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Synthesis of Biorenewable and Water-Degradable Polylactam Esters from Itaconic Acid

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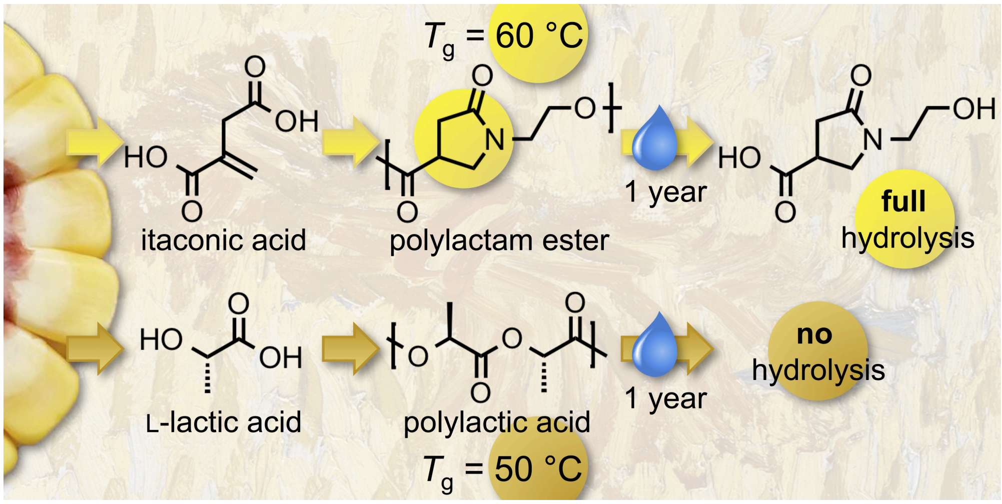
Supporting Information

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

Table of Contents



General Considerations and Instrumentation

Materials

Itaconic acid (99%) was purchased from Alfa Aesar and used without further purification. Ethanolamine (99%), Ethylene diamine (redistilled, 99.95+%), 1,3-propanediol(99.60+%), 1,4-butanediol(99%), 1,5-pentanediol(99%) and 1,6-hexanediol(99%) were bought from Sigma-Aldrich and used as received. Antimony Oxide (Sb_2O_3, 99.5%), the catalyst for polymerization, was purchased from Acros and used as received without any purification. Ethylene glycol, deionized water, acetone and concentrated aqueous HCl solution were purchased from Fisher Scientific. NMR solvents, including deuterated dimethyl sulfoxide (DMSO-d_6) and deuterium oxide (D_2O), 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, quintet; m, multiplet; br, broad.

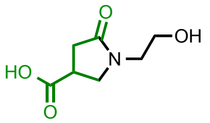
Differential scanning calorimetry thermograms were obtained with a DSC Q1000 from TA instruments. About 3-5 mg of each sample were massed and added to a sealed pan that passed through a heat/cool/heat cycle at 10 °C/min. Reported data are from the second full cycle. The temperature ranged from –50 to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

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

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

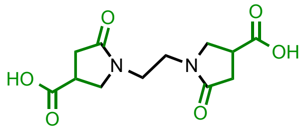
Monomer Preparation

N-(2-hydroxyethyl)-2-pyrrolidone-4-carboxylic acid (HEPC)



13.01 g (100.0 mmol) of itaconic acid was dissolved in 100 mL of water. 3.32 mL (55.0 mmol) of ethanolamine was added dropwise to the solution with continuous stirring. The mixture was refluxed overnight and cooled down to room temperature. After removing most of the solvent by rotary evaporation, ethanol was added and a white product started to precipitate. After filtration, the raw product was recrystallized in ethanol and dried under vacuum with a yield of 71%. ^{1}H NMR (500 MHz, DMSO-d_6): δ ppm 12.65 (br, 1H), 4.71 (br, 1H), 3.63 (t, *J* = 9.4 Hz, 1H), 3.53 (dd, *J* = 9.8, 6.1 Hz, 1H), 3.47 (t, *J* = 5.8 Hz, 2H), 3.27 – 3.14 (m, 3H), 2.44 (t, *J* = 7.3 Hz, 2H). ^{13}C NMR (125 MHz, DMSO-d_6): δ ppm 175.0, 172.4, 58.9, 49.9, 45.0, 36.0, 34.0.

Ethylene bis(pyrrolidone carboxylic acid) (EBPC)



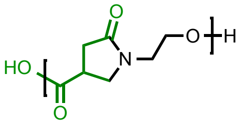
13.01 g (100.0 mmol) of itaconic acid was dissolved in 100 mL of water. 3.67 mL (55.0 mmol) of ethylene diamine was syringed out from the bottle and then added dropwise to the solution with continuous stirring. The mixture was refluxed overnight and cooled down to room temperature. The yellow product started to precipitate after removing three quarters of the solvent by rotary evaporation. 0.5 M of cold aqueous HCl solution was added to wash the product three times. The white powder was obtained by filtration and dried, affording a yield of 78%. ^{1}H NMR (500 MHz, DMSO-d_6): major diastereoisomer (1) (55%): δ ppm 12.61 (br, 2H), 3.58 (dd, *J* = 10.0, 10 Hz, 2H), 3.51 – 3.37 (m, 4H), 3.27 – 3.17 (m, 2H), 3.17 – 3.06 (m, 2H), 2.45 – 2.33 (m, 4H); minor diastereoisomer (2) (45%): δ ppm 12.61 (br, 2H), 3.55 (dd, *J* = 10.0, 10 Hz, 2H), 3.51 – 3.37 (m, 4H), 3.27 – 3.17 (m, 2H), 3.17 – 3.06 (m, 2H), 2.45 – 2.33 (m, 4H). ^{13}C NMR (125 MHz, DMSO-d_6): δ ppm 174.3, 172.3, 48.2, 38.8, 35.5, 33.4.

Polymerizations

Polymerization apparatus

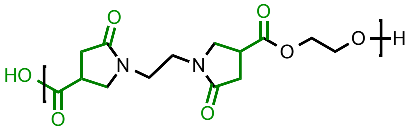
The polymerization was usually performed in a 25 mL round bottom flask, which was connected to a rotary evaporation bump trap, and together linked to a vacuum line. With this setup water, as the byproduct of condensation, can be collected and seen in the bump trap. Furthermore, all other volatile compounds could be removed without further treatment.

Poly(ethylene pyrrolidone carboxylate) (PEPC)



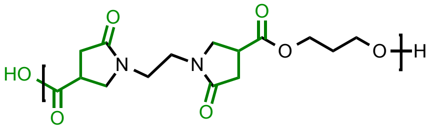
1.73 g (10.0 mmol) of monomer and 58.3 mg (2.0 mol %) Sb_2O_3 were added to a 25 mL round bottom flask and melted under a nitrogen atmosphere at 180 °C for 4 hours. Then dynamic vacuum was slowly introduced into the system to increase the reaction rate by removing byproduct (water) from the system and help shift the equilibrium to completion. The temperature was steadily increased from 180 °C to 240 °C over a period of 8 hours. After cooling down, the polymer was melted and removed without further purification, giving a milky white polymer in 84.3% yield. ^{1}H NMR (500 MHz, DMSO-d_6): δ ppm 4.18 (t, *J* = 5.2 Hz, 2H), 3.62 (t, *J* = 9.0 Hz, 1H), 3.53 (dd, *J* = 9.8, 5.6 Hz, 1H), 3.44 (s, 2H), 3.27 (p, *J* = 7.8 Hz, 1H), 2.56 – 2.38 (m, 2H). ^{13}C NMR (125 MHz, DMSO-d_6): δ 172.7, 172.2, 61.6, 48.5, 40.8, 35.4, 33.1.

Polyethylene/[ethylene bis(pyrrolidone carboxylate)]



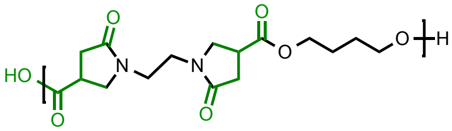
2.843 g (10.0 mmol) of ethylene bis(pyrrolidone carboxylic acid), 0.745 g (12.0 mmol) of ethylene glycol and 58.3 mg (2.0 mol %) Sb_2O_3 were added to a 25 mL round bottom flask and melted under a nitrogen atmosphere at 180 °C for 4 hours. Then dynamic vacuum was slowly introduced into the system to increase the reaction rate by removing byproduct (water) from the system and help shift the equilibrium to completion. The temperature was steadily increased from 180 °C to 240 °C over a period of 8 hours. After cooling down, the polymer was melted and removed without further purification, giving a brown polymer in 88.3% yield. ^1H NMR (500 MHz, DMSO-*d*$_6$): δ ppm 4.29 (s, 4H), 3.61 (q, *J* = 8.7 Hz, 2H), 3.52 – 3.43 (m, 2H), 3.39 (d, *J* = 9.4 Hz, 2H), 3.29 – 3.18 (m, 4H), 2.48 – 2.34 (m, 4H). ^{13}C NMR (125 MHz, DMSO-*d*$_6$): δ ppm 172.7, 172.1, 62.5, 47.9, 38.7, 35.4, 33.2.

Polypropylene/[ethylene bis(pyrrolidone carboxylate)]



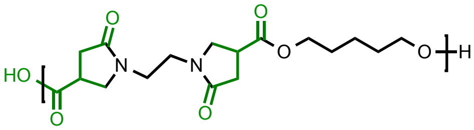
2.843 g (10.0 mmol) of ethylene bis(pyrrolidone carboxylic acid), 0.837 g (11.0 mmol) of 1,3-propanediol and 58.3 mg (2.0 mol %) Sb_2O_3 were added to a 25 mL round bottom flask and melted under a nitrogen atmosphere at 180 °C for 4 hours. Then dynamic vacuum was slowly introduced into the system to increase the reaction rate by removing byproduct (water) from the system and help shift the equilibrium to completion. The temperature was steadily increased from 180 °C to 240 °C over a period of 8 hours. After cooling down, the polymer was melted and removed without further purification, giving a brown polymer in 89.8% yield. ^1H NMR (500 MHz, DMSO-*d*$_6$): δ ppm 4.14 (t, *J* = 6.4 Hz, 4H), 3.60 (q, *J* = 9.3 Hz, 2H), 3.51 – 3.42 (m, 2H), 3.37 (d, *J* = 9.5 Hz, 2H), 3.29 – 3.18 (m, 4H), 2.49 – 2.34 (m, 4H), 1.94 (t, *J* = 6.4 Hz, 2H). ^{13}C NMR (125 MHz, DMSO-*d*$_6$): δ ppm 172.7, 172.1, 61.4, 48.0, 38.7, 35.4, 33.2, 27.4.

Polybutylene/[ethylene bis(pyrrolidone carboxylate)]



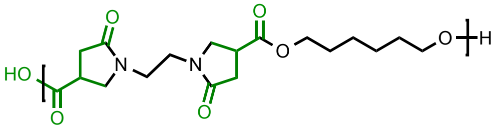
2.843 g (10.0 mmol) of ethylene bis(pyrrolidone carboxylic acid), 0.991 g (11.0 mmol) of 1,4-butanediol and 58.3 mg (2.0 mol %) Sb_2O_3 were added to a 25 mL round bottom flask and melted under a nitrogen atmosphere at 180 °C for 4 hours. Then dynamic vacuum was slowly introduced into the system to increase the reaction rate by removing byproduct (water) from the system and help shift the equilibrium to completion. The temperature was steadily increased from 180 °C to 240 °C over a period of 8 hours. After cooling down, the polymer was melted and removed without further purification, giving a brown polymer in 87.6% yield. ^1H NMR (500 MHz, DMSO-*d*$_6$): δ 4.09 (s, 4H), 3.60 (q, *J* = 9.6 Hz, 2H), 3.54 – 3.42 (m, 2H), 3.38 (d, *J* = 9.7 Hz, 2H), 3.29 – 3.16 (m, 4H), 2.49 – 2.29 (m, 4H), 1.65 (s, 4H). ^{13}C NMR (125 MHz, DMSO-*d*$_6$): δ ppm 172.7, 172.1, 64.2, 48.0, 38.7, 35.4, 33.2, 24.6.

Polypentylene/[ethylene bis(pyrrolidone carboxylate)]



2.843 g (10.0mmol) of ethylene bis(pyrrolidone carboxylic acid), 1.094 g (10.5 mmol) of 1,5-heptanediol and 58.3 mg (2.0 mol %) Sb_2O_3 were added to a 25 mL round bottom flask and melted under a nitrogen atmosphere at 180 °C for 4 hours. Then dynamic vacuum was slowly introduced into the system to increase the reaction rate by removing byproduct (water) from the system and help shift the equilibrium to completion. The temperature was steadily increased from 180 °C to 240 °C over a period of 8 hours. After cooling down, the polymer was melted and removed without further purification, giving a brown polymer in 90.8% yield. ^1H NMR (500 MHz, DMSO-*d*$_6$): δ ppm 4.06 (t, *J* = 6.5 Hz, 4H), 3.60 (q, *J* = 9.3 Hz, 2H), 3.51 – 3.43 (m, 2H), 3.38 (d, *J* = 9.5 Hz, 2H), 3.28 – 3.15 (m, 4H), 2.49 – 2.30 (m, 4H), 1.61 (quint, *J* = 7.0 Hz, 4H), 1.36 (quint, *J* = 7.4 Hz, 2H). ^{13}C NMR (125 MHz, DMSO-*d*$_6$): δ ppm 172.7, 172.1, 64.4, 48.0, 38.8, 35.5, 33.24, 27.6, 21.8.

Polyhexylene/[ethylene bis(pyrrolidone carboxylate)]



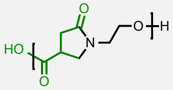
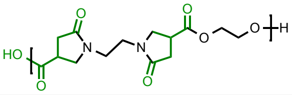
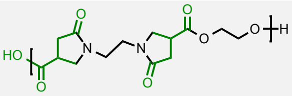
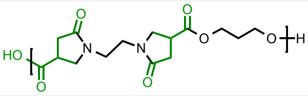
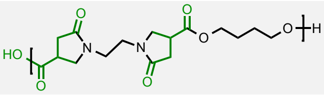
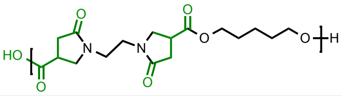
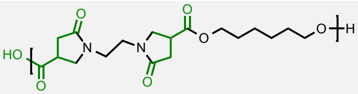
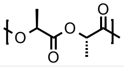
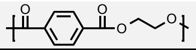
2.843 g (10.0 mmol) of ethylene bis(pyrrolidone carboxylic acid), 1.241 g (10.5 mmol) of 1,6-hexanediol and 58.3 mg (2.0 mol %) Sb_2O_3 were added to a 25 mL round bottom flask and melted under a nitrogen atmosphere at 180 °C for 4 hours. Then dynamic vacuum was slowly introduced into the system to increase the reaction rate by removing byproduct (water) from the system and help shift the equilibrium to completion. The temperature was steadily increased from 180 °C to 240 °C over a period of 8 hours. After cooling down, the polymer was melted and removed without further purification, giving a brown polymer in 86.2% yield. ^1H NMR (500 MHz, DMSO-*d*$_6$): δ ppm 4.04 (t, *J* = 6.6 Hz, 4H), 3.59 (q, *J* = 9.2 Hz, 2H), 3.49 – 3.41 (m, 2H), 3.37 (d, *J* = 9.4 Hz, 2H), 3.27 – 3.14 (m, 4H), 2.46 – 2.30 (m, 4H), 1.57 (t, *J* = 6.7 Hz, 4H), 1.31 (s, 4H). ^{13}C NMR (125 MHz, DMSO-*d*$_6$): δ ppm 172.7, 172.1, 64.5, 48.0, 38.7, 35.5, 33.2, 27.9, 24.9.

Degradation study

Six different polylactam esters (Table S1, Entries 1 and 3–7) were molded into approximately 5 mm flattened pellets and placed in scintillation vials with ~10 mL deionized water. The vials were continuously shaken on an orbital shaker. For comparison, a set of the same polymers was stored in scintillation vials with air-permeable caps. The molecular weight and structure of these polymers were analyzed by GPC and ^1H NMR, initially and after one year. A detailed degradation study of polypropylene/[ethylene bis(pyrrolidone carboxylate)] (Table S1, Entry 4) was conducted by GPC and ^1H NMR at the initial time, and subsequent times of 15 days, 30 days, 90 days, 180 days, and 360 days. Samples were prepared by taking 0.5 mL of the solution and drying under dynamic vacuum at room temperature before analysis. Note that the polymers agitated in water all fully dissolved within 30 days.

Summary of Polymerization Data

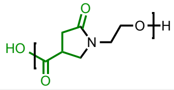
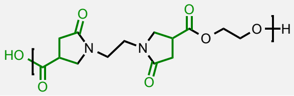
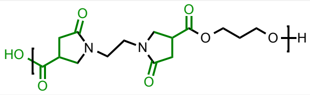
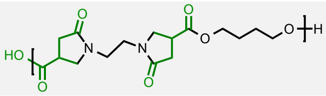
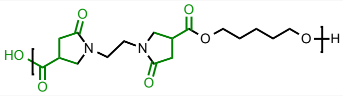
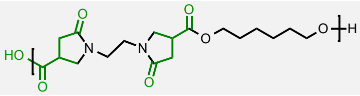
Table S1. Molecular weight and thermal data for PEPC (Entry 1), PAEBPC polymers made from diols of varying length (Entries 2–7), and commercial samples of PLA (Entry 8) and PET (Entry 9).[a]

Entry	Polymers	monomer ratio (diacid:diol)	Yield (%)	M_n [b] (Da)	M_w [b] (Da)	PDI [b]	T_g (°C) [c]	T_{50} (°C) [d]
1			84	20,800	44,700	2.1	60	387
2		1.0:1.0	63	10,000	40,800	4.1	56	359
3		1.0:1.2	88	23,200	52,500	2.3	62	374
4		1.0:1.1	90	19,500	50,300	2.6	50	368
5		1.0:1.1	88	24,900	59,800	2.4	39	373
6		1.0:1.05	91	21,200	47,300	2.2	29	373
7		1.0:1.05	86	23,400	78,200	3.3	24	376
8		commercial sample[e]		91,200	201,800	2.2	52	343
9		commercial sample[f]		34,100	75,500	2.2	83	414

[a] With 2.0 mol % Sb_2O_3, 180°C under nitrogen for 4 hours, followed by a temperature ramp over 8 hours to 240°C with dynamic vacuum. [b] GPC in hexafluoroisopropanol (HFIP) at 40°C vs. polymethyl methacrylate standards. [c] Determined by DSC. [d] TGA temperature at which 50% mass loss was observed under nitrogen. [e] Ingeo® PLA cup sample from NatureWorks, LLC. [f] Bottle grade PET copolymer from Trader Joe's® Natural Mountain Spring Water.

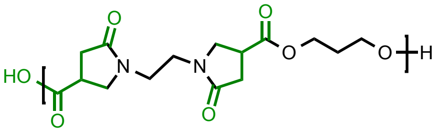
Summary of Polymer Degradation Data

Table S2. Molecular weight data of original polymers and corresponding degraded polymers after agitation in deionized water for one year.[a]

Entry	Polymers	Original polymer			Degraded polymer after one year		
		M_n (Da)	M_w (Da)	PDI	M_n (Da)	M_w (Da)	PDI
1		20,800	44,700	2.1	490	1,030	2.1
2		23,200	52,500	2.3	570	680	1.2
3		19,500	50,300	2.6	570	690	1.2
4		24,900	59,800	2.4	570	680	1.2
5		21,200	47,300	2.2	530	690	1.3
6		23,400	78,200	3.3	520	690	1.3

[a] Obtained by GPC in hexafluoroisopropanol (HFIP) at 40°C versus polymethyl methacrylate standards.

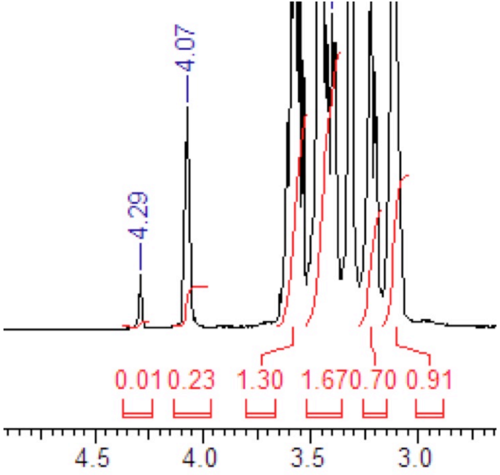
Table S3. Time dependent degradation study of polypropylene/[ethylene bis(pyrrolidone carboxylate)] (Table S2, Entry 3).



Entry	Time (Days)	M_n (Da)[a]	
		Polymer in water	Polymer in air
1	0	19,500	19,500
2	15	17,100	19,400
3	30	14,000	19,000
4	90	10,400	18,800
5	180	5,900	18,200
6	360	570	17,600

[a] Obtained by GPC in hexafluoroisopropanol (HFIP) at 40°C versus polymethyl methacrylate standards.

After one year, the ethylene glycol CH_2 peaks from the PEEBPC polymer integrate to 0.01, while the ethylene glycol CH_2 peaks from ethylene glycol itself integrate to 0.23. Thus, the extent of degradation is 0.23/(0.01+0.23) = 96%. See the NMR spectrum of Figure S5, part of which is below. This is the same ^1H NMR spectrum in Figure 3 (middle) of the main paper.



^{1}H NMR Spectra

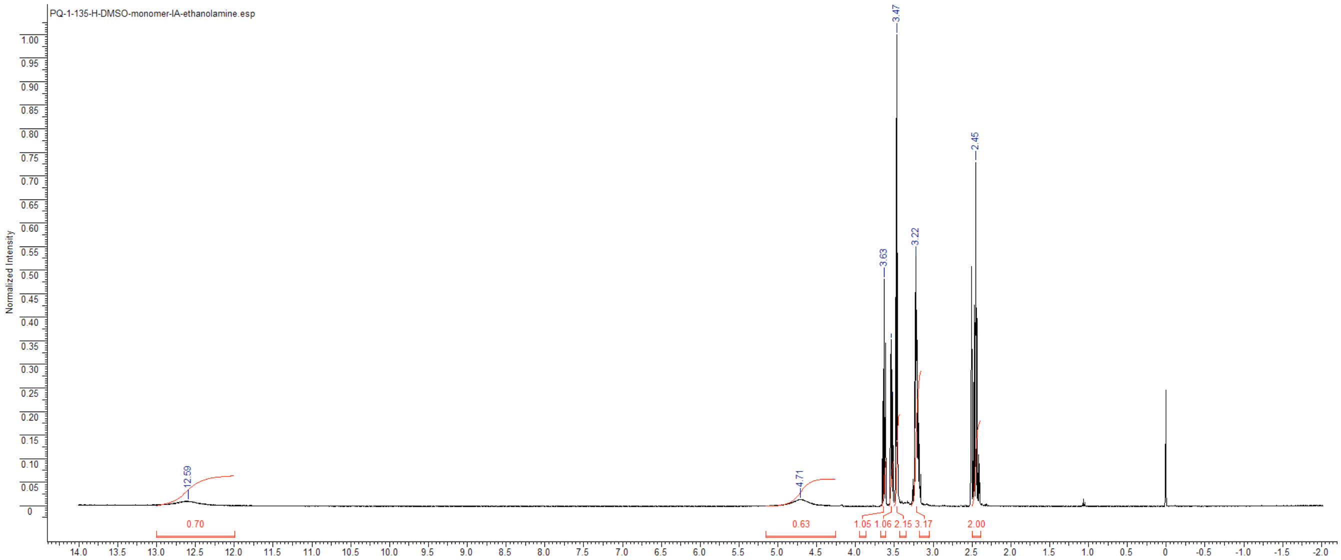


Figure S1. ^{1}H NMR spectrum of *N*-(2-hydroxyethyl)-2-pyrrolidone-4-carboxylic acid.

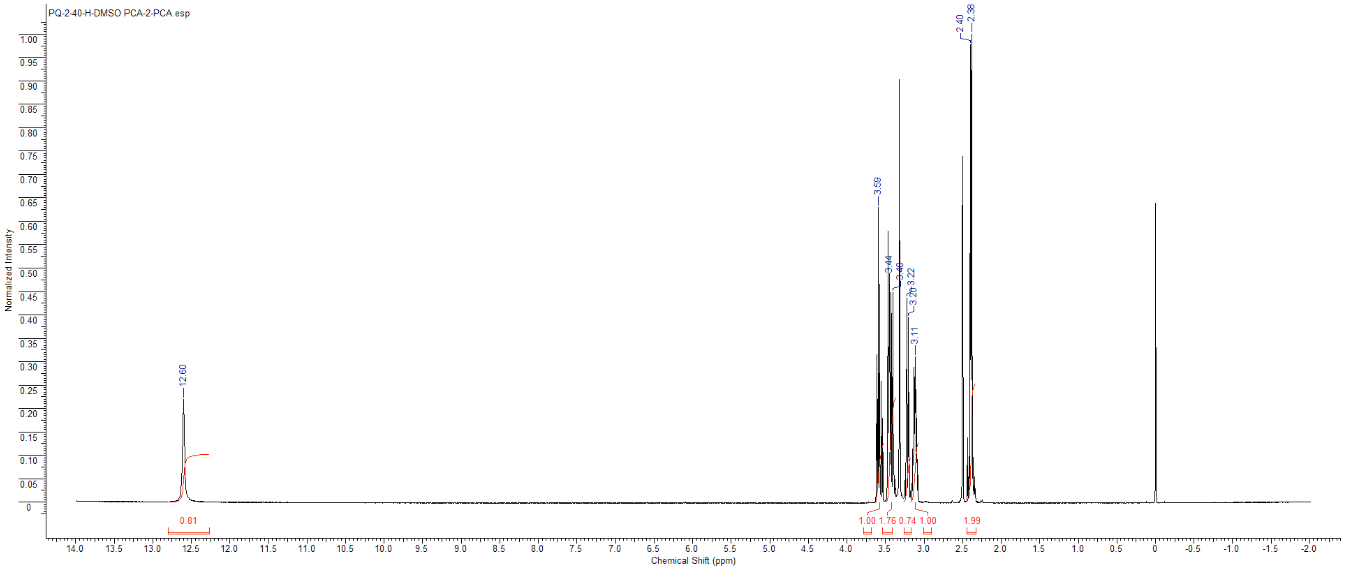


Figure S2. ^{1}H NMR spectrum of Ethylene bis(pyrrolidone carboxylic acid) (EBPC).

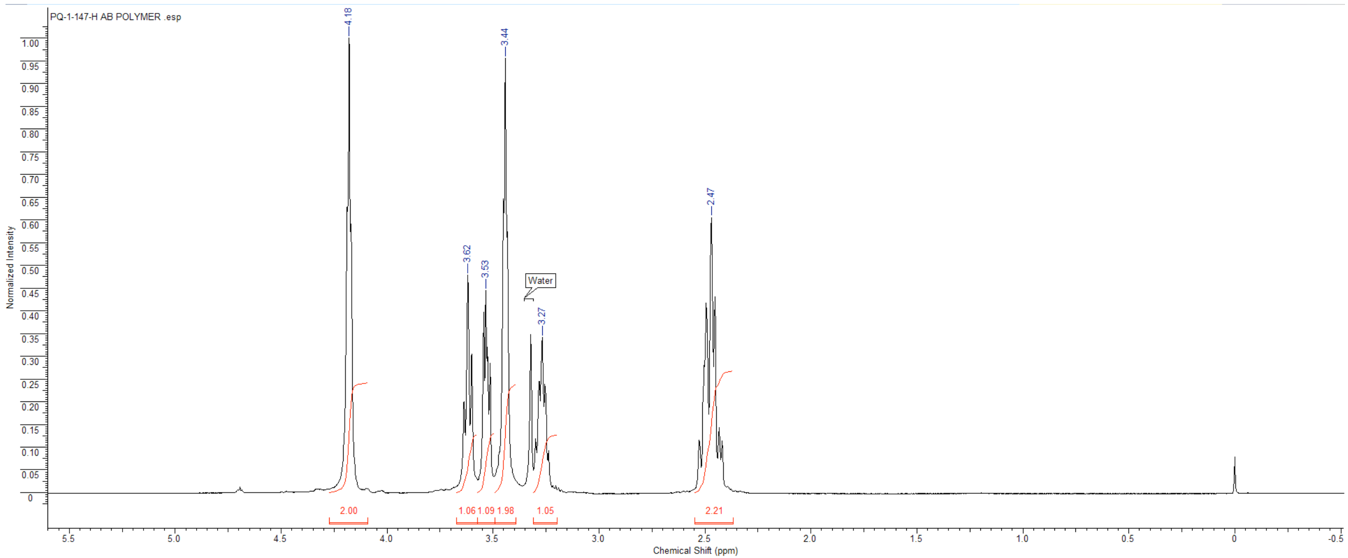


Figure S3. ^{1}H NMR spectrum of Poly(ethylene pyrrolidone carboxylate) (Table S1, Entry 1).

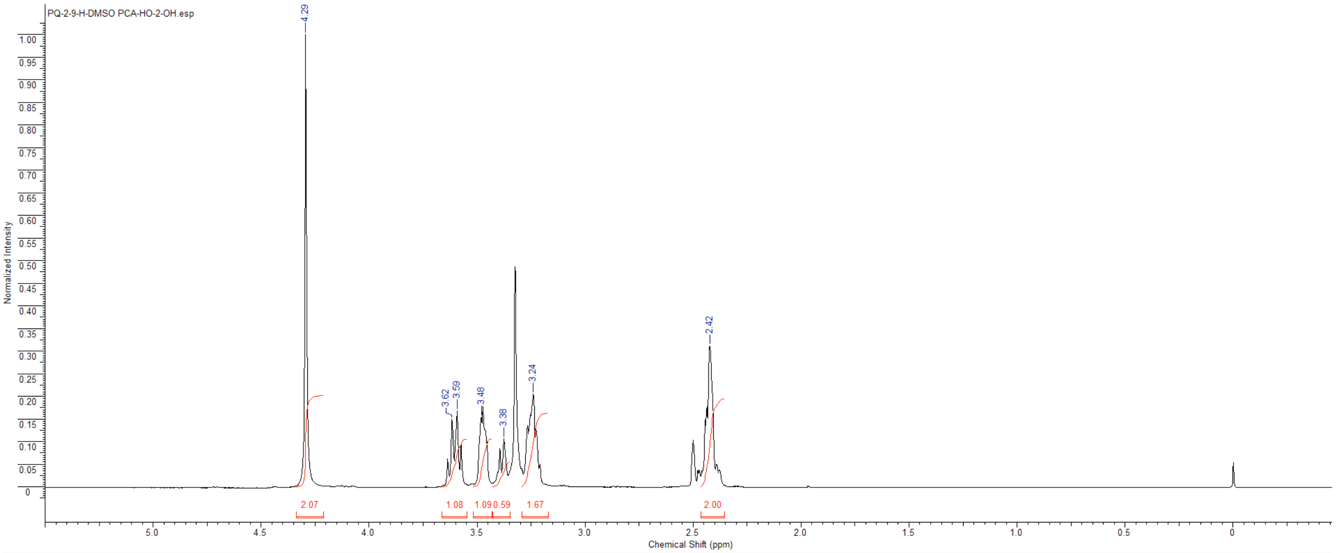


Figure S4. ^{1}H NMR spectrum of Polyethylene/[ethylene bis(pyrrolidone carboxylate)] (Table S1, Entry 3).

