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Polyglycolic Acid from the Direct Polymerization of Renewable C1 Feedstocks

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Electronic Supplementary Information (ESI)

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

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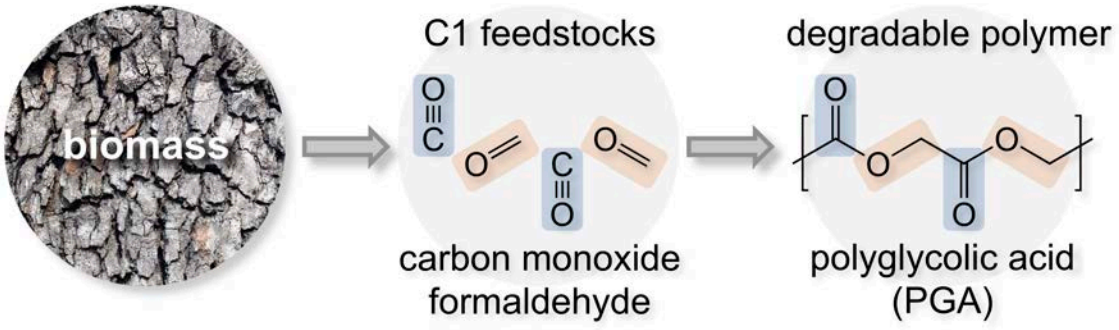


General Considerations and Instrumentation

Unless otherwise noted, all solvents were purified by stirring over calcium hydride for 24 hours and then vacuum transfer into an oven dried Straus flask. Xylenes were purchased from Sigma Aldrich and stored over molecular sieves. Solvents were purchased from Sigma Aldrich and utilized after further purification. Paraformaldehyde was purchased from Sigma Aldrich. Trioxane was purchased from Acros Organics and used after recrystallization in $CHCl_3$. The initiators *para*-toluenesulfonic acid (*p*-TSA) and BF_3•OEt_2 were purchased from Sigma Aldrich and used as received. Triflic acid (TfOH) was purchased from Oakwood Chemical and used as received. A Parr 4768Q 600 mL high pressure autoclave was used for the experiments with a magnetic stir bar.

Nuclear magnetic resonance (^{1}H NMR and ^{13}C NMR) spectra were recorded using an Inova 500 MHz spectrometer. NMR sample preparation: 0.5 g of sample was dissolved in 0.4 g of HFIP, and 1.0 g of $CDCl_3$ (or C_6D_6) was added to the mixture.; HFIP-d_2 was also used for some NMR spectra. For ^{1}H NMR, number of scans = 32 with a 5 s relaxation delay. For ^{13}C NMR (125 MHz), number of scans = 10,000 with a 3 s relaxation delay. Chemical shifts are reported in parts per million (ppm) downfield relative to tetramethylsilane (TMS, 0.0 ppm) or residual protons in the specified solvent.

Differential scanning calorimetry thermograms were obtained with a DSC Q1000 from TA instruments. About 1.5-3 mg of each sample was weighed and sealed in a pan. Thermal history was established by a heat/cool/heat cycle at 10 °C/min, and the data were obtained for the second heating ramp.

Thermogravimetric analyses were performed under nitrogen with a TGA Q5000 from TA Instruments. About 5-10 mg of each sample was heated at 10 °C/min from RT to 500 °C.

Gel permeation chromatography (GPC) was performed at 40 ˚C using an Agilent Technologies 1260 Infinity Series liquid chromatography system with an internal differential refractive index detector, and two Waters Styragel HR-5E columns (7.8 mm i.d., 300 mm length, guard column 7.8 mm i.d., 25 mm length) using a solution of 0.1% potassium triflate (K(OTf)) in HPLC grade hexafluoroisopropanol (HFIP) as the mobile phase at a flow rate of 0.5 mL/min. Calibration was performed with narrow polydispersity polymethyl methacrylate (PMMA) standards.

Representative Polymerization Procedure for Table S1

Under a nitrogen atmosphere, a mixture of trioxane (9.03 g, 0.1 mol), and an acid initiator (1 mmol) in 100 mL of a solvent was placed in a 600 mL high pressure reactor, charged with the desired pressure of CO, and heated to the desired reaction temperature. The reaction was stirred under CO pressure for the desired reaction time at the same temperature. After cooling to room temperature, the pressure was released and the mixture was poured into cold basic methanol. The product was isolated by filtration, washed with methanol and dichloromethane (DCM), and dried under vacuum.

PGA formation (Table S1 entry 17)= ^{1}H NMR (500 MHz, HFIP-$CDCl_3$) δ ppm 4.84 (s, 2H). ^{13}C NMR (125 MHz, HFIP-$CDCl_3$) δ ppm 168.4, 61.4.

POM formation (Table S1 entry 2)= ^{1}H NMR (500 MHz, HFIP-$CDCl_3$) δ ppm 5.18 (s, 2H), 4.98 (s, 2H), 4.94 (s, 2H). ^{13}C NMR (125 MHz, HFIP-$CDCl_3$) δ ppm 89.9.

General Polymerization Procedure for Table S2

Under a nitrogen atmosphere, a mixture of trioxane (9.03 g, 0.1 mol), glycerol (0.073 mL, 1 mmol) and triflic acid (0.088 mL, 1 mmol) in 100 mL of DCM was placed in a 600 mL high pressure reactor, charged with 800 psi CO, and heated to the desired reaction temperature. The reaction was stirred under CO pressure for one day at the same temperature. After cooling to room temperature, the pressure was released and the mixture was poured into cold basic methanol. The product was isolated by filtration, washed with methanol and DCM, and dried under vacuum. ^{1}H NMR (500 MHz, HFIP-$CDCl_3$) δ ppm 4.86 (s, 2H). ^{13}C NMR (125 MHz, HFIP-$CDCl_3$) δ ppm 168.2, 60.9.

General Polymerization Procedure for Table S3

Under a nitrogen atmosphere, a mixture of the desired amount of paraformaldehyde and triflic acid (1 mol%) in 100 mL of DCM was placed in a 600 mL high pressure reactor, charged with 800 psi CO, and heated to the desired reaction temperature. The reaction was stirred under CO pressure for three days at the same temperature. After cooling to room temperature, the pressure was released and the mixture was poured into cold basic methanol. The product was isolated by filtration, washed with methanol and DCM, and dried under vacuum.

The Production of PGA from POM (entry 27)

Under a nitrogen atmosphere, a mixture of trioxane (9.03 g, 0.1 mol), and triflic acid (0.088 mL, 1 mmol) in 100 mL of DCM was placed in a 600 mL high pressure reactor. The reaction was stirred at room temperature for 12 hours. Then, without terminating the polymerization, the vessel was charged with 800 psi CO, and heated to 170 ^{o}C. The reaction

was stirred under CO pressure for three days. After cooling to room temperature, the pressure was released and the mixture was poured into cold basic methanol. The product was isolated by filtration, washed with methanol and DCM, and dried under vacuum. ^{1}H NMR (500 MHz, HFIP-$CDCl_3$) δ ppm 4.39 (s, 2H). ^{13}C NMR (125 MHz, HFIP-$CDCl_3$) δ ppm 168.2, 60.9.

Polycondensation of Oligomeric Glycolic Acid (OGA) (entry 28)

A 2.0 g amount of OGA (from Table S1 entry 17) was weighed into a 50 mL reaction flask equipped with a magnetic stirrer. Then, 0.5 weight % of $Zn(OAc)_2 \cdot 2H_2O$ relative to OGA was added. The mixture was heated at 200 ^{o}C with stirring under nitrogen for 2h, then heating continued under reduced pressure for 12 h. After cooling to room temperature, the mixture was poured into cold basic methanol. The product was isolated by filtration, washed with methanol and DCM to remove oligomeric residue, and dried under vacuum. Yield: 1.55 g brown solid. ^{1}H NMR (500 MHz, HFIP-$CDCl_3$) δ ppm 4.89 (s, 2H). ^{13}C NMR (125 MHz, HFIP-CDCl3) δ ppm 168.3, 60.9.

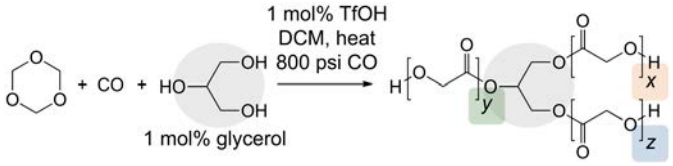
Summary of Polymerization Data

Table S1. Polymerization results: trioxane and carbon monoxide.

Entry[a]	CO (psi)	Initiator[b]	Solvent	T_p (°C)	Time	Yield (g)	Yield (%)	M_w (g/mol)	M_n (g/mol)	PDI	T_g (°C)	T_m (°C)
1	250	BF_3•OEt_2	DCM	RT	1 day	4.76	28	13,000	9,200	1.42	c	c
2	480	BF_3•OEt_2	DCM	RT	1 day	7.03	41	15,000	8,700	1.76	c	c
3	800	BF_3•OEt_2	DCM	100	1 day	NR	0	–	–	–	–	–
4	800	*p*-TSA	DCM	120	2 days	5.45	31	1,100	720	1.48	–22	133
5	800	TfOH	DCM	50	1 day	4.09	24	34,000	13,400	2.54	c	c
6	800	TfOH	DCM	60	1 day	4.26	25	38,000	12,400	3.05	c	c
7	800	TfOH	DCM	80	1 day	2.63	15	11,000	4,000	2.64	c	c
8	800	TfOH	DCM	100	1 day	2.51	14	1,000	740	1.43	c	115
9	800	TfOH	DCE	100	1 day	2.00	11	1,100	900	1.23	c	141
10	800	TfOH	Heptane	100	1 day	3.50	20	1,100	830	1.32	–18	119
11	800	TfOH	DCM	105	1 day	2.58	15	1,100	550	2.04	17	c
12	800	TfOH	DCM	130	1 day	3.53	20	1,600	1,100	1.50	3	c
13	800	TfOH	DCM	120	2 days	6.70	39	1,500	1,000	1.48	–39	143
14	800	TfOH	DCM	110	3 days	8.25	47	2,300	1,400	1.69	37	161
15	800	TfOH	DCM	130	3 days	11.00	63	1,500	1,000	1.48	c	164
16	800	TfOH	DCM	150	3 days	14.40	83	2,400	1,600	1.52	c	181
17	800	TfOH	DCM	170	3 days	16.00	92	3,200	1,800	1.73	13	192
18	800	TfOH	DCM	180	3 days	9.80	56	1,500	1,000	1.43	15	c
19[d]	800	TfOH	HFIP	170	3 days	2.44	56	2,200	1,400	1.59	38	c
20	800	TfOH	Xylenes	130	3 days	NR	0	–	–	–	–	–

[a]Reactions conducted with 0.100 mol (9.03 g) of trioxane. [b]Initiator loading was 1 mol % of trioxane. [c]Missing thermal response (T_g) or low decomposition temperatures (T_m) prevented conclusive thermal analysis by DSC. [d]0.020 mol (1.8 g) of trioxane employed.

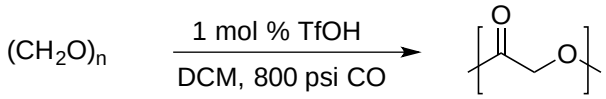
Table S2. Polymerization results: trioxane, carbon monoxide, and glycerol.



Entry[a]	T_p (°C)	Time	Yield (g)	Yield (%)	M_n (g/mol)	PDI	T_g (°C)	T_m (°C)
21	100	1 day	7.12	40	1,700	1.56	45	172
22	150	1 day	14.2	81	3,100	1.83	50	206
23	150	2 days	14.0	80	3,700	2.46	47	205
24	170	1 day	5.02	28	1,600	1.37	51	b

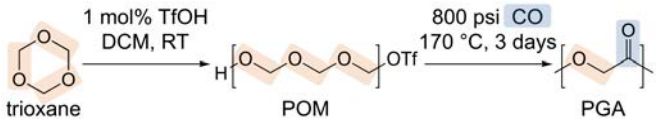
[a]Reactions conducted with 0.100 mol (9.03 g) of trioxane. Initiator (TfOH) loading was 1.0 mol % of trioxane. [b]Low decomposition temperature prevented conclusive T_m analysis by DSC.

Table S3. Polymerization results: paraformaldehyde and carbon monoxide.

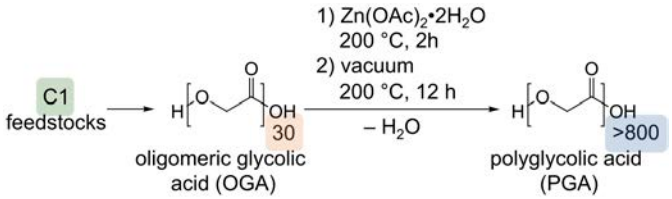


Entry	Paraformaldehyde (g)	T_p (°C)	Time	Yield (g)	M_n (g/mol)	PDI	T_g (°C)	T_m (°C)
25	3.0	100	1 day	4.4	1,000	1.30	–19	162
26	9.0	170	3 days	6.2	1,500	1.49	51	a

[a]Low decomposition temperature prevented conclusive T_m analysis by DSC



Scheme S1. PGA production (entry 27) from polyoxymethylene and CO.



Scheme S2. High molecular weight PGA (entry 28) production from polycondensation of oligomeric glyocolic acid (OGA).

FTIR Spectra

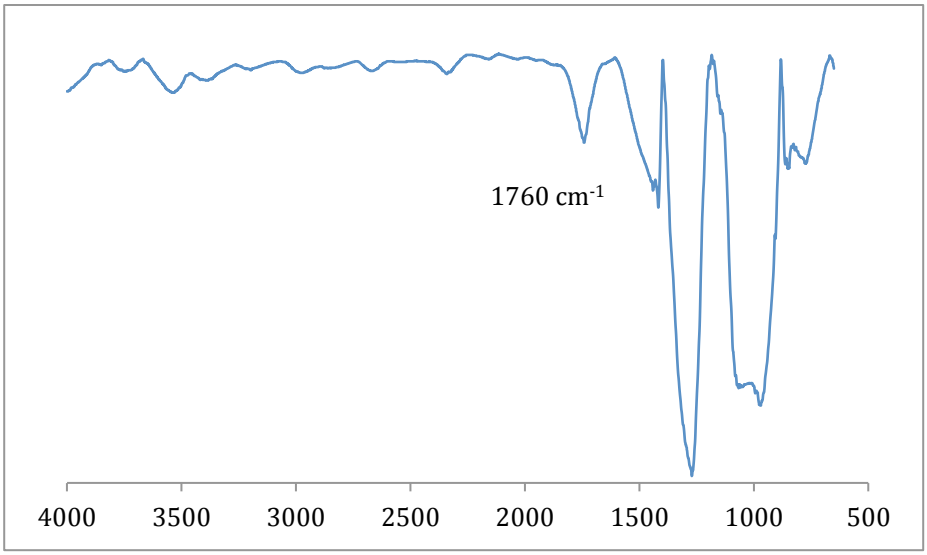


Figure S1. FTIR spectrum of polymer commercial polyglycolic acid.

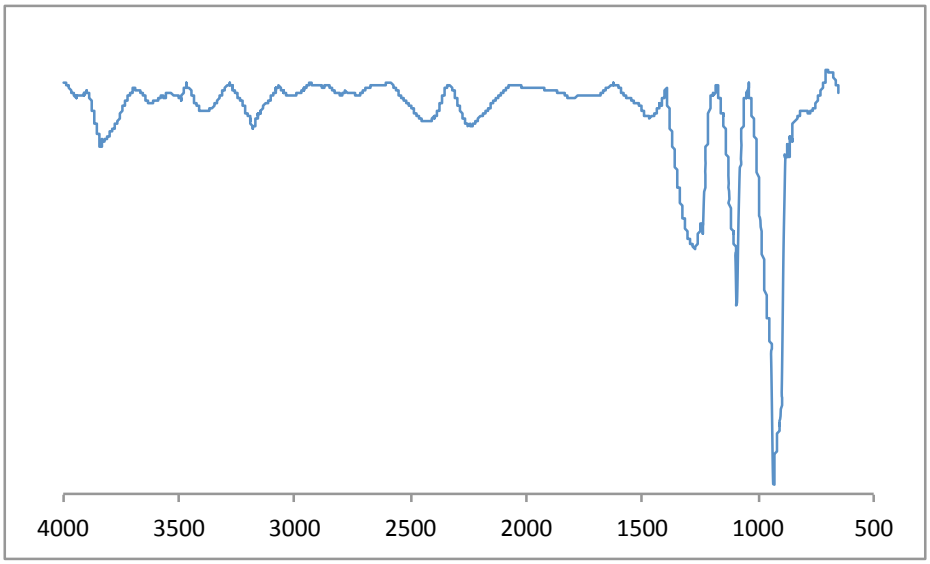


Figure S2. FTIR spectrum of polymer **1** (Table S1 entry 1).

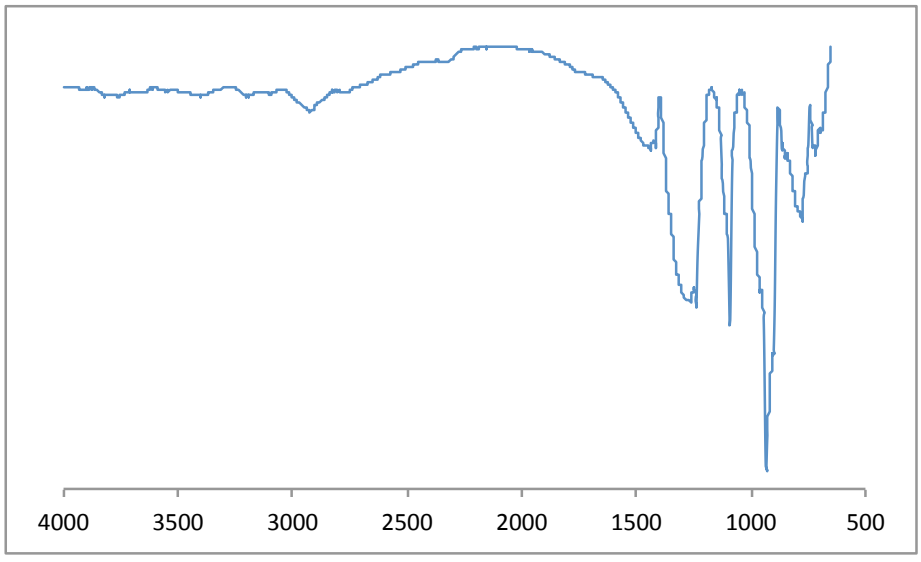


Figure S3. FTIR spectrum of polymer **2** (Table S1 entry 2).

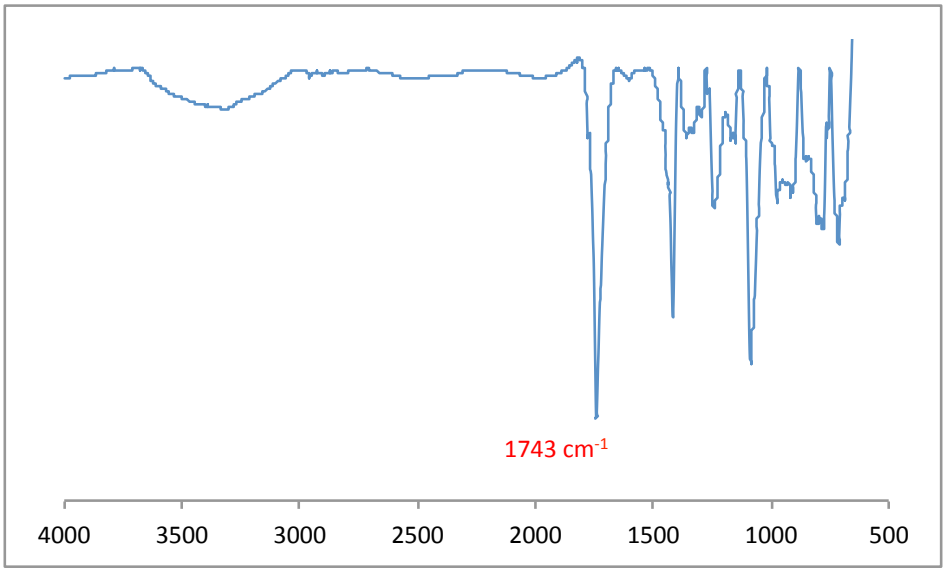


Figure S4. FTIR spectrum of polymer **4** (Table S1 entry 4).

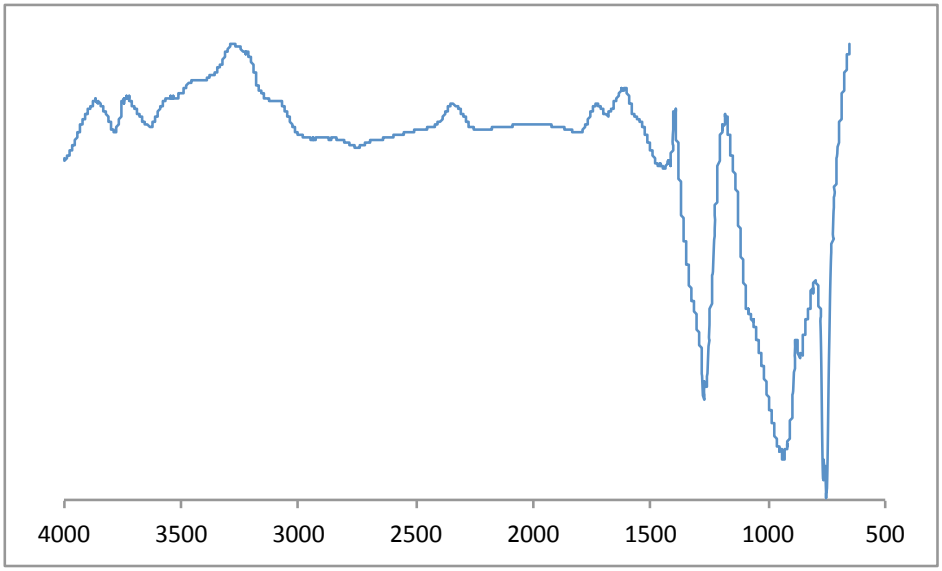


Figure S5. FTIR spectrum of polymer **5** (Table S1 entry 5).

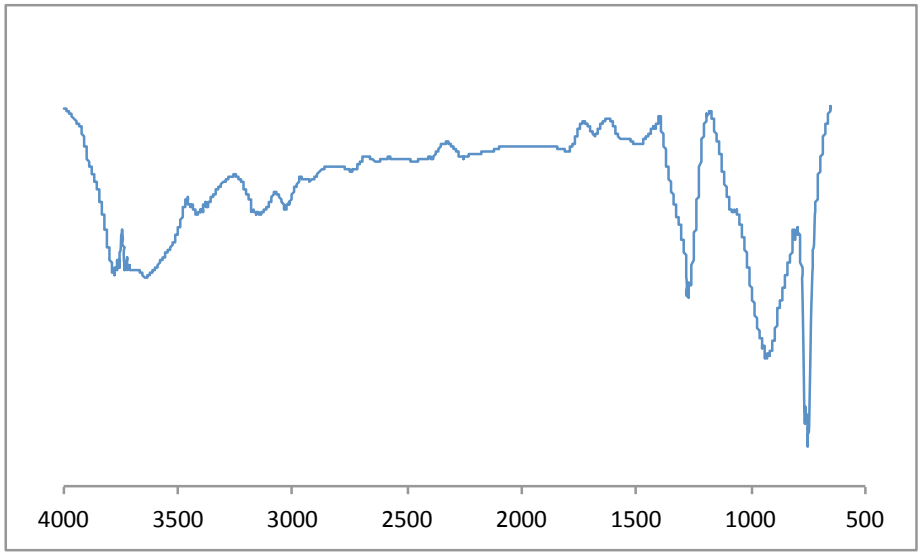


Figure S6. FTIR spectrum of polymer **6** (Table S1 entry 6).

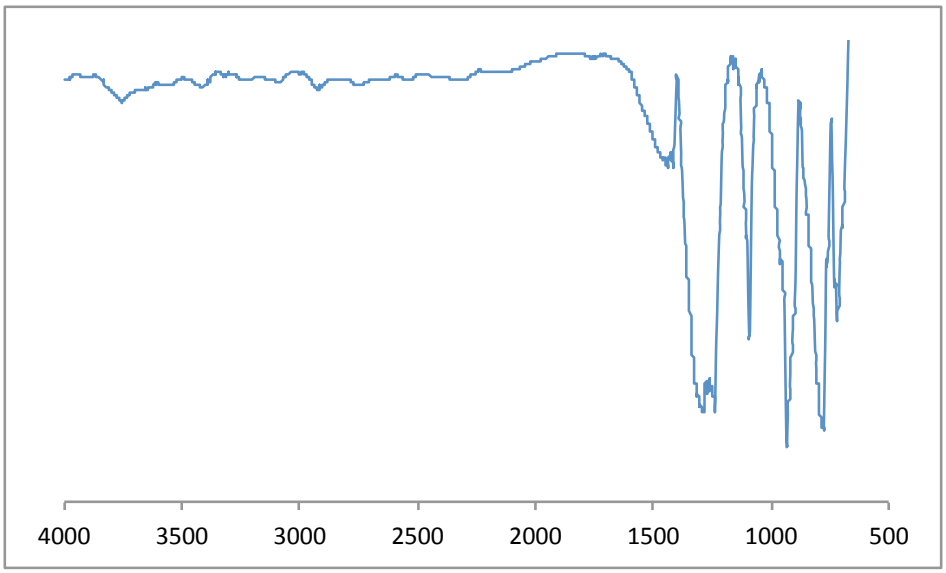


Figure S7. FTIR spectrum of polymer **7** (Table S1 entry 7).

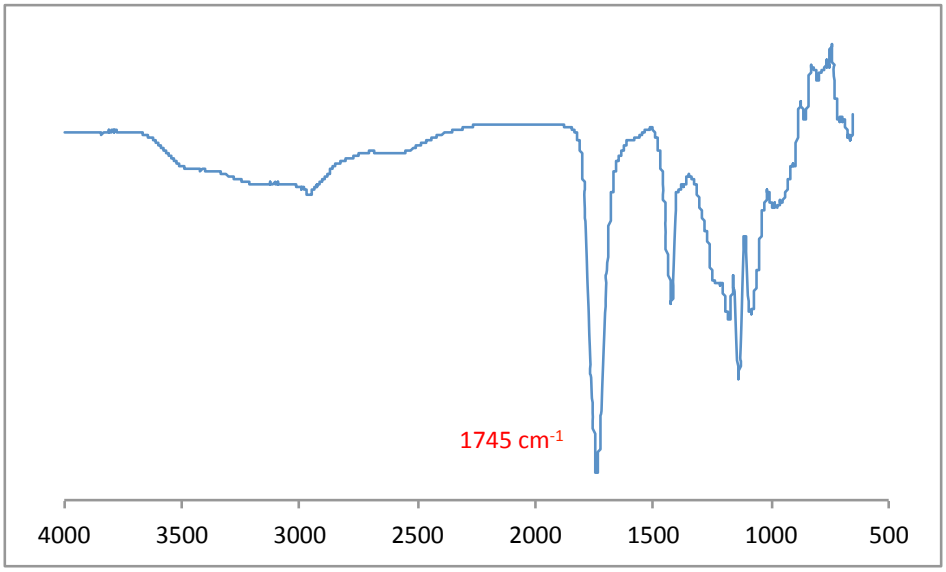


Figure S8. FTIR spectrum of polymer **8** (Table S1 entry 8).

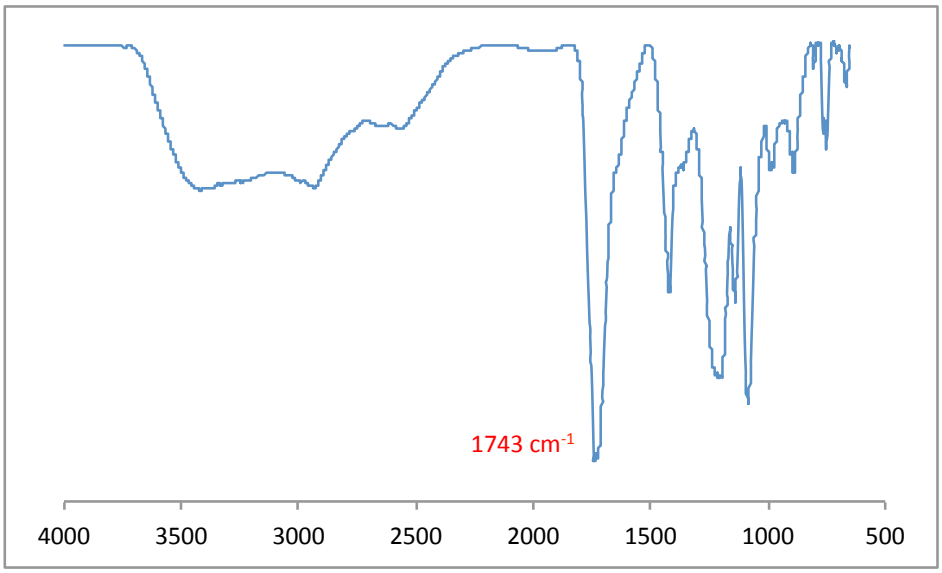


Figure S9. FTIR spectrum of polymer **9** (Table S1 entry 9).

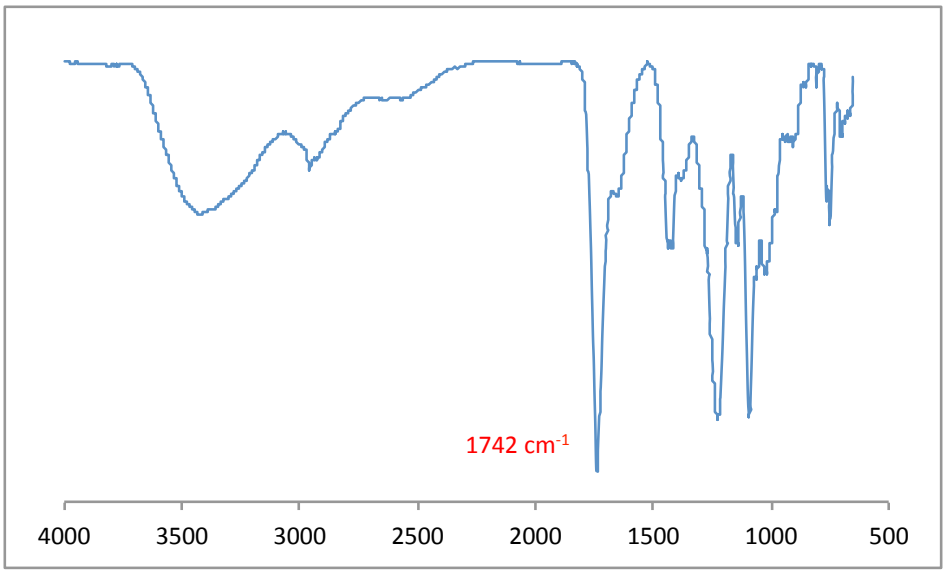


Figure S10. FTIR spectrum of polymer **10** (Table S1 entry 10).

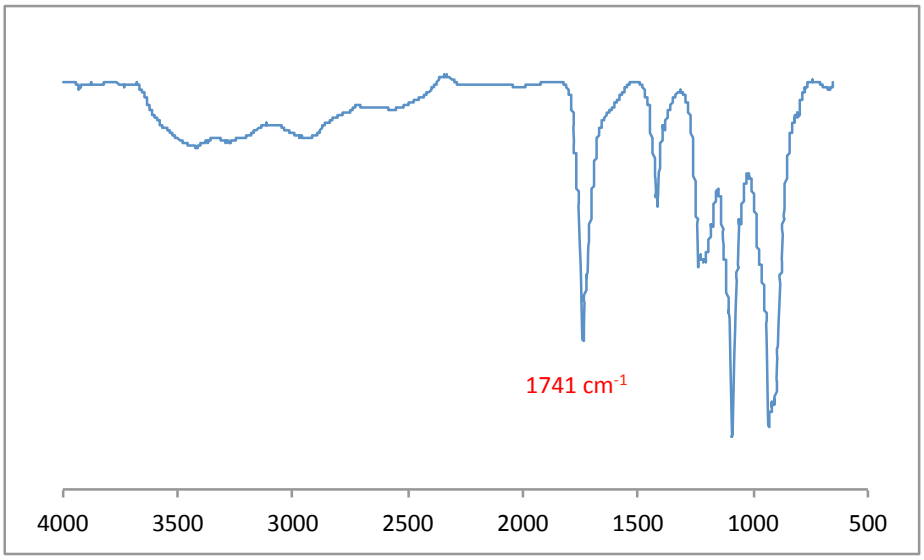


Figure S11. FTIR spectrum of polymer **11** (Table S1 entry 11).

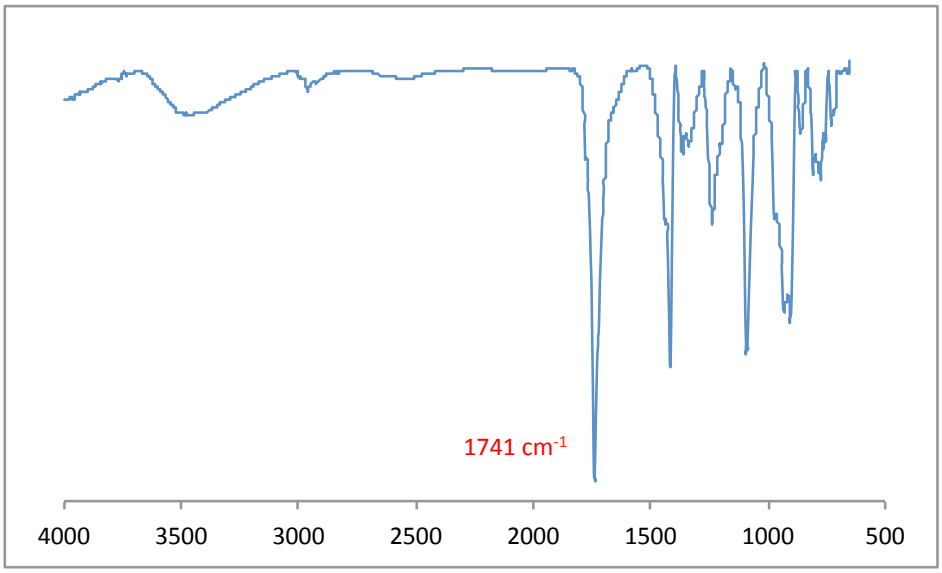


Figure S12. FTIR spectrum of polymer **12** (Table S1 entry 12).

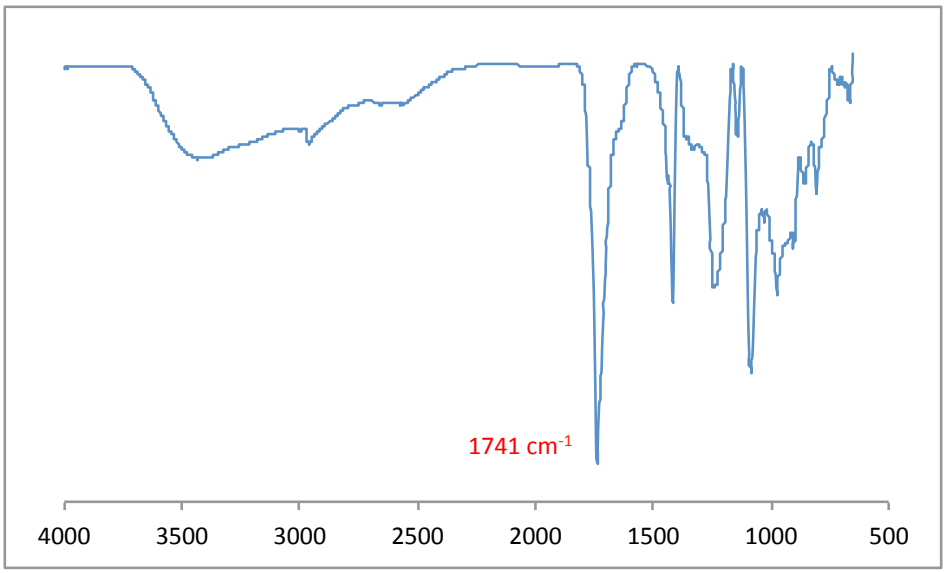


Figure S13. FTIR spectrum of polymer **13** (Table S1 entry 13).

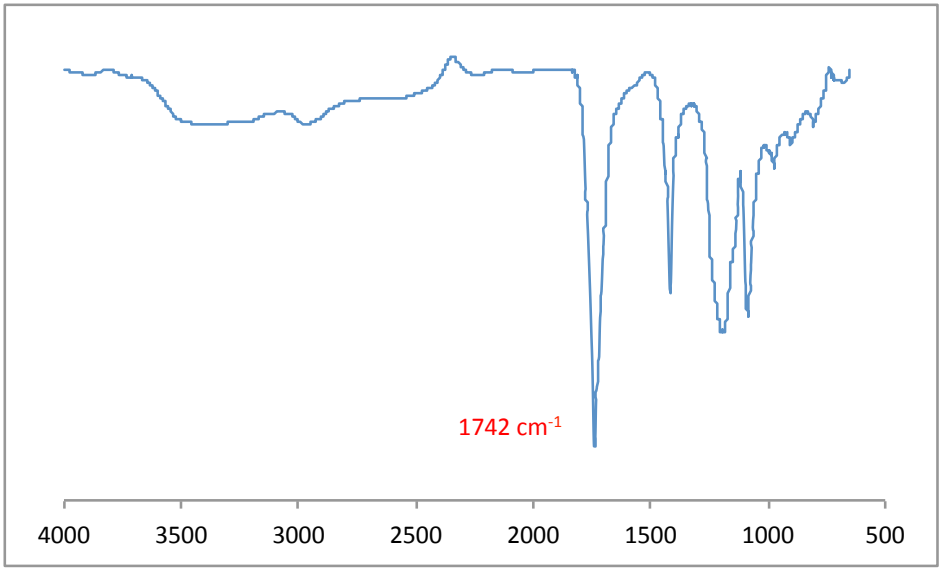


Figure S14. FTIR spectrum of polymer **14** (Table S1 entry 14).

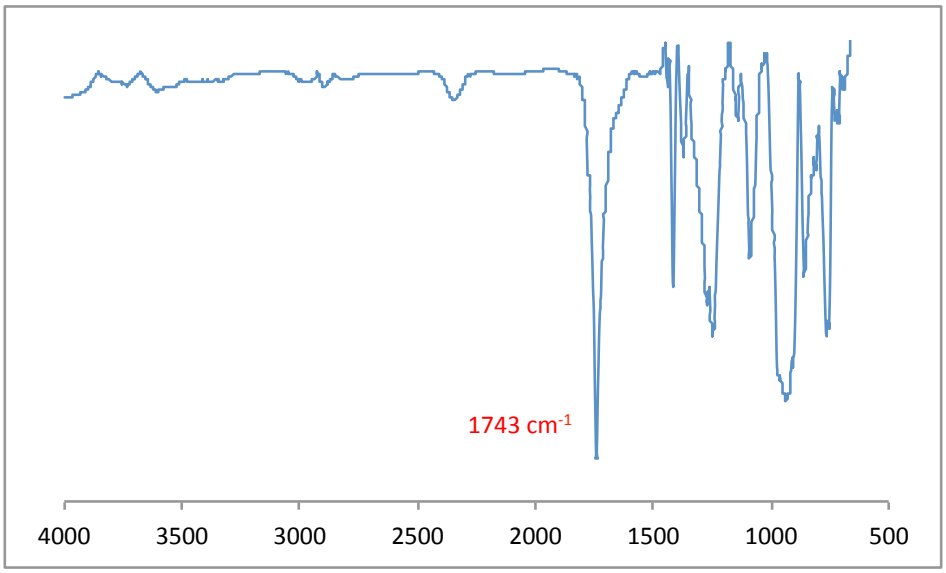


Figure S15. FTIR spectrum of polymer **15** (Table S1 entry 15).

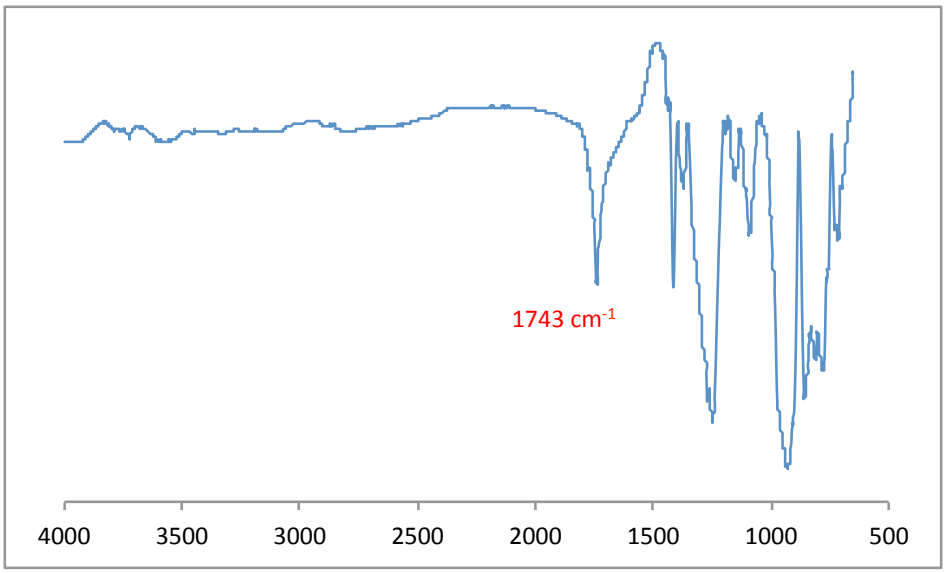


Figure S16. FTIR spectrum of polymer **16** (Table S1 entry 16).

