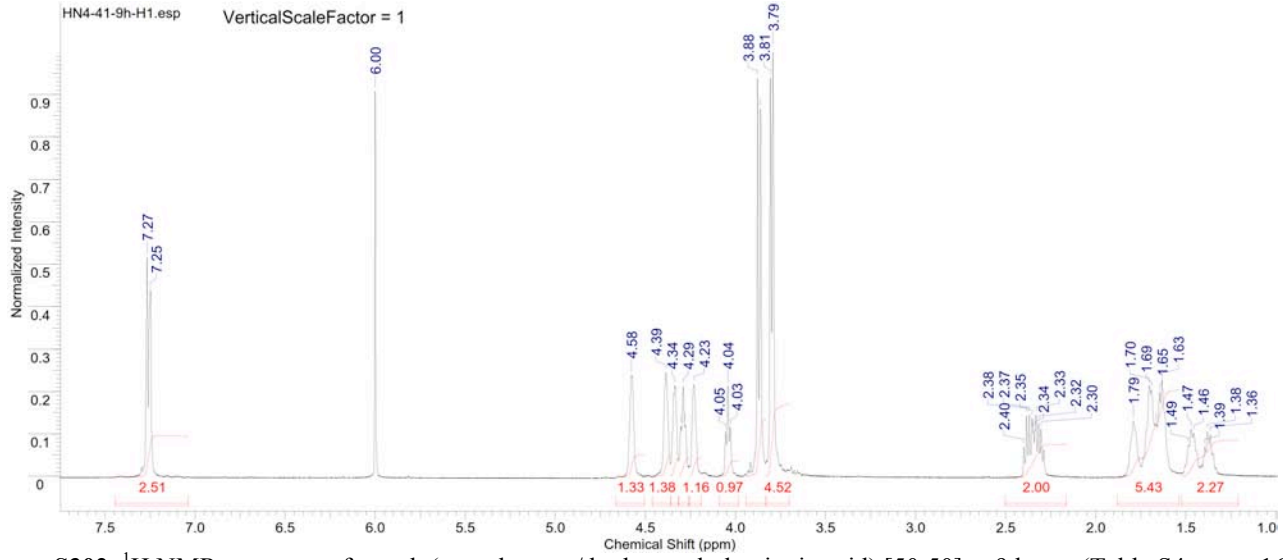


Figure S302. [1]H NMR spectrum of copoly(caprolactone/ hydroxyethylsyringic acid) [50:50] at 9 hours (Table S4, entry 16).

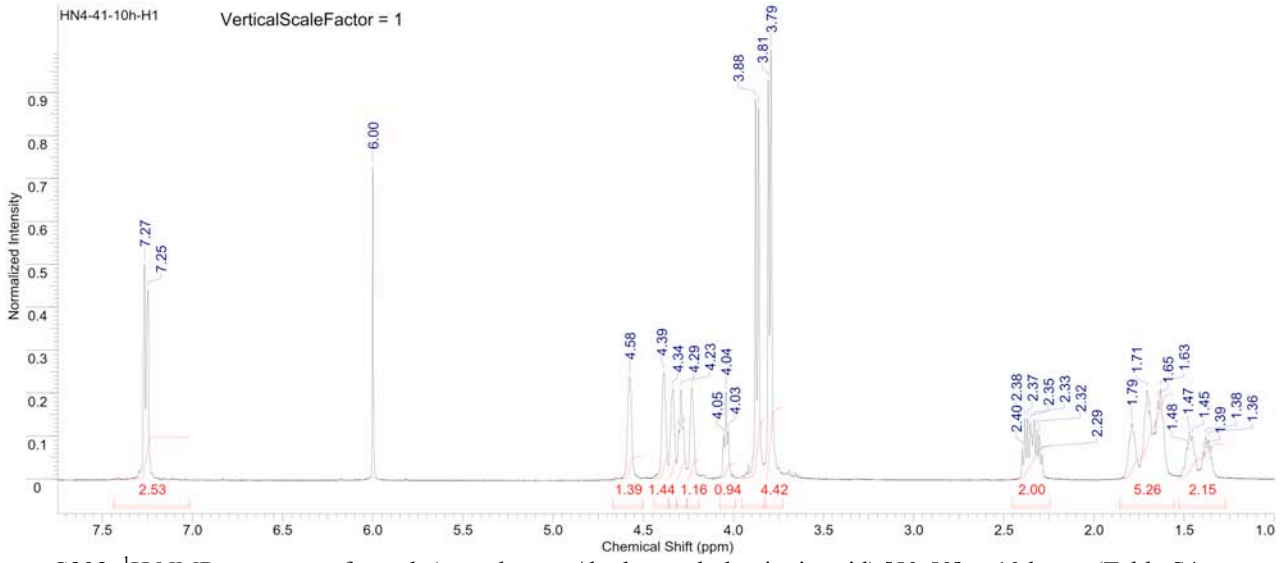


Figure S303. ^{1}H NMR spectrum of copoly(caprolactone/ hydroxyethylsyringic acid) [50:50] at 10 hours (Table S4, entry 17).

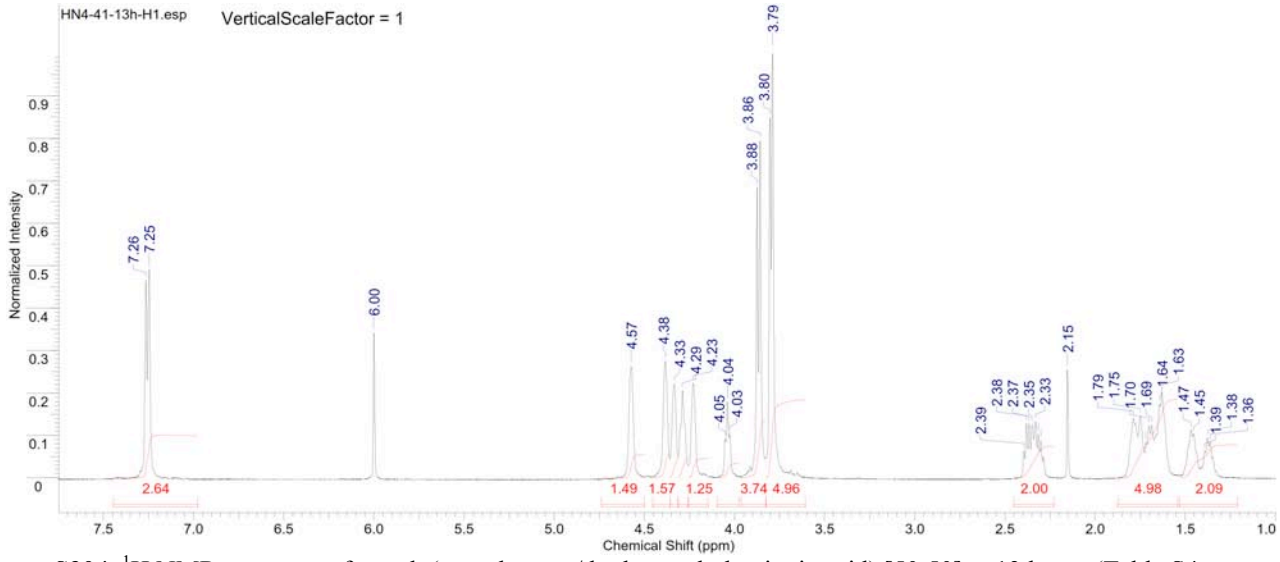


Figure S304. ^{1}H NMR spectrum of copoly(caprolactone/ hydroxyethylsyringic acid) [50:50] at 13 hours (Table S4, entry 18).

^{13}C NMR Spectra

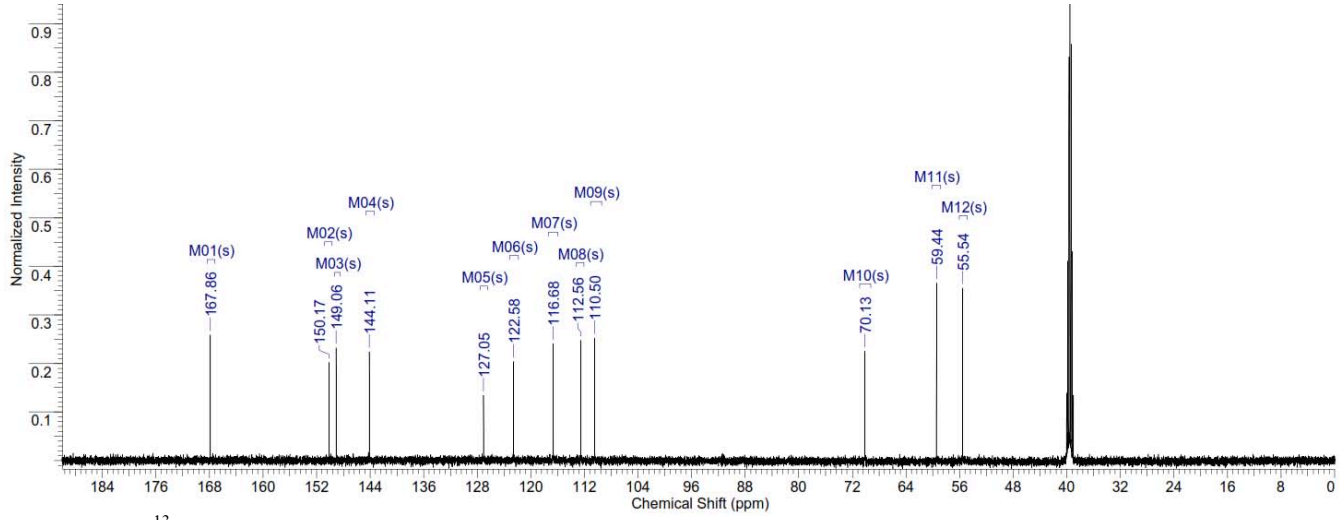


Figure S305. ^{13}C NMR spectrum of hydroxyethylferulic acid.

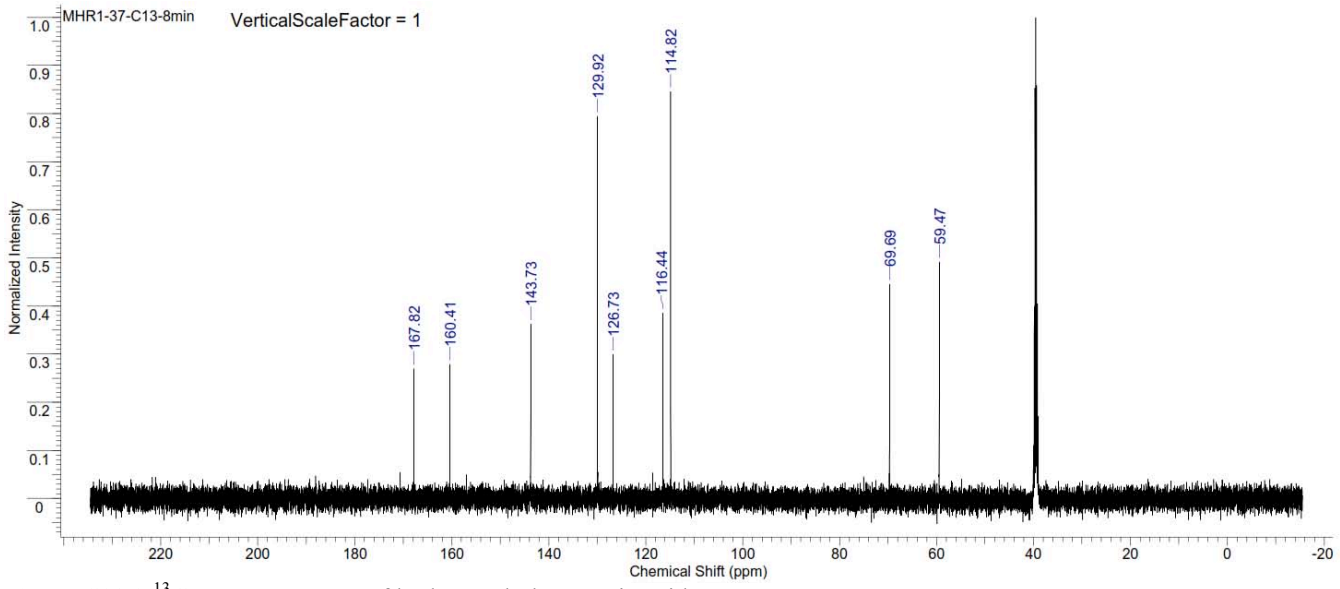


Figure S306. ^{13}C NMR spectrum of hydroxyethylcoumaric acid.

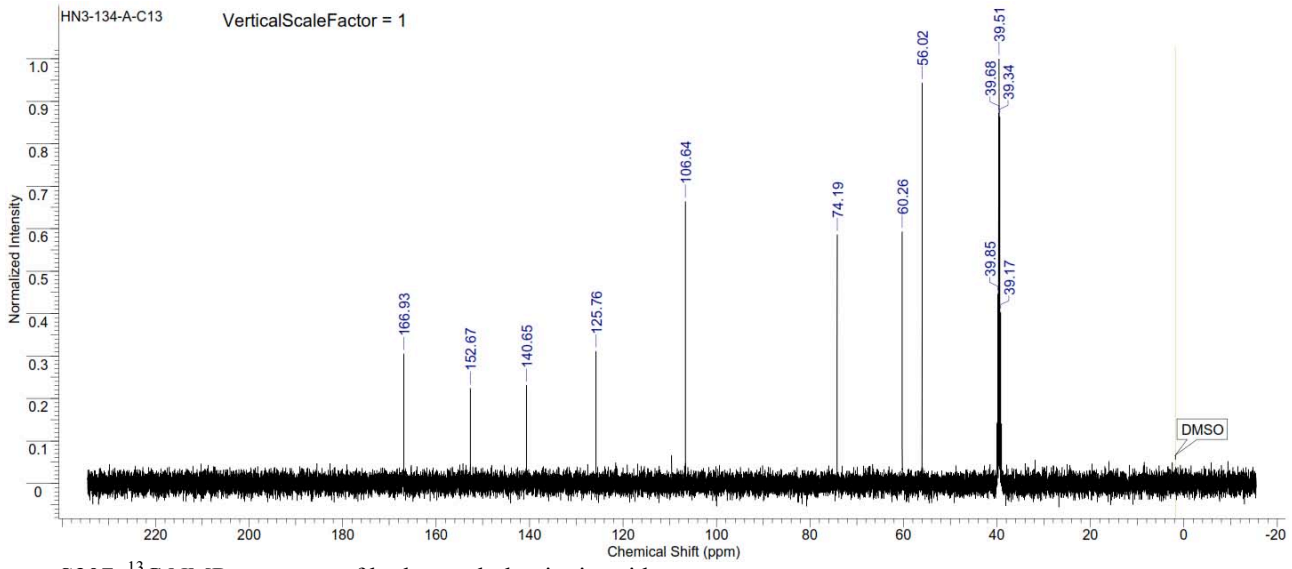


Figure S307. ^{13}C NMR spectrum of hydroxyethylsyringic acid.

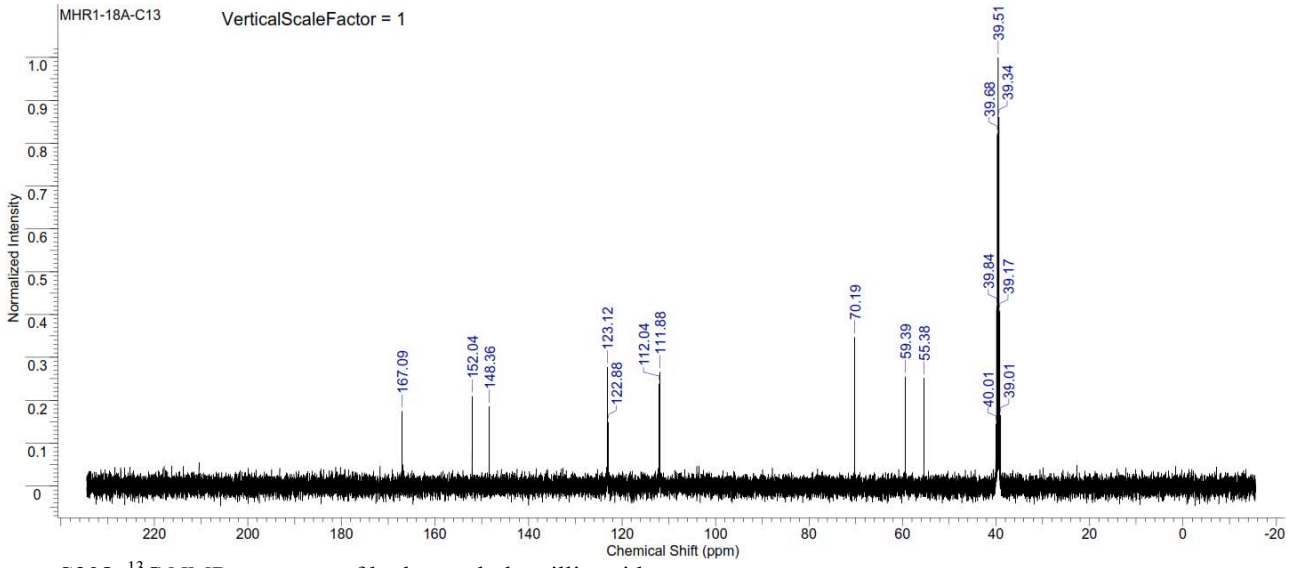


Figure S308. ^{13}C NMR spectrum of hydroxyethylvanillic acid.

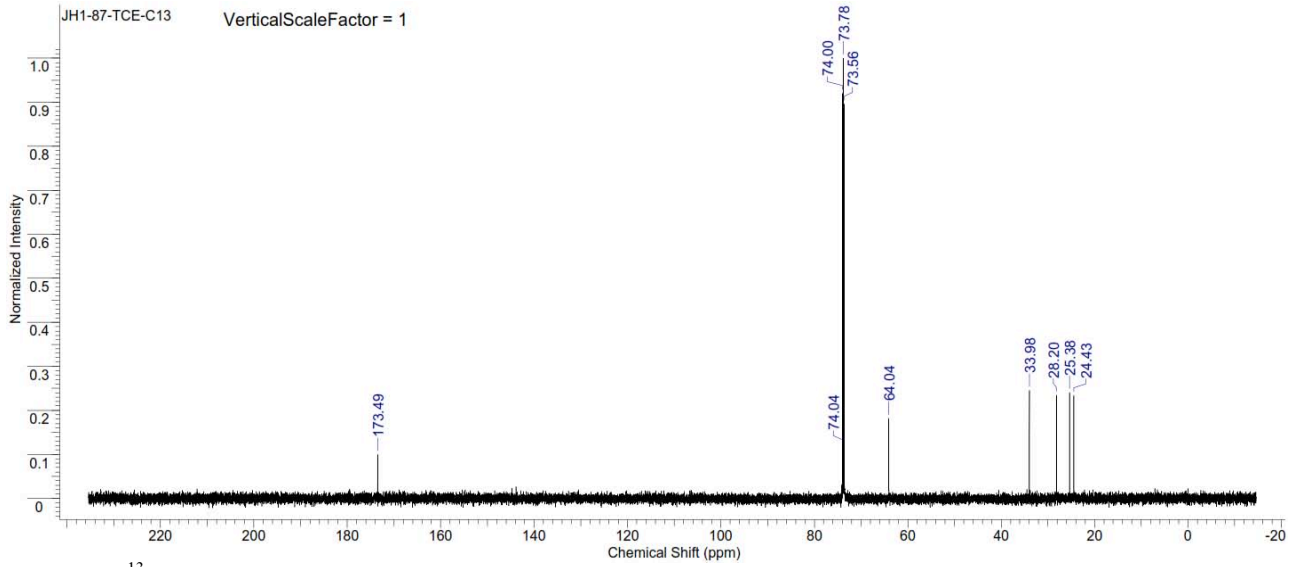


Figure S309. ^{13}C NMR spectrum of polycaprolactone (Table S2, entry 1)

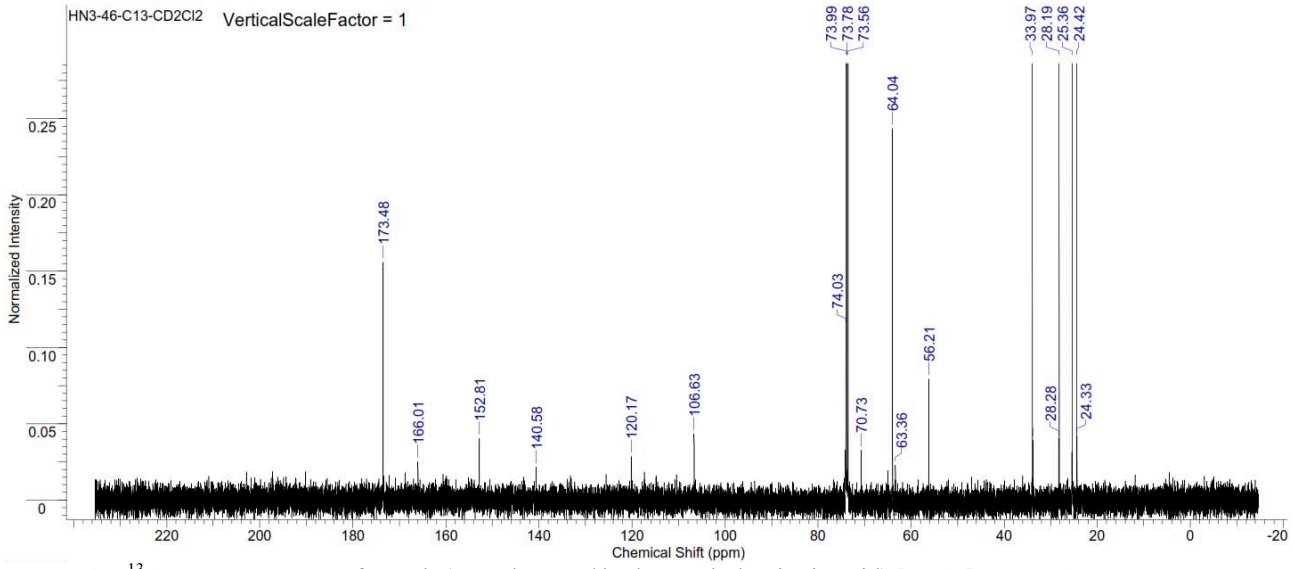


Figure S310. ^{13}C NMR spectrum of copoly(caprolactone/ hydroxyethylsyringic acid) [90:10] (Table S2, entry 2).

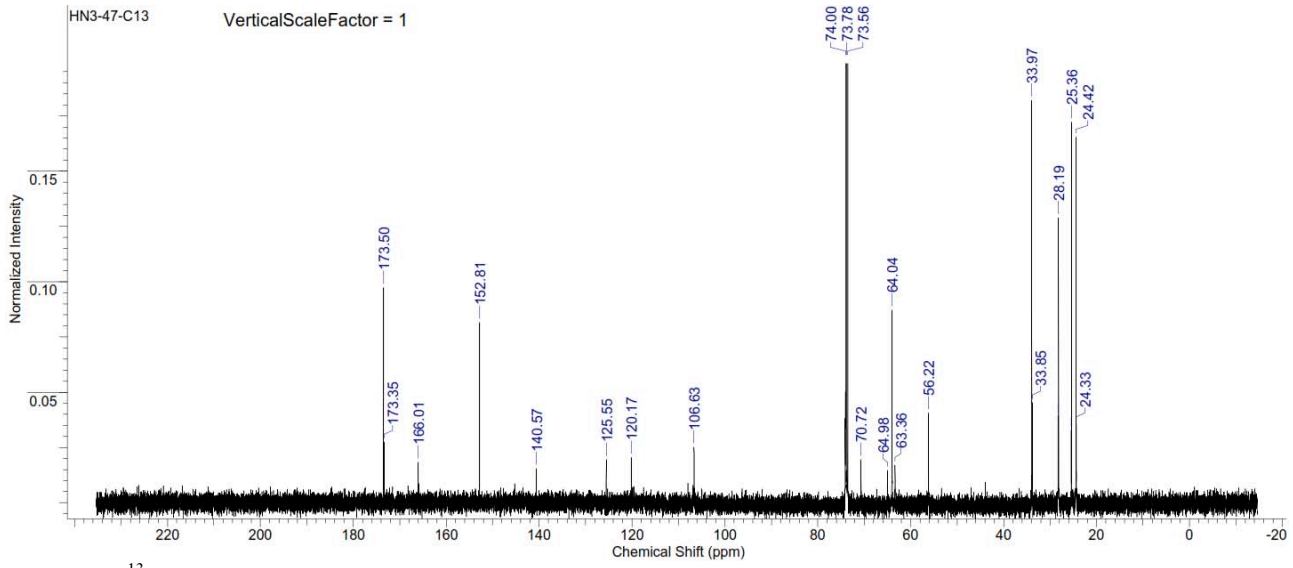


Figure S311. ^{13}C NMR spectrum of copoly(caprolactone/ hydroxyethylsyringic acid) [80:20] (Table S2, entry 3).

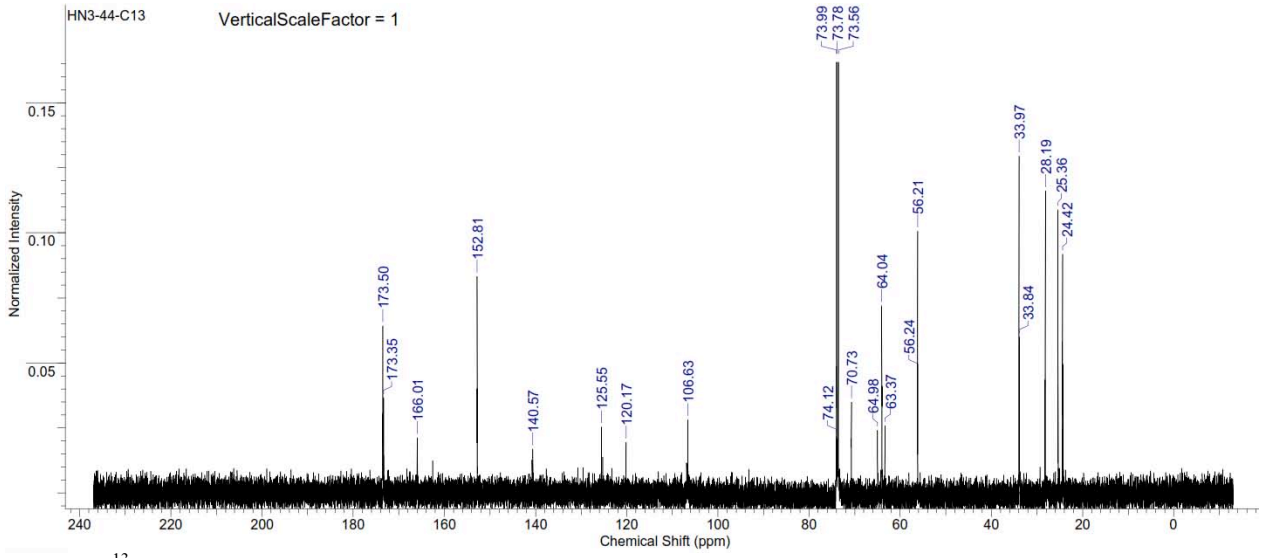


Figure S312. ^{13}C NMR spectrum of copoly(caprolactone/ hydroxyethylsyringic acid) [70:30] (Table S2, entry 4).

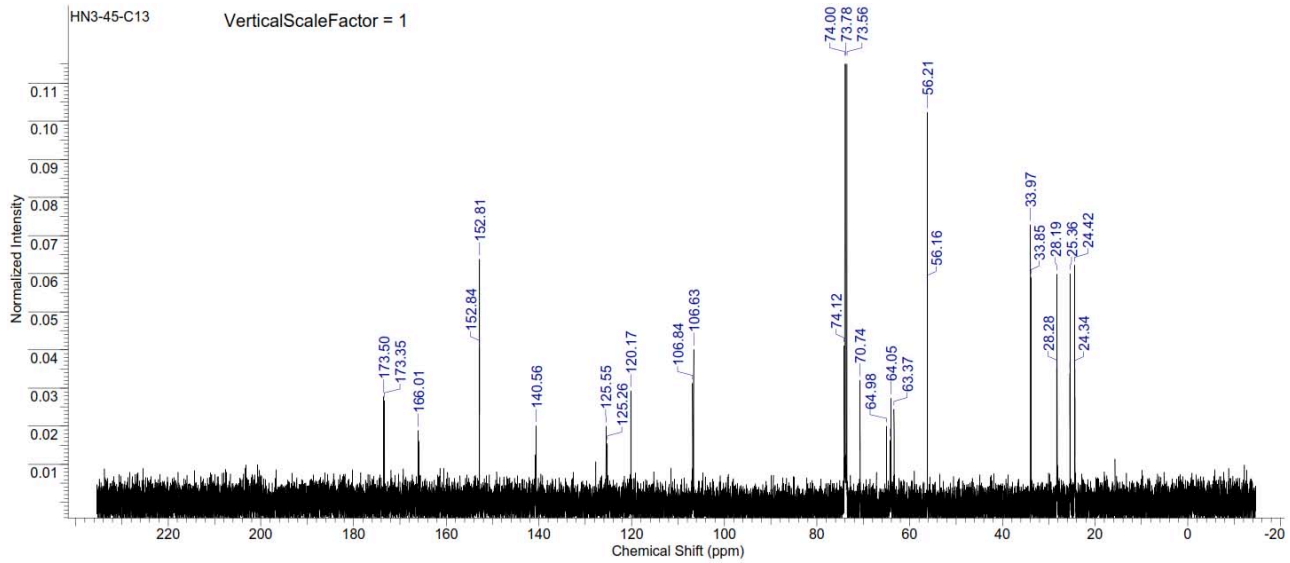


Figure S313. ^{13}C NMR spectrum of copoly(caprolactone/ hydroxyethylsyringic acid) [60:40] (Table S2, entry 5).

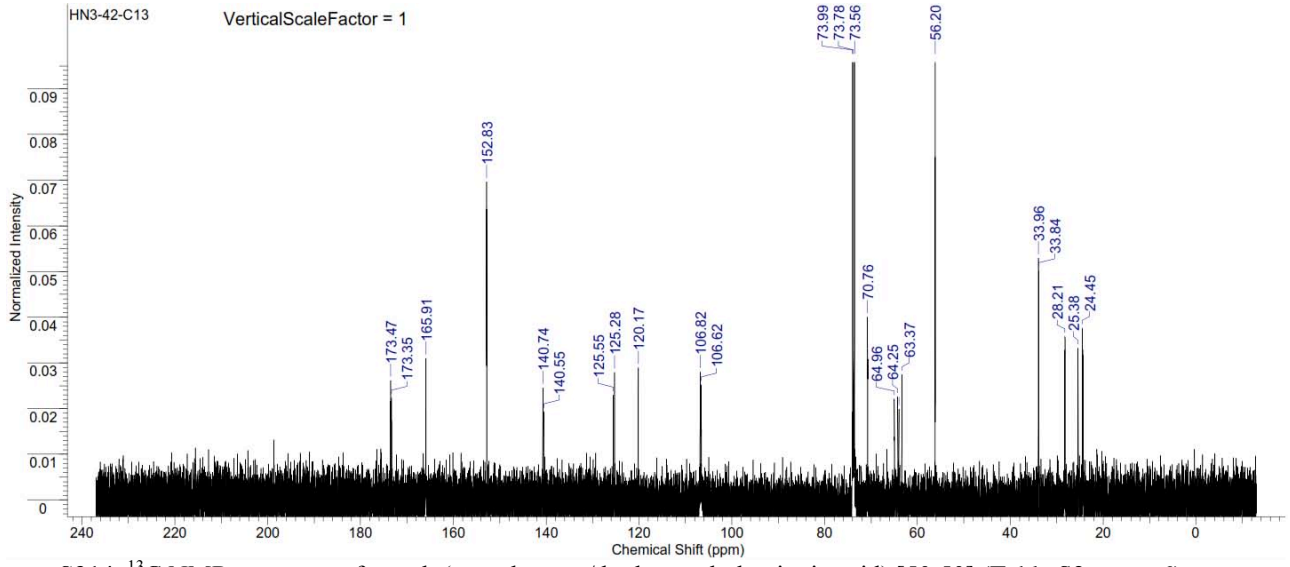


Figure S314. ^{13}C NMR spectrum of copoly(caprolactone/ hydroxyethylsyringic acid) [50:50] (Table S2, entry 6).

