Electronic Supplementary Material (ESI) for Polymer Chemistry.

Supporting Information

Lewis acids modulation in phosphorus phenol nickel catalyzed ethylene polymerization and copolymerization

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Content

1. Supplementary Figures and Tables

Supplementary Table S1 Ethylene homopolymerization.[a]

Ent.	Cat.	Lewis Acid	Yield/g	Act.[b]	T_m(°C)[c]	M_n (10^3)[d]	PDI[d]
1	-	$Ni(OAc)_2$	-	-	-	-	-
2	-	$Zn(OAc)_2$	-	-	-	-	-
3	-	$Zn(TMEDA)(OAc)_2$	-	-	-	-	-

[a]Conditions: Lewis Acid 1 μmol, ethylene 8 atm, toluene 20 mL, t=15 min. [b] Activity is in unit of 10^6 g mol^{-1} h^{-1}. [c] Determined by differential scanning calorimetry (DSC; second heating). [d] Determined by GPC in trichlorobenzene at 160 °C with polystyrene standards. M_n is in unit of kg mol^{-1}.

Supplementary Table S2 Ethylene homopolymerization.[a]

Ent.	Cat.	Lewis Acid	Yield/g	Act.[b]	T_m(°C)[c]	M_n (10^3)[d]	PDI[d]
1	Ni1	$Ni(COD)_2$	1.2	4.8	119.1	6.8	2.4
2	Ni2	$Ni(COD)_2$	1.8	7.2	129.1	12.4	3.7
3	Ni3	$Ni(COD)_2$	3.3	13.2	130.5	28.6	5.3

[a]Conditions: **Ni** catalyst 1 μmol, ethylene 8 atm, toluene 20 mL, $Ni(COD)_2$ 1eq, t=15 min. [b] Activity is in unit of 10^6 g mol^{-1} h^{-1}. [c] Determined by differential scanning calorimetry (DSC; second heating). [d] Determined by GPC in trichlorobenzene at 160 °C with polystyrene standards. M_n is in unit of kg mol^{-1}.

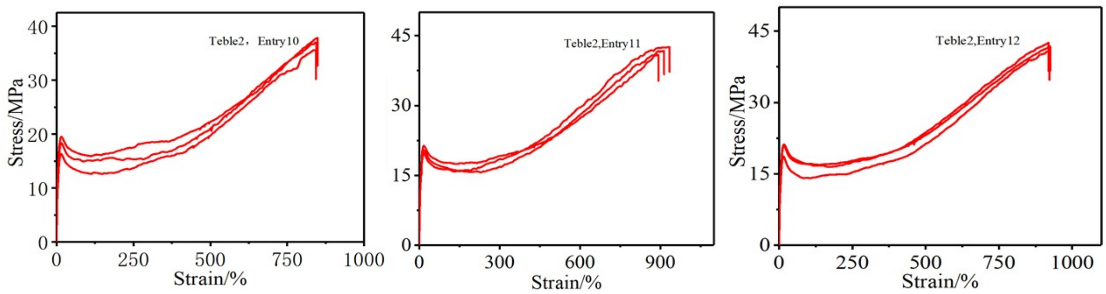


Figure S1 Stress-strain curves for every copolymer tested three times in Figure 4a.

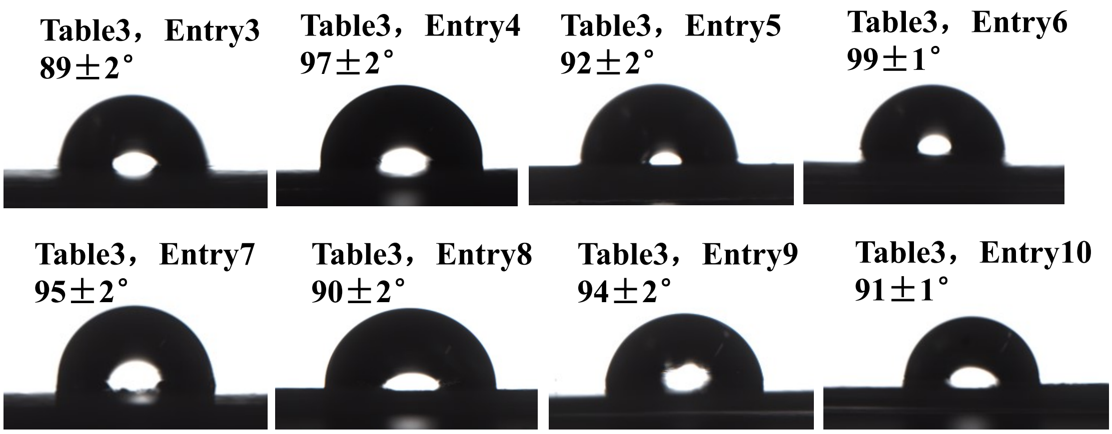


Figure S2 The values and figures of copolymers' WCAs in Figure 4b.

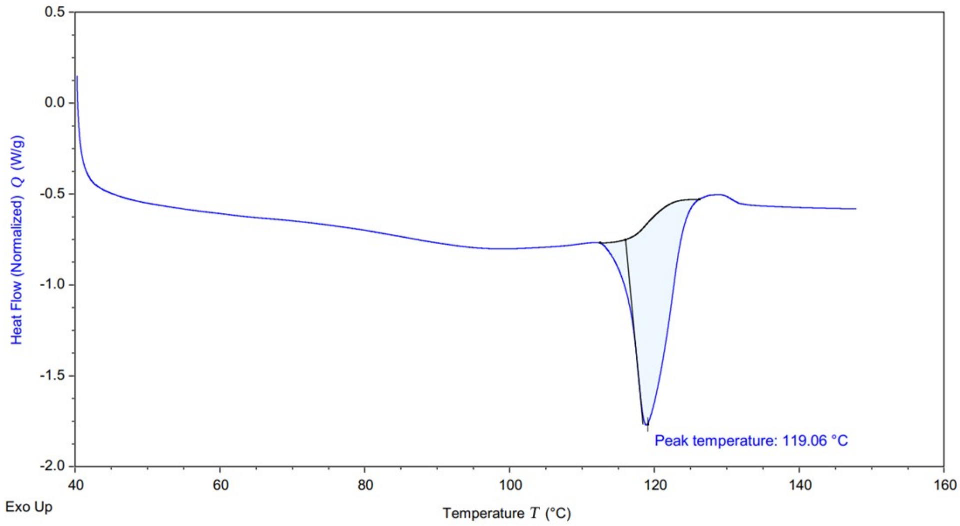


Figure S3 DSC of the polymer from Table S2, Entry 1.

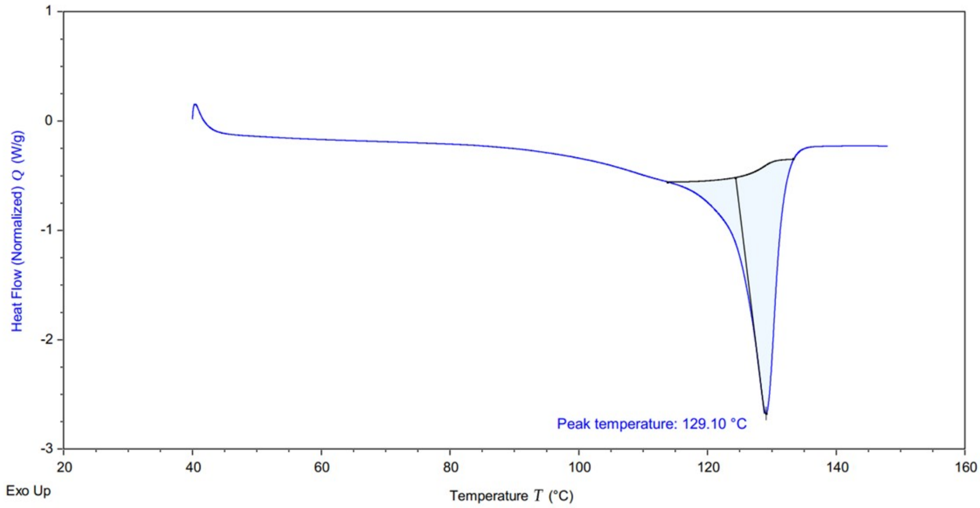


Figure S4 DSC of the polymer from Table S2, Entry 2.

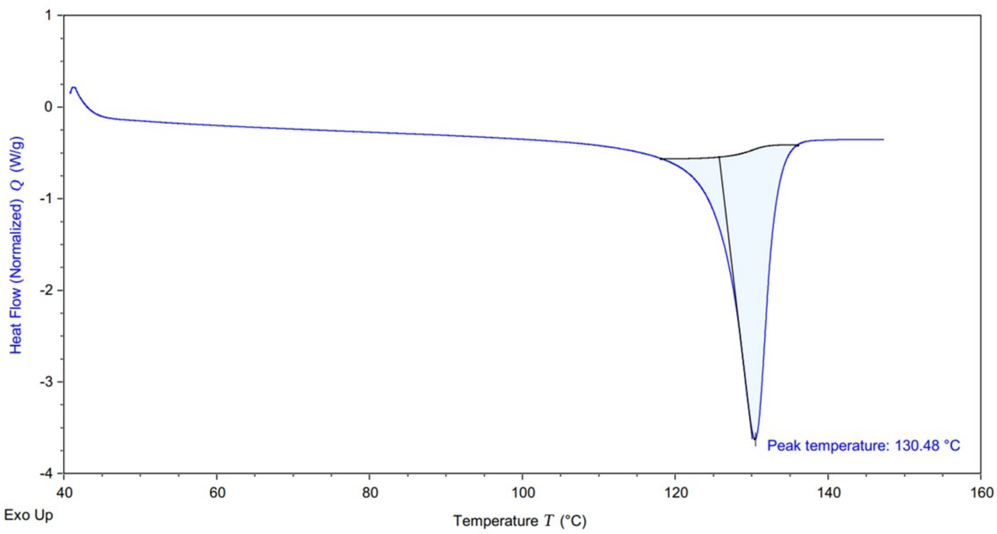
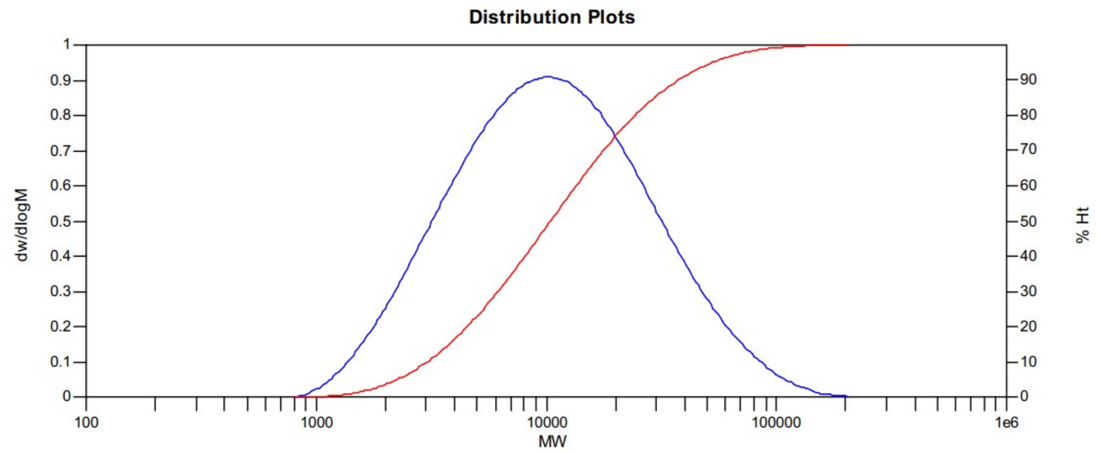


Figure S5 DSC of the polymer from Table S2, Entry 3.



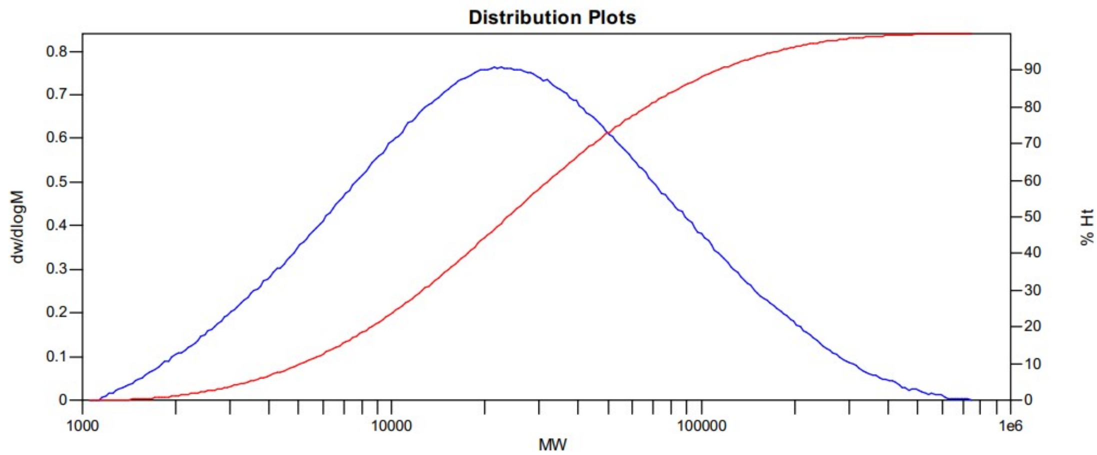
MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	10027	6832	16388	36397	63228	14289	2.39871

Processed Peaks

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1		13.13	15.23	16.90	-17.9506	0	1861.13	100

Figure S6 GPC of the polymer from Table S2, Entry 1.



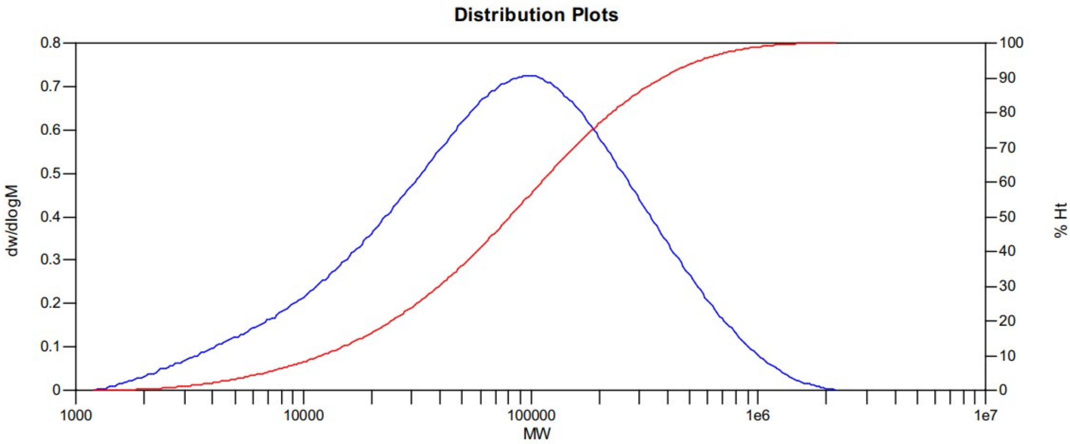
MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	22496	12449	45903	134279	249239	37693	3.68728

Processed Peaks

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1		12.25	14.67	16.72	-6.88011	0	848.833	100

Figure S7 GPC of the polymer from Table S1, Entry 2.



MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	100181	28619	150784	421403	745770	123397	5.26867

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	13.67	16.63	-8.66449	0	1124.82	100

Figure S8 GPC of the polymer from Table S1, Entry 3.

2. Experimental

2.1 General consideration

All manipulations of air- and water-sensitive compounds were carried out using standard Schlenk, high-vacuum, and glovebox techniques. Deuterated solvents used for NMR were dried and distilled prior to use. ^{1}H NMR spectra was recorded by a Bruker Ascend Tm 400 spectrometer at ambient temperature unless otherwise stated. The chemical shifts of the ^{1}H NMR spectra were referenced to the residual solvent; Coupling constants are in Hz. Molecular weight and molecular weight distribution of the polymer were determined by gel permeation chromatography (GPC) with a PL-220 equipped with two Agilent PLgel Olexis columns at 160 °C using trichlorobenzene as a solvent, and the calibration was made using polystyrene standard and are corrected for linear polyethylene by universal calibration using the Mark-Houwink parameters of Rudin: K = 1.75×10^{-2} cm^3/g and R = 0.67 for polystyrene and K = 5.90×10^{-2} cm^3/g and R = 0.69 for polyethylene. DSC measurements were performed on a TA Instruments DSC250. Samples (ca. 5 mg) were annealed by heating to 150 °C at 10 °C /min, cooled to 40 °C at 10 °C /min, and then analyzed while being heated to 150 °C at 10 °C /min.

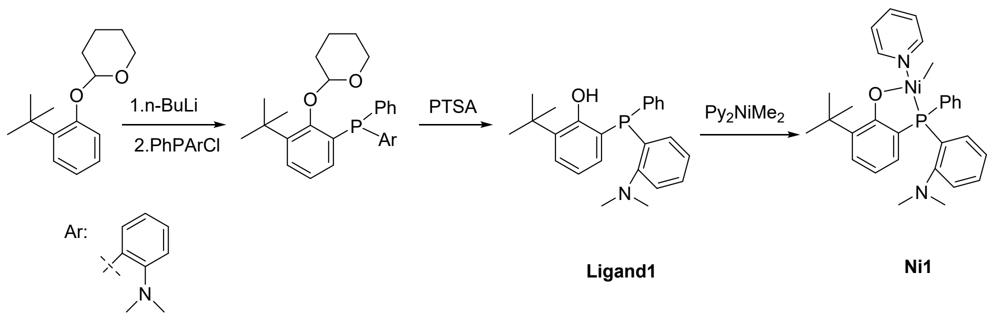
The water contact angles on polymer films were measured with a Contact Angle Meter SL200B (Solon Tech. Co., Ltd.) using the dynamic sessile drop method. Samples for water contact angle measurements were prepared via evaporation of 3 to 5 % (w/w) solutions in toluene onto glass slides under ambient conditions. The solvent was evaporated on top of a glass slide for 10 minutes, and a second layer of the polymer solution was then applied to increase thickness. The water contact angles of the polymer thin films were measured using a contact angle goniometer at 25 °C with an accuracy of ±3°. The reported values are the average of at least six measurements made at different positions of the film.

A standard test method, ASTM 638, was followed to measure the tensile properties of the polyethylene samples. Polymers were melt-pressed at 30 to 35^{o}C above their melting point to obtain the dog-bone-shaped tensile-test specimens. The test specimens showed 25-mm gauge length, 2-mm width, and thickness of 0.4 mm. Stress/strain experiments were performed at 10 m/min using a Universal Test Machine (UTM2502) at room temperature. At least three specimens of each copolymer were tested.

2.2 Ethylene polymerization procedure.

For the polymerization reaction of ethylene at 8 atm pressures, a 350 mL glass thick-walled pressure vessel was charged with toluene, a desired amount of comonomer, and a magnetic stir bar in the glovebox. The pressure vessel was connected to a high-pressure line, and the solution was degassed. The vessel was warmed to the desired temperature using an oil bath and allowed to equilibrate for 5 min. The metal catalyst Ni1-Ni3 in toluene was injected into the polymerization system via syringe. With rapid stirring, the reactor was pressurized, maintained at a desired ethylene pressure, and stirred continuously for a desired period. The pressure vessel was vented, the polymerization was quenched via the addition of MeOH (5 mL), and the polymer was precipitated using excess MeOH. After filtration, the polymer sample was obtained and dried at 80 °C for 24 h under vacuum. The polar monomer incorporation (mol%) was calculated from NMR analysis. In particular, 30 atm ethylene polymerization takes place in a closed mechanical stirring kettle.

2.3 Ligand preparation procedures.

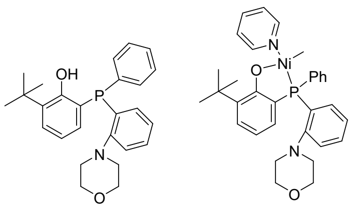


Ni 1: Under nitrogen, 2-(2-(*tert*-butyl)phenoxy)tetrahydro-2*H*-pyran (2.34g,10 mmol) was dissolved in 50 mL of dried THF. n-BuLi(4.6mL,2.4 M in hexane,11 mmol,1.1 equiv) was added dropwise and the reaction mixture was stirred for 2 h at 0 ^{o}C. The flask was transferred to a -78 ^{o}C bath, and the THF solution of PhPArCl (10 mmol,1.0 equiv) was added dropwise. The mixture was stirred for 1 hour, and warmed to room temperature to react for 12 hours. After quenching, the suspension was transferred to a round bottom flask and the THF was evaporated on a rotary evaporator. The crude material was then extracted with DCM (3 x 200 mL), washed with H_2O (3 x 100 mL), and then collect the organic phase and dried with Na_2SO_4. After filtration and concentration, the crude product of the protected ligand can be obtained, which can be directly used for the next reaction without further purification. Then, the protected ligand was dissolved in methanol under nitrogen, 3.0 eq of p-toluenesulfonic acid was added to react for 6 hours. Then, the reaction solution was evaporated with a rotary evaporator to evaporate methanol, the crude material was then extracted with DCM (3 x 200 mL), washed with H_2O (3 x 100 mL), and then collect the organic phase and dried with Na_2SO_4. After filtration and concentration, the pure ligand 1 was obtained by column chromatography as a white solid (1.80 g, 48%). Under nitrogen, a toluene solution of 1 mmol (377 mg) of the ligand and 1.2 eq Py_2NiMe_2 was stirred for 1 hour at room temperature. After concentrating, adding nhexane for recrystallization resulted in the formation of **Ni 1** (428 mg, 81%) as a yellow solid.

Ligand 1: ^{1}H NMR (400 MHz, $CDCl_3$) ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 (s, 1H), 7.43 – 7.28 (m, 6H), 7.23 – 7.15 (m, 1H), 7.11 (s, 2H), 6.91 (s, 1H), 6.76 (t, *J* = 7.5 Hz, 1H), 2.54 (s, 6H), 1.42 (s, 9H). ^{31}P NMR (162 MHz, $CDCl_3$) δ -41.48. ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.61, 157.40, 132.15, 131.98, 128.97, 127.29, 127.22, 127.18, 127.04, 121.19, 120.40, 120.37, 118.90, 118.89, 76.30, 75.98, 75.67, 44.34, 44.31. ESI-MS (m/z): $[M+H]^+$ Calcd for $C_{24}H_{29}ONP$, 378.19813; Found: 378.19809.

Ni 1: ^{1}H NMR (400 MHz, C_6D_6) δ 8.50 (s, 2H), 7.58 (t, J = 7.7 Hz, 2H), 7.19 - 7.01 (m, 2H), 6.79 (s, 5H), 6.54 (s, 2H), 6.24 (d, J = 5.8 Hz, 3H), 2.44 (s, 6H), 1.32 (s, 9H), -0.78 (d, J = 4.6 Hz, 3H). ^{31}P NMR (162 MHz, C_6D_6) δ 13.36. ^{13}C NMR (101 MHz, C_6D_6) δ 173.98, 173.77, 157.25, 157.14, 137.11, 137.02, 132.60, 131.84, 131.75, 130.10, 129.48, 126.88, 126.64, 126.39, 123.62, 123.54, 122.11, 122.05, 118.69, 118.17, 112.08, 112.01, 44.72, 33.87, 28.30, -17.19 (d, J = 38.5 Hz，Ni-*Me*). Anal. Calcd for $C_{30}H_{36}N_2NiOP$: C, 67.95; H, 6.84; N, 5.28. Found: C, 67.76; H, 6.87; N, 5.33.

Ni 2: A procedure similar to the **Ni 1;**



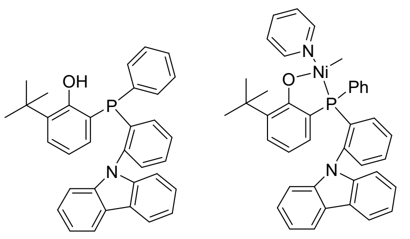
Ligand 2 Ni 2

Ligand 2(10mmol,1.90g,46%):^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 - 7.34 (m, 7H), 7.31 (dd, J = 7.5, 1.8 Hz, 1H), 7.22 (m, J = 7.8, 4.7, 0.9 Hz, 1H), 7.12 (t, J = 7.5 Hz, 1H), 6.94 (m, J = 7.6, 4.7, 1.5 Hz, 1H), 6.87 - 6.75 (m, 2H), 3.59 (t, J = 4.4 Hz, 4H), 2.97 - 2.84 (m, 2H), 2.63 (d, J = 10.5 Hz, 2H), 1.46 (s, 9H). ^{31}P NMR (162 MHz, $CDCl_3$) δ -41.83. ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.27, 158.06, 155.19, 155.03, 135.95, 133.85, 133.66, 133.06, 132.46, 130.18, 128.77,128.60, 128.53, 125.98, 125.96, 122.43, 122.41, 120.14, 120.11, 77.40, 77.08, 76.76, 67.19, 52.82, 34.98, 34.96, 29.62. ESI-MS (m/z): $[M+H]^+$ Calcd for $C_{26}H_{31}O_2NP$, 420.20869; Found: 420.20844.

Ni 2 (1mmol,468 mg, 82%): ^{1}H NMR (400 MHz, C_6D_6) δ 8.49 (s, 2H), 7.66 (dd, J =

8.3, 4.8 Hz, 2H), 7.08 - 6.94 (m, 2H), 6.89 - 6.75 (m, 7H), 6.63 (s, 1H), 6.51 (s, 2H), 6.26 - 6.12 (m, 3H), 4.19 - 3.68 (m, 4H), 2.84 (s, 2H), 2.45 (s, 2H), 1.29 (s, 9H), -0.78 (d, J = 4.9 Hz, 3H). ^{31}P NMR (162 MHz, C_6D_6) δ 18.72. ^{13}C NMR (101 MHz, C_6D_6) δ 156.64, 156.55, 138.26，138.17, 134.64, 134.61, 133.26, 133.17, 131.60, 131.54, 131.53, 129.92, 129.25, 129.23, 129.00, 128.49, 128.40, 127.95, 127.83, 127.71, 127.59, 127.46, 125.25, 125.17, 124.05, 123.99, 121.13, 113.15, 113.08, 67.34, 53.97, 34.89, 34.87, 29.44, -15.82 (d, J = 39.2 Hz, Ni-*Me*). Anal. Calcd for $C_{32}H_{38}N_2NiO_2P$: C, 67.16; H, 6.69; N, 4.89. Found: C, 67.02; H, 6.77; N, 4.92.

Ni 3: A procedure similar to the **Ni 1;**



Ligand 3 Ni 3

Ligand 3(10mmol,2.25g,45%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (dd, *J* = 17.7, 7.5 Hz, 2H), 7.57 (d, *J* = 7.5 Hz, 1H), 7.50 (s, 1H), 7.38 (d, *J* = 16.1 Hz, 2H), 7.31 (s, 1H), 7.26 – 7.20 (m, 4H), 7.20 – 7.10 (m, 5H), 7.04 (d, *J* = 8.1 Hz, 1H), 6.88 (dd, *J* = 6.8, 5.7 Hz, 1H), 6.73 (t, *J* = 7.6 Hz, 1H), 6.64 (d, *J* = 8.0 Hz, 1H), 1.19 (s, 9H). ^{31}P NMR (162 MHz, $CDCl_3$) δ -44.19. ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.54, 158.32, 133.63, 133.44, 128.50, 128.43, 125.46, 120.17, 119.95, 119.67, 119.64, 77.35, 77.24, 77.04, 76.72, 34.68, 34.66, 29.35. ESI-MS (m/z): $[M+H]^+$ Calcd for $C_{34}H_{30}NOP$, 500.21378; Found: 500.21375.

N**i 3** (1mmol,527 mg, 81%): ^{1}H NMR (400 MHz, C_6D_6) δ 8.06 - 7.97 (m, 2H), 7.75 (dd, *J* = 23.7, 13.9 Hz, 6H), 7.43 - 7.22 (m, 4H), 7.03 (m, *J* = 40.8, 21.5, 5.6 Hz, 8H), 6.77 - 6.56 (m, 4H), 6.33 (s, 2H), 1.30 (d, *J* = 3.4 Hz, 9H), -0.83 (t, *J* = 4.4 Hz, 3H). ^{31}P NMR (162 MHz, C_6D_6) δ -18.94. ^{13}C NMR (101 MHz, C_6D_6) δ 149.09, 143.00, 142.61, 137.59, 134.83, 134.10, 133.08, 131.79, 131.70, 130.80, 128.95, 128.26, 127.56, 127.46, 127.09, 126.85, 126.61, 125.13, 124.24, 123.84, 122.95, 121.55, 119.02, 118.79, 118.43, 116.82, 112.59, 111.71, 110.76, 33.77, 28.43, -14.59 (d, *J* =

36.3 Hz, Ni-*Me*). Anal. Calcd for $C_{40}H_{38}N_2NiOP$: C, 73.64; H, 5.87; N, 4.29. Found: C, 73.52; H, 5.78; N, 4.22.

3. **[1]H NMR** and **[13]C NMR** of the ligands and catalyst

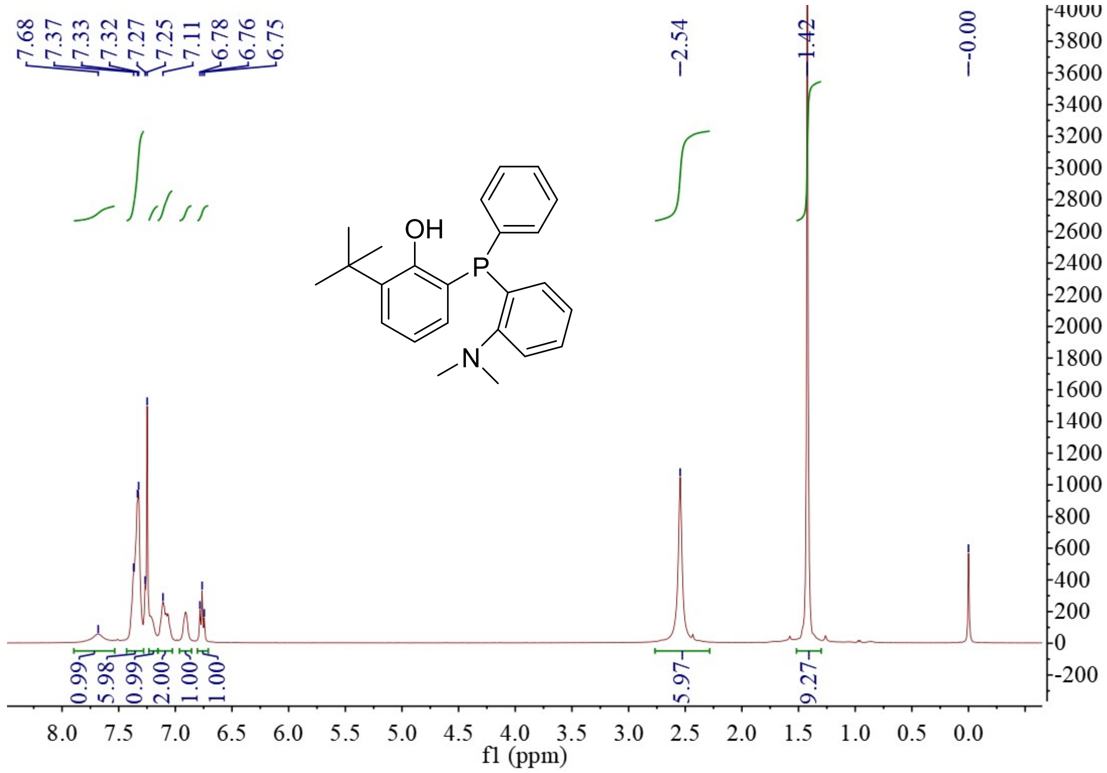


Figure S9 [1]H NMR spectrum of **L1**. (400 MHz, $CDCl_3$).