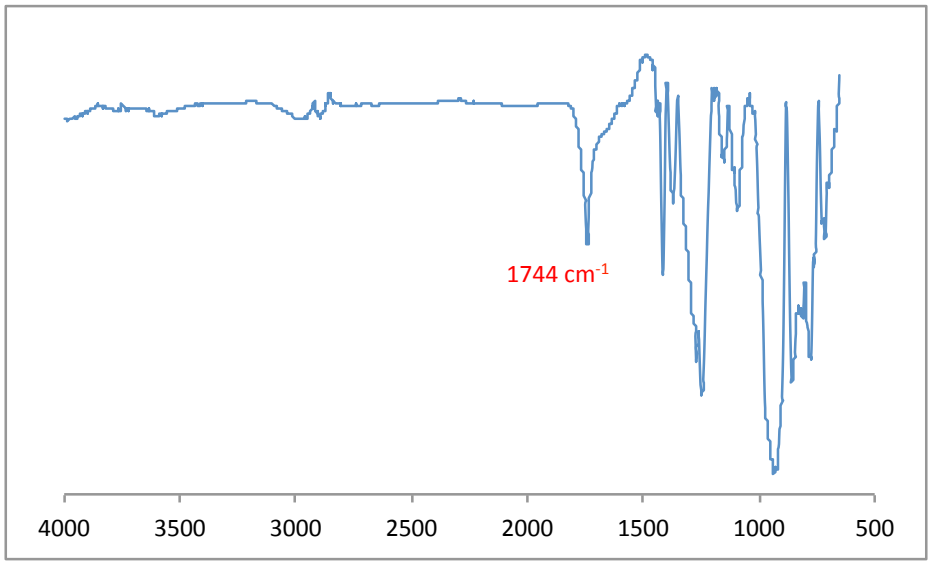


Figure S17. FTIR spectrum of polymer **17** (Table S1 entry 17).

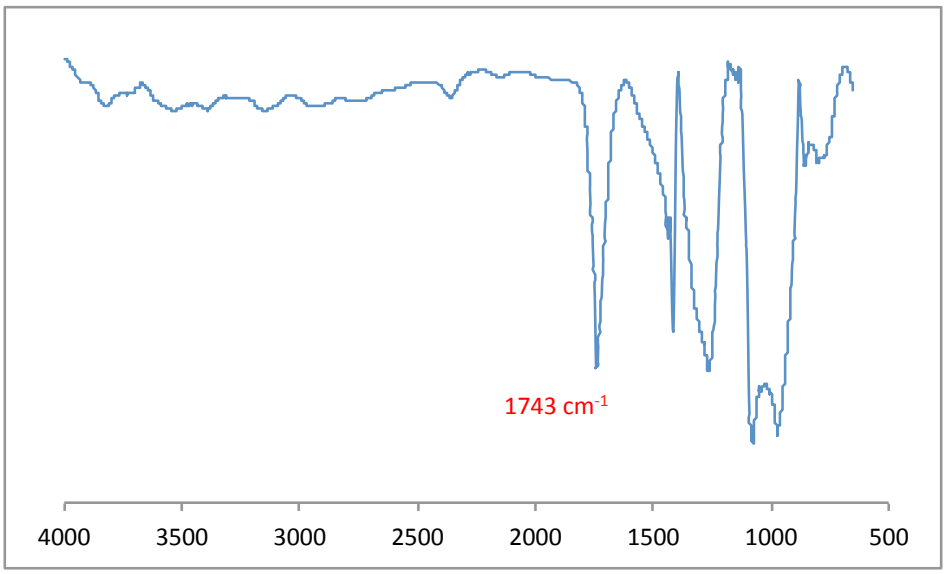


Figure S18. FTIR spectrum of polymer **18** (Table S1 entry 18).

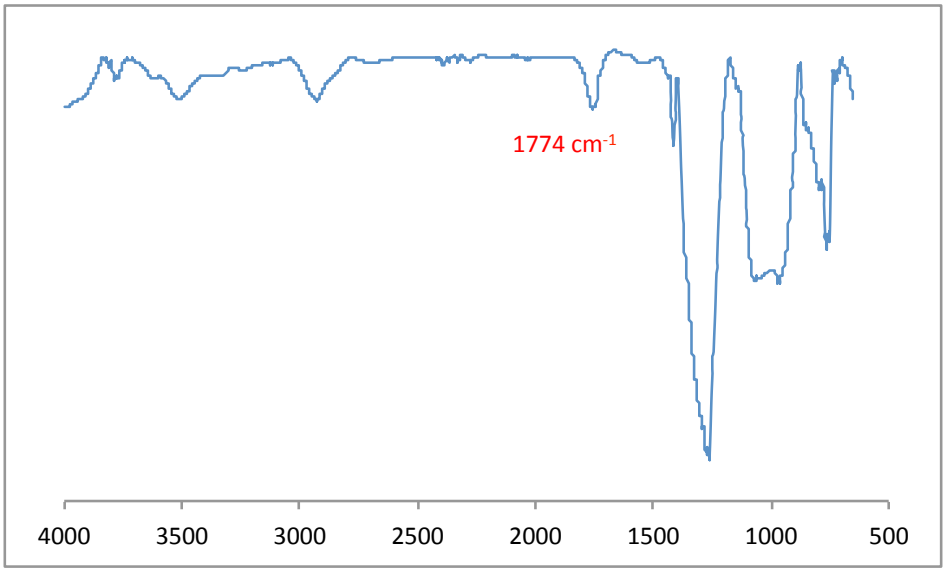


Figure S19. FTIR spectrum of polymer **19** (Table S1 entry 19).

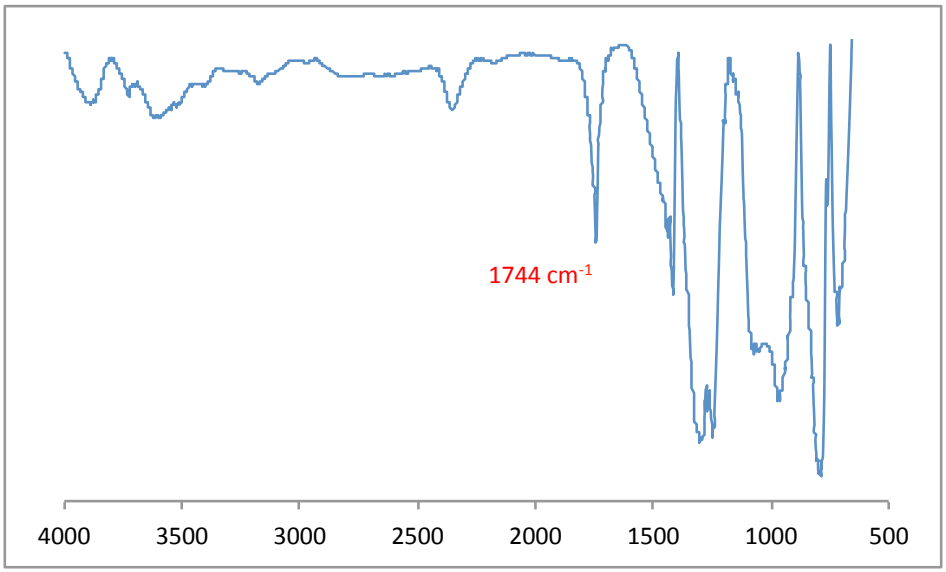


Figure S20. FTIR spectrum of polymer **21** (Table S2 entry 21).

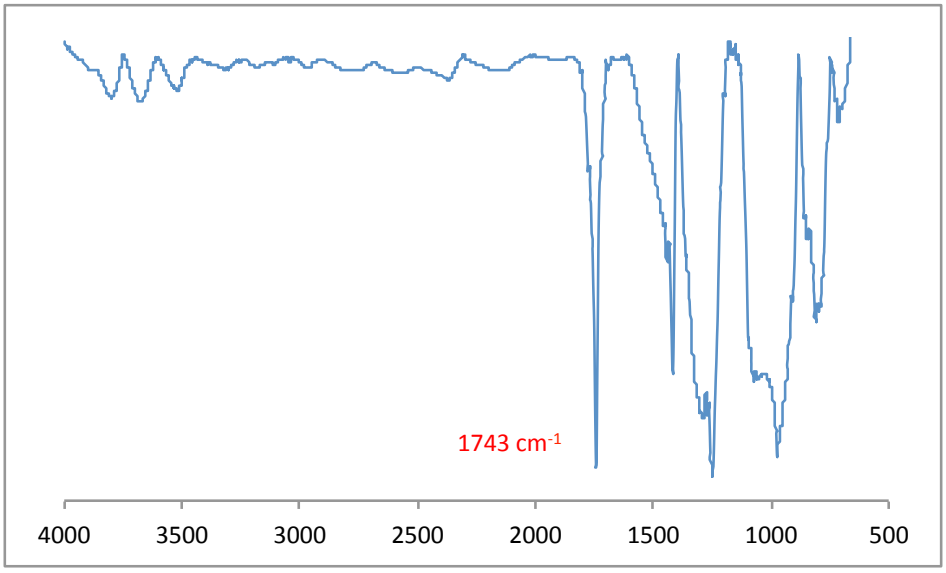


Figure S21. FTIR spectrum of polymer **22** (Table S2 entry 22).

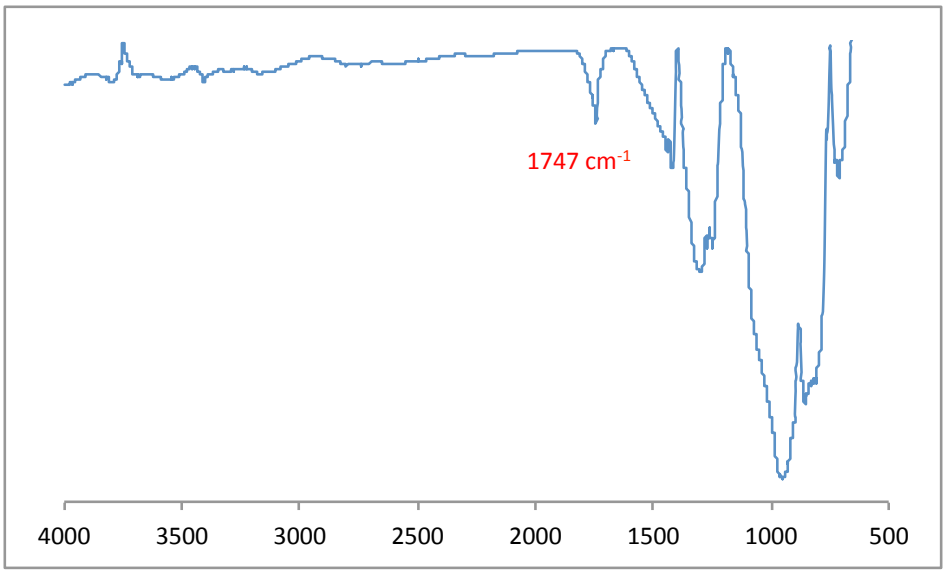


Figure S22. FTIR spectrum of polymer **23** (Table S2 entry 23).

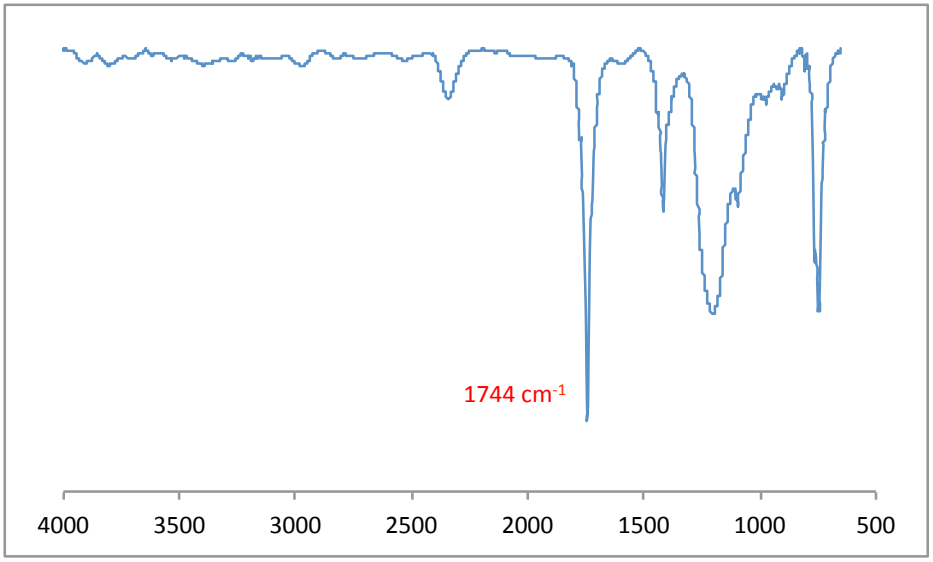


Figure S23. FTIR spectrum of polymer **24** (Table S2 entry 24).

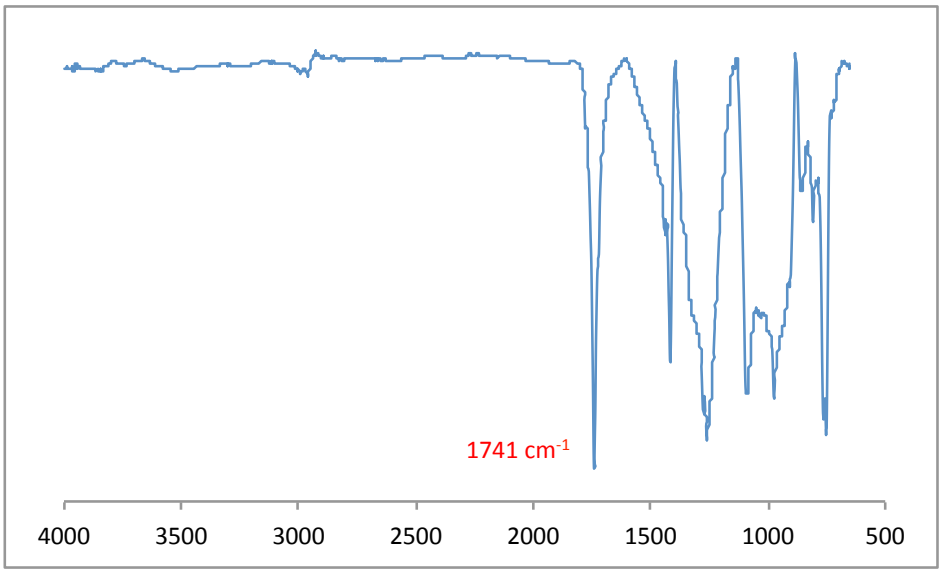


Figure S24. FTIR spectrum of polymer **25** (Table S3 entry 25).

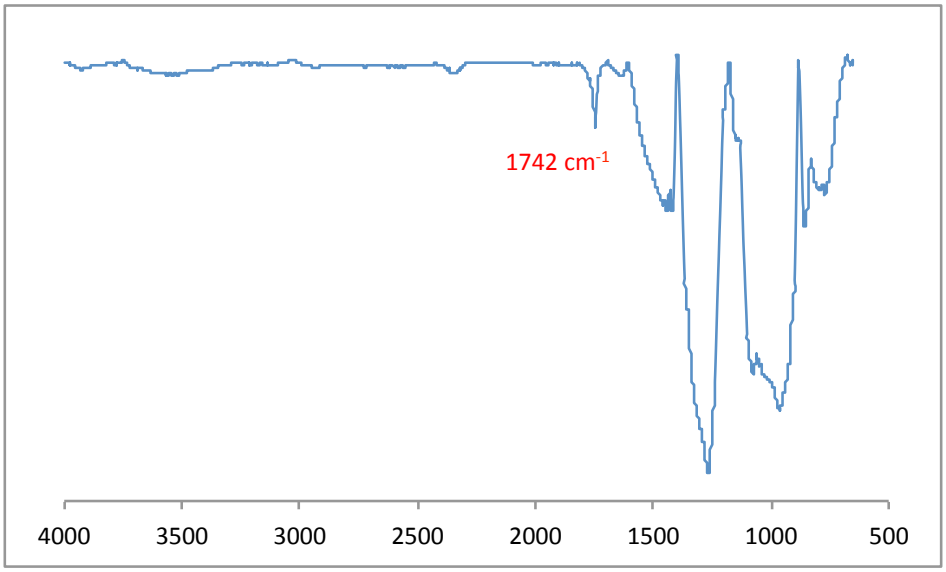


Figure S25. FTIR spectrum of polymer **26** (Table S3 entry 26).

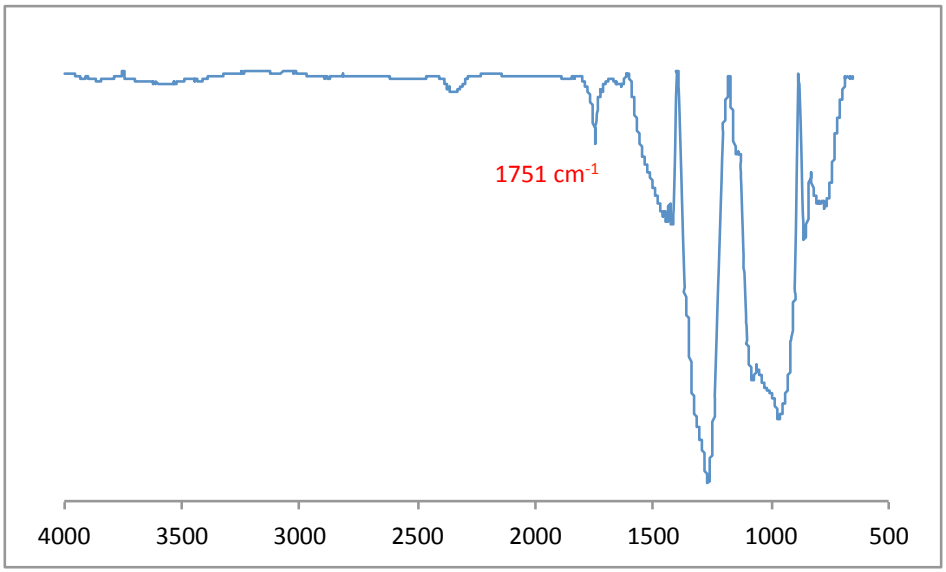


Figure S26. FTIR spectrum of polymer **27** (Scheme S1 entry 27).

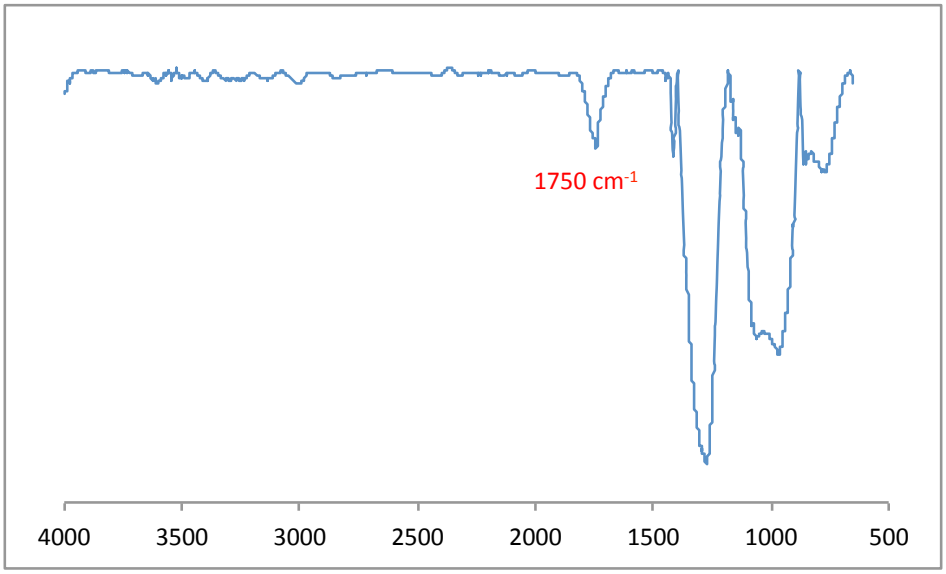


Figure S27. FTIR spectrum of polymer **28** (Scheme S2 entry 28).

Thermogravimetric Analyses

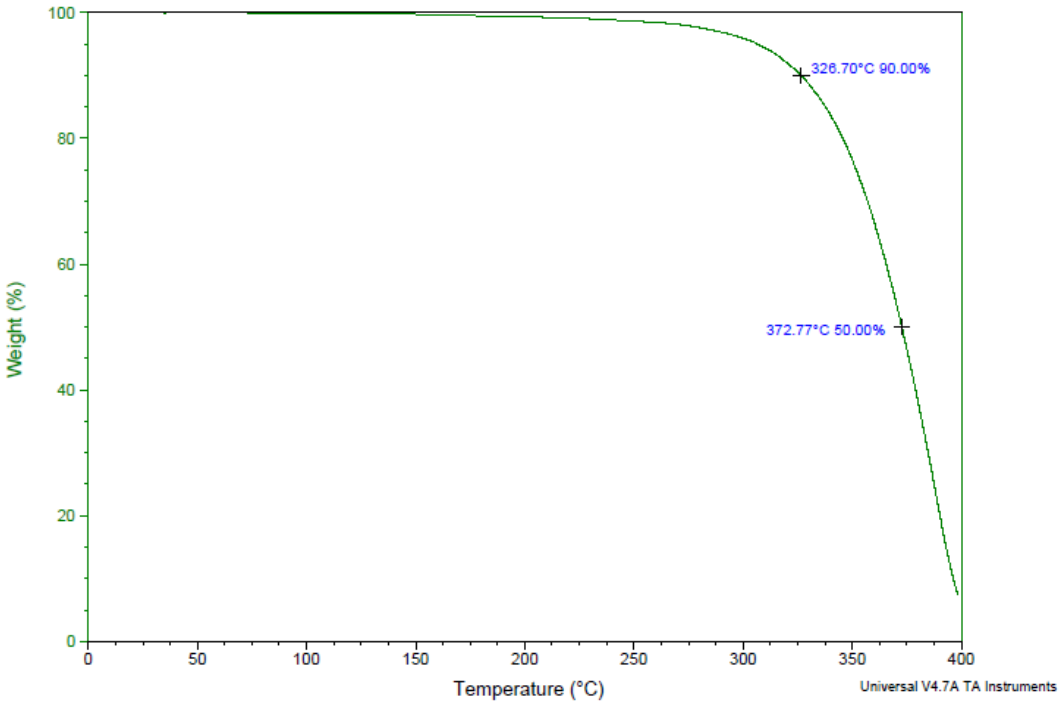


Figure S28. TGA Thermogram of commercial polyglycolic acid.

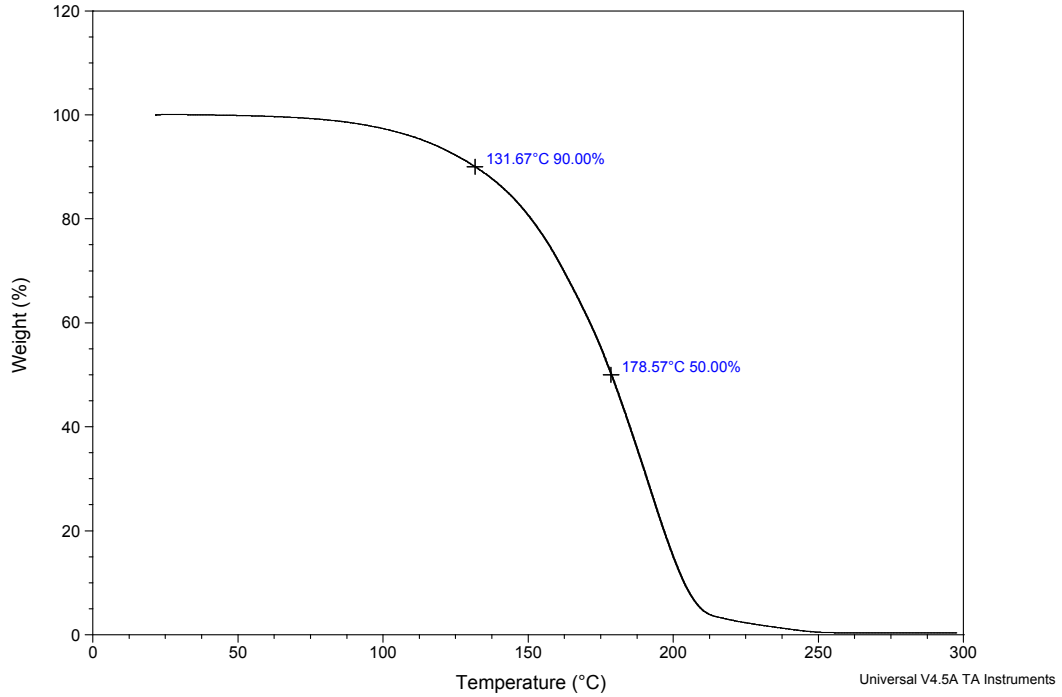


Figure S29. TGA Thermogram of polymer **1** (Table S1 entry 1).

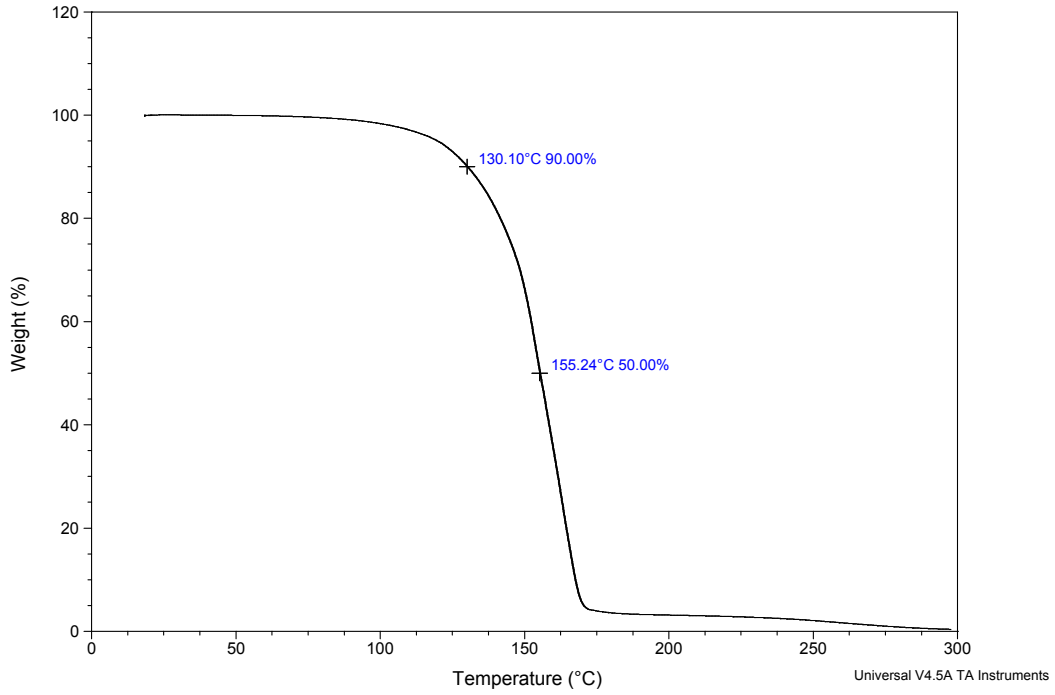


Figure S30. TGA Thermogram of polymer **2** (Table S1 entry 2).

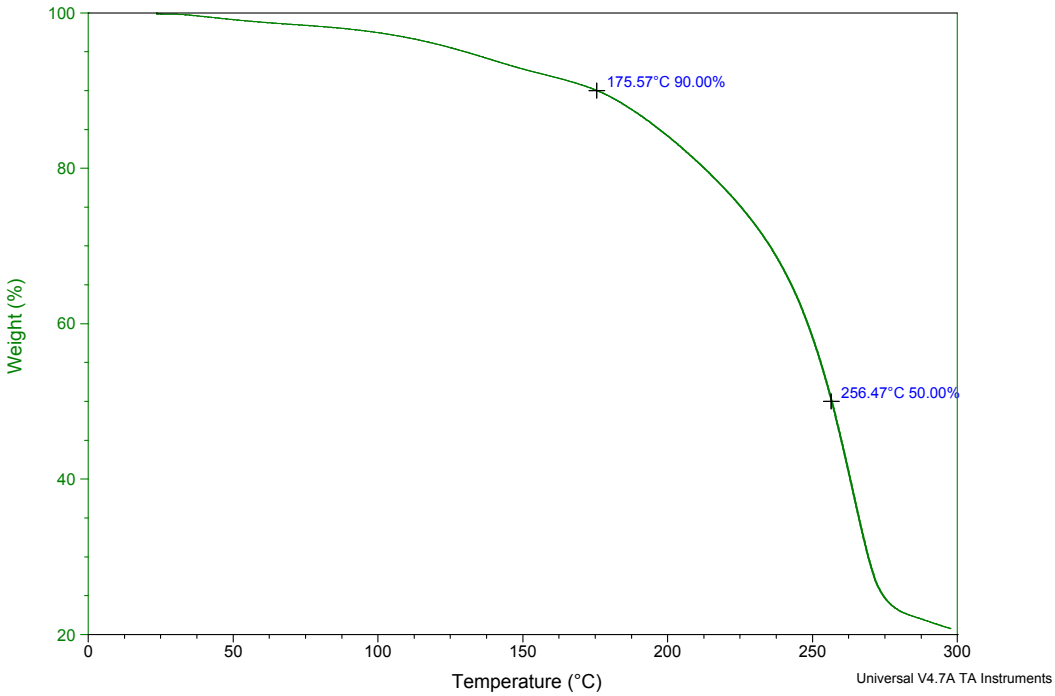


Figure S31. TGA Thermogram of polymer **4** (Table S1 entry 4).

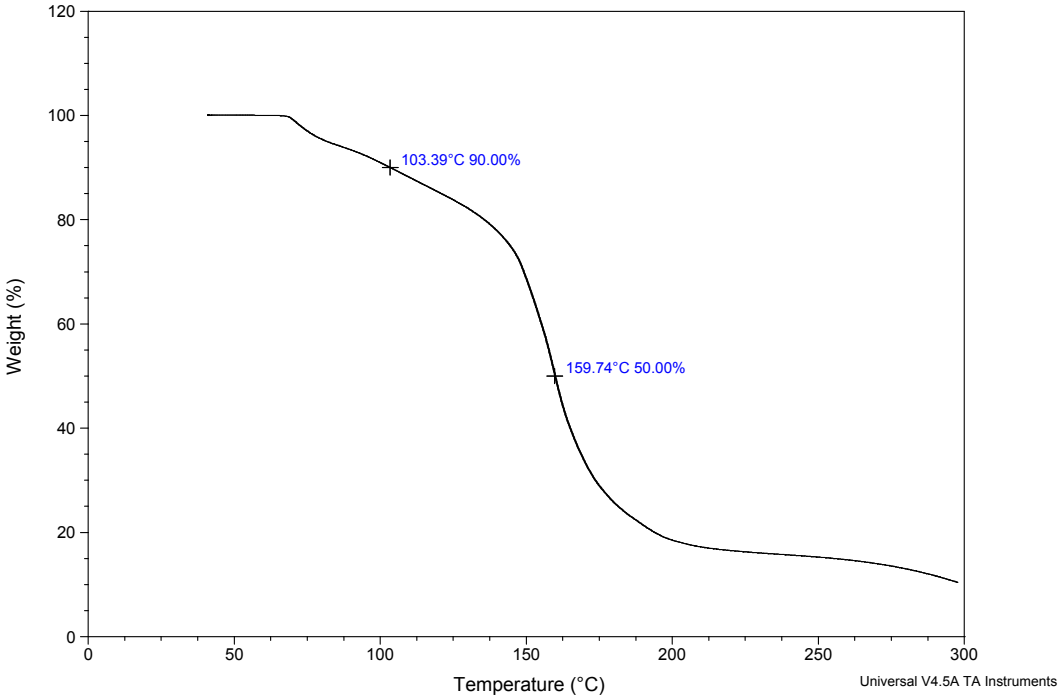


Figure S32. TGA Thermogram of polymer **5** (Table S1 entry 5).

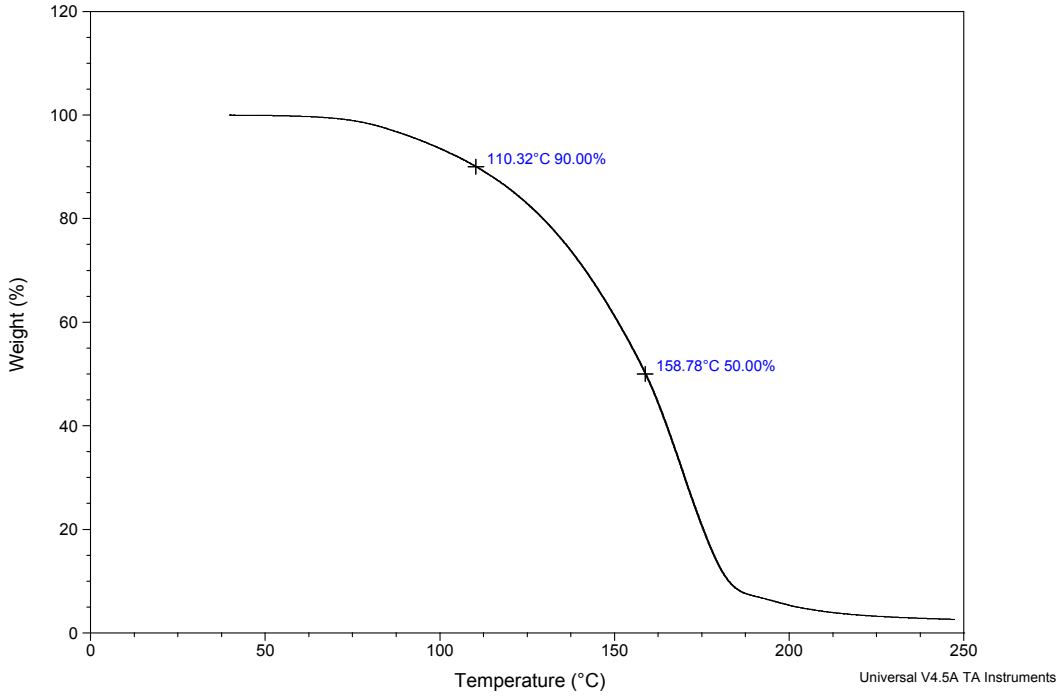


Figure S33. TGA Thermogram of polymer **6** (Table S1 entry 6).

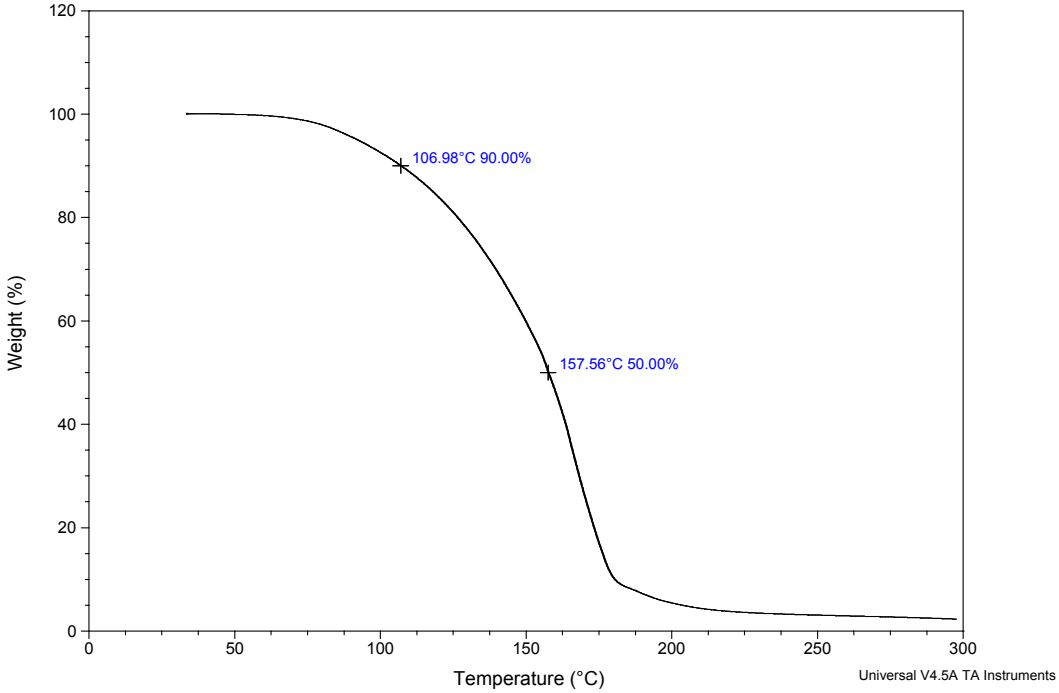


Figure S34. TGA Thermogram of polymer **7** (Table S1 entry 7).

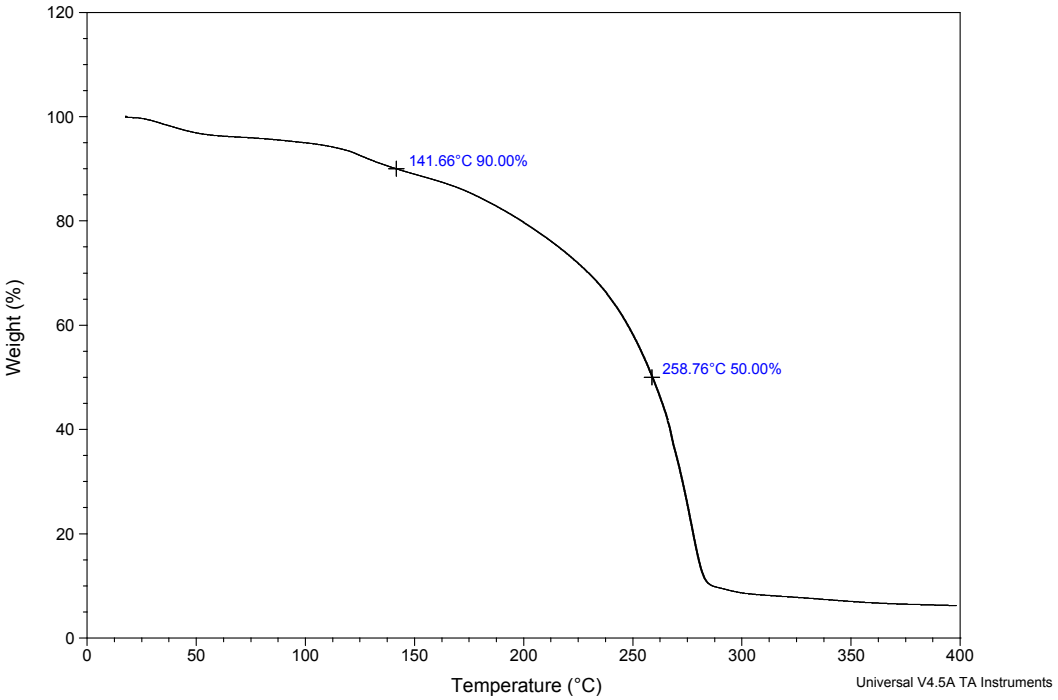


Figure S35. TGA Thermogram of polymer **8** (Table S1 entry 8).

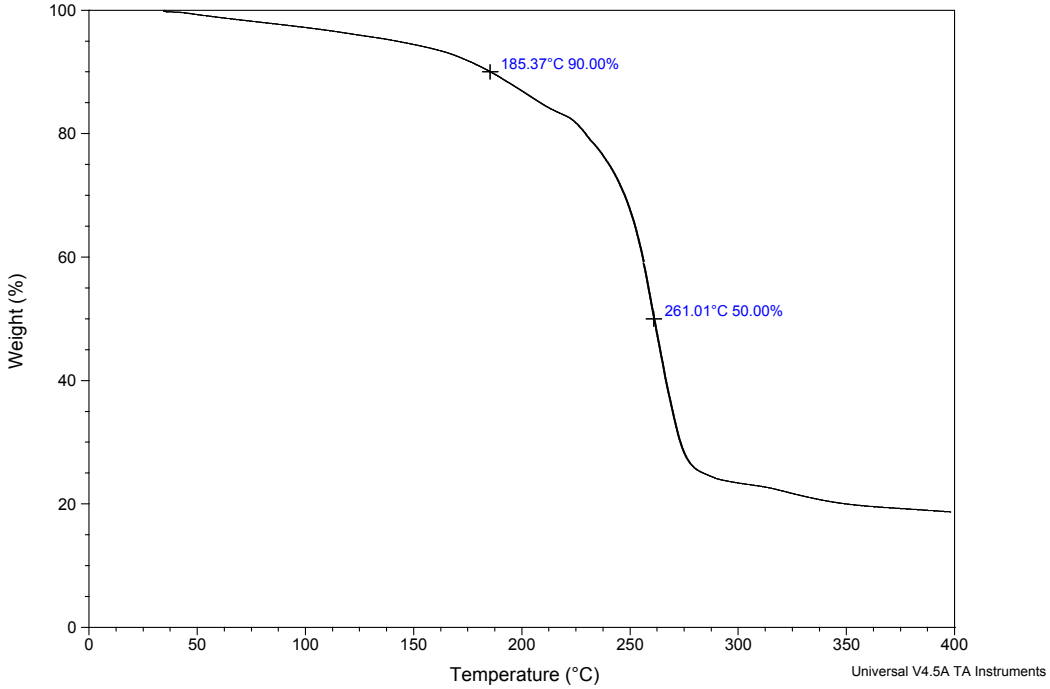


Figure S36. TGA Thermogram of polymer **9** (Table S1 entry 9).

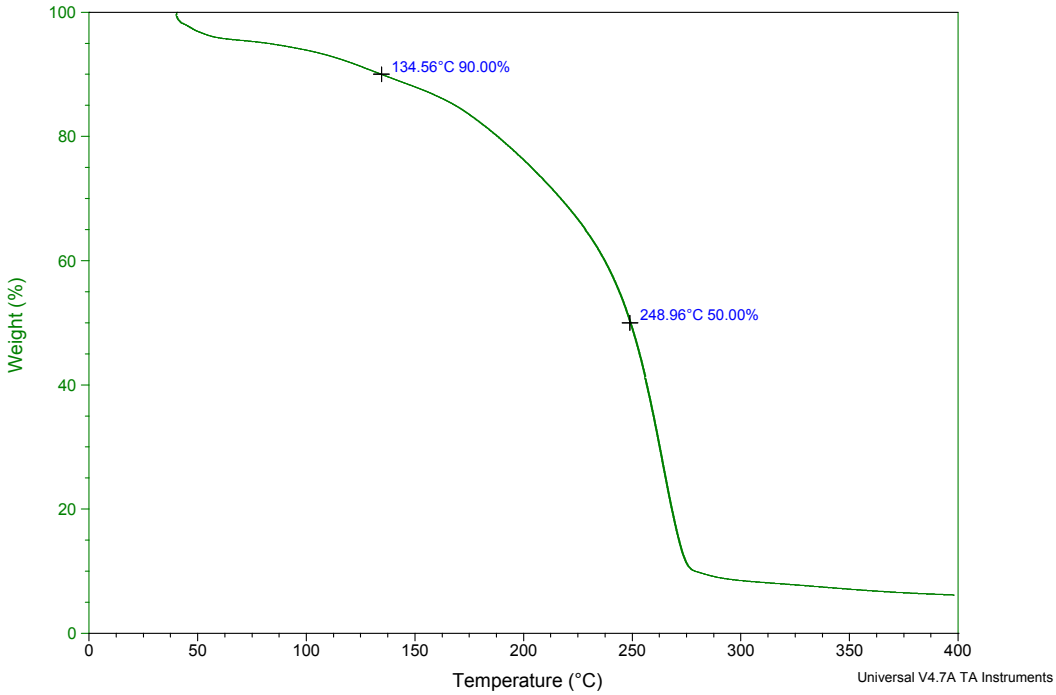


Figure S37. TGA Thermogram of polymer **10** (Table S1 entry 10).