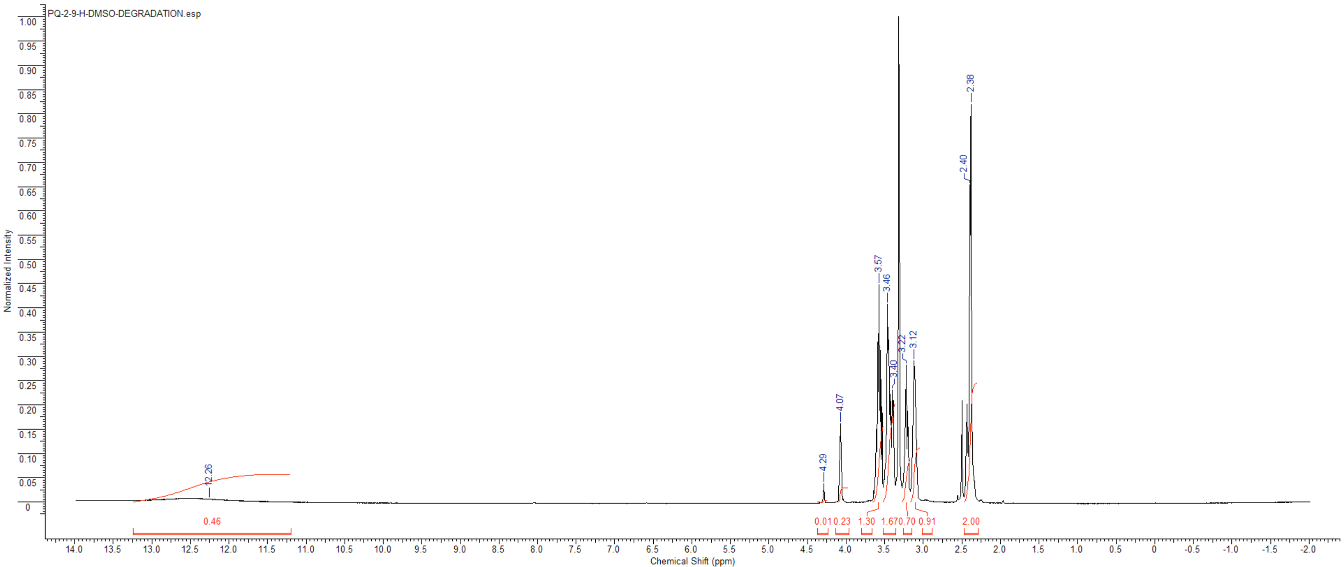


Figure S5. ^{1}H NMR spectrum of degraded Polyethylene/[ethylene bis(pyrrolidone carboxylate)] after a year.

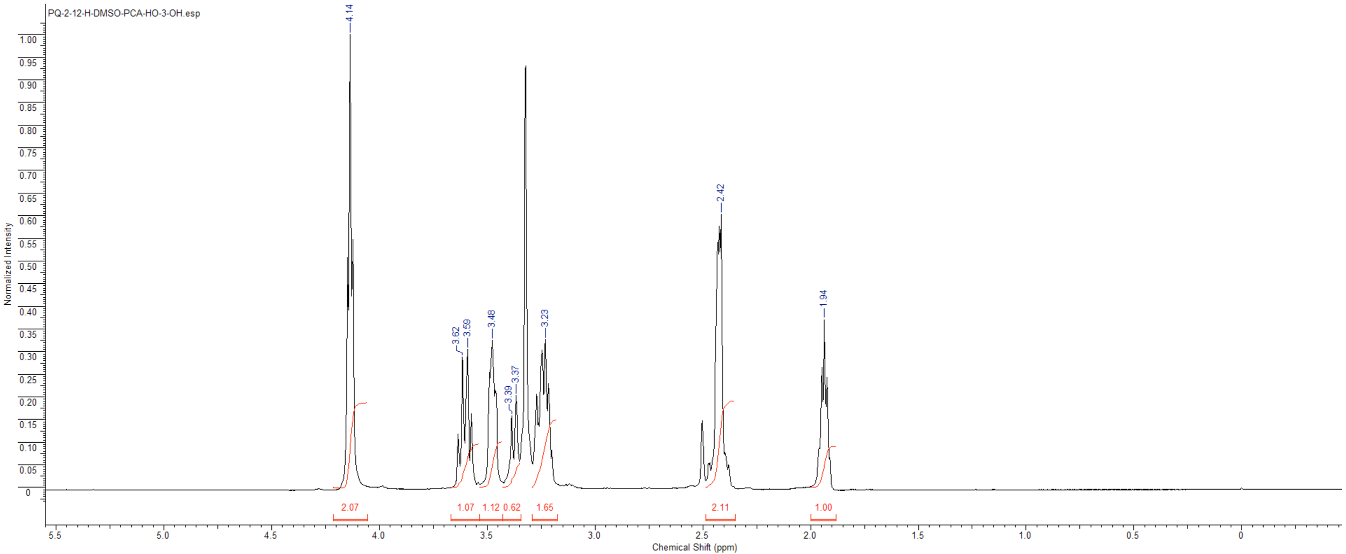


Figure S6. ^{1}H NMR spectrum of Polypropylene/[ethylene bis(pyrrolidone carboxylate)] (Table S1, Entry 4).

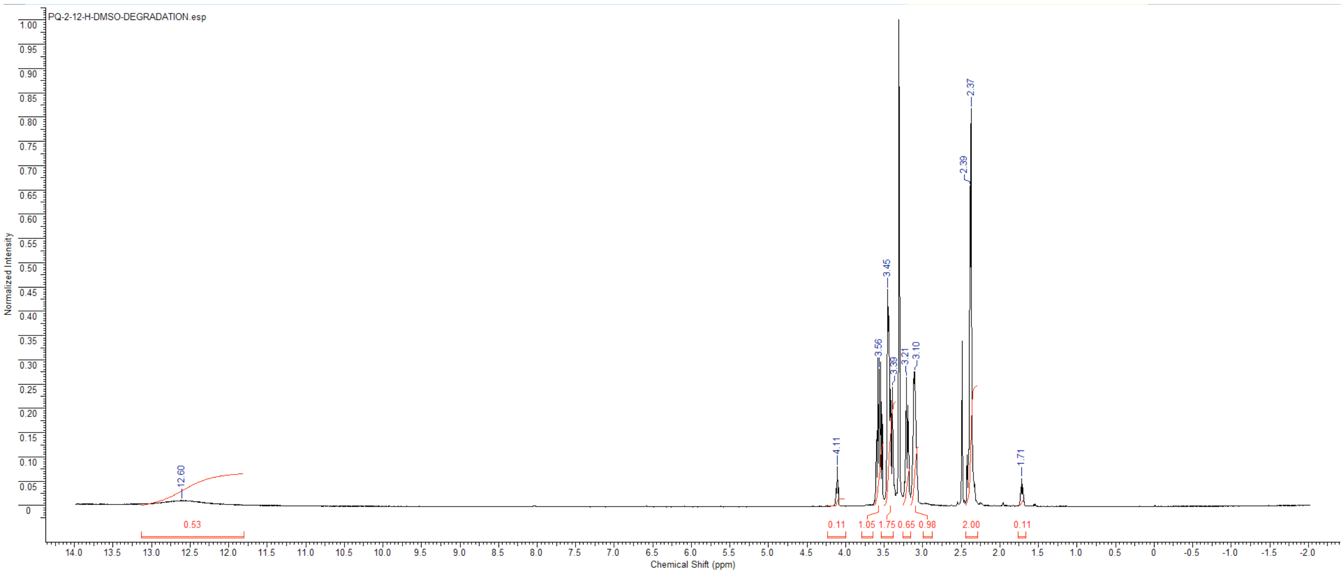


Figure S7. ^{1}H NMR spectrum of degraded Polypropylene/[ethylene bis(pyrrolidone carboxylate)] after a year.

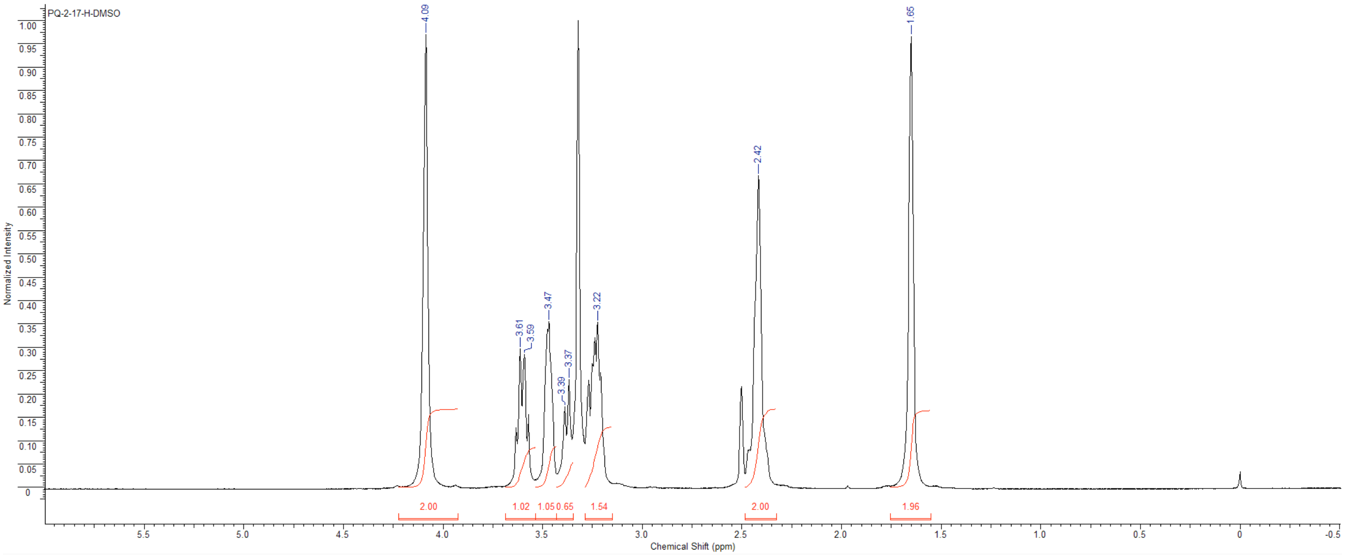


Figure S8. ^{1}H NMR spectrum of Polybutylene/[ethylene bis(pyrrolidone carboxylate)] (Table S1, Entry 5).

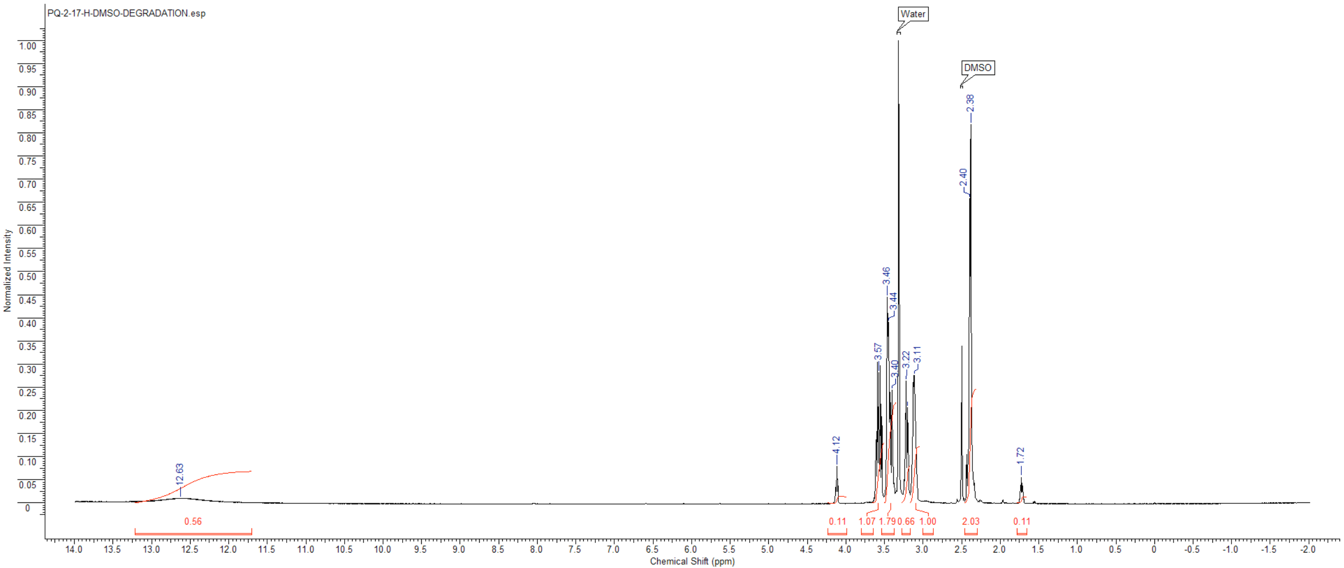


Figure S9. ^{1}H NMR spectrum of degraded Polybutylene/[ethylene bis(pyrrolidone carboxylate)] after a year.

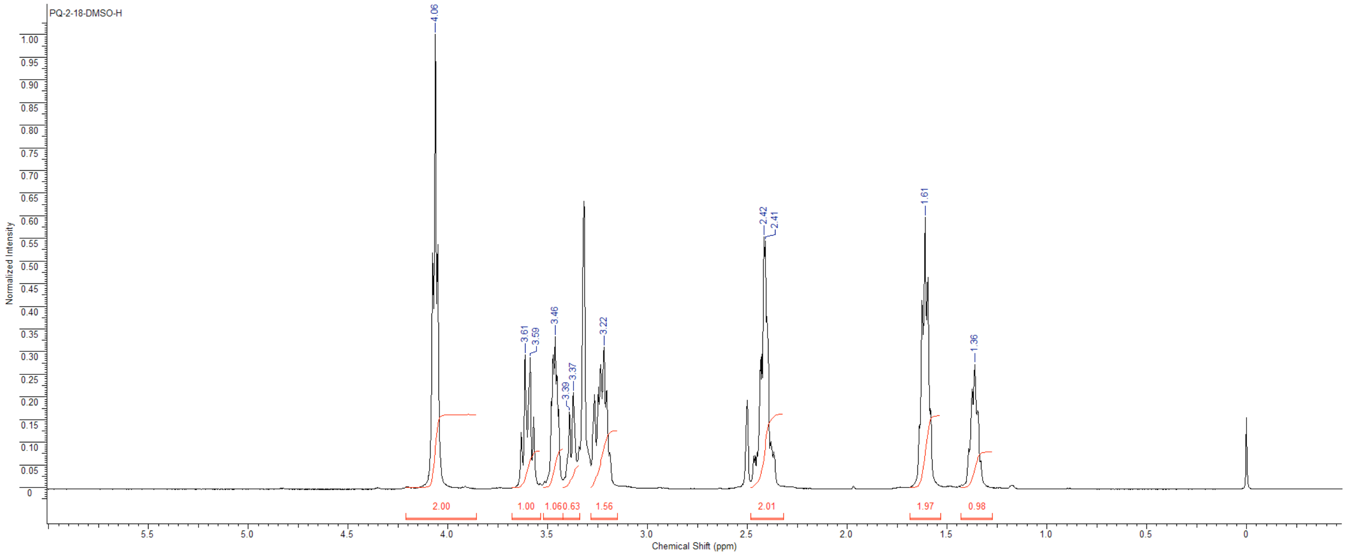


Figure S10. ^{1}H NMR spectrum of Polypentylene/[ethylene bis(pyrrolidone carboxylate)] (Table S1, Entry 6).

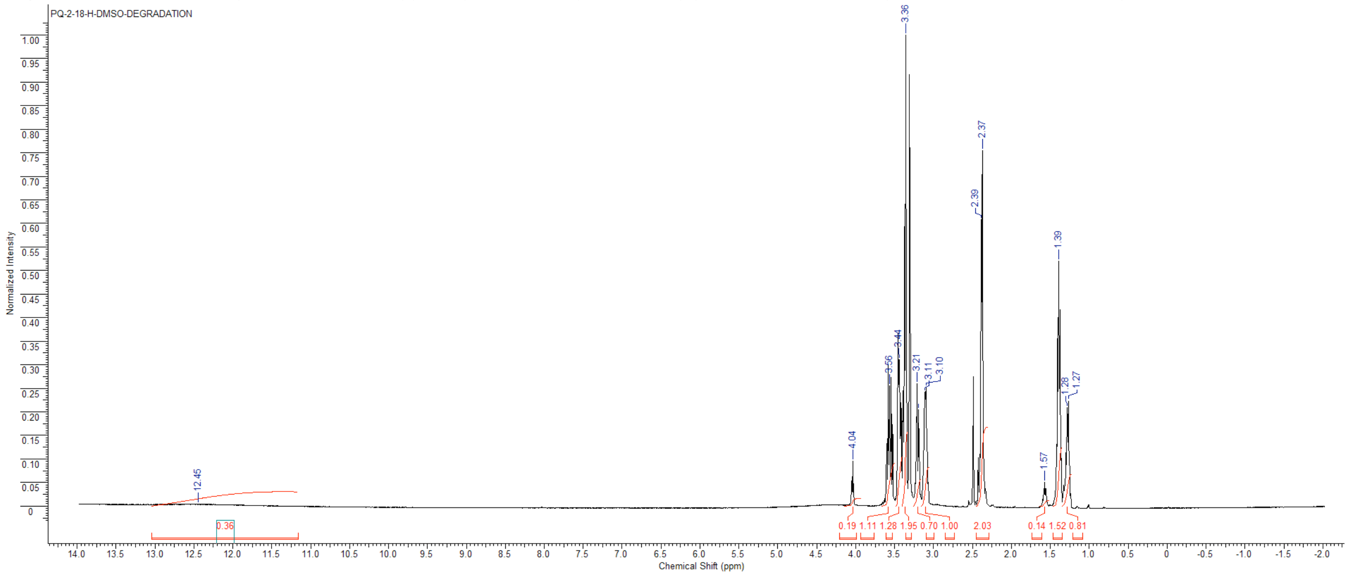


Figure S11. ^{1}H NMR spectrum of degraded Polypentylene/[ethylene bis(pyrrolidone carboxylate)] after a year.

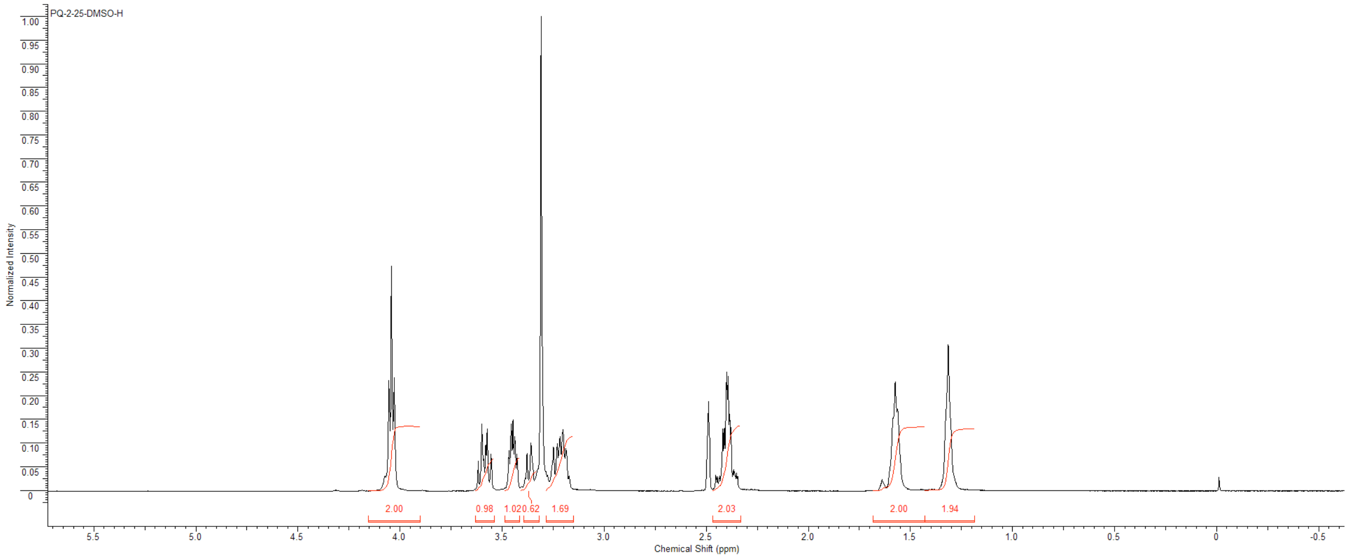


Figure S12. ^{1}H NMR spectrum of Polyhexylene/[ethylene bis(pyrrolidone carboxylate)] (Table S1, Entry 7).

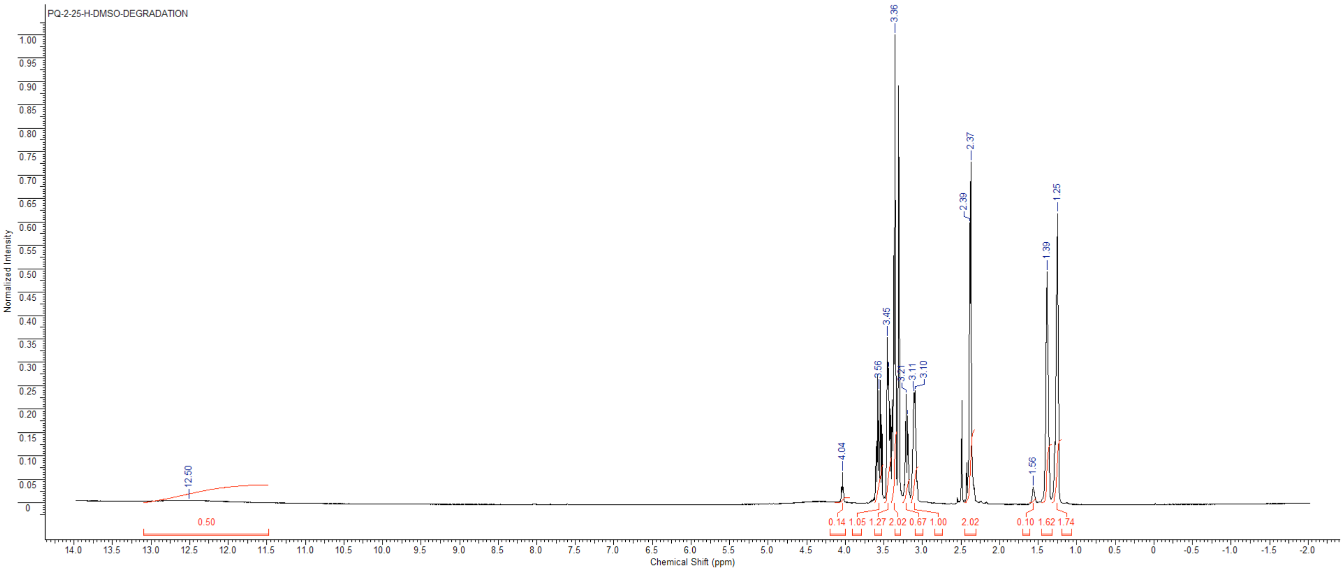


Figure S13. ^{1}H NMR spectrum of degraded Polyhexylene/[ethylene bis(pyrrolidone carboxylate)] after a year.

^{13}C NMR Spectra

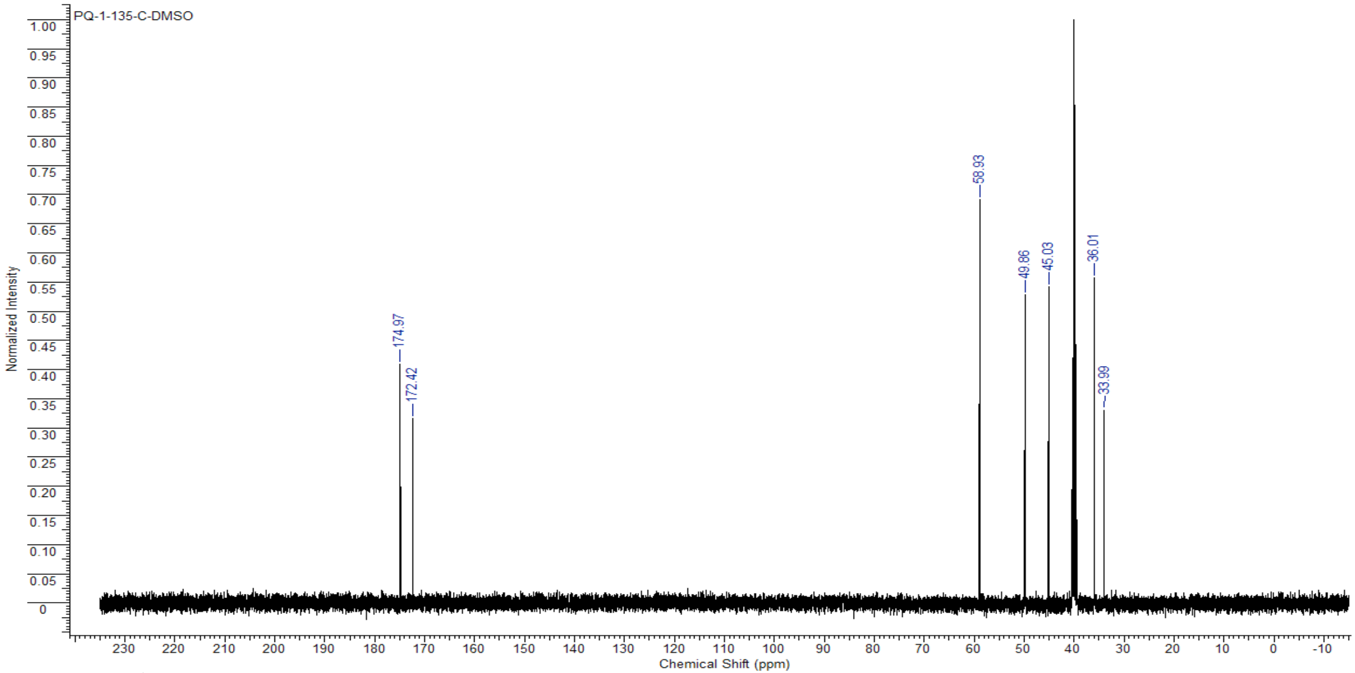


Figure S14. ^{13}C NMR spectrum of *N*-(2-hydroxyethyl)-2-pyrrolidone-4-carboxylic acid.

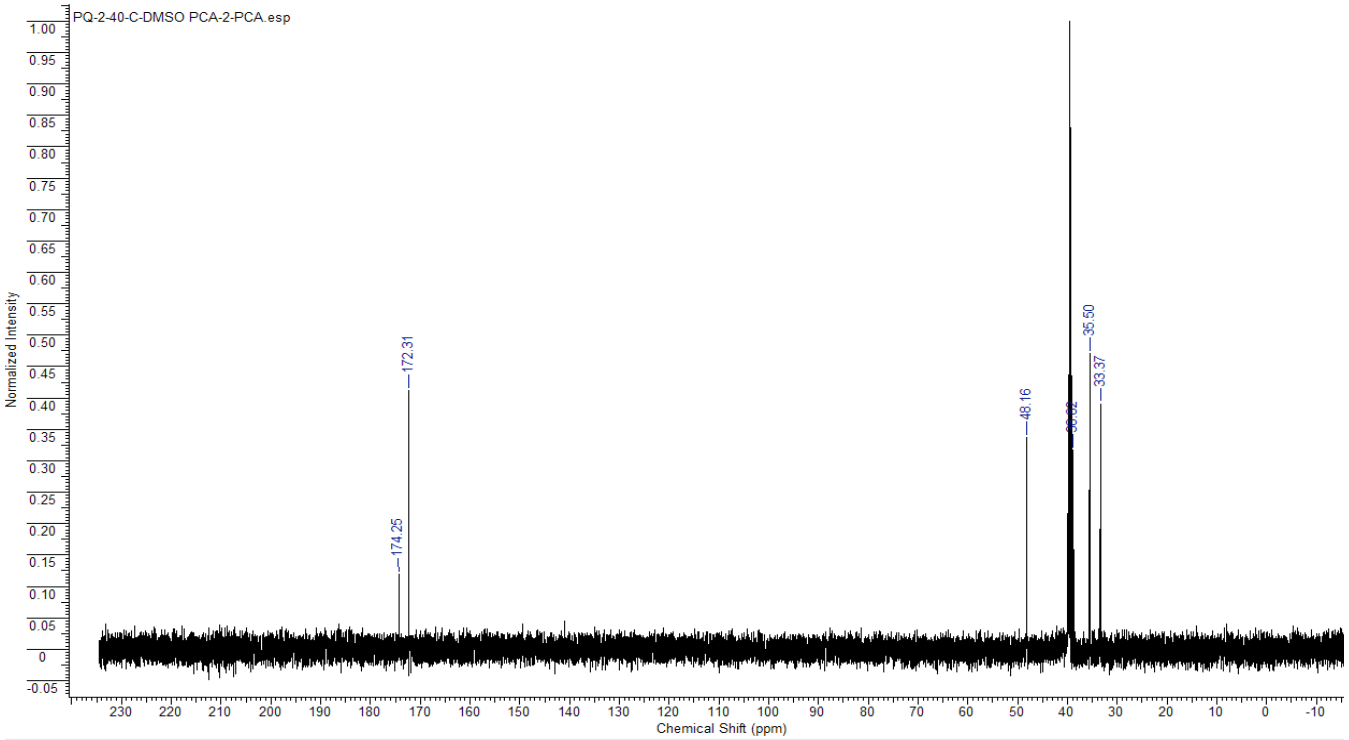


Figure S15. ^{13}C NMR spectrum of Ethylene bis(pyrrolidone carboxylic acid) (EBPC).

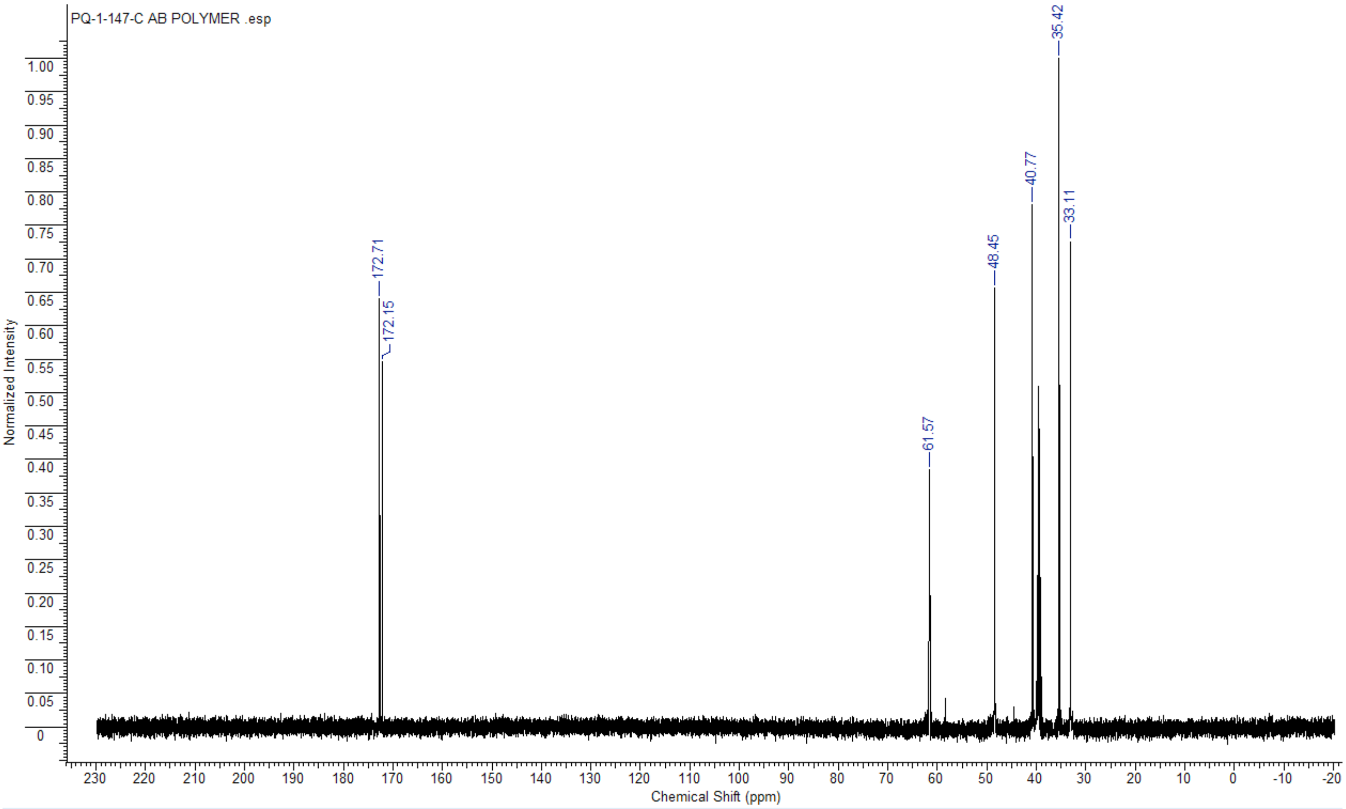


Figure S16. ^{13}C NMR spectrum of Poly(ethylene pyrrolidone carboxylate) (Table S1, Entry 1).

