Electronic Supplementary Information (ESI)

Influence of initiating groups on phosphino-phenolate nickel catalyzed ethylene (co)polymerizations

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1 NMR figures of ligands and catalysts

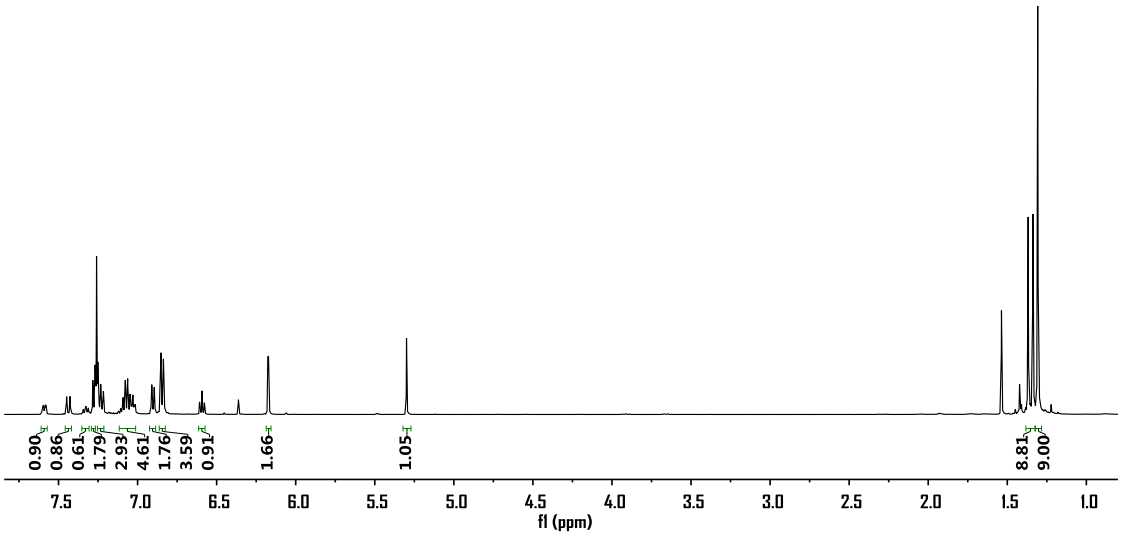


Figure S1. ^{1}H NMR spectrum of **PO-H** in $CDCl_3$.

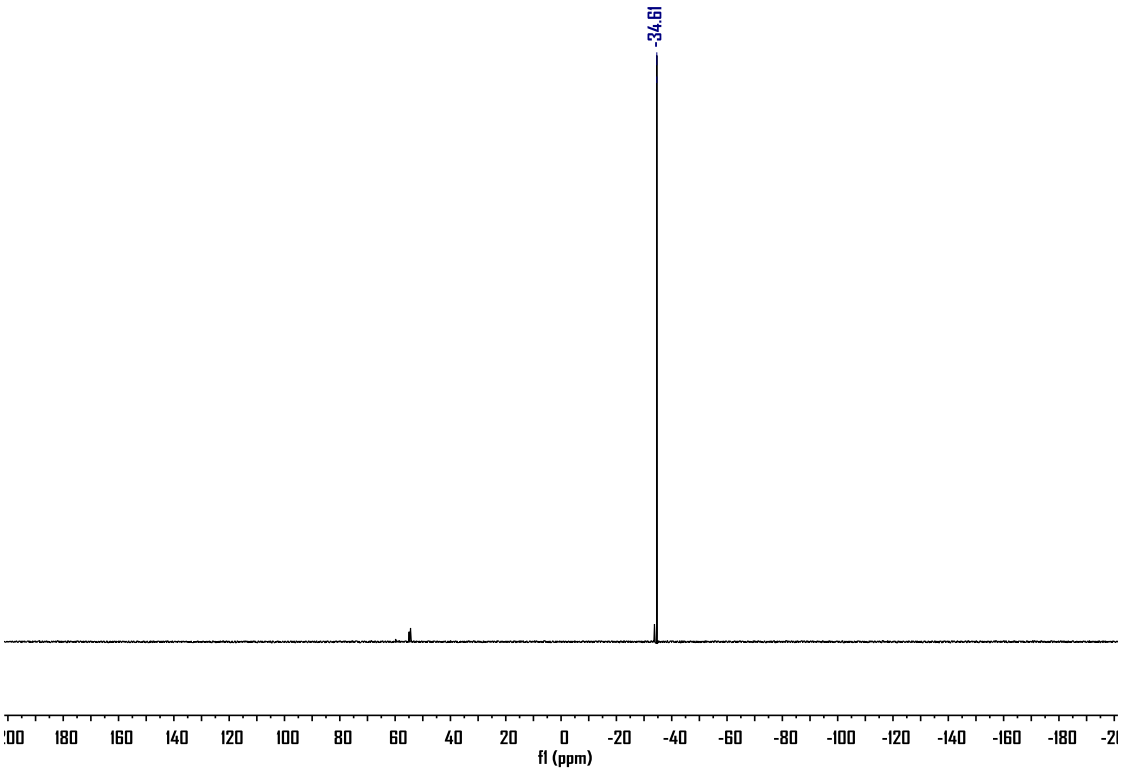


Figure S2. $^{31}P\{^{1}H\}$ NMR spectrum of **PO-H** in $CDCl_3$.

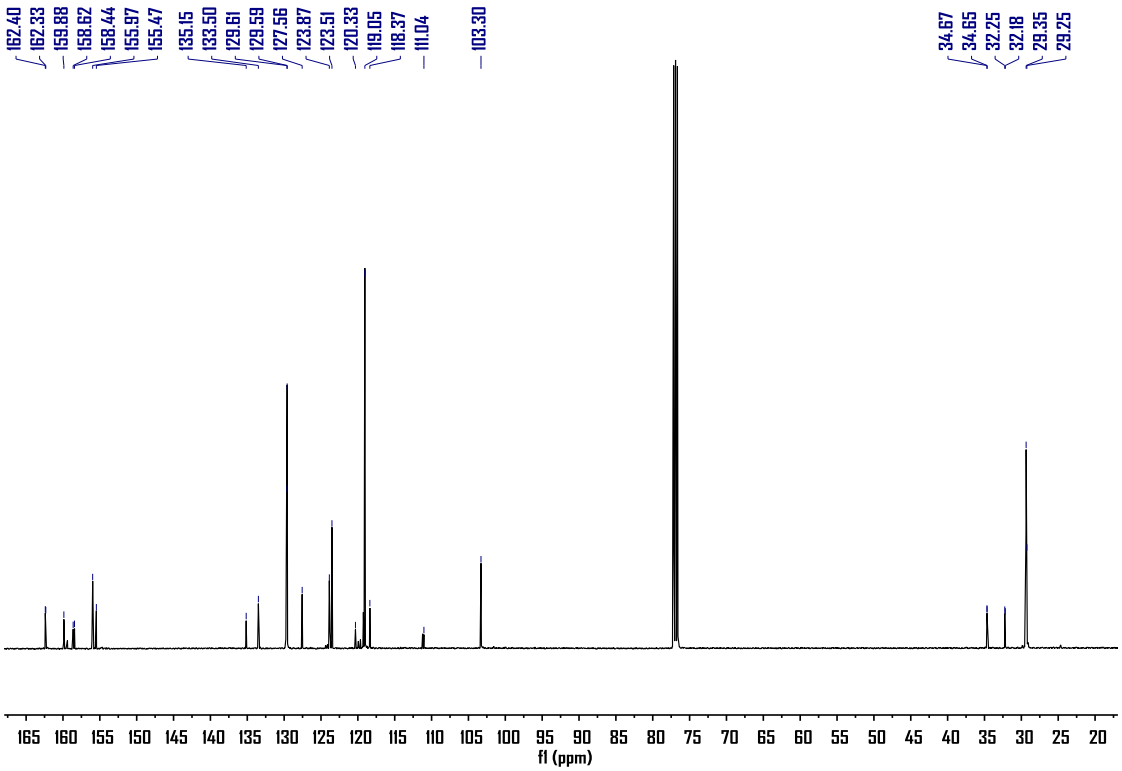


Figure S3. $^{13}C\{^{1}H\}$ NMR spectrum of **PO-H** in $CDCl_3$.

^{1}H, ^{13}C, ^{31}P, COSY, HSQC, HMBC NMR of Ni(II) Complexes

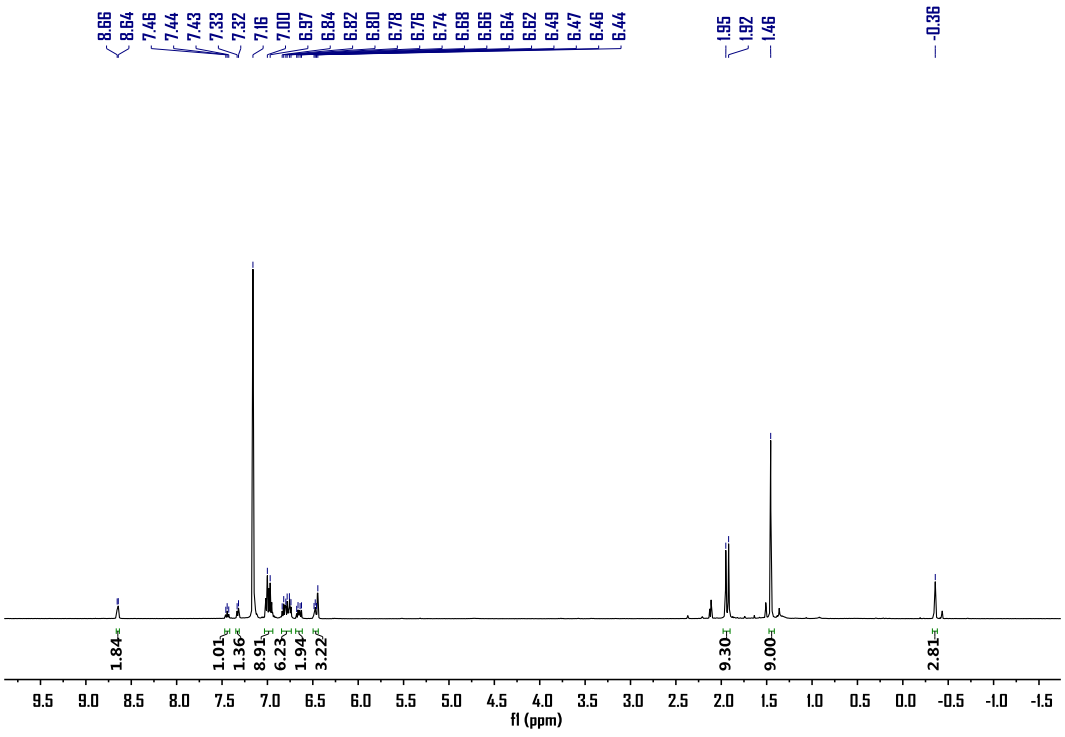


Figure S4. ^{1}H NMR spectrum of **Ni1-pyr** in C_6D_6.

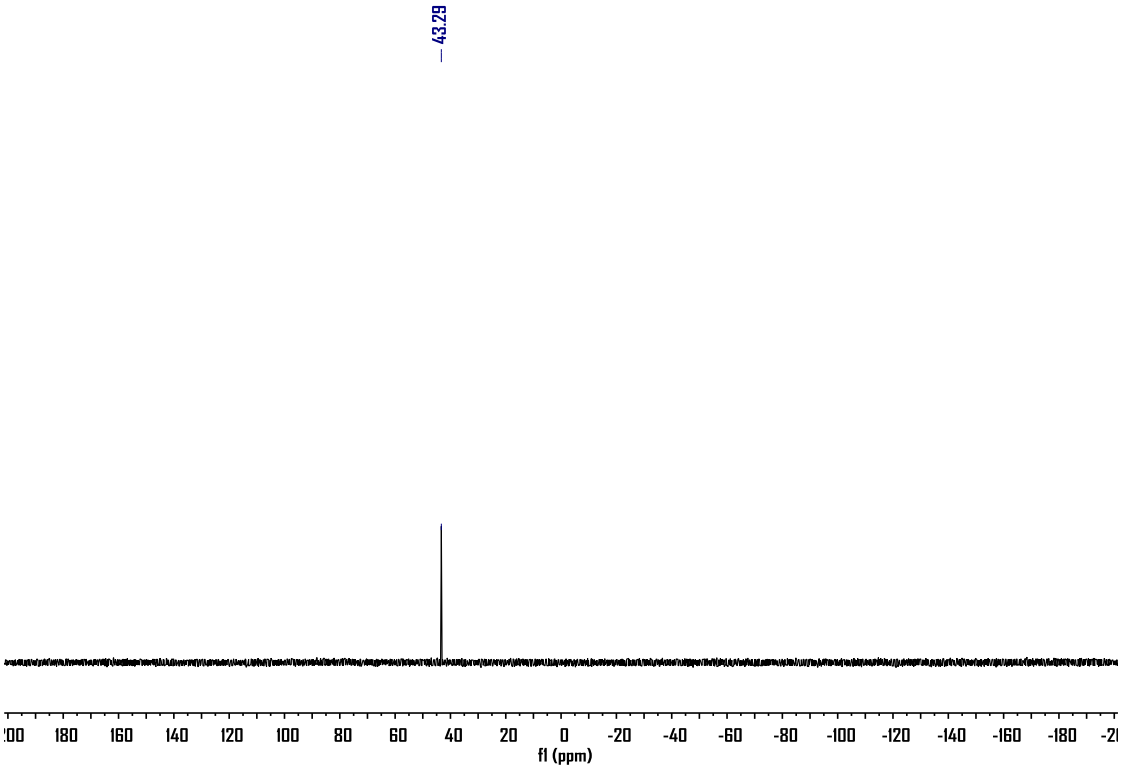


Figure S5. $^{31}P\{^{1}H\}$ NMR spectrum of **Ni1-pyr** in C_6D_6.

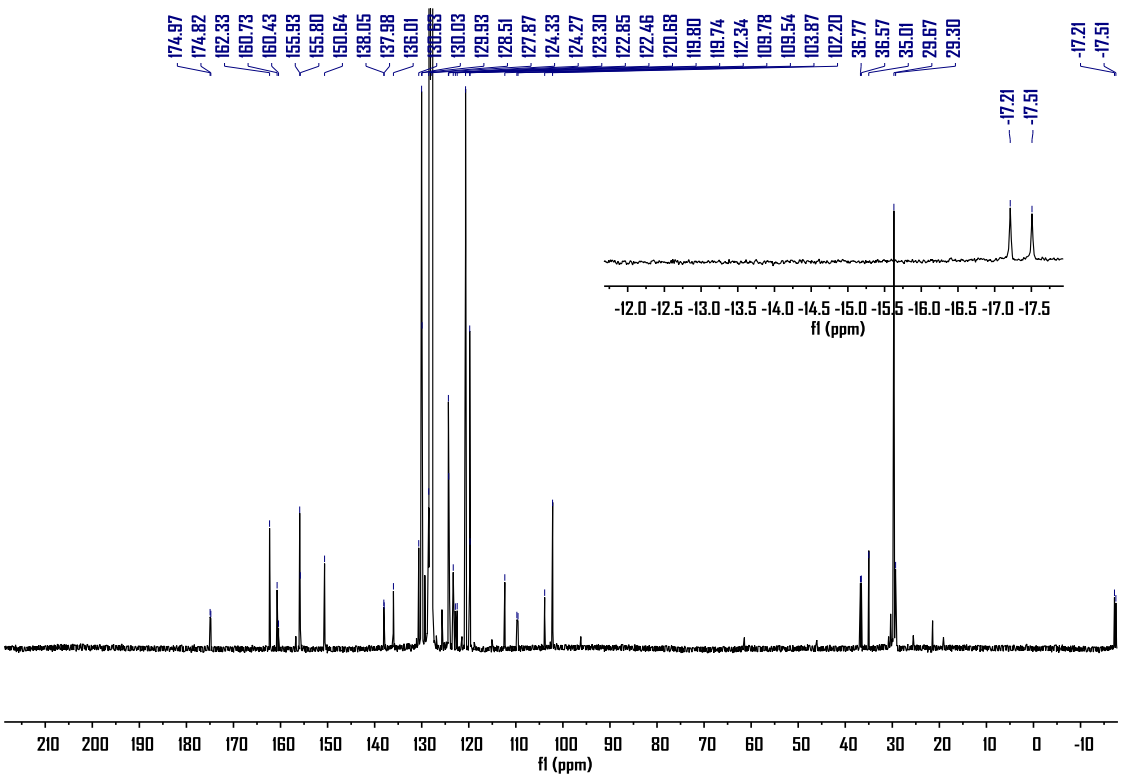


Figure S6. $^{13}C\{^{1}H\}$ NMR spectrum of **Ni1-pyr** in C_6D_6.

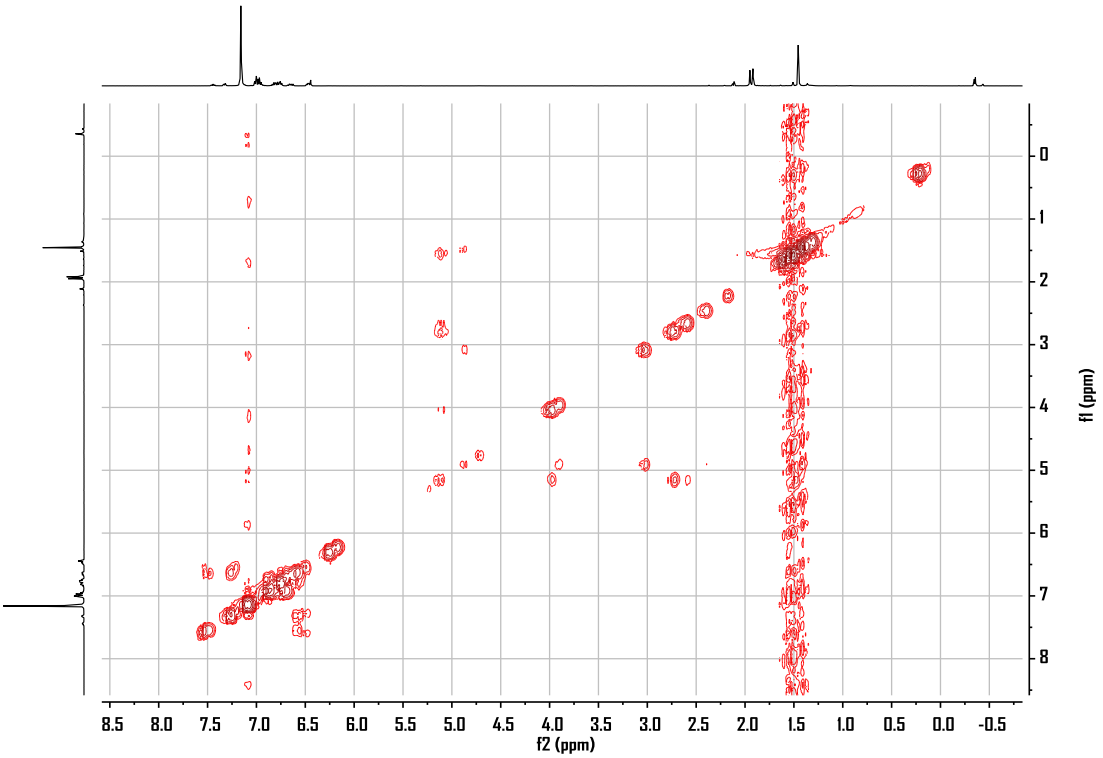


Figure S7. ^{1}H-^{1}H COSY spectrum of **Ni1-pyr** in C_6D_6.

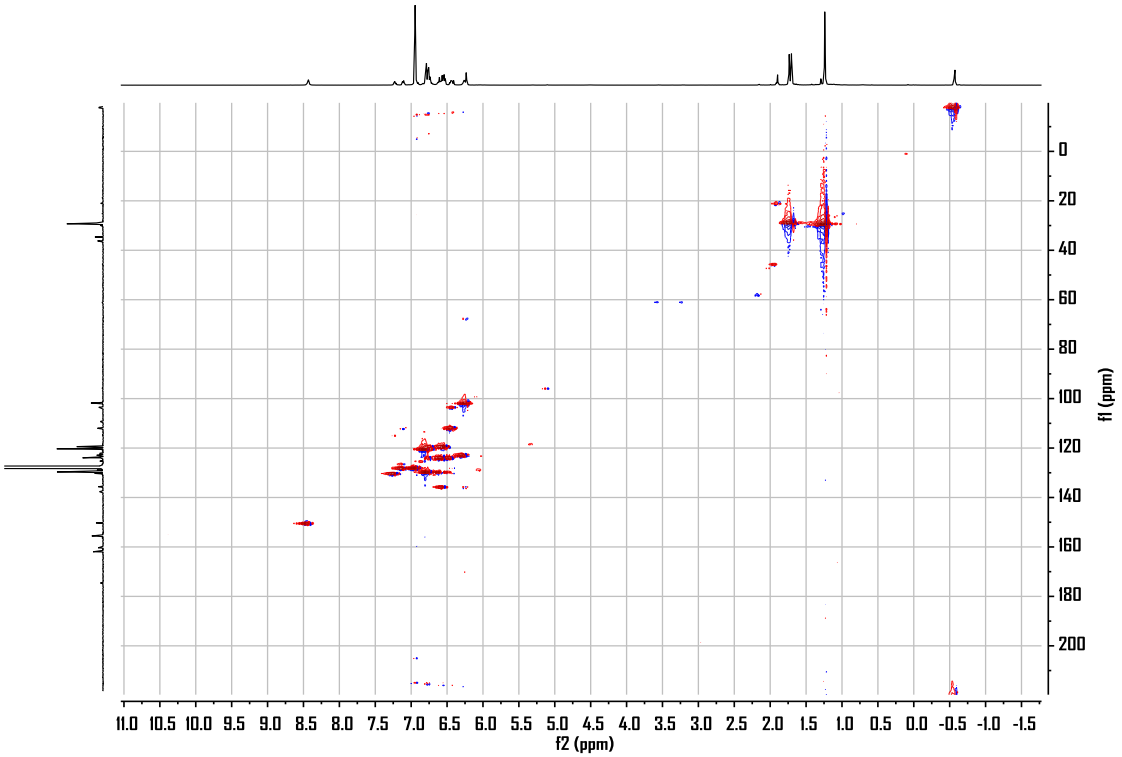


Figure S8. ^{1}H-^{13}C HSQC NMR spectrum of **Ni1-pyr** in C_6D_6.