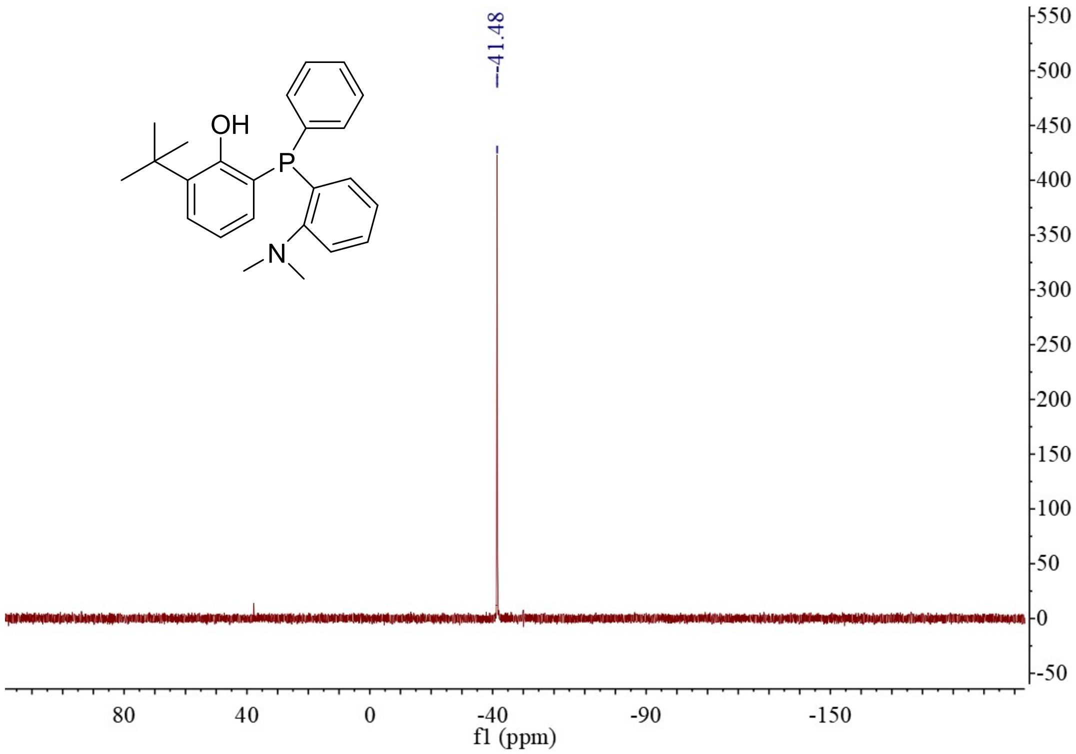


Figure S10 ^{31}P NMR spectrum of **L1**. (162 MHz, $CDCl_3$).

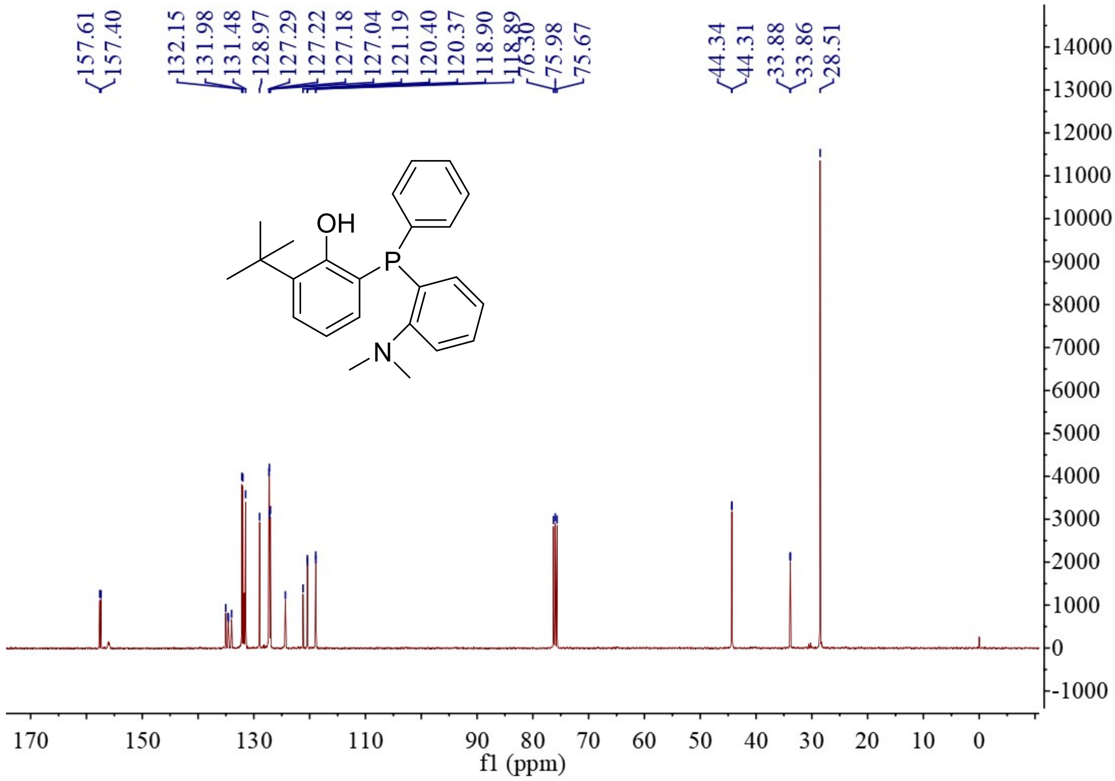


Figure S11 ^{13}C NMR spectrum of **L1**. (101 MHz, $CDCl_3$).

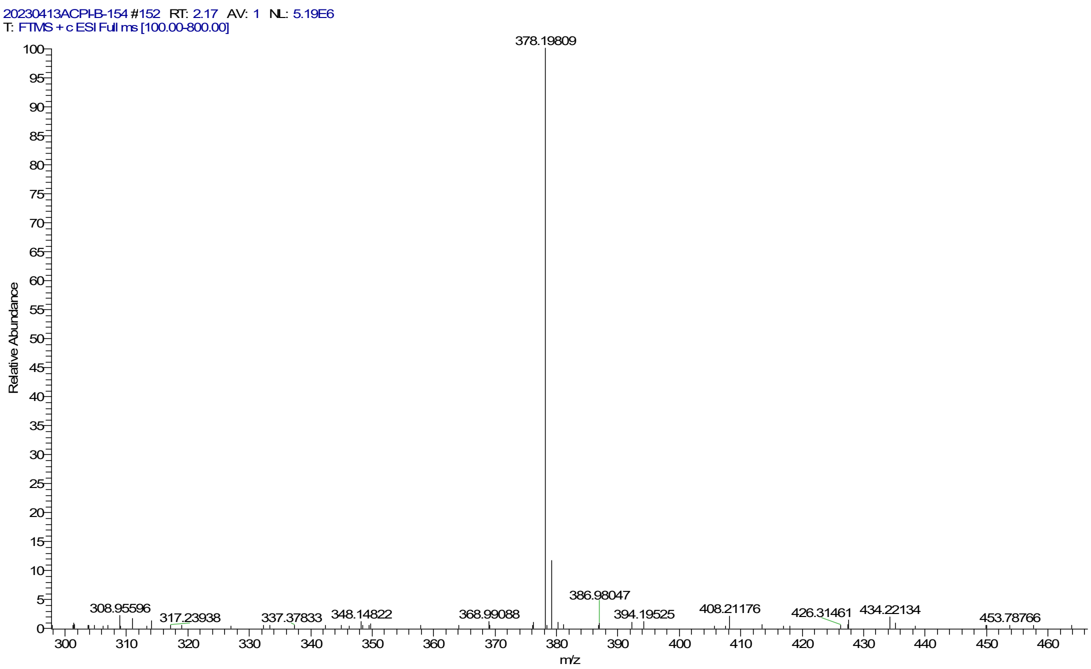


Figure S12 ESI-MS spectrum of **L1.**

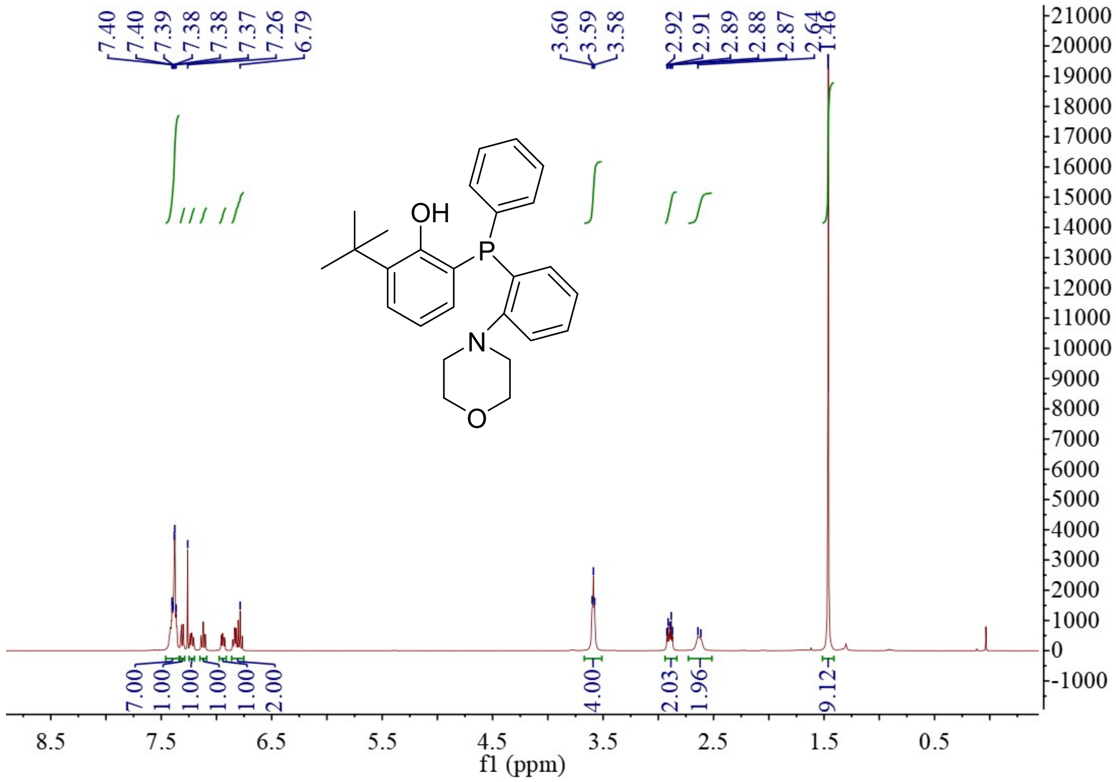


Figure S13 ^{1}H NMR spectrum of **L2**. (400 MHz, $CDCl_3$).

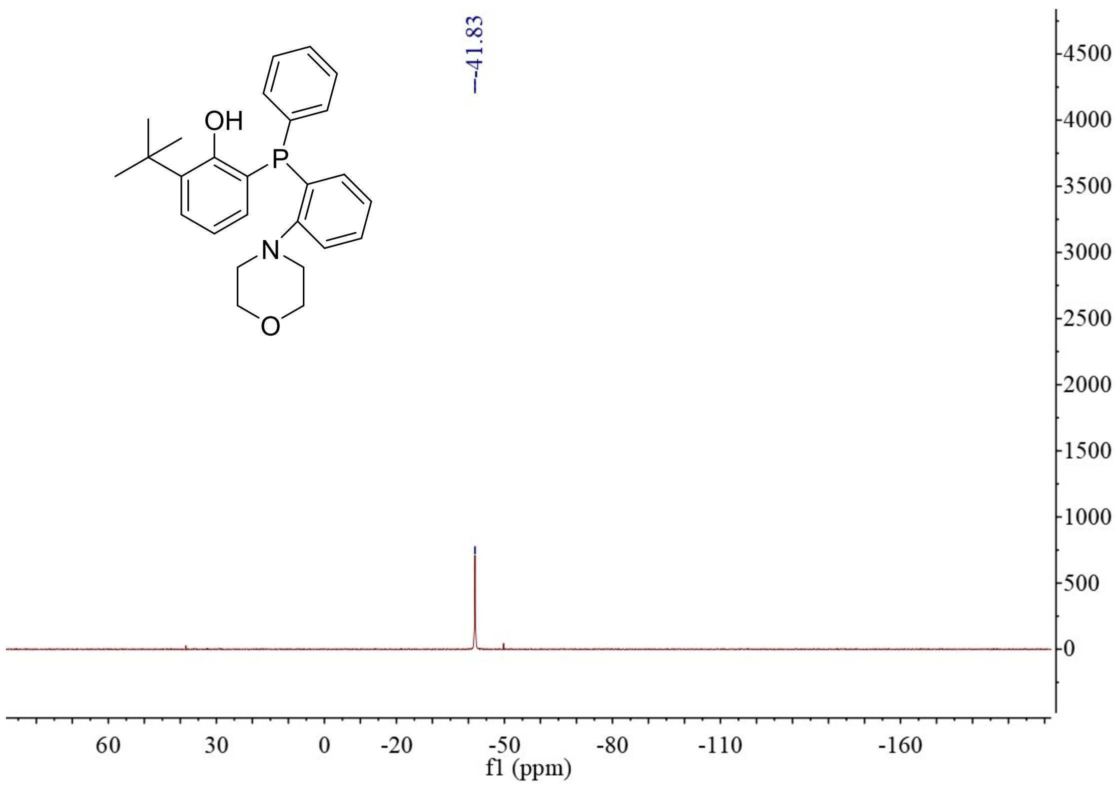


Figure S14 ^{31}P NMR spectrum of **L2**. (162 MHz, $CDCl_3$).

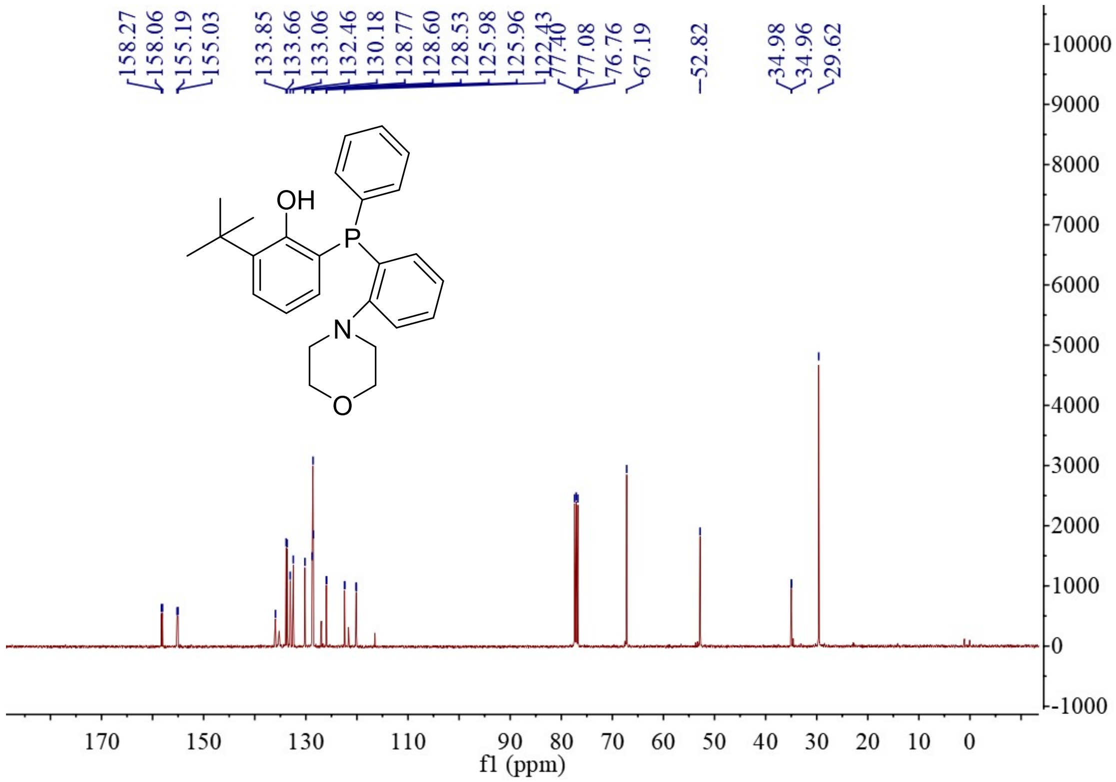


Figure S15 ^{13}C NMR spectrum of **L2**. (101 MHz, $CDCl_3$).

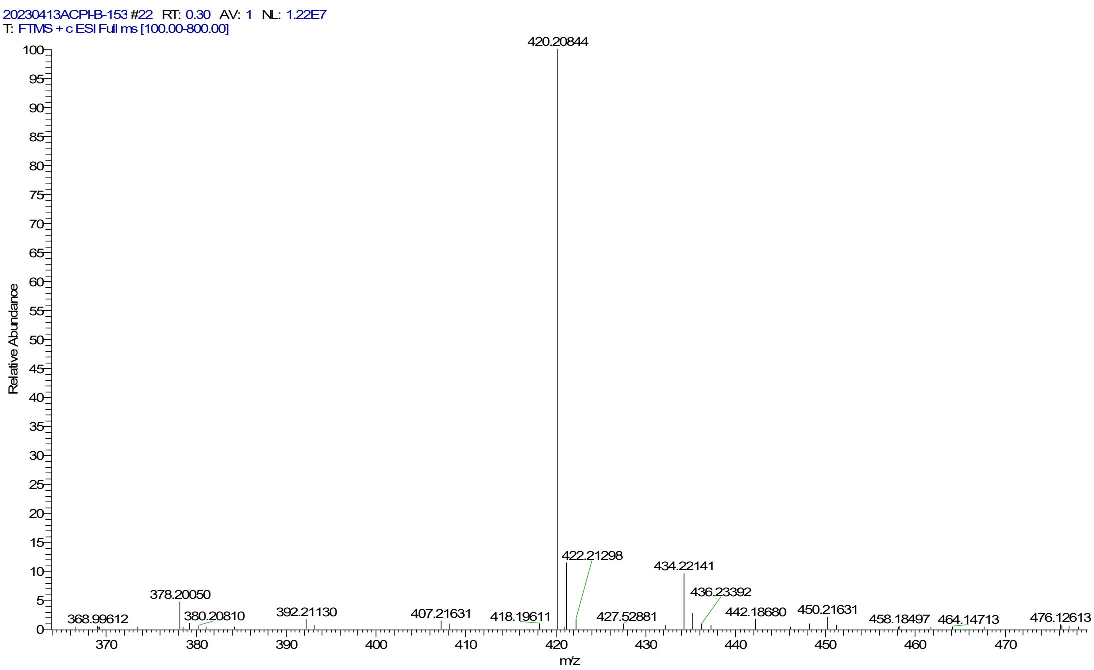


Figure S16 ESI-MS spectrum of **L2.**

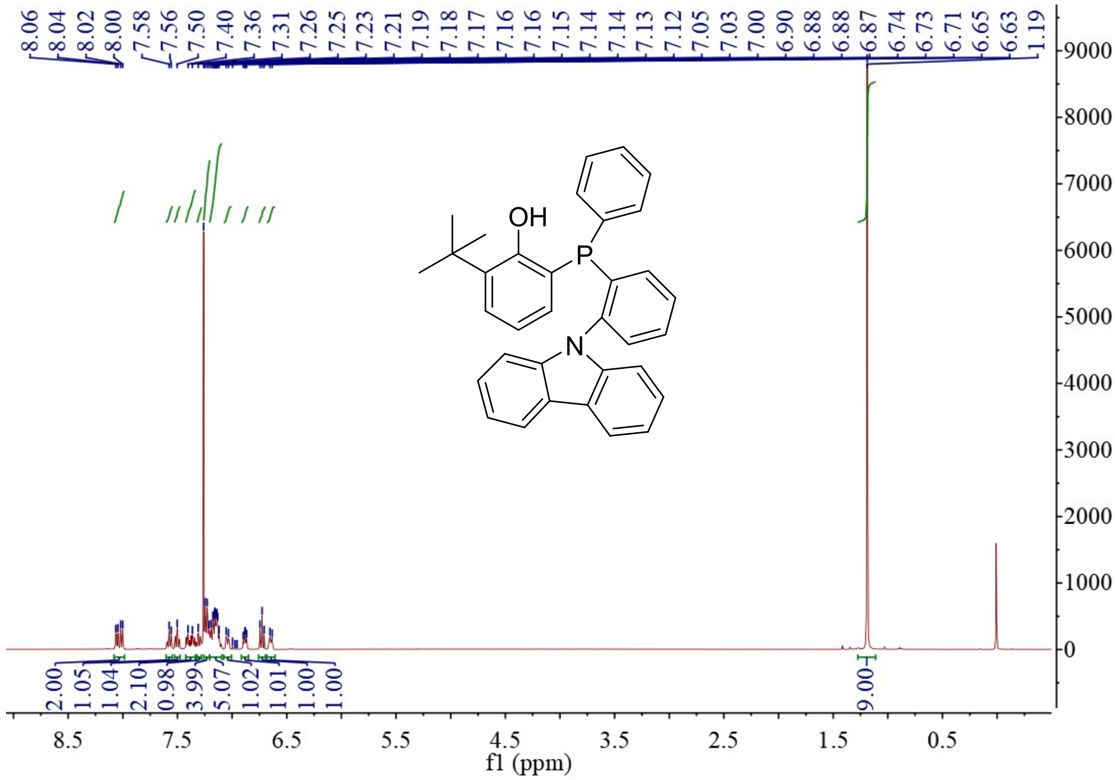


Figure S17 ^{1}H NMR spectrum of **L3**. (400 MHz, $CDCl_3$).

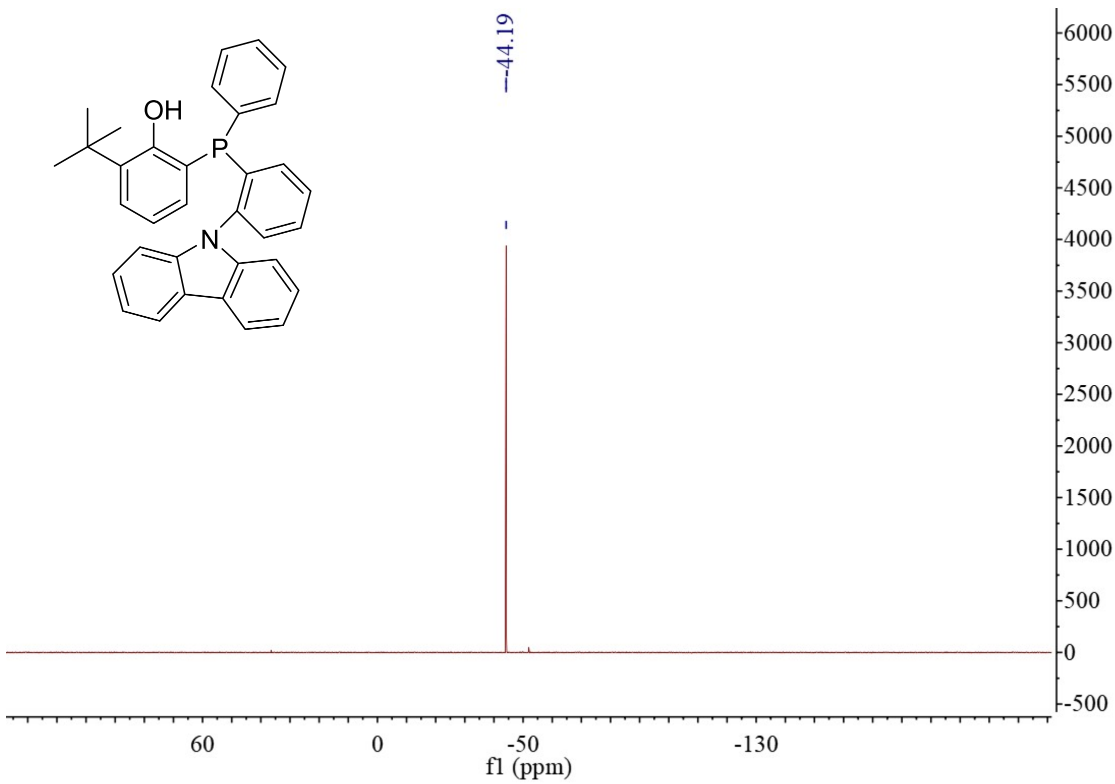


Figure S18 ^{31}P NMR spectrum of **L3**. (162 MHz, $CDCl_3$).

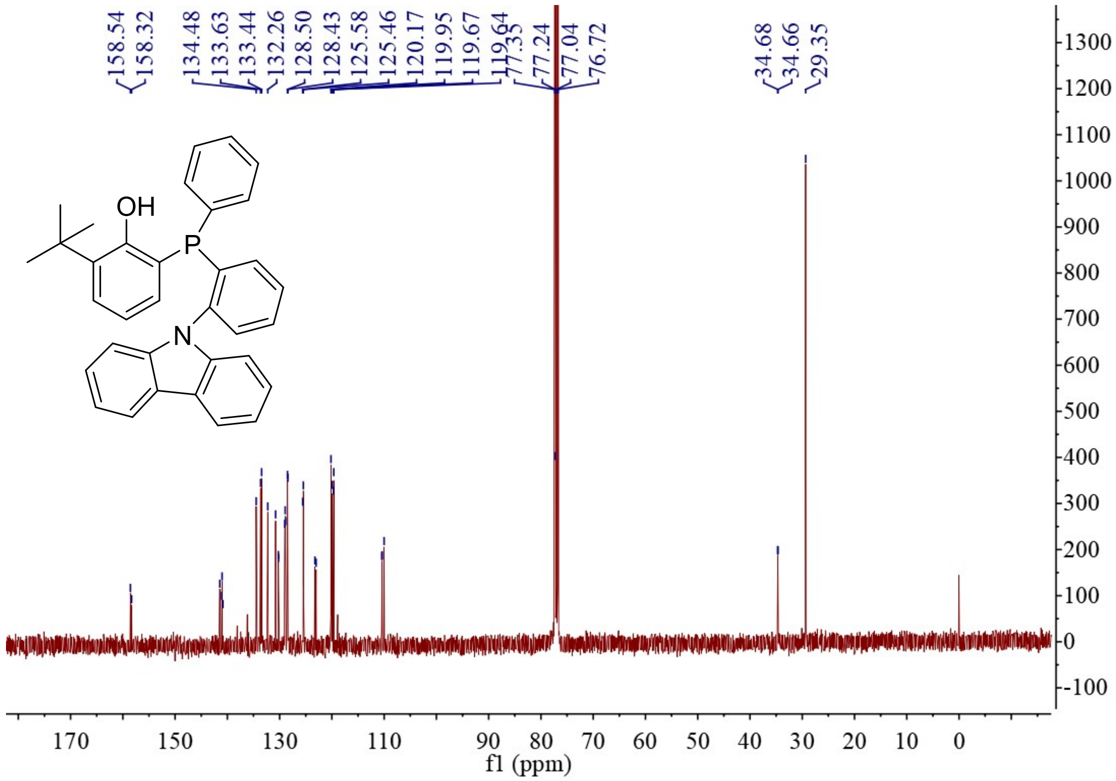


Figure S19 ^{13}C NMR spectrum of **L3**. (101 MHz, $CDCl_3$).

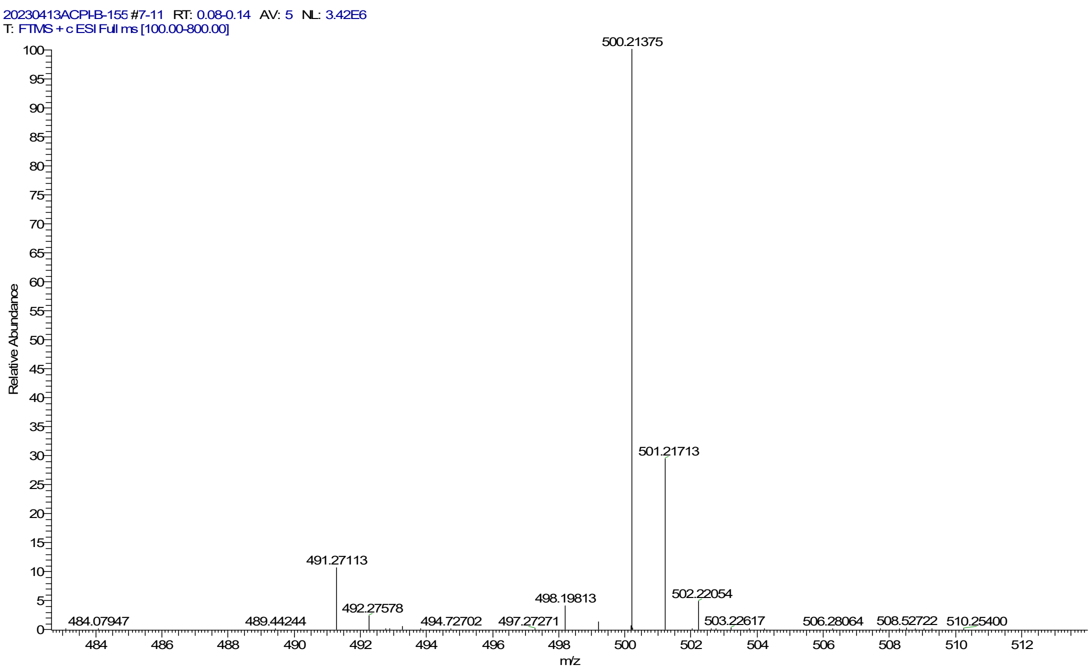


Figure S20 ESI-MS spectrum of **L3.**

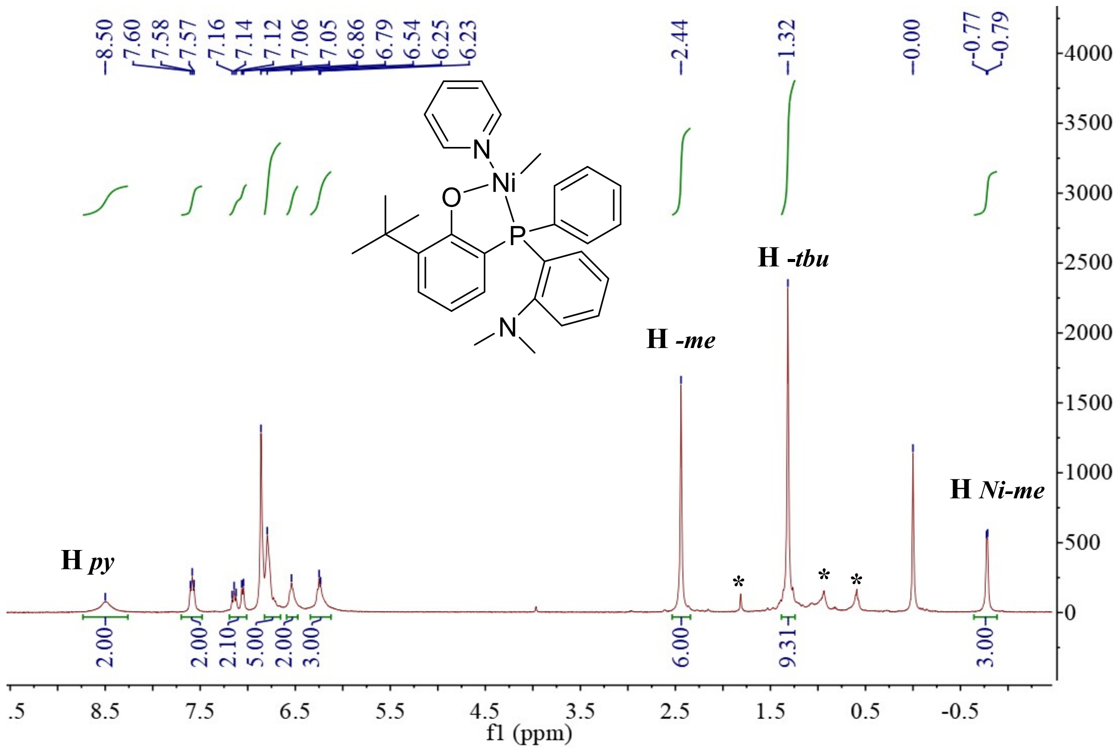


Figure S21 ^{1}H NMR spectrum of **Ni1**. (400 MHz, C_6D_6). (*solution)

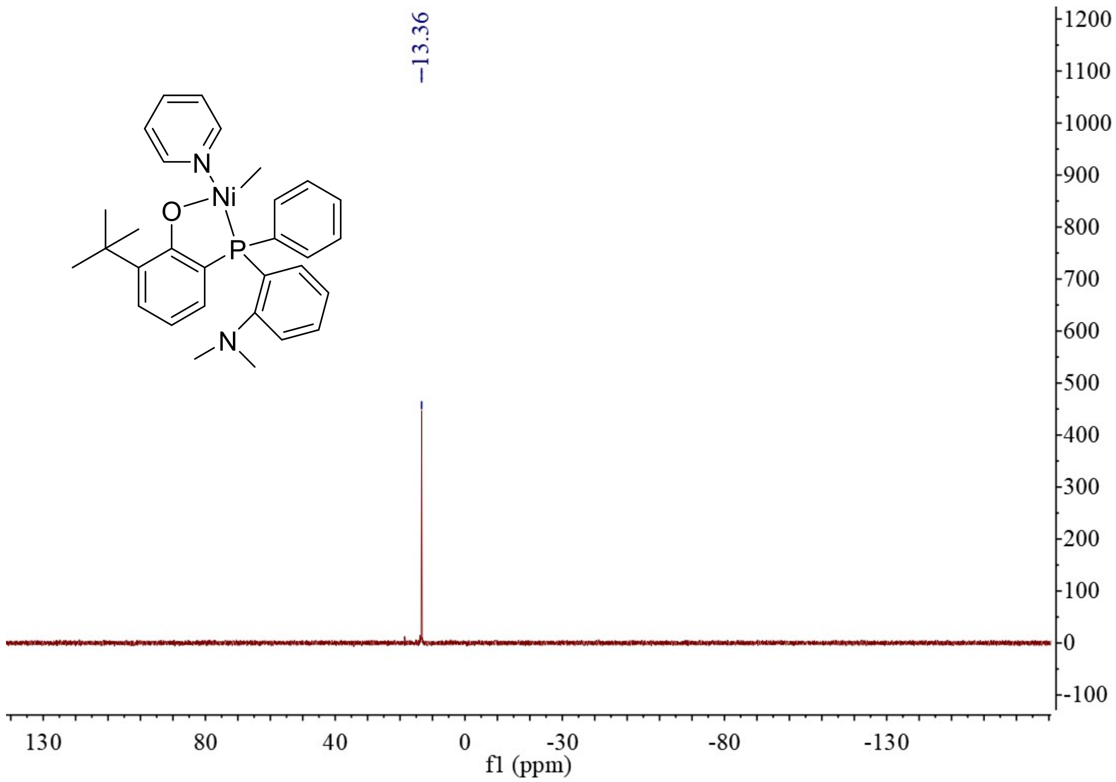


Figure S22 ^{31}P NMR spectrum of **Ni1**. (162 MHz, C_6D_6).