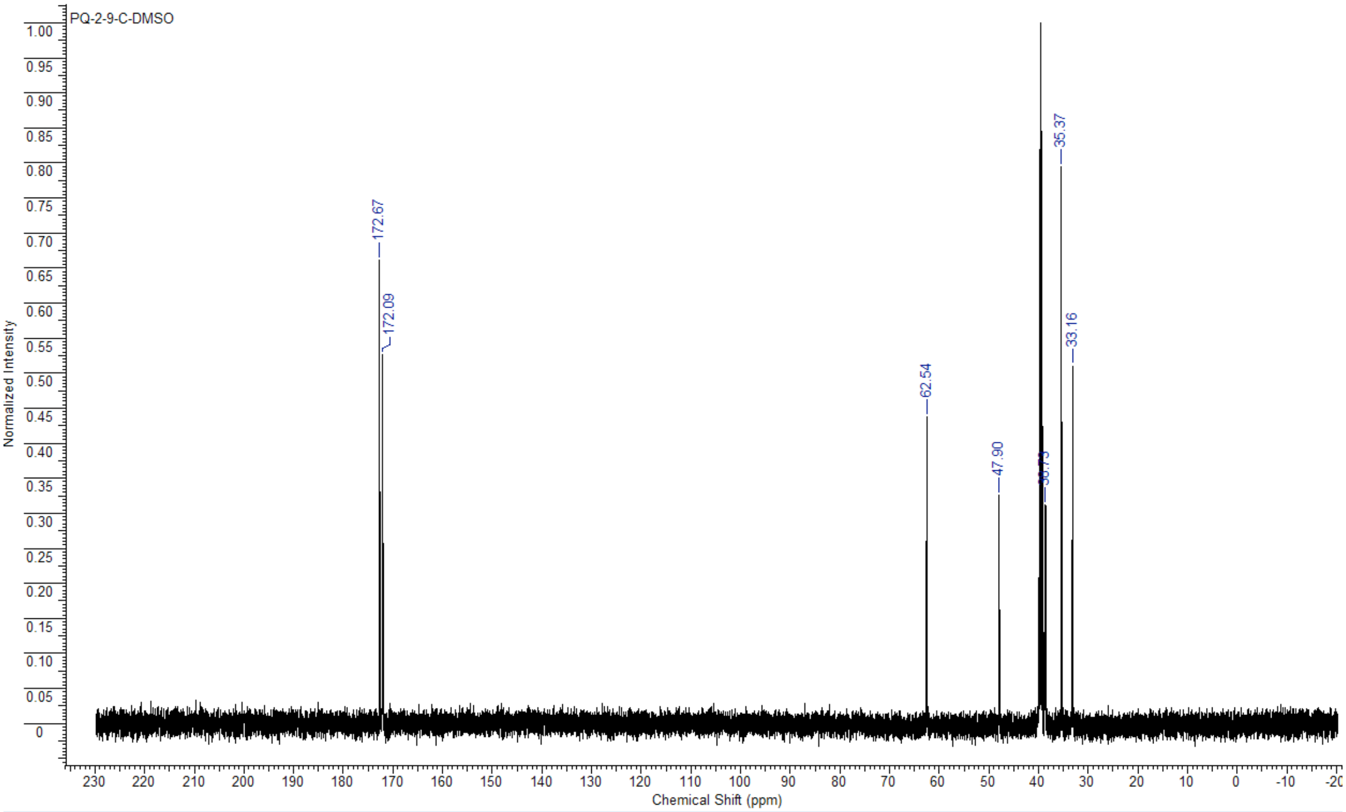


Figure S17. ^{13}C NMR spectrum of Polyethylene/[ethylene bis(pyrrolidone carboxylate)] (Table S1, Entry 3).

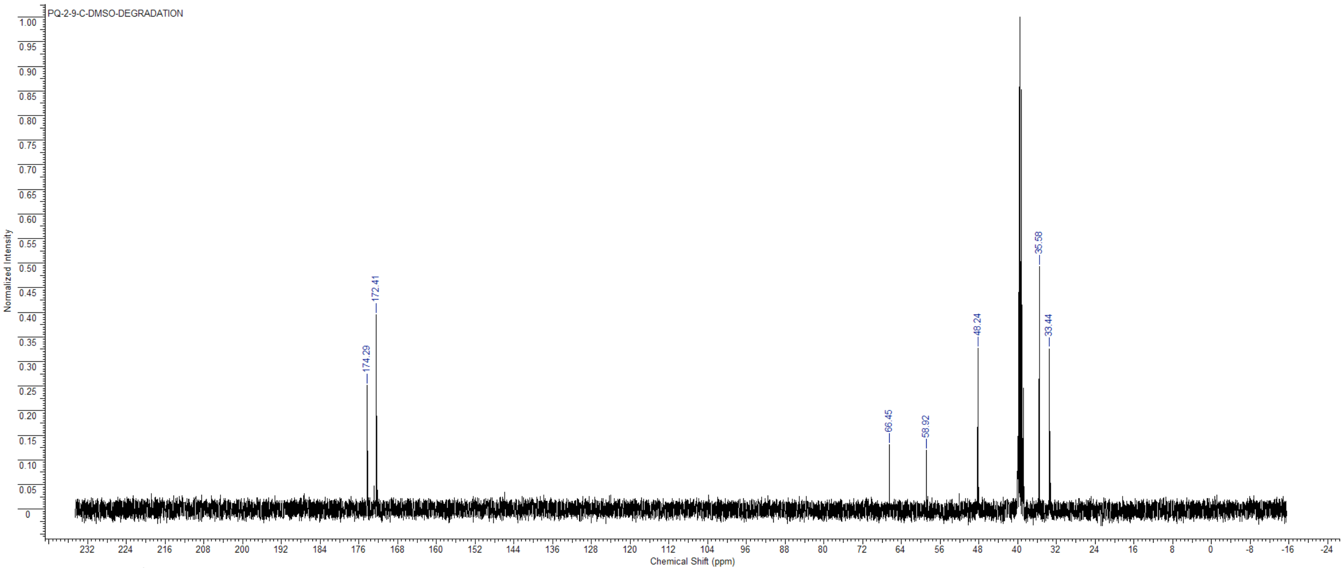


Figure S18. ^{13}C NMR spectrum of degraded Polyethylene/[ethylene bis(pyrrolidone carboxylate)] after a year.

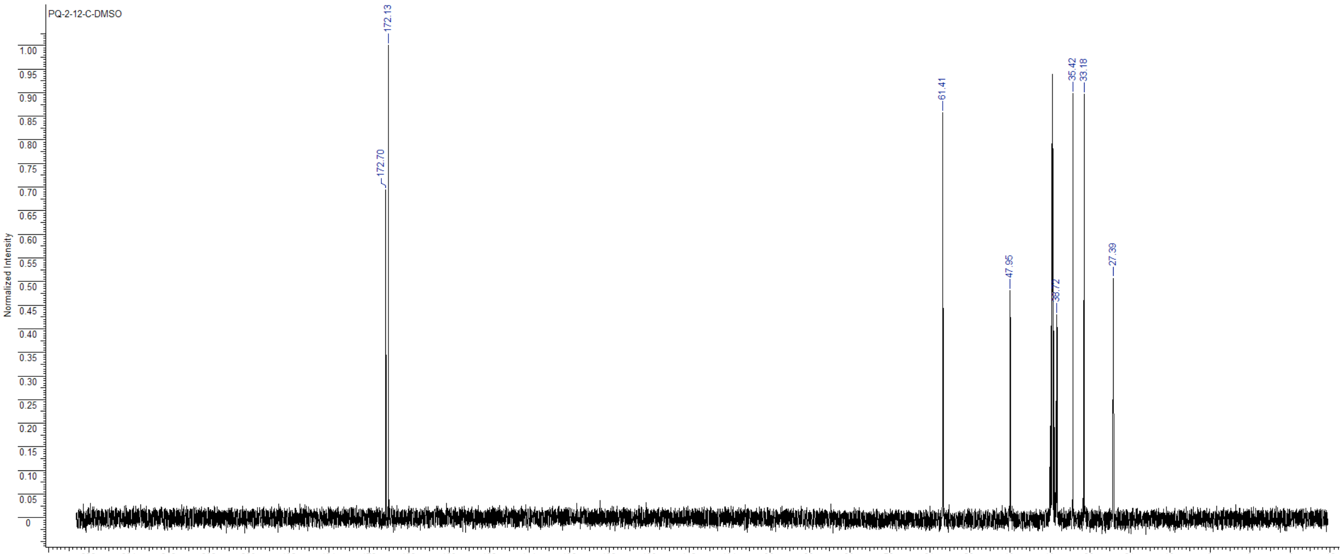


Figure S19. ^{13}C NMR spectrum of Polypropylene/[ethylene bis(pyrrolidone carboxylate)] (Table S1, Entry 4).

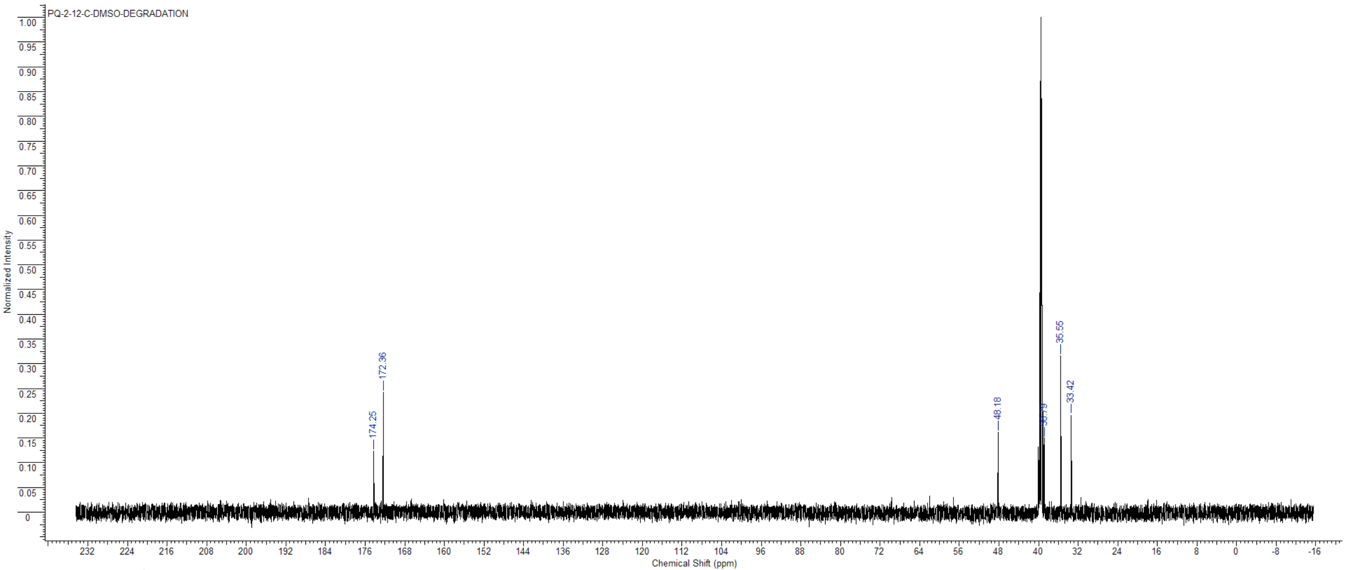


Figure S20. ^{13}C NMR spectrum of degraded Polypropylene/[ethylene bis(pyrrolidone carboxylate)] after a year.

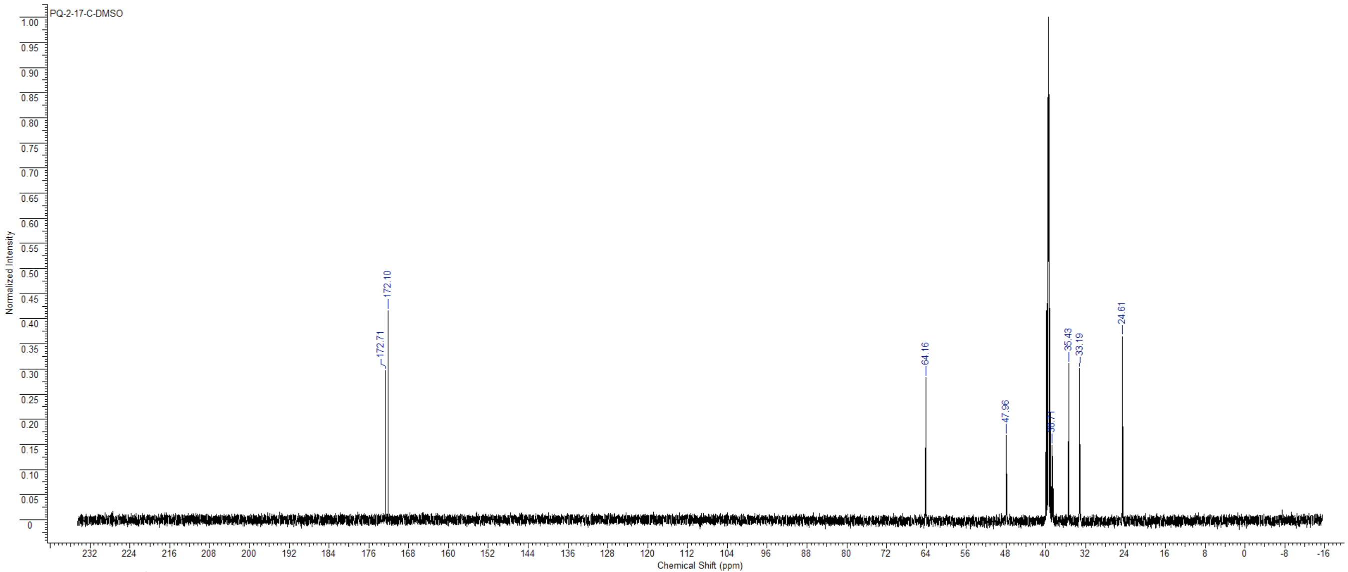


Figure S21. ^{13}C NMR spectrum of Polybutylene/[ethylene bis(pyrrolidone carboxylate)] (Table S1, Entry 5).

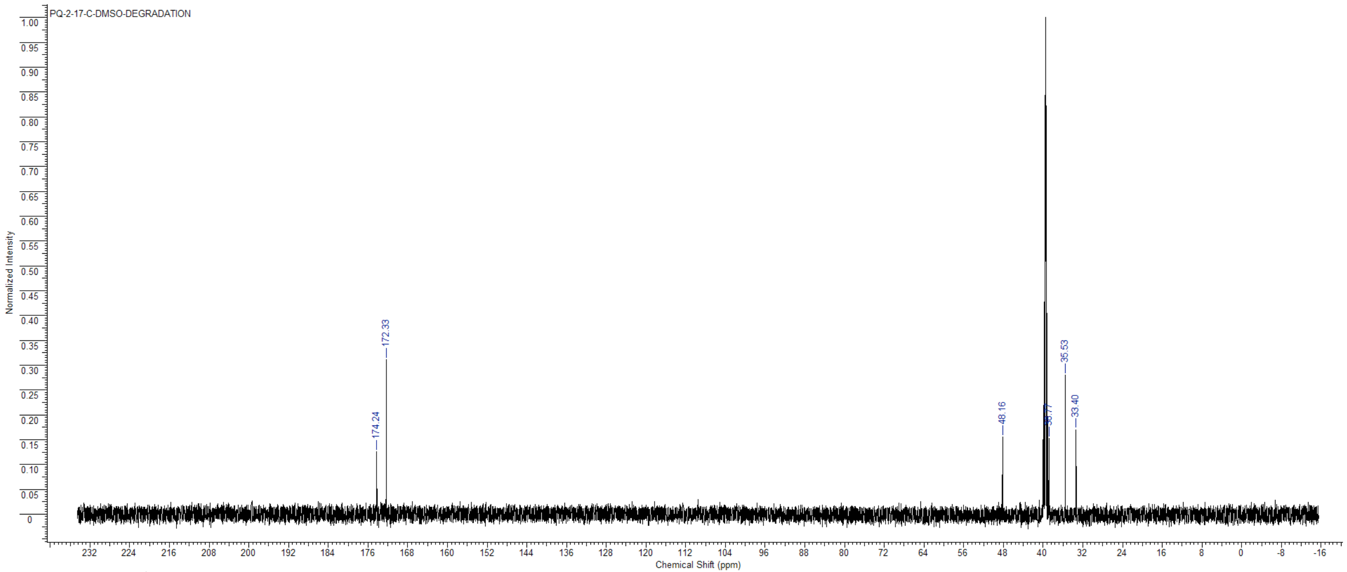


Figure S22. ^{13}C NMR spectrum of degraded Polybutylene/[ethylene bis(pyrrolidone carboxylate)] after a year.

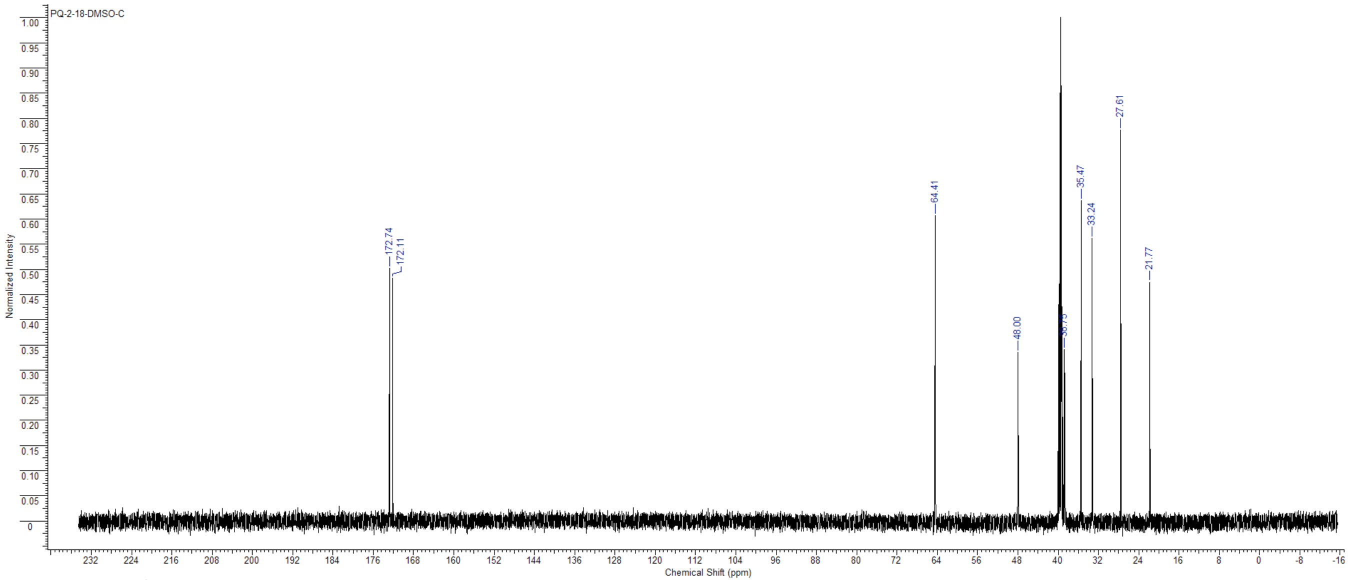


Figure S23. ^{13}C NMR spectrum of Polypentylene/[ethylene bis(pyrrolidone carboxylate)] (Table S1, Entry 6).

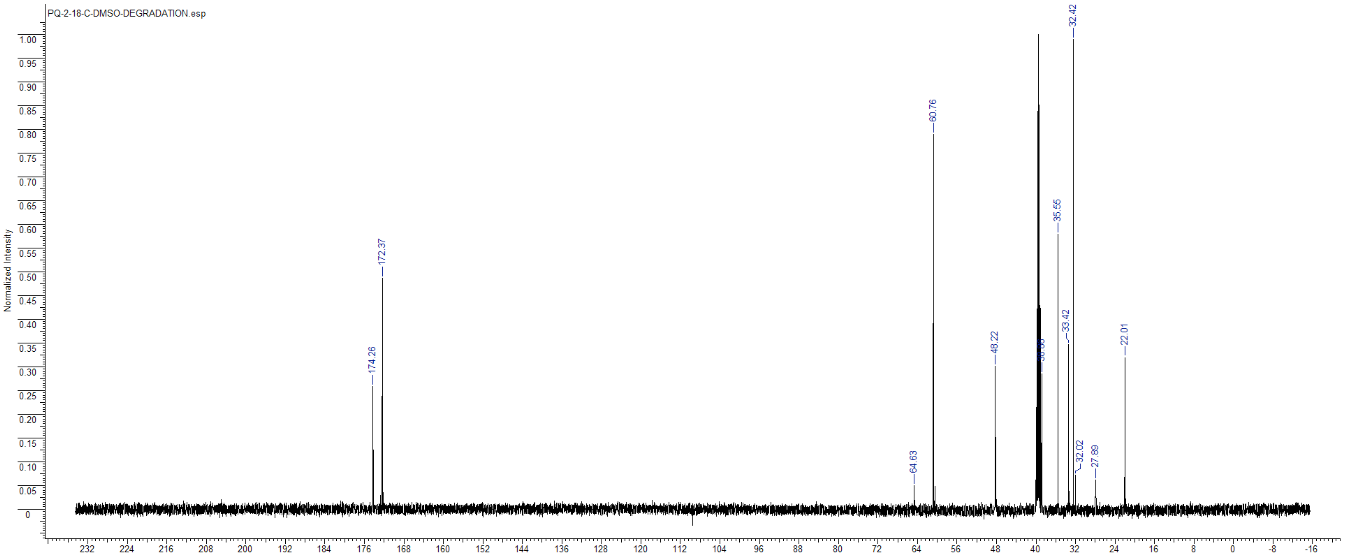


Figure S24. ^{13}C NMR spectrum of degraded Polypentylene/[ethylene bis(pyrrolidone carboxylate)] after a year.

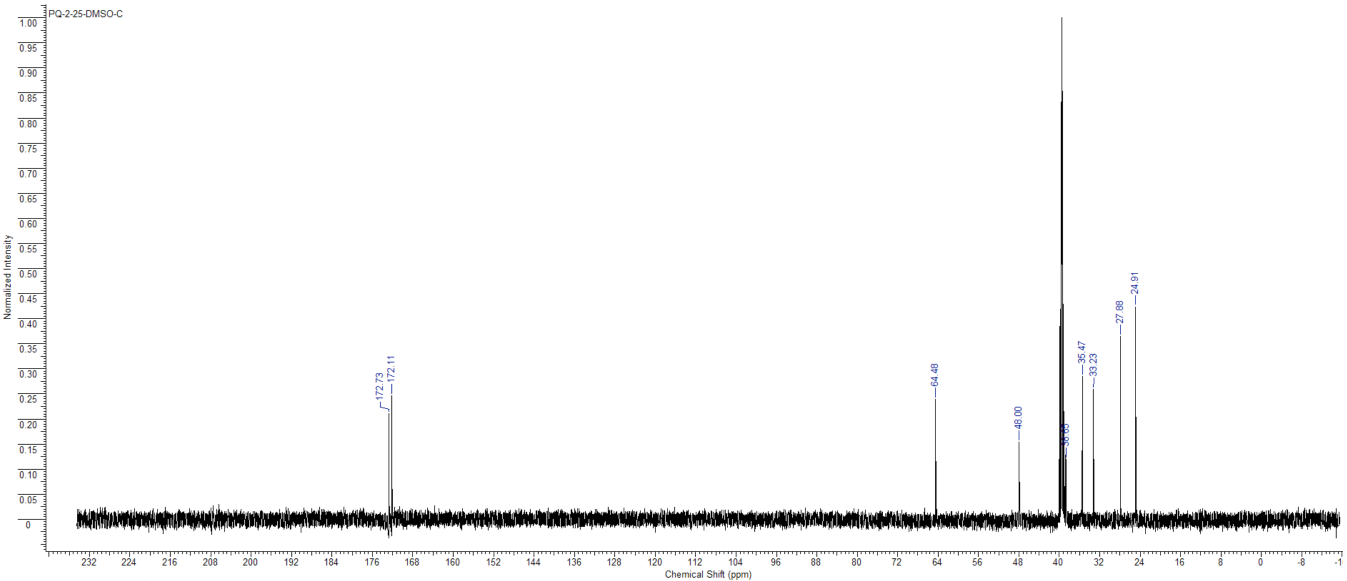


Figure S25. ^{13}C NMR spectrum of Polyhexylene/[ethylene bis(pyrrolidone carboxylate)] (Table S1, Entry 7).

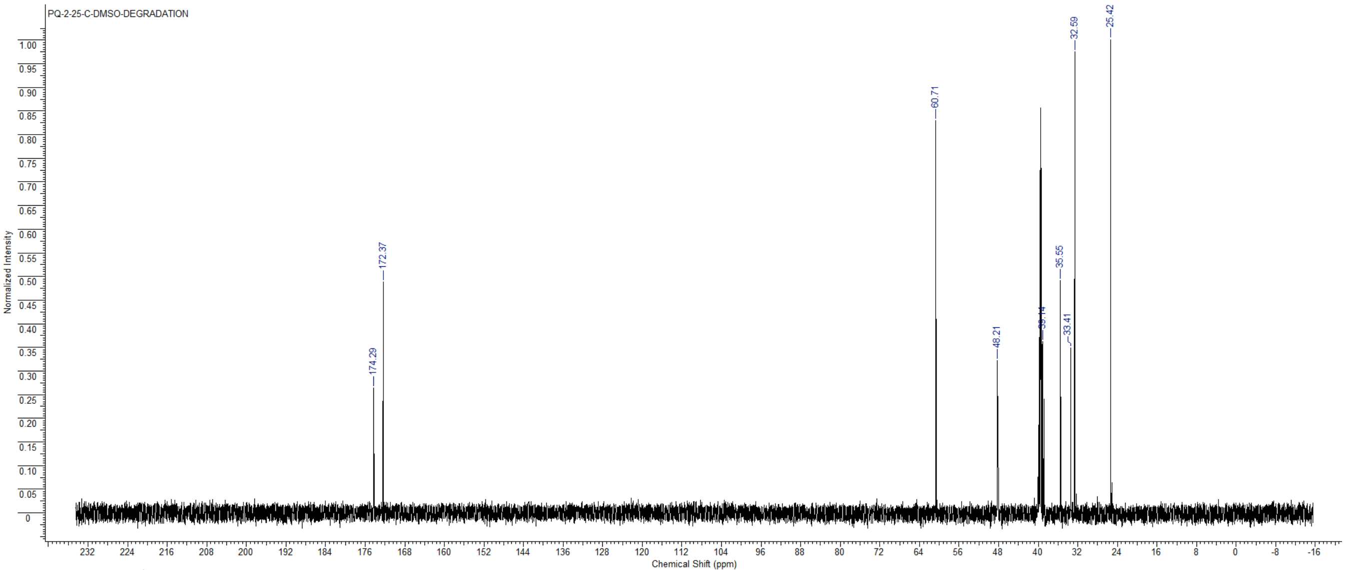


Figure S26. ^{13}C NMR spectrum of degraded Polyhexylene/[ethylene bis(pyrrolidone carboxylate)] after a year.

Differential Scanning Calorimetry (DSC) Thermograms

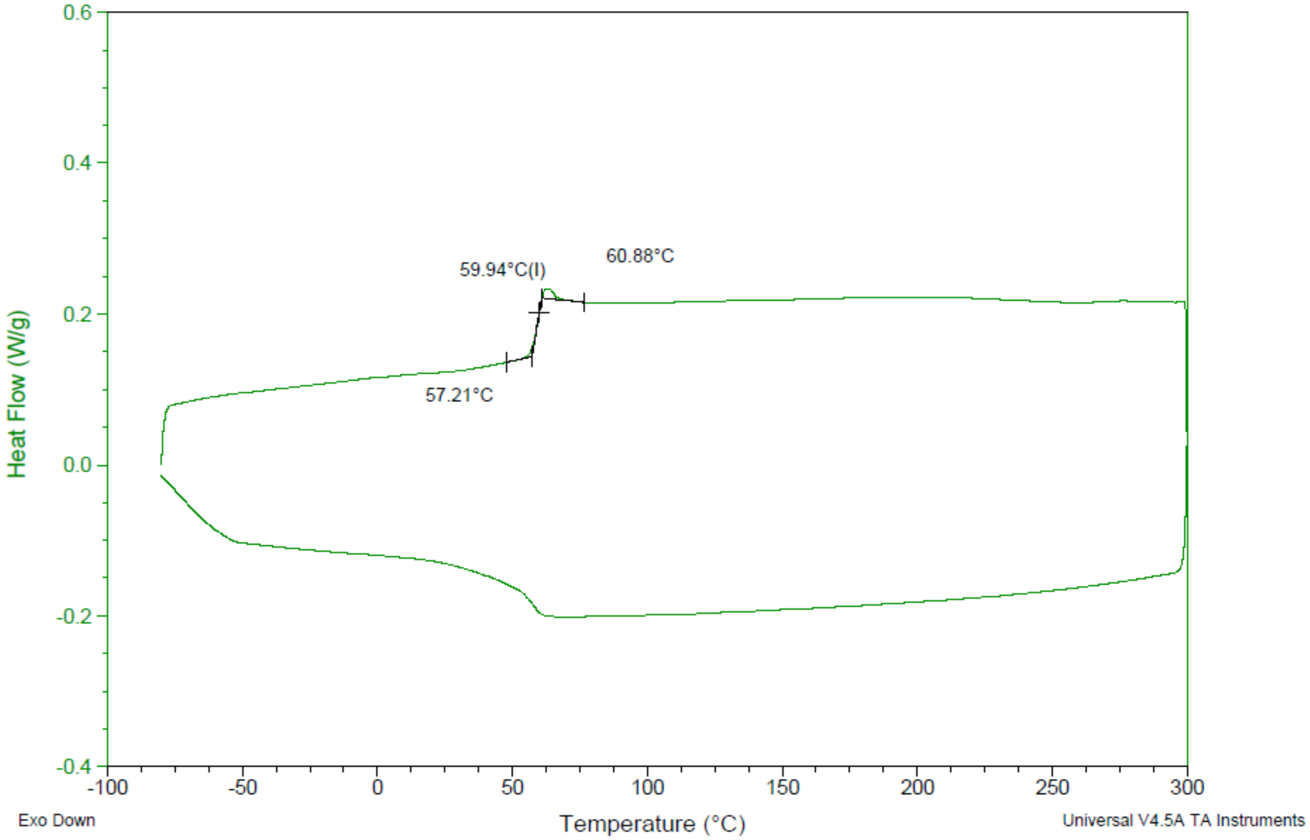


Figure S27. DSC Thermogram of Poly(ethylene pyrrolidone carboxylate) (Table S1, Entry 1).