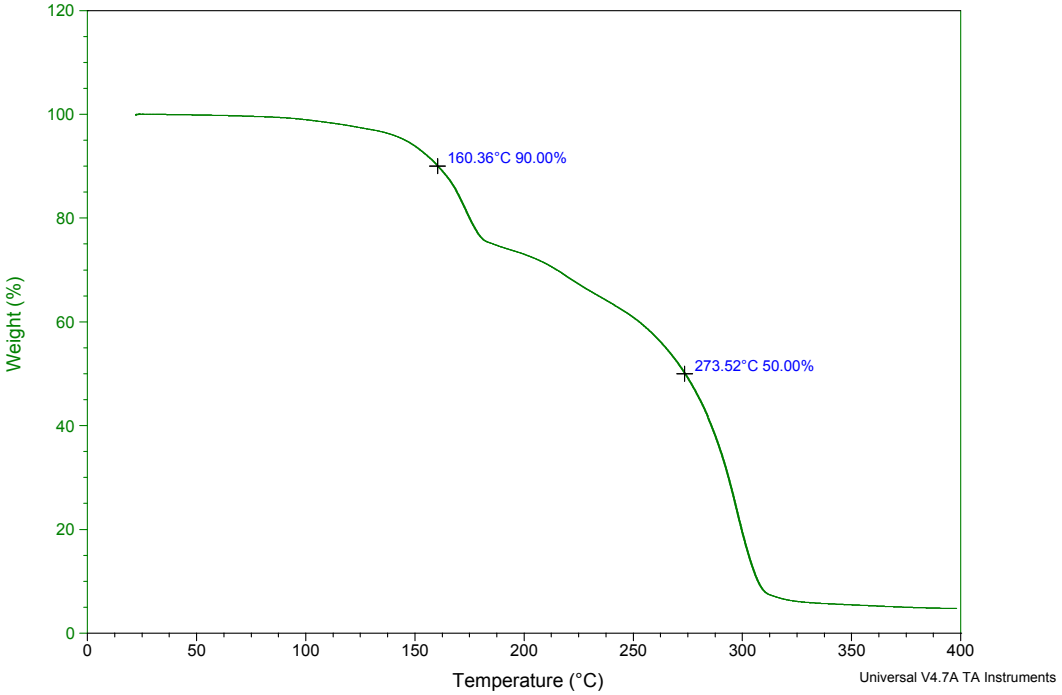


Figure S38. TGA Thermogram of polymer **11** (Table S1 entry 11).

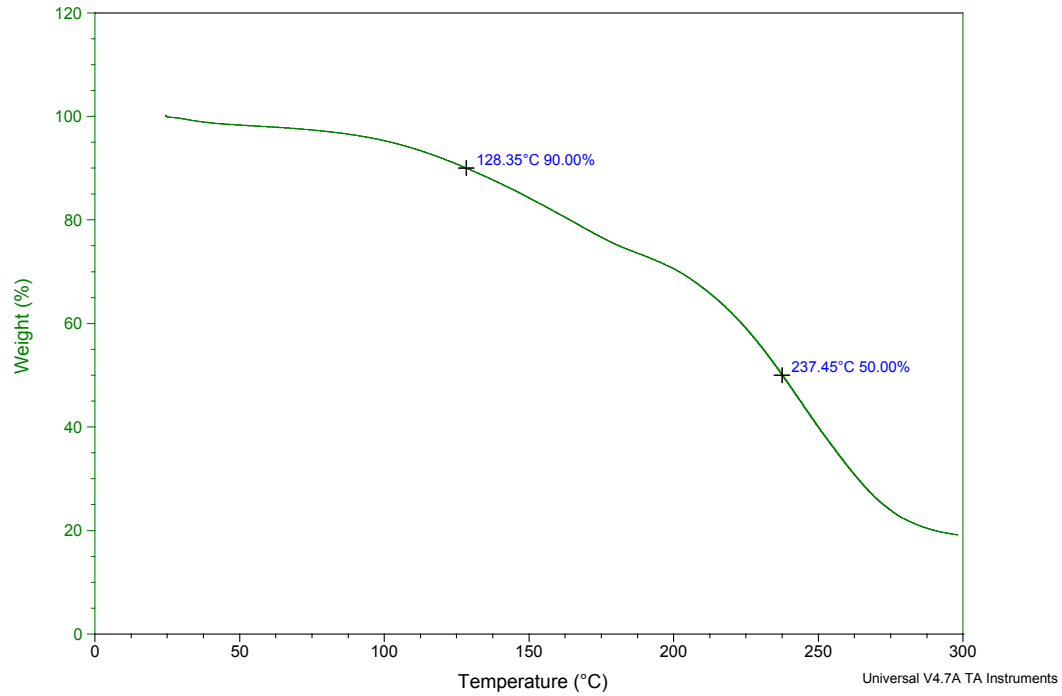


Figure S39. TGA Thermogram of polymer **12** (Table S1 entry 12).

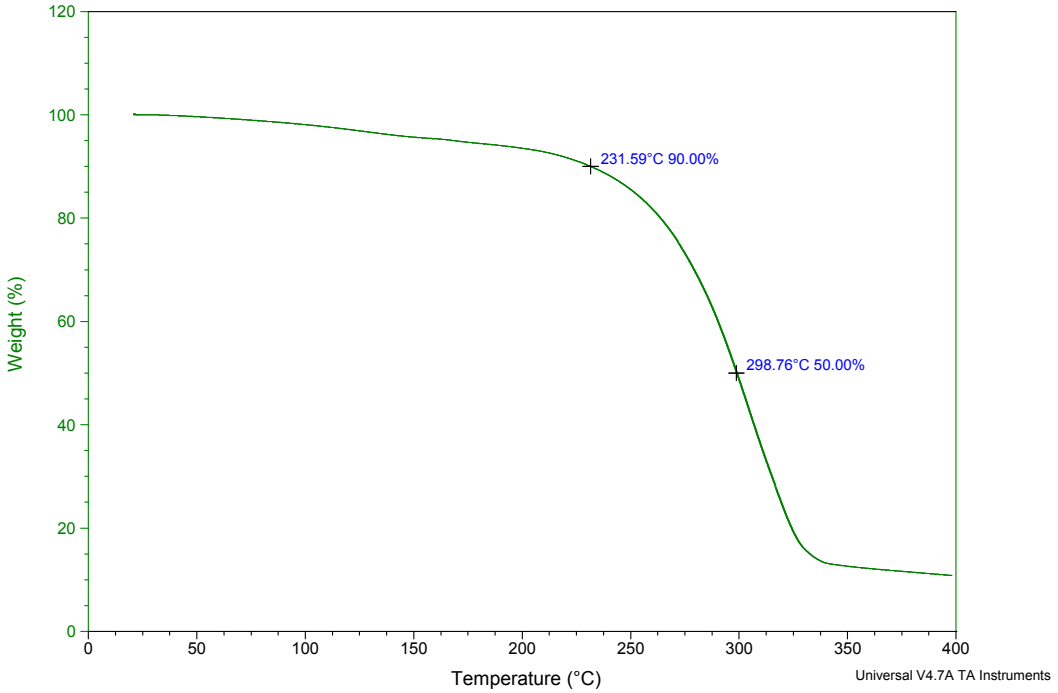


Figure S40. TGA Thermogram of polymer **13** (Table S1 entry 13).

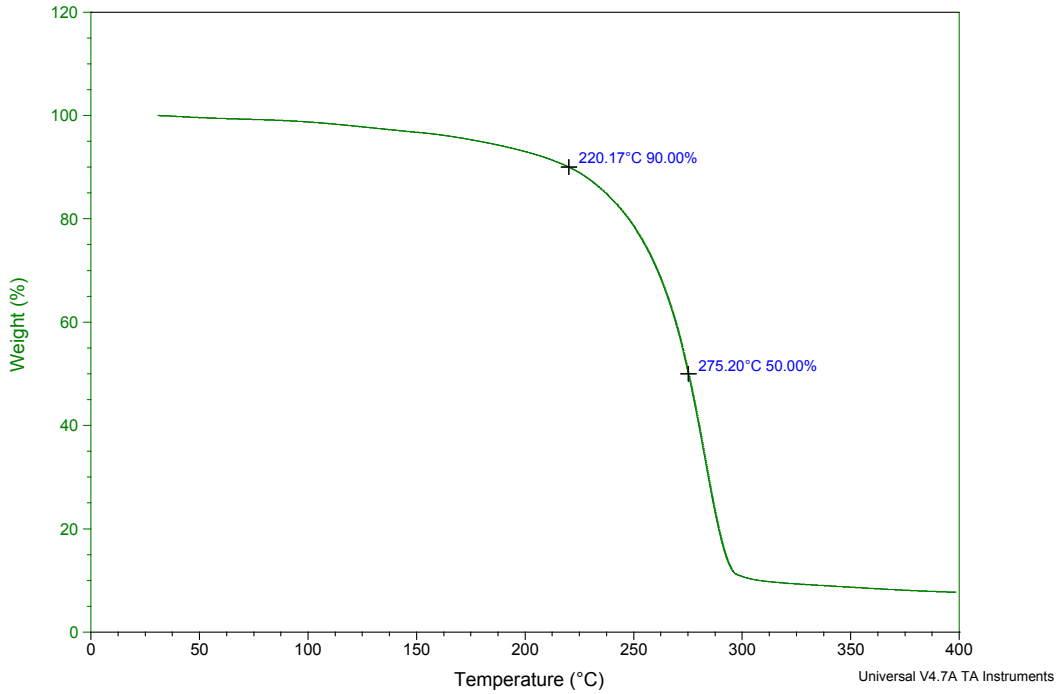


Figure S41. TGA Thermogram of polymer **14** (Table S1 entry 14).

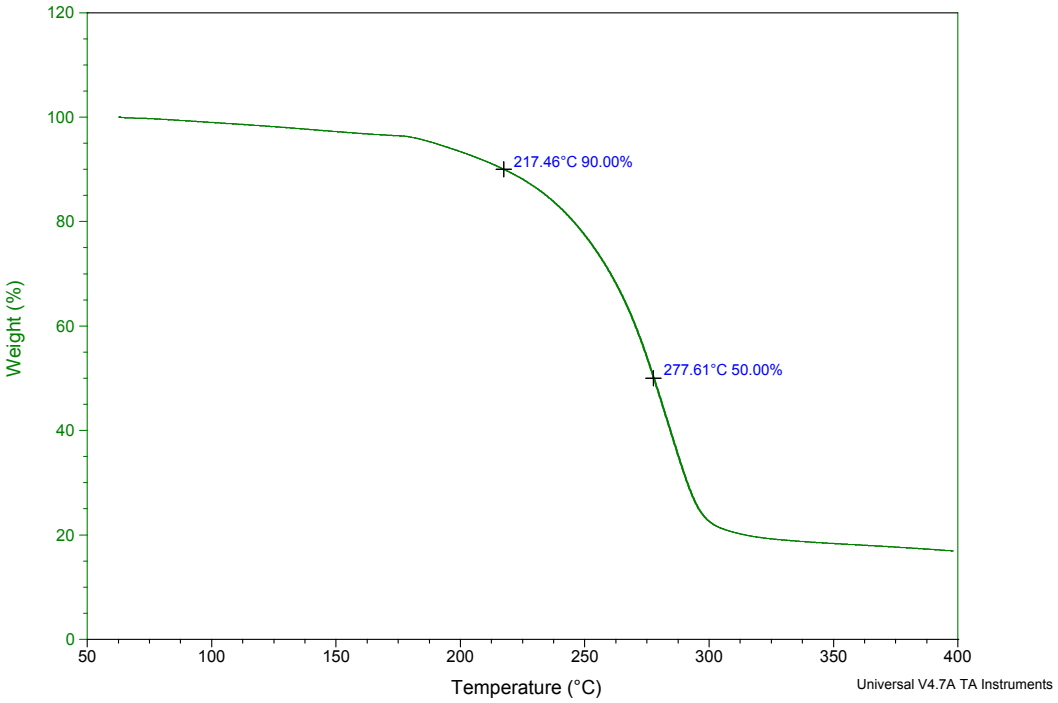


Figure S42. TGA Thermogram of polymer **15** (Table S1 entry 15).

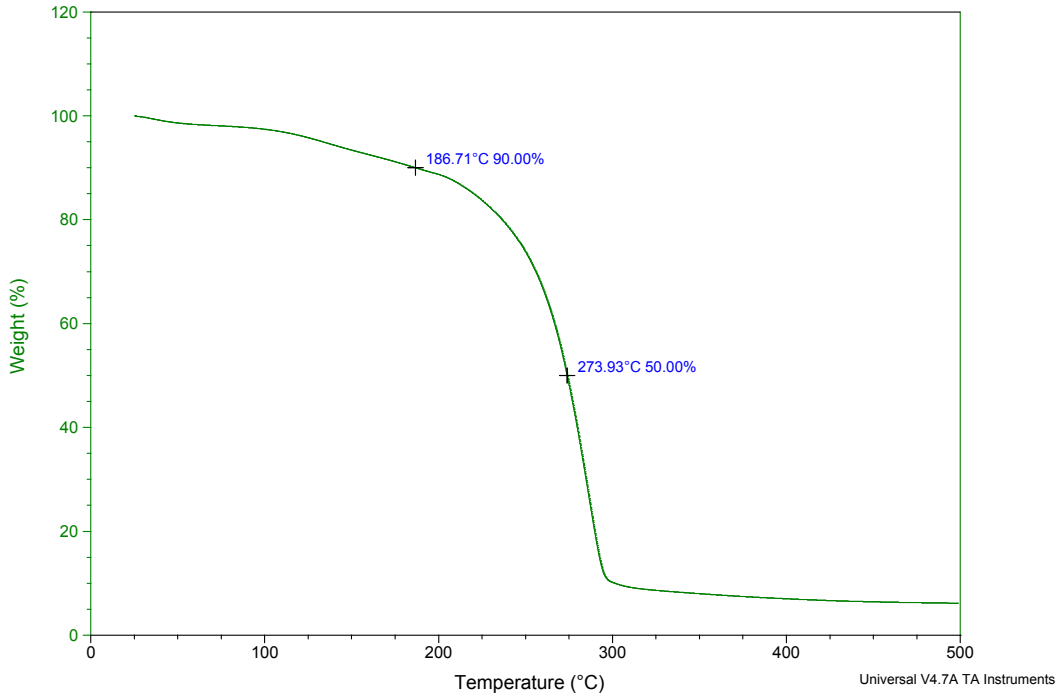


Figure S43. TGA Thermogram of polymer **16** (Table S1 entry 16).

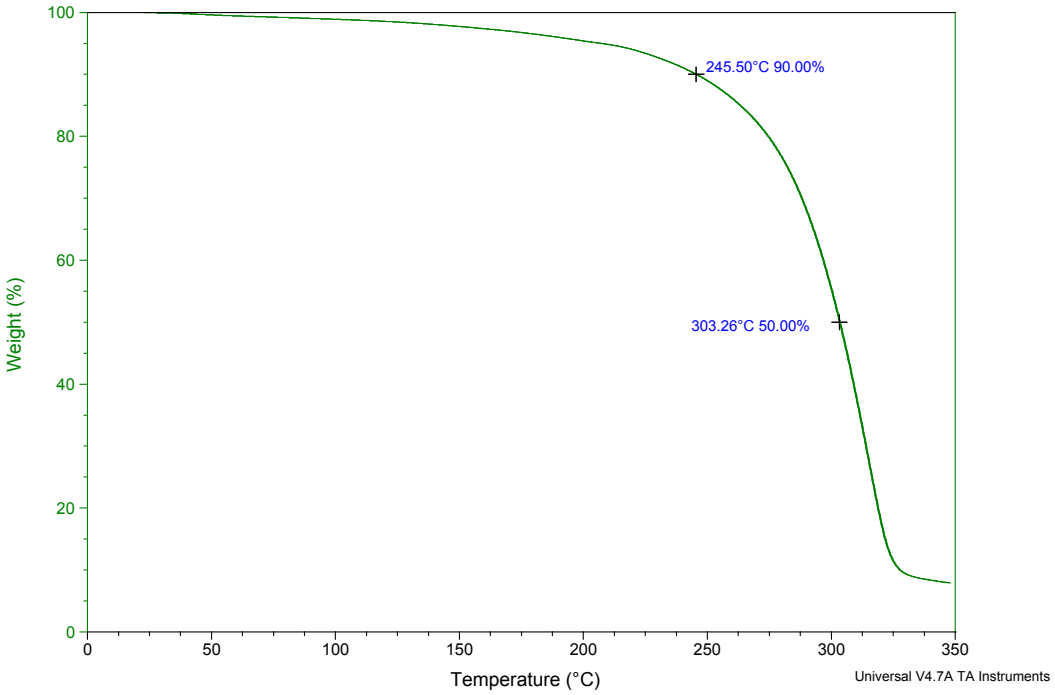


Figure S44. TGA Thermogram of polymer **17** (Table S1 entry 17).

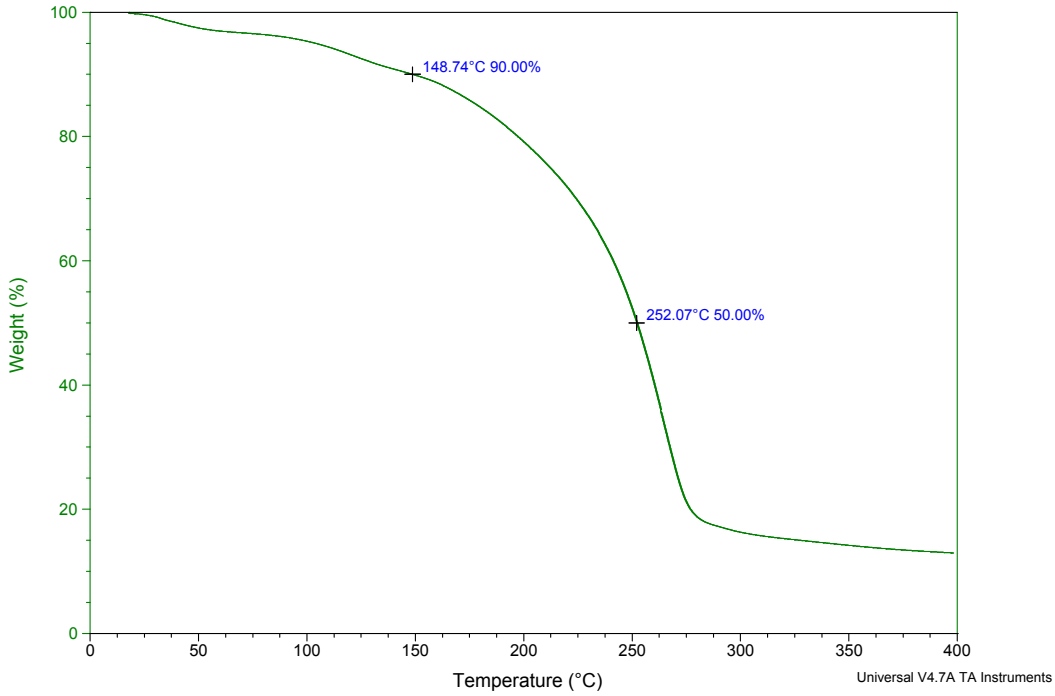


Figure S45. TGA Thermogram of polymer **18** (Table S1 entry 18).

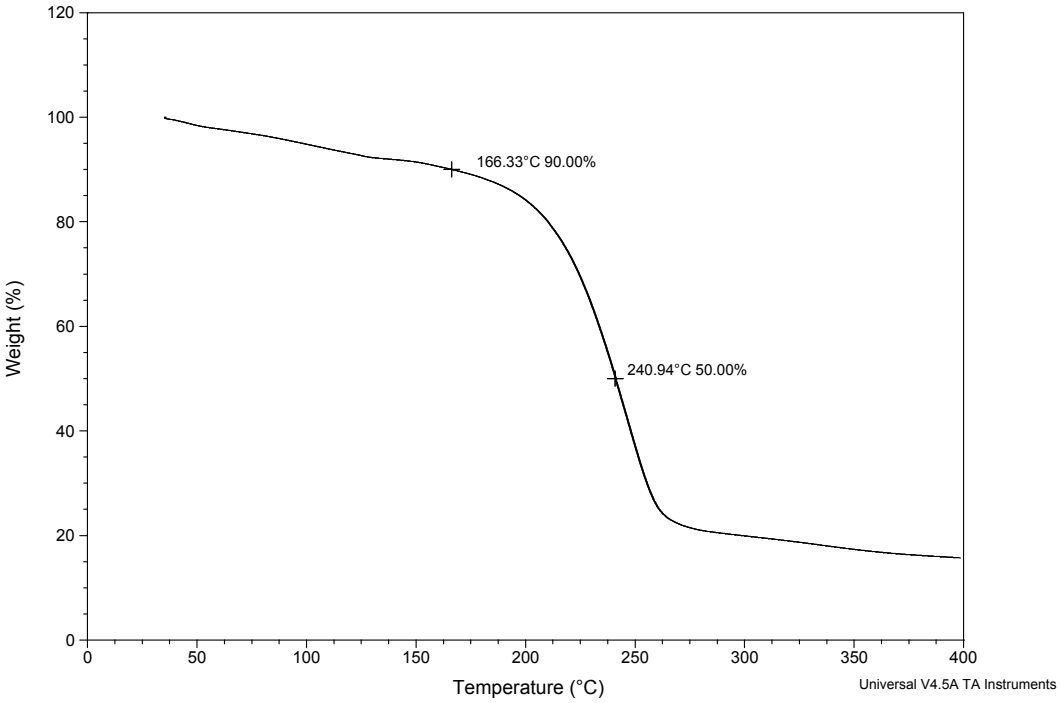


Figure S46. TGA Thermogram of polymer **19** (Table S1 entry 19).

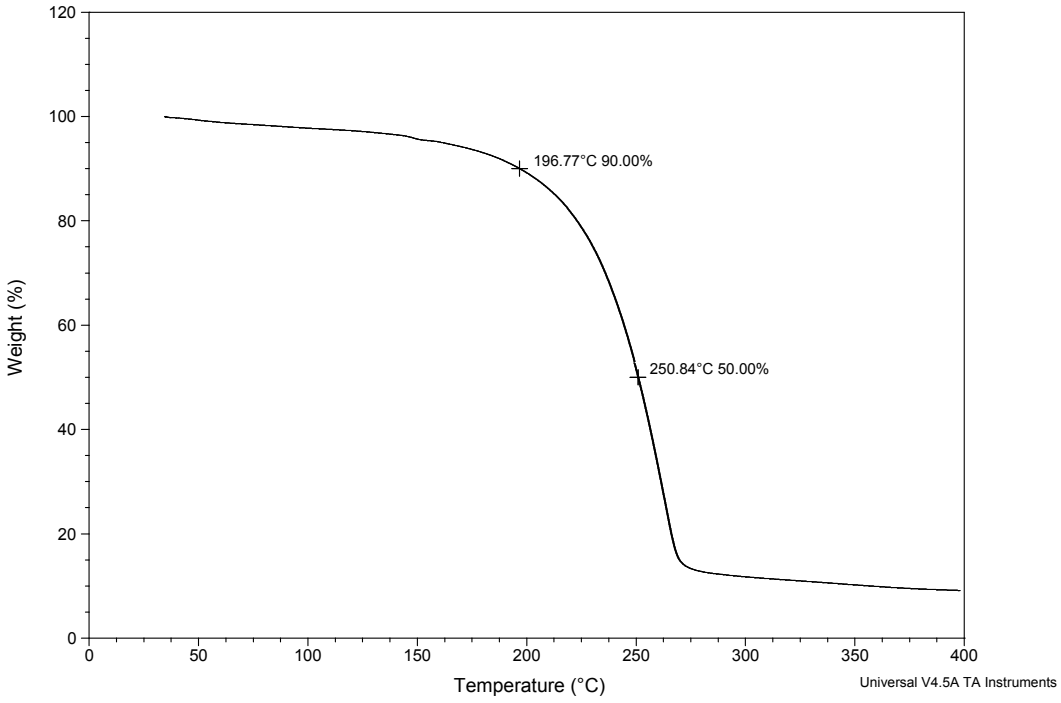


Figure S47. TGA Thermogram of polymer **21** (Table S2 entry 21).

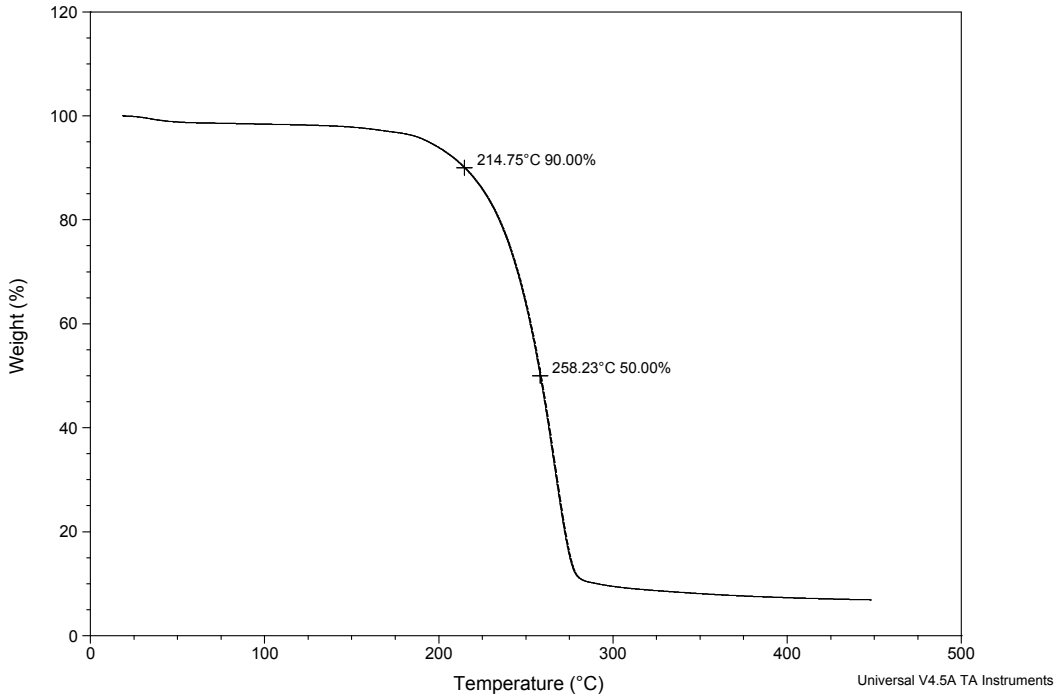


Figure S48. TGA Thermogram of polymer **22** (Table S2 entry 22).

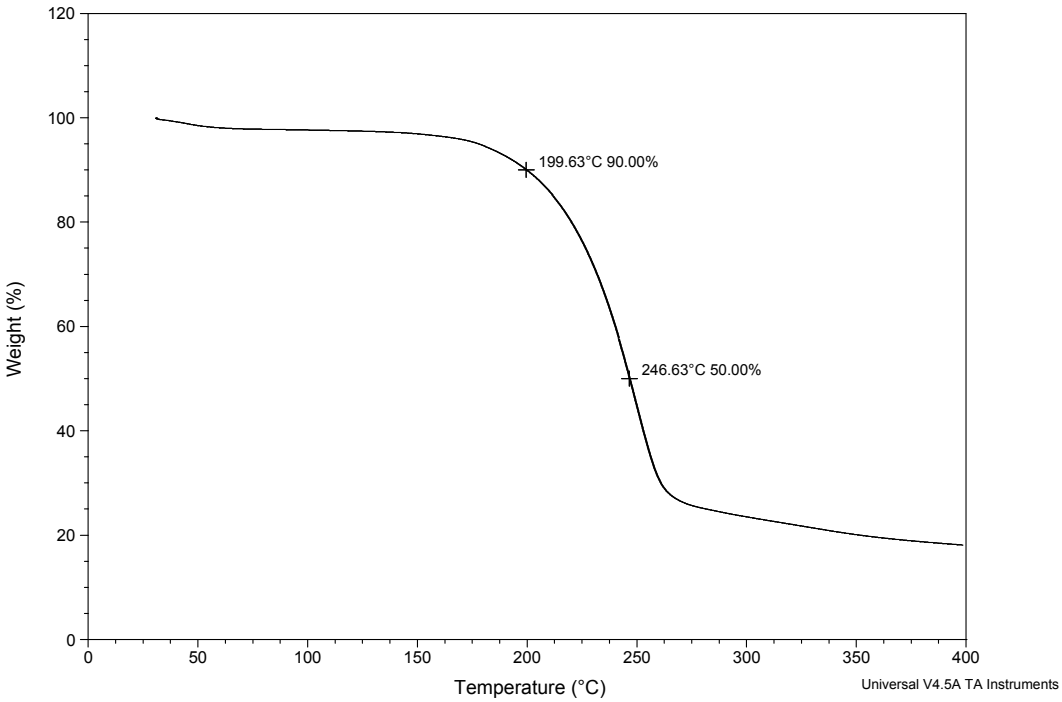


Figure S49. TGA Thermogram of polymer **23** (Table S2 entry 23).

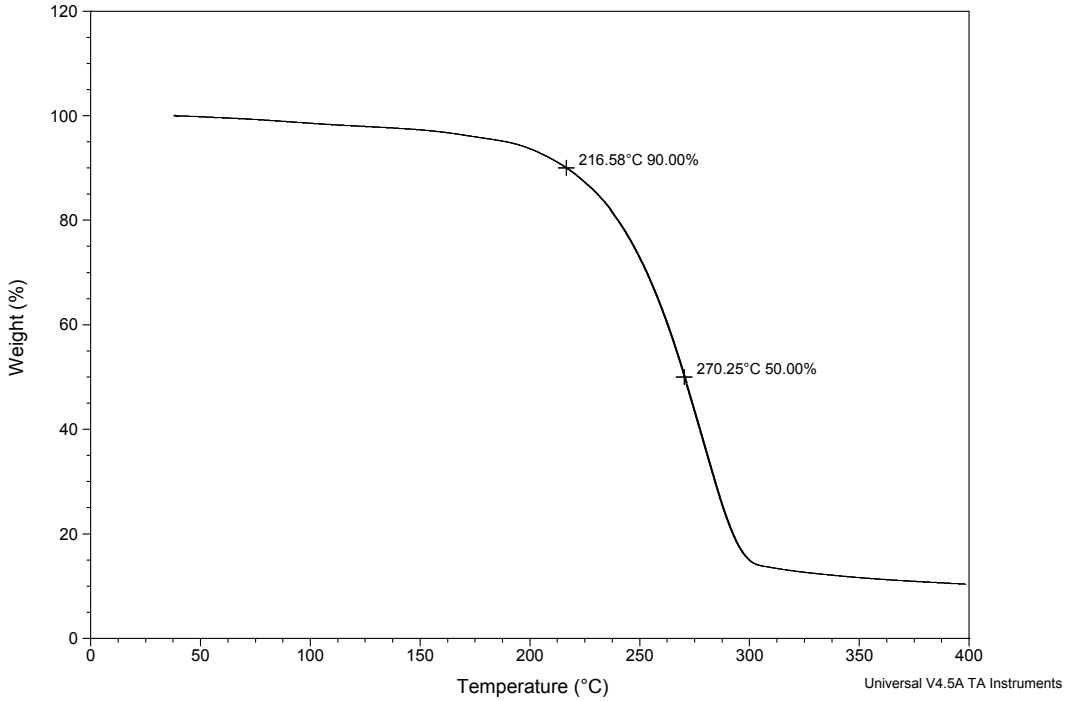


Figure S50. TGA Thermogram of polymer **24** (Table S2 entry 24).

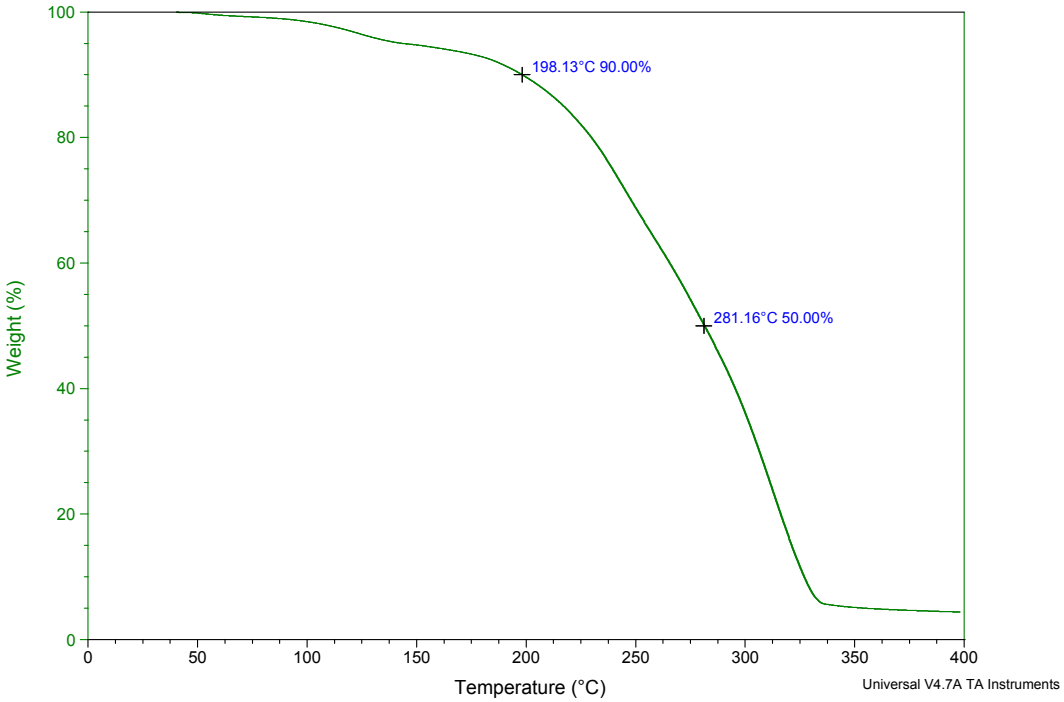


Figure S51. TGA Thermogram of polymer **25** (Table S3 entry 25).

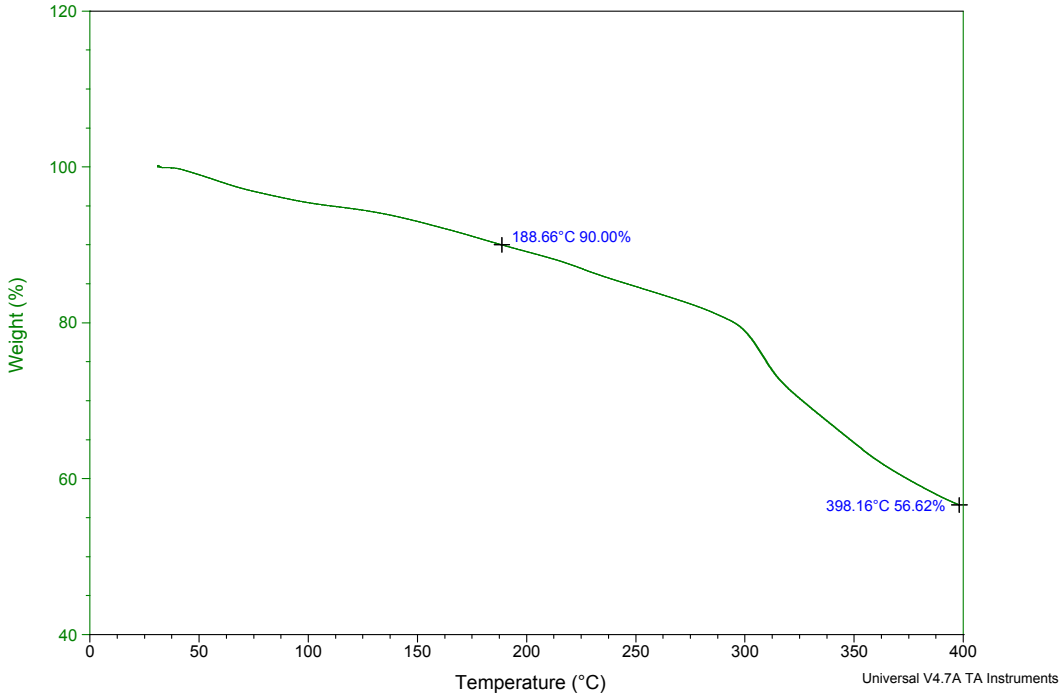


Figure S52. TGA Thermogram of polymer **26** (Table S3 entry 26).

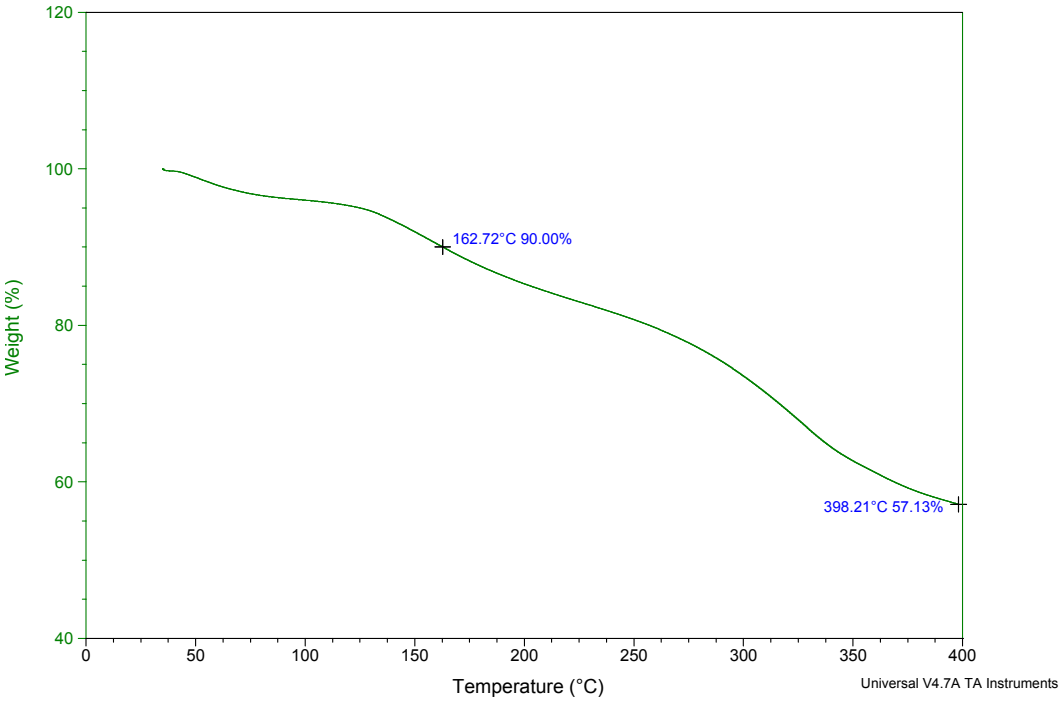


Figure S53. TGA Thermogram of polymer **27** (Scheme S1 entry 27).

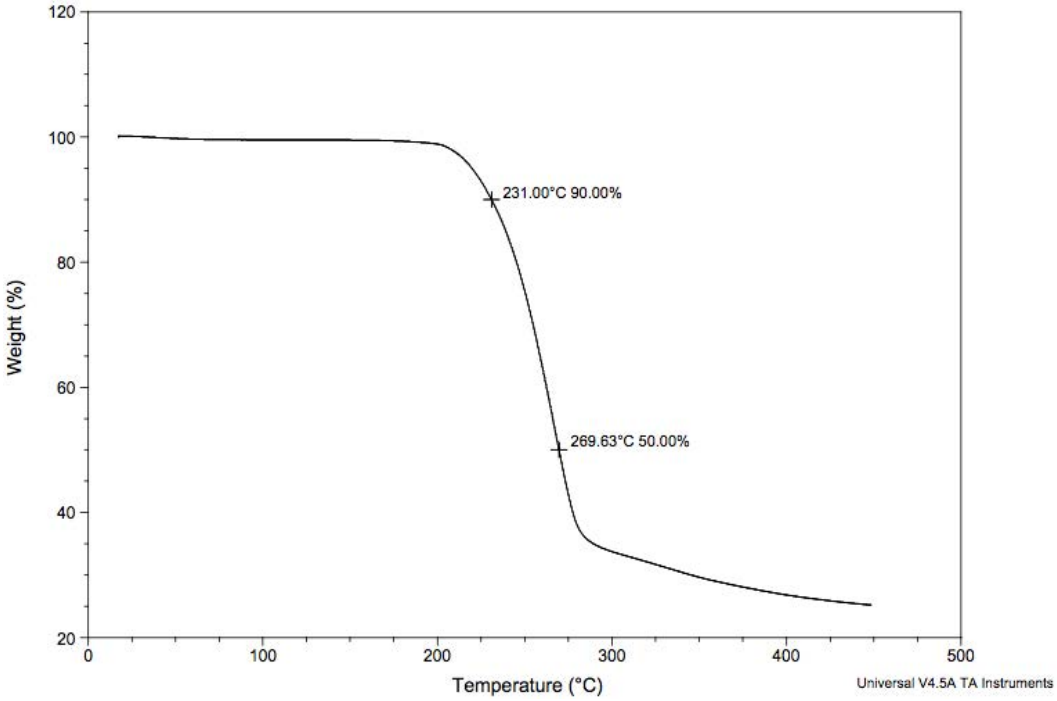


Figure S54. TGA Thermogram of polymer **28** (Scheme S2 entry 28).

