Supporting Information:

Ligand-Metal Secondary Interaction in Phosphine-Sulfonate Palladium and Nickel Catalyzed Ethylene (Co)Polymerization

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Content

1. Experimental

General

All manipulations of air and moisture sensitive materials were performed under a dry N_2 atmosphere using a glove-box or standard Schlenk techniques. Ethylene gas was purified by passing through an Agilent oxygen/moisture trap. Solvents (tetrahydrofuran, toluene, hexanes) and deuterated solvents were dried before use. Other chemicals were purchased from J&K Chemical, Energy Chemical and Nine Ding Chemistry Shanghai Co. Ltd. and were used as received. *N*-(2-bromophenyl) carbazole,[1] 1-(2-bromophenyl)-2,5-dimethylpyrrole,[2] Pd(TMEDA)Me_2,[3] PdMeCl(COD)[4] and *trans*-[$(PPh_3)_2$Ni(Cl)Ph][5] were prepared using literature mehods. Nuclear magnetic resonance (^{1}H, ^{13}C and ^{31}P NMR) spectra were recorded on a Bruker 400 MHz spectrometer. ^{1}H NMR and ^{13}C NMR chemical shifts were referenced to residual deuterated solvent resonance or tetramethylsilane signal (0 ppm). ^{31}P NMR chemical shifts were referenced to an external 85% H_3PO_4 (aq.) standard. Elemental analyses were performed using a VarioELIII. Mass spectra were recorded on a Thermo LTQ Orbitrap XL (ESI^+). X-ray Diffraction data were collected at 298(2) K on a Bruker Smart CCD area detector with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). 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 150 °C using o-dichlorobenzene 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: $K = 1.75 \times 10^{-2}$ cm^3/g and R = 0.67 for polystyrene and $K = 5.90 \times 10^{-2}$ cm^3/g and R = 0.69 for polyethylene.[6]

Preparation of L1. At 0 °C, ^{n}BuLi (2.5 M in hexanes, 8 mL, 20 mmol) was added slowly to a solution of anhydrous benzenesulfonic acid (1.58 g, 10 mmol) in THF (25 mL). The suspension was stirred for 1 h before the addition of a solution of $PhPCl_2$ (0.87 mL, 20.0 mmol) in THF (30 mL) at -78 °C. The mixture was stirred for 1 h at -78 °C. *N*-(2-bromophenyl) carbazole (5.06 g, 20 mmol) was dissolved in dry THF (40 mL) under nitrogen and cooled to -78 °C. ^{n}BuLi (2.5 M in hexanes, 8 mL, 20 mmol) was added dropwise. The resulting solution was stirred for 1h at -78 °C before added

into the solution of lithium [chloro(phenyl)phosphino]benzenesulfonate. The mixture was stirred for 1 h at -78 °C, and warmed room temperature and stirred for 24 h. The volatiles were removed, and the residue was taken up in distilled water. The mixture was acidified with concentrated HCl/H_2O solution, and extracted three times with CH_2Cl_2. The extracts were combined, dried over $MgSO_4$, and concentrated under vacuum. The crude product was recrystallized from CH_2Cl_2/ether at room temperature. The resulting white powder was filtered and dried to give the desired ligand **L1**. Yield: 82%. ^{1}H NMR (400MHz, $CDCl_3$): δ 8.38 (t, *J* = 6 Hz, 1H), 8.00 (d, *J* = 8 Hz, 1H), 7.90-7.88 (m, 1H), 7.83 (d, *J* = 4 Hz, 1H), 7.76-7.68 (m, 4H), 7.57-7.55 (m,1H), 7.34 (t, *J* = 8 Hz, 2H), 7.23 (t, *J* = 8 Hz, 1H), 7.13-7.05 (m, 4H), 6.94 (br, 2H), 6.63 (d, *J* = 8Hz, 1H). ^{31}P NMR (162 MHz, $CDCl_3$): δ 3.70. ^{13}C NMR (100 MHz, $CDCl_3$): 140.28 (d, *J* = 5 Hz), 139.97 (s), 136.44 (s), 136.35 (s), 135.93 (d, *J* = 2 Hz), 135.51 (d, *J* = 3 Hz), 134.58 (s), 134.45 (s), 133.61 (d, *J* = 2 Hz), 132.42 (s), 132.30 (s), 130.74 (s), 130.65 (s), 130.27 (s), 130.14 (s), 129.72 (s), 129.58 (s), 129.54 (s), 129.41 (s), 129.34 (s), 127.64 (s), 125.58 (s), 123.46 (s), 123.39 (s), 121.55 (s), 120.77 (s), 120.27 (s), 120.01 (s), 111.37 (d, *J* = 1 Hz), 109.51 (s). ESI-MS (m/z): Anal. Calcd. for $C_{30}H_{22}NO_3PS$: 507.1058, found: 508.1131 ($[M+H]^+$).

***Preparation of L2*.** At 0 °C, ^{n}BuLi (2.5 M, 20 mL, 50 mmol) was slowly added to a solution of benzenesulfonic acid (3.95g, 25 mmol) in THF (100 mL). The suspension was stirred for 1 h before the addition of a solution of $PhPCl_2$ (3.4 mL, 25 mmol) in THF (20 mL) at -78 °C. The mixture was stirred for another 2 h at 25 °C to yield lithium [chloro(phenyl)phosphino]benzenesulfonate. 1-(2-Bromophenyl)-2,5-dimethylpyrrole (6.25g, 25mmol) was dissolved in dry THF (100 mL) under nitrogen. After cooling to -78 °C, ^{n}BuLi (2.5 M in hexane, 4 mL, 10 mmol) was added dropwise. The resulting solution was stirred for 1 h at -78 °C before adding to the lithium [chloro(phenyl)phosphino]benzenesulfonate at -78 °C. The mixture was stirred for another 24h at room temperature. THF was removed under vacuum, and the residue was washed with CH_2Cl_2 and ether. The product was sensitive to air, and was used directly for subsequent reactions. Yield: 69%. ^{1}H NMR (400MHz, DMSO-d^6): δ 7.88 (br, 1H), 7.30-7.26 (m, 1H), 7.17 (t, *J* = 8 Hz, 1H), 7.11-6.98 (m, 8H), 6.95-6.93 (m, 3H), 5.55 (s, 2H), 1.63 (s, 2H), 1.53 (s, 2H). ^{31}P NMR (162 MHz, DMSO-d^6): -18.71. ^{13}C NMR (162 MHz, DMSO-d^6): 152.50 (d, *J* = 26 Hz), 148.13 (s), 141.83 (d, *J* = 25 Hz), 140.47 (d, *J* = 20 Hz), 138.61 (d, *J* = 17 Hz), 134.97 (s), 134.73 (s), 134.39 (s),

129.42 (s), 129.14 (s), 128.93 (s), 128.64 (s), 128.59 (s), 128.11 (s), 128.05 (s), 127.77 (s), 127.56 (s), 125.60 (s), 105.31 (d, *J* = 10 Hz), 13.60 (d, *J* = 7 Hz), 12.49 (d, *J* = 2 Hz).MALDI-TOF-MS (m/z): Anal. Calcd. for $C_{24}H_{21}NO_3PSLi$: 441.1140, found: 441.1260.

Preparation of Pd1. Ligand **L1** (0.5 mmol) was suspended in 1,4-dioxane (4 mL). Pd(TMEDA)Me_2 (132 mg, 1.05 eq) was added at room temperature. Then the solution was stirred at -5 °C for 8 h and the solution became turbid. The resulting white precipitate was filtered, washed with diethyl ether and dried under reduced pressure. The solid was dissolved in DMSO (4 mL) at room temperature. The solvent was removed under reduced pressure at 80 °C. After the removing DMSO, the resulting solid was dispersed in diethyl ether, and isolated by filtration to yield an off-white solid. Yield: 75%. ^{1}H NMR (400MHz, $CDCl_3$): δ 8.10 (br, 1H), 8.01 (d, J = 8 Hz, 1H), 7.95 (br, 1H), 7.70-7.52 (m, 3H), 7.44-7.33 (m, 7H), 7.25-7.13 (m, 4H), 6.88-6.86 (m, 1H), 6.69 (br, 1H), 2.67 (s, 6H), -0.22 (s, 3H). ^{31}P NMR (162 MHz, $CDCl_3$): δ 23.52. ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.13 (d, J = 5 Hz), 142.70 (s), 142.24 (s), 134.59 (d, J = 12 Hz), 134.09 (d, J = 7 Hz), 133.26 (s), 132.10 (d, J = 4 Hz), 131.09 (s), 130.77 (s), 129.84 (s), 129.18 (s), 128.61 (s), 128.54 (s), 128.44 (s), 128.41 (s), 128.37 (s), 126.49 (s), 125.96 (s), 125.86 (s), 125.44 (s), 124.36 (d, J = 2 Hz), 124.02 (s), 120.30 (s), 120.23 (s), 120.15 (s), 120.09 (s), 120.01 (s), 112.65 (d, J = 10 Hz), 111.08 (s), 41.11 (s), 0.13 (s).Anal. Calcd. for $C_{33}H_{30}NO_4PPdS_2$: C, 56.13; H, 4.28; N, 1.98 Found: C, 56.02; H, 4.33; N, 2.03.

Preparation of Ni1. A suspension of ligand **L1** (0.5 mmol) and Na_2CO_3 (159mg, 1.5 mmol) in 15 ml CH_2Cl_2 was stirred for 8 h at room temperature. Solid *trans*-[$(PPh_3)_2$Ni(Cl)Ph] (347mg, 0.5 mmol) was added in small portions. The reaction was stirred for 8 h at room temperature. The resulting orange mixture was filtered over Celite and the volatiles were removed under vacuum. Toluene (3 mL) was added to the orange residue to afford a slurry, then hexanes (20 mL) were added and the mixture was stirred for 2 h. The precipitate was recovered by filtration, washed with hexanes (3 x 10 ml) and dried under vacuum to yield an off-white solid. Yield: 62%. ^{1}H NMR (400MHz, $CDCl_3$): δ 8.19 (dd, J = 12 Hz, J = 8 Hz, 1H), 7.84 (t, J = 8 Hz, 2H), 7.70-7.52 (m, 5H), 7.48-7.45 (m, 2H), 7.39-7.28 (m, 12H), 7.19-7.09 (m, 6H), 7.07-6.94 (m, 5H), 6.69-6.63 (m, 2H), 6.56 (t, J = 8 Hz, 2H), 6.44 (d, J = 8 Hz, 1H), 6.37 (t, J = 8 Hz,

1H), 6.24 (t, J = 8 Hz, 1H), 6.09 (t, J = 8 Hz, 1H). ^{31}P NMR (162 MHz, $CDCl_3$): δ 13.90 (d, J = 282 Hz), -0.46 (d, J = 282 Hz). ^{13}C NMR (100 MHz, d^6-DMSO) δ 141.51 (s), 141.36 (d, J = 1Hz), 140.13 (s), 134.55 (s), 134.16 (s), 133.94 (s), 133.18 (s), 133.03 (s), 131.99 (s), 131.43 (d, J = 9 Hz), 129.43 (s), 129.26 (s), 128.87 (s), 128.83 (s), 128.76 (s), 128.64 (s), 128.61 (s), 128.58 (s), 128.50 (s), 128.34 (s), 128.29 (s), 128.23 (s), 128.14 (s), 128.02 (d, J = 2Hz), 127.95 (s), 127.65 (s), 127.54 (d, J = 1Hz), 127.36 (s), 126.62 (s), 125.57 (s), 125.25 (s), 124.87 (s), 122.92 (s), 122.46 (s), 119.56 (s), 119.35 (s), 119.21 (s), 119.02 (s), 113.60 (d, J = 5Hz), 110.20 (s). Anal. Calcd. for $C_{54}H_{41}NO_3P_2NiS$: C, 71.70; H, 4.57; N, 1.55. Found: C, 71.62; H, 4.68; N, 1.52.

Preparation of Pd2. At room temperature, a 25 mL Schlenk tube was charged with 0.5 mmol PdMeCl(COD), 0.5 mmol **L2** and 20 mL CH_2Cl_2. The solution was stirred for 10 min, and 156 mg (2.0 mmol, 2 equiv) of DMSO was added. The solution was further stirred for 10 min and was filtered through a syringe filter. The solution was evaporated, and the resulting solid was washed with ether. The solid was dissolved in CH_2Cl_2 (10 mL), and 3 equiv. of $AgBF_4$ was added. The solution was stirred for 10 min and was filtered through a syringe filter. The solvent was removed. The resulting solid was washed with ether and hexanes, and dried under vacuum to give **Pd2**. Yield: 52%. ^{1}H NMR (400MHz, $CDCl_3$): δ 8.14 (br, 1H), 7.56-7.53 (m, 1H), 7.45-7.36 (m, 7H), 7.17 (t, J = 8 Hz, 1H), 7.08 (t, J = 8 Hz, 1H), 6.52-6.47 (m, 1H), 6.08 (br, 1H), 5.66 (br, 1H), 2.68 (br, 6H), 2.38 (br, 3H), 1.36 (br, 3H), 0.51 (br, 3H). ^{31}P NMR (162 MHz, $CDCl_3$): δ 21.21. ^{13}C NMR (100 MHz, d^6-DMSO): 148.96 (d, J = 14 Hz), 142.52(d, J = 9 Hz), 135.94 (d, J = 7 Hz), 134.62 (s), 134.50 (s), 134.01 (d, J = 2 Hz), 131.89 (d, J = 6 Hz), 131.81 (s), 130.86 (d, J = 1 Hz), 130.40 (s), 129.62 (s), 129.52 (s), 129.34 (s), 129.09 (s), 128.59 (s), 128.33 (s), 128.22 (s), 128.00 (d, J = 8 Hz), 127.23 (d, J = 8 Hz), 107.27 (s), 106.63 (s), 40.43 (s), 14.31 (s), 13.06 (s). Anal. Calcd. for $C_{27}H_{30}NO_4PPdS_2$: C, 51.15; H, 4.77; N, 2.21 Found: C, 51.09; H, 4.85; N, 2.17.

Procedure for ethylene homopolymerization. Polymerizations were performed in a Biotage Endeavor housed in a nitrogen-filled glovebox with eight parallel reactors and an overhead stirrer. In a typical experiment, the reaction vessels were charged with desired amount of catalyst in DCM (0.2 mL) and toluene (3

mL). The vessel was heated to 80 °C and allowed to equilibrate for 5 min. With rapid stirring, the vessel was pressurized and maintained at 8.0 atm of ethylene. After 1h, the pressure vessel was vented and the polymer was precipitated in methanol and dried at 50 °C for 24 h under vacuum. Polymer-branching (B) density was determined by ^{1}H NMR spectroscopy. B = 1000 × (2/3) ×(I_{CH3})/(I_{CH2+CH}+I_{CH3}). CH_3 (m, 0.77–0.95 ppm); CH_2 and CH (m, ~1.0–1.45 ppm).. For the low molecular weight polymers and oligomers, chain end groups were excluded. The branches were calculated according to the following equation.[7,8]

$$\frac{Branches}{1000C} = \frac{2 \times 1000 \times I_{CH}}{\frac{2 \times I_{CH_3}}{3} + I_{CH_2+CH} + I_{CH} + I_{CH_2,\,allyl} + 2 \times (I_{CH_2,\,vinyl} + I_{CH_2,vinylene})}$$

$$I_{CH} = \frac{I_{CH_3}}{3} - \frac{I_{CH_2,\,vinyl}}{2} - I_{CH_2,vinylene}$$

Procedure for copolymerization of ethylene with polar comonomers. In a typical experiment, the reaction vessels were charged with desired amount of catalyst and comonomer (for MA and AA, 20 mg of BHT, i.e. butylated hydroxytoluene, was added) in DCM (0.2 mL) and toluene (3 mL). The vessels were heated to 80 °C and allowed to equilibrate for 5 min. With rapid stirring, the vessel was pressurized and maintained at 8.0 atm of ethylene. After 1 h, the pressure vessel was vented and the polymer was precipitated in ethanol and dried at 50 °C for 24 h under vacuum. The incorporation ratio was calculated by ^{1}H NMR analysis.

2. X-ray Crystallographic Studies

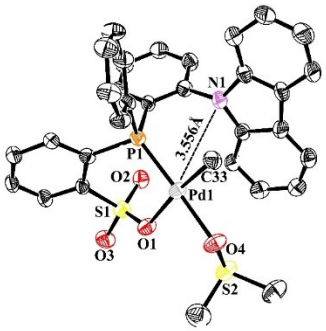


Table S1 Crystal data and structure refinement for **Pd1**.

Entry	**Pd1**
Formula	C_{33} H_{30} N O_4 P Pd S_2
Formula weight	706.07
Temperature[K]	298(2)
λ(Mo-Kα)[Å]	0.71073
Crystal system	Triclinic
Space group	P -1
a[Å]	10.1100(9)
b[Å]	12.7449(11)
c[Å]	14.2331(12)
α[°]	85.456(2)
β[°]	75.6790(10)
γ[°]	87.617(3)
Volume[$Å^3$]	1770.9(3)
Z	2
D(calc)[$g \cdot cm^{-3}$]	1.324
μ[mm^{-1}]	0.721
F(000)	720
θ min-max (º)	2.238 -27.095
h	-12→12
k	-15→10
l	-16→16
Reflections collected	8768
Reflections unique	6129
R(int)	0.0864
Data / restraints / parameters	6129 /0 / 382
Final R indices [I>2σ(I)]	R_1 = 0.0864 wR_2 = 0.1419
R indices (all data)	R_1 =0.1870 wR_2 = 0.1555
GOF on F^2	1.062

3. NMR spectra of ligands and catalysts.

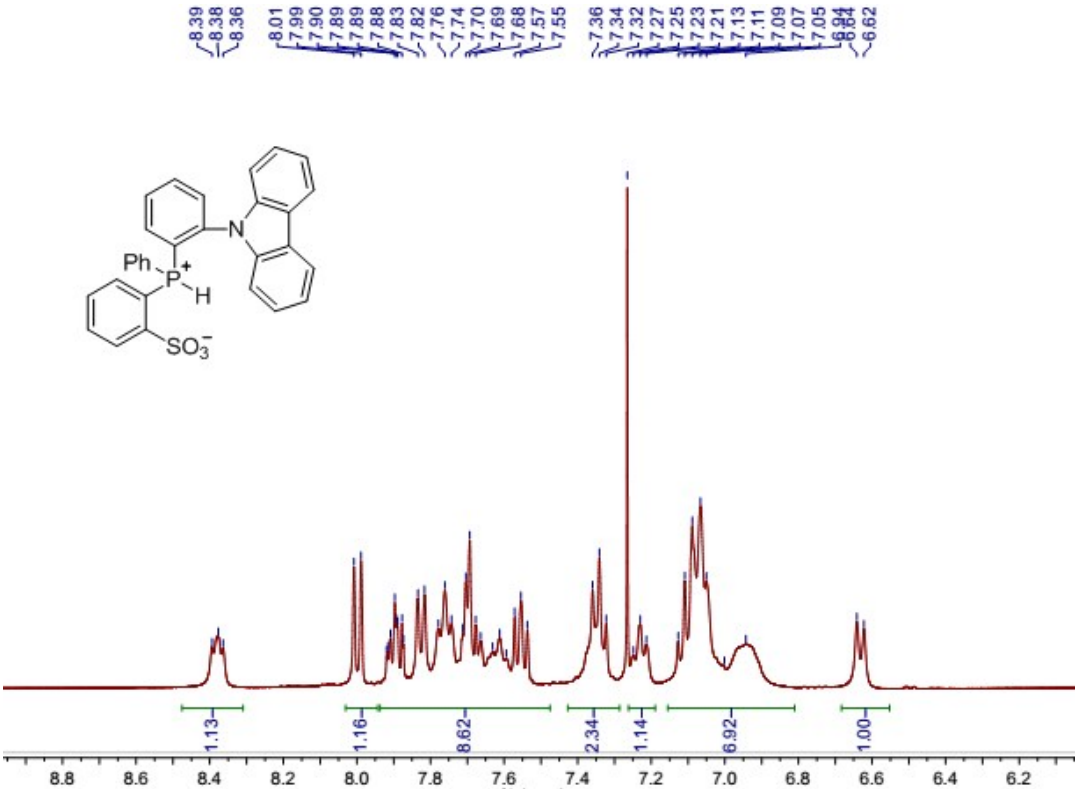


Figure S1 ^{1}H NMR of **L1**.

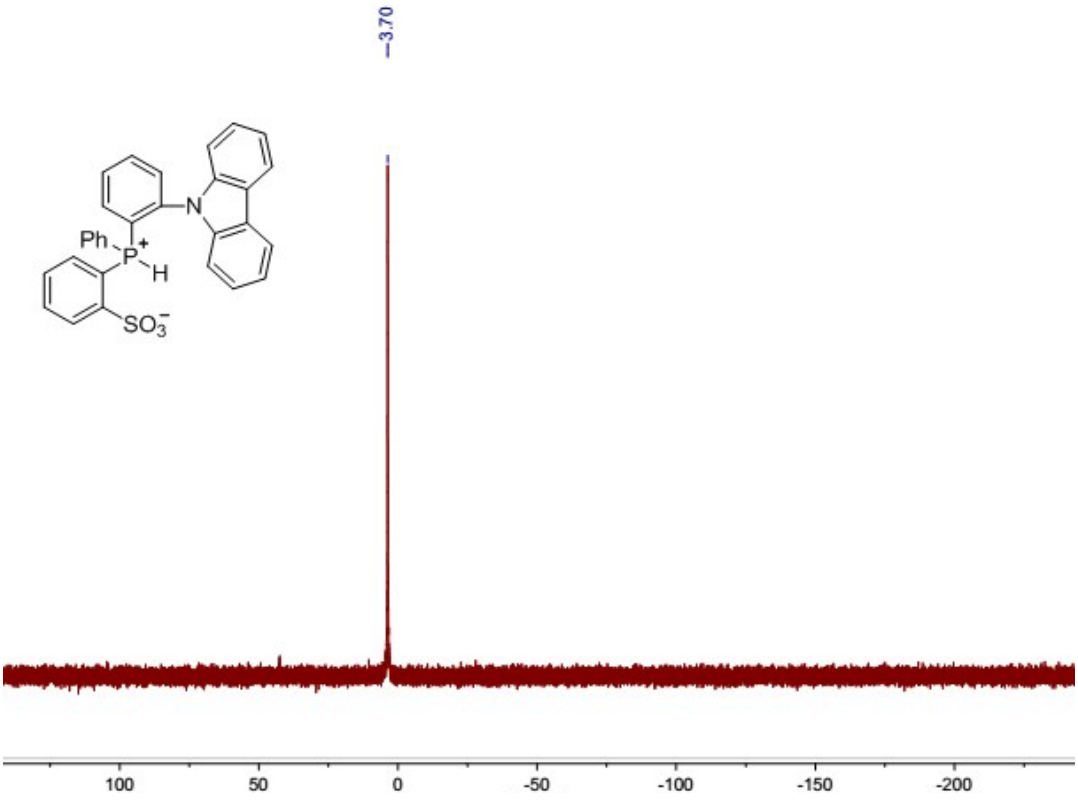


Figure S2 ^{31}P NMR of **L1**.