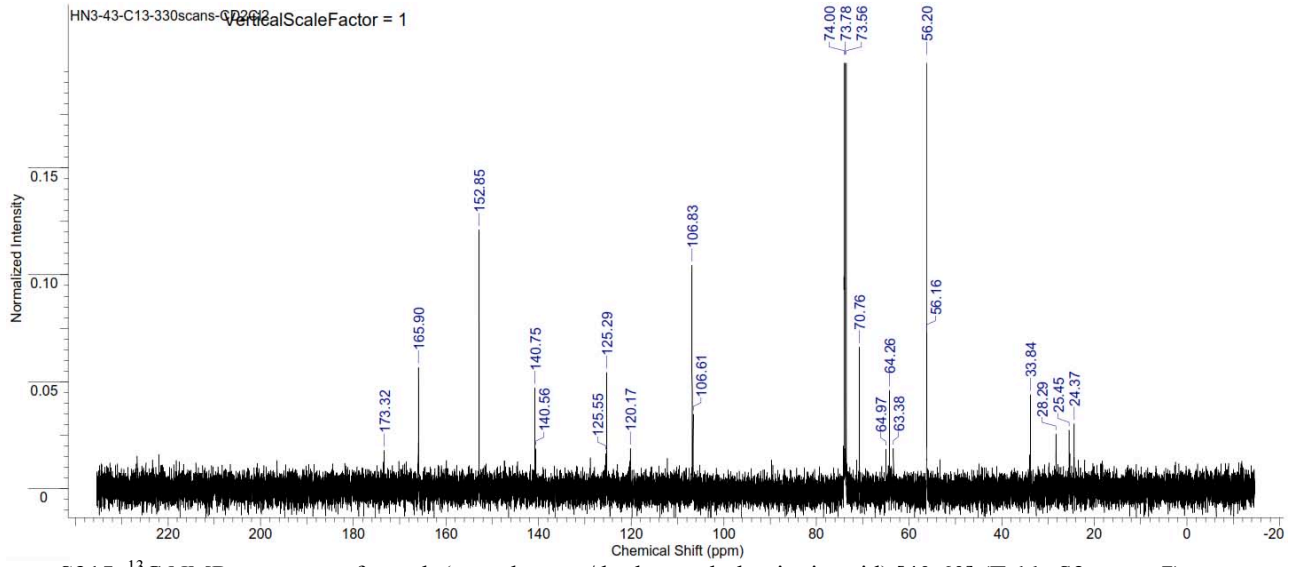


Figure S315. ^{13}C NMR spectrum of copoly(caprolactone/ hydroxyethylsyringic acid) [40:60] (Table S2, entry 7).

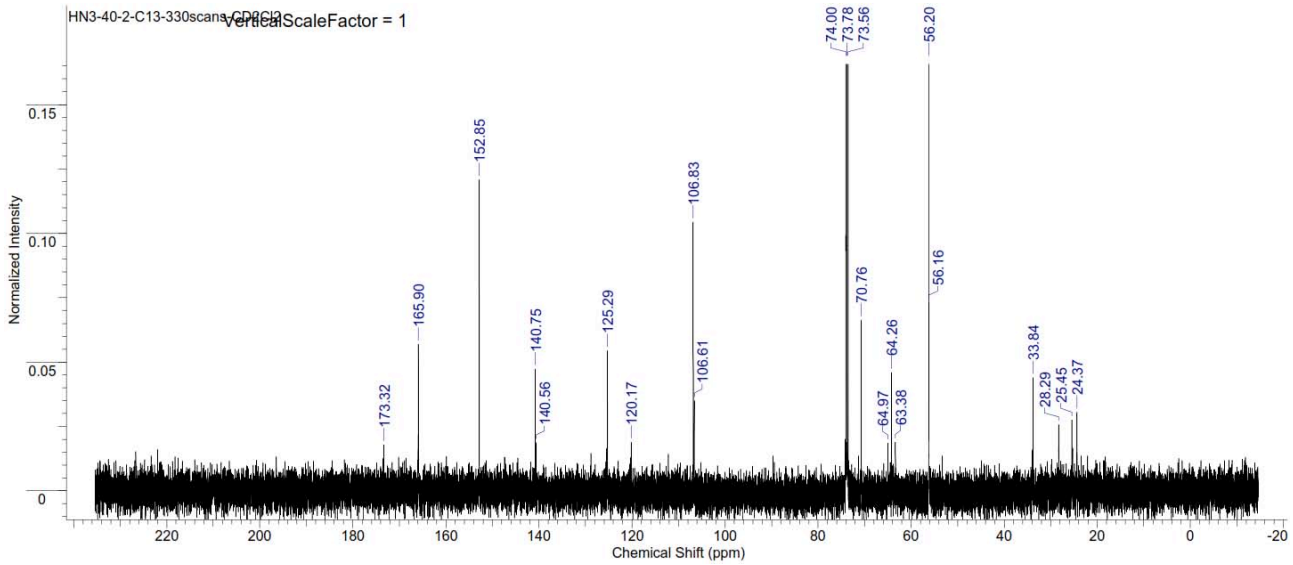


Figure S316. ^{13}C NMR spectrum of copoly(caprolactone/ hydroxyethylsyringic acid) [30:70] (Table S2, entry 8).

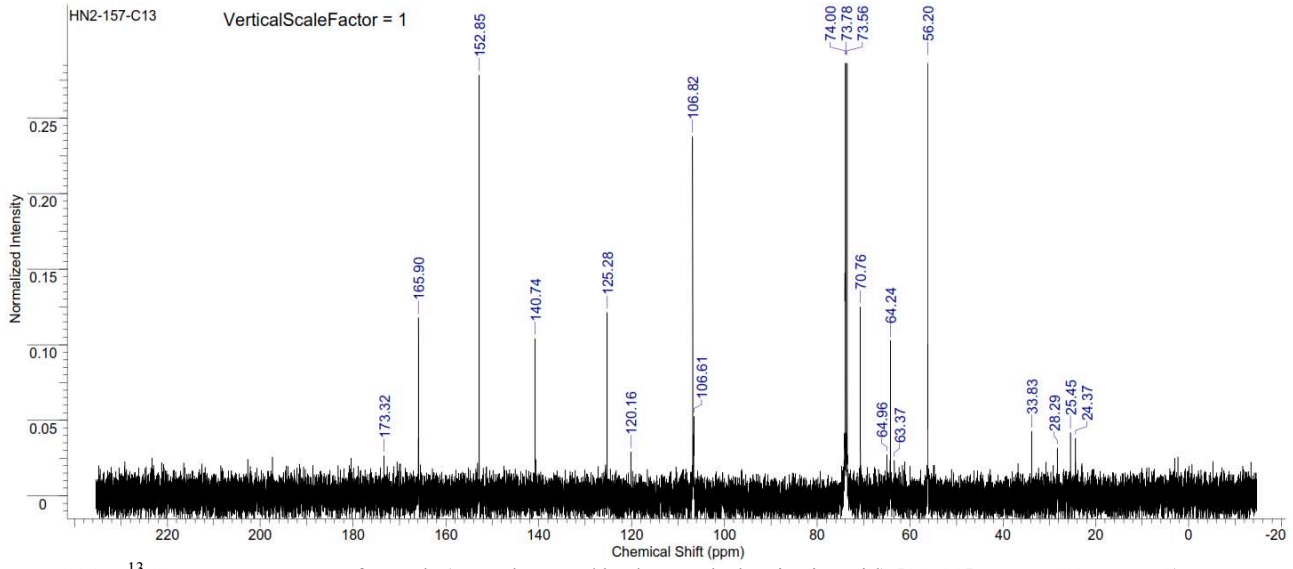


Figure S317. ^{13}C NMR spectrum of copoly(caprolactone/ hydroxyethylsyringic acid) [20:80] (Table S2, entry 9).

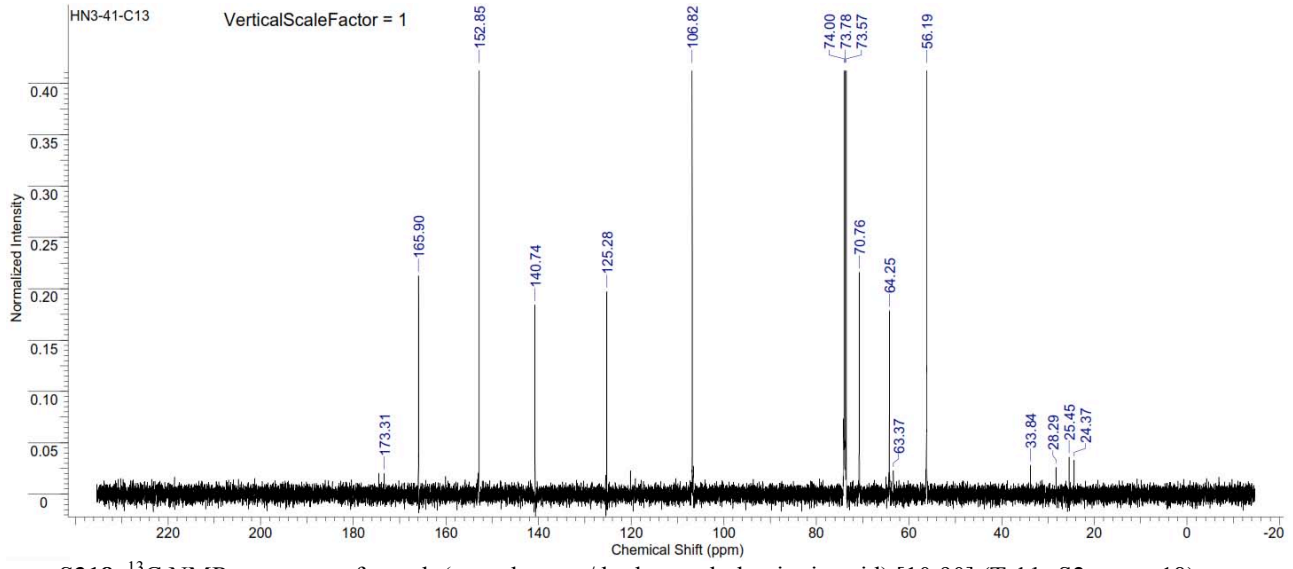


Figure S318. ^{13}C NMR spectrum of copoly(caprolactone/ hydroxyethylsyringic acid) [10:90] (Table S2, entry 10).

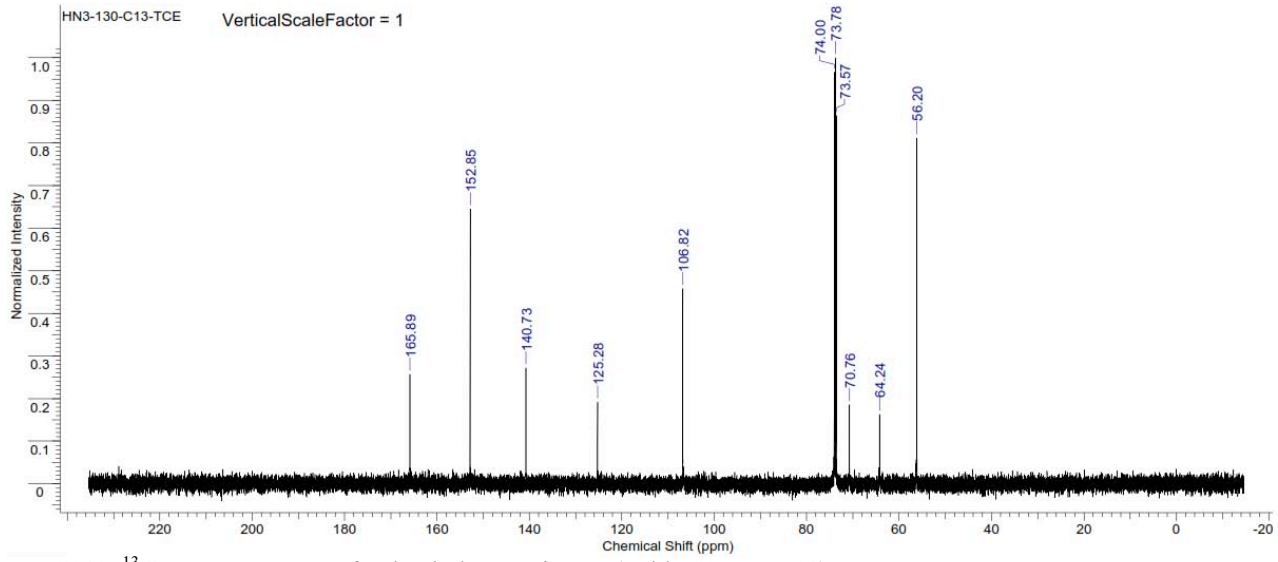


Figure S319. ^{13}C NMR spectrum of polyethylene syringate (Table S2, entry 11).

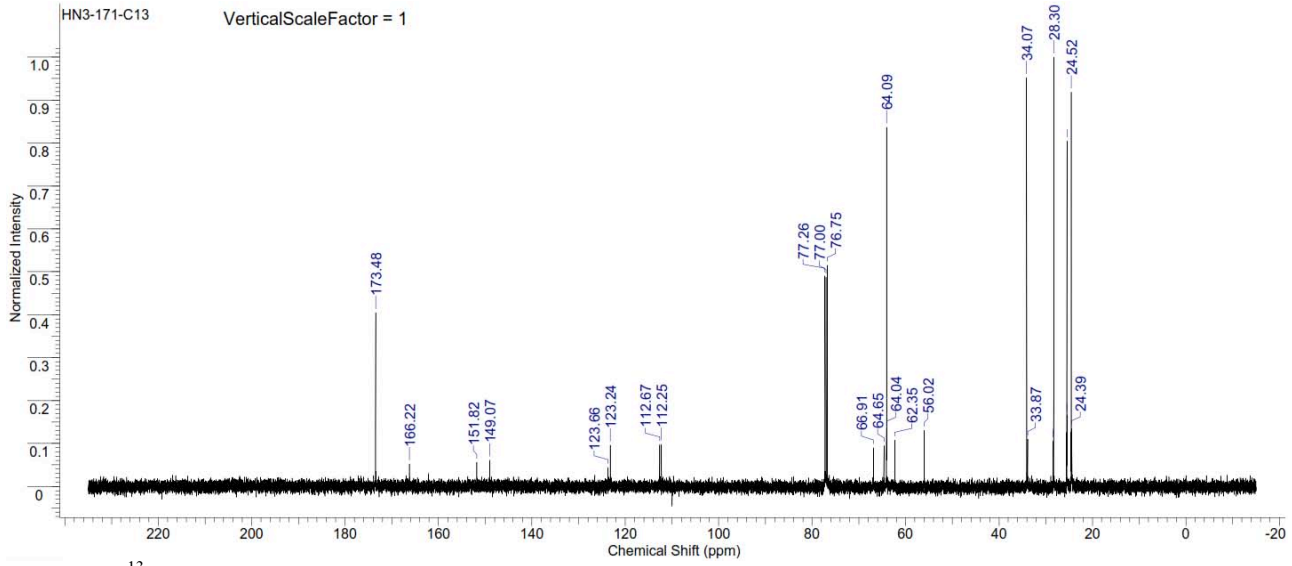


Figure S320. ^{13}C NMR spectrum of copoly(caprolactone/ hydroxyethylvanillic acid) [90:10] (Table S3, entry 12).

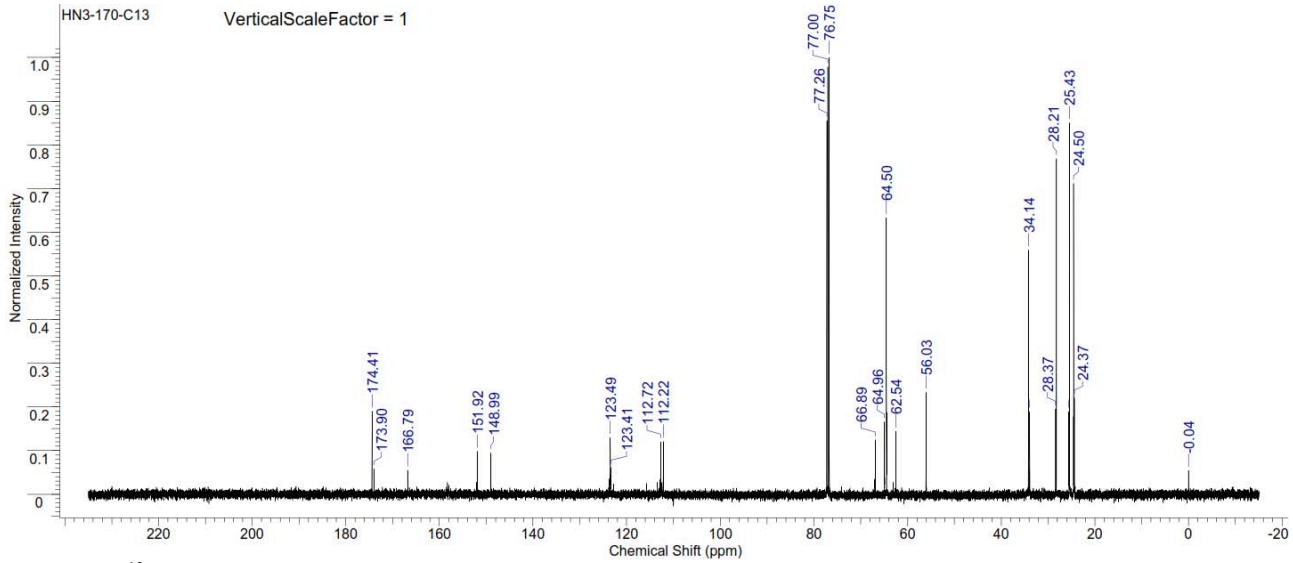


Figure S321. ^{13}C NMR spectrum of copoly(caprolactone/ hydroxyethylvanillic acid) [80:20] (Table S2, entry 13).

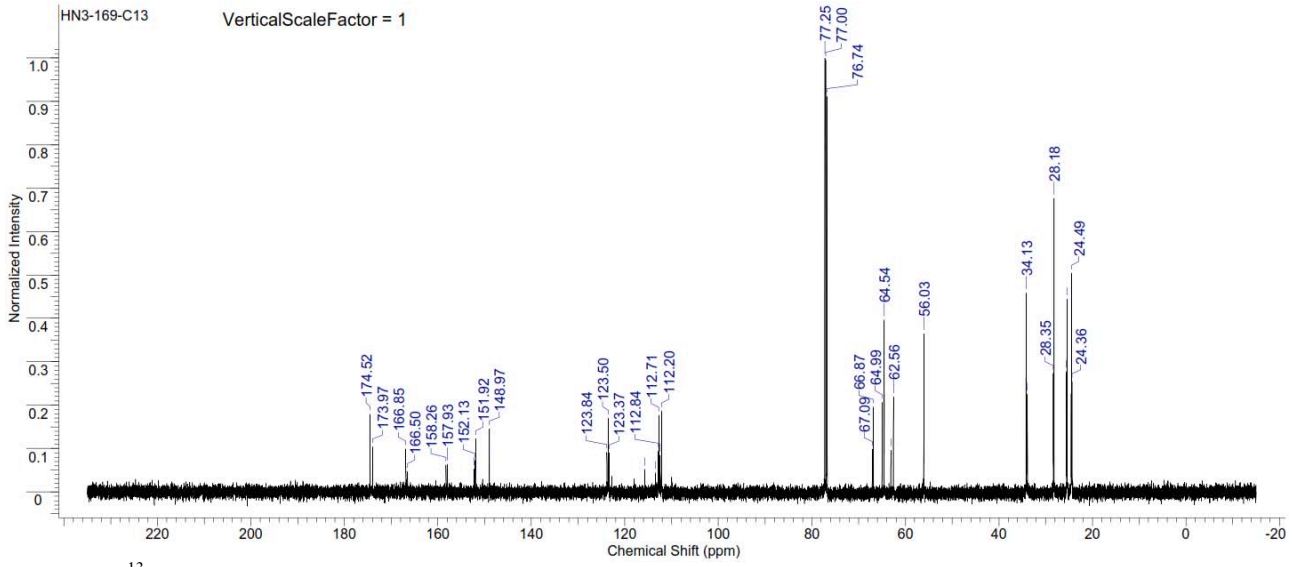


Figure S322. ^{13}C NMR spectrum of copoly(caprolactone/ hydroxyethylvanillic acid) [70:30] (Table S2, entry 14).

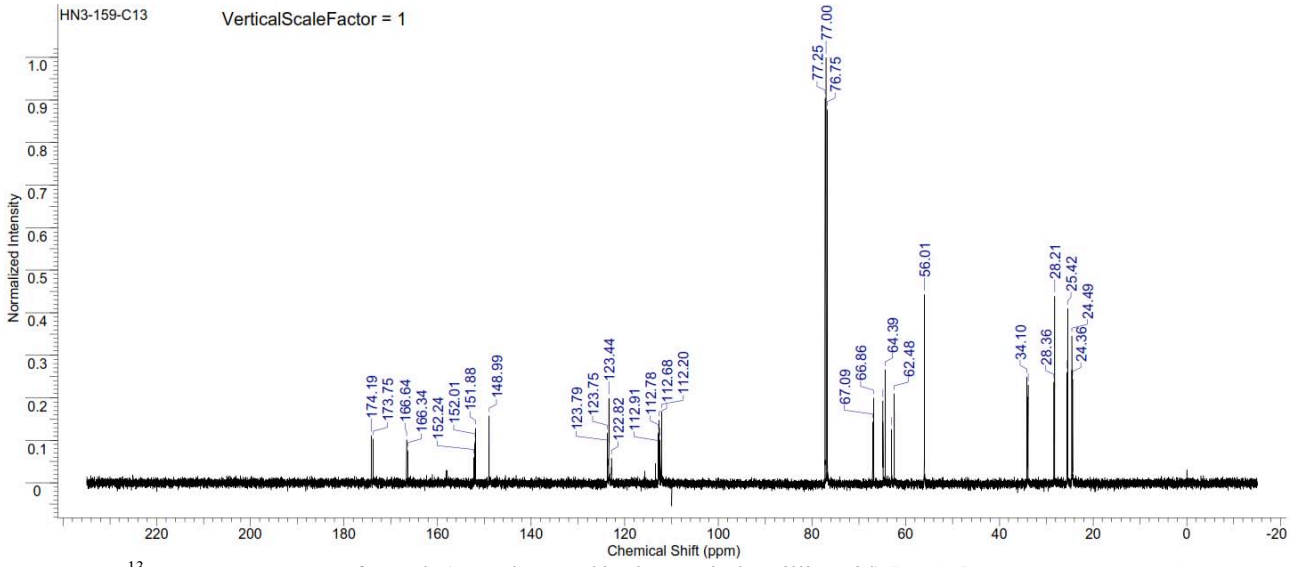


Figure S323. ^{13}C NMR spectrum of copoly(caprolactone/ hydroxyethylvanillic acid) [60:40] (Table S2, entry 15).

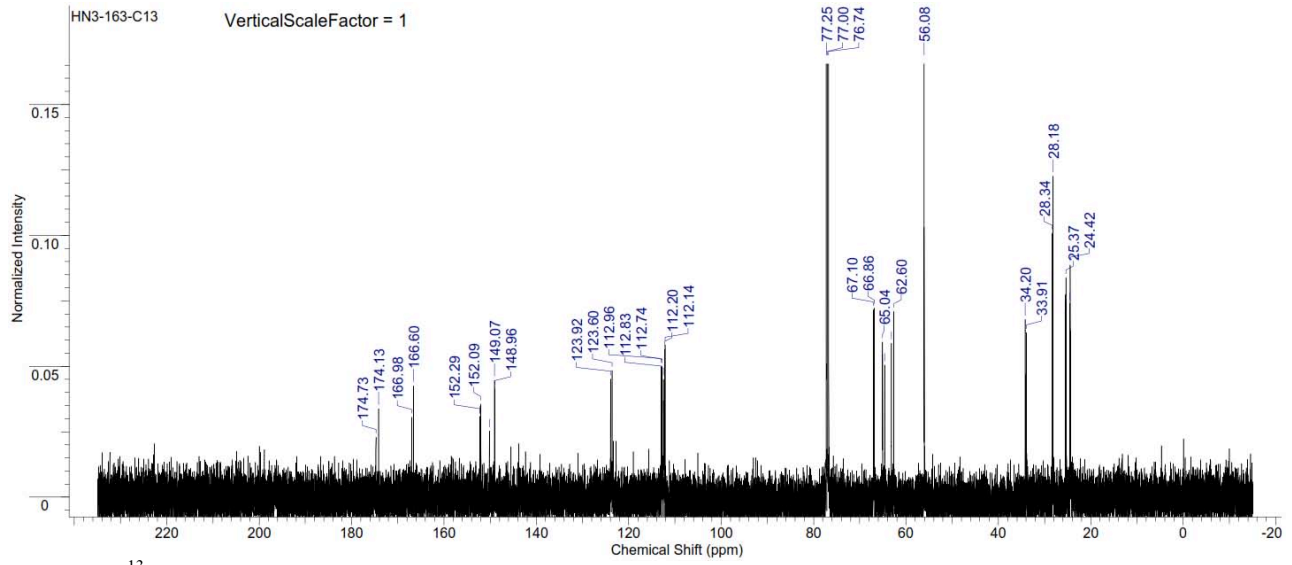


Figure S324. ^{13}C NMR spectrum of copoly(caprolactone/ hydroxyethylvanillic acid) [50:50] (Table S2, entry 16).

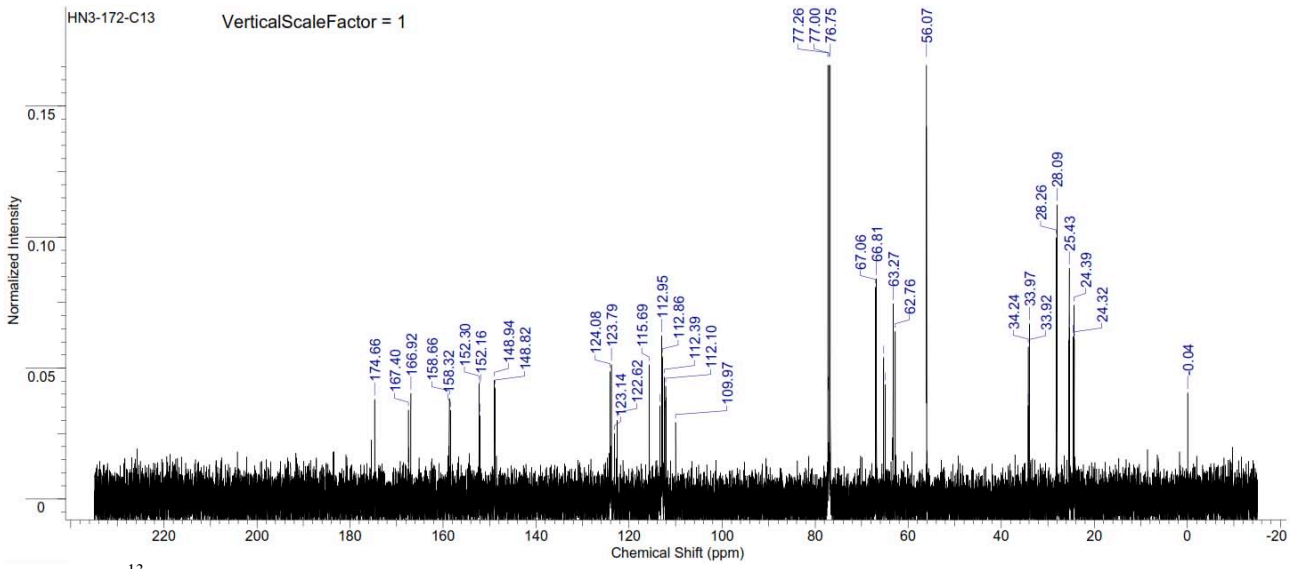


Figure S325. ^{13}C NMR spectrum of copoly(caprolactone/ hydroxyethylvanillic acid) [40:60] (Table S2, entry 17).

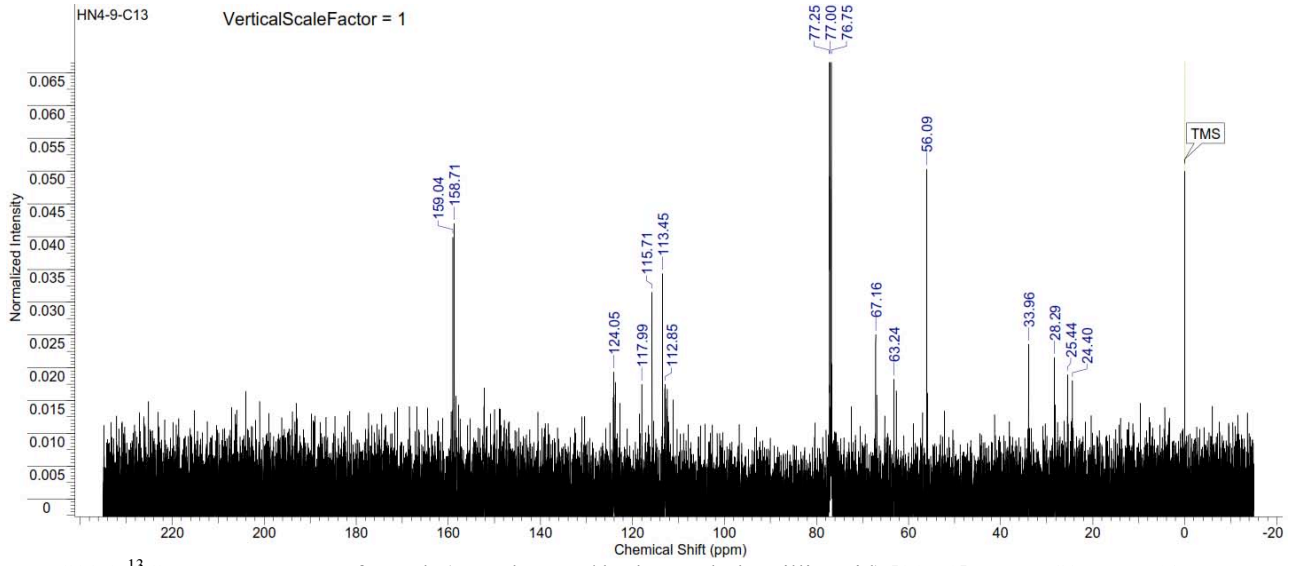


Figure S326. ^{13}C NMR spectrum of copoly(caprolactone/ hydroxyethylvanillic acid) [30:70] (Table S2, entry 18).

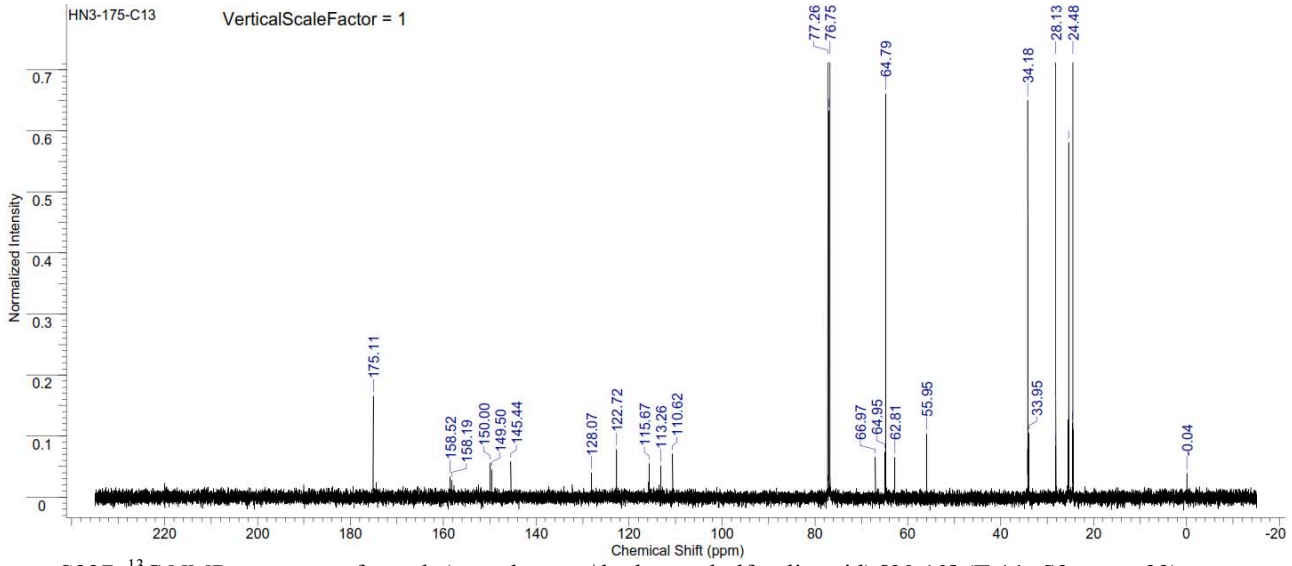


Figure S327. ^{13}C NMR spectrum of copoly(caprolactone/ hydroxyethylferulic acid) [90:10] (Table S2, entry 22).