Differential Scanning Calorimetry (DSC) Thermograms

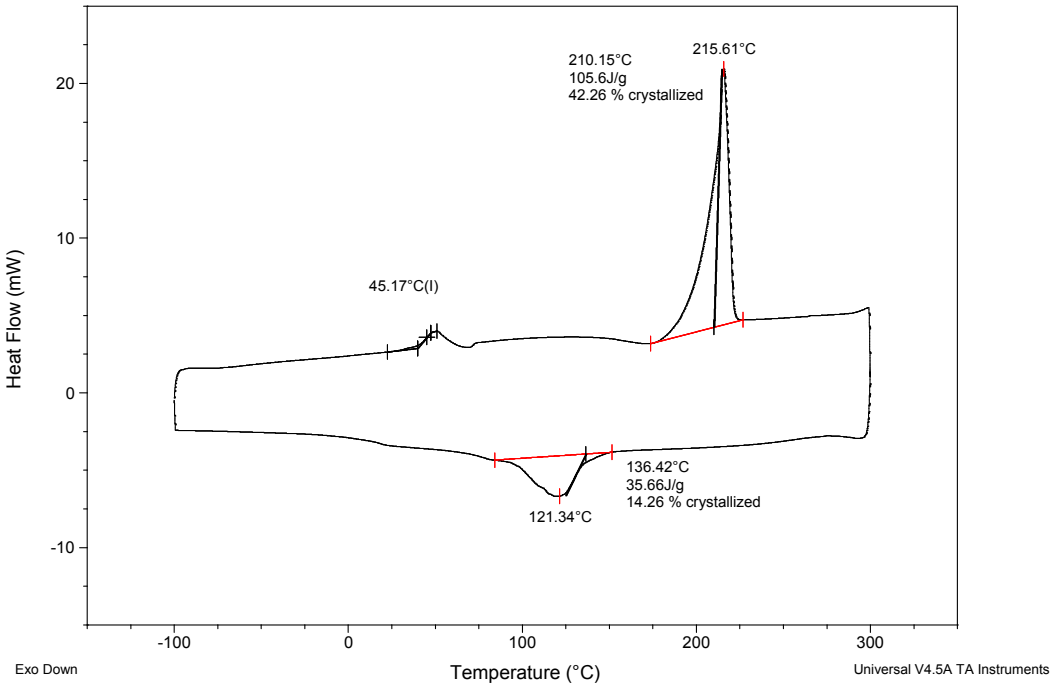


Figure S55. DSC Thermogram of commercial polyglycolic acid.

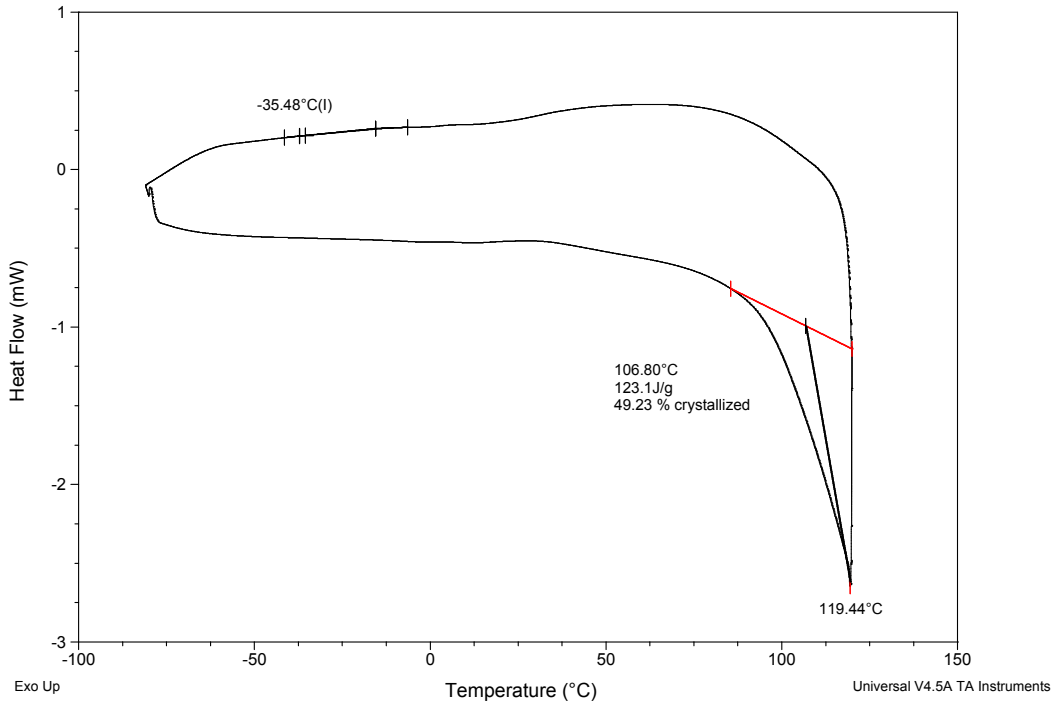


Figure S56. DSC Thermogram of polymer **1** (Table S1 entry 1).

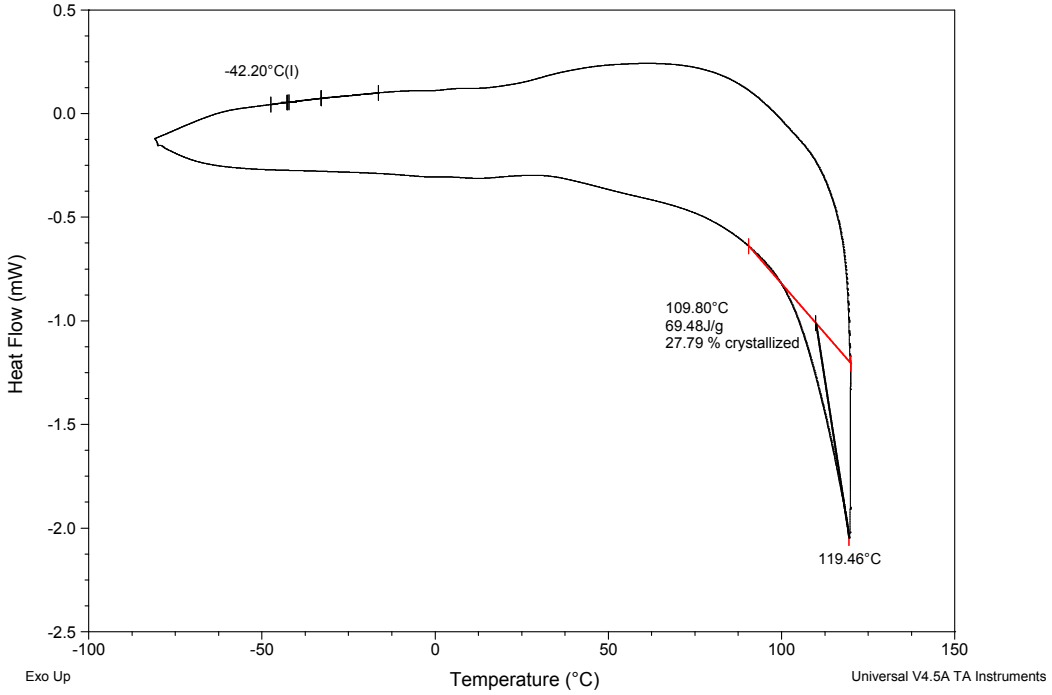


Figure S57. DSC Thermogram of polymer **2** (Table S1 entry 2).

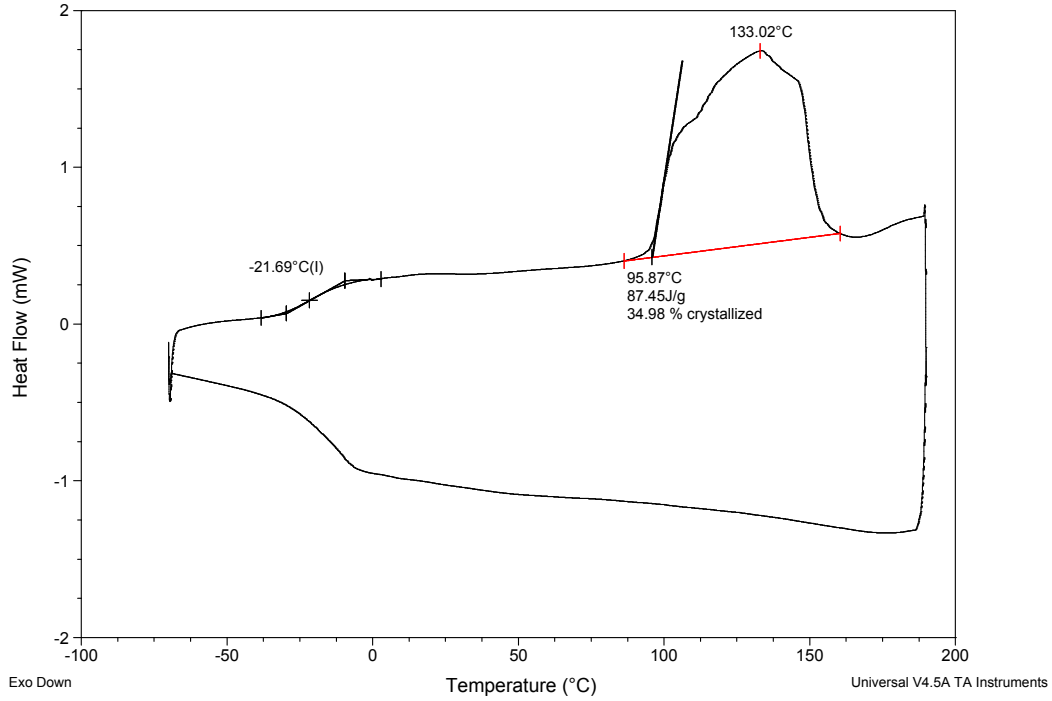


Figure S58. DSC Thermogram of polymer **4** (Table S1 entry 4).

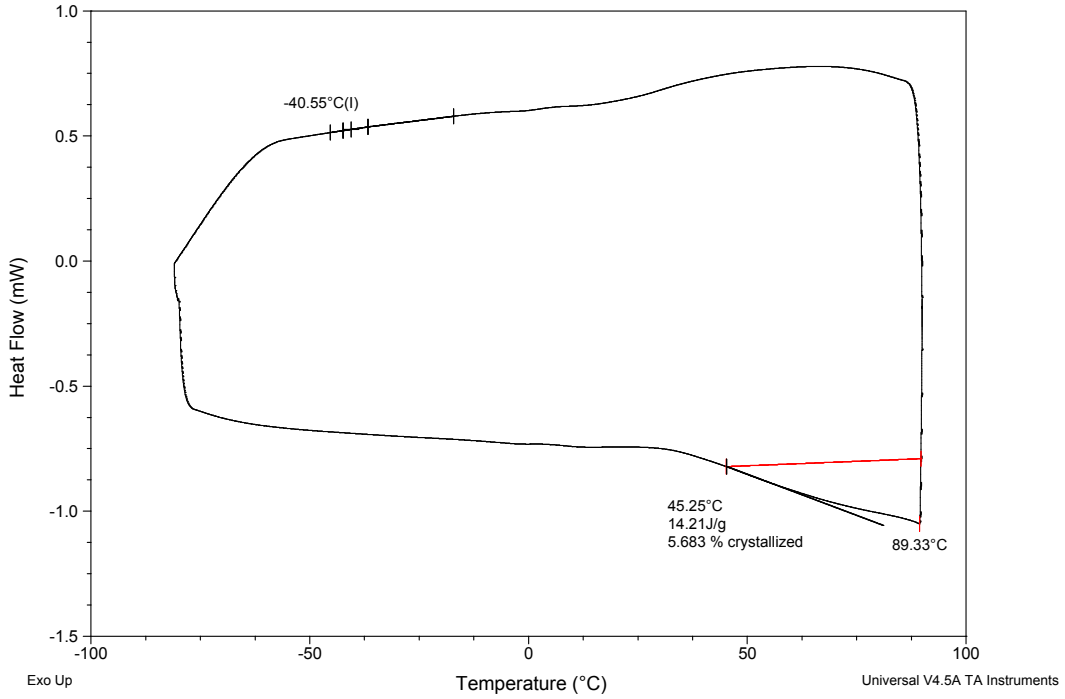


Figure S59. DSC Thermogram of polymer **5** (Table S1 entry 5).

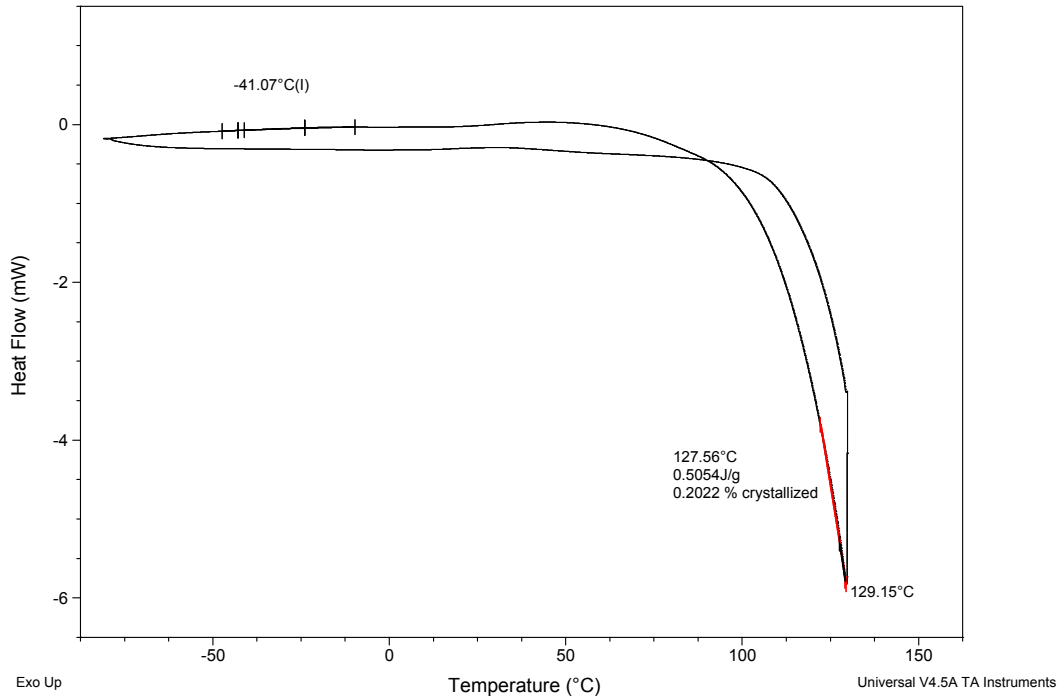


Figure S60. DSC Thermogram of polymer **6** (Table S1 entry 6).

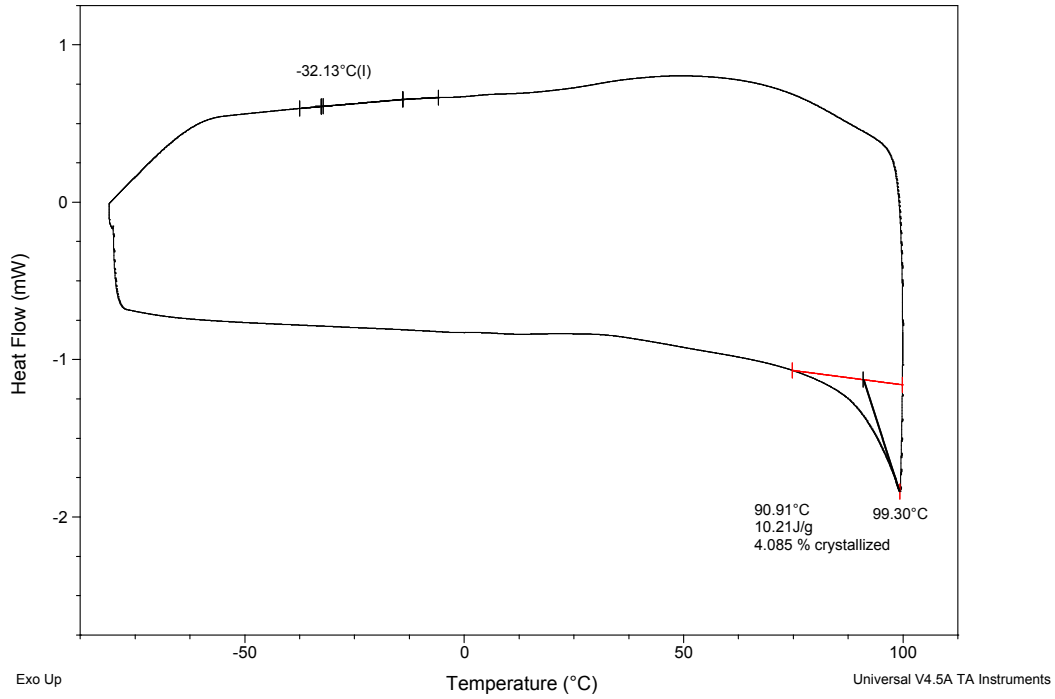


Figure S61. DSC Thermogram of polymer **7** (Table S1 entry 7).

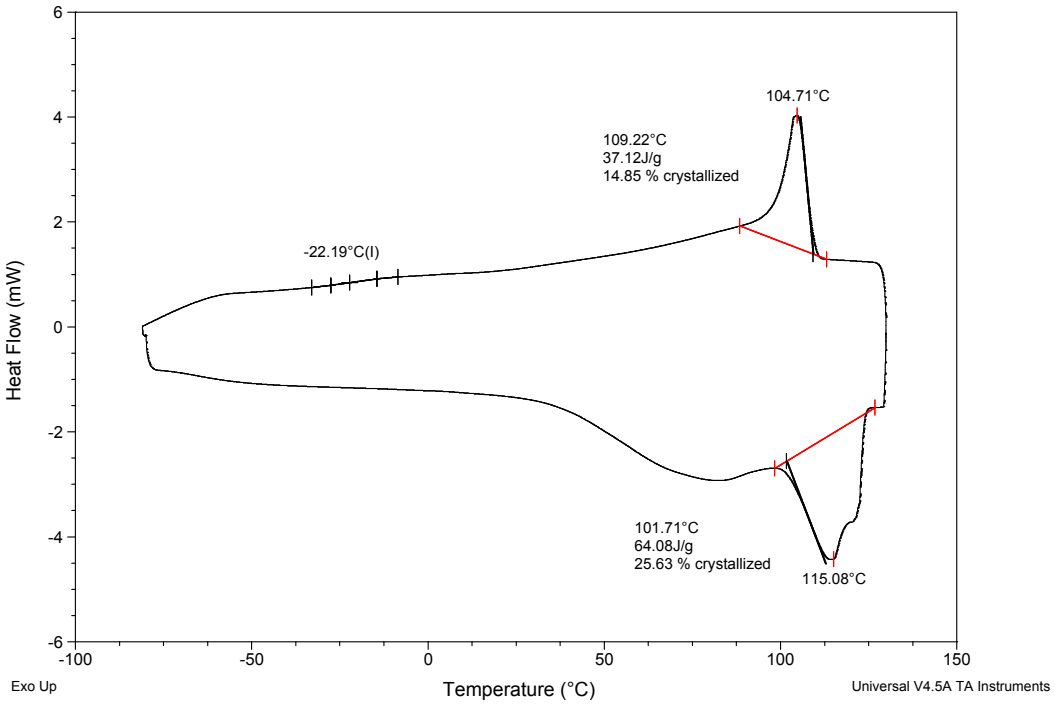


Figure S62. DSC Thermogram of polymer **8** (Table S1 entry 8).

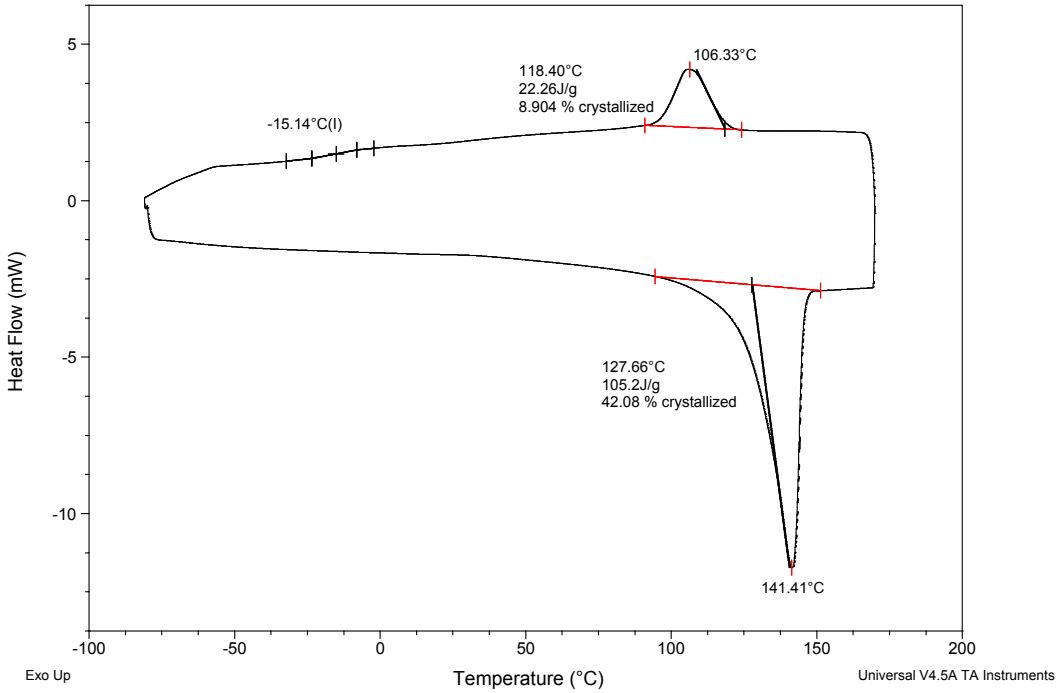


Figure S63. DSC Thermogram of polymer **9** (Table S1 entry 9).

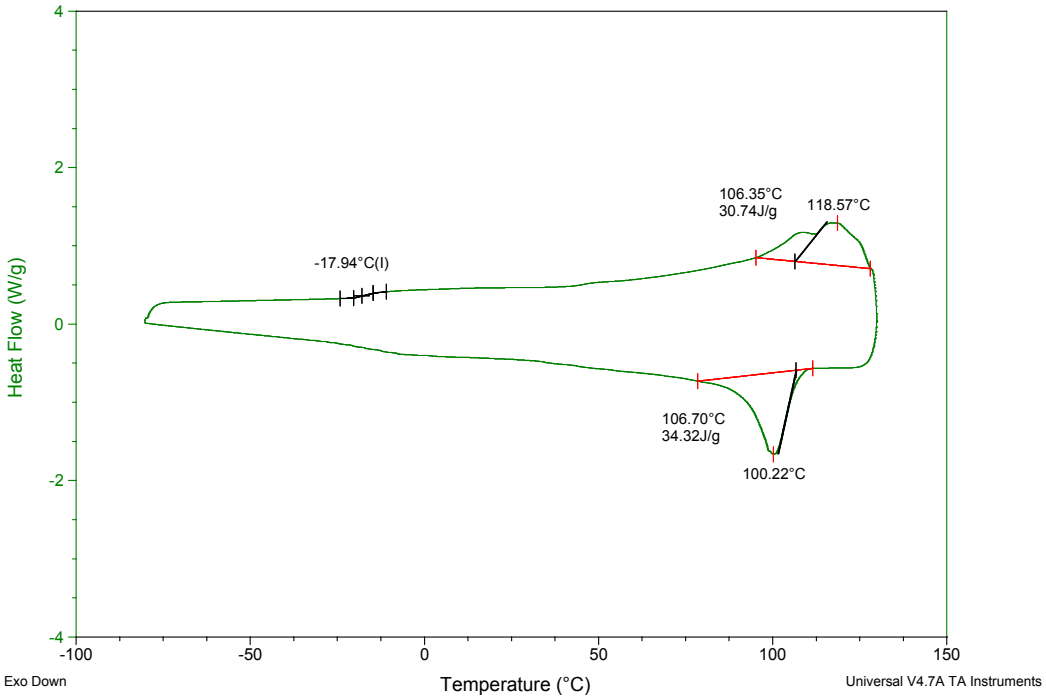


Figure S64. DSC Thermogram of polymer **10** (Table S1 entry 10).

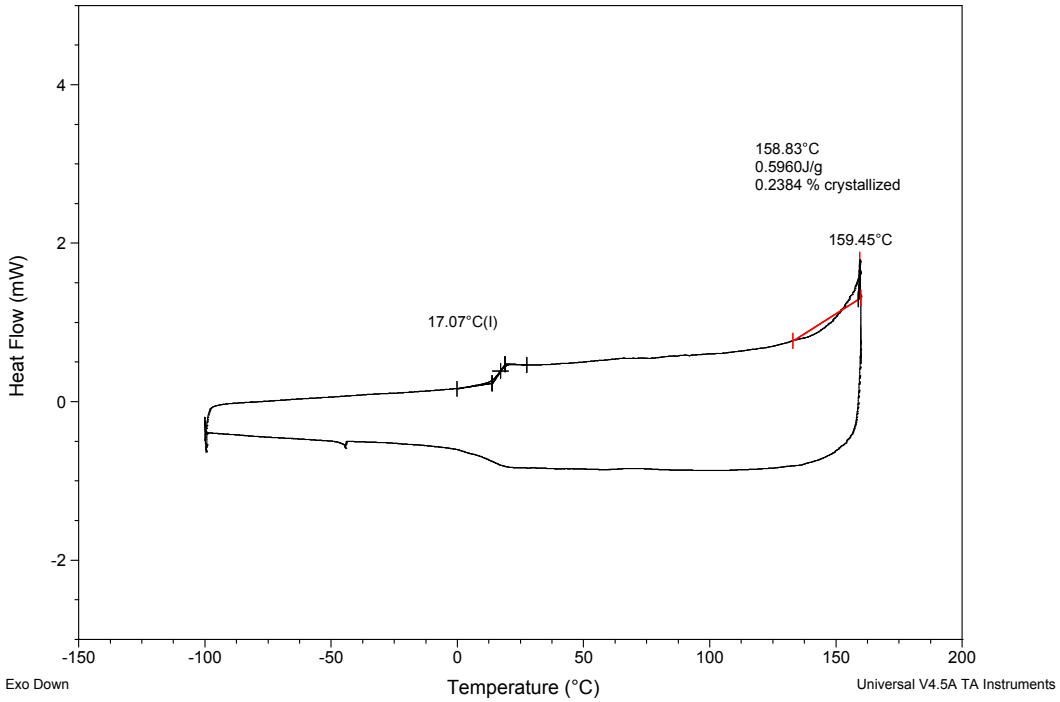


Figure S65. DSC Thermogram of polymer **11** (Table S1 entry 11).

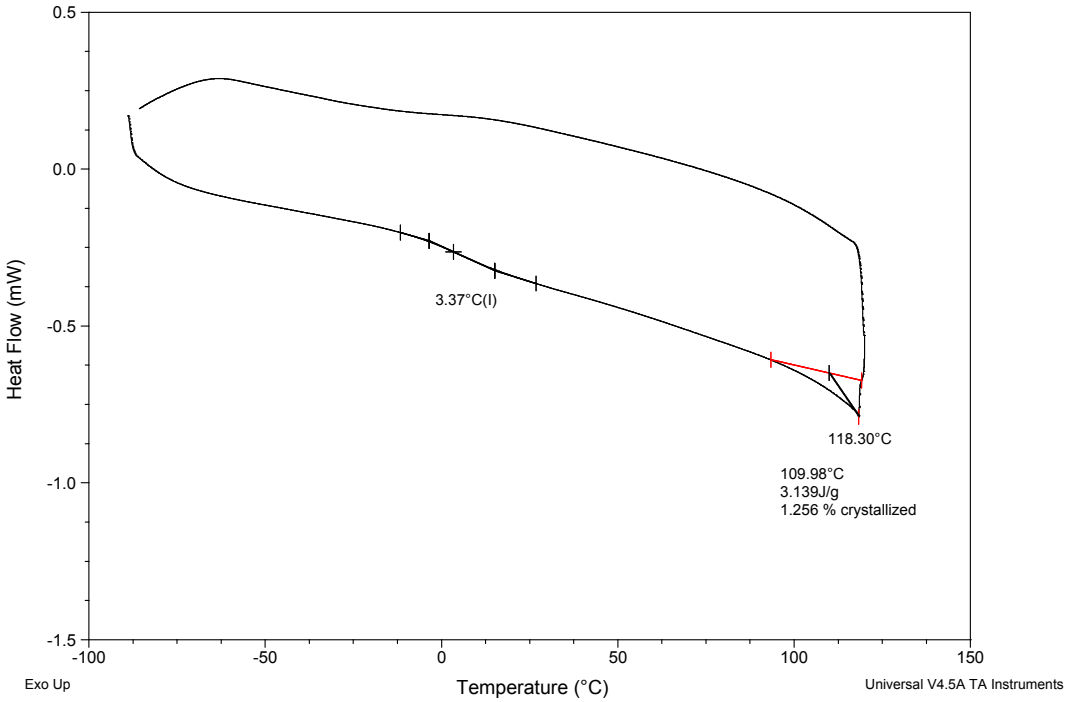


Figure S66. DSC Thermogram of polymer **12** (Table S1 entry 12).

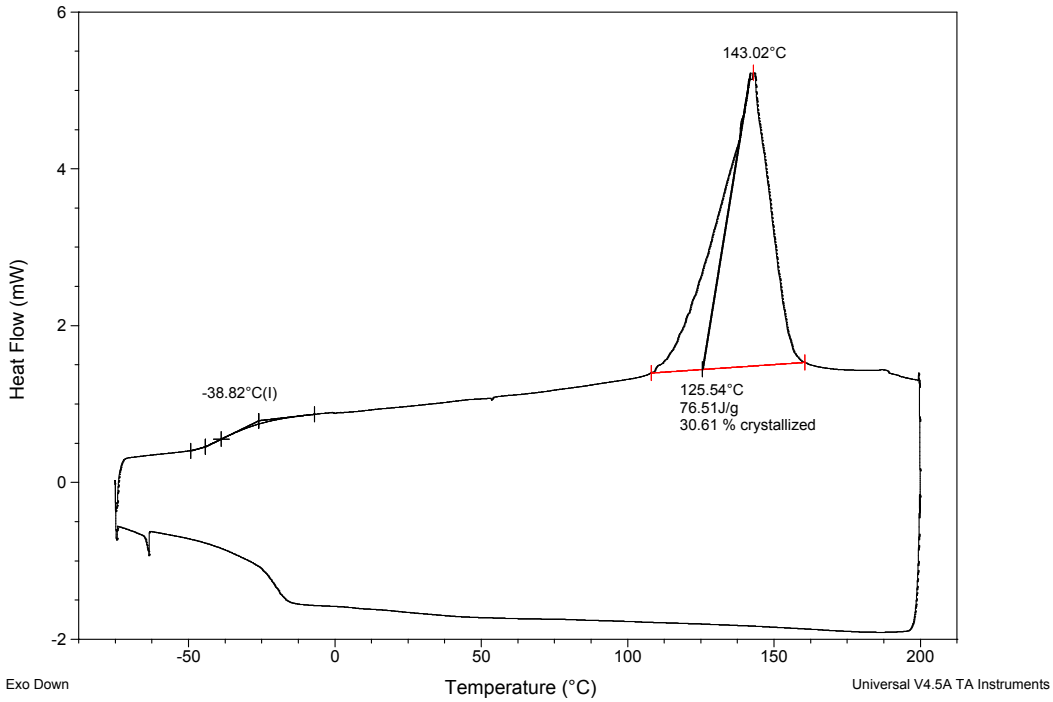


Figure S67. DSC Thermogram of polymer **13** (Table S1 entry 13).

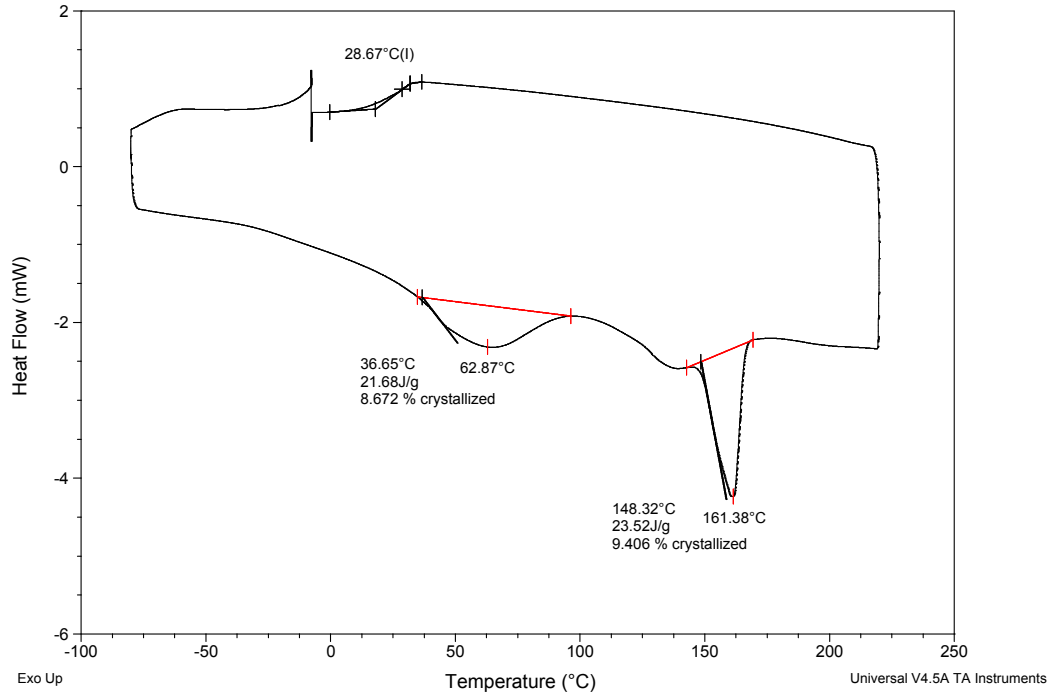


Figure S68. DSC Thermogram of polymer **14** (Table S1 entry 14).

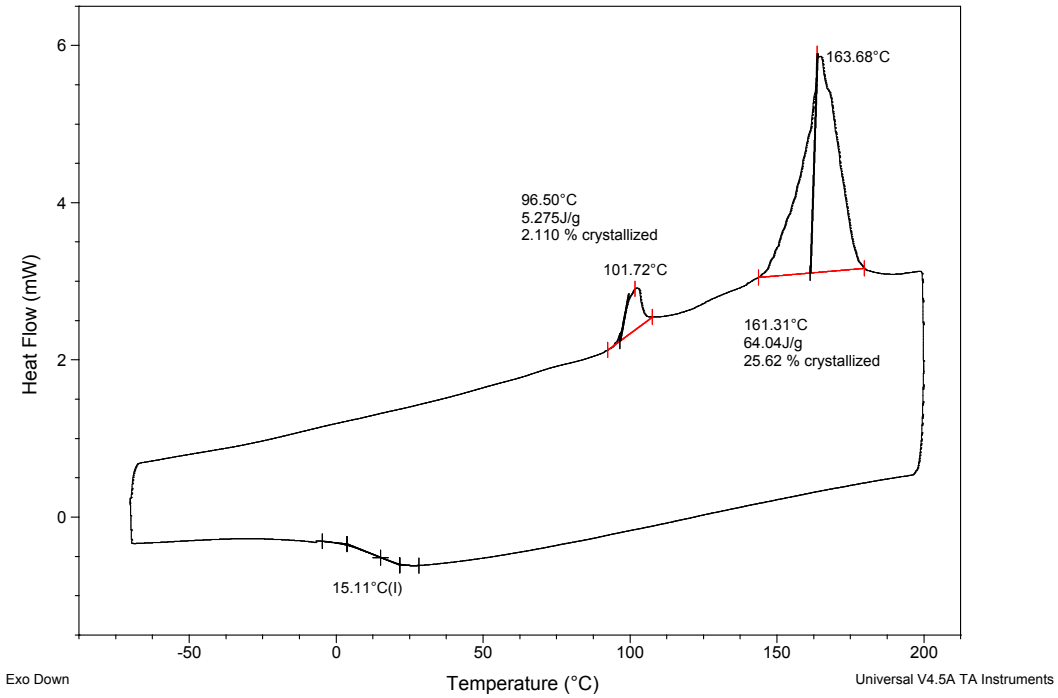


Figure S69. DSC Thermogram of polymer **15** (Table S1 entry 15).

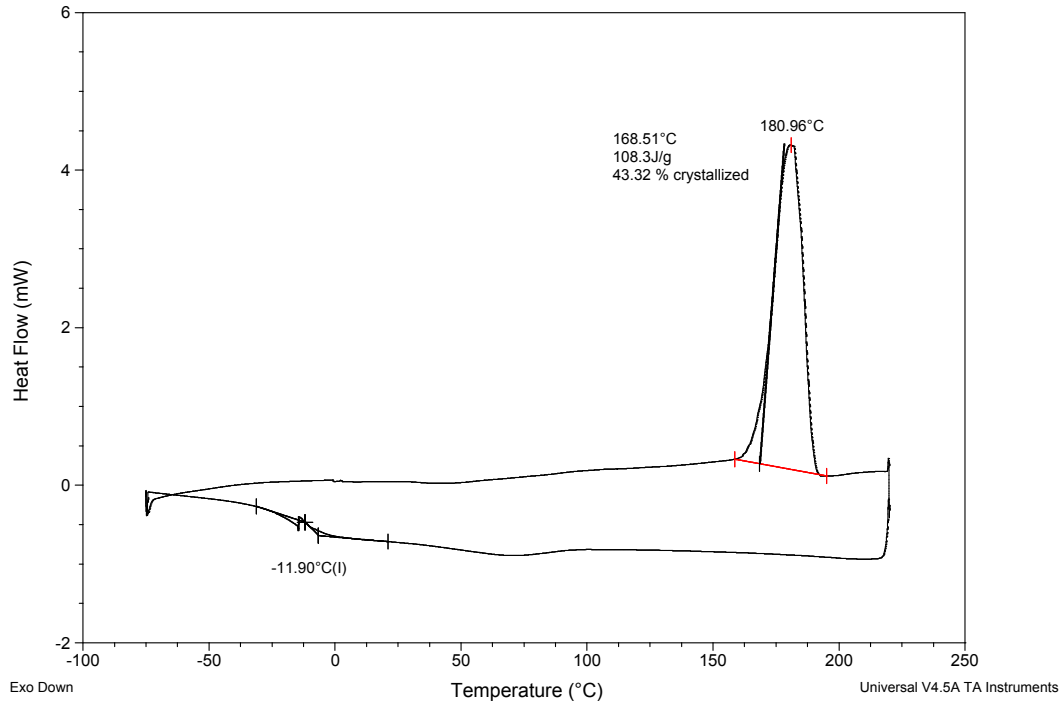


Figure S70. DSC Thermogram of polymer **16** (Table S1 entry 16).

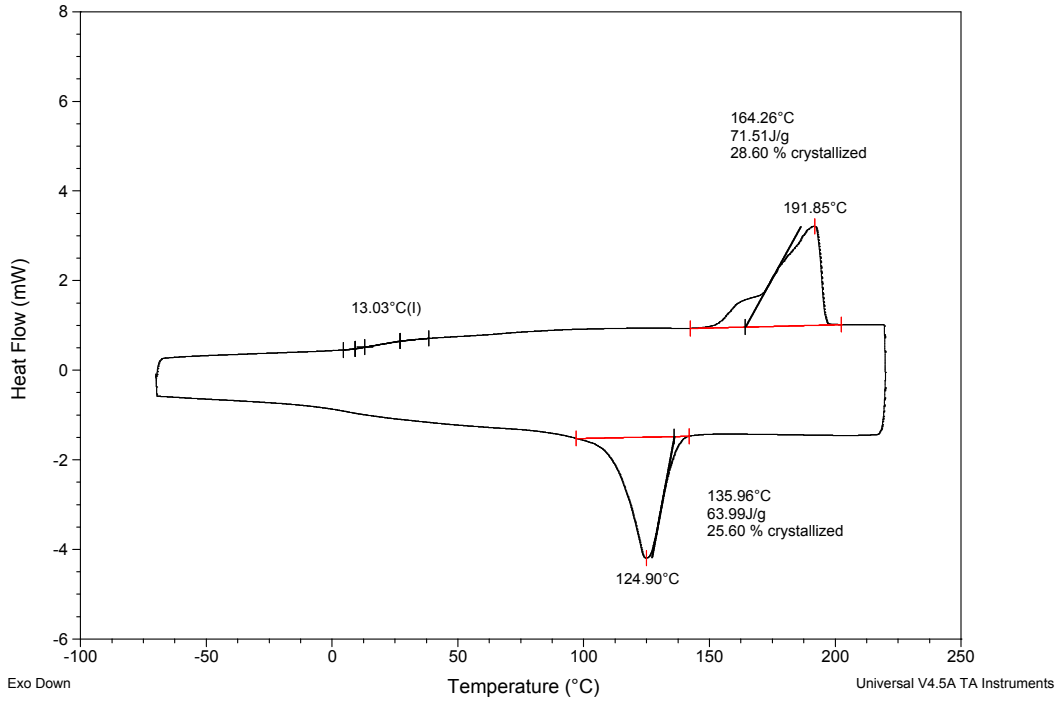


Figure S71. DSC Thermogram of polymer **17** (Table S1 entry 17).