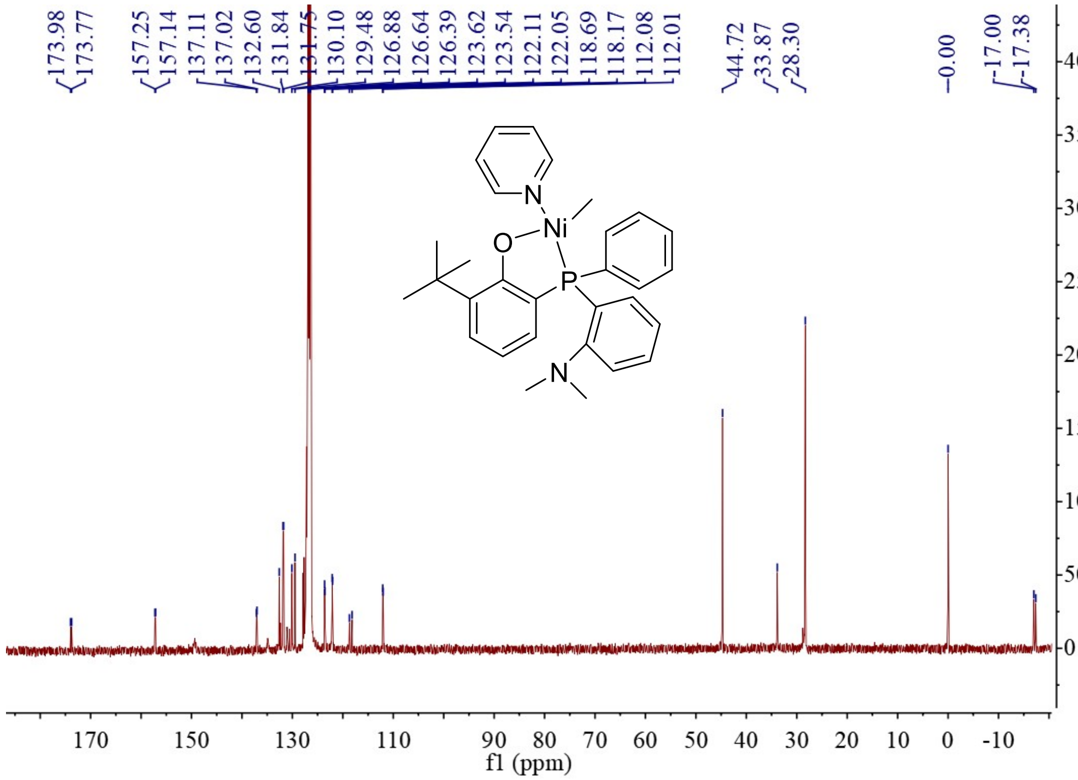


Figure S23 ^{13}C NMR spectrum of **Ni1**. (101 MHz, C_6D_6).

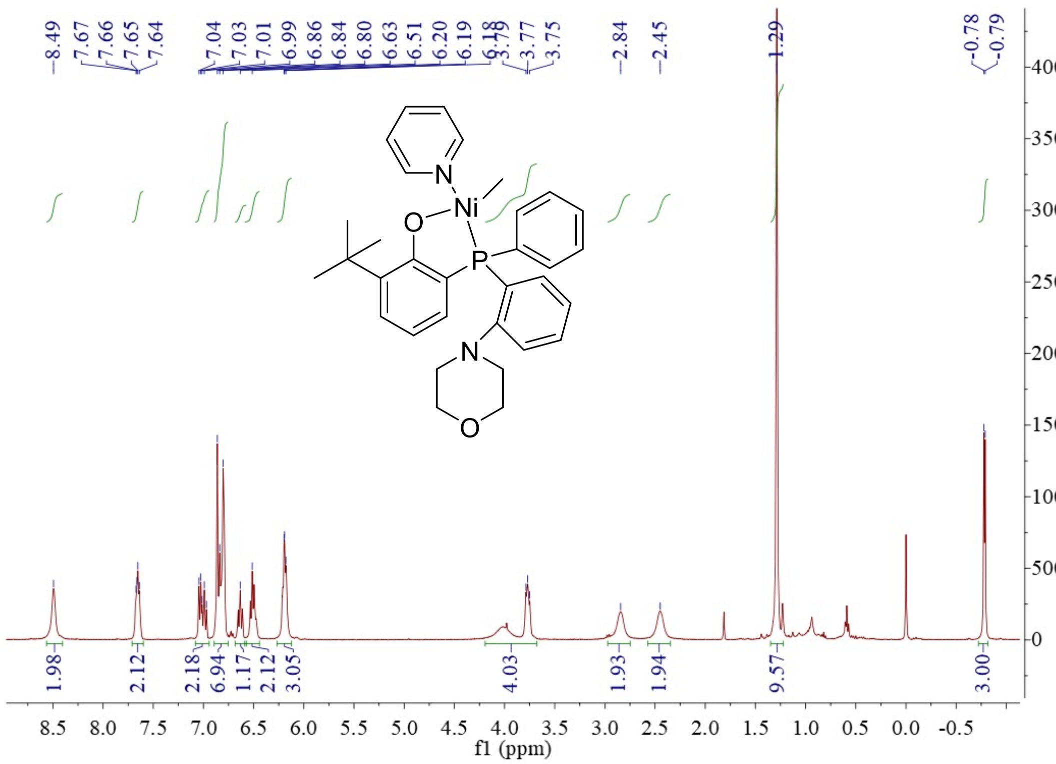


Figure S24 ^{1}H NMR spectrum of **Ni2**. (400 MHz, C_6D_6). (*solution)

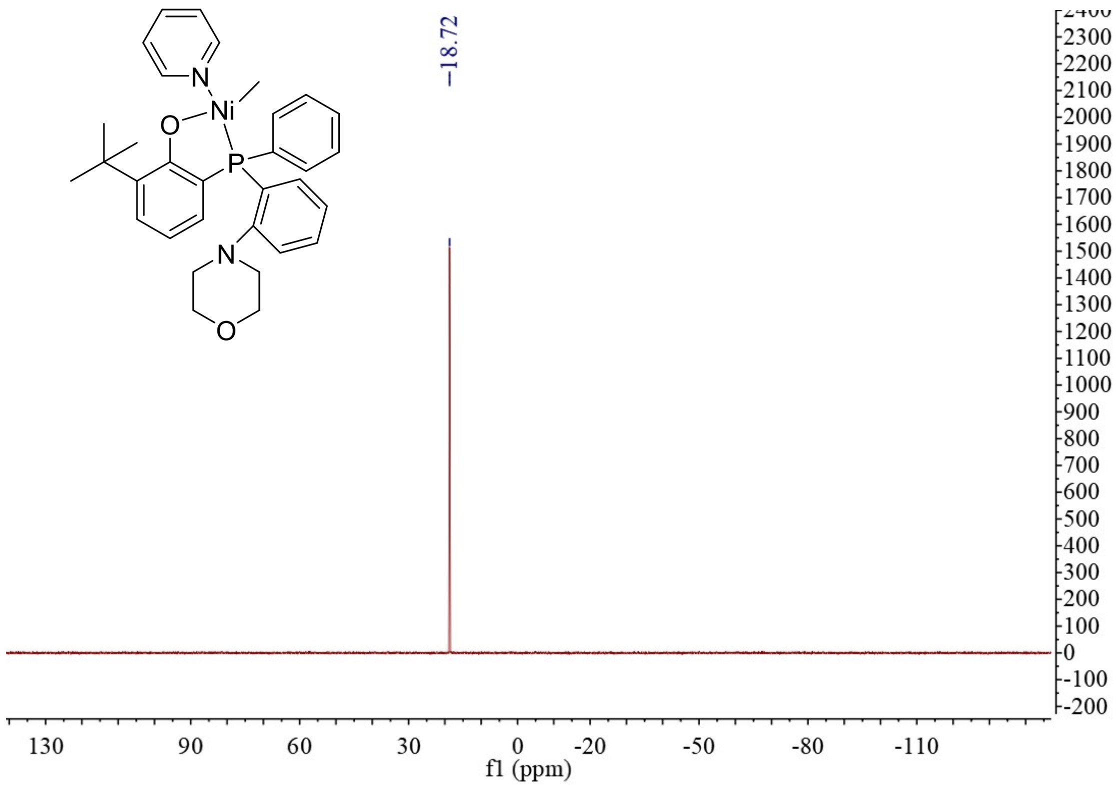


Figure S25 ^{31}P NMR spectrum of **Ni2**. (162 MHz, C_6D_6).

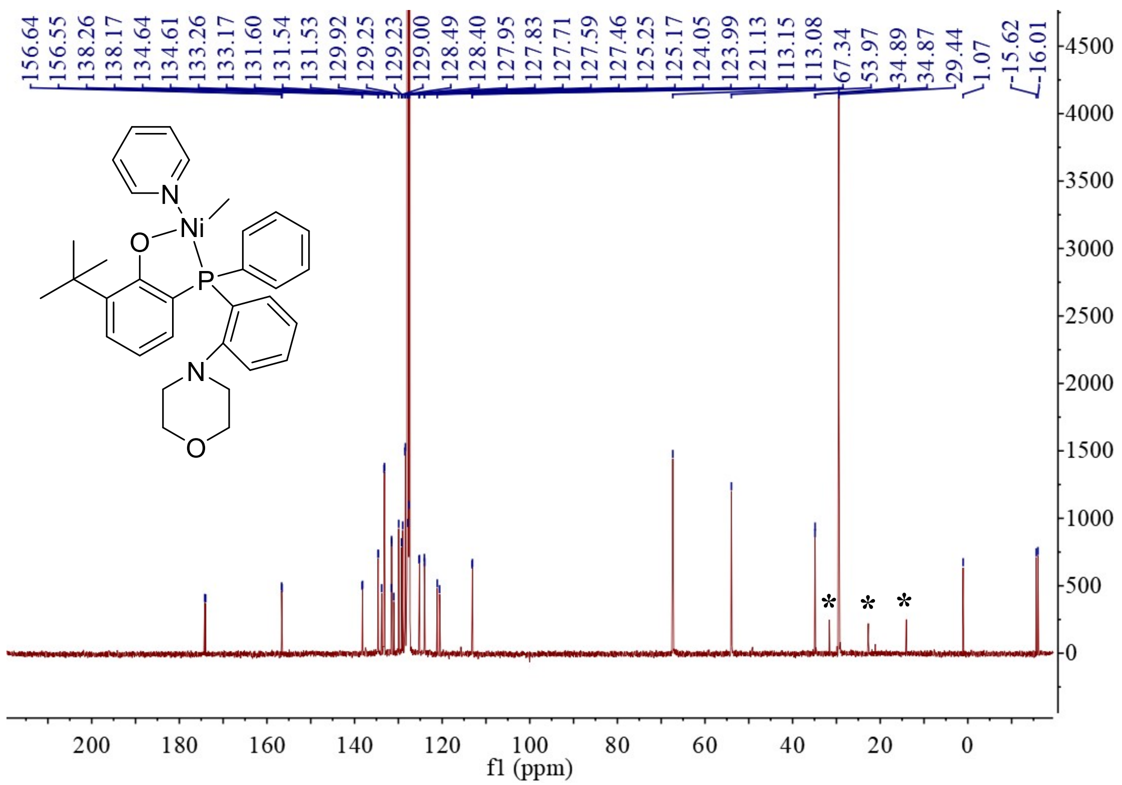


Figure S26 ^{13}C NMR spectrum of **Ni2**. (101 MHz, C_6D_6). (*Hex)

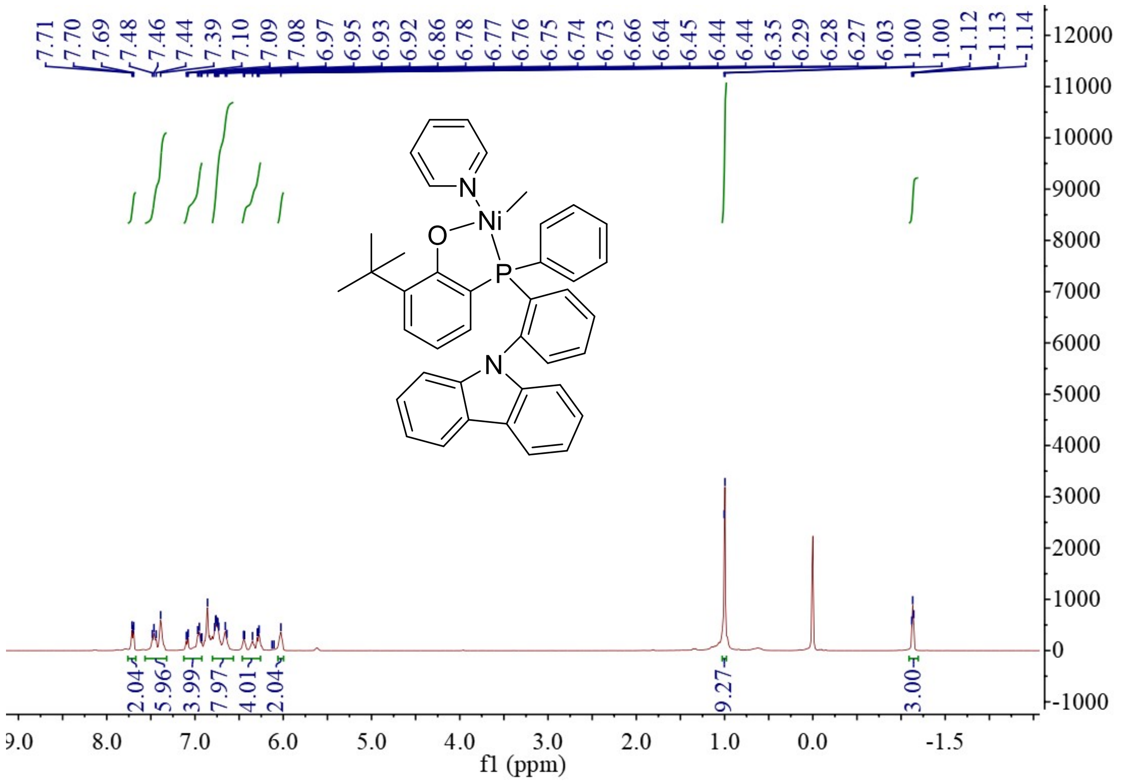


Figure S27 [1]H NMR spectrum of **Ni3**. (400 MHz, C_6D_6).

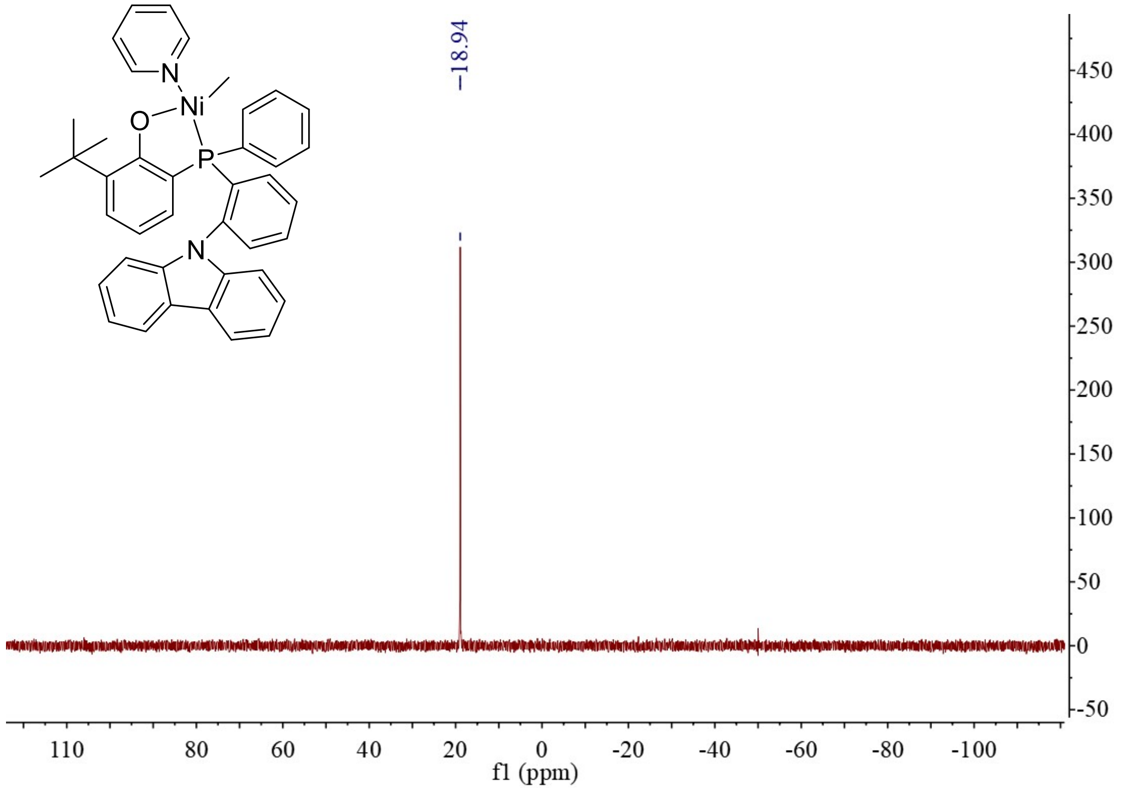


Figure S28 [31]P NMR spectrum of **Ni3**. (162 MHz, C_6D_6).

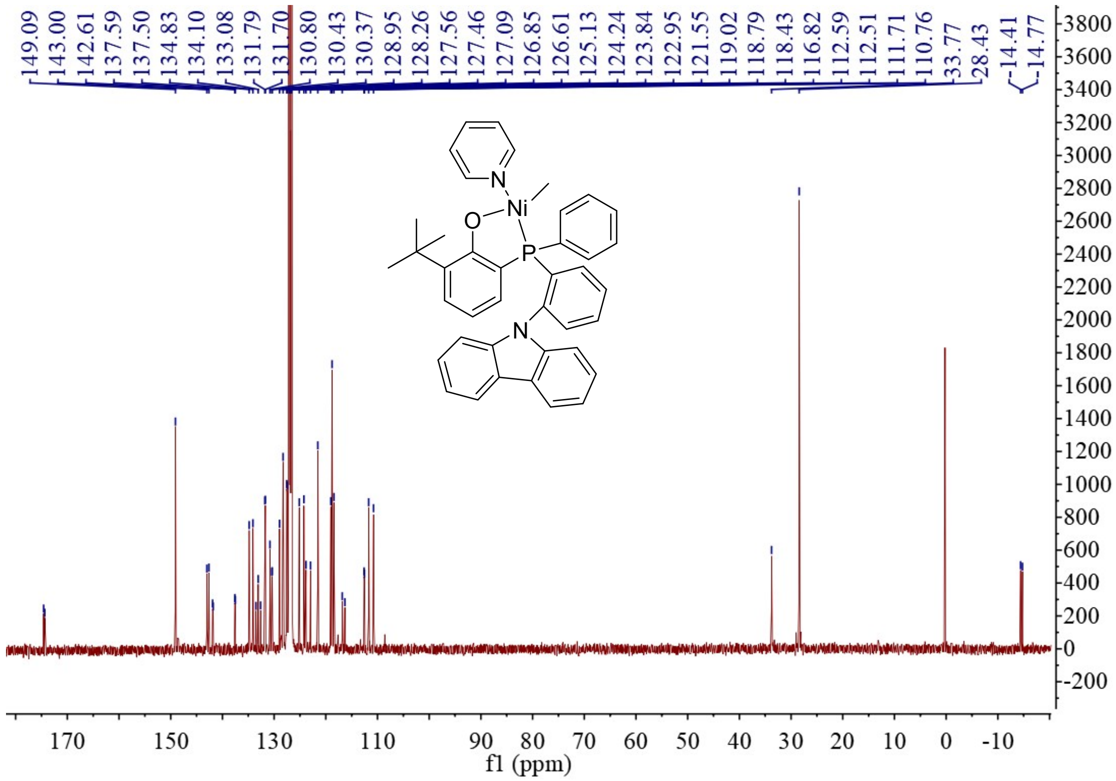


Figure S29 ^{13}C NMR spectrum of **Ni3**. (101 MHz, C_6D_6).

4. ^1H NMR of the polymers

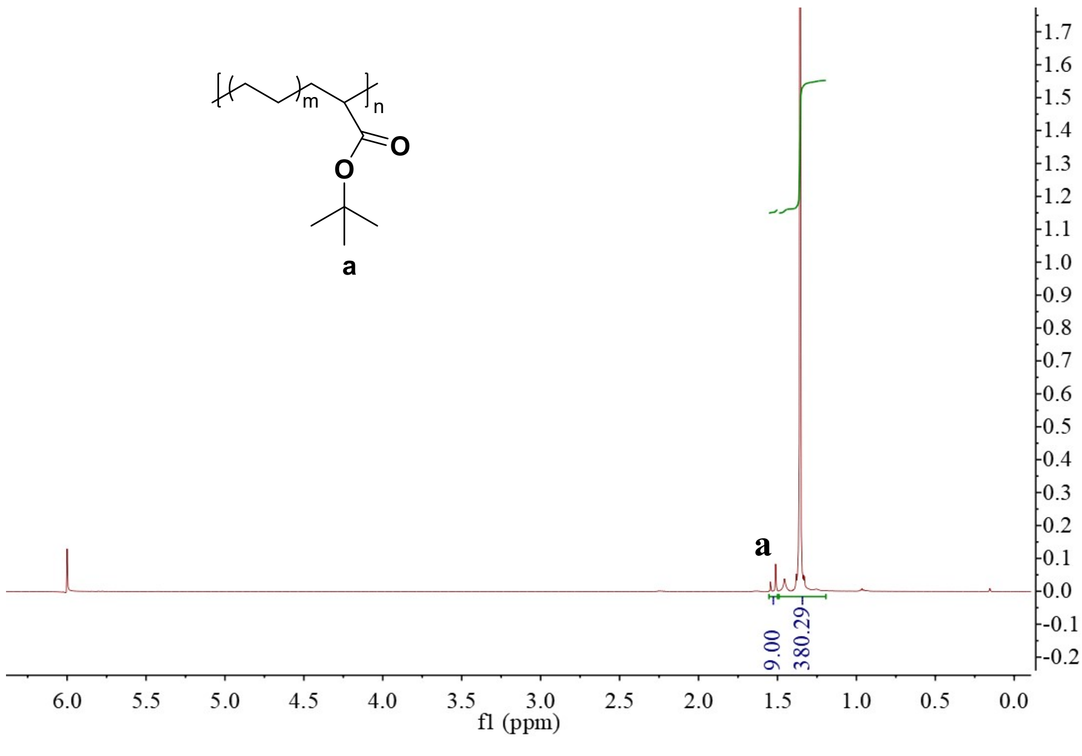


Figure S30 ^1H NMR of the polymer from Table 3, Entry 1. ($C_2D_2Cl_4$, 120 °C)

$$\text{Incorporation (\%)} = \frac{I(a)/9}{\frac{I(a)}{9} + \frac{I(CH2) - 3}{4}} * 100\% = 1.0\%$$

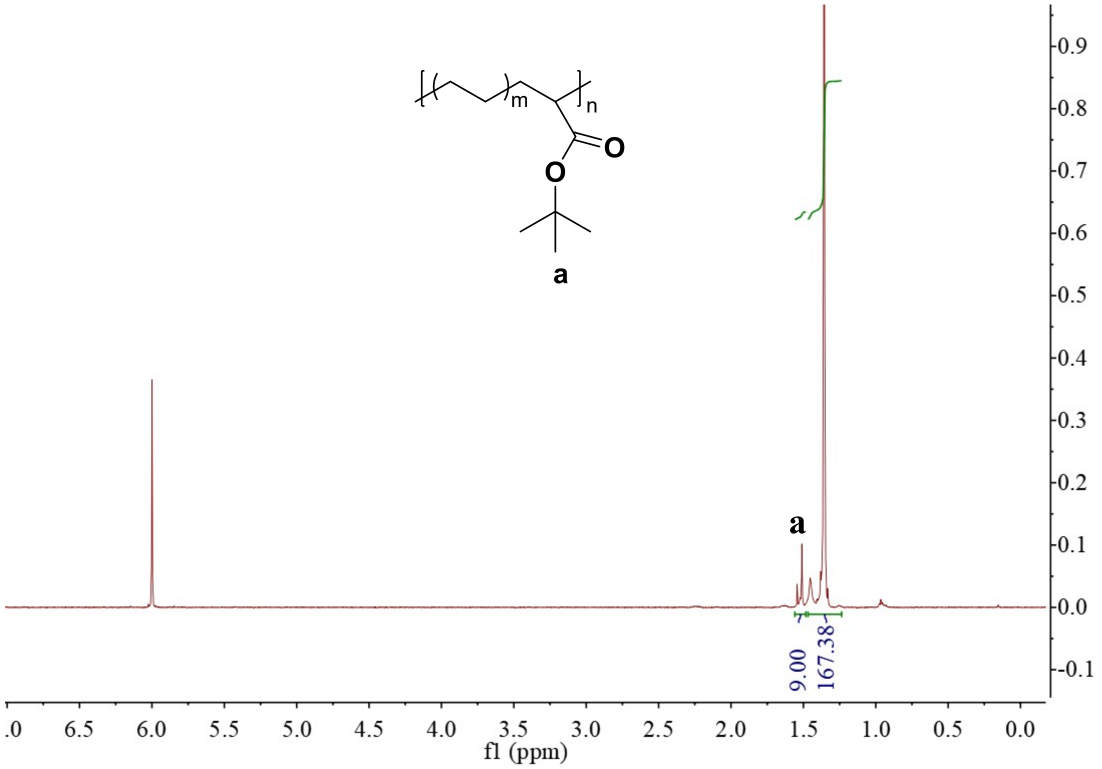


Figure S31 ^{1}H NMR of the polymer from Table 3, Entry 2. ($C_2D_2Cl_4$, 120 °C)

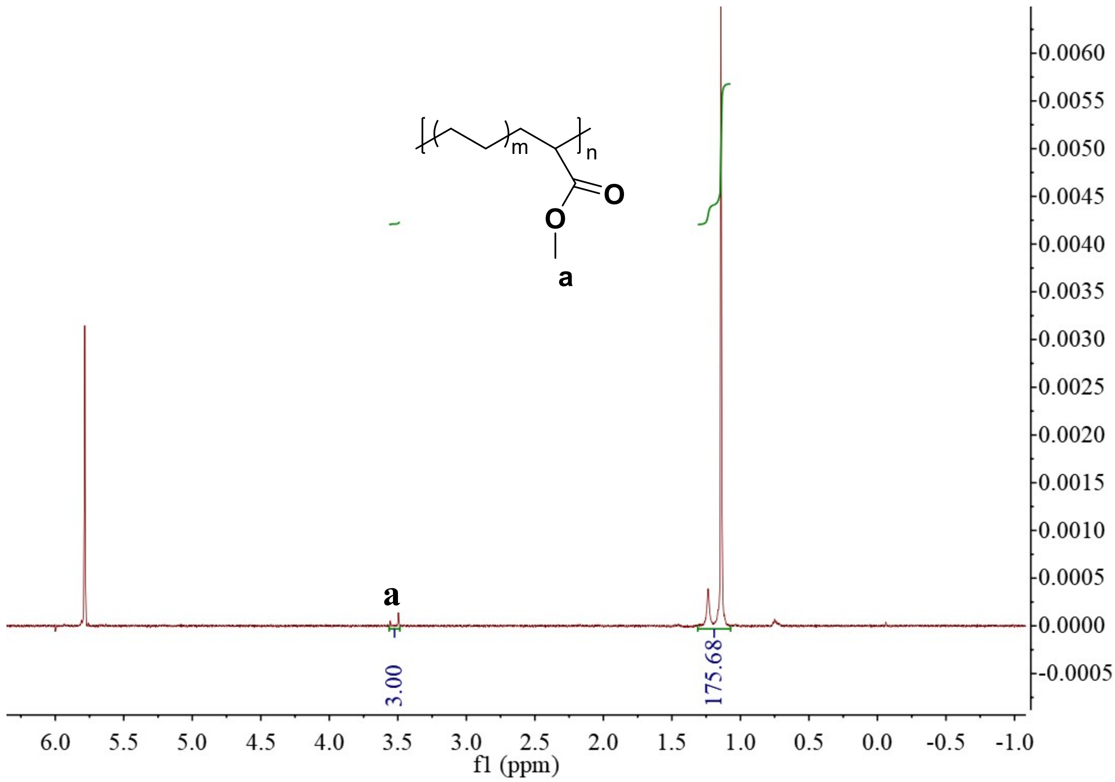


Figure S32 ^{1}H NMR of the polymer from Table 3, Entry 3. ($C_2D_2Cl_4$, 120 °C)

$$\text{Incorporation (\%)} = \frac{I(a)/3}{\frac{I(a)}{3} + \frac{I(CH2) - 3}{4}} * 100\% = 2.3\%$$

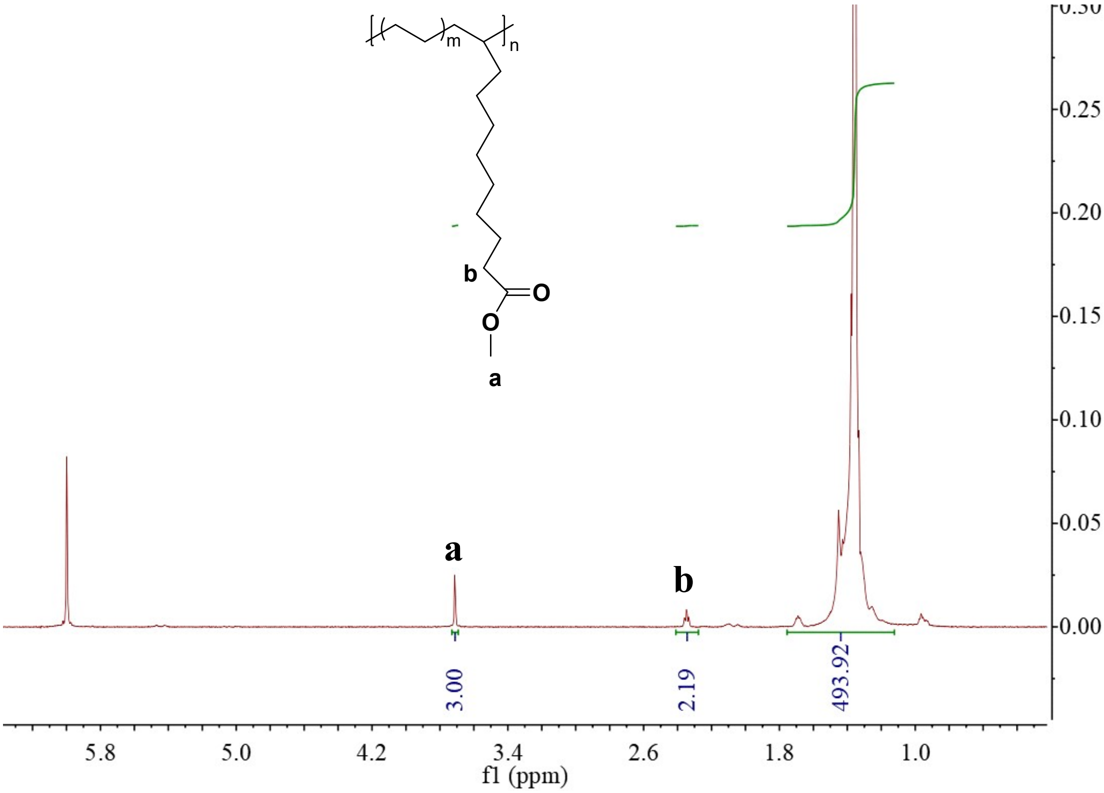


Figure S33 [1]H NMR of the polymer from Table 3, Entry 4. ($C_2D_2Cl_4$, 120 °C)

$$\text{Incorporation (\%)} = \frac{I(a)/3}{\frac{I(a)}{3} + \frac{I(CH2) - 17}{4}} * 100\% = 0.8\%$$

