Polyoxalates from Biorenewable Diols via Oxalate Metathesis Polymerization

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Electronic Supplementary Information (ESI)

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

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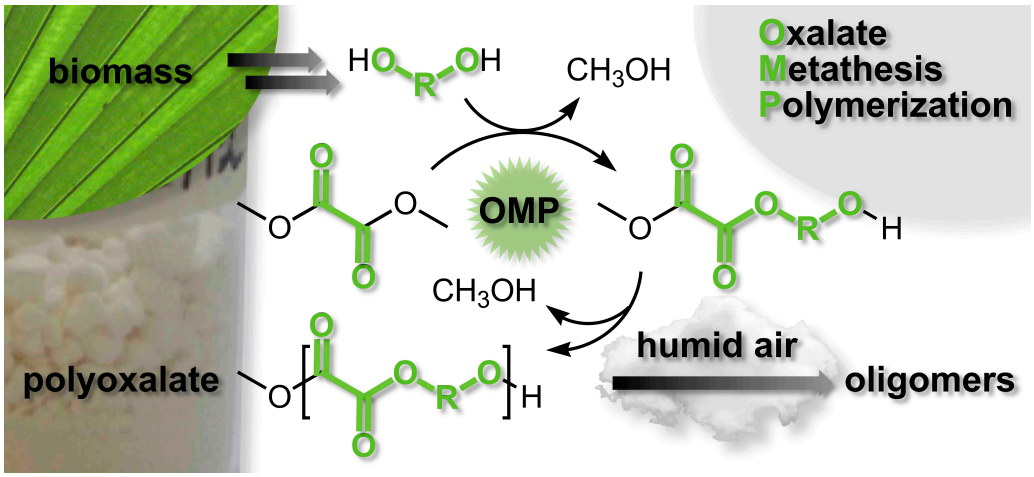


General Considerations and Instrumentation

Proton nuclear magnetic resonance (^{1}H NMR) spectra were recorded using a Varian Mercury 300 MHz and Inova 500 MHz spectrometer. Chemical shifts are reported in parts per million (ppm) downfield relative to tetramethylsilane (TMS, 0.0 ppm) or residual proton 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 theromograms were obtained with a DSC Q1000 from TA instruments. About 1.5-3 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 –100 to 200 ºC.

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

Gel permeation chromatography (GPC) was performed at 40 °C using a Waters Associates GPCV2000 liquid chromatography system with an internal differential refractive index detector and two Waters Styragel HR-5E columns (10 μm PD, 7.8 mm i.d., 300 mm length) using HPLC grade tetrahydrofuran (THF) as the mobile phase at a flow rate of 1.0 mL/min. Calibration was performed with narrow polydispersity polystyrene standards.

Monomer Preparation

1,3-propanediol. 1,3-propanediol was purchased from Aldrich as a liquid in 99.6% purity.

2,2-dimethyl-1,3-propanediol. Was purchased from Aldrich as a solid in 99% purity

1,4-butanediol. 1,4-butanediol was purchased from Aldrich as a liquid in 99% purity.

1,5-pentanediol. 1,5-pentanediol was purchased from Acros Organics as a liquid in 98% purity. The monomer was further purified by first stirring it over calcium hydride for 24 hours followed by vacuum distillation. The purified monomer was stored over molecular sieves.

1,6-hexanediol. 1,6-hexanediol was purchased from Acros Organics as a crystalline solid in 97 % purity. The monomer was further purified by recrystallization from ethyl acetate.

1,7-heptanediol. 1,7-pentanediol was purchased from Aldrich as a liquid in 95% purity. The monomer was further purified by first stirring it over calcium hydride for 24 hours followed by vacuum distillation. The purified monomer was stored over molecular sieves.

1,8-octanediol. 1,8-octanediol was purchased from Acros Organics as a crystalline solid in 99% purity. The monomer was further purified by recrystallization from ethyl acetate.

1,9-nonanediol. 1,9-nonanediol was purchased from Acros Organics as a crystalline solid in 99% purity. The monomer was further purified by recrystallization from ethyl acetate.

1,10-decanediol. 1,10-decanediol was purchased from Acros Organics as a crystalline solid in 99% purity. The monomer was further purified by recrystallization from 1,2-dichloroethane.

1,11-undecanediol. 1,11-undecanediol was purchased from Accela as a crystalline solid in 97% purity.

1,12-dodecanediol. 1,12-dodecanediol was purchased from Aldrich as a crystalline solid in 99% purity. The monomer was further purified by recrystallization from 1,2-dichloroethane.

Resorcinol bis(beta-hydroxyethyl)ether. 1 mol of Resorcinol reacted with 2 moles of ethylene carbonate and catalytic amount of Triphenylphosphine (PPh_3) at 150 °C for 24 hours, then cooled. 200 mL of methanol in ice bath were added, crystals were filtered and washed with more cold methanol, giving 64% yield of final product.

Hydroquinone bis(beta-hydroxyethyl)ether. Hydroquinone bis(beta-hydroxyethyl)ether. Was purchased from Aldrich as a solid in 99+% purity.

Dimethyl oxalate. Dimethyl oxalate was purchased from Aldrich as a crystalline solid in 99% purity.

Polymerizations

Polymerization device. 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 molecules of condensation could be collected and visualized in the bump trap, followed by removal of all volatiles—without changing the initial glassware configuration. See below.

General polymerization and workup procedure. A 50 mL round bottom flask was charged with one equivalent of dimethyl oxalate, one equivalent of the corresponding diol, and about 2 mol% of *para*-toluenesulfonic acid (*p*-TSA). The mixture was stirred under a nitrogen atmosphere for 1 hour at 100 ºC. After that the temperature was increased to 130 ºC for 2 hours. Then, vacuum was pulled for 1 hour, and finally temperature was increased to 220 ºC for 3 hours. The product was dissolved in about 30-40 mL of methylene chloride or dimethyl sulfoxide. The polymer was reprecipitated by the addition of the solution in about 100 mL of cold methanol. The system was filtered and polymer was dried under vacuum.

Polypropylene oxalate

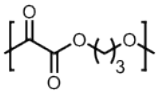


Table S1, Entry 1. 44.8% yield. ^{1}H NMR ($CDCl_3$): ppm 4.42 (t, J = 6.1 Hz, 4 H), 2.20 (quin, J = 6.1 Hz, 2 H). ^{13}C NMR ($CDCl_3$): δ ppm 157.4, 63.5, 27.3.

Polyneopentylene oxalate

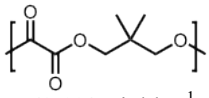


Table S1, Entry 2. 62.9% yield. ^{1}H NMR ($CDCl_3$): ppm 4.12 (s, 4 H), 1.07 (s, 6 H). ^{13}C NMR ($CDCl_3$): δ ppm 157.1, 70.9, 35.0, 21.5.

Polybutylene oxalate

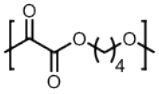


Table S1, Entry 3. 72.2% yield. ^{1}H NMR ($CDCl_3$): ppm 4.38 – 4.31 (m, 4 H), 1.92 – 1.84 (m, 4 H). ^{13}C NMR ($CDCl_3$): δ ppm 157.6, 66.3, 24.8.

Polypentylene oxalate

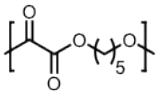


Table S1, Entry 4. 79.1% yield. ^{1}H NMR ($CDCl_3$): ppm 4.30 (t, J = 6.6 Hz, 4 H), 1.80 (quin, J = 7.2 Hz, 4 H), 1.51 (quin, J = 7.5 Hz, 2 H). ^{13}C NMR ($CDCl_3$): δ ppm 157.8, 66.7, 27.8, 22.1.

Polyhexylene oxalate

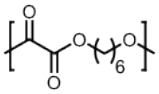


Table S1, Entry 5. 77.7% yield. ^{1}H NMR ($CDCl_3$): ppm 4.29 (t, J = 6.6 Hz, 4 H), 1.76 (quin, J = 7.0 Hz, 4 H), 1.49 – 1.40 (m, 4 H). ^{13}C NMR ($CDCl_3$): δ ppm 157.9, 66.8, 28.1, 25.3.

Polyheptylene oxalate

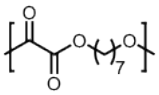


Table S1, Entry 6. 68.6% yield. ^{1}H NMR ($CDCl_3$): ppm 4.28 (t, J = 6.9 Hz, 4 H), 1.83 – 1.66 (m, 4 H), 1.49 – 1.32 (m, 6 H). ^{13}C NMR ($CDCl_3$): δ ppm 157.9, 67.0, 28.6, 28.1, 25.5.

Polyoctylene oxalate

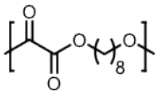


Table S1, Entry 7. 85.1% yield. ^{1}H NMR ($CDCl_3$): ppm 4.28 (t, J = 6.6 Hz, 4 H), 1.74 (quin, J = 7.1 Hz, 4 H), 1.44 – 1.30 (m, 8 H). ^{13}C NMR ($CDCl_3$): δ ppm 158.0, 67.0, 28.9, 28.2, 25.6.

Polynonylene oxalate

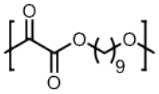


Table S1, Entry 8. 76.7% yield. ^{1}H NMR ($CDCl_3$): ppm 4.28 (t, J = 6.8 Hz, 4 H), 1.73 (quin, J = 6.8 Hz, 4 H), 1.44 – 1.27 (m, 10 H). ^{13}C NMR ($CDCl_3$): δ ppm 158.0, 67.1, 29.2, 29.0, 28.2, 25.6.

Polydecylene oxalate

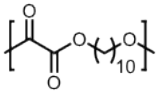


Table S1, Entry 9. 83.2% yield. ^{1}H NMR ($CDCl_3$): ppm 4.28 (t, J = 6.8 Hz, 4 H), 1.73 (quin, J = 7.2 Hz, 4 H), 1.42 – 1.26 (m, 12 H). ^{13}C NMR ($CDCl_3$): δ ppm 158.1, 67.1, 29.3, 29.1, 28.3, 25.7.

Polyundecylene oxalate

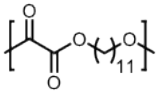


Table S1, Entry 10. 73.4% yield. ^{1}H NMR ($CDCl_3$): ppm 4.28 (t, J = 6.8 Hz, 4 H), 1.73 (quin, J = 7.0 Hz, 4 H), 1.43 – 1.23 (m, 14 H). ^{13}C NMR ($CDCl_3$): δ ppm 158.0, 67.1, 29.4, 29.4, 29.1, 28.2, 25.7.

Polydodecylene oxalate

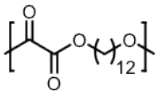


Table S1, Entry 11. 84.7% yield. ^{1}H NMR ($CDCl_3$): ppm 4.30 (t, J = 7.1 Hz, 4 H), 1.76 (quin, J = 7.0 Hz, 4 H), 1.44 – 1.25 (m, 16 H). ^{13}C NMR ($CDCl_3$): δ ppm 158.0, 67.2, 29.5, 29.4, 29.1, 28.3, 25.7.

Poly(decylene-*co*-RBHE) oxalate [50:50]

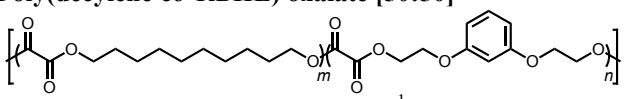


Table S2, Entry 5. 75.8% yield. ^{1}H NMR ($CDCl_3$): ppm 7.06 – 7.25 (m, 1 H), 6.39 – 6.63 (m, 3 H), 4.62 (br s, 4 H), 4.09 – 4.40 (m, 8 H), 1.61 – 1.86 (m, 4 H), 1.30 ppm (br s, 12 H). ^{13}C NMR ($CDCl_3$): δ ppm 159.4, 158.0, 157.8, 157.5, 157.3, 130.1, 107.5, 101.9, 67.3, 67.1, 65.2, 65.1, 64.9, 29.3, 29.1, 28.2, 25.7.

Poly(RBHE) oxalate

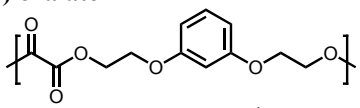


Table S2, Entry 10. 56.4% yield. ^{1}H NMR (DMSO-d_6): ppm 7.16 (t, J = 8.8 Hz, 1 H), 6.59 – 6.46 (m, 3 H), 4.62 – 4.45 (m, 4 H), 4.33 - 4.14 (m, 4 H). ^{13}C NMR (DMSO-d_6): δ ppm 159.2, 157.0, 130.0, 107.3, 101.2, 65.3, 65.0.

Poly(decylene-*co*-HBHE) oxalate [50:50]

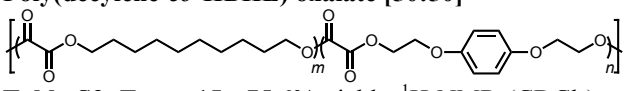


Table S2, Entry 15. 75.6% yield. ^{1}H NMR ($CDCl_3$): ppm 6.88 – 6.80 (m, 4 H), 4.60 (br s, 4 H), 4.28 (q, J = 6.2 Hz, 4 H), 4.21 (d, J = 3.9 Hz, 4 H), 1.79 – 1.68 (m, 4 H), 1.44 – 1.24 (m, 12 H). ^{13}C NMR ($CDCl_3$): δ ppm 158.0, 157.8, 157.5, 157.3, 152.9, 115.8, 115.8, 67.3, 67.1, 65.9, 65.2, 65.0, 29.2, 29.0, 28.2, 25.6.

Poly(HBHE) oxalate

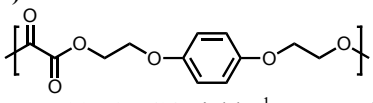
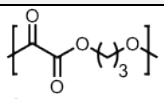
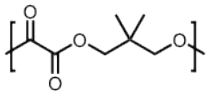
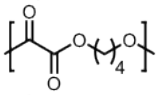
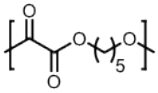
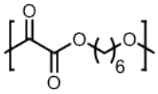
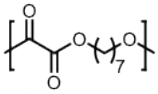
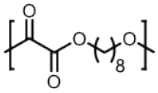
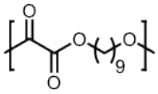
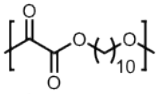
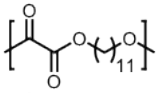
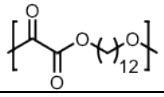


Table S2, Entry 20. 87.6% yield. ^{1}H NMR (DMSO-d_6): ppm 6.99 – 6.73 (m, 4 H), 4.18 (br s, 4 H) 4.53 (br s, 4 H). ^{13}C NMR (DMSO-d_6): δ ppm 157.0, 152.3, 115.5, 65.7, 65.1.

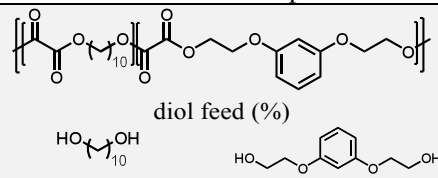
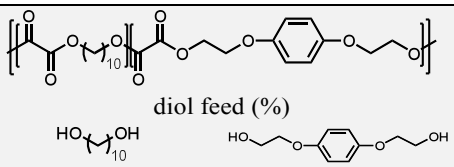
Summary of Polymerization Data

Table S1. Molecular weight and thermal properties of polyalkylene oxalates.[a]

Entry	Polymer	% Yield	M_w (Da)	M_n (Da)	PDI	T_g (°C)	T_m (°C)	H_m (J/g)	H_c (J/g)	T_{50} (°C)[c]
1		45	n.a.	n.a.	n.a.	-2	78[b]	53[b]	n.o.	314
2		63	19,400	11,200	1.73	7	103[b]	57[b]	n.o.	350
3		72	n.a.	n.a.	n.a.	n.o.	98	64	64	327
4		79	41,400	21,800	1.90	-34	56[b]	56[b]	n.o.	357
5		78	40,700	24,300	1.68	n.o.	76	65	62	354
6		69	39,600	22,000	1.80	-48	35[b]	20[b]	n.o.	369
7		85	62,400	36,900	1.69	n.o.	76	55	64	366
8		77	71,300	40,400	1.76	-47	40	52	51	371
9		83	67,600	36,600	1.85	n.o.	79	57	65	369
10		73	33,300	15,600	2.14	-29	55	71	71	342
11		85	69,300	39,500	1.76	n.o.	80	76	73	369

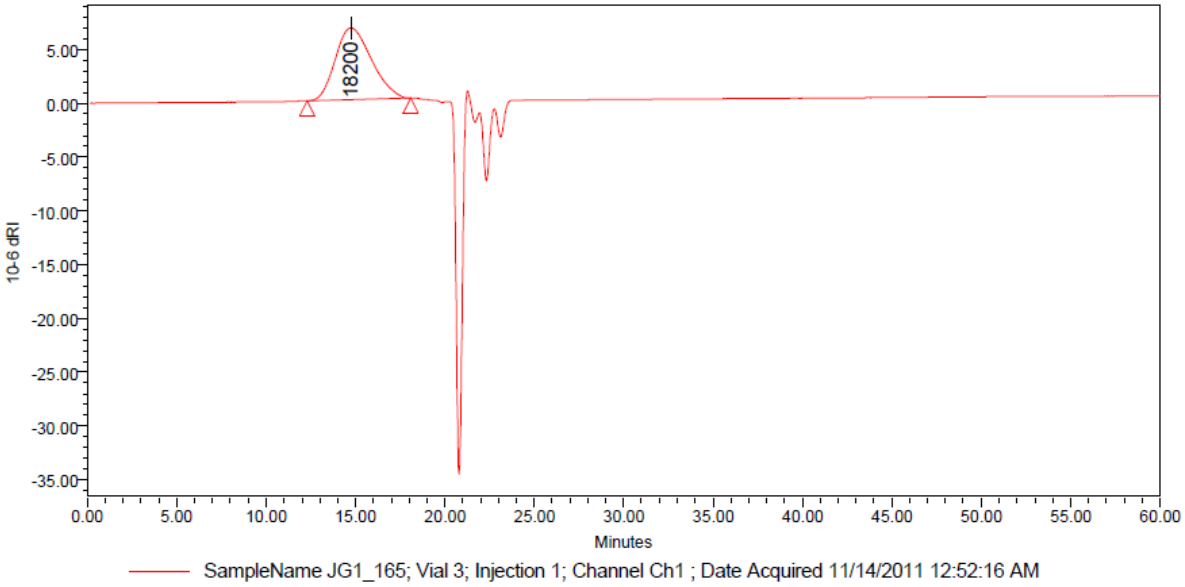
[a]Molecular weight data obtained by GPC versus polystyrene standards; n.a. indicates data not available because of insolubility in the GPC solvent, THF. Thermal DSC data obtained from the second cycle unless otherwise noted; n.o. indicates a thermal transition not observed. [b]Thermal DSC data obtained from the first cycle. [c]Temperature for 50% mass loss by TGA under nitrogen.

Table S2. Characterization of aliphatic/aromatic copolyoxalates synthesized from diols and dimethyl oxalate.[a]

Entry	 diol feed (%)		Yield (%)	% Aromatic incorp. ^{1}H NMR (%)	M_w (Da)	M_n (Da)	PDI	T_g (°C)	T_m (°C)	H_m (°C)
1	90	10	76	11	64,900	36,100	1.80	–24	70	52
2	80	20	80	22	71,300	39,900	1.79	–20	66	46
3	70	30	83	26	59,800	32,500	1.84	–15	64	51
4	60	40	71	38	62,400	32,100	1.95	–18	58	7
5	50	50	76	48	63,700	30,000	2.12	–5	95[b]	25[b]
6	40	60	61	57	57,500	27,700	2.07	4	103[b]	41[b]
7	30	70	73	68	43,700	22,300	1.95	14	122[b]	20[b]
8	20	80	73	77	n.a.	n.a.	n.a.	25	133[b]	35[b]
9	10	90	46	84	n.a.	n.a.	n.a.	29	138[b]	41[b]
10	0	100	56	100	n.a.	n.a.	n.a.	34	156[b]	50[b]
Entry	 diol feed (%)		Yield (%)	% Aromatic incorp. ^{1}H NMR (%)	M_w (Da)	M_n (Da)	PDI	T_g (°C)	T_m (°C)	H_m (°C)
11	90	10	81	7	36,200	16,900	2.13	n.o.	74	69
12	80	20	78	17	68,600	40,100	1.71	–21	67	35
13	70	30	70	20	62,300	35,800	1.74	–16	66	61
14	60	40	78	38	53,800	27,000	1.99	–16	62	57
15	50	50	76	49	52,200	26,100	2.00	–14	137	29
16	40	60	73	56	19,300	10,300	1.87	–12	151	27
17	30	70	78	70	n.a.	n.a.	n.a.	10	164	31
18	20	80	79	82	n.a.	n.a.	n.a.	17	171	38
19	10	90	78	90	n.a.	n.a.	n.a.	27	186	56
20	0	100	88	100	n.a.	n.a.	n.a.	45	190	68

[a]Molecular weight data obtained by GPC versus polystyrene standards; n.a. indicates data not available because of insolubility in the GPC solvent, THF. Thermal DSC data obtained from the second cycle unless otherwise noted; n.o. indicates a thermal transition not observed. [b]Thermal DSC data obtained from the first cycle.

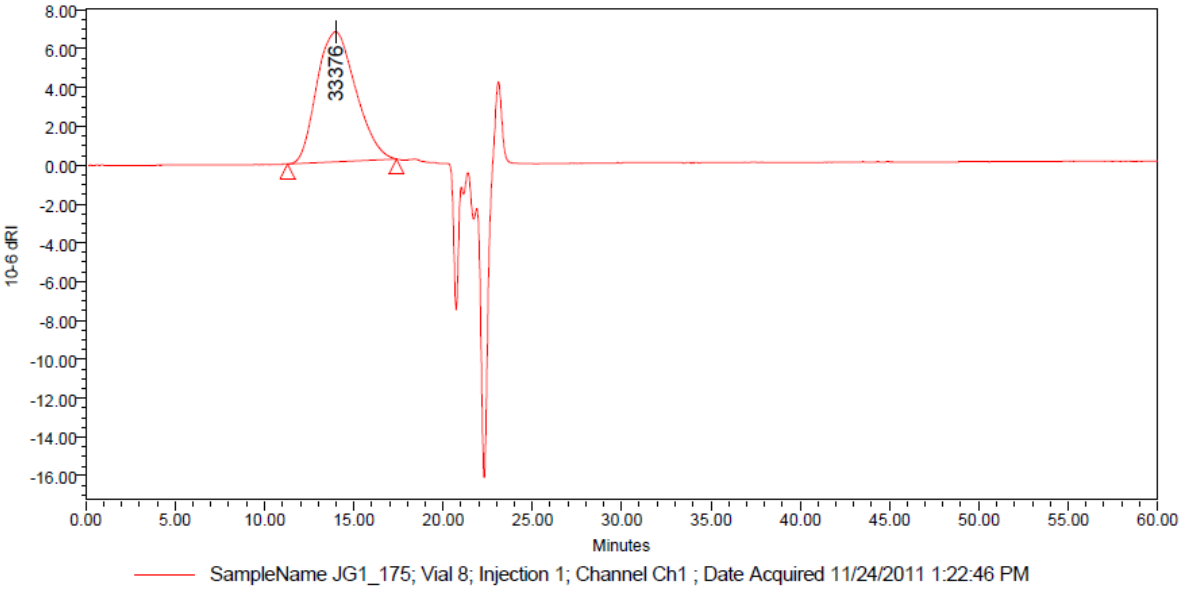
Gel Permeation Chromatography (GPC) Analysis



GPC Results

	Dist Name	Mn	Mw	MP	Mz	Mz+1	Mv	Polydispersity	MW Marker 1	MW Marker 2
1		11187	19382	18200	29744	41256		1.732527		

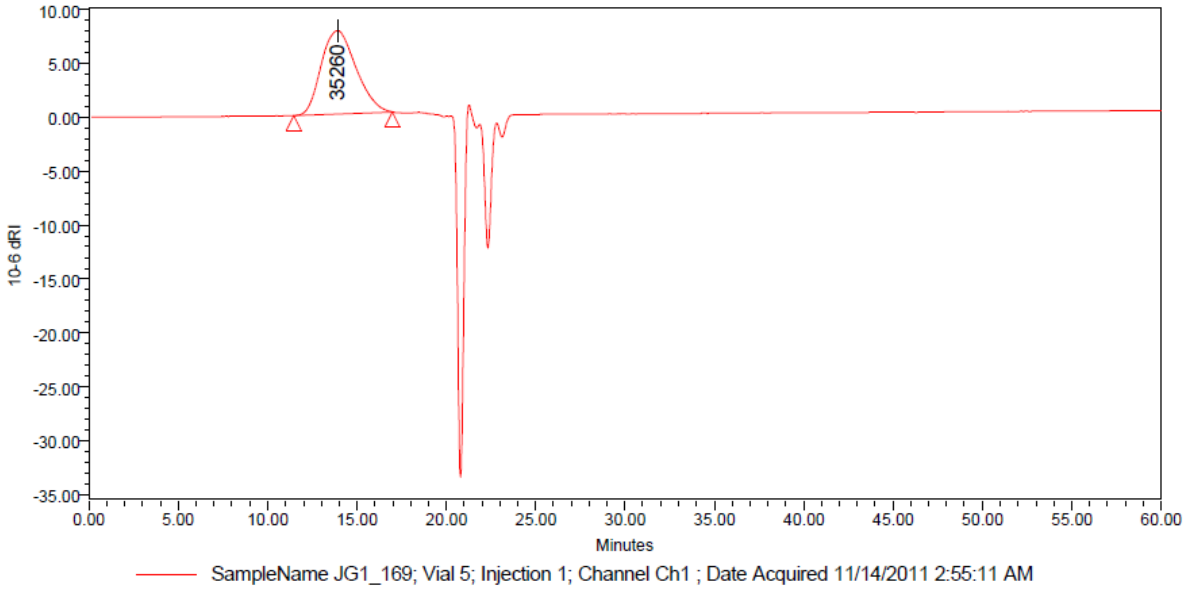
Figure S1. GPC Chromatogram of polyneopentylene oxalate (Table S1, entry 2).



GPC Results

	Dist Name	Mn	Mw	MP	Mz	Mz+1	Mv	Polydispersity	MW Marker 1	MW Marker 2
1		21806	41361	33376	68721	99347		1.896792		

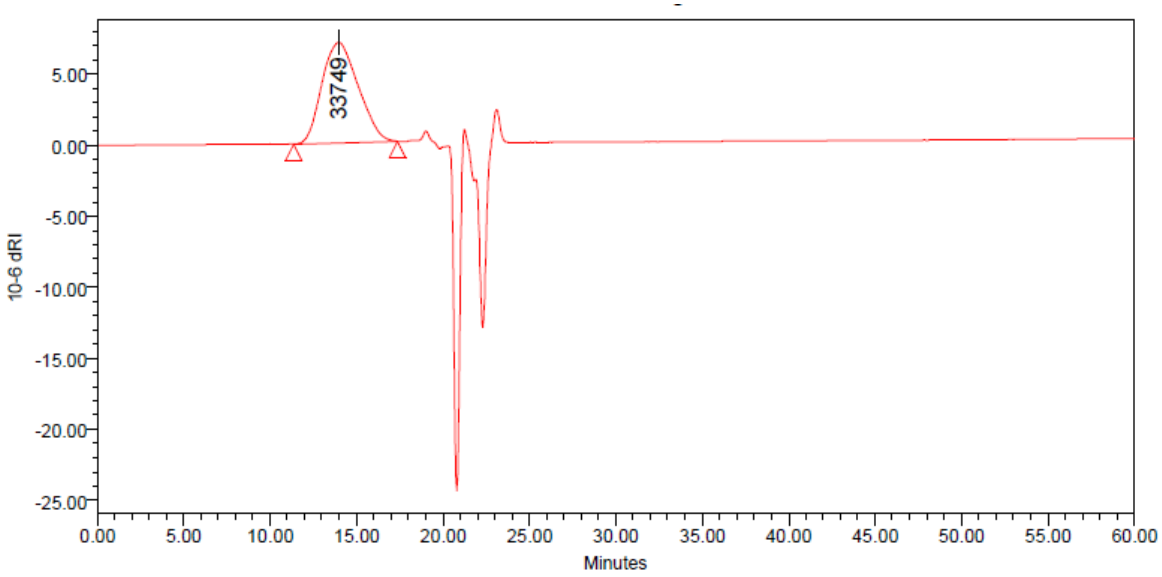
Figure S2. GPC Chromatogram of polypentylene oxalate (Table S1, entry 4).



GPC Results

	Dist Name	Mn	Mw	MP	Mz	Mz+1	Mv	Polydispersity	MW Marker 1	MW Marker 2
1		24310	40749	35260	62132	86121		1.676242		

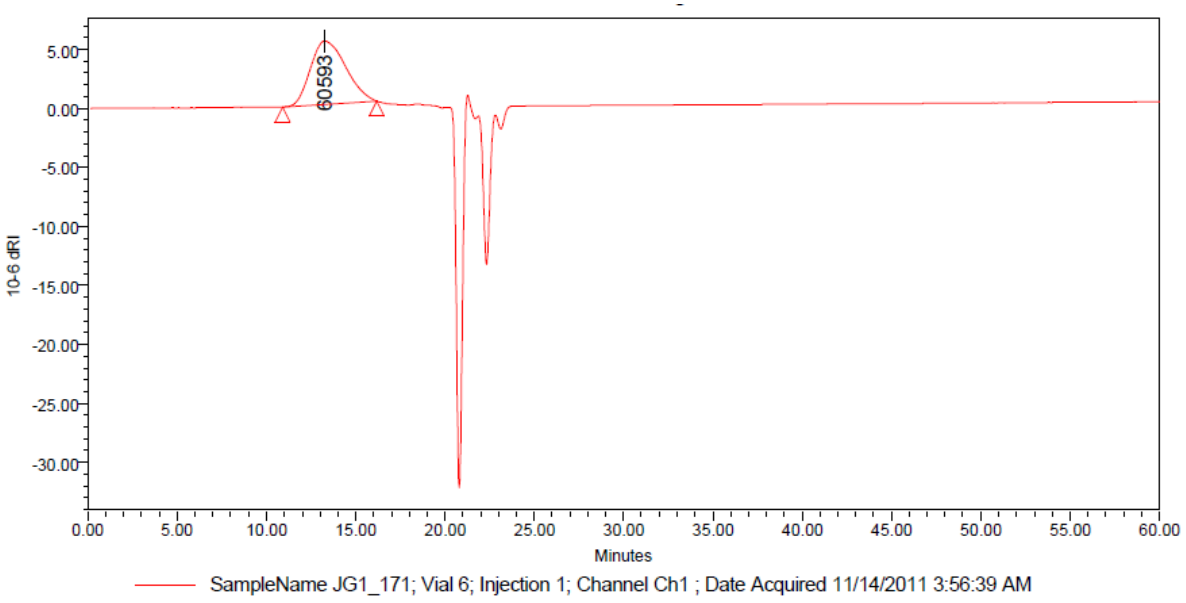
Figure S3. GPC Chromatogram of polyhexylene oxalate (Table S1, entry 5).



GPC Results

	Dist Name	Mn	Mw	MP	Mz	Mz+1	Mv	Polydispersity	MW Marker 1	MW Marker 2
1		21957	39557	33749	63846	91408		1.801545		

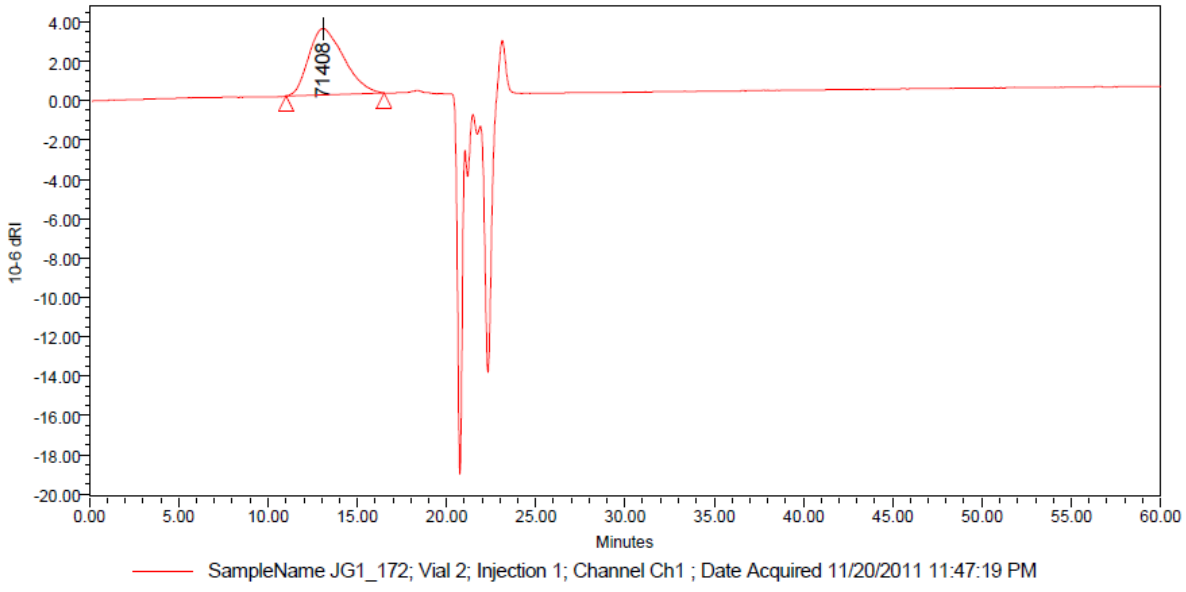
Figure S4. GPC Chromatogram of polyheptylene oxalate (Table S1, entry 6).



GPC Results

	Dist Name	Mn	Mw	MP	Mz	Mz+1	Mv	Polydispersity	MW Marker 1	MW Marker 2
1		36858	62444	60593	95137	127573		1.694195		

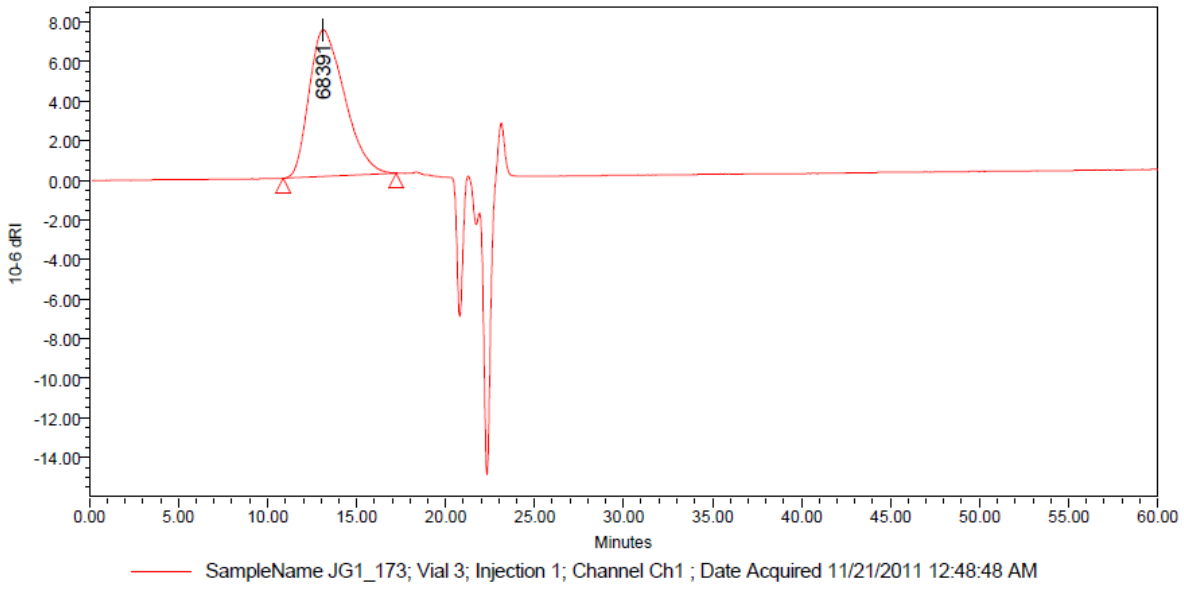
Figure S5. GPC Chromatogram of polyoctylene oxalate (Table S1, entry 7).



GPC Results

	Dist Name	Mn	Mw	MP	Mz	Mz+1	Mv	Polydispersity	MW Marker 1	MW Marker 2
1		40405	71276	71408	107177	139682		1.764028		

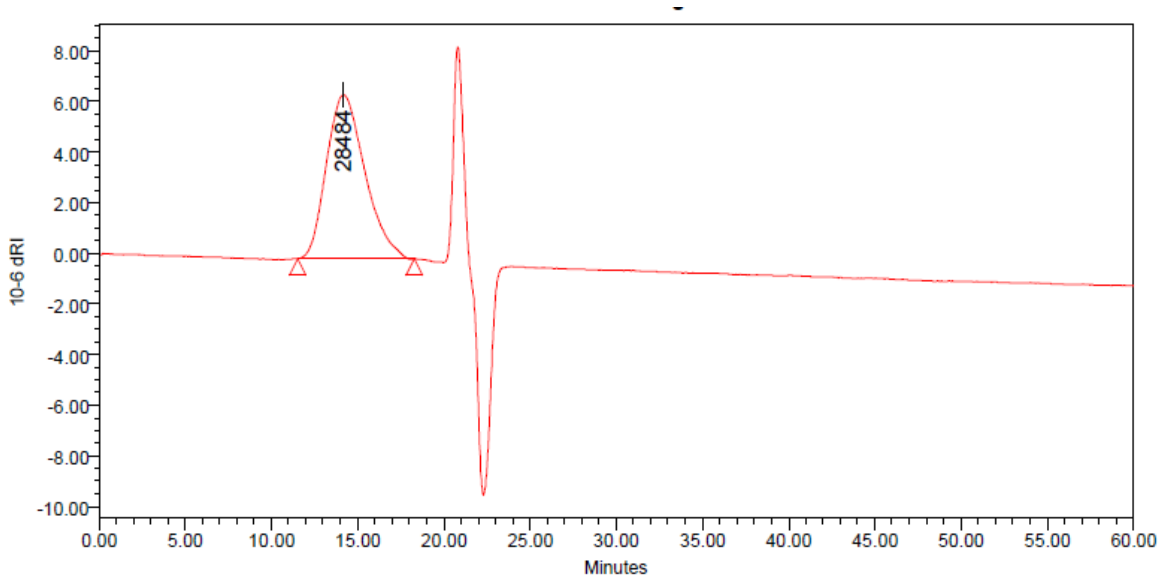
Figure S6. GPC Chromatogram of polynonylene oxalate (Table S1, entry 8).



GPC Results

	Dist Name	Mn	Mw	MP	Mz	Mz+1	Mv	Polydispersity	MW Marker 1	MW Marker 2
1		36614	67614	68391	103172	135730		1.846656		

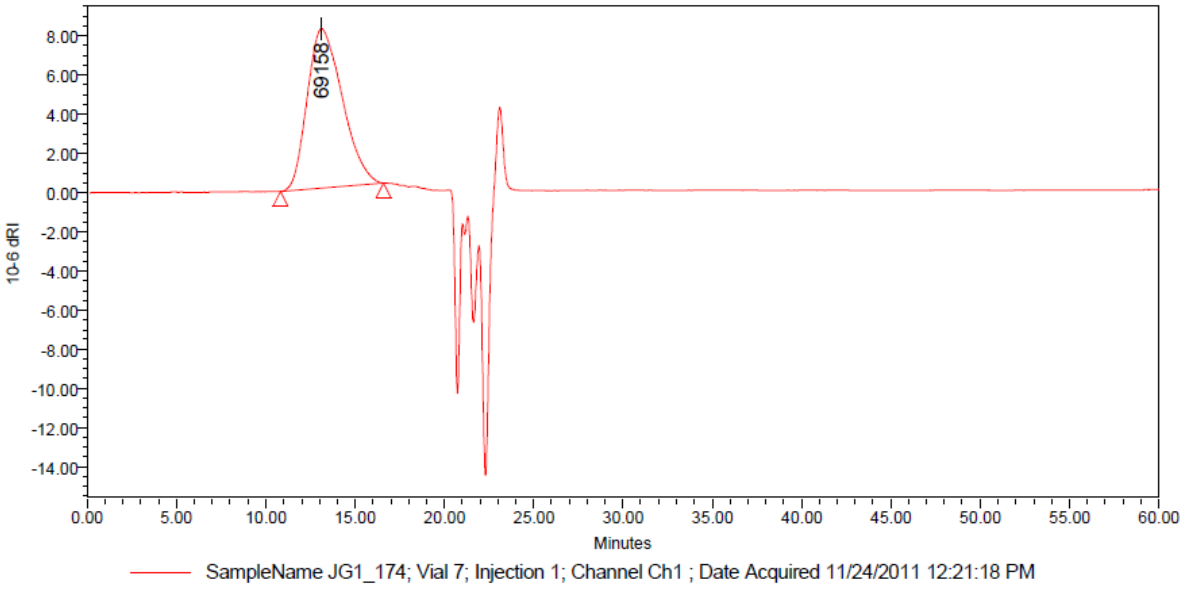
Figure S7. GPC Chromatogram of polydecylene oxalate (Table S1, entry 9).



GPC Results

	Dist Name	Mn	Mw	MP	Mz	Mz+1	Mv	Polydispersity	MW Marker 1	MW Marker 2
1		15582	33309	28484	59082	90356		2.137647		

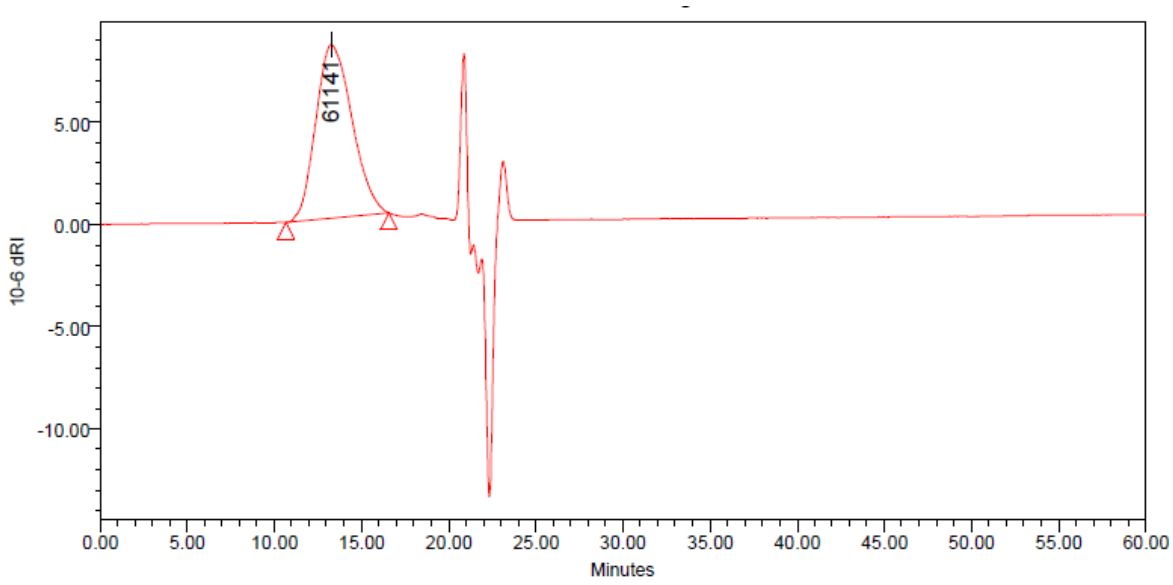
Figure S8. GPC Chromatogram of polyundecylene oxalate (Table S1, entry 10).



GPC Results

	Dist Name	Mn	Mw	MP	Mz	Mz+1	Mv	Polydispersity	MW Marker 1	MW Marker 2
1		39498	69342	69158	104758	137539		1.755562		

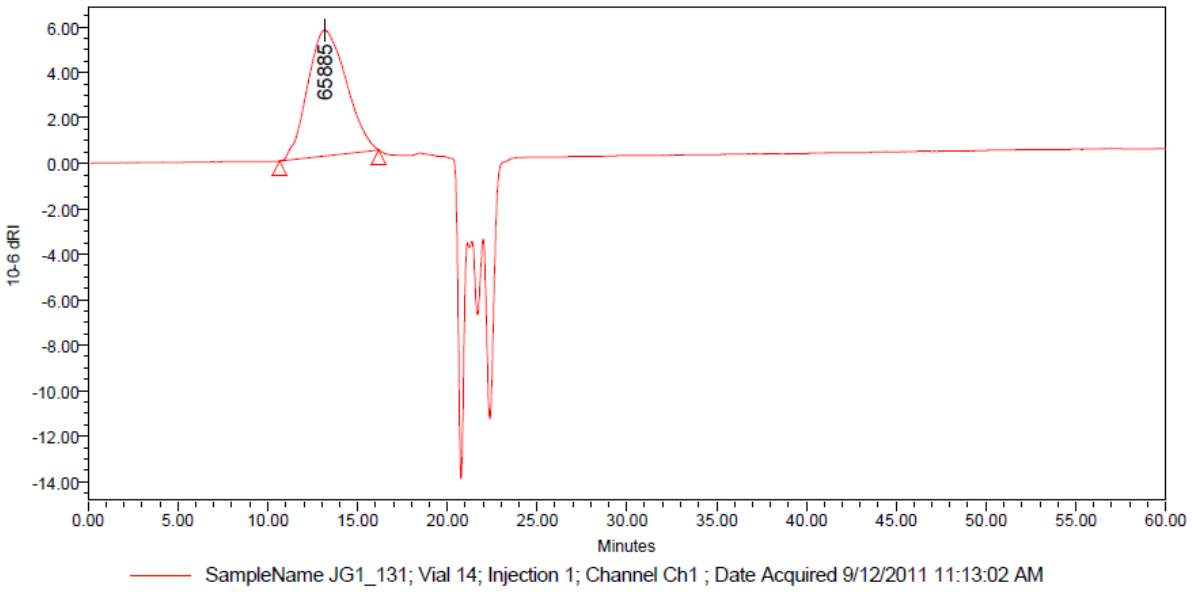
Figure S9. GPC Chromatogram of polydodecylene oxalate (Table S1, entry 11).



GPC Results

	Dist Name	Mn	Mw	MP	Mz	Mz+1	Mv	Polydispersity	MW Marker 1	MW Marker 2
1		36060	64926	61141	101644	136753		1.800480		

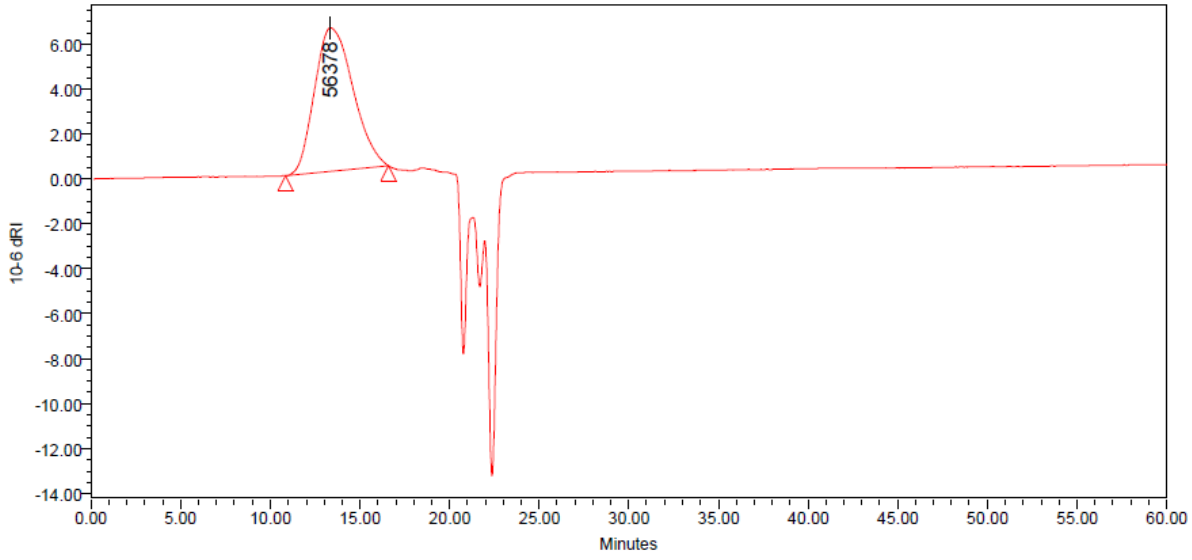
Figure S10. GPC Chromatogram of poly(decylene-*co*-RBHE) oxalate [90:10] (Table S2, entry 1).



GPC Results

	Dist Name	Mn	Mw	MP	Mz	Mz+1	Mv	Polydispersity	MW Marker 1	MW Marker 2
1		39896	71265	65885	110677	146177		1.786259		

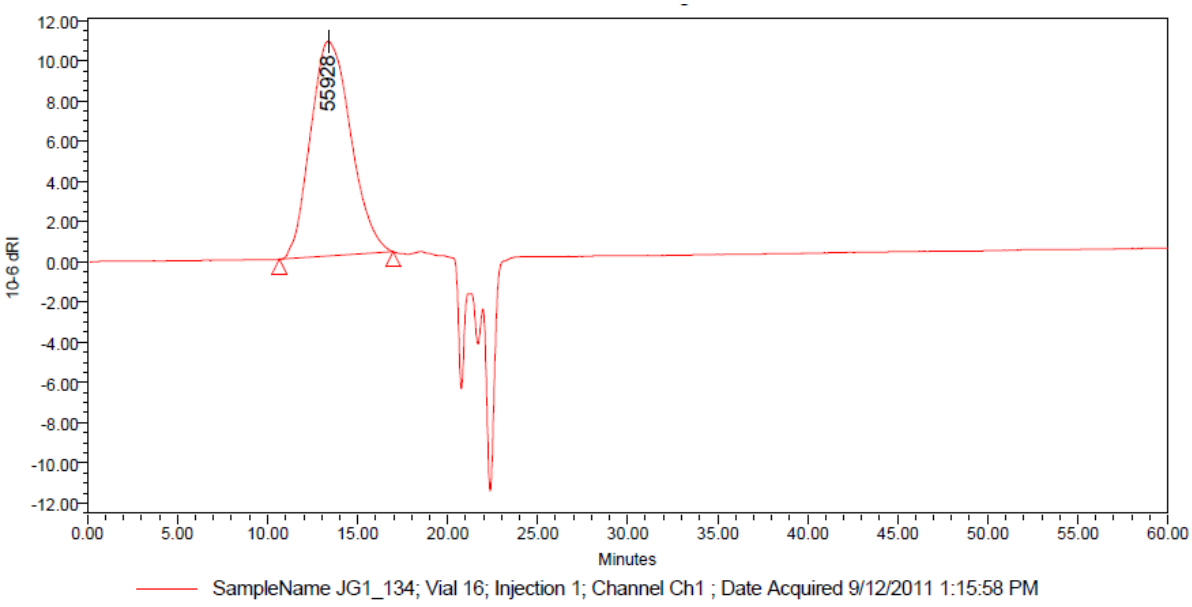
Figure S11. GPC Chromatogram of oly(decylene-*co*-RBHE) oxalate [80:20] (Table S2, entry 2).



GPC Results

	Dist Name	Mn	Mw	MP	Mz	Mz+1	Mv	Polydispersity	MW Marker 1	MW Marker 2
1		32472	59803	56378	95869	131215		1.841678		

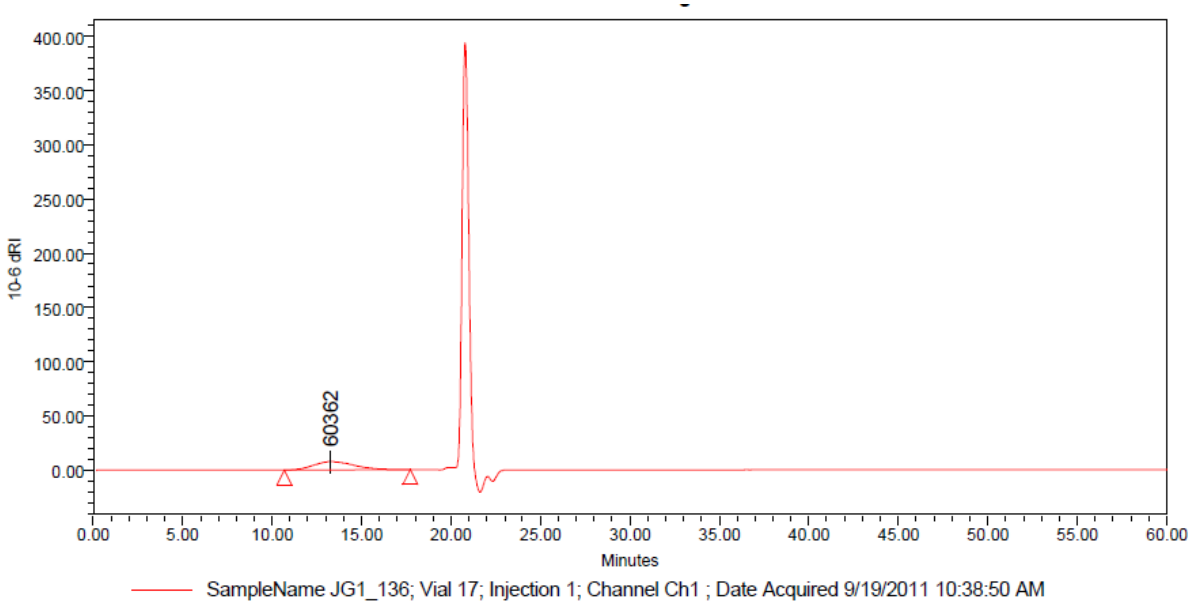
Figure S12. GPC Chromatogram of poly(decylene-*co*-RBHE) oxalate [70:30] (Table S2, entry 3).



