

Supporting Information

for

Correlating Chlorinated Polyethylene Molecular Structure to Compatibilization Efficiency for Mixed Polymer Waste

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^1H NMR Spectra of Cl_2COE Monomer:

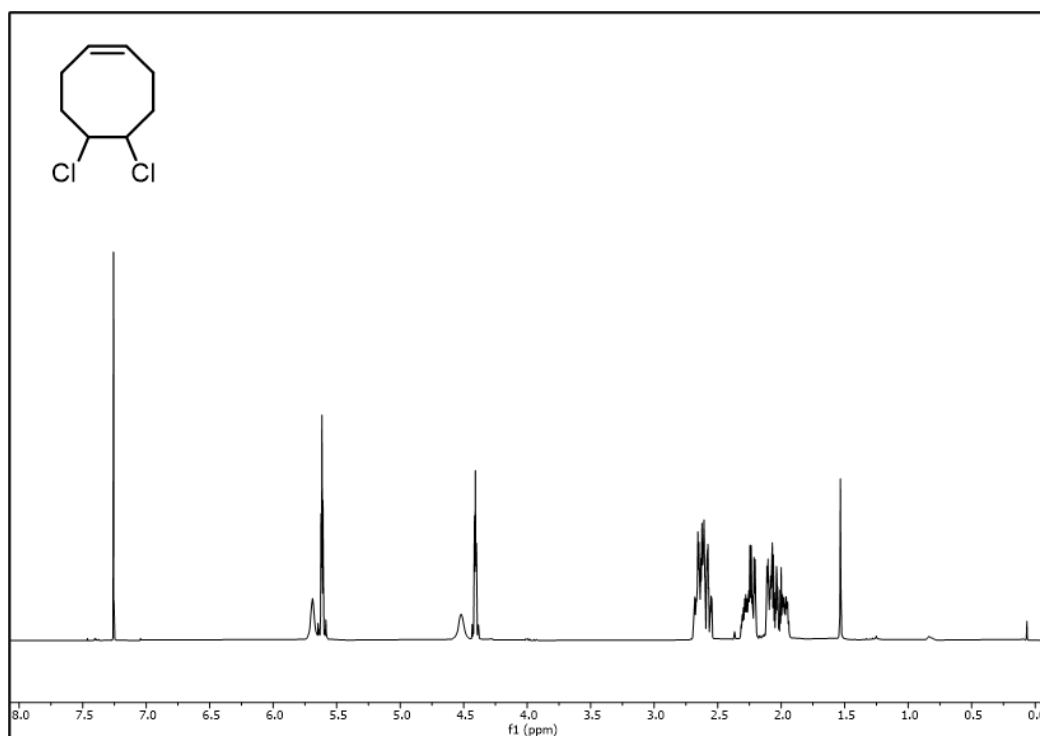


Figure S1. ^1H NMR spectrum of Cl_2COE monomer in CDCl_3 .

^1H NMR Spectra of Synthesized c-PE Compatibilizers:

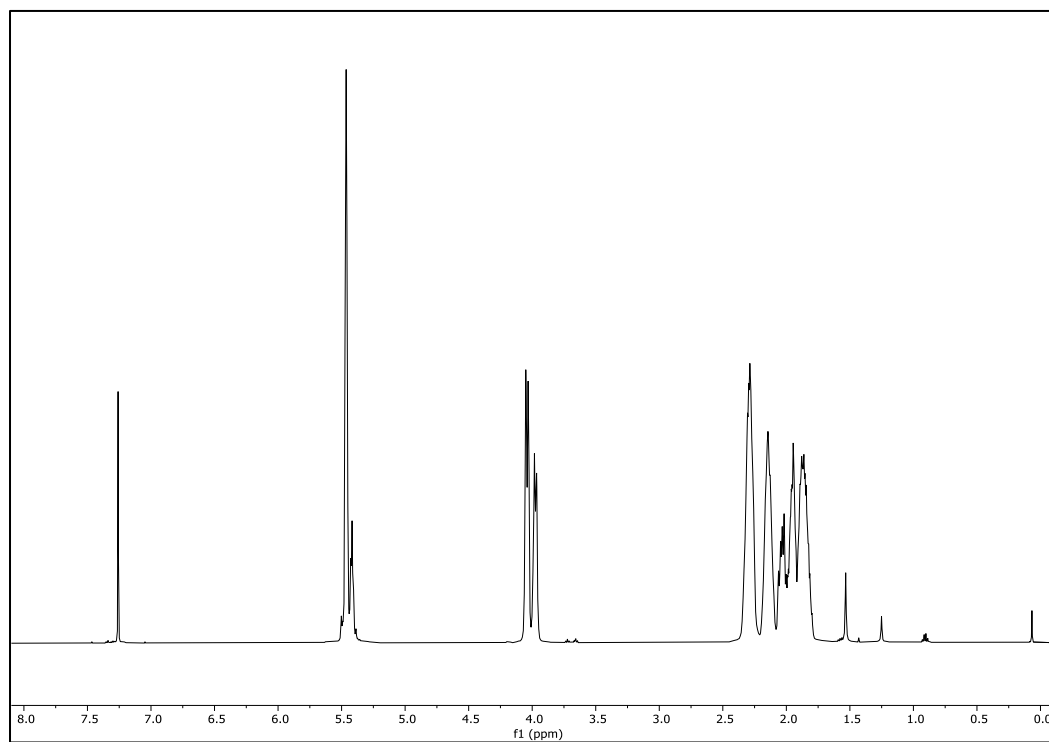


Figure S2. ^1H NMR spectrum of S100-3 prior to hydrogenation in CDCl_3 .

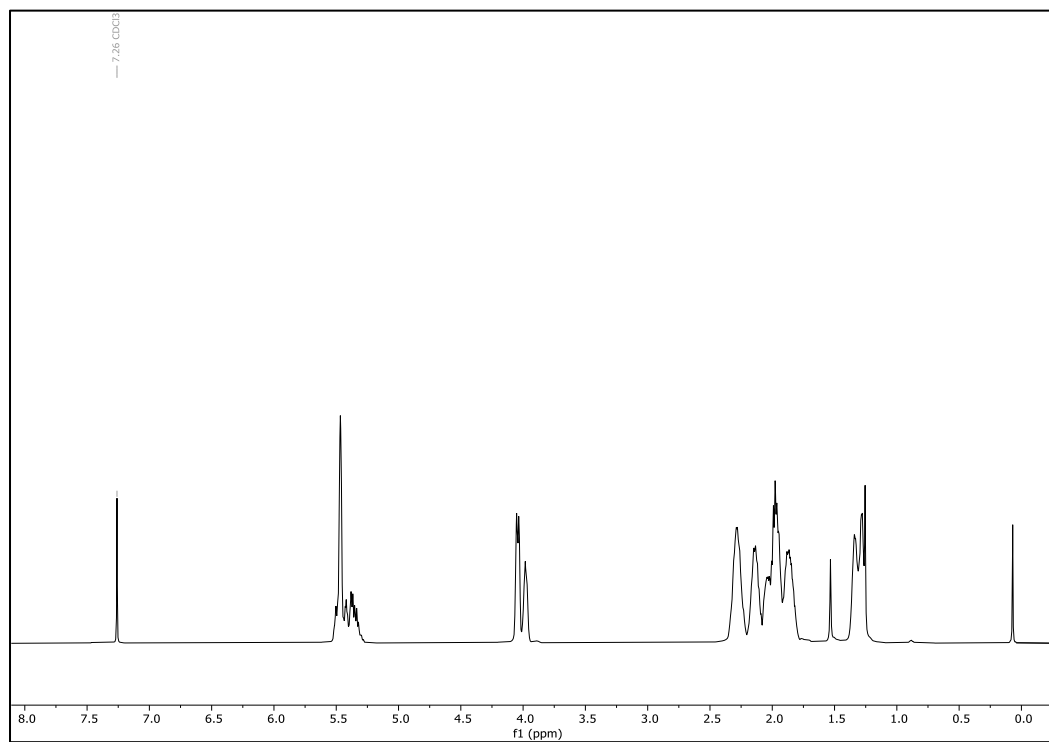


Figure S3. ^1H NMR spectrum of S75-3 prior to hydrogenation in CDCl_3 .

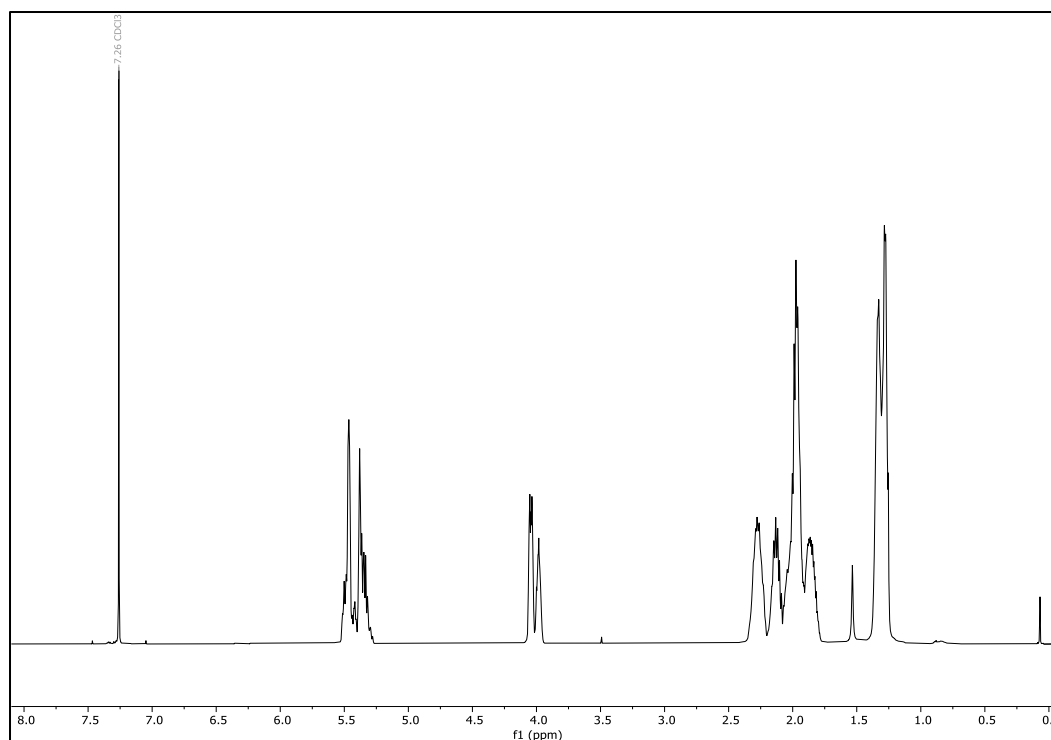


Figure S4. ^1H NMR spectrum of S50-1 prior to hydrogenation in CDCl_3 .

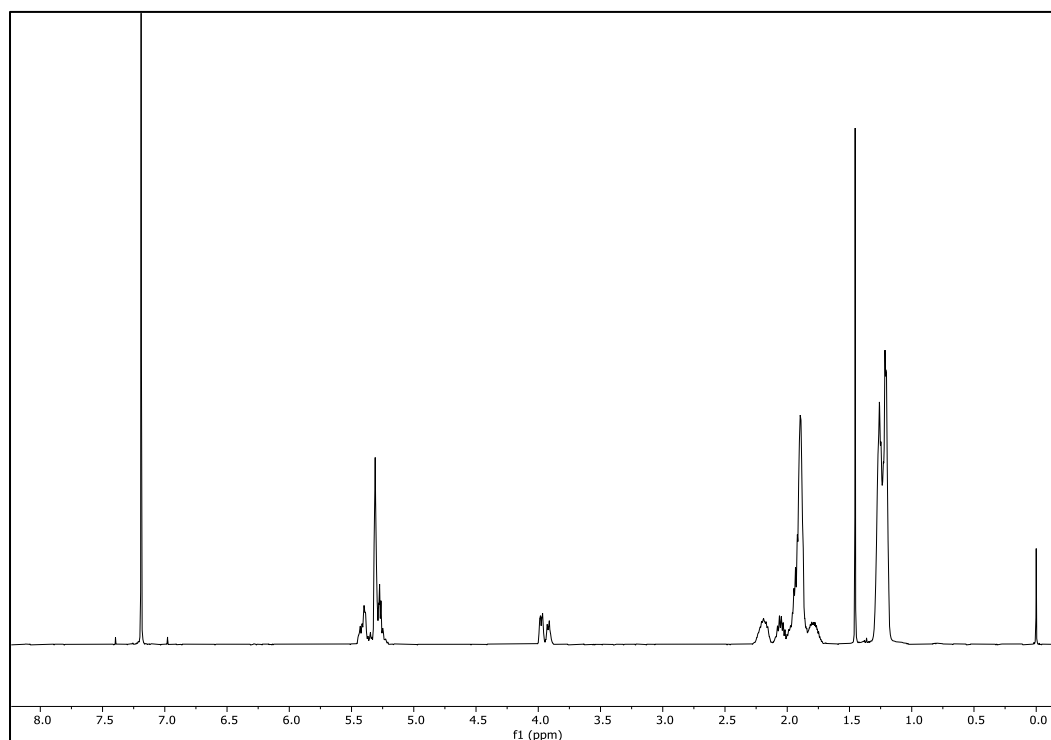


Figure S5. ^1H NMR spectrum of S25-1 prior to hydrogenation in CDCl_3 .

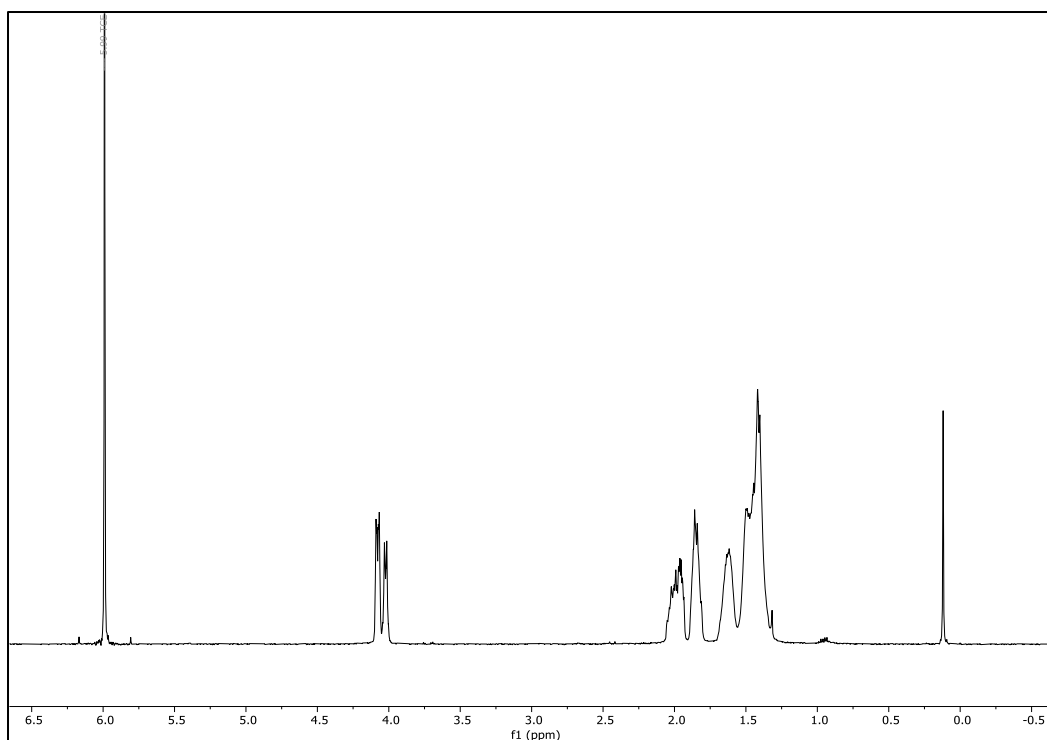


Figure S6. ^1H NMR spectrum of S100-3 dissolved in 1,1,2,2-tetrachloroethane- d_2 .

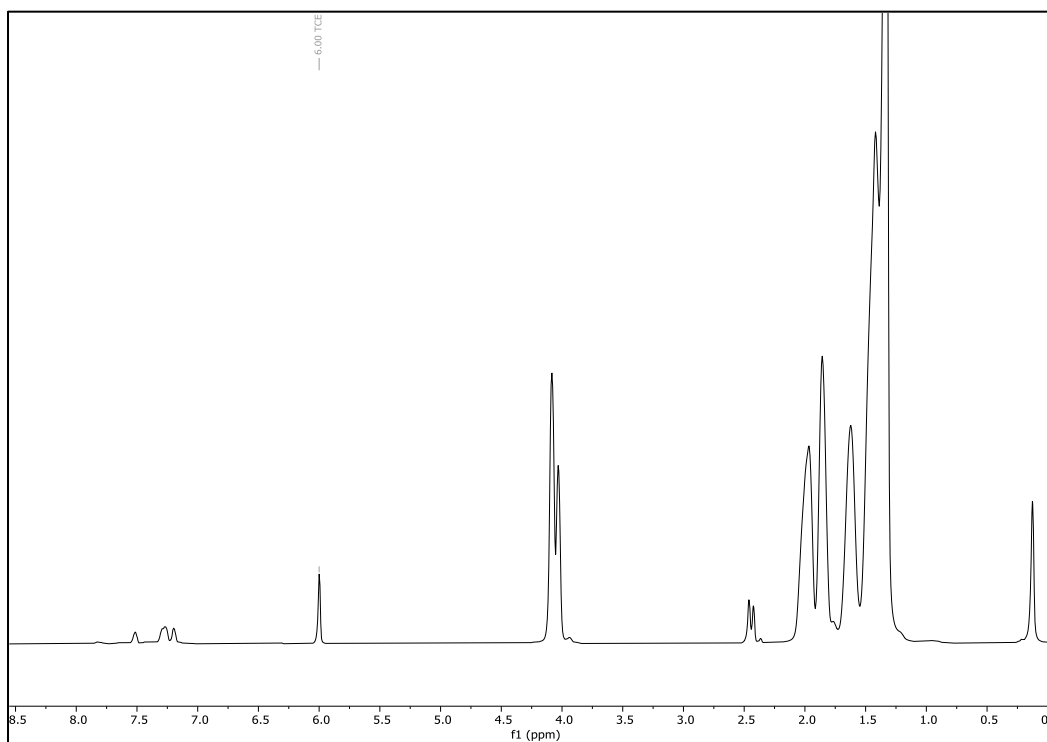


Figure S7. ^1H NMR spectrum of S75-3 dissolved in 1,1,2,2-tetrachloroethane- d_2 .

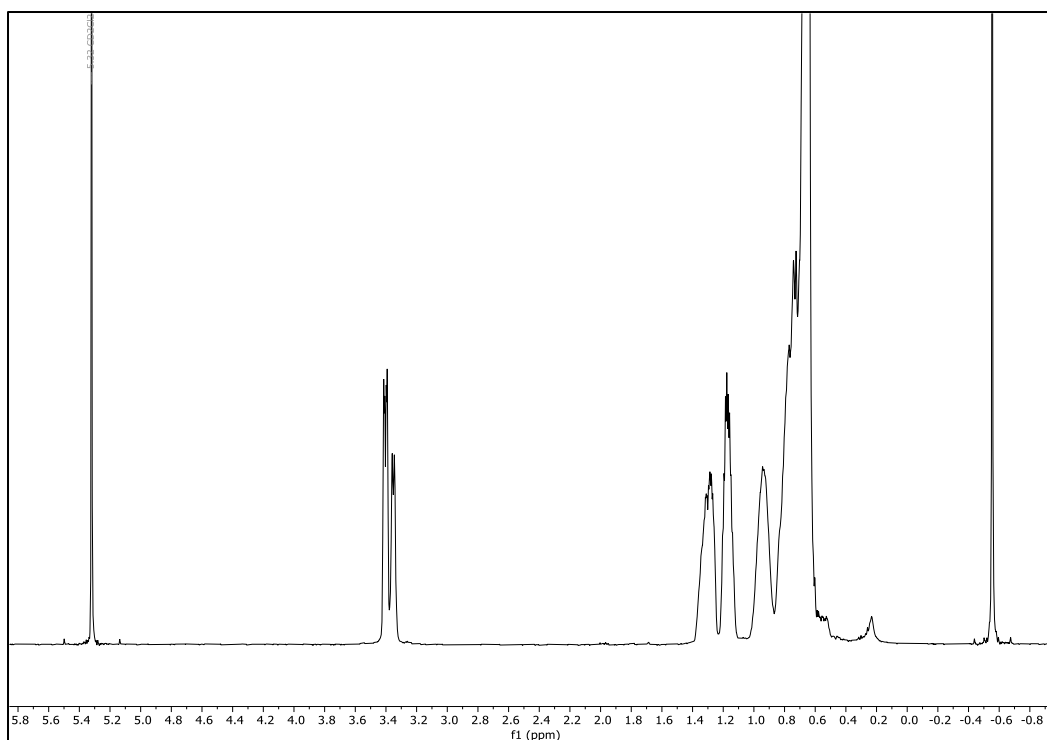


Figure S8. ^1H NMR spectrum of S50-1 dissolved in 1,1,2,2-tetrachloroethane- d_2 .

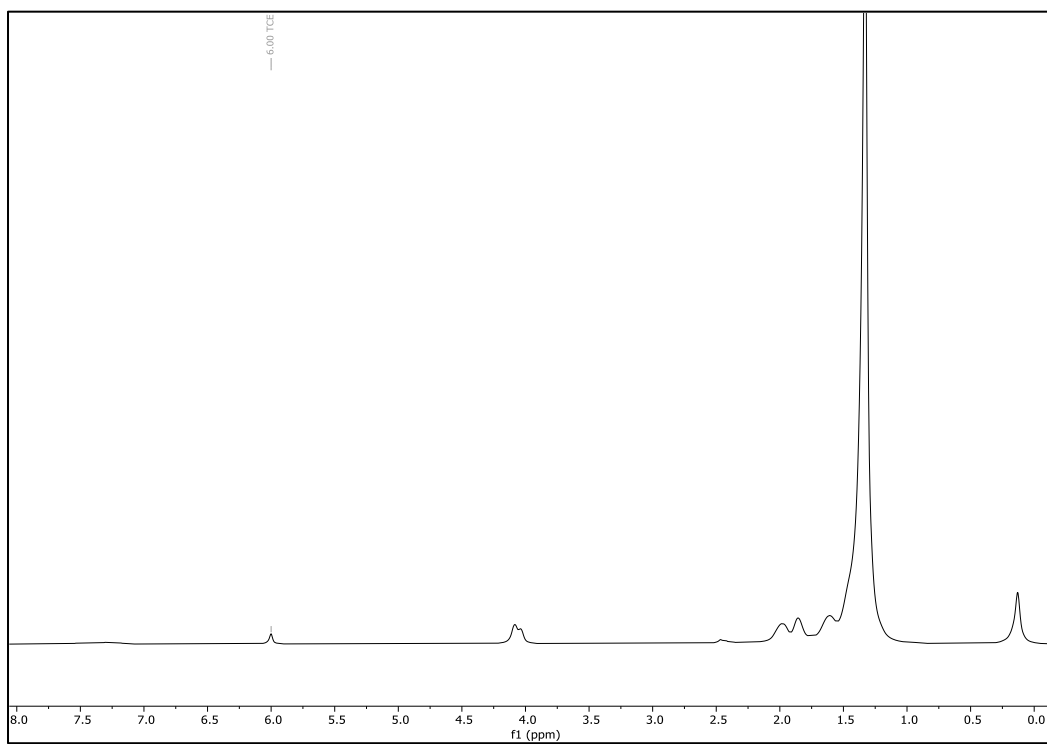


Figure S9. ^1H NMR spectrum of S25-1 dissolved in 1,1,2,2-tetrachloroethane- d_2 .