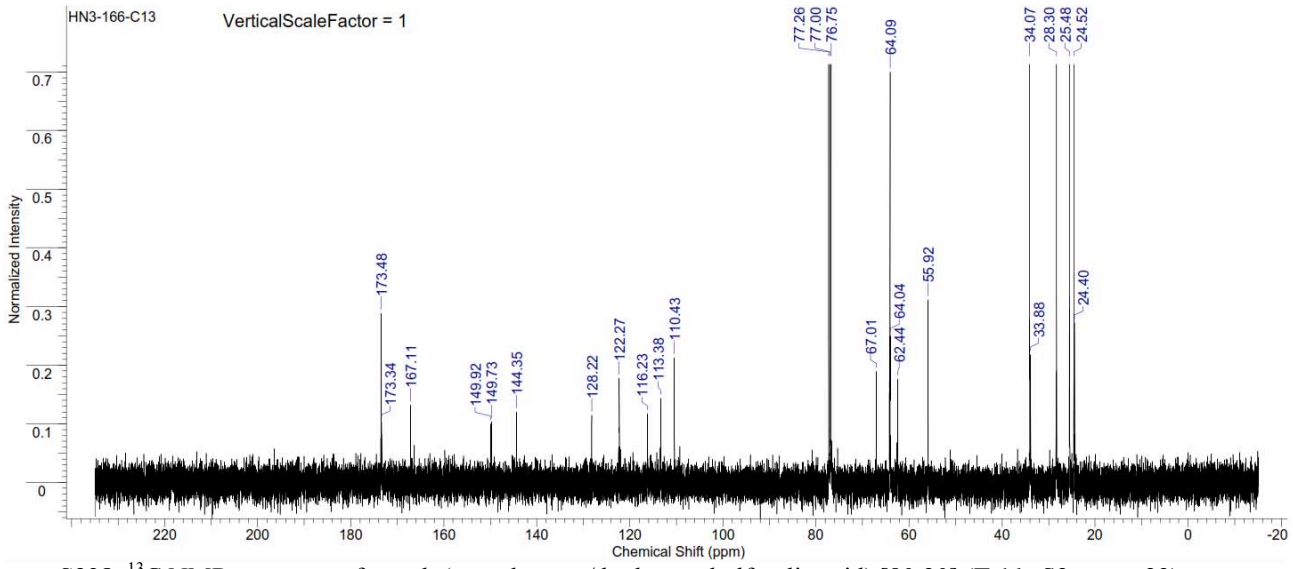


Figure S328. ^{13}C NMR spectrum of copoly(caprolactone/ hydroxyethylferulic acid) [80:20] (Table S2, entry 23).

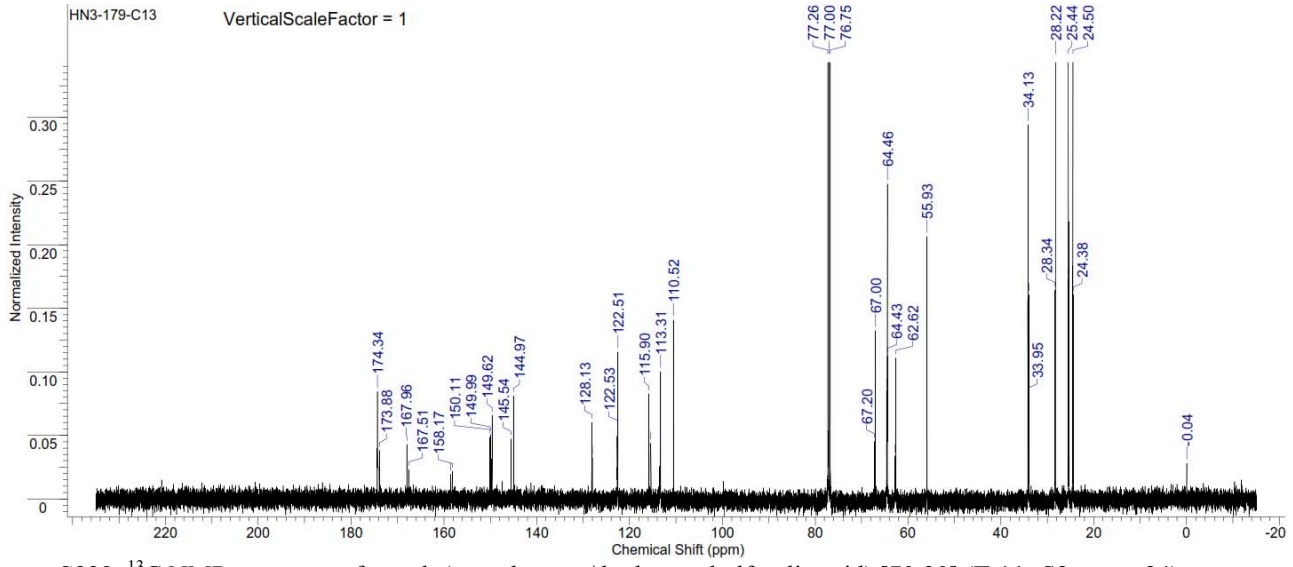


Figure S329. ^{13}C NMR spectrum of copoly(caprolactone/ hydroxyethylferulic acid) [70:30] (Table S2, entry 24).

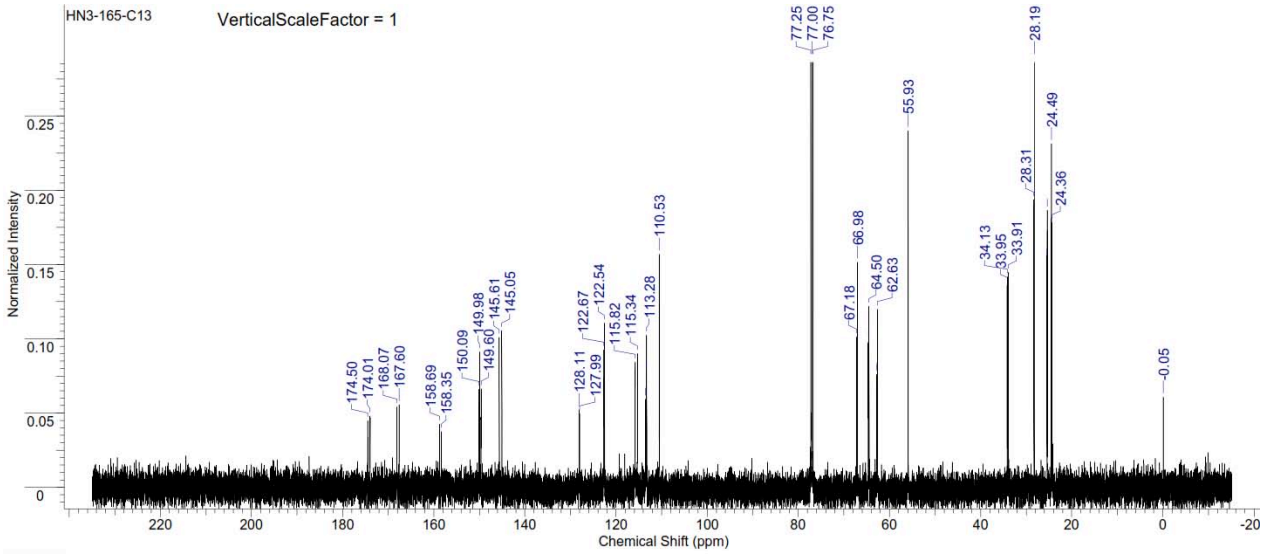


Figure S330. ^{13}C NMR spectrum of copoly(caprolactone/ hydroxyethylferulic acid) [60:40] (Table S2, entry 25).

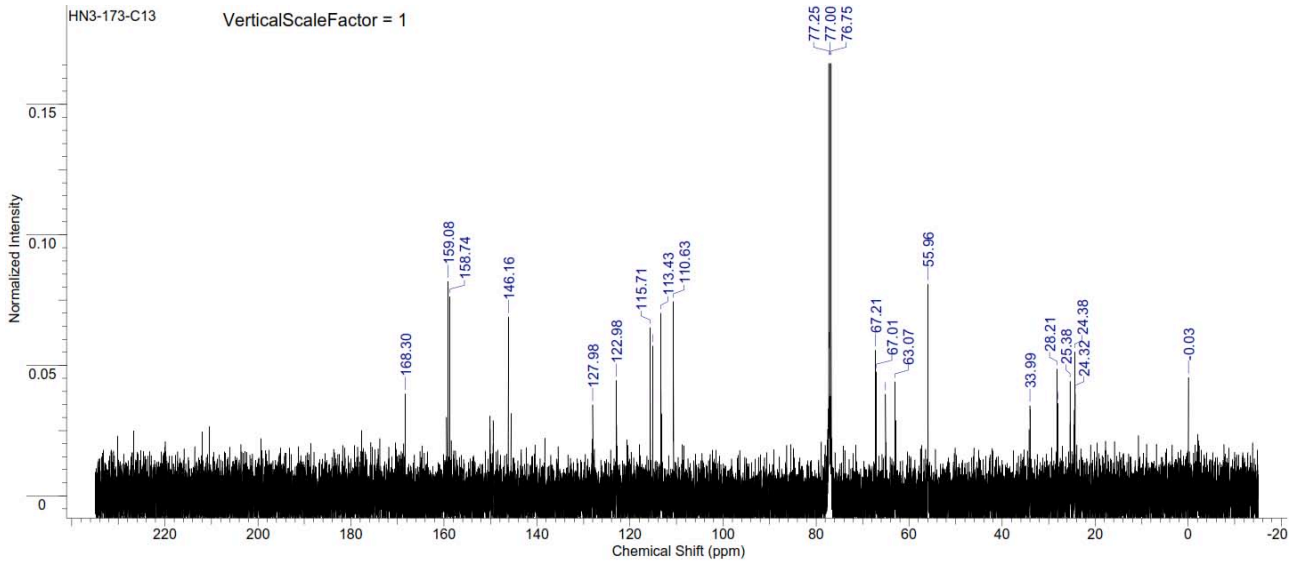


Figure S331. ^{13}C NMR spectrum of copoly(caprolactone/ hydroxyethylferulic acid) [50:50] (Table S2, entry 26).

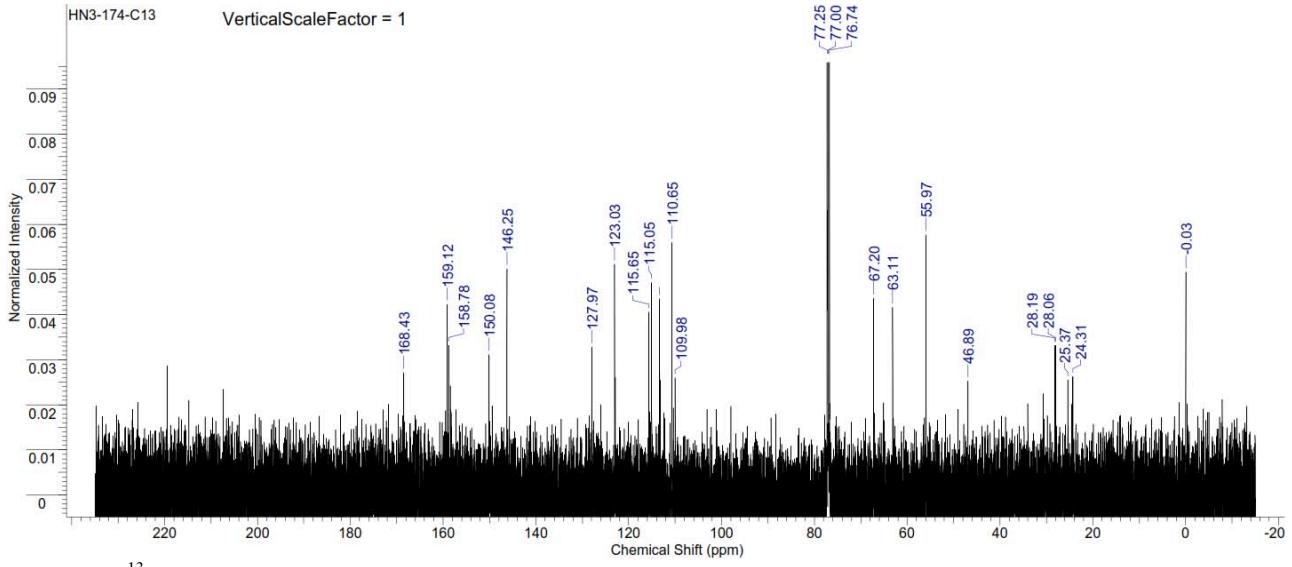


Figure S332. ^{13}C NMR spectrum of copoly(caprolactone/ hydroxyethylferulic acid) [40:60] (Table S2, entry 27).

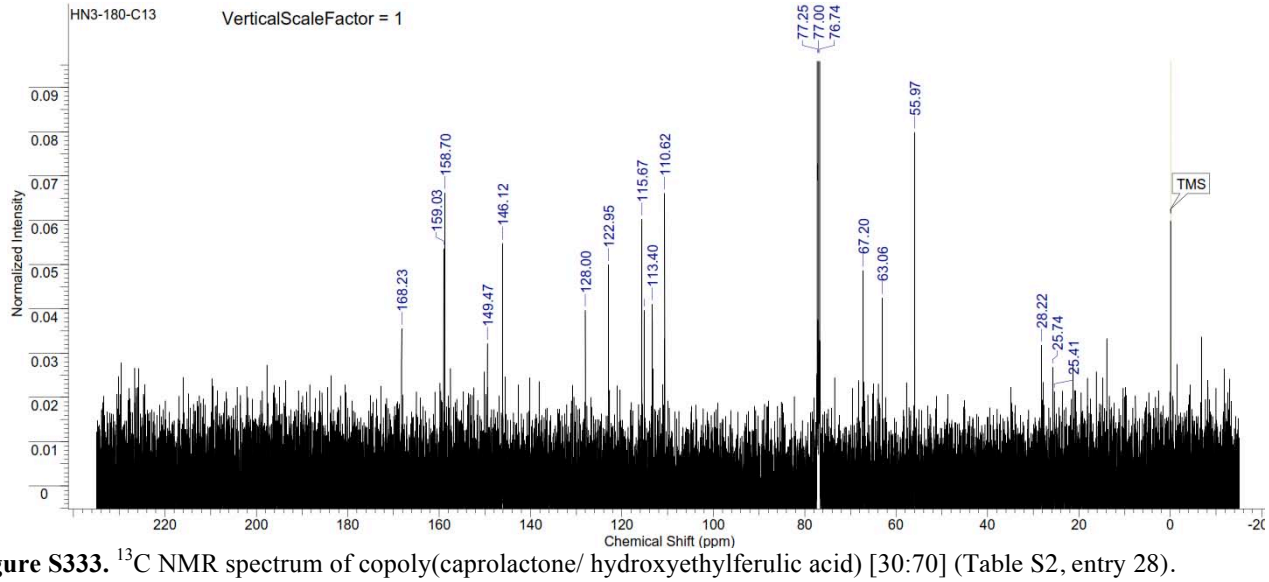


Figure S333. ^{13}C NMR spectrum of copoly(caprolactone/ hydroxyethylferulic acid) [30:70] (Table S2, entry 28).

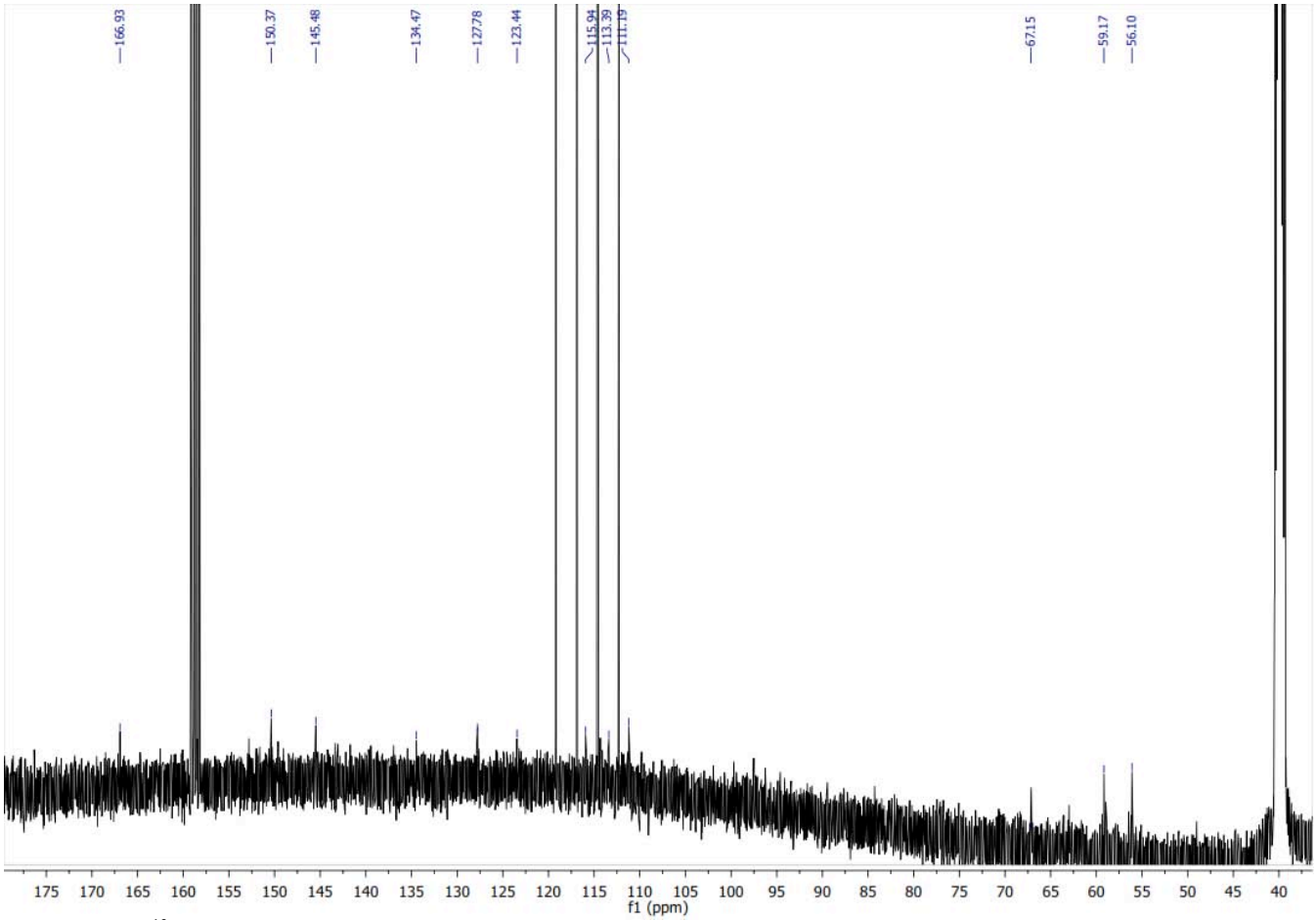


Figure S334. ^{13}C NMR spectrum of polyethylene ferulate (Table S2, entry 31).

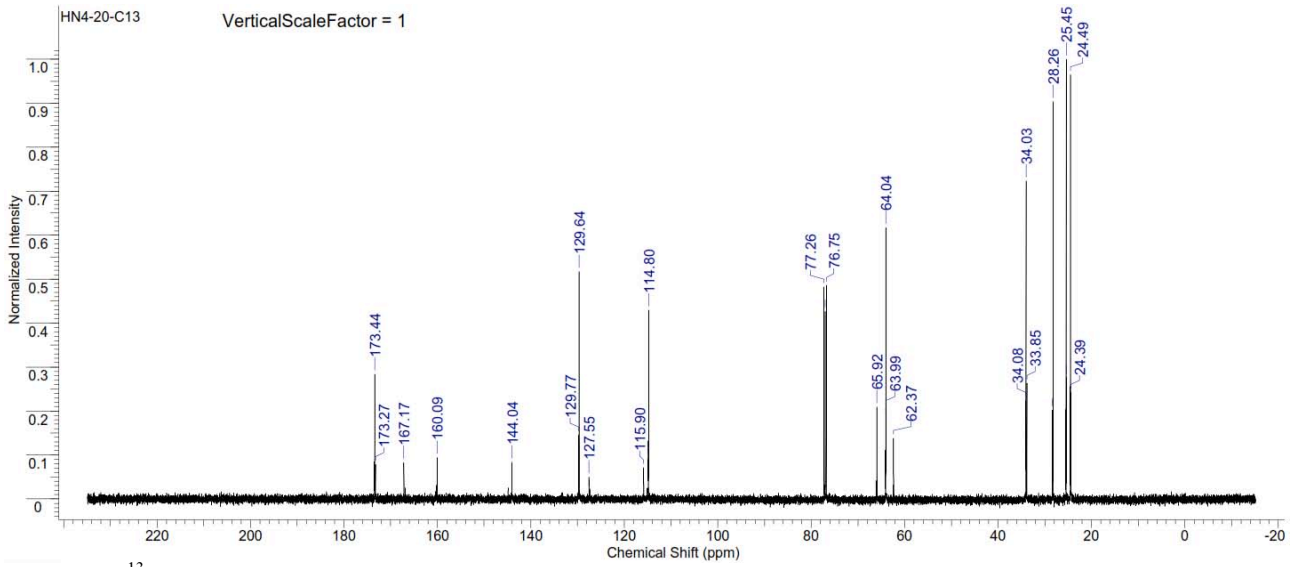


Figure S335. ^{13}C NMR spectrum of copoly(caprolactone/ hydroxyethylcoumaric acid) [80:20] (Table S2, entry 32).

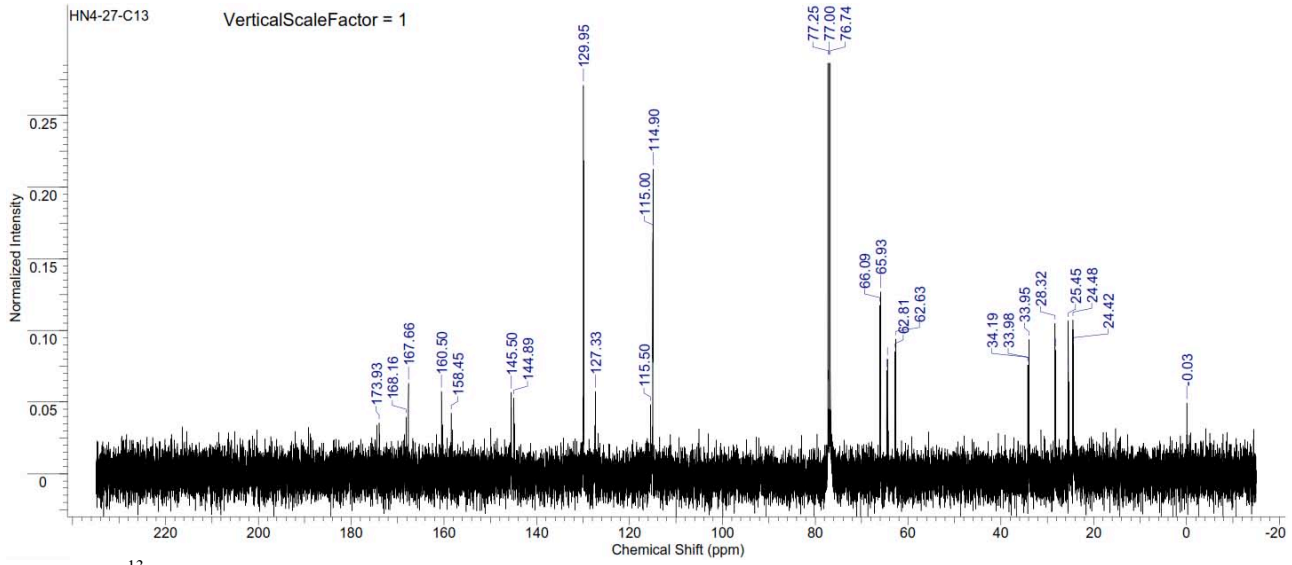


Figure S336. ^{13}C NMR spectrum of copoly(caprolactone/ hydroxyethylcoumaric acid) [50:50] (Table S2, entry 33).

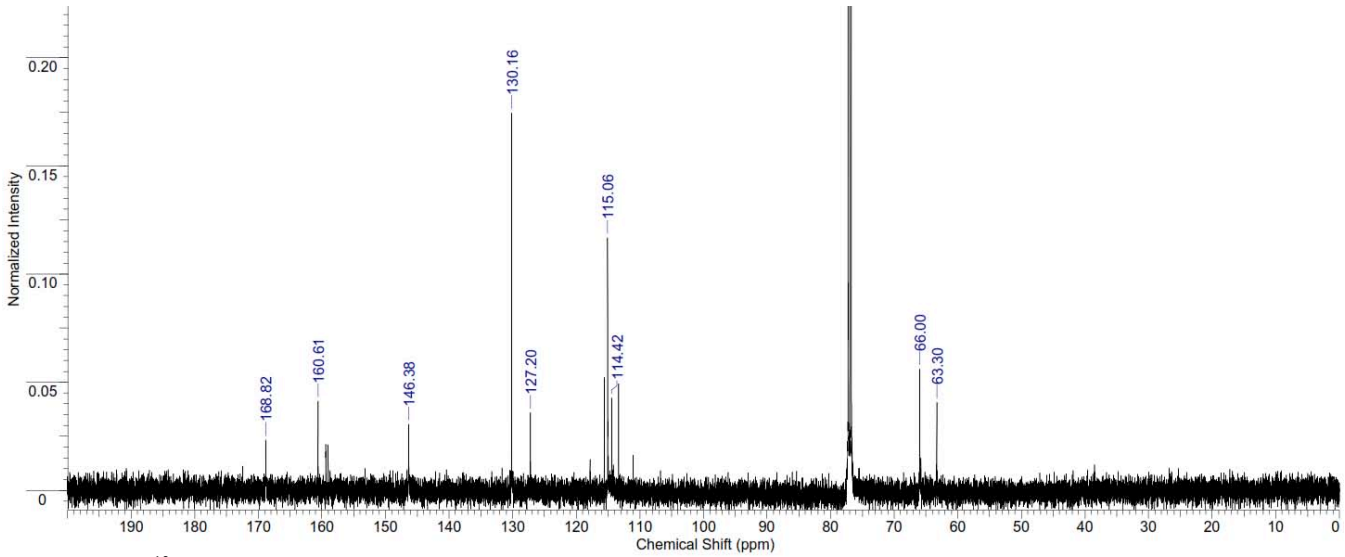


Figure S337. ^{13}C NMR spectrum of polyethylene coumarate (Table S2, entry 35).

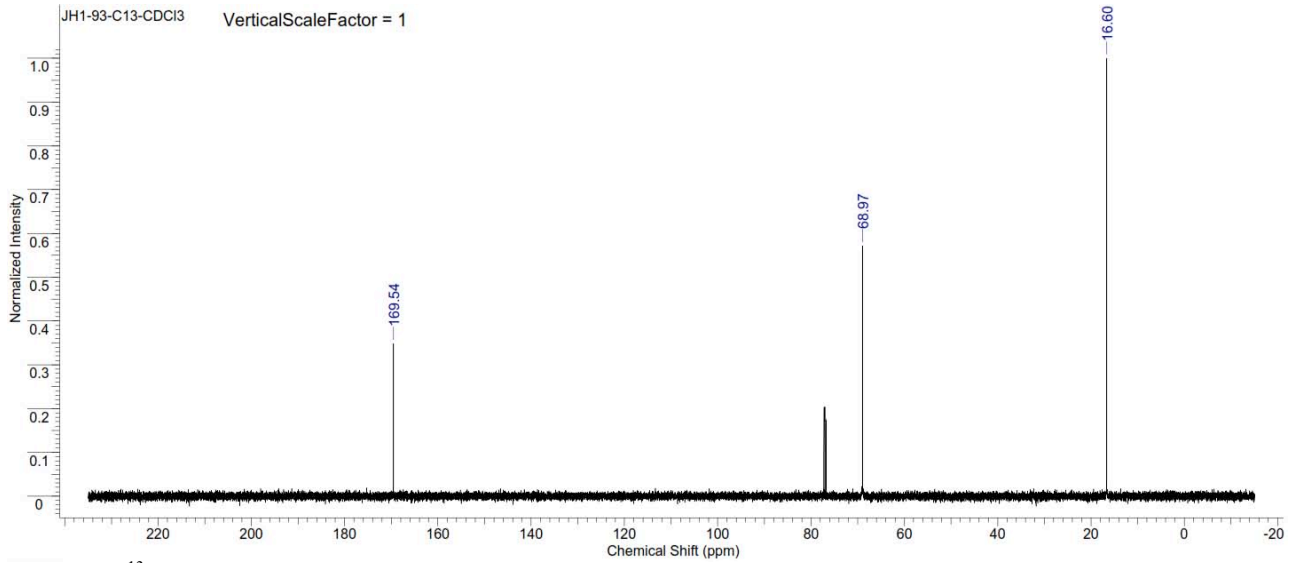


Figure S338. ^{13}C NMR spectrum of polylactic acid (Table S3, entry 1).

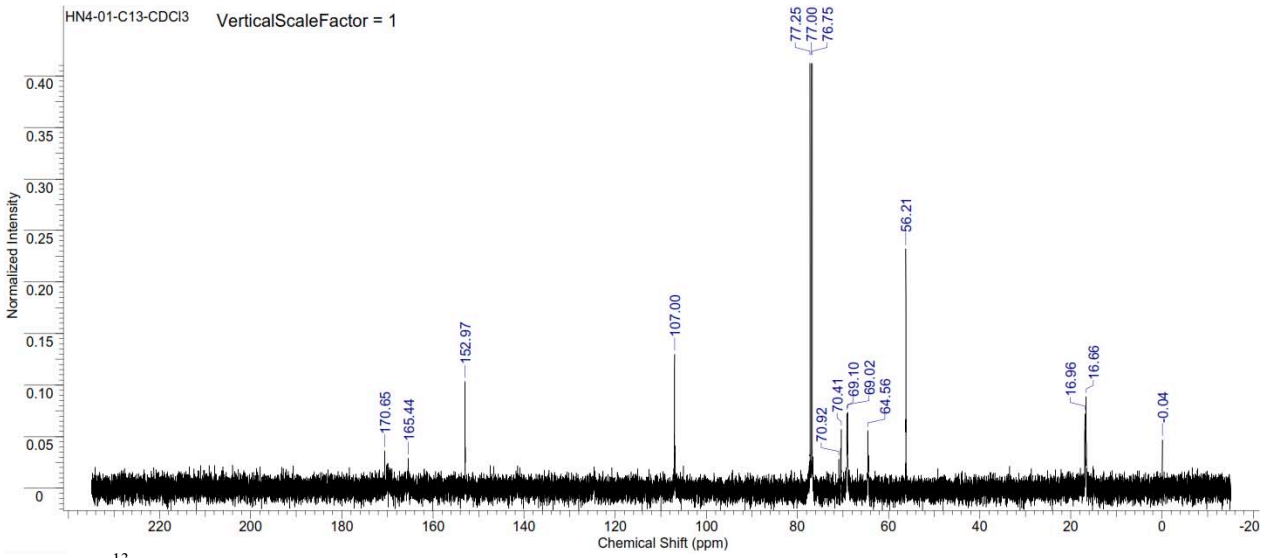


Figure S339. ^{13}C NMR spectrum of copoly(L-lactide/ hydroxyethylsyringic acid) [80:20] (Table S3, entry 2).

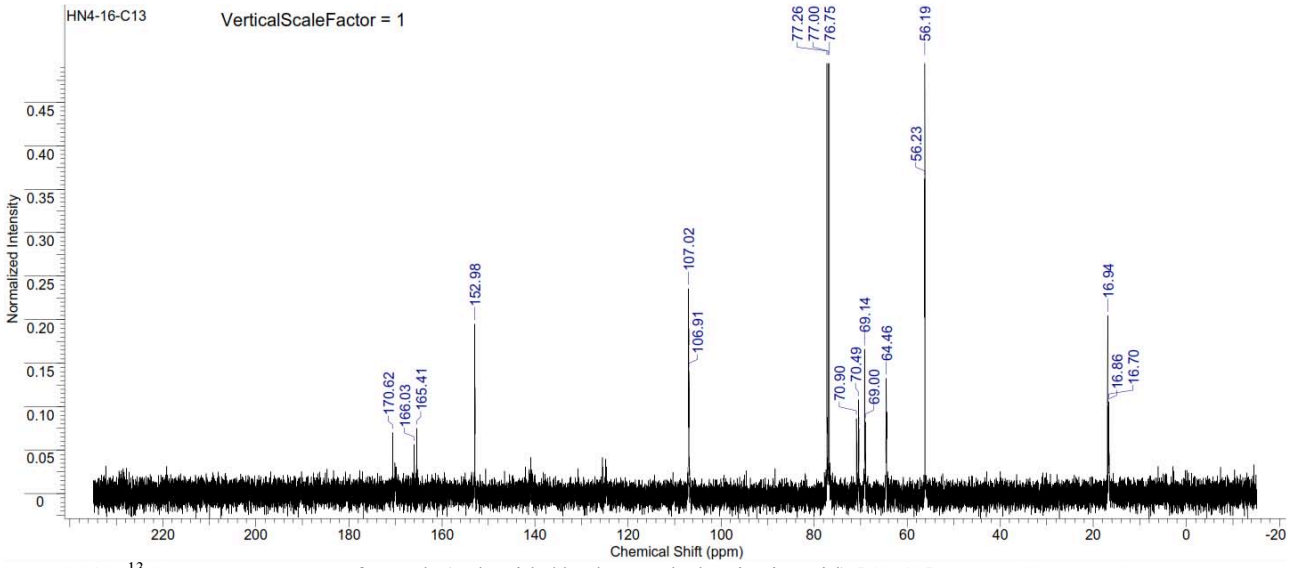


Figure S340. ^{13}C NMR spectrum of copoly(L-lactide/ hydroxyethylsyringic acid) [60:40] (Table S3, entry 3).