GPC Results

	Dist Name	Mn	Mw	MP	Mz	Mz+1	Mv	Polydispersity	MW Marker 1	MW Marker 2
1		32069	62384	55928	102144	139549		1.945287		

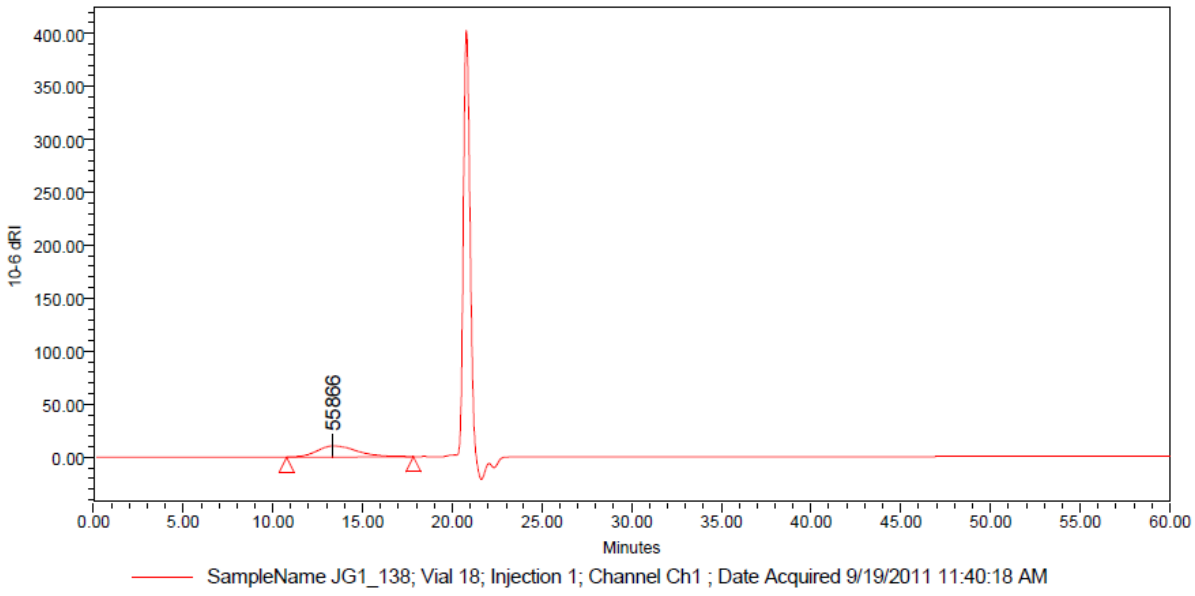
Figure S13. GPC Chromatogram of poly(decylene-*co*-RBHE) oxalate [60:40] (Table S2, entry 4).



GPC Results

	Dist Name	Mn	Mw	MP	Mz	Mz+1	Mv	Polydispersity	MW Marker 1	MW Marker 2
1		30015	63735	60362	105303	142513		2.123403		

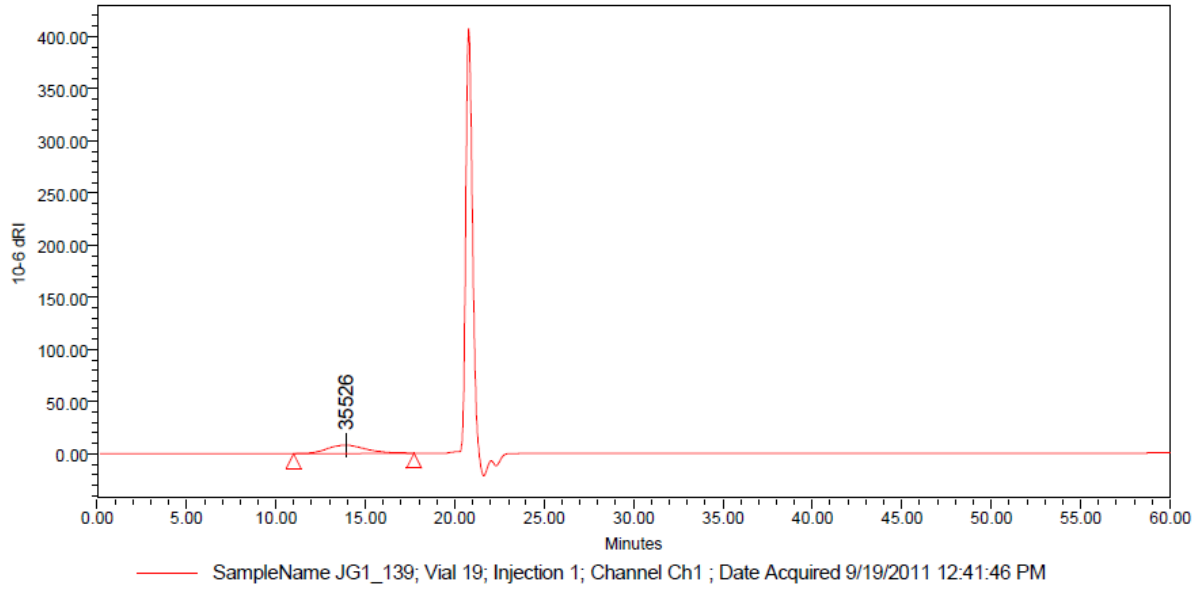
Figure S14. GPC Chromatogram of poly(decylene-*co*-RBHE) oxalate [50:50] (Table S2, entry 5).



GPC Results

	Dist Name	Mn	Mw	MP	Mz	Mz+1	Mv	Polydispersity	MW Marker 1	MW Marker 2
1		27725	57470	55866	94549	130544		2.072852		

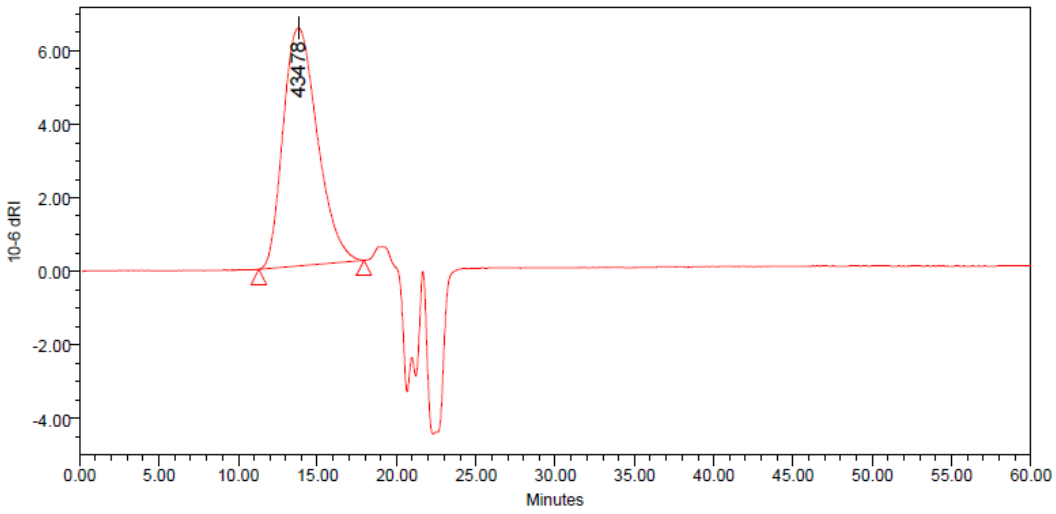
Figure S15. GPC Chromatogram of poly(decylene-*co*-RBHE) oxalate [40:60] (Table S2, entry 6).



GPC Results

	Dist Name	Mn	Mw	MP	Mz	Mz+1	Mv	Polydispersity	MW Marker 1	MW Marker 2
1		22374	43688	35526	72954	105910		1.952661		

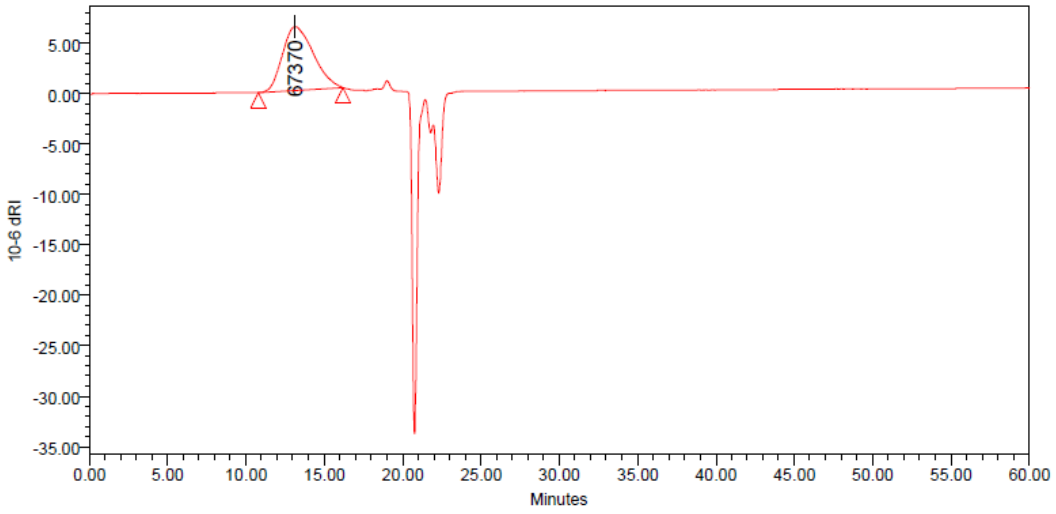
Figure S16. GPC Chromatogram of poly(decylene-*co*-RBHE) oxalate [30:70] (Table S2, entry 7).



GPC Results

	Dist Name	Mn	Mw	MP	Mz	Mz+1	Mv	Polydispersity	MW Marker 1	MW Marker 2
1		24659	49067	43478	80146	112472		1.989814		

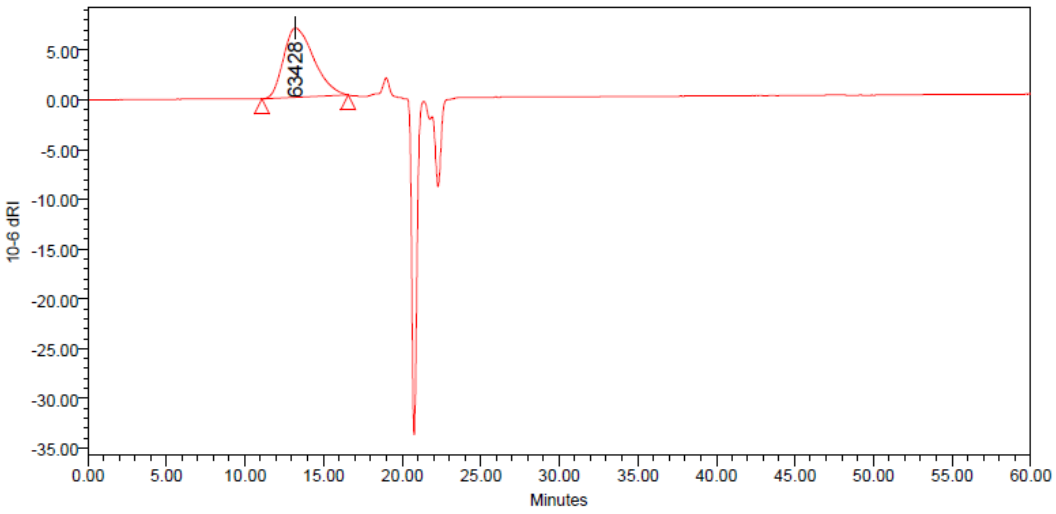
Figure S17. GPC Chromatogram of poly(decylene-*co*-HBHE) oxalate [90:10] (Table S2, entry 11).



GPC Results

	Dist Name	Mn	Mw	MP	Mz	Mz+1	Mv	Polydispersity	MW Marker 1	MW Marker 2
1		40134	68597	67370	103259	135877		1.709206		

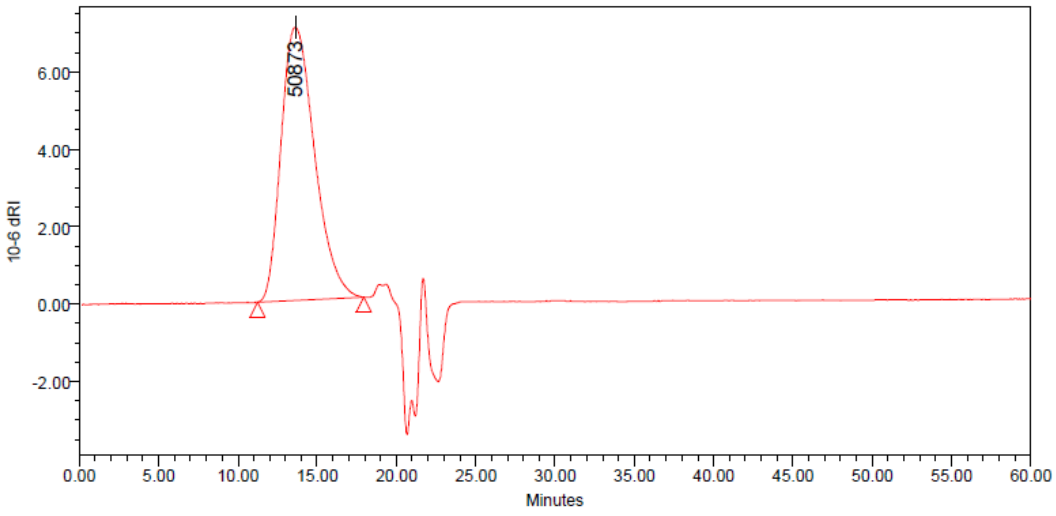
Figure S18. GPC Chromatogram of poly(decylene-*co*-HBHE) oxalate [80:20] (Table S2, entry 12).



GPC Results

	Dist Name	Mn	Mw	MP	Mz	Mz+1	Mv	Polydispersity	MW Marker 1	MW Marker 2
1		35787	62280	63428	93903	124645		1.740287		

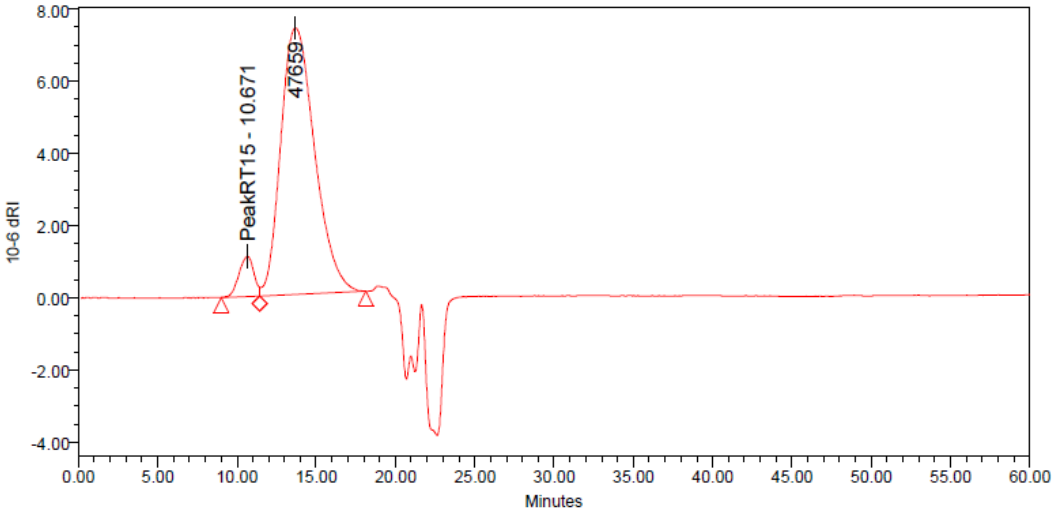
Figure S19. GPC Chromatogram of poly(decylene-*co*-HBHE) oxalate [70:30] (Table S2, entry 13).



GPC Results

	Dist Name	Mn	Mw	MP	Mz	Mz+1	Mv	Polydispersity	MW Marker 1	MW Marker 2
1		27034	53800	50873	86195	118666		1.990088		

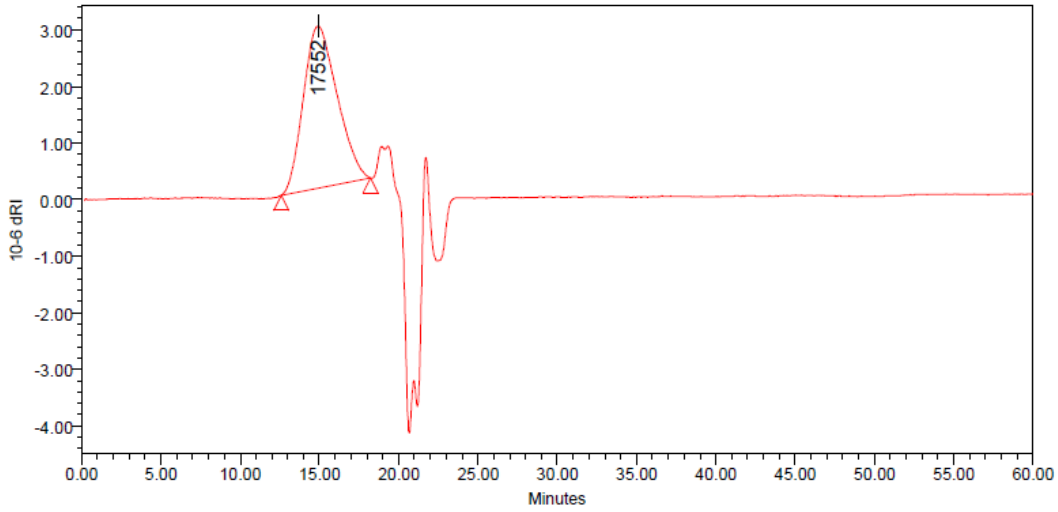
Figure S20. GPC Chromatogram of poly(decylene-*co*-HBHE) oxalate [60:40] (Table S2, entry 14).



GPC Results

	Dist Name	Mn	Mw	MP	Mz	Mz+1	Mv	Polydispersity	MW Marker 1	MW Marker 2
1										
2		26149	52202	47659	84851	118538		1.996324		

Figure S21. GPC Chromatogram of poly(decylene-*co*-HBHE) oxalate [50:50] (Table S2, entry 15).



GPC Results

	Dist Name	Mn	Mw	MP	Mz	Mz+1	Mv	Polydispersity	MW Marker 1	MW Marker 2
1		10304	19297	17552	30831	43040		1.872834		

Figure S22. GPC Chromatogram of poly(decylene-*co*-HBHE) oxalate [40:60] (Table S2, entry 16).

Differential Scanning Calorimetry (DSC) Thermograms

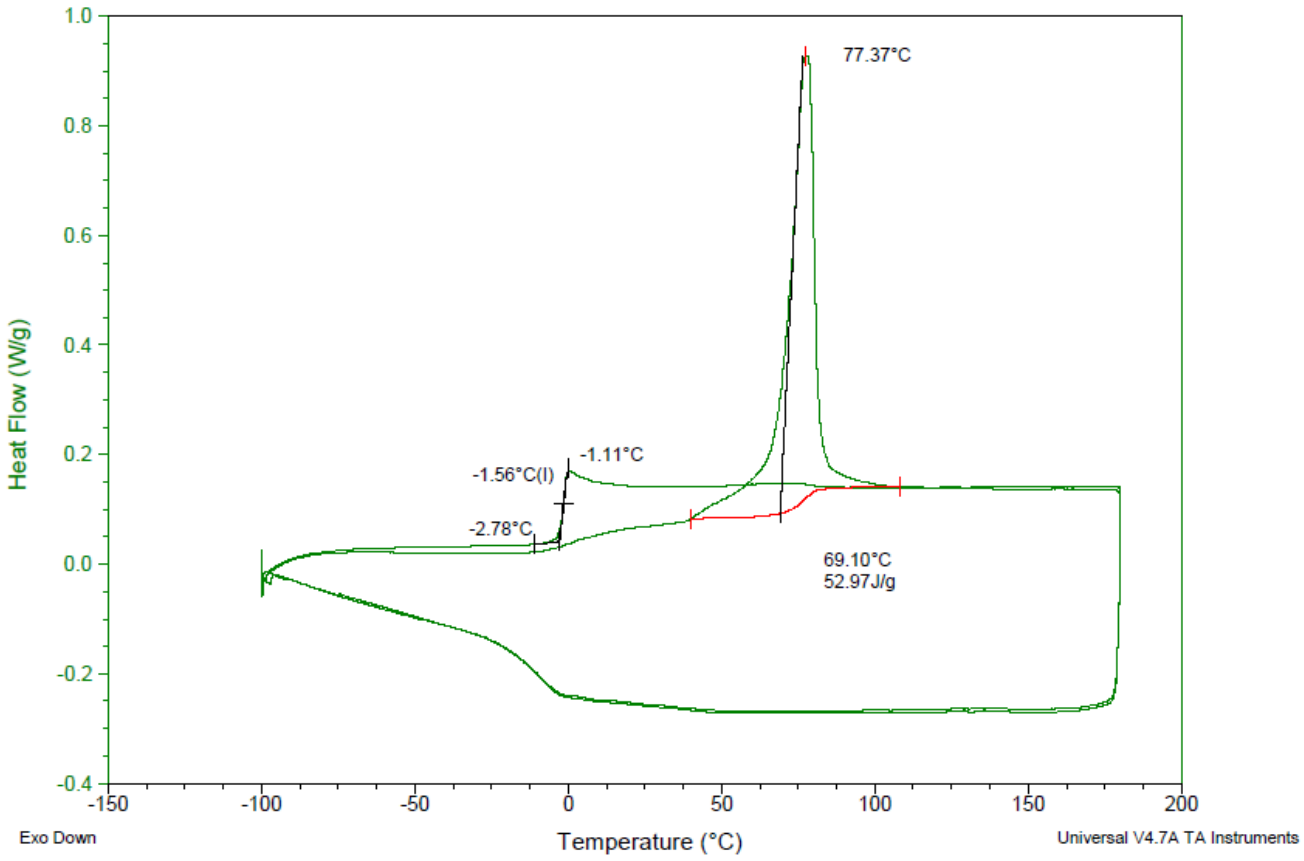


Figure S23. DSC Thermogram of polypropylene oxalate (Table S1, entry 1).

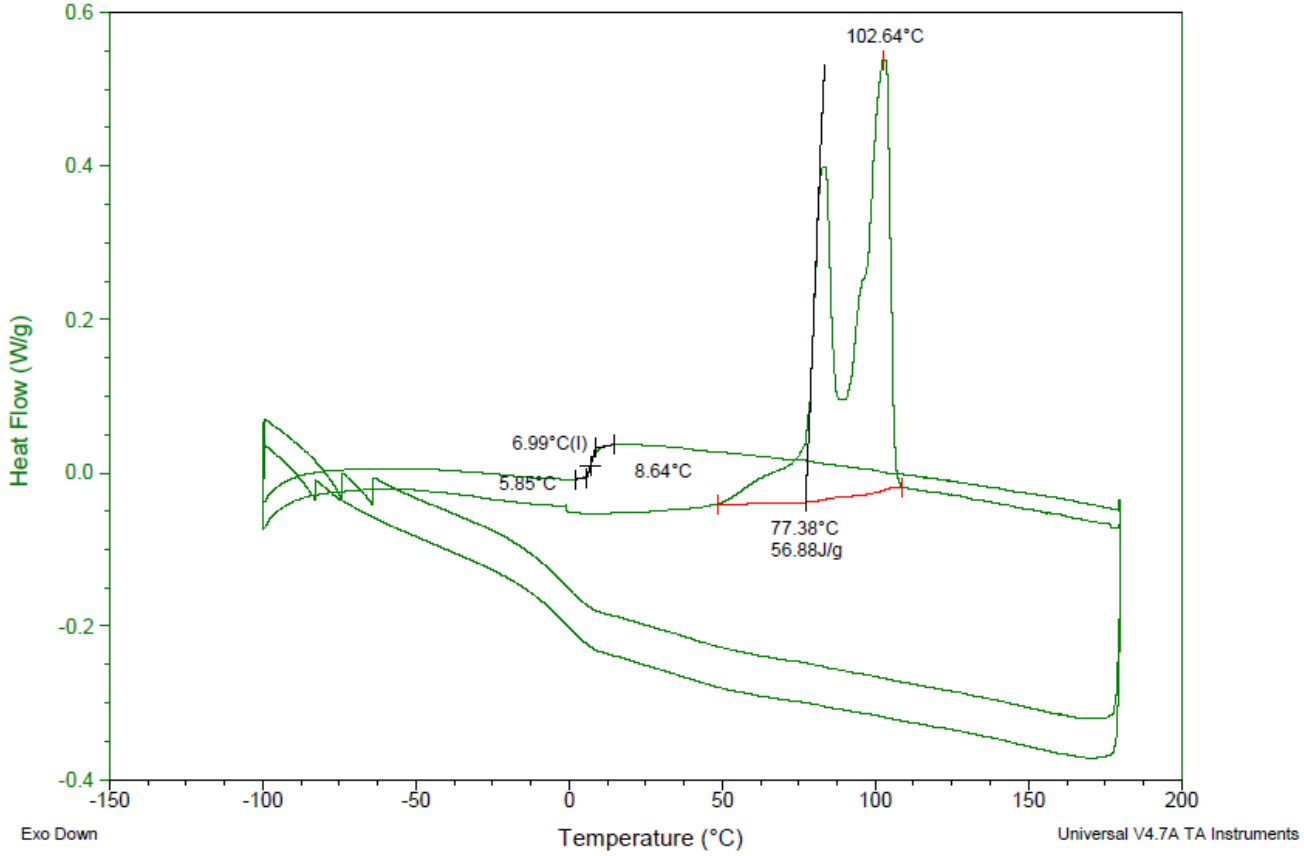


Figure S24. DSC Thermogram of polyneopentylene oxalate (Table S1, entry 2).

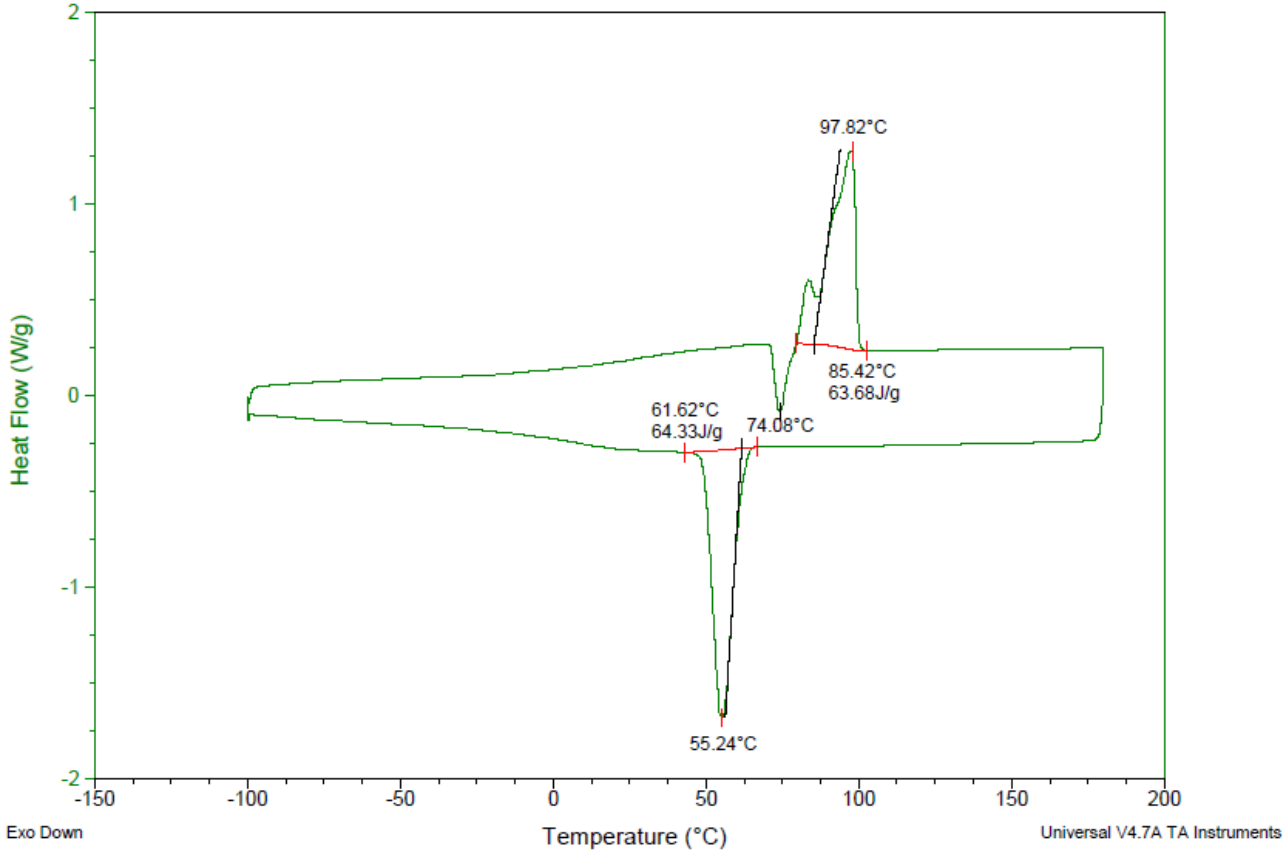


Figure S25. DSC Thermogram of polybutylene oxalate (Table S1, entry 3).

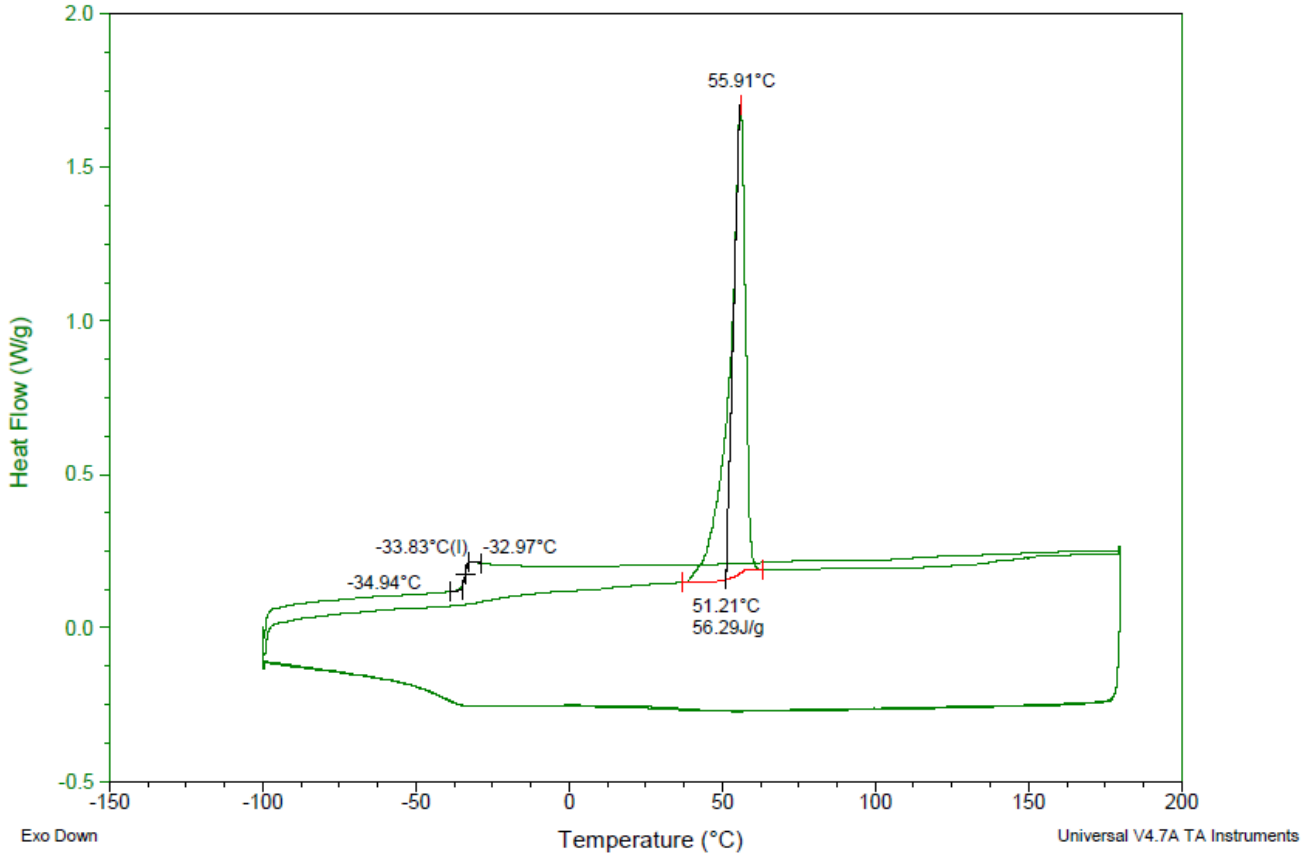


Figure S26. DSC Thermogram of polypentylene oxalate (Table S1, entry 4).

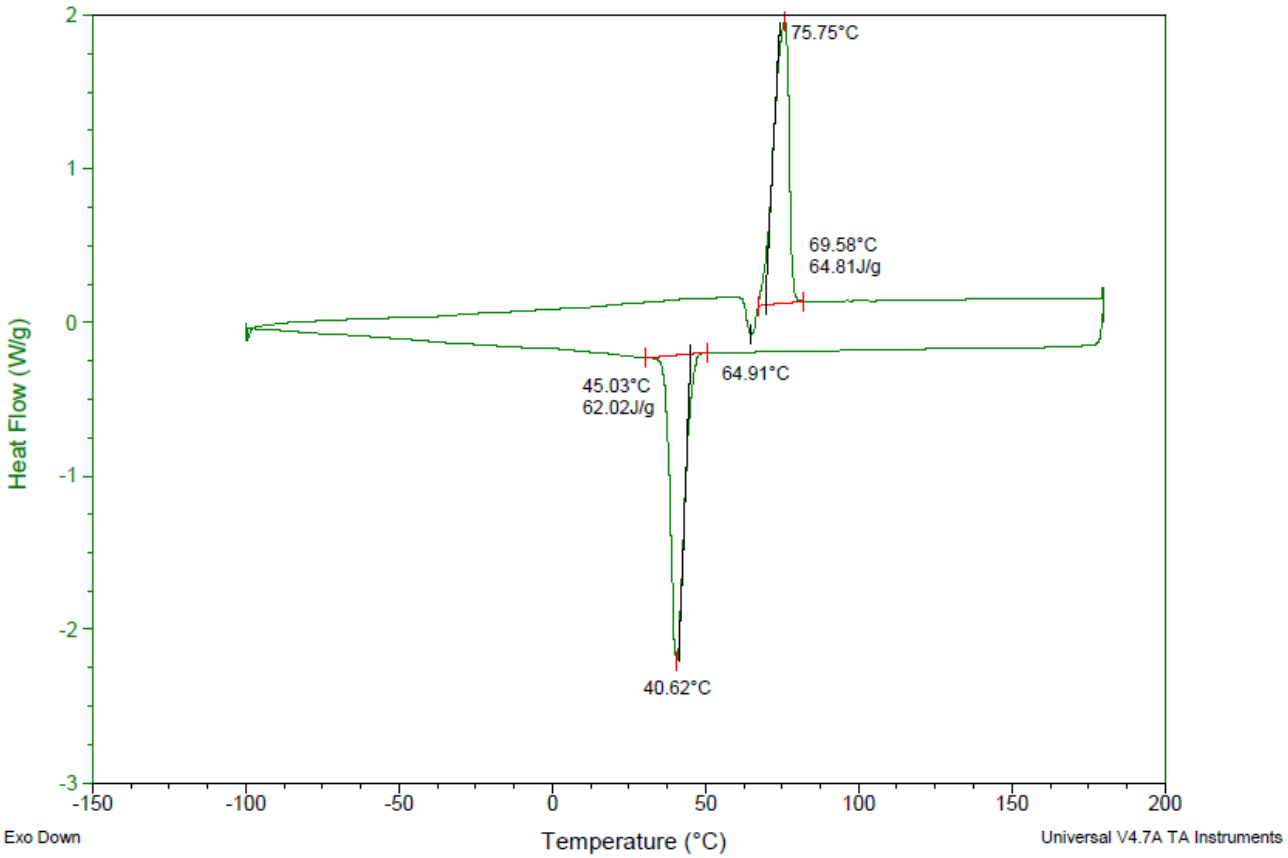


Figure S27. DSC Thermogram of polyhexylene oxalate (Table S1, entry 5).

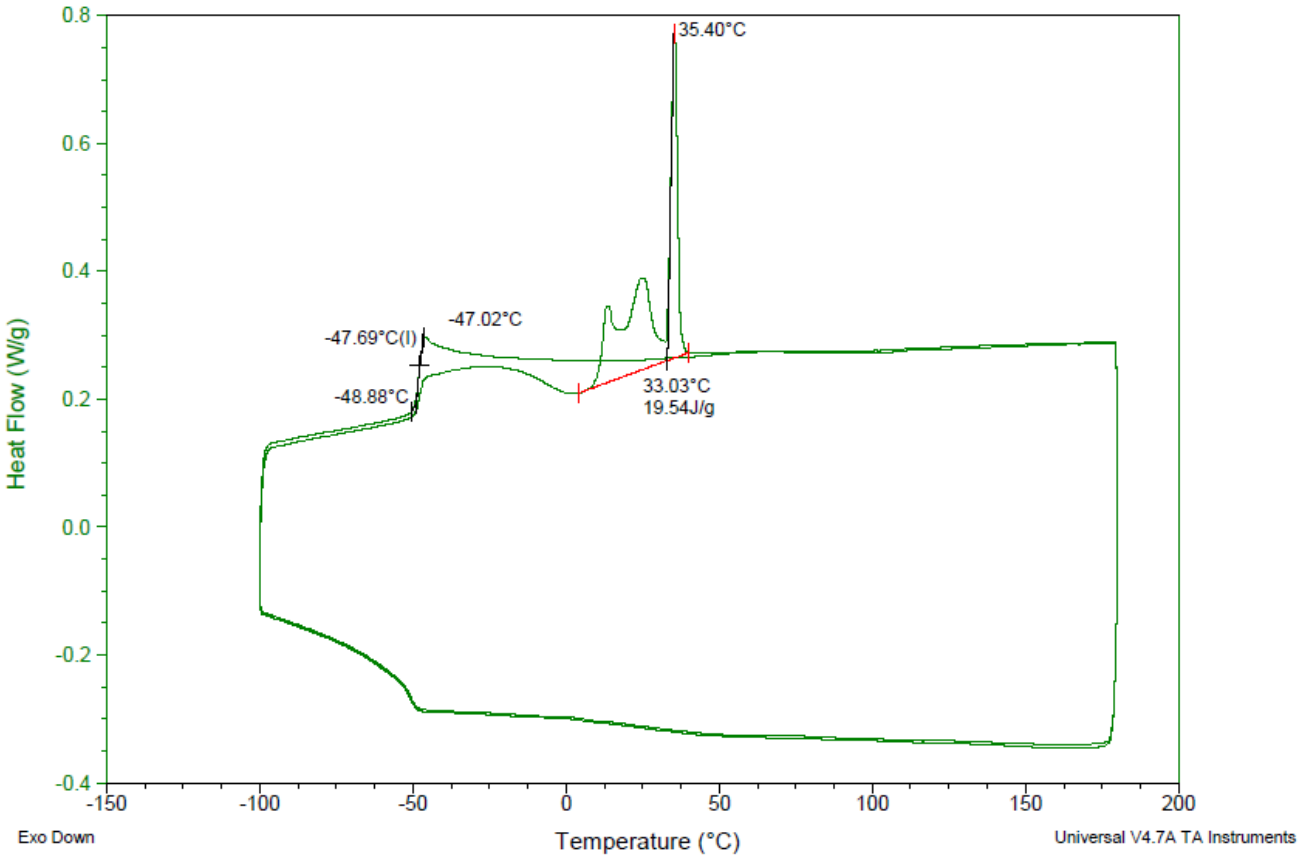


Figure S28. DSC Thermogram of polyheptylene oxalate (Table S1, entry 6).

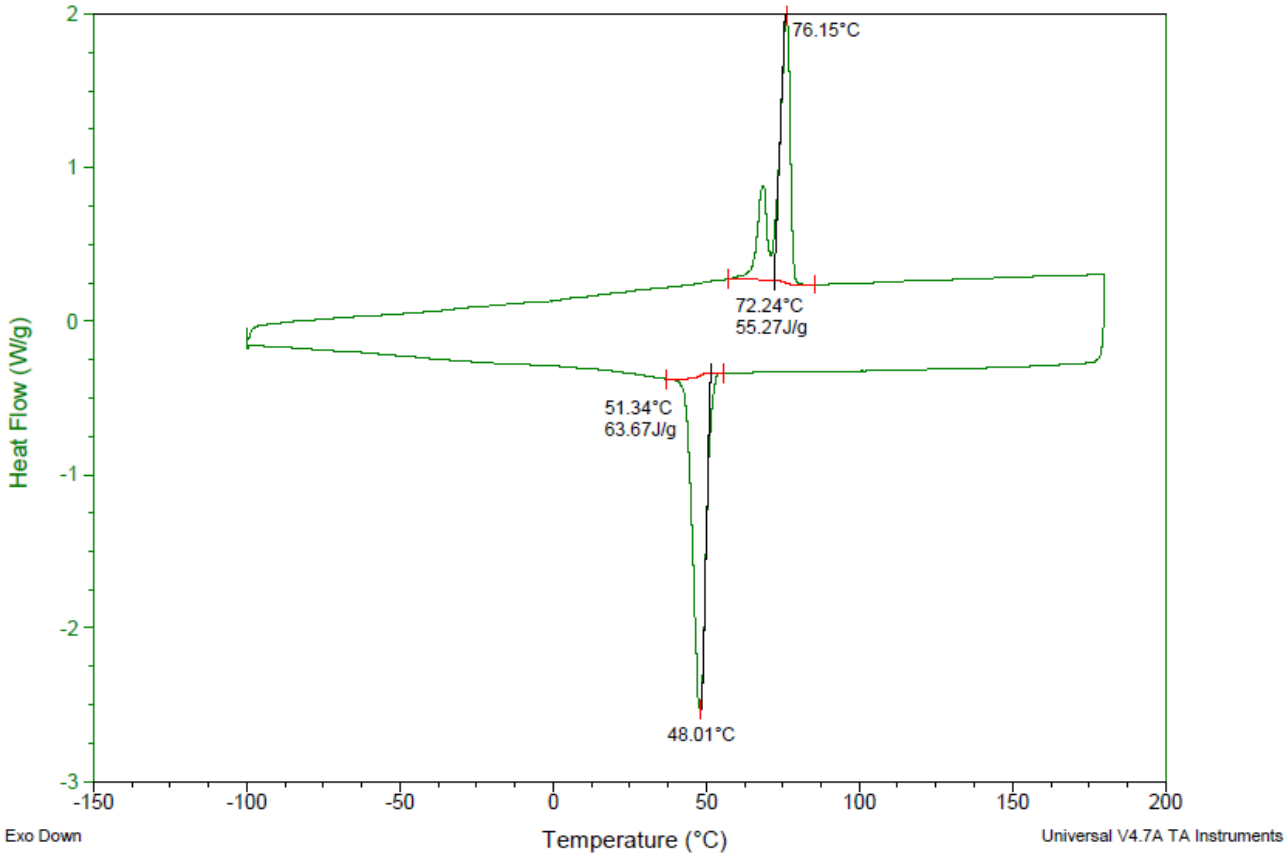


Figure S29. DSC Thermogram of polyoctylene oxalate (Table S1, entry 7).

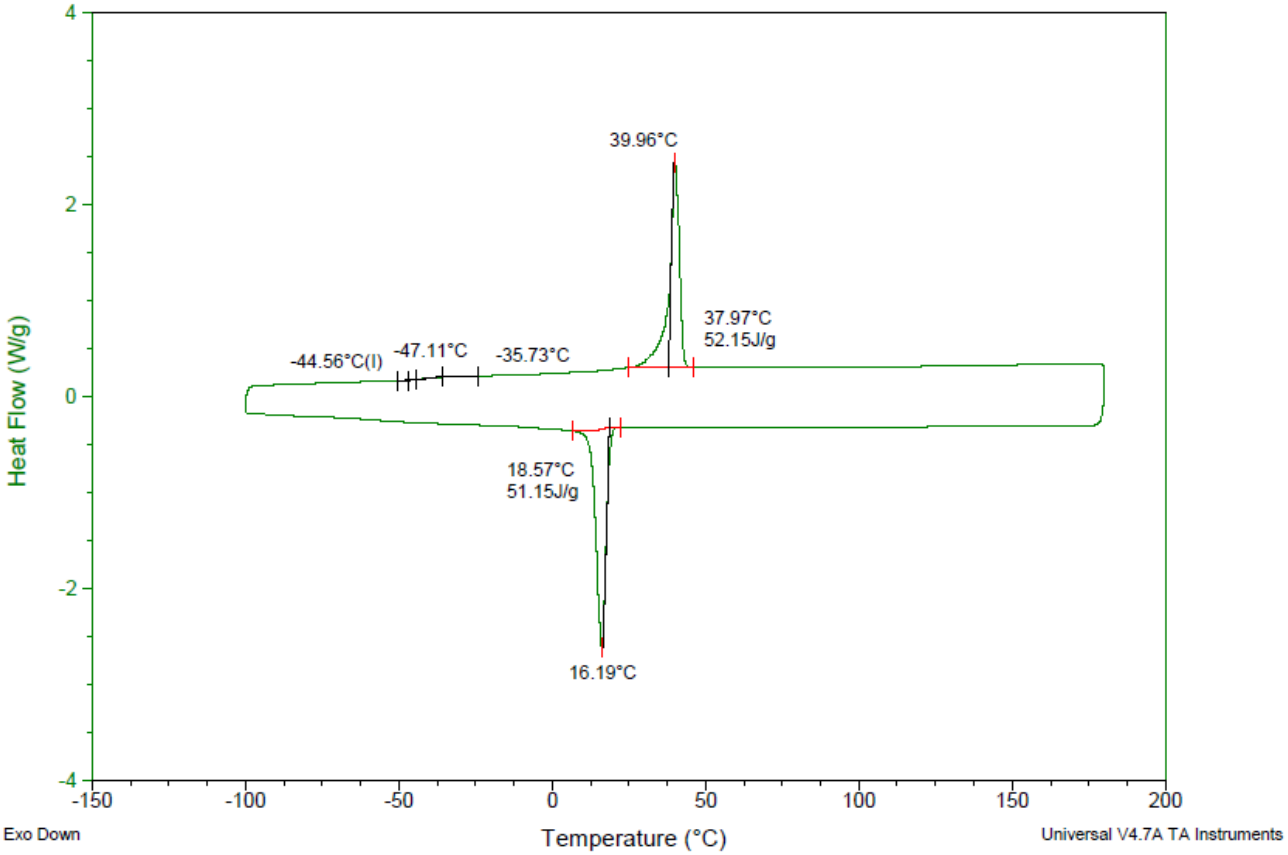


Figure S30. DSC Thermogram of polynonylene oxalate (Table S1, entry 8).

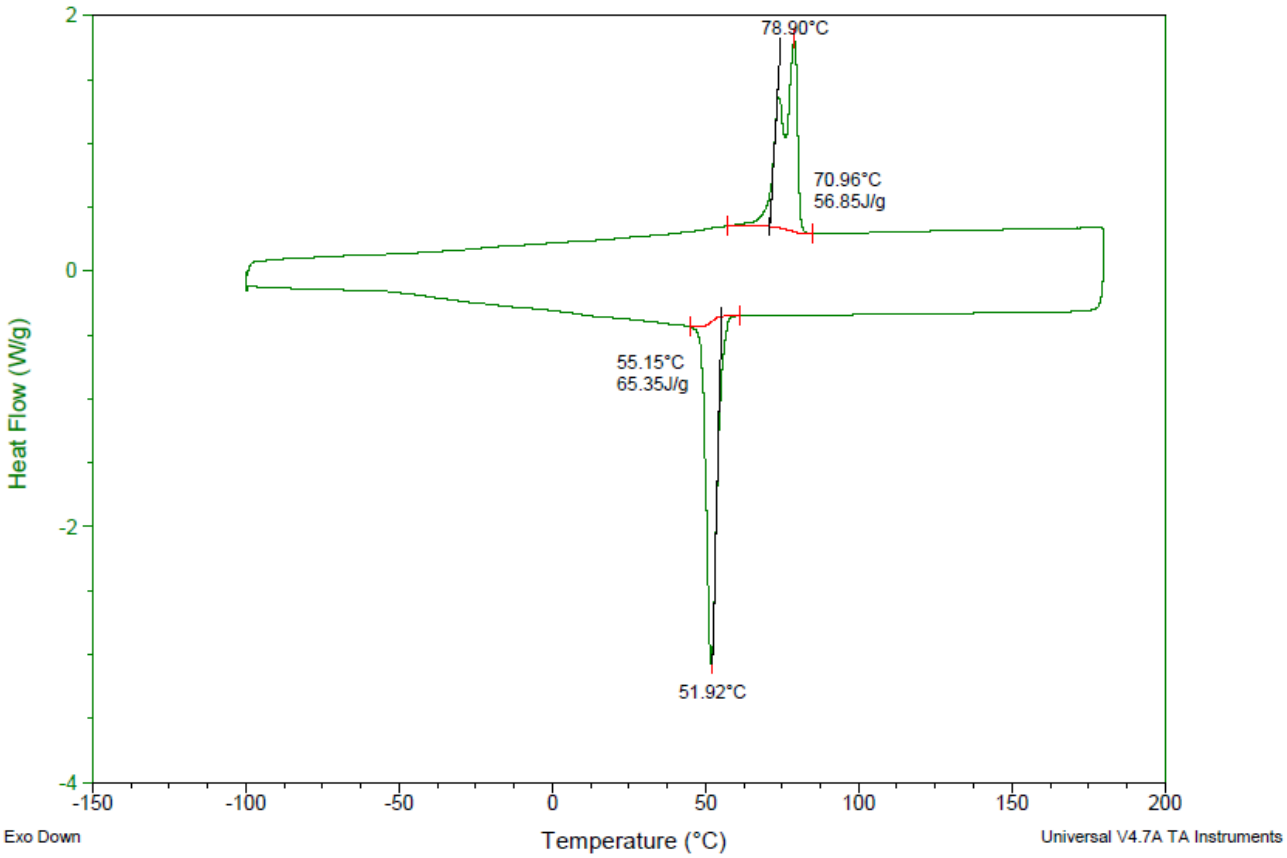


Figure S31. DSC Thermogram of polydecylene oxalate (Table S1, entry 9).

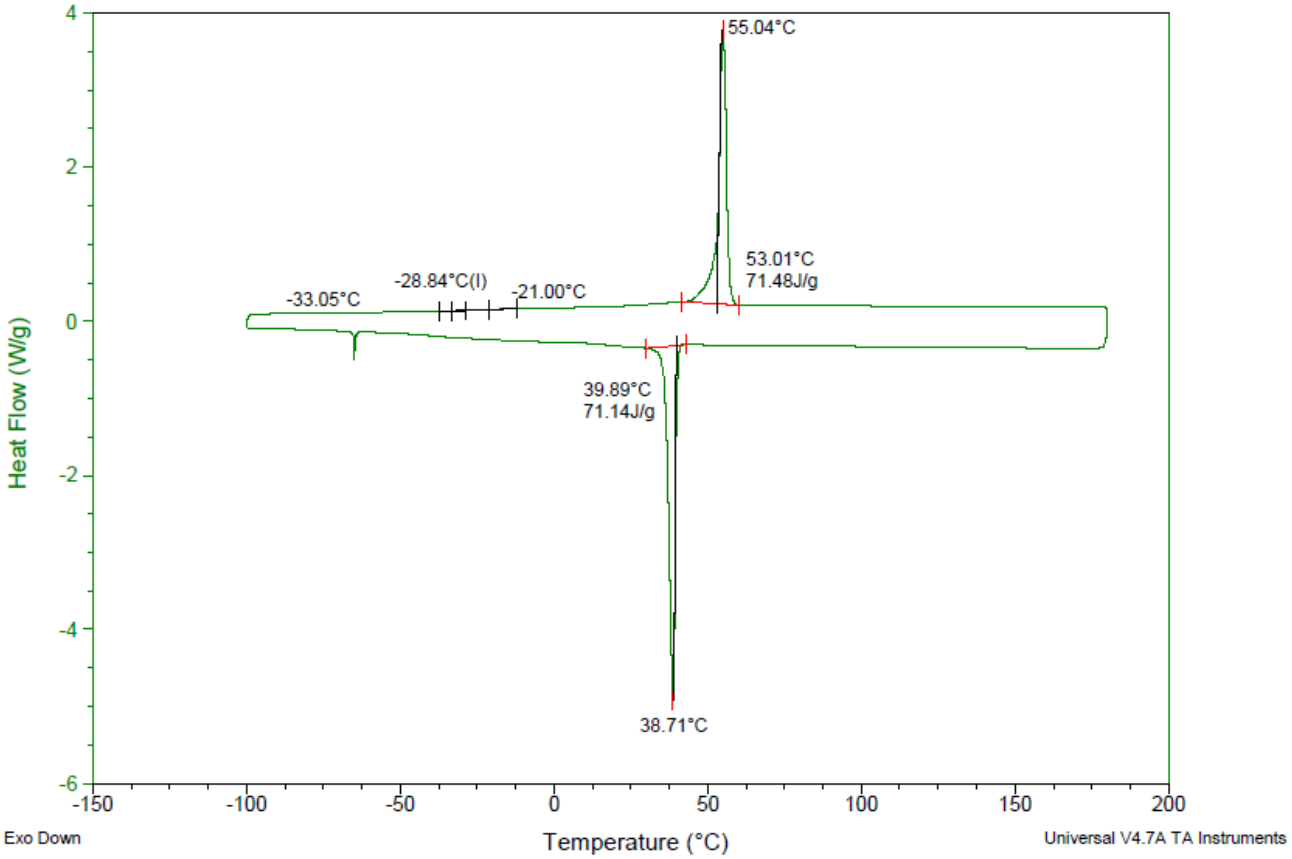


Figure S32. DSC Thermogram of polyundecylene oxalate (Table S1, entry 10).

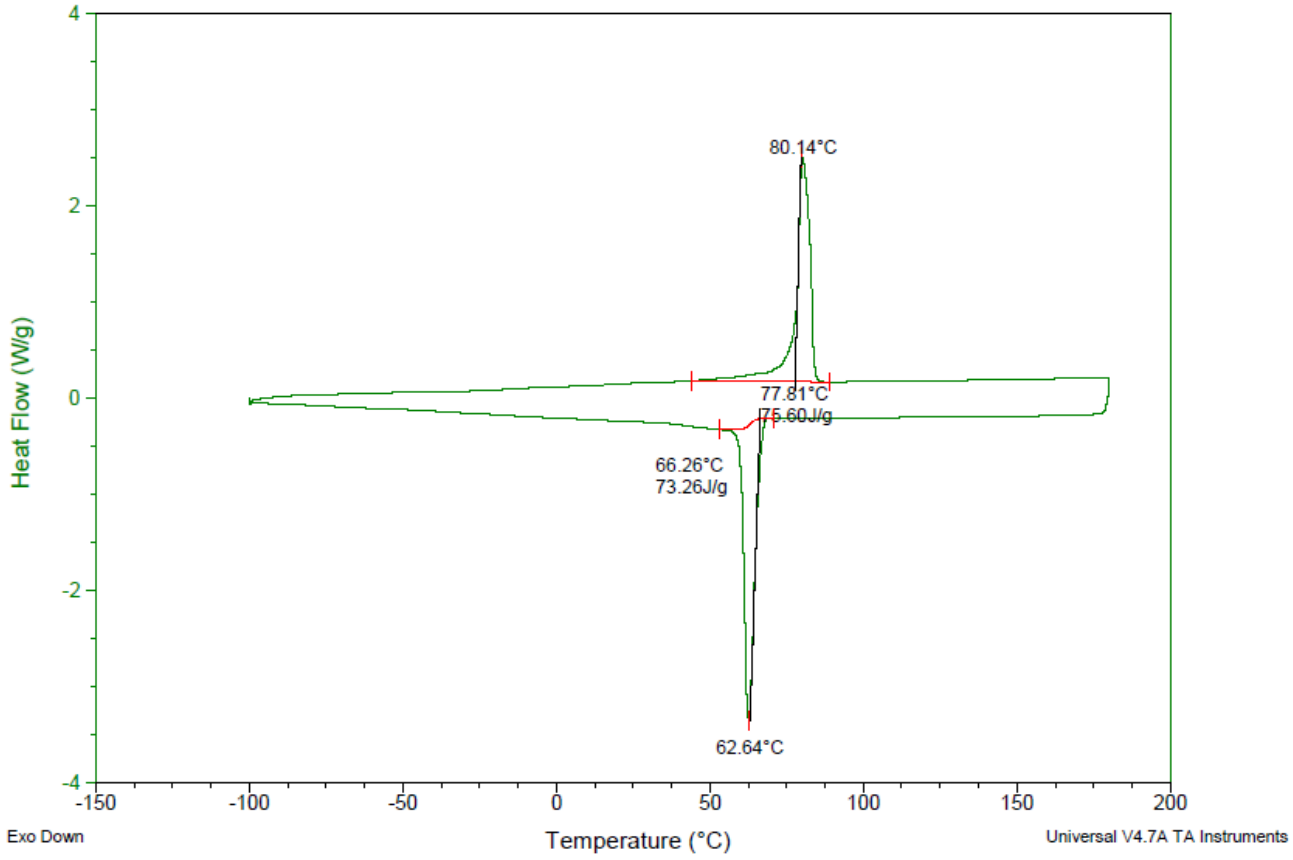


Figure S33. DSC Thermogram of polydodecylene oxalate (Table S1, entry 11).

