Supplementary Information for:

Dearomatized Diimines for Nickel(II) and Palladium(II) Catalyzed Ethylene Polymerization and Copolymerization

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1. Figures

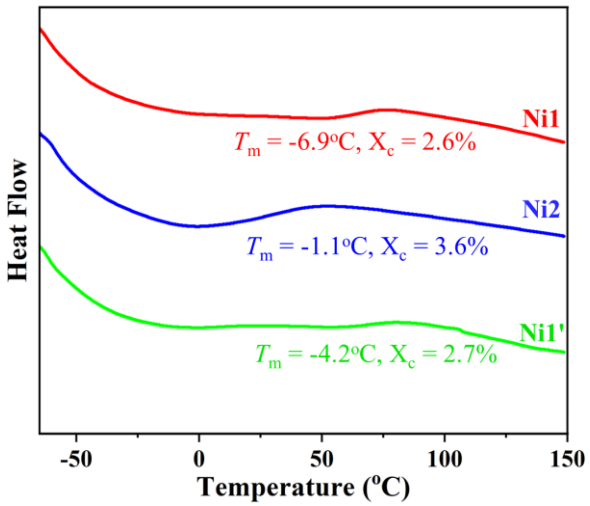


Figure S1. Comparisons on the melting points (T_m) and crystallinity (X_c) of polyethylene generated by **Ni1**, **Ni2** and **Ni1'**.

2. General Considerations

All experiments were performed under a dry nitrogen atmosphere using a glove-box or standard Schlenk techniques. Solvent including dichloromethane, n-hexane and toluene were dried and distillated before. Other reagents were obtained from commercial sources and used without purification. Deuterated solvents used for NMR were dried and distilled prior to use.

NMR spectra of ligands and complexes was acquired at 25 °C on Bruker DPX 500 spectrometers using $CDCl_3$ as solvent and TMS as an internal standard. The NMR data of polymer samples produced by **Pd1** and **Pd2** were obtained at 25 °C on a Bruker DPX 500 spectrometer, using $CDCl_3$ as solvent, while the NMR data of polymer samples produced by **Ni1**-**Ni4**, **Ni1'** and **Pd3**-**Pd4** were obtained at 120 °C on a Bruker ARX400 NMR spectrometer, using $C_6D_4Cl_2$ or $C_2D_2Cl_4$ as solvent. The chemical shifts of the ^1H and ^{13}C NMR spectra were referenced to the tetramethylsilane signal (0 ppm) or residual solvent resonance. Coupling constants are in Hz. Mass spectra were obtained using electro spray ionization (ESI) LCMS-2010A for **L2**, **L4**, **Pd2** and **Pd4**. Mass spectra of **Ni2** and **Ni4** were determined on a bruker ultraflextreme MALDI-TOF-MS. Elemental analysis was performed by the Analytical

Center of the Anhui University. X-ray Diffraction data were collected at 298(2) K on a Bruker Smart CCD area detector with graphite-monochromated Mo K^{α} radiation (λ = 0.71073 Å). Molecular weight and molecular weight distribution of the polymer obtained by **Pd1** and **Pd2** were determined by GPC eluting with THF on a Tosh instrument (Tosh, Tokyo, Japan) equipped with two linear Styragel columns. The system was calibrated with polystyrene standards and operated at 40 ℃ with a flow rate of 0.35 mL/min. Molecular weight and molecular weight distribution of the polymer obtained by **Ni1-Ni4**, **Ni1'** and **Pd3-Pd4** were determined by gel permeation chromatography (GPC) with a PL-220 equipped with two Agilent PLgel Olexis columns at 150 ^{o}C using trichlorobenzene as a solvent, and the calibration was made using polystyrene standard. DSC was performed by a DSC 25 from TA Instruments. Samples were quickly heated to 150 ℃ and kept for 5 min to remove thermal history, then cooled to -70 ℃ (or 30 ℃) at a rate of 10 K/min, and finally reheated to 150 ℃ at the same rate under a nitrogen flow (50 mL/min). The maximum points endotherm (heating scan) were taken as the melting temperature (T_m).

3. ^{1}H and ^{13}C NMR of the Synthetic Compounds.

3.1. ^{1}H and ^{13}C NMR of ligands

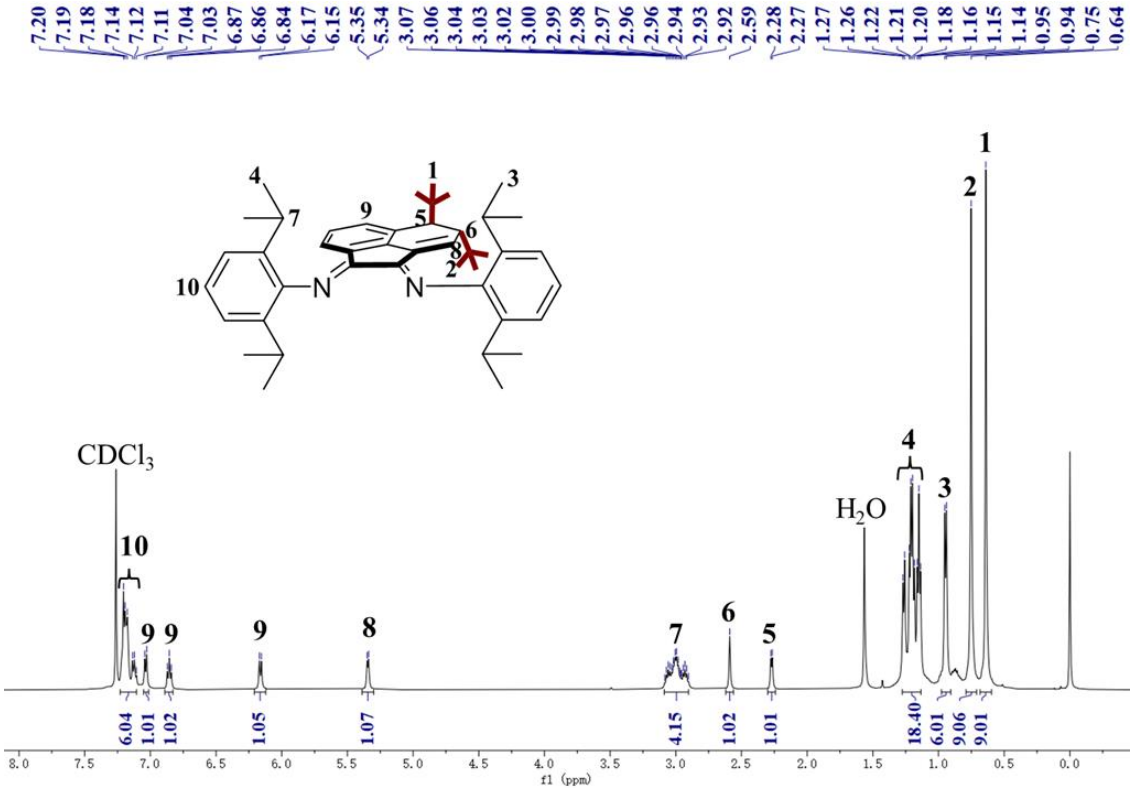


Figure S2. ^{1}H NMR spectrum of **L2** in $CDCl_3$.

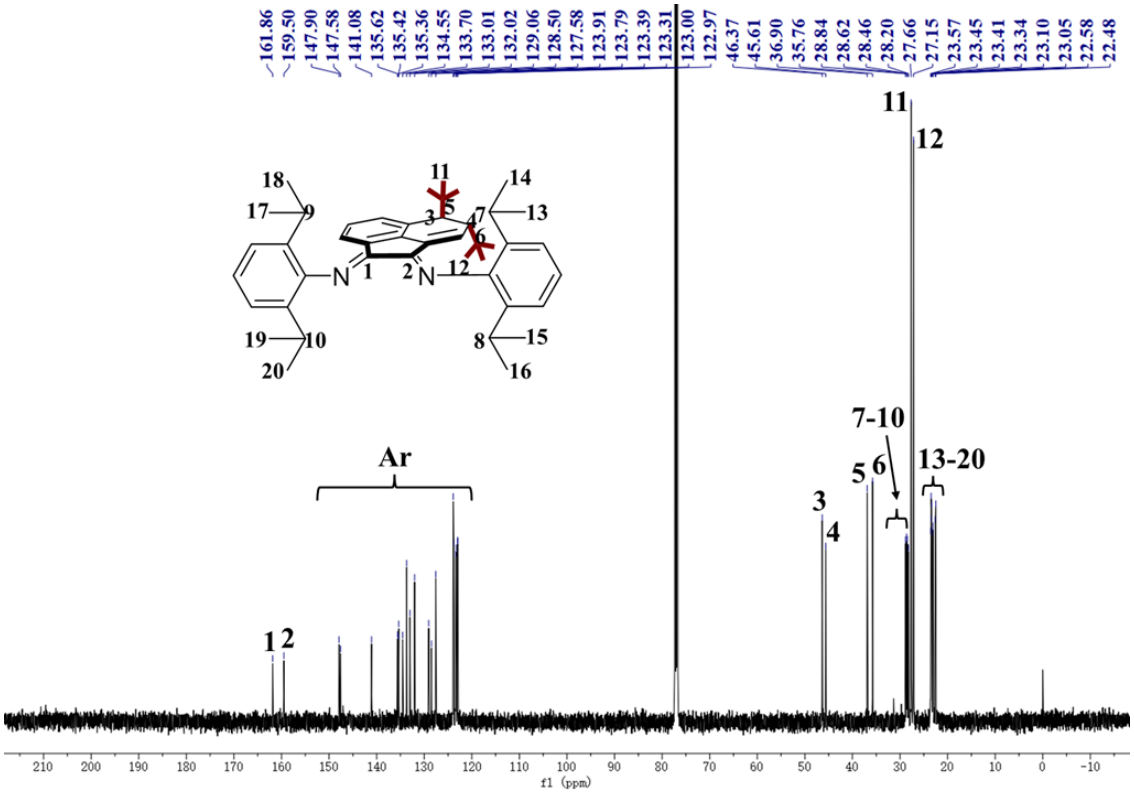


Figure S3. ^{13}C NMR spectrum of **L2** in $CDCl_3$.

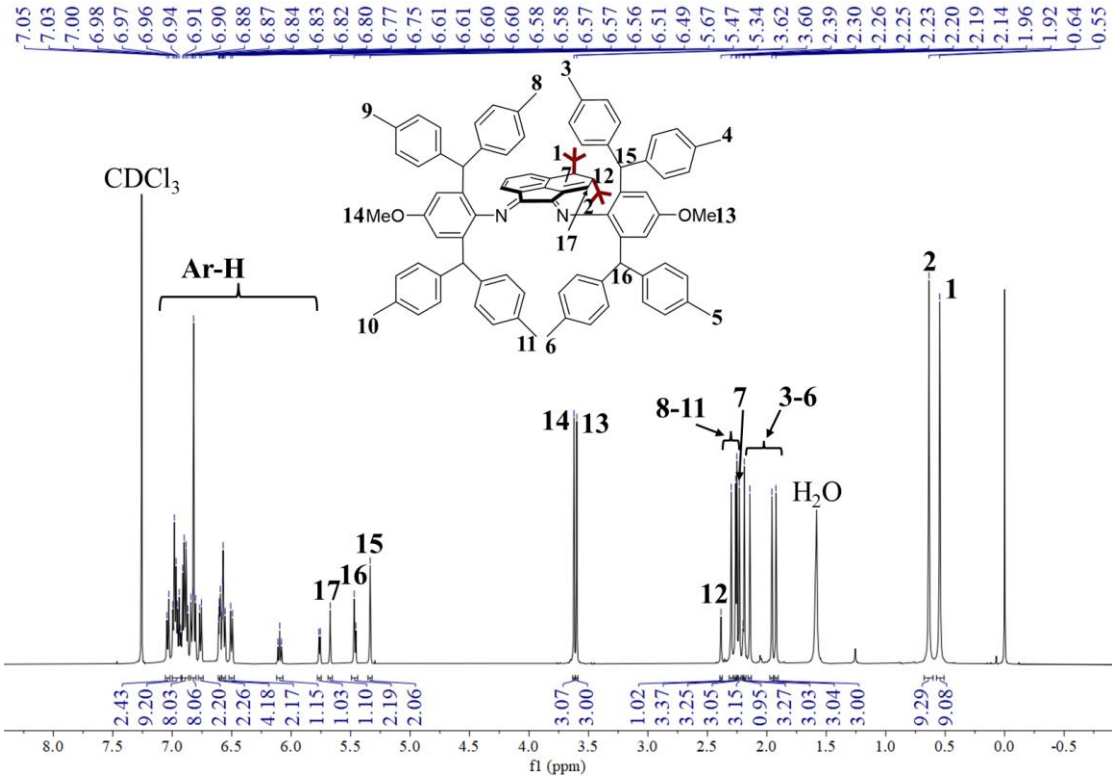


Figure S4. ^{1}H NMR spectrum of **L4** in $CDCl_3$.

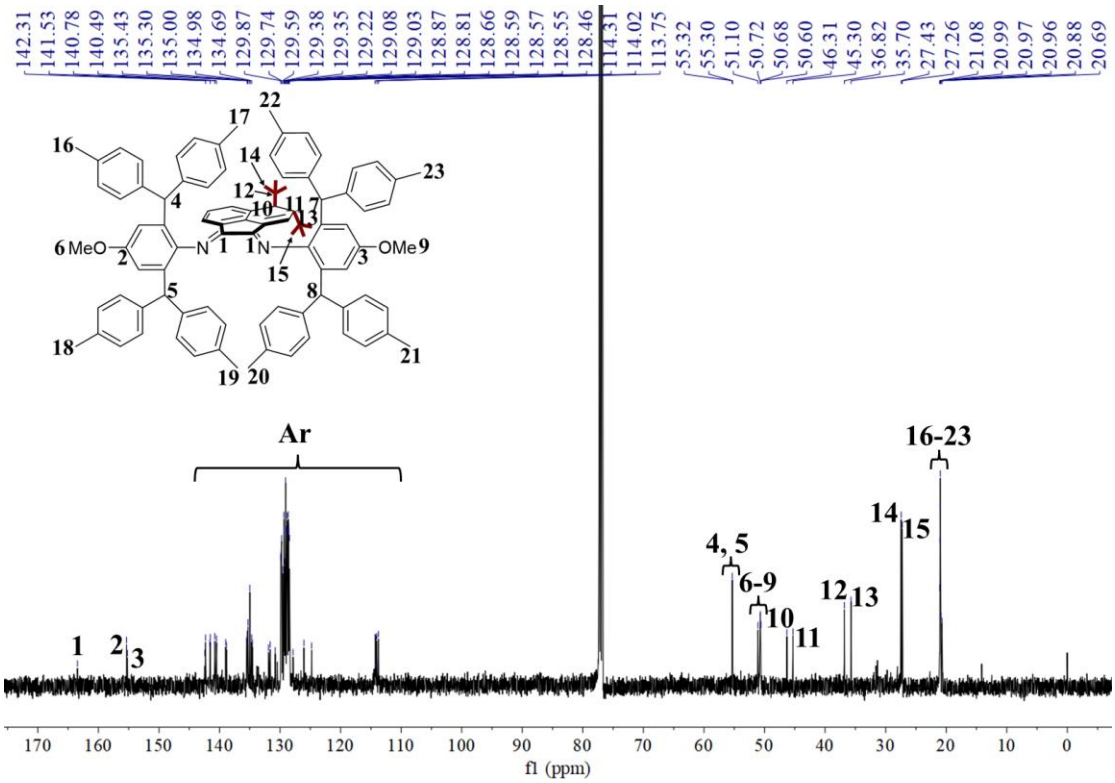


Figure S5. ^{13}C NMR spectrum of **L4** in $CDCl_3$.

3.2. ^{1}H and ^{13}C NMR of Palladium Complexes

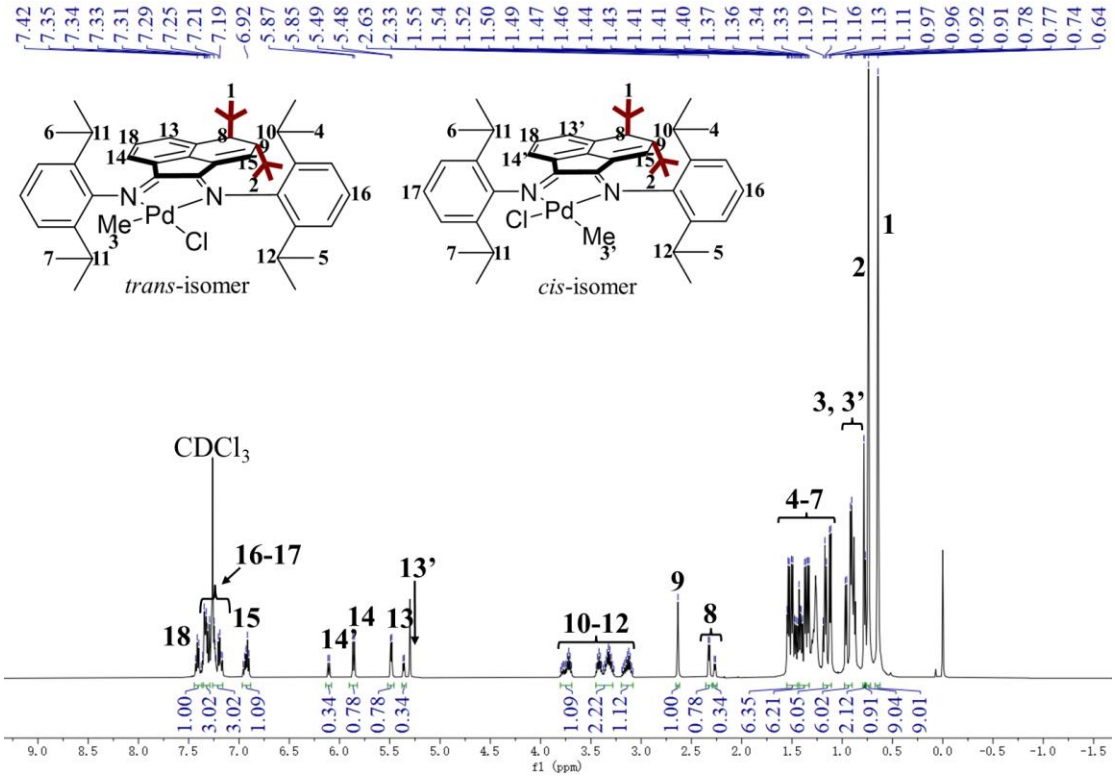


Figure S6. ^{1}H NMR spectrum of **Pd2** in $CDCl_3$.

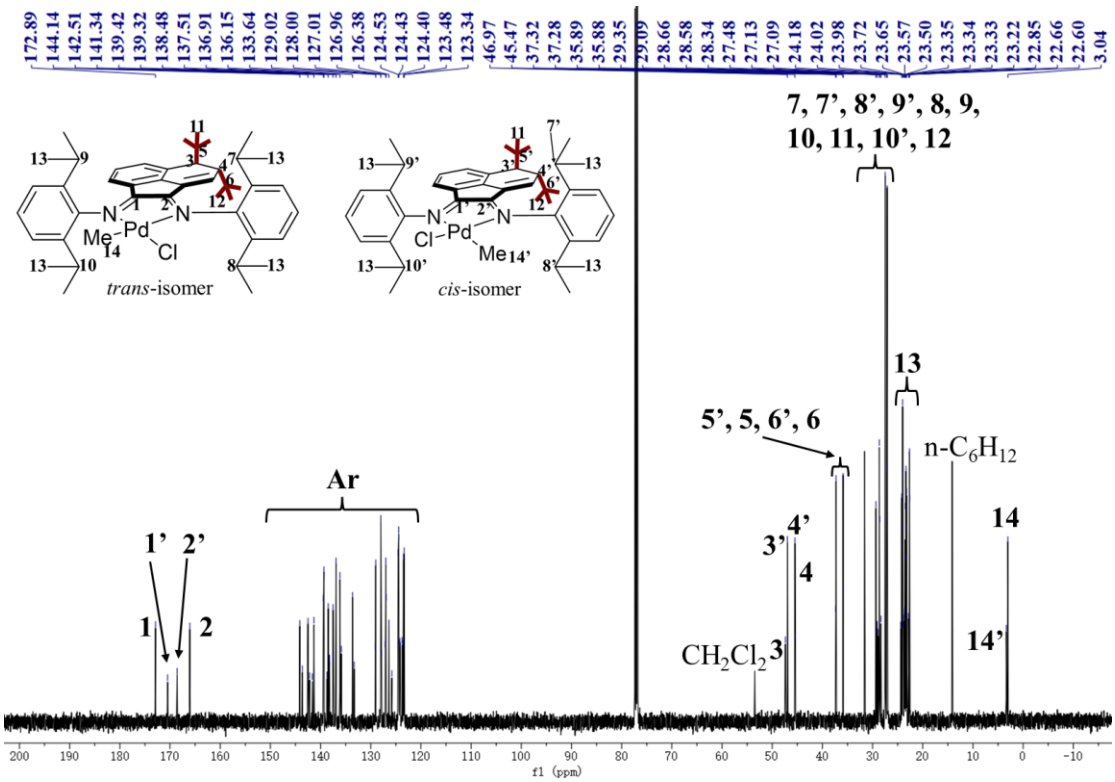


Figure S7. ^{13}C NMR spectrum of **Pd2** in $CDCl_3$.

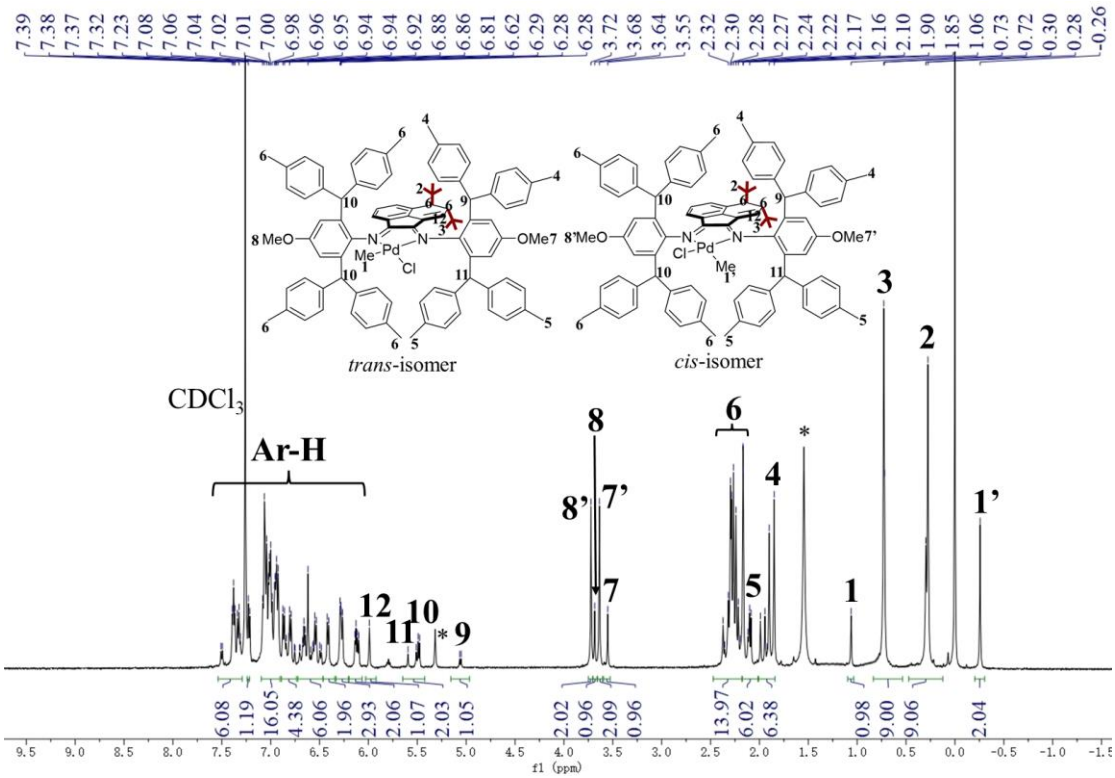


Figure S8. ^{1}H NMR spectrum of **Pd4** in $CDCl_3$. * CH_2Cl_2; H_2O

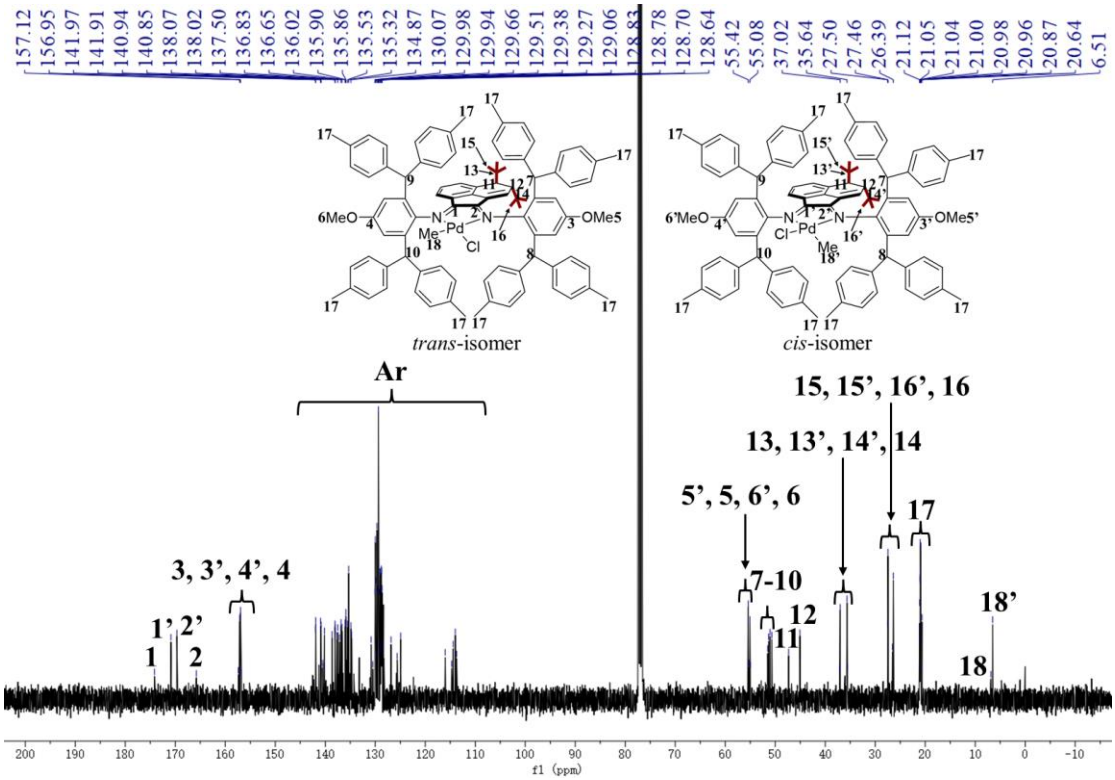


Figure S9. ^{13}C NMR spectrum of **Pd4** in $CDCl_3$.

3.3. ESI-MS Data

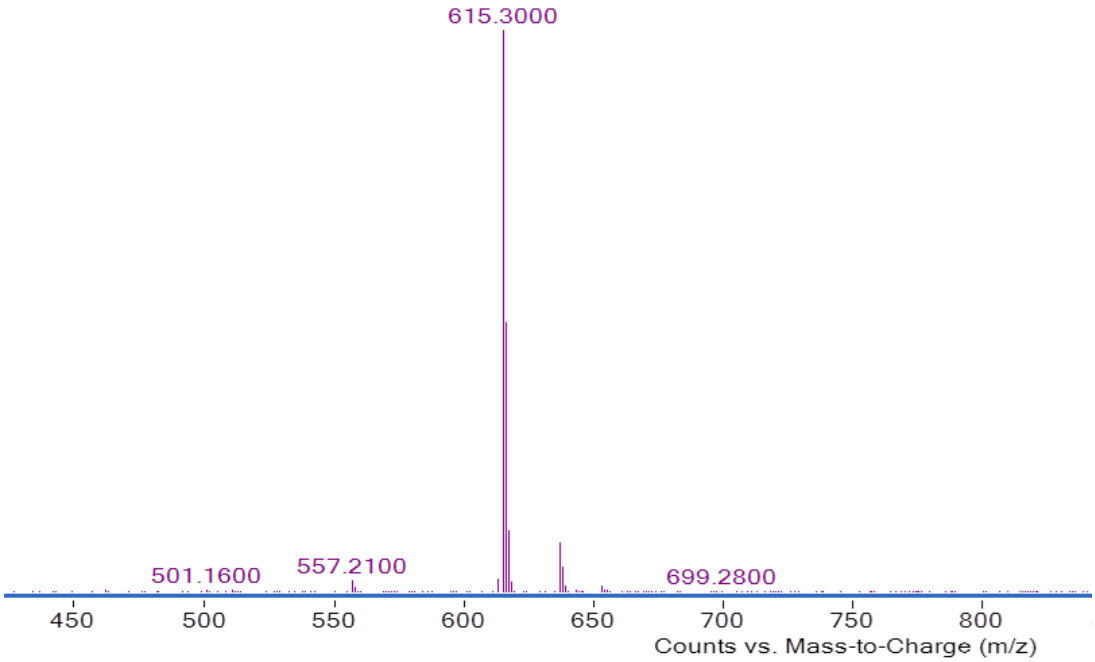


Figure S10. ESI-MS of **L2**.

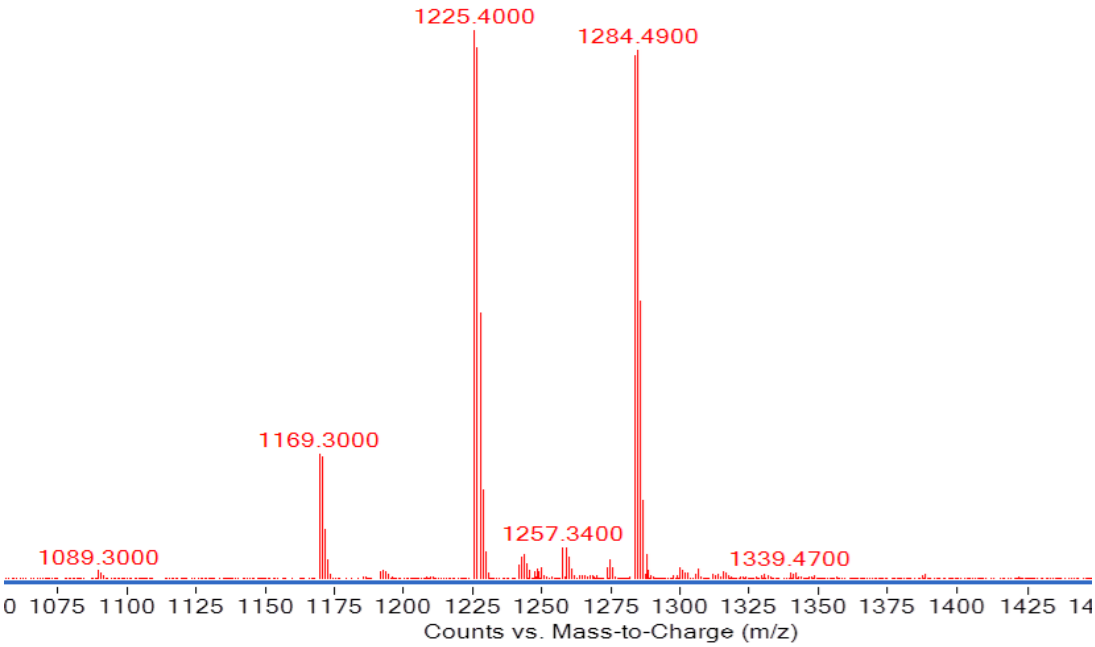


Figure S11. ESI-MS of **L4**.

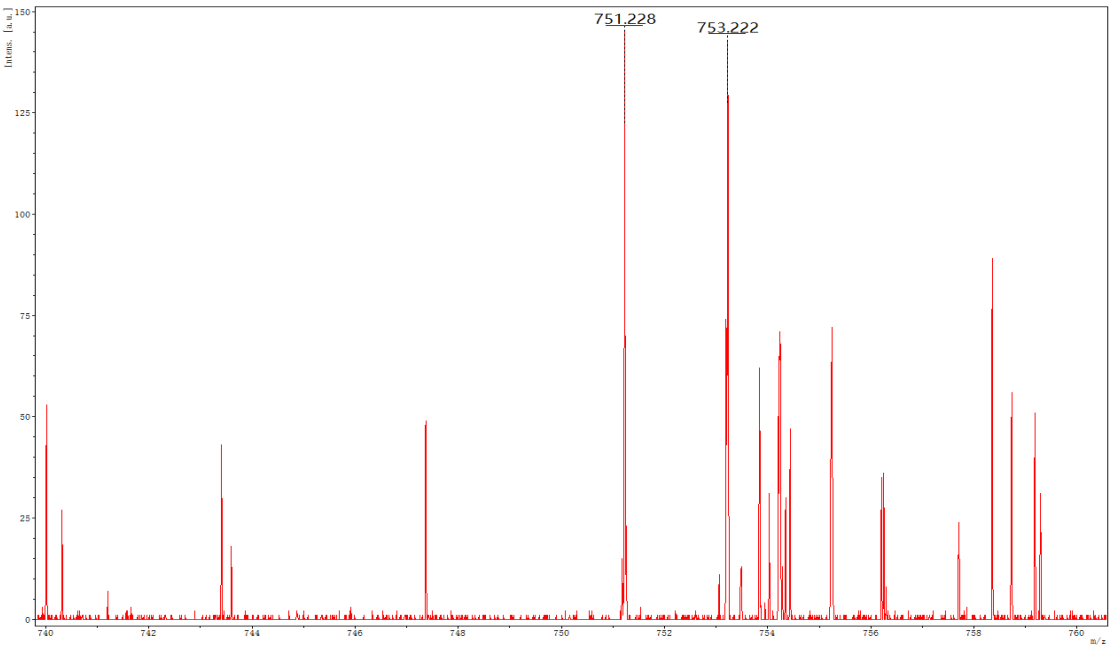


Figure S12. MALDI-TOF/TOF of **Ni2**.

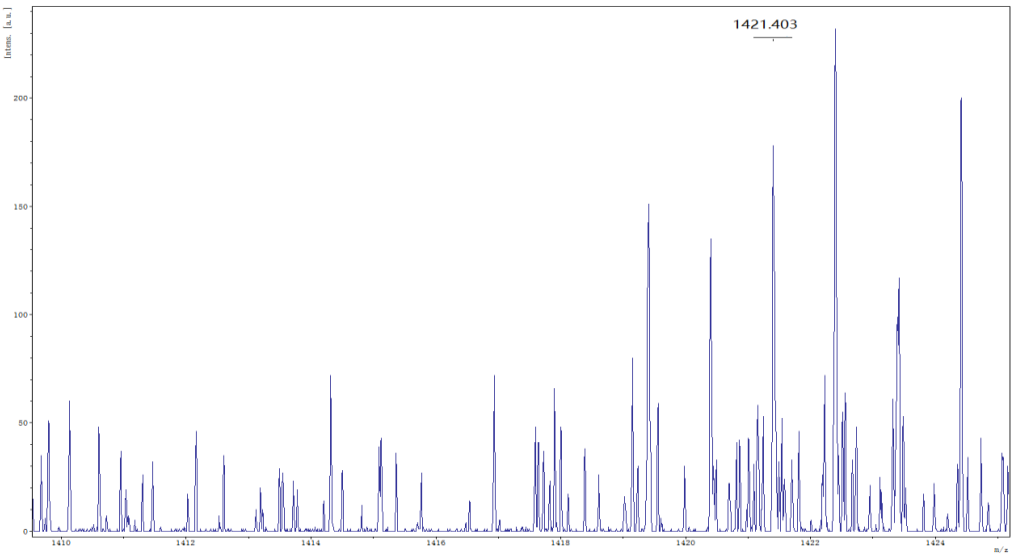


Figure S13. MALDI-TOF/TOF of **Ni4**.

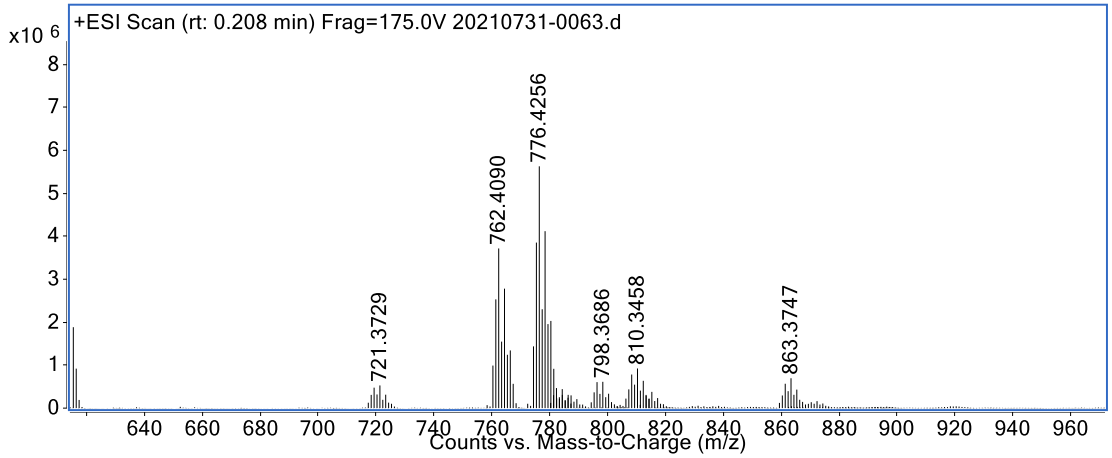


Figure S14. ESI-MS of **Pd2**.