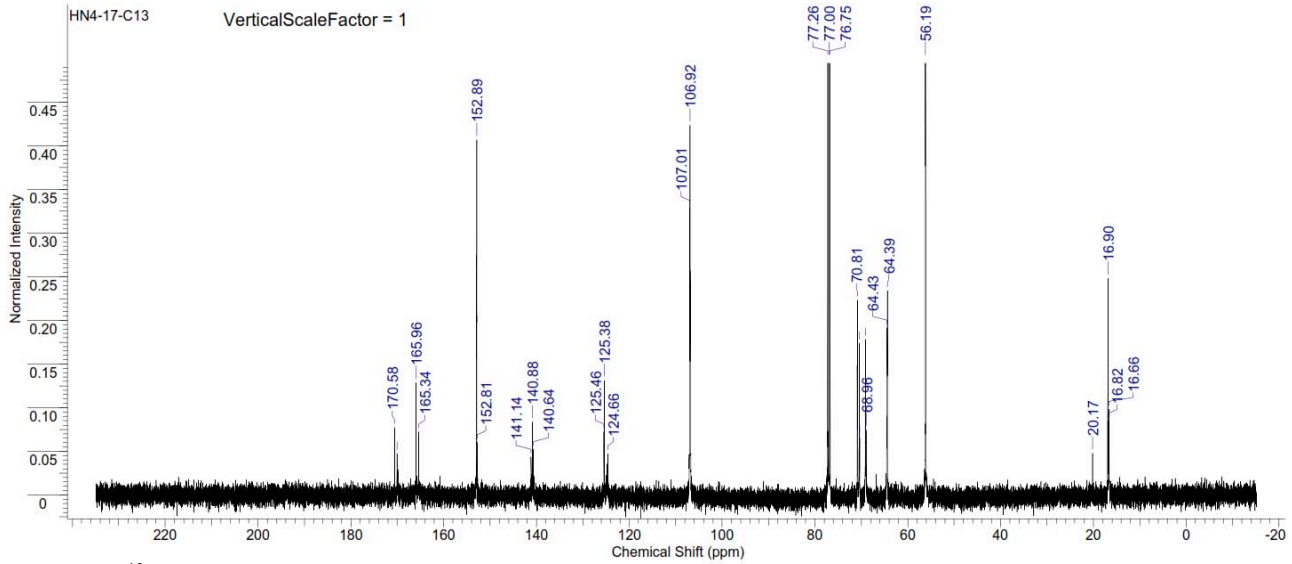


Figure S341. ^{13}C NMR spectrum of copoly(L-lactide/ hydroxyethylsyringic acid) [40:60] (Table S3, entry 4).

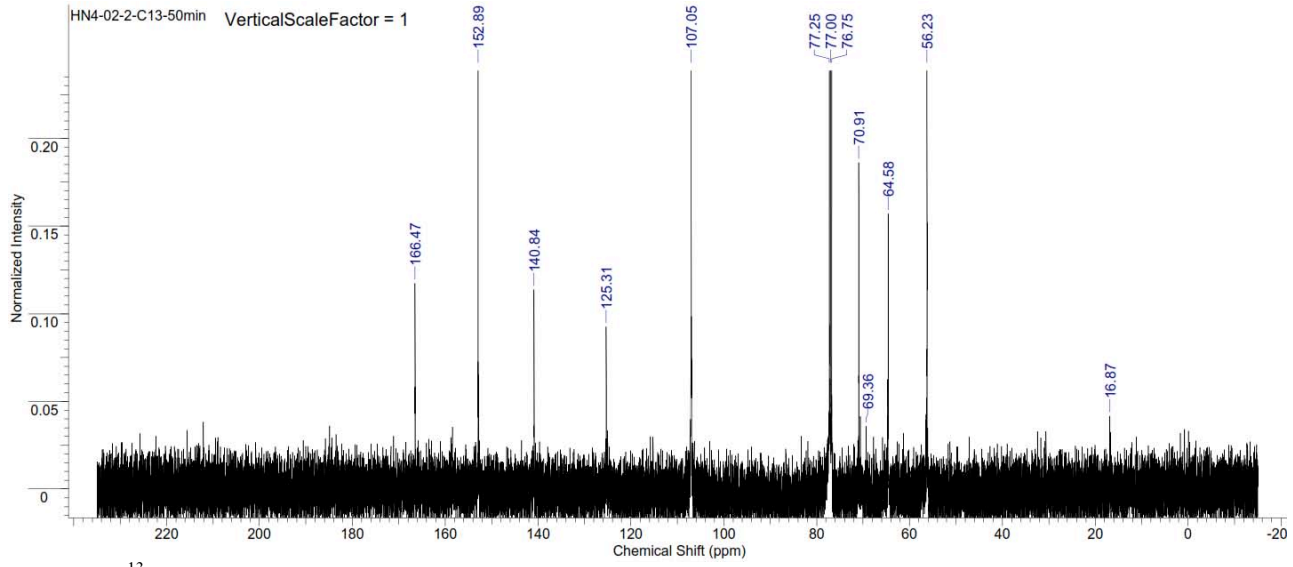


Figure S342. ^{13}C NMR spectrum of copoly(L-lactide/ hydroxyethylsyringic acid) [20:80] (Table S3, entry 5).

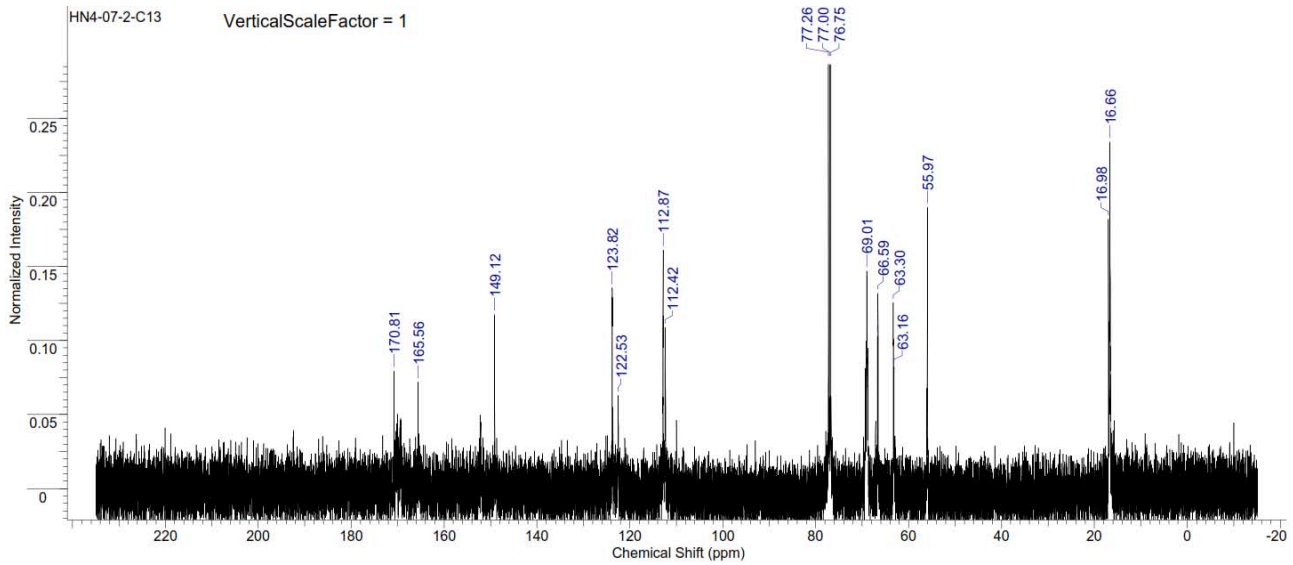


Figure S343. ^{13}C NMR spectrum of copoly(L-lactide/ hydroxyethylvanillic acid) [80:20] (Table S3, entry 7).

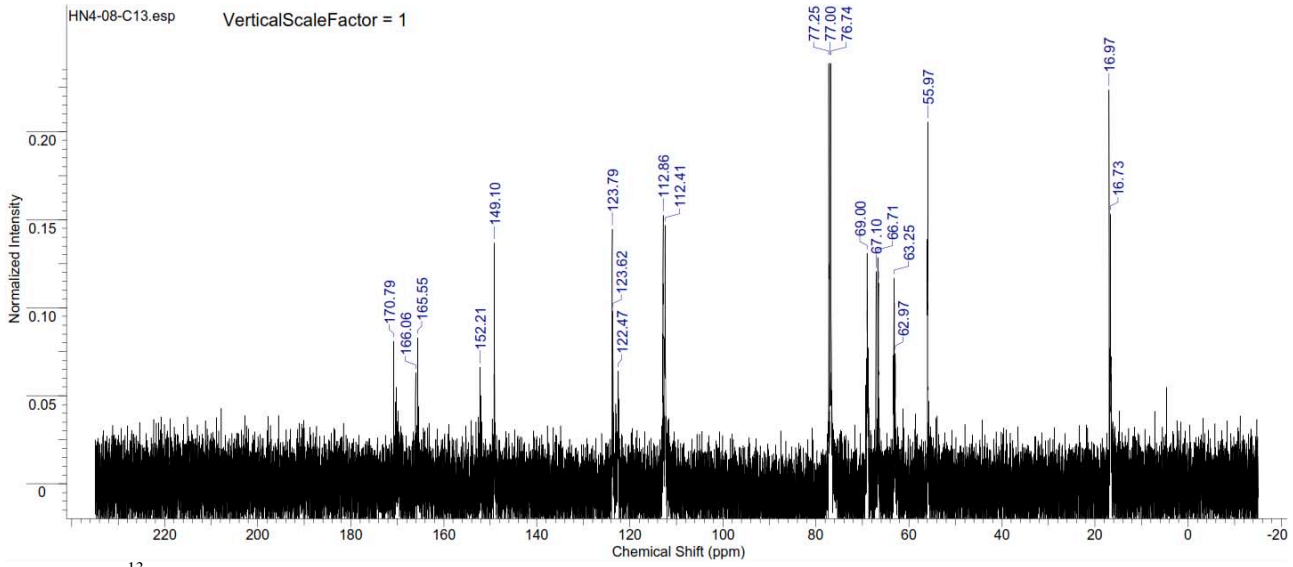


Figure S344. ^{13}C NMR spectrum of copoly(L-lactide/ hydroxyethylvanillic acid) [60:40] (Table S3, entry 8).

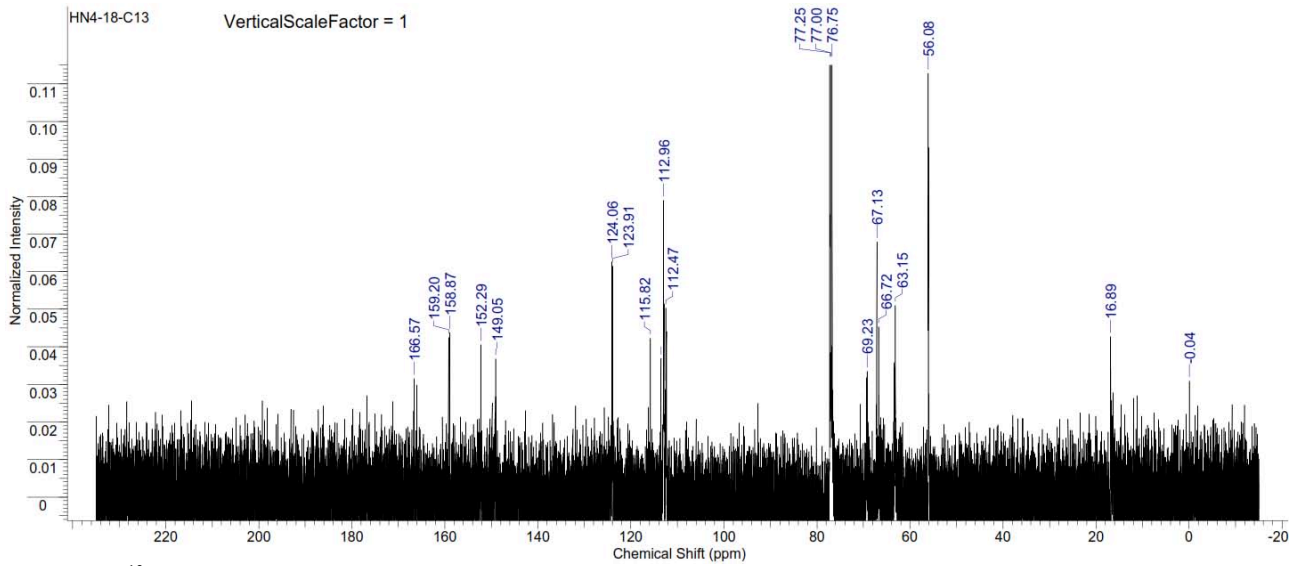


Figure S345. ^{13}C NMR spectrum of copoly(L-lactide/ hydroxyethylvanillic acid) [40:60] (Table S3, entry 9).

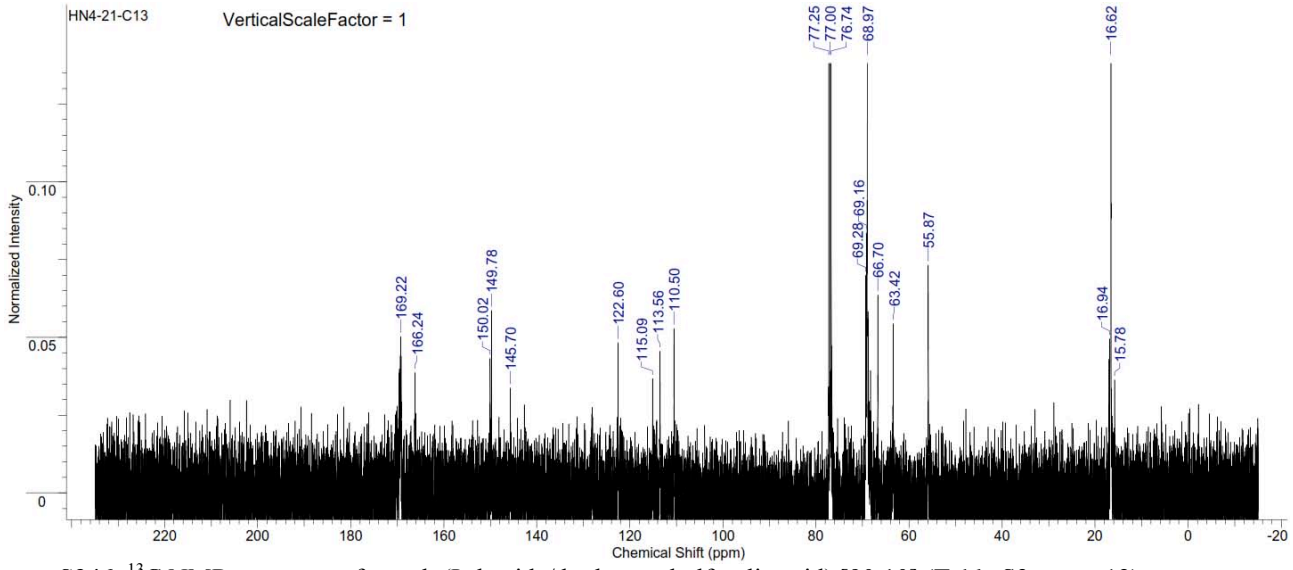


Figure S346. ^{13}C NMR spectrum of copoly(L-lactide/ hydroxyethylferulic acid) [90:10] (Table S3, entry 12).

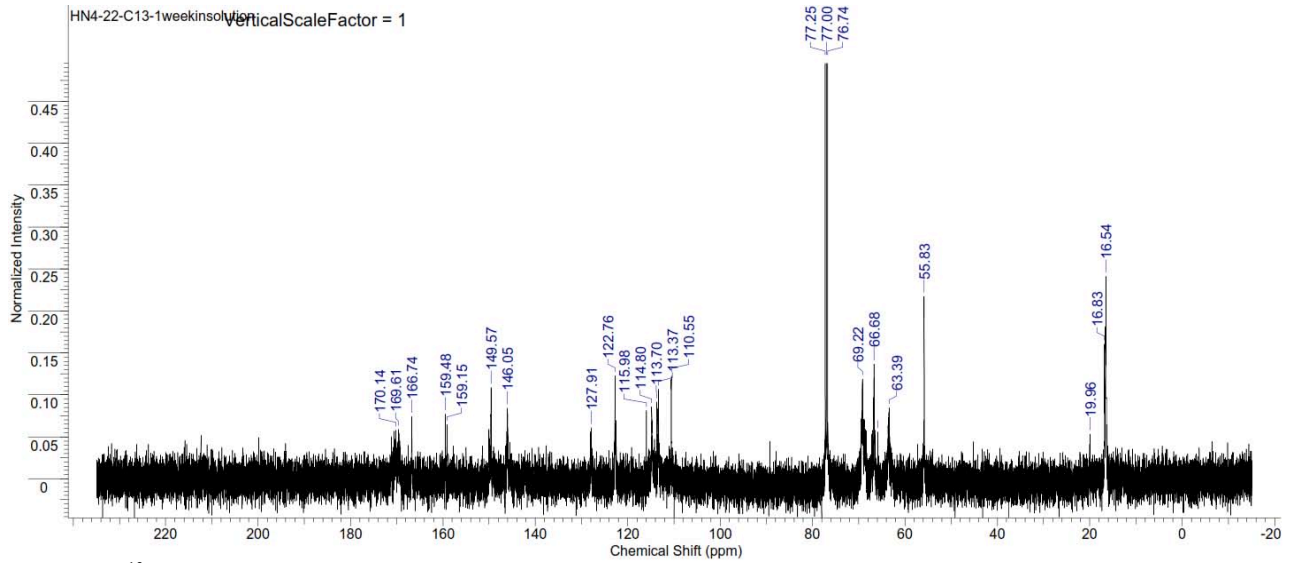


Figure S347. ^{13}C NMR spectrum of c copoly(L-lactide/ hydroxyethylferulic acid) [80:20] (Table S3, entry 13).

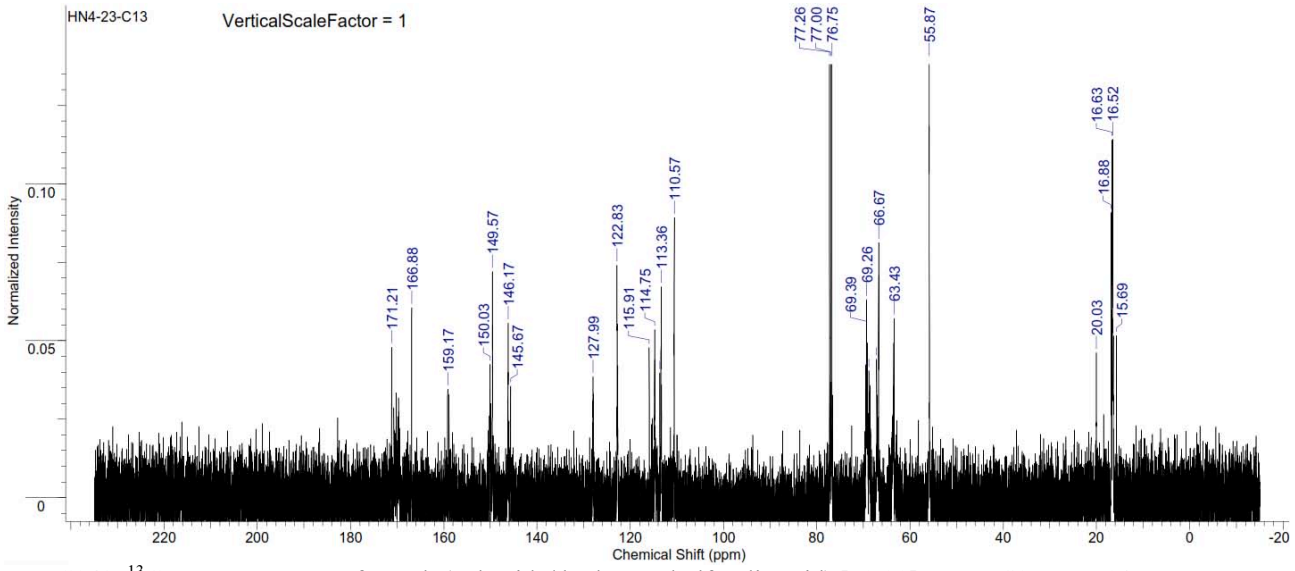


Figure S348. ^{13}C NMR spectrum of copoly(L-lactide/ hydroxyethylferulic acid) [70:30] (Table S3, entry 14).

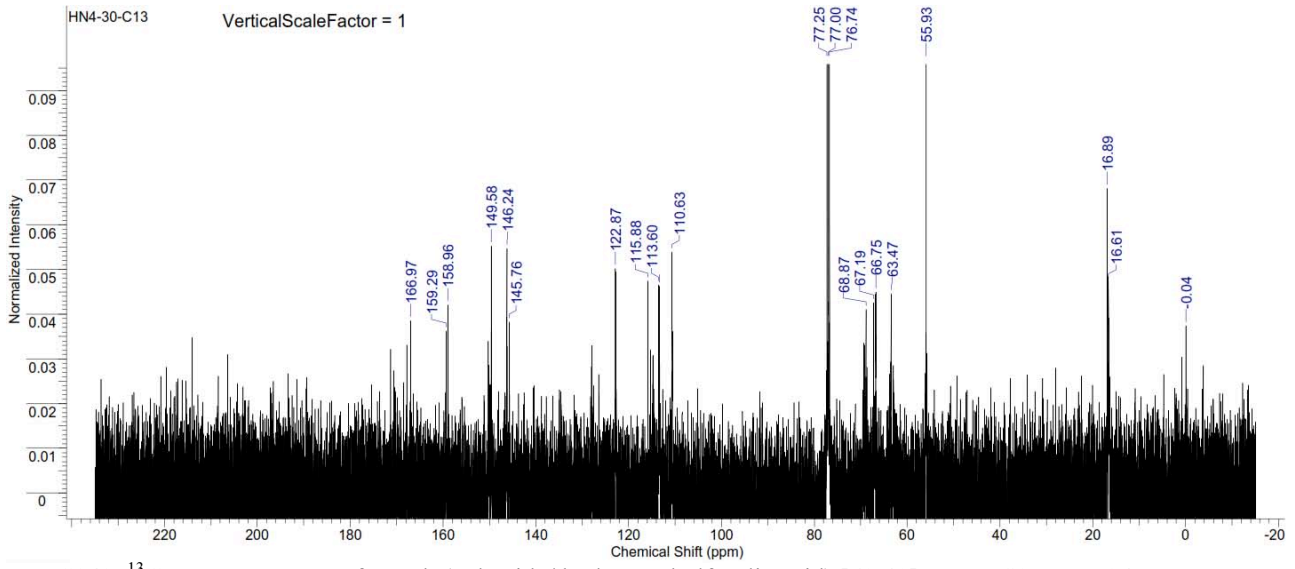


Figure S349. ^{13}C NMR spectrum of copoly(L-lactide/ hydroxyethylferulic acid) [60:40] (Table S3, entry 15).

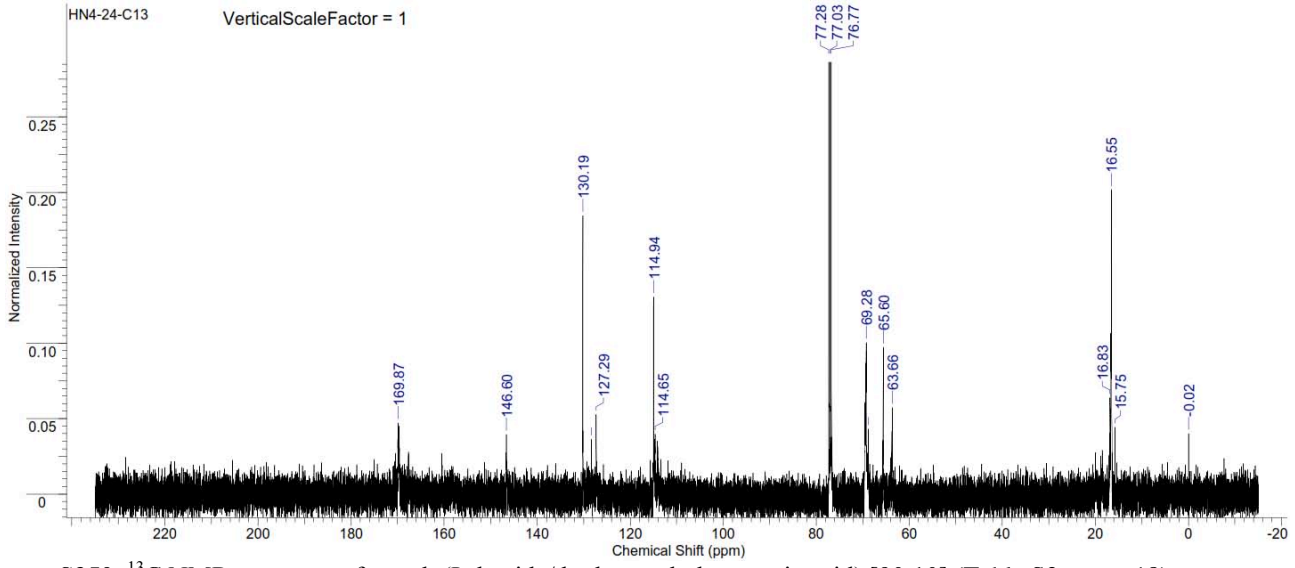


Figure S350. ^{13}C NMR spectrum of copoly(L-lactide/ hydroxyethylcoumaric acid) [90:10] (Table S3, entry 18).

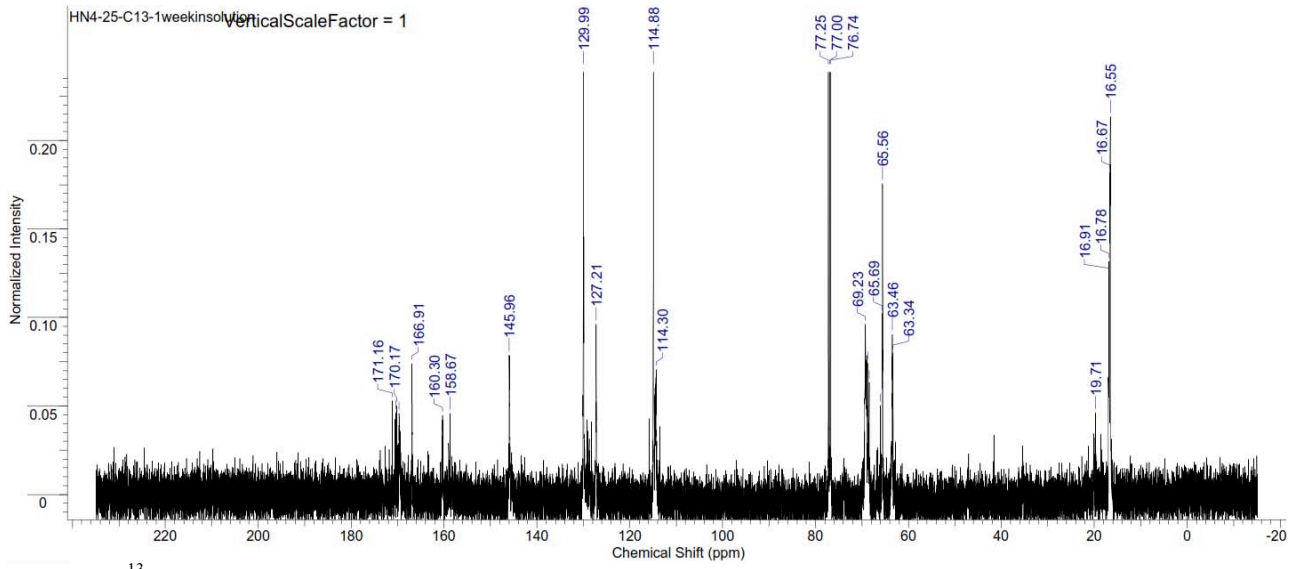


Figure S351. ^{13}C NMR spectrum of c copoly(L-lactide/ hydroxyethylcoumaric acid) [80:20] (Table S3, entry 19).

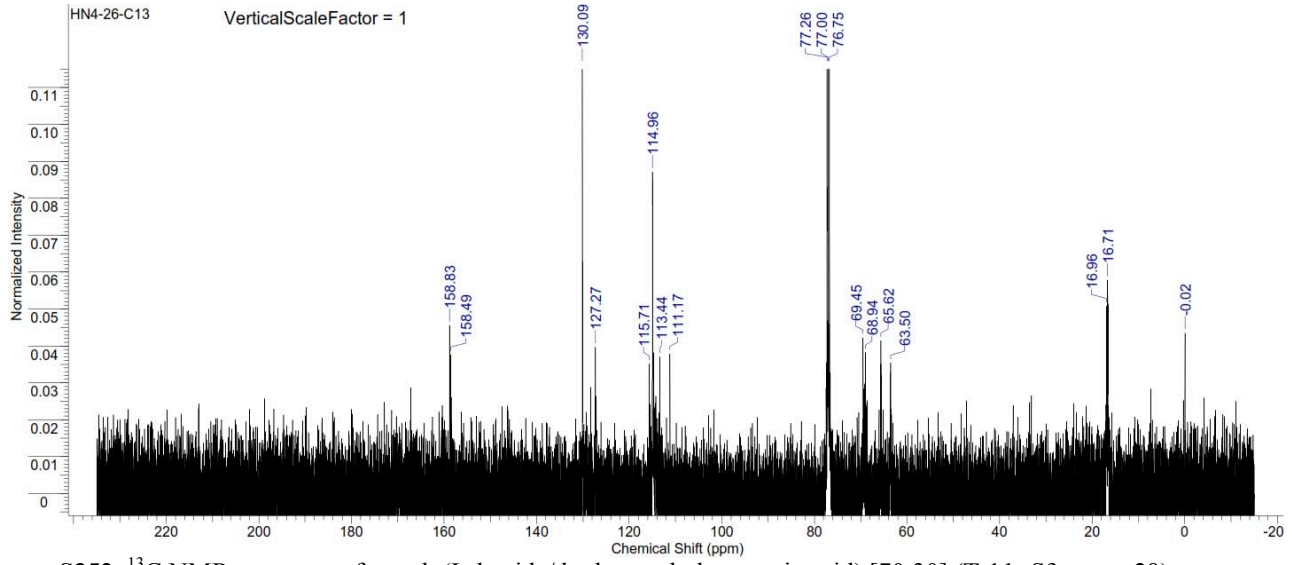


Figure S352. ^{13}C NMR spectrum of copoly(L-lactide/ hydroxyethylcoumaric acid) [70:30] (Table S3, entry 20).

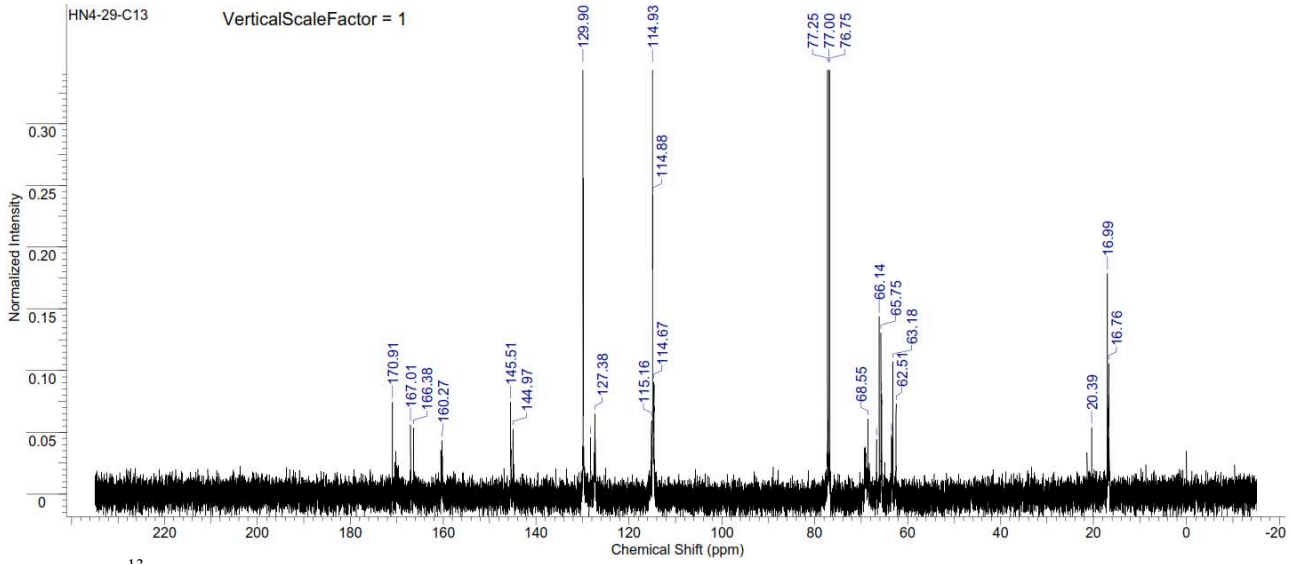


Figure S353. ^{13}C NMR spectrum of copoly(L-lactide/ hydroxyethylcoumaric acid) [60:40] (Table S3, entry 21).