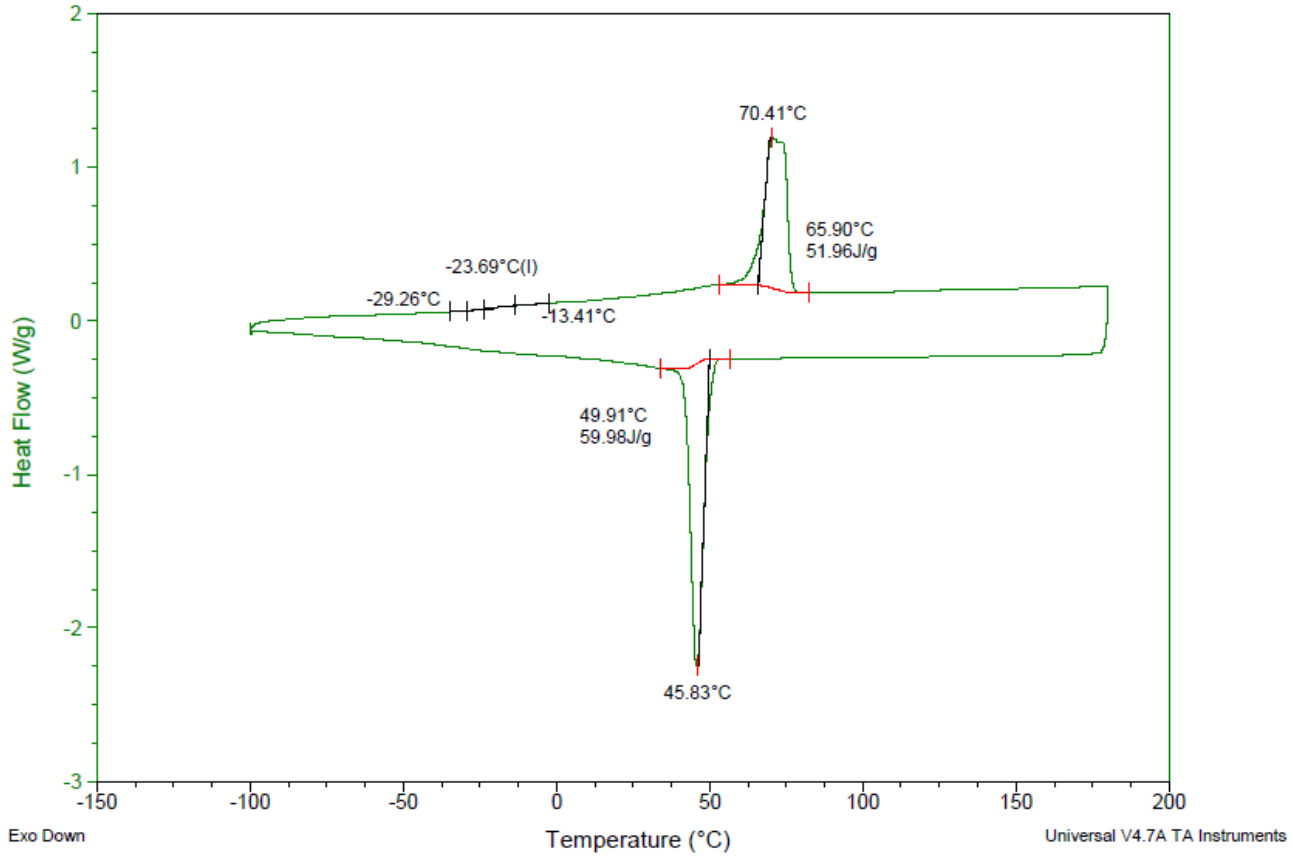


Figure S34. DSC Thermogram of poly(decylene-*co*-RBHE) oxalate [90:10] (Table S2, entry 1).

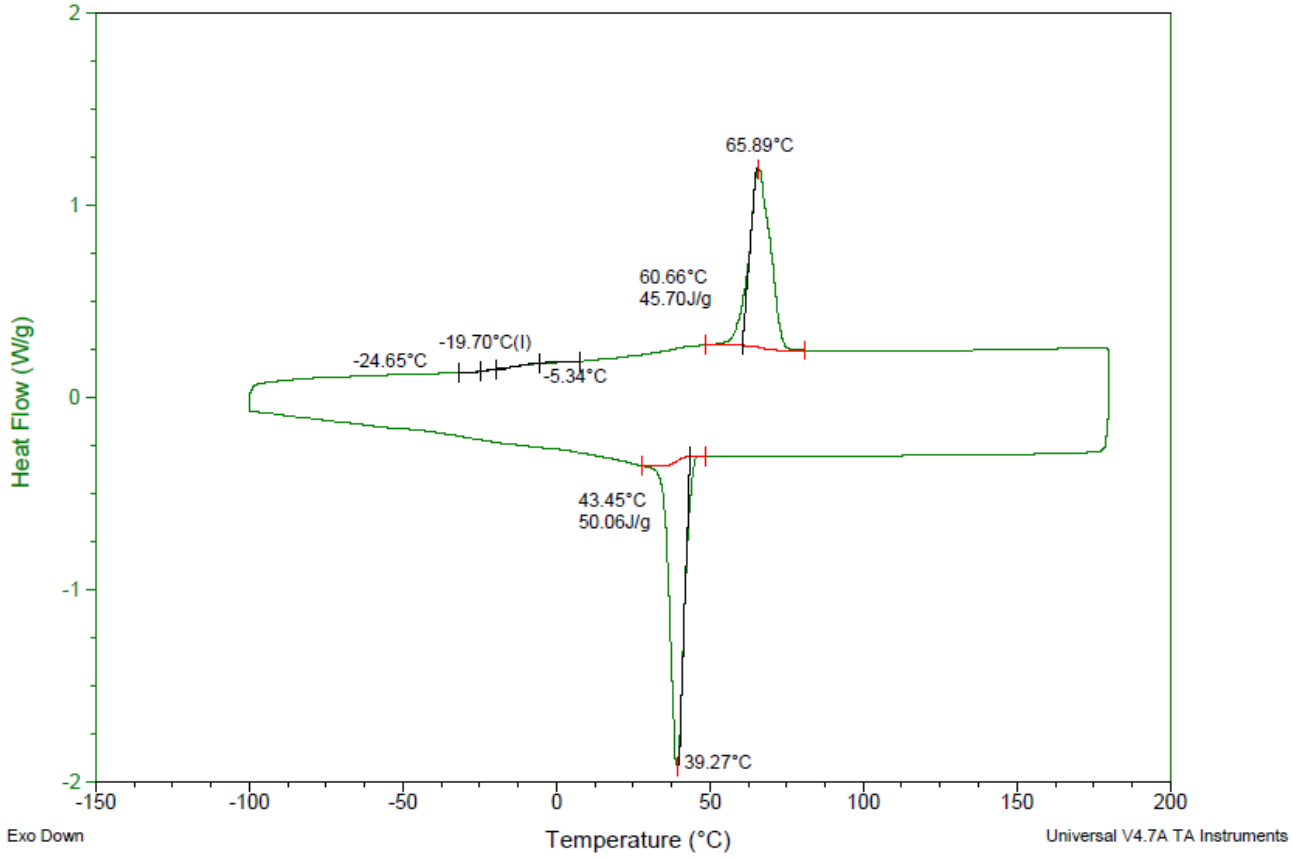


Figure S35. DSC Thermogram of poly(decylene-*co*-RBHE) oxalate [80:20] (Table S2, entry 2).

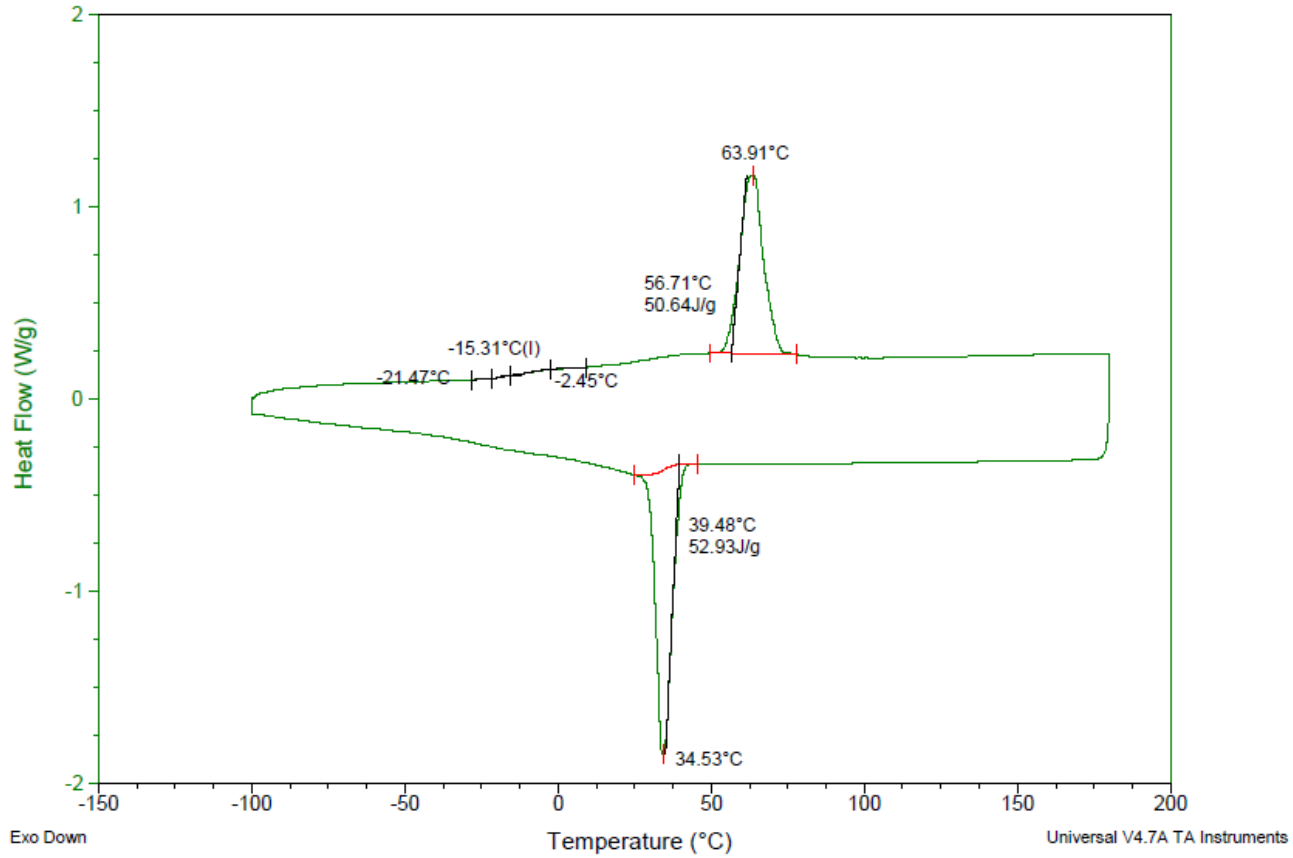


Figure S36. DSC Thermogram of poly(decylene-*co*-RBHE) oxalate [70:30] (Table S2, entry 3).

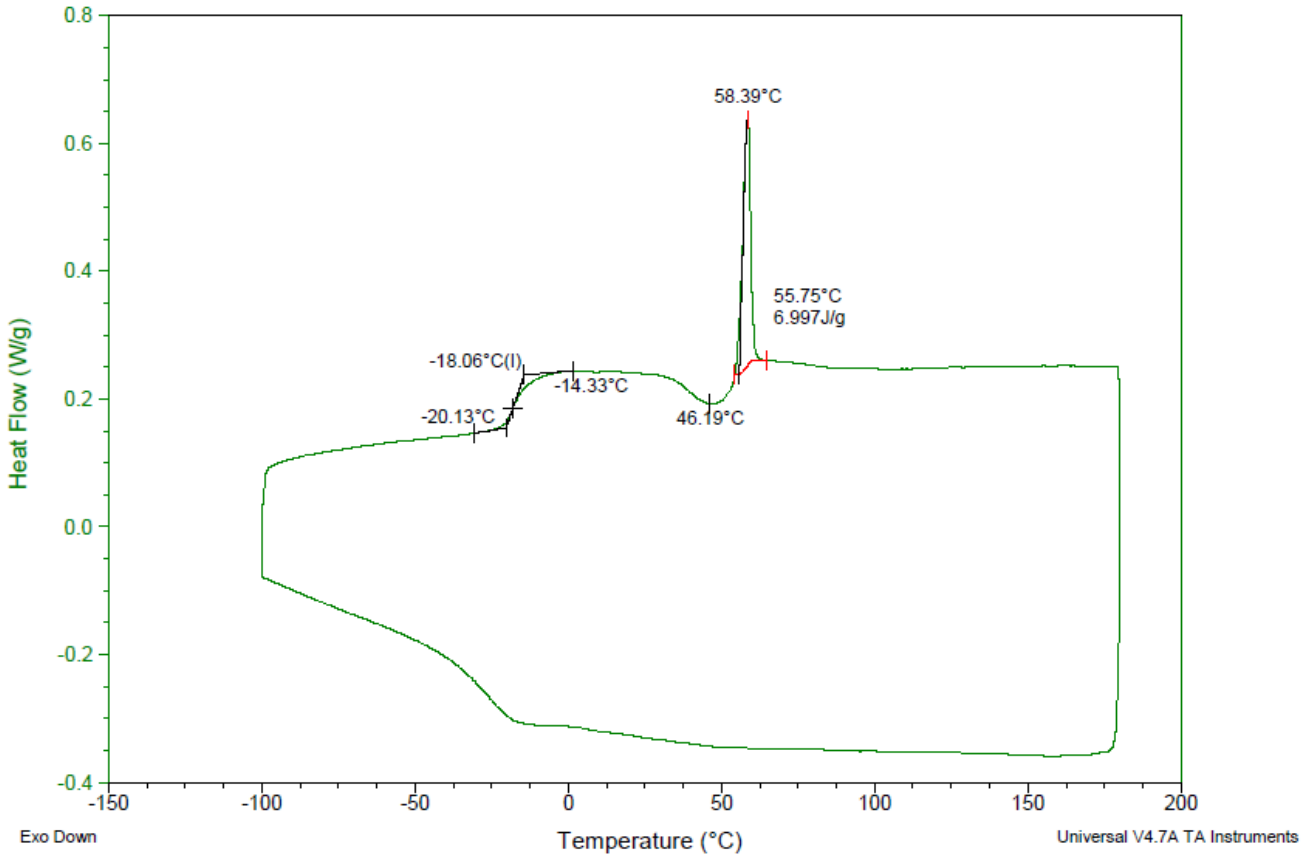


Figure S37. DSC Thermogram of poly(decylene-*co*-RBHE) oxalate [60:40] (Table S2, entry 4).

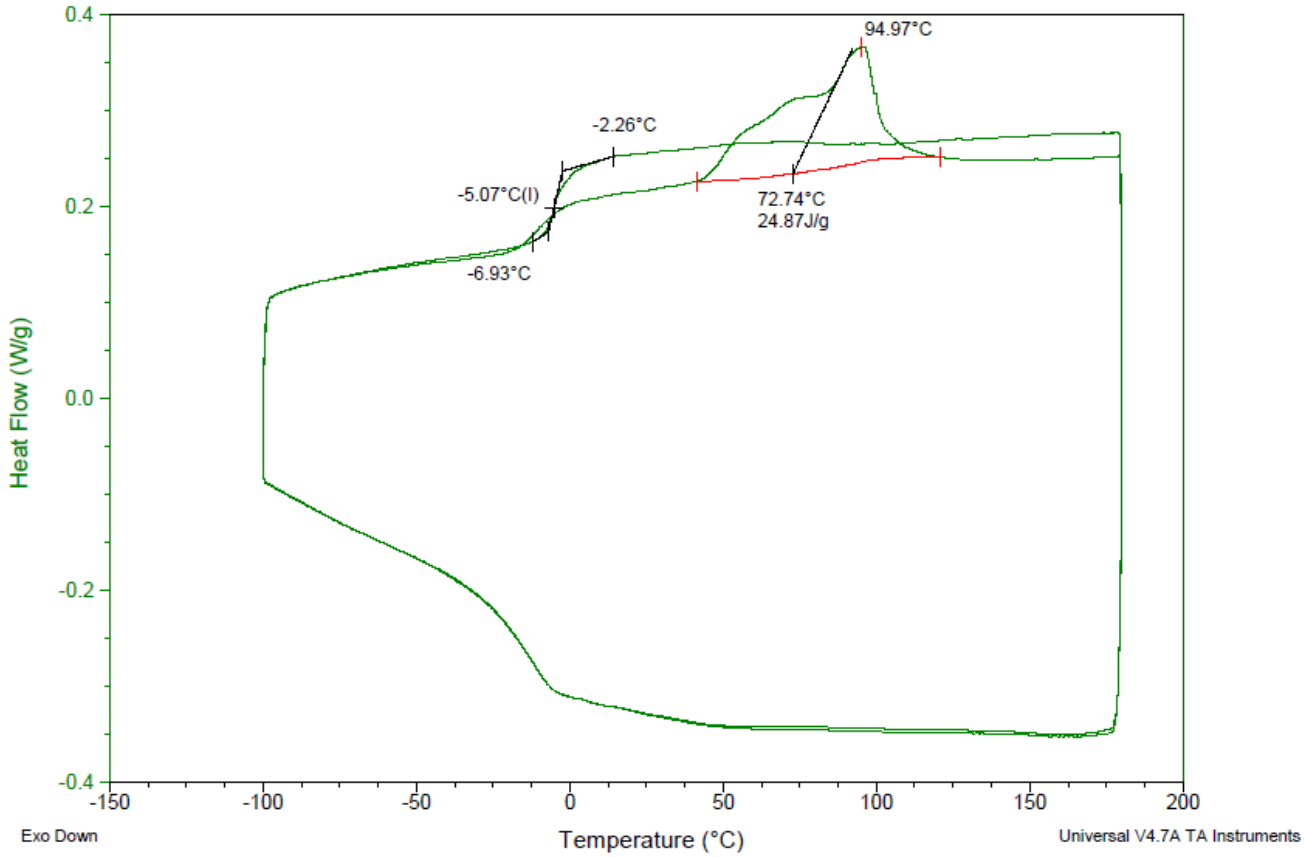


Figure S38. DSC Thermogram of poly(decylene-*co*-RBHE) oxalate [50:50] (Table S2, entry 5).

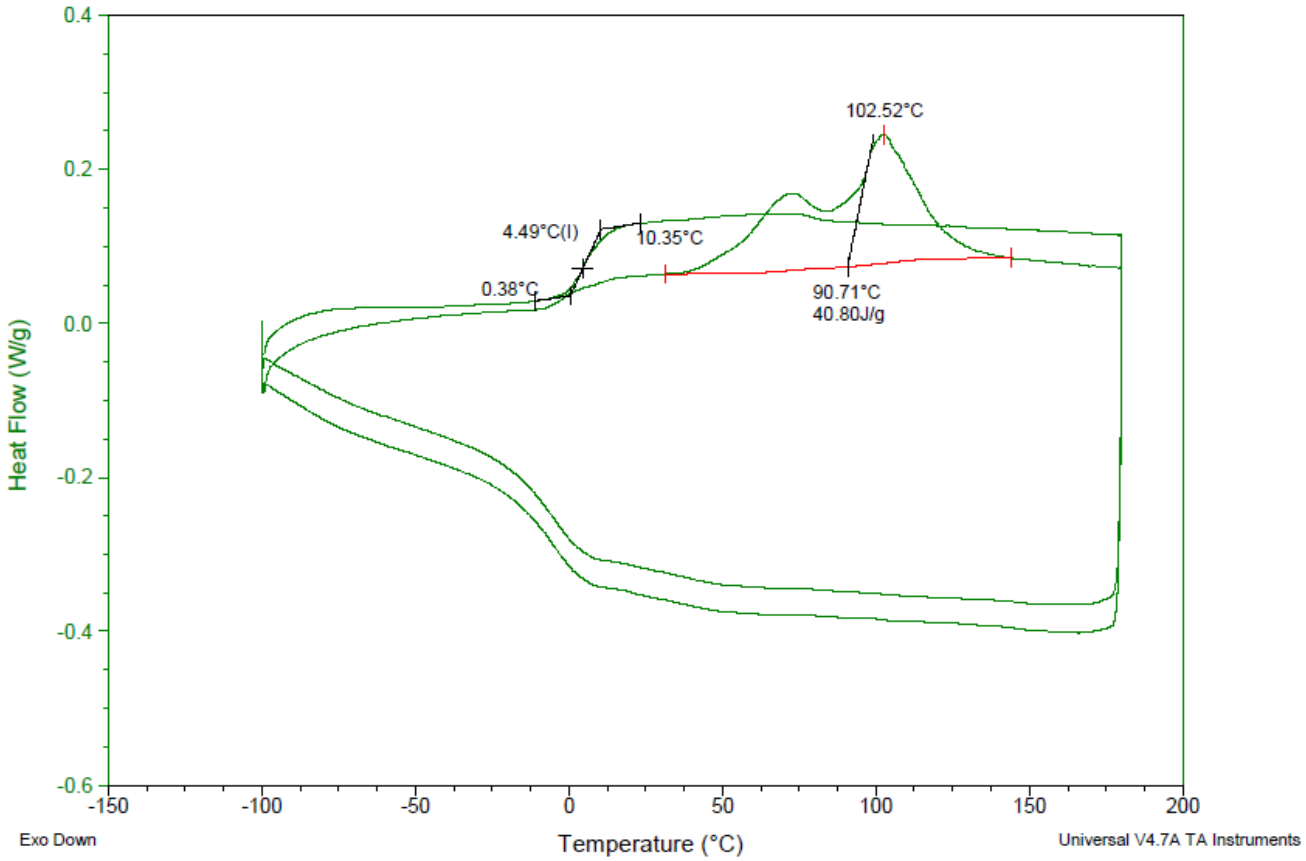


Figure S39. DSC Thermogram of poly(decylene-*co*-RBHE) oxalate [40:60] (Table S2, entry 6).

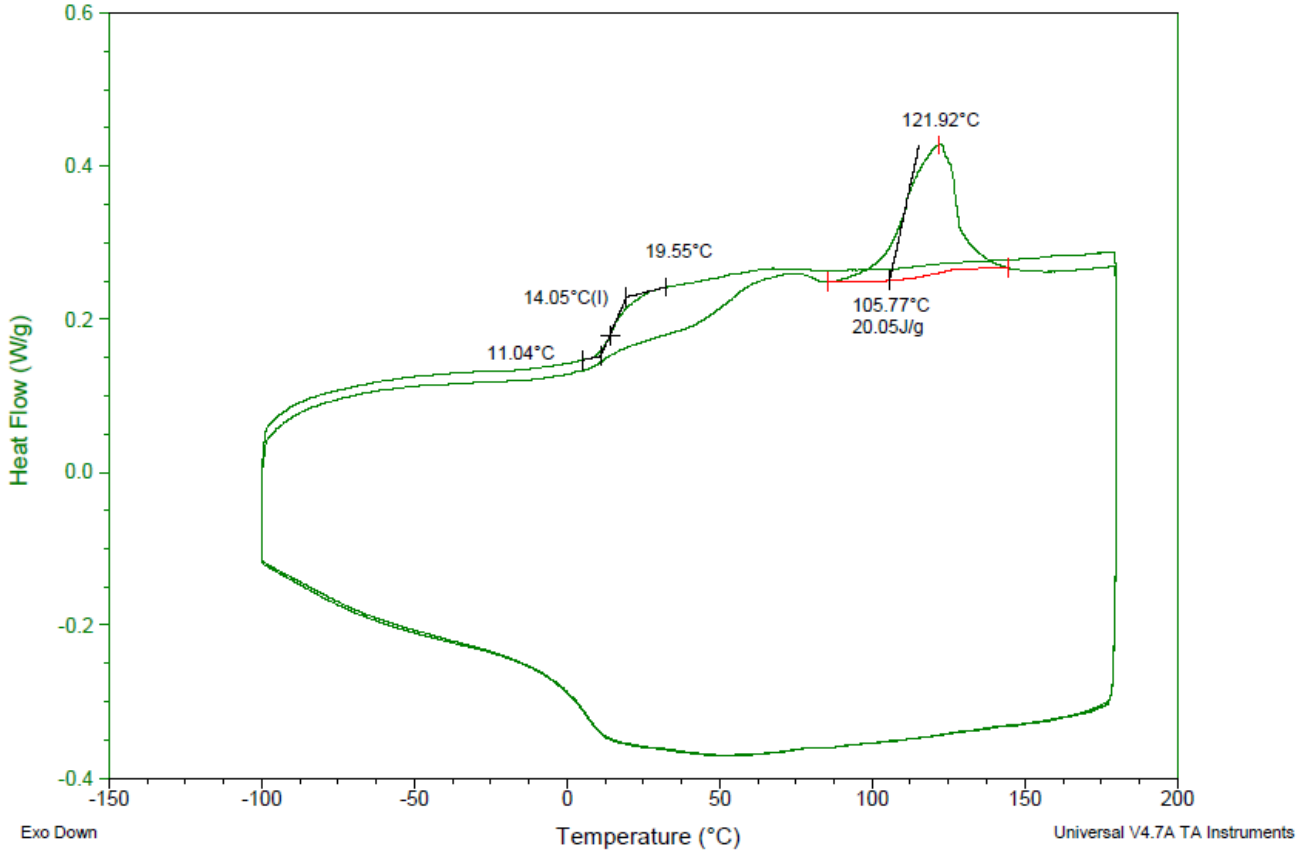


Figure S40. DSC Thermogram of poly(decylene-*co*-RBHE) oxalate [30:70] (Table S2, entry 7).

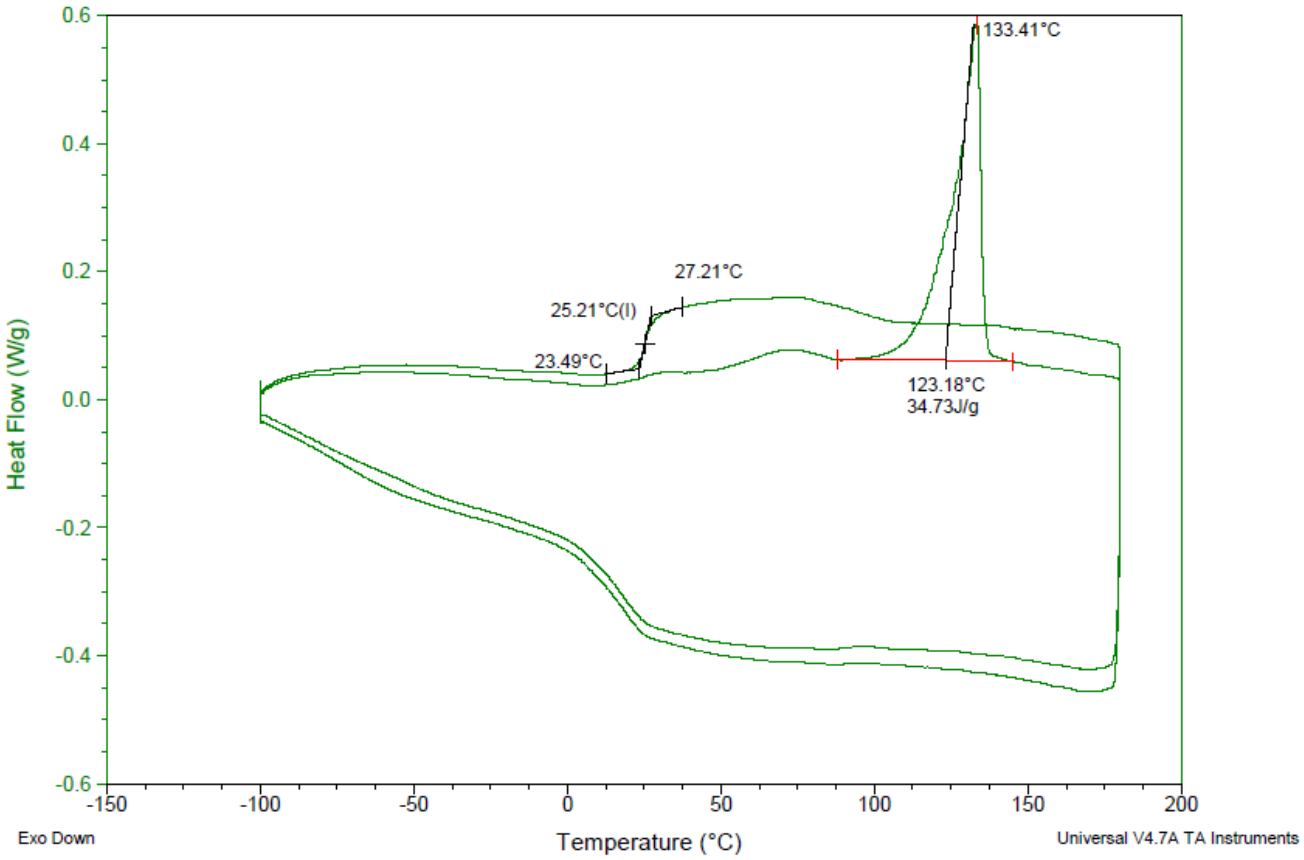


Figure S41. DSC Thermogram of poly(decylene-*co*-RBHE) oxalate [20:80] (Table S2, entry 8).

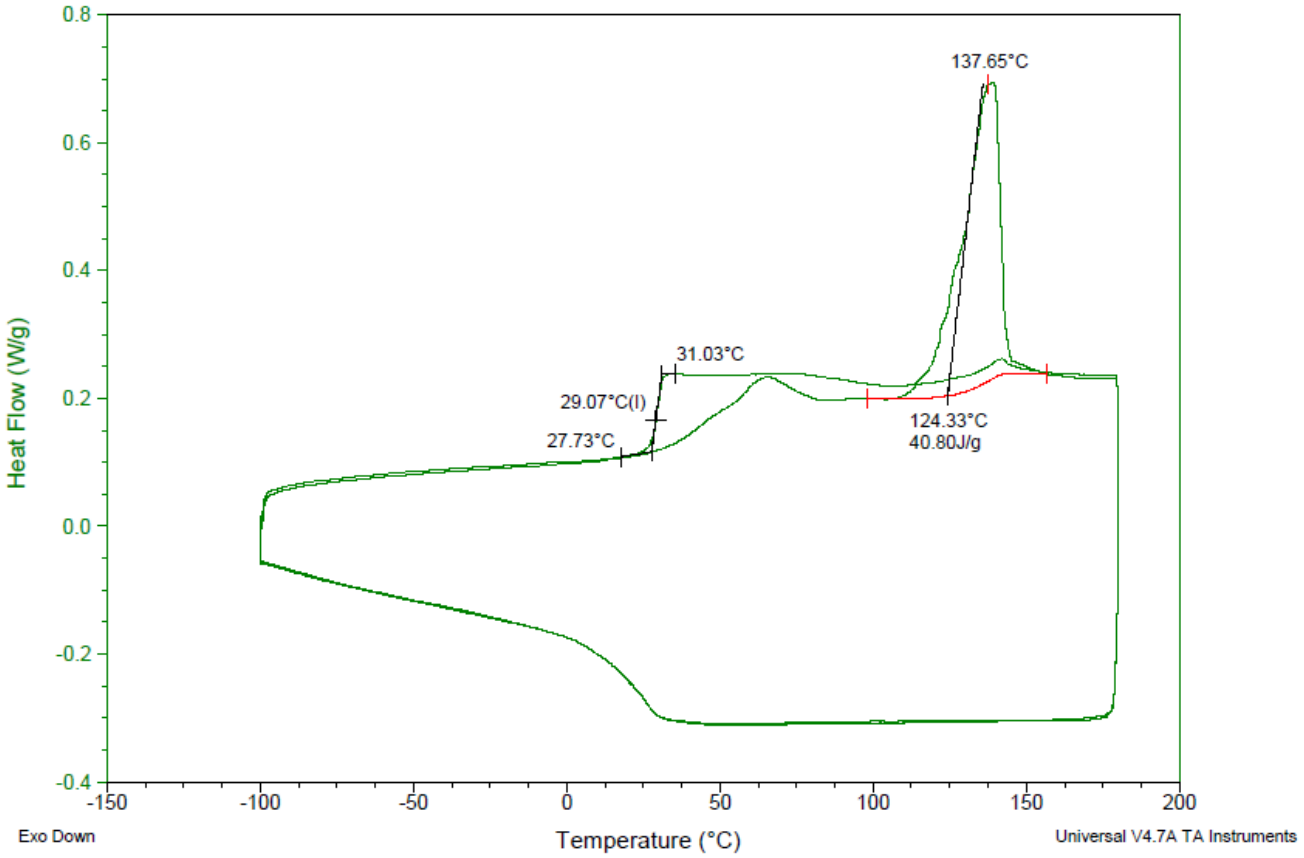


Figure S42. DSC Thermogram of poly(decylene-*co*-RBHE) oxalate [10:90] (Table S2, entry 9).

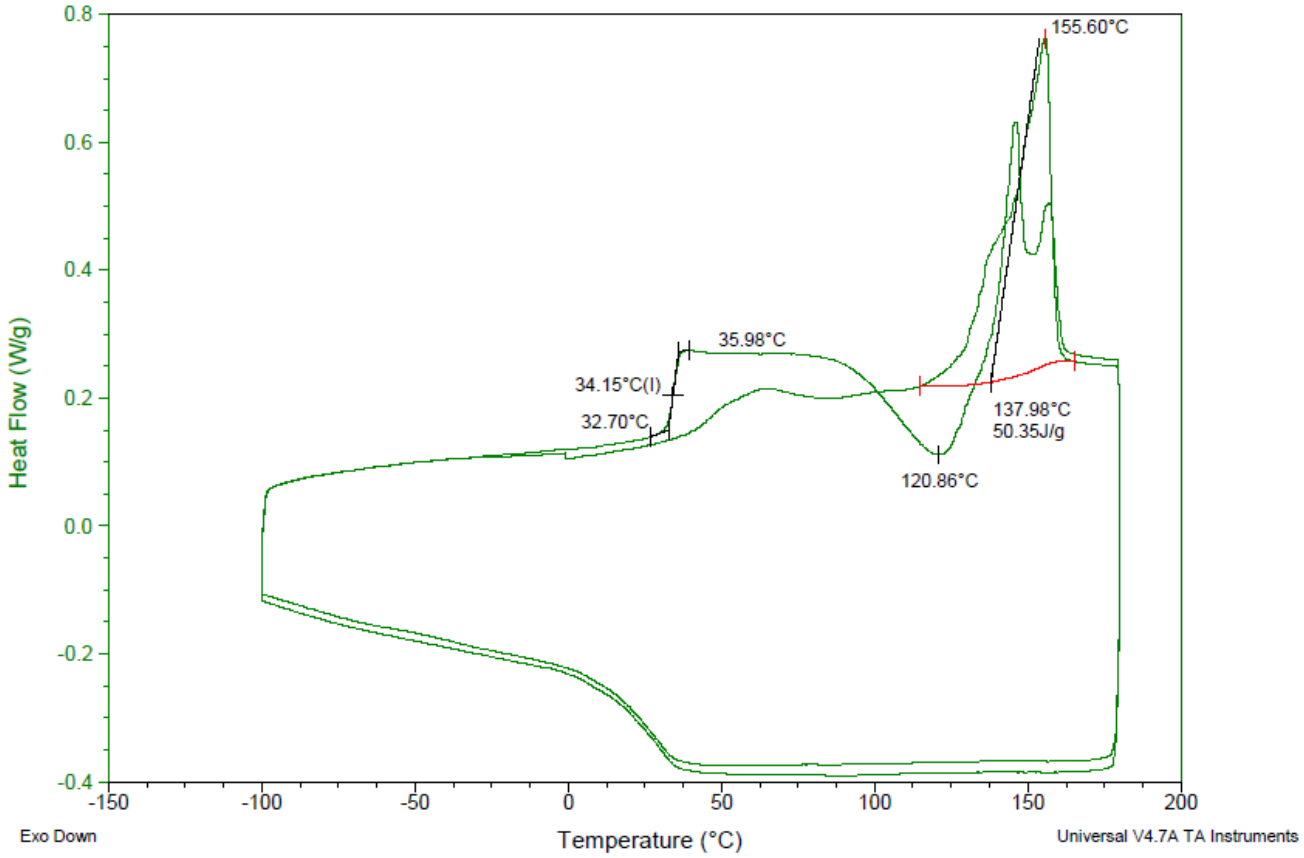


Figure S43. DSC Thermogram of poly(RBHE) oxalate (Table S2, entry 10).

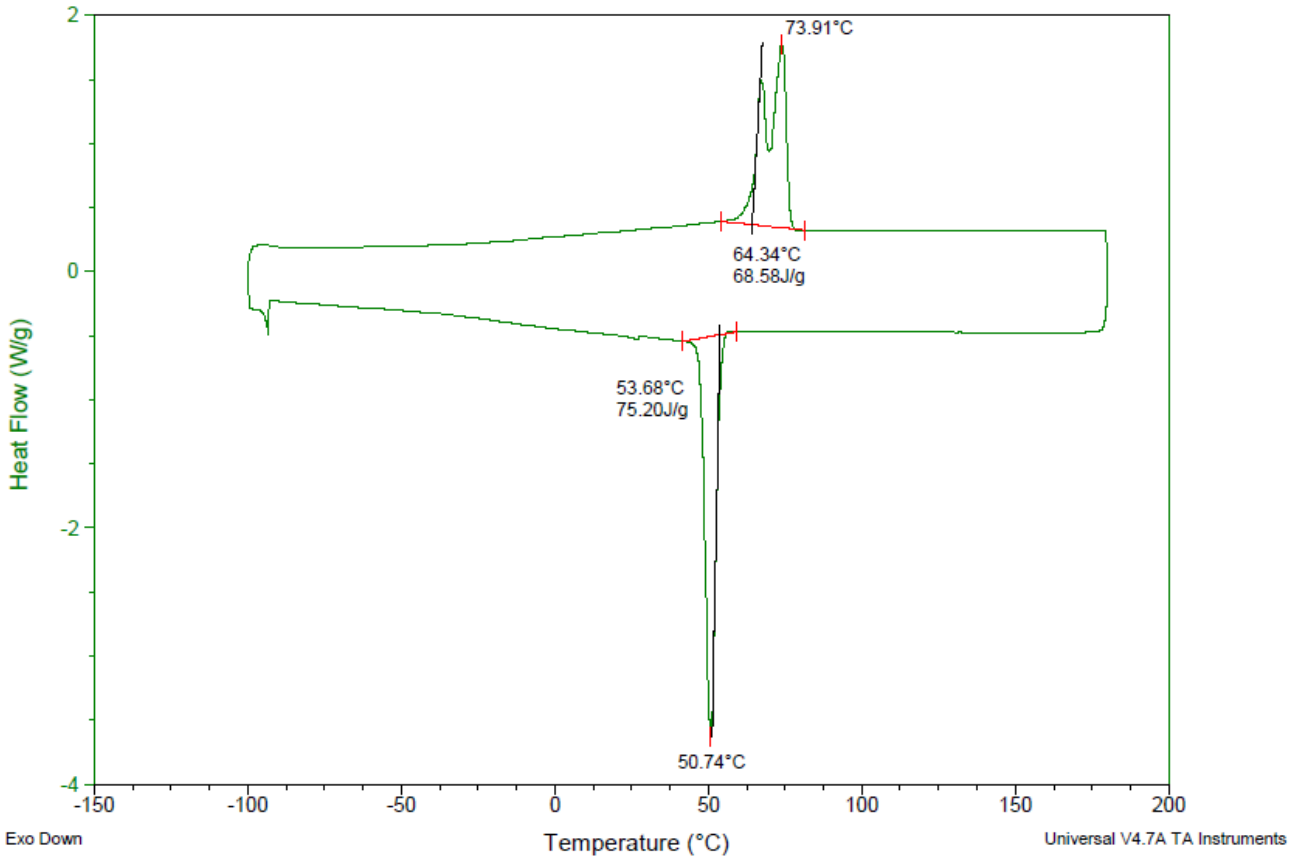


Figure S44. DSC Thermogram of poly(decylene-*co*-HBHE) oxalate [90:10] (Table S2, entry 11).

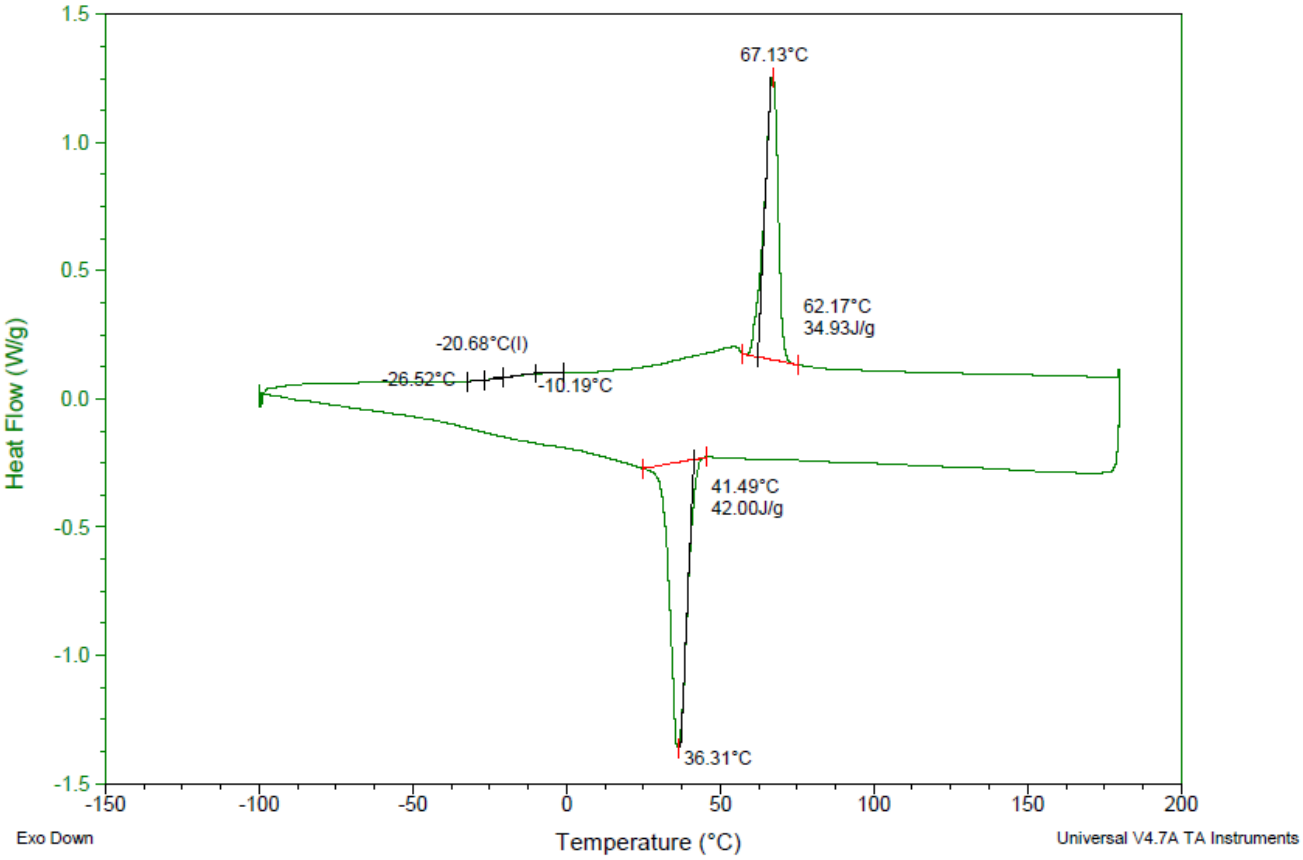


Figure S45. DSC Thermogram of poly(decylene-*co*-HBHE) oxalate [80:20] (Table S2, entry 12).

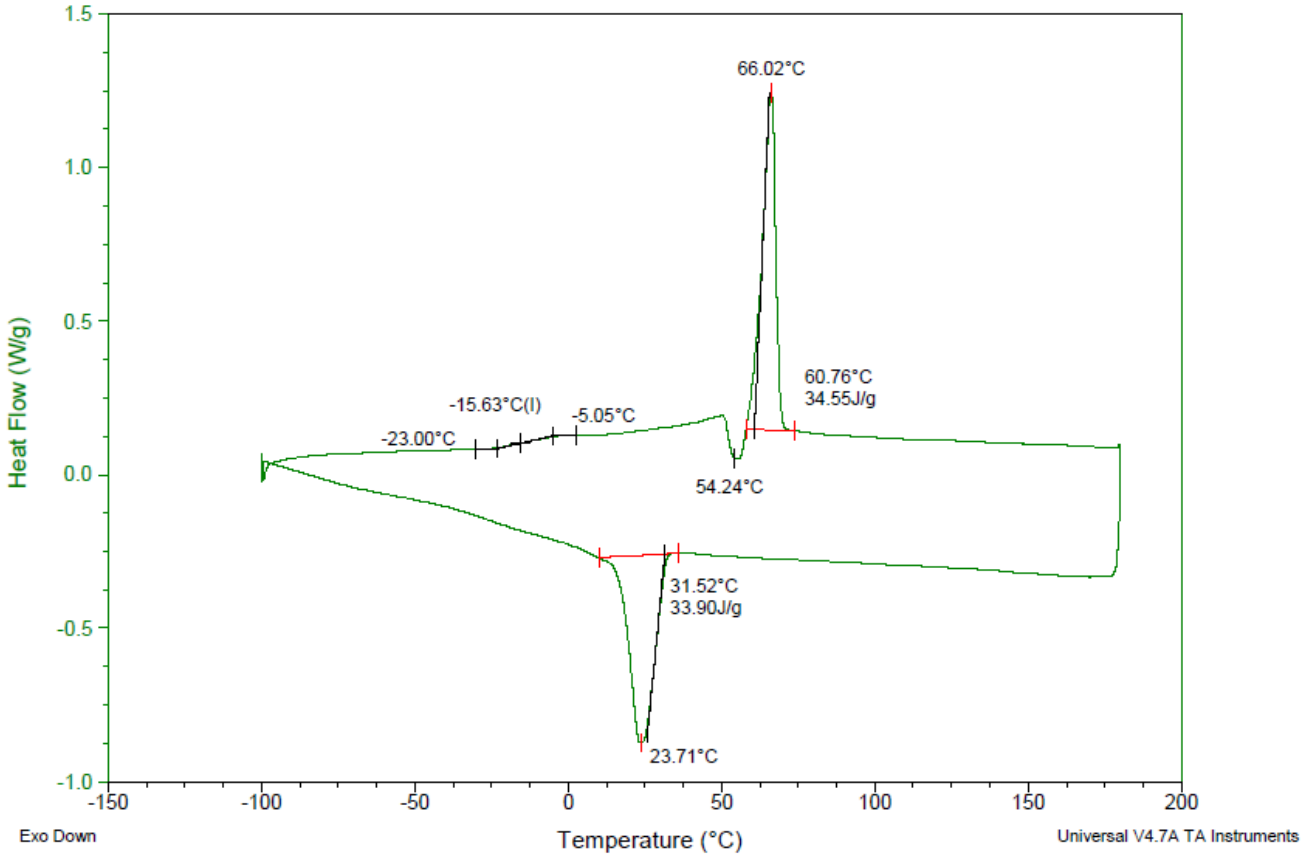


Figure S46. DSC Thermogram of poly(decylene-*co*-HBHE) oxalate [70:30] (Table S2, entry 13).

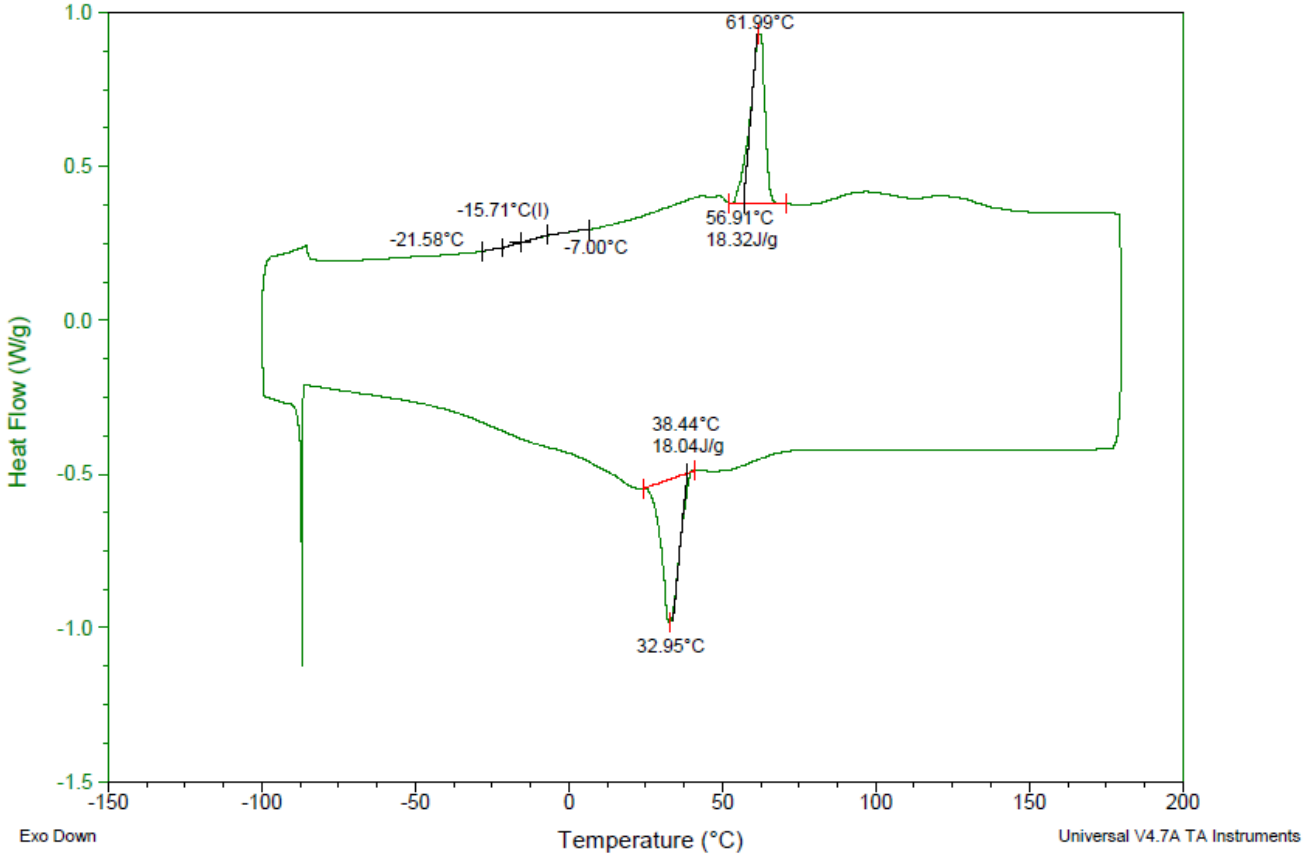


Figure S47. DSC Thermogram of poly(decylene-*co*-HBHE) oxalate [60:40] (Table S2, entry 14).

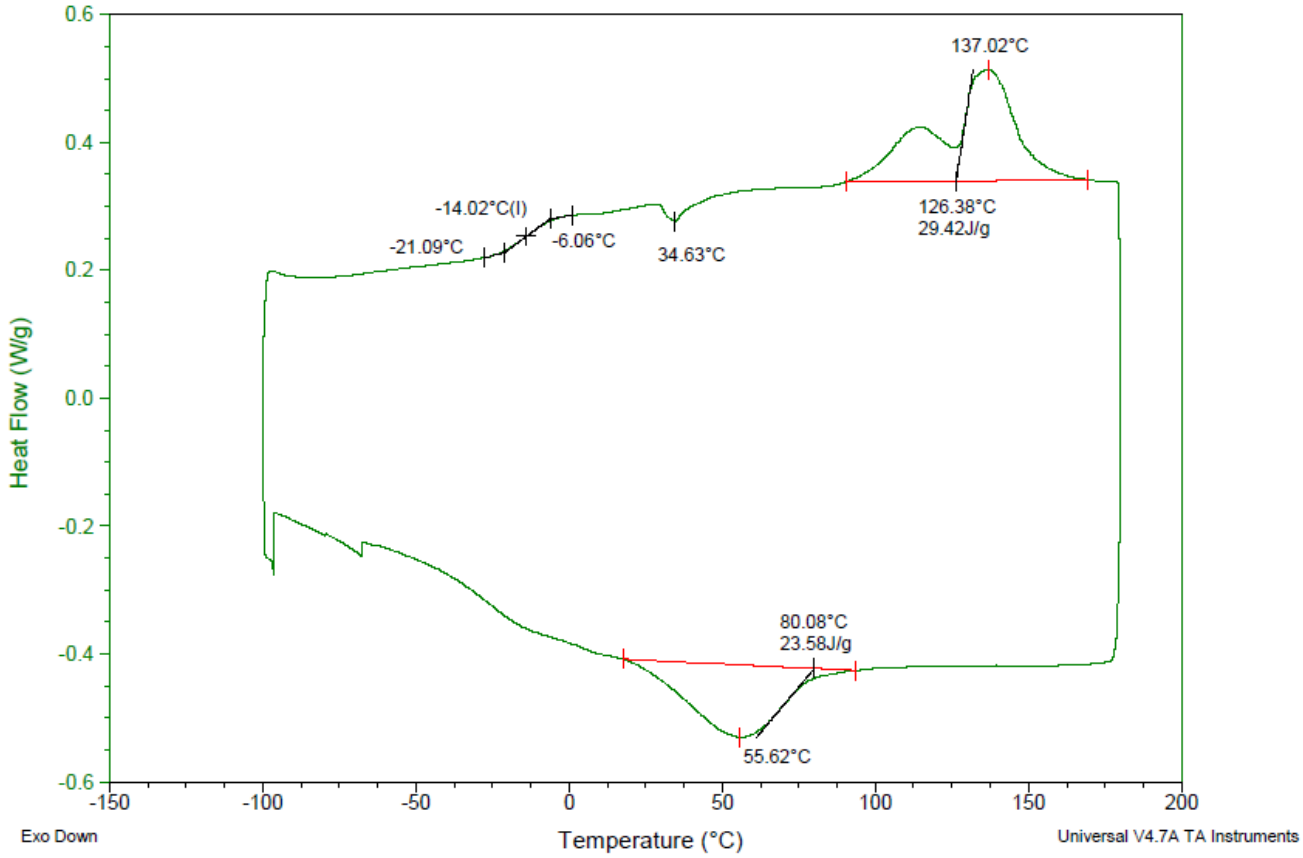


Figure S48. DSC Thermogram of poly(decylene-*co*-HBHE) oxalate [50:50] (Table S2, entry 15).

