Synthesis of Lightly Branched Ultrahigh-Molecular-Weight Polyethylene Using Cationic Benzocyclohexyl Nickel Catalysts

Zhengpeng Yan[†a], Guanru Chang[†a,b], Wenping Zou[c], Gen Luo[a]*, Shengyu Dai[a]*

[a]Institutes of Physical Science and Information Technology, Key Laboratory of Structure and Functional Regulation of Hybrid Materials of Ministry of Education, Anhui University, Hefei, Anhui, 230601, China.
[b]School of Chemistry and Chemical Engineering, Key Laboratory of Inorganic Functional Material, Huangshan University, Huangshan, Anhui 245041, China
[c]Department of Chemistry, University of Houston, 4800 Calhoun Rd, Houston, TX 77004, USA

[†]The first two authors are equal first authors.

*To whom correspondence should be addressed. luogen@ahu.edu.cn (Gen Luo); daiyu@ustc.edu.cn (Shengyu Dai).

1. Experimental sections

1.1 General Considerations

All chemicals were commercially sourced, except those whose synthesis is described. All experiments were carried out under a dry nitrogen atmosphere using standard Schlenk techniques or in a glove-box. Deuterated solvents used for NMR were dried and distilled prior to use. ^{1}H, ^{13}C NMR spectra were recorded by a JNM-ECZ600R or JNM-ECZ400R spectrometer at ambient temperature unless otherwise stated. The chemical shifts of the ^{1}H and ^{13}C NMR spectra were referenced to the residual solvent; Coupling constants are in Hz. Mass spectra were obtained by the Analytical Center of Anhui University. Elemental analysis was performed by the Analytical Center of 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 polymers were determined by gel permeation chromatography (GPC) with a PL 210 equipped

with one Shodex AT-803S and two Shodex AT-806MS columns at 150 °C using trichlorobenzene as a solvent and calibrated with polystyrene standards. Stress/strain experiments were performed at 10 mm/min by means of a Universal Test Machine (UTM2502) at room temperature. Polymers were melt-pressed at 50 °C above their melting point to obtain the test specimens. The test specimens have 14-mm gauge length, 2-mm width, and thickness of 0.5 mm. Differential scanning calorimetry (DSC) was performed by a DSC Q25 from TA Instruments. Samples were quickly heated to 150°C and kept for 5 min to remove thermal history, then cooled to -70°C at a rate of 10 K/min, and finally reheated to 150°C 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).

**1.2 Procedure for the Synthesis of Ligands L1-L2.**
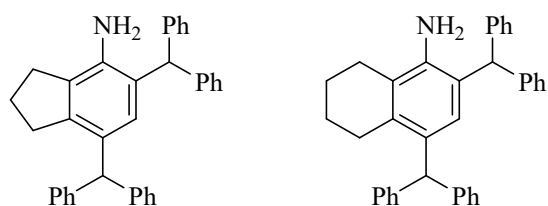
These compounds were synthesized by the reported literature.[1]
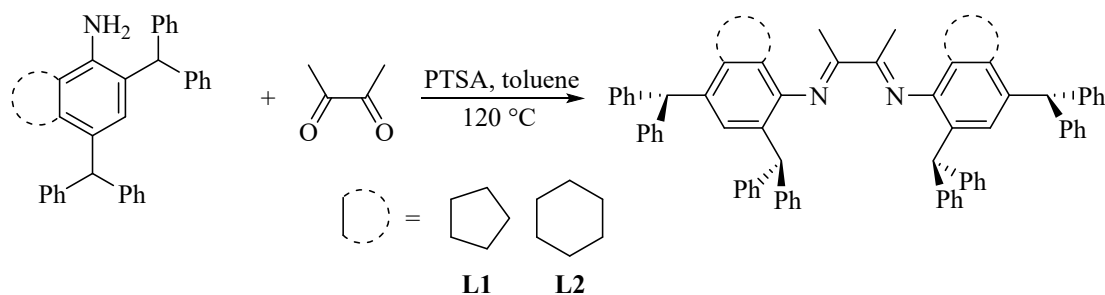
A mixture of aniline (4.2 mmol), 2,3-butanedione (0.172 g, 2 mmol), and a catalytic amount of *p*-toluenesulfonic acid in 20 mL toluene was refluxed for 72 h. The solution was evaporated at reduced pressure, and the remaining solution was diluted in ethanol (20 mL). The yellow solid was isolated by filtration, followed by recrystallization from dichloromethane and ethanol.
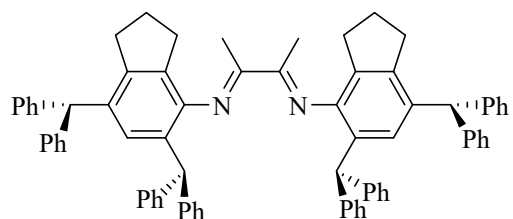
L1 (1.33 g, 68%). ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.15 - 6.97 (m, 24H, Ar-*H*), 6.93 (d, *J* = 7.1 Hz, 4H, Ar-*H*), 6.83 (dd, *J* = 16.6, 7.7 Hz, 12H, Ar-*H*), 6.19 (s, 2H, Ar-*H*), 5.38 (s, 2H, -C*H*-), 5.19 (s, 2H, -C*H*-), 2.62 (dd, *J* = 26.9, 7.1 Hz, 4H, -C*H$_2$*-), 2.44 (dd, *J* = 16.4, 10.1 Hz, 2H, -C*H$_2$*-), 2.40-2.29 (m, 2H, -C*H$_2$*-), 1.99 - 1.86 (m, 4H, -C*H$_2$*-), 1.24 (s, 6H, Ar-C(C*H$_3$*)=N). ^{13}C NMR (101 MHz, CDCl$_3$) δ 167.19 (*C*=N), 142.41, 141.10, 133.34, 130.15, 129.91, 128.44, 128.29, 128.12, 127.92, 127.20, 127.07, 126.98, 126.81, 124.96, 124.87, 124.75, 53.08 (-*C*H-), 51.31 (-*C*H-), 30.60 (-*C*H$_2$-), 29.68 (-*C*H$_2$-), 28.68 (-*C*H$_2$-), 14.64 (Ar-C(*C*H$_3$)=N). APCI-MS (m/z): calcd for C$_{74}$H$_{65}$N$_2$: 981.5148, Found, 981.5129, [M+H]$^+$.
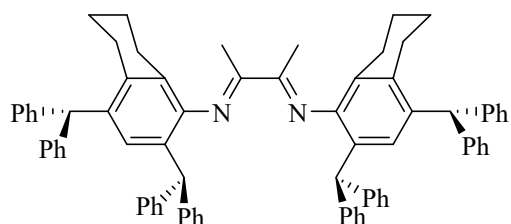

L2 (1.21 g, 60%). ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.19 - 6.93 (m, 24H, Ar-*H*), 6.88 (d, *J* = 7.0 Hz, 4H, Ar-*H*), 6.80 (t, *J* = 6.5 Hz, 8H, Ar-*H*), 6.74 (d, *J* = 6.1 Hz, 4H, Ar-*H*), 6.16 (s, 2H, Ar-*H*), 5.51 (s, 2H, -C*H*-), 5.09 (s, 2H, -C*H*-), 2.67 (d, *J* = 16.5 Hz, 2H, -C*H$_2$*-), 2.41 (d, *J* = 16.8 Hz, 2H, -C*H$_2$*-), 2.25 (d, *J* = 16.7 Hz, 2H, -C*H$_2$*-), 1.99 (dd, *J* = 15.2, 7.3 Hz, 2H, -C*H$_2$*-), 1.75 (d, *J* = 5.5 Hz, 4H, -C*H$_2$*-), 1.55 (s, 4H, -C*H$_2$*-), 1.18 (s, 6H, Ar-C(C*H$_3$*)=N). ^{13}C NMR (101 MHz, CDCl$_3$) δ 168.82 (*C*=N), 145.69, 144.05, 143.72, 143.33, 142.79, 136.64, 133.94, 129.53, 129.47, 129.26, 129.07, 128.53, 128.24, 128.08, 128.01, 127.80, 126.07, 125.93, 125.85, 125.73, 123.82, 52.59 (-*C*H-), 52.28 (-*C*H-), 26.59 (-*C*H$_2$-), 26.13 (-*C*H$_2$-), 23.03 (-*C*H$_2$-), 22.57 (-*C*H$_2$-), 15.94 (Ar-C(*C*H$_3$)=N). APCI-MS (m/z): calcd for C$_{76}$H$_{69}$N$_2$: 1009.5461, Found, 1009.5456, [M+H]$^+$.

1.3 Procedure for the Synthesis of Ligands L3-L4.
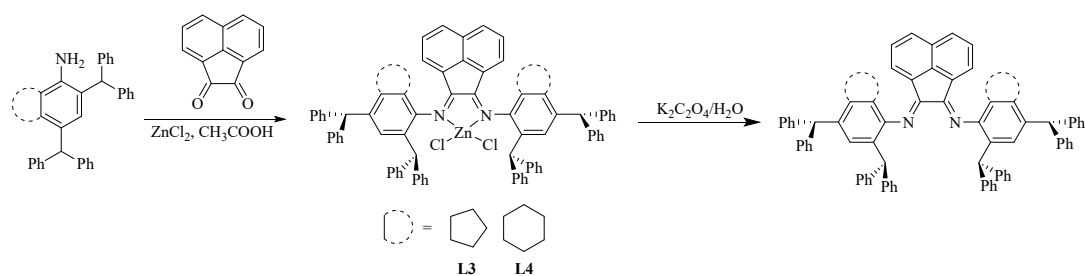
The ligands **L3-L4** were prepared as follows: $ZnCl_2$ (0.34 g, 2.5 mmol) and acenaphthoquinone (2.0 mmol), were suspended in glacial acetic acid (5 mL). Anilines (4.2 mmol) was added, and the reaction mixture was refluxed under stirring for 4 h. The solution was allowed to cool to room temperature, and a bright yellow solid precipitated. The solid was separated by filtration and washed with acetic acid (3 × 5 mL) and diethyl ether (5 × 5 mL), to remove remaining acetic acid. Drying under vacuum gave bright yellow, poorly soluble solid. Then the zinc was removed from the zinc diimine complex. The product of the previous step was suspended in methylene chloride (30 mL), and a solution of potassium oxalate (0.41 g, 2.2 mmol) in water (5 mL) was added. The reaction mixture was stirred vigorously for 1 h. The two phases were separated, and the organic layer was washed with water (3 × 20 mL) and dried with $MgSO_4$. After filtration, the solvent was removed under vacuum to afford the product as a yellow powder.
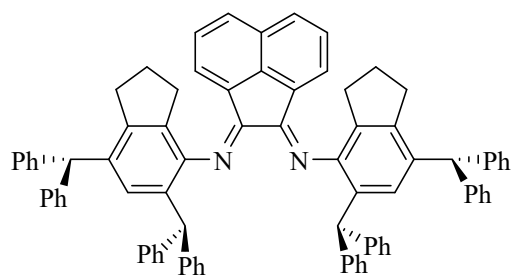
L3 (1.53 g, 71%). ^1H NMR (400 MHz, $CDCl_3$) δ 7.61 (d, *J* = 8.2 Hz, 2H, Ar-*H*), 7.35 - 7.22 (m, 8H, Ar-*H*), 7.21 - 7.11 (m, 10H, Ar-*H*), 7.10 - 6.98 (m, 12H, Ar-*H*), 6.92 (d, *J* = 7.3 Hz, 4H, Ar-*H*), 6.83 (d, *J* = 7.5 Hz, 4H, Ar-*H*), 6.37 (dd, *J* = 15.8, 8.2 Hz, 4H, Ar-*H*), 6.25 (d, *J* = 7.1 Hz, 2H, Ar-*H*), 6.11 (t, *J* = 7.3 Hz, 2H, Ar-*H*), 5.69 (d, *J* = 6.7 Hz, 2H, -C*H*-), 5.57 (d, *J* = 11.2 Hz, 2H, -C*H*-), 3.05 - 2.93 (m, 2H, -C*H*₂-), 2.87 -

2.75 (m, 2H, -CH_2-), 2.73 - 2.63 (m, 2H, -CH_2-), 2.63 - 2.51 (m, 2H, -CH_2-), 2.10 - 1.86 (m, 4H, -CH_2-). ^{13}C NMR (101 MHz, CDCl$_3$) δ 162.19 (*C*=N), 144.83, 143.81, 143.31, 143.23, 142.15, 142.06, 139.89, 135.09, 131.58, 129.74, 129.41, 129.20, 129.11, 129.06, 128.17, 128.06, 127.70, 127.13, 126.85, 126.08, 125.99, 125.65, 124.70, 122.34, 54.20 (-*C*H-), 52.32 (-*C*H-), 31.71 (-*C*H$_2$-), 30.31 (-*C*H$_2$-), 24.73 (-*C*H$_2$-). APCI-MS (m/z): calcd for C$_{82}$H$_{65}$N$_2$: 1077.5148, Found, 1077.5150, [M+H]$^+$.
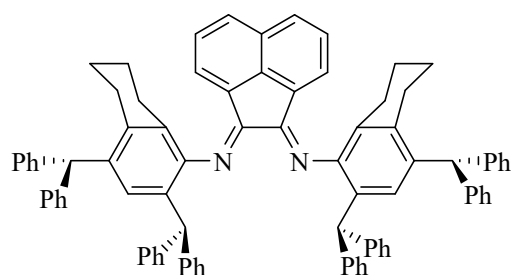
L4 (1.70 g, 77%). ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.60 (d, *J* = 8.2 Hz, 2H, Ar-*H*), 7.32 - 7.19 (m, 8H, Ar-*H*), 7.16 - 7.05 (m, 12H, Ar-*H*), 7.01 (d, *J* = 5.6 Hz, 6H, Ar-*H*), 6.92 (d, *J* = 7.3 Hz, 4H, Ar-*H*), 6.86 - 6.80 (m, 4H, Ar-*H*), 6.74 (d, *J* = 7.6 Hz, 4H, Ar-*H*), 6.29 (dd, *J* = 14.6, 6.8 Hz, 6H, Ar-*H*), 6.08 (t, *J* = 7.2 Hz, 2H, Ar-*H*), 5.69 (s, 2H, -C*H*-), 5.58 (s, 2H, -C*H*-), 2.98 - 2.84 (m, 2H, -CH_2-), 2.70 (t, *J* = 5.9 Hz, 4H, -CH_2-), 2.50 - 2.33 (m, 2H, -CH_2-), 1.86 - 1.77 (m, 2H, -CH_2-), 1.74 - 1.63 (m, 4H, -CH_2-), 1.61 - 1.53 (m, 2H, -CH_2-). ^{13}C NMR (101 MHz, CDCl$_3$) δ 162.84 (*C*=N), 147.05, 144.23, 143.71, 143.34, 141.76, 139.73, 137.31, 133.80, 129.73, 129.47, 129.34, 129.14, 129.09, 128.16, 128.01, 127.67, 126.98, 126.82, 126.06, 125.90, 125.61, 124.85, 124.70, 122.24, 52.62 (-*C*H-), 52.25 (-*C*H-), 26.65 (-*C*H$_2$-), 25.88 (-*C*H$_2$-), 23.07 (-*C*H$_2$-), 22.57 (-*C*H$_2$-). APCI-MS (m/z): calcd for C$_{84}$H$_{69}$N$_2$: 1105.5461, Found, 1105.5443, [M+H]$^+$.

1.4 Procedure for the Synthesis of Nickel Complexes Ni1-Ni4.

Complexes **Ni1-Ni4** were synthesized by the reaction of 1 equiv. of (DME)NiBr$_2$ with the corresponding ligands in methylene chloride. The ligand (0.2 mmol) was added in 5 mL of methylene chloride in a Schlenk tube under a nitrogen atmosphere. (DME)NiBr$_2$ (0.2 mmol, 62 mg) was added to the above solution. The resulting
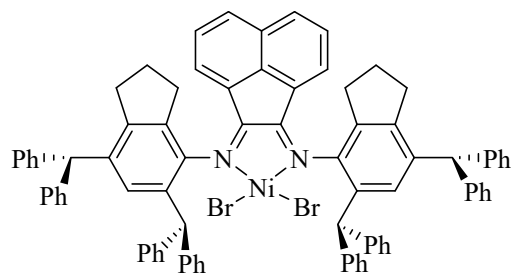
mixture was stirred at room temperature overnight. The solvent was evaporated under reduced pressure to afford a solid. The product was washed with 4 × 5 mL diethyl ether and dried under vacuum.
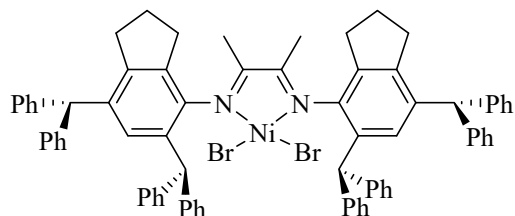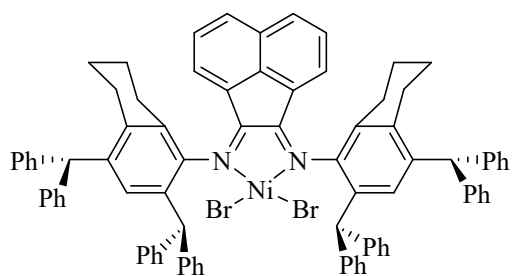

Ni1 (187 mg, 78%). Elem. Anal. Calcd for $C_{74}H_{64}Br_2N_2Ni$: C, 74.08; H, 5.38; N, 2.33. Found: C, 73.99; H, 5.47; N, 2.31.
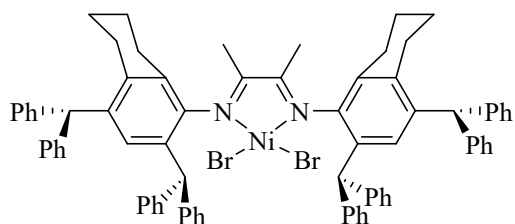
Ni2 (184 mg, 75%). Elem. Anal. Calcd for $C_{76}H_{68}Br_2N_2Ni$: C, 74.34; H, 5.58; N, 2.28. Found: C, 74.28; H, 5.64; N, 2.21.

Ni3 (223 mg, 86%). Elem. Anal. Calcd for $C_{82}H_{64}Br_2N_2Ni$: C, 76.00; H, 4.98; N, 2.16. Found: C, 75.89; H, 4.87; N, 2.08.

Ni4 (233 mg, 88%). Elem. Anal. Calcd for $C_{84}H_{68}Br_2N_2Ni$: C, 76.20; H, 5.18; N, 2.12. Found: C, 76.23; H, 5.26; N, 2.20.

1.5 A general procedure for the homopolymerization of ethylene using Ni(II) complexes.

In a typical experiment, a 350 mL stainless pressure reactor connected with a high pressure gas line was firstly dried at 90 °C under vacuum for at least 1 h. The reactor was then adjusted to the desired polymerization temperature. 20 mL of toluene and the desired amount Et_2AlCl was added to the reactor under N_2 atmosphere, then the 1 μmol Ni(II) catalyst in 1 mL of CH_2Cl_2 was injected into the polymerization system via syringe. With a rapid stirring, the reactor was pressurized and maintained at 6 atm of ethylene. After 10 min, the pressure reactor was vented and the polymer was precipitated in ethanol, filtered and dried at 50 °C for at least 24 h under vacuum.