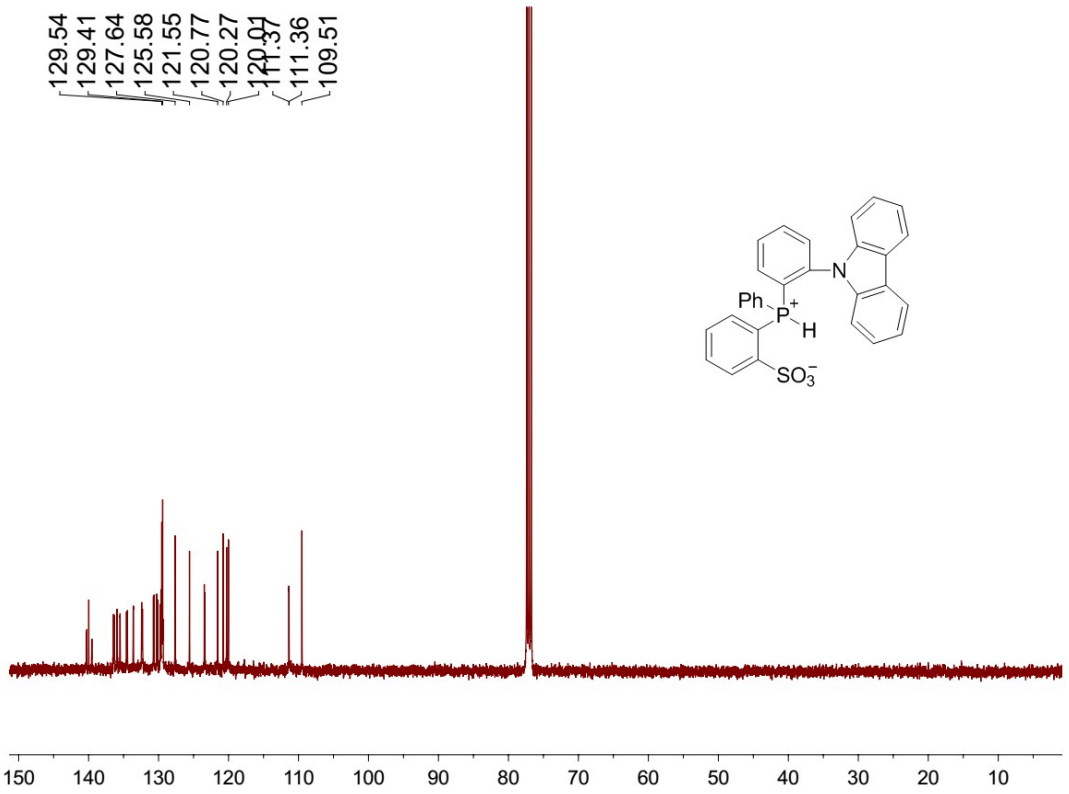


Figure S3 ^{13}C NMR of **L1**.

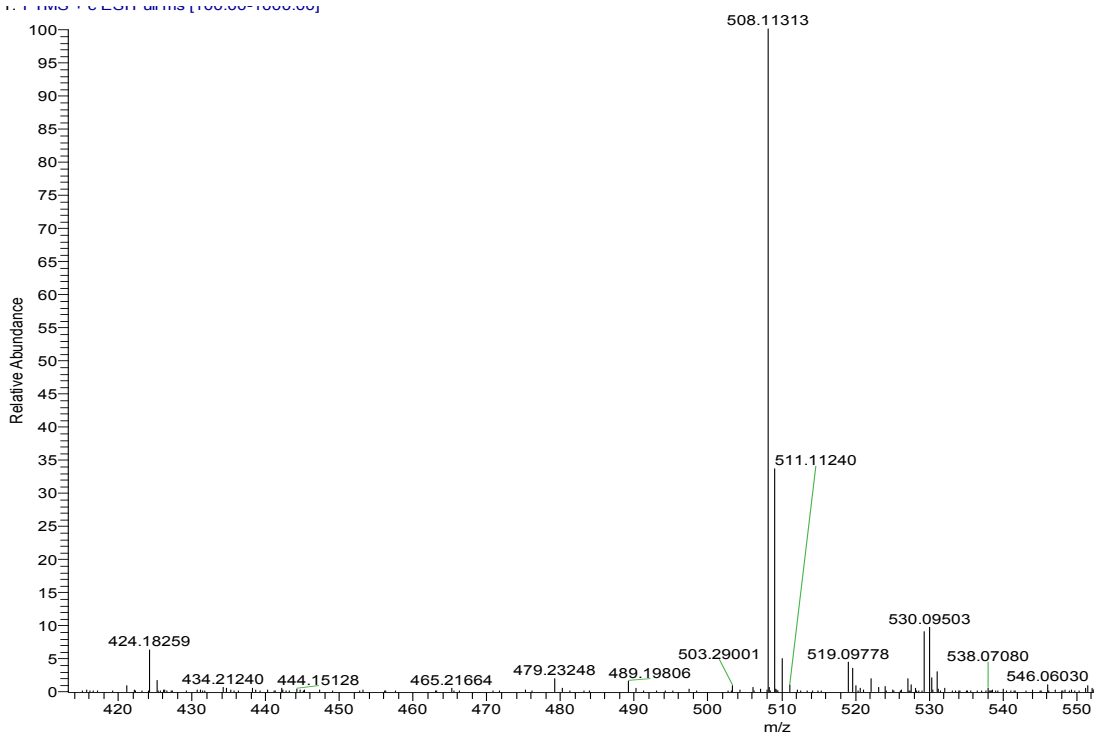


Figure S4 ESI-MS of **L1**.

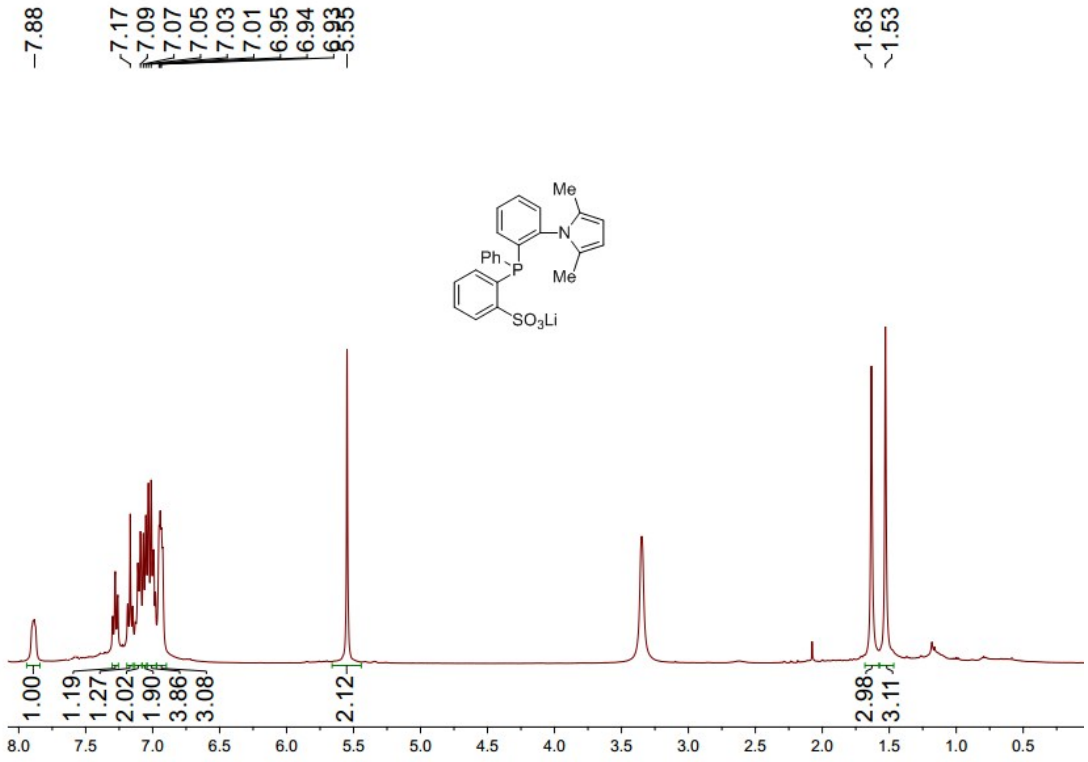


Figure S5 ^{1}H NMR of **L2-Li**.

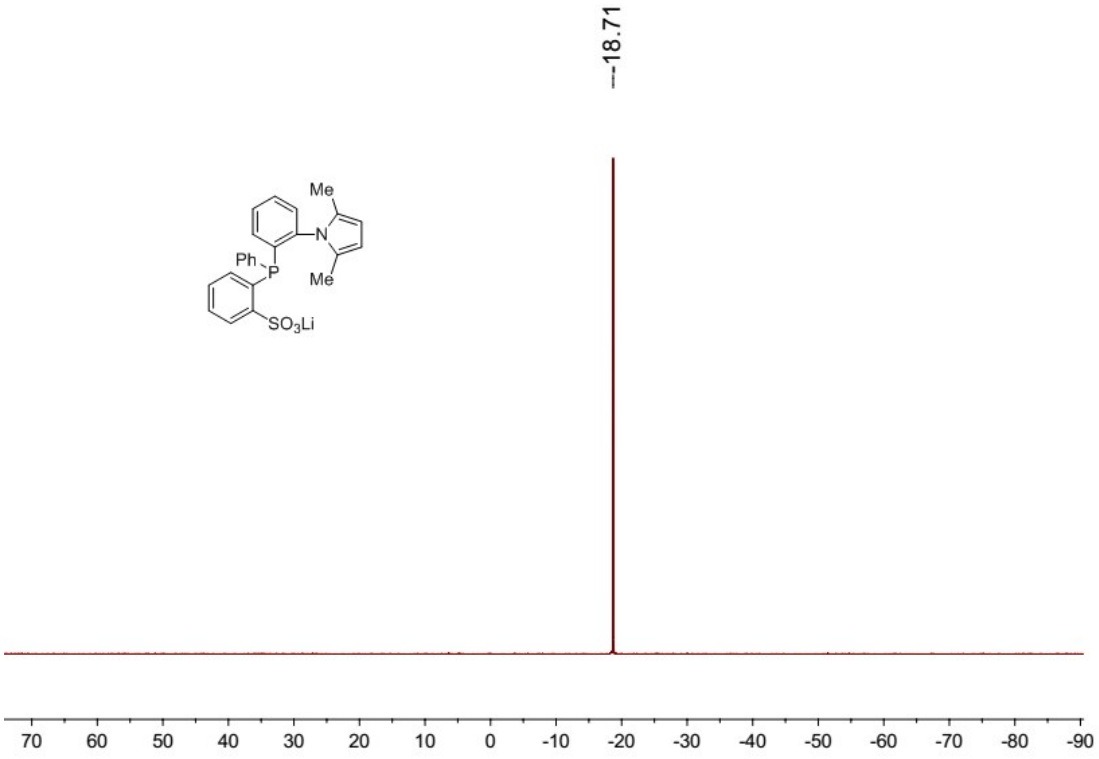


Figure S6 ^{31}P NMR of **L2-Li**.

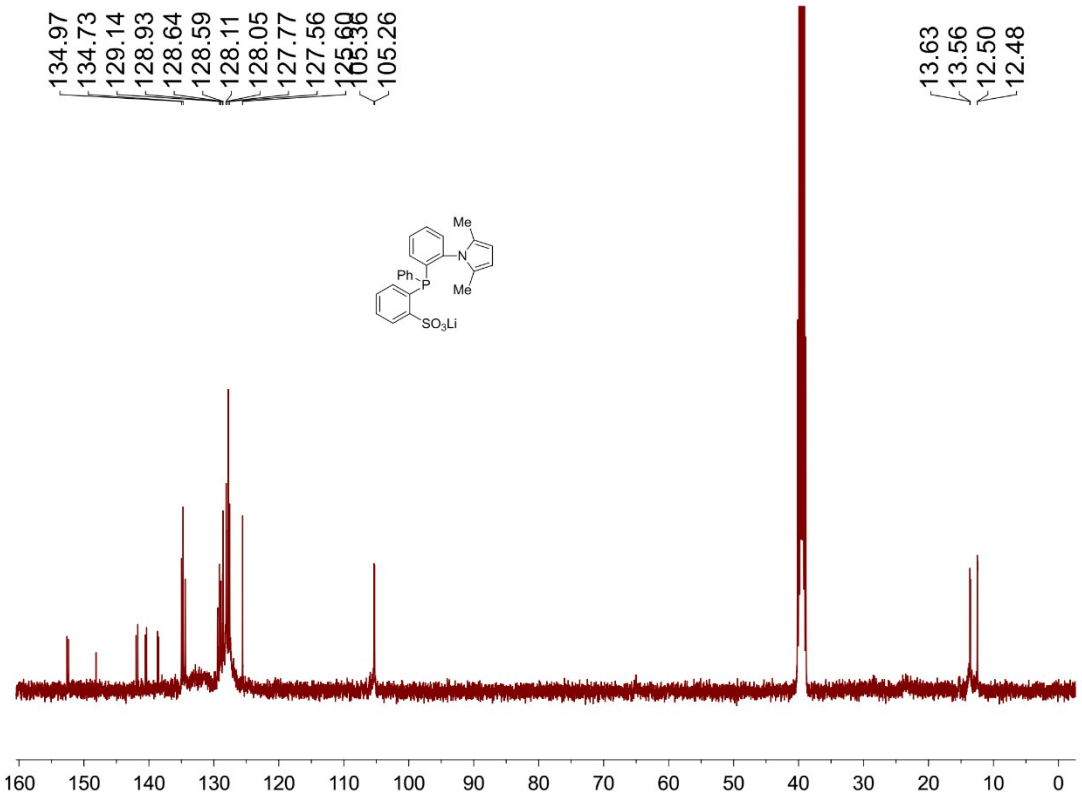


Figure S7 ^{13}C NMR of **L2-Li**.

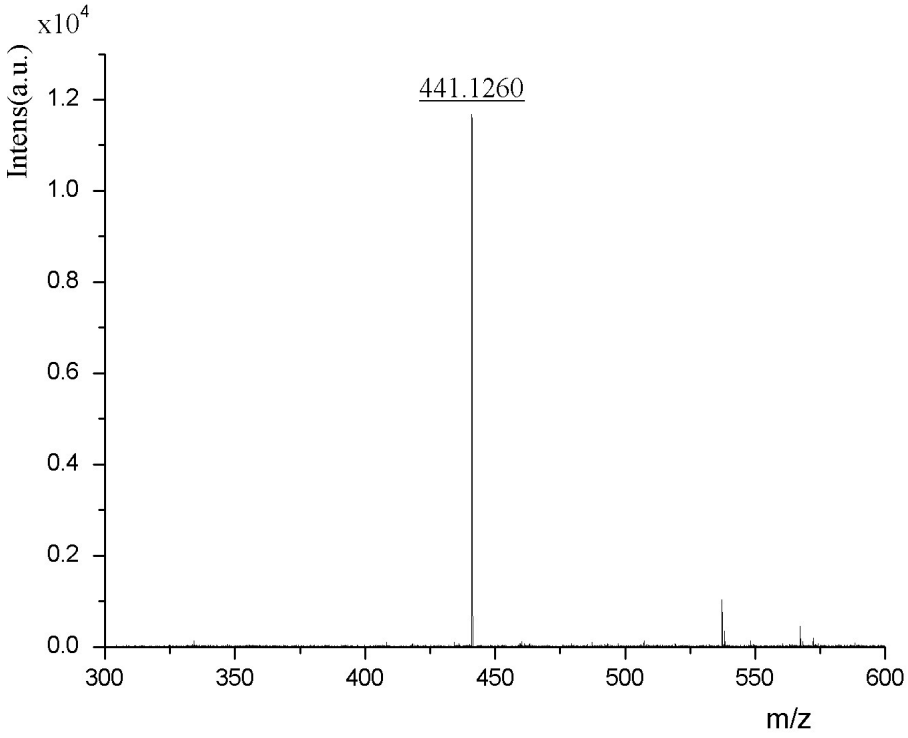


Figure S8 MALDI-TOF-MS of **L2-Li**..

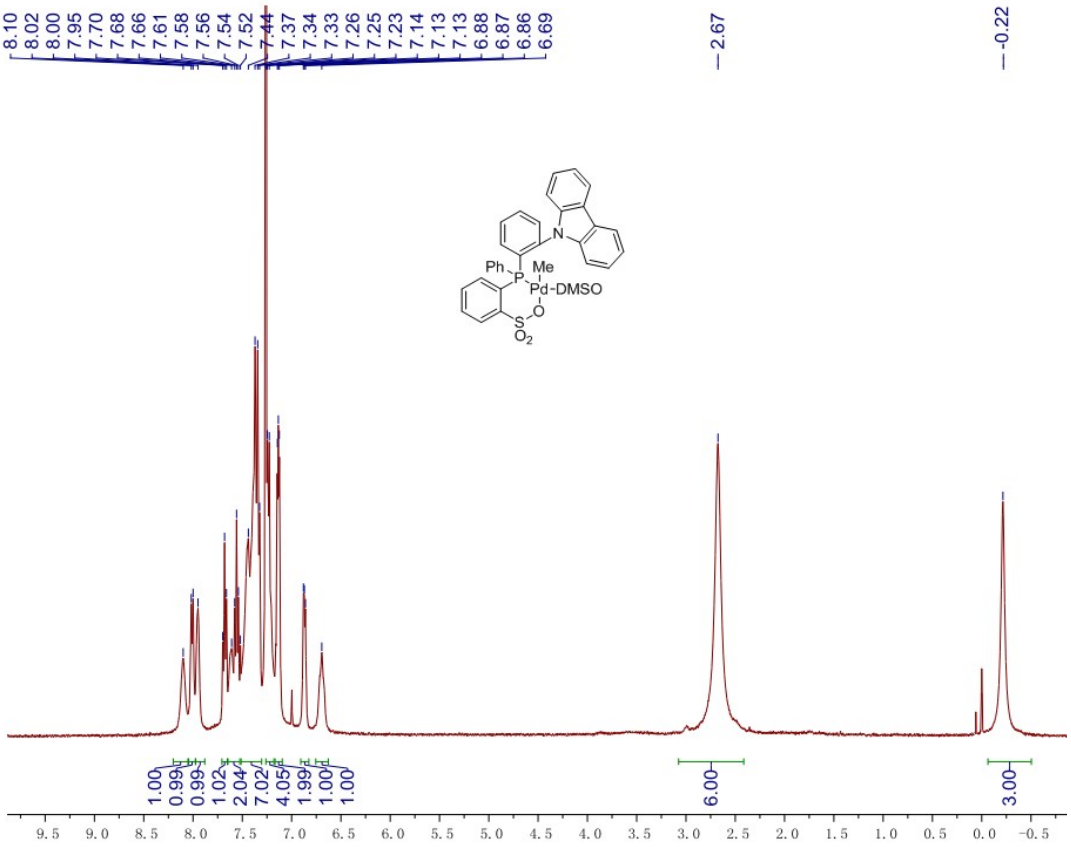


Figure S9 ^{1}H NMR of **Pd1**.

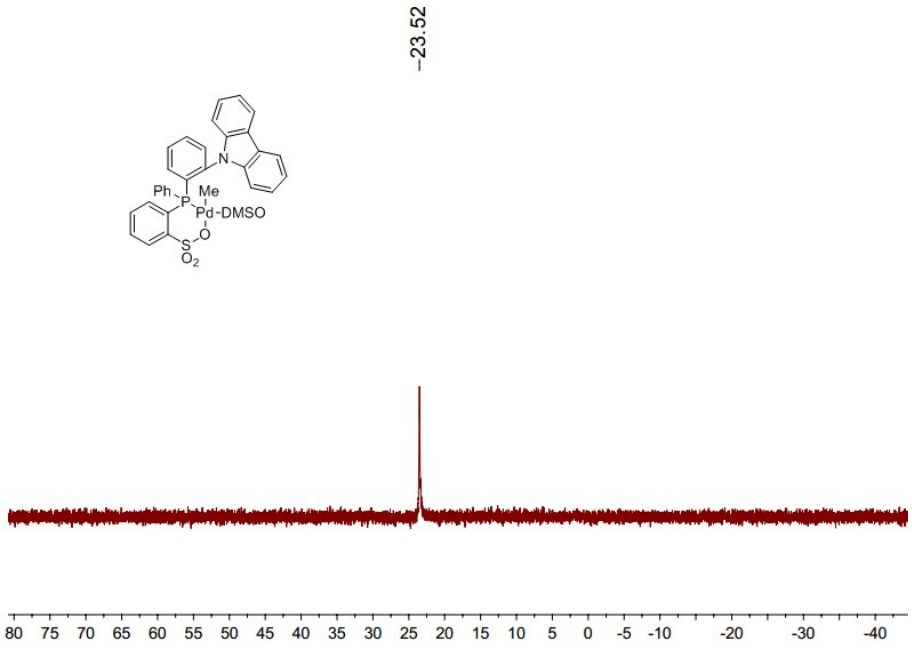


Figure S10 ^{31}P NMR of **Pd1**.

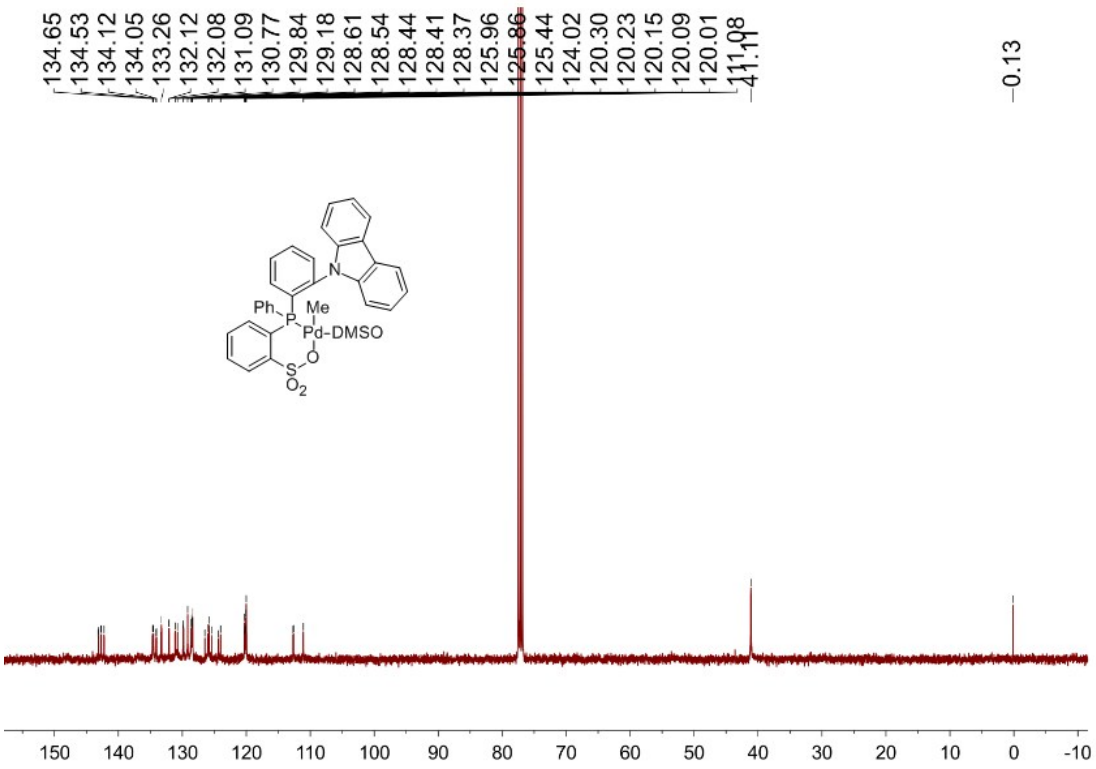


Figure S11 ^{13}C NMR of **Pd1**.

