Supporting Information for:

Ethylene Polymerization and Copolymerization using Nickel 2-Iminopyridine-*N*-oxide Catalysts: Modulation of Polymer Molecular Weights and Molecular-weight Distributions

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1. Figures

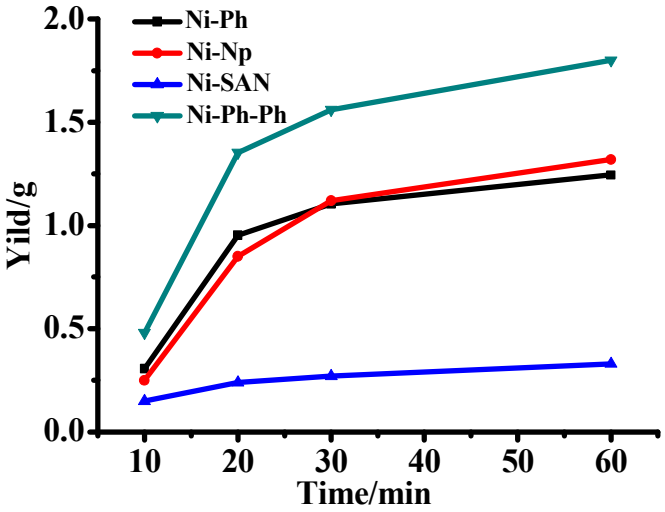


Figure S1. Yield versus time for nickel catalysts at 60 ^{o}C.

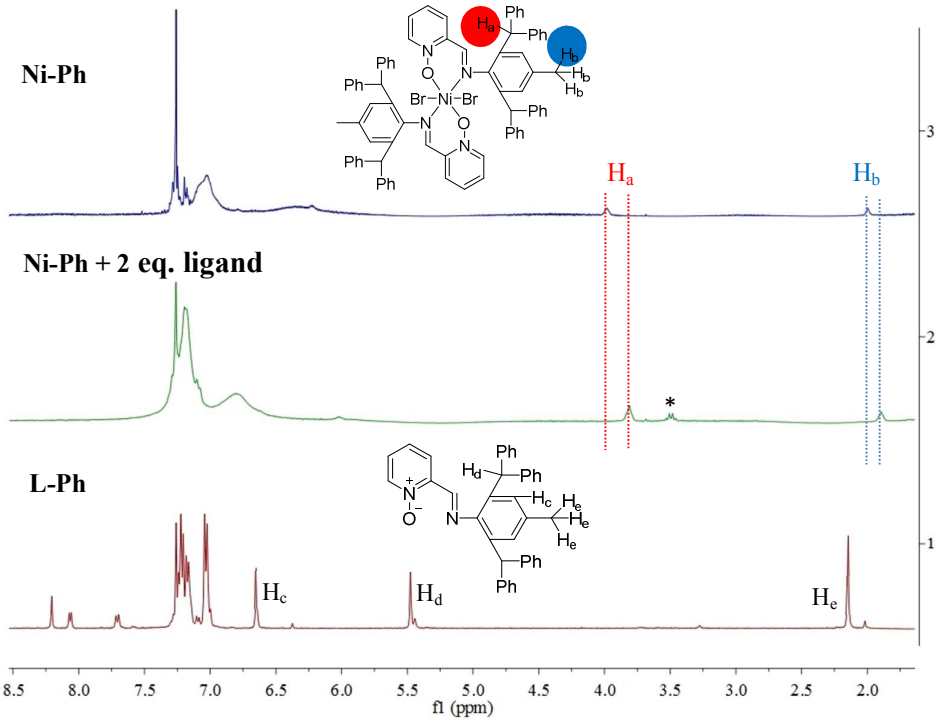


Figure S2. ^{1}H NMR spectrum of the **Ni-Ph**, **Ni-Ph** plus 2 eq. ligand, and **L-Ph** in $CDCl_3$. *Solvent impurity in $CDCl_3$.

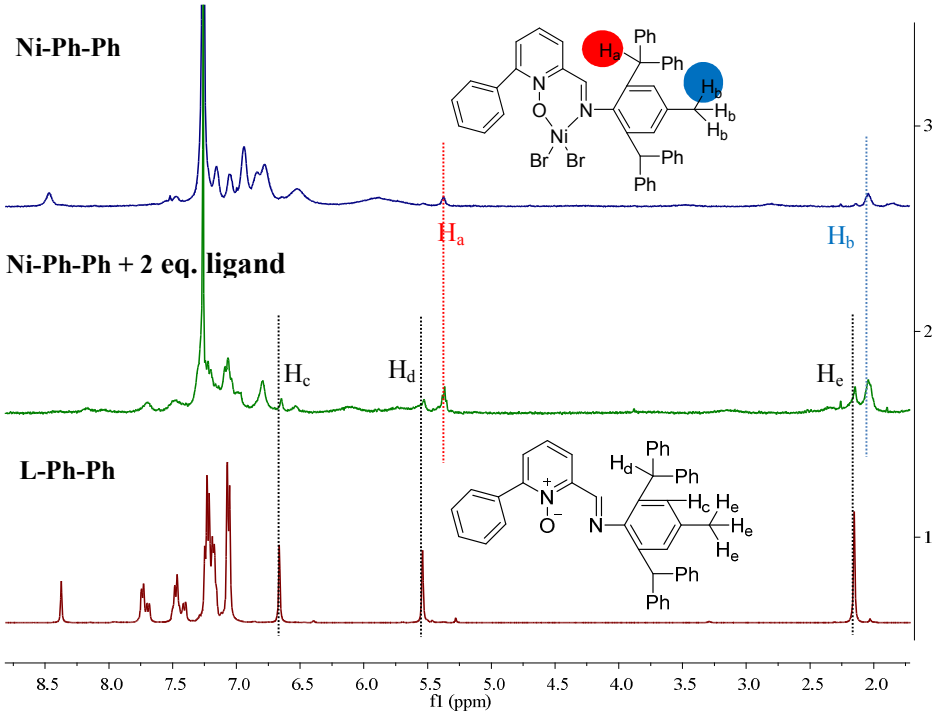


Figure S3. ^{1}H NMR spectrum of the **Ni-Ph-Ph**, **Ni-Ph-Ph** plus 2 eq. ligand, and **L-Ph-Ph** in $CDCl_3$.

2. Fractionation Data

Table S1. Fractionation data of bimodal polyethylene (Table 1, entry 2).

	Yield/mg	T_m [a]/°C	B [b]	M_w [c]	M_w/M_n [c]
entry 2	500	127.6	17	75.8	59.7
Fraction 1	165	127.9	6	221.4	2.5
Fraction 2	195	121.1	17	50.4	9.6
Fraction 3	86	89.0	25	1.5	2.2

[a]Melting temperature determined by DSC. [b]Branching numbers per 1000C were determined by ^{1}H NMR. [c]M_n: 10^4 g mol^{-1}, M_n and M_w/M_n determined by GPC.

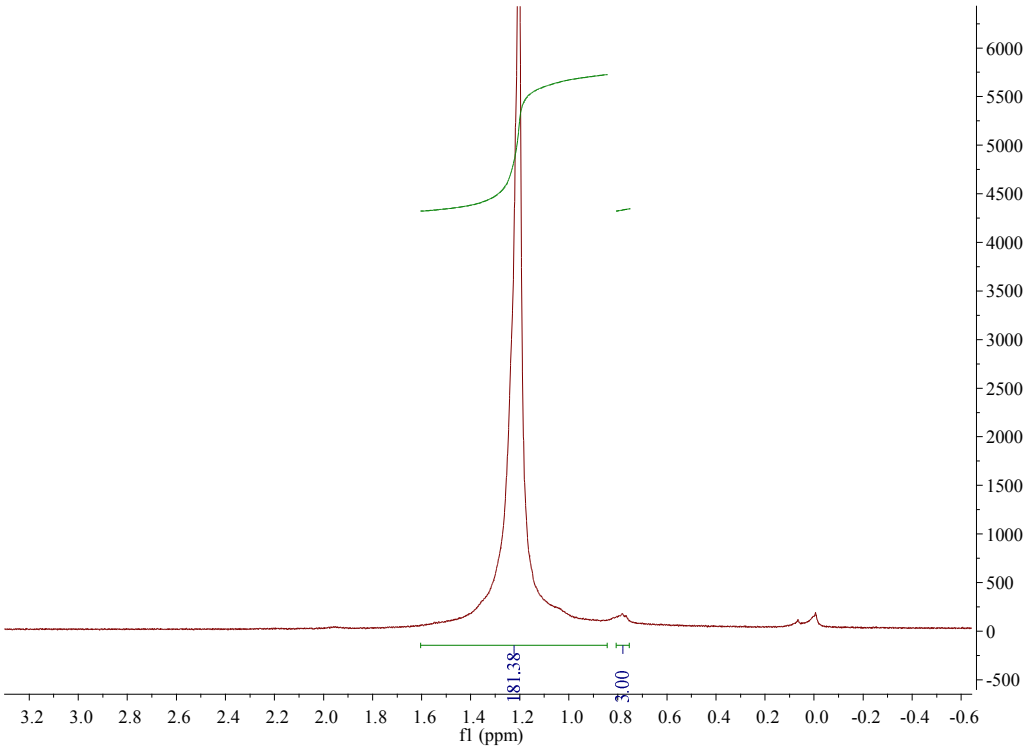


Figure S4a. ^{1}H NMR spectrum of the table S1, Fraction 1($C_2D_2Cl_4$, 120°C). *Solvent impurity in $C_2D_2Cl_4$.

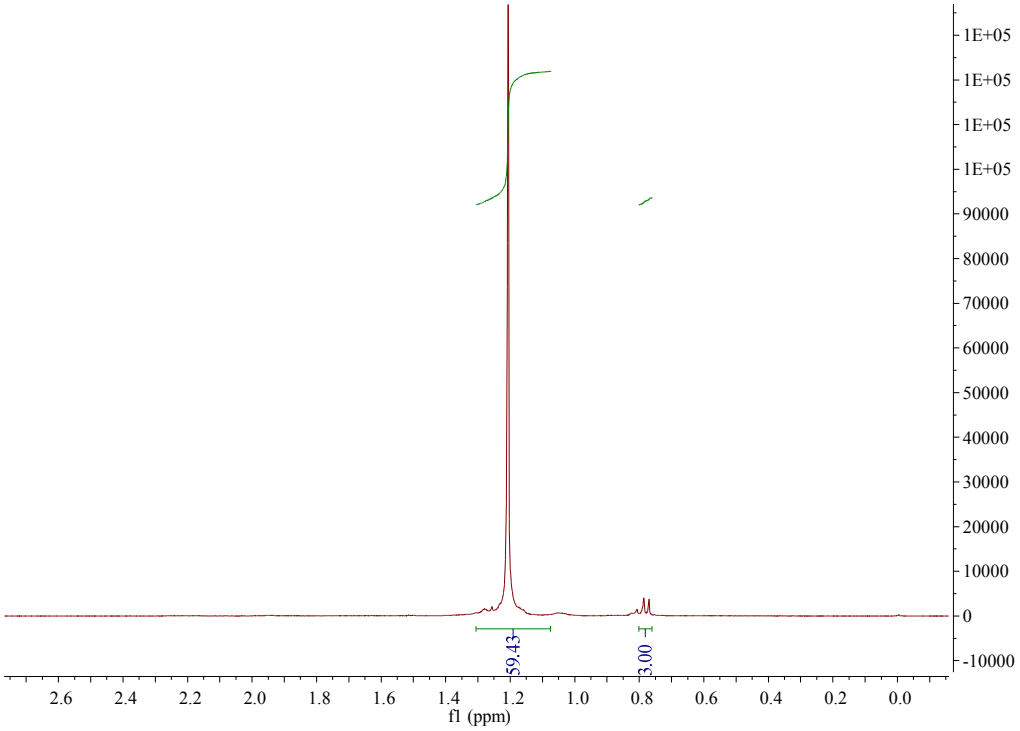


Figure S4b. ^{1}H NMR spectrum of the table S1, Fraction 2($C_2D_2Cl_4$, 120°C). *Solvent impurity in $C_2D_2Cl_4$.

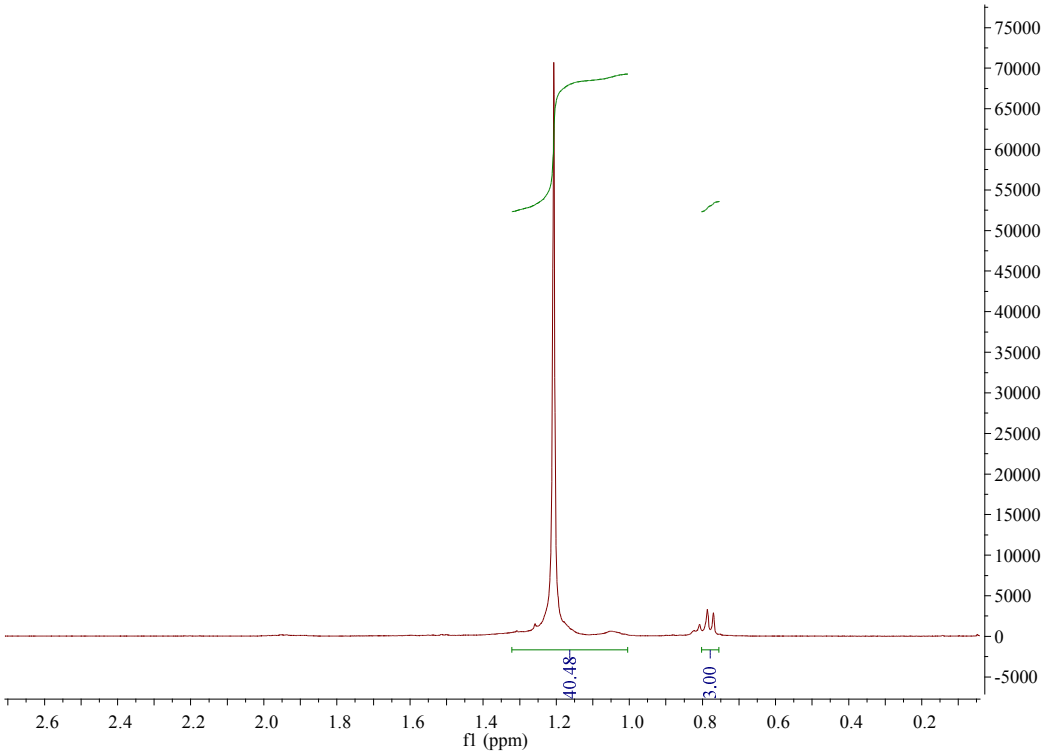


Figure S4c. ^{1}H NMR spectrum of the table S1, Fraction 3($C_2D_2Cl_4$, 120°C). *Solvent impurity in $C_2D_2Cl_4$.

Table S2. Fractionation data of bimodal ethylene/methyl 10-undecenoate copolymer(Table 2, entry 11).

	Yield/mg	$T_m{}^a$/^{o}C	Comonomer incorp.[mol%]*b*
entry 11	93	79.8/119.1	0.3
Fraction 1	15	121.7	0.1
Fraction 2	16	87.0/116.1	0.3
Fraction 3	33	73.8	0.9

^{a}Melting temperature determined by DSC. ^{b}Determined by ^{1}H NMR spectroscopy.

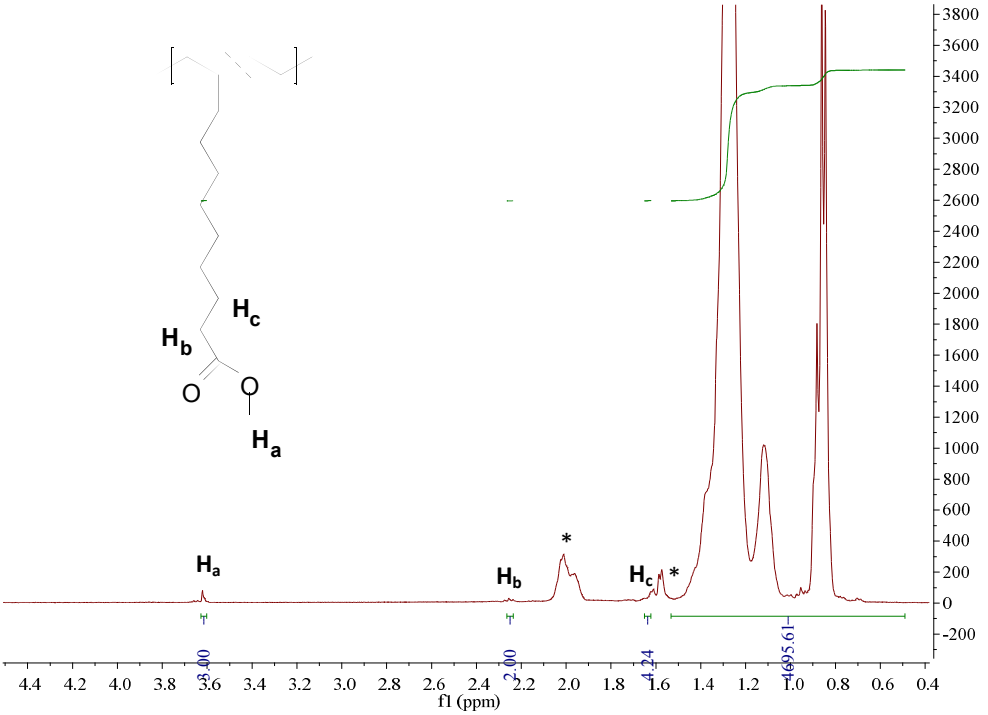


Figure S5a. ^{1}H NMR spectrum of the table S2, Fraction 1($C_2D_2Cl_4$, 120°C). *Solvent impurity in $C_2D_2Cl_4$.

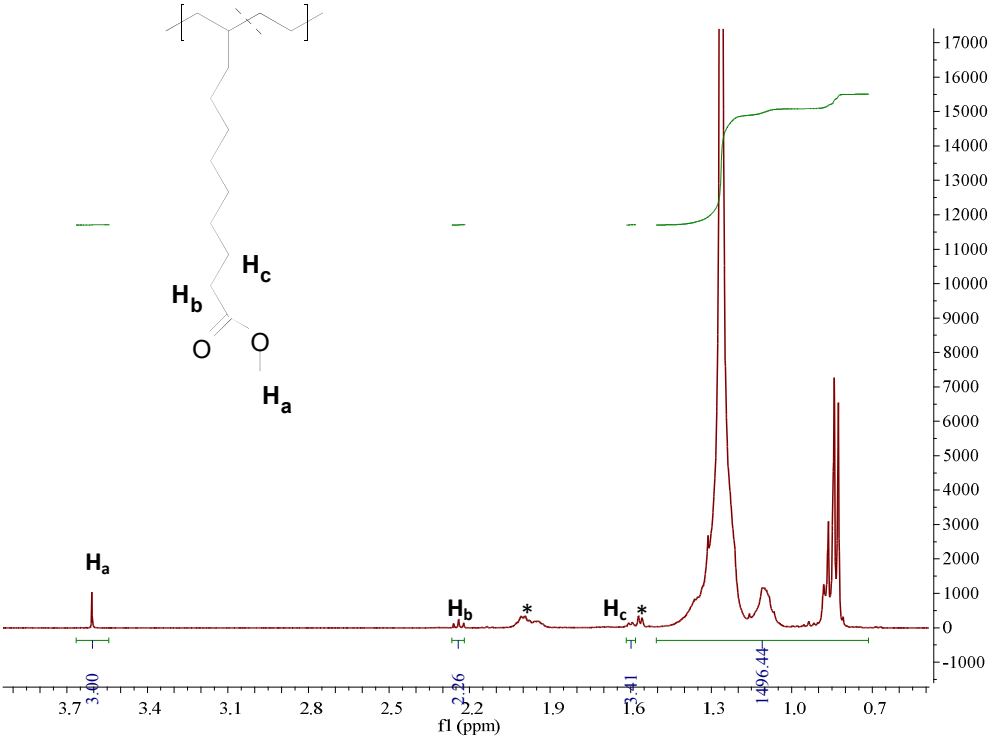


Figure S5b. ^{1}H NMR spectrum of the table S2, Fraction 2($C_2D_2Cl_4$, 120°C). *Solvent impurity in $C_2D_2Cl_4$.

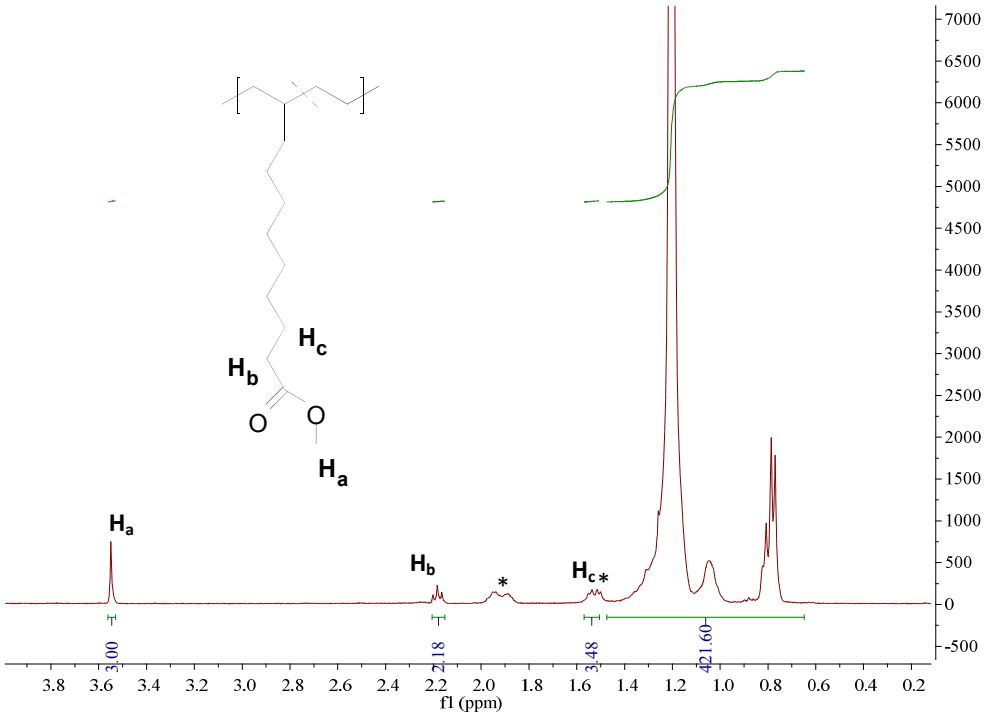
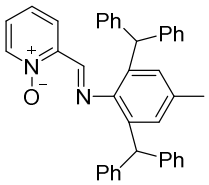


Figure S5c. ^{1}H NMR spectrum of the table S2, Fraction 3($C_2D_2Cl_4$, 120°C). *Solvent impurity in $C_2D_2Cl_4$.

3. Experimental sections

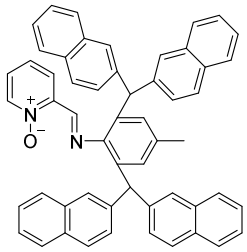
3.1 Ligand Synthesis.



Ligand L-Ph

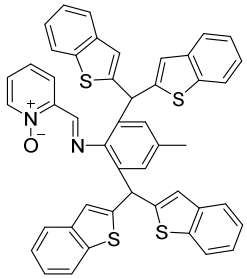
A mixture of 2-pyridinecarboxaldehyde-*N*-oxide (123 mg, 1.0 mmol), 2,6-bis(diphenylmethyl)-4-methylaniline (**NH_2-Ph**) (440 mg, 1.0 mmol) and *p*-toluenesulfonic acid (20 mg) in toluene (50 mL) was stirred at 130 °C for 24 h. The solvent was partially evaporated under reduced pressure until a gray solid formed. The remaining solution was diluted with methanol (30 mL) and the gray solid was collected by filtration, washed three times with 10 mL of methanol to afford **L-Ph** (480 mg, 62.9 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.21 (*Py*, s, 1H), 8.06 (*Py*, d, *J* = 6.4 Hz, 1H), 7.71 (*Py*, d, *J* = 8.4 Hz, 1H), 7.33 – 7.12 (m, 14H), 7.09 (*Py*, d, *J* = 6.8 Hz, 1H), 7.03 (m, 7H), 6.65 (s, 2H), 5.47 (s, 2H), 2.15 (*CH_3*, s, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ 156.35, 147.47, 145.24, 143.49, 139.63,

133.26, 132.85, 129.61, 128.98, 128.25, 127.13, 126.25, 124.66, 124.51, 51.80, 21.44.HRMS (m/z): calcd for $C_{39}H_{33}ON_2$: [M] 545.2587 found:545.2605.



Ligand L-Np

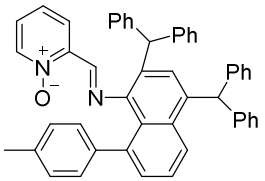
Using the same procedure as for the synthesis of **L-Ph**, except for 2,6-bis(di(naphthalen-2-yl)methyl)-4-methylaniline (**NH_2-Np**) (640 mg, 1.0 mmol), **L-Np** was obtained as a yellow powder (522 mg, 72%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.49 (*Py*, s, 1H), 7.93 (*Py*, d, *J* = 6.8 Hz, 1H), 7.79 (d, *J* = 6.8 Hz, 4H), 7.73 (d, *J* = 8.4 Hz, 4H), 7.64 (d, *J* = 6.4 Hz, 4H), 7.50 (d, *J* = 10.4 Hz, 2H), 7.47 – 7.36 (m, 12H), 7.14 (t, *J* = 9.2 Hz, 1H), 6.98 (t, *J* = 8.8 Hz, 1H), 6.79 (s, 2H), 5.83 (s, 2H), 2.13 (*CH_3*, s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.00, 146.72, 144.12, 139.78, 139.11, 138.39, 132.59, 132.46, 132.37, 131.55, 131.36, 131.17, 128.51, 128.42, 127.97, 127.26, 127.12, 126.84, 126.81, 126.51, 125.95, 124.96, 124.81, 124.70, 124.50, 123.43, 123.39, 51.64, 51.14, 20.35, 19.95. HRMS (m/z): calcd for $C_{55}H_{41}ON_2$: [M] 745.3213, found: 745.3225.



Ligand L-Bz

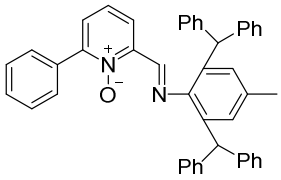
Using the same procedure as for the synthesis of **L-Ph**, except for 2,6-bis(bis(benzothiophen-2-yl)methyl)-4-methylaniline **(NH_2-Bz)** (566 mg, 1.0 mmol),**L-Bz** was obtained as a yellow powder (431 mg, 56%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (*Py*, s, 1H), 7.82 (*Py*, d, *J* = 8.0 Hz, 1H),7.72 (d, *J* = 8.0 Hz, 4H),7.70 (*Py*, d, *J* = 6.8 Hz, 1H),7.66 (*Py*, d, *J* = 7.2 Hz, 1H), 7.53 (d, *J* = 8.0 Hz, 1H), 7.45 (d, *J* = 7.2 Hz,1H), 7.38 – 7.28 (m, 6H),7.27(s, 1H),7.22(s, 1H),7.16(m, 3H) 7.02 (d, *J* = 4.0 Hz,2H), 6.95 (s, 1H), 6.75 (m, 2H), 6.55 (s, 1H), 6.36 (t, *J* = 7.8 Hz, 1H), 6.01 (s, 1H), 2.26 (*CH_3*, s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) ^{13}C NMR (101 MHz, $CDCl_3$) δ 150.88, 150.06, 145.42, 144.41, 144.32, 143.81, 138.96, 138.88, 138.76, 138.72, 138.68, 138.50, 138.44, 137.96, 137.61, 133.55, 128.75, 128.30, 125.73, 123.79, 123.68, 123.57, 123.53, 123.46, 123.42, 123.35, 123.15, 123.11,

122.84, 122.81, 122.75, 122.63, 122.60, 122.56, 122.55, 121.68, 121.36, 121.26, 121.11, 120.66, 68.40, 59.88, 43.91, 20.18. HRMS (m/z): calcd for $C_{47}H_{33}ON_2S_4$: [M] 769.1470, found: 769.1462.



Ligand L-An

Using the same procedure as for the synthesis of **L-Ph**, except for 2,4-dibenzhydryl-8-(p-tolyl)naphthalen-1-amine (**NH_2-An**) (566 mg, 1.0 mmol) **L-An** was obtained as a yellow powder (576 mg, 86%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (t, *J* = 8.0 Hz, 2H), 7.95 (s, 1H), 7.53 (*Py*, d, *J* = 8.1 Hz, 1H), 7.38 (*Py*, t, *J* = 8.8 Hz,1H), 7.13-7.25 (m, 8H), 7.11 – 6.98 (m, 13H), 6.89 (d, *J* = 8.0 Hz, 2H), 6.87 – 6.79 (m, 4H), 6.67 (s, 1H), 6.22 (s, 1H), 5.67 (s, 1H), 1.98 (*CH_3*, s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.11, 145.19, 143.86, 142.71, 142.44, 141.30, 138.27, 138.19, 135.30, 134.36, 131.61, 129.51, 129.25, 129.18, 128.47, 128.19, 127.77, 127.41, 127.29, 126.99, 125.45, 125.23, 124.93, 124.13, 123.55, 122.89, 122.72, 52.35, 50.58, 19.79. HRMS (m/z): calcd for $C_{49}H_{39}ON_2$ [M]: 671.3057, found: 671.3055.

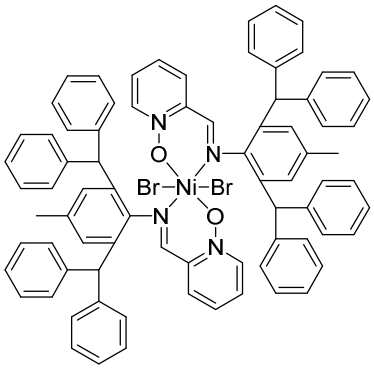


Ligand L-Ph-Ph

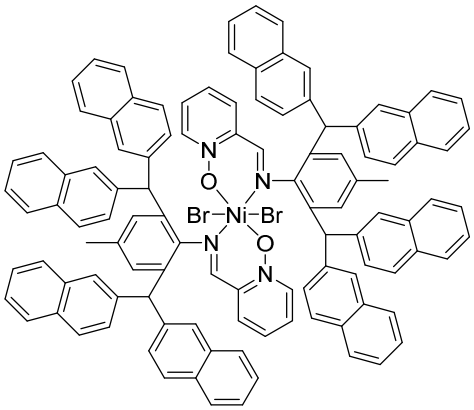
A mixture of 2-carbaldehyde-6-phenylpyridine *N*-Oxide (199 mg, 1.0 mmol), 2,6-bis(diphenylmethyl)-4-methylaniline (**NH_2-Ph**) (440 mg, 1.0mmol) and p-toluenesulfonic acid (20 mg) in toluene (50 mL) was stirred at 130 °C for 24 h. The solvent was partially evaporated under reduced pressure until the formation of a gray solid, and the remaining solution was diluted in methanol (30 mL). The gray solid was isolated by filtration, washed three times by 10 mL methanol to afford ligand **L-Ph-Ph** (550 mg, 90 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.36 (*Py*, s, 1H), 7.72 (*Py*, d, *J* = 7.2 Hz, 2H), 7.68 (*Py*, d, *J* = 8.0 Hz, 1H), 7.46 (m, 3H), 7.41 (d, *J* = 7.6 Hz, 1H), 7.13- 7.25(m, 13H), 7.04 (d, *J* = 7.2 Hz, 2H), 6.65 (s, 2H), 5.52 (s, 2H), 2.15 (*CH_3*, s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.42, 149.42, 147.87, 145.84, 143.41, 133.04, 132.82, 132.56, 129.67, 129.59, 129.29, 128.89, 128.52, 128.33, 128.22, 126.22, 124.07, 123.40, 51.74, 21.44. HRMS (m/z): calcd for $C_{49}H_{39}ON_2$ [M]: 621.2900, found: 621.2885.

3.2 Syntheses of the Complexes.

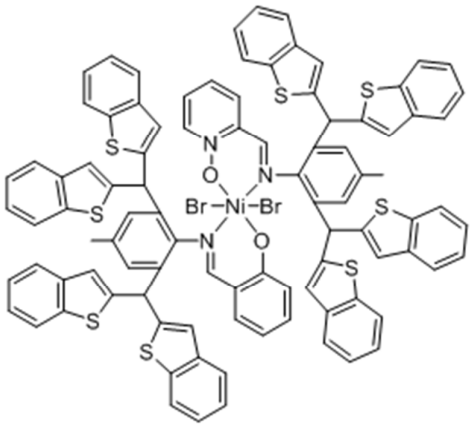
A Schlenk tube was charged with (DME)$NiBr_2$ (0.5 mmol for **Ni-Ph**, **Ni-Np**, and **Ni-Bz**; 1.0 mmol for **Ni-Ph-Ph**, and **Ni-An**), the ligand (1.0 mmol) and 20 mL dichloromethane. The reaction mixture was stirred at room temperature for 12 h, followed by the addition of diethyl ether (20 mL) to precipitate the metal complex. The precipitate was washed with diethyl ether and dried under reduced pressure at room temperature for 12 h.



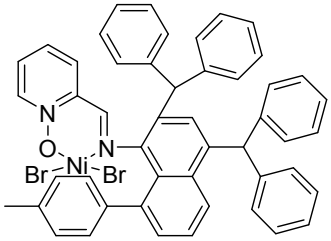
Complexes Ni-Ph, light red solid (589 mg, 90%). Anal. Calcd for $C_{78}H_{64}Br_2N_4NiO_2$: C, 71.63; H, 4.93; N, 4.28. Found: C, 71.45; H, 4.97; N, 4.35. MALDI-TOF: m/z 680.8602 $[M\text{-}L\text{-}Br]^+$; 682.8975 $[M\text{-}L\text{-}Br + 2H]^+$.



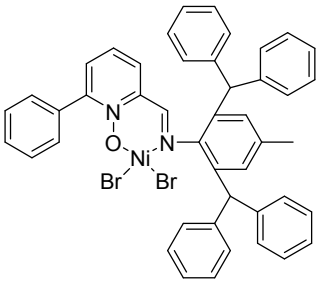
Complexes Ni-Np, light brown-red solid (734 mg, 86%). Anal. Calcd for $C_{110}H_{80}Br_2N_4NiO_2$: C, 77.34; H, 4.72; N, 3.28. Found: C, 77.55; H, 4.57; N, 3.35. MALDI-TOF: m/z 880.8529 $[M\text{-}L\text{-}Br]^+$; 882.8887 $[M\text{-}L\text{-}Br + 2H]^+$.



Complexes Ni-Bz, yellow solid (686 mg, 78%). Anal. Calcd for $C_{94}H_{66}Br_2N_4NiO_2S_8$: C, 64.20; H, 3.78; N, 3.19. Found: C, 64.45; H, 3.57; N, 3.18. MALDI-TOF: m/z 903.9476 $[M\text{-}L\text{-}Br]^+$; 906.0133 $[M\text{-}L\text{-}Br + 2H]^+$.



Complexes Ni-An, light brown-red solid (718 mg, 92%). Anal. Calcd for $C_{37}H_{30}Br_2N_2NiO$: C, 60.29; H, 4.10; N, 3.80. Found: C, 60.37; H, 4.15; N, 3.65. MALDI-TOF: m/z 806.7671 $[M - Br]^+$; 808.7863 $[M\text{-}Br + 2H]^+$.



Complexes Ni-Ph-Ph, light brown-red solid (730 mg, 87%). Anal. Calcd for $C_{45}H_{36}Br_2N_2NiO$: C, 64.40; H, 4.32;N, 3.34. Found: C, 64.28; H, 4.38; N, 3.45. MALDI-TOF: m/z 756.8963 $[M - Br]^+$; 758.8924 $[M\text{-}Br + 2H]^+$.

4. Spectra Data

4.1 ^{1}H and ^{13}C NMR of Ligands.

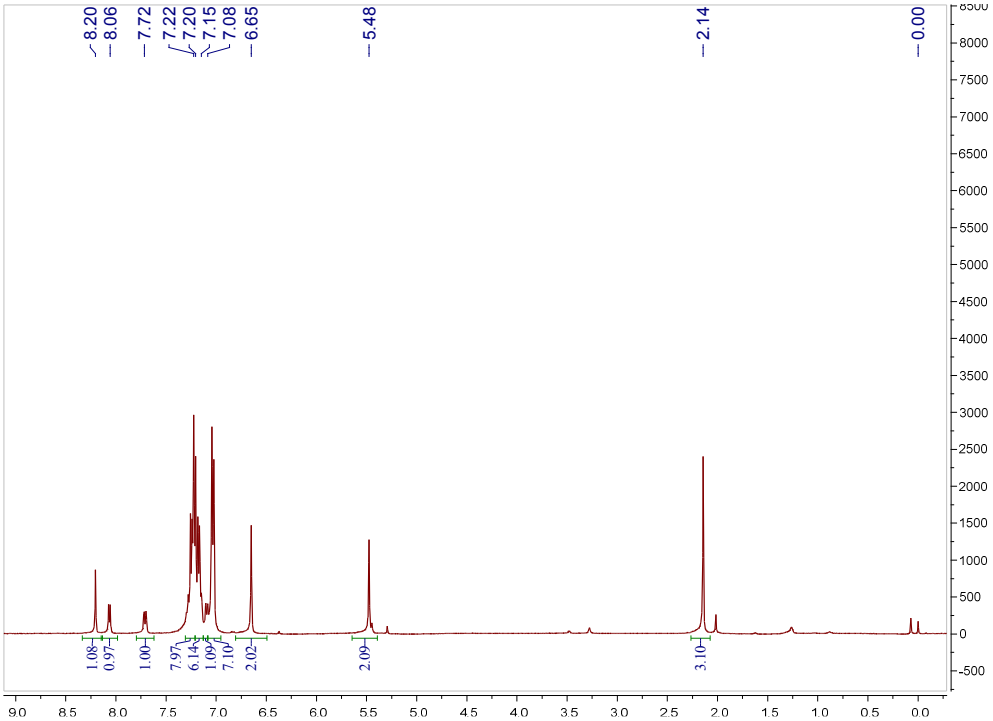


Figure S6. ^{1}H NMR spectrum of **L-Ph** in $CDCl_3$.

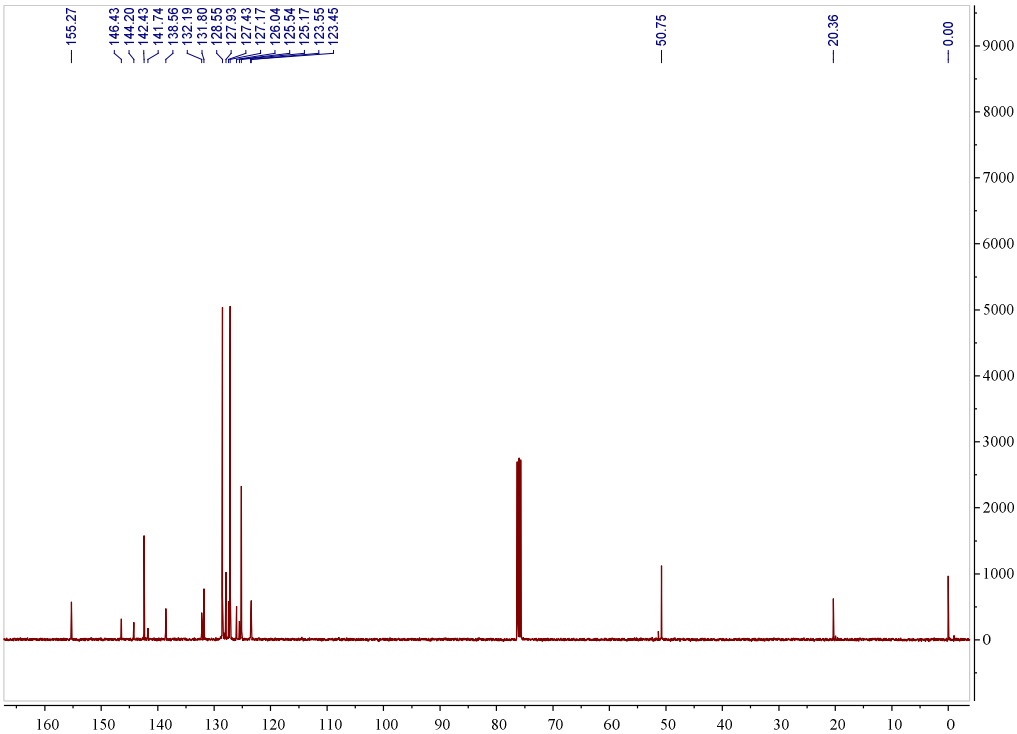


Figure S7. ^{13}C NMR spectrum of **L-Ph** in $CDCl_3$.

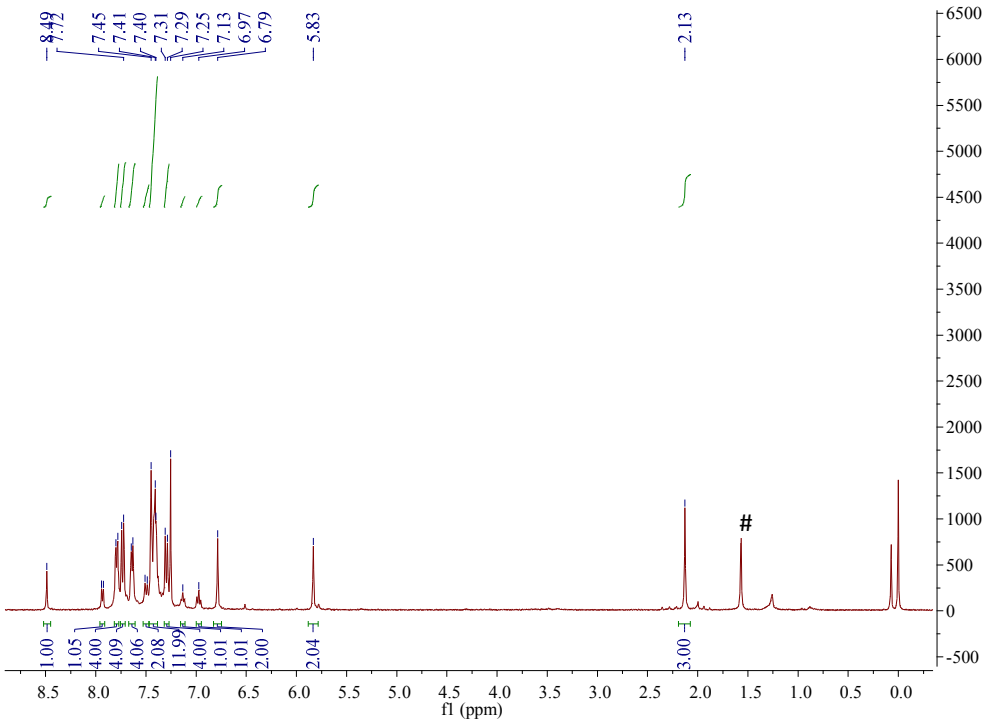


Figure S8. ^{1}H NMR spectrum of **L-Np** in $CDCl_3$. (# H_2O)

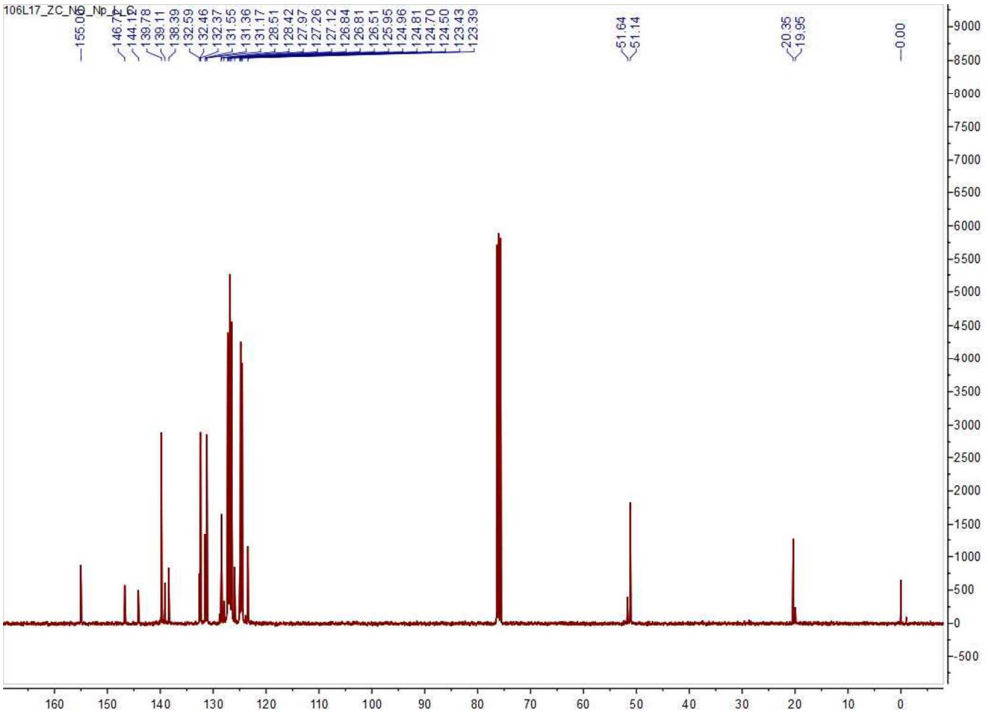


Figure S9. ^{13}C NMR spectrum of **L-Np** in $CDCl_3$. (# H_2O)

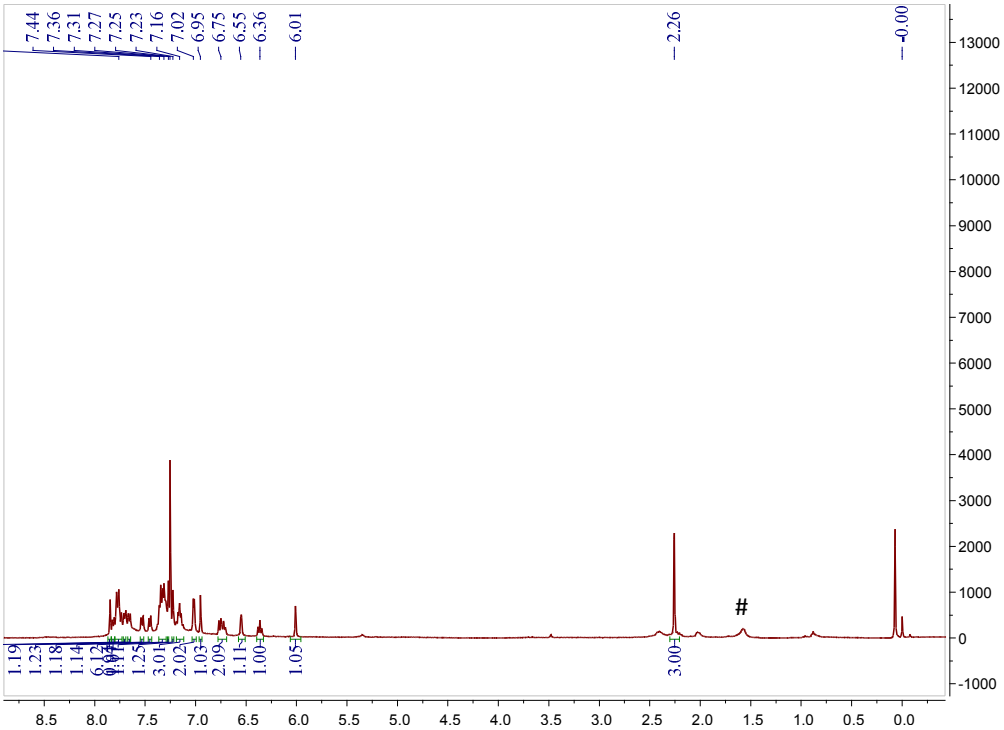


Figure S10. ^{1}H NMR spectrum of **L-Bz** in $CDCl_3$. (# H_2O)

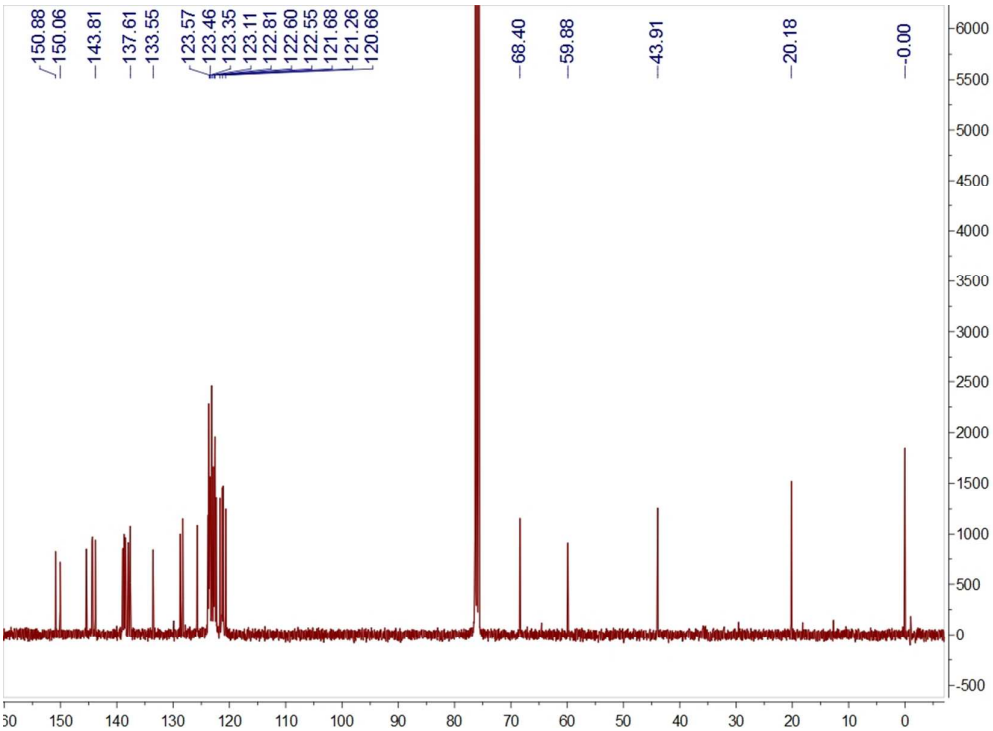


Figure S11. ^{13}C NMR spectrum of **L-Bz** in $CDCl_3$.