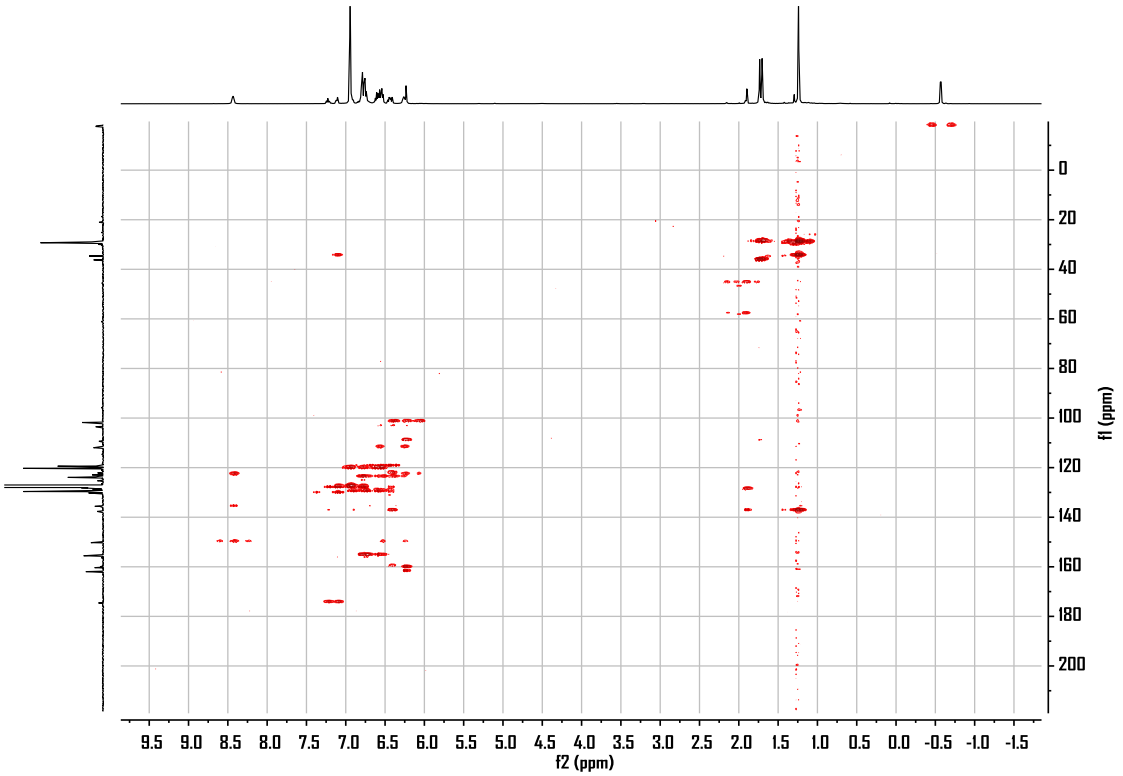


Figure S9. ^{1}H-^{13}C HMBC NMR spectrum of **Ni1-pyr** in C_6D_6.

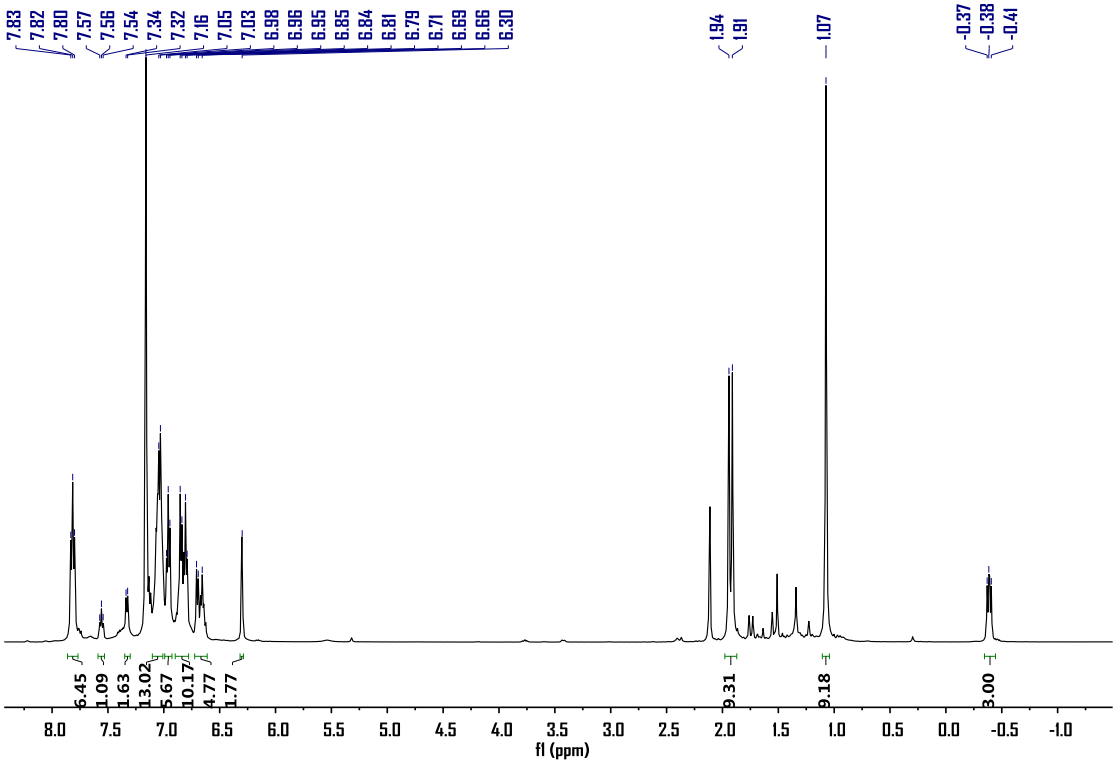


Figure S10. ^{1}H NMR spectrum of **Ni1-PPh$_3$** in C_6D_6.

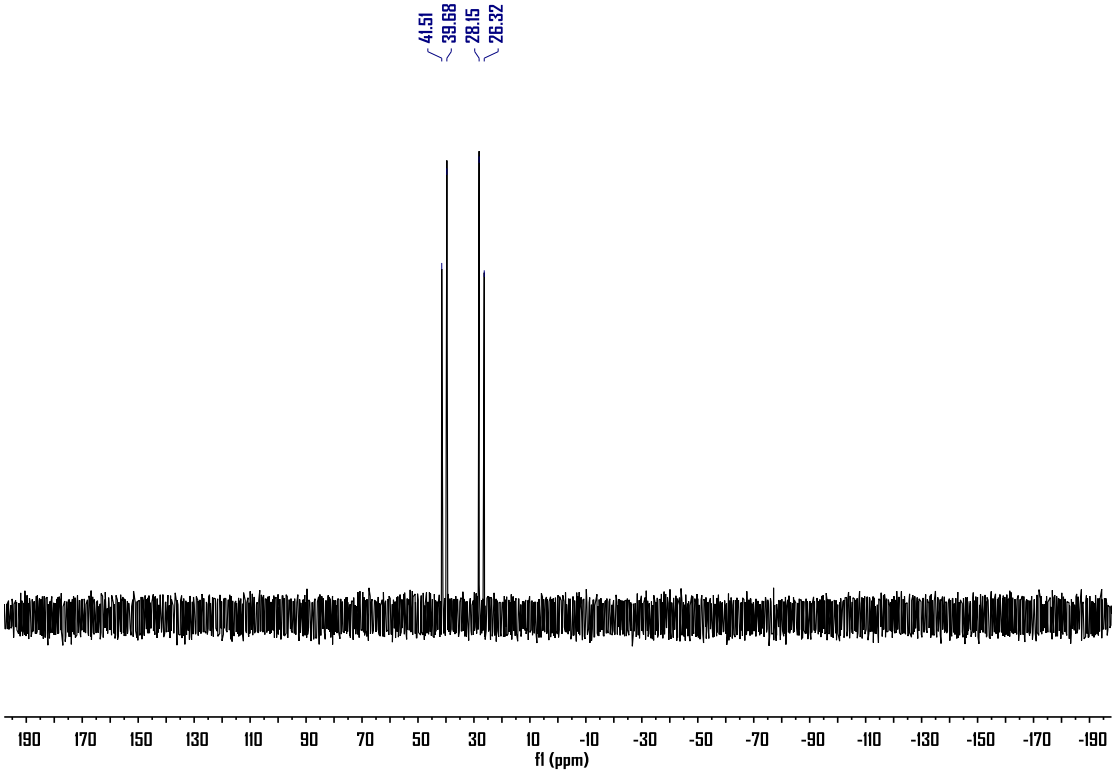


Figure S11. $^{31}P\{^{1}H\}$ NMR spectrum of **Ni1-PPh$_3$** in C_6D_6.

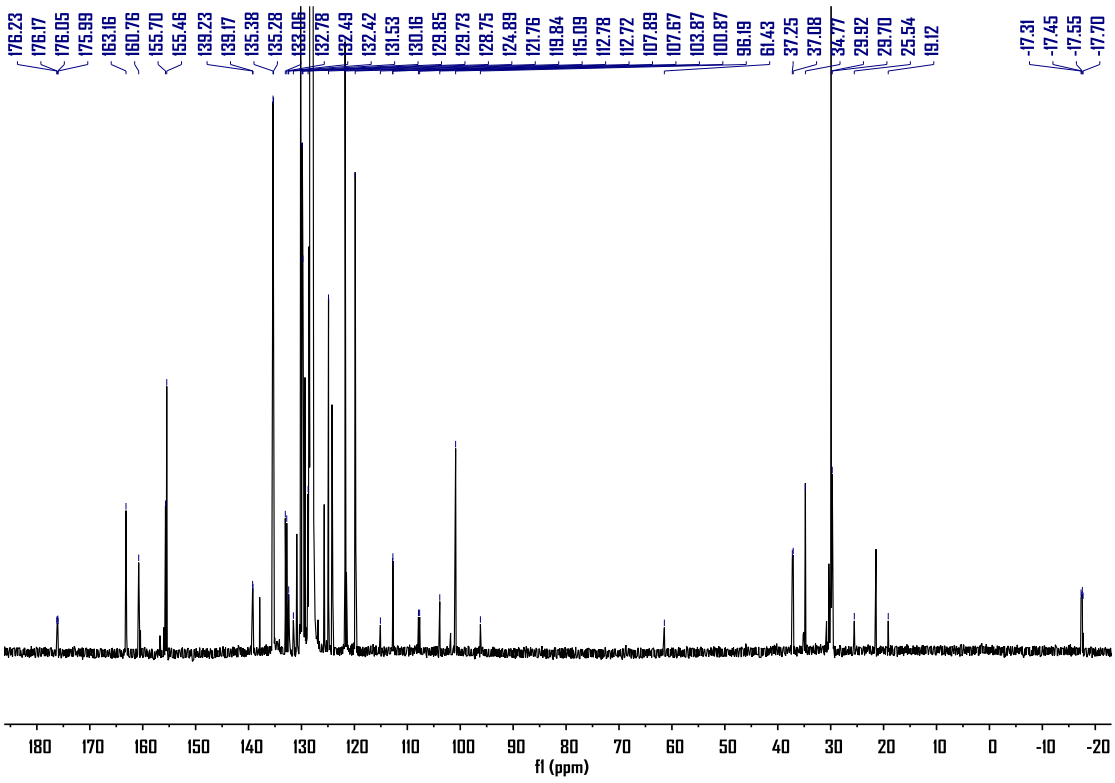


Figure S12. $^{13}C\{^{1}H\}$ NMR spectrum of **Ni1-PPh$_3$** in C_6D_6.

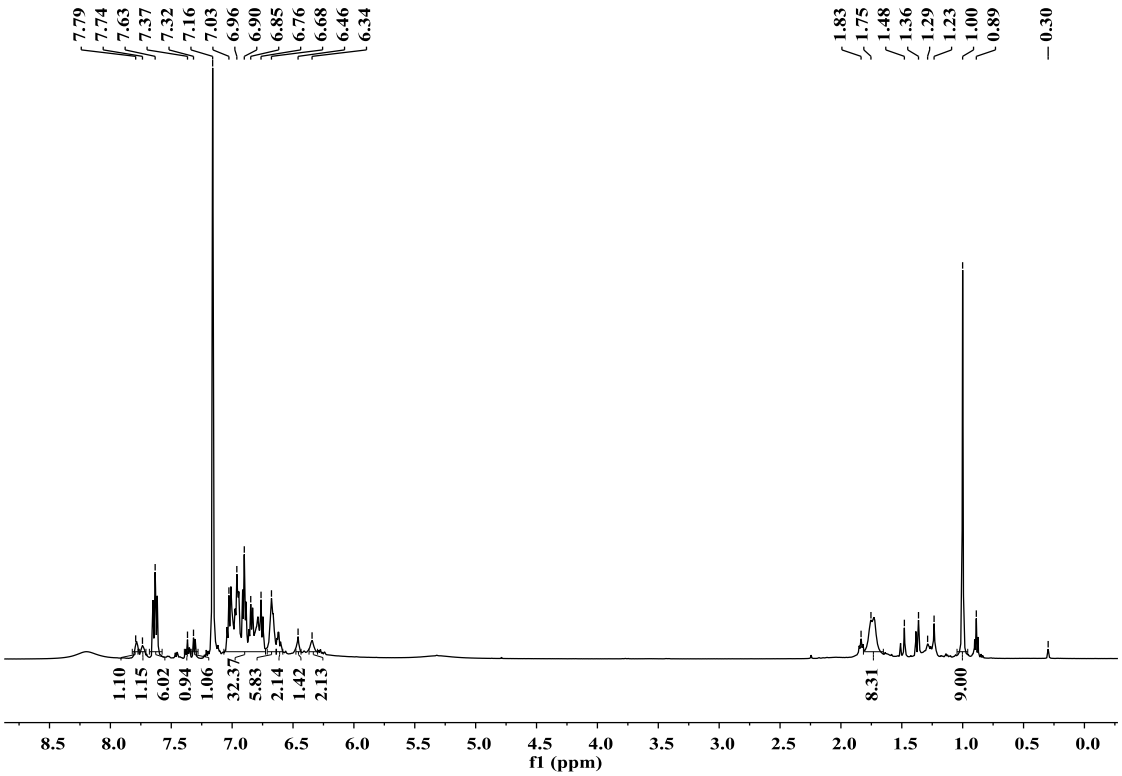


Figure S13. ^{1}H NMR spectrum of **Ni2** in C_6D_6.

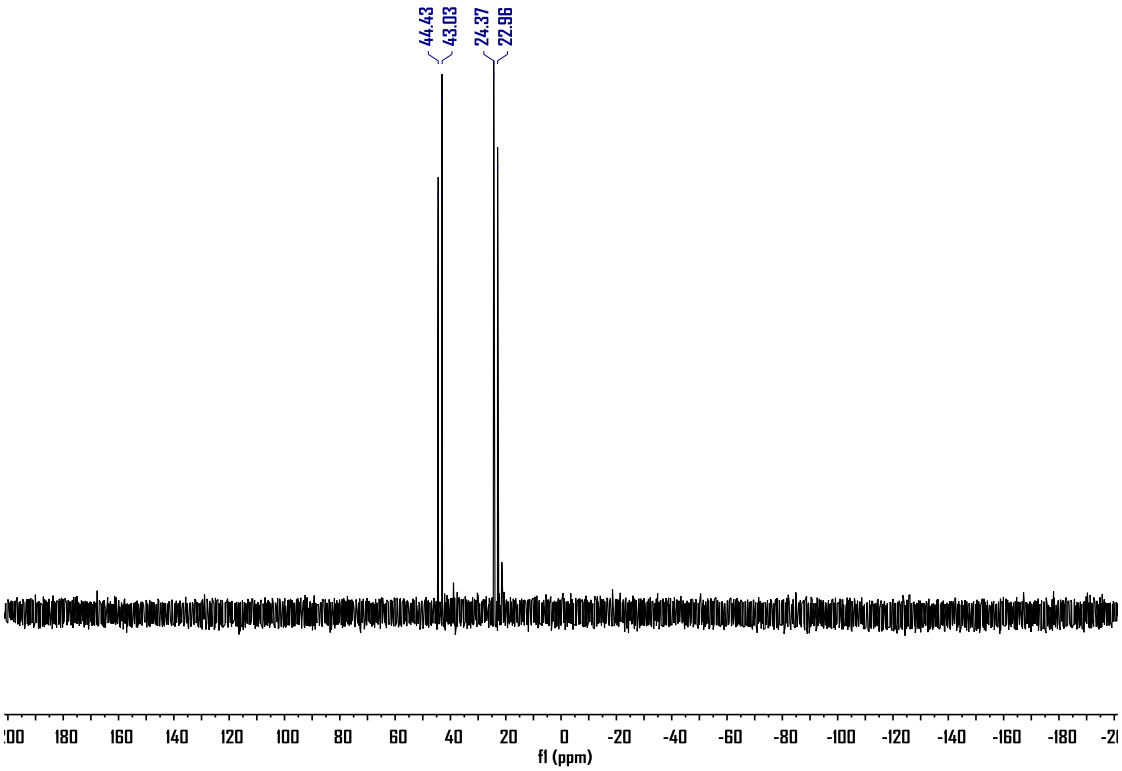


Figure S14. ^{31}P{^{1}H} NMR spectrum of **Ni2** in C_6D_6.

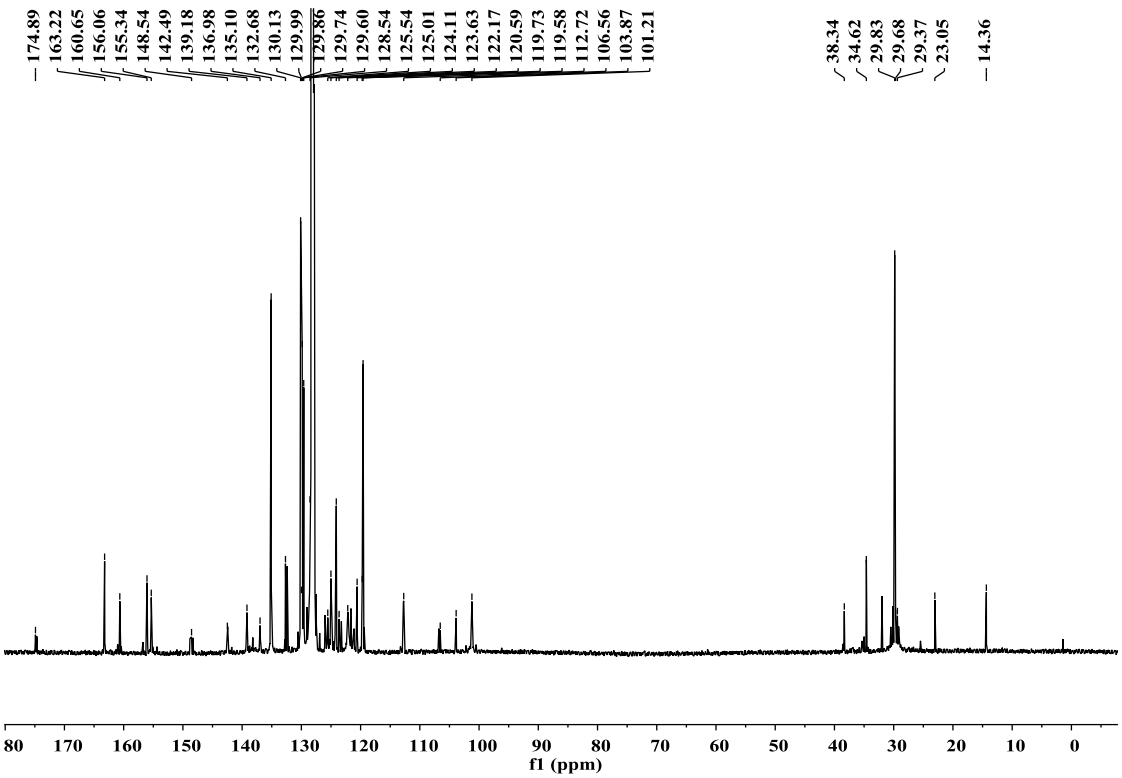


Figure S15. $^{13}C\{^{1}H\}$ NMR spectrum of **Ni2** in C_6D_6.