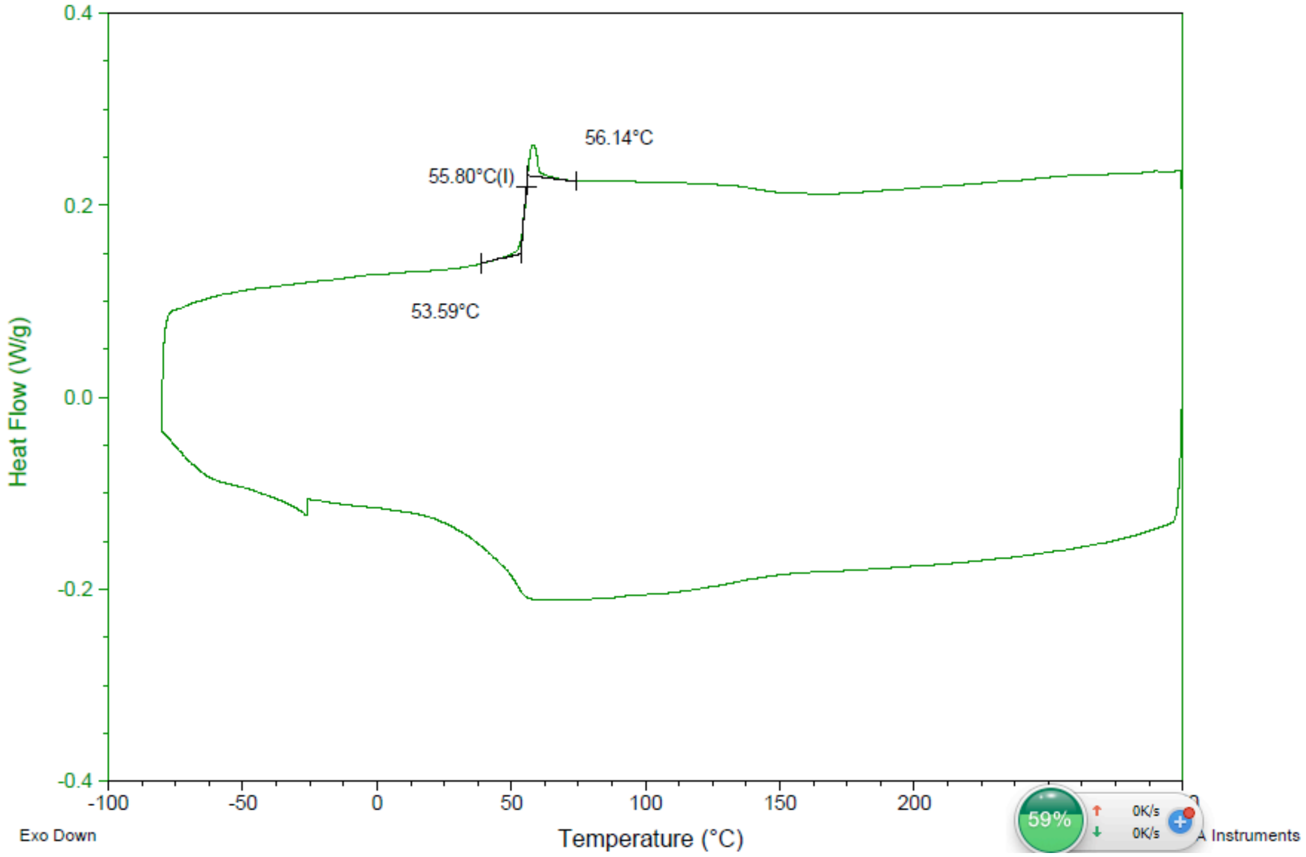


Figure S28. DSC Thermogram of Polyethylene/[ethylene bis(pyrrolidone carboxylate)] (Table S1, Entry 2).

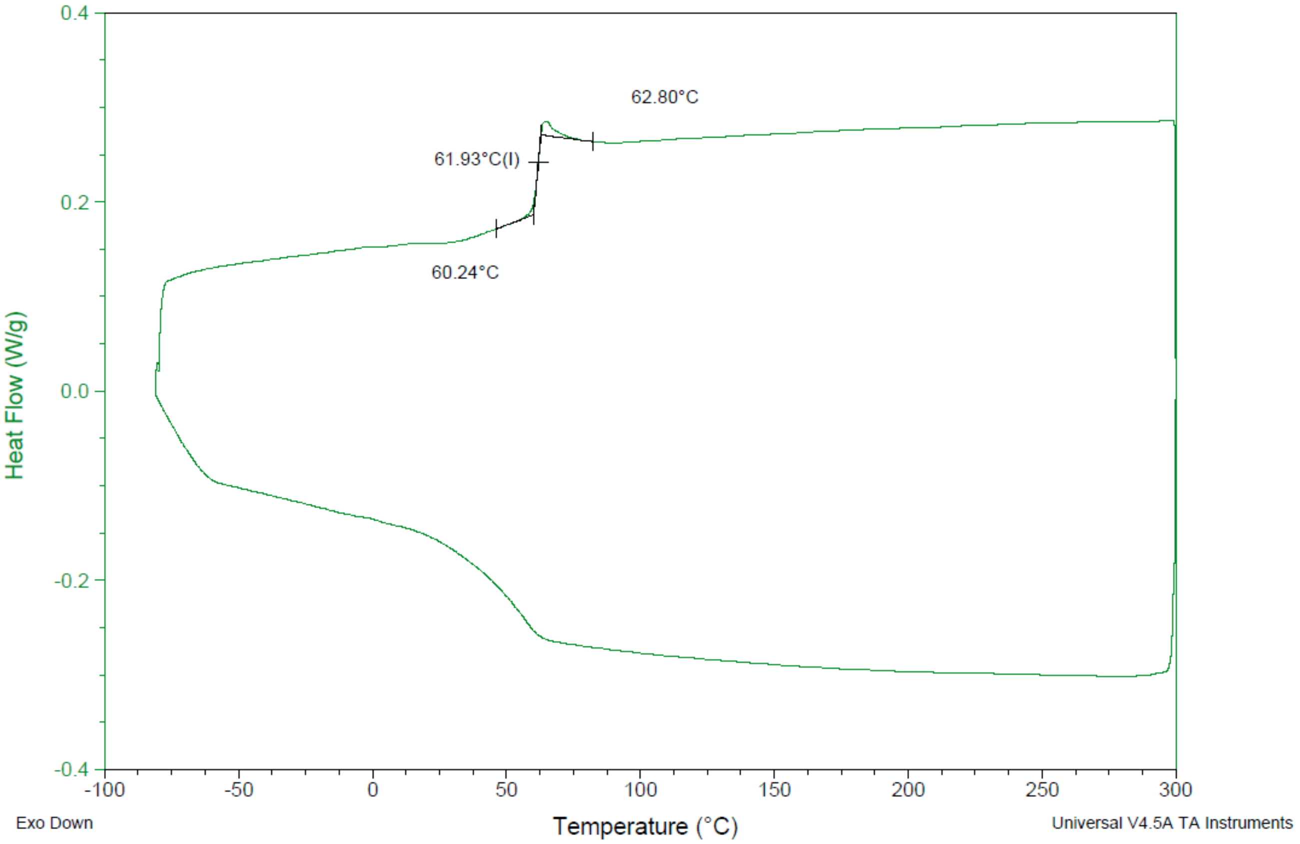


Figure S29. DSC Thermogram of Polyethylene/[ethylene bis(pyrrolidone carboxylate)] (Table S1, Entry 3)

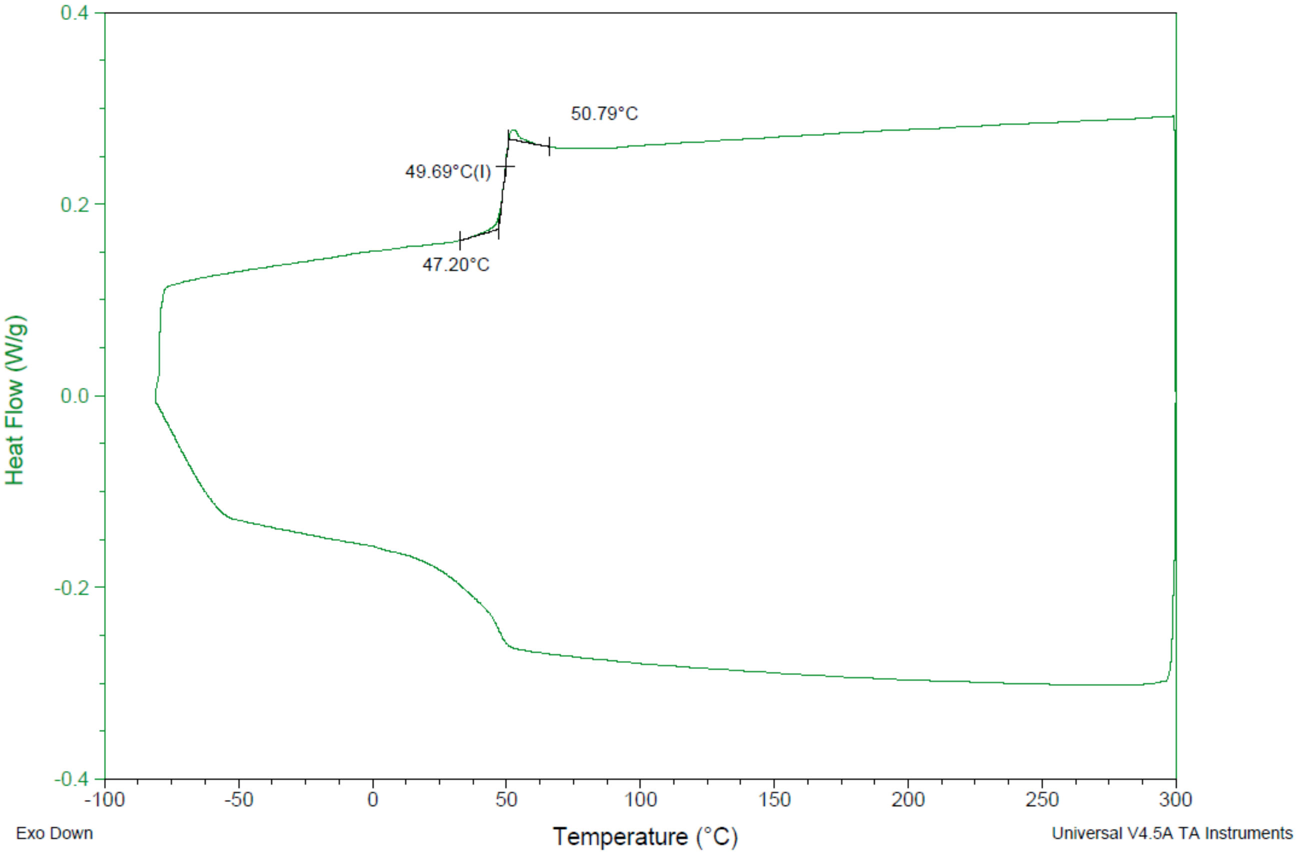


Figure S30. DSC Thermogram of Polypropylene/[ethylene bis(pyrrolidone carboxylate)] (Table S1, Entry 4).

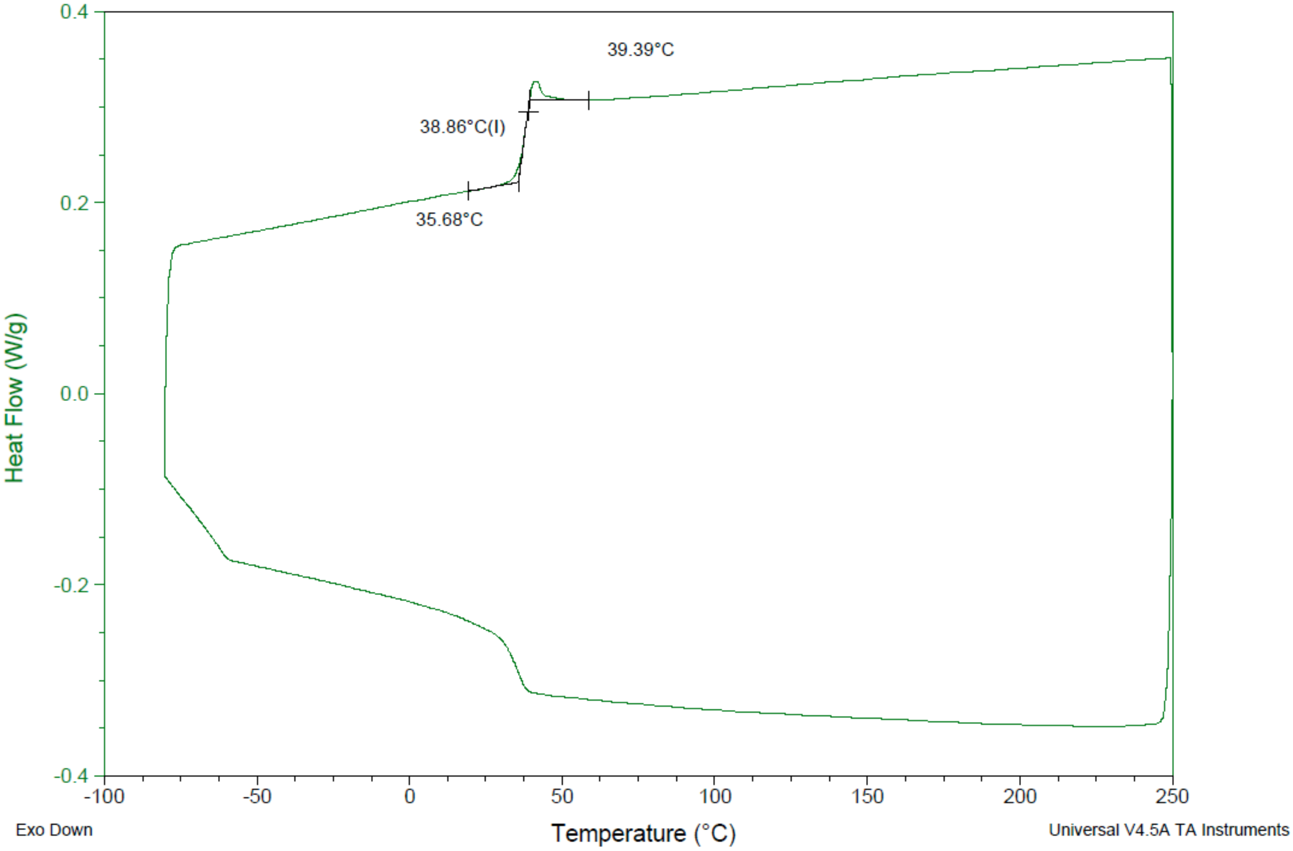


Figure S31. DSC Thermogram of Polybutylene/[ethylene bis(pyrrolidone carboxylate)] (Table S1, Entry 5).

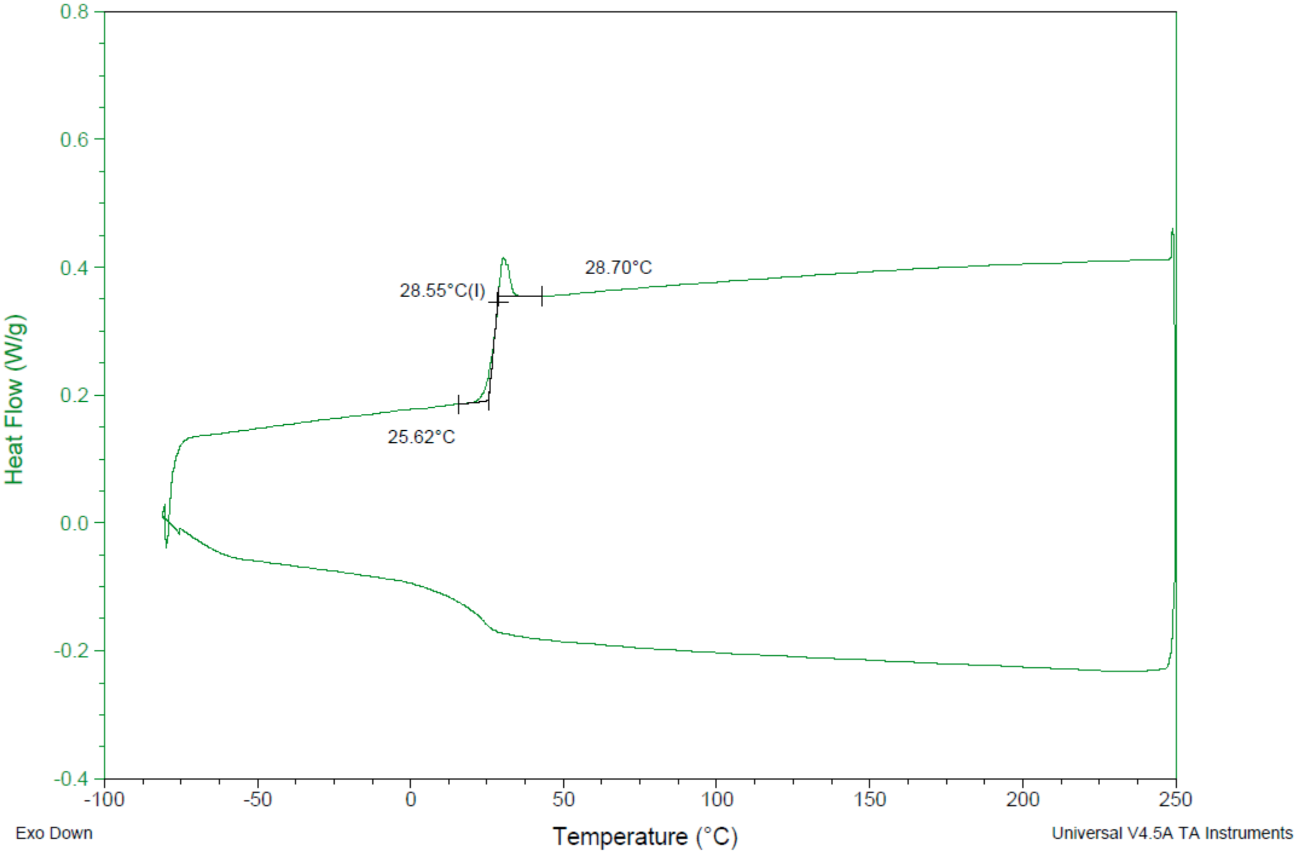


Figure S32. DSC Thermogram of Polypentylene/[ethylene bis(pyrrolidone carboxylate)] (Table S1, Entry 6).

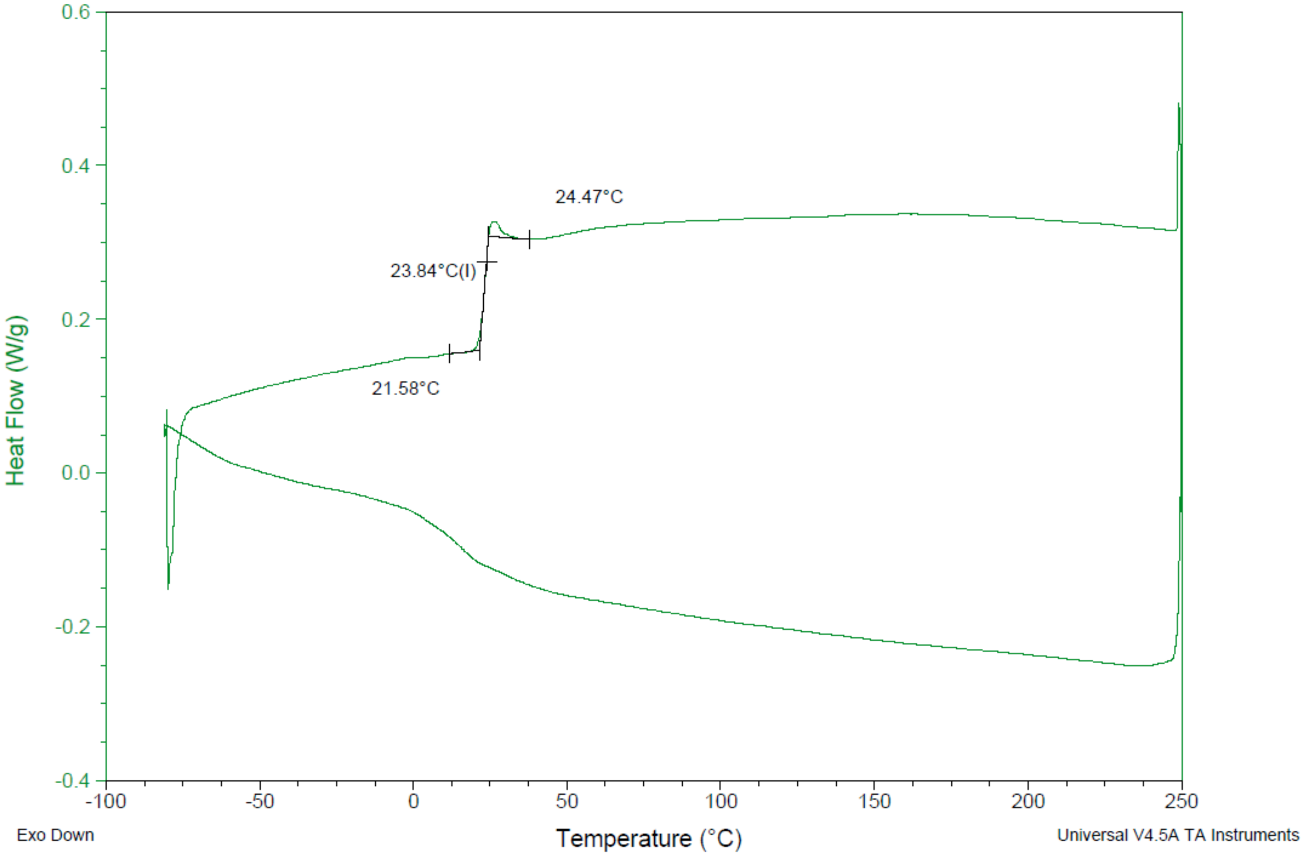


Figure S33. DSC Thermogram of Polyhexylene/[ethylene bis(pyrrolidone carboxylate)] (Table S1, Entry 7).

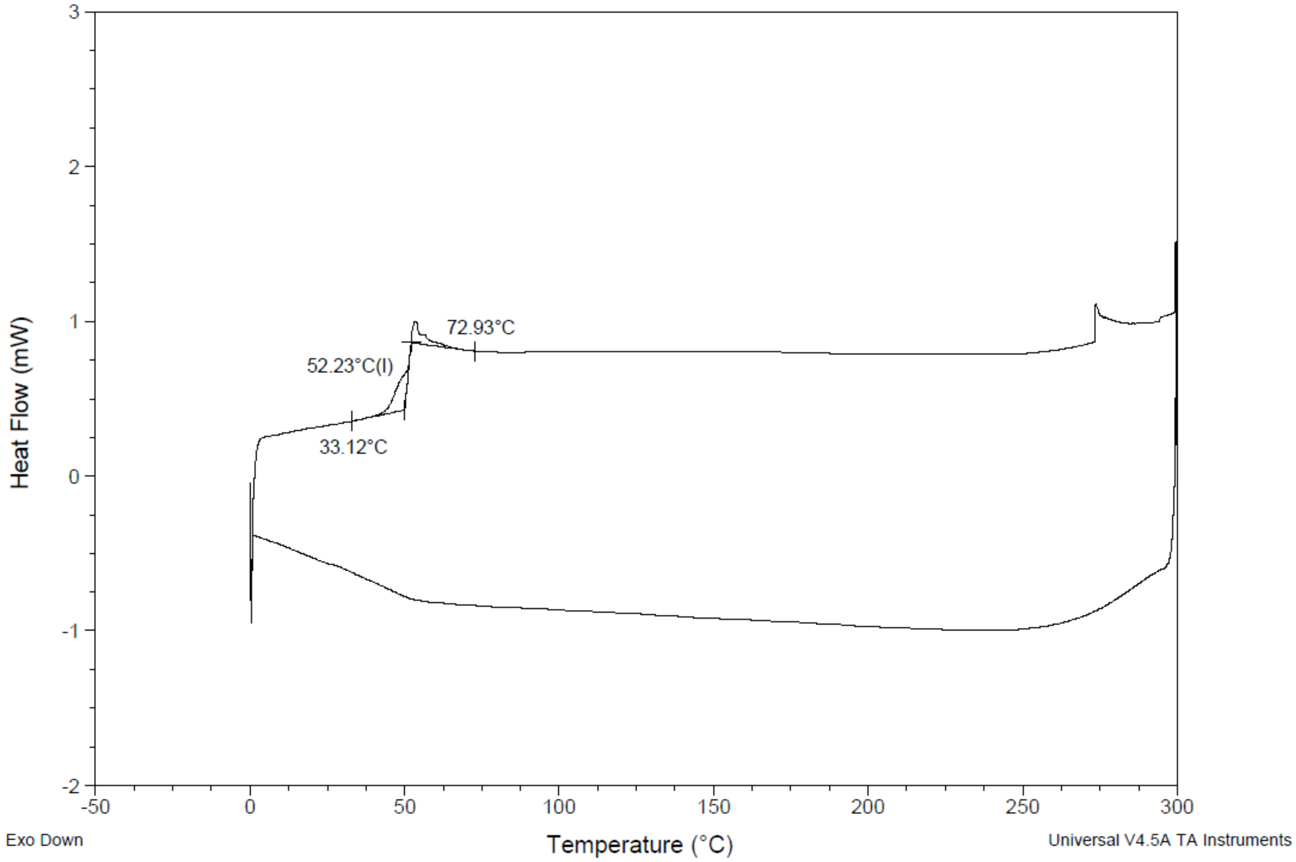


Figure S34. DSC Thermogram of commercially available poly(lactic acid) (PLA) (Table S1, Entry 8).

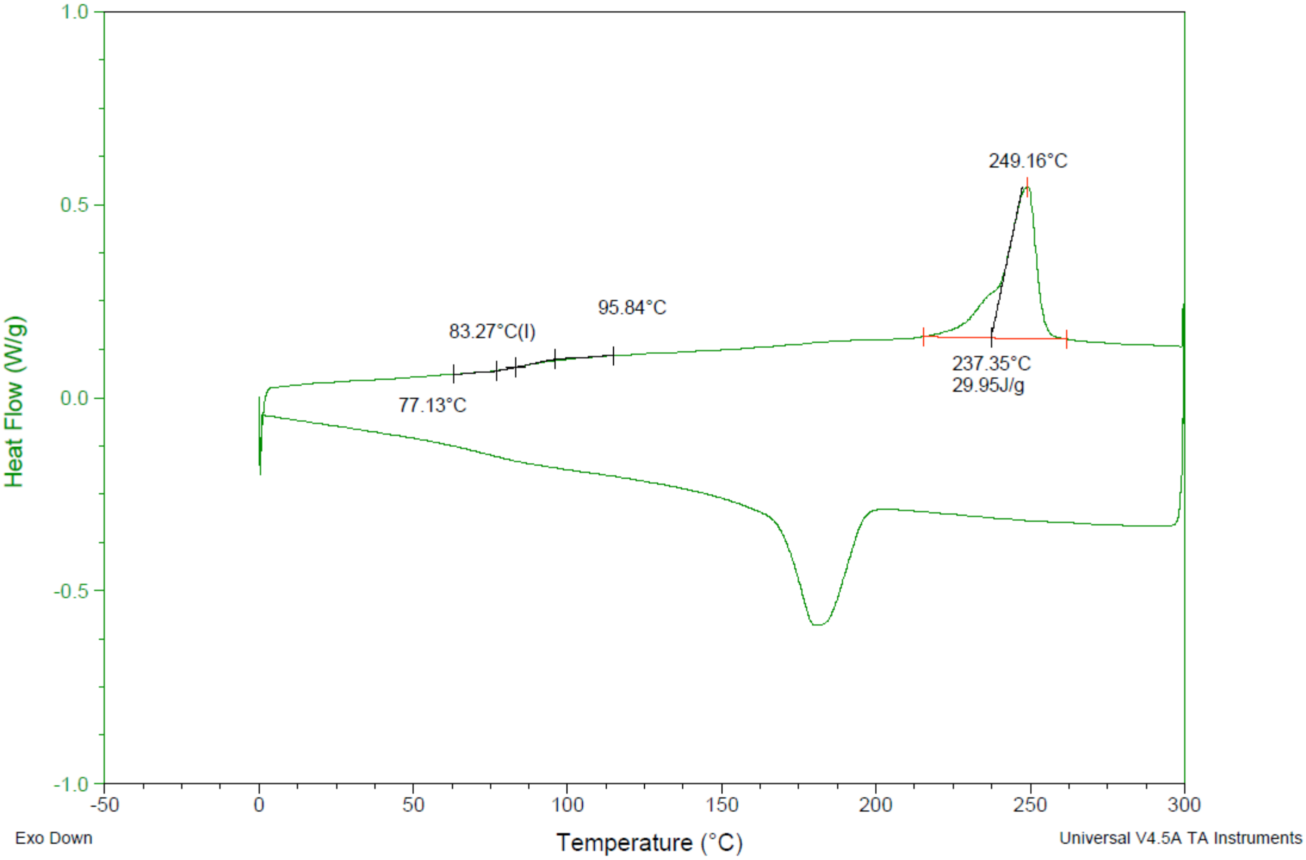


Figure S35. DSC Thermogram of commercially available poly(ethylene terephthalate) (PET) (Table S1, Entry 9).

Thermogravimetric Analysis (TGA) Thermograms

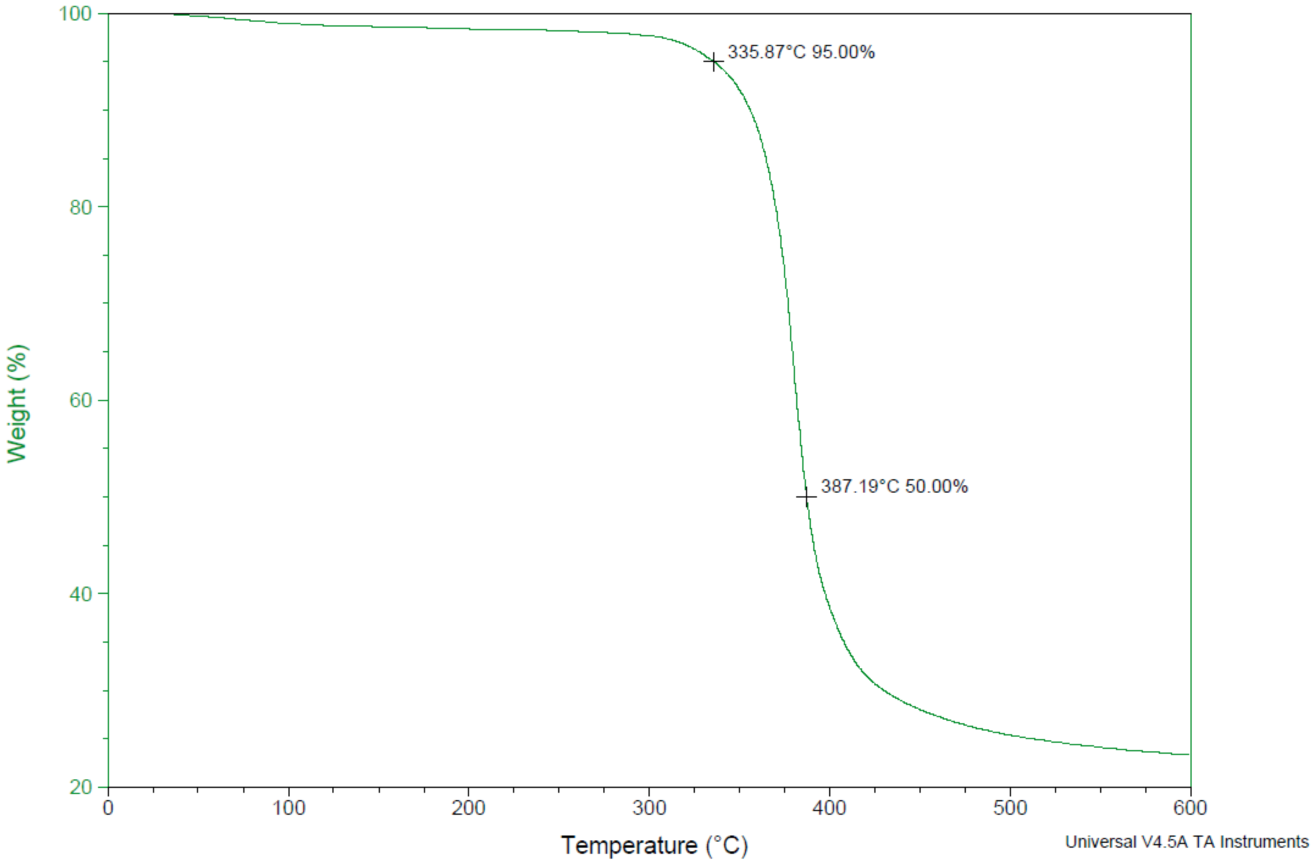


Figure S36. TGA Thermogram of Poly(ethylene pyrrolidone carboxylate) (Table S1, Entry 1).