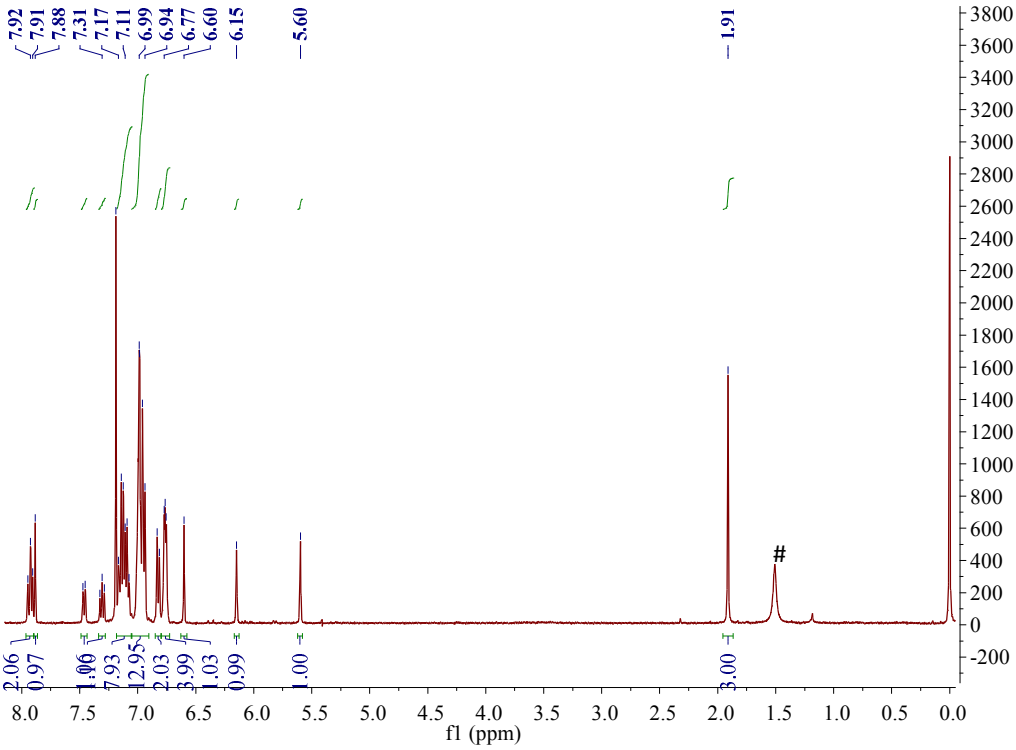


Figure S12. ^{1}H NMR spectrum of **L-An** in $CDCl_3$. (# H_2O)

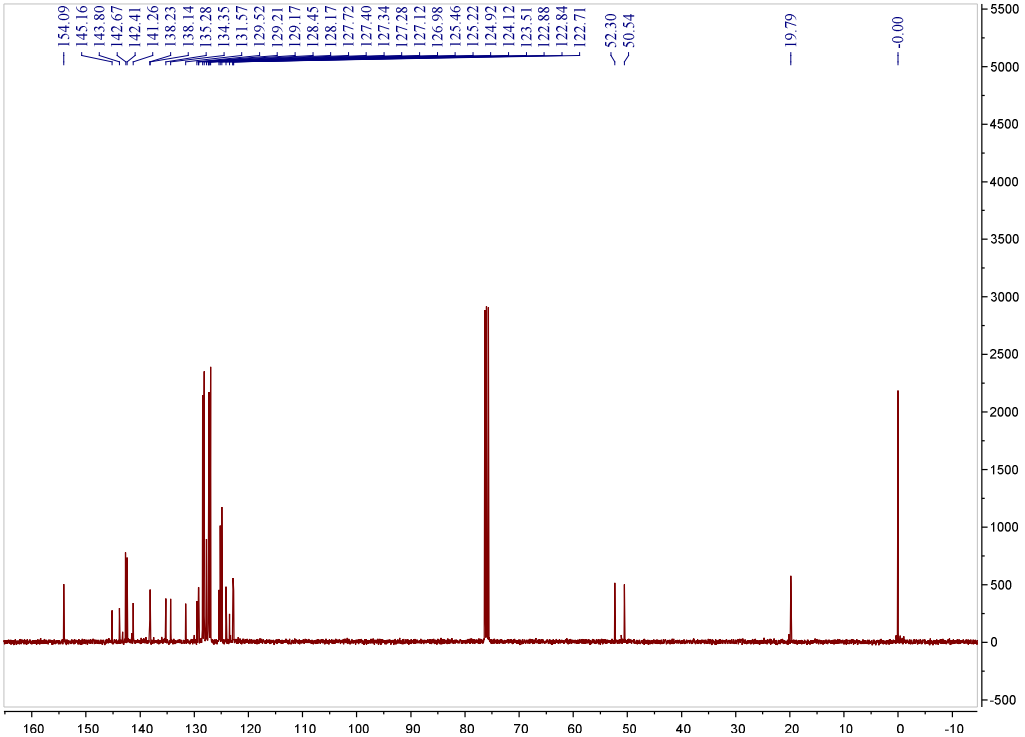


Figure S13. ^{13}C NMR spectrum of **L-An** in $CDCl_3$.

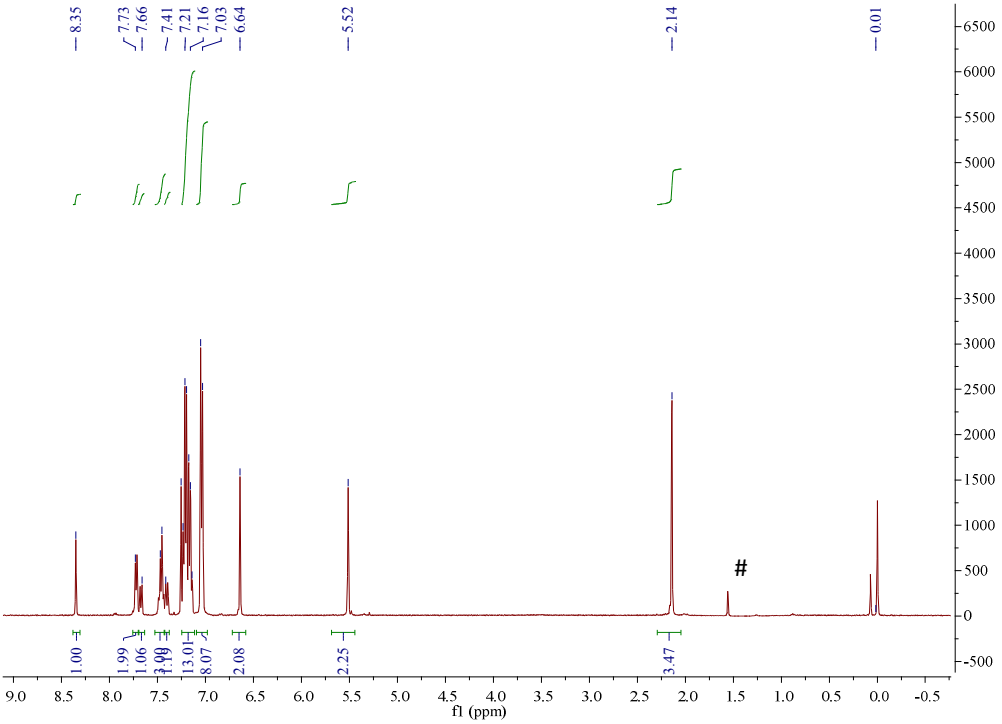


Figure S14. ^{1}H NMR spectrum of **L-Ph-Ph** in $CDCl_3$. (# H_2O)

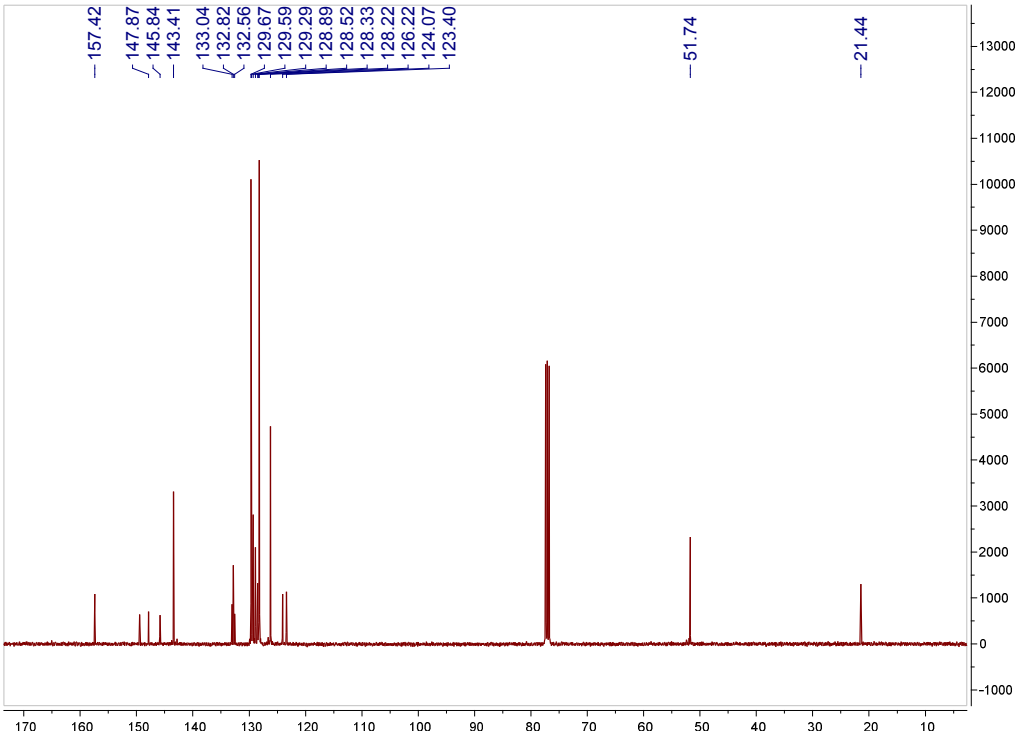


Figure S15. ^{13}C NMR spectrum of **L-Ph-Ph** in $CDCl_3$.

4.2 MALDI-TOF of Complexes.

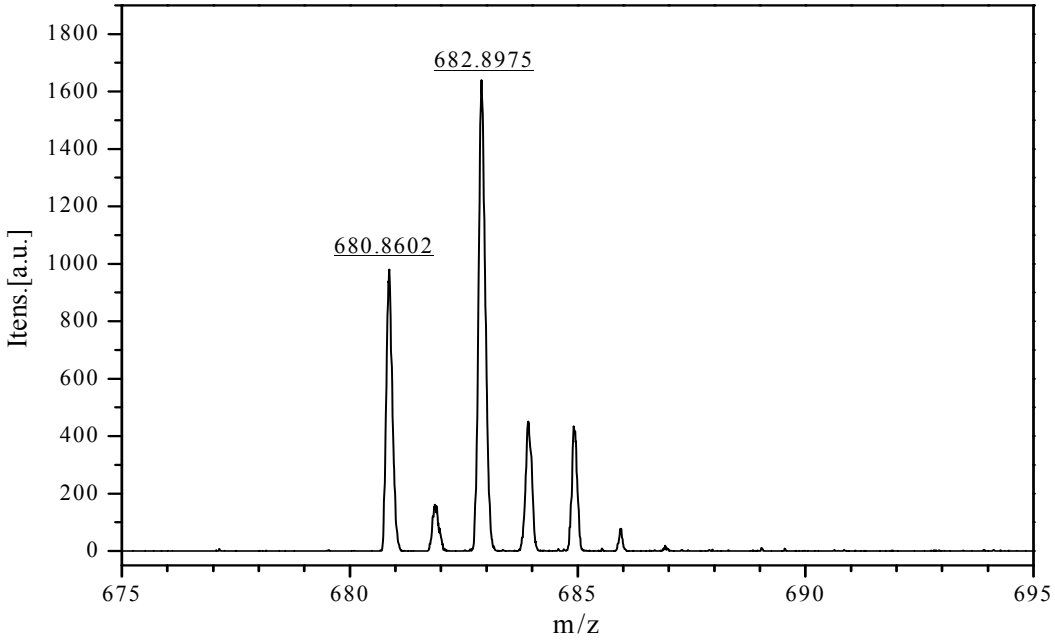


Figure S16. MALDI-TOF of Complexes **Ni-Ph**.

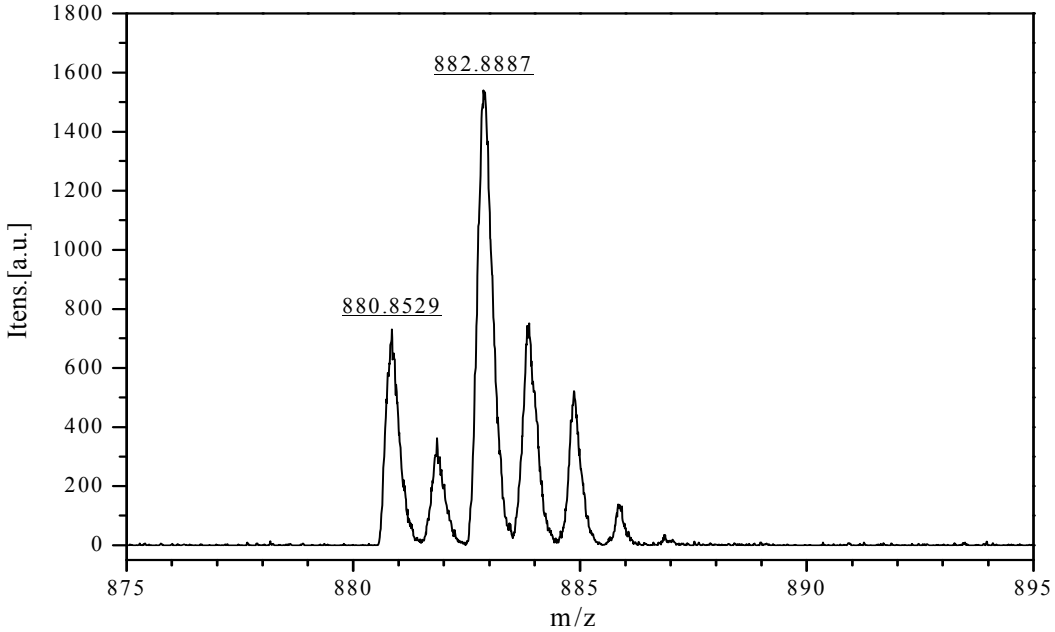


Figure S17. MALDI-TOF of Complexes **Ni-Np**.

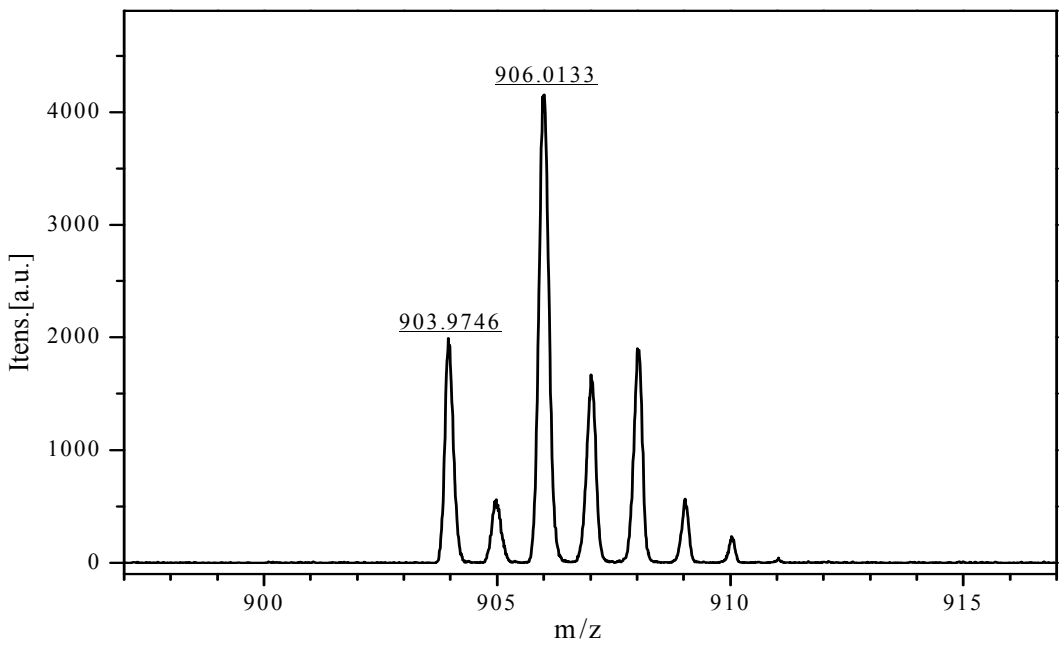


Figure S18. MALDI-TOF of Complexes **Ni-Bz**.

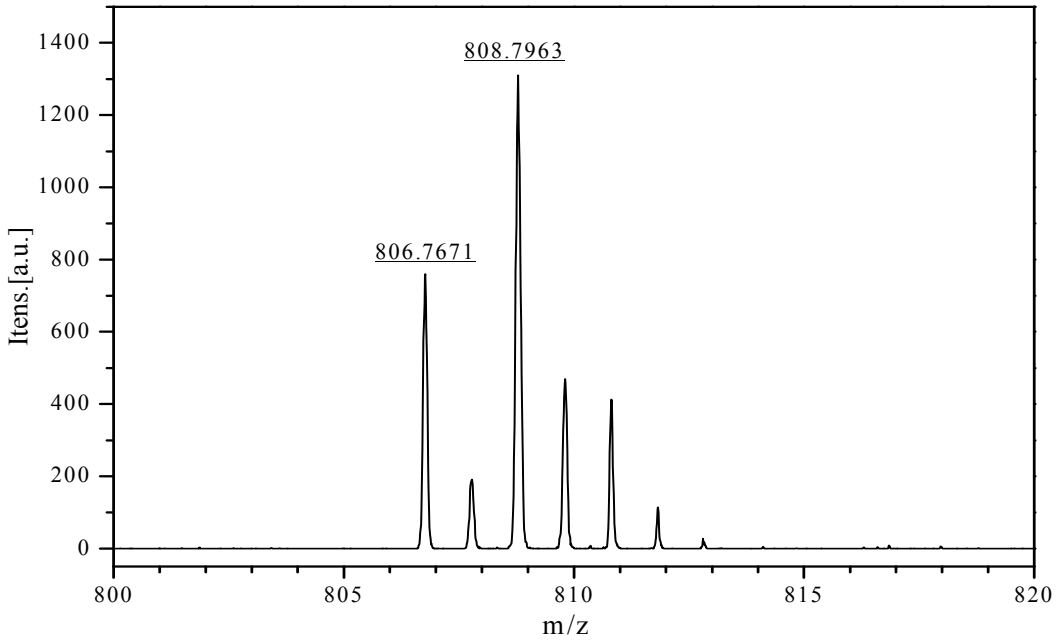


Figure S19. MALDI-TOF of Complexes **Ni-An**.

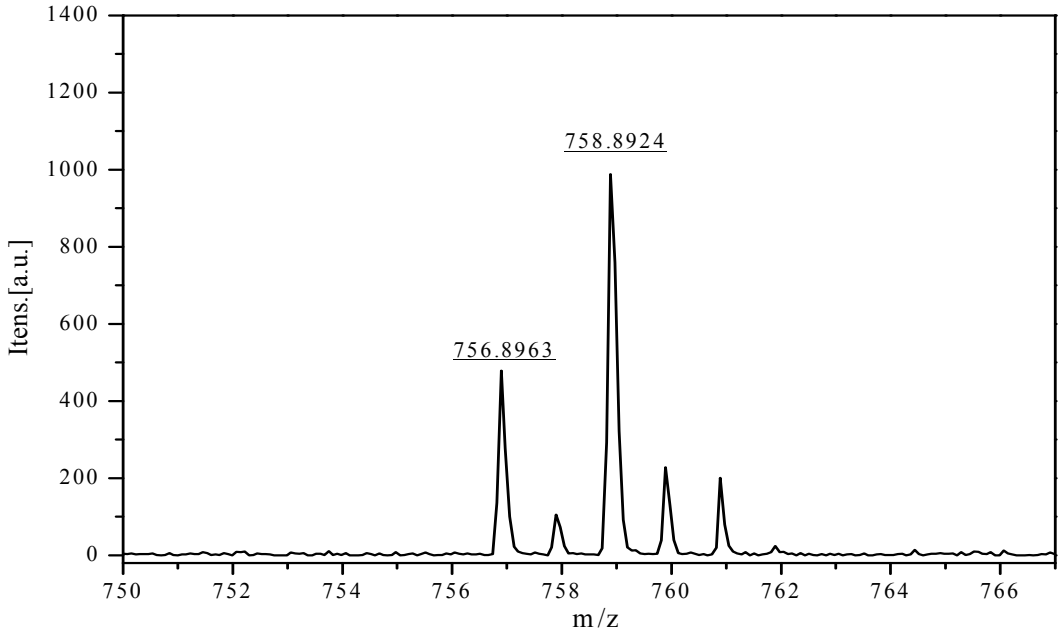


Figure S20. MALDI-TOF of Complexes **Ni-Ph-Ph**.

4.3 ^{1}H NMR of polymer and copolymer.

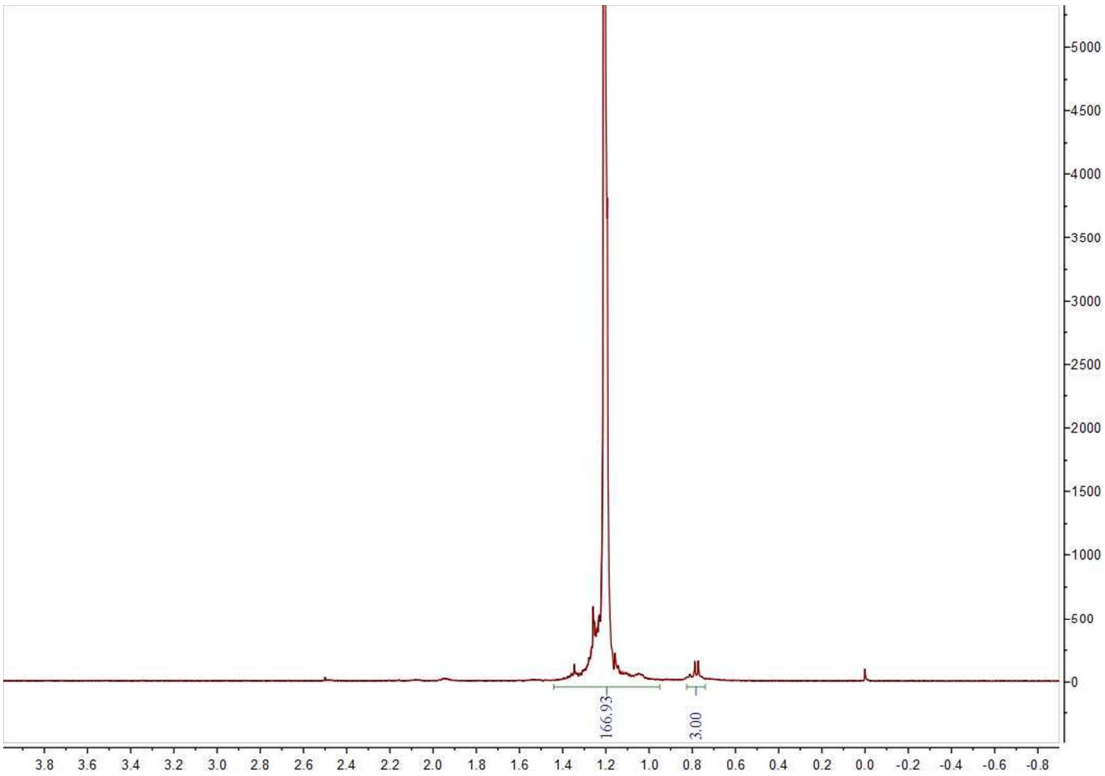


Figure S21. ^{1}H NMR spectrum of the polymer from table 1, entry 1 ($C_2D_2Cl_4$, 120°C).

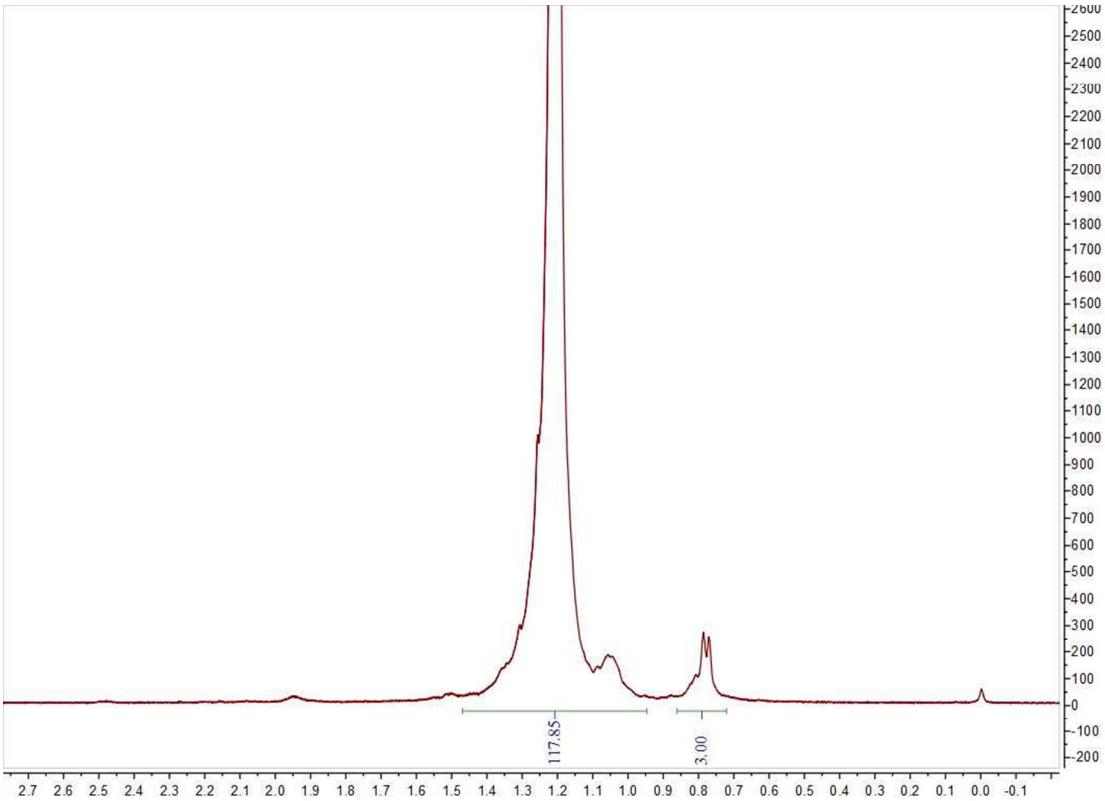


Figure S22. ^{1}H NMR spectrum of the polymer from table 1, entry 2 ($C_2D_2Cl_4$, 120°C).

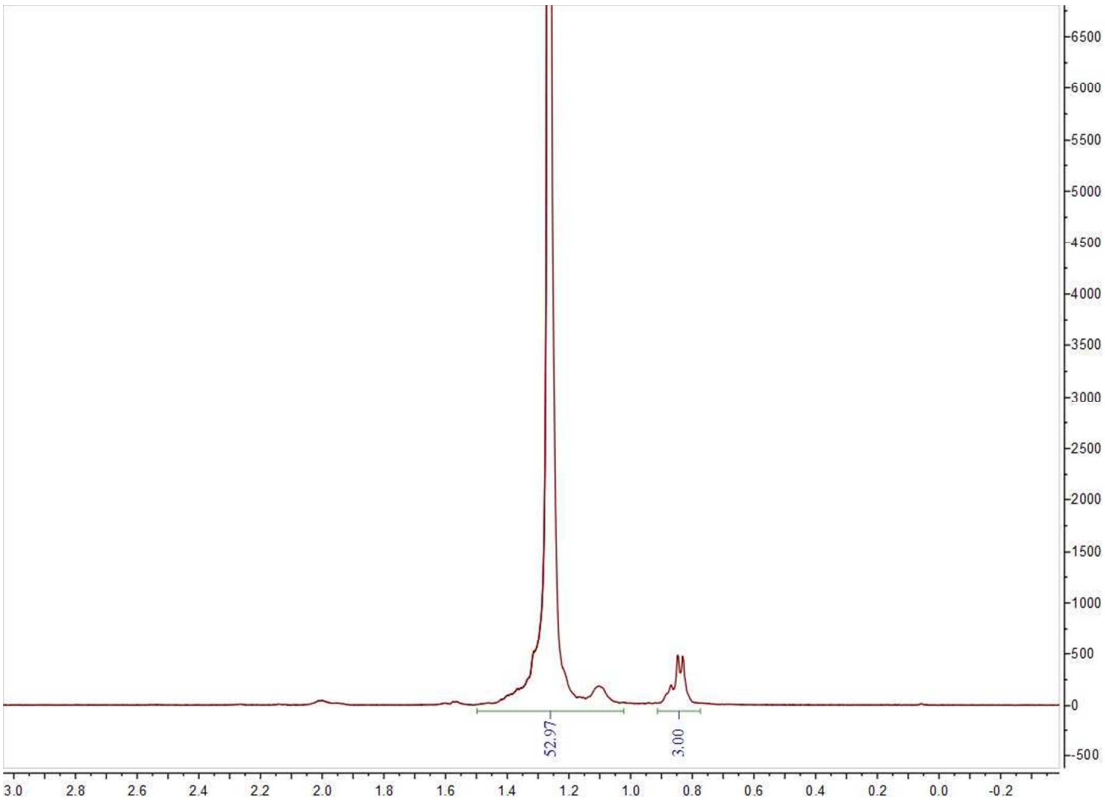


Figure S23. ^{1}H NMR spectrum of the polymer from table 1, entry3 ($C_2D_2Cl_4$, 120°C).

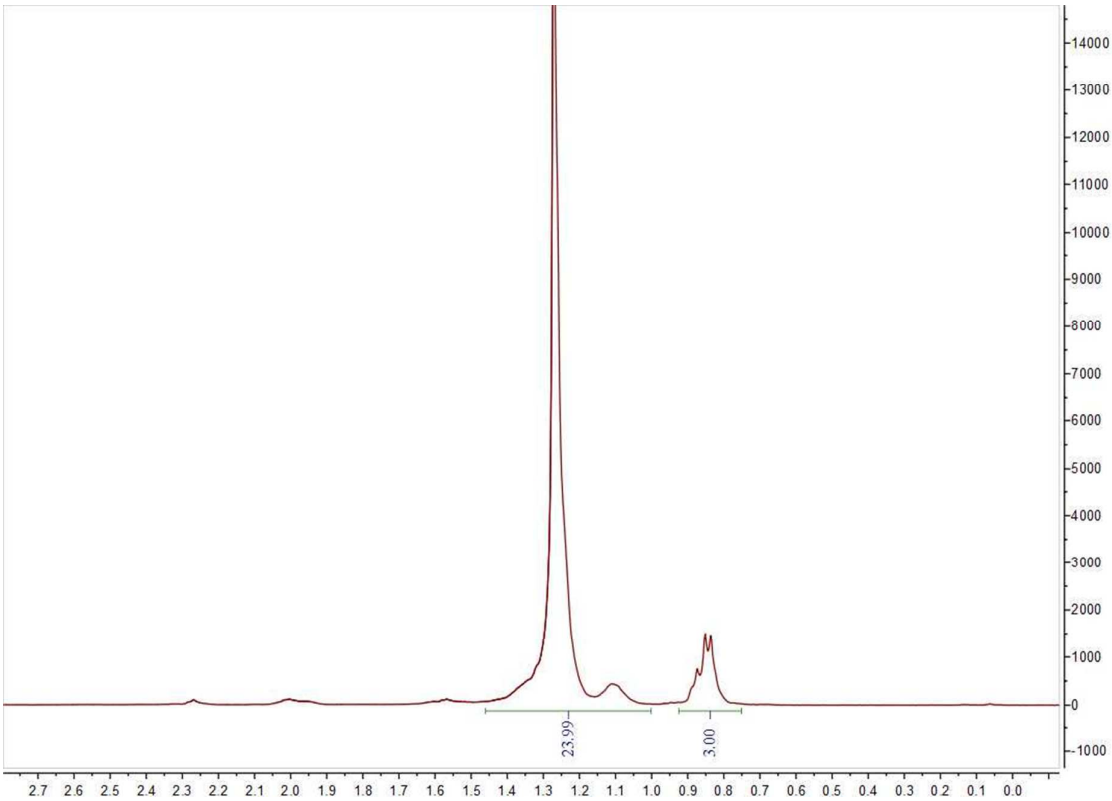


Figure S24. ^{1}H NMR spectrum of the polymer from table 1, entry 4 ($C_2D_2Cl_4$, 120°C).

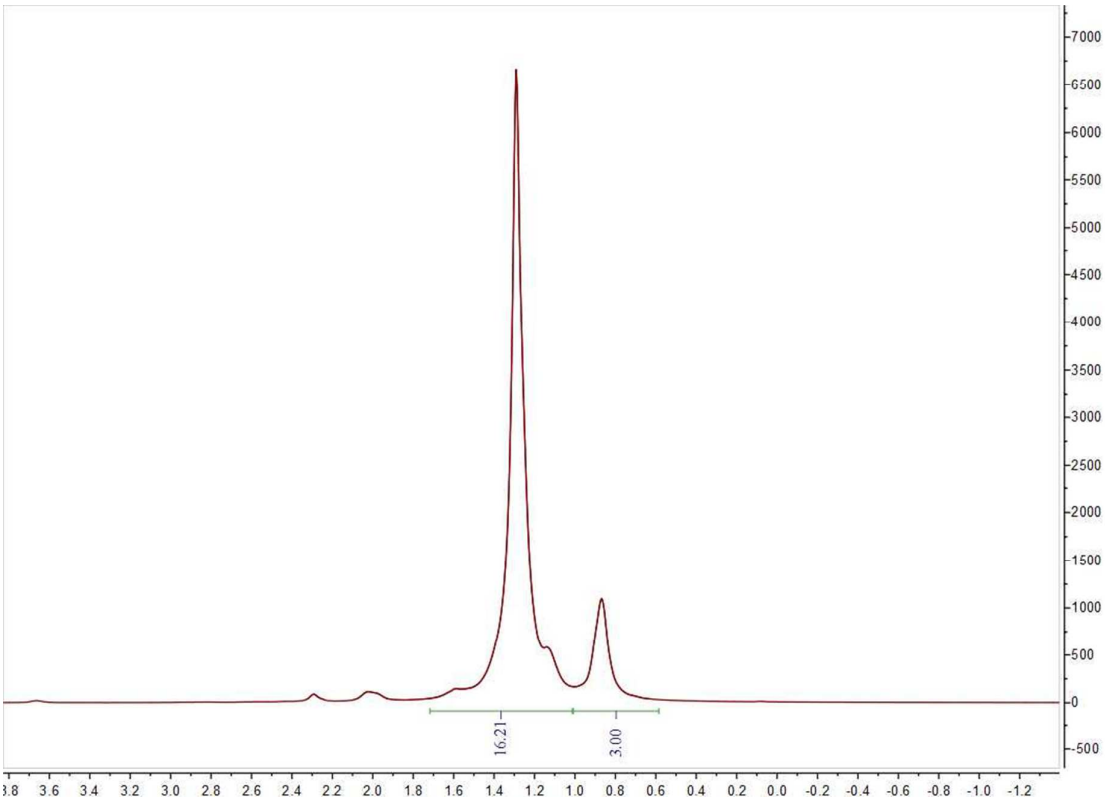


Figure S25. ^{1}H NMR spectrum of the polymer from table 1, entry 5 ($C_2D_2Cl_4$, 120°C).

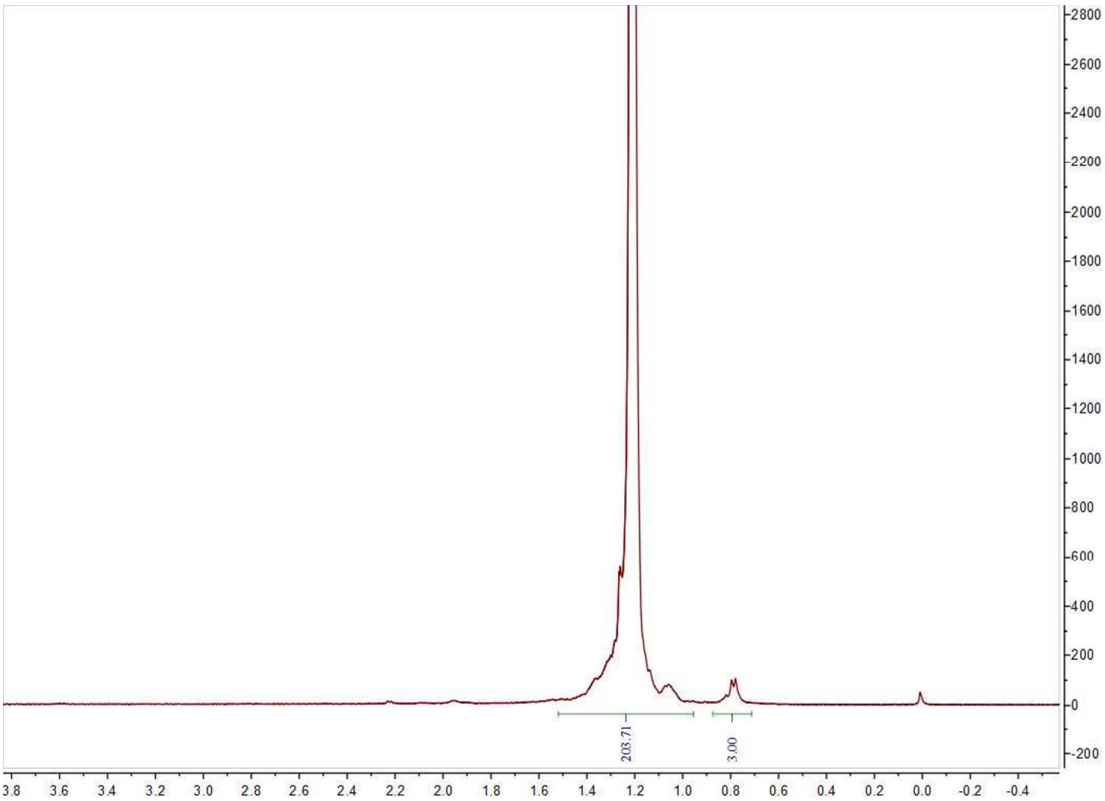


Figure S26. ^{1}H NMR spectrum of the polymer from table 1, entry 9($C_2D_2Cl_4$, 120°C).

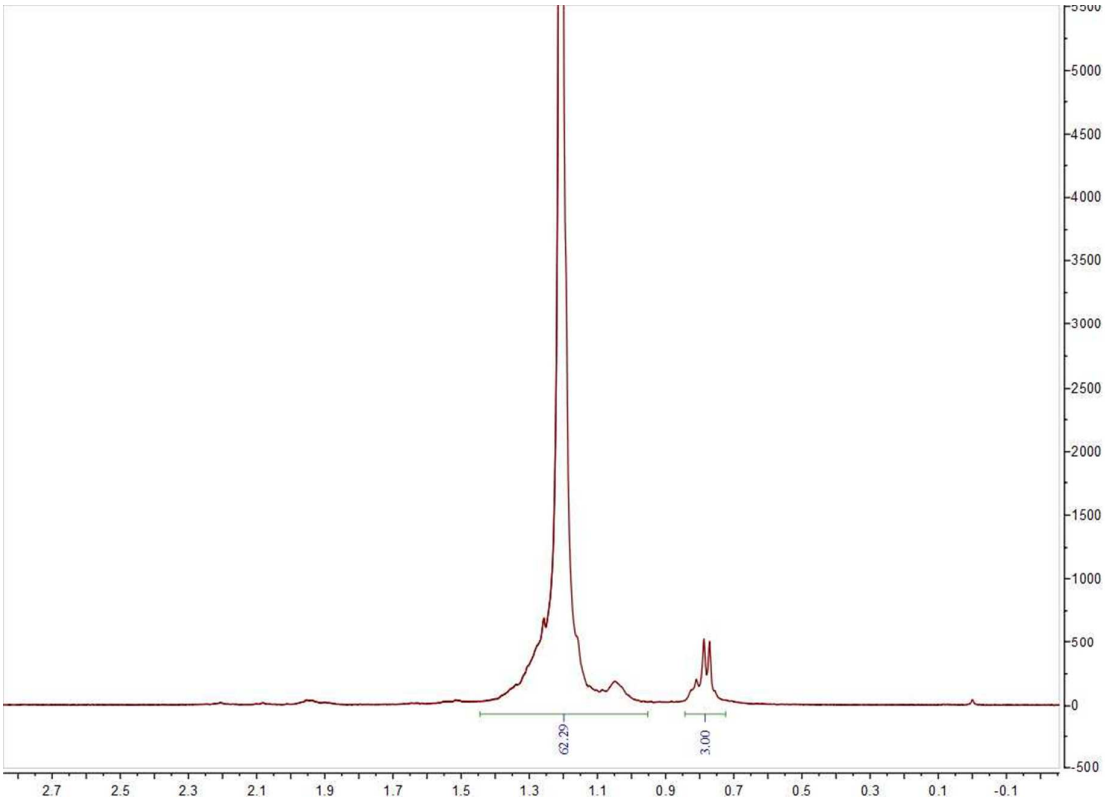


Figure S27. ^{1}H NMR spectrum of the polymer from table 1, entry 10 ($C_2D_2Cl_4$, 120°C).

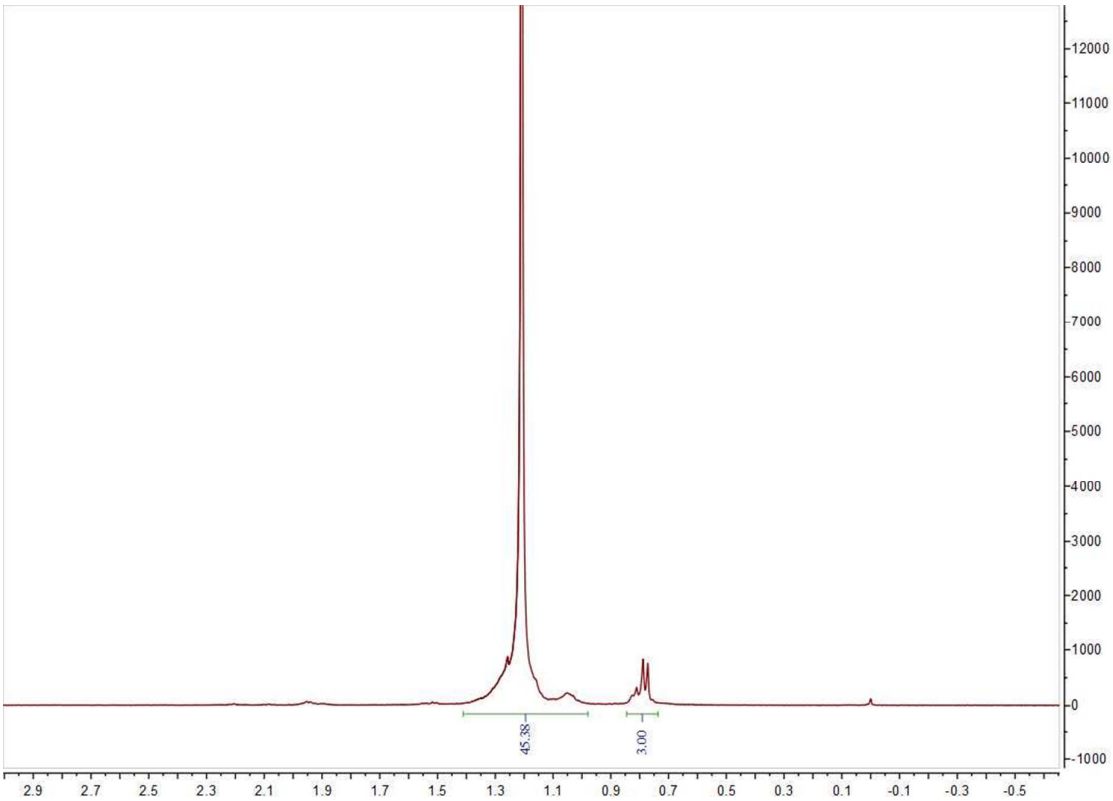


Figure S28. ^{1}H NMR spectrum of the polymer from table 1, entry 11 ($C_2D_2Cl_4$, 120°C).

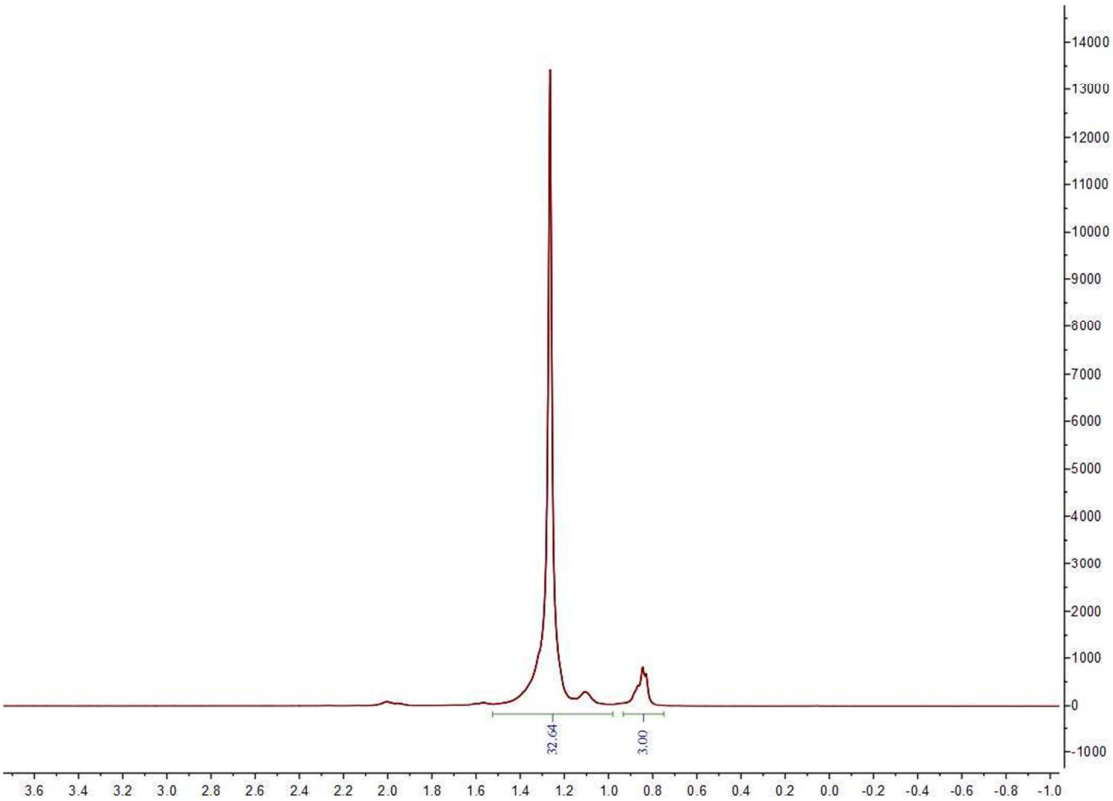


Figure S29. ^{1}H NMR spectrum of the polymer from table 1, entry 12 ($C_2D_2Cl_4$, 120°C).

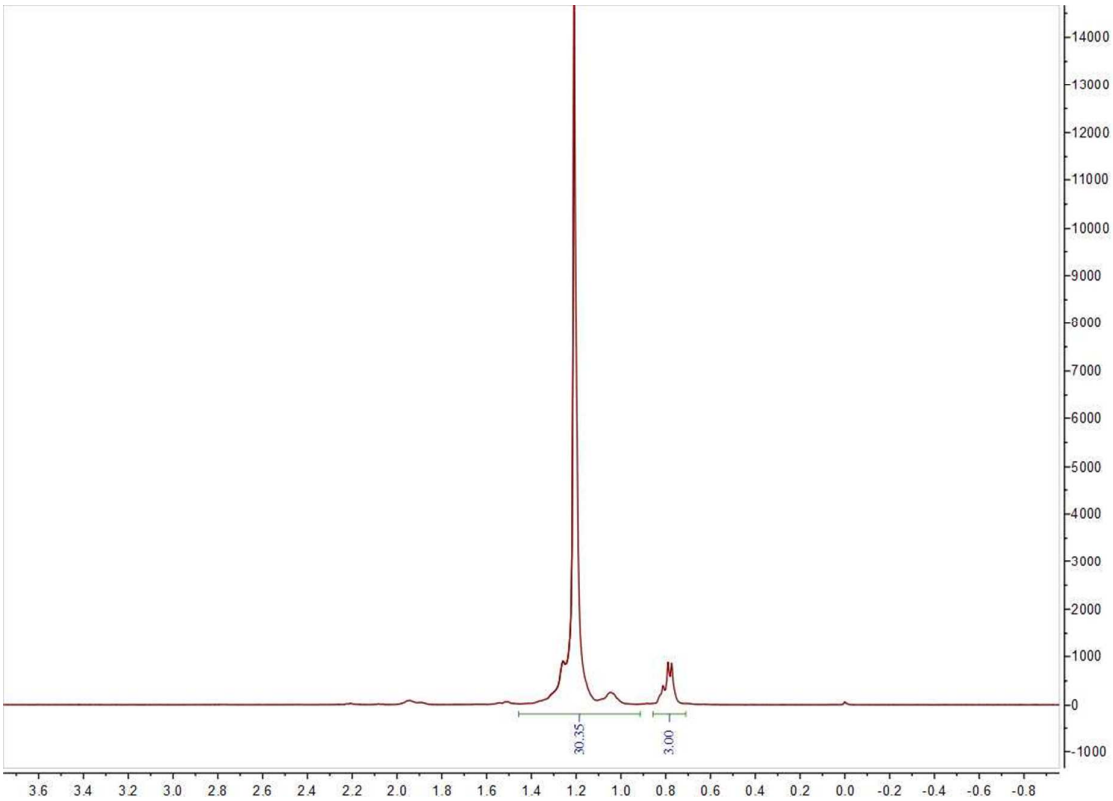


Figure S30. ^{1}H NMR spectrum of the polymer from table 1, entry 13 ($C_2D_2Cl_4$, 120°C).