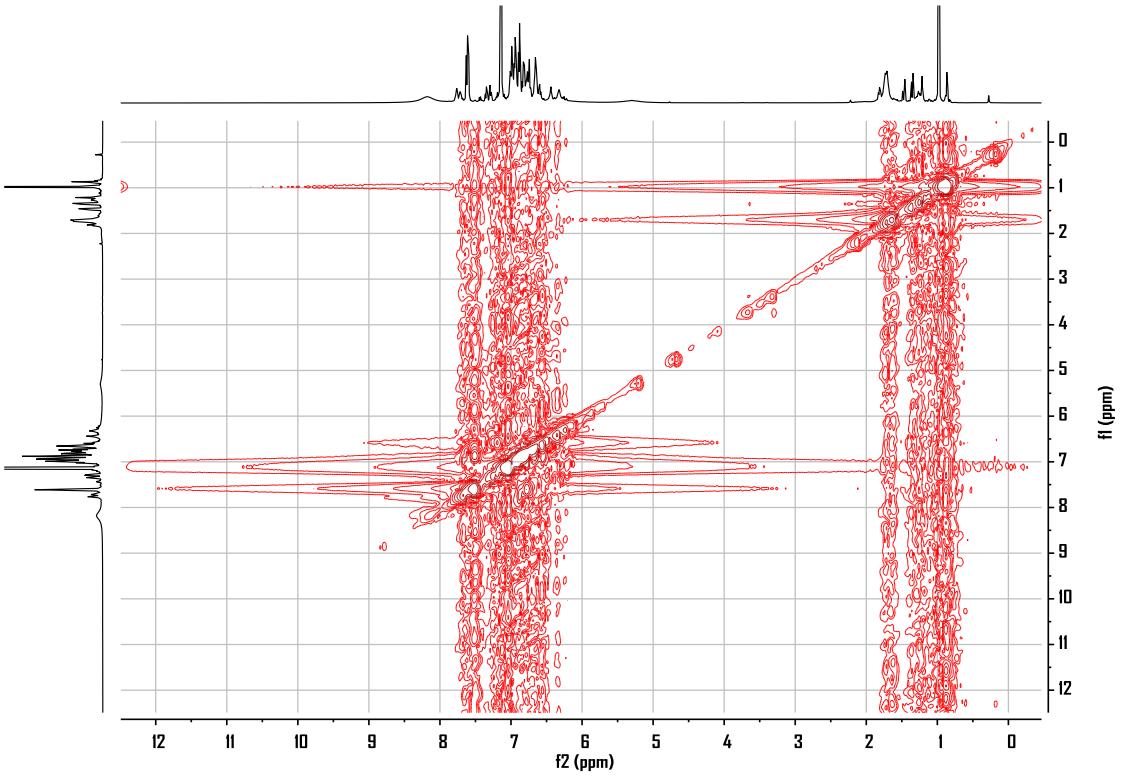


Figure S16. ^{1}H-^{1}H COSY spectrum of **Ni2** in C_6D_6.

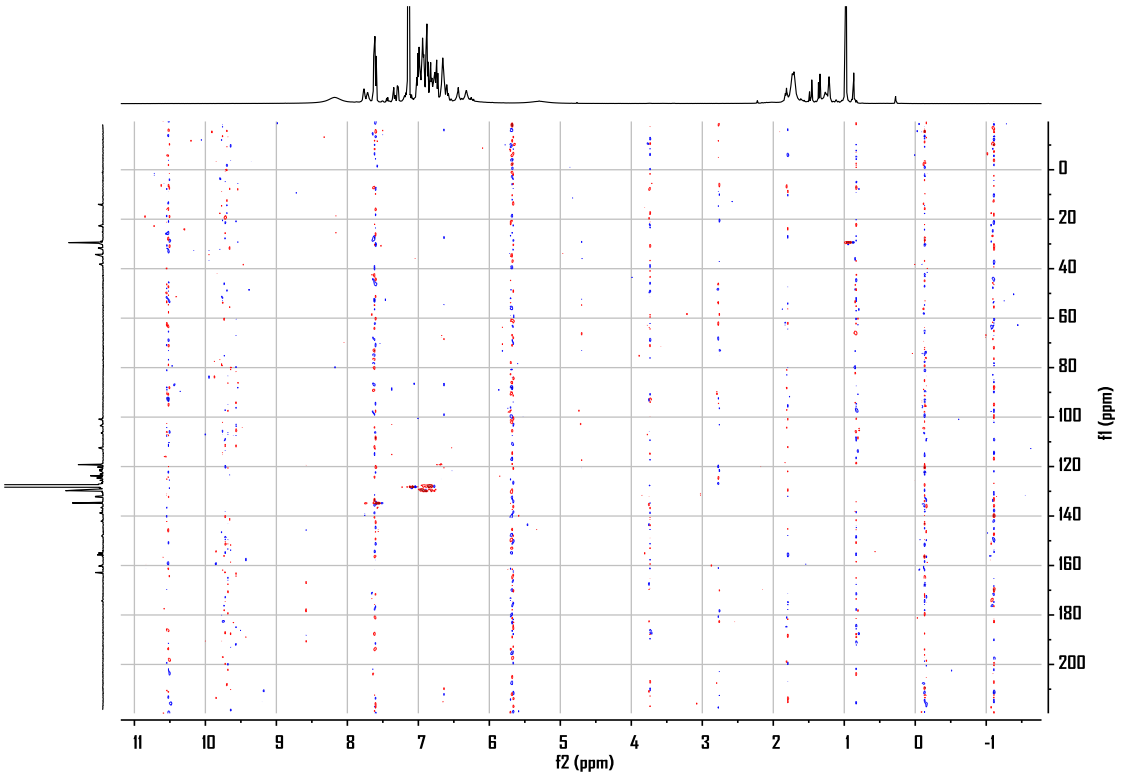


Figure S17. ^{1}H-^{13}C HSQC NMR spectrum of **Ni2** in C_6D_6.

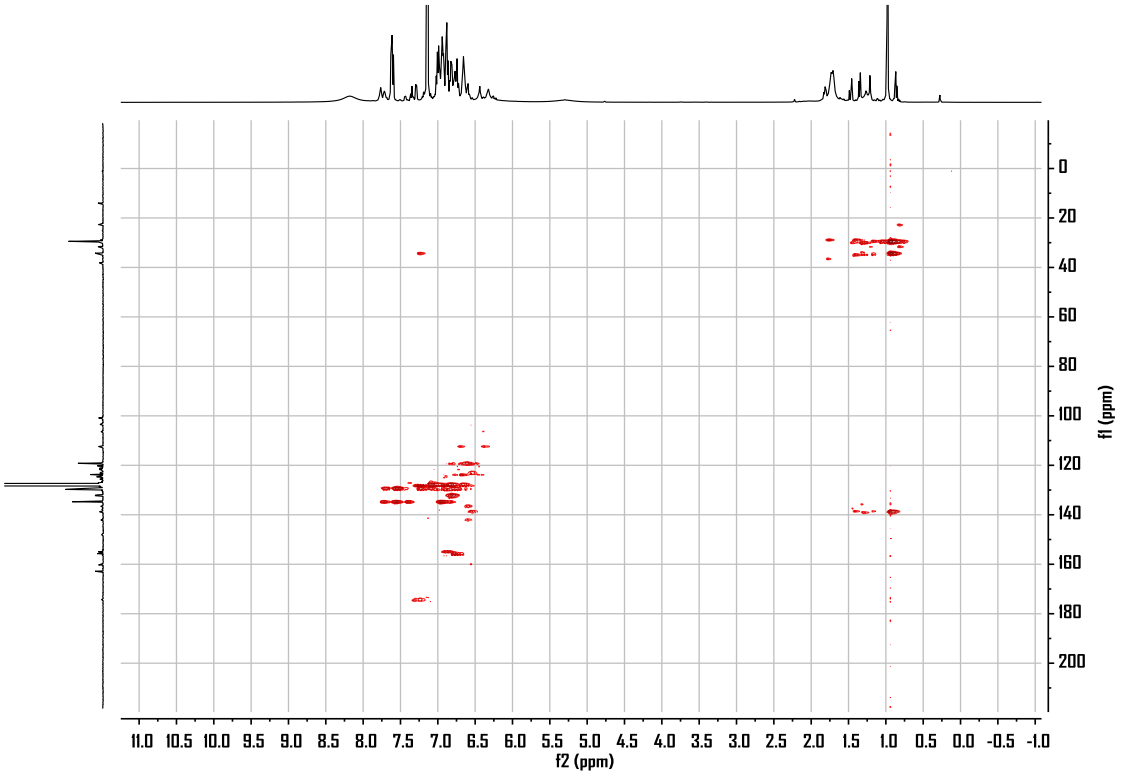


Figure S18. ^{1}H-^{13}C HMBC NMR spectrum of **Ni2** in C_6D_6.

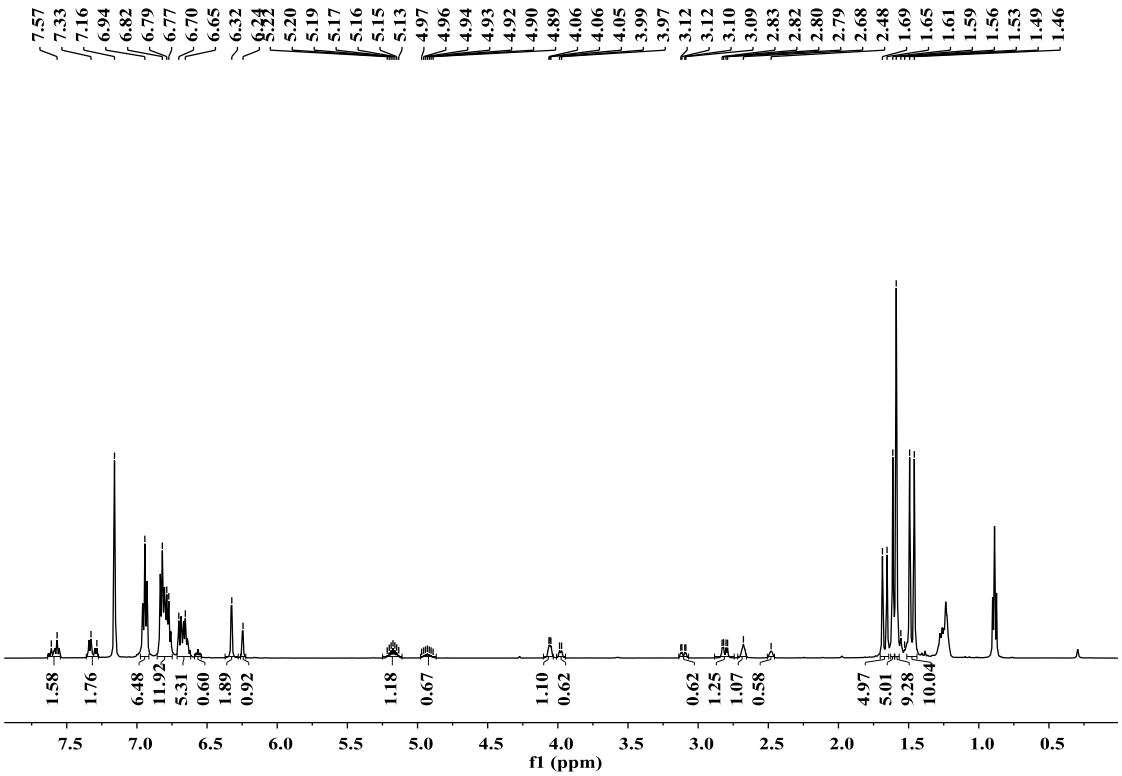


Figure S19. ^{1}H NMR spectrum of **Ni3** in C_6D_6.

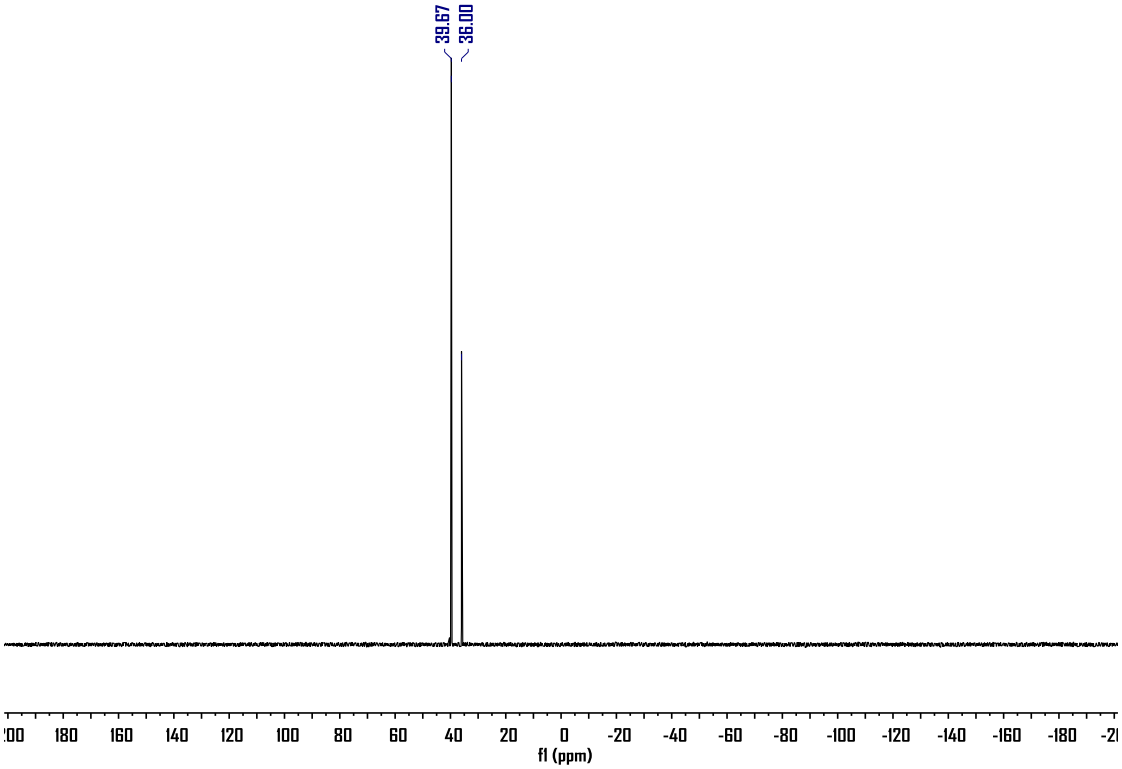


Figure S20. $^{31}P\{^{1}H\}$ NMR spectrum of **Ni3** in C_6D_6.

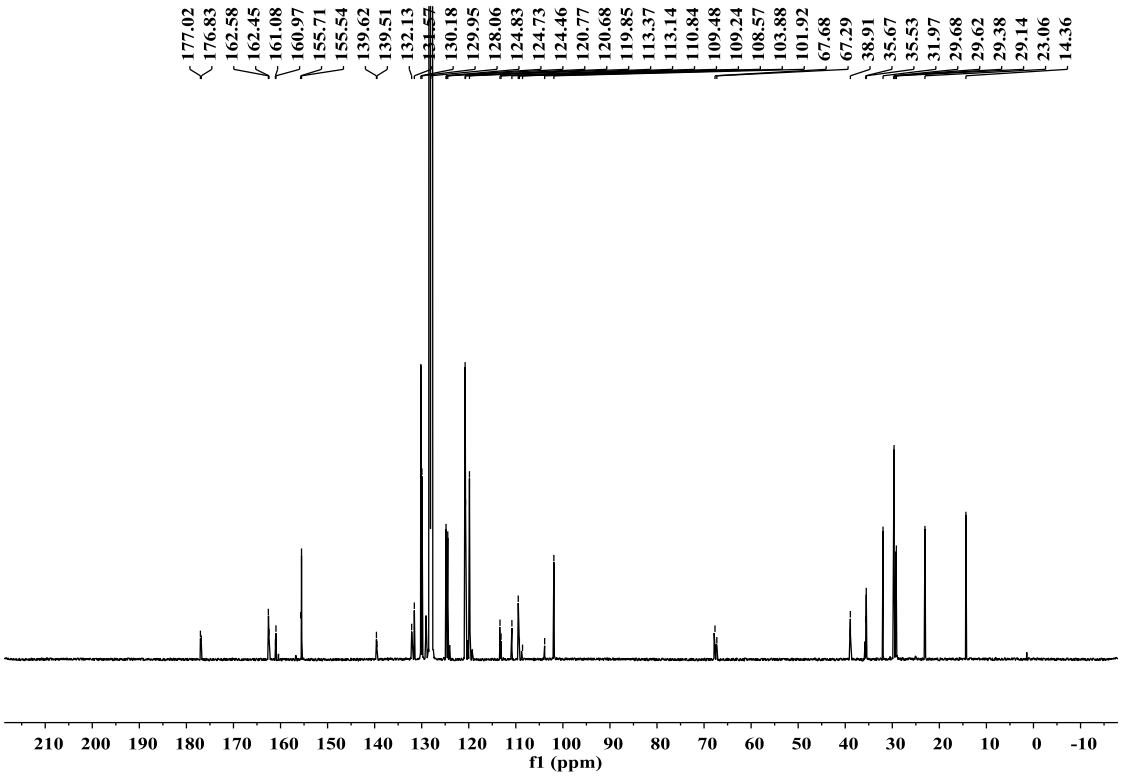


Figure S21. $^{13}C\{^{1}H\}$ NMR spectrum of **Ni3** in C_6D_6.

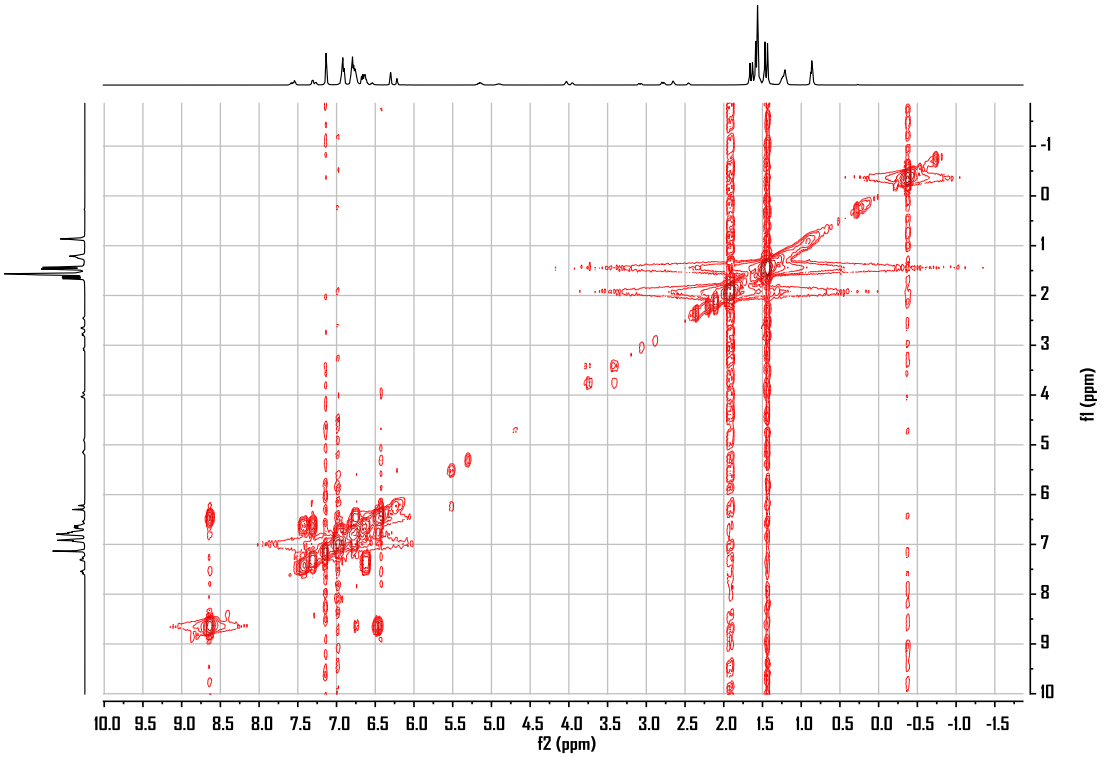


Figure S22. ^{1}H-^{1}H COSY spectrum of **Ni3** in C_6D_6.