1.6 A general procedure for the copolymerization of MU with ethylene using Ni(II) complexes.

In a typical experiment, a 350 mL stainless pressure reactor connected with a high pressure gas line was firstly dried at 90 °C under vacuum for at least 1 h. The reactor was then adjusted to the desired polymerization temperature. 18 mL of toluene and the desired amount MU and Et_2AlCl was added to the reactor under N_2 atmosphere, then 5 μmol Ni(II) catalyst in 1 mL of CH_2Cl_2 was injected into the polymerization system via syringe. With a rapid stirring, the reactor was pressurized and maintained at desired pressure of ethylene. After 10 min, the pressure reactor was

vented and the copolymer was precipitated in ethanol, filtered and dried at 50 °C for at least 24 h under vacuum.

1.7, Table S1. Mechanical properties.[a]

Ent.	Precat.	$T/^oC$	Strain (%)[b]	Stress (MPa)[b]
1	**Ni1**	30	338	16.4
2	**Ni1**	50	712	30.5
3	**Ni1**	70	752	29.0
4	**Ni2**	30	353	20.4
5	**Ni2**	50	514	28.2
6	**Ni2**	70	555	20.9
7	**Ni3**	30	706	24.3
8	**Ni3**	50	771	21.9
9	**Ni3**	70	998	30.4
10	**Ni4**	30	347	14.9
11	**Ni4**	50	479	19.5
12	**Ni4**	70	552	17.7

[a]Conditions: performed at 10 mm/min by means of a Universal Test Machine (UTM2502) at room temperature (25 °C). [b]Strain and stress at break values.

2. Spectra Data

2.1 ^{1}H and ^{13}C NMR of the Synthetic Compounds.
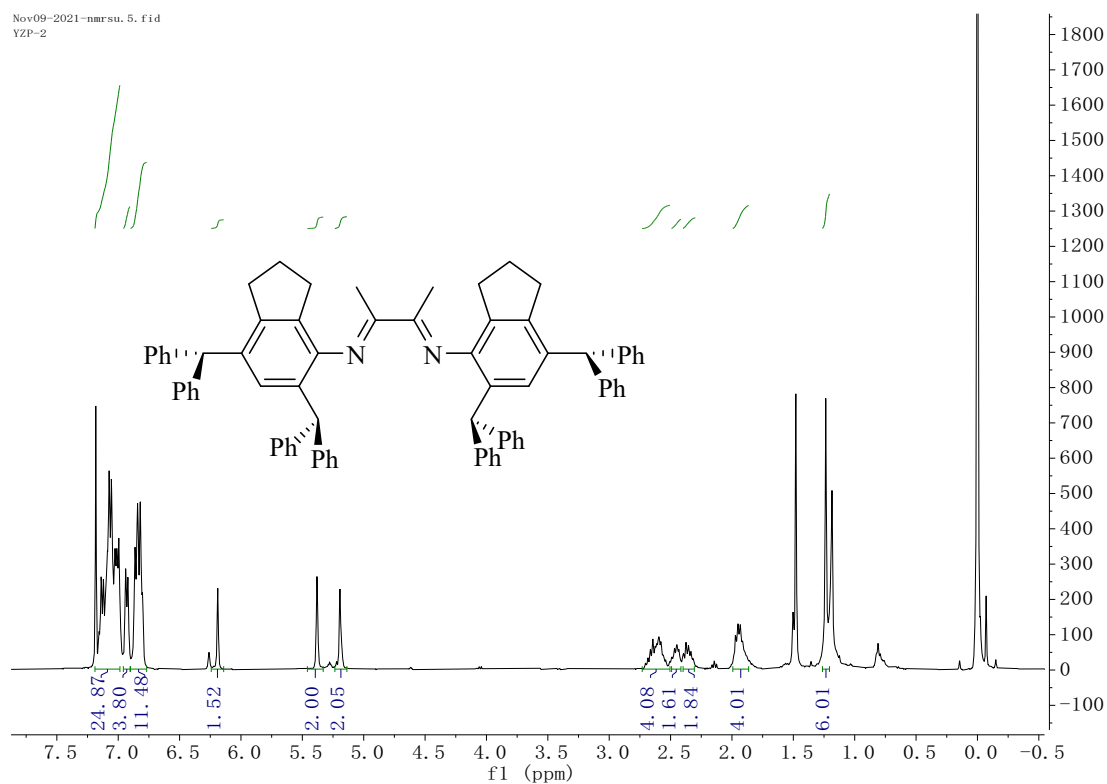
Figure S1. ^{1}H NMR spectrum of **L1** in CDCl$_3$.
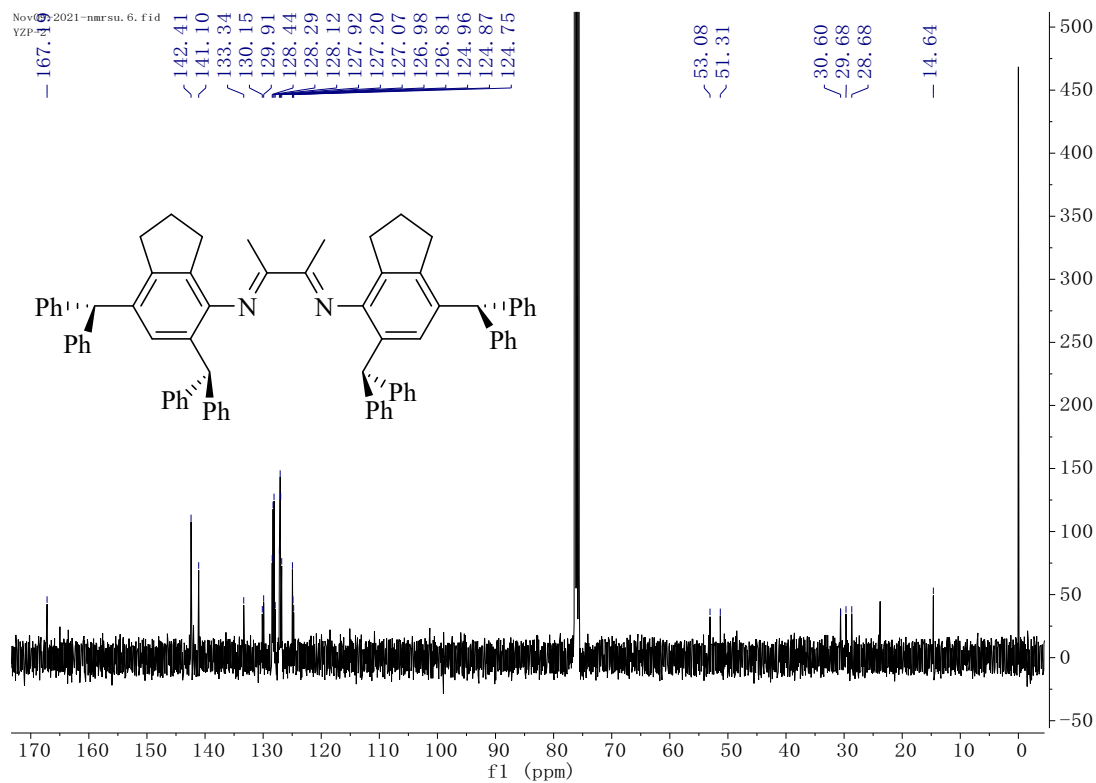
Figure S2. ^{13}C NMR spectrum of **L1** in CDCl$_3$.
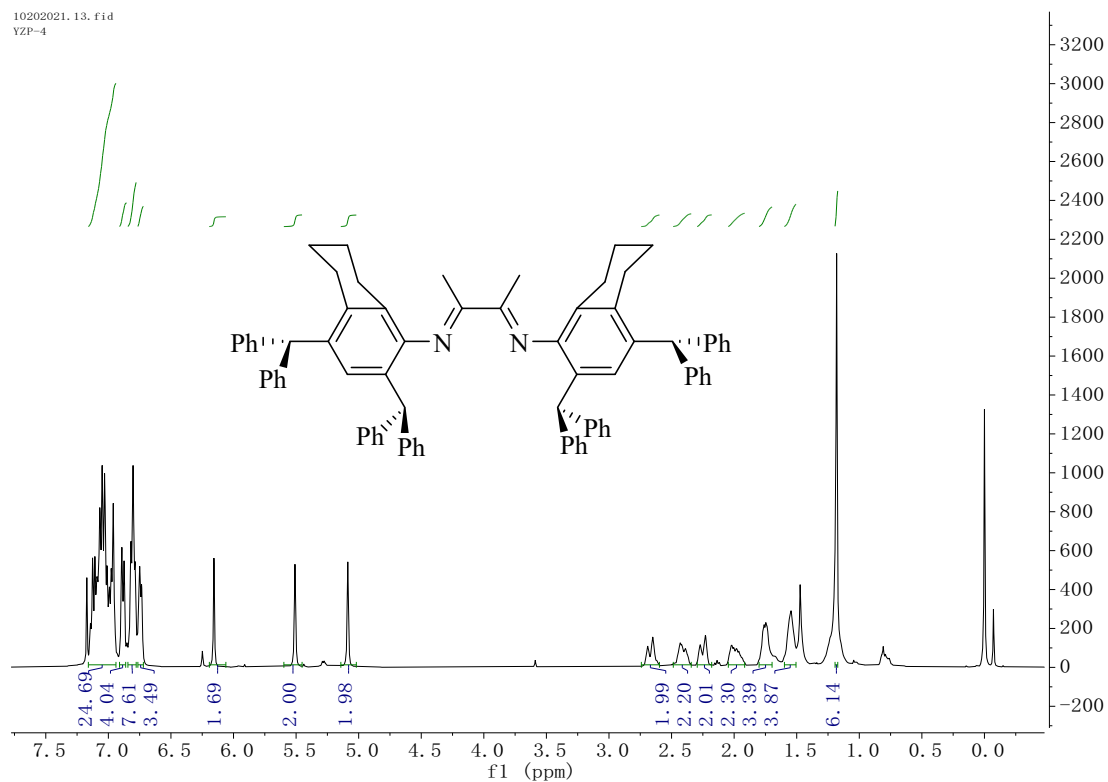
Figure S3. ^{1}H NMR spectrum of **L2** in CDCl$_3$.
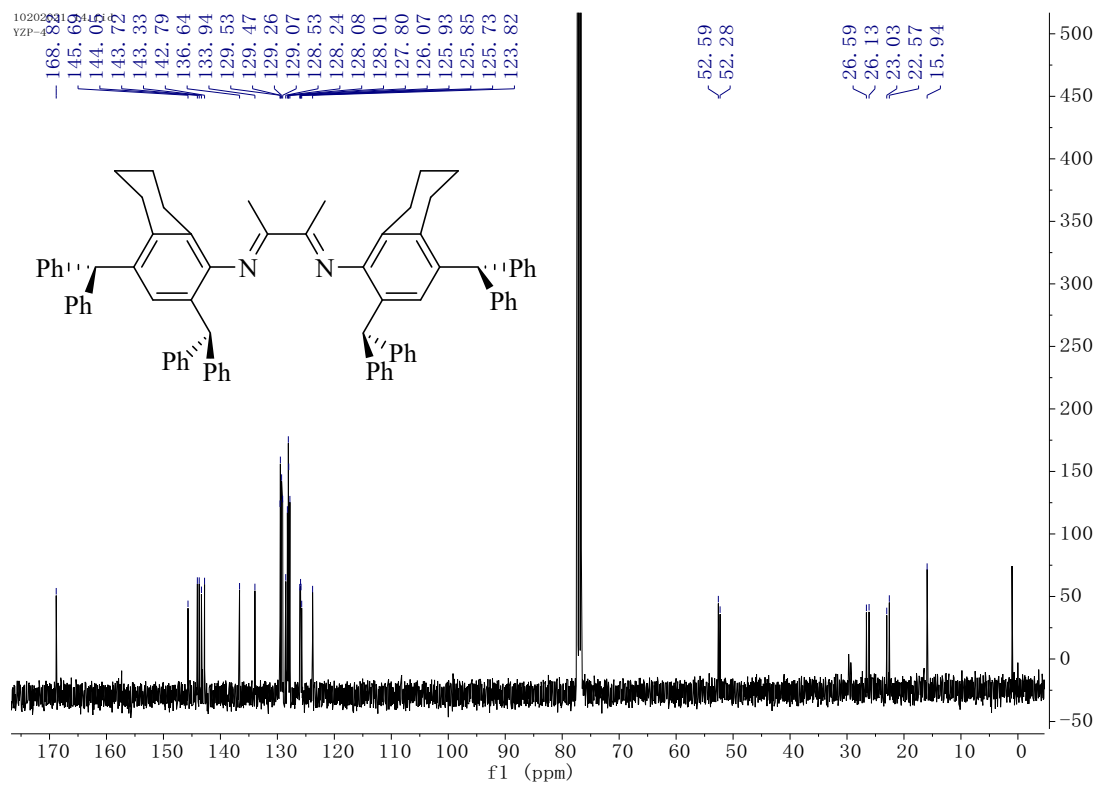
Figure S4. ^{13}C NMR spectrum of **L2** in CDCl$_3$.
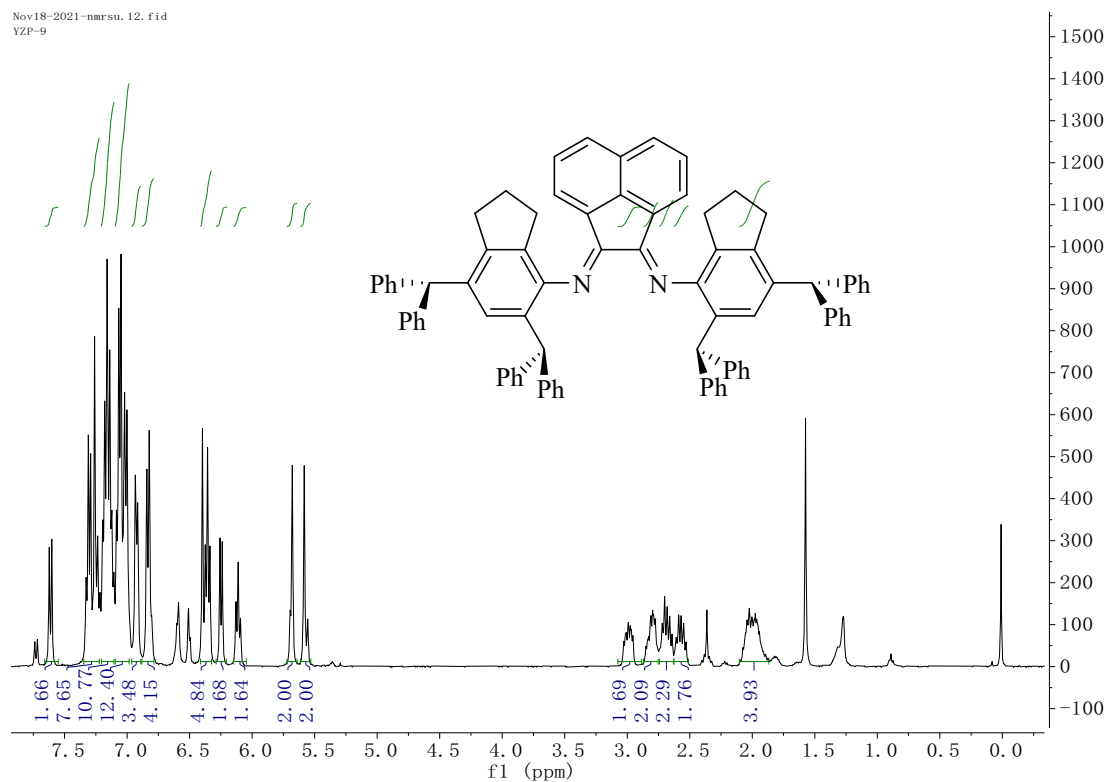
Figure S5. ^{1}H NMR spectrum of **L3** in CDCl$_3$.
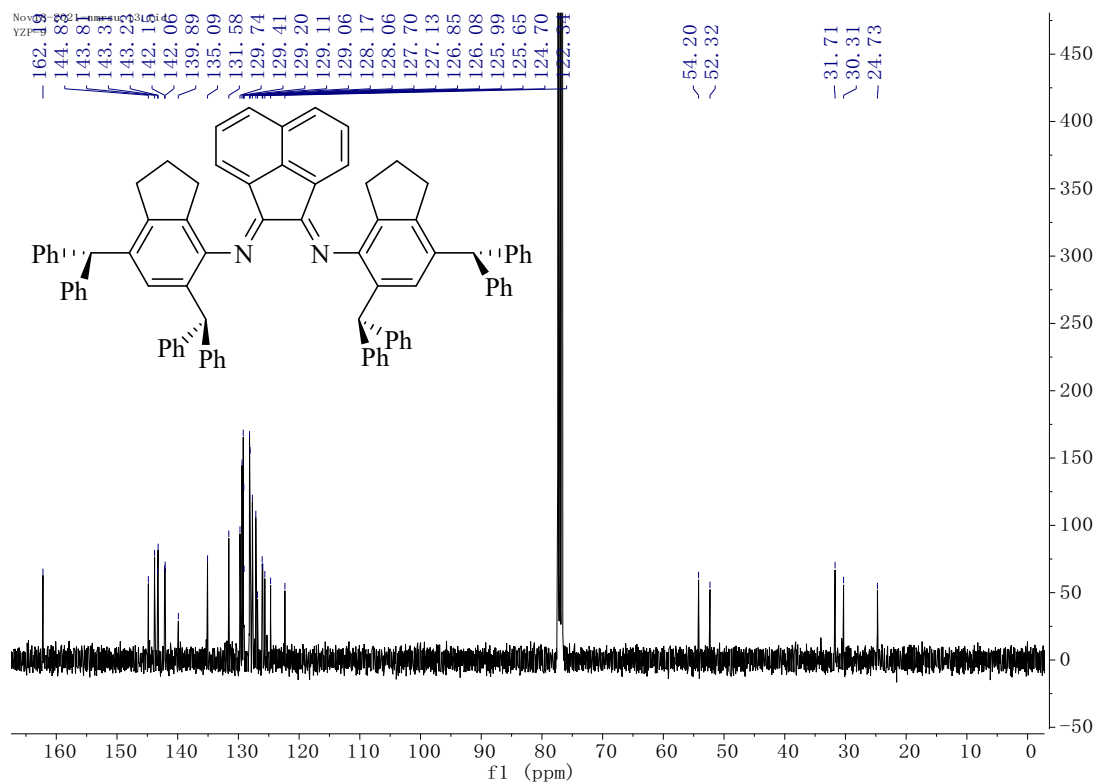
Figure S6. ^{13}C NMR spectrum of **L3** in CDCl$_3$.
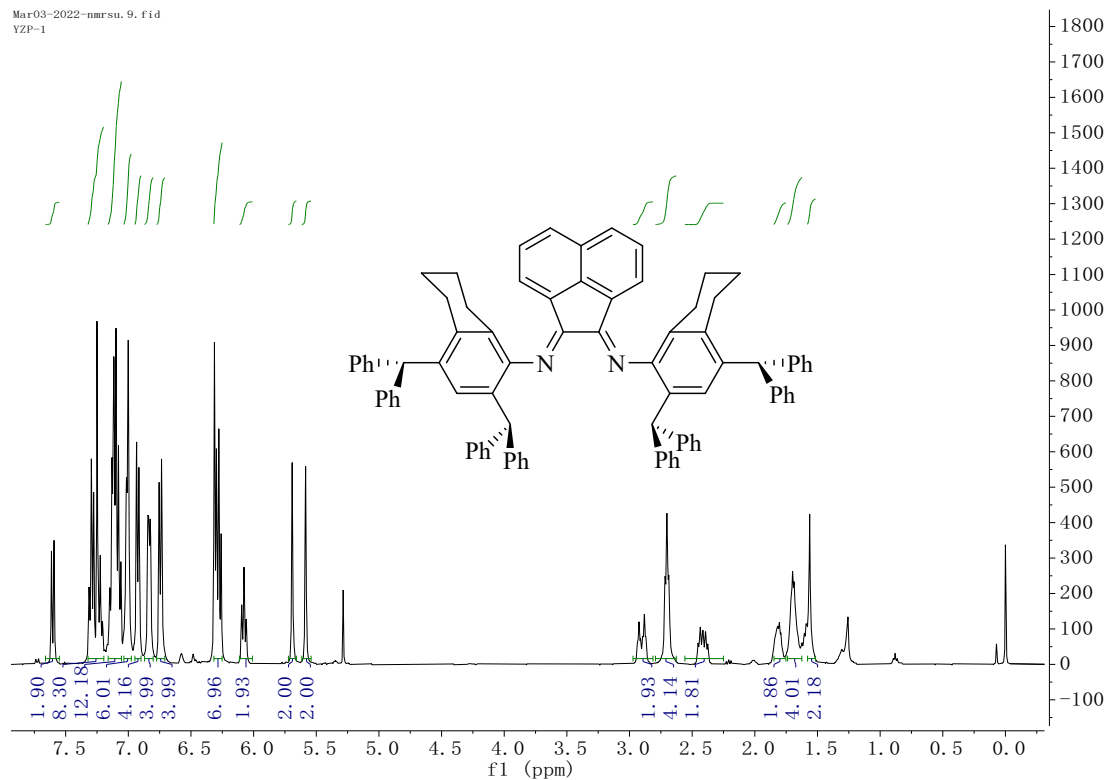
Figure S7. ^{1}H NMR spectrum of **L4** in CDCl$_3$.
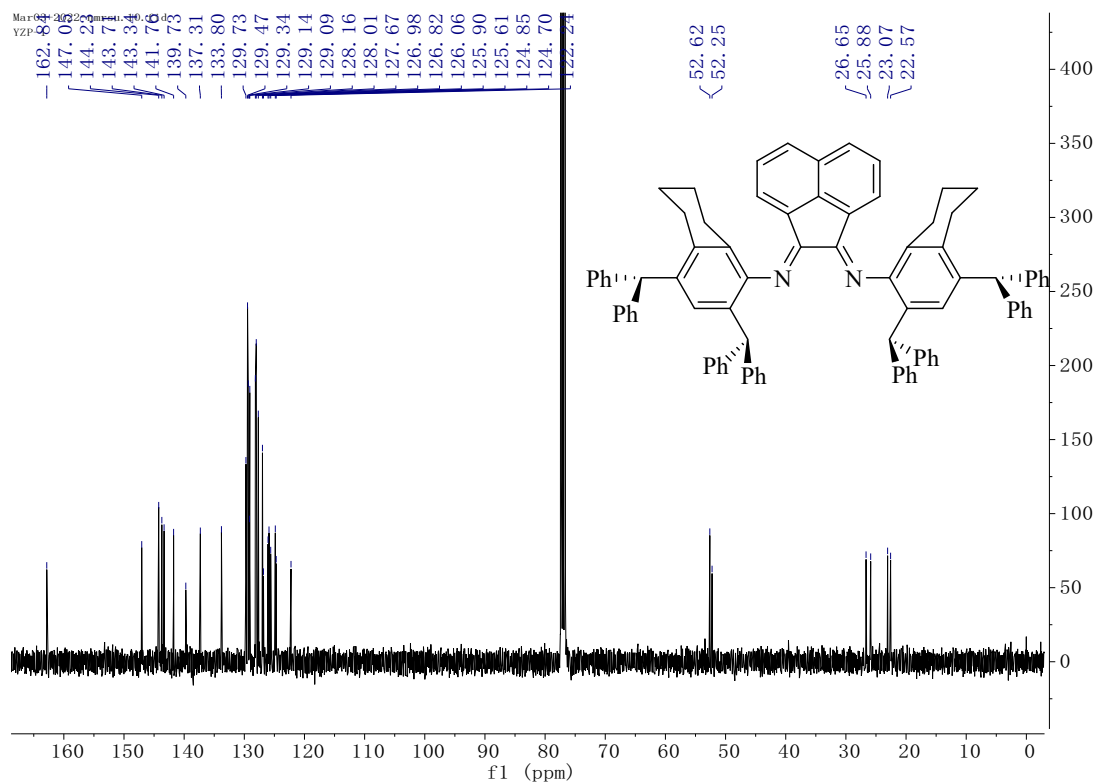
Figure S8. ^{13}C NMR spectrum of **L4** in CDCl$_3$.