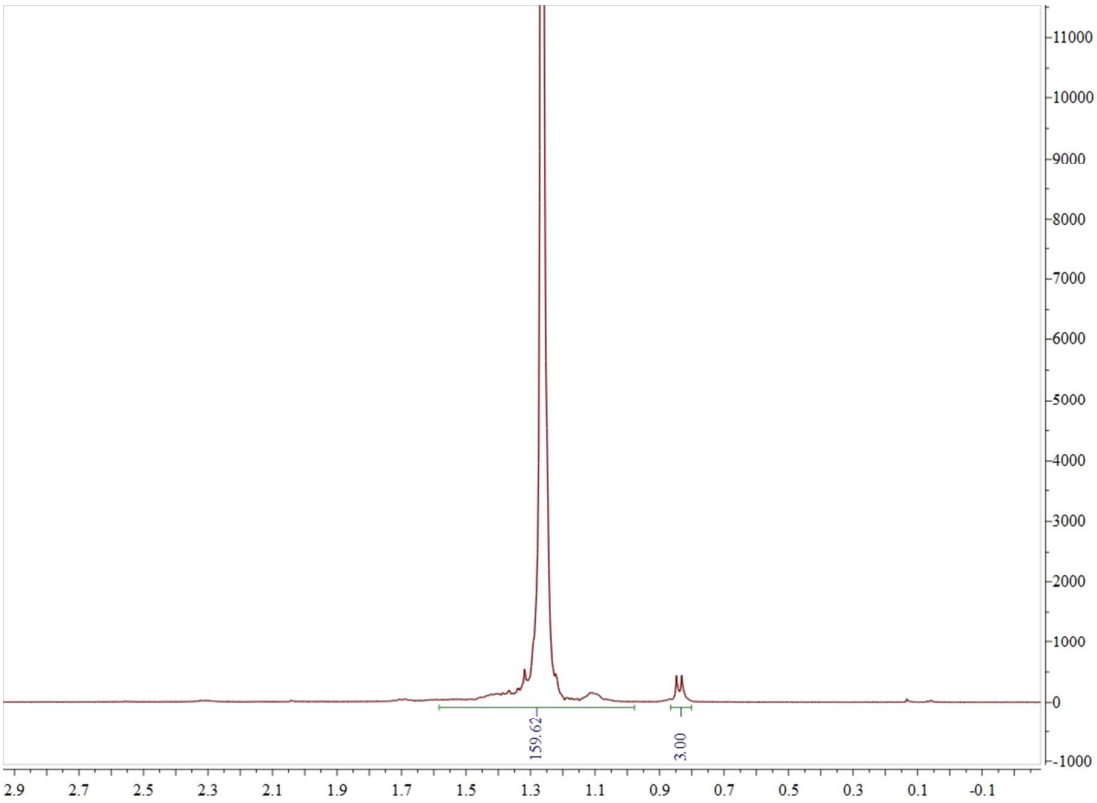


Figure S31. ^{1}H NMR spectrum of the polymer from table 1, entry 17 ($C_2D_2Cl_4$, 120°C).

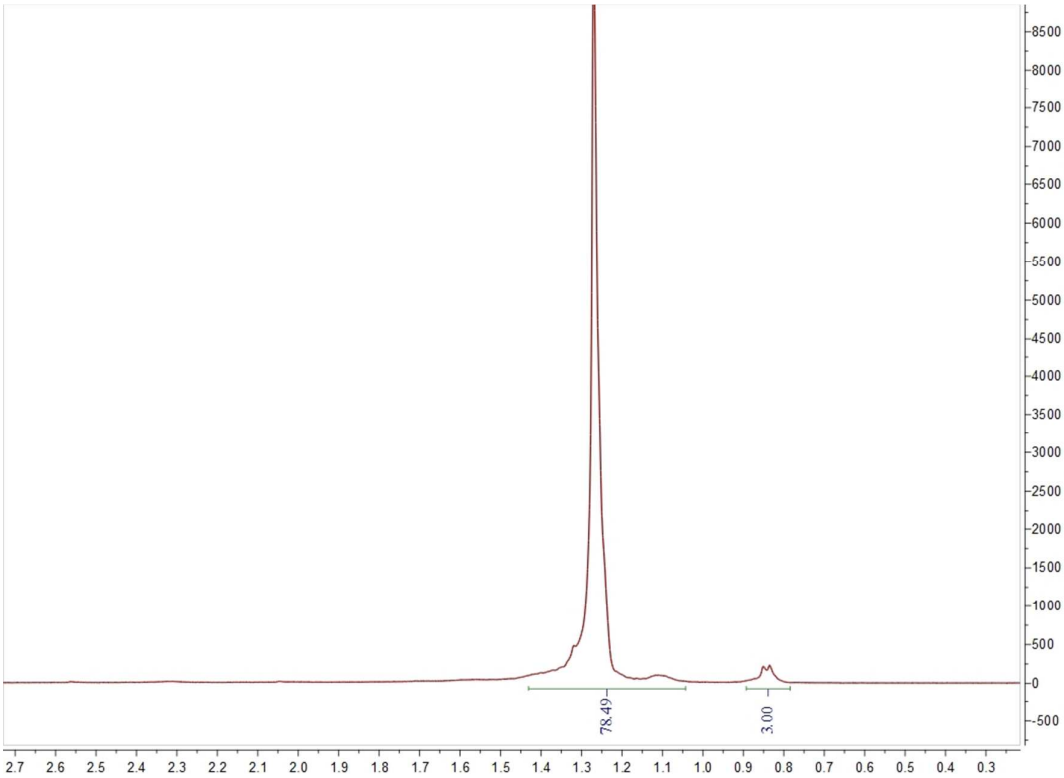


Figure S32. ^{1}H NMR spectrum of the polymer from table 1, entry 18 ($C_2D_2Cl_4$, 120°C).

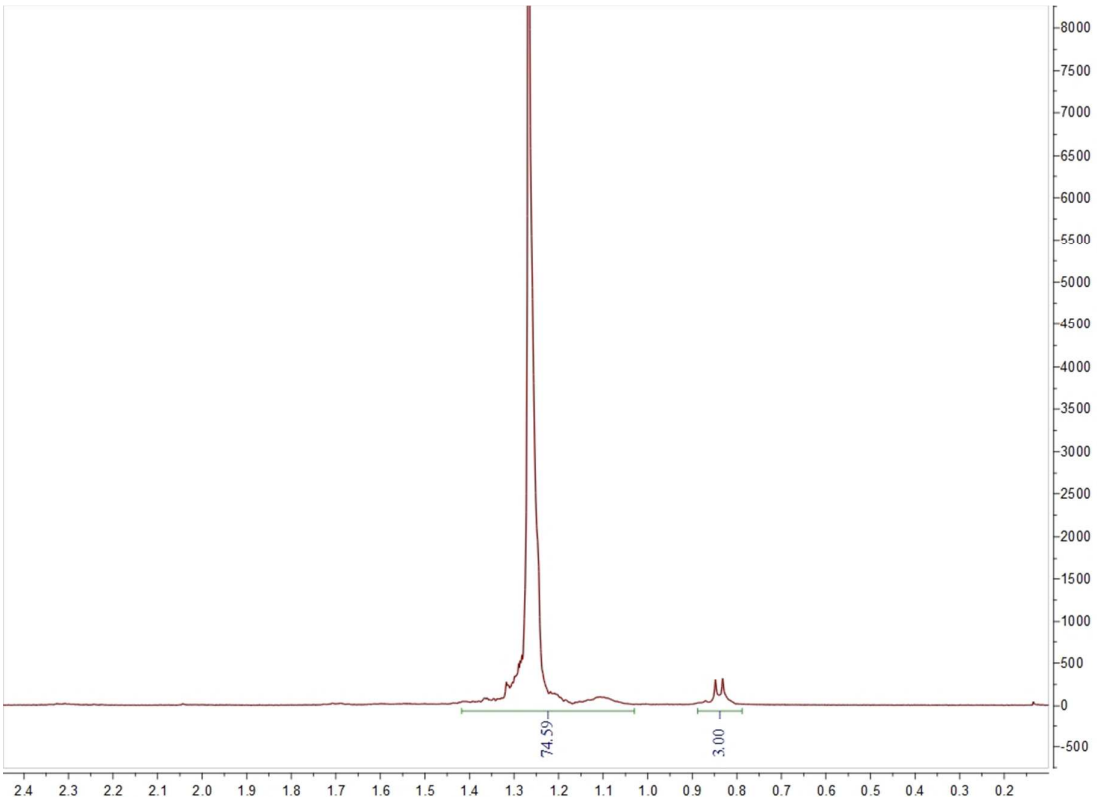


Figure S33. ^{1}H NMR spectrum of the polymer from table 1, entry 19 ($C_2D_2Cl_4$, 120°C).

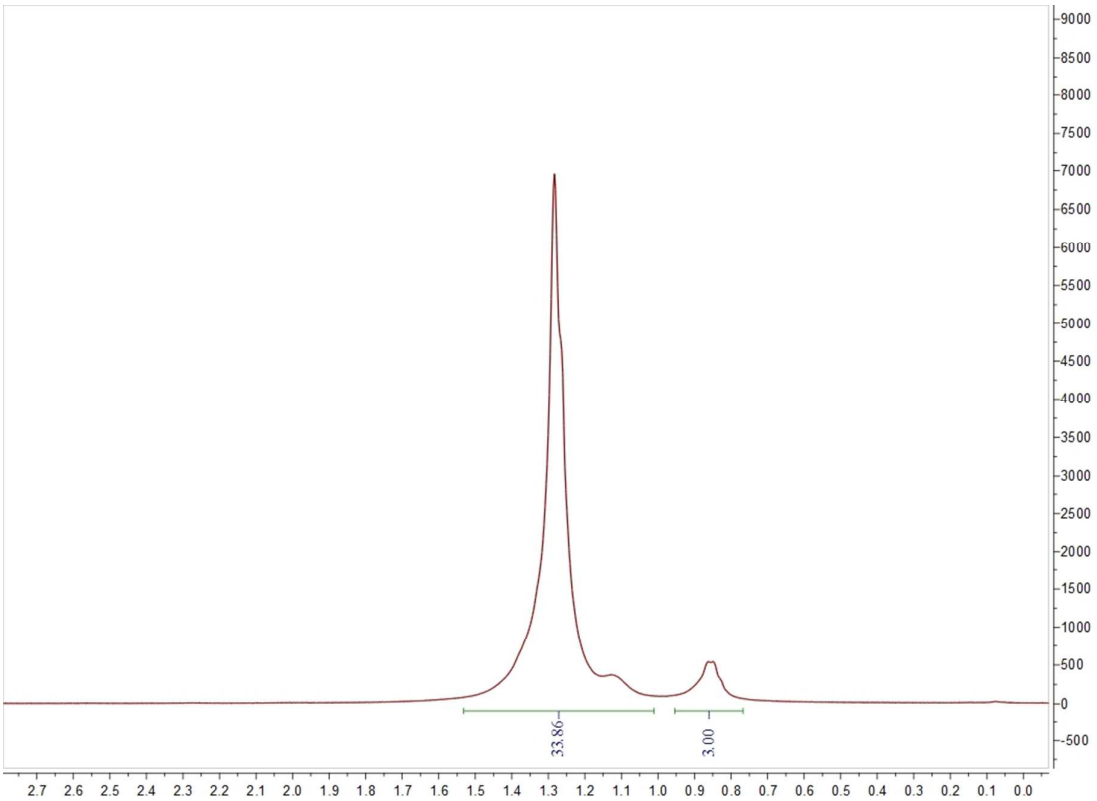


Figure S34. ^{1}H NMR spectrum of the polymer from table 1, entry 20($C_2D_2Cl_4$, 120°C).

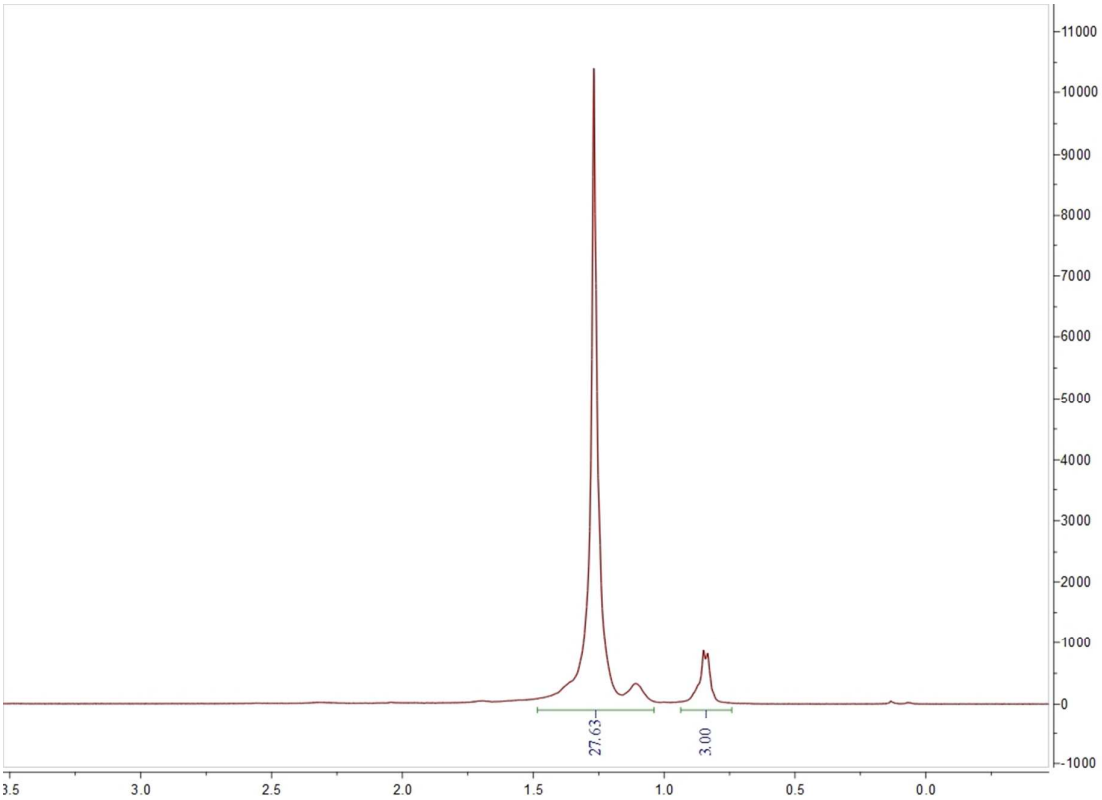


Figure S35. ^{1}H NMR spectrum of the polymer from table 1, entry 21 ($C_2D_2Cl_4$, 120°C).

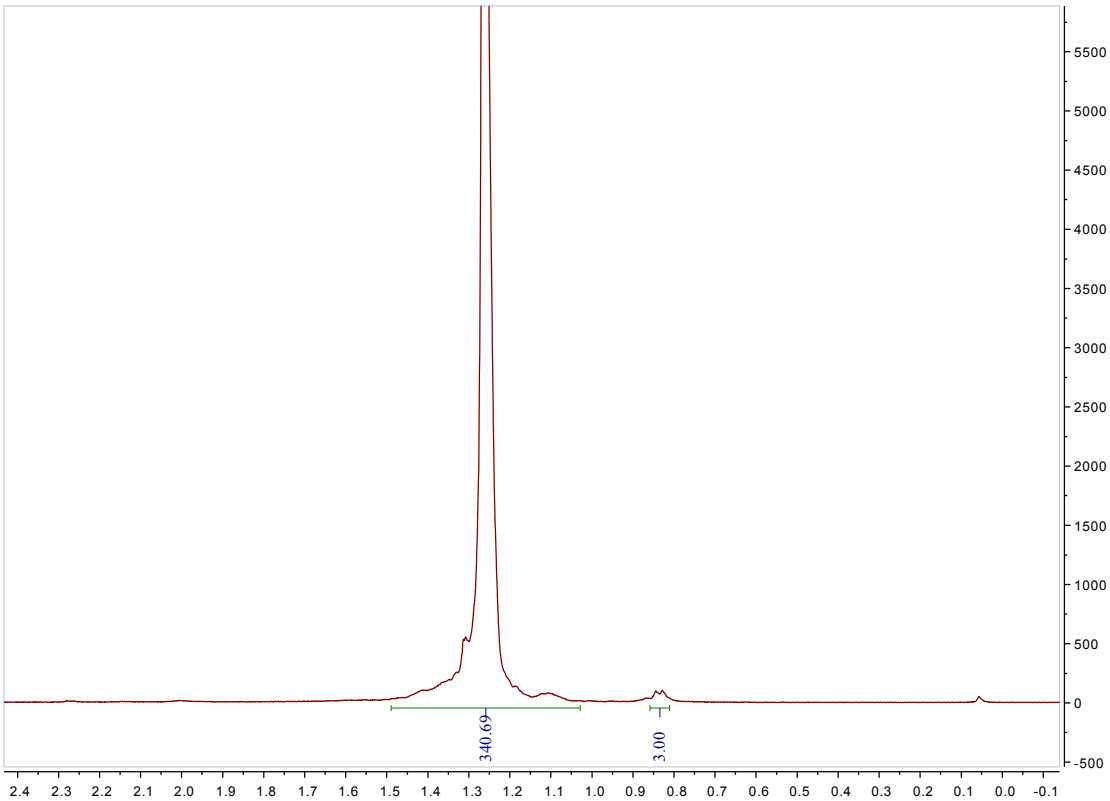


Figure S36. ^{1}H NMR spectrum of the polymer from table 1, entry 23 ($C_2D_2Cl_4$, 120°C).

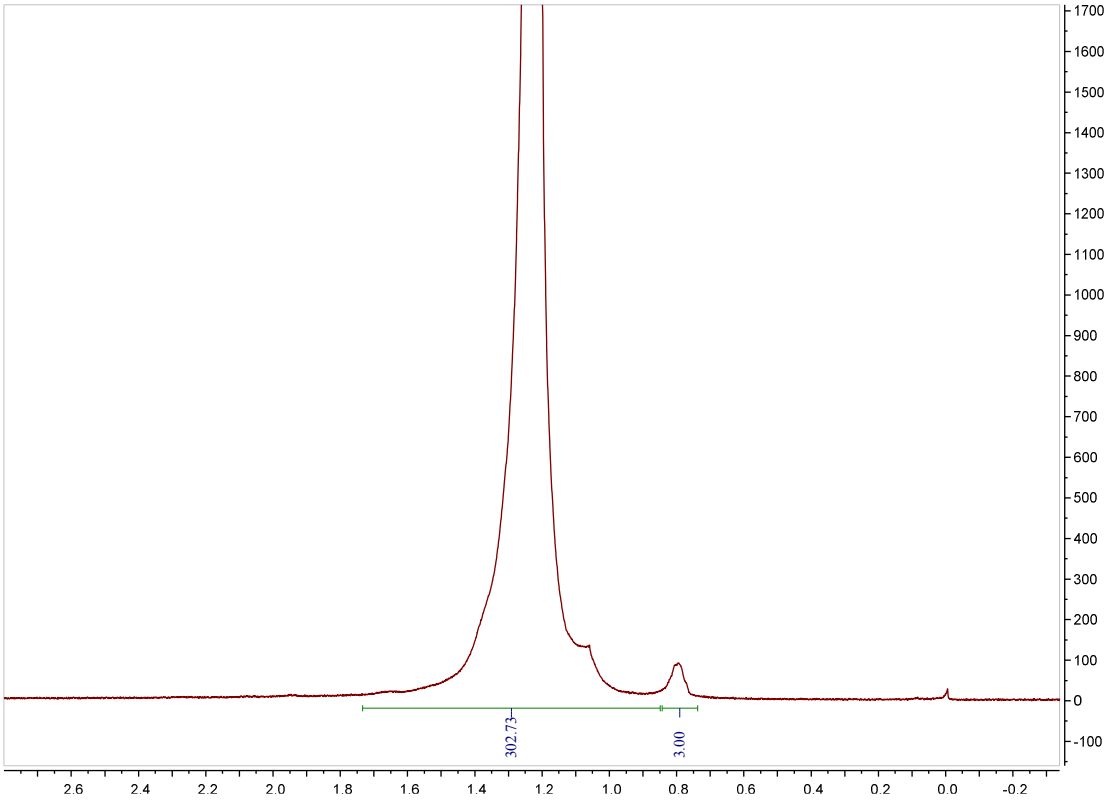


Figure S37. ^{1}H NMR spectrum of the polymer from table 1, entry 24 ($C_2D_2Cl_4$, 120°C).

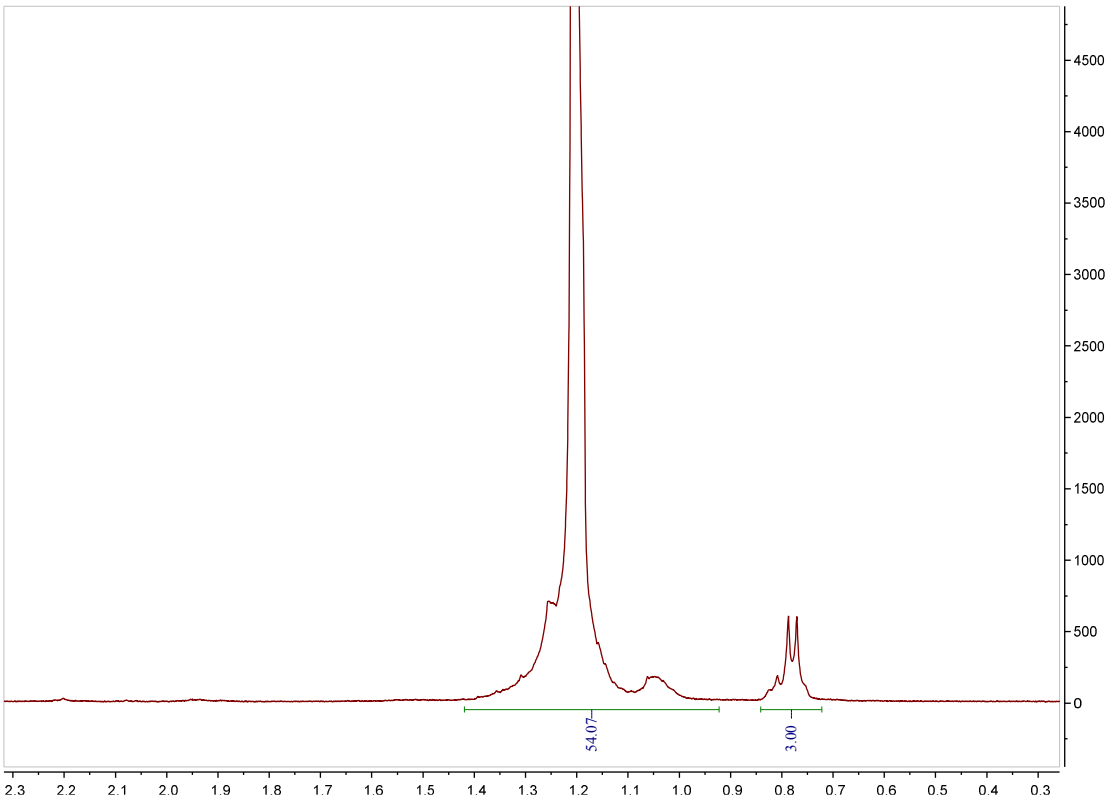


Figure S38. ^{1}H NMR spectrum of the polymer from table 1, entry 25 ($C_2D_2Cl_4$, 120°C).

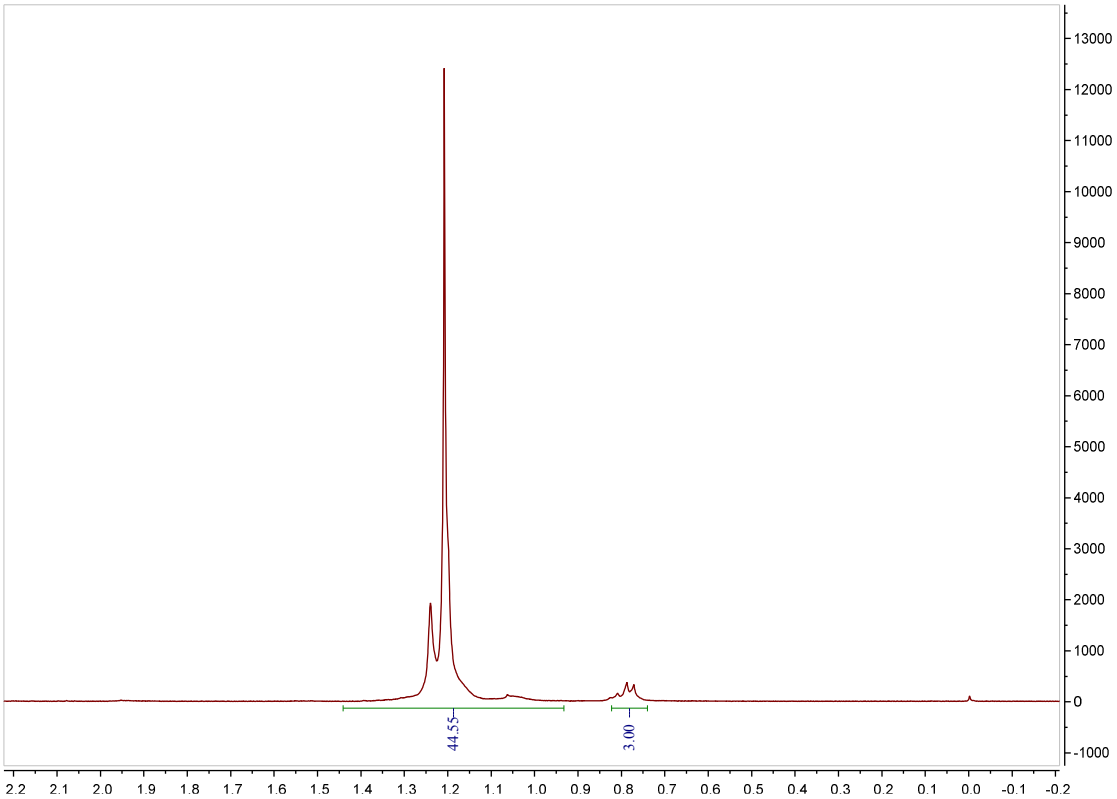


Figure S39. ^{1}H NMR spectrum of the polymer from table 1, entry 26 ($C_2D_2Cl_4$, 120°C).

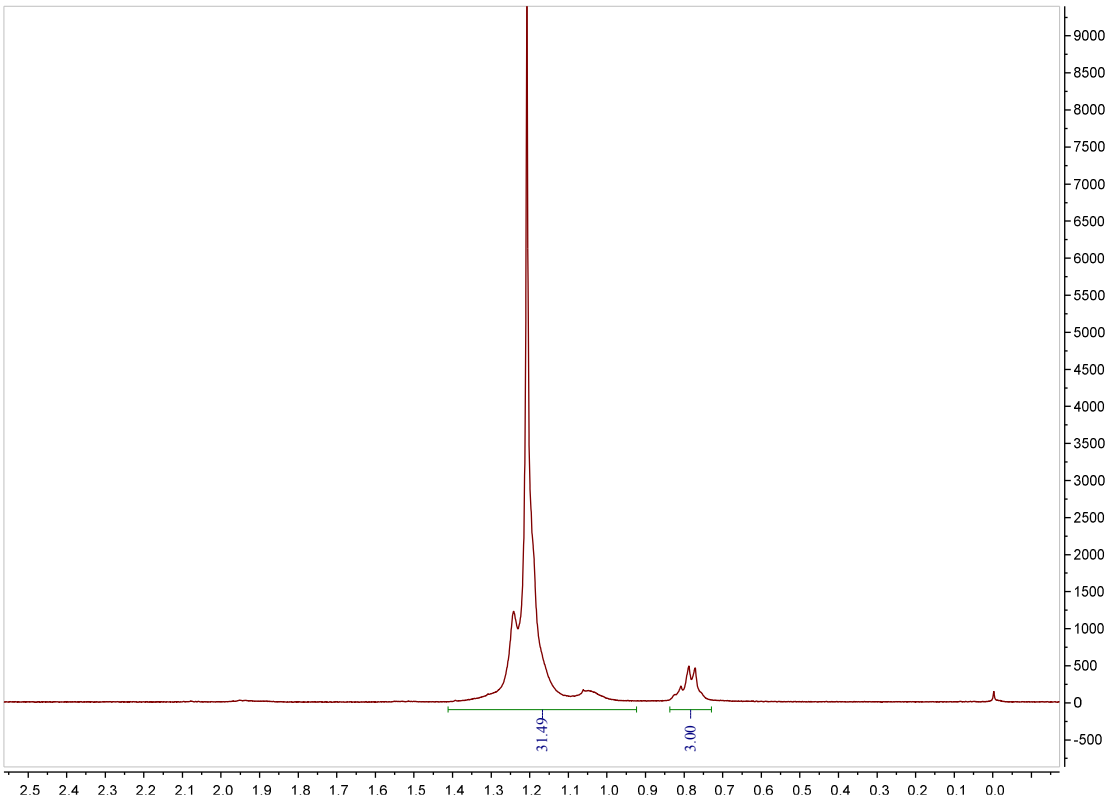


Figure S40. ^{1}H NMR spectrum of the polymer from table 1, entry 27 ($C_2D_2Cl_4$, 120°C).

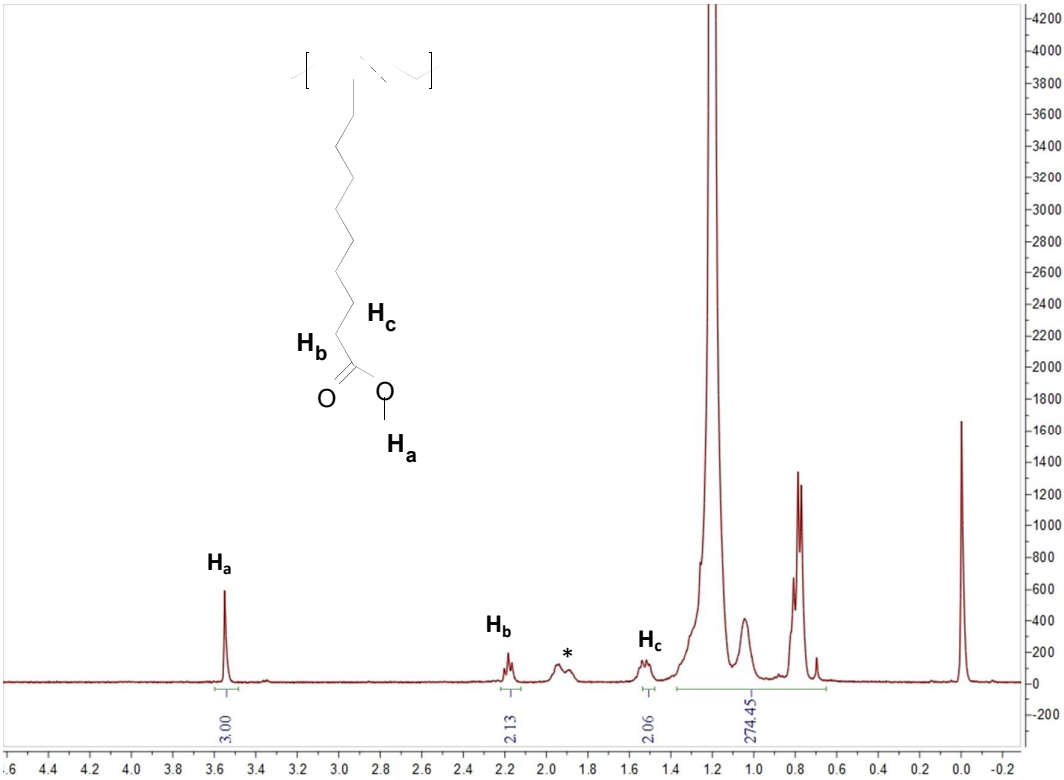


Figure S41. ^{1}H NMR spectrum of the polymer from table 2, entry 1 ($C_2D_2Cl_4$, 120°C). *Solvent impurity in $C_2D_2Cl_4$.

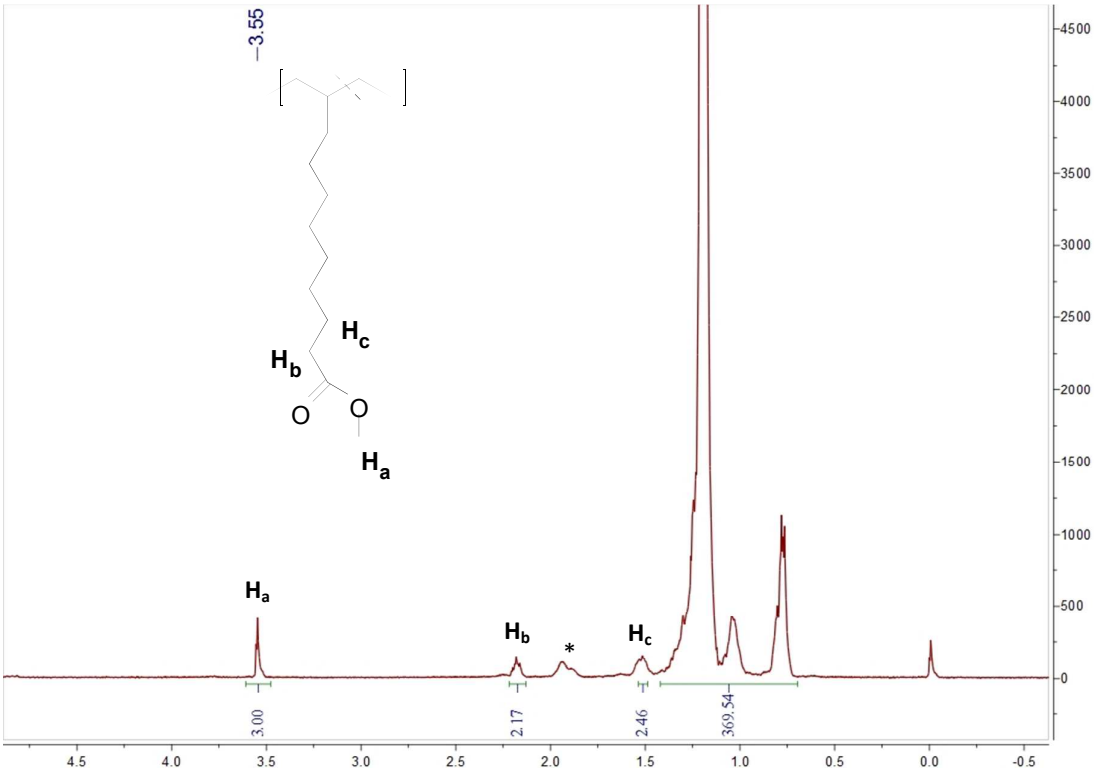


Figure S42. ^{1}H NMR spectrum of the polymer from table2, entry 2($C_2D_2Cl_4$, 120°C). *Solvent impurity in $C_2D_2Cl_4$.

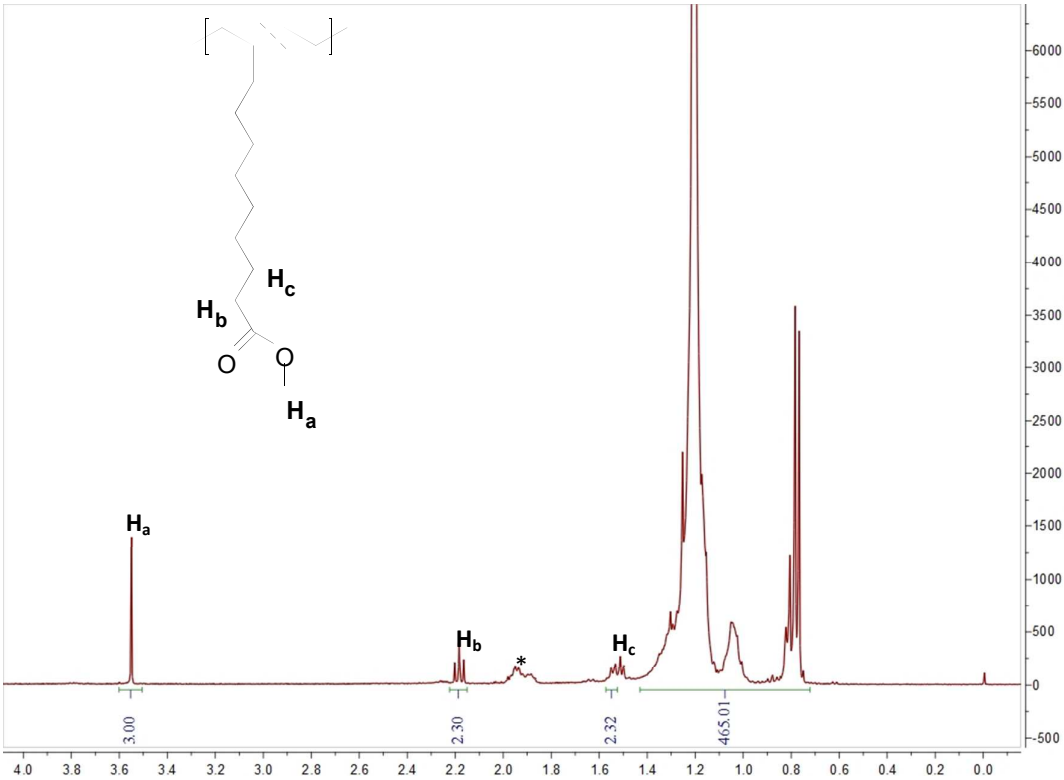


Figure S43. ^{1}H NMR spectrum of the polymer from table2, entry 3($C_2D_2Cl_4$, 120°C). *Solvent impurity in $C_2D_2Cl_4$.

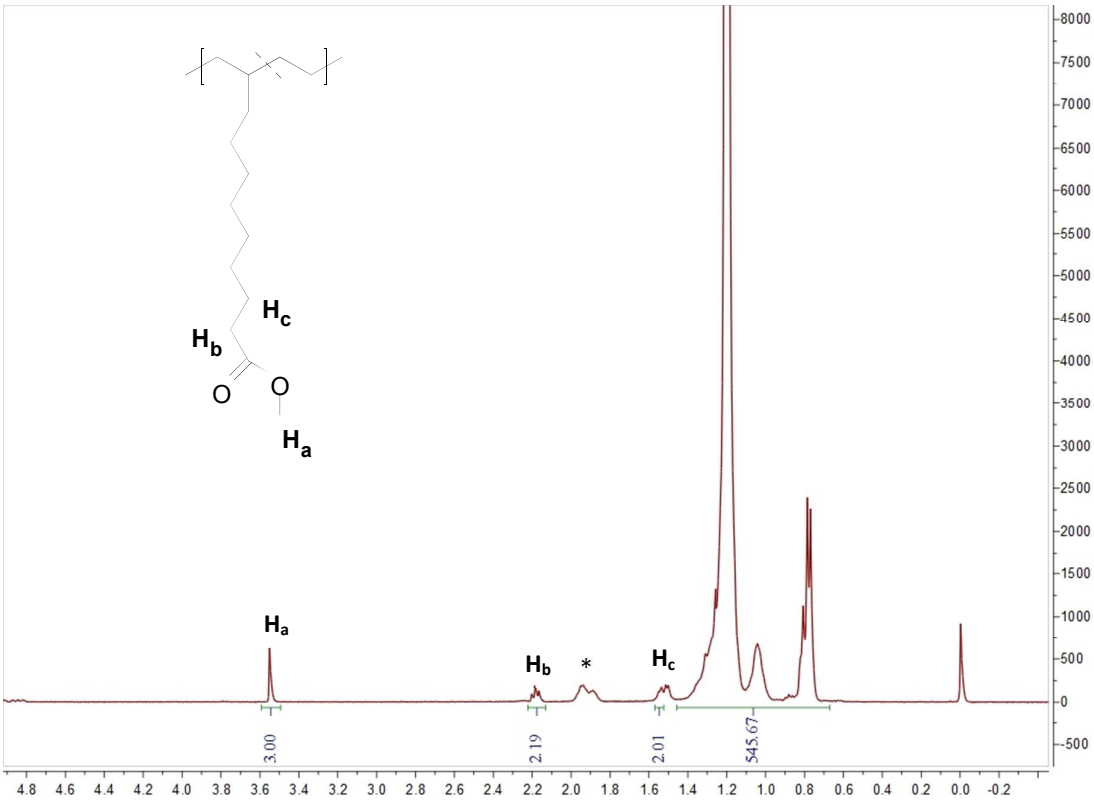


Figure S44. ^{1}H NMR spectrum of the polymer from table2, entry 4($C_2D_2Cl_4$, 120°C).

*Solvent impurity in $C_2D_2Cl_4$.

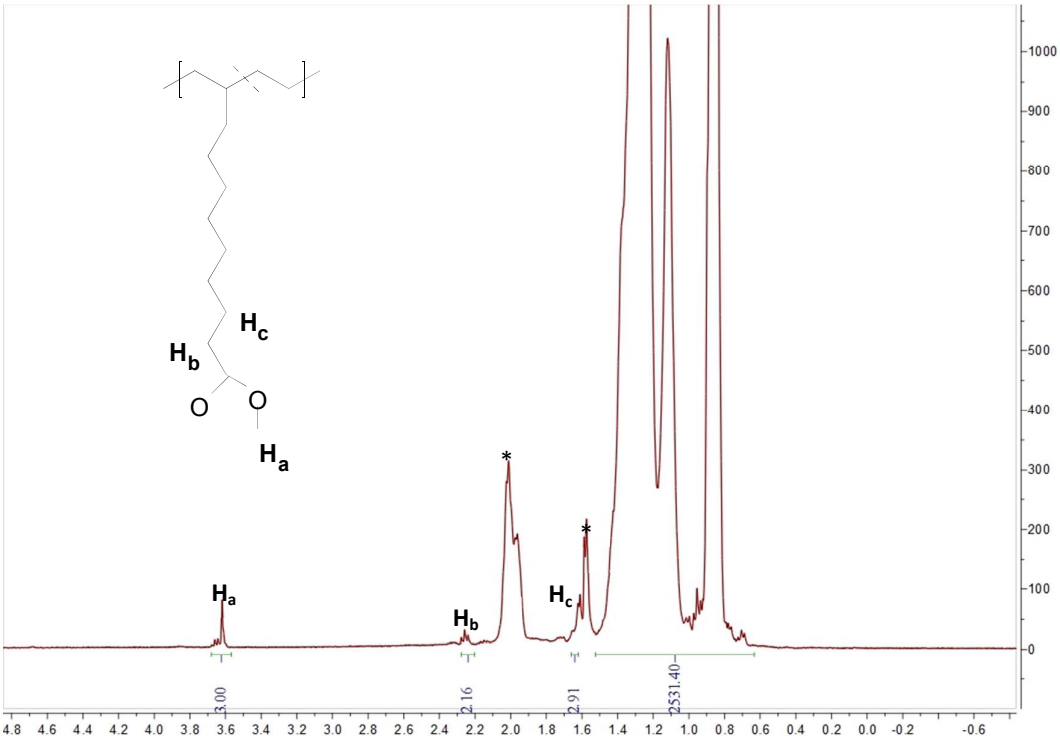


Figure S45. ^{1}H NMR spectrum of the polymer from table2, entry 5($C_2D_2Cl_4$, 120°C). *Solvent impurity in $C_2D_2Cl_4$.

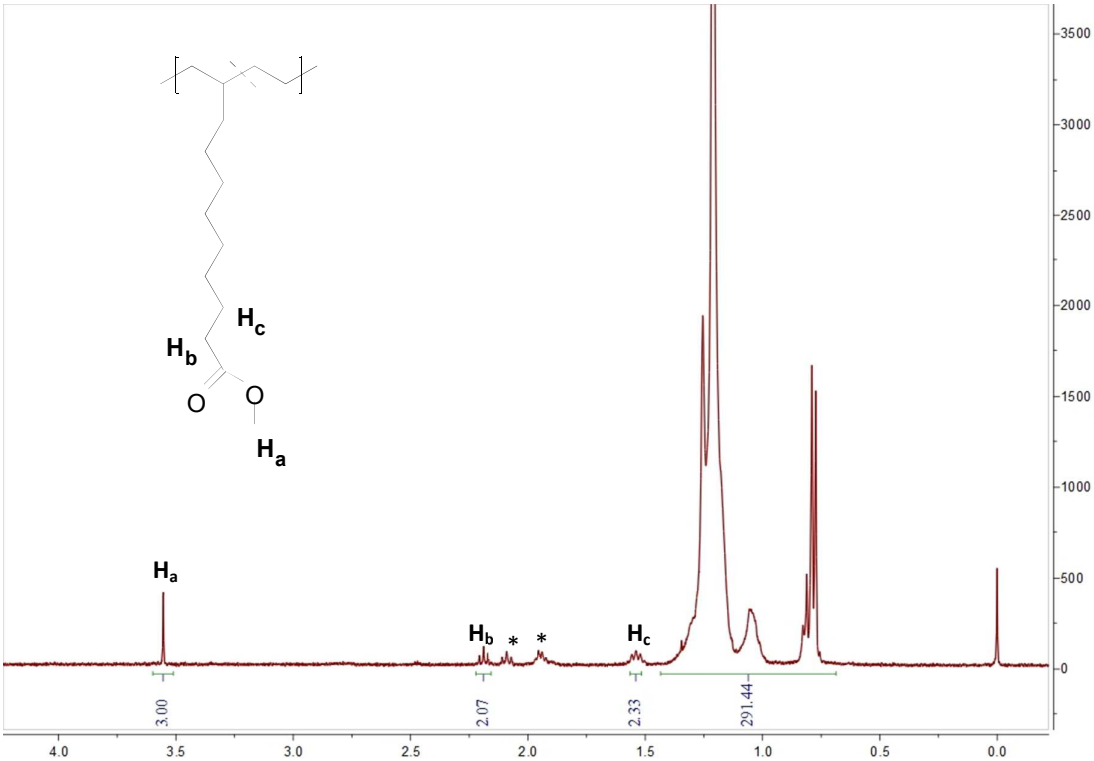


Figure S46. ^{1}H NMR spectrum of the polymer from table2, entry 6($C_2D_2Cl_4$, 120°C). *Solvent impurity in $C_2D_2Cl_4$.

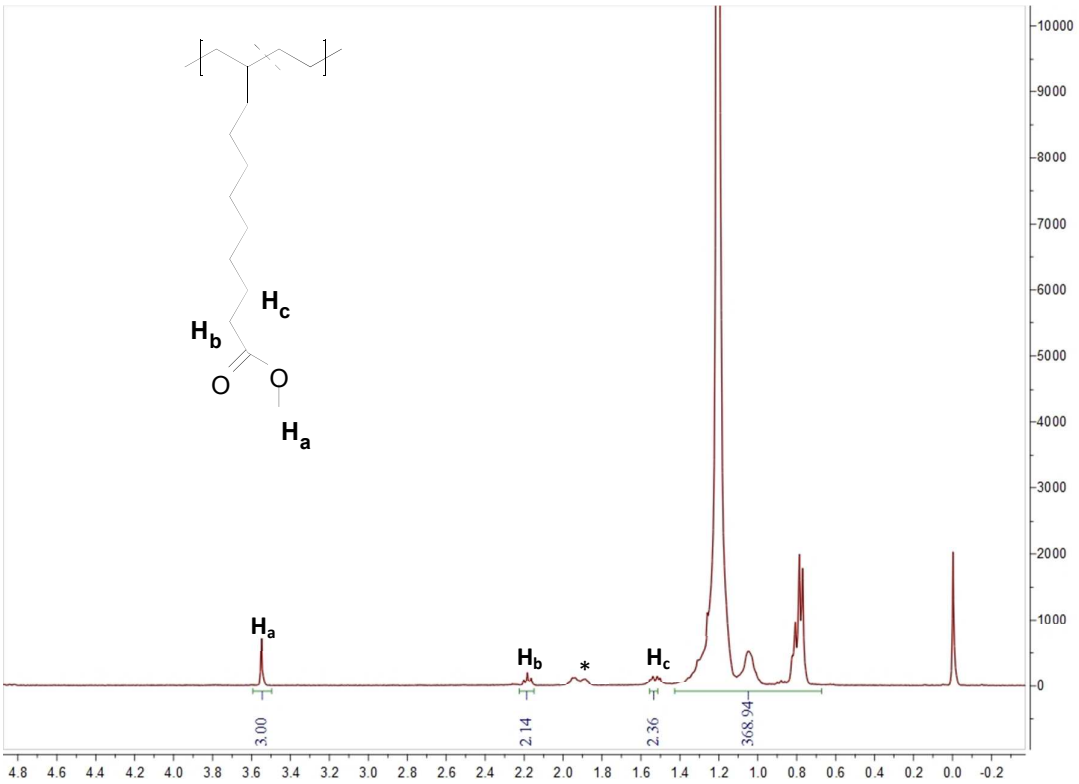


Figure S47. ^{1}H NMR spectrum of the polymer from table2, entry 7($C_2D_2Cl_4$, 120°C). *Solvent impurity in $C_2D_2Cl_4$.

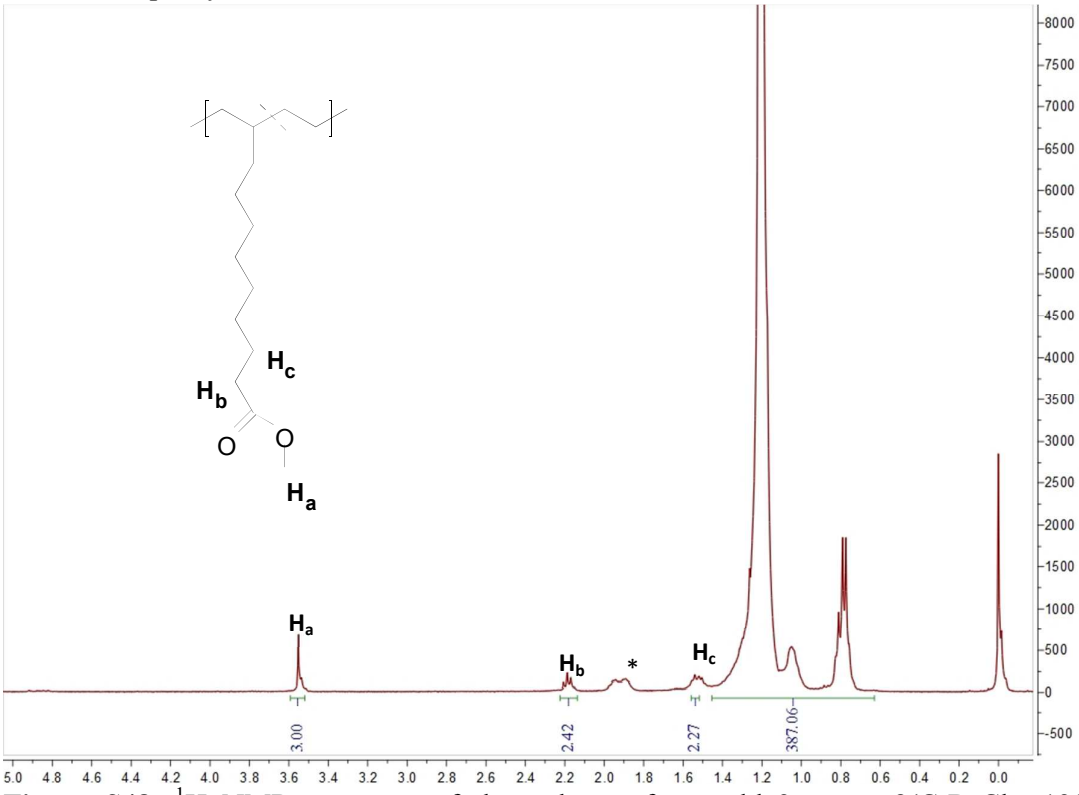


Figure S48. ^{1}H NMR spectrum of the polymer from table2, entry 8($C_2D_2Cl_4$, 120°C). *Solvent impurity in $C_2D_2Cl_4$.