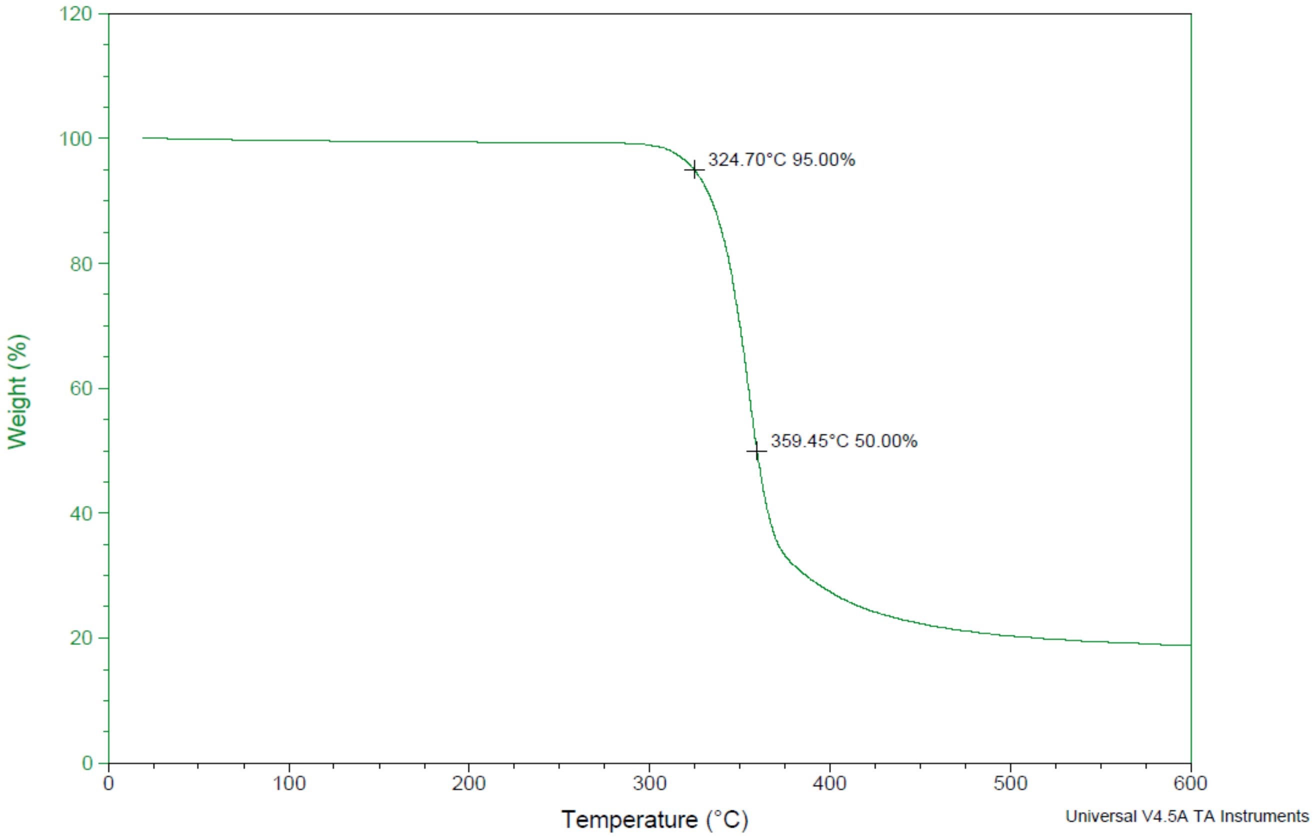


Figure S37. TGA Thermogram of Polyethylene/[ethylene bis(pyrrolidone carboxylate)] (Table S1, Entry 2).

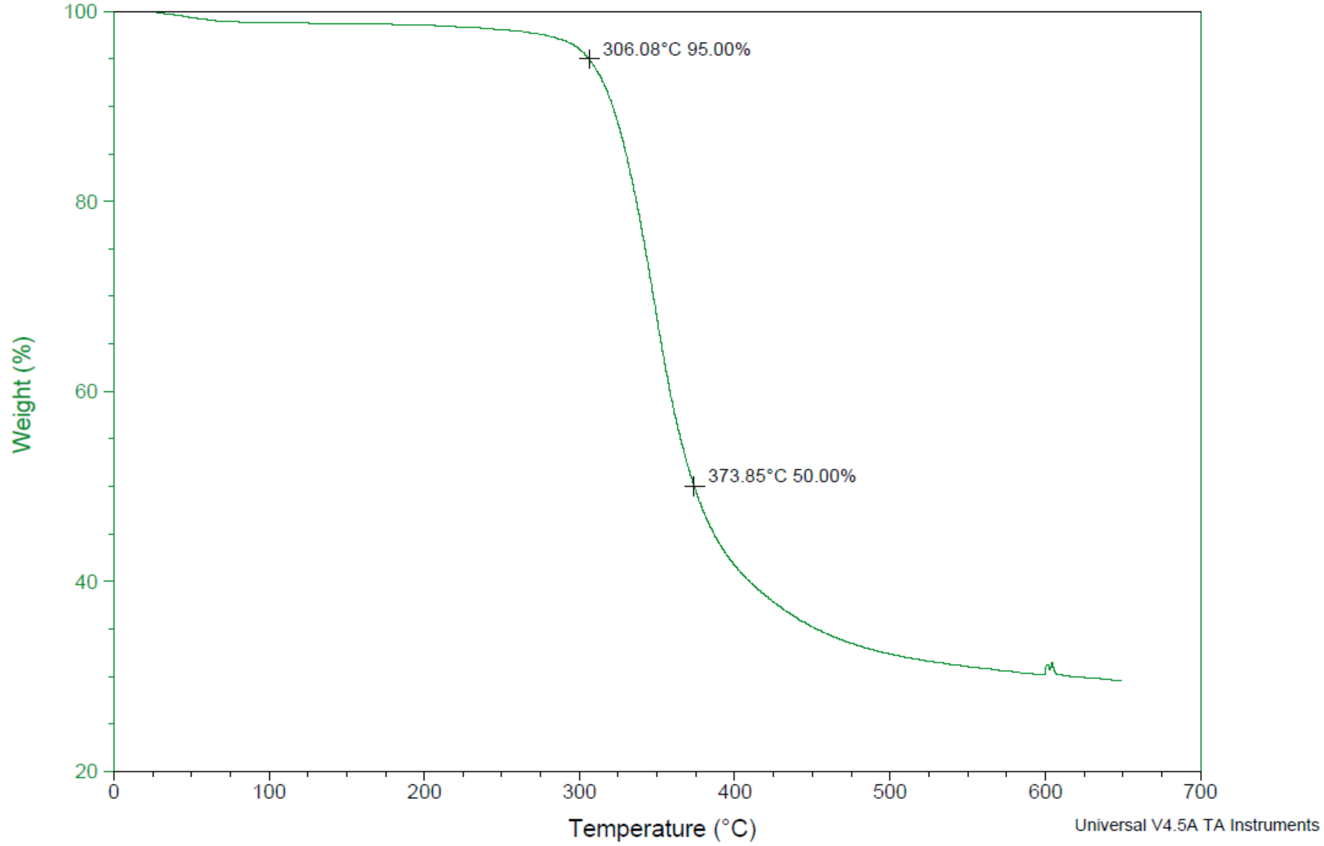


Figure S38. TGA Thermogram of Polyhexylene/[ethylene bis(pyrrolidone carboxylate)] (Table S1, Entry 3).

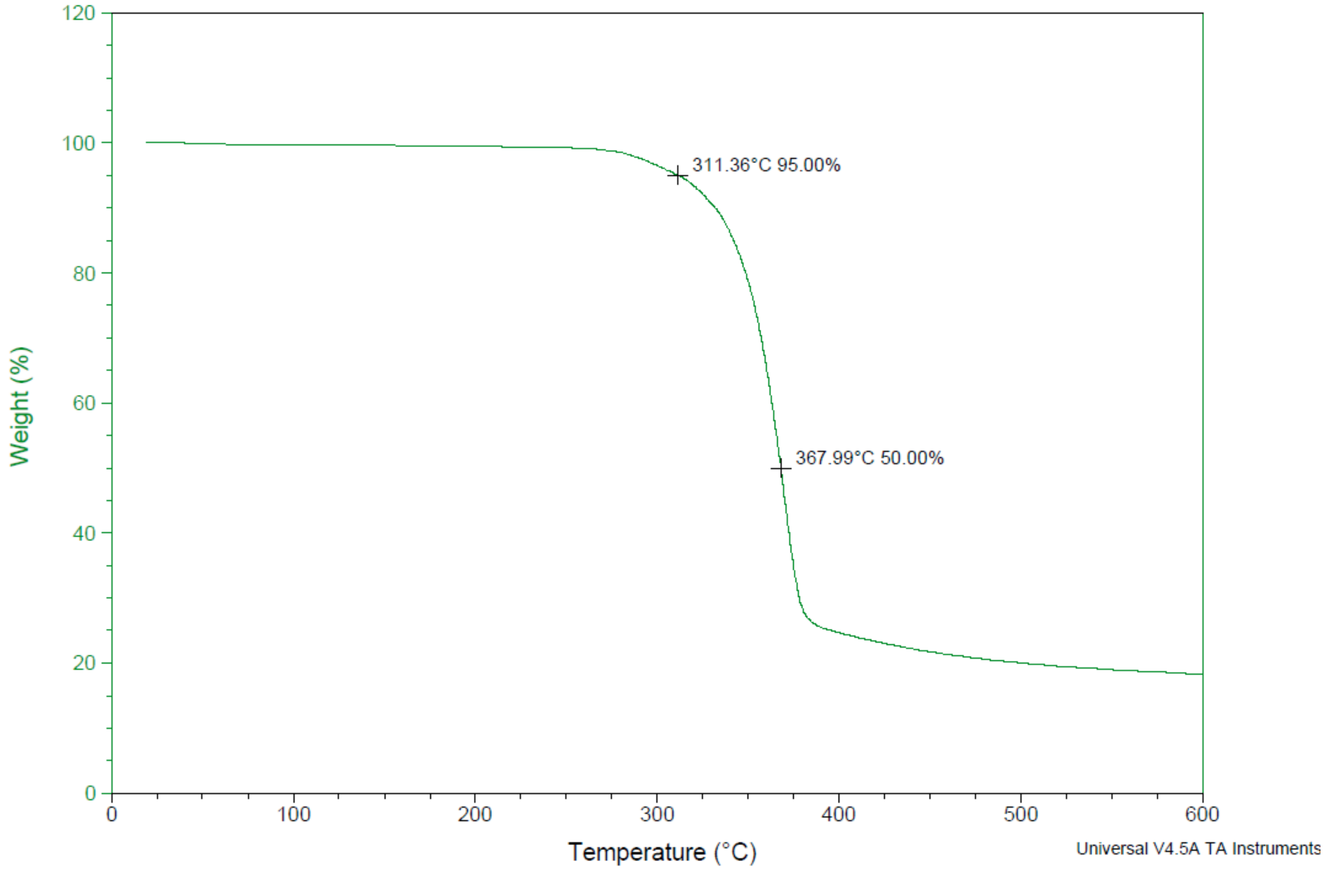


Figure S39. TGA Thermogram of Polypropylene/[ethylene bis(pyrrolidone carboxylate)] (Table S1, Entry 4).

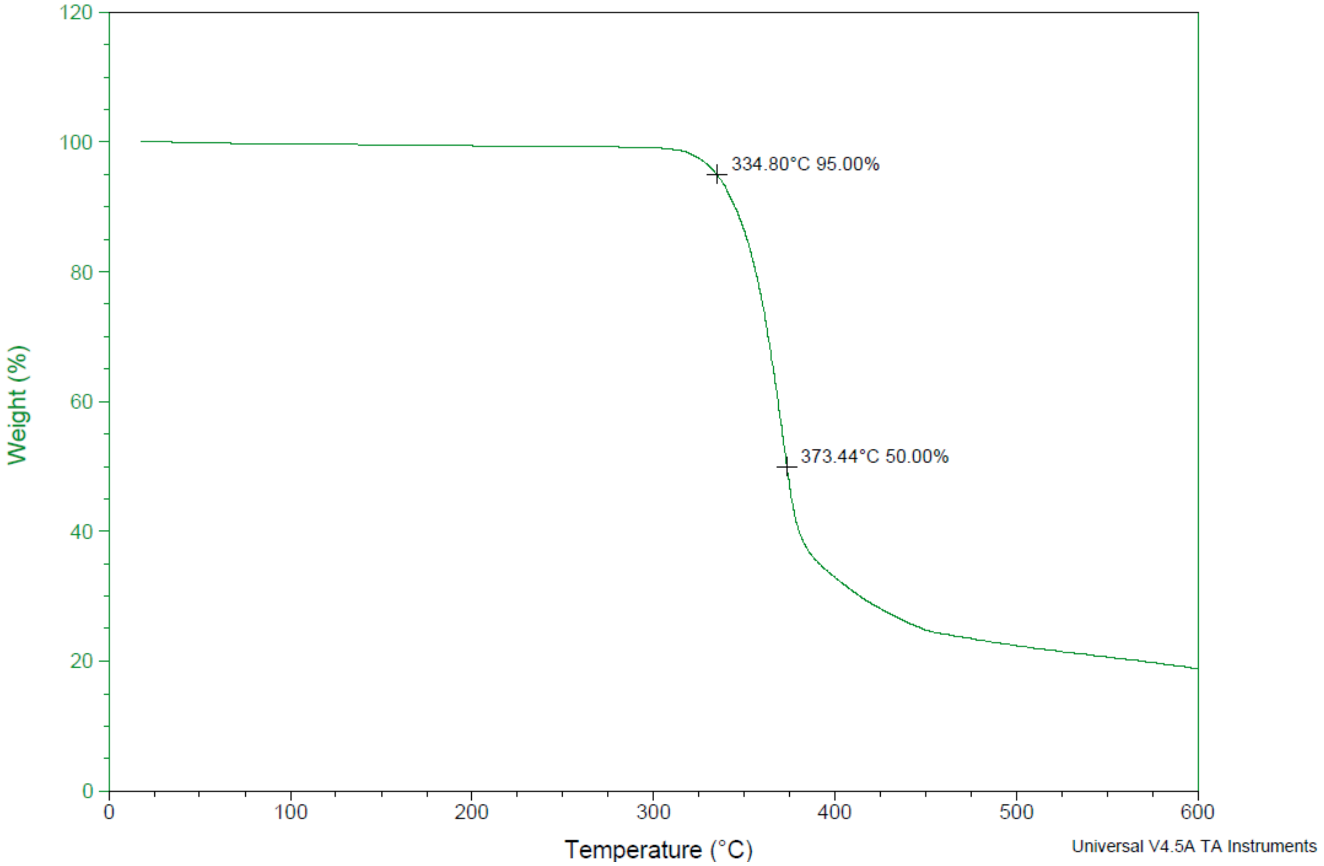


Figure S40. TGA Thermogram of Polybutylene/[ethylene bis(pyrrolidone carboxylate)] (Table S1, Entry 5).

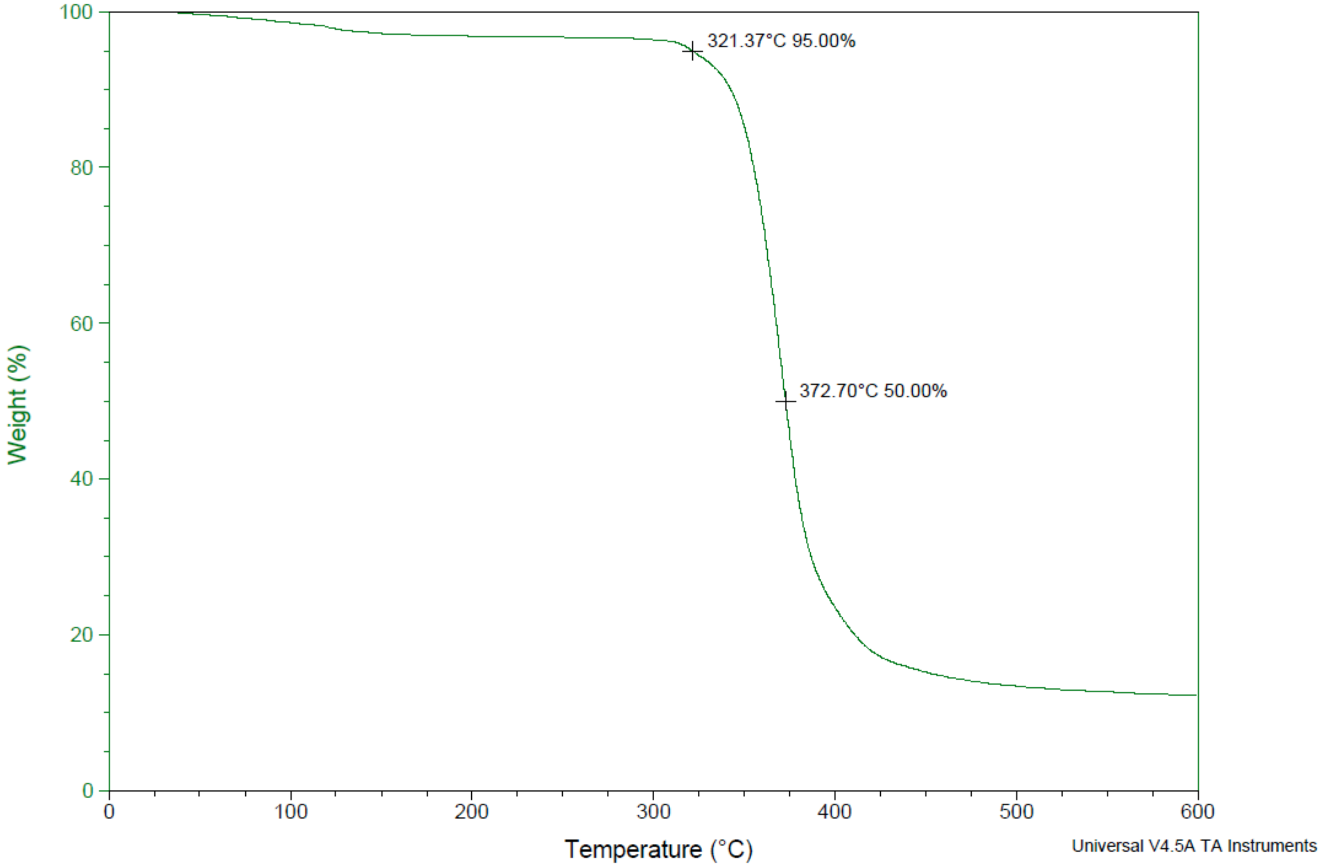


Figure S41. TGA Thermogram of Polypentylene/[ethylene bis(pyrrolidone carboxylate)] (Table S1, Entry 6).

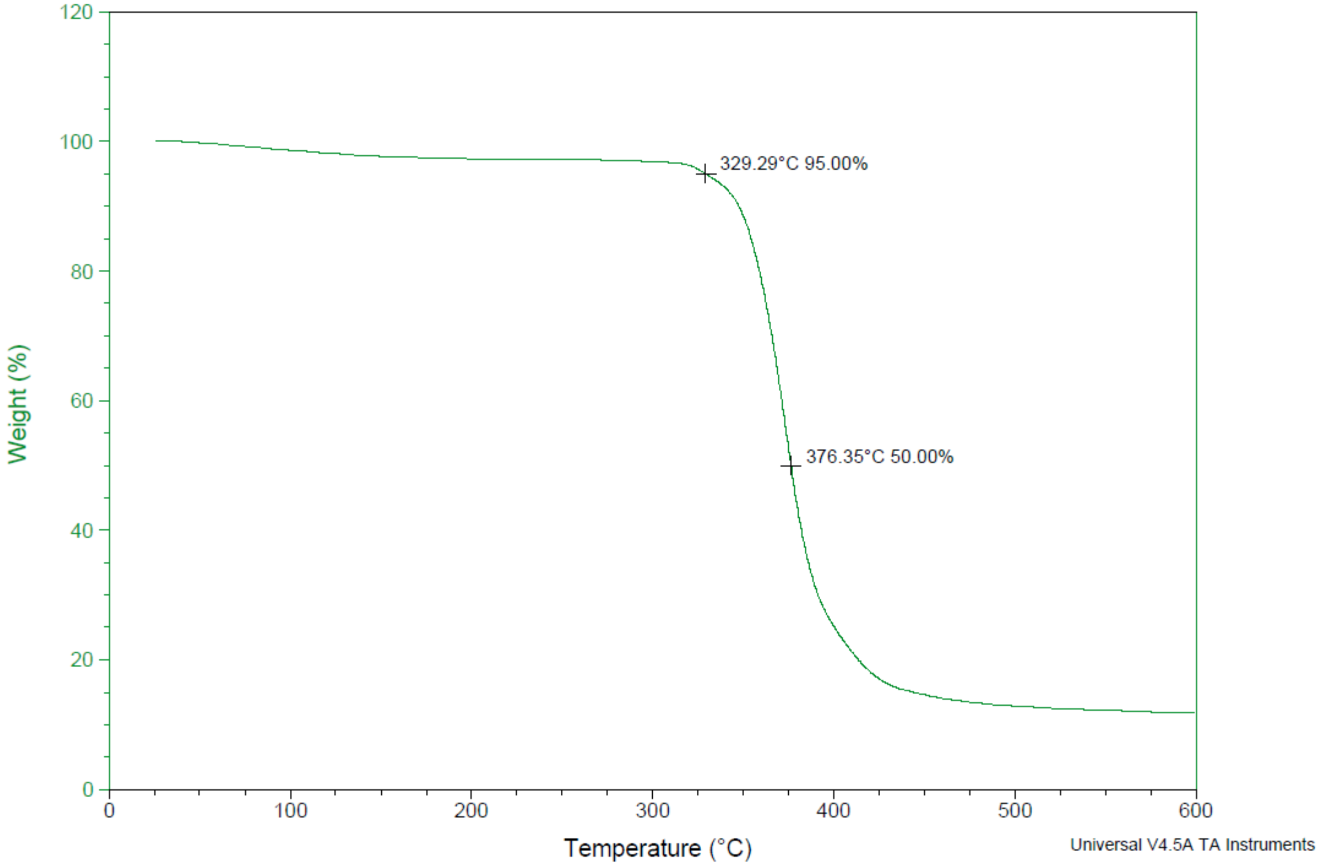


Figure S42. TGA Thermogram of Polyhexylene/[ethylene bis(pyrrolidone carboxylate)] (Table S1, Entry 7).

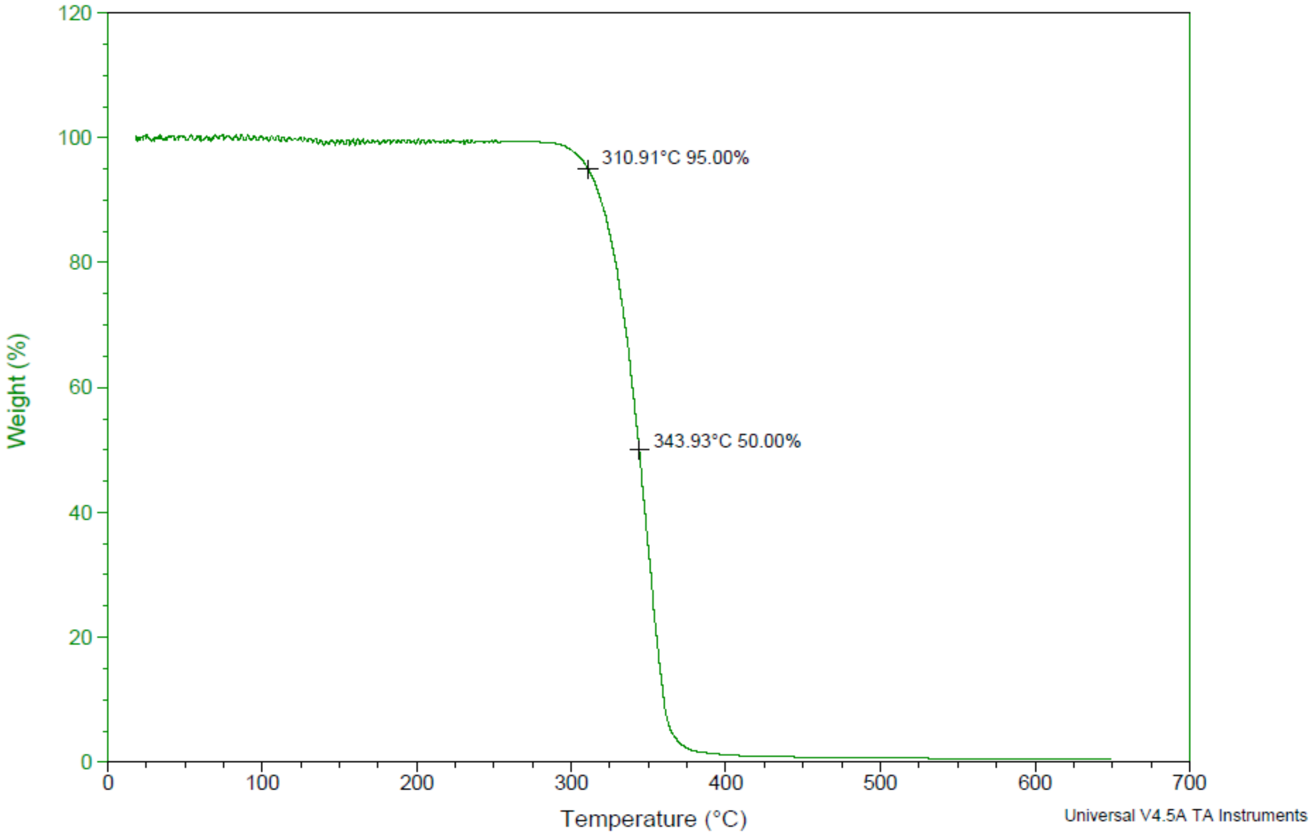


Figure S43. TGA Thermogram of commercially available poly(lactic acid) (PLA) (Table S1, Entry 8).

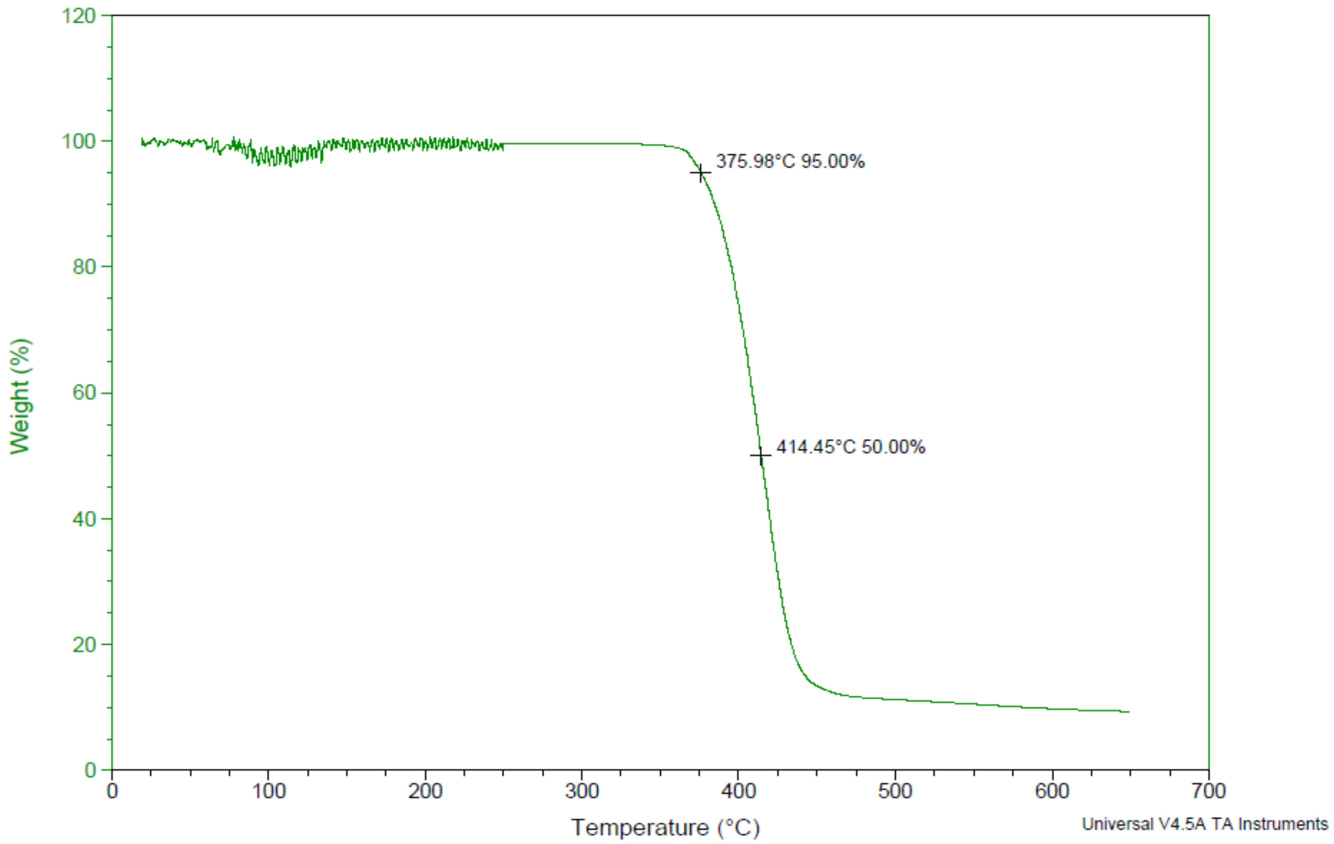
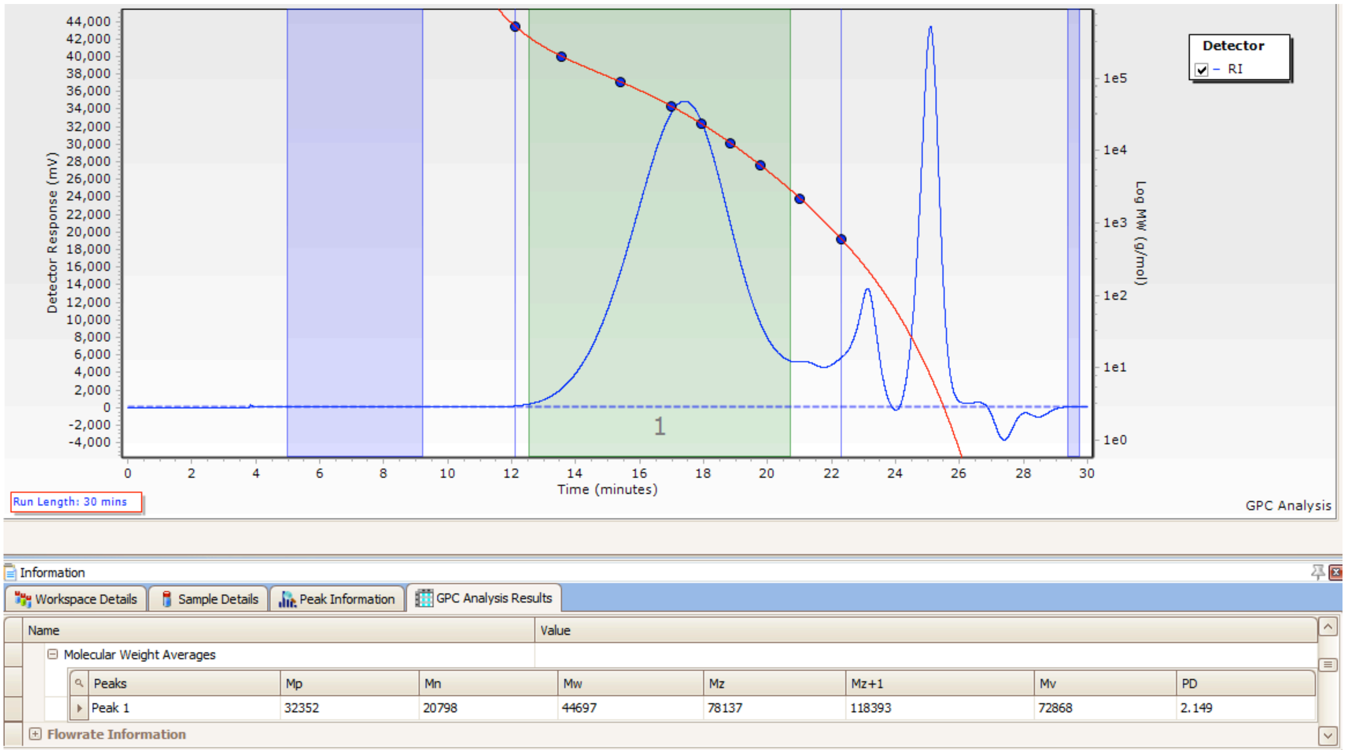


Figure S44. TGA Thermogram of commercially available poly(ethylene terephthalate) (PET) (Table S1, Entry 9).

