Supplementary Information (SI)

Pentiptycenyl Substituents in Insertion Polymerization with α-Diimine Nickel and Palladium Species

Yudan Liao,[a,b] Yixin Zhang,[a] Lei Cui,[a] Hongliang Mu[a] and Zhongbao Jian[a,*]

[a] State Key Laboratory of Polymer Physics and Chemistry, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Renmin Street 5625, Changchun 130022, China
[b] University of Chinese Academy of Sciences, Beijing 100049, China

Contents

Figures and Tables

Table S1. Result for ethylene polymerizations at different temperatures and times[a]

Entry	Cat.	*T*/°C	Time/min	Yield/g	Act.[b]
1	**Ipty-Ni4**	20	10	0.64	1.92
2	**Ipty-Ni4**	20	20	1.52	2.28
3	**Ipty-Ni4**	20	30	2.13	2.13
4	**Ipty-Ni4**	40	10	0.73	2.19
5	**Ipty-Ni4**	40	20	1.74	2.61
6	**Ipty-Ni4**	40	30	2.53	2.53
7	**Ipty-Ni4**	60	10	1.06	3.18
8	**Ipty-Ni4**	60	20	2.31	3.47
9	**Ipty-Ni4**	60	30	3.13	3.13
10	**Ipty-Ni4**	80	10	1.02	3.06
11	**Ipty-Ni4**	80	20	2.21	3.31
12	**Ipty-Ni4**	80	30	2.67	2.67
13	**Ph-Ni4**	20	10	0.17	0.51
14	**Ph-Ni4**	20	20	0.39	0.59
15	**Ph-Ni4**	20	30	0.57	0.57
16	**Ph-Ni4**	40	10	0.28	0.84
17	**Ph-Ni4**	40	20	0.56	0.84
18	**Ph-Ni4**	40	30	0.83	0.83
19	**Ph-Ni4**	60	10	0.52	1.56
20	**Ph-Ni4**	60	20	1.01	1.52
21	**Ph-Ni4**	60	30	1.54	1.54
22	**Ph-Ni4**	80	10	0.65	1.95
23	**Ph-Ni4**	80	20	1.25	1.88
24	**Ph-Ni4**	80	30	1.83	1.83

[a] Reaction conditions: Ni catalyst (2 μmol), MAO (500 equiv.), toluene/CH_2Cl_2 (19 mL/1 mL).
[b]Activity (Act.) = 10^6 g/(mol Ni ·h).

Table S2. Polyethylene Branching Distribution based on ^{13}C NMR analysis[a]

polymer	methyl	ethyl	propyl	butyl+	Branching density (/1000C)[b]
PE-1	23.4	1.2	0.7	2.7	28
PE-2	26.5	2.5	1.0	5.0	35

[a] Sample from Table 1, entries 4 (**PE-1**), 11 (**PE-2**). [b] Measured by ^{13}C NMR in $CDCl_2CDCl_2$ at 110 °C.

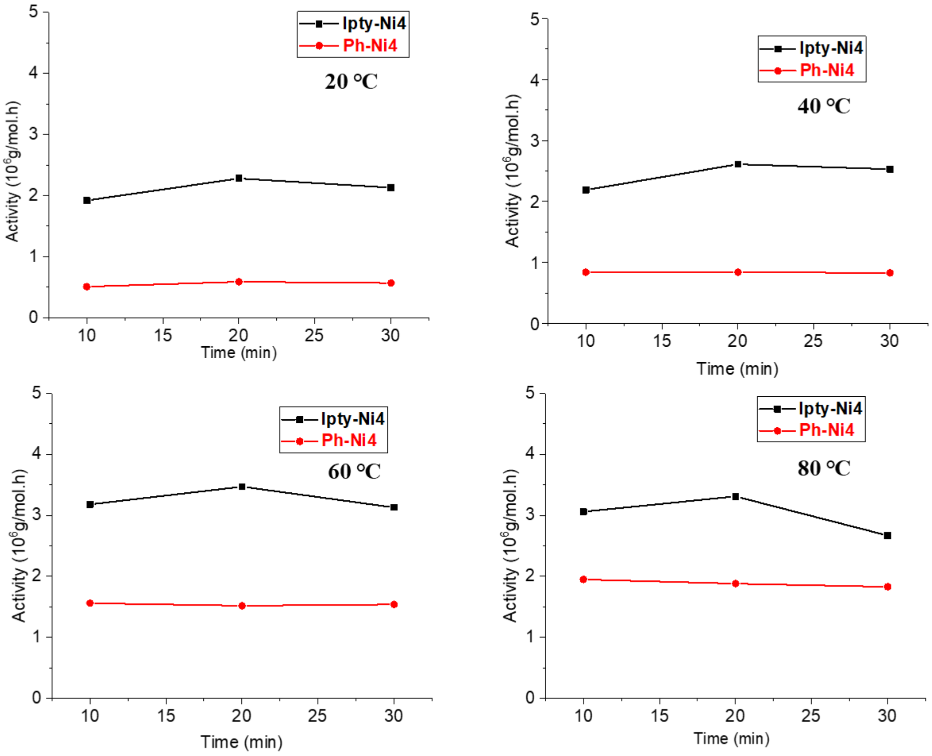


Figure S1. Plots of activity versus time and for **Ipty-Ni4** (black) and **Ph-Ni4** (red) at 20, 40, 60, 80 °C.

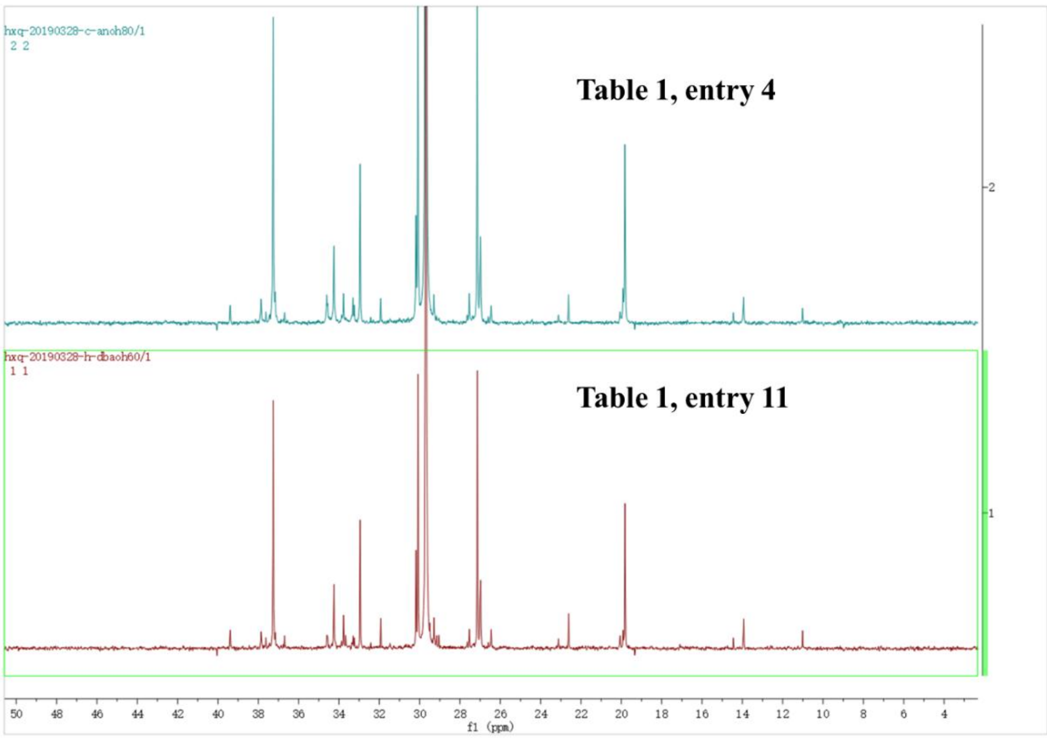


Figure S2. ^{13}C NMR spectra (400 MHz, $C_2D_2Cl_4$, 110 ℃) of the polymers from table 1, entries 4 and 11.

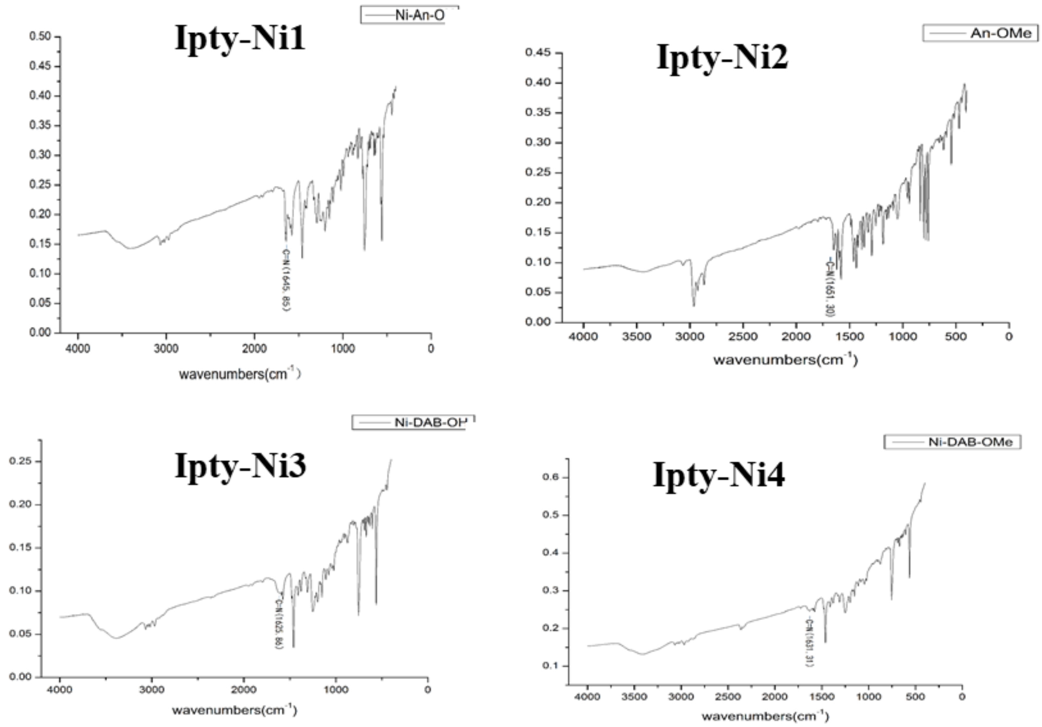
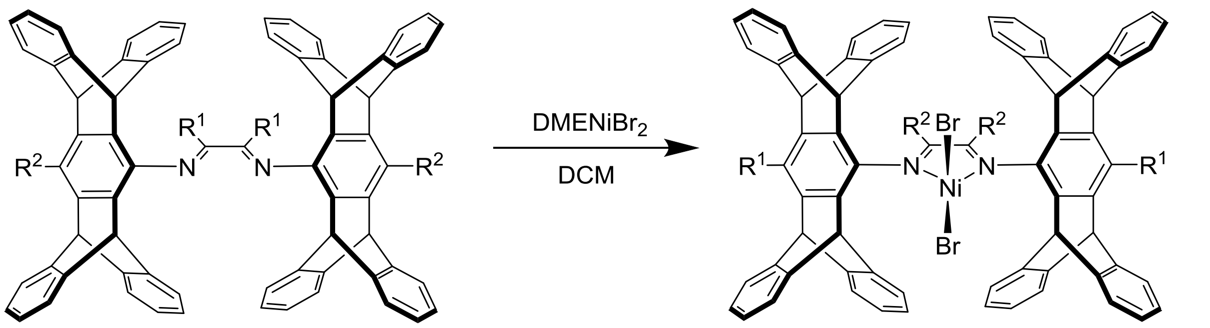


Figure S3. FT-IR spectra of the **Ipty-Ni1~4** complexes.

General Considerations: All experiments were carried out under a dry Nitrogen atmosphere using standard Schlenk techniques or in a glove-box. Deuterated solvents used for NMR were dried and distilled prior to use. ^{1}H, ^{13}C NMR spectra were recorded by a Bruker Ascend Tm 400 spectrometer at ambient temperature unless otherwise stated. The chemical shifts of the ^{1}H and ^{13}C NMR spectra were referenced to the residual solvent; Coupling constants are in Hz. Elemental analysis were performed at the National Analytical Research Centre of Changchun Institute of Applied Chemistry. 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 polymers with low solubility at room temperature were determined by gel permeation chromatography (GPC) with a PL 210 equipped with one Shodex AT-803S and two Shodex AT-806MS columns at 150 ^{o}C using trichlorobenzene as a solvent and calibrated with polystyrene standards. The molecular weight and the molecular weight distribution of the polymers with good solubility at room temperature were determined by gel permeation chromatography (GPC) equipped with two linear Styragel columns (HR2 and HR4) at 40 ℃ using THF as a solvent and calibrated with polystyrene standards, and THF was employed as the eluent at a flow rate of 1.0 mL/min. Melting points (T_m) of polyethylenes and copolymers were measured through DSC analyses, which were carried out under a nitrogen atmosphere at heating and cooling rates of 10 ℃/min.

Preparation of Ligands and Catalysts

The ligands (**Ipty-OH1**, **Ipty-OH3**, **Ipty-OMe2** and **Ipty-OMe4**) were prepared using literature procedure.[1] The ligand **Ph-L4** and the corresponding nickel complexes **Ph-Ni4** and the palladium complexes **Ph-Pd4** were previously reported by the Chen group.[2,3]



Ipty-Ni1: R^1 = OH, R^2 = acenaphthene
Ipty-Ni2: R^1 = OMe, R^2 = acenaphthene
Ipty-Ni3: R^1 = OH, R^2 = Me
Ipty-Ni4: R^1 = OMe, R^2 = Me

Preparation of Ipty-Ni complexes: The nickel complexes were prepared in a similar manner by the reaction of 0.2 mmol ligand with 1 equivalent $NiBr_2$(DME) in dichloromethane. After stirring overnight, the solvent was removed, and the brown solid powder was washed with ether (10 mL × 2) and dried under vacuum to give the corresponding nickel complexes.

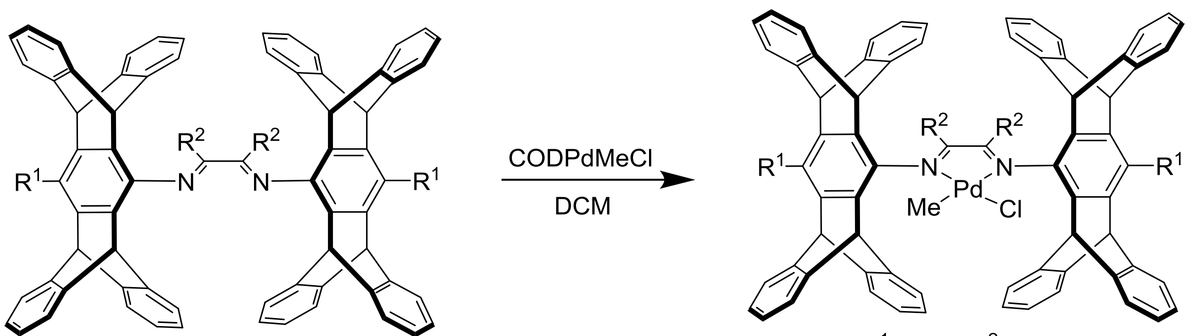
Ipty-Ni1: (0.206 g, 80%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 19.45 (s, 2H, C*H*Ar_3), 16.27 (s, 2H, C*H*Ar_3), 9.63 (s, 2H, O*H*). FT-IR: 1645.85 cm^{-1} (C=N). MALDI-TOF-MS (m/z): Calcd for $C_{80}H_{48}Br_2N_2NiO_2$: 1286.14; Found: 1207.17 [M-Br]$^+$. Elemental analysis: calc. For

$C_{80}H_{48}Br_2N_2NiO_2$ (1287.78 g mol^{-1}): C, 74.62; H, 3.76; N, 2.18. Found: C, 74.48; H, 3.74; N, 2.23.

Ipty-Ni2: (0.221 g, 84%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 17.93 (s, 2H, C*H*Ar$_3$), 15.46 (s, 2H, C*H*Ar$_3$), 4.26 (s, 6H, O*Me*). FT-IR: 1651.30 cm^{-1} (C=N) MALDI-TOF-MS (m/z): Calcd for $C_{82}H_{52}Br_2N_2NiO_2$: 1314.17; Found: 1235.20 [M-Br]$^+$. Elemental analysis: calc. For $C_{82}H_{52}Br_2N_2NiO_2$ (1315.83 g mol^{-1}): C, 74.85; H,3.98; N, 2.13. Found: C, 74.59; H, 3.89; N, 2.07.

Ipty-Ni3: (0.195 g, 83%). ^{1}H NMR (300 MHz, THF-*d*$_8$) δ 12.82 (s, 2H, O*H*), -20.53 (s, 6H, C*H*$_3$). FT-IR: 1625.86 cm^{-1} (C=N) MALDI-TOF-MS (m/z): Calcd for $C_{72}H_{48}Br_2N_2NiO_2$: 1190.14; Found: 1111.19 [M-Br]$^+$. Elemental analysis: calc. For $C_{72}H_{48}Br_2N_2NiO_2$ (1191.69 g mol^{-1}): C, 72.57; H, 4.06; N, 2.35. Found: C, 72.29; H, 3.89; N, 2.23.

Ipty-Ni4: (0.207 g, 85%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 17.28 (d, *J* = 6.8 Hz, 4H, C*H*Ar$_3$), -15.91 (s, 6H, C*H*$_3$). FT-IR: 1631.31 cm^{-1} (C=N). MALDI-TOF-MS (m/z): Calcd for $C_{74}H_{52}Br_2N_2NiO_2$: 1218.17; Found: 1139.02 [M-Br]$^+$. Elemental analysis: calc. For $C_{74}H_{52}Br_2N_2NiO_2$ (1219.74 g mol^{-1}): C, 72.87; H, 4.30; N, 2.30. Found: C, 72.99; H, 4.39; N, 2.17.



Ipty-Pd1: R^1 = OH, R^2 = acenaphthene
Ipty-Pd2: R^1 = OMe, R^2 = acenaphthene
Ipty-Pd3: R^1 = OH, R^2 = Me
Ipty-Pd4: R^1 = OMe, R^2 = Me

Preparation of Ipty-Pd complexes: To a solution of ligand (1 mmol) in dry CH_2Cl_2 (40 mL) was added 265 mg (1 mmol) of PdMeCl(COD). After stirring the mixture for 3 days at room temperature, Complex **Ipty-Pd2** was isolated using column chromatography. The mixture was eluted on silica gel with first 1:1 hexanes/CH_2Cl_2 then pure CH_2Cl_2 as the mobile phase. The pure complex **Ipty-Pd2** was obtained as an orange solid. Complexes **Ipty-Pd1, Ipty-Pd3, Ipty-Pd4** was isolated by filtration, washed three times by 20 mL CH_2Cl_2 to remove the excess PdMeCl(COD) and ligand. The pure compound was obtained as an orange or yellow solid. Complexes **Ipty-Pd1, Ipty-Pd3, Ipty-Pd4** have poor solubility in almost all solvents, so the ^{13}C NMR spectrum of these complexes can't be collected.

Ipty-Pd1: (0.91 g, 74%). ^{1}H NMR (400 MHz, DMSO) δ 9.81 (s, 2H, O*H*), 7.99 (d, *J* = 8.2 Hz, 2H, Ar-*H*), 7.62 (d, *J* = 7.0 Hz, 4H, Ar-*H*), 7.50 (d, *J* = 5.5 Hz, 4H, Ar-*H*), 7.44 (d, *J* = 7.1 Hz, 4H, Ar-*H*), 7.10-7.00 (m, 8H, Ar-*H*), 6.85 (d, *J* = 6.9 Hz, 4H, Ar-*H*), 6.72 – 6.43 (m, 10H, Ar-

H), 6.14 (s, 4H, C*H*Ar$_3$), 5.92 (s, 4H, C*H*Ar$_3$), 5.18 (s, 2H, Ar-*H*), 0.98 (s, 3H, Pd-*Me*). Elemental analysis: calc. For $C_{81}H_{51}ClN_2O_2Pd$ (1226.18 g mol^{-1}): C, 79.34; H, 4.19; N, 2.28. Found: C, 79.57; H, 4.25; N, 2.36. MALDI-TOF-MS (m/z): Calcd for $C_{81}H_{51}ClN_2O_2Pd$: 1224.27; Found: 1175.73 [M-Me-Cl]$^+$.

Ipty-Pd2: (1.18 g, 94%). ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.83 – 7.56 (m, 4H，Ar-*H*), 7.51 – 7.27 (m, 10H, Ar-*H*), 7.08-6.97 (m, 8H, Ar-*H*), 6.86 – 6.68 (m, 4H, Ar-*H*), 6.54-6.37 (m, 10H, Ar-*H*), 5.89-5.76 (m, 8H, C*H*Ar$_3$), 5.13 (d, *J* = 7.2 Hz, 1H, Ar-*H*), 5.07 (d, *J* = 7.2 Hz, 1H, Ar-*H*), 4.14 (s, 6H, O*Me*), 0.76 (s, 3H, Pd-*Me*). ^{13}C NMR (101 MHz, CDCl$_3$) δ 173.57 (*C*=N-Ar), 170.16 (*C*=N-Ar), 149.32 (*C*-OMe), 149.04 (*C*-OMe), 145.70, 145.10, 145.05, 144.52, 144.22, 144.01, 143.87, 143.64, 137.54, 136.78, 136.21, 135.48, 128.19, 125.90, 125.83, 125.69, 125.35, 125.15, 124.84, 124.75, 124.49, 123.81, 123.68, 123.47, 123.29, 123.03, 122.75, 63.49 (O*Me*), 63.44 (O*Me*), 50.11 (*C*HAr$_3$), 49.68 (*C*HAr$_3$), 4.26 (Pd-*Me*). Elemental analysis: calc. For $C_{83}H_{55}ClN_2O_2Pd$ (1252.30 g mol^{-1}): C, 79.48; H, 4.42; N, 2.23. Found: C, 79.34; H, 4.36; N, 2.52. MALDI-TOF-MS (m/z): Calcd for $C_{83}H_{55}ClN_2O_2Pd$: 1252.30; Found: 1204.09 [M-Me-Cl]$^+$.

Ipty-Pd3: (0.54 g, 48%). ^{1}H NMR (400 MHz, DMSO) δ 9.24 (s, 2H, O*H*), δ 7.52 – 7.30 (m, 16H, Ar-*H*), 7.08 –6.90 (m, 16H, Ar-*H*), 6.04 (s, 4H, C*H*Ar$_3$), 5.38 (s, 4H, C*H*Ar$_3$), 2.05 (s, 6H, *Me*-C=N), 0.97 (s, 3H, Pd-*Me*). Elemental analysis: calc. For $C_{73}H_{51}ClN_2O_2Pd$ (1128.27 g mol^{-1}): C, 77.59; H, 4.55; N, 2.48. Found: C, 77.76; H, 4.45; N, 2.43. MALDI-TOF-MS (m/z): Calcd for $C_{73}H_{51}ClN_2O_2Pd$: 1128.27; Found: 1079.79 [M-Me-Cl]$^+$.

Ipty-Pd4: (0.74 g, 64%). ^{1}H NMR (400 MHz, DMSO) δ 7.52 (s, 12H, Ar-*H*), 7.39 (d, *J* = 6.0 Hz, 4H, Ar-*H*), 7.20 – 6.88 (m, 16H, Ar-*H*), 5.91 (s, 4H, C*H*Ar$_3$), 5.44 (s, 4H, C*H*Ar$_3$), 3.93 (s, 6H, O*Me*), 2.08 (s, 6H, *Me*-C=N), 0.96 (s, 3H, Pd-*Me*). Elemental analysis: calc. For $C_{75}H_{55}ClN_2O_2Pd$ (1158.15 g mol^{-1}): C, 77.78; H, 4.79; N, 2.42. Found: C, 77.65; H, 4.66; N, 2.36. MALDI-TOF-MS (m/z): Calcd for $C_{75}H_{55}ClN_2O_2Pd$: 1156.30; Found: 1108.03 [M-Me-Cl]$^+$.