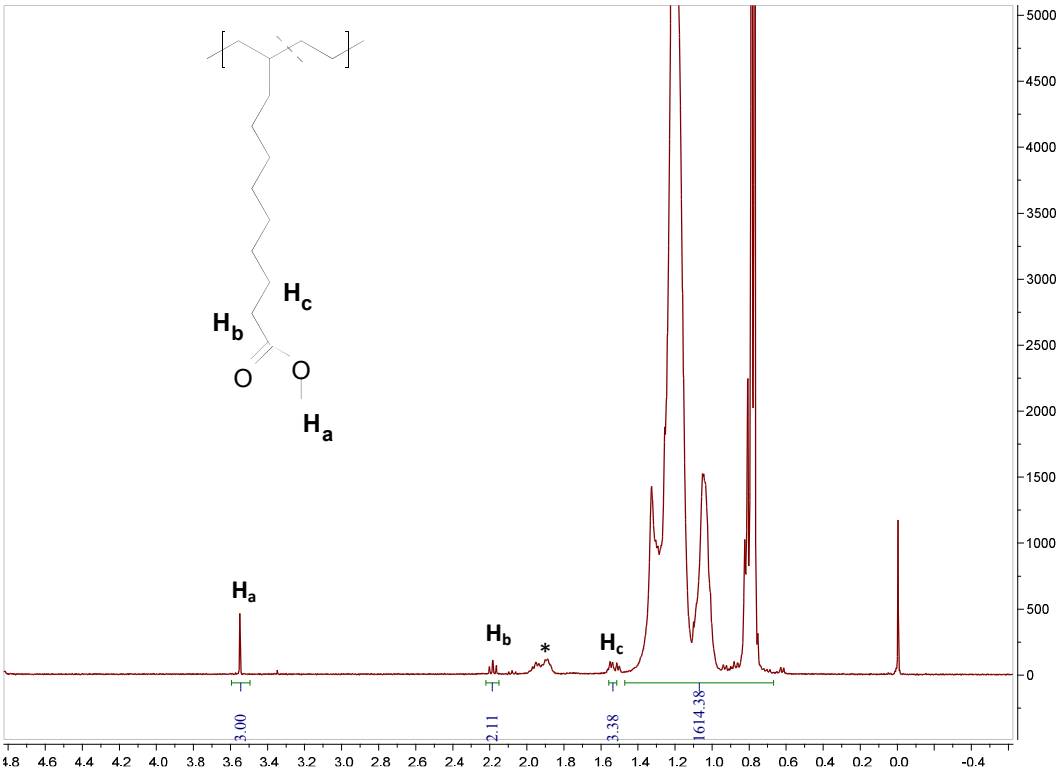


Figure S49. ^{1}H NMR spectrum of the polymer from table2, entry 9($C_2D_2Cl_4$, 120°C). *Solvent impurity in $C_2D_2Cl_4$.

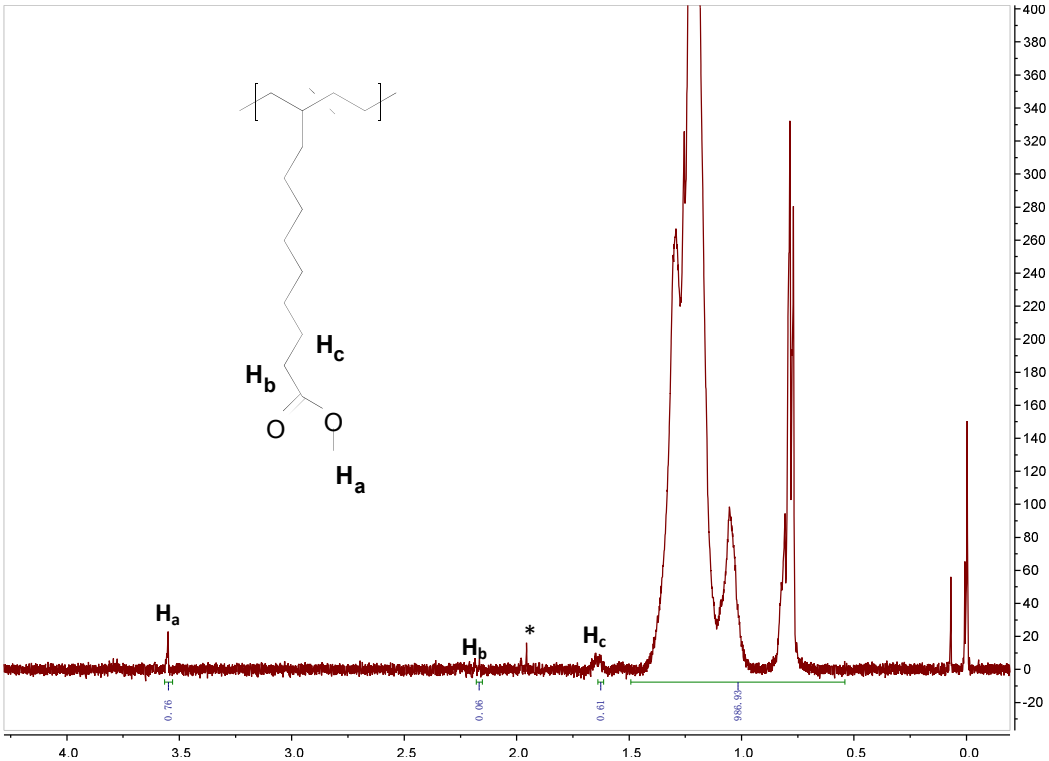


Figure S50. ^{1}H NMR spectrum of the polymer from table2, entry 10($C_2D_2Cl_4$, 120°C). *Solvent impurity in $C_2D_2Cl_4$.

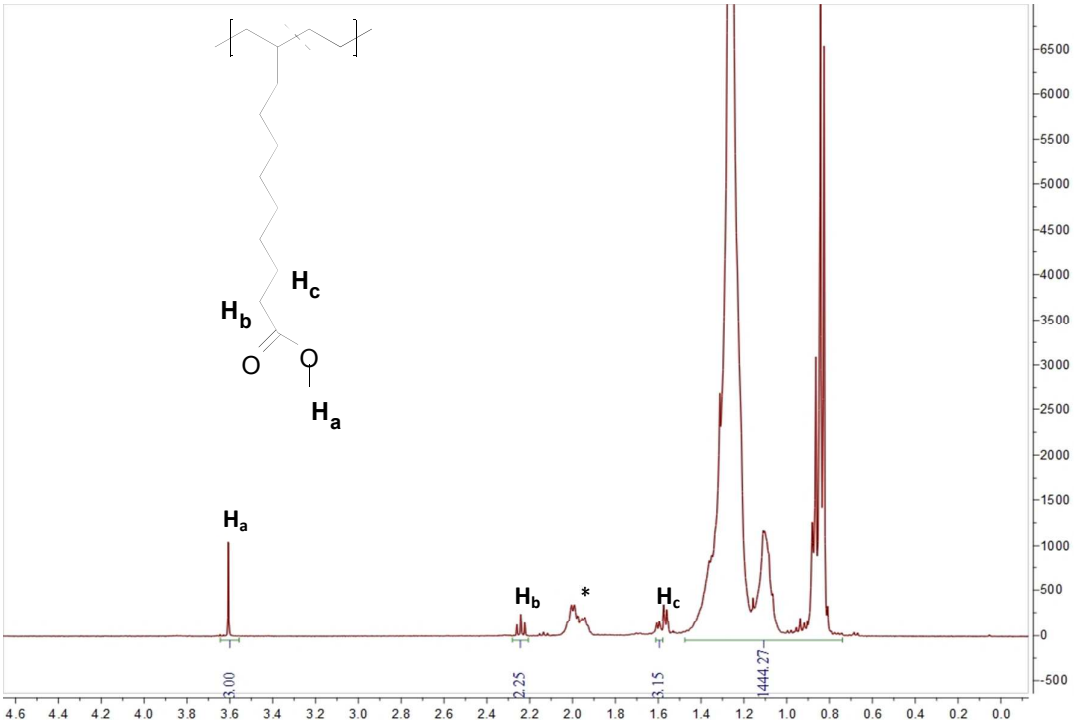


Figure S51. ^{1}H NMR spectrum of the polymer from table2, entry 11($C_2D_2Cl_4$, 120°C). *Solvent impurity in $C_2D_2Cl_4$.

4.4 DSC of polymer and copolymer.

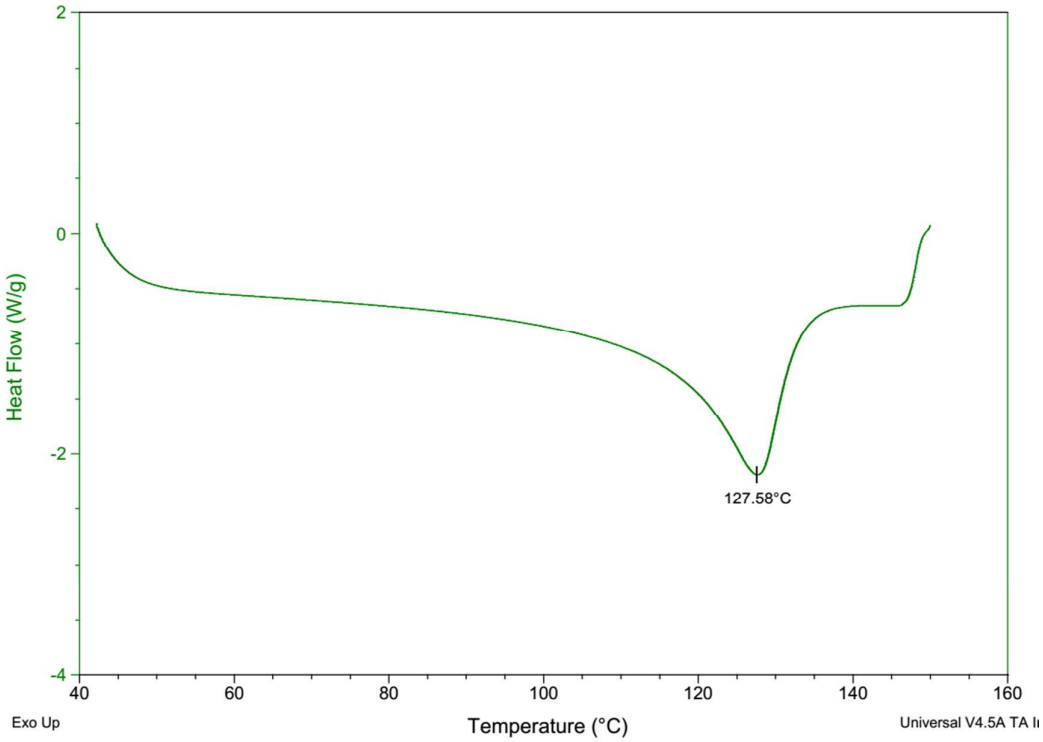


Figure S52. DSC of the polymer from table 1, entry 1.

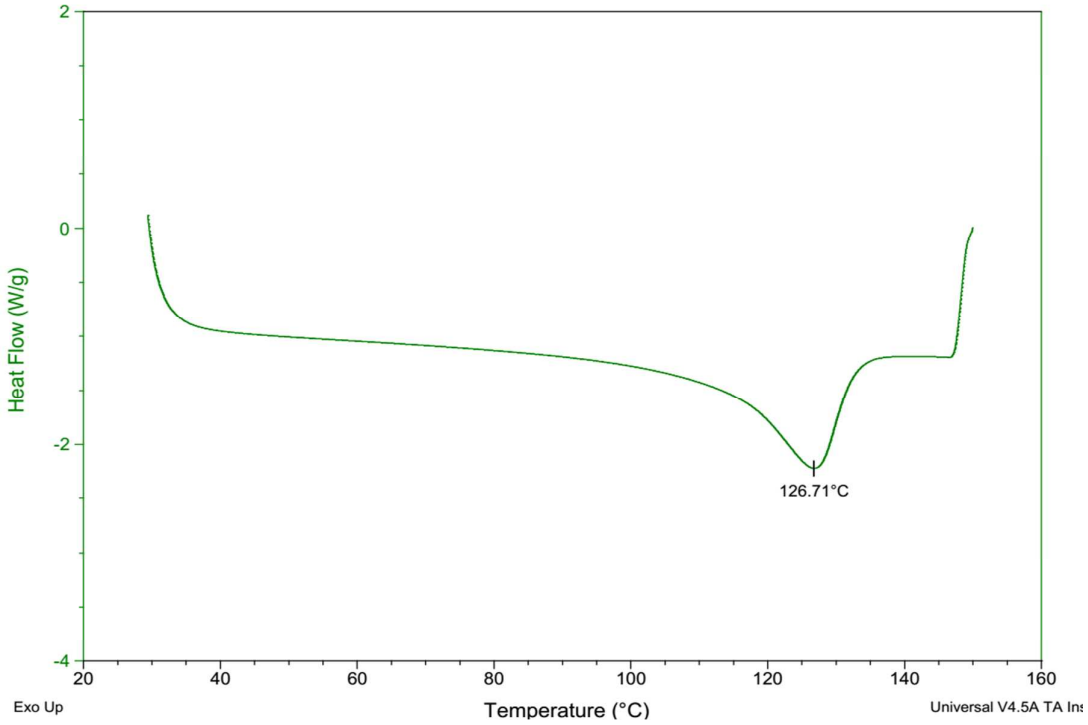


Figure S53. DSC of the polymer from table 1, entry 2.

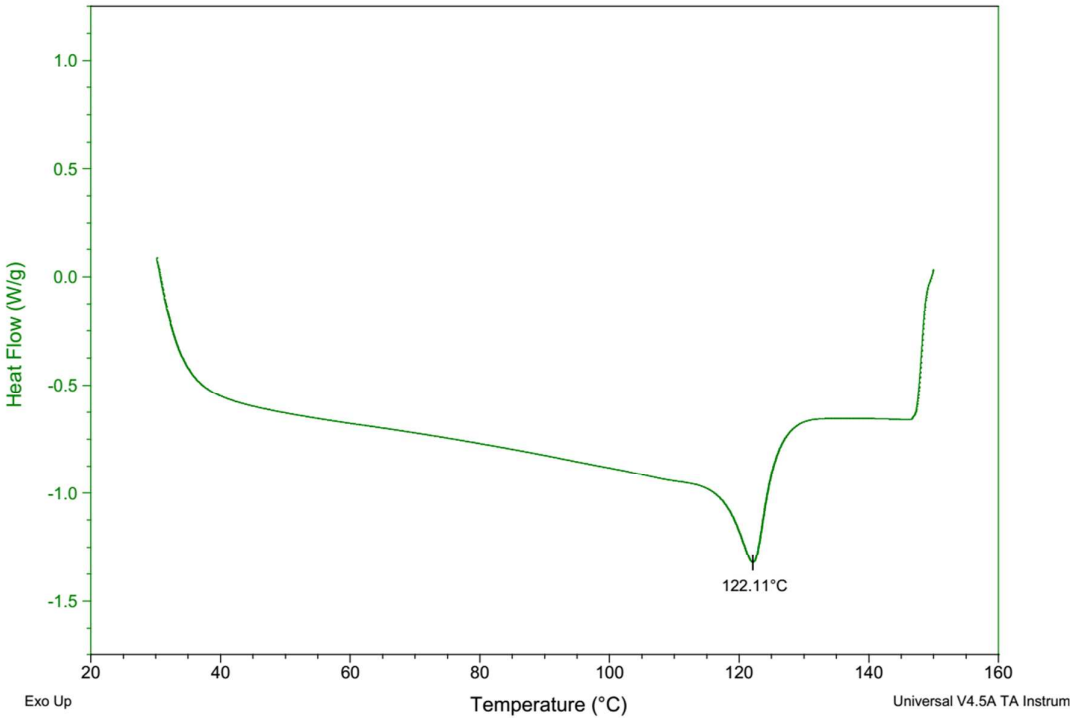


Figure S54. DSC of the polymer from table 1, entry 3.

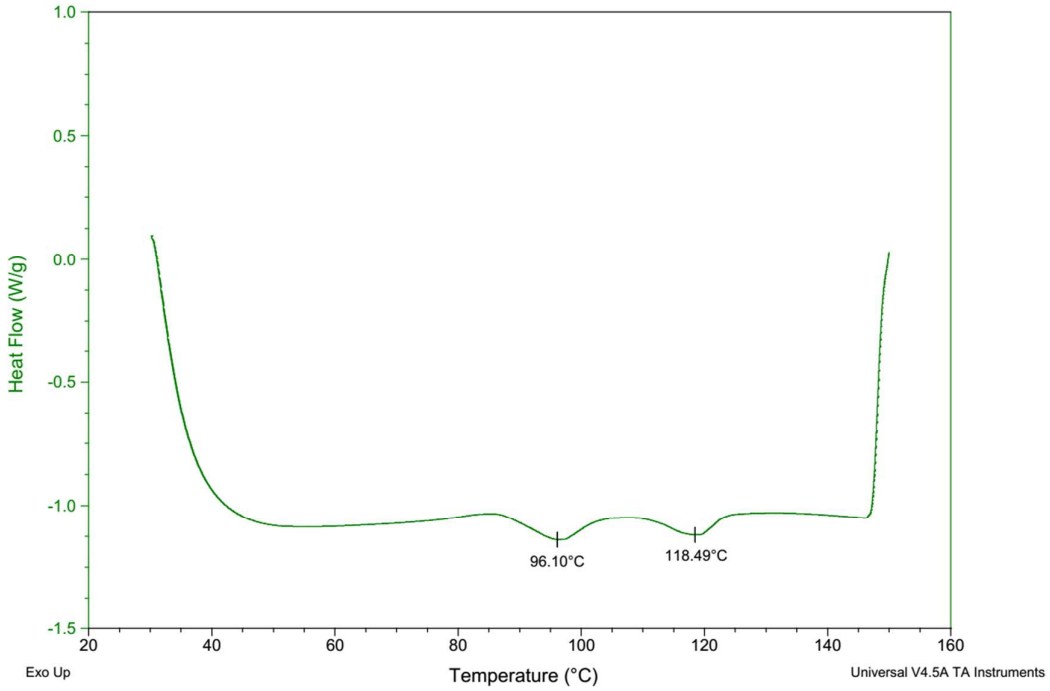


Figure S55. DSC of the polymer from table 1, entry 4.

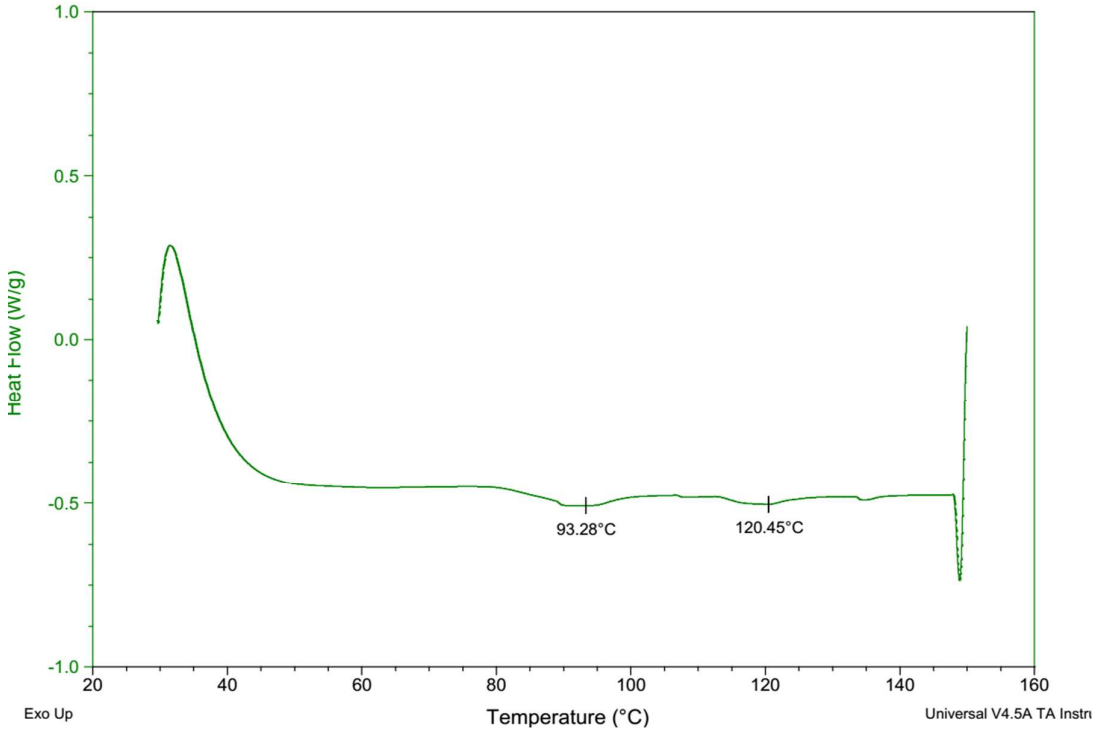


Figure S56. DSC of the polymer from table 1, entry 5.

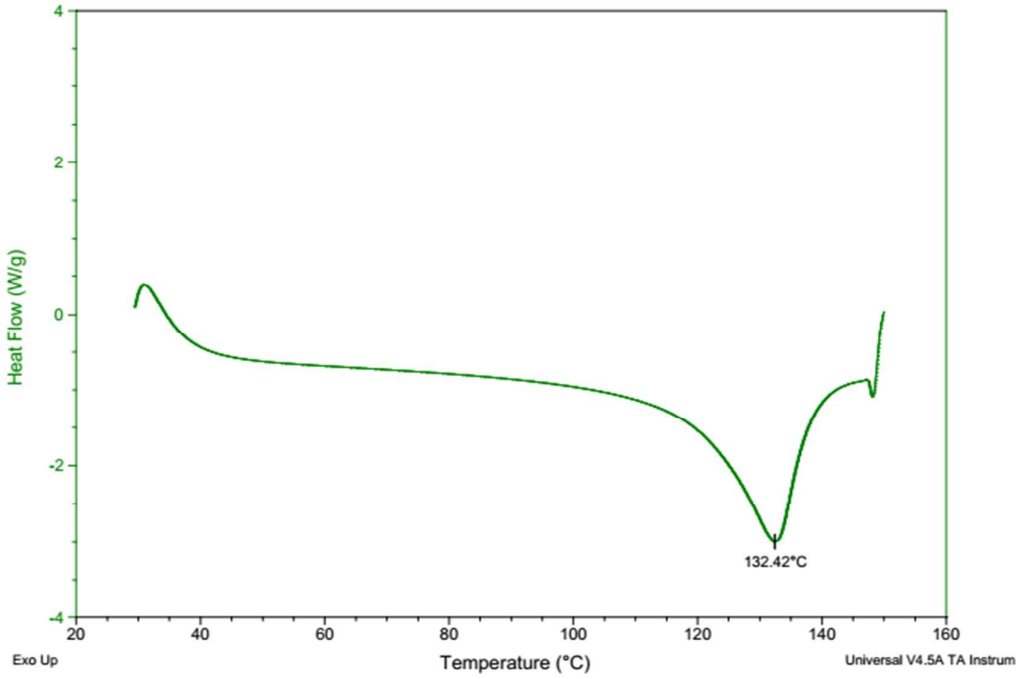


Figure S57. DSC of the polymer from table 1, entry 6.

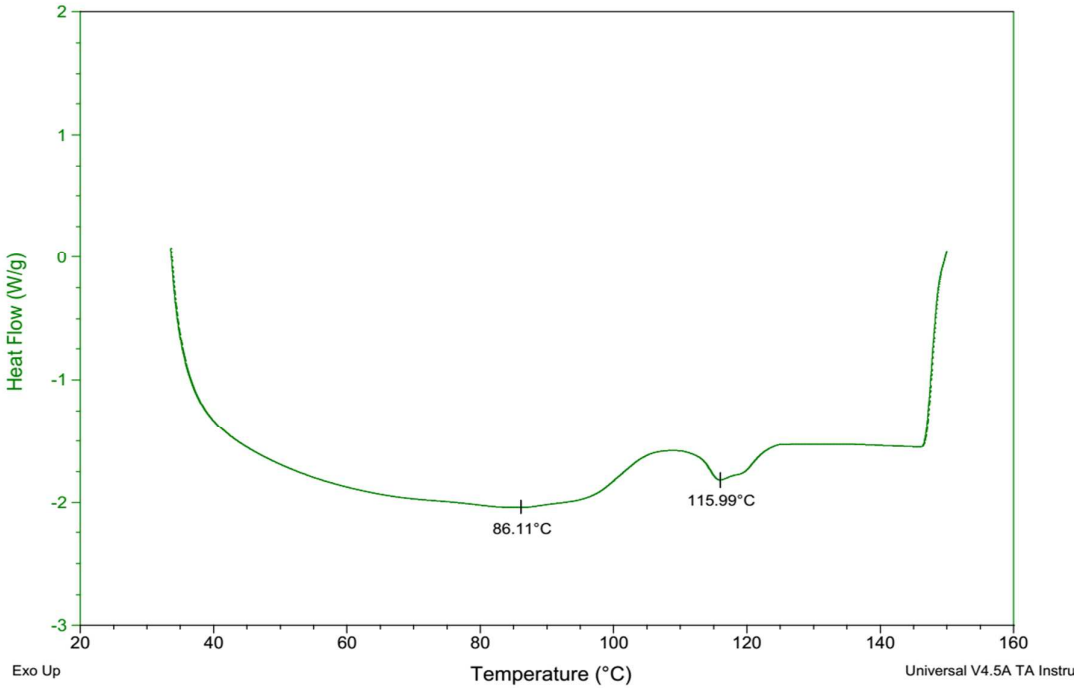


Figure S58. DSC of the polymer from table 1, entry 7.

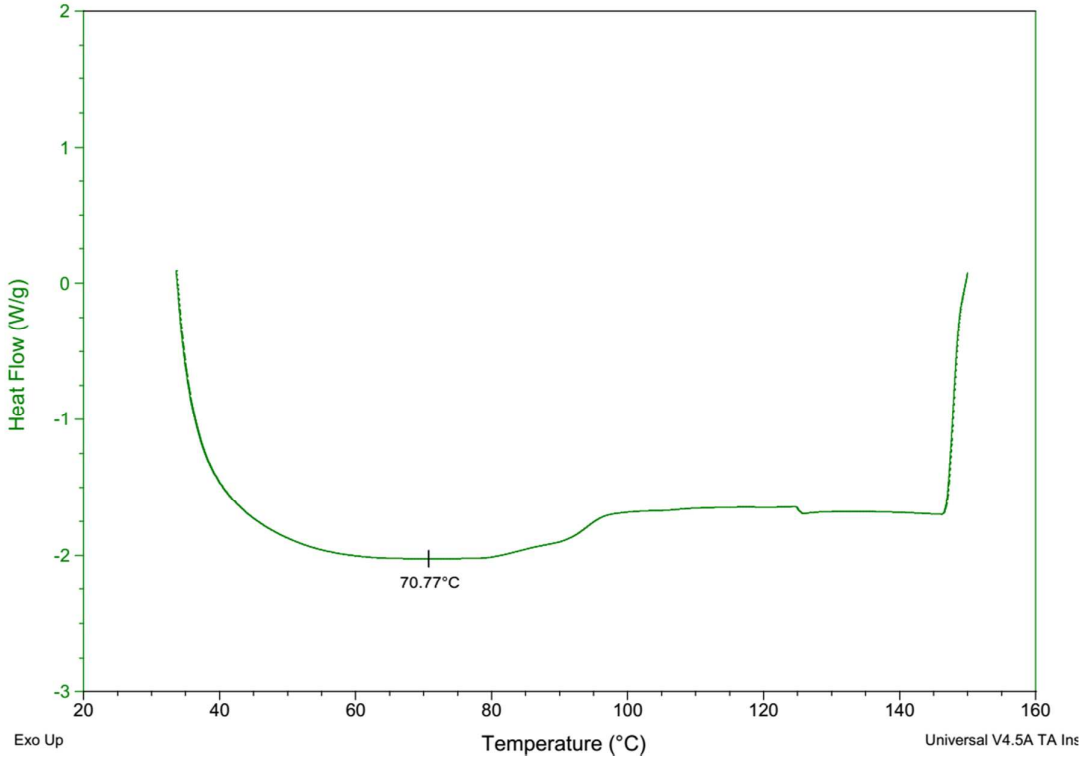


Figure S59. DSC of the polymer from table 1, entry 8.

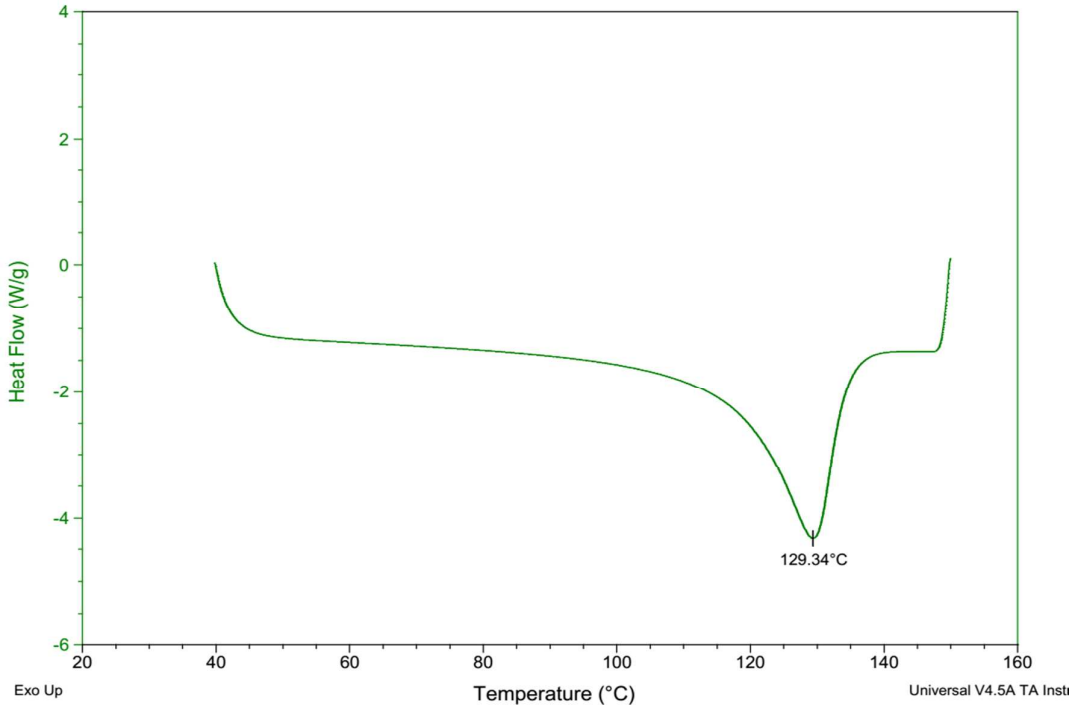


Figure S60. DSC of the polymer from table 1, entry 9.

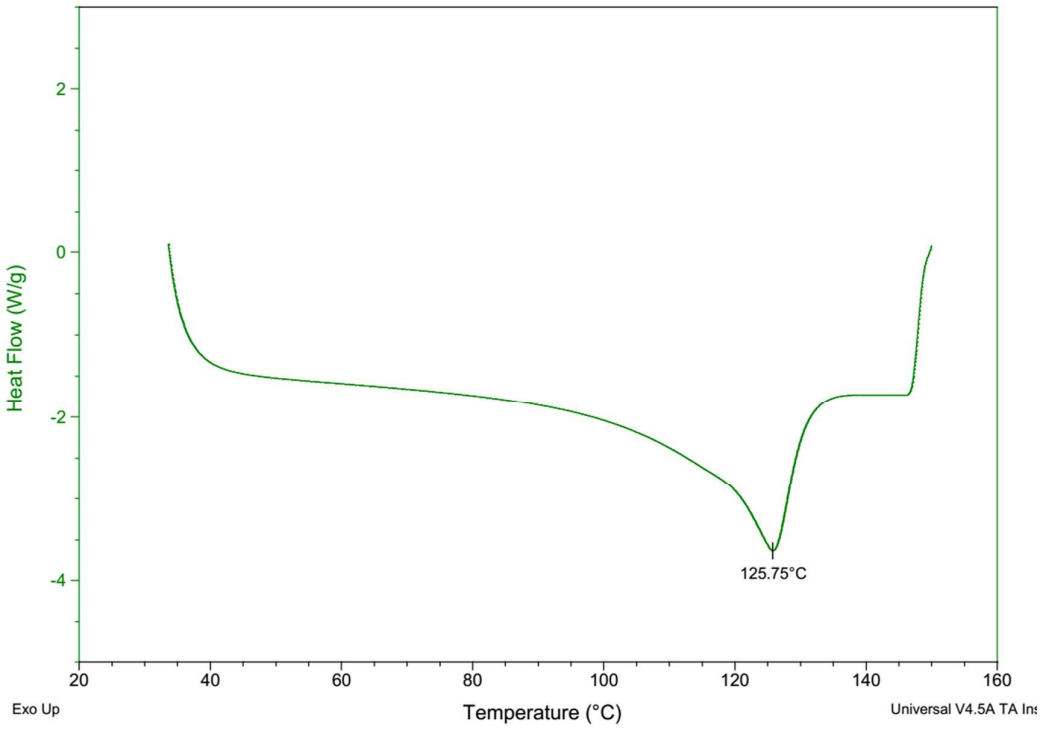


Figure S61. DSC of the polymer from table 1, entry 10.

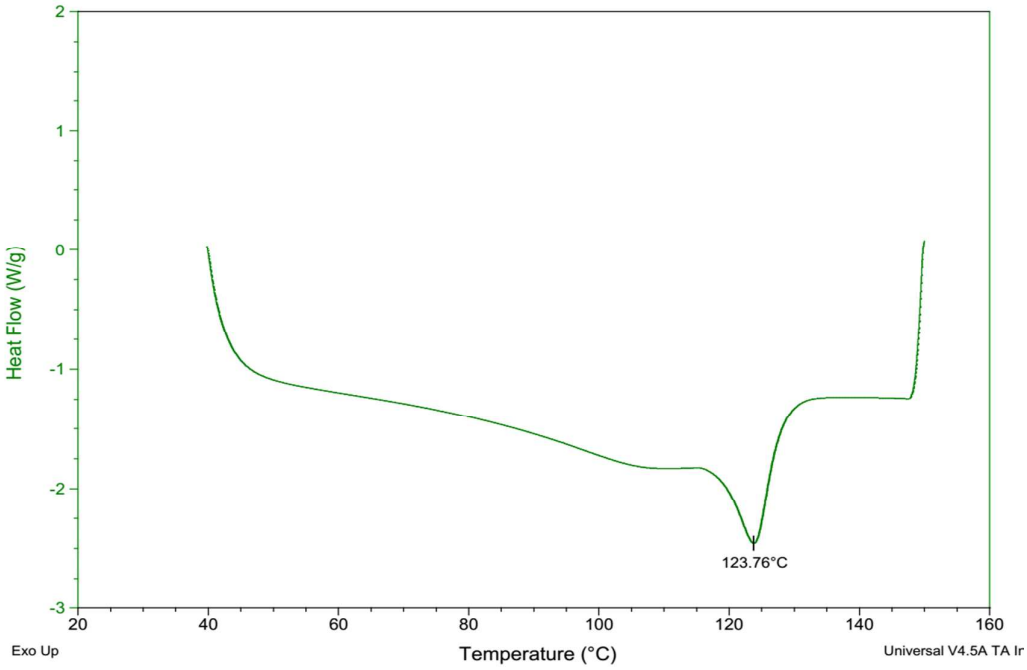


Figure S62. DSC of the polymer from table 1, entry 11.

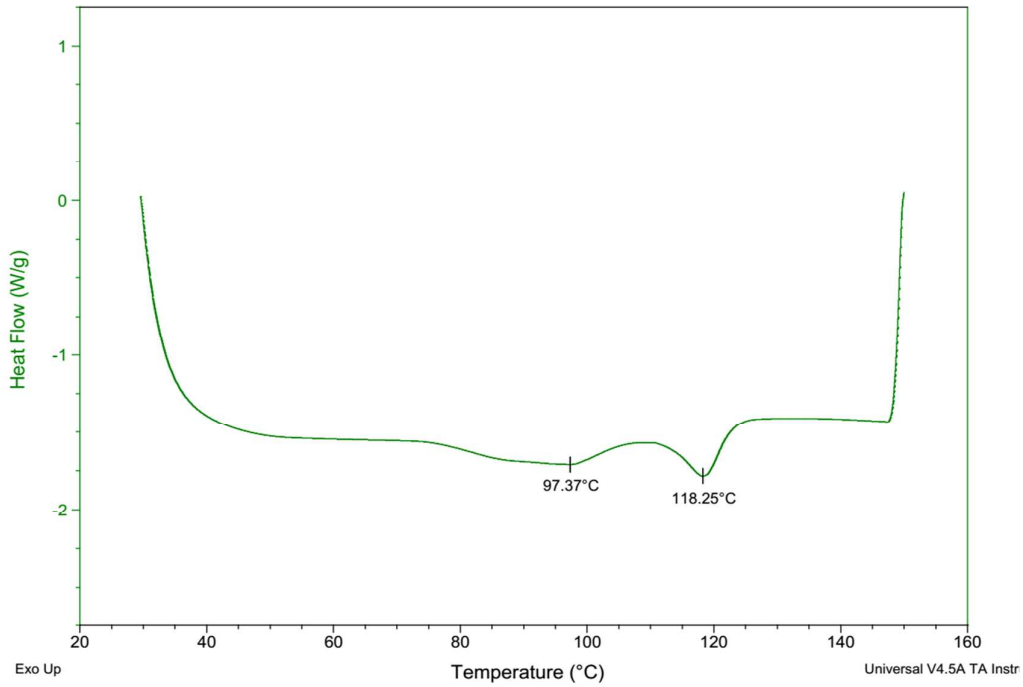


Figure S63. DSC of the polymer from table 1, entry 12.

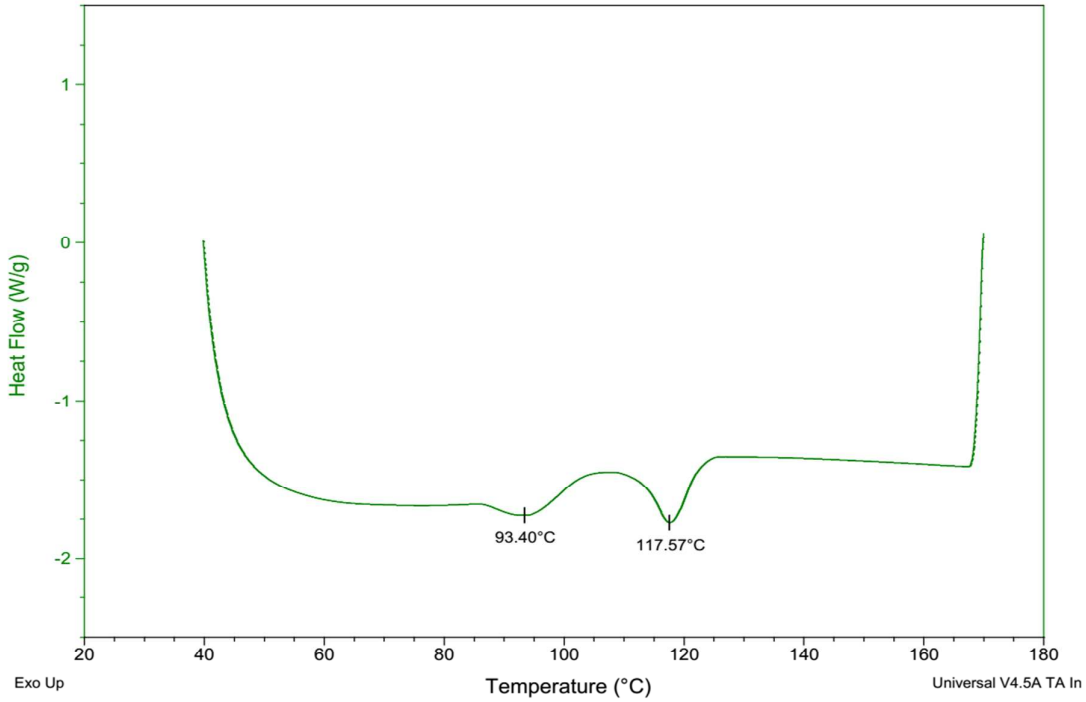


Figure S64. DSC of the polymer from table 1, entry 13.

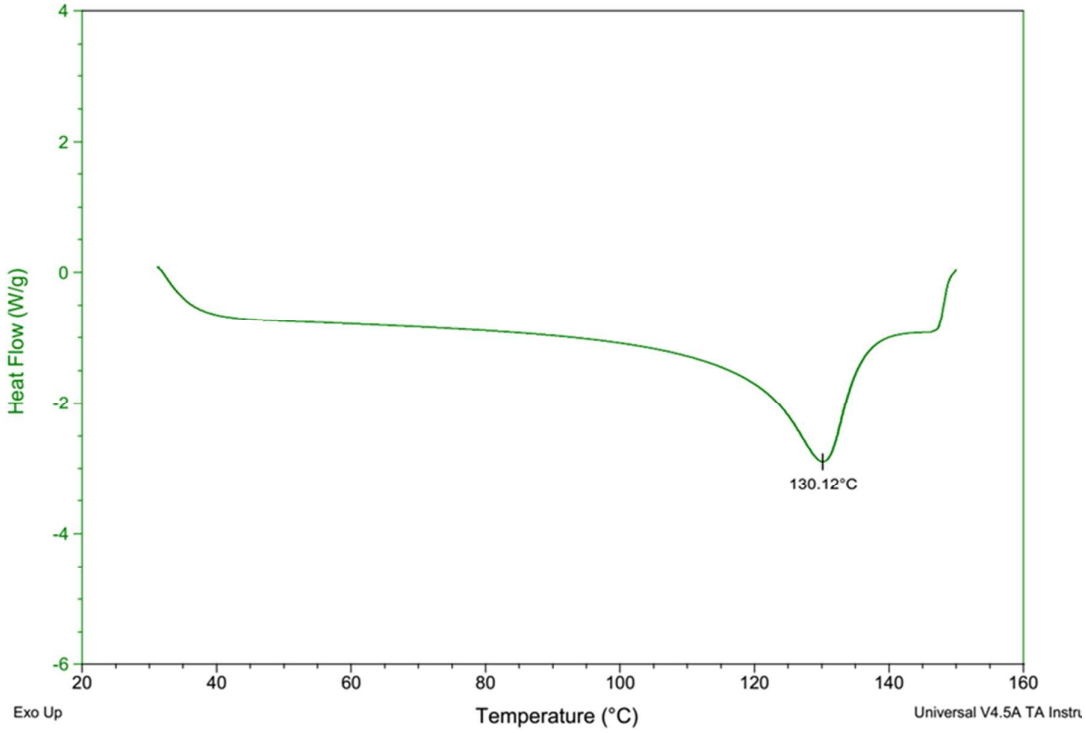


Figure S65. DSC of the polymer from table 1, entry 14.

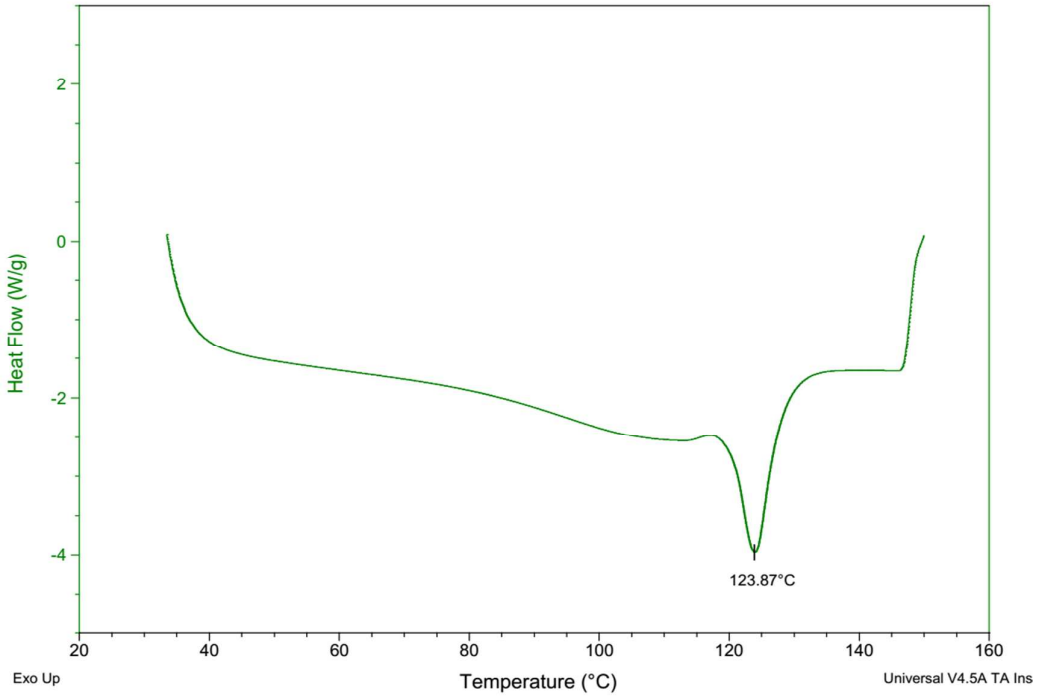


Figure S66. DSC of the polymer from table 1, entry 15.

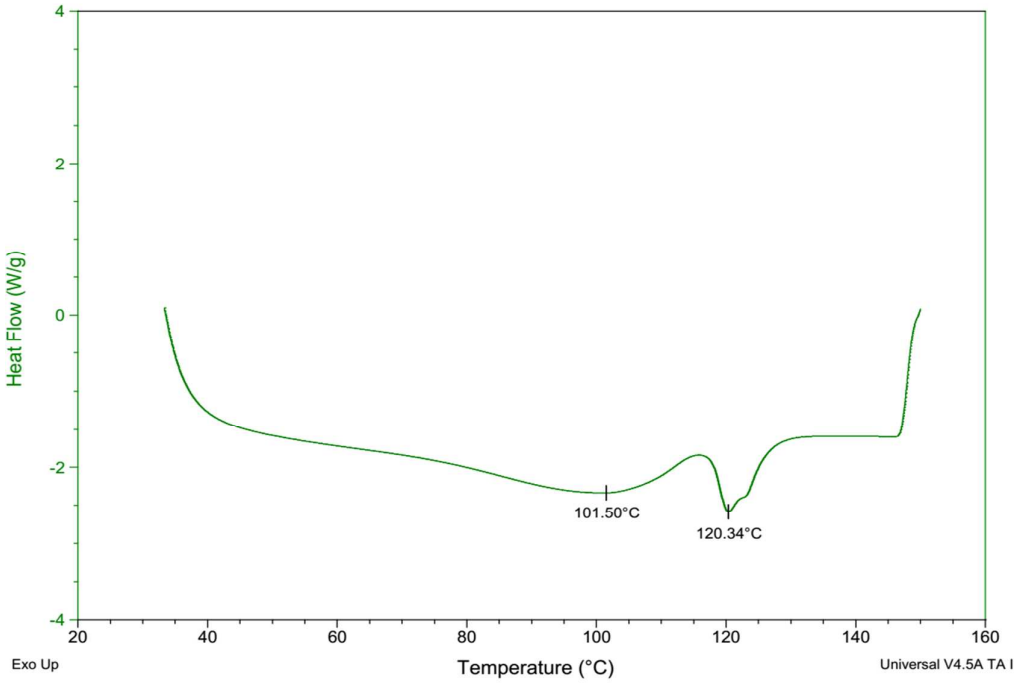


Figure S67. DSC of the polymer from table 1, entry 16.

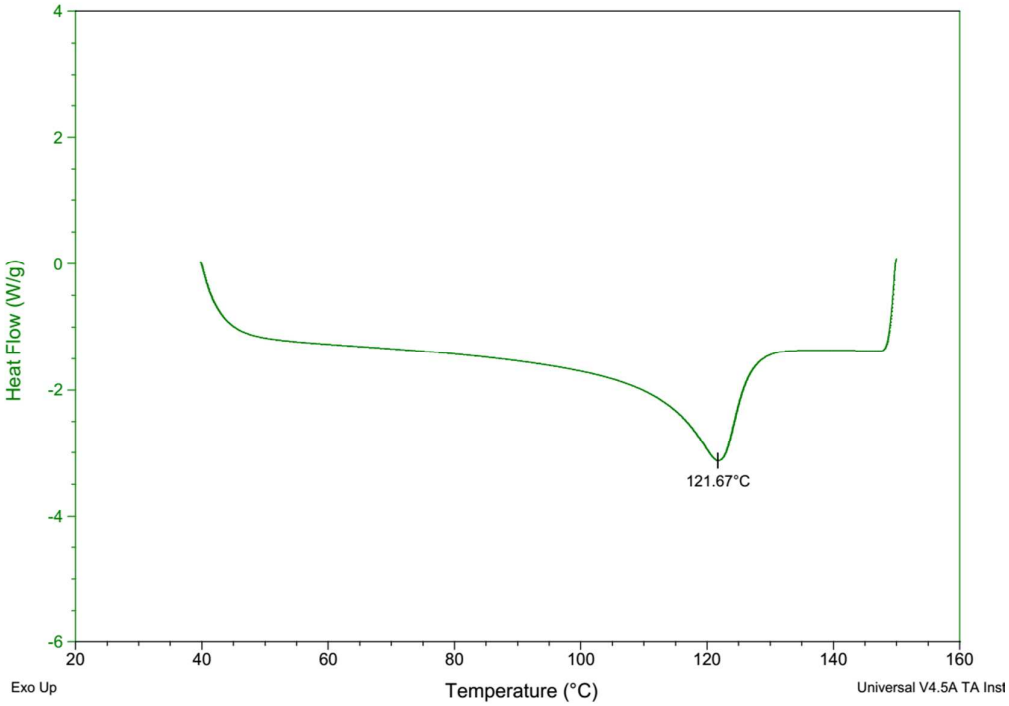


Figure S68. DSC of the polymer from table 1, entry 17.