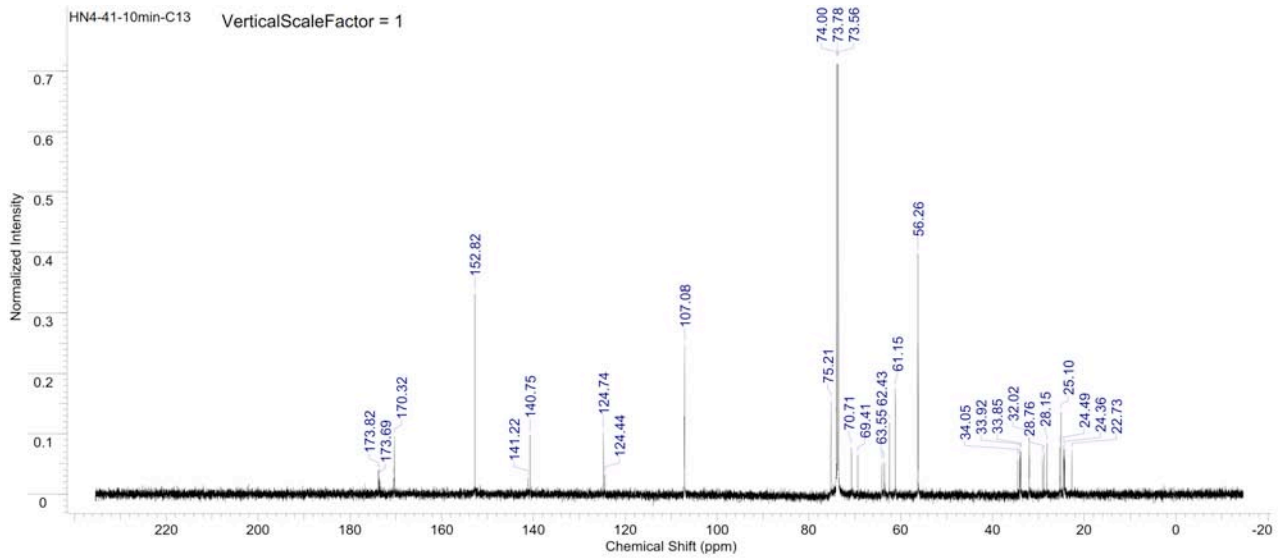


Figure S354. ^{13}C NMR spectrum of copoly(caprolactone/ hydroxyethylsyringic acid) [50:50] at 10 min. (Table S4, entry 1).

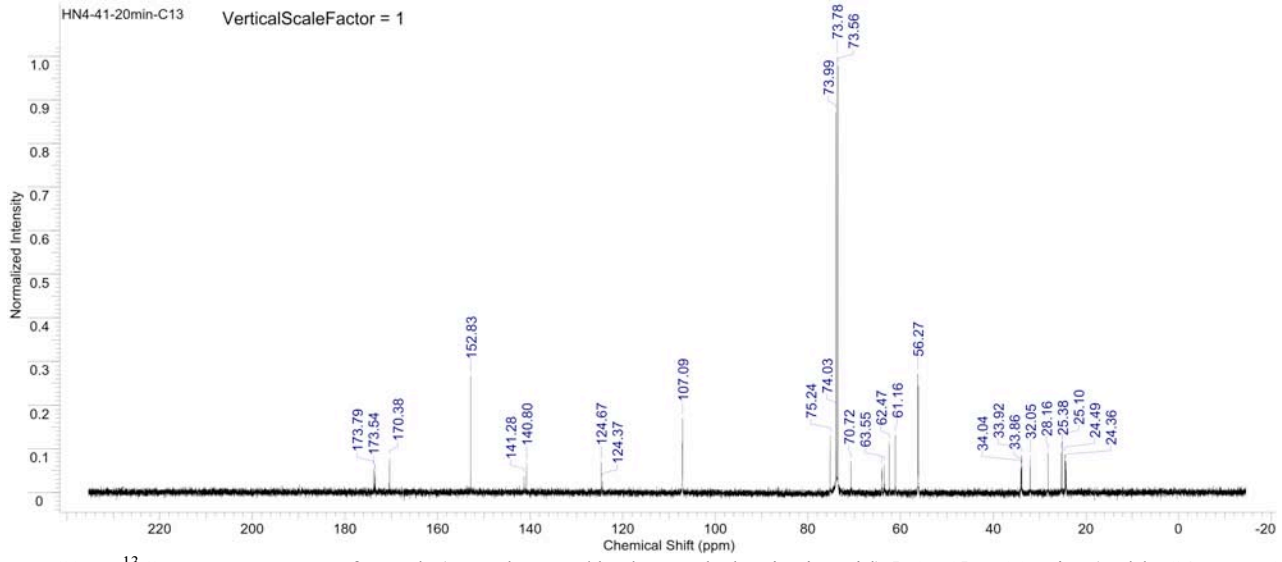


Figure S355. ^{13}C NMR spectrum of copoly(caprolactone/ hydroxyethylsyringic acid) [50:50] at 20 min. (Table S4, entry 2).

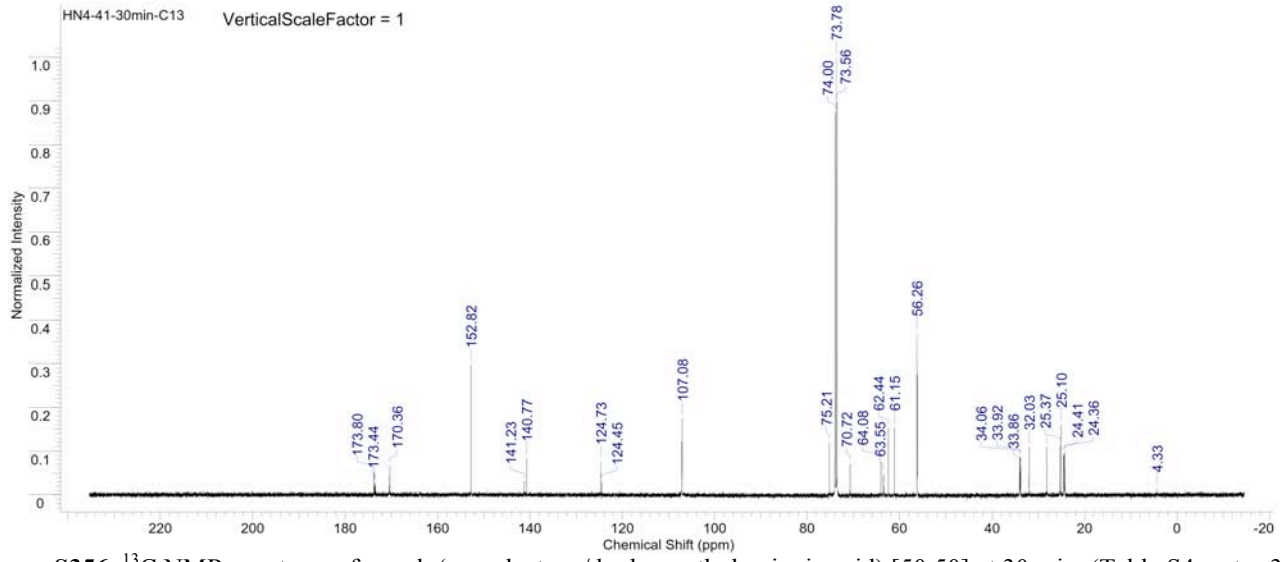


Figure S356. ^{13}C NMR spectrum of copoly(caprolactone/ hydroxyethylsyringic acid) [50:50] at 30 min. (Table S4, entry 3).

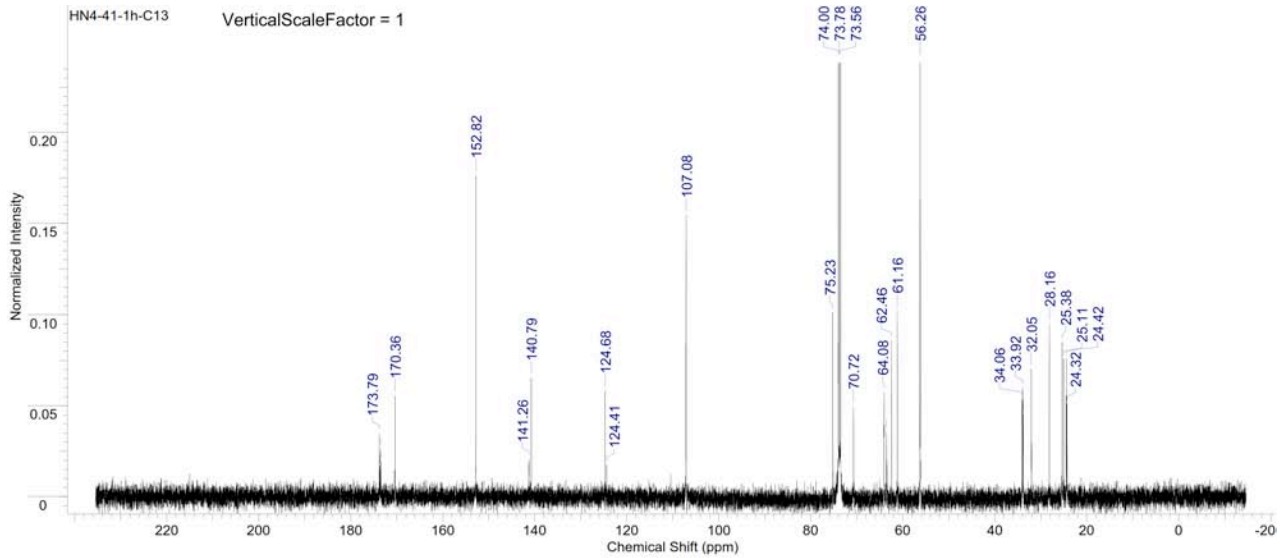


Figure S357. ^{13}C NMR spectrum of copoly(caprolactone/ hydroxyethylsyringic acid) [50:50] at 1 hour (Table S4, entry 4).

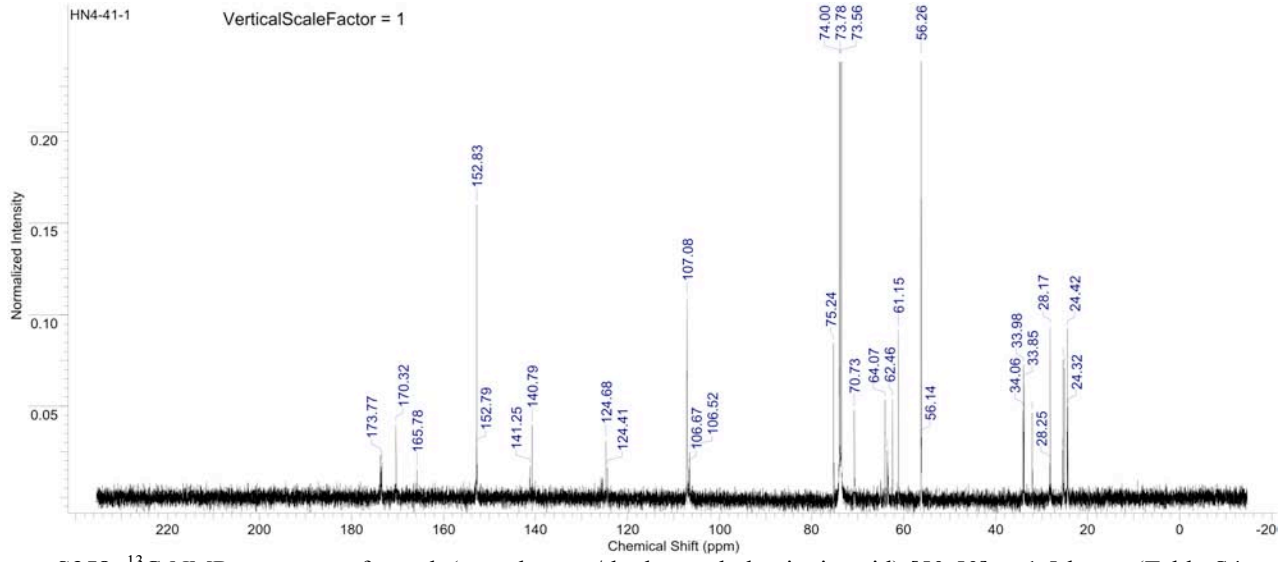


Figure S358. ^{13}C NMR spectrum of copoly(caprolactone/ hydroxyethylsyringic acid) [50:50] at 1.5 hours (Table S4, entry 5).

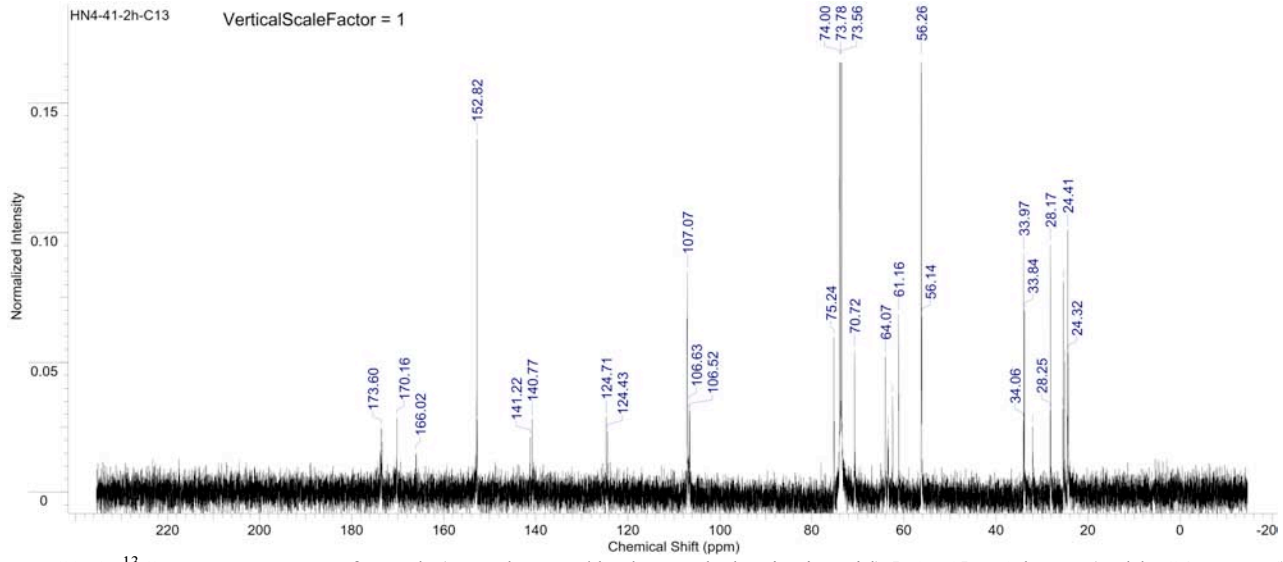


Figure S359. ^{13}C NMR spectrum of copoly(caprolactone/ hydroxyethylsyringic acid) [50:50] at 2 hours (Table S4, entry 6).

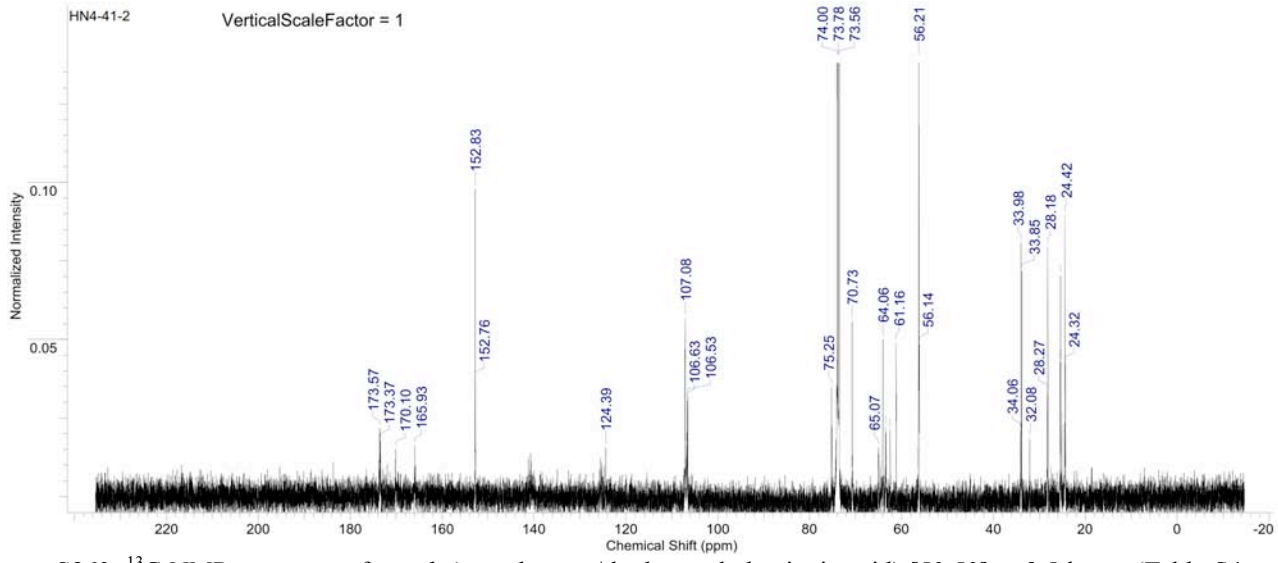


Figure S360. ^{13}C NMR spectrum of copoly(caprolactone/ hydroxyethylsyringic acid) [50:50] at 2.5 hours (Table S4, entry 7).

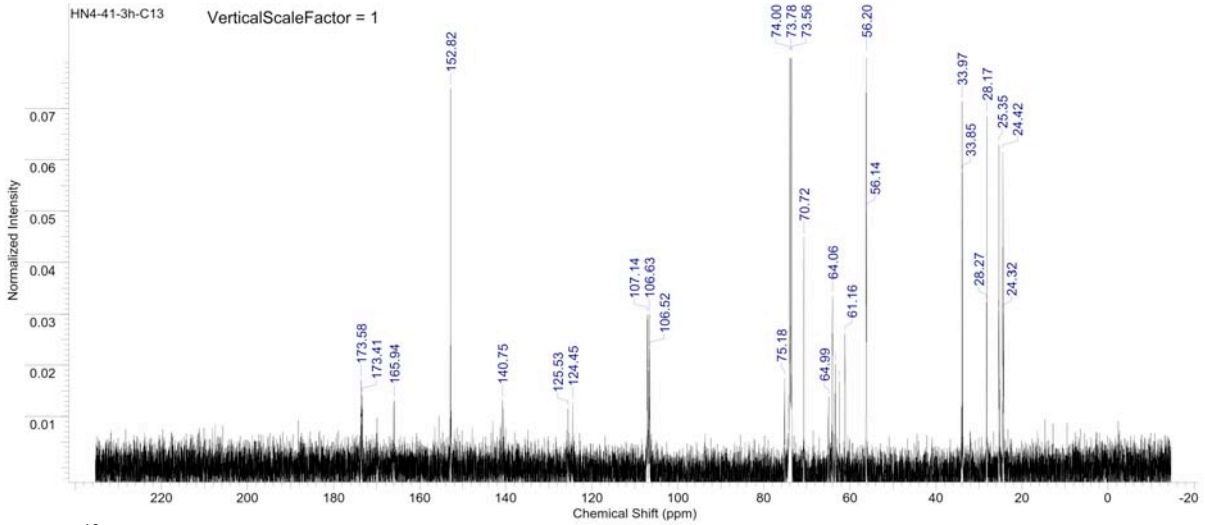


Figure S361. ^{13}C NMR spectrum of copoly(caprolactone/ hydroxyethylsyringic acid) [50:50] at 3 hours (Table S4, entry 8).

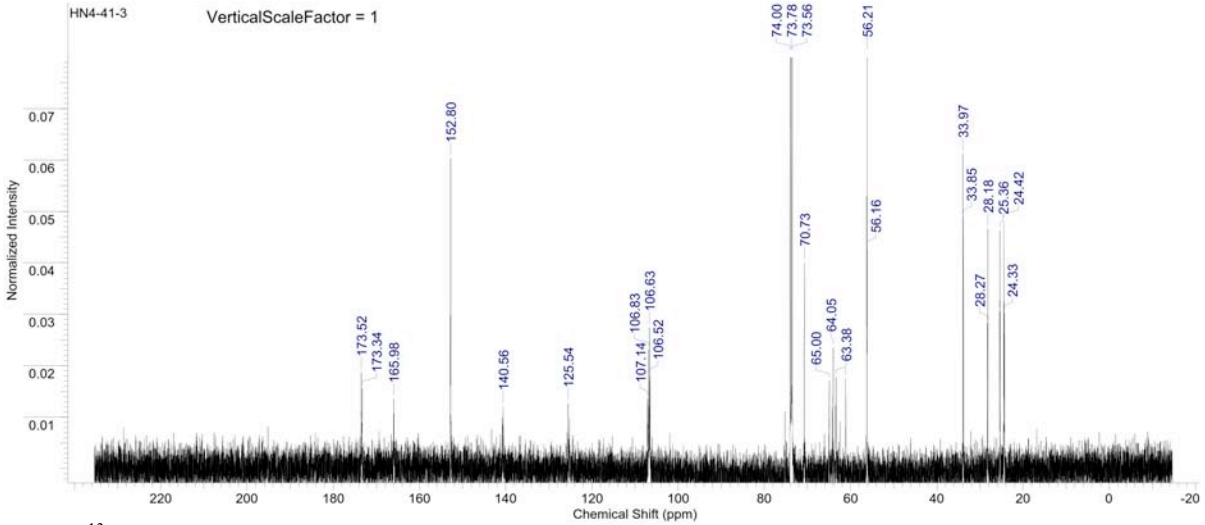


Figure S362. ^{13}C NMR spectrum of copoly(caprolactone/ hydroxyethylsyringic acid) [50:50] at 3.5 hours (Table S4, entry 9).

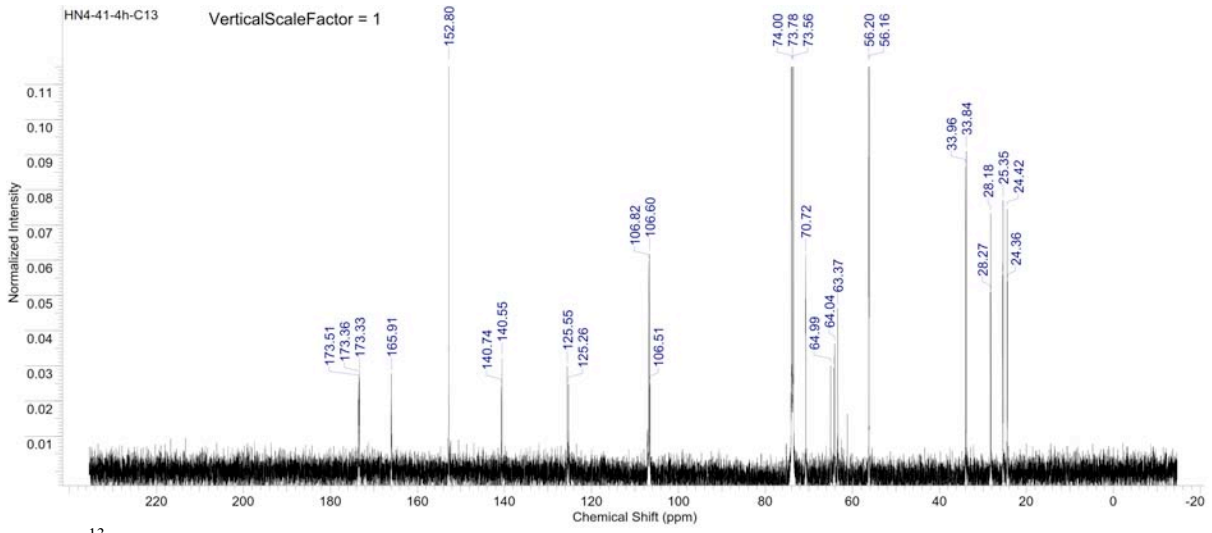


Figure S363. ^{13}C NMR spectrum of copoly(caprolactone/ hydroxyethylsyringic acid) [50:50] at 4 hours (Table S4, entry 10).

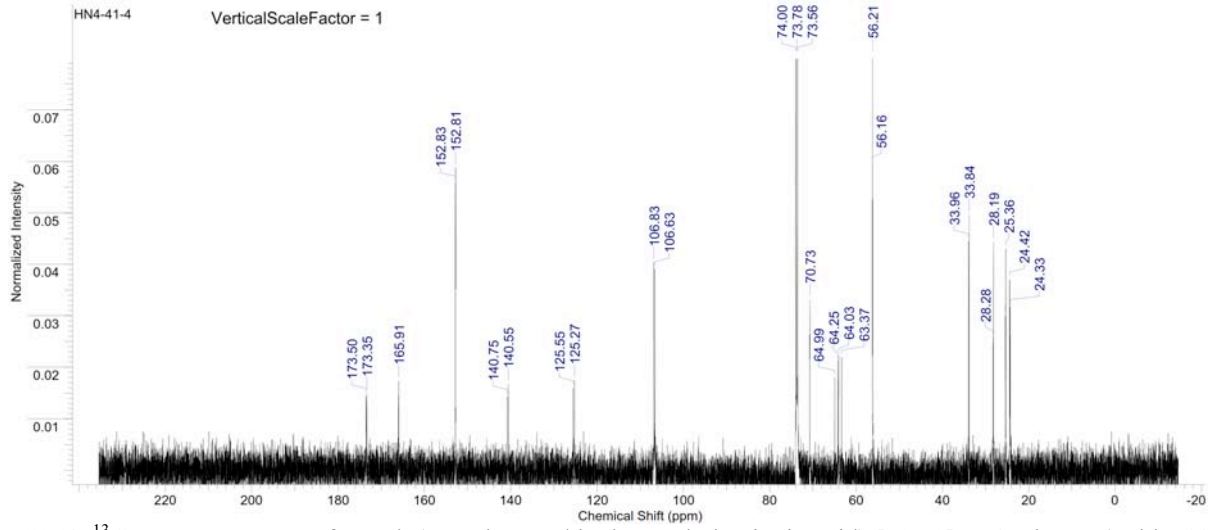


Figure S364. ^{13}C NMR spectrum of copoly(caprolactone/ hydroxyethylsyringic acid) [50:50] at 4.5 hours (Table S4, entry 11).

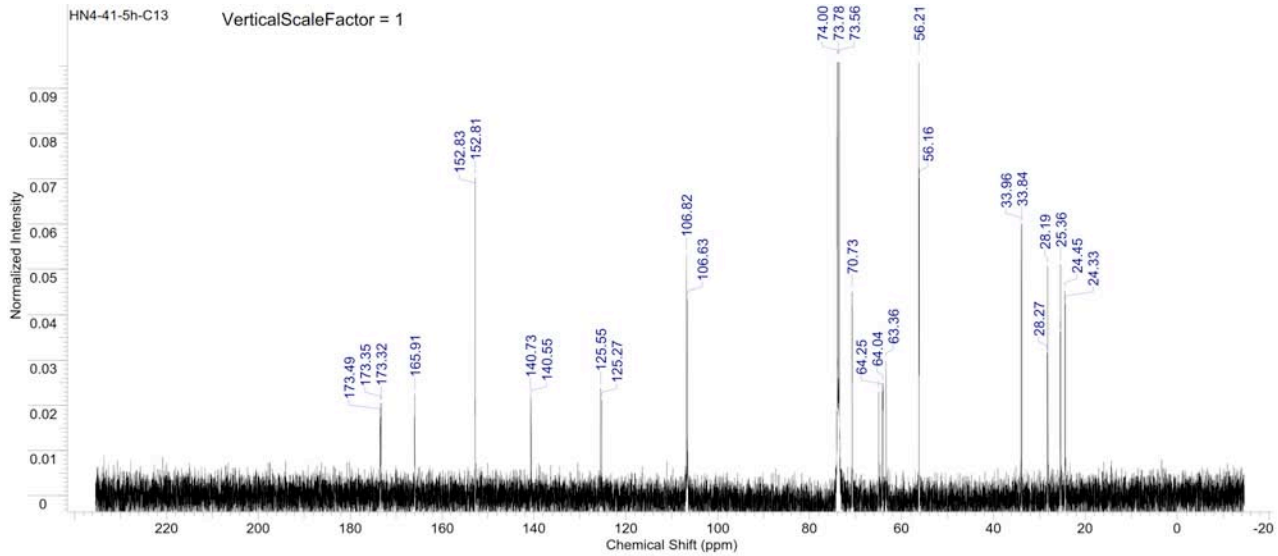


Figure S365. ^{13}C NMR spectrum of copoly(caprolactone/ hydroxyethylsyringic acid) [50:50] at 5 hours (Table S4, entry 12).

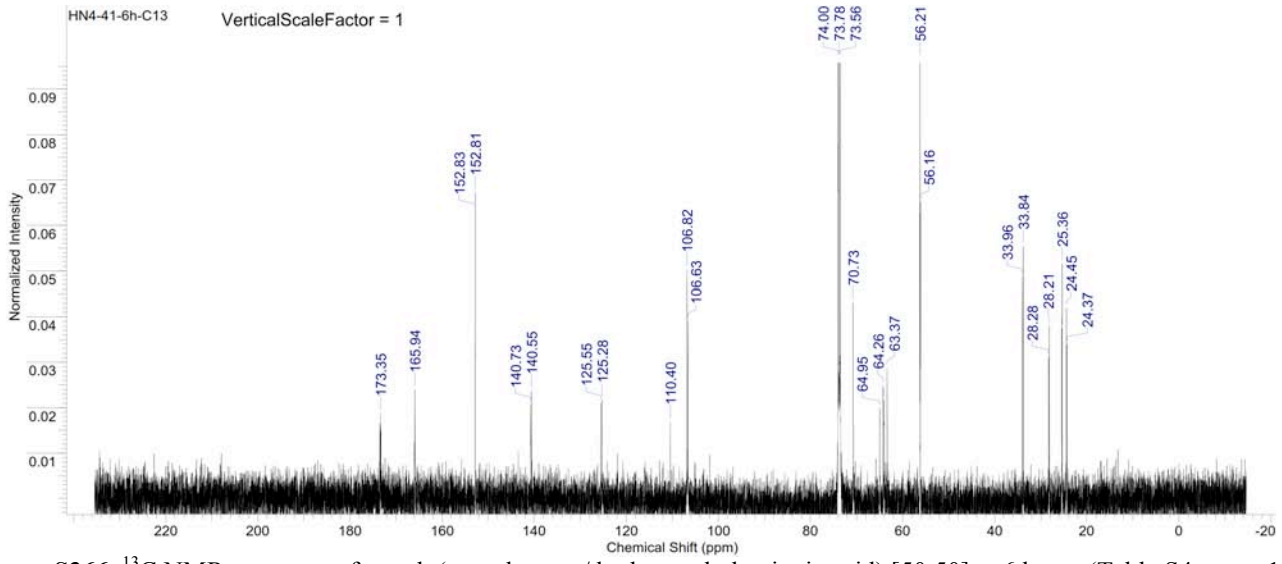


Figure S366. ^{13}C NMR spectrum of copoly(caprolactone/ hydroxyethylsyringic acid) [50:50] at 6 hours (Table S4, entry 13).

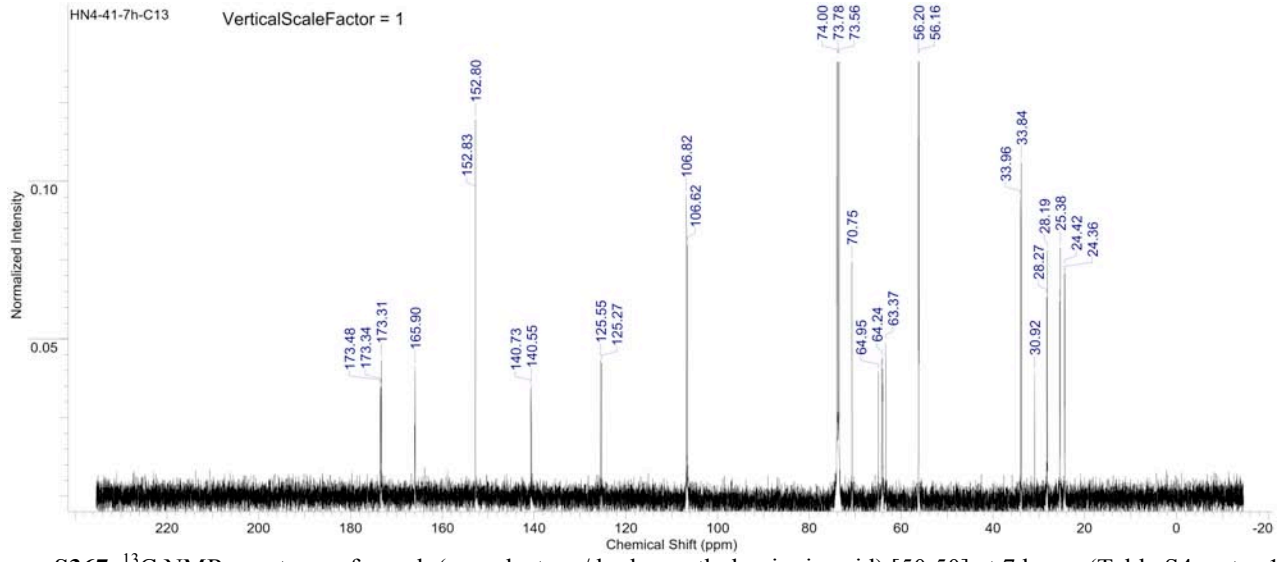


Figure S367. ^{13}C NMR spectrum of copoly(caprolactone/ hydroxyethylsyringic acid) [50:50] at 7 hours (Table S4, entry 14).