A general procedure for the homopolymerization of ethylene using Ipty-Ni complexes.

In a typical experiment, a 300 mL stainless pressure reactor connected with a high pressure gas line was firstly dried at 90 ℃ under vacuum for at least 1 h. The reactor was then adjusted to the desired polymerization temperature. 20 mL of toluene and the desired amount MAO was added to the reactor under N_2 atmosphere, then the desired amount of catalyst in 1 mL of CH_2Cl_2 was injected into the polymerization system via syringe. With a rapid stirring, the reactor was pressurized and maintained at 6 atm of ethylene. After 30 min, the pressure reactor was vented and the polymer was precipitated in ethanol, filtered and dried at 50 ℃ for at least 24 h under vacuum.

A general procedure for the homopolymerization of ethylene using Ipty-Pd complexes.

In a typical experiment, a 300 mL stainless pressure reactor connected with a high pressure gas line was firstly dried at 90 ℃ under vacuum for at least 1 h. The reactor was then adjusted to the desired polymerization temperature. 38 mL of DCM and the desired amount NaBArF was added to the reactor under N_2 atmosphere, then the desired amount of catalyst in 2 mL of CH_2Cl_2

was injected into the polymerization system via syringe. With a rapid stirring, the reactor was pressurized and maintained at 4 atm of ethylene. After 12 h, the pressure reactor was vented and the polymer was dried under vacuum overnight.

A general procedure for the copolymerization of polar monomer with ethylene using Ipty-Pd complexes.

In a typical experiment, a 300 mL stainless pressure reactor connected with a high pressure gas line was firstly dried at 90 ℃ under vacuum for at least 1 h. The reactor was then adjusted to the desired polymerization temperature. 18 mL of DCM with the desired amount NaBArF was added to the reactor under N_2 atmosphere, then the desired polar monomer and the desired amount of Pd catalyst in 2 mL of CH_2Cl_2 was injected into the polymerization system via syringe subsequently. With a rapid stirring, the reactor was pressurized and maintained at the desired pressure of ethylene. After 12 h, the pressure reactor was vented and the copolymer was dried under vacuum overnight.

NMR figures of ligands and catalysts

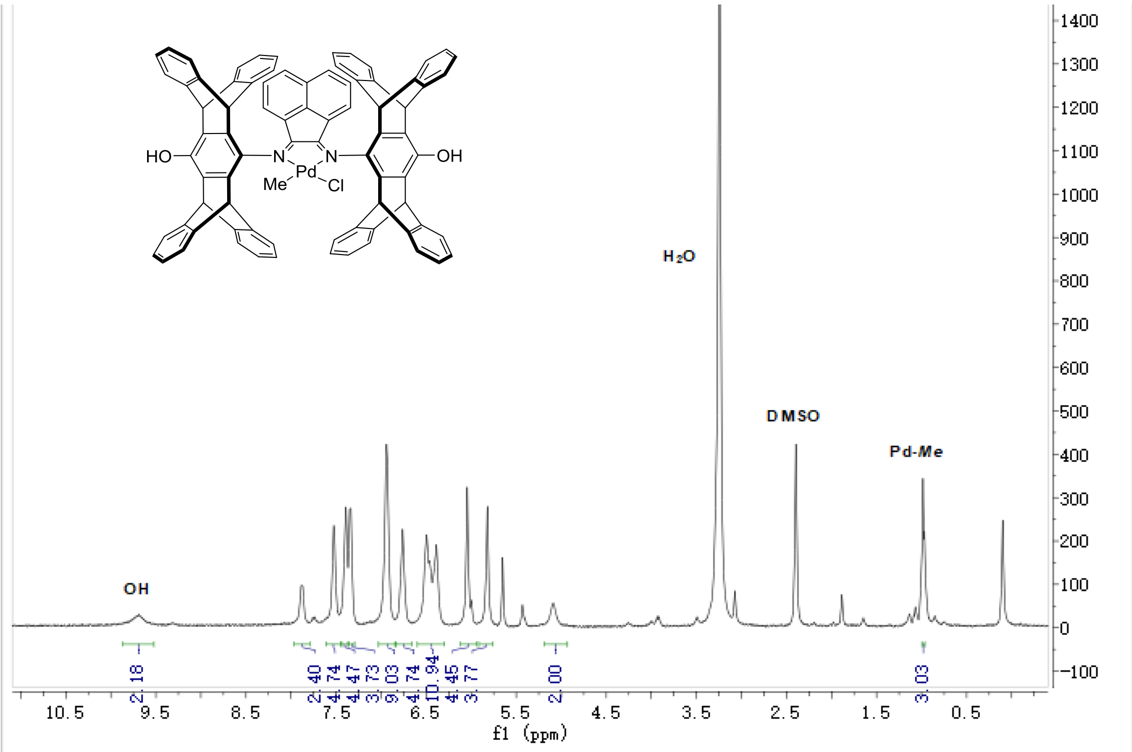


Figure S4. ¹H NMR spectrum (400 MHz, $CDCl_3$) of **Ipty-Pd1**.

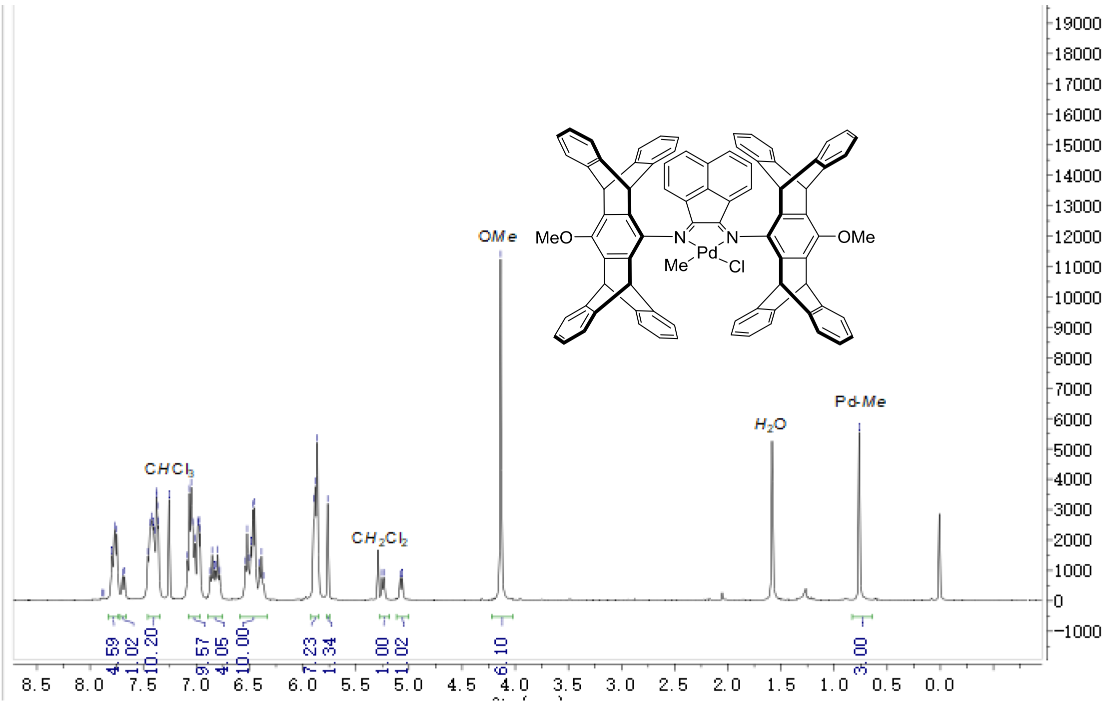


Figure S5. ¹H NMR spectrum (400 MHz, $CDCl_3$) of **Ipty-Pd2**.

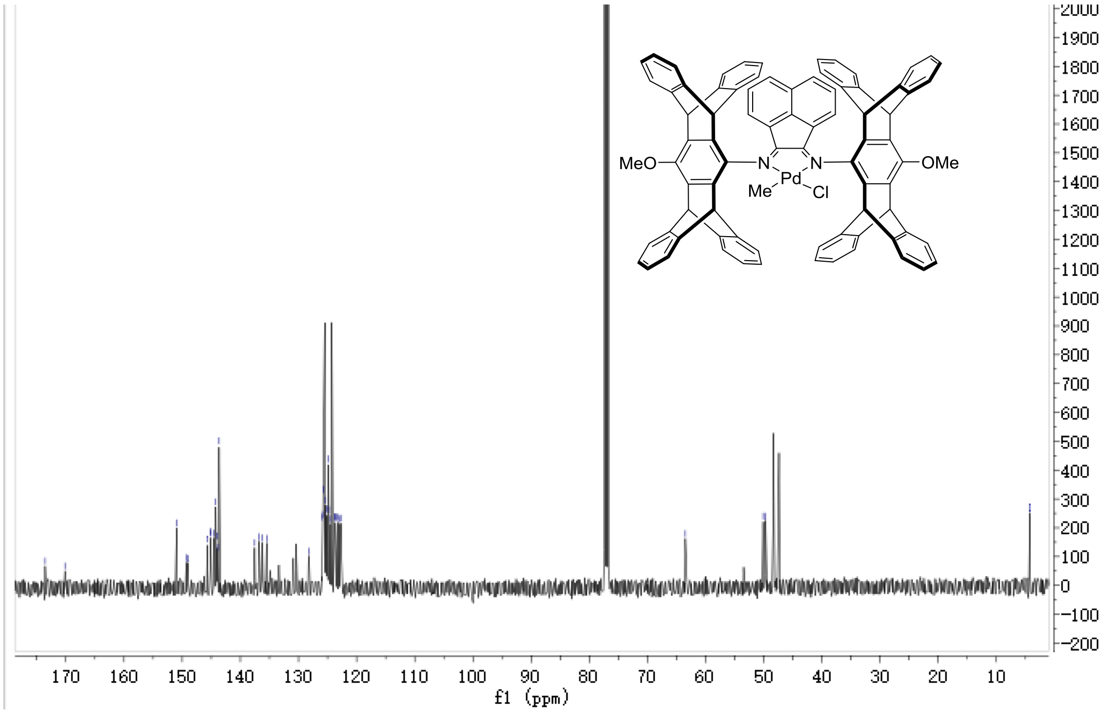


Figure S6. ^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **Ipty-Pd2**.

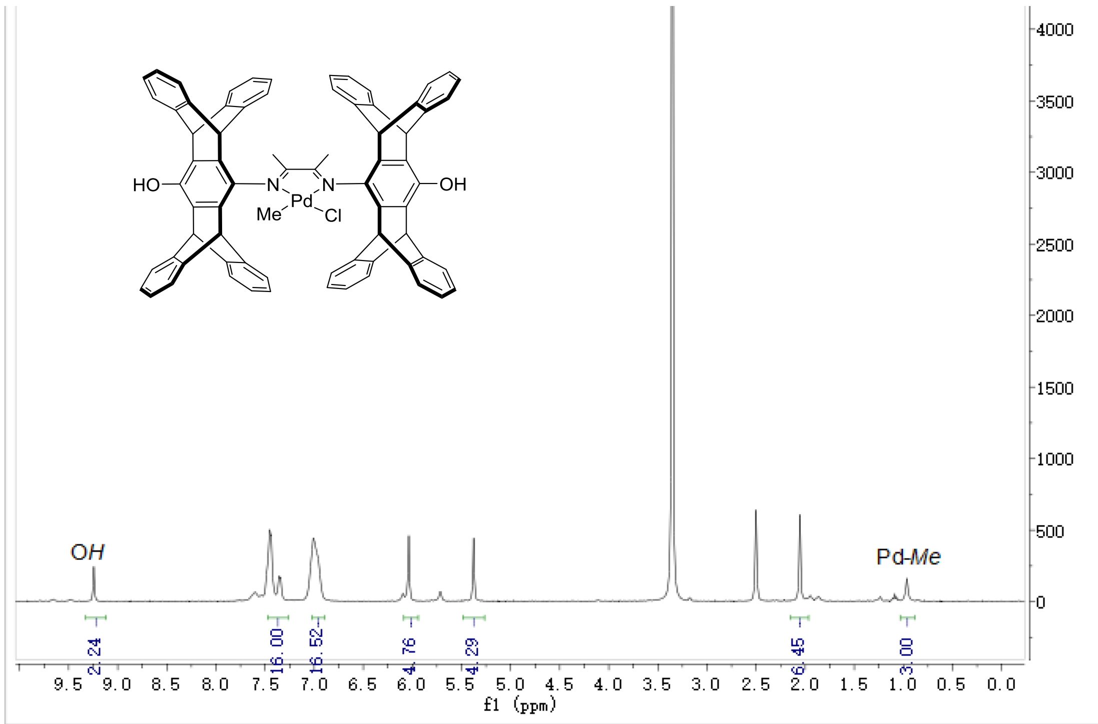


Figure S7. ^{1}H NMR spectrum (400 MHz, DMSO) of **Ipty-Pd3**.

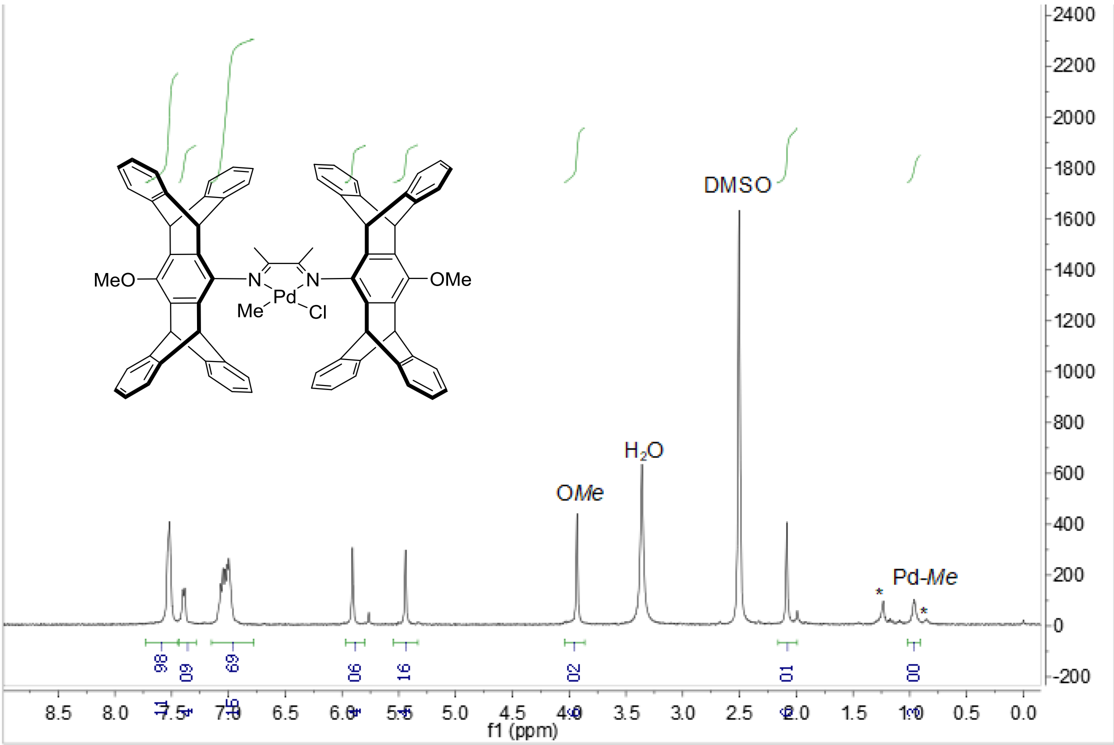


Figure S8. [1]H NMR spectrum (400 MHz, DMSO) of **Ipty-Pd4**.

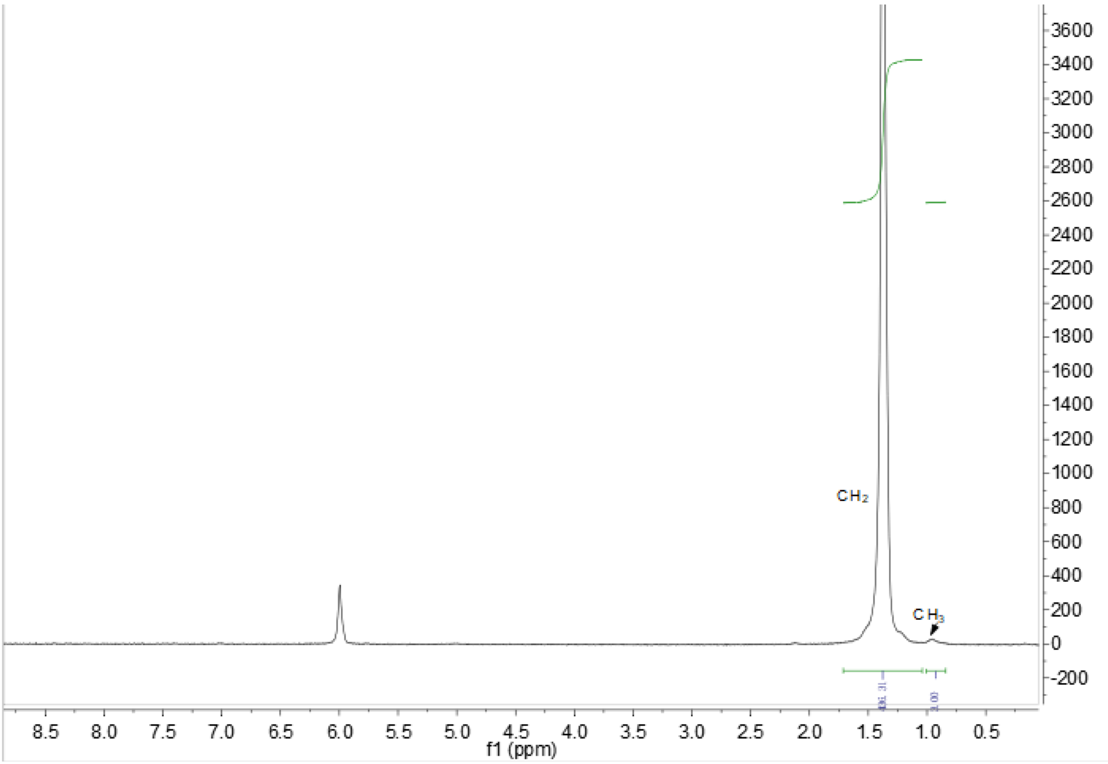


Figure S9. [1]H NMR spectrum (400 MHz, $C_2D_2Cl_4$, 120 ℃) of the polymer from table 1, entry 1.

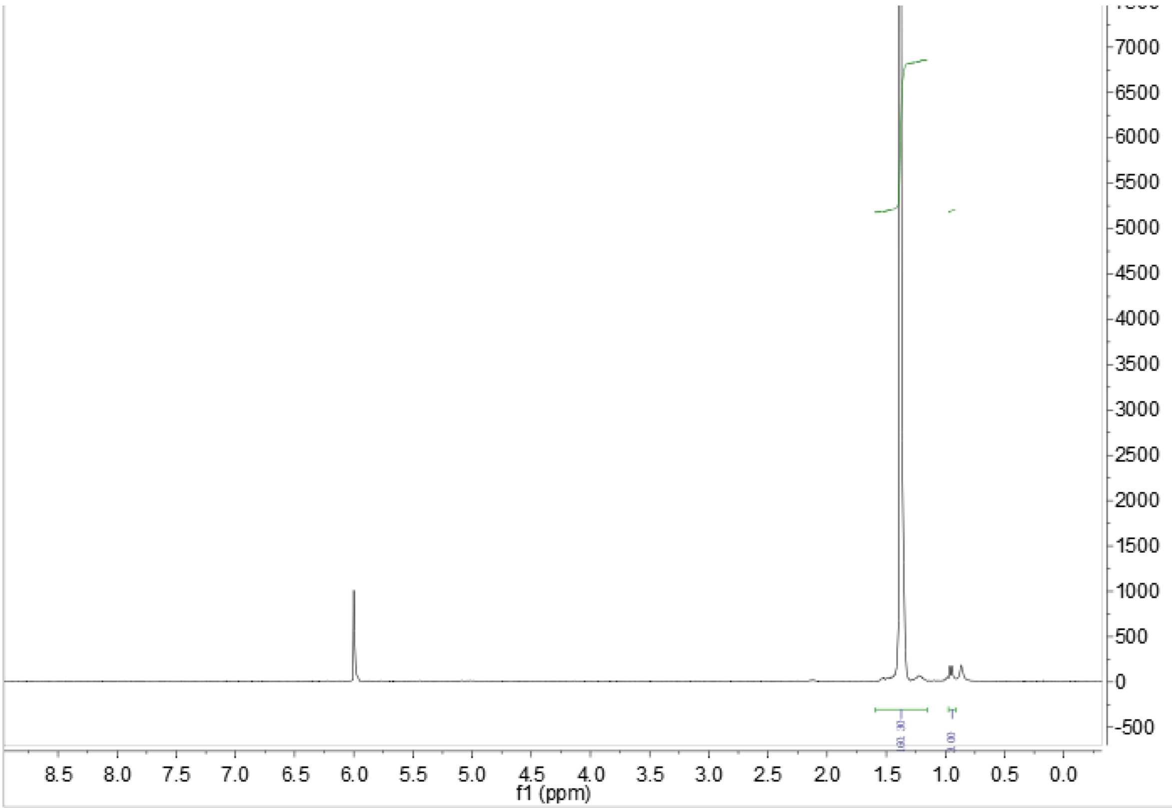


Figure S10. [1]H NMR spectrum (400 MHz, $C_2D_2Cl_4$, 120 ℃) of the polymer from table 1, entry 2.

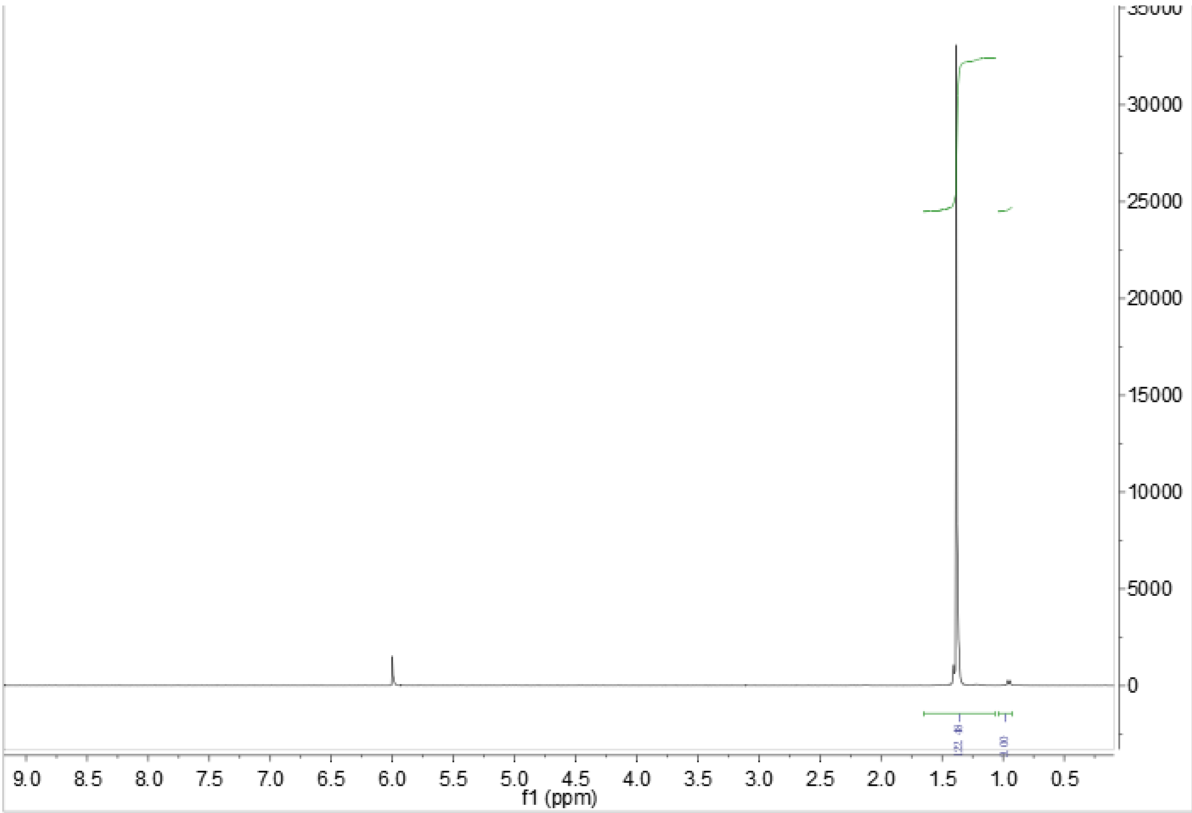


Figure S11. [1]H NMR spectrum (400 MHz, $C_2D_2Cl_4$, 120 ℃) of the polymer from table 1, entry 3.