2.2 MS of Ligands L1-L4.

YZP-3 #18 RT: 0.15 AV: 1 SB: 1 0.09 NL: 3.46E7
T: FTMS + c APCI corona Full ms [150.00-1250.00]
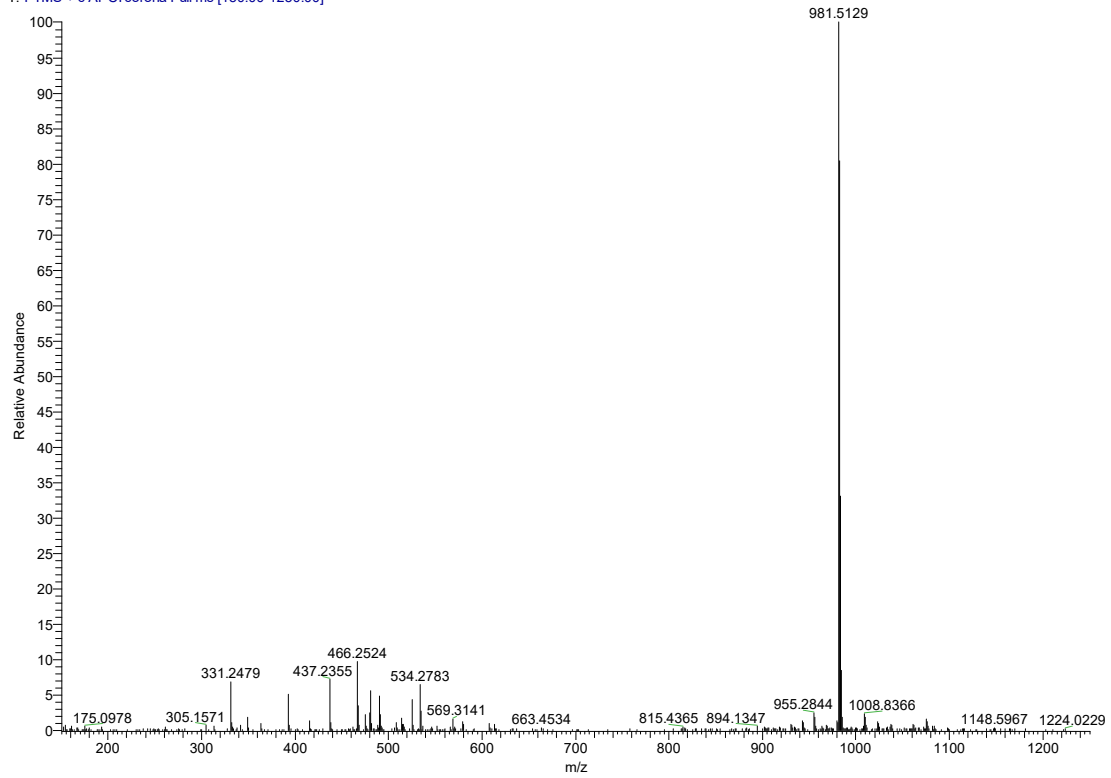
Figure S9. APCI-MS of **L1**.

YZP-4 #21 RT: 0.17 AV: 1 SB: 1 0.10 NL: 2.78E7
T: FTMS + c APCI corona Full ms [150.00-1250.00]
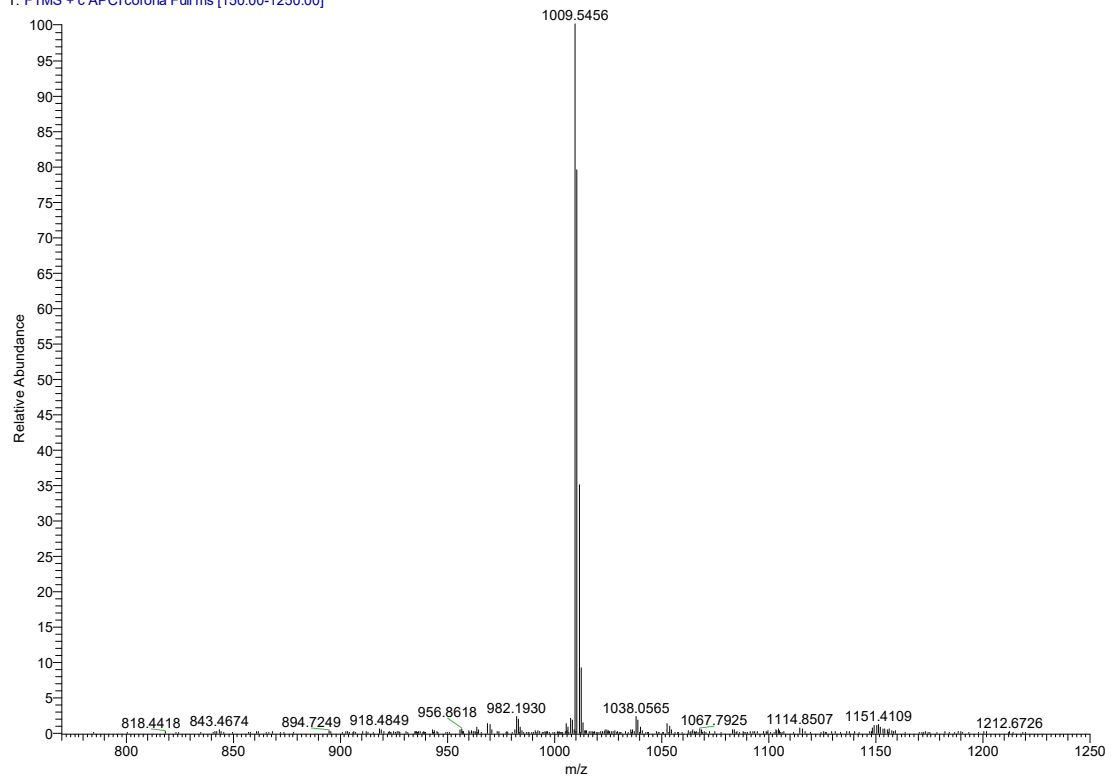
Figure S10. APCI-MS of **L2**.

1077.5150

Relative Abundance

1099.4966

613.3411   657.3677   701.3942   821.7075   851.5394   911.4366   1005.3849   1047.3748   1125.2235   1172.5729   1230.6625

m/z

Figure S11. APCI-MS of **L3**.

1105.5443

Relative Abundance

1128.5287

1139.2974

613.3403   657.3665   701.3923   745.4194   819.3366   851.5391   925.5419   963.7283   1001.5236   1074.2285   1199.6128

m/z
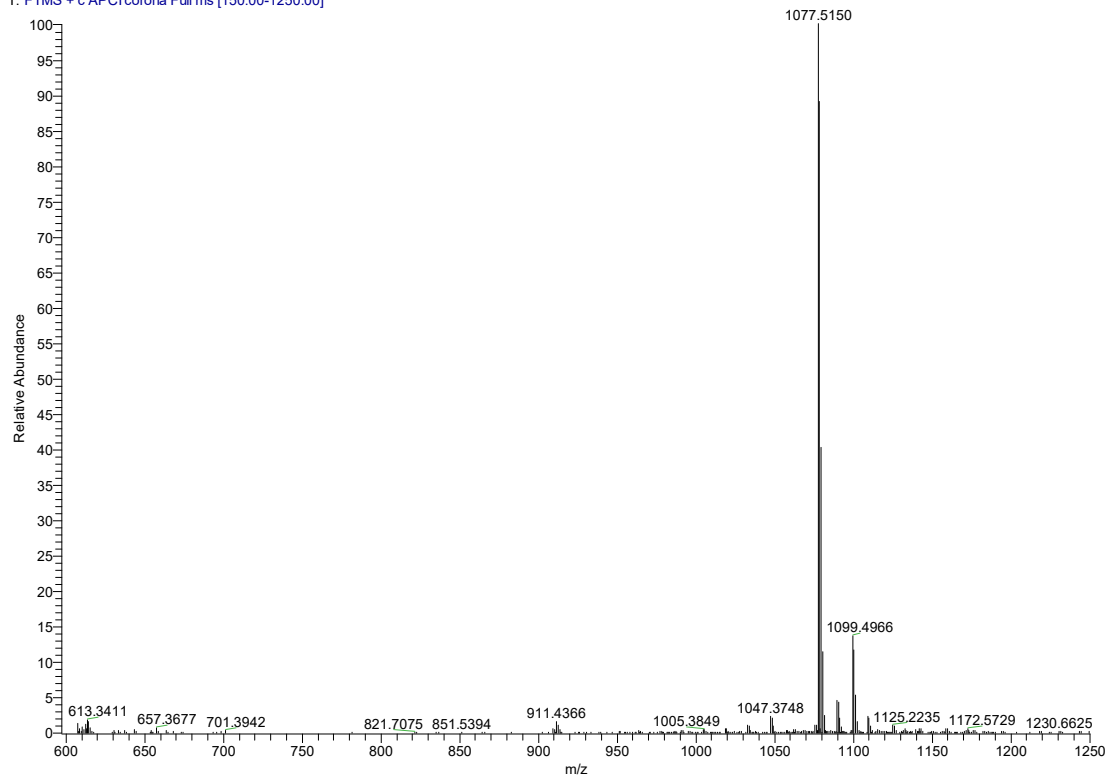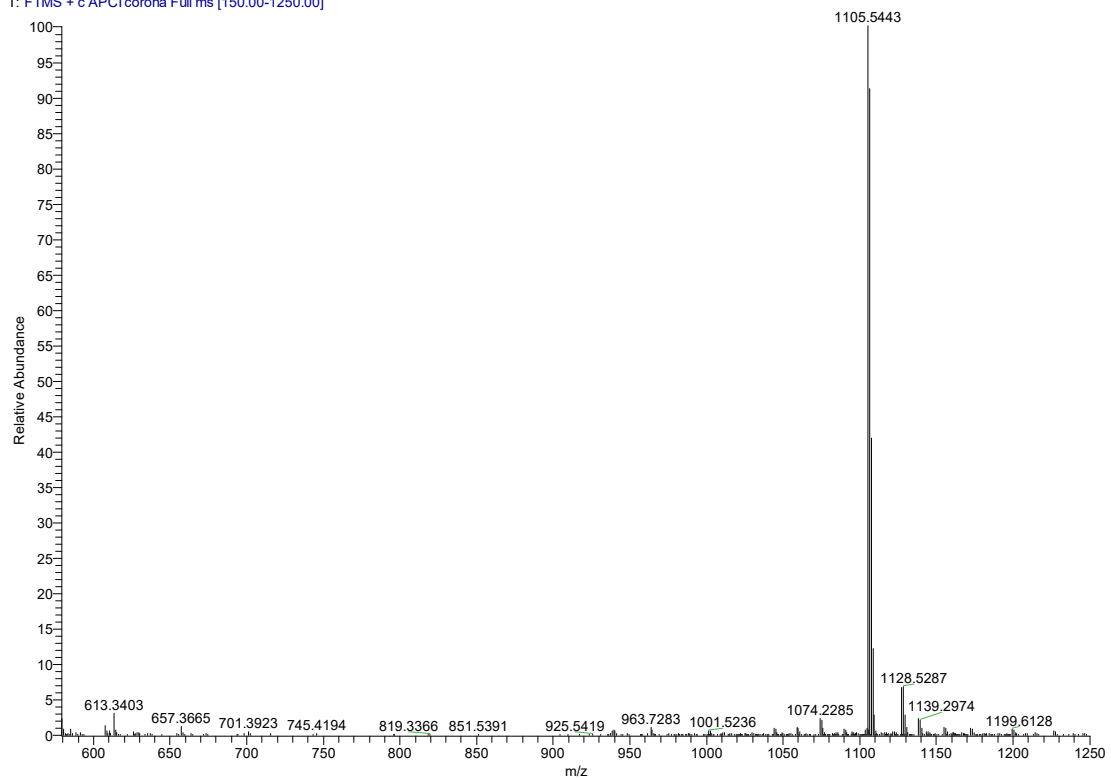
Figure S12. APCI-MS of **L4**.