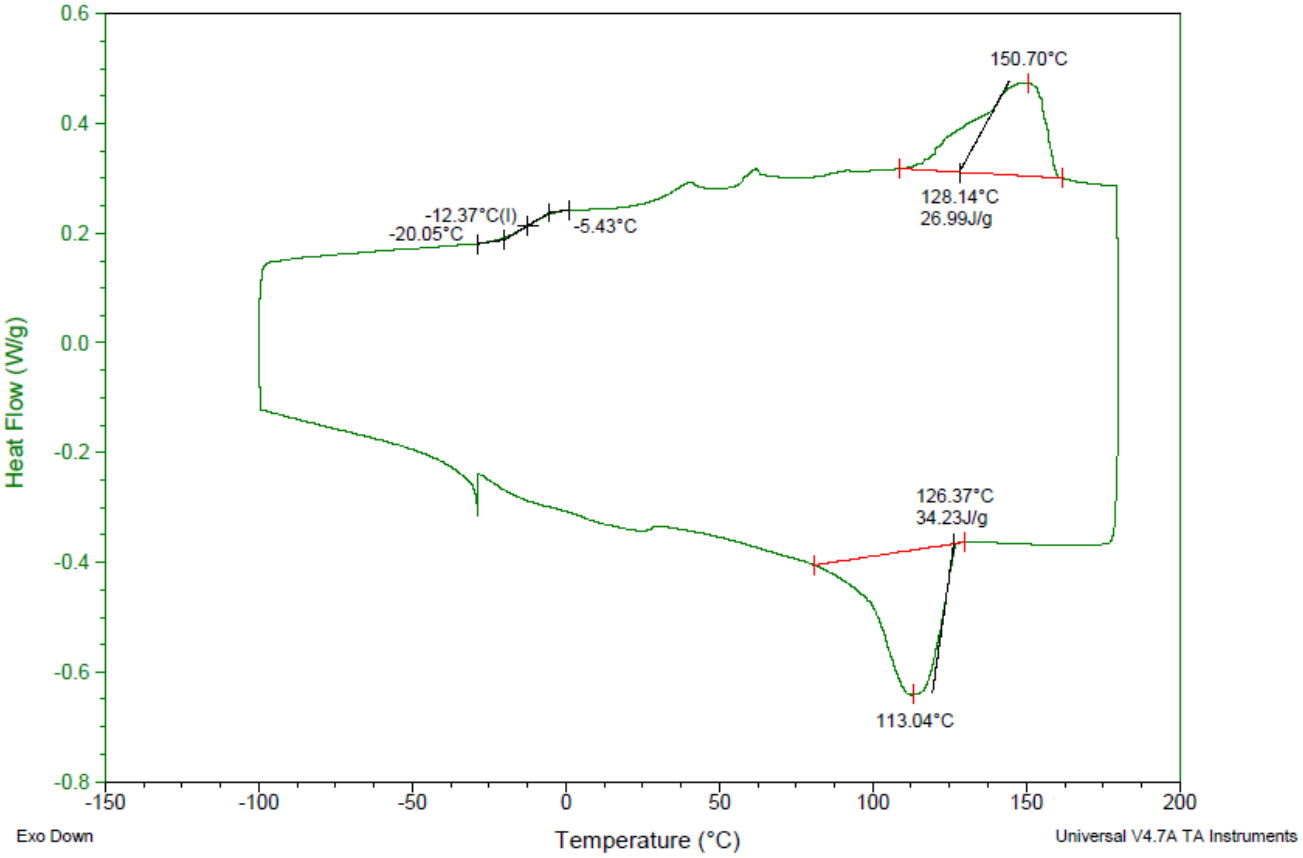


Figure S49. DSC Thermogram of poly(decylene-*co*-HBHE) oxalate [40:60] (Table S2, entry 16).

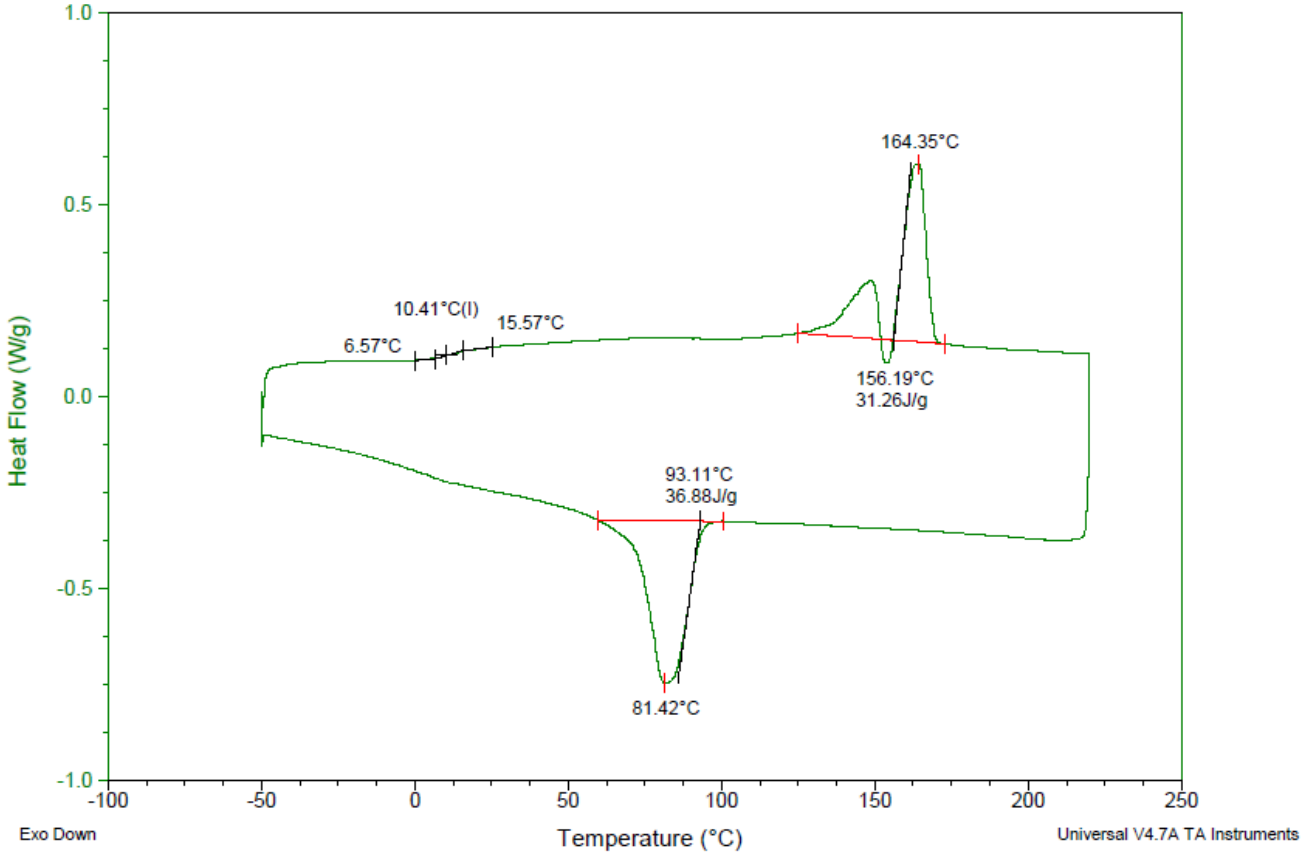


Figure S50. DSC Thermogram of poly(decylene-*co*-HBHE) oxalate [30:70] (Table S2, entry 17).

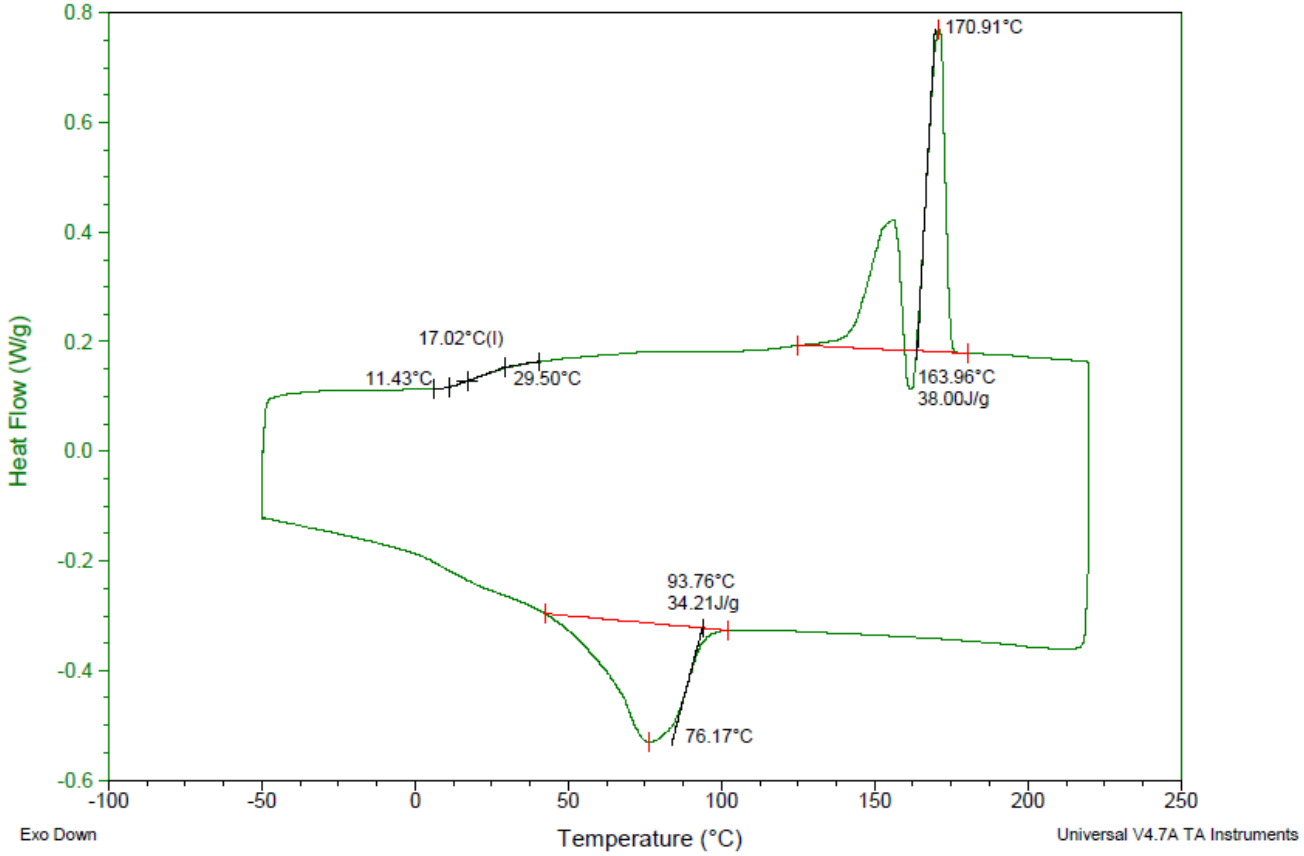


Figure S51. DSC Thermogram of poly(decylene-*co*-HBHE) oxalate [20:80] (Table S2, entry 18).

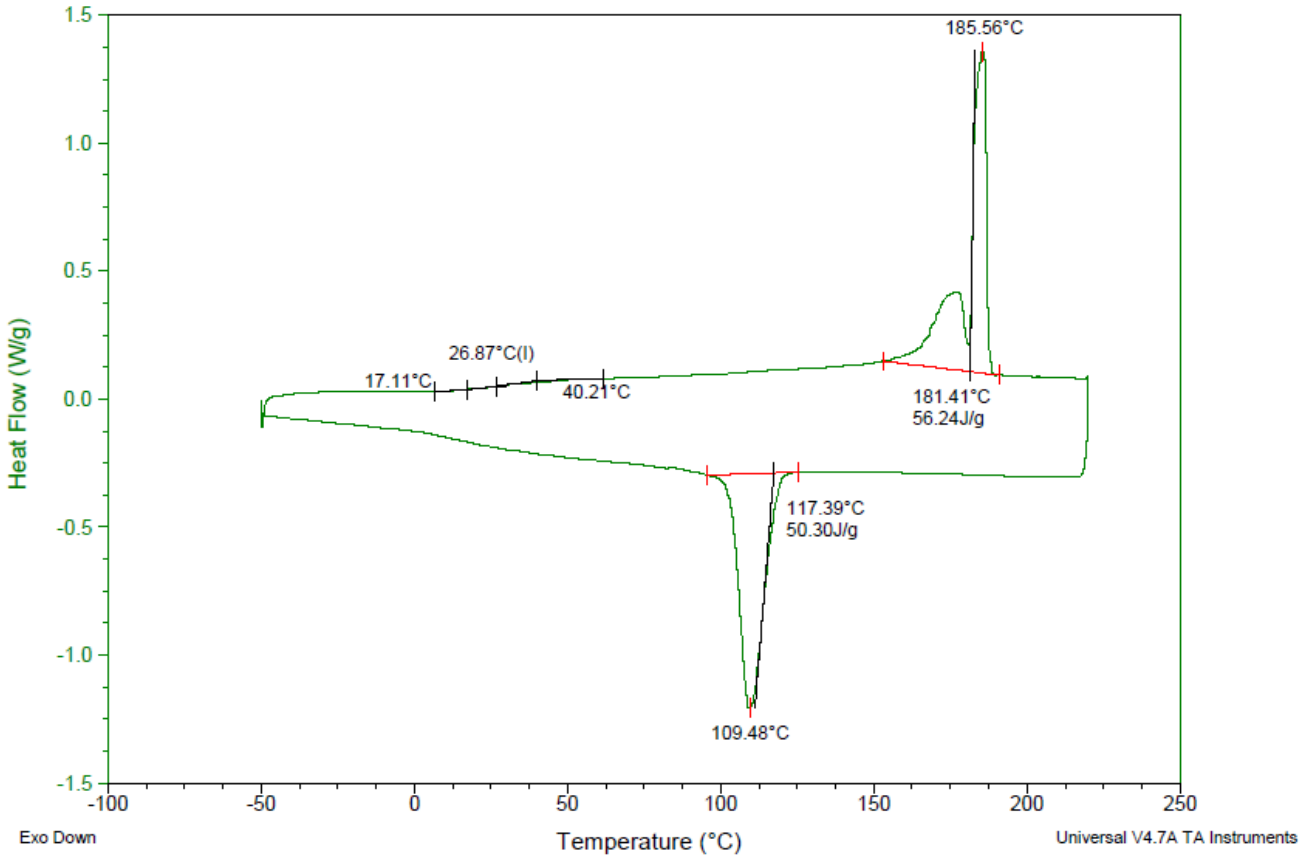


Figure S52. DSC Thermogram of poly(decylene-*co*-HBHE) oxalate [10:90] (Table S2, entry 19).

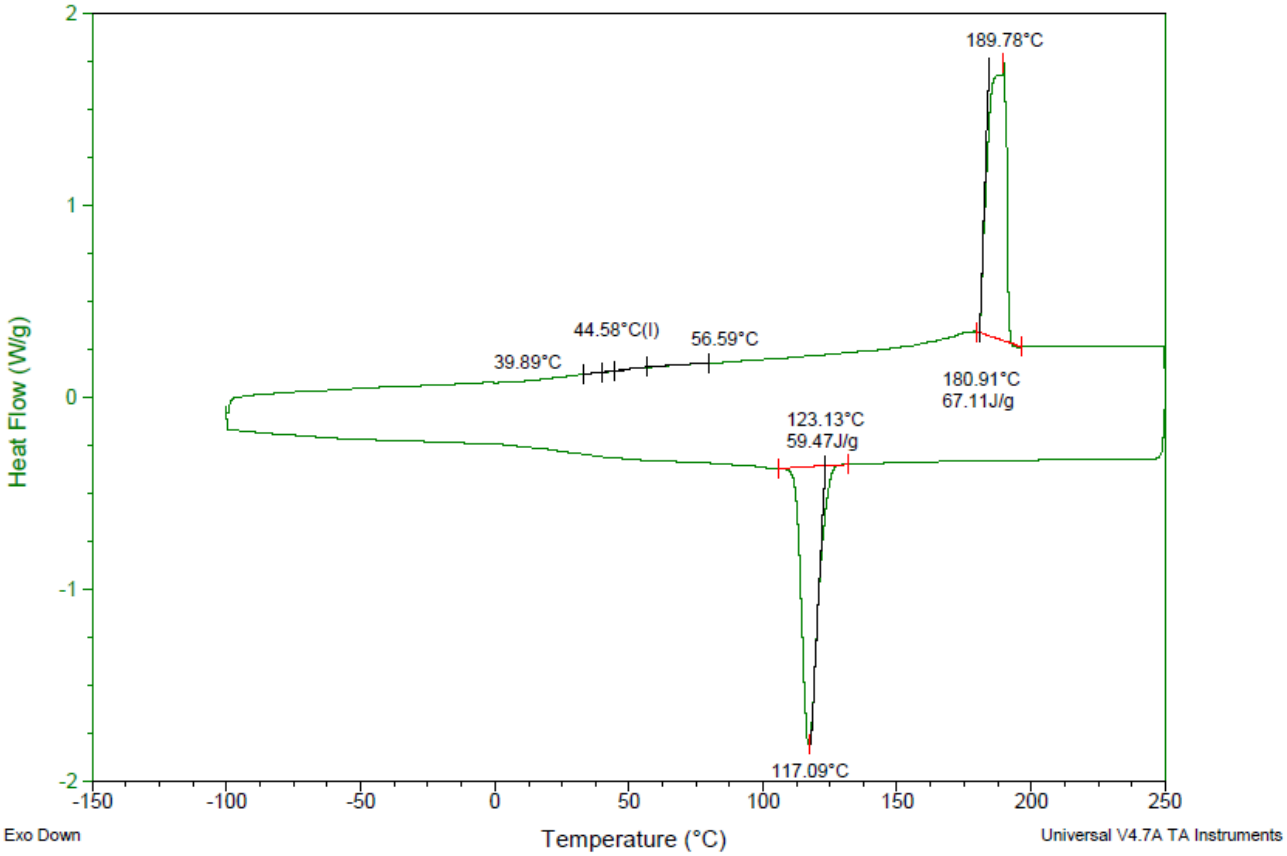


Figure S53. DSC Thermogram of poly(HBHE) oxalate (Table S2, entry 20).

Thermogravimetric Analysis (TGA) Thermograms

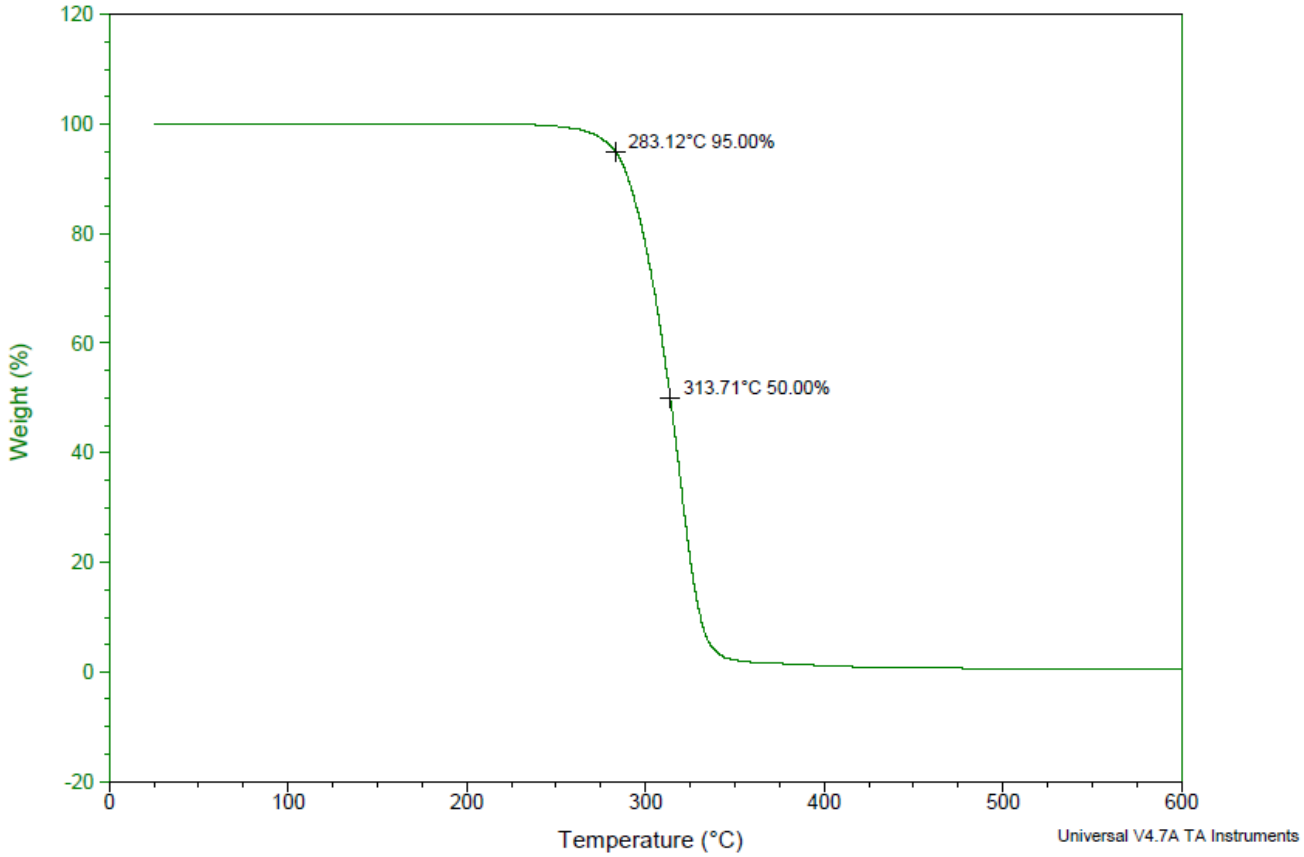


Figure S54. TGA Thermogram of polypropylene oxalate (Table S1, entry 1).

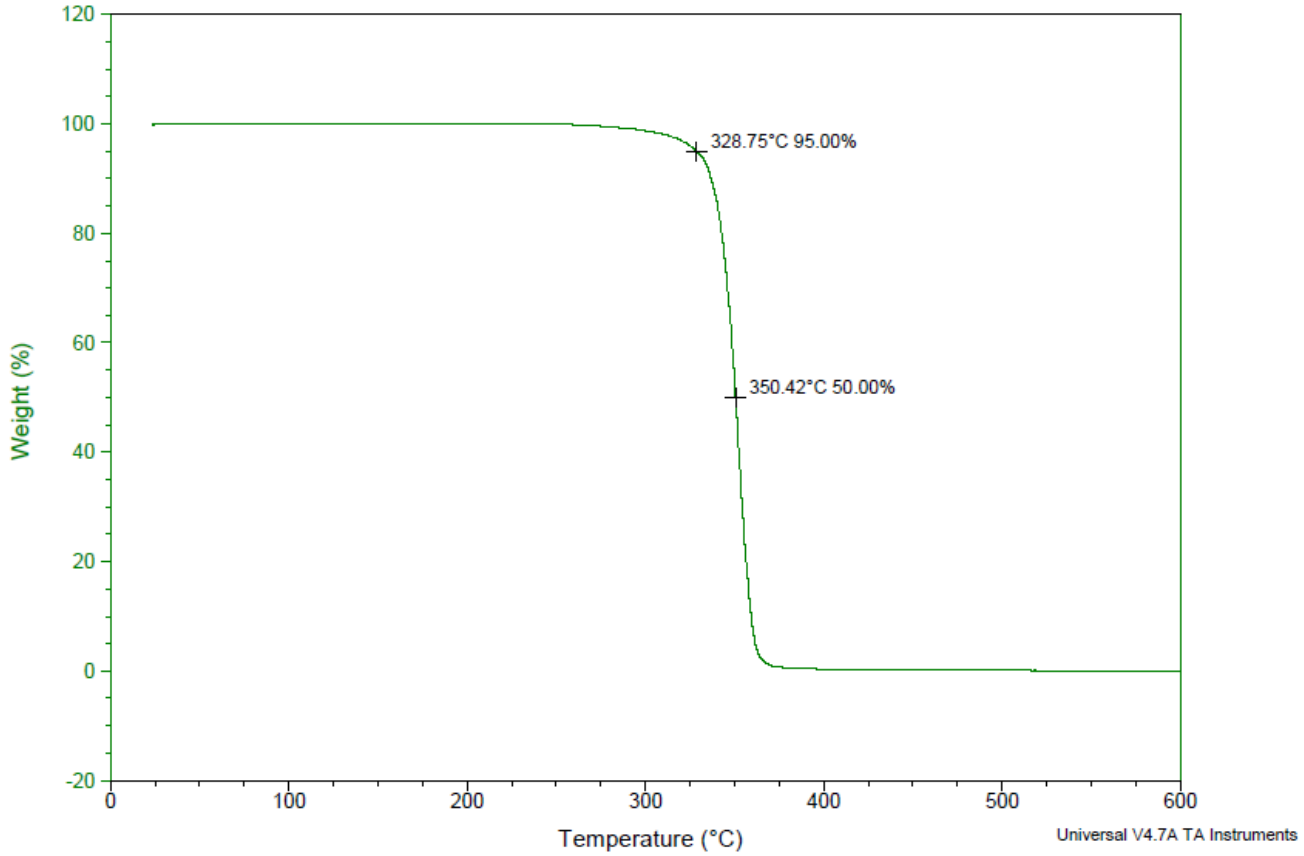


Figure S55. TGA Thermogram of polyneopentyl oxalate (Table S1, entry 2).

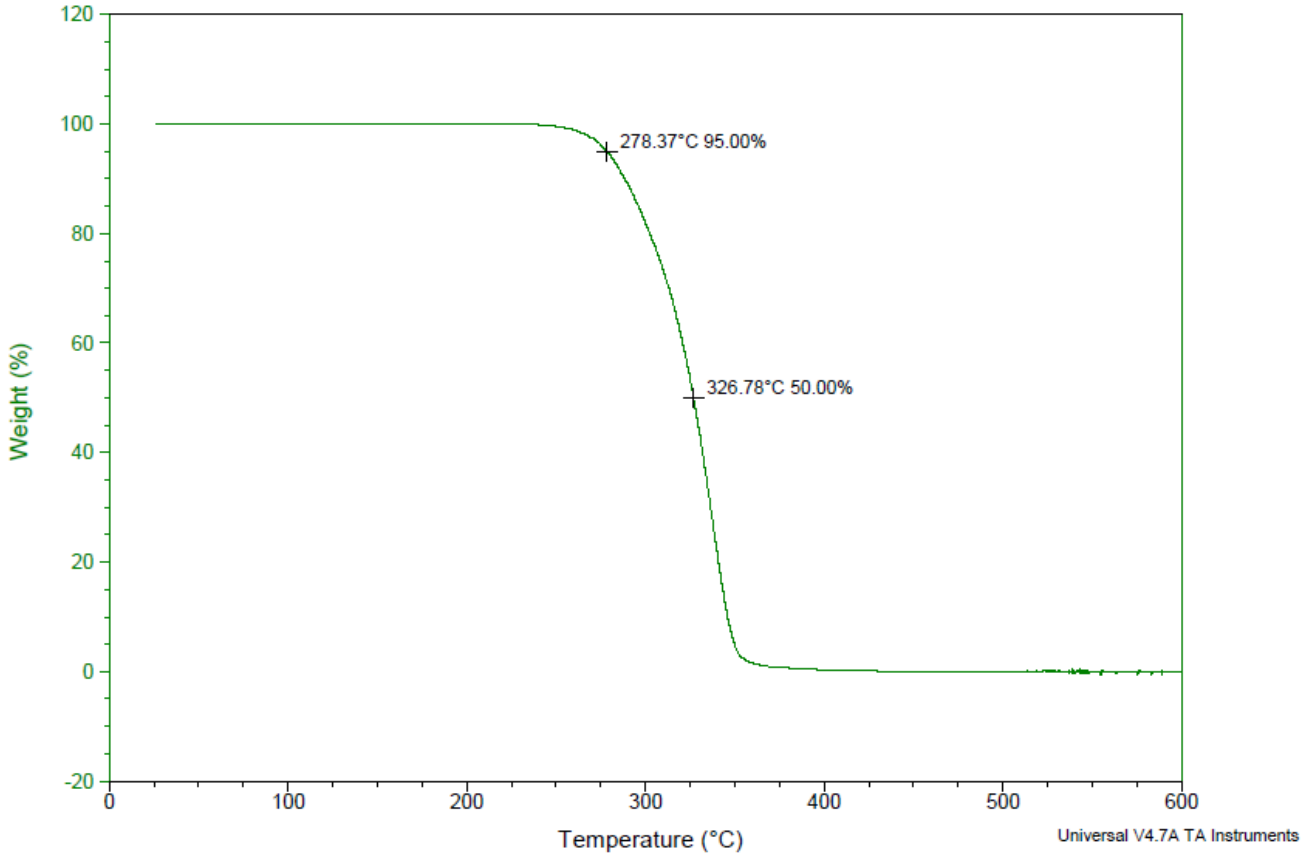


Figure S56. TGA Thermogram of polybutylene oxalate (Table S1, entry 3).

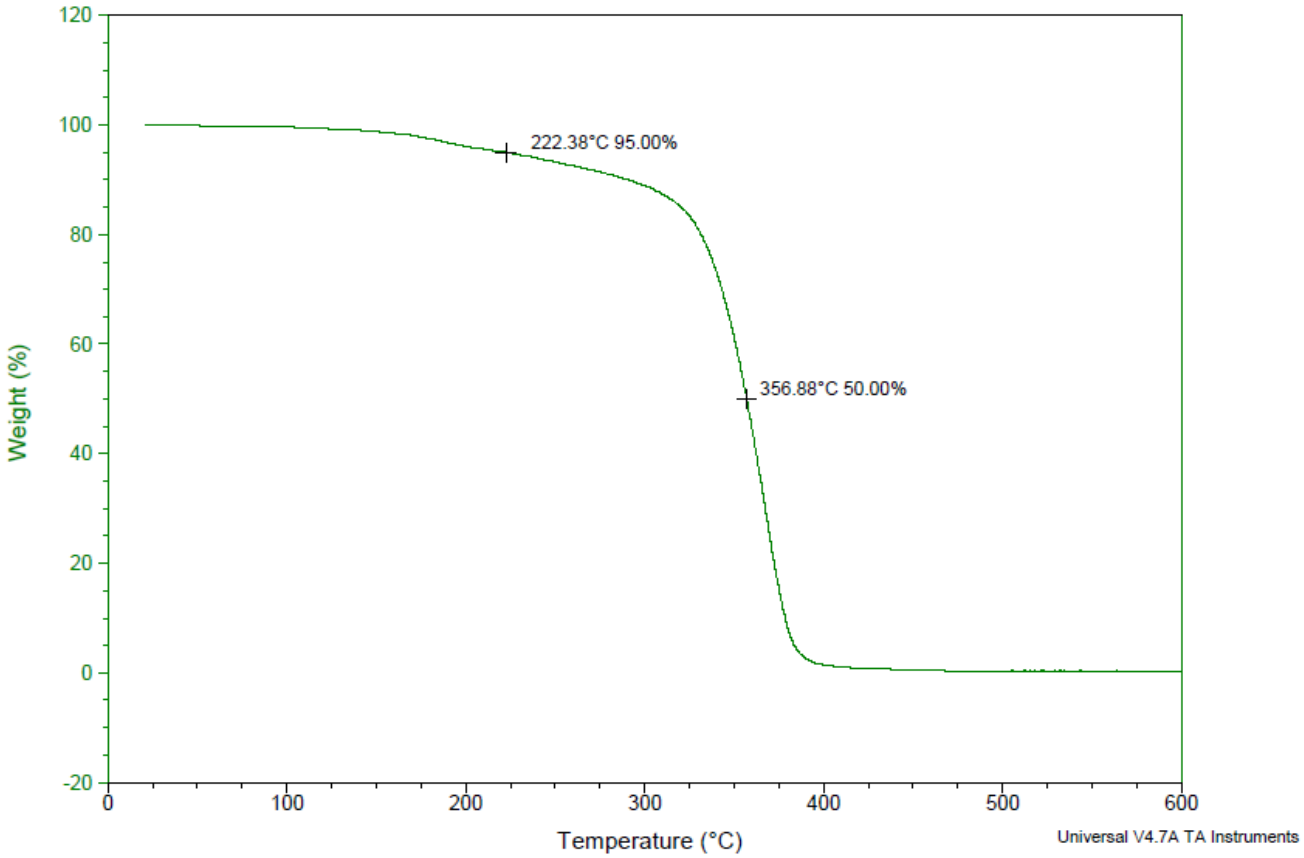


Figure S57. TGA Thermogram of polypentylene oxalate (Table S1, entry 4).

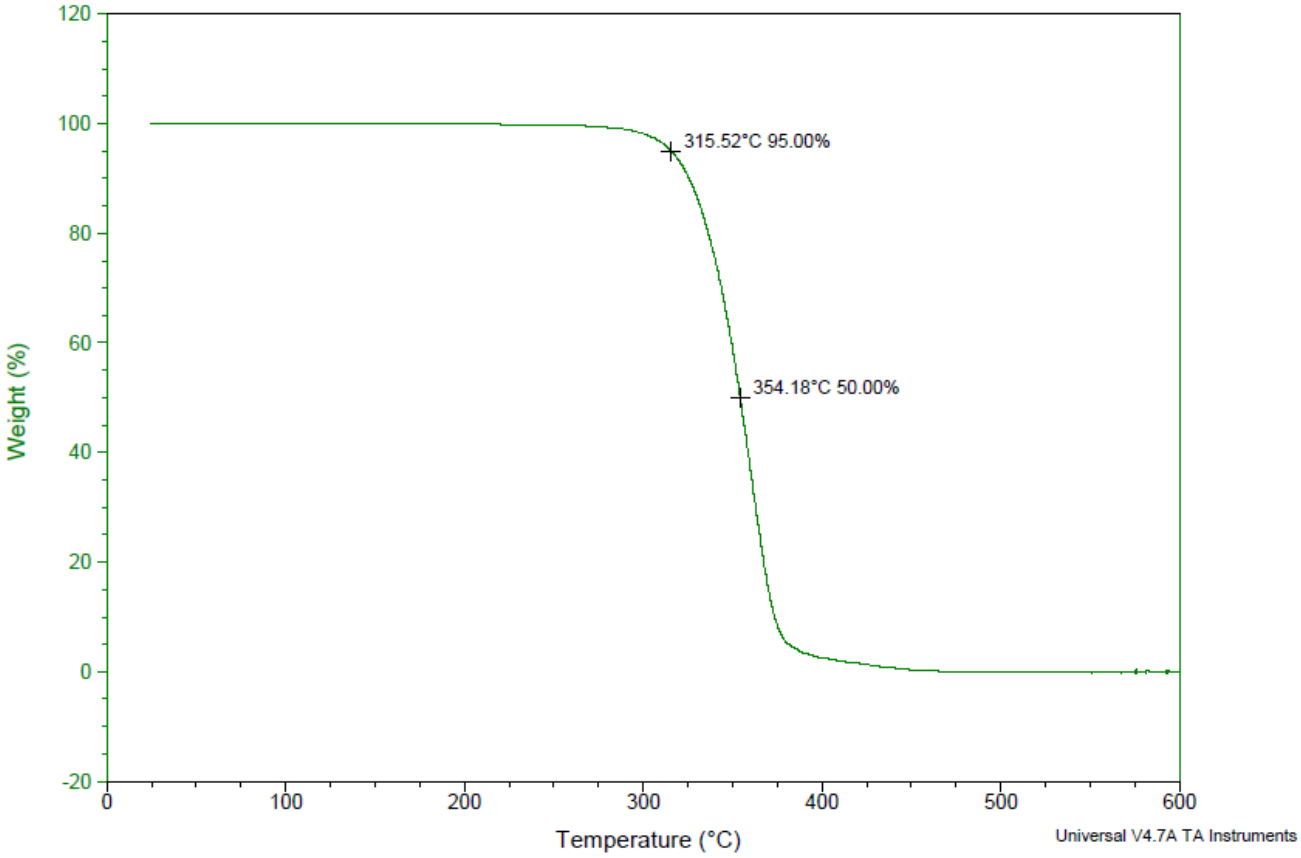


Figure S58. TGA Thermogram of polyhexylene oxalate (Table S1, entry 5).

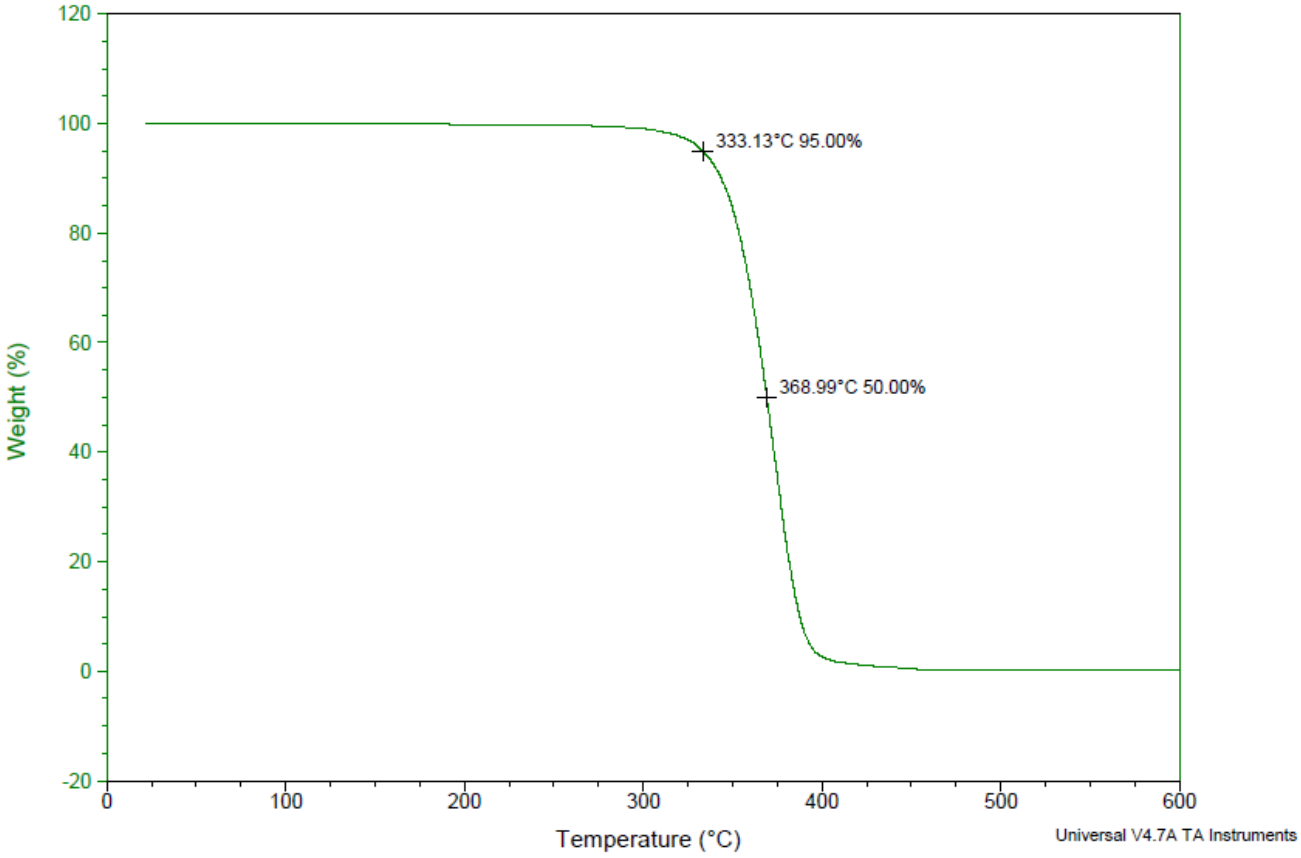


Figure S59. TGA Thermogram of polyheptylene oxalate (Table S1, entry 6).

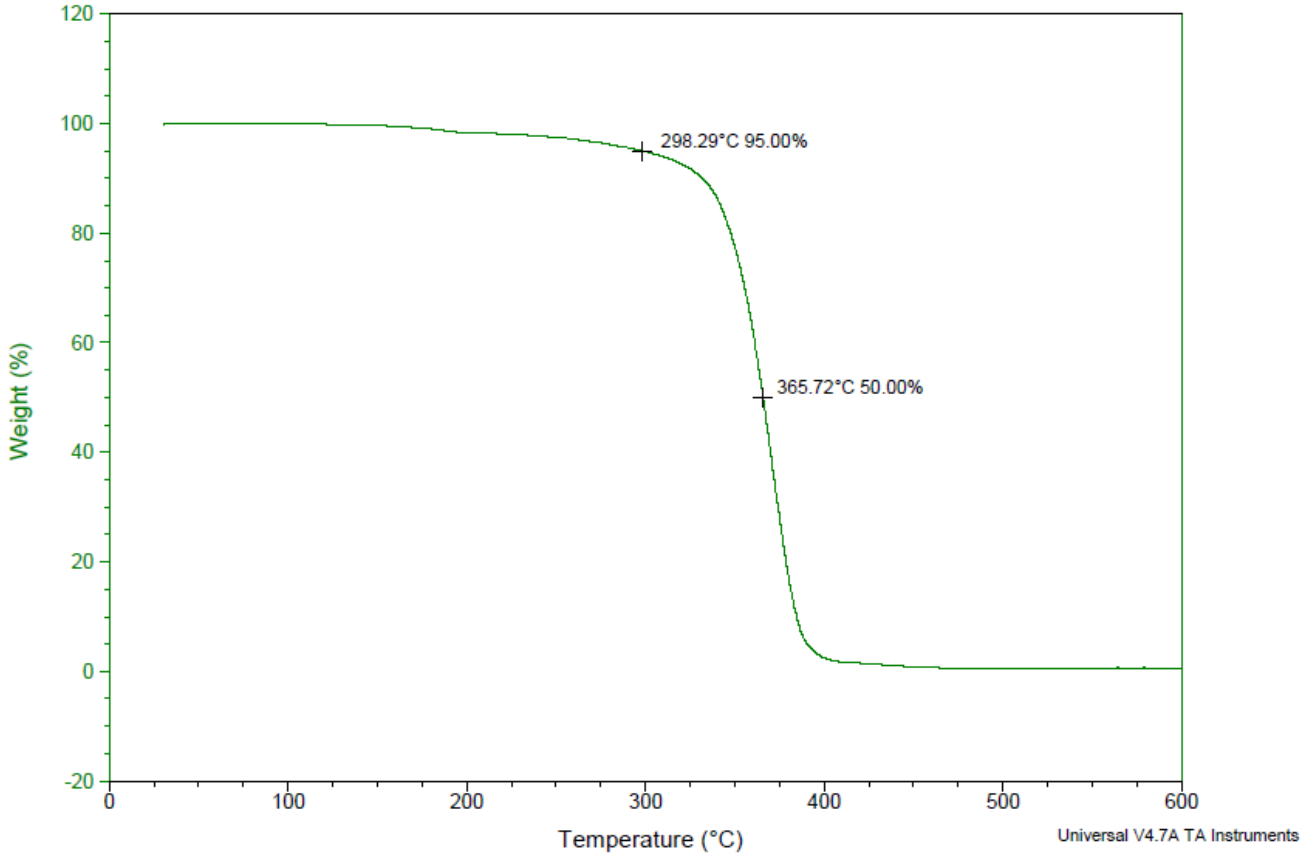


Figure S60. TGA Thermogram of polyoctylene oxalate (Table S1, entry 7).

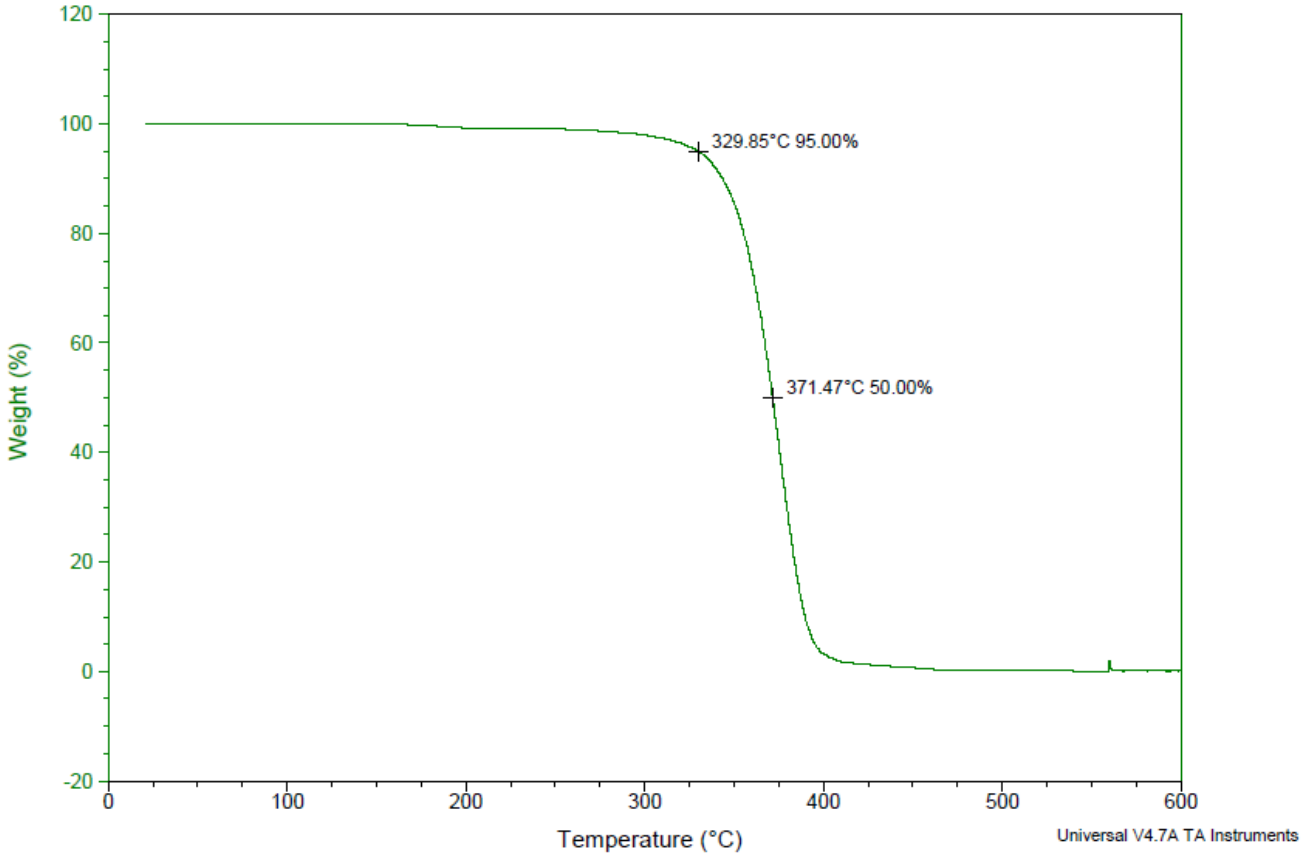


Figure S61. TGA Thermogram of polynonylene oxalate (Table S1, entry 8).

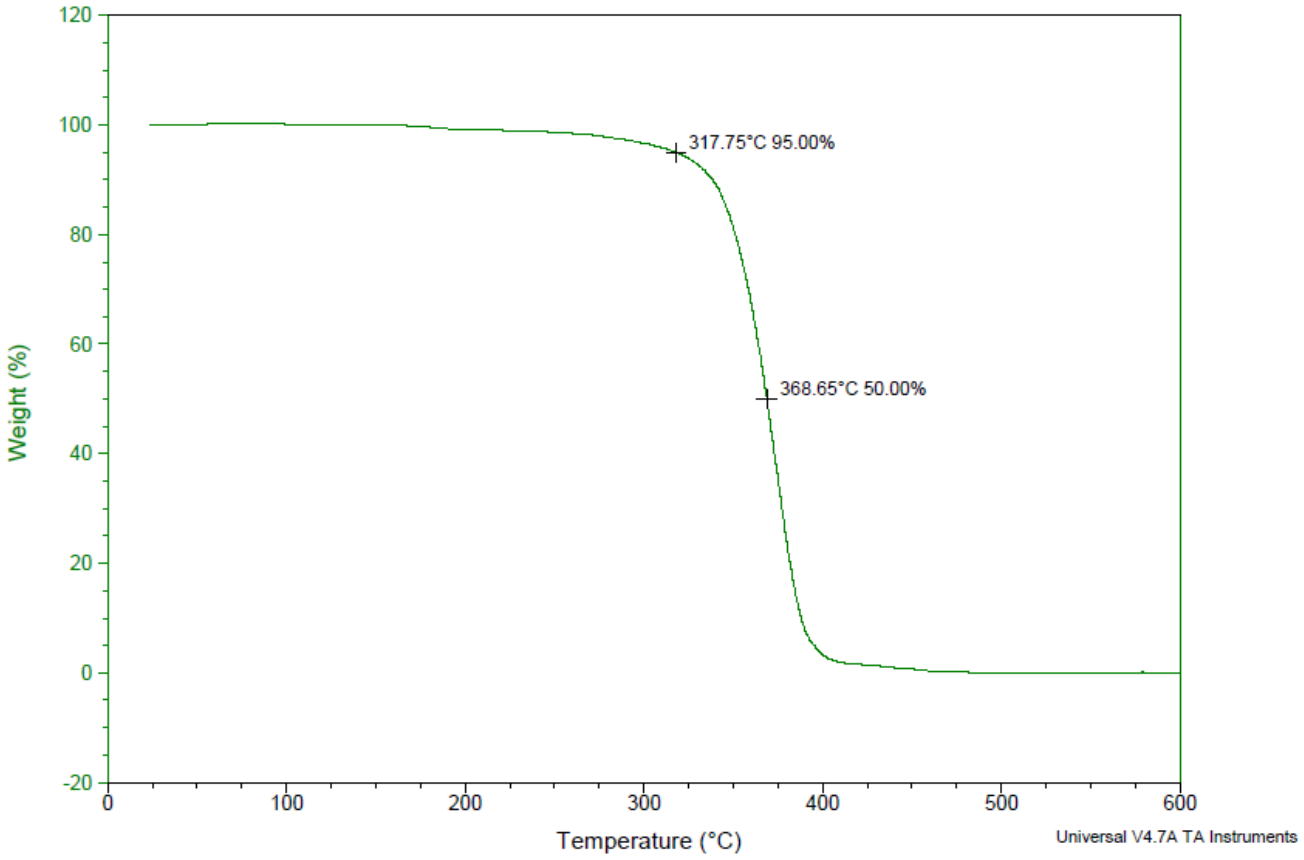


Figure S62. TGA Thermogram of polydecylene oxalate (Table S1, entry 9).

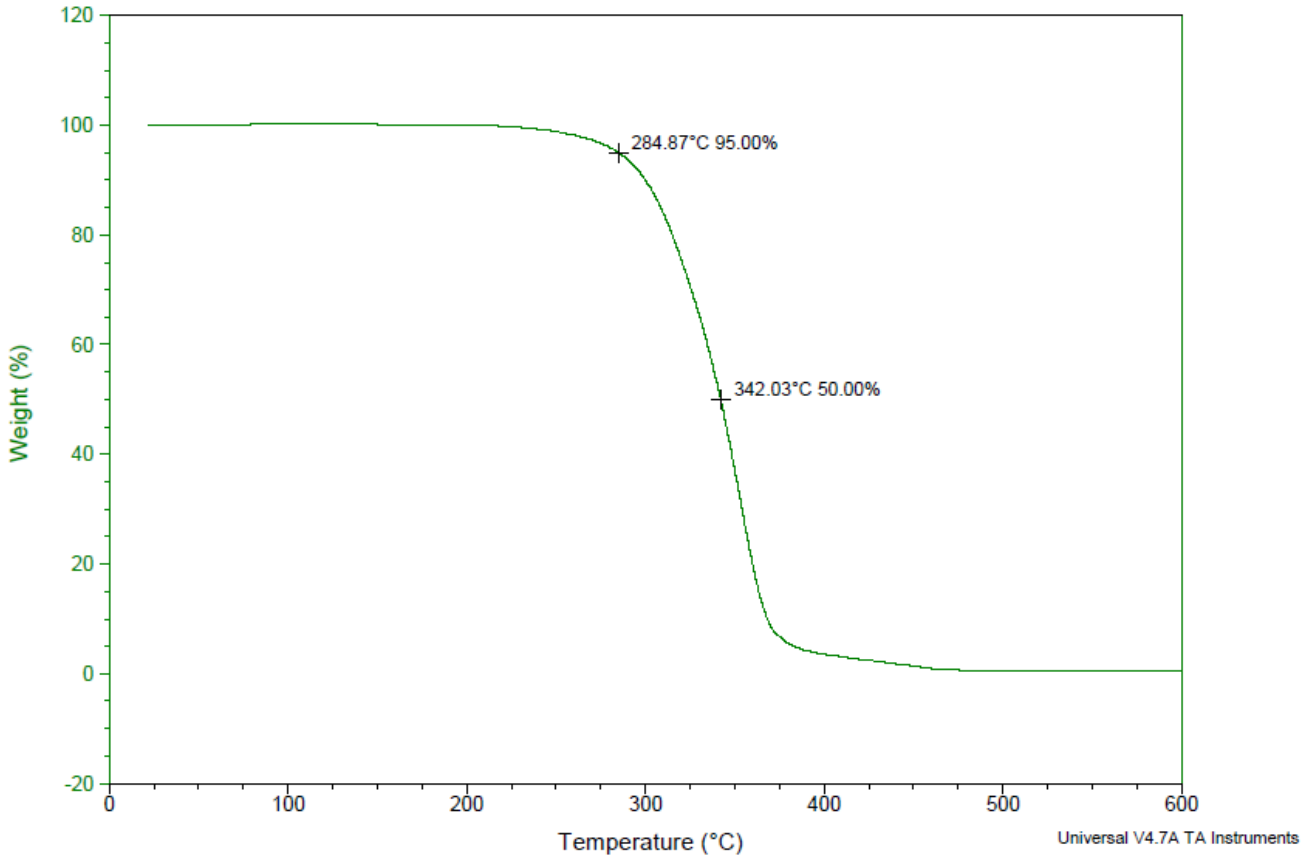


Figure S63. TGA Thermogram of polyundecylene oxalate (Table S1, entry 10).