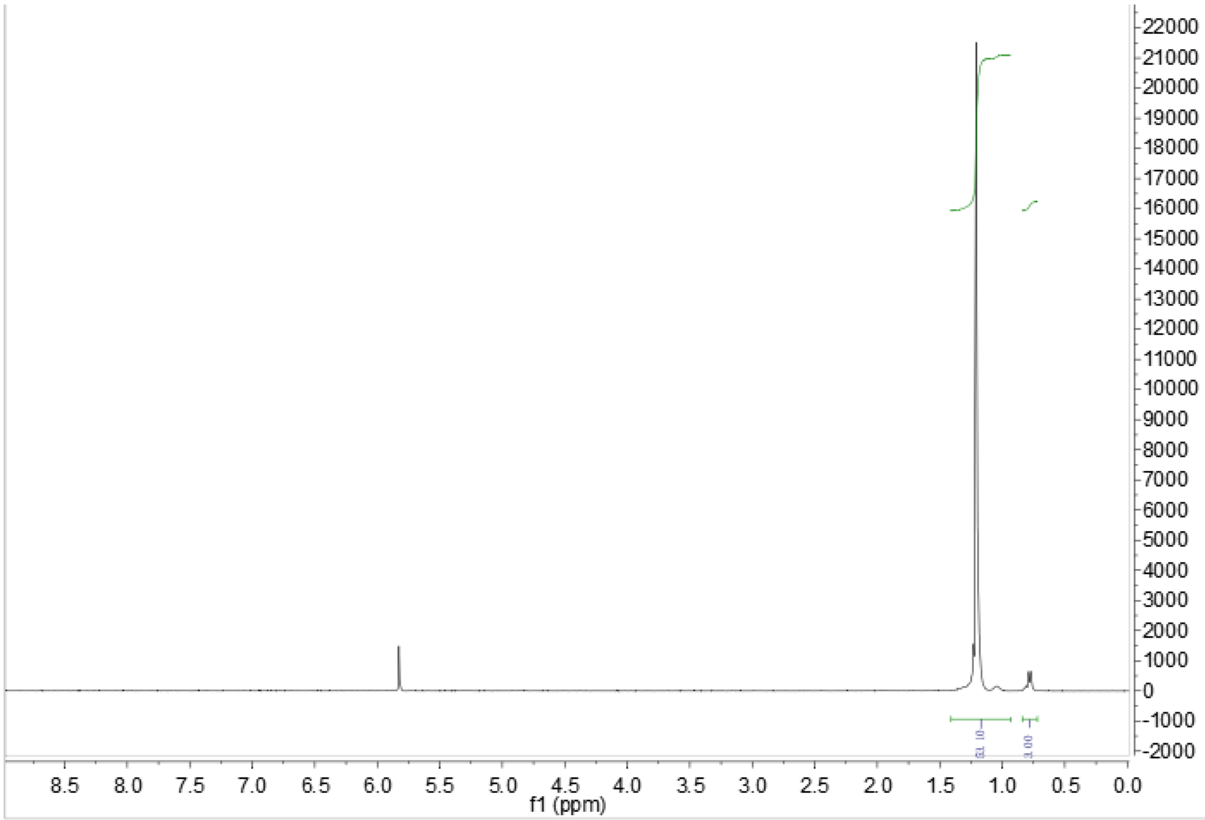


Figure S12. [1]H NMR spectrum (400 MHz, $C_2D_2Cl_4$, 120 ℃) of the polymer from table 1, entry 4.

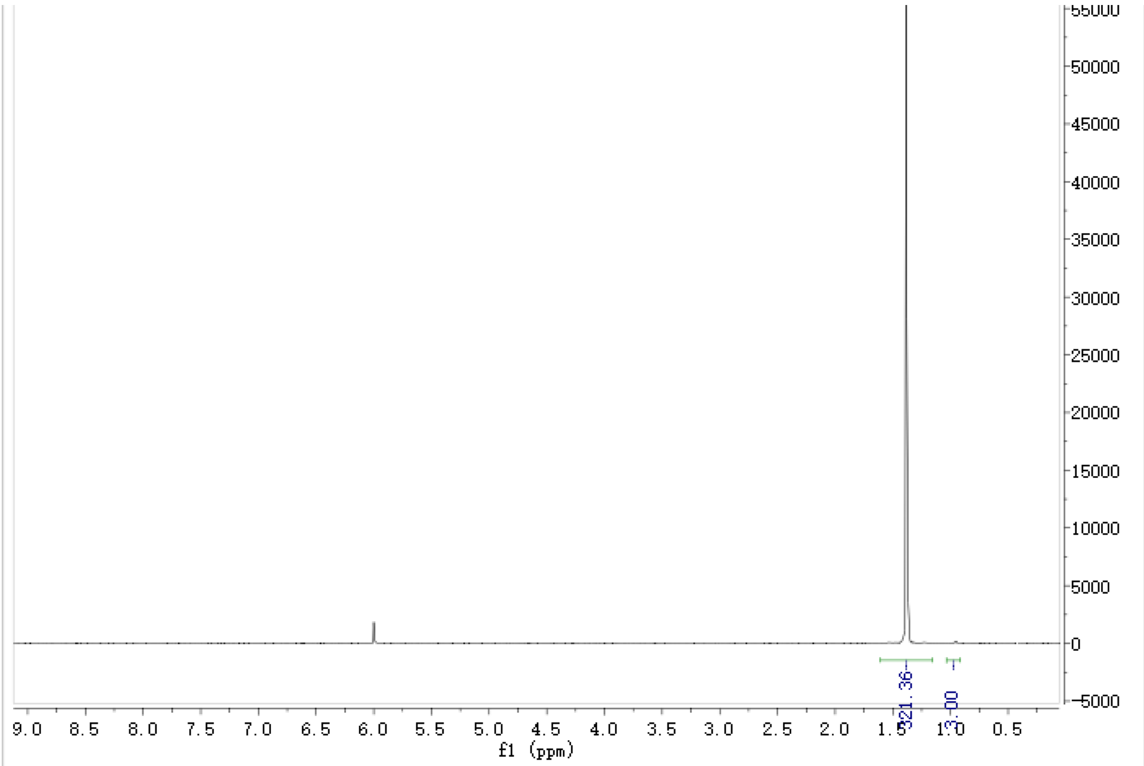


Figure S13. [1]H NMR spectrum (400 MHz, $C_2D_2Cl_4$, 120 ℃) of the polymer from table 1, entry 5.

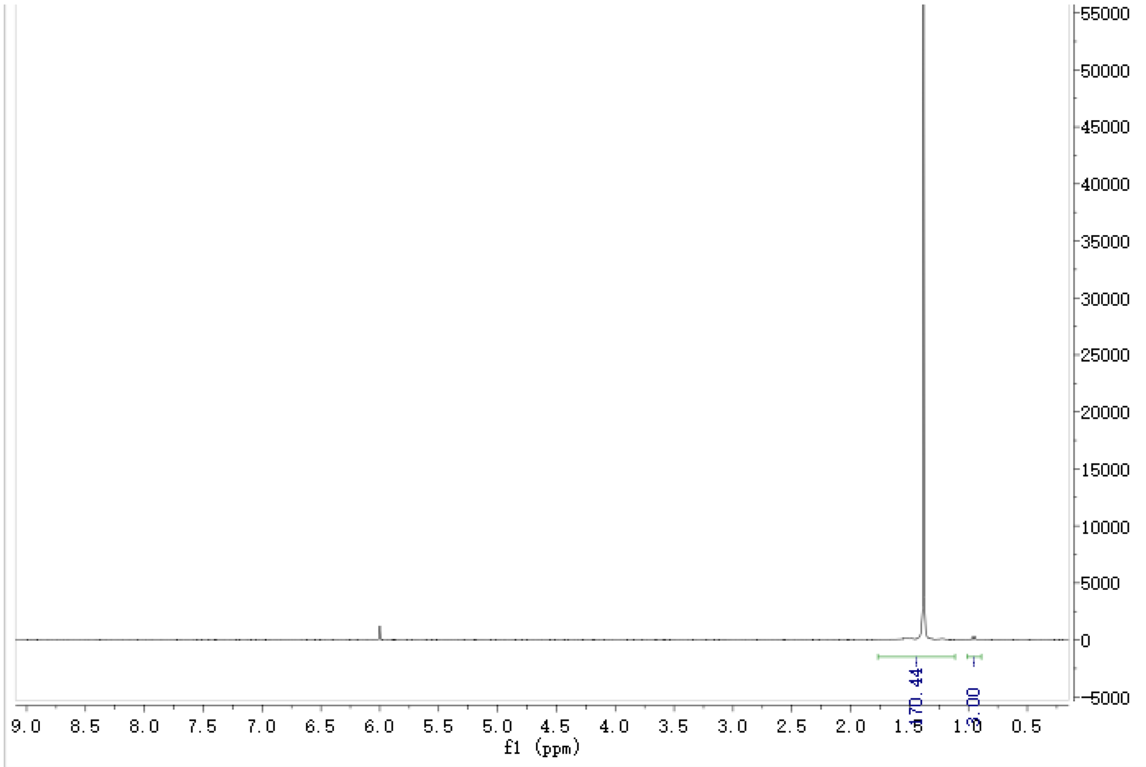


Figure S14. [1]H NMR spectrum (400 MHz, $C_2D_2Cl_4$, 120 ℃) of the polymer from table 1, entry 6.

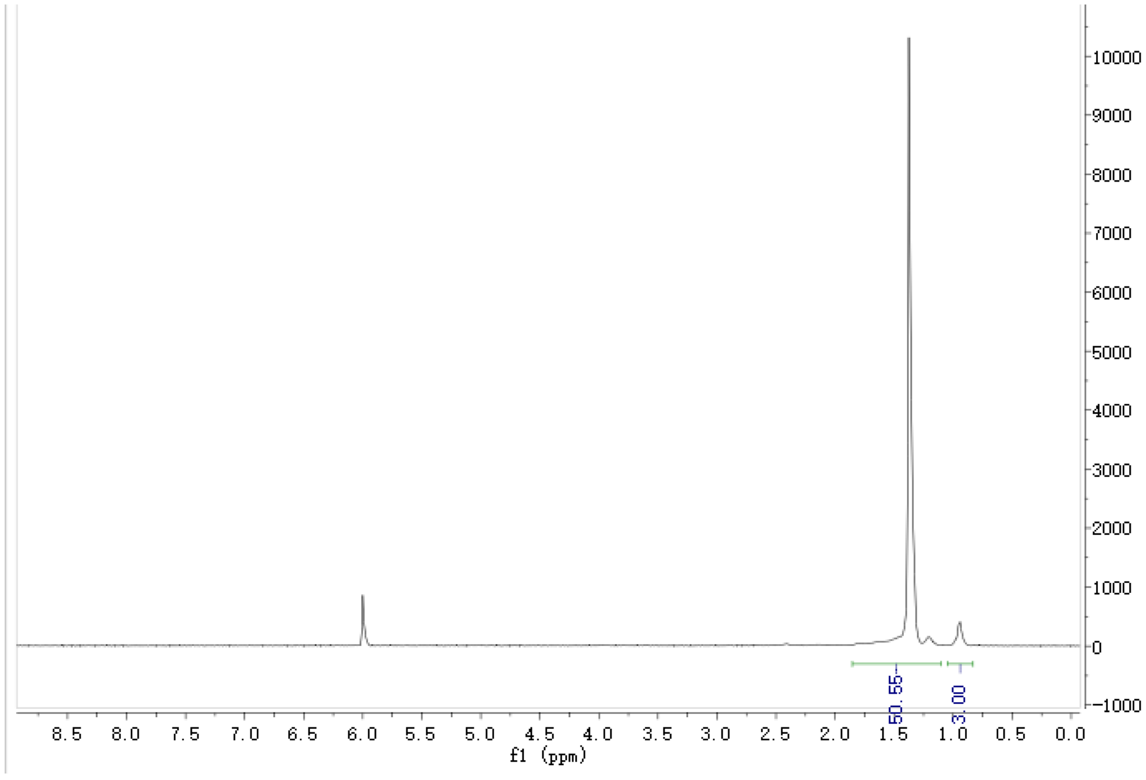


Figure S15. [1]H NMR spectrum (400 MHz, $C_2D_2Cl_4$, 120 ℃) of the polymer from table 1, entry 8.

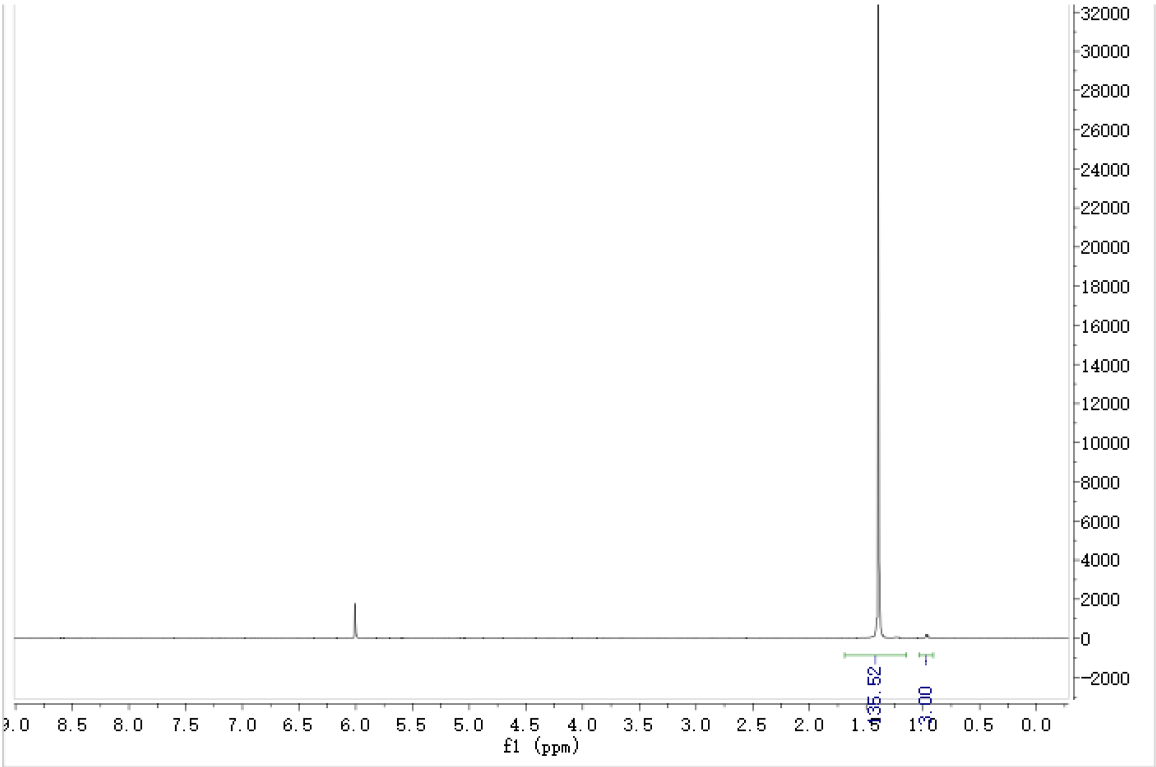


Figure S16. [1]H NMR spectrum (400 MHz, $C_2D_2Cl_4$, 120 ℃) of the polymer from table 1, entry 9.

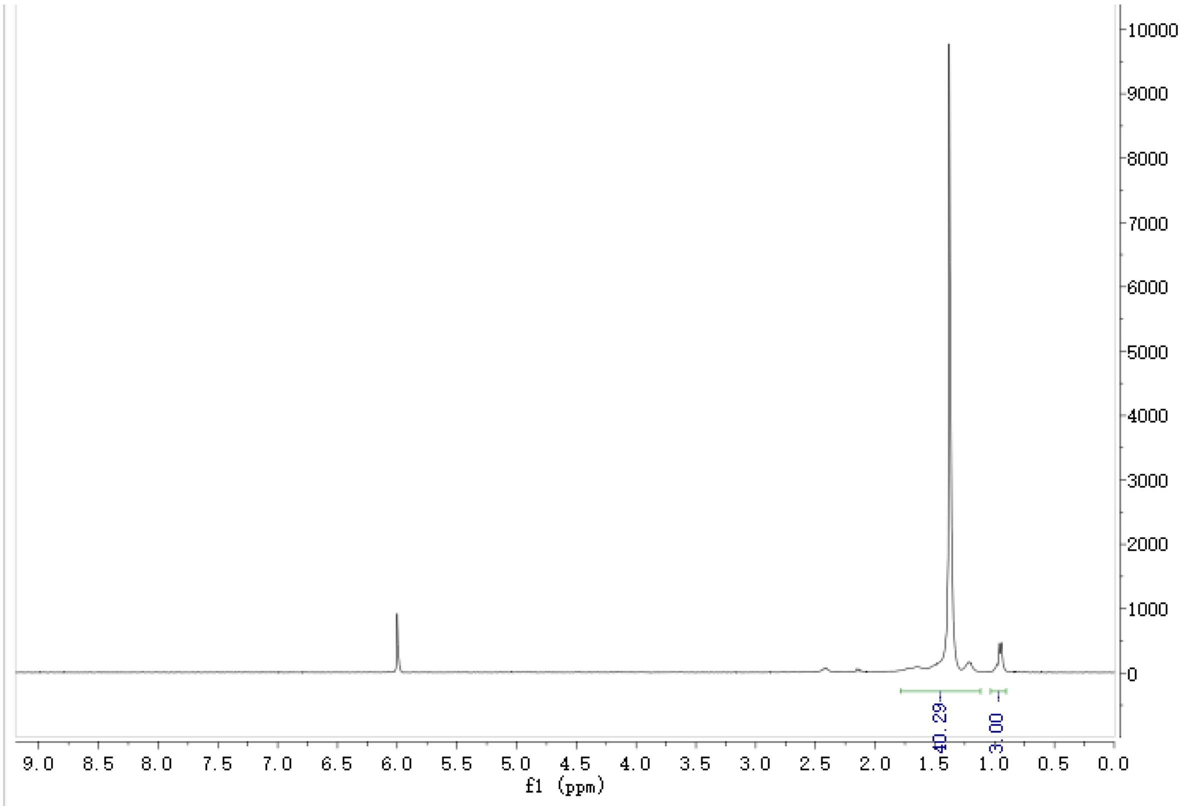


Figure S17. [1]H NMR spectrum (400 MHz, $C_2D_2Cl_4$, 120 ℃) of the polymer from table 1, entry 12.

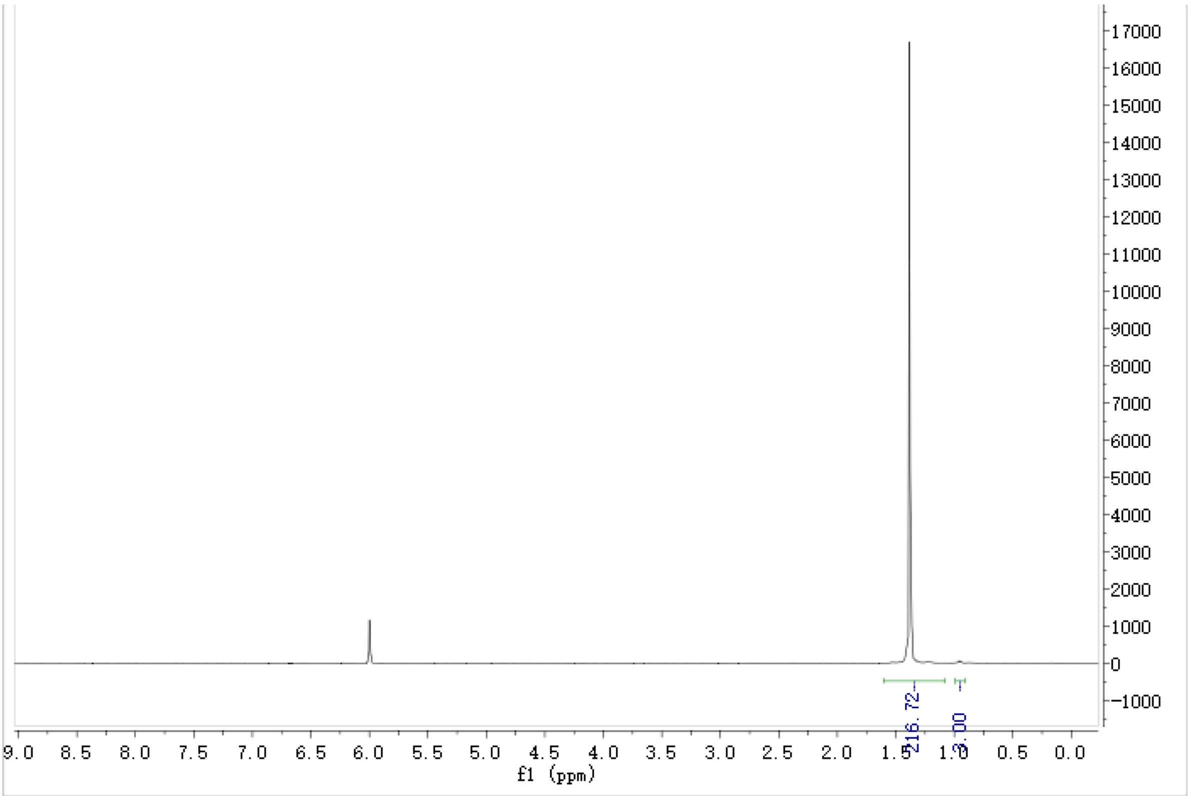


Figure S18. [1]H NMR spectrum (400 MHz, $C_2D_2Cl_4$, 120 ℃) of the polymer from table 1, entry 13.

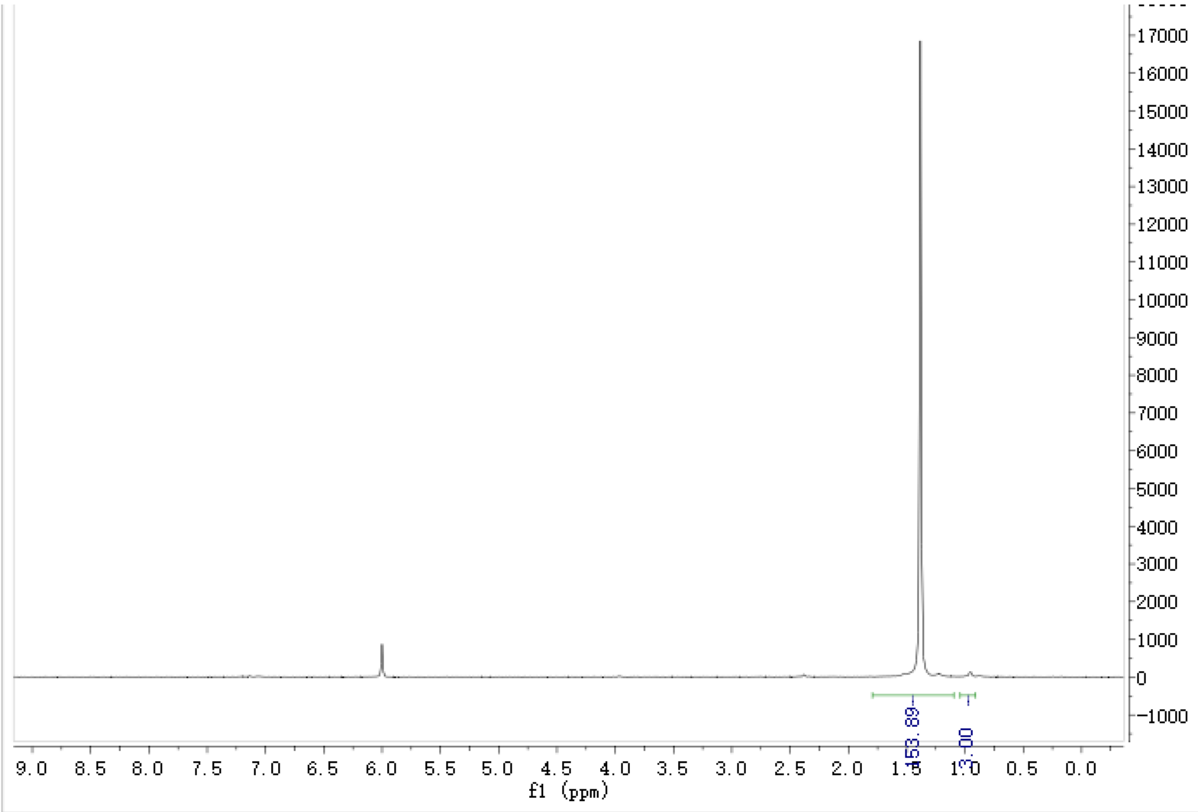


Figure S19. [1]H NMR spectrum (400 MHz, $C_2D_2Cl_4$, 120 ℃) of the polymer from table 1, entry 14.