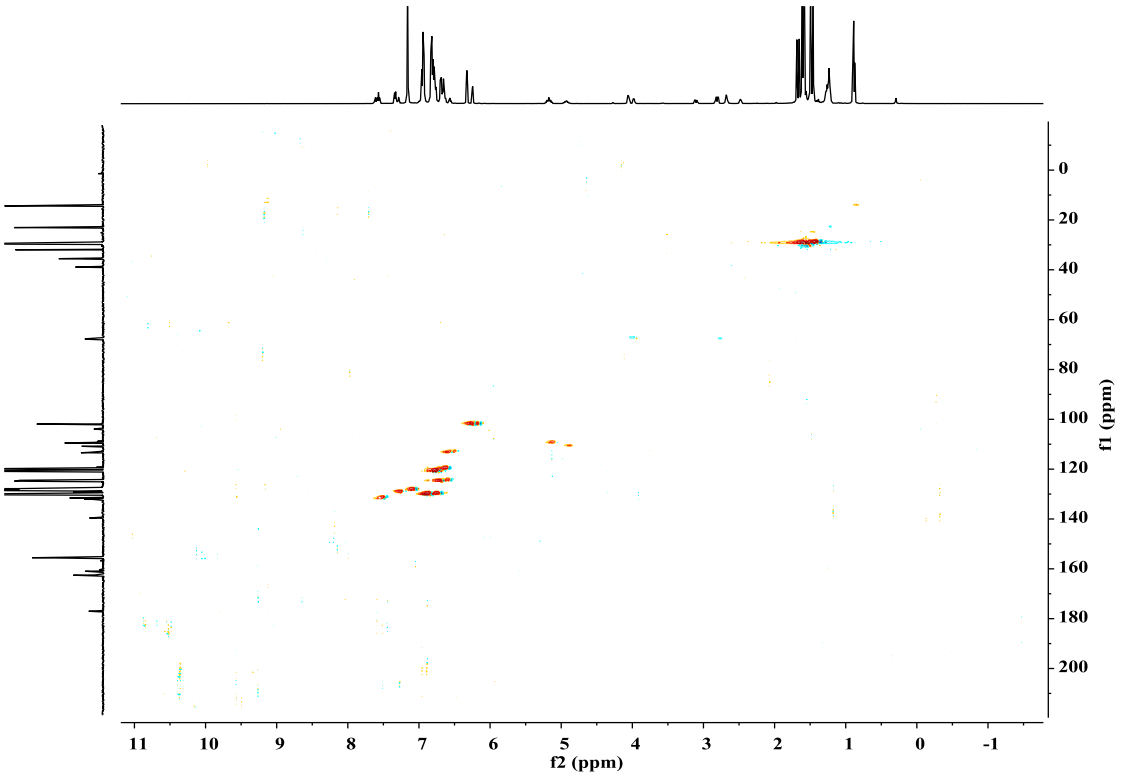


Figure S23. ^{1}H-^{13}C HSQC NMR spectrum of **Ni3** in C_6D_6.

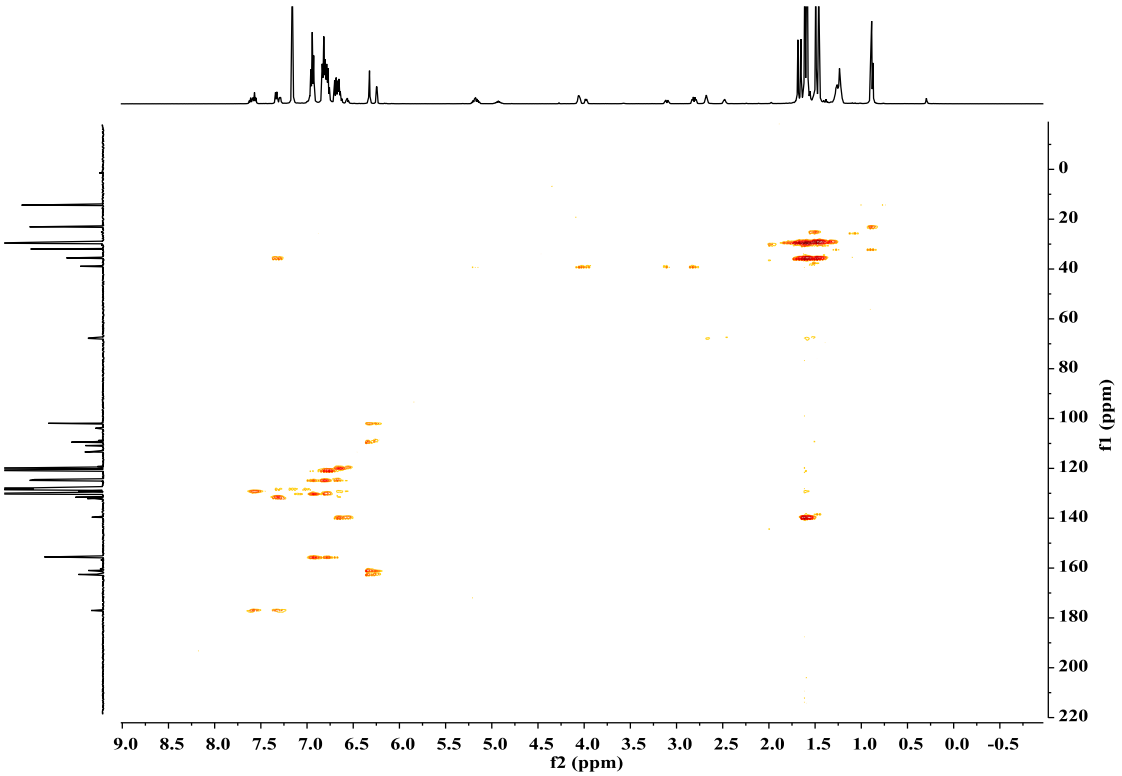


Figure S24. ^{1}H-^{13}C HMBC NMR spectrum of **Ni3** in C_6D_6.

2 NMR figures of (co)polymers

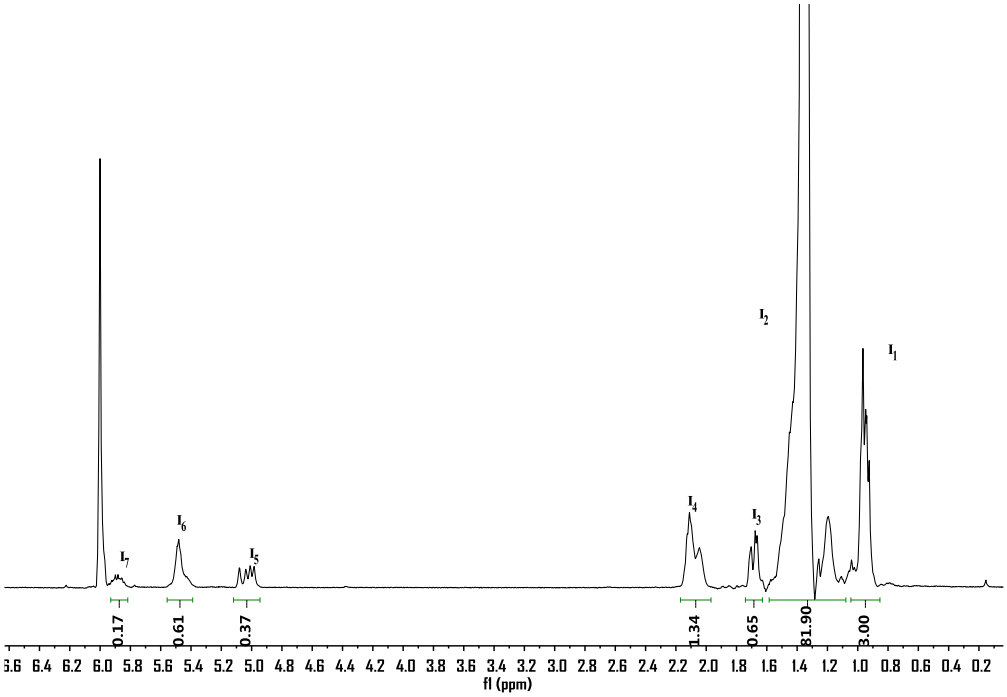


Figure S25. ^{1}H NMR spectrum (400 MHz, $C_2D_2Cl_4$, 110 ℃) of the polyethylene generated from table 1,entry 4.

Me Branches / 1000C = $\frac{\left(3-0.37\times\frac{3}{2}-0.61\times3\right)/3}{88.04/2}\times1000=5$

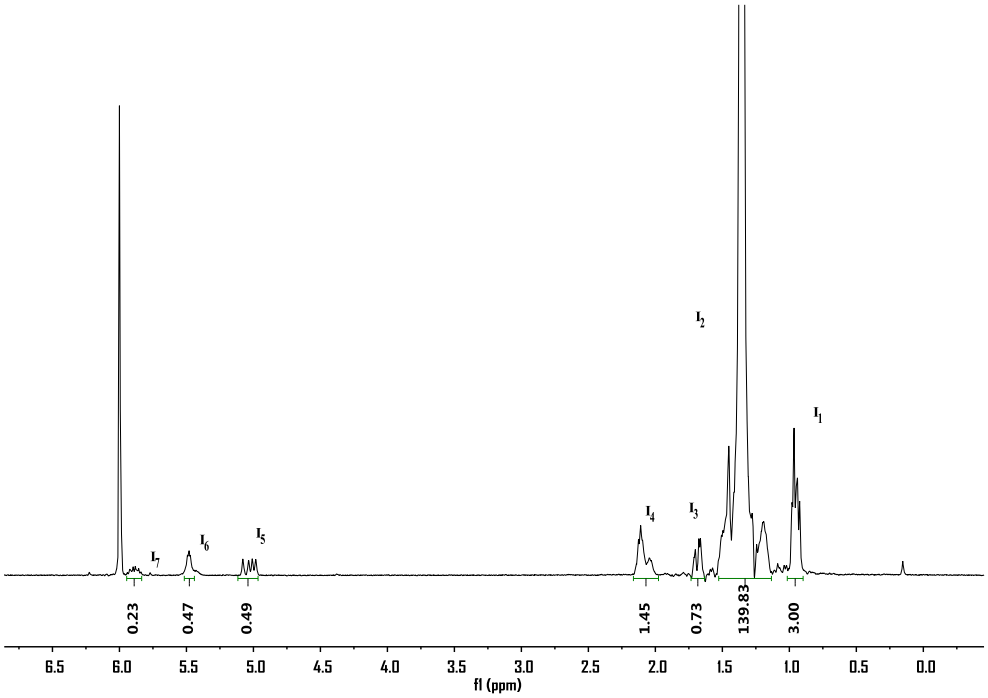


Figure S26. ^{1}H NMR spectrum (400 MHz, $C_2D_2Cl_4$, 110 ℃) of the polyethylene generated from table 1, entry 12.

Me Branches / 1000C = $\frac{\left(3-0.49\times\frac{3}{2}-0.47\times3\right)/3}{146.2/2}\times1000=4$

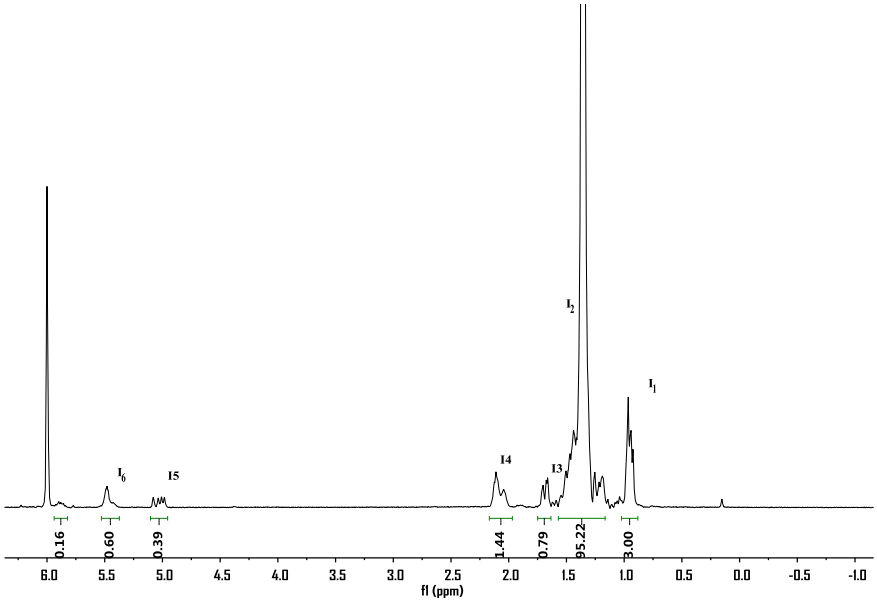


Figure S27. ^{1}H NMR spectrum (400 MHz, $C_2D_2Cl_4$, 110 ℃) of the polyethylene generated by from table 1, entry 20.

Me Branches / 1000C = $\frac{\left(3-0.39\times\frac{3}{2}-0.60\times3\right)/3}{101.6/2}\times 1000=4$

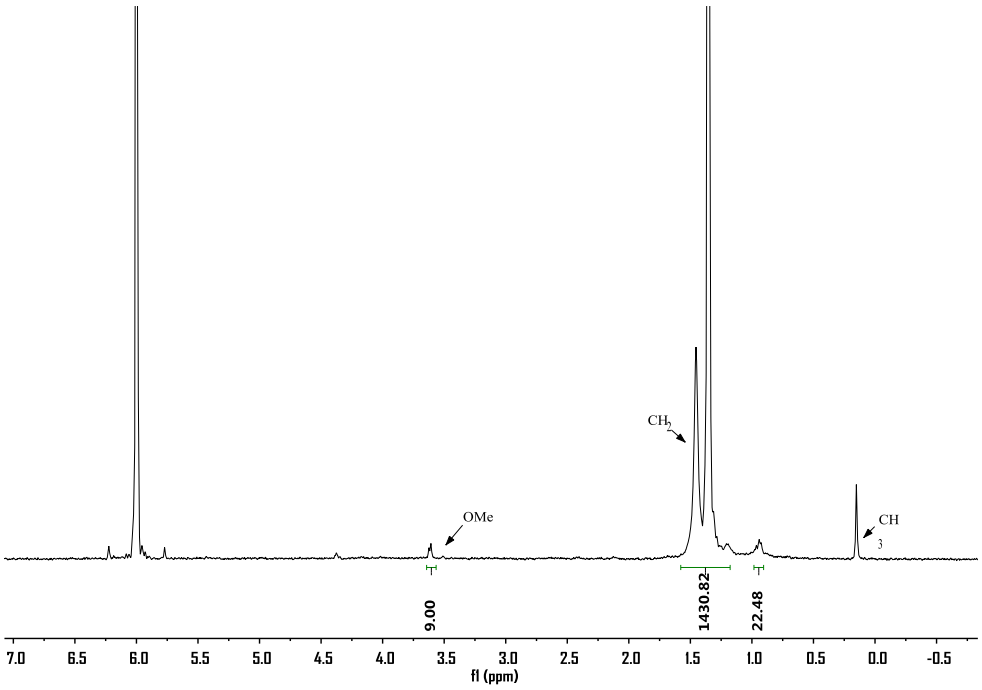


Figure S28. ^{1}H NMR spectrum (400 MHz, $C_2D_2Cl_4$, 100 ℃) of the VTMoS copolymer from table 2, entry 1.

Me Branches / 1000C = $\frac{22.48/3}{1462.3/2}\times 1000=10$

VTMoS%= $\frac{I_{OMe}/9}{(I_{CH2}+I_{CH3})/4}\times 100\% = \frac{9/9}{(1430.82+22.48)/4}\times 100\%=0.3\%$

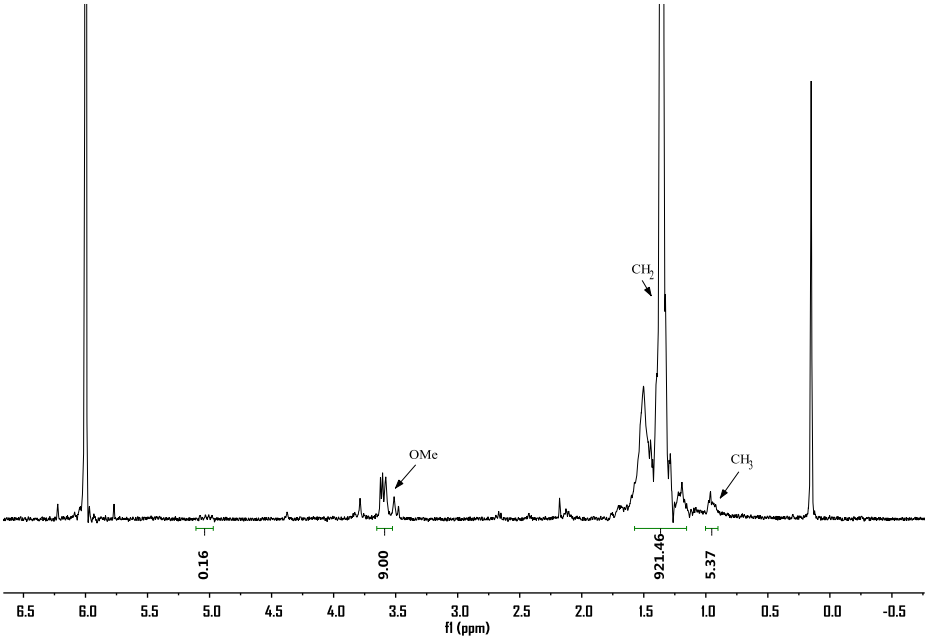


Figure S29. ^{1}H NMR spectrum (400 MHz, $C_2D_2Cl_4$, 100 ℃) of the VTMoS copolymer from table 2, entry 2.

Me Branches / 1000C = $\frac{5.37/3}{935.99/2} \times 1000=4$

VTMoS%= $\frac{I_{OMe}/9}{(I_{CH2}+I_{CH3})/4} \times 100\% = \frac{9/9}{(921.46+5.37)/4} \times 100\%=0.43\%$

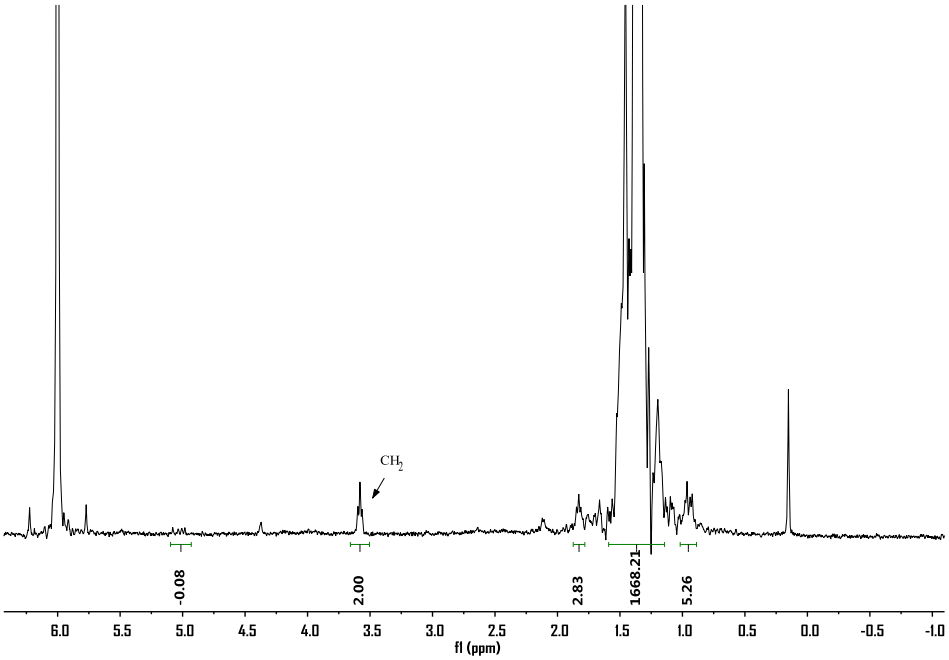


Figure S30. ^{1}H NMR spectrum (400 MHz, $C_2D_2Cl_4$, 100 ℃) of the 6-Cl-Hex copolymer from table 2, entry 3.

Me Branches / 1000C = $\frac{\left(5.26-\frac{0.08\times3}{2}\right)/3}{1678.38/2} \times 1000=2$

6-Cl-Hex %= $\frac{I_{CH2}/2}{\frac{I_{CH2}}{2}+\left(I_{tol}-\frac{I_{CH2}}{2}\times11\right)/4} \times 100\% = \frac{2/2}{1+(1678.38-11)/4} \times 100\%=0.24\%$

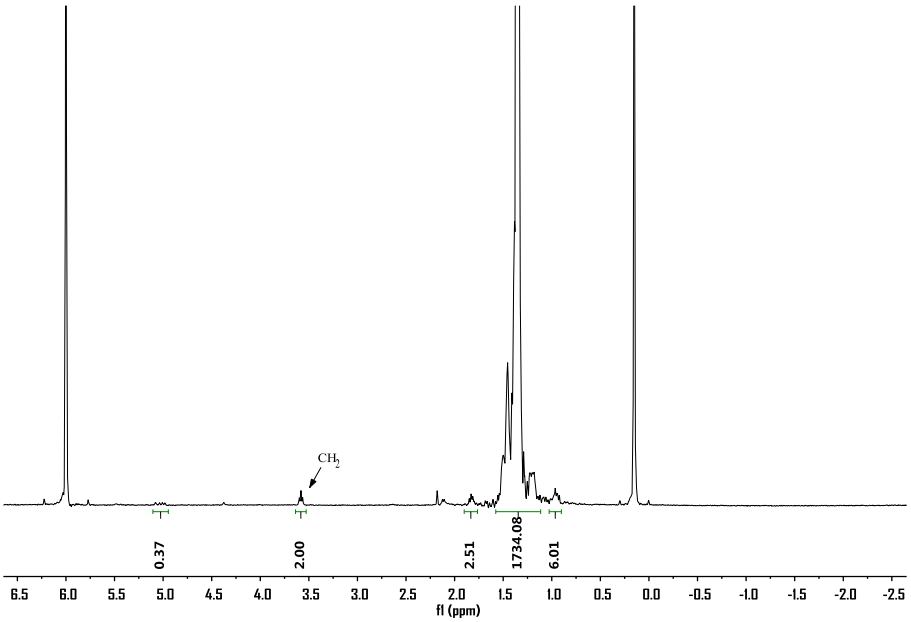


Figure S31. ^{1}H NMR spectrum (400 MHz, $C_2D_2Cl_4$, 100 ℃) of the 6-Cl-Hex copolymer from table 2,entry 4.