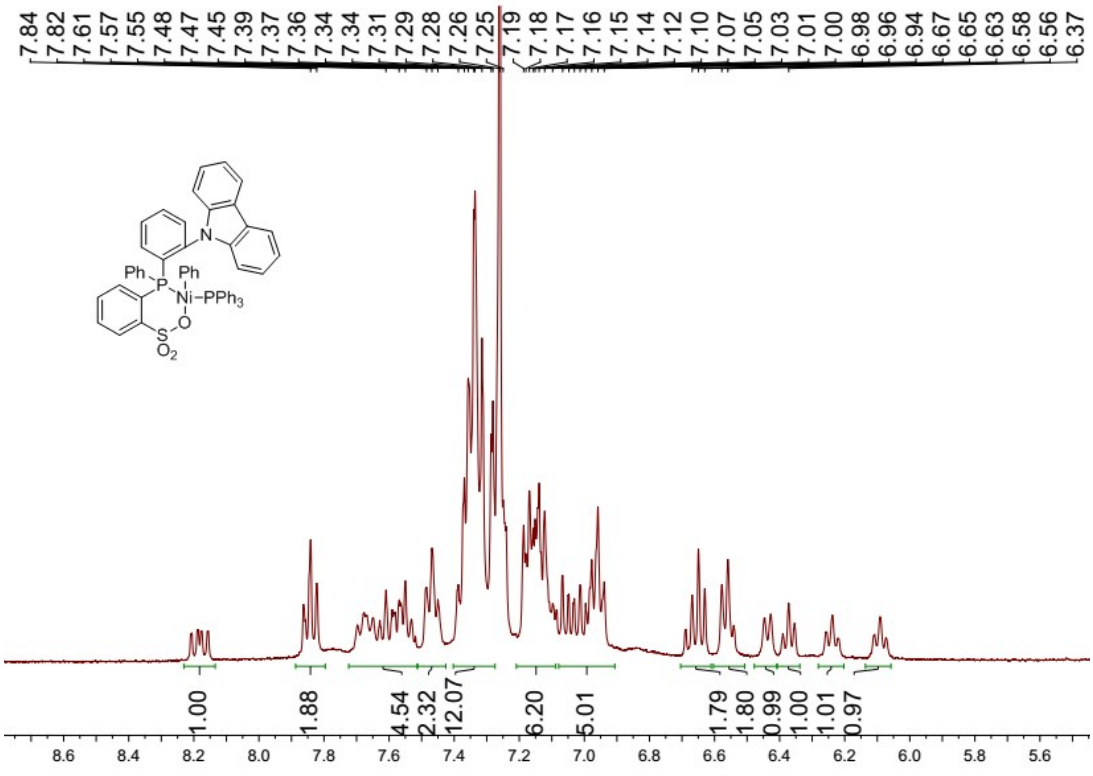


Figure S12 ^{1}H NMR of **Ni1**.

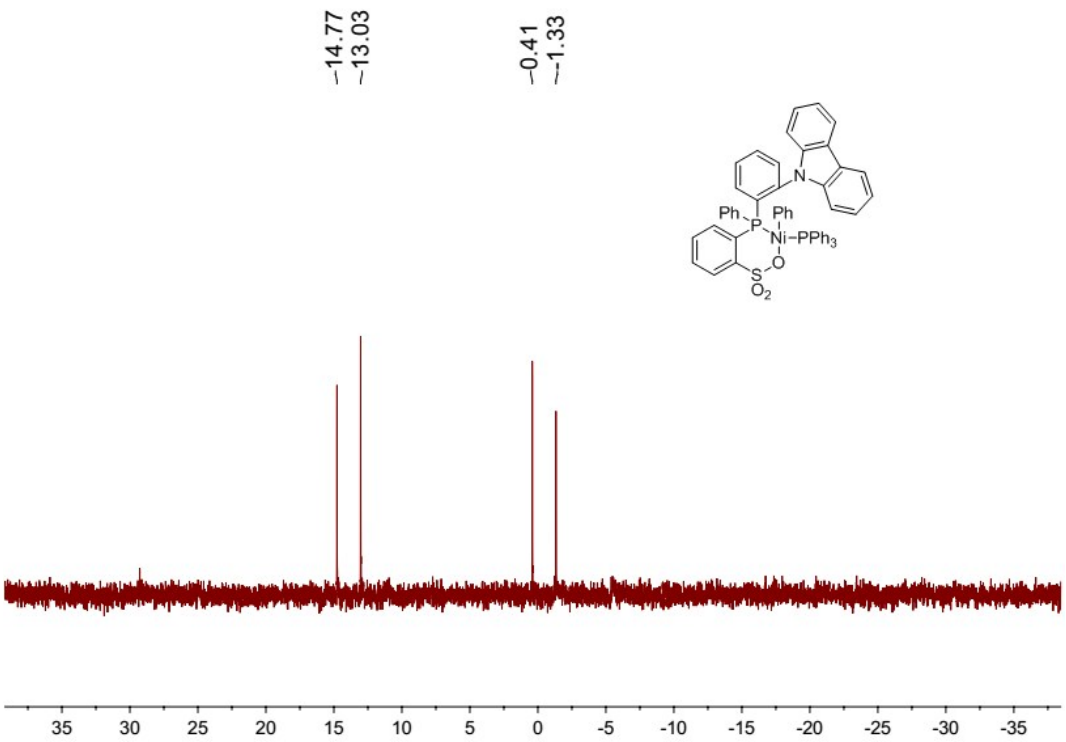


Figure S13 ^{31}P NMR of **Ni1**.

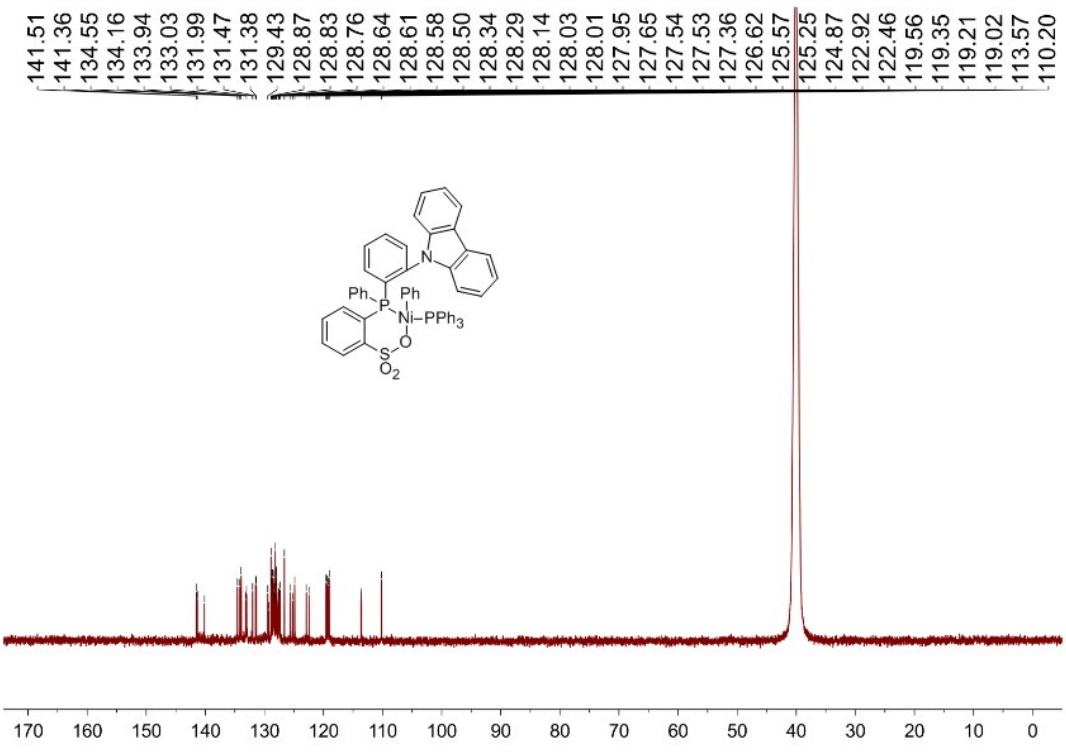


Figure S14 ^{13}C NMR of **Ni1**.

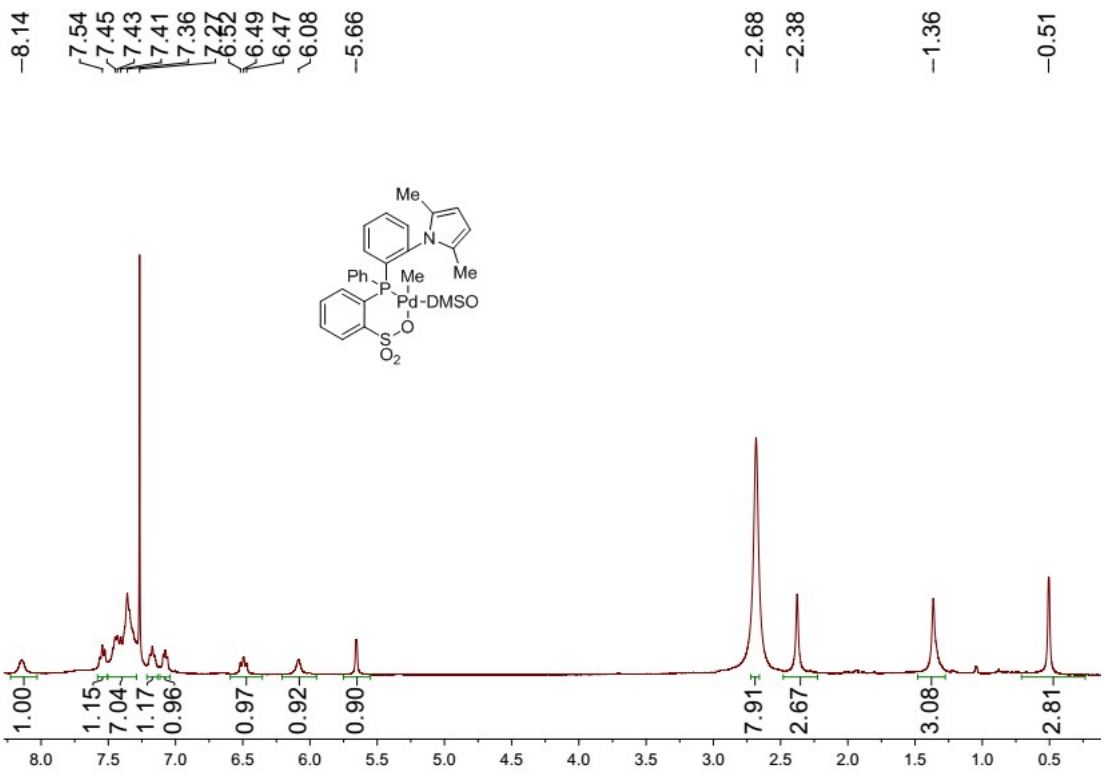


Figure S15 ^{1}H NMR of **Pd2**.

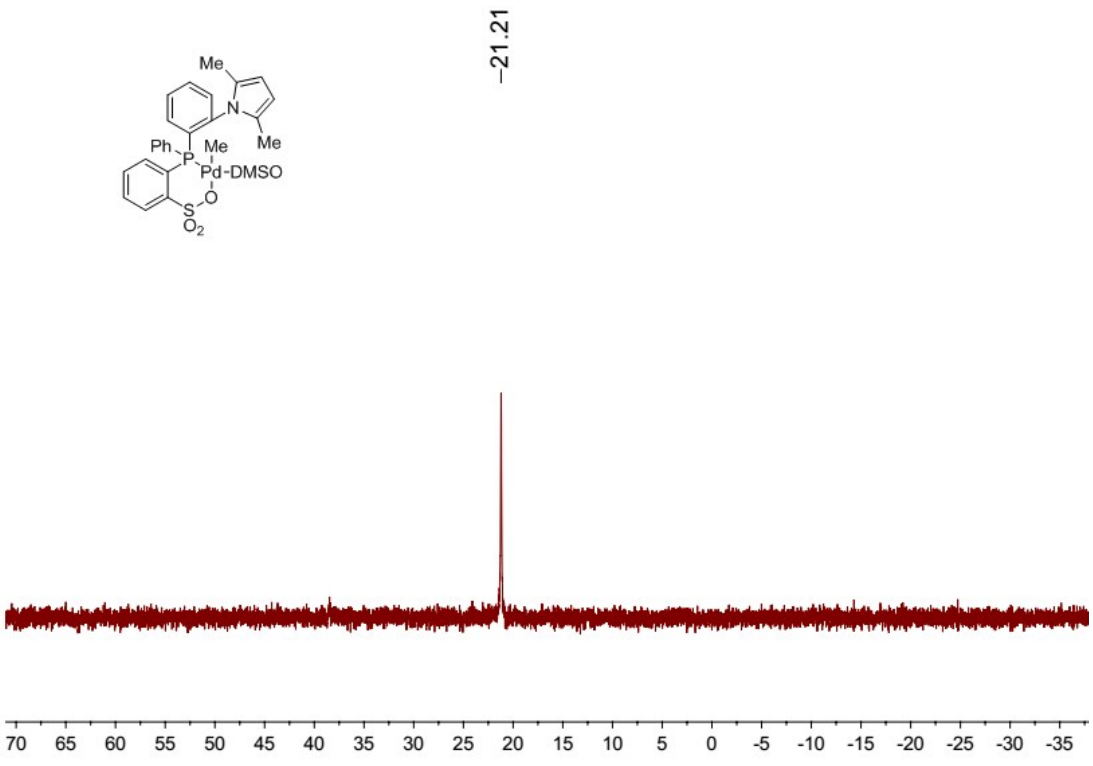


Figure S16 ^{31}P NMR of **Pd2**.

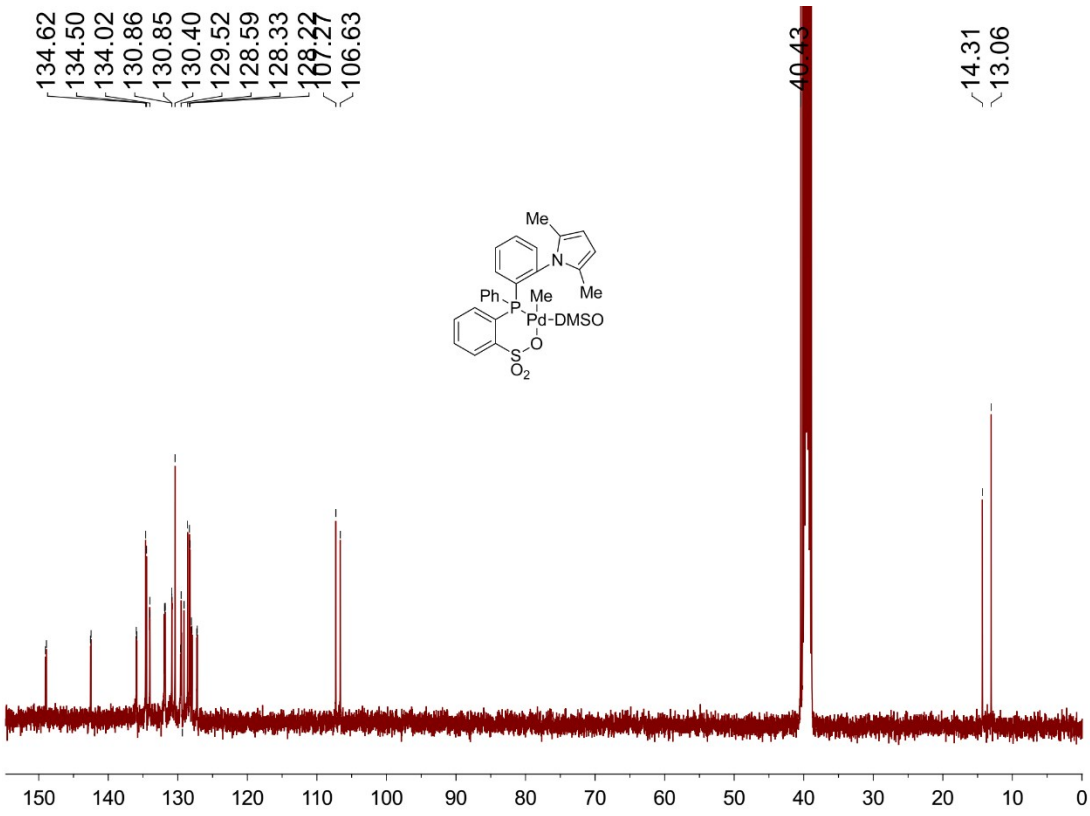


Figure S17 ^{13}C NMR of **Pd2**.

4. ^{1}H NMR Spectra of Polymers

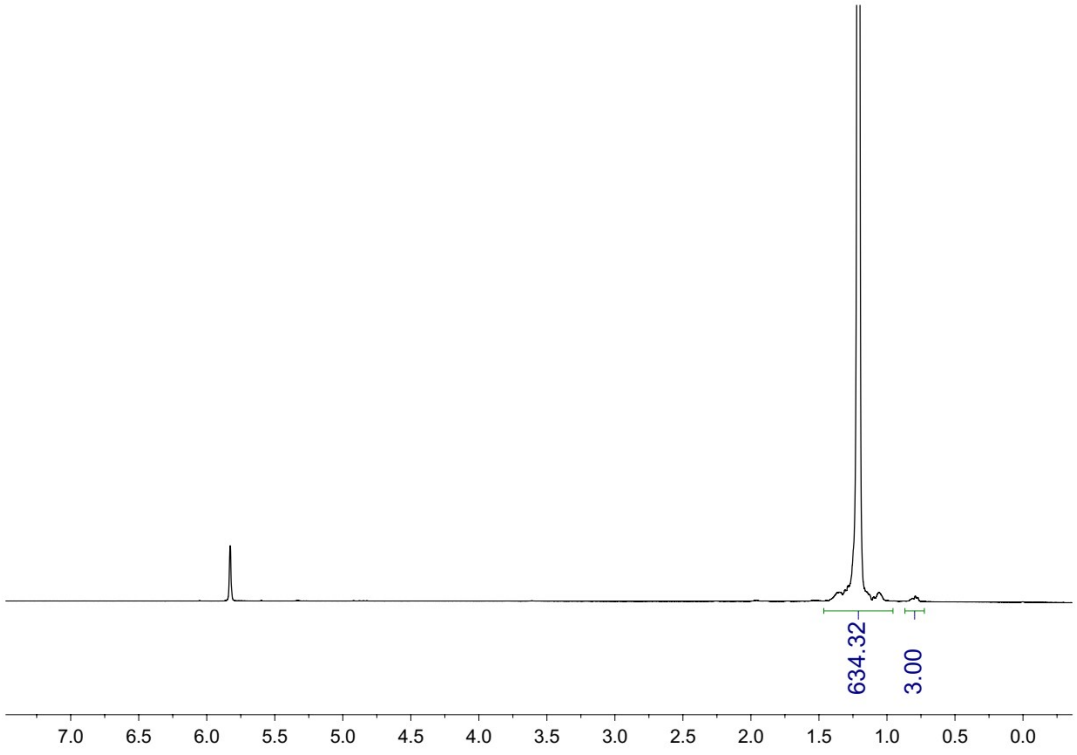


Figure S18 ^{1}H NMR of the polymer (table 1, entry 1).

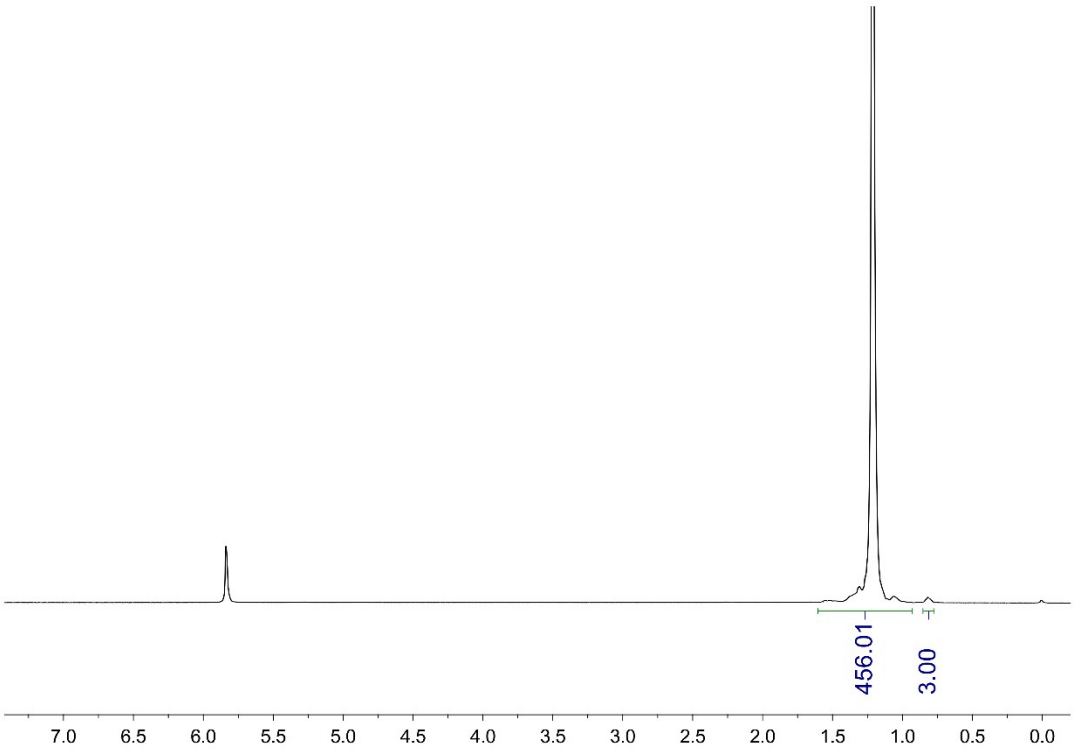


Figure S19 ^{1}H NMR of the polymer (table 1, entry 2).