Gel Permeation Chromatography (GPC) Data

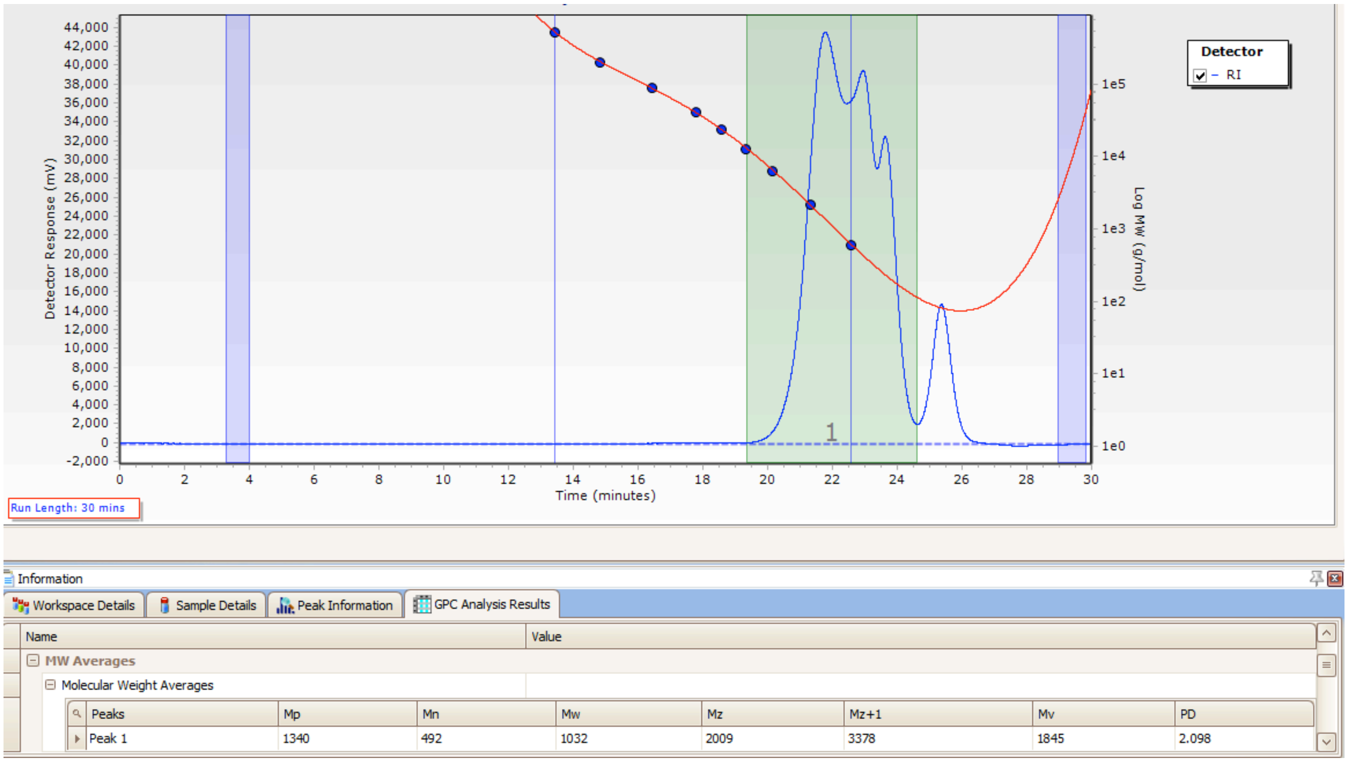


Name	Value
⊟ Molecular Weight Averages	

Peaks	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
Peak 1	32352	20798	44697	78137	118393	72868	2.149

⊞ Flowrate Information

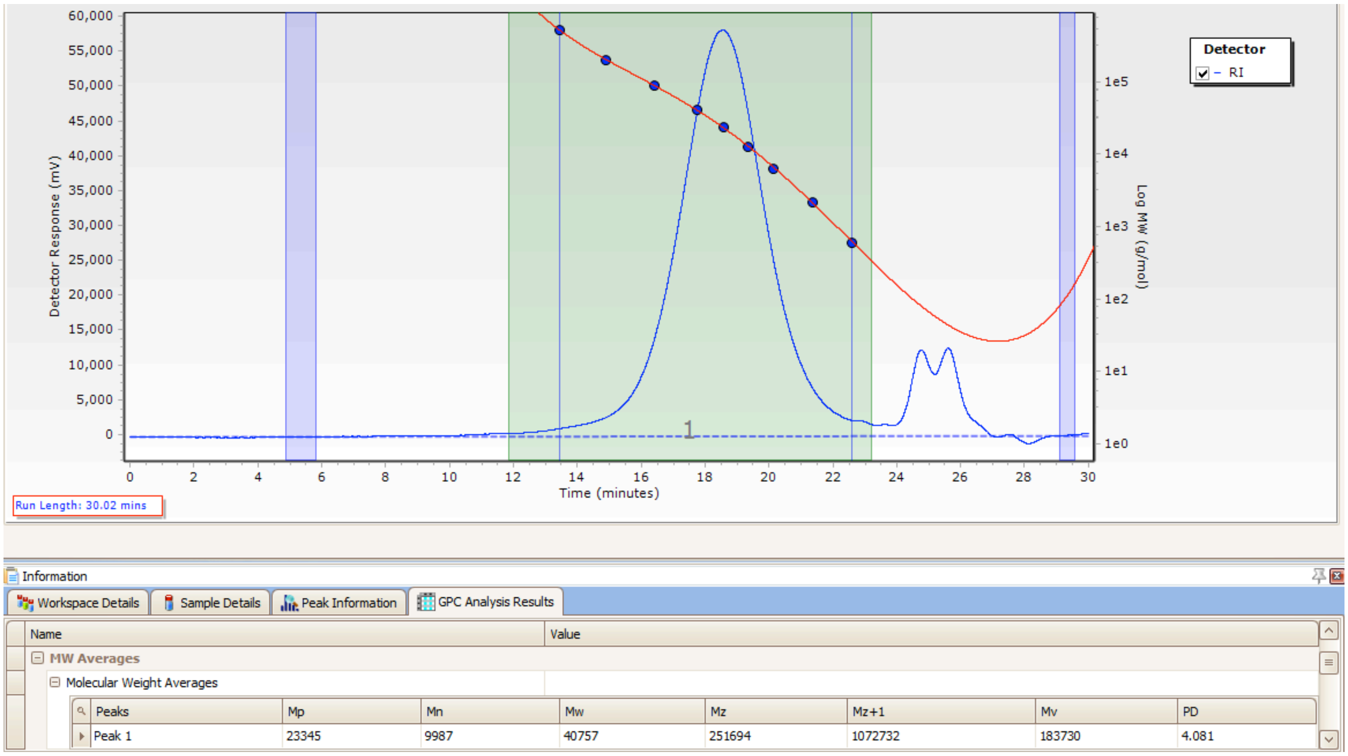
Figure S45. GPC Chromatogram of poly(ethylene pyrrolidone carboxylate) (Table S1, Entry 1 and Table S2, Entry 1).



Name	Value
⊟ MW Averages	
⊟ Molecular Weight Averages	

Peaks	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
Peak 1	1340	492	1032	2009	3378	1845	2.098

Figure S46. GPC Chromatogram of degraded poly(ethylene pyrrolidone carboxylate) after a year (Table S2, Entry 1).



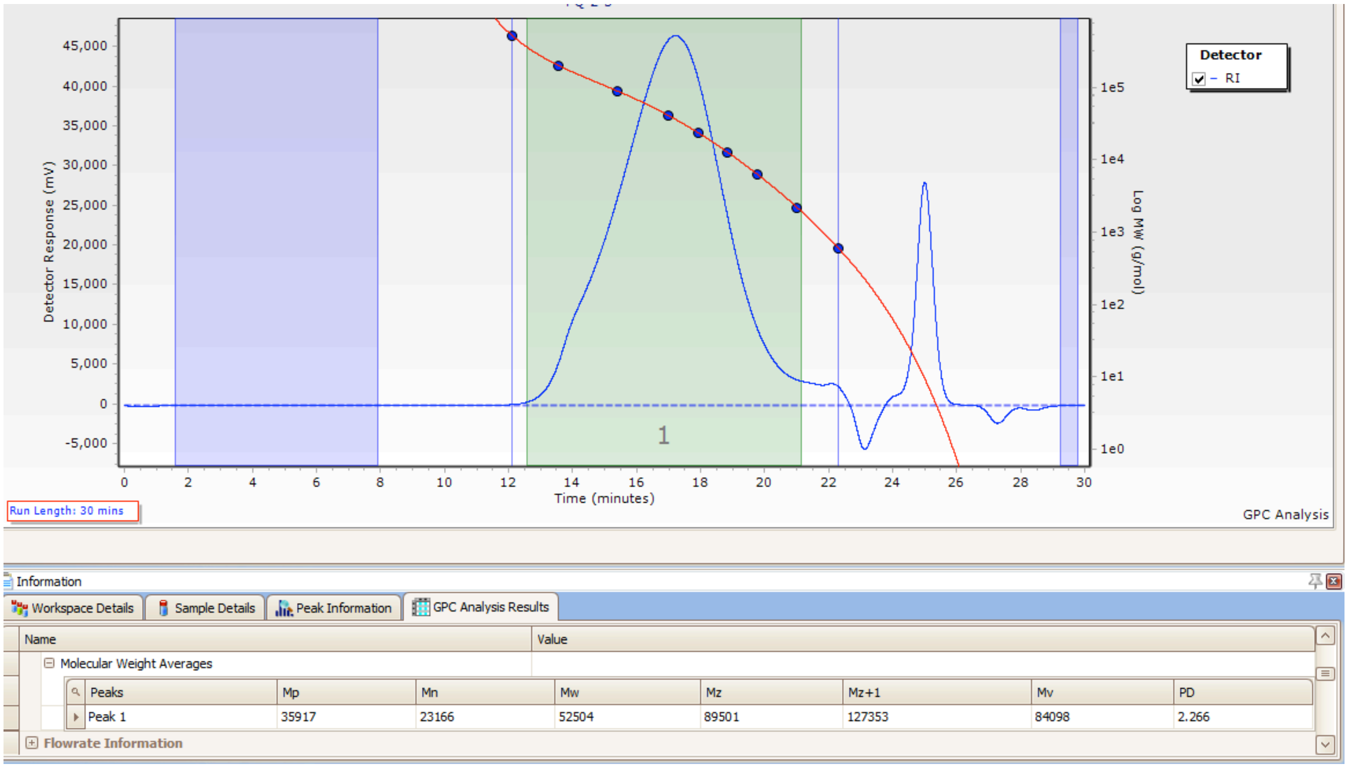
Name | Value

⊟ MW Averages

⊟ Molecular Weight Averages

Peaks	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
Peak 1	23345	9987	40757	251694	1072732	183730	4.081

Figure S47. GPC Chromatogram of Polyethylene/[ethylene bis(pyrrolidone carboxylate)] (Table S1, Entry 2).



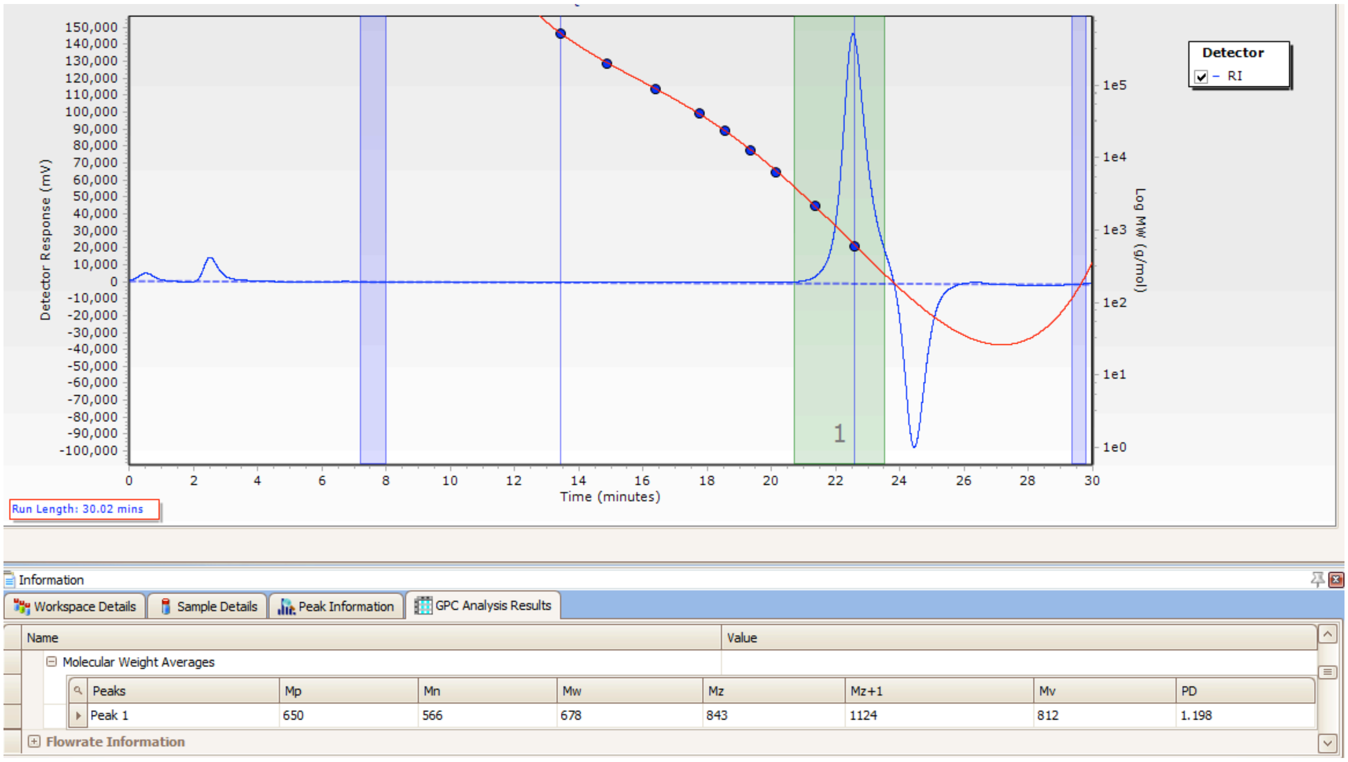
Name | Value

⊟ Molecular Weight Averages

Peaks	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
Peak 1	35917	23166	52504	89501	127353	84098	2.266

⊞ Flowrate Information

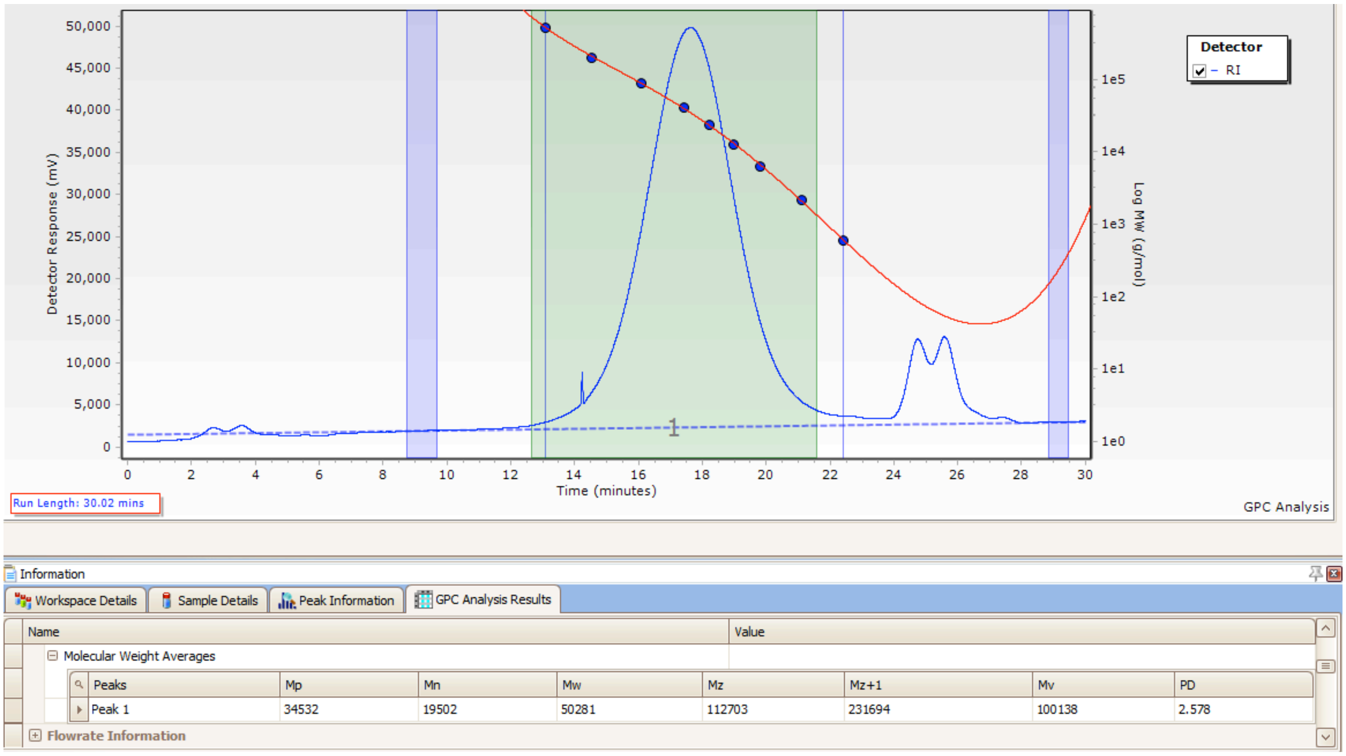
Figure S48. GPC Chromatogram of Polyethylene/[ethylene bis(pyrrolidone carboxylate)] (Table S1, Entry 3 and Table S2, Entry 2).



Name	Value
⊟ Molecular Weight Averages	

Peaks	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
Peak 1	650	566	678	843	1124	812	1.198

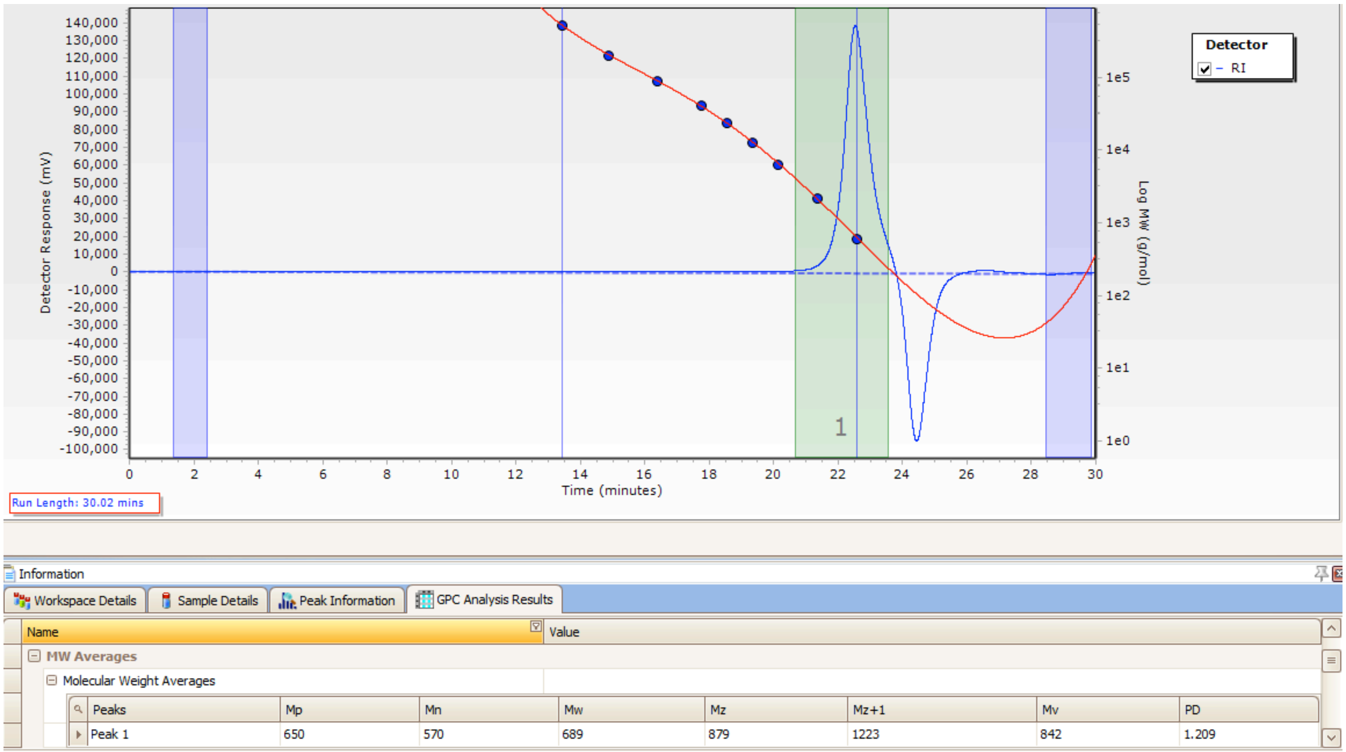
Figure S49. GPC Chromatogram of degraded Polyethylene/[ethylene bis(pyrrolidone carboxylate)] in water after one year (Table S2, Entry 2).



Name	Value
⊟ Molecular Weight Averages	

Peaks	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
Peak 1	34532	19502	50281	112703	231694	100138	2.578

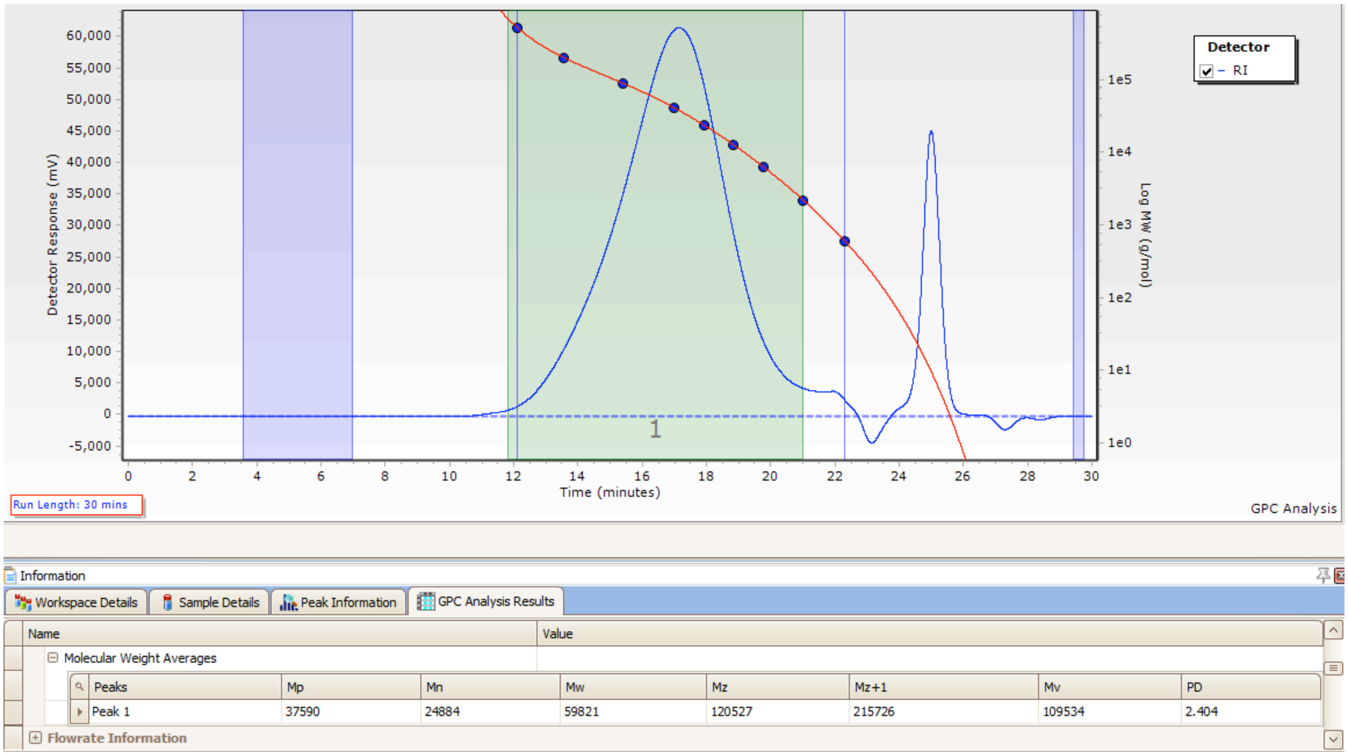
Figure S50. GPC Chromatogram of Polypropylene/[ethylene bis(pyrrolidone carboxylate)] (Table S1, Entry 4, Table S2, Entry 3 and Table S3, Entry 1).



Name	Value
⊟ MW Averages	
⊟ Molecular Weight Averages	

Peaks	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
Peak 1	650	570	689	879	1223	842	1.209

Figure S51. GPC Chromatogram of degraded Polypropylene/[ethylene bis(pyrrolidone carboxylate)] in water after one year (Table S2, Entry 3 and Table S3, Entry 6).

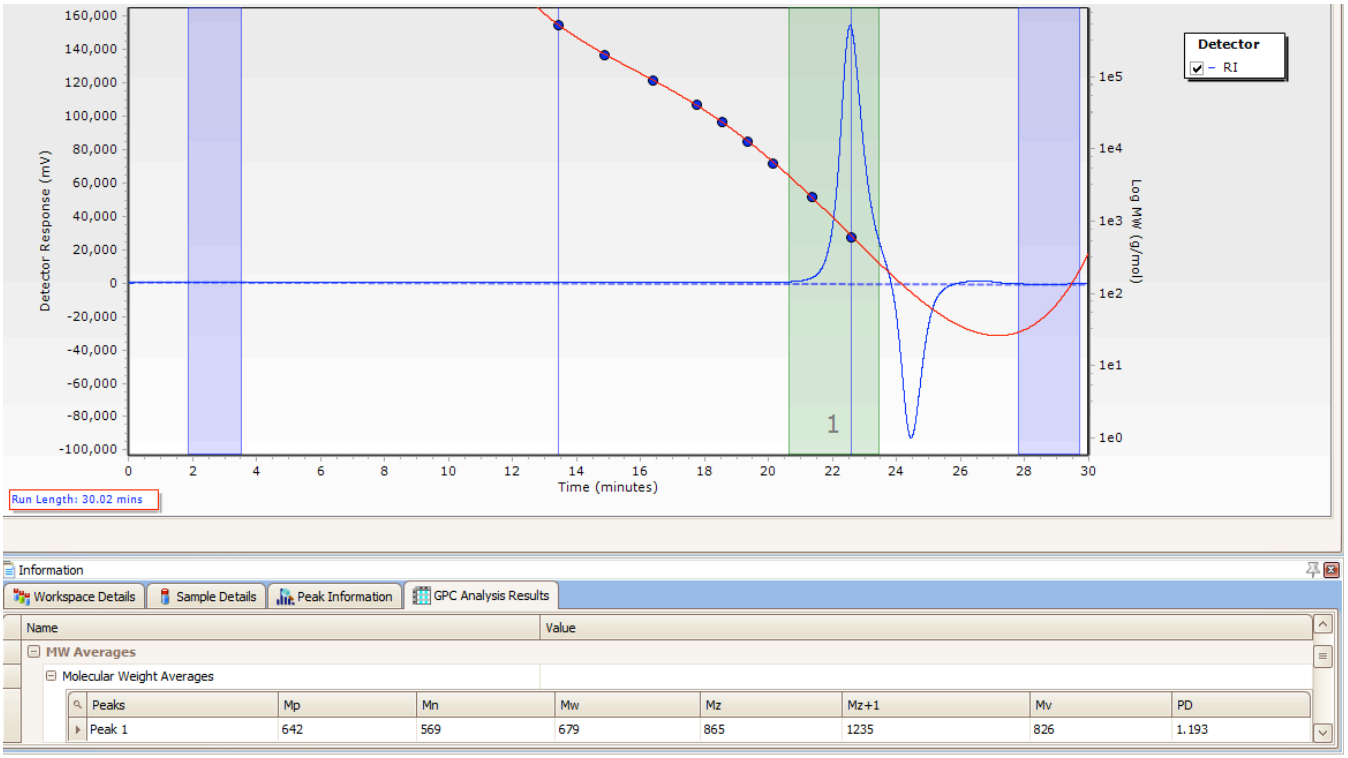


Name	Value
⊟ Molecular Weight Averages	

Peaks	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
Peak 1	37590	24884	59821	120527	215726	109534	2.404

⊞ Flowrate Information

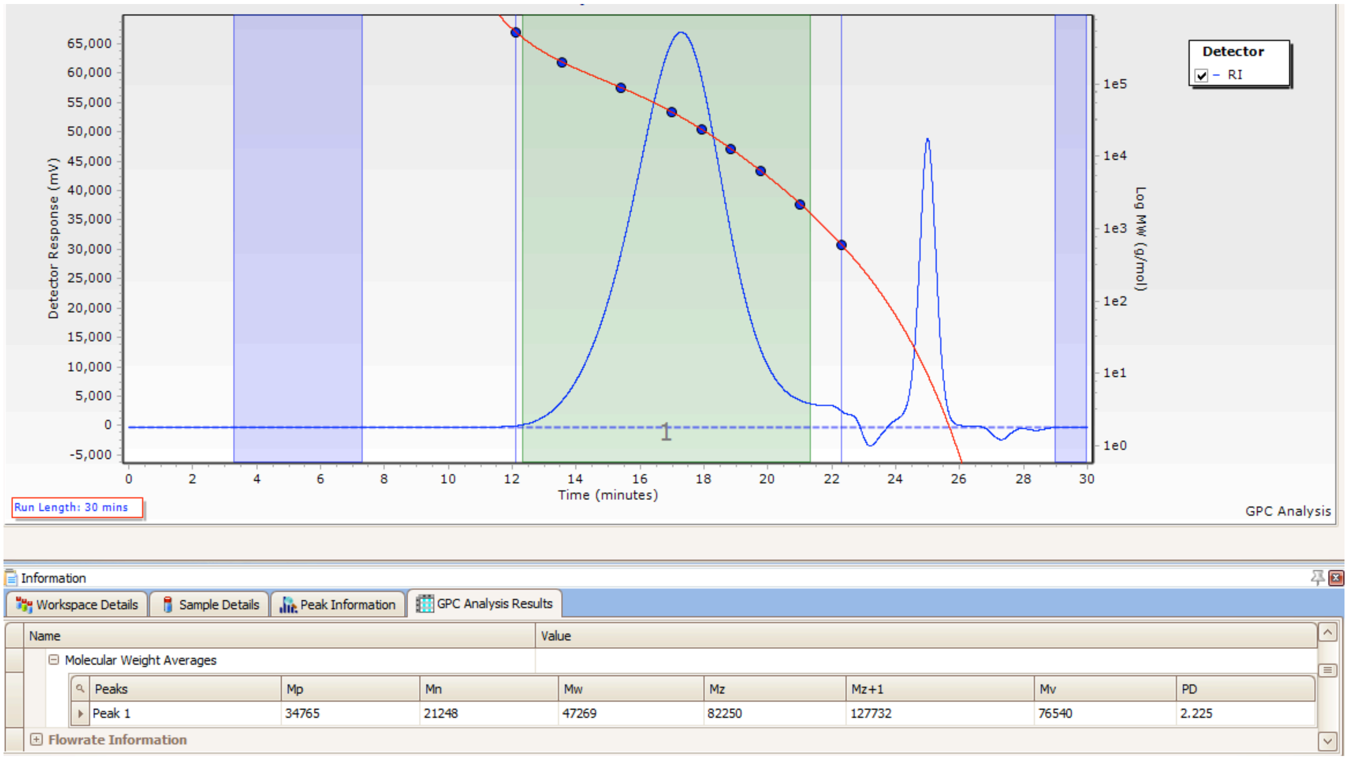
Figure S52. GPC Chromatogram of Polybutylene/[ethylene bis(pyrrolidone carboxylate)] (Table S1, Entry 5 and Table S2, Entry 4).