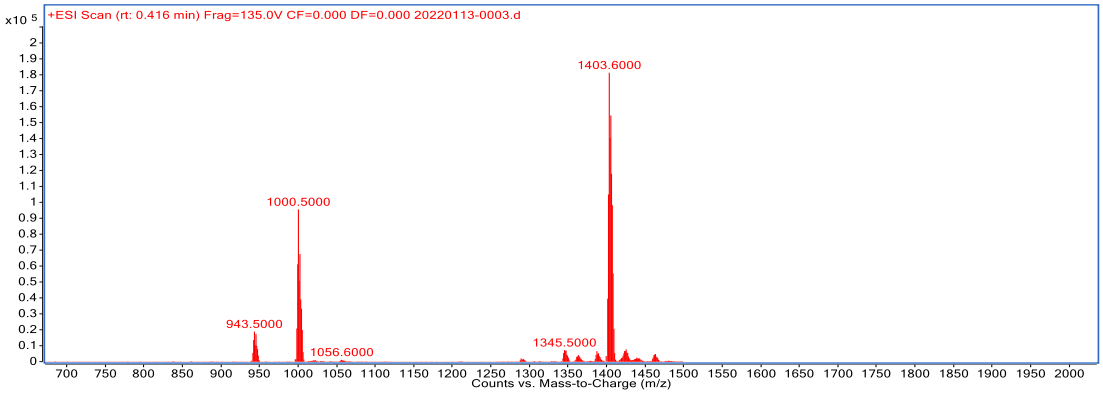


Figure S15. ESI-MS of **Pd4**.

3.4. ^{1}H and ^{13}C NMR of Polymers

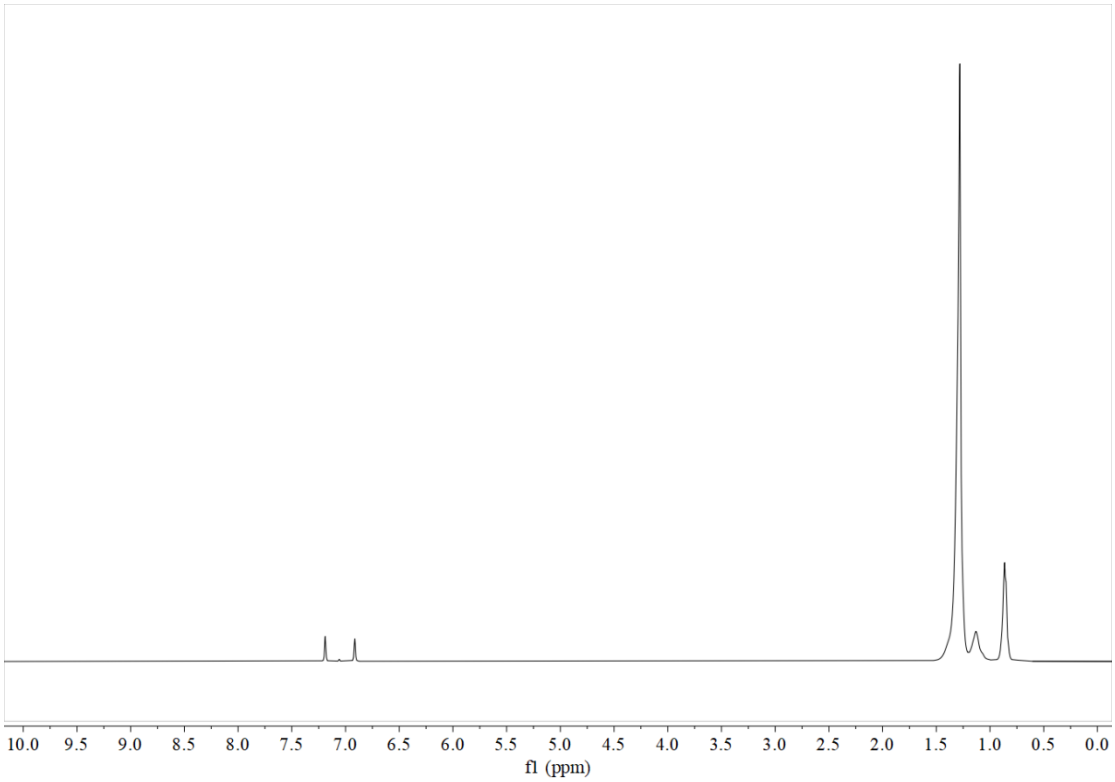


Figure S16. ^{1}H NMR spectrum of the polymer from table 1, entry 1($C_6D_4Cl_2$, 120 ℃).

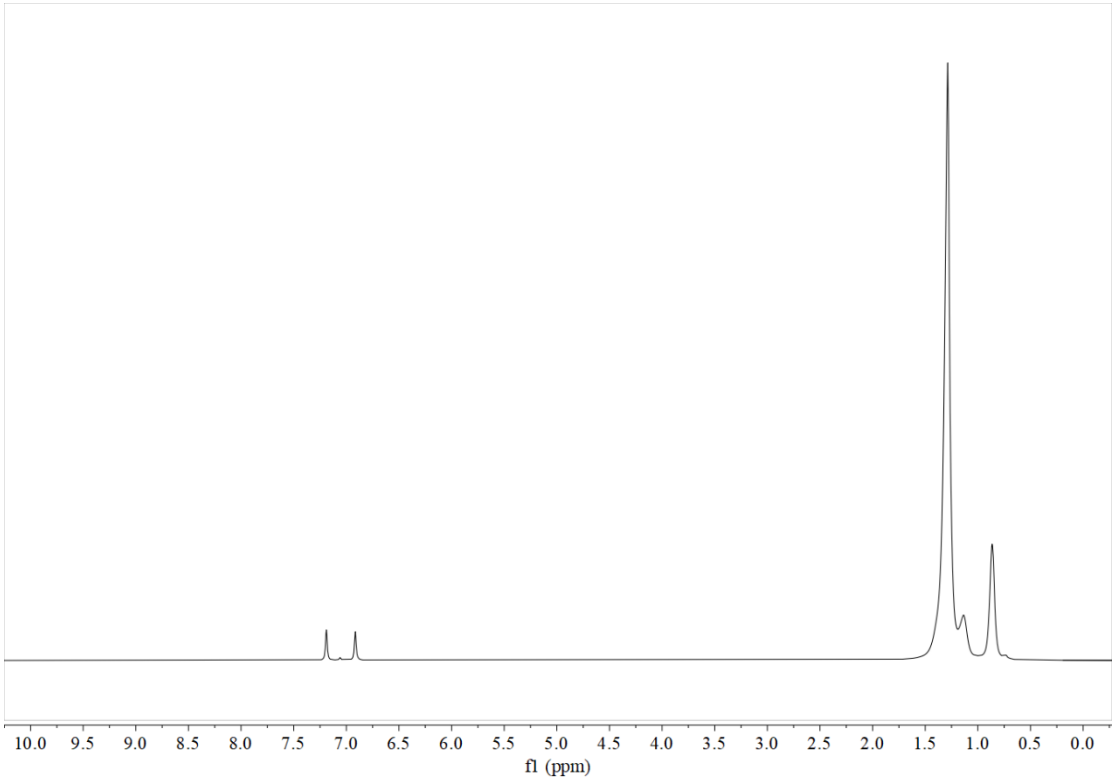


Figure S17. ^{1}H NMR spectrum of the polymer from table 1, entry 2($C_6D_4Cl_2$, 120 ℃).

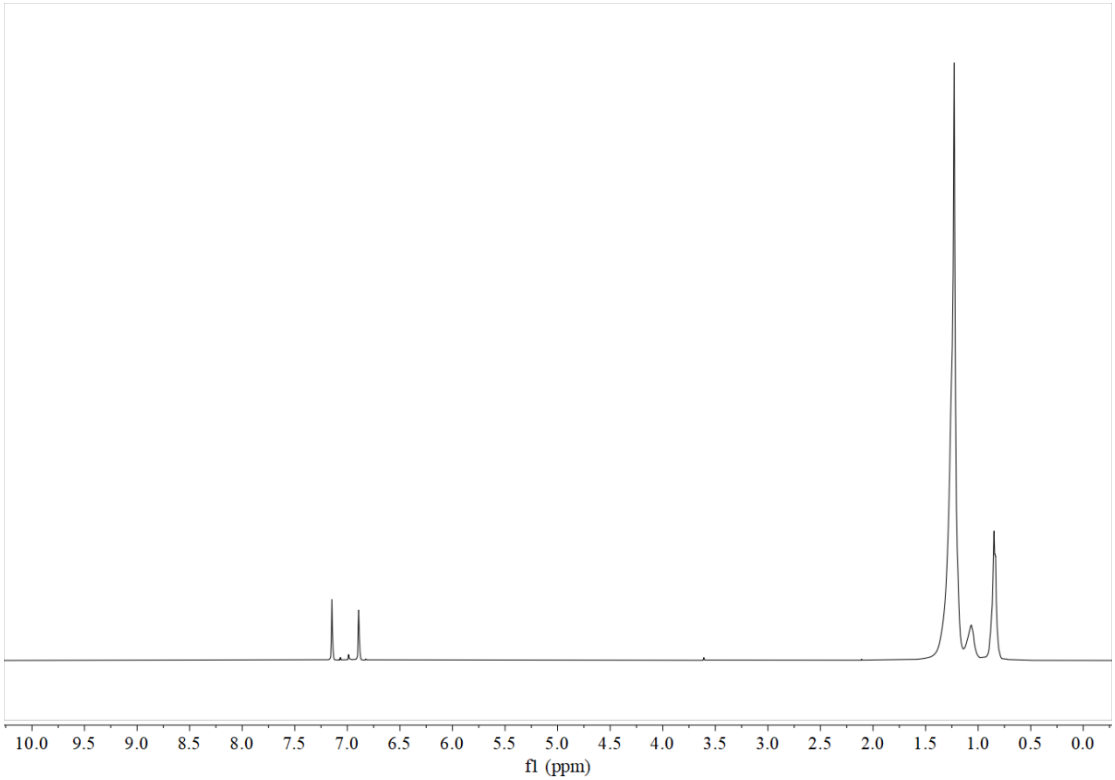


Figure S18. ^{1}H NMR spectrum of the polymer from table 1, entry 3($C_6D_4Cl_2$, 120 ℃).

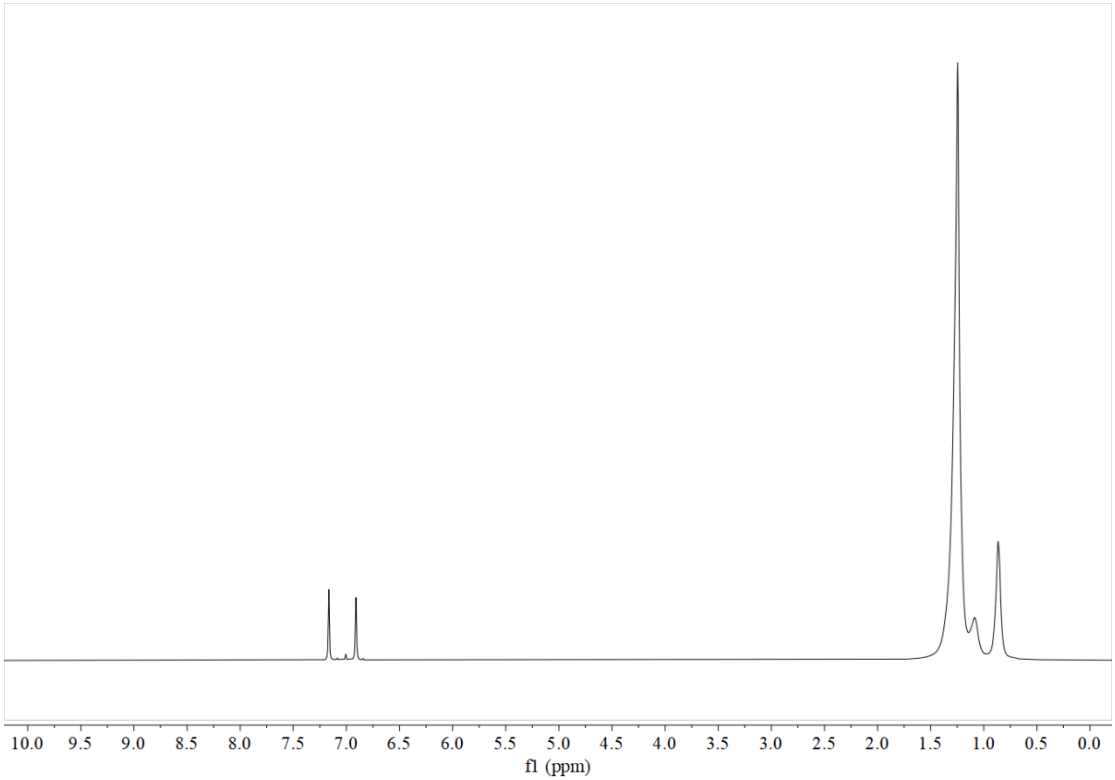


Figure S19. ^{1}H NMR spectrum of the polymer from table 1, entry 4($C_6D_4Cl_2$, 120 ℃).

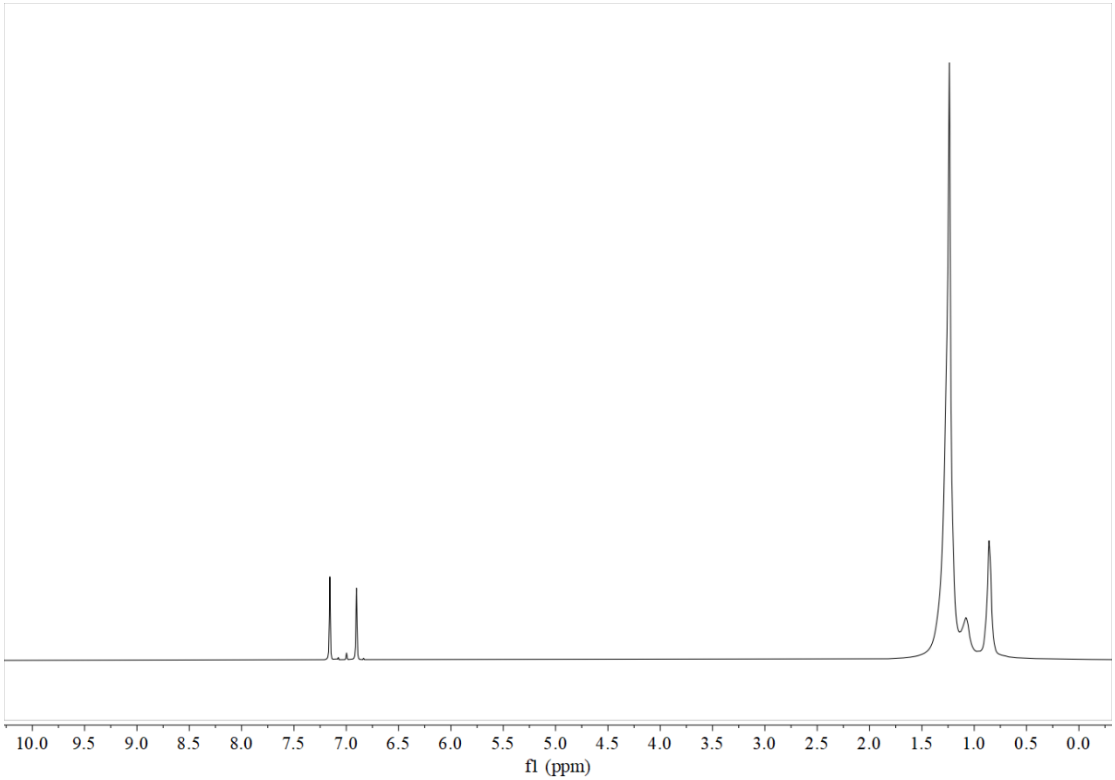


Figure S20. ^{1}H NMR spectrum of the polymer from table 1, entry 5($C_6D_4Cl_2$, 120 ℃).

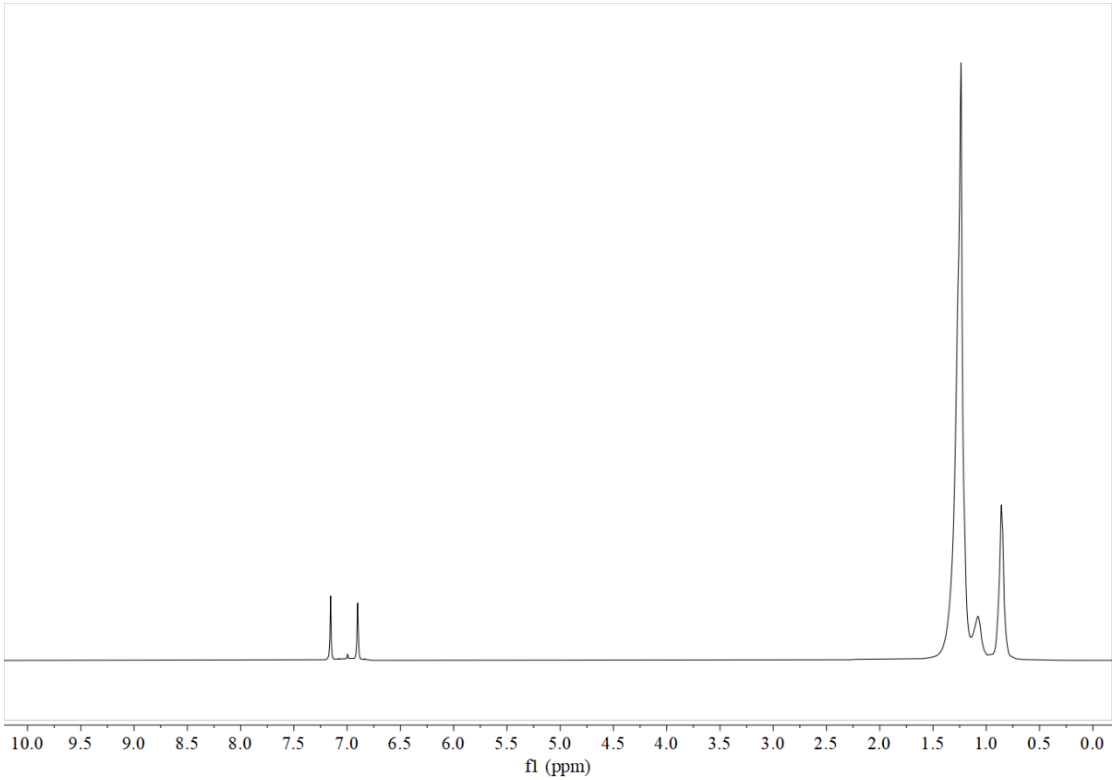


Figure S21. ^{1}H NMR spectrum of the polymer from table 1, entry 6($C_6D_4Cl_2$, 120 ℃).

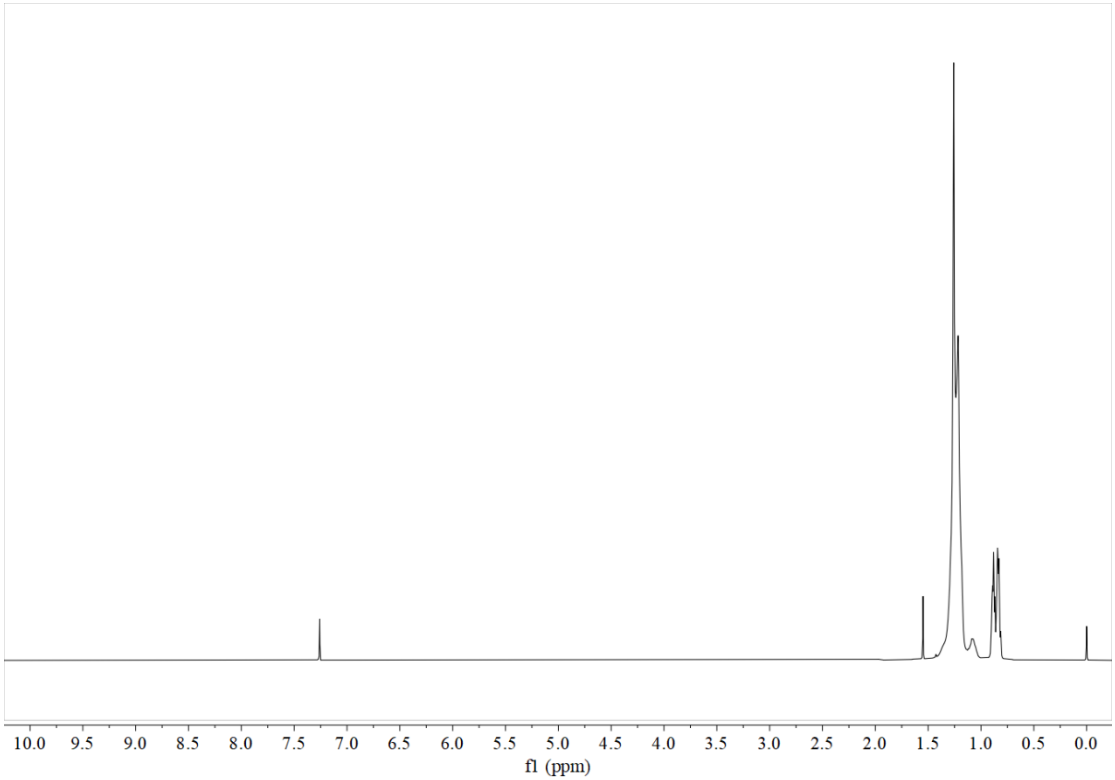


Figure S22. ^{1}H NMR spectrum of the polymer from table 1, entry 10($CDCl_3$, 25°C).

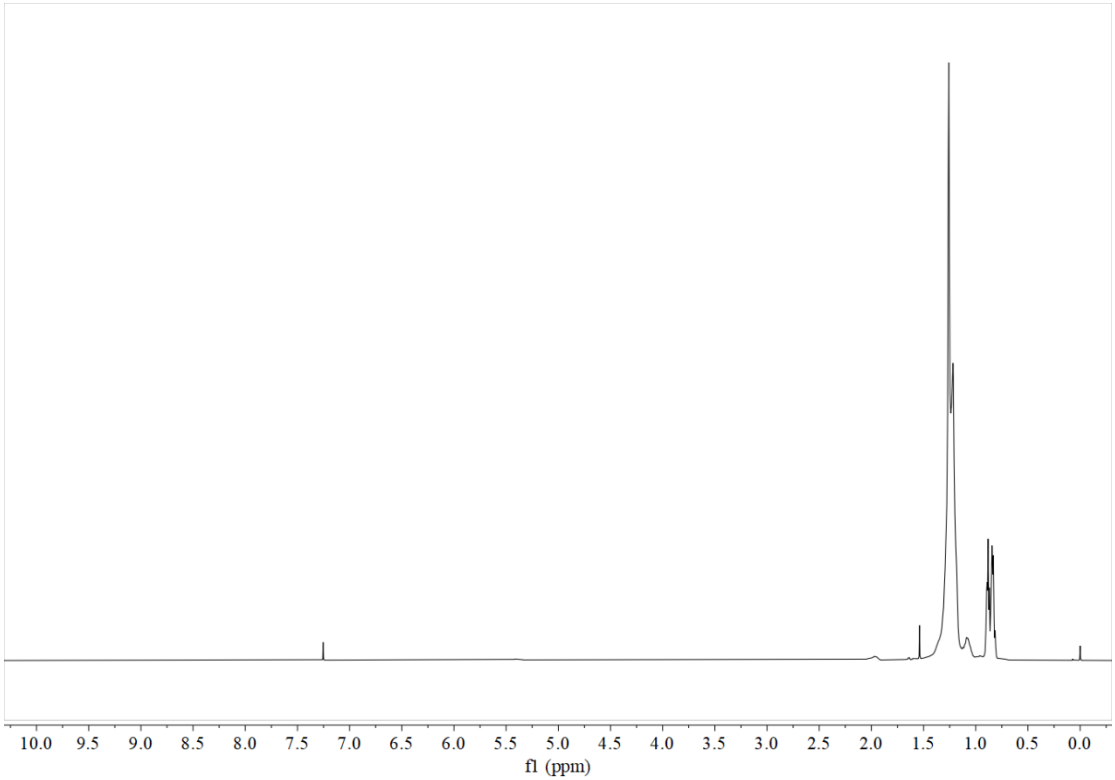


Figure S23. ^{1}H NMR spectrum of the polymer from table 1, entry 11($CDCl_3$, 25°C).

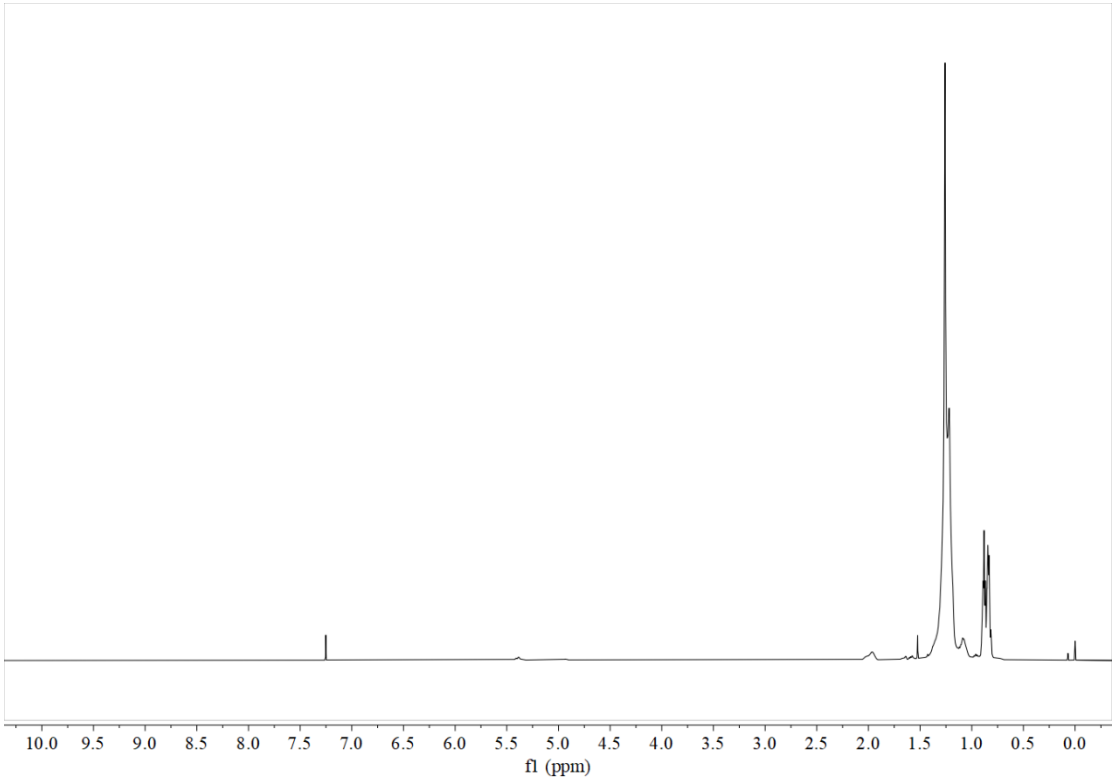


Figure S24. ^{1}H NMR spectrum of the polymer from table 1, entry 12($CDCl_3$, 25 ℃).

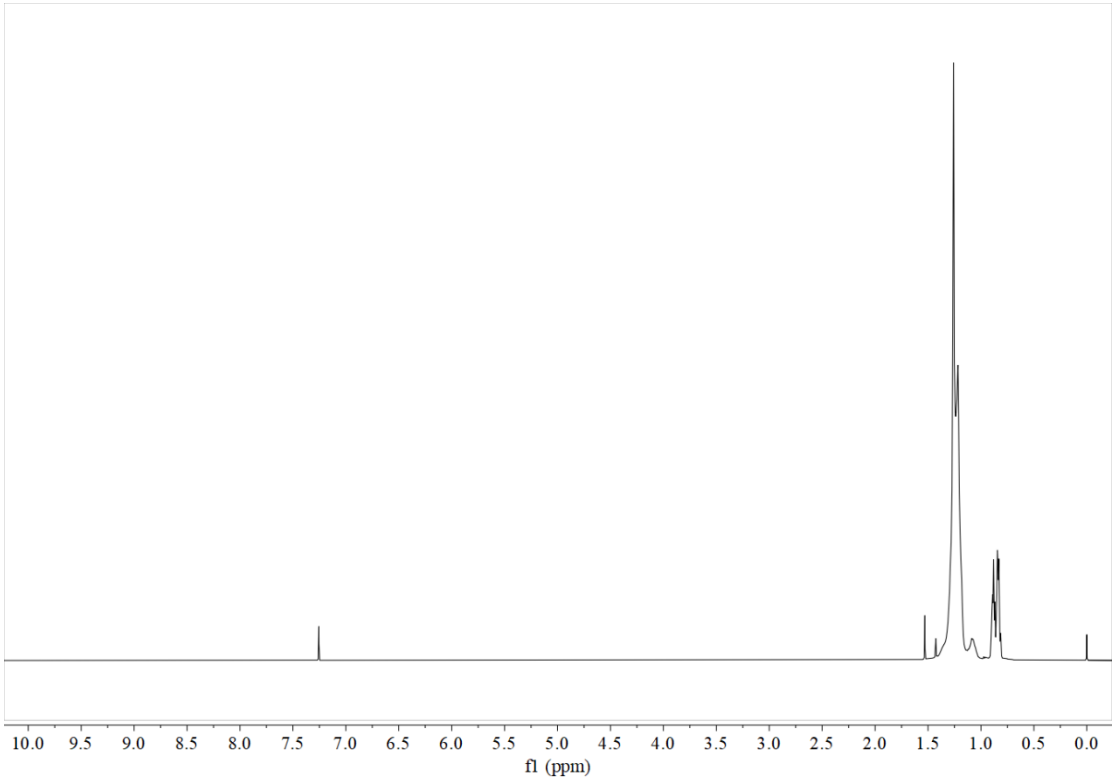


Figure S25. ^{1}H NMR spectrum of the polymer from table 1, entry 13($CDCl_3$, 25 ℃).

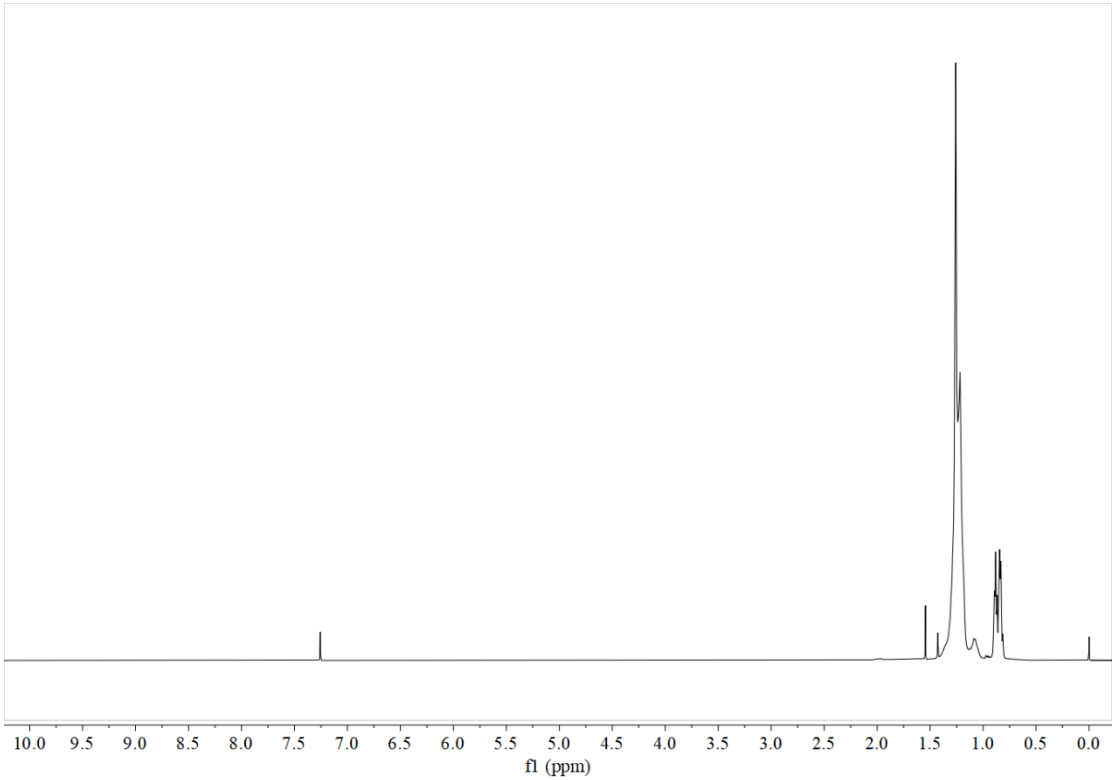


Figure S26. ^{1}H NMR spectrum of the polymer from table 1, entry 14($CDCl_3$, 25 °C).

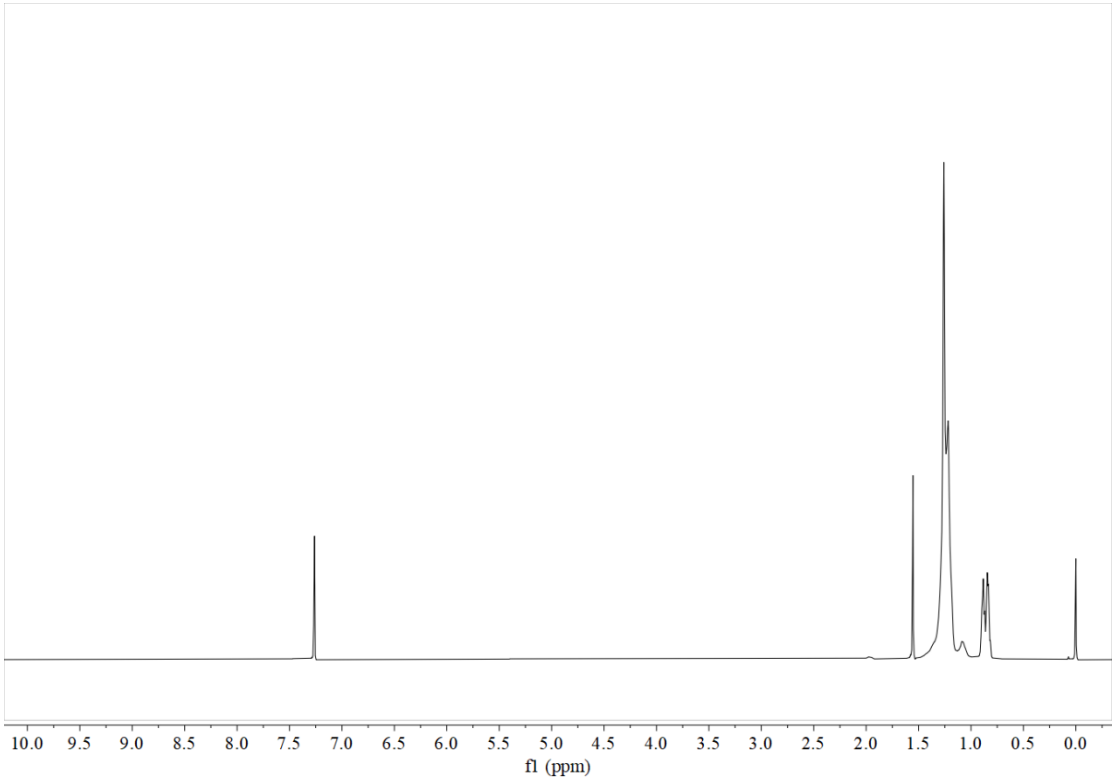


Figure S27. ^{1}H NMR spectrum of the polymer from table 1, entry 15 ($CDCl_3$, 25 °C).