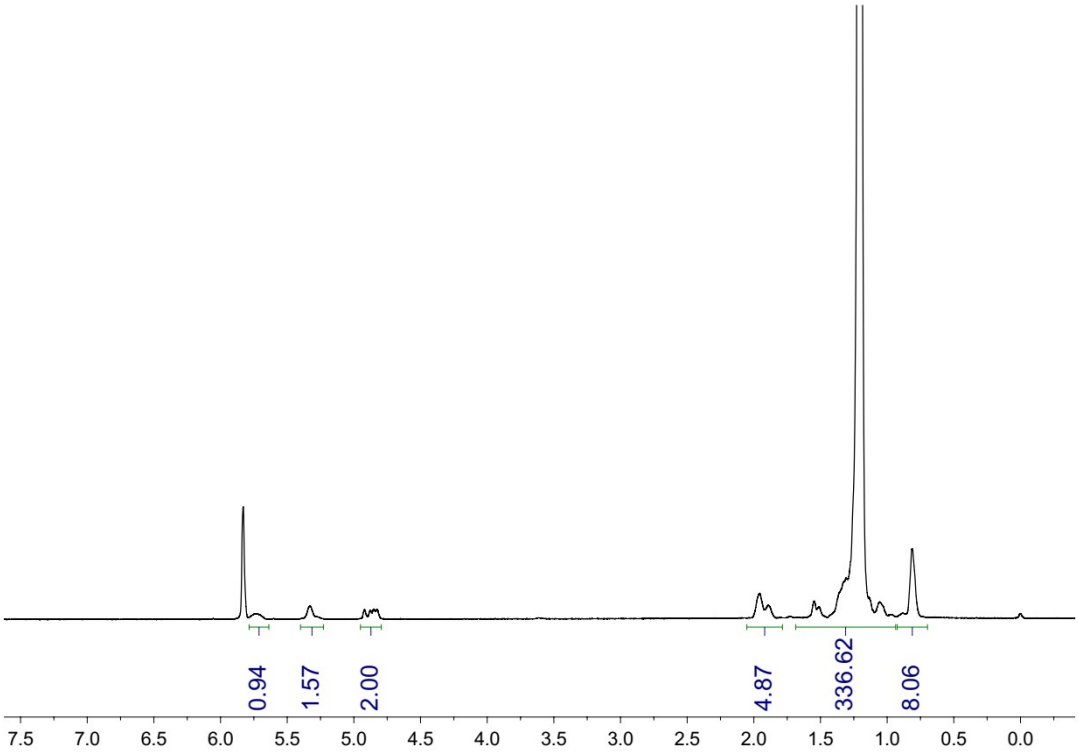


Figure S20 ^{1}H NMR of the polymer (table 1, entry 3).

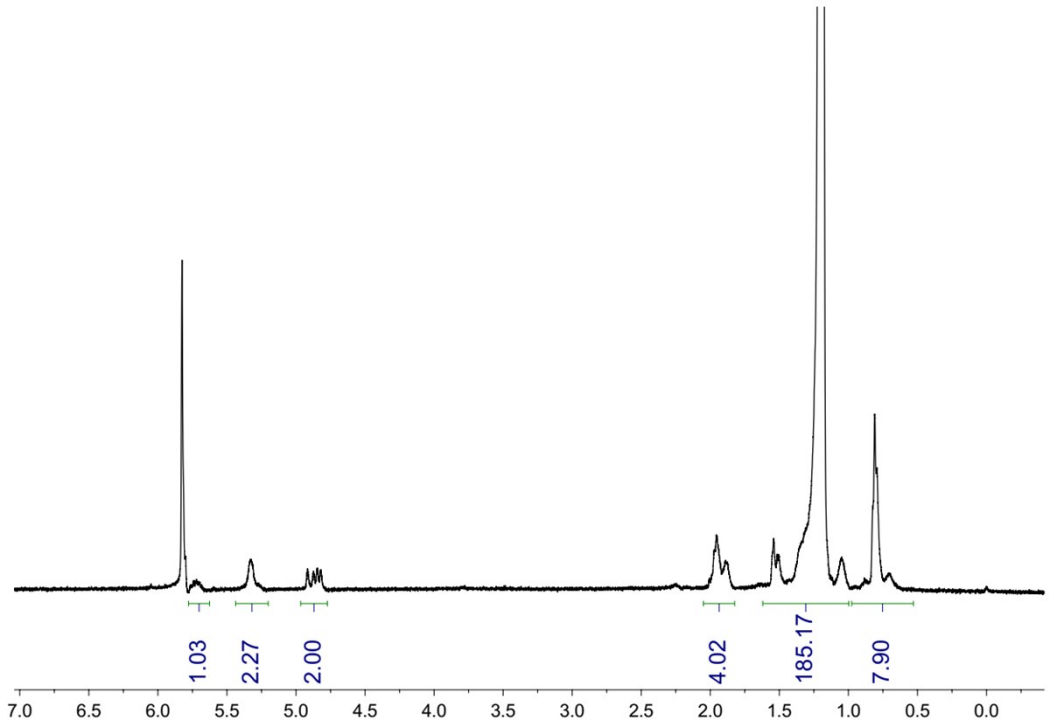


Figure S21 ^{1}H NMR of the polymer (table 1, entry 4).

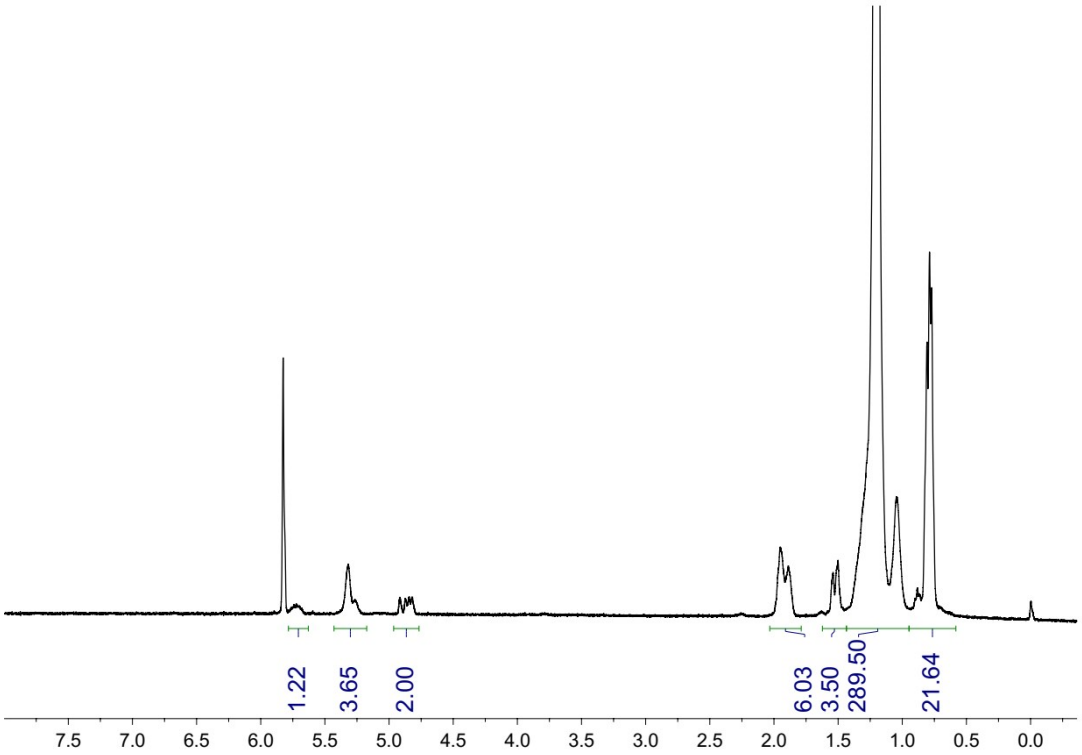


Figure S22. [1]H NMR of the polymer (table 1, entry 7).

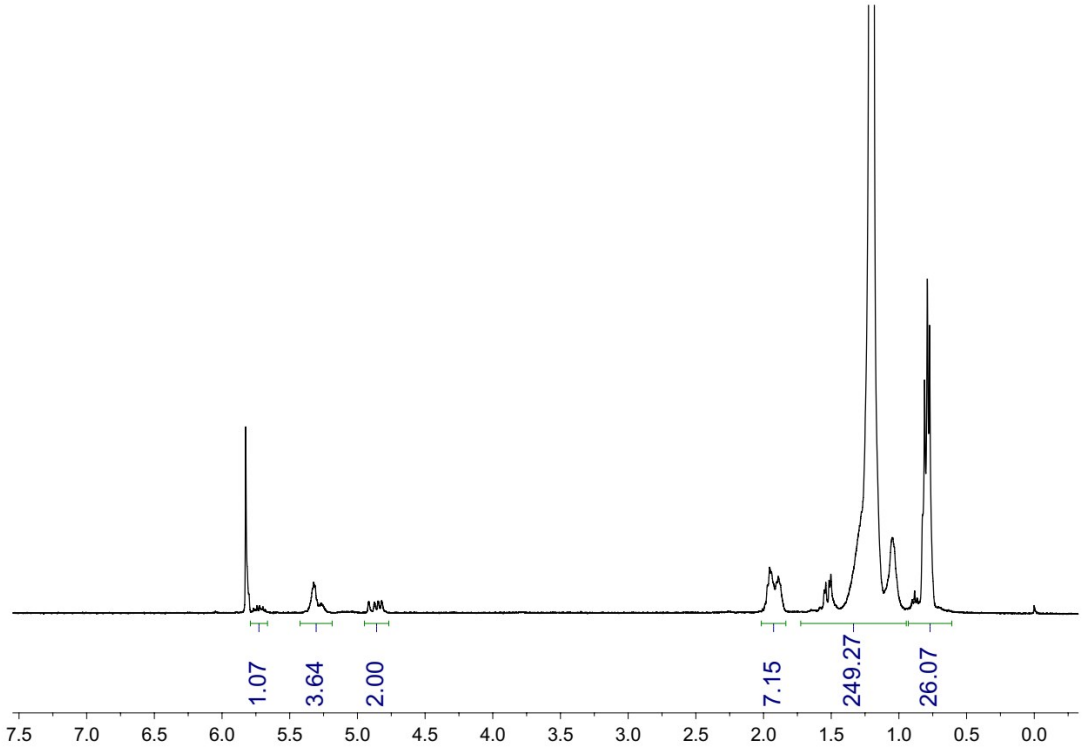


Figure S23 [1]H NMR of the polymer (table 1, entry 8).

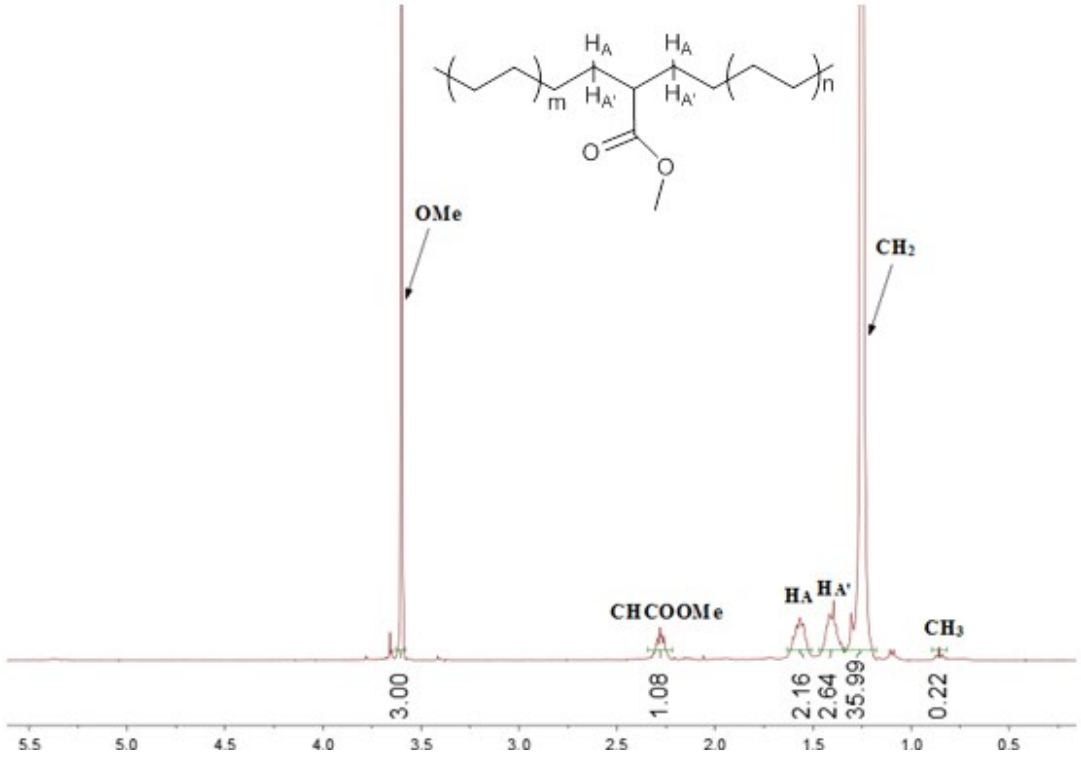


Figure S24 ^{1}H NMR of the copolymer (table 2, entry 1).

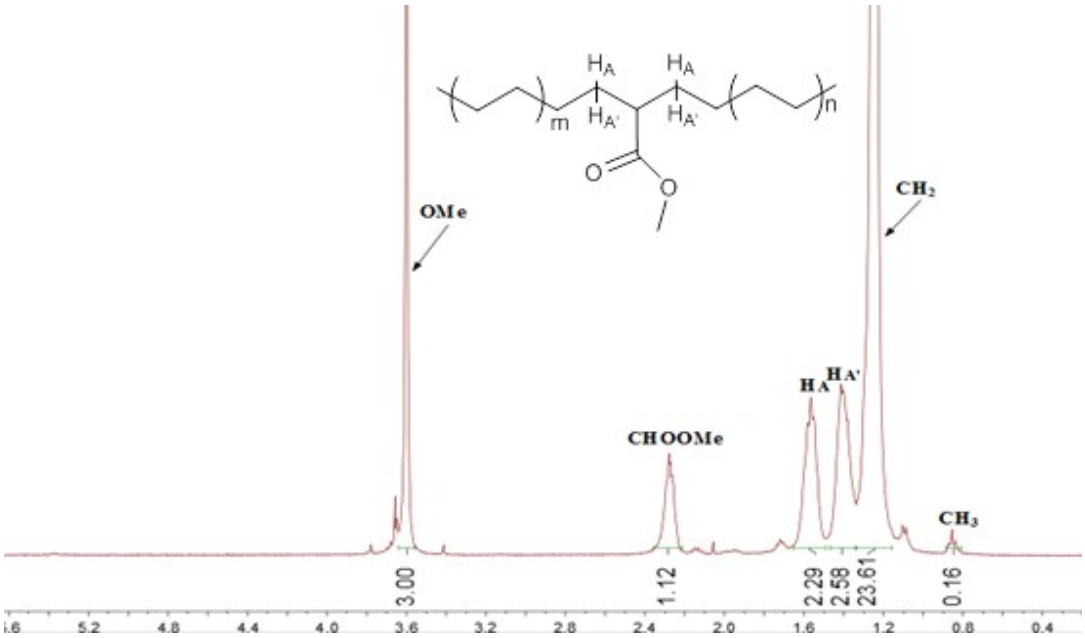


Figure S25 ^{1}H NMR of the copolymer (table 2, entry 2).

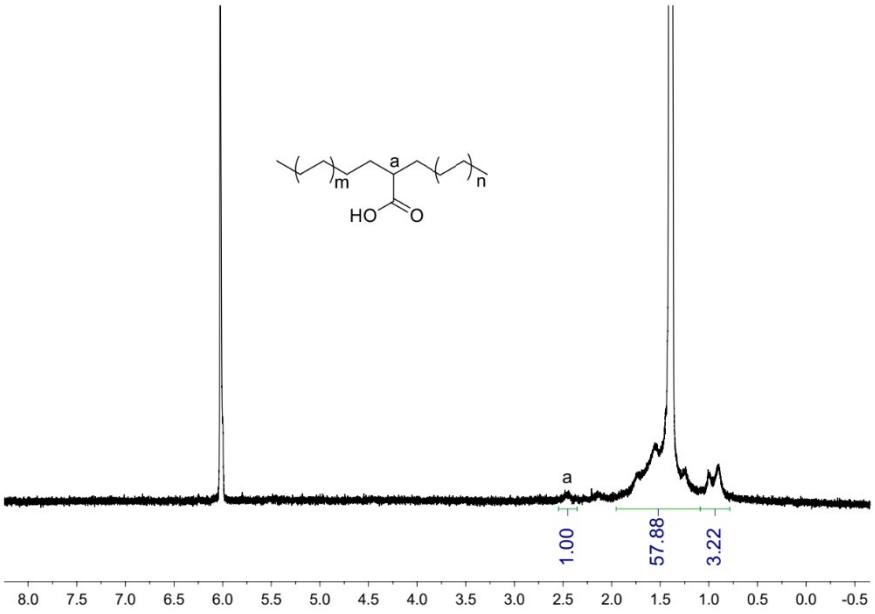


Figure S26 [1]H NMR of the copolymer (table 2, entry 3).

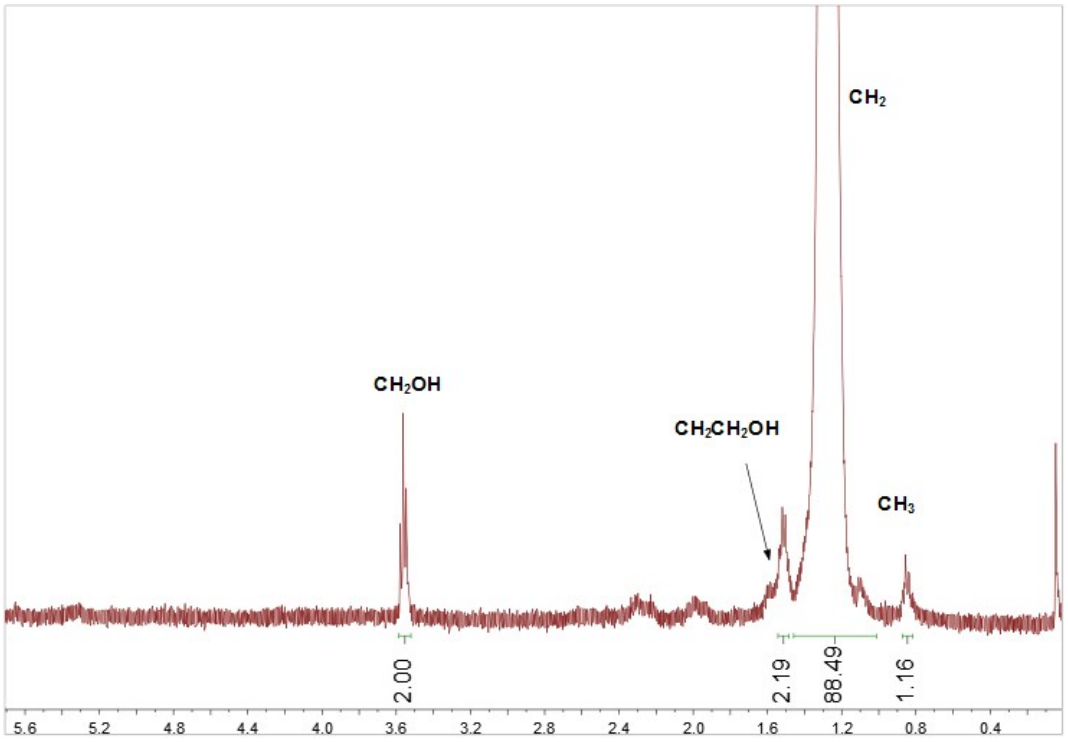


Figure S27 [1]H NMR of the copolymer (table 2, entry 4).

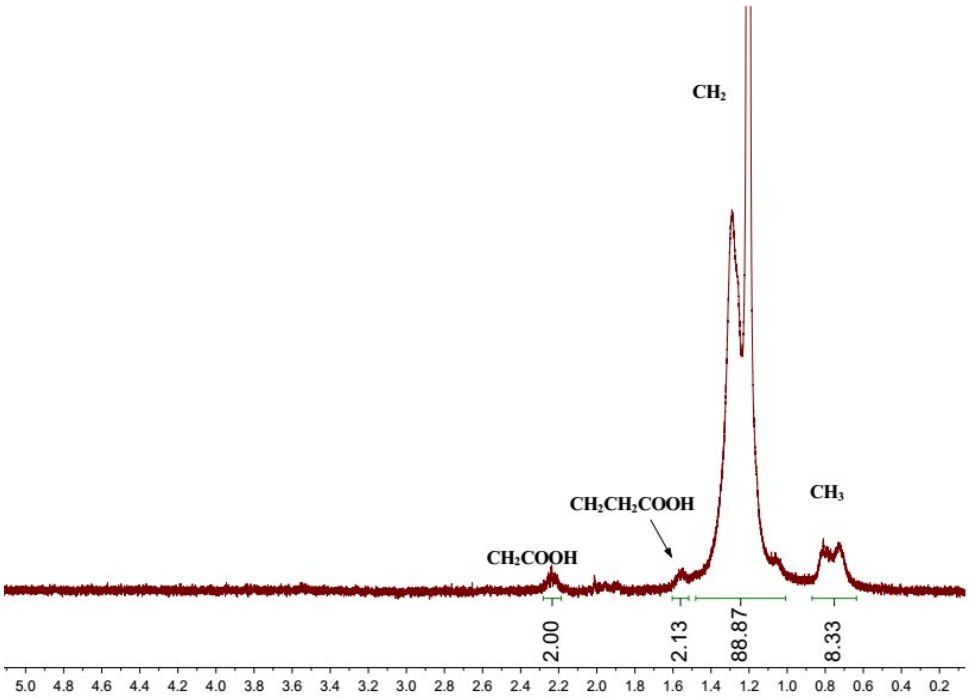


Figure S28 [1]H NMR of the copolymer (table 2, entry 5).