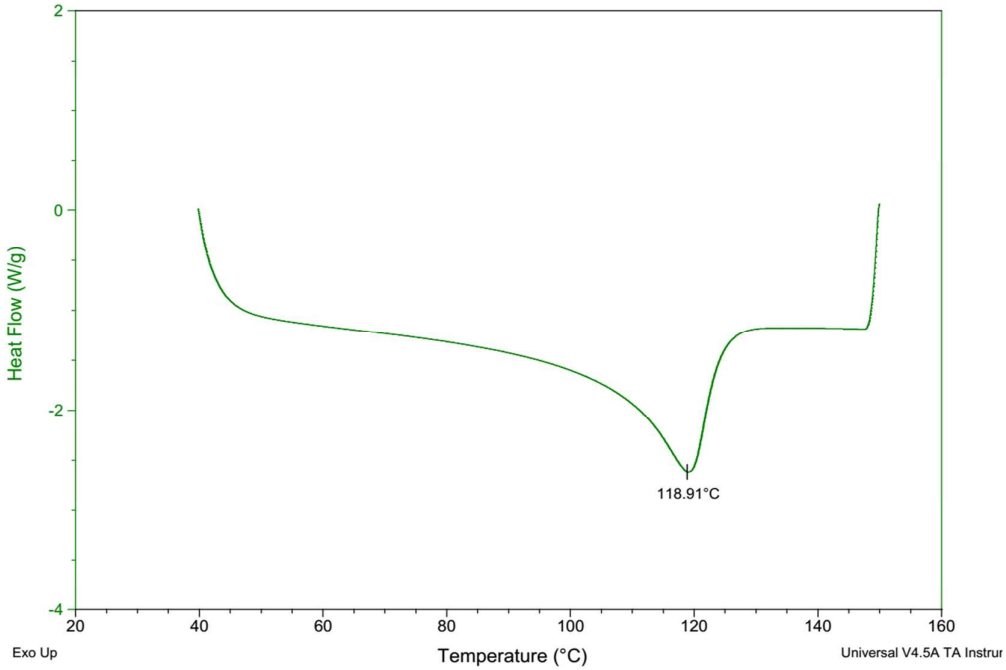


Figure S69. DSC of the polymer from table 1, entry 18.

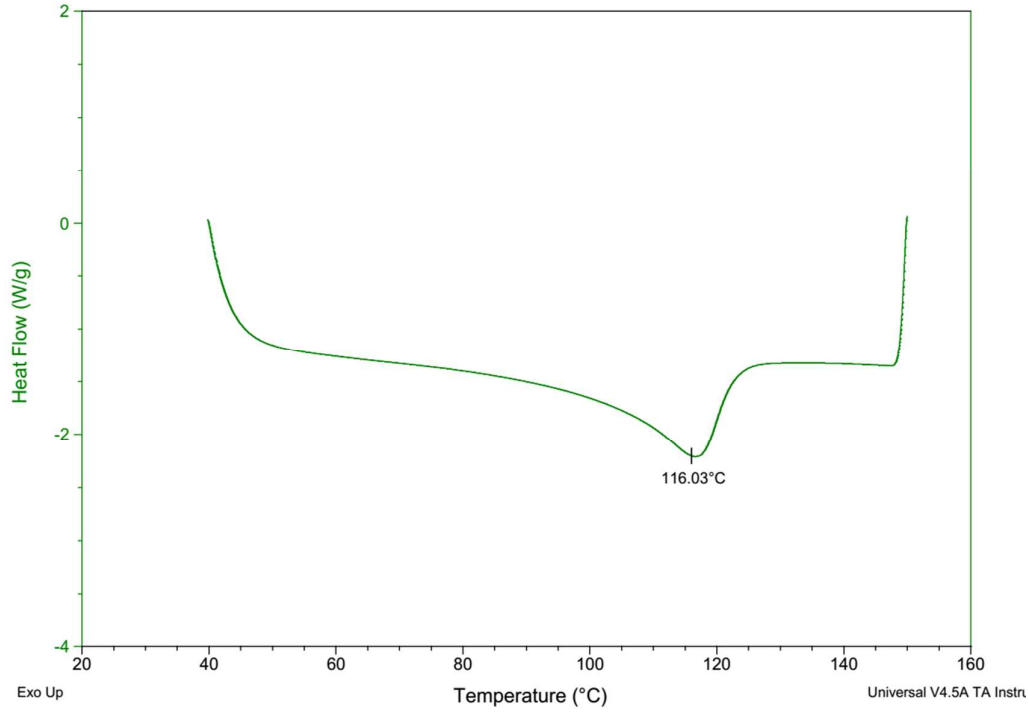


Figure S70. DSC of the polymer from table 1, entry 19.

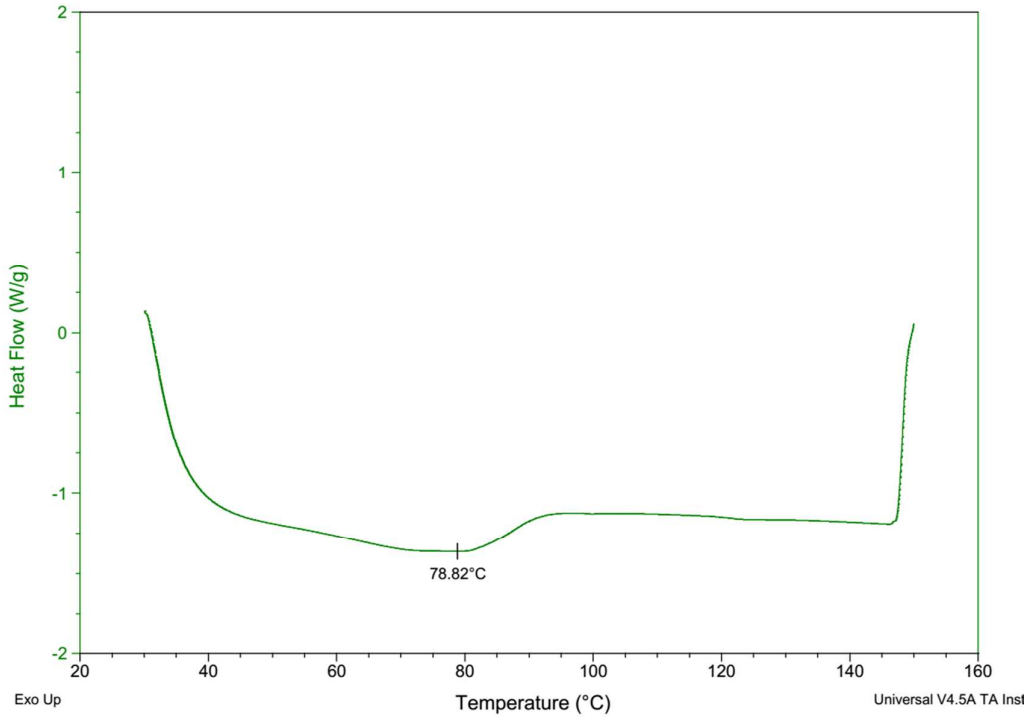


Figure S71. DSC of the polymer from table 1, entry 20.

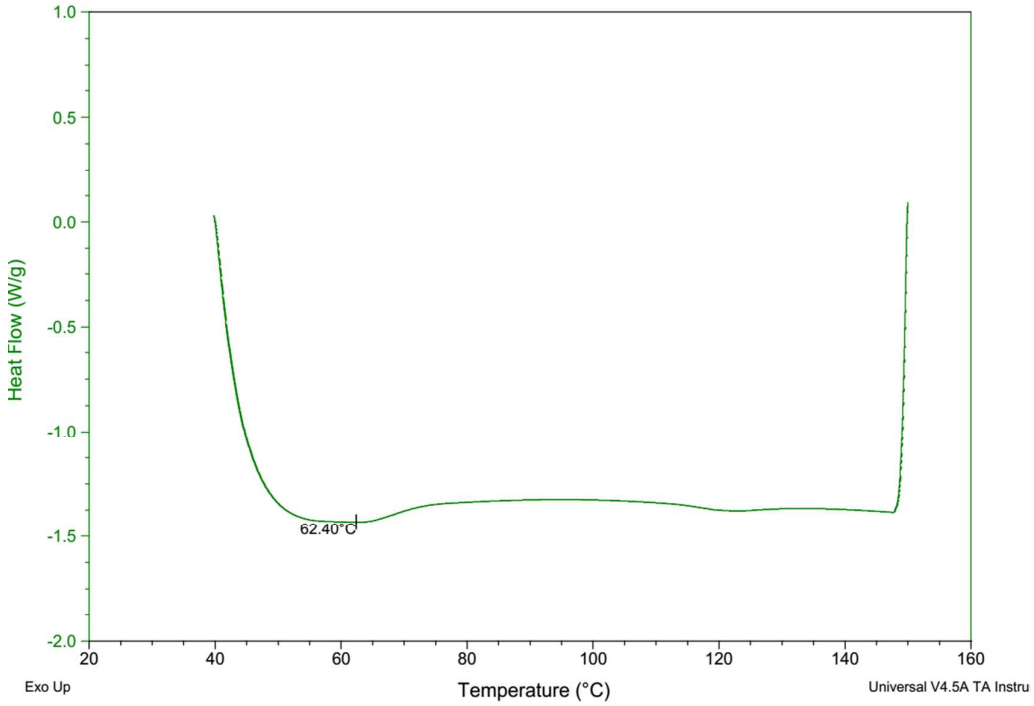


Figure S72. DSC of the polymer from table 1, entry 21.

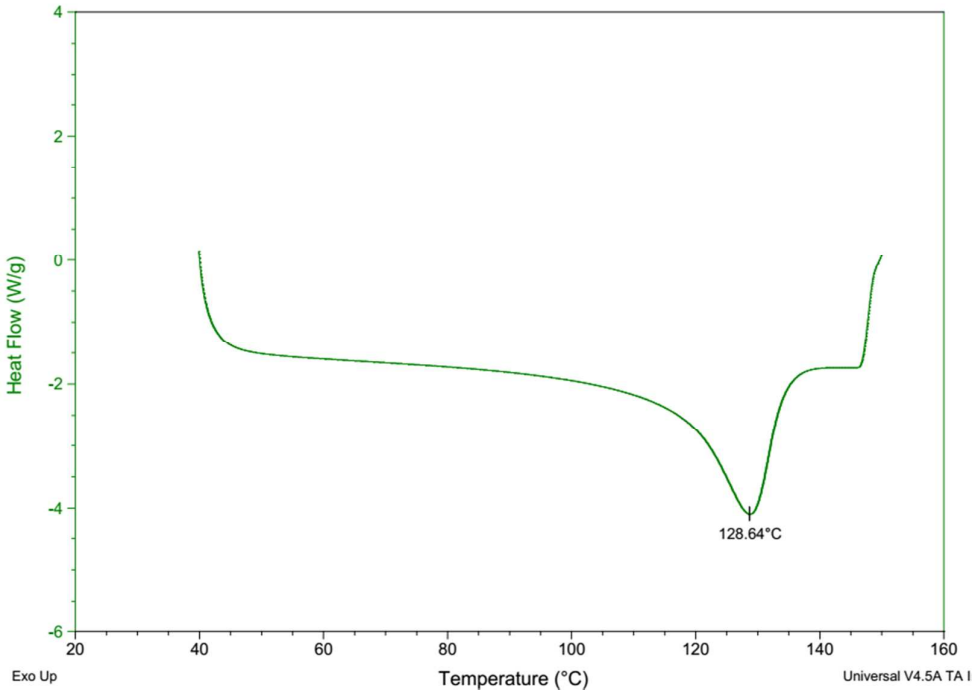


Figure S73. DSC of the polymer from table 1, entry 23.

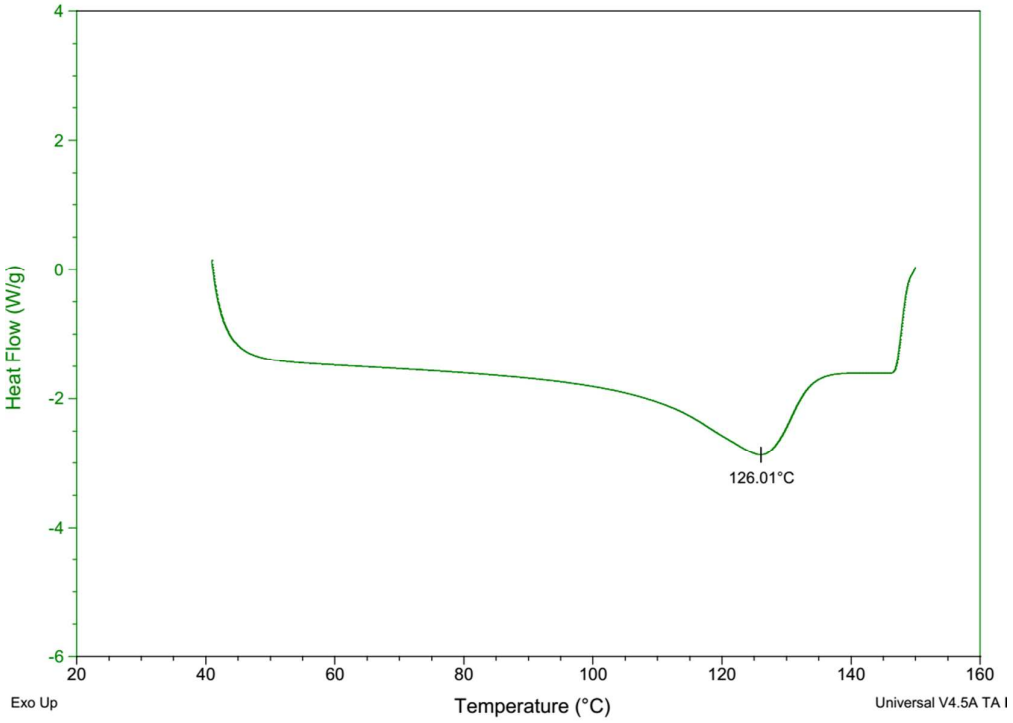


Figure S74. DSC of the polymer from table 1, entry 24.

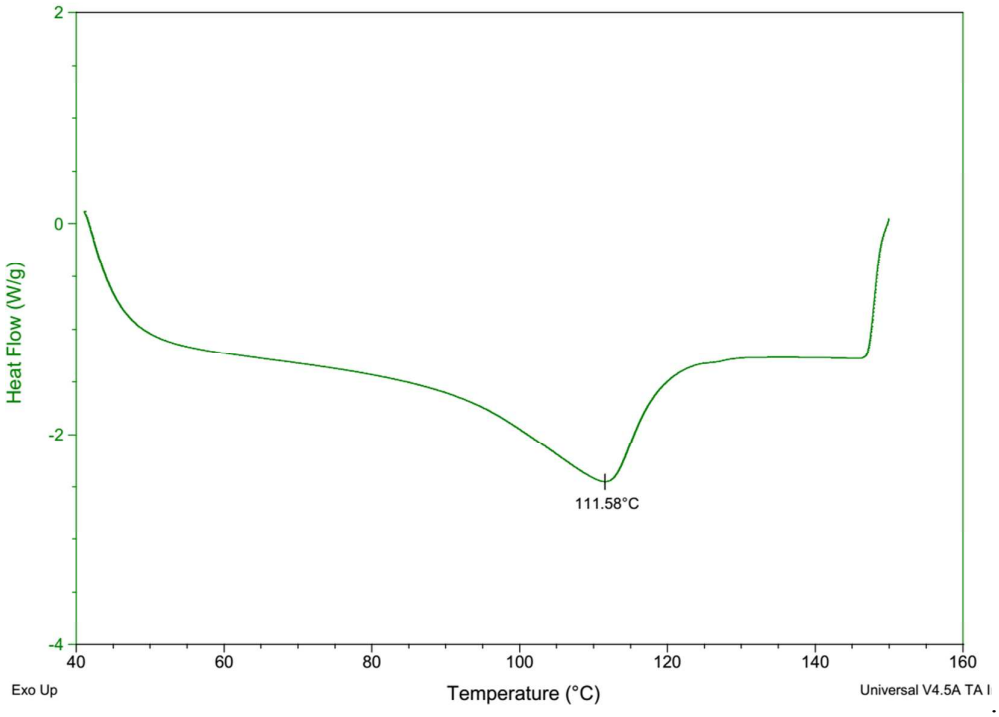


Figure S75. DSC of the polymer from table 1, entry 25.

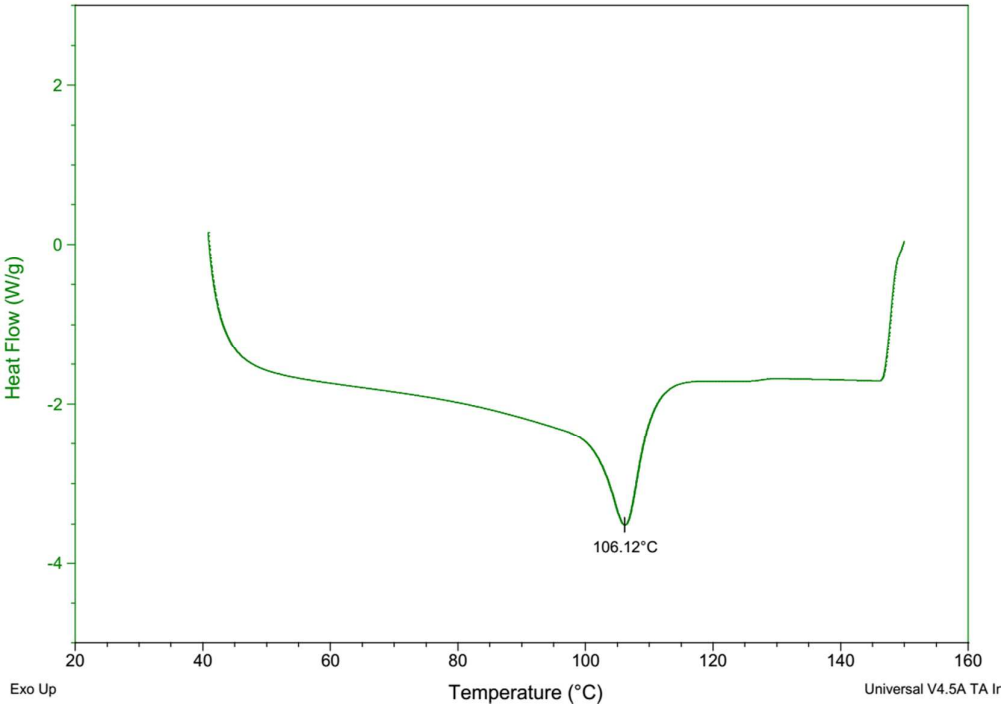


Figure S76. DSC of the polymer from table 1, entry 26.

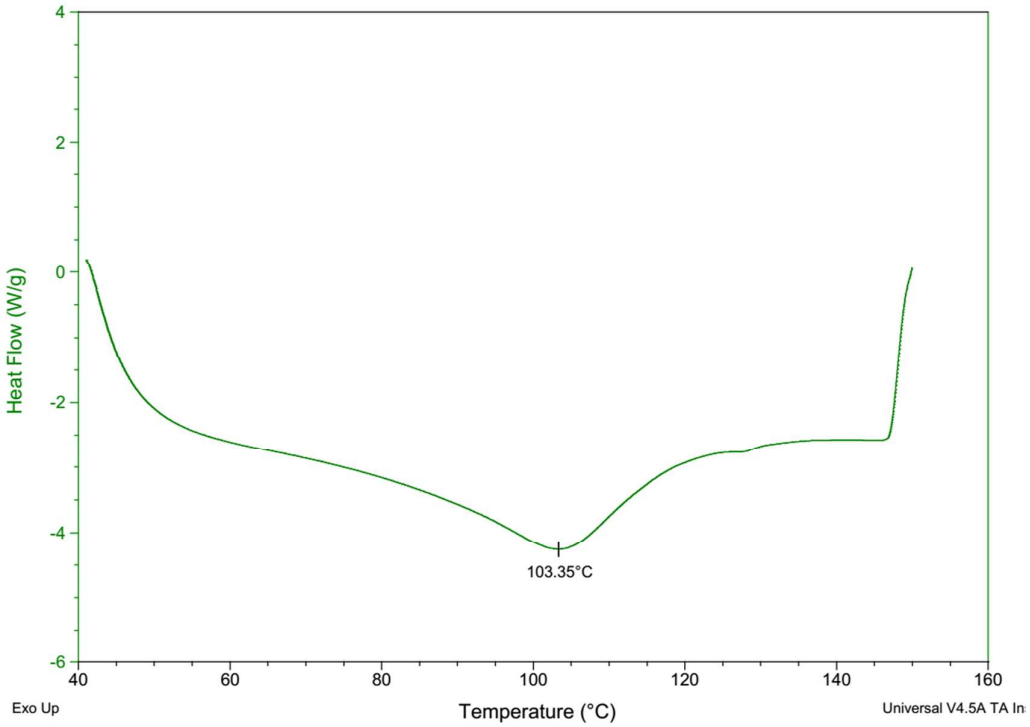


Figure S77. DSC of the polymer from table 1, entry 27.

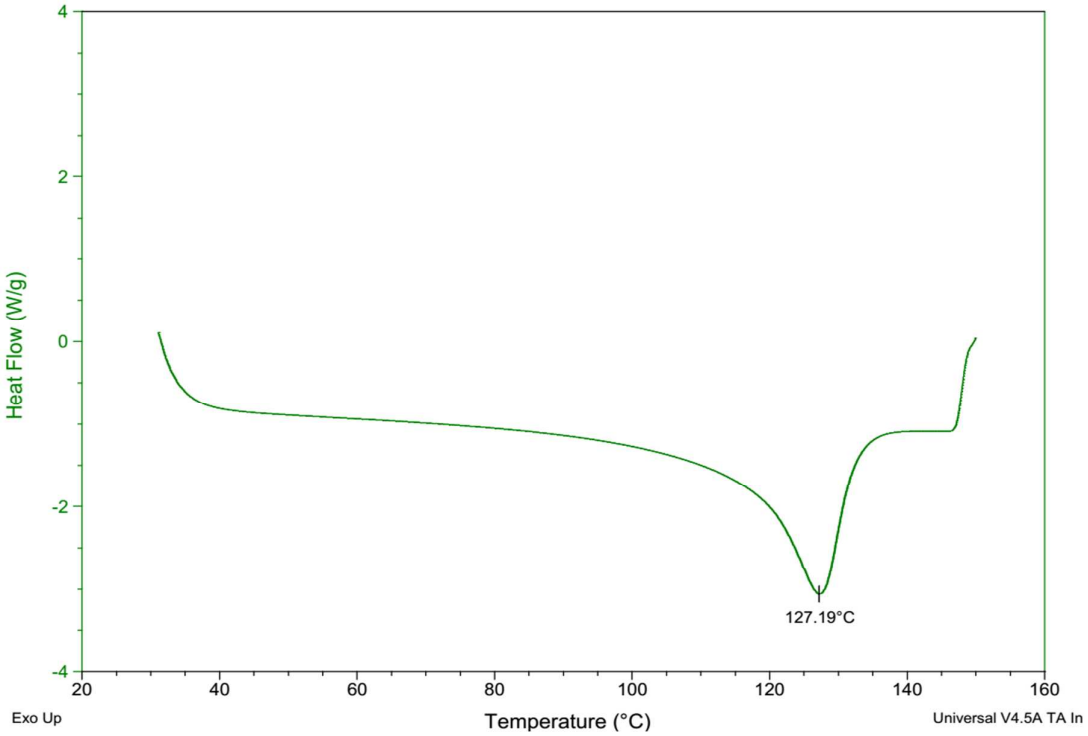


Figure S78. DSC of the polymer from table 1, entry 28.

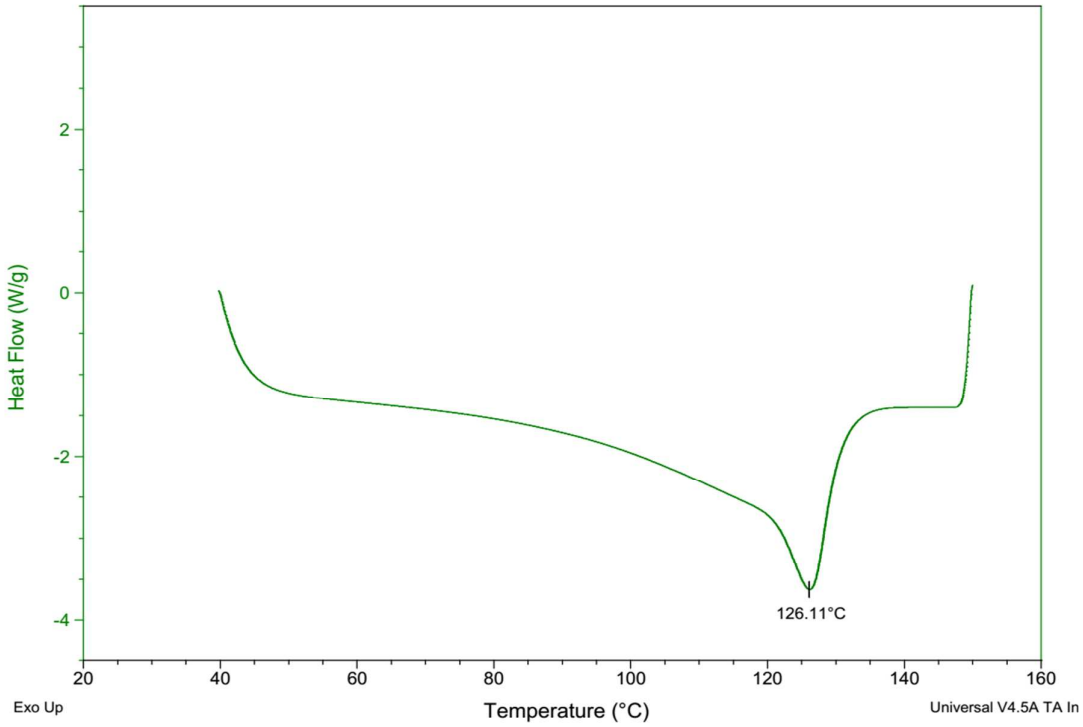


Figure S79. DSC of the polymer from table 1, entry 29.

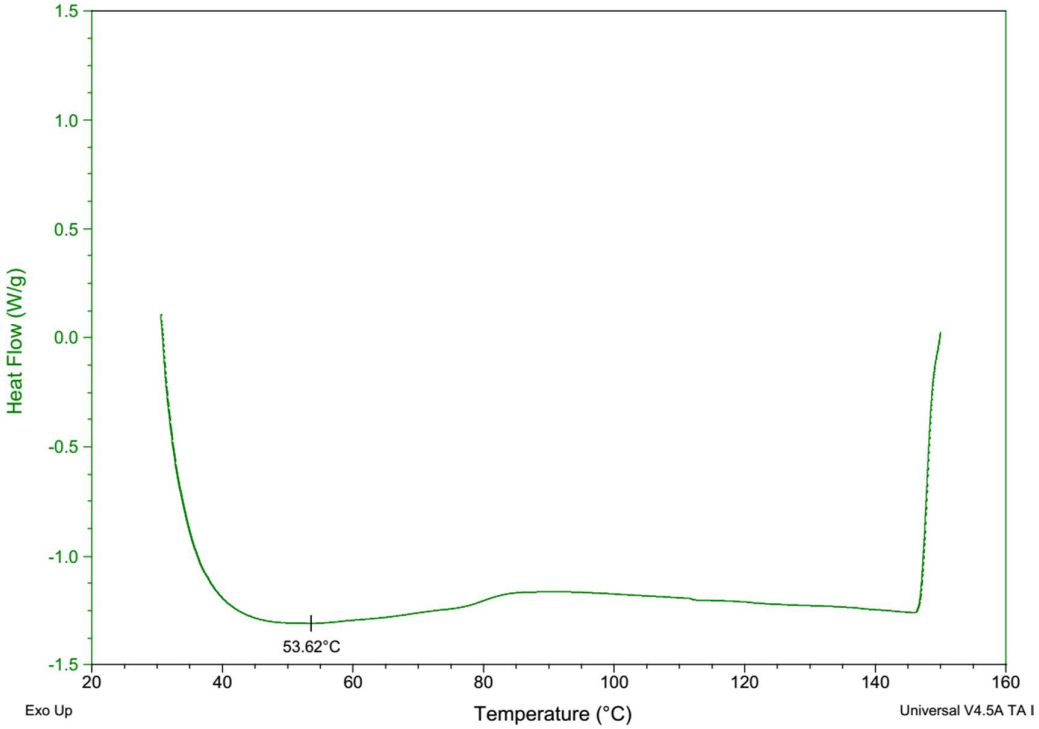


Figure S80. DSC of the polymer from table 2, entry 1.

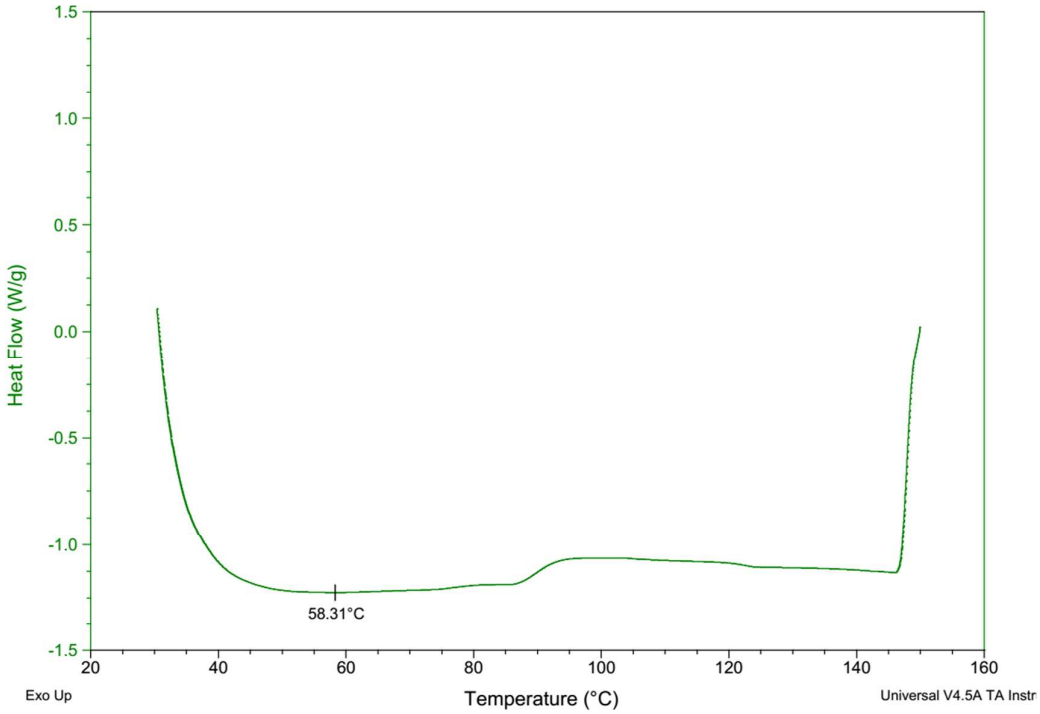


Figure S81. DSC of the polymer from table 2, entry 2.

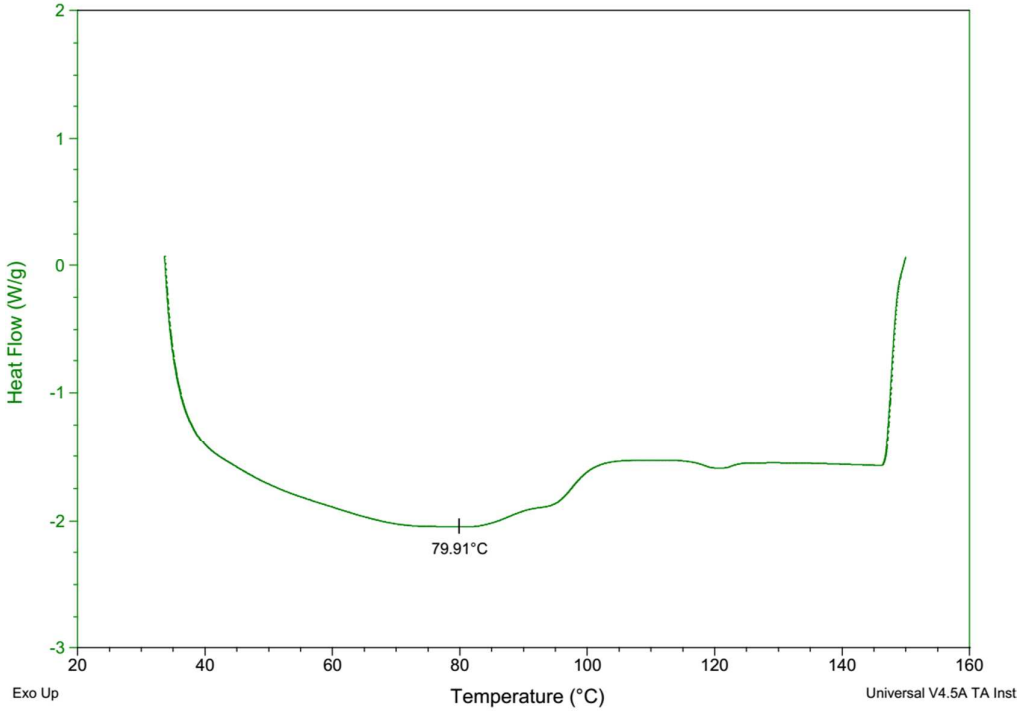


Figure S82. DSC of the polymer from table 2, entry 3.

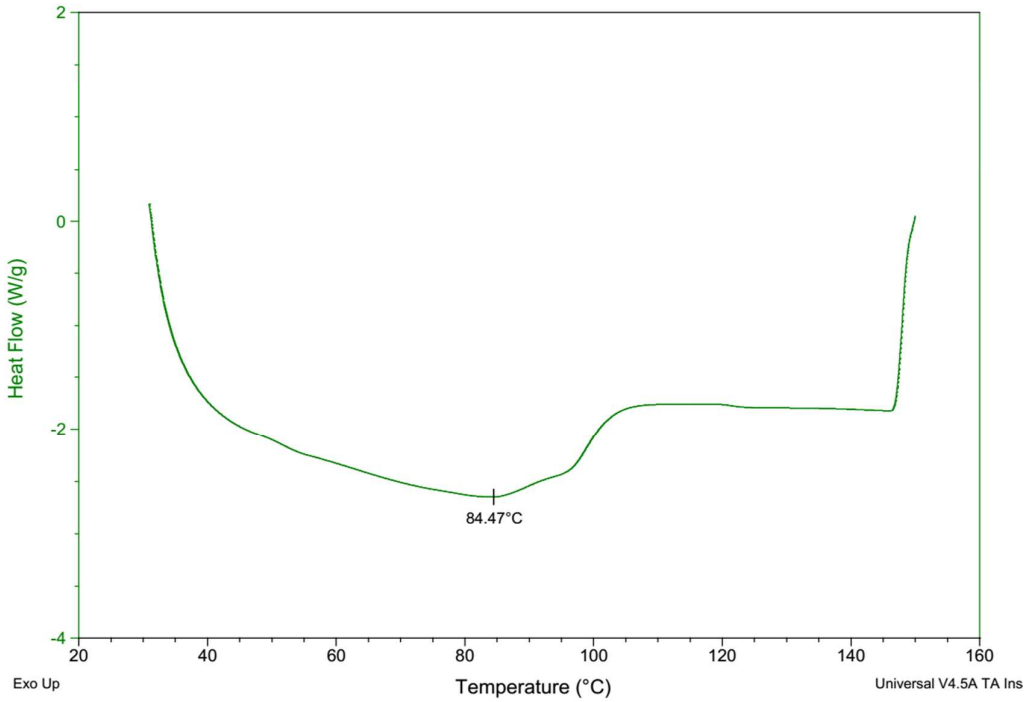


Figure S83. DSC of the polymer from table 2, entry 4.

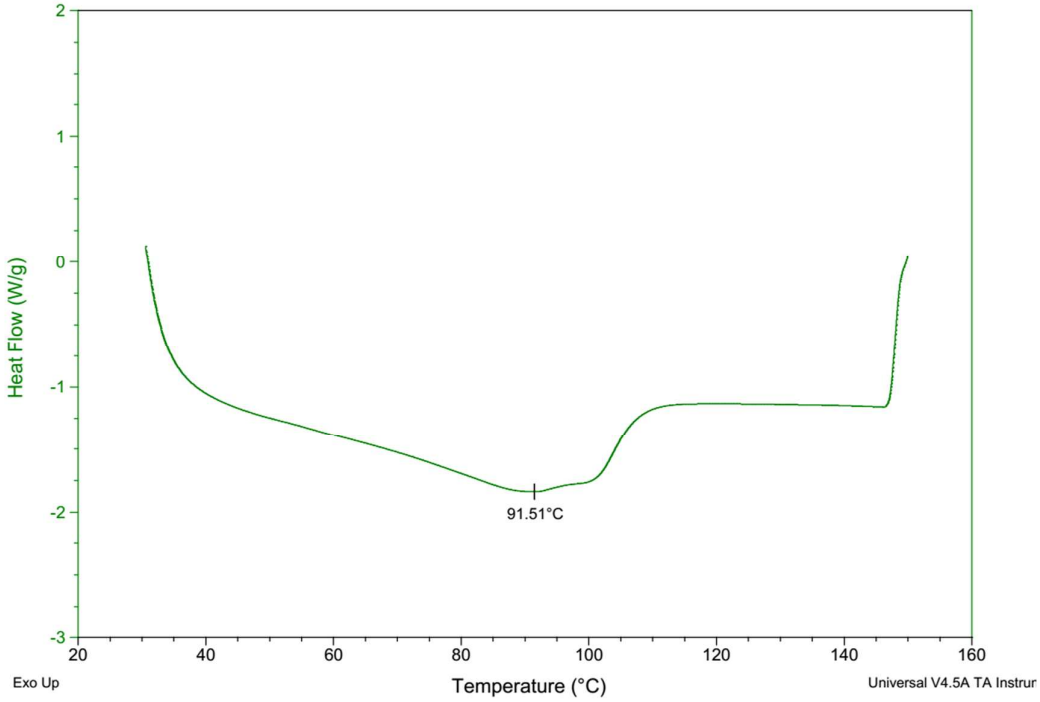


Figure S84. DSC of the polymer from table 2, entry 5.

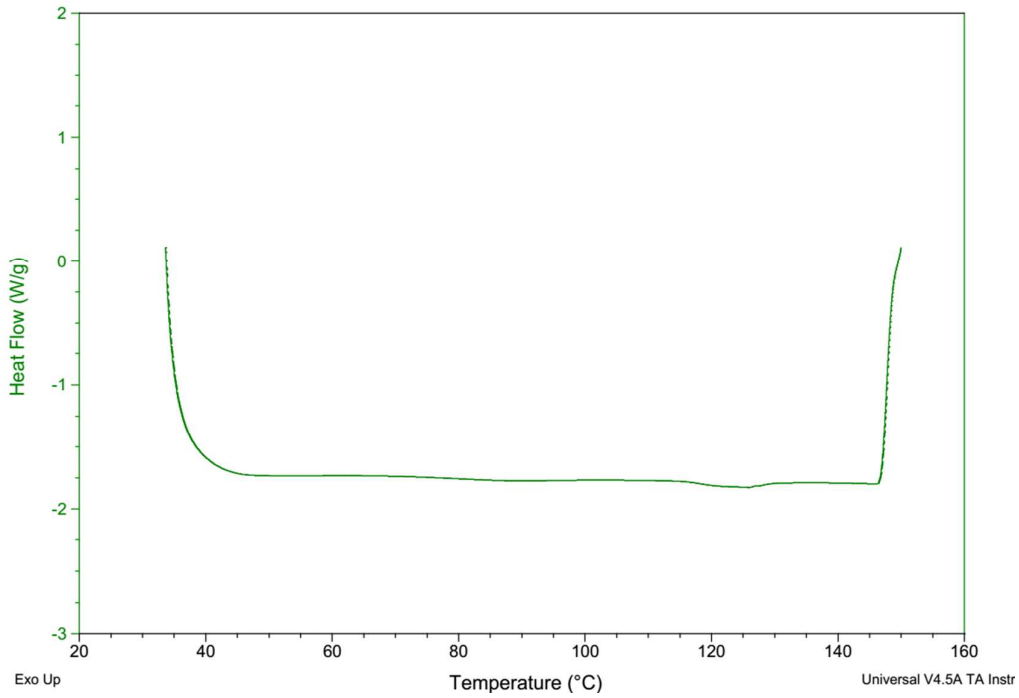


Figure S85. DSC of the polymer from table 2, entry 6.

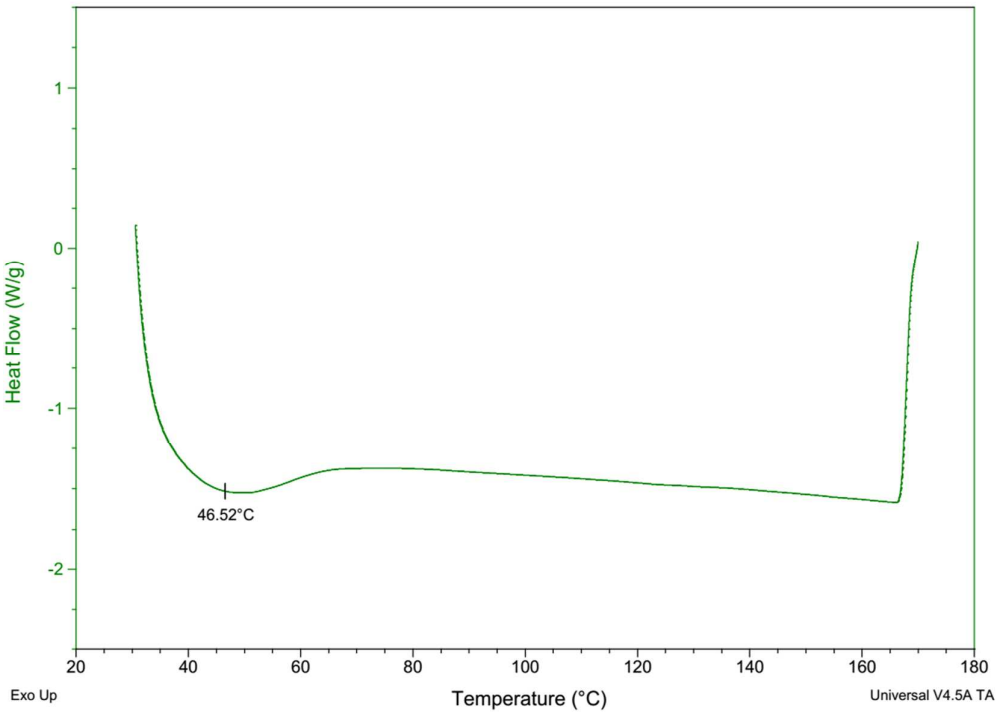


Figure S86. DSC of the polymer from table 2, entry 7.

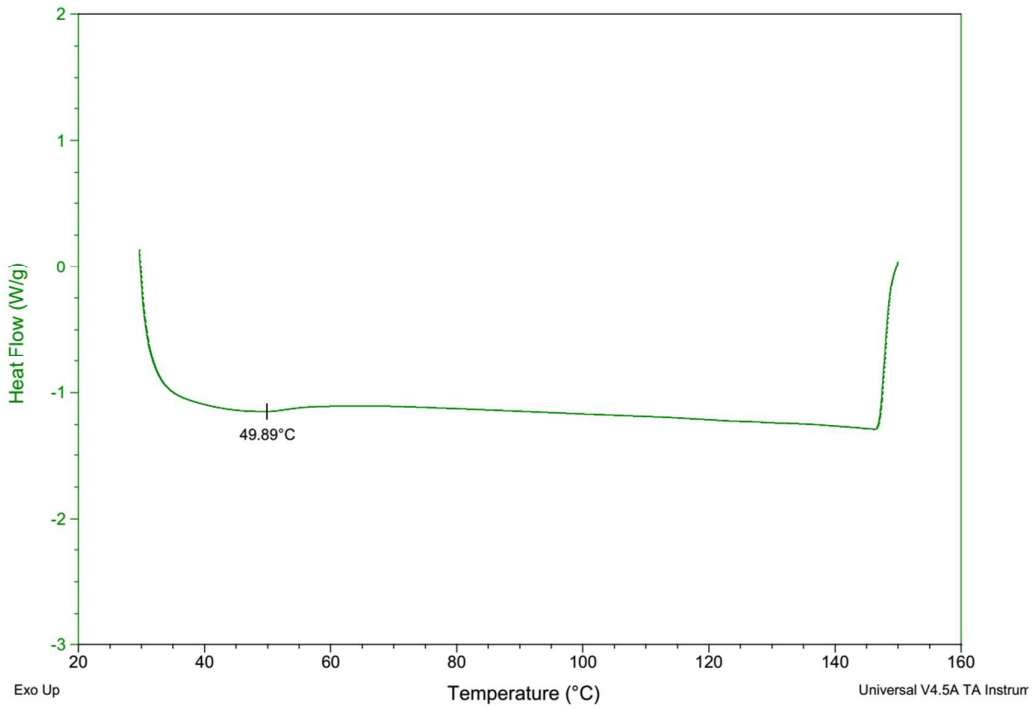


Figure S87. DSC of the polymer from table 2, entry 8.

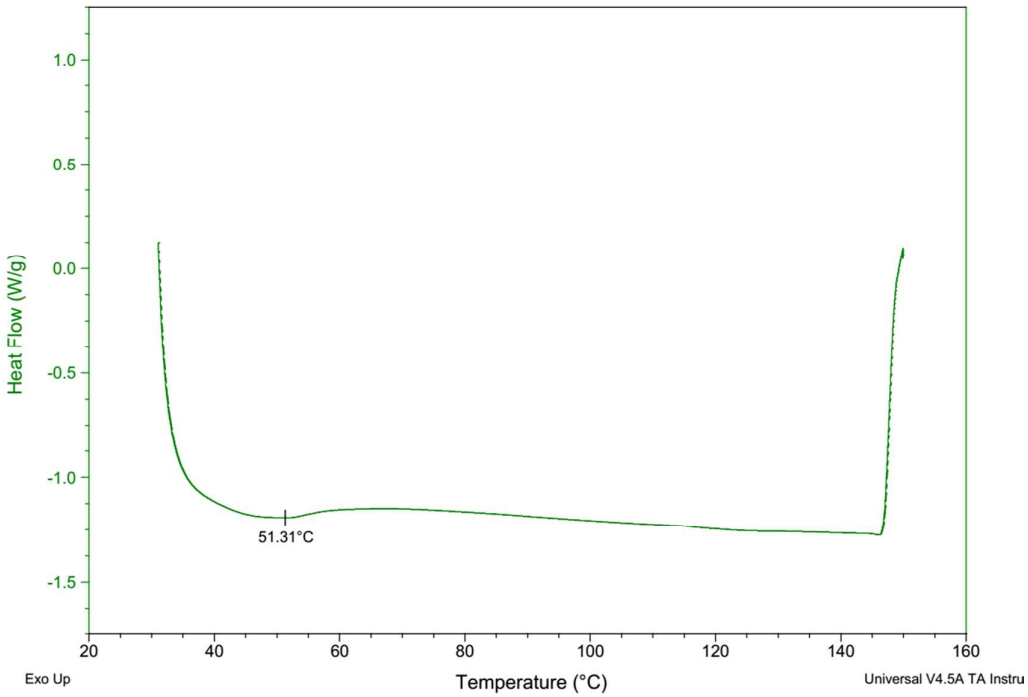


Figure S88. DSC of the polymer from table 2, entry 9.

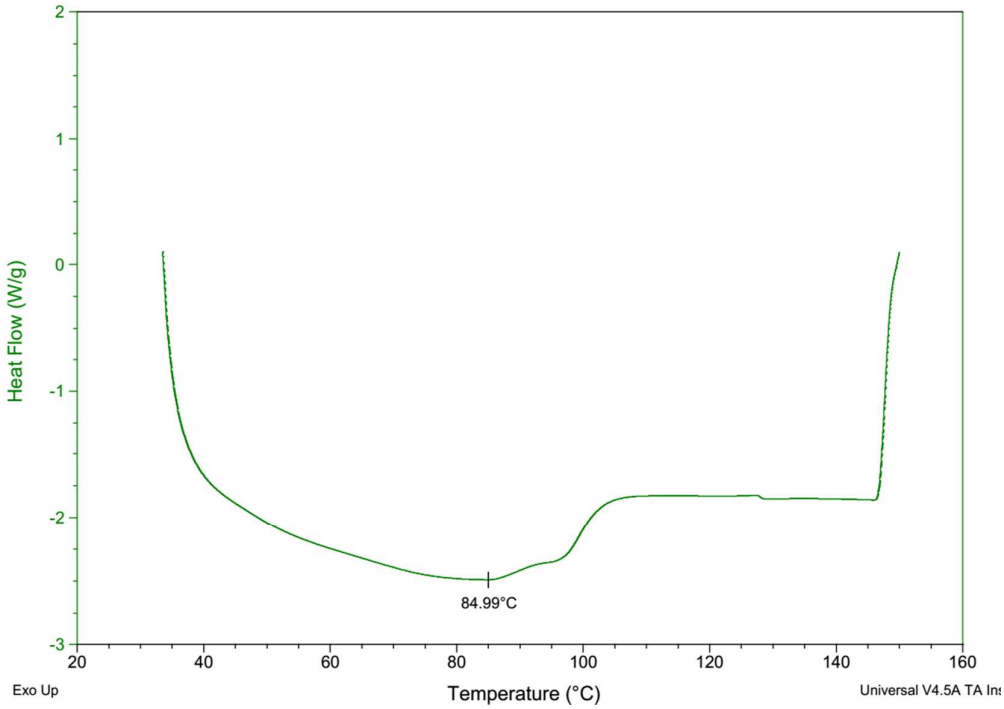


Figure S89. DSC of the polymer from table 2, entry 10.