2.3 ¹H and ¹³C NMR of Representative Polymers and Copolymers.
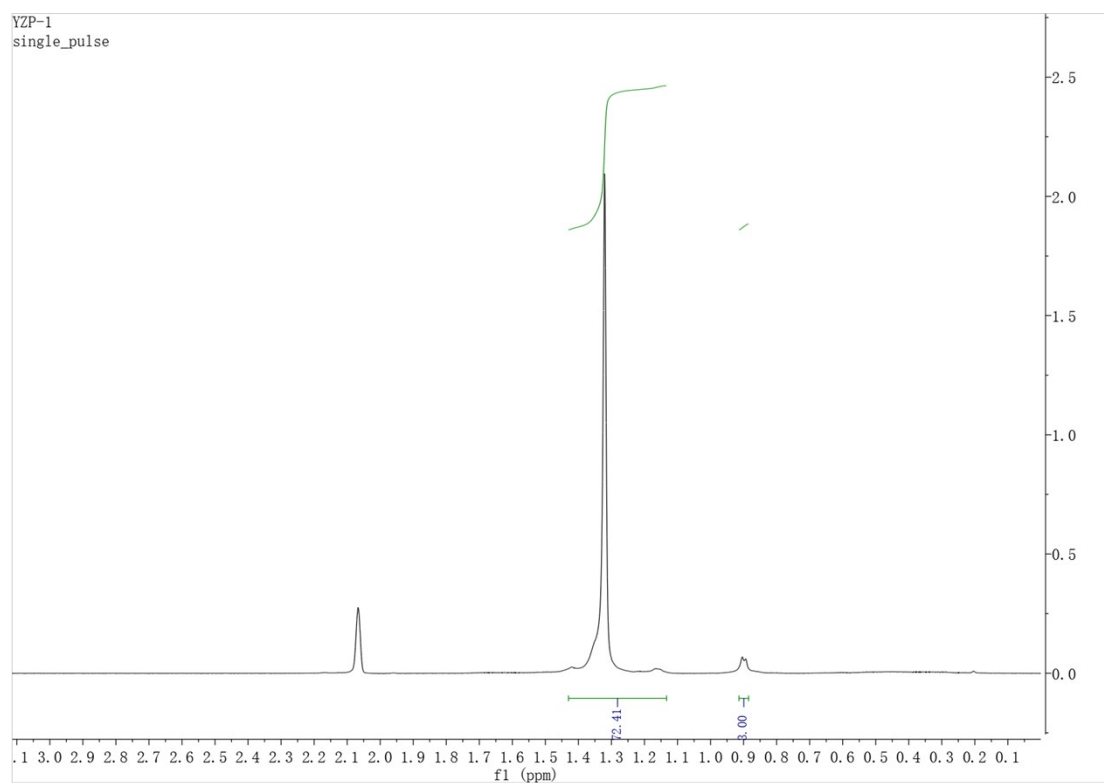
Figure S13. ¹H NMR spectrum of the polymer from table 1, entry 1 (d⁸-toluene, 100 ºC).
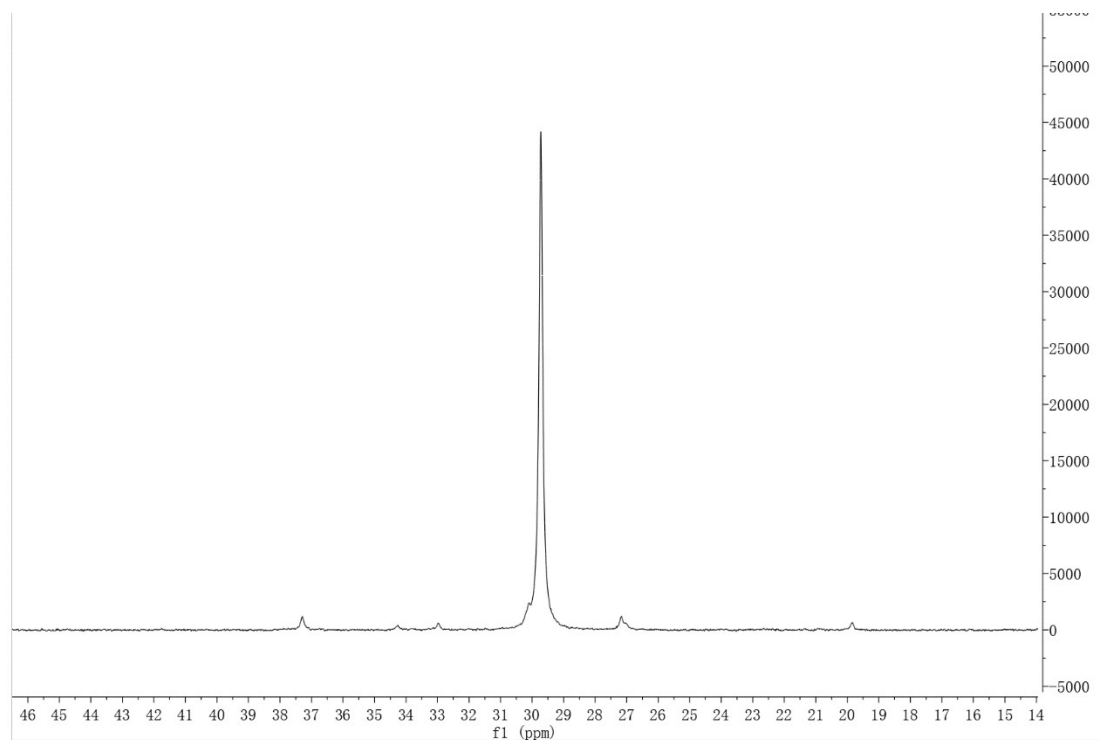
Figure S14. ¹³C NMR spectrum of the polymer from table 1, entry 1 (CDCl₂CDCl₂, 120 ºC).
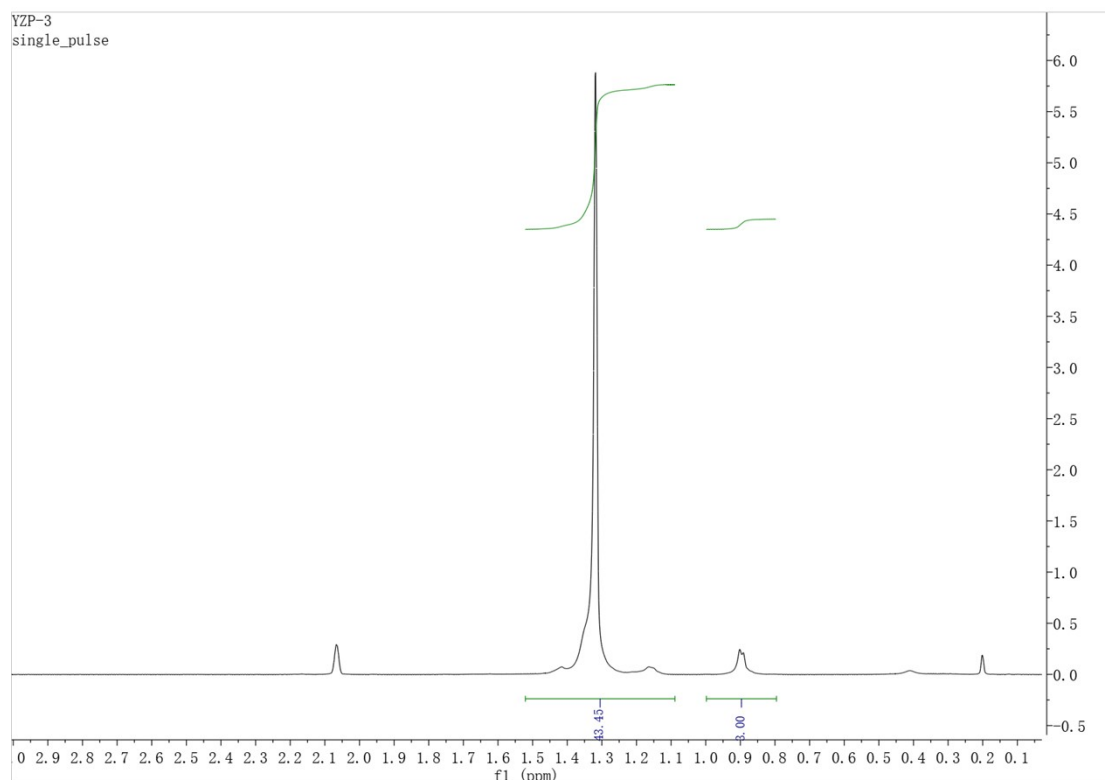
Figure S15. ^{1}H NMR spectrum of the polymer from table 1, entry 3 (d^8-toluene, 100 ^{o}C).
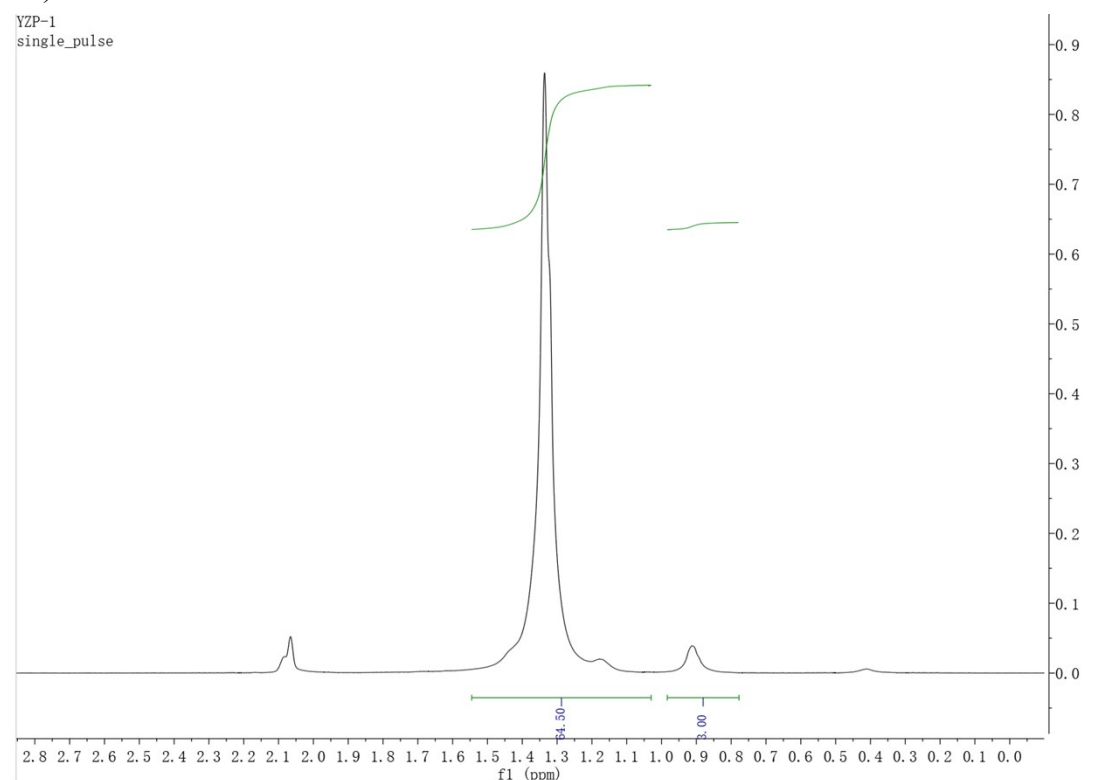
Figure S16. ^{1}H NMR spectrum of the polymer from table 1, entry 4 (d^8-toluene, 100 ^{o}C).
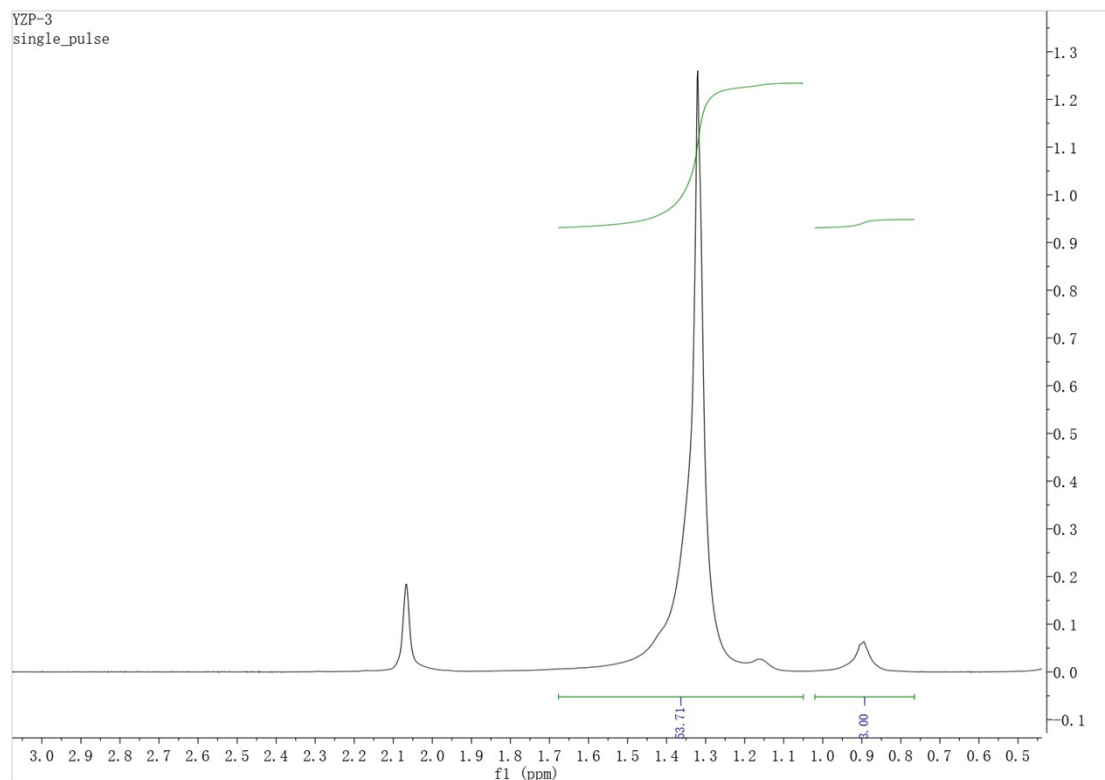
Figure S17. ^{1}H NMR spectrum of the polymer from table 1, entry 6 (d^8-toluene, 100 °C).
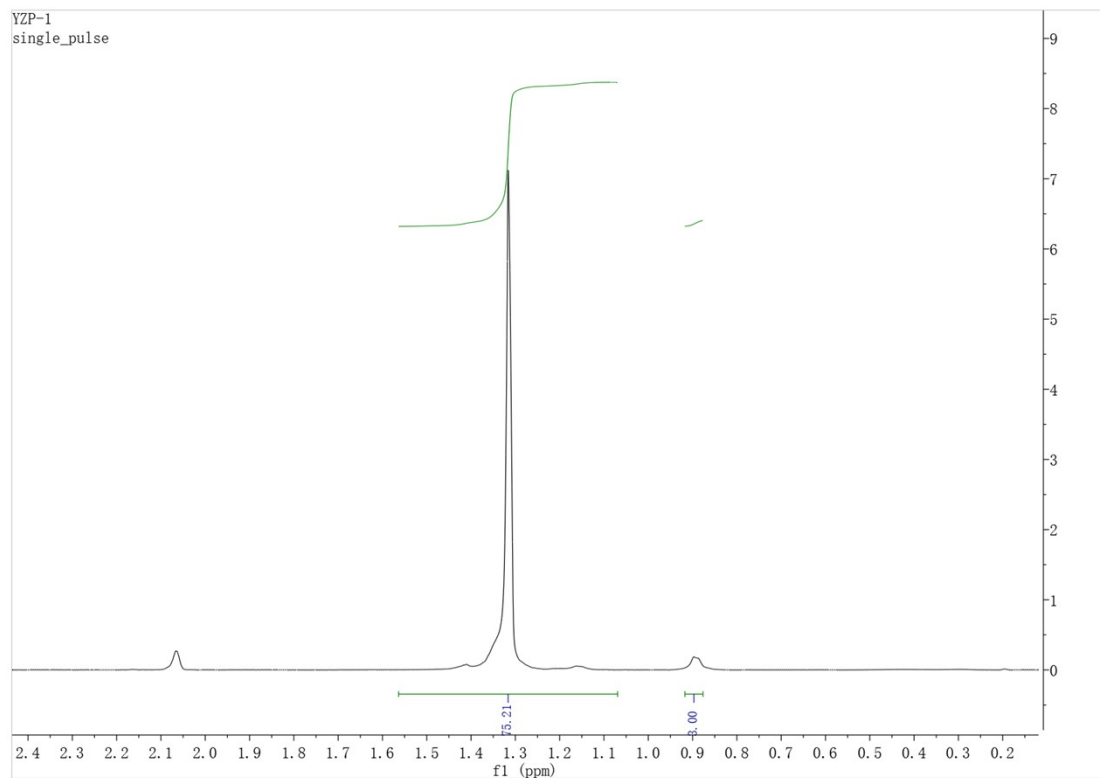
Figure S18. ^{1}H NMR spectrum of the polymer from table 1, entry 7 (d^8-toluene, 100 °C).
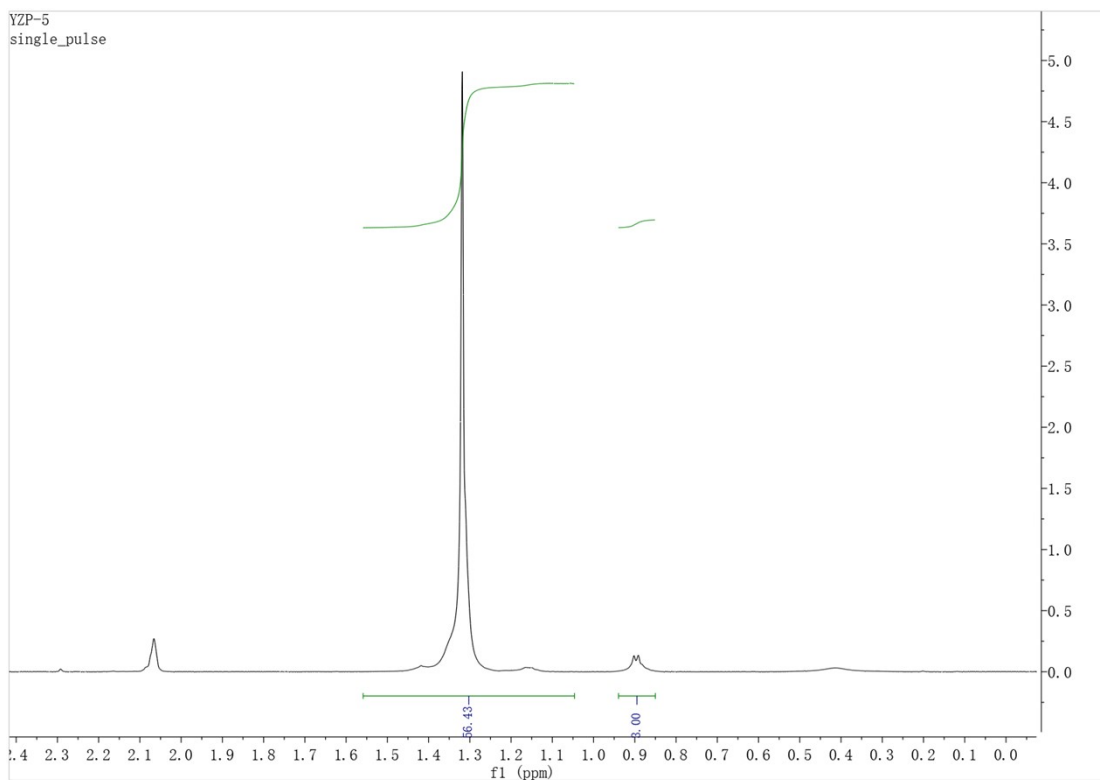
Figure S19. ^{1}H NMR spectrum of the polymer from table 1, entry 11 (d^8-toluene, 100 °C).
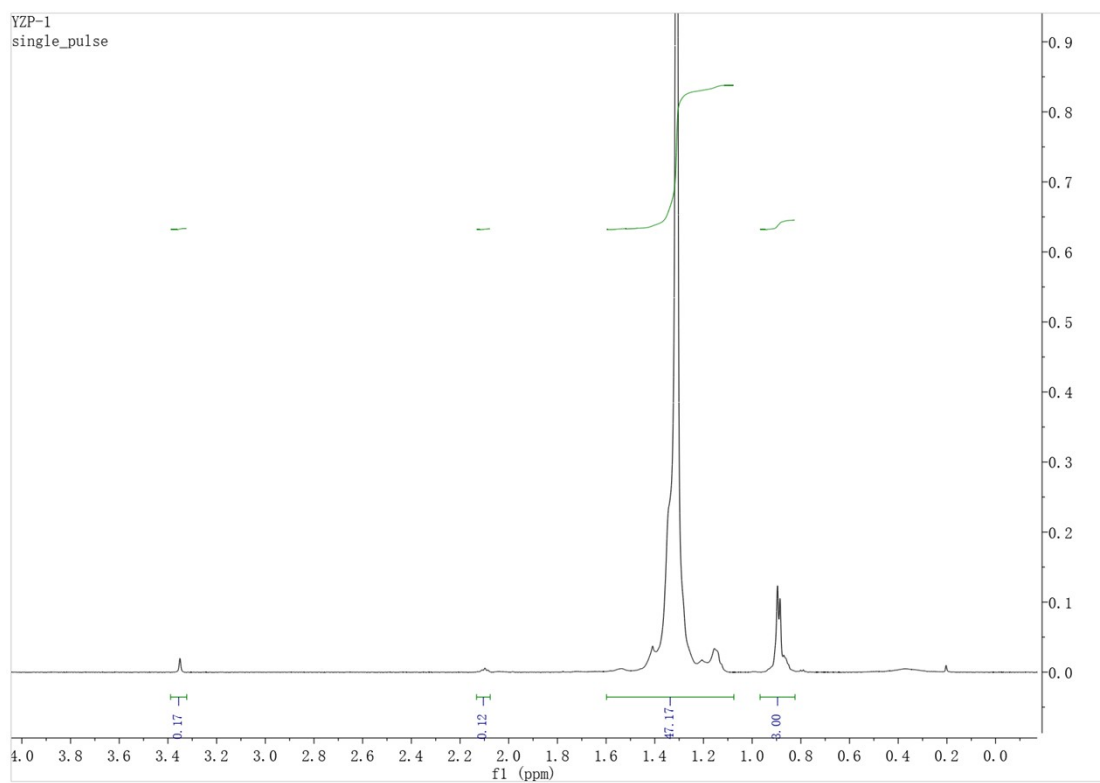
Figure S20. ^{1}H NMR spectrum of the E-MU copolymer from table 2, entry 1 (C$_6$D$_6$, 75 °C).
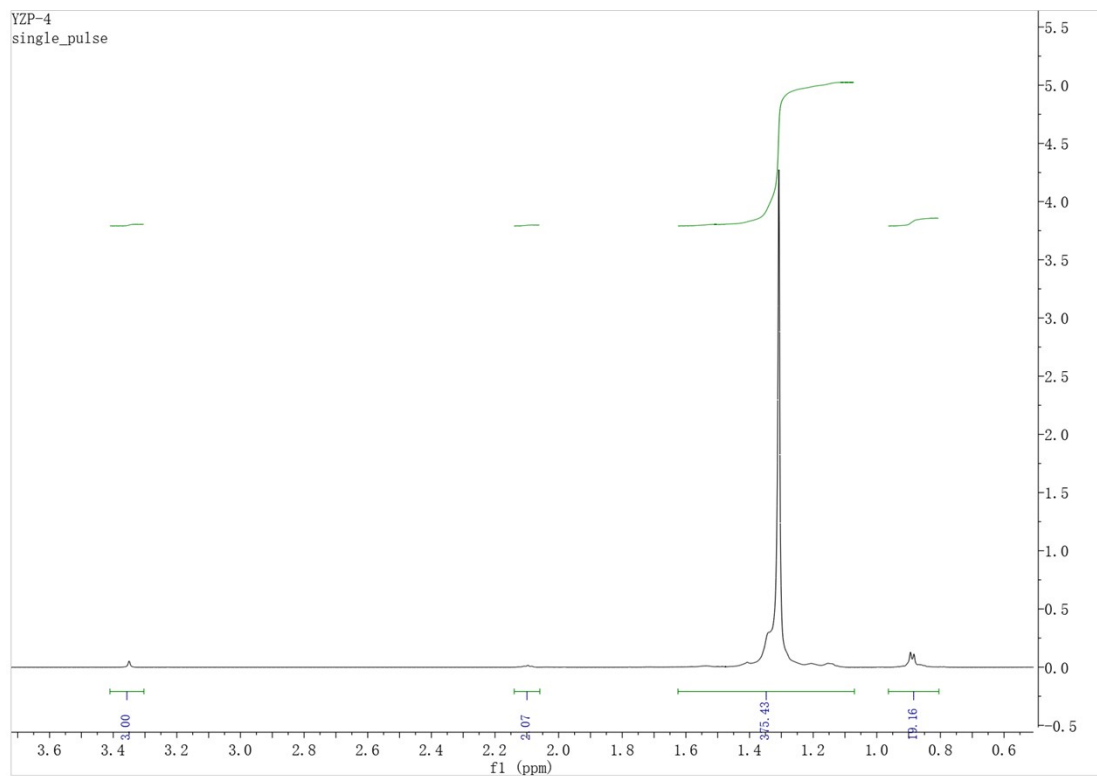
Figure S21. ^{1}H NMR spectrum of the E-MU copolymer from table 2, entry 4 (C_6D_6, 75 °C).
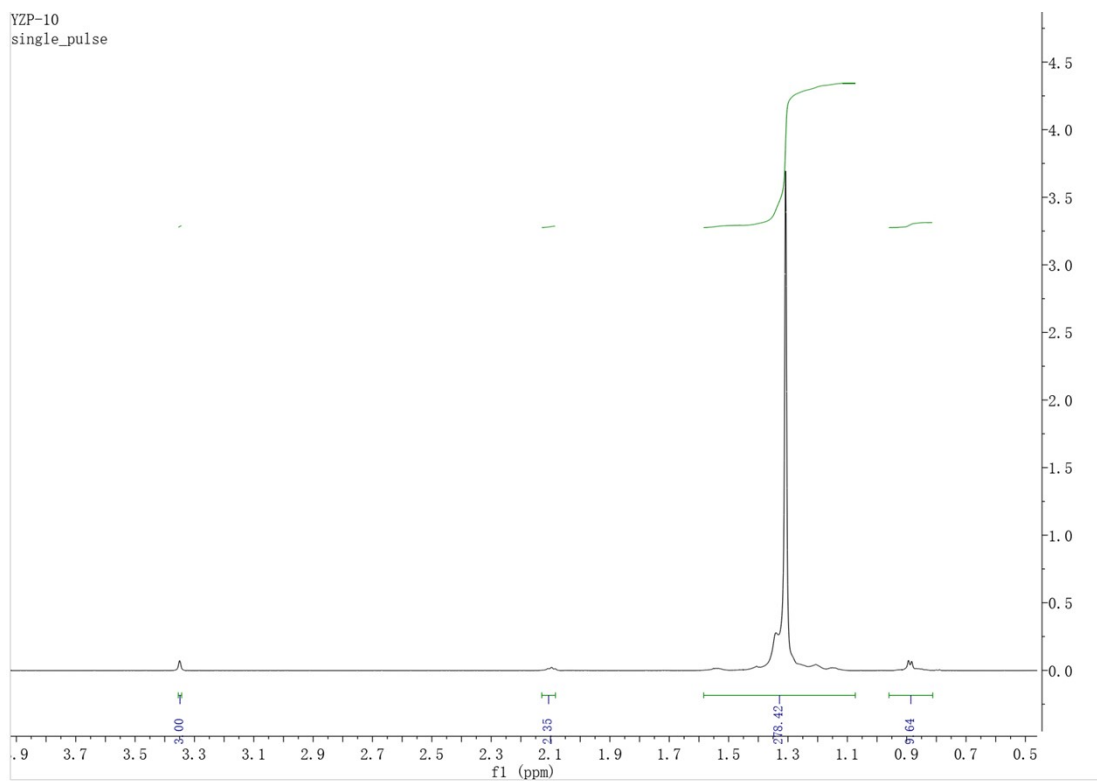
Figure S22. ^{1}H NMR spectrum of the E-MU copolymer from table 2, entry 10 (C_6D_6, 75 °C).