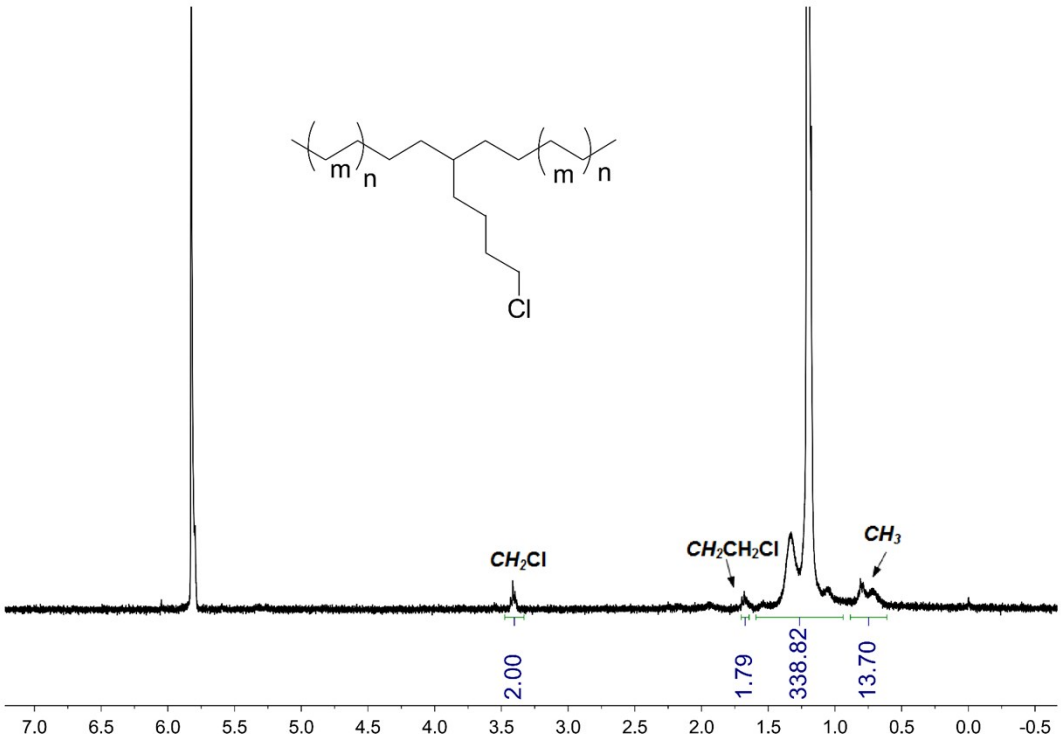


Figure S29 [1]H NMR of the copolymer (table 2, entry 6).

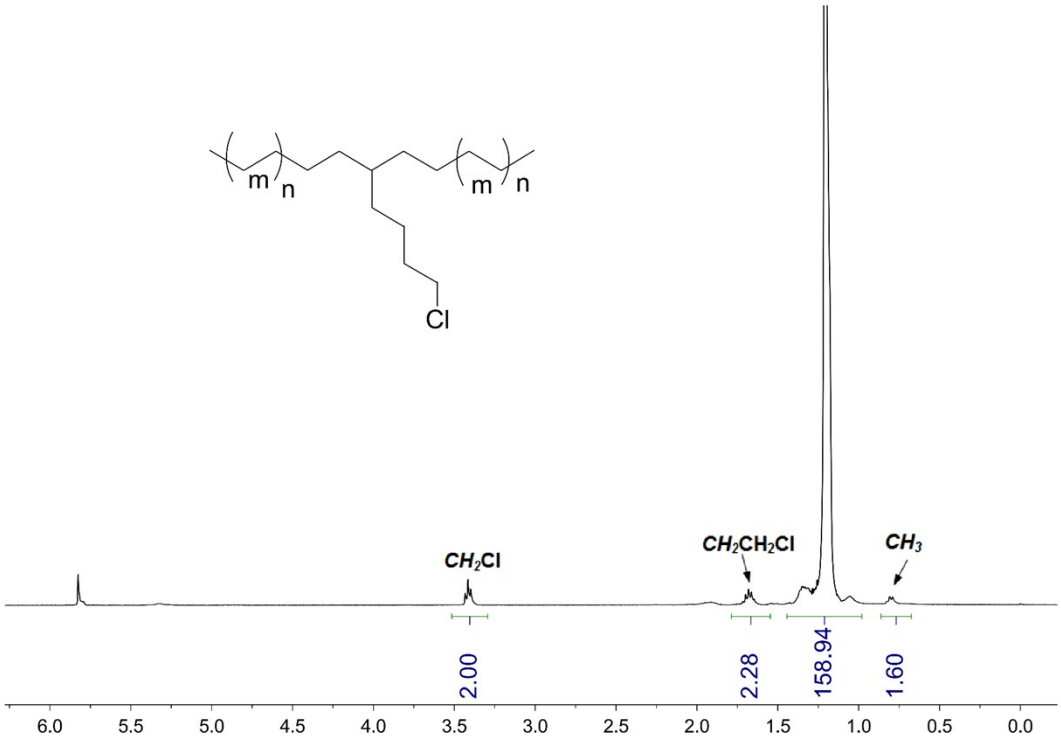


Figure S30 ^{1}H NMR of the copolymer (table 2, entry 7).

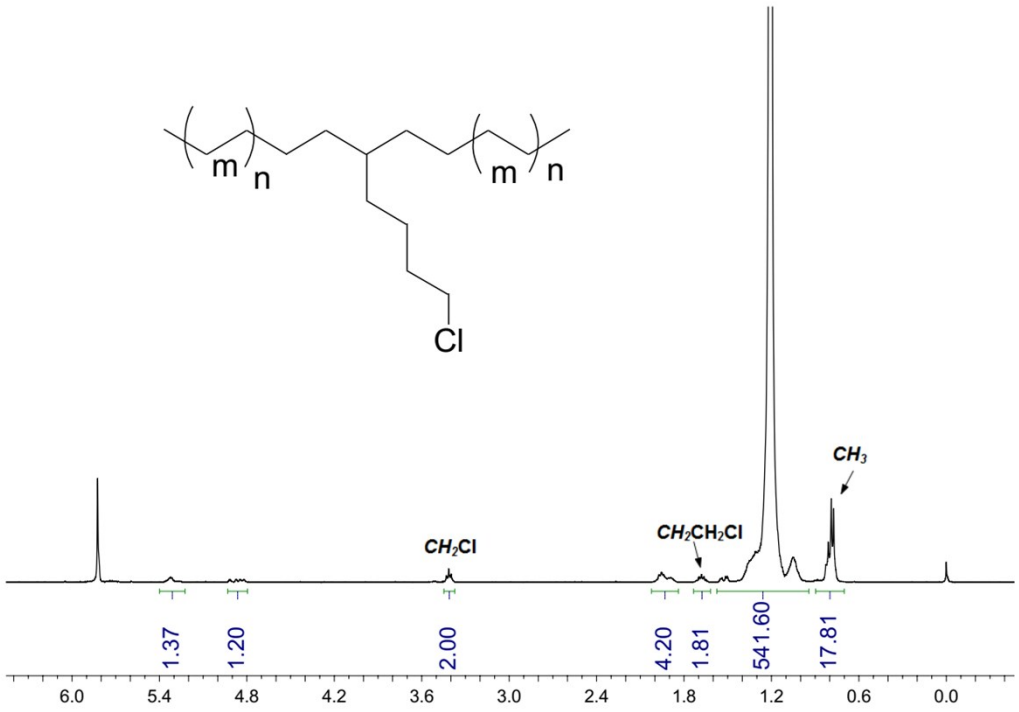


Figure S31 ^{1}H NMR of the copolymer (table 2, entry 8).

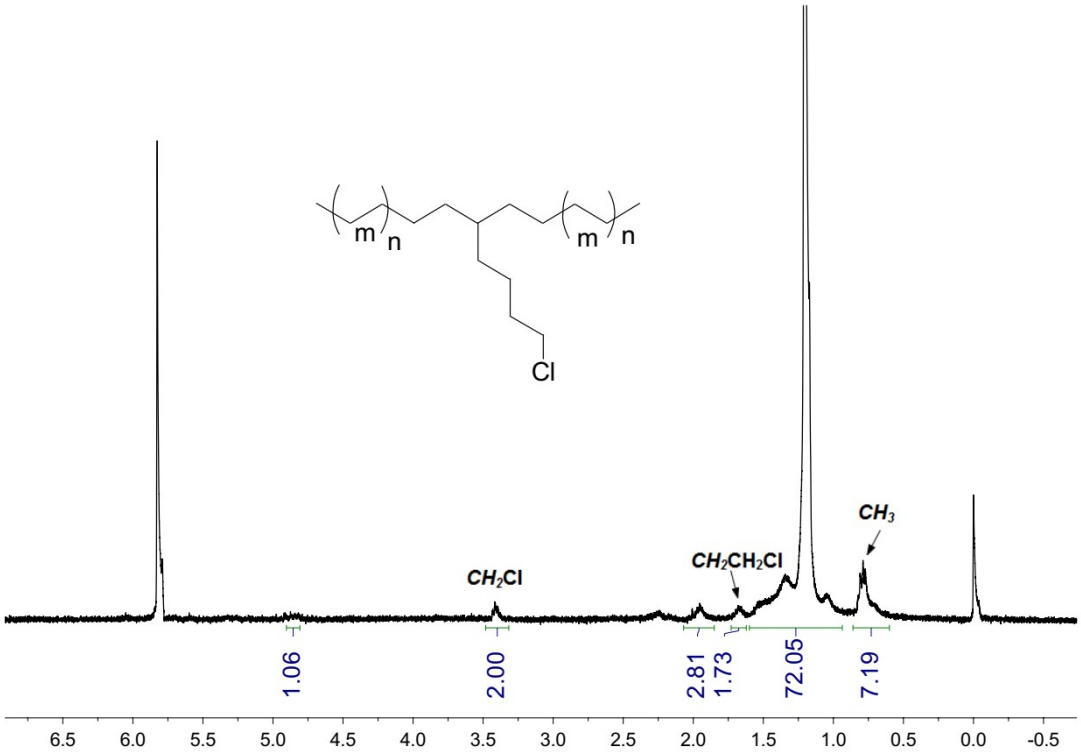


Figure S32 [1]H NMR of the copolymer (table 2, entry 9).

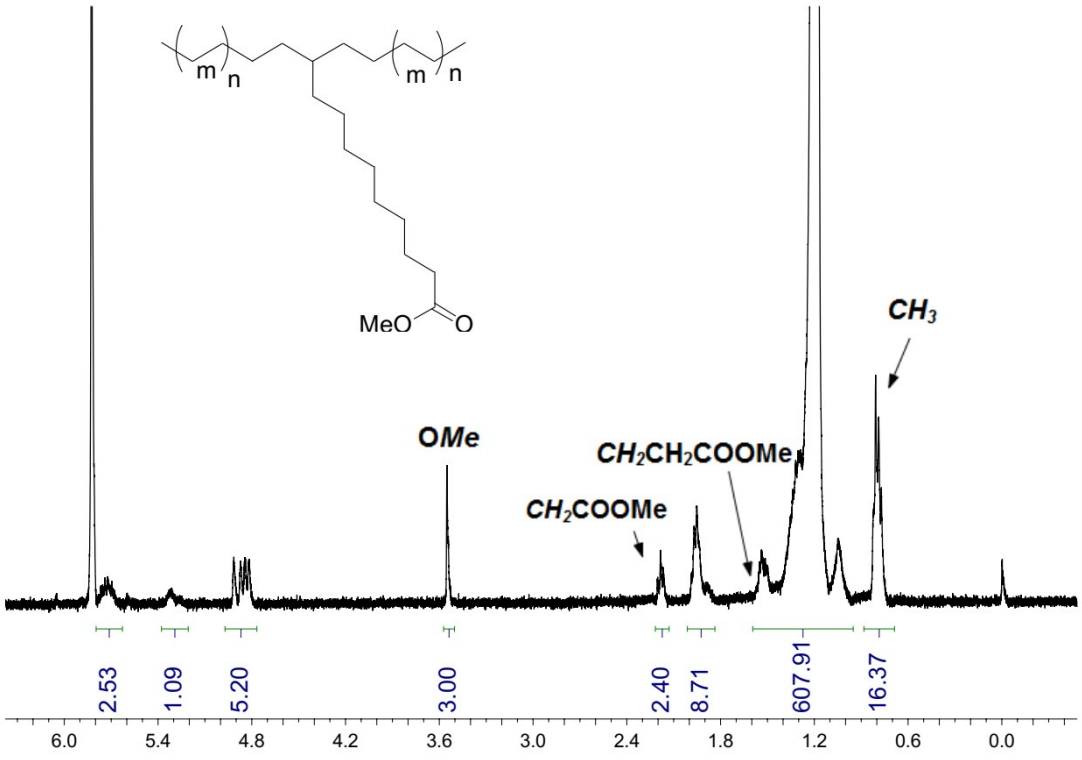


Figure S33 [1]H NMR of the copolymer (table 2, entry 10).

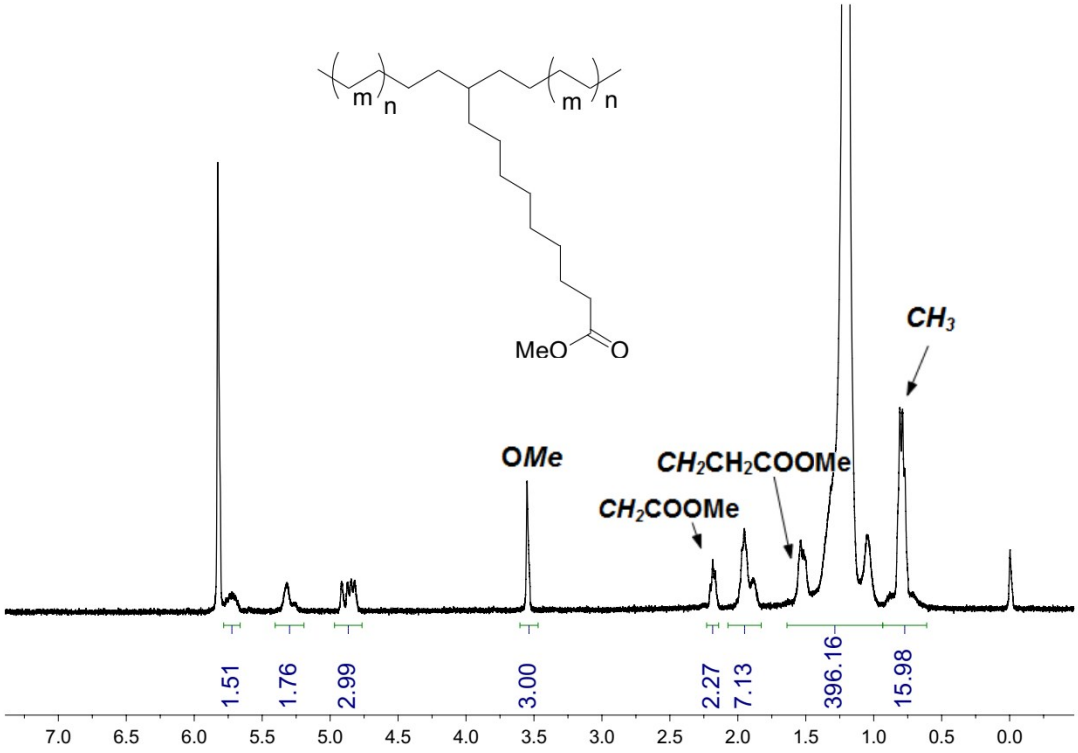
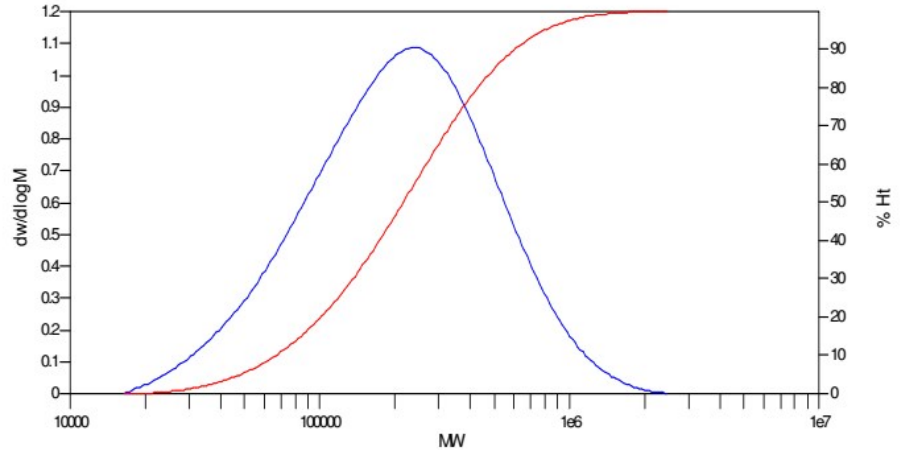


Figure S34 ^{1}H NMR of the copolymer (table 2, entry 11).

5. GPC of Polymers



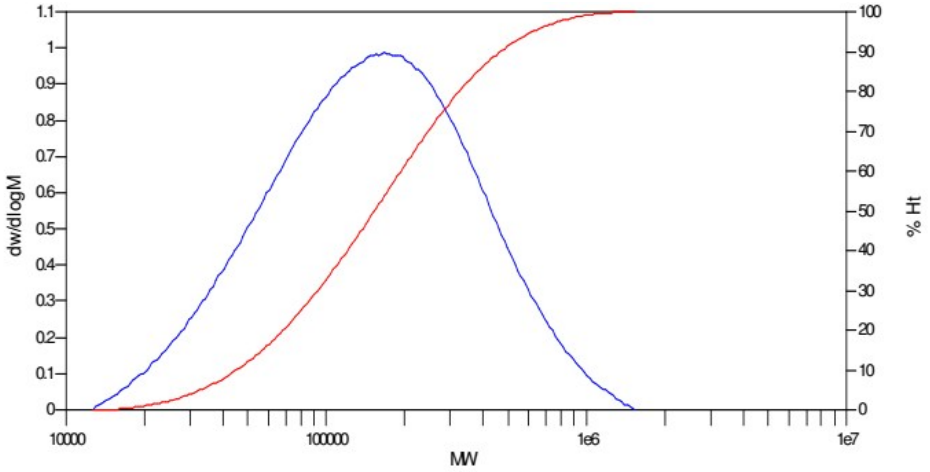
MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	237993	142907	285923	504444	770819	259218	2.00076

Processed Peaks

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1		11.37	13.02	14.90	27.7202	100	2485.22	100

Figure S35 GPC of the polymer (table 1, entry 1).



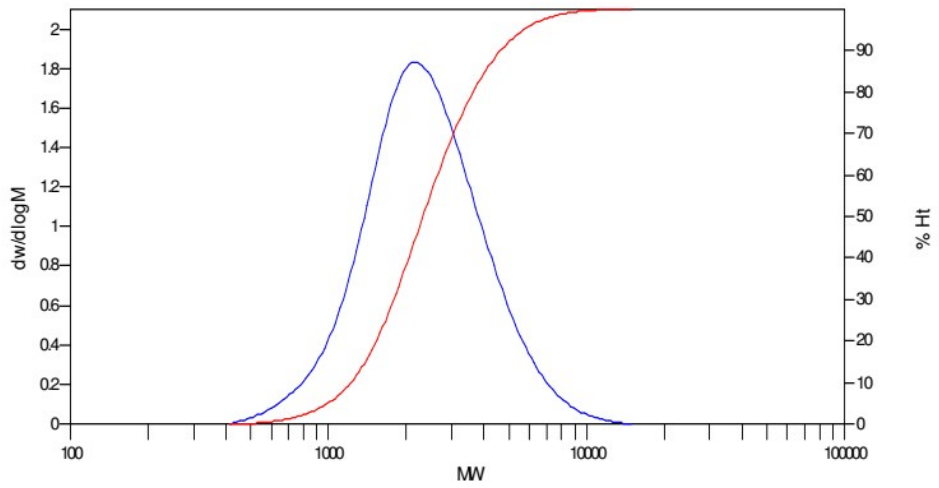
MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	166933	99776	213088	392852	593380	191152	2.13566

Processed Peaks

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1		11.70	13.27	15.08	8.7073	100	859.003	100

Figure S36 GPC of the polymer (table 1, entry 2).



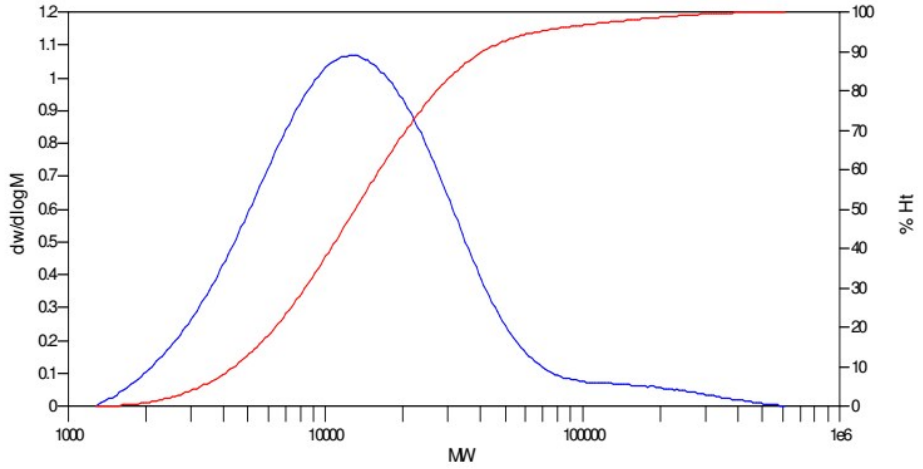
MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	2153	2026	2668	3536	4661	2555	1.31688

Processed Peaks

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1		14.97	16.33	17.50	39.3692	100	2094.61	100

Figure S37 GPC of the polymer (table 1, entry 3).



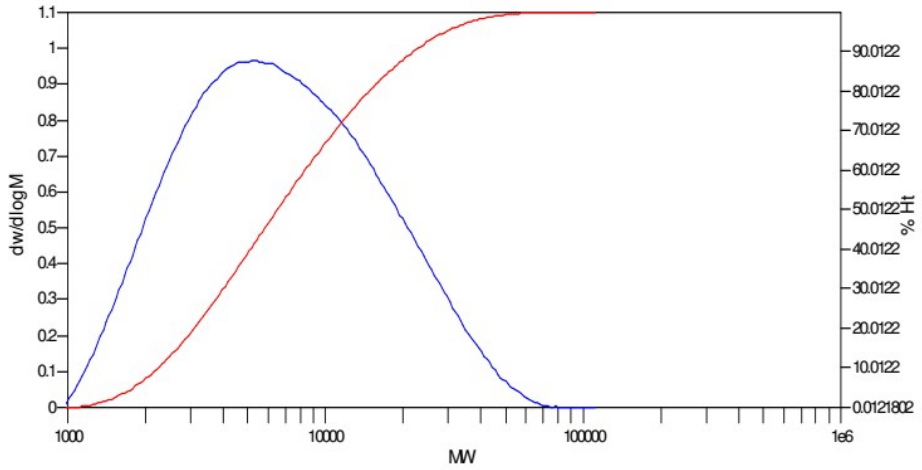
MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	12685	9297	23037	92213	237356	19040	2.4779

Processed Peaks

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1		12.35	15.08	16.70	27.1503	100	2479.35	100

Figure S38 GPC of the polymer (table 1, entry 5).