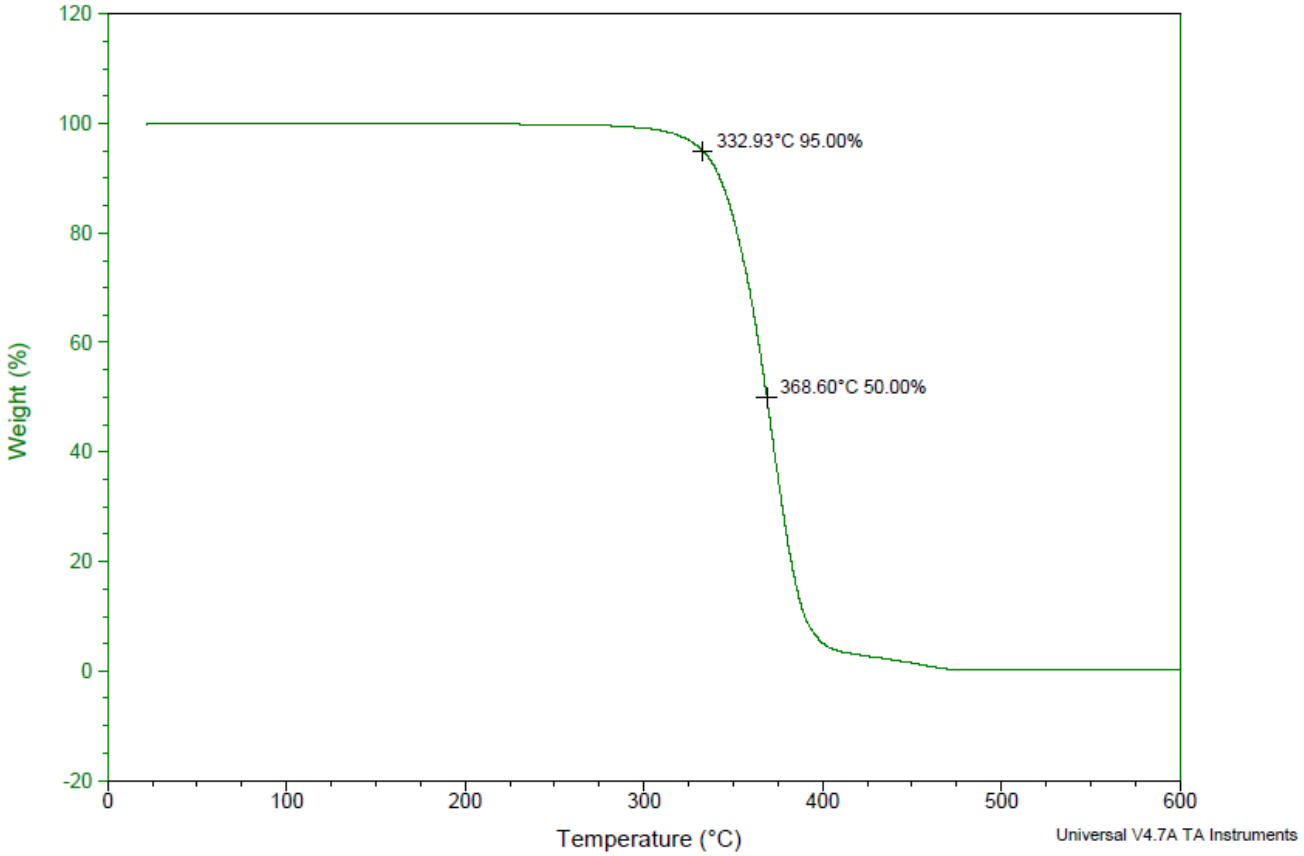


Figure S64. TGA Thermogram of polydodecylene oxalate (Table S1, entry 11).

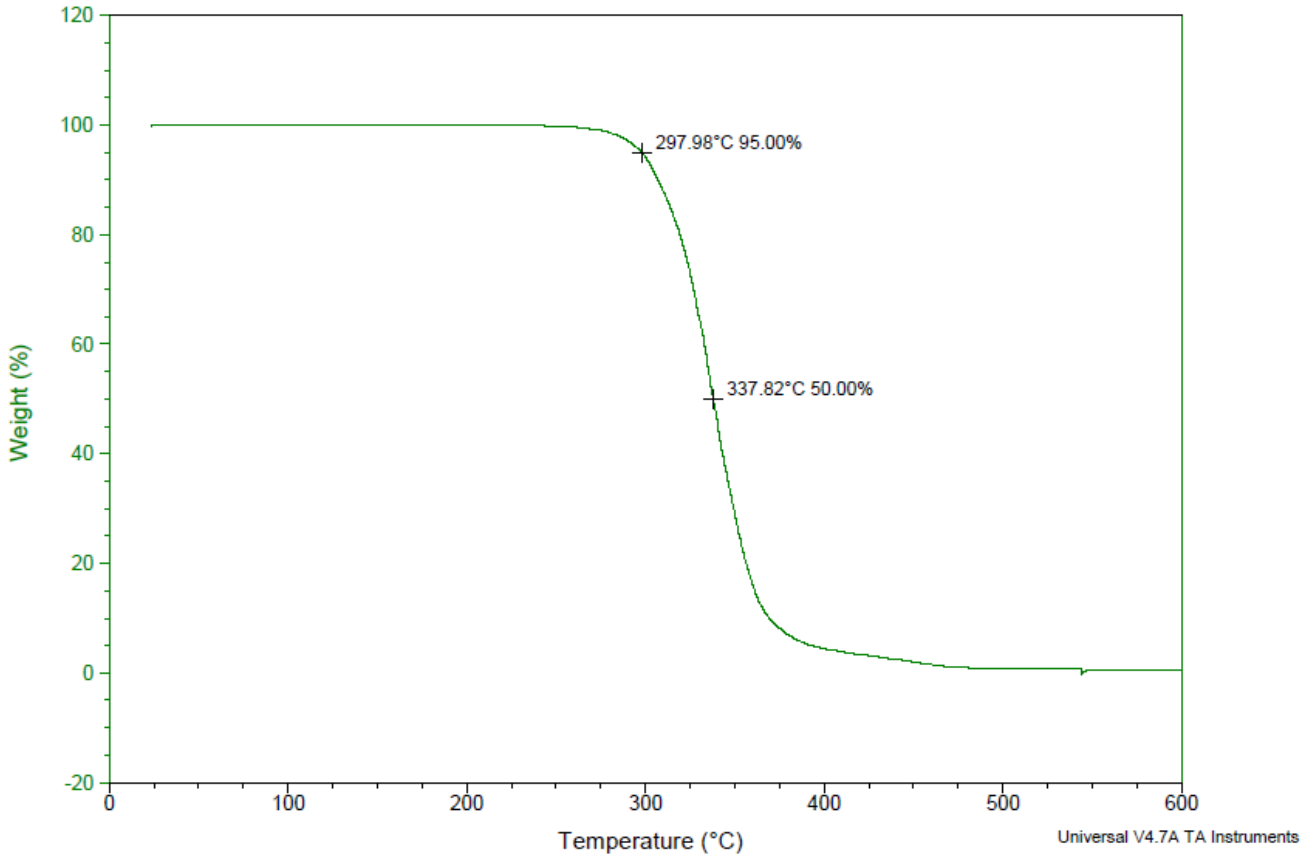


Figure S65. TGA Thermogram of poly(decylene-*co*-RBHE) oxalate [90:10] (Table S2, entry 1).

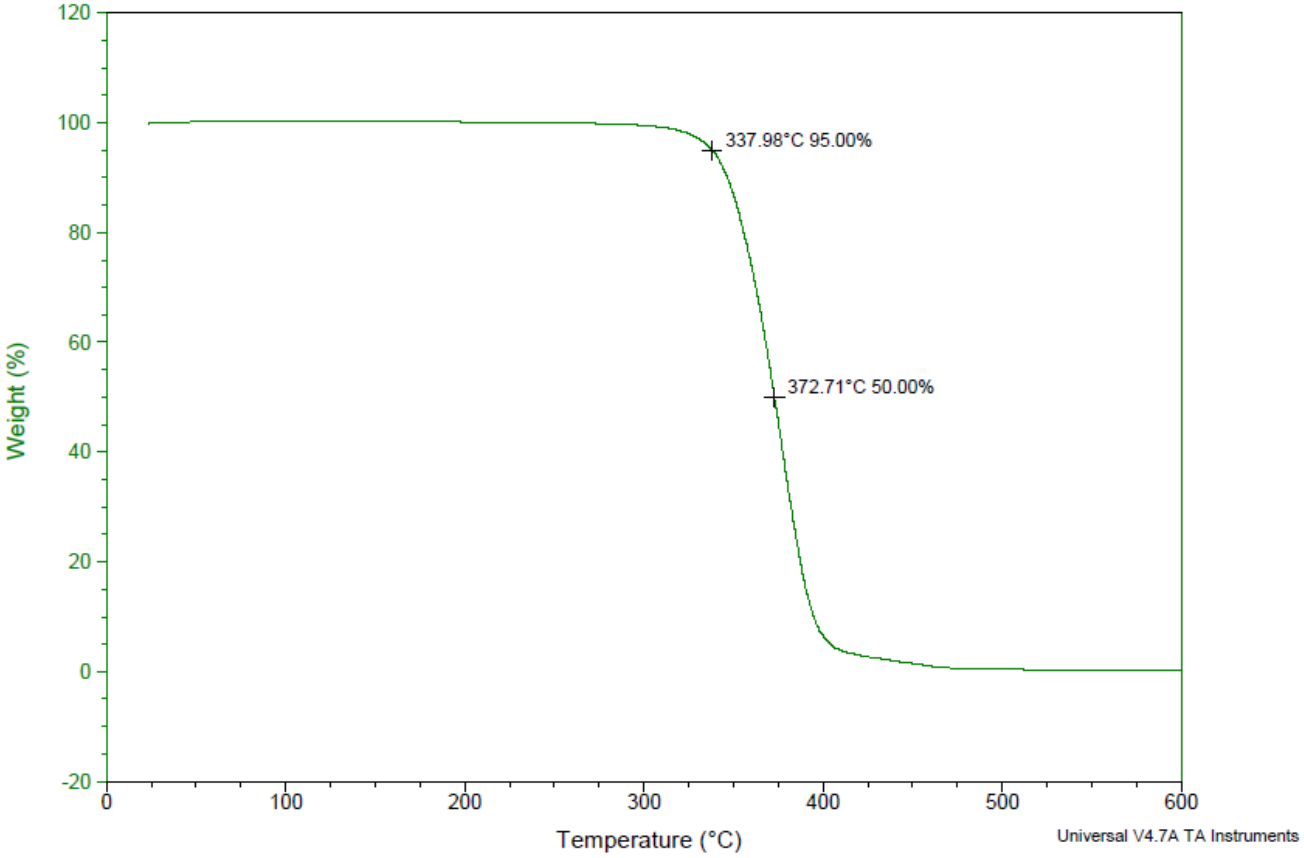


Figure S66. TGA Thermogram of poly(decylene-*co*-RBHE) oxalate [80:20] (Table S2, entry 2).

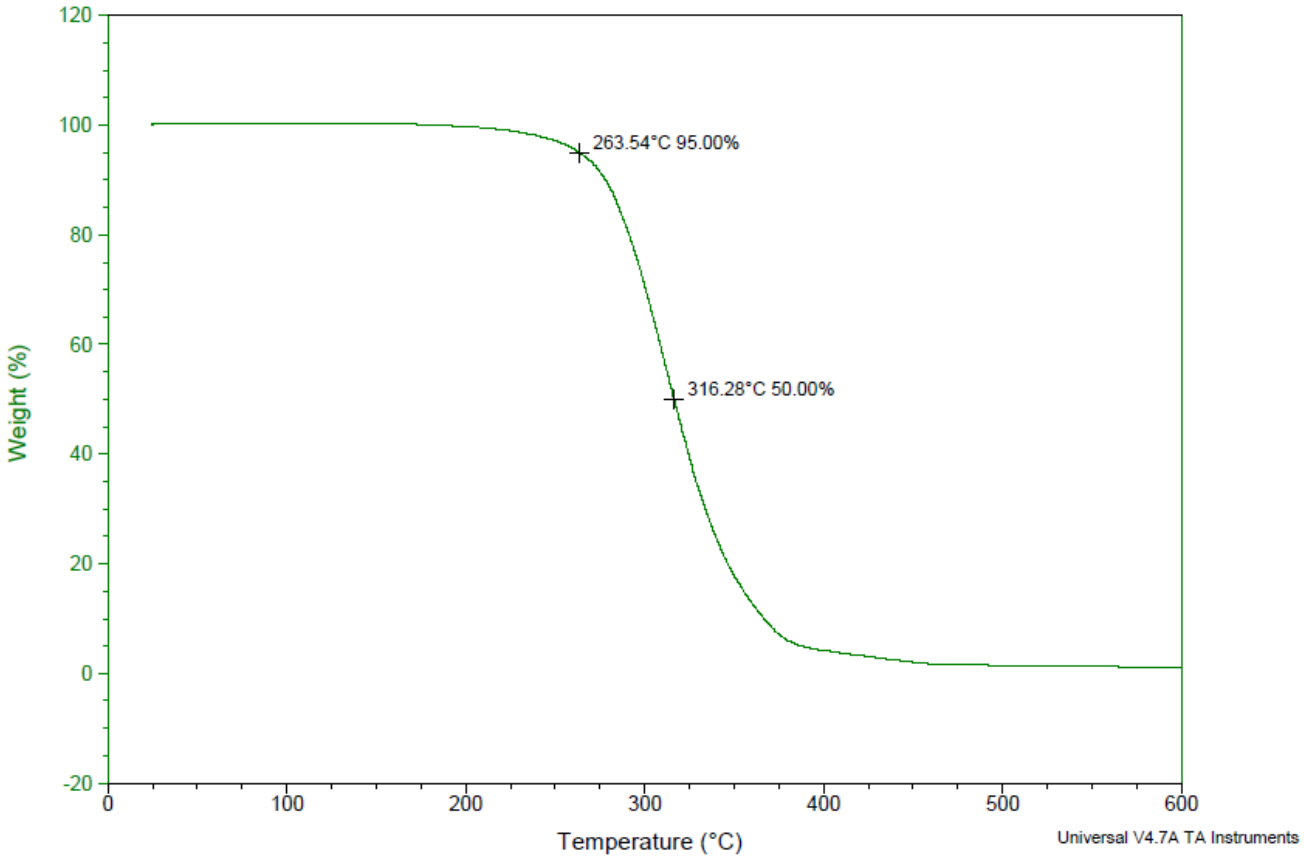


Figure S67. TGA Thermogram of poly(decylene-*co*-RBHE) oxalate [70:30] (Table S2, entry 3).

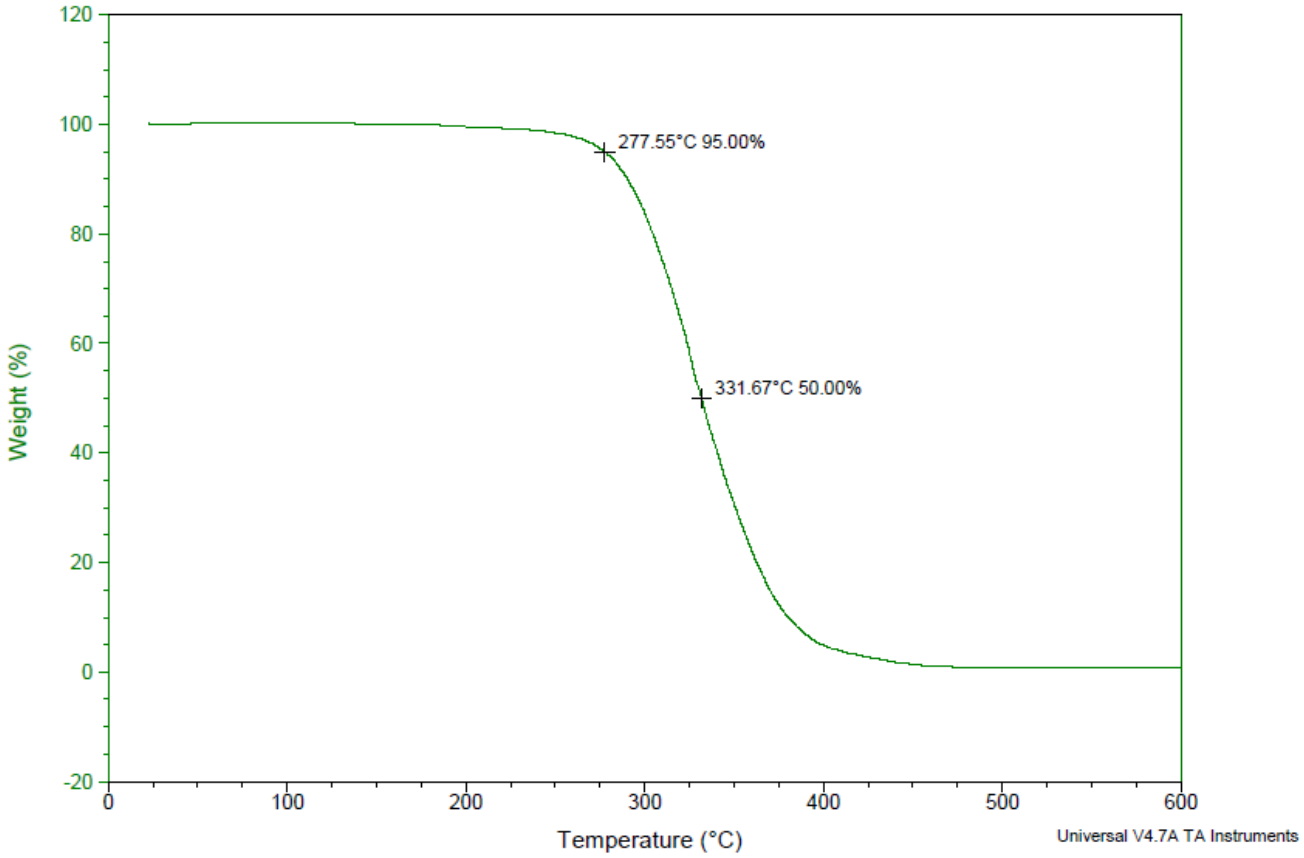


Figure S68. TGA Thermogram of poly(decylene-*co*-RBHE) oxalate [60:40] (Table S2, entry 4).

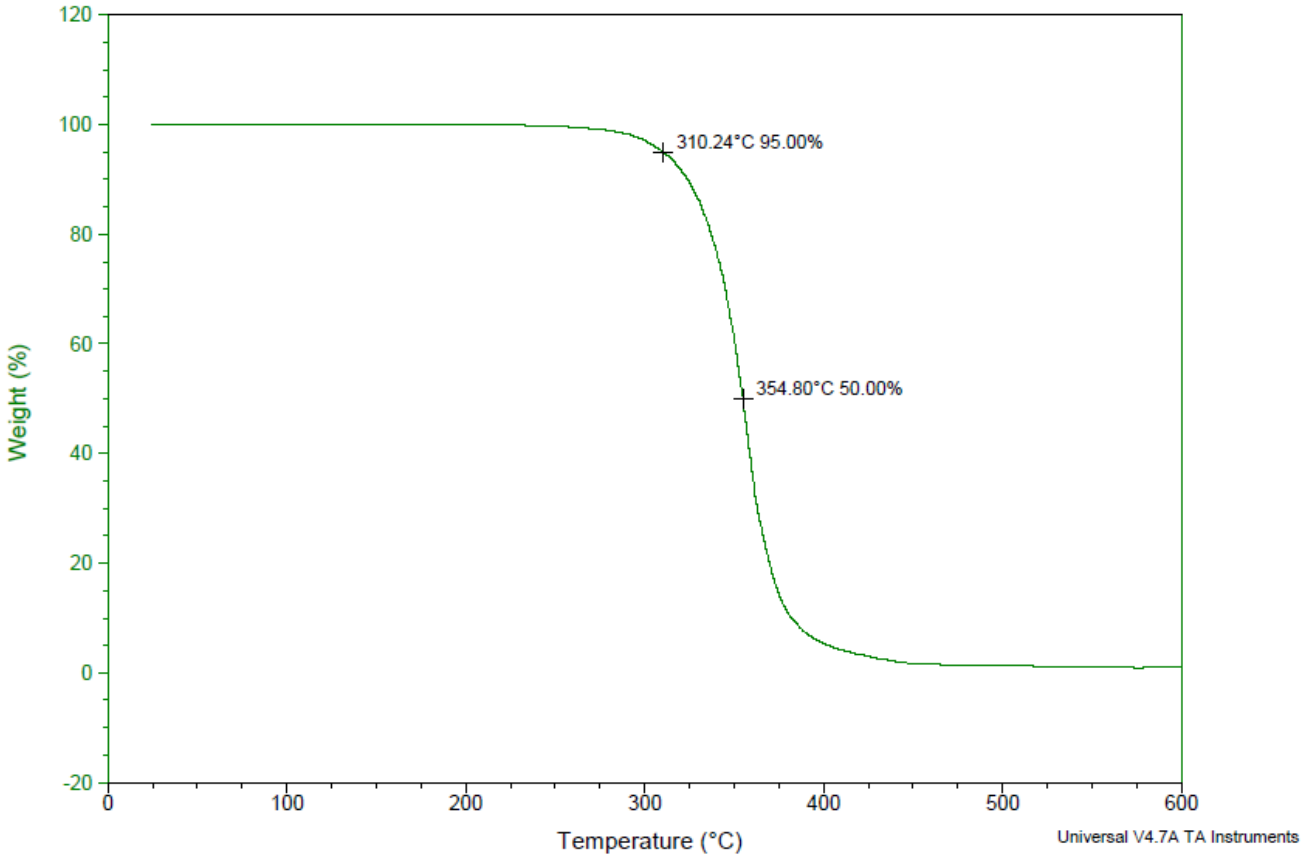


Figure S69. TGA Thermogram of poly(decylene-*co*-RBHE) oxalate [50:50] (Table S2, entry 5).

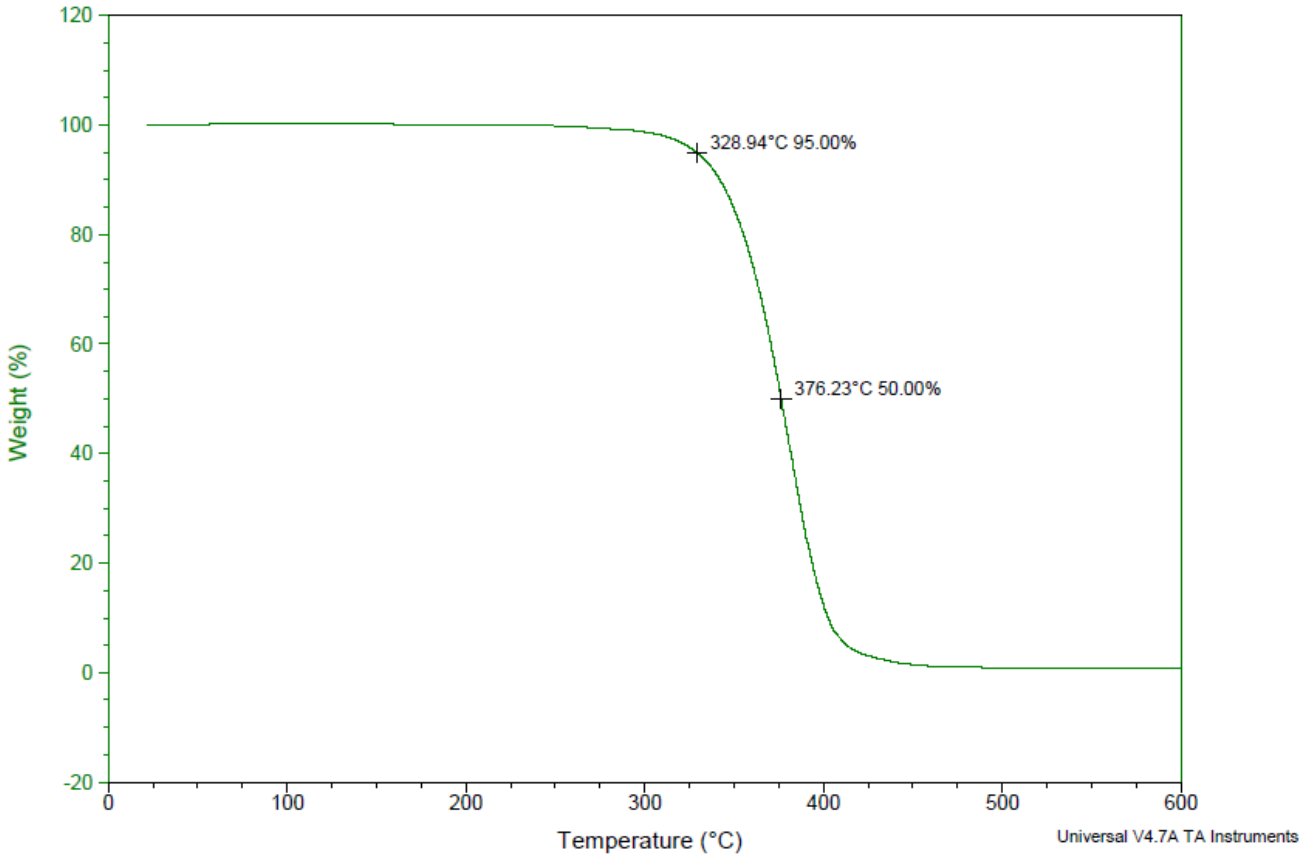


Figure S70. TGA Thermogram of poly(decylene-*co*-RBHE) oxalate [40:60] (Table S2, entry 6).

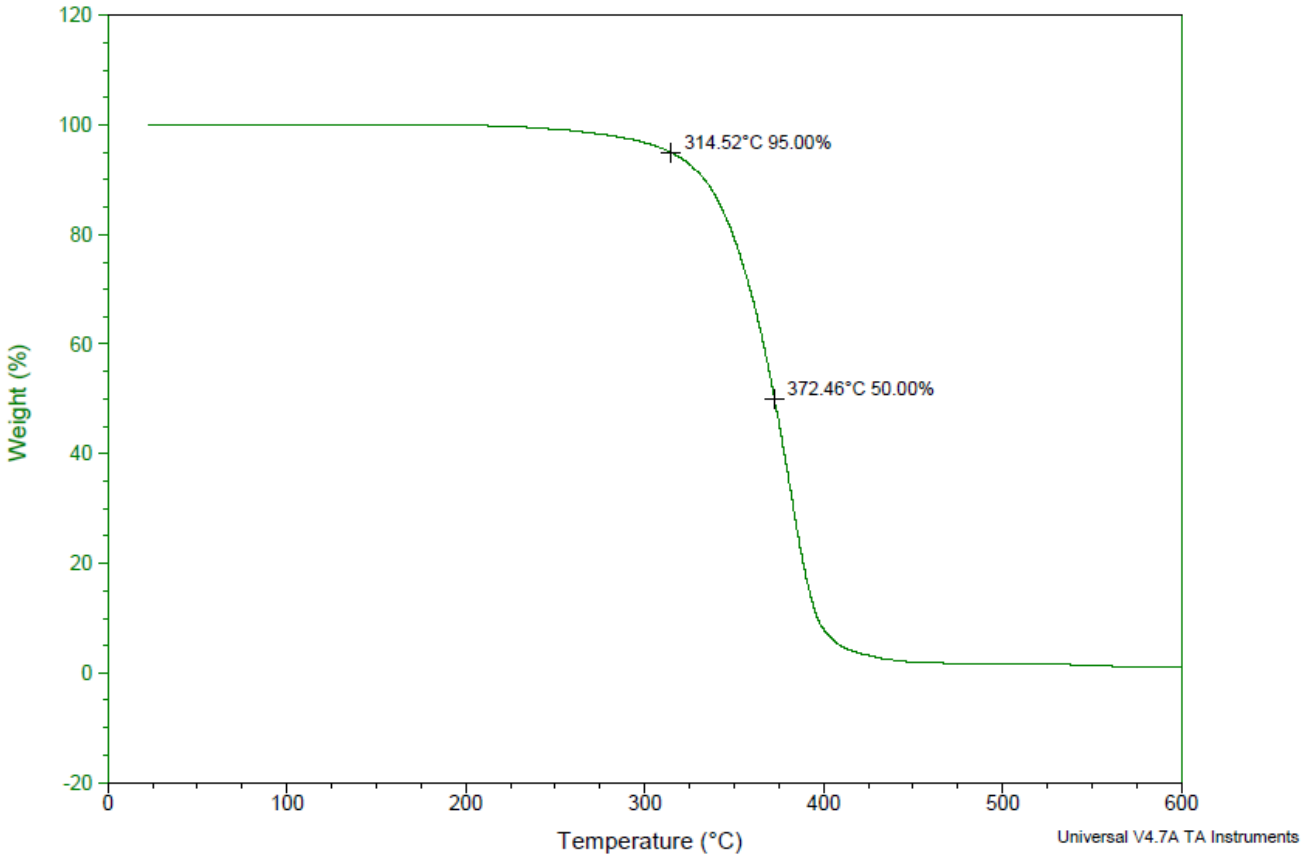


Figure S71. TGA Thermogram of poly(decylene-*co*-RBHE) oxalate [30:70] (Table S2, entry 7).

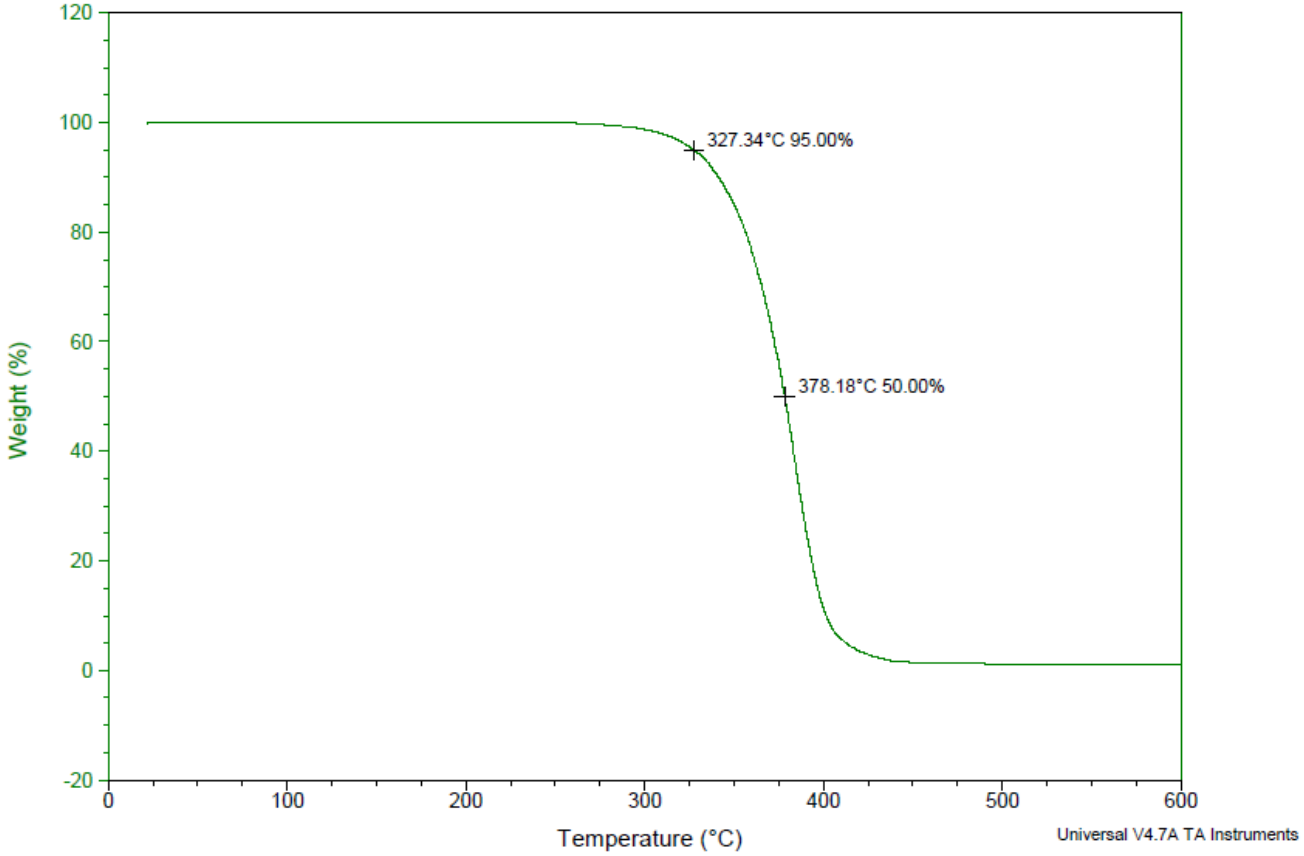


Figure S72. TGA Thermogram of poly(decylene-*co*-RBHE) oxalate [20:80] (Table S2, entry 8).

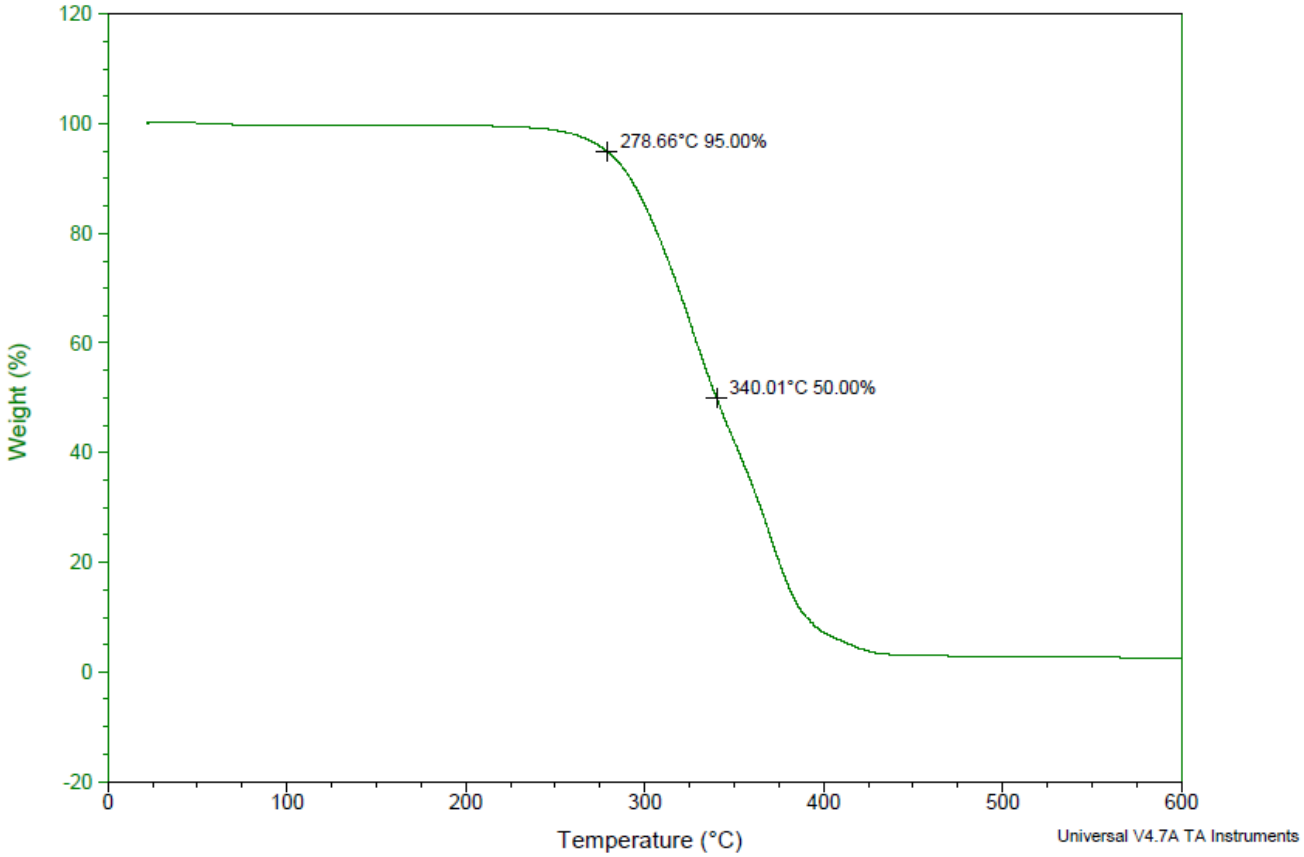


Figure S73. TGA Thermogram of poly(decylene-*co*-RBHE) oxalate [10:90] (Table S2, entry 9).

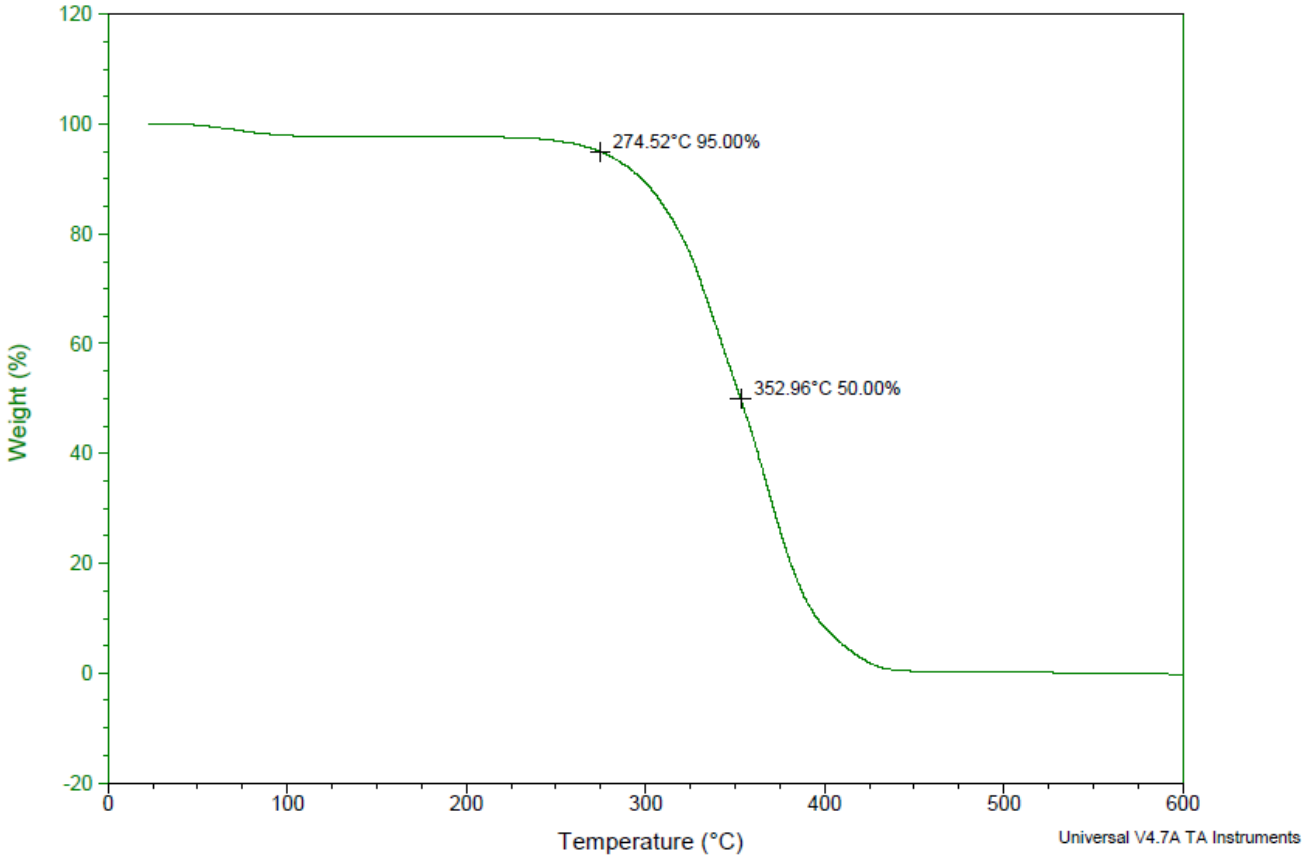


Figure S74. TGA Thermogram of poly(RBHE) oxalate (Table S2, entry 10).

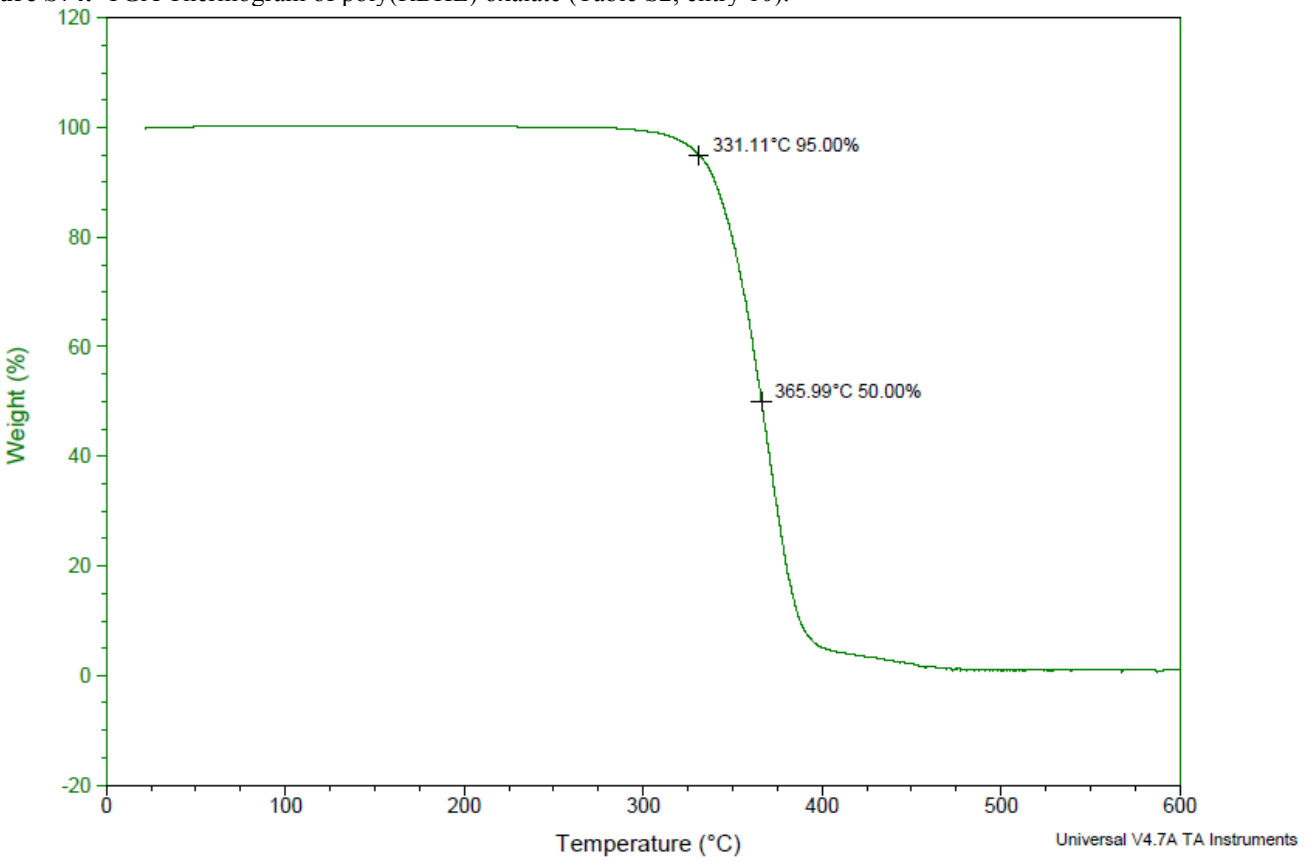


Figure S75. TGA Thermogram of poly(decylene-*co*-HBHE) oxalate [90:10] (Table S2, entry 11).

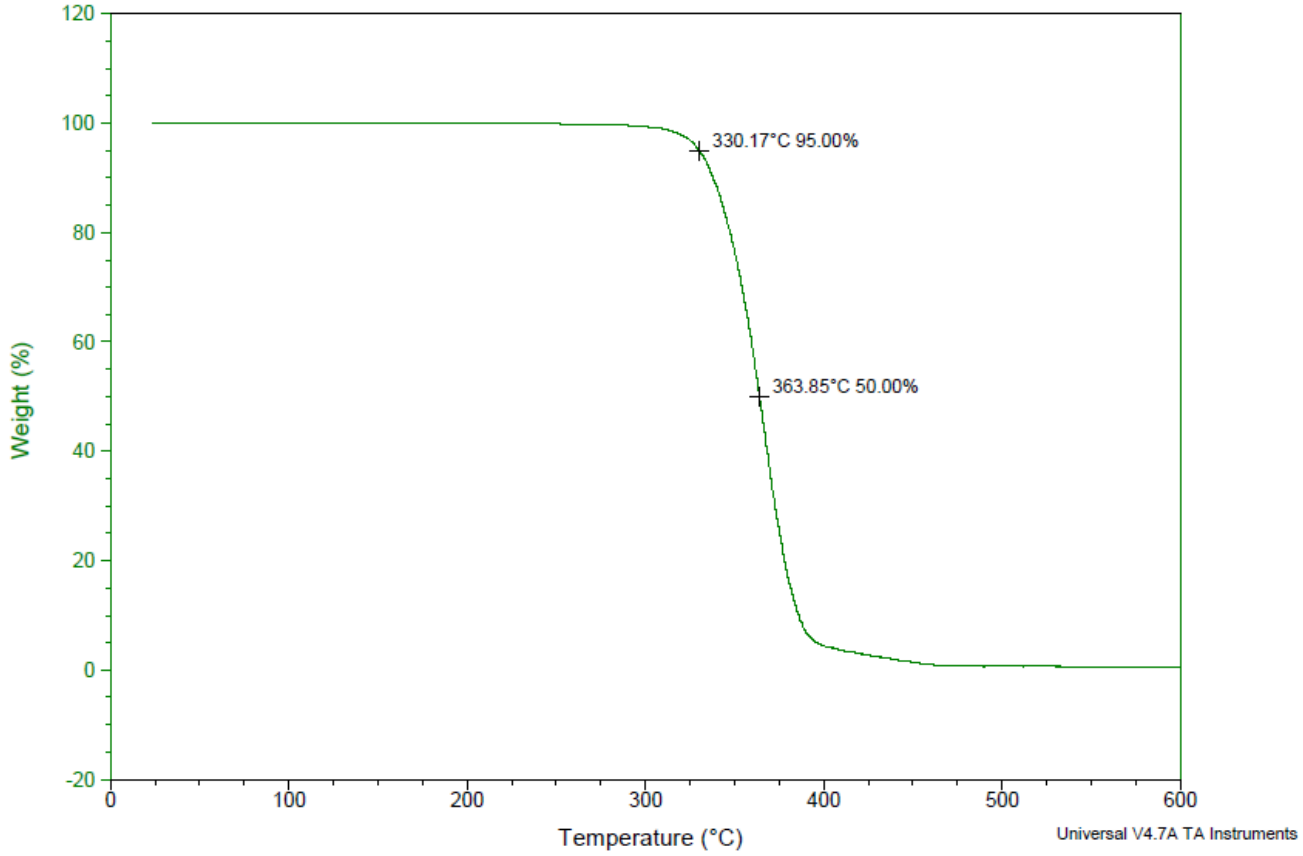


Figure S76. TGA Thermogram of poly(decylene-*co*-HBHE) oxalate [80:20] (Table S2, entry 12).

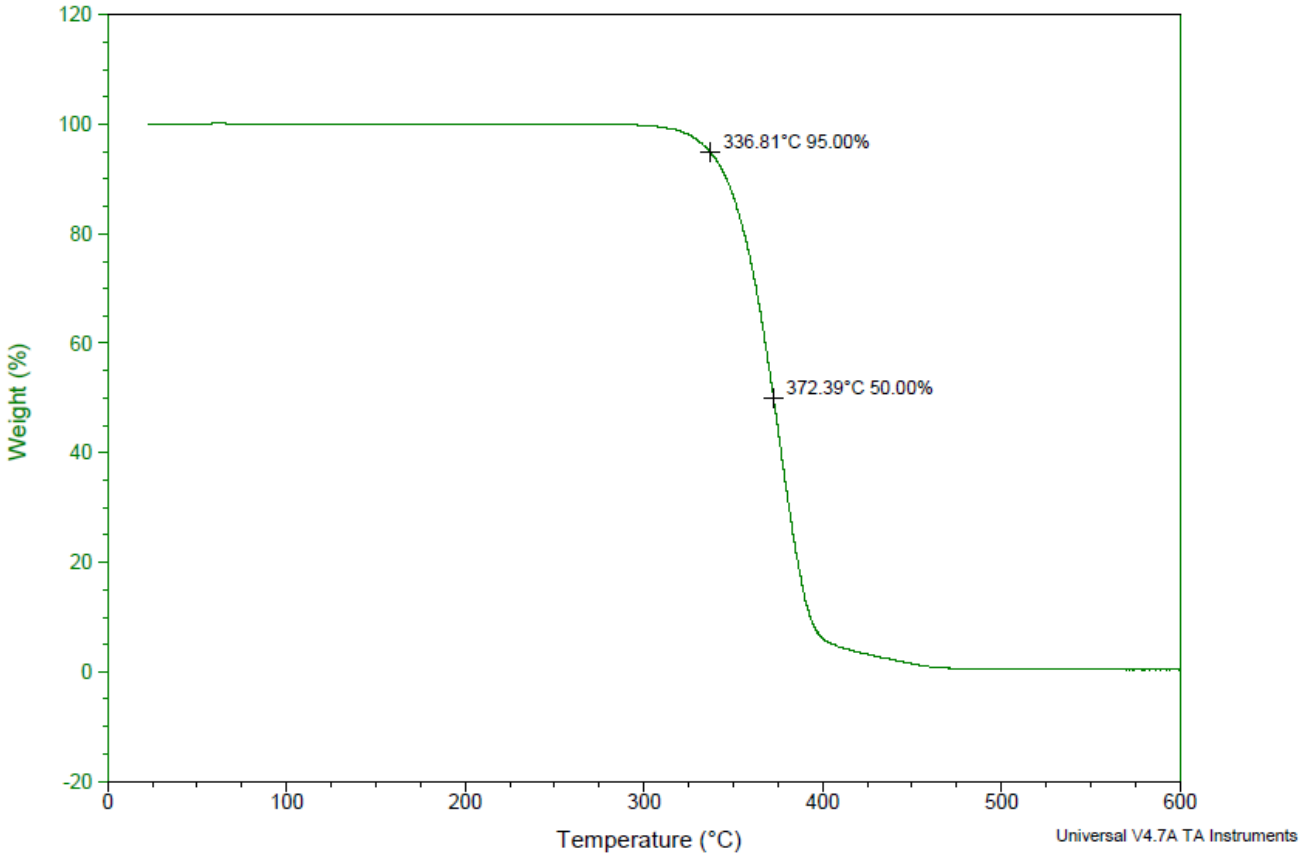


Figure S77. TGA Thermogram of poly(decylene-*co*-HBHE) oxalate [70:30] (Table S2, entry 13).

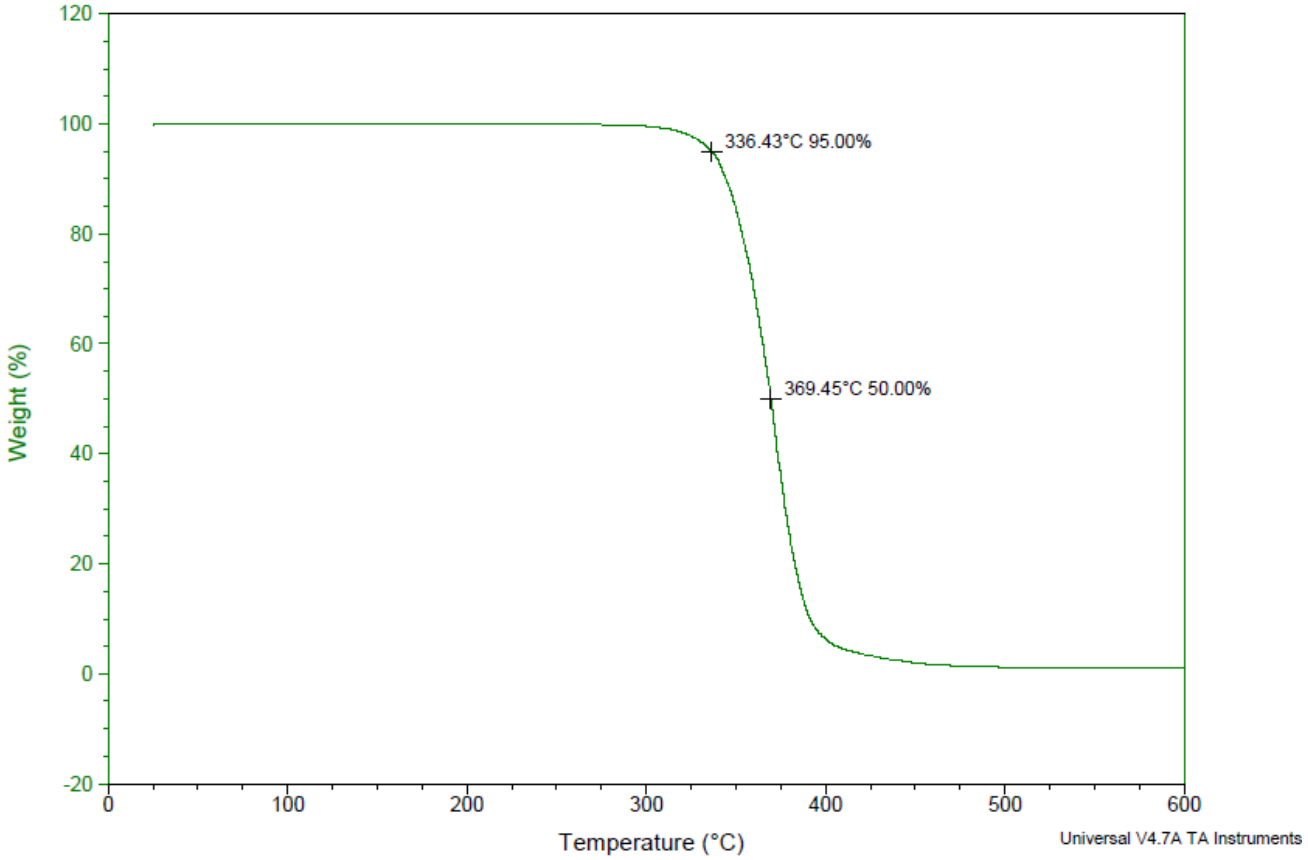


Figure S78. TGA Thermogram of poly(decylene-*co*-HBHE) oxalate [60:40] (Table S2, entry 14).