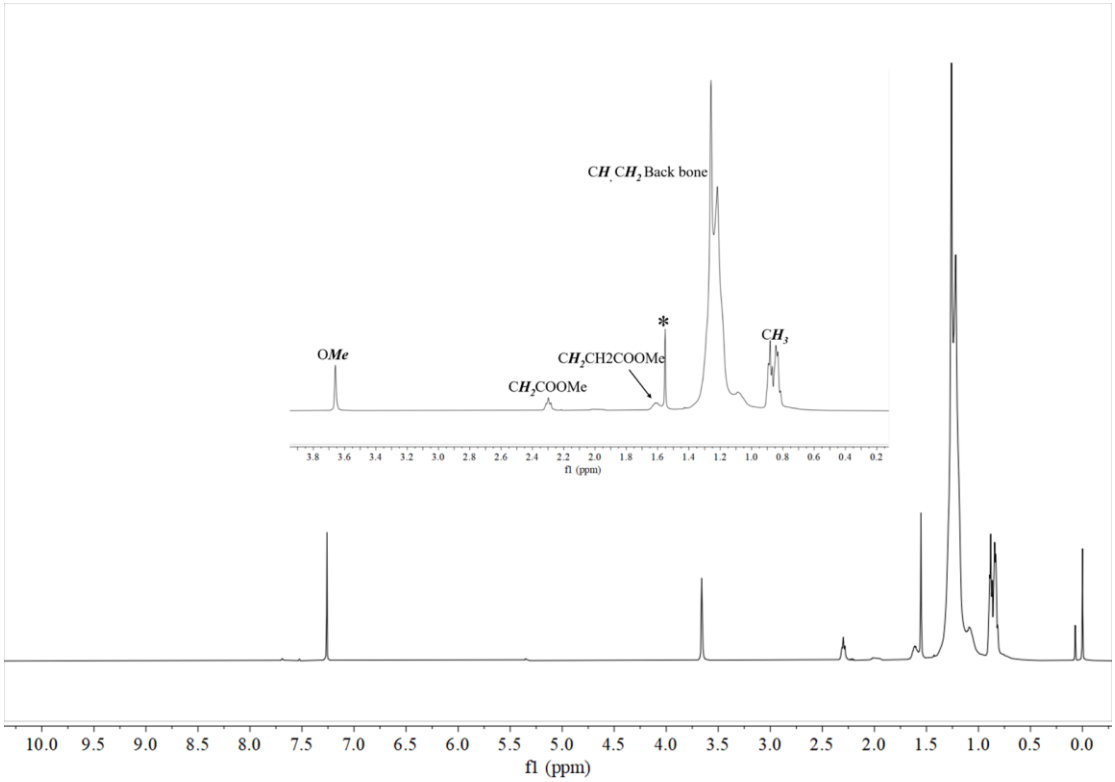


Figure S28. ^{1}H NMR spectrum of the polymer from table 3, entry 2 ($CDCl_3$, 25 ℃). * H_2O

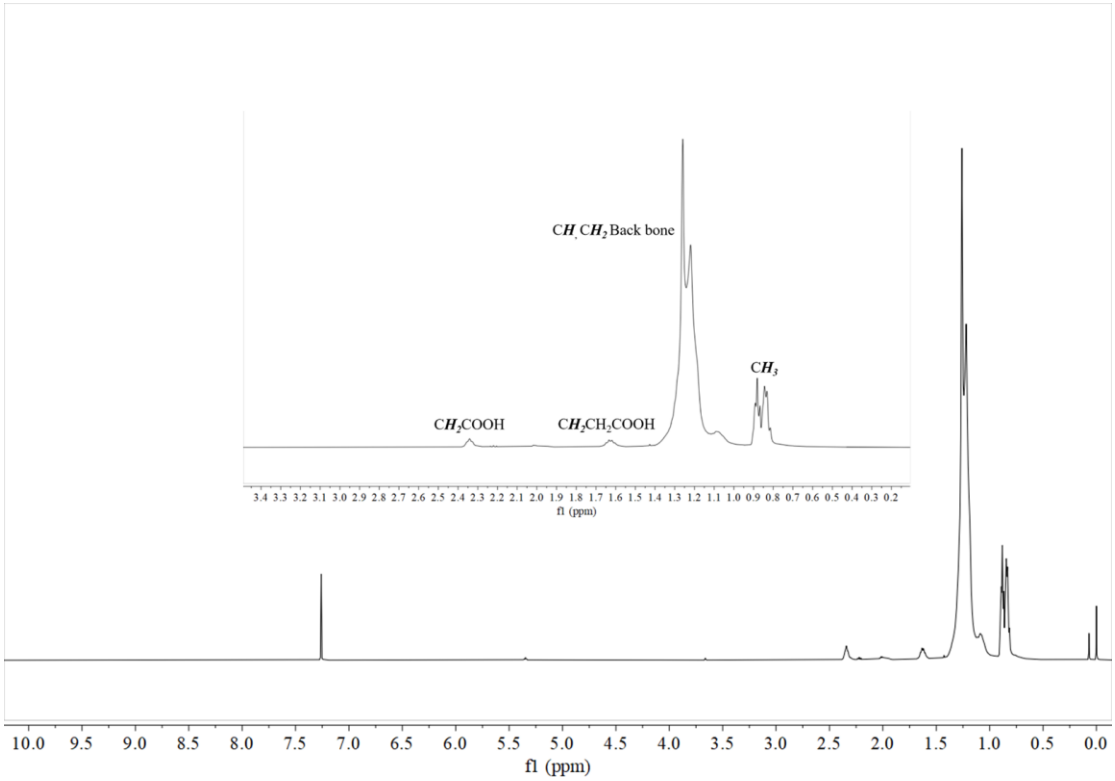


Figure S29. ^{1}H NMR spectrum of the polymer from table 3, entry 4($CDCl_3$, 25 ℃).

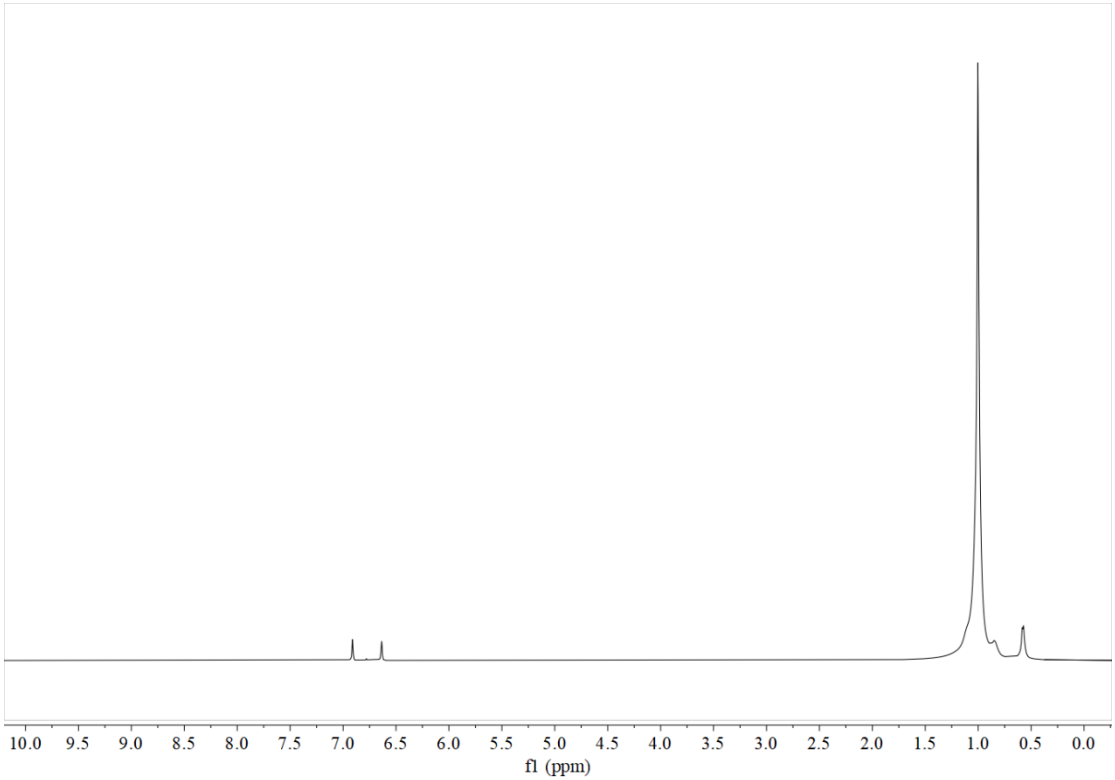


Figure S30. ^{1}H NMR spectrum of the polymer from table 4, entry 1($C_6D_4Cl_2$, 120 ℃).

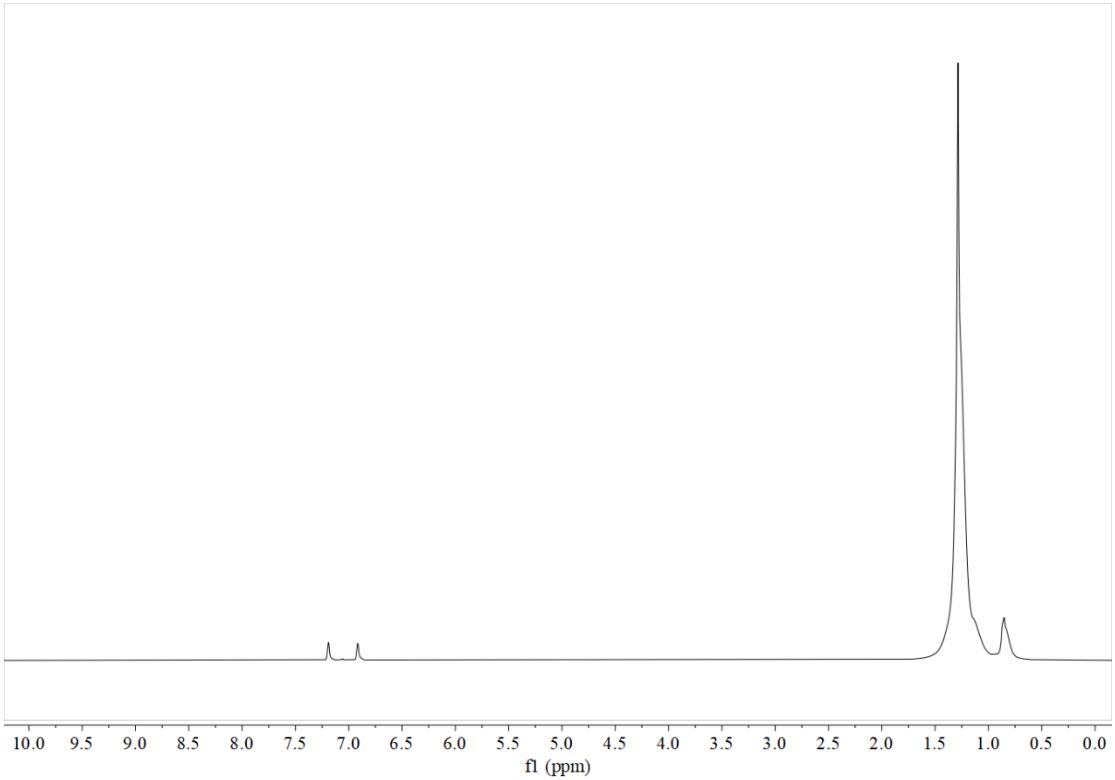


Figure S31. ^{1}H NMR spectrum of the polymer from table 4, entry 2($C_6D_4Cl_2$, 120 ℃).

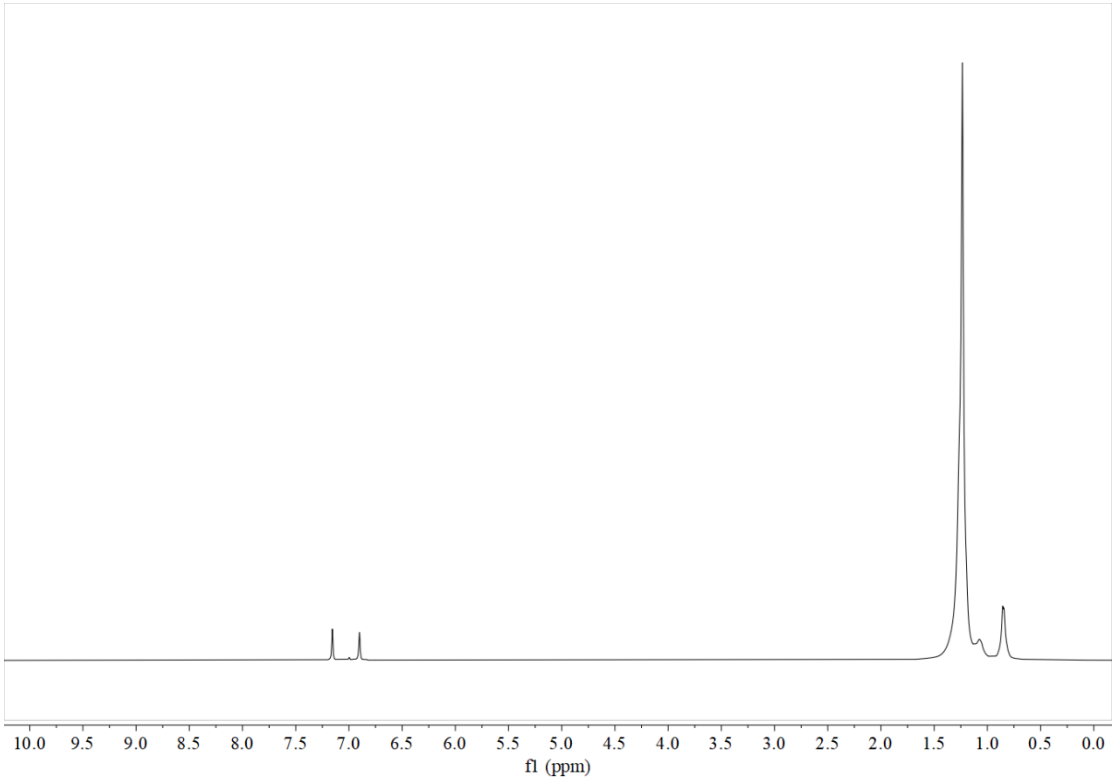


Figure S32. ^{1}H NMR spectrum of the polymer from table 4, entry 3($C_6D_4Cl_2$, 120 ℃).

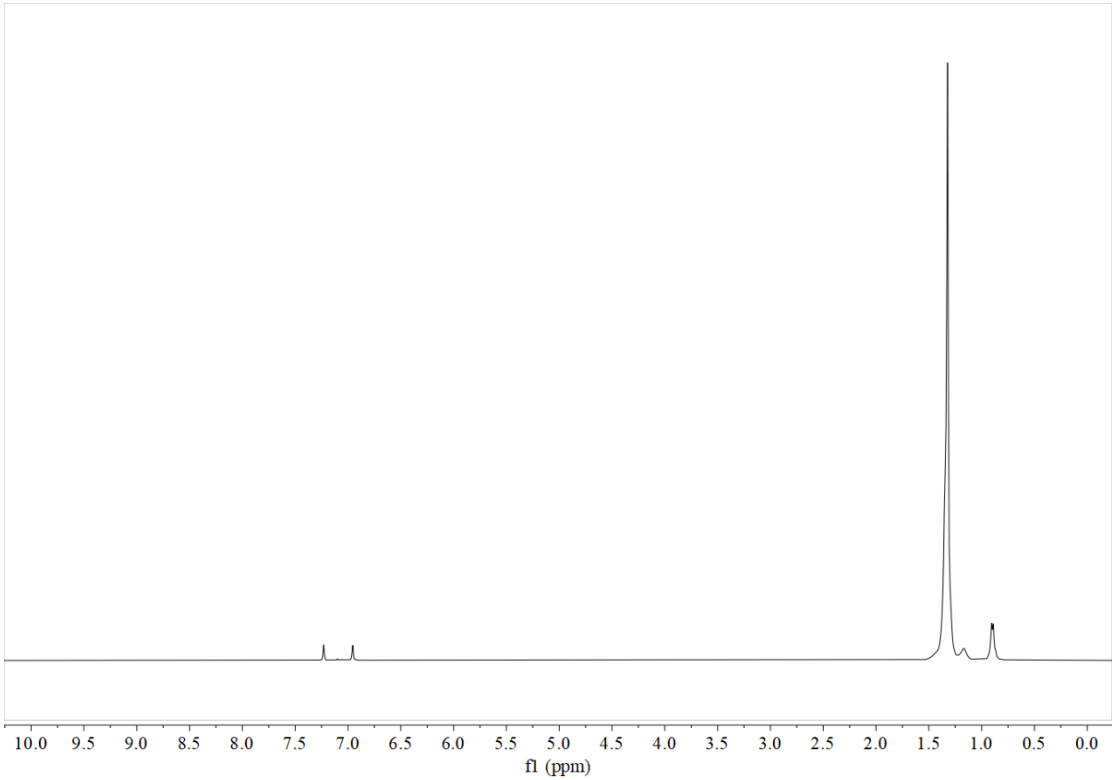


Figure S33. ^{1}H NMR spectrum of the polymer from table 4, entry4 ($C_6D_4Cl_2$, 120 ℃).

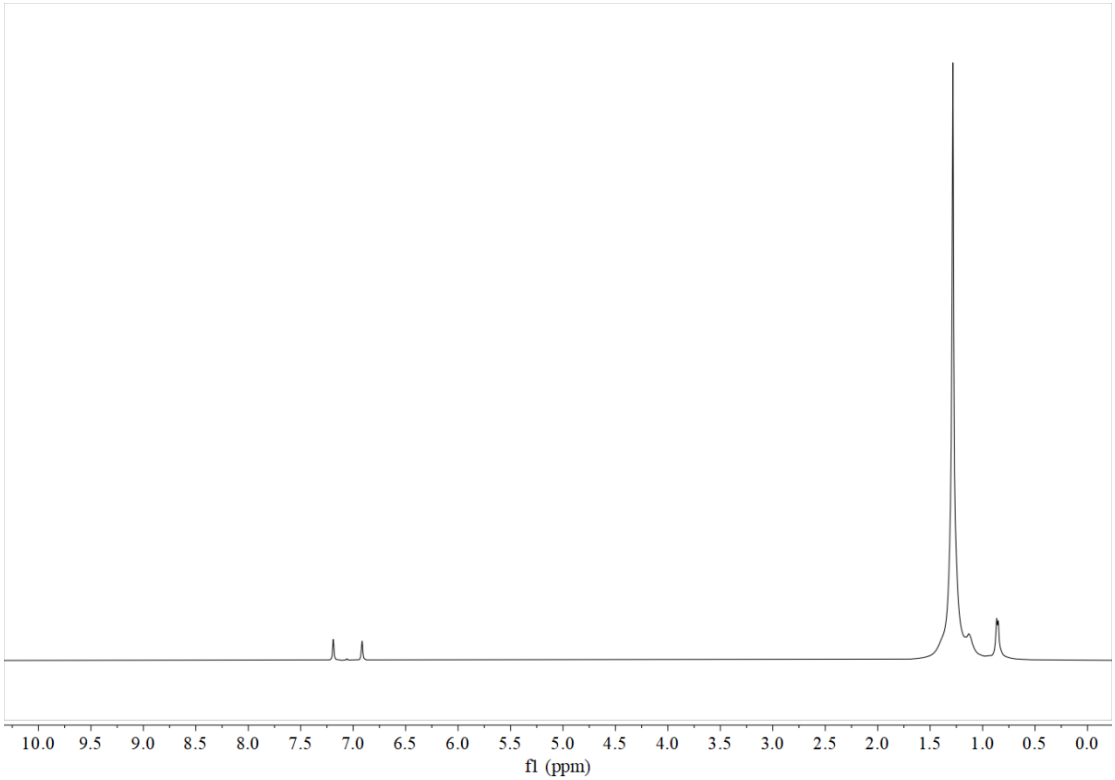


Figure S34. ^{1}H NMR spectrum of the polymer from table 4, entry 5 ($C_6D_4Cl_2$, 120 ℃).

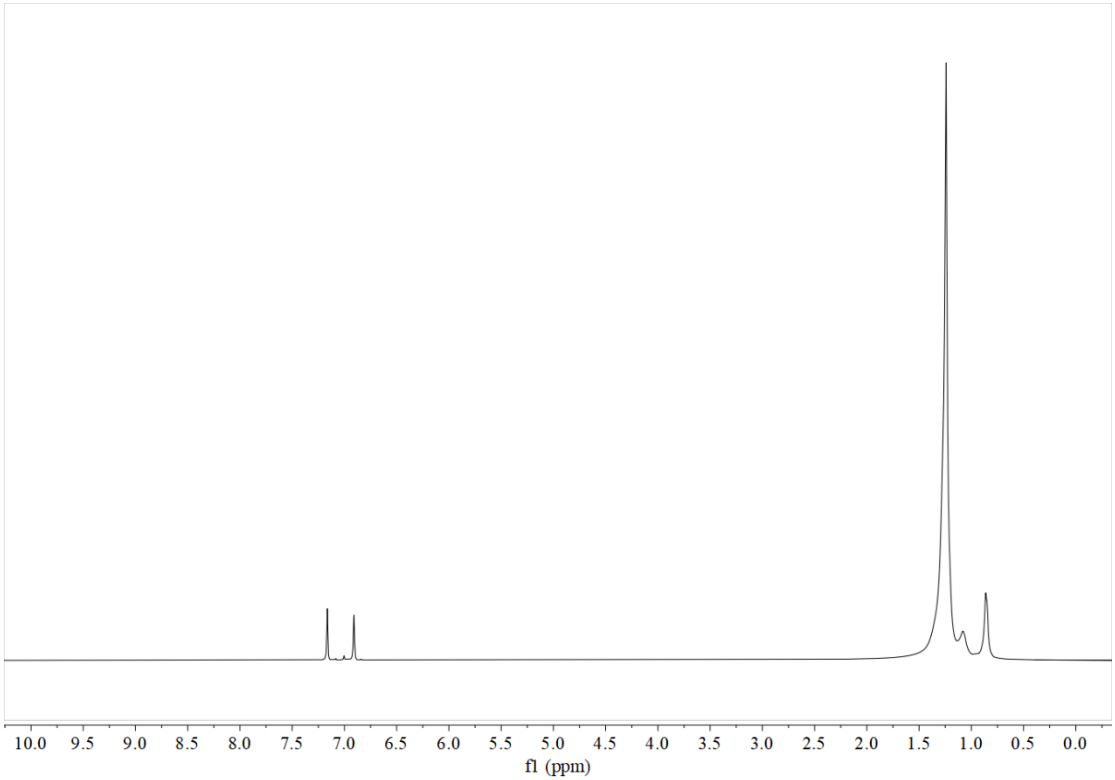


Figure S35. ^{1}H NMR spectrum of the polymer from table 4, entry 6($C_6D_4Cl_2$, 120 ℃).

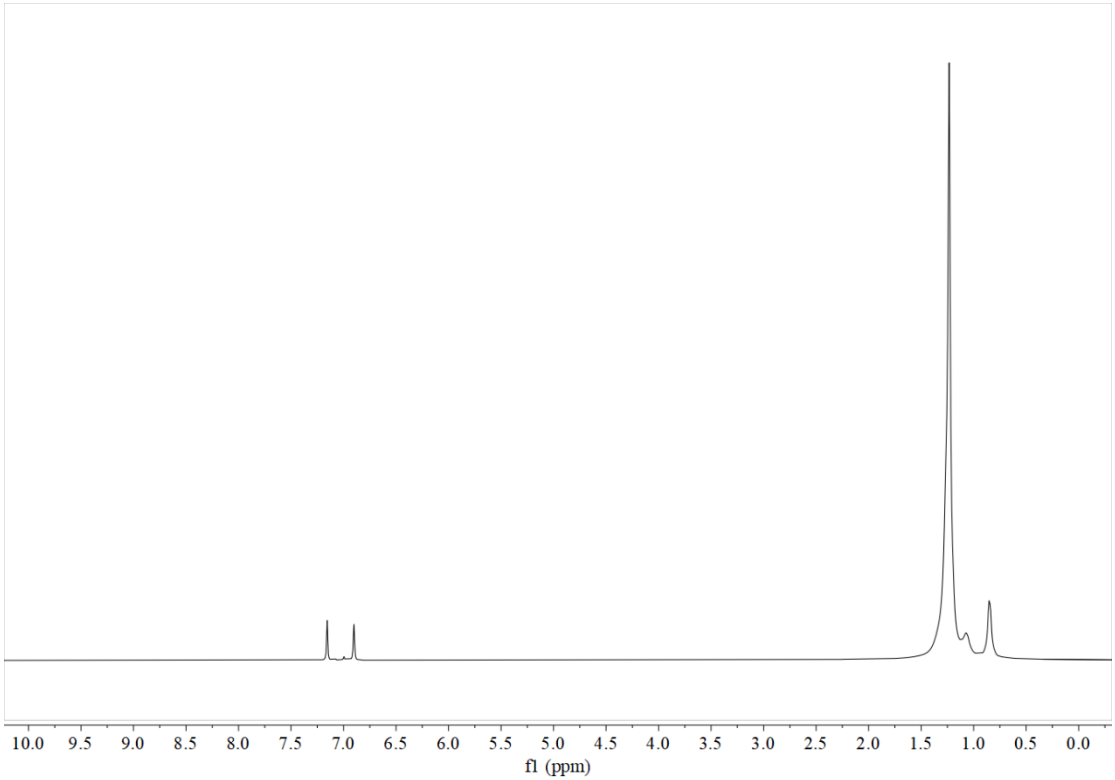


Figure S36. ^{1}H NMR spectrum of the polymer from table 4, entry 7 ($C_6D_4Cl_2$, 120 °C).

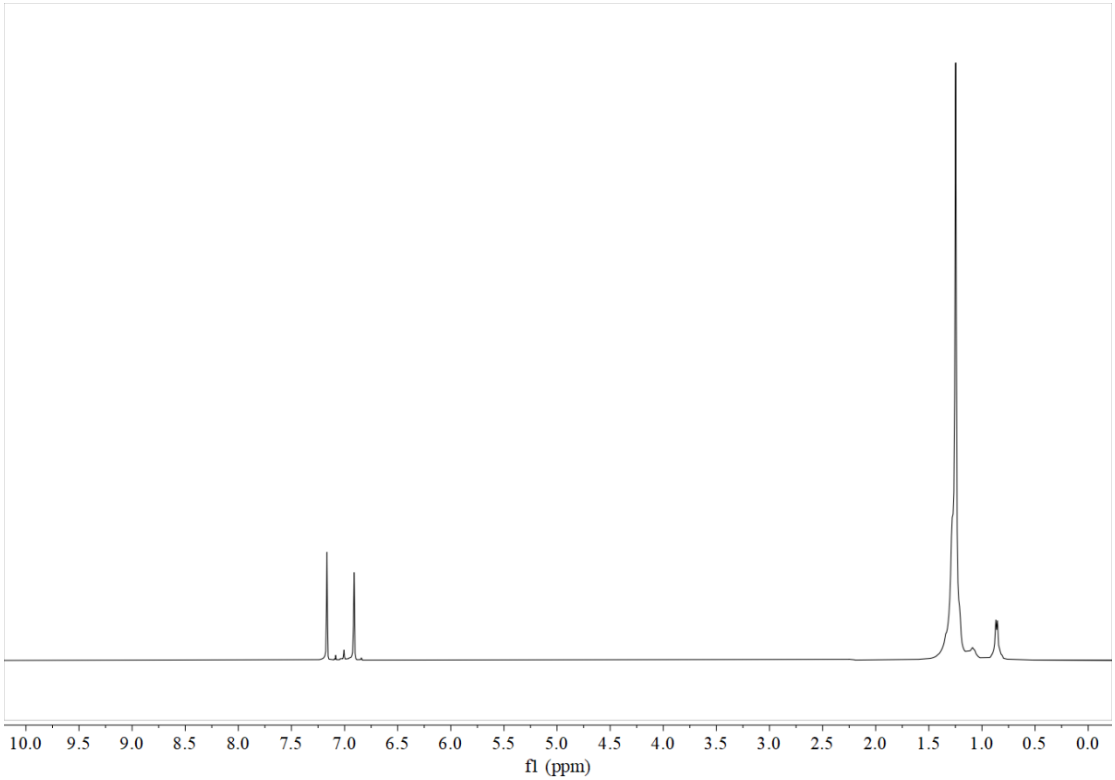


Figure S37. ^{1}H NMR spectrum of the polymer from table 4, entry 8 ($C_6D_4Cl_2$, 120 °C).

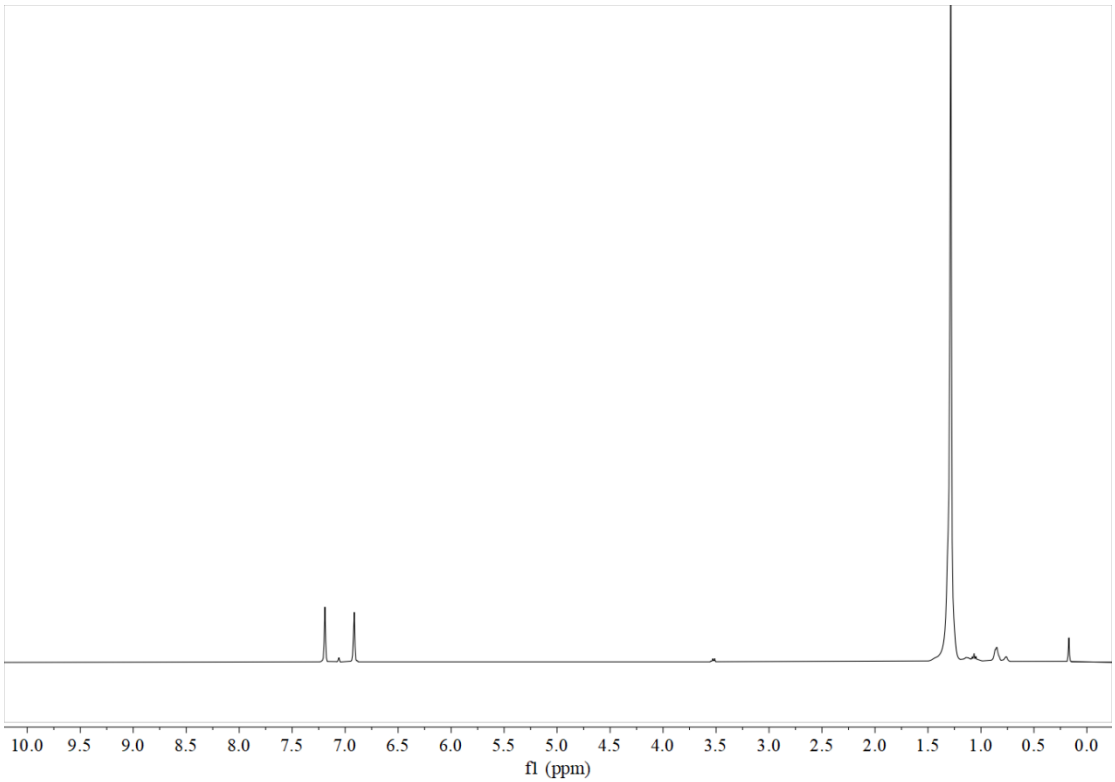


Figure S38. ^{1}H NMR spectrum of the polymer from table 4, entry 9 ($C_6D_4Cl_2$, 120 °C).

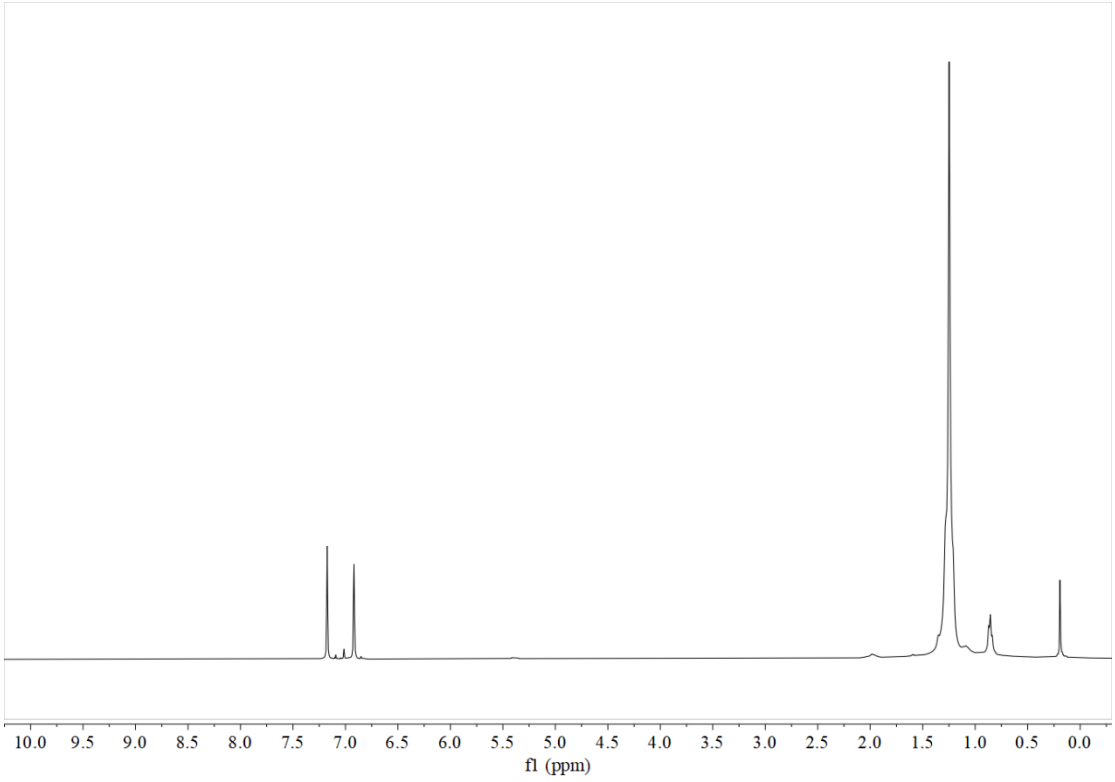


Figure S39. ^{1}H NMR spectrum of the polymer from table 4, entry 10 ($C_6D_4Cl_2$, 120 °C).

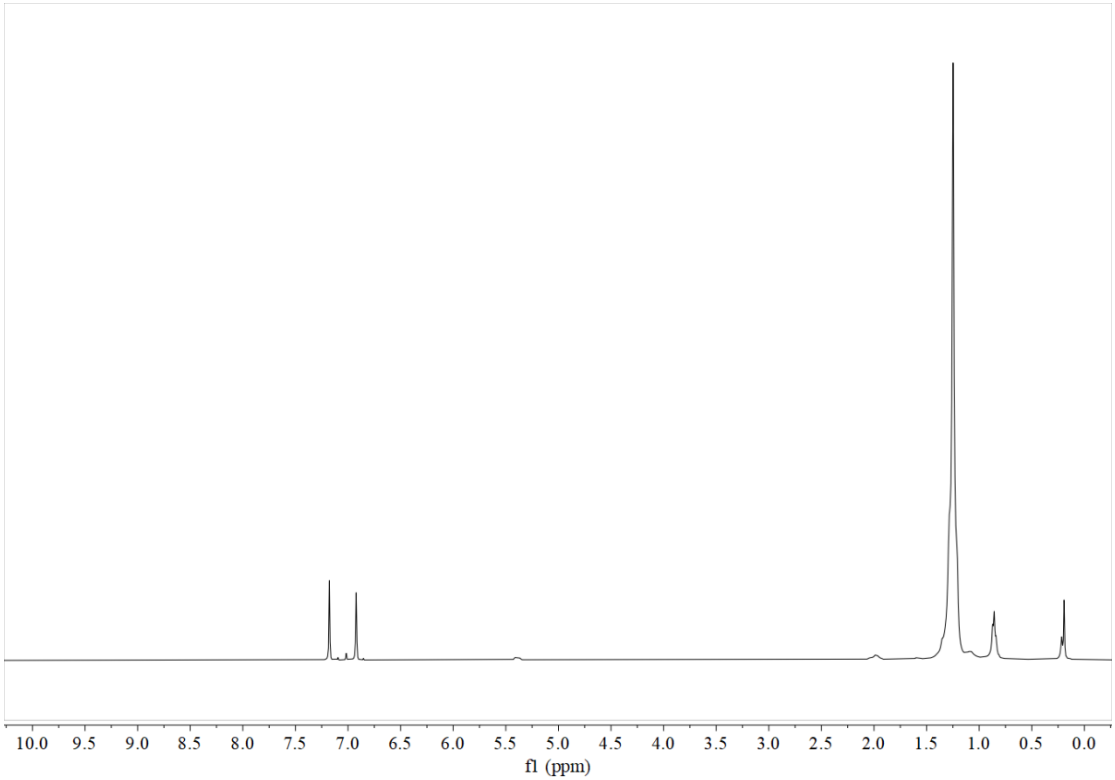


Figure S40. ^{1}H NMR spectrum of the polymer from table 4, entry 11 ($C_6D_4Cl_2$, 120 °C).

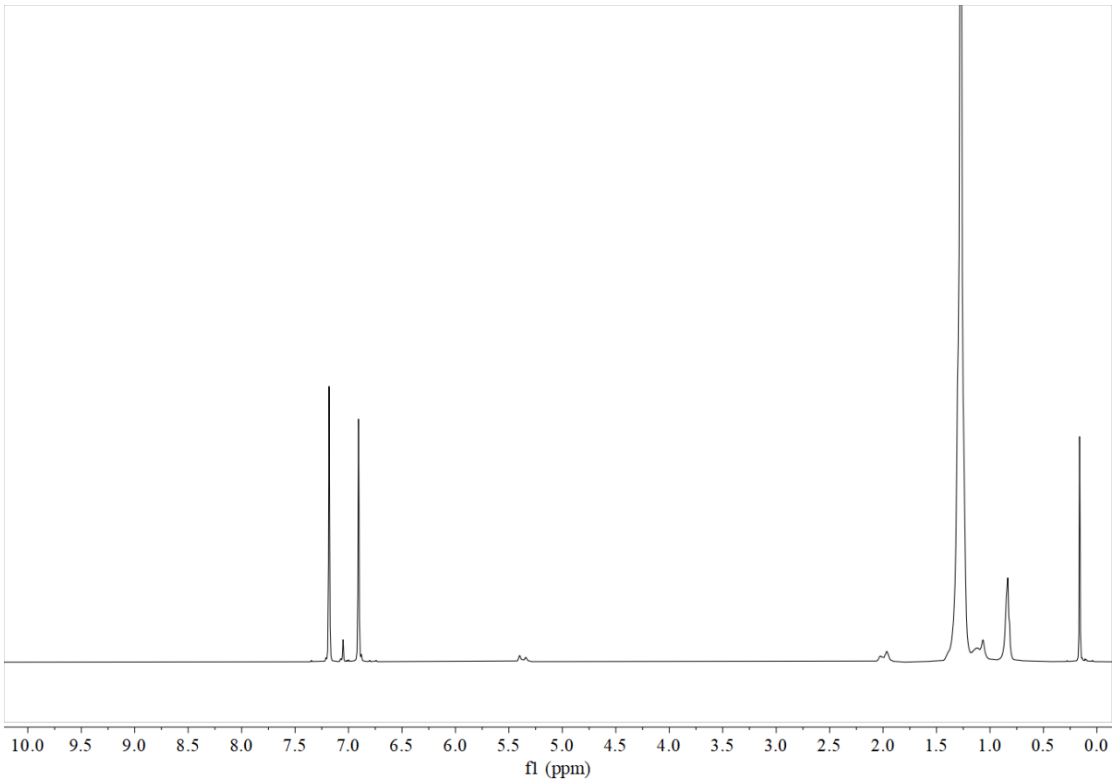


Figure S41. ^{1}H NMR spectrum of the polymer from table 4, entry 12 ($C_6D_4Cl_2$, 120 °C).