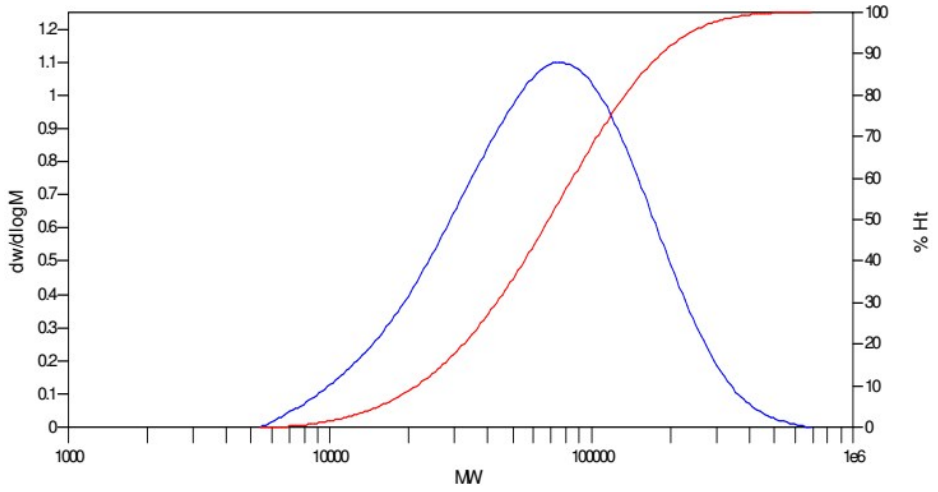
MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	5289	4796	9613	18189	27706	8603	2.00438

Processed Peaks

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1		13.55	15.72	16.90	8.9551	0	902.443	100

Figure S39 GPC of the polymer (table 1, entry 6).



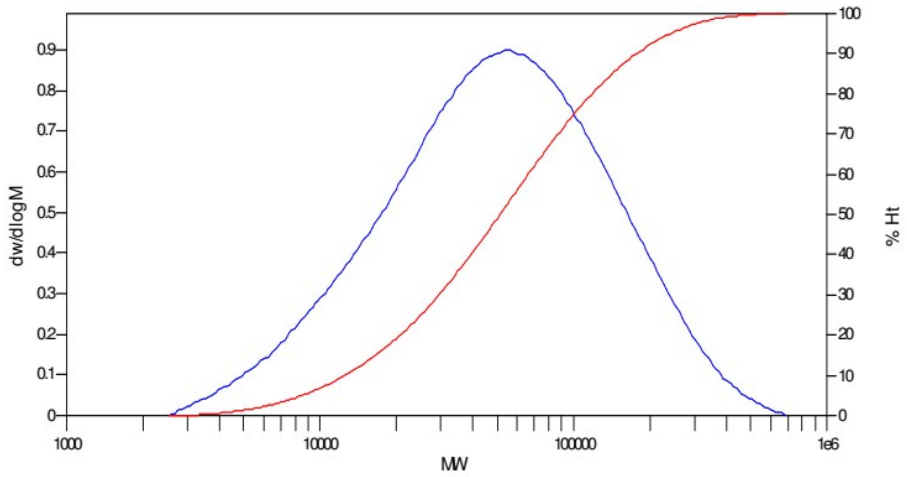
MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	74718	45584	88705	149741	219768	80923	1.94597

Processed Peaks

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1		12.27	13.83	15.68	22.2579	100	1971.44	100

Figure S40 GPC of the polymer (table 2, entry 1).



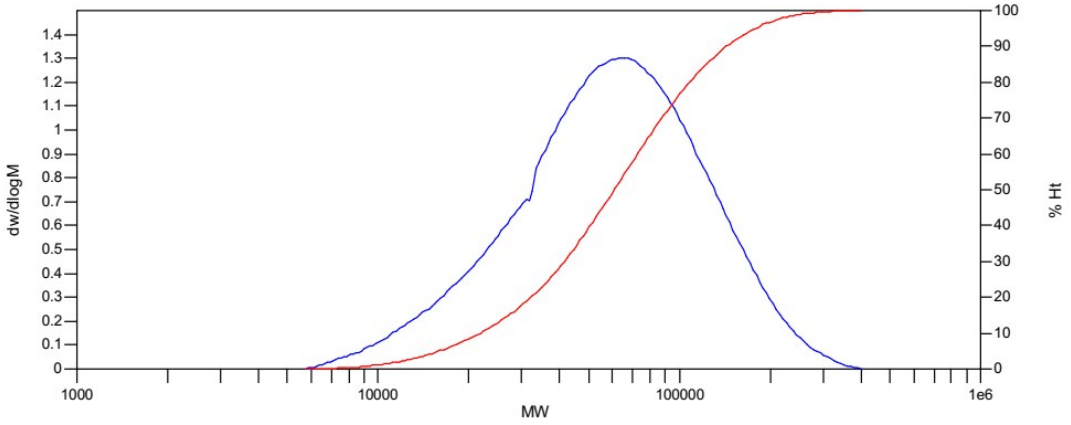
MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	56261	28955	76807	158076	249550	67280	2.65263

Processed Peaks

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1		12.27	14.05	16.22	9.15006	100	989.367	100

Figure S41 GPC of the polymer (table 2, entry 2).



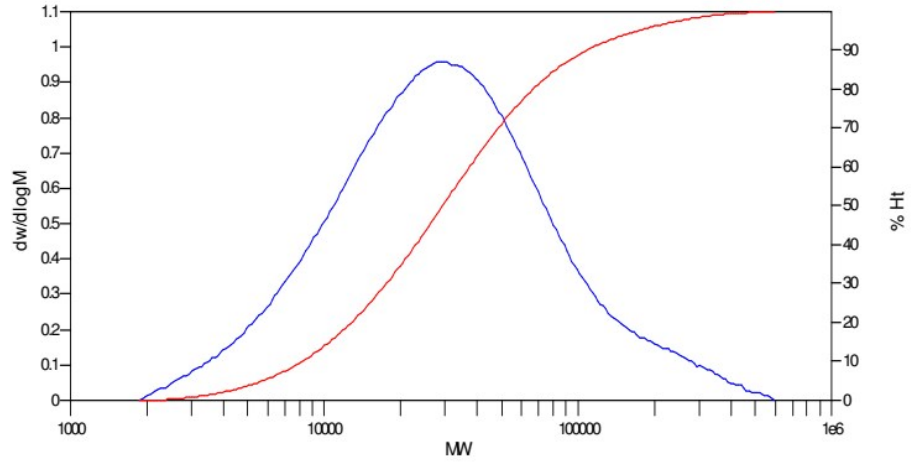
MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	65955	42535	71705	108088	147102	66768	1.68579

Processed Peaks

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1		12.73	13.93	15.68	-25.5163	100	1827.98	100

Figure S42 GPC of the polymer (table 2, entry 3).



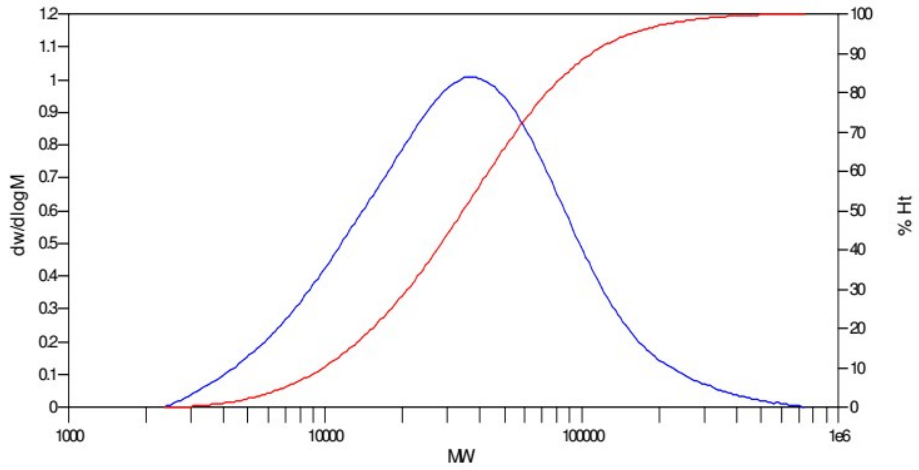
MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	29714	18199	48759	127044	237568	41566	2.67921

Processed Peaks

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1		12.37	14.53	16.43	7.00427	100	711.584	100

Figure S43 GPC of the polymer (table 2, entry 4).



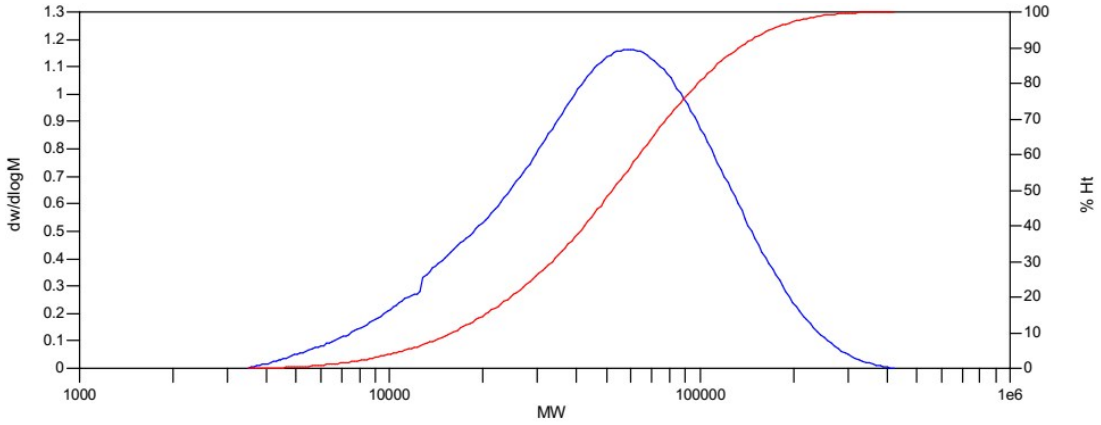
MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	36760	21766	51552	118473	230800	45105	2.36846

Processed Peaks

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1		12.22	14.33	16.27	22.2879	100	2157.9	100

Figure S44 GPC of the polymer (table 2, entry 5).



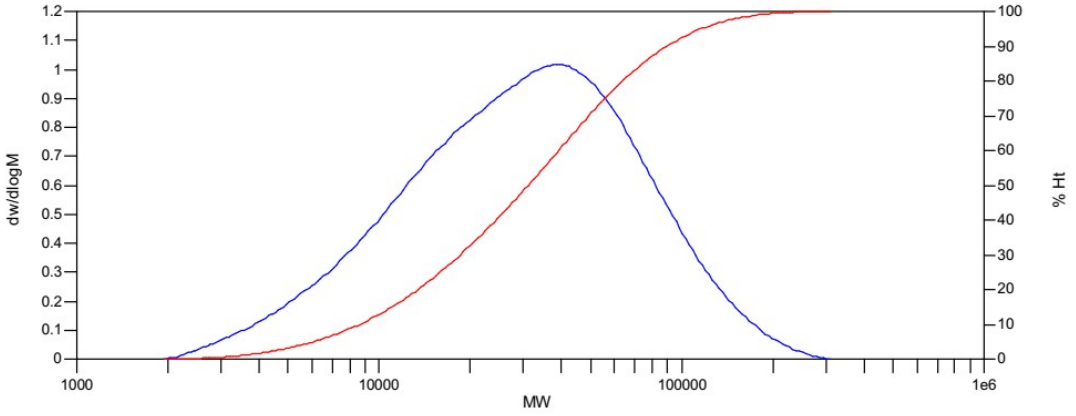
MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	59760	32349	63468	103618	146431	58118	1.96198

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	13.98	16.08	-32.1144	100	2581.24	100

Figure S45 GPC of the polymer (table 2, entry 6).



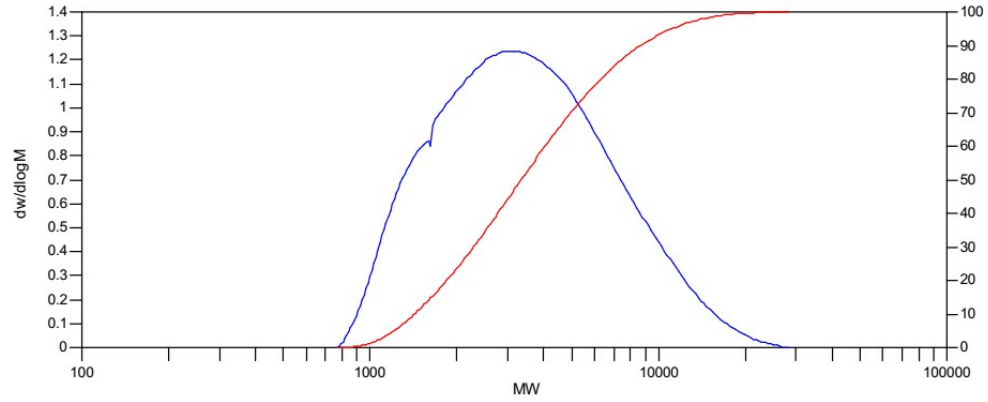
MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	40443	18033	39906	72111	107409	35847	2.21294

Processed Peaks

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1		12.90	14.27	16.60	-32.4226	100	3036.71	100

Figure S46 GPC of the polymer (table 2, entry 7).



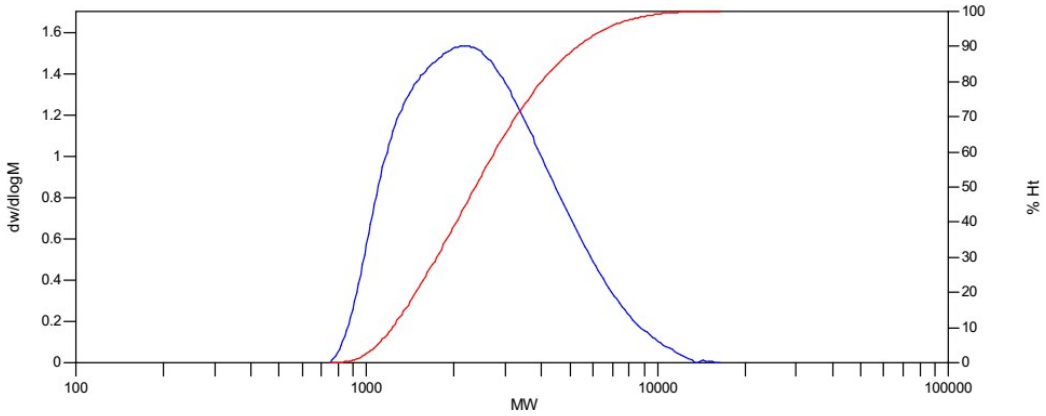
MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	3437	2611	4070	6497	9533	3778	1.55879

Processed Peaks

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1		14.50	16.10	17.53	-32.1236	100	3037.02	100

Figure S47 GPC of the polymer (table 2, entry 8).



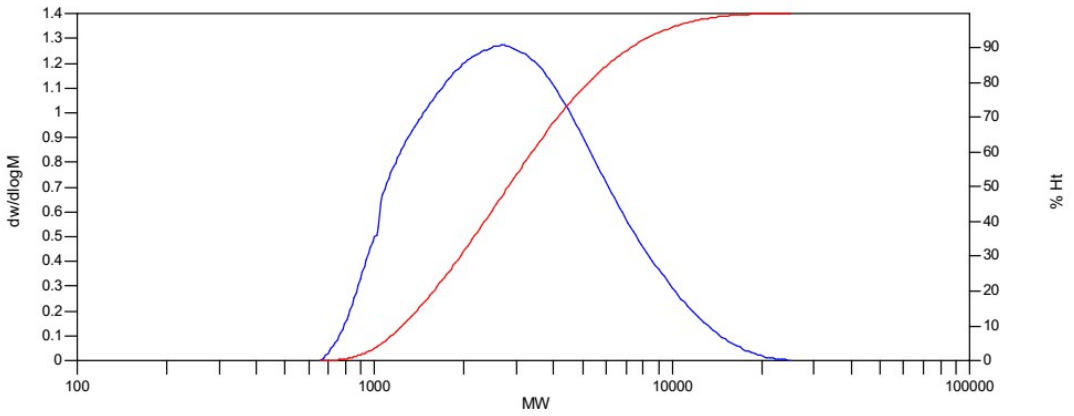
MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	2336	2033	2733	3831	5255	2597	1.34432

Processed Peaks

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1		14.88	16.43	17.57	-62.3372	100	5011.39	100

Figure S48 GPC of the polymer (table 2, entry 9).



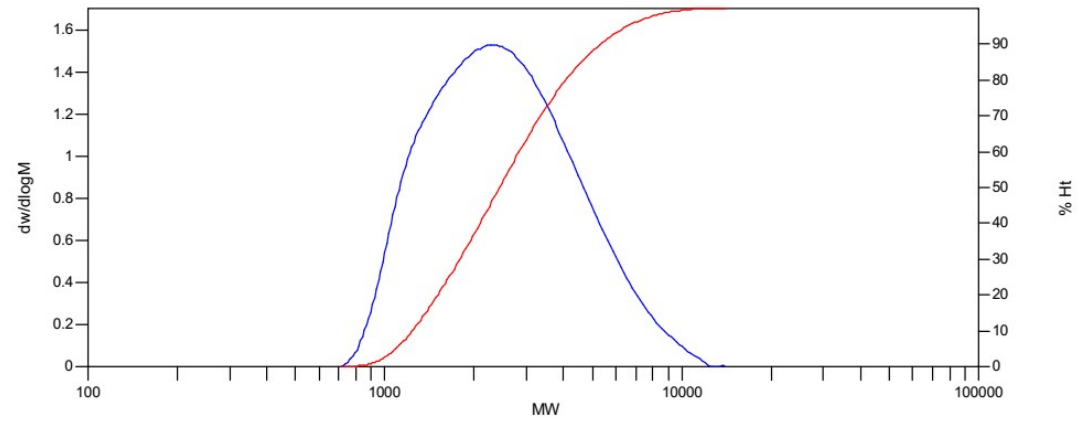
MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	2826	2222	3405	5424	8056	3166	1.5324

Processed Peaks

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1		14.58	16.25	17.72	-36.1892	100	3404.98	100

Figure S49 GPC of the polymer (table 2, entry 10).



MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	2519	2067	2767	3790	5022	2635	1.33866

Processed Peaks

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1		15.00	16.37	17.62	-44.1675	100	3538.48	100

Figure S50 GPC of the polymer (table 2, entry 11).

6. DSC of Polymers

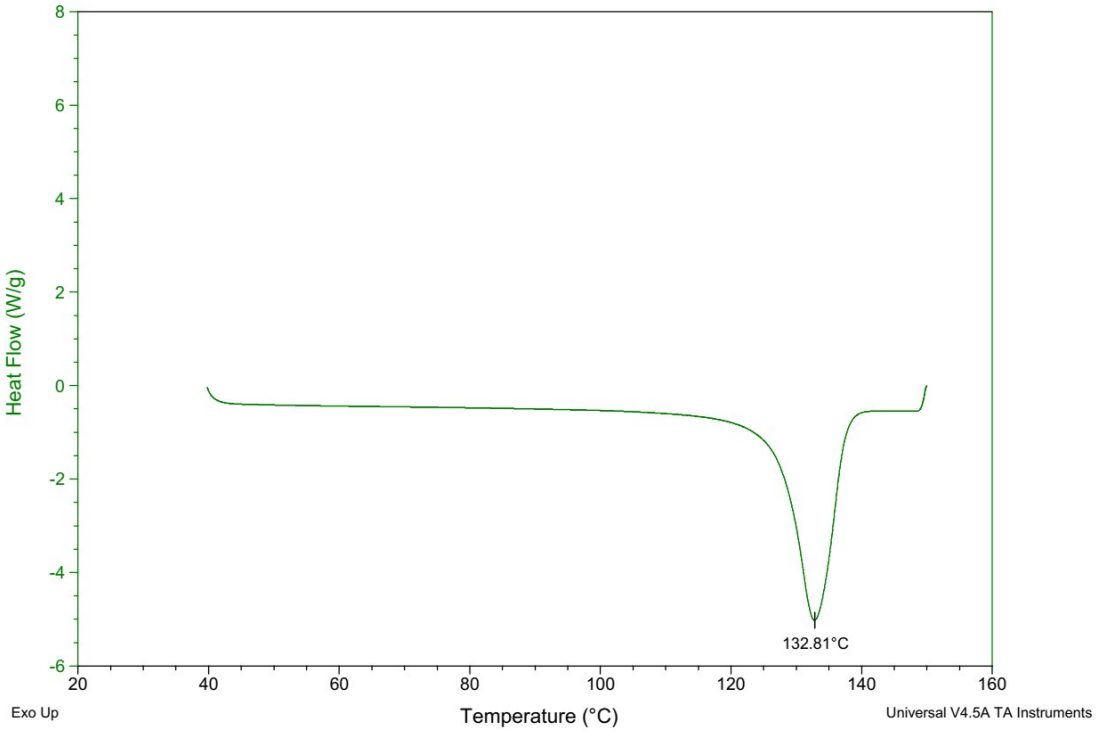


Figure S51 DSC of the polymer (table 1, entry 1).

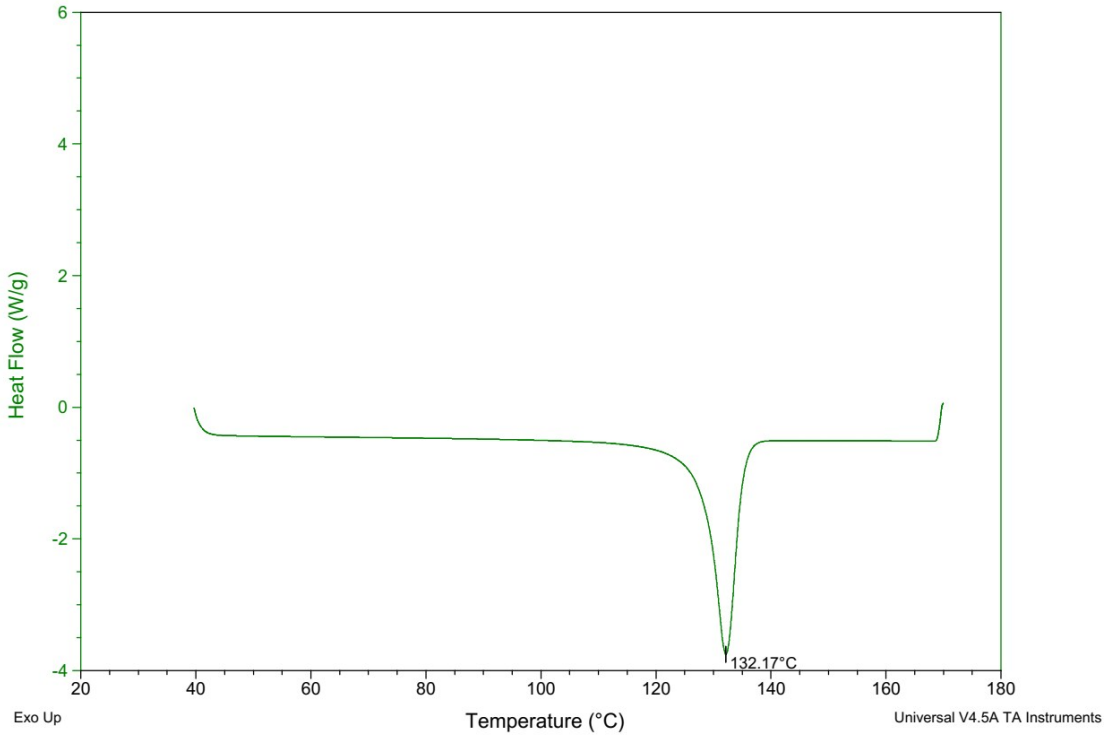


Figure S52 DSC of the polymer (table 1, entry 2).