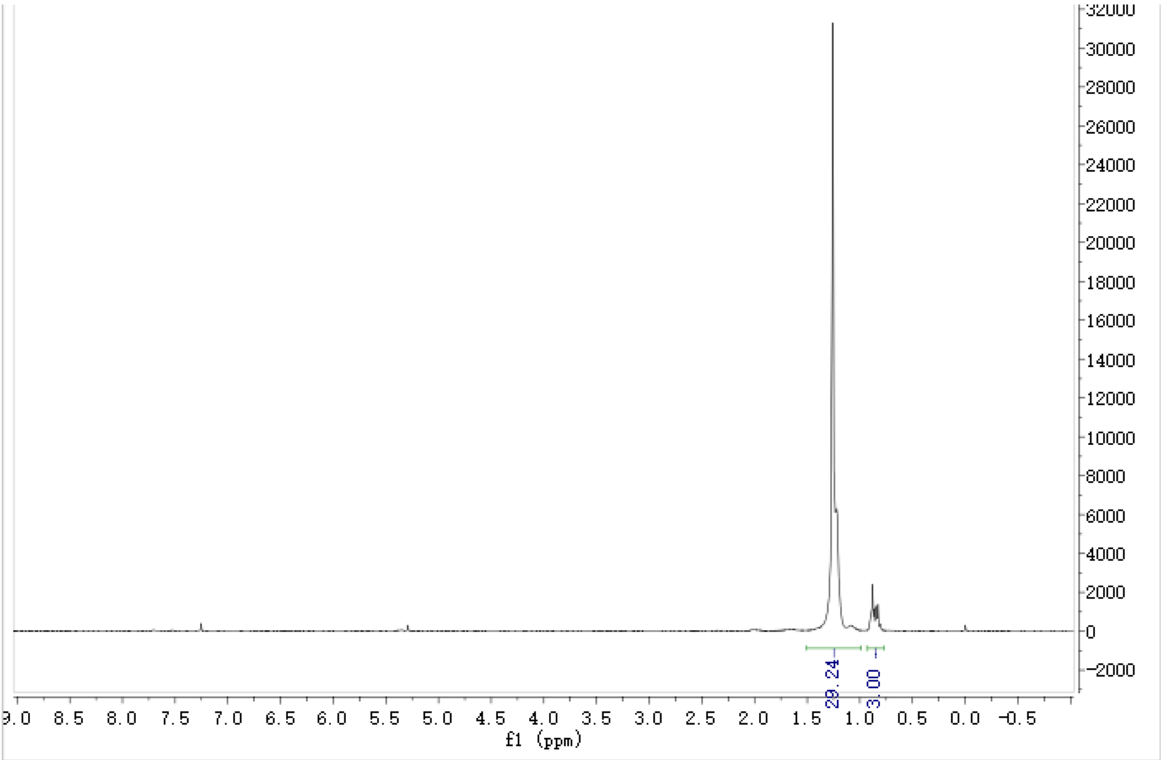


Figure S20. [1]H NMR spectrum (400 MHz, $CDCl_3$, 20 ℃) of the polymer from table 2, entry 1.

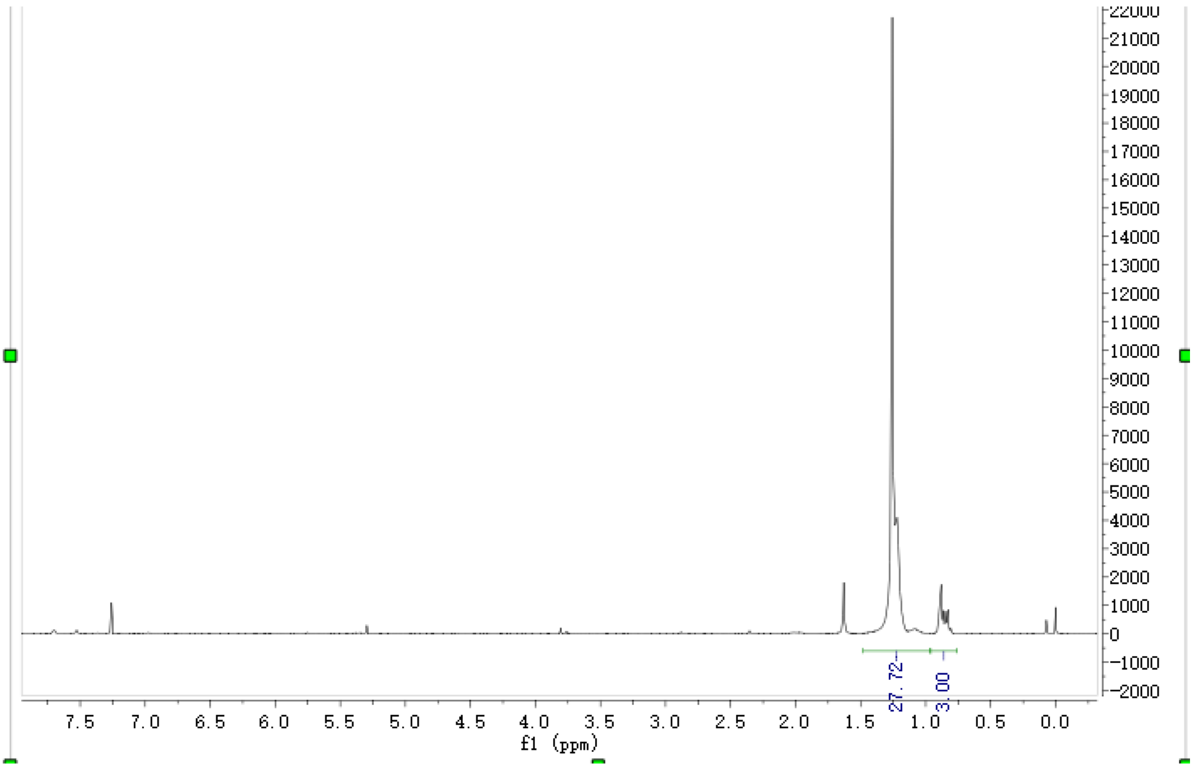


Figure S21. [1]H NMR spectrum (400 MHz, $CDCl_3$, 20 ℃) of the polymer from table 2, entry 2.

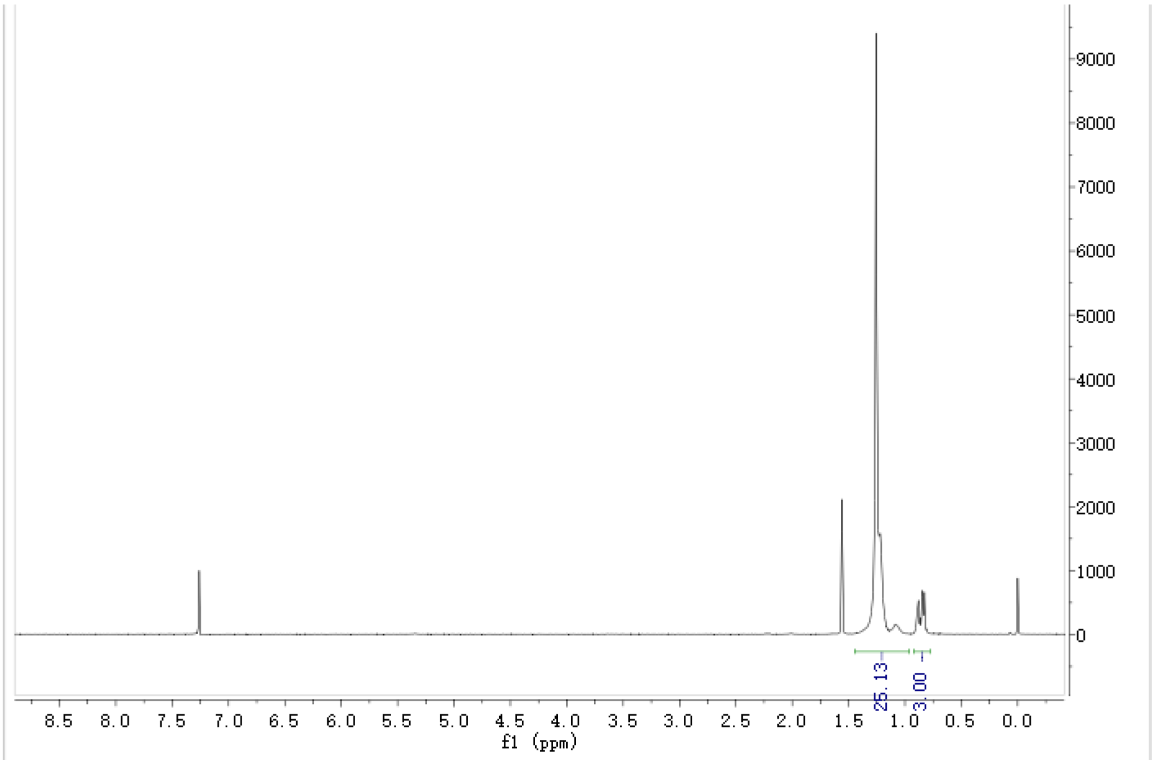


Figure S22. [1]H NMR spectrum (400 MHz, $CDCl_3$, 20 ℃) of the polymer from table 2, entry 3.

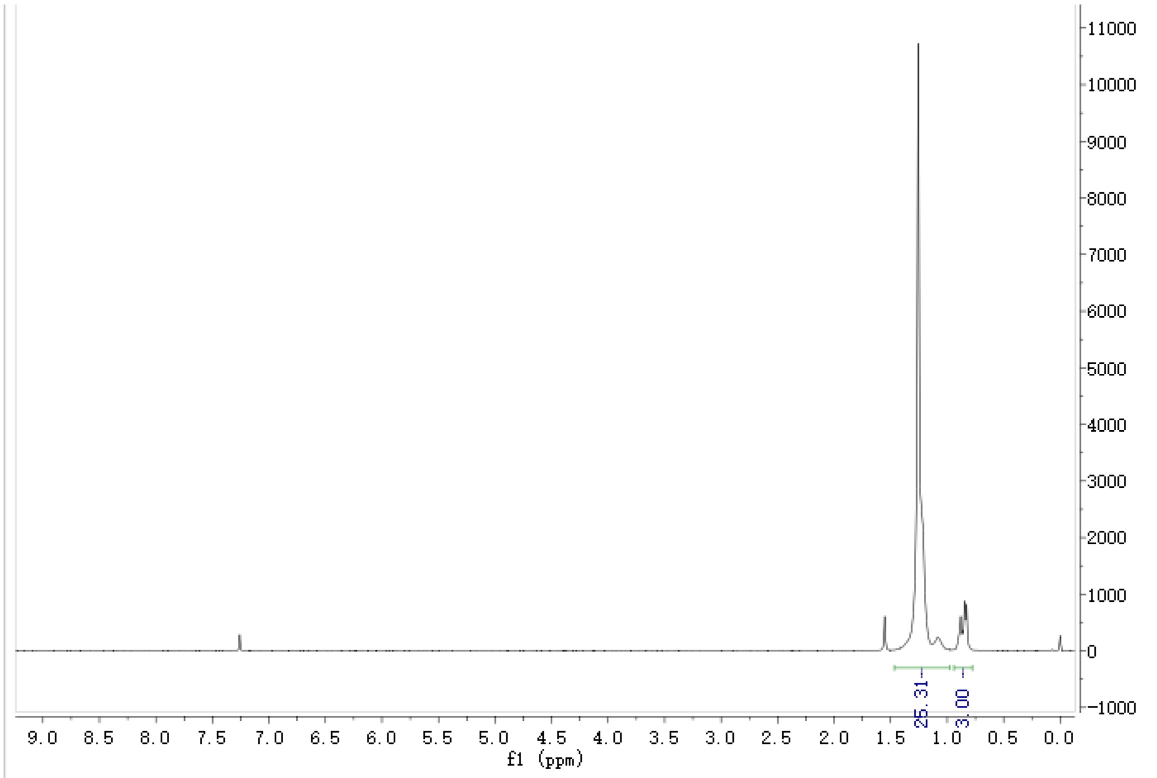


Figure S23. [1]H NMR spectrum (400 MHz, $CDCl_3$, 20 ℃) of the polymer from table 2, entry 4.

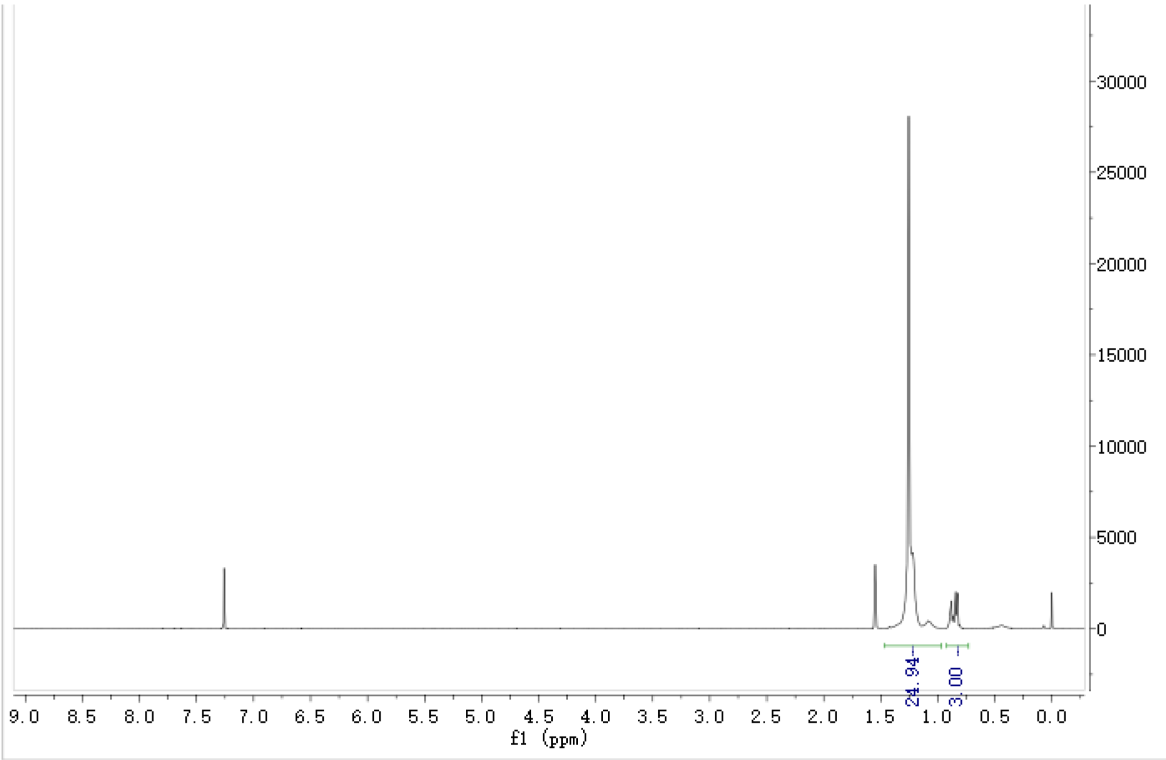
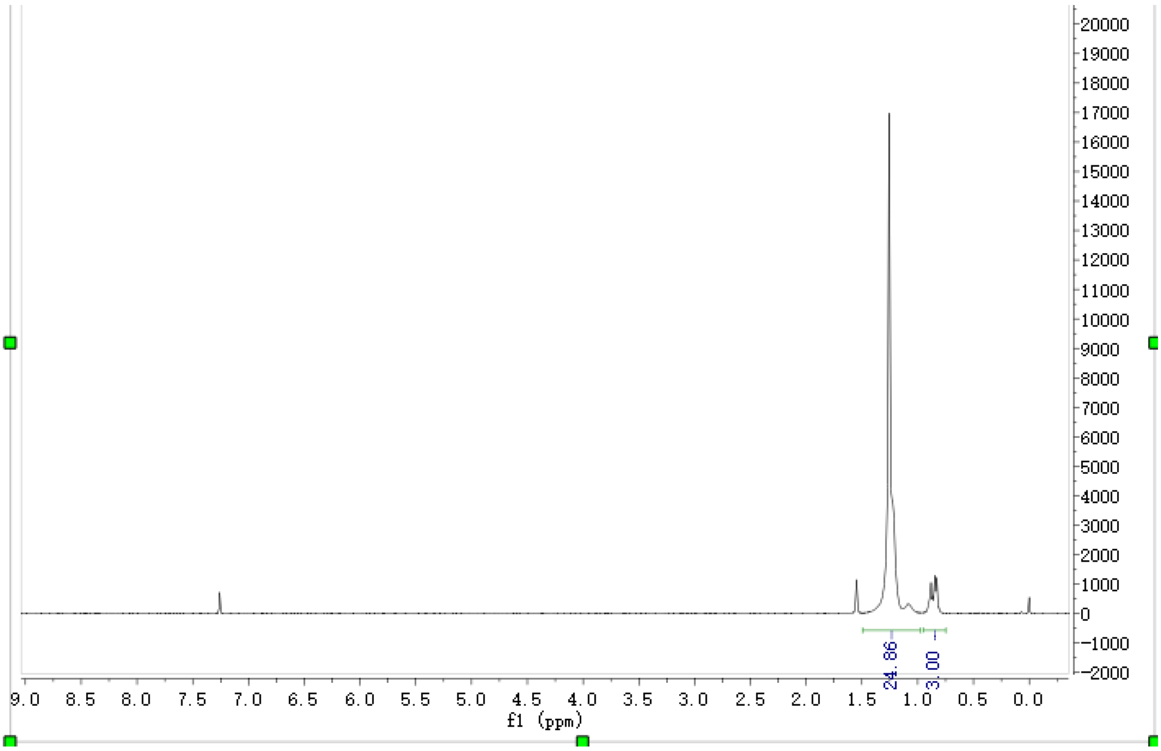


Figure S24. [1]H NMR spectrum (400 MHz, $CDCl_3$, 20 ℃) of the polymer from table 2, entry 5



.

Figure S25. [1]H NMR spectrum (400 MHz, $CDCl_3$, 20 ℃) of the polymer from table 2, entry 6.

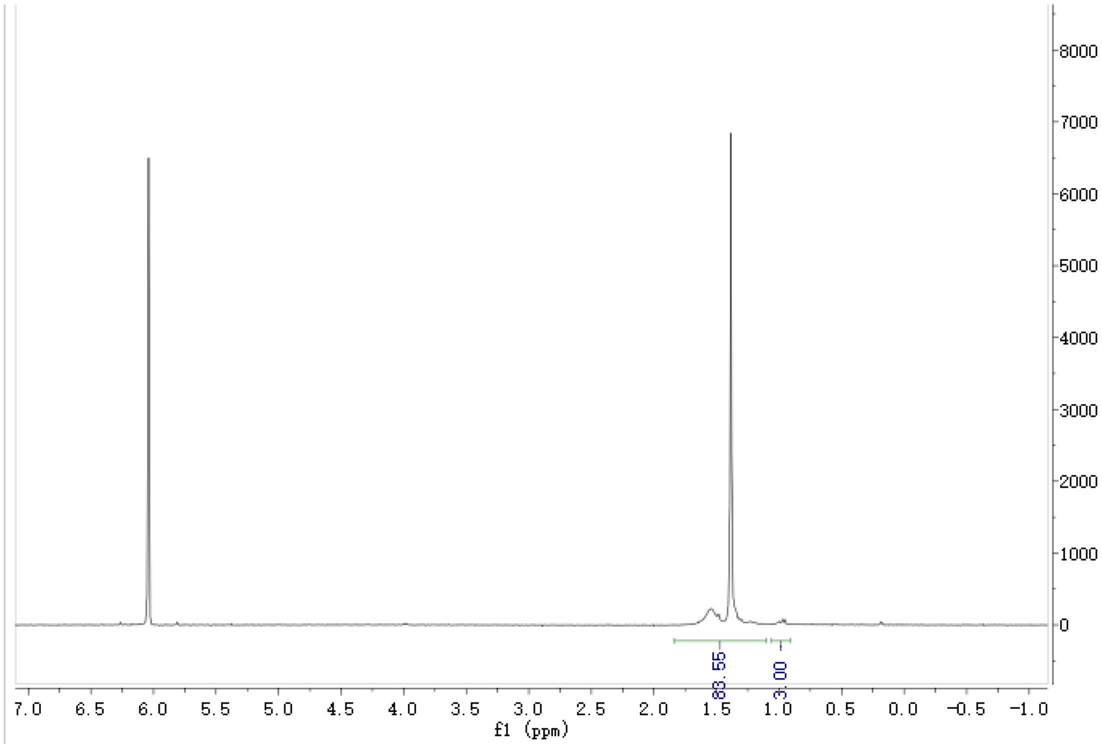


Figure S26. ^{1}H NMR spectrum (400 MHz, $C_2D_2Cl_4$, 120 ℃) of the polymer from table 2, entry 7.

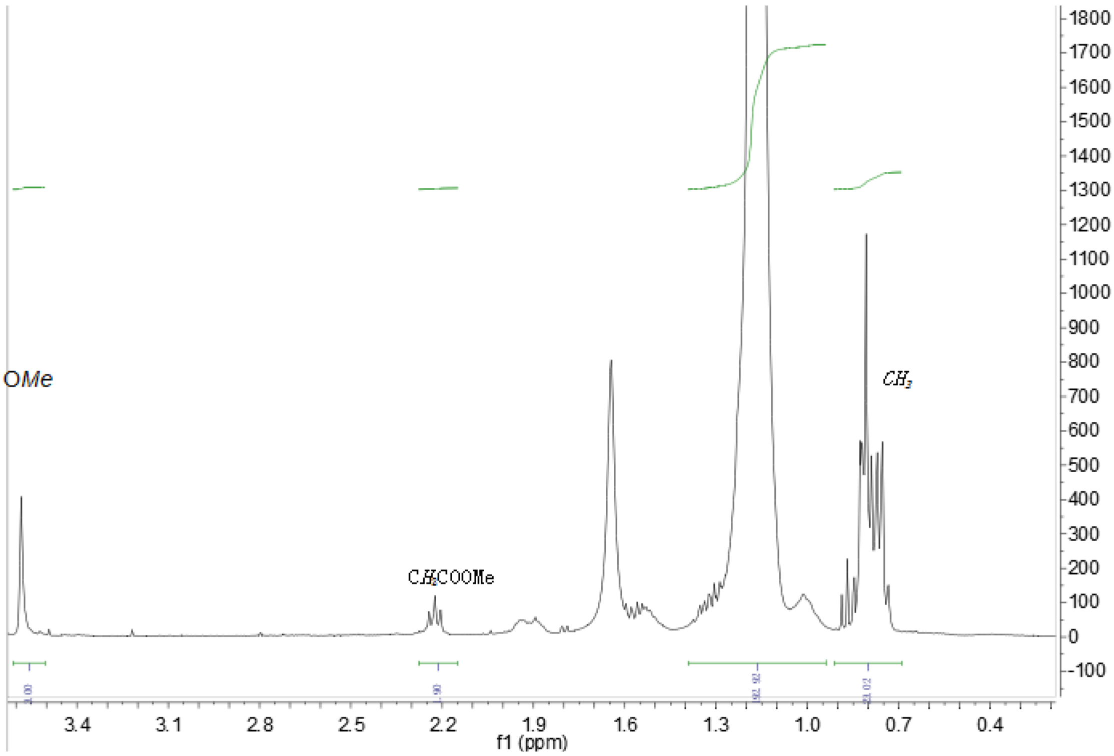


Figure S27. ^{1}H NMR spectrum (400 MHz, $CDCl_3$, 20 ℃) of the polymer from table 3, entry 1.