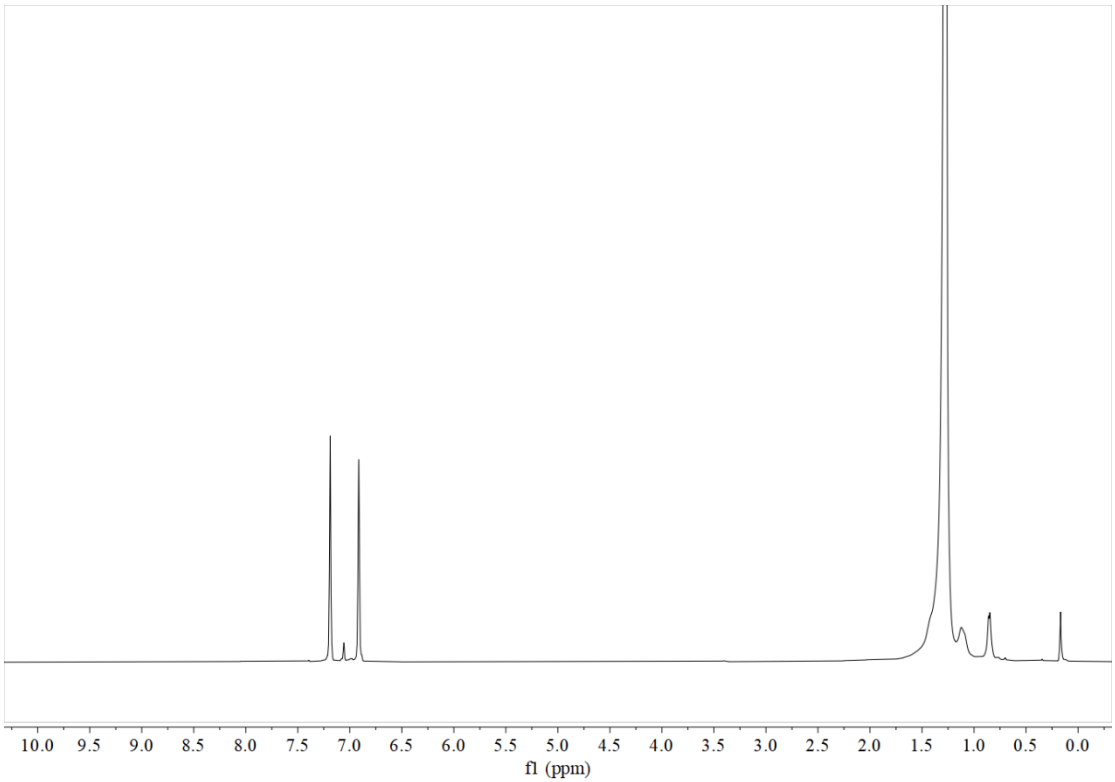


Figure S42. ^{1}H NMR spectrum of the polymer from table 4, entry 13 ($C_6D_4Cl_2$, 120 °C).

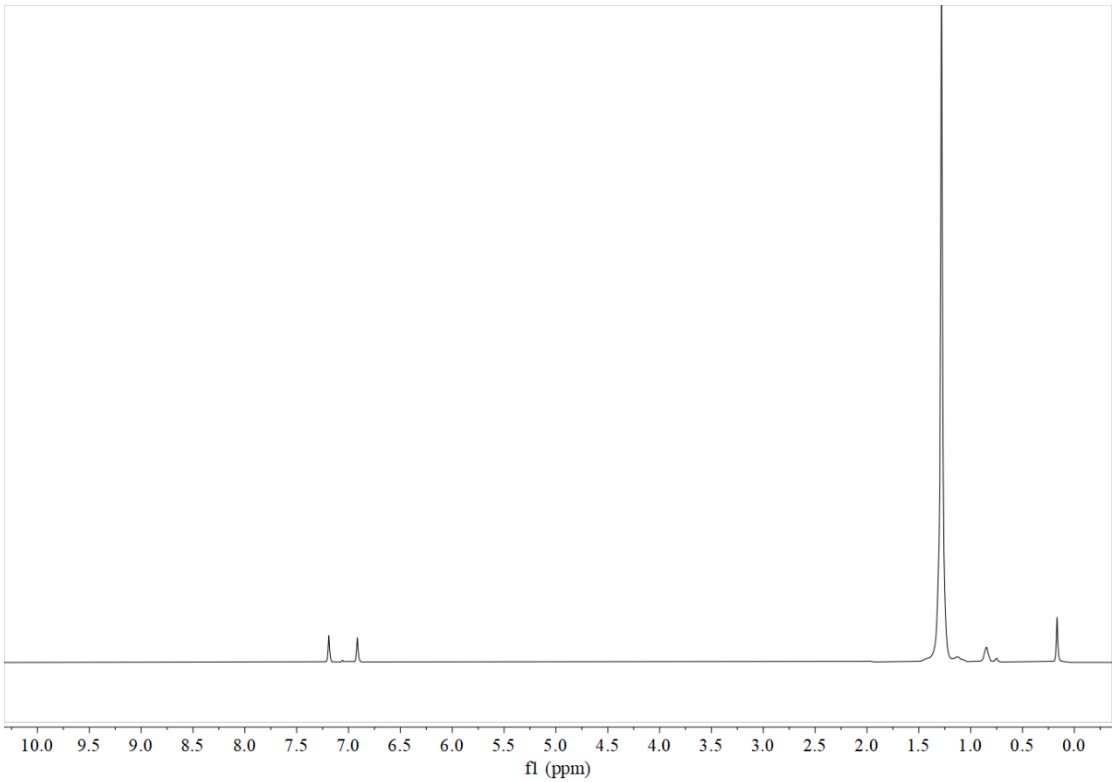


Figure S43. ^{1}H NMR spectrum of the polymer from table 4, entry 14 ($C_6D_4Cl_2$, 120 °C).

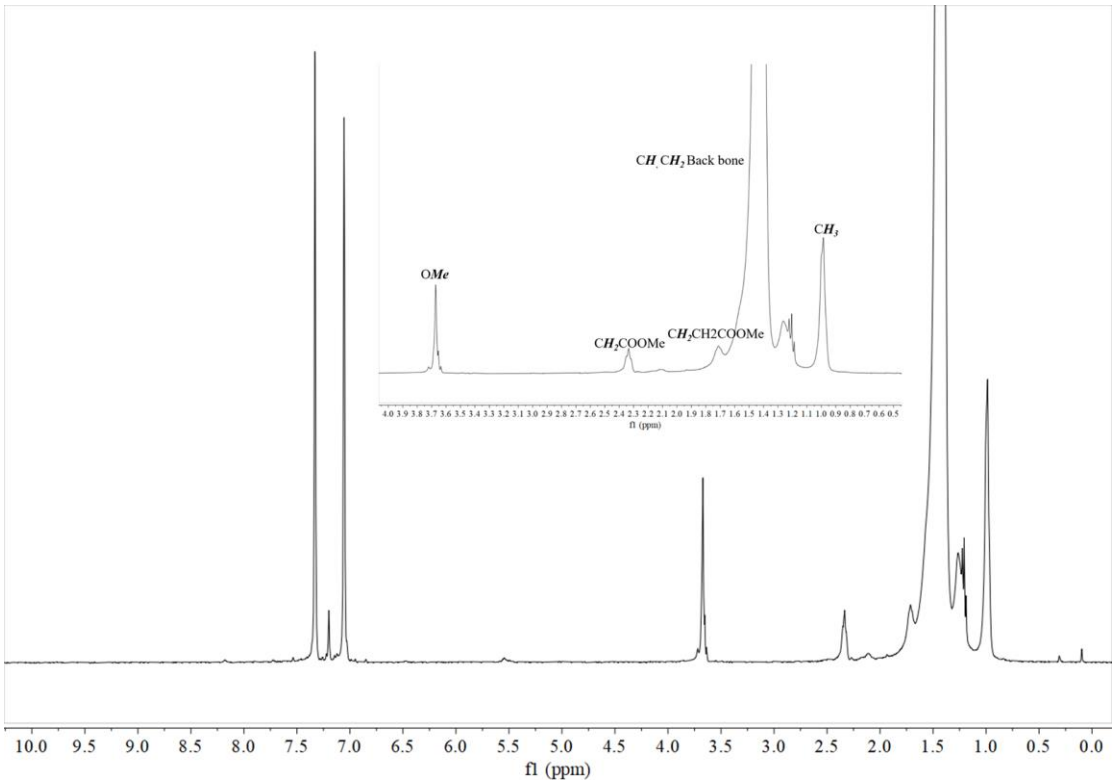


Figure S44. ^{1}H NMR spectrum of the polymer from table 5, entry 1 ($C_6D_4Cl_2$, 120 °C).

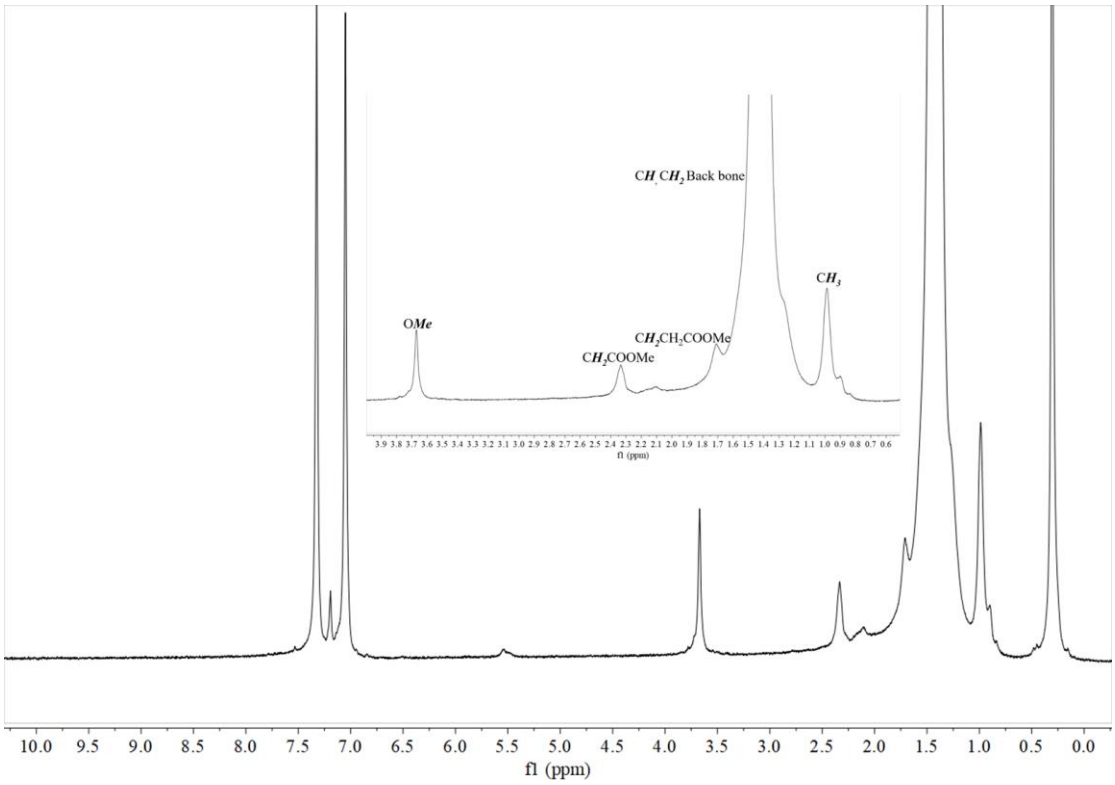


Figure S45. ^{1}H NMR spectrum of the polymer from table 5, entry 2 ($C_6D_4Cl_2$, 120 °C).

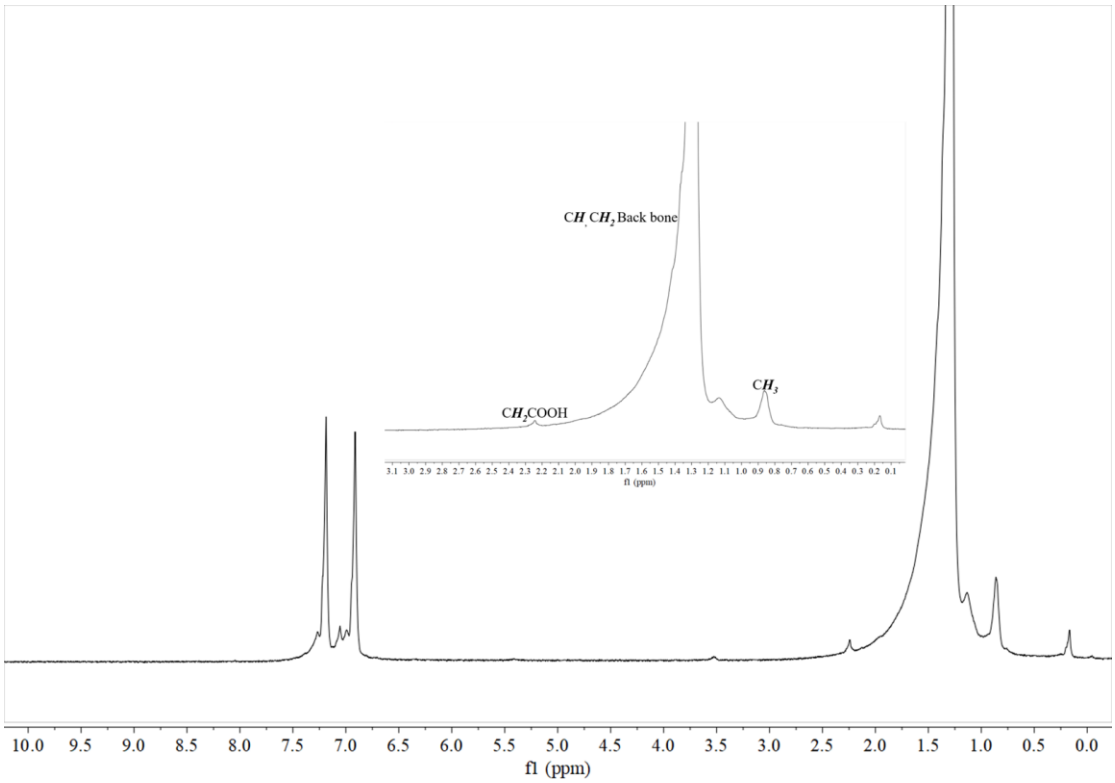


Figure S46. ^{1}H NMR spectrum of the polymer from table 5, entry 5 ($C_6D_4Cl_2$, 120 °C).

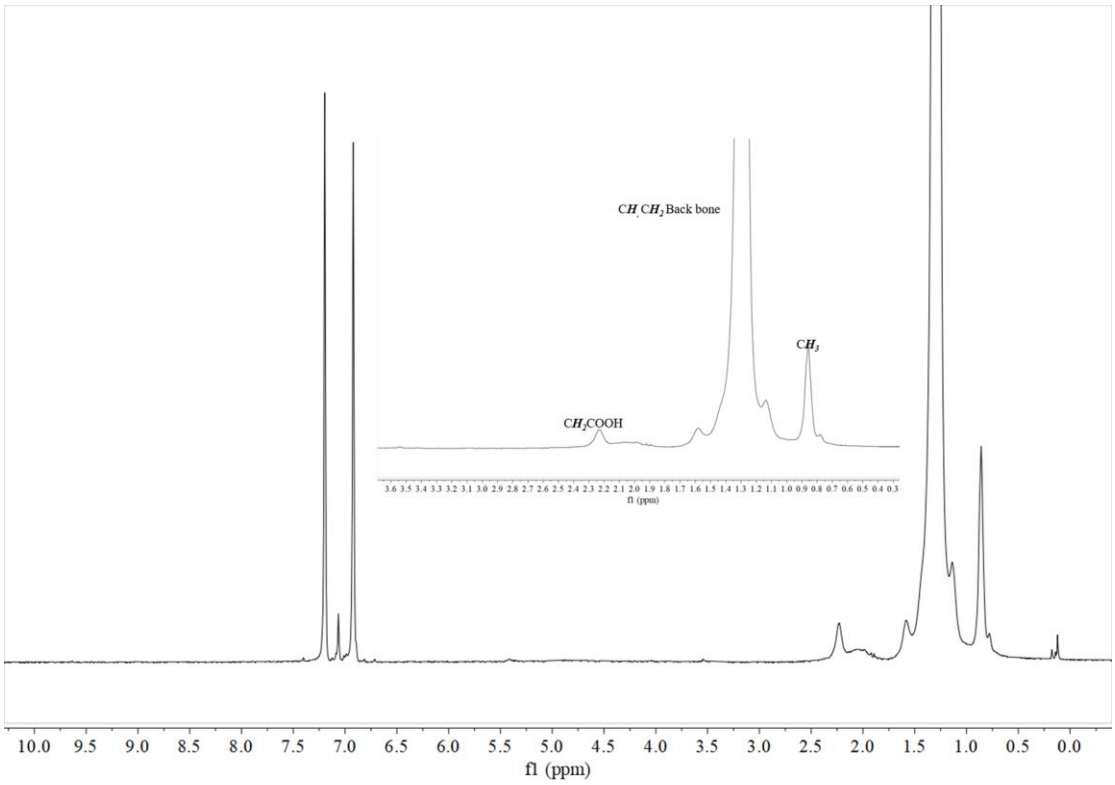


Figure S47. ^{1}H NMR spectrum of the polymer from table 5, entry 6 ($C_6D_4Cl_2$, 120 °C).

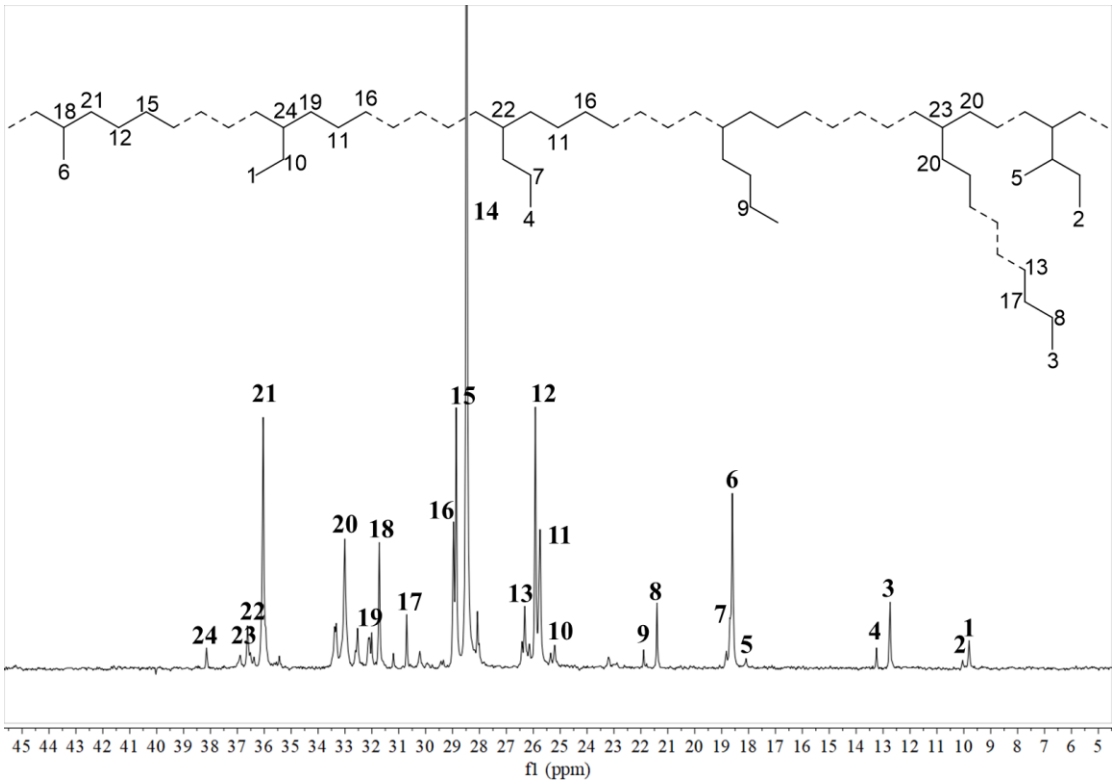


Figure S48. ^{13}C NMR spectrum of the polymer from table 1, entry 1 ($C_2D_2Cl_4$, 120 °C).

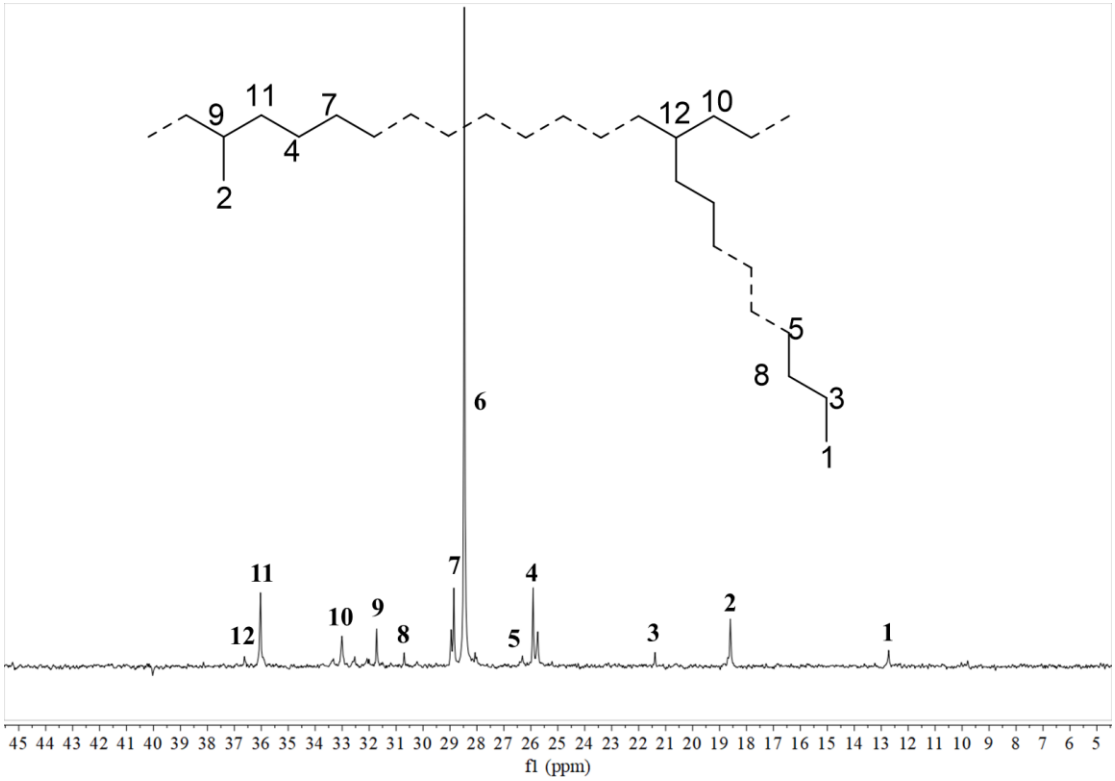


Figure S49. ^{13}C NMR spectrum of the polymer from table 1, entry 4 ($C_2D_2Cl_4$, 120 °C).

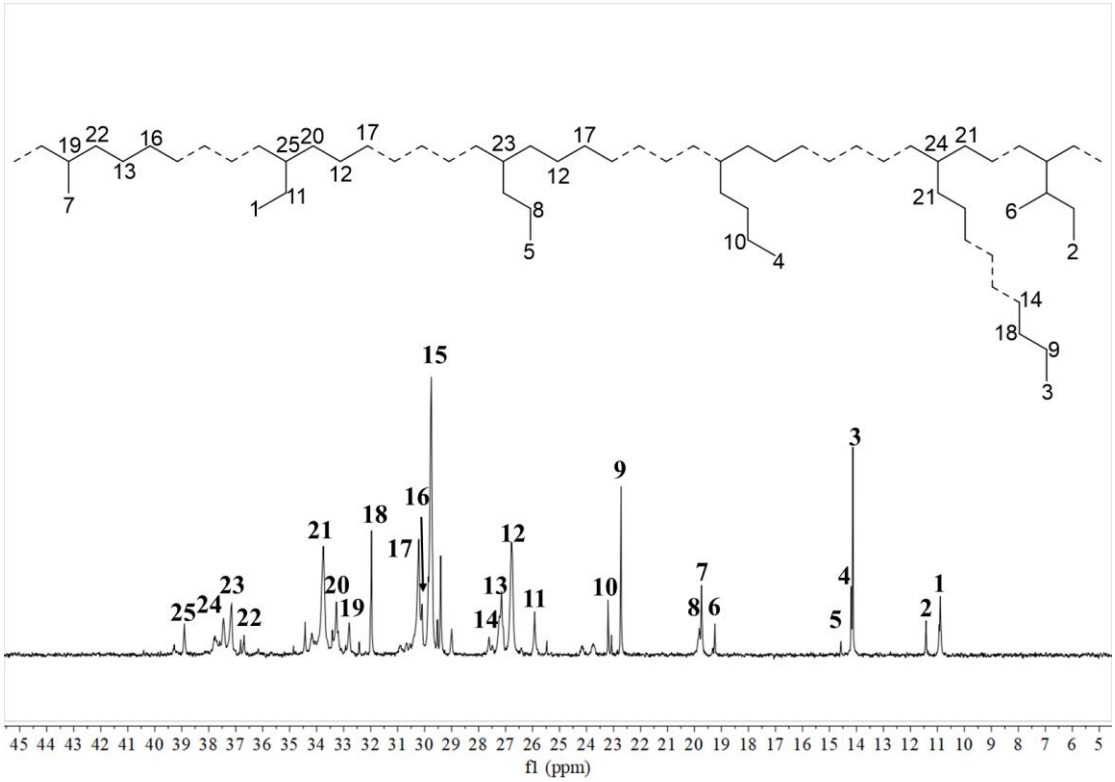


Figure S50. ^{13}C NMR spectrum of the polymer from table 1, entry 10 ($CDCl_3$, 25 °C).

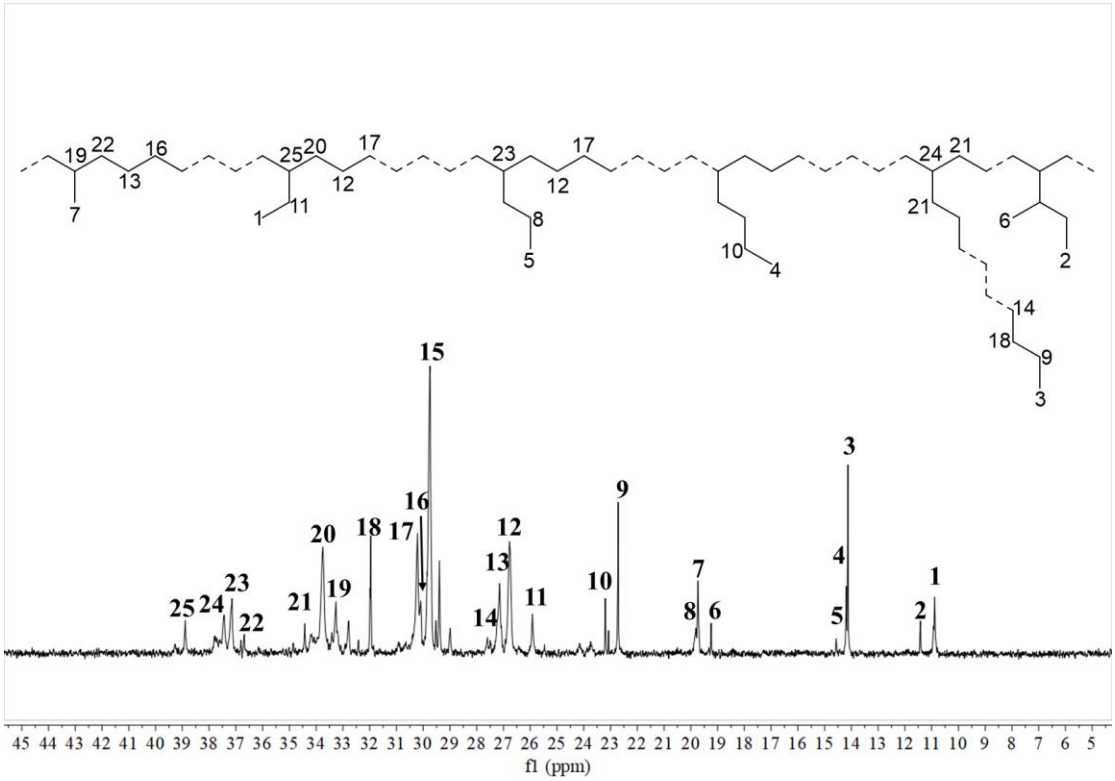


Figure S51. ^{13}C NMR spectrum of the polymer from table 1, entry 13 ($CDCl_3$, 25 °C).

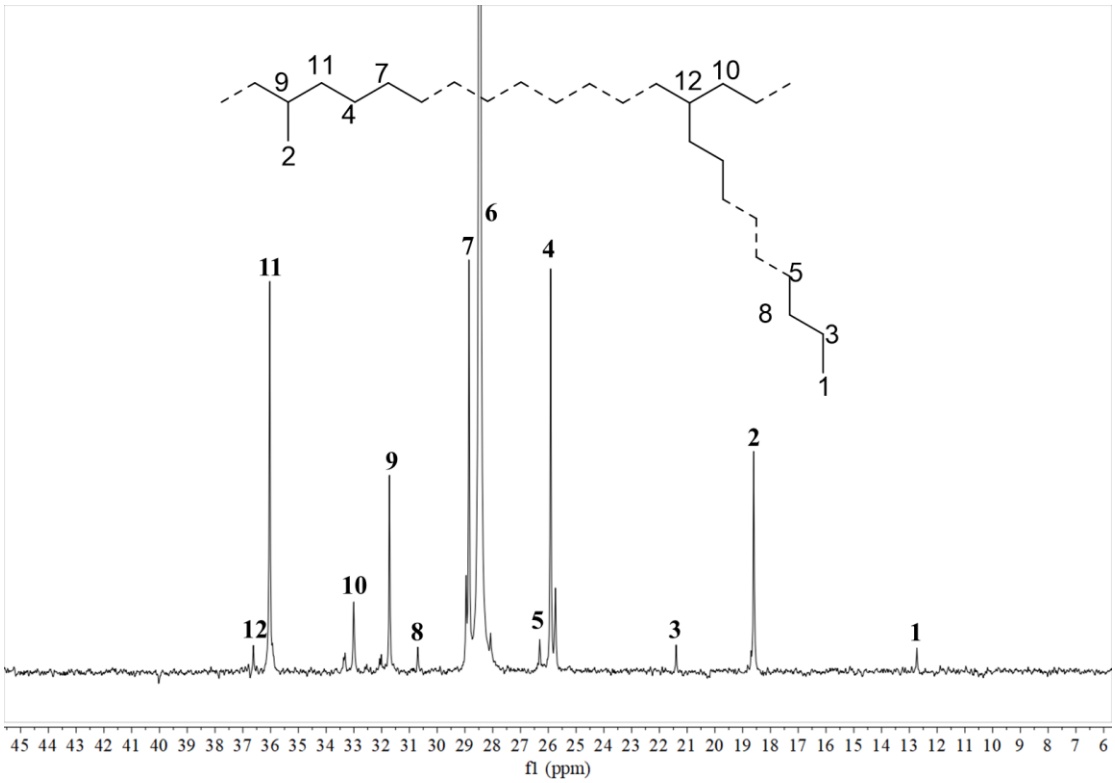


Figure S52. ^{13}C NMR spectrum of the polymer from table 4, entry 1 ($C_2D_2Cl_4$, 120 °C).

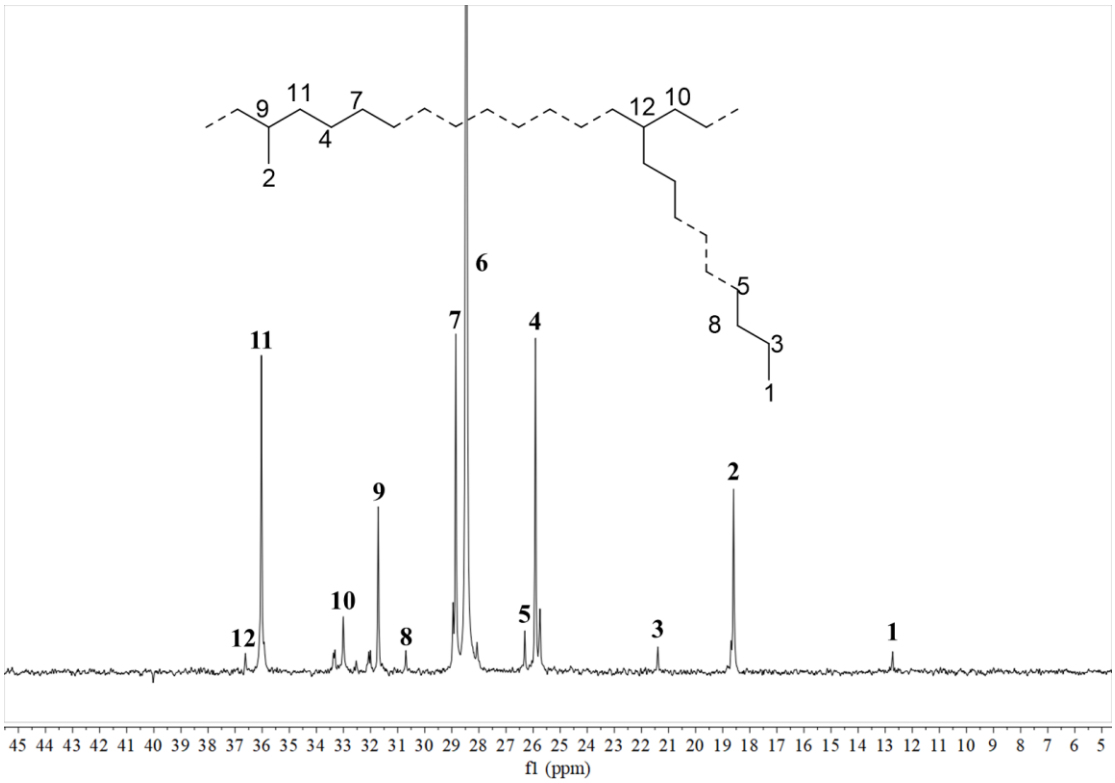


Figure S53. ^{13}C NMR spectrum of the polymer from table 4, entry 5 ($C_2D_2Cl_4$, 120 °C).

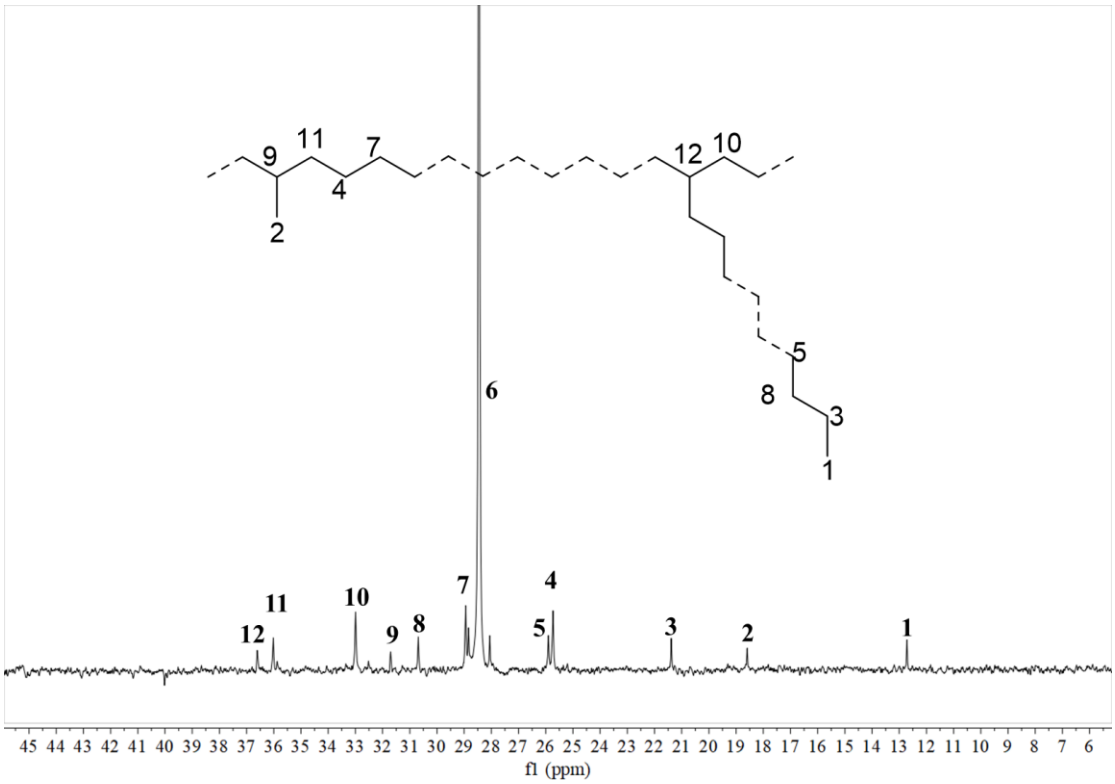


Figure S54. ^{13}C NMR spectrum of the polymer from table 4, entry 9 ($C_2D_2Cl_4$, 120 °C).