Me Branches / 1000C = $\frac{\left(6.01-\frac{0.37\times3}{2}\right)/3}{1744.97/2}\times1000=2$

6-Cl-Hex %= $\frac{I_{CH2}/2}{\frac{I_{CH2}}{2}+\left(I_{tol}-\frac{I_{CH2}}{2}\times11\right)/4}\times100\% = \frac{2/2}{1+(1678.38-11)/4}\times100\%=0.24\%$

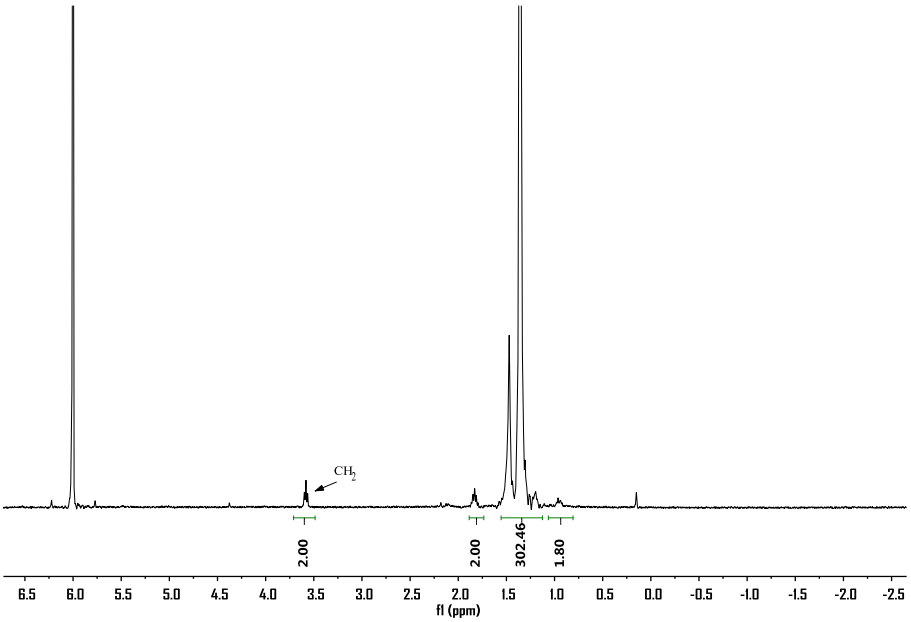


Figure S32. ^{1}H NMR spectrum (400 MHz, $C_2D_2Cl_4$, 100 ℃) of the 6-Cl-Hex copolymer from table 2,entry 5.

Me Branches / 1000C = $\frac{(1.8)/3}{308.26/2}\times1000=4$

6-Cl-Hex %= $\frac{I_{CH2}/2}{\frac{I_{CH2}}{2}+\left(I_{tol}-\frac{I_{CH2}}{2}\times11\right)/4}\times100\% = \frac{2/2}{1+(308.26-11)/4}\times100\%=1.28\%$

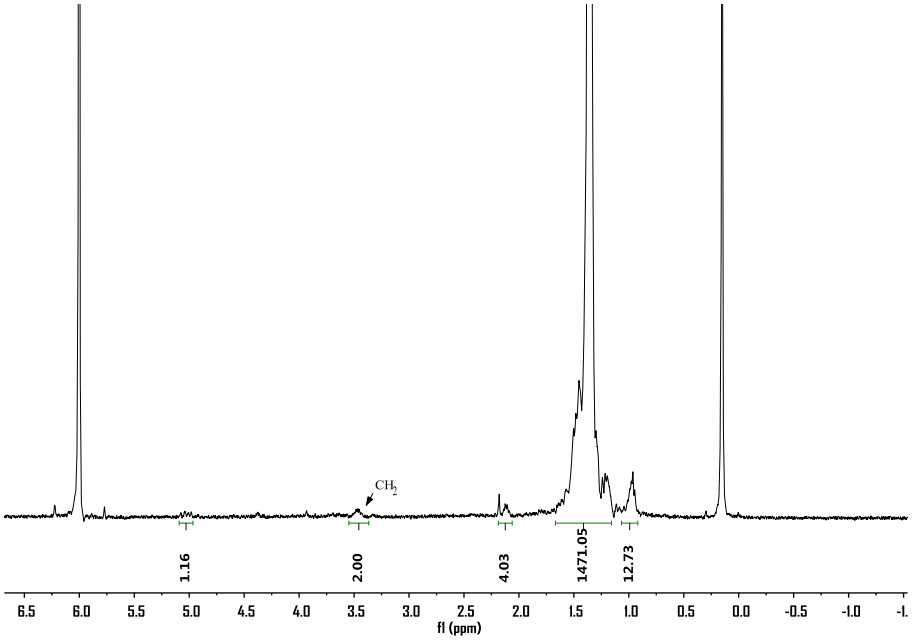
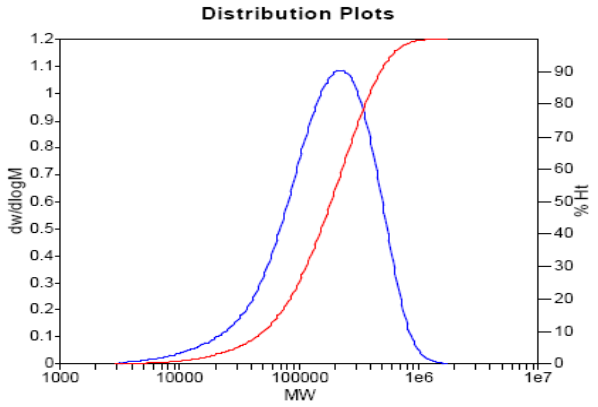


Figure S33.[1]H NMR spectrum (400 MHz, $C_2D_2Cl_4$, 100 ℃) of the E-^{n}BuAE copolymer from table 2, entry 6.

Me Branches / 1000C = $\frac{(12.73)/3}{1490.97/2} \times 1000=6$

^{n}BuAE% = $\frac{I_{CH_2}/2}{(I_{CH2}+I_{CH3})/4} \times 100\%$ = $\frac{2/2}{(1490.97)/4} \times 100\%$ = 0.27%

3. GPC data of (co)polymers



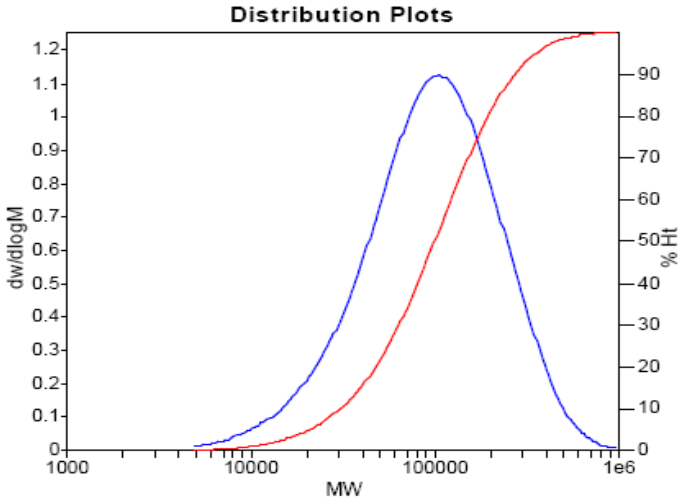
MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	228154	95493	229021	371170	512790	211325	2.3983

Processed Peaks

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1		11.12	12.48	15.45	-16.7845	100	1444.05	100

Figure S34. GPC trace of the polymer from table 1, entry 1.



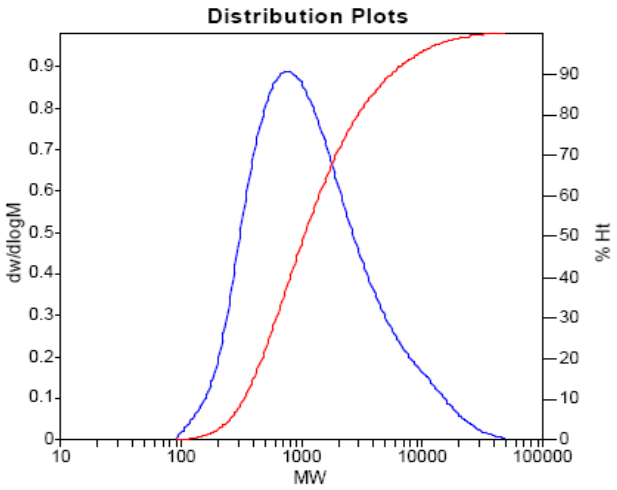
MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	103768	62398	128352	219186	325420	118122	2.05699

Processed Peaks

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1		11.52	13.02	15.08	-15.586	100	1296.84	100

Figure S35. GPC trace of the polymer from table 1, entry 2.



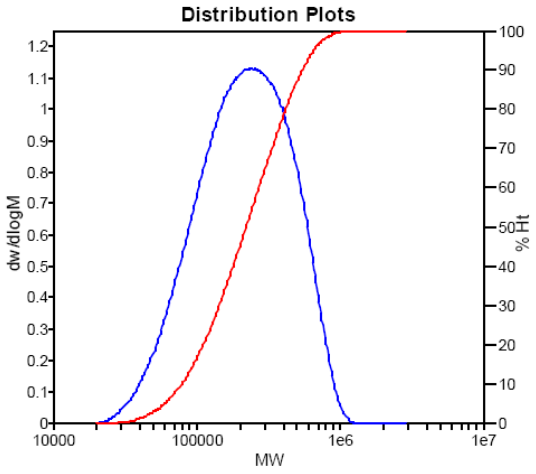
MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	792	726	2314	8560	17897	1899	3.18733

Processed Peaks

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1		13.53	16.37	17.78	-12.9743	100	1363.7	100

Figure S36. GPC trace of the polymer from table 1, entry 4.



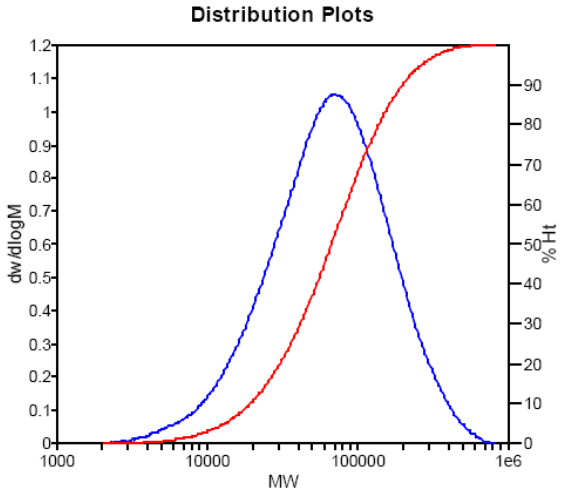
MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	236353	159341	269150	399581	518530	252656	1.68914

Processed Peaks

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1		15.77	18.40	21.02	-10.1055	100	1305.45	100

Figure S37. GPC trace of the polymer from table 1, entry 5.



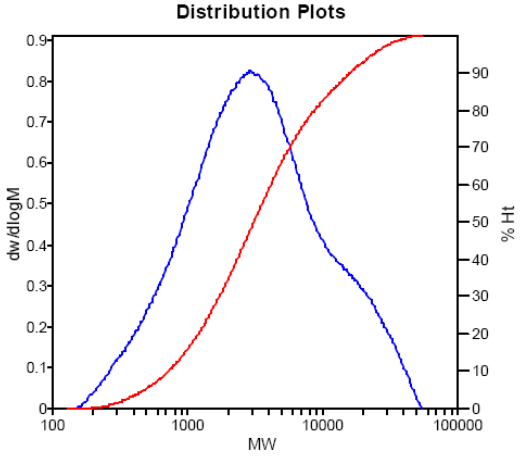
MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	71285	40732	91945	169896	262525	83565	2.25732

Processed Peaks

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1		17.10	19.67	23.42	-12.6874	100	1758.47	100

Figure S38. GPC trace of the polymer from table 1, entry 6.



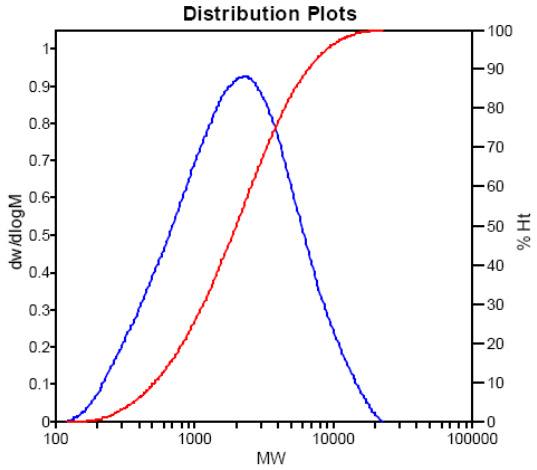
MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	2947	1722	5998	15838	25324	5086	3.48316

Processed Peaks

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1		19.95	23.03	26.32	-5.94699	100	1054.12	100

Figure S39. GPC trace of the polymer from table 1, entry 7.



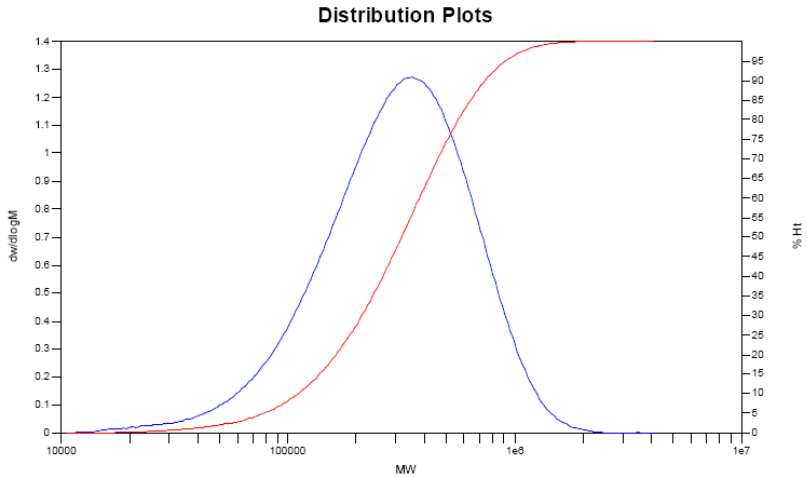
MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	2254	1205	2923	5778	8879	2620	2.42573

Processed Peaks

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1		20.88	23.32	26.40	-10.0504	100	1583.83	100

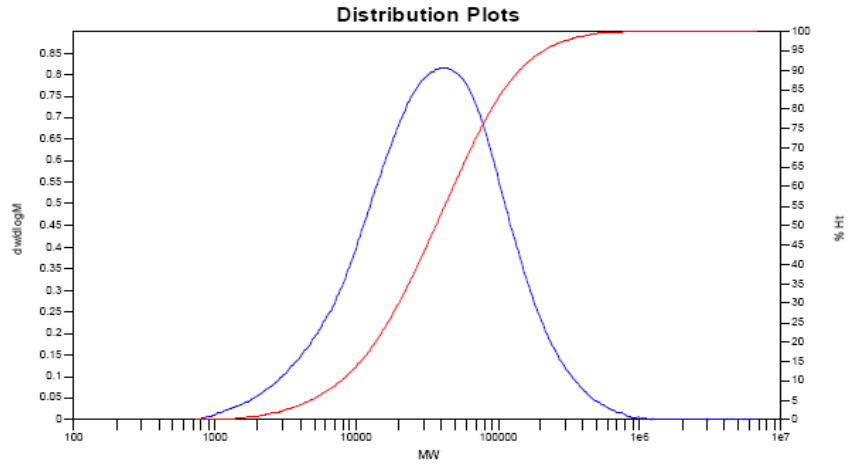
Figure S40. GPC trace of the polymer from table 1, entry 8.



MW Averages

Mp: 351176	Mn: 211433	Mv: 352708	Mw: 378170
Mz: 569750	Mz+1: 783278	PD: 1.7886	

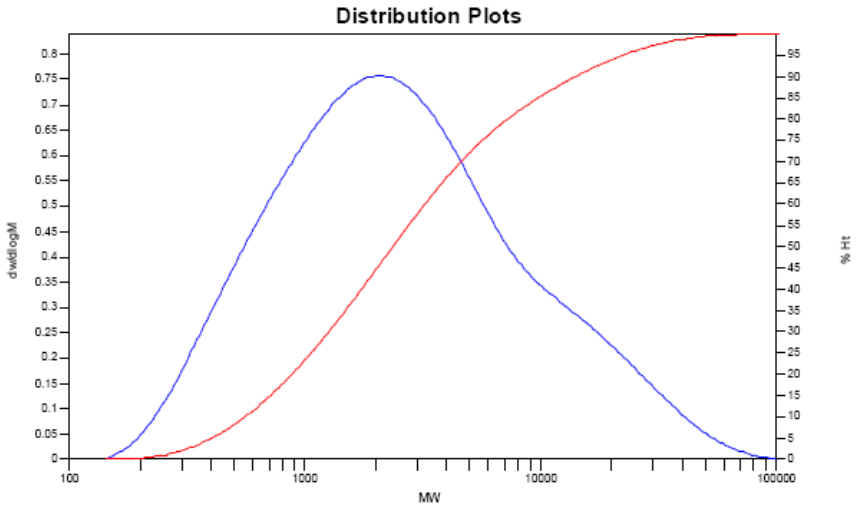
Figure S41. GPC trace of the polymer from table 1, entry 9.



MW Averages

Mp: 38971	Mn: 17166	Mv: 52865	Mw: 63102
Mz: 232559	Mz+1: 1674749	PD: 3.6760	

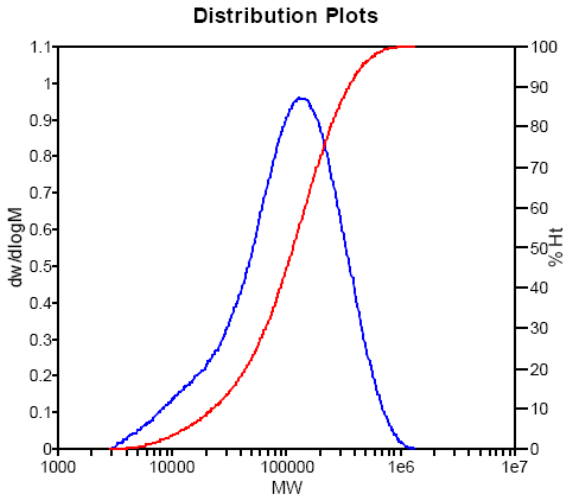
Figure S42. GPC trace of the polymer from table 1, entry 10.



MW Averages

Mp: 2095	Mn: 1363	Mv: 4301	Mw: 5381
Mz: 18531	Mz+1: 34555	PD: 3.9479	

Figure S43. GPC trace of the polymer from table 1, entry 12.



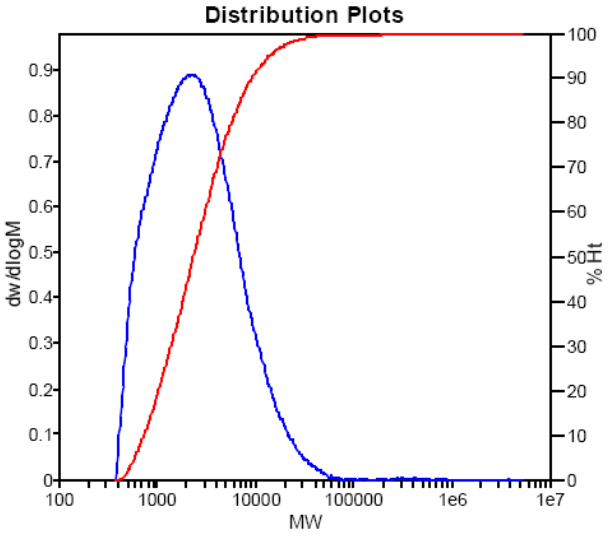
MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	132118	52383	157763	296507	440314	140311	3.01172

Processed Peaks

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1		16.77	19.15	23.07	-9.42904	100	1392.22	100

Figure S44. GPC trace of the polymer from table 1, entry 18.



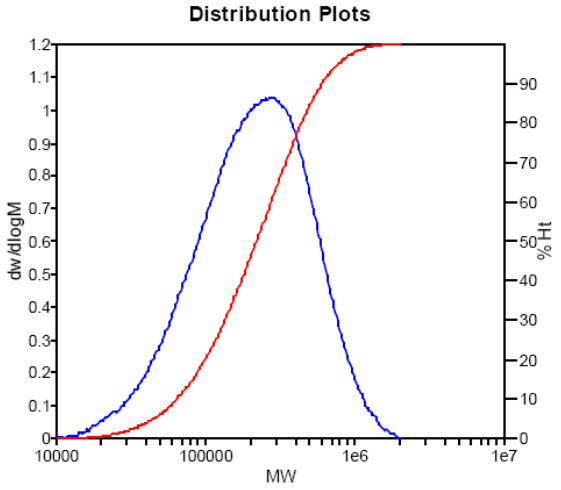
MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	2171	1666	5185	267522	2714158	3899	3.11224

Processed Peaks

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1		15.17	23.25	25.07	-9.96733	100	1608.56	100

Figure S45. GPC trace of the polymer from table 1, entry 19.



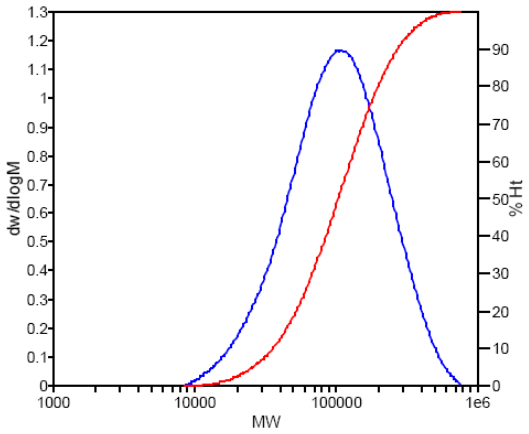
MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	280825	137793	286906	488734	706643	263558	2.08215

Processed Peaks

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1		16.05	18.08	21.50	-6.88015	100	943.764	100

Figure S46. GPC trace of the polymer from table 1, entry 25.