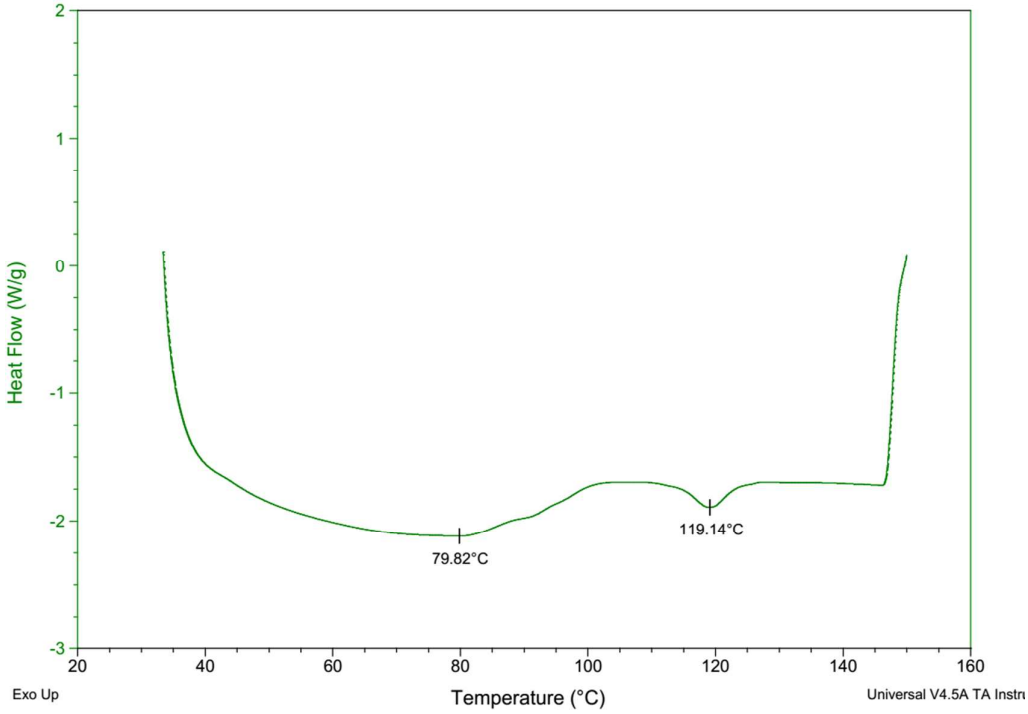


Figure S90. DSC of the polymer from table 2, entry 11.

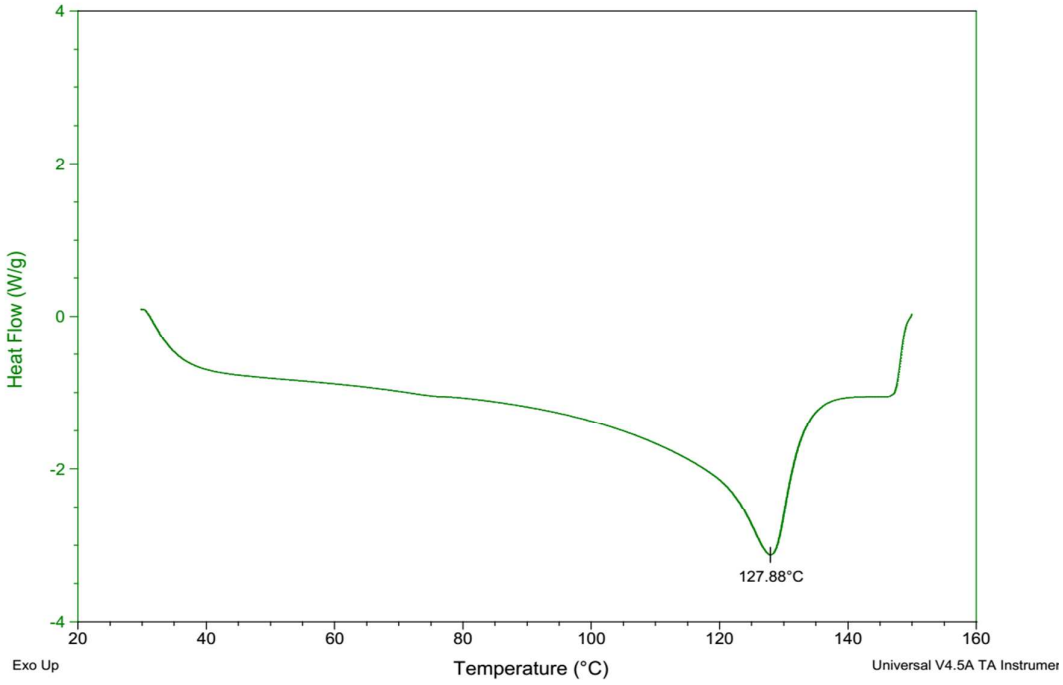


Figure S91. DSC of the polymer from table S1, Fraction 1.

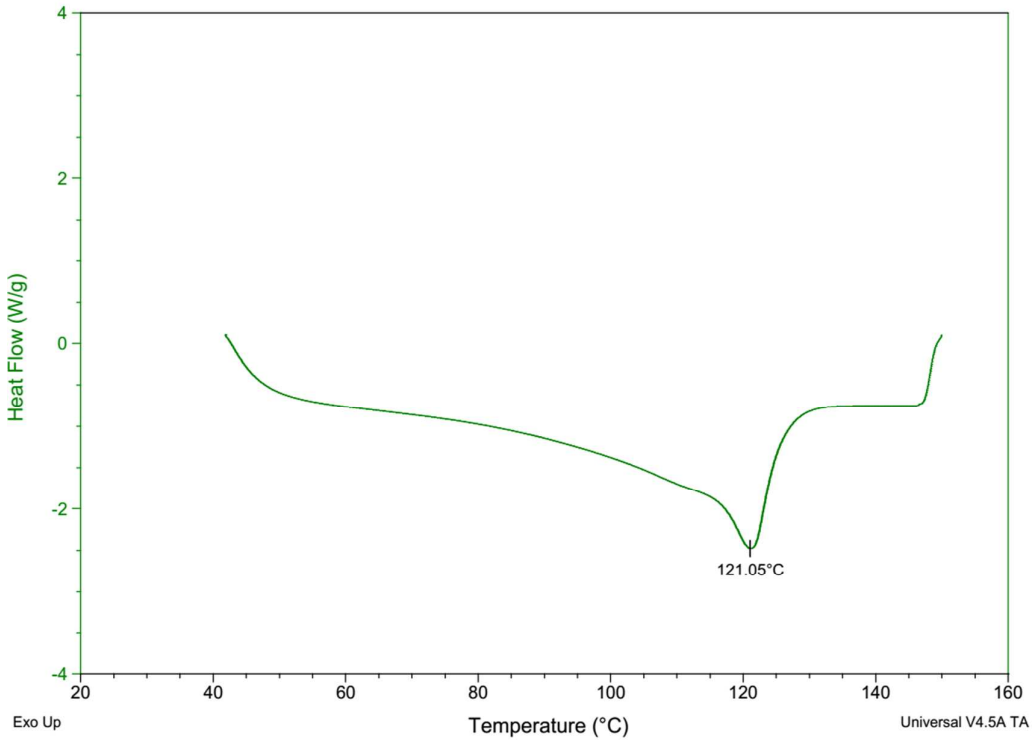


Figure S92. DSC of the polymer from table S1, Fraction 2.

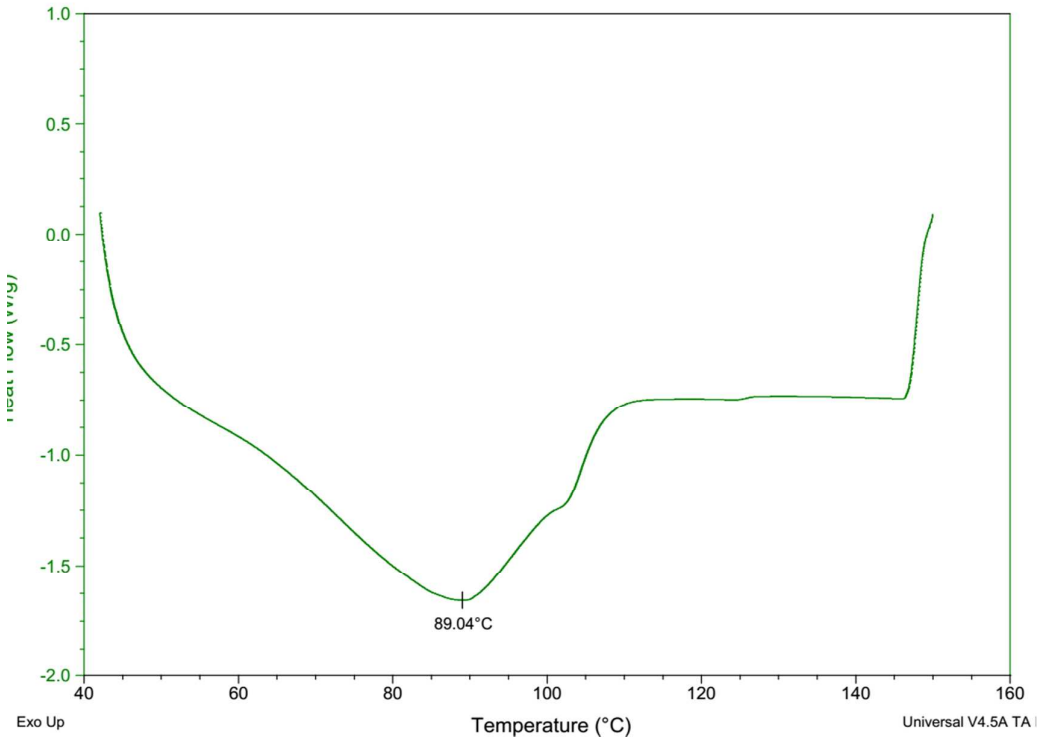


Figure S93. DSC of the polymer from table S1, Fraction 3.

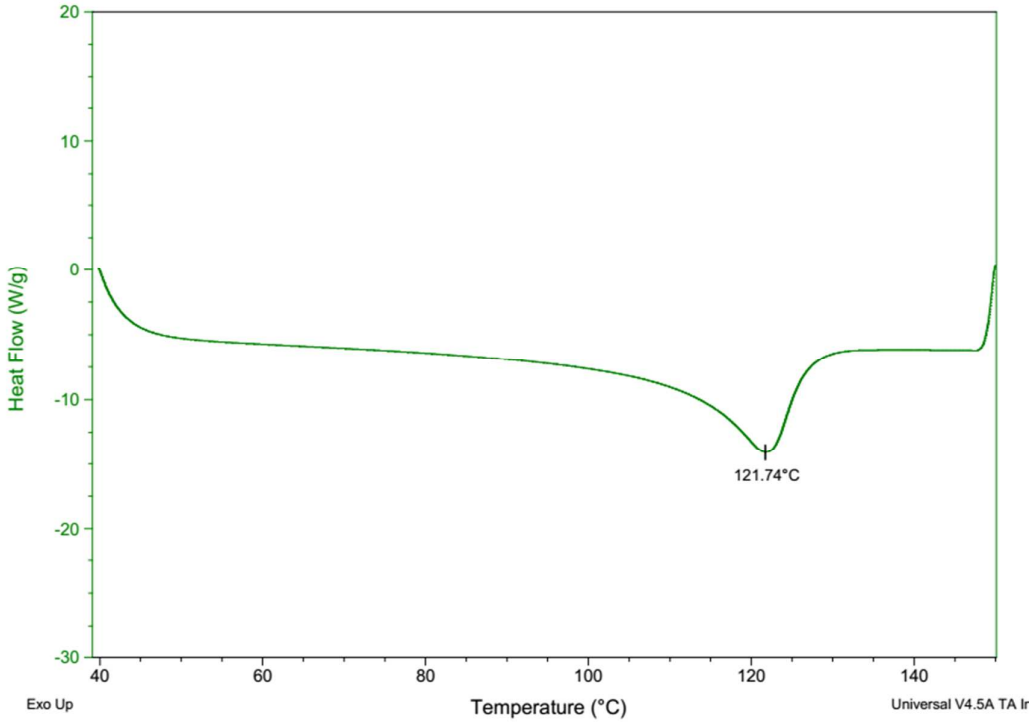


Figure S94. DSC of the polymer from table S2, Fraction 1.

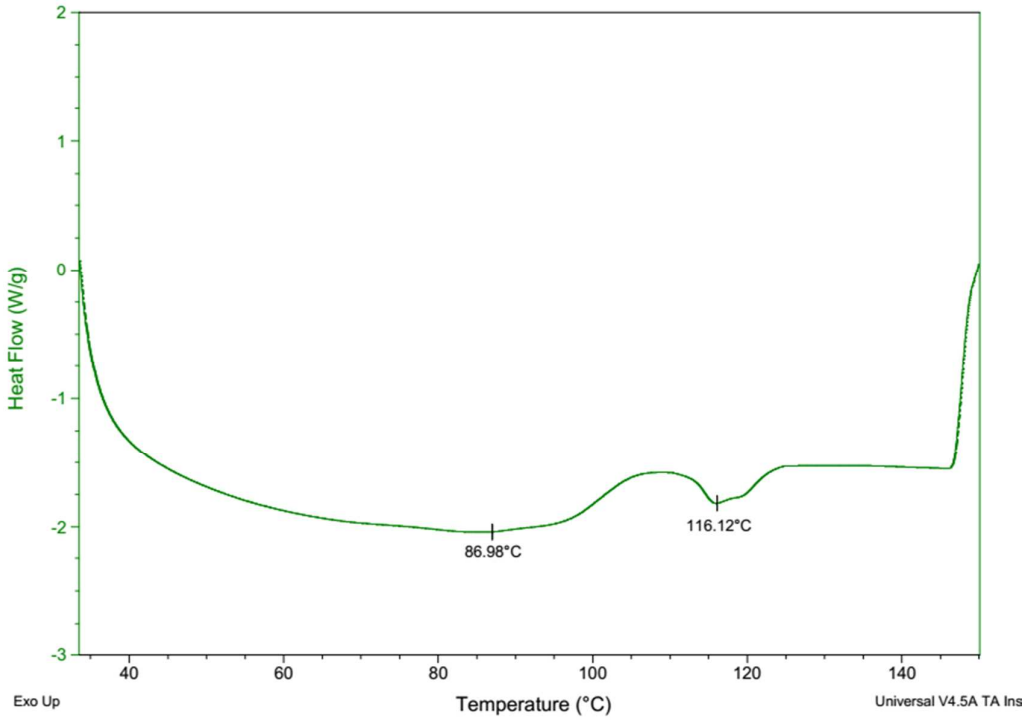


Figure S95. DSC of the polymer from table S2, Fraction 2.

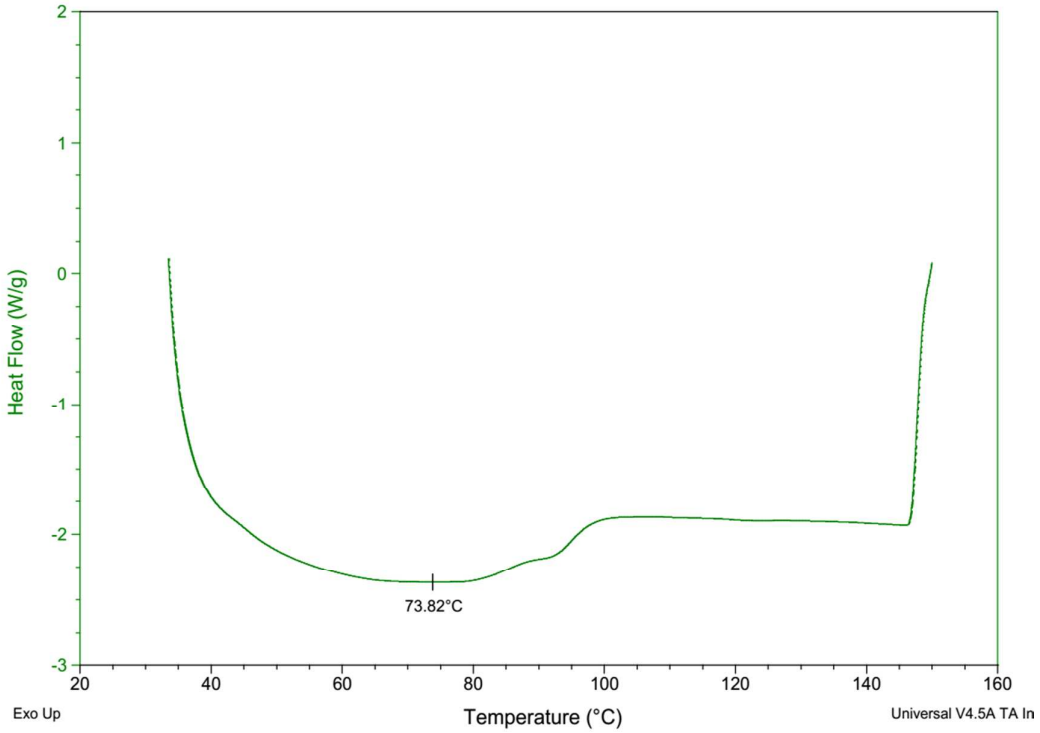
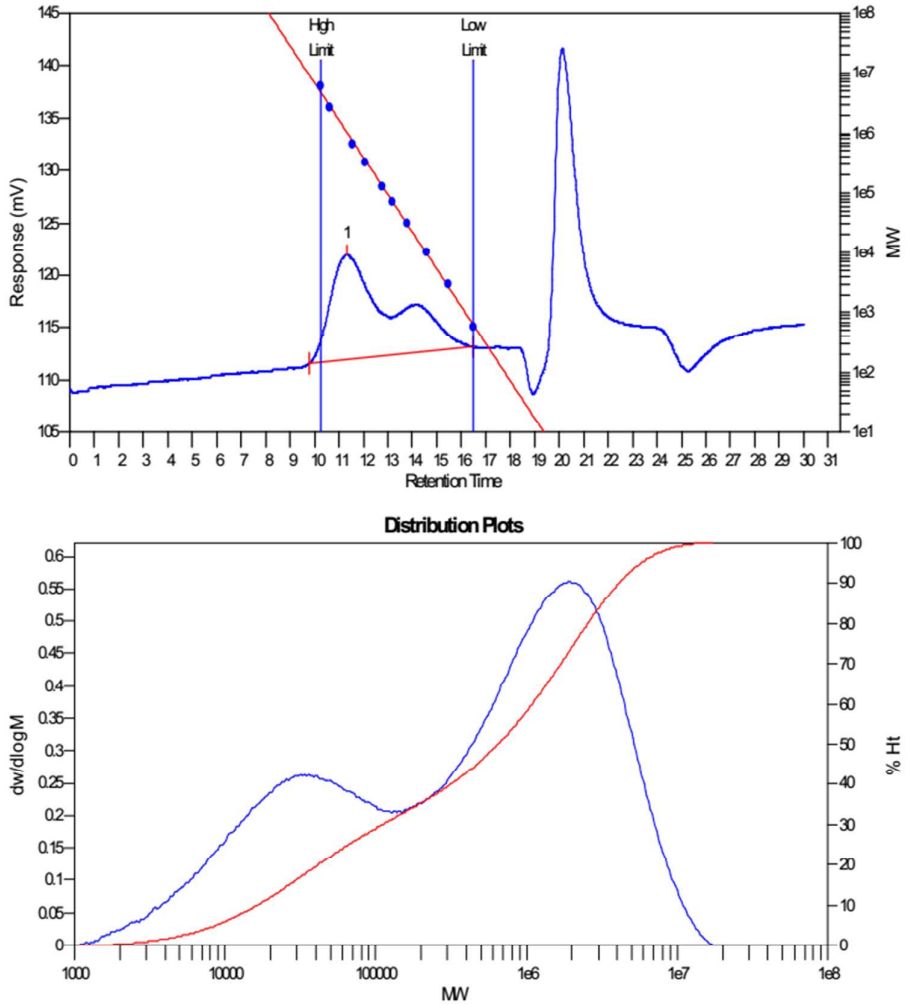


Figure S96. DSC of the polymer from table S2, Fraction 3.

4.5 GPC of polymer and copolymer.



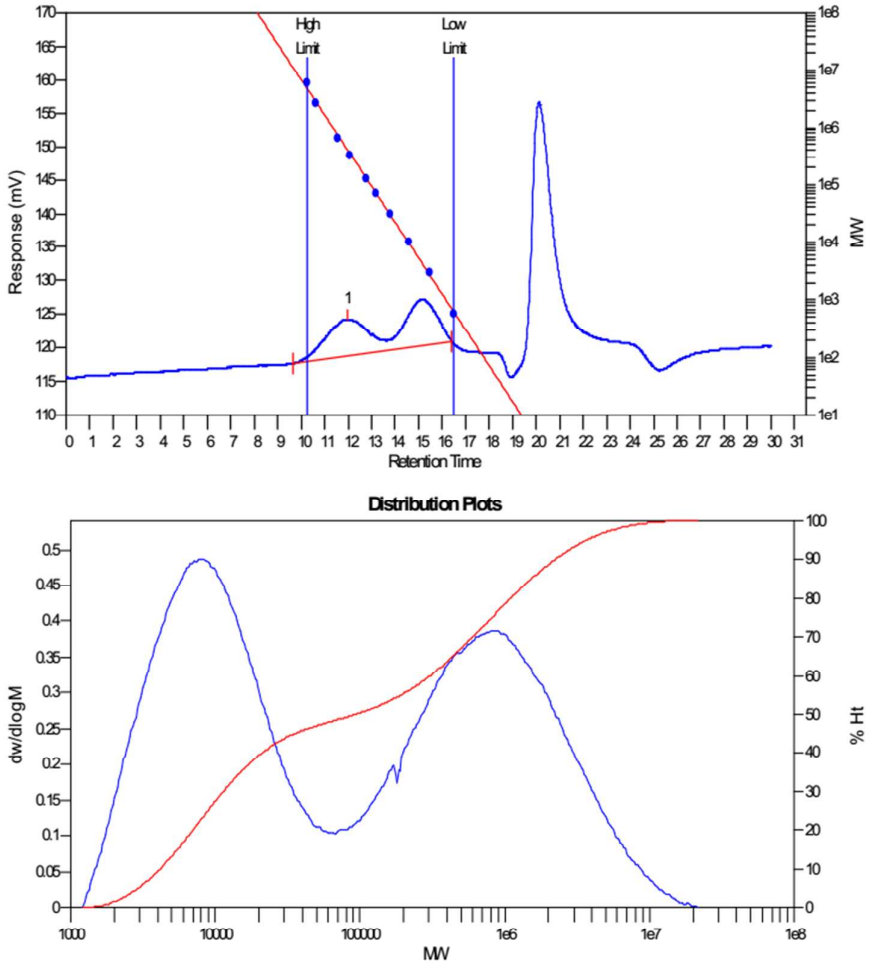
MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	1945040	43930	1456340	4293277	6528570	1104868	33.1514

Processed Peaks

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1		9.78	11.30	16.50	9.98301	0	1704.47	100

Figure S97. GPC of the polymer from table 1, entry 1.



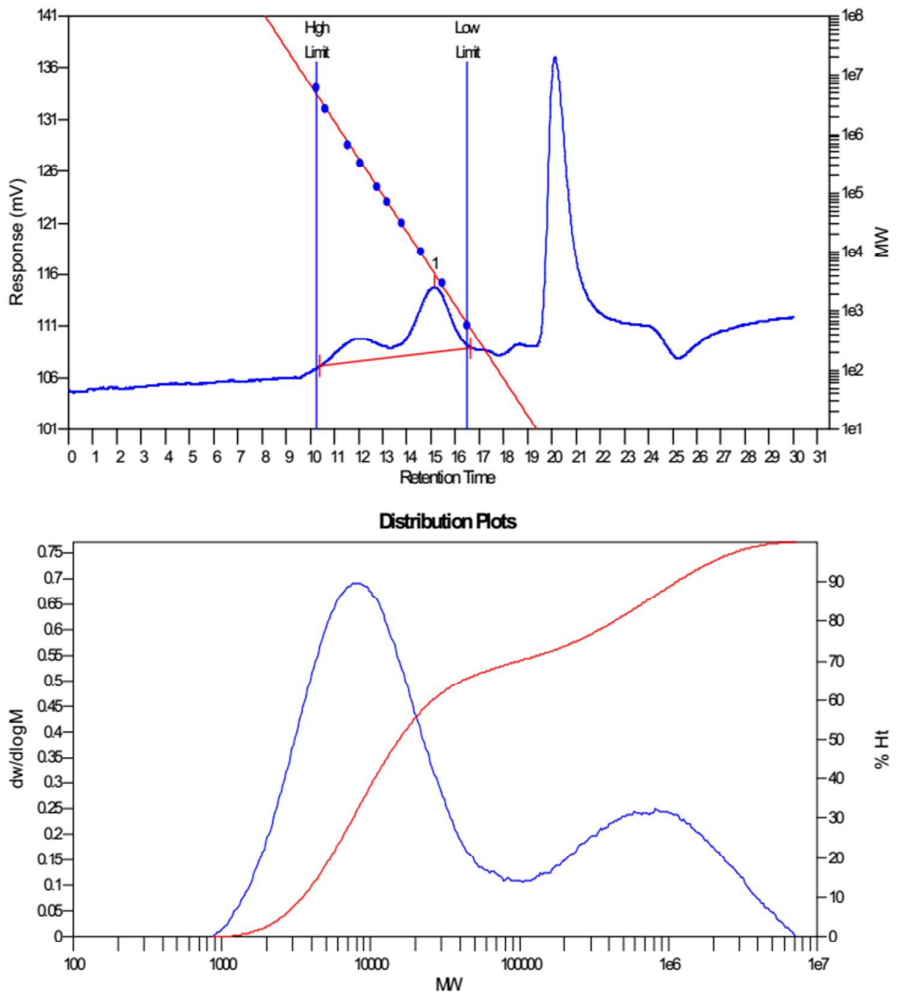
MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	8313	12700	757809	4039891	7397198	487069	59.67

Processed Peaks

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1		9.63	11.97	16.42	5.52035	0	1373.38	100

Figure S98. GPC of the polymer from table 1, entry 2.



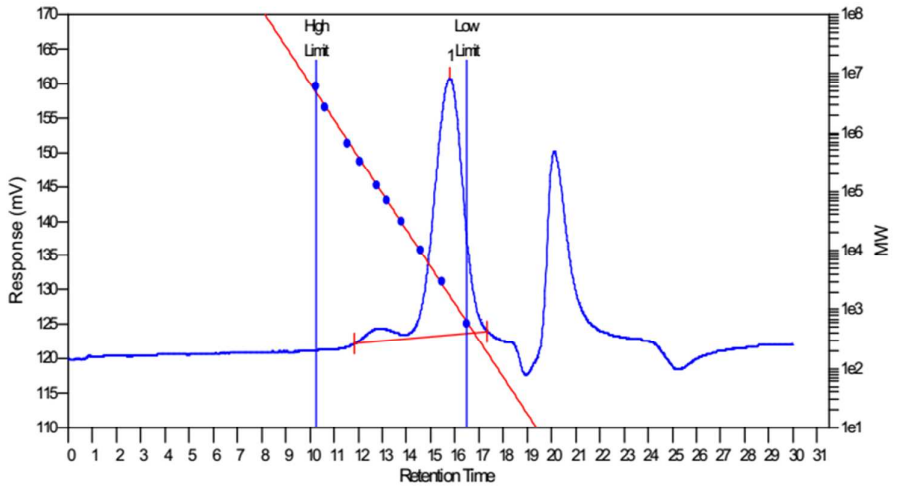
MW Averages

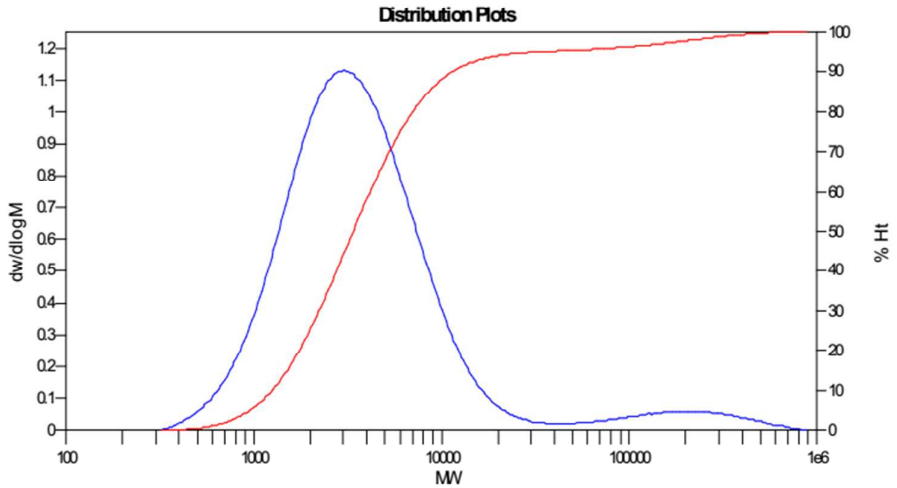
Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	7735	8974	335104	2119677	3234920	194872	37.3417

Processed Peaks

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1		10.40	15.13	16.65	6.29762	0	872.256	100

Figure S99. GPC of the polymer from table 1, entry 3.





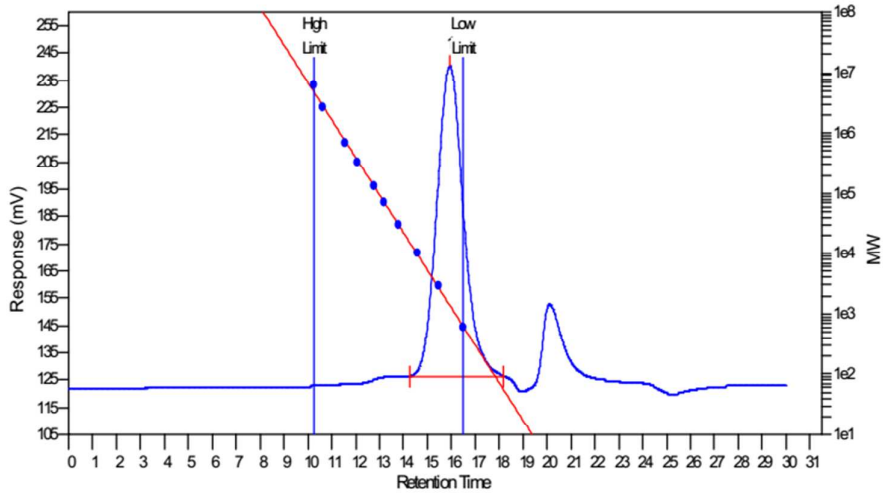
MW Averages

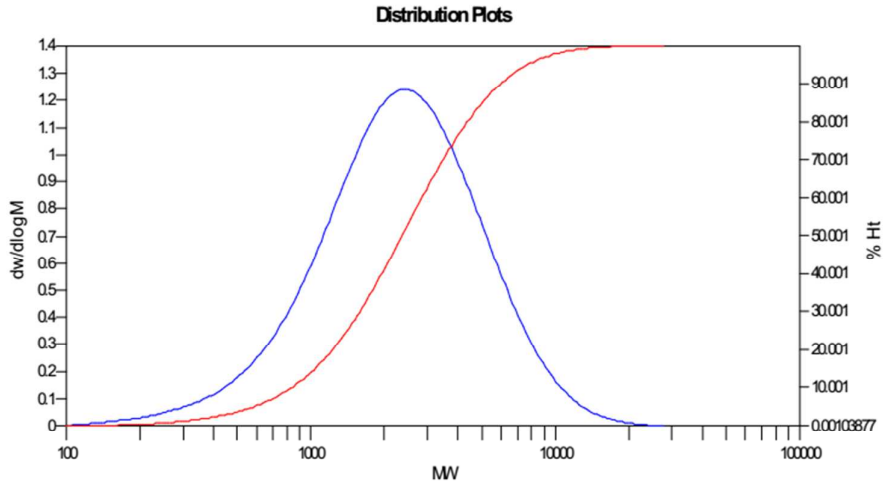
Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	3030	2553	14631	229724	404960	8416	5.7309

Processed Peaks

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1		11.85	15.78	17.33	37.2451	0	3160.05	100

Figure S100. GPC of the polymer from table 1, entry 4.





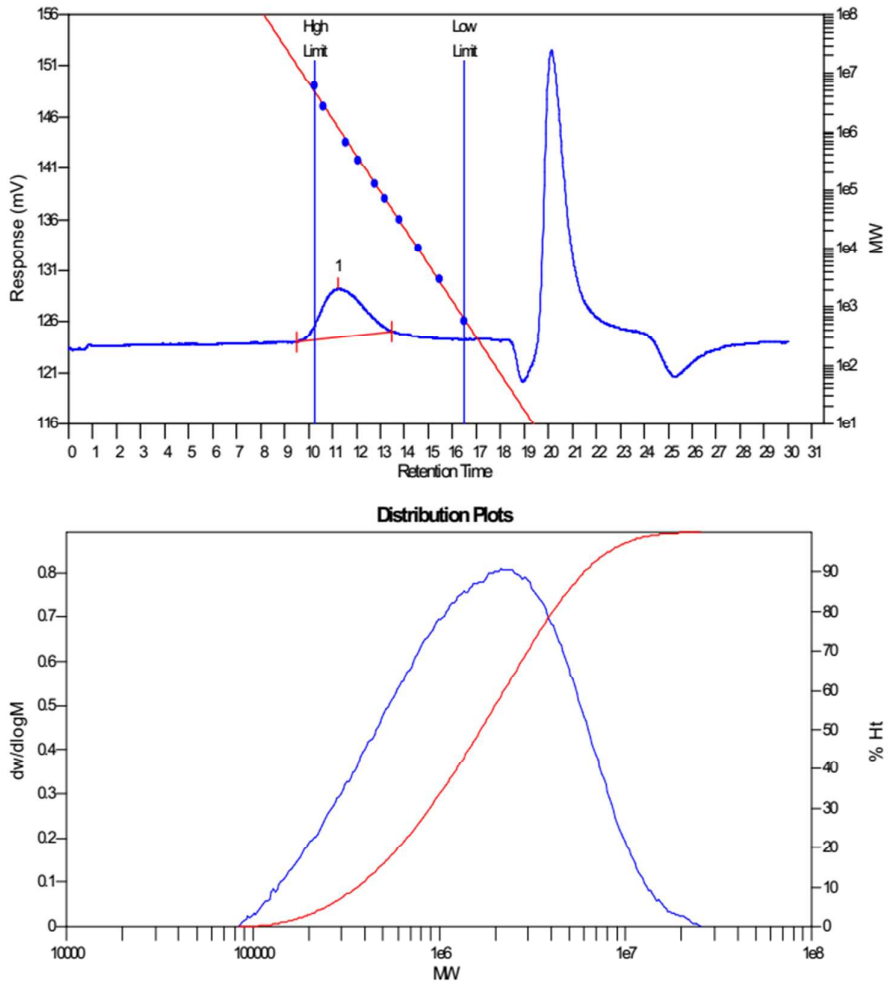
MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	2440	1602	2971	4867	7331	2735	1.85456

Processed Peaks

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1		14.25	15.93	18.17	113.911	0	8794.95	100

Figure S101. GPC of the polymer from table 1, entry 5.



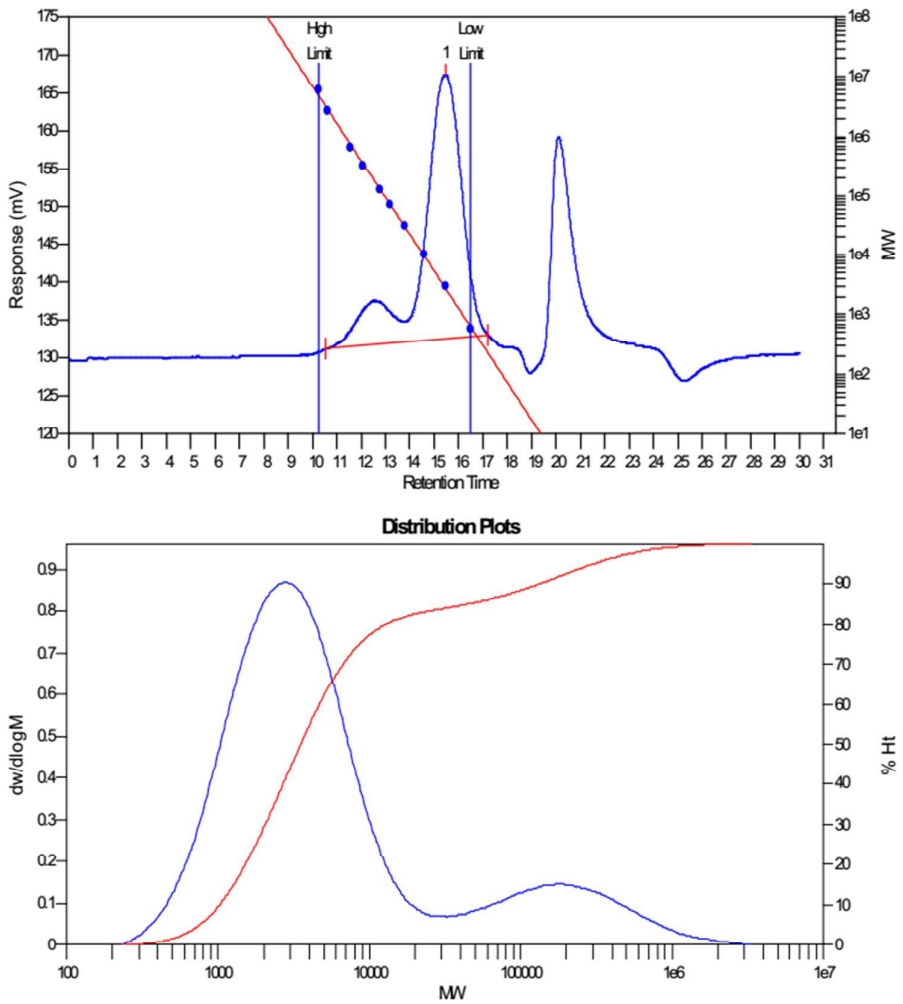
MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	2141290	880851	2571842	5477630	8761060	2229990	2.91972

Processed Peaks

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1		9.52	11.23	13.48	4.77189	0	565.974	100

Figure S102. GPC of the polymer from table 1, entry 6.



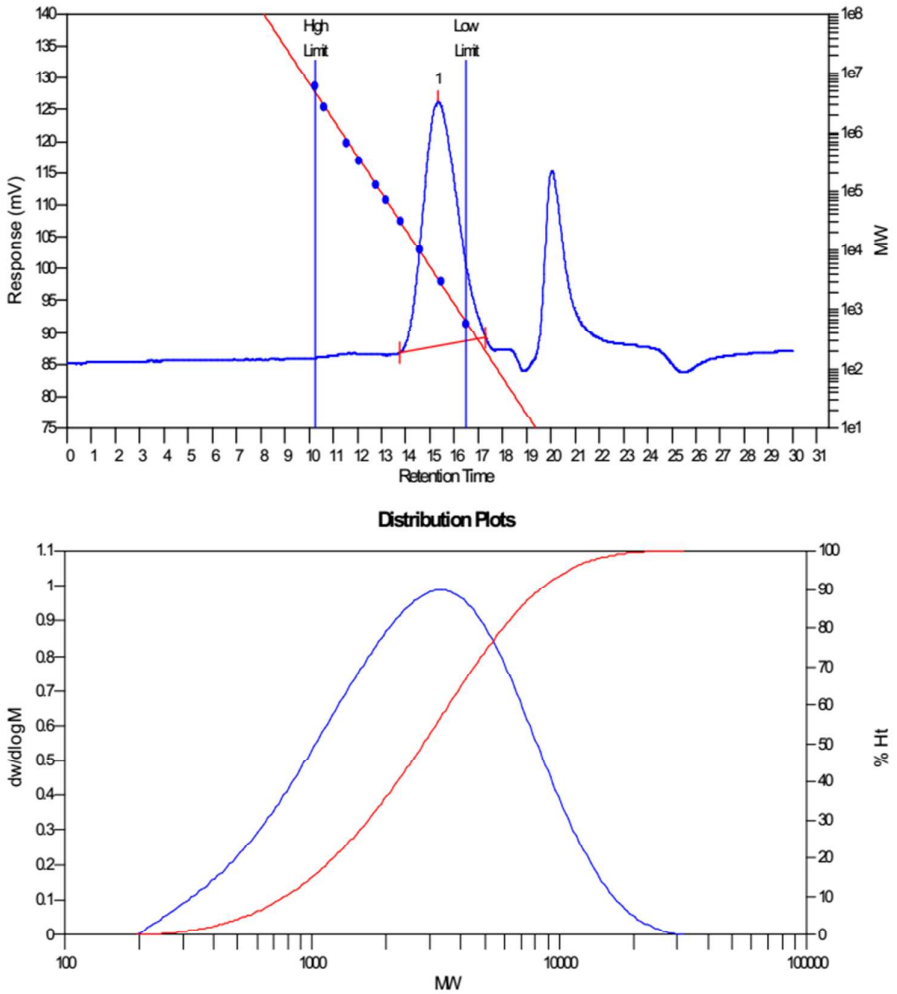
MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	2791	2361	49690	610409	1149995	26008	21.0462

Processed Peaks

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1		10.52	15.45	17.18	34.9147	0	3877.95	100

Figure S103. GPC of the polymer from table 1, entry 7.



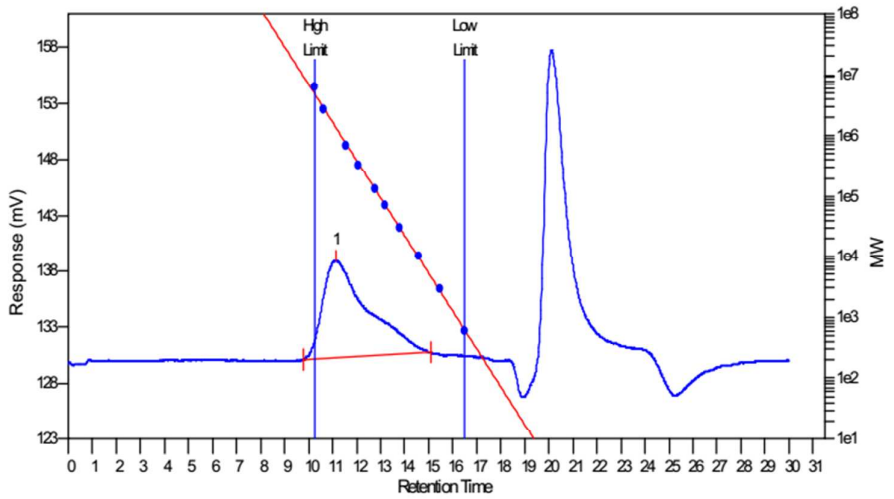
MW Averages

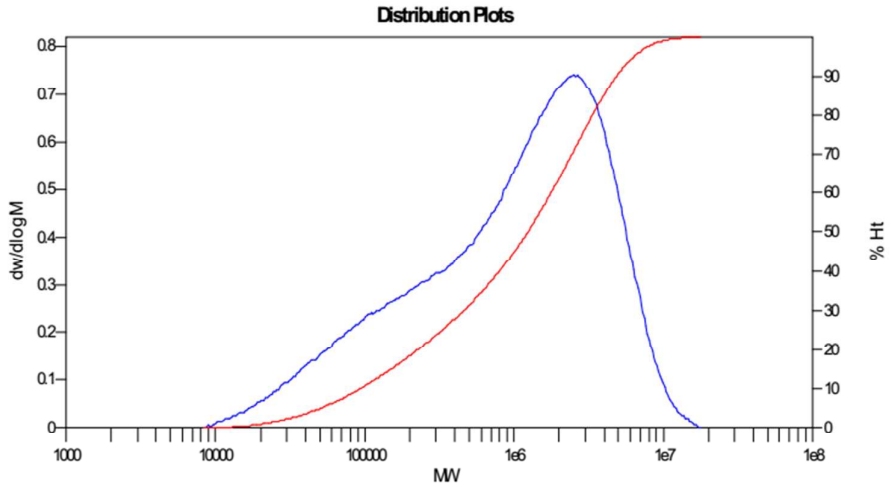
Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	3300	1742	3837	6929	10334	3460	2.20264

Processed Peaks

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1		13.75	15.35	17.30	38.2771	0	3735.9	100

Figure S104. GPC of the polymer from table 1, entry 8.





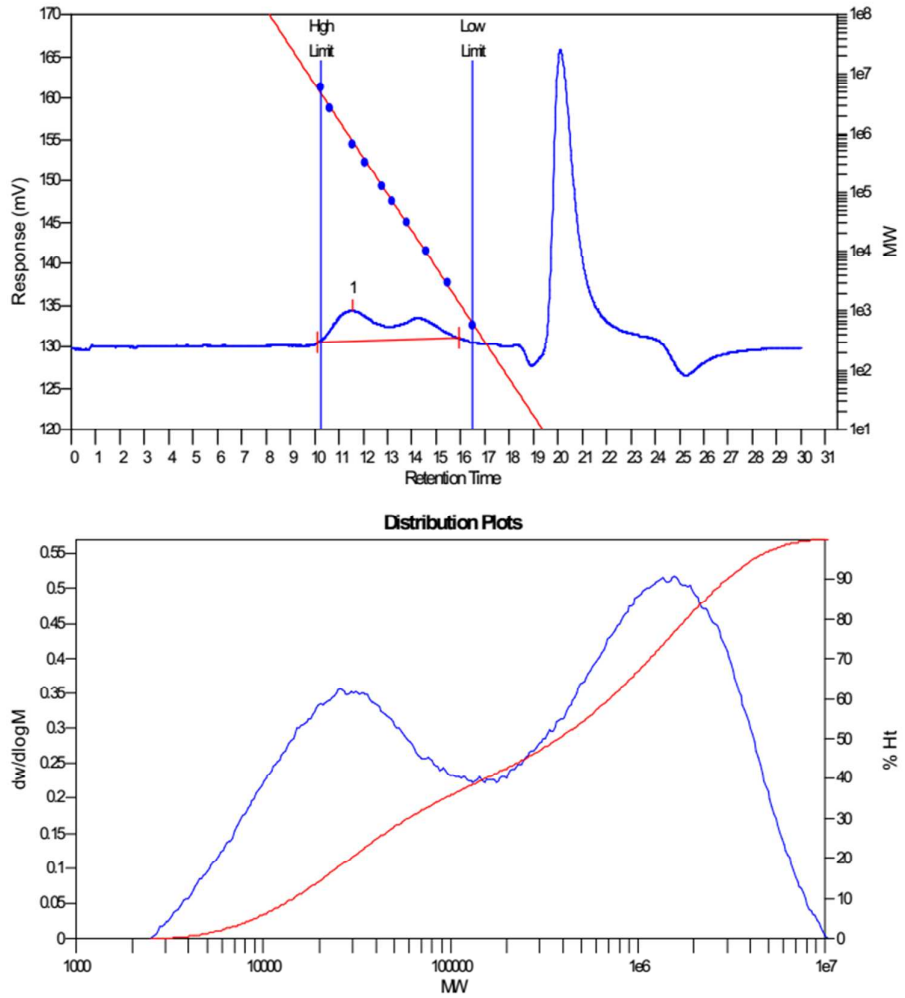
MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	2473409	246399	1926626	4276046	6236653	1606293	7.81913

Processed Peaks

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1		9.77	11.13	15.08	8.72171	0	1126.39	100

Figure S105. GPC of the polymer from table 1, entry 9.



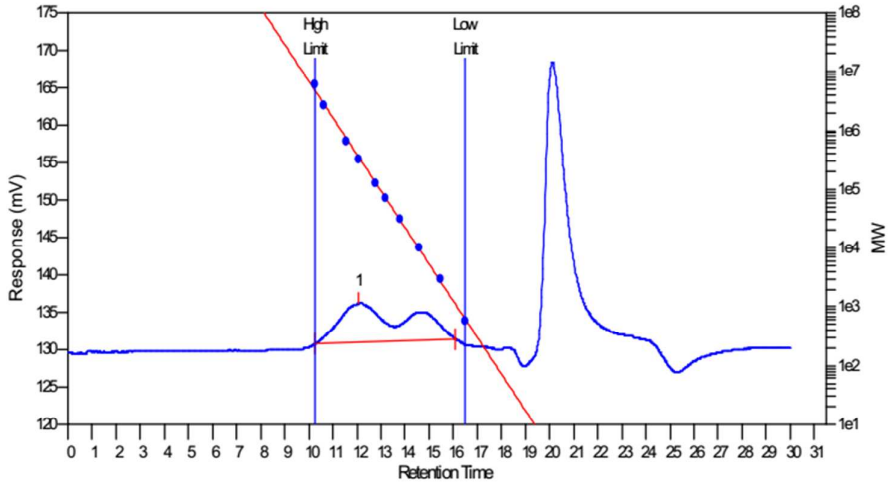
MW Averages

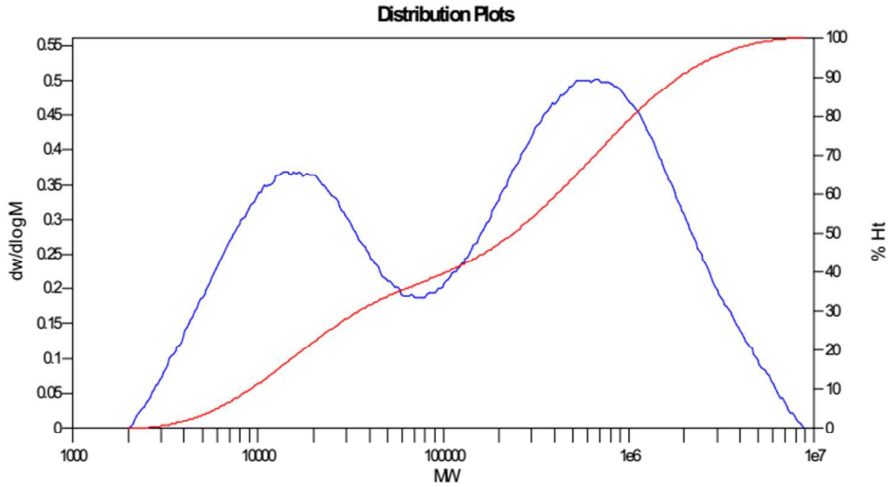
Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	1566743	44278	1007301	3038930	4414172	752582	22.7495

Processed Peaks

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1		10.13	11.55	15.92	3.72305	0	690.408	100

Figure S106. GPC of the polymer from table 1, entry 10.