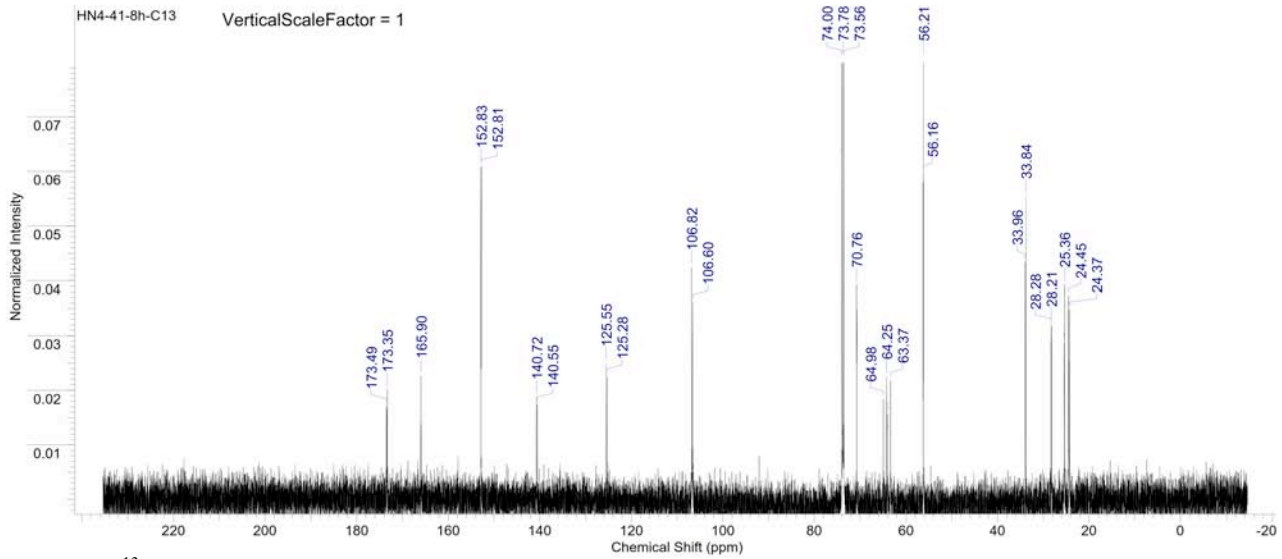


Figure S368. ^{13}C NMR spectrum of copoly(caprolactone/ hydroxyethylsyringic acid) [50:50] at 8 hours (Table S4, entry 15).

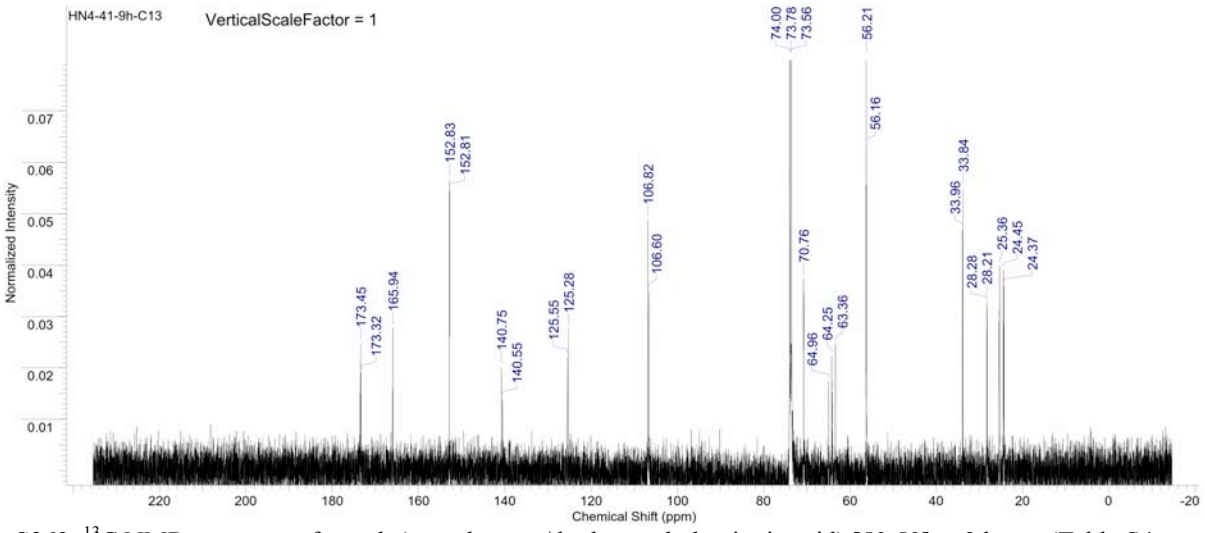


Figure S369. ^{13}C NMR spectrum of copoly(caprolactone/ hydroxyethylsyringic acid) [50:50] at 9 hours (Table S4, entry 16).

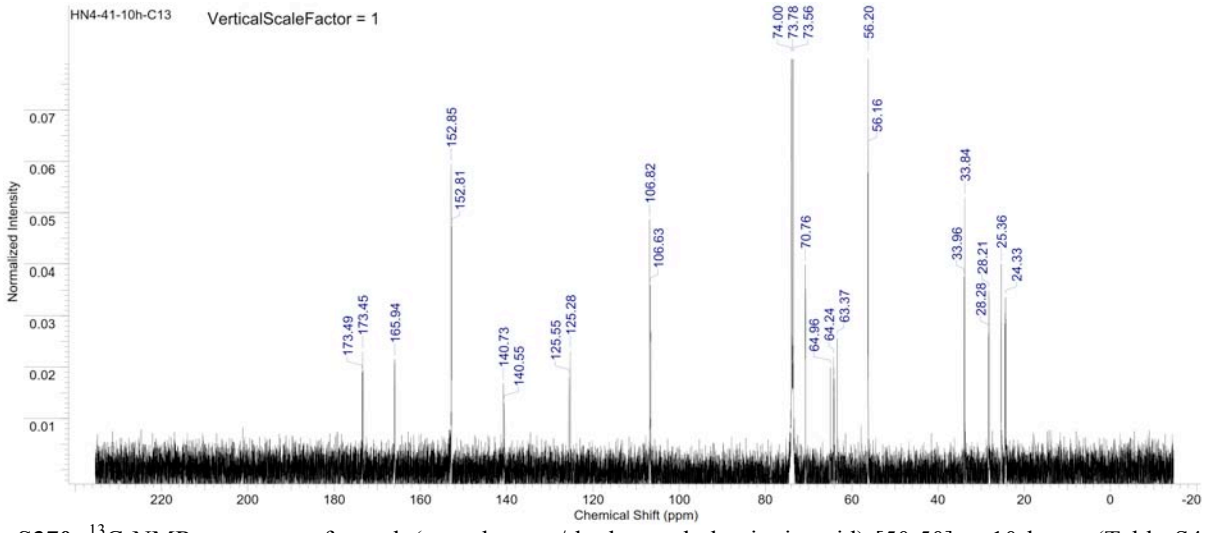


Figure S370. ^{13}C NMR spectrum of copoly(caprolactone/ hydroxyethylsyringic acid) [50:50] at 10 hours (Table S4, entry 17).

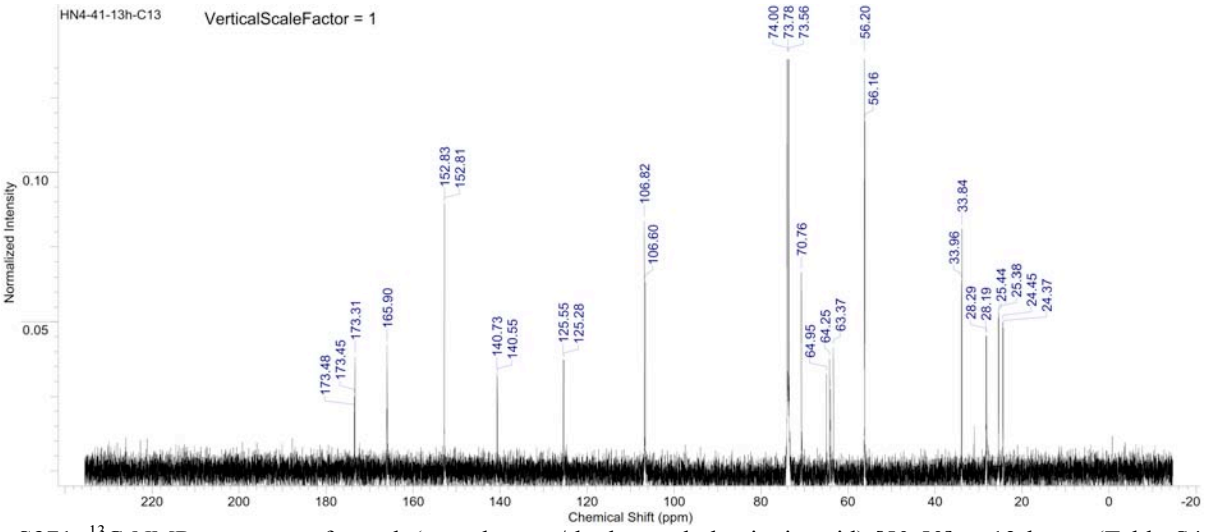


Figure S371. ^{13}C NMR spectrum of copoly(caprolactone/ hydroxyethylsyringic acid) [50:50] at 13 hours (Table S4, entry 18).

^{1}H NMR Analysis for Copolymer Composition

For copoly(caprolactone/hydroxyethylsyringic acid) series:

Figure S372 depicts exemplary ^{1}H NMR spectra for the homopolymers and copolymer with hydroxyethylsyringic acid (HESA) feed fractions of 100%, 40%, and 0%. Of particular use are the methoxy hydrogens of the hydroxyethylsyringic acid (HESA) repeat units (3.6 to 3.9 ppm) and the eight methylene hydrogens of the caprolactone repeat units (1.2 to 2.4 ppm). Relative integration provided the incorporation values reported in Table S2.

- the polycaprolactone (PCL) (from Table S2, Entry 1)
- the 60:40 (feed ratio, CL:HESA) copolymer (from Table S2, Entry 5)
- and the polyethylene syringate (PES) (from Table S2, Entry 11)

Integration of the peaks for the 60:40 caprolactone:HESA copolymer spectrum gives an area of 23.52 corresponding to the 6 methoxy protons for the HESA repeat unit at 3.6 to 3.9 ppm and an area of 39.24 (= 29.65 + 9.59) corresponding to the 8 methylene protons for caprolactone repeat units at 1.2 to 2.4 ppm. Thus we have:

([23.52/6] /([23.52/6] + [39.24/8])*100 = 44% HESA monomers present in the copolymer.
This computes to 100 – 44 = 56% caprolactone monomers present in the copolymer.

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

For copoly(caprolactone/hydroxyethylvanillic acid) series:

Figure S373 depicts exemplary ^{1}H NMR spectra for the homopolymers and copolymer with hydroxyethylvanillic acid (HEVA) feed fractions of 0%, 40%, and 100%. Of particular use are the methoxy hydrogens of the hydroxyethylvanillic acid (HEVA) repeat units (3.70 to 3.95 ppm) and the eight methylene hydrogens of the caprolactone repeat unit (1.25 to 2.5 ppm). Relative integration provided the incorporation values reported in Table S2.

- the polycaprolactone (PCL) (from Table S2, Entry 1)
- and the 60:40 (feed ratio, CL:HEVA) copolymer (from Table S2, Entry 15)

Integration of the peaks for the 60:40 caprolactone:HEVA copolymer spectrum gives an area of 2.53 corresponding to the 3 methoxy protons for the HEVA repeat unit at 3.70 to 3.95 ppm and an area of 8.19 (= 2.00 + 4.15 + 2.04) corresponding to the 8 methylene protons for the caprolactone repeat unit at 1.25 to 2.5 ppm. Thus we have:

([2.53/3] /([2.53/3] + [8.19/8])*100 = 45% HEVA monomers present in the copolymer.
This computes to 100 – 45 = 55% caprolactone monomers present in the copolymer.

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

For copoly(caprolactone/hydroxyethylferulic acid) series:

Figure S374 depicts exemplary ^{1}H NMR spectra for the homopolymers and copolymer with hydroxyethylferulic acid (HEFA) feed fractions of 0%, 40%, and 100%. Of particular use are the methoxy hydrogens of the hydroxyethylferulic acid (HEFA) repeat units (3.7 to 4.0 ppm) and the eight methylene hydrogens of the caprolactone repeat unit (1.2 to 2.5 ppm). Relative integration provided the incorporation values reported in Table S2.

- the polycaprolactone (PCL) (from Table S2, Entry 1)
- the 60:40 (feed ratio, CL:HEFA) copolymer (from Table S2, Entry 25)
- and the polyethylene ferulate (PEF) (from Table S2, Entry 31)

Integration of the peaks for the 60:40 caprolactone:HEFA copolymer spectrum gives an area of 2.87 corresponding to the 3 methoxy protons for the HEFA repeat unit at 3.7 to 4.0 ppm and an area of 8.06 (= 2.00 + 4.10 + 1.96) corresponding to the 8 methylene protons for caprolactone repeat units at 1.2 to 2.5 ppm. Thus we have:

([2.87/3] /([2.87/3] + [8.06/8])*100 = 49% HEFA monomers present in the copolymer.
This computes to 100 – 49 = 51% caprolactone monomers present in the copolymer.

This is in close agreement with the 60:40 feed ratio of caprolactone: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(caprolactone/hydroxyethylcoumaric acid) series:

Figure S375 depicts exemplary ^{1}H NMR spectra for the homopolymers and copolymer with hydroxyethylcoumaric acid (HECA) feed fractions of 0%, 50%, and 100%. Of particular use are the six protons of sp^2 hybridized carbons of the hydroxyethylcoumaric acid (HECA) repeat units (6.1 to 8.0 ppm) and eight methylene hydrogens of the caprolactone repeat units (1.1 to 2.5 ppm). Relative integration provided the incorporation values reported in Table S2.

- the polycaprolactone (PCL) (from Table S2, Entry 1)
- the 50:50 (feed ratio, CL:HECA) copolymer (from Table S2, Entry 33)
- and the polyethylene coumarate (PEC) (from Table S2, Entry 35)

Integration of the peaks for the 50:50 caprolactone:HECA copolymer spectrum gives an area of 8.54 (= 2.31 + 2.58 + 2.50 + 1.15) corresponding to the 6 protons of sp^2 hybridized carbons for the HECA repeat unit at 6.0 to 7.8 ppm and an area of 8.36 (= 2.00 + 4.23 + 2.13) corresponding to the 8 methylene protons for caprolactone repeat units at 1.1 to 2.5 ppm. Thus we have:

([8.54/6] /([8.54/6] + [8.36/8])*100 = 54% HECA monomers present in the copolymer.
This computes to 100 – 54 = 46% caprolactone monomers present in the copolymer.

This is in close agreement with the 50:50 feed ratio of caprolactone:HECA monomers employed. All the other compositions (from Table S2) displayed a similar agreement between the feed ratio and the measured incorporation ratio.

For copoly(L-lactide/hydroxyethylsyringic acid) series:

Figure S376 depicts exemplary ^{1}H NMR spectra for the homopolymers and copolymer with hydroxyethylsyringic acid (HESA) fractions of 0%, 40%, and 100%. Of particular use are the methoxy hydrogens of the hydroxyethylsyringic acid (HESA) repeat units (3.5 to 4.1 ppm) and six methyl hydrogens of the L-lactide repeat units (1.0 to 2.0 ppm). Relative integration provided the incorporation values reported in Table S3.

- the polylactic acid (PLA) (from Table S3, Entry 1)
- the 60:40 (feed ratio, L-lactide:HESA) copolymer (from Table S3, Entry 3)
- and the polyethylene syringate (PES) (from Table S3, Entry 6)

Integration of the peaks for the 60:40 L-lactide:HESA copolymer spectrum gives an area of 31.82 corresponding to the 6 methoxy protons for the HESA repeat unit at 3.5 to 4.1 ppm and an area of 20.00 corresponding to the 6 methyl protons for L-lactide repeat units at 1.0 to 2.0 ppm. Thus we have:

([31.81/6] /([31.81/6] + [20.00/6])*100 = 61% HESA monomers present in the copolymer.
This computes to 100 – 61 = 39% L-lactide monomers present in the copolymer.

Overall the final composition of HESA into the copolymer is routinely greater than its feed fraction (Table S3). This difference is likely caused by the facile loss of L-lactide through sublimation before its polymerization and after its polymerization via back-biting during prolonged heating of the polymer.

For copoly(L-lactide/hydroxyethylvanillic acid) series:

Figure S377 depicts exemplary ^{1}H NMR spectra for the homopolymers and copolymer with hydroxyethylvanillic acid (HEVA) feed fractions of 0% and 40%. Of particular use are the peaks attributed to the three methoxy hydrogens of the hydroxyethylvanillic acid (HEVA) repeat units (3.5 to 4.1 ppm) and six methyl hydrogens of the L-lactide repeat units (1.0 to 2.0 ppm). Relative integration provided the incorporation values reported in Table S3.

- the polylactic acid (PLA) (from Table S3, Entry 1)
- and the 60:40 (feed ratio, L-lactide:HEVA) copolymer (from Table S3, Entry 8)

Integration of the peaks for the 60:40 L-lactide:HEVA copolymer spectrum gives an area of 12.32 corresponding to the 3 methoxy protons for the HEVA repeat unit at 3.5 to 4.1 ppm and an area of 20.00 corresponding to the 6 methyl protons for L-lactide repeat units at 1.0 to 2.0 ppm. Thus we have:

([12.32/3] /([12.32/3] + [20.00/6])*100 = 55% HEVA monomers present in the copolymer.
This computes to 100 – 55 = 45% L-lactide monomers present in the copolymer.

Overall the final composition of HEVA into the copolymer is routinely greater than its feed fraction (Table S3). This difference is likely caused by the facile loss of L-lactide through sublimation before its polymerization and after its polymerization via back-biting during prolonged heating of the polymer.

For copoly(L-lactide/hydroxyethylferulic acid) series:

Figure S378 depicts exemplary ^{1}H NMR spectra for the homopolymers and copolymer with hydroxyethylferulic acid (HEFA) feed fractions of 0%, 40%, and 100%. Of particular use are the three methoxy hydrogens of hydroxyethylferulic acid (HEFA) repeat units (3.60 to 4.05 ppm) and the six methyl hydrogens of the L-lactide repeat units (1.3 to 1.9 ppm). Relative integration provided the incorporation values reported in Table S3.

- the polylactic acid (PLA) (from Table S3, Entry 1)
- the 60:40 (feed ratio, L-lactide:HEFA) copolymer (from Table S3, Entry 15)
- and the polyethylene ferulate (PEF) (from Table S3, Entry 17)

Integration of the peaks for the 60:40 L-lactide:HEFA copolymer spectrum gives an area of 14.3 corresponding to the 3 methoxy protons for the HEFA repeat unit at 3.60 to 4.05 ppm and an area of 20.0 corresponding to the 6 methyl protons for L-lactide repeat units at 1.3 to 1.9 ppm. Thus we have:

([14.3/3] /([14.3/3] + [20/6])*100 = 59% HEFA monomers present in the copolymer.
This computes to 100 – 59 = 41% L-lactide monomers present in the copolymer.

Overall the final composition of HEFA into the copolymer is routinely greater than its feed fraction (Table S3). This difference is likely caused by the facile loss of L-lactide through sublimation before its polymerization and after its polymerization via back-biting during prolonged heating of the polymer.

For copoly(L-lactide/hydroxyethylcoumaric acid) series:

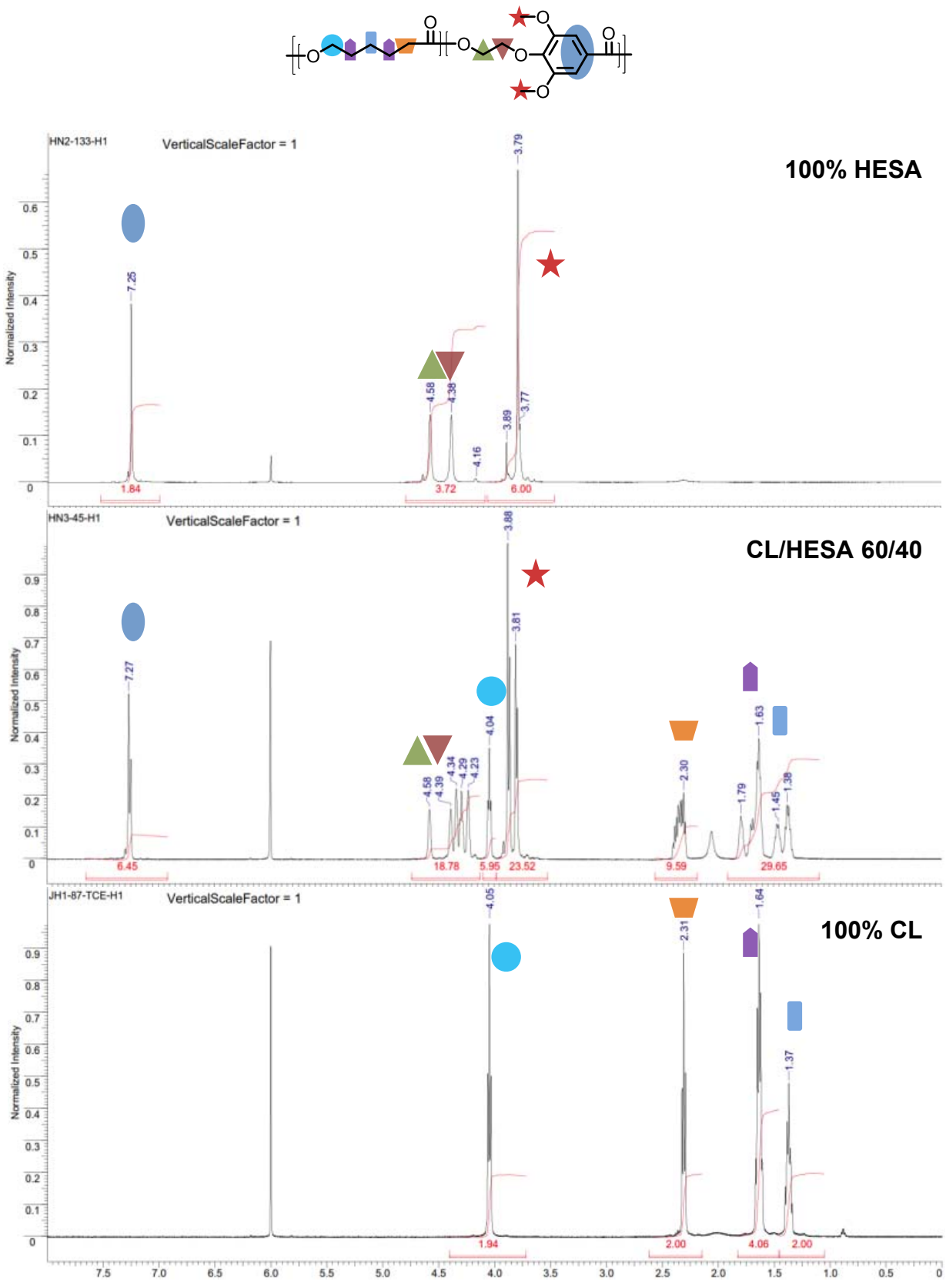
Figure S379 depicts exemplary ^{1}H NMR spectra for the homopolymers and copolymer with hydroxyethylcoumaric acid (HECA) feed fractions of 0%, 40%, and 100%. Of particular use are the six protons of sp^2 hybridized carbons of the hydroxyethylcoumaric acid (HECA) repeat units (6.25 to 7.90 ppm) and six methyl hydrogens of the L-lactide repeat units (1.25 to 1.90 ppm). Relative integration provided the incorporation values reported in Table S3.

- the polylactic acid (PLA) (from Table S3, Entry 1)
- the 60:40 (feed ratio, L-lactide:HECA) copolymer (from Table S3, Entry 21)
- and the polyethylene coumarate (PEC) (from Table S3, Entry 23)

Integration of the peaks for the 60:40 L-lactide:HECA copolymer spectrum gives an area of 41.34 (= 6.21 + 16.51 + 12.55 + 6.07) corresponding to the 6 protons of sp^2 hybridized carbons for the HECA repeat unit at 6.25 to 7.90 ppm and an area of 30.00 corresponding to the 6 methyl protons for L-lactide repeat units at 1.25 to 1.90 ppm. Thus we have:

([41.34/6] /([41.34/6] + [30.00/6])*100 = 58% HECA monomers present in the copolymer.
This computes to 100 – 58 = 42% L-lactide monomers present in the copolymer.

Overall the final composition of HECA into the copolymer is routinely greater than its feed fraction (Table S3). This difference is likely caused by the facile loss of L-lactide through sublimation before its polymerization and after its polymerization via back-biting during prolonged heating of the polymer.



1

Figure S372. [1]H NMR spectra of copoly(caprolactone/hydroxyethylsyringic acid) with hydroxyethylsyringic acid (HESA) feed fractions of 100%, 40%, and 0%.

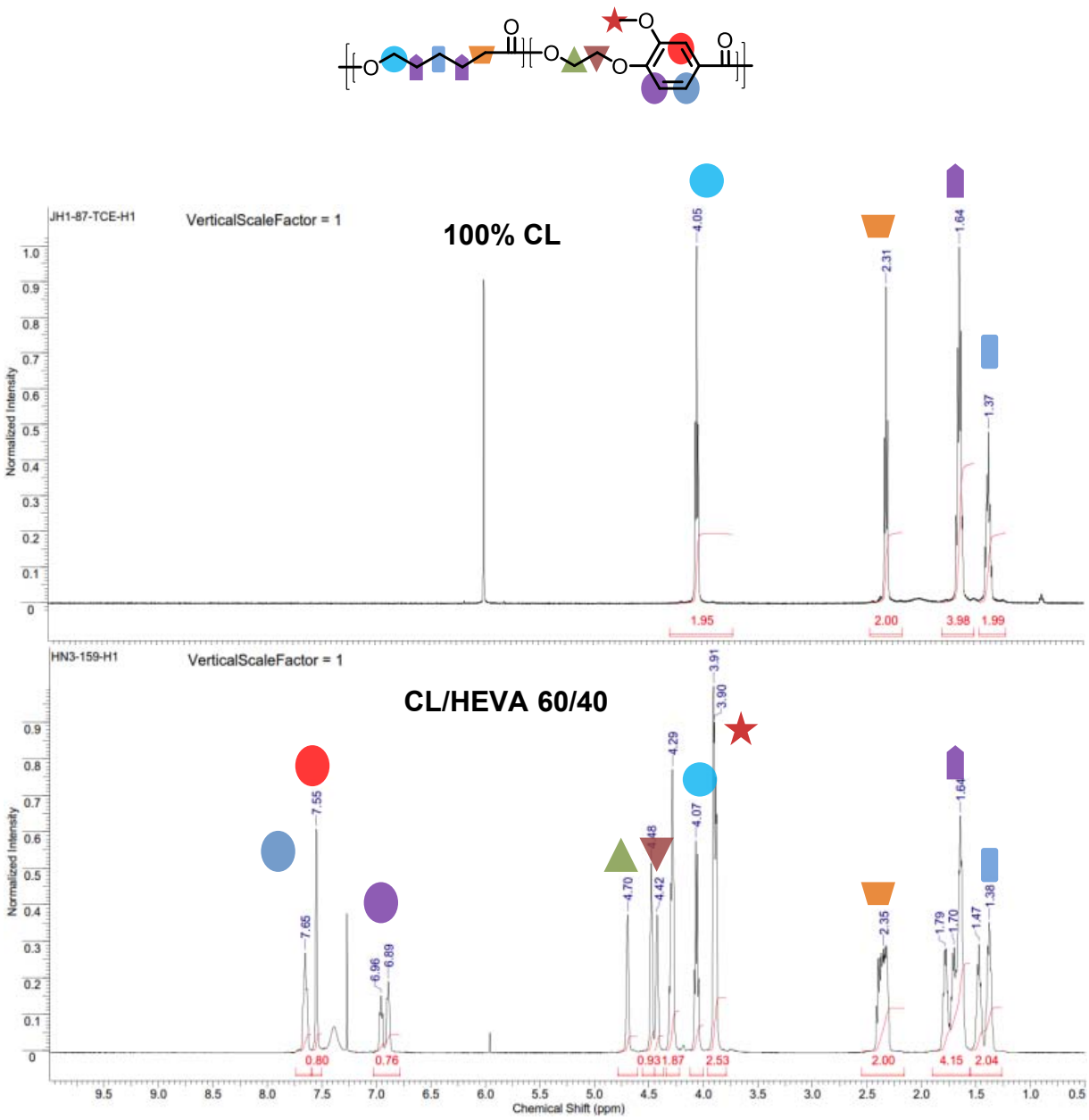


Figure S373. ^{1}H NMR spectra of copoly(caprolactone/hydroxyethylvanillic acid) with hydroxyethylvanillic acid (HEVA) feed fractions of 0% and 40%.

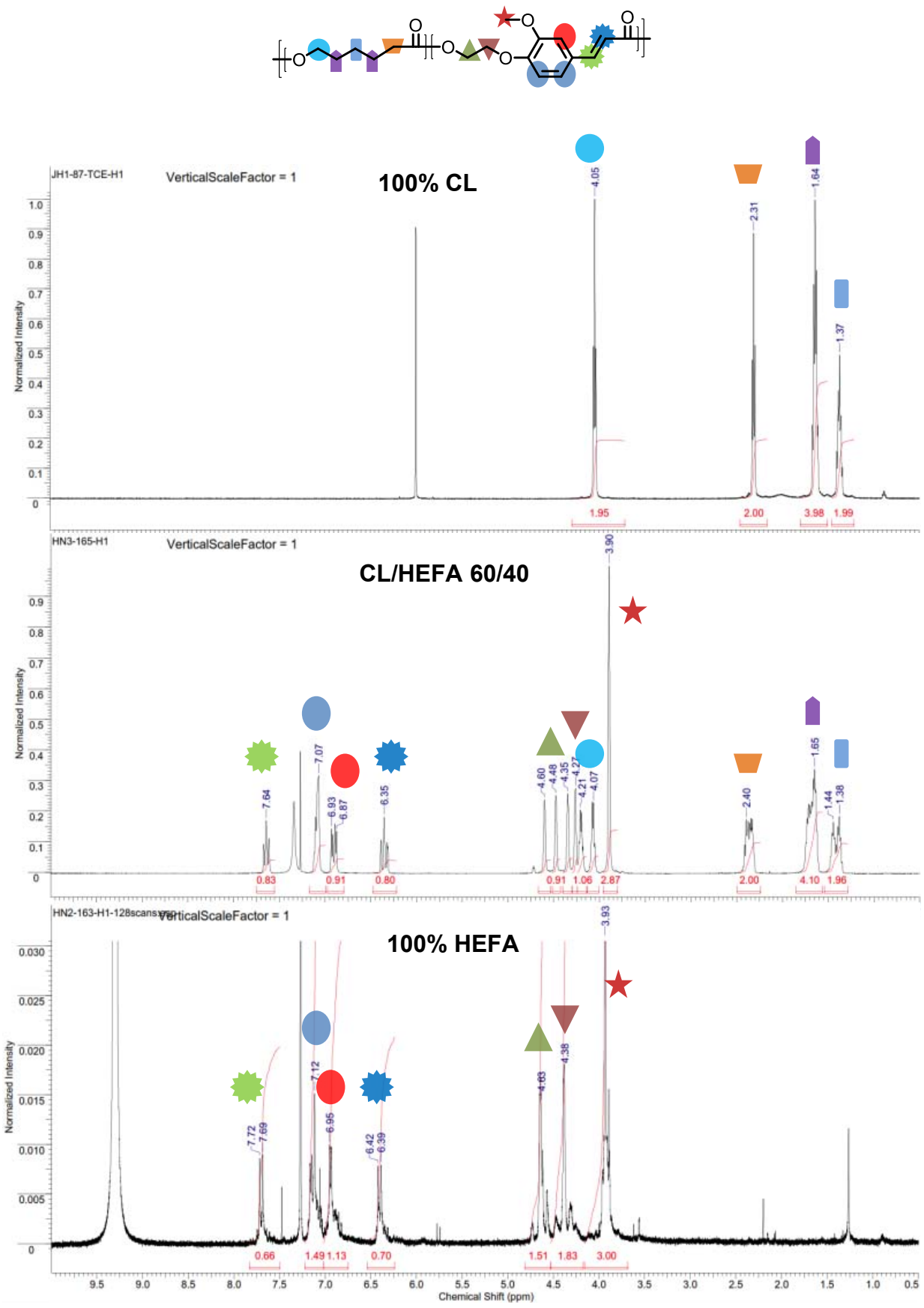


Figure S374. [1]H NMR spectra of copoly(caprolactone/hydroxyethylferulic acid) with hydroxyethylferulic acid (HEFA) feed fractions of 0%, 40%, and 100%.