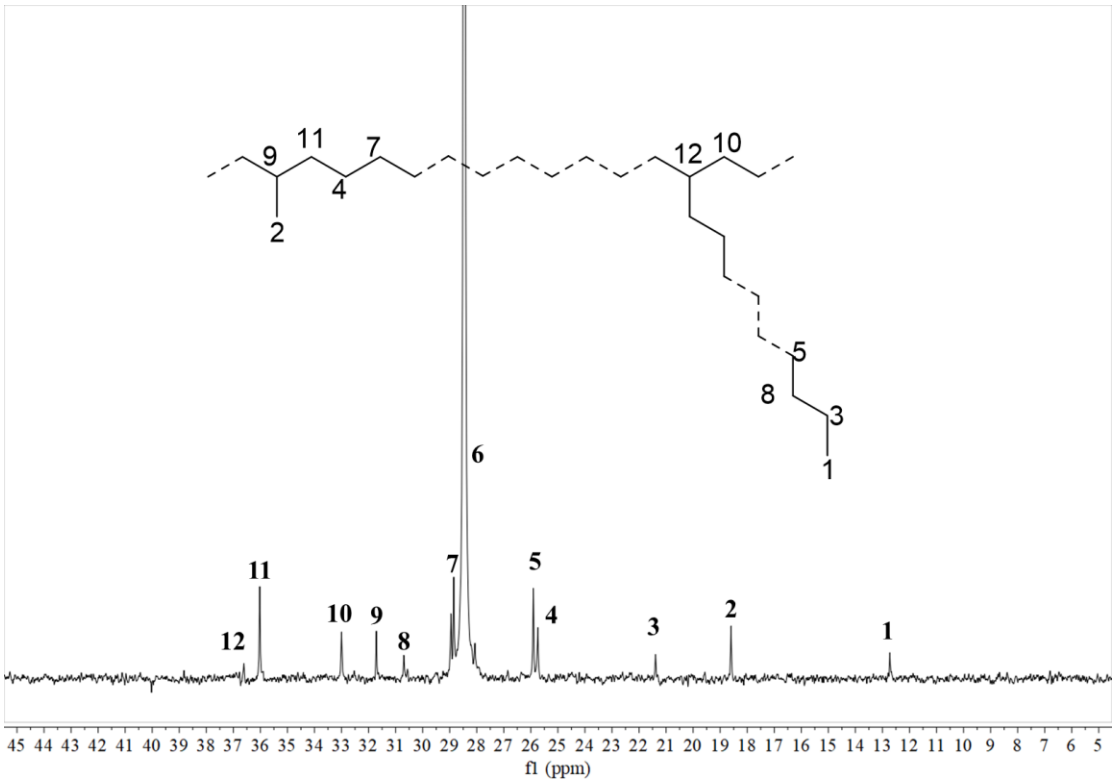


Figure S55. ^{13}C NMR spectrum of the polymer from table 4, entry 13 ($C_2D_2Cl_4$, 120 °C).

3.5. DSC, GPC of Polymers

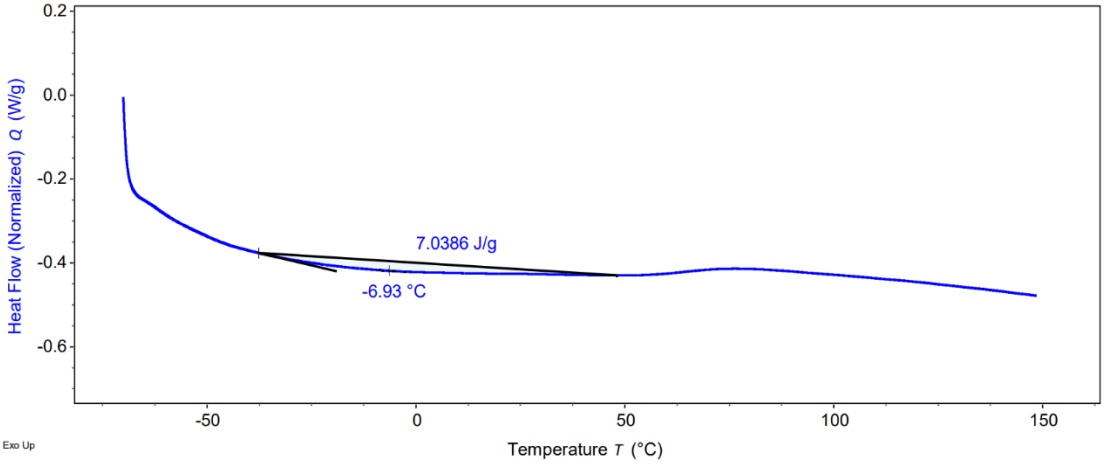


Figure S56. DSC of the polymer from table 1, entry 1.

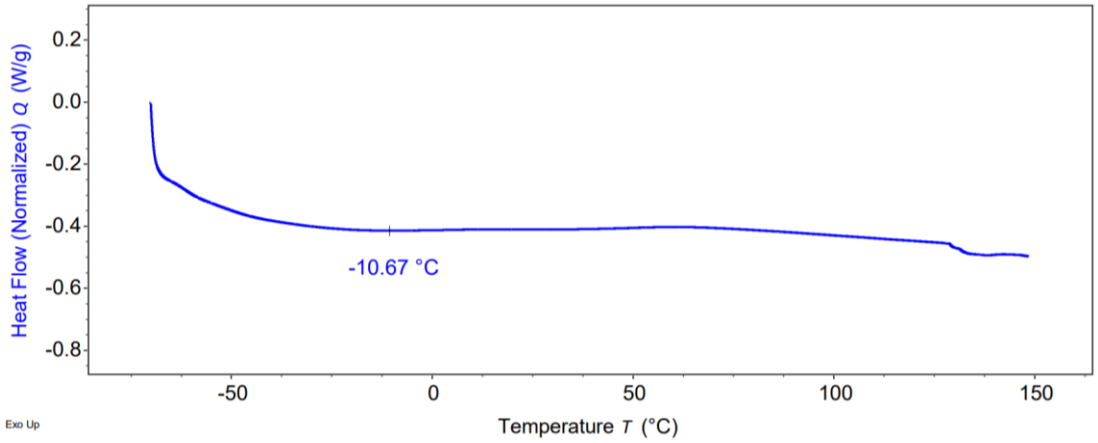


Figure S57. DSC of the polymer from table 1, entry 2.

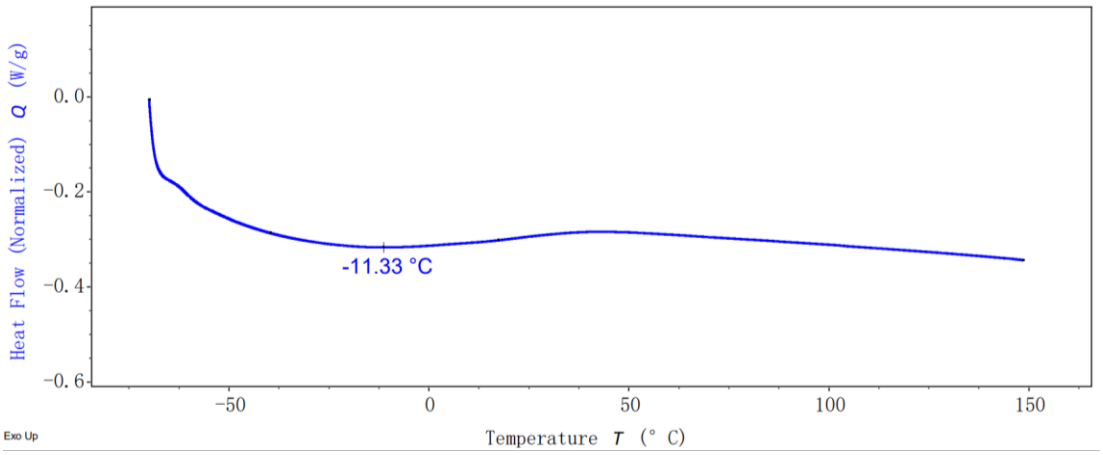


Figure S58. DSC of the polymer from table 1, entry 3.

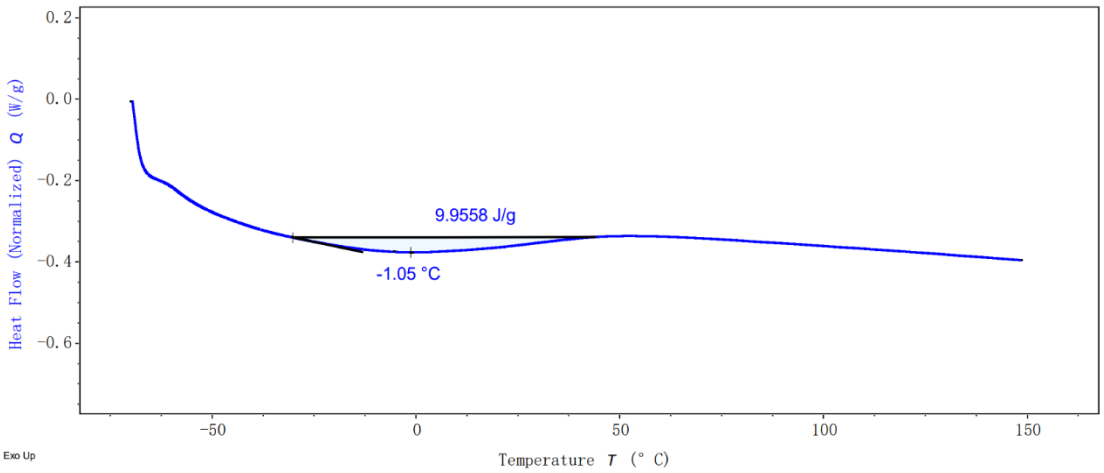


Figure S59. DSC of the polymer from table 1, entry 4.

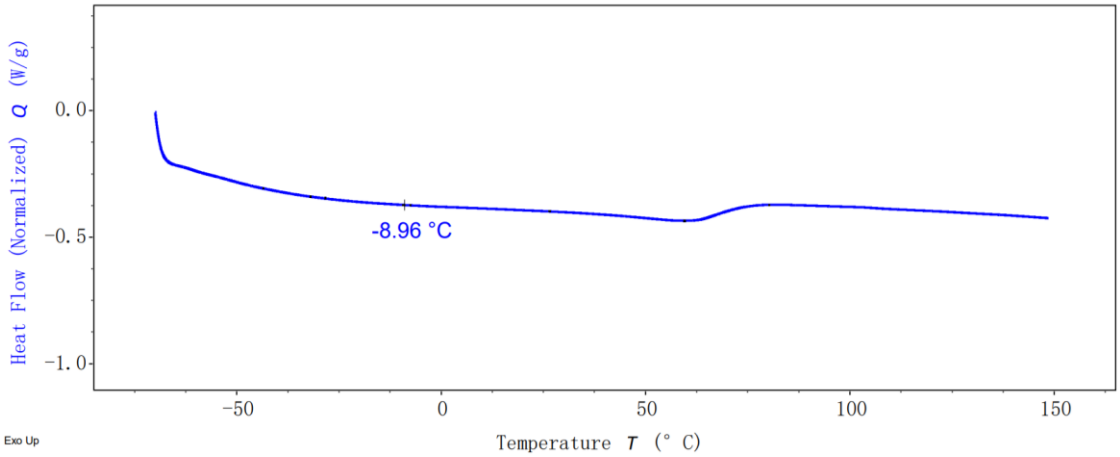


Figure S60. DSC of the polymer from table 1, entry 5.

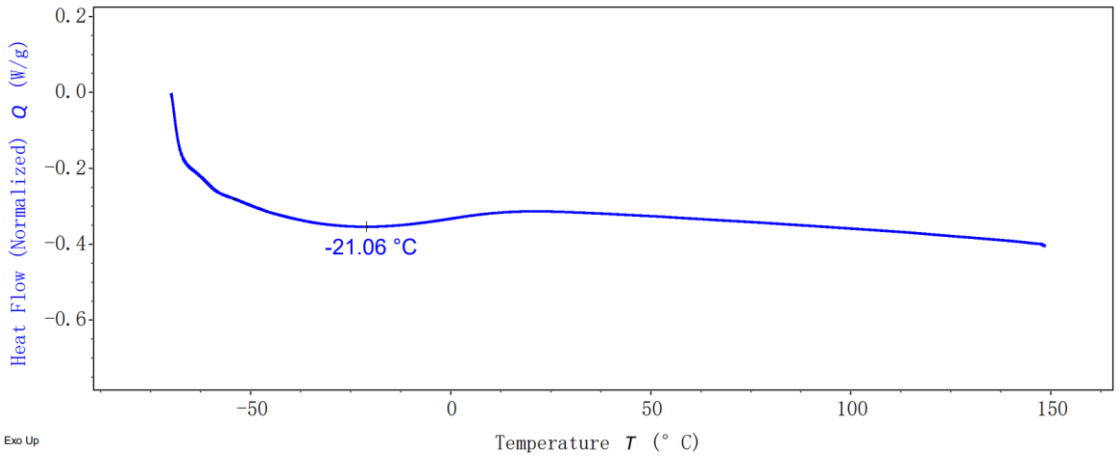


Figure S61. DSC of the polymer from table 1, entry 6.

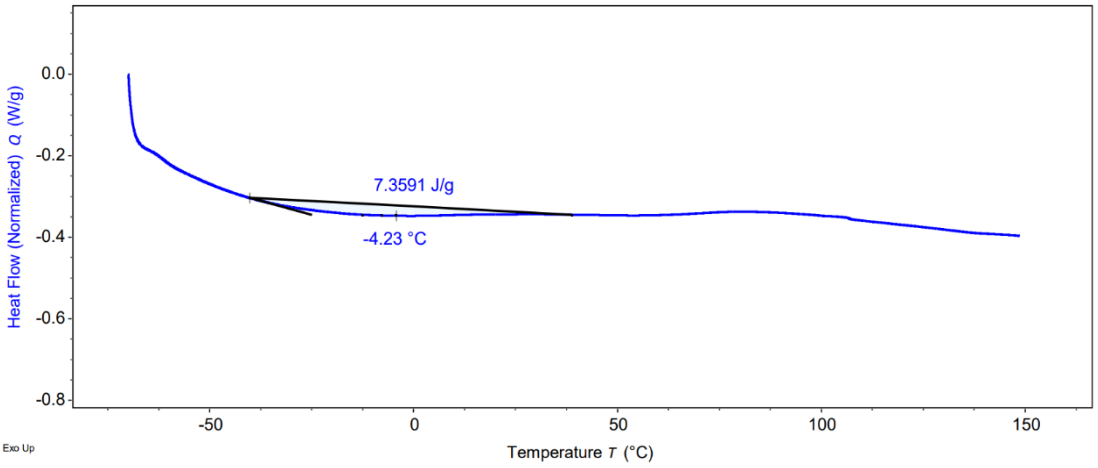


Figure S62. DSC of the polymer from table 1, entry 7.

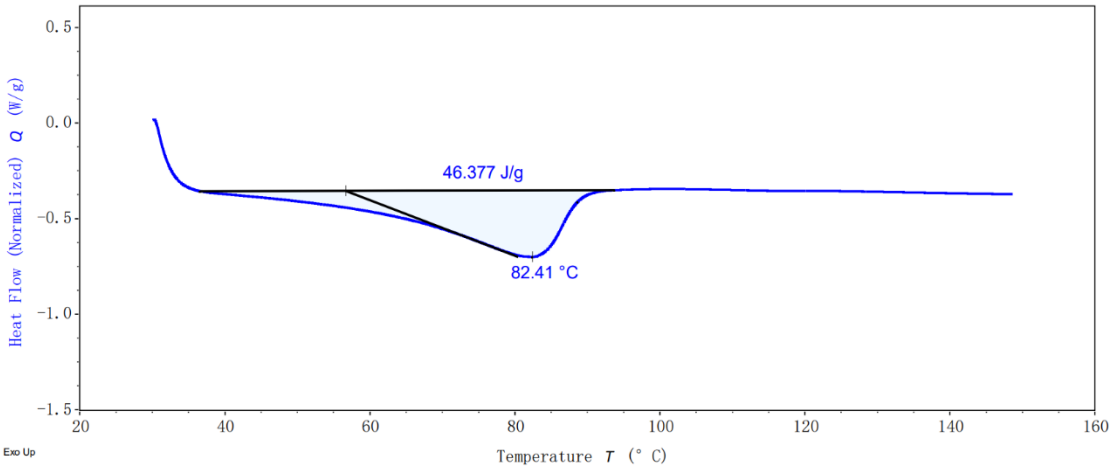


Figure S63. DSC of the polymer from table 4, entry 1.

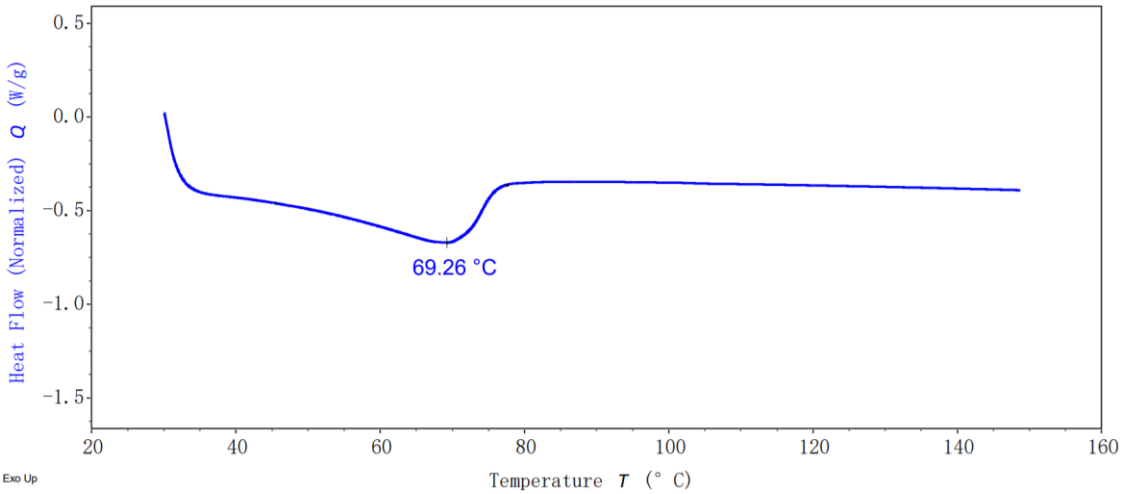


Figure S64. DSC of the polymer from table 4, entry 2.

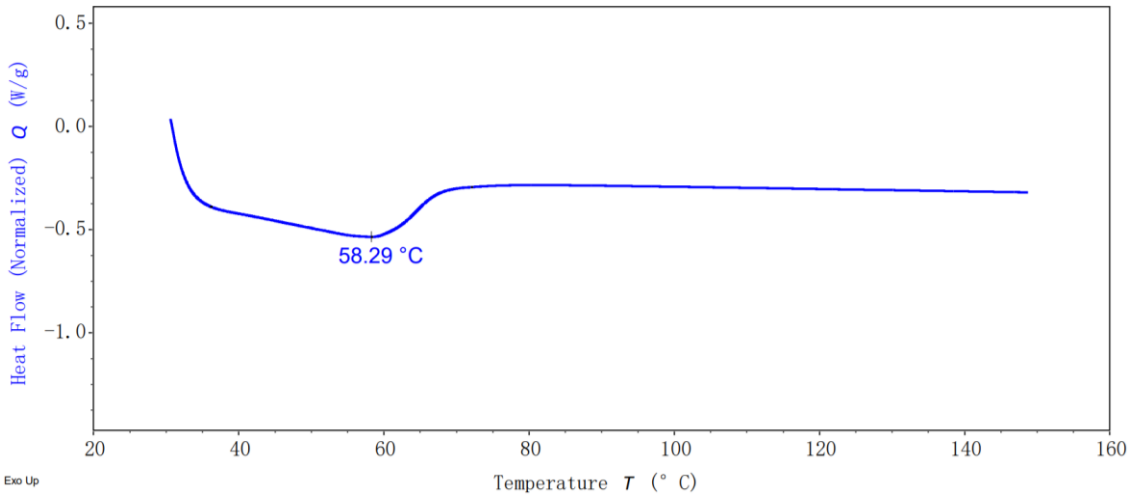


Figure S65. DSC of the polymer from table 4, entry 3.

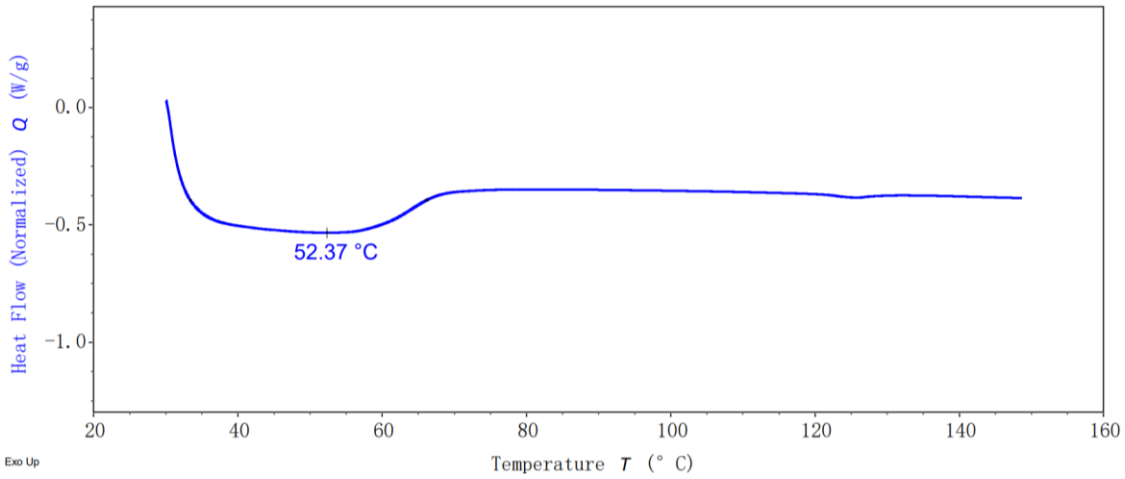


Figure S66. DSC of the polymer from table 4, entry 4.

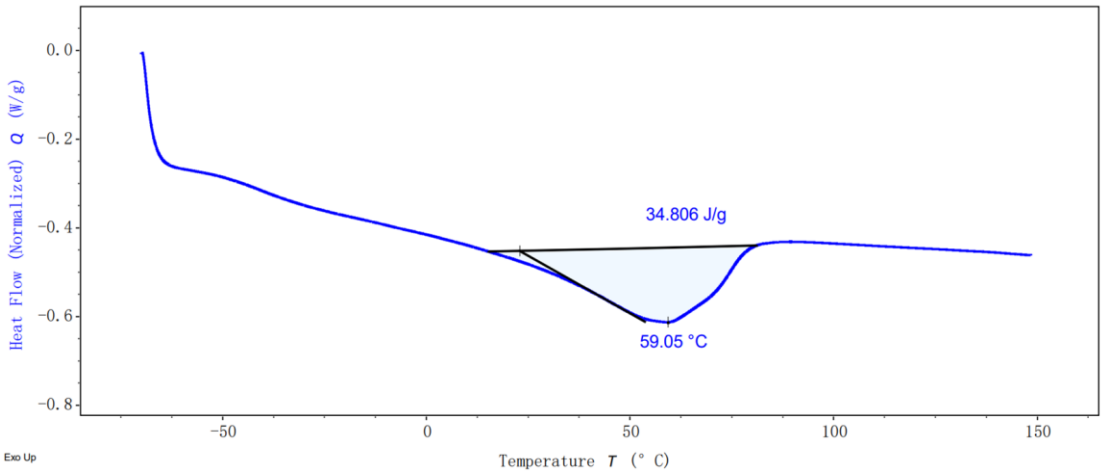


Figure S67. DSC of the polymer from table 4, entry 5.

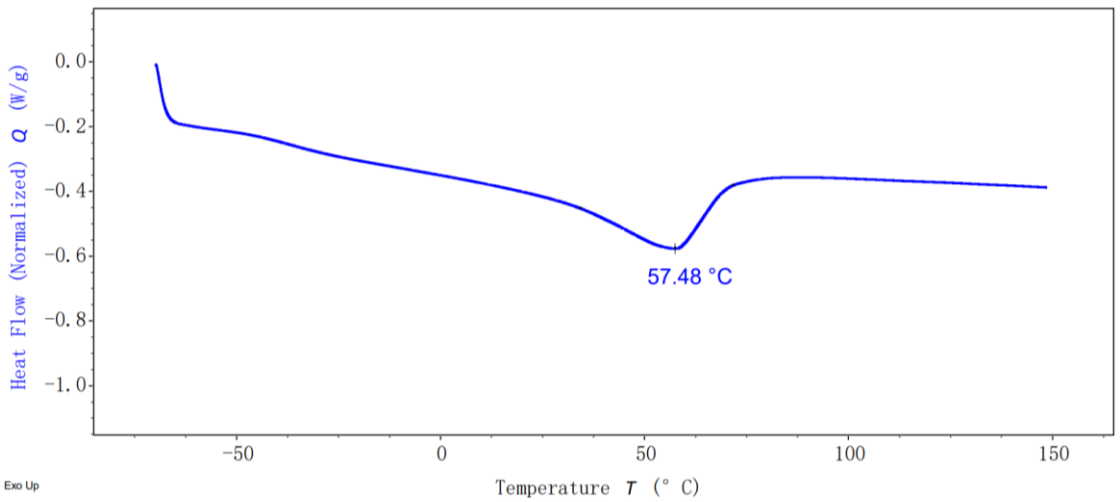


Figure S68. DSC of the polymer from table 4, entry 6.

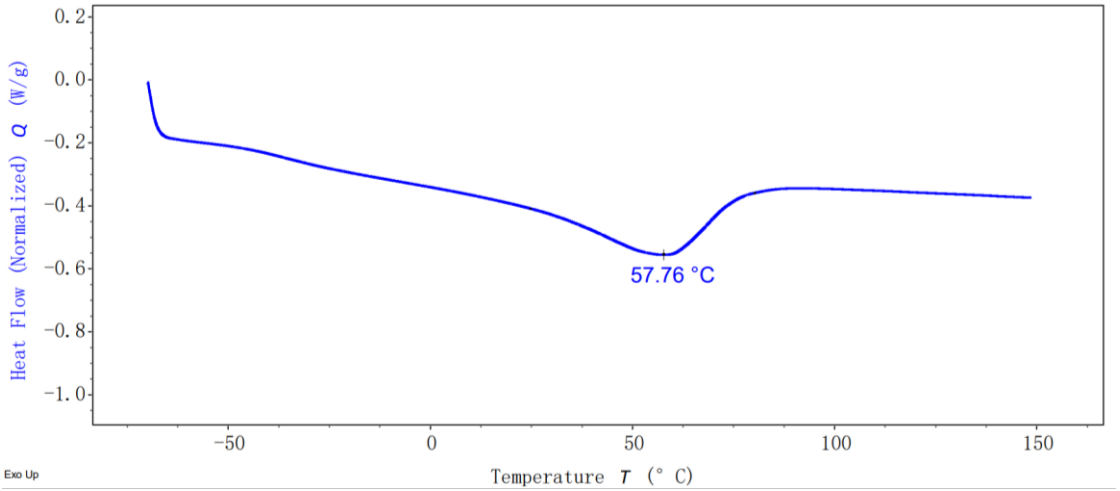


Figure S69. DSC of the polymer from table 4, entry 7.

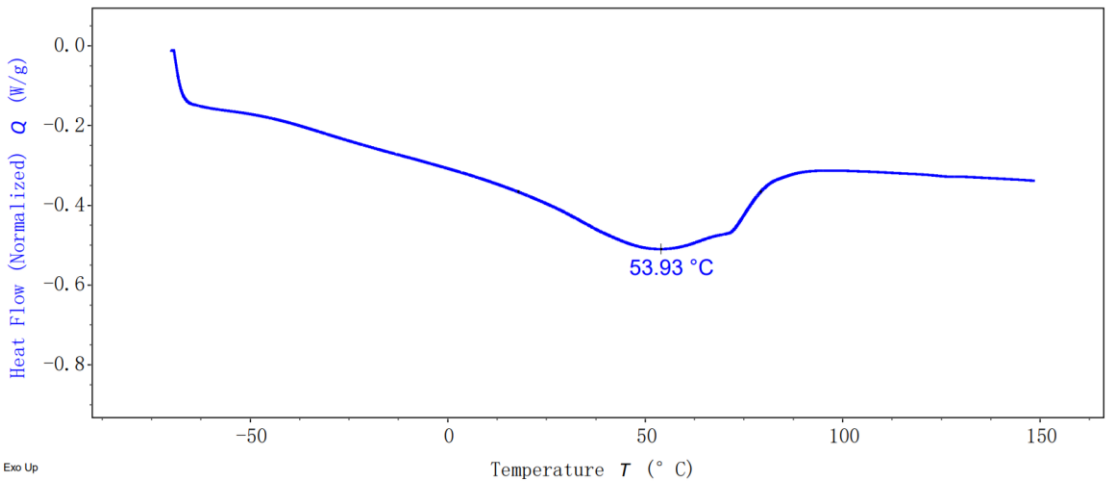


Figure S70. DSC of the polymer from table 4, entry 8.

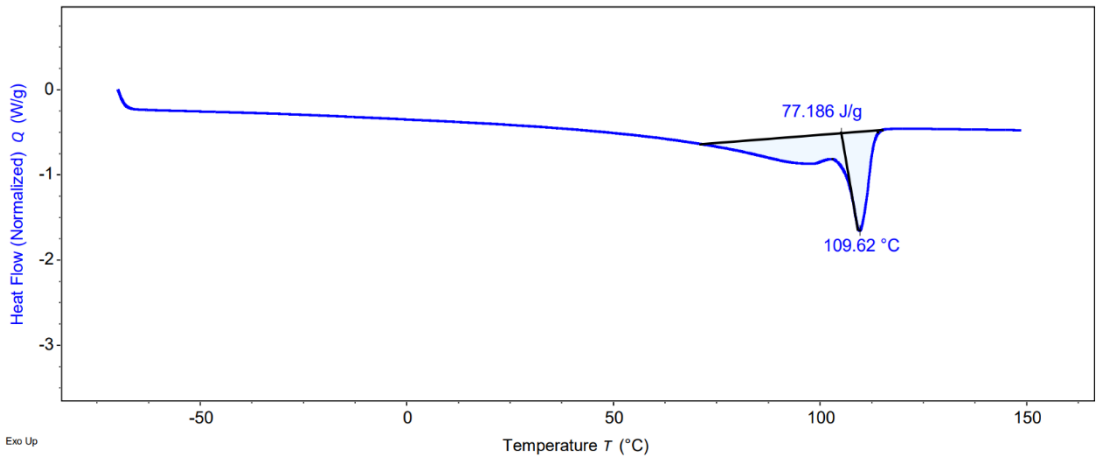


Figure S71. DSC of the polymer from table 4, entry 9.

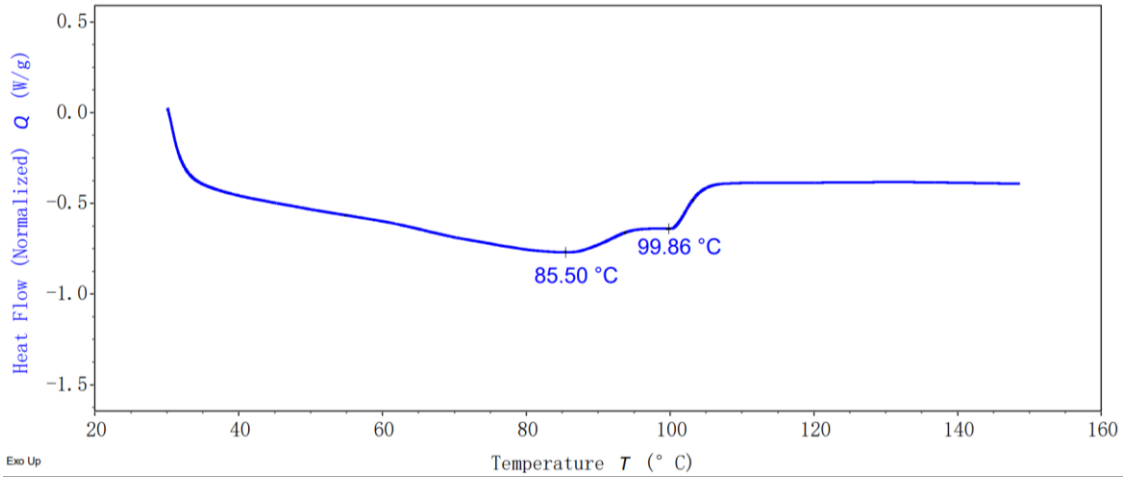


Figure S72. DSC of the polymer from table 4, entry 10.

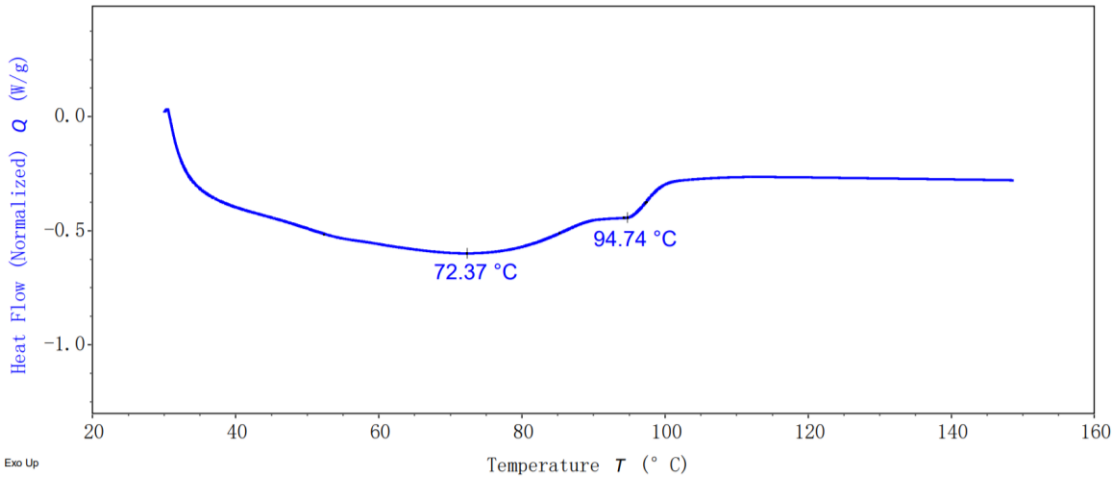


Figure S73. DSC of the polymer from table 4, entry 11.

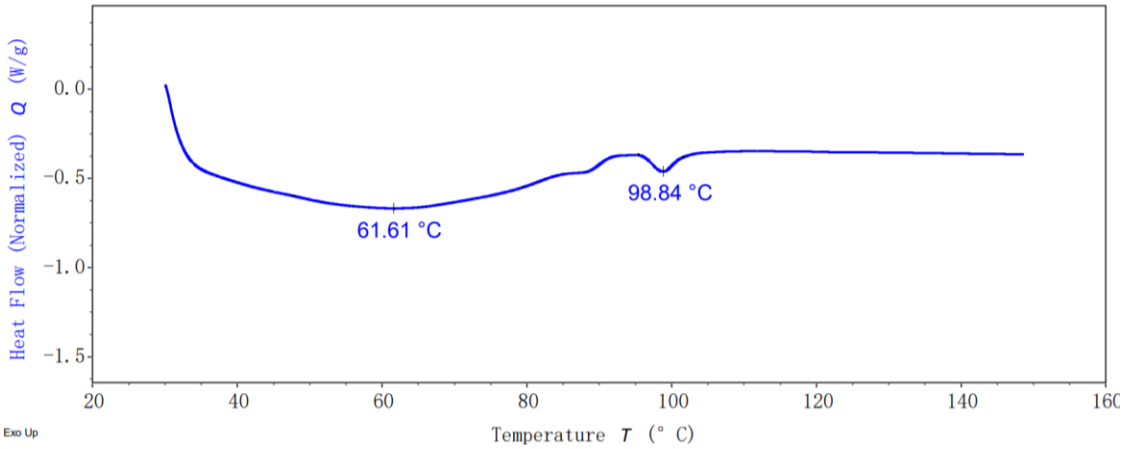


Figure S74. DSC of the polymer from table 4, entry 12.