2.4 DSC and GPC of Representative Polymers and Copolymers.
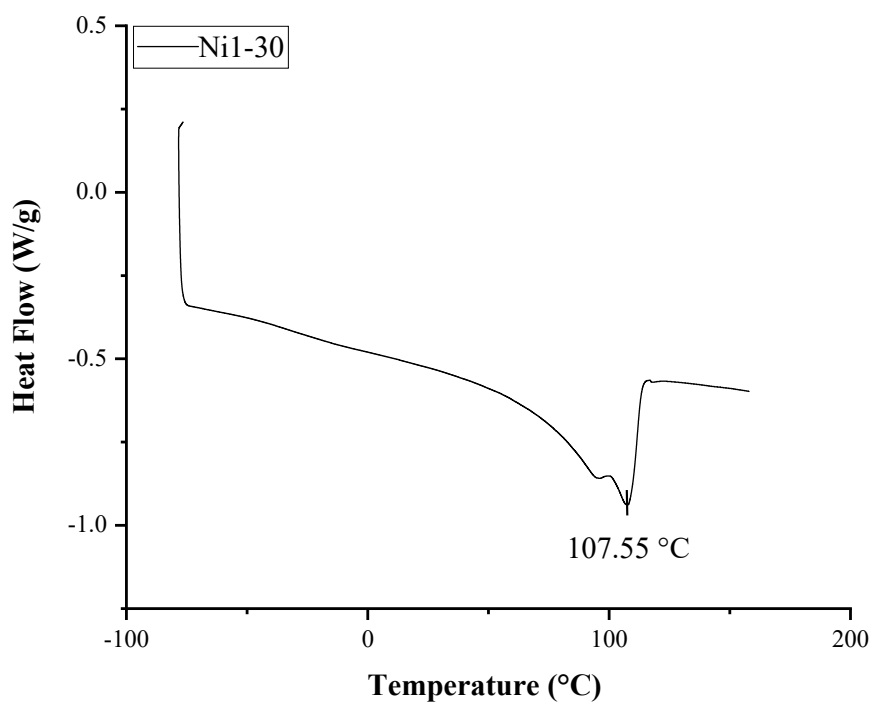
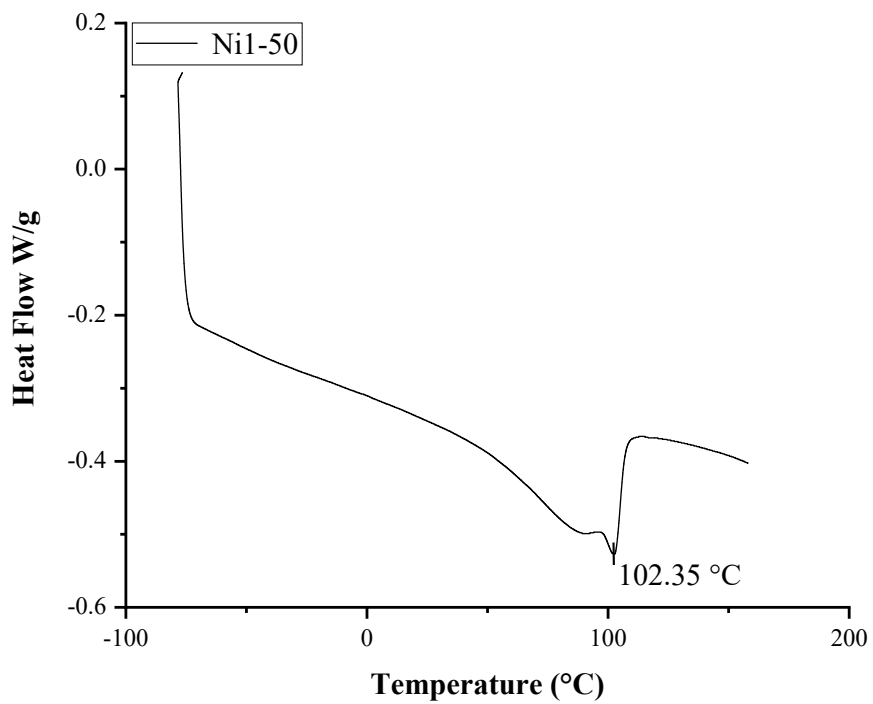**Figure S23**. DSC of the polymer from table 1, entry 1.
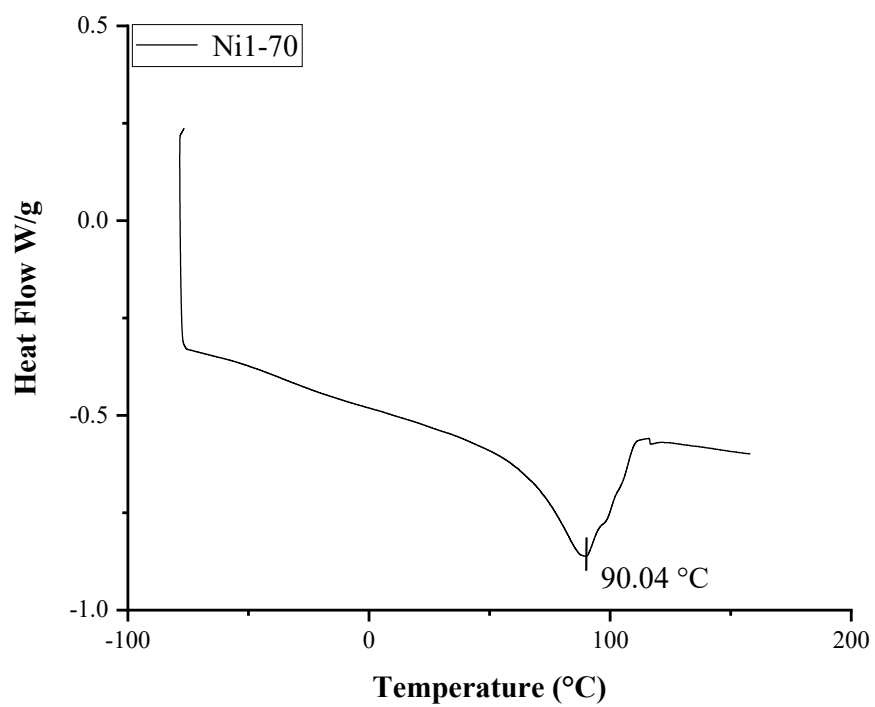

Figure S24. DSC of the polymer from table 1, entry 2.

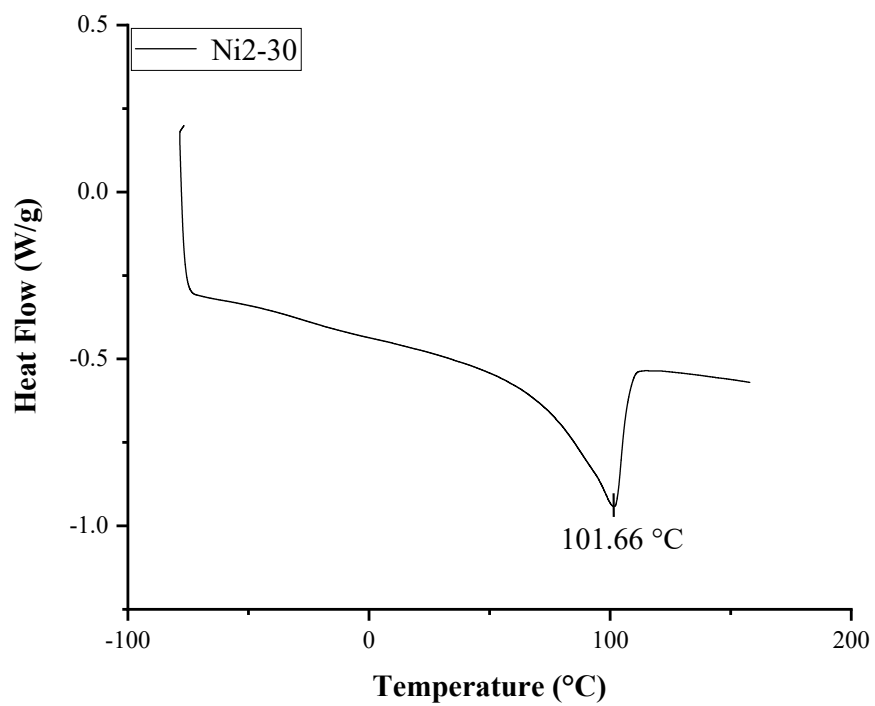**Figure S25**. DSC of the polymer from table 1, entry 3.

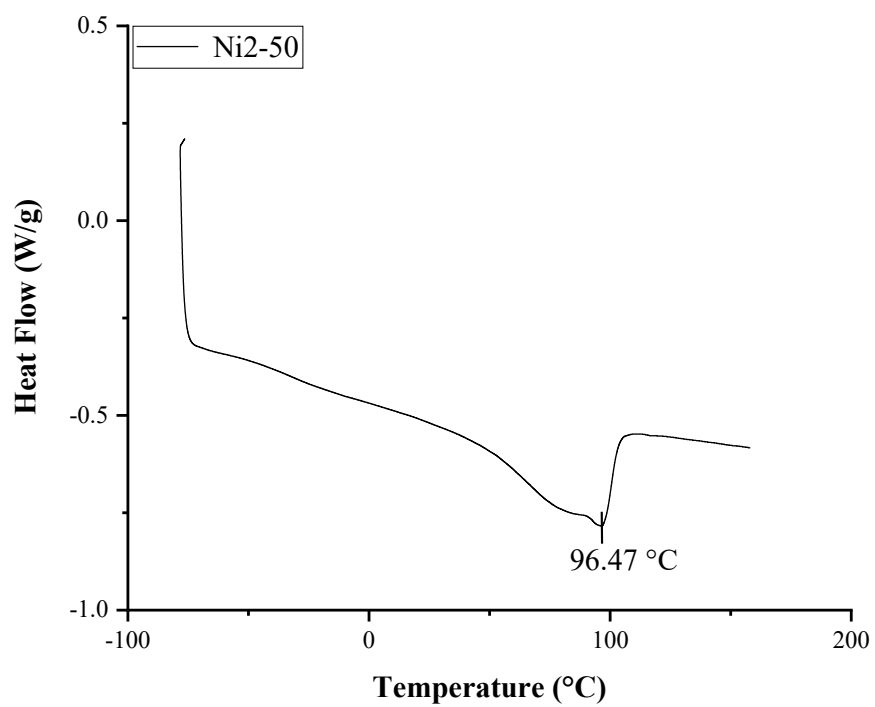**Figure S26**. DSC of the polymer from table 1, entry 4.

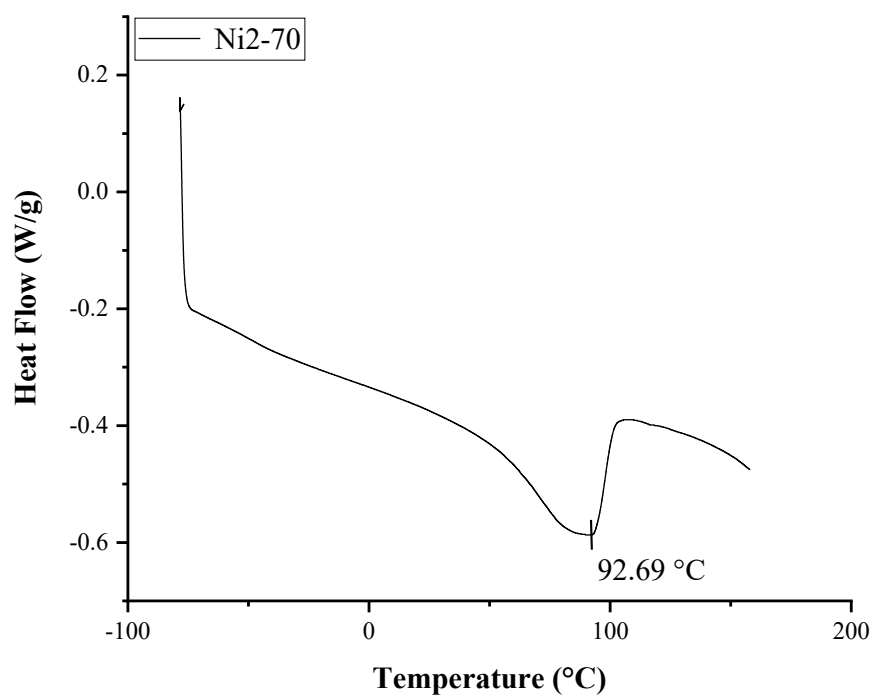**Figure S27**. DSC of the polymer from table 1, entry 5.