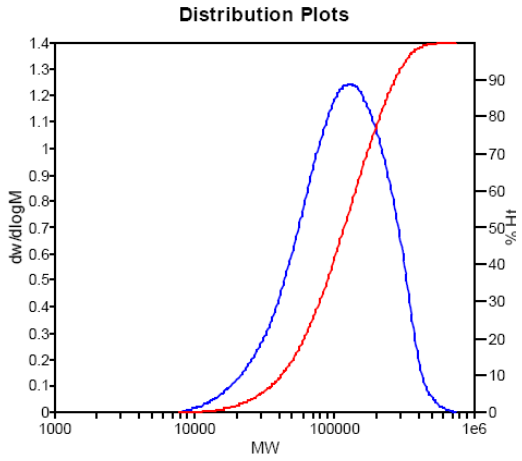
MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	109128	73053	132309	212987	299994	122939	1.81114

Processed Peaks

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1		17.17	19.22	21.92	-14.1586	100	1769.45	100

Figure S47. GPC trace of the polymer from table 1, entry 26.



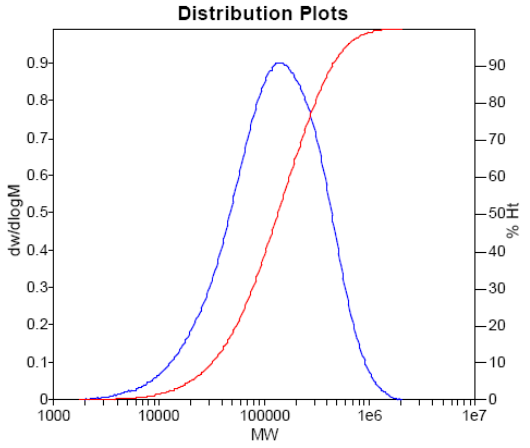
MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	129802	82549	138960	200559	258812	131038	1.68336

Processed Peaks

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1		17.20	19.05	22.02	-15.4164	100	1808.21	100

Figure S48. GPC trace of the polymer from table 1, entry 27.



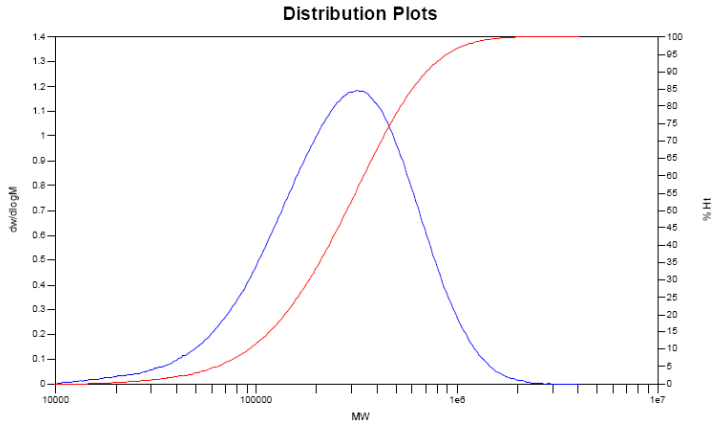
MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	142912	67001	194659	386858	609032	173997	2.90531

Processed Peaks

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1		11.00	12.80	15.78	-13.037	100	1353.42	100

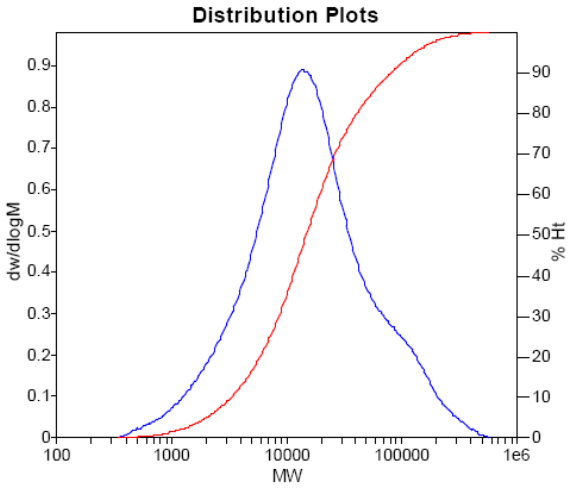
Figure S49. GPC trace of the polymer from table 1, entry 28.



MW Averages

Mp: 317779	Mn: 179615	Mv: 322502	Mw: 349576
Mz: 562983	Mz+1: 816282	PD: 1.9463	

Figure S50. GPC trace of the polymer from table 1, entry 29.



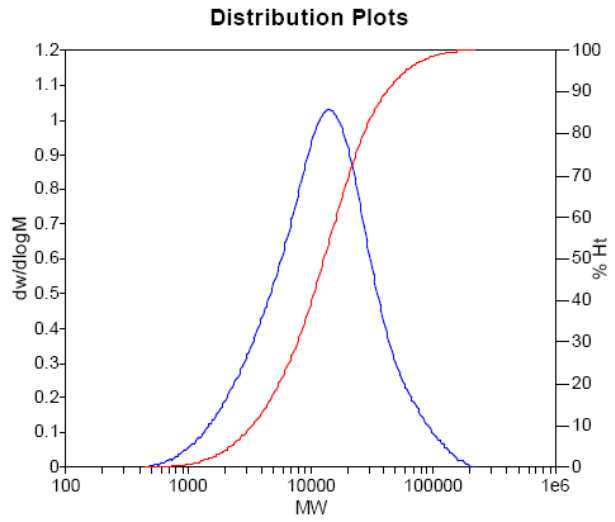
MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	14124	7342	31655	109360	210325	25935	4.3115

Processed Peaks

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1		11.87	14.37	16.87	-9.46533	100	995.816	100

Figure S51. GPC trace of the polymer from table 2, entry 1.



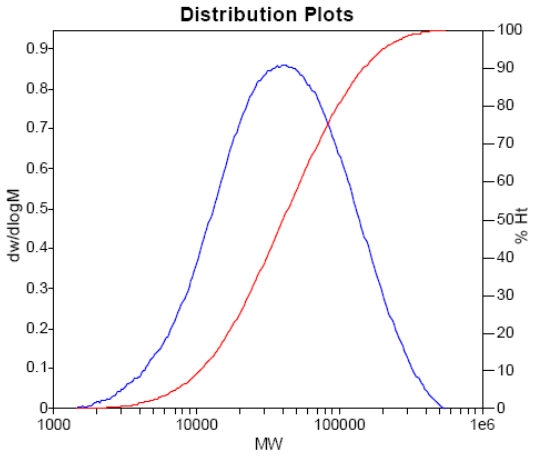
MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	13780	7390	19069	41920	73902	16942	2.58038

Processed Peaks

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1		12.52	14.38	16.72	-8.0259	100	729.131	100

Figure S52. GPC trace of the polymer from table 2, entry 2.



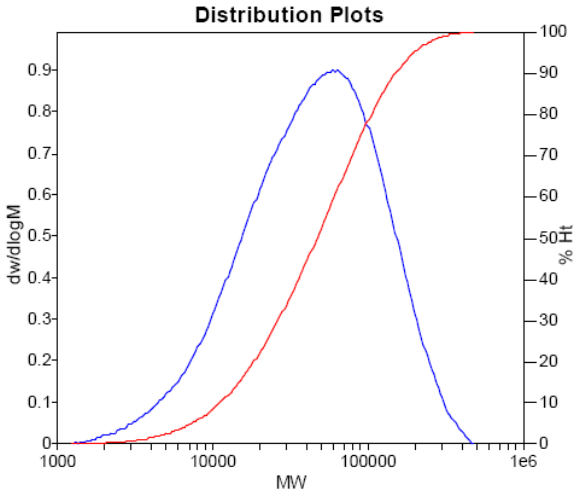
MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	41729	23273	62645	131272	206199	55540	2.69175

Processed Peaks

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1		11.90	13.63	15.90	-6.3578	100	692.592	100

Figure S53. GPC trace of the polymer from table 2, entry 3.



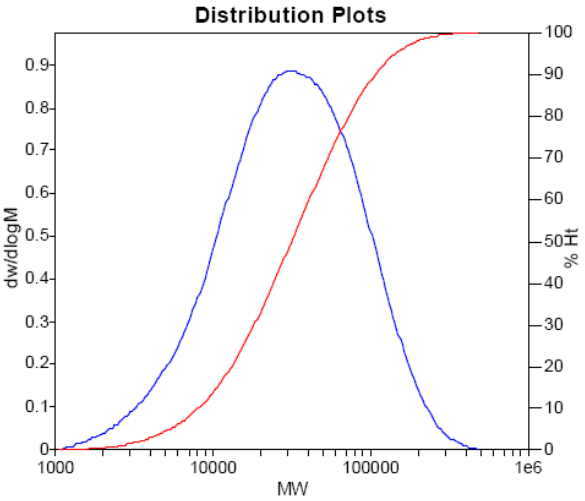
MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	58903	24644	65901	124552	183244	59227	2.67412

Processed Peaks

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1		11.98	13.40	16.02	-7.81307	100	811.244	100

Figure S54. GPC trace of the polymer from table 2, entry 4.



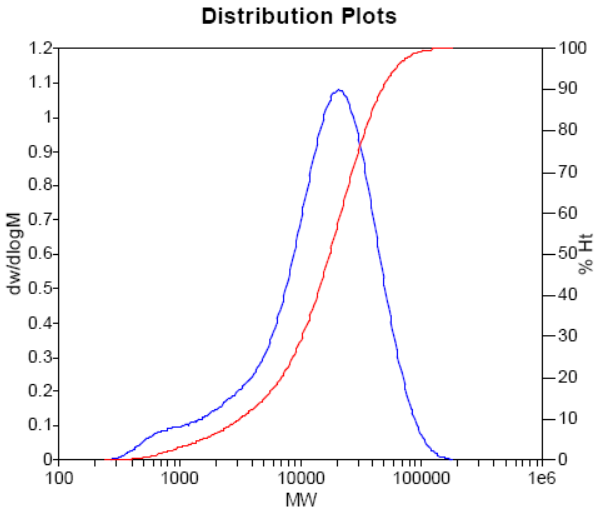
MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	30299	17673	46730	95074	152429	41697	2.64415

Processed Peaks

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1		11.98	13.85	16.13	-7.84762	100	827.975	100

Figure S55. GPC trace of the polymer from table 2, entry 5.



MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	20868	6552	22031	38785	56276	19798	3.36248

Processed Peaks

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1		12.75	14.20	17.18	-11.5082	100	981.335	100

Figure S56. GPC trace of the polymer from table 2, entry 6.

4 DSC data of (co)polymers

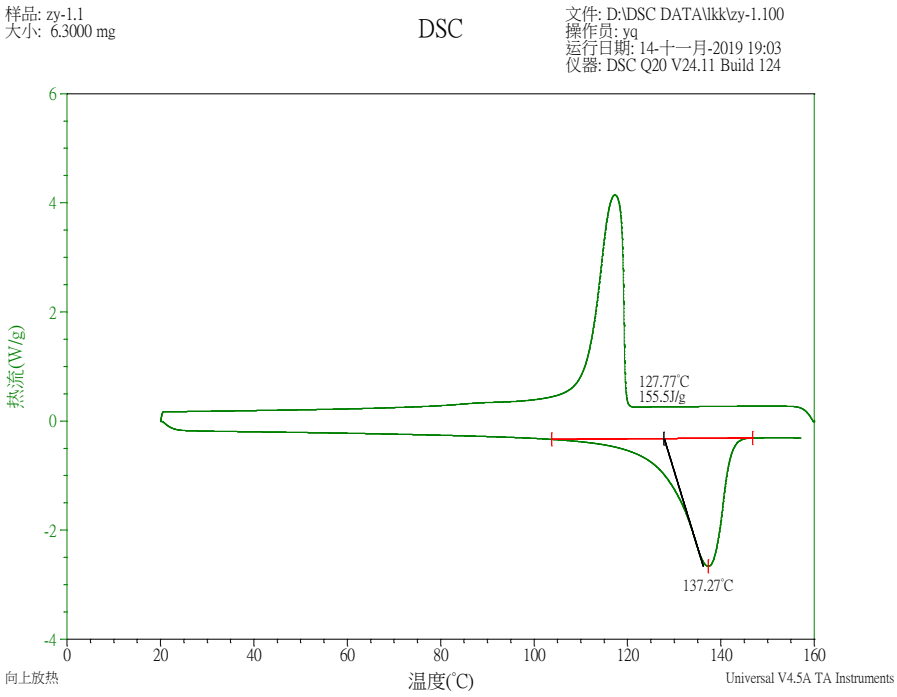


Figure S57. DSC data of the polymer from table 1, entry 1.

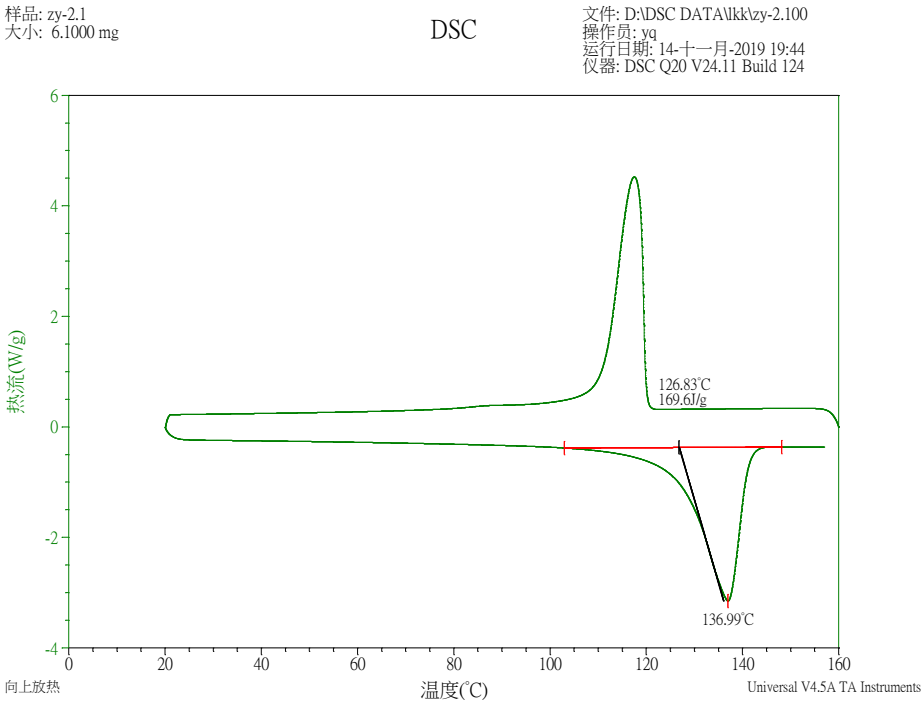


Figure S58. DSC data of the polymer from table 1, entry 2.

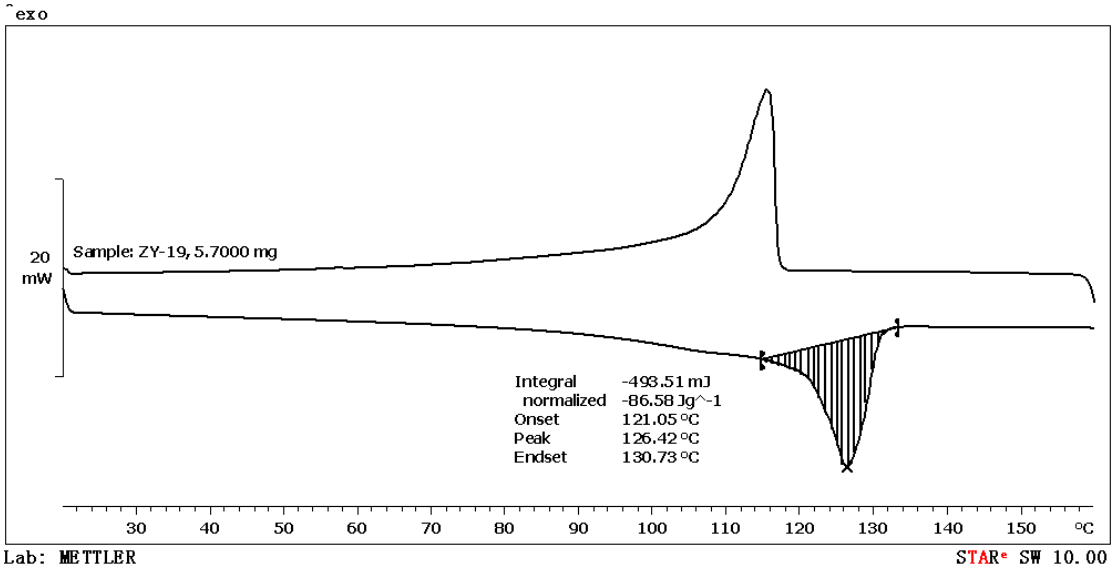


Figure S59. DSC data of the polymer from table 1, entry 3.

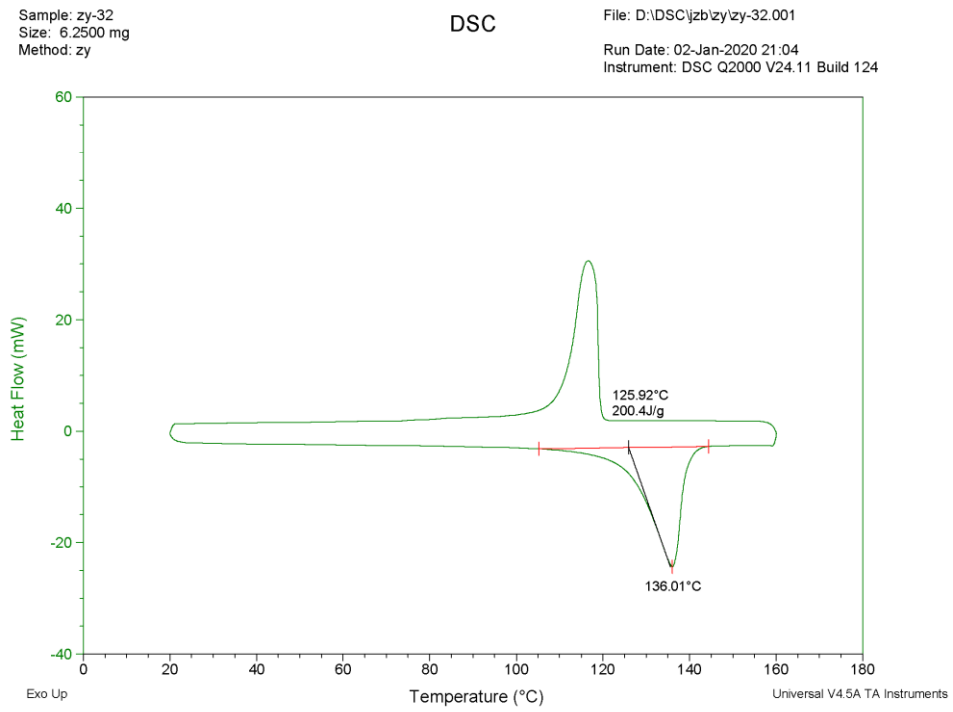


Figure S60. DSC data of the polymer from table 1, entry 5.

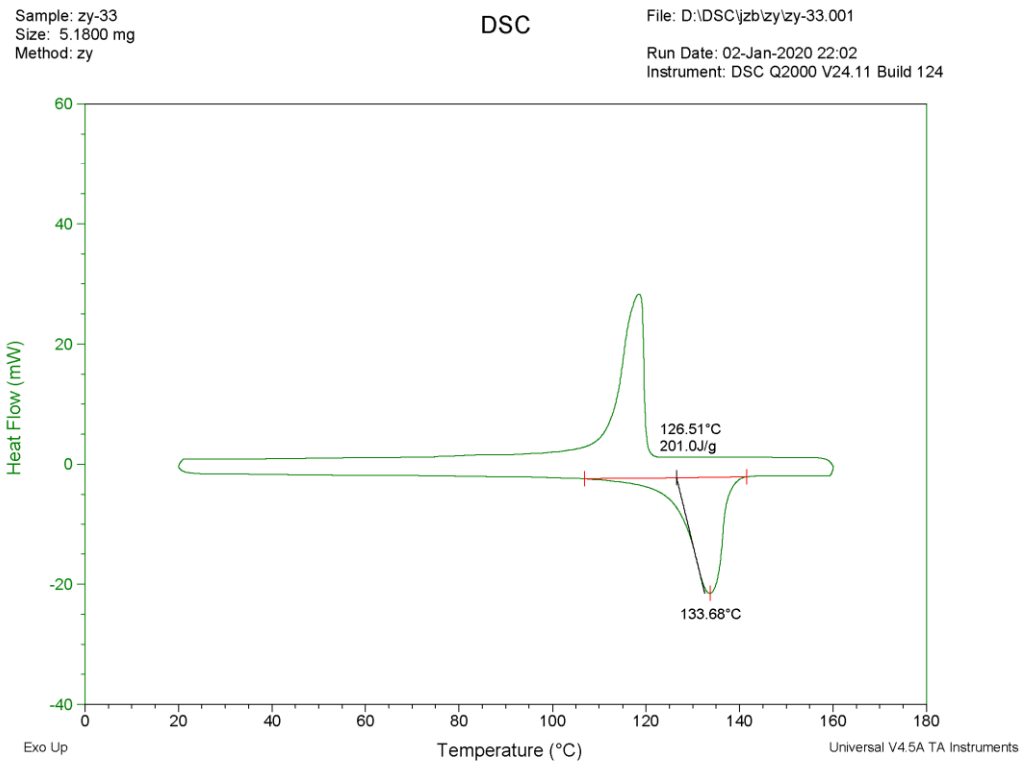


Figure S61. DSC data of the polymer from table 1, entry 6.