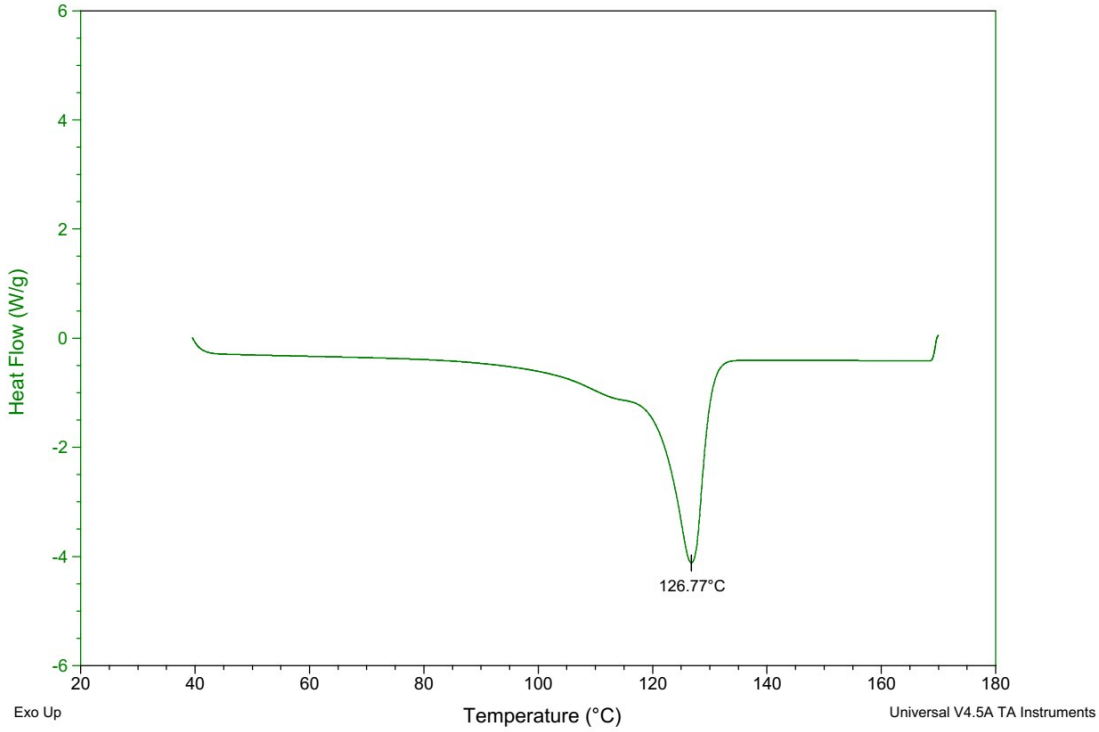


Figure S53 DSC of the polymer (table 1, entry 3).

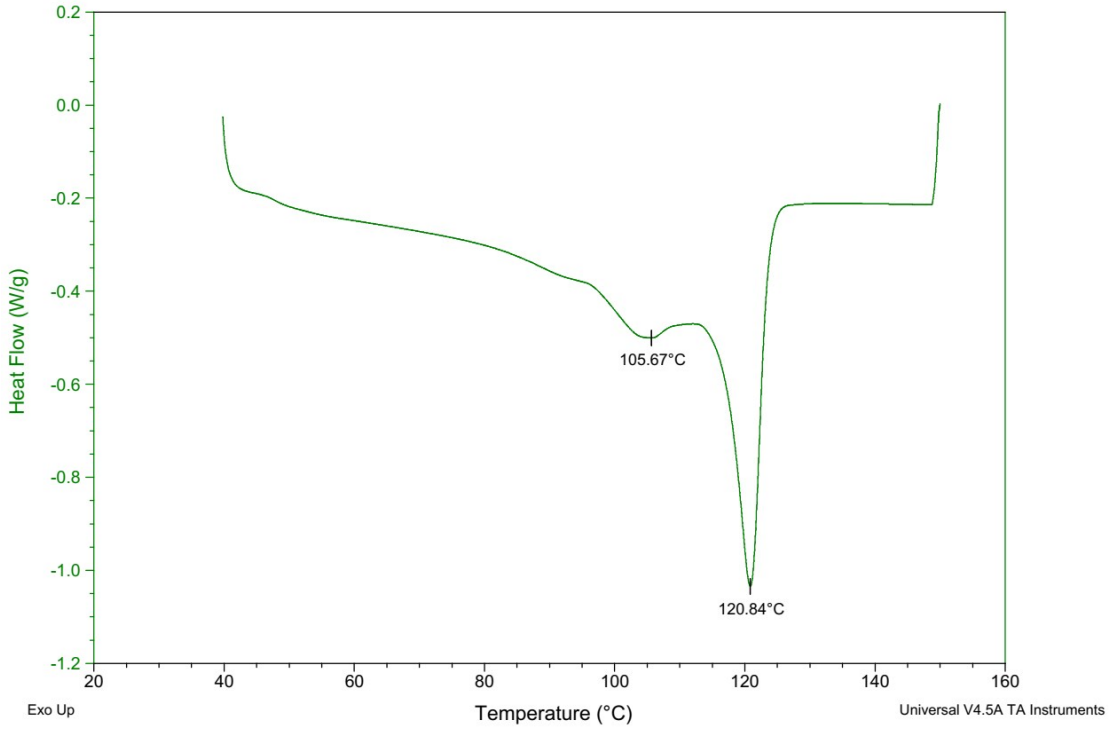


Figure S54 DSC of the polymer (table 1, entry 4).

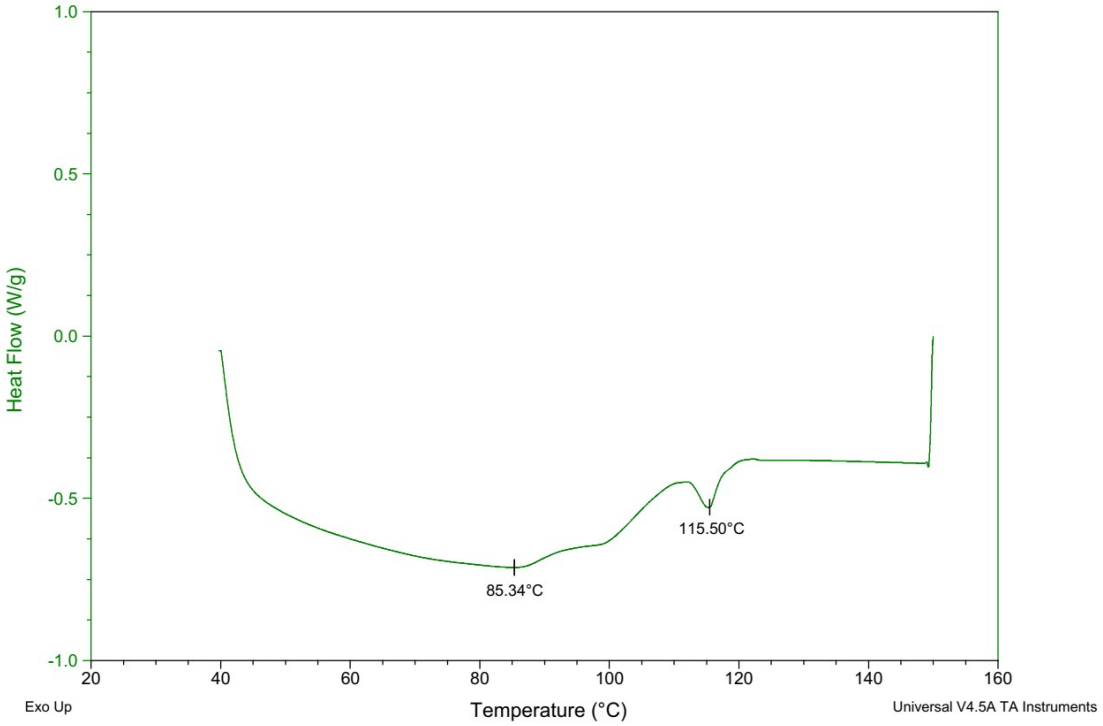


Figure S55 DSC of the polymer (table 1, entry 5).

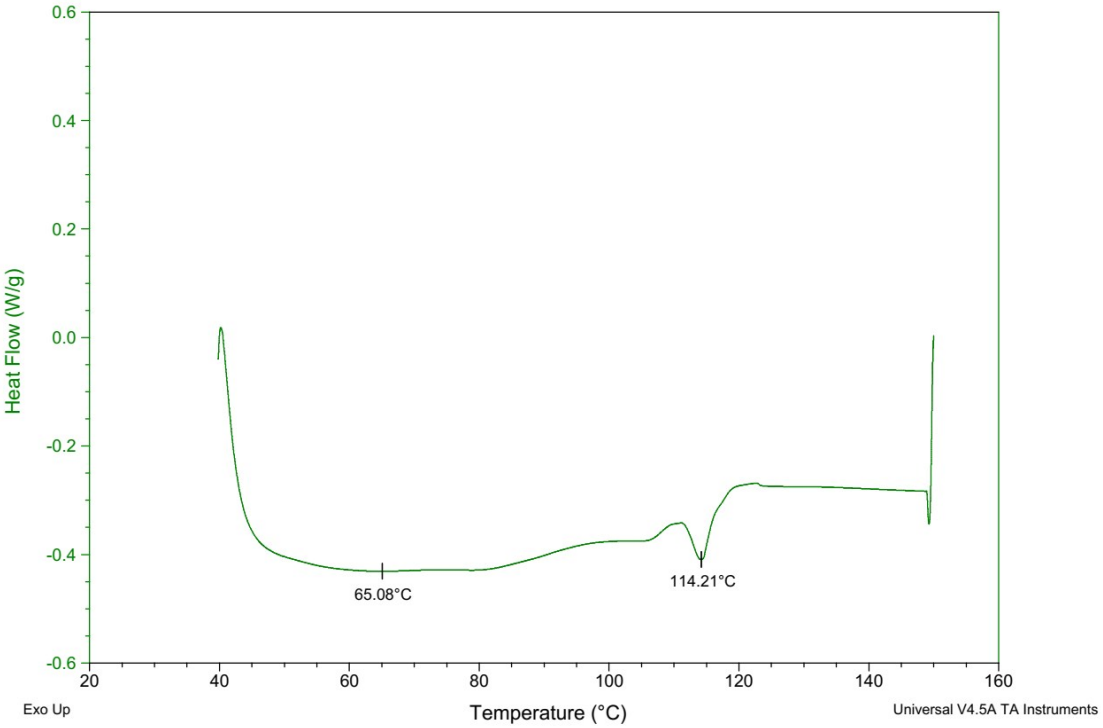


Figure S56 DSC of the polymer (table 1, entry 6).

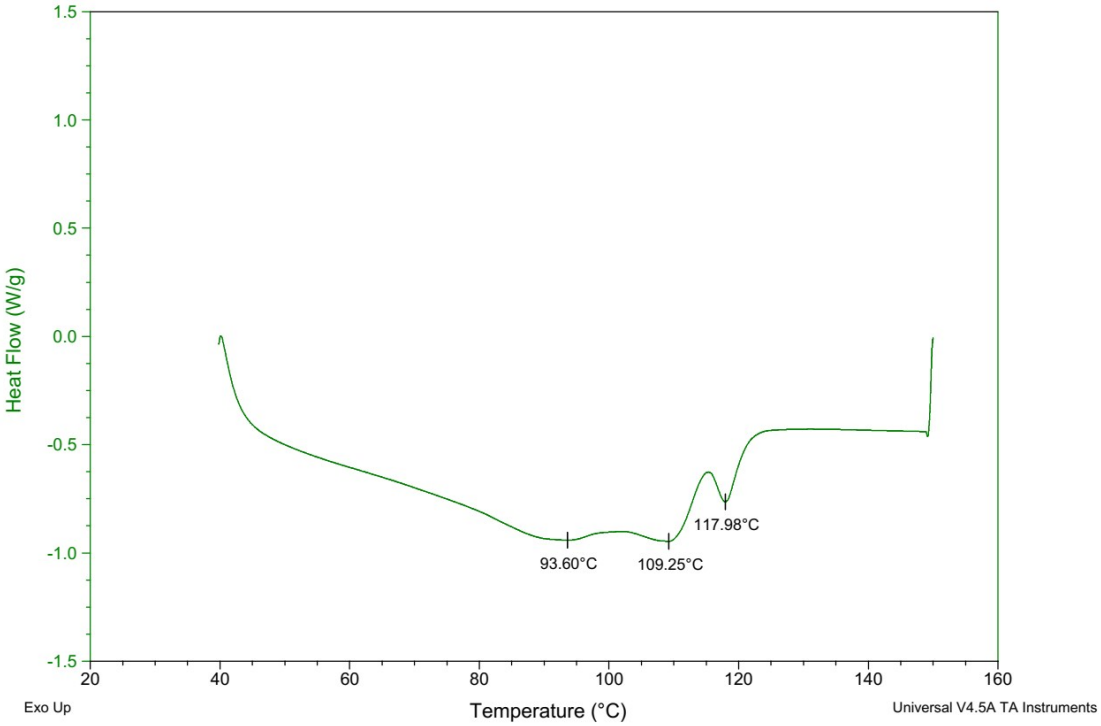


Figure S57 DSC of the polymer (table 1, entry 7).

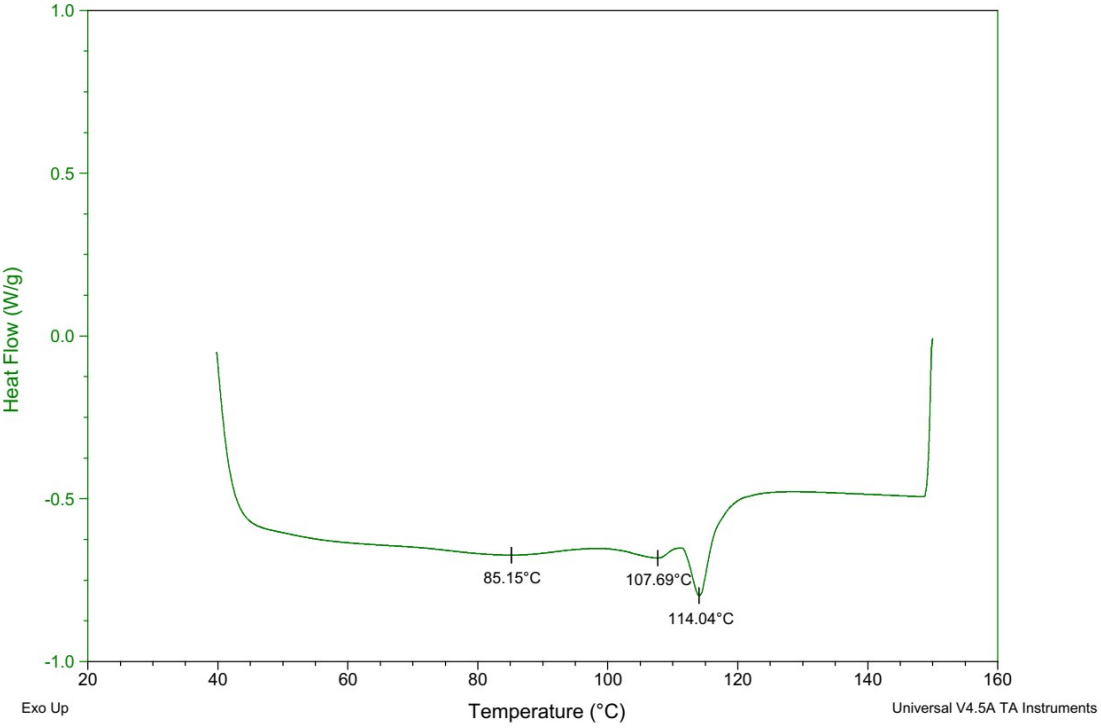


Figure S58 DSC of the polymer (table 1, entry 8).

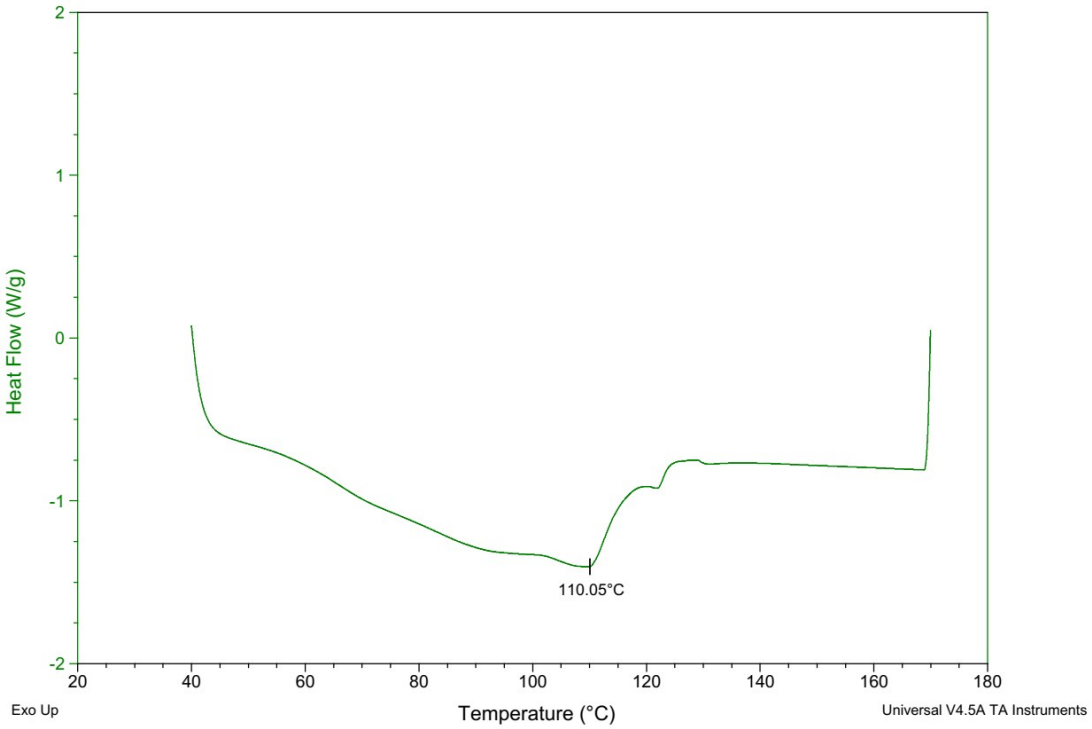


Figure S59 DSC of the polymer (table 2, entry 1).

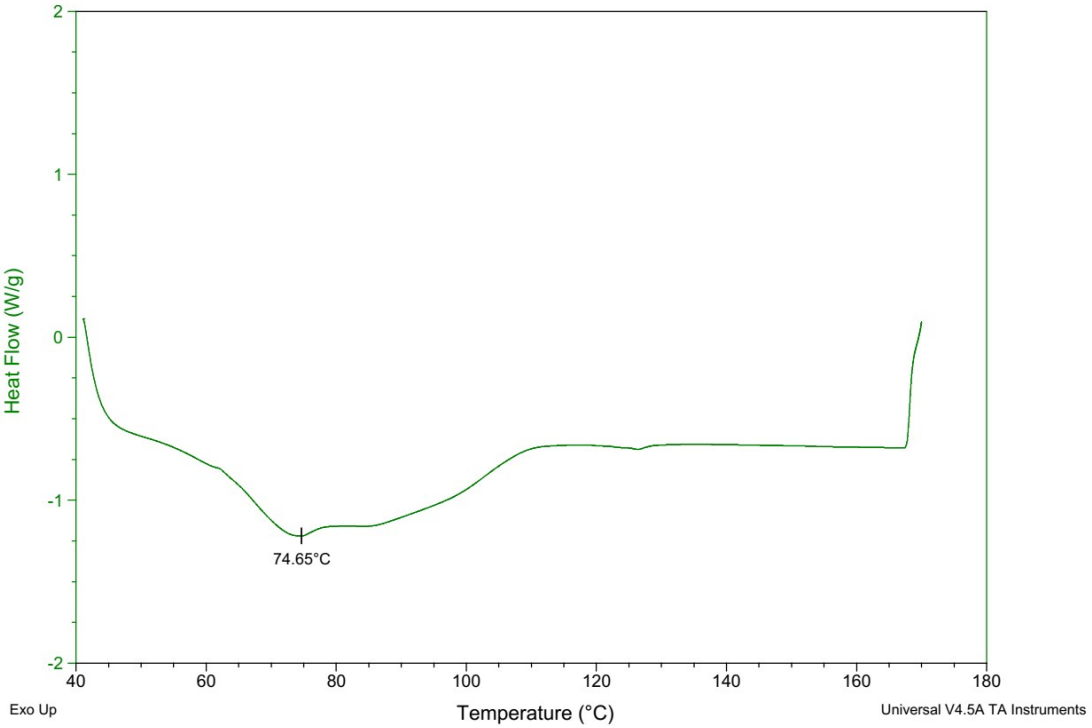


Figure S60 DSC of the polymer (table 2, entry 2).