Figure S28. DSC of the polymer from table 1, entry 6.

Figure S29. DSC of the polymer from table 1, entry 7.

Figure S30. DSC of the polymer from table 1, entry 8.

Figure S31. DSC of the polymer from table 1, entry 9.

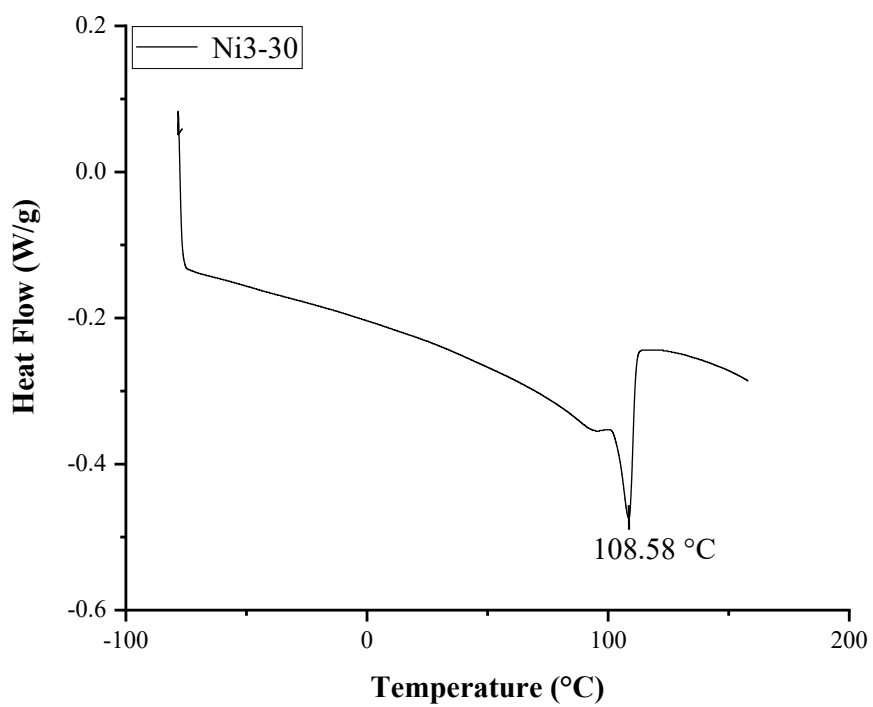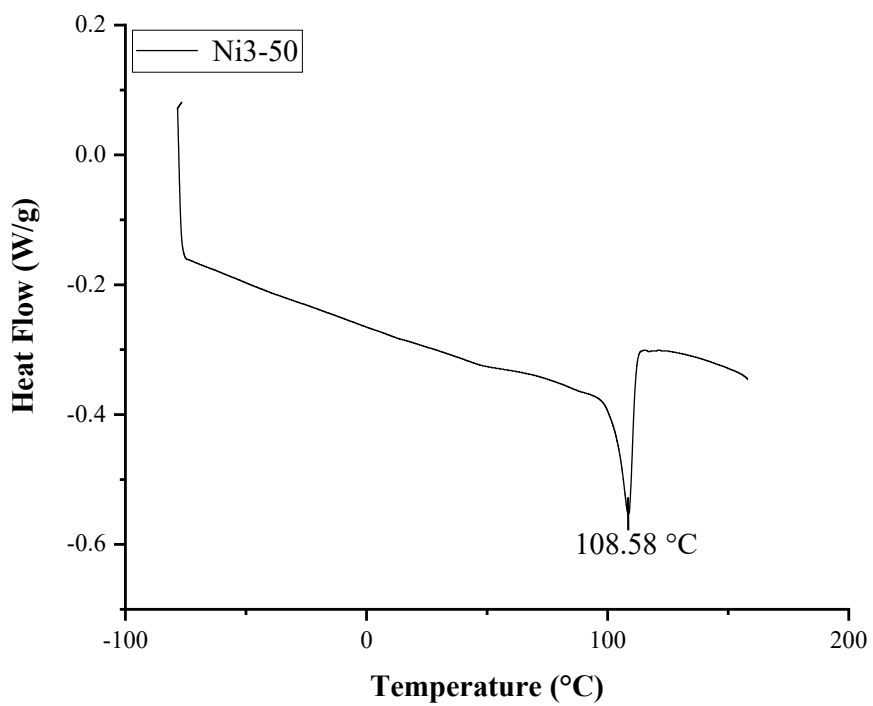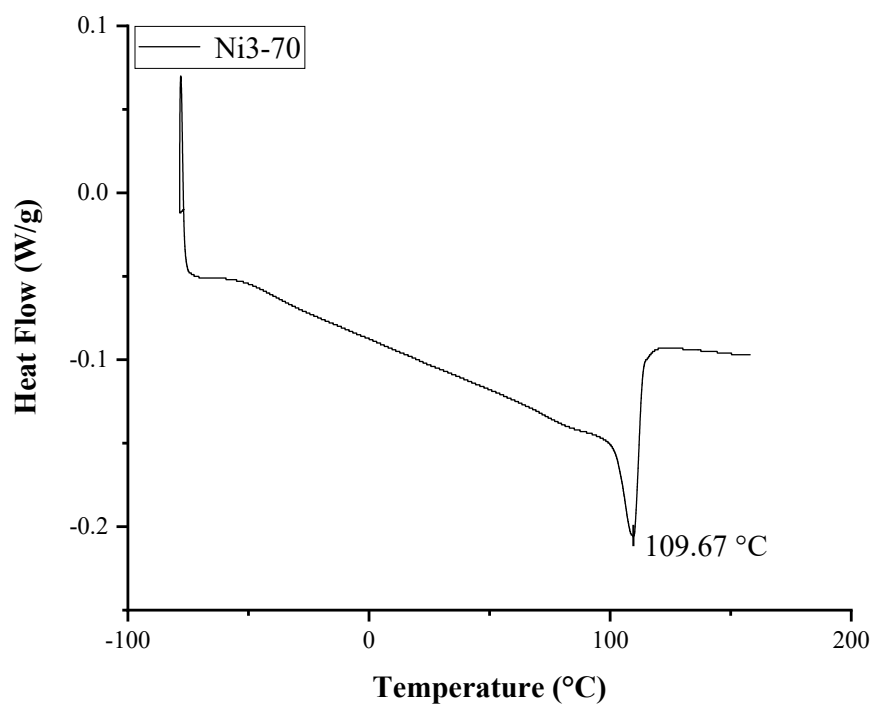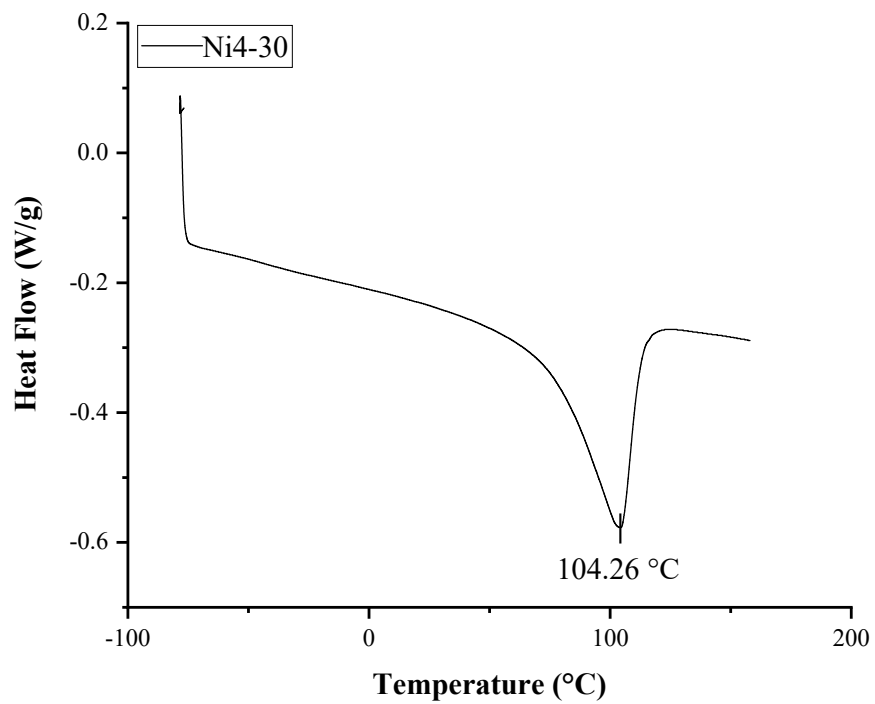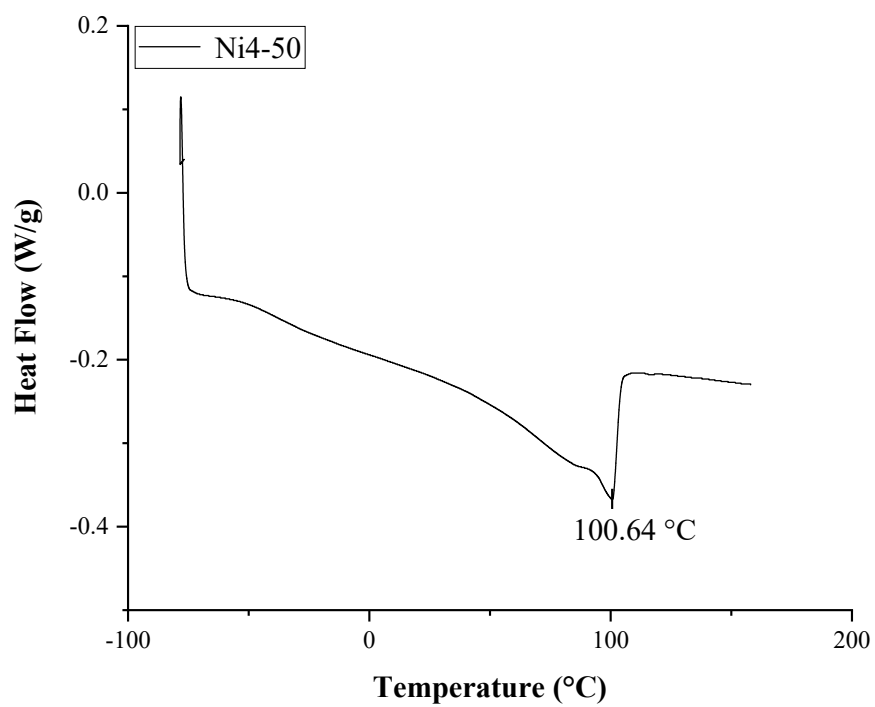**Figure S32**. DSC of the polymer from table 1, entry 10.

Figure S33. DSC of the polymer from table 1, entry 11.
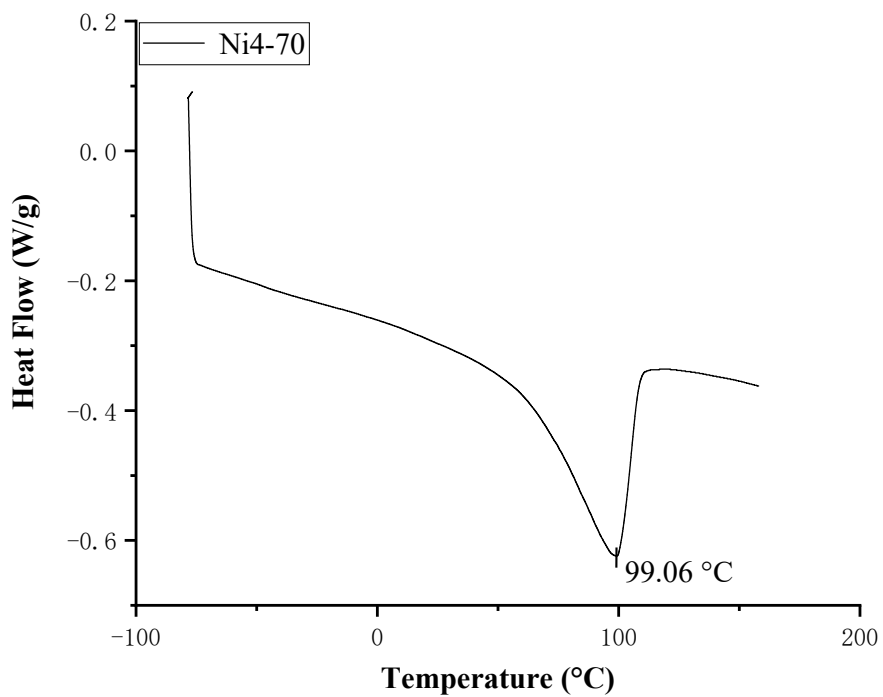
Figure S34. DSC of the polymer from table 1, entry 12.
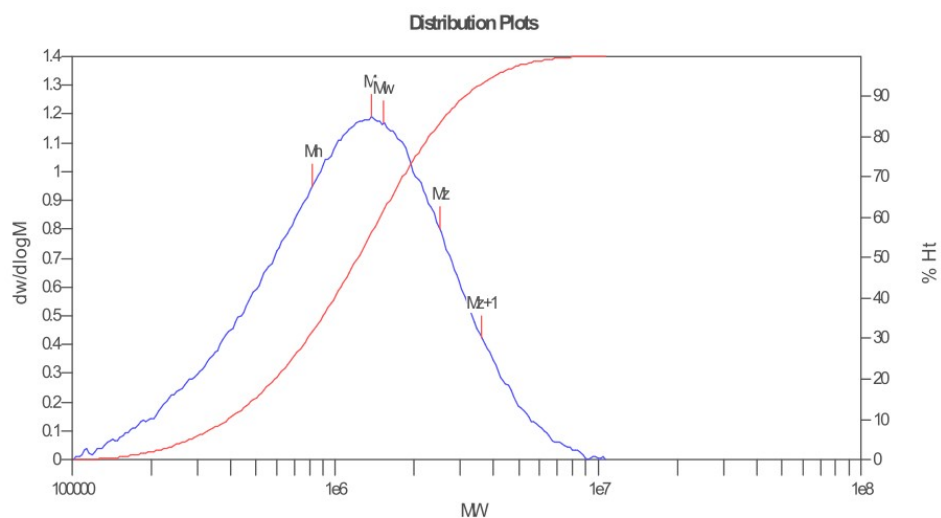
MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	1379463	819846	1526361	2495404	3616847	1405547	1.86177

Figure S35. GPC of the polymer from table 1, entry 1.
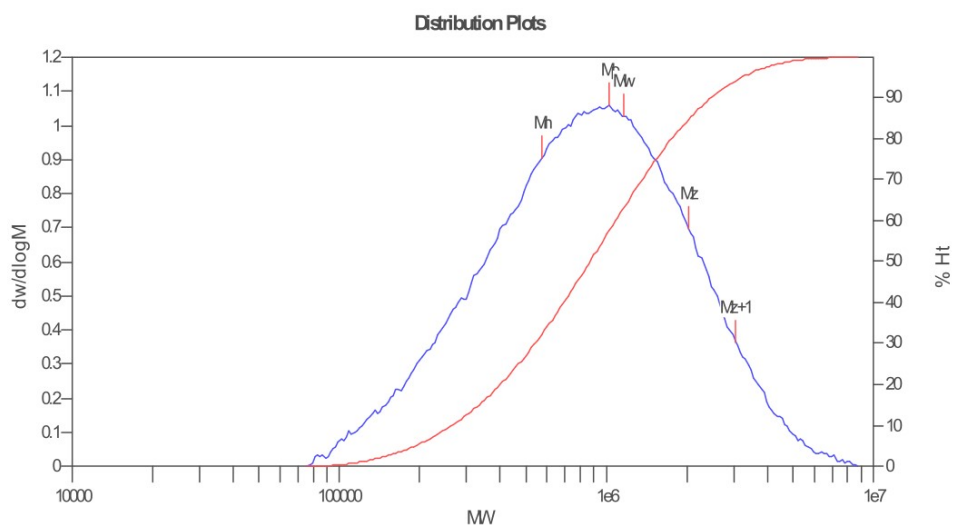
MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	1029535	575296	1156114	2027892	3039748	1051098	2.0096

Figure S36. GPC of the polymer from table 1, entry 2.
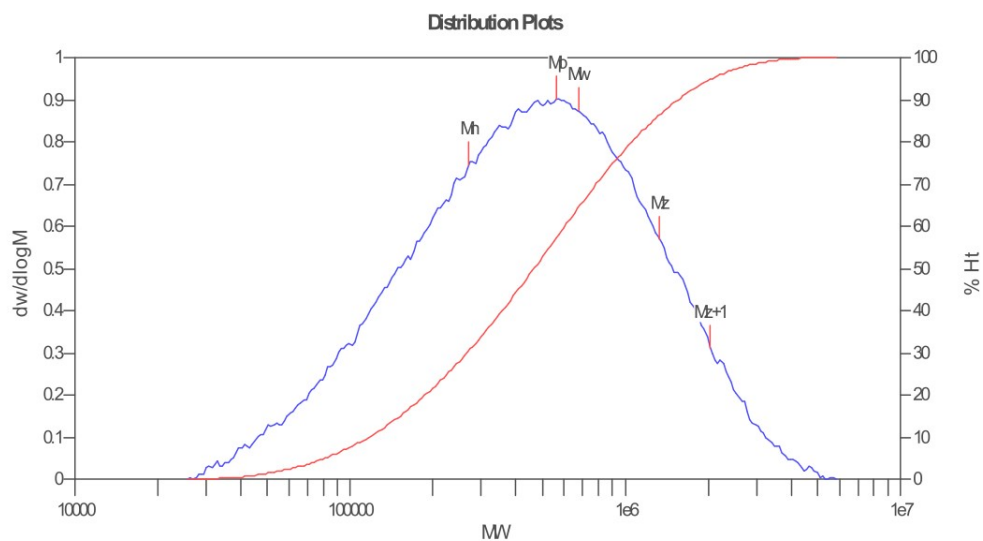
MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	560698	269254	678109	1332790	2038238	600961	2.51847