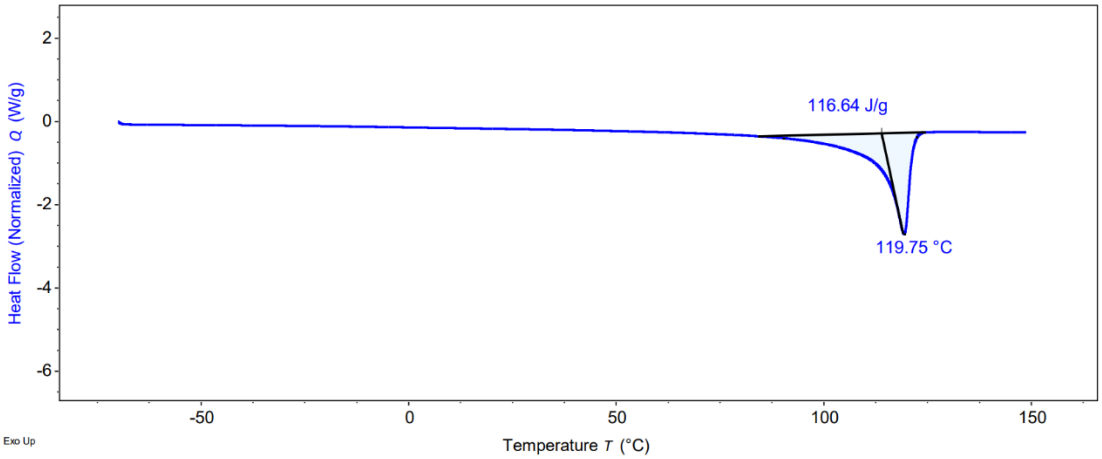


Figure S75. DSC of the polymer from table 4, entry 13.

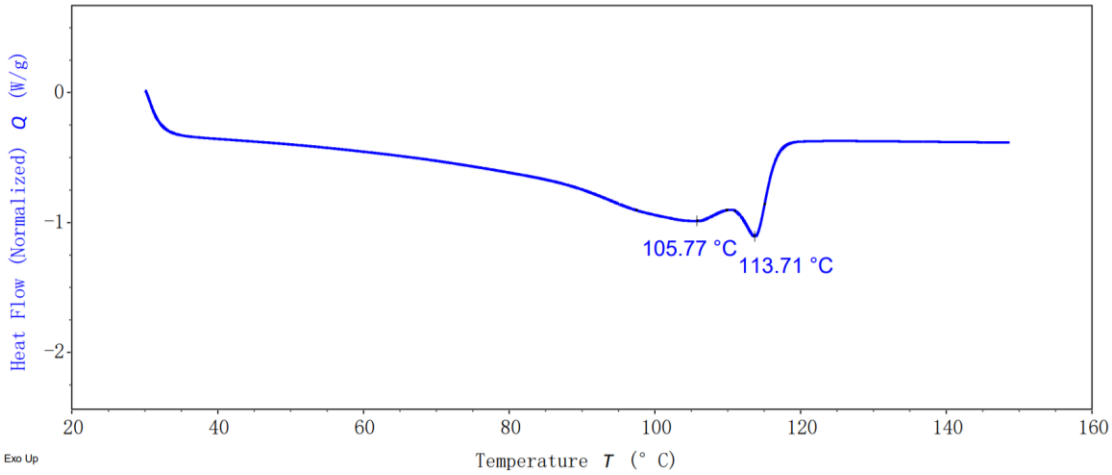


Figure S76. DSC of the polymer from table 4, entry 14.

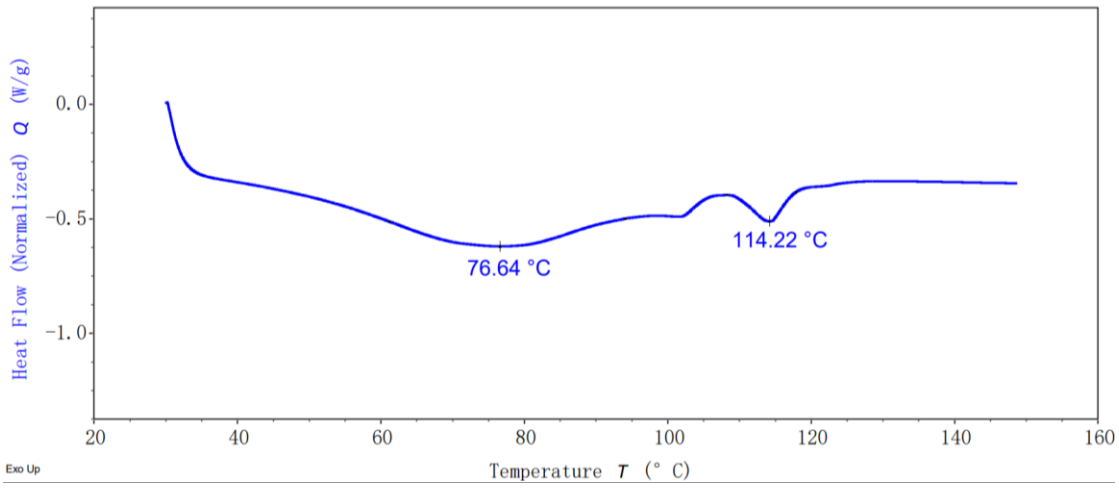


Figure S77. DSC of the polymer from table 4, entry 15.

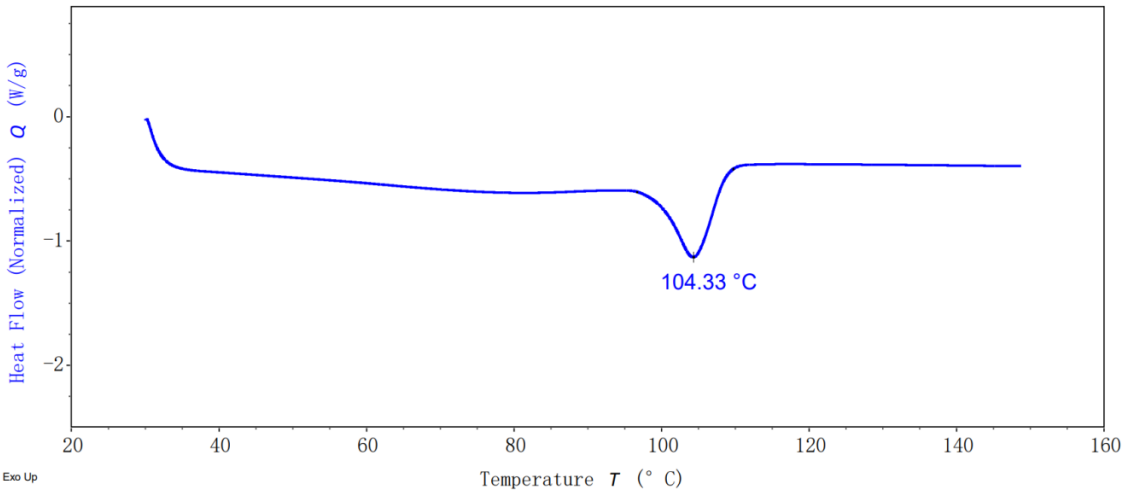


Figure S78. DSC of the polymer from table 5, entry 1.

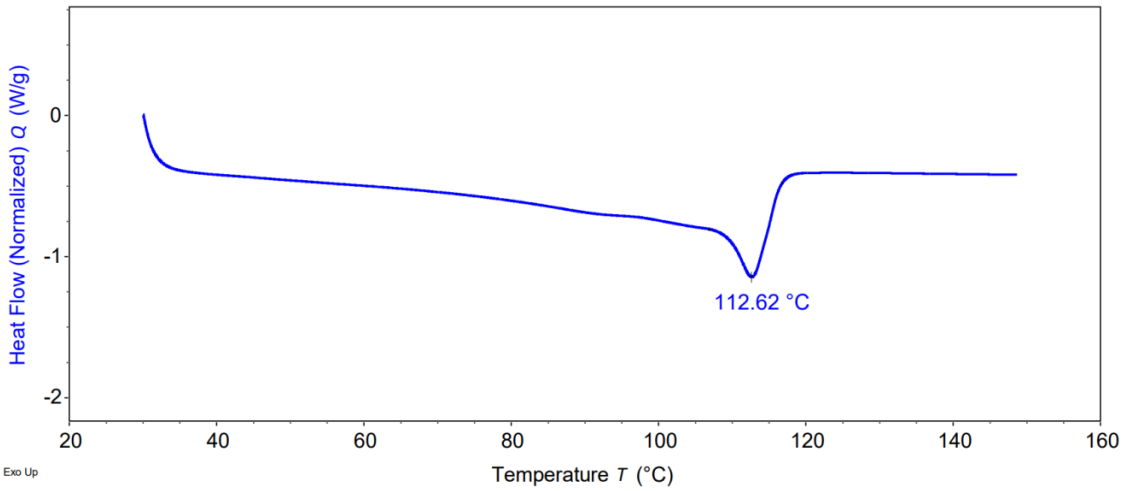


Figure S79. DSC of the polymer from table 5, entry 2.

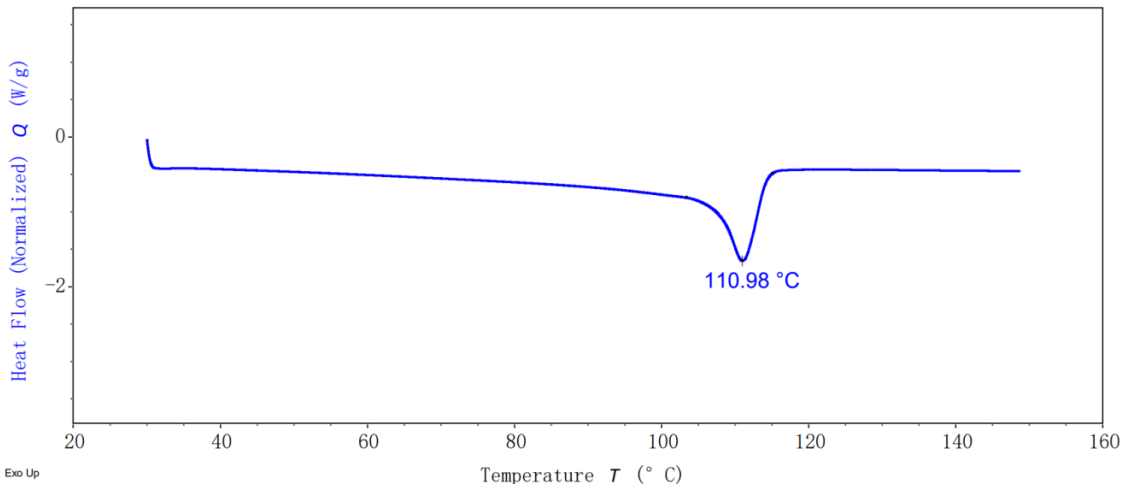


Figure S80. DSC of the polymer from table 5, entry 5.

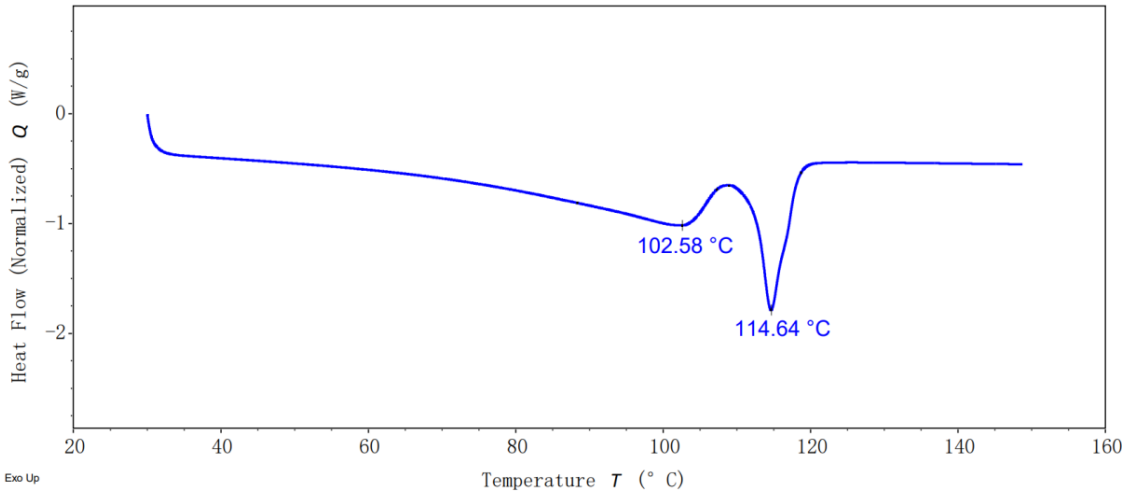
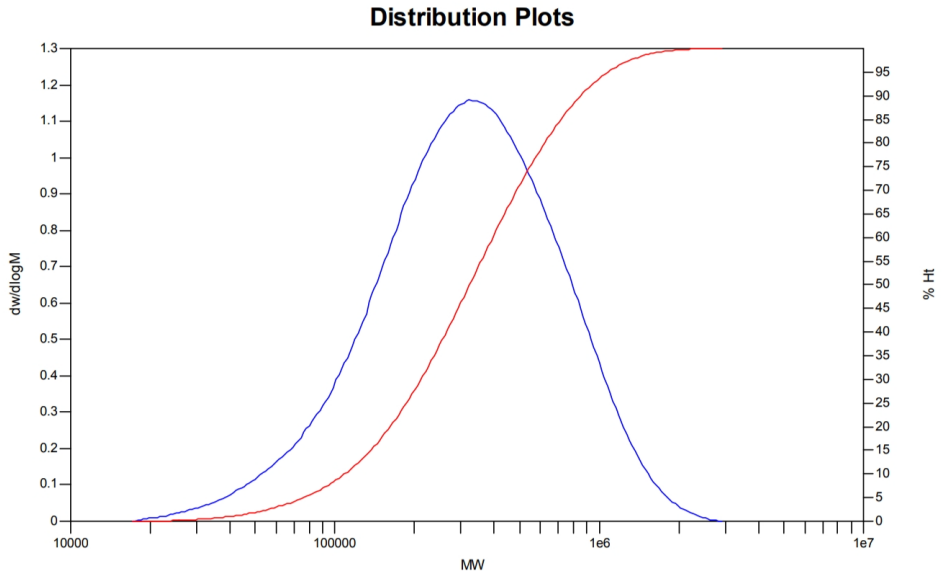


Figure S81. DSC of the polymer from table 5, entry 6.

Cirrus GPC Sample Peak Report

MW Averages

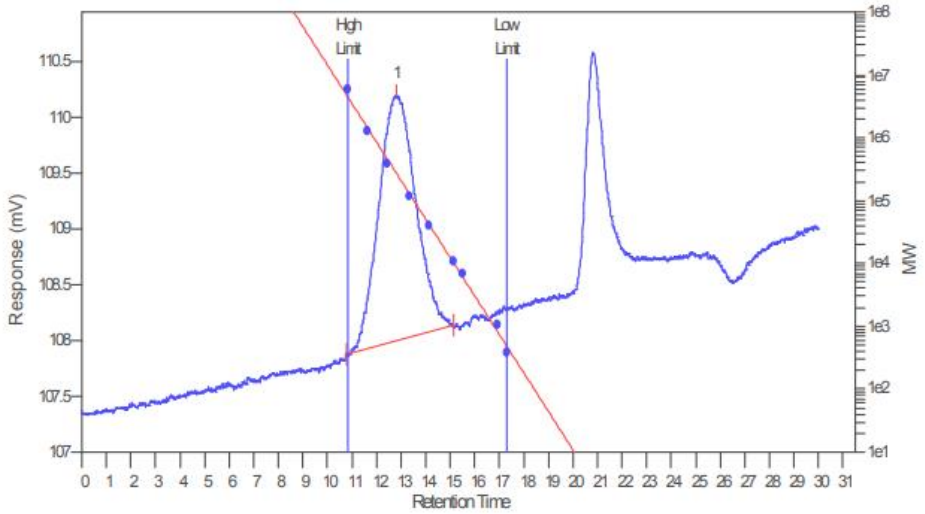
Mp: 322062	Mn: 217886	Mv: 379375	Mw: 411978
Mz: 670246	Mz+1: 956760	PD: 1.8908	

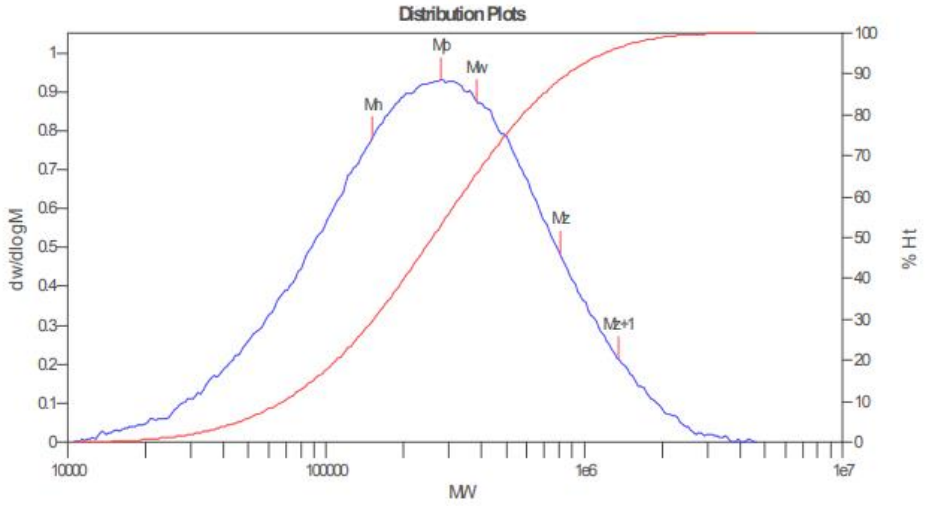


MW Ranges

Range No	High Limit	Low Limit	%Area
1	2902778	50000	98.097
2	50000	40000	0.891
3	40000	30000	0.642
4	30000	20000	0.348
5	20000	17170	0.022

Figure S82. GPC of the polymer from table 1, entry 1.





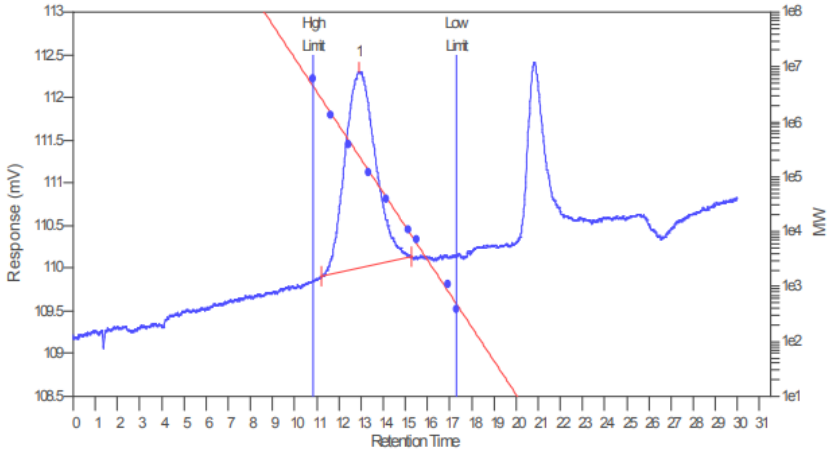
MW Averages

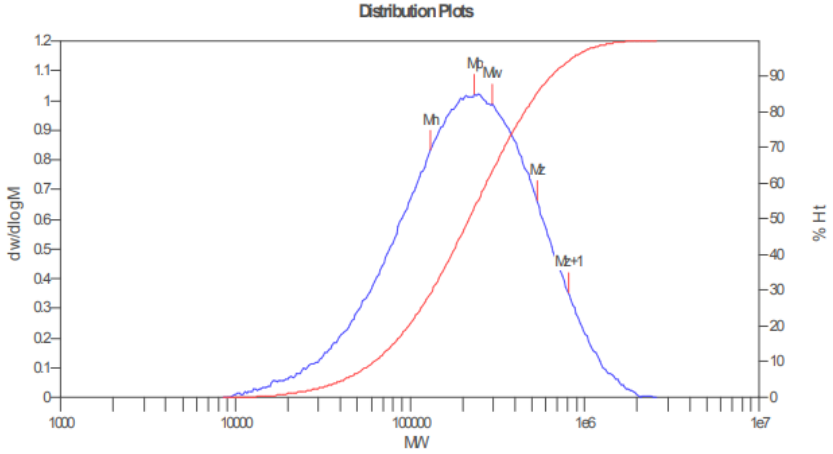
Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	277312	150175	383802	803325	1350570	338487	2.5557

Processed Peaks

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1		10.80	12.80	15.12	2.21118	0	232.494	100

Figure S83. GPC of the polymer from table 1, entry 2.





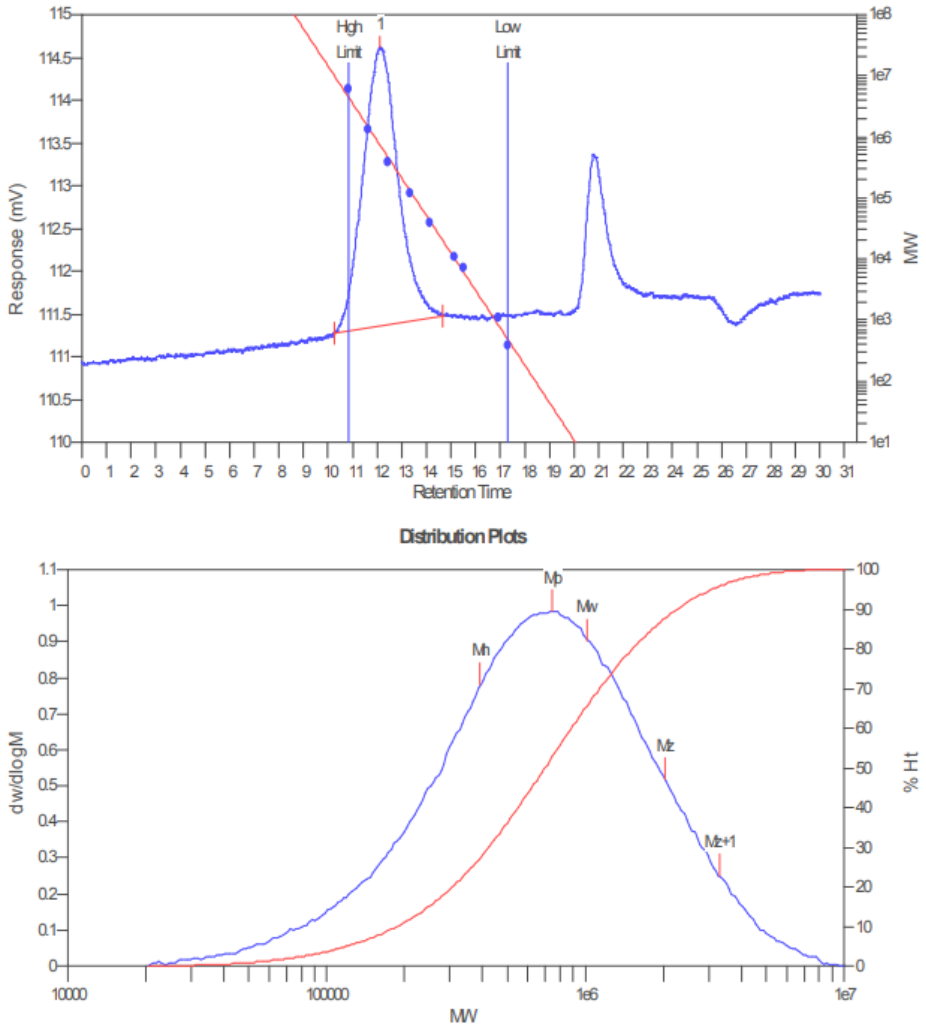
MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	235247	131180	295409	533497	804770	266668	2.25194

Processed Peaks

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1		11.22	12.92	15.27	2.29767	0	220.843	100

Figure S84. GPC of the polymer from table 1, entry 3.



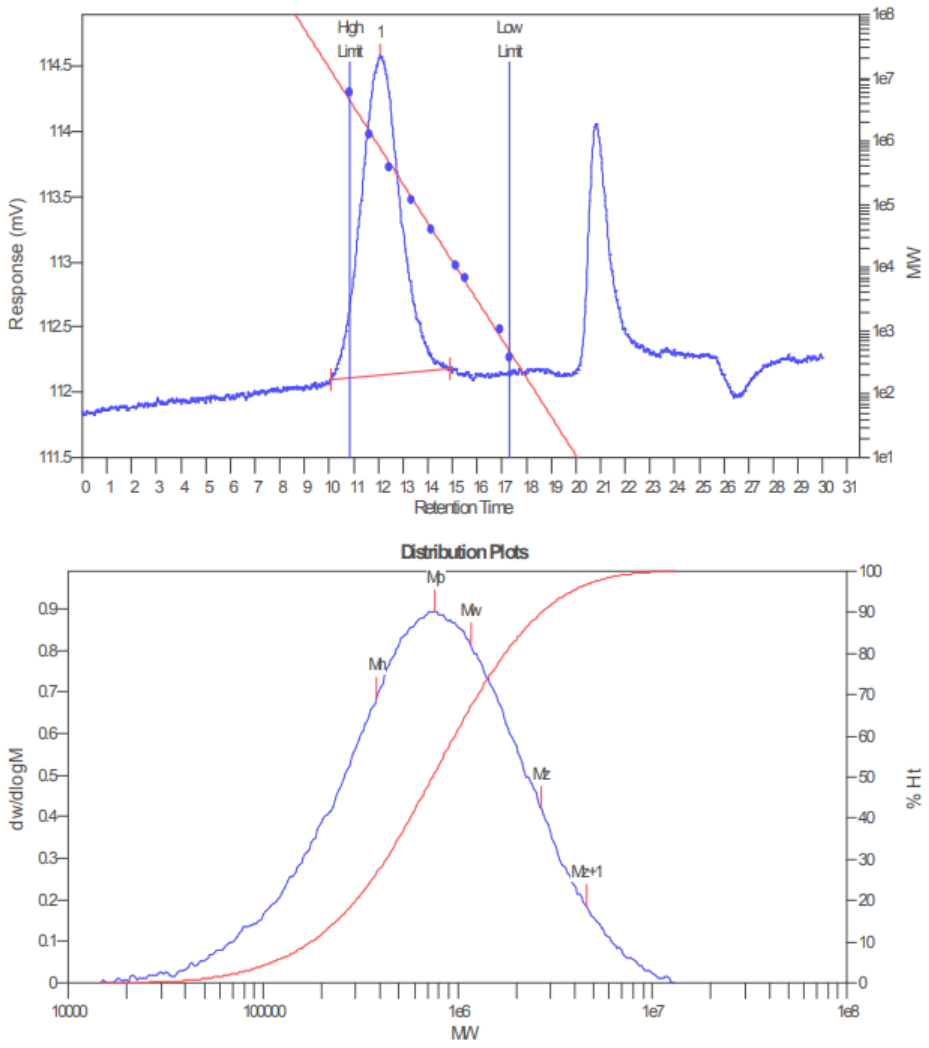
MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	744119	392455	1012324	2035417	3290233	898090	2.57947

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	12.10	14.65	3.25376	0	323.794	100

Figure S85. GPC of the polymer from table 1, entry 4.



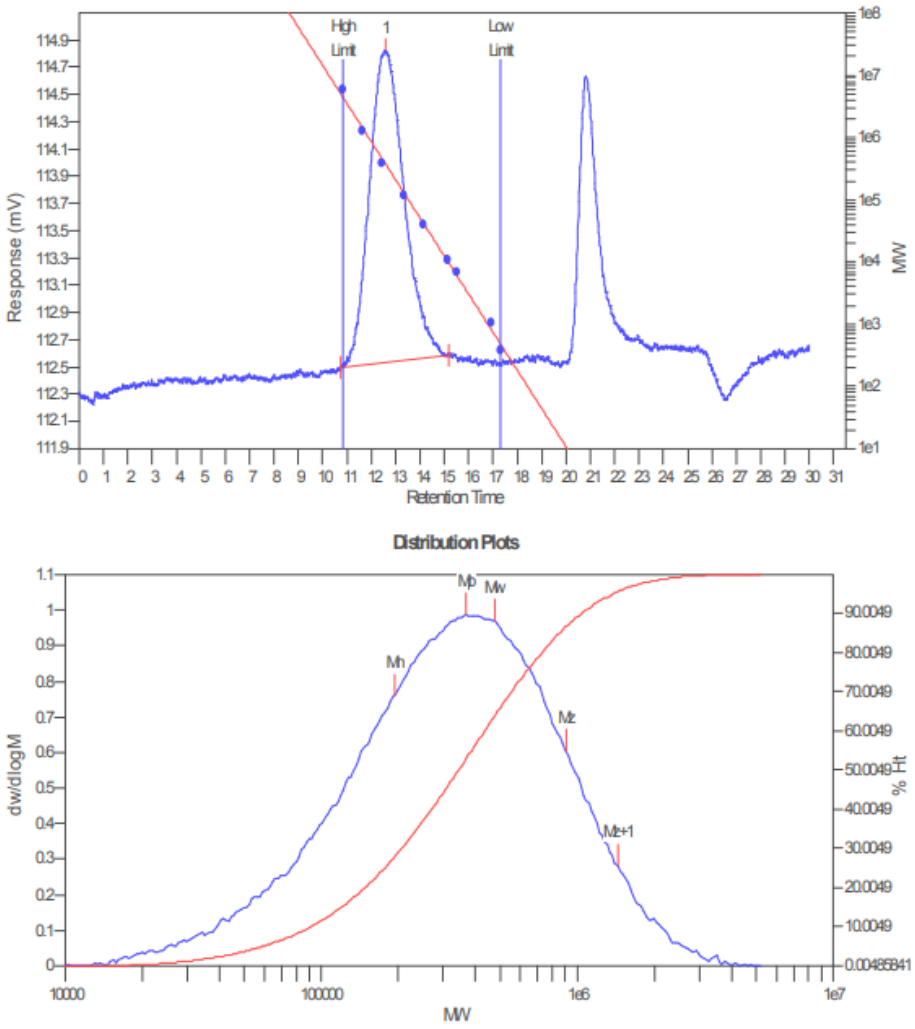
MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	761814	382755	1172752	2680704	4608172	1016351	3.06398

Processed Peaks

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1		10.07	12.08	14.88	2.45017	0	268.568	100

Figure S86. GPC of the polymer from table 1, entry 5.



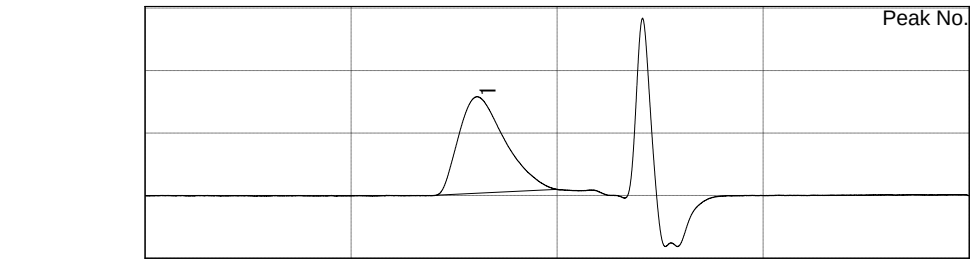
MW Averages

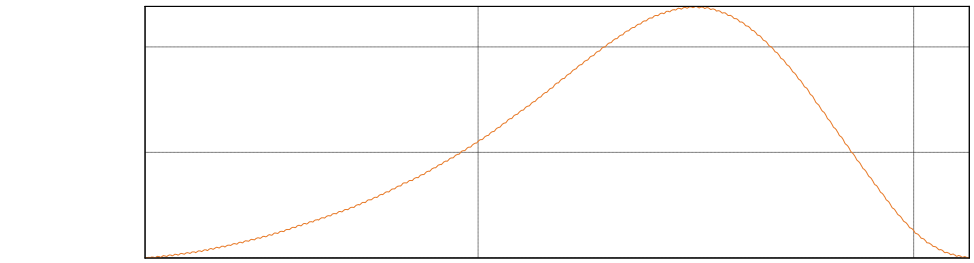
Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	367661	194236	475207	906238	1442344	425205	2.44654

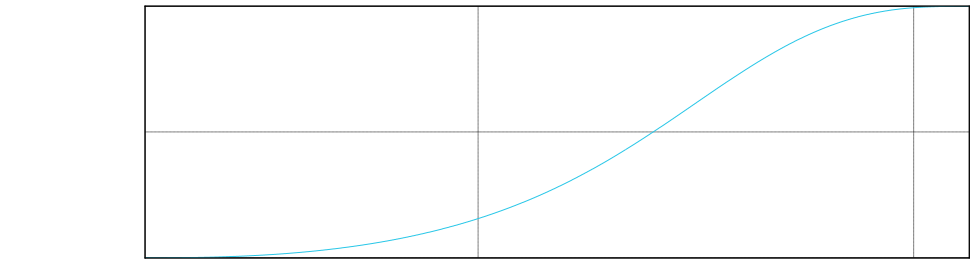
Processed Peaks

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1		10.72	12.60	15.18	2.28653	0	226.575	100

Figure S87. GPC of the polymer from table 1, entry 6.







Result of molecular weight calculation (RI)

Peak 1 Base Peak

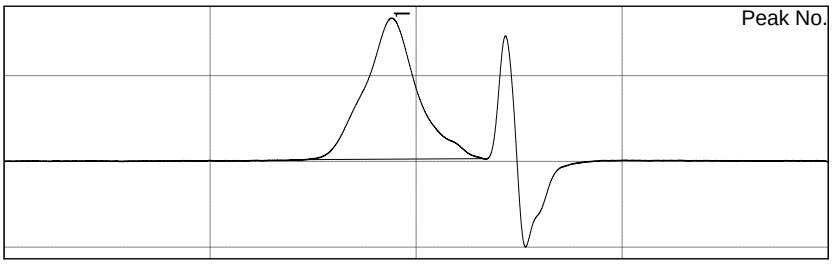
	[min]	[mV]	[mol]		
Peak start	7.078	0.068	134,085	Mn	16,418
Peak top	8.048	15.848	31,590	Mw	30,044
Peak end	10.002	1.000	1,718	Mz	44,573
				Mz+1	57,169
				Mv	30,044
Height [mV]			15.471	Mp	31,590
Area [mV*sec]			1203.522	Mz/Mw	1.484
Area% [%]			100.000	Mw/Mn	1.830
[eta]			30044.05312	Mz+1/Mw	1.903

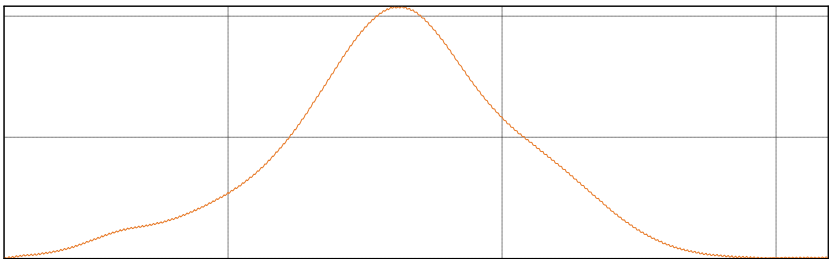
Result of molecular weight calculation (RI)

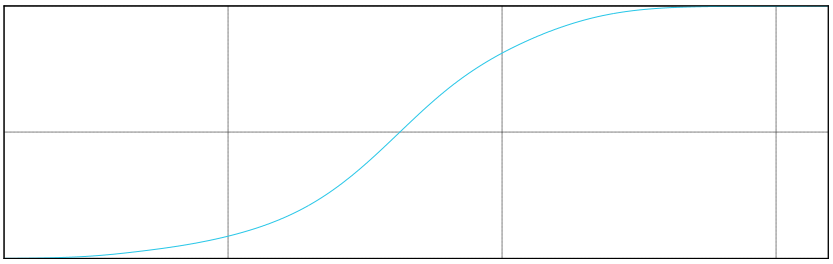
Total

	[min]	[mV]	[mol]		
Peak start	7.078	0.068	134,085	Mn	16,418
Peak top	8.048	15.848	31,590	Mw	30,044
Peak end	10.002	1.000	1,718	Mz	44,573
				Mz+1	57,169
				Mv	30,044
Height [mV]			15.471	Mp	31,590
Area [mV*sec]			1203.522	Mz/Mw	1.484
Area% [%]			100.000	Mw/Mn	1.830
[eta]			30044.05312	Mz+1/Mw	1.903

Figure S88. GPC of the polymer from table 1, entry 10.