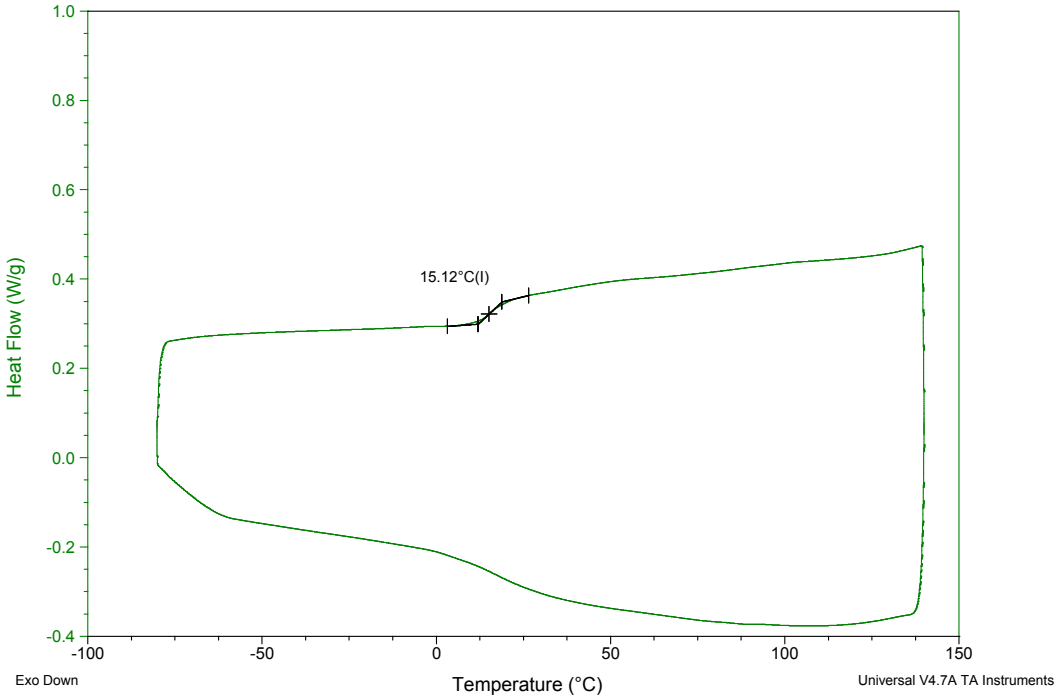


Figure S72. DSC Thermogram of polymer **18** (Table S1 entry 18).

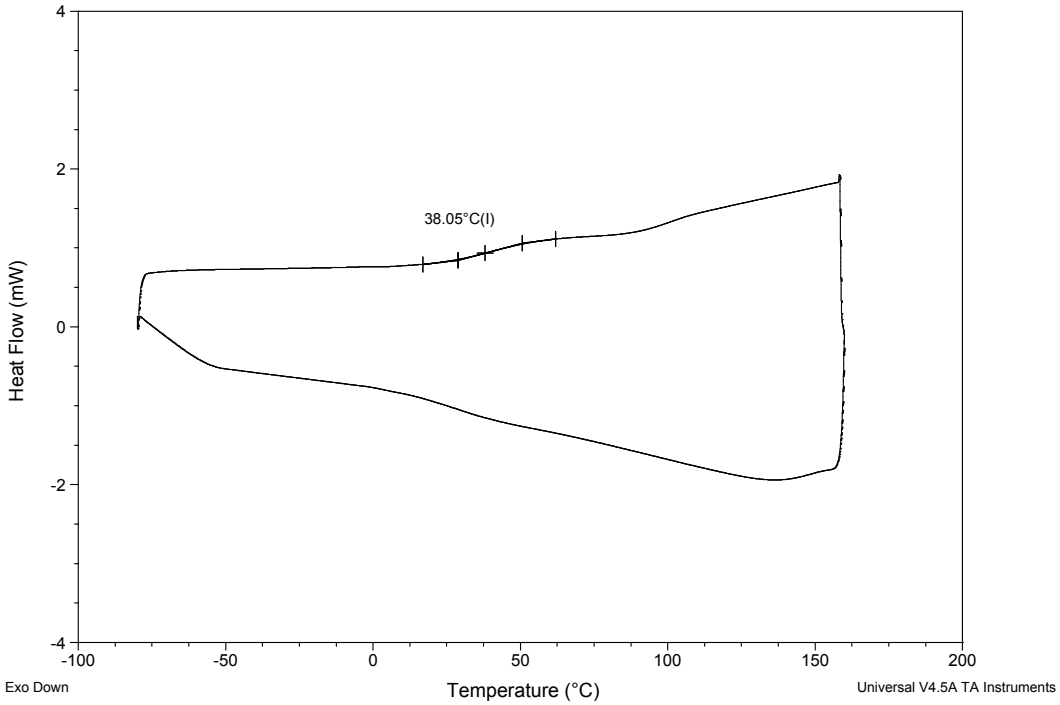


Figure S73. DSC Thermogram of polymer **19** (Table S1 entry 19).

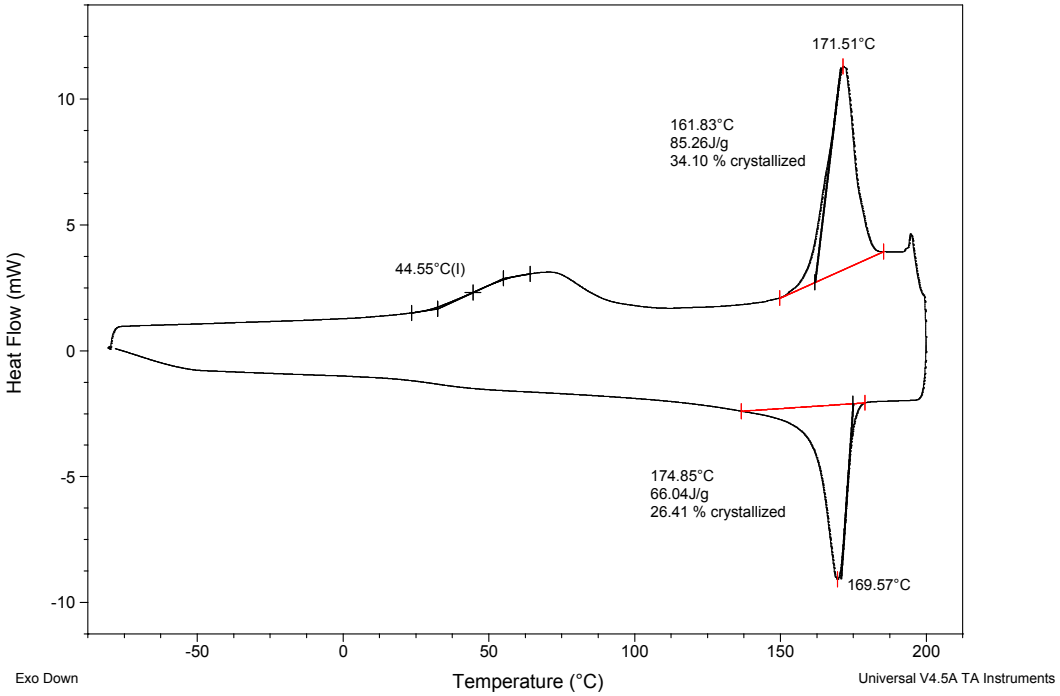


Figure S74. DSC Thermogram of polymer **21** (Table S2 entry 21).

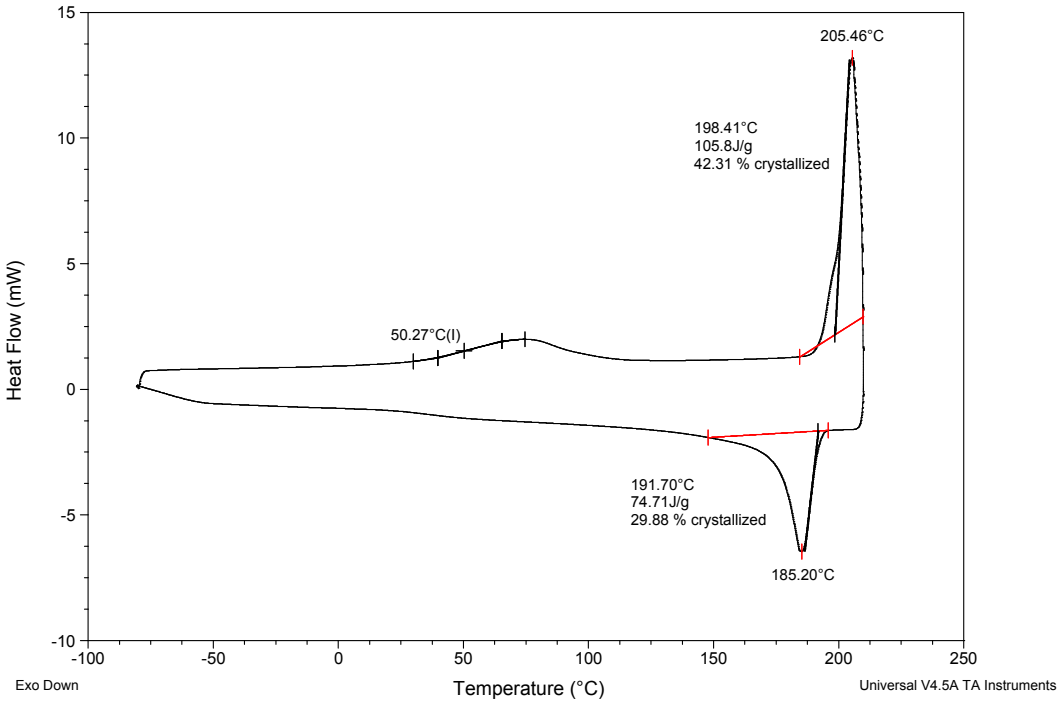


Figure S75. DSC Thermogram of polymer **22** (Table S2 entry 22).

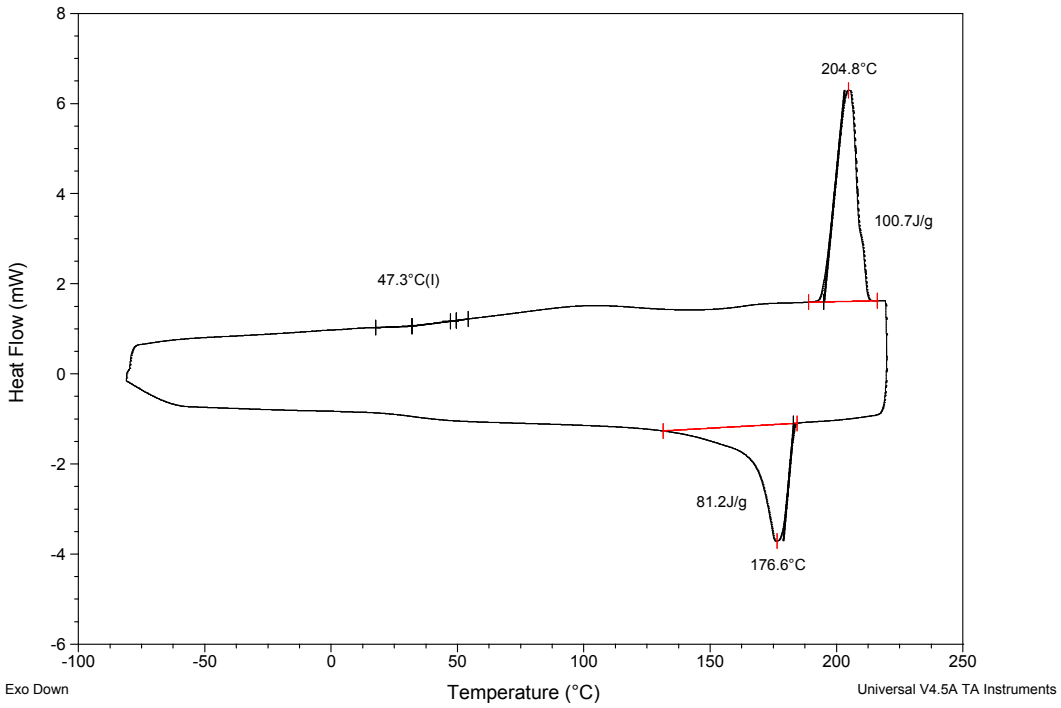


Figure S76. DSC Thermogram of polymer **23** (Table S2 entry 23).

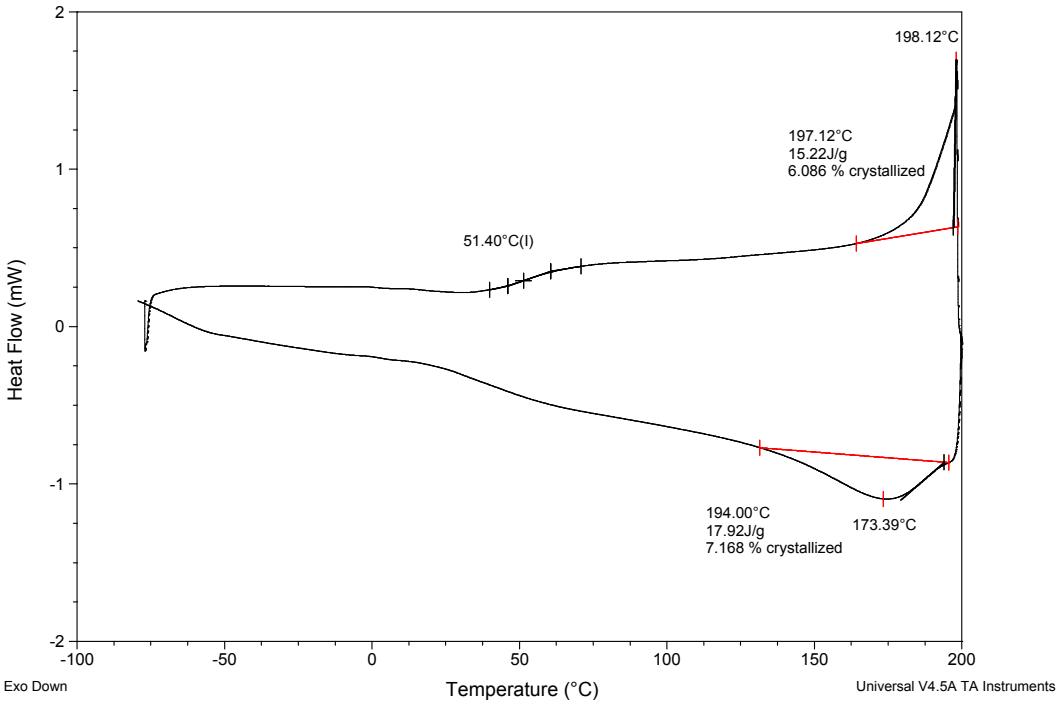


Figure S77. DSC Thermogram of polymer **24** (Table S2 entry 24).

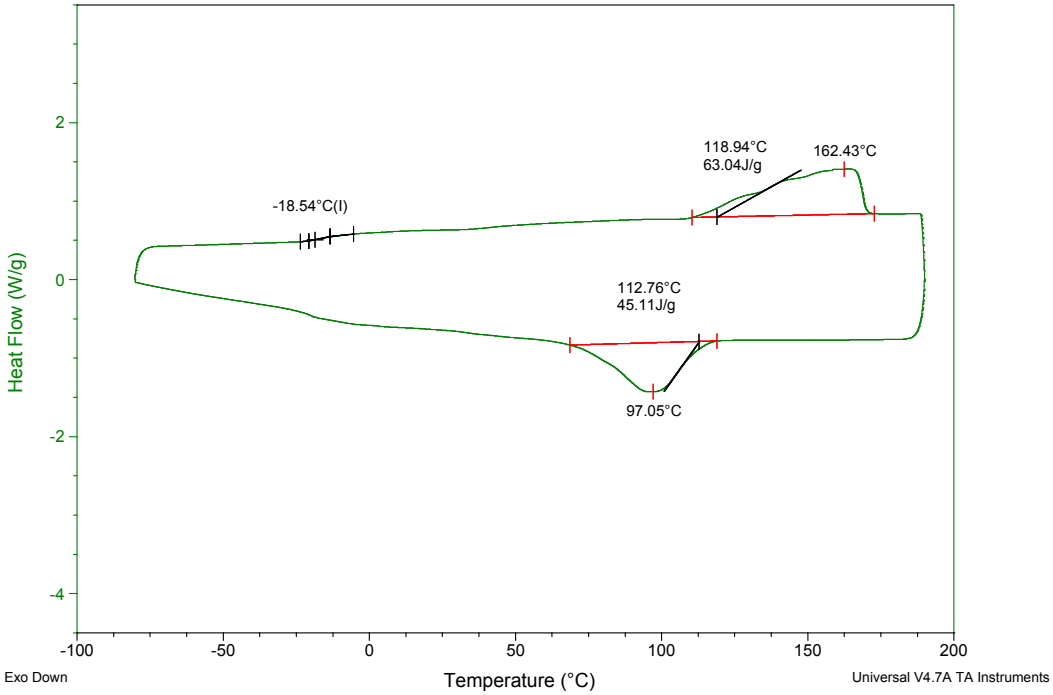


Figure S78. DSC Thermogram of polymer **25** (Table S3 entry 25).

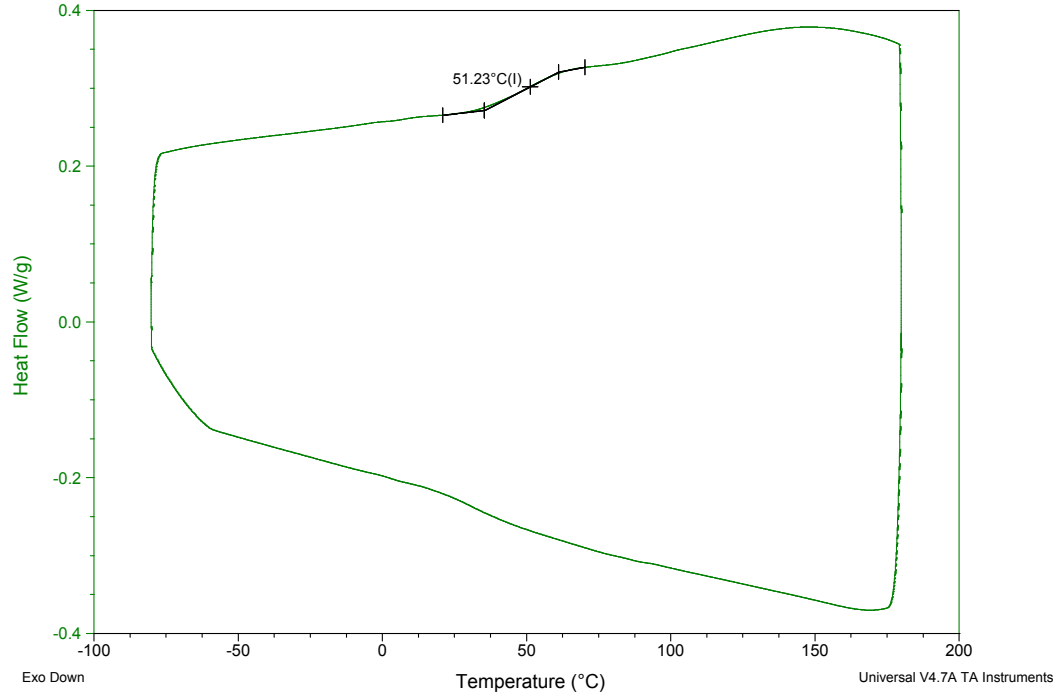


Figure S79. DSC Thermogram of polymer **26** (Table S3 entry 26).

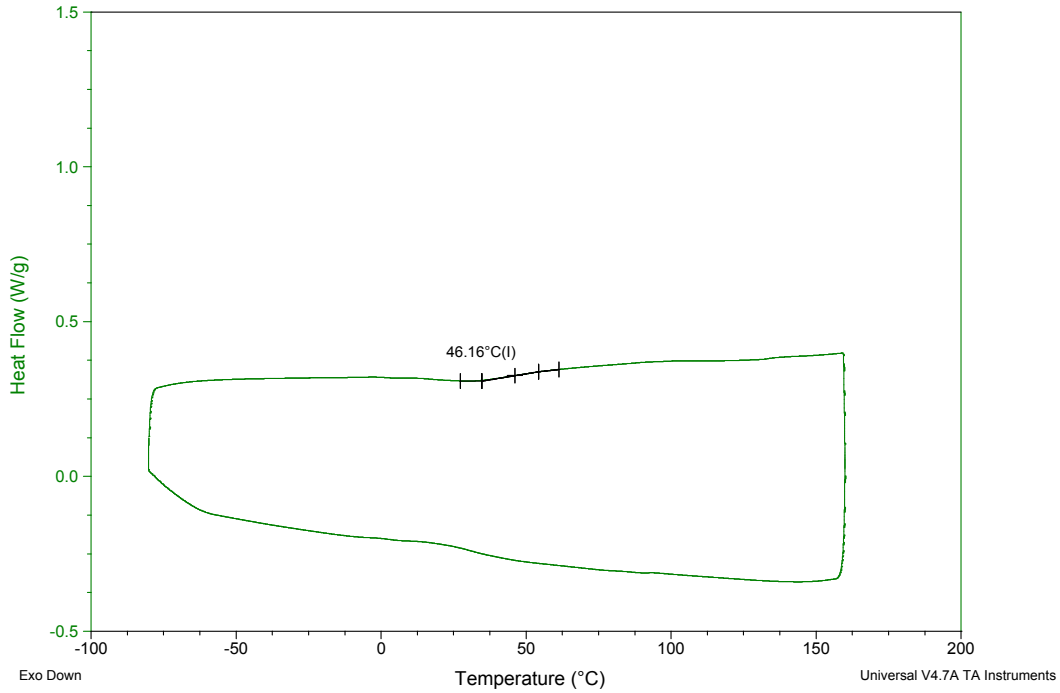


Figure S80. DSC Thermogram of polymer **27** (Scheme S1 entry 27).

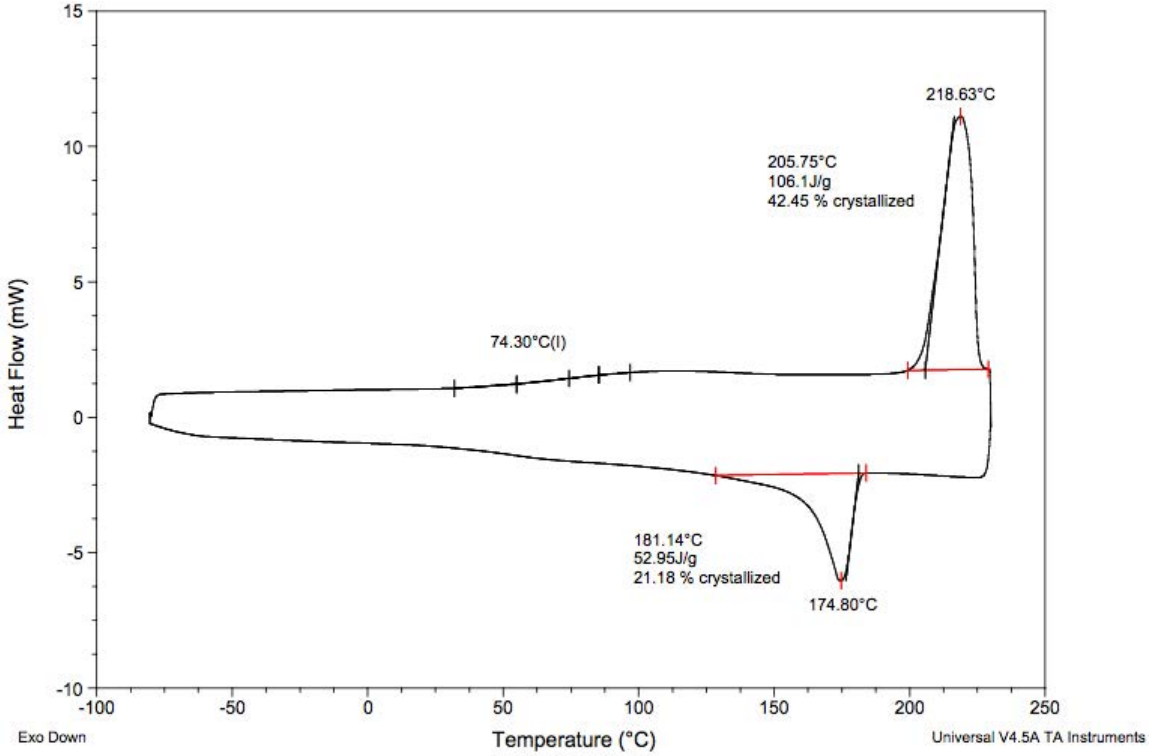


Figure S81. DSC Thermogram of polymer **28** (Scheme S2 entry 28).

^{1}H NMR Spectra

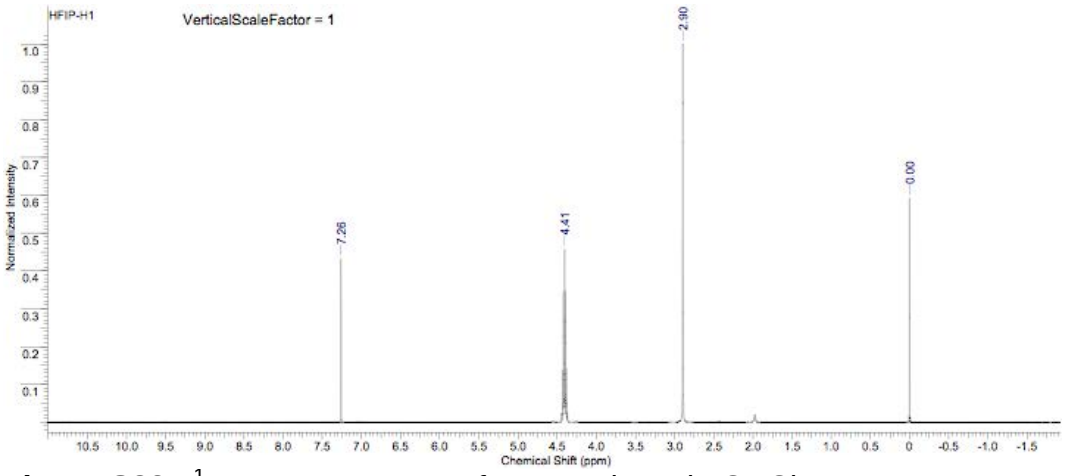


Figure S82. ^{1}H NMR spectrum of HFIP solvent in $CDCl_3$.

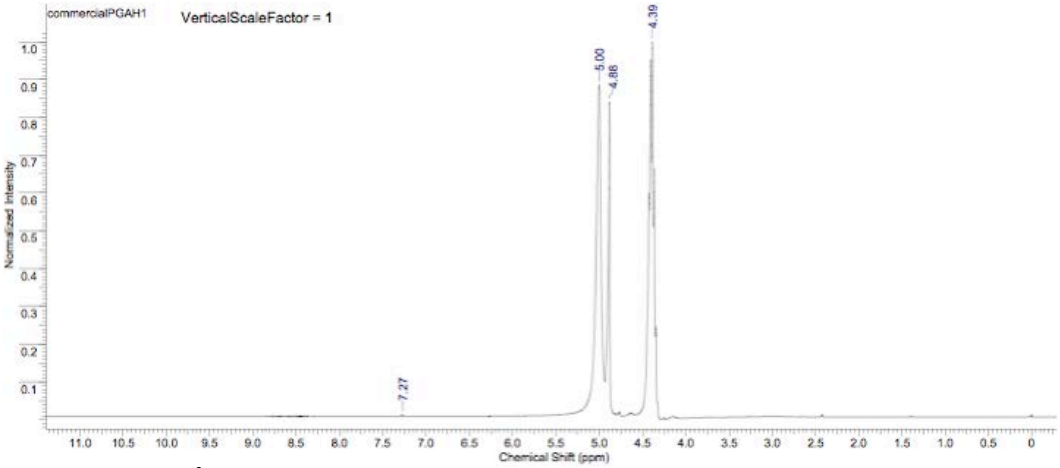


Figure S83. ^{1}H NMR spectrum of commercial polyglycolic acid in HFIP solvent and $CDCl_3$.

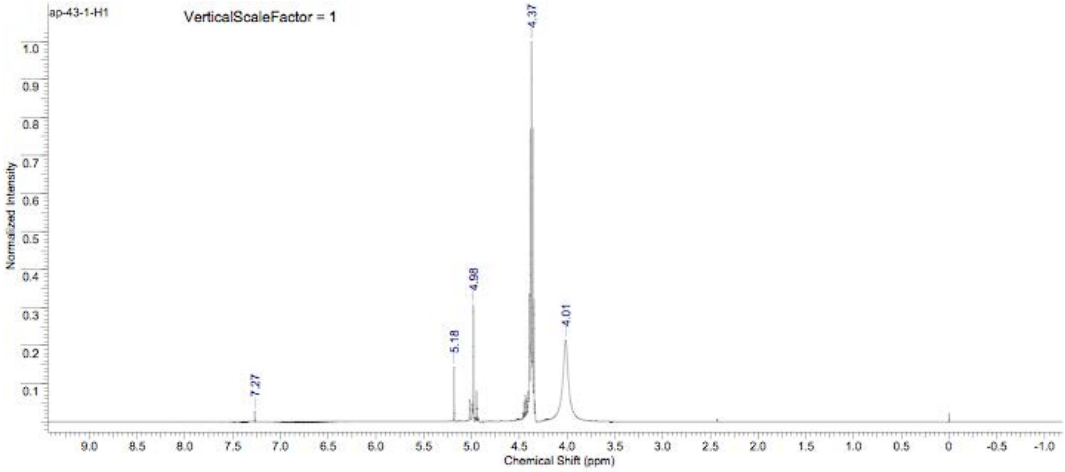


Figure S84. ^{1}H NMR spectrum of polymer **1** in HFIP solvent and $CDCl_3$ (Table S1 entry 1).

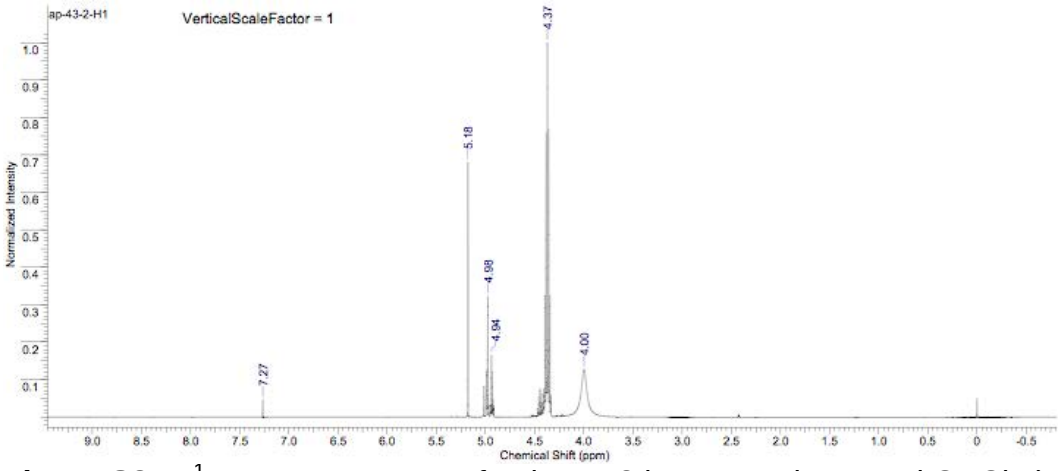


Figure S85. ^{1}H NMR spectrum of polymer **2** in HFIP solvent and $CDCl_3$ (Table S1 entry 2).

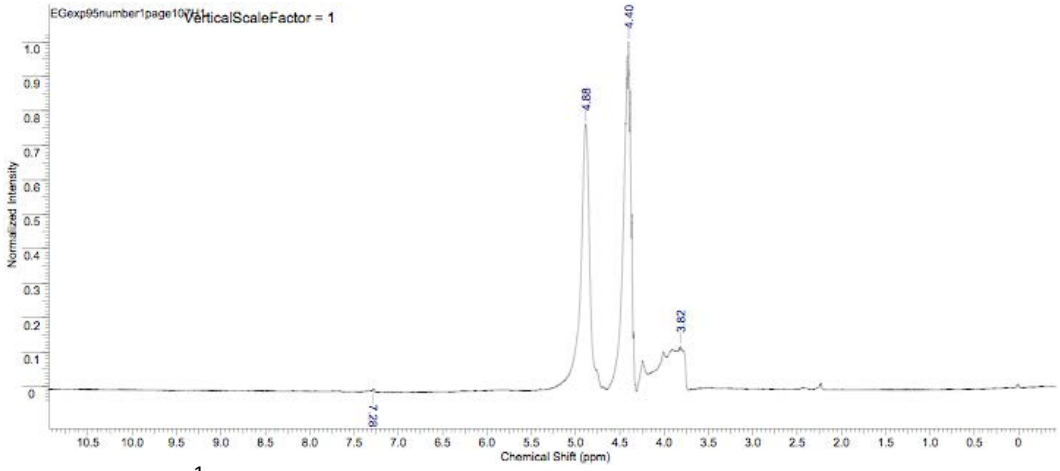


Figure S86. ^{1}H NMR spectrum of polymer **4** in HFIP solvent and $CDCl_3$ (Table S1 entry 4).

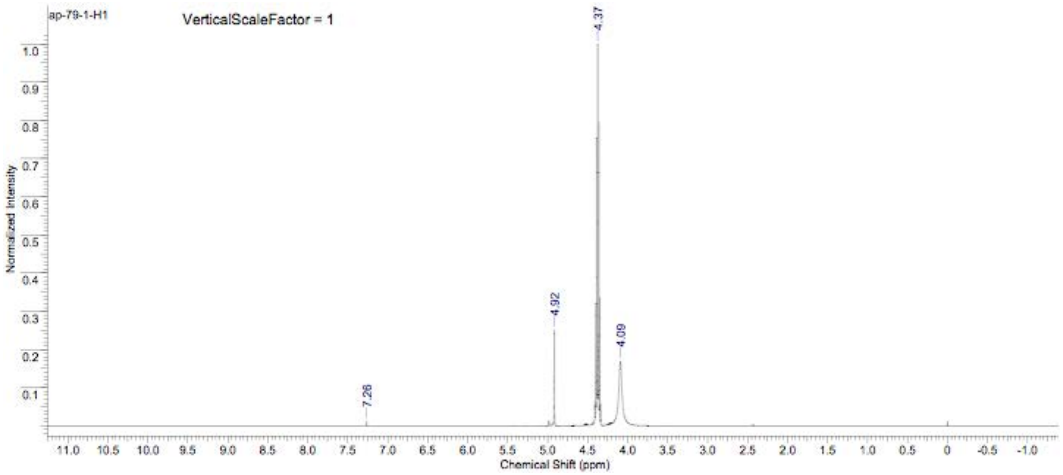


Figure S87. ^{1}H NMR spectrum of polymer **5** in HFIP solvent and $CDCl_3$ (Table S1 entry 5).

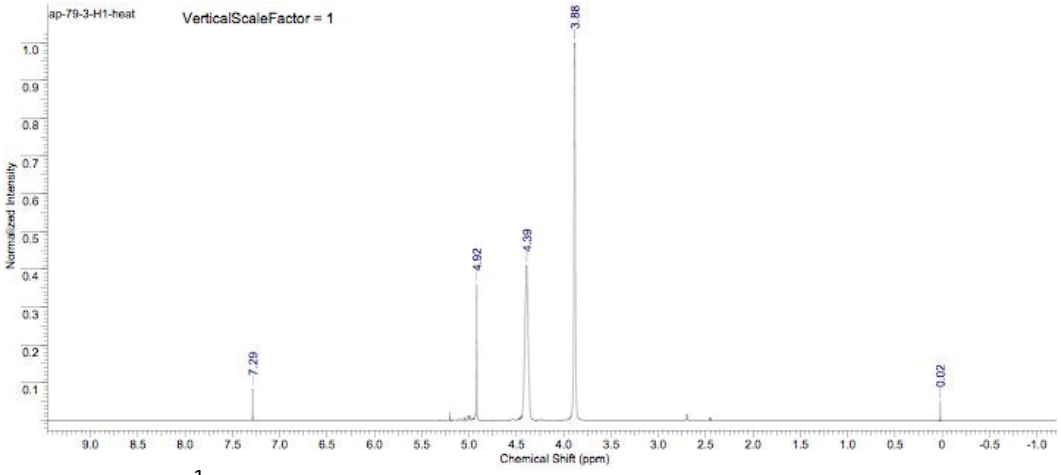


Figure S88. ^{1}H NMR spectrum of polymer **6** in HFIP solvent and $CDCl_3$ (Table S1 entry 6).

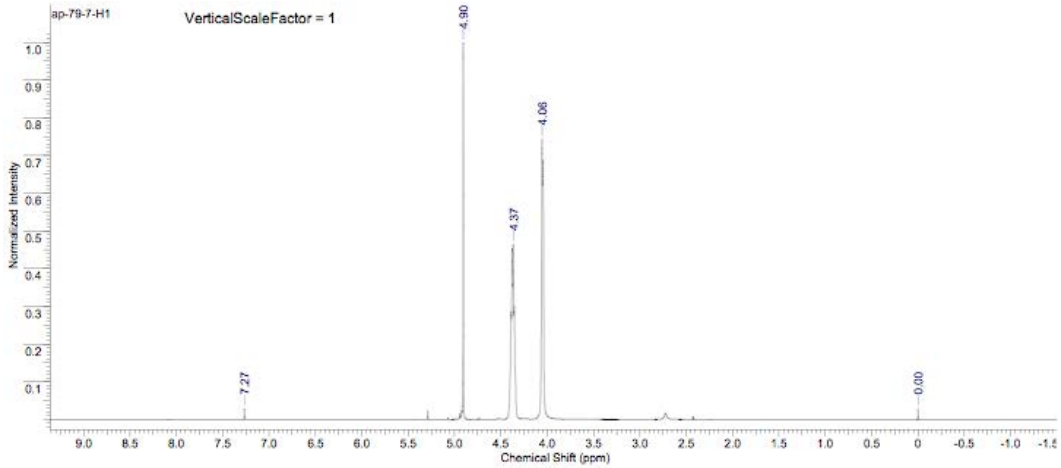


Figure S89. ^{1}H NMR spectrum of polymer **7** in HFIP solvent and $CDCl_3$ (Table S1 entry 7).

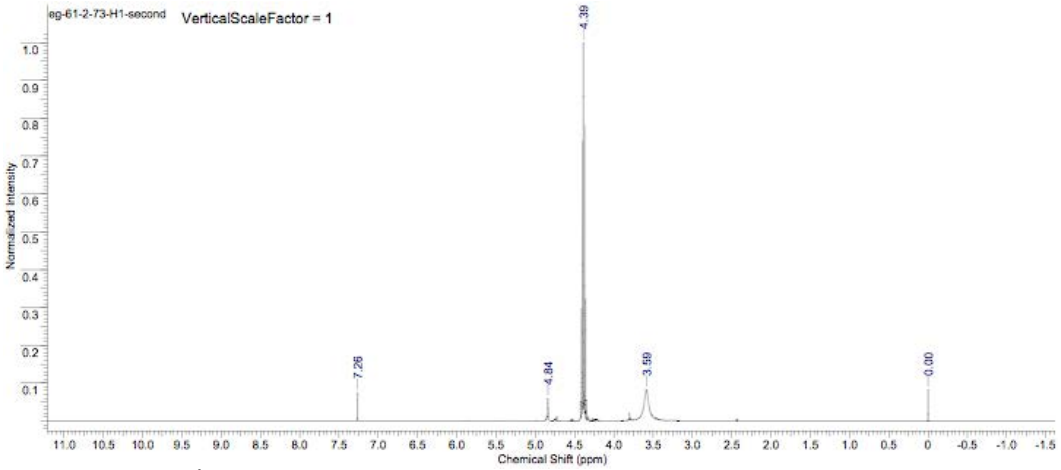


Figure S90. ^{1}H NMR spectrum of polymer **8** in HFIP solvent and $CDCl_3$ (Table S1 entry 8).

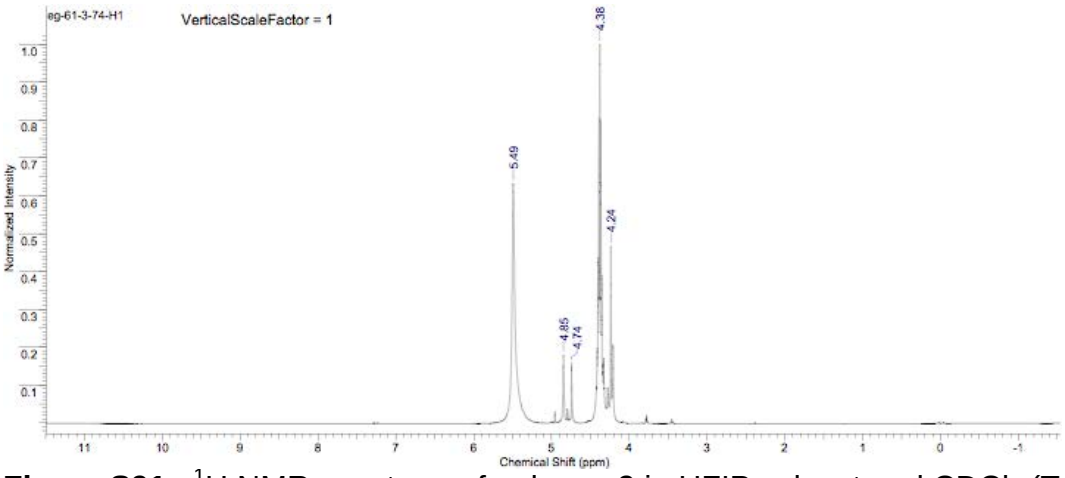


Figure S91. ^{1}H NMR spectrum of polymer **9** in HFIP solvent and $CDCl_3$ (Table S1 entry 9).

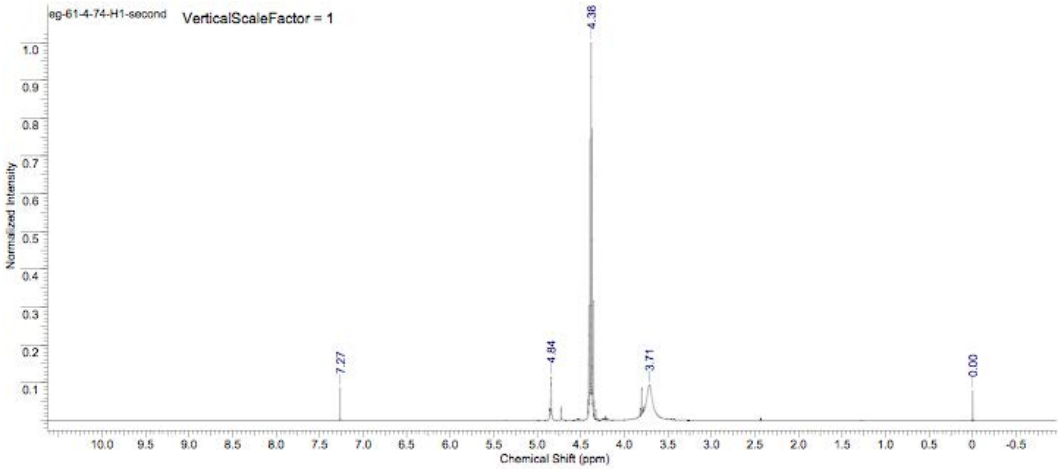


Figure S92. ^{1}H NMR spectrum of polymer **10** in HFIP solvent and $CDCl_3$ (Table S1 entry 10).