Figure S37. GPC of the polymer from table 1, entry 3.
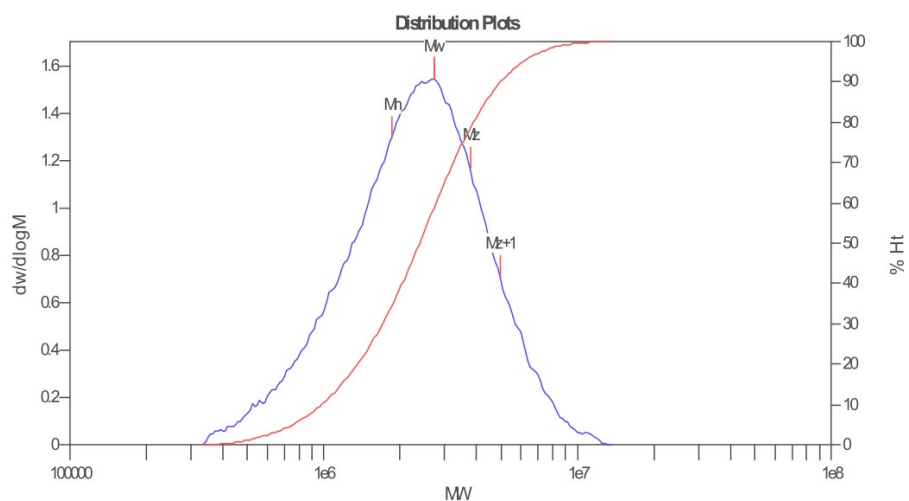
MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	2709854	1845960	2722676	3774762	4943548	2582084	1.47494

Figure S38. GPC of the polymer from table 1, entry 4.
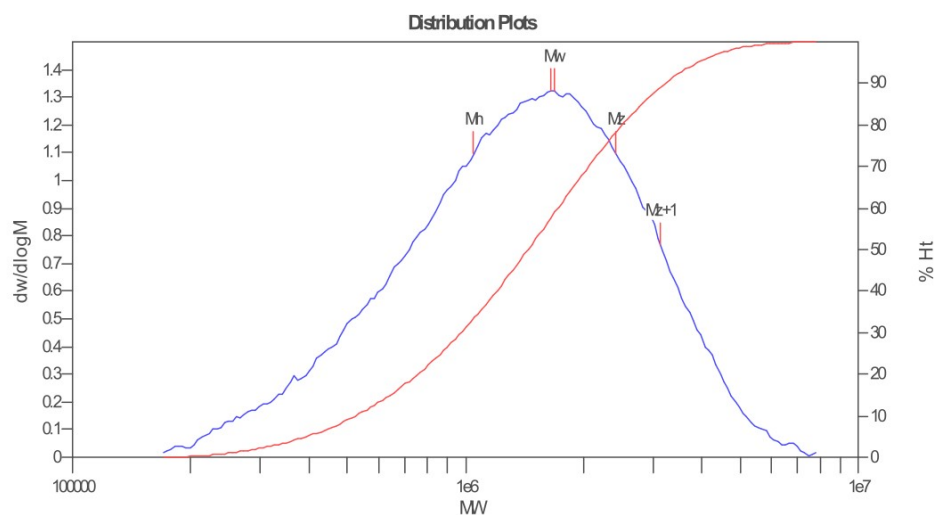
MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	1651605	1047775	1680566	2409726	3136467	1580279	1.60394

Figure S39. GPC of the polymer from table 1, entry 5.
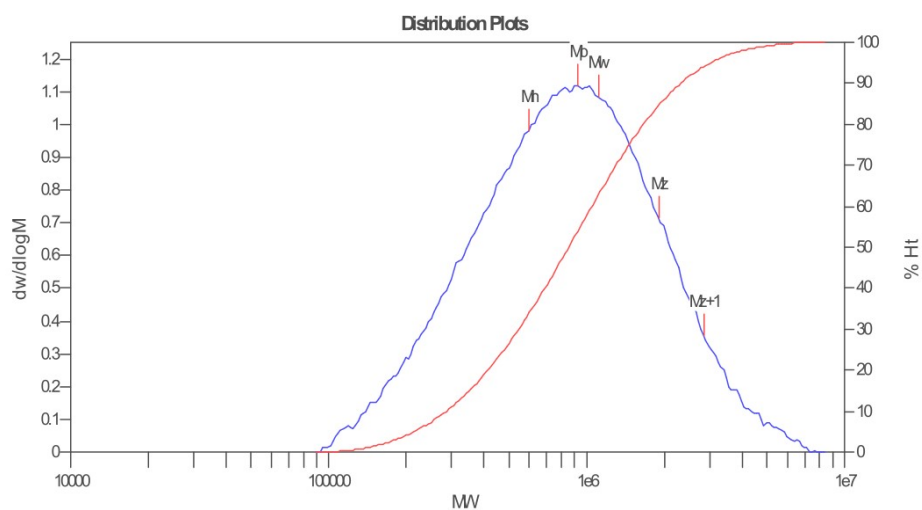
MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	919959	600176	1115148	1904897	2848204	1021017	1.85803

Figure S40. GPC of the polymer from table 1, entry 6.
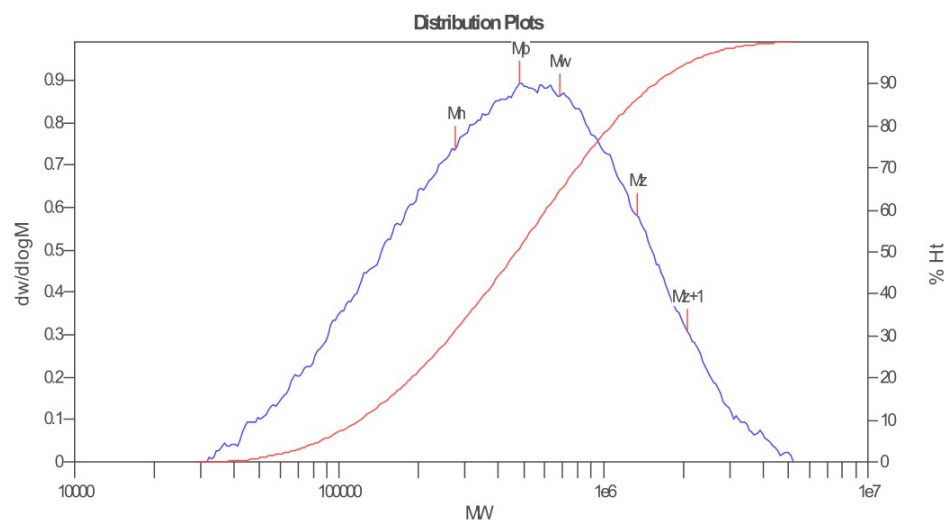
MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	478969	276355	682439	1347853	2070969	604628	2.46943

Figure S41. GPC of the polymer from table 1, entry 7.
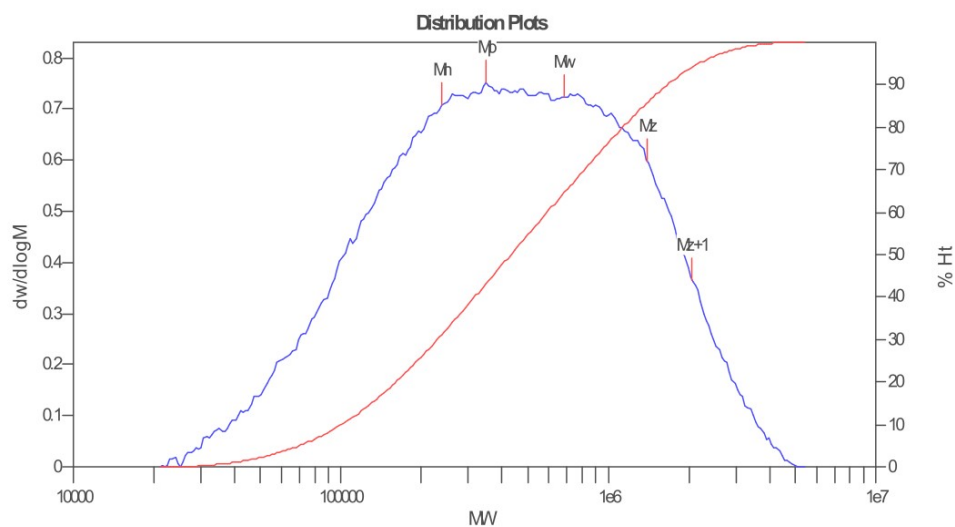
MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	349513	237795	684366	1399550	2051726	597285	2.87797

Figure S42. GPC of the polymer from table 1, entry 8.
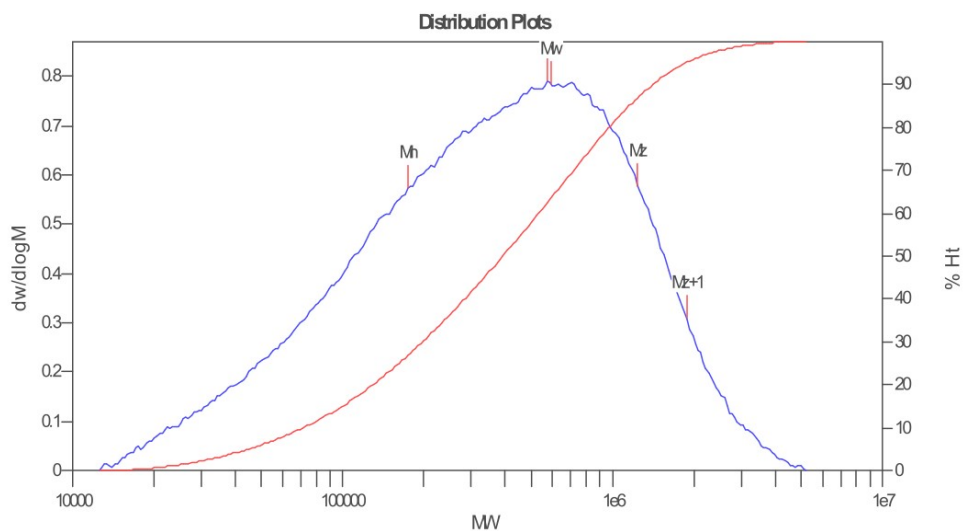
MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	573460	174688	594602	1239810	1885677	516393	3.40379

Figure S43. GPC of the polymer from table 1, entry 9.
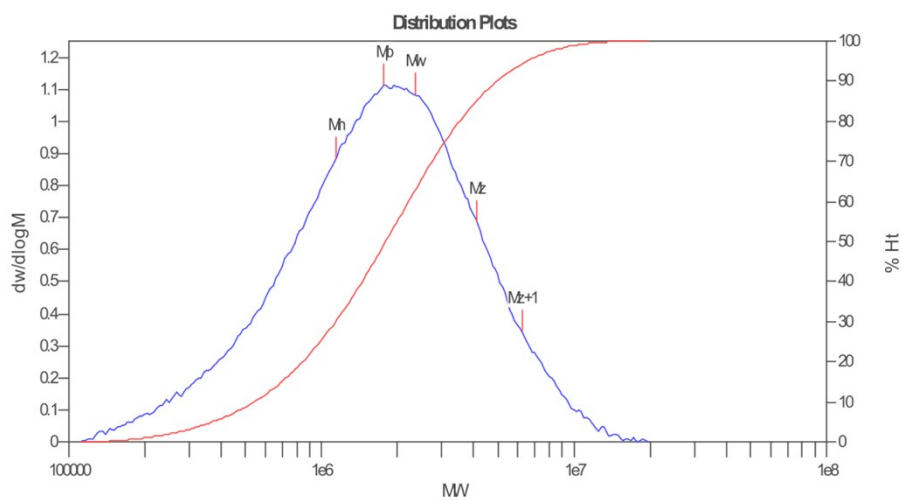
MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	1766973	1142570	2353479	4111595	6211115	2142044	2.05981

Figure S44. GPC of the polymer from table 1, entry 10.

Distribution Plots
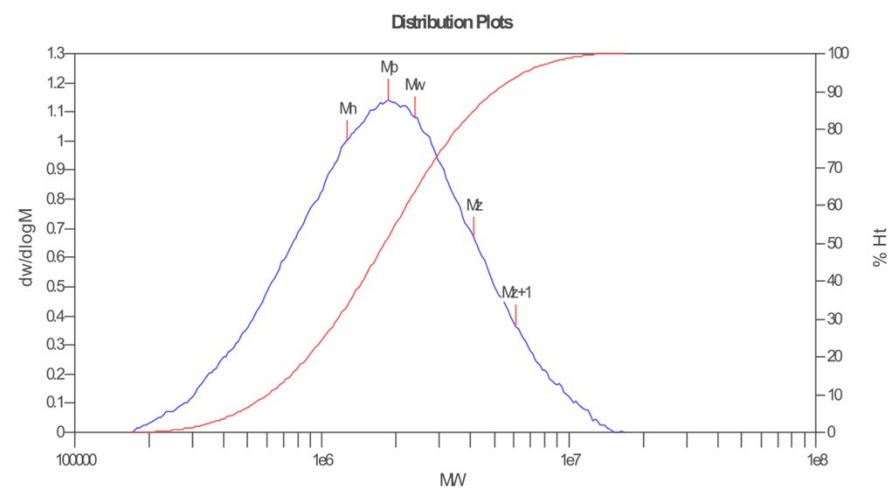
MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	1848327	1260029	2379224	4098218	6083779	2174214	1.88823

Figure S45. GPC of the polymer from table 1, entry 11.

Distribution Plots
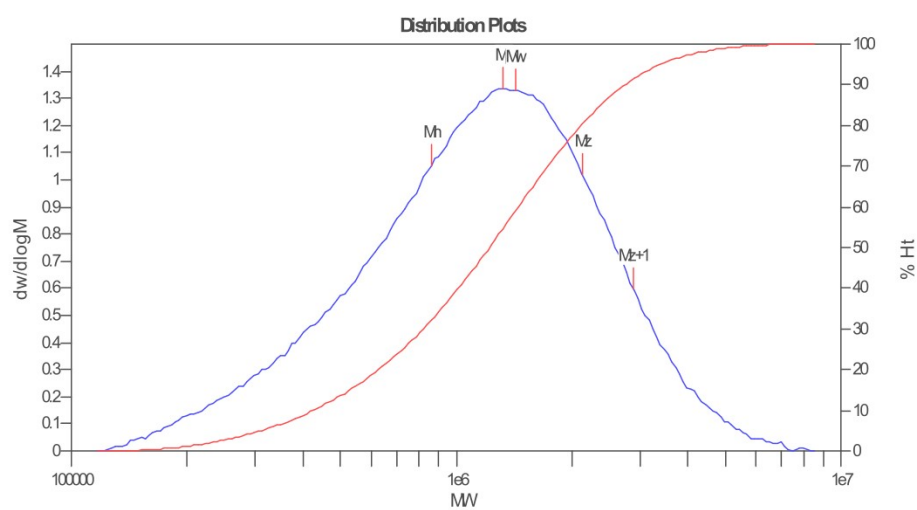
MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	1318746	861315	1431836	2124284	2887235	1340148	1.66238

Figure S46. GPC of the polymer from table 1, entry 12.
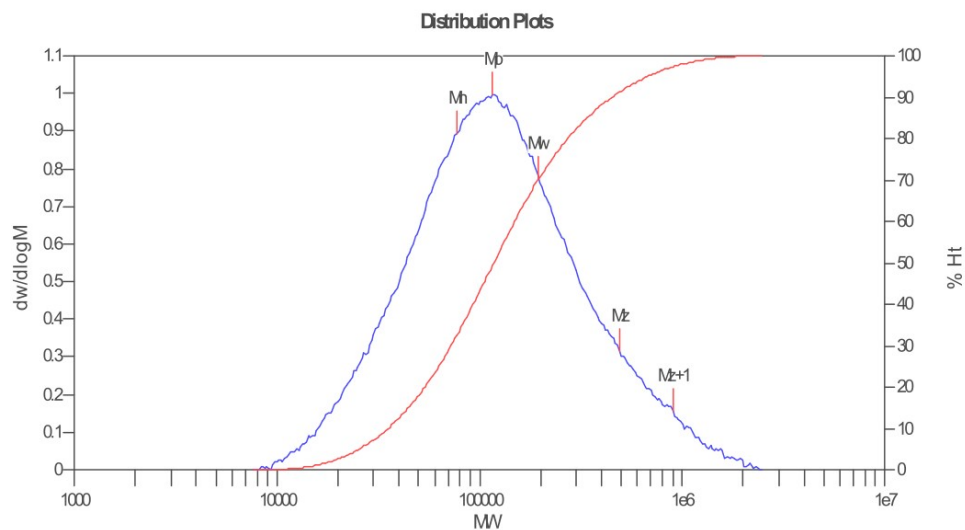
MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	116014	77826	196483	490664	901680	169456	2.52464

Figure S47. GPC of the polymer from table 2, entry 1.
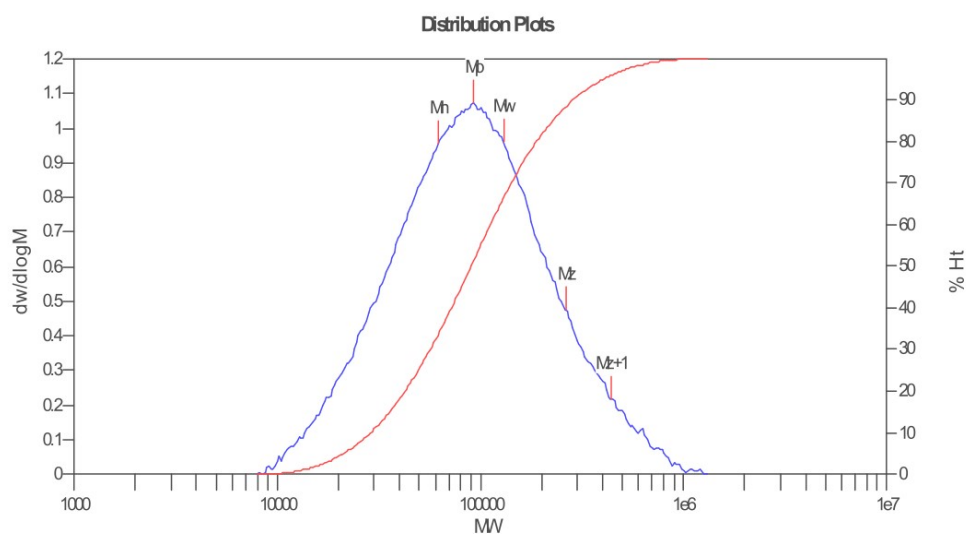
MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	92633	62008	130653	263216	439993	116701	2.10703

Figure S48. GPC of the polymer from table 2, entry 2.
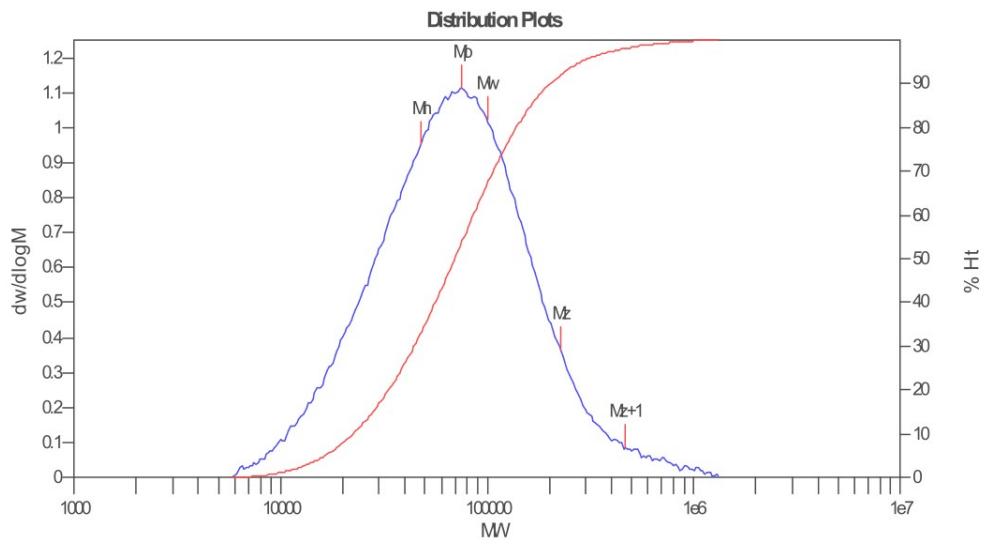
MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	75647	47561	100215	226762	465649	89009	2.10708