^1H NMR Spectra of Commercial c-PE Compatibilizers:

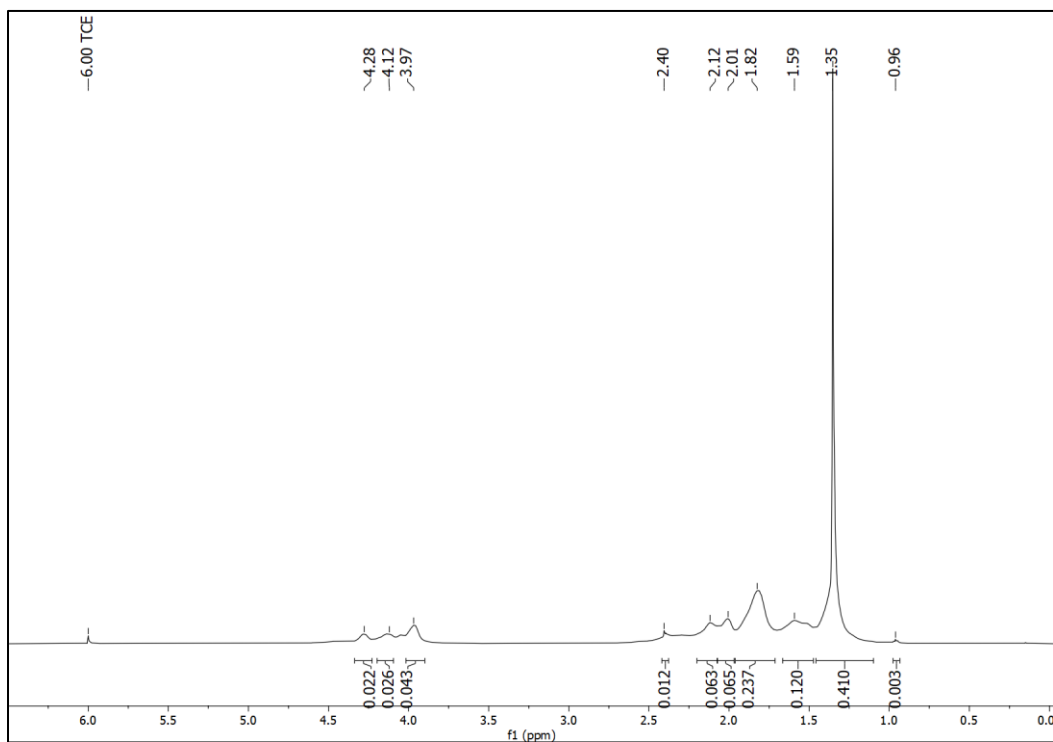


Figure S10. ^1H NMR spectrum of R1 dissolved in 1,1,2,2-tetrachloroethane- d_2 .

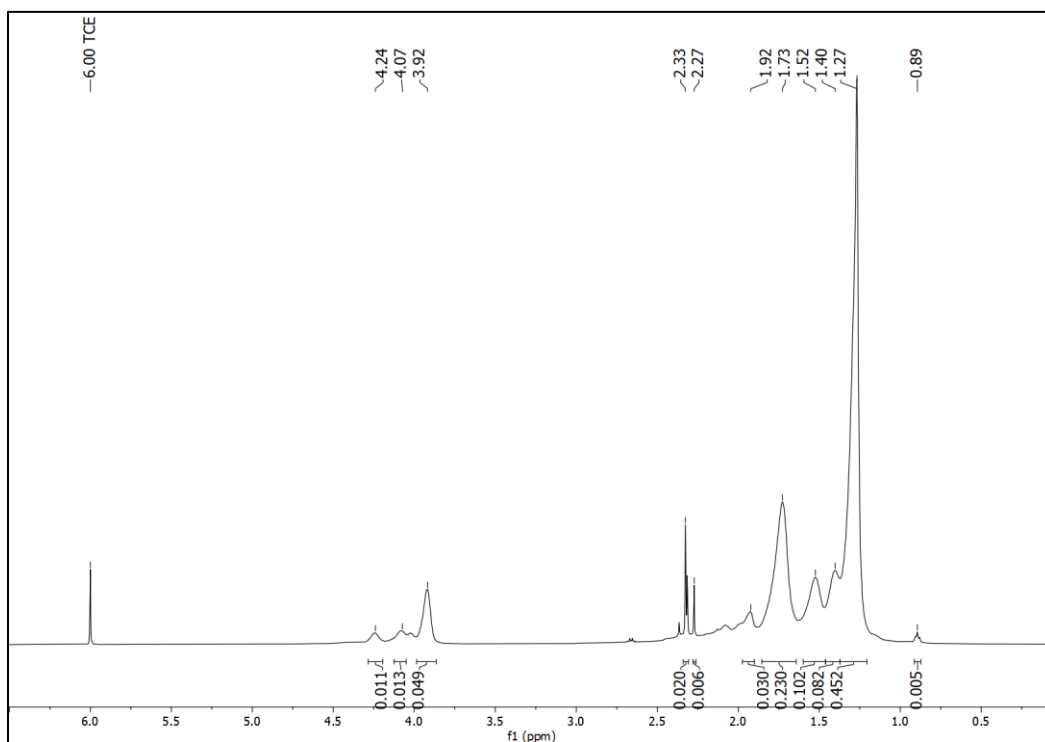


Figure S11. ^1H NMR spectrum of B1 dissolved in 1,1,2,2-tetrachloroethane- d_2 .

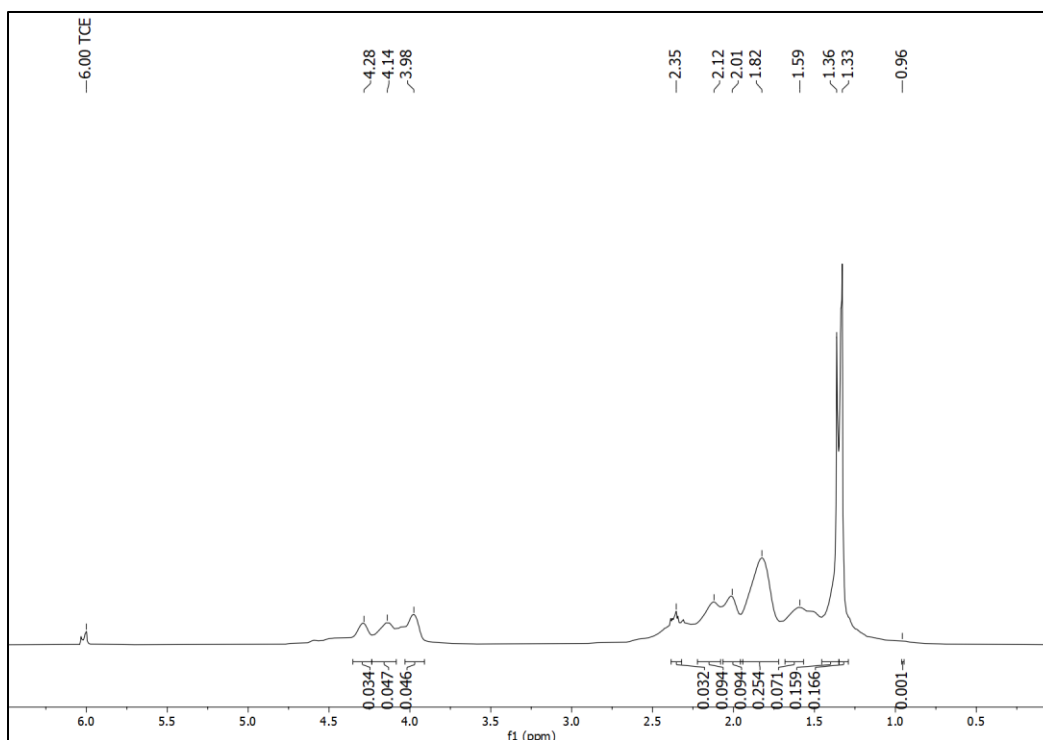


Figure S12. ^1H NMR spectrum of B2 dissolved in 1,1,2,2-tetrachloroethane- d_2 .

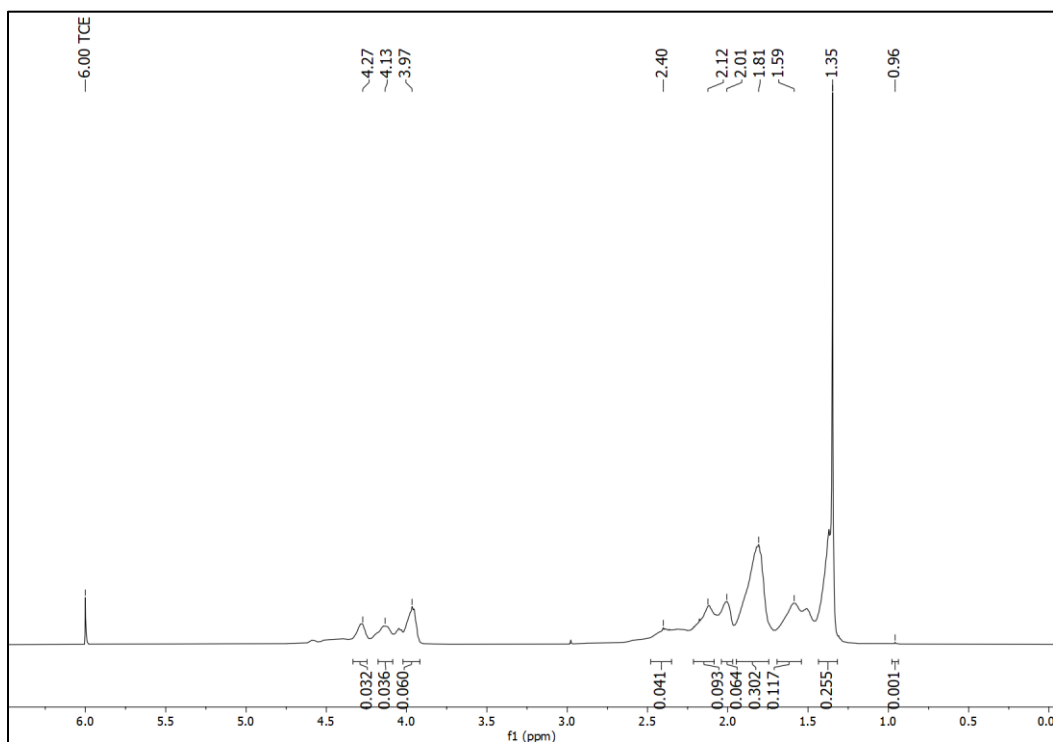


Figure S13. ^1H NMR spectrum of B3 dissolved in 1,1,2,2-tetrachloroethane- d_2 .

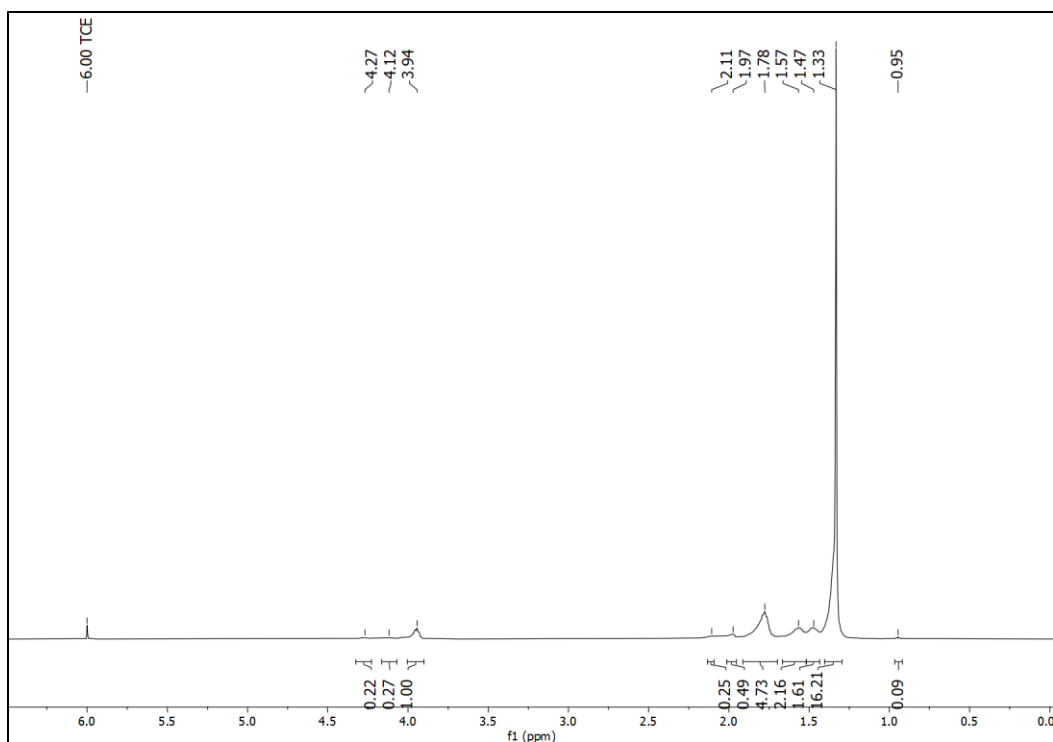


Figure S14. ¹H NMR spectrum of **B4** dissolved in 1,1,2,2-tetrachloroethane-d₂.

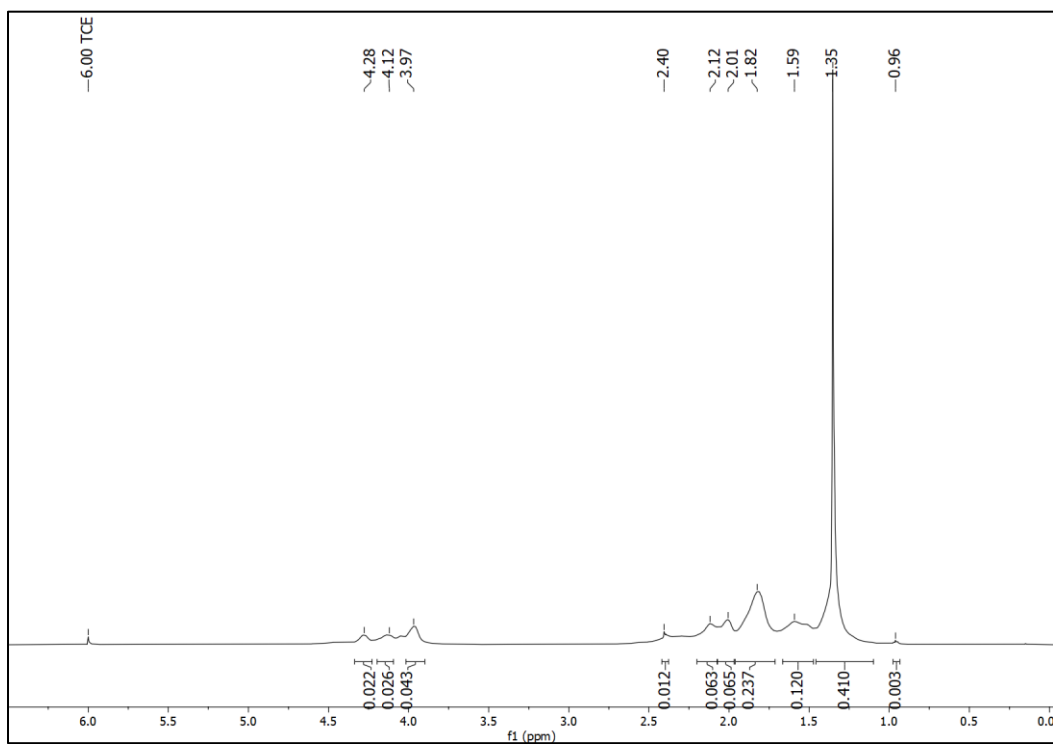


Figure S15. ¹H NMR spectrum of **B5** dissolved in 1,1,2,2-tetrachloroethane-d₂.

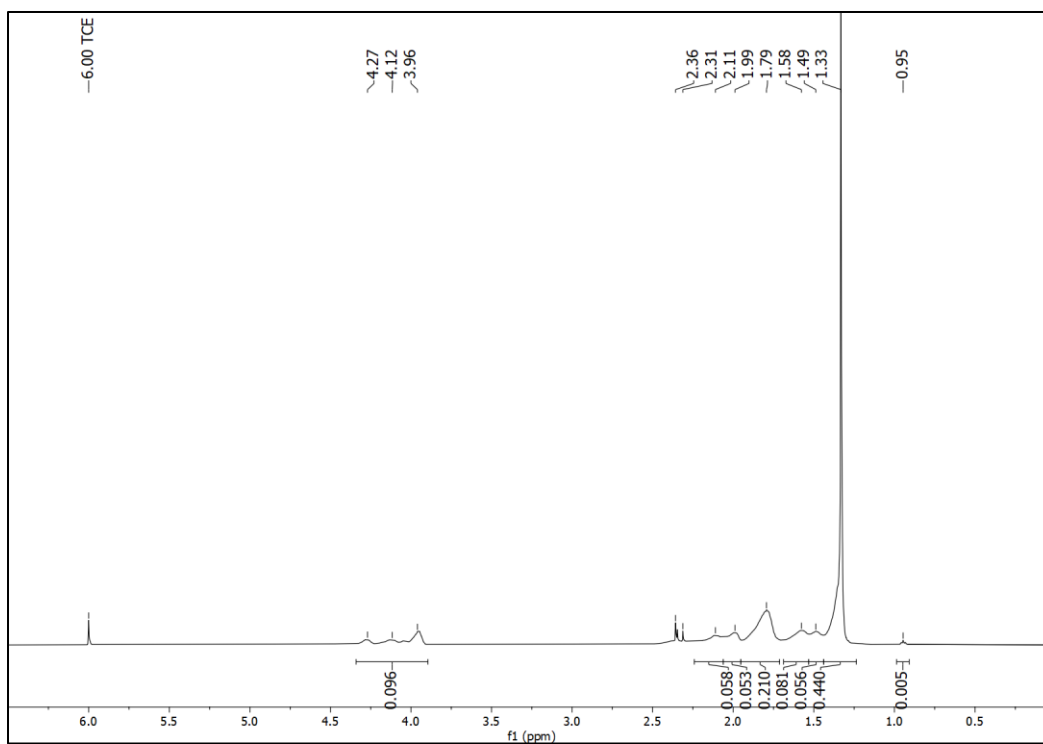


Figure S16. ¹H NMR spectrum of **B6** dissolved in 1,1,2,2-tetrachloroethane-*d*₂.

Quantitative ^{13}C NMR Spectra of c-PE Compatibilizers:

Samples of 5 wt% c-PE in 1,1,2,2-tetrachloroethylene- d_2 (Cambridge Isotope Labs) were prepared for NMR analysis.¹ For the commercial c-PEs, the samples were heated to 110 °C in a glove box to ensure solubility and prevent oxidation. Quantitative ^{13}C NMRs were run on a Bruker Avance 400 MHz at 90 °C to prevent precipitation. The synthesized c-PE ^{13}C samples were run on a Varian 500 MHz NMR at temperatures between 60 - 80 °C depending on solubility.

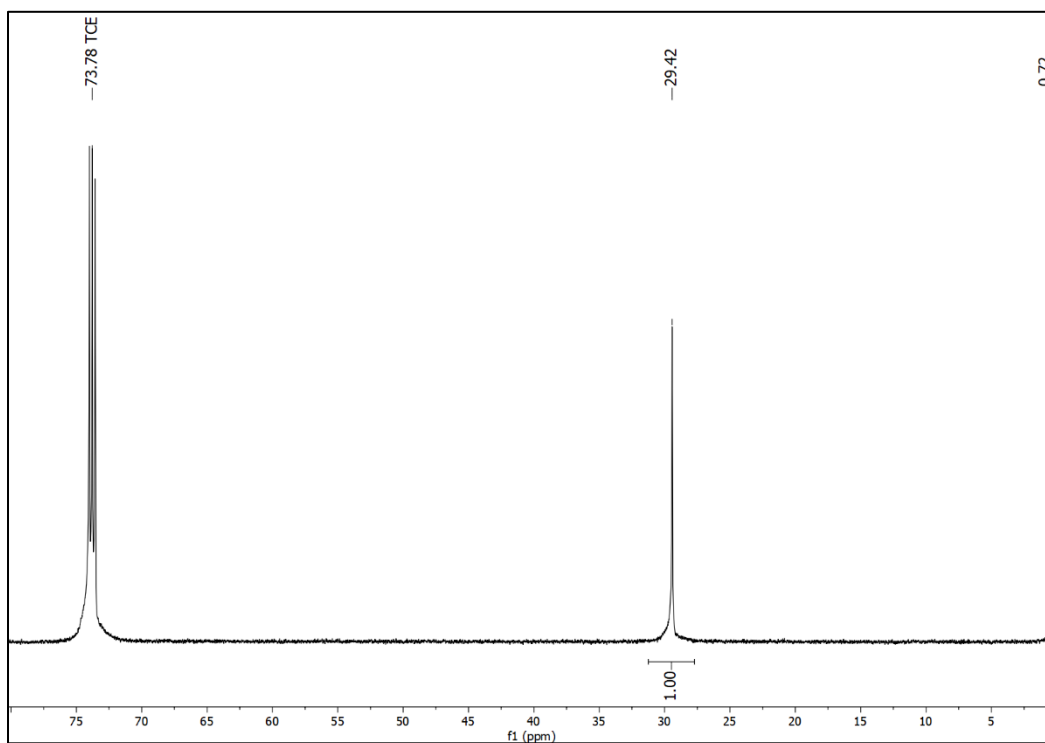


Figure S17. Quantitative ^{13}C NMR of PCOE dissolved in 1,1,2,2-tetrachloroethane- d_2 .

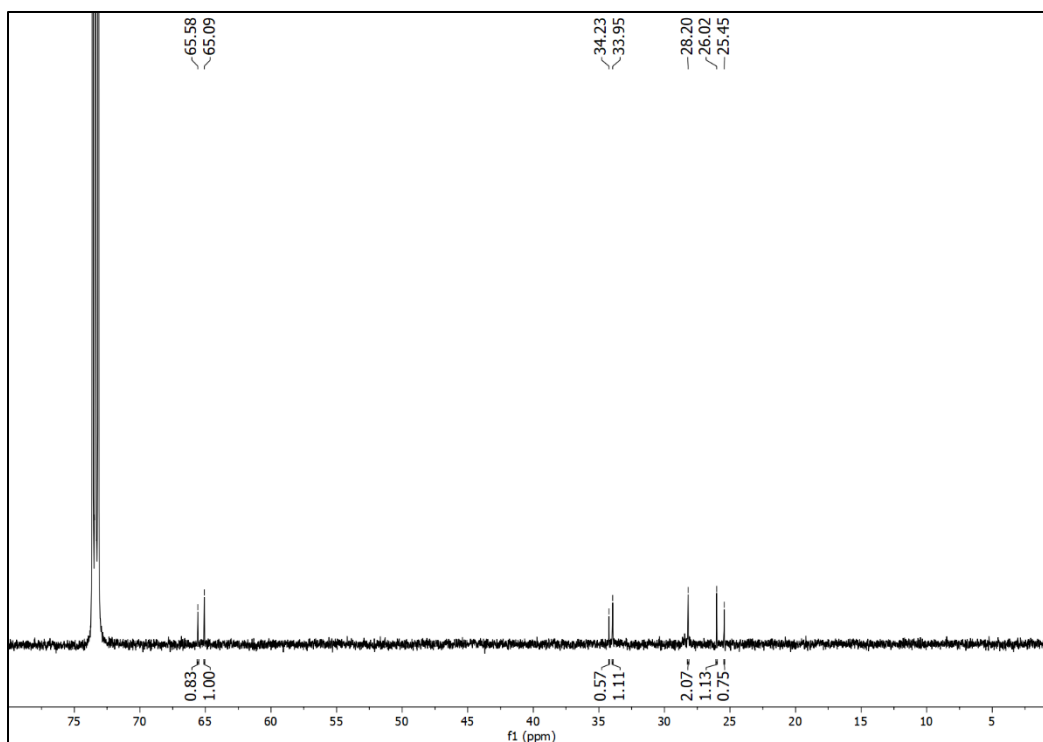


Figure S18. Quantitative ^{13}C NMR of S100-3 dissolved in 1,1,2,2-tetrachloroethane- d_2 .