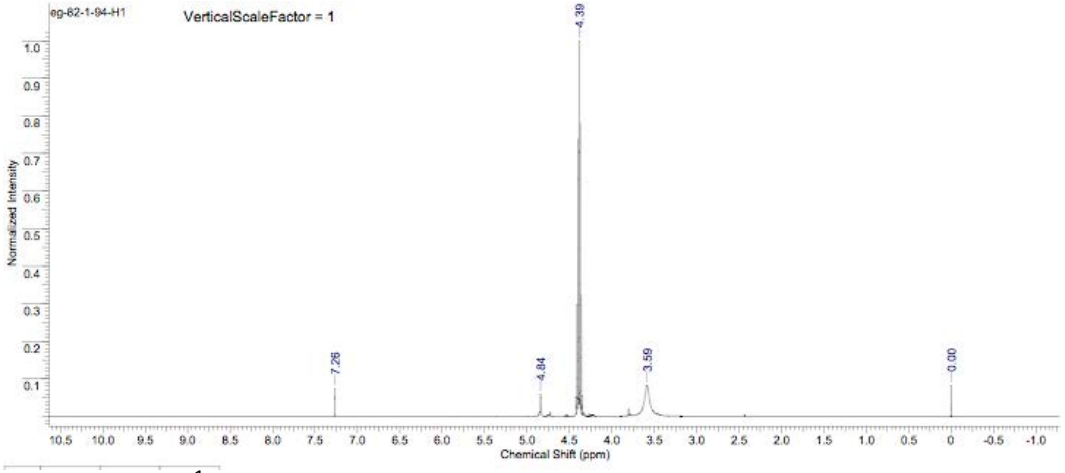


Figure S93. ^{1}H NMR spectrum of polymer **11** in HFIP solvent and $CDCl_3$ (Table S1 entry 11).

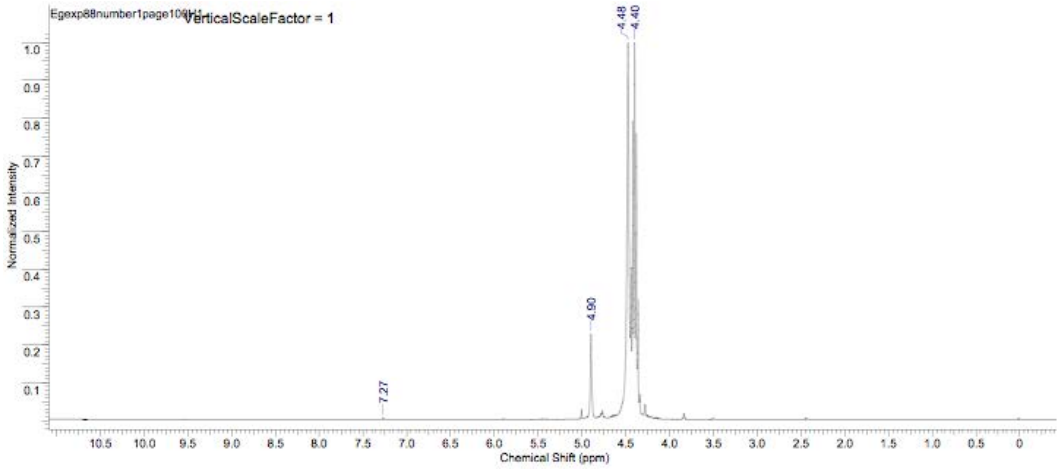


Figure S94. ^{1}H NMR spectrum of polymer **12** in HFIP solvent and $CDCl_3$ (Table S1 entry 12).

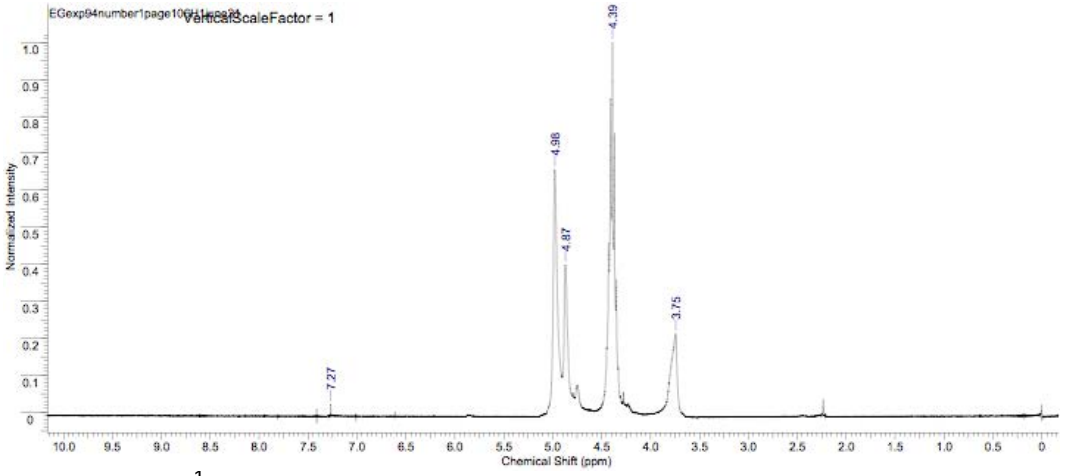


Figure S95. ^{1}H NMR spectrum of polymer **13** in HFIP solvent and $CDCl_3$ (Table S1 entry 13).

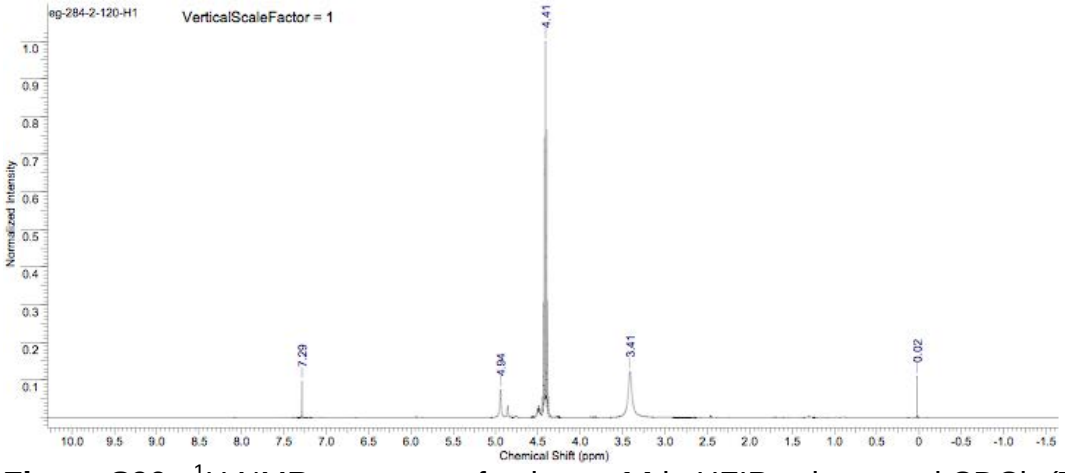


Figure S96. ^{1}H NMR spectrum of polymer **14** in HFIP solvent and $CDCl_3$ (Table S1 entry 14).

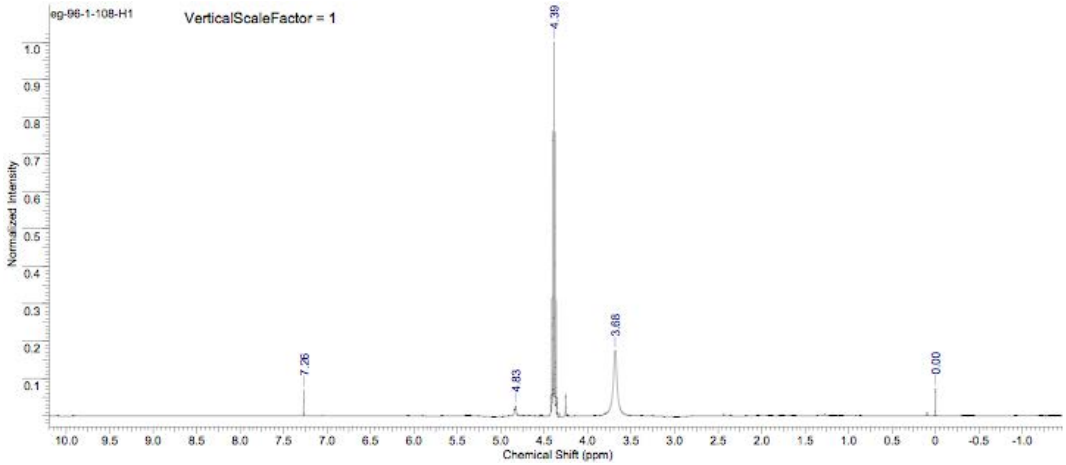


Figure S97. ^{1}H NMR spectrum of polymer **15** in HFIP solvent and $CDCl_3$ (Table S1 entry 15).

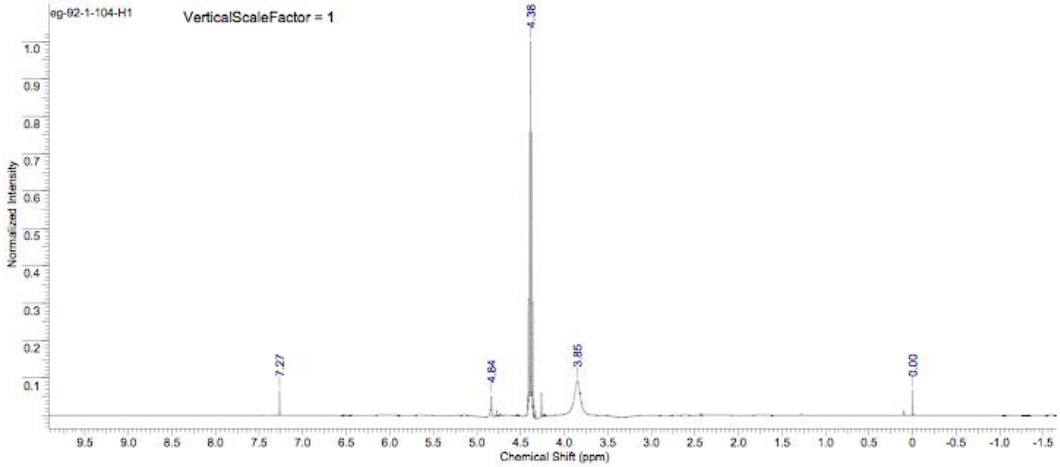


Figure S98. ^{1}H NMR spectrum of polymer **16** in HFIP solvent and $CDCl_3$ (Table S1 entry 16).

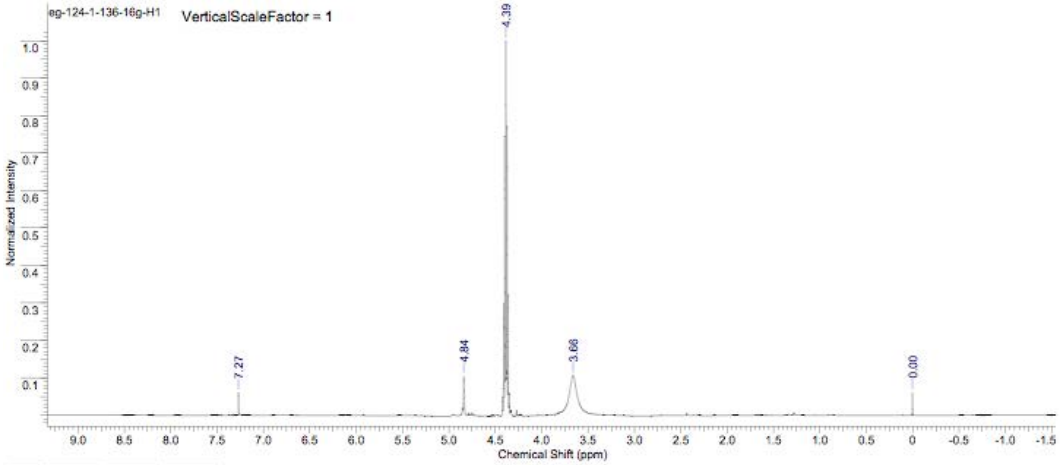


Figure S99. ^{1}H NMR spectrum of polymer **17** in HFIP solvent and $CDCl_3$ (Table S1 entry 17).

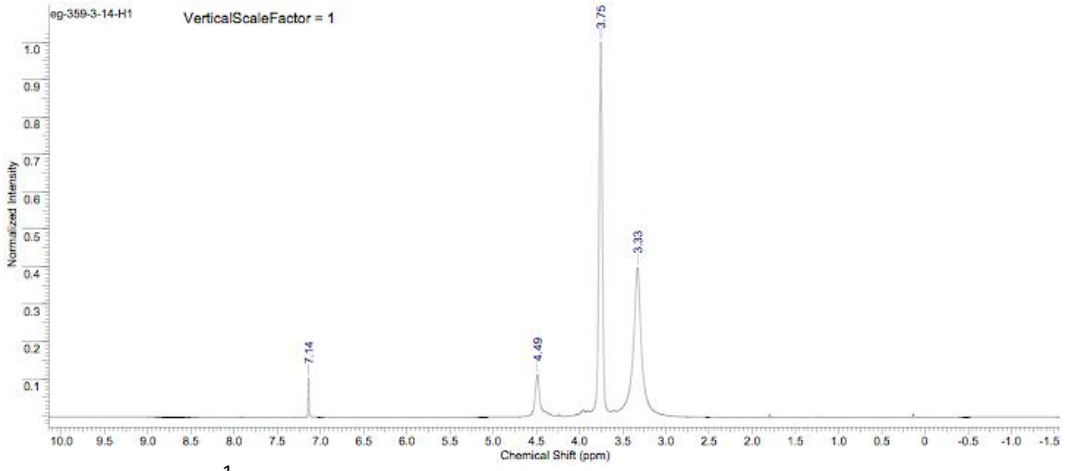


Figure S100. ^{1}H NMR spectrum of polymer **18** in HFIP solvent and $CDCl_3$ (Table S1 entry 18).

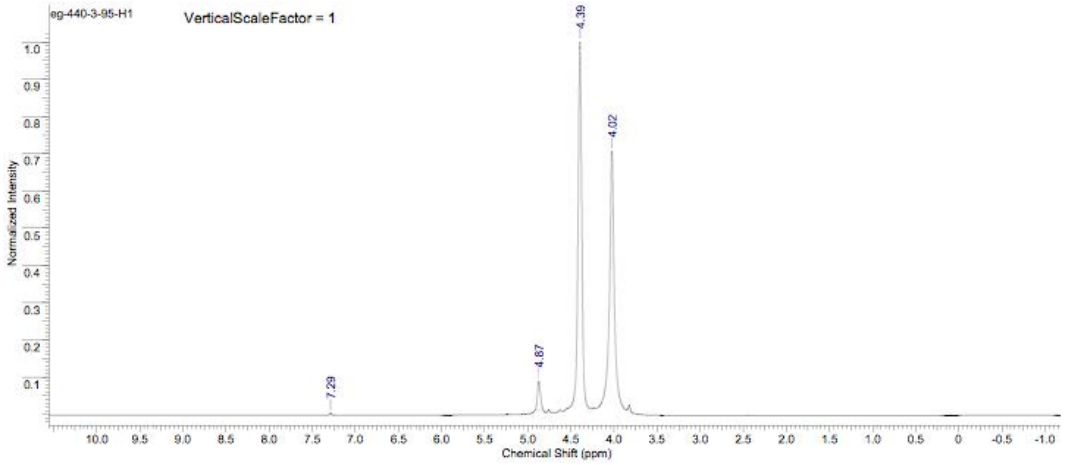


Figure S101. ^{1}H NMR spectrum of polymer **19** in HFIP solvent and $CDCl_3$ (Table S1 entry 19).

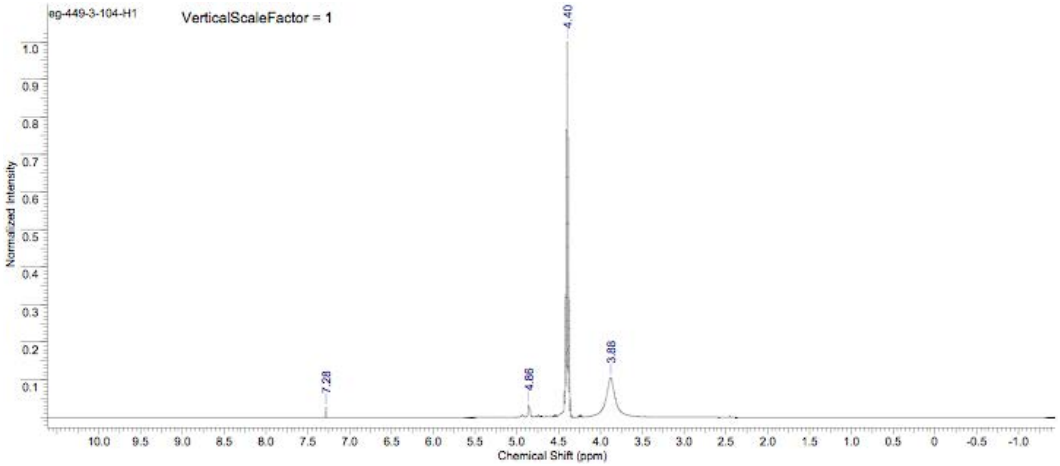


Figure S102. ^{1}H NMR spectrum of polymer **21** in HFIP solvent and $CDCl_3$ (Table S2 entry 21).

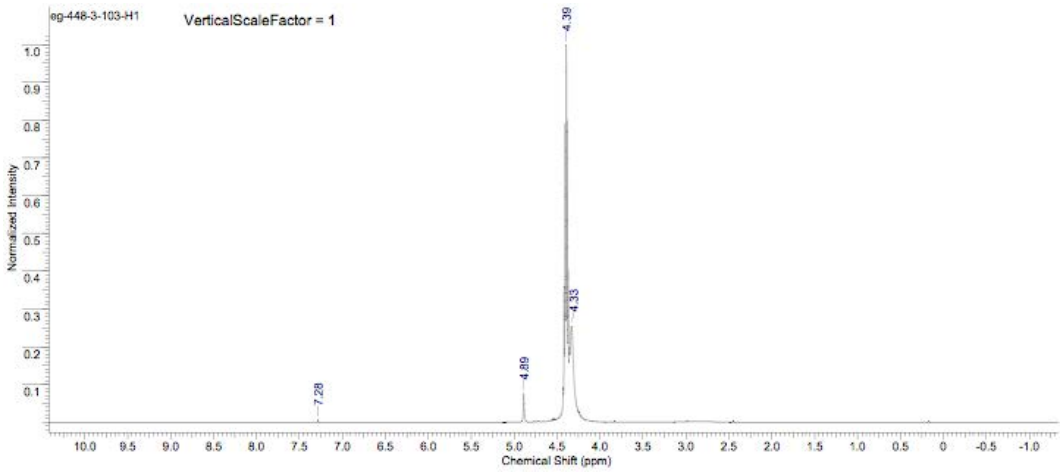


Figure S103. ^{1}H NMR spectrum of polymer **22** in HFIP solvent and $CDCl_3$ (Table S2 entry 22).

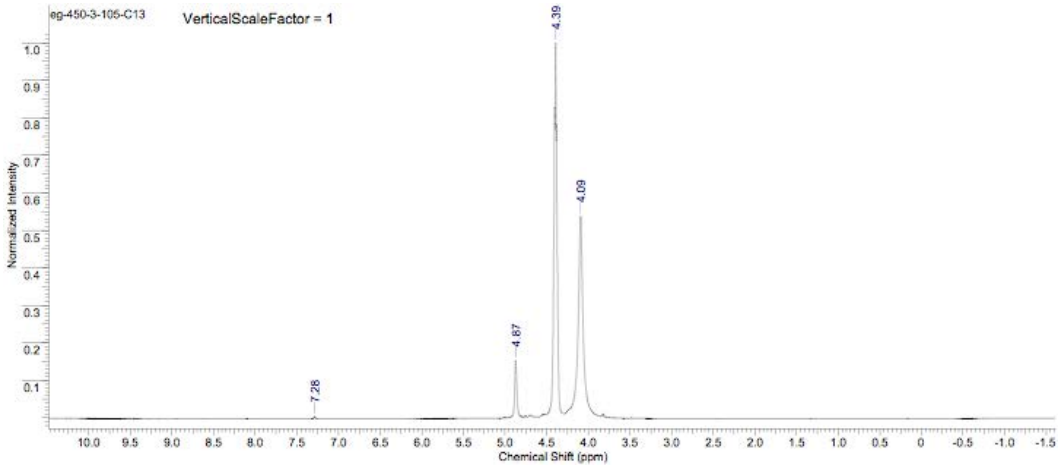


Figure S104. ^{1}H NMR spectrum of polymer **23** in HFIP solvent and $CDCl_3$ (Table S2 entry 23).

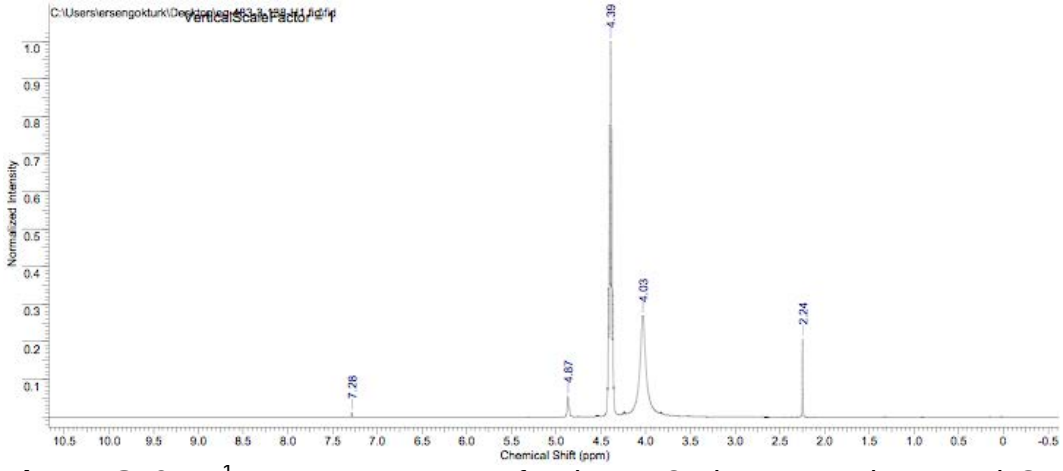


Figure S105. ^{1}H NMR spectrum of polymer **24** in HFIP solvent and $CDCl_3$ (Table S2 entry 24).

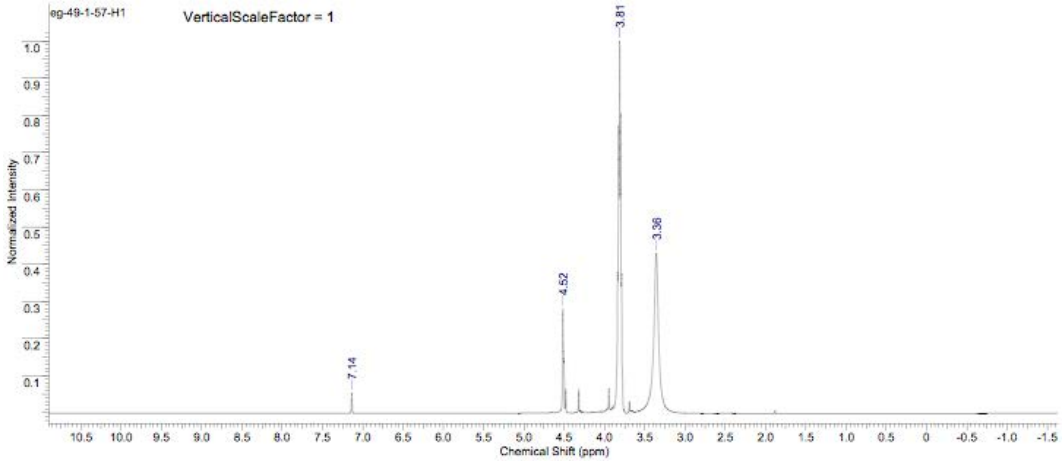


Figure S106. ^{1}H NMR spectrum of polymer **25** in HFIP solvent and $CDCl_3$ (Table S3 entry 25).

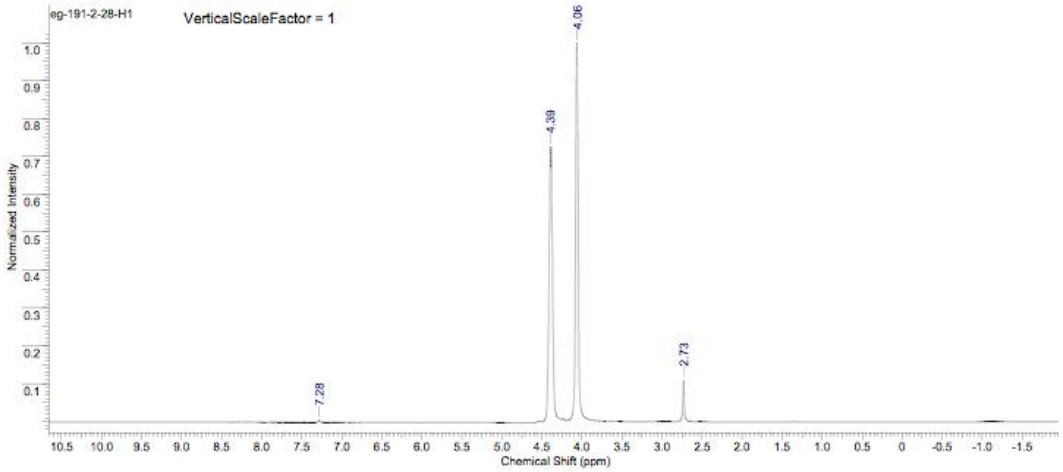


Figure S107. ^{1}H NMR spectrum of polymer **26** in HFIP solvent and $CDCl_3$ (Table S3 entry 26).

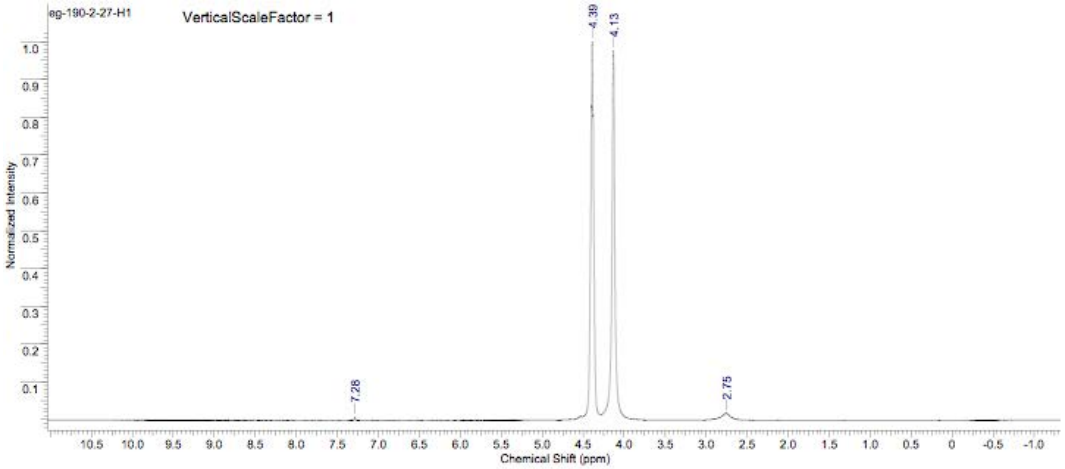


Figure S108. ^{1}H NMR spectrum of polymer **27** in HFIP solvent and $CDCl_3$ (Scheme S1 entry 27).

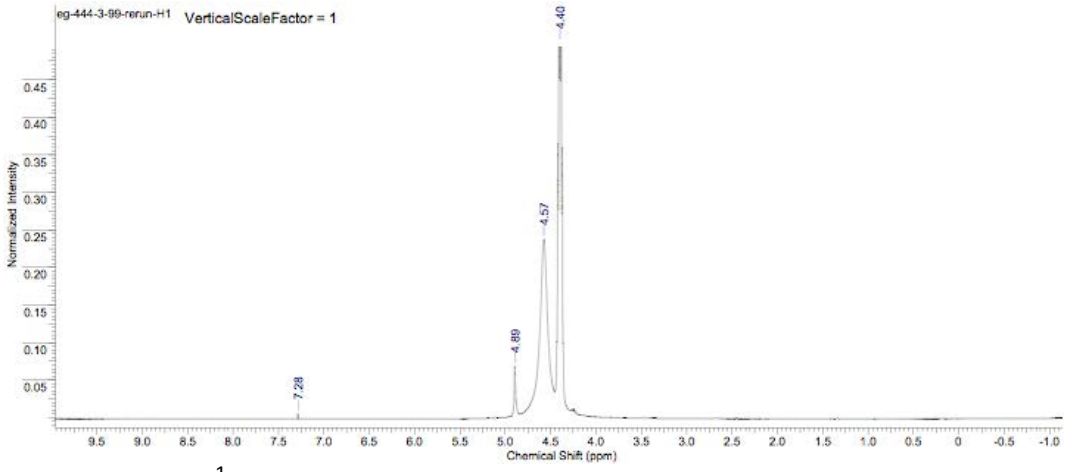


Figure S109. ^{1}H NMR spectrum of polymer **28** in HFIP solvent and $CDCl_3$ (Scheme S2 entry 28).

^{13}C NMR Spectra

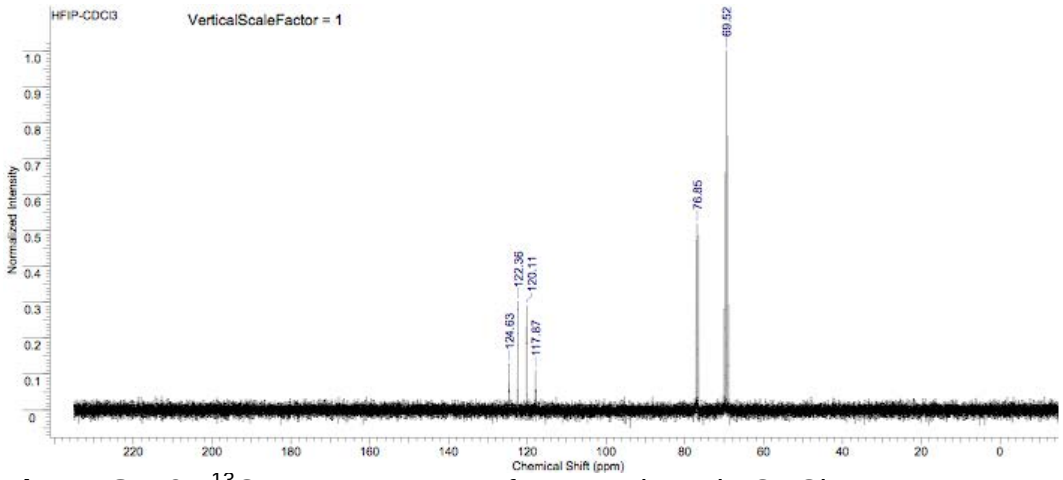


Figure S110. ^{13}C NMR spectrum of HFIP solvent in $CDCl_3$.

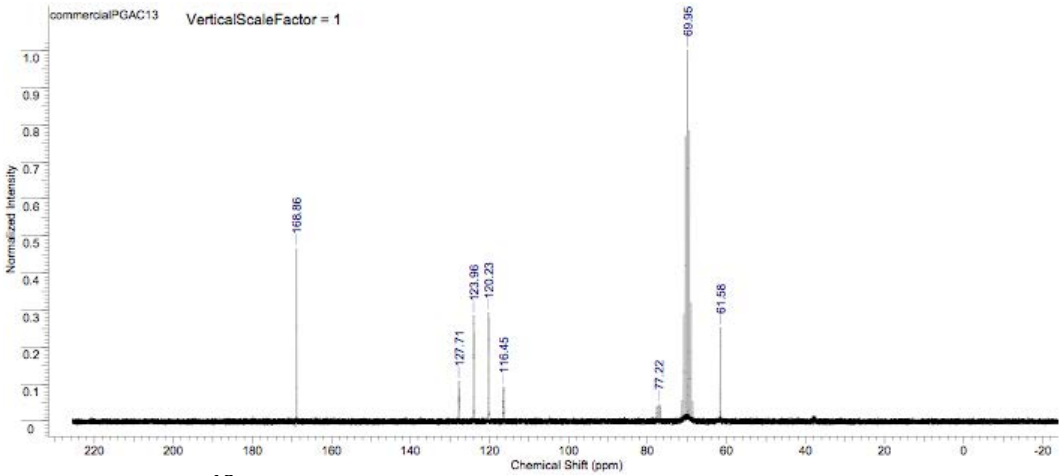


Figure S111. ^{13}C NMR spectrum of commercial polyglycolic acid in HFIP solvent and $CDCl_3$.

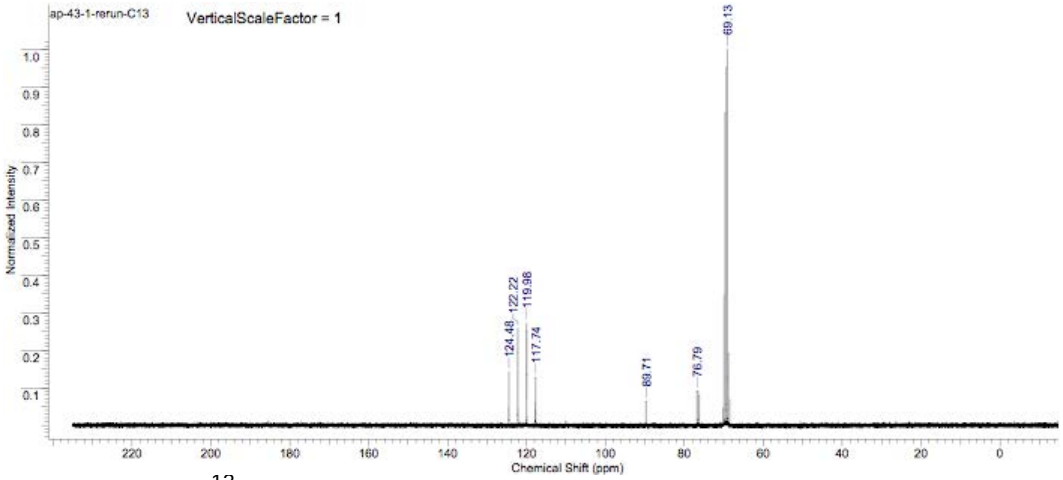


Figure S112. ^{13}C NMR spectrum of polymer **1** in HFIP solvent and $CDCl_3$ (Table S1 entry 1).

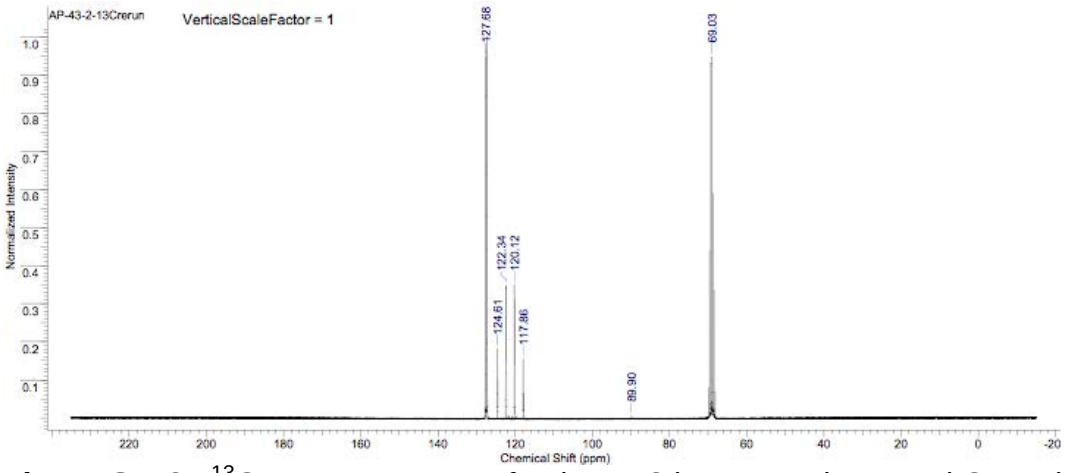


Figure S113. ^{13}C NMR spectrum of polymer **2** in HFIP solvent and C_6D_6 (Table S1 entry 2).

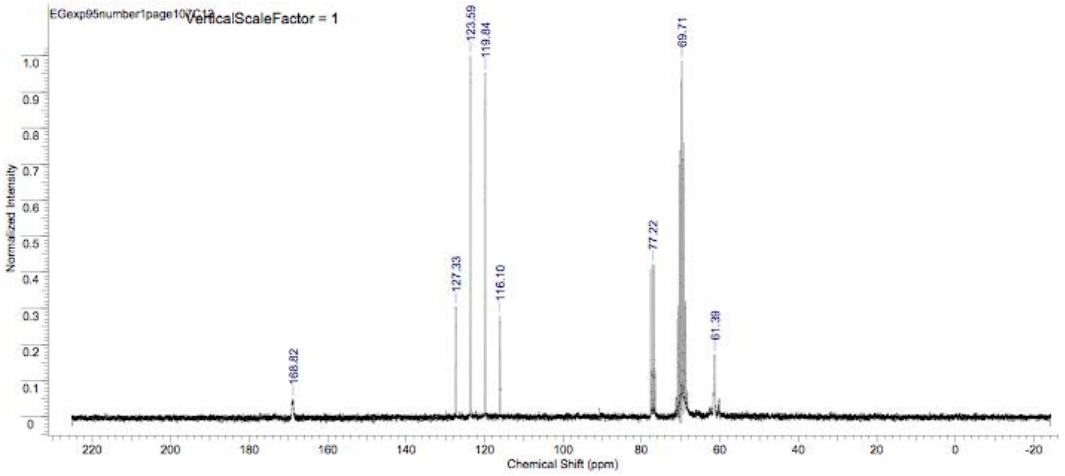


Figure S114. ^{13}C NMR spectrum of polymer **4** in HFIP solvent and $CDCl_3$ (Table S1 entry 4).

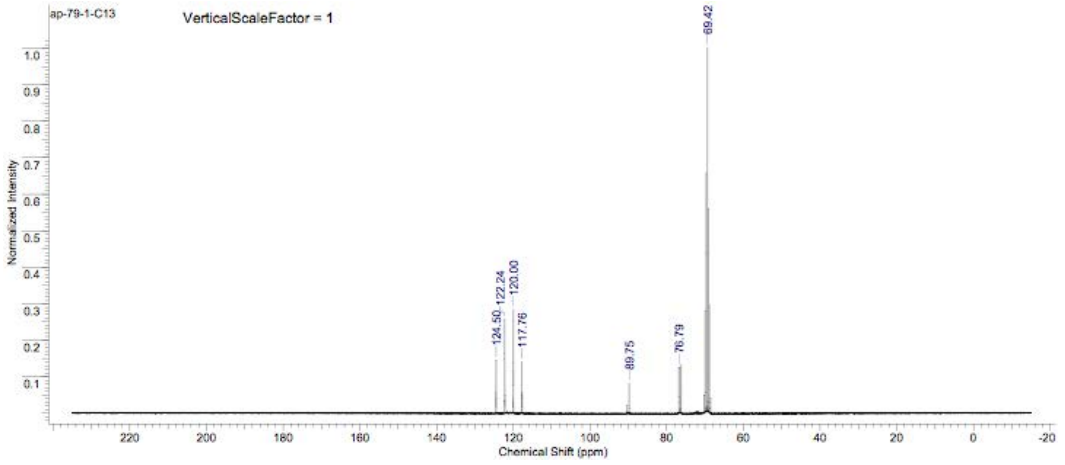


Figure S115. ^{13}C NMR spectrum of polymer **5** in HFIP solvent and $CDCl_3$ (Table S1 entry 5).

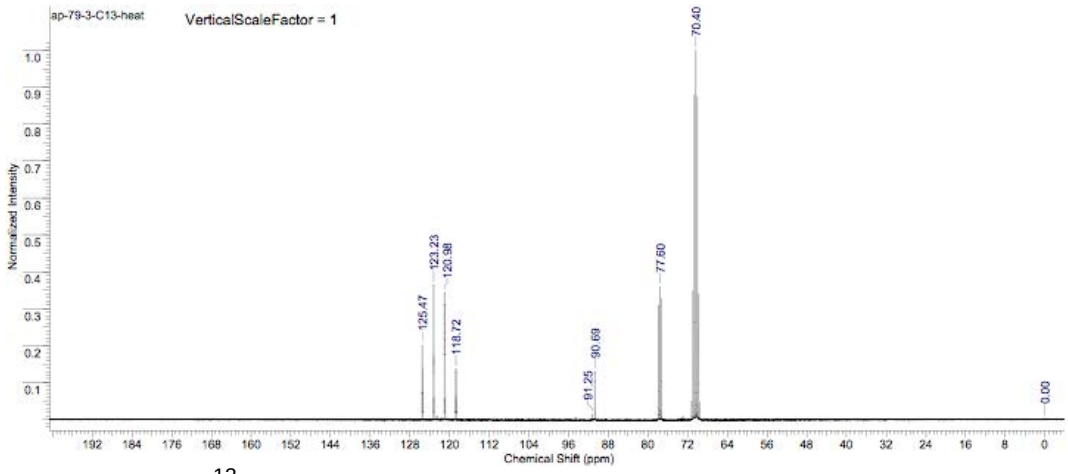


Figure S116. ^{13}C NMR spectrum of polymer **6** in HFIP solvent and $CDCl_3$ (Table S1 entry 6).