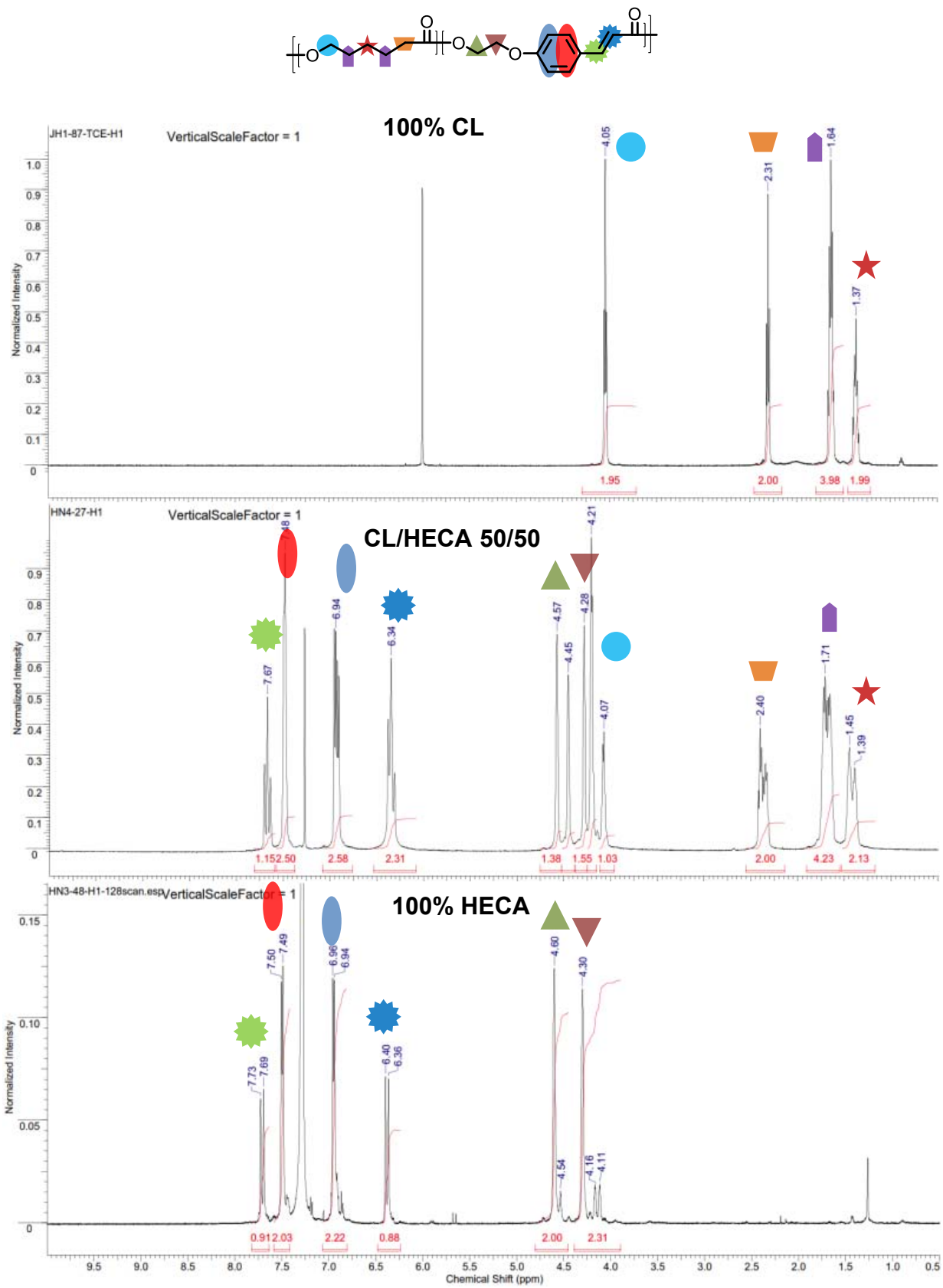


Figure S375. ^{1}H NMR spectra of copoly(caprolactone/hydroxyethylcoumaric acid) with hydroxyethylcoumaric acid (HECA) feed fractions of 0%, 50%, and 100%.

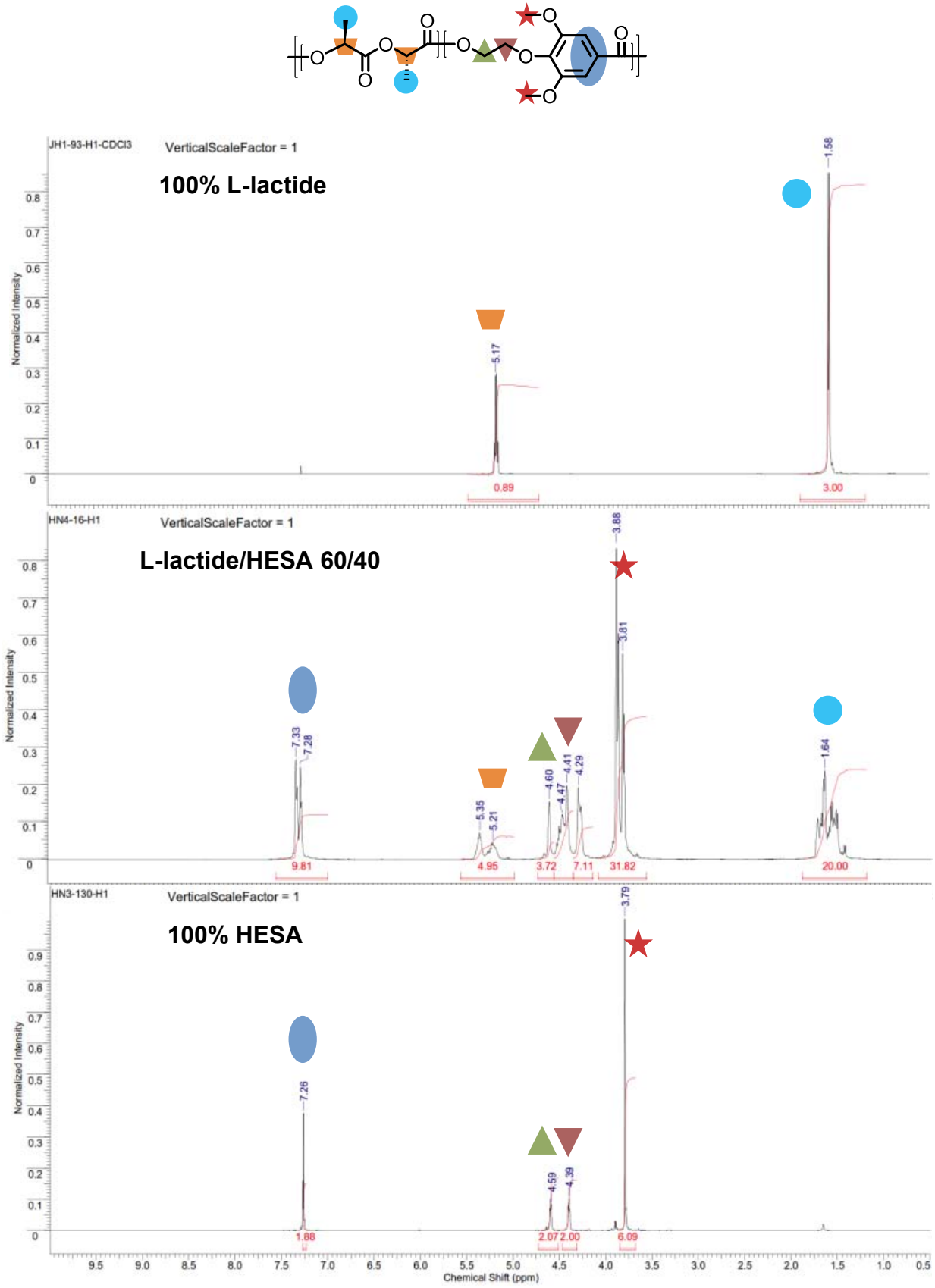


Figure S376. [1]H NMR spectra of copoly(L-lactide/hydroxyethylsyringic acid) with hydroxyethylsyringic acid (HESA) feed fractions of 0%, 40%, and 100%.

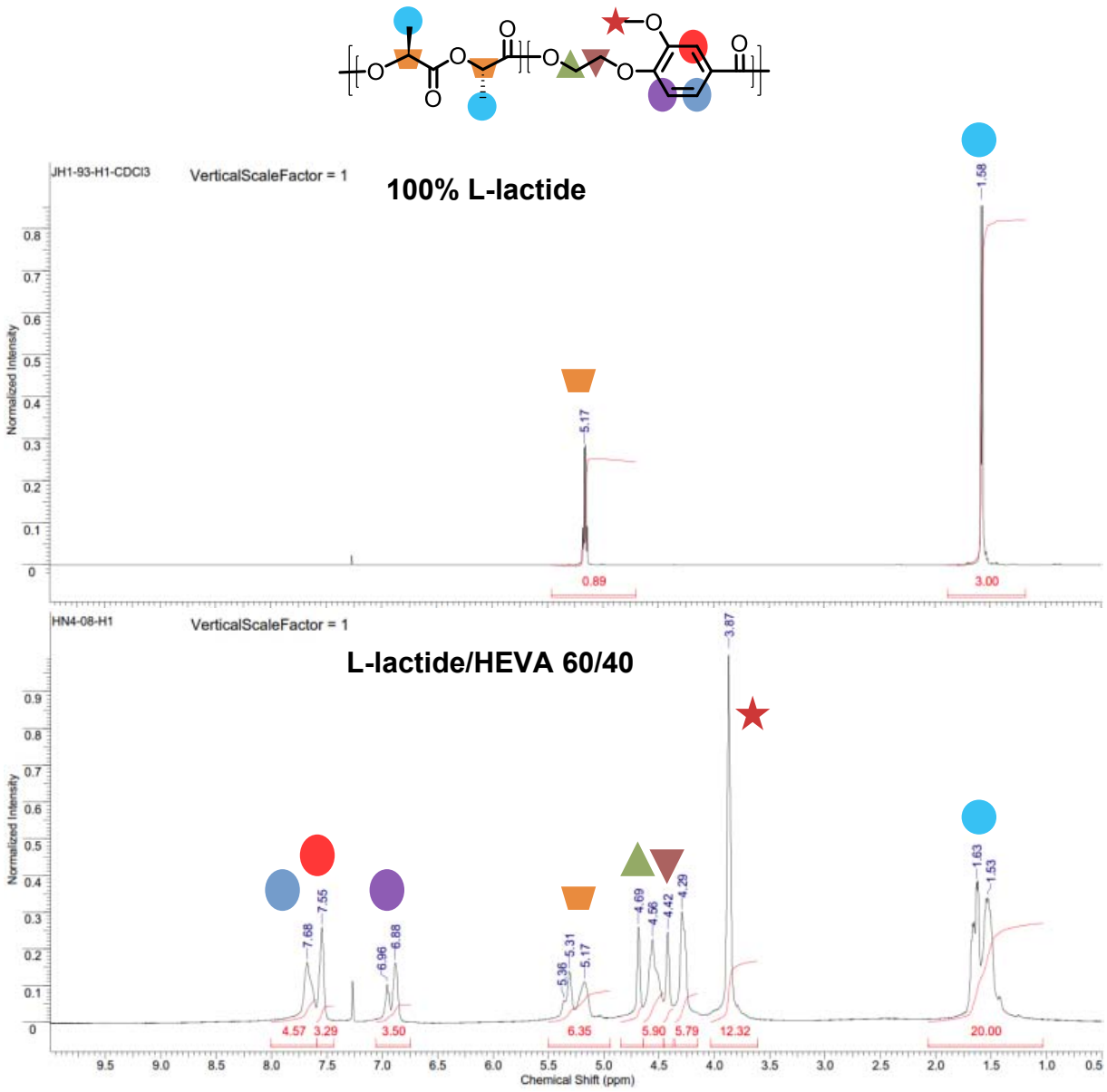


Figure S377. [1]H NMR spectra of copoly(L-lactide/hydroxyethylvanillic acid) with hydroxyethylvanillic acid (HEVA) feed fractions of 0% and 40%.

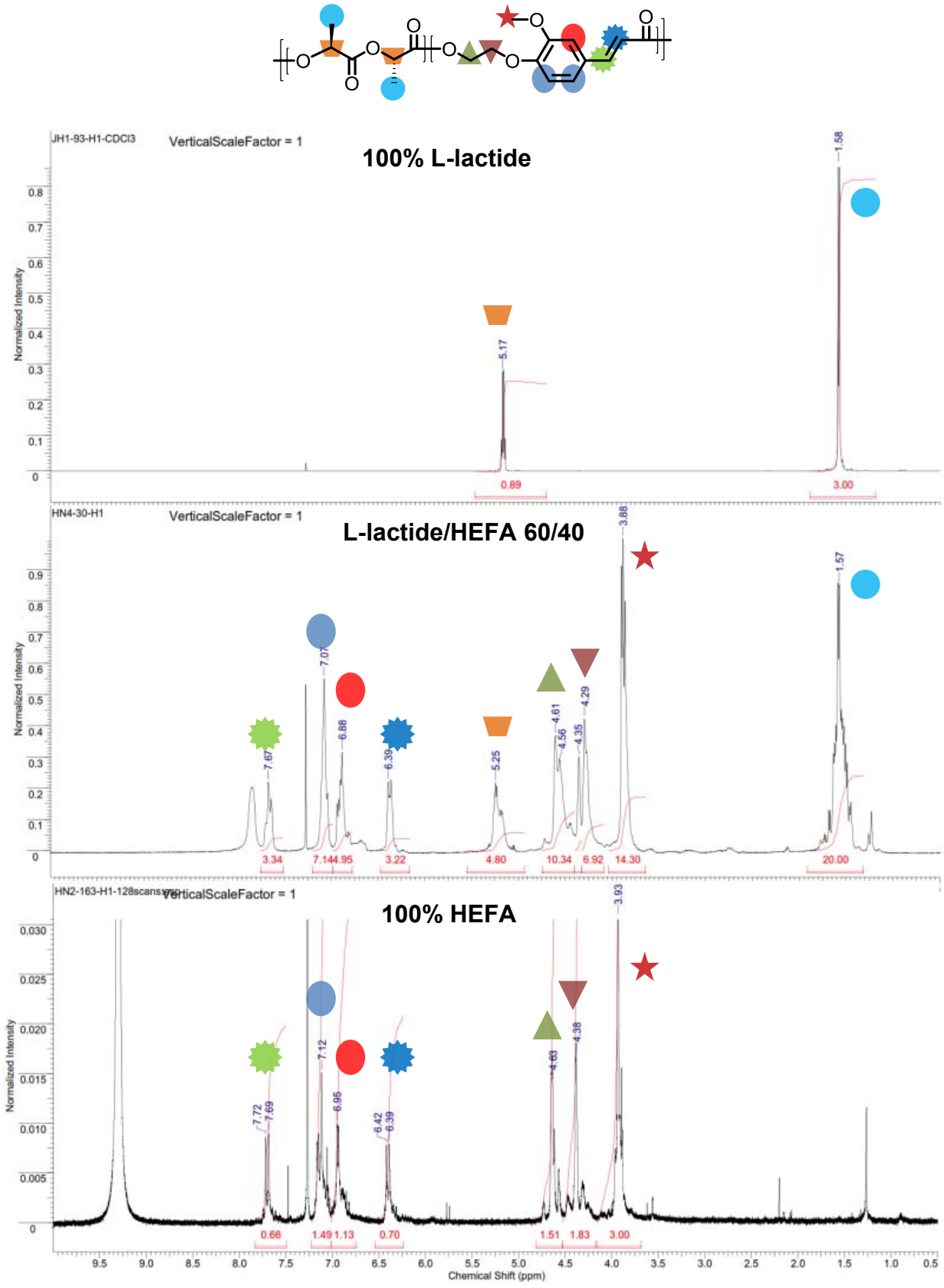


Figure S378. ^{1}H NMR spectra of copoly(L-lactide/hydroxyethylferulic acid) with hydroxyethylferulic acid (HEFA) feed fractions of 0%, 40%, and 100%.

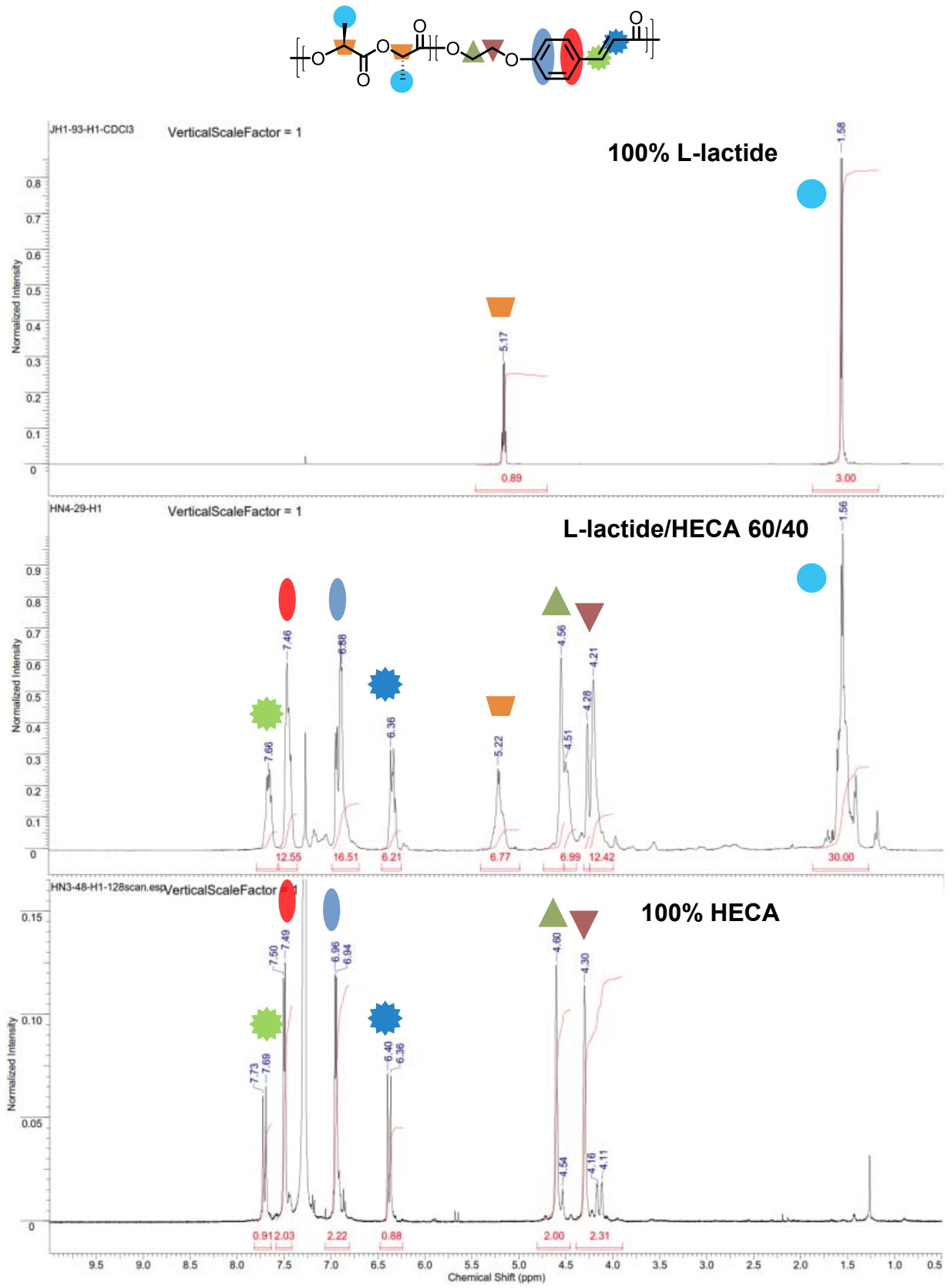


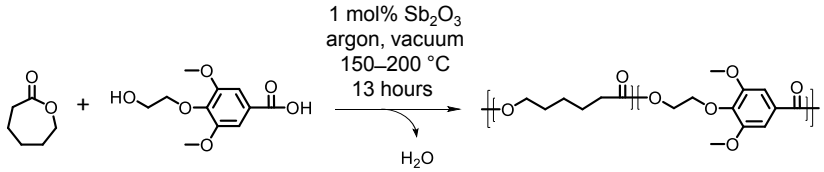
Figure S379. [1]H NMR spectra of copoly(L-lactide/hydroxyethylcoumaric acid) with hydroxyethylcoumaric acid (HECA) feed fractions of 0%, 40%, and 100%.

Kinetic study

Polymerization procedure

A 50 mL round bottom flask connected to a bump trap containing 1.2 eq. of P_2O_5 was charged with 3.18 g of hydroxyethylsyringic acid (13.1 mmol), 1.50 g of ε-caprolactone (13.1 mmol), and 77 mg of Sb_2O_3 (1 mol%). 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. During the polymerization, 18 aliquot samples were removed. Three aliquots were sampled after 10 minute intervals for the first half hour; nine aliquots were sampled after 30 minute intervals from one hour until 5 hours; five aliquots were sampled after 1 hour intervals until 10 hours; finally, one aliquot was taken at the end of the reaction, 13 hours.

Table S4. Kinetic study for ROP polycondensation for the copolymer of ε-caprolactone and hydroxyethylsyringic acid prepared with a 50:50 ratio of monomers.



Entry	Reaction condition[a]	Reaction time (hours)	Reaction temperature (°C)	M_n [b] (Da)	M_w [b] (Da)	PDI [b]	T_g [c] (°C)	$T_{95\%}$ [d] (°C)	$T_{50\%}$ [e] (°C)
1	Argon	0.17	150	220	360	1.6	-39	178	329
2		0.33	150	255	420	1.7	-38	185	321
3		0.5	150	262	460	1.8	-38	190	327
4		1	150	280	570	2	-31	189	323
5		1.5	180	340	820	2.4	-22	198	329
6		2	180	780	1,400	1.8	-15	197	329
7		2.5	180	950	1,700	1.8	-11	205	333
8		3	200	1,100	2,200	2.0	-4	233	352
9		3.5	200	1,700	3,700	2.2	0	250	354
10		4	200	3,100	7,200	2.4	4	258	352
11		4.5	200	4,600	11,400	2.5	8	274	352
12		5	200	6,400	15,900	2.5	10	276	352
13	Vacuum	6	200	9,200	23,200	2.5	13	293	355
14		7	200	14,700	33,600	2.3	15	301	354
15		8	200	20,300	45,600	2.2	15	304	353
16		9	200	23,200	50,500	2.2	17	311	353
17		10	200	27,100	55,800	2.1	20	314	353
18		13	200	28,800	57,200	2.0	20	315	359

[a]1.2 eq. of P_2O_5; mixture was melted under argon for 5 hour temperature ramp from 150 to 200 °C; then dynamic vacuum was applied for 8 hours at 200 °C. [b]Obtained by GPC in hexafluoroisopropanol (HFIP) at 40 °C versus polymethyl methacrylate (PMMA) standards. [c]Determined by DSC. [d]Temperature at which 5% mass loss is observed under nitrogen. [f]Temperature at which 50% mass loss is observed under nitrogen.

ESI-TOF Analysis Protocol

Accurate mass experiments were performed on an Agilent 6220 ESI TOF (Santa Clara, CA) mass spectrometer equipped with an electrospray source operated in positive ion mode. Agilent ESI Low Concentration Tuning Mix was used for mass calibration for a calibration range of m/z 100 – 4000. Samples were prepared in a solution containing acidified methanol (0.1% formic acid), 20% of hexafluoroisopropanol and adventitious sodium salts; 1 µL was injected into the electrospray source at a rate of 100 µL min^{-1}. Optimal conditions were: capillary voltage 4000 V, source temperature 350 °C, and a cone voltage of 60 V. The TOF analyzer was scanned over m/z 100.00–3200.00 with a 1 s integration time. Data was acquired in continuum mode until acceptable averaged data was obtained.

The National Science Foundation is acknowledged for this instrument via the CRIF-MU program, CHE-0541761.

Table S5. Relative abundance of monomers and oligomers as a function of time according to ESI mass spectrometry.

		10 min.		20 min.		30 min.		1 hour		1.5 hours.	
oligomer+ Na	mass	abundance	percent	abundance	percent	abundance	percent	abundance	percent	abundance	percent
CL (+H+)	115.15	20598.6	0.3	21735	0.3	16826.4	0.2	17161.1	0.2	13797.5	0.7
HESA	265.07	639849.5	9.8	841041	10.0	1250311.5	14.4	1188952.1	16.3	295502.2	14.6
LL	269.14	41031.6	0.6	20530	0.2	16838.9	0.2	11635.4	0.2	5113.1	0.3
LA	379.14	640793.5	9.8	1594925	18.9	1396029.9	16.1	750702.1	10.3	199433.6	9.8
AA	489.14	13853.5	0.2	17973	0.2	13562.2	0.2	32131.5	0.4	81536.8	4.0
LLA	493.2	1909137.8	29.2	2112282	25.0	2095847.1	24.2	1910100.9	26.1	474813.1	23.4
ALA and LAA	603.3	22036.8	0.3	25063	0.3	24672.1	0.3	51829.8	0.7	97644.2	4.8
LLLA	607.27	1891091.7	28.9	2002425	23.7	2006297.1	23.2	1863554.8	25.5	285947.3	14.1
LALA	717.33	17351.7	0.3	19452	0.2	37627.4	0.4	74600.9	1.0	120455	5.9
LLLLA	721.33	1081673.5	16.5	1507322	17.9	1416140.4	16.4	1003511.6	13.7	207035.5	10.2
LLLLLA	835.41	184170.3	2.8	187177	2.2	231844.1	2.7	223602.7	3.1	127826.7	6.3
LLLLLLA	949.47	60680.4	0.9	68112	0.8	101340.5	1.2	116117.3	1.6	72303	3.6
LLLLLLLA	1063.54	14838.7	0.2	18788	0.2	35814.5	0.4	49529.7	0.7	33897.4	1.7
LLLLLLLLA	1177.61	3073.3	0.0	4546	0.1	10561.8	0.1	17583.1	0.2	13906	0.7
Total		6540180.9	100.0	8441371.2	100.0	8653713.9	100.0	7311013.0	100.0	2029211.4	100.0

		2 hours		2.5 hours		3 hours		3.5 hours		4 hours	
oligomer+ Na	mass	abundance	percent	abundance	percent	abundance	percent	abundance	percent	abundance	percent
CL (+H+)	115.15	12666	0.8	226.9	0.0	443	0.1	591.2	0.1	1244.4	0.4
HESA	265.07	293643.9	18.4	191720.2	19.3	138774	19.9	95725.8	20.2	72739.5	21.1
LL	269.14	4722.5	0.3	2940.8	0.3	2464	0.4	2745.5	0.6	4929	1.4
LA	379.14	148626.6	9.3	83444.1	8.4	52863	7.6	33189	7.0	26248.9	7.6
AA	489.14	120004.3	7.5	102075.3	10.3	86790	12.4	73513.3	15.5	58778.5	17.0
LLA	493.2	246370	15.4	143053.4	14.4	92281	13.2	55782.5	11.8	41527.3	12.0
ALA and LAA	603.3	128379.9	8.0	102662.9	10.3	84035	12.0	67766	14.3	56094.3	16.3
LLLA	607.27	196684.7	12.3	107244.4	10.8	66510	9.5	36554.5	7.7	25941.5	7.5
LALA	717.33	142504.7	8.9	107621	10.8	84317	12.1	62805	13.3	26502.3	7.7
LLLLA	721.33	139088.8	8.7	72966.5	7.3	43507	6.2	22523	4.8	15945.7	4.6
LLLLLA	835.41	84481	5.3	43160.2	4.3	24668	3.5	12162.1	2.6	8337.6	2.4
LLLLLLA	949.47	47882.3	3.0	23171.7	2.3	13128	1.9	6255	1.3	4103.3	1.2
LLLLLLLA	1063.54	23216.8	1.5	11005.3	1.1	5963	0.9	2805.2	0.6	1825.4	0.5
LLLLLLLLA	1177.61	9832.1	0.6	4527.6	0.5	2458	0.4	1260.2	0.3	738.1	0.2
Total		1598103.6	100.0	995820.3	100.0	698201.4	100.0	473678.3	100.0	344955.8	100.0

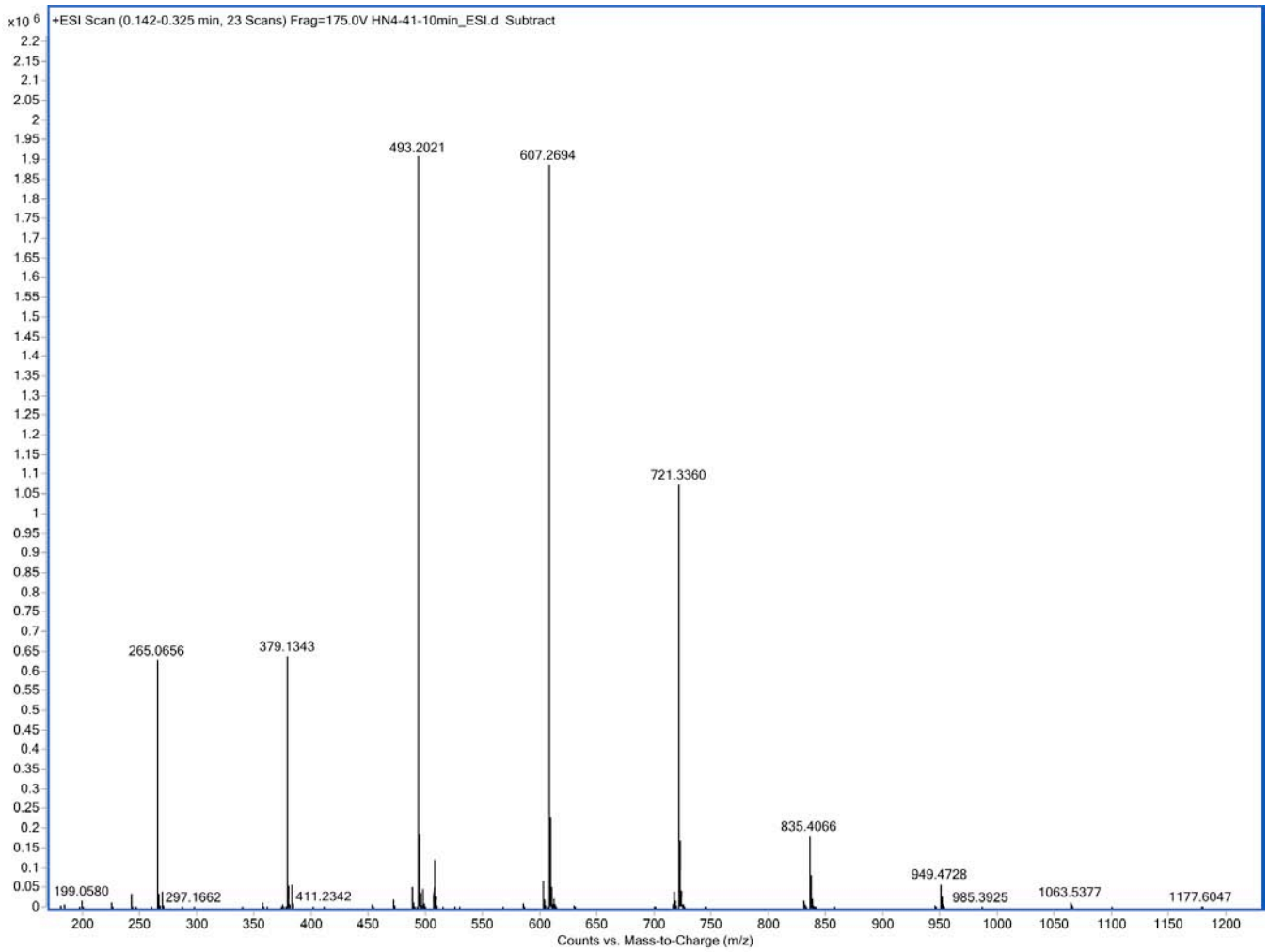


Figure S380. ESI spectra of copoly(caprolactone/hydroxyethylsyringic acid) [50:50] at 10 min. (Table S4, entry 1)

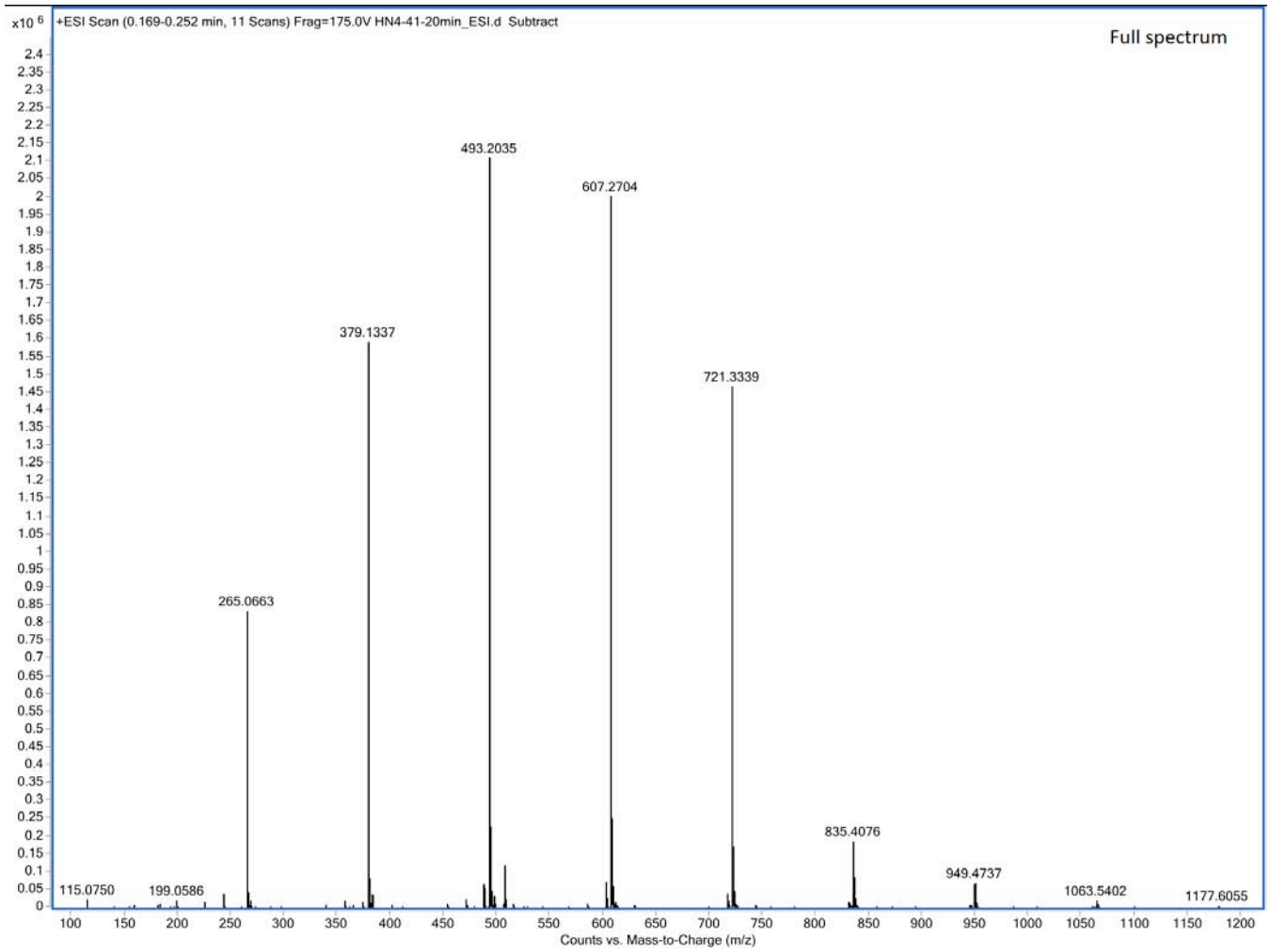


Figure S381. ESI spectra of copoly(caprolactone/hydroxyethylsyringic acid) [50:50] at 20 min. (Table S4, entry 2)