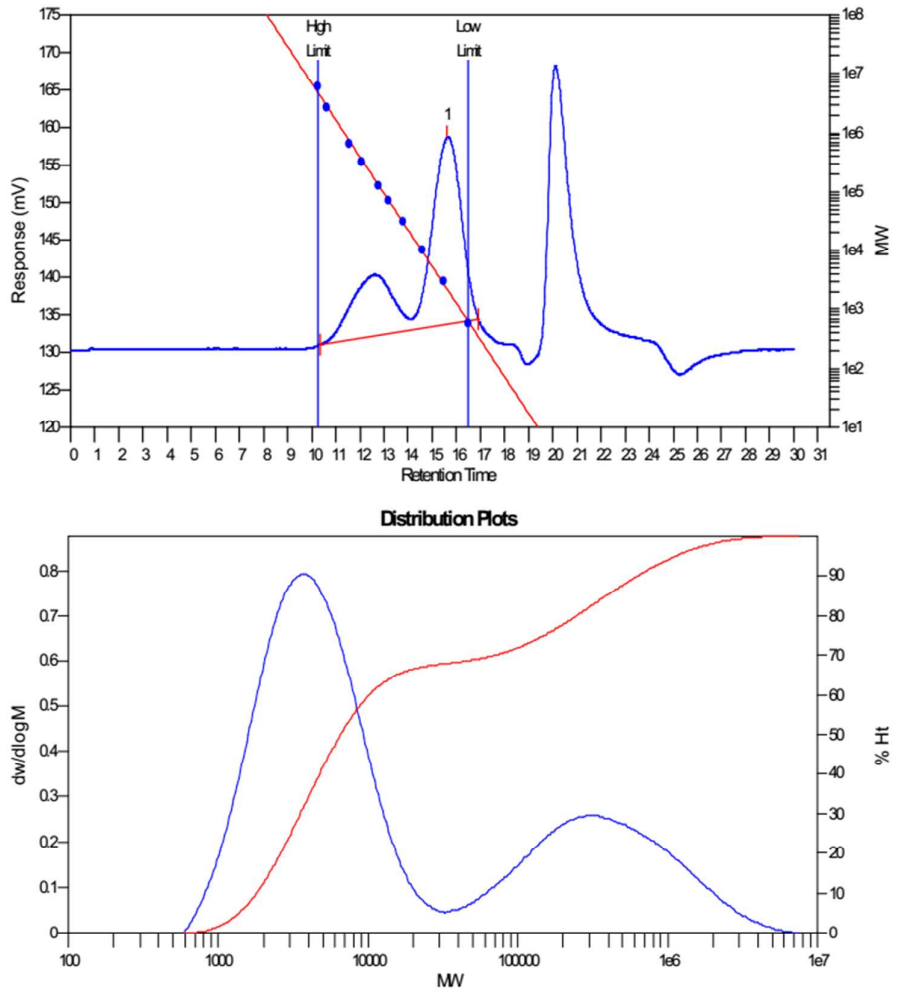
MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	659591	28917	651867	2314676	3726786	475877	22.5427

Processed Peaks

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1		10.25	12.05	16.07	5.1636	0	984.445	100

. **Figure S107.** GPC of the polymer from table 1, entry 11.



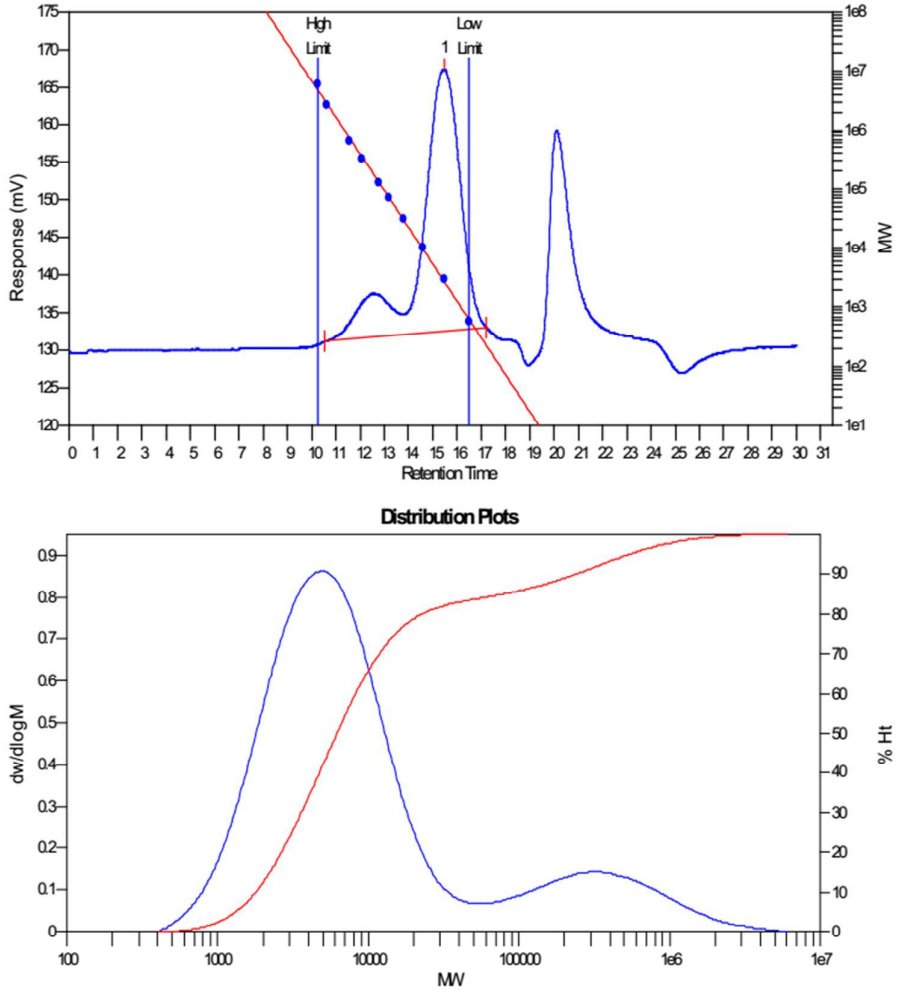
MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	3853	4498	199838	1461992	2546345	112592	44.4282

Processed Peaks

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1		10.37	15.62	16.92	25.0072	0	3025.38	100

Figure S108. GPC of the polymer from table 1, entry 12.



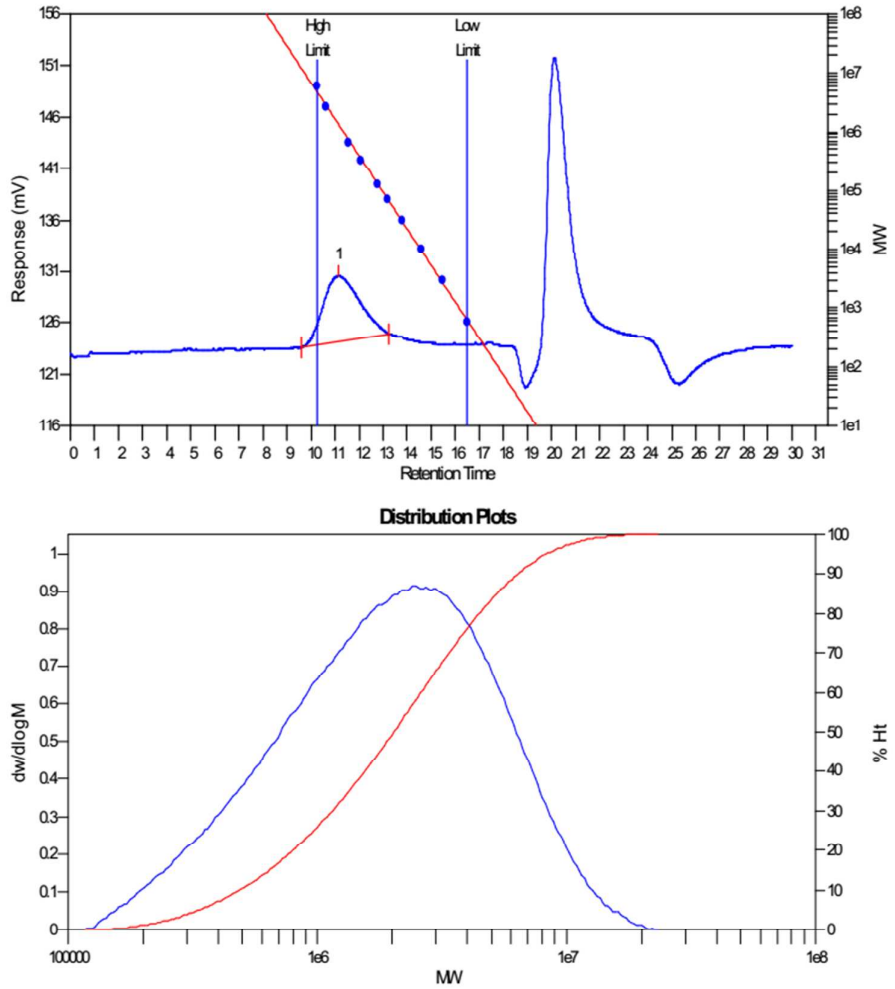
MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	4899	4127	89711	1115164	2104610	45598	21.7376

Processed Peaks

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1		10.52	15.45	17.18	34.9147	0	3877.95	100

Figure S109. GPC of the polymer from table 1, entry 13.



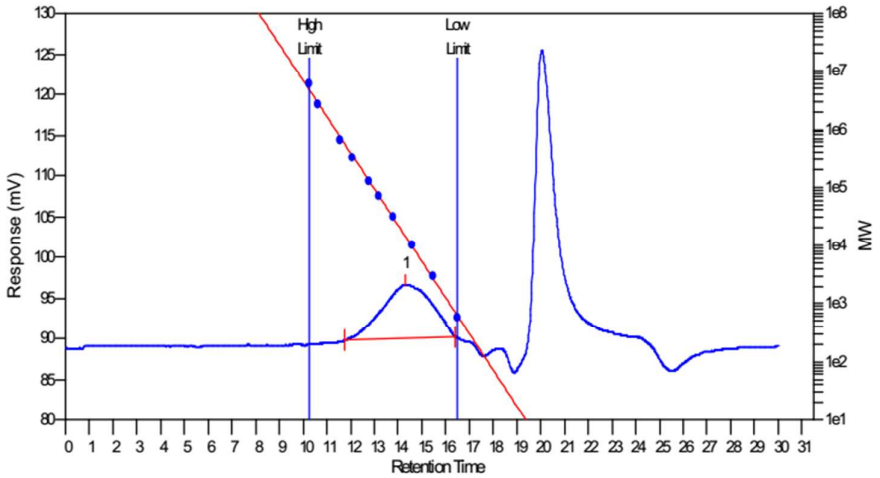
MW Averages

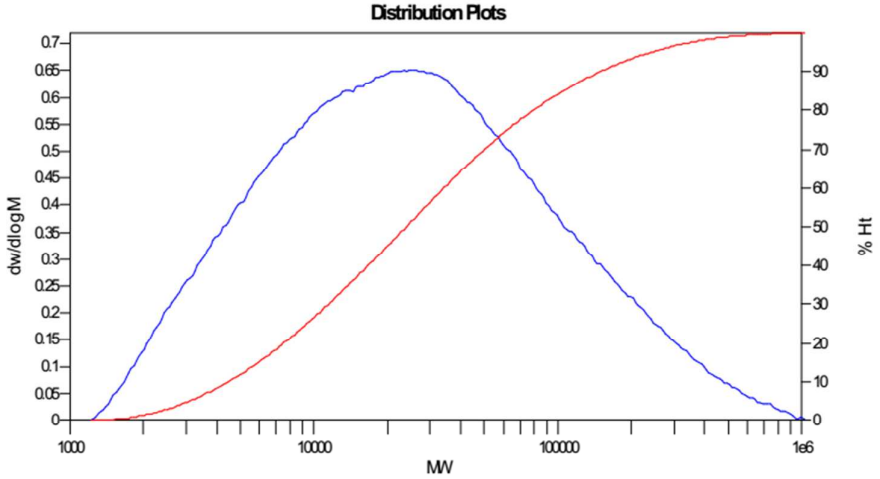
Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	2473409	1144378	2825872	5312204	7919528	2511000	2.46935

Processed Peaks

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1		9.58	11.13	13.25	6.4382	0	673.53	100

Figure S110. GPC of the polymer from table 1, entry 14.





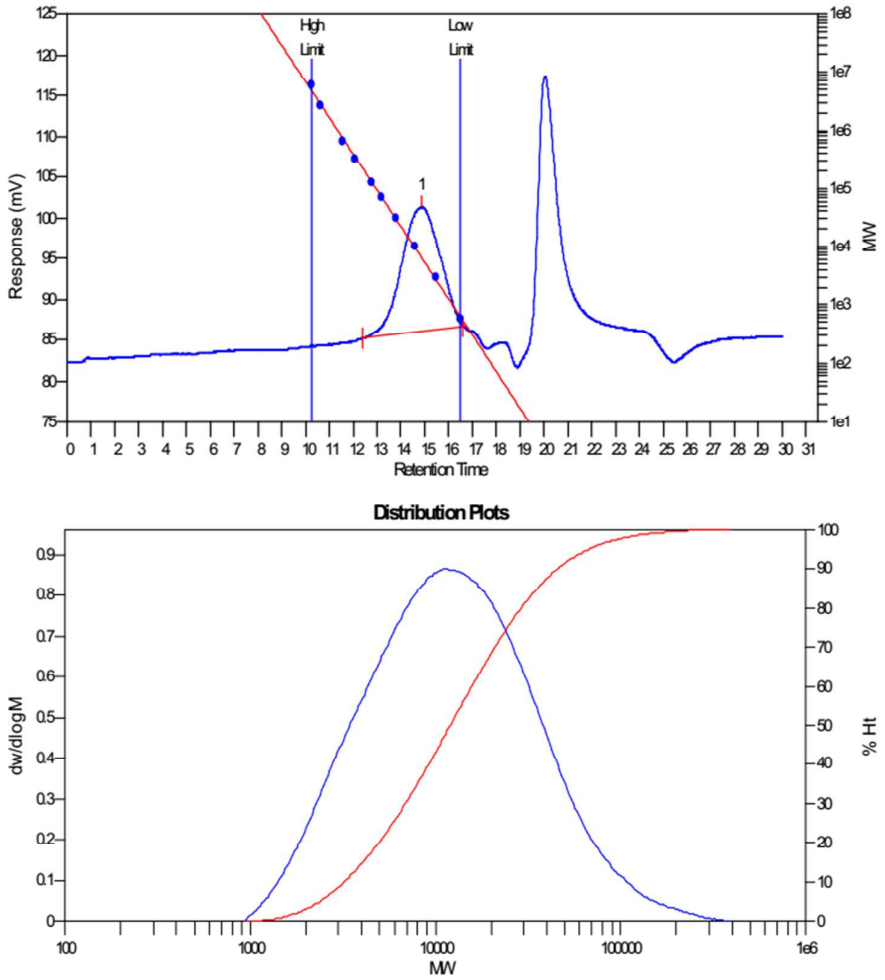
MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	26348	11698	57782	213693	403712	44855	4.93948

Processed Peaks

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1		11.73	14.32	16.42	6.56181	0	963.625	100

Figure S111. GPC of the polymer from table 1, entry 15.



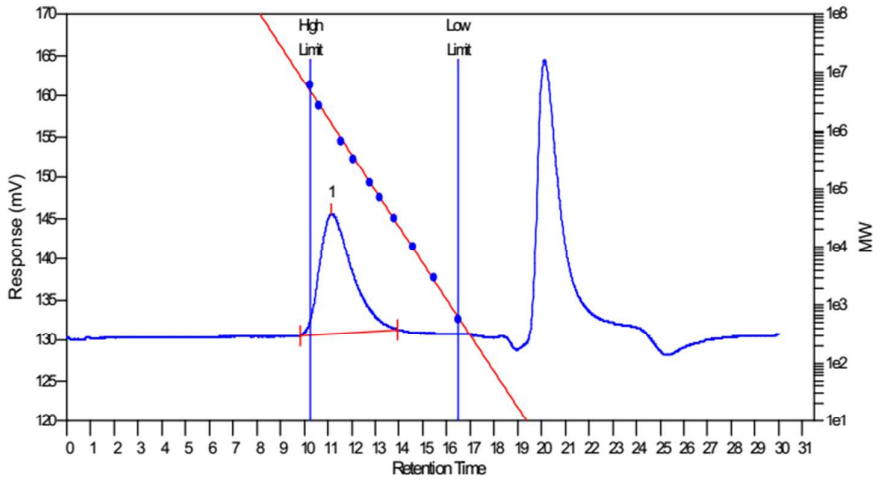
MW Averages

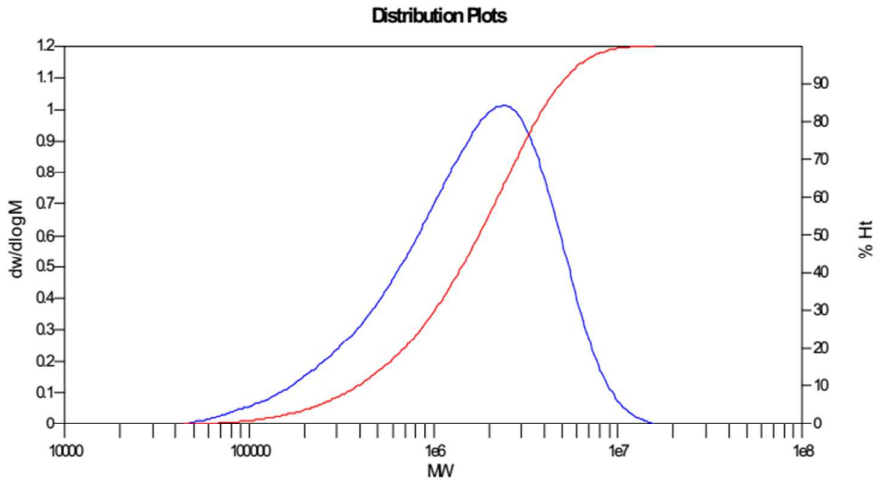
Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	11638	7518	20393	55394	115440	17315	2.71256

Processed Peaks

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1		12.42	14.85	16.60	15.2446	0	1686.69	100

Figure S112. GPC of the polymer from table 1, entry 16.





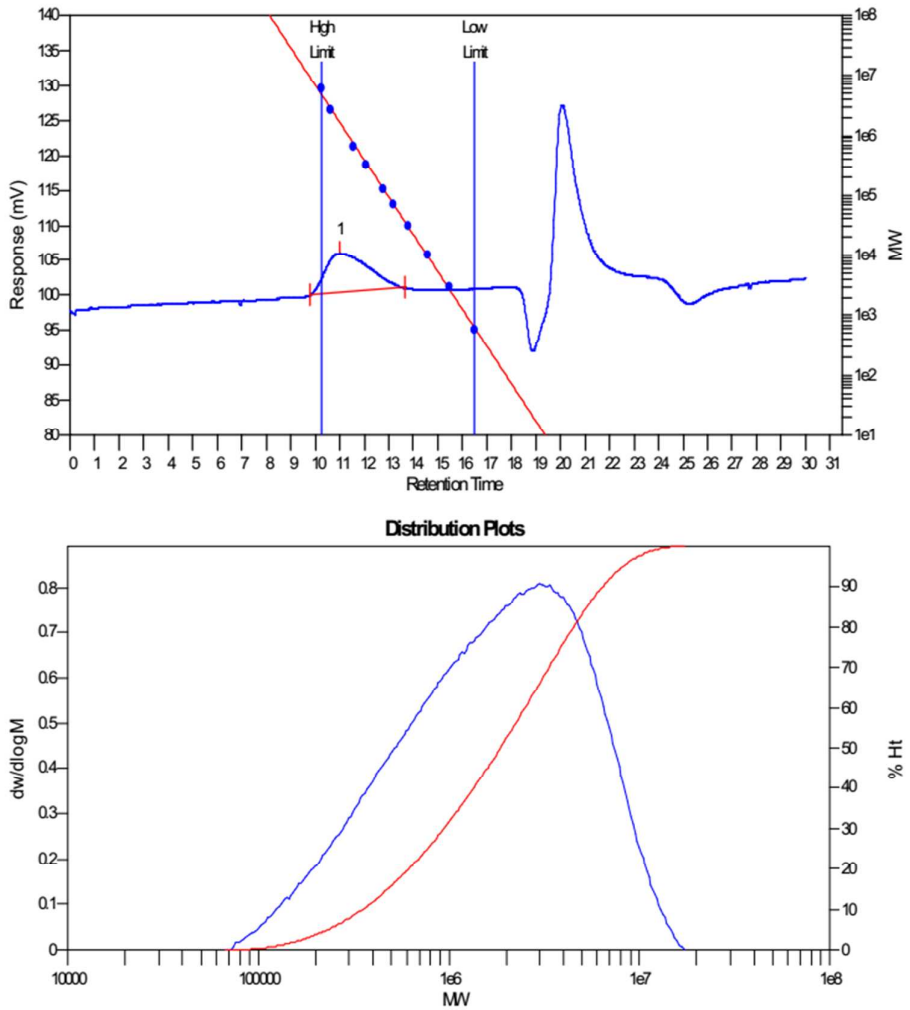
MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	2473409	862519	2257722	3888418	5458161	2031328	2.61759

Processed Peaks

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1		9.85	11.13	13.92	14.6604	0	1388.67	100

Figure S113. GPC of the polymer from table 1, entry 17.



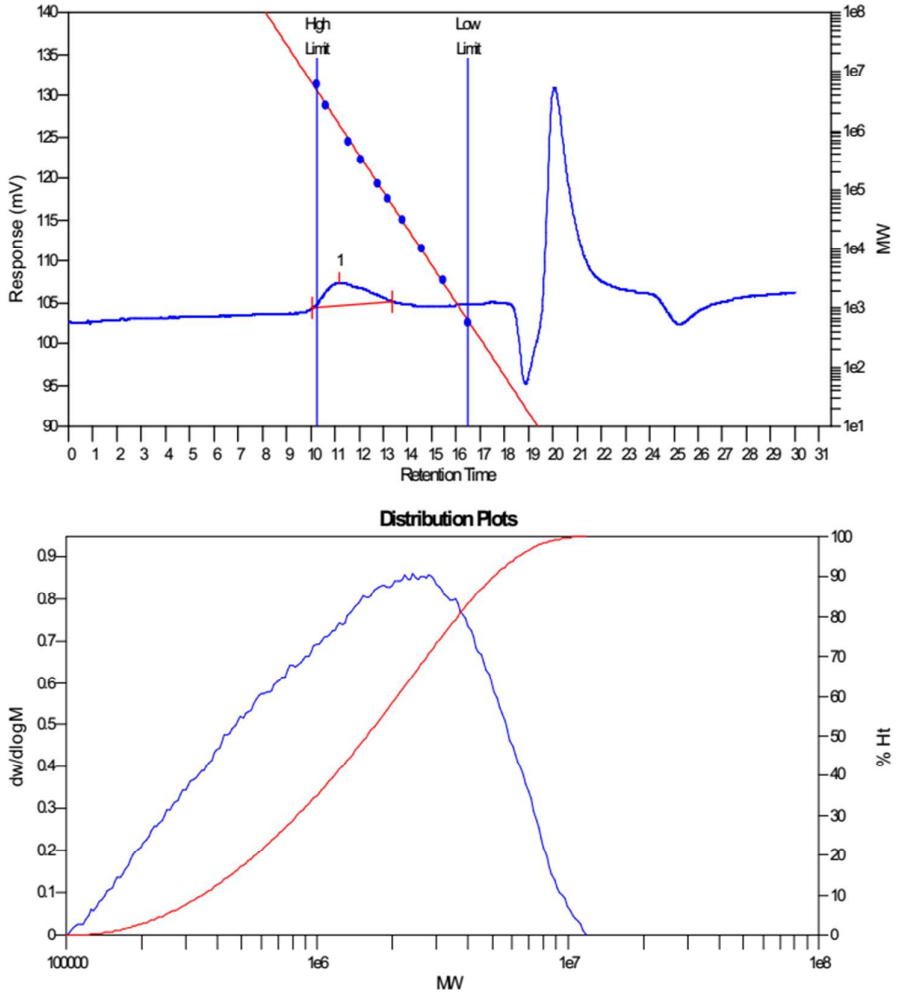
MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	2997713	873335	2697676	5175988	7258052	2360976	3.08894

Processed Peaks

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1		9.78	11.00	13.63	5.71127	0	677.646	100

Figure S114. GPC of the polymer from table 1, entry 18.



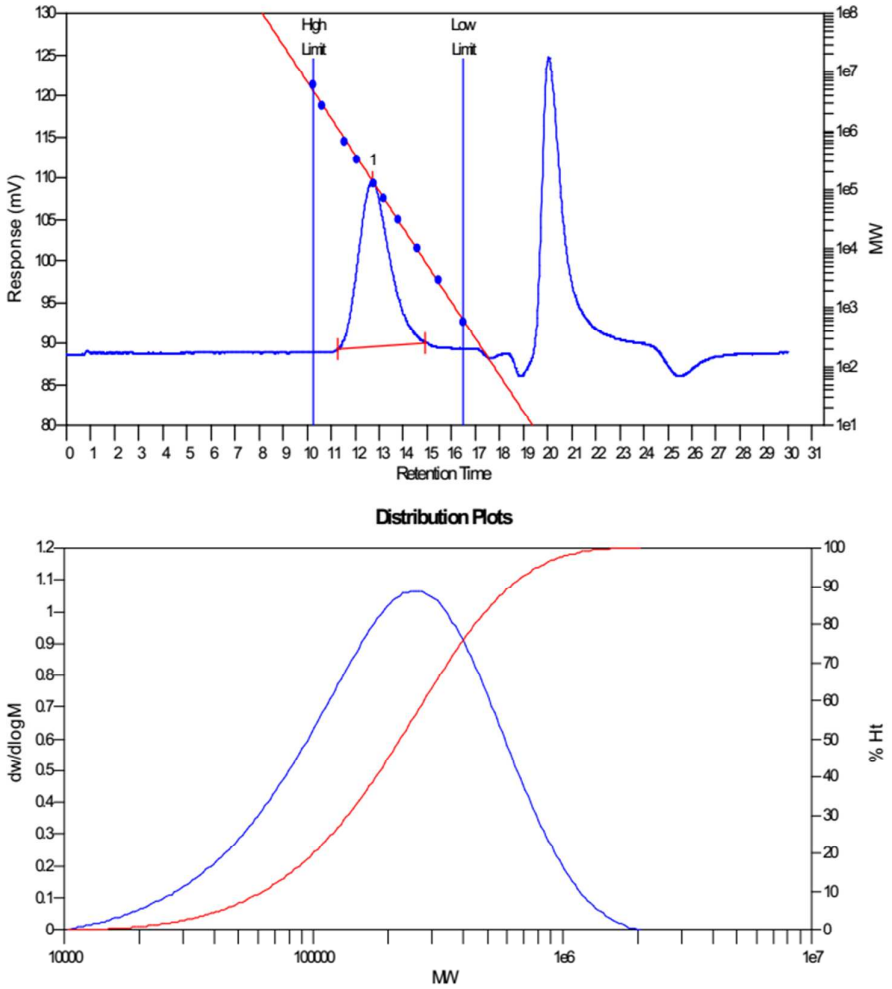
MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	2414678	853466	2176893	3905785	5317000	1935899	2.55065

Processed Peaks

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1		10.05	11.20	13.37	2.74049	0	306.774	100

Figure S115. GPC of the polymer from table 1, entry 19.



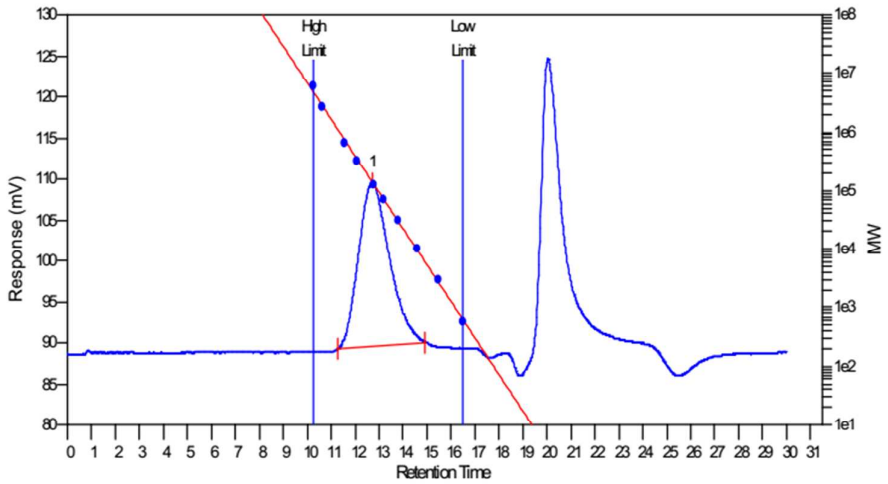
MW Averages

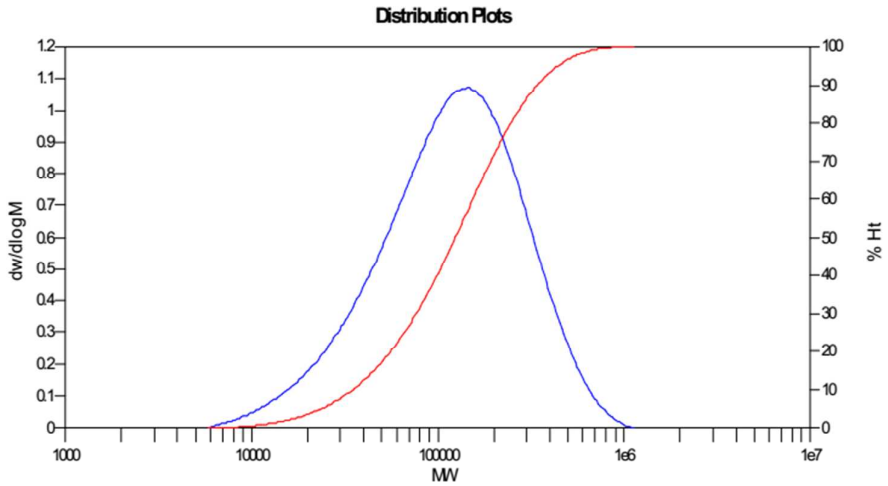
Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	258369	134661	290529	497947	718774	263417	2.15748

Processed Peaks

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1		11.27	12.70	14.93	19.9302	0	1793.09	100

Figure S116. GPC of the polymer from table 1, entry 20.





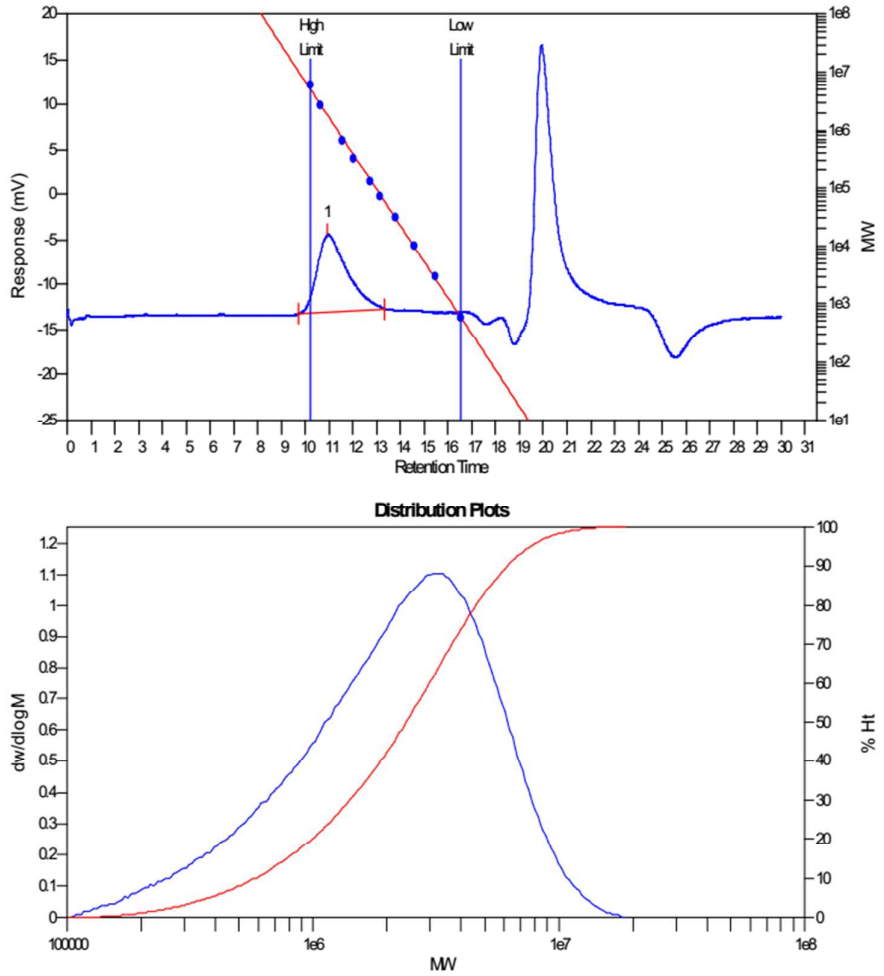
MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	143825	75446	161329	275075	395985	146900	2.13834

Processed Peaks

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1		11.27	12.70	14.93	19.9302	0	1793.09	100

Figure S117. GPC of the polymer from table 1, entry 21.



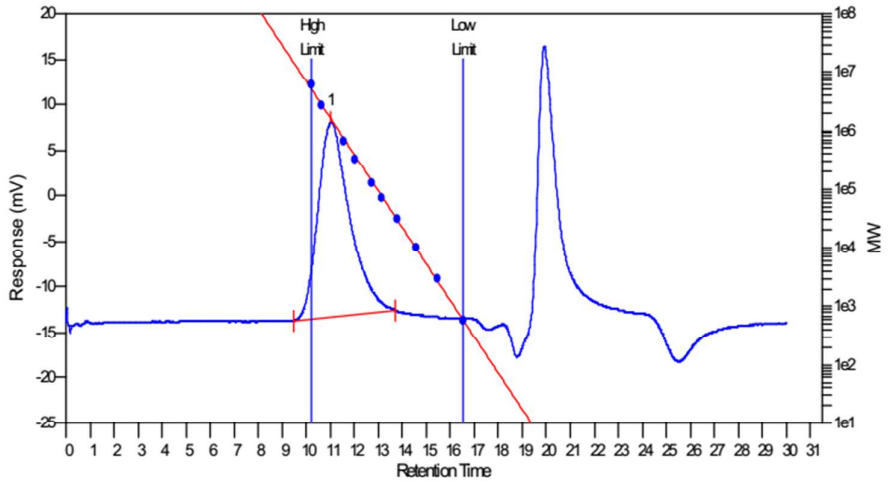
MW Averages

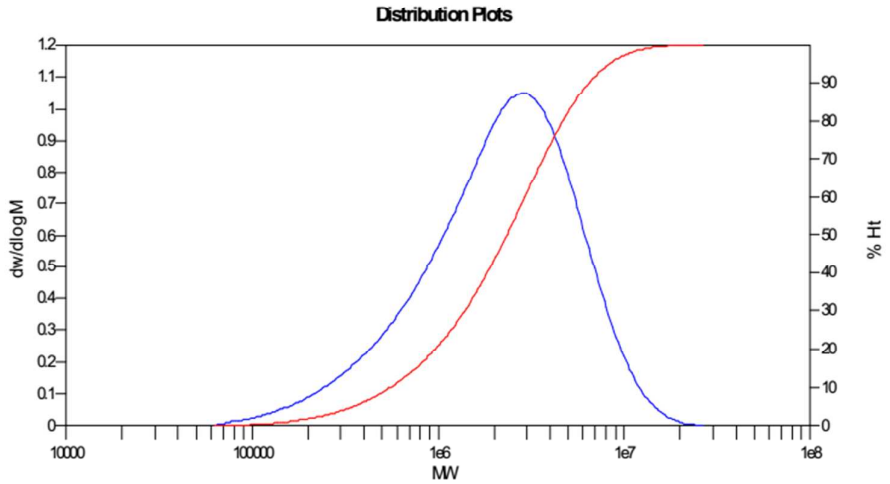
Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	3300175	1300989	2938342	4802320	6589563	2674999	2.25854

Processed Peaks

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1		9.73	10.93	13.35	8.61883	0	748.545	100

Figure S118. GPC of the polymer from table 1, entry 23.





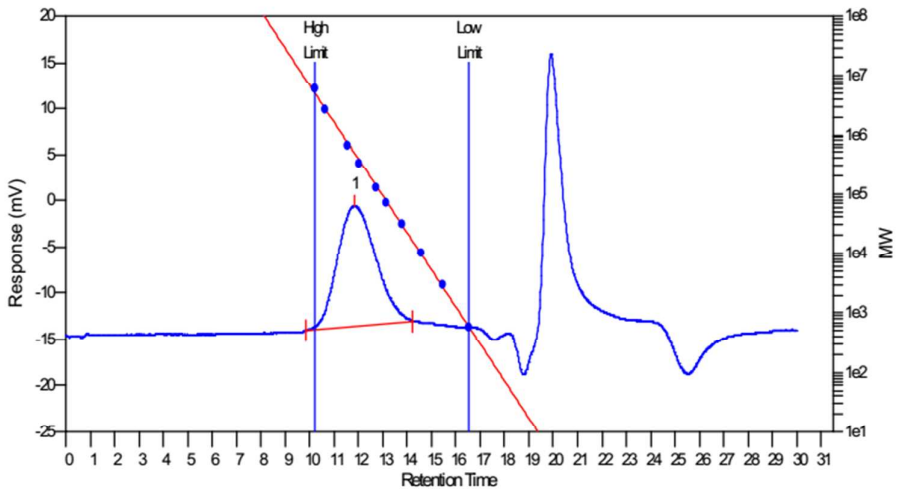
MW Averages

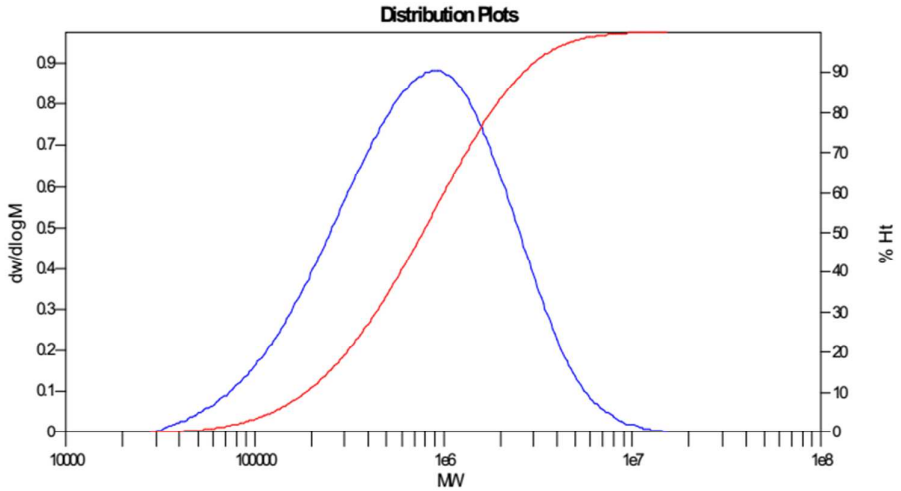
Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	2926532	1213802	3016507	5288479	7755845	2716599	2.48517

Processed Peaks

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1		9.48	11.02	13.68	21.2559	0	1943.55	100

Figure S119. GPC of the polymer from table 1, entry 24.





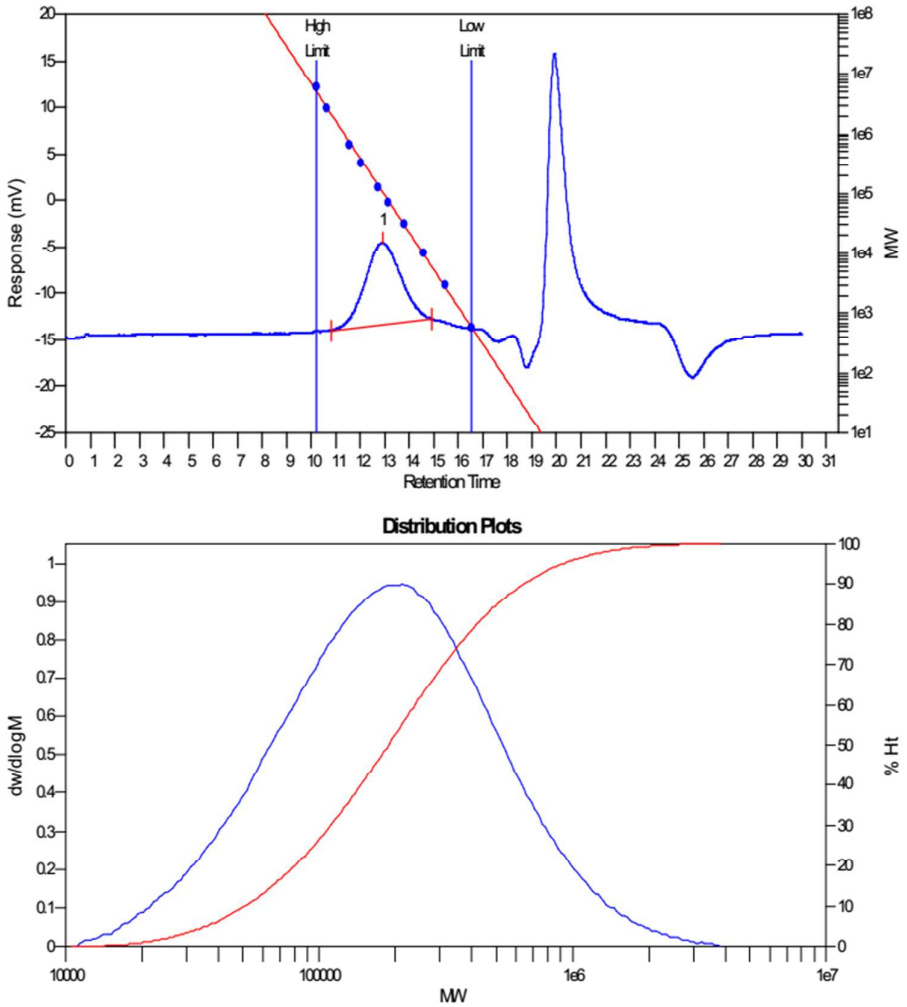
MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	923399	423280	1166371	2515389	4337124	1017114	2.75555

Processed Peaks

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1		9.87	11.87	14.23	12.9464	0	1405.69	100

Figure S120. GPC of the polymer from table 1, entry 25.



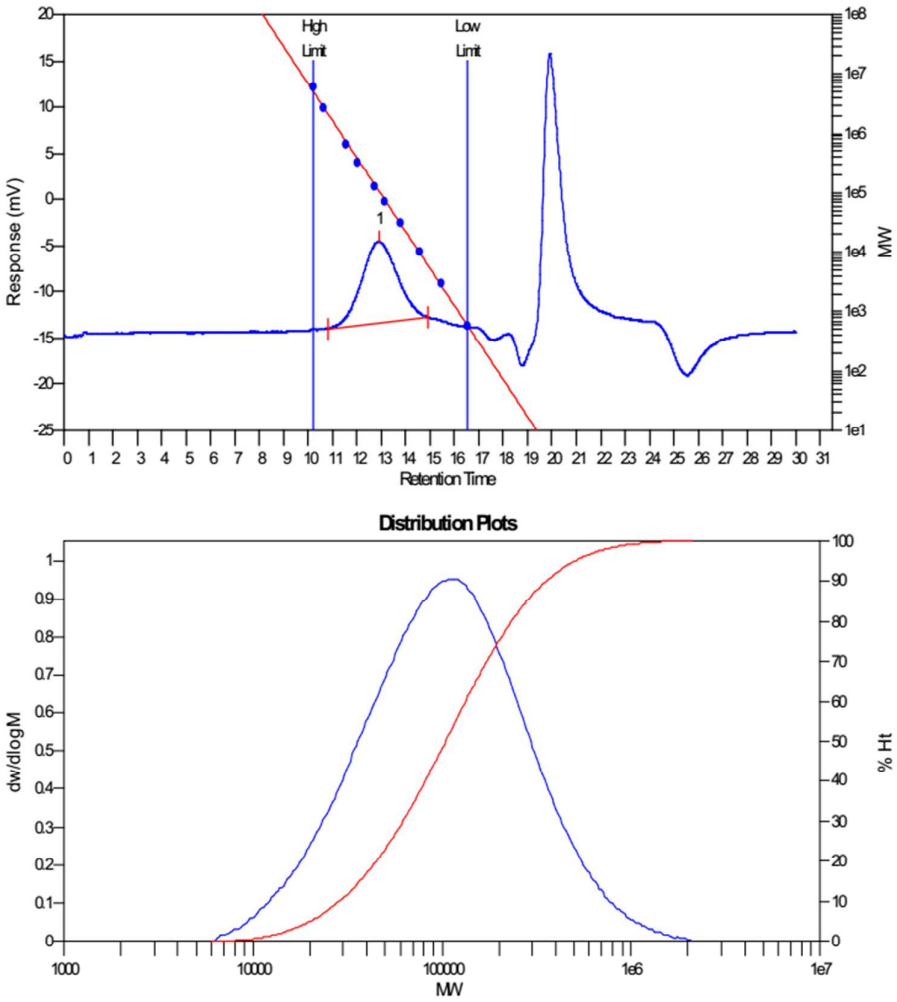
MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	213180	114573	287887	660587	1230852	250531	2.51269

Processed Peaks

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1		10.83	12.90	14.92	8.76582	0	890.119	100

Figure S121. GPC of the polymer from table 1, entry 26.



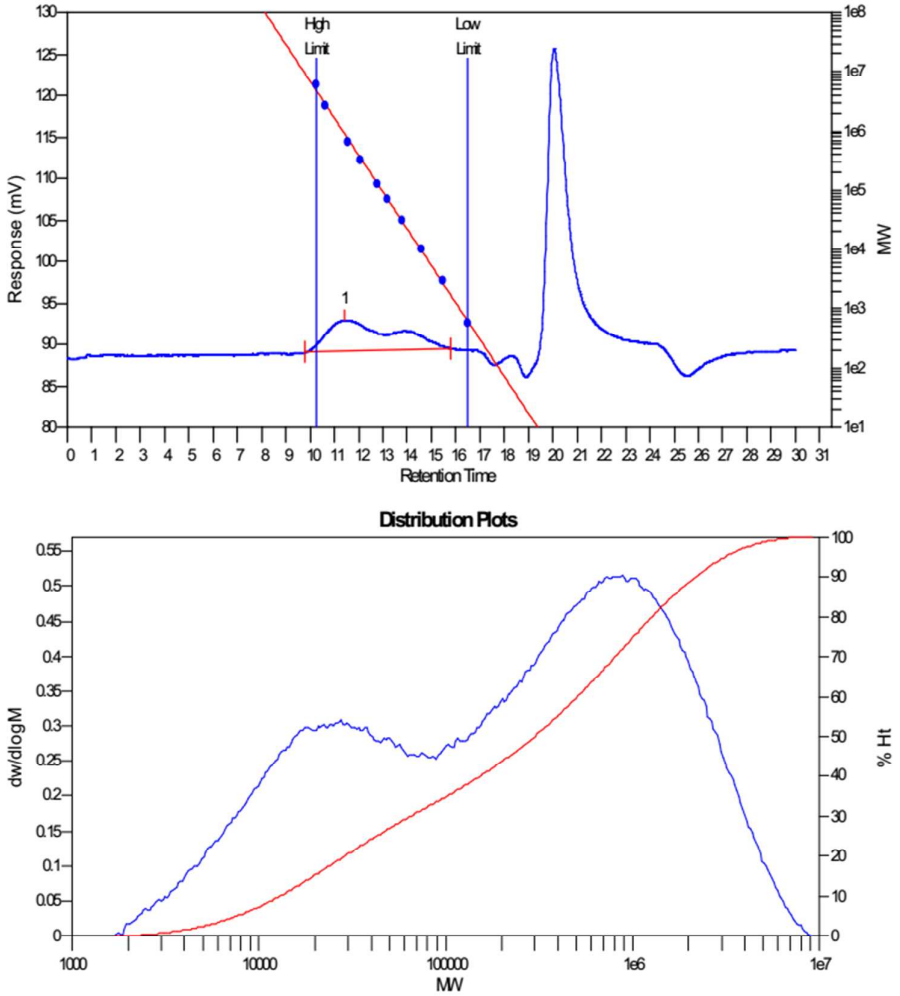
MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	118804	64252	159741	363368	674032	139858	2.48616

Processed Peaks

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1		10.83	12.90	14.92	8.76582	0	890.119	100

Figure S122. GPC of the polymer from table 1, entry 27.



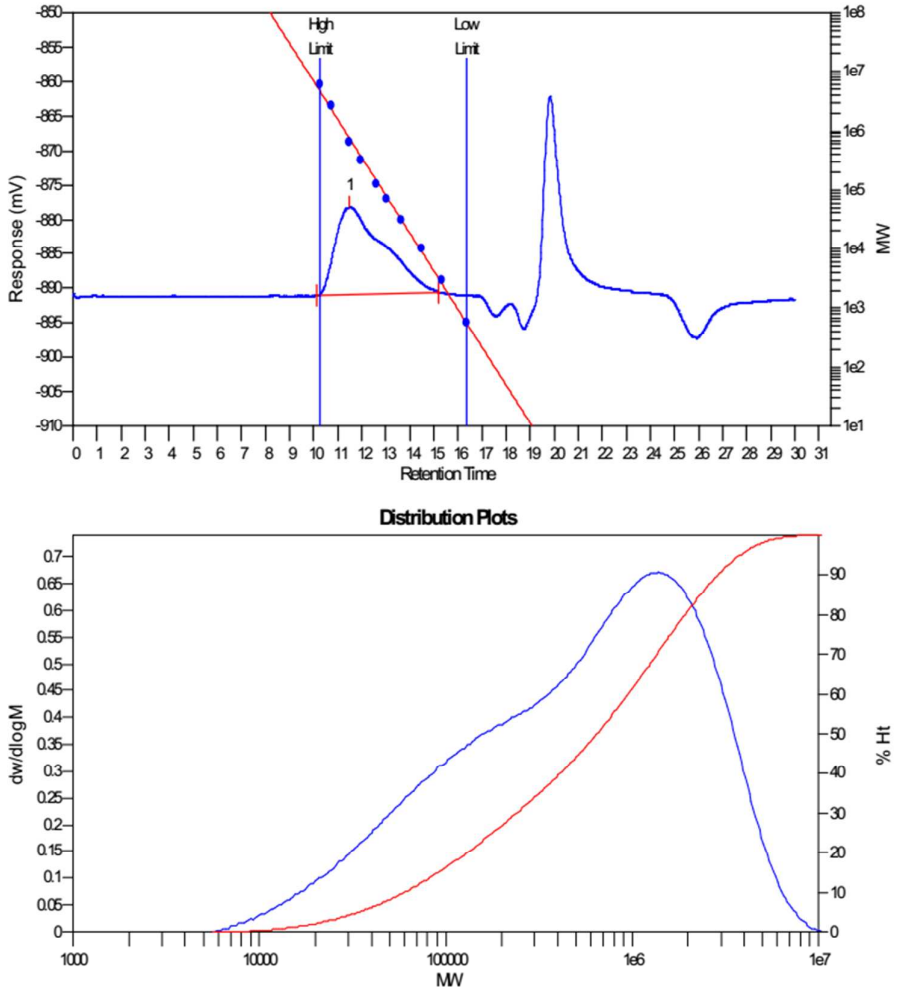
MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	883818	38248	748418	2342142	3600345	570063	19.5675

Processed Peaks

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1		9.80	11.43	15.80	3.82719	0	715.724	100

Figure S123. GPC of the polymer from table 1, entry 28.