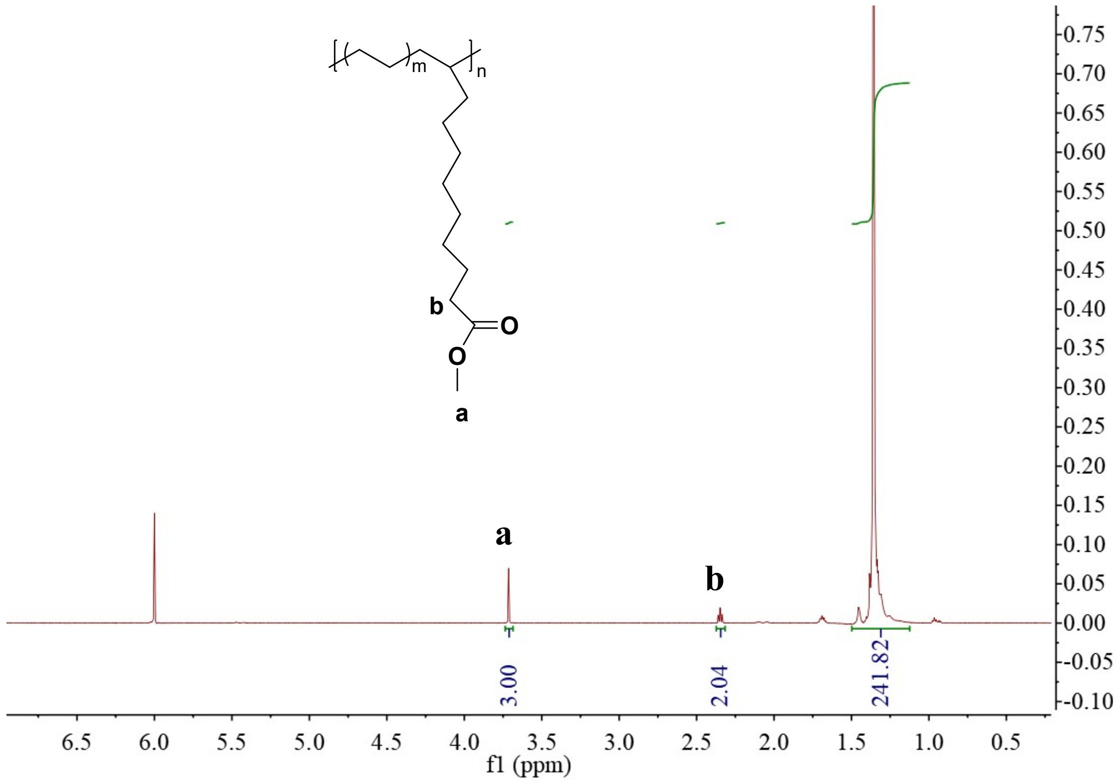


Figure S34 ^{1}H NMR of the polymer from Table 3, Entry 5. ($C_2D_2Cl_4$, 120 °C)

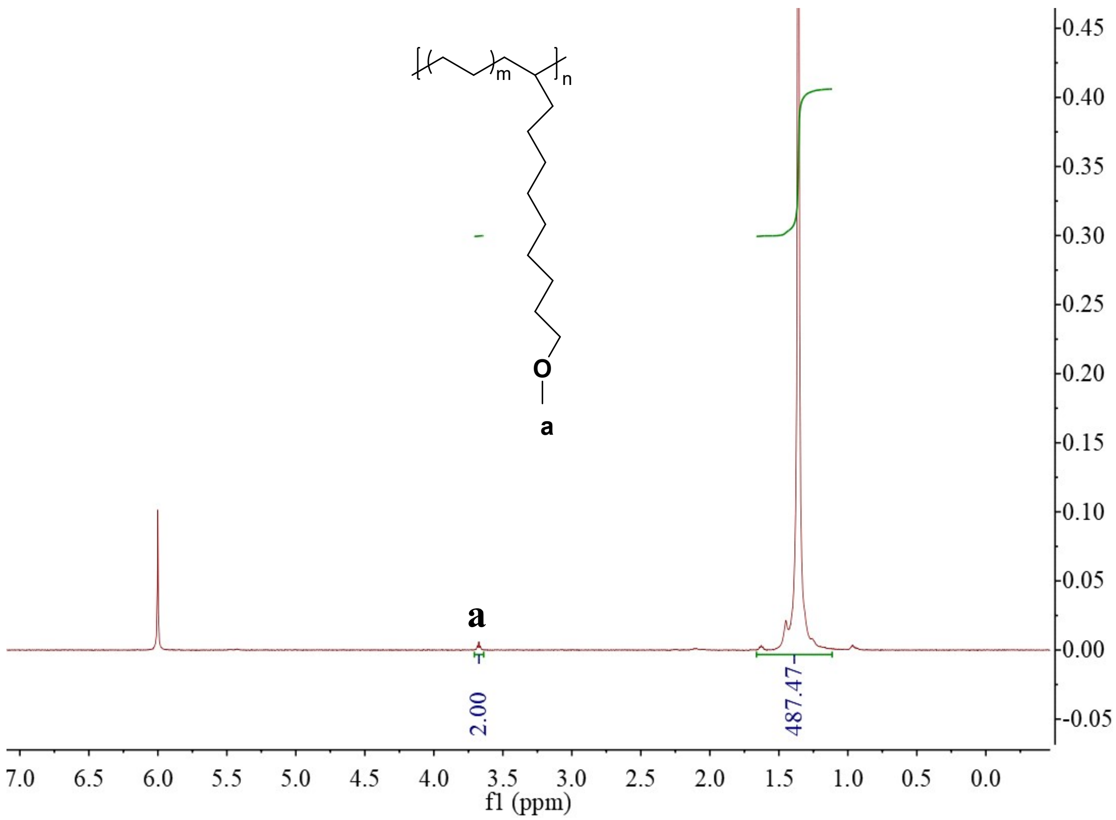


Figure S35 ^{1}H NMR of the polymer from Table 3, Entry 7. ($C_2D_2Cl_4$, 120 °C)

$$\text{Incorporation (\%)} = \frac{I(a)/2}{\frac{I(a)}{2} + \frac{I(CH2) - 17}{4}} * 100\% = 0.8\%$$

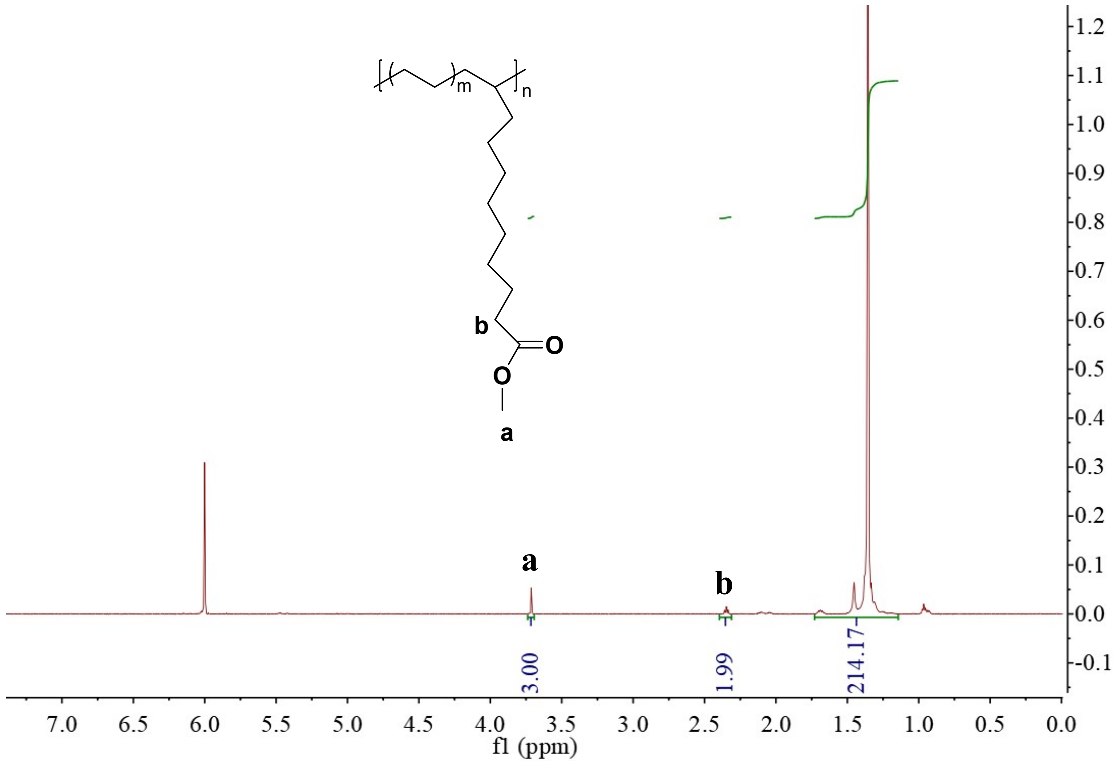


Figure S36 ^{1}H NMR of the polymer from Table 3, Entry 8. ($C_2D_2Cl_4$, 120 °C)

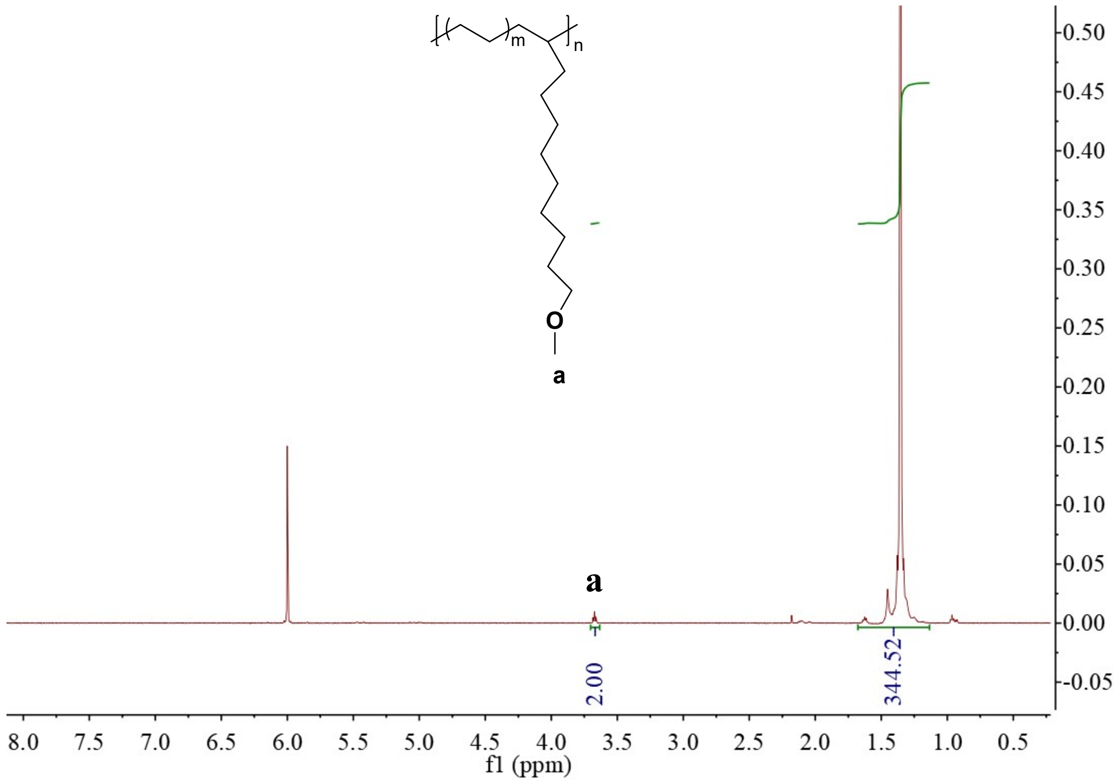


Figure S37 ^{1}H NMR of the polymer from Table 3, Entry 9. ($C_2D_2Cl_4$, 120 °C)

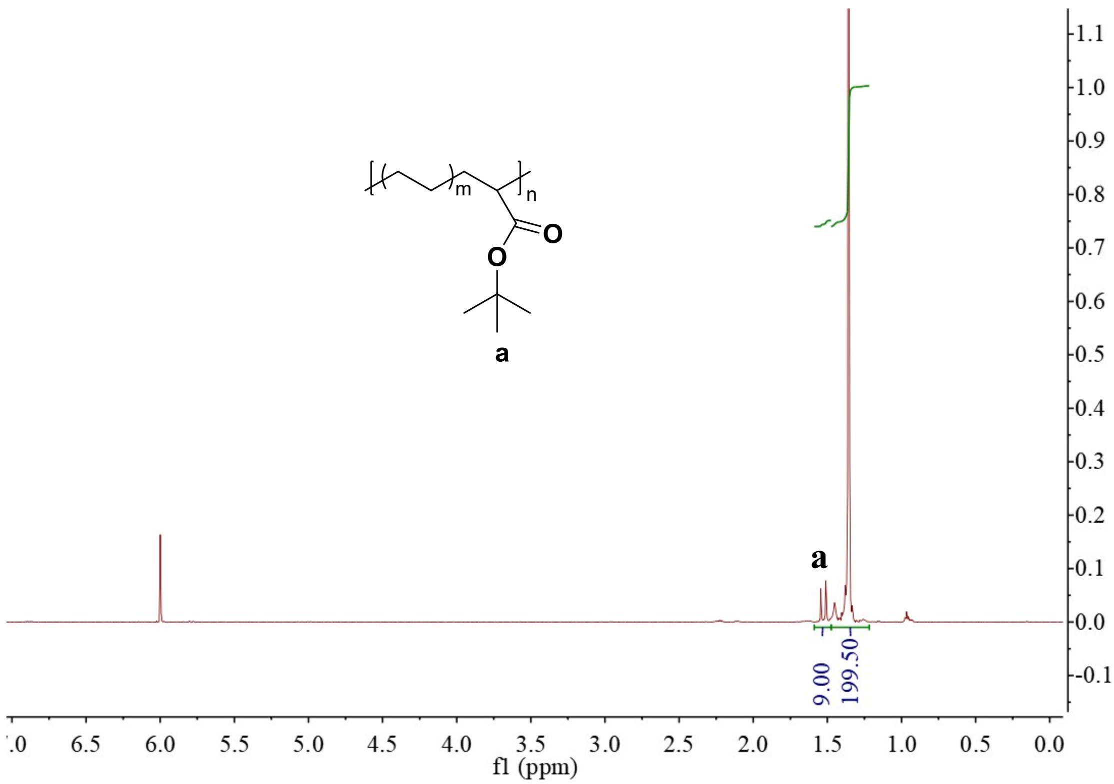


Figure S38 ^{1}H NMR of the polymer from Table 3, Entry 10. ($C_2D_2Cl_4$, 120 °C)

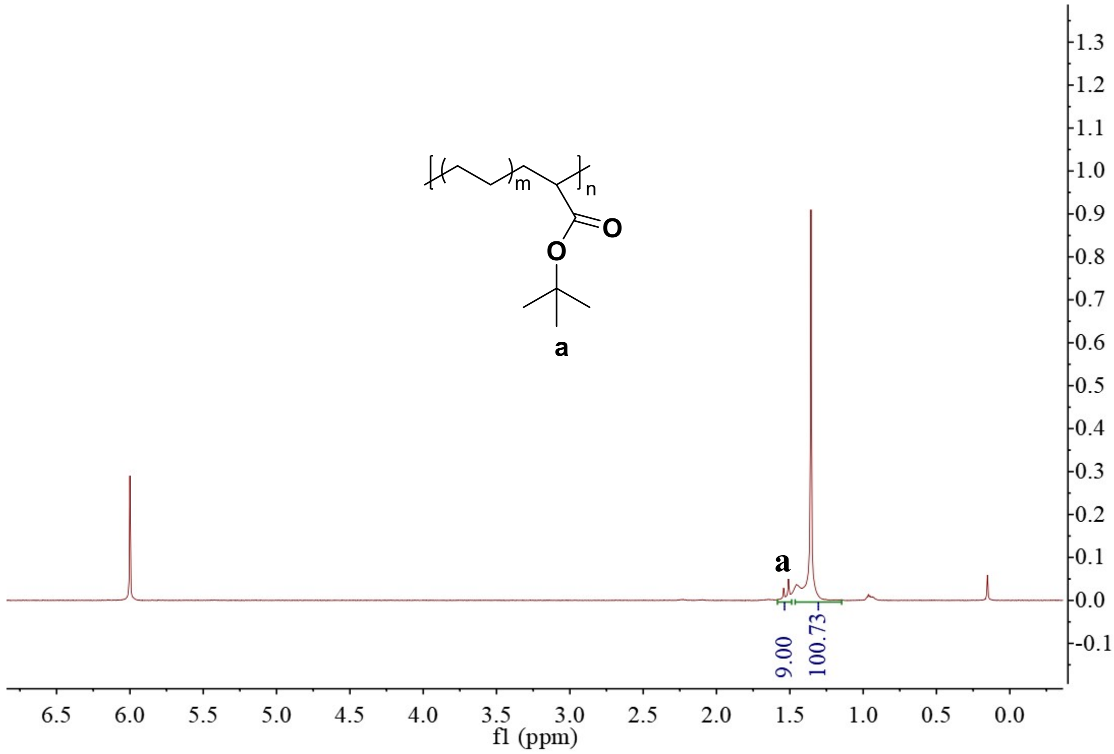


Figure S39 ^{1}H NMR of the polymer from Table 3, Entry 11. ($C_2D_2Cl_4$, 120 °C)

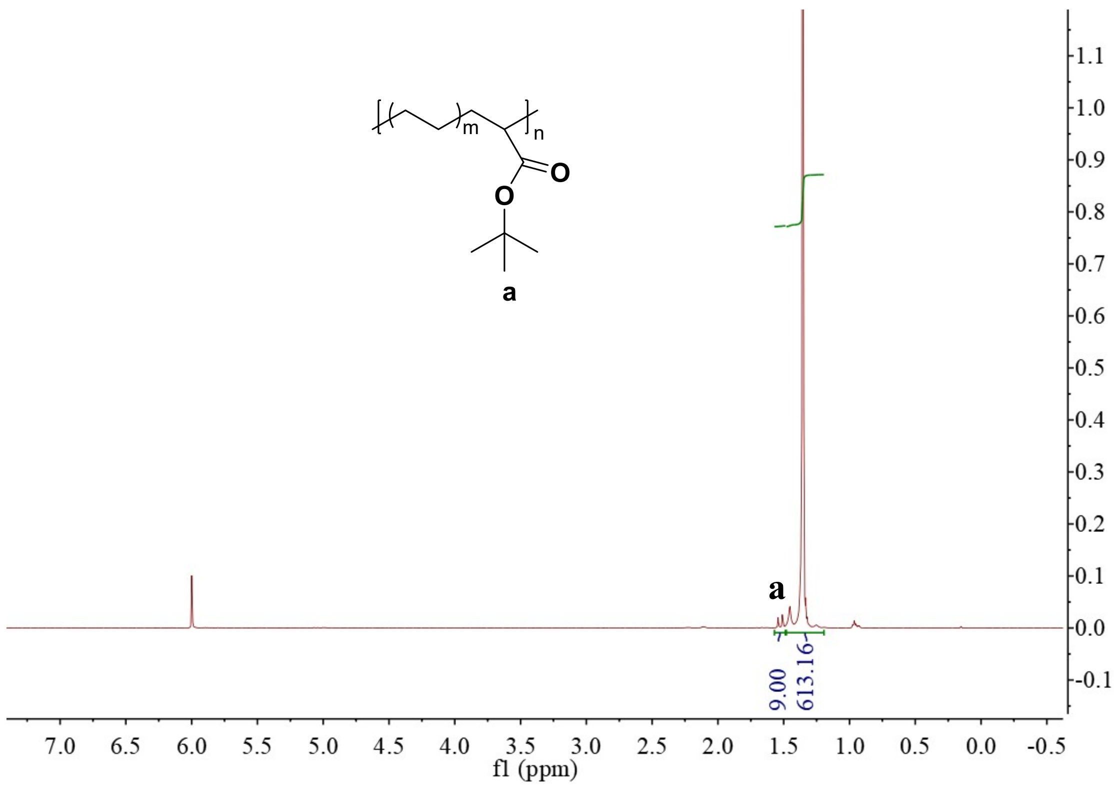


Figure S40 ^{1}H NMR of the polymer from Table 3, Entry 12. ($C_2D_2Cl_4$, 120 °C)

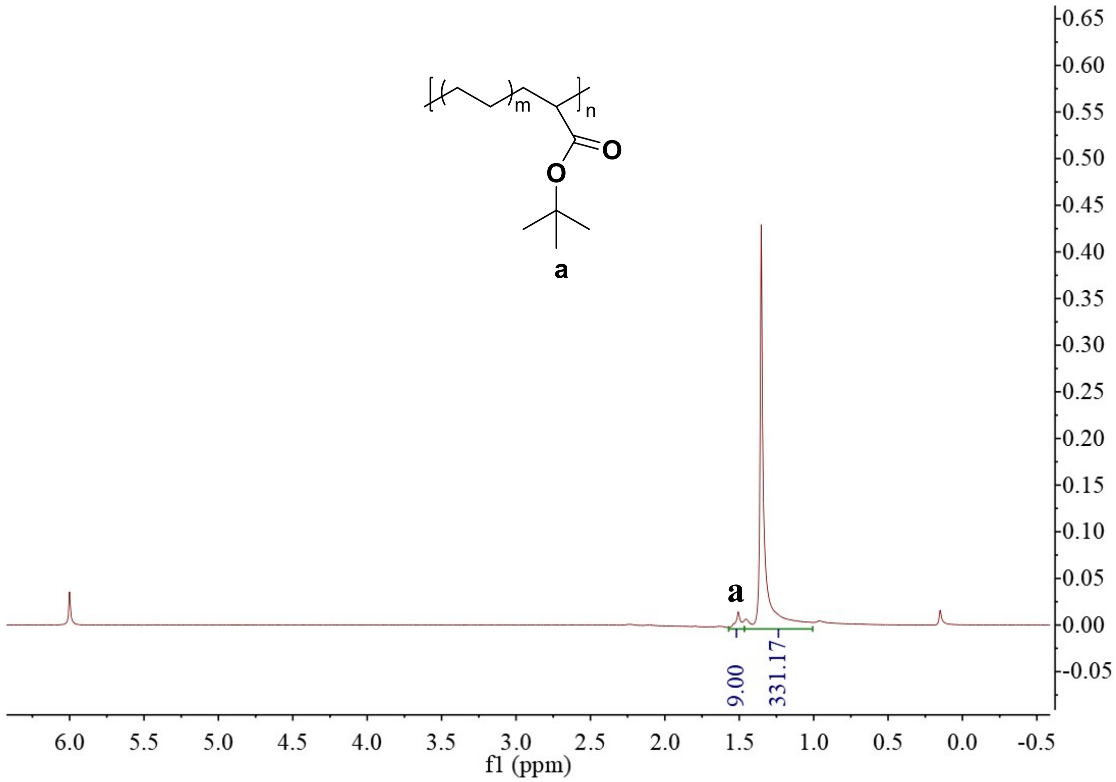


Figure S41 [1]H NMR of the polymer from Table 3, Entry 13. ($C_2D_2Cl_4$, 120 °C)

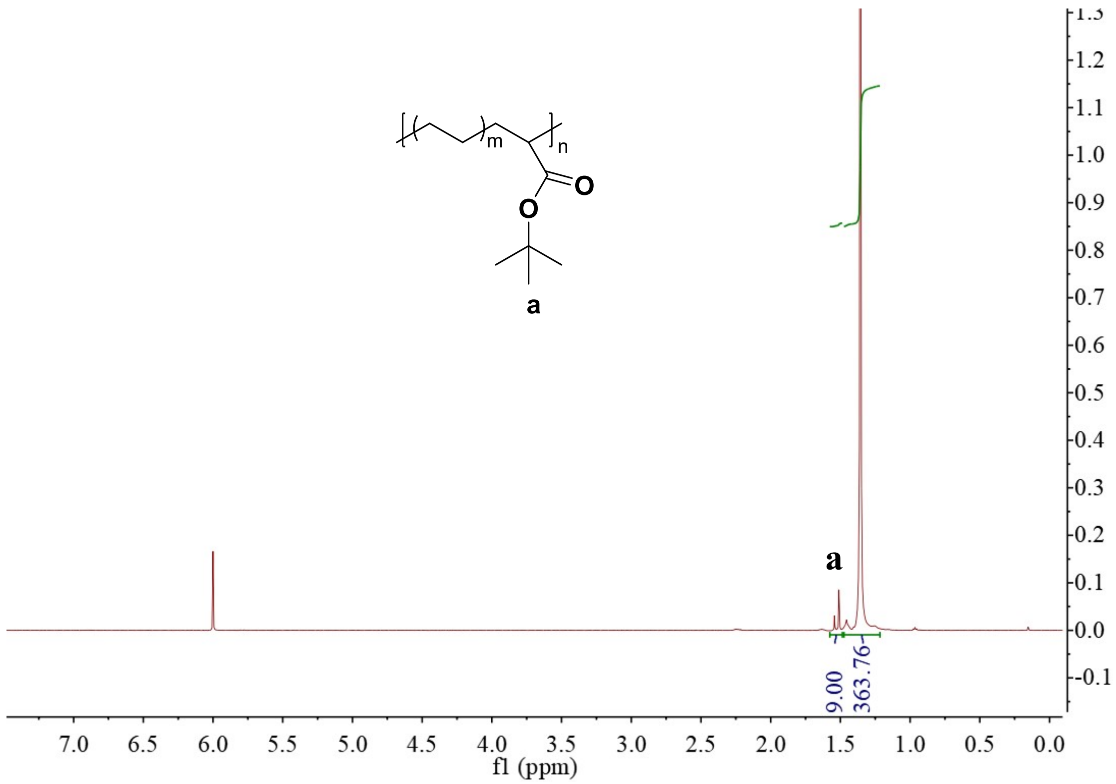


Figure S42 [1]H NMR of the polymer from Table 3, Entry 14. ($C_2D_2Cl_4$, 120 °C)

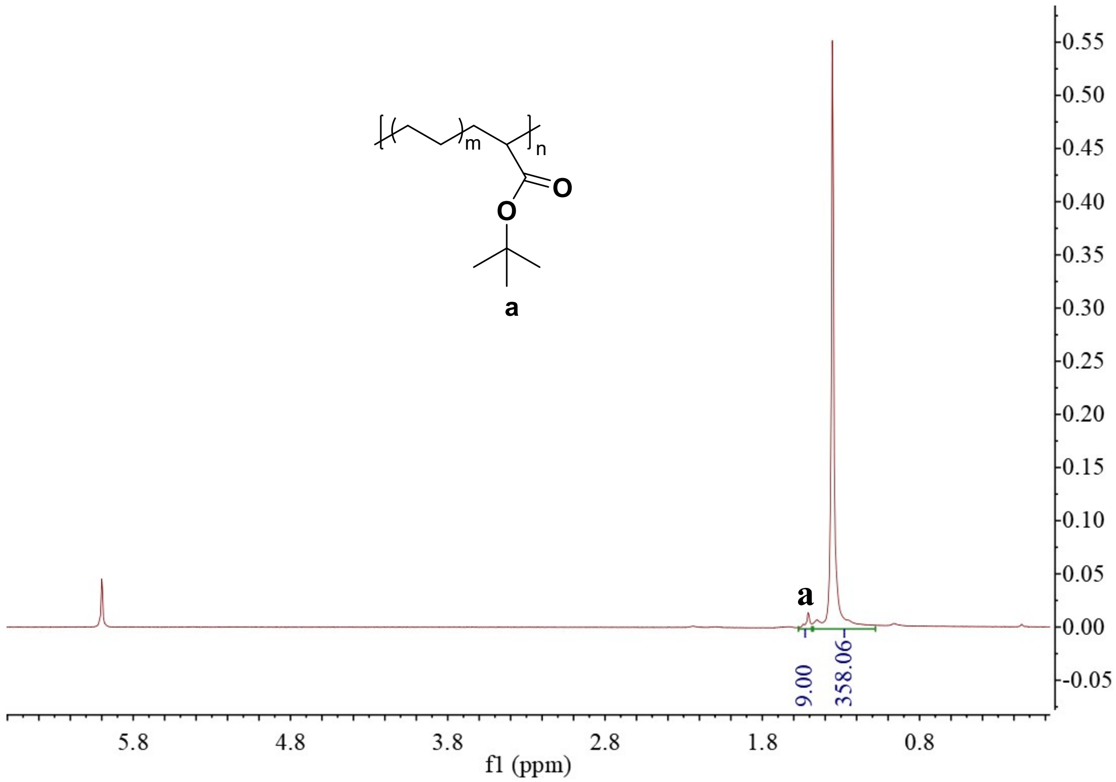


Figure S43 [1]H NMR of the polymer from Table 3, Entry 15. ($C_2D_2Cl_4$, 120 °C)

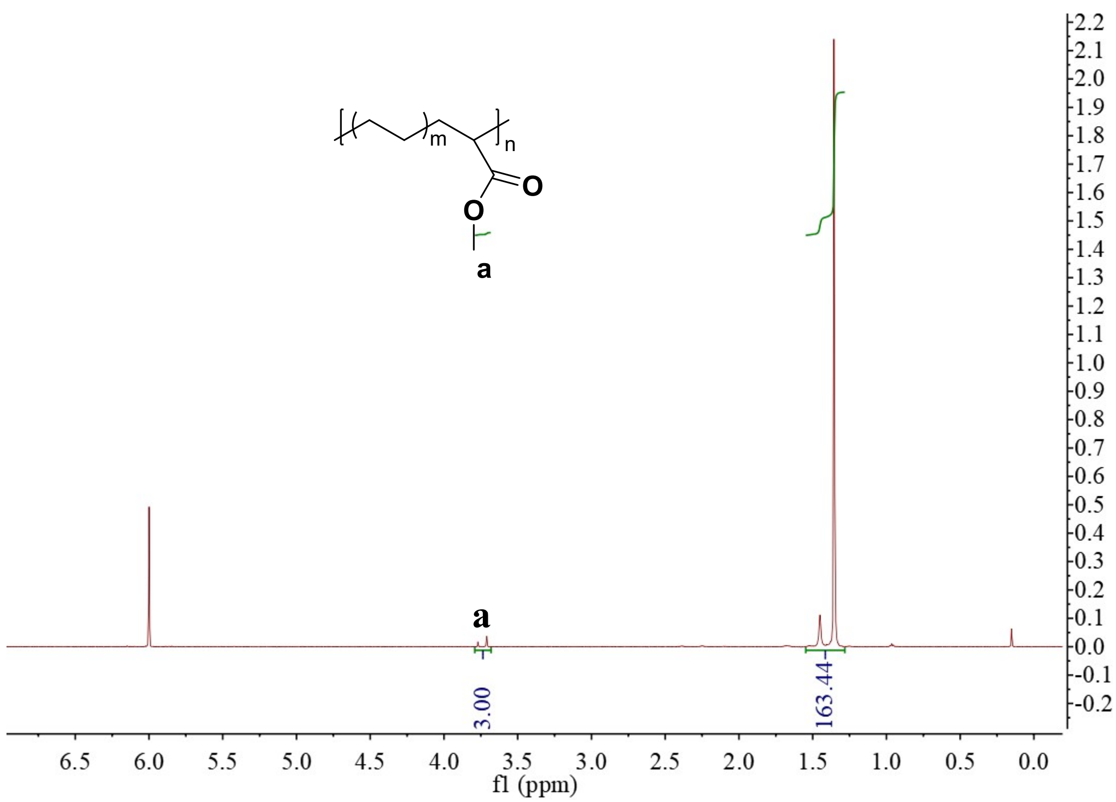


Figure S44 [1]H NMR of the polymer from Table 3, Entry 16. ($C_2D_2Cl_4$, 120 °C)

5. DSC of polymers

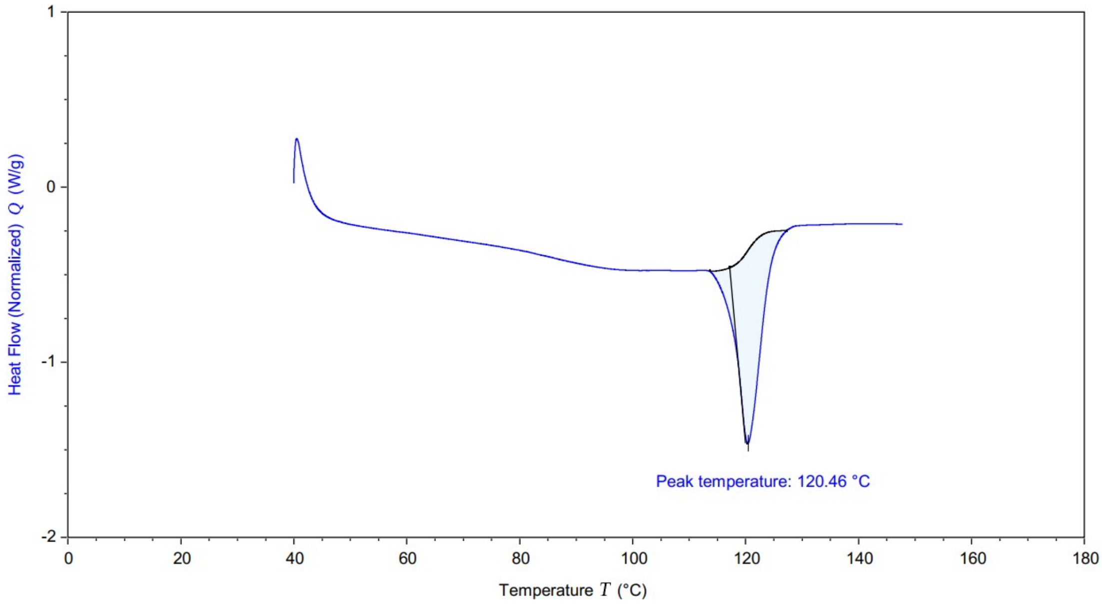


Figure S45 DSC of the polymer from Table 1, Entry 1.