Name	Value
⊟ MW Averages	
⊟ Molecular Weight Averages	

Peaks	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
Peak 1	642	569	679	865	1235	826	1.193

Figure S53. GPC Chromatogram of degraded Polybutylene/[ethylene bis(pyrrolidone carboxylate)] in water after one year (Table S2, Entry 4).

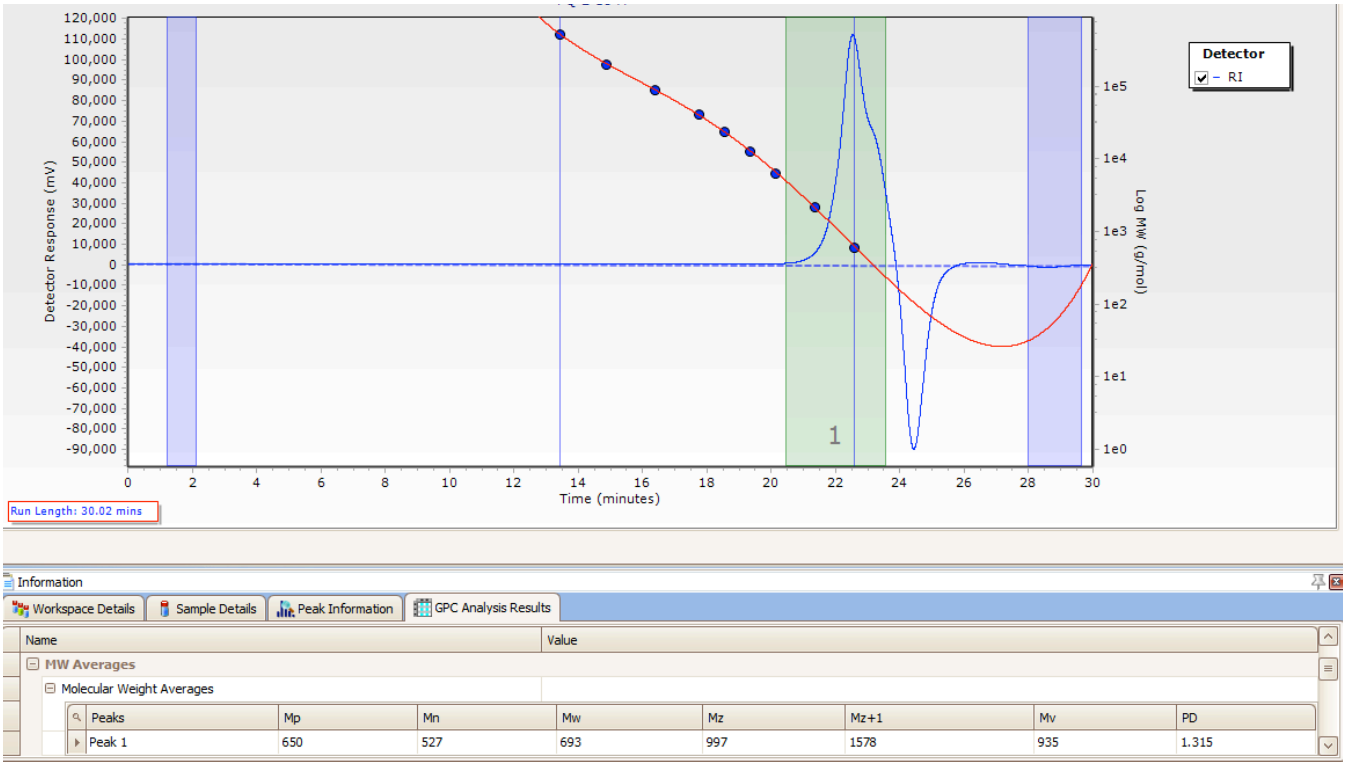


Name	Value
⊟ Molecular Weight Averages	

Peaks	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
Peak 1	34765	21248	47269	82250	127732	76540	2.225

⊞ Flowrate Information

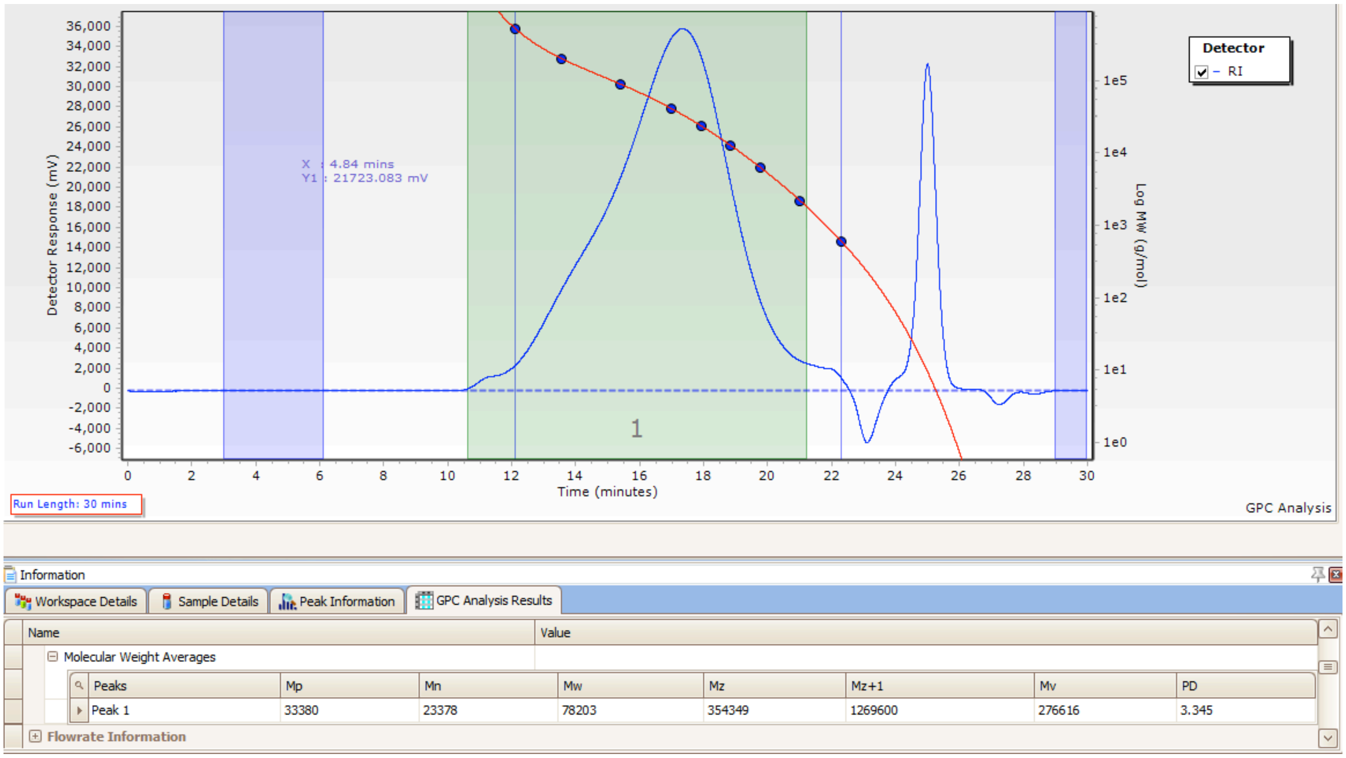
Figure S54. GPC Chromatogram of Polypentylene/[ethylene bis(pyrrolidone carboxylate)] (Table S1, Entry 6 and Table S2, Entry 5).



Name	Value
⊟ MW Averages	
⊟ Molecular Weight Averages	

Peaks	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
Peak 1	650	527	693	997	1578	935	1.315

Figure S55. GPC Chromatogram of degraded Polypentylene/[ethylene bis(pyrrolidone carboxylate)] in water after one year (Table S2, Entry 5).

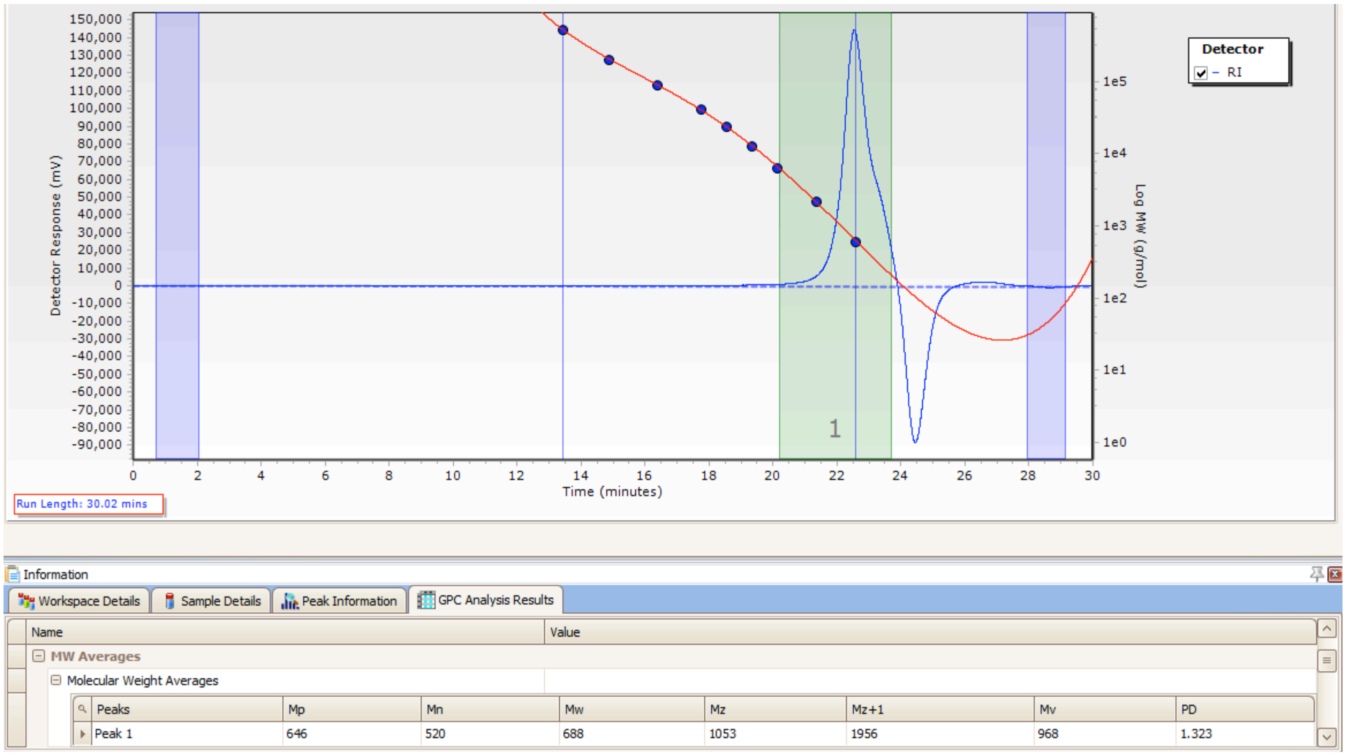


Name	Value
⊟ Molecular Weight Averages	

Peaks	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
Peak 1	33380	23378	78203	354349	1269600	276616	3.345

⊞ Flowrate Information

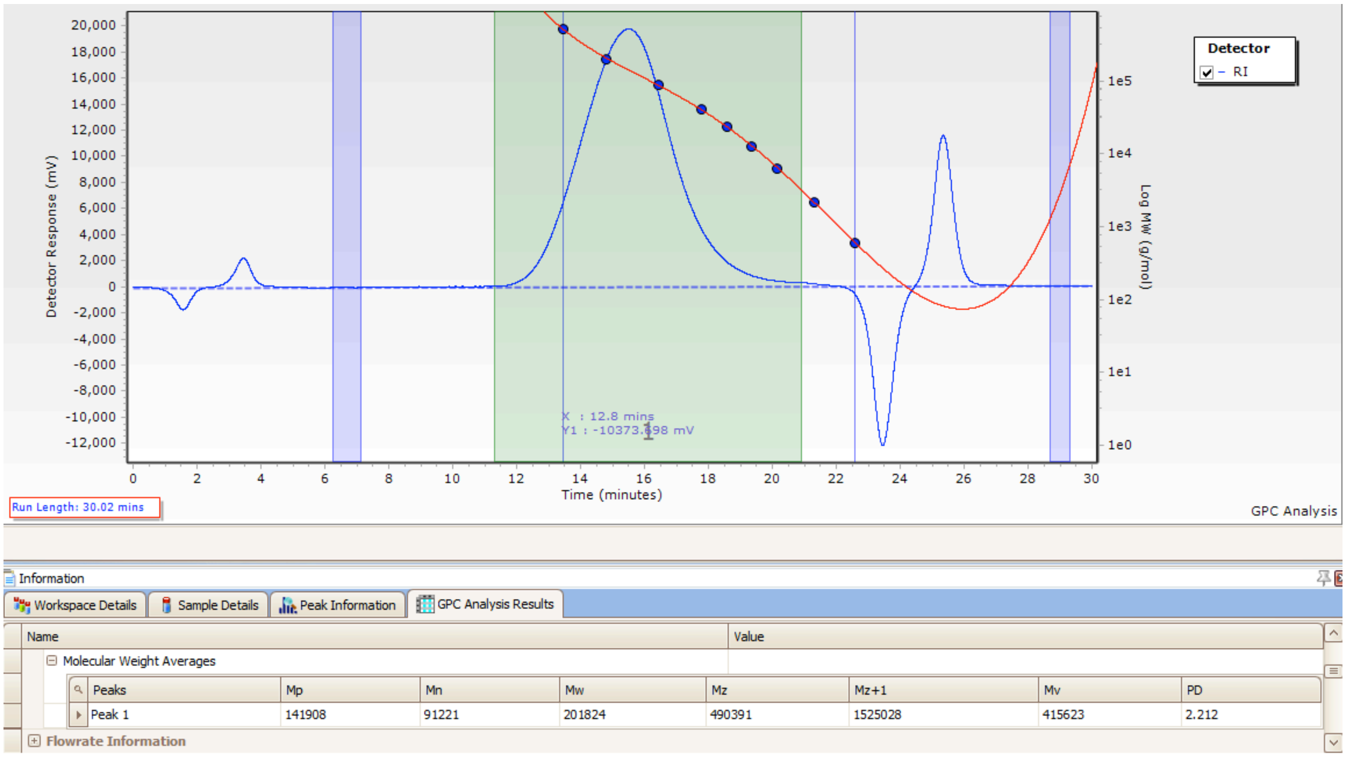
Figure S56. GPC Chromatogram of Polyhexylene/[ethylene bis(pyrrolidone carboxylate)] (Table S1, Entry 7 and Table S2, Entry 6).



Name	Value
⊟ MW Averages	
⊟ Molecular Weight Averages	

Peaks	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
Peak 1	646	520	688	1053	1956	968	1.323

Figure S57. GPC Chromatogram of degraded Polyhexylene/[ethylene bis(pyrrolidone carboxylate)] in water after one year (Table S2, Entry 6).

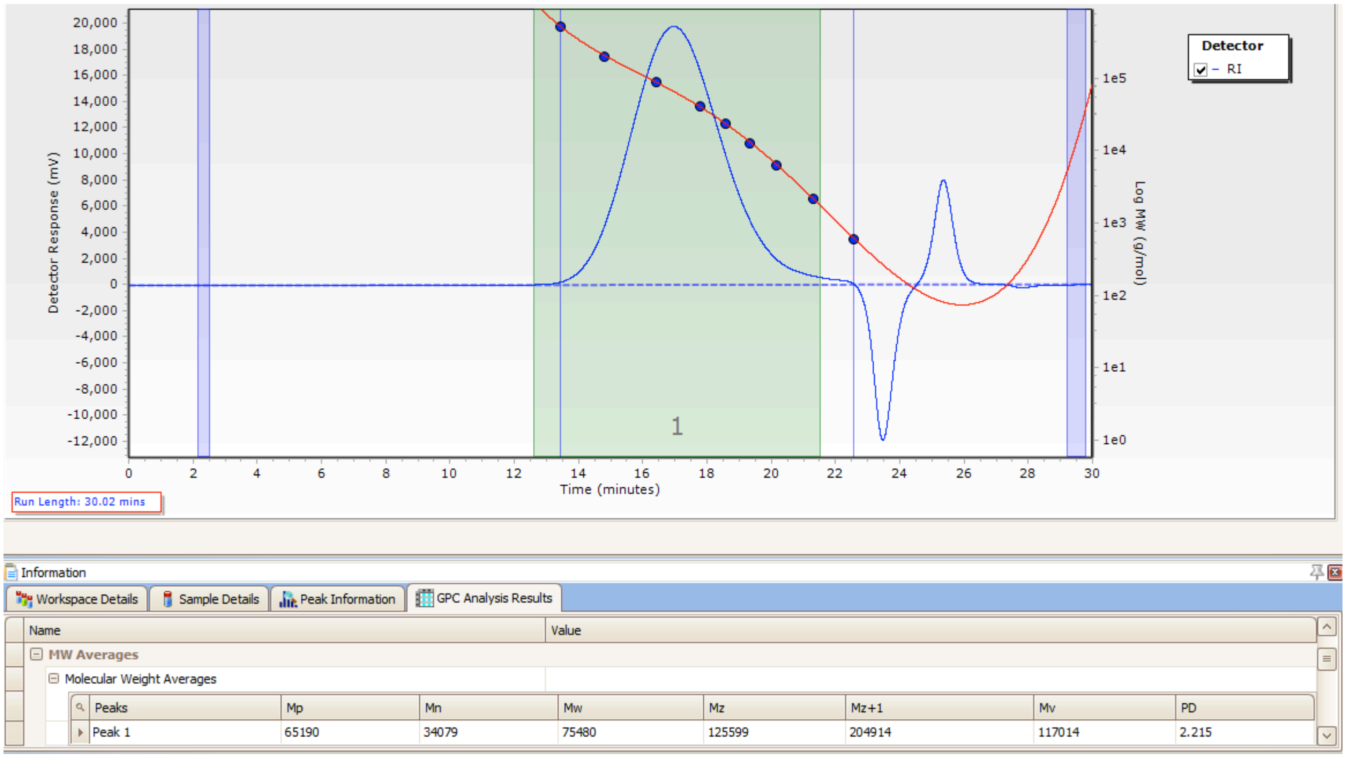


Name	Value
⊟ Molecular Weight Averages	

Peaks	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
Peak 1	141908	91221	201824	490391	1525028	415623	2.212

⊞ Flowrate Information

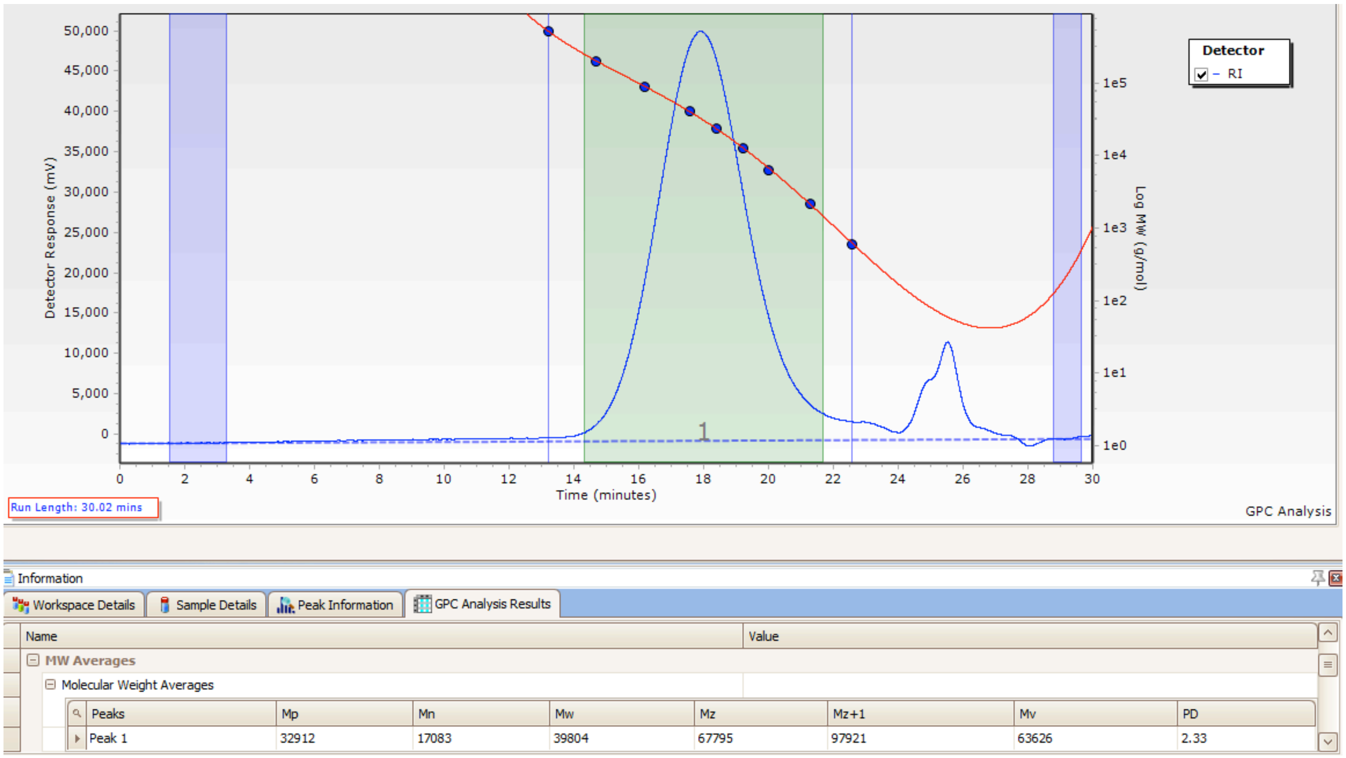
Figure S58. GPC Chromatogram of commercially available poly(lactic acid) (PLA) (Table S1, Entry 8).



Name	Value
MW Averages	
Molecular Weight Averages	

Peaks	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
Peak 1	65190	34079	75480	125599	204914	117014	2.215

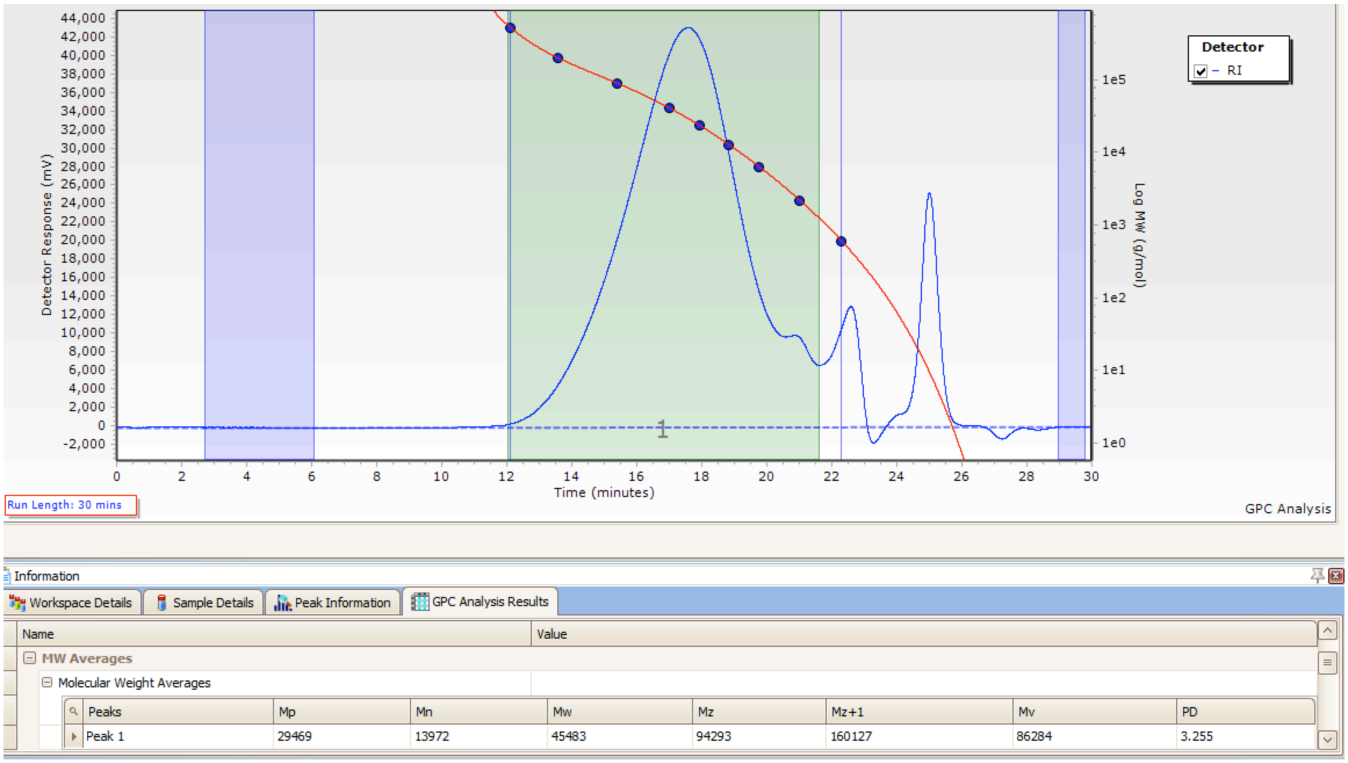
Figure S59. GPC Chromatogram of commercially available poly(ethylene terephthalate) (PET) (Table S1, Entry 9).



Name	Value
MW Averages	
Molecular Weight Averages	

Peaks	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
Peak 1	32912	17083	39804	67795	97921	63626	2.33

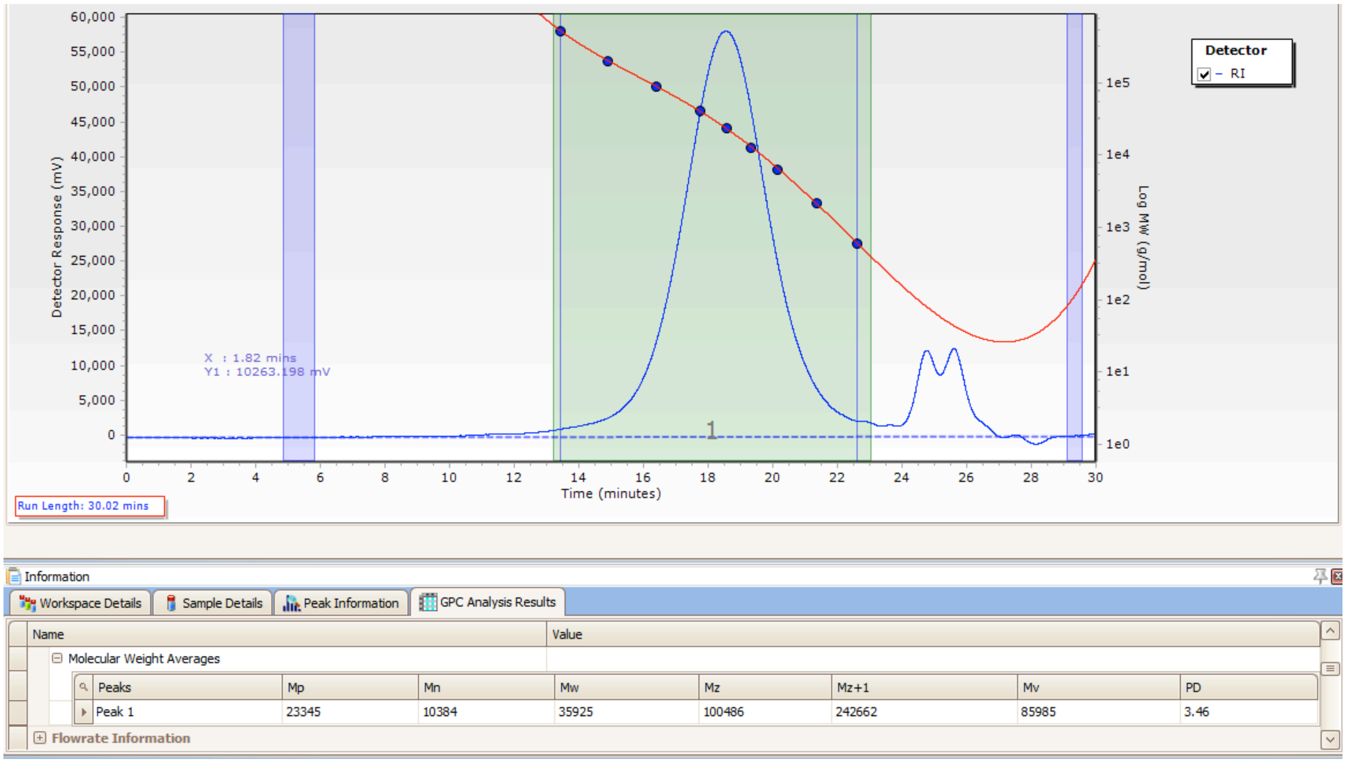
Figure S60. GPC Chromatogram of Polypropylene/[ethylene bis(pyrrolidone carboxylate)] in water after 15 days (Table S3, Entry 2).



Name	Value
⊟ **MW Averages**	
⊟ Molecular Weight Averages	

Peaks	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
Peak 1	29469	13972	45483	94293	160127	86284	3.255

Figure S61. GPC Chromatogram of Polypropylene/[ethylene bis(pyrrolidone carboxylate)] in water after 30 days (Table S3, Entry 3).

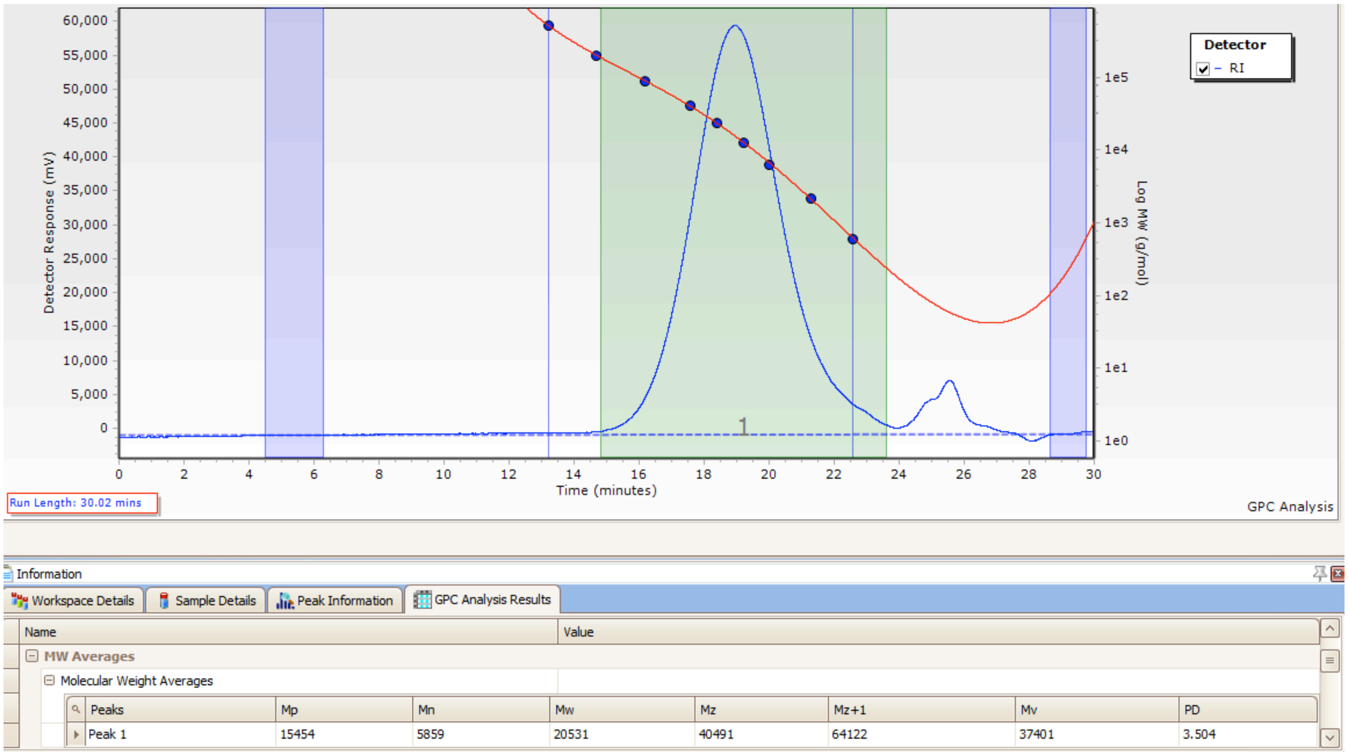


Name	Value
⊟ Molecular Weight Averages	

Peaks	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
Peak 1	23345	10384	35925	100486	242662	85985	3.46

⊞ **Flowrate Information**

Figure S62. GPC Chromatogram of Polypropylene/[ethylene bis(pyrrolidone carboxylate)] in water after 90 days (Table S3, Entry 4).