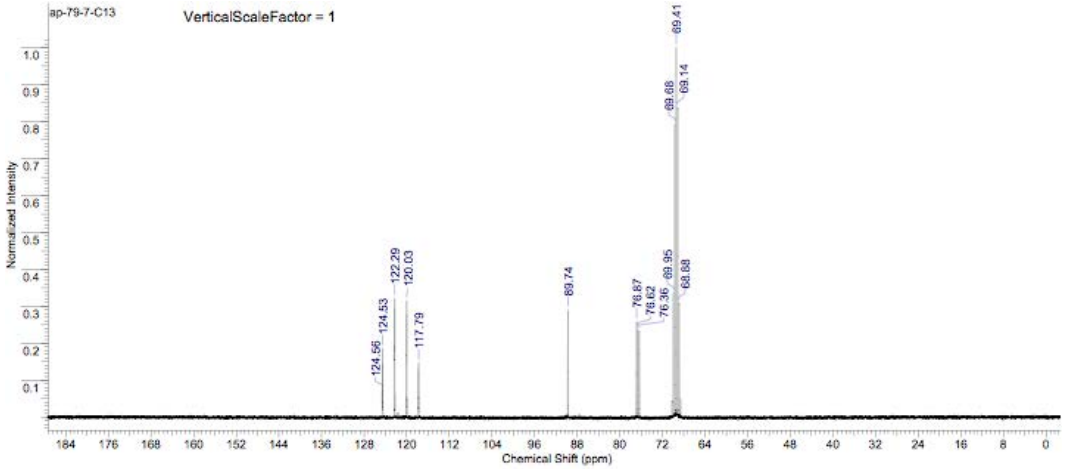


Figure S117. ^{13}C NMR spectrum of polymer **7** in HFIP solvent and $CDCl_3$ (Table S1 entry 7).

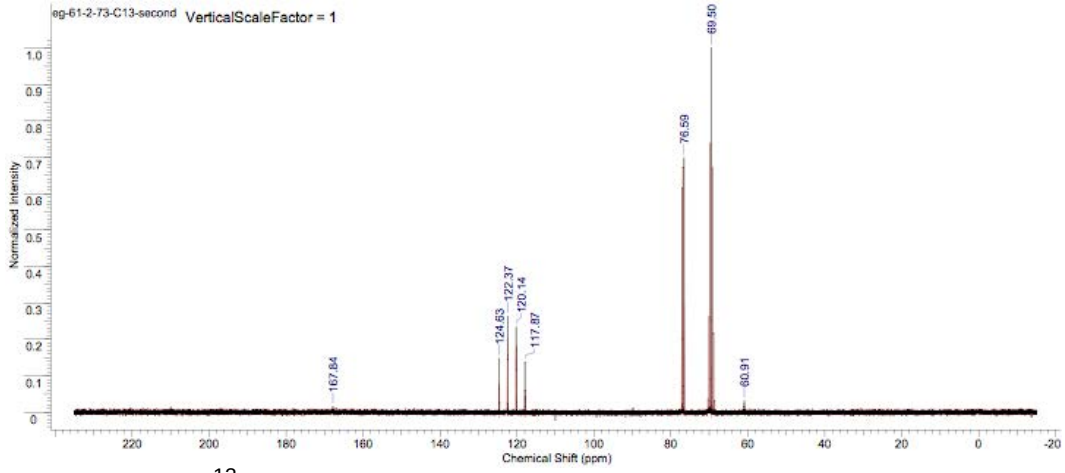


Figure S118. ^{13}C NMR spectrum of polymer **8** in HFIP solvent and $CDCl_3$ (Table S1 entry 8).

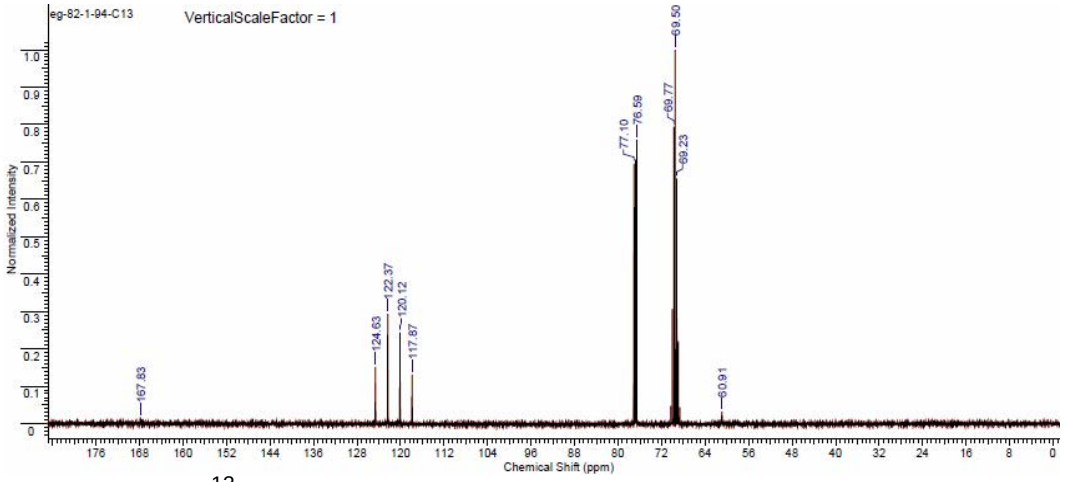


Figure S119. ^{13}C NMR spectrum of polymer **9** in HFIP solvent and $CDCl_3$ (Table S1 entry 9).

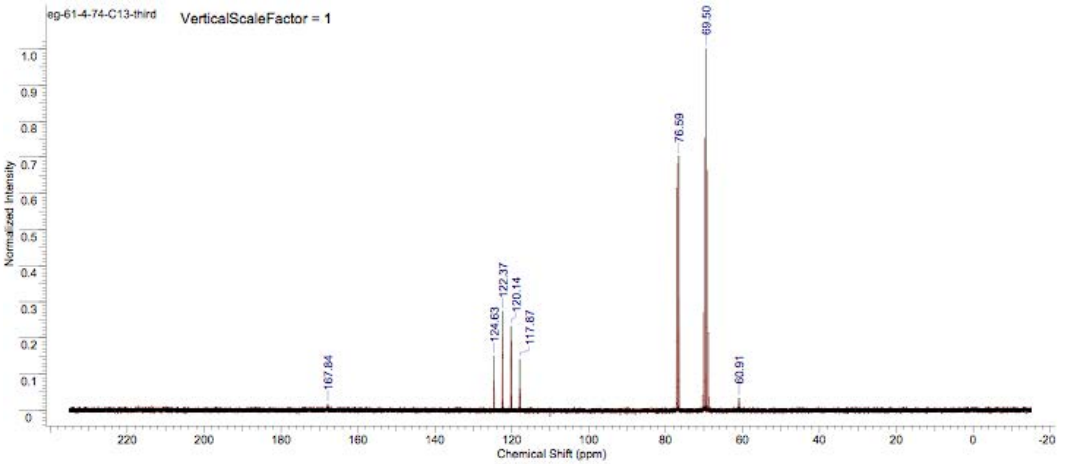


Figure S120. ^{13}C NMR spectrum of polymer **10** in HFIP solvent and C_6D_6 (Table S1 entry 10).

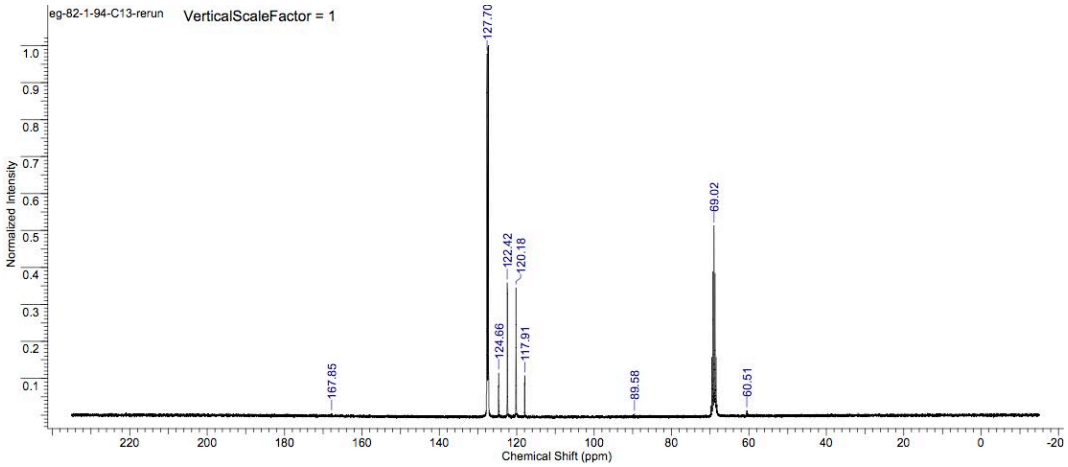


Figure S121. ^{13}C NMR spectrum of polymer **11** in HFIP solvent and $CDCl_3$ (Table S1 entry 11).

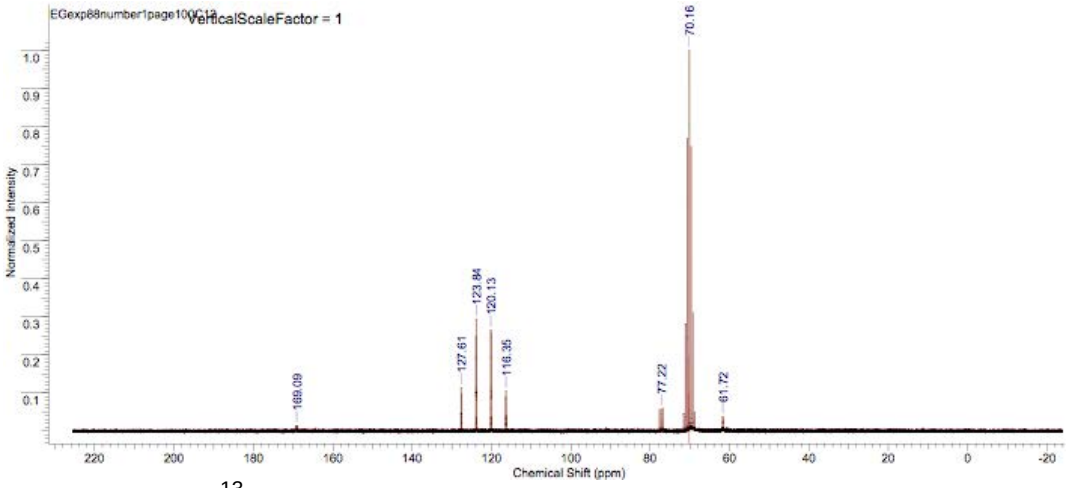


Figure S122. ^{13}C NMR spectrum of polymer **12** in HFIP solvent and $CDCl_3$ (Table S1 entry 12).

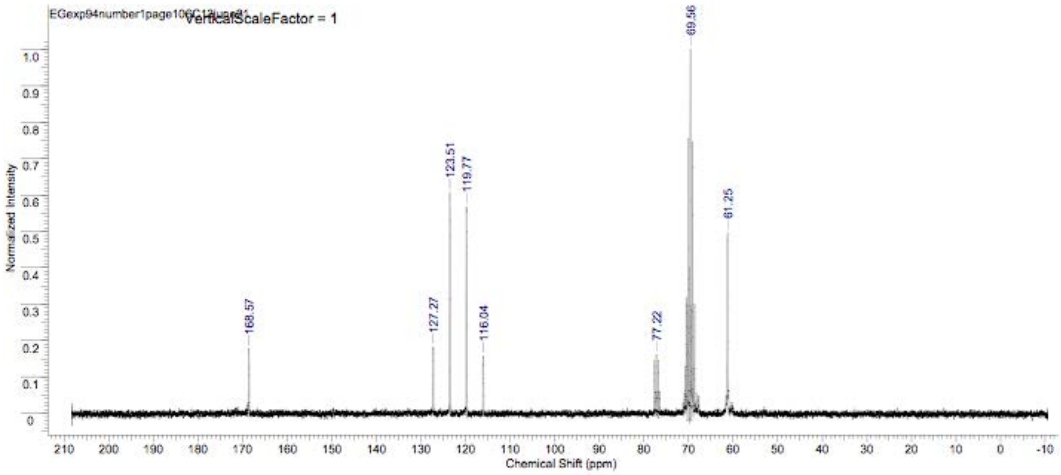


Figure S123. ^{13}C NMR spectrum of polymer **13** in HFIP solvent and $CDCl_3$ (Table S1 entry 13).

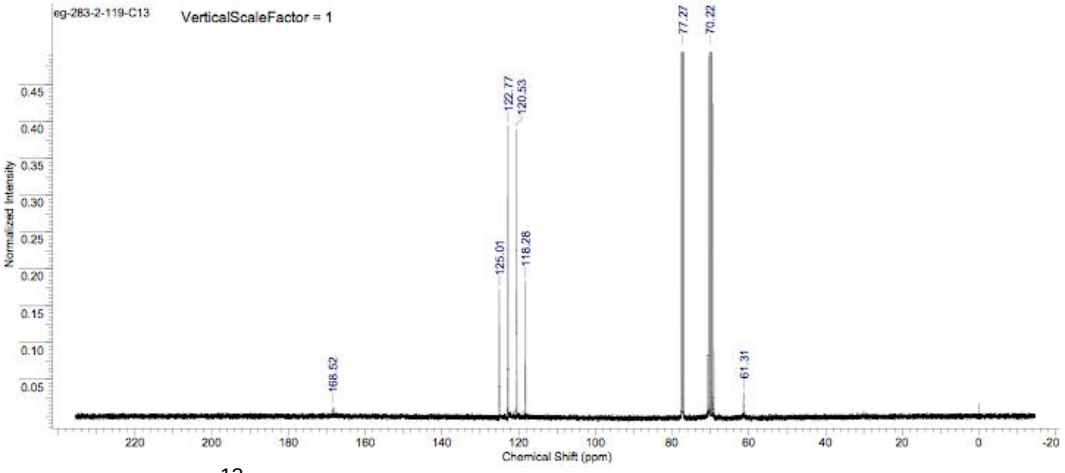


Figure S124. ^{13}C NMR spectrum of polymer **14** in HFIP solvent and $CDCl_3$ (Table S1 entry 14).

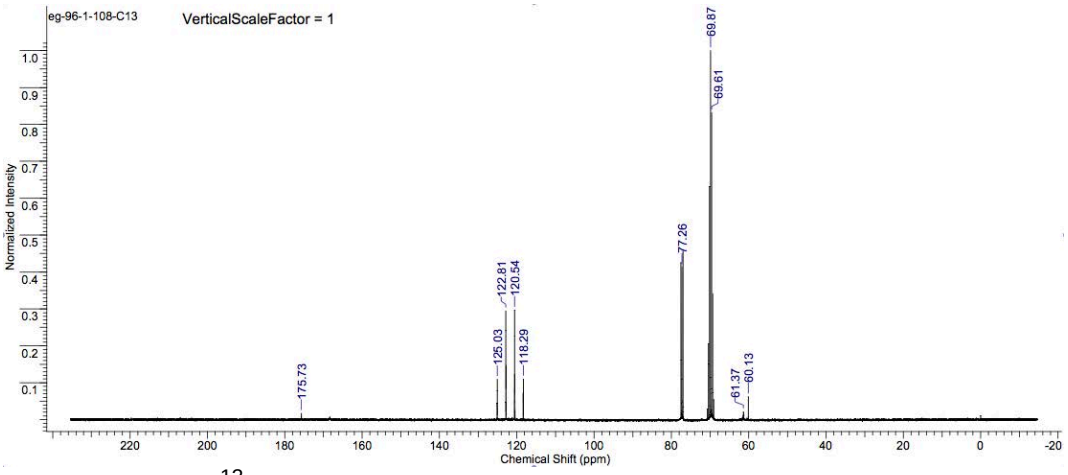


Figure S125. ^{13}C NMR spectrum of polymer **15** in HFIP solvent and $CDCl_3$ (Table S1 entry 15).

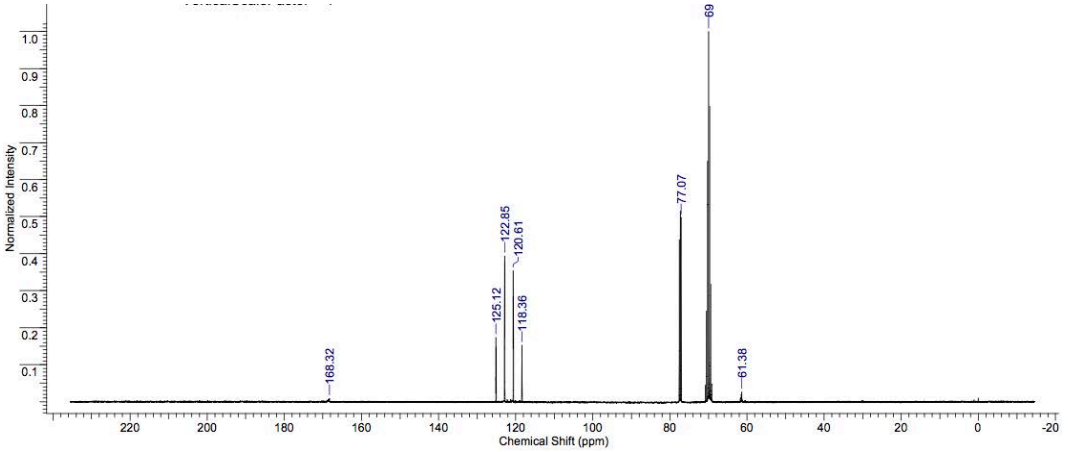


Figure S126. ^{13}C NMR spectrum of polymer **16** in HFIP solvent and $CDCl_3$ (Table S1 entry 16).

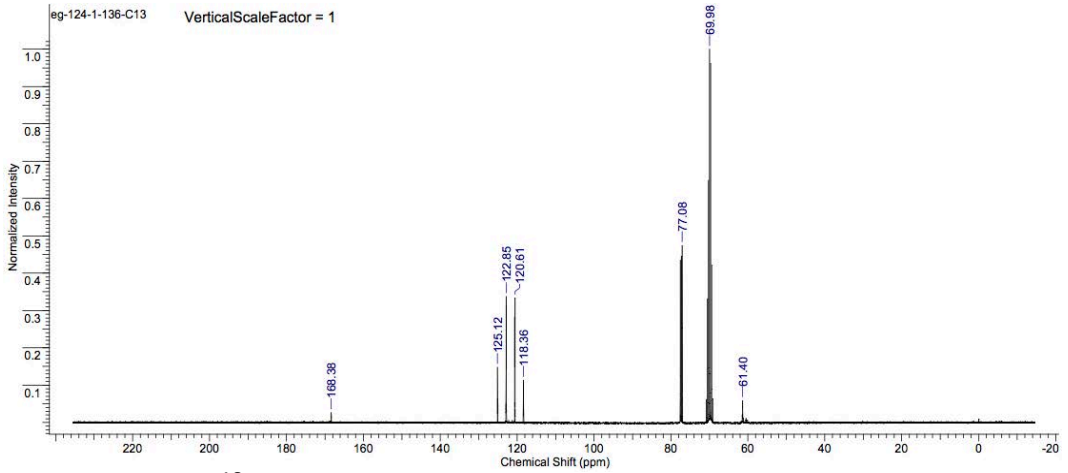


Figure S127. ^{13}C NMR spectrum of polymer **17** in HFIP solvent and $CDCl_3$ (Table S1 entry 17).

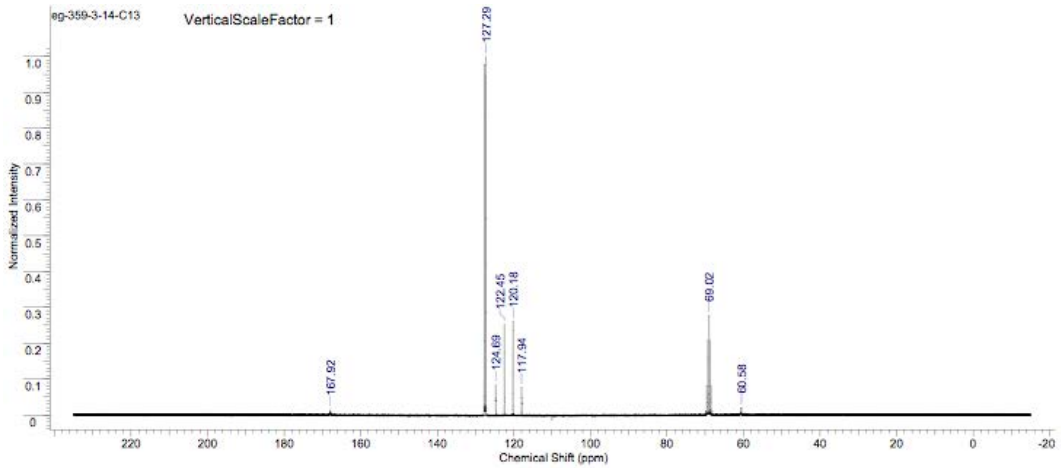


Figure S128. ^{13}C NMR spectrum of polymer **18** in HFIP solvent and C_6D_6 (Table S1 entry 18).

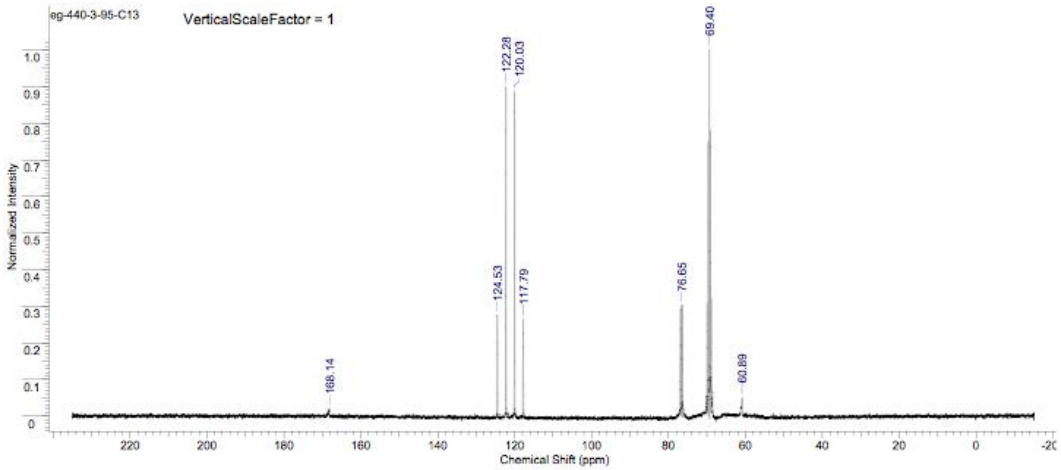


Figure S129. ^{13}C NMR spectrum of polymer **19** in HFIP solvent and $CDCl_3$ (Table S1 entry 19).

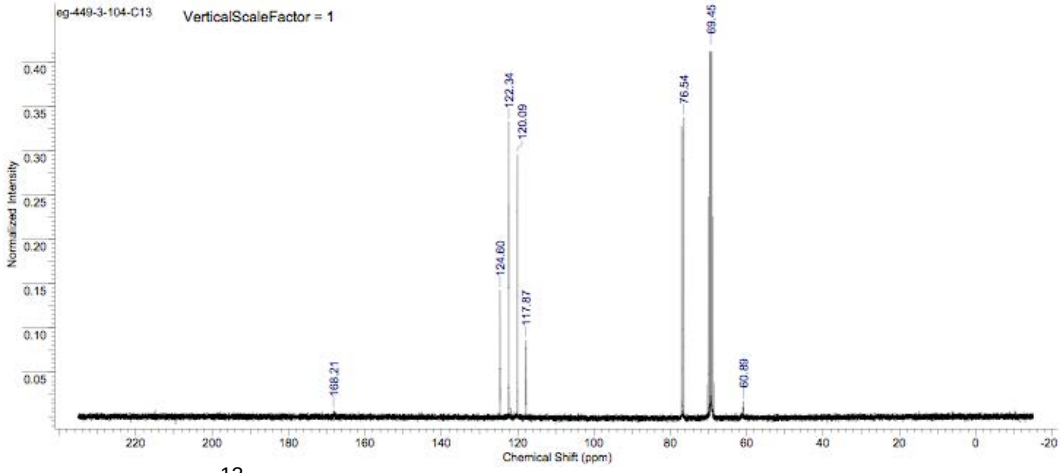


Figure S130. ^{13}C NMR spectrum of polymer **21** in HFIP solvent and $CDCl_3$ (Table S2 entry 21).

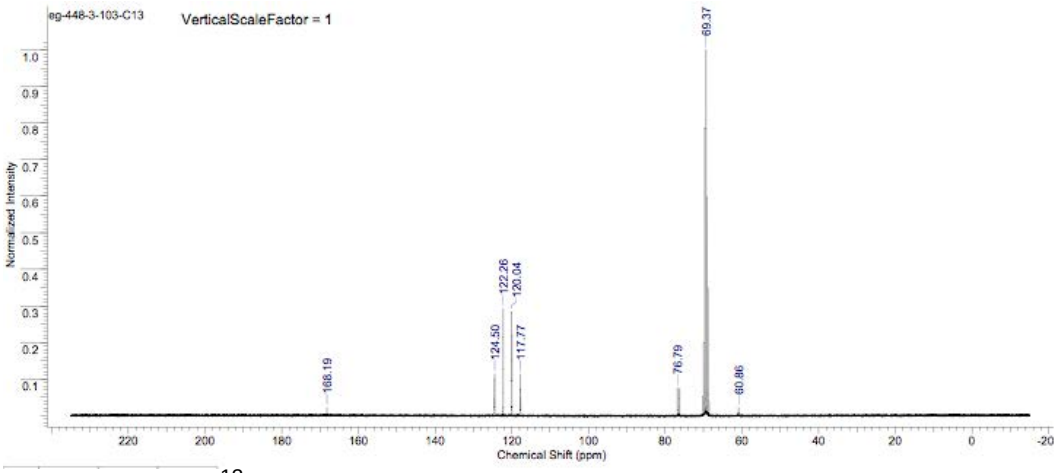


Figure S131. ^{13}C NMR spectrum of polymer **22** in HFIP solvent and $CDCl_3$ (Table S2 entry 22).

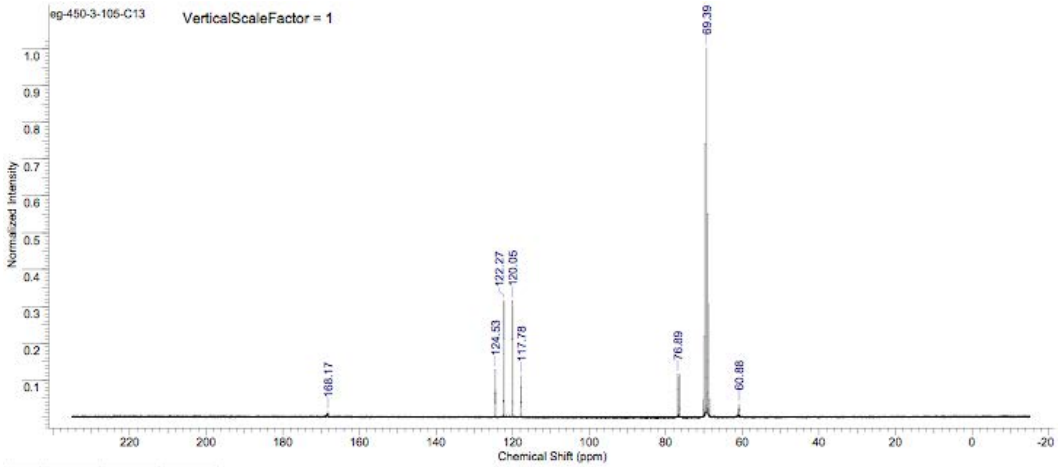


Figure S132. ^{13}C NMR spectrum of polymer **23** in HFIP solvent and $CDCl_3$ (Table S2 entry 23).

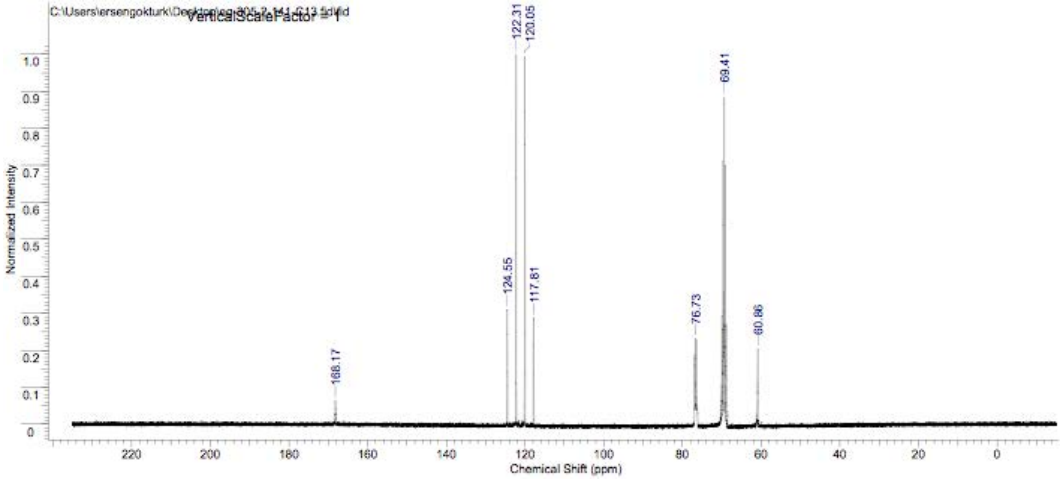


Figure S133. ^{13}C NMR spectrum of polymer **24** in HFIP solvent and $CDCl_3$ (Table S2 entry 24).

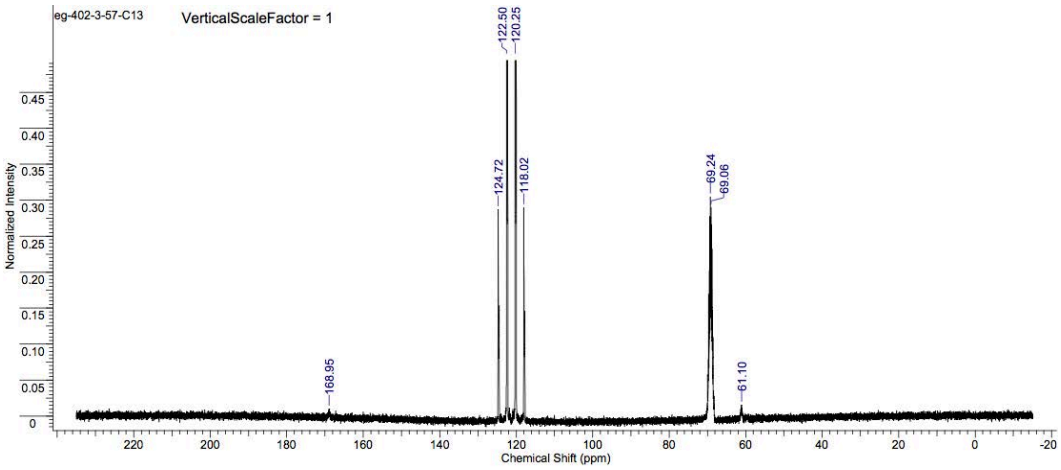


Figure S134. ^{13}C NMR spectrum of polymer **25** in HFIP-d_2 (Table S3 entry 25).

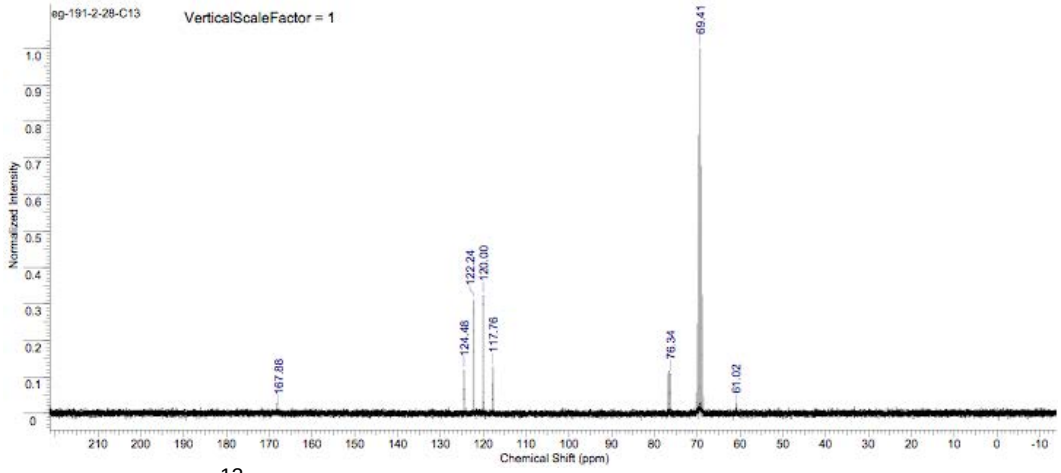


Figure S135. ^{13}C NMR spectrum of polymer **26** in HFIP solvent and $CDCl_3$ (Table S3 entry 26).

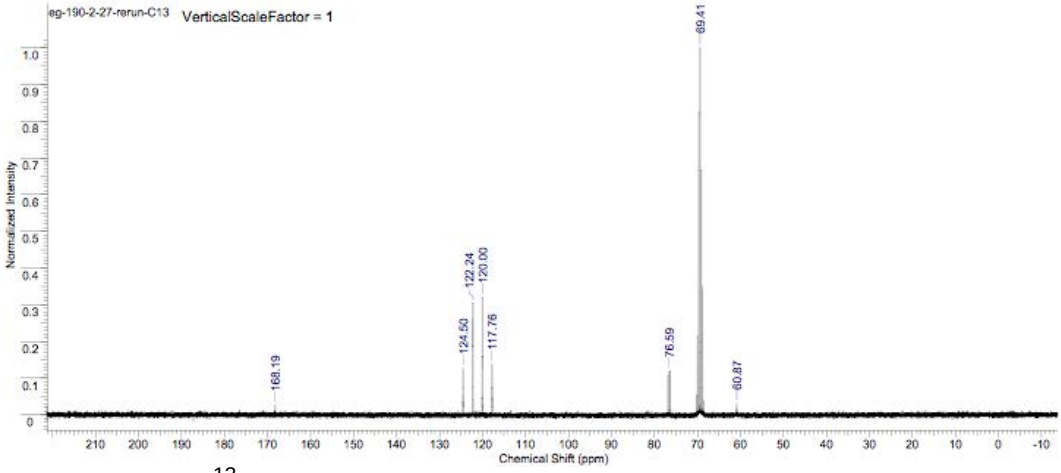


Figure S136. ^{13}C NMR spectrum of polymer **27** in HFIP solvent and $CDCl_3$ (Scheme S1 entry 27).

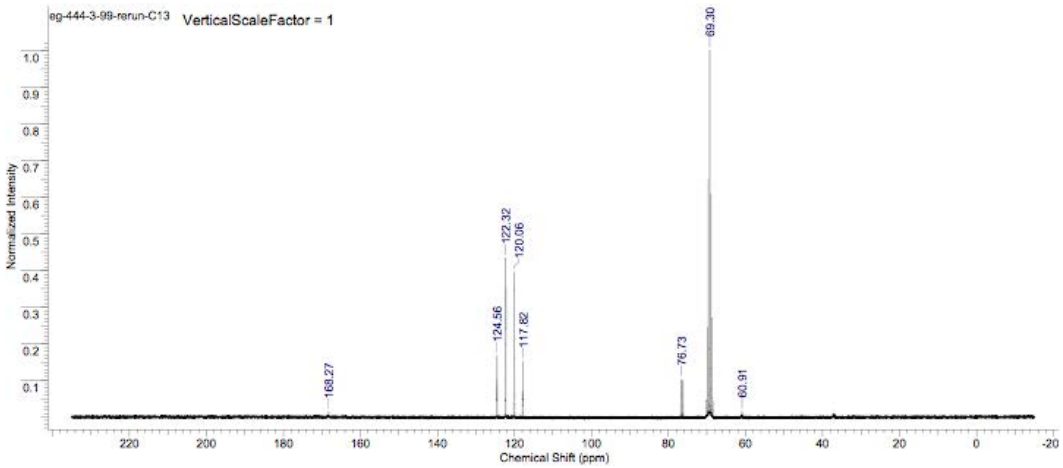
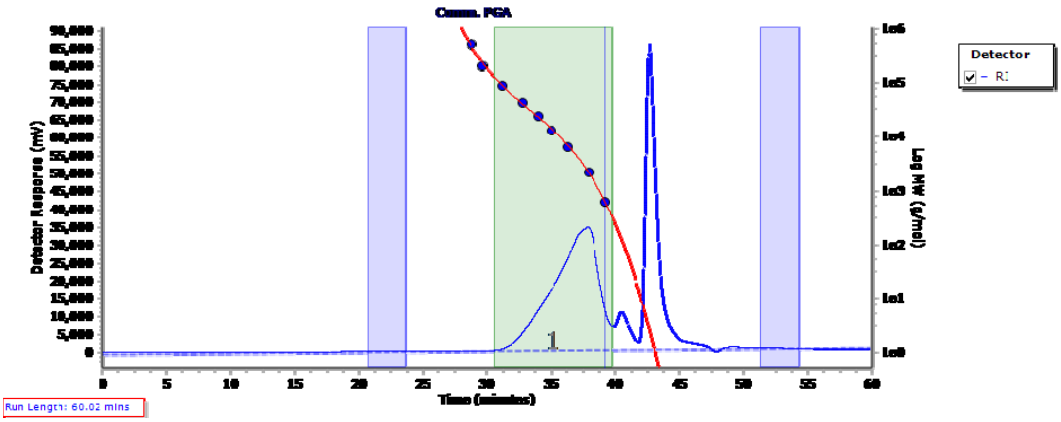


Figure S137. ^{13}C NMR spectrum of polymer **28** in HFIP solvent and $CDCl_3$ (Scheme S2 entry 28).

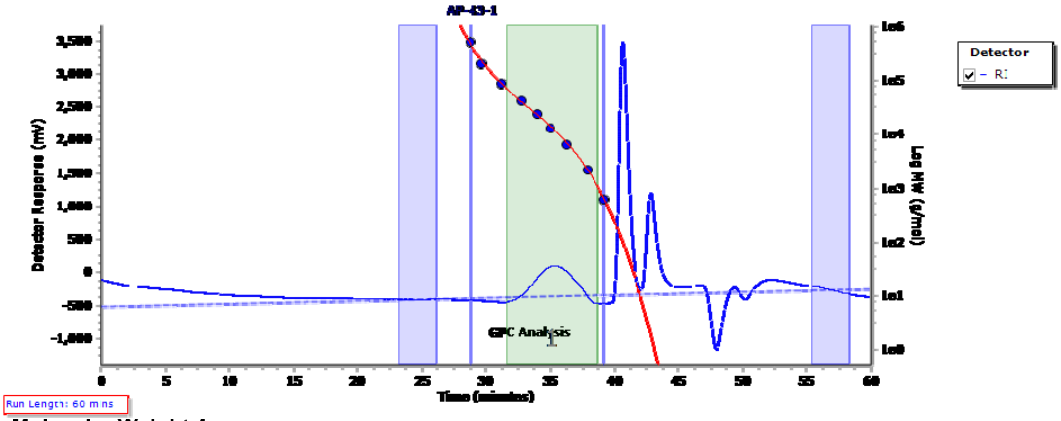
Gel Permeation Chromatography (GPC) Data



Molecular Weight Averages

Peak	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
Peak 1	2197	2500	8612	21601	36540	19575	3.445

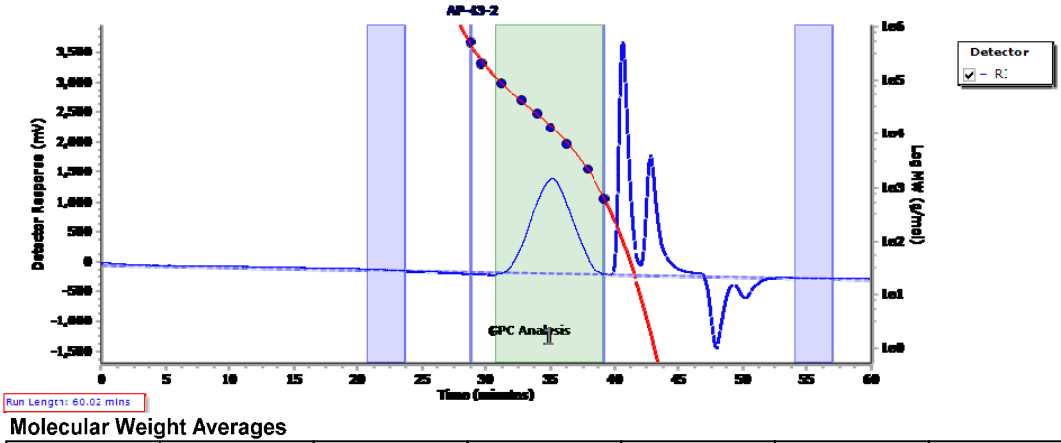
Figure S138. GPC Chromatogram of commercial polyglycolic acid in HFIP solvent.



Molecular Weight Averages

Peak	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
Peak 1	11734	9224	13049	17177	20883	16603	1.415

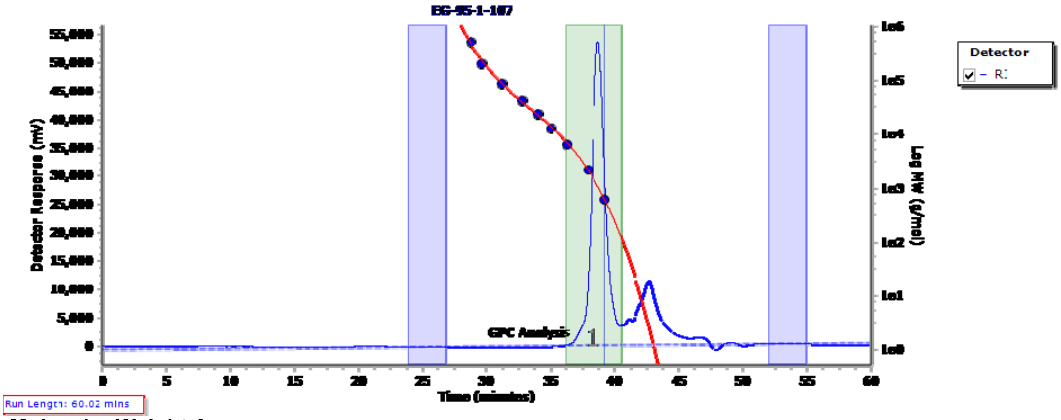
Figure S139. GPC Chromatogram of polymer **1** in HFIP solvent (Table S1 entry 1).