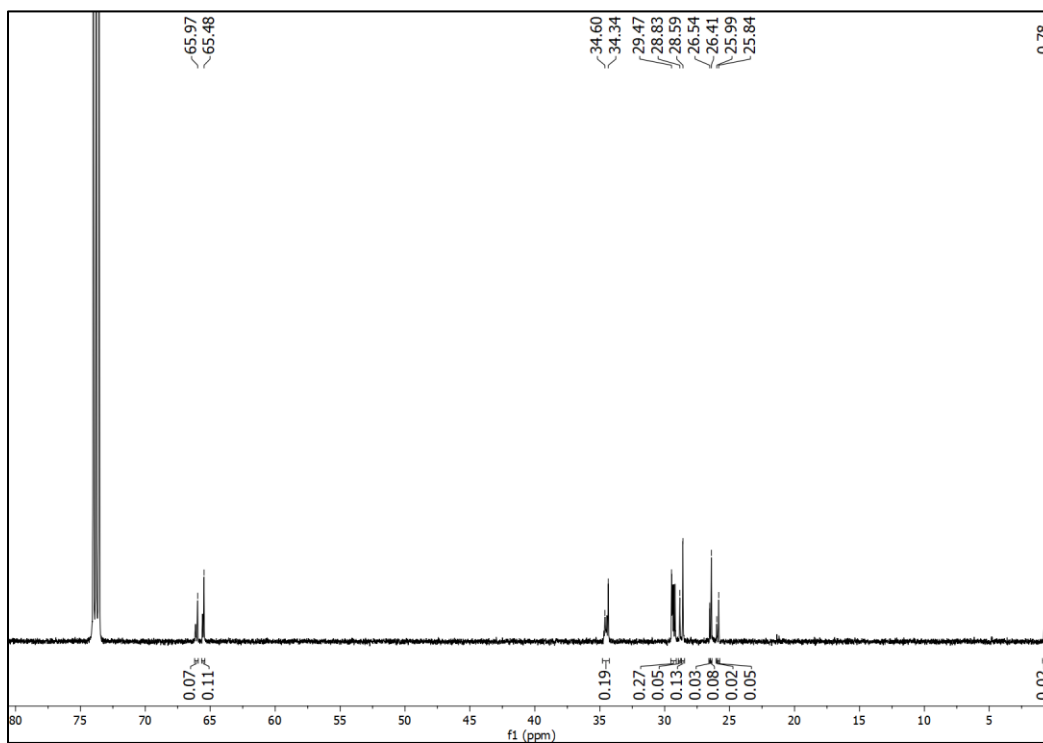


Figure S19. Quantitative ^{13}C NMR of S75-3 dissolved in 1,1,2,2-tetrachloroethane- d_2 .

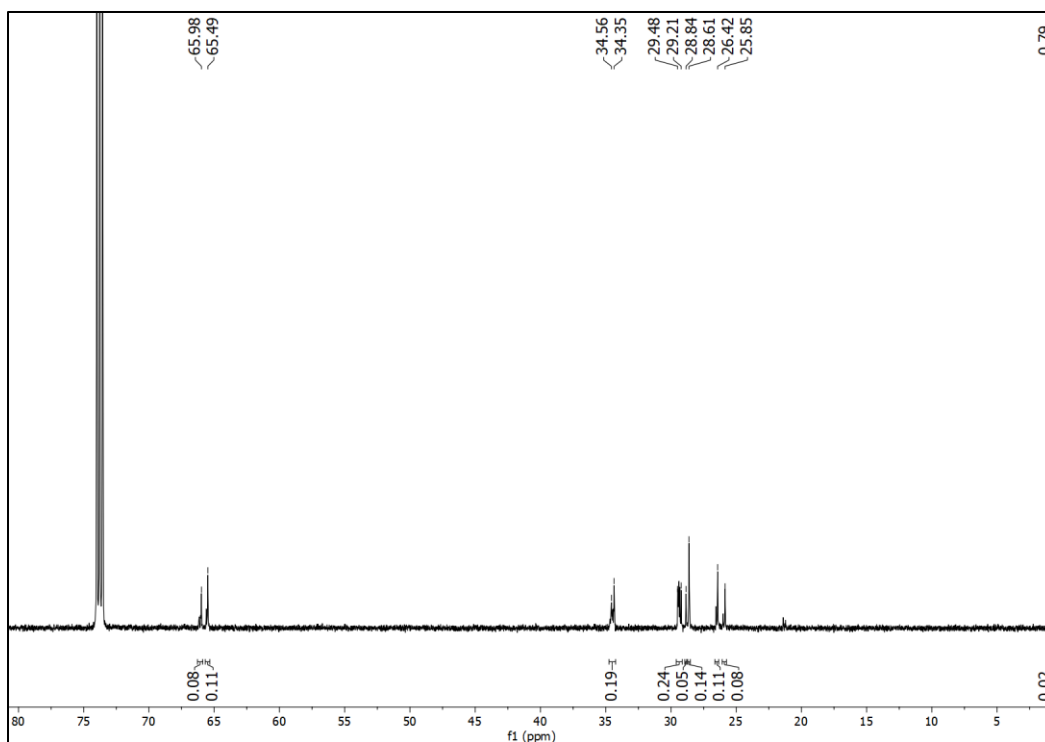


Figure S20. Quantitative ^{13}C NMR of S75-4 dissolved in 1,1,2,2-tetrachloroethane- d_2 .

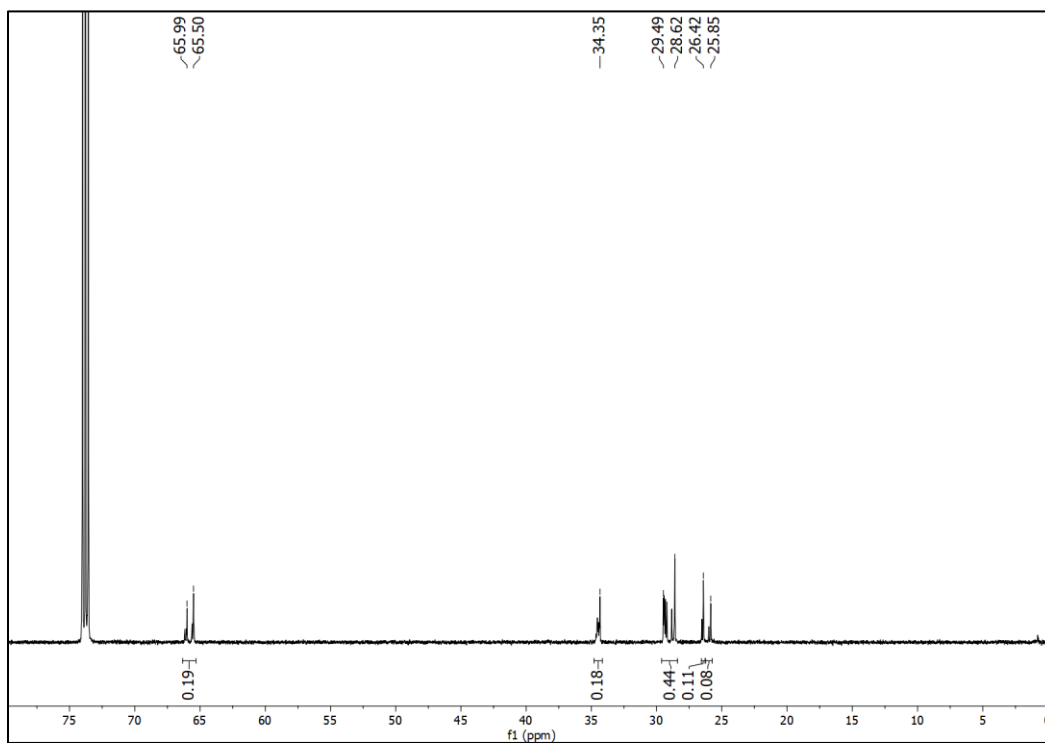


Figure S21. Quantitative ^{13}C NMR of S75-5 dissolved in 1,1,2,2-tetrachloroethane- d_2 .

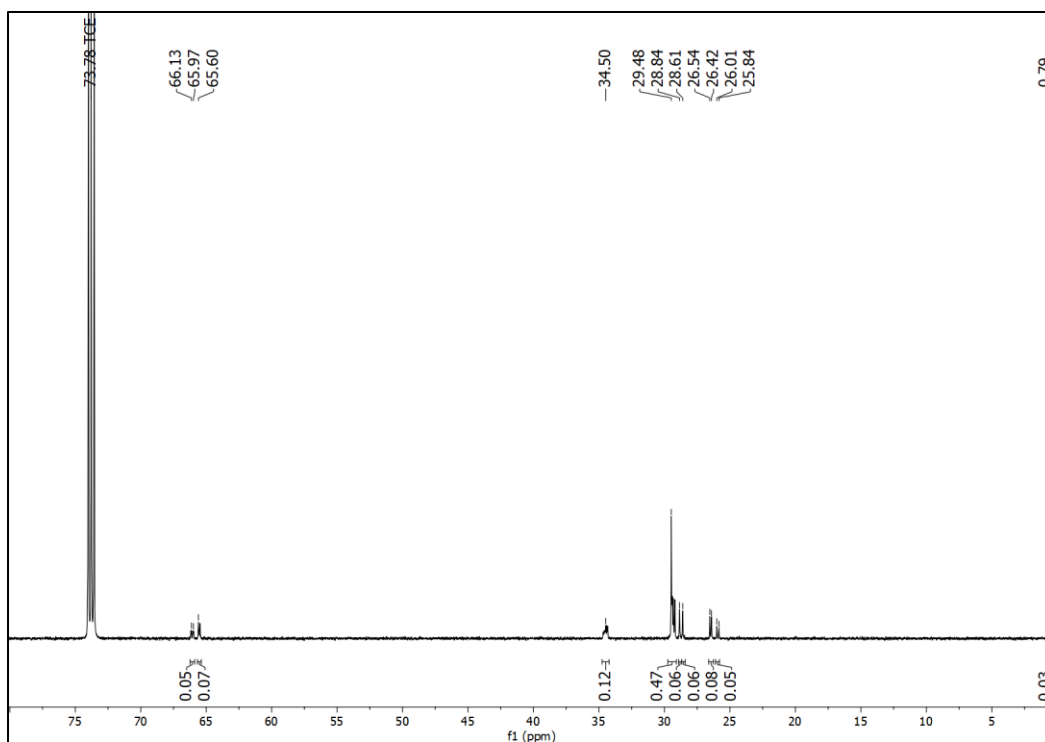


Figure S22. Quantitative ^{13}C NMR of S50-2 dissolved in 1,1,2,2-tetrachloroethane- d_2 .

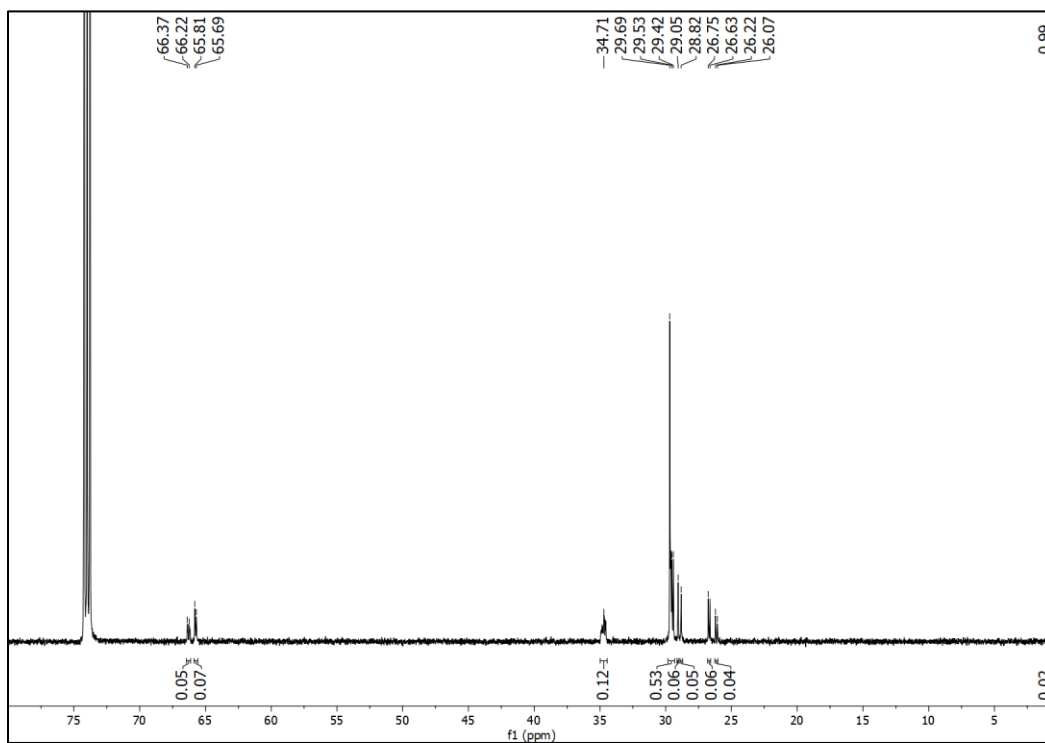


Figure S23. Quantitative ^{13}C NMR of S50-3 dissolved in 1,1,2,2-tetrachloroethane- d_2 .

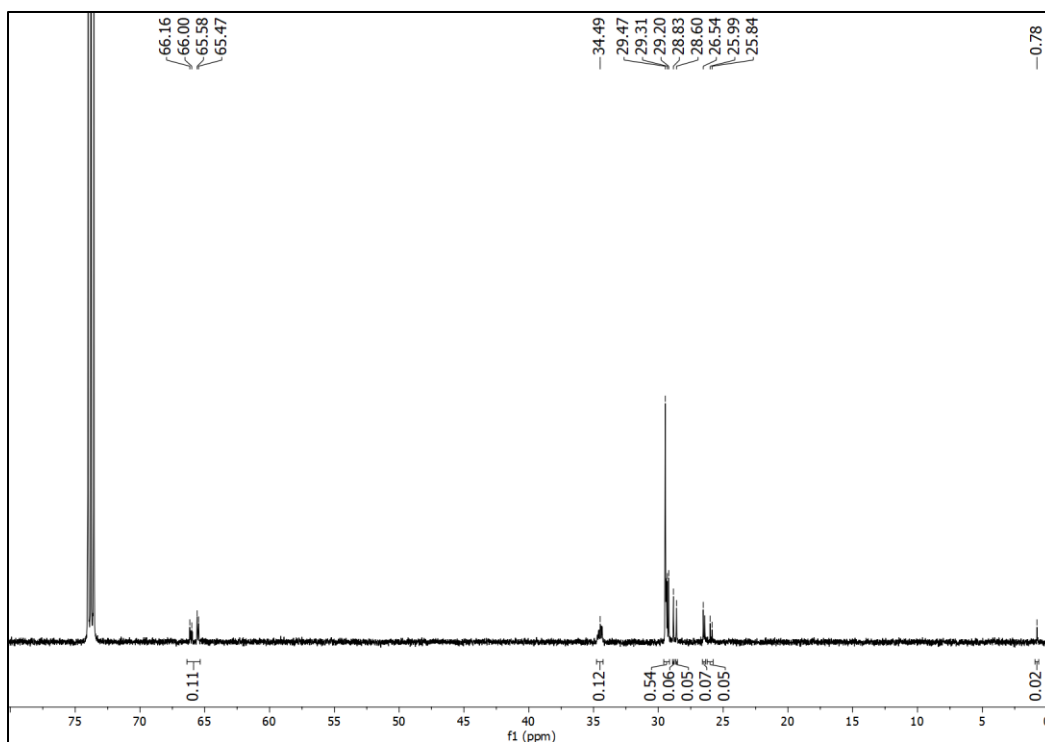


Figure S24. Quantitative ^{13}C NMR of S50-5 dissolved in 1,1,2,2-tetrachloroethane- d_2 .

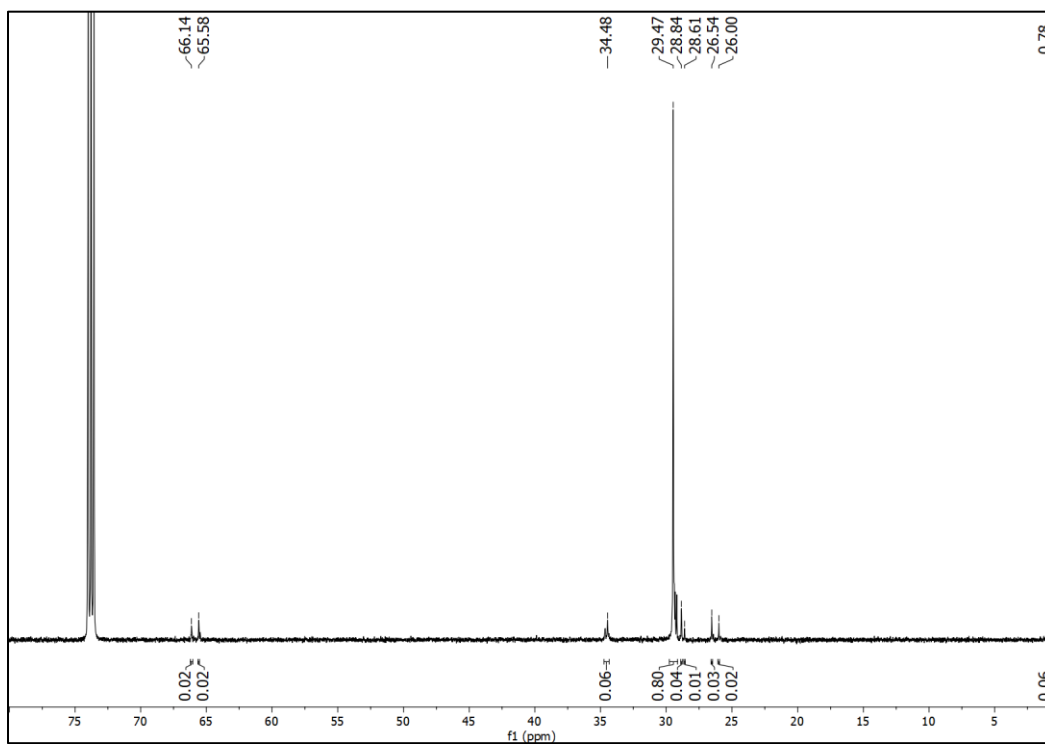


Figure S25. Quantitative ^{13}C NMR of S25-1 dissolved in 1,1,2,2-tetrachloroethane- d_2 .

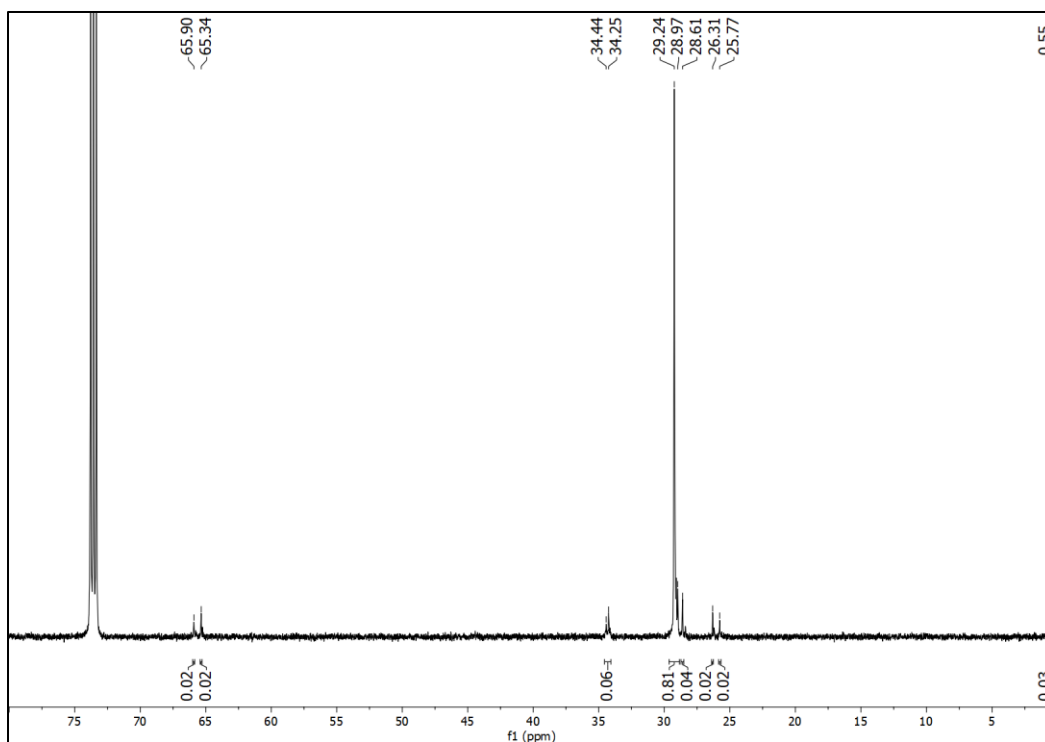


Figure S26. Quantitative ^{13}C NMR of S25-3 dissolved in 1,1,2,2-tetrachloroethane- d_2 .

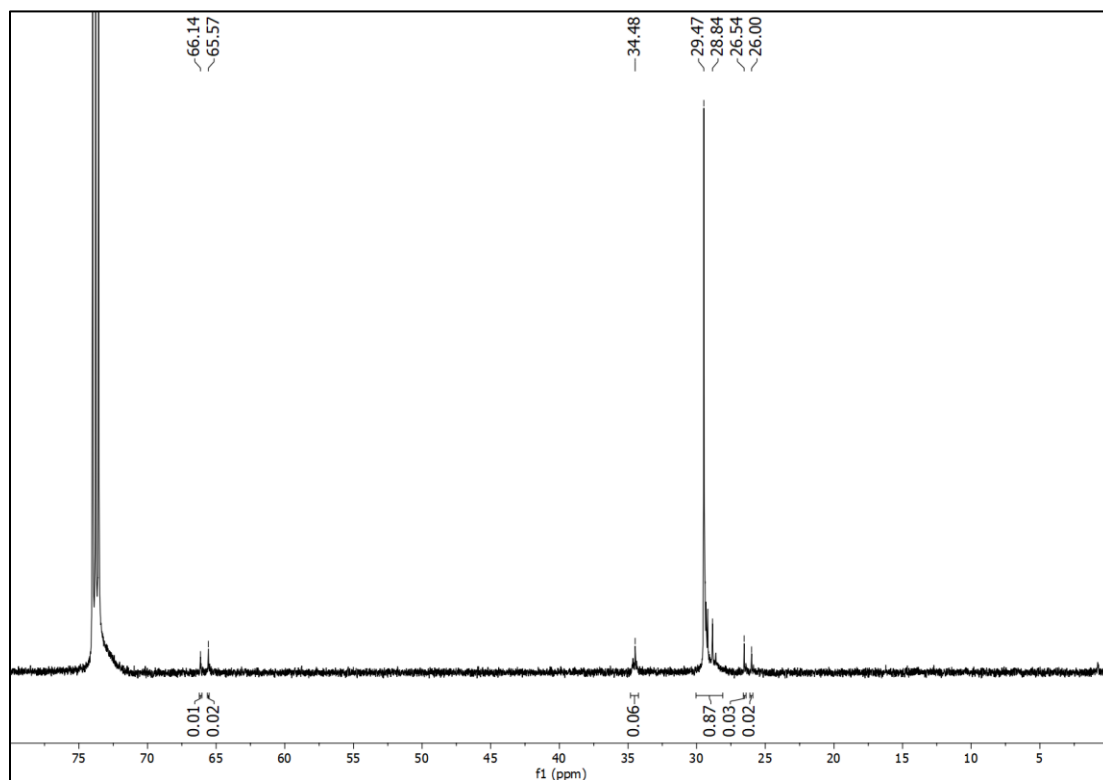


Figure S27. Quantitative ^{13}C NMR of S25-4 dissolved in 1,1,2,2-tetrachloroethane- d_2 .