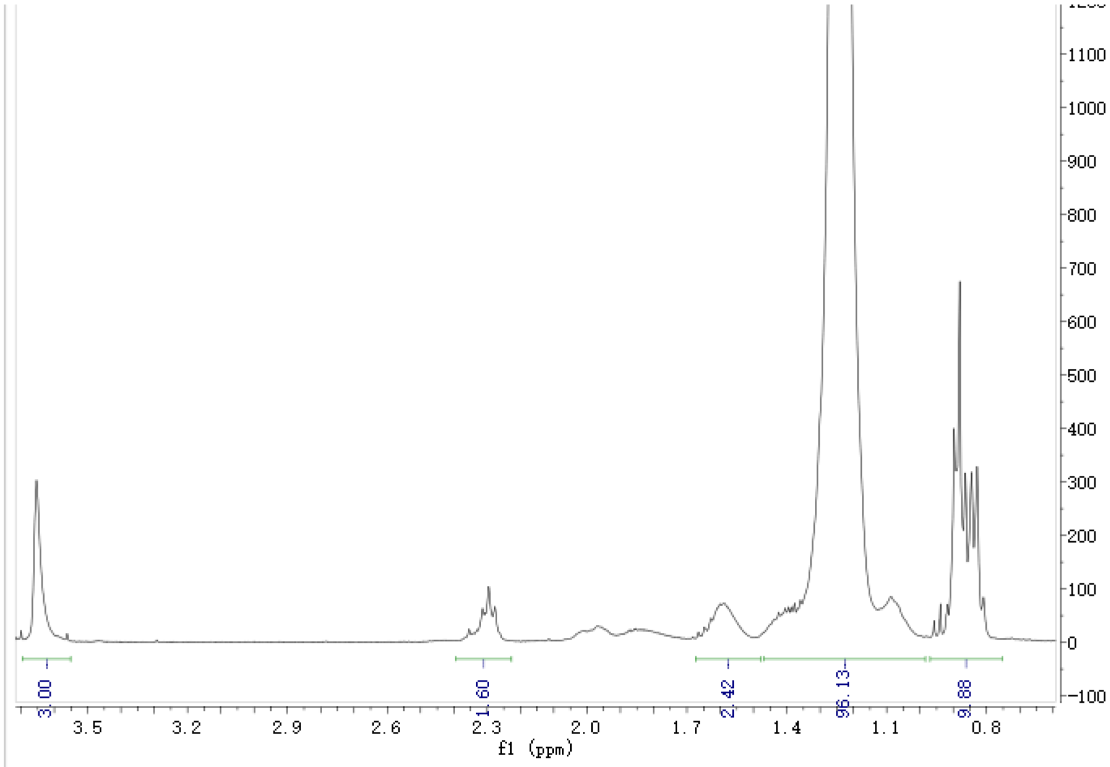


Figure S28. [1]H NMR spectrum (400 MHz, $CDCl_3$, 20 ℃) of the polymer from table 3, entry 2.

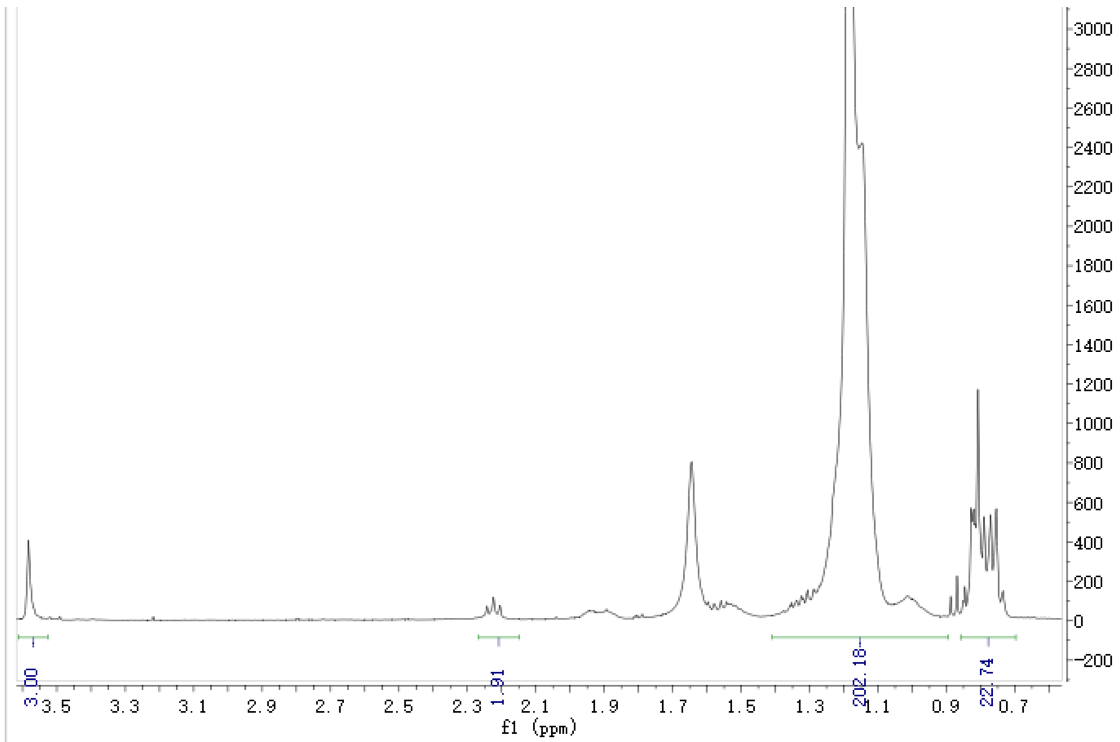


Figure S29. [1]H NMR spectrum (400 MHz, $CDCl_3$, 20 ℃) of the polymer from table 3, entry 4.

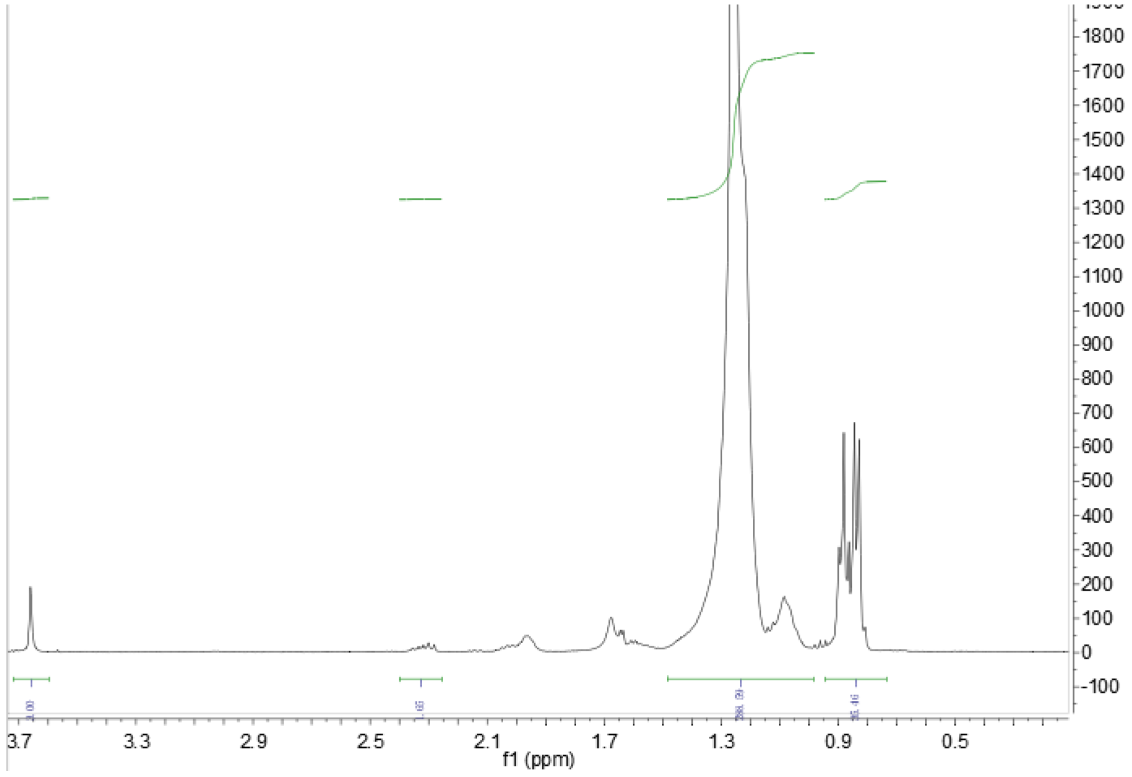


Figure S30. [1]H NMR spectrum (400 MHz, $CDCl_3$, 20 ℃) of the polymer from table 3, entry 7.

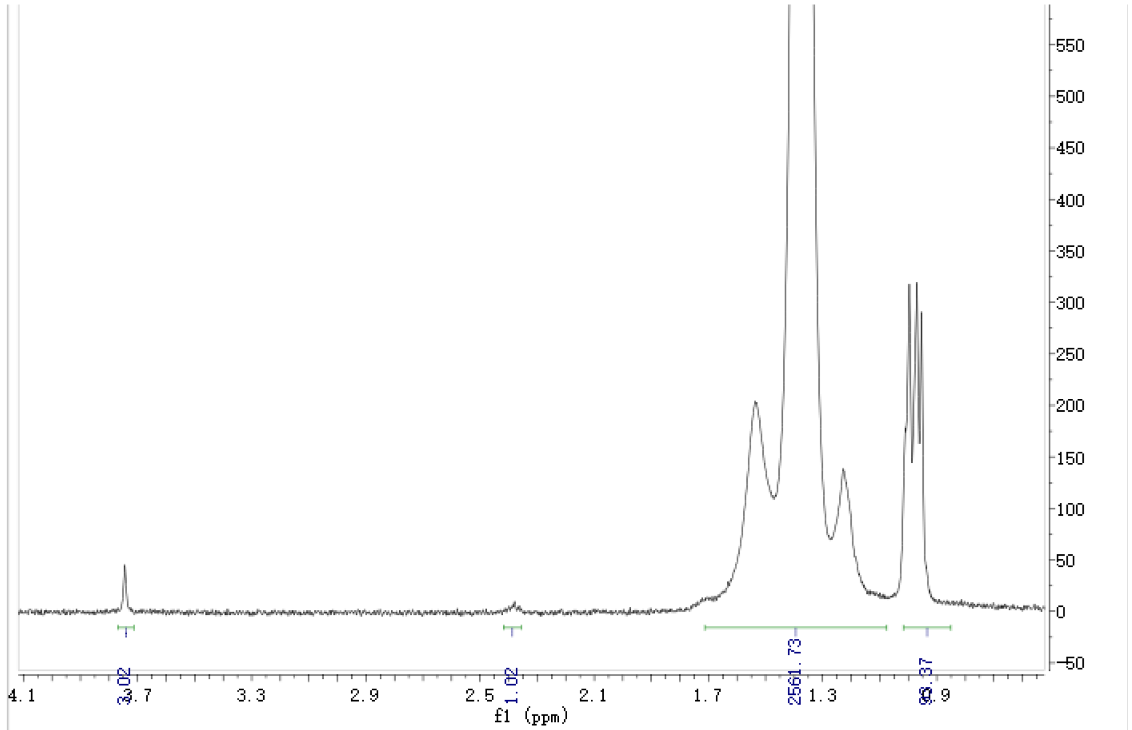
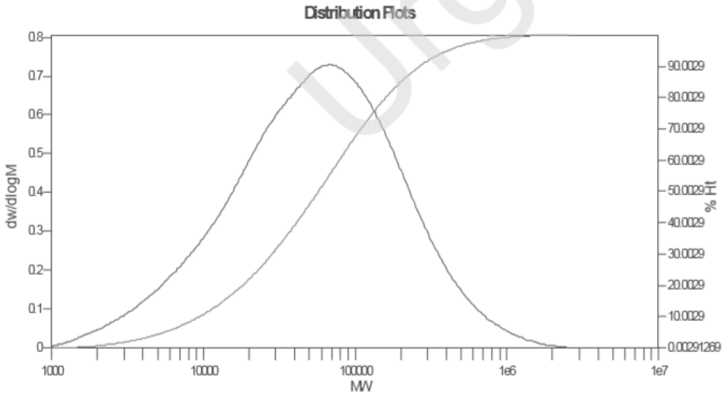


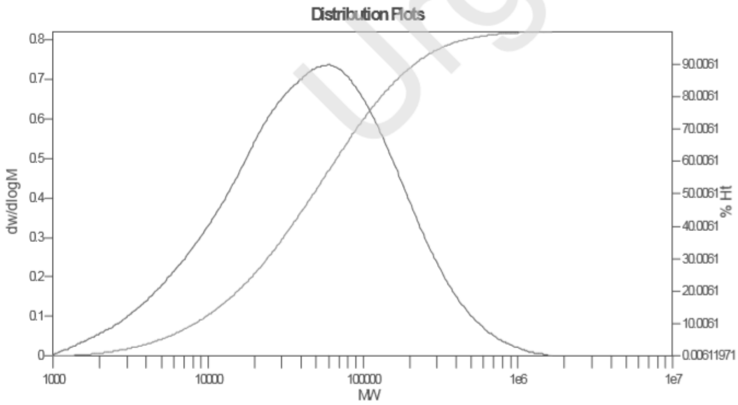
Figure S31. [1]H NMR spectrum (400 MHz, $C_2D_2Cl_4$, 120 ℃) of the polymer from table 3, entry 13.



MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	68303	22260	111295	365066	774592	90463	4.99978

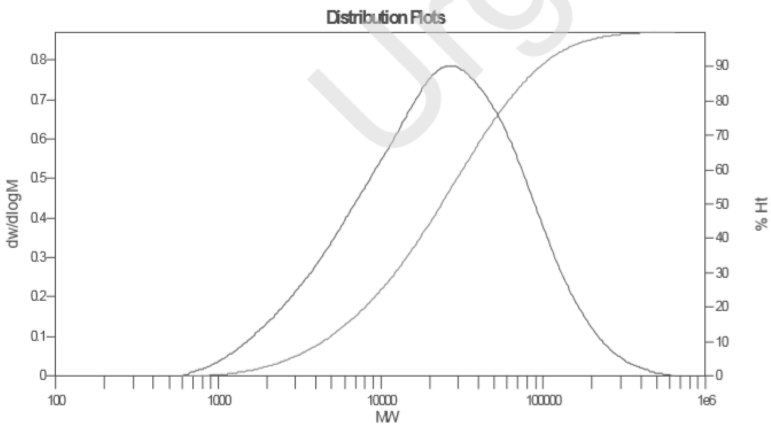
Figure S32. GPC trace of the polymer from table 1, entry 2.



MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	59530	19532	88740	260618	510447	73261	4.54331

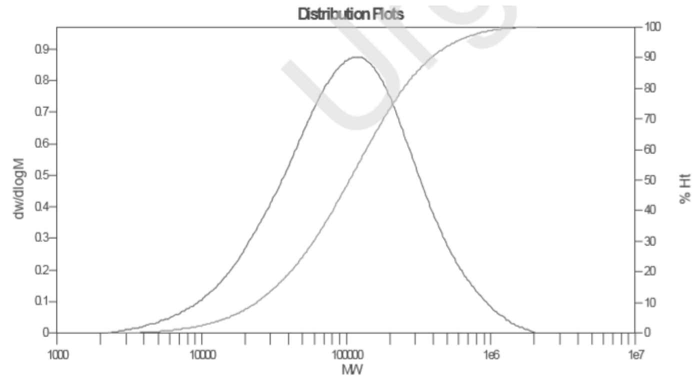
Figure S33. GPC trace of the polymer from table 1, entry 3.



MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	26093	10662	40234	103685	190902	33997	3.77359

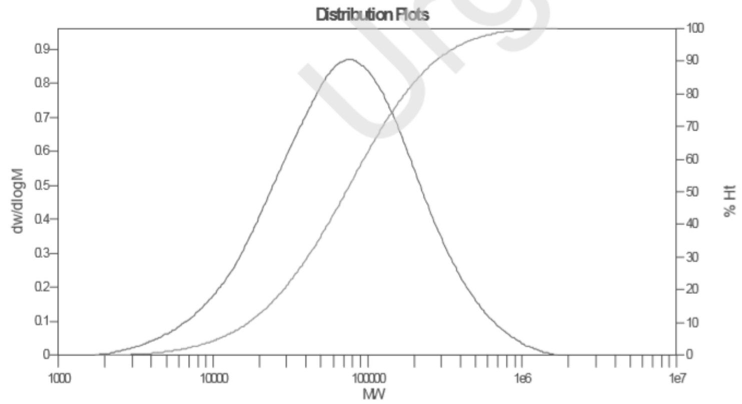
Figure S34. GPC trace of the polymer from table 1, entry 4.



MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	113070	52878	169097	402890	712884	145595	3.19787

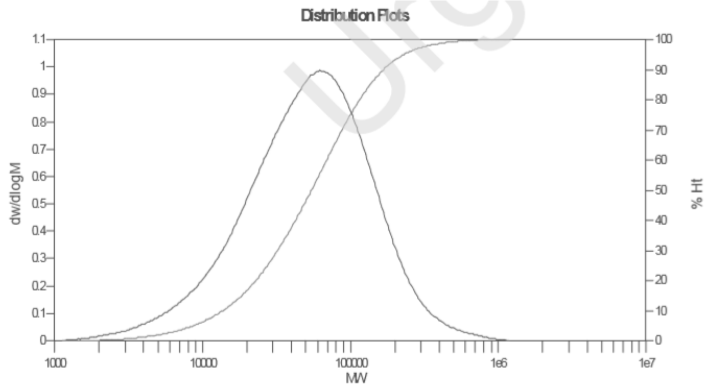
Figure S35. GPC trace of the polymer from table 1, entry 5.



MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	74859	37680	119378	297012	545326	102248	3.16821

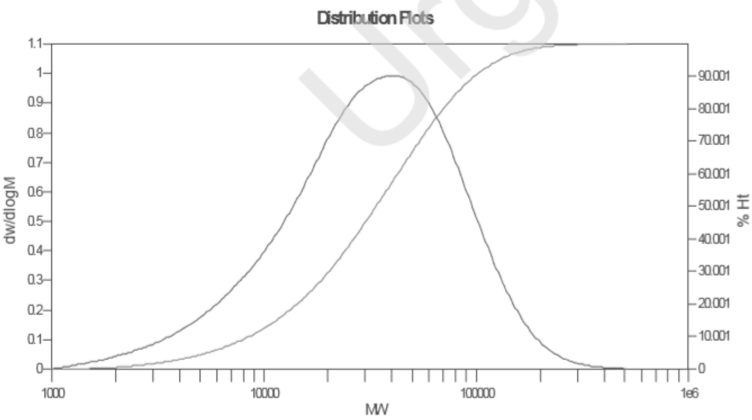
Figure S36. GPC trace of the polymer from table 1, entry 6.



MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	62322	28859	78688	173561	335193	69308	2.72664

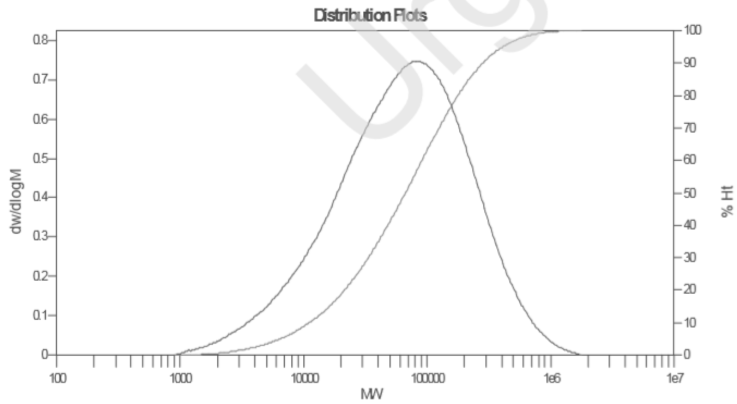
Figure S37. GPC trace of the polymer from table 1, entry 7.



MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	41260	18175	45335	84300	134278	40709	2.49436

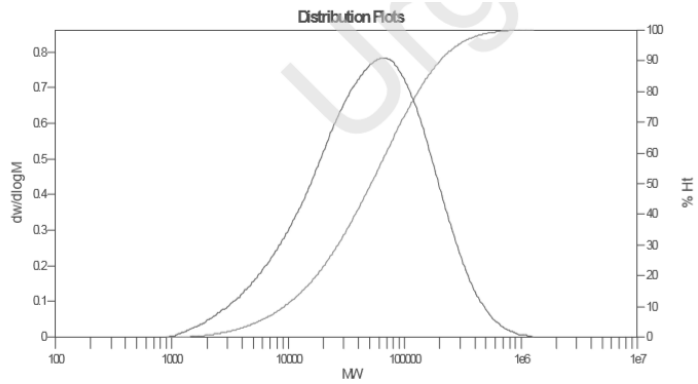
Figure S38. GPC trace of the polymer from table 1, entry 8.



MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	79202	25492	116930	311254	565003	97782	4.58693

Figure S39. GPC trace of the polymer from table 1, entry 11.



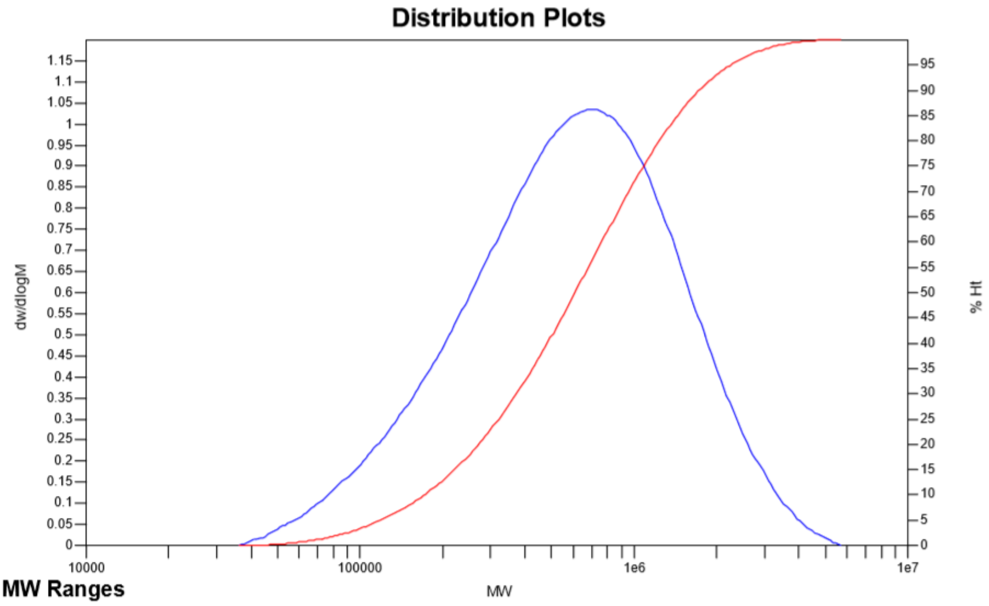
MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	67329	21446	84761	208363	373663	72057	3.9523

Figure S40. GPC trace of the polymer from table 1, entry 12.