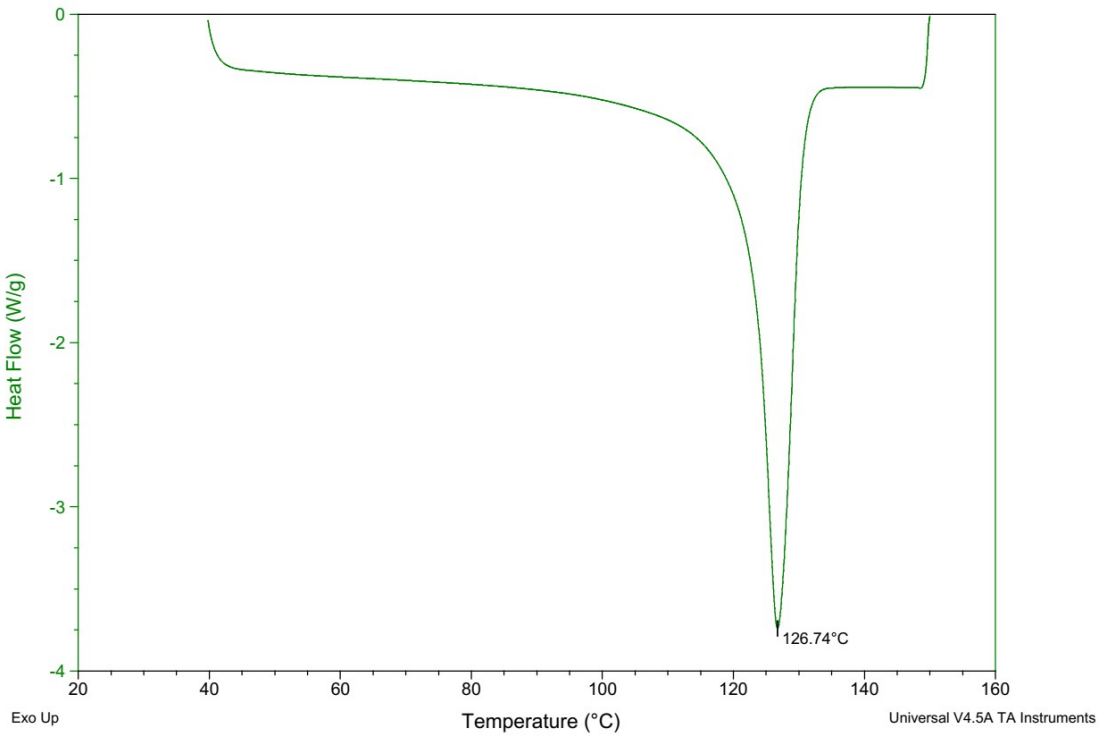


Figure S61 DSC of the polymer (table 2, entry 3).

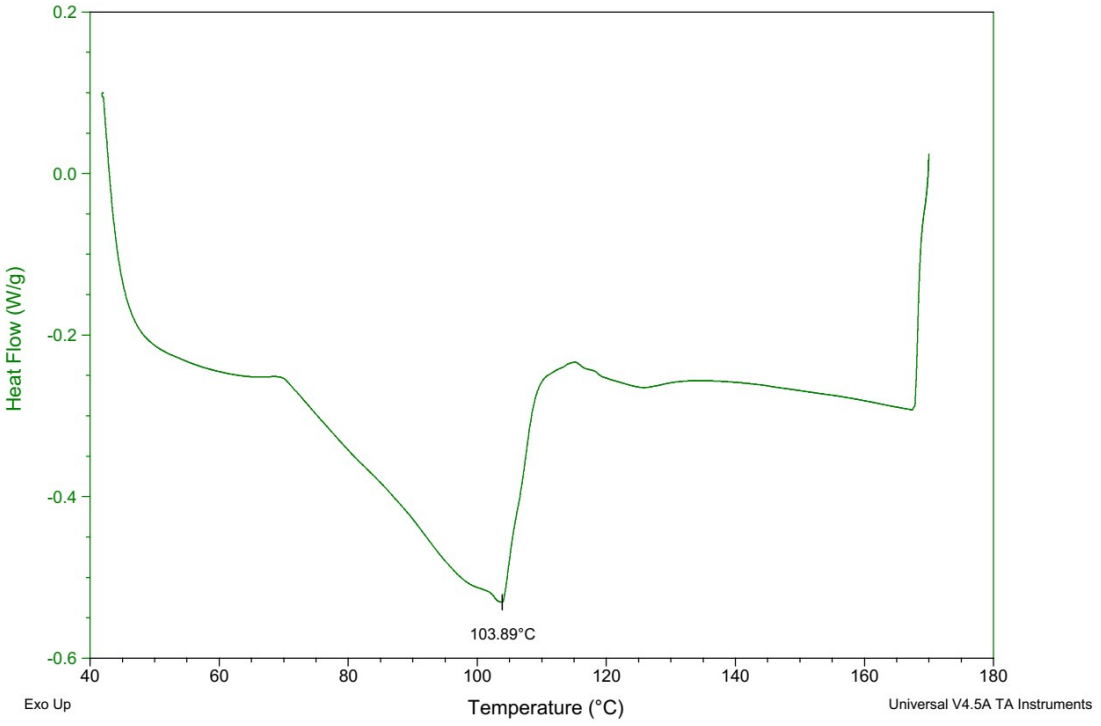


Figure S62 DSC of the polymer (table 2, entry 4).

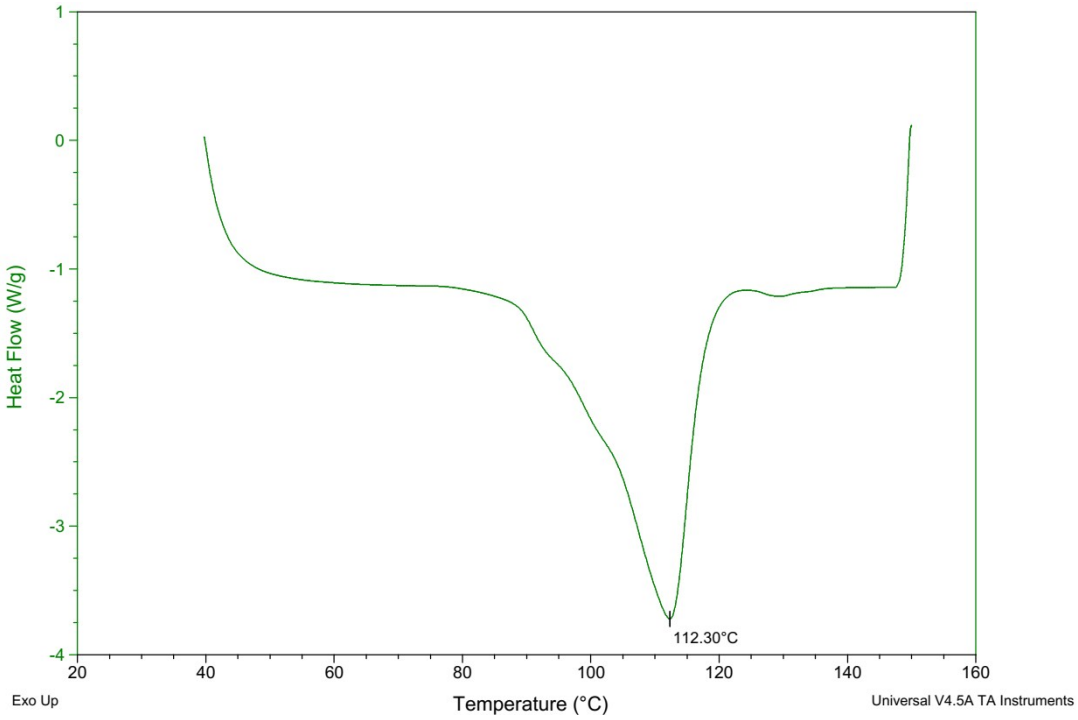


Figure S63 DSC of the polymer (table 2, entry 5).

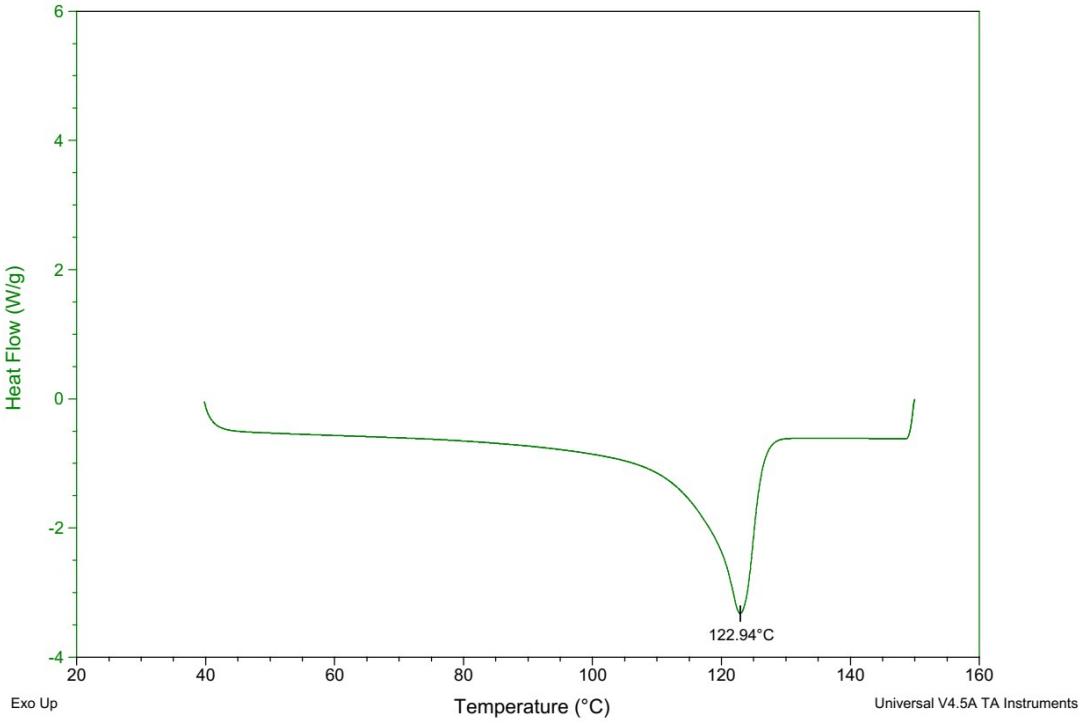


Figure S64 DSC of the polymer (table 2, entry 6).

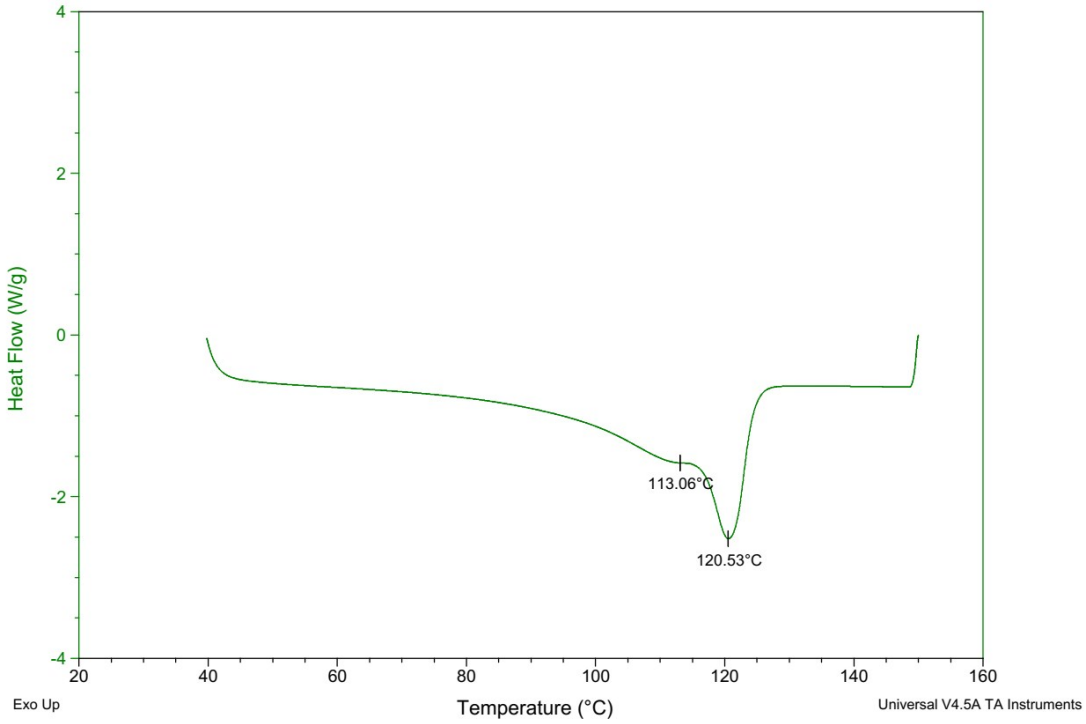


Figure S65 DSC of the polymer (table 2, entry 7).

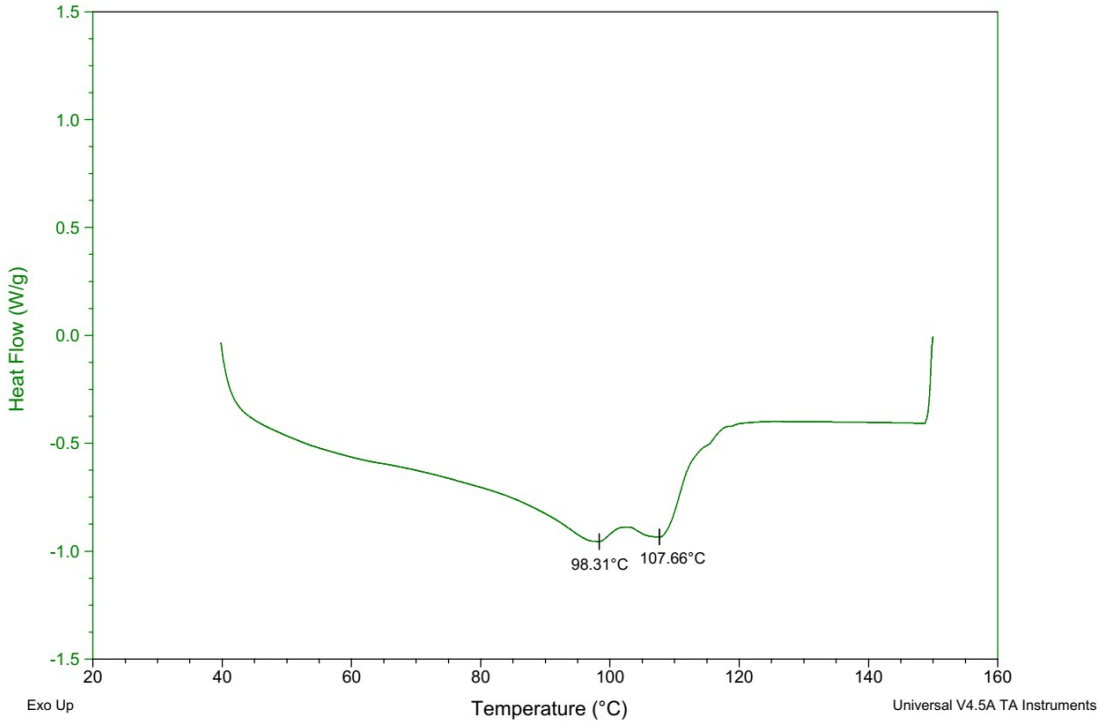


Figure S66 DSC of the polymer (table 2, entry 8).

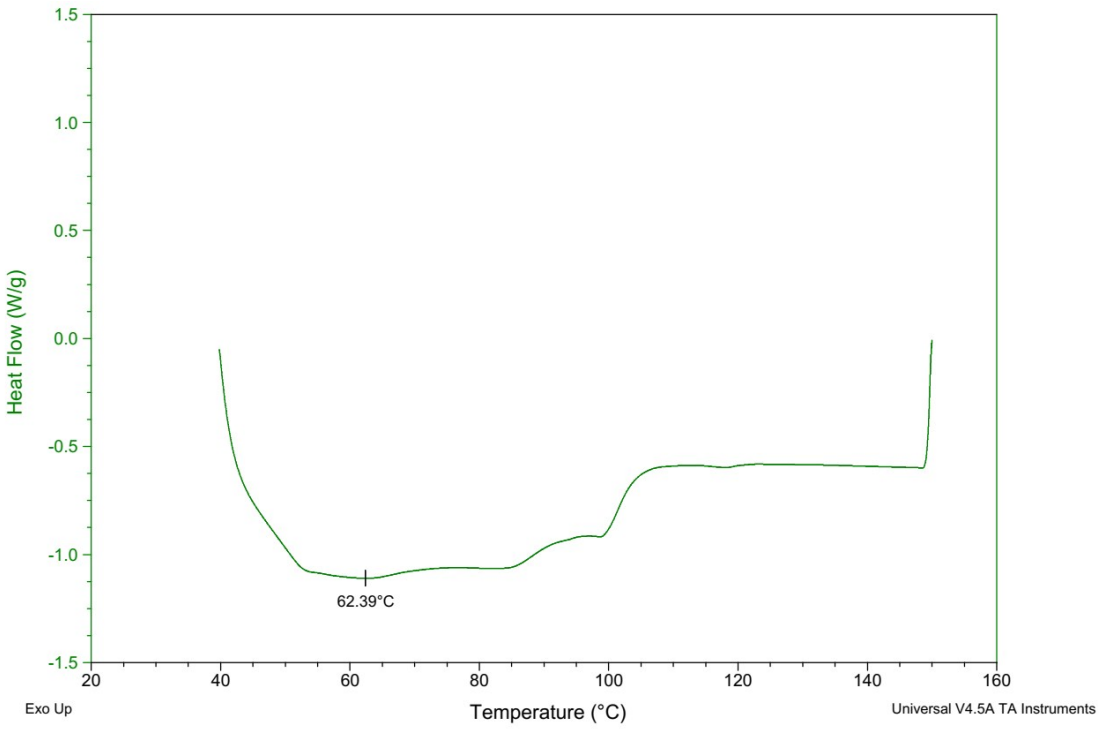


Figure S67 DSC of the polymer (table 2, entry 9).

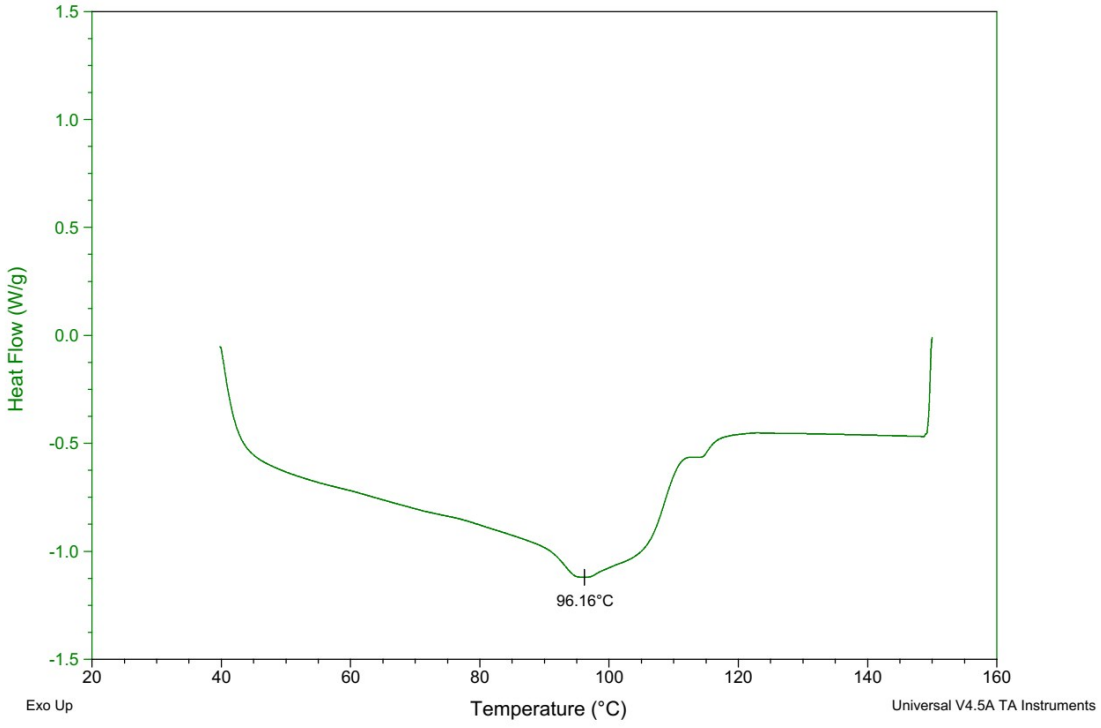


Figure S68 DSC of the polymer (table 2, entry 10).

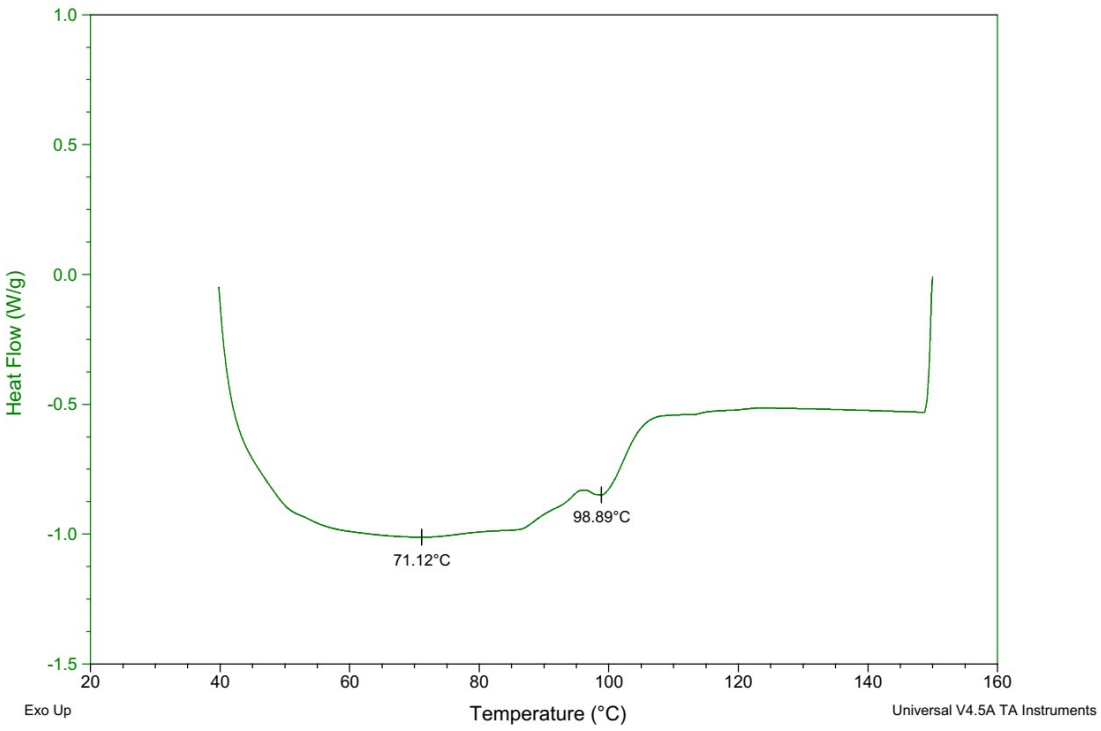


Figure S69 DSC of the polymer (table 2, entry 11).

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