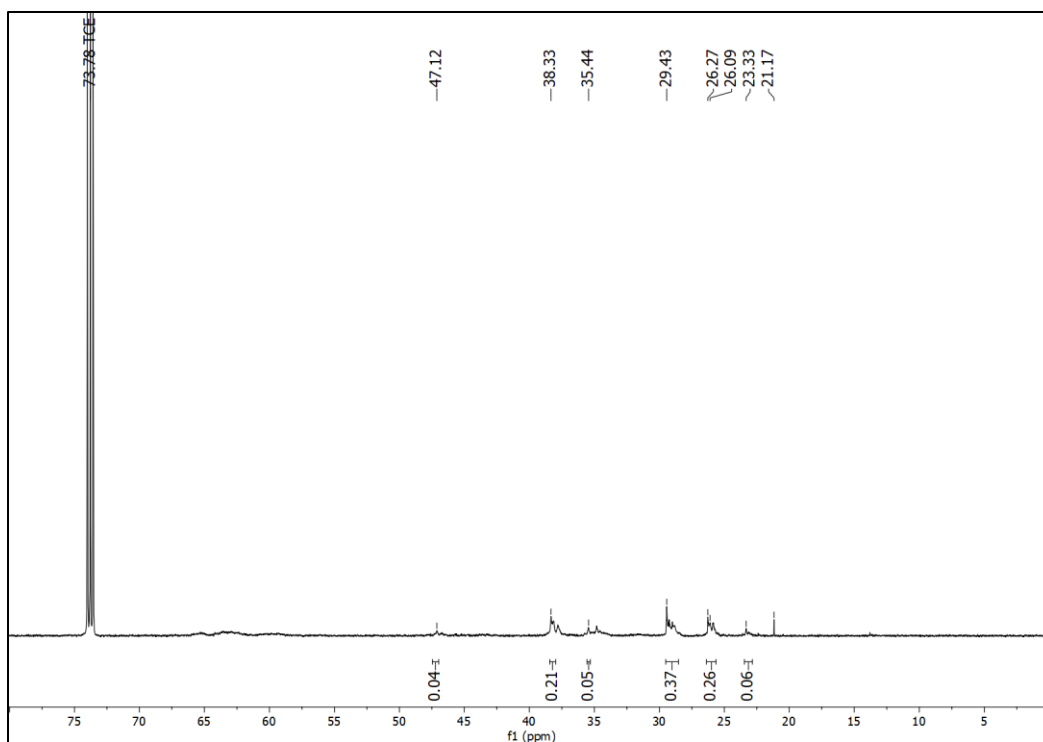


Figure S28. Quantitative ^{13}C NMR of **R1** dissolved in 1,1,2,2-tetrachloroethane- d_2 .

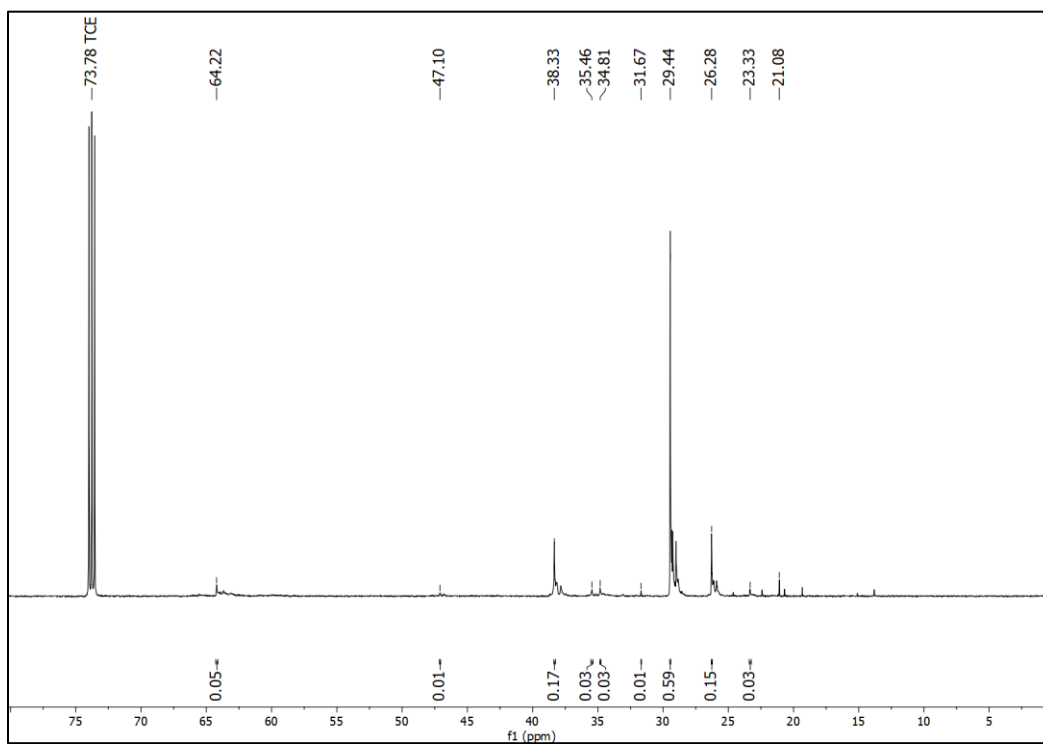


Figure S29. Quantitative ^{13}C NMR of **B1** dissolved in 1,1,2,2-tetrachloroethane- d_2 .

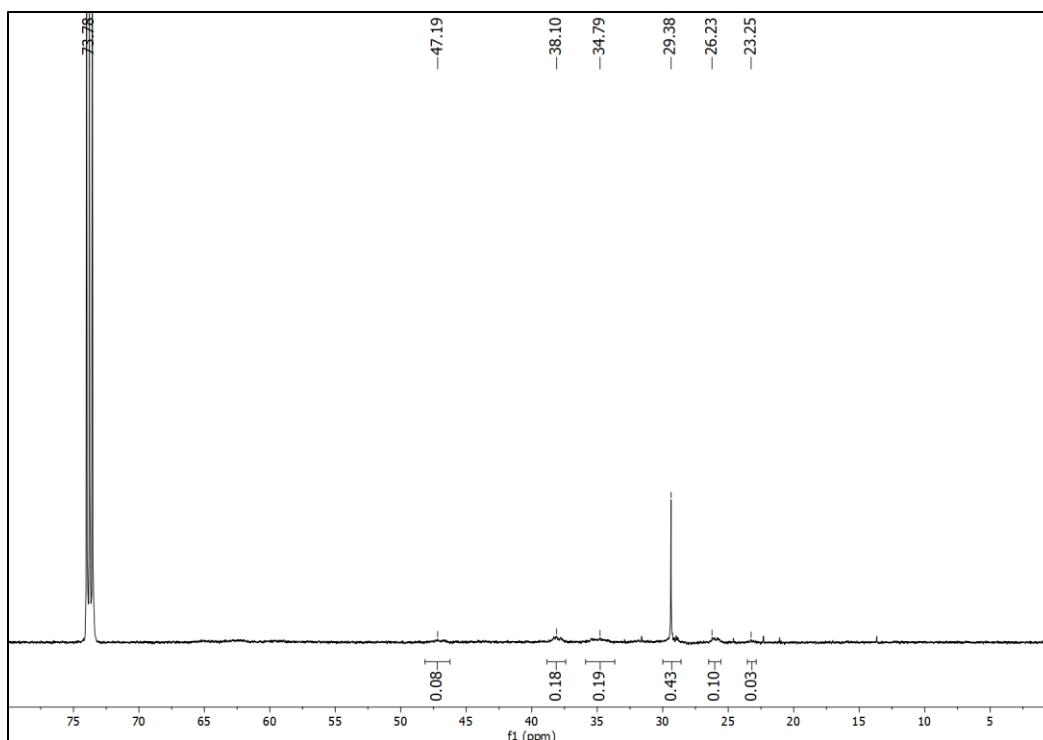


Figure S30. Quantitative ^{13}C NMR of B2 dissolved in 1,1,2,2-tetrachloroethane- d_2 .

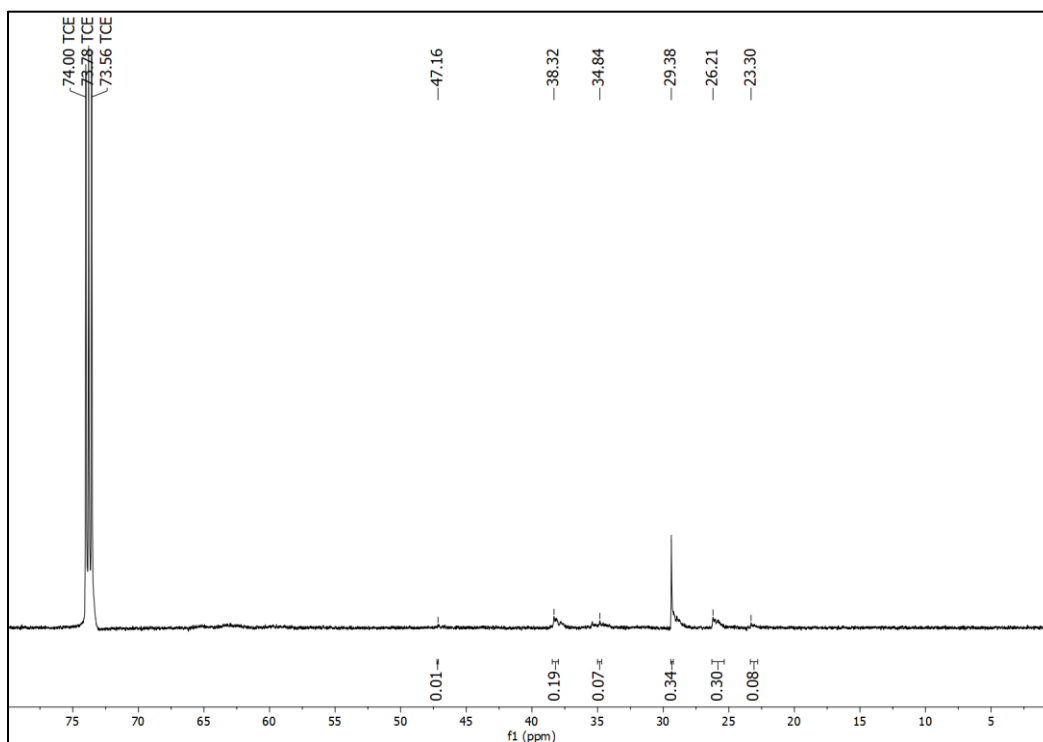


Figure S31. Quantitative ^{13}C NMR of B3 dissolved in 1,1,2,2-tetrachloroethane- d_2 .

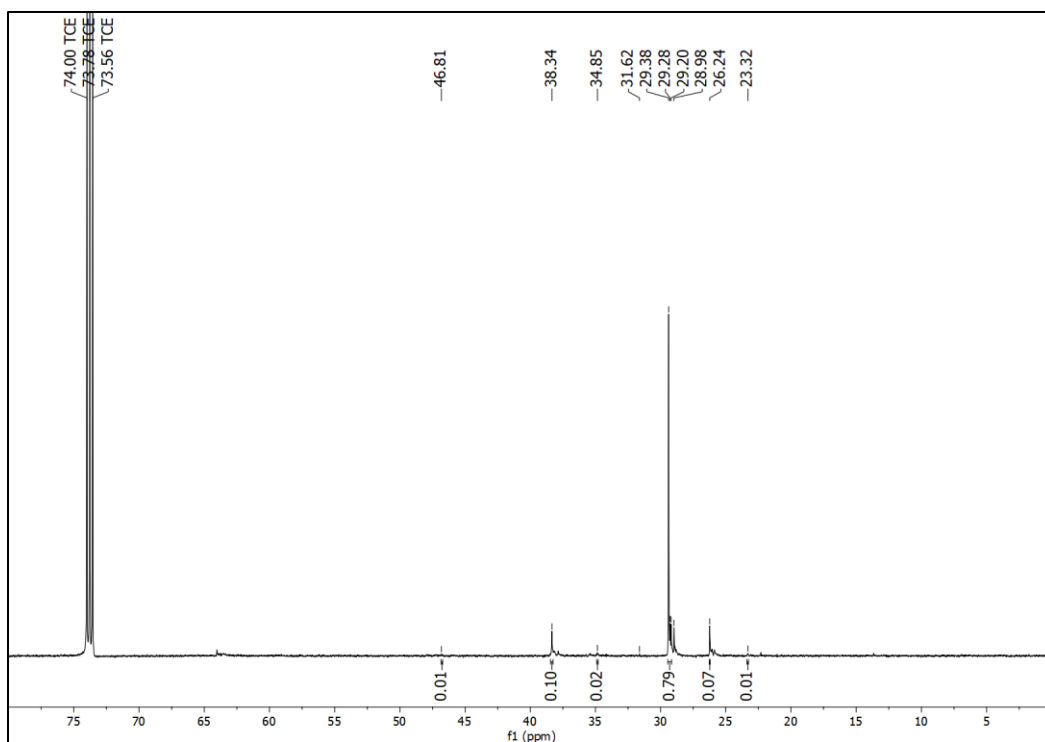


Figure S32. Quantitative ^{13}C NMR of B4 dissolved in 1,1,2,2-tetrachloroethane- d_2 .

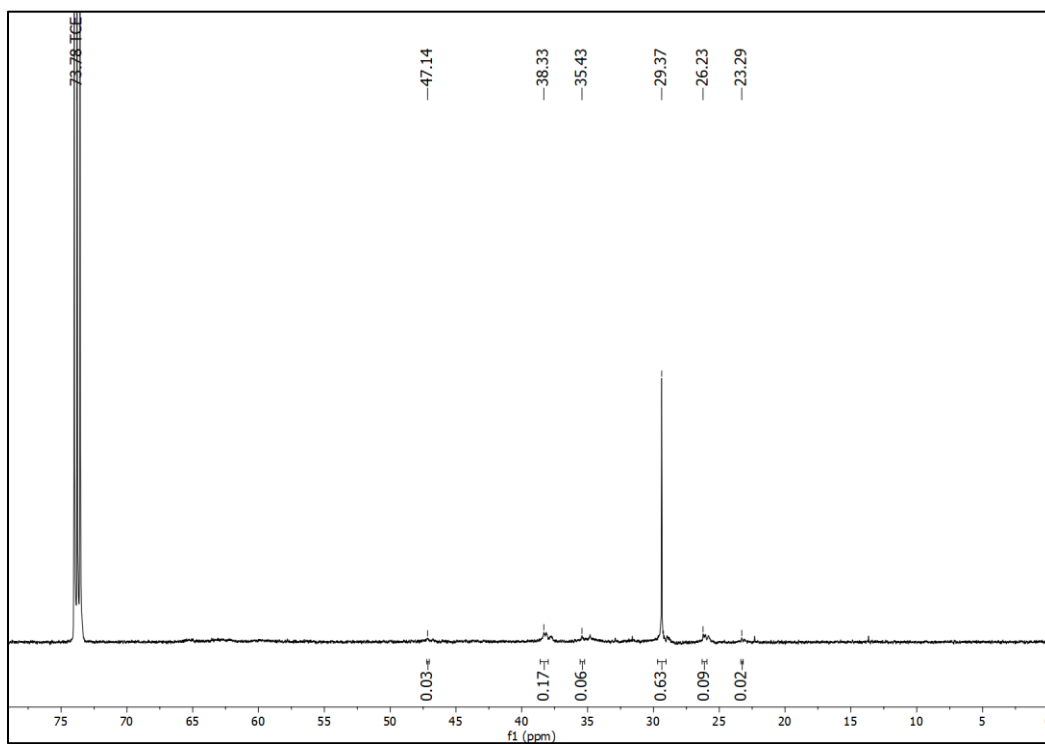


Figure S33. Quantitative ^{13}C NMR of B5 dissolved in 1,1,2,2-tetrachloroethane- d_2 .

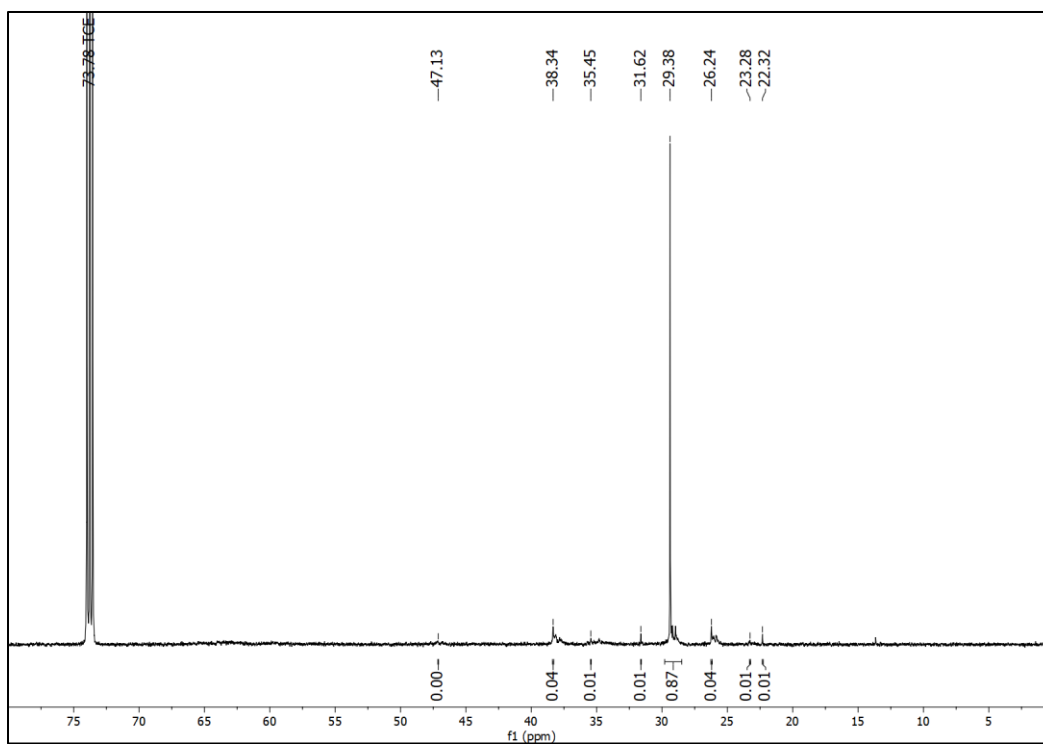


Figure S34. Quantitative ^{13}C NMR of B6 dissolved in 1,1,2,2-tetrachloroethane- d_2 .

GPC Chromatograms of c-PE Compatibilizers:

Molar masses were obtained from gel permeation chromatography (GPC). The synthesized compatibilizers were tested in their pre-hydrogenated form. The material was run on a Tosch EcoSEC GPC system equipped with RI detection in tetrahydrofuran. The post-hydrogenated samples were not tested by GPC due to their insolubility in THF and the fact that they are isorefractive with 1,2,4-trichlorobenzene. We assume their molar mass stays the same post hydrogenation due to the nature of the diimide reduction they undergo and therefore only obtained molar mass of the initial polymer materials. The commercial c-PEs were run on a Viscotek 350A HT-GPC system at 150 °C in 1,2,4-trichlorobenzene.

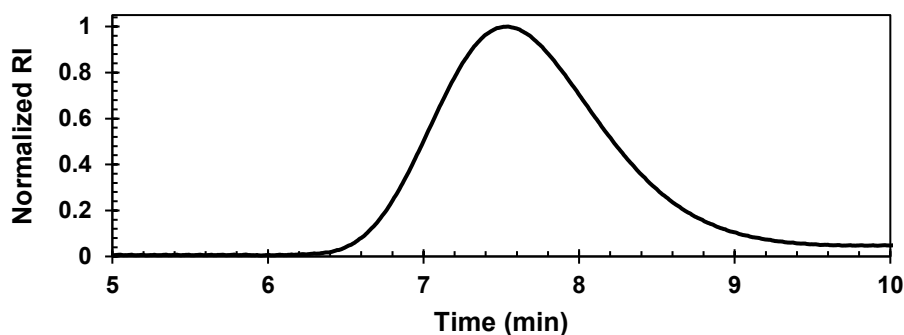


Figure S35. GPC chromatograph of S100-3 prior to hydrogenation.

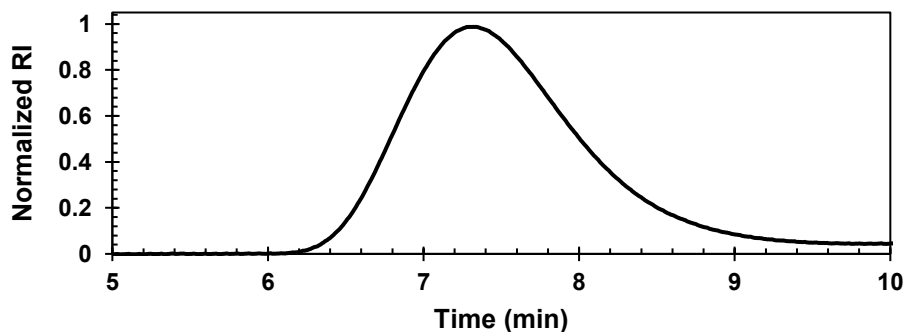


Figure S36. GPC chromatograph of S75-3 prior to hydrogenation.

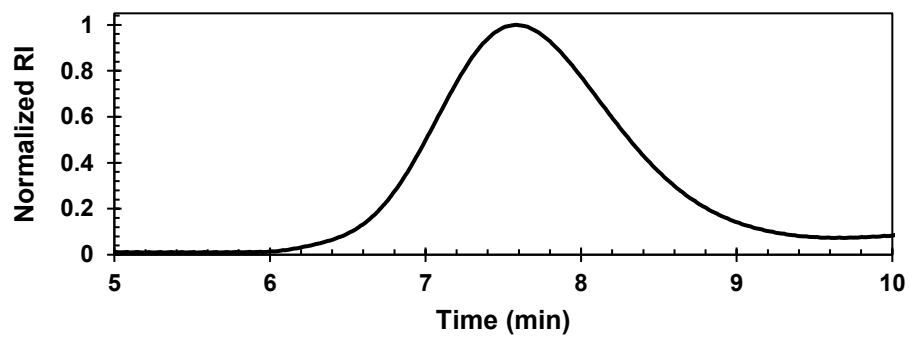


Figure S37. GPC chromatograph of S50-1 prior to hydrogenation.

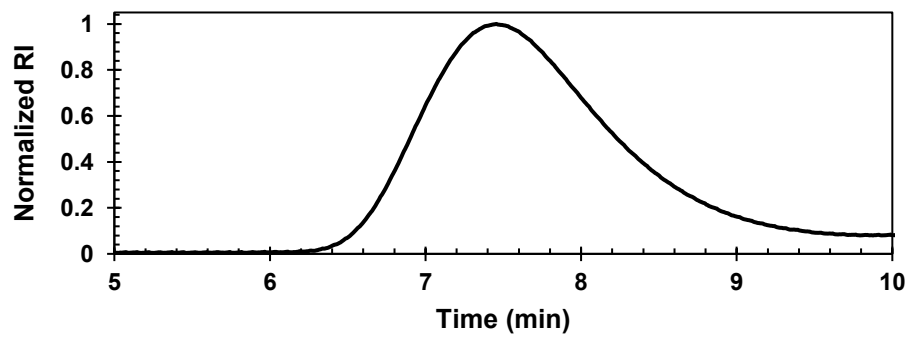


Figure S38. GPC chromatograph of S25-1 prior to hydrogenation.

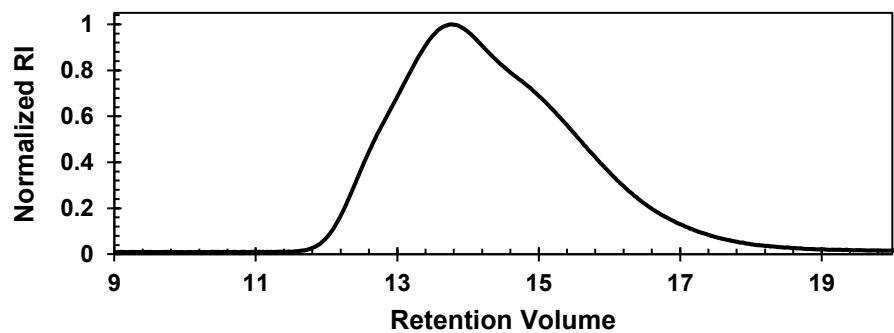


Figure S39. GPC chromatograph of R1.

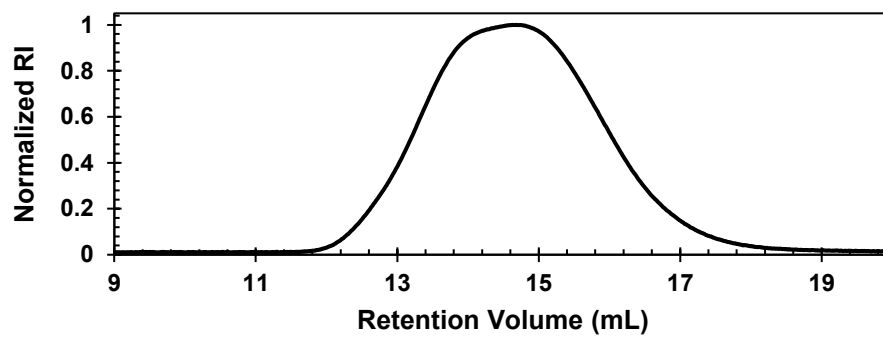


Figure S40. GPC chromatograph of B1.