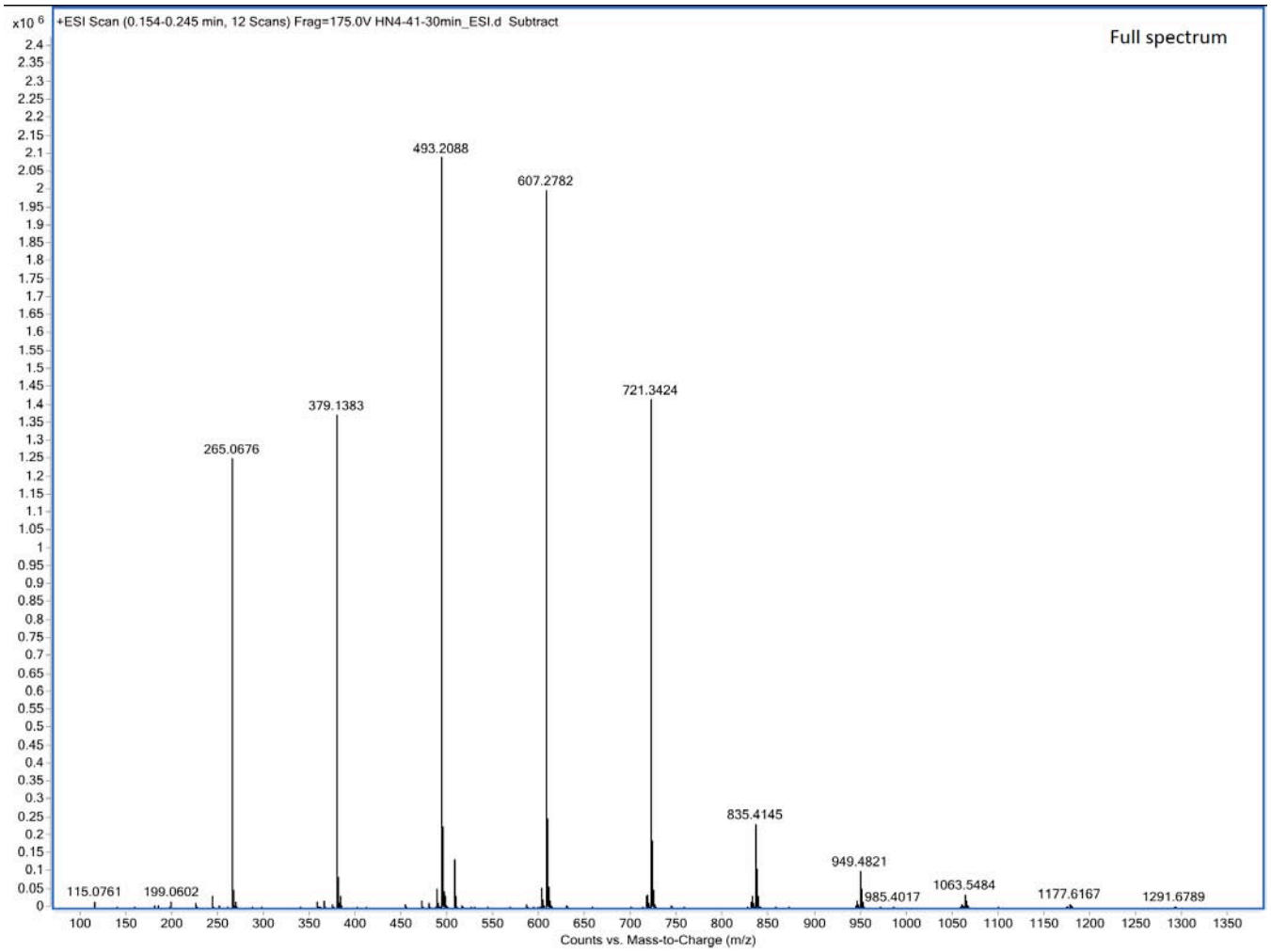


Figure S382. ESI spectra of copoly(caprolactone/hydroxyethylsyringic acid) [50:50] at 30 min. (Table S4, entry 3)

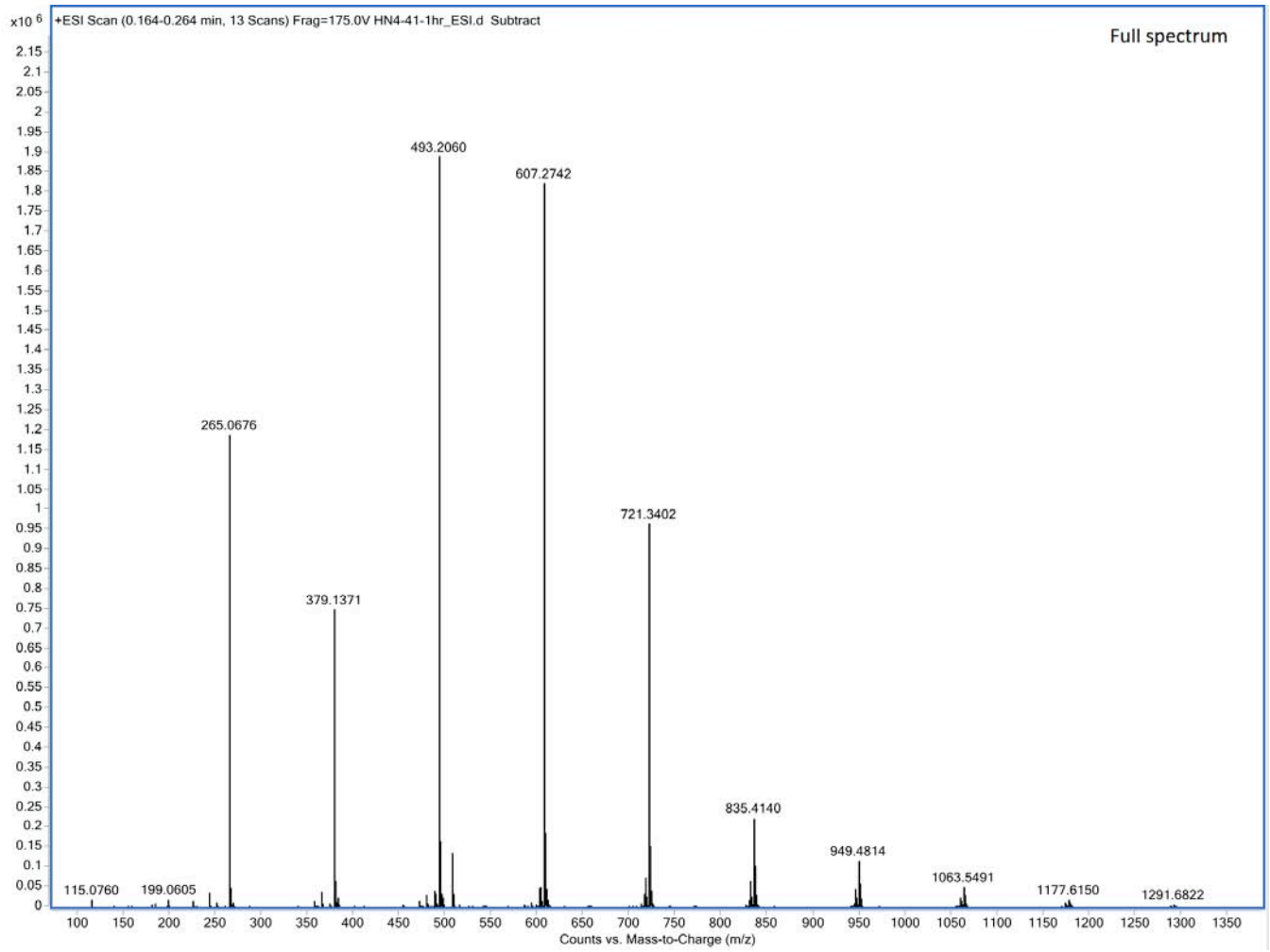


Figure S383. ESI spectra of copoly(caprolactone/hydroxyethylsyringic acid) [50:50] at 1 hour (Table S4, entry 4)

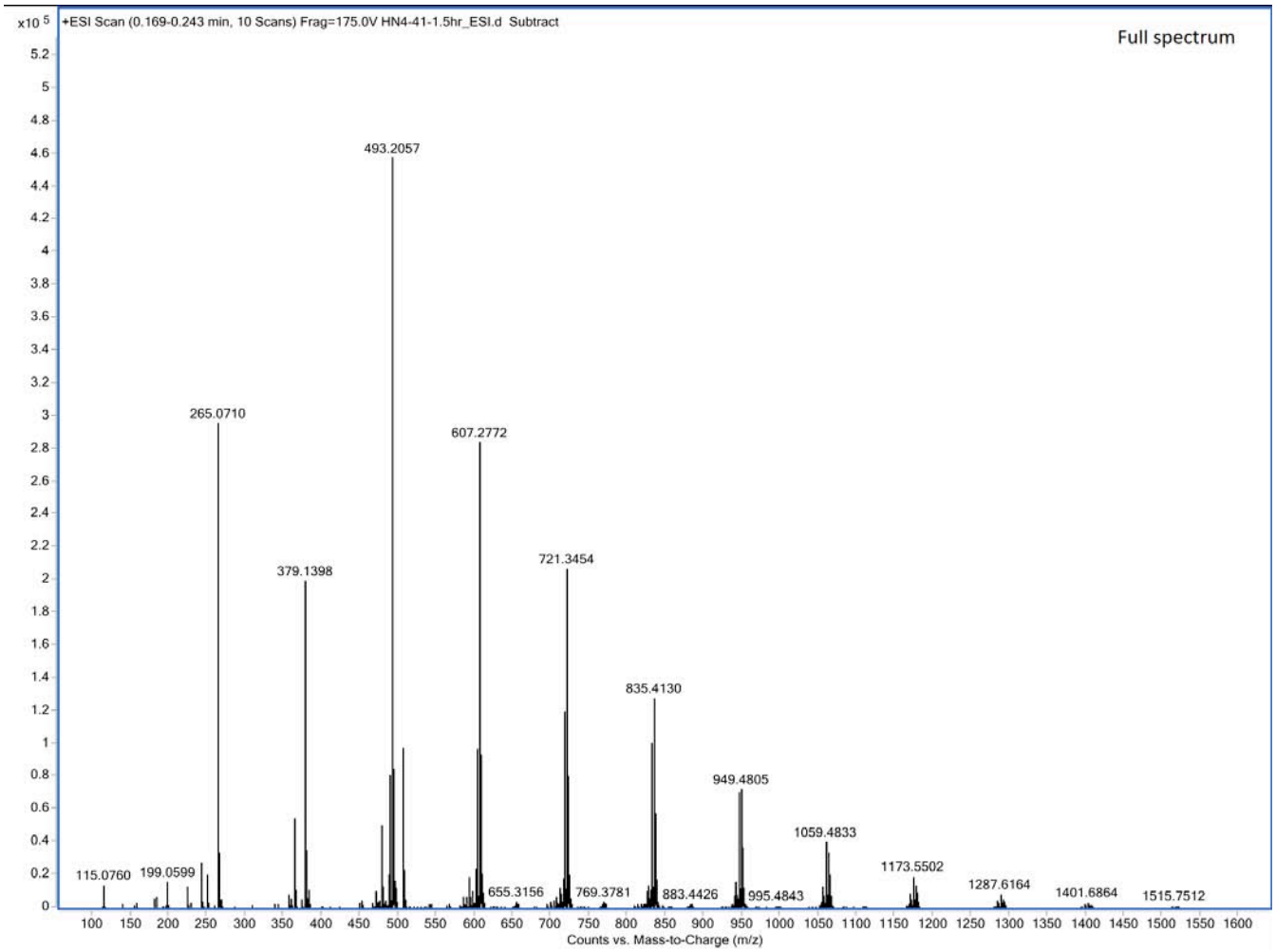


Figure S384. ESI spectra of copoly(caprolactone/hydroxyethylsyringic acid) [50:50] at 1.5 hours (Table S4, entry 5)

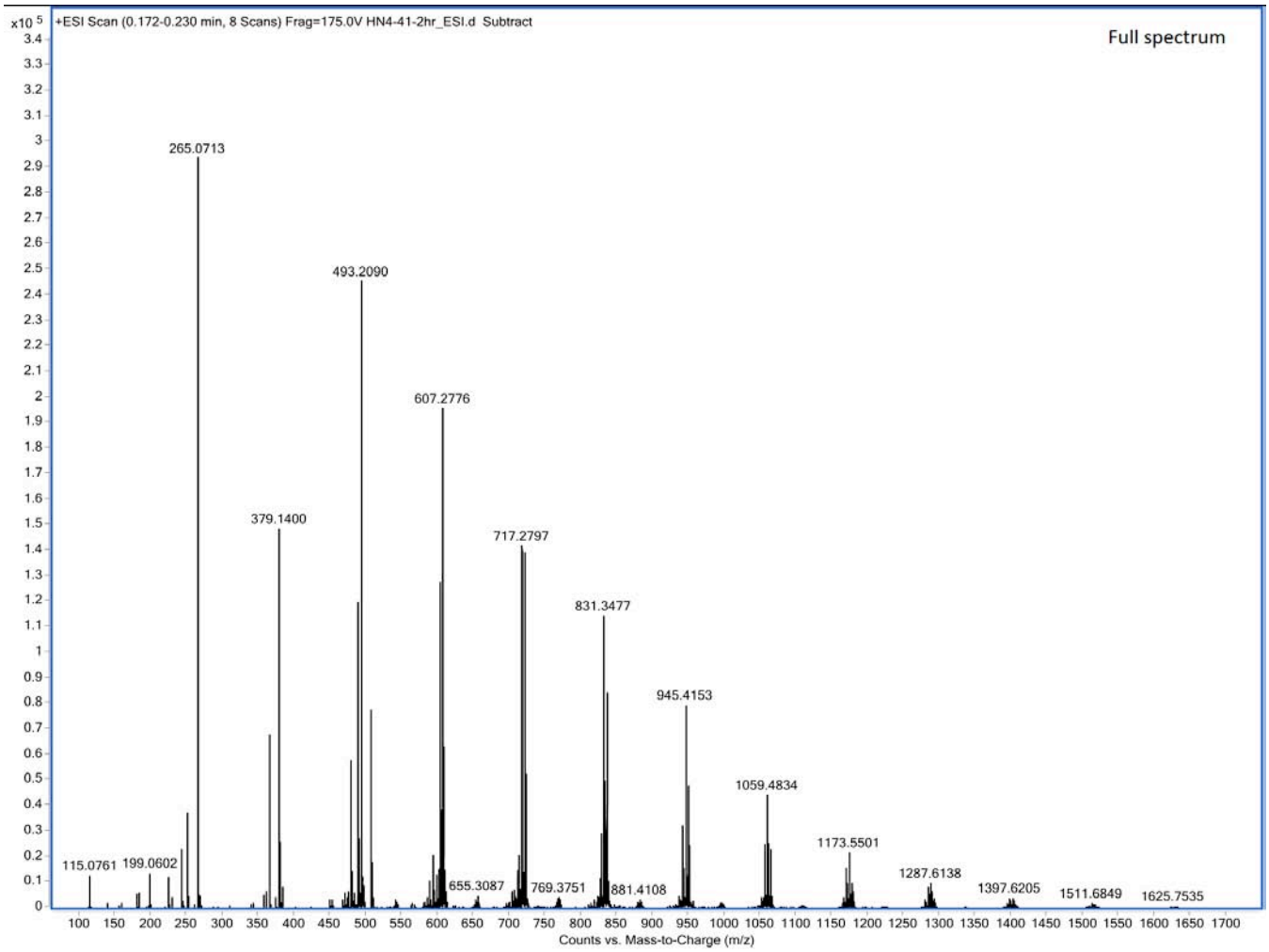


Figure S385. ESI spectra of copoly(caprolactone/hydroxyethylsyringic acid) [50:50] at 2 hours (Table S4, entry 6)

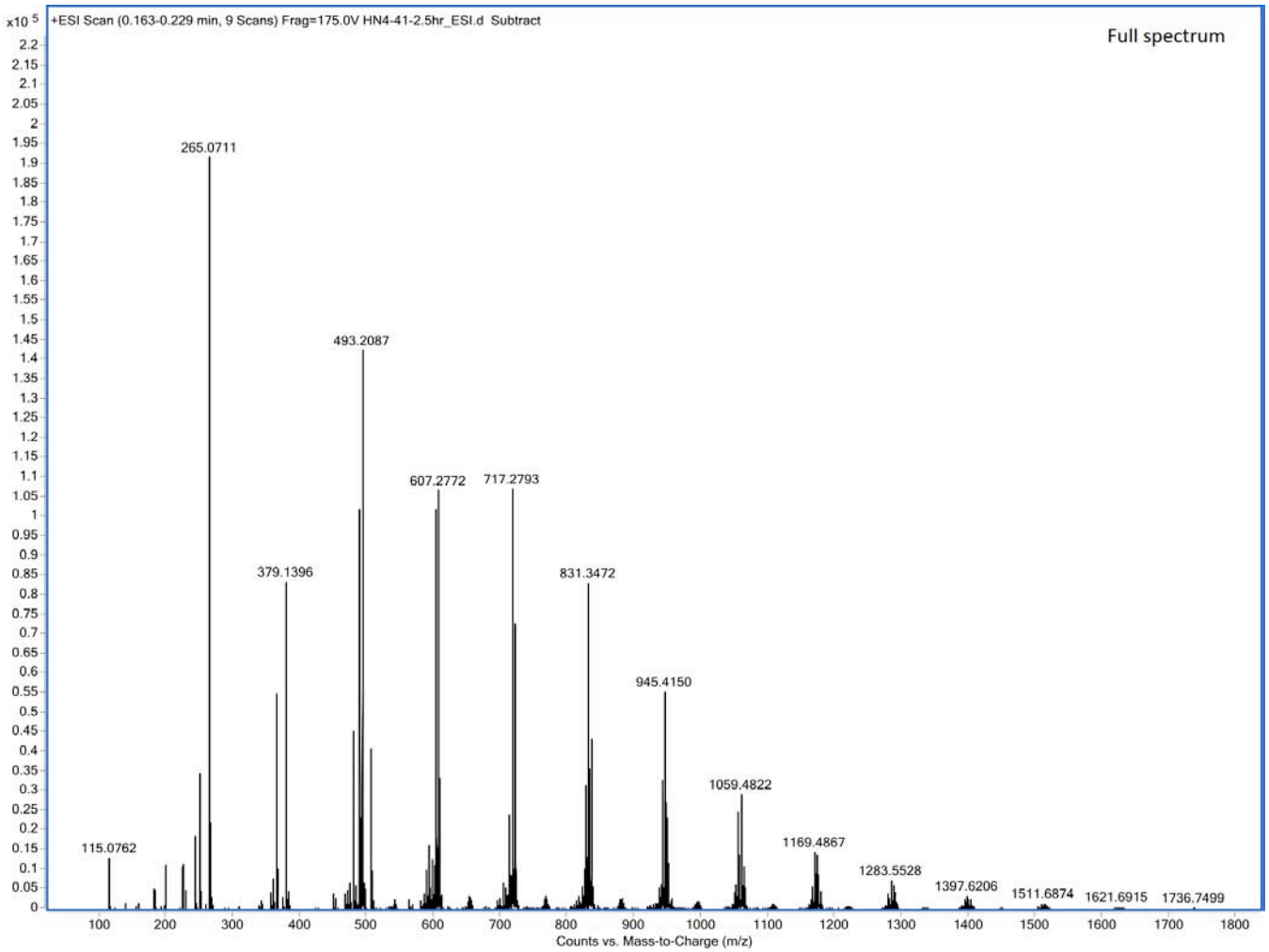


Figure S386. ESI spectra of copoly(caprolactone/hydroxyethylsyringic acid) [50:50] at 2.5 hours (Table S4, entry 7)

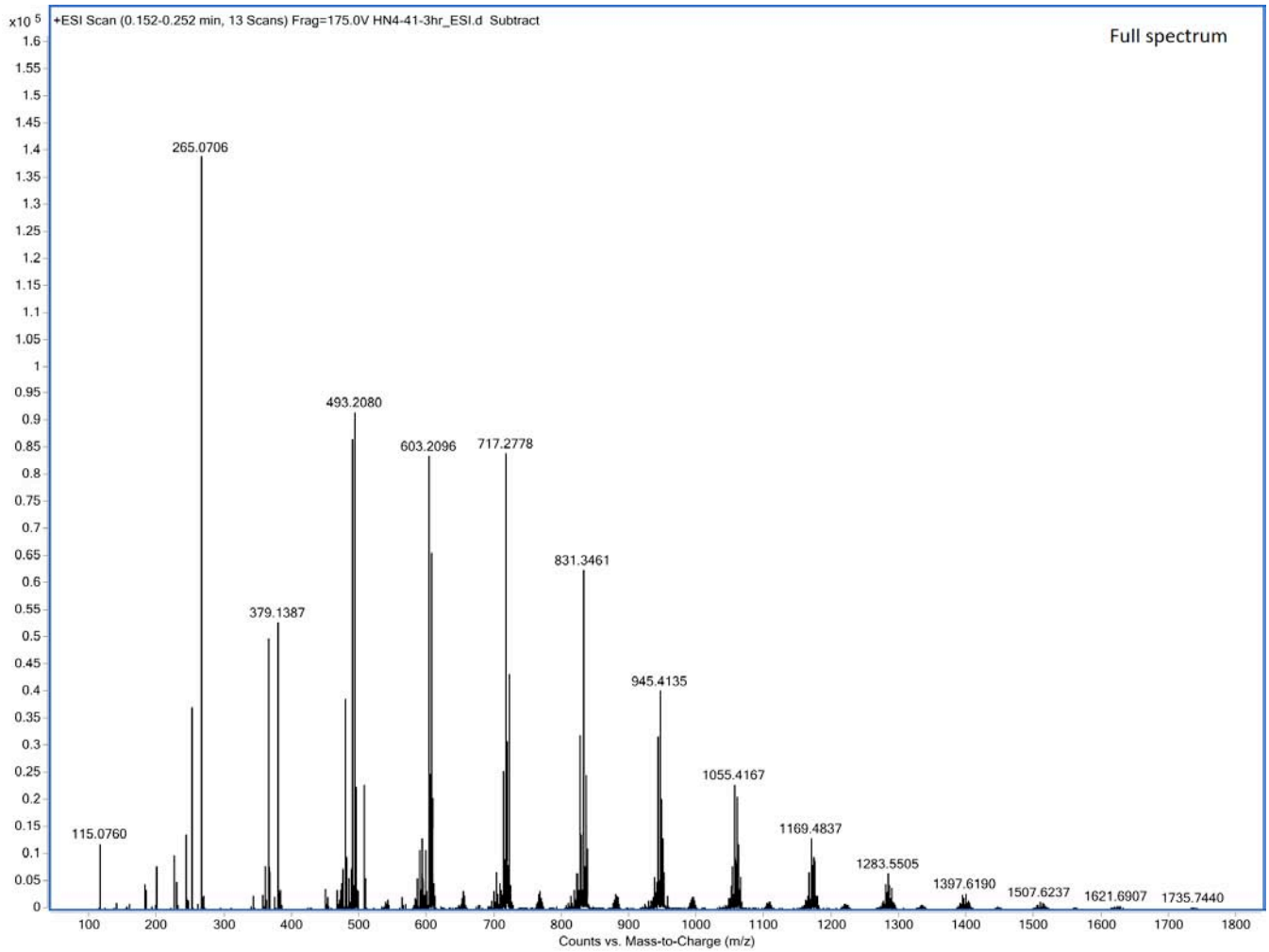


Figure S387. ESI spectra of copoly(caprolactone/hydroxyethylsyringic acid) [50:50] at 3 hours (Table S4, entry 8)

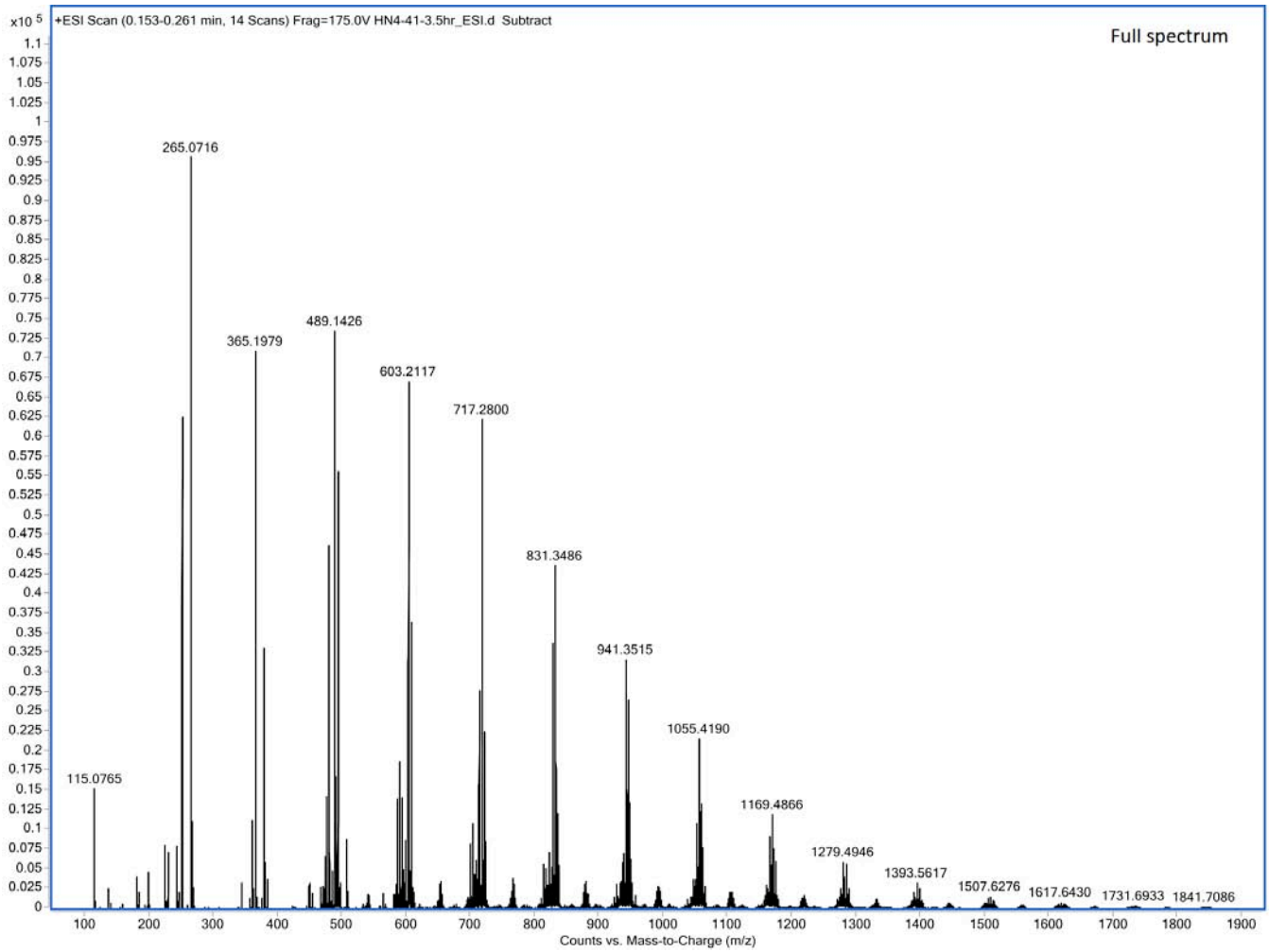


Figure S388. ESI spectra of copoly(caprolactone/hydroxyethylsyringic acid) [50:50] at 3.5 hours (Table S4, entry 9)

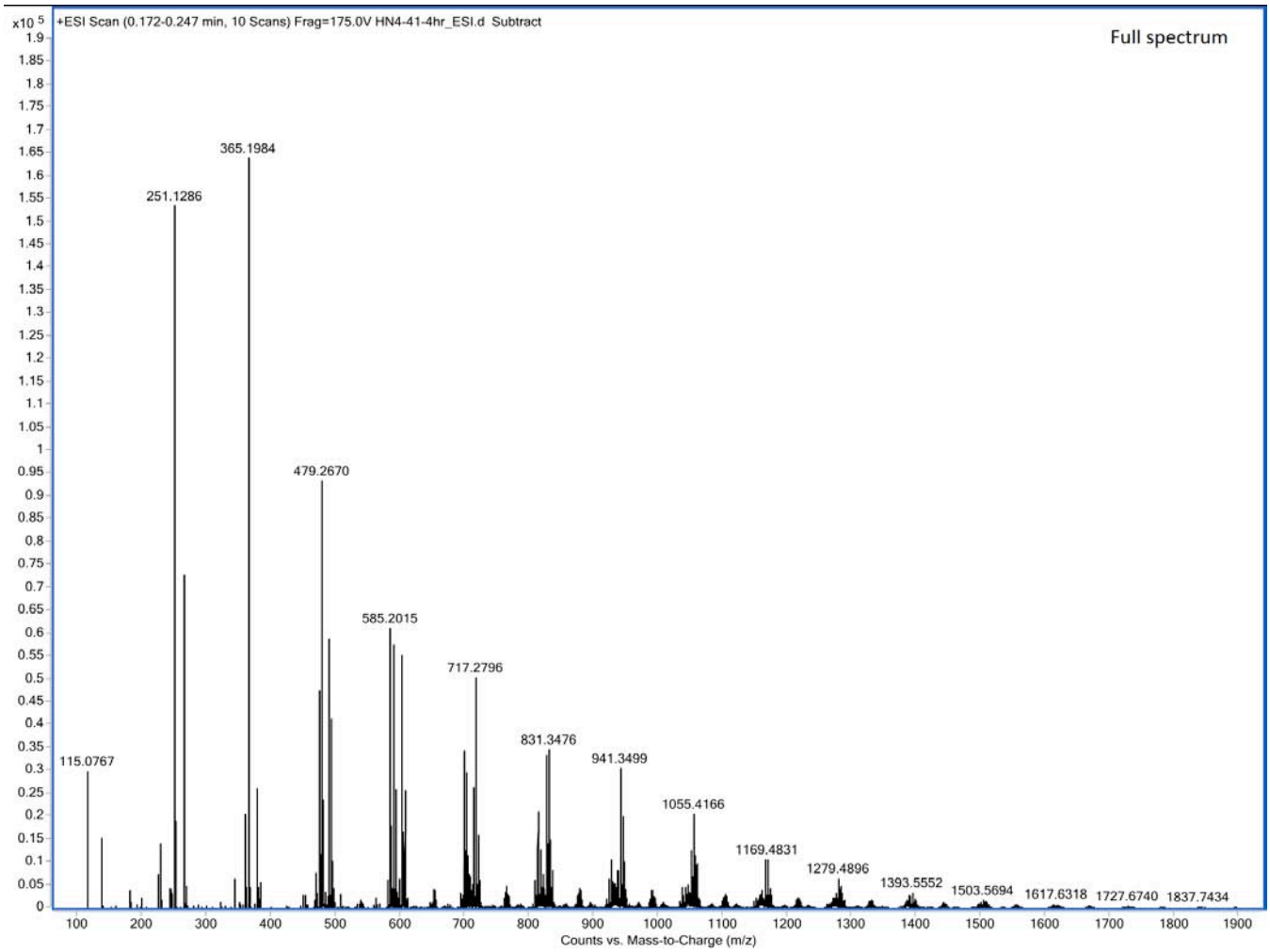


Figure S389. ESI spectra of copoly(caprolactone/hydroxyethylsyringic acid) [50:50] at 4 hours (Table S4, entry 10)