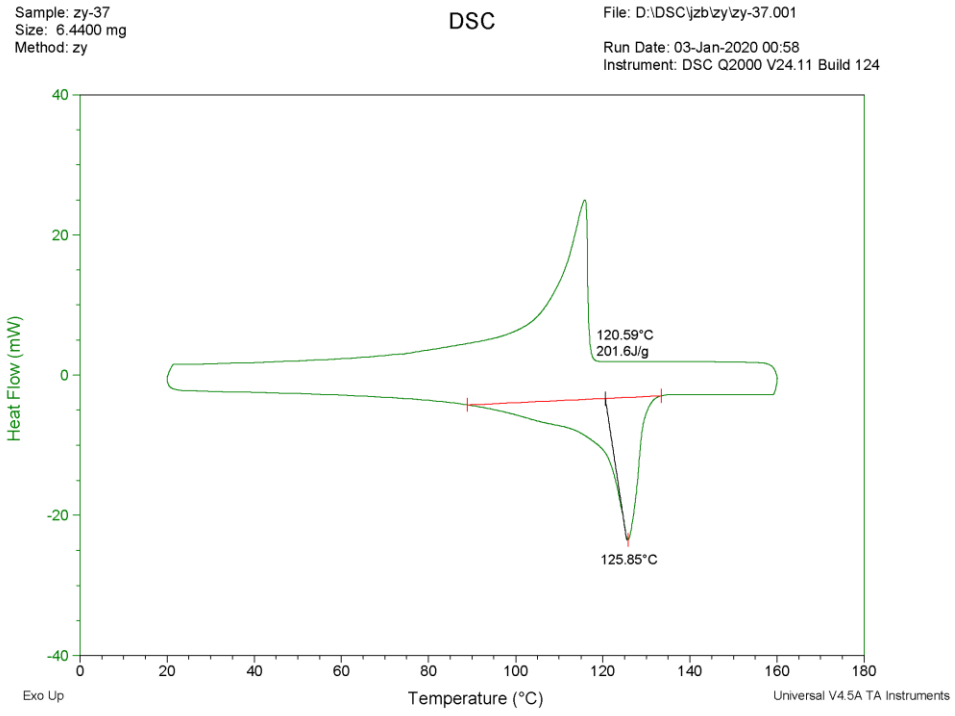


Figure S62. DSC data of the polymer from table 1, entry 7.

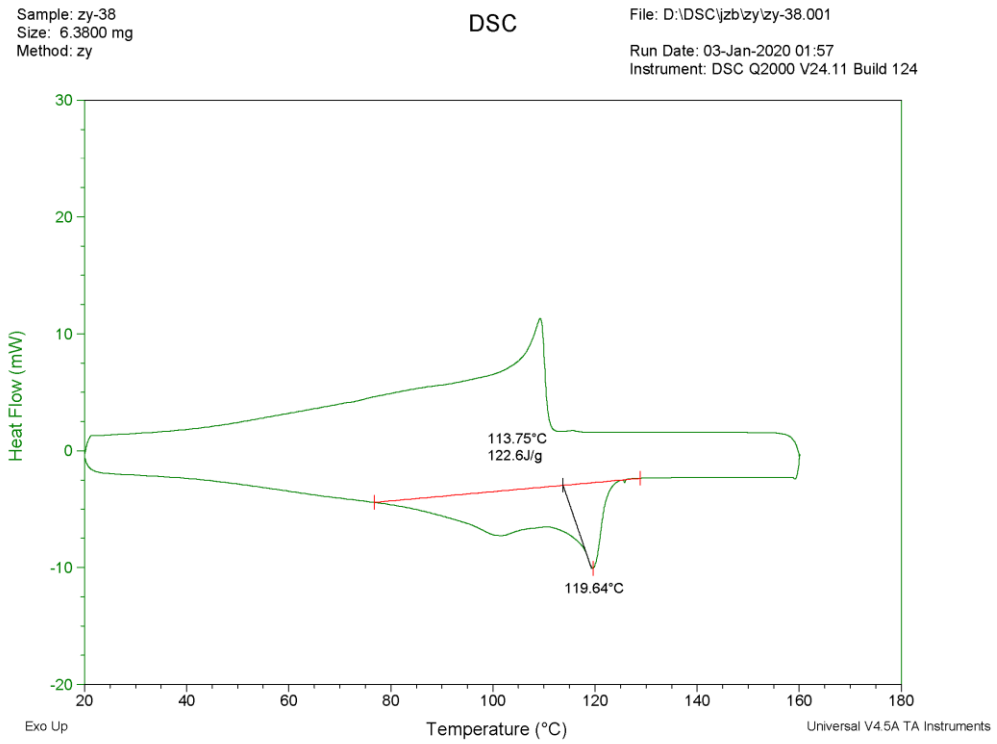


Figure S63. DSC data of the polymer from table 1, entry 8.

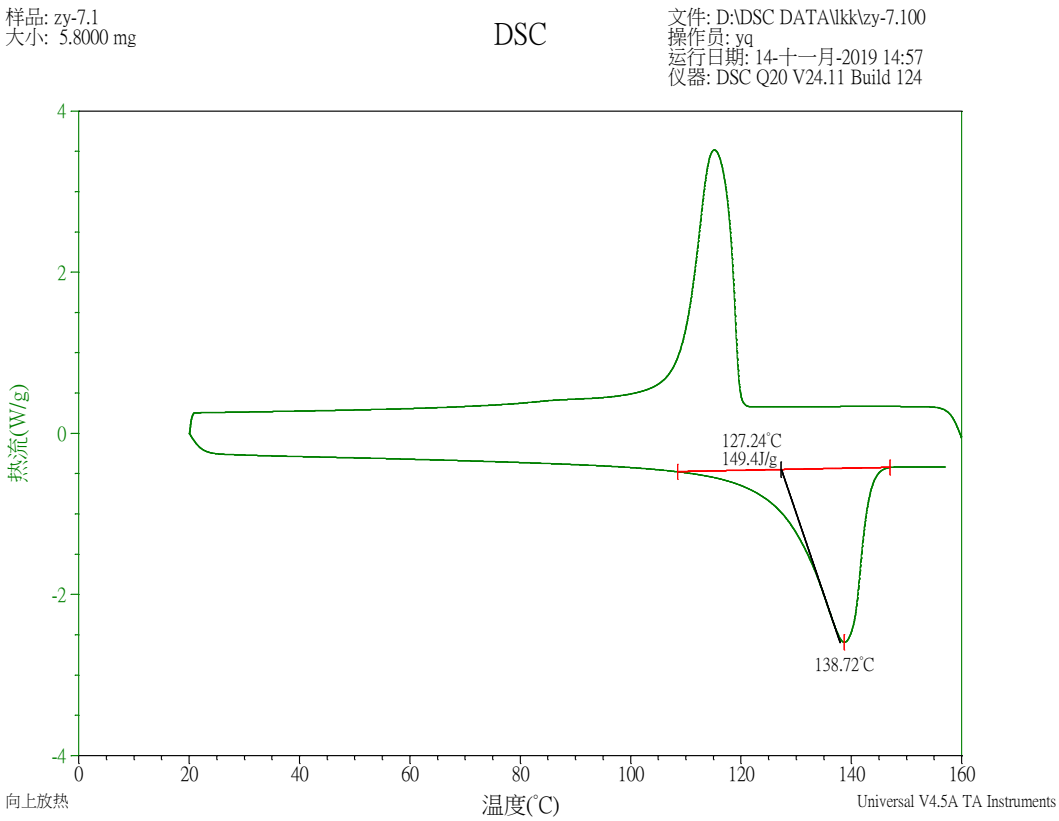


Figure S64. DSC data of the polymer from table 1, entry 9.

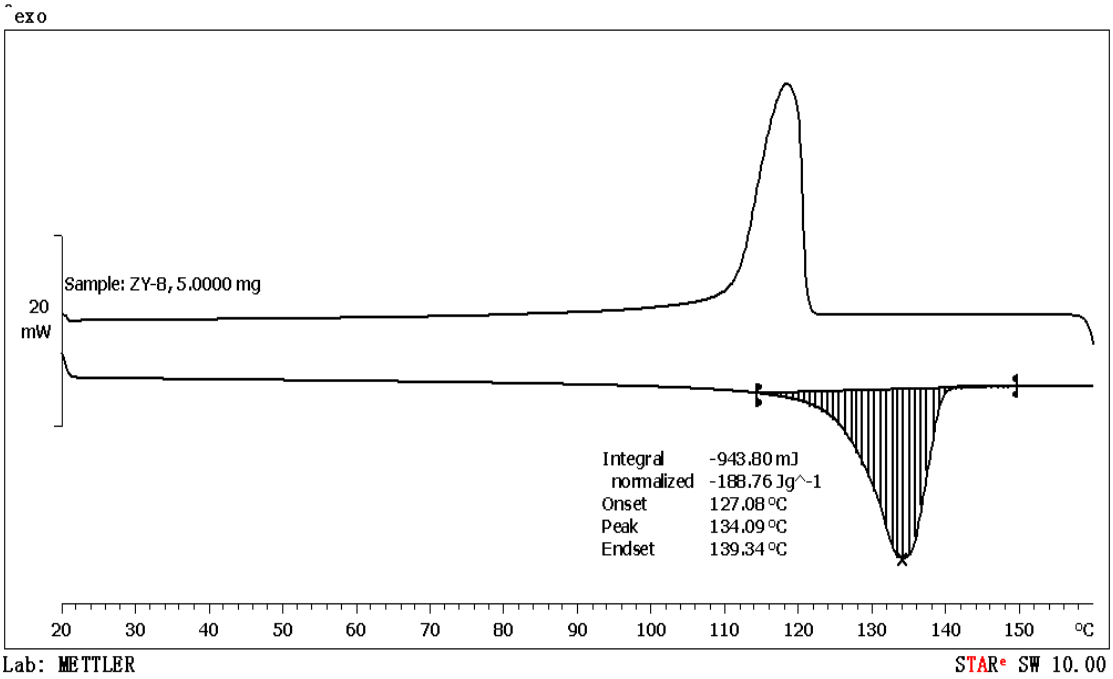


Figure S65. DSC data of the polymer from table 1, entry 10.

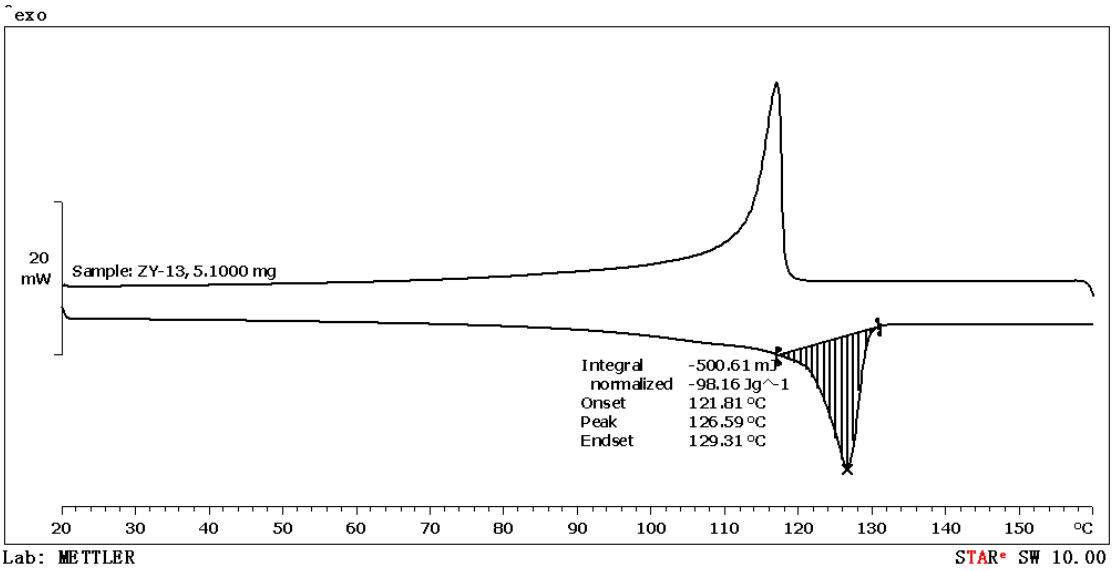


Figure S66. DSC data of the polymer from table 1, entry 11.

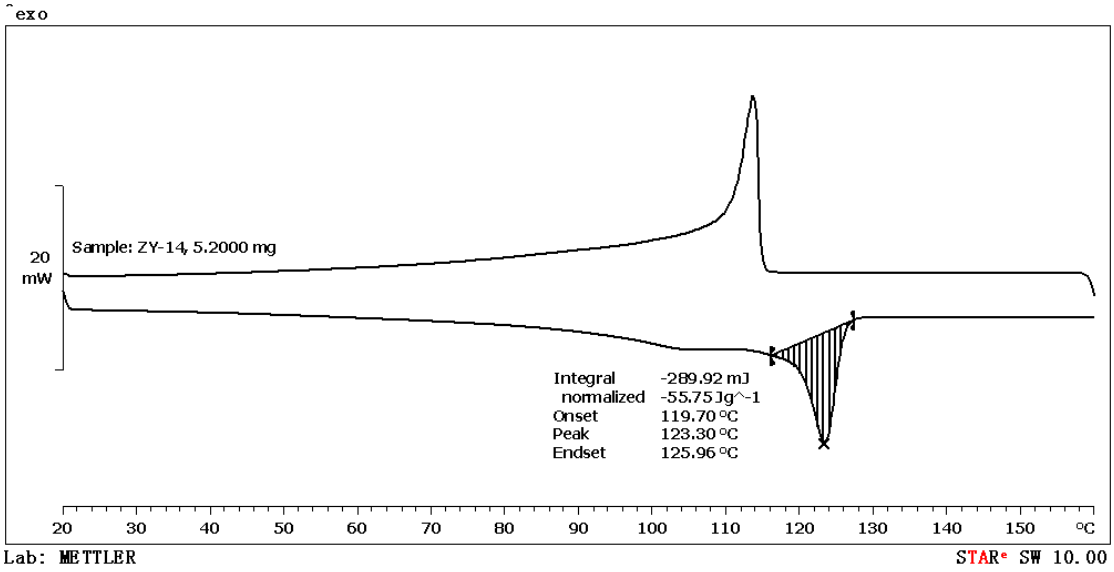


Figure S67. DSC data of the polymer from table 1, entry 12.

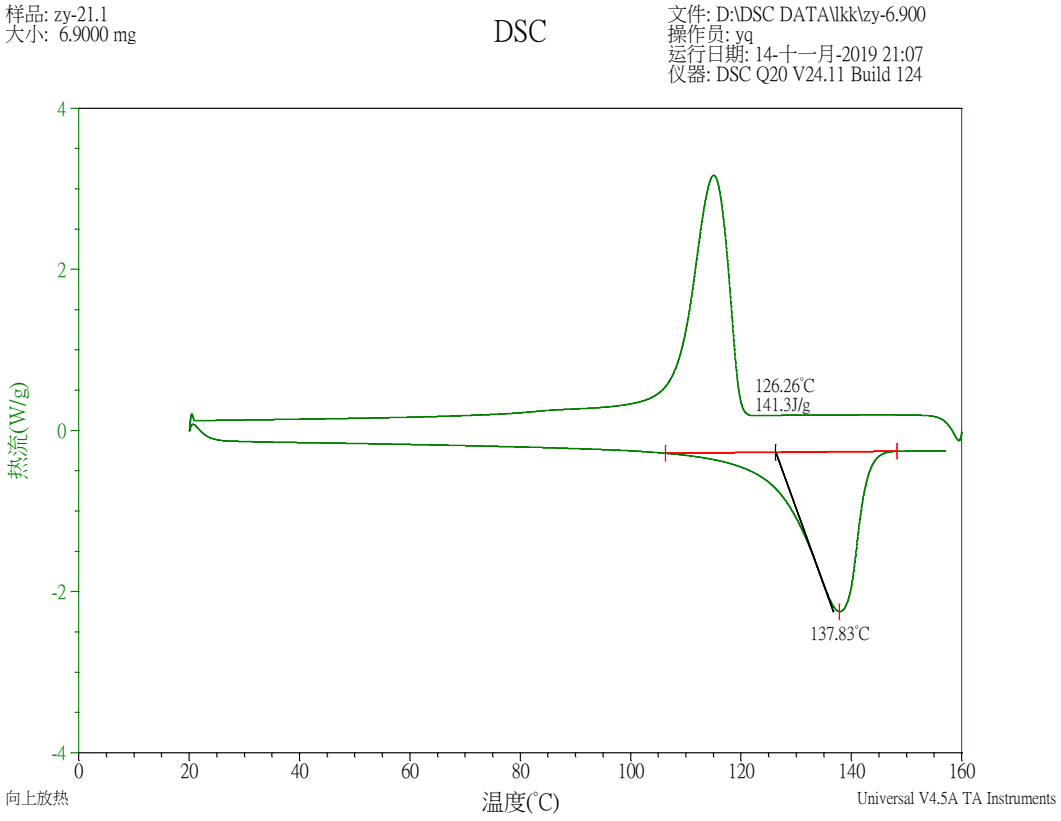


Figure S68. DSC data of the polymer from table 1, entry 18.

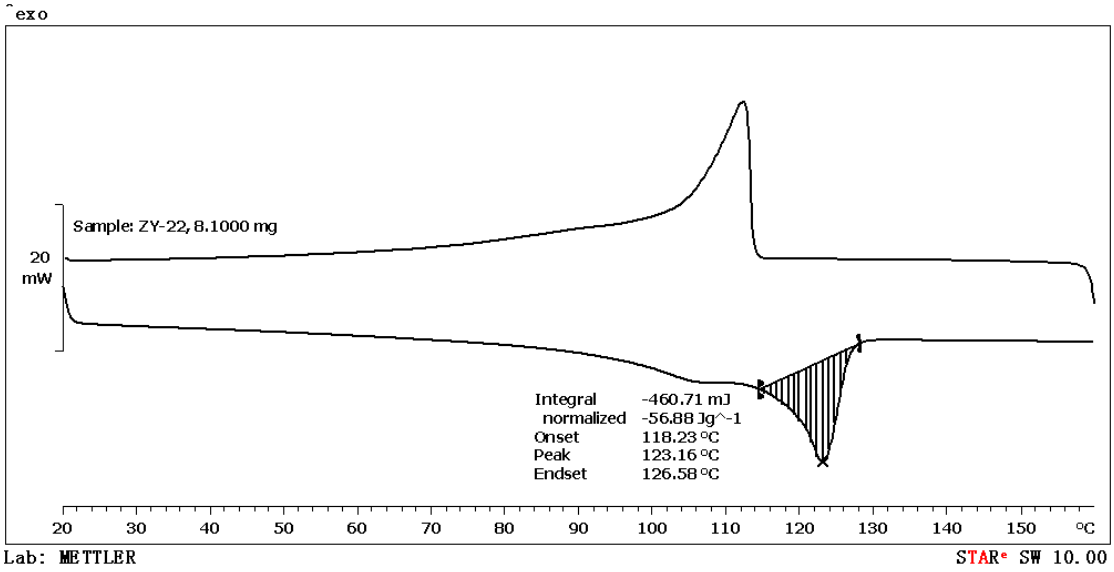


Figure S69. DSC data of the polymer from table 1, entry 19.

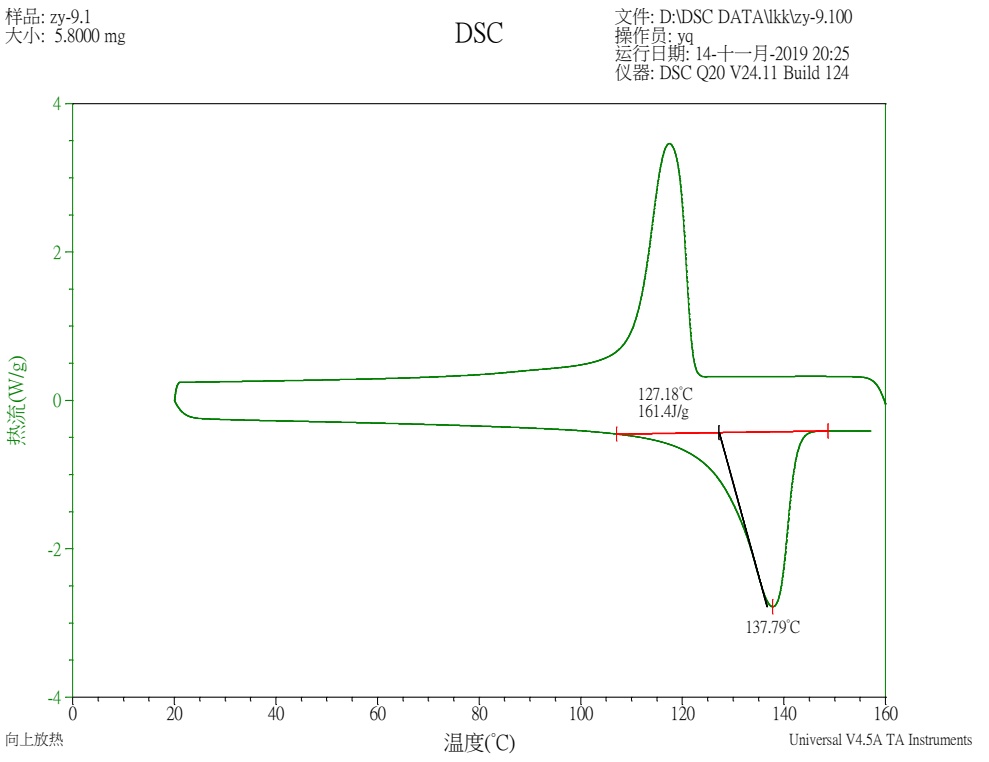


Figure S70. DSC data of the polymer from table 1, entry 25.