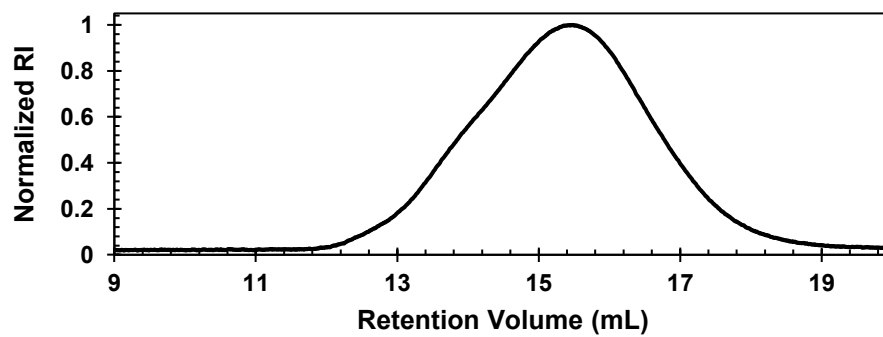


Figure S41. GPC chromatograph of B2.

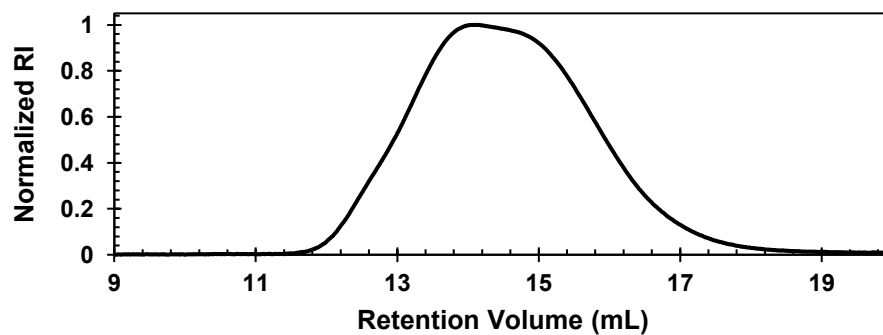


Figure S42. GPC chromatograph of B3.

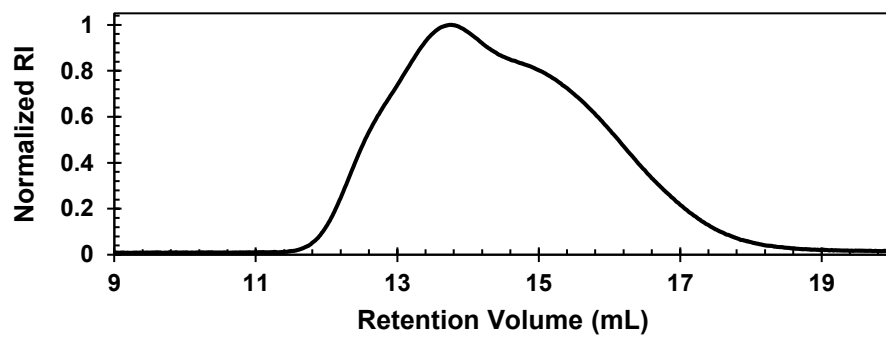


Figure S43. GPC chromatograph of B4.

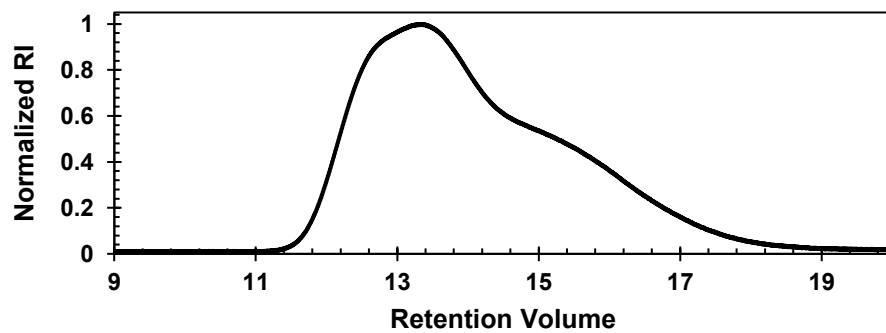


Figure S44. GPC chromatograph of B5.

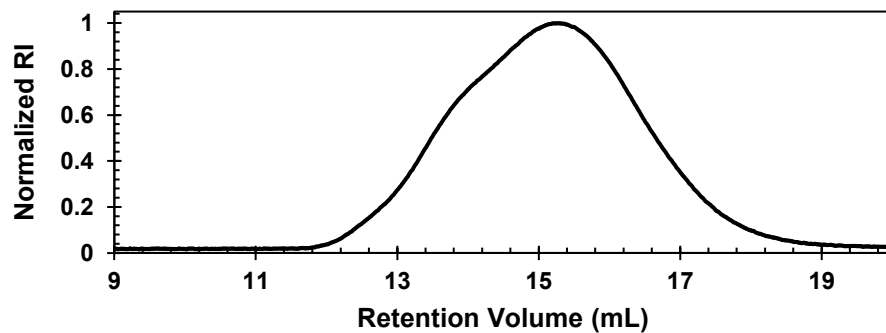


Figure S45. GPC chromatograph of B6.

DSC Thermograms of c-PE Compatibilizers:

Differential scanning calorimetry (DSC) was used to obtain heat of fusion and melting temperatures using a TA Instruments Q-2000 DSC. C-PE samples (5 – 10 mg) were analyzed via a heat-cool-heat cycles with heating and cooling rates of 10 °C/min. All DSC thermograms below depict the cooling cycle and second heating cycles. All quantitative measurements were made using the second heating cycle, and integrations of the melting peak are used to calculate the heat fusion, which is a representation of the extent of crystallinity, since there is no known theoretical 100% crystallinity value for this material.²

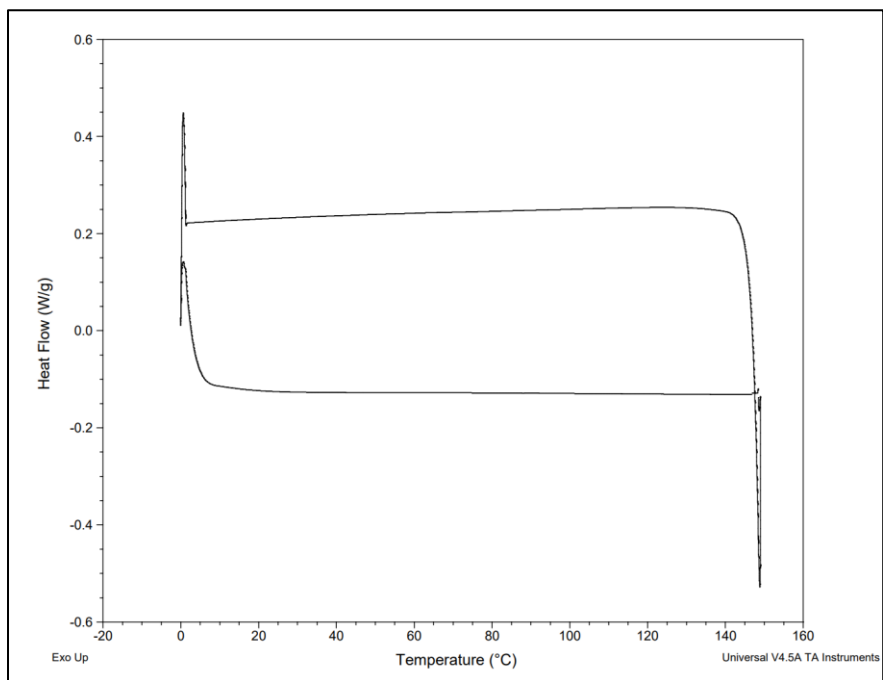


Figure S46. DSC thermogram for S100-1.

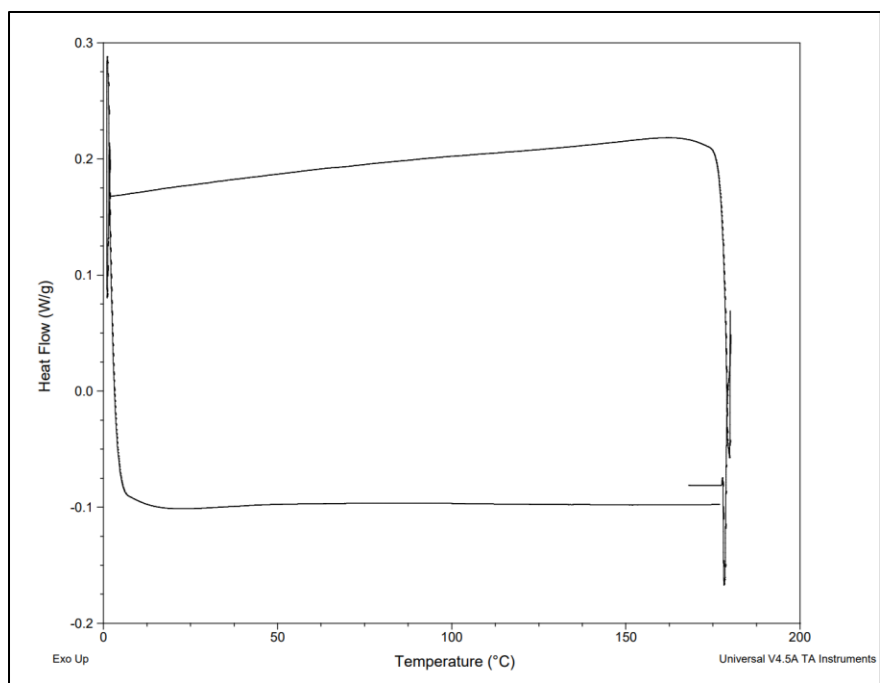


Figure S47. DSC thermogram for S100-2.

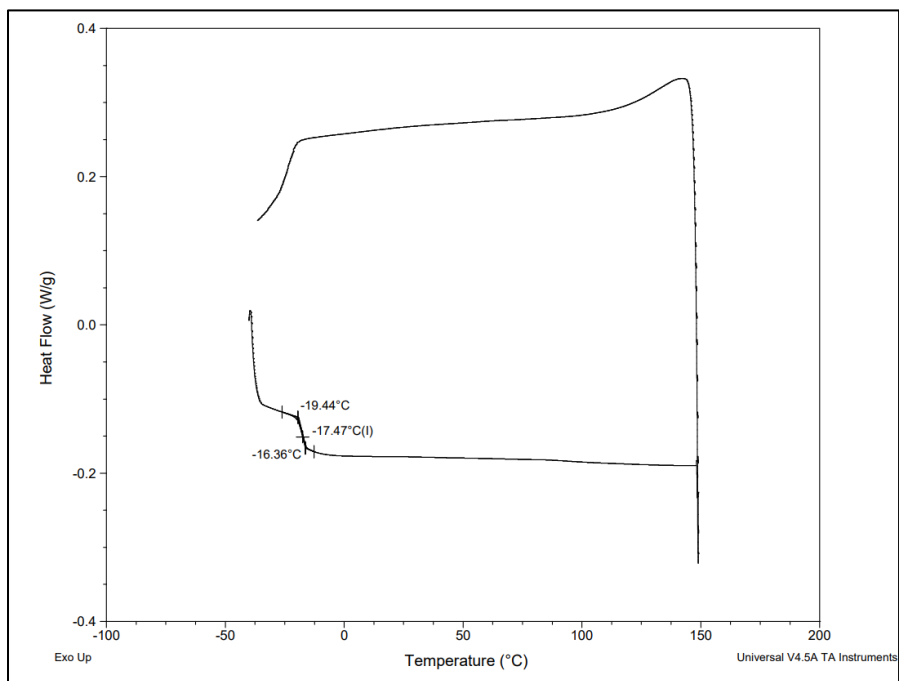


Figure S48. DSC thermogram for S100-3.

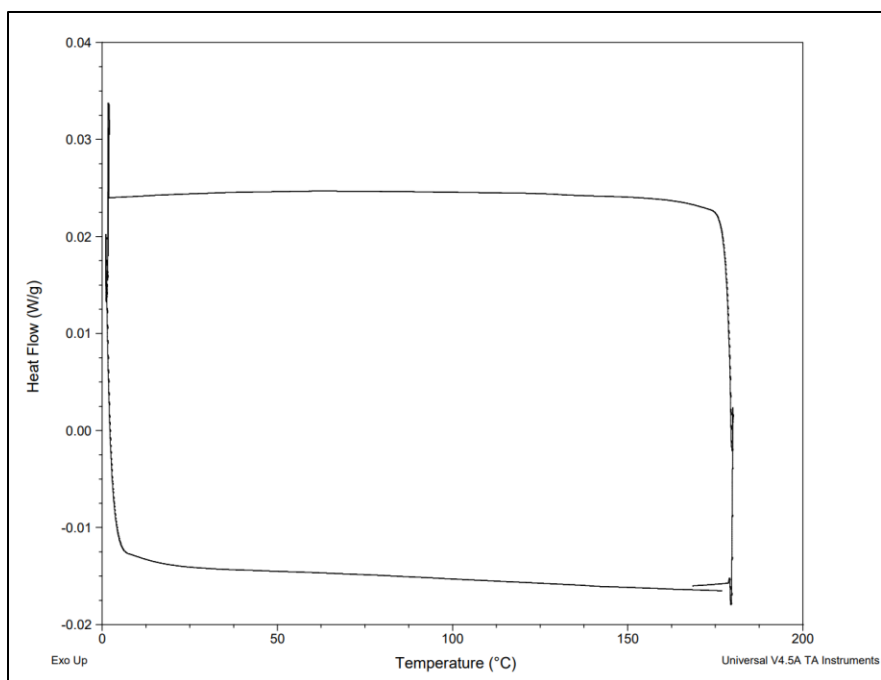


Figure S49. DSC thermogram for S100-4.

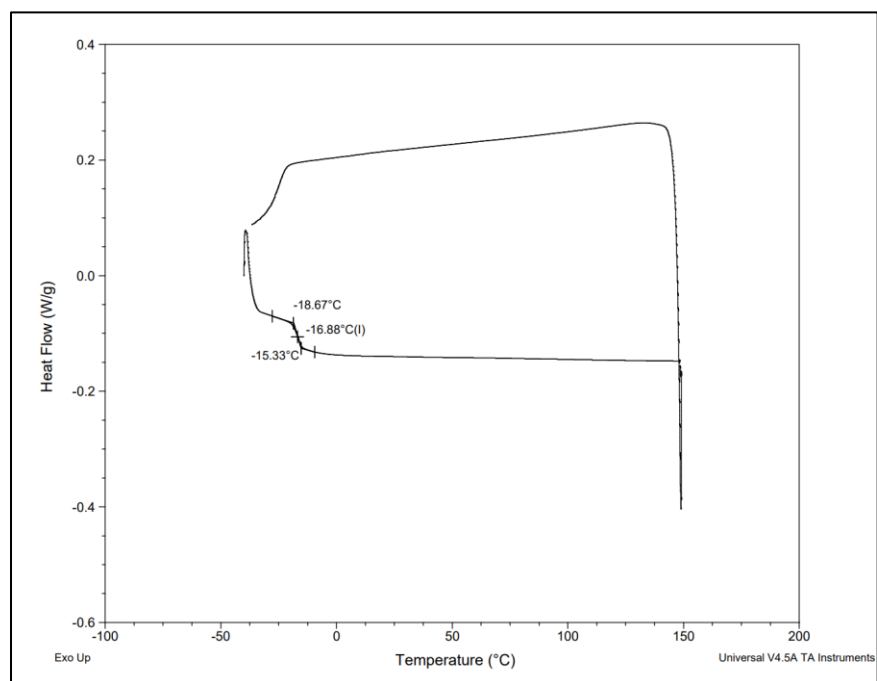


Figure S50. DSC thermogram for S100-5.

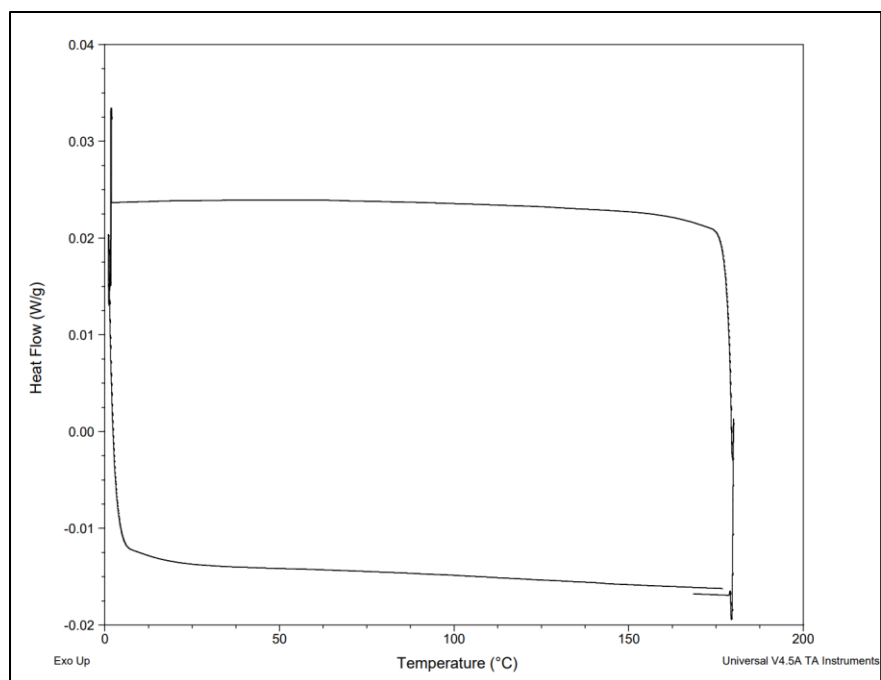


Figure S51. DSC thermogram for S100-6.

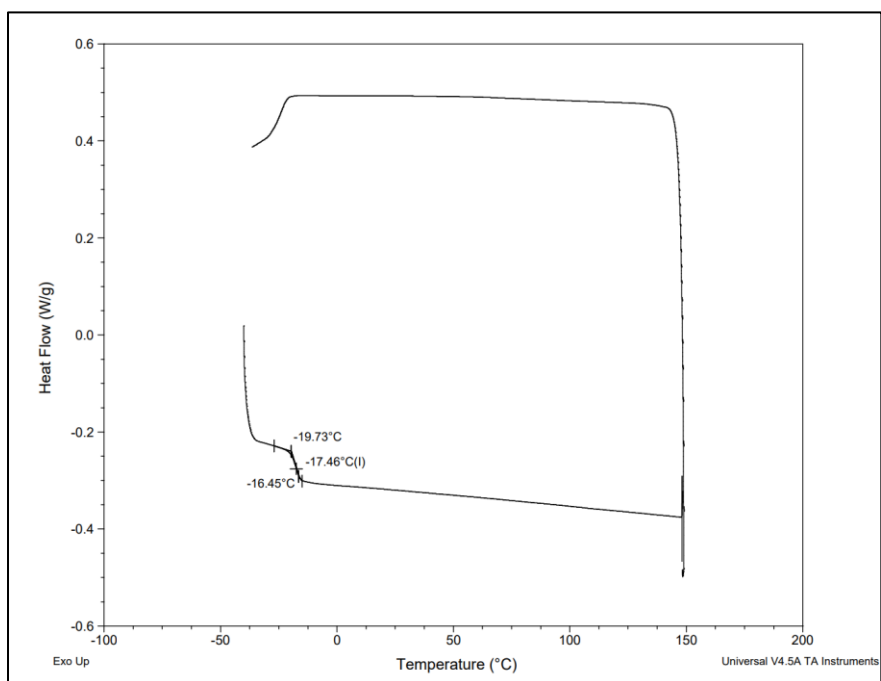


Figure S52. DSC thermogram for S100-7.

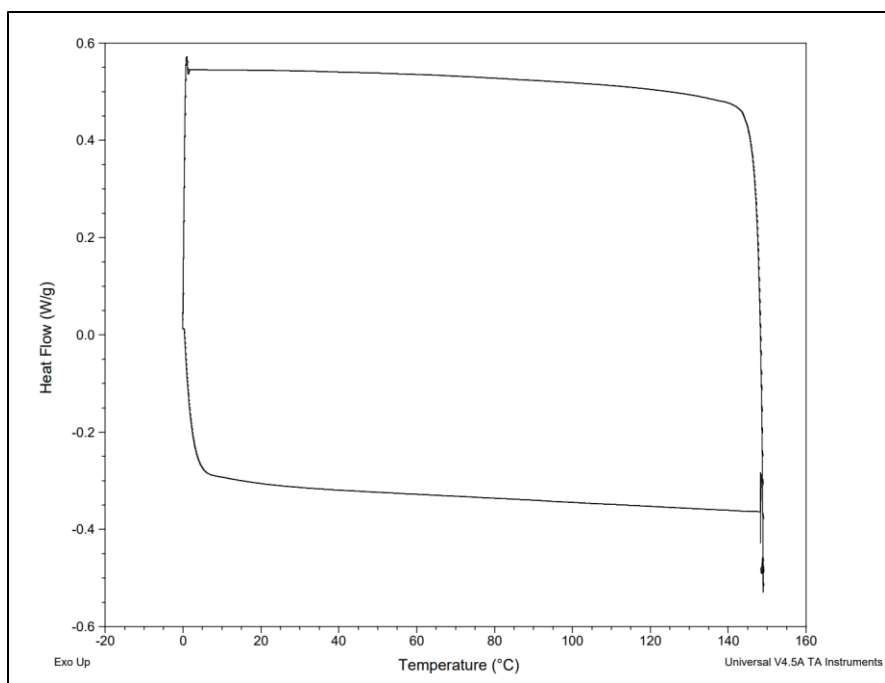


Figure S53. DSC thermogram for S100-8.

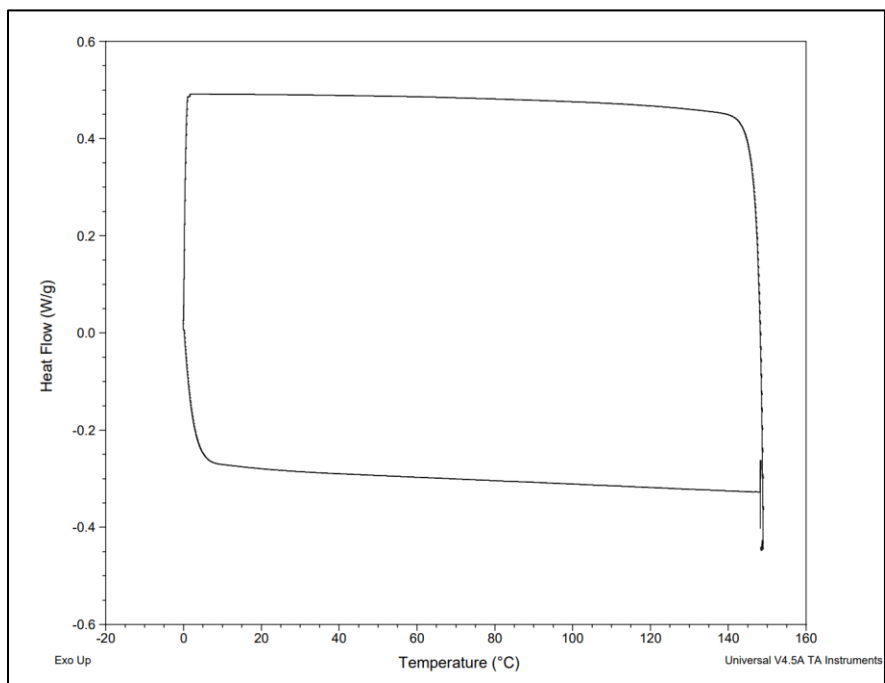


Figure S54. DSC thermogram for S100-9.