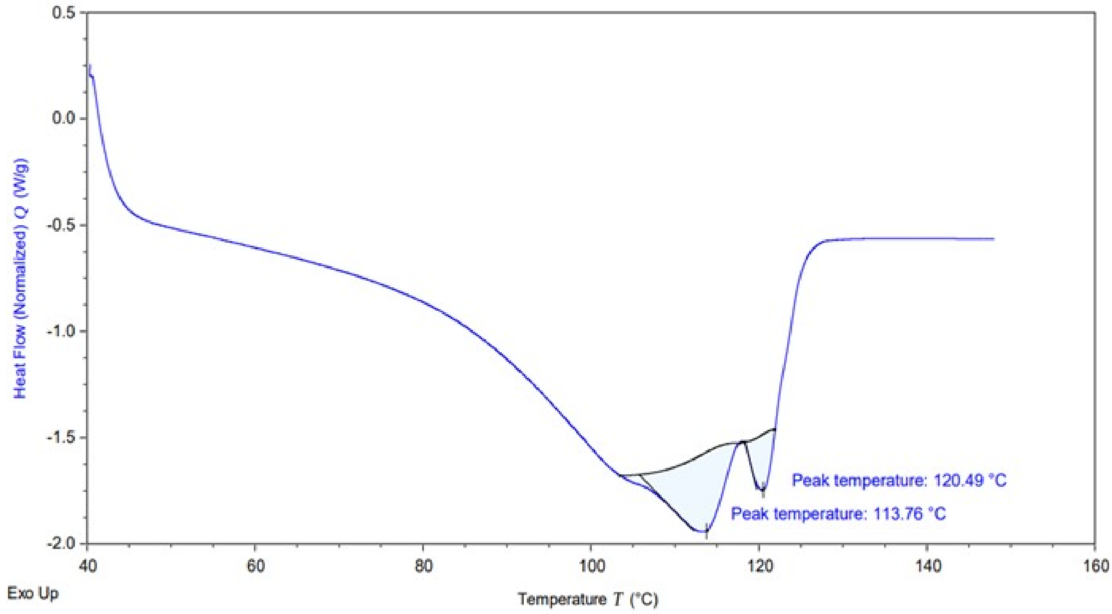


Figure S46 DSC of the polymer from Table 1, Entry 2.

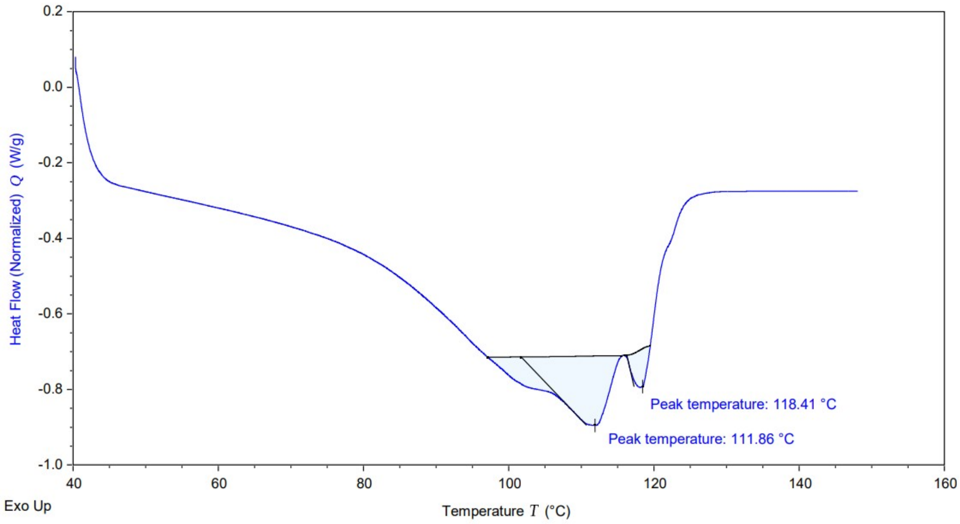


Figure S47 DSC of the polymer from Table 1, Entry 3.

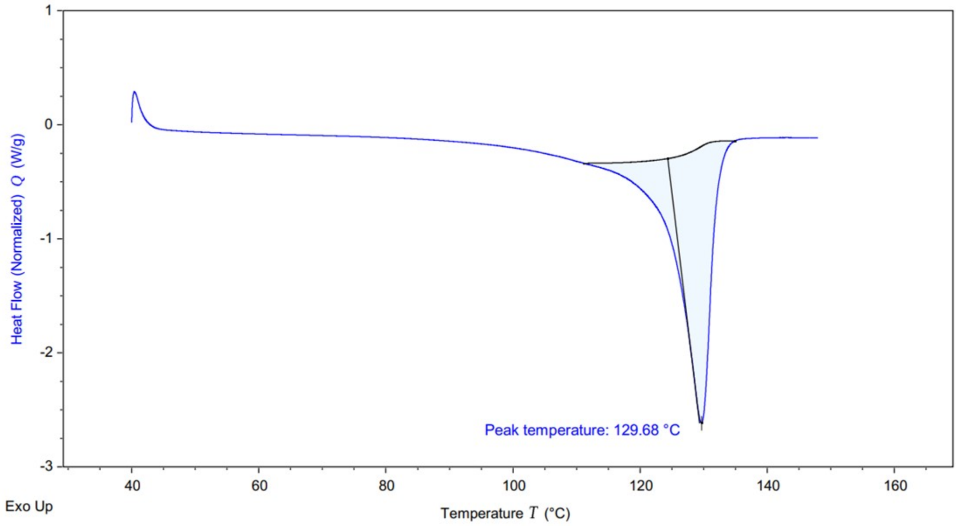


Figure S48 DSC of the polymer from Table 1, Entry 4.

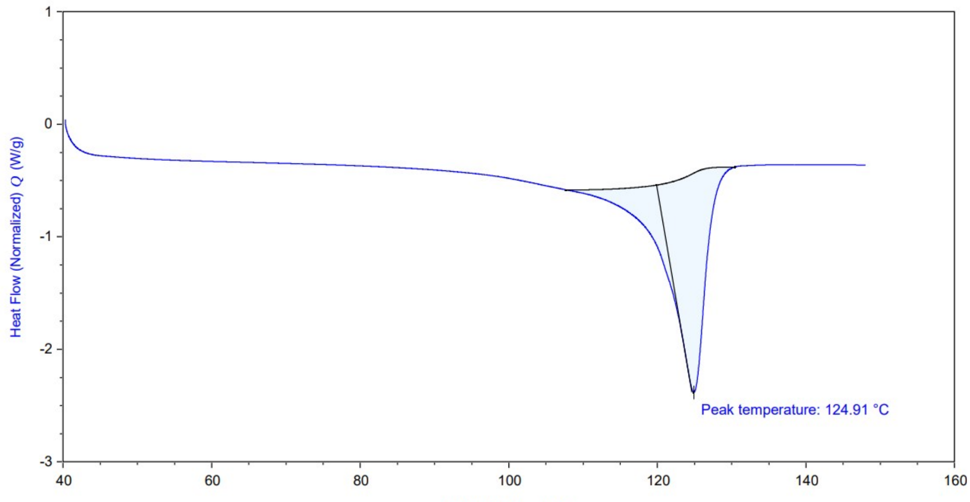


Figure S49 DSC of the polymer from Table 1, Entry 5.

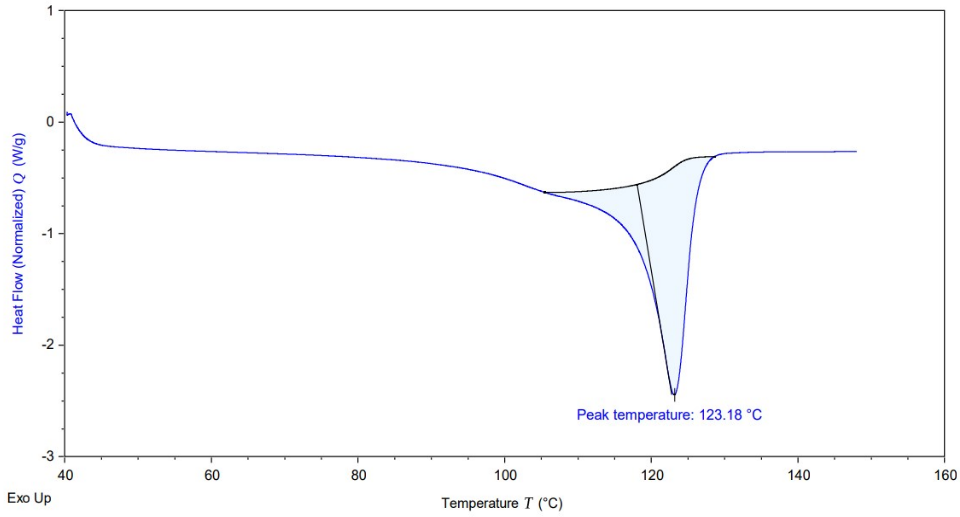


Figure S50 DSC of the polymer from Table 1, Entry 6.

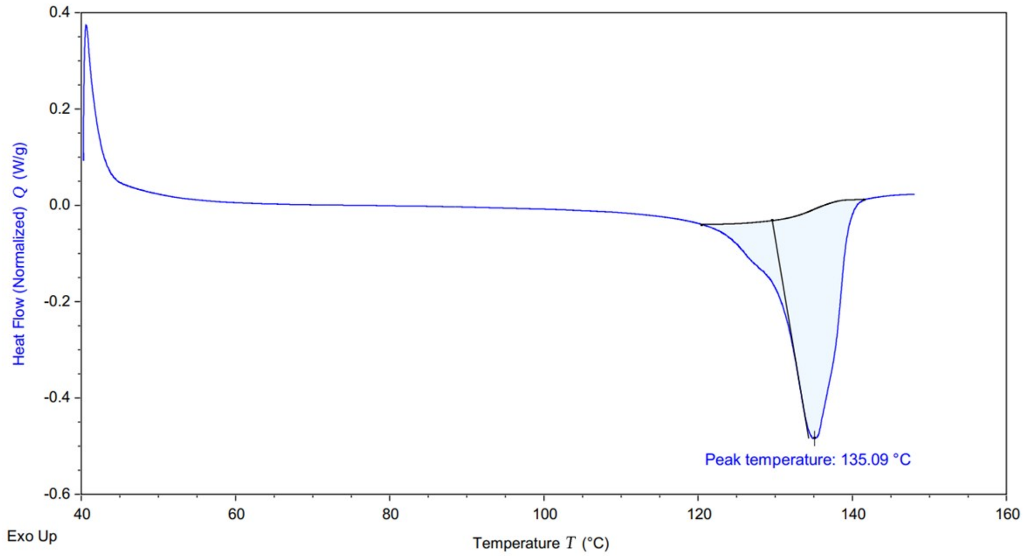


Figure S51 DSC of the polymer from Table 1, Entry 7.

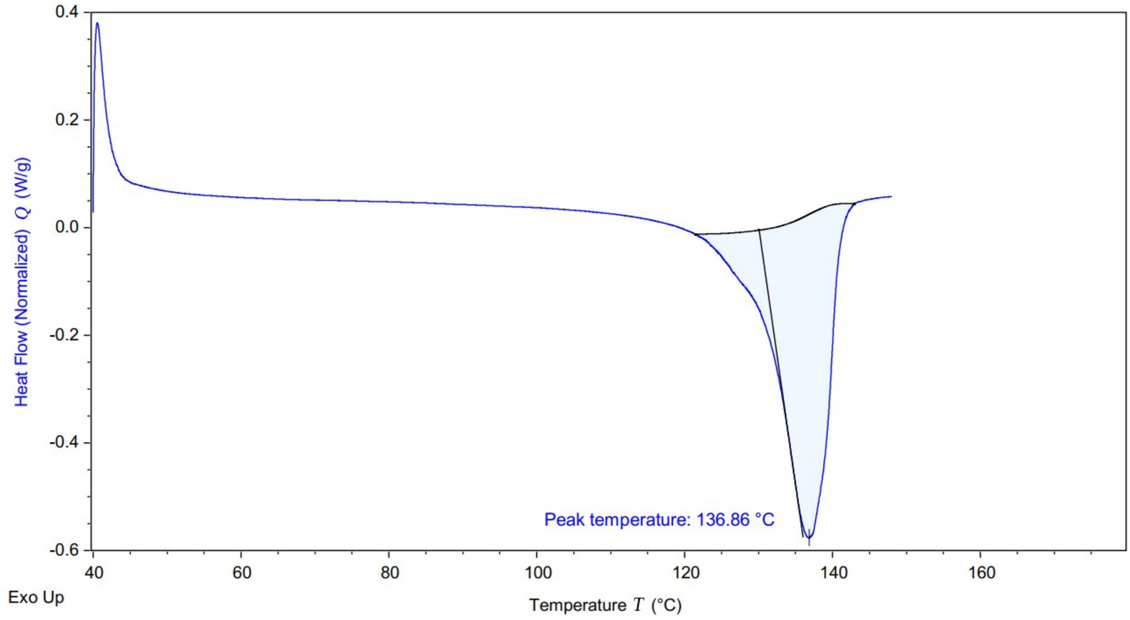


Figure S52 DSC of the polymer from Table 1, Entry 8.

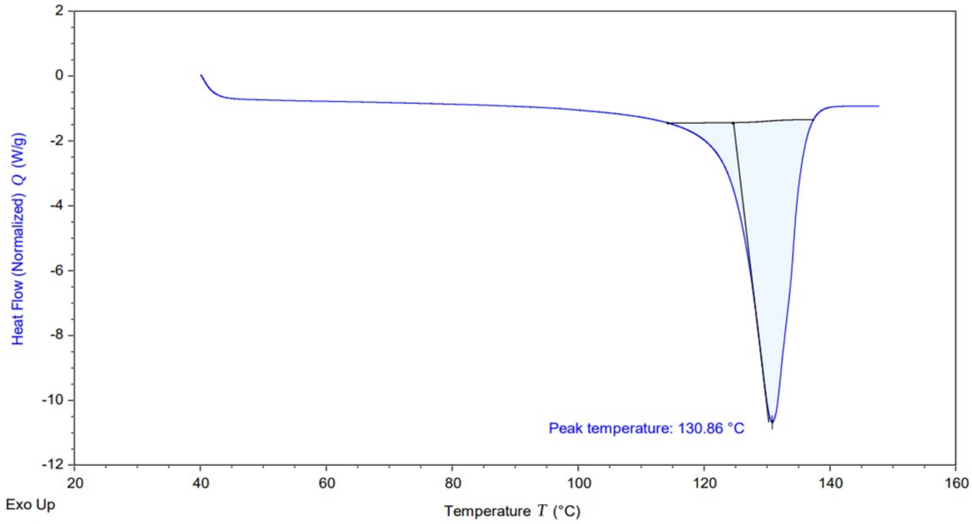


Figure S53 DSC of the polymer from Table 1, Entry 9.

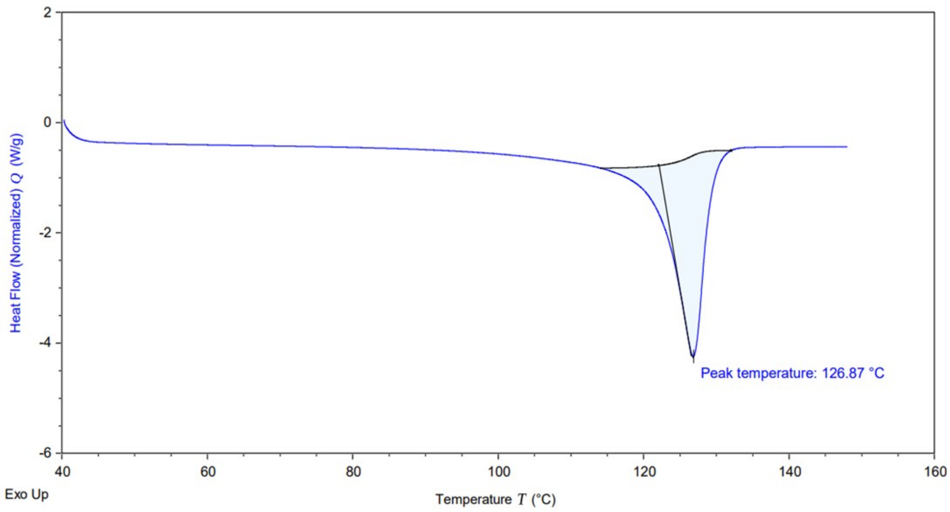


Figure S54 DSC of the polymer from Table 1, Entry 10.

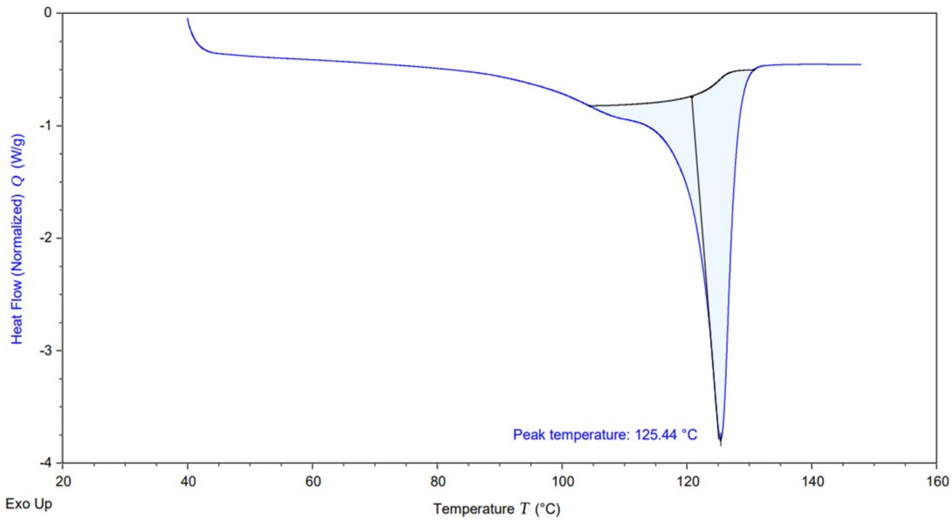


Figure S55 DSC of the polymer from Table 1, Entry 11.

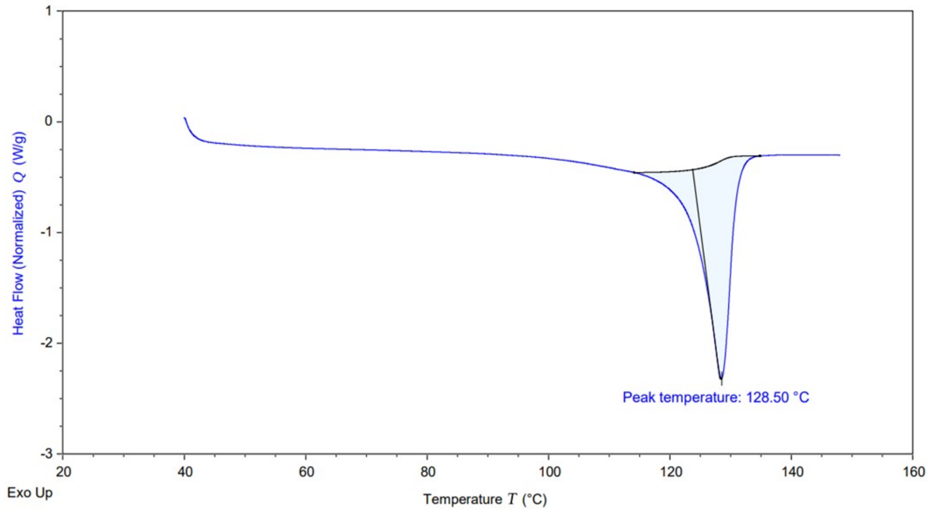


Figure S56 DSC of the polymer from Table 1, Entry 12.

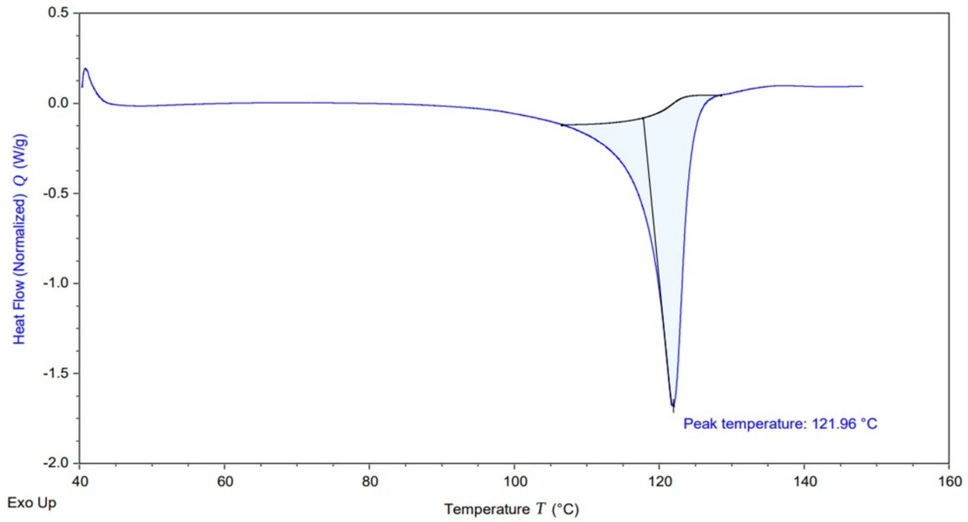


Figure S57 DSC of the polymer from Table 2, Entry 2.

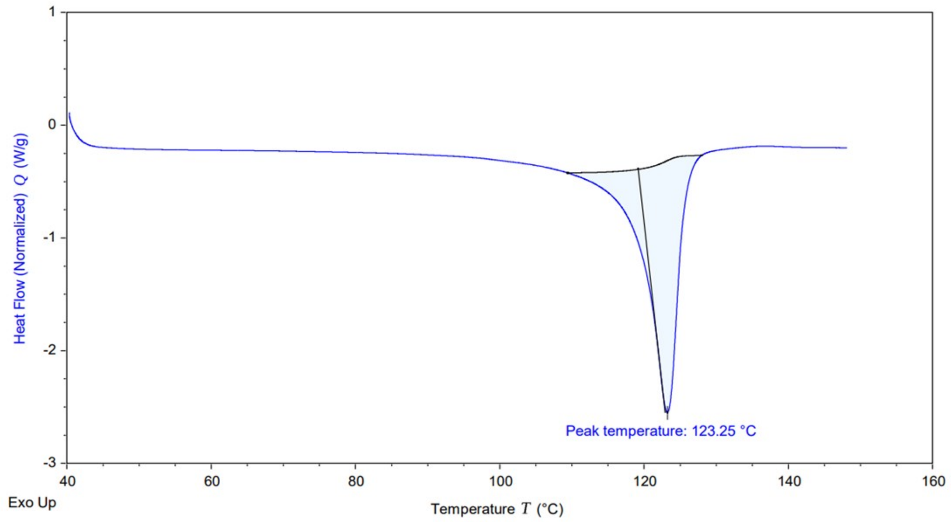


Figure S58 DSC of the polymer from Table 2, Entry 3.

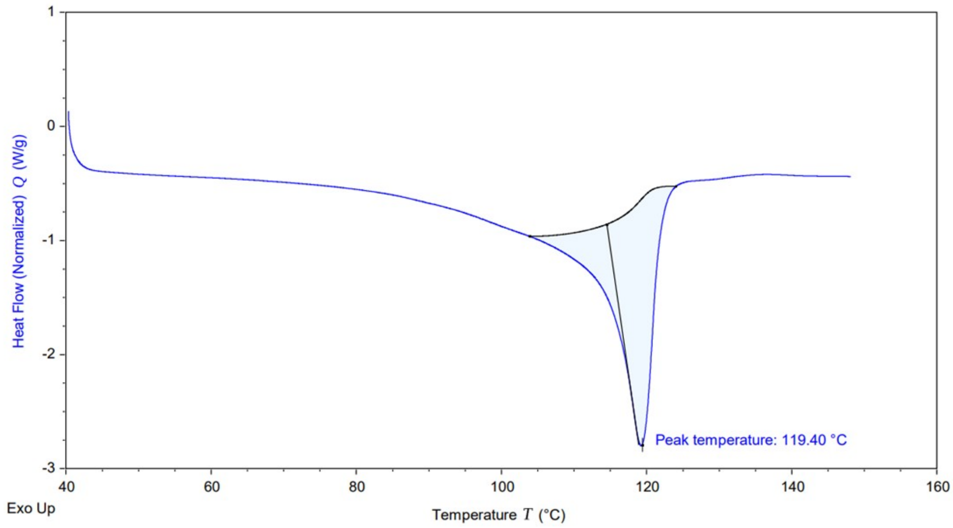


Figure S59 DSC of the polymer from Table 2, Entry 4.

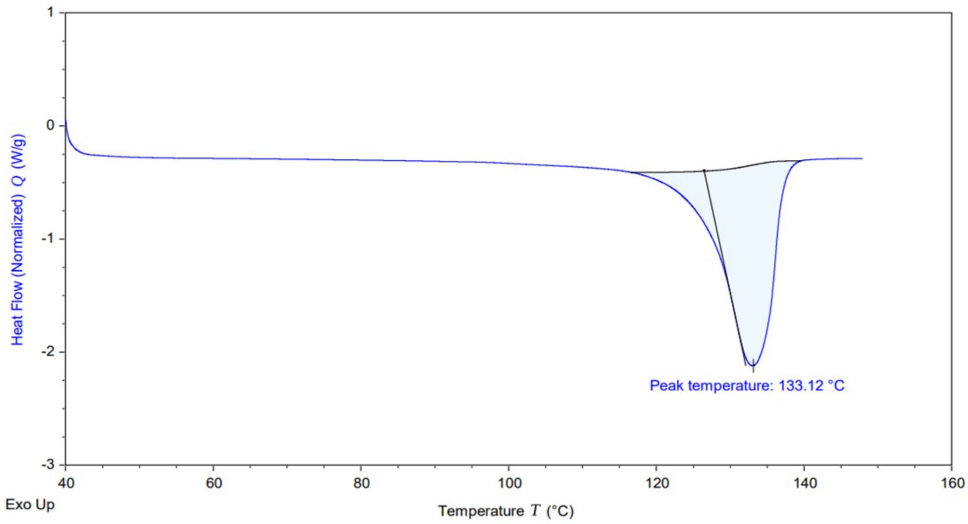


Figure S60 DSC of the polymer from Table 2, Entry 6.

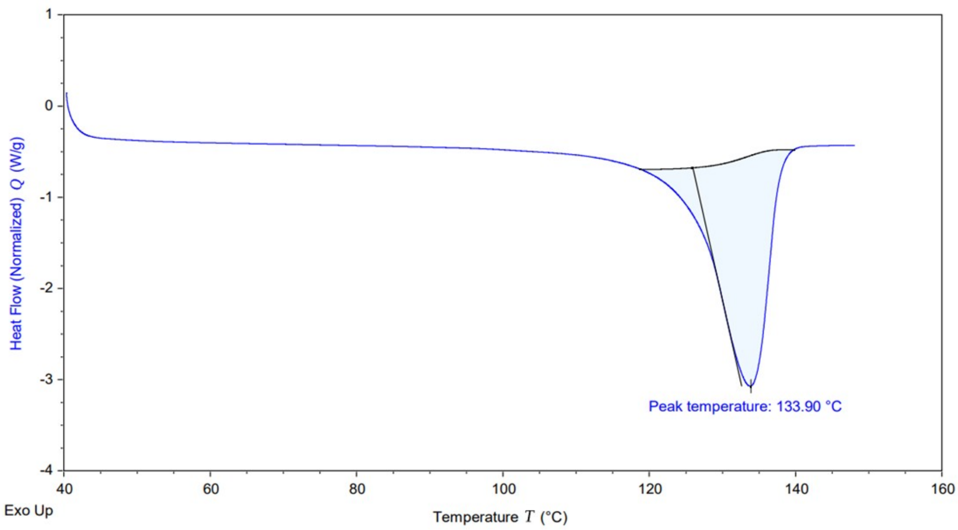


Figure S61 DSC of the polymer from Table 2, Entry 7.

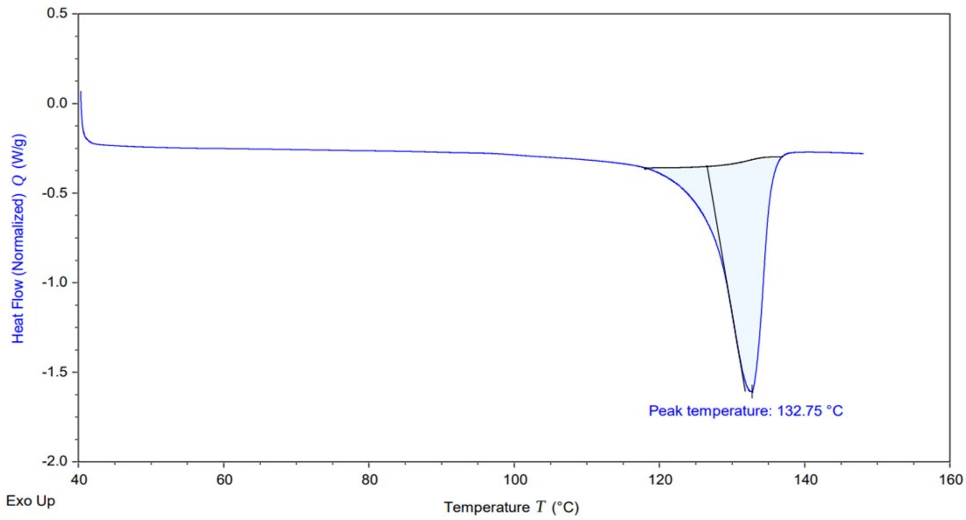


Figure S62 DSC of the polymer from Table 2, Entry 8.