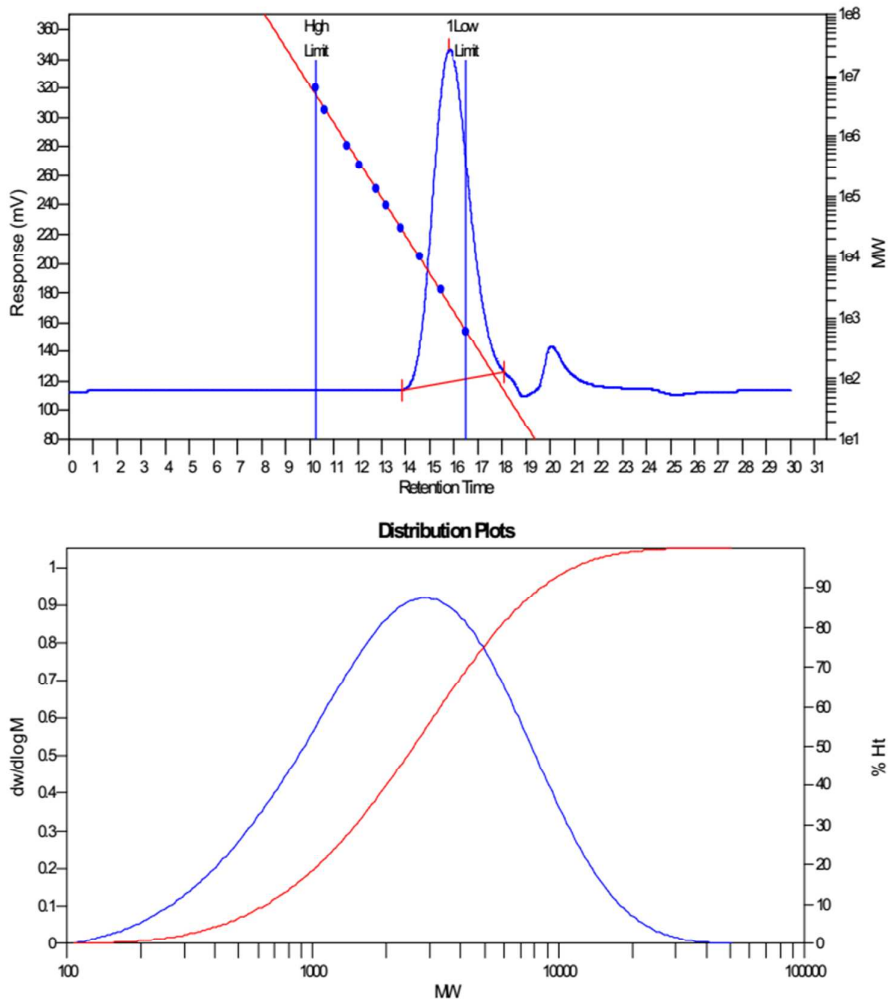
MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	1391478	155754	1104610	2572869	3764584	911919	7.09202

Processed Peaks

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1		10.12	11.48	15.18	12.7253	0	1757.3	100

Figure S124. GPC of the polymer from table 1, entry 29.



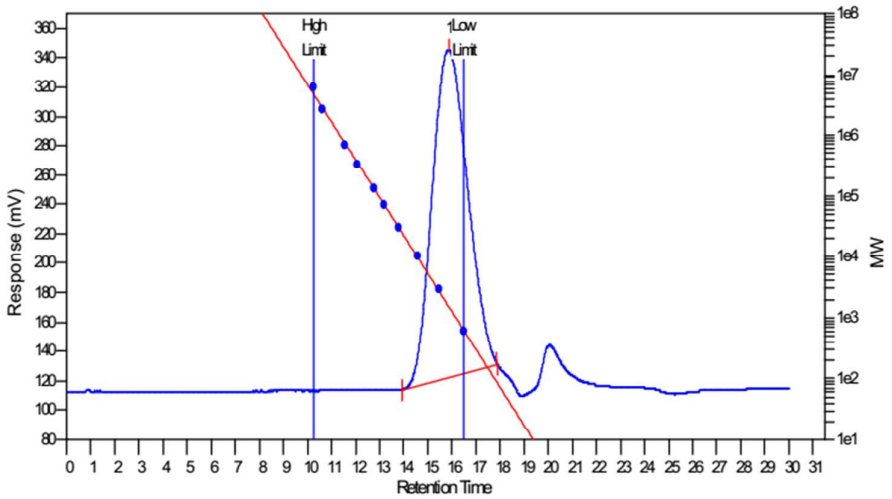
MW Averages

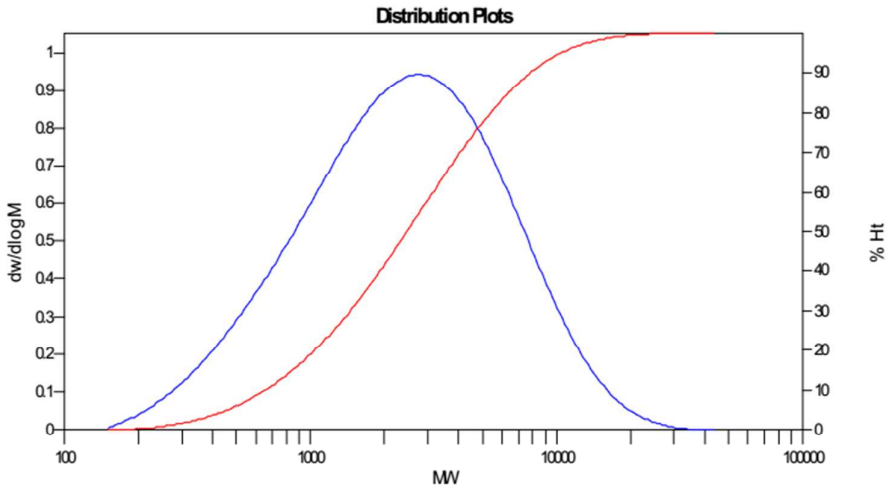
Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	2887	1464	3767	7708	12704	3315	2.57309

Processed Peaks

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1		13.83	15.82	18.10	227.209	0	23721.1	100

Figure S125. GPC of the polymer from table 2, entry 1.





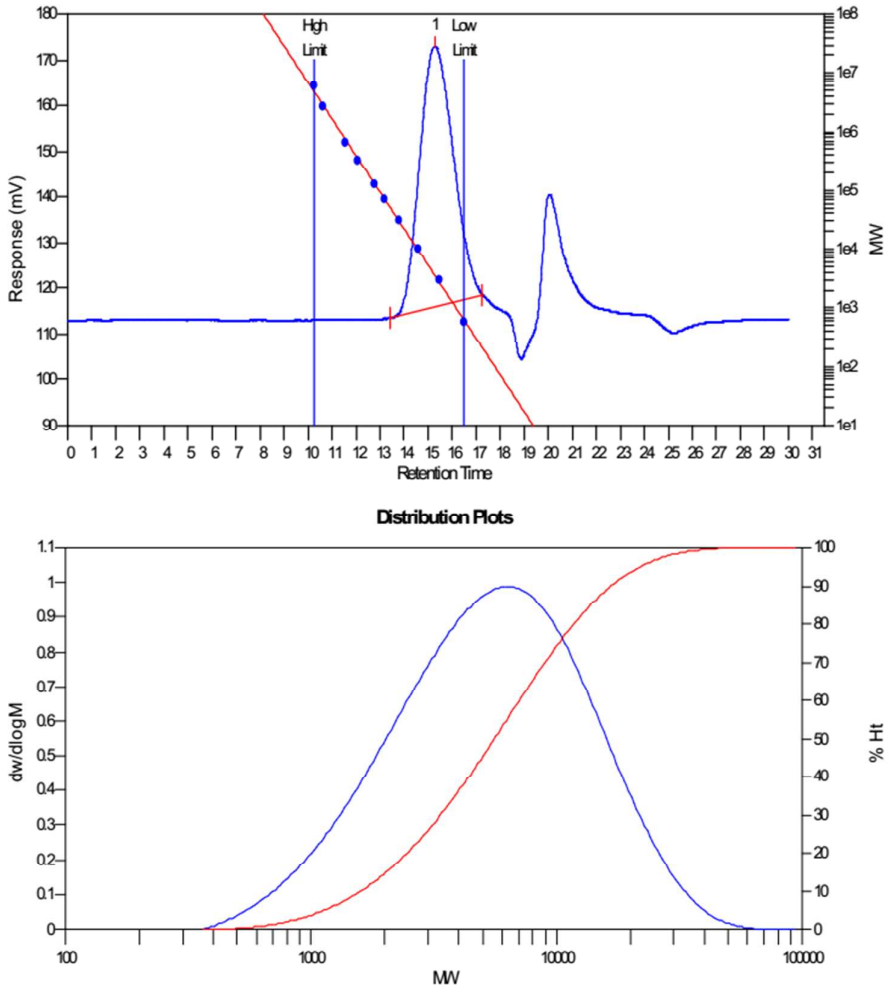
MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	2752	1486	3505	6822	10858	3112	2.35868

Processed Peaks

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1		13.93	15.87	17.87	223.488	0	22751.8	100

Figure S126. GPC of the polymer from table 2, entry 2.



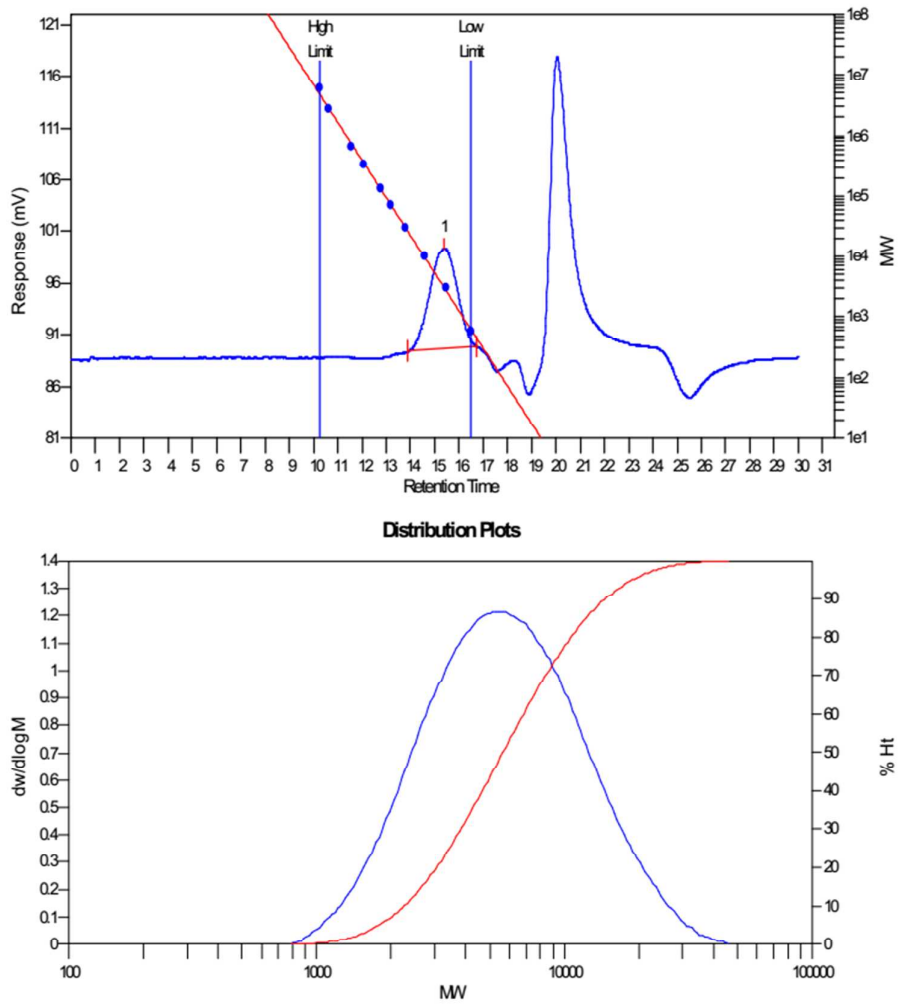
MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	6382	3526	7652	13954	21175	6874	2.17016

Processed Peaks

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1		13.40	15.28	17.25	56.9606	0	5523.54	100

Figure S127. GPC of the polymer from table 2, entry 3.



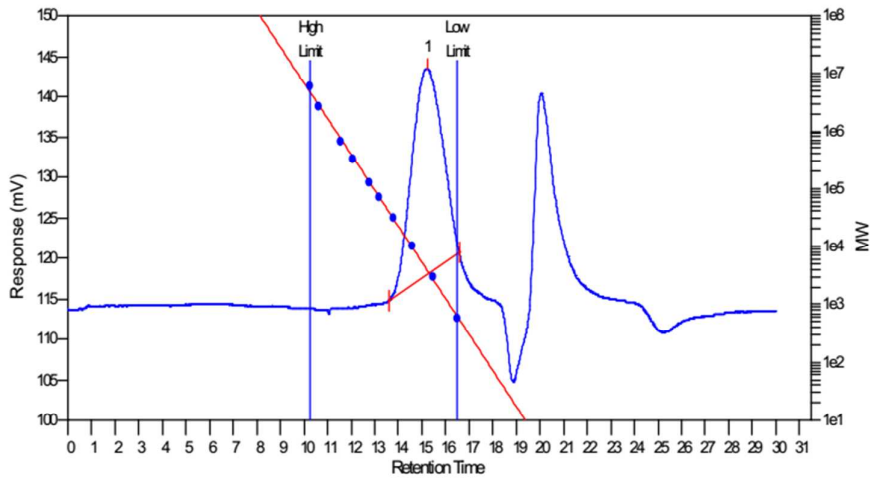
MW Averages

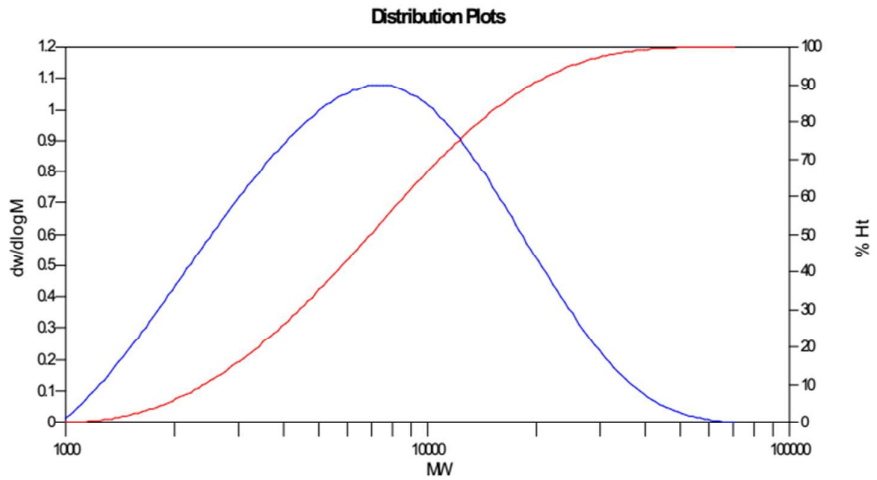
Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	5525	4412	7213	11429	16394	6684	1.63486

Processed Peaks

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1		13.90	15.38	16.72	9.76641	0	769.773	100

Figure S128. GPC of the polymer from table 2, entry 4.





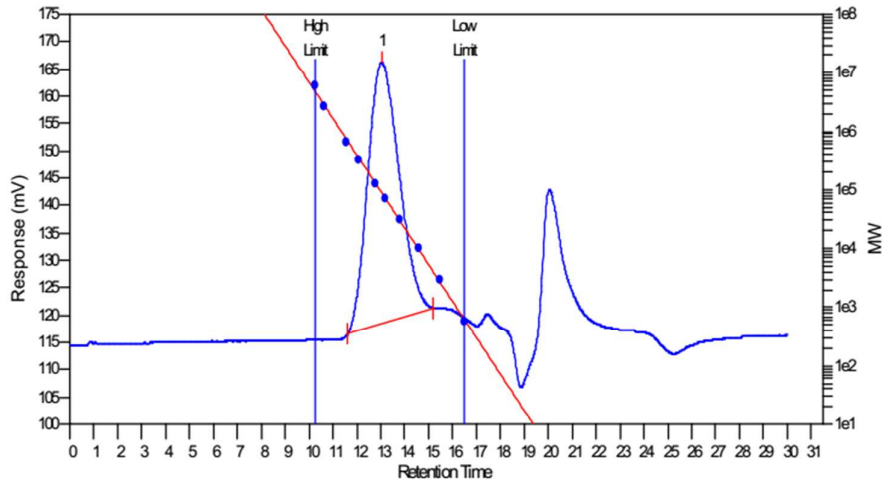
MW Averages

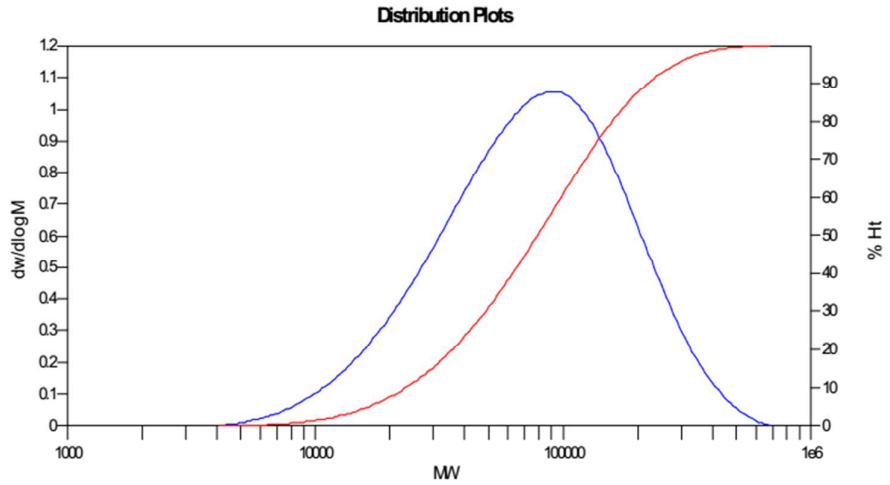
Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	7551	5087	9207	15518	22694	8418	1.80991

Processed Peaks

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1		13.60	15.22	16.57	25.4827	0	2270.57	100

Figure S129. GPC of the polymer from table 2, entry 5.





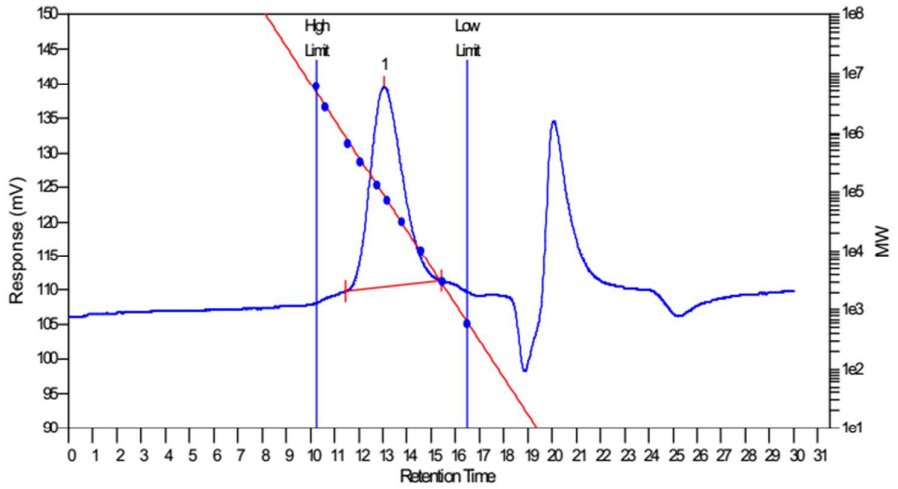
MW Averages

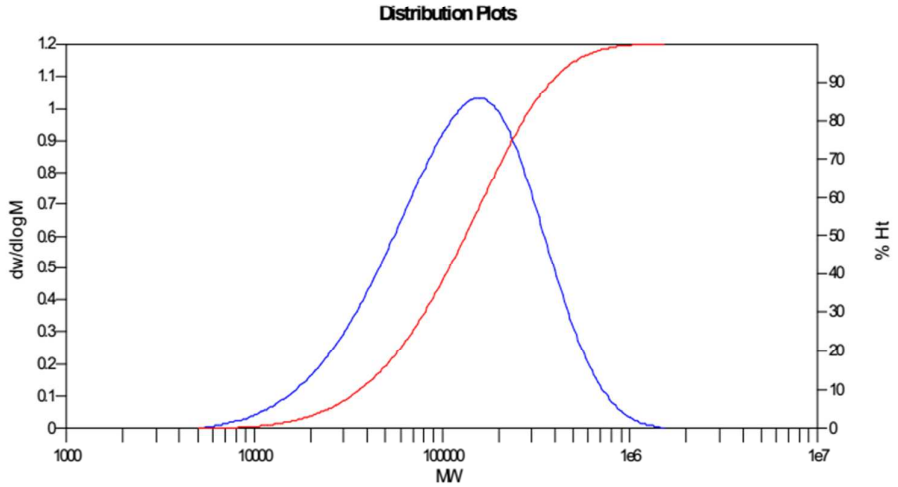
Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	91349	49986	102465	174185	250165	93421	2.04987

Processed Peaks

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1		11.62	13.03	15.18	47.6893	0	4354.54	100

Figure S130. GPC of the polymer from table 2, entry 6.





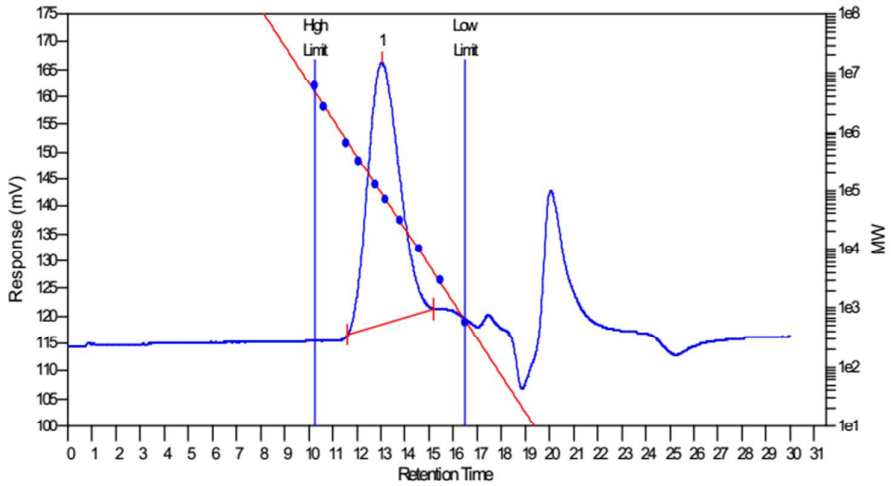
MW Averages

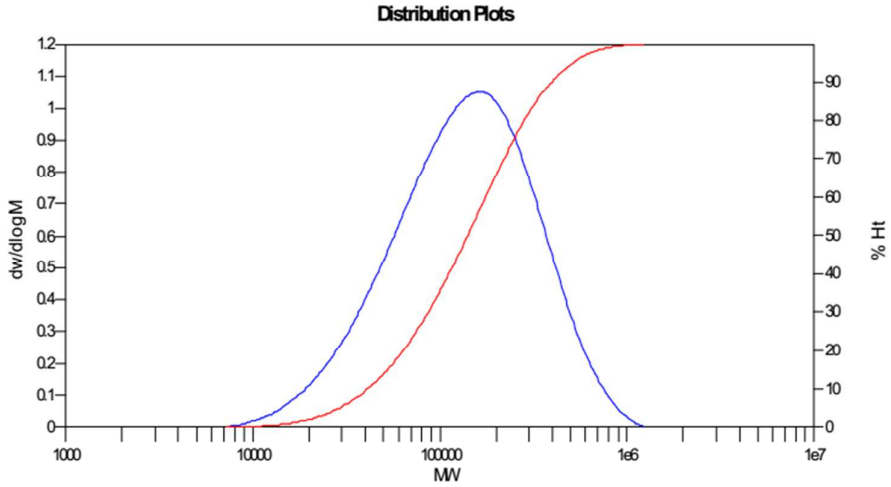
Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	155980	79188	176304	313803	472793	158977	2.2264

Processed Peaks

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1		11.47	13.05	15.43	28.9855	0	2692.74	100

Figure S131. GPC of the polymer from table 2, entry 7.





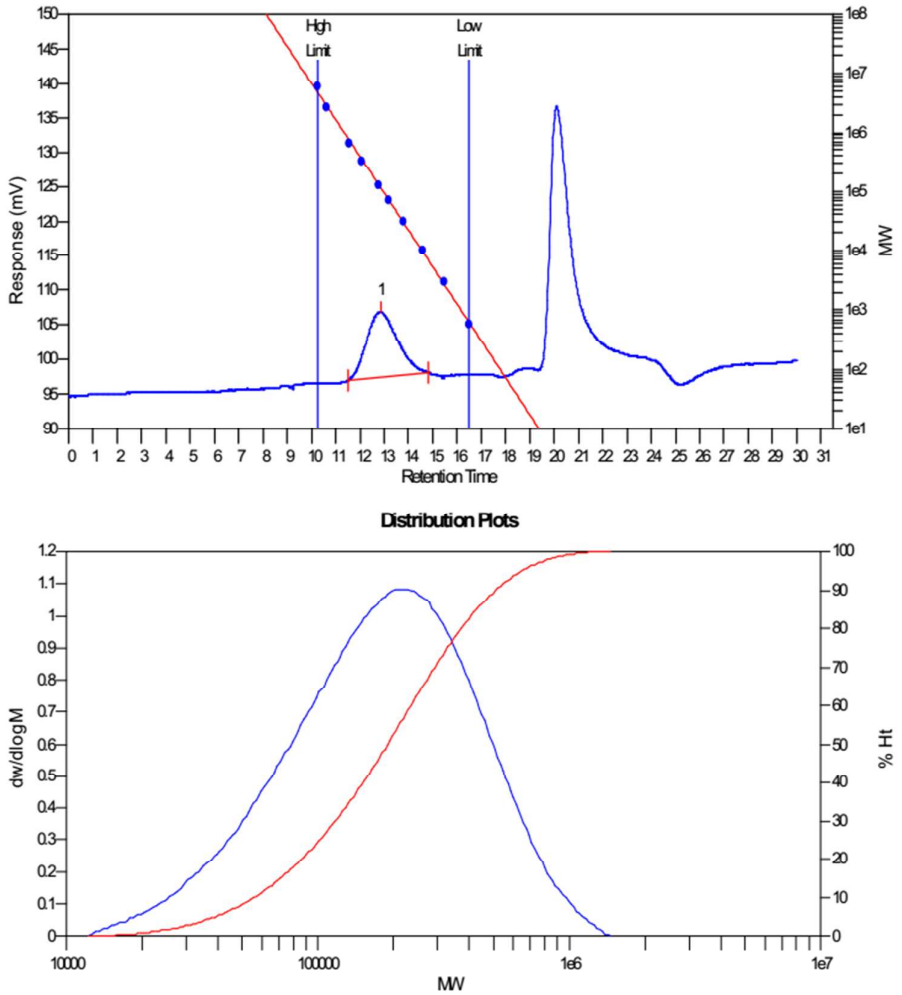
MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	163660	89026	184027	314461	452826	167078	2.06712

Processed Peaks

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1		11.62	13.03	15.18	47.6893	0	4354.54	100

Figure S132. GPC of the polymer from table 2, entry 8.



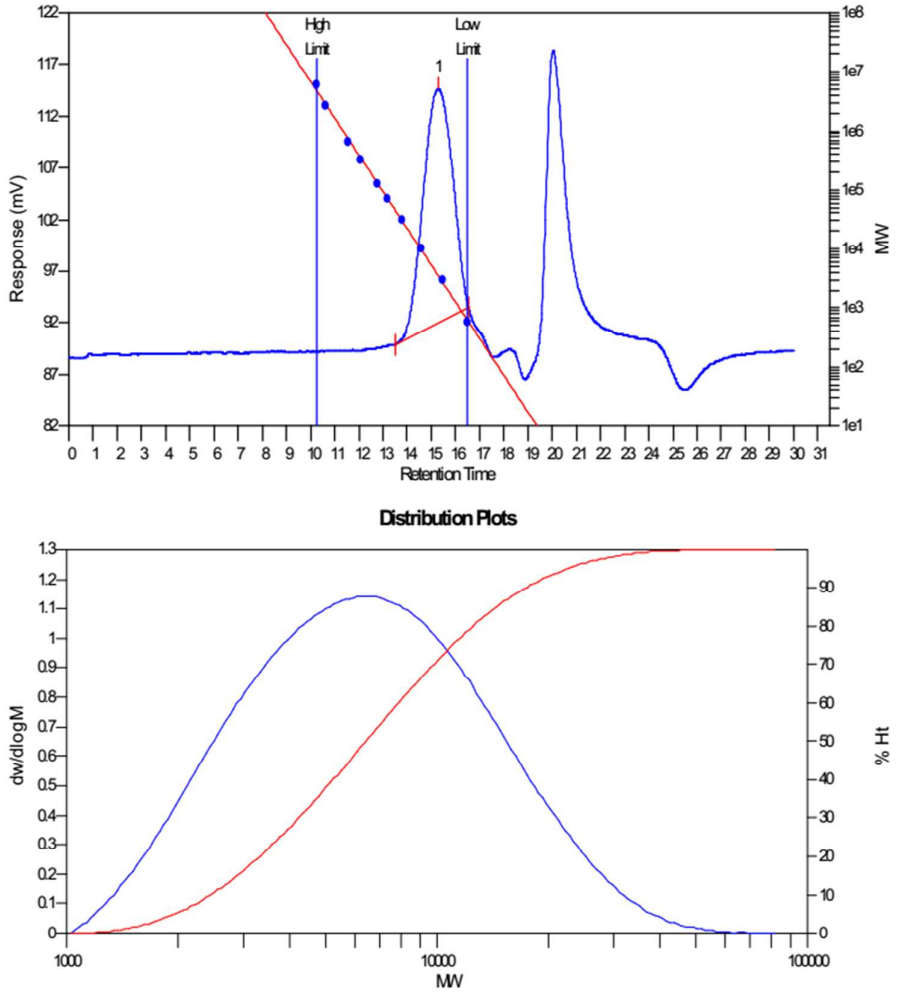
MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	208118	119976	242195	402196	566771	220901	2.0187

Processed Peaks

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1		11.50	12.85	14.82	9.43962	0	835.158	100

Figure S133. GPC of the polymer from table 2, entry 9.



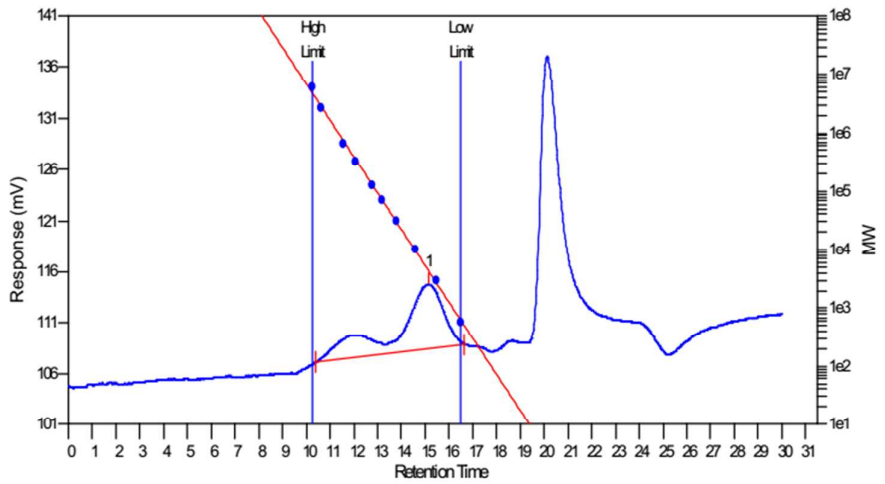
MW Averages

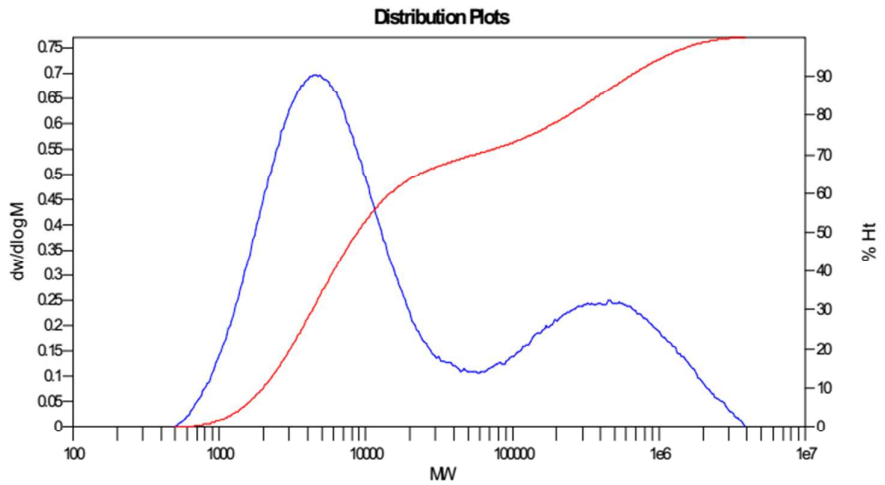
Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	6382	4945	8403	13900	20725	7732	1.69929

Processed Peaks

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1		13.50	15.28	16.53	22.6451	0	1897.21	100

Figure S134. GPC of the polymer from table 2, entry 10.





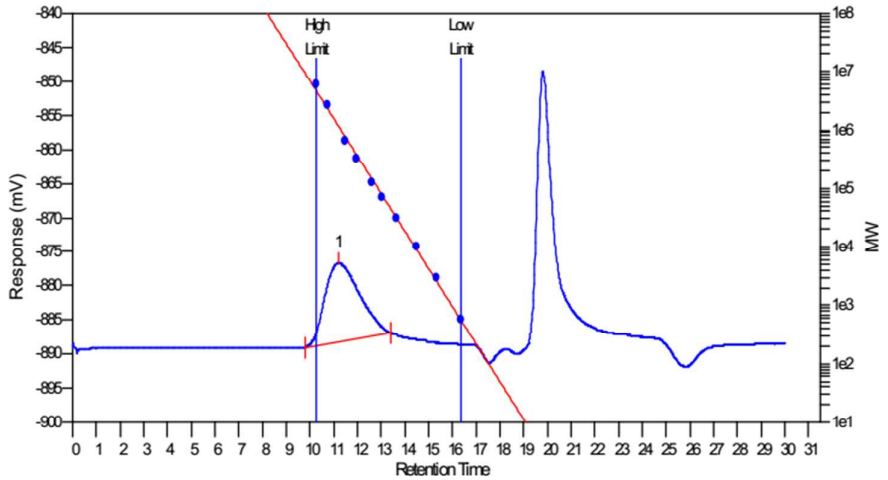
MW Averages

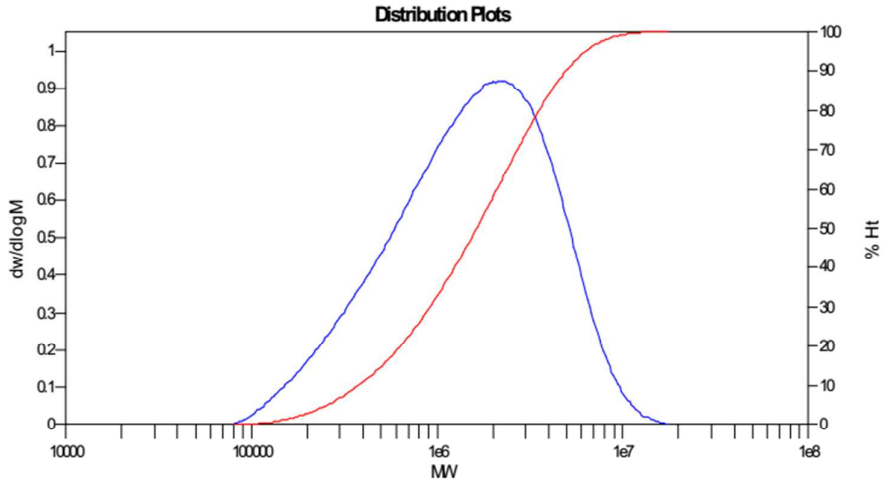
Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	4395	5115	184673	1159145	1766902	109981	36.1042

Processed Peaks

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1		10.40	15.13	16.65	6.29762	0	872.256	100

Figure S135. GPC of the polymer from table 2, entry 11.





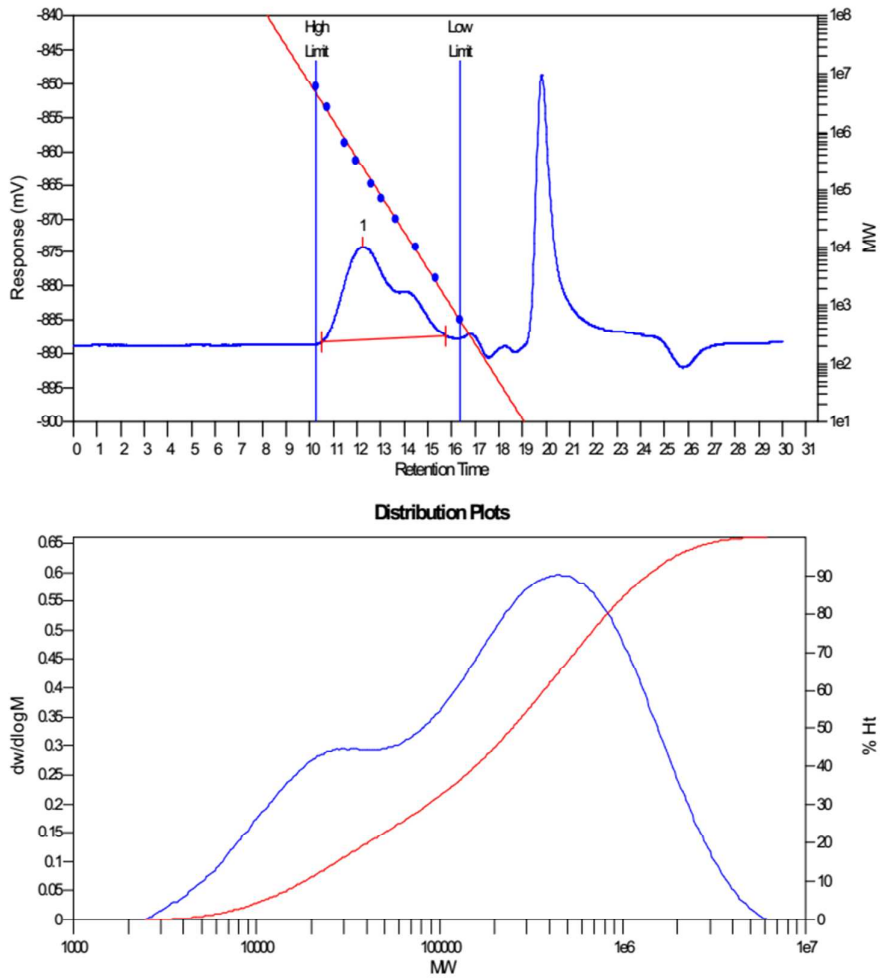
MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	2230032	892985	2214194	4020364	5828324	1976164	2.47954

Processed Peaks

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1		9.78	11.20	13.40	11.5047	0	1160.97	100

Figure S136. GPC of the table S1, Fraction 1.



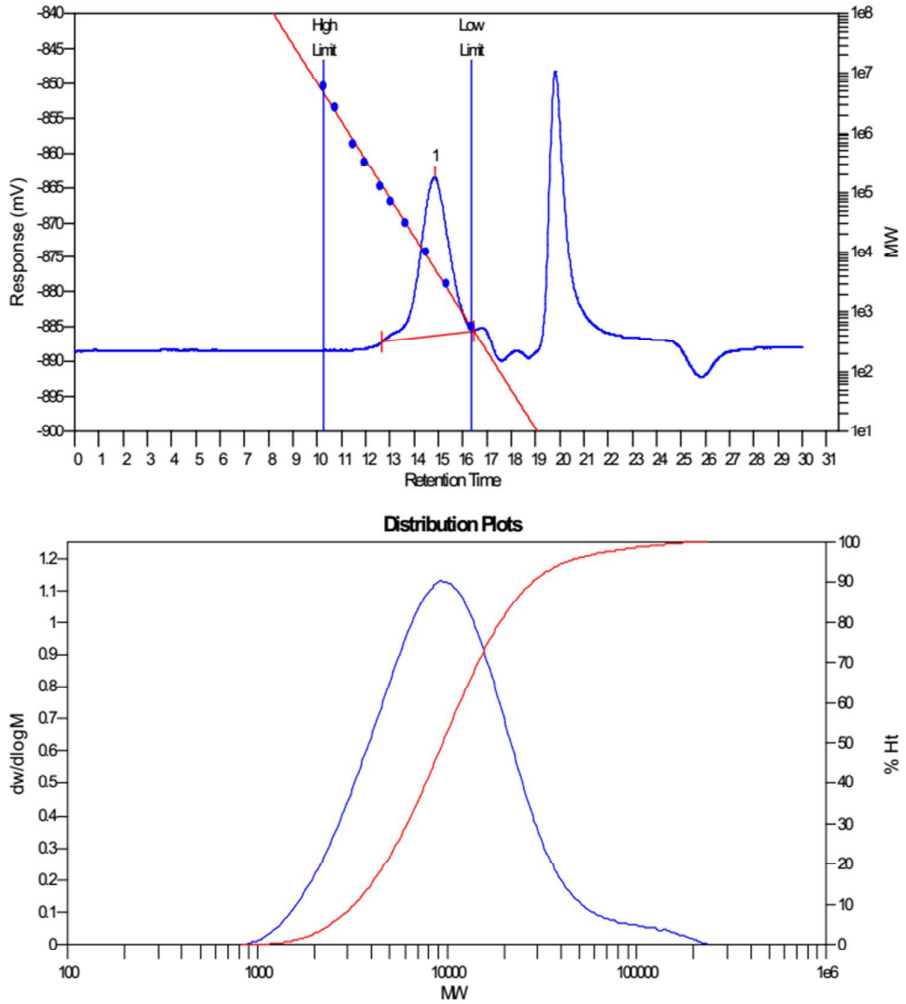
MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	444181	52572	503877	1436182	2306520	398478	9.58451

Processed Peaks

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1		10.48	12.25	15.73	13.7454	0	2138.33	100

Figure S137. GPC of the table S1, Fraction 2.



MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	9241	6810	14679	40390	92590	12725	2.15551

Processed Peaks

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1		12.67	14.85	16.47	22.66	0	1859.01	100

Figure S138. GPC of the table S1, Fraction 3.

5. References

(1) Brasse M., Campora J., Palma P., Álvarez E., Cruz V., Ramos J, Reyes M.L.. Nickel 2-iminopyridine N-oxide (PymNox) complexes: cationic counterparts of salicylaldiminate-based neutral ethylene polymerization catalysts. *Organometallics*. **2008**, *27*, 4711–4723

(2) Berthon-Gelloz G., Siegler M.A., Spek A.L., Tinant B., Reek J.N., Markó I.E.. IPr* an easily accessible highly hindered N-heterocyclic carbene. *Dalton Trans.* **2010**, *39*, 1444-1446.

(3) Dierick S., Dewez D.F., Markó I.E.. IPr*(2-Np)□ An Exceedingly Bulky N-Heterocyclic Carbene. *Organometallics* **2014**, *33*, 677−683.

(4) Dai, S. Y.; Chen, C. L. Direct synthesis of functionalized high‐molecular‐weight polyethylene by copolymerization of ethylene with polar monomers. *Angew. Chem., Int. Ed.* **2016**, *55*, 13281-13285.

(5) Dai S. Y., Sui, X. L., Chen, C. L. Synthesis of high molecular weight polyethylene using iminopyridyl nickel catalysts. *Chem. Commun.* **2016**, *52*, 9113-9116.

6. X-ray Crystallography

Complexes Ni-Ph:

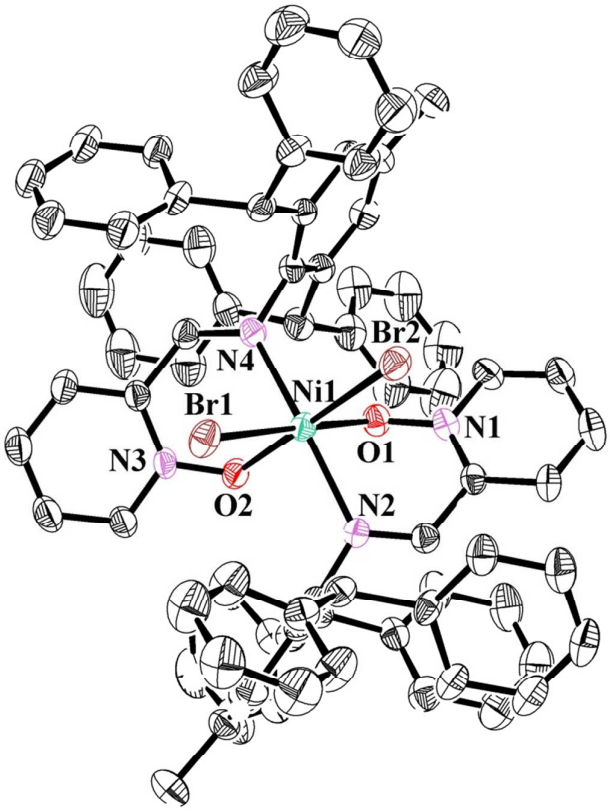


Figure S139. Molecular structure of complex **Ni-Ph**. Selected bond lengths (Å) and angles (deg): Ni1-Br1 2.5239(14), Ni1-Br2 2.5220(14), Ni1-O1 2.044(5), Ni1-O2 2.066(5), Ni1-N2 2.158(6), Ni1-N4 2.151(6); Br2-Ni1-Br1 91.78(5), O1-Ni1-O2 86.69(19), N4-Ni1-N2 161.9(2). Hydrogen atoms have been omitted for clarity. Atoms are drawn at the 30% probability level.

Table S3. Crystal data and structure refinement for Ni-Ph.

Entry	**Ni-Ph**
Formula	C79 H66 Br2 Cl2 N4 Ni O2
Formula weight	1392.79
Temperature[K]	293(2)
λ(Mo-Kα)[Å]	1.54178
Crystal system	Triclinic
Space group	P-1
a[Å]	16.5810(9)
b[Å]	16.5963(16)
c[Å]	16.8376(12)
α[°]	85.765(2)
β[°]	68.6950(10)
γ[°]	66.2460(10)
Volume[$Å^3$]	3936.8(5)
Z	2
D(calc)[$g \cdot cm^{-3}$]	1.175
μ[mm^{-1}]	2.504
F(000)	1432
θ min-max (º)	3.7170- 67.3470
h	-19→19
k	-19→19
l	-19→19
Reflections collected	13715
Reflections unique	13715
R(int)	0.0000
Data / restraints / parameters	13715 /0 / 815
Final R indices [I>2σ(I)]	R_1 = 0.1009 wR_2 = 0.2429
R indices (all data)	R_1 =0.1409 wR_2 = 0.2703
GOF on F^2	1.120

Complexes Ni-Ph-Ph:

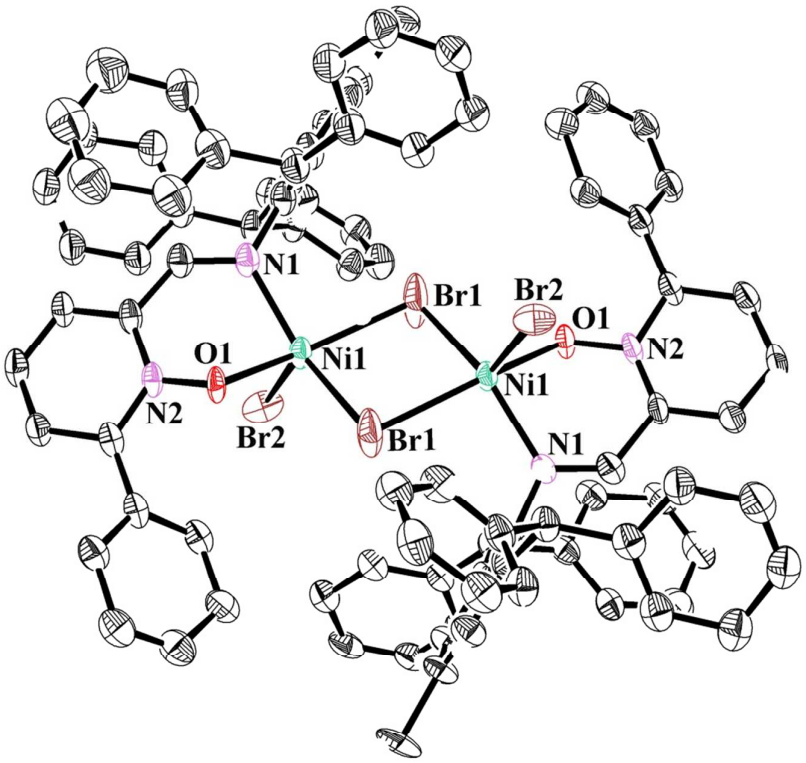


Figure S150.Molecular structure of complex **Ni-Ph-Ph**. Selected bond lengths (Å) and angles (deg): Ni1 Br1 2.461(2), Ni1 Br2 2.405(3), Ni1 O1 1.998(9), Ni1 N1 2.046(12); Br2 Ni1 Br1 105.24(9), O1 Ni1 N1 84.9(4). Hydrogen atoms have been omitted for clarity. Atoms are drawn at the 30% probability level.

Table S4. Crystal data and structure refinement for Ni-Ph-Ph.

Entry	**Ni-Ph-Ph**
Formula	C90 H72 Br4 N4 Ni2 O2
Formula weight	1678.58
Temperature[K]	298(2)
λ(Mo-Kα)[Å]	0.71073
Crystal system	Triclinic
Space group	P -1
a[Å]	11.8392(9)
b[Å]	14.1257(12)
c[Å]	14.3685(13)
α[°]	90.9240(10)
β[°]	102.292(2)
γ[°]	113.080(3)
Volume[$Å^3$]	2146.6(3)
Z	1
D(calc)[$g \cdot cm^{-3}$]	1.298
μ[mm^{-1}]	2.346
F(000)	852
θ min-max (°)	2.588 -22.095
h	-14→13
k	-15→16
l	-12→17
Reflections collected	10807
Reflections unique	7374
R(int)	0.1592
Data / restraints / parameters	7374 /0 /461
Final R indices [I>2σ(I)]	R_1 = 0.1567 wR_2 = 0.3638
R indices (all data)	R_1 =0.2193 wR_2 = 0.4024
GOF on F^2	1.143