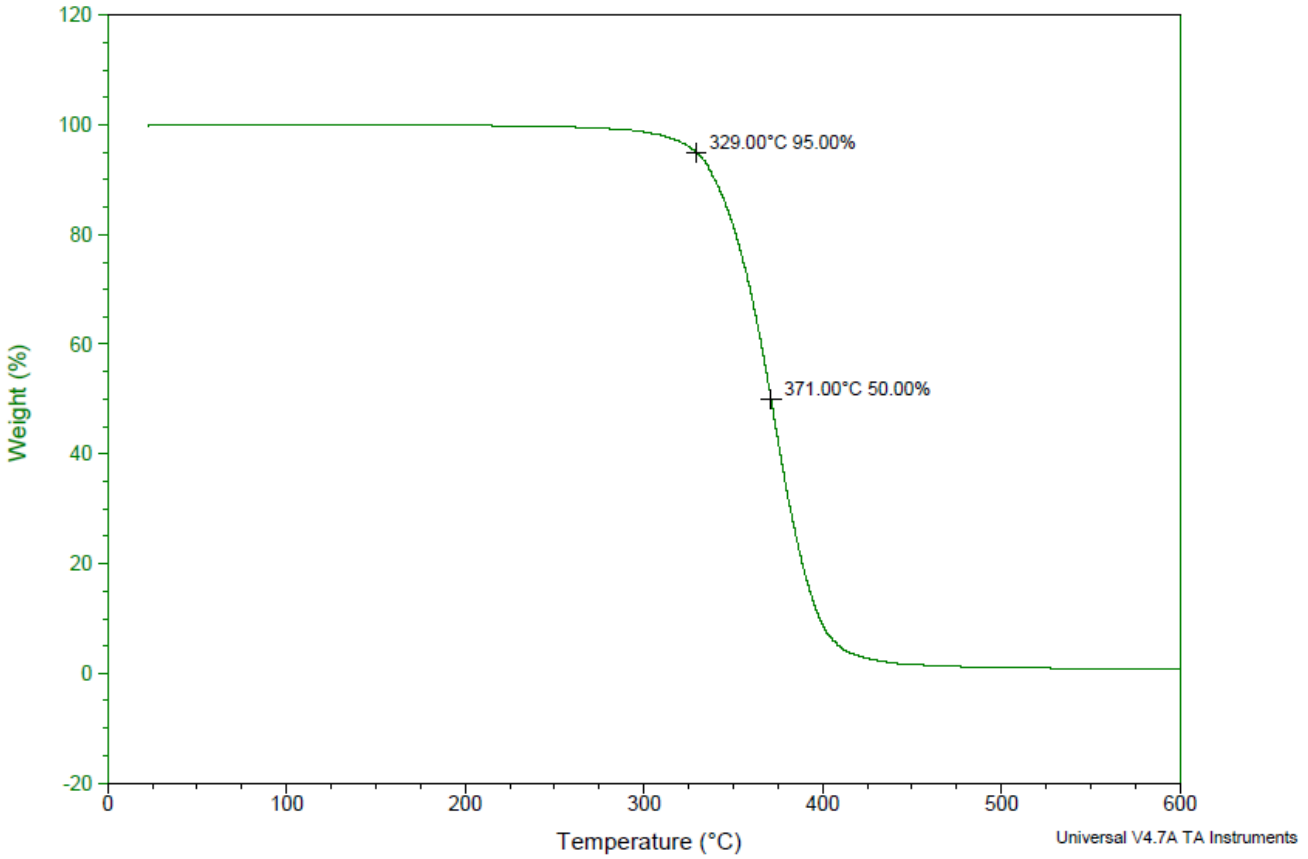


Figure S79. TGA Thermogram of poly(decylene-*co*-HBHE) oxalate [50:50] (Table S2, entry 15).

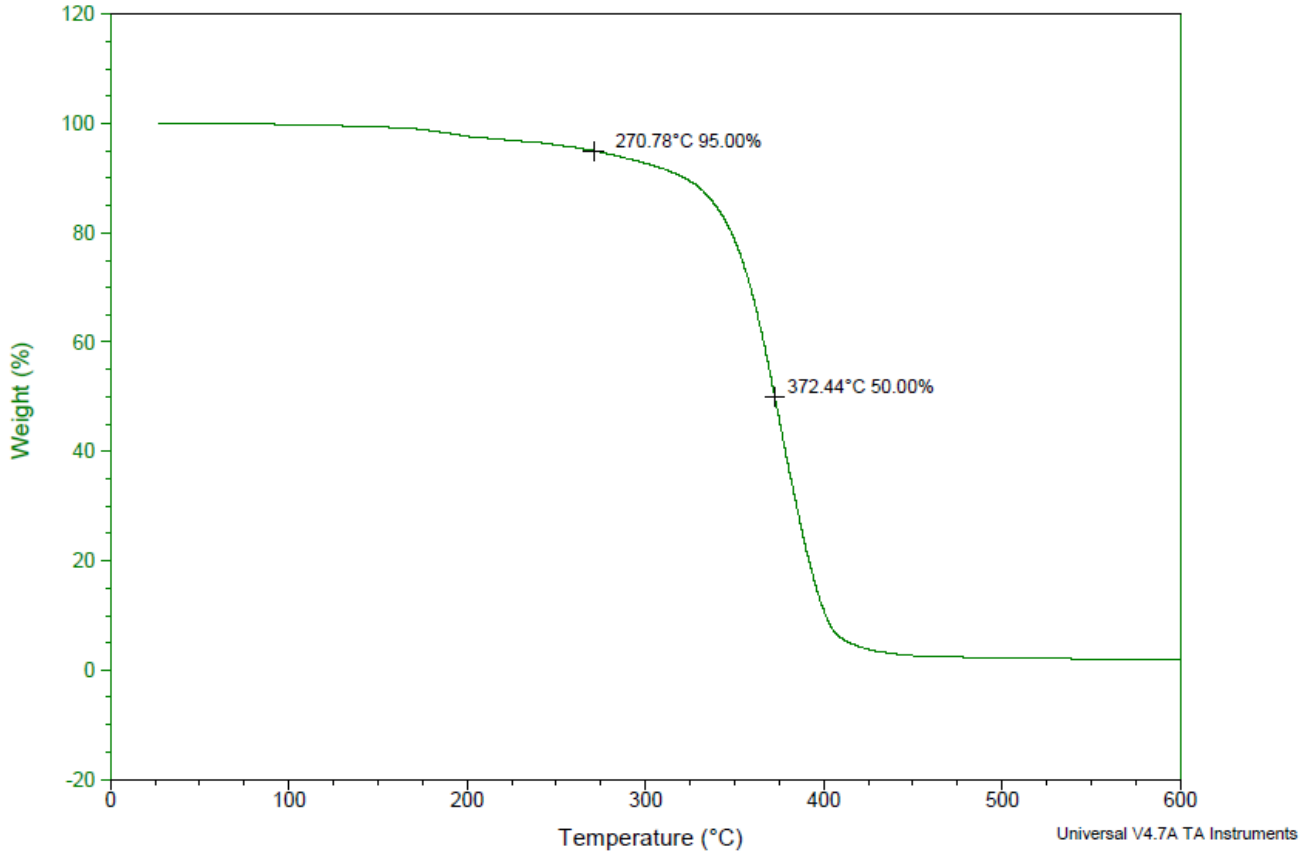


Figure S80. TGA Thermogram of poly(decylene-*co*-HBHE) oxalate [40:60] (Table S2, entry 16).

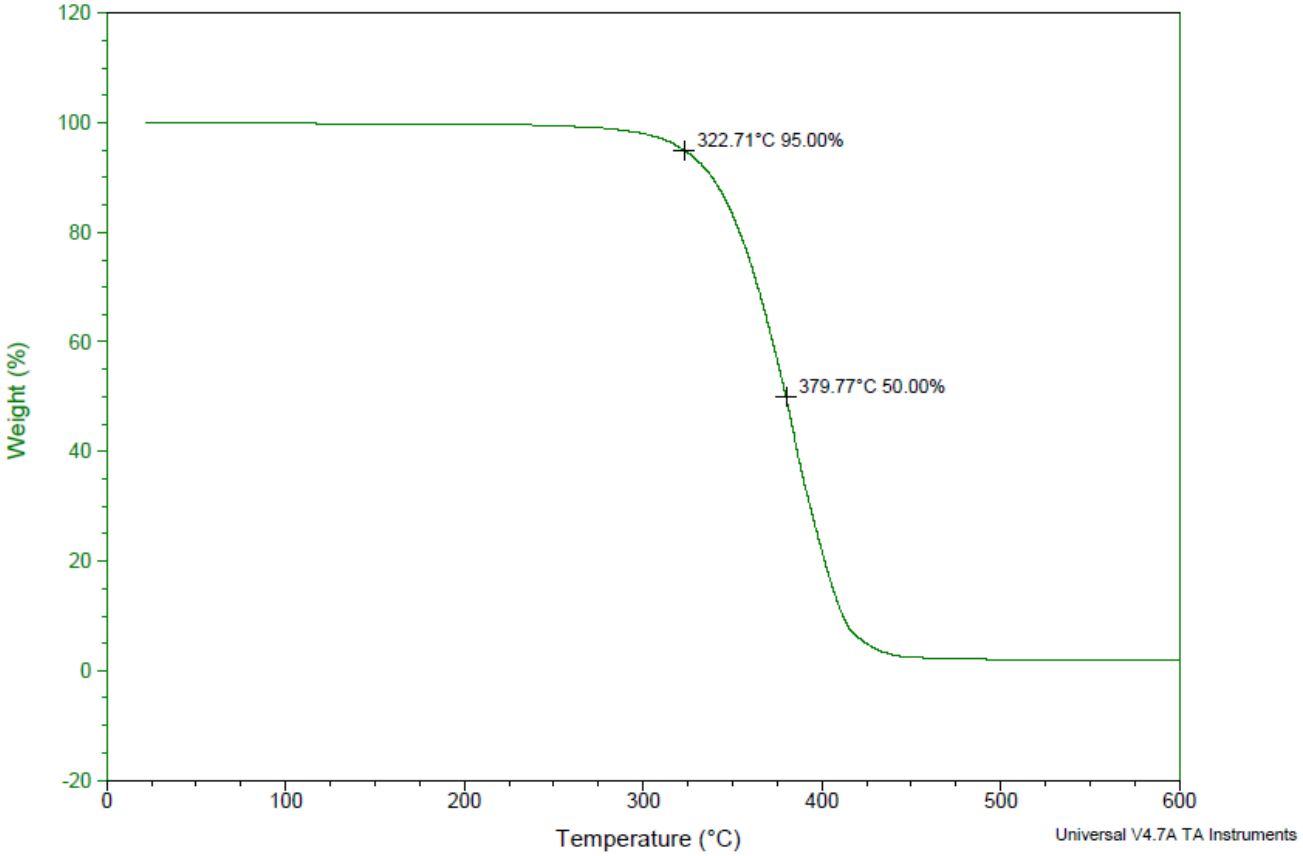


Figure S81. TGA Thermogram of poly(decylene-*co*-HBHE) oxalate [30:70] (Table S2, entry 17).

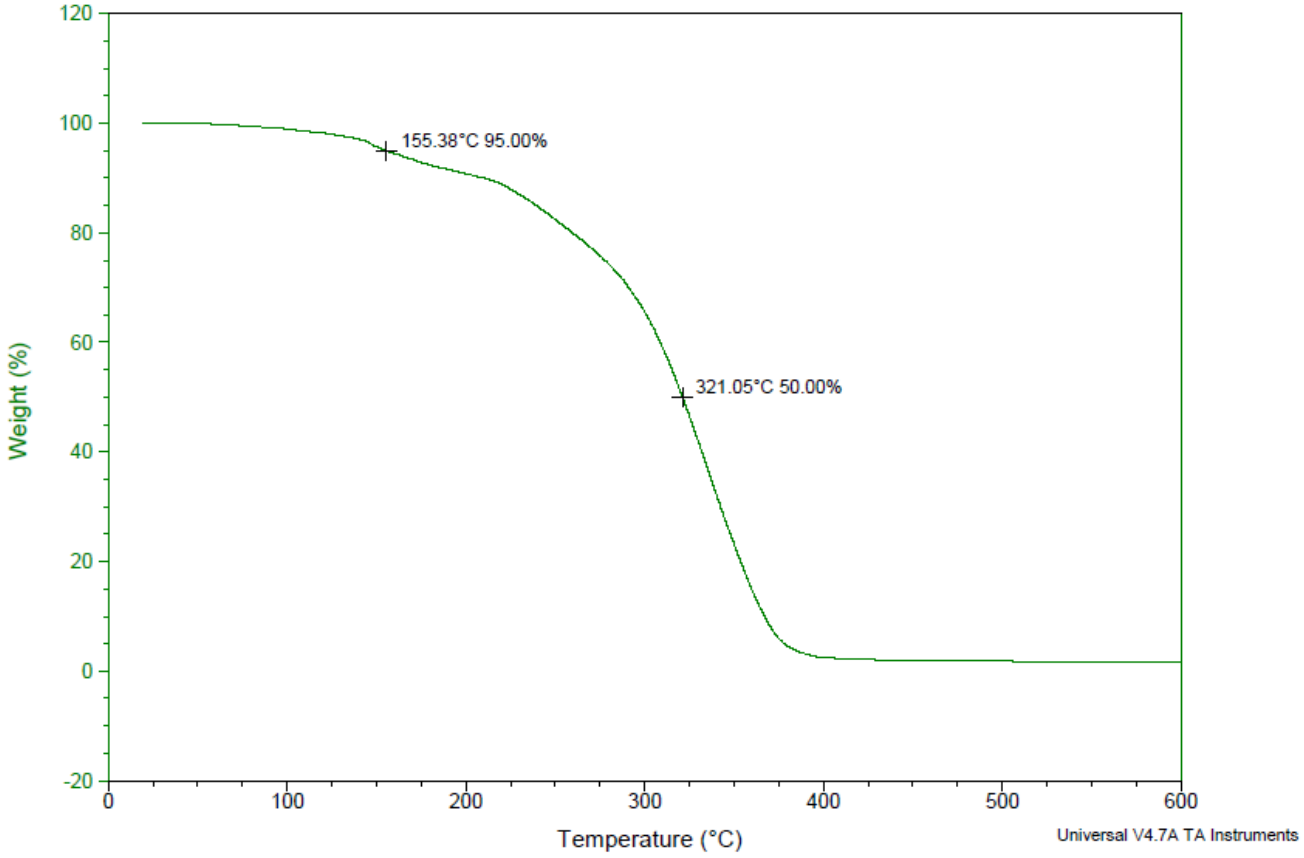


Figure S82. TGA Thermogram of poly(decylene-*co*-HBHE) oxalate [20:80] (Table S2, entry 18).

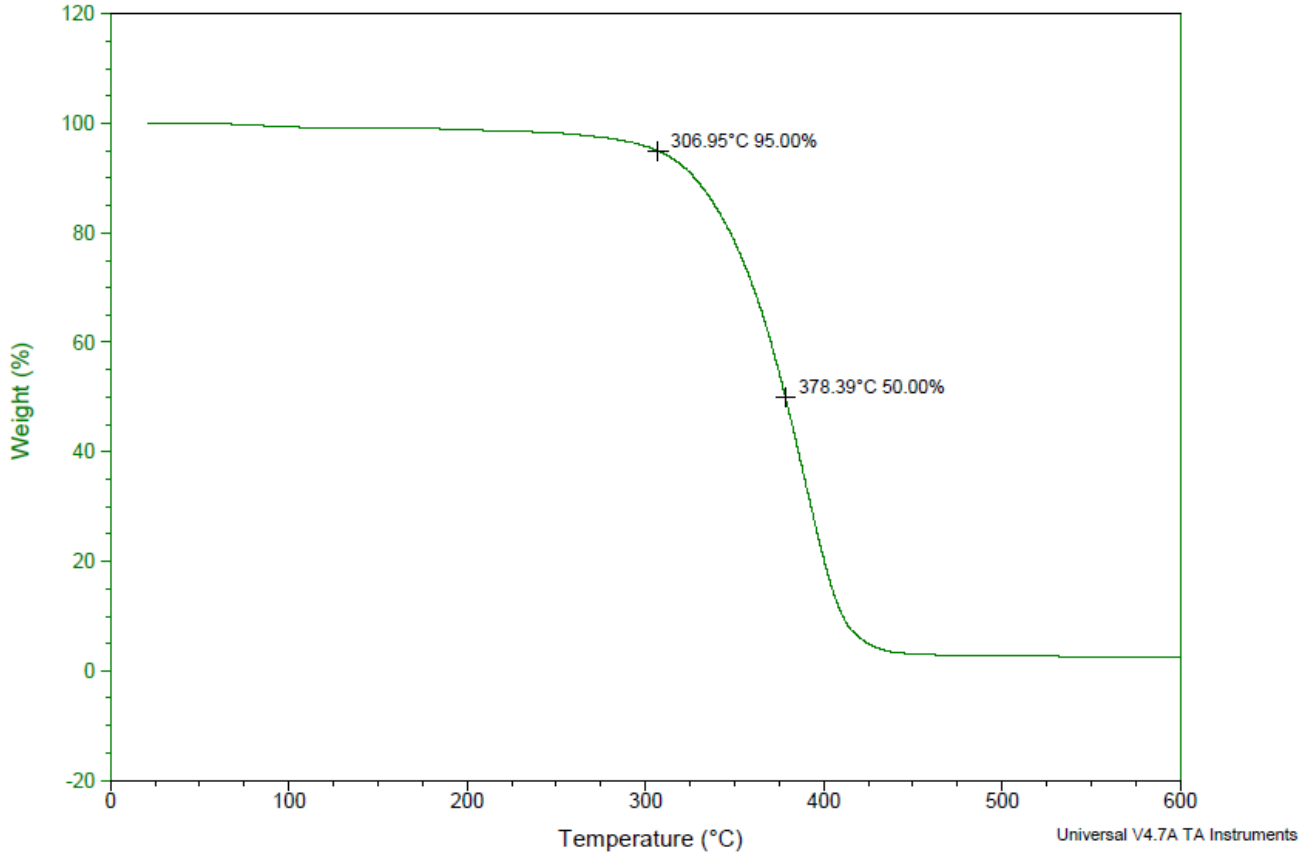


Figure S83. TGA Thermogram of poly(decylene-*co*-HBHE) oxalate [10:90] (Table S2, entry 19).

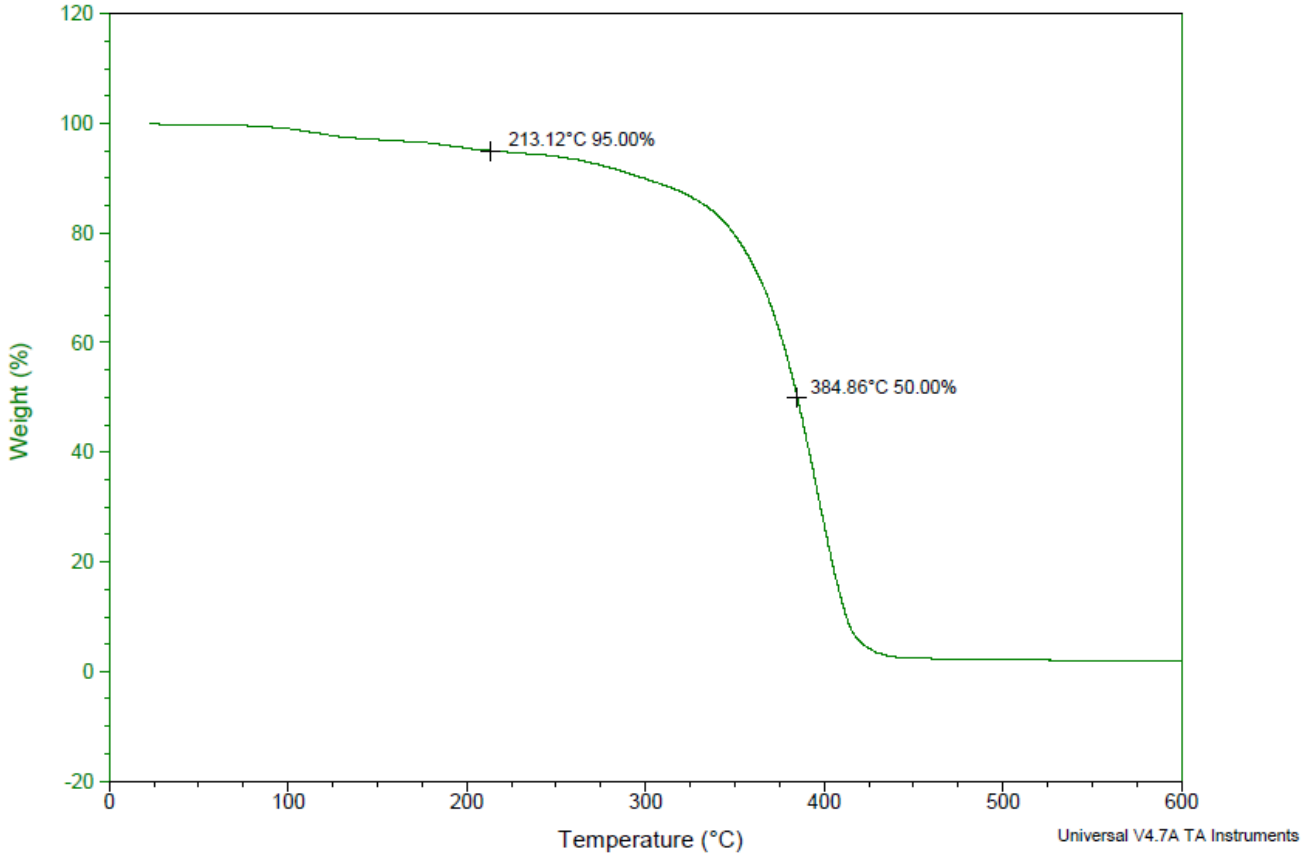


Figure S84. TGA Thermogram of poly(HBHE) oxalate (Table S2, entry 20).

^{1}H NMR Spectra

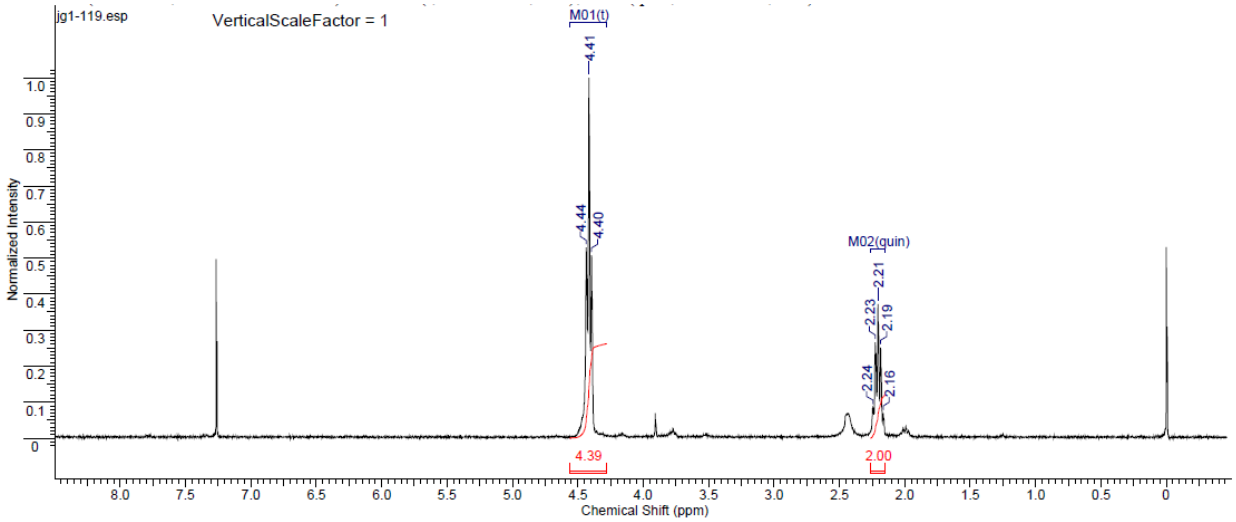


Figure S85. ^{1}H NMR spectrum of polypropylene oxalate (Table S1, entry 1).

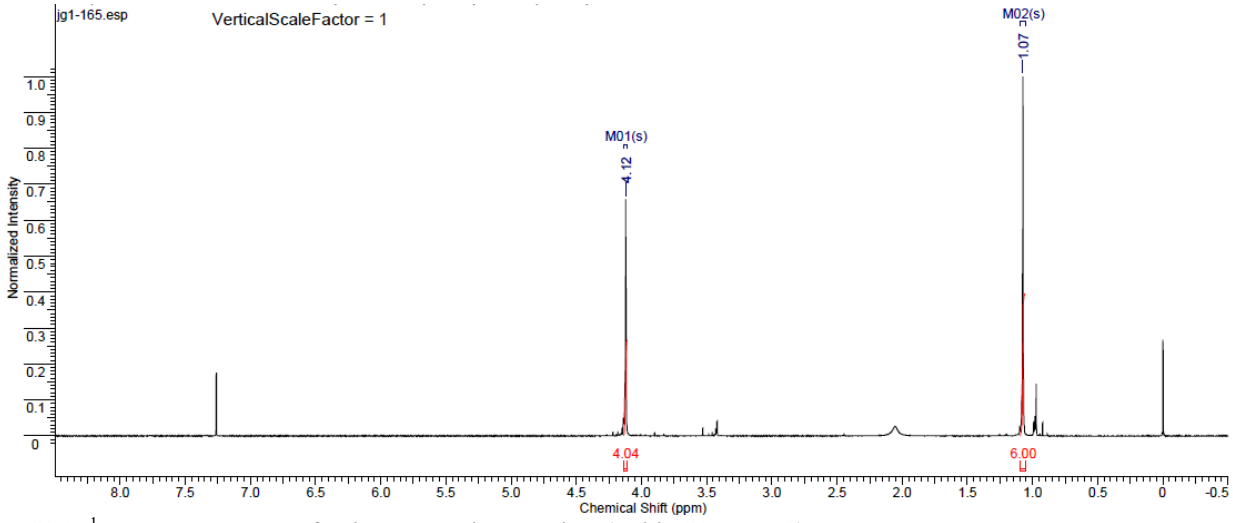


Figure S86. ^{1}H NMR spectrum of polyneopentylene oxalate (Table S1, entry 2).

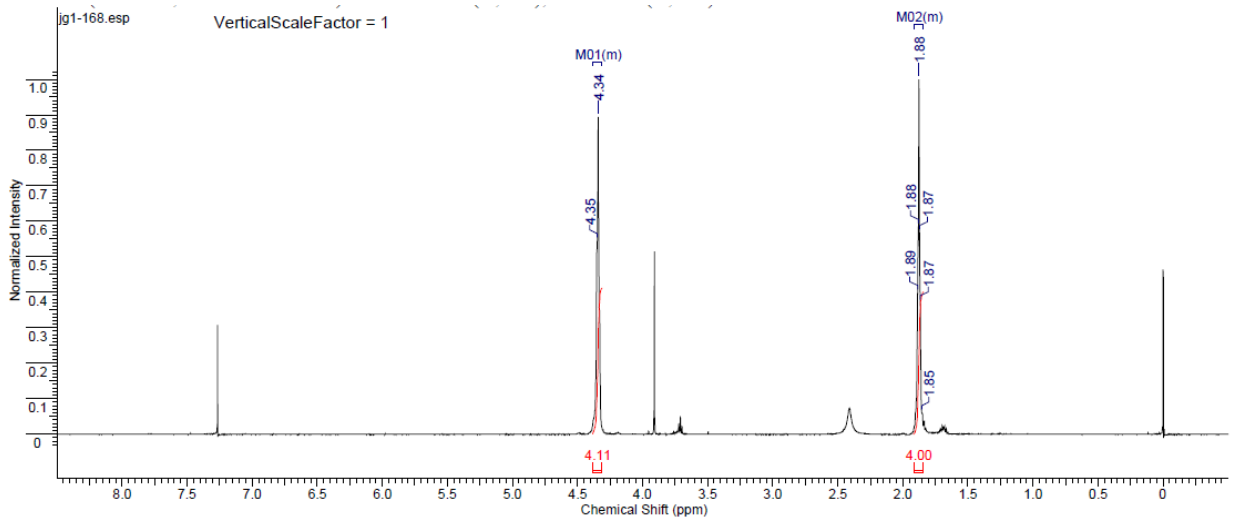


Figure S87. ^{1}H NMR spectrum of polybutylene oxalate (Table S1, entry 3).

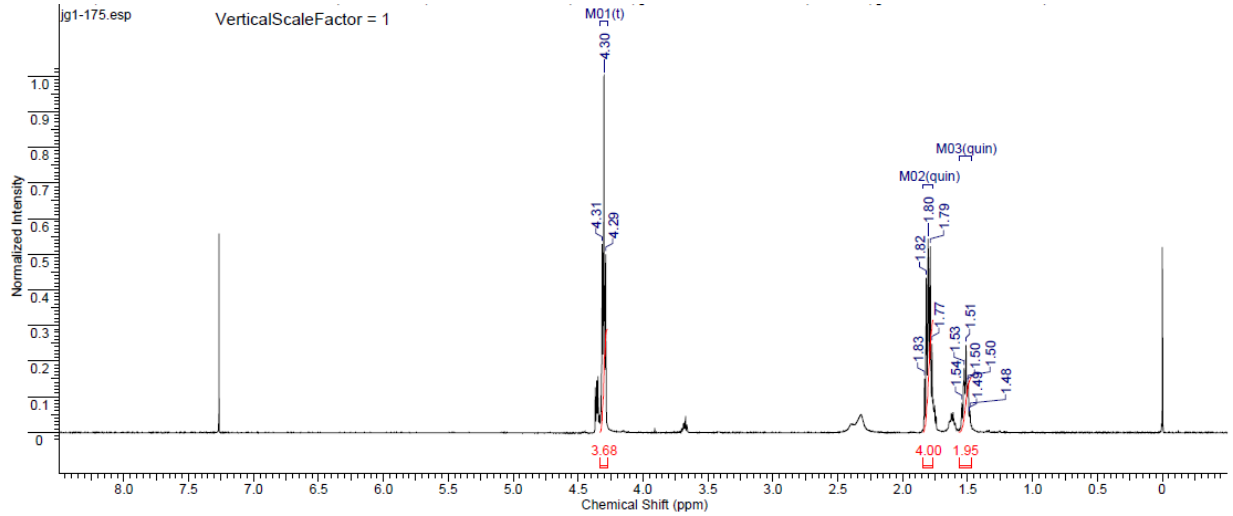


Figure S88. ^{1}H NMR spectrum of polypentylene oxalate (Table S1, entry 4).

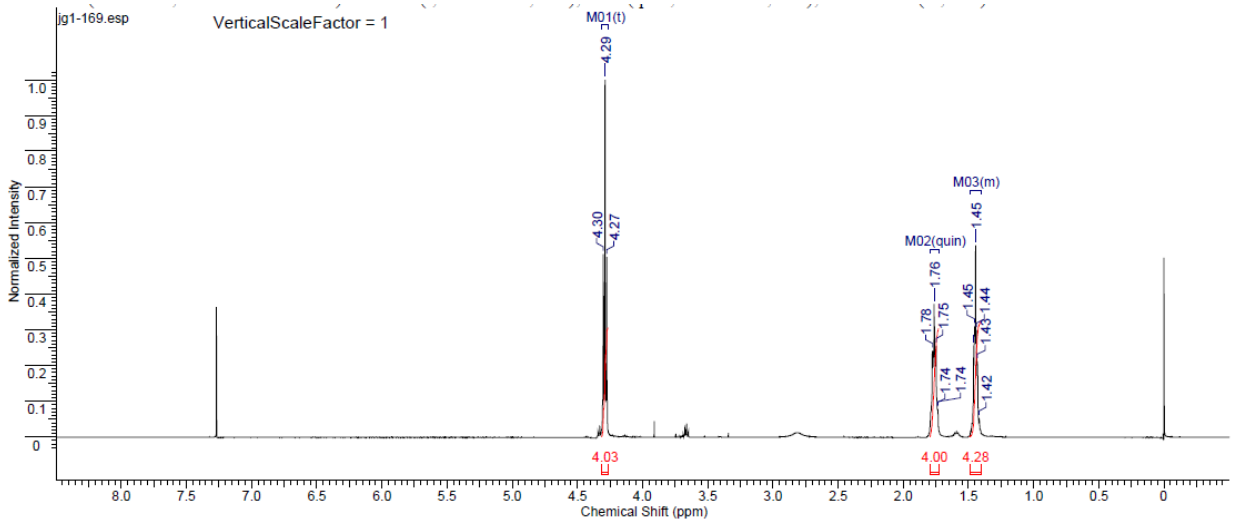


Figure S89. ^{1}H NMR spectrum of polyhexylene oxalate (Table S1, entry 5).

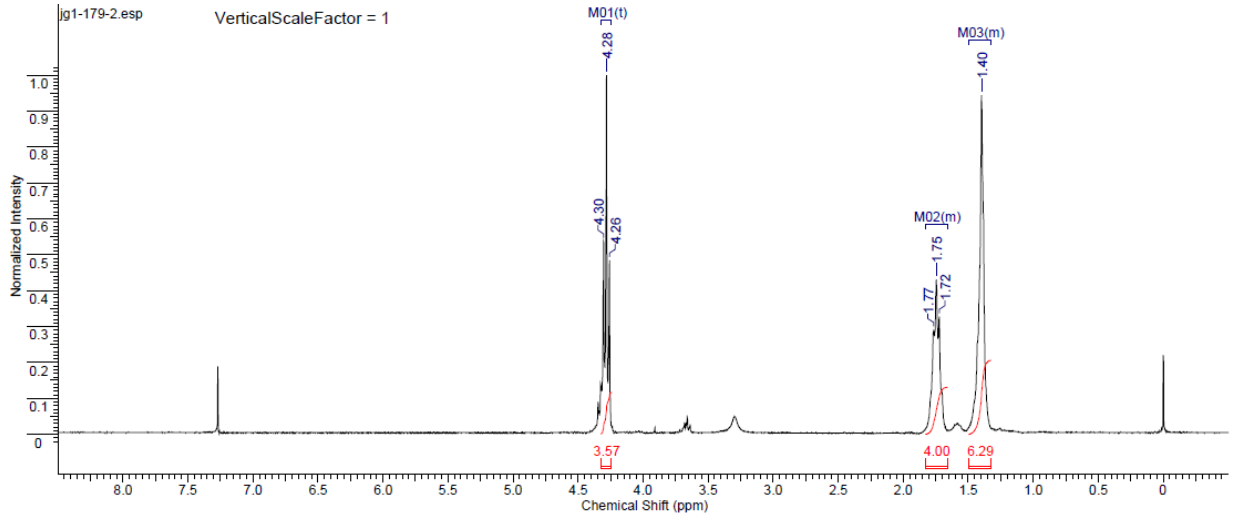


Figure S90. ^{1}H NMR spectrum of polyheptylene oxalate (Table S1, entry 6).

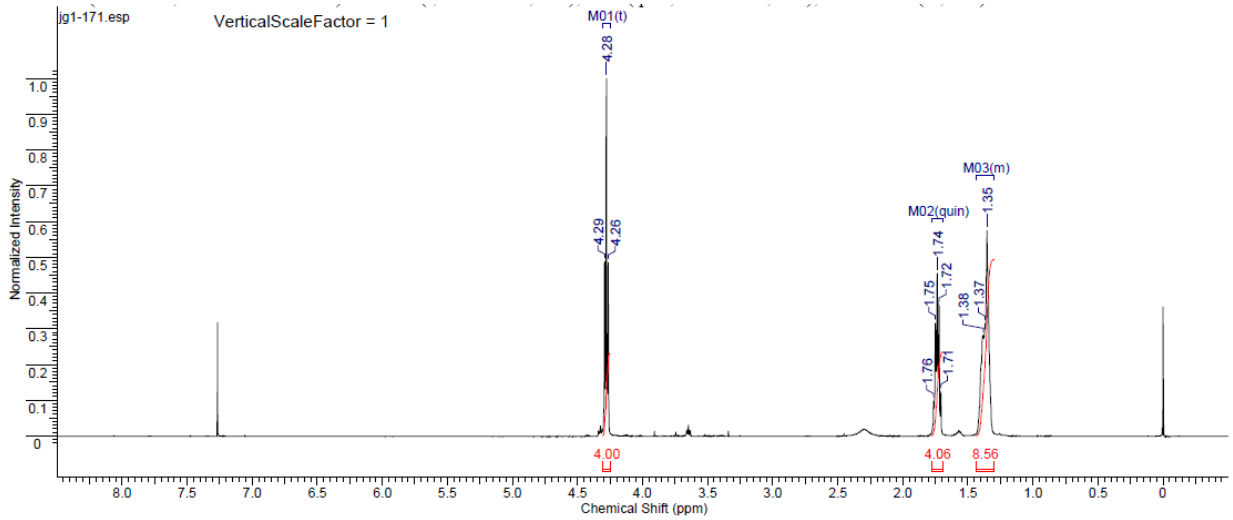


Figure S91. ^{1}H NMR spectrum of polyoctylene oxalate (Table S1, entry 7).

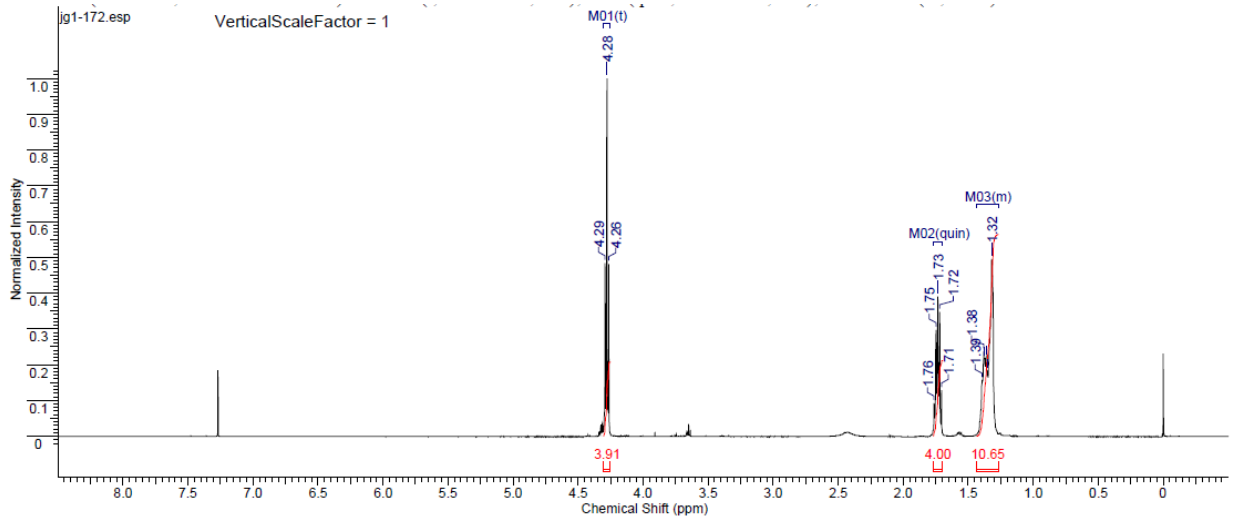


Figure S92. ^{1}H NMR spectrum of polynonylene oxalate (Table S1, entry 8).

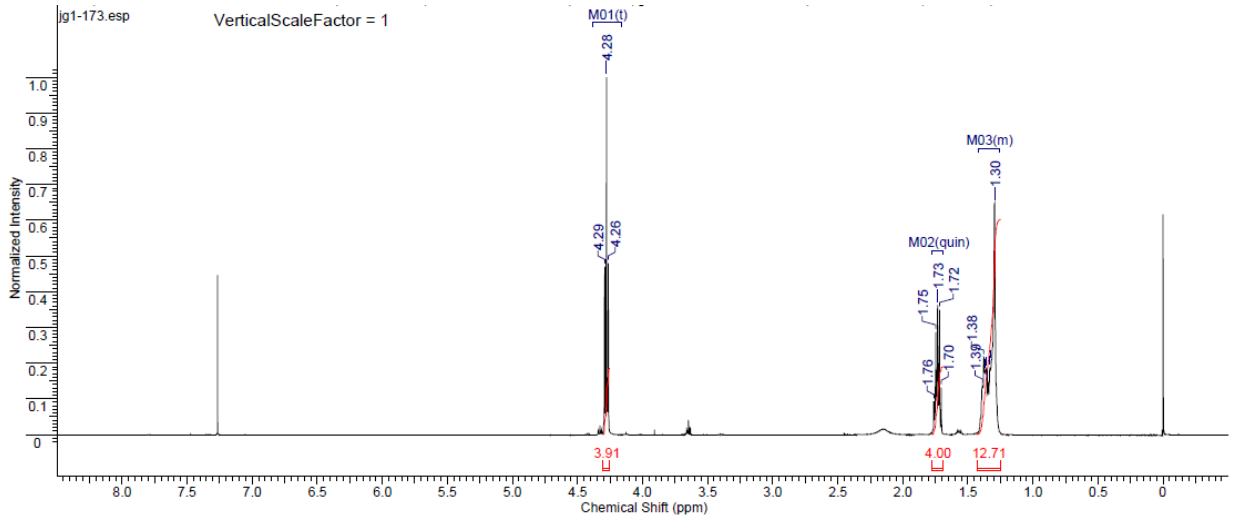


Figure S93. ^{1}H NMR spectrum of polydecylene oxalate (Table S1, entry 9).

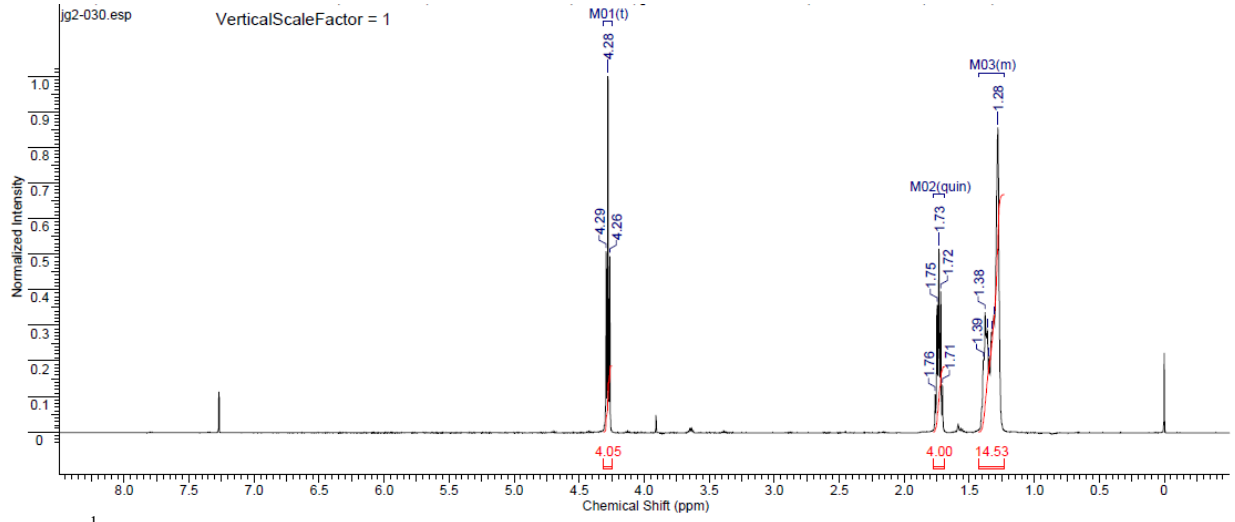


Figure S94. ^{1}H NMR spectrum of polyundecylene oxalate (Table S1, entry 10).

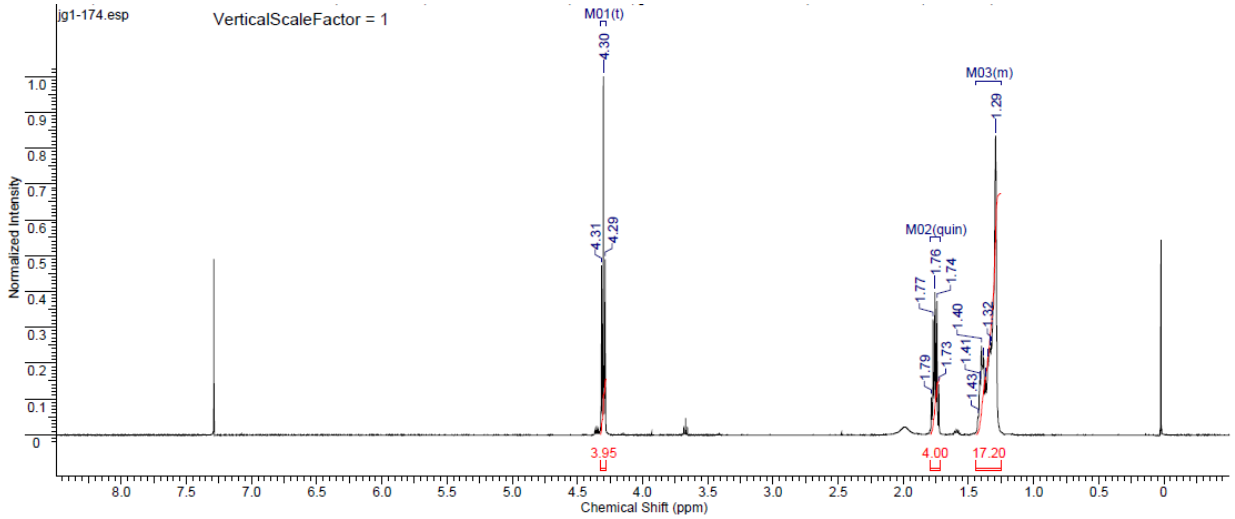


Figure S95. ^{1}H NMR spectrum of polydodecylene oxalate (Table S1, entry 11).

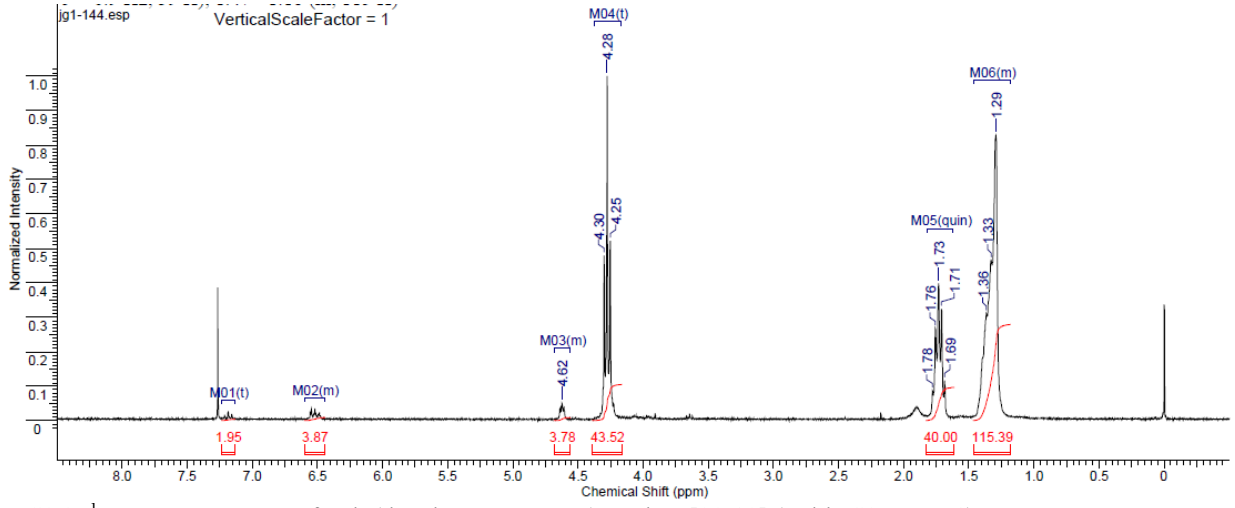


Figure S96. ^{1}H NMR spectrum of poly(decylene-*co*-RBHE) oxalate [90:10] (Table S2, entry 1).

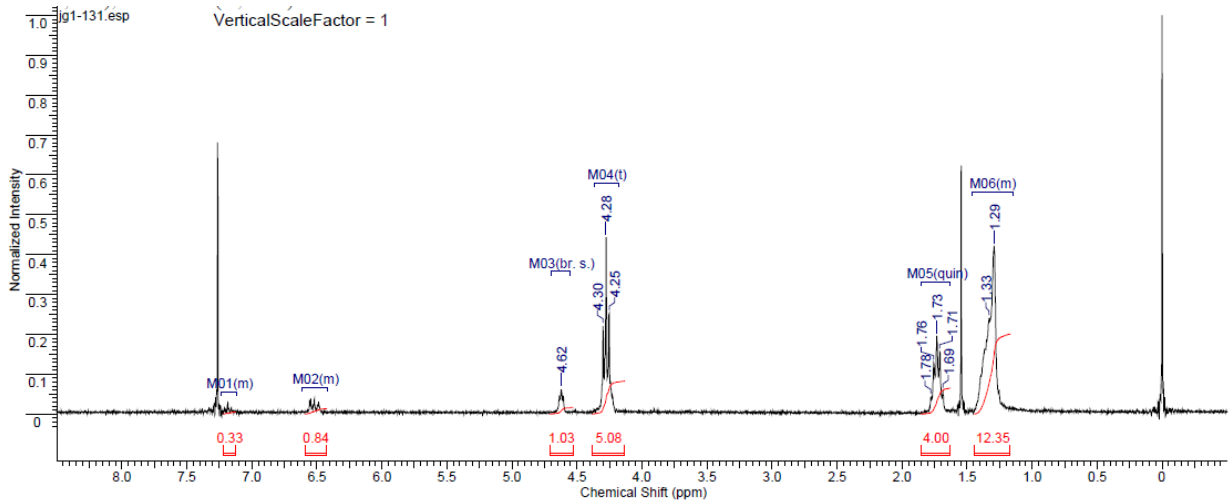


Figure S97. ^{1}H NMR spectrum of poly(decylene-*co*-RBHE) oxalate [80:20] (Table S2, entry 2).

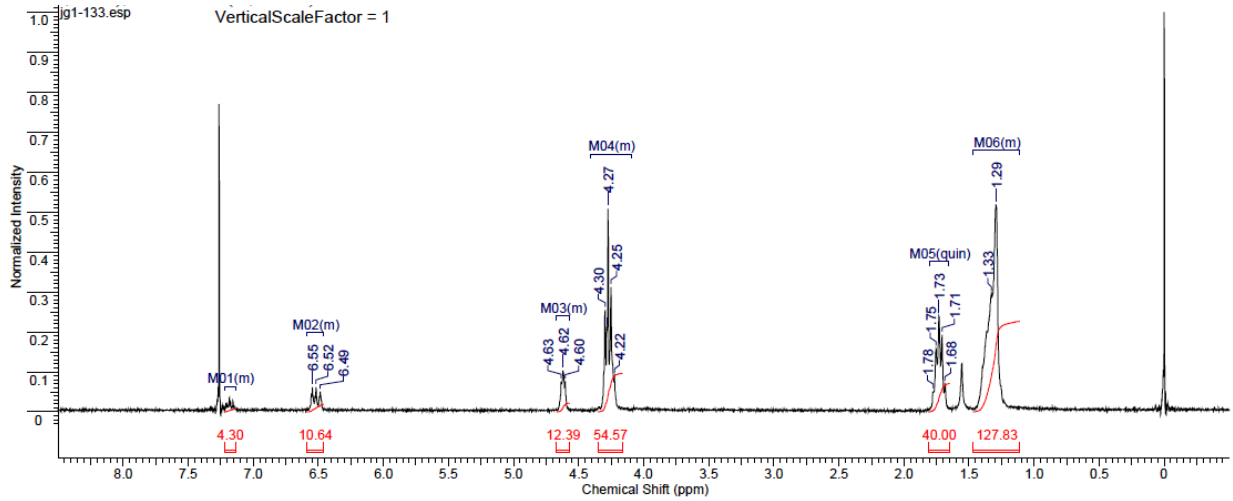


Figure S98. ^{1}H NMR spectrum of poly(decylene-*co*-RBHE) oxalate [70:30] (Table S2, entry 3).

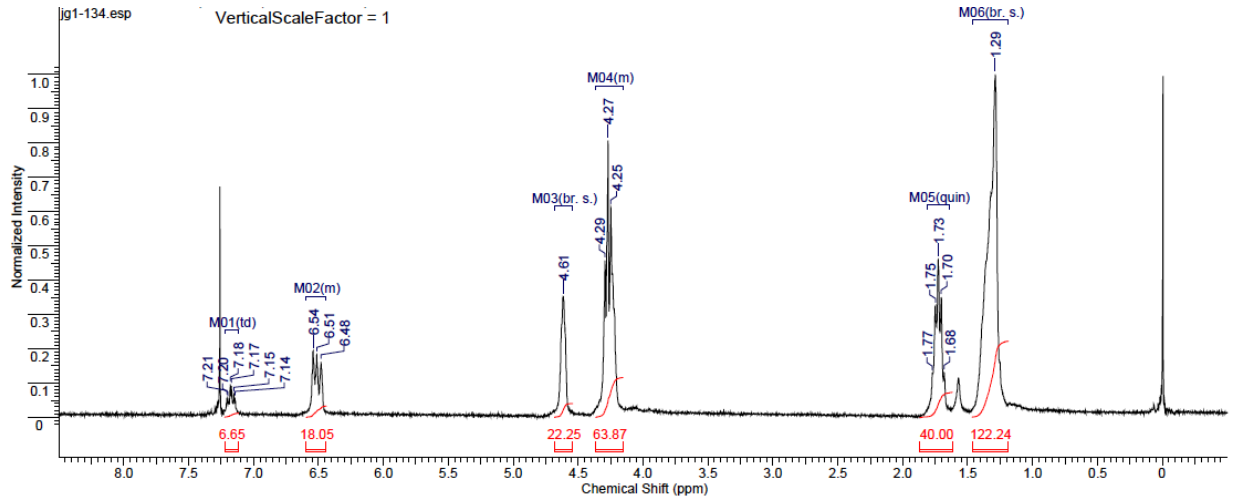


Figure S99. ^{1}H NMR spectrum of poly(decylene-*co*-RBHE) oxalate [60:40] (Table S2, entry 4).