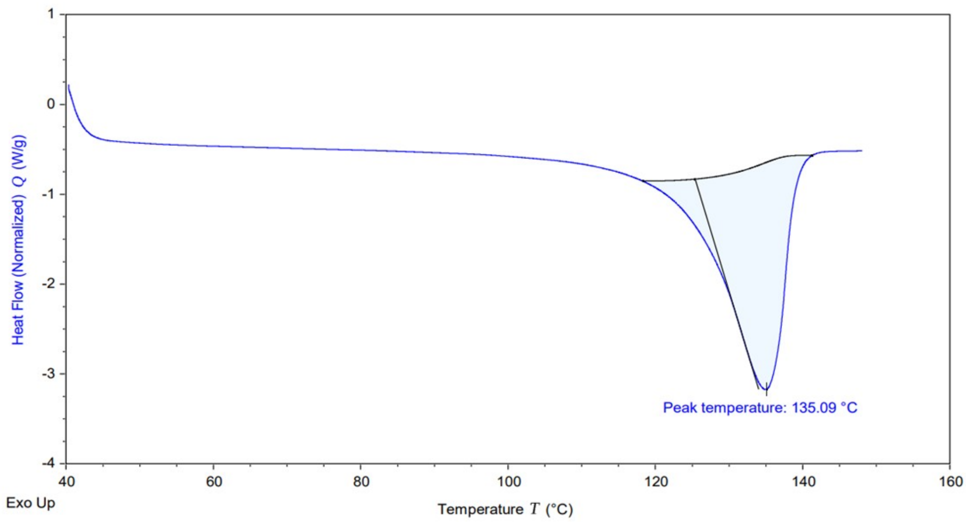


Figure S63 DSC of the polymer from Table 2, Entry 10.

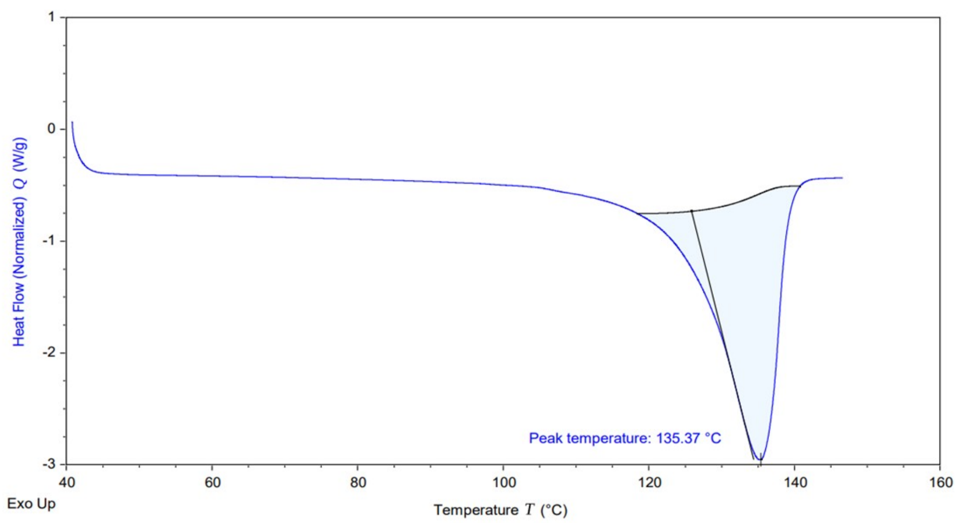


Figure S64 DSC of the polymer from Table 2, Entry 11.

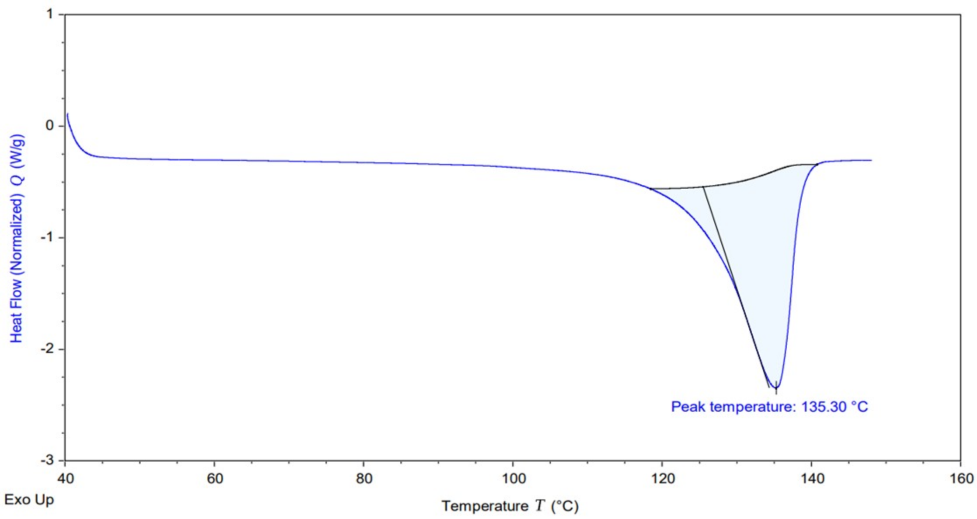


Figure S65 DSC of the polymer from Table 2, Entry 12.

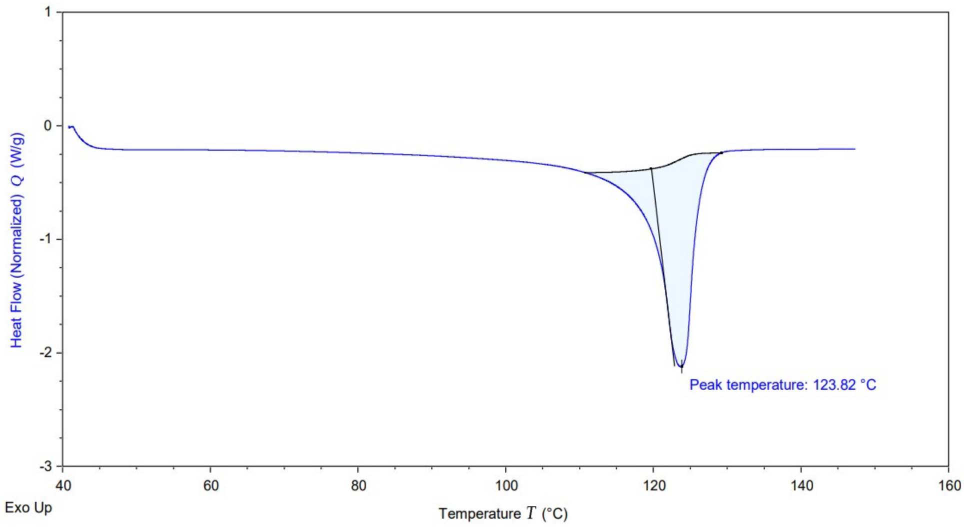


Figure S66 DSC of the polymer from Table 3, Entry 1.

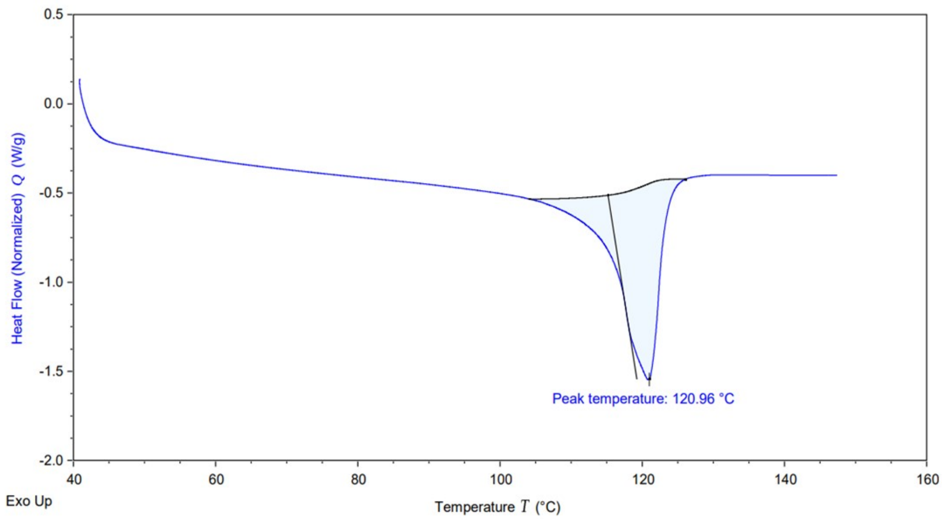


Figure S67 DSC of the polymer from Table 3, Entry 2.

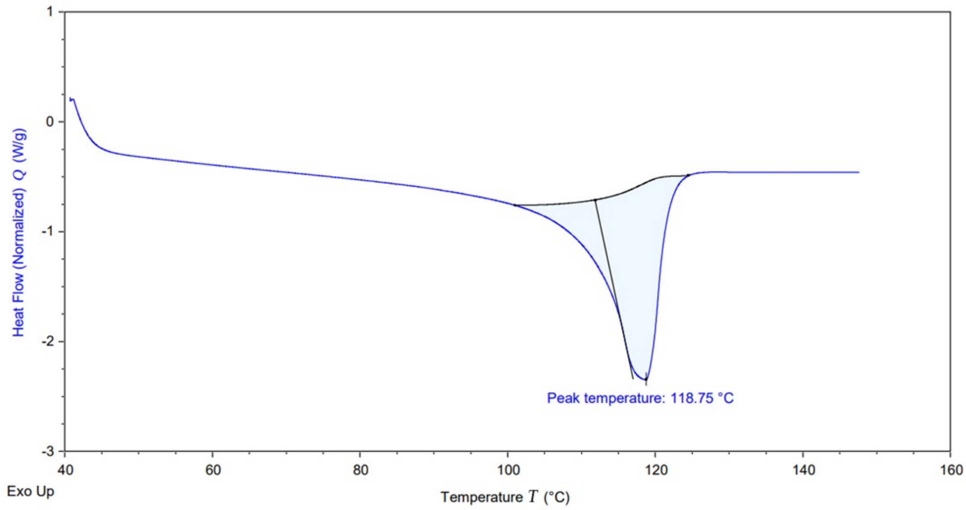


Figure S68 DSC of the polymer from Table 3, Entry 3.

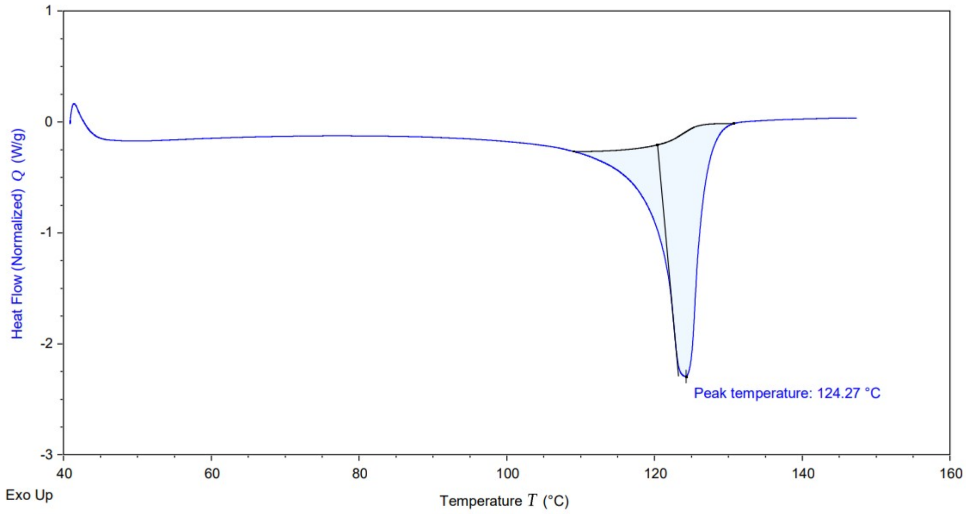


Figure S69 DSC of the polymer from Table 3, Entry 4.

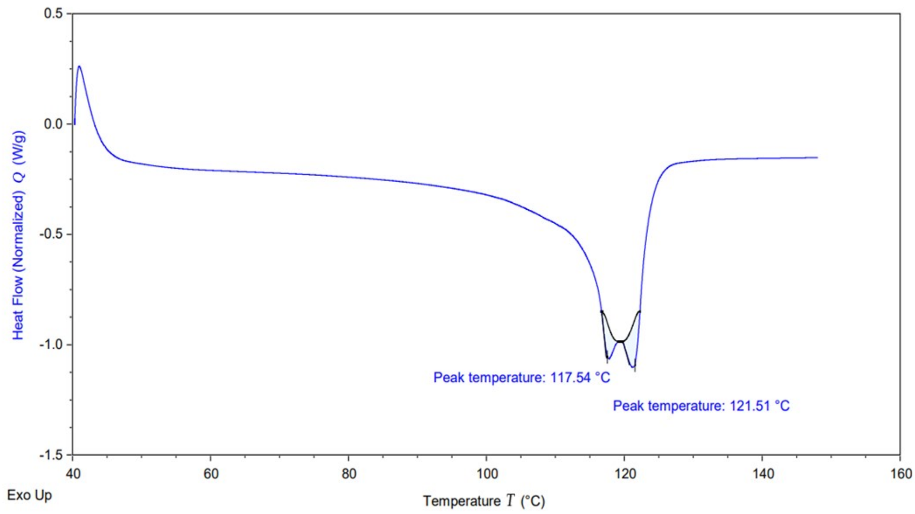


Figure S70 DSC of the polymer from Table 3, Entry 5.

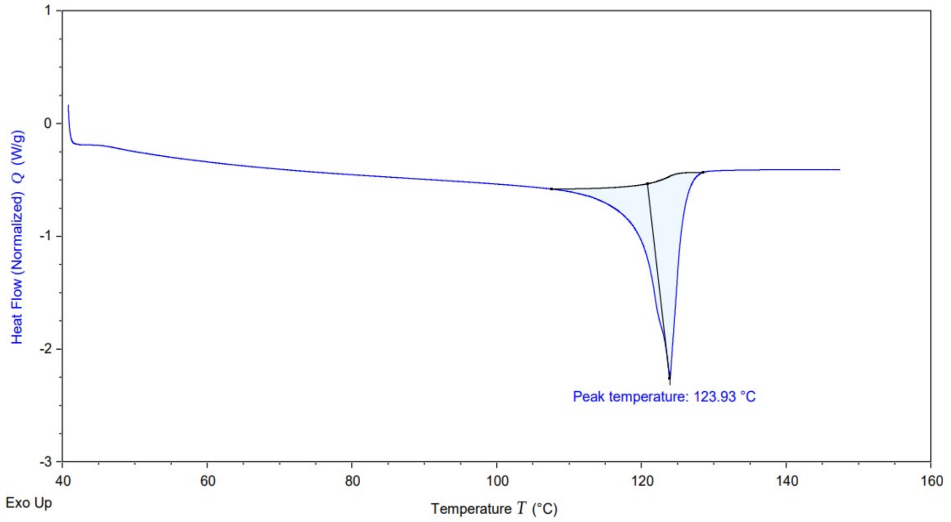


Figure S71 DSC of the polymer from Table 3, Entry 6.

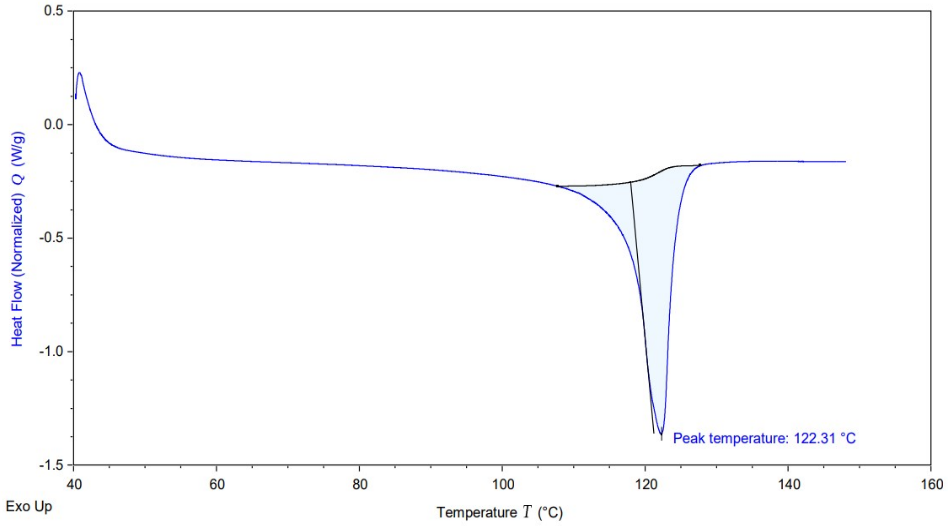


Figure S72 DSC of the polymer from Table 3, Entry 7.

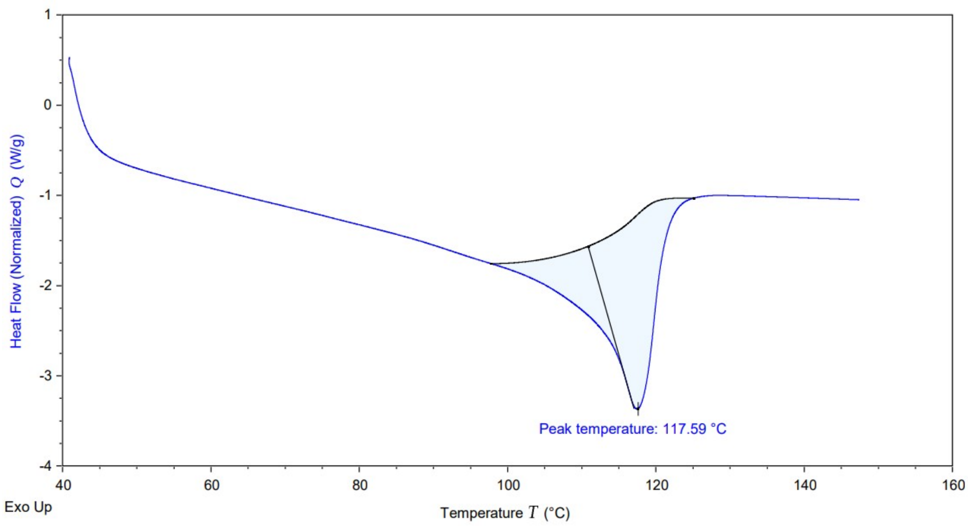


Figure S73 DSC of the polymer from Table 3, Entry 8.

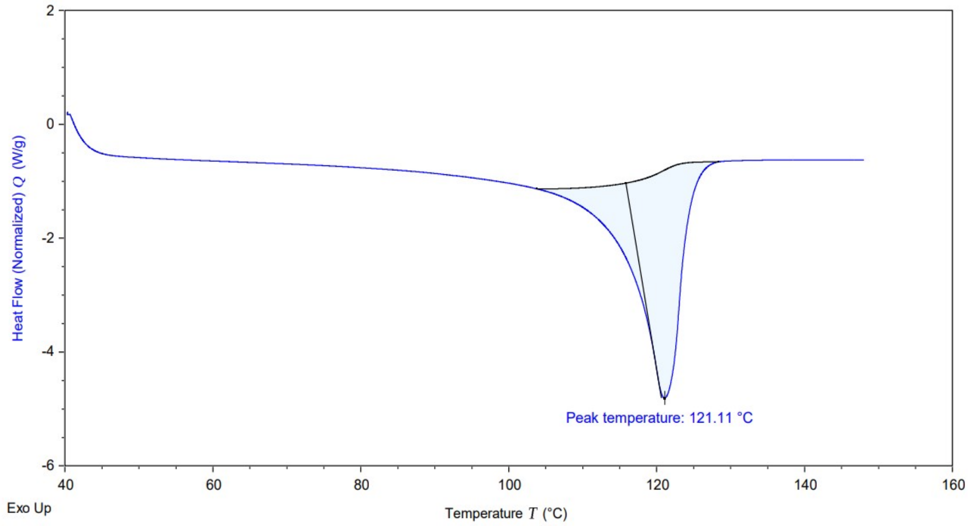


Figure S74 DSC of the polymer from Table 3, Entry 9.

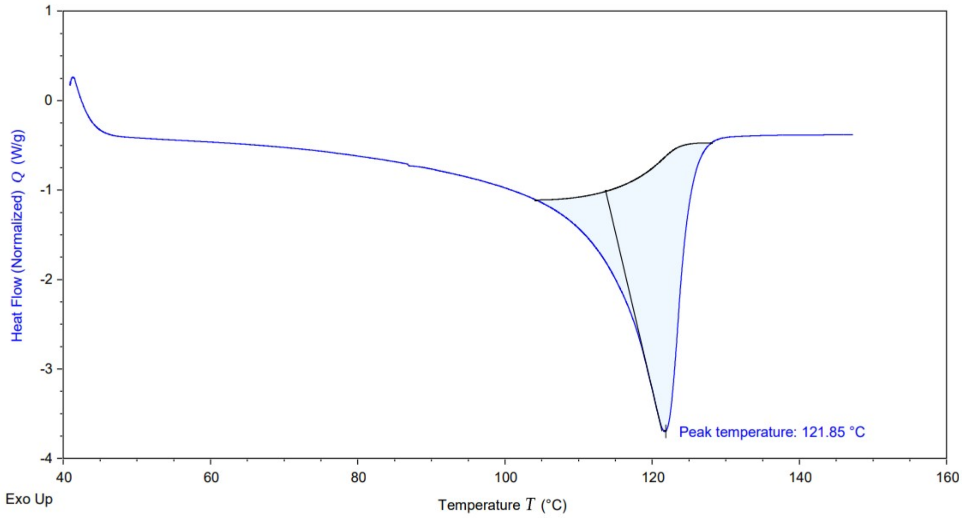


Figure S75 DSC of the polymer from Table 3, Entry 10.

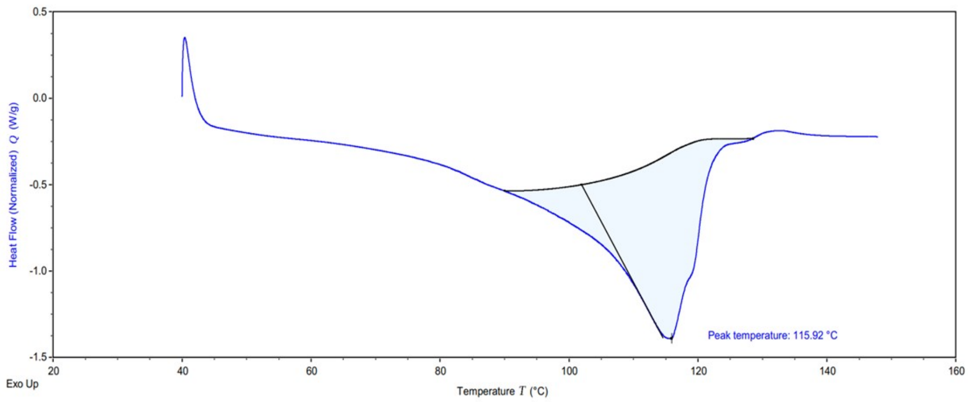


Figure S76 DSC of the polymer from Table 3, Entry 11.

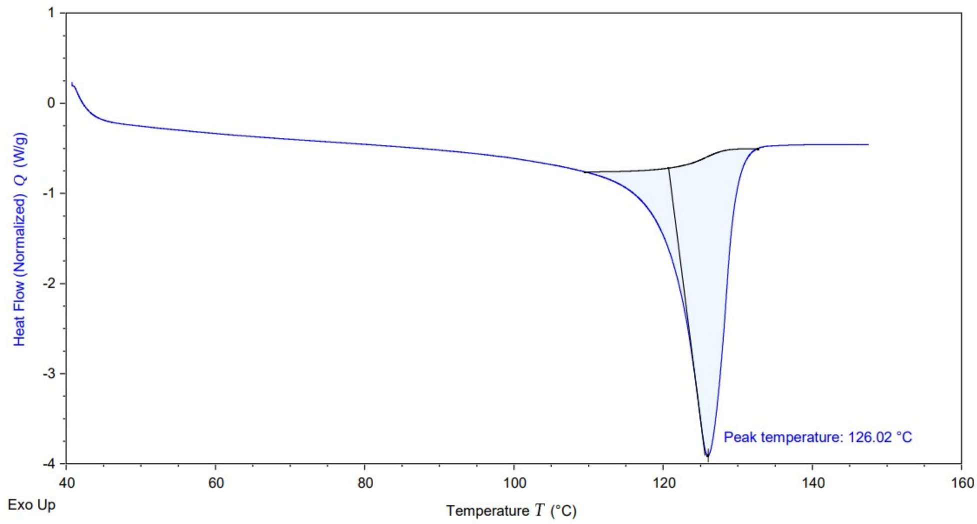


Figure S77 DSC of the polymer from Table 3, Entry 12.

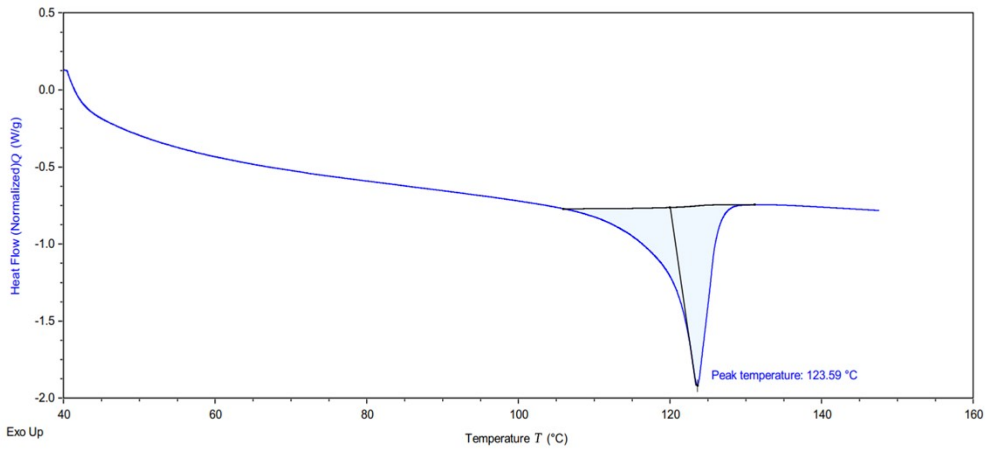


Figure S78 DSC of the polymer from Table 3, Entry 13.

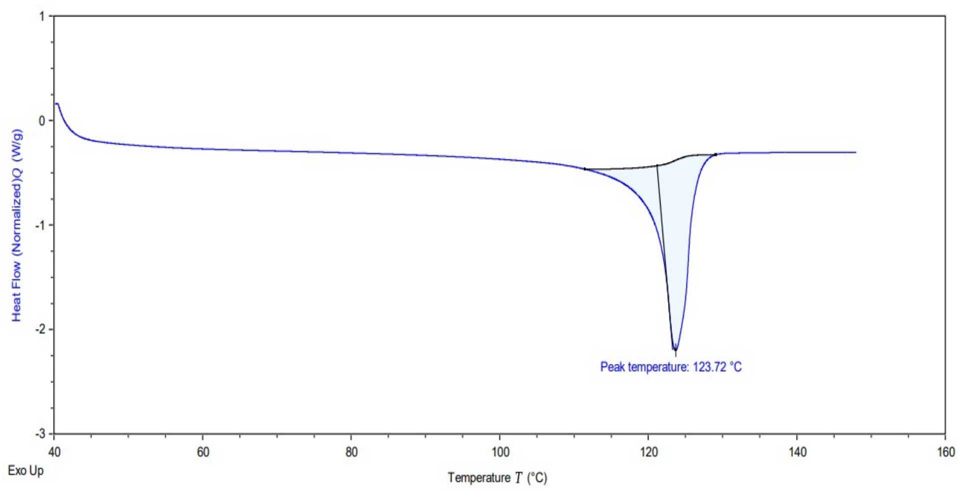


Figure S79 DSC of the polymer from Table 3, Entry 14.

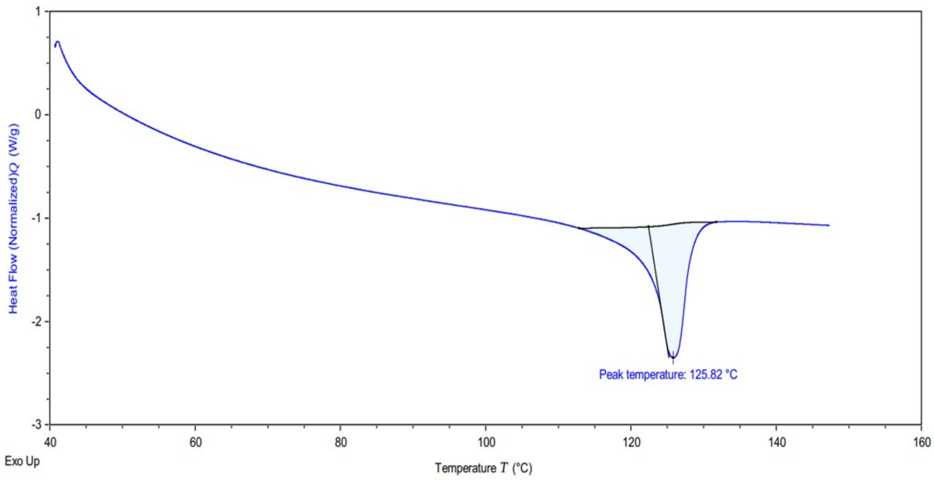


Figure S80 DSC of the polymer from Table 3, Entry 15.

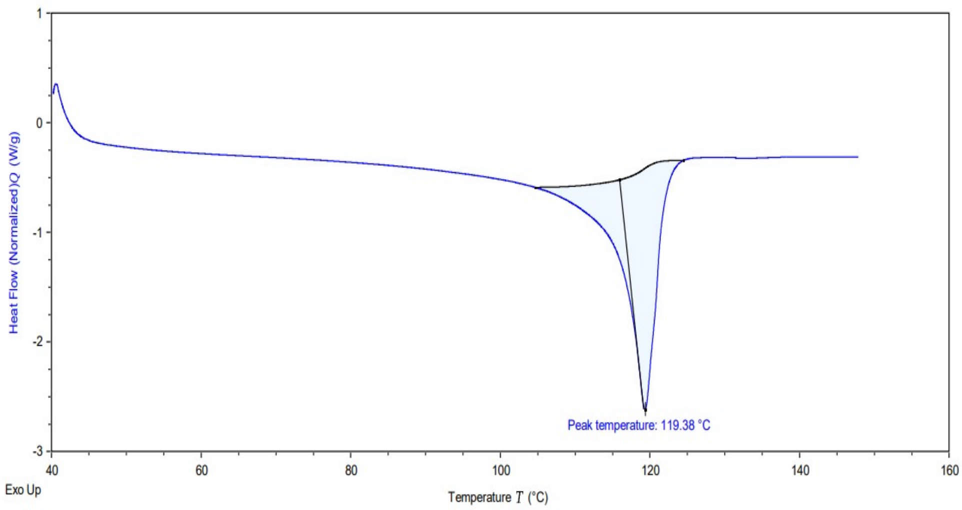
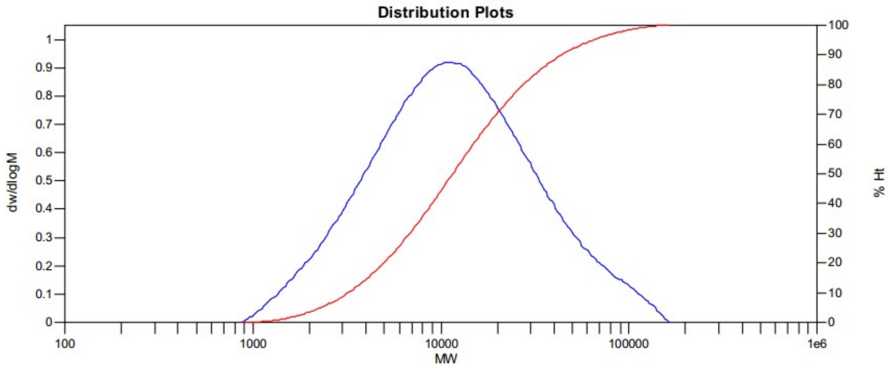


Figure S81 DSC of the polymer from Table 3, Entry 16.

6. GPC of polymers



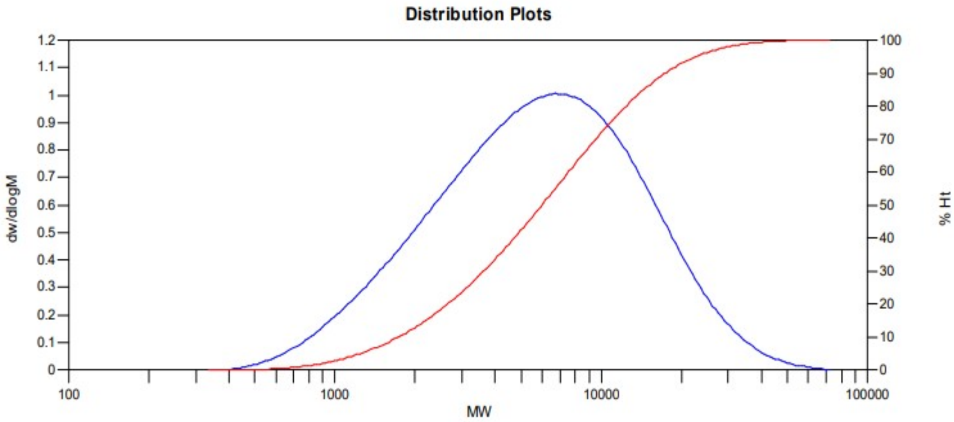
MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	11248	7312	18768	42920	71095	16295	2.56674

Processed Peaks

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1		12.88	14.65	16.47	-7.92508	100	818.611	100

Figure S82 GPC of the polymer from Table 1, Entry 1.