MW Averages

Mp: 687147	Mn: 376946	Mv: 739855	Mw: 808652
Mz: 1418258	Mz+1: 2079764	PD: 2.1453	

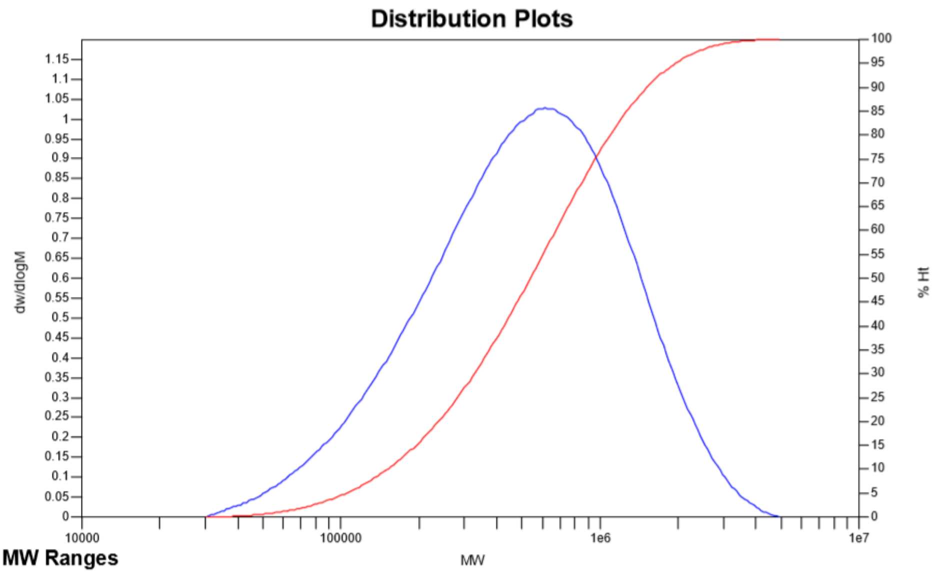


MW Ranges

Figure S41. GPC trace of the polymer from table 1, entry 13.

MW Averages

Mp: 616100	Mn: 330829	Mv: 649727	Mw: 709099
Mz: 1225327	Mz+1: 1766562	PD: 2.1434	



MW Ranges

Figure S42. GPC trace of the polymer from table 1, entry 14.

MW Averages

Mp: 177547	Mn: 104650	Mv: 221818	Mw: 246221
Mz: 480766	Mz+1: 758797	PD: 2.3528	

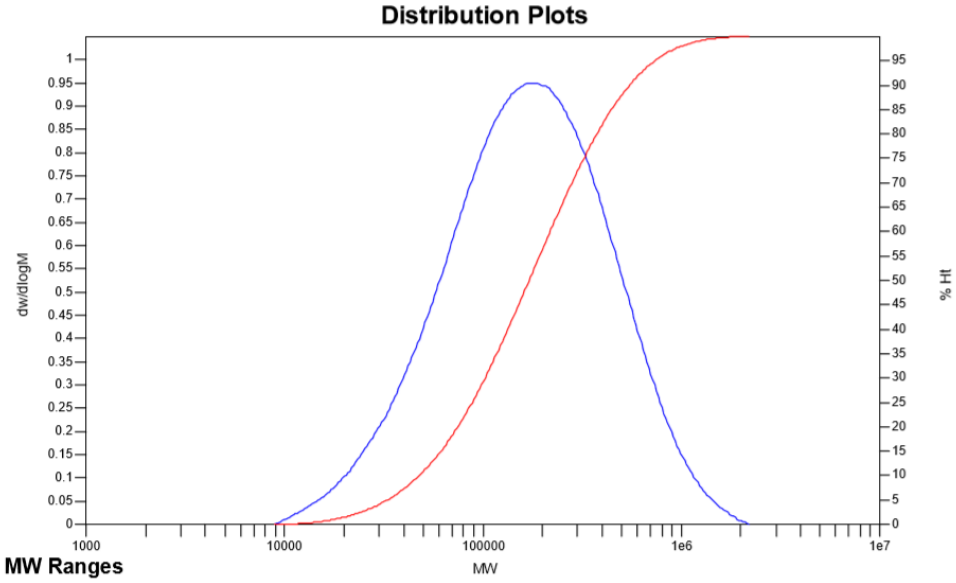


Figure S43. GPC trace of the polymer from table 1, entry 15.

MW Averages

Mp: 144325	Mn: 86333	Mv: 176753	Mw: 197321
Mz: 377572	Mz+1: 598615	PD: 2.2856	

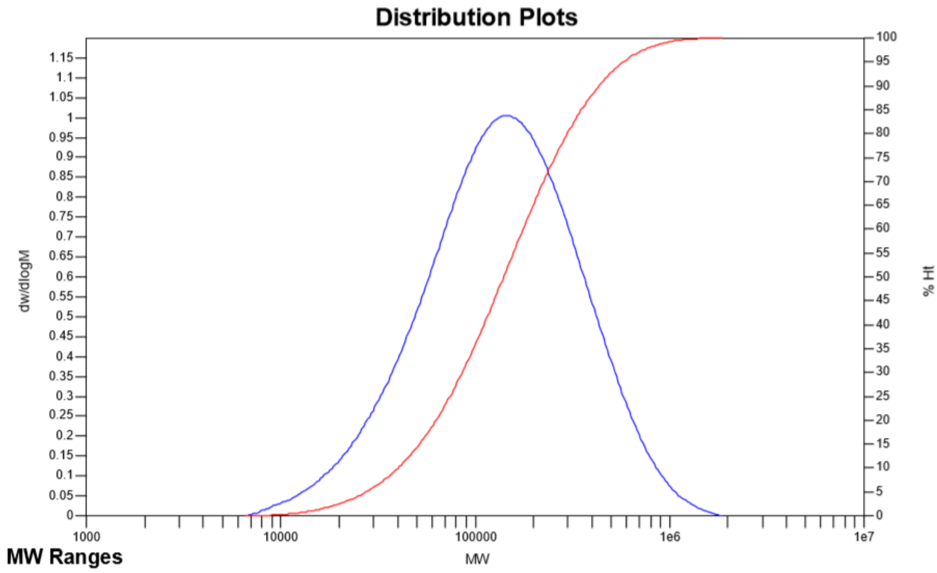
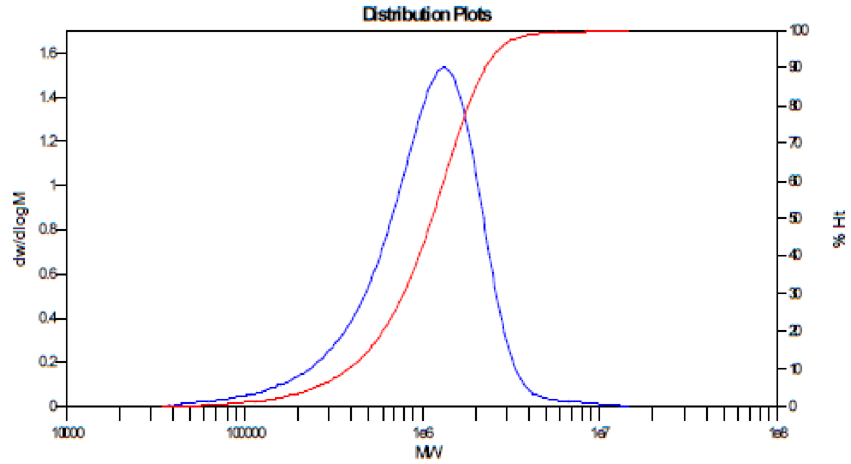


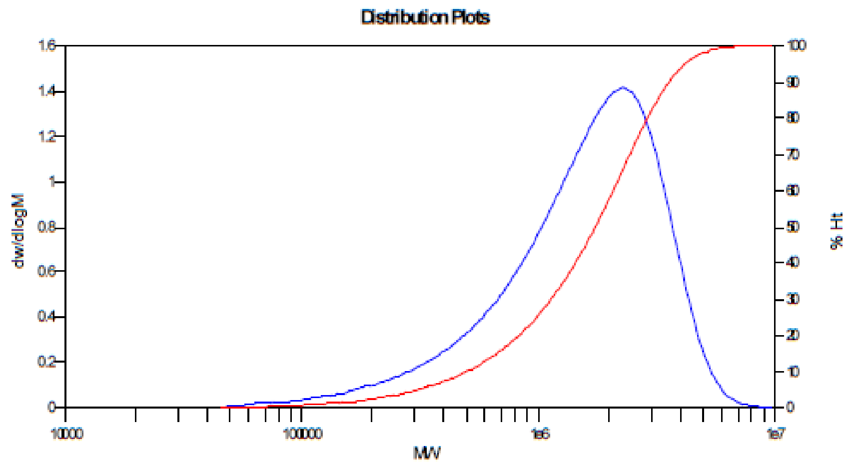
Figure S44. GPC trace of the polymer from table 1, entry 16.



MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	1357361	715464	1280788	1930878	3100315	1198739	1.79015

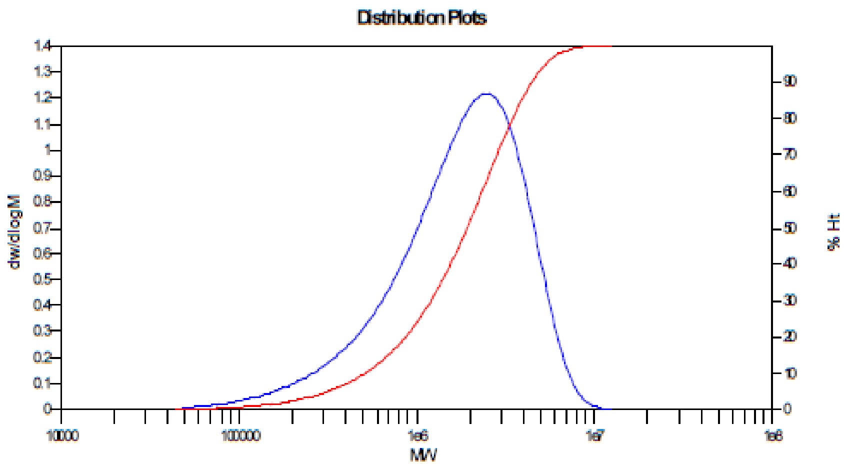
Figure S45. GPC trace of the polymer from table 1, entry 17.



MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	2286083	976843	1904313	2659150	3280858	1783344	1.94946

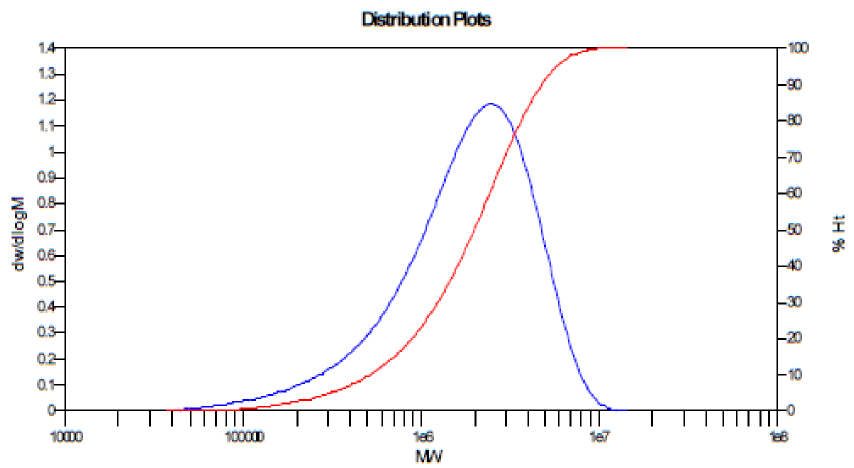
Figure S46. GPC trace of the polymer from table 1, entry 18.



MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	2462829	1045794	2234794	3335552	4283757	2066908	2.13694

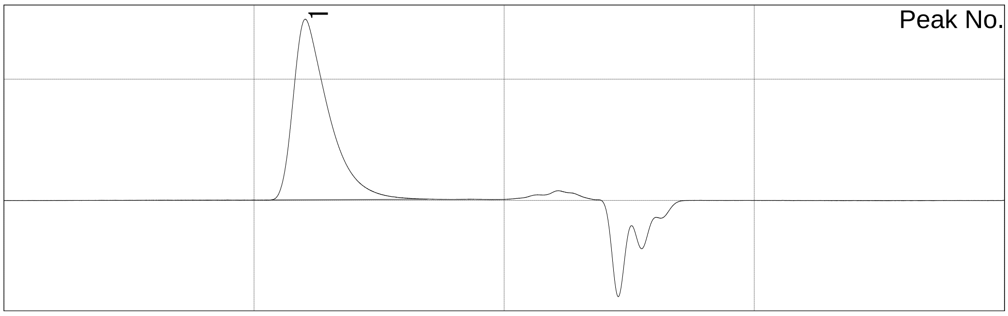
Figure S47. GPC trace of the polymer from table 1, entry 19.



MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	2462829	1032977	2353027	3612196	4746593	2165376	2.27791

Figure S48. GPC trace of the polymer from table 1, entry 20.



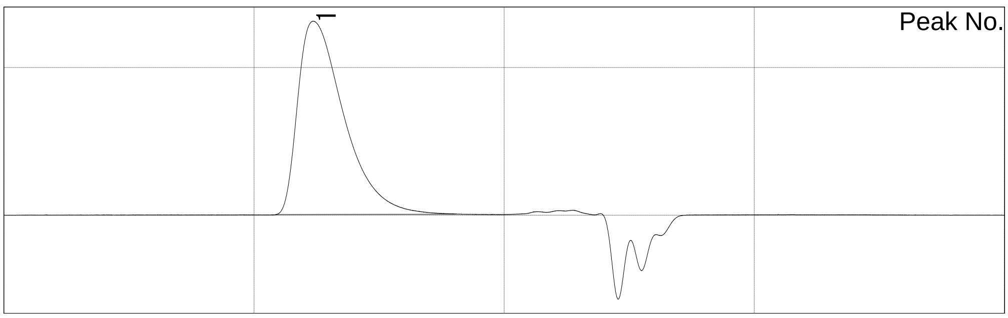
Result of molecular weight calculation (RI)

Peak 1 Base Peak

	[min]	[mV]	[mol]
Peak start	5.348	0.217	1,785,831
Peak top	6.018	74.868	680,026
Peak end	8.455	0.513	20,302
Height [mV]			74.587
Area [mV*sec]			3638.775
Area% [%]			100.000
[eta]			570209.70717

Mn	395,852
Mw	570,210
Mz	698,842
Mz+1	800,983
Mv	570,210
Mp	680,026
Mz/Mw	1.226
Mw/Mn	1.440
Mz+1/Mw	1.405

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



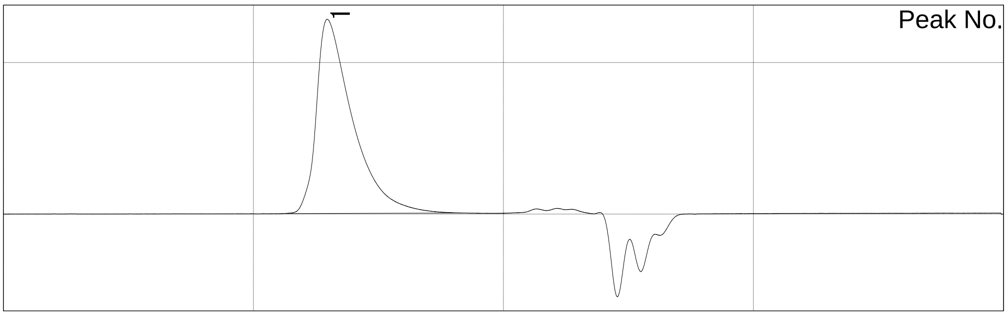
Result of molecular weight calculation (RI)

Peak 1 Base Peak

	[min]	[mV]	[mol]
Peak start	5.430	0.262	1,587,559
Peak top	6.177	65.727	541,294
Peak end	9.037	0.395	8,780
Height [mV]			65.437
Area [mV*sec]			4186.401
Area% [%]			100.000
[eta]			441883.72025

Mn	261,466
Mw	441,884
Mz	581,570
Mz+1	690,459
Mv	441,884
Mp	541,295
Mz/Mw	1.316
Mw/Mn	1.690
Mz+1/Mw	1.563

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

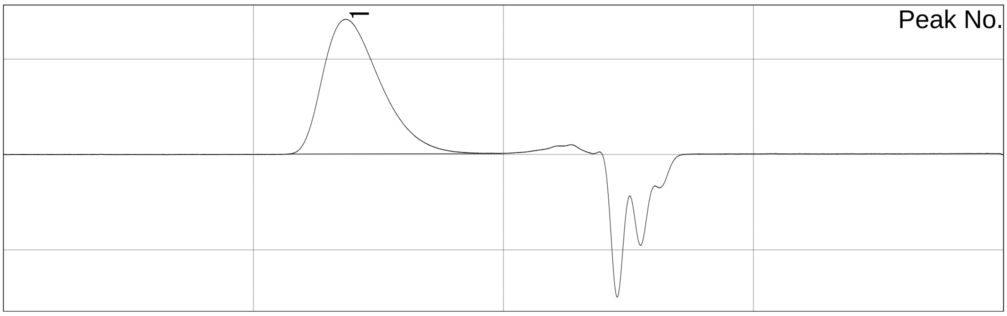


Result of molecular weight calculation (RI)

Peak 1 Base Peak

	[min]	[mV]	[mol]		
				Mn	182,379
Peak start	5.652	0.224	1,153,457	Mw	280,513
Peak top	6.472	64.344	353,842	Mz	351,315
Peak end	9.137	0.384	7,602	Mz+1	408,976
				Mv	280,513
Height [mV]			64.082	Mp	353,843
Area [mV*sec]			3224.836	Mz/Mw	1.252
Area% [%]			100.000	Mw/Mn	1.538
[eta]			280513.16636	Mz+1/Mw	1.458

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



Result of molecular weight calculation (RI)

Peak 1 Base Peak

	[min]	[mV]	[mol]		
				Mn	98,672
Peak start	5.707	0.115	1,065,565	Mw	197,392
Peak top	6.852	28.401	204,639	Mz	294,797
Peak end	9.958	0.206	2,326	Mz+1	382,809
				Mv	197,392
Height [mV]			28.261	Mp	204,640
Area [mV*sec]			2258.530	Mz/Mw	1.493
Area% [%]			100.000	Mw/Mn	2.001
[eta]			197392.45047	Mz+1/Mw	1.939

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

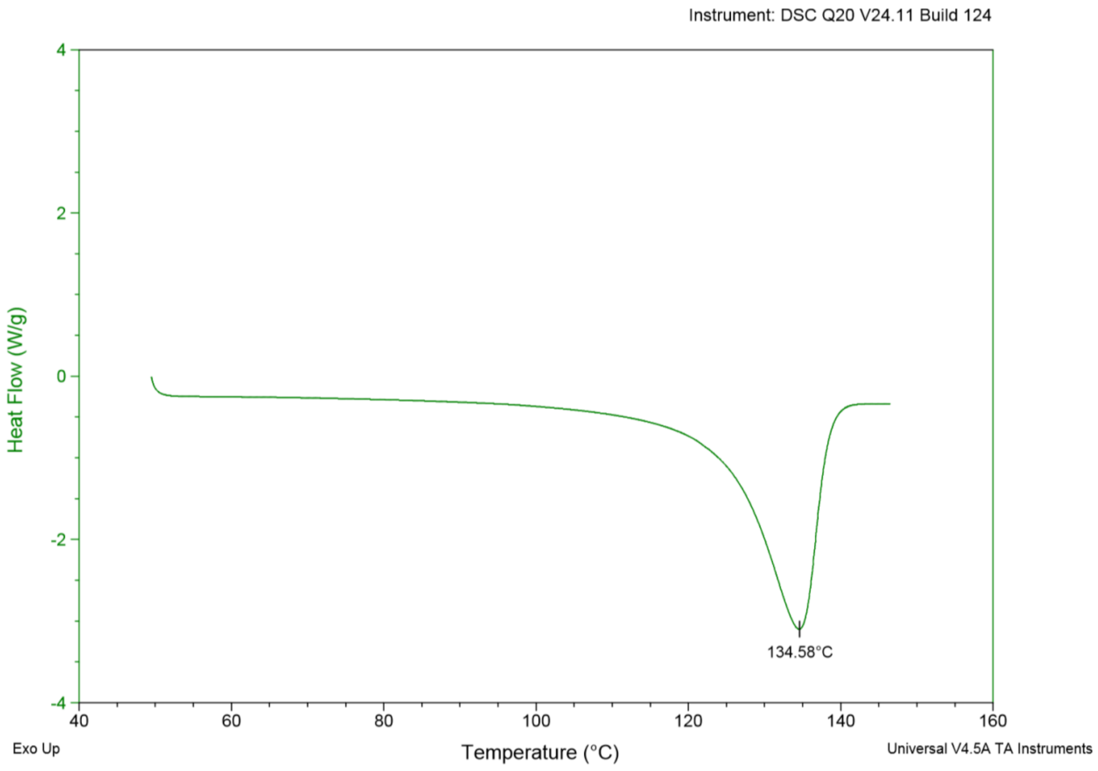


Figure S53. DSC data of the polymer from table 1, entry 1.

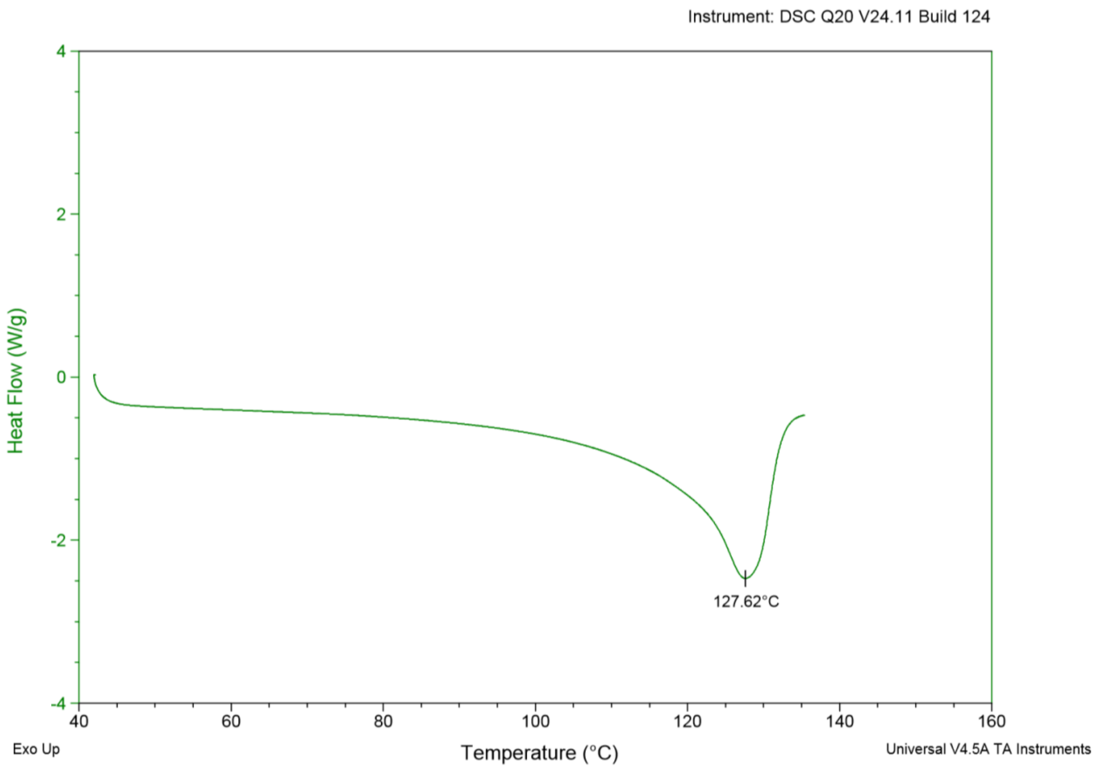


Figure S54. DSC data of the polymer from table 1, entry 2.