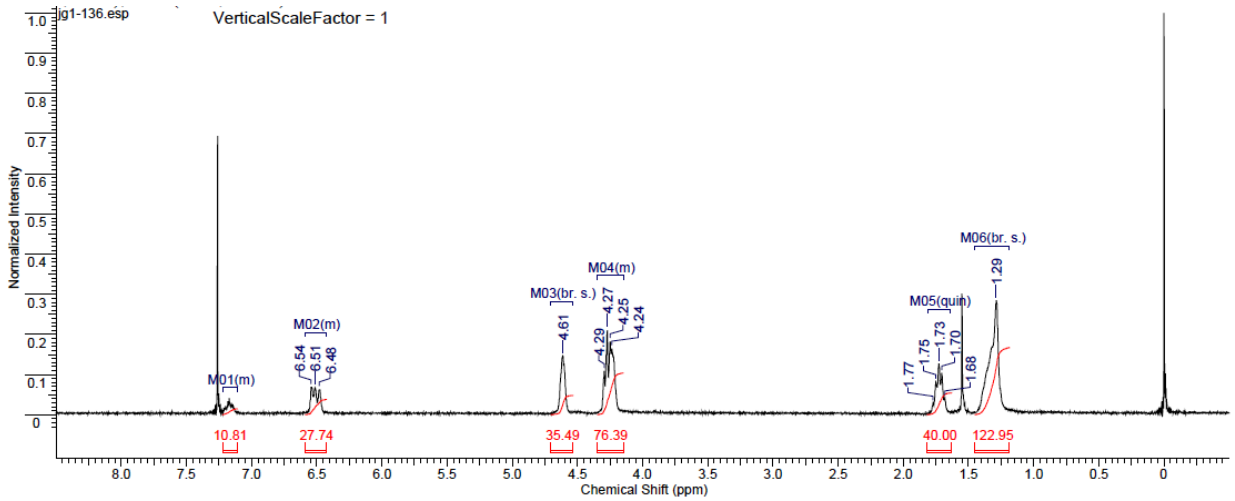


Figure S100. ^{1}H NMR spectrum of poly(decylene-*co*-RBHE) oxalate [50:50] (Table S2, entry 5).

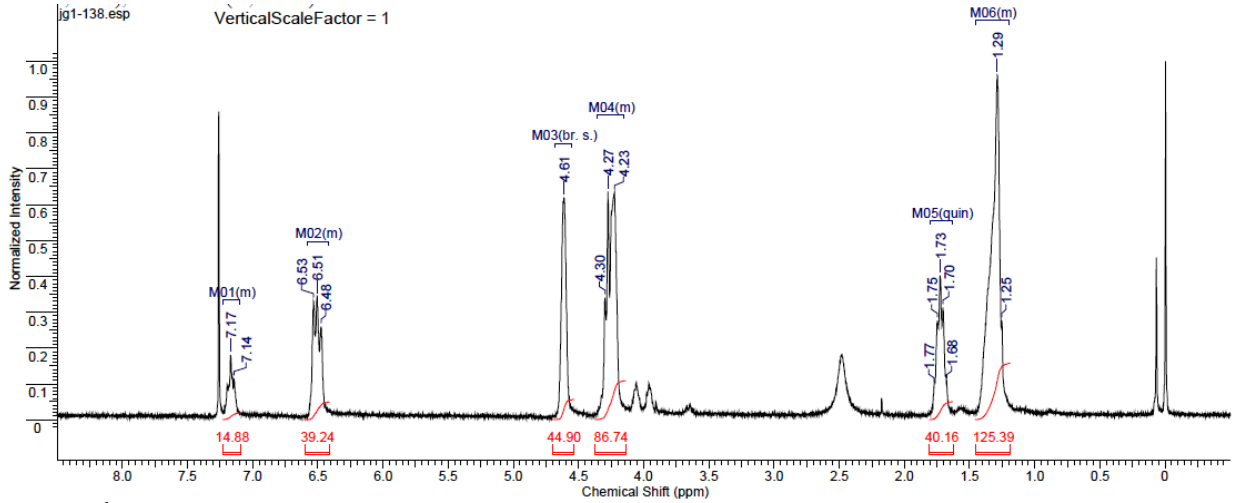


Figure S101. ^{1}H NMR spectrum of poly(decylene-*co*-RBHE) oxalate [40:60] (Table S2, entry 6).

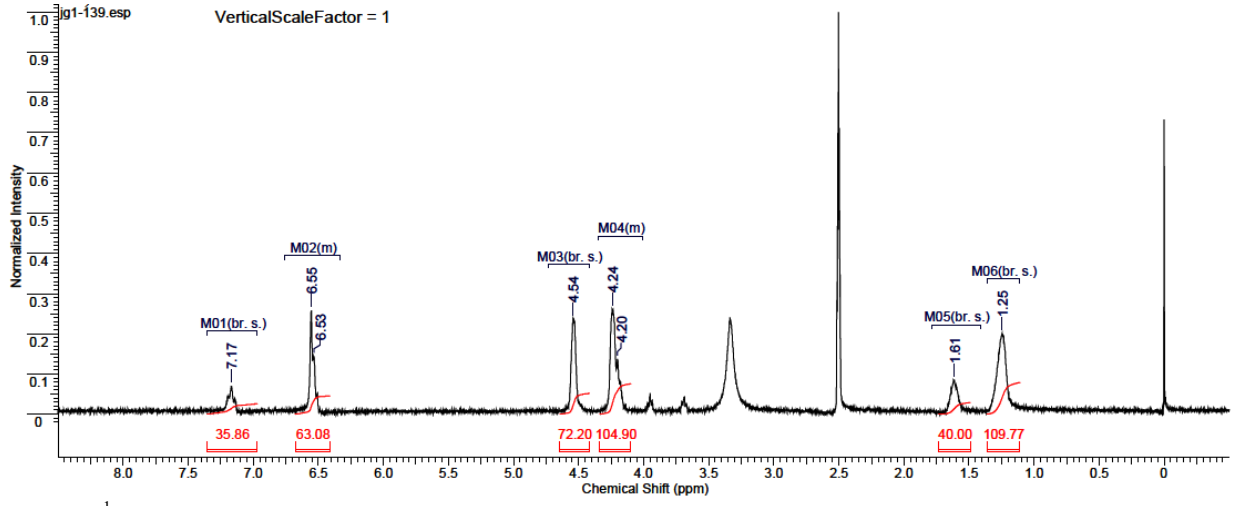


Figure S102. ^{1}H NMR spectrum of poly(decylene-*co*-RBHE) oxalate [30:70] (Table S2, entry 7).

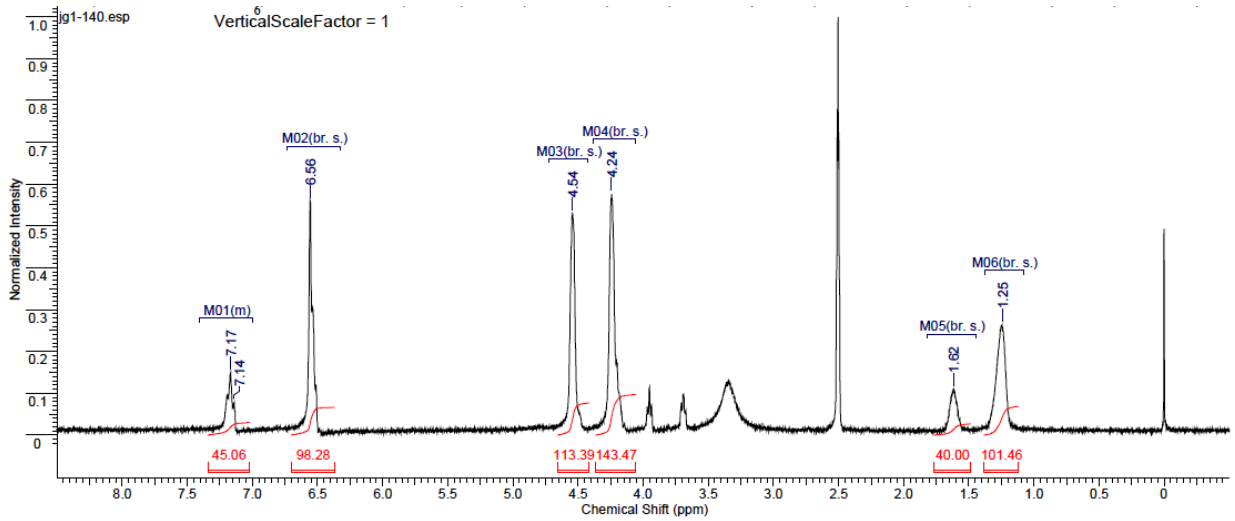


Figure S103. [1]H NMR spectrum of poly(decylene-*co*-RBHE) oxalate [20:80] (Table S2, entry 8).

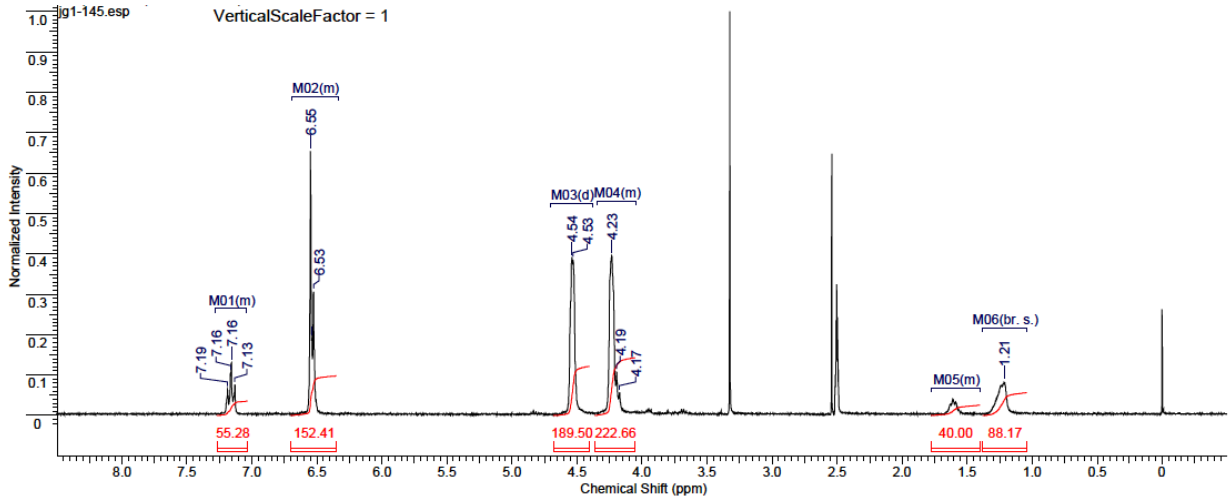


Figure S104. [1]H NMR spectrum of poly(decylene-*co*-RBHE) oxalate [10:90] (Table S2, entry 9).

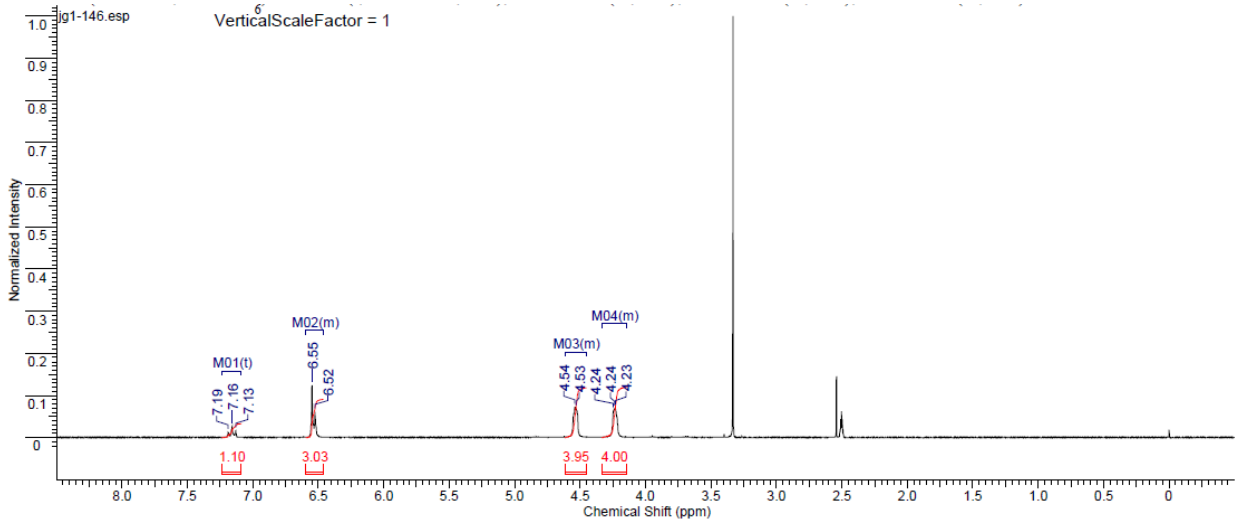


Figure S105. [1]H NMR spectrum of poly(RBHE) oxalate (Table S2, entry 10).

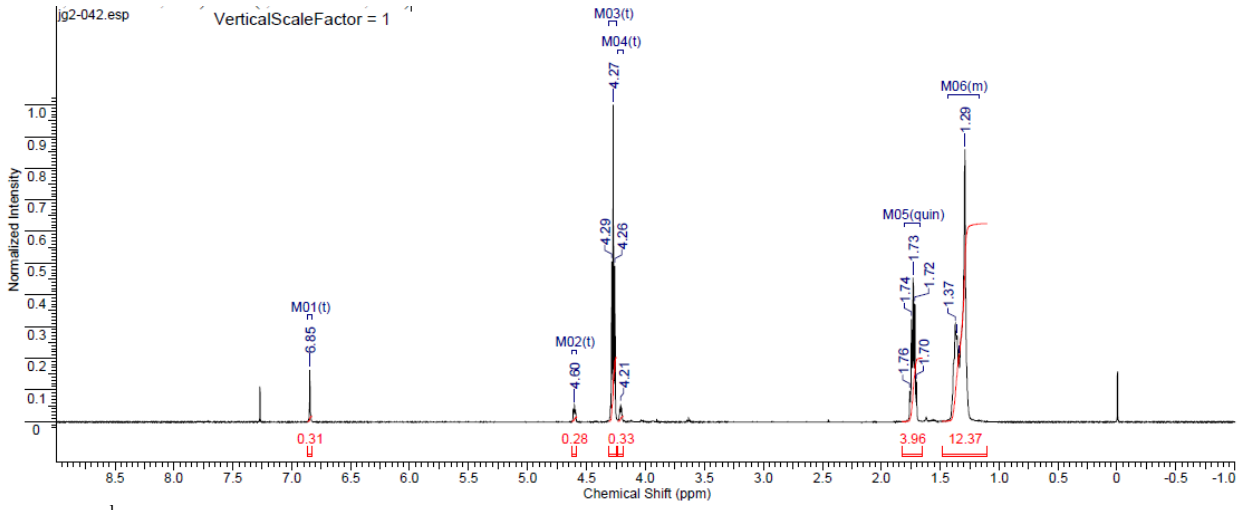


Figure S106. ^{1}H NMR spectrum of poly(decylene-*co*-HBHE) oxalate [90:10] (Table S2, entry 11).

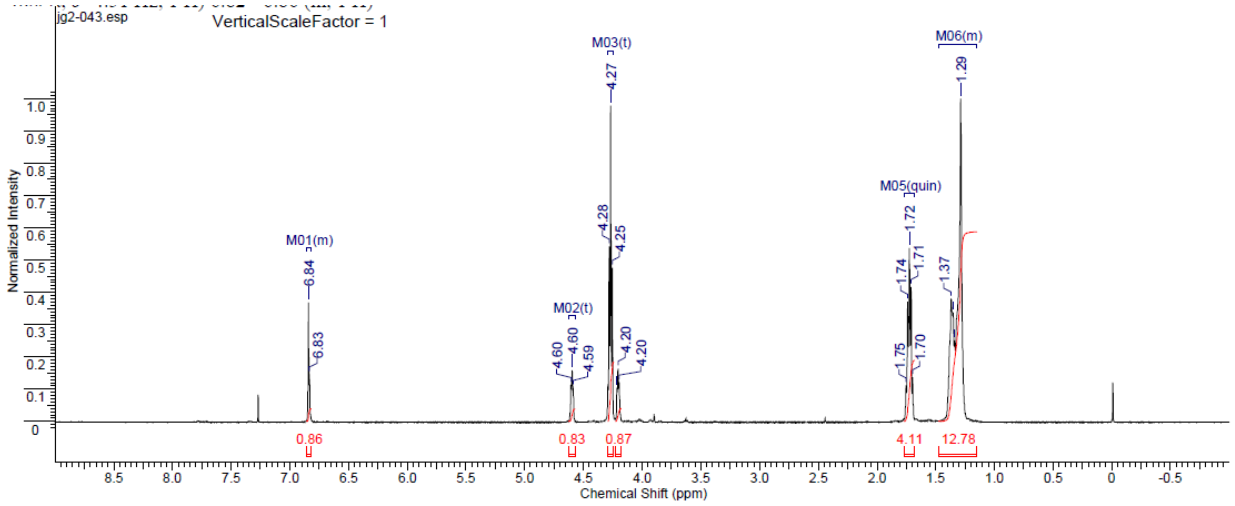


Figure S107. ^{1}H NMR spectrum of poly(decylene-*co*-HBHE) oxalate [80:20] (Table S2, entry 12).

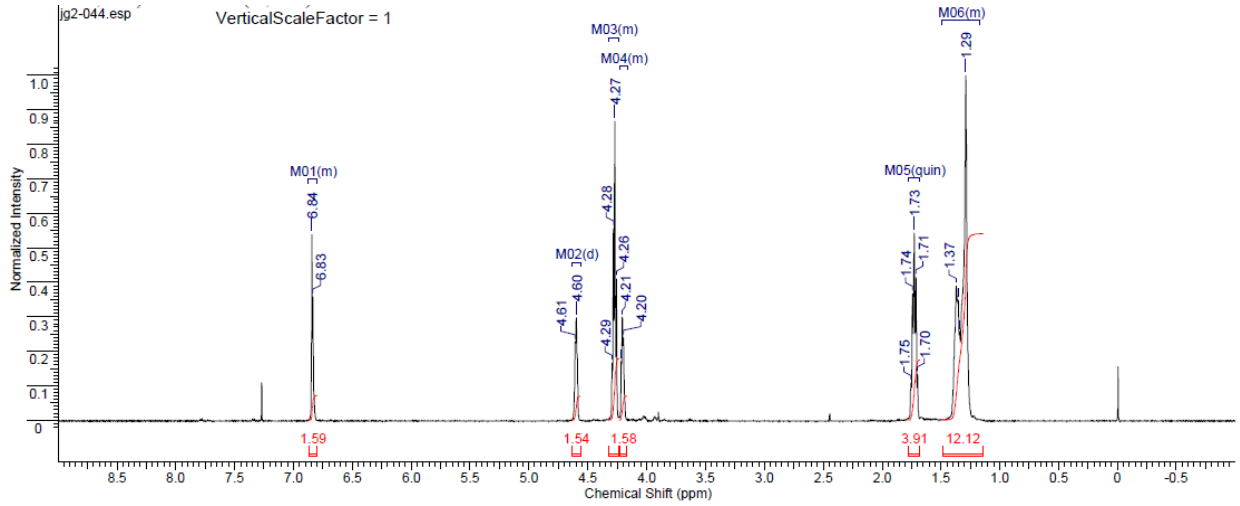


Figure S108. ^{1}H NMR spectrum of poly(decylene-*co*-HBHE) oxalate [70:30] (Table S2, entry 13).

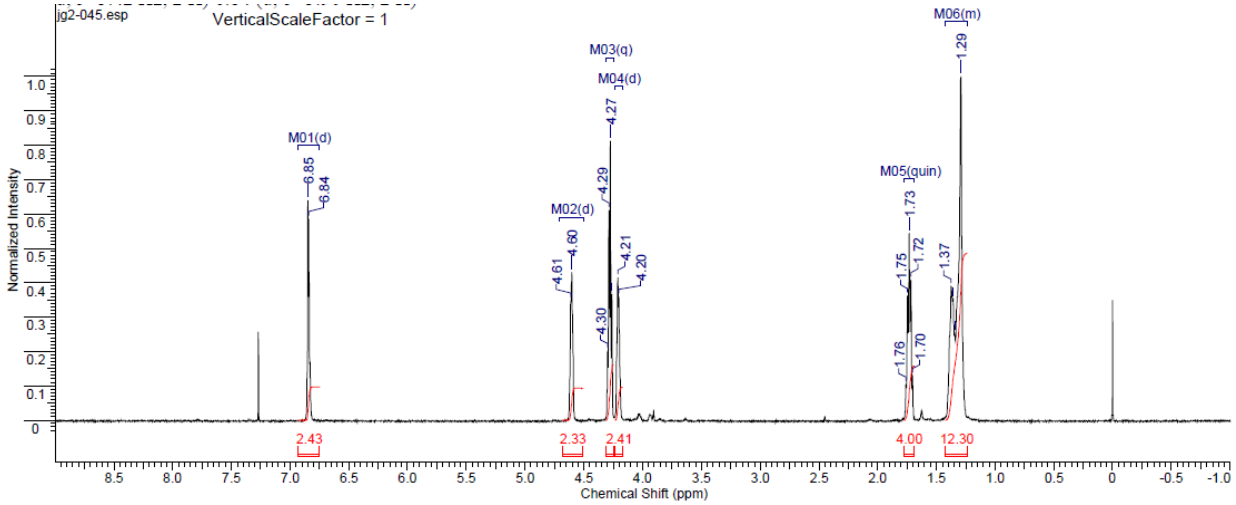


Figure S109. ^{1}H NMR spectrum of poly(decylene-*co*-HBHE) oxalate [60:40] (Table S2, entry 14).

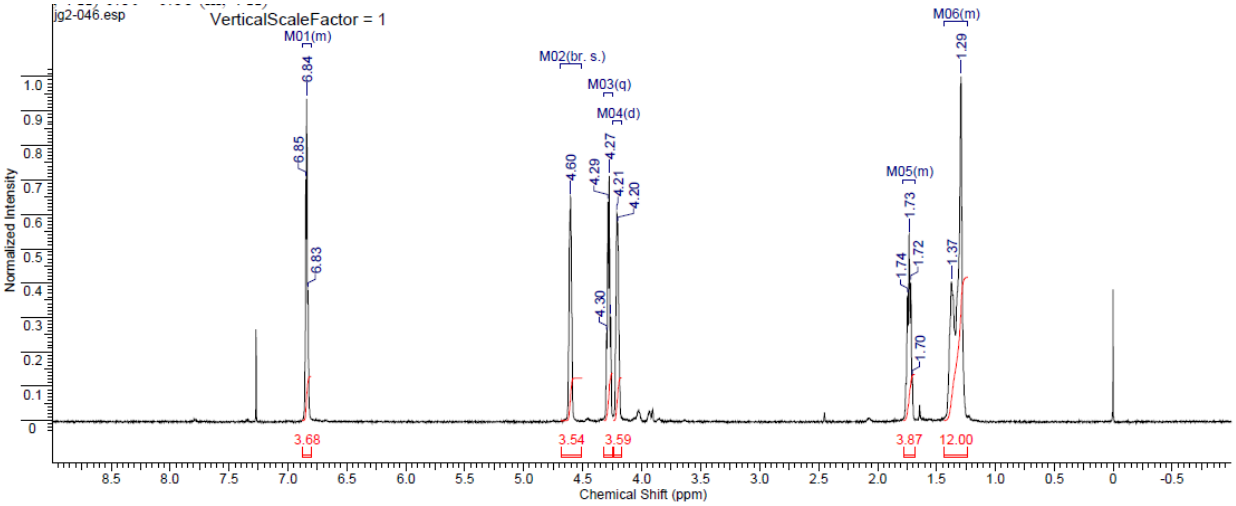


Figure S110. ^{1}H NMR spectrum of poly(decylene-*co*-HBHE) oxalate [50:50] (Table S2, entry 15).

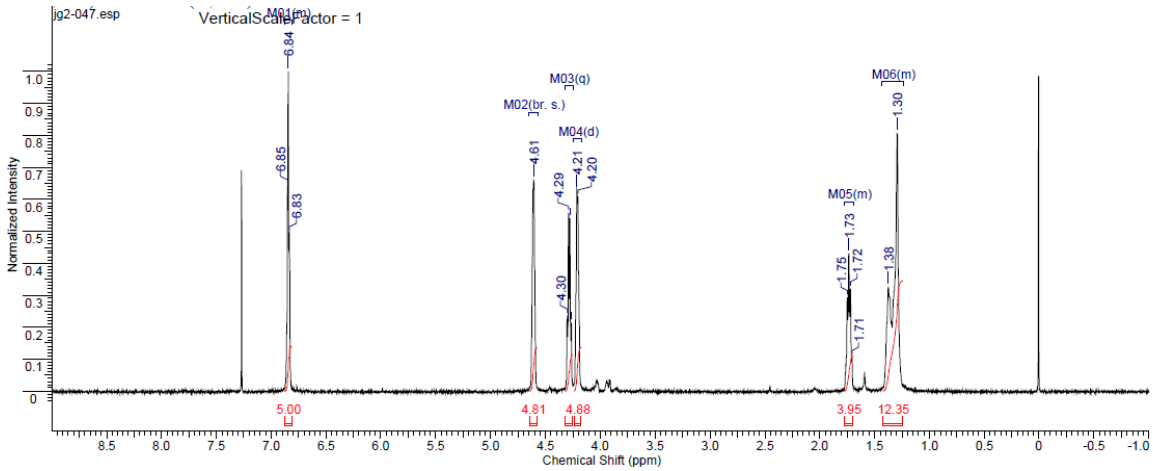


Figure S111. ^{1}H NMR spectrum of poly(decylene-*co*-HBHE) oxalate [40:60] (Table S2, entry 16).

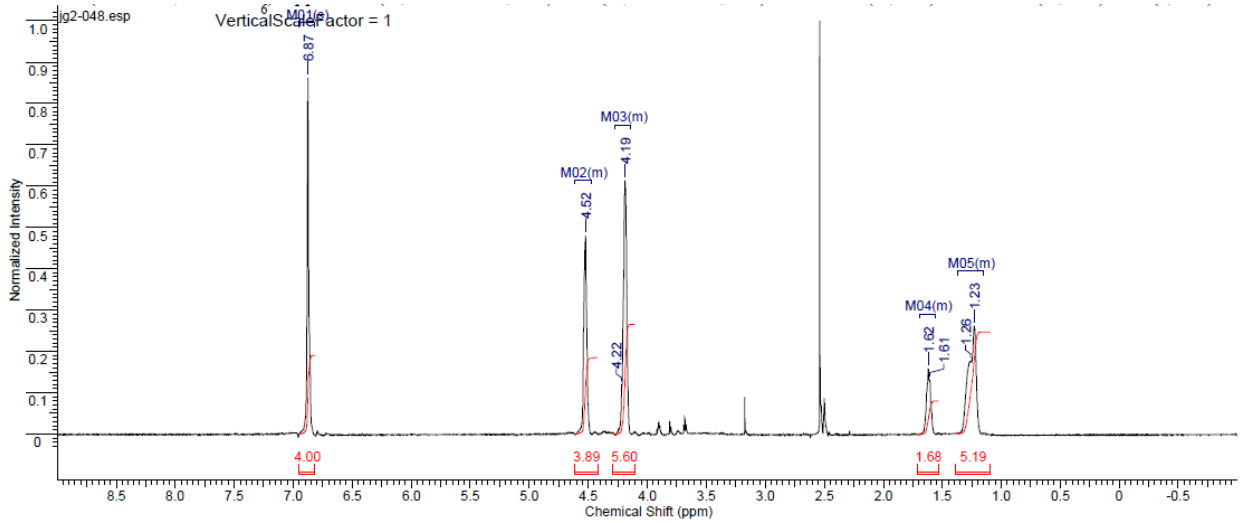


Figure S112. ^{1}H NMR spectrum of poly(decylene-*co*-HBHE) oxalate [30:70] (Table S2, entry 17).

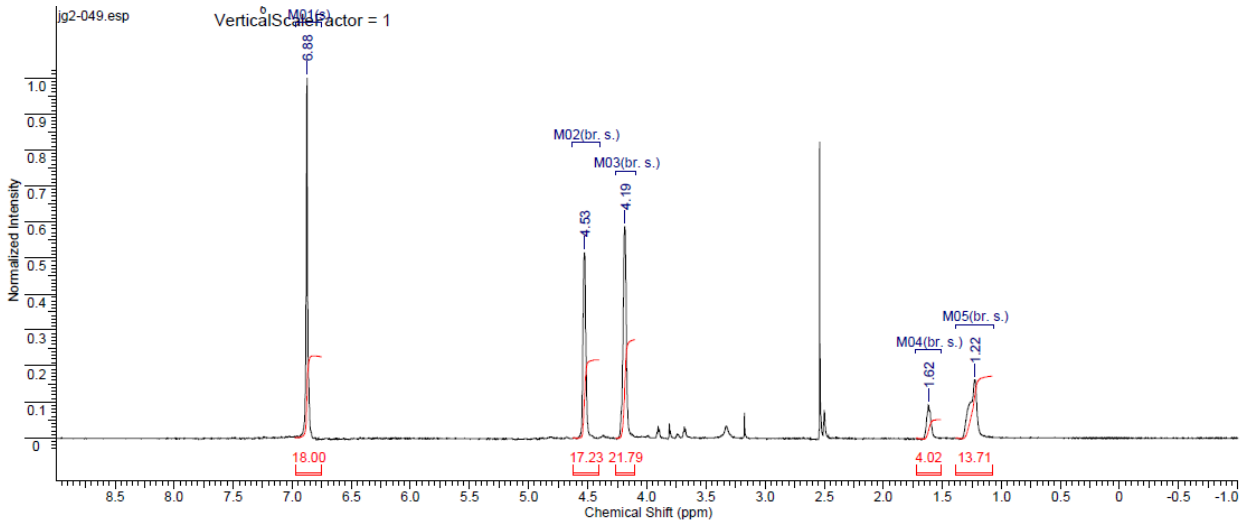


Figure S113. ^{1}H NMR spectrum of poly(decylene-*co*-HBHE) oxalate [20:80] (Table S2, entry 18).

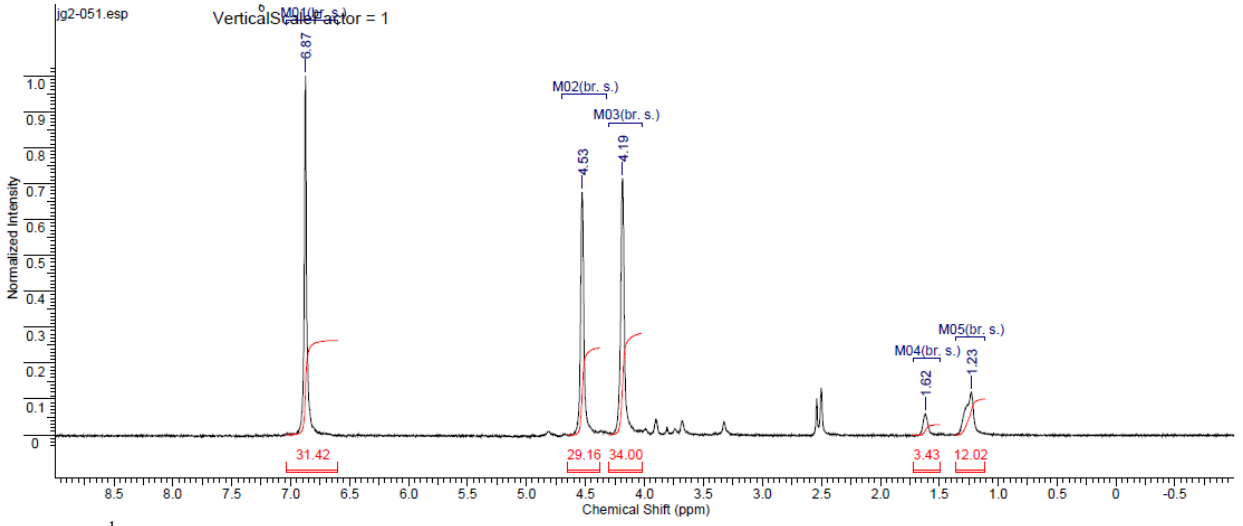


Figure S114. ^{1}H NMR spectrum of poly(decylene-*co*-HBHE) oxalate [10:90] (Table S2, entry 19).

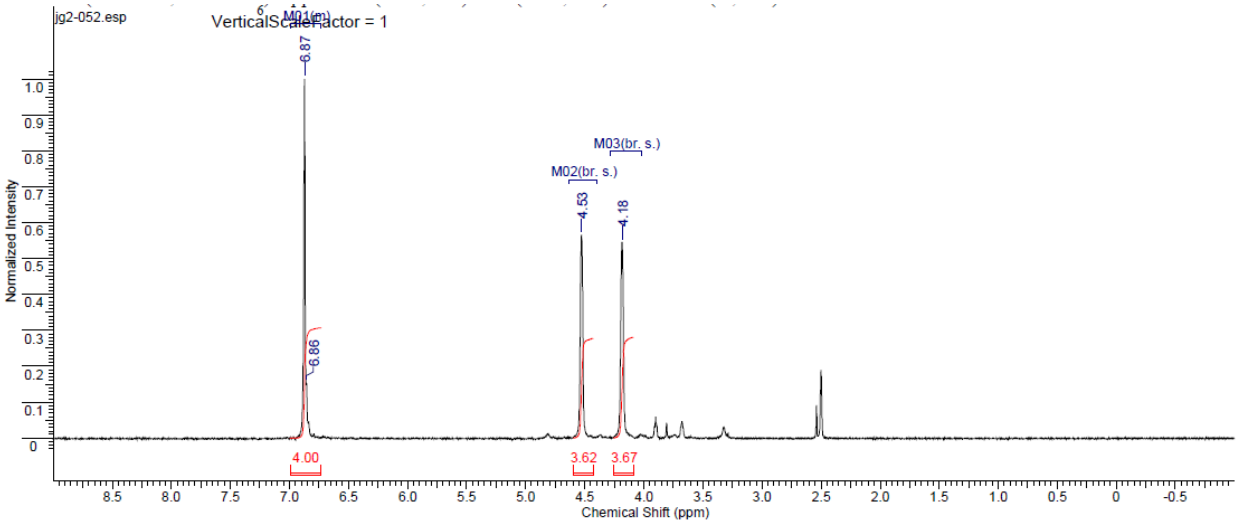


Figure S115. ^{1}H NMR spectrum of poly(HBHE) oxalate (Table S2, entry 20).

^{13}C NMR Spectra

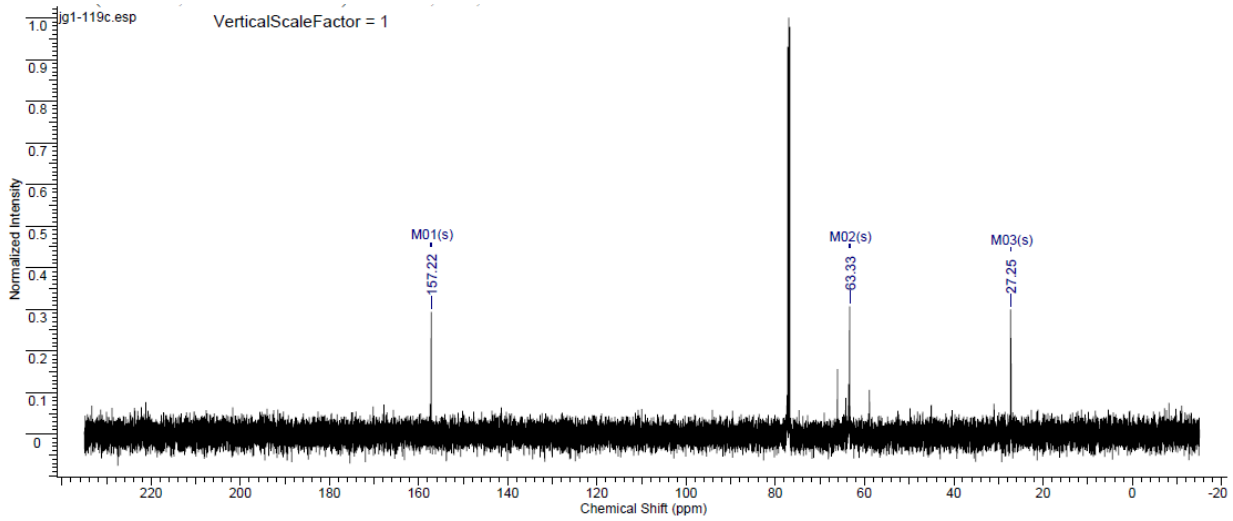


Figure S116. ^{13}C NMR spectrum of polypropylene oxalate (Table S1, entry 1).

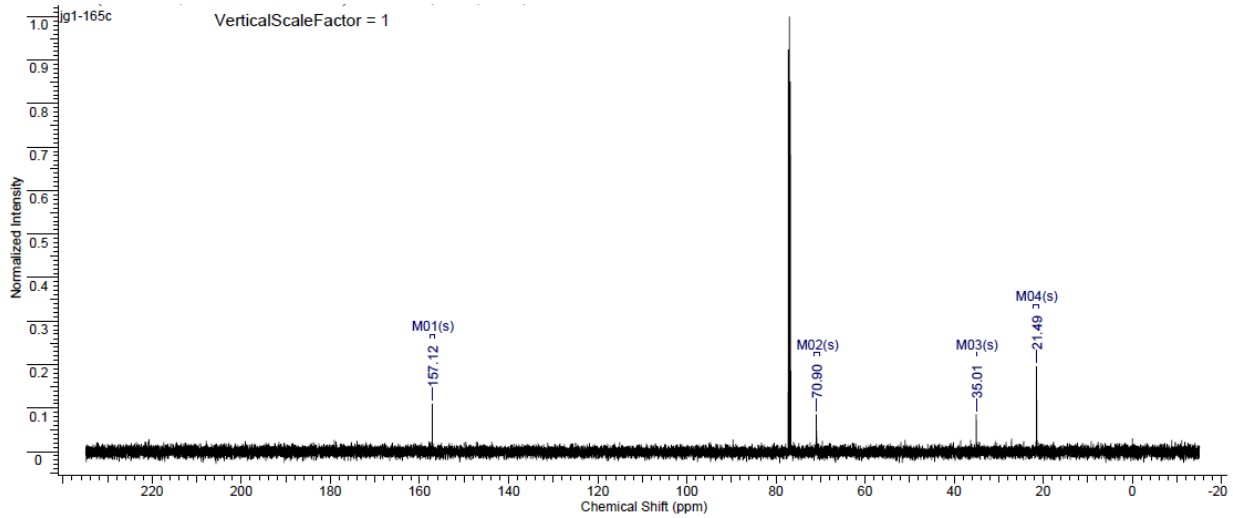


Figure S117. ^{13}C NMR spectrum of polyneopentylene oxalate (Table S1, entry 2).

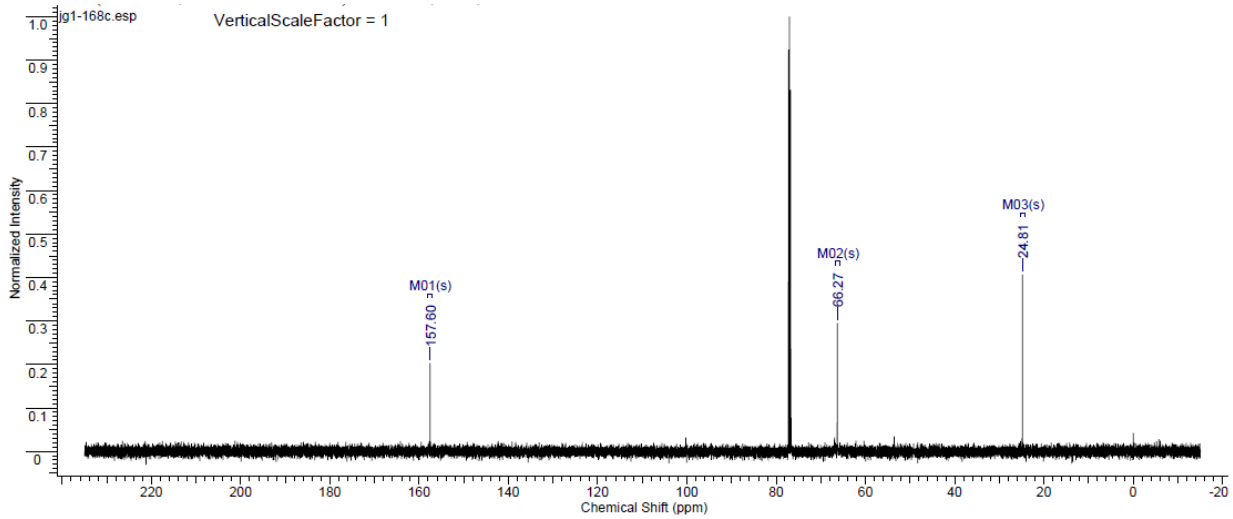


Figure S118. ^{13}C NMR spectrum of polybutylene oxalate (Table S1, entry 3).

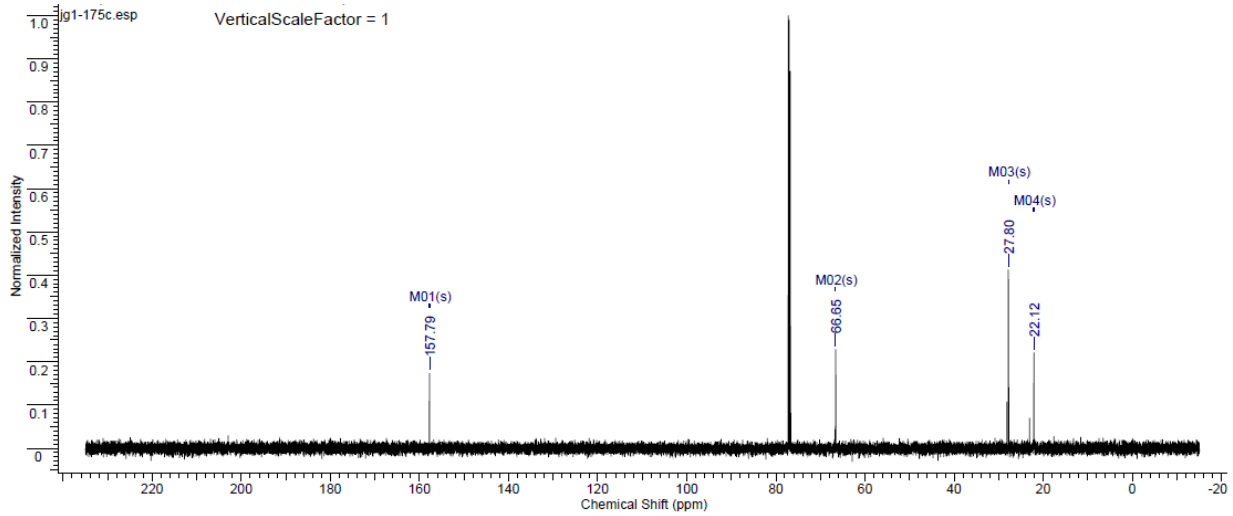


Figure S119. ^{13}C NMR spectrum of polypentylene oxalate (Table S1, entry 4).

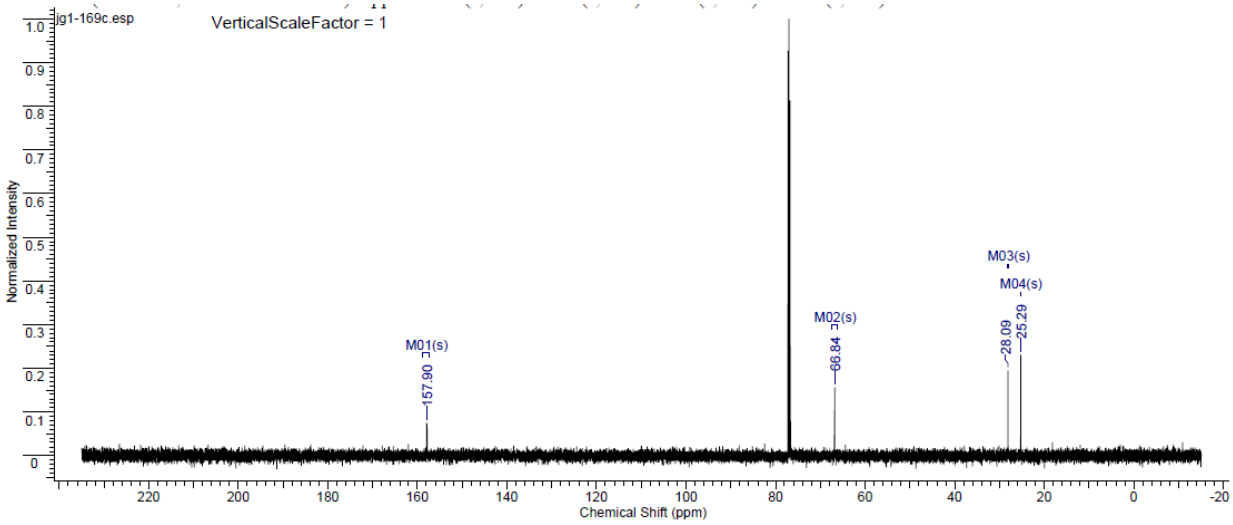


Figure S120. ^{13}C NMR spectrum of polyhexylene oxalate (Table S1, entry 5).

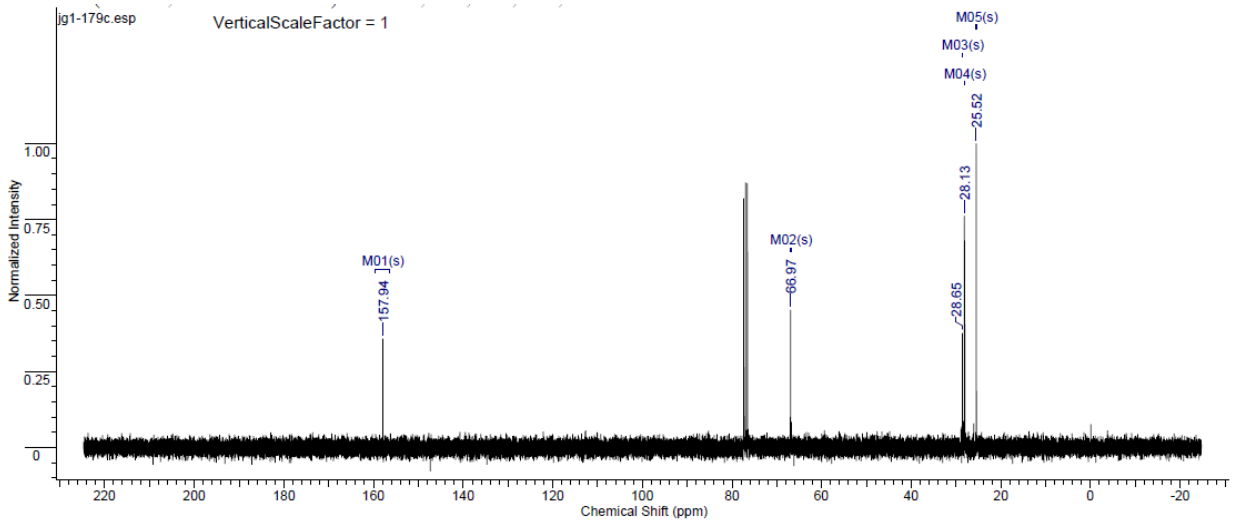


Figure S121. ^{13}C NMR spectrum of polyheptylene oxalate (Table S1, entry 6).

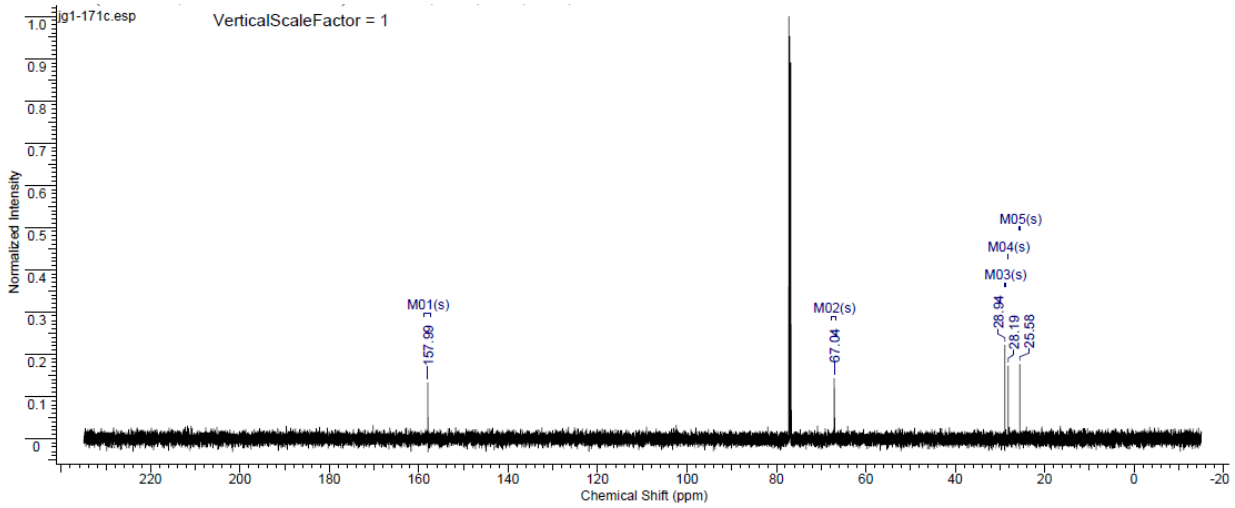


Figure S122. ^{13}C NMR spectrum of polyoctylene oxalate (Table S1, entry 7).

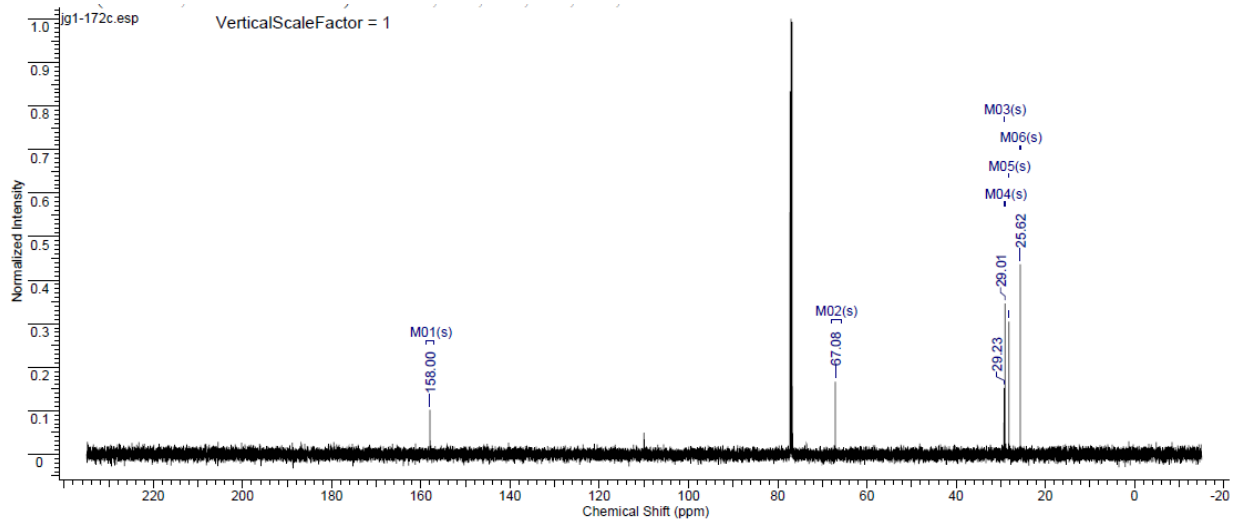


Figure S123. ^{13}C NMR spectrum of polynonylene oxalate (Table S1, entry 8).

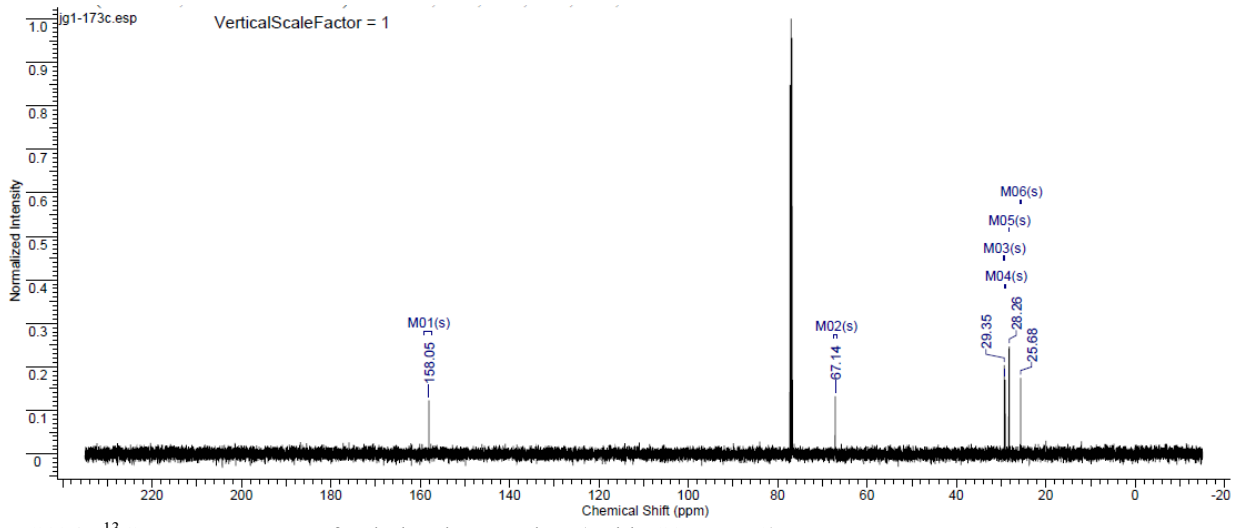


Figure S124. ^{13}C NMR spectrum of polydecylene oxalate (Table S1, entry 9).

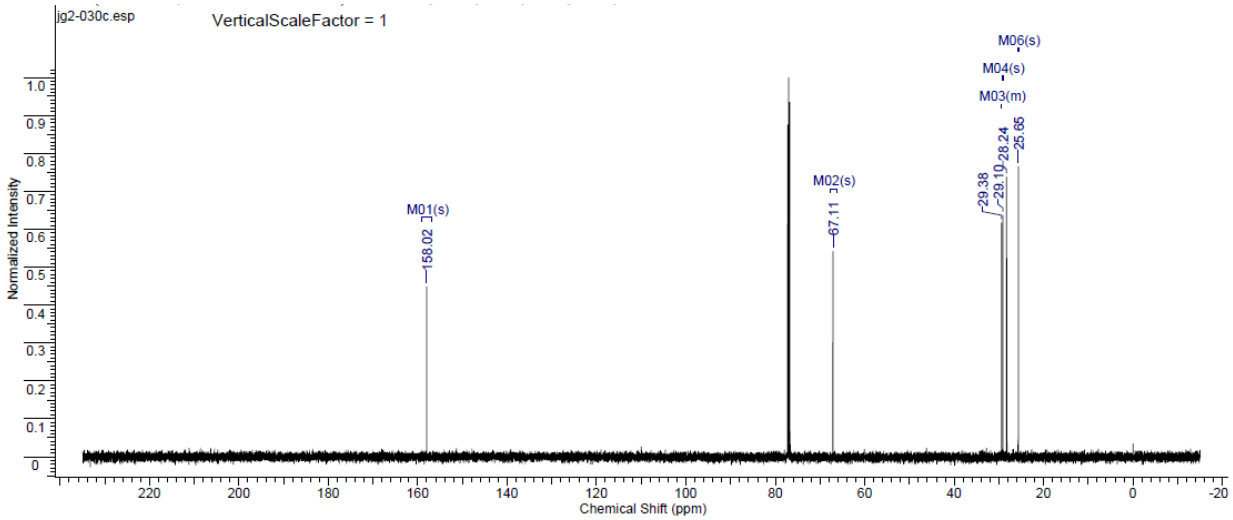


Figure S125. ^{13}C NMR spectrum of polyundecylene oxalate (Table S1, entry 10).