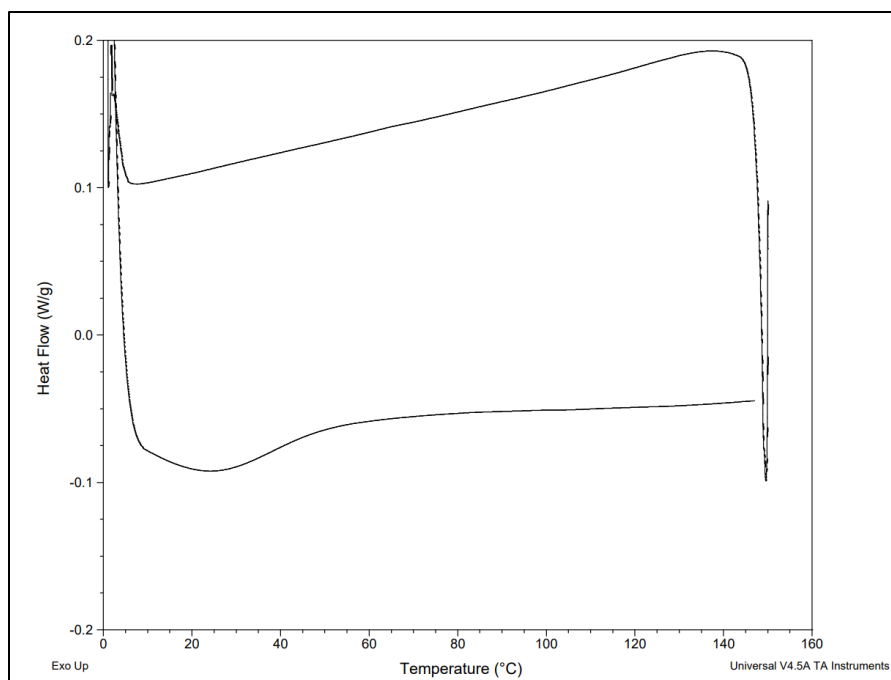


Figure S55. DSC thermogram for S75-1.

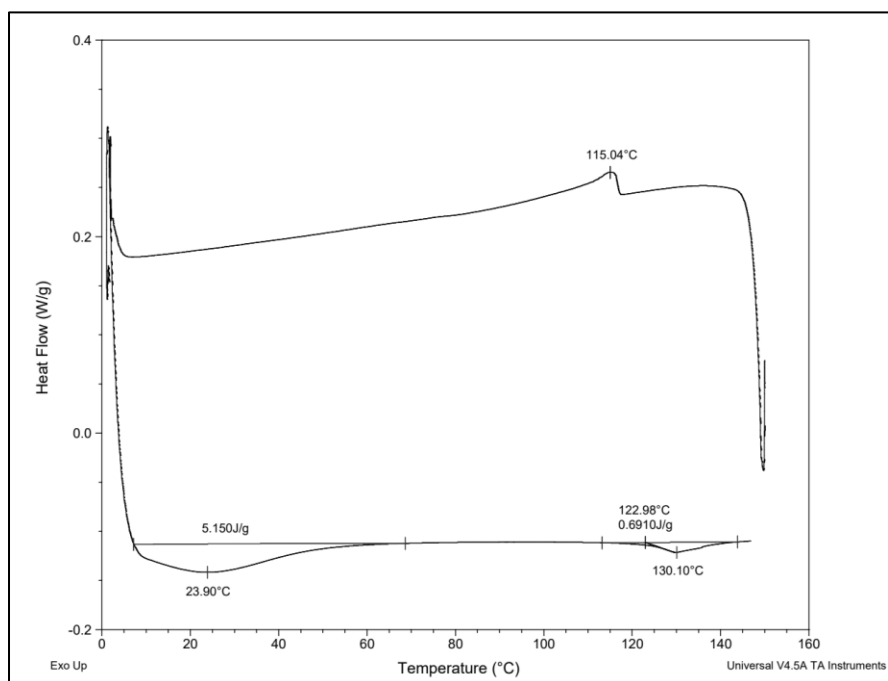


Figure S56. DSC thermogram for S75-2.

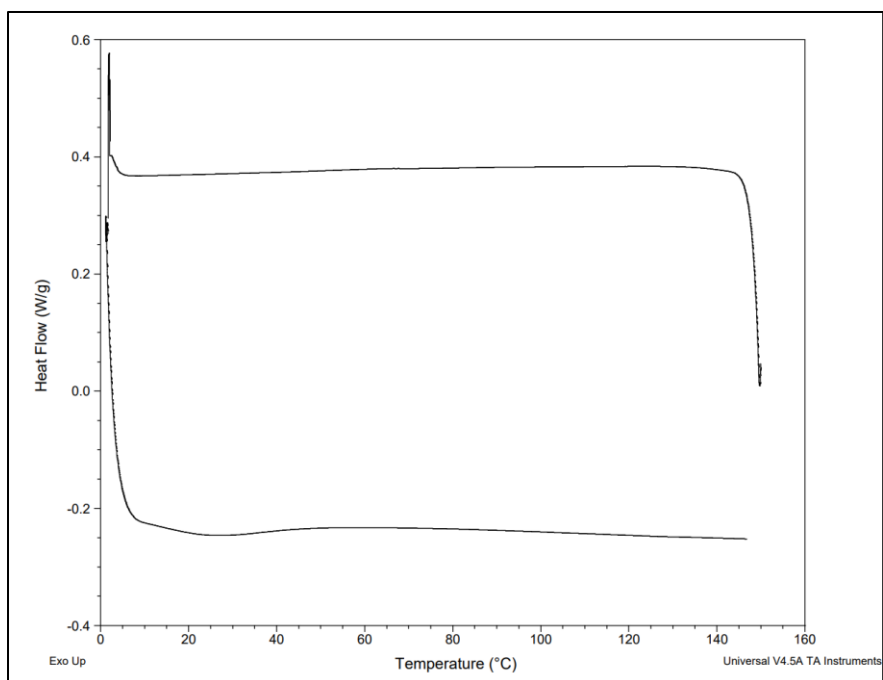


Figure S57. DSC thermogram for S75-3.

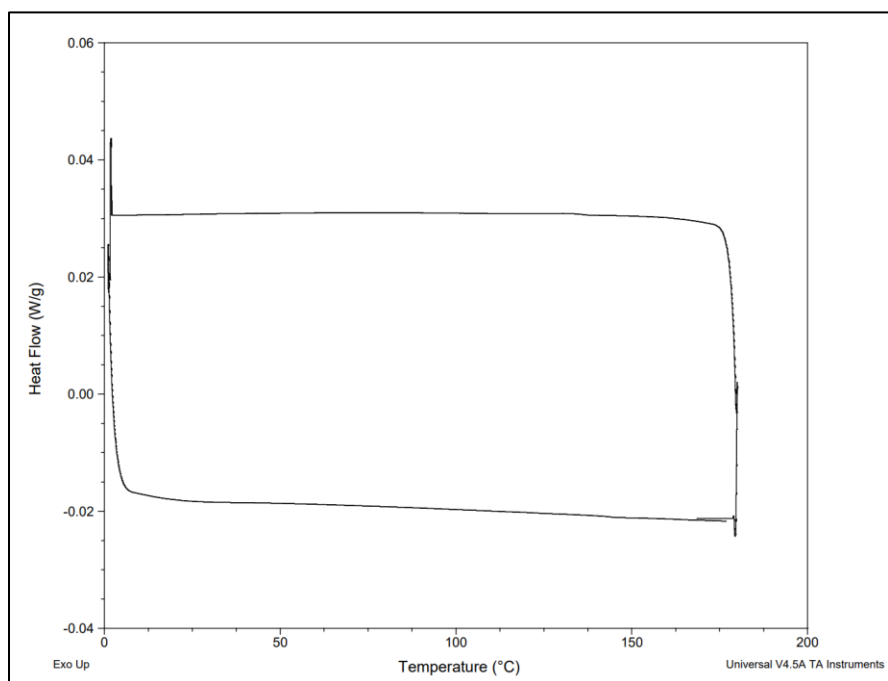


Figure S58. DSC thermogram for S75-4.

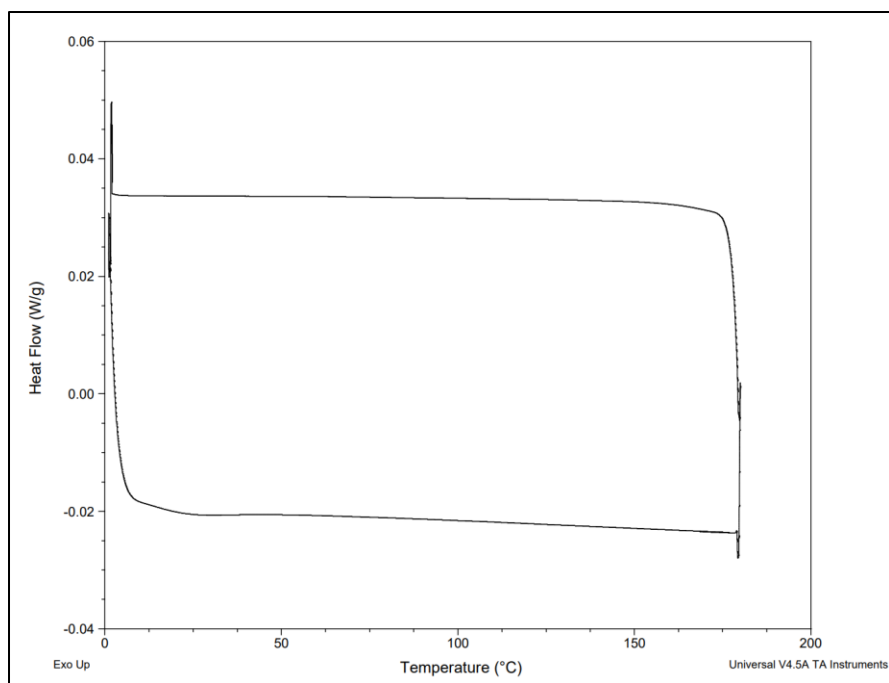


Figure S59. DSC thermogram for S75-5.

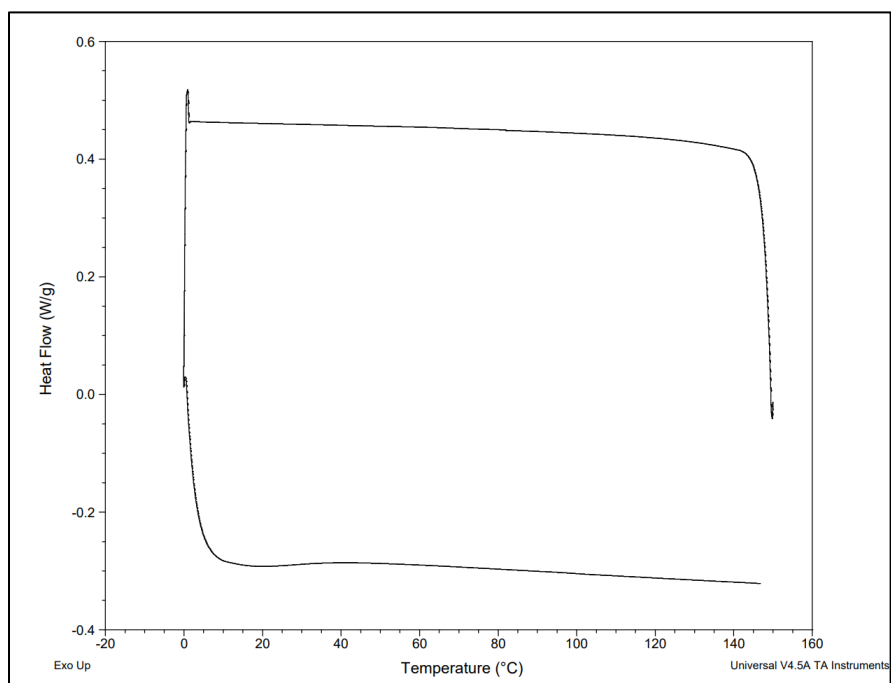


Figure S60. DSC thermogram for S75-6.

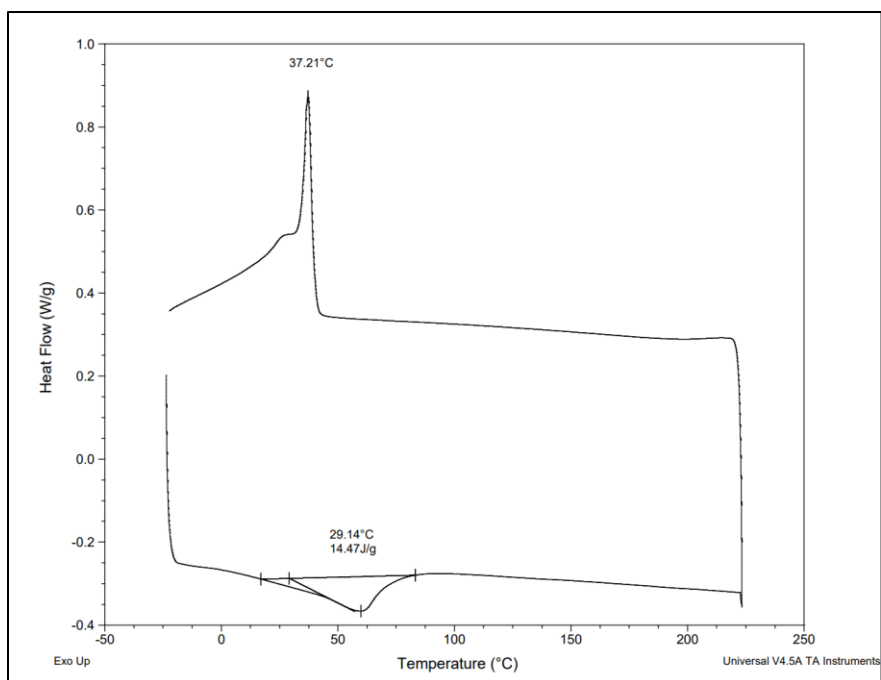


Figure S61. DSC thermogram for S50-1.

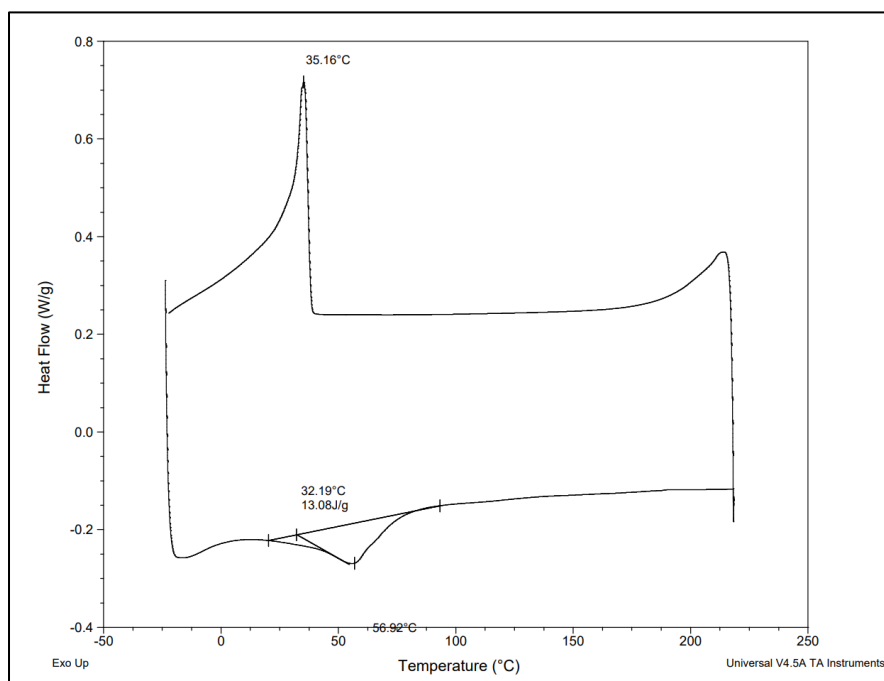


Figure S62. DSC thermogram for S50-2.

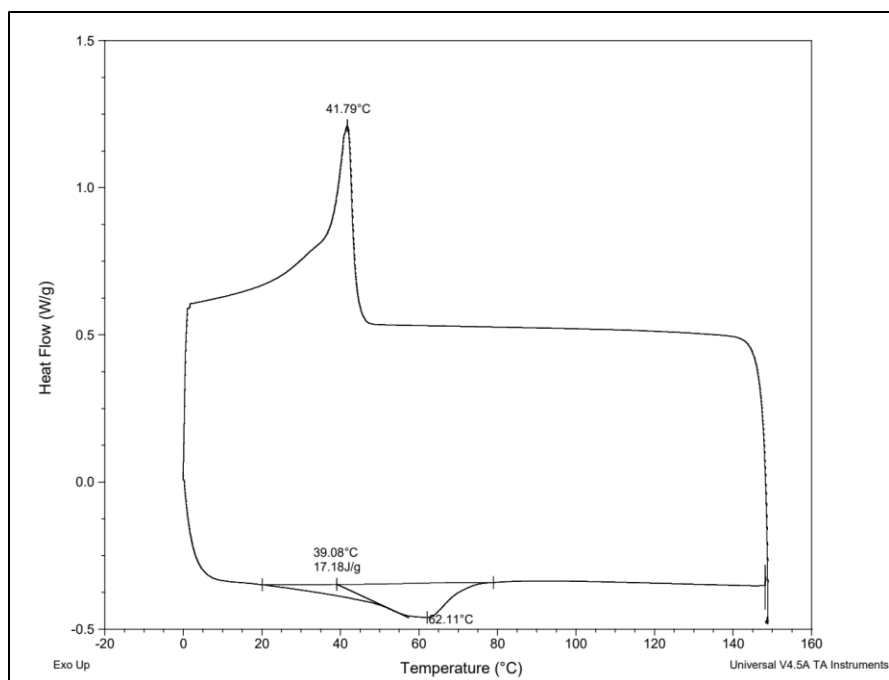


Figure S63. DSC thermogram for S50-3.

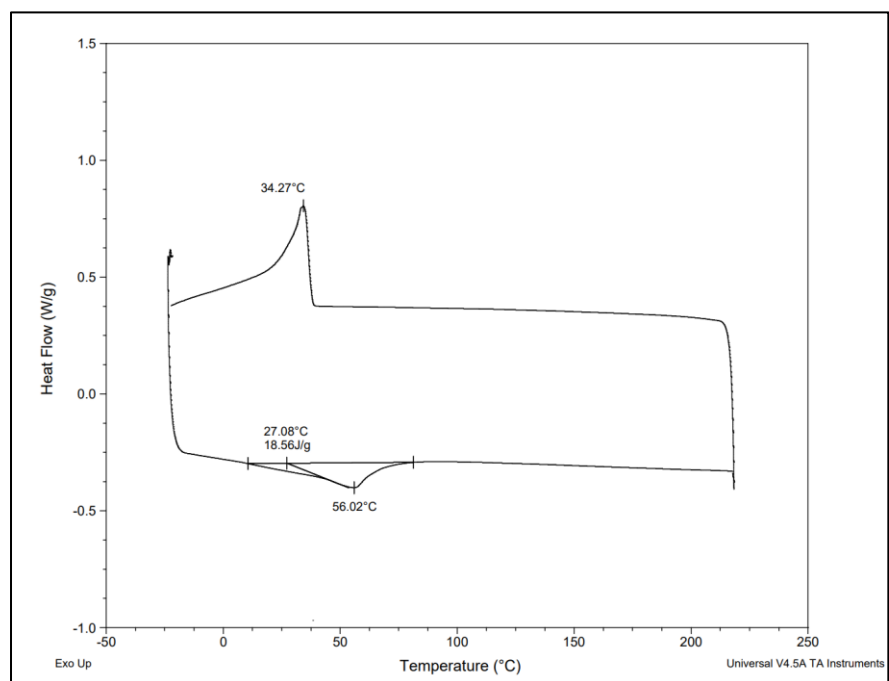


Figure S64. DSC thermogram for S50-4.

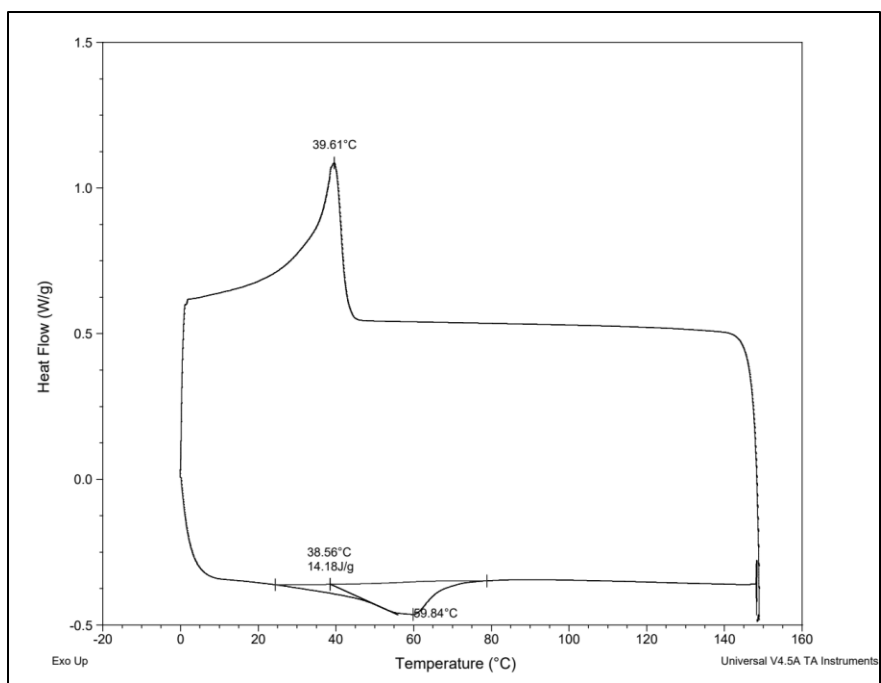


Figure S65. DSC thermogram for S50-5.

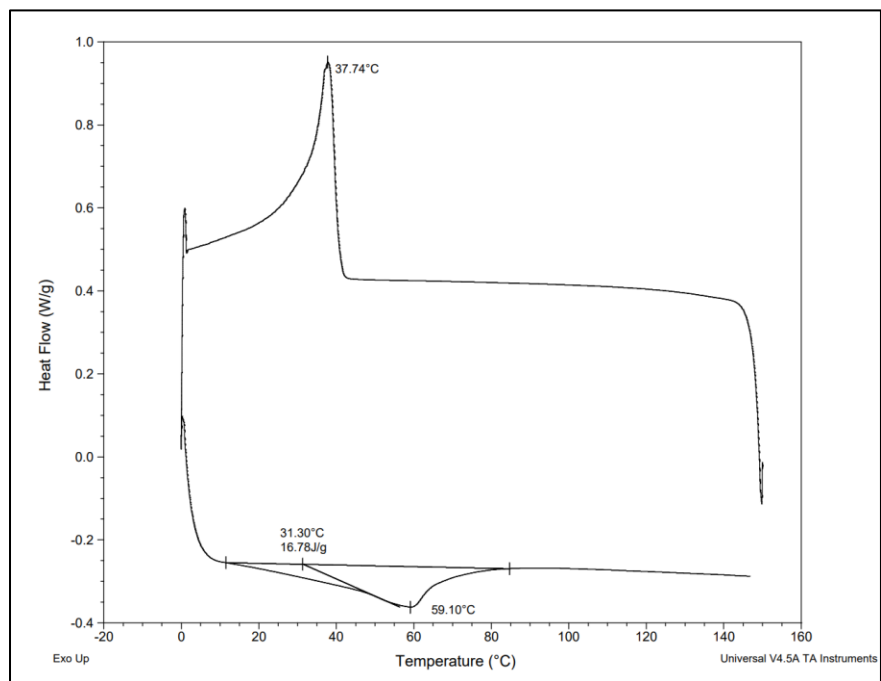


Figure S66. DSC thermogram for S50-6.