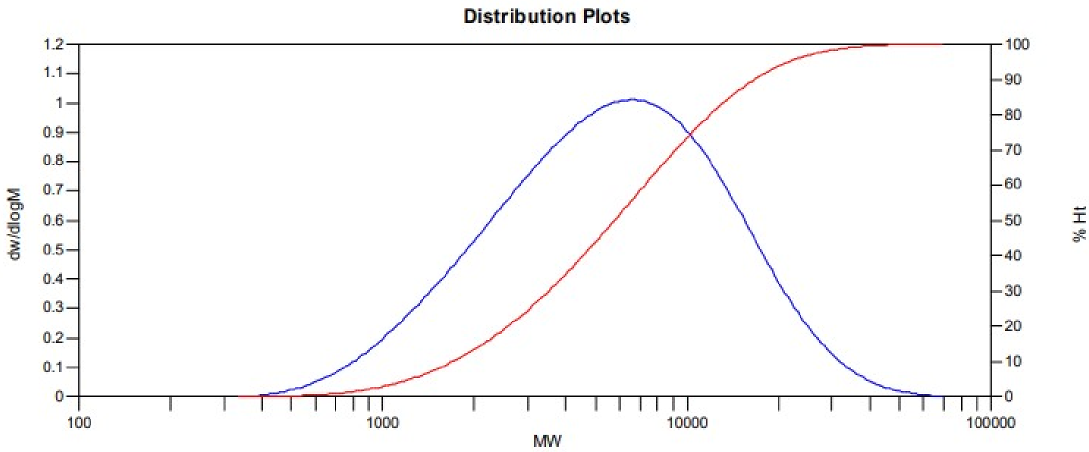
MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	6702	3832	8099	14628	22323	7295	2.11352

Processed Peaks

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1		13.62	15.22	17.23	-19.9255	0	1840.58	100

Figure S83 GPC of the polymer from Table 1, Entry 2.



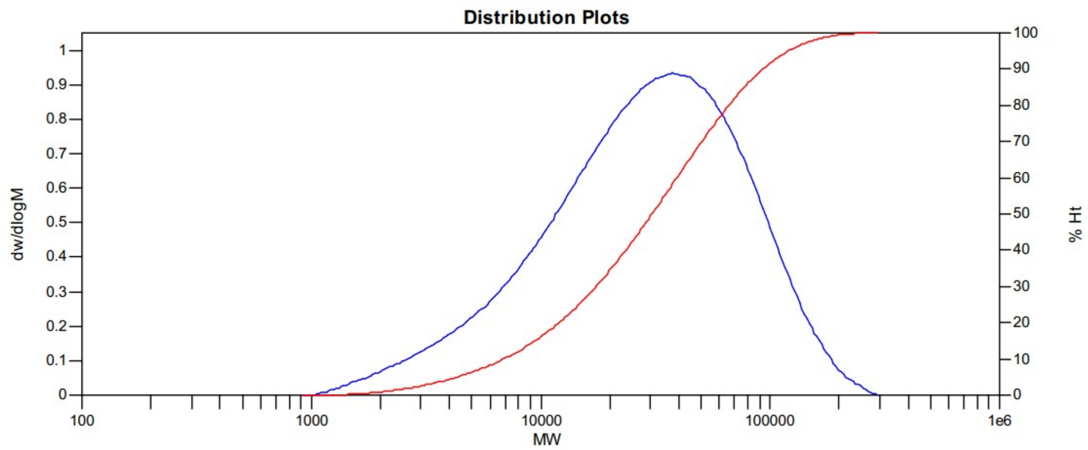
MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	6538	3731	7777	13882	20941	7019	2.08443

Processed Peaks

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1		13.65	15.23	17.23	-26.1884	0	2405.66	100

Figure S84 GPC of the polymer from Table 1, Entry 3.



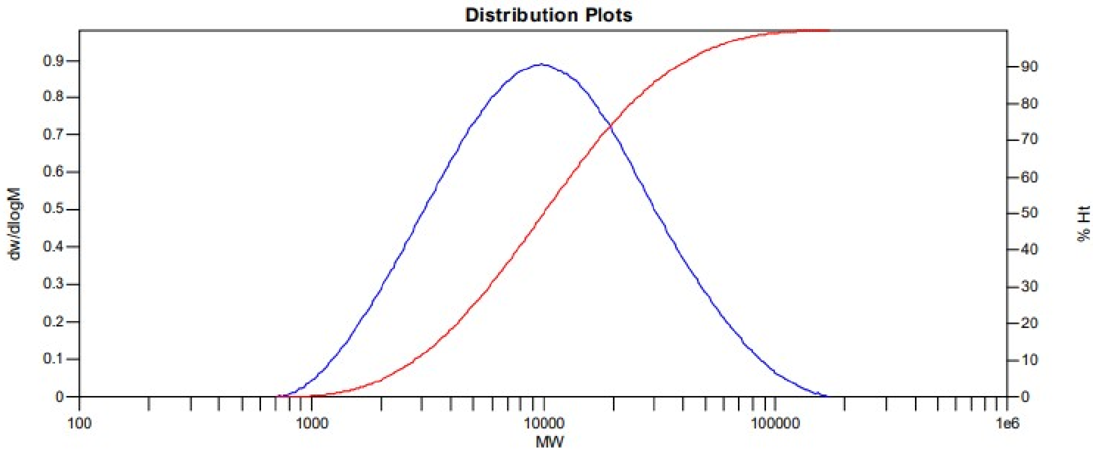
MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	37621	15567	41563	75953	109769	37018	2.66994

Processed Peaks

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1		12.88	14.28	16.82	-10.4162	0	1049.57	100

Figure S85 GPC of the polymer from Table 1, Entry 4.



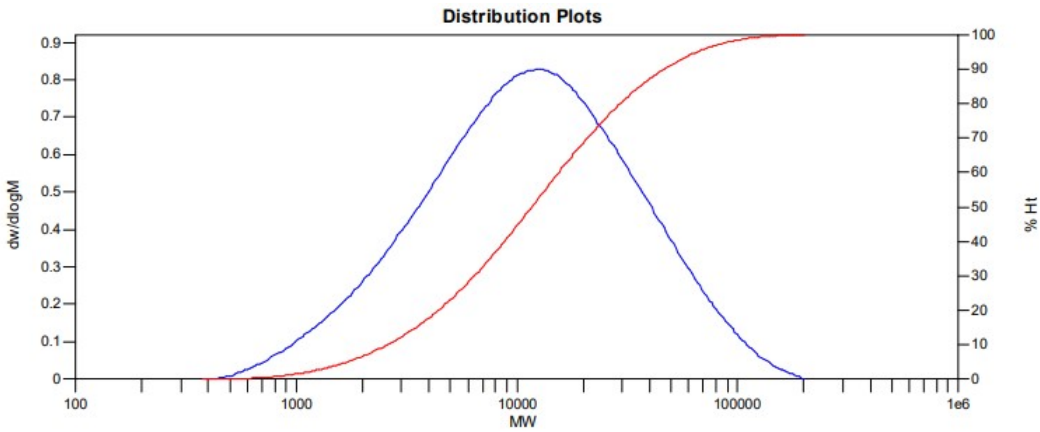
MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	9785	6371	15992	35746	60023	13879	2.51012

Processed Peaks

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1		13.25	15.20	16.98	-11.0357	0	1166.28	100

Figure S86 GPC of the polymer from Table 1, Entry 5.



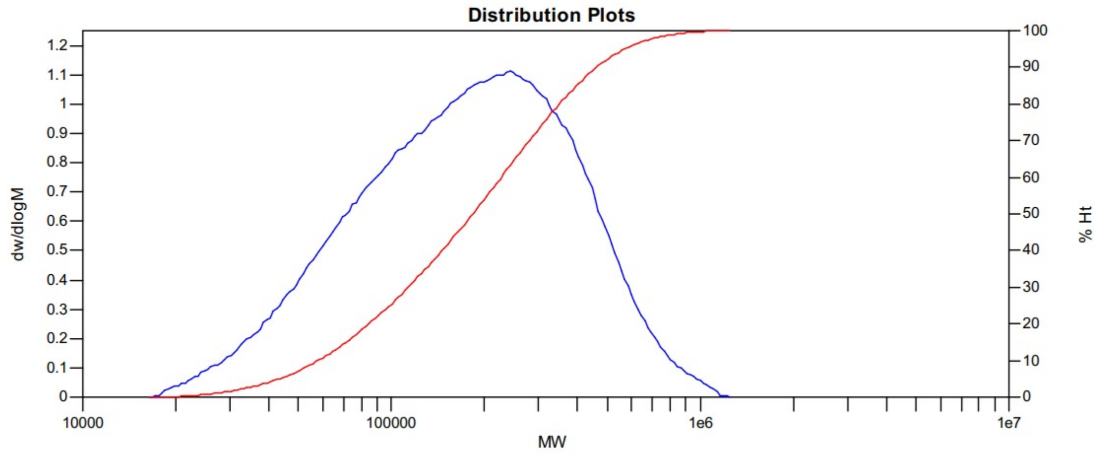
MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	12772	6128	19249	44767	73974	16452	3.14116

Processed Peaks

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1		12.93	14.78	17.15	-9.78375	0	1095.16	100

Figure S87 GPC of the polymer from Table 1, Entry 6.



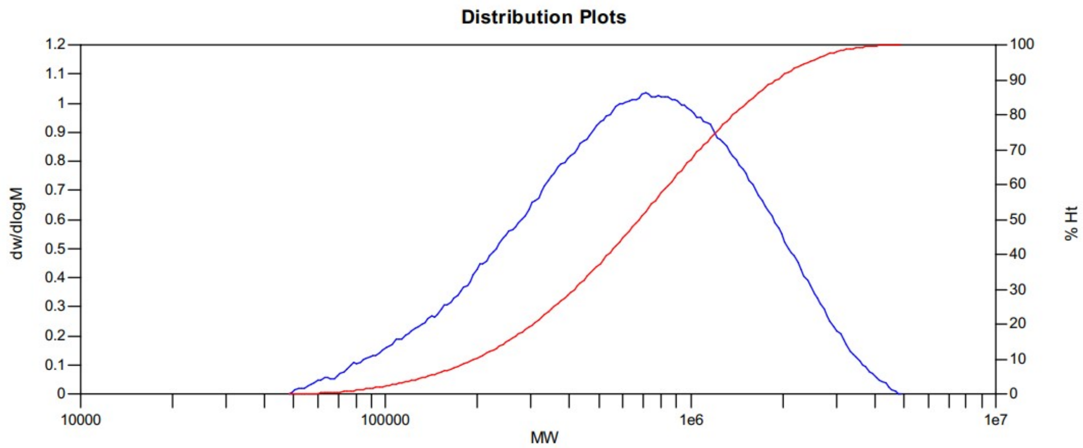
MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	241881	123068	225996	355357	483397	208199	1.83635

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	13.02	14.85	-3.92012	0	331.897	100

Figure S88 GPC of the polymer from Table 1, Entry 7.



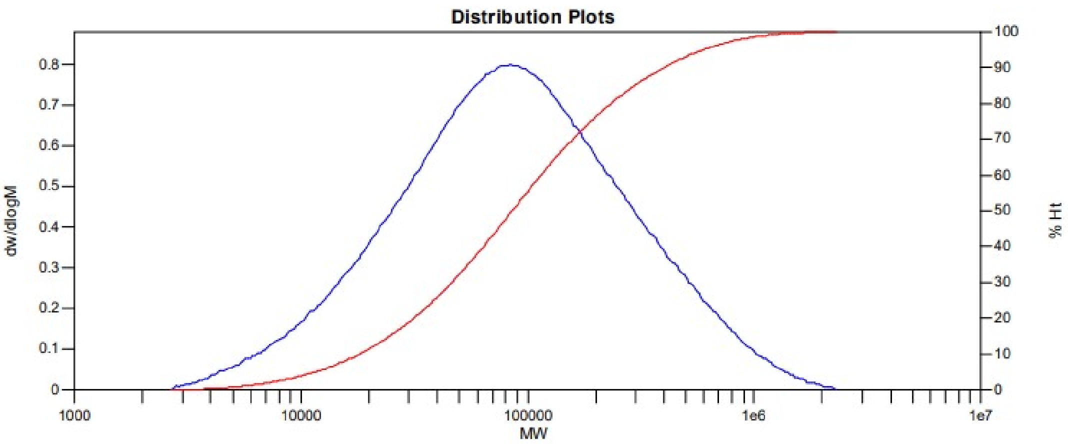
MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	710379	427578	882707	1474860	2039431	802627	2.06444

Processed Peaks

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1		10.97	12.28	14.12	-3.53988	0	321.729	100

Figure S89 GPC of the polymer from Table 1, Entry 8.



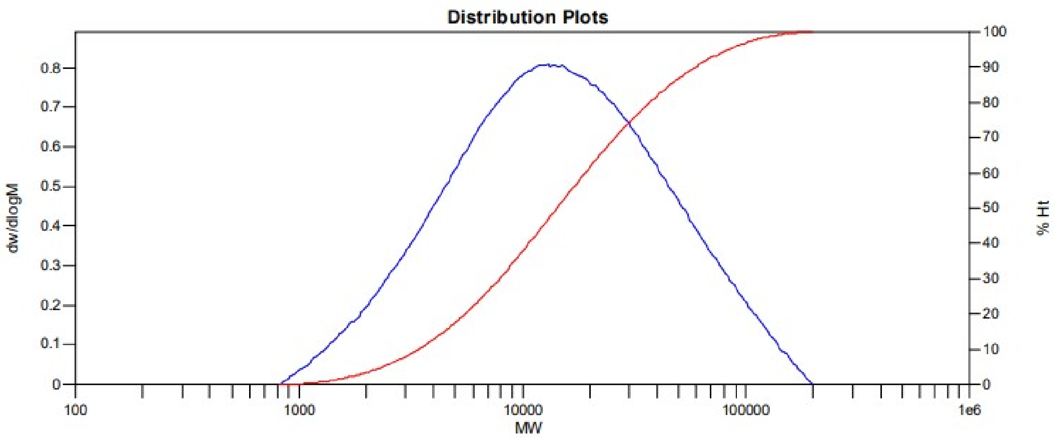
MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	84401	42629	161084	455022	829482	133072	3.77874

Processed Peaks

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1		11.48	13.73	16.08	-6.77933	0	797.235	100

Figure S90 GPC of the polymer from Table 1, Entry 9.



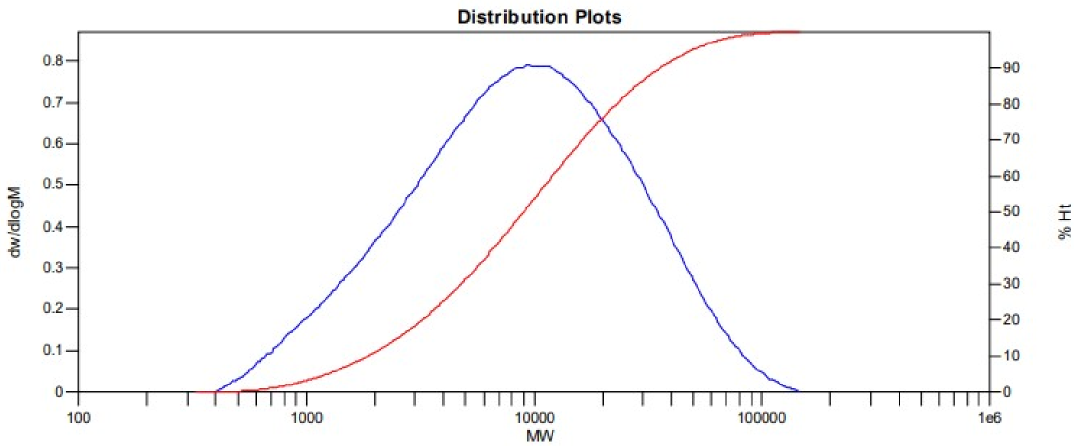
MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	13017	8115	24013	54656	85883	20662	2.95909

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	14.62	16.52	-8.0319	100	939.764	100

Figure S91 GPC of the polymer from Table 1, Entry 10.



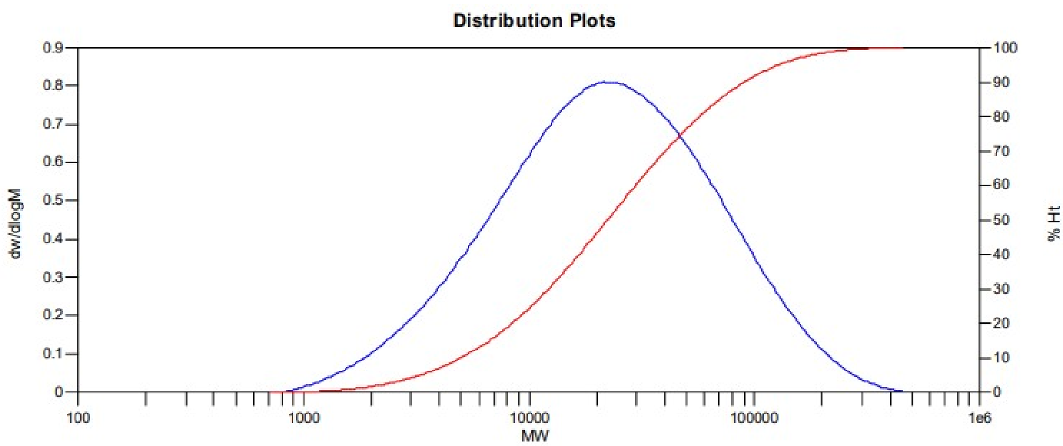
MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	9315	4580	14675	33273	53362	12553	3.20415

Processed Peaks

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1		13.05	14.90	17.15	-8.77272	0	1029.38	100

Figure S92 GPC of the polymer from Table 1, Entry 11.



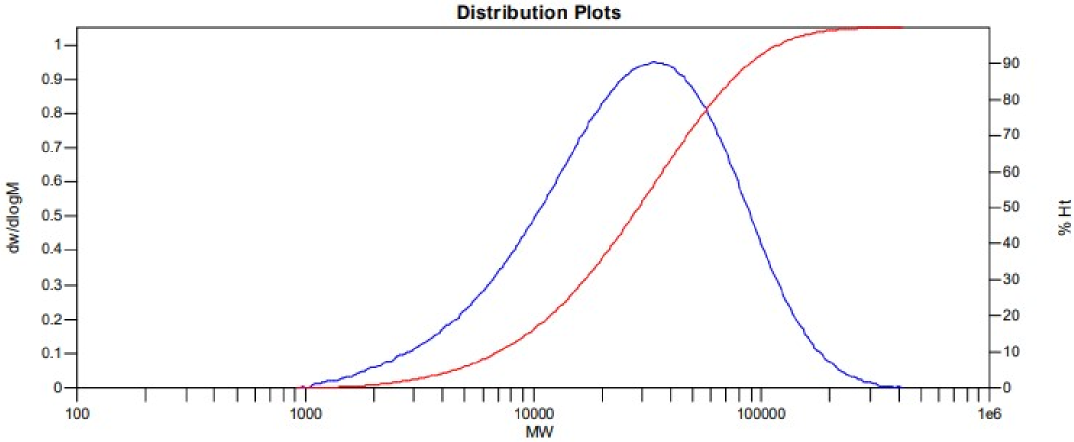
MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	21421	11789	37592	90643	155250	31972	3.18874

Processed Peaks

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1		12.58	14.67	16.98	-17.7935	100	2065.54	100

Figure S93 GPC of the polymer from Table 1, Entry 12.



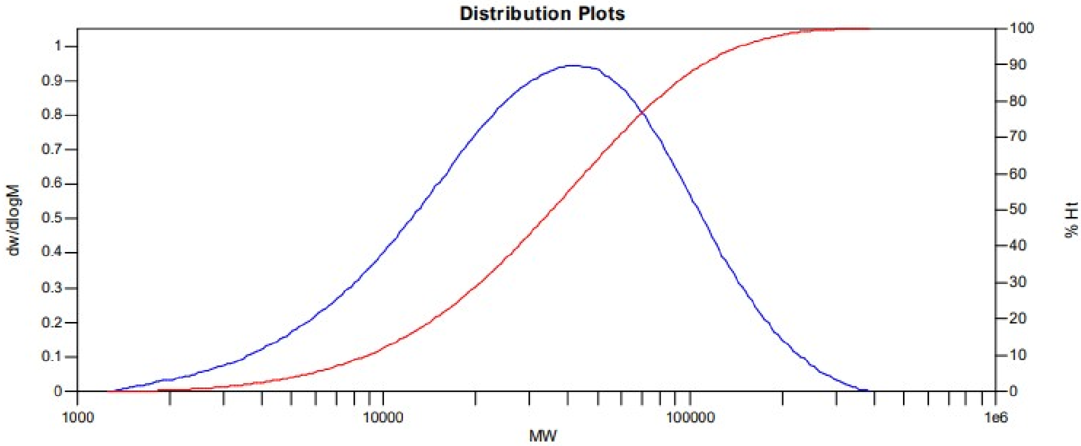
MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	33286	15568	40171	77018	120938	35675	2.58036

Processed Peaks

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1		12.65	14.37	16.82	-9.23924	0	914.999	100

Figure S94 GPC of the polymer from Table 2, Entry 2.



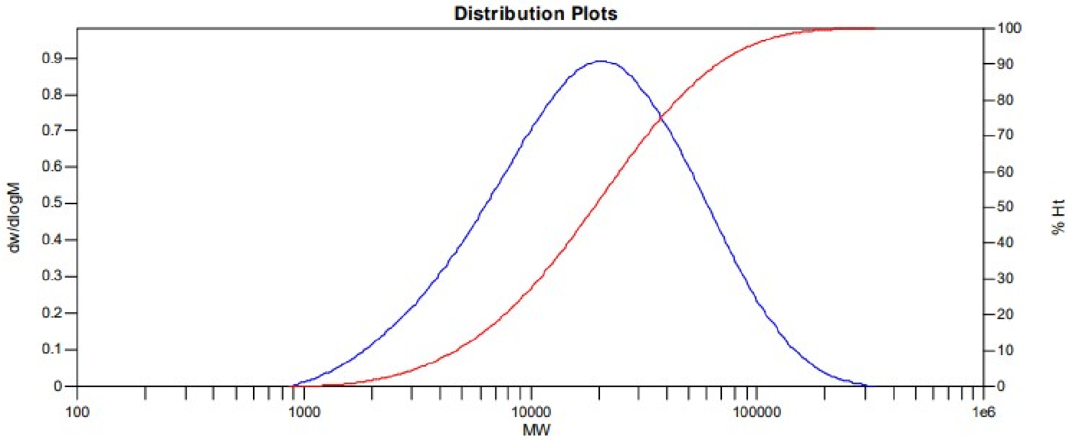
MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	42520	19556	49312	92706	139299	43874	2.52158

Processed Peaks

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1		12.70	14.20	16.60	-11.9419	0	1189.69	100

Figure S95 GPC of the polymer from Table 2, Entry 3.



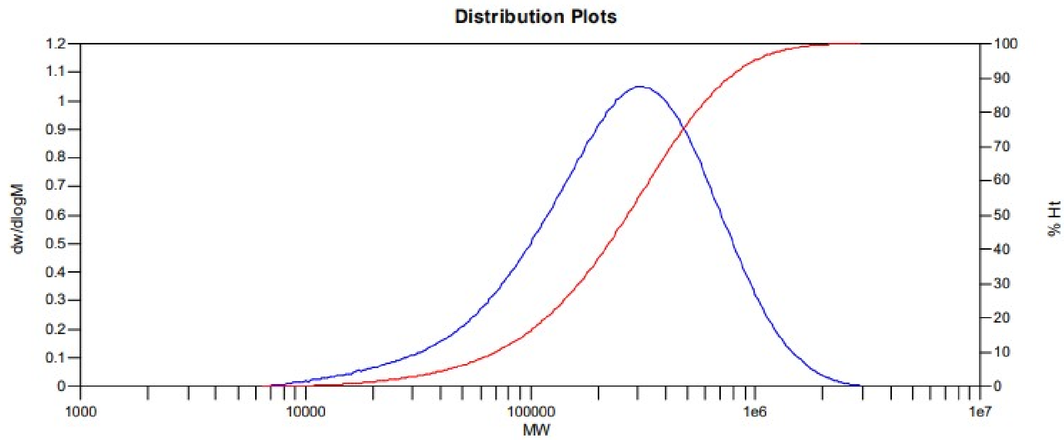
MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	19904	10772	29033	62109	102630	25313	2.69523

Processed Peaks

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1		12.80	14.72	16.85	-15.3728	0	1622.11	100

Figure S96 GPC of the polymer from Table 2, Entry 4.



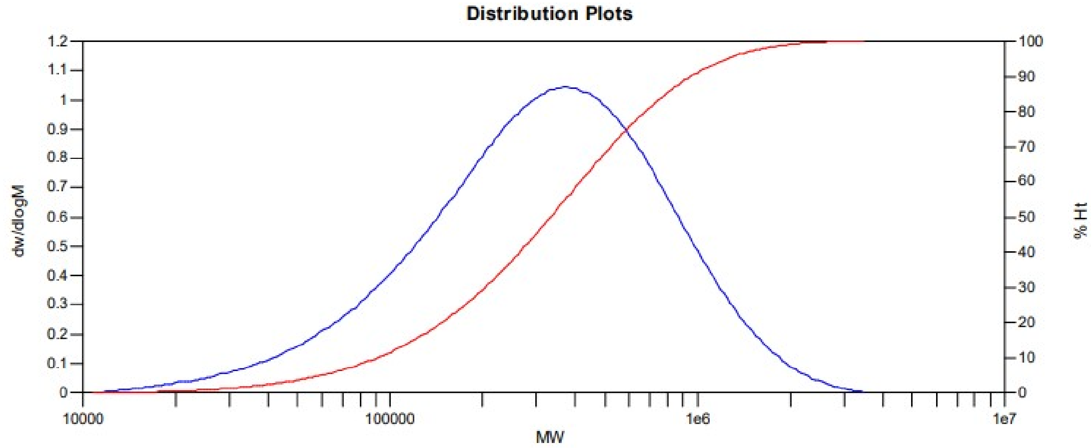
MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	308987	144788	356603	636793	955183	320819	2.46293

Processed Peaks

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1		11.32	12.85	15.48	-15.7281	0	1409.1	100

Figure S97 GPC of the polymer from Table 2, Entry 6.



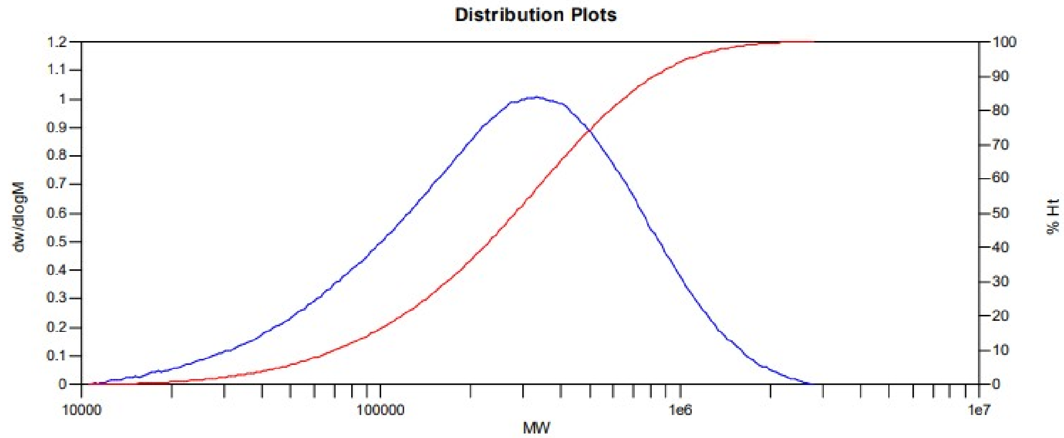
MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	375847	192731	443387	794337	1193853	399201	2.30055

Processed Peaks

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1		11.20	12.72	15.13	-12.1787	0	1096.9	100

Figure S98 GPC of the polymer from Table 2, Entry 7.



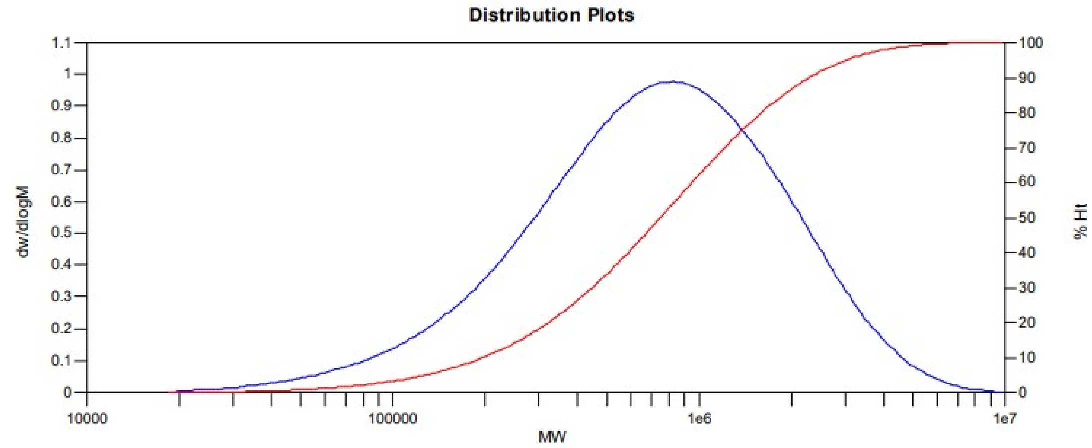
MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	332538	156499	376500	678613	1000584	337629	2.40577

Processed Peaks

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1		11.35	12.80	15.15	-8.26655	0	773.127	100

Figure S99 GPC of the polymer from Table 2, Entry 8.



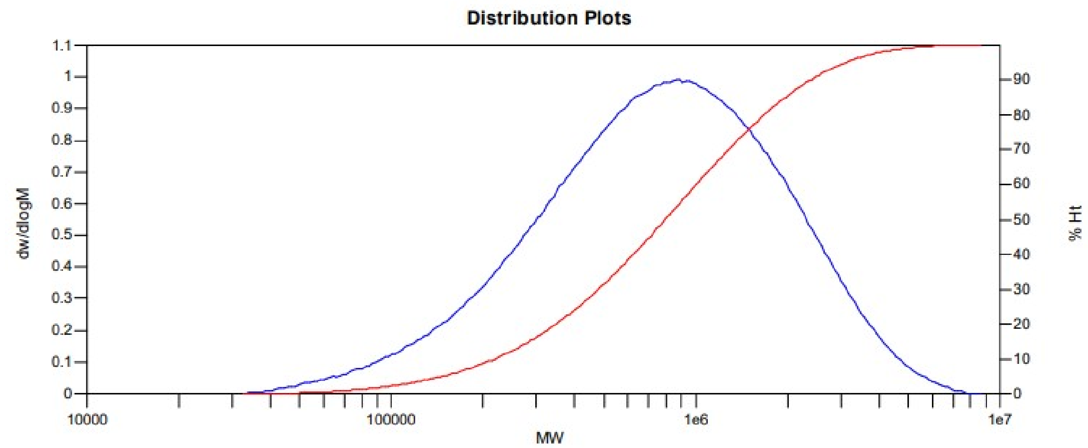
MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	822797	415864	1040081	1955677	3004301	927353	2.50101

Processed Peaks

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1		10.50	12.18	14.77	-17.7542	0	1708.23	100

Figure S100 GPC of the polymer from Table 2, Entry 10.