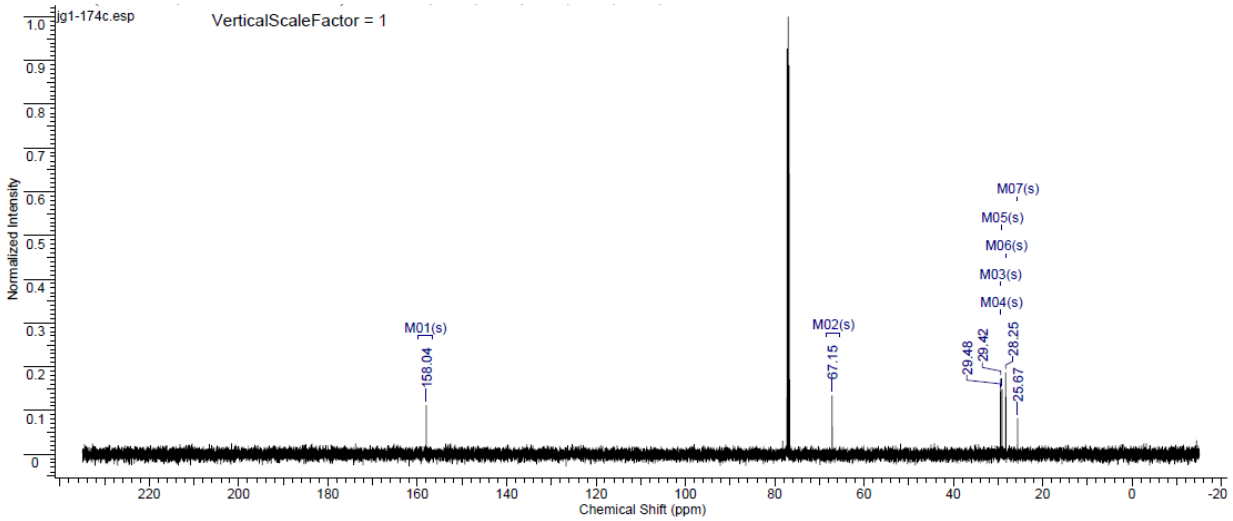


Figure S126. ^{13}C NMR spectrum of polydodecylene oxalate (Table S1, entry 11).

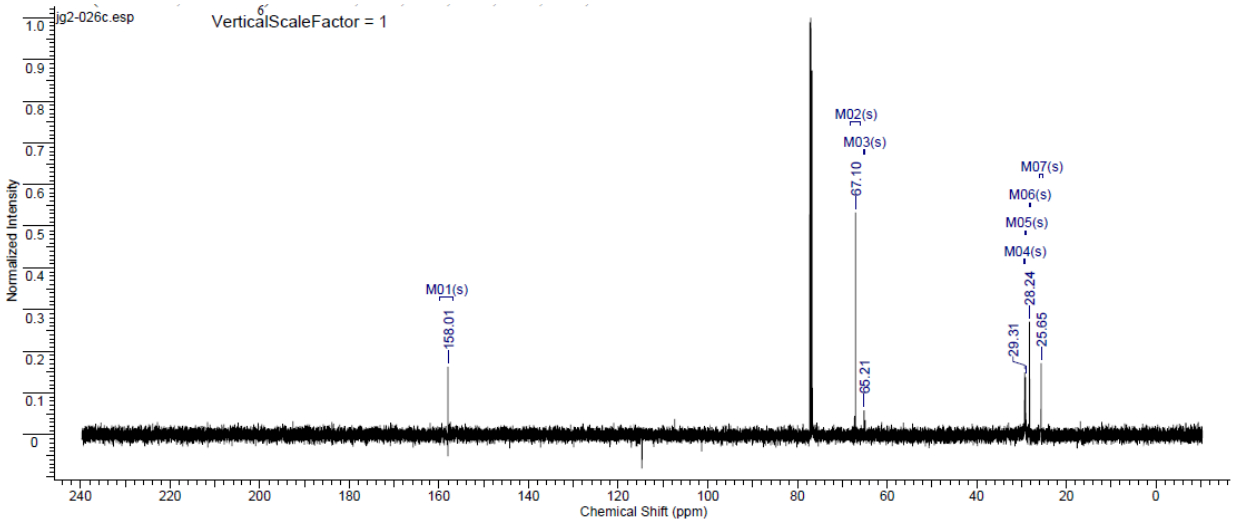


Figure S127. ^{13}C NMR spectrum of poly(decylene-*co*-RBHE) oxalate [90:10] (Table S2, entry 1).

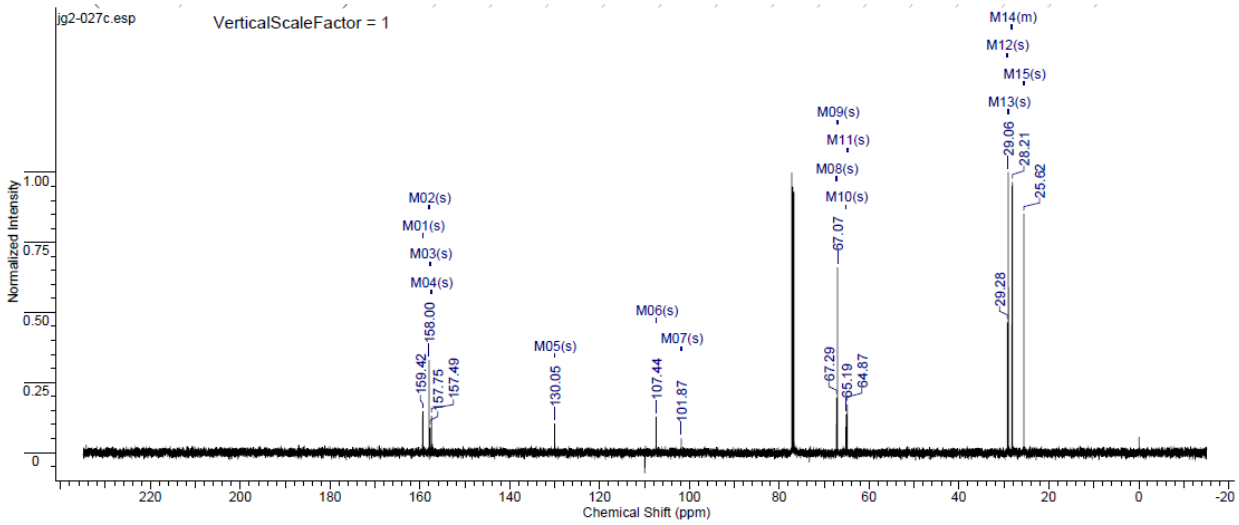


Figure S128. ^{13}C NMR spectrum of poly(decylene-*co*-RBHE) oxalate [80:20] (Table S2, entry 2).

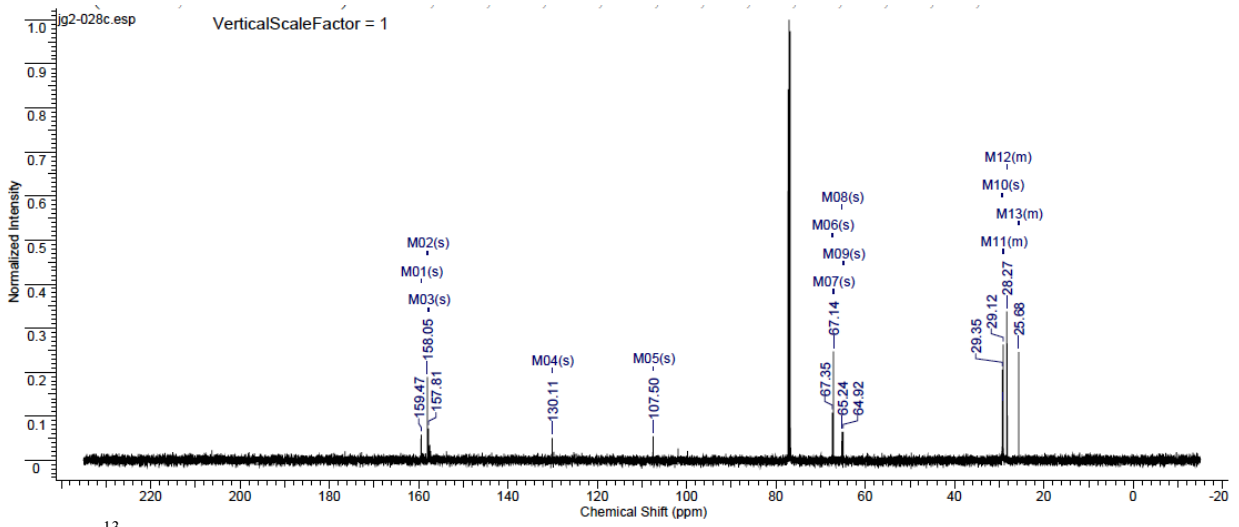


Figure S129. ^{13}C NMR spectrum of poly(decylene-*co*-RBHE) oxalate [70:30] (Table S2, entry 3).

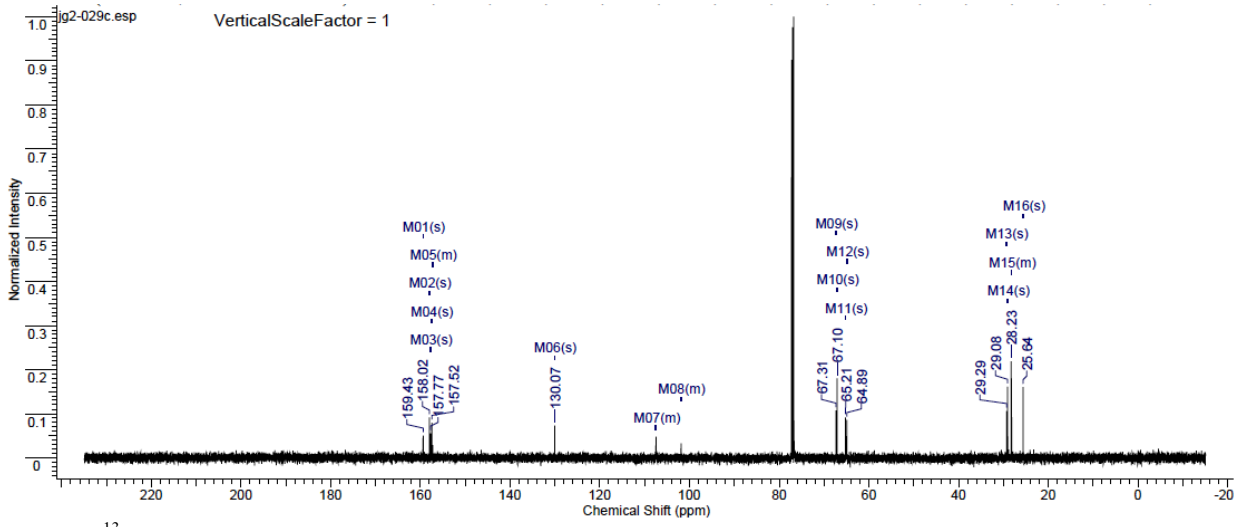


Figure S130. ^{13}C NMR spectrum of poly(decylene-*co*-RBHE) oxalate [60:40] (Table S2, entry 4).

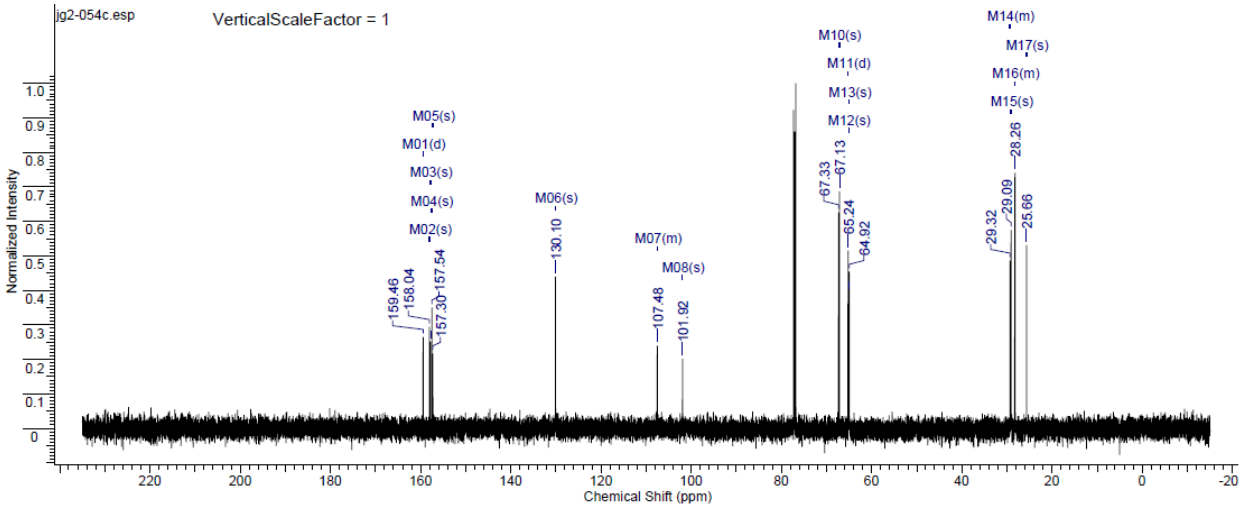


Figure S131. ^{13}C NMR spectrum of poly(decylene-*co*-RBHE) oxalate [50:50] (Table S2, entry 5).

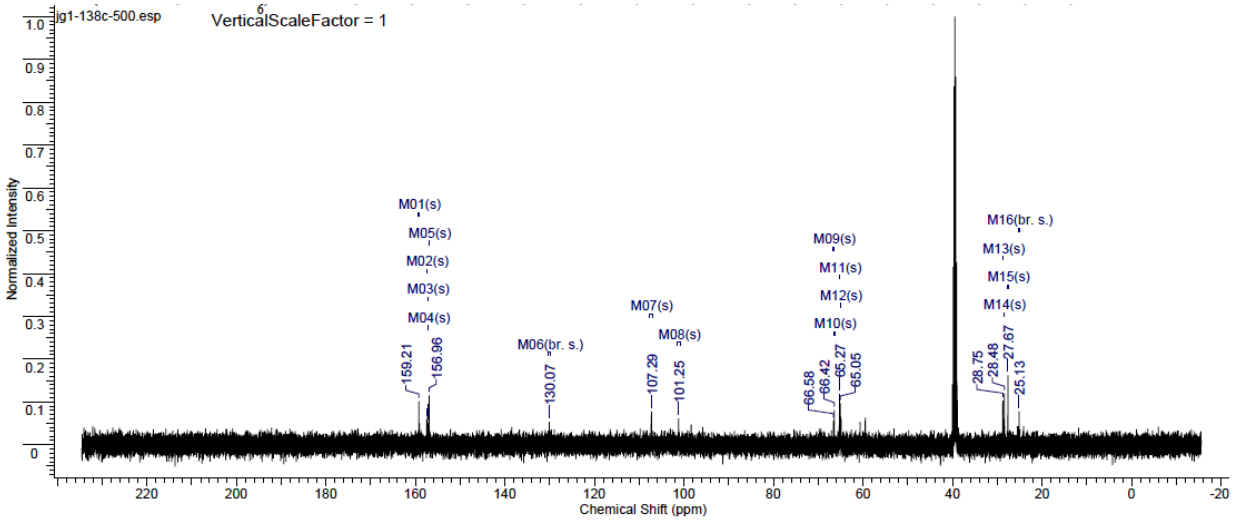


Figure S132. ^{13}C NMR spectrum of poly(decylene-*co*-RBHE) oxalate [40:60] (Table S2, entry 6).

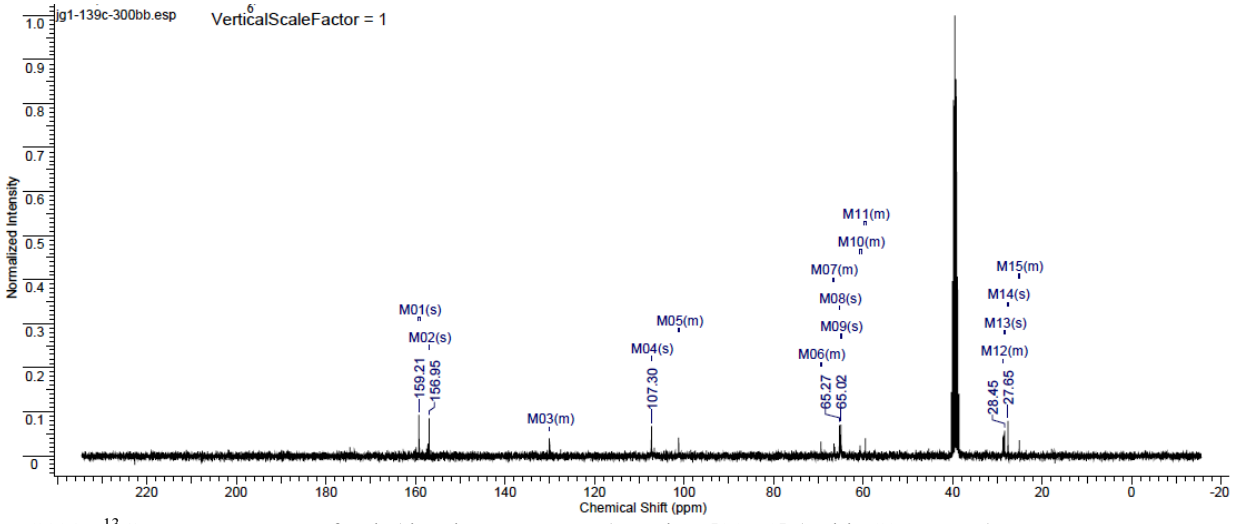


Figure S133. ^{13}C NMR spectrum of poly(decylene-*co*-RBHE) oxalate [30:70] (Table S2, entry 7).

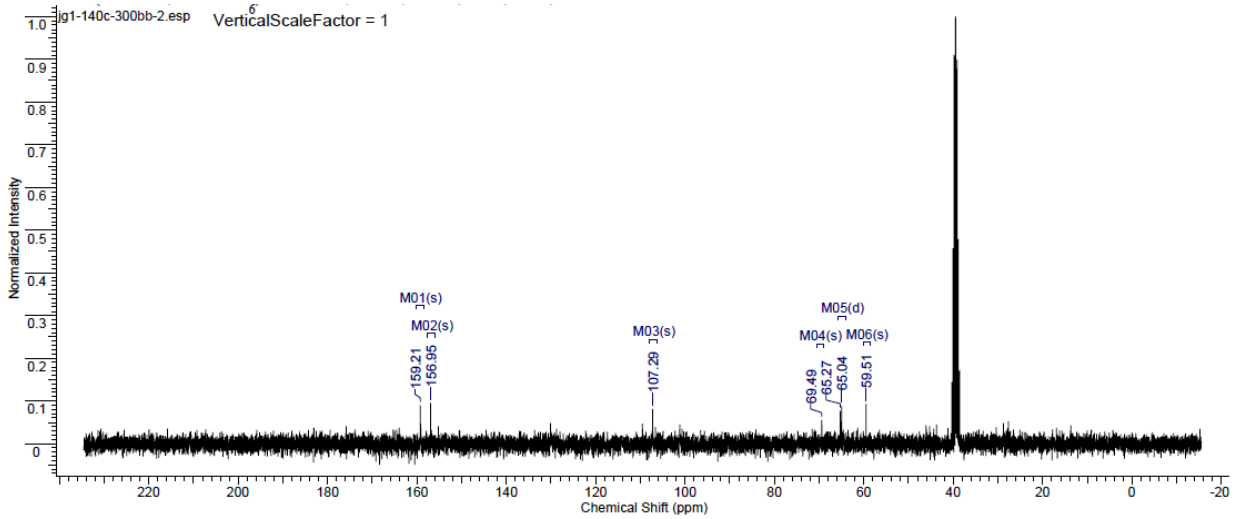


Figure S134. ^{13}C NMR spectrum of poly(decylene-*co*-RBHE) oxalate [20:80] (Table S2, entry 8).

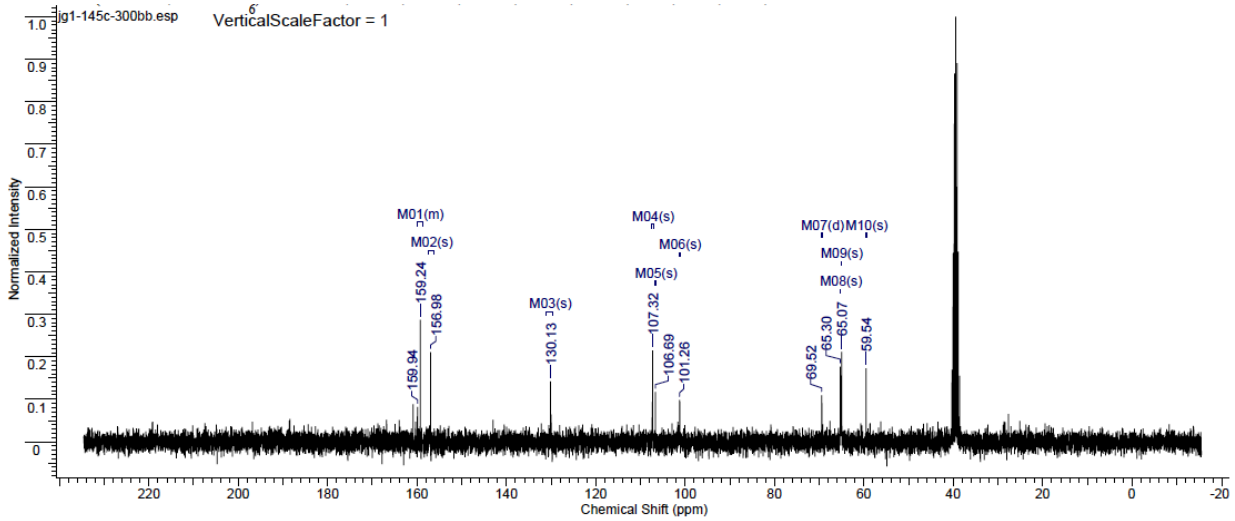


Figure S135. ^{13}C NMR spectrum of poly(decylene-*co*-RBHE) oxalate [10:90] (Table S2, entry 9).

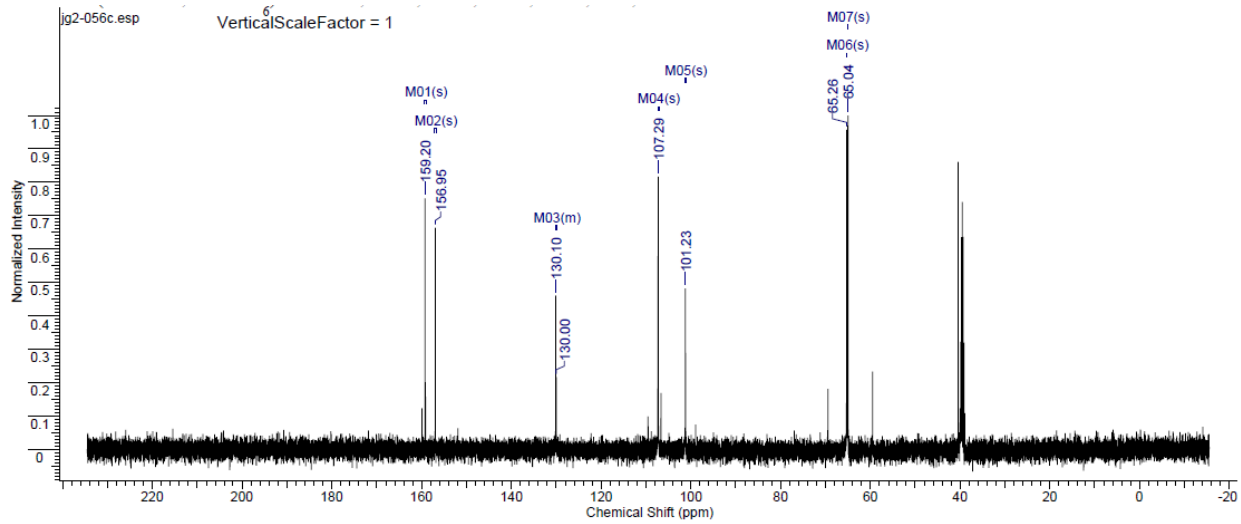


Figure S136. ^{13}C NMR spectrum of poly(RBHE) oxalate (Table S2, entry 10).

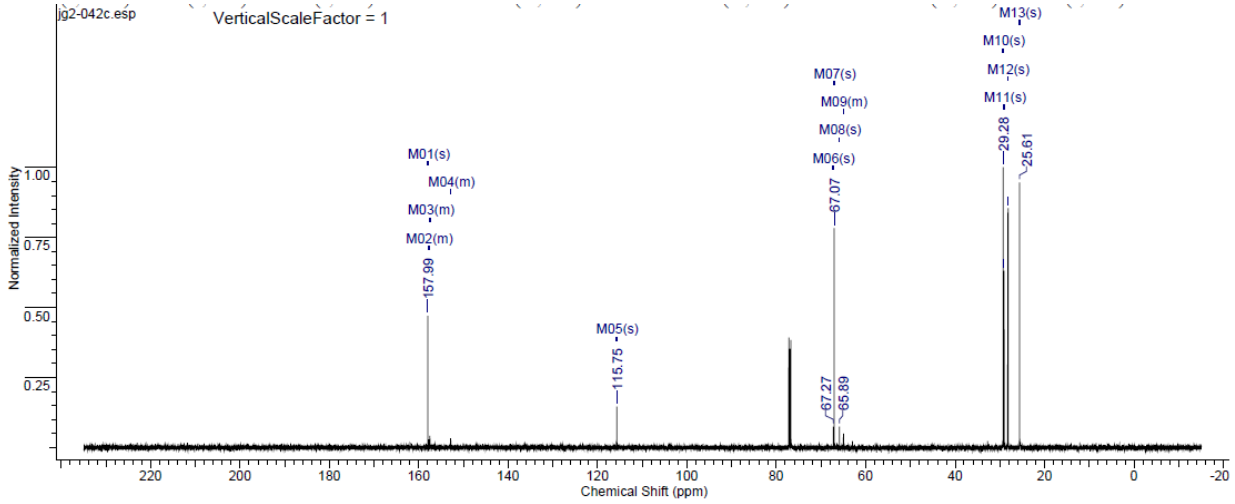


Figure S137. ^{13}C NMR spectrum of poly(decylene-*co*-HBHE) oxalate [90:10] (Table S2, entry 11).

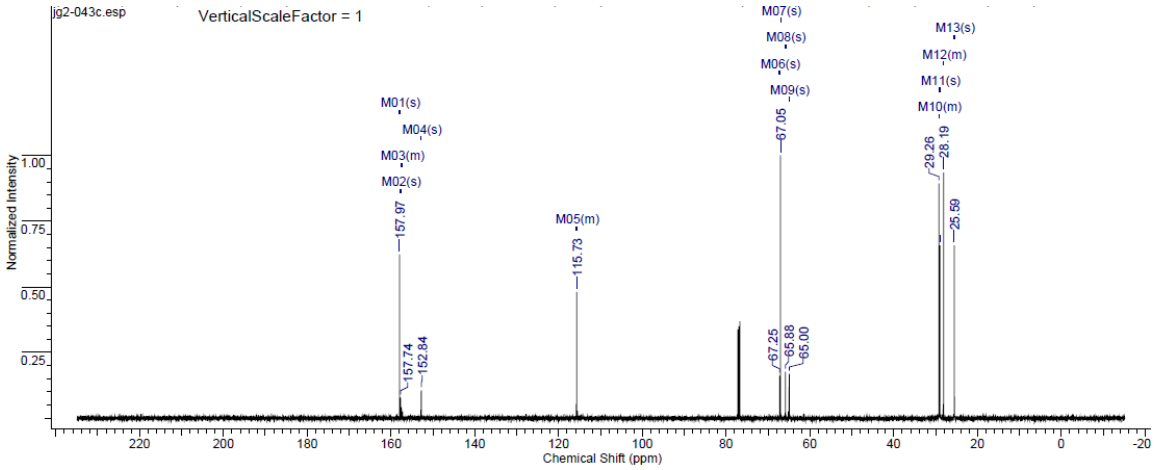


Figure S138. ^{13}C NMR spectrum of poly(decylene-*co*-HBHE) oxalate [80:20] (Table S2, entry 12).

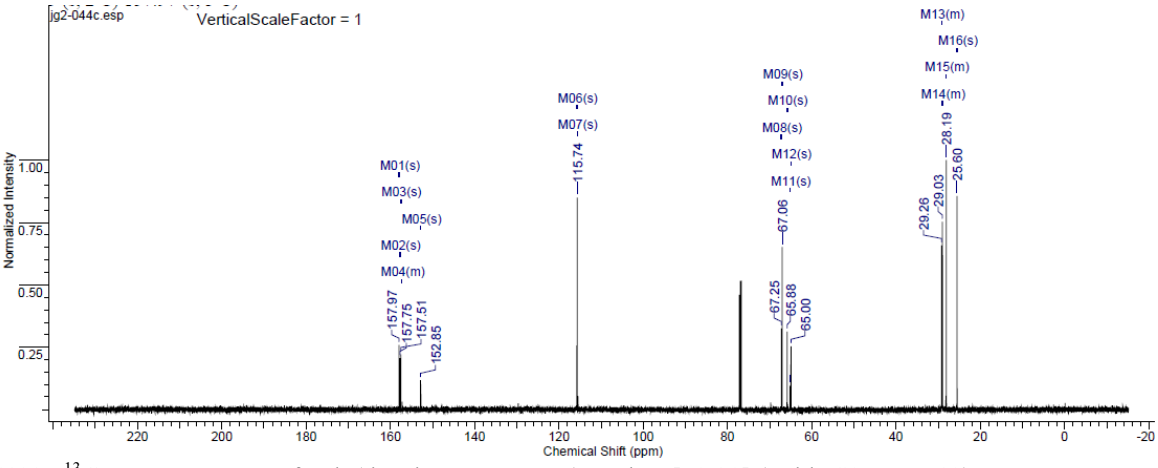


Figure S139. ^{13}C NMR spectrum of poly(decylene-*co*-HBHE) oxalate [70:30] (Table S2, entry 13).

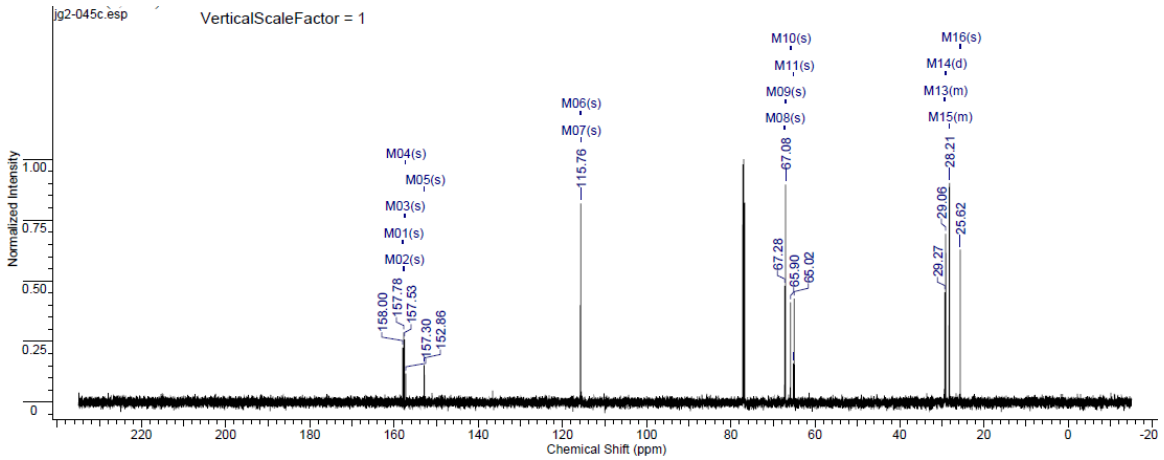


Figure S140. ^{13}C NMR spectrum of poly(decylene-*co*-HBHE) oxalate [60:40] (Table S2, entry 14).

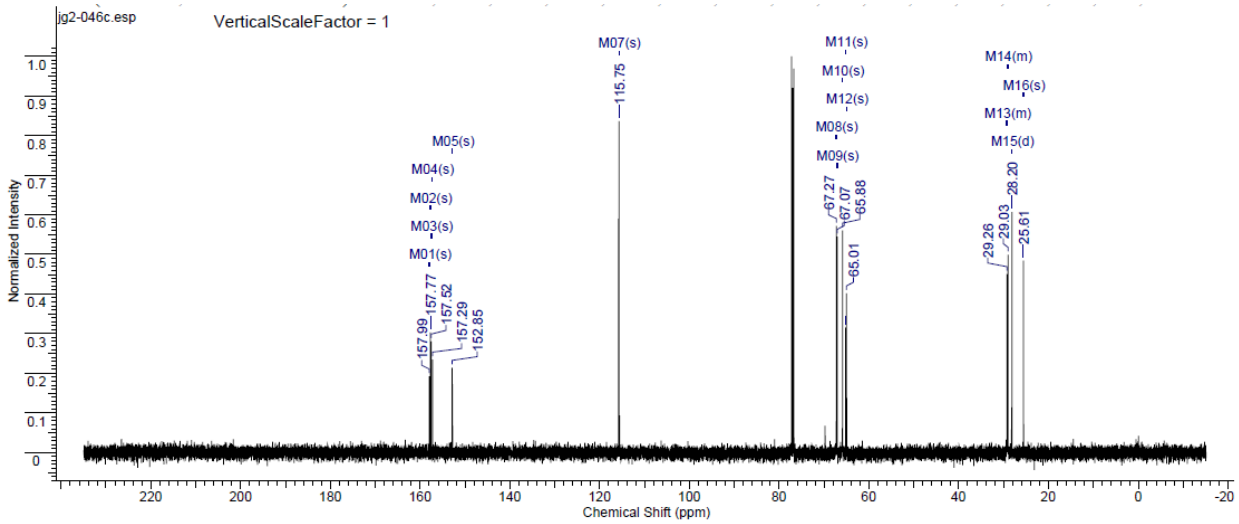


Figure S141. ^{13}C NMR spectrum of poly(decylene-*co*-HBHE) oxalate [50:50] (Table S2, entry 15).

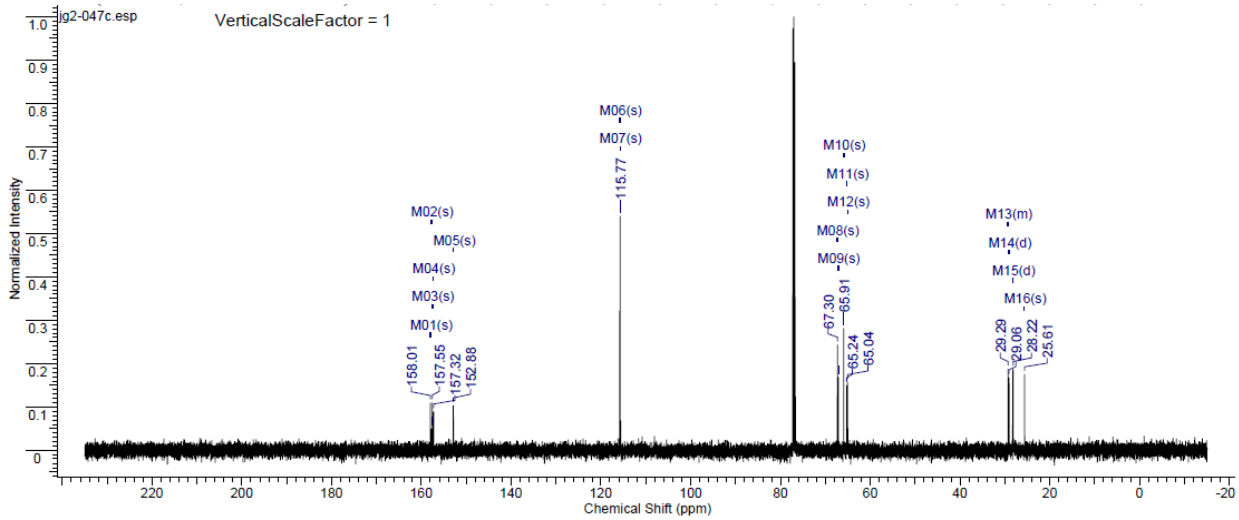


Figure S142. ^{13}C NMR spectrum of poly(decylene-*co*-HBHE) oxalate [40:60] (Table S2, entry 16).

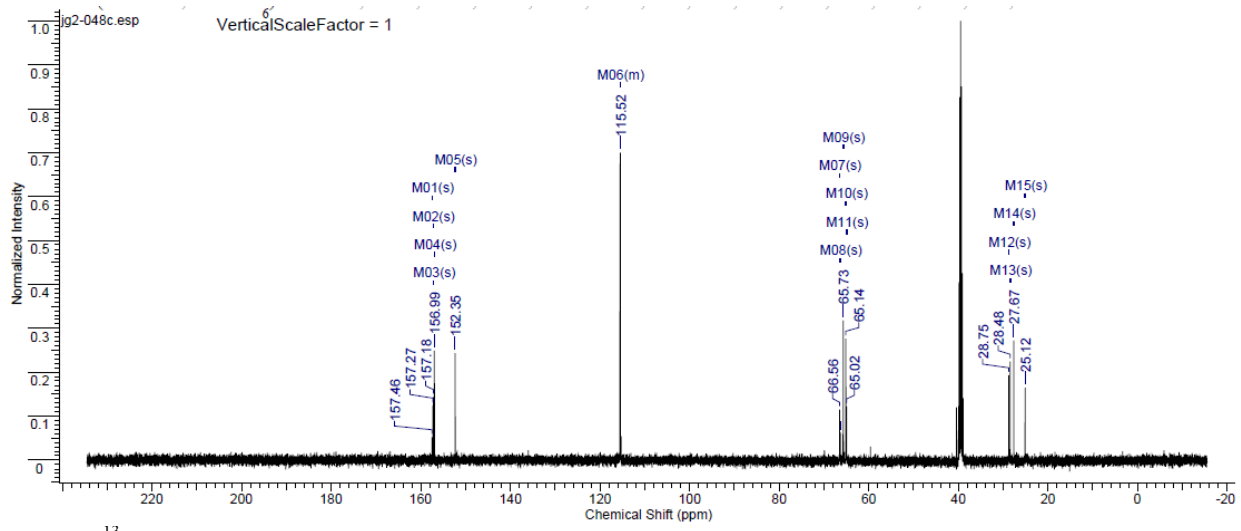


Figure S143. ^{13}C NMR spectrum of poly(decylene-*co*-HBHE) oxalate [30:70] (Table S2, entry 17).

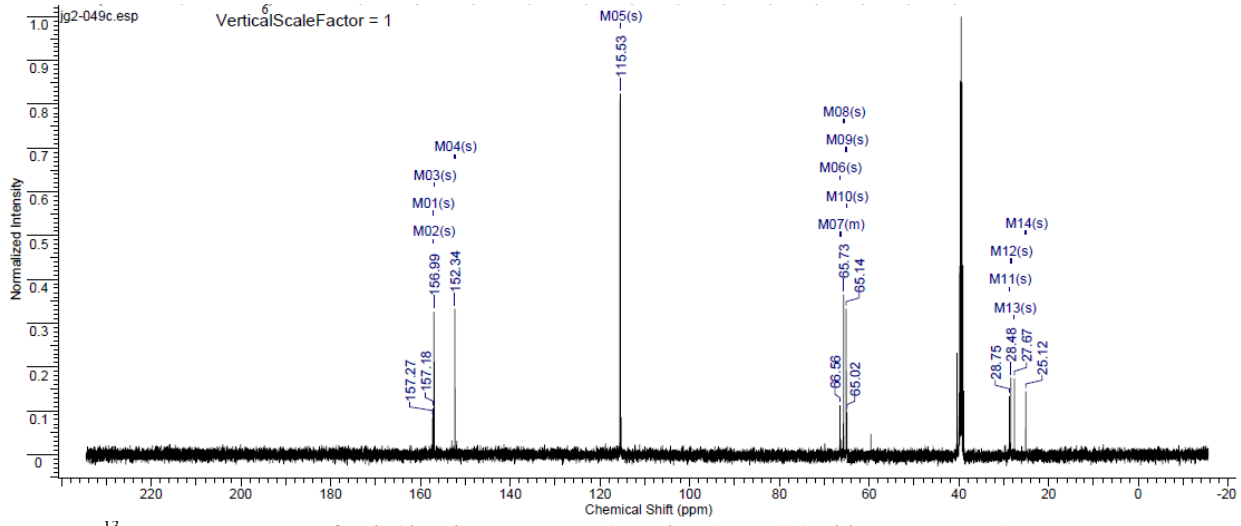


Figure S144. ^{13}C NMR spectrum of poly(decylene-*co*-HBHE) oxalate [20:80] (Table S2, entry 18).

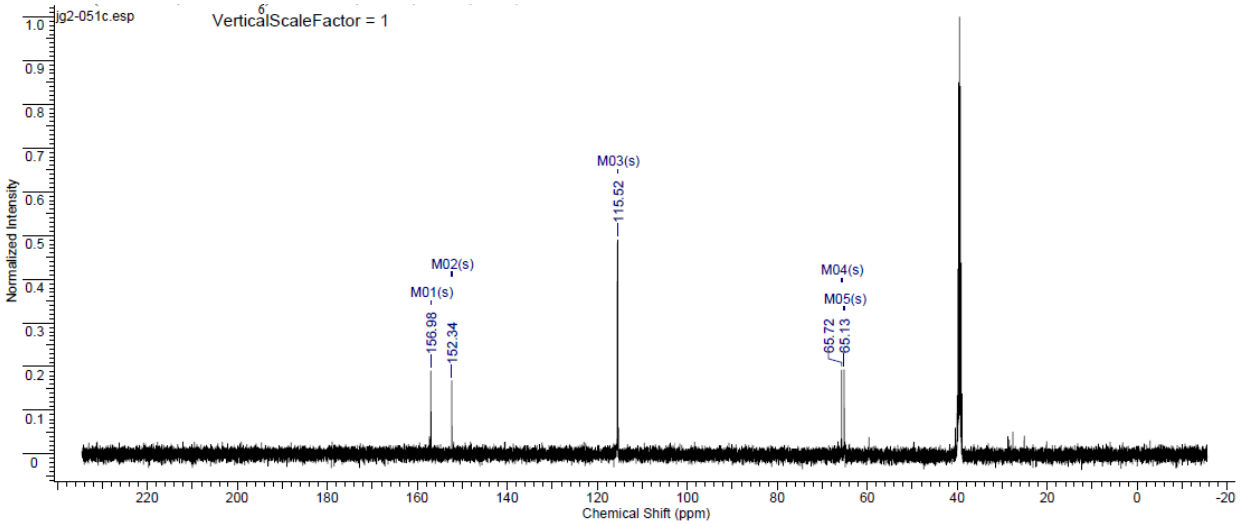


Figure S145. ^{13}C NMR spectrum of poly(decylene-*co*-HBHE) oxalate [10:90] (Table S2, entry 19).

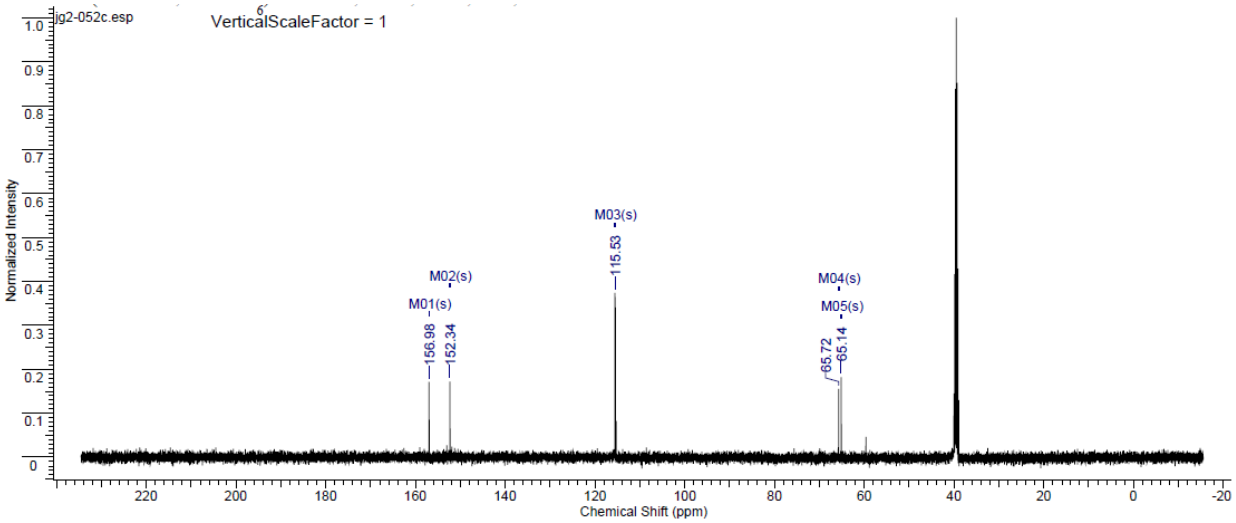
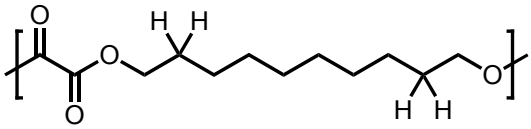


Figure S146. ^{13}C NMR spectrum of poly(HBHE) oxalate (Table S2, entry 20).

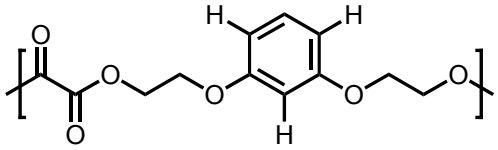
^{1}H NMR Analysis for Copolymer Composition

To check the incorporation of the aromatic monomer for the polymers of Table 2, the NMR spectrum of **polydecylene oxalate** was compared with that of **poly(resorcinol bis(2-hydroxyethyl)ether) oxalate**. The aliphatic copolymer (polydecylene oxalate) has specific peaks near 1.7 ppm that are assigned to the four hydrogens beta to the ester oxygen.



polydecylene oxalate

In contrast, the aromatic copolymer (poly(RBHE) oxalate) shows peaks near 6.5 ppm that correspond to the three hydrogens ortho to oxygen in the aromatic part of the repeat unit.

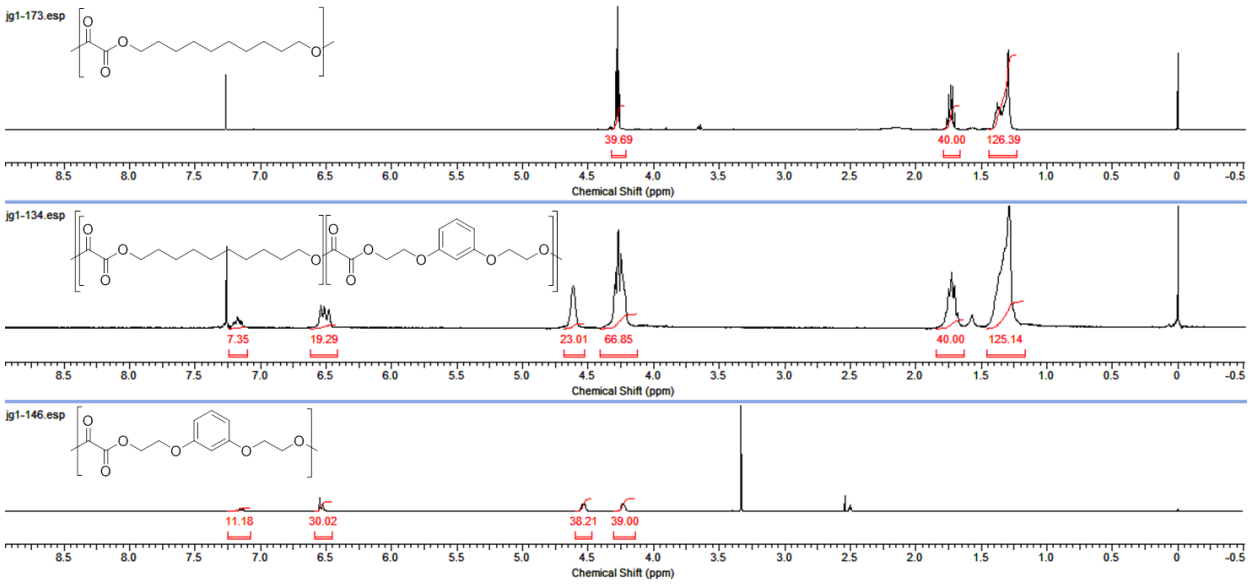


poly(resorcinol bis(2-hydroxyethyl)ether) oxalate

Aliphatic/aromatic copolymers should show peaks in both regions and by measuring the intensity of these peaks and calculating the ratio, the relative incorporation can be obtained. The figure below shows, respectively, the ^{1}H NMR spectra of:

- the aliphatic polydecylene oxalate (from Table S1, Entry 9),
- the 60:40 (feed ratio, aliphatic:aromatic) copolymer (from Table S2, Entry 4),
- and the aromatic poly(RBHE) oxalate (from Table S2, Entry 10).

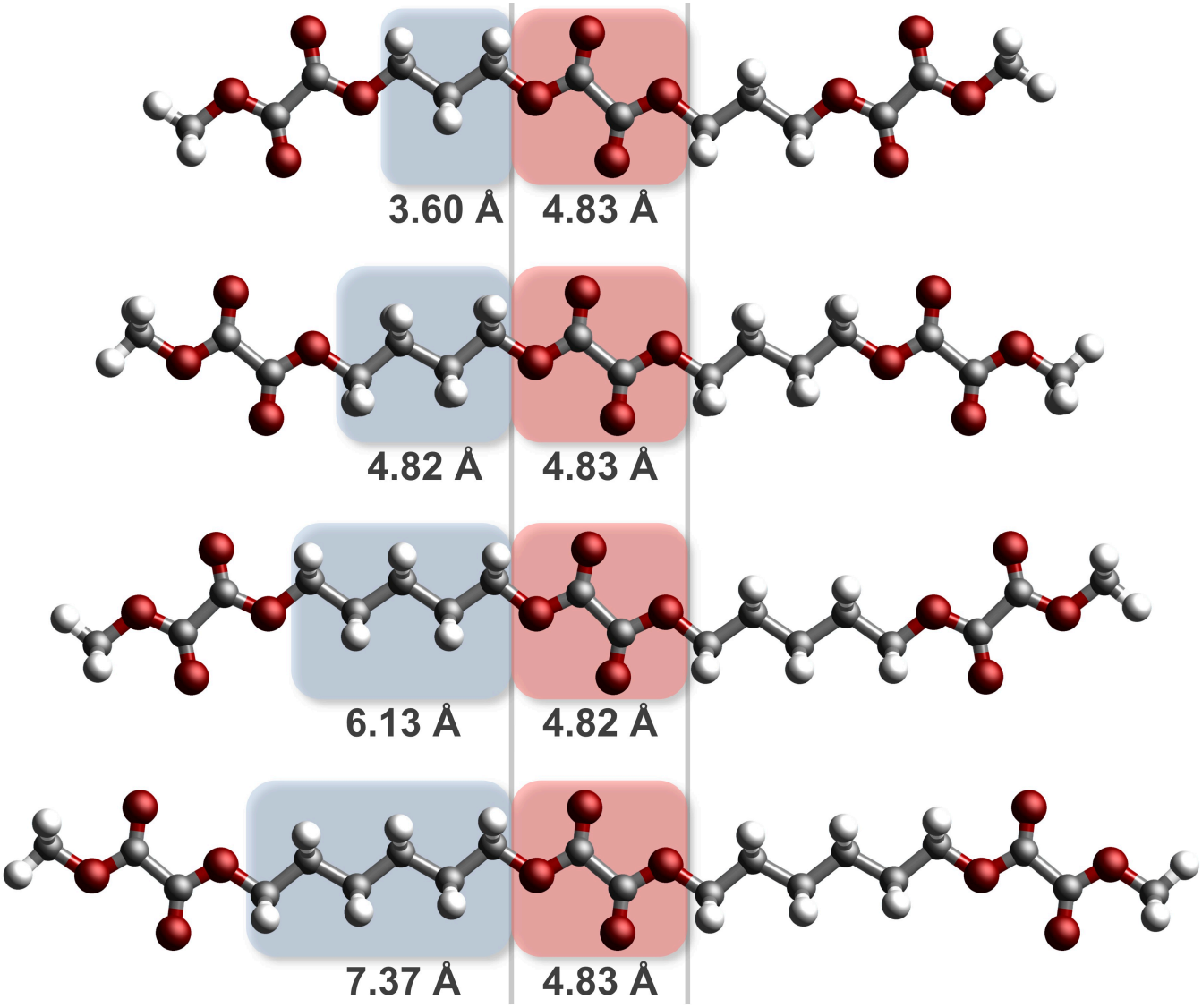
Integration of the peaks for the 60:40 aliphatic:aromatic copolymer spectrum gives an area of 40 related to 4 aliphatic protons at 1.7 ppm and an area of 19.29 related to 3 aromatic protons at 6.5 ppm. Thus we have a [40/4]:[19.29/3] = 10:6.43 ratio of aliphatic:aromatic blocks present. This computes to 10/[10+6.43] = 60.9% aliphatic composition and 6.43/[10+6.43] = 39.1% aromatic composition. This is in close agreement with the 60:40 feed ratio of aliphatic:aromatic monomers employed. All the other compositions (from Table S2) displayed a similar agreement between the feed ratio and the measured incorporation ratio.



In a similar way, the calculation of the aromatic incorporation of the poly(HBHE) oxalate copolymers was calculated. In this case, the four beta hydrogens of the aliphatic segment were compared with the four aromatic hydrogens of the aromatic segment.

Computational Studies of Polyoxalate Segments

Polyoxalate segments were created in the extended chain conformation and subjected to energy minimization with DFT calculations (B3LYP 6-31G*) in the gas phase with MacSpartan '10 sofware. The extended chain conformation was enforced by locking all dihedral angles at 180°. These are not necessarily conformational minima, but are local minima employed to estimate lengths of the component aliphatic segments (blue) and oxalate segments (red) of the chain. Distances were measured between bond midpoints.



Shown are segments representing polypropylene oxalate, polybutylene oxalate, polypentylene oxalate, and polyhexylene oxalate, respectively.