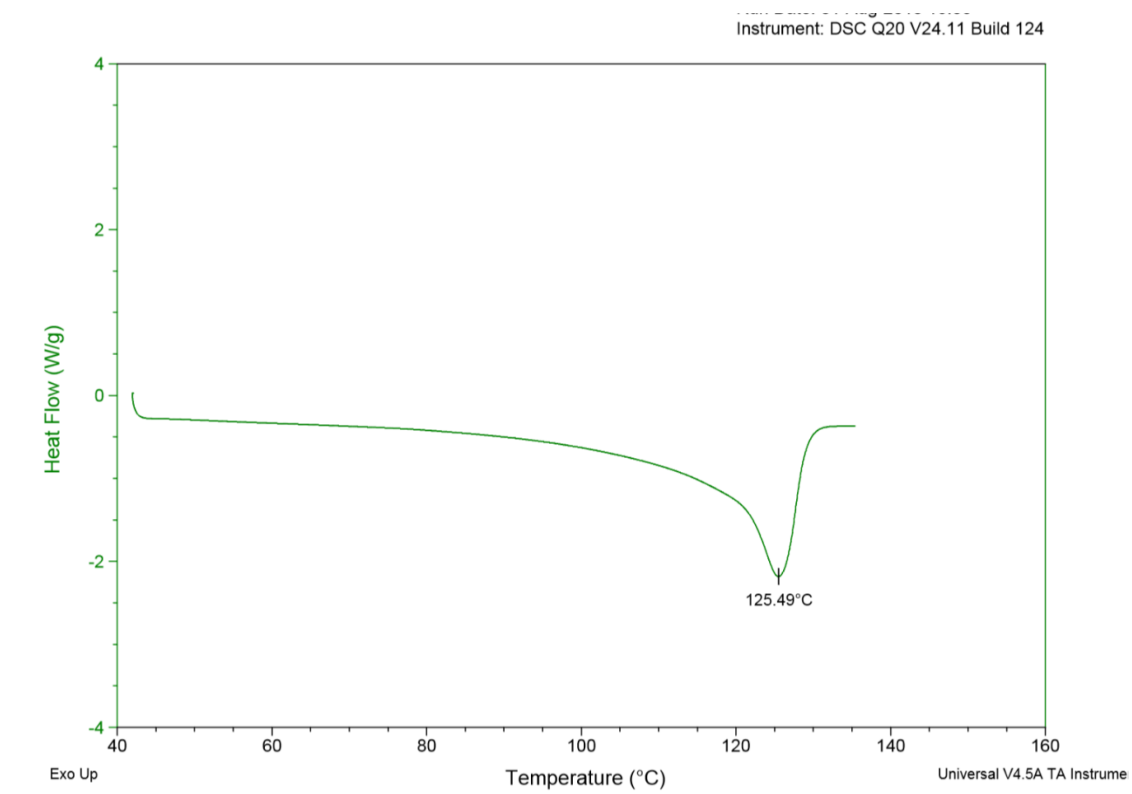


Figure S55. DSC data of the polymer from table 1, entry 3.

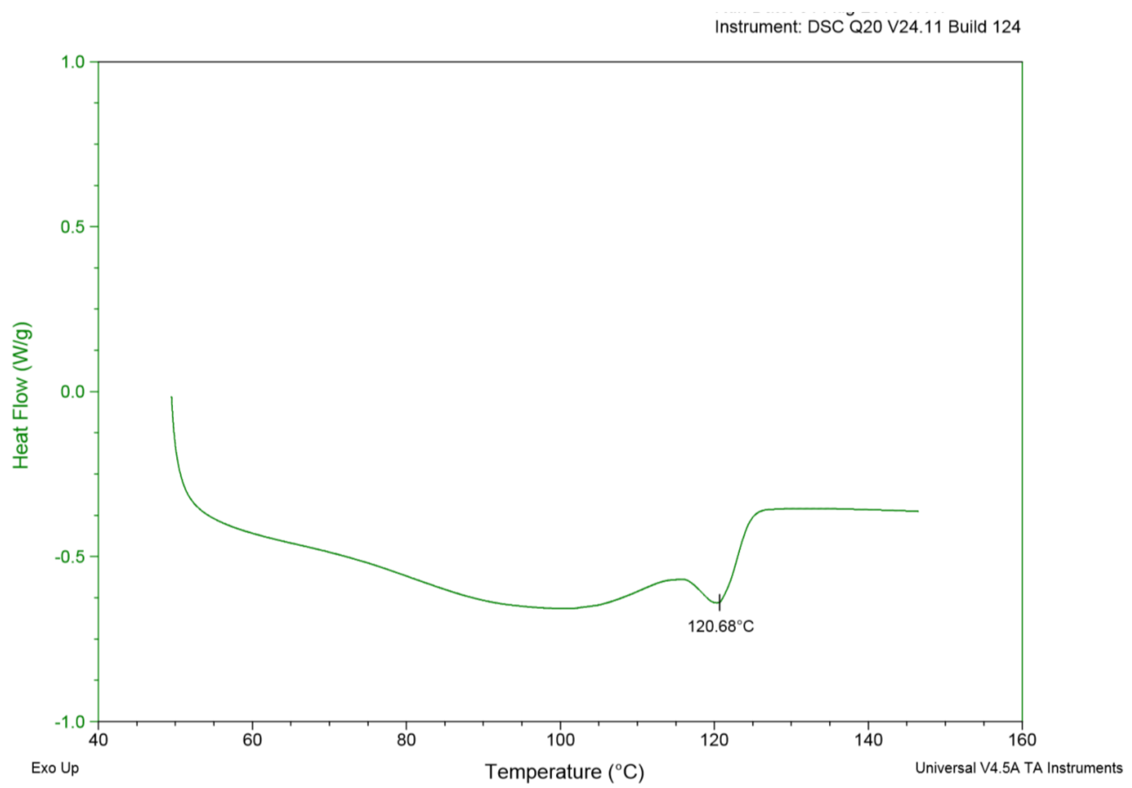


Figure S56. DSC data of the polymer from table 1, entry 4.

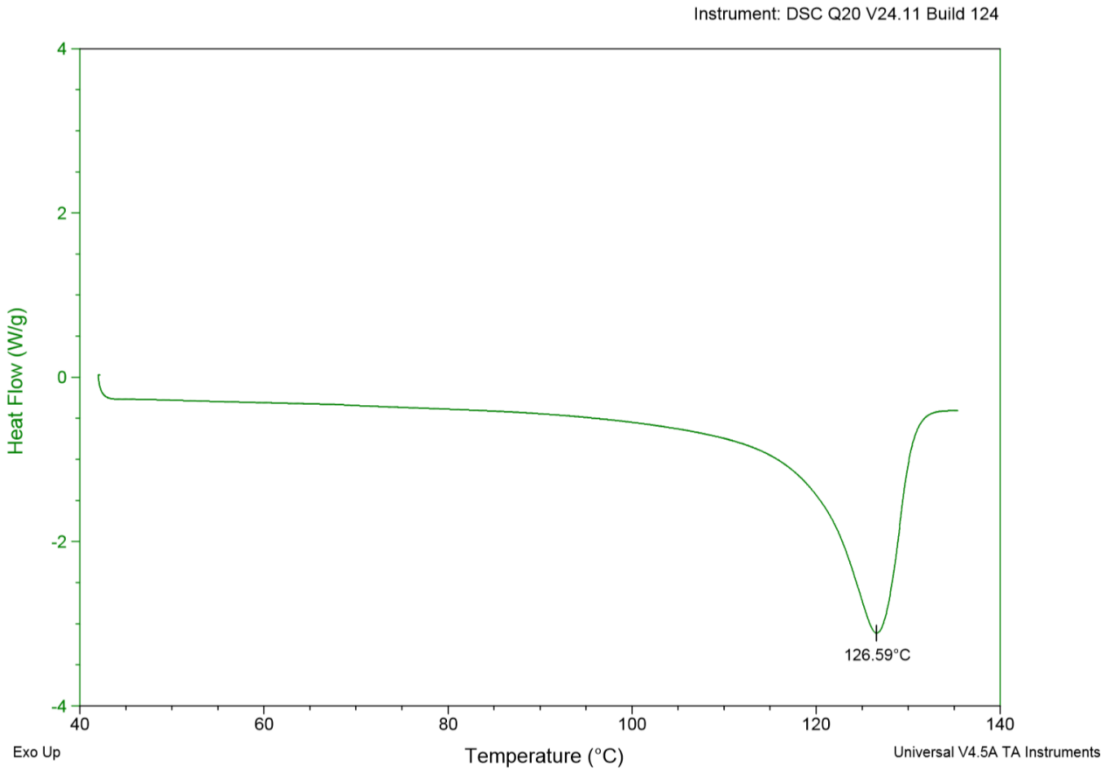


Figure S57. DSC data of the polymer from table 1, entry 6.

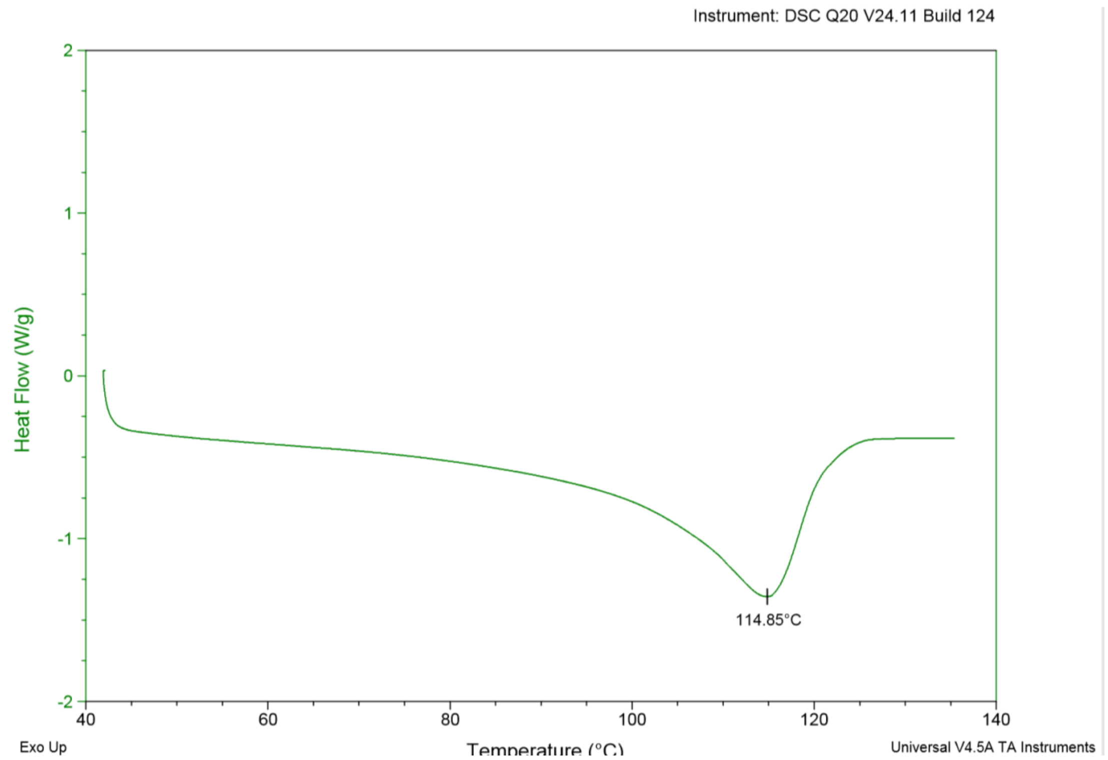


Figure S58. DSC data of the polymer from table 1, entry 7.

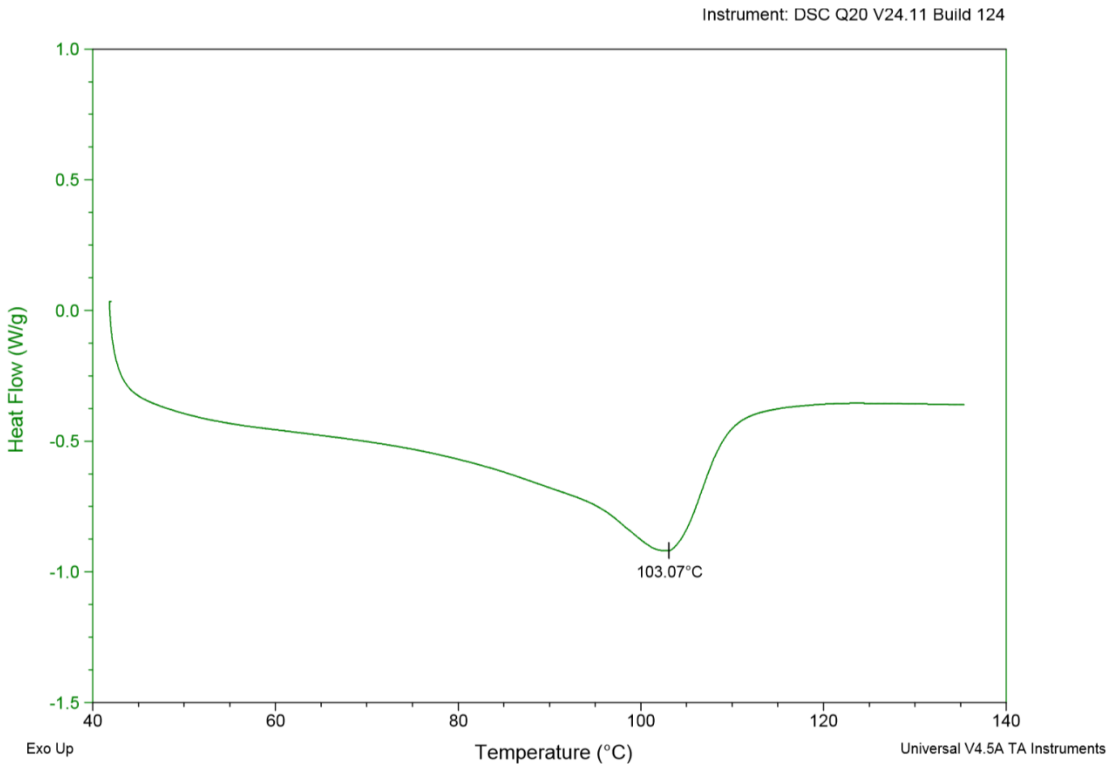


Figure S59. DSC data of the polymer from table 1, entry 8.

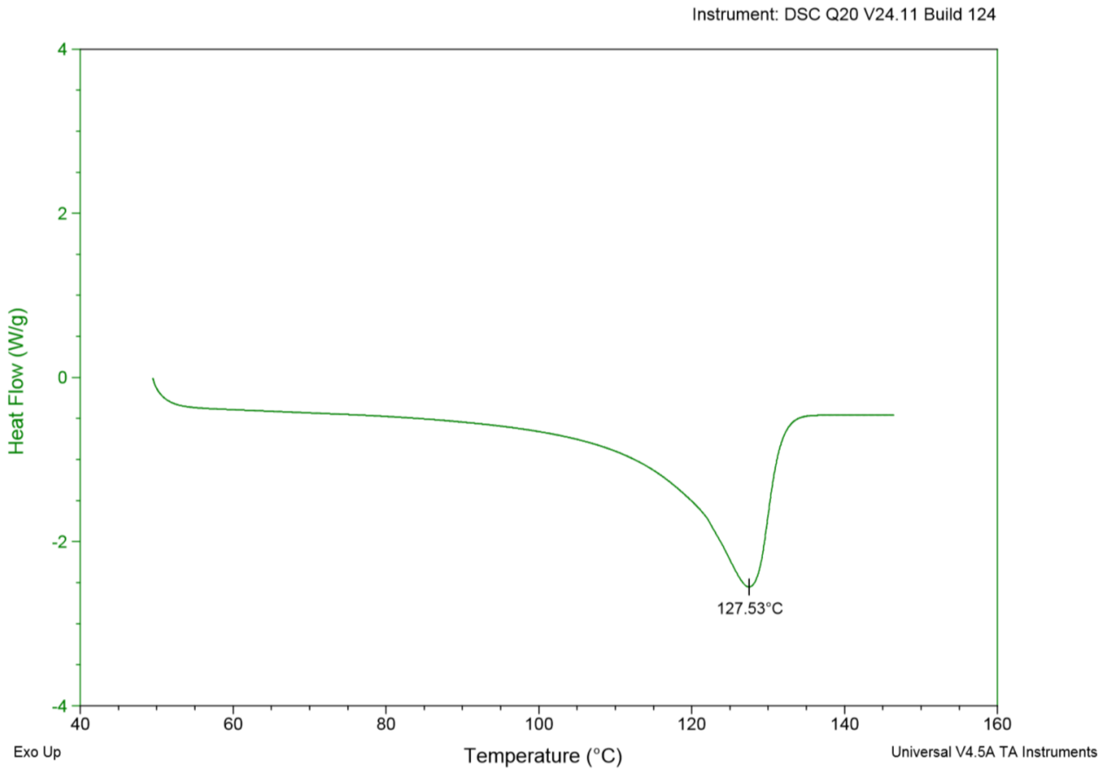


Figure S60. DSC data of the polymer from table 1, entry 9.

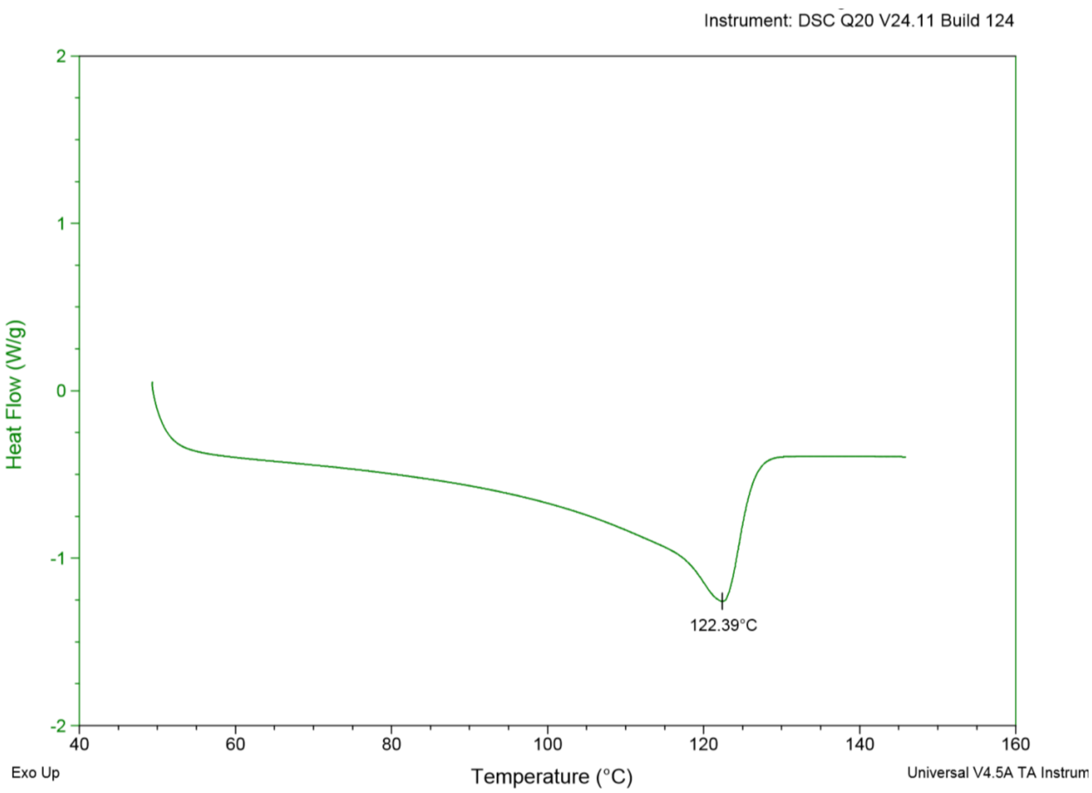


Figure S61. DSC data of the polymer from table 1, entry 10.

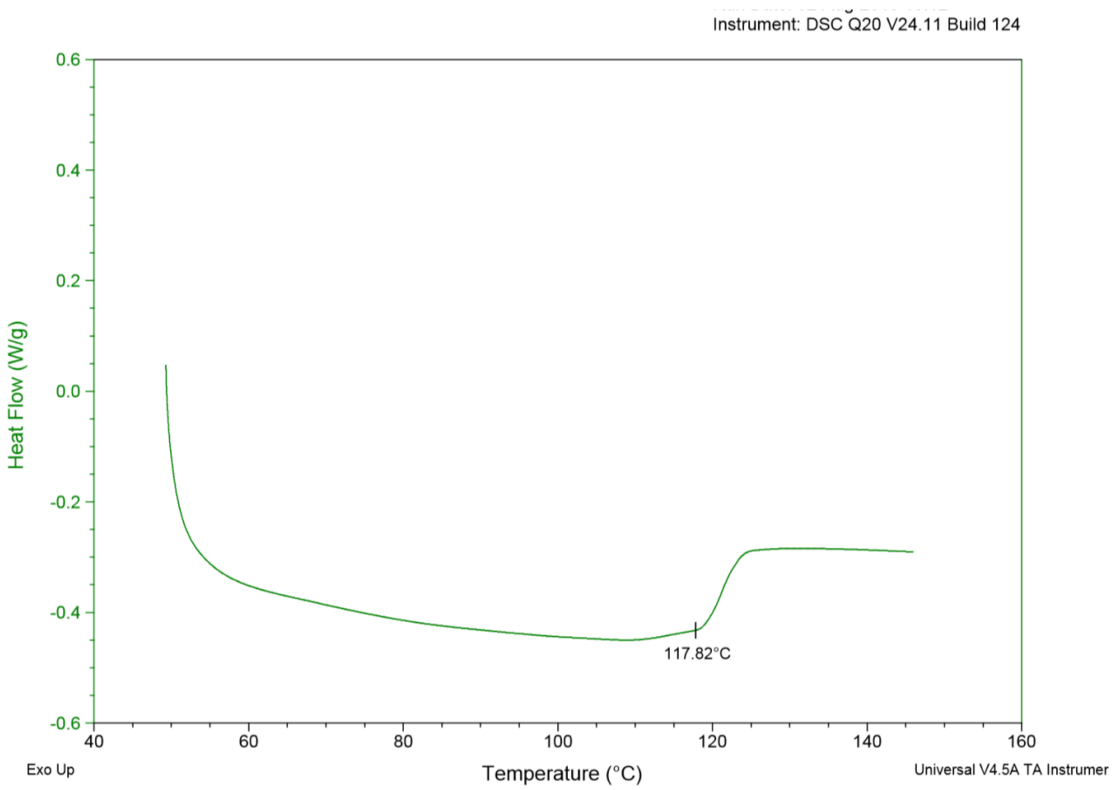


Figure S62. DSC data of the polymer from table 1, entry 11.

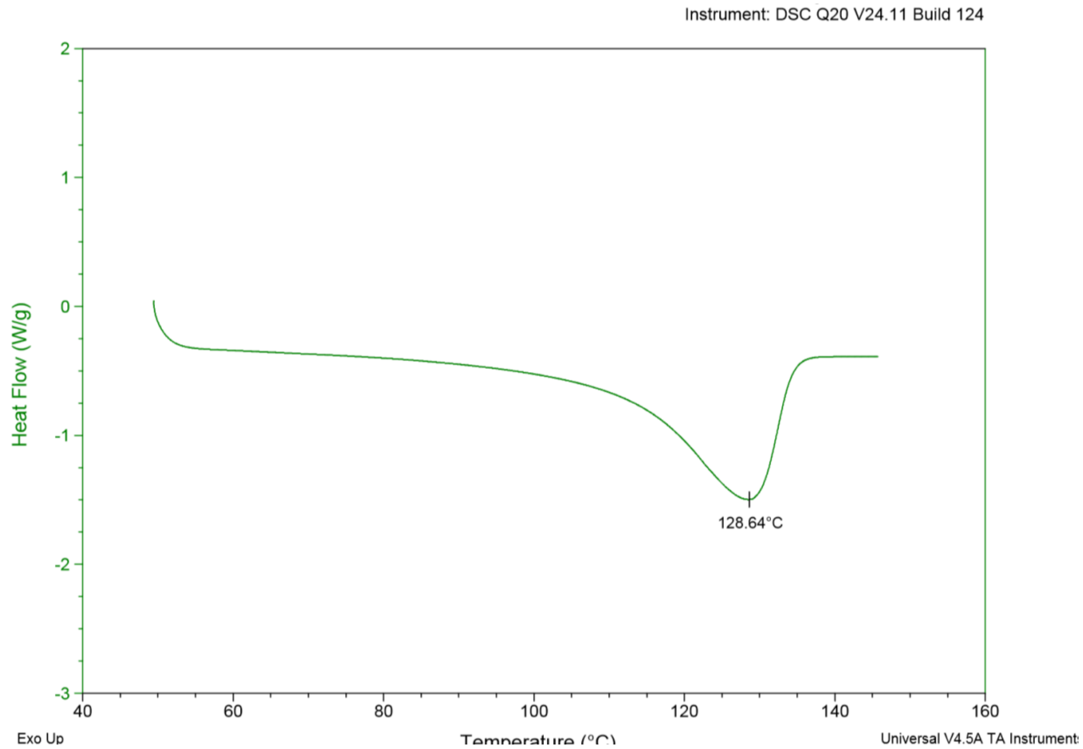


Figure S63. DSC data of the polymer from table 1, entry 13.

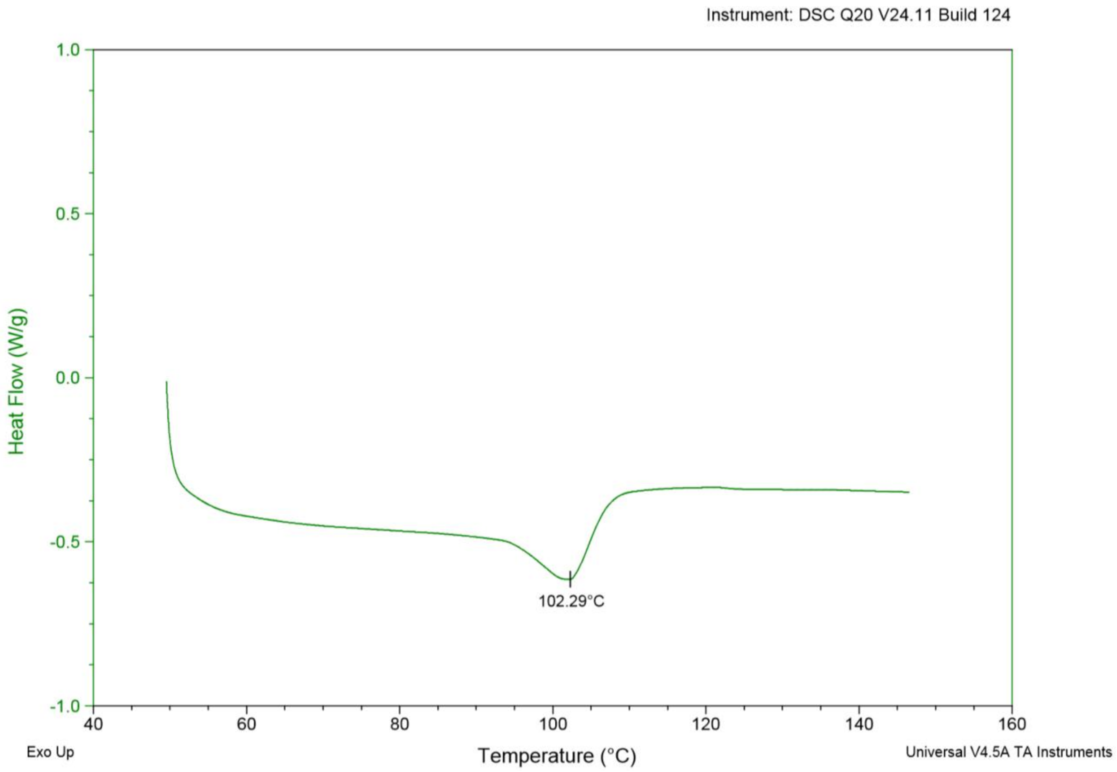


Figure S64. DSC data of the polymer from table 1, entry 15.

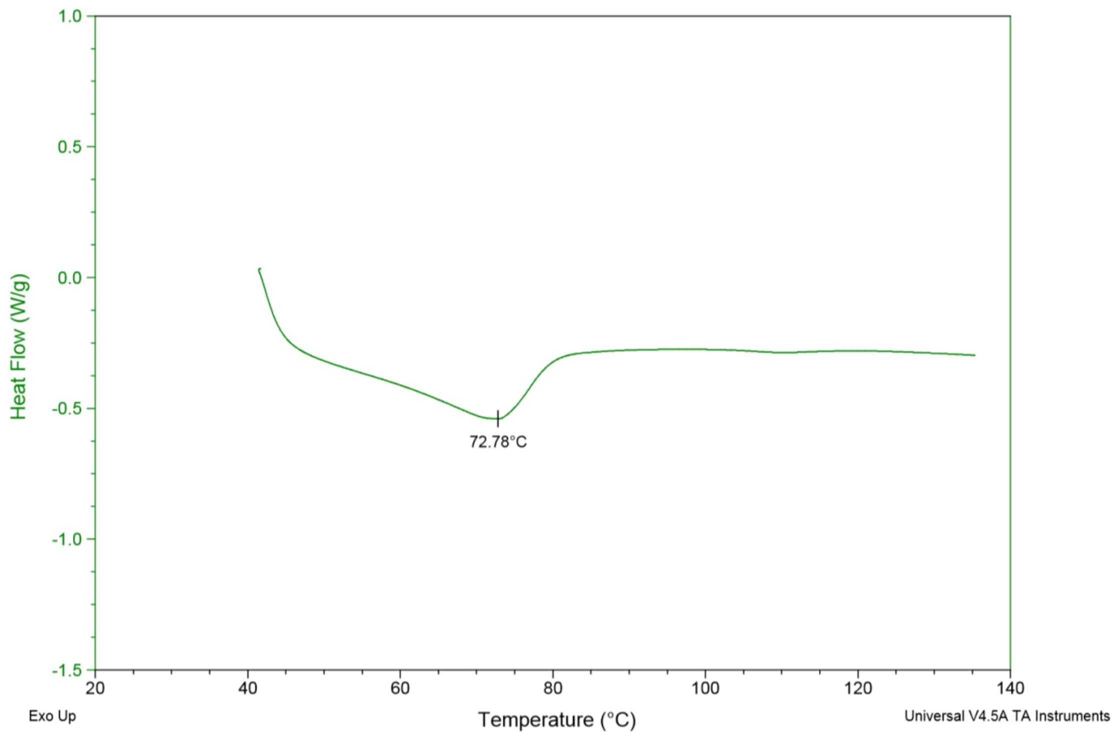


Figure S65. DSC data of the polymer from table 1, entry 17.

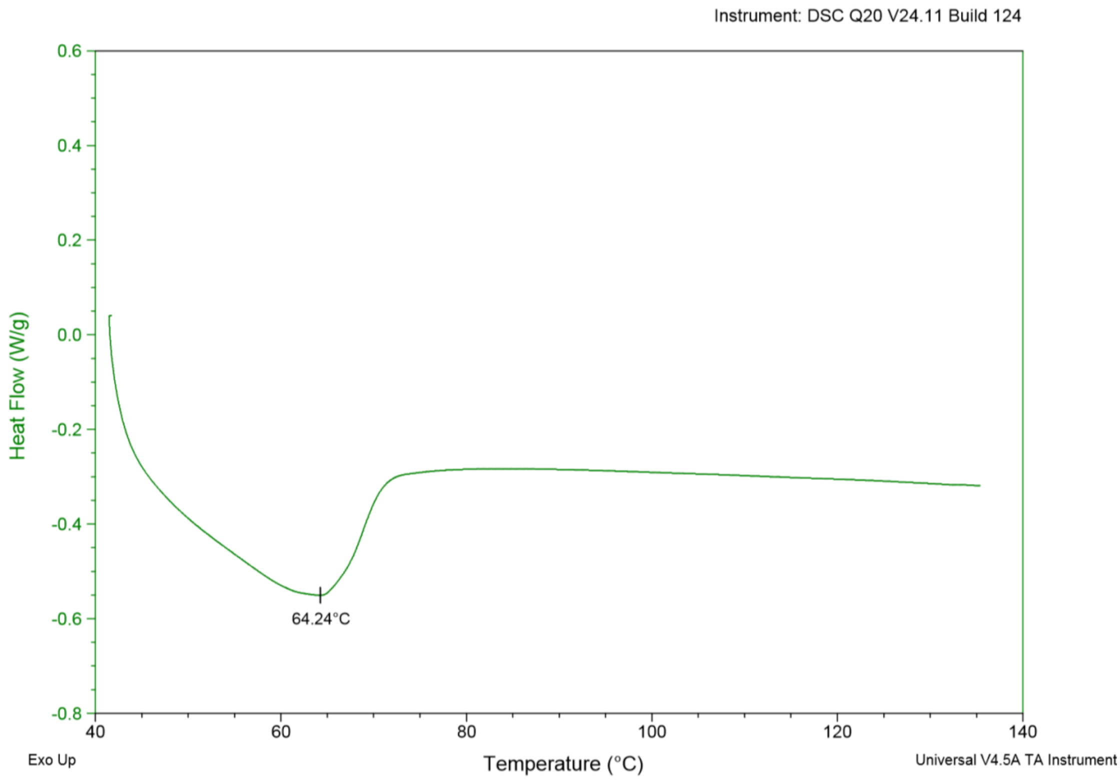


Figure S66. DSC data of the polymer from table 1, entry 18.

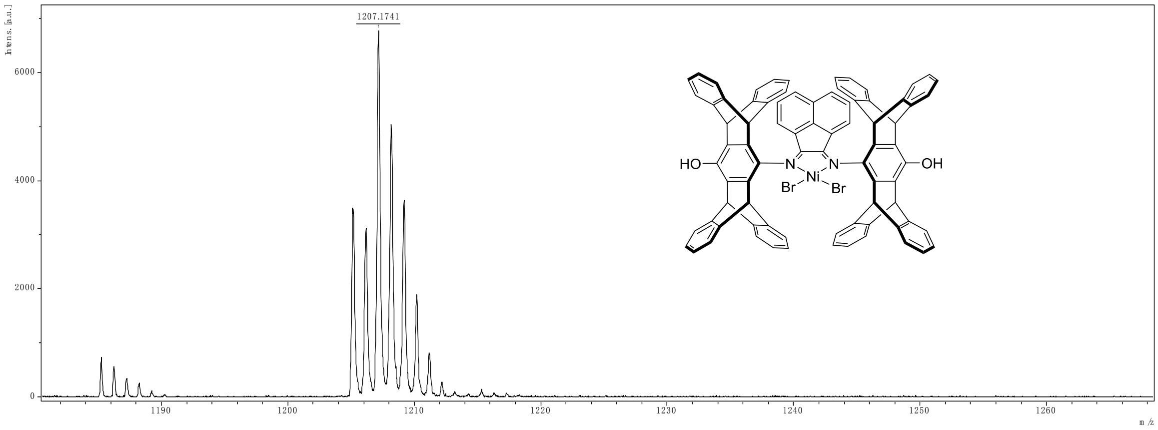


Figure S67. MALDI-TOF-MS of complex **Ipty-Ni1**.

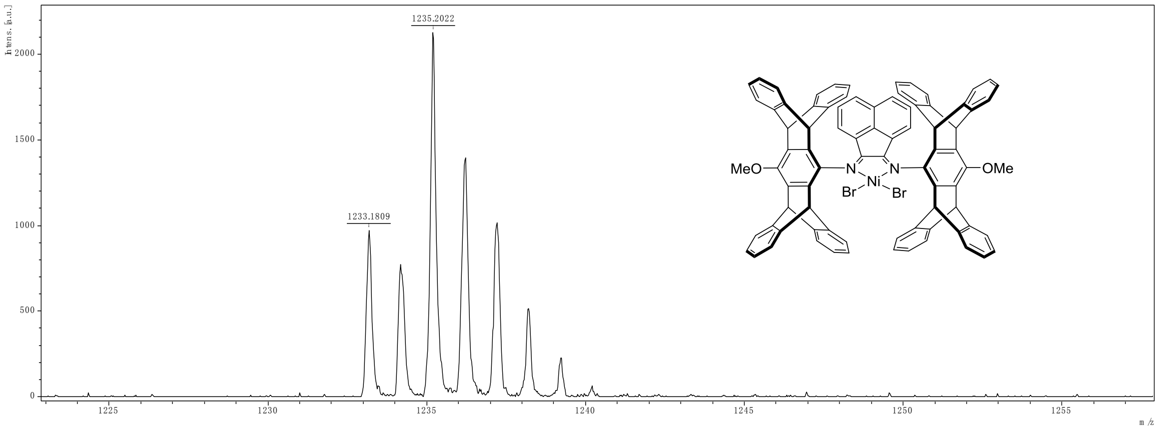


Figure S68. MALDI-TOF-MS of complex **Ipty-Ni2**.

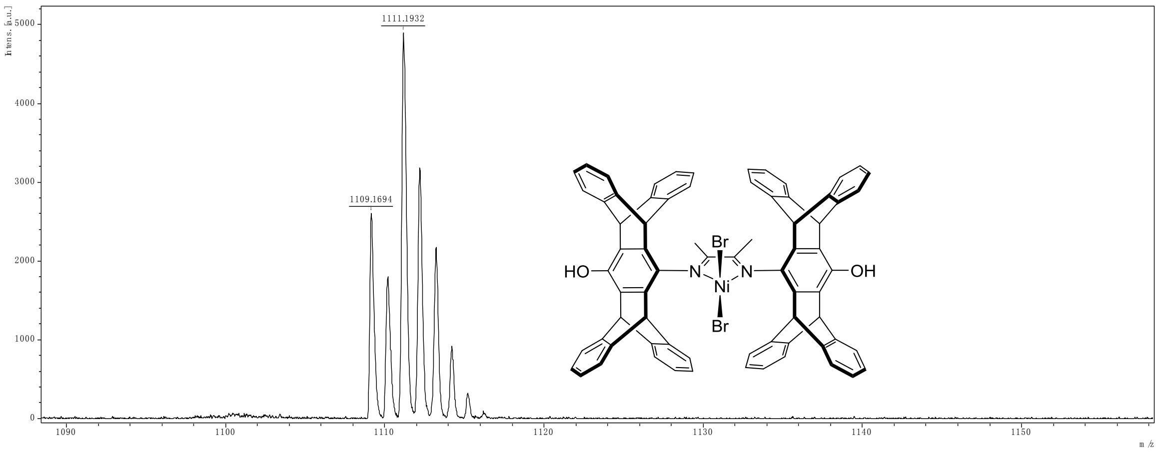


Figure S69. MALDI-TOF-MS of complex **Ipty-Ni3**.

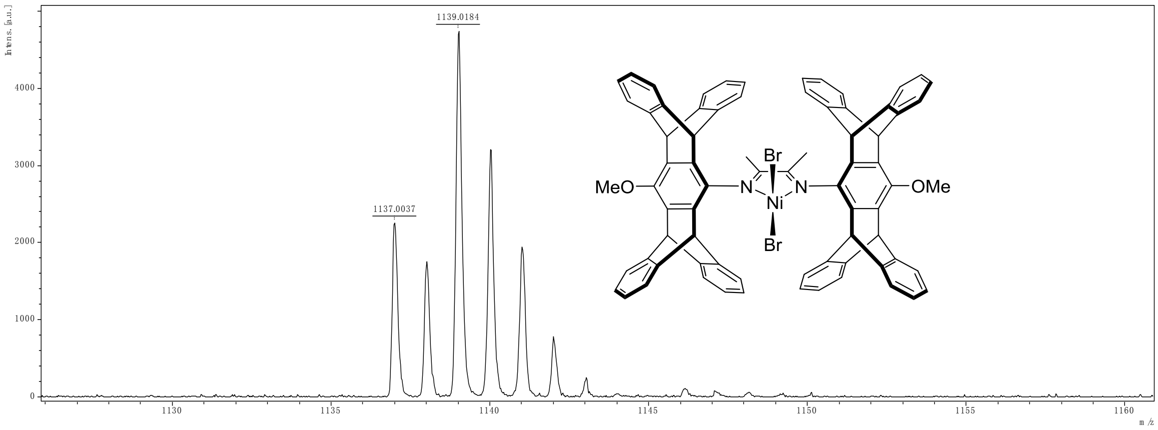


Figure S70. MALDI-TOF-MS of complex **Ipty-Ni4**.

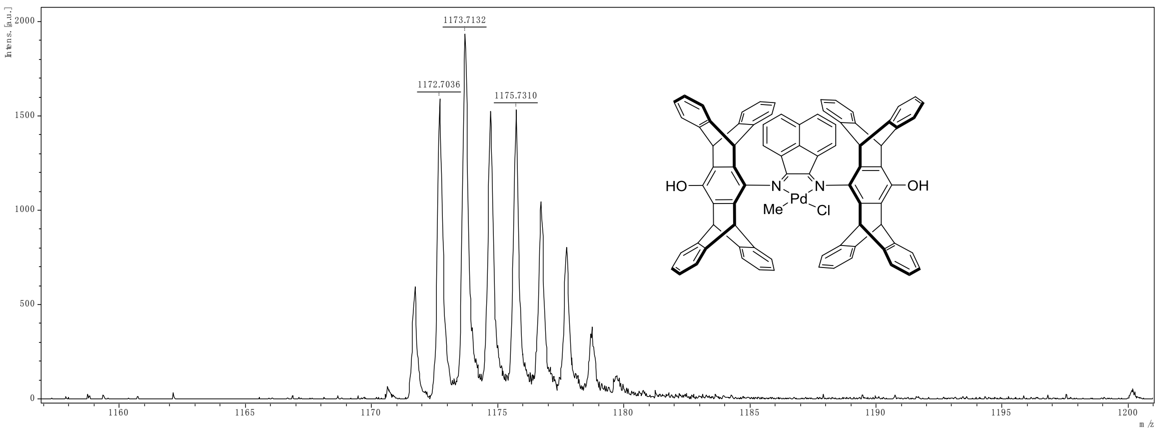


Figure S71. MALDI-TOF-MS of complex **Ipty-Pd1**.

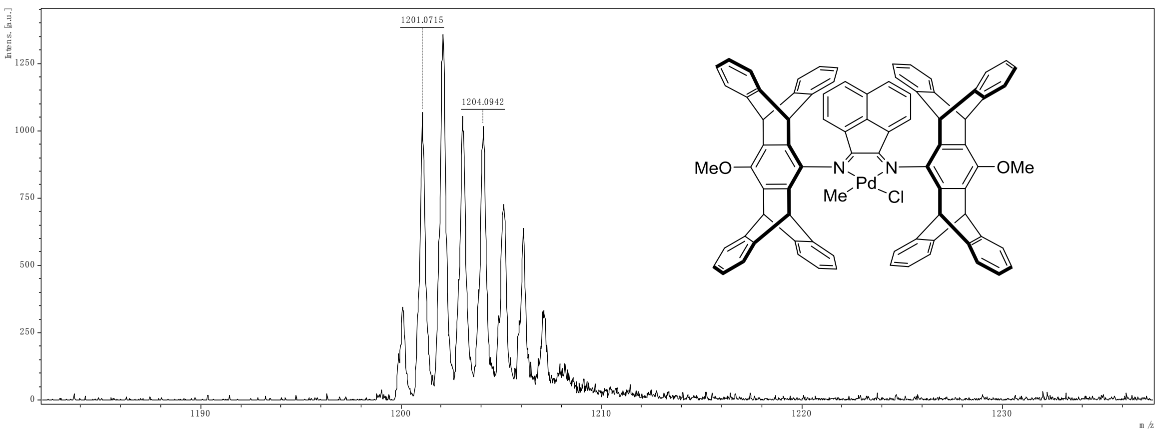


Figure S72. MALDI-TOF-MS of complex **Ipty-Pd2**.

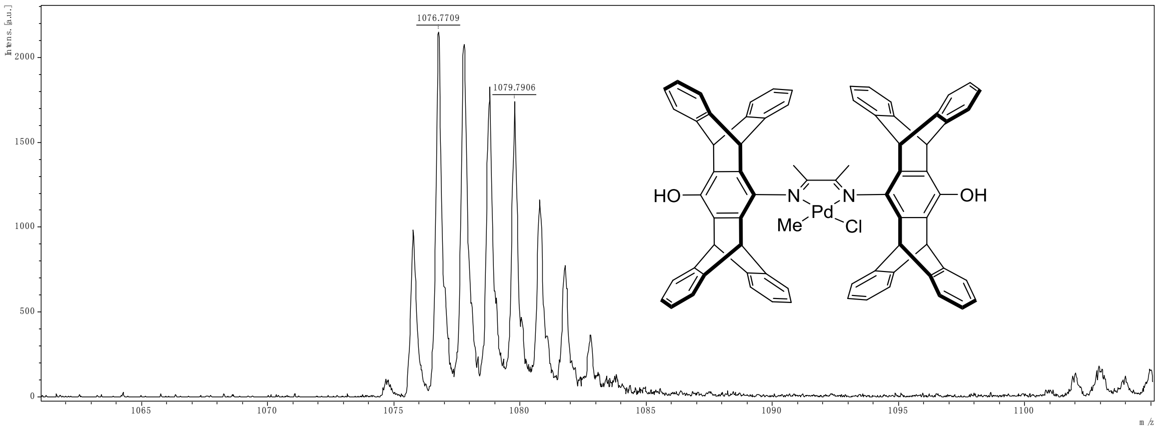


Figure S73. MALDI-TOF-MS of complex **Ipty-Pd3**.

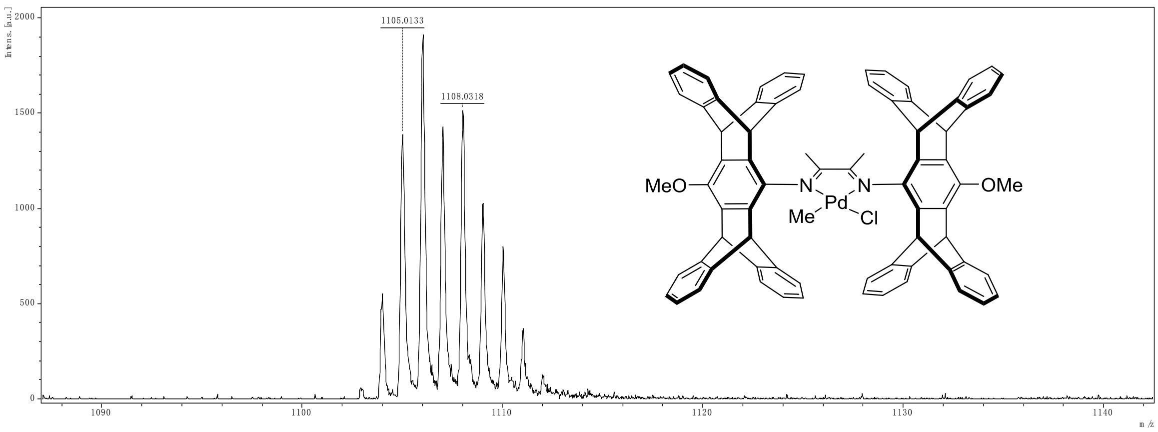


Figure S74. MALDI-TOF-MS of complex **Ipty-Pd4**.

References

1, Savka, R.; Foro, S.; Plenio, H. Pentiptycene-based concave NHC–metal complexes. *Dalton Transactions*, **2016**, *45*, 11015-11024.

2, Guo, L. H.; Zou, C.; Dai, S. Y.; Chen, C. L. Direct synthesis of branched carboxylic acid functionalized poly(1-octene) by α-diimine palladium catalysts. *Polymers*, **2017**, *9*, 122.

3, Dai, S. Y.; Sui, X. L.; Chen, C. L. Highly robust palladium(II) α-diimine catalysts for slow-chain-walking polymerization of ethylene and copolymerization with methyl acrylate. *Angew. Chem. Int. Ed.*, **2015**, *54*, 9948-9953.