Name | Value

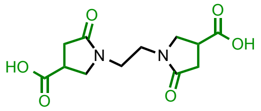
MW Averages

Molecular Weight Averages

Peaks	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
Peak 1	15454	5859	20531	40491	64122	37401	3.504

Figure S63. GPC Chromatogram of Polypropylene/[ethylene bis(pyrrolidone carboxylate)] in water after 180 days (Table S3, Entry 5).

2D NMR Analysis/Diastereomeric ratio of EBPC



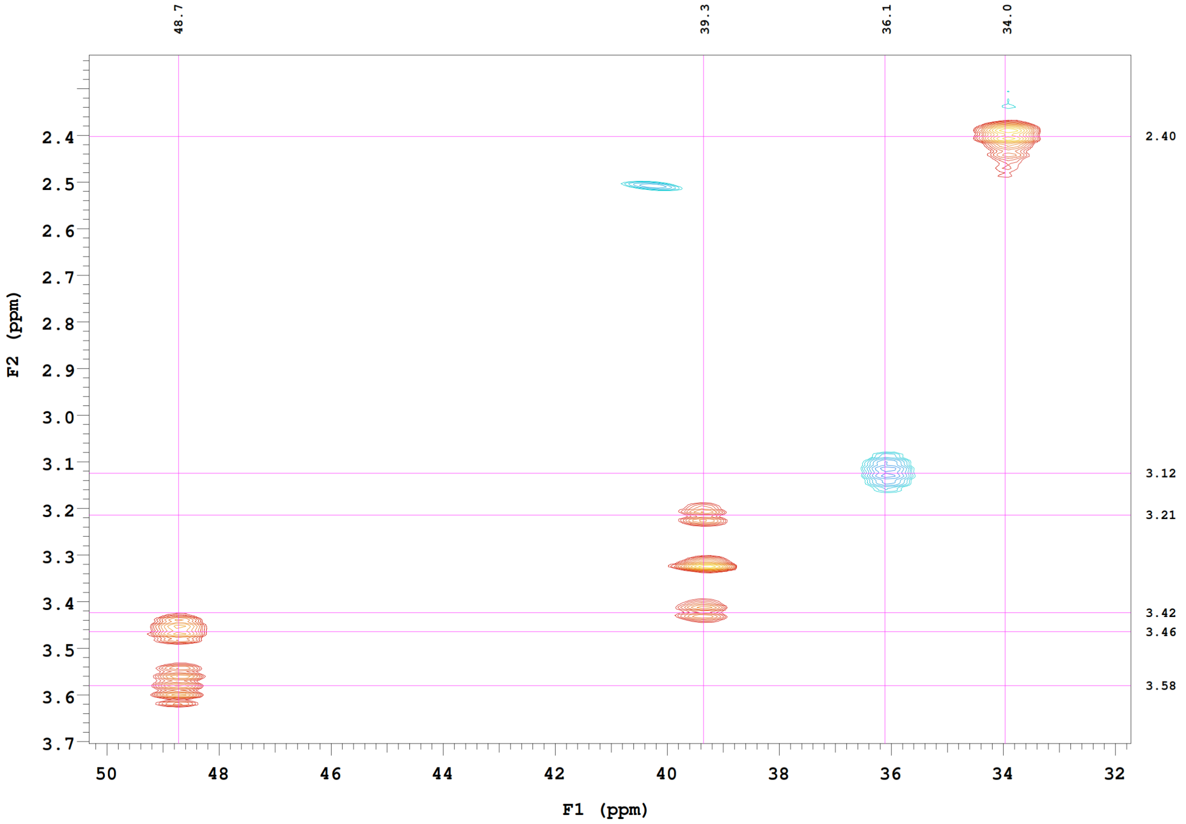


Figure S64. HSQC spectrum of ethylene bis(pyrrolidone carboxylic acid) (EBPC).

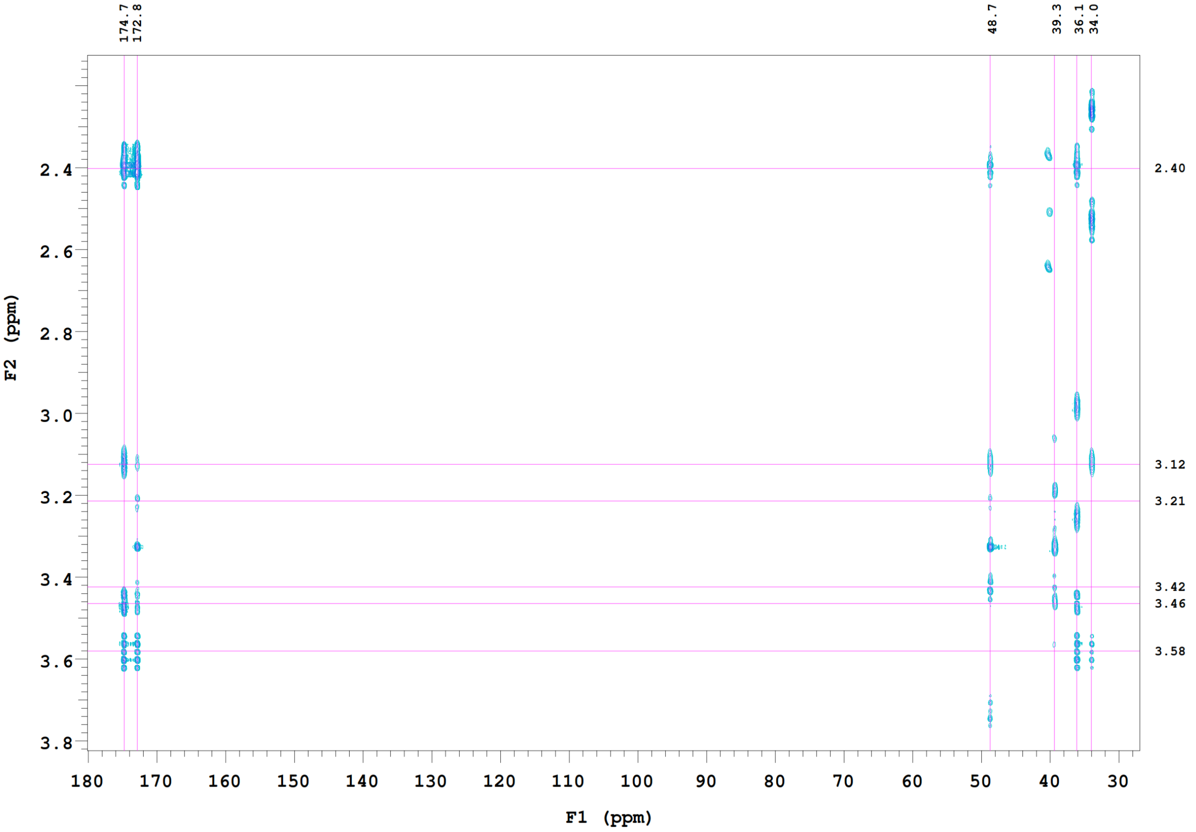


Figure S65. HMBC spectrum of ethylene bis(pyrrolidone carboxylic acid) (EBPC).

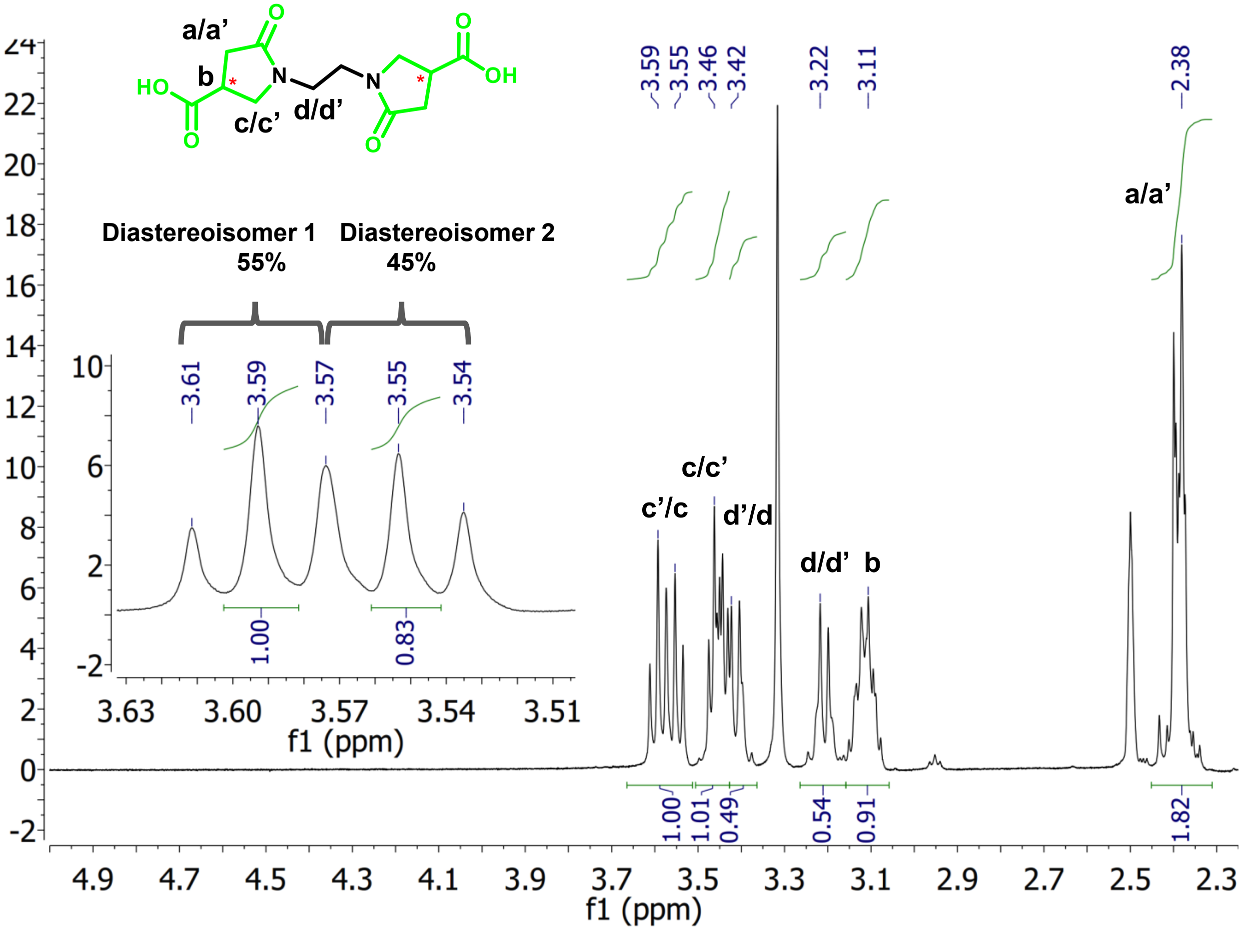


Figure S66. ^{1}H NMR of ethylene bis(pyrrolidone carboxylic acid) (EBPC) with peak assignments.

Based on the HSQC and HMBC spectra, we are able to identify all the ^{1}H NMR peaks. Protons a, a', b, d, and d' of both diastereoisomers are completely overlapped which made only one signal area for each proton. However, the protons c and c' (3.51 – 3.63 ppm) of these two diastereoisomers are only slightly overlapped, which allows the determination of the diastereoisomeric ratio.

- Diastereoisomer 1: central peak at 3.59 ppm has an integration of 1.00
- Diastereoisomer 2: central peak at 3.55 ppm has an integration of 0.83

So the relative abundance of diastereoisomer 1 = [1.00/(1.00 + 0.83)]*100 = **55%**.
And the relative abundance of diastereoisomer 2 = [0.83/(1.00 + 0.83)]*100 = **45%**.

MALDI-TOF Analysis of Polymers and ESI-TOF Analysis of Degradation Products

MALDI-TOF Analysis Protocol

Matrix assisted laser desorption/ionization time-of- flight (MALDI-TOF) was performed on a **Bruker Daltonics Microflex LRF MALDI-TOF** mass spectrometer (Bruker Daltonics, Breman, Germany) operated in linear, positive ion mode with a N_2 laser. Laser power was used at the threshold level required to generate signal until suitable data was obtained. The instrument was calibrated with Protein Calibration Standards purchased from Bruker Daltonics bracketing the molecular weights of the samples (typically mixtures of myoglobin and cytochrome c using doubly charged, singly charged and dimer peaks as appropriate). Samples were prepared in 100% hexafluoroisopropanol at an approximate concentration of 1 pmol/μL. Dithranol in 10 mmol sodium iodide in hexafluoroisopropanol was used as the matrix. Allotments of 1 μL of matrix and 1 μL of sample were thoroughly mixed together; 0.5 μL of this was spotted on the target plate and allowed to dry.

ESI-TOF Analysis Protocol

Accurate mass experiments were performed on a **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 - 2000. Samples were prepared in a solution containing acidified methanol (0.1% formic acid) and adventitious sodium salts; 1 µL was injected into the electrospray source at a rate of 200 µL min-1. Optimal conditions were: capillary voltage 4000 V, source temperature 350 ^{o}C and a cone voltage of 60 V. The TOF analyzer was scanned over m/z 130.00–3200.00 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.

Polymers PEPC (Table S1, entry 1) and PPEBPC (Table S1, entry 4) were subject to MALDI-TOF analysis (ionized by Na^+). For PEPC (Figure S67), the repeat unit analyzed to be 155 Daltons ($C_7H_9NO_3$), as predicted by the assumed polymeric structure. For PPEBPC (Figure S68), the repeat unit analyzed to be 324 Daltons ($C_{15}H_{20}N_2O_6$), as predicted by the assumed polymeric structure.

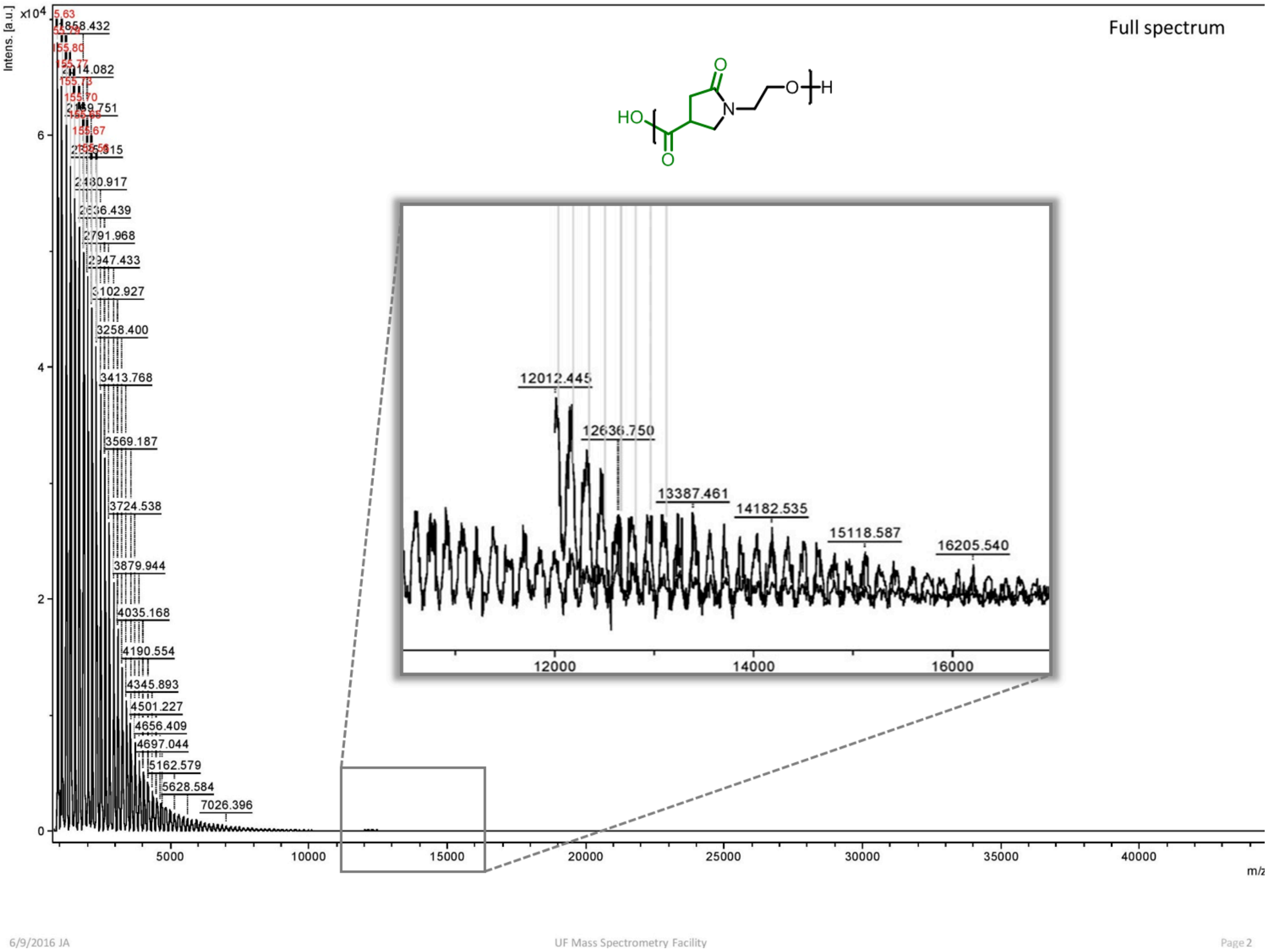


Figure S67. MALDI-TOF analysis of polymer PEPC (Table S1, entry 1).

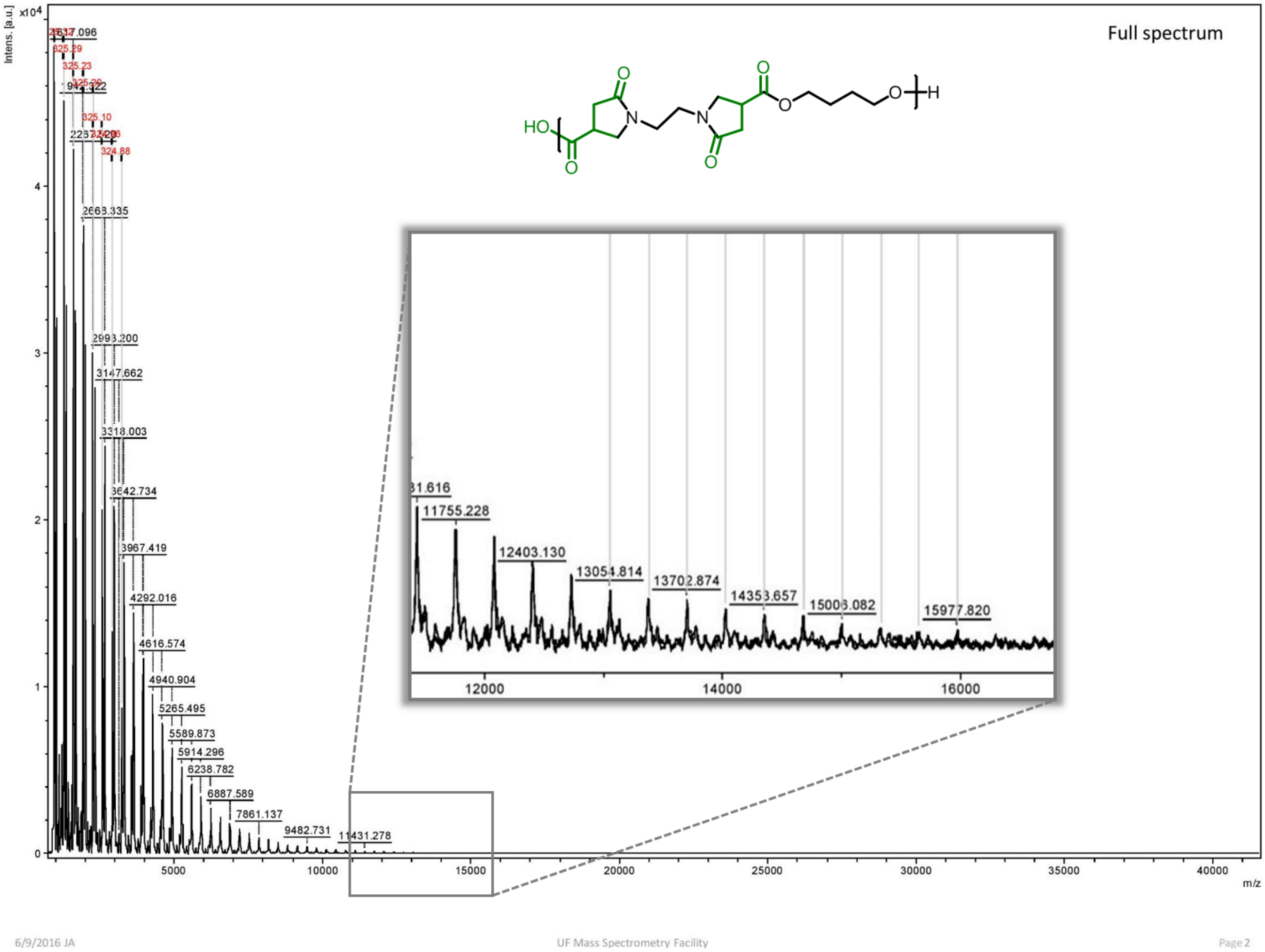


Figure S68. MALDI-TOF analysis of polymer PPEBPC (Table S1, entry 4).

Polymers PEPC and PPEBPC were each subjected to hydrolytic degradation under the following conditions: 6M aqueous HCl solution with continuous agitation on an orbital shaker for 20 days.

ESI-TOF analysis of the degraded PEPC clearly indicated the hydroxy-acid HEPC (Figure S69), with a peak at 196 Da = HEPC (173 Da) + sodium (23 Da), along with higher oligomers separated by the predicted mass of 155 Da, consistent with the lactam HEPC repeat unit—and not a hydrolyzed lactam.

ESI-TOF analysis of the degraded PPEBPC clearly indicated the presumed PEBPC repeat unit (AB, 324 Da, Figure S70), with a peak at 365 Da = PEBPC (342 Da) + sodium (23 Da), along with higher oligomers separated by the predicted masses of the A repeat unit (from EBPC, 266 Da) and the B repeat unit (from 1,3-propanediol, 58 Da). This is consistent with the repeat unit containing intact lactams—and not hydrolyzed lactams.

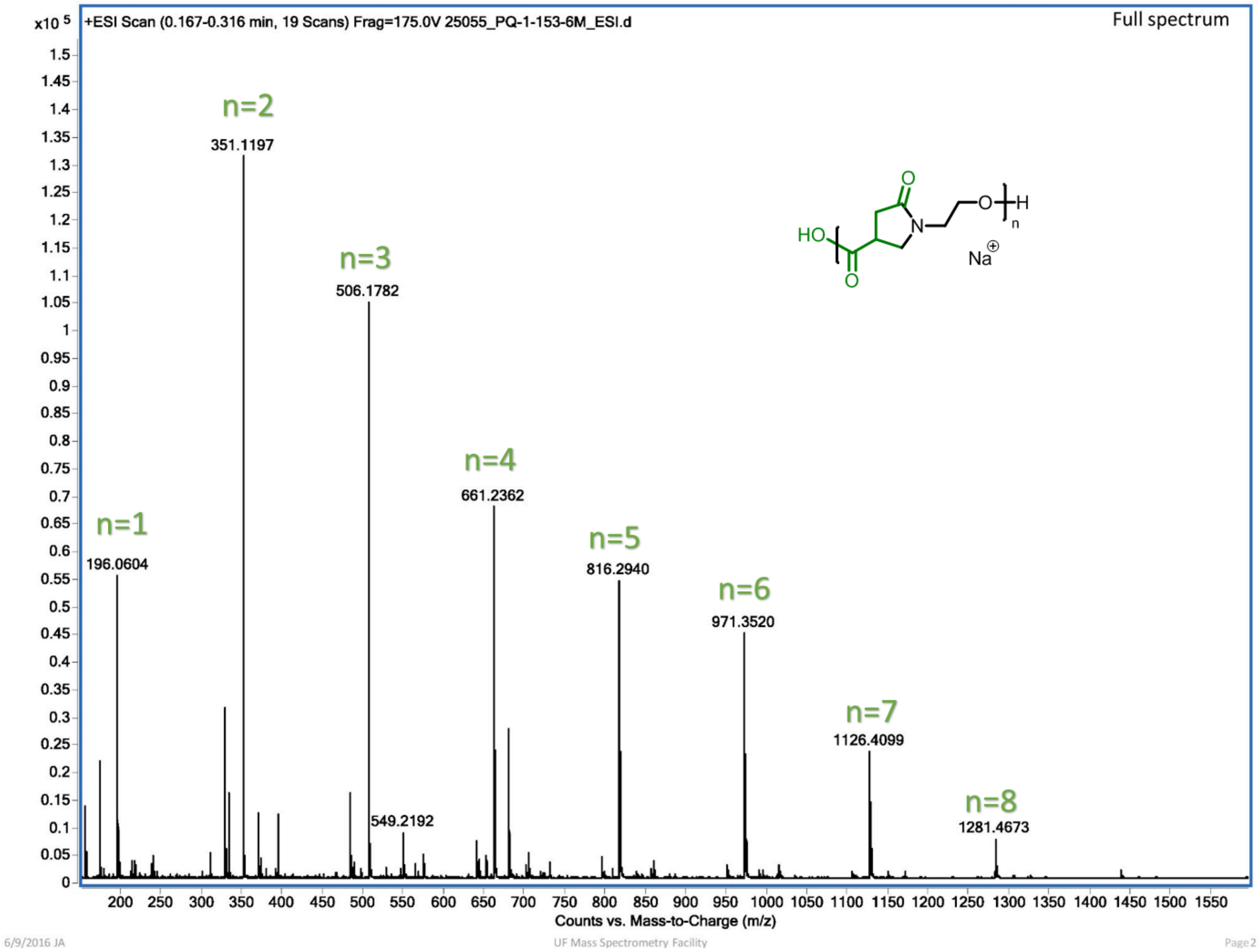


Figure S69. ESI-TOF analysis of degradation products from polymer PEPC, showing HEPC (173 Da) + sodium (23 DA) = 196 Da (for n =1) and higher oligomers with a repeat unit of 155 Da. Thus, 18 Da + 23 Da + n(155 Da) = 196, 351, 506, 661, 816, 971, 1126, 1281 Da for n = 1 through 8, respectively.

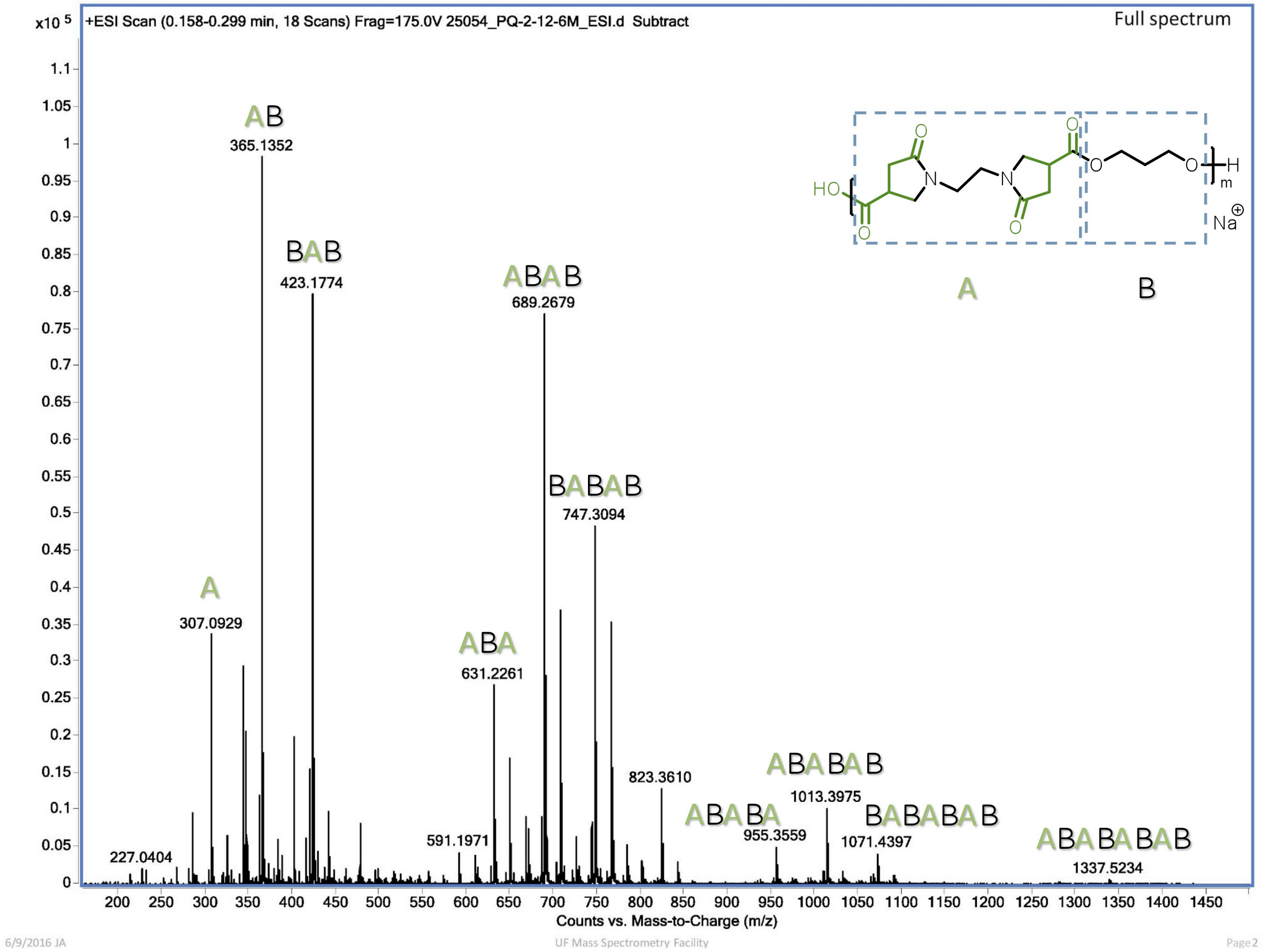


Figure S70. ESI-TOF analysis of degradation products from polymer PPEBPC, showing PEBPC (342 Da) + sodium (23 Da) = 365 Da and higher oligomers made from both A (266 Da) and B (58 Da) segments, according to Table S4.

Table S4. Computation of oligmer peaks in the ESI-TOF spectrum from degraded (hyrolyzed) PPEBPC.

oligomer	#A 266 Da	#B 58 Da	water 18 Da	sodium 23 Da	total
A	1	0	18	23	307
AB	1	1	18	23	365
BAB	1	2	18	23	423
ABA	2	1	18	23	631
ABAB	2	2	18	23	689
BABAB	2	3	18	23	747
ABABA	3	2	18	23	955
ABABAB	3	3	18	23	1013
BABABAB	3	4	18	23	1071
ABABABAB	4	4	18	23	1337