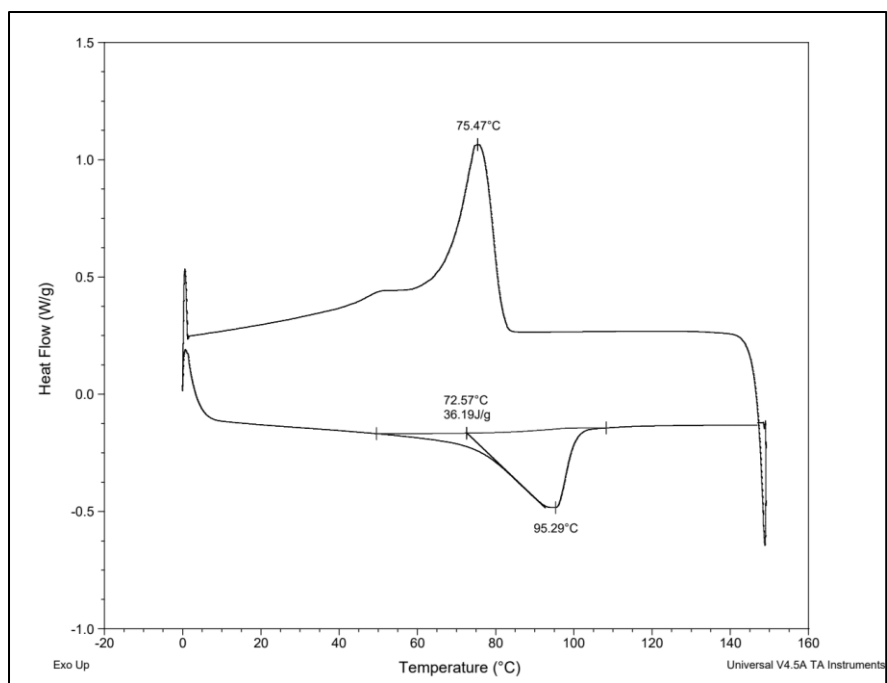


Figure S67. DSC thermogram for S25-1.

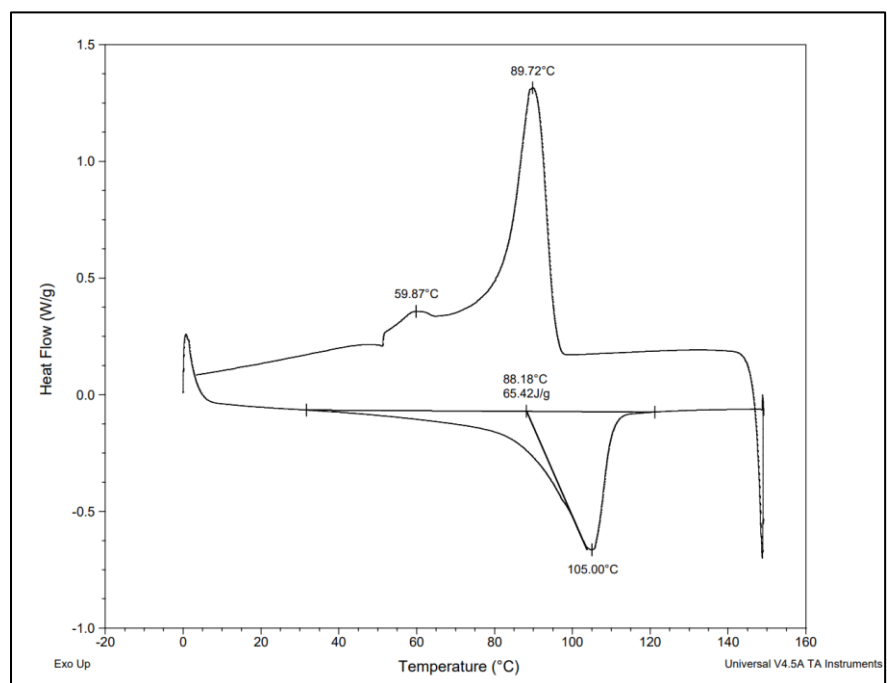


Figure S68. DSC thermogram for S25-2.

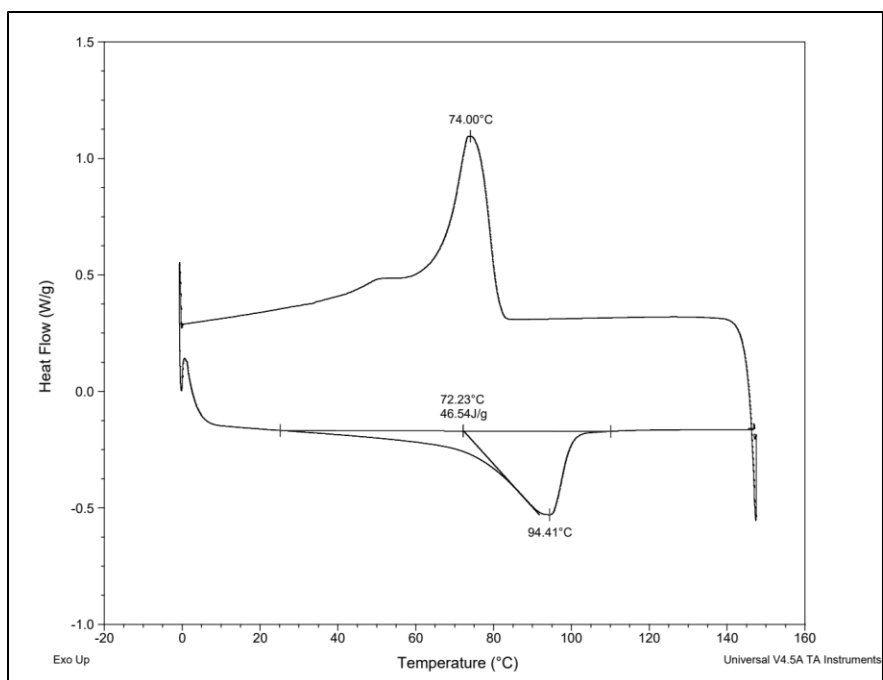


Figure S69. DSC thermogram for S25-3.

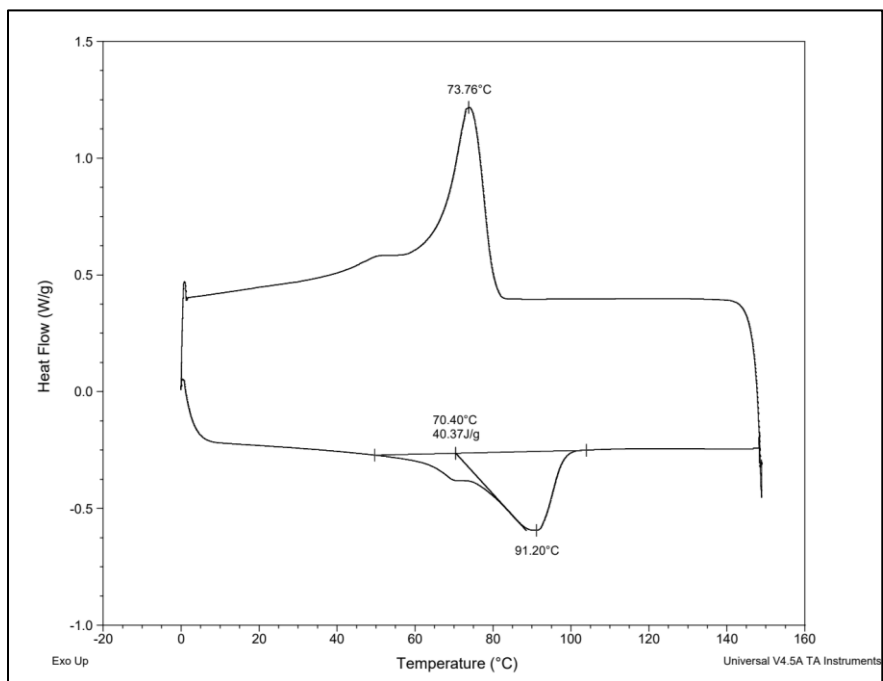


Figure S70. DSC thermogram for S25-4.

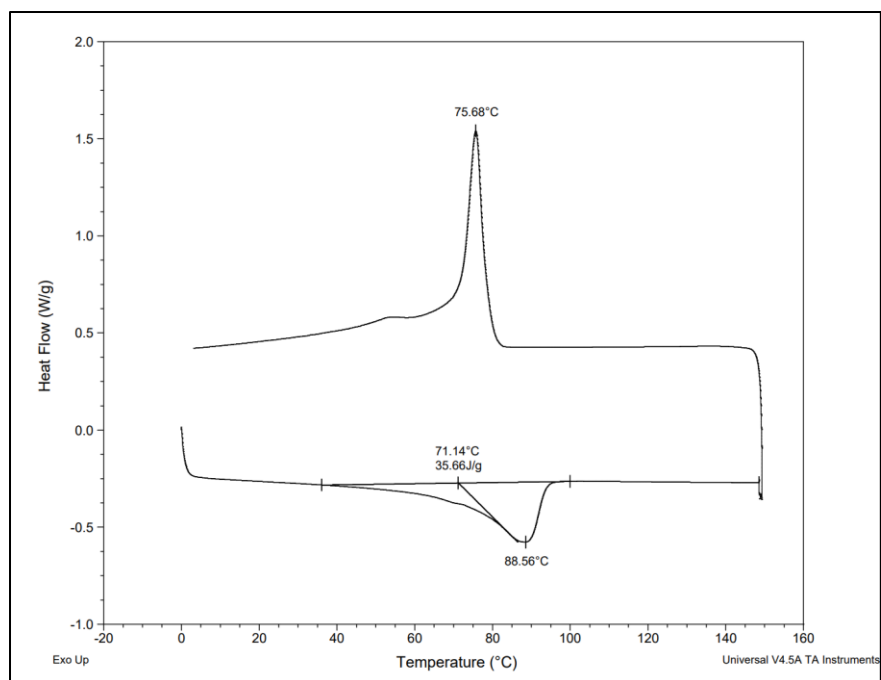


Figure S71. DSC thermogram for S25-5.

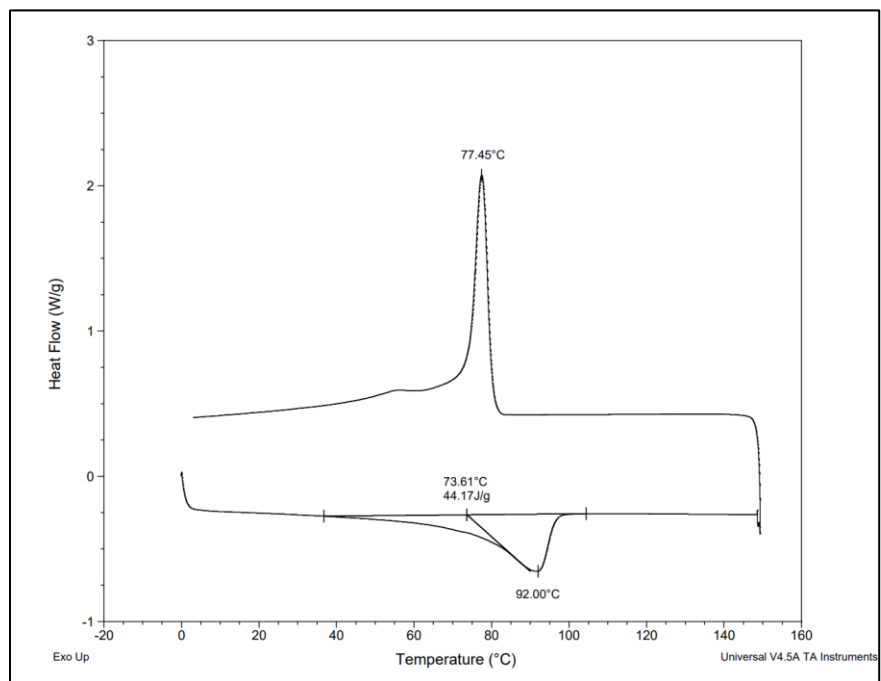


Figure S72. DSC thermogram for S25-6.

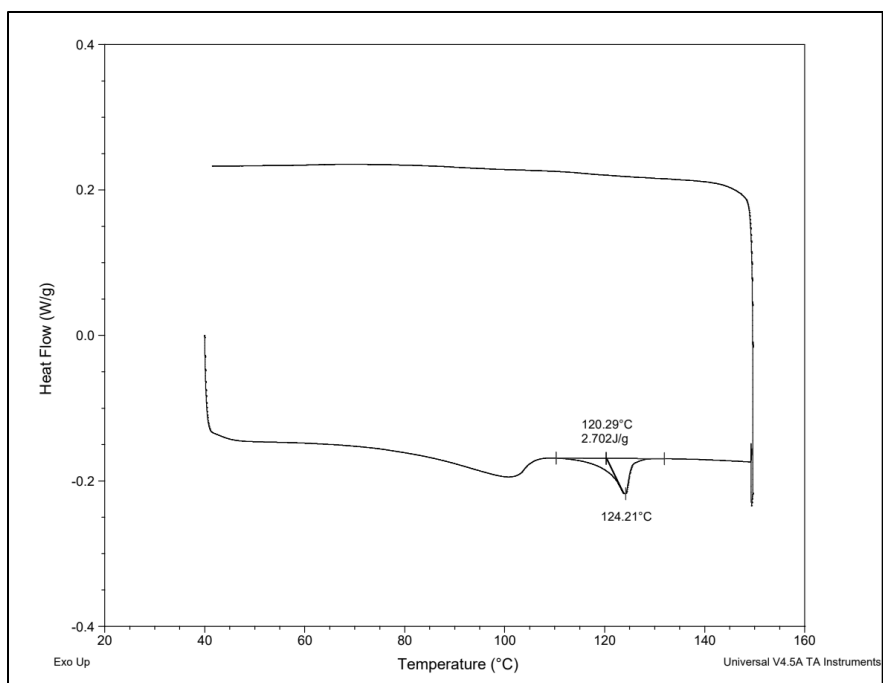


Figure S73. DSC thermogram for R1.

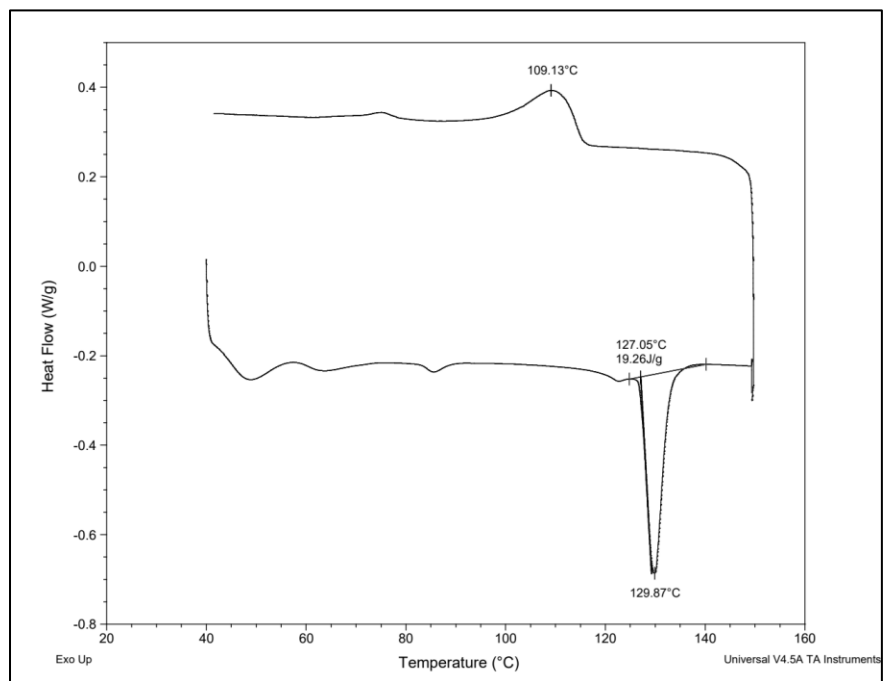


Figure S74. DSC thermogram for B1.

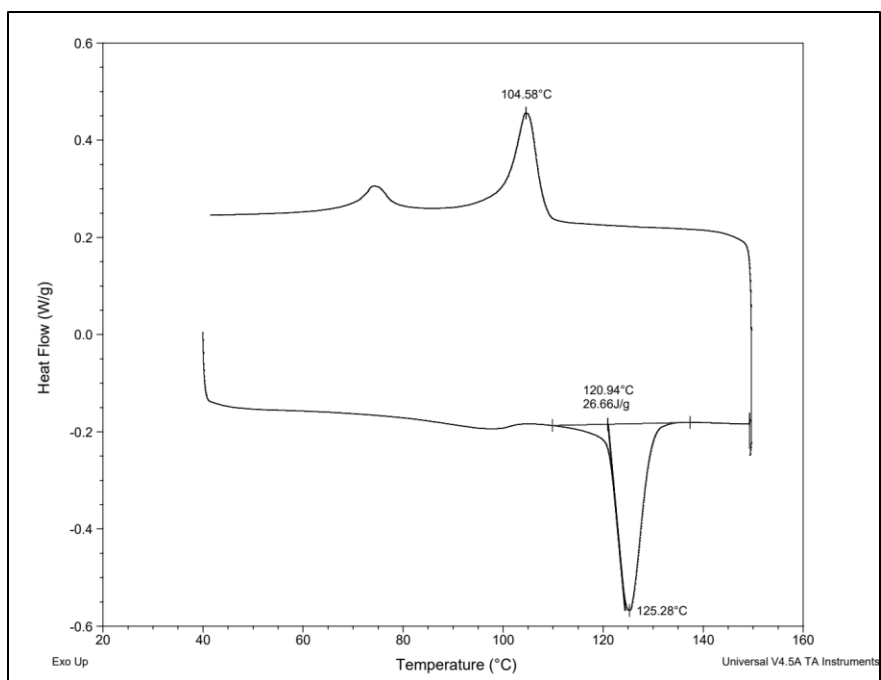


Figure S75. DSC thermogram for B2.

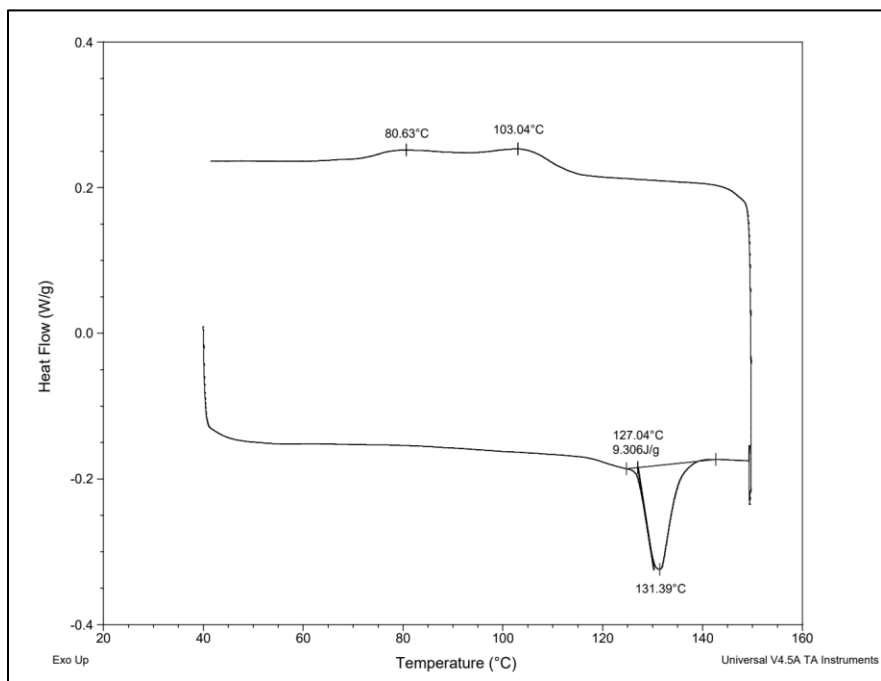


Figure S76. DSC thermogram for B3.

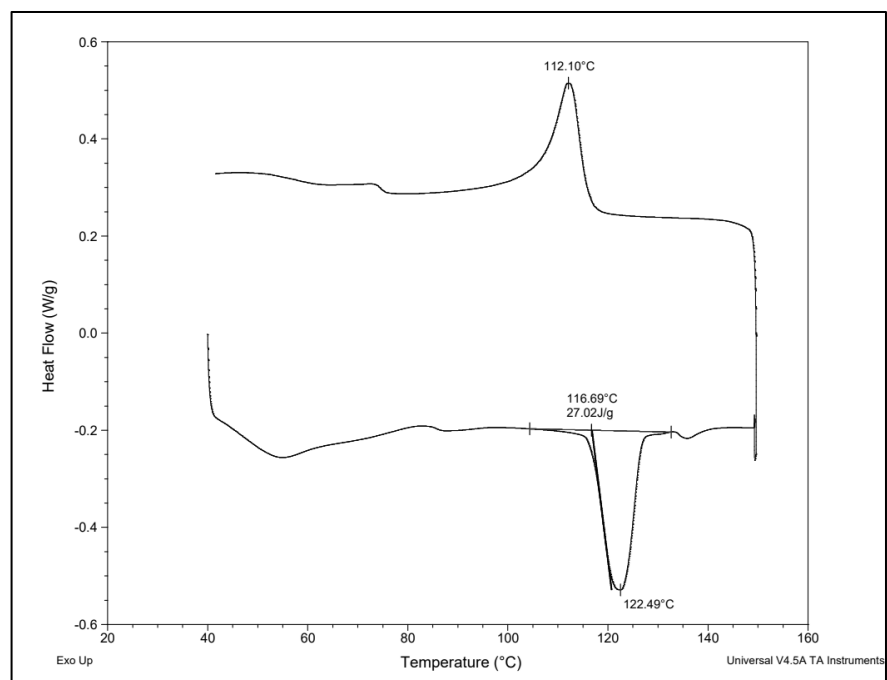


Figure S77. DSC thermogram for B4.

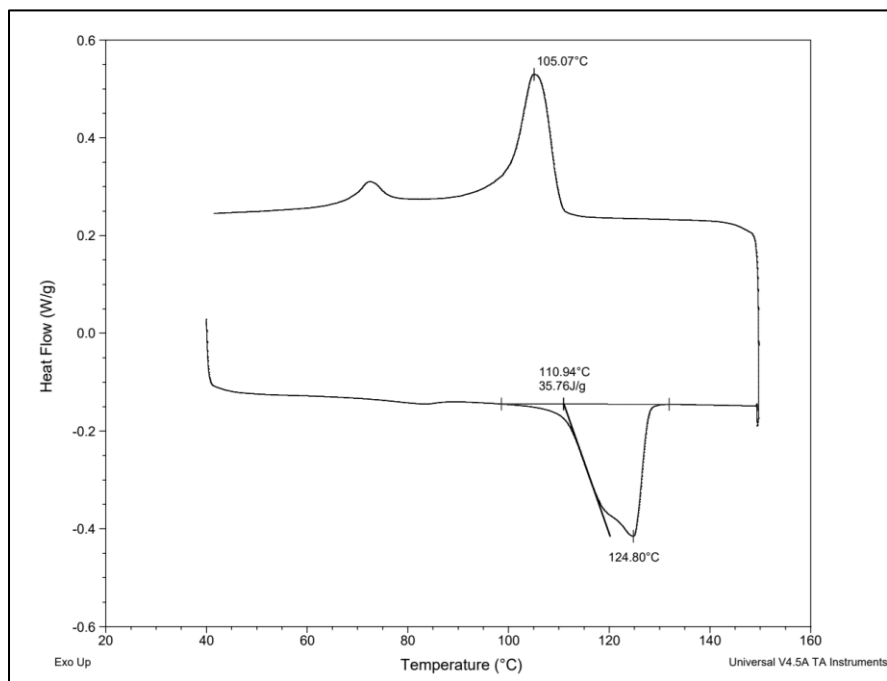


Figure S78. DSC thermogram for B5.