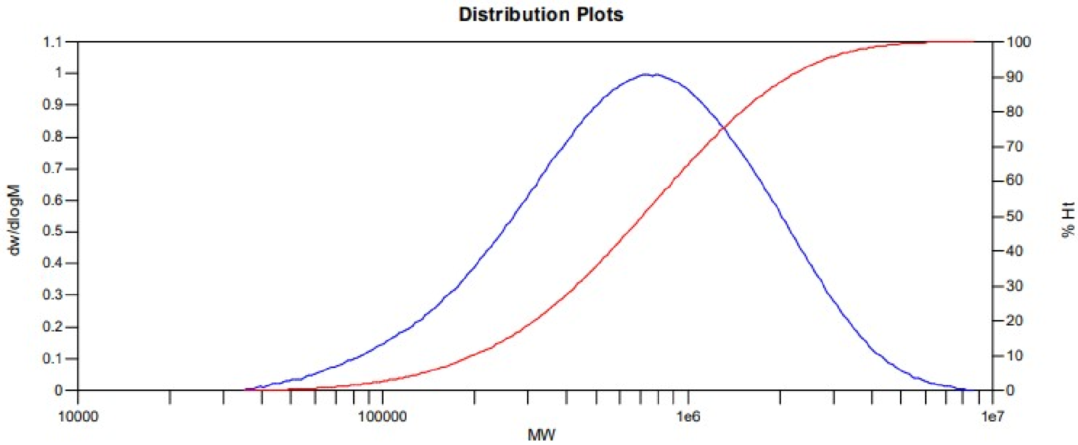
MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	864093	472071	1081851	1946250	2866644	971681	2.29171

Processed Peaks

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1		10.58	12.15	14.38	-8.22666	0	780.9	100

Figure S101 GPC of the polymer from Table 2, Entry 11.



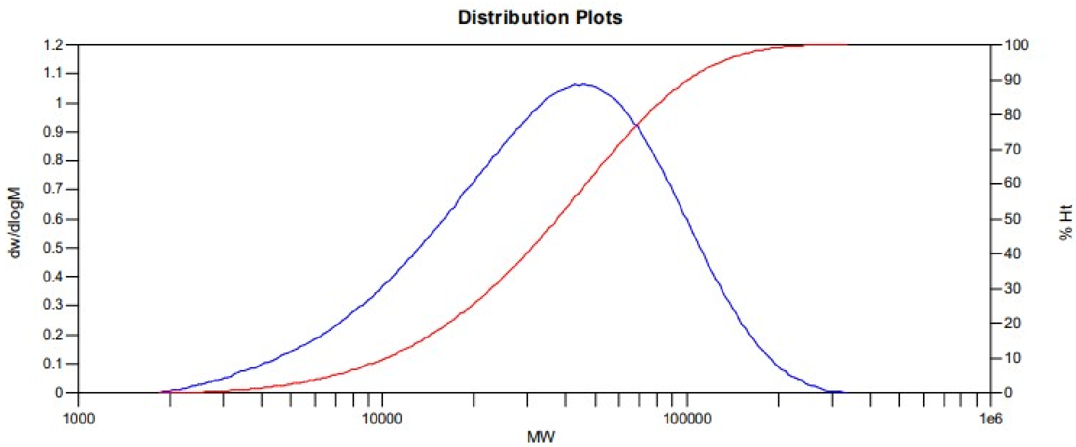
MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	727987	429798	979016	1813822	2775201	876699	2.27785

Processed Peaks

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1		10.58	12.27	14.33	-11.8658	0	1118.18	100

Figure S102 GPC of the polymer from Table 2, Entry 12.



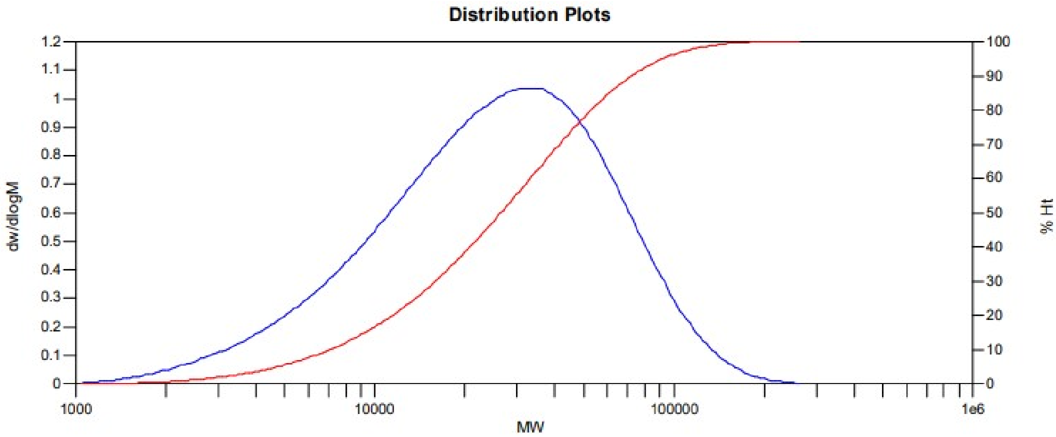
MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	45242	22290	47873	80407	113843	43506	2.14773

Processed Peaks

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1		12.58	13.97	16.08	-14.3308	0	1253.4	100

Figure S103 GPC of the polymer from Table 3, Entry 1.



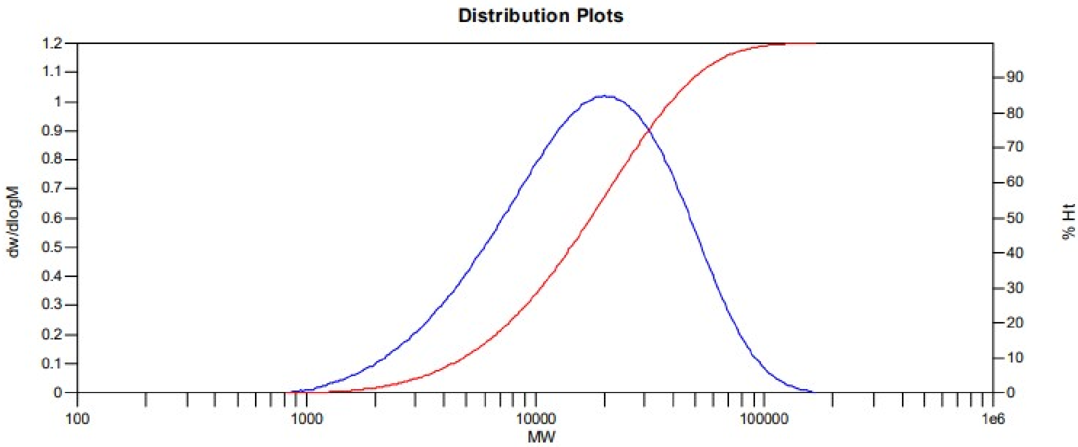
MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	31971	15382	34079	58155	83567	30881	2.21551

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	14.17	16.47	-12.518	0	1121.34	100

Figure S104 GPC of the polymer from Table 3, Entry 2.



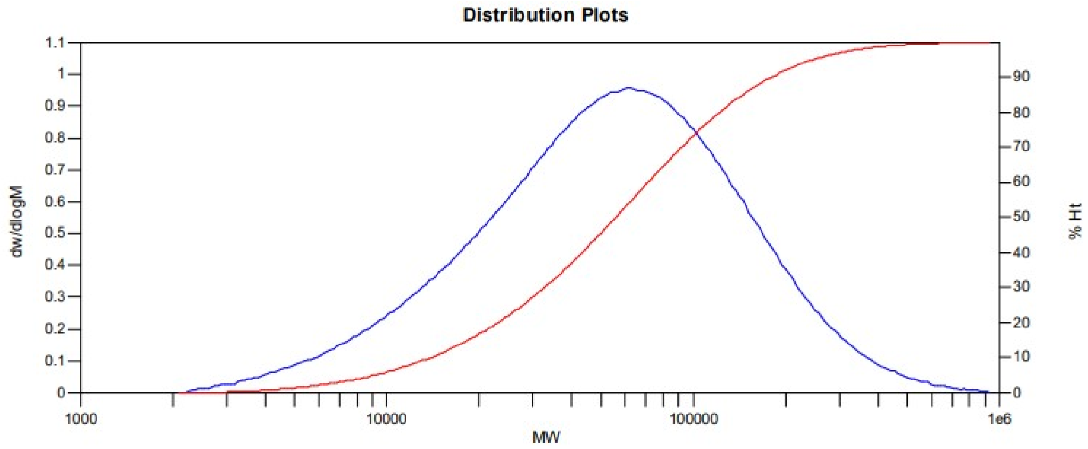
MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	19958	10582	22900	39539	57173	20724	2.16405

Processed Peaks

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1		13.05	14.48	16.63	-14.4653	0	1318.02	100

Figure S105 GPC of the polymer from Table 3, Entry 3.



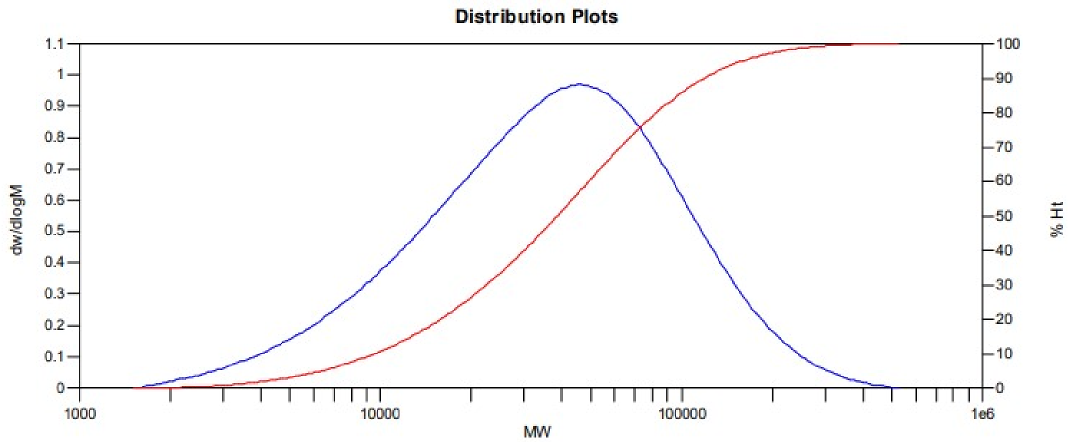
MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	62453	30849	80929	169083	289518	71125	2.62339

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	13.72	16.00	-12.6424	0	1227.18	100

Figure S106 GPC of the polymer from Table 3, Entry 4.



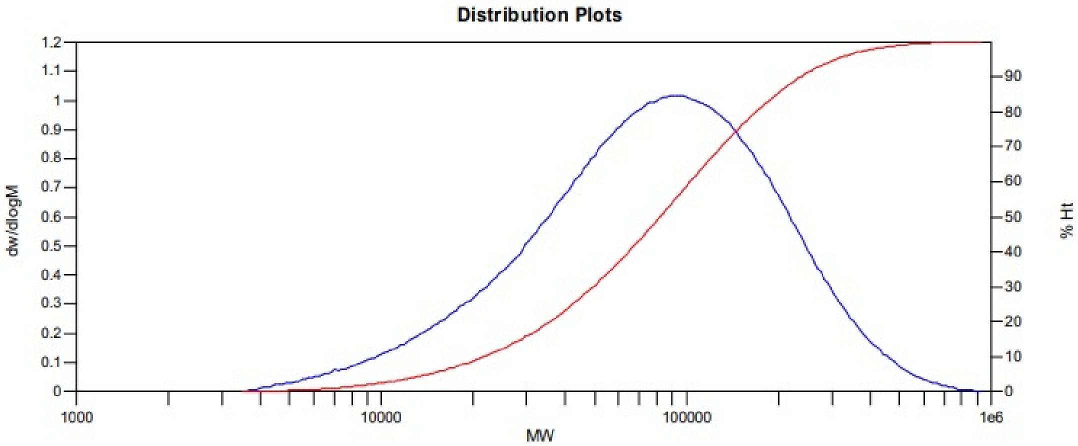
MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	45242	21448	54081	105500	167855	47949	2.52149

Processed Peaks

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1		12.28	13.93	16.22	-15.4098	100	1475.37	100

Figure S107 GPC of the polymer from Table 3, Entry 5.



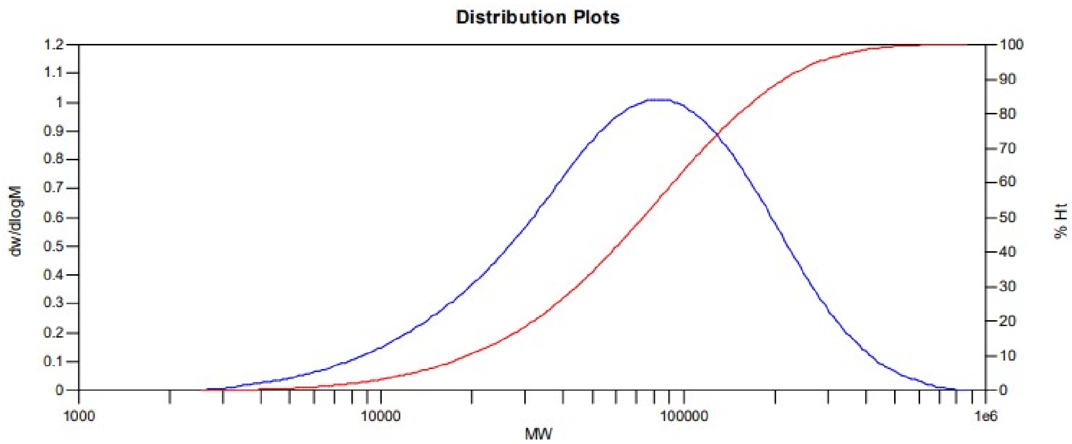
MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	90596	47570	109435	196028	292770	98442	2.3005

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	13.47	15.65	-10.0106	0	912.513	100

Figure S108 GPC of the polymer from Table 3, Entry 6.



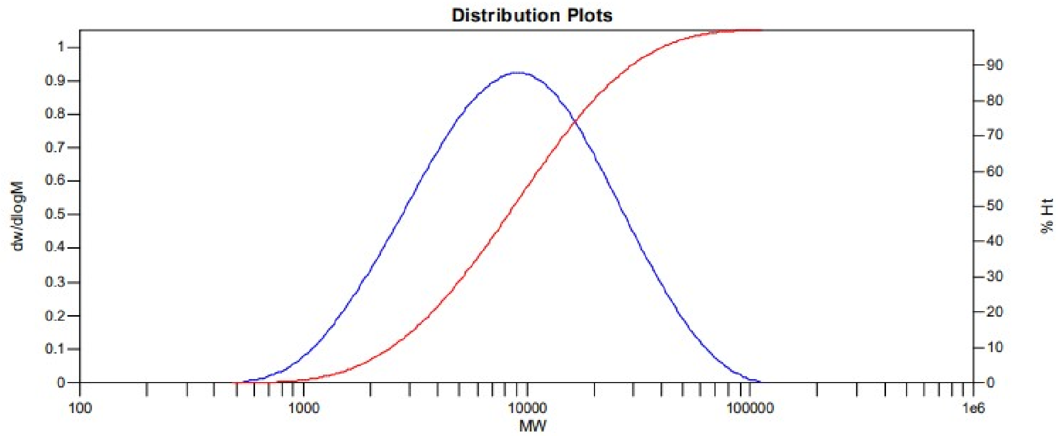
MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	80031	41961	99203	180836	273702	88979	2.36417

Processed Peaks

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1		11.95	13.55	15.87	-16.5856	0	1526.4	100

Figure S109 GPC of the polymer from Table 3, Entry 7.



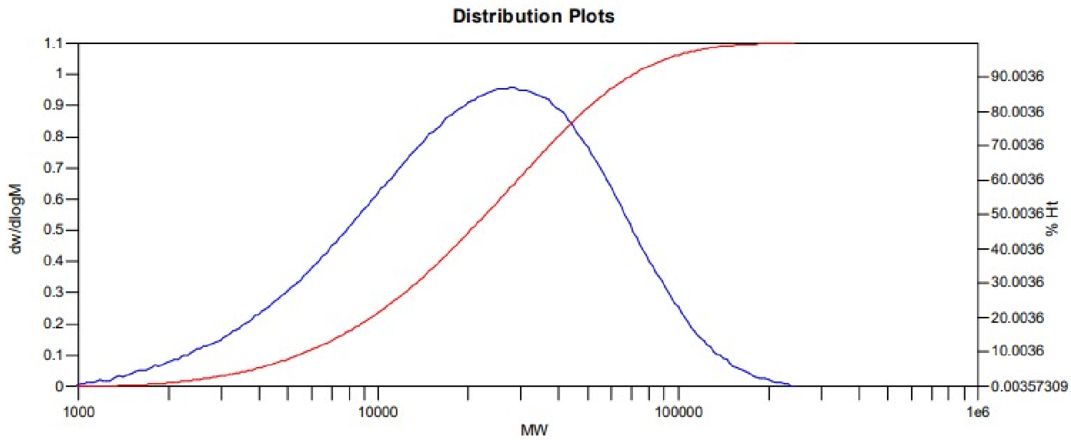
MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	8804	5534	12925	25697	40200	11429	2.33556

Processed Peaks

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1		13.32	15.03	16.98	-18.5911	100	1869.49	100

Figure S110 GPC of the polymer from Table 3, Entry 8.



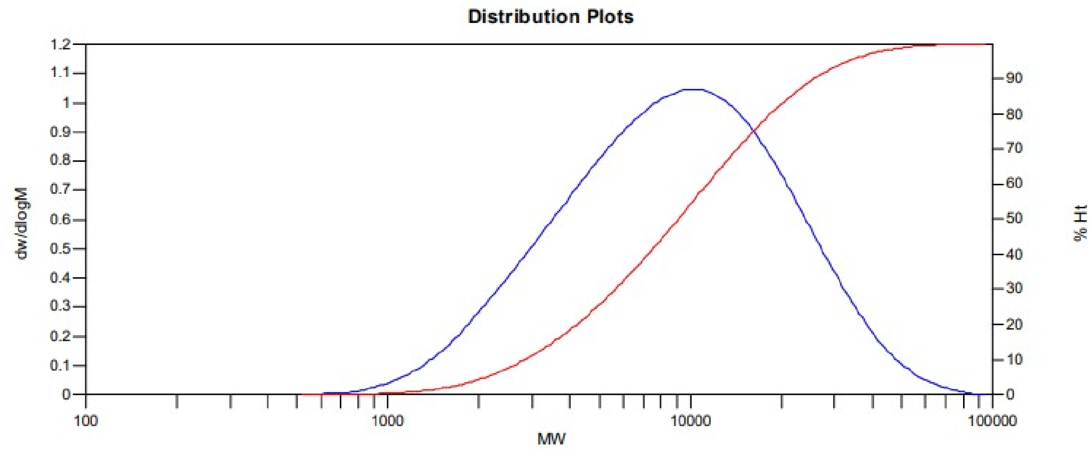
MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	27551	12806	30968	56736	84705	27691	2.41824

Processed Peaks

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1		12.80	14.27	16.52	-7.70159	0	747.811	100

Figure S111 GPC of the polymer from Table 3, Entry 9.



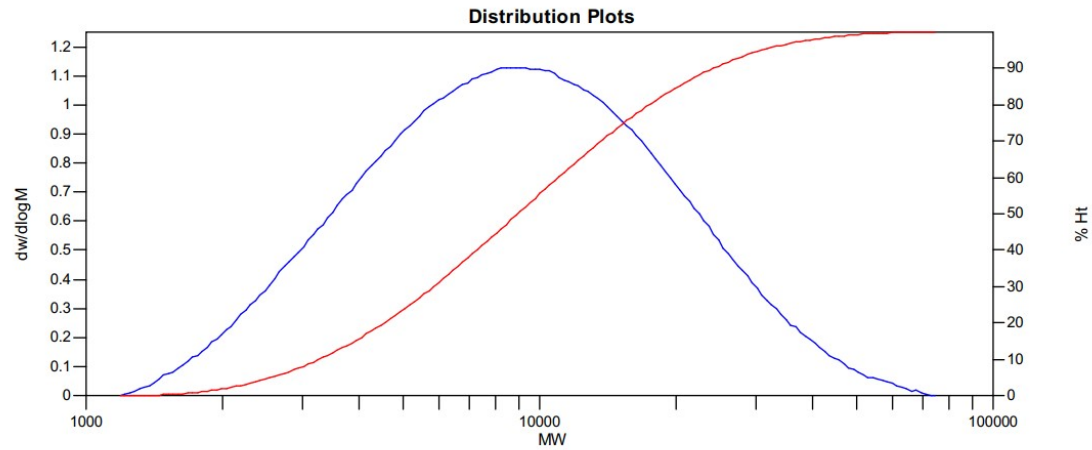
MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	10473	6103	12014	20620	30173	10921	1.96854

Processed Peaks

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1		13.43	14.92	16.93	-15.7381	0	1396.6	100

Figure S112 GPC of the polymer from Table 3, Entry 10.



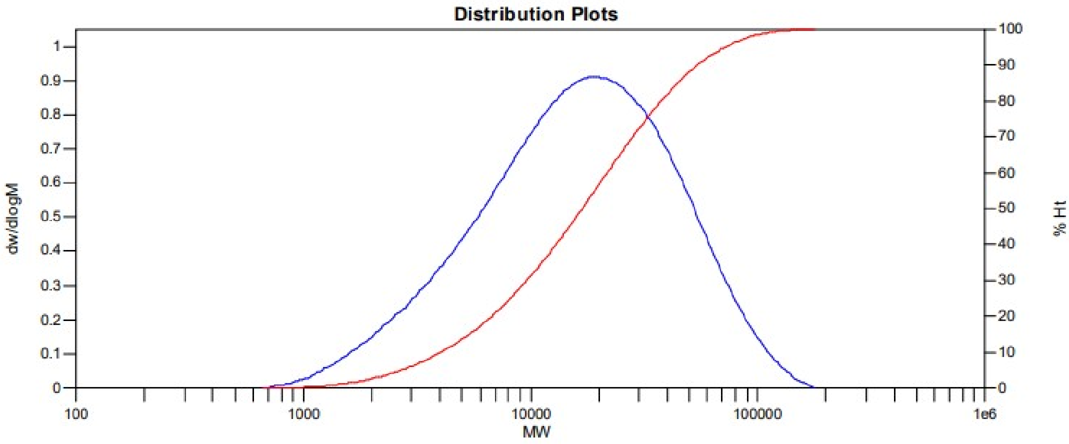
MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	8243	6698	11653	19104	27570	10714	1.73977

Processed Peaks

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1		13.82	15.32	16.63	-6.53222	0	545.336	100

Figure S113 GPC of the polymer from Table 3, Entry 11.



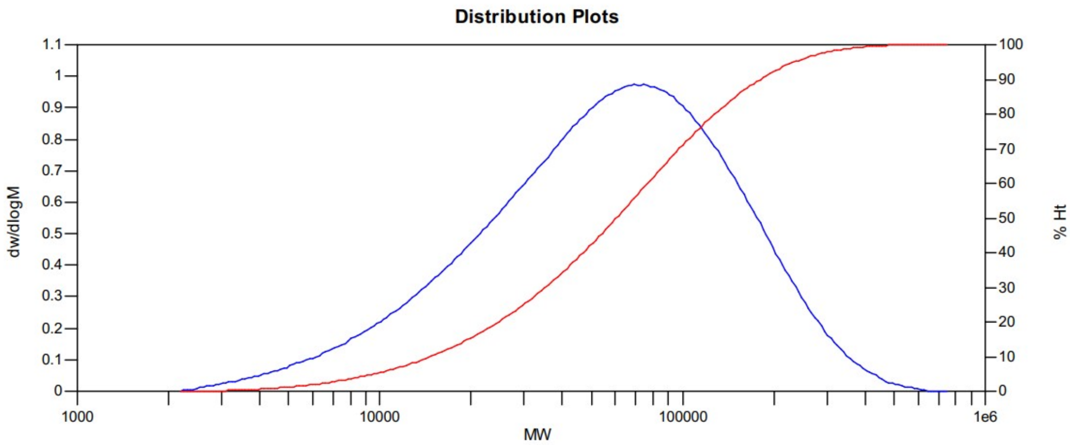
MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	19469	9318	23885	45429	67554	21167	2.56332

Processed Peaks

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1		13.02	14.45	16.77	-12.4454	0	1273.76	100

Figure S114 GPC of the polymer from Table 3, Entry 12.



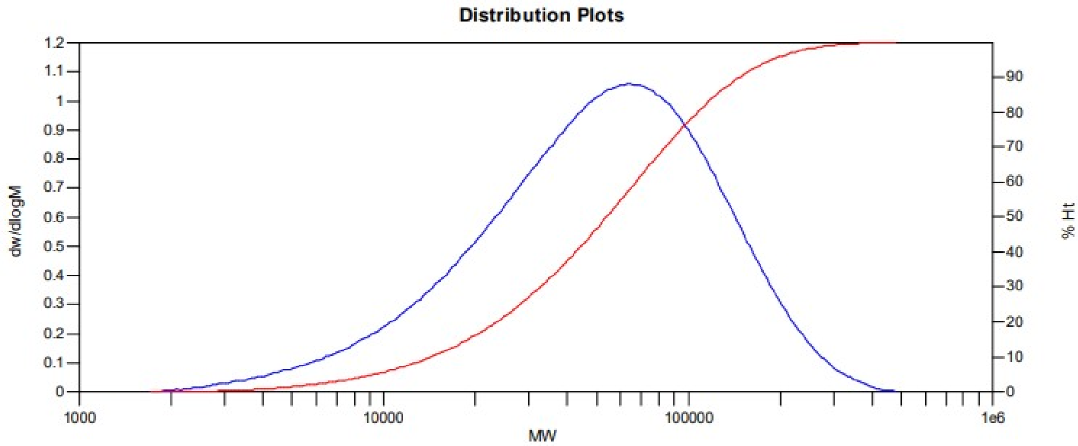
MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	74675	32751	81829	149985	223305	73100	2.49852

Processed Peaks

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1		12.25	13.82	16.22	-12.0205	0	1161.29	100

Figure S115 GPC of the polymer from Table 3, Entry 13.



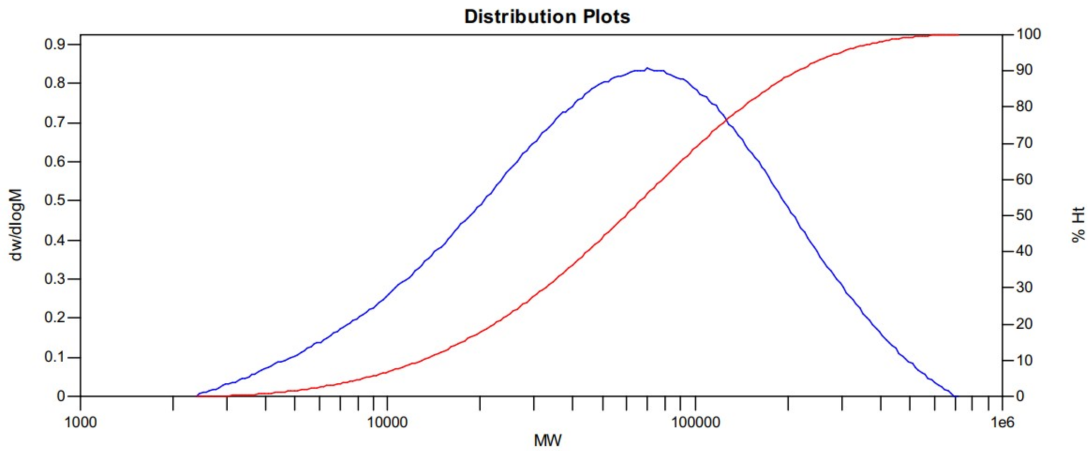
MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	62913	30558	69099	117441	167348	62631	2.26124

Processed Peaks

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1		12.55	13.93	16.38	-13.6434	0	1212.57	100

Figure S116 GPC of the polymer from Table 3, Entry 14.



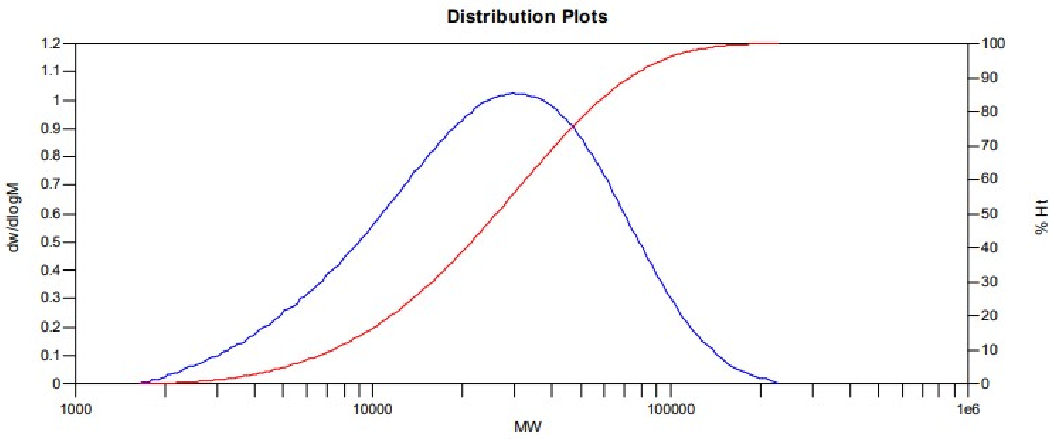
MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	69932	30352	90865	189940	290248	78905	2.99371

Processed Peaks

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1		12.50	14.08	16.38	-7.29707	0	818.363	100

Figure S117 GPC of the polymer from Table 3, Entry 15.



MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	29450	16103	34091	58669	84567	30882	2.11706

Processed Peaks

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1		13.05	14.45	16.42	-8.24736	0	757.584	100

Figure S118 GPC of the polymer from Table 3, Entry 16.

7. X-ray Crystallography

Entry	Ni1
Empirical formula	$C_{30}H_{35}N_2NiOP$
Formula weight	529.28
Temperature/K	100
Crystal system	orthorhombic
Space group	$P2_12_12_1$
a/Å	8.6966(6)
b/Å	15.9160(12)
c/Å	19.1276(19)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	2647.5(4)
Z	4
ρcalcg/cm^3	1.328
μ/mm^{-1}	0.819
F(000)	1120.0
Crystal size/mm^3	0.19 × 0.08 × 0.05
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.97 to 52.76
Index ranges	$-10 \leq h \leq 10$, $-19 \leq k \leq 18$, $-23 \leq l \leq 16$
Reflections collected	11685
Independent reflections	5167 [Rint = 0.0826, Rsigma = 0.1291]
Data/restraints/parameters	5167/0/322
Goodness-of-fit on F^2	1.043

Final R indexes [I>=2σ (I)]	R_1 = 0.0572, wR_2 = 0.0925
Final R indexes [all data]	R_1 = 0.0973, wR_2 = 0.1121
Largest diff. peak/hole / e Å^{-3}	0.43/-0.44

Summary of Data – CCDC. **2257728**

Entry	Ni2
Empirical formula	$C_{32}H_{37}N_2NiO_2P$
Formula weight	571.31
Temperature/K	100
Crystal system	triclinic
Space group	P-1
a/Å	9.1318(5)
b/Å	9.5917(4)
c/Å	16.6693(9)
α/°	96.988(2)
β/°	92.616(2)
γ/°	104.598(2)
Volume/Å^3	1397.99(12)
Z	2
ρcalcg/cm^3	1.357
μ/mm^{-1}	0.783
F(000)	604.0
Crystal size/mm^3	0.15 × 0.08 × 0.05
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.43 to 52.864
Index ranges	-11 ≤ h ≤ 11, -11 ≤ k ≤ 12, -20 ≤ l ≤ 20
Reflections collected	16326
Independent reflections	5710 [Rint = 0.0533, Rsigma = 0.0636]
Data/restraints/parameters	5710/0/347
Goodness-of-fit on F^2	1.045
Final R indexes [I>=2σ (I)]	R1 = 0.0428, wR_2 = 0.0823
Final R indexes [all data]	R1 = 0.0657, wR_2 = 0.0939
Largest diff. peak/hole / e Å^{-3}	0.35/-0.40

Summary of Data – CCDC. **2257729**

Entry	Ni3
Empirical formula	$C_{40}H_{37}N_2NiOP$
Formula weight	651.39
Temperature/K	170.0
Crystal system	triclinic
Space group	P-1
a/Å	10.4219(8)
b/Å	12.3823(10)
c/Å	12.6499(9)
α/°	88.716(2)
β/°	83.981(2)
γ/°	85.981(3)
Volume/Å^3	1619.3(2)
Z	2
ρcalcg/cm^3	1.336

μ/mm^{-1}	0.684
F(000)	684.0
Crystal size/mm^3	0.12 × 0.07 × 0.05
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.962 to 52.826
Index ranges	$-13 \le h \le 13$, $-15 \le k \le 15$, $-14 \le l \le 15$
Reflections collected	18704
Independent reflections	6567 [Rint = 0.0351, Rsigma = 0.0416]
Data/restraints/parameters	6567/0/410
Goodness-of-fit on F^2	0.990
Final R indexes [I>=2σ (I)]	R1 = 0.0353, wR$_2$ = 0.0756
Final R indexes [all data]	R1 = 0.0448, wR$_2$ = 0.0818
Largest diff. peak/hole / e Å^{-3}	0.50/-0.33

Summary of Data – CCDC. **2257730**