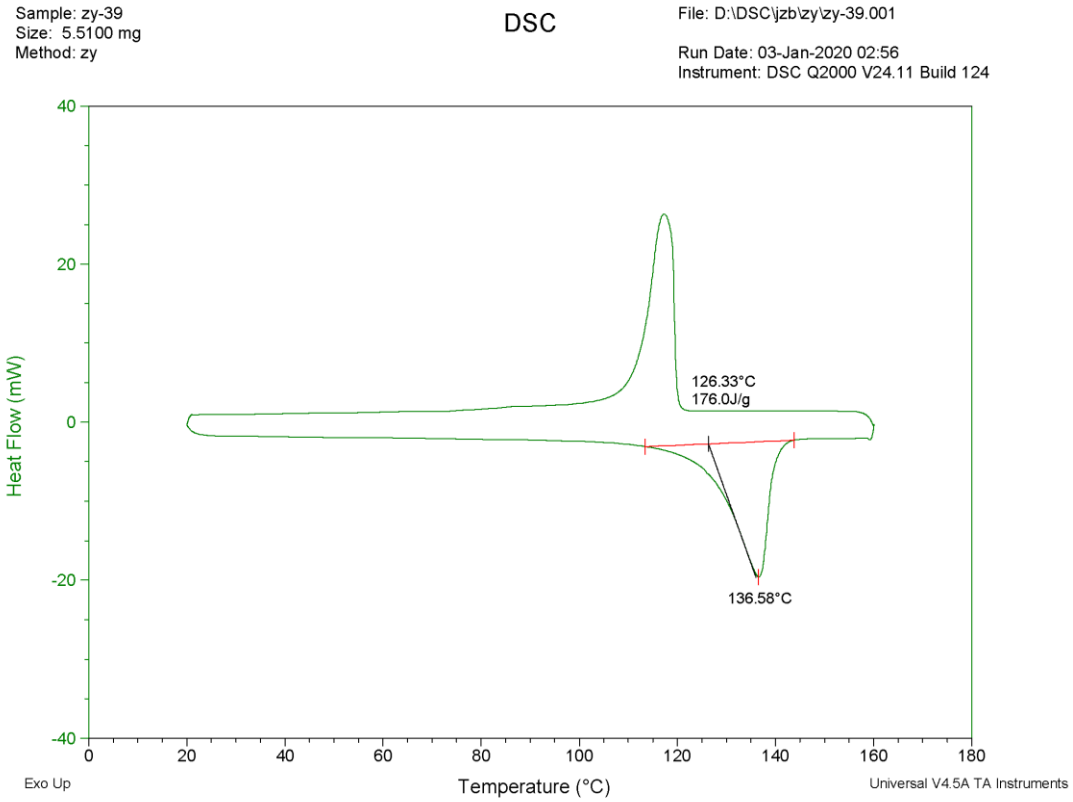


Figure S71. DSC data of the polymer from table 1, entry 26.

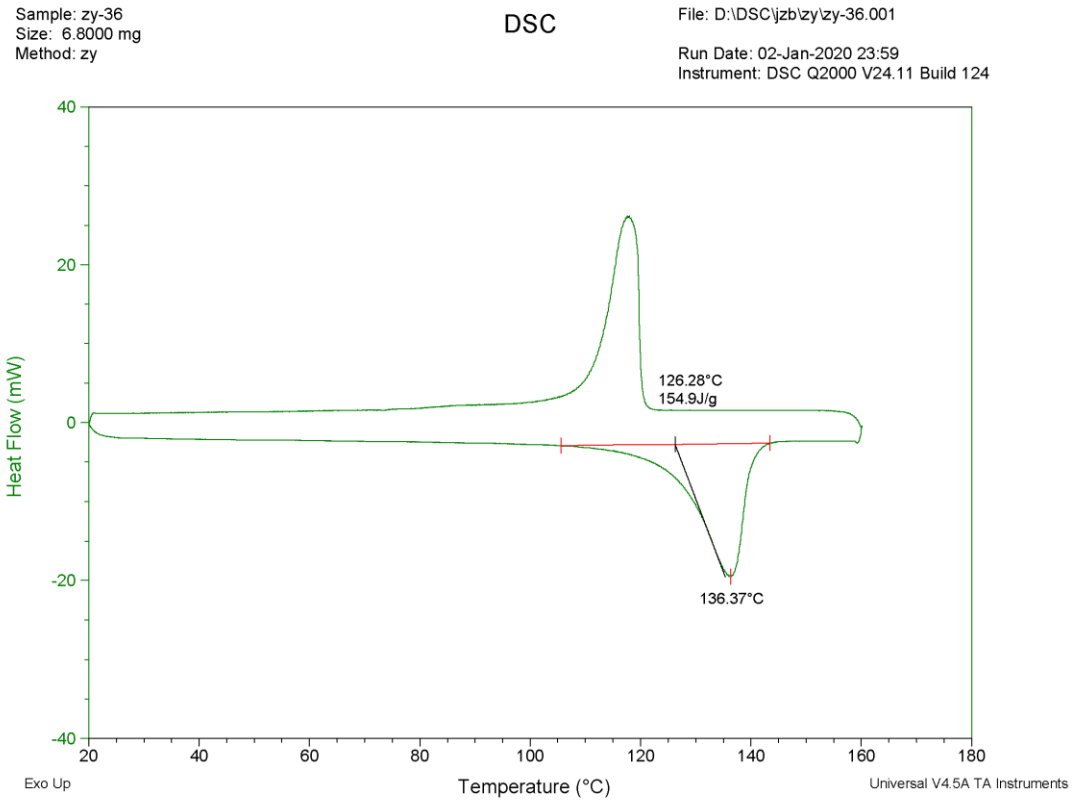


Figure S72. DSC data of the polymer from table 1, entry 27.

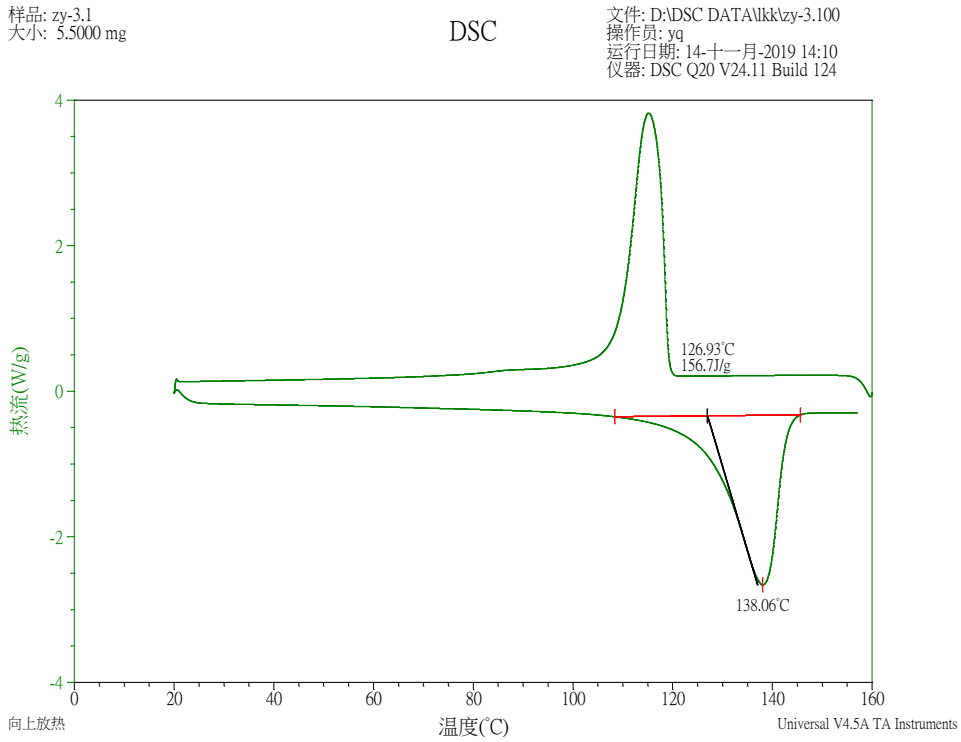


Figure S73. DSC data of the polymer from table 1, entry 28.

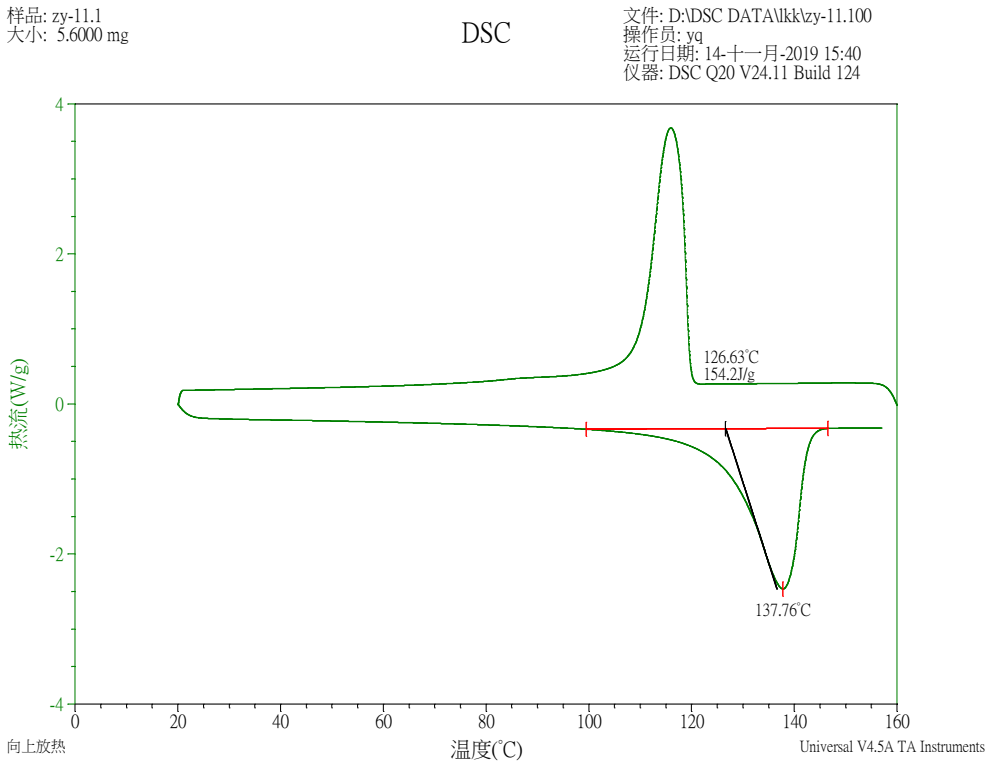


Figure S74. DSC data of the polymer from table 1, entry 29.

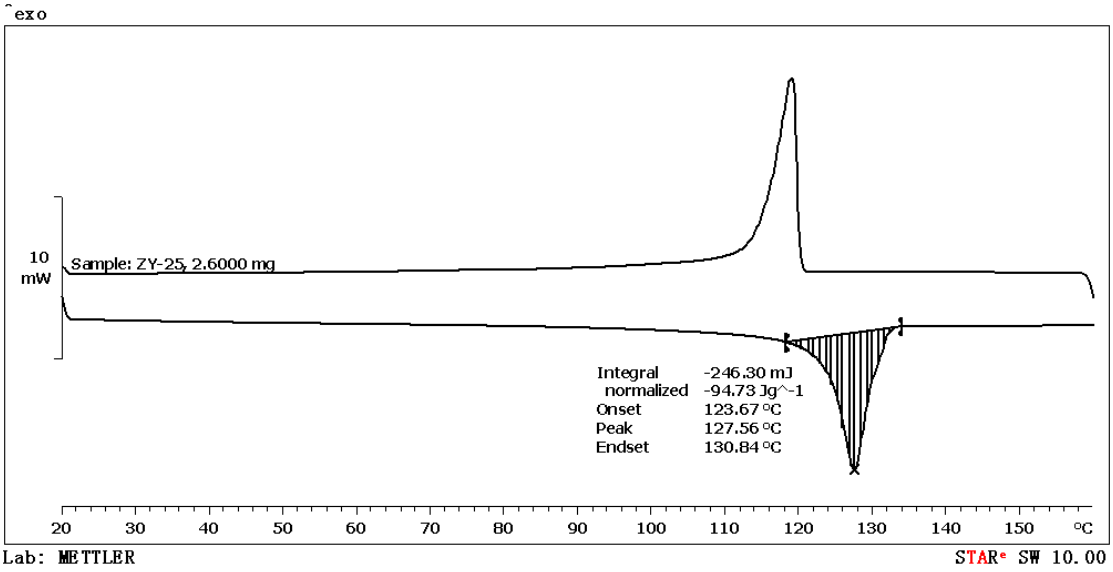


Figure S75. DSC data of the polymer from table 2, entry 1.

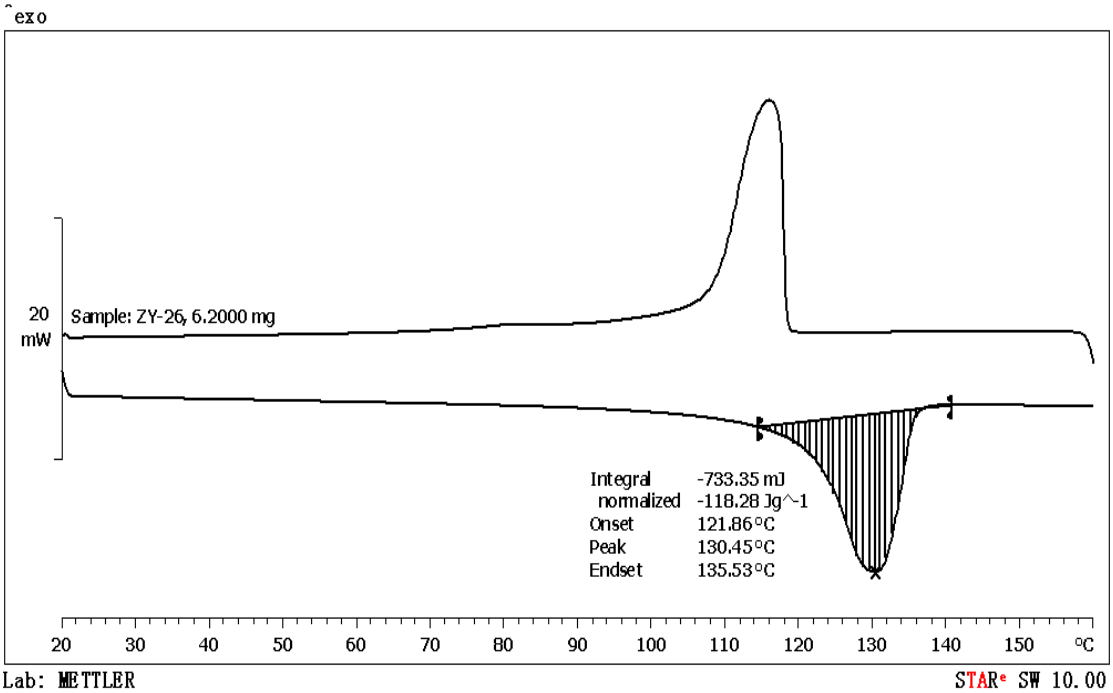


Figure S76. DSC data of the polymer from table 2, entry 3.

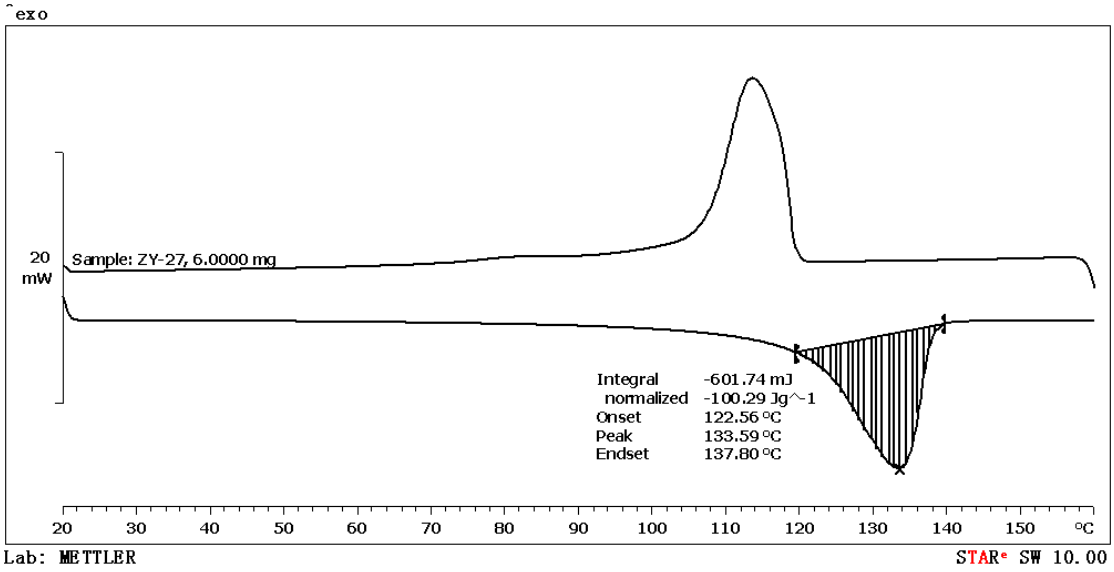


Figure S77. DSC data of the polymer from table 2, entry 4.

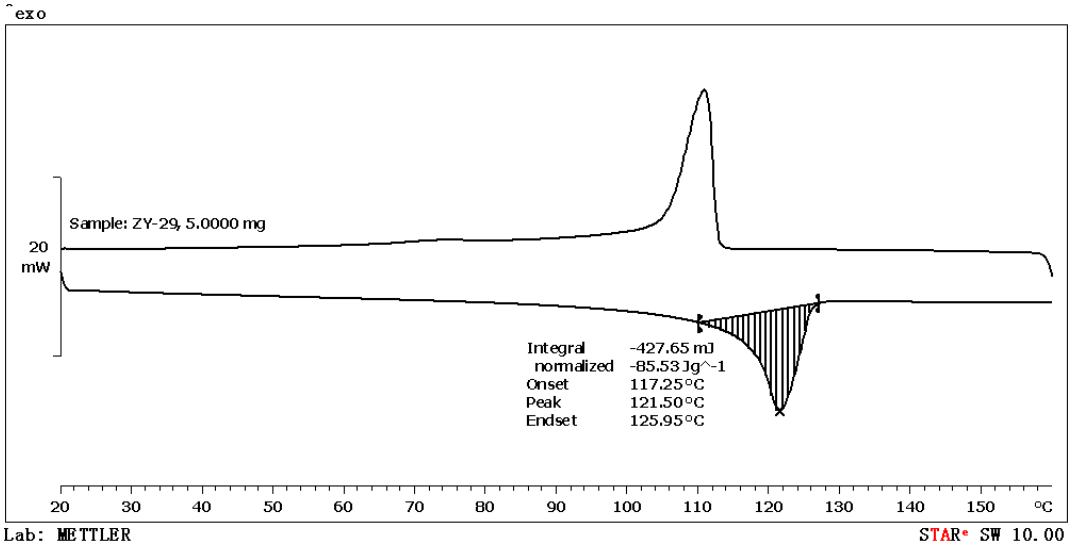


Figure S78. DSC data of the polymer from table 2, entry 5.

5 Crystallographic data for Ni2

Table S1. Crystallographic data for **Ni2**.

	Ni2
Formula	$C_{62}H_{116}NiO_4P_2$
Formula weight	987.73
Crystal dimensions (mm^3)	0.30 × 0.28 × 0.27
Crystal system	triclinic
Space group	P^{-1}
a (Å)	13.6395(4)
b (Å)	14.5011(4)
c (Å)	16.4868(5)
α (°)	98.6220(10)
β (°)	96.0890(10)
γ (°)	98.2070(10)
Volume ($Å^3$)	3163.83(16)
Z	2
T (K)	173(2)
D_{calcd} (g cm^{-3})	1.037
μ (mm^{-1})	1.223
F (000)	1040
No. of rflns. collected	20156
No. of indep. rflns. /R_{int}	8767 / 0.0617
No. of obsd. rflns. [$I_0 > 2\sigma(I_0)$]	7392
Data / restraints / parameters	8767 / 0 / 622
R_1 / wR_2 [$I_0 > 2\sigma(I_0)$]	0.0719 / 0.1812
R_1 / wR_2 (all data)	0.0815 / 0.1898
GOF (on F^2)	1.053
Largest diff. peak and hole (e $Å^{-3}$)	0.666 / -0.768
CCDC No.	1965065