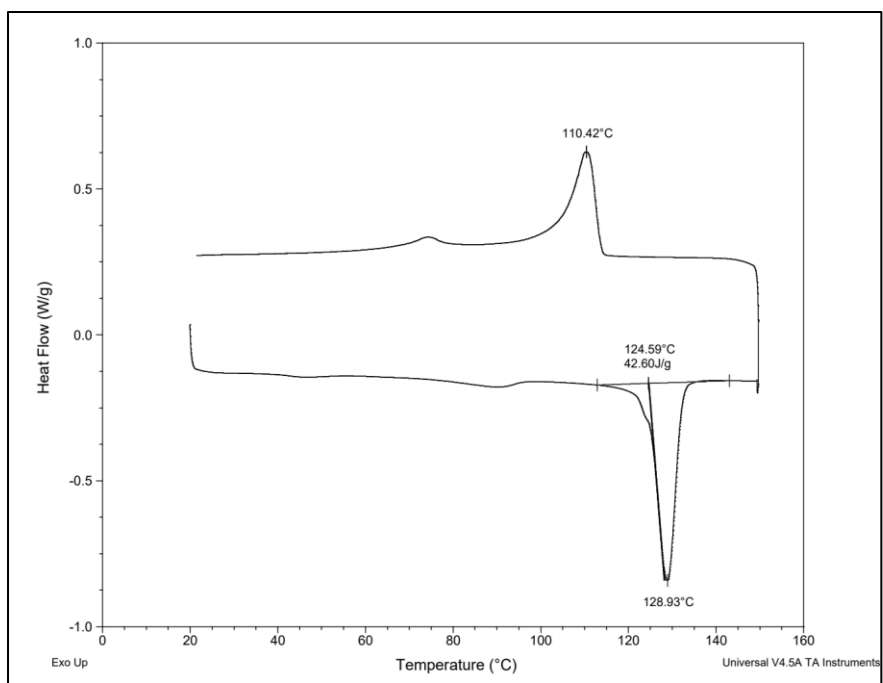


Figure S79. DSC thermogram for B6.

Determination of Chlorine Content:

To determine chlorine content per 100 carbons, high-temperature ^1H NMR of all c-PEs was obtained using a Bruker AVANCE NEO 500 MHz at 60-80 $^{\circ}\text{C}$. Equation 1 is used, where S_1 is the integration of the methyl protons, S_2 is the integration of the methylene protons, and S_3 is the methine protons geminal to the chlorine atoms.³ An example spectra can be found in Figure S80.

$$(1) \text{ Chlorines per 100 carbons} = \frac{(S_3)}{(S_3/1)+(S_2/2)+(S_1/3)} \times 100$$

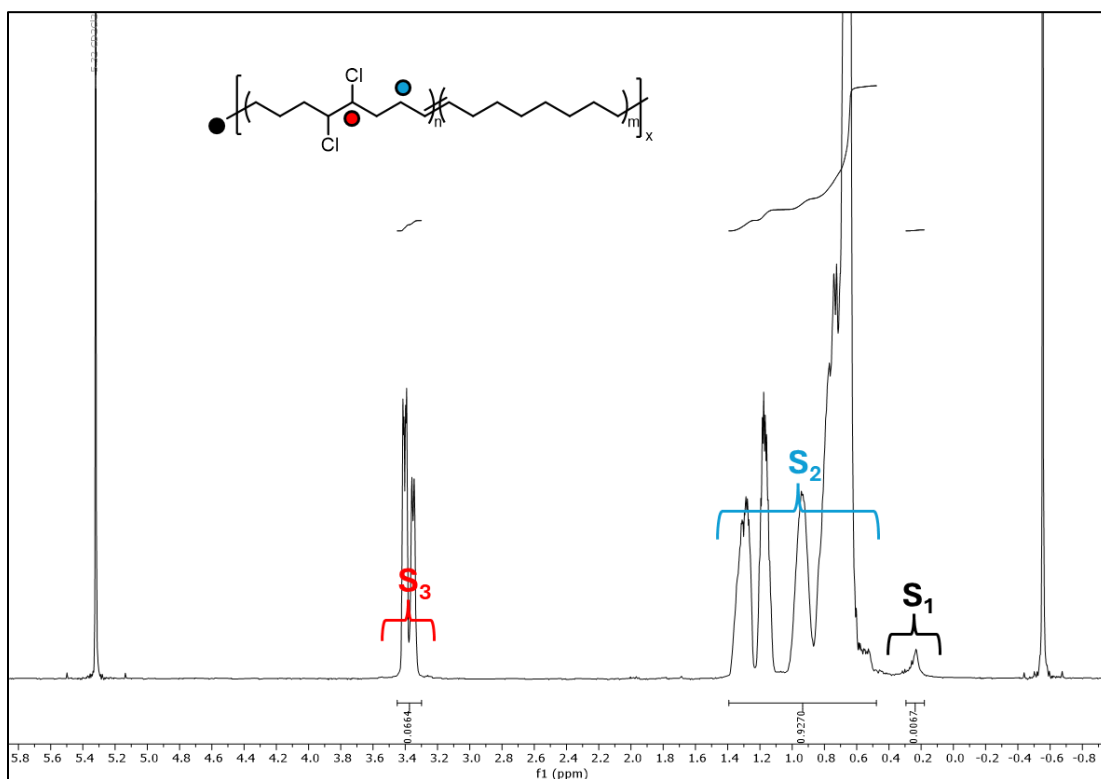


Figure S80. ^1H NMR spectrum of S50-1 dissolved in 1,1,2,2-tetrachloroethane- d_2 with integrations of S_1 , S_2 , and S_3 identified.

Determination of Relative Blockiness:

Relative blockiness is determined by comparing the normalized integration of non-chlorinated PE pentads (ISO) at ~29.4 ppm from $q^{13}\text{C}$ NMR to the integration from a statistical randomly chlorinated polyethylene model.^{4,5} The statistical model is based on calculated Bernoullian probabilities dependent on the chlorine content of the sample. For the ISO peak integration, the expected value from the statistical model, determined by H. Chang et al, is $(1-x/2)^8$, where x is the mole ratio of chlorine. The peaks present in the carbon NMR are normalized to a sum of 1 before comparison to fit the model. The percent difference between the observed ISO integration and the model integration is the relative blockiness, as shown in Equation 2. The larger the difference between the statistical and actual NMR peak integrations, the more similar the structure of the polymer is to a multiblock copolymer compared to a random copolymer.

$$(2) \text{ Relative Blockiness(ISO)} = |ISO_{obs} - ISO_{model}| / ISO_{model} \times 100\%$$

Sample calculation for R1

Table S1. ^{13}C NMR integrations for **R1** which has a chlorine content of 23 mol% Cl.

Integrations	ISO
Expected	0.377
Observed	0.368

$$\text{Relative Blockiness(ISO)} = \frac{|0.377 - 0.368|}{0.377} \times 100\% = 2.25\%$$

Sample calculation for B6

Table S2. ^{13}C NMR integrations for **B6** which has a chlorine content of 19 mol% Cl.

Integrations	ISO
Expected	0.441
Observed	0.874

$$\text{Relative Blockiness(ISO)} = \frac{|0.441 - 0.874|}{0.441} \times 100\% = 98.2\%$$

Determination of Reactivity Ratios:

To determine reactivity ratios of these monomers, the nonterminal or Beckingham-Sanoja-Lynd (BSL) model was then used to determine reactivity ratios due to the nature of the monomers used.⁶ These copolymerizations are classified as “ideal” meaning they depend on the chemistry of the monomer, and in this case the interaction with the ruthenium metal center of **G3**, not the polymer chain end to determine which monomer will add next. This method of determining reactivity ratios was chosen because of the BSL model’s ability to distinguish between random and gradient copolymers.⁶ To do this, ¹H NMR was used to monitor conversion over time and total monomer conversion versus individual monomer conversion was plotted. A standard polymerization reaction was set up where both monomers were added to a vial in a 1:1 mixture with deuterated chloroform as the solvent and trimethoxy benzene as an internal standard added in 1 equivalence. ¹H NMRs were obtained on a Varian 500 MHz NMR of the initial monomer mixture before Grubbs 3rd generation catalyst was added and of aliquots over a period of several minutes (0 s, 10 s, 20 s, 30 s, 1 min, 2 min, 3 min, 4 min, 5 min, and 6 min) after the catalyst was added. All samples were quenched with ethyl vinyl ether, including the initial timepoint, before taking NMR to ensure consistency. A sample ¹H NMR of a 10 s timepoint is included in Figure S81.

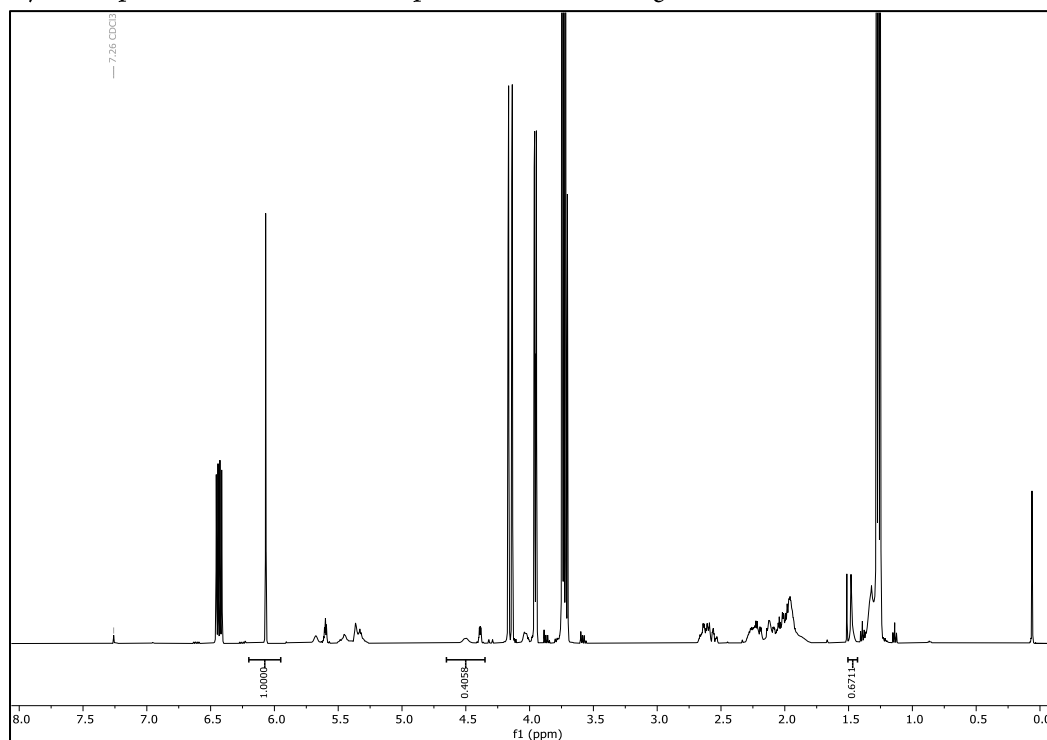


Figure S81. ¹H NMR of copolymerization ran for 10 seconds with trimethoxy benzene as internal standard in deuterated chloroform.

Trimethoxy benzene was integrated from 6.01-6.14 ppm and set to 1 for the other integrations to be referenced against. Cl₂COE (monomer A) was integrated from 4.35-4.63 ppm, as this encompasses both protons geminal to the chlorine in both isomers, and COE (monomer B) was integrated from 1.44-1.51 ppm. These integrations were monitored over time, and the monomer conversion (p_A and p_B) was calculated over a period of 6 minutes.

For the BSL method, the total conversion (p_{AB}), individual monomer conversions (p_A and p_B), and initial monomer molar fractions (n_A and n_B) were used in equations 3-5 to solve for the reactivity ratios (r_A and r_B).⁶ Total monomer conversion was found using Equation 3, where n_A and n_B are the initial mole fractions of each respective

monomer.⁷ Data acquired within the first minute of the reaction were analyzed with a linearized form of Equations 3 and 4 using linear regression in Python. The optimized values of r_A and r_B are reported with the statistically derived uncertainty.

$$(3) \quad p_{AB} = 1 - n_A \left(\frac{[M_A]_t}{[M_A]_0} \right) - (1 - n_A) \left(\frac{[M_B]_t}{[M_B]_0} \right)$$

$$(4) \quad p_{AB}(p_A) = 1 - n_A \times (1 - p_A) - (1 - n_A) \times (1 - p_A)^{r_B}$$

$$(5) \quad p_{AB}(p_A) = 1 - n_A \times (1 - p_B)^{r_A} - (1 - n_A) \times (1 - p_B)$$

Additionally, the Mayo Lewis model was used to validate the reactivity ratios determined from the non-terminal BSL model. To do so, homopolymerization experiments were performed to determine the self-propagating homopolymerization rate constants (k_A and k_B). These rate constants were used as input to solve for the cross-propagation rate constants (k_{AB} and k_{BA}) using equations 4-8, where M_A , M_B , M_A^* , and M_B^* are time-dependent monomer concentrations.⁸ The reactivity ratios were calculated using the rate constants (equations 8-9) and a nonlinear regression analysis in Python.

$$(6) \quad -\frac{d[M_A]_t}{dt} = k_A[M_A^*]_t[M_A]_t + k_{BA}[M_B^*]_t[M_A]_t$$

$$(7) \quad -\frac{d[M_B]_t}{dt} = k_{AB}[M_A^*]_t[M_B]_t + k_B[M_B^*]_t[M_B]_t$$

$$(8) \quad -\frac{d[M_A^*]_t}{dt} = k_{AB}[M_A^*]_t[M_B]_t - k_{BA}[M_B^*]_t[M_A]_t$$

$$(9) \quad -\frac{d[M_B^*]_t}{dt} = k_{BA}[M_B^*]_t[M_A]_t - k_{AB}[M_A^*]_t[M_B]_t$$

$$(10) \quad r_A = \frac{k_A}{k_{AB}}$$

$$(11) \quad r_B = \frac{k_B}{k_{BA}}$$

The reactivity ratios identified from this data and the monomer concentration vs time plot can be found in Figure S82.

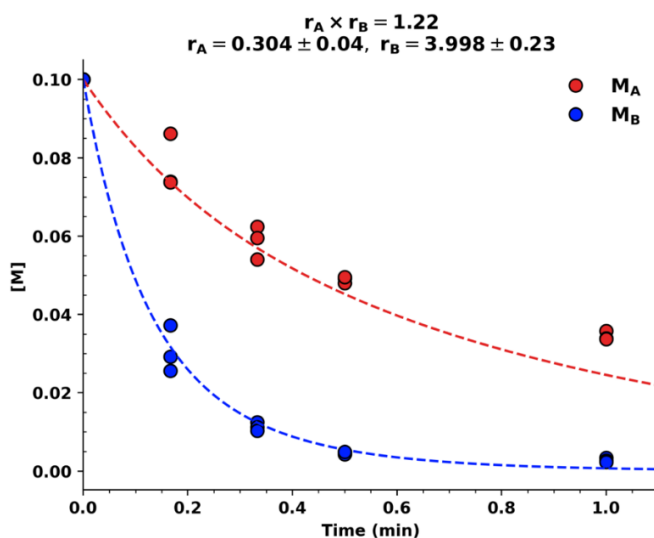


Figure S82. Mayo Lewis terminal model used to determine reactivity ratios from kinetic plots of monomer concentration vs time

Determination of Interfacial Adhesion:

Interfacial adhesion (G_a) was calculated using Equation 12 with force collected from an Instron Universal Tester (5kN) and width measured using a caliper at the exact point force was collected.⁵ This value for interfacial adhesion can quantify how the strength of the interface between the incompatible polymers is improving with the addition of compatibilizers. A combination T+U peel test is an average of a 90° peel for a T test and a 180° U peel test.

$$(12) G_a = \frac{F}{w}$$

Determination of Trilayer Procedure:

Previous work by our group prepared the trilayer samples at 200 °C for 15 minutes, however, several studies were performed to determine if this was the best procedure for these samples.⁵ A 200 °C processing temperature is required to ensure the PVC is significantly above its T_g (85 °C) without degrading. This was verified with Thermogravimetric Analysis (TGA) (Figure S83) collected from a TA Instruments Q-50 TGA of PVC thermally stabilized with Mark1900. Next, we varied the time the samples were in the Carver press at 200 °C (Figure S84). It was determined that 15 minutes was the maximum amount of time the samples could be held at that temperature before obvious yellowing from oxidation became prevalent. This also likely accounts for the consistent decrease in interfacial adhesion across all compatibilizers tested after 20 minutes in the Carver press.

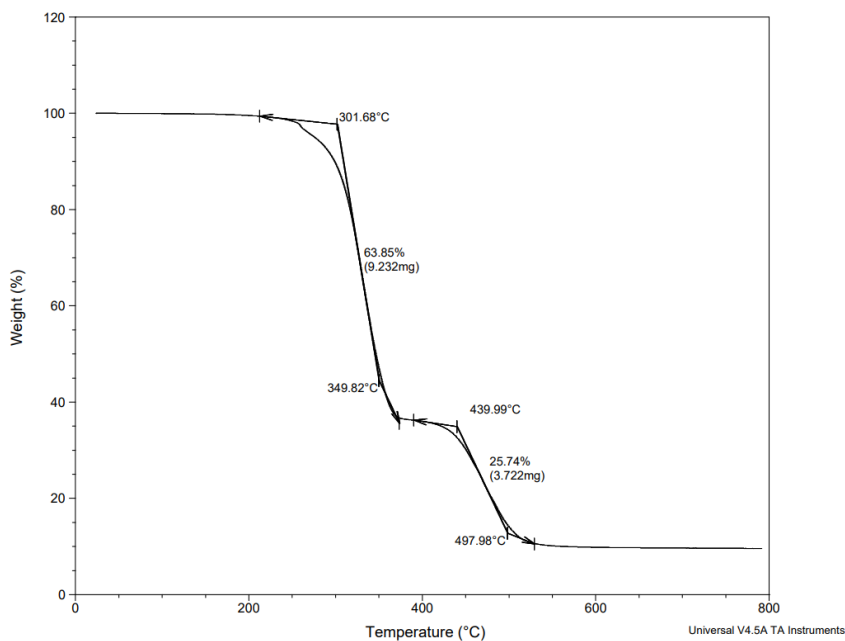


Figure S83. TGA thermogram for thermally stabilized PVC powder.

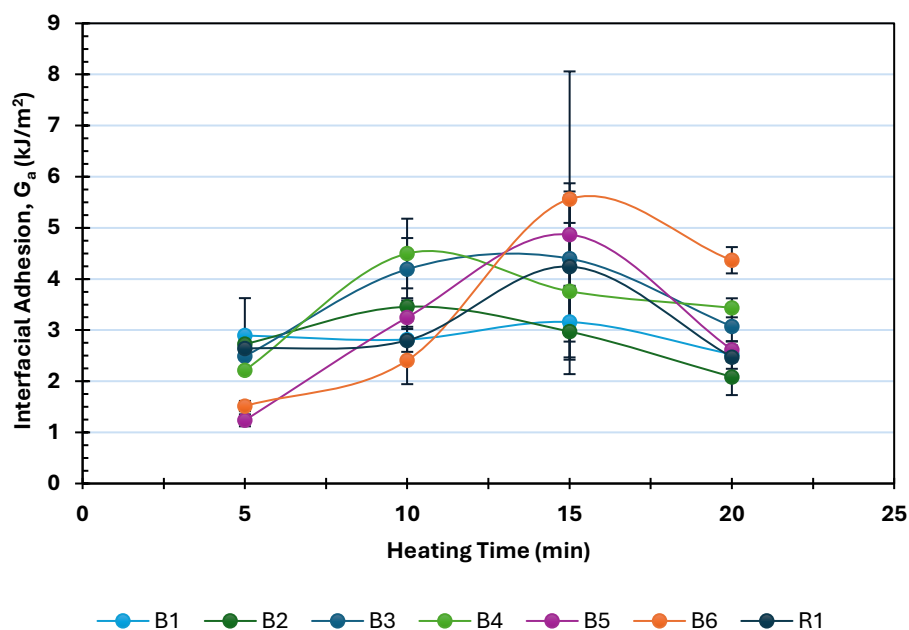


Figure S84. Interfacial adhesion of commercial compatibilizers at varying trilayer heating times in the Carver press.

Polymer Characterization Data:

Table S3. Compatibilizer characterization for all commercial and synthesized c-PEs. ^aCommercial materials denoted by their blocky or random structure. ^bSynthesized homopolymers containing 100% molar ratio of Cl₂COE monomer content. ^cSynthesized copolymers containing 75, 50, and 25% molar ratios of Cl₂COE monomer content. ^dMonomer feed ratios are Cl₂COE:COE.

Sample	Feed Ratio ^d	Actual Monomer Ratio ^d	Polymer Sequence Distribution	Relative % Blockiness	M _n (kg/mol)	Đ	Chlorines per 100 carbons	Heat of Fusion (J/g)	G _a (kJ/m ²)
^a B1	N/A	N/A	Blocky	6.9	62.6	3.8	14.4	19.3	3.2 ± 0.69
^a B2	N/A	N/A	Blocky	11.1	24.3	3.7	22.7	26.7	3.0 ± 0.83
^a B3	N/A	N/A	Blocky	11.1	87.2	5.1	17.7	35.8	4.9 ± 1.00
^a B4	N/A	N/A	Blocky	27.2	67.1	4.1	10.4	27.0	3.4 ± 1.34
^a B5	N/A	N/A	Blocky	33.1	35.6	5.1	17.7	35.8	4.9 ± 1.00
^a B6	N/A	N/A	Blocky	98.2	30.8	6.2	19.3	42.6	5.6 ± 2.50
^a R1	N/A	N/A	Random	2.3	128.0	12.	23.1	2.7	4.2 ± 1.47
^b S100-1	100:0	100:0	homo	N/A	19.9	4.1	24.0	0.0	3.3 ± 0.56
^b S100-2	100:0	100:0	homo	N/A	62.7	3.5	22.4	0.0	2.8 ± 0.44
^b S100-3	100:0	100:0	homo	N/A	68.8	1.8	22.2	0.0	2.9 ± 0.60
^b S100-4	100:0	100:0	homo	N/A	71.2	2.5	24.2	0.0	2.6 ± 0.31
^b S100-5	100:0	100:0	homo	N/A	99.6	1.8	23.5	0.0	2.4 ± 0.28
^b S100-6	100:0	100:0	homo	N/A	115.0	2.3	23.5	0.0	2.6 ± 0.16

^b S100-7	100:0	100:0	homo	N/A	124.5	2.0	23.7	0.0	3.4 ± 0.23
^b S100-8	100:0	100:0	homo	N/A	129.2	2.2	23.3	0.0	2.5 ± 0.37
^b S100-9	100:0	100:0	homo	N/A	140.0	2.1	24.1	0.0	3.3 ± 0.56
^c S75-1	75:25	74:26	Gradient	-	40.2	2.2	18.0	9.3	2.3 ± 0.46
^c S75-2	75:25	72:28	Gradient	-	64.4	2.2	17.8	5.8	3.1 ± 0.48
^c S75-3	75:25	73:27	Gradient	5.7	78.8	2.1	17.9	7.2	3.2 ± 0.64
^c S75-4	75:25	77:23	Gradient	6.0	101.8	2.1	18.5	0.0	3.5 ± 0.45
^c S75-5	75:25	76:24	Gradient	5.2	128.0	2.1	18.5	0.0	3.8 ± 0.67
^c S75-6	75:25	78:22	Gradient	-	120.9	1.9	19.0	0.0	3.7 ± 0.63
^c S50-1	50:50	54:46	Gradient	-	55.4	2.1	12.5	14.5	2.0 ± 0.34
^c S50-2	50:50	54:46	Gradient	18.2	57.3	2.9	12.5	13.1	3.1 ± 0.95
^c S50-3	50:50	48:52	Gradient	13.3	90.6	2.3	11.6	17.2	2.9 ± 0.39
^c S50-4	50:50	53:47	Gradient	-	106.2	2.3	12.2	18.6	3.2 ± 0.39
^c S50-5	50:50	48:52	Gradient	10.8	137.1	2.3	11.7	14.2	2.8 ± 0.78
^c S50-6	50:50	50:50	Gradient	-	147.3	2.1	11.8	16.8	4.5 ± 0.63
^c S25-1	25:75	25:75	Gradient	8.5	65.6	2.4	6.0	36.2	2.7 ± 0.37
^c S25-2	25:75	17:83	Gradient	-	73.7	2.3	4.1	65.4	3.1 ± 0.95
^c S25-3	25:75	24:76	Gradient	-	94.5	2.2	5.8	46.5	2.9 ± 0.39
^c S25-4	25:75	25:75	Gradient	14.0	100.1	2.2	6.0	40.4	2.5 ± 0.58
^c S25-5	25:75	24:76	Gradient	-	136.7	2.1	5.8	35.7	3.1 ± 0.30
^c S25-6	25:75	24:76	Gradient	6.0	149.2	2.4	5.7	44.2	2.1 ± 0.23

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