Result of molecular weight calculation (RI)

Peak 1 Base Peak

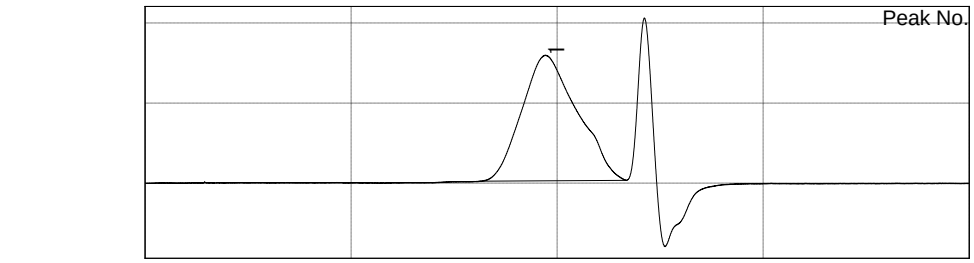
	[min]	[mV]	[mol]		
Peak start	7.003	0.203	154,886	Mn	2,399
Peak top	9.390	16.746	4,306	Mw	6,632
Peak end	11.617	0.324	152	Mz	15,778
				Mz+1	34,744
				Mv	6,632
Height [mV]			16.480	Mp	4,307
Area [mV*sec]			1457.361	Mz/Mw	2.379
Area% [%]			100.000	Mw/Mn	2.765
[eta]			6632.04971	Mz+1/Mw	5.239

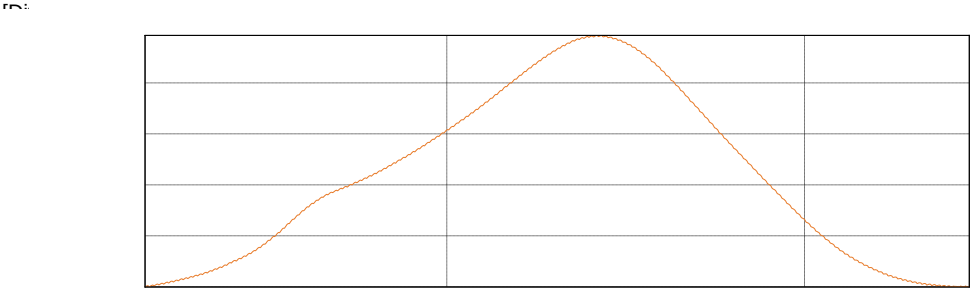
Result of molecular weight calculation (RI)

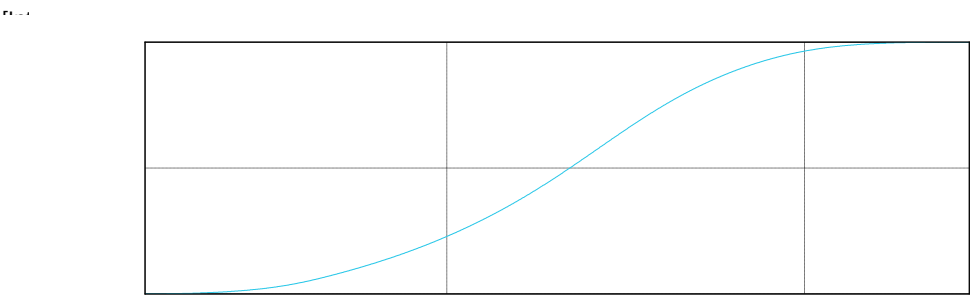
Total

	[min]	[mV]	[mol]		
Peak start	7.003	0.203	154,886	Mn	2,399
Peak top	9.390	16.746	4,306	Mw	6,632
Peak end	11.617	0.324	152	Mz	15,778
				Mz+1	34,744
				Mv	6,632
Height [mV]			16.480	Mp	4,307
Area [mV*sec]			1457.361	Mz/Mw	2.379
Area% [%]			100.000	Mw/Mn	2.765
[eta]			6632.04971	Mz+1/Mw	5.239

Figure S89. GPC of the polymer from table 1, entry 11.







Result of molecular weight calculation (RI)

Peak 1 Base Peak

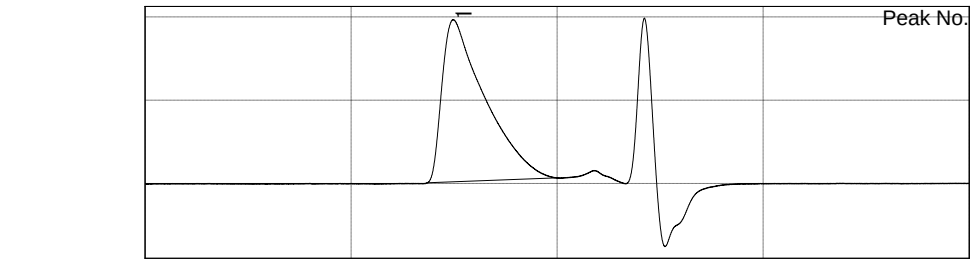
	[min]	[mV]	[mol]		
Peak start	8.120	0.249	28,860	Mn	1,331
Peak top	9.720	15.990	2,627	Mw	3,079
Peak end	11.662	0.351	143	Mz	5,778
				Mz+1	8,776
				Mv	3,079
Height [mV]			15.695	Mp	2,628
Area [mV*sec]			1468.270	Mz/Mw	1.876
Area% [%]			100.000	Mw/Mn	2.314
[eta]			3079.47790	Mz+1/Mw	2.850

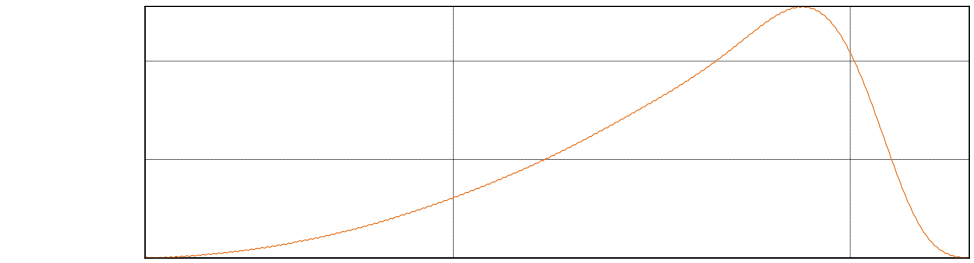
Result of molecular weight calculation (RI)

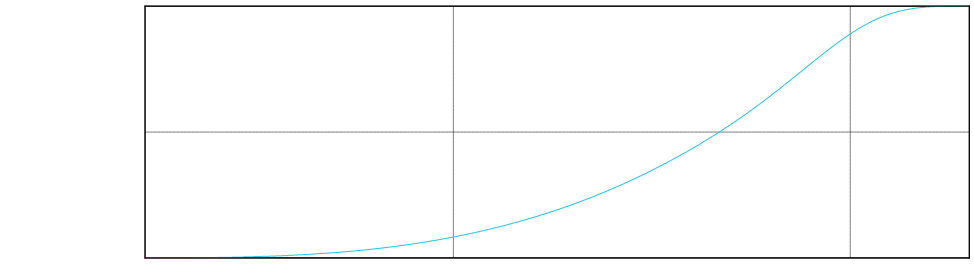
Total

	[min]	[mV]	[mol]		
Peak start	8.120	0.249	28,860	Mn	1,331
Peak top	9.720	15.990	2,627	Mw	3,079
Peak end	11.662	0.351	143	Mz	5,778
				Mz+1	8,776
				Mv	3,079
Height [mV]			15.695	Mp	2,628
Area [mV*sec]			1468.270	Mz/Mw	1.876
Area% [%]			100.000	Mw/Mn	2.314
[eta]			3079.47790	Mz+1/Mw	2.850

Figure S90. GPC of the polymer from table 1, entry 12.







Result of molecular weight calculation (RI)

Peak 1 Base Peak

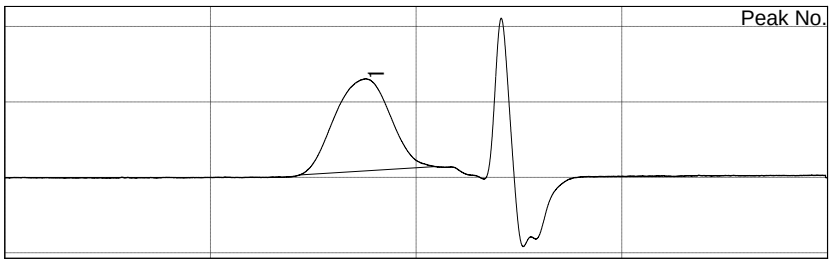
	[min]	[mV]	[mol]		
Peak start	6.830	0.086	199,255	Mn	25,456
Peak top	7.473	19.687	76,022	Mw	52,450
Peak end	10.022	0.677	1,672	Mz	75,588
				Mz+1	91,441
				Mv	52,450
Height [mV]			19.482	Mp	76,022
Area [mV*sec]			1406.282	Mz/Mw	1.441
Area% [%]			100.000	Mw/Mn	2.060
[eta]			52449.57864	Mz+1/Mw	1.743

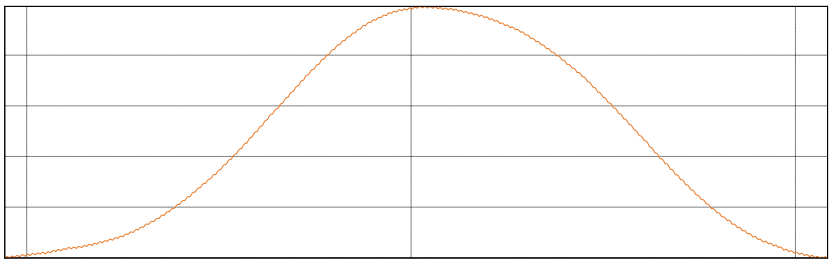
Result of molecular weight calculation (RI)

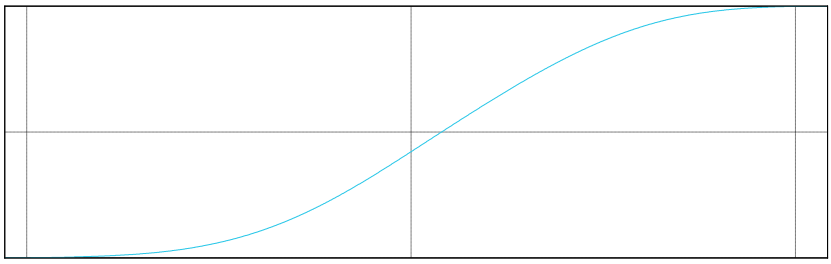
Total

	[min]	[mV]	[mol]		
Peak start	6.830	0.086	199,255	Mn	25,456
Peak top	7.473	19.687	76,022	Mw	52,450
Peak end	10.022	0.677	1,672	Mz	75,588
				Mz+1	91,441
				Mv	52,450
Height [mV]			19.482	Mp	76,022
Area [mV*sec]			1406.282	Mz/Mw	1.441
Area% [%]			100.000	Mw/Mn	2.060
[eta]			52449.57864	Mz+1/Mw	1.743

Figure S91. GPC of the polymer from table 1, entry 13.







Result of molecular weight calculation (RI)

Peak 1 Base Peak

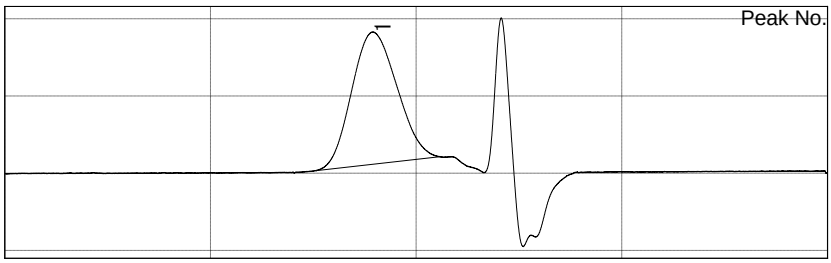
	[min]	[mV]	[mol]		
Peak start	7.147	0.312	121,102	Mn	8,352
Peak top	8.765	13.089	10,856	Mw	16,855
Peak end	10.453	1.425	876	Mz	29,906
				Mz+1	43,908
				Mv	16,855
Height [mV]			12.232	Mp	10,512
Area [mV*sec]			1143.026	Mz/Mw	1.774
Area% [%]			100.000	Mw/Mn	2.018
[eta]			16855.27798	Mz+1/Mw	2.605

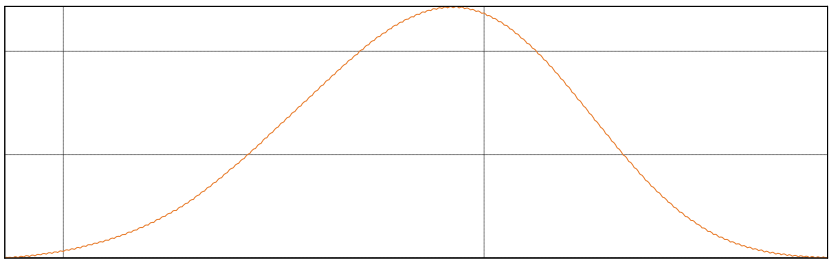
Result of molecular weight calculation (RI)

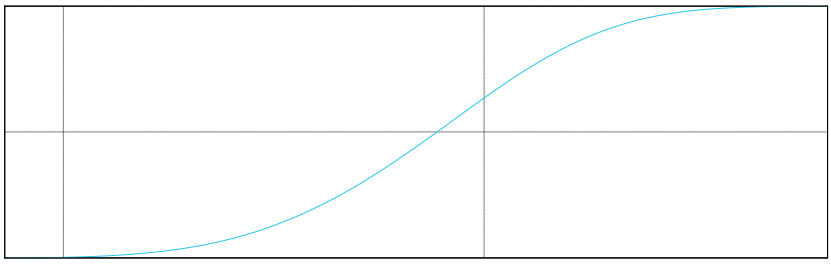
Total

	[min]	[mV]	[mol]		
Peak start	7.147	0.312	121,102	Mn	8,352
Peak top	8.765	13.089	10,856	Mw	16,855
Peak end	10.453	1.425	876	Mz	29,906
				Mz+1	43,908
				Mv	16,855
Height [mV]			12.232	Mp	10,512
Area [mV*sec]			1143.026	Mz/Mw	1.774
Area% [%]			100.000	Mw/Mn	2.018
[eta]			16855.27798	Mz+1/Mw	2.605

Figure S92. GPC of the polymer from table 1, entry 14.







Result of molecular weight calculation (RI)

Peak 1 Base Peak

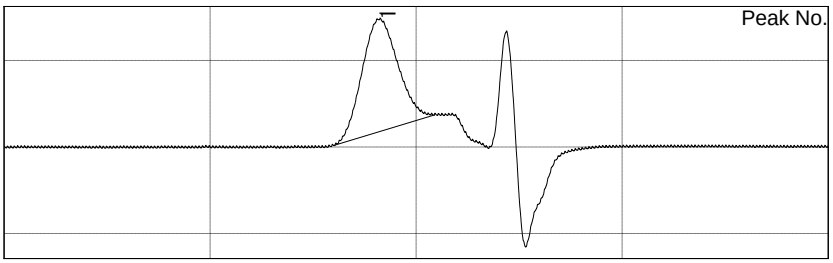
	[min]	[mV]	[mol]		
Peak start	7.560	0.322	65,407	Mn	5,706
Peak top	8.923	18.302	8,574	Mw	9,657
Peak end	10.580	2.143	726	Mz	14,999
				Mz+1	21,062
				Mv	9,657
Height [mV]			17.158	Mp	8,575
Area [mV*sec]			1306.359	Mz/Mw	1.553
Area% [%]			100.000	Mw/Mn	1.692
[eta]			9657.00982	Mz+1/Mw	2.181

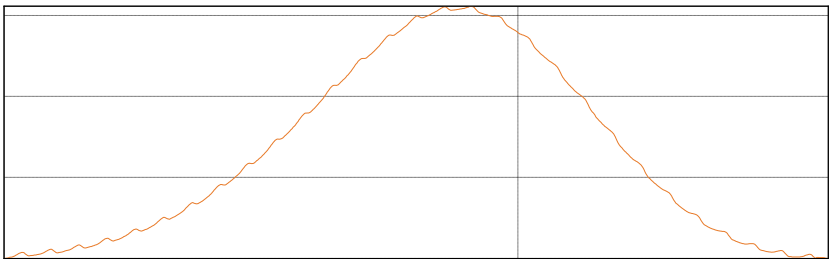
Result of molecular weight calculation (RI)

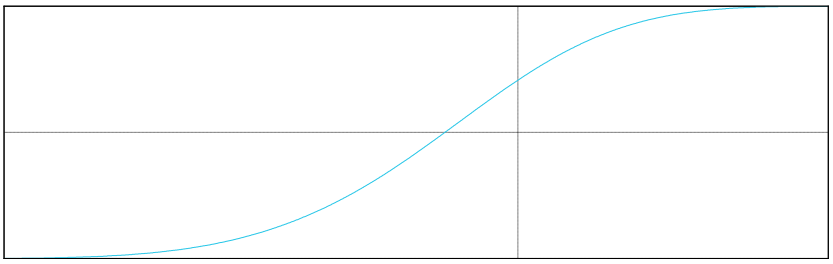
Total

	[min]	[mV]	[mol]		
Peak start	7.560	0.322	65,407	Mn	5,706
Peak top	8.923	18.302	8,574	Mw	9,657
Peak end	10.580	2.143	726	Mz	14,999
				Mz+1	21,062
				Mv	9,657
Height [mV]			17.158	Mp	8,575
Area [mV*sec]			1306.359	Mz/Mw	1.553
Area% [%]			100.000	Mw/Mn	1.692
[eta]			9657.00982	Mz+1/Mw	2.181

Figure S93. GPC of the polymer from table 1, entry 15.







Result of molecular weight calculation (RI)

Peak 1 Base Peak

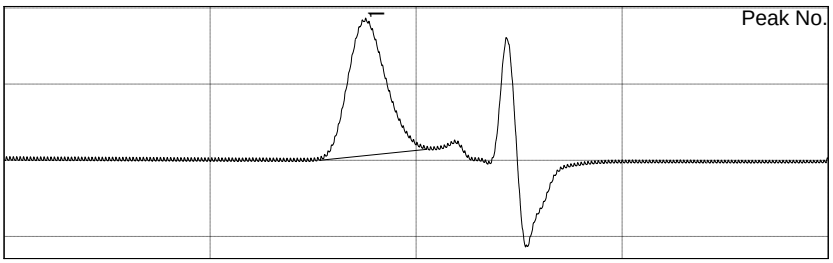
	[min]	[mV]	[mol]		
Peak start	7.995	0.177	38,427	Mn	5,941
Peak top	9.048	14.827	8,165	Mw	8,367
Peak end	10.427	3.677	1,075	Mz	11,225
				Mz+1	14,279
				Mv	8,367
Height [mV]			13.134	Mp	8,165
Area [mV*sec]			792.664	Mz/Mw	1.342
Area% [%]			100.000	Mw/Mn	1.408
[eta]			8366.60230	Mz+1/Mw	1.707

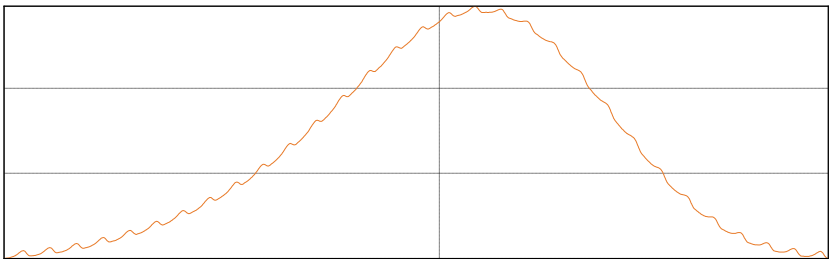
Result of molecular weight calculation (RI)

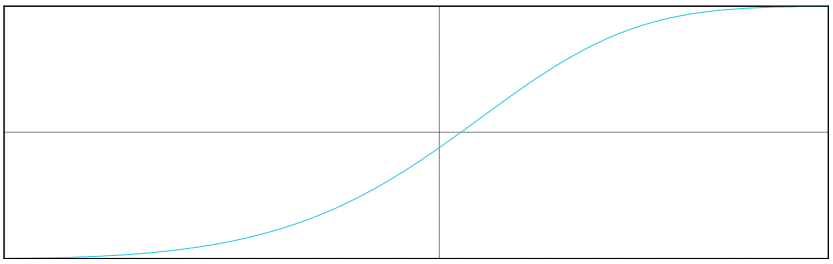
Total

	[min]	[mV]	[mol]		
Peak start	7.995	0.177	38,427	Mn	5,941
Peak top	9.048	14.827	8,165	Mw	8,367
Peak end	10.427	3.677	1,075	Mz	11,225
				Mz+1	14,279
				Mv	8,367
Height [mV]			13.134	Mp	8,165
Area [mV*sec]			792.664	Mz/Mw	1.342
Area% [%]			100.000	Mw/Mn	1.408
[eta]			8366.60230	Mz+1/Mw	1.707

Figure S94. GPC of the polymer from table 3, entry 1.







Result of molecular weight calculation (RI)

Peak 1 Base Peak

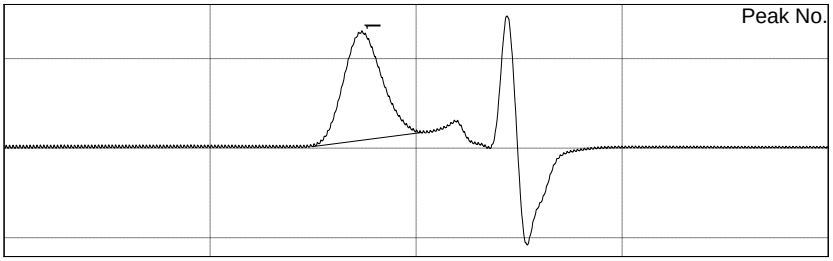
	[min]	[mV]	[mol]		
Peak start	7.670	0.020	59,057	Mn	8,585
Peak top	8.773	18.681	11,761	Mw	12,777
Peak end	10.243	1.438	1,369	Mz	17,677
				Mz+1	22,907
				Mv	12,777
Height [mV]			18.053	Mp	11,761
Area [mV*sec]			1150.451	Mz/Mw	1.384
Area% [%]			100.000	Mw/Mn	1.488
[eta]			12776.88391	Mz+1/Mw	1.793

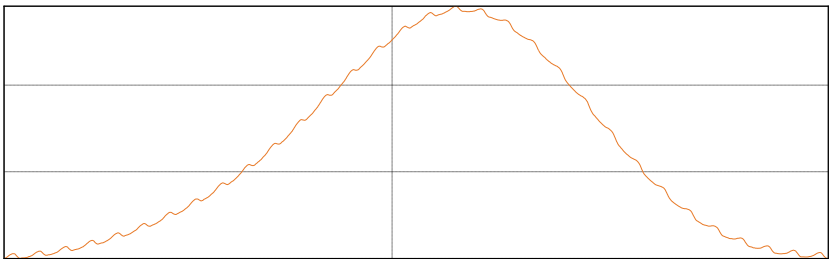
Result of molecular weight calculation (RI)

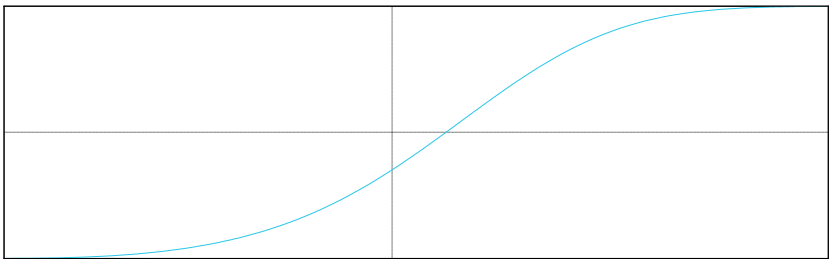
Total

	[min]	[mV]	[mol]		
Peak start	7.670	0.020	59,057	Mn	8,585
Peak top	8.773	18.681	11,761	Mw	12,777
Peak end	10.243	1.438	1,369	Mz	17,677
				Mz+1	22,907
				Mv	12,777
Height [mV]			18.053	Mp	11,761
Area [mV*sec]			1150.451	Mz/Mw	1.384
Area% [%]			100.000	Mw/Mn	1.488
[eta]			12776.88391	Mz+1/Mw	1.793

Figure S95. GPC of the polymer from table 3, entry 2.







Result of molecular weight calculation (RI)

Peak 1 Base Peak

	[min]	[mV]	[mol]		
Peak start	7.493	0.189	76,469	Mn	10,116
Peak top	8.680	13.116	13,481	Mw	15,112
Peak end	10.122	1.750	1,636	Mz	21,285
				Mz+1	28,192
				Mv	15,112
Height [mV]			12.222	Mp	13,448
Area [mV*sec]			792.958	Mz/Mw	1.409
Area% [%]			100.000	Mw/Mn	1.494
[eta]			15112.06837	Mz+1/Mw	1.866

Result of molecular weight calculation (RI)

Total

	[min]	[mV]	[mol]		
Peak start	7.493	0.189	76,469	Mn	10,116
Peak top	8.680	13.116	13,481	Mw	15,112
Peak end	10.122	1.750	1,636	Mz	21,285
				Mz+1	28,192
				Mv	15,112
Height [mV]			12.222	Mp	13,448
Area [mV*sec]			792.958	Mz/Mw	1.409
Area% [%]			100.000	Mw/Mn	1.494
[eta]			15112.06837	Mz+1/Mw	1.866

Figure S96. GPC of the polymer from table 3, entry 4.

Cirrus GPC Sample Peak Report

Sample Details

Acquired: 2023/6/1 19:30:06

Batch Name: 20230601

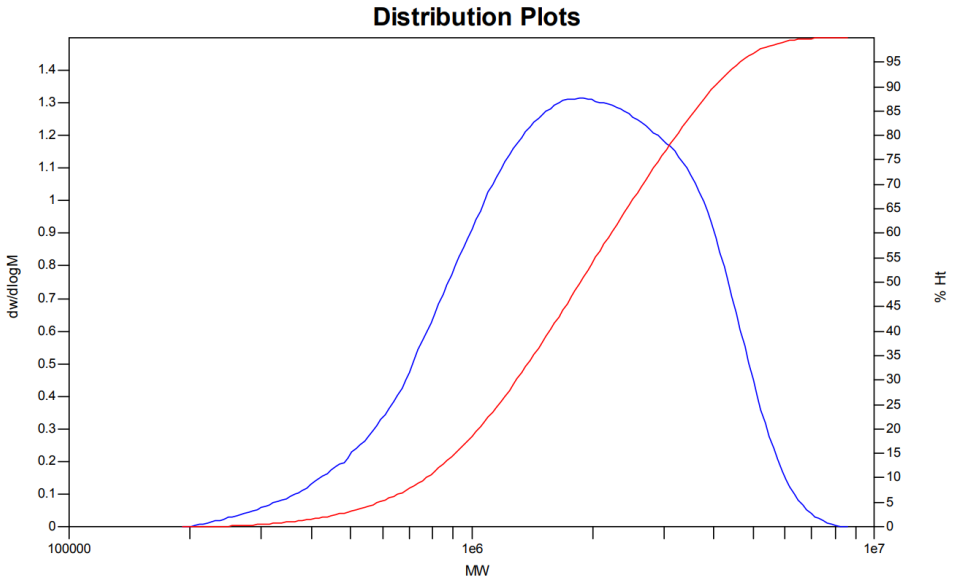
Filename: E:\Cirrus Workbooks\JC\20230601-0013.cgrm

Concentration: 0.10 mg/ml

Injection Volume: 200.0 ul LIMS ID:

MW Averages

Mp: 1852389	Mn: 1431658	Mv: 2026924	Mw: 2134794
Mz: 2883372	Mz+1: 3552334	PD: 1.4911	



Sample Peak Report

MW Ranges

Range No	High Limit	Low Limit	%Area
1	8612253	191450	100.000

Figure S97. GPC of the polymer from table 4, entry 1.

Cirrus GPC Sample Peak Report

Sample Details

Acquired: 2023/6/1 15:44:01

Batch Name: 20230601

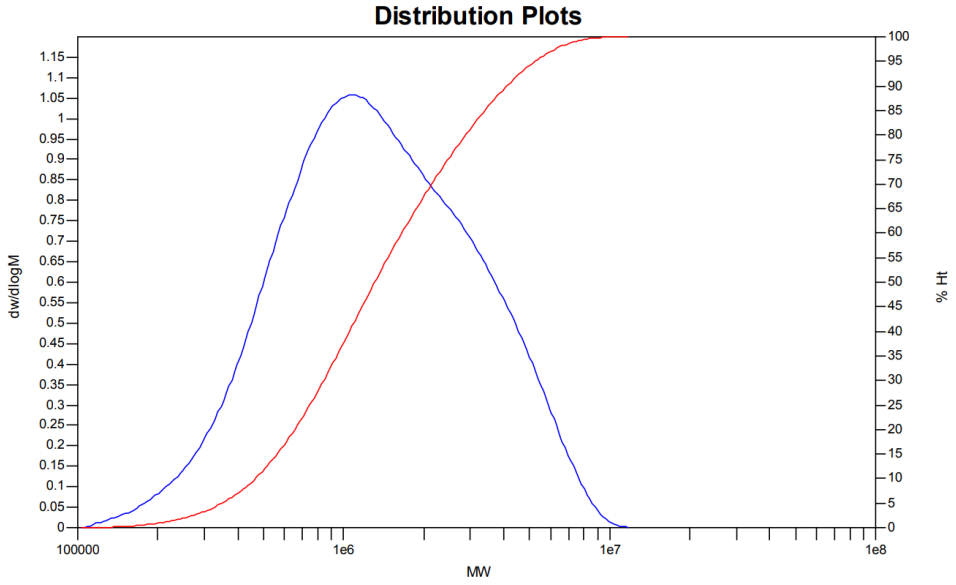
Filename: E:\Cirrus Workbooks\JC\20230601-0008.cgrm

Concentration: 0.10 mg/ml

Injection Volume: 200.0 ul LIMS ID:

MW Averages

Mp: 1075426	Mn: 947234	Mv: 1672383	Mw: 1837448
Mz: 3171400	Mz+1: 4496942	PD: 1.9398	



Sample Peak Report

MW Ranges

Range No	High Limit	Low Limit	%Area
1	11710992	103538	100.000

Figure S98. GPC of the polymer from table 4, entry 2.

Cirrus GPC Sample Peak Report

Sample Details

Acquired: 2023/6/1 15:02:55

Batch Name: 20230601

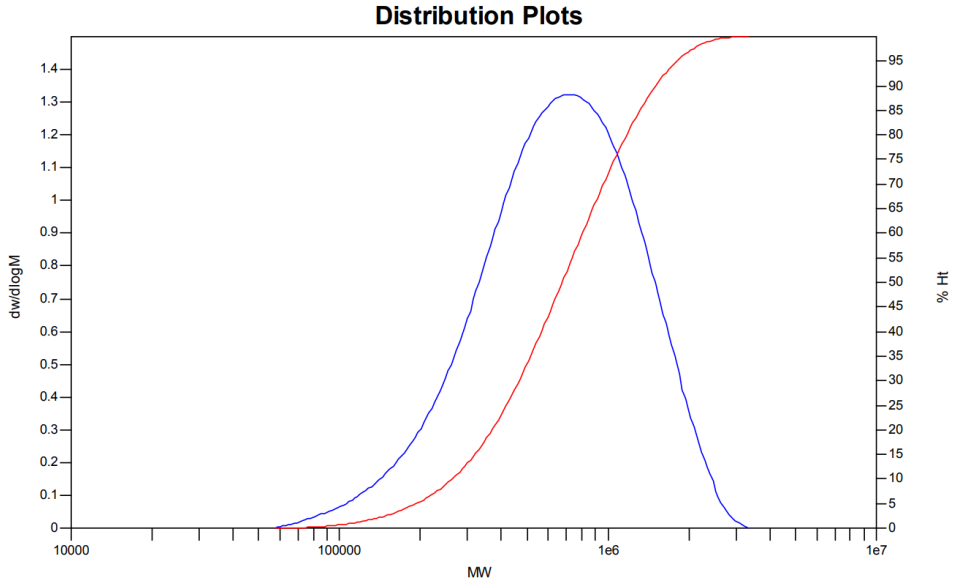
Filename: E:\Cirrus Workbooks\JC\20230601-0007.cgrm

Concentration: 0.10 mg/ml

Injection Volume: 200.0 ul LIMS ID:

MW Averages

Mp: 719505	Mn: 498967	Mv: 741361	Mw: 785604
Mz: 1101029	Mz+1: 1399359	PD: 1.5745	



MW Ranges

Range No	High Limit	Low Limit	%Area
1	3345173	57334	100.000

Figure S99. GPC of the polymer from table 4, entry 3.

Cirrus GPC Sample Peak Report

Sample Details

Acquired: 2023/6/1 14:21:52

Batch Name: 20230601

Filename: E:\Cirrus Workbooks\JC\20230601-0006.cgrm

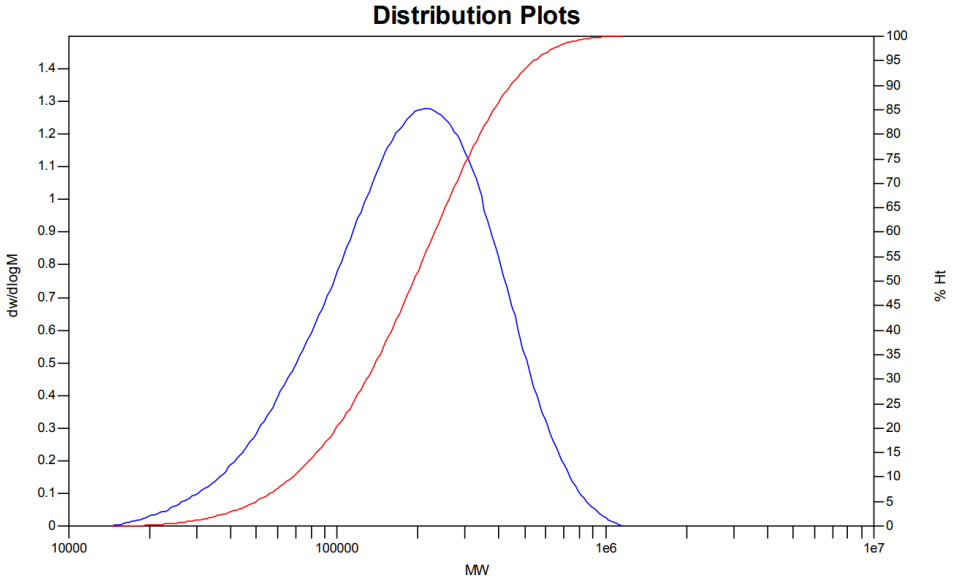
Concentration: 0.10 mg/ml

Injection Volume: 200.0 ul LIMS ID:

MW Averages

Mp: 215473	Mn: 135327	Mv: 212856	Mw: 227386
Mz: 334198	Mz+1: 441881	PD: 1.6803	

Distribution Plots



Sample Peak Report

MW Ranges

Range No	High Limit	Low Limit	%Area
1	1154471	50000	94.921
2	50000	40000	2.208
3	40000	30000	1.661
4	30000	20000	1.040
5	20000	14551	0.171

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

Cirrus GPC Sample Peak Report

Sample Details

Acquired: 2023/4/19 11:17:08

Batch Name: 20230419

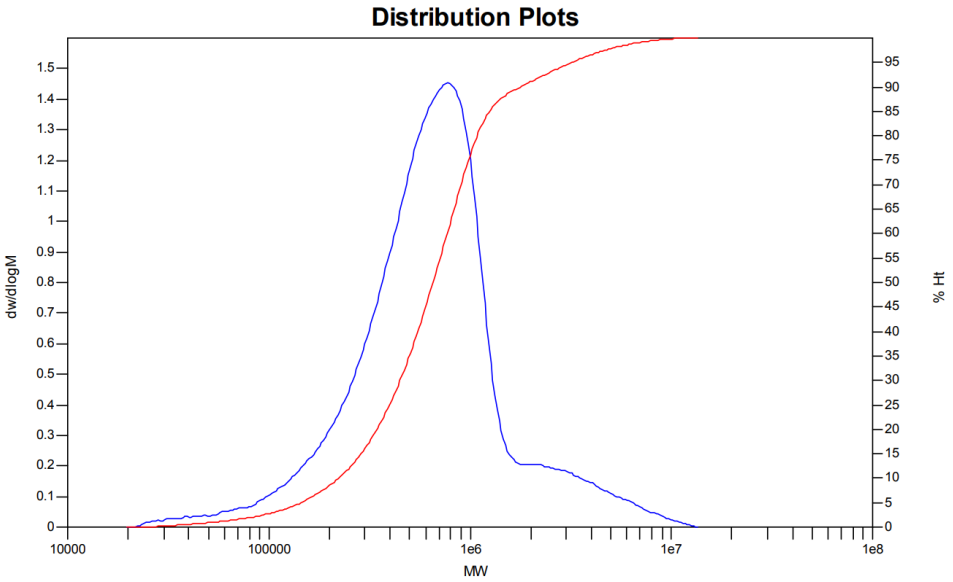
Filename: E:\Cirrus Workbooks\JC\20230419-0003.cgrm

Concentration: 0.10 mg/ml

Injection Volume: 200.0 ul LIMS ID:

MW Averages

Mp: 772389	Mn: 408859	Mv: 830305	Mw: 947114
Mz: 2423106	Mz+1: 5026942	PD: 2.3165	



Sample Peak Report

MW Ranges

Range No	High Limit	Low Limit	%Area
1	13495793	50000	99.099
2	50000	40000	0.346
3	40000	30000	0.356
4	30000	20000	0.192
5	20000	19787	0.008

Figure S101. GPC of the polymer from table 4, entry 6.