Molecular Weight Averages

Peak	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
Peak 1	12683	8706	15275	22682	29921	21621	1.755

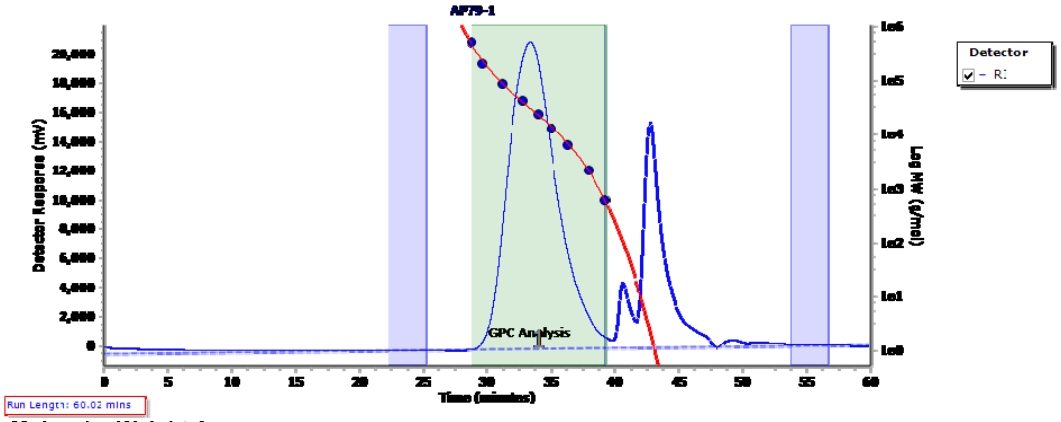
Figure S140. GPC Chromatogram of polymer **2** in HFIP solvent (Table S1 entry 2).



Molecular Weight Averages

Peak	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
Peak 1	1011	723	1070	1477	2052	1407	1.48

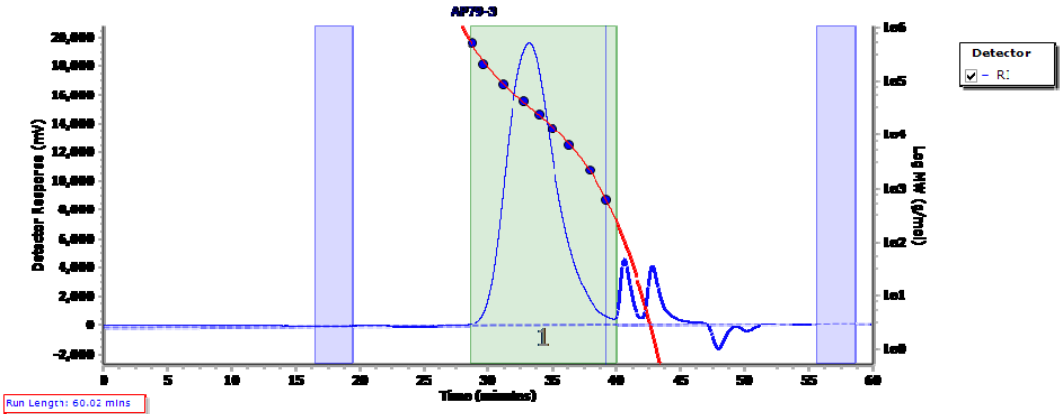
Figure S141. GPC Chromatogram of polymer **4** in HFIP solvent (Table S1 entry 4).



Molecular Weight Averages

Peak	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
Peak 1	29519	13465	34179	59021	90968	55031	2.538

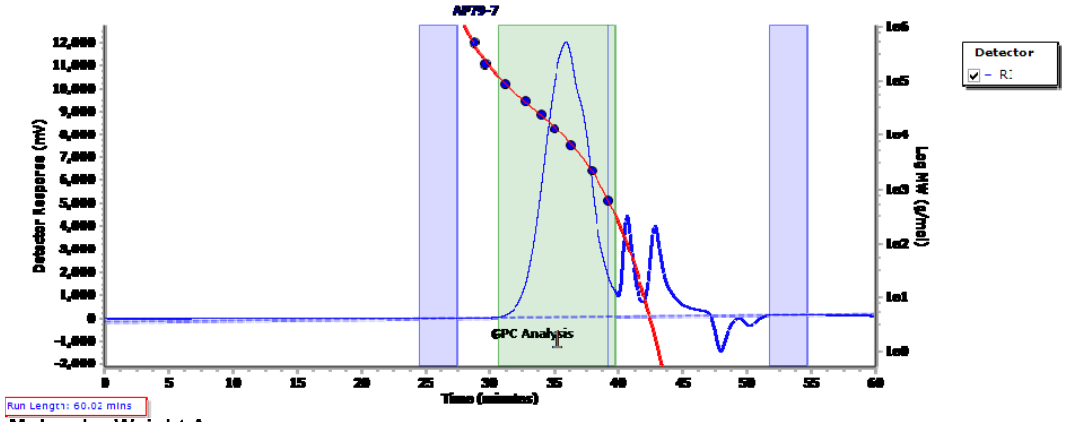
Figure S142. GPC Chromatogram of polymer **5** in HFIP solvent (Table S1 entry 5).



Molecular Weight Averages

Peak	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
Peak 1	31741	12427	37924	70586	123573	64765	3.052

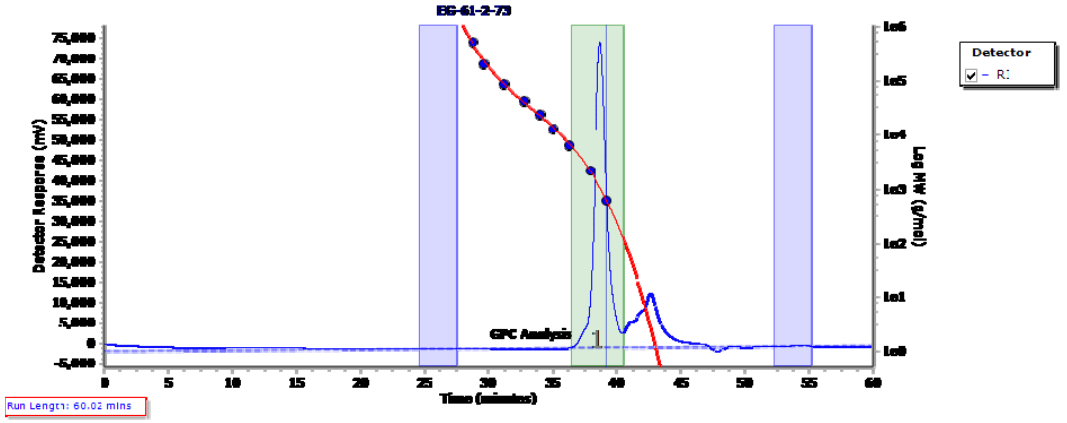
Figure S143. GPC Chromatogram of polymer **6** in HFIP solvent (Table S1 entry 6).



Molecular Weight Averages

Peak	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
Peak 1	8298	4076	10743	19367	30059	18023	2.636

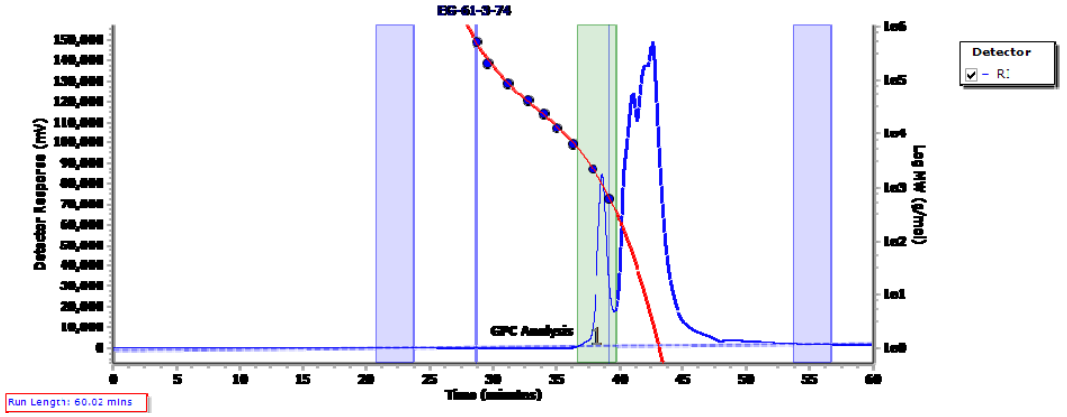
Figure S144. GPC Chromatogram of polymer **7** in HFIP solvent (Table S1 entry 7).



Molecular Weight Averages

Peak	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
Peak 1	991	736	1049	1403	1882	1343	1.425

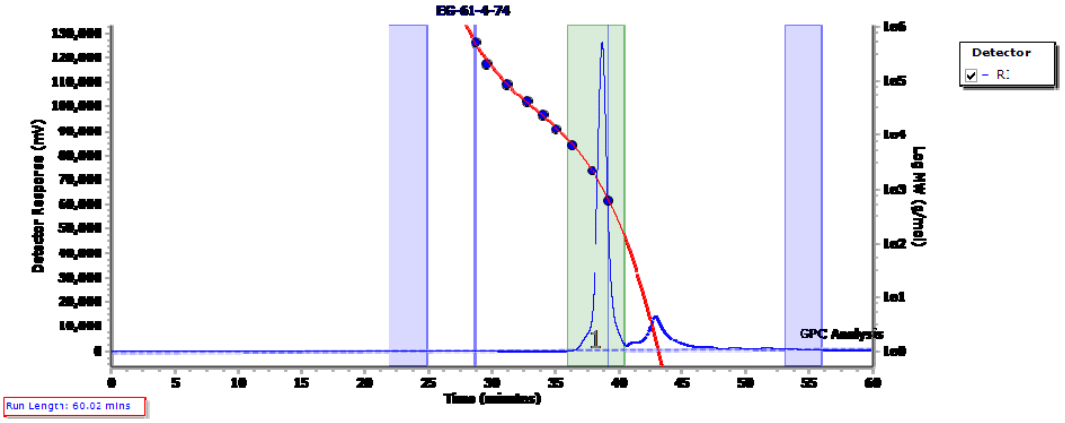
Figure S145. GPC Chromatogram of polymer **8** in HFIP solvent (Table S1 entry 8).



Molecular Weight Averages

Peak	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
Peak 1	1073	898	1102	1343	1663	1303	1.227

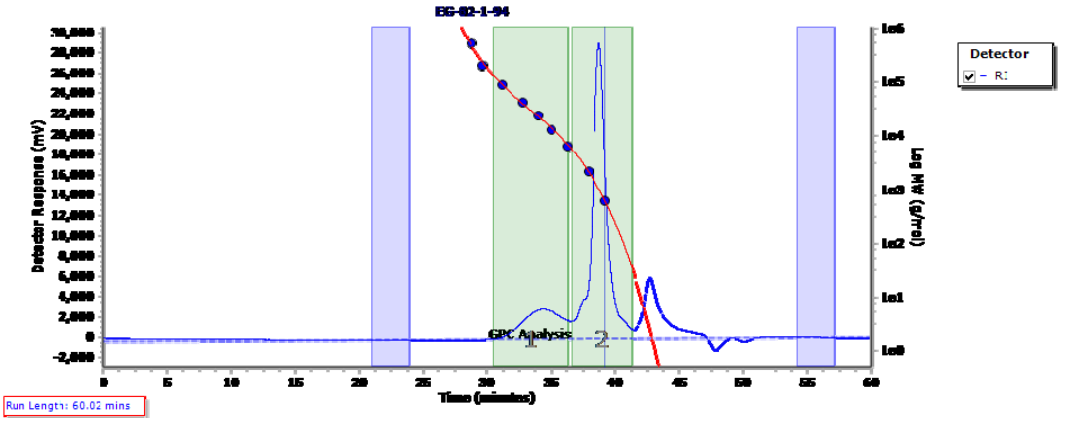
Figure S146. GPC Chromatogram of polymer **9** in HFIP solvent (Table S1 entry 9).



Molecular Weight Averages

Peak	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
Peak 1	991	825	1089	1413	1889	1355	1.32

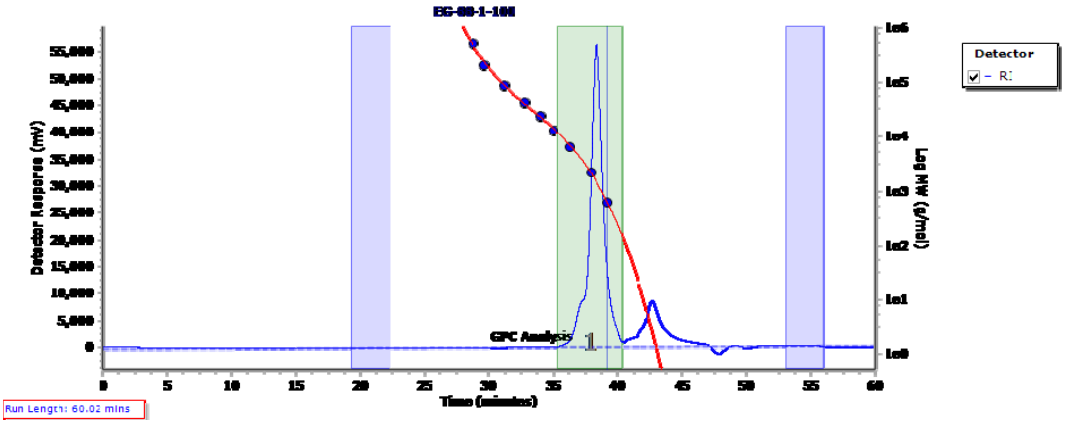
Figure S147. GPC Chromatogram of polymer **10** in HFIP solvent (Table S1 entry 10).



Molecular Weight Averages

Peak	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
Peak 1	18506	16476	23209	32680	43694	31155	1.409
Peak 2	964	546	1111	1750	2557	1643	2.035

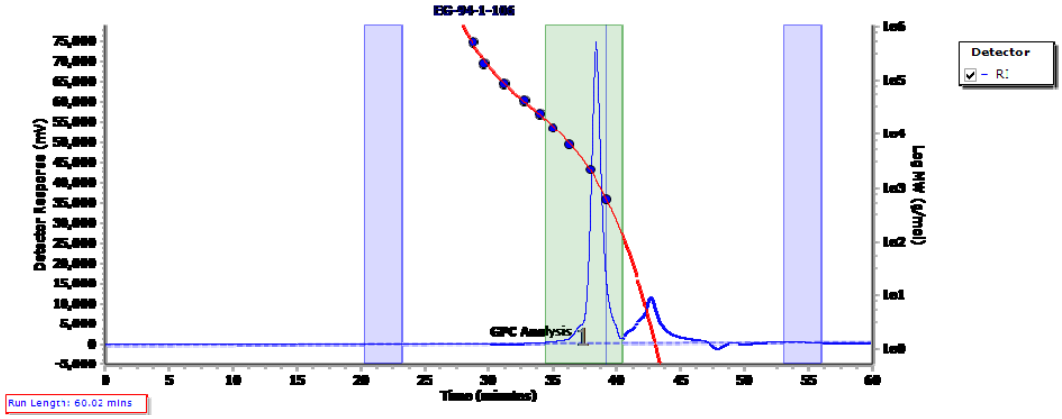
Figure S148. GPC Chromatogram of polymer **11** in HFIP solvent (Table S1 entry 11).



Molecular Weight Averages

Peak	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
Peak 1	1403	1097	1640	2413	3535	2274	1.495

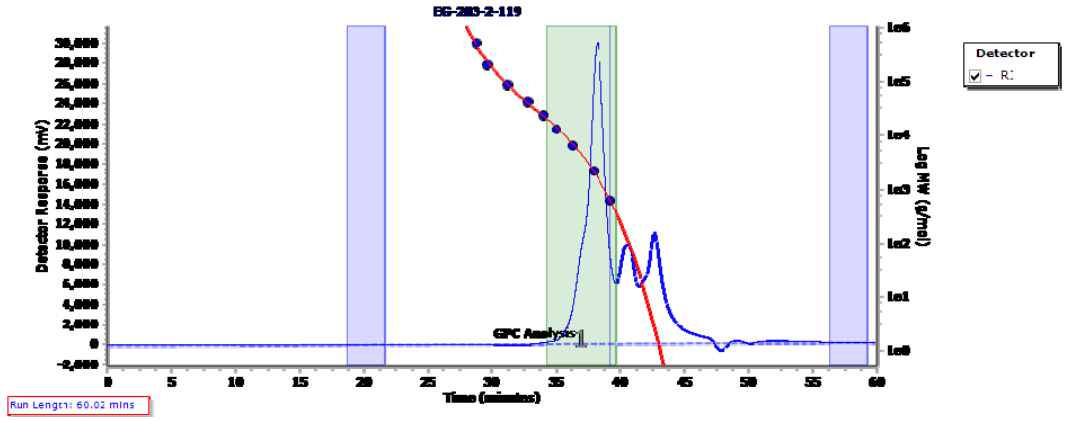
Figure S149. GPC Chromatogram of polymer **12** in HFIP solvent (Table S1 entry 12).



Molecular Weight Averages

Peak	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
Peak 1	1343	1038	1534	2666	5938	2382	1.478

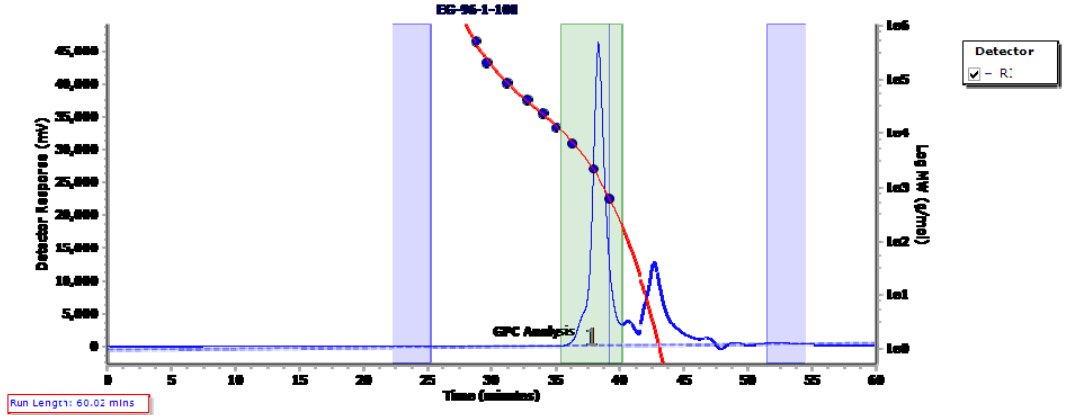
Figure S150. GPC Chromatogram of polymer **13** in HFIP solvent (Table S1 entry 13).



Molecular Weight Averages

Peak	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
Peak 1	1606	1366	2314	3981	6523	3676	1.694

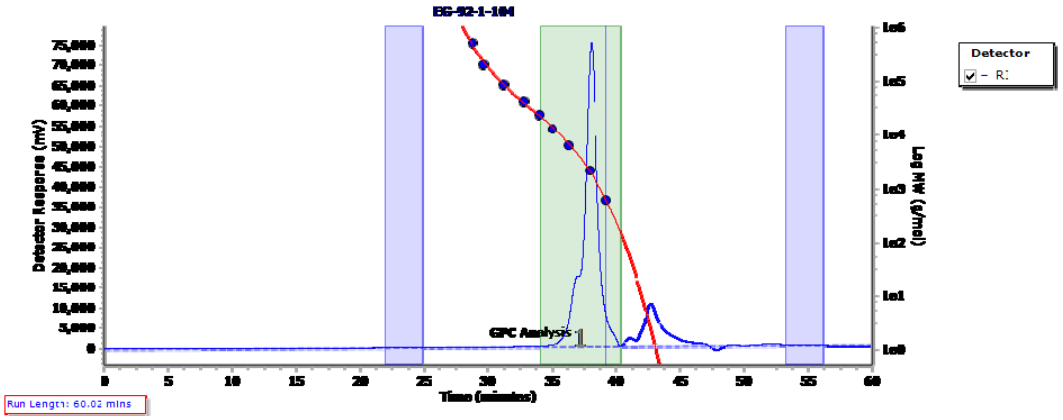
Figure S151. GPC Chromatogram of polymer **14** in HFIP solvent (Table S1 entry 14).



Molecular Weight Averages

Peak	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
Peak 1	1425	1036	1531	2128	2929	2027	1.478

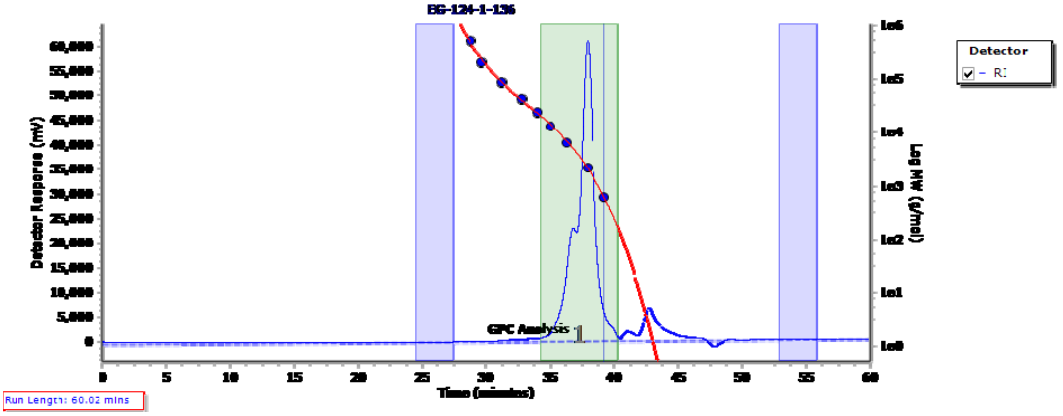
Figure S152. GPC Chromatogram of polymer **15** in HFIP solvent (Table S1 entry 15).



Molecular Weight Averages

Peak	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
Peak 1	1835	1579	2405	3747	6101	3487	1.523

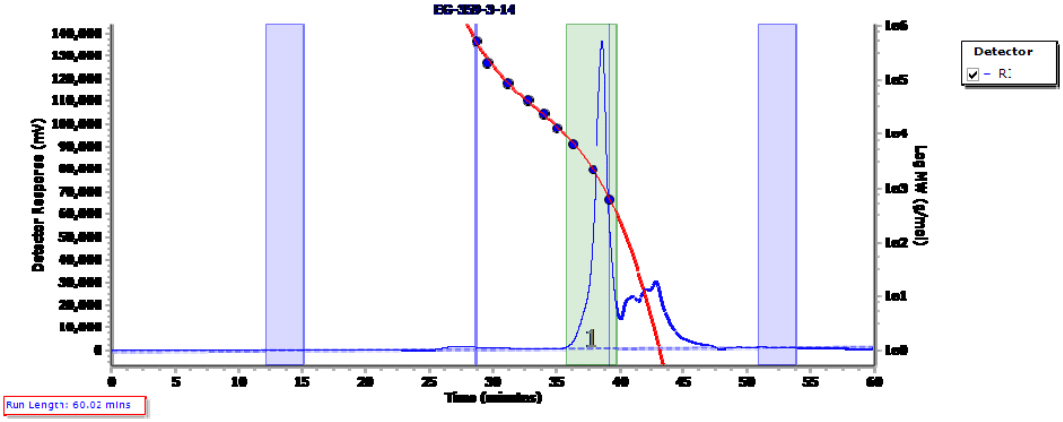
Figure S153. GPC Chromatogram of polymer **16** in HFIP solvent (Table S1 entry 16).



Molecular Weight Averages

Peak	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
Peak 1	2059	1823	3151	5114	7683	4779	1.728

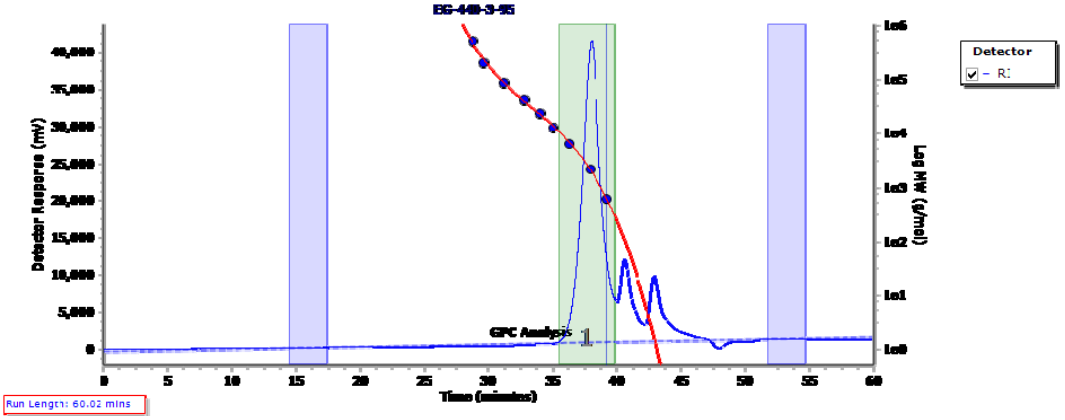
Figure S154. GPC Chromatogram of polymer **17** in HFIP solvent (Table S1 entry 17).



Molecular Weight Averages

Peak	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
Peak 1	1094	1041	1490	2234	3305	2099	1.431

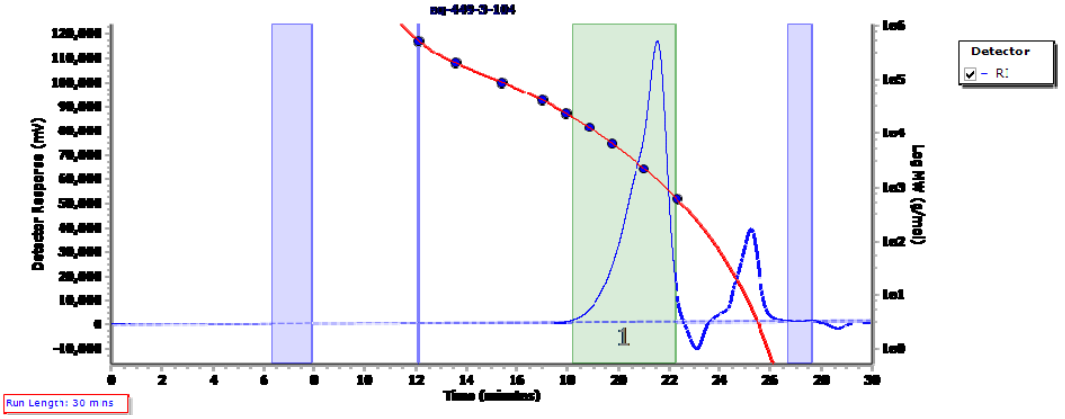
Figure S155. GPC Chromatogram of polymer **18** in HFIP solvent (Table S1 entry 18).



Molecular Weight Averages

Peak	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
Peak 1	1895	1363	2161	3058	4015	2923	1.585

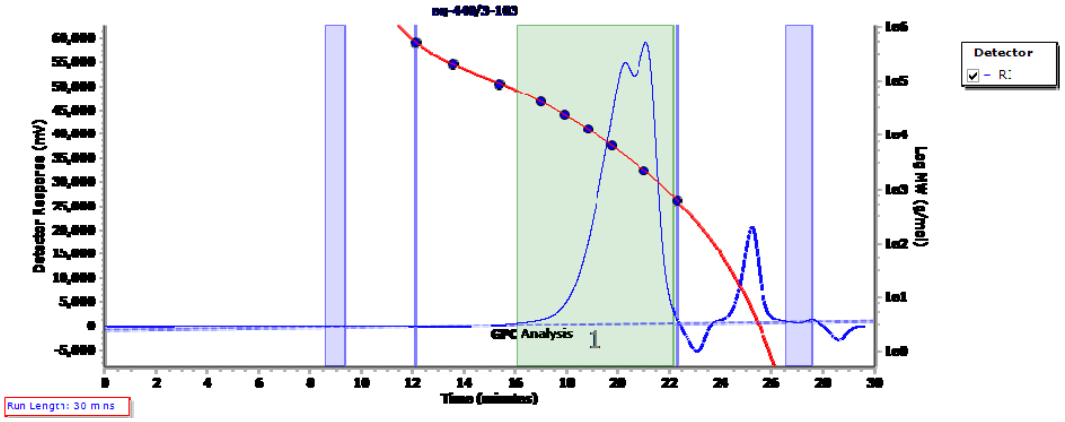
Figure S156. GPC Chromatogram of polymer **19** in HFIP solvent (Table S1 entry 19).



Molecular Weight Averages

Peak	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
Peak 1	1321	1737	2717	4756	7659	4382	1.564

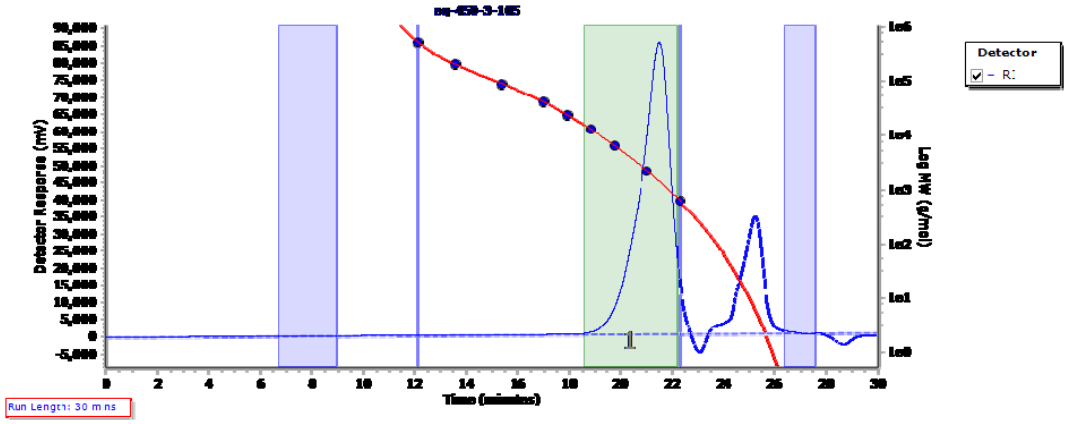
Figure S157. GPC Chromatogram of polymer **21** in HFIP solvent (Table S2 entry 21).



Molecular Weight Averages

Peak	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
Peak 1	2028	3075	5613	11552	22251	10361	1.825

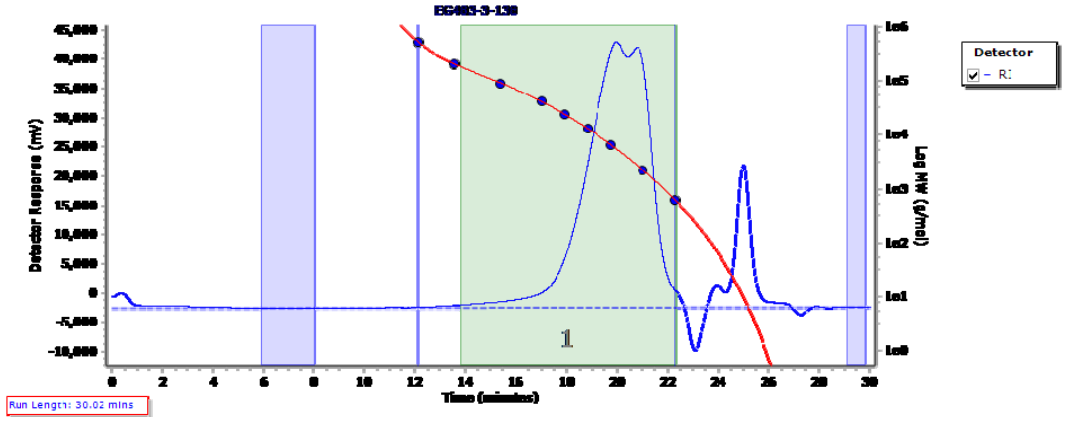
Figure S158. GPC Chromatogram of polymer **22** in HFIP solvent (Table S2 entry 22).



Molecular Weight Averages

Peak	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
Peak 1	1369	1565	2141	3207	4868	3006	1.368

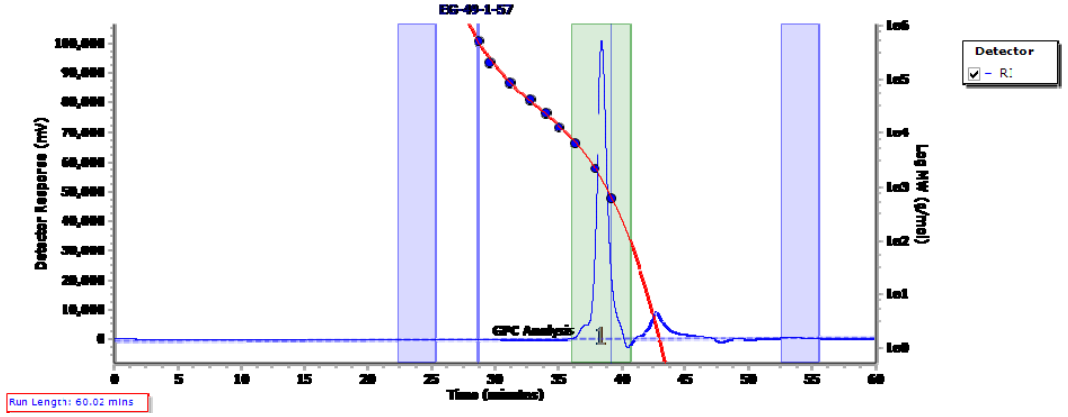
Figure S159. GPC Chromatogram of polymer **23** in HFIP solvent (Table S2 entry 23).



Molecular Weight Averages

Peak	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
Peak 1	5288	3655	8989	32274	82157	26725	2.459

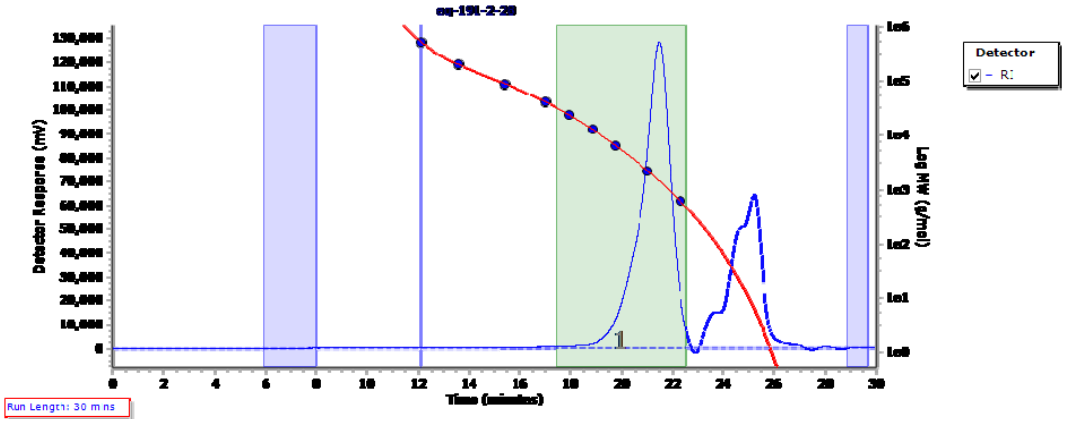
Figure S160. GPC Chromatogram of polymer **24** in HFIP solvent (Table S2 entry 24).



Molecular Weight Averages

Peak	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
Peak 1	1294	1080	1399	1814	2456	1739	1.295

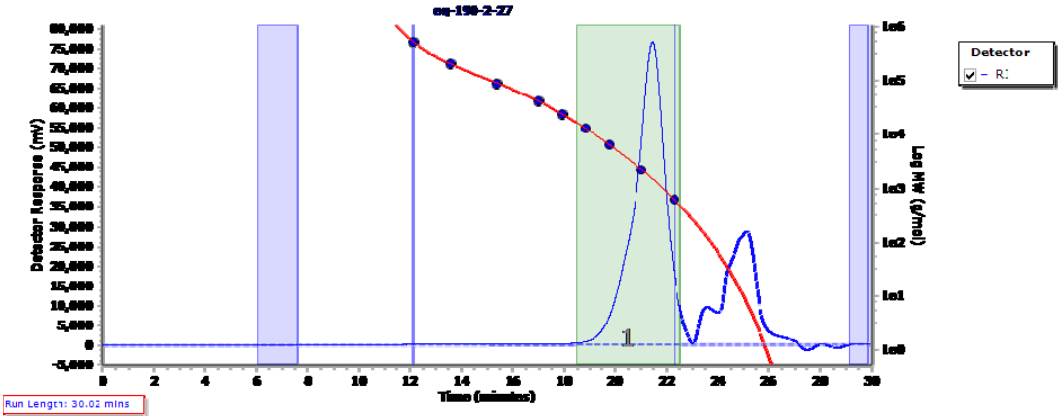
Figure S161. GPC Chromatogram of polymer **25** in HFIP solvent (Table S3 entry 25).



Molecular Weight Averages

Peak	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
Peak 1	1401	1486	2208	4238	9815	3743	1.486

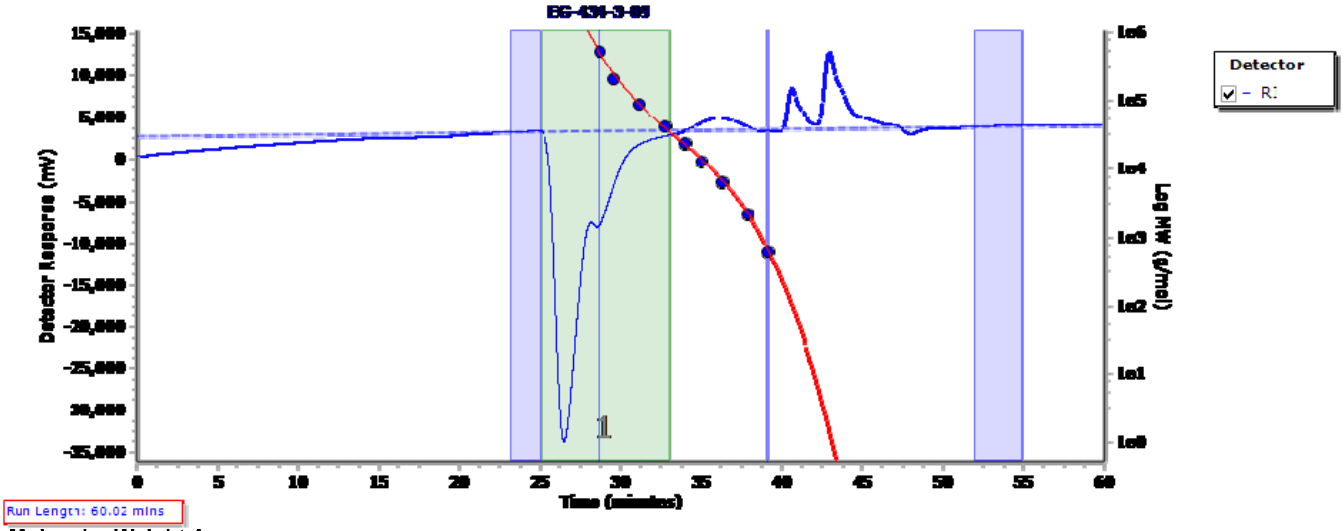
Figure S162. GPC Chromatogram of polymer **26** in HFIP solvent (Table S3 entry 26).



Molecular Weight Averages

Peak	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
Peak 1	1438	1440	2073	3253	5172	3027	1.44

Figure S163. GPC Chromatogram of polymer **27** in HFIP solvent (Scheme S1 entry 27).



Molecular Weight Averages

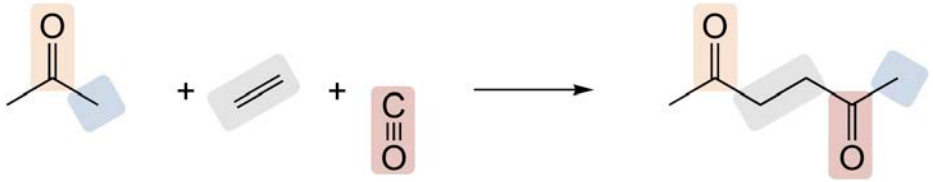
Peak	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
Peak 1	5708445	636010	4288208	9714490	14953486	8997050	6.742

Figure S164. GPC Chromatogram of polymer **28** in HFIP solvent (Scheme S2 entry 28).

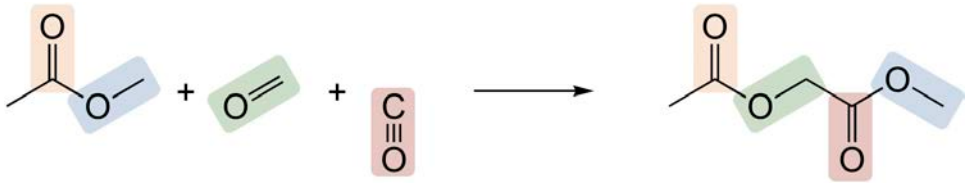
Computational Study for Copolymerization Thermodynamics

Computational studies were performed with Spartan `10 for Macintosh, version 1.1.0. ΔH values for the reactions were determined from heat of formations (HOF), determined by the **G3 (MP2) method**. Entropy (S) and ΔS values were determined by **DFT B3LYP 6-311++G****. The units for HOF, ΔH, and ΔG are kcal/mol and the units for S and ΔS are cal/molK.

Table S4. G3(MP2)/DFT thermodynamic calculations for gas phase model copolymerizations.



HOF	–16.64	35.31	–15.23	–29.09	ΔH_{rxn} = –32.53
S	67.89	52.32	47.20	87.43	ΔS_{rxn} = –79.98
					ΔG_{298} = –8.70



HOF	–60.14	–11.07	–15.23	–111.60	ΔH_{rxn} = –25.16
S	73.80	53.60	47.20	90.75	ΔS_{rxn} = –83.85
					ΔG_{298} = –0.17

Polymer Photographs

Figure S165. Photograph of commercial PGA (left) and entry **17** from Table S1 (right).

Figure S166. Photograph of mostly waxy, amorphous, oligomeric material (Table S1 entry 8) obtained according to the trioxane/CO copolymerization method described by G. Cevidalli, M. Ragazzini, and M. Modena, *U.S. Patent* 3,673,156, **1972**.