Figure S49. GPC of the polymer from table 2, entry 3.
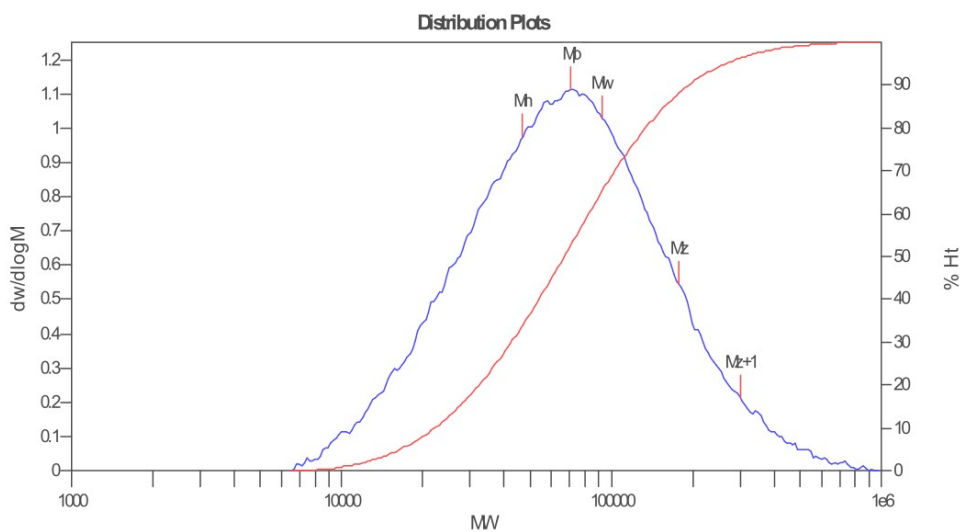
MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	70708	46751	92446	177431	300260	83435	1.97741

Figure S50. GPC of the polymer from table 2, entry 4.
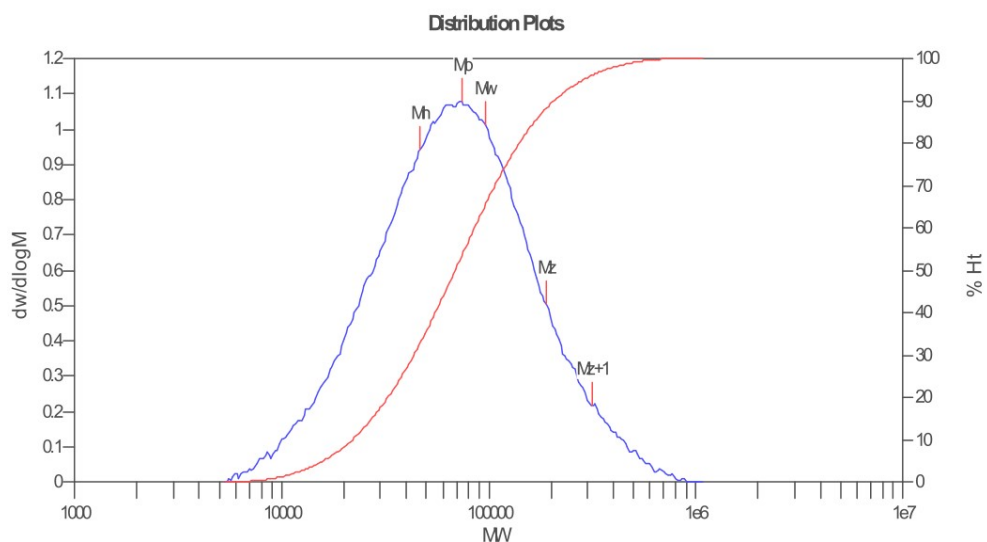
MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	73964	46586	97038	189839	315860	87119	2.08299

Figure S51. GPC of the polymer from table 2, entry 5.
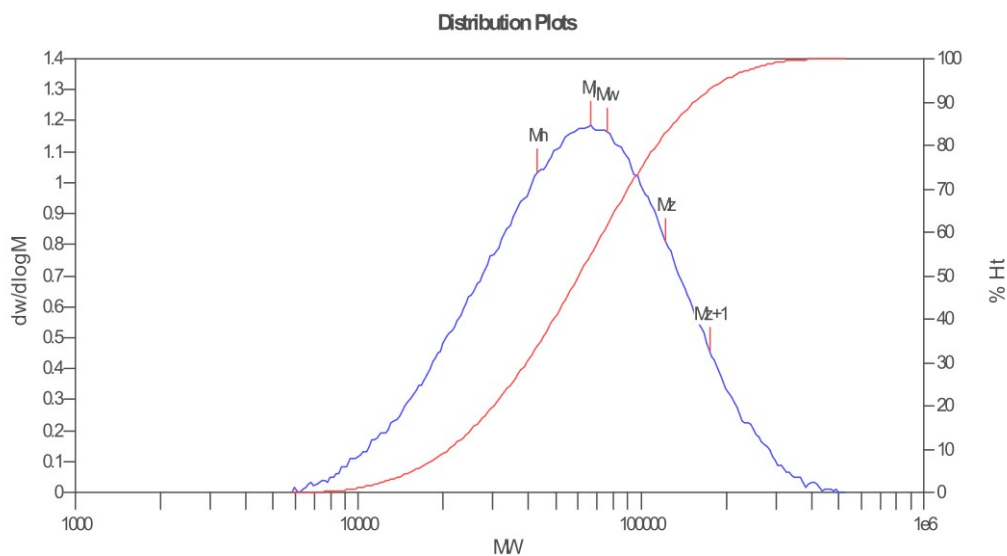
MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	66092	42919	76005	122403	175513	70224	1.77089

Figure S52. GPC of the polymer from table 2, entry 6.
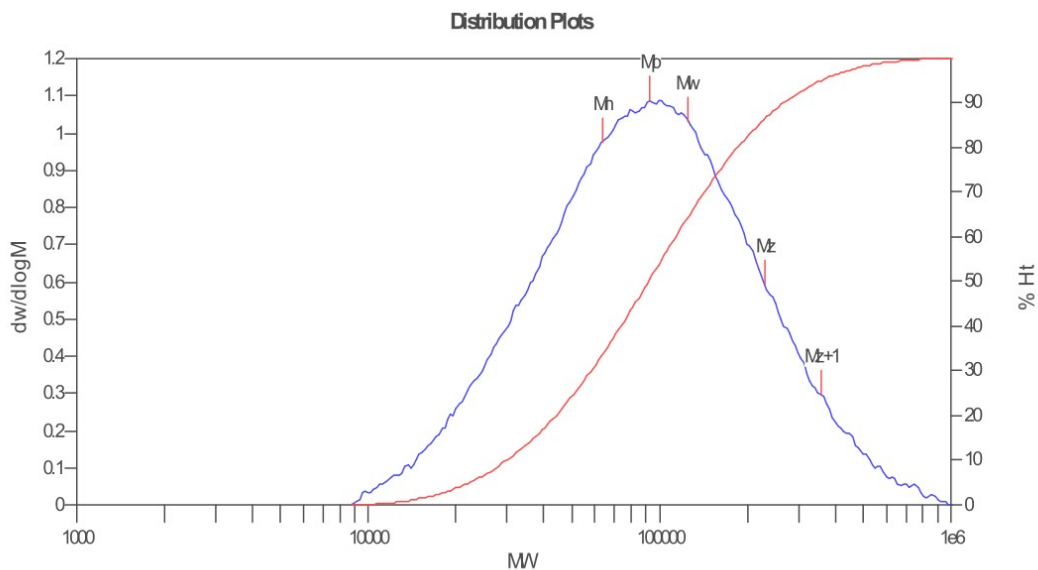
MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	92633	63387	125059	228684	359624	113324	1.97294

Figure S53. GPC of the polymer from table 2, entry 7.
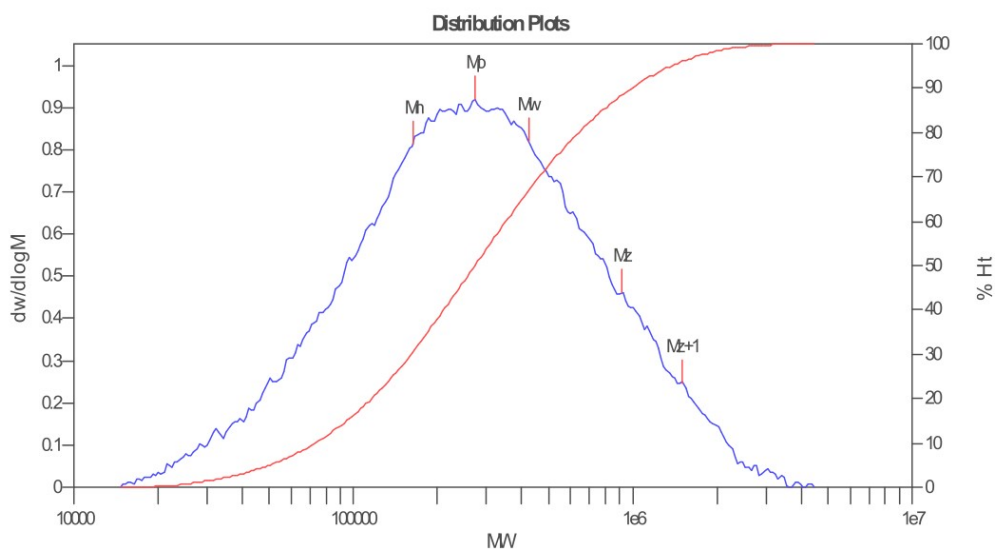
MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	272862	163324	423819	911827	1496337	371222	2.59496

Figure S54. GPC of the polymer from table 2, entry 8.
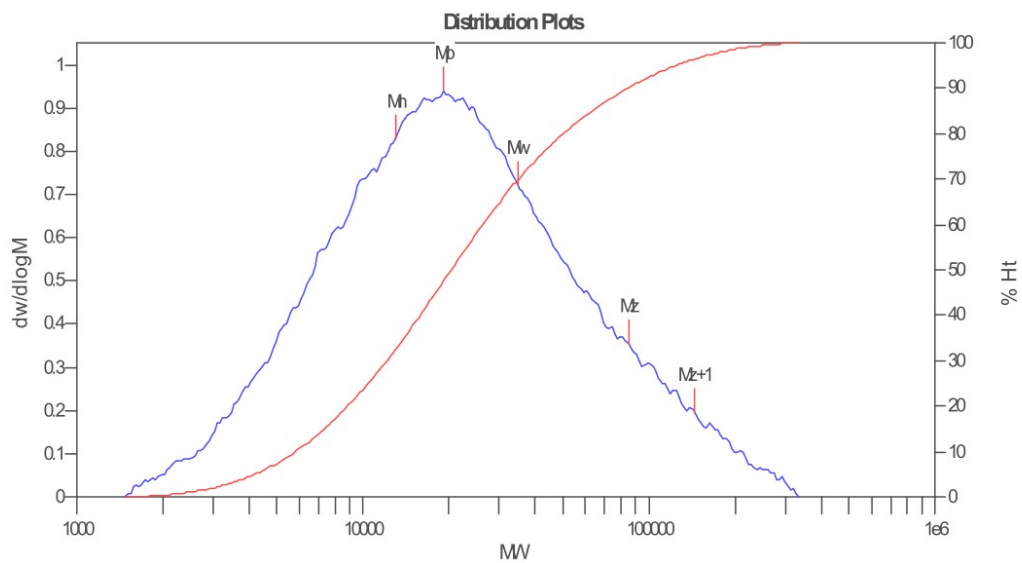
MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	19166	13034	34918	85079	144483	29992	2.67899

Figure S55. GPC of the polymer from table 2, entry 9.
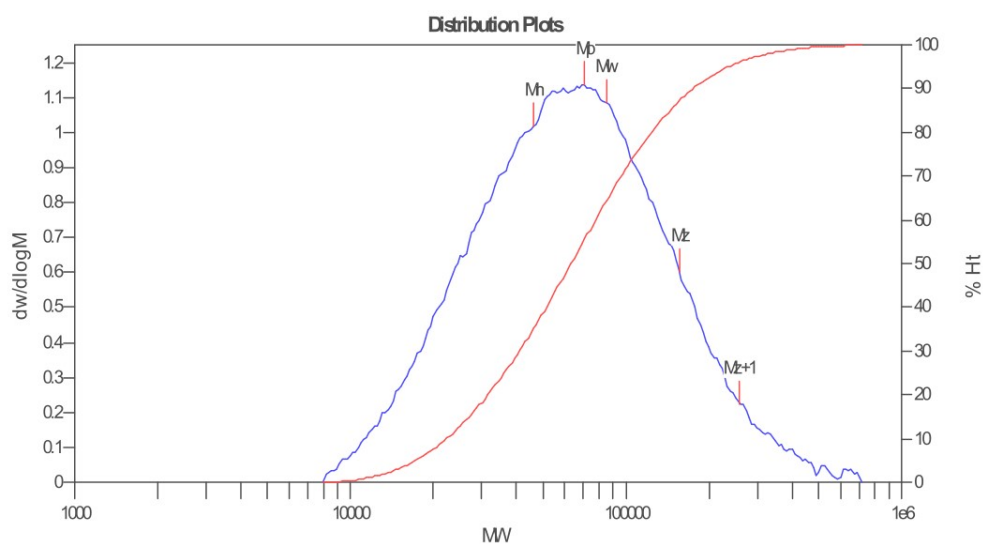
MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	70708	46280	85345	156148	258793	77702	1.8441

Figure S56. GPC of the polymer from table 2, entry 10.

2.5 Water Contact Angle of Polymer

(a) (b)
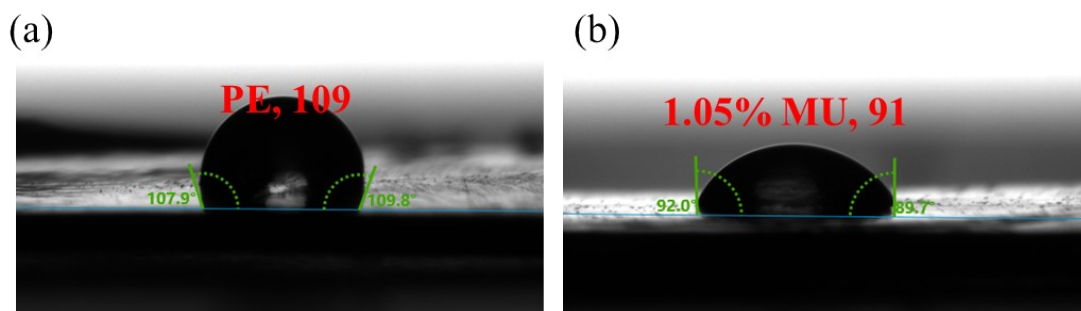
Figure S57. Water contact angle of the polyethylene **(a)** (sample from Table 1, entry 1) and E-MU copolymer **(b)** (sample from Table 2, entry 4)

3. References

1 B. Ding, G. Chang, Z. Yan and S. Dai, Ethylene (co) oligomerization using iminopyridyl Ni(II) and Pd(II) complexes bearing benzocycloalkyl moieties to access hyperbranched ethylene oligomers and ethylene-MA co-oligomers, *Front. Chem.*, 2022, **10**, 961426.

4. X-ray Crystallography.
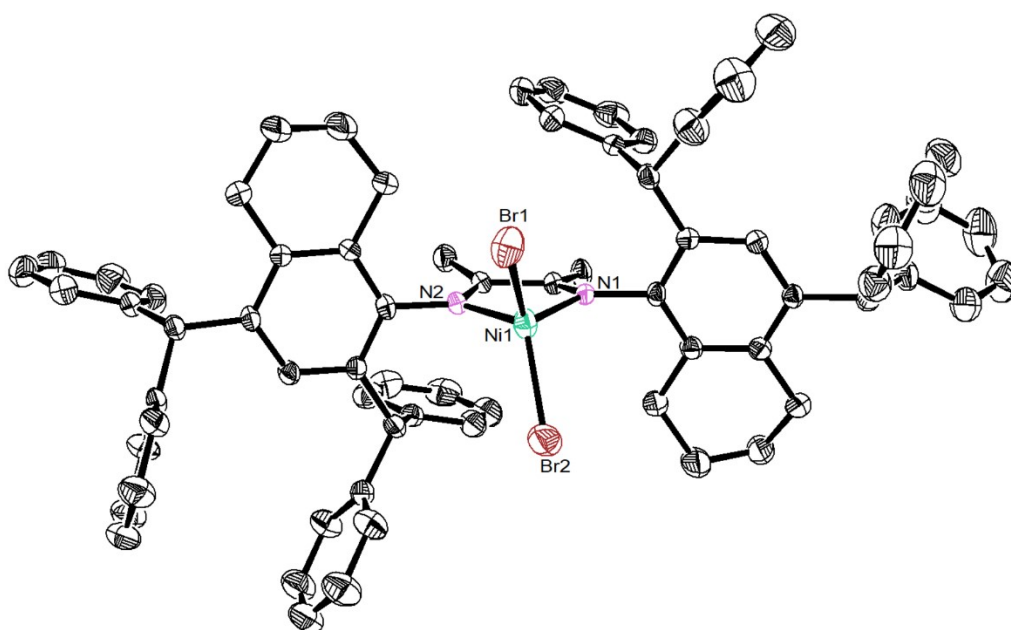
Table S2 Crystal data and structure refinement for Ni2.	
Identification code	**Ni2**

Empirical formula	C77 H70 Br2 Cl2 N2 Ni
Formula weight	1312.78
Temperature/K	298(2)
Crystal system	Monoclinic
Space group	P2(1)/c
a/Å	15.8351(15)
b/Å	23.180(2)
c/Å	17.8789(18)
α/°	90.00
β/°	103.973(4)
γ/°	90.00
Volume/Å^3	6368.3(11)
Z	4
ρ_{calc}g/cm^3	1.369
μ/mm^{-1}	1.689
F(000)	2712
Crystal size/mm^3	0.43 x 0.15 x 0.12
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	2.11 to 25.02
Index ranges	-18<=h<=18, -27<=k<=14, -21<=l<=21
Reflections collected	31023
Independent reflections	11223 [R(int) = 0.0908]
Data/restraints/parameters	11223 / 1156 / 759
Goodness-of-fit on F^2	1.067
Final R indexes [I>=2σ (I)]	R1 = 0.0503, wR2 = 0.0757
Final R indexes [all data]	R1 = 0.1312, wR2 = 0.0843
Largest diff. peak/hole / e Å^{-3}	0.569 and -0.670