Cirrus GPC Sample Peak Report

Sample Details

Acquired: 2023/4/19 10:39:16

Batch Name: 20230419

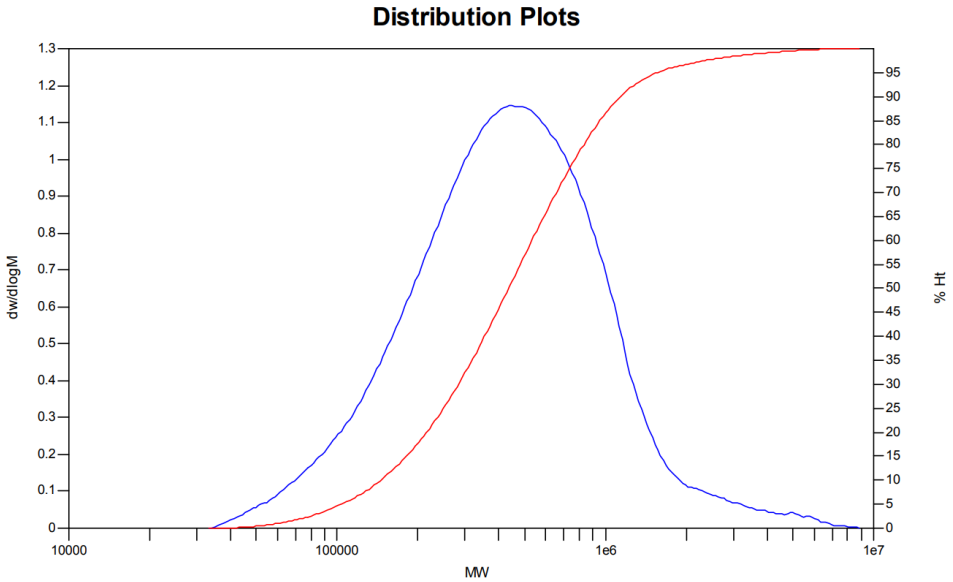
Filename: E:\Cirrus Workbooks\JC\20230419-0002.cgrm

Concentration: 0.10 mg/ml

Injection Volume: 200.0 ul LIMS ID:

MW Averages

Mp: 437942	Mn: 299203	Mv: 538601	Mw: 601271
Mz: 1323979	Mz+1: 2820311	PD: 2.0096	



MW Ranges

Range No	High Limit	Low Limit	%Area
1	8818287	50000	99.572
2	50000	40000	0.365
3	40000	33286	0.062

Figure S102. GPC of the polymer from table 4, entry 7.

Cirrus GPC Sample Peak Report

Sample Details

Acquired: 2023/4/19 13:48:38

Batch Name: 20230419

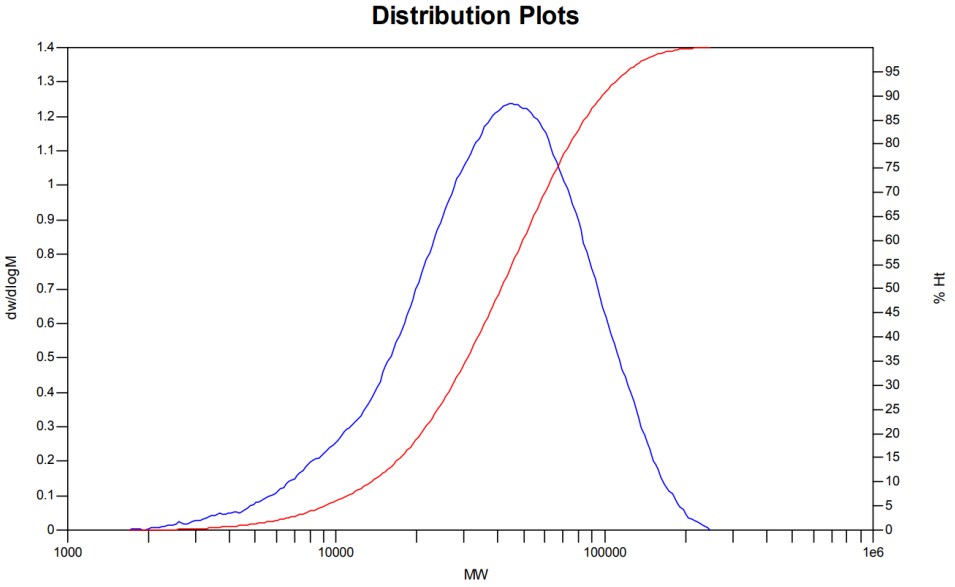
Filename: E:\Cirrus Workbooks\JC\20230419-0007.cgrm

Concentration: 0.10 mg/ml

Injection Volume: 200.0 ul LIMS ID:

MW Averages

Mp: 44205	Mn: 26677	Mv: 45715	Mw: 49120
Mz: 73918	Mz+1: 98133	PD: 1.8413	



MW Ranges

Range No	High Limit	Low Limit	%Area
1	248312	50000	39.432
2	50000	40000	11.912
3	40000	30000	14.231
4	30000	20000	15.517
5	20000	10000	12.925
6	10000	1692	5.984

Figure S103. GPC of the polymer from table 4, entry 8.

Cirrus GPC Sample Peak Report

Sample Details

Acquired: 2023/6/1 16:25:04

Batch Name: 20230601

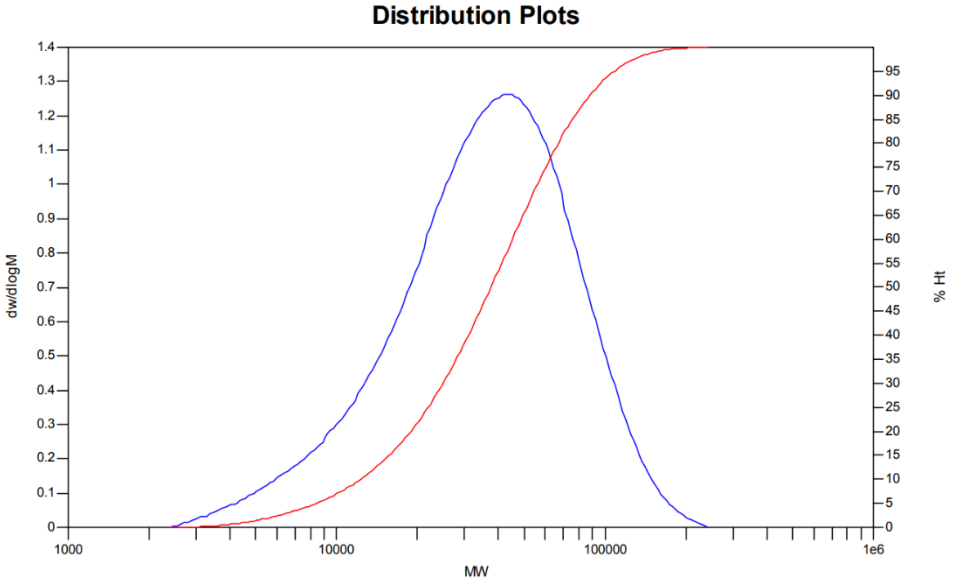
Filename: E:\Cirrus Workbooks\JC\20230601-0009.cgrm

Concentration: 0.10 mg/ml

Injection Volume: 200.0 ul LIMS ID:

MW Averages

Mp: 44205	Mn: 24832	Mv: 41578	Mw: 44627
Mz: 66995	Mz+1: 89649	PD: 1.7972	



Sample Peak Report

MW Ranges

Range No	High Limit	Low Limit	%Area
1	242510	50000	34.527
2	50000	40000	12.161
3	40000	30000	14.930
4	30000	20000	16.601
5	20000	10000	14.797
6	10000	2413	6.985

Figure S104. GPC of the polymer from table 4, entry 9.

Cirrus GPC Sample Peak Report

Sample Details

Acquired: 2023/4/19 13:10:46

Batch Name: 20230419

Filename: E:\Cirrus Workbooks\JC\20230419-0006.cgrm

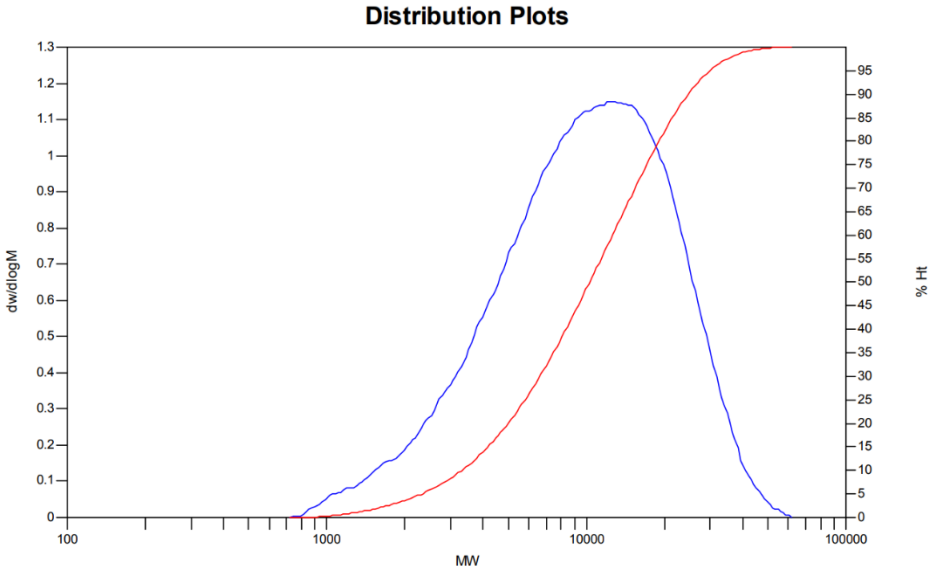
Concentration: 0.10 mg/ml

Injection Volume: 200.0 ul LIMS ID:

MW Averages

Mp: 12331	Mn: 6787	Mv: 11469	Mw: 12332
Mz: 18517	Mz+1: 24249	PD: 1.8170	

Distribution Plots



Sample Peak Report

MW Ranges

Range No	High Limit	Low Limit	%Area
1	61548	50000	0.186
2	50000	40000	0.890
3	40000	30000	3.872
4	30000	20000	12.926
5	20000	10000	33.478
6	10000	722	48.648

Figure S105. GPC of the polymer from table 4, entry 10.

Cirrus GPC Sample Peak Report

Sample Details

Acquired: 2023/6/14 18:09:23

Batch Name: 20230614

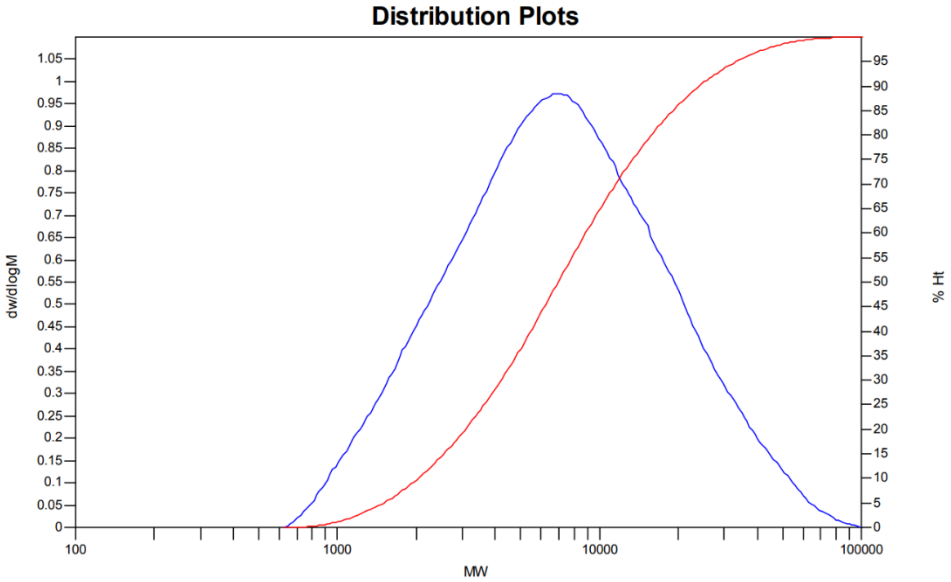
Filename: E:\Cirrus Workbooks\JC\20230614-0011.cgrm

Concentration: 0.10 mg/ml

Injection Volume: 200.0 ul LIMS ID:

MW Averages

Mp: 6828	Mn: 4587	Mv: 9320	Mw: 10536
Mz: 21736	Mz+1: 35063	PD: 2.2969	



Sample Peak Report

MW Ranges

Range No	High Limit	Low Limit	%Area
1	101119	50000	1.450
2	50000	40000	1.620
3	40000	30000	3.302
4	30000	20000	7.469
5	20000	10000	21.395
6	10000	627	64.763

Figure S106. GPC of the polymer from table 4, entry 11.

Cirrus GPC Sample Peak Report

Sample Details

Acquired: 2023/4/12 12:49:29

Batch Name: 20230412

Filename: E:\Cirrus Workbooks\JC\20230412-0005.cgrm

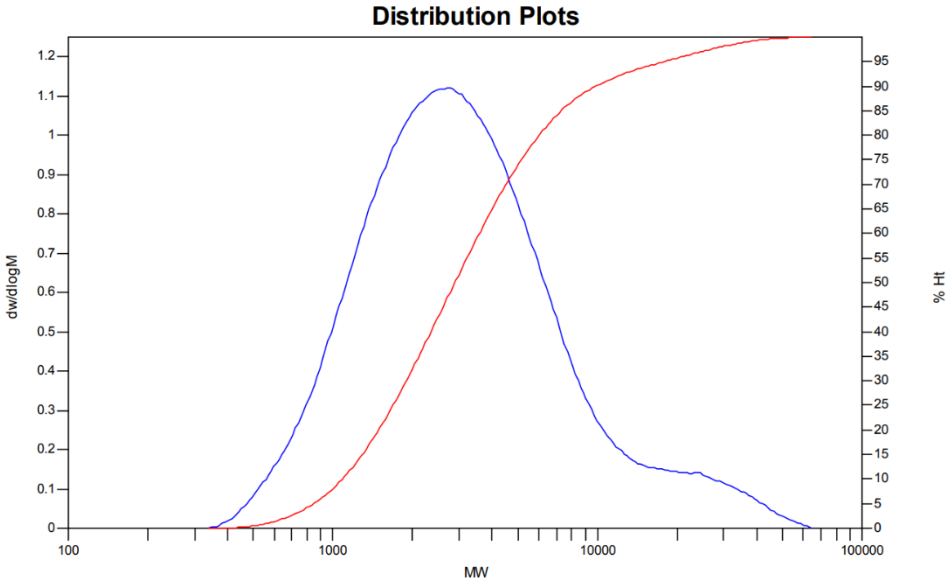
Concentration: 0.10 mg/ml

Injection Volume: 200.0 ul LIMS ID:

MW Averages

Mp: 2780	Mn: 2210	Mv: 4201	Mw: 4887
Mz: 13587	Mz+1: 26704	PD: 2.2113	

Distribution Plots

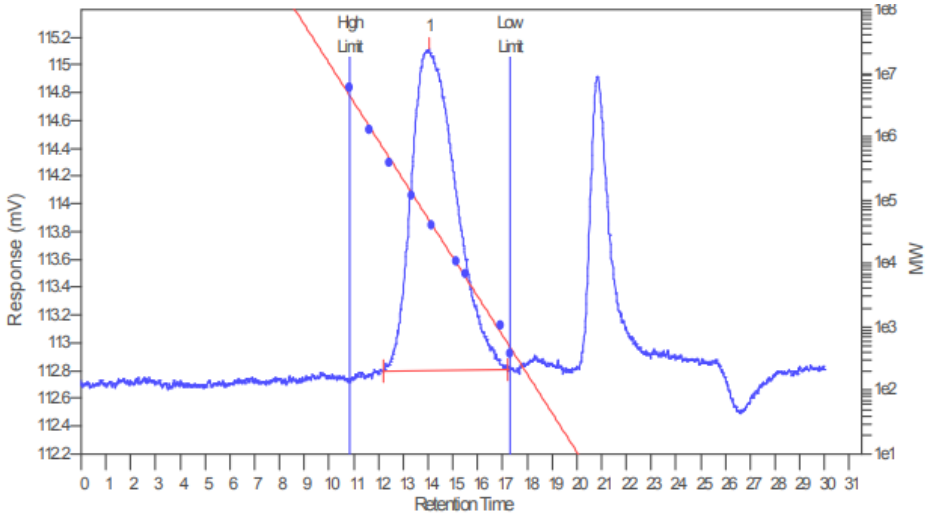


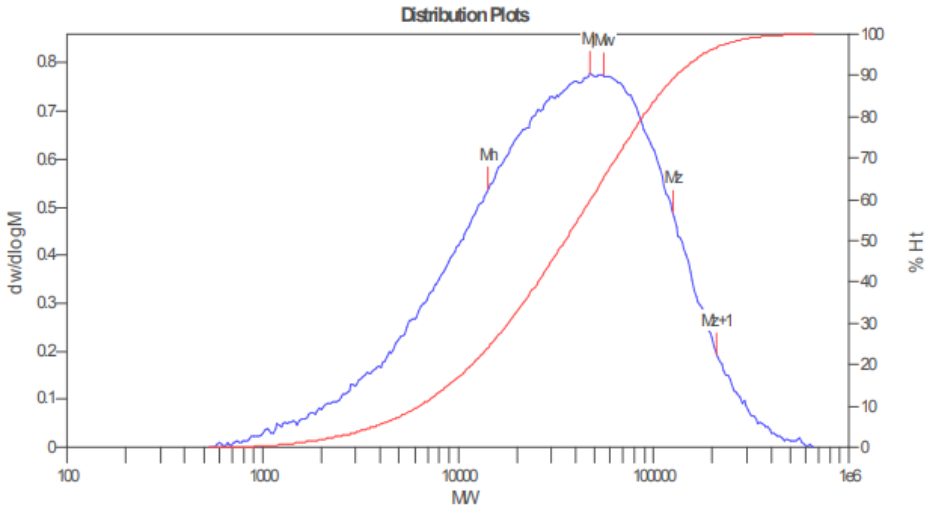
Sample Peak Report

MW Ranges

Range No	High Limit	Low Limit	%Area
1	64528	50000	0.178
2	50000	40000	0.497
3	40000	30000	1.210
4	30000	20000	2.364
5	20000	10000	5.520
6	10000	339	90.230

Figure S107. GPC of the polymer from table 4, entry 12.





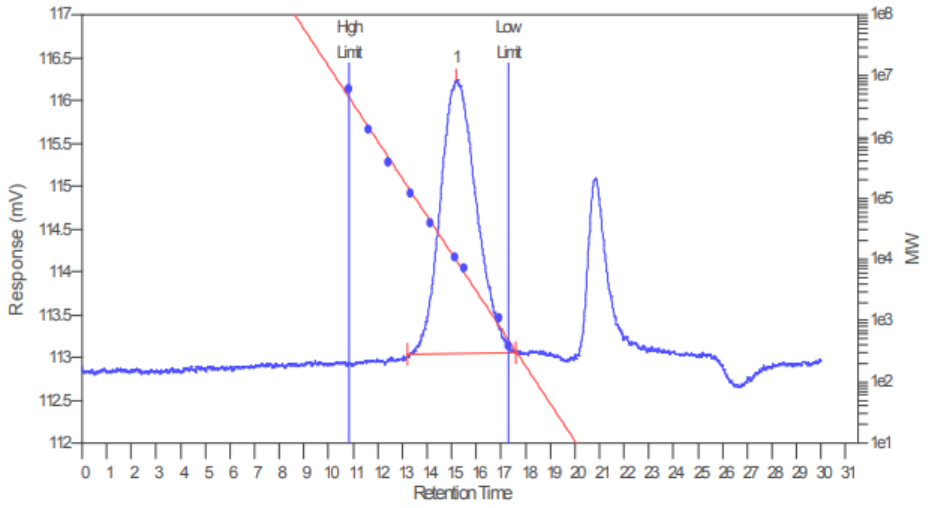
MW Averages

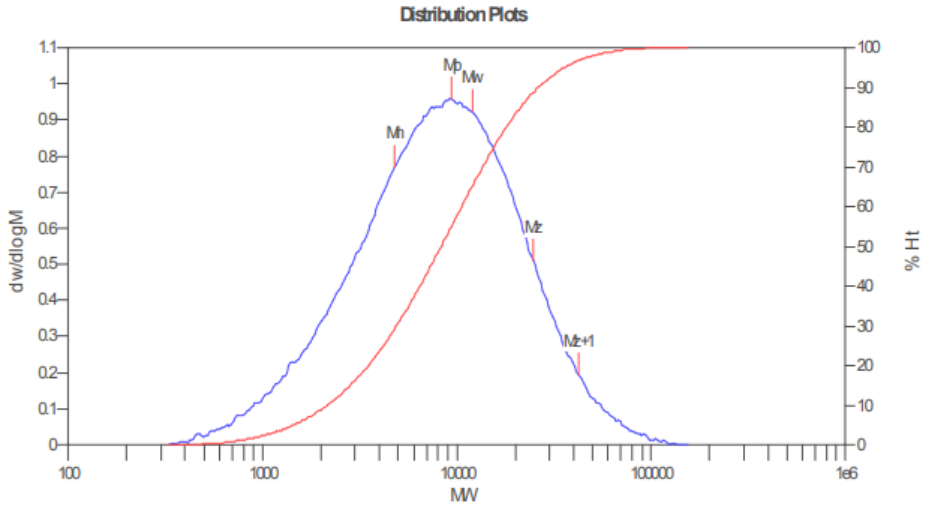
Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	47586	14305	55572	125868	211353	47757	3.8848

Processed Peaks

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1		12.18	14.05	17.23	2.31983	0	291.554	100

Figure S108. GPC of the polymer from table 4, entry 13.





MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	9402	4783	12014	24795	42367	10637	2.51181

Processed Peaks

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1		13.22	15.20	17.58	3.20768	0	327.954	100

Figure S109. GPC of the polymer from table 4, entry 14.

Cirrus GPC Sample Peak Report

Sample Details

Acquired: 2023/4/12 13:27:21

Batch Name: 20230412

Filename: E:\Cirrus Workbooks\JC\20230412-0006.cgrm

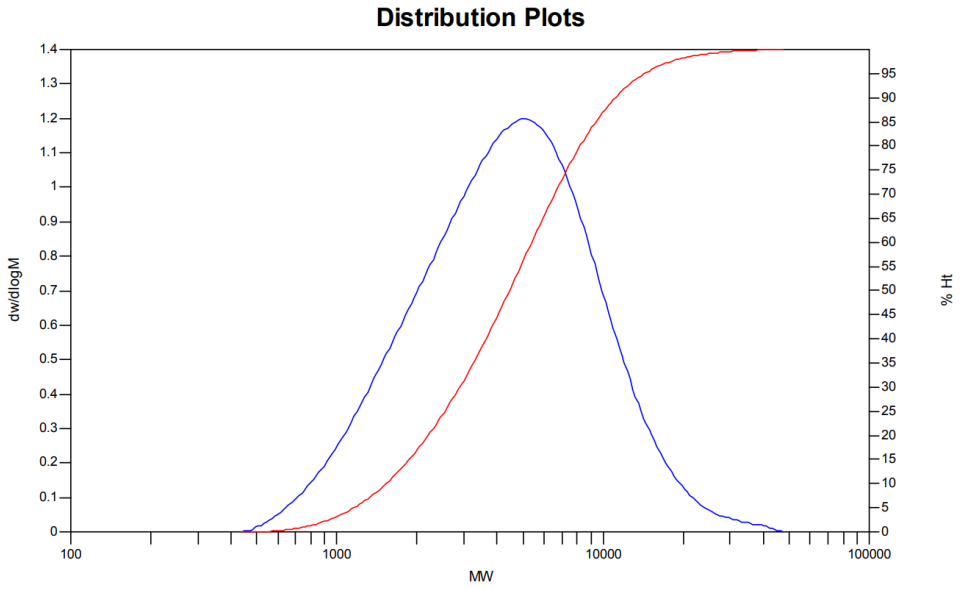
Concentration: 0.10 mg/ml

Injection Volume: 200.0 ul LIMS ID:

MW Averages

Mp: 5021	Mn: 3162	Mv: 5168	Mw: 5610
Mz: 9428	Mz+1: 14793	PD: 1.7742	

Distribution Plots



Sample Peak Report

MW Ranges

Range No	High Limit	Low Limit	%Area
1	47454	40000	0.074
2	40000	30000	0.357
3	30000	20000	1.327
4	20000	10000	11.191
5	10000	439	87.052

Figure S110. GPC of the polymer from table 4, entry 15.

Cirrus GPC Sample Peak Report

Sample Details

Acquired: 2023/6/1 18:49:03

Batch Name: 20230601

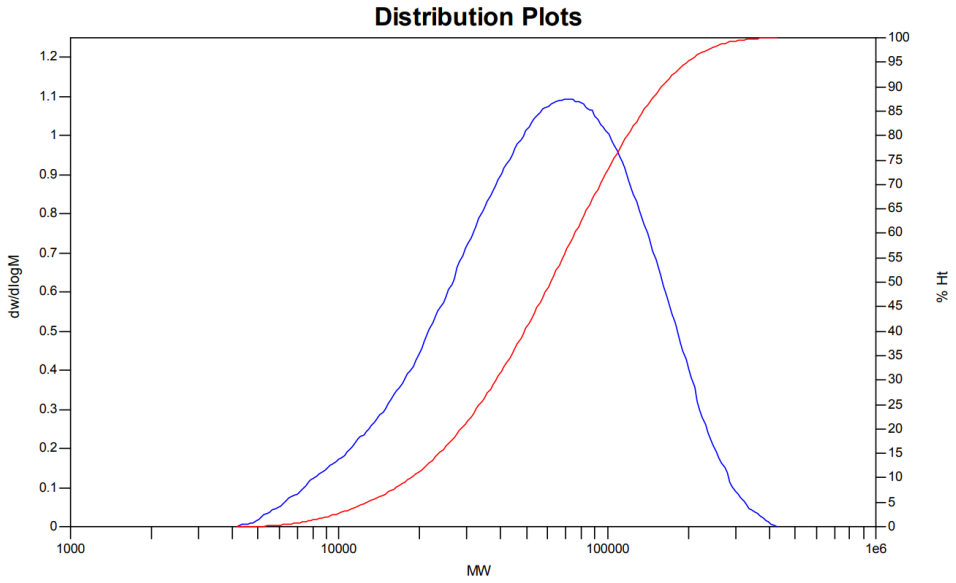
Filename: E:\Cirrus Workbooks\JC\20230601-0012.cgrm

Concentration: 0.10 mg/ml

Injection Volume: 200.0 ul LIMS ID:

MW Averages

Mp: 70928	Mn: 39408	Mv: 70548	Mw: 76640
Mz: 122170	Mz+1: 166295	PD: 1.9448	



Sample Peak Report

MW Ranges

Range No	High Limit	Low Limit	%Area
1	427710	50000	59.264
2	50000	40000	9.220
3	40000	30000	10.036
4	30000	20000	10.075
5	20000	10000	8.650
6	10000	4156	2.755

Figure S111. GPC of the polymer from table 5, entry 1.

Cirrus GPC Sample Peak Report

Sample Details

Acquired: 2023/6/14 13:21:48

Batch Name: 20230614

Filename: E:\Cirrus Workbooks\JC\20230614-0004.cgrm

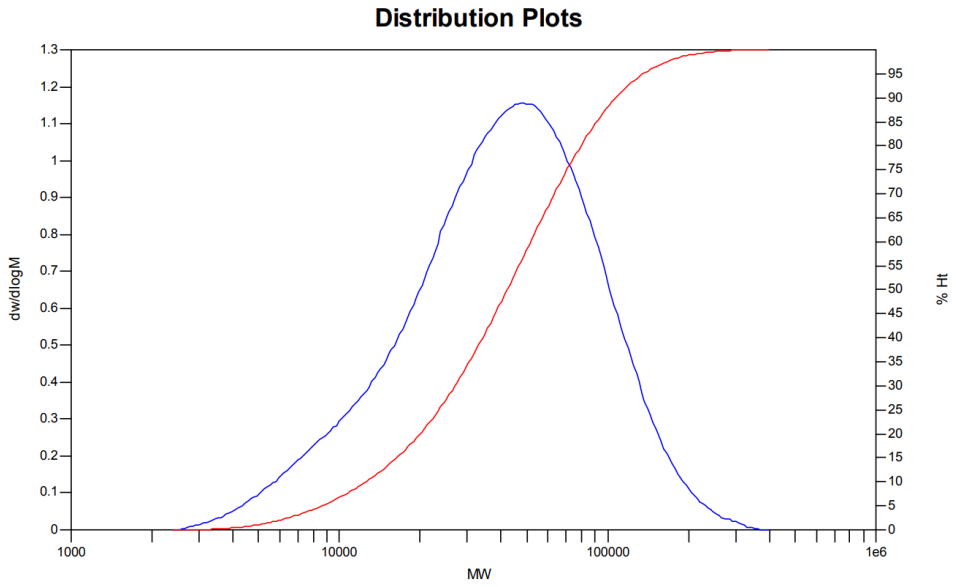
Concentration: 0.10 mg/ml

Injection Volume: 200.0 ul LIMS ID:

MW Averages

Mp: 48589	Mn: 26786	Mv: 48355	Mw: 52602
Mz: 85797	Mz+1: 122998	PD: 1.9638	

Distribution Plots



Sample Peak Report

MW Ranges

Range No	High Limit	Low Limit	%Area
1	398426	50000	41.534
2	50000	40000	11.072
3	40000	30000	13.111
4	30000	20000	14.234
5	20000	10000	13.268
6	10000	2413	6.781

Figure S112. GPC of the polymer from table 5, entry 2.

Cirrus GPC Sample Peak Report

Sample Details

Acquired: 2023/5/27 14:28:17

Batch Name: 20230527

Filename: E:\Cirrus Workbooks\JC\20230527-0007.cgrm

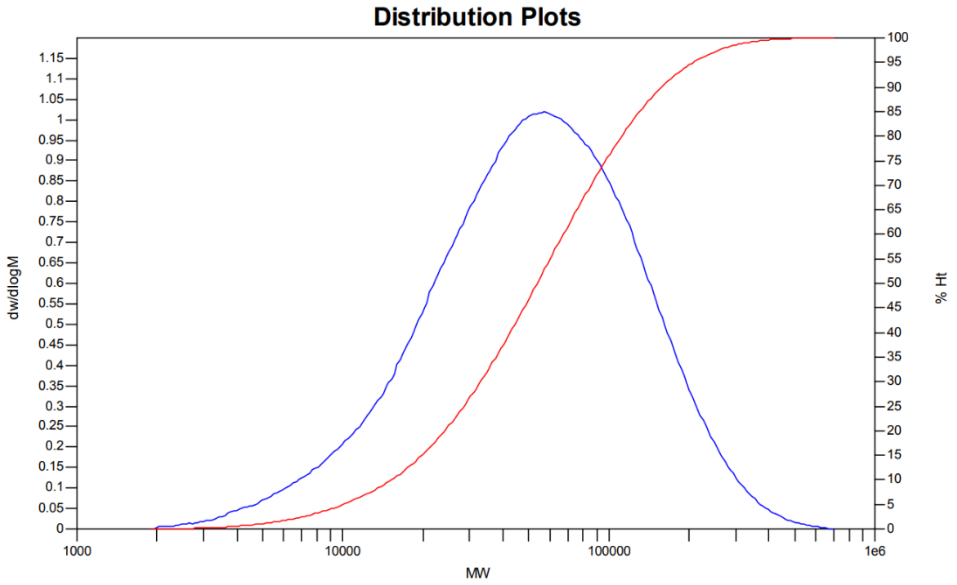
Concentration: 0.10 mg/ml

Injection Volume: 200.0 ul LIMS ID:

MW Averages

Mp: 57334	Mn: 32016	Mv: 65990	Mw: 73229
Mz: 134248	Mz+1: 207389	PD: 2.2873	

Distribution Plots



Sample Peak Report

MW Ranges

Range No	High Limit	Low Limit	%Area
1	702694	50000	53.160
2	50000	40000	9.433
3	40000	30000	10.682
4	30000	20000	11.541
5	20000	10000	10.256
6	10000	1905	4.929

Figure S113. GPC of the polymer from table 5, entry 5.

Cirrus GPC Sample Peak Report

Sample Details

Acquired: 2023/5/27 12:25:03

Batch Name: 20230527

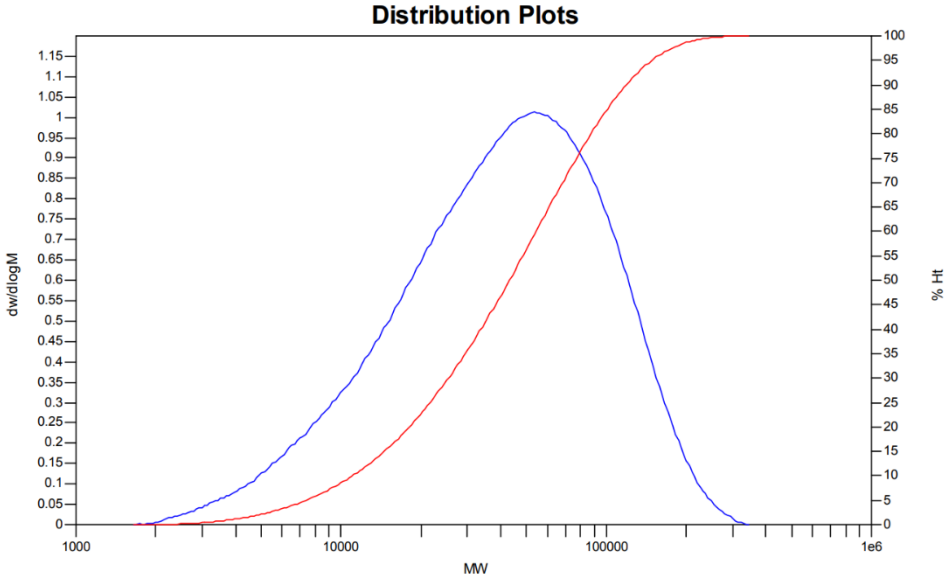
Filename: E:\Cirrus Workbooks\JC\20230527-0004.cgrm

Concentration: 0.10 mg/ml

Injection Volume: 200.0 ul LIMS ID:

MW Averages

Mp: 53408	Mn: 24439	Mv: 50248	Mw: 55265
Mz: 92628	Mz+1: 127521	PD: 2.2613	



Sample Peak Report

MW Ranges

Range No	High Limit	Low Limit	%Area
1	345734	50000	43.613
2	50000	40000	9.506
3	40000	30000	11.146
4	30000	20000	13.044
5	20000	10000	14.104
6	10000	1653	8.587

Figure S114. GPC of the polymer from table 5, entry 6.

4. X-ray Crystallography

CCDC numbers of complexes **Pd2**, **Ni4** and **Pd4** are **2280677**, **2280679** and **2280680**, respectively.

Table S1. Crystallographic and structural refinement data for **Pd2**, **Ni4** and **Pd4.**

Identification code	**Pd2**	**Ni4**	**Pd4**
Empirical formula	$C_{45}H_{61}ClN_2$ Pd	$C_{94}H_{94}Br_2N_2NiO_2$ •CH_2Cl_2	$C_{95}H_{97}ClN_2O_2Pd$
Formula weight	771.80	1587.17	1440.59
Temperature/K	298(2) K	298(2) K	293(2) K
Crystal system	Monoclinic	Triclinic	Triclinic
Space group	P 21/n	P-1	P -1
a/Å	14.8764(13) Å	12.5341(12) Å	13.7030(13) Å
b/Å	17.0627(18) Å	14.1985(14) Å	16.3525(15) Å
c/Å	19.043(2) Å	24.945(3) Å	18.4107(17) Å
α/°	90 °.	99.731(3) °.	86.973(3) °.
β/°	95.432(2) °.	93.888(2) °.	74.385(2) °.
γ/°	90 °.	110.972(4) °.	86.344(3) °.
Volume/Å^3	4812.0(9) Å^3	4045.7(7) Å^3	3962.4(6) Å^3
Z	4	2	2
ρcalcg/cm^3	1.065 Mg/m^3	1.303 Mg/m^3	1.207 Mg/m^3
μ/mm^{-1}	0.468 mm^{-1}	1.344 mm^{-1}	0.318 mm^{-1}
F(000)	1632	1656	1520
Crystal size/mm^3	0.430 x 0.400 x 0.320 mm^3	0.30 x 0.13 x 0.09 mm^3	0.430 x 0.380 x 0.210 mm^3
θ min-max/ º	2.047 to 25.020 °.	1.84 to 25.02 °.	2.036 to 25.020 °.
Limiting indices	-16<=h<=17, -20<=k<=17, -22<=l<=15	-14<=h<=14, -16<=k<=14, -29<=l<=24	-16<=h<=16, -18<=k<=19, -21<=l<=17
Reflections collected	23326	20792	19253
Reflections unique	8471 [R(int) = 0.0609]	14044 [R(int) = 0.0507]	13602 [R(int) = 0.1415]
Data/restraints/parameters	8471 / 486 / 458	14044 / 147 / 947	13602 / 45 / 911
Goodness-of-fit on F^2	1.056	1.083	1.071
Final R indexes [I>=2σ (I)]	R1 = 0.0448, wR2 = 0.1036	R1 = 0.0640, wR2 = 0.0950	R1 = 0.1430, wR2 = 0.2882
R indexes [all data]	R1 = 0.0812, wR2 = 0.1146	R1 = 0.1465, wR2 = 0.1048	R1 = 0.2264, wR2 = 0.3169
Largest diff. peak/hole / e Å^{-3}	0.554 and -0.612 e.Å^{-3}	0.827 and -0.599 e.Å^{-3}	1.867 and -2.486 e.Å^{-3}