Enhanced mechanical properties of acrylate and 5-vinyl-2-norbornene based ethylene terpolymers: rational design and synthesis using remotely modulated phosphine-sulfonate palladium complexes

Yong-Qing Li[a,b], *Gui-Ping Cao*[a,*], *Yu-Cai Cao*[b,*]

[a]UNILAB State Key Laboratory of Chemical Engineering, East China University of Science and Technology, Shanghai, 200237, P. R. China

[b]State Key Laboratory of Polyolefins and Catalysis, Shanghai Key Laboratory of Catalysis Technology for Polyolefins, Shanghai Research Institute of Chemical Industry Co., Ltd, Shanghai, 200062, P. R. China

Supporting Information

Experimental

General

Nitrogen was purified by passage through columns containing activated molecular sieves. Toluene, THF, CH_2Cl_2 and diethyl ether were purified by a MBraun SPS system. Deuterated solvents used for NMR spectroscopy were dried and distilled prior to use. Butyl acrylate (BA) was dried over calcium hydride (CaH_2), distilled under reduced pressure, and stored at −25°C. Other chemicals and reagents were obtained from commercial sources and used without further purification.

^{1}H NMR and ^{13}C NMR spectra were recorded on a JEOL JNM-ECZR 500 MHz spectrometer at ambient temperature unless otherwise indicated. The chemical shifts for protons and carbons were referenced to the residual proton and carbon resonance of chloroform-*d* (δ: 7.26 and 77.16, respectively). ^{1}H NMR analyses of polymers were performed using 5 wt% solutions of the polymers in an NMR tube in $CDCl_2CDCl_2$ at 120°C using a 30° pulse of 50.0 μs, a spectral width of 10 kHz, a relaxation time of 5.0 s, an acquisition time of 3.2 s. Quantitative ^{13}C NMR analyses of polymers were performed using 10 wt% solutions of the polymers in an NMR tube in1,2,4-trichlorobenzene at 125°C using a 30° pulse of 16.8 μs, a spectral width of 20 kHz, a relaxation time of 2.0 s, an acquisition time of 0.65 s, and inverse gated decoupling. Samples were preheated for at least 30 min before acquiring data. The molecular weights and molecular weight distributions of the polymers were determined using gel permeation chromatography (GPC) with a PL-220 equipped with two Agilent PLgel Olexis columns at 150 °C using 1,2,4-trichlorobenzene as a solvent. The calibration curve was constructed from polystyrene standard and was corrected for linear polyethylene by universal calibration using the Mark–Houwink parameters of Rudin:

$K = 5.90 \times 10^{-2}$ cm^3/g and $\alpha = 0.69$ for polyethylene. Melting points of polymers were measured on a TA Instruments DSC Q100 at heating and cooling rates of 10 °C/min with a temperature range of 30-160°C.

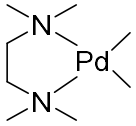
A standard test method, ASTM 638, was followed to measure the tensile properties of the polyethylene samples. Polymers were melt-pressed at 30 to 35℃ above their melting point to obtain the dog-bone-shaped tensile-test specimens. The test specimens showed 25-mm gauge length, 2-mm width, and thickness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

The water contact angles on polymer films were measured 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.

Preparation of sulfur vulcanized crosslinked polymer. A total amount of 3.0 g polymer sample was dissolved in 100 mL of toluene at 80 ℃ under nitrogen. After 30 min of reaction, add sulfuric acid (ie 150 mg ZnO, 30 mg stearic acid, 15 mg accelerator MBT, accelerator 20 mg TMTD, 30 mg sulfur), the solvent was drained and dried under vacuum at 45 °C for 24 hours. The rubber mixture was thermoformed using a hydraulic press at 10 MPa, 160 °C, and cured for 20 minutes to produce a 1 mm thick sheet for subsequent use.

Synthesis of Pd and Ni complexes

(TMEDA)$PdMe_2$[1-3]

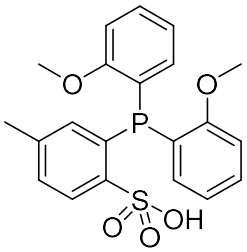


$PdCl_2$ (10 g, 56.39 mmol) was added to CH_3CN (300 mL) and refluxed for 2 h. After $PdCl_2$ was dissolved completely, the mixture was cooled to room tempterature. TMEDA (9.9 g, 93.22 mmol) was aded and the mixture was stirred overnight. The yellow slurry was filtrated and washed by Et_2O (60 mL), then dried in vacuo to obtain (TMEDA)$PdCl_2$ 15.88 g.

(TMEDA)$PdCl_2$ (4.62 g, 15.66 mmol) was added to Et_2O (49.3 mL), stirred for 10 min，then MeLi (19.6 mL, 1.6 M in Et_2O, 31.36 mmol) was added dropwise at –10 °C. The mixture was stirred at 0 °C for 0.5 h and at room temperature for 1 h，then cold water (20 mL) was added to the mixture to form a transparent organic layer and a black aqueous layer. The aqueous layer was extracted with Et_2O (20 mL×2)。All the organic phase was combined and dried over anhydrous sodium sulfate. The solvent was removed under vacumm to obtain the white solid (2.3 g, yield 52.8%).

^1H NMR (500 MHz, Chloroform-d) δ 2.51 (s, 4H), 2.45 (s, 12H), -0.16 (s, 6H).

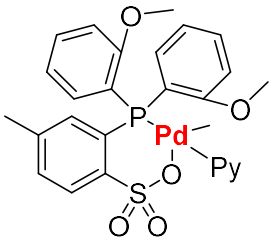
***ortho*-(Bis(2-methoxyphenyl)phosphino)toluenesulfonic acid (L3)[4]**



A flask was charged with p-toluenesulfonic acid (4.20 g, 24.4 mmol, dehydrated) and THF (50 mL), cooled to 0 °C, stirred for 10 min, and nBuLi (19.6 mL of a 2.5 M solution in hexane, 48.8 mmol) was added dropwise. The mixture was warmed to 25℃ and stirred for 2 h. A second flask was charged with THF (25 mL) and PCl_3 (3.35 g, 24.4 mmol), cooled to –30℃, and the solution of dilithiated p-toluenesulfonic acid was added and then stirred at room temperature for 1 h. A third flask was charged with THF (50 mL) and anisole (5.28 g, 48.8 mmol), cooled to 0 °C, and nBuLi (19.6 mL of a 2.5 M solution in hexane, 48.8 mmol) was added dropwise. The mixture was warmed to 25 °C and stirred for 4h, then transferred to the second flask at 0°C. The mixture was warmed to room temperature and stirred over night. The volatiles were removed under vacuum and the residue was taken up in water (50 mL). The aqueous mixture was acidified with dilute HCl to pH~2. The mixture was extracted with CH_2Cl_2 (3 × 25 mL) and the extracts were combined, dried over Na_2SO_4, and evaporated under vacuum to yield a solid. The solid was recrystallized with 8 mL DCM and 5 mL Et_2O at –25 ℃, filtrated and dried to afford a white powder **L3·0.5 CH_2Cl_2** . Yield 12.6 g, 24.8%.

^{1}H NMR (500 MHz, Chloroform-d) δ 8.25 (dd, J = 8.0, 5.4 Hz, 1H), 7.68 (td, J = 8.2, 1.6 Hz, 2H), 7.54 (dt, J = 8.0, 1.8 Hz, 1H), 7.12 – 6.97 (m, 6H), 6.87 (dd, J = 15.2, 1.7 Hz, 1H), 5.29 (s, 1H, C$\underline{H_2}$Cl$_2$), 3.78 (s, 6H), 2.29 (s, 3H). ^{13}C NMR (126 MHz, CHLOROFORM-D) δ 161.20, 149.67, 140.48, 139.87, 137.55, 135.20, 134.51, 134.45, 129.34, 129.26, 123.15, 121.19, 113.01, 112.22, 111.92, 107.64, 105.85, 55.57, 53.55, 18.72. ^{31}P NMR (202 MHz, CHLOROFORM-*D*) δ -10.98. HRMS (AP-MALDI): *m/z* calcd for $C_{21}H_{21}O_5PS$: 417.0920 [M+H]; found: 417.0918.

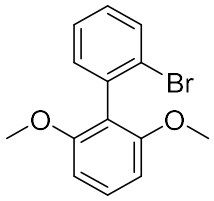
(P(2-OMe-Ph)$_2$(2-SO$_3$-5-Me-Ph))Pd(Me)(Py) (Pd3)



A flask was charged with **L3·0.5 CH_2Cl_2** (458.9 mg, 1.0 mmol), **(TMEDA)PdMe$_2$** (252.7 mg, 1.0 mmol) and THF (10 mL). The mixture was stirred at room temperature for 1 h, then pyridine (395.5 mg, 5 mmol) was added and stirred for 1 h. Et_2O (30 mL) was added to precipitate the solid. The solid was filtrated, washed with Et_2O and dried under vacuum to afford a white powder. Yield: 0.35 g, 56.8%.

^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.79 (d, *J* = 6.6 Hz, 2H), 8.09 (dd, *J* = 8.0, 4.9 Hz, 1H), 7.85 – 7.77 (m, 1H), 7.62 (s, 2H), 7.53 – 7.47 (m, 2H), 7.44 – 7.37 (m, 2H), 7.24 (d, *J* = 8.2 Hz, 1H), 7.08 – 6.98 (m, 3H), 6.92 (dd, *J* = 8.3, 4.7 Hz, 2H), 3.64 (s, 6H), 2.24 (s, 3H), 0.24 (d, *J* = 2.8 Hz, 3H). ^{13}C NMR (126 MHz, CHLOROFORM-*D*) δ 159.94, 150.58, 150.44, 145.96, 145.40, 139.60, 138.29, 138.21, 137.66, 135.73, 134.82, 133.27, 133.17, 131.43, 130.57, 128.06, 127.55, 127.16, 125.59, 125.04, 124.93, 120.86, 120.76, 120.66, 120.57, 116.72, 116.27, 111.56, 111.39, 55.46, 55.40, 21.37, 0.45.

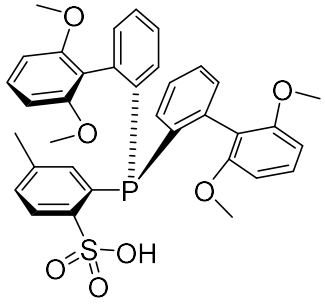
2'-bromo-2,6-dimethoxybiphenyl[5]



A flask was charged with 1,3-Dimethoxy benzene (70 g, 0.5 mol) and THF (1000 mL). nBuLi (2.5 M solution in hexane, 200 mL, 0.5 mmol) was added to the mixture at room temperature and stirred for 1 h. Then 1,2-dibromobenzene (100 g, 0.42 mol) was added dropwise at room temperature and stirred for 3 h. The solvent was removed under vacumm and warer (200 mL) was added. The aqueous layer was extracted with Et_2O (3×200 mL) and the extracts were combined, dried over Na_2SO_4, filtrated and dried under vacuum to afford a white powder. Yield: 108 g, 87.7%。

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.66 (dd, *J* = 8.0, 1.3 Hz, 1H), 7.38 – 7.32 (m, 2H), 7.25 – 7.18 (m, 2H), 6.66 (d, *J* = 8.4 Hz, 2H), 3.74 (s, 6H). ^{13}C NMR (126 MHz, CHLOROFORM-*D*) δ 157.74, 136.18, 132.42, 132.39, 129.56, 128.67, 127.01, 125.32, 118.89, 104.10, 56.07.

***ortho*-(Bis(2,6-dimethoxybiphenyl)phosphino)toluenesulfonic acid (L4)[6,7]**

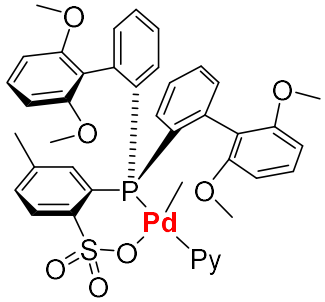


A flask was charged with p-toluenesulfonic acid (4.14 g, 24.0 mmol, dehydrated) and THF (50 mL), cooled to 0 °C, stirred for 10 min, and nBuLi (19.2 mL of a 2.5 M solution in hexane, 48.0 mmol) was added dropwise. The mixture was warmed to 25℃ and stirred for 2 h. A second flask was charged with THF (60 mL) and PCl_3 (3.3 g, 24.0 mmol), cooled to –78℃, and the solution of dilithiated p-toluenesulfonic acid was added and then stirred at 0 °C for 1.5 h. A third flask was charged with THF (300 mL) and 2'-bromo-2,6-dimethoxybiphenyl (14.0 g, 48.0 mmol), cooled to –78℃, and nBuLi

(20.0 mL of a 2.5 M solution in hexane, 50.0 mmol) was added dropwise. The mixture was kept at –78°C for 1 h and then transferred to the second flask at –78°C. The mixture was warmed to room temperature and stirred over night. The volatiles were removed under vacuum and the residue was taken up in water (200 mL). The aqueous mixture was acidified with dilute HCl to pH~2. The mixture was extracted with CH_2Cl_2 (3 × 50 mL) and the extracts were combined, dried over Na_2SO_4, and evaporated under vacuum to yield a solid. The solid was slurried with 10 mL DCM and 20 mL Et_2O, filtrated and dried to afford a white powder **L4** . Yield 7.45 g, 49.7%.

^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.03 (dd, *J* = 7.9, 5.3 Hz, 1H), 7.68 – 7.57 (m, 2H), 7.45 – 7.13 (m, 9H), 6.83 (d, *J* = 13.0 Hz, 1H), 6.33 (d, *J* = 91.4 Hz, 4H), 3.46 (q, *J* = 7.0 Hz, 12H), 2.26 (s, 3H). HRMS (AP-MALDI): *m/z* calcd for $C_{35}H_{33}O_7PS$: 629.1757 [M+H]; found: 629.1756.

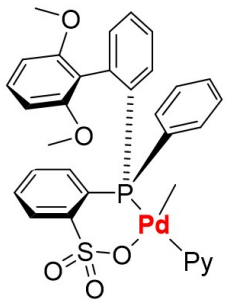
(P(2,6-diOMePh-Ph)$_2$(2-SO$_3$-5-Me-Ph))Pd(Me)(Py) (Pd4)



A flask was charged with **L4** (628.9 mg, 1.0 mmol), **(TMEDA)PdMe$_2$** (252.7 mg, 1.0 mmol) and THF (10 mL). The mixture was stirred at room temperature for 1 h, then pyridine (395.5 mg, 5 mmol) was added and stirred for 1 h. Et_2O (30 mL) was added to precipitate the solid at –25°C. The solid was filtrated, washed with Et_2O and dried under vacuum to afford a white powder. Yield: 0.71 g, 85.7%.

^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.57 (dd, *J* = 4.7, 1.8 Hz, 2H), 7.85 – 7.67 (m, 4H), 7.43 (t, *J* = 8.6 Hz, 3H), 7.37 – 7.29 (m, 4H), 7.13 (ddd, *J* = 7.7, 4.4, 1.5 Hz, 2H), 6.95 (t, *J* = 8.3 Hz, 3H), 6.41 (d, *J* = 9.2 Hz, 2H), 6.25 (d, *J* = 8.4 Hz, 2H), 3.68 (s, 6H), 3.41 (s, 6H), 2.16 (s, 3H), 0.18 (d, *J* = 2.3 Hz, 3H). ^{13}C NMR (126 MHz, Methylene Chloride-d_2) δ 157.93, 157.66, 150.82, 138.19, 136.77, 135.79, 134.38, 134.31, 131.15, 129.91, 129.29, 128.22, 126.25, 124.80, 119.15, 103.72, 103.62, 55.51, 21.54, 3.54. Anal. Calcd. for $C_{41}H_{40}NO_7PPdS$: C, 59.46; H, 4.87. Found: C, 58.07; H, 4.95.

(P(2,6-diOMePh-Ph)$_2$(2-SO$_3$-Ph))Pd(Me)(Py) (Pd5)

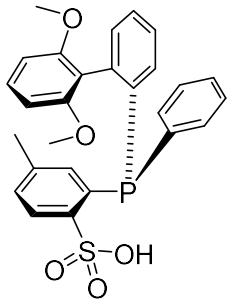


A flask was charged with benzenesulfonic acid (3.8 g, 24.0 mmol, dehydrated) and THF (60 mL), cooled to 0 °C, stirred for 10 min, and nBuLi (19.2 mL of a 2.5 M solution in hexane, 48.0 mmol) was added dropwise. The mixture was warmed to 25℃ and stirred for 2 h. A second flask was charged with THF (60 mL) and $PPhCl_2$ (3.25 mL, 24 mmol), cooled to –78℃, and the solution of dilithiated p-toluenesulfonic acid was added and then stirred at –78℃ for 1.5 h. A third flask was charged with THF (300 mL) and 2'-bromo-2,6-dimethoxybiphenyl (7.0 g, 24.0 mmol), cooled to –78℃, and nBuLi (11.2 mL of a 2.5 M solution in hexane, 28.0 mmol) was added dropwise. The mixture was kept at –78℃ for 1 h and then transferred to the second flask at –78℃. The mixture was warmed to room temperature and stirred over night. The volatiles were removed under vacuum and the residue was taken up in water (200 mL). The aqueous mixture was acidified with dilute HCl to pH~2. The mixture was extracted with CH_2Cl_2 (3 × 50 mL) and the extracts were combined, dried over Na_2SO_4, and evaporated under vacuum to yield a solid. The solid was slurried with 10 mL DCM and 20 mL Et_2O, filtrated and dried to afford a white powder 4.9 g.

A flask was charged with white powder (520.0 mg), **(TMEDA)PdMe$_2$** (252.7 mg, 1.0 mmol) and THF (10 mL). The mixture was stirred at room temperature for 1 h, then pyridine (395.5 mg, 5 mmol) was added and stirred for 1 h. Et_2O (30 mL) was added to precipitate the solid at –25℃. The solid was filtrated, washed with Et_2O and dried under vacuum to afford a white powder. Yield: 0.53 g, 78.2%.

^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.36 (s, 3H), 7.74 (t, *J* = 7.7 Hz, 1H), 7.60 (q, *J* = 8.1, 7.2 Hz, 2H), 7.52 (t, *J* = 7.4 Hz, 1H), 7.45 – 7.37 (m, 4H), 7.35 – 7.25 (m, 7H), 7.20 (t, *J* = 8.3 Hz, 1H), 6.50 (dd, *J* = 8.3, 4.6 Hz, 2H), 3.66 (s, 3H), 2.73 (s, 3H), 0.32 (d, *J* = 2.5 Hz, 3H). ^{13}C NMR (126 MHz, CHLOROFORM-D) δ 158.16, 157.28, 151.08, 149.22, 141.83, 137.63, 136.18, 134.76, 134.26, 133.24, 131.48, 130.22, 129.76, 129.48, 129.05, 128.68, 128.35, 128.12, 126.46, 124.63, 117.05, 104.11, 103.04, 56.39, 54.17, 0.24. Anal. Calcd. for $C_{32}H_{30}NO_5PPdS$: C, 56.69; H, 4.46. Found: C, 55.46; H, 4.63.

***ortho*-((2,6-dimethoxybiphenyl)(phenyl)phosphino)toluenesulfonic acid (L1)** [8]
2-[(2',6'-dimethoxy[1,1'-biphenyl]-2-yl)phenylphosphino]-4-methyl benzenesulfonic acid

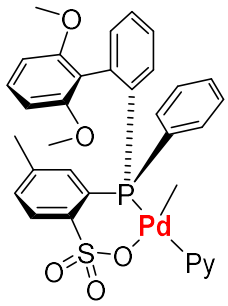


A flask was charged with p-toluenesulfonic acid (4.14 g, 24.0 mmol, dehydrated) and THF (60 mL), cooled to 0 °C, stirred for 10 min, and nBuLi (19.2 mL of a 2.5 M

solution in hexane, 48.0 mmol) was added dropwise. The mixture was warmed to 25℃ and stirred for 2 h. A second flask was charged with THF (60 mL) and $PPhCl_2$ (3.25 mL, 24 mmol), cooled to –78℃, and the solution of dilithiated p-toluenesulfonic acid was added and then stirred at –78℃ for 1.5 h. A third flask was charged with THF (300 mL) and 2'-bromo-2,6-dimethoxybiphenyl (7.0 g, 24.0 mmol), cooled to –78℃, and nBuLi (11.2 mL of a 2.5 M solution in hexane, 28.0 mmol) was added dropwise. The mixture was kept at –78℃ for 1 h and then transferred to the second flask at –78℃. The mixture was warmed to room temperature and stirred over night. The volatiles were removed under vacuum and the residue was taken up in water (200 mL). The aqueous mixture was acidified with dilute HCl to pH~2. The mixture was extracted with CH_2Cl_2 (3 × 50 mL) and the extracts were combined, dried over Na_2SO_4, and evaporated under vacuum to yield a solid. The solid was slurried with 10 mL DCM and 20 mL Et_2O, filtrated and dried to afford a white powder **L1·0.5 CH_2Cl_2**. Yield 9.1 g, 77%.

^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.19 (dd, *J* = 7.9, 5.2 Hz, 1H), 7.73 (t, *J* = 7.7 Hz, 1H), 7.60 – 7.54 (m, 1H), 7.53 – 7.30 (m, 8H), 7.23 (t, *J* = 8.4 Hz, 1H), 7.07 – 7.01 (m, 1H), 6.47 (d, *J* = 8.3 Hz, 1H), 6.39 (d, *J* = 8.4 Hz, 1H), 5.28 (s, 1H), 3.60 (s, 3H), 3.42 (s, 3H), 2.31 (s, 3H). ^{13}C NMR (126 MHz, CHLOROFORM-*D*) δ 156.97, 156.57, 149.89, 149.82, 140.93, 140.85, 139.80, 139.70, 135.05, 134.05, 133.48, 132.66, 131.69, 131.54, 131.39, 129.22, 128.78, 127.96, 120.30, 119.57, 119.47, 118.74, 113.88, 113.83, 113.15, 112.40, 103.82, 103.73, 55.48, 55.41, 55.35, 55.33, 21.29, 21.24. ^{31}P NMR (202 MHz, CHLOROFORM-*D*) δ 1.53. HRMS (AP-MALDI): *m/z* calcd for $C_{27}H_{25}O_5PS$: 493.1233 [M+H]; found: 493.1232.

(P(2,6-diOMePh-Ph)$_2$(2-SO$_3$-5-Me-Ph))Pd(Me)(Py) (Pd1)

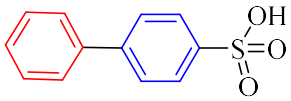


A flask was charged with **L1·0.5 CH_2Cl_2** (535.0 mg, 1.0 mmol), **(TMEDA)PdMe$_2$** (252.7 mg, 1.0 mmol) and THF (10 mL). The mixture was stirred at room temperature for 1 h, then pyridine (395.5 mg, 5 mmol) was added and stirred for 1 h. Et_2O (30 mL) was added to precipitate the solid at –25℃. The solid was filtrated, washed with Et_2O and dried under vacuum to afford a white powder. Yield: 0.41 g, 59.2%.

^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.38 (dd, *J* = 4.7, 1.9 Hz, 2H), 8.25 (dd, *J* = 8.0, 4.7 Hz, 1H), 7.77 – 7.71 (m, 1H), 7.69 – 7.56 (m, 2H), 7.48 – 7.40 (m, 2H), 7.34 – 7.27 (m, 8H), 7.23 – 7.19 (m, 2H), 6.52 (d, *J* = 8.4 Hz, 2H), 3.67 (s, 3H), 2.77 (s, 3H), 2.26 (s, 3H), 0.30 (d, *J* = 2.5 Hz, 3H). ^{13}C NMR (126 MHz, CHLOROFORM-*D*) δ

158.16, 157.23, 150.38, 150.29, 150.18, 146.81, 146.27, 142.70, 141.73, 140.64, 140.21, 137.91, 136.22, 134.75, 134.09, 133.98, 133.76, 133.35, 133.22, 130.94, 130.17, 129.67, 129.51, 129.08, 128.45, 128.37, 128.11, 126.27, 124.62, 124.52, 118.25, 118.20, 103.64, 103.60, 103.02, 102.97, 55.45, 55.40, 54.35, 54.27, 21.59, 0.34. Anal. Calcd. for $C_{33}H_{32}NO_5PPdS$: C, 57.27; H, 4.66. Found: C, 57.05; H, 4.91.

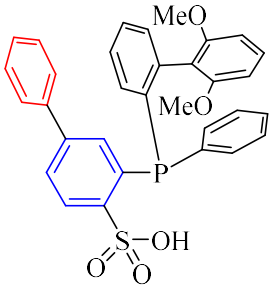
4-phenylbenzenesulfonic Acid



A flask was charged with biphenyl (10 g, 0.067 mol) and $CHCl_3$ (50 mL). Sulfurochloridic acid (9.6 g, 0.083 mol) in $CHCl_3$ (10 mL) was added dropwise for 1 h. The mixture was stirred for 0.5 h, filtrated, and washed by $CHCl_3$. The solid was dried under vacuum to afford a white powder. Yied: 10.7 g, 68.2%.

^{1}H NMR (500 MHz, THF-d_8) δ 8.85 (d, J = 9.6 Hz, 2H), 8.28 – 7.59 (m, 5H), 7.41 (ddd, J = 35.6, 7.4, 3.5 Hz, 2H).

***2*-((2,6-dimethoxybiphenyl)(phenyl)phosphino)-4-phenylbenzenesulfonic acid (L2)**

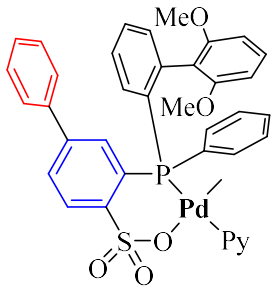


A flask was charged with 4-phenylbenzenesulfonic acid (5.62 g, 24.0 mmol, dehydrated) and THF (60 mL), cooled to 0 °C, stirred for 10 min, and nBuLi (19.2 mL of a 2.5 M solution in hexane, 48.0 mmol) was added dropwise. The mixture was warmed to 25°C and stirred for 2 h. A second flask was charged with THF (60 mL) and $PPhCl_2$ (3.25 mL, 24 mmol), cooled to –78°C, and the solution of dilithiated p-toluenesulfonic acid was added and then stirred at –78°C for 1.5 h. A third flask was charged with THF (300 mL) and 2'-bromo-2,6-dimethoxybiphenyl (7.0 g, 24.0 mmol), cooled to –78°C, and nBuLi (11.2 mL of a 2.5 M solution in hexane, 28.0 mmol) was added dropwise. The mixture was kept at –78°C for 1 h and then transferred to the second flask at –78°C. The mixture was warmed to room temperature and stirred over night. The volatiles were removed under vacuum and the residue was taken up in water (200 mL). The aqueous mixture was acidified with dilute HCl to pH~2. The mixture was extracted with CH_2Cl_2 (3 × 50 mL) and the extracts were combined, dried over Na_2SO_4, and evaporated under vacuum to yield a solid. The solid was slurried with 10 mL DCM and 20 mL Et_2O, filtrated and dried to afford a white powder **L2·0.5 CH_2Cl_2**. Yield 7.2 g, 54.2%.

^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.45 – 8.29 (m, 1H), 7.94 (d, *J* = 8.1 Hz, 1H), 7.77 (s, 1H), 7.61 (s, 1H), 7.43 (d, *J* = 41.5 Hz, 14H), 6.47 (t, *J* = 7.0 Hz, 2H), 5.30 (s, 1H), 3.66 (s, 3H), 3.33 (s, 3H).

HRMS (AP-MALDI): *m/z* calcd for $C_{32}H_{27}O_5PS$: 555.1390 [M+H]; found: 555.1386.

(P(2,6-diOMePh-Ph)$_2$(2-SO$_3$-5-Ph-Ph))Pd(Me)(Py) (Pd2)



A flask was charged with **L2** (554.6.0 mg, 1.0 mmol), **(TMEDA)PdMe$_2$** (252.7 mg, 1.0 mmol) and THF (10 mL). The mixture was stirred at room temperature for 1 h, then pyridine (395.5 mg, 5 mmol) was added and stirred for 1 h. Et_2O (30 mL) was added to precipitate the solid at –25℃. The solid was filtrated, washed with Et_2O and dried under vacuum to afford a white powder. Yield: 0.59 g, 78.4%.

^{1}H NMR (500 MHz, Methylene Chloride-d_2) δ 8.38 (s, 2H), 8.27 (dd, *J* = 8.1, 4.5 Hz, 1H), 7.87 – 7.75 (m, 2H), 7.63 (s, 3H), 7.46 – 7.30 (m, 14H), 7.26 (s, 1H), 6.58 – 6.44 (m, 2H), 3.62 (s, 3H), 2.76 (s, 3H), 0.39 (s, 3H).

^{13}C NMR (126 MHz, Methylene Chloride-d_2) δ 158.46, 157.69, 150.93, 148.42, 148.31, 142.73, 142.26, 142.13, 139.55, 138.51, 136.31, 135.04, 133.76, 133.44, 133.11, 131.33, 130.27, 130.16, 129.78, 129.36, 128.84, 128.50, 127.23, 126.71, 125.12, 118.35, 104.59, 102.74, 56.32, 54.41, -1.59.

Anal. Calcd. for $C_{38}H_{33}NO_5PPdS$: C, 60.6; H, 4.42 Found: C, 58.82; H, 4.60.

General procedure for homopolymerization

A 1000 mL stainless steel reactor was charged with toluene (400 mL) and desired amount of Pd complex in 2 mL CH_2Cl_2. The pressure vessel was connected to a high pressure line and the solution was degassed. The reactor was warmed to the desired temperature using an water bath. The reactor was pressurized and maintained at the desired pressure of ethylene. After desired amount of time, the reactor was vented and the polymer was precipitated in ethanol (400 mL), filtrated and dried at 80 °C for 24 h under vacuum.

General procedure for copolymerization and terpolymerization

A 1000 mL stainless steel reactor was charged with toluene (200 mL), polar monomer, BHT (2 mg) in toluene (2 mL) and desired amount of Pd complex in 2 mL CH_2Cl_2. The pressure vessel was connected to a high pressure line and the solution was degassed. The reactor was warmed to the desired temperature using an water bath. The

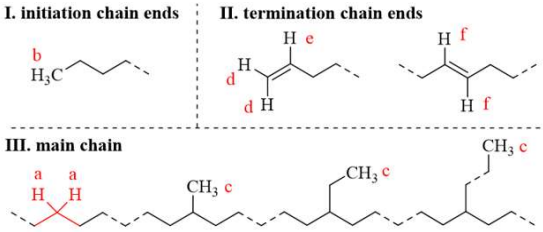
reactor was pressurized and maintained at the desired pressure of ethylene. After desired amount of time, the reactor was vented and the polymer was precipitated in ethanol (400 mL), filtrated and dried at 80 °C for 24 h under vacuum.

Computational Methods

Density functional theory (DFT) calculations were performed using the Gaussian 09 Program, revision E.01.[9] DFT calculations for structure optimizations were performed with the B3LYP functional[10] with empirical disperision correction, DFT-D3[11], the Lanl2dz basis set[12] for palladium, and the 6-31G(d) basis set[13] for the light atoms (C, H, O, N, P and S). Single point calculations were performed with the B3LYP functional with empirical dispersion correction, DFT-D3, the SDD basis set[14] for palladium, and the 6-311G(d,p) basis sets[15] for the light atoms. The solvation effect of toluene (ε = 2.37) was considered through the SMD model[16] in single-point calculations. Electrostatic potential (ESP) maps were performed by Multiwfn[17] and VMD[18]. Steric maps were drawn by Sambvca 2.1[19] based on the DFT optimized structures or molecuar structures from X-ray diffraction analysis of single crystals.

Equations to calculate comonomer incorporation ratio, U_{int}, and number of branches

For PE[20-25]:



assignment	chemical shift in ^{1}H NMR
a	1.32
b	0.96
c	0.90
d	4.95
e	5.8
f	5.4
aliphatic	0.5~2.5

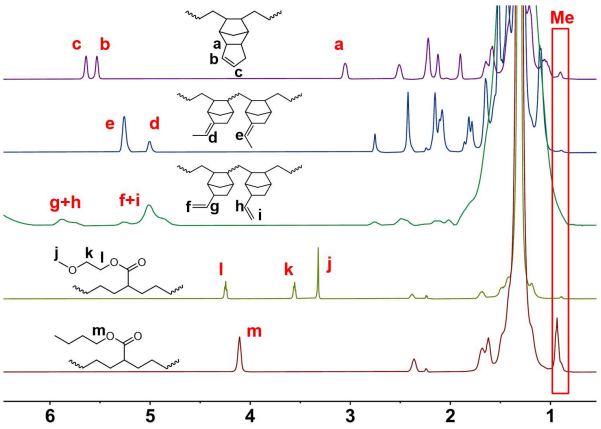
number of branches[26]

$$B = \frac{\frac{I_b + I_c}{3} - \frac{I_d + I_f}{2}}{\frac{I_b + I_c}{3} + \frac{I_a}{2}} \times 1000$$

internal unsaturation[27]

$$U_{int} = \frac{I_f}{I_d + I_f} \times 100\%$$

For copolymers and terpolymers:



EBA: Incorporation ratio of BA

$$x = \frac{\frac{I_m}{2}}{I_{aliphatic} - \frac{I_m}{2} \times 10} \times 100\%$$

E-EGMA: Incorporation ratio of EGMA

$$x_{EGMA} = \frac{\frac{I_l}{2}}{I_{aliphatic} - \frac{I_l}{2} \times 3} \times 100\%$$

E-ENB: Incorporation ratio of ENB $x_{\mathrm{ENB}} = \dfrac{I_{\mathrm{e+d}}}{\dfrac{I_{\mathrm{aliphatic}} - I_{\mathrm{e+d}} \times 11}{4} + I_{\mathrm{e+d}}} \times 100\%$

E-VNB: Incorporation ratio of VNB $x_{\mathrm{VNB}} = \dfrac{\dfrac{I_{\mathrm{f+g+h+i}}}{3}}{\dfrac{I_{\mathrm{aliphatic}} - \dfrac{I_{\mathrm{f+g+h+i}}}{3} \times 9}{4} + \dfrac{I_{\mathrm{f+g+h+i}}}{3}} \times 100\%$

E-DCPD: Incorporation ratio of DCPD $x_{\mathrm{DCPD}} = \dfrac{I_{\mathrm{a}}}{\dfrac{I_{\mathrm{aliphatic}} - I_{\mathrm{a}} \times 9}{4} + I_{\mathrm{a}}} \times 100\%$

E-BA-EGMA: Incorporation ratio of BA $x_{\mathrm{BA}} = \dfrac{\dfrac{I_{\mathrm{m}}}{2}}{\dfrac{I_{\mathrm{aliphatic}} - \dfrac{I_{\mathrm{m}}}{2} \times 10 - \dfrac{I_{\mathrm{l}}}{2} \times 3}{4} + \dfrac{I_{\mathrm{m}}}{2} + \dfrac{I_{\mathrm{l}}}{2}} \times 100\%$

Incorporation ratio of EGMA $x_{\mathrm{EGMA}} = \dfrac{\dfrac{I_{\mathrm{l}}}{2}}{\dfrac{I_{\mathrm{aliphatic}} - \dfrac{I_{\mathrm{m}}}{2} \times 10 - \dfrac{I_{\mathrm{l}}}{2} \times 3}{4} + \dfrac{I_{\mathrm{m}}}{2} + \dfrac{I_{\mathrm{l}}}{2}} \times 100\%$

E-BA-VNB: Incorporation ratio of BA $x_{\mathrm{BA}} = \dfrac{\dfrac{I_{\mathrm{m}}}{2}}{\dfrac{I_{\mathrm{aliphatic}} - \dfrac{I_{\mathrm{m}}}{2} \times 10 - \dfrac{I_{\mathrm{f+g+h+i}}}{3} \times 9}{4} + \dfrac{I_{\mathrm{m}}}{2} + \dfrac{I_{\mathrm{f+g+h+i}}}{3}} \times 100\%$

Incorporation ratio of VNB $x_{\mathrm{VNB}} = \dfrac{\dfrac{I_{\mathrm{f+g+h+i}}}{3}}{\dfrac{I_{\mathrm{aliphatic}} - \dfrac{I_{\mathrm{m}}}{2} \times 10 - \dfrac{I_{\mathrm{f+g+h+i}}}{3} \times 9}{4} + \dfrac{I_{\mathrm{m}}}{2} + \dfrac{I_{\mathrm{f+g+h+i}}}{3}} \times 100\%$

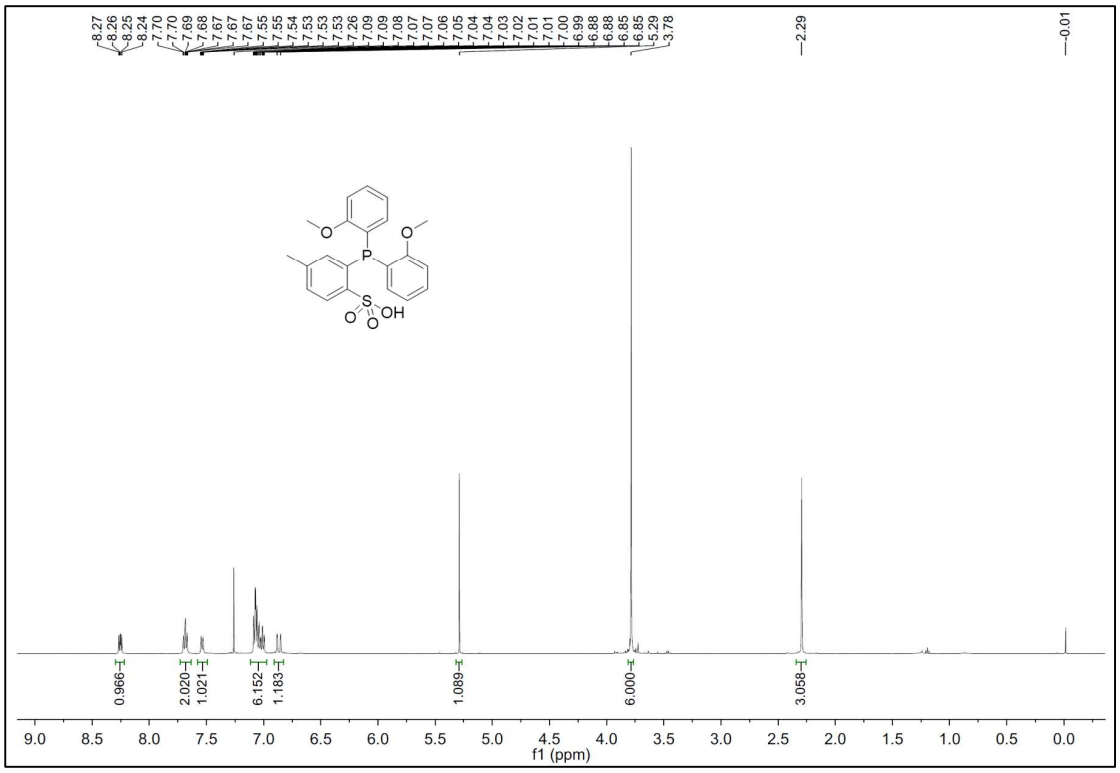
E-BA-ENB: Incorporation ratio of BA $x_{\mathrm{BA}} = \dfrac{\dfrac{I_{\mathrm{m}}}{2}}{\dfrac{I_{\mathrm{aliphatic}} - \dfrac{I_{\mathrm{m}}}{2} \times 10 - I_{\mathrm{e+d}} \times 11}{4} + \dfrac{I_{\mathrm{m}}}{2} + I_{\mathrm{e+d}}} \times 100\%$

Incorporation ratio of ENB $x_{\mathrm{ENB}} = \dfrac{I_{\mathrm{e+d}}}{\dfrac{I_{\mathrm{aliphatic}} - \dfrac{I_{\mathrm{m}}}{2} \times 10 - I_{\mathrm{e+d}} \times 11}{4} + \dfrac{I_{\mathrm{m}}}{2} + I_{\mathrm{e+d}}} \times 100\%$

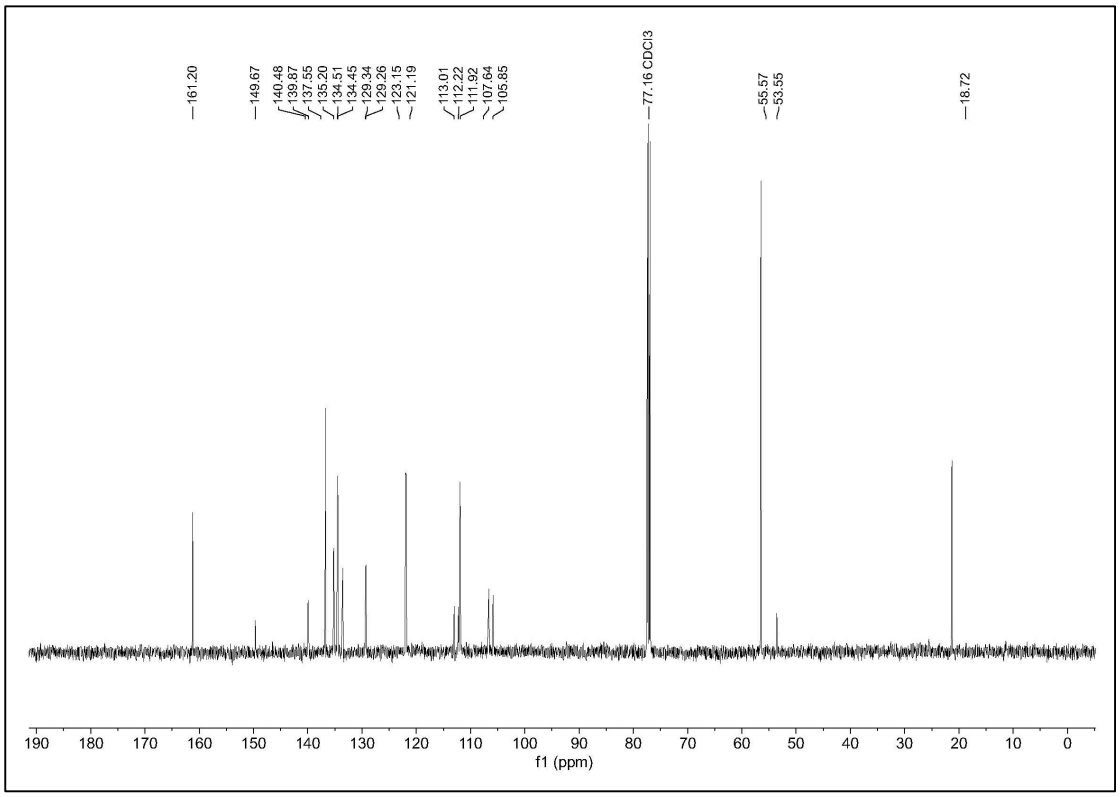
E-BA-DCPD: Incorporation ratio of BA $x_{\mathrm{BA}} = \dfrac{\dfrac{I_{\mathrm{m}}}{2}}{\dfrac{I_{\mathrm{aliphatic}} - \dfrac{I_{\mathrm{m}}}{2} \times 10 - I_{\mathrm{a}} \times 9}{4} + \dfrac{I_{\mathrm{m}}}{2} + I_{\mathrm{a}}} \times 100\%$

Incorporation ratio of DCPD $x_{\mathrm{DCPD}} = \dfrac{I_{\mathrm{a}}}{\dfrac{I_{\mathrm{aliphatic}} - \dfrac{I_{\mathrm{m}}}{2} \times 10 - I_{\mathrm{a}} \times 9}{4} + \dfrac{I_{\mathrm{m}}}{2} + I_{\mathrm{a}}} \times 100\%$

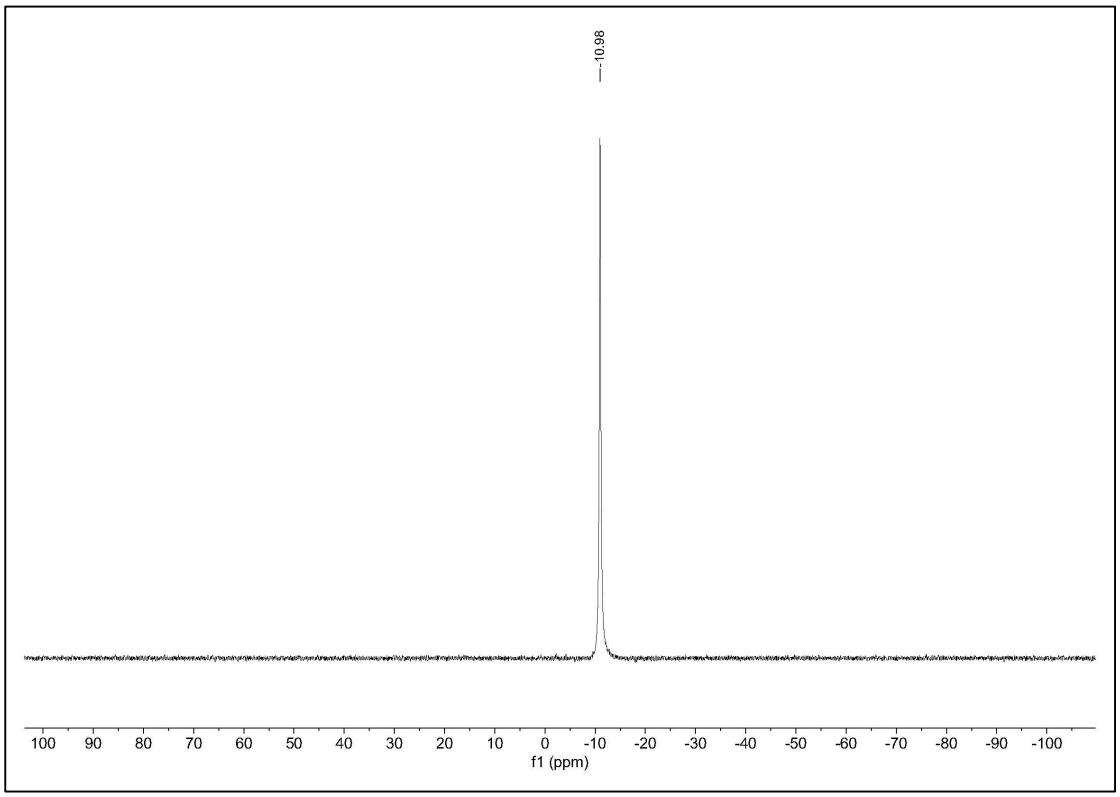
NMR spectra of prepared compounds



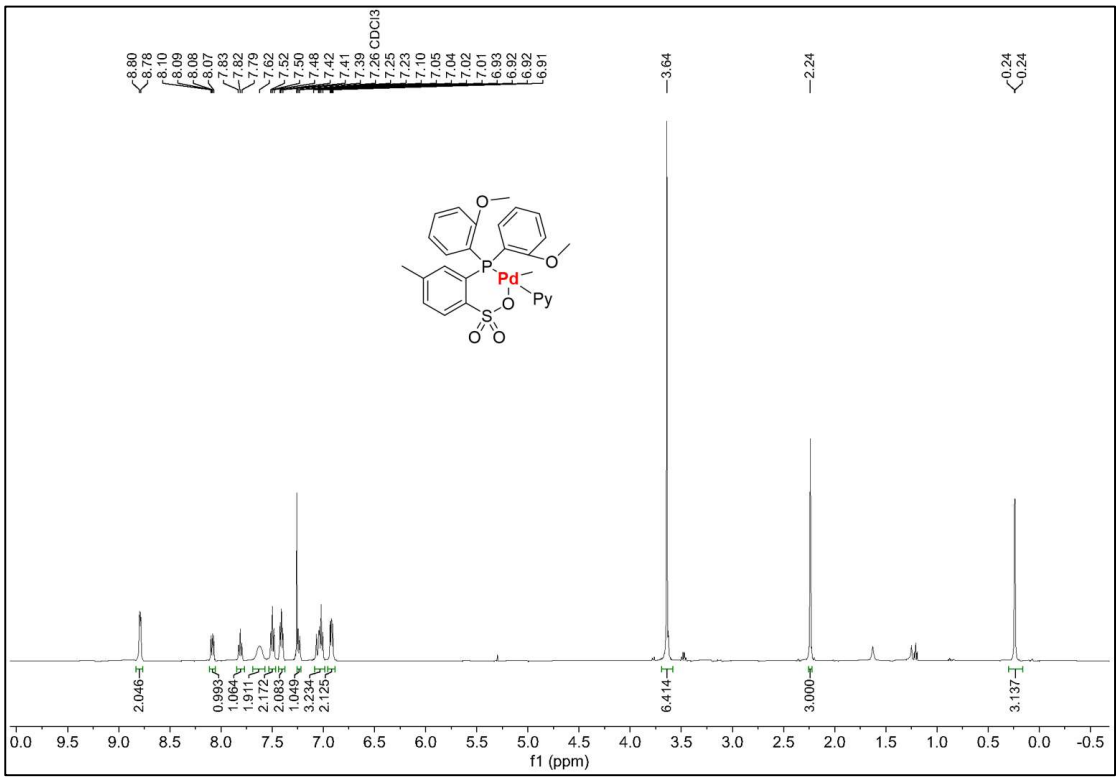
^{1}H NMR spectrum of L3·0.5CH_2Cl_2 (in $CDCl_3$)



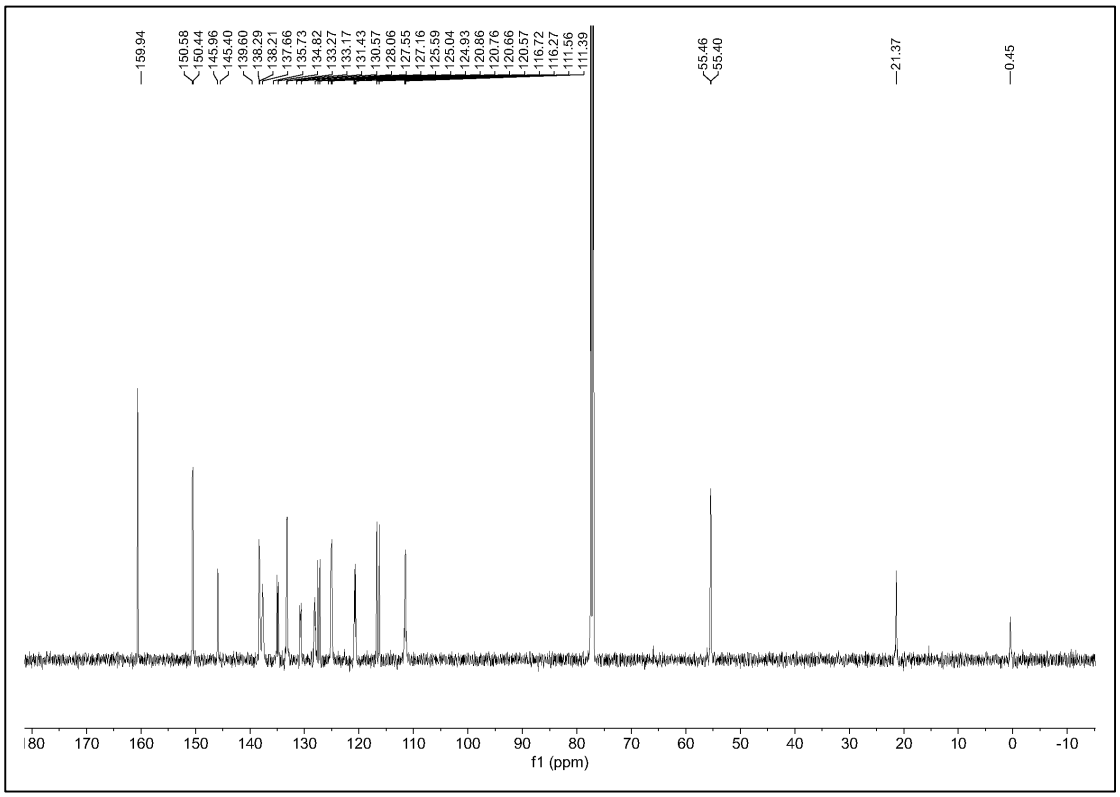
^{13}C NMR spectrum of L3·0.5CH_2Cl_2 (in $CDCl_3$)



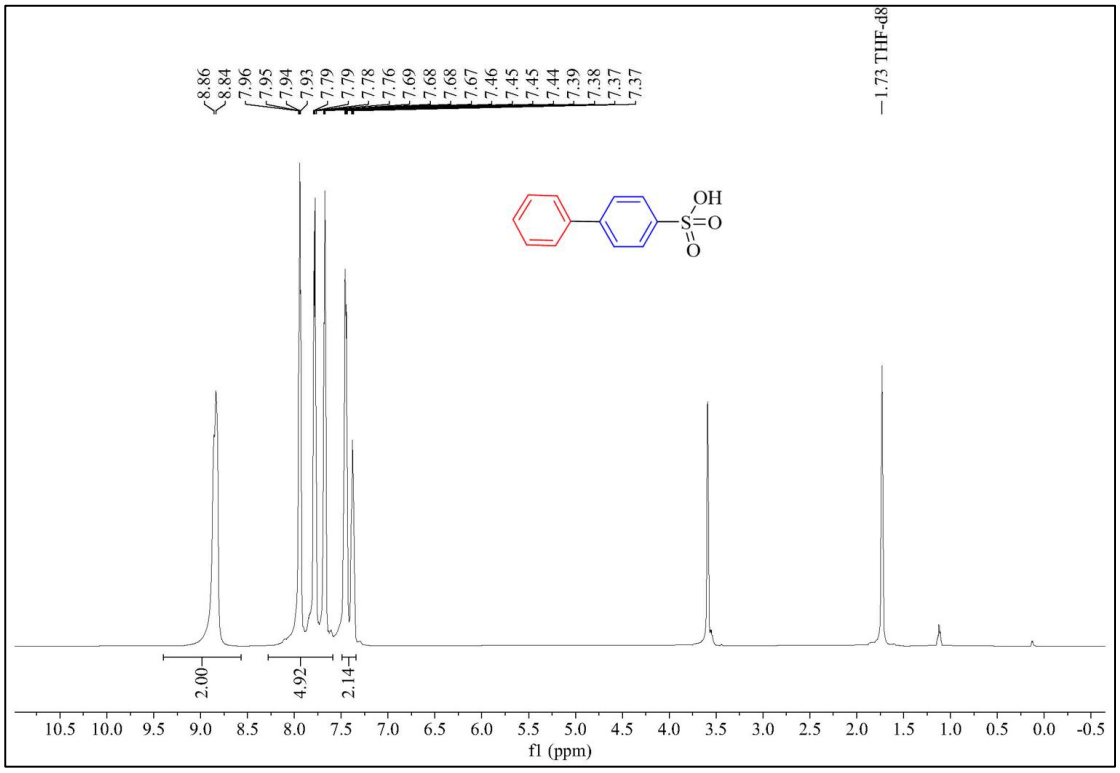
^{31}P NMR spectrum of L3·0.5CH_2Cl_2 (in $CDCl_3$)



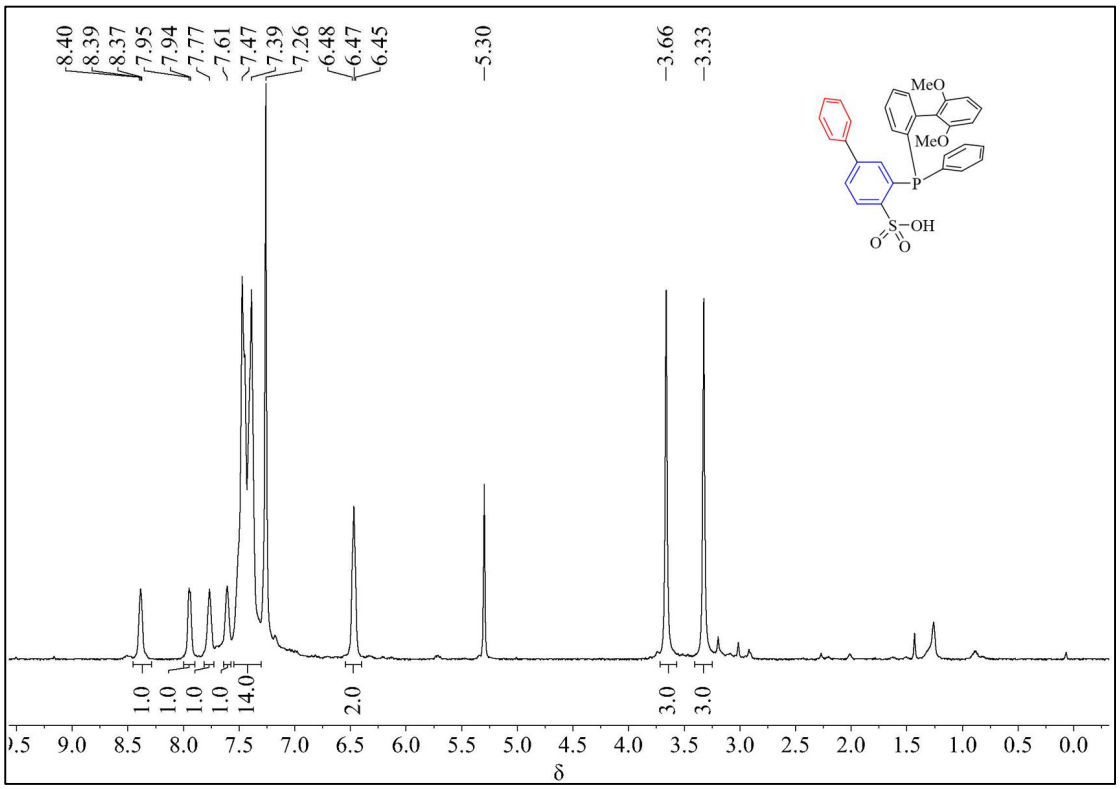
^{1}H NMR spectrum of Pd3 (in $CDCl_3$)



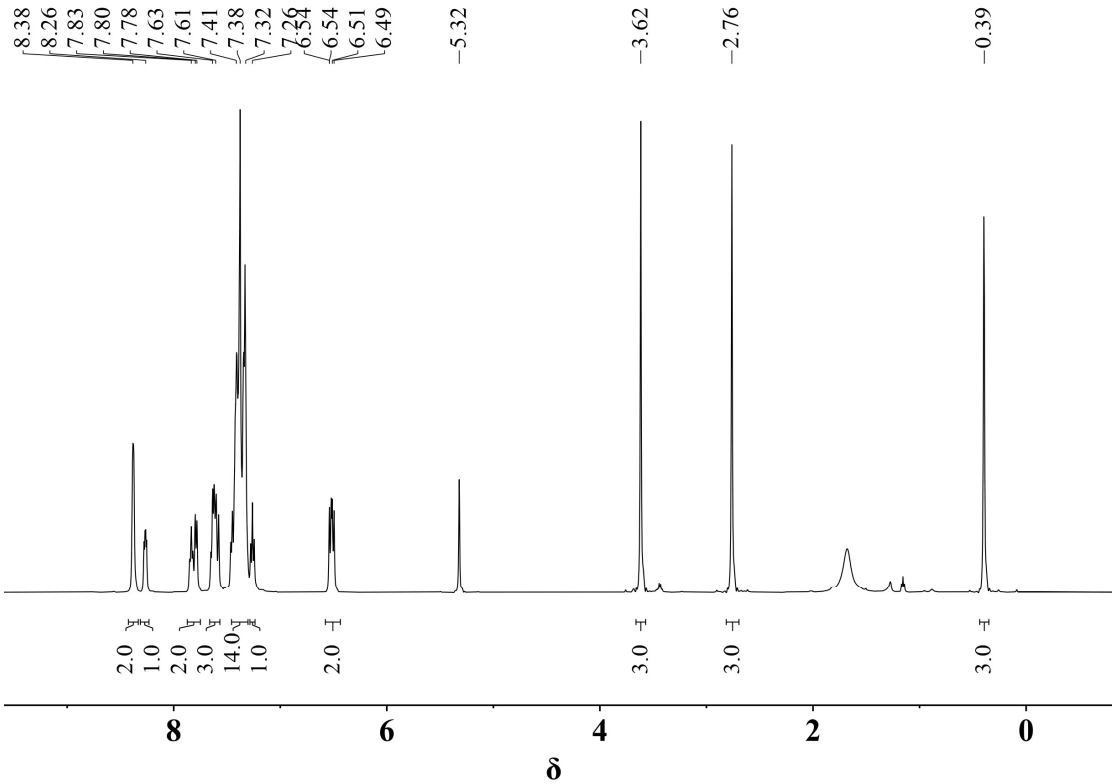
^{13}C NMR spectrum of Pd3 (in $CDCl_3$)



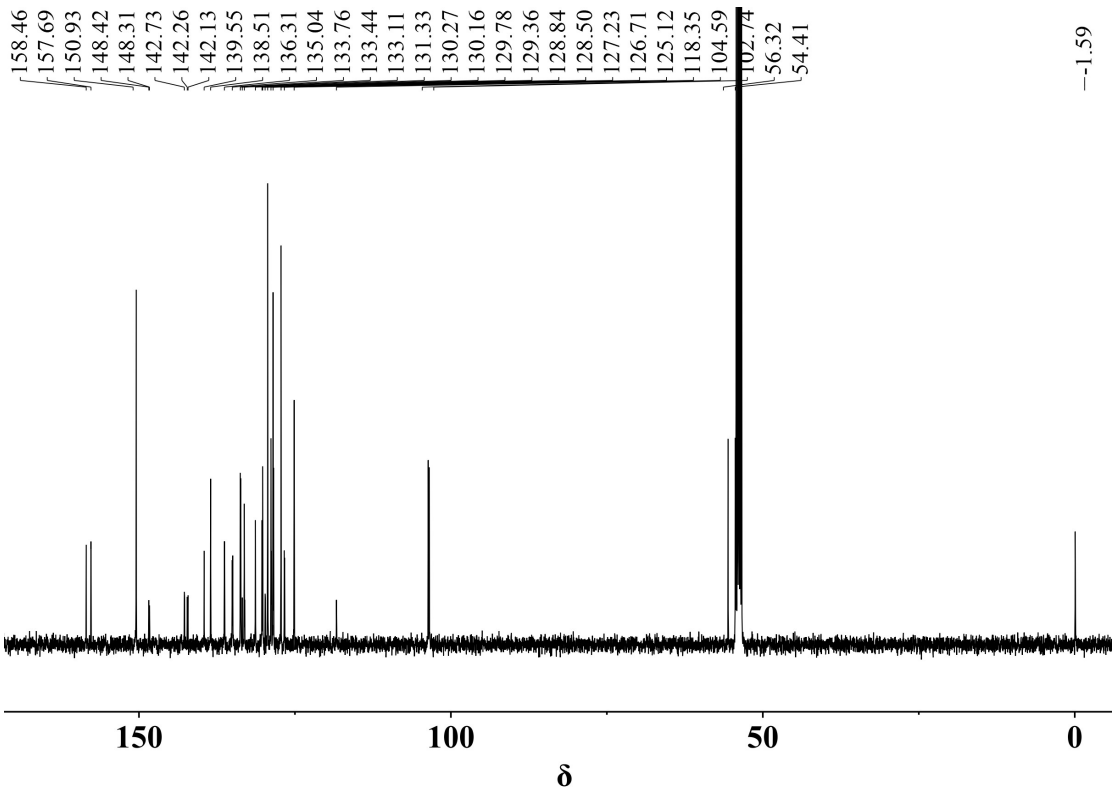
^{1}H NMR spectrum of L2 (in THF-d_8)



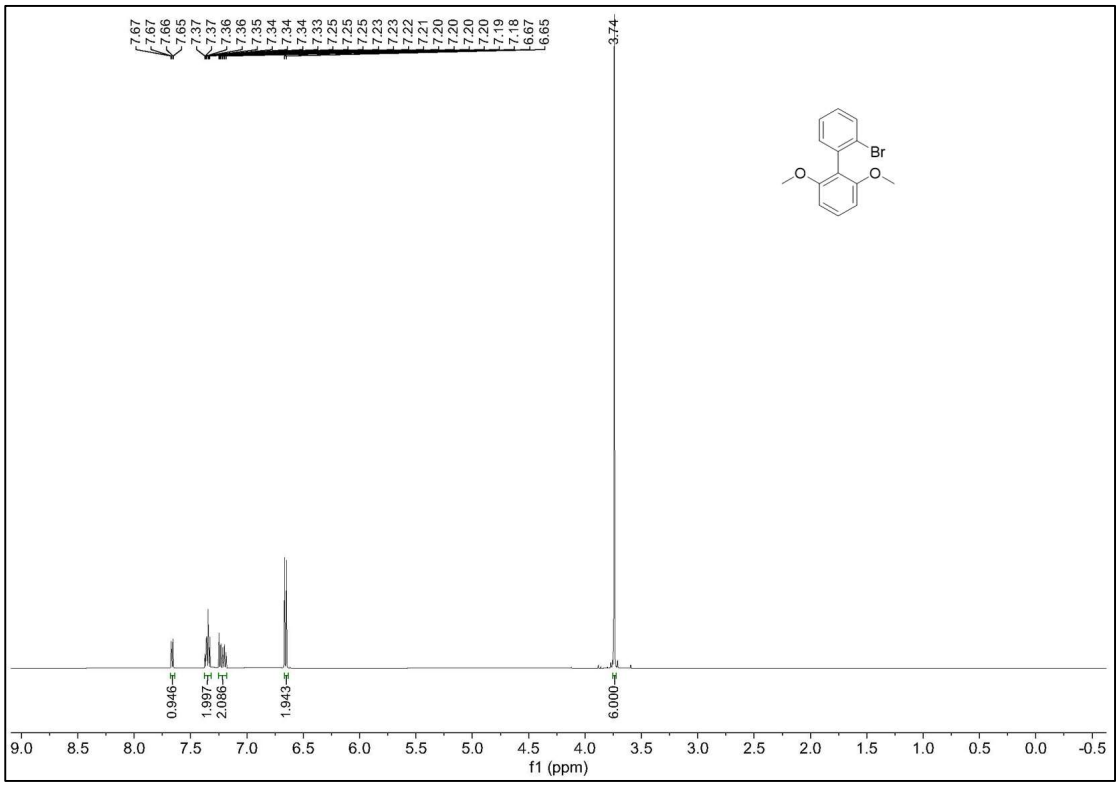
^{1}H NMR spectrum of L2 (in $CDCl_3$)



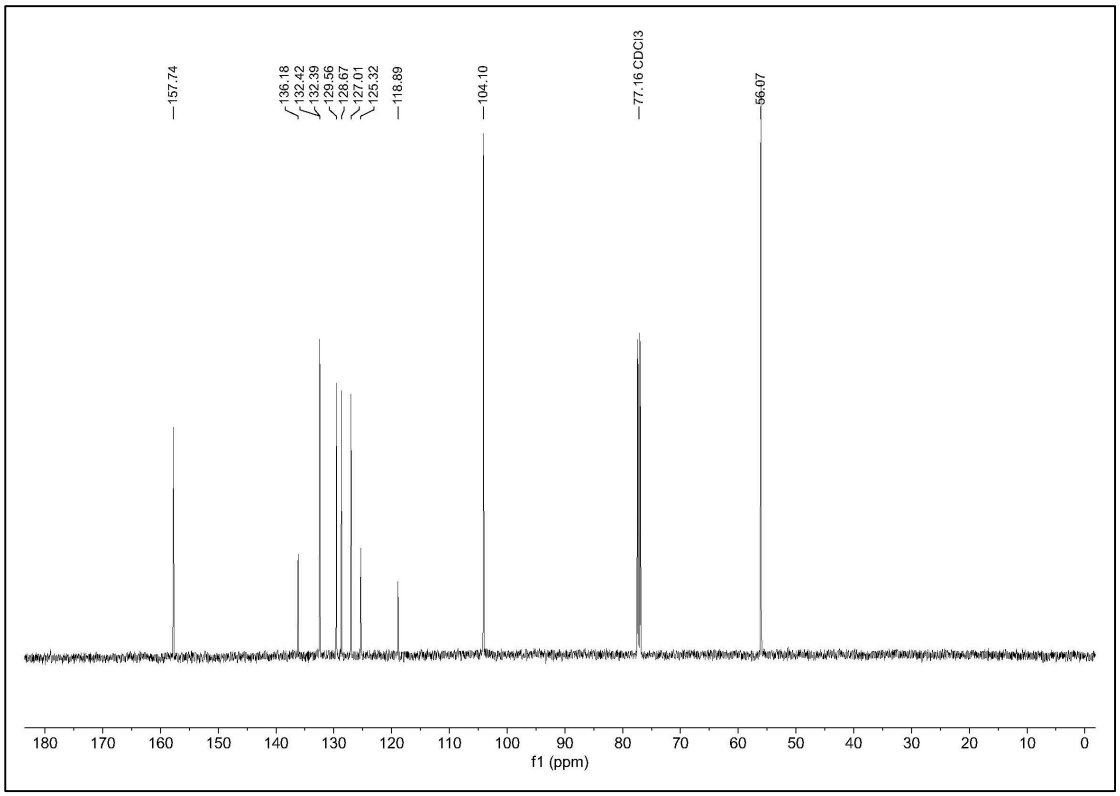
^{1}H NMR spectrum of Pd2 (in CD_2Cl_2)



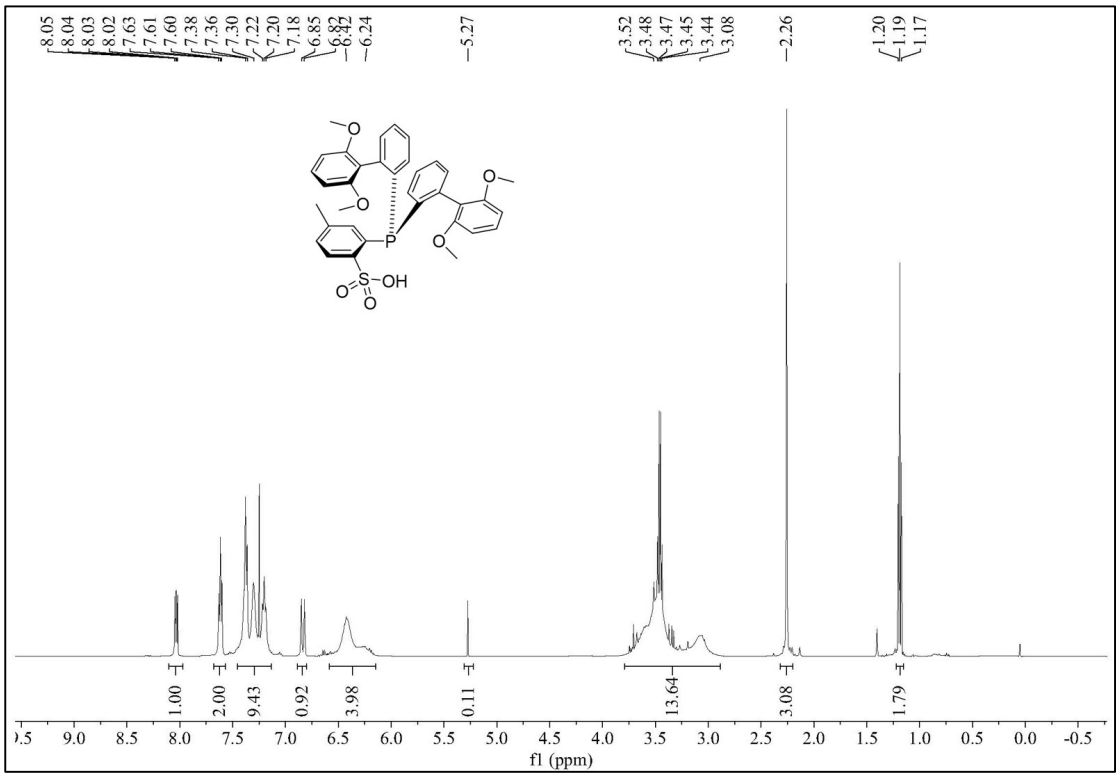
^{13}C NMR spectrum of Pd2 (in CD_2Cl_2)



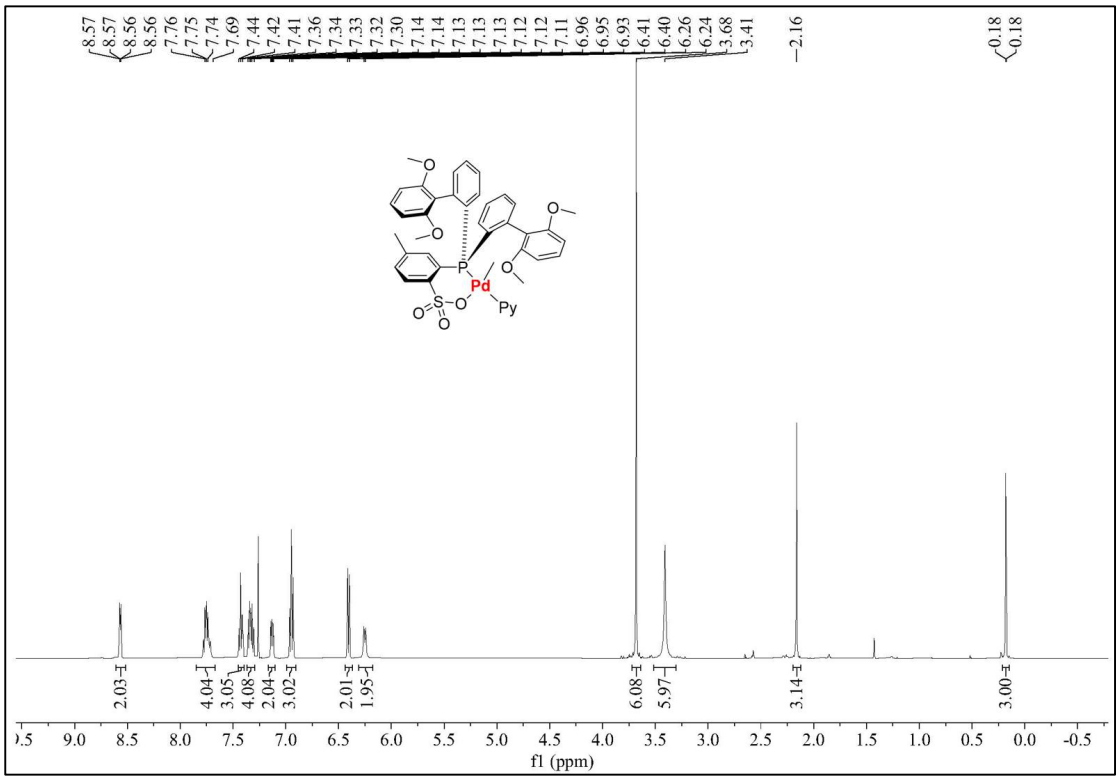
^{1}H NMR spectrum of 2'-bromo-2,6-dimethoxybiphenyl (in $CDCl_3$)



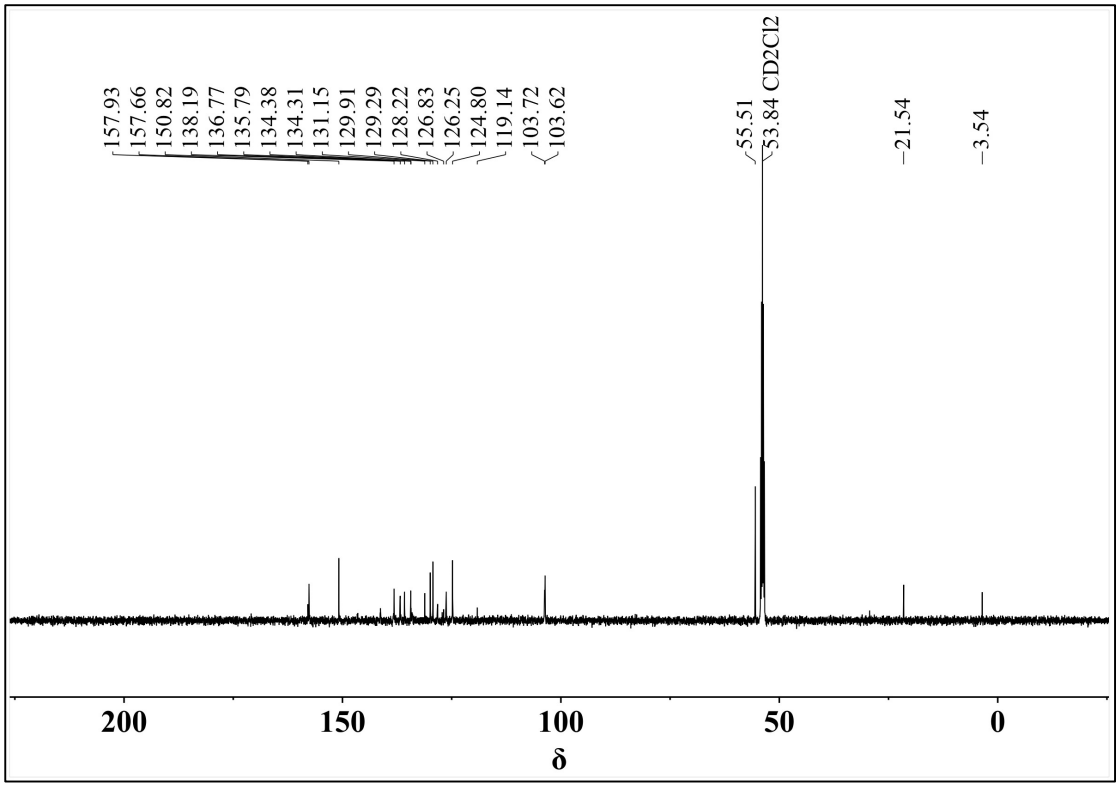
^{13}C NMR spectrum of 2'-bromo-2,6-dimethoxybiphenyl (in $CDCl_3$)



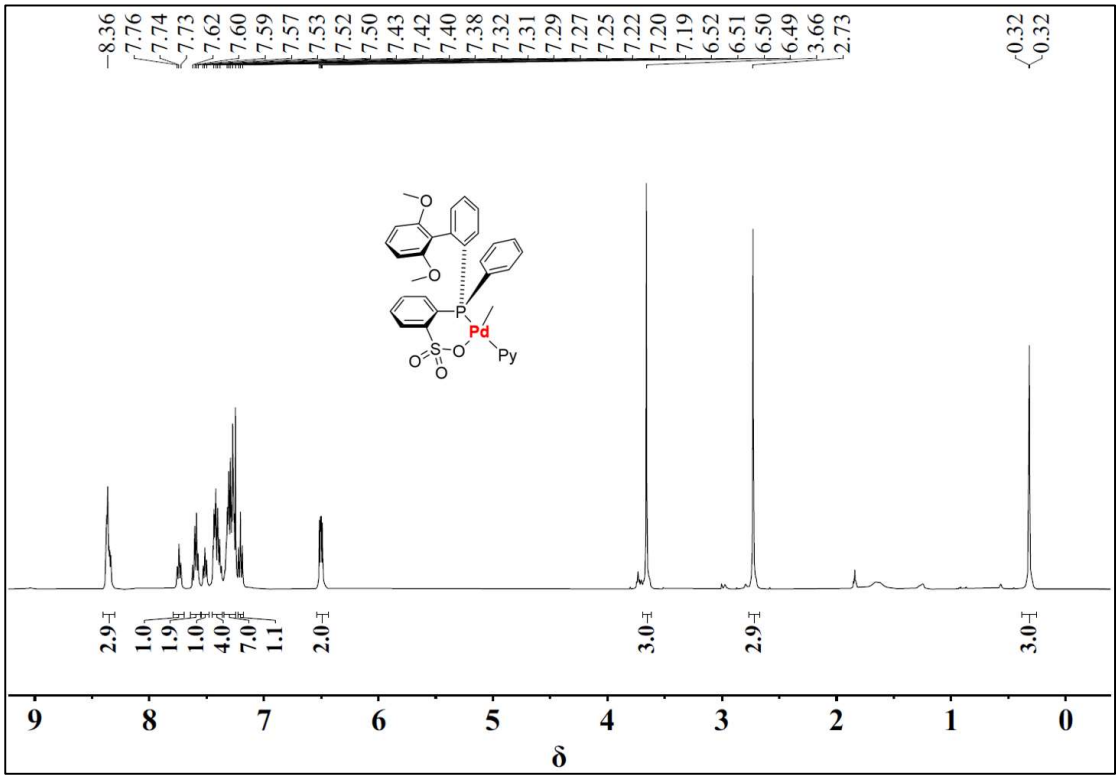
^{1}H NMR spectrum of L4 (in $CDCl_3$)



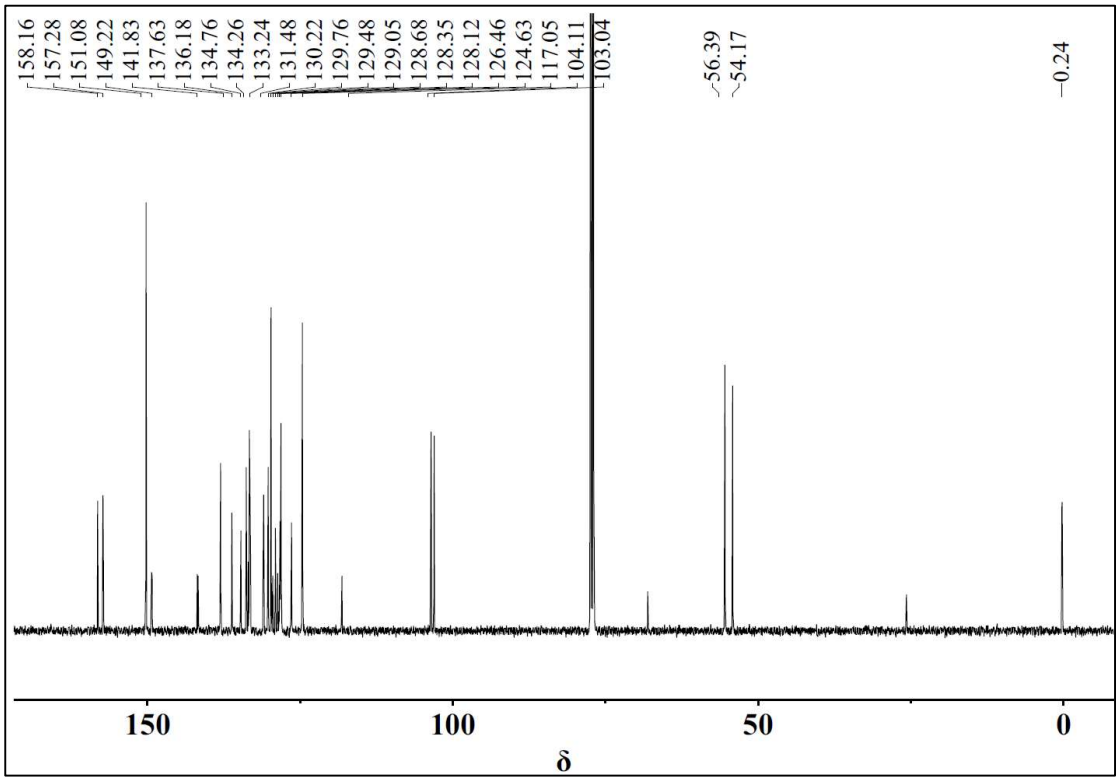
^{1}H NMR spectrum of Pd4 (in $CDCl_3$)



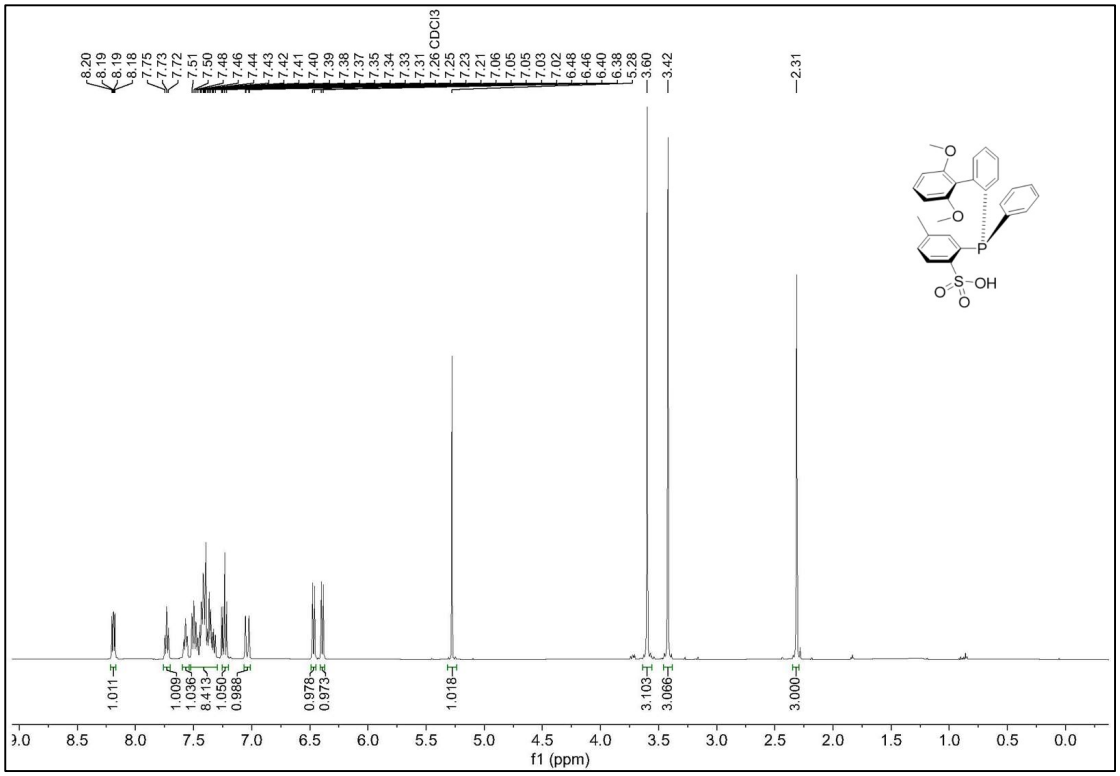
^{13}C NMR spectrum of Pd4 (in CD_2Cl_2)



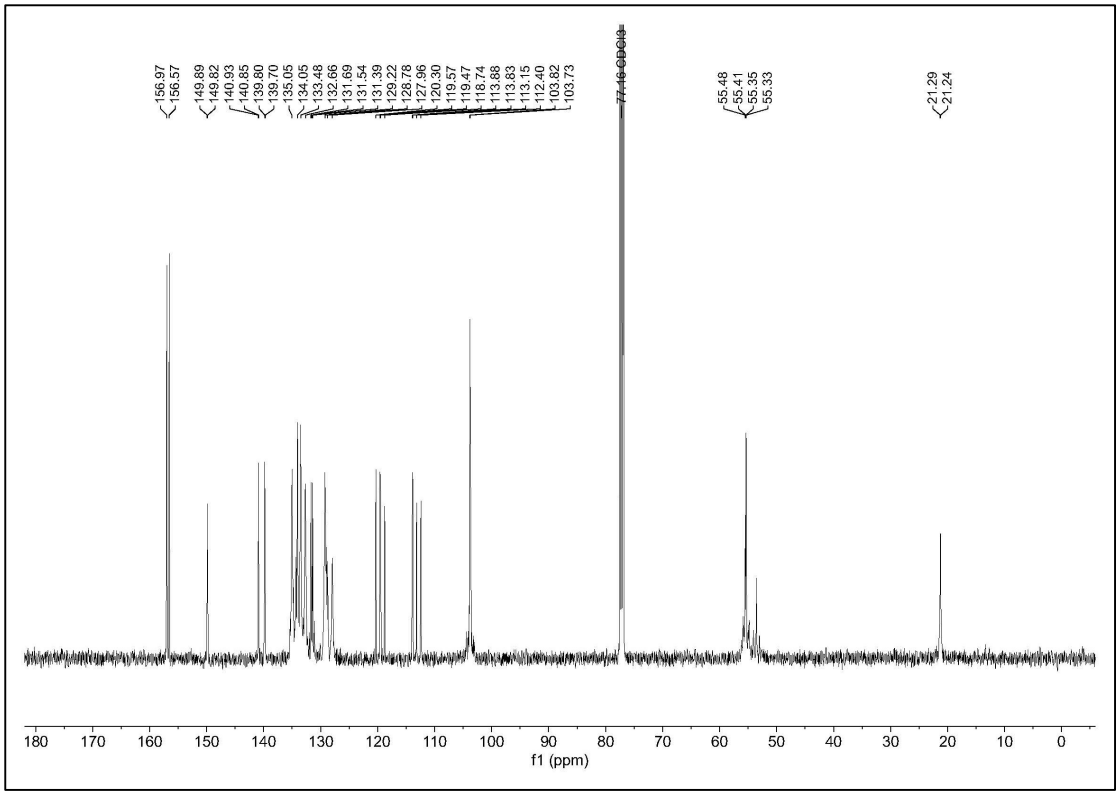
^{1}H NMR spectrum of Pd5 (in $CDCl_3$)



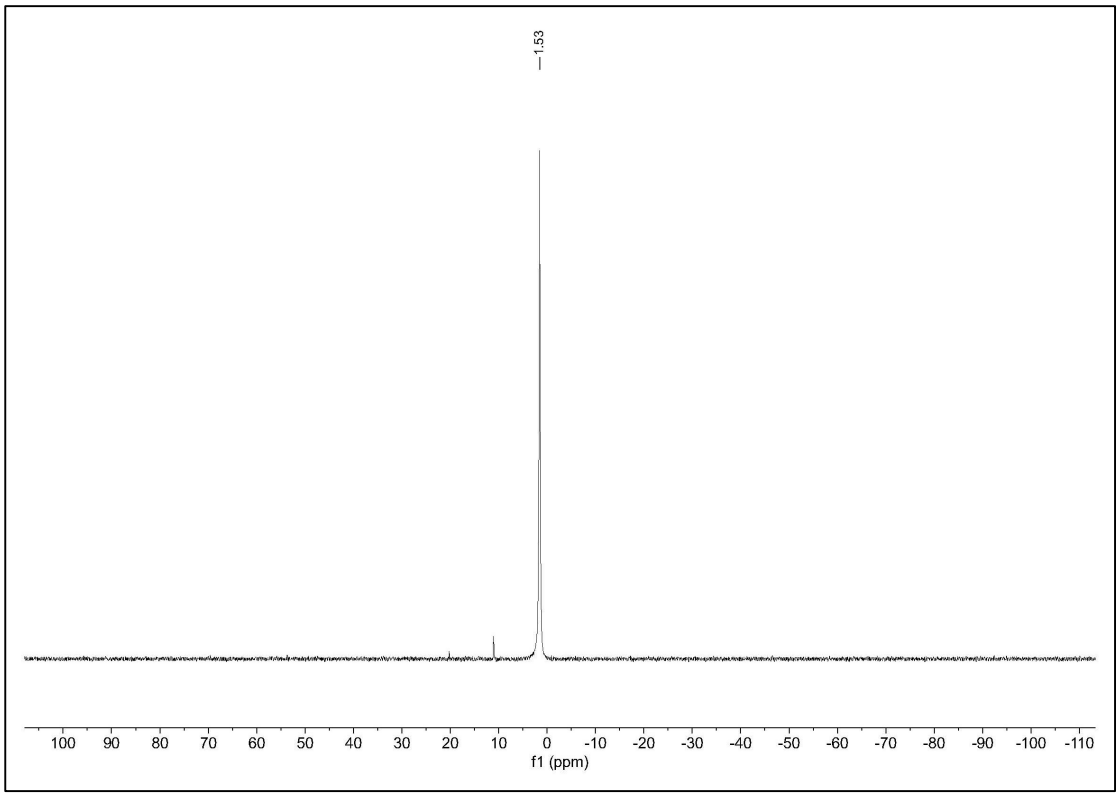
^{13}C NMR spectrum of Pd5 (in $CDCl_3$)



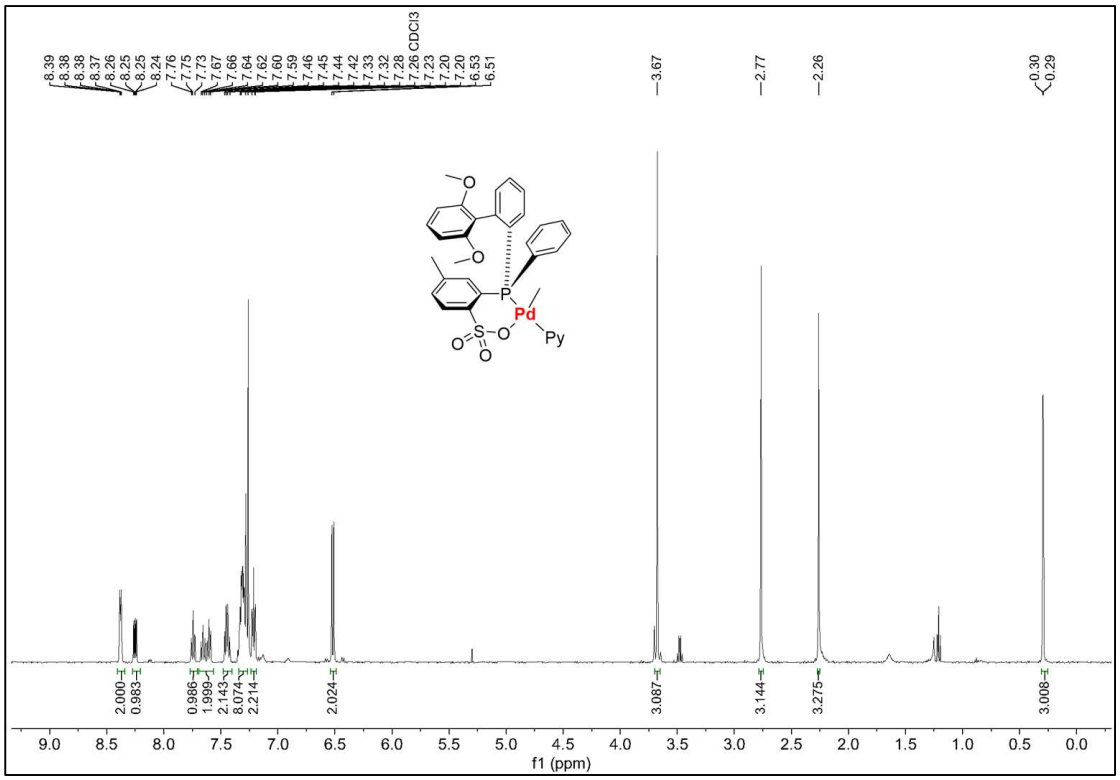
^{1}H NMR spectrum of L1 (in $CDCl_3$)



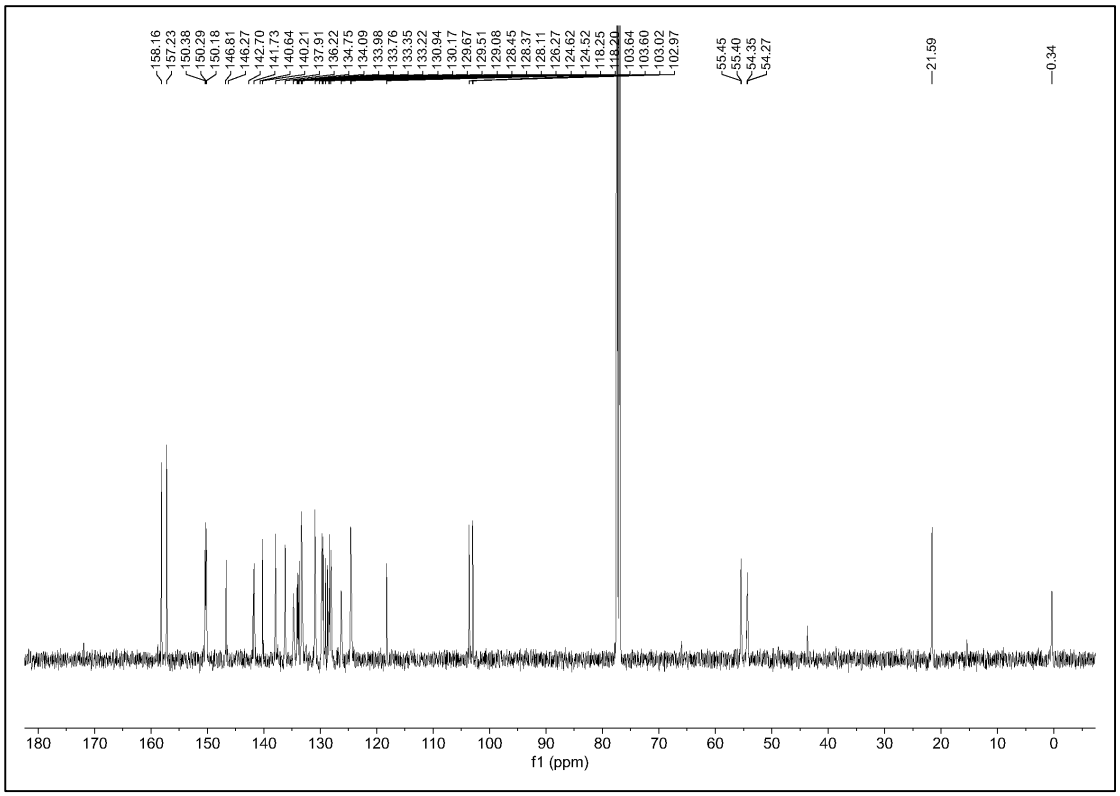
^{13}C NMR spectrum of L1 (in $CDCl_3$)



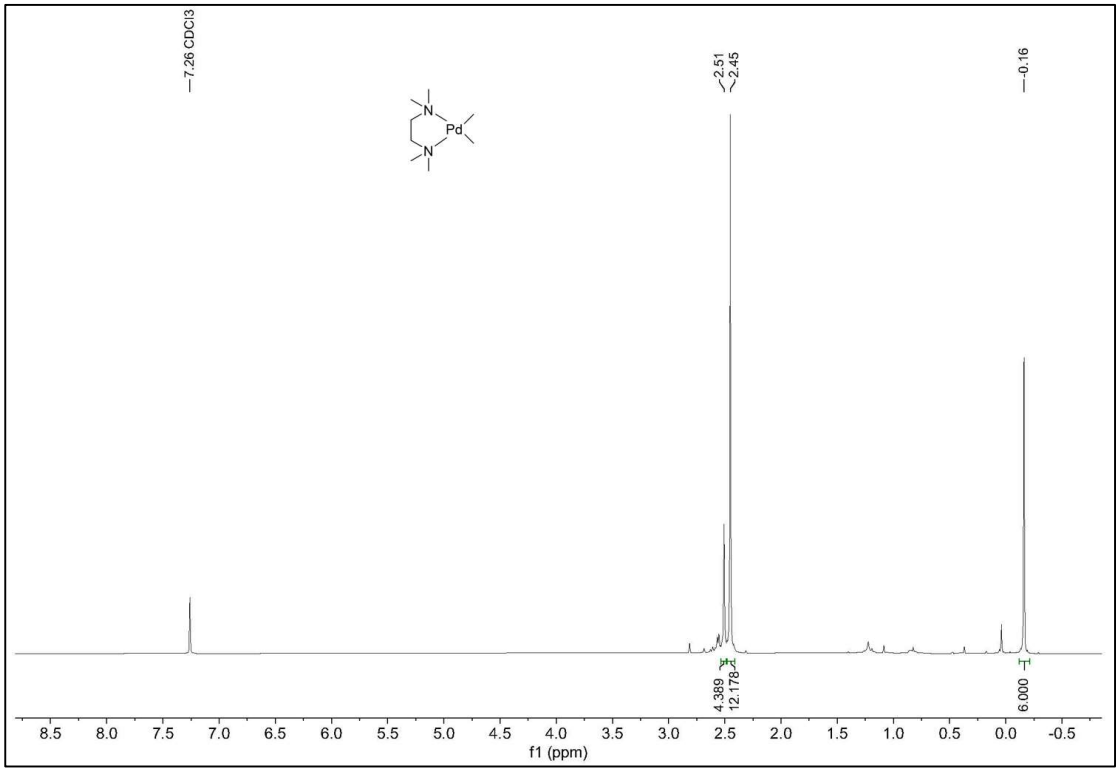
^{31}P NMR spectrum of L1 (in $CDCl_3$)



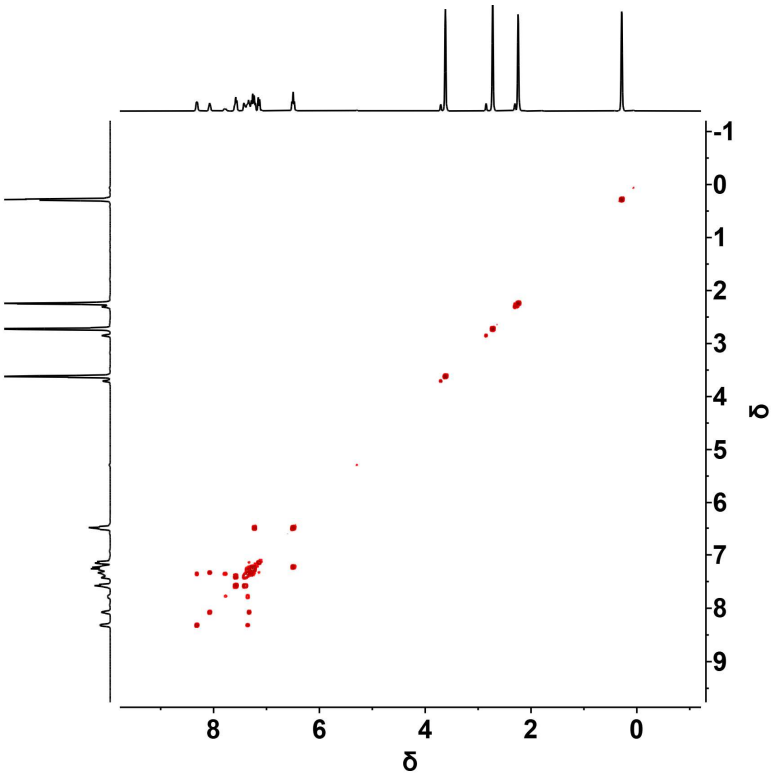
^{1}H NMR spectrum of Pd1 (in $CDCl_3$)



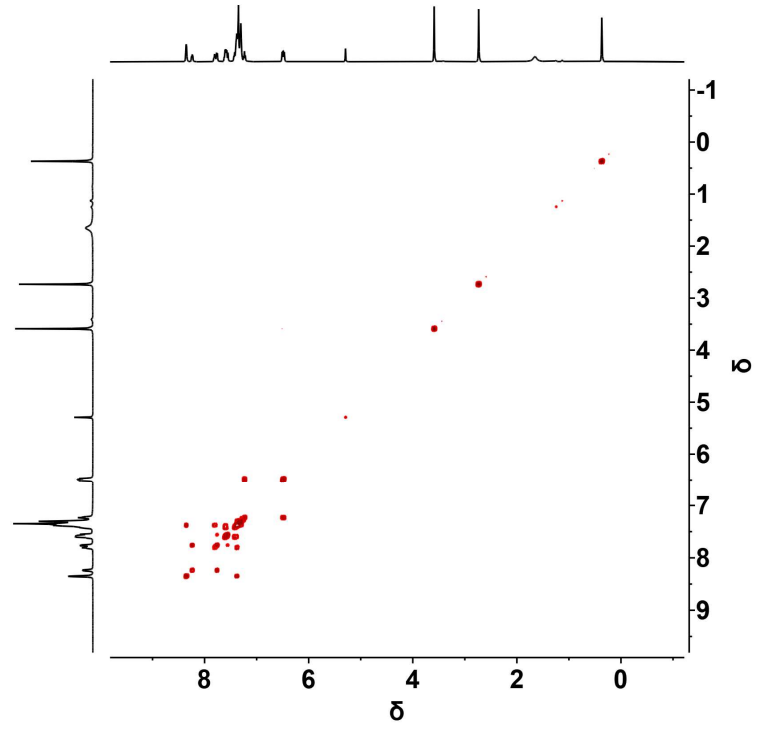
^{13}C NMR spectrum of Pd1 (in $CDCl_3$)



^{1}H NMR spectrum of (TMEDA)$PdMe_2$ (in $CDCl_3$)

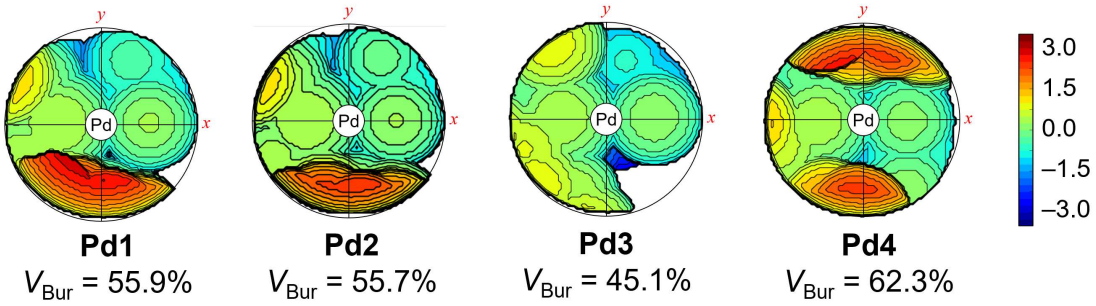


$^{1}H-^{1}H$ COSY NMR spectrum of **Pd1** in CD_2Cl_2 solution



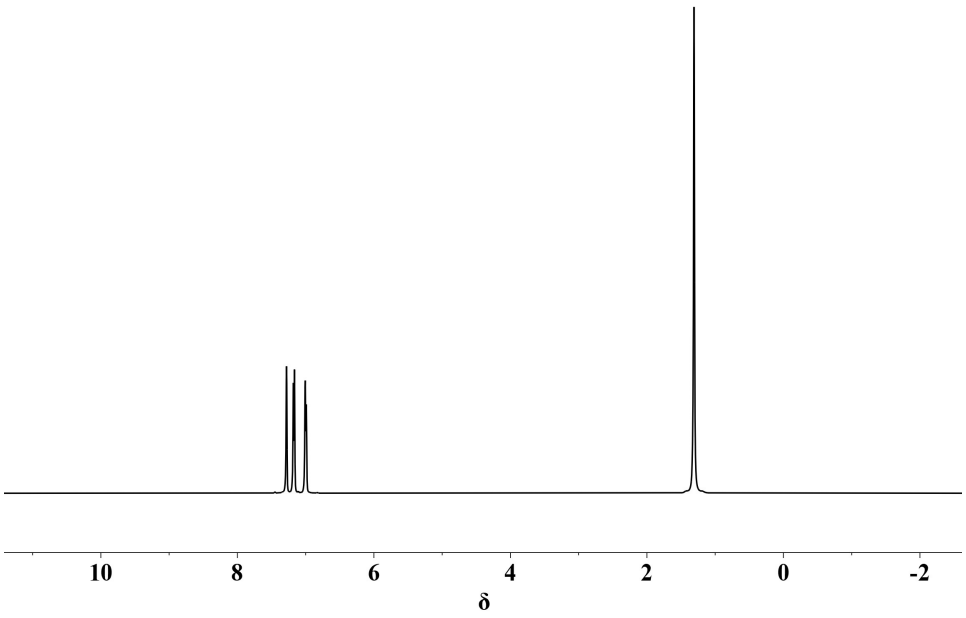
$^{1}H-^{1}H$ COSY NMR spectrum of **Pd2** in CD_2Cl_2 solution

Topographic steric maps

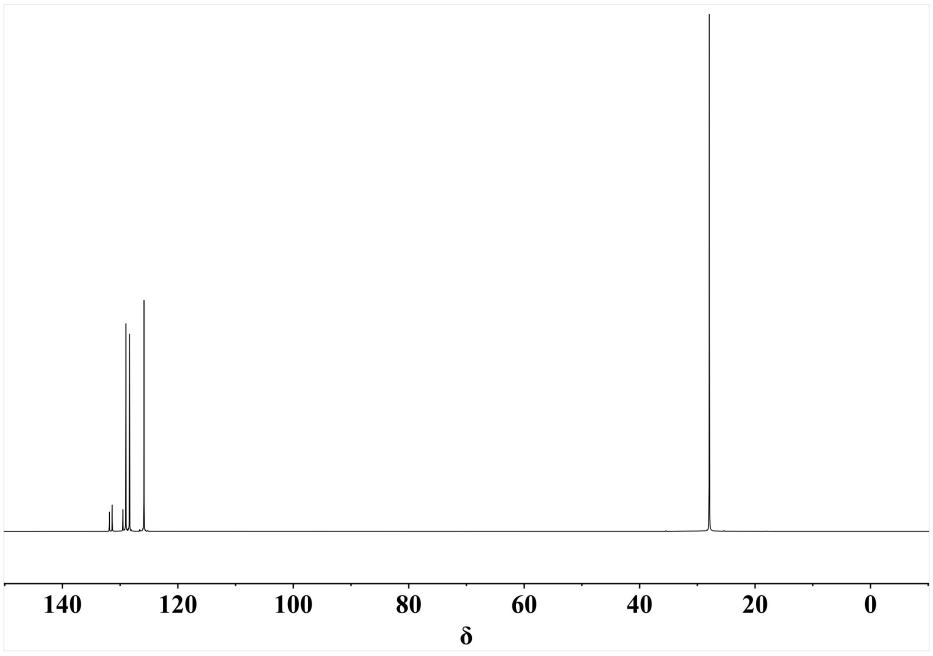


Topographic steric maps of **Pd1**, **Pd2, Pd3, and Pd4**.

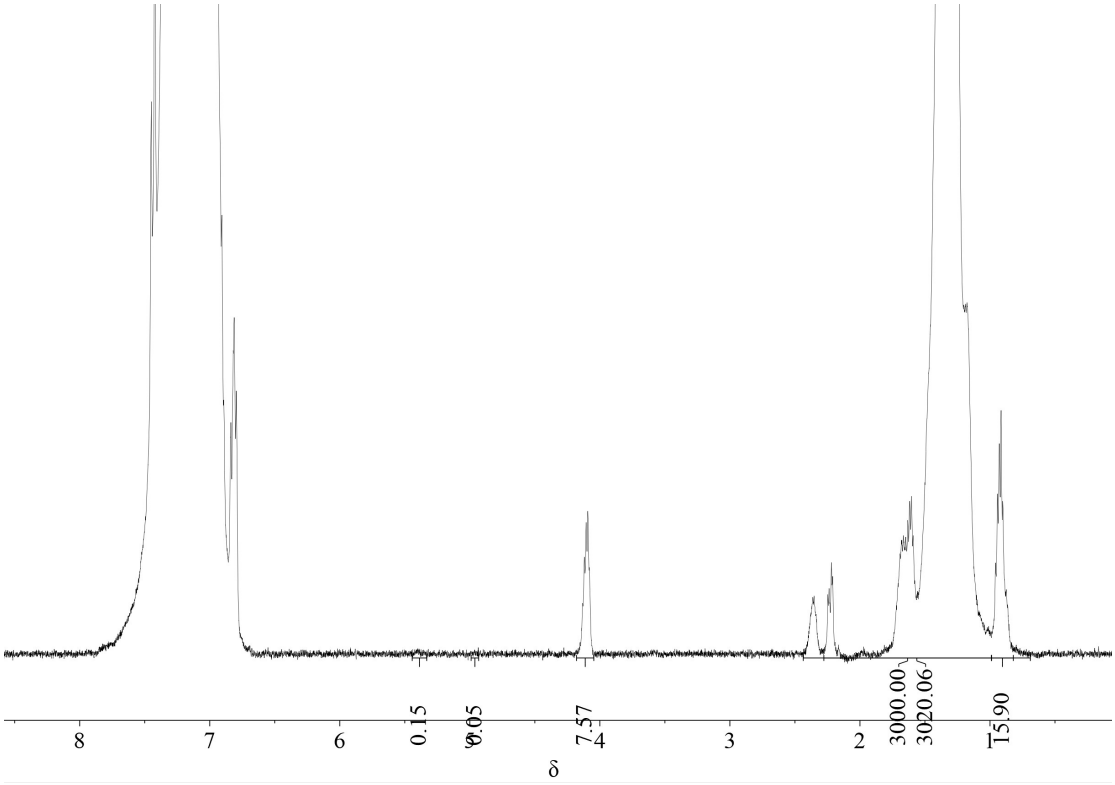
NMR spectra of polymers



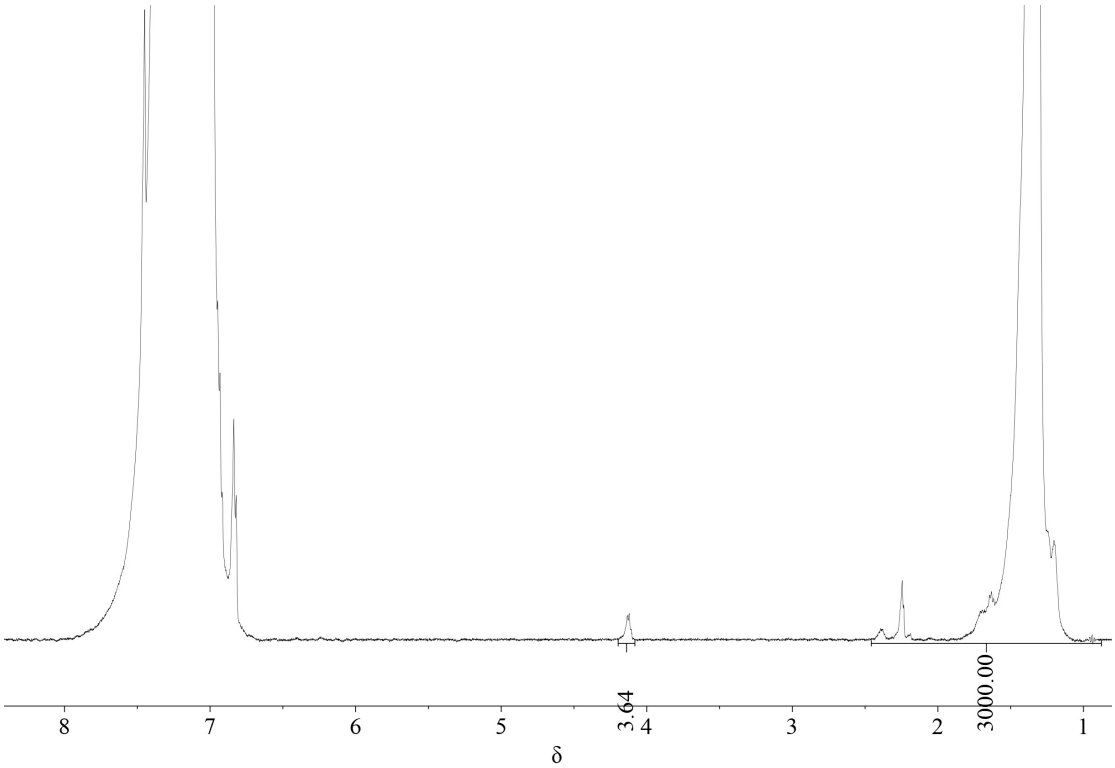
^{1}H NMR spectrum of highly linear PE in Table 1, Entry 11



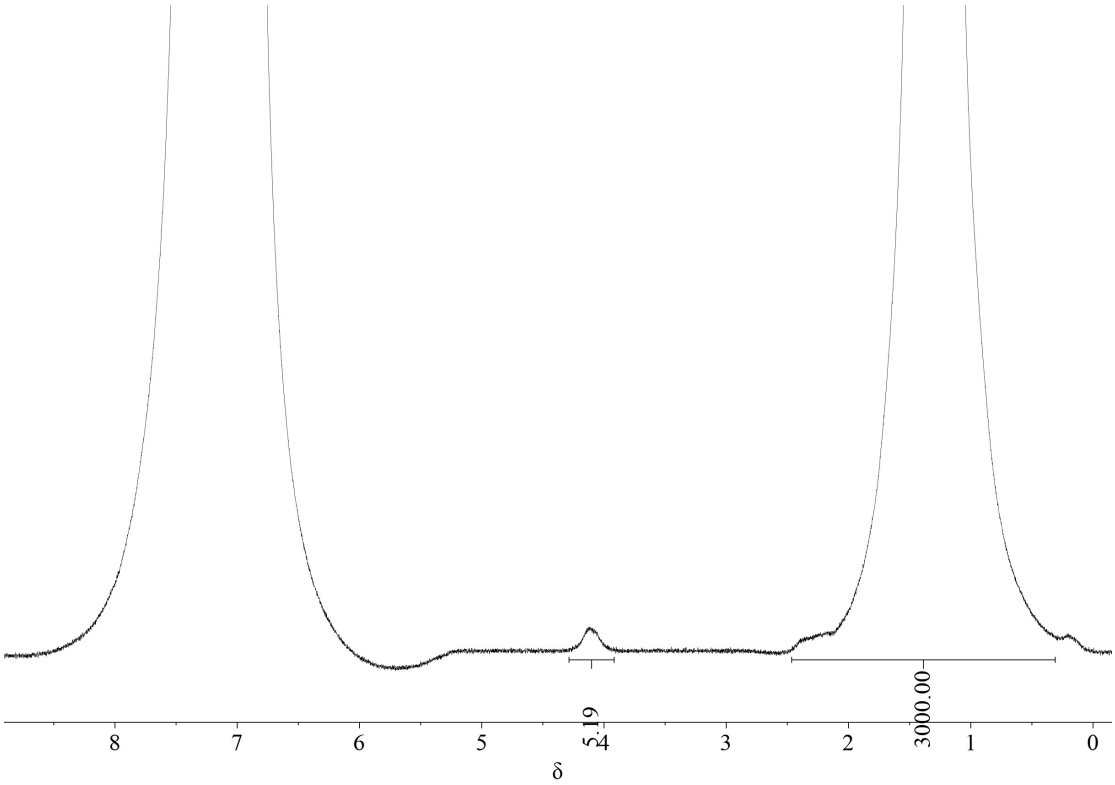
^{13}C NMR spectrum of highly linear PE in Table 1, Entry 11



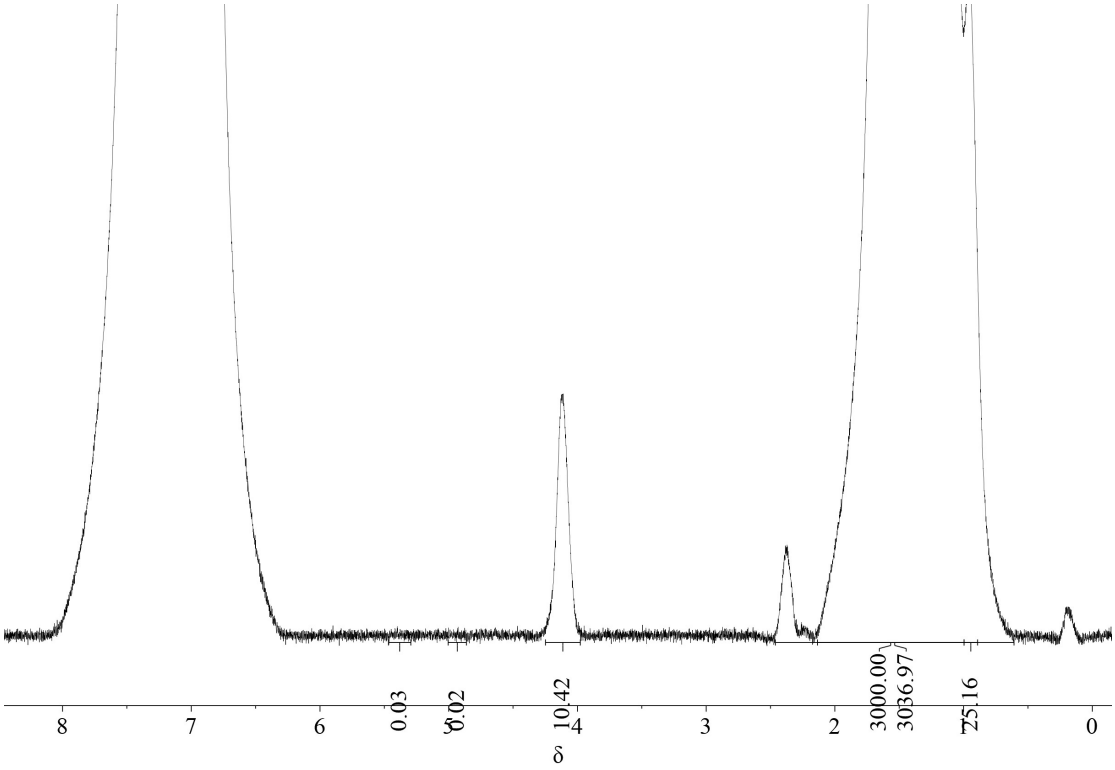
^{1}H NMR spectrum of polymer in Entry 1, Table2



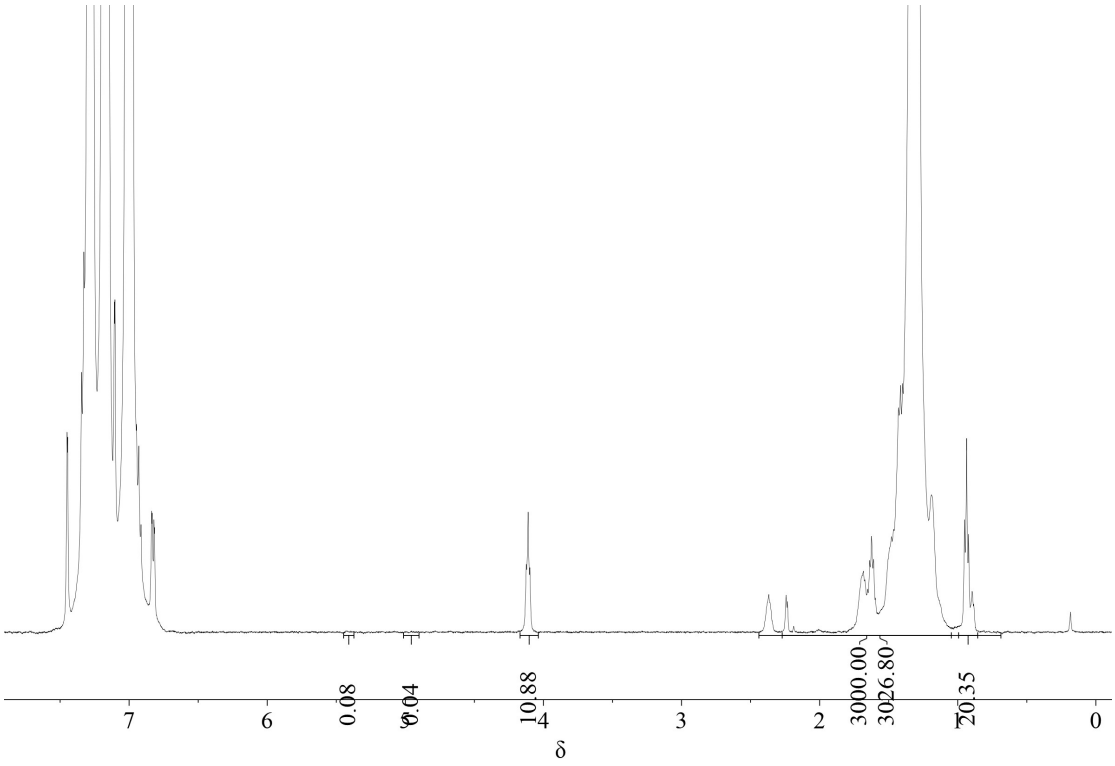
^{1}H NMR spectrum of polymer in Entry 2, Table2



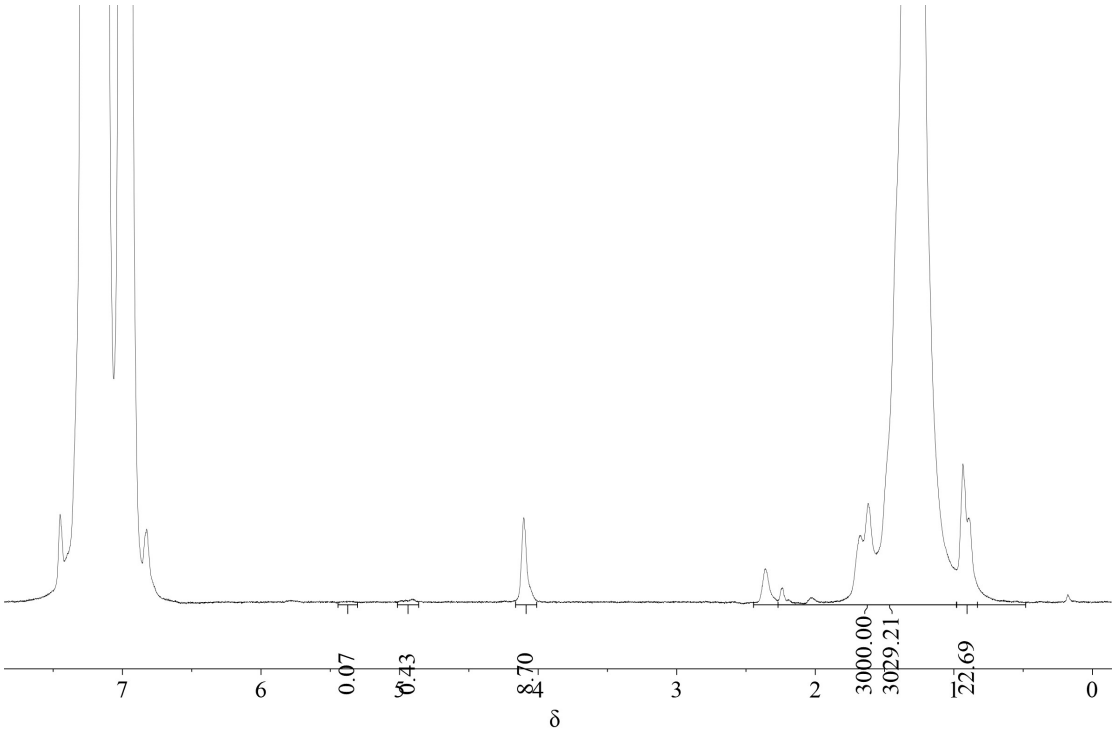
^{1}H NMR spectrum of polymer in Entry 3, Table2



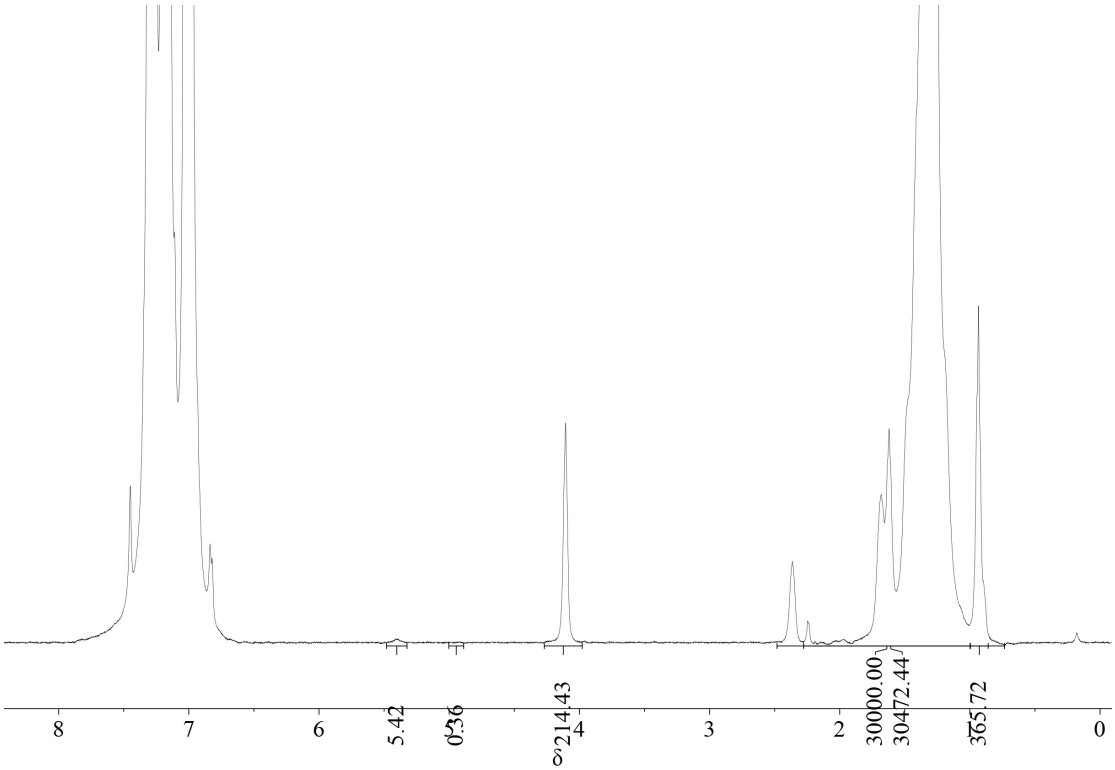
^{1}H NMR spectrum of polymer in Entry 4, Table2



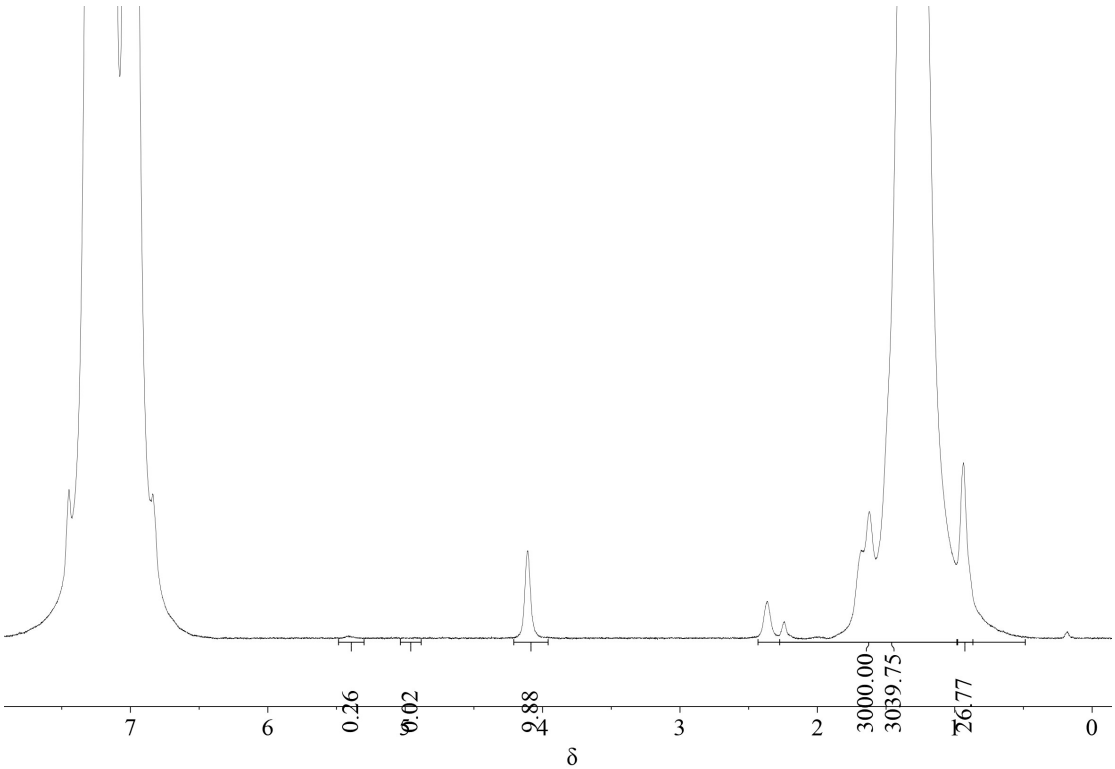
^{1}H NMR spectrum of polymer in Entry 5, Table2



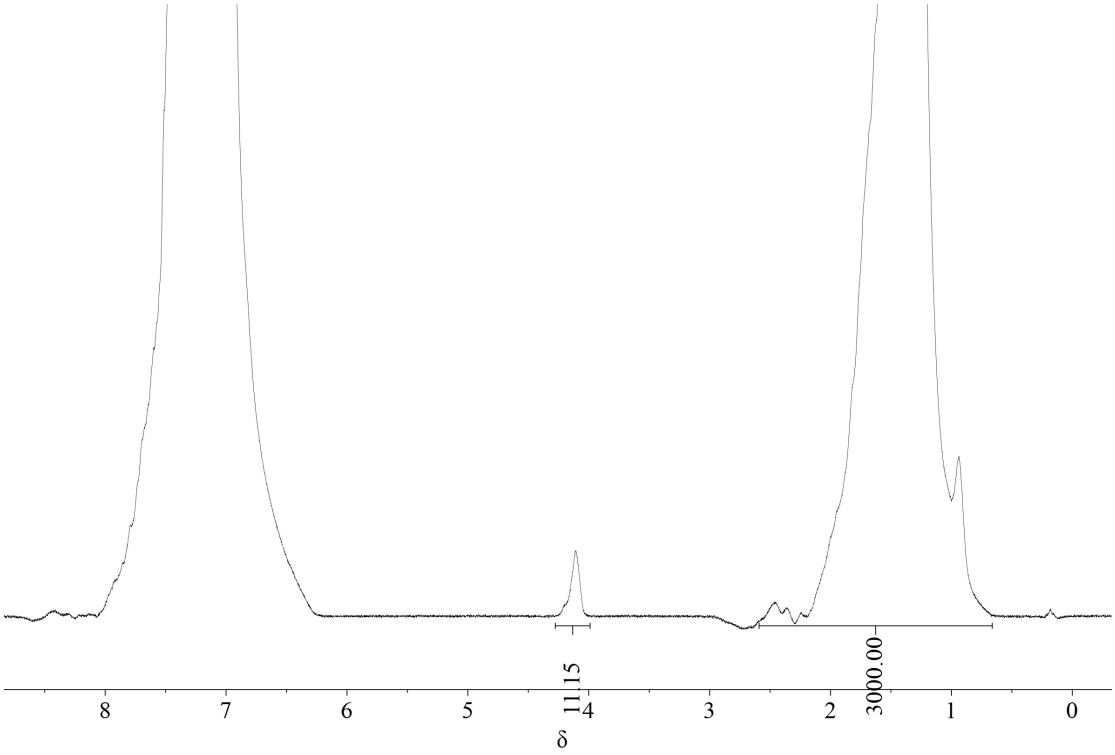
^{1}H NMR spectrum of polymer in Entry 6, Table2



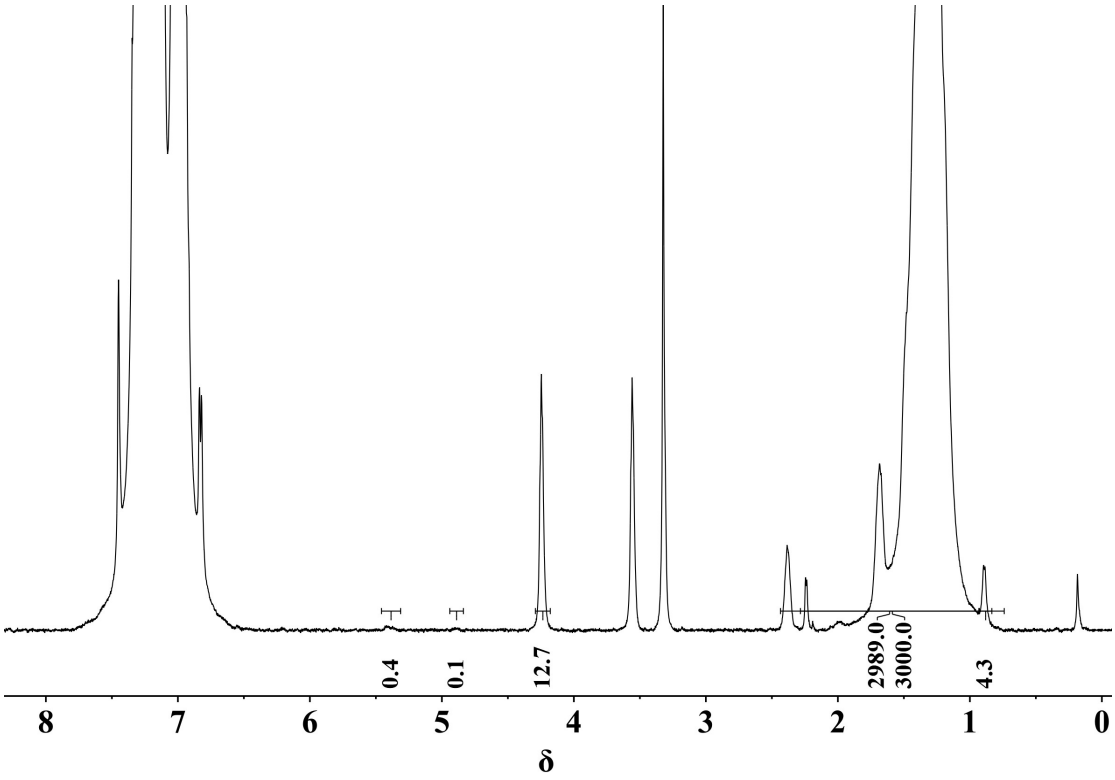
^{1}H NMR spectrum of polymer in Entry 7, Table2



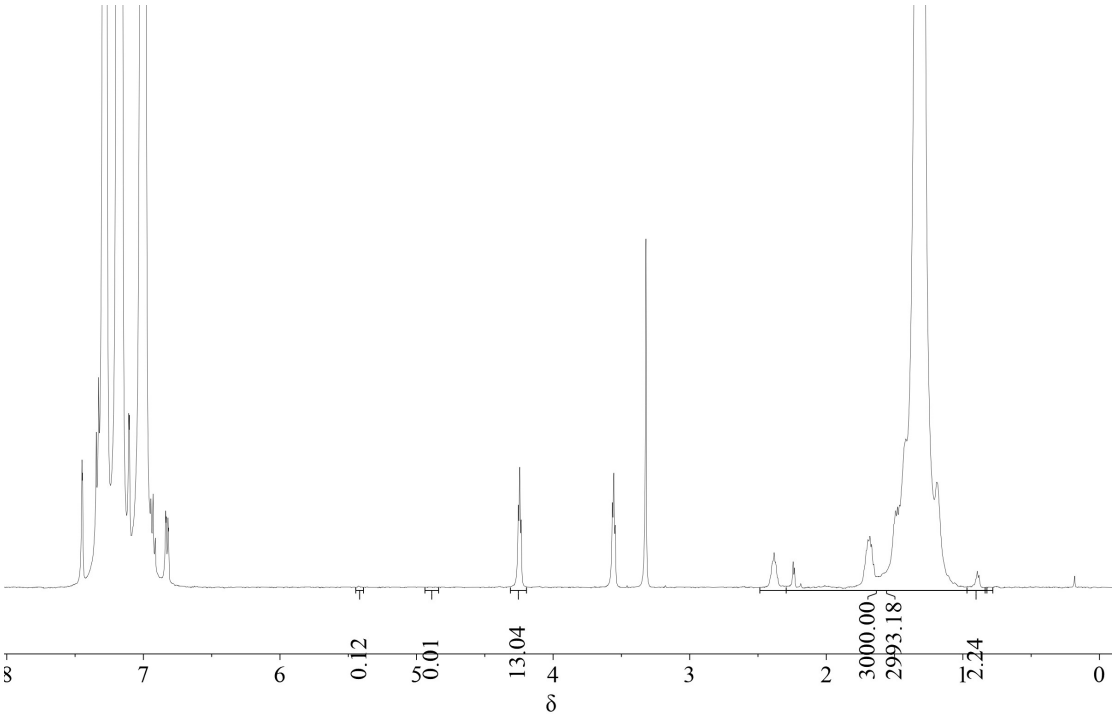
^{1}H NMR spectrum of polymer in Entry 8, Table2



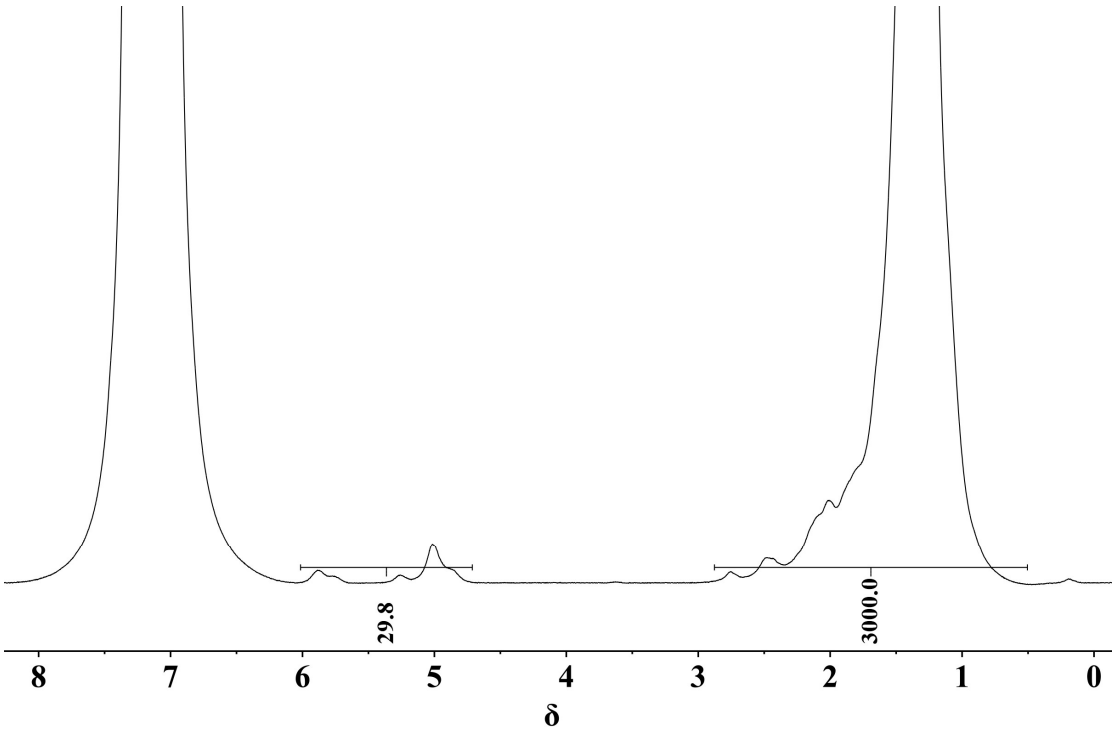
^{1}H NMR spectrum of polymer in Entry 10, Table2



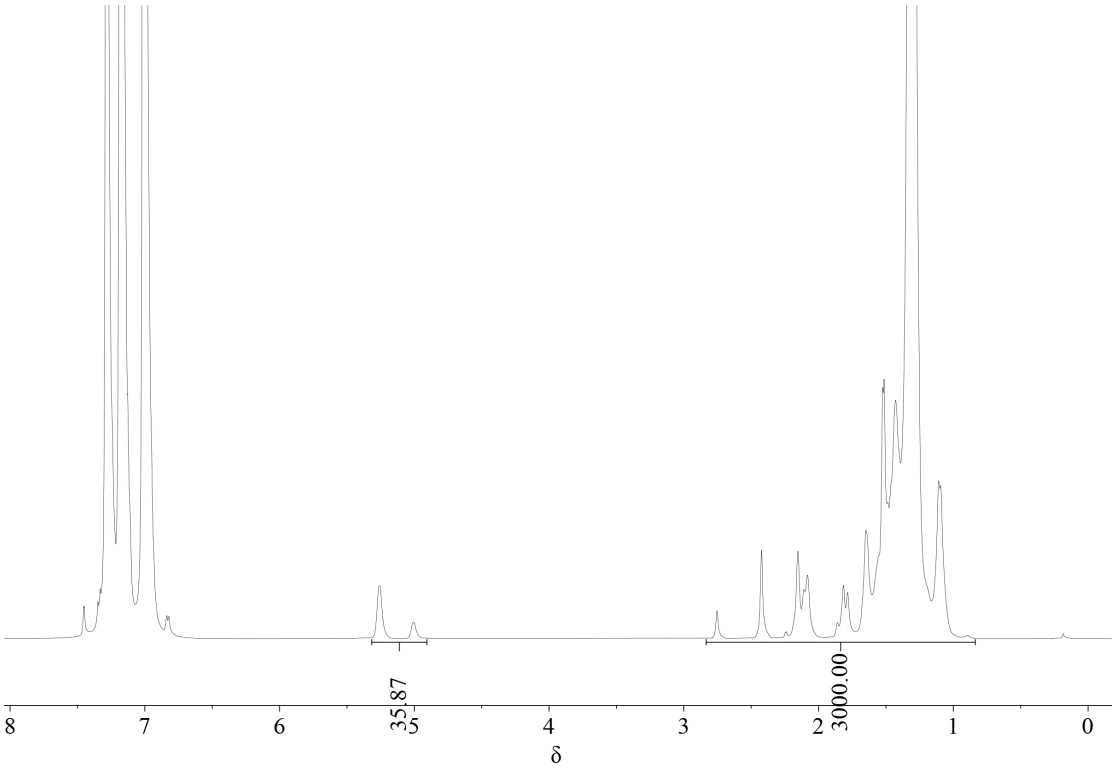
^{1}H NMR spectrum of polymer in Entry 11, Table2



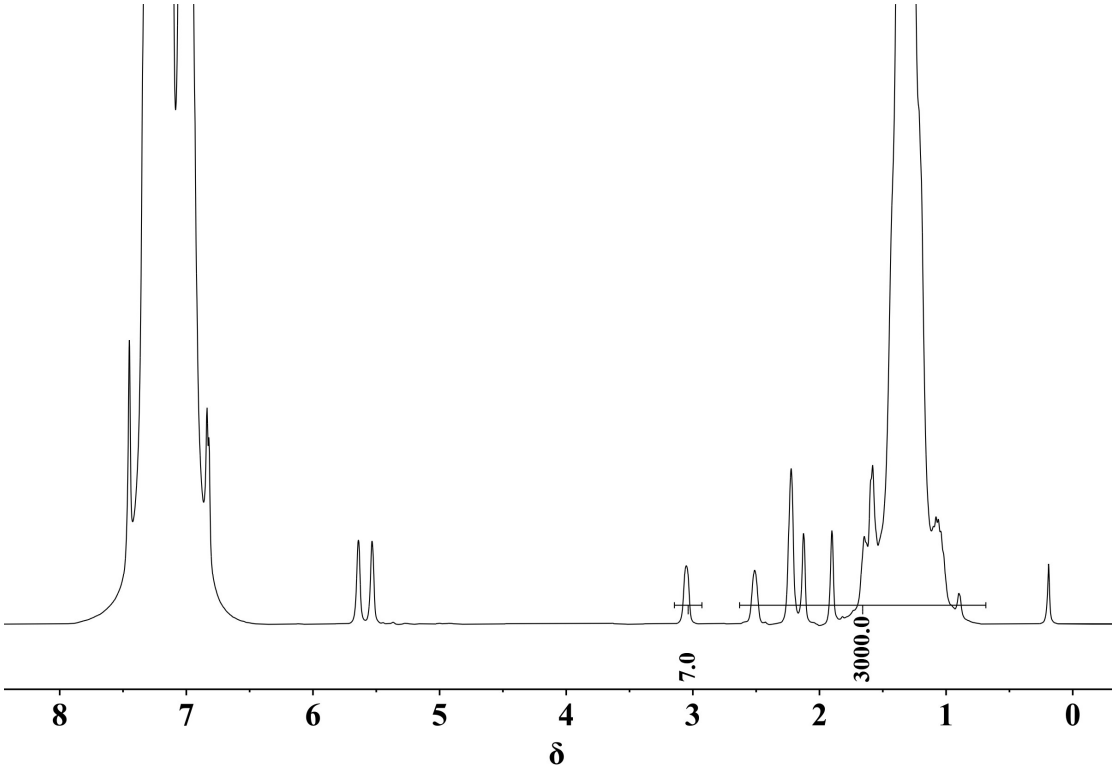
^{1}H NMR spectrum of polymer in Entry 12, Table2



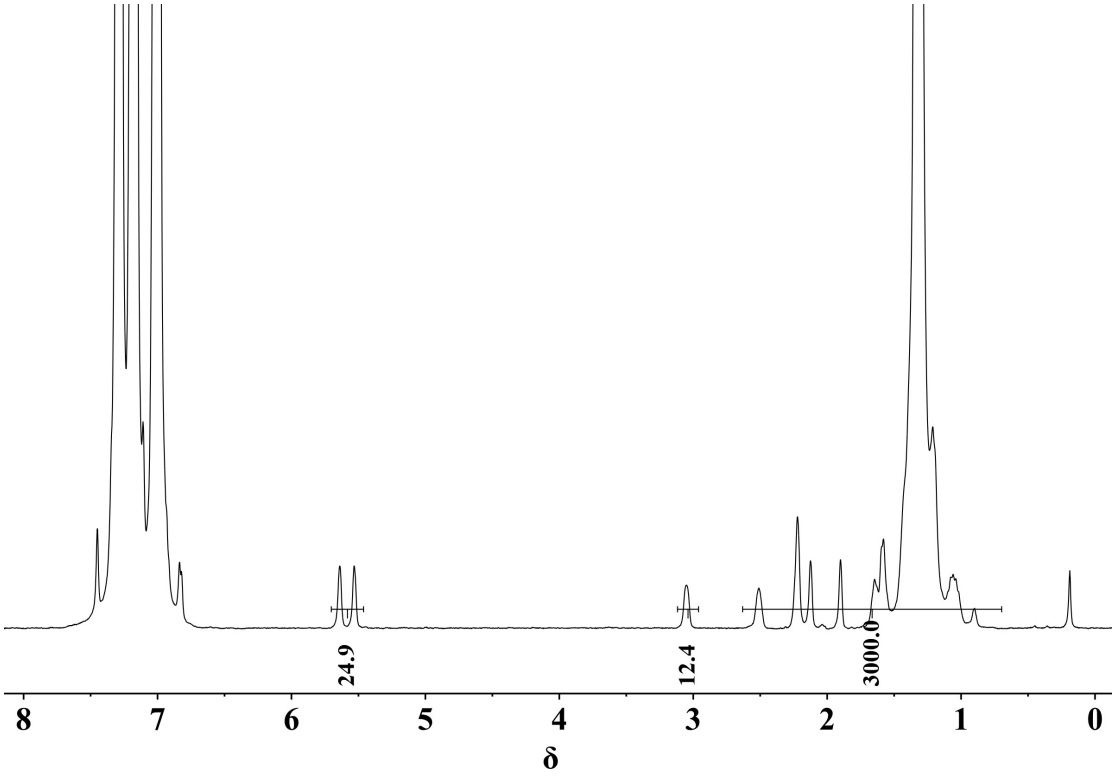
^{1}H NMR spectrum of polymer in Entry 13, Table2



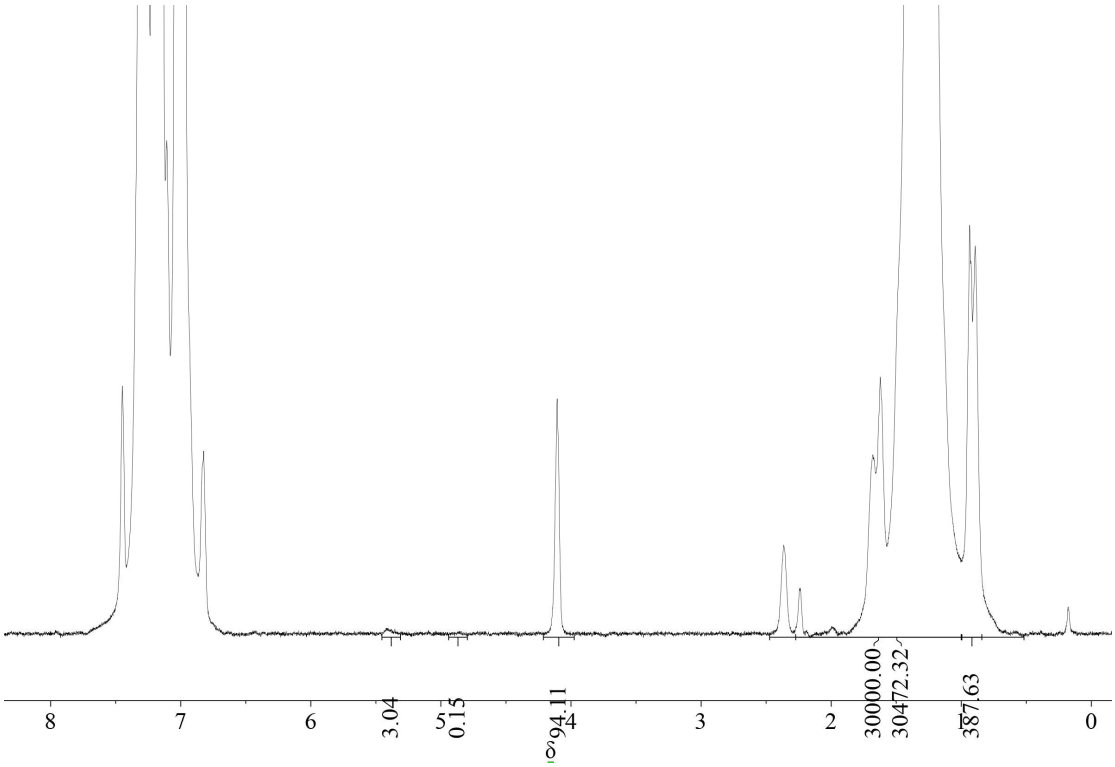
^{1}H NMR spectrum of polymer in Entry 14, Table2



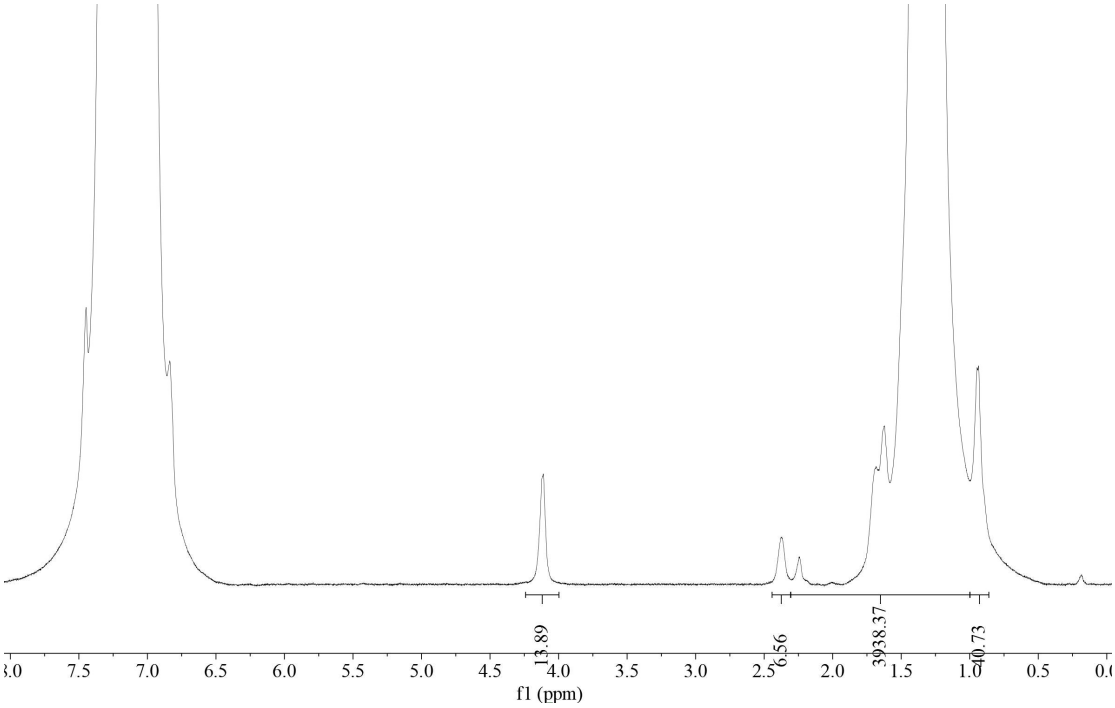
^{1}H NMR spectrum of polymer in Entry 15, Table2



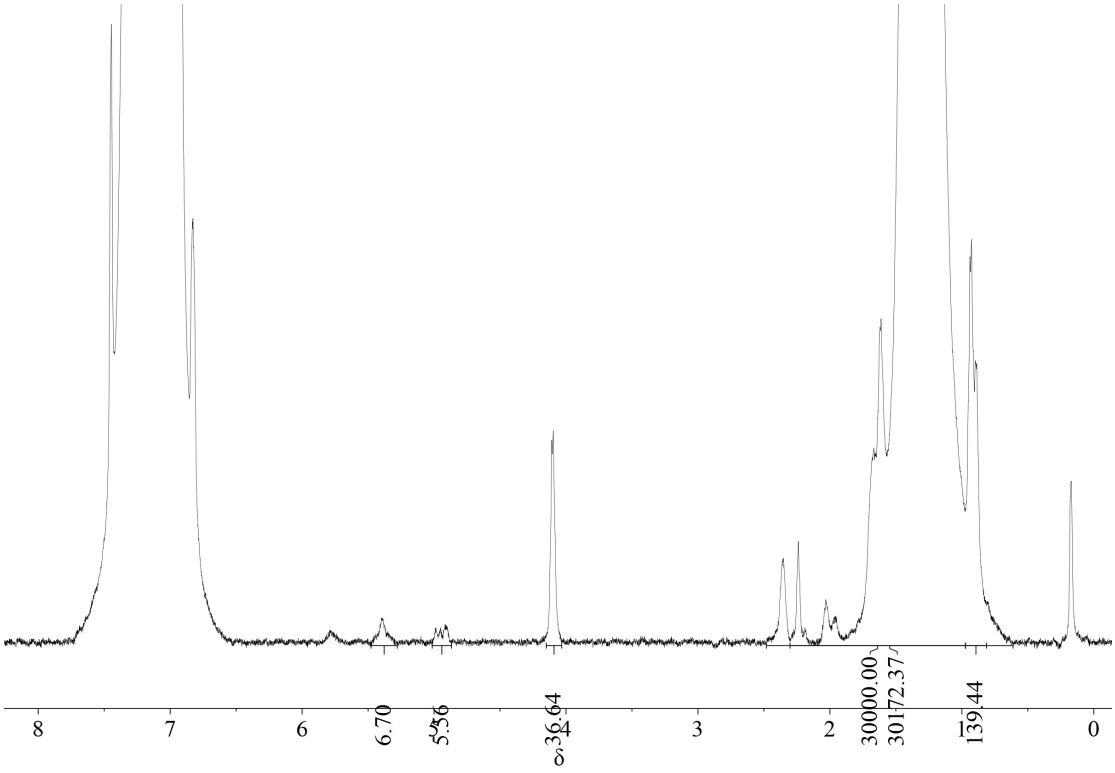
^{1}H NMR spectrum of polymer in Entry 16, Table2



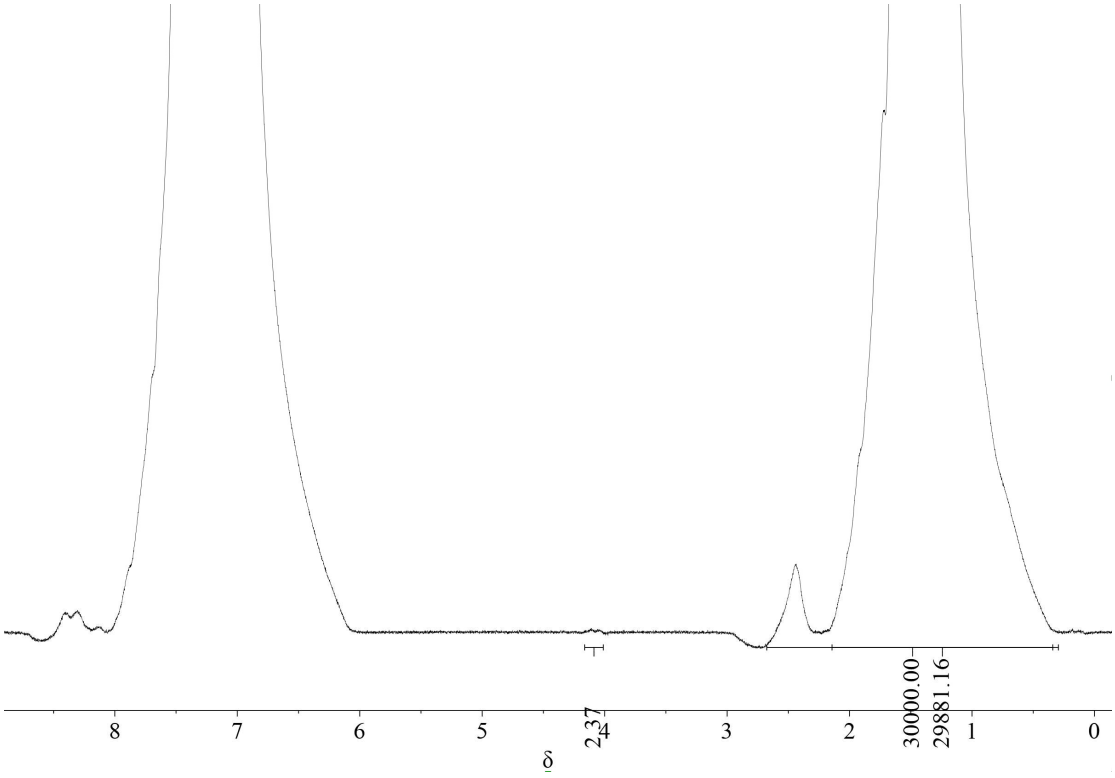
^{1}H NMR spectrum of polymer in Entry 17, Table2



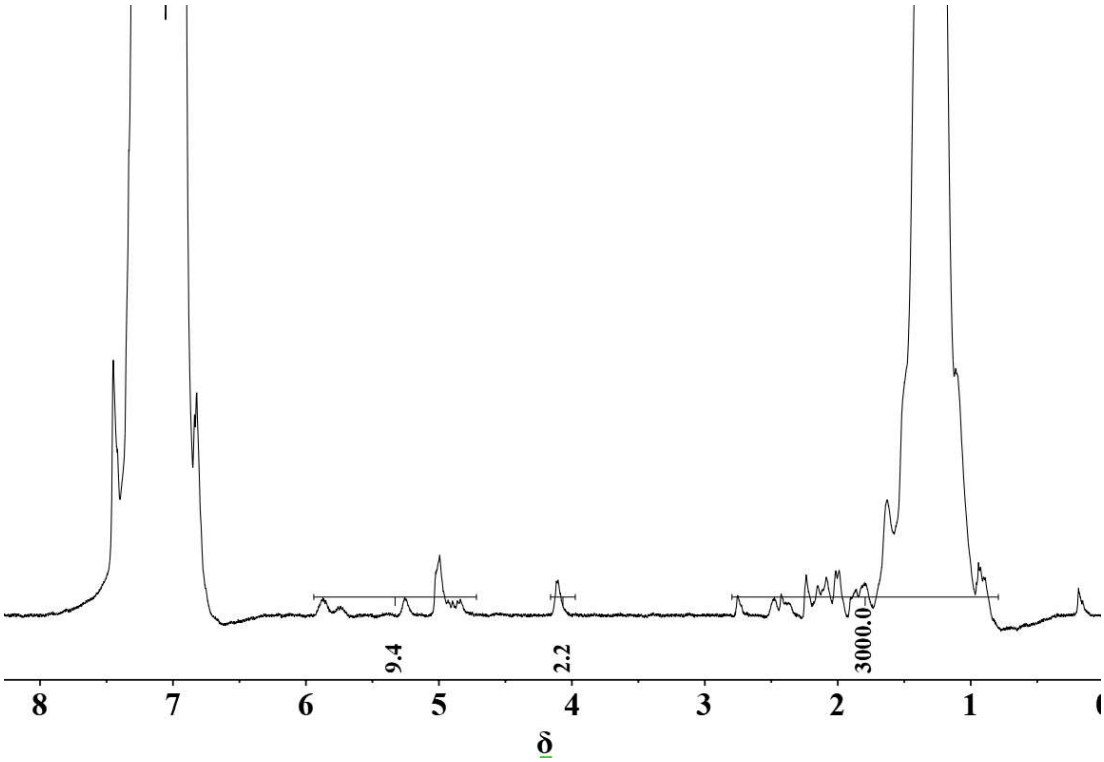
^{1}H NMR spectrum of polymer in Entry 18, Table2



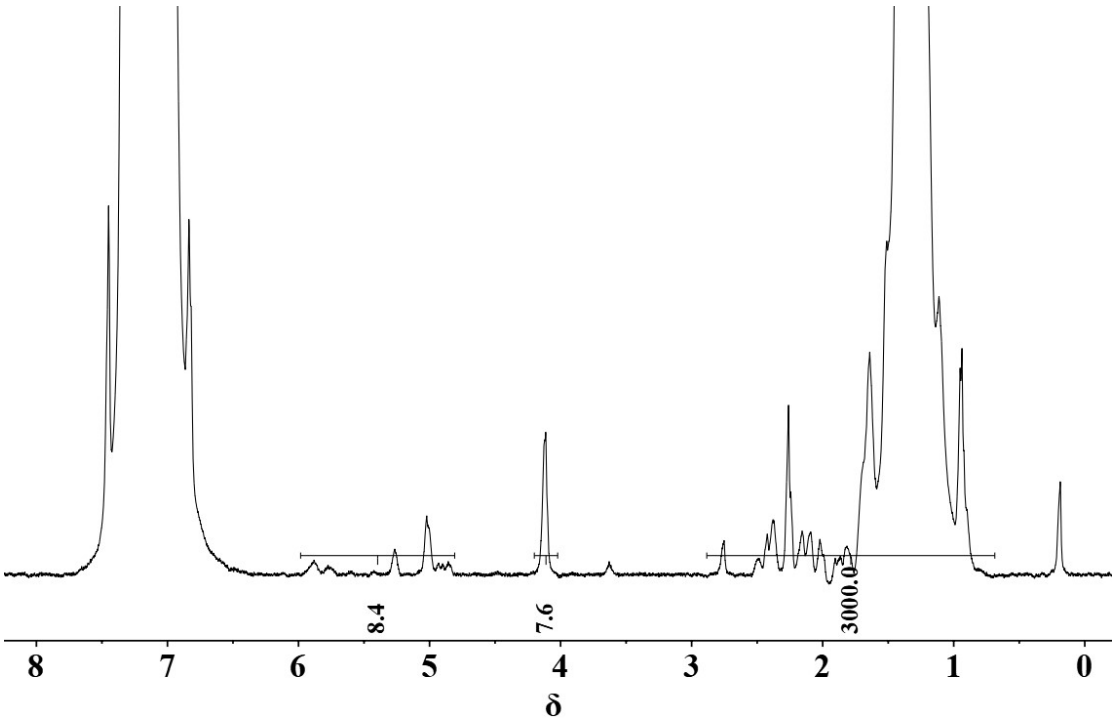
^{1}H NMR spectrum of polymer in Entry 19, Table2



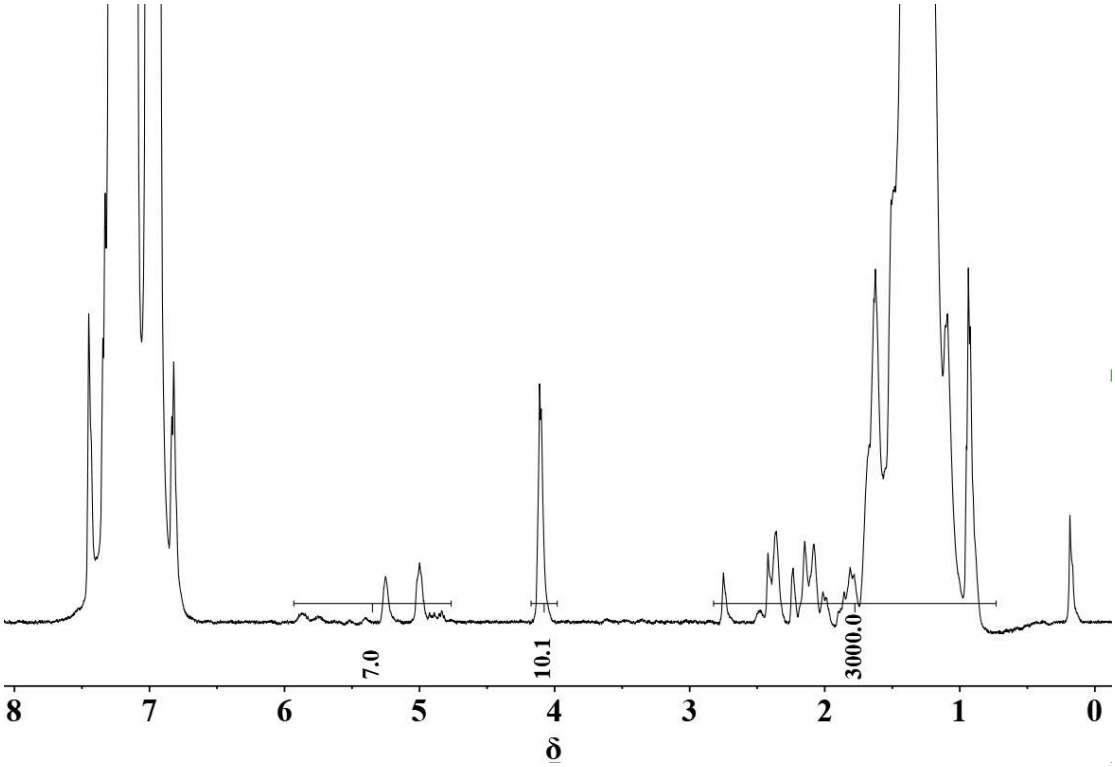
^{1}H NMR spectrum of polymer in Entry 20, Table2



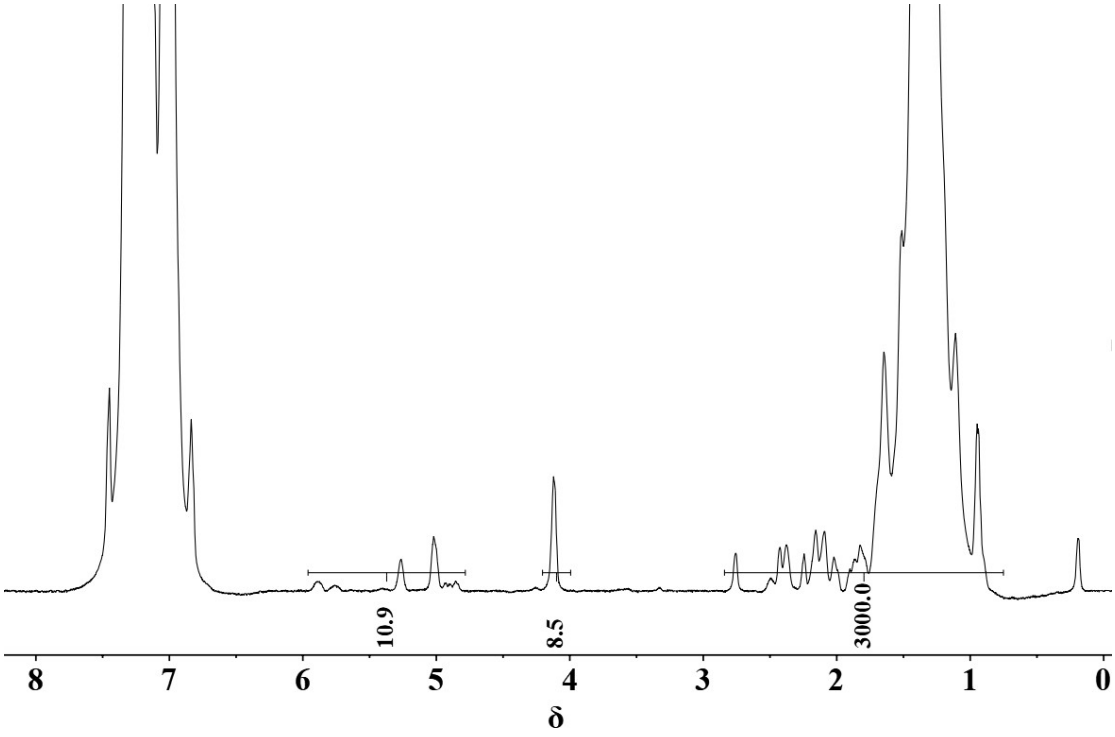
^{1}H NMR spectrum of polymer in Entry 1, Table3



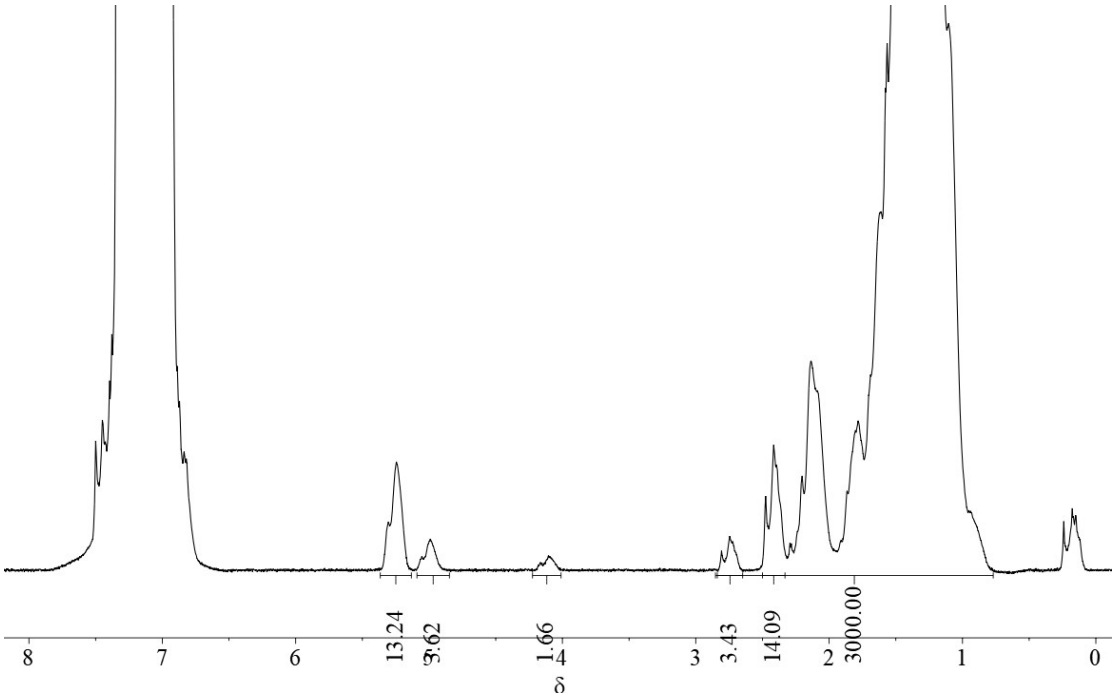
^{1}H NMR spectrum of polymer in Entry 2, Table3



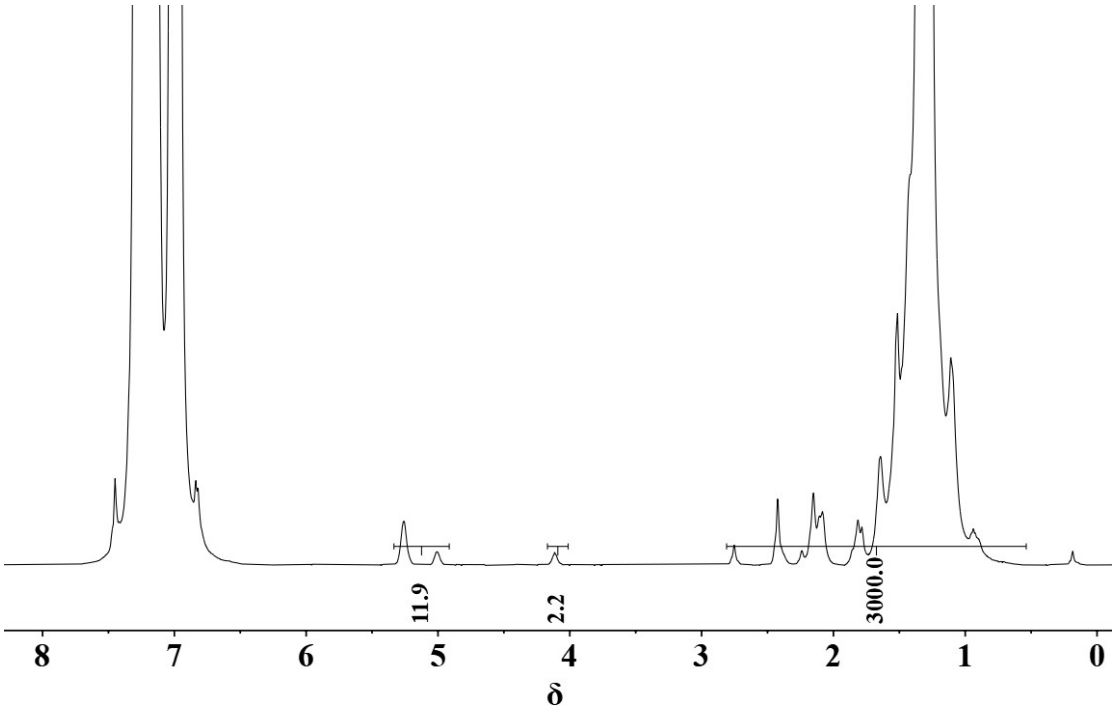
^{1}H NMR spectrum of polymer in Entry 3, Table3



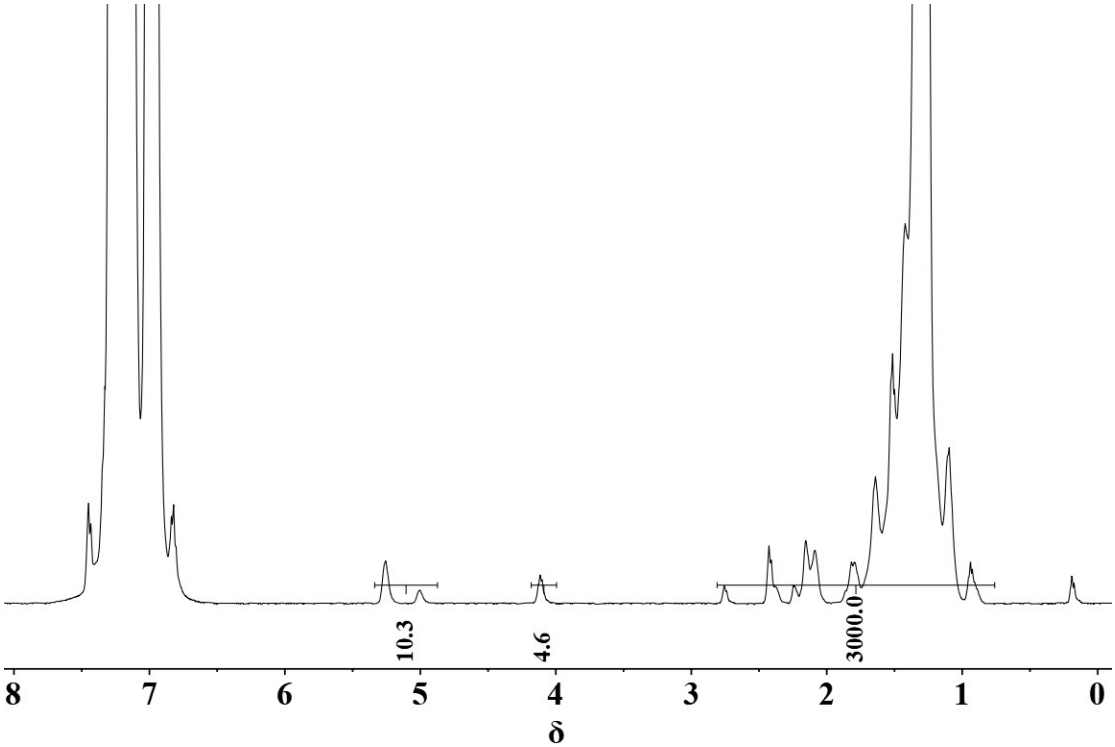
^{1}H NMR spectrum of polymer in Entry 4, Table3



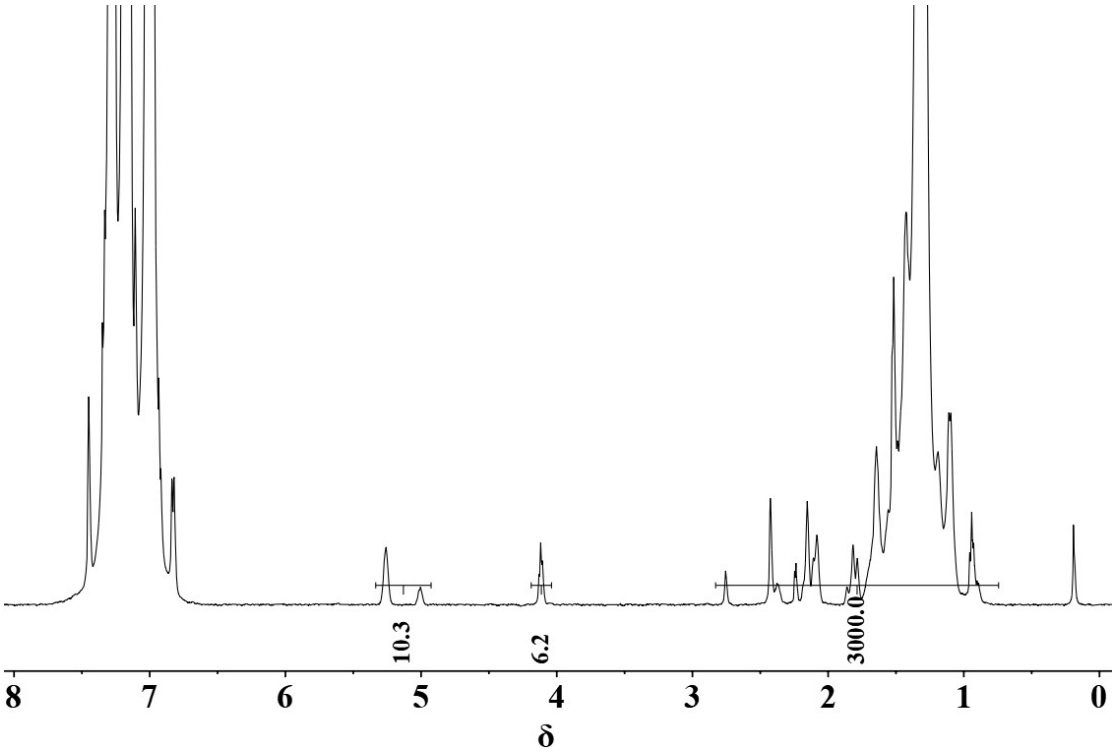
^{1}H NMR spectrum of polymer in Entry 5, Table3



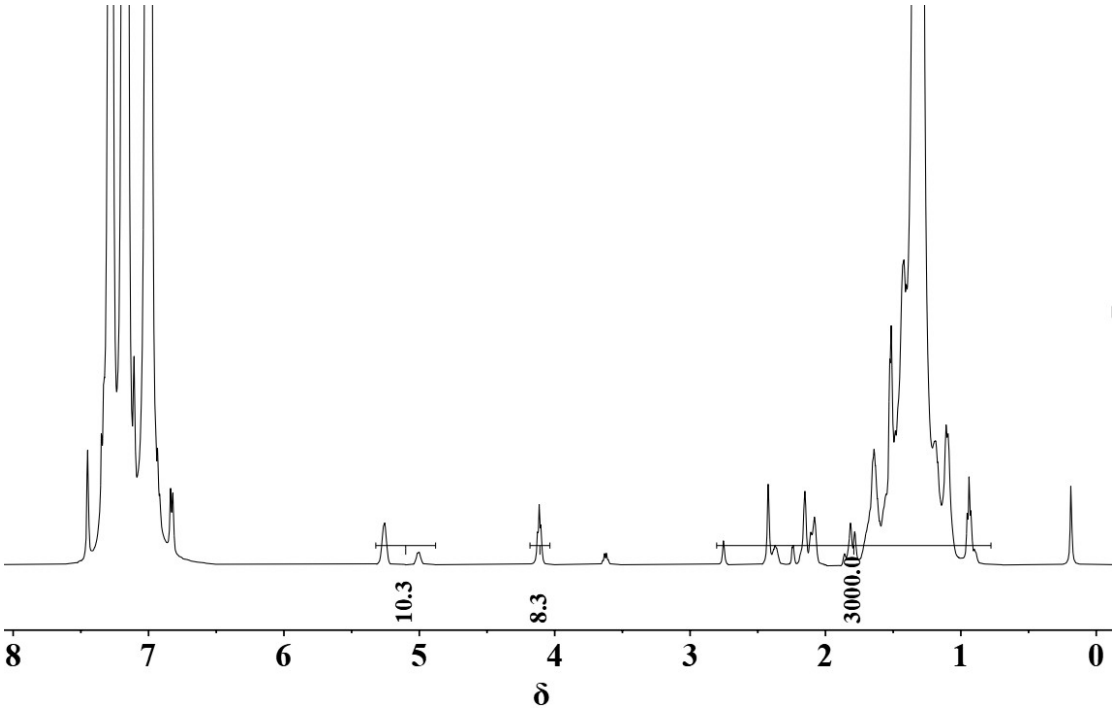
^{1}H NMR spectrum of polymer in Entry 6, Table3



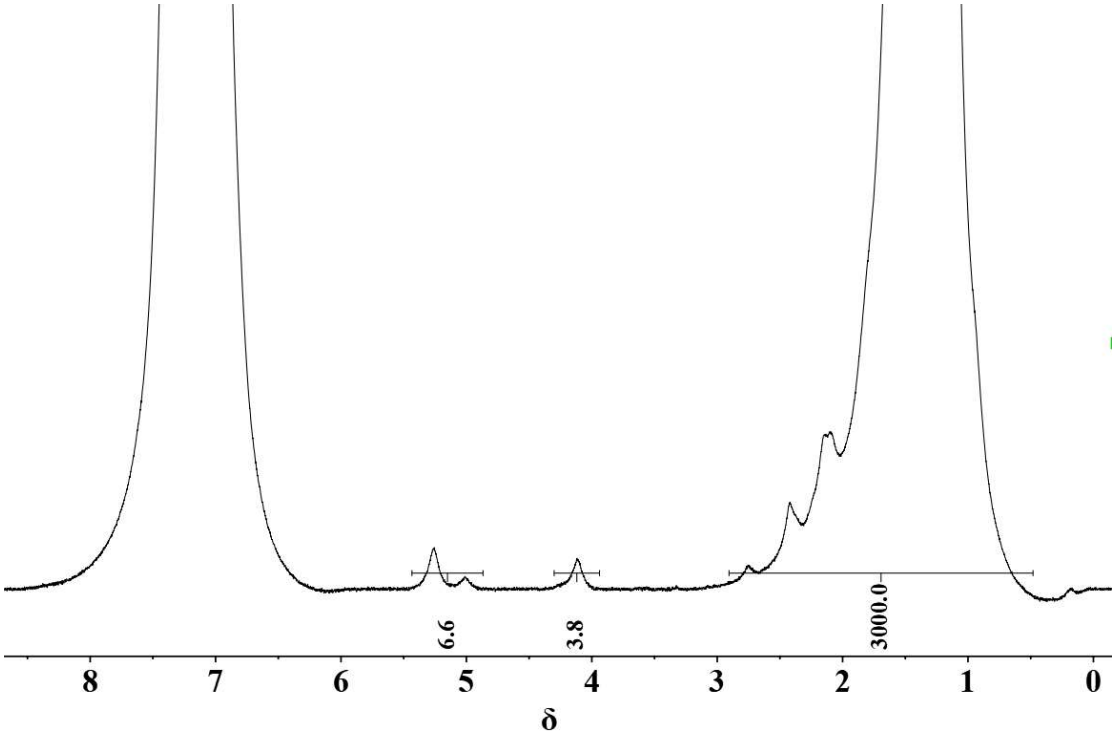
^{1}H NMR spectrum of polymer in Entry 7, Table3



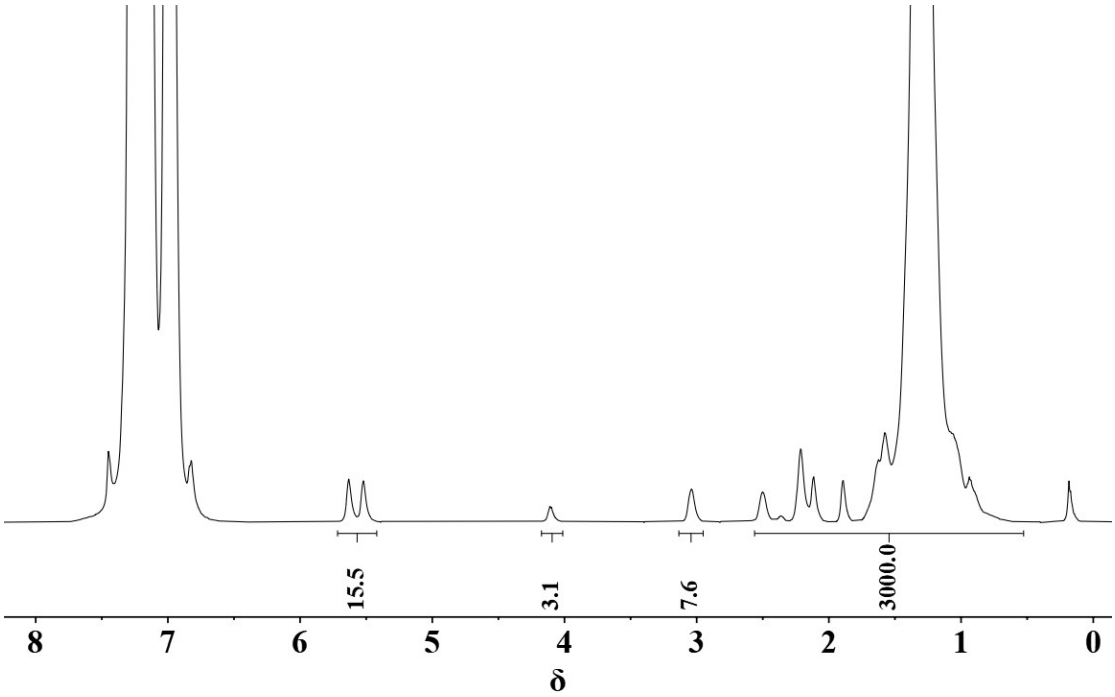
^{1}H NMR spectrum of polymer in Entry 8, Table3



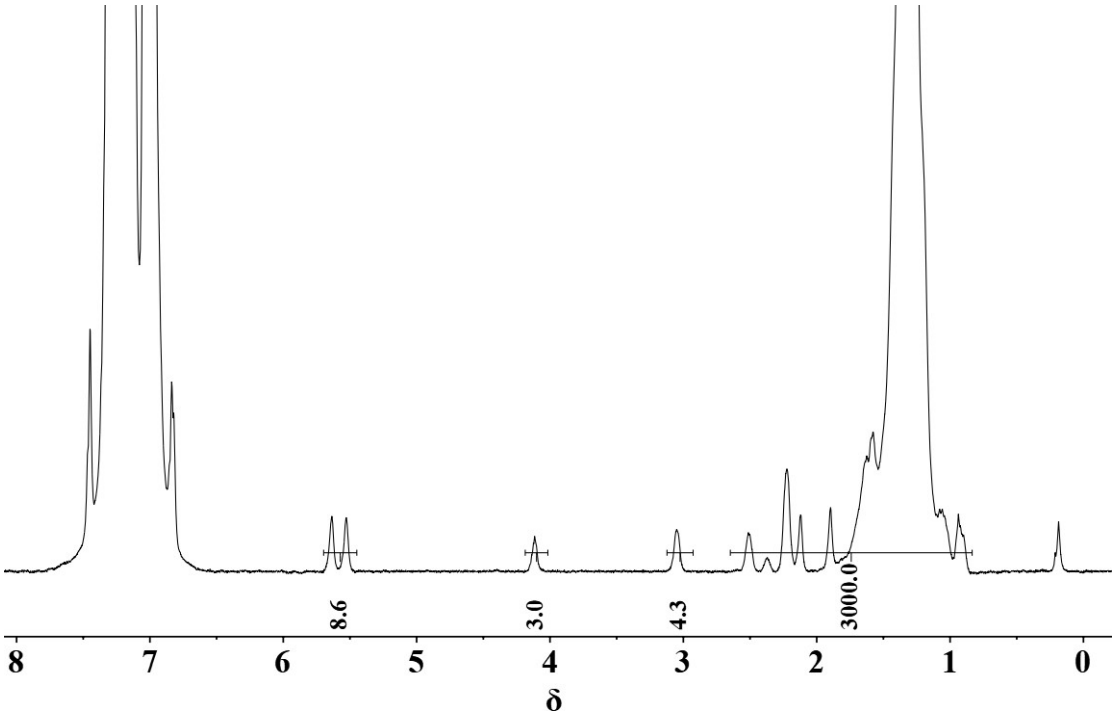
^{1}H NMR spectrum of polymer in Entry 9, Table3



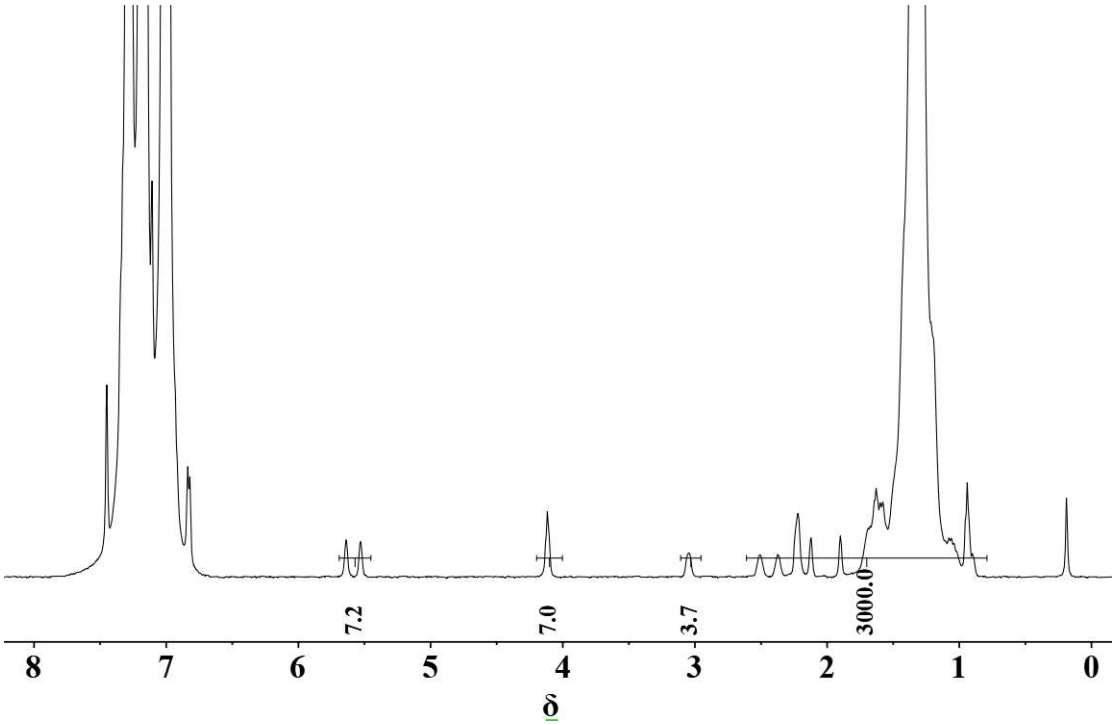
^{1}H NMR spectrum of polymer in Entry 10, Table3



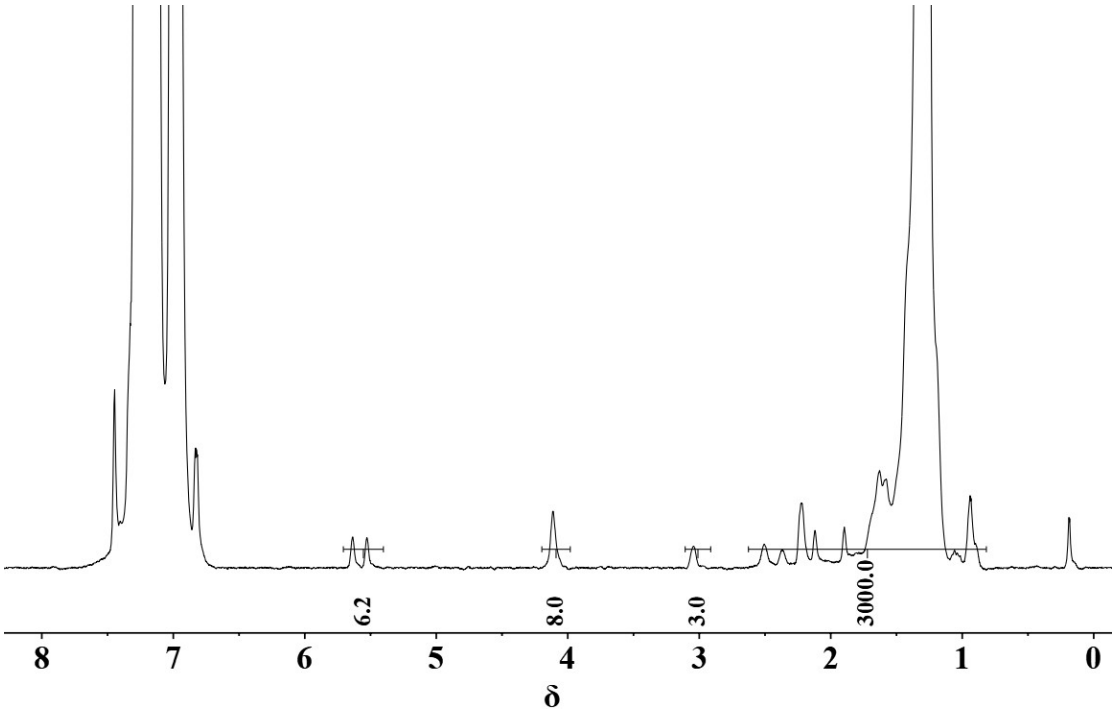
^{1}H NMR spectrum of polymer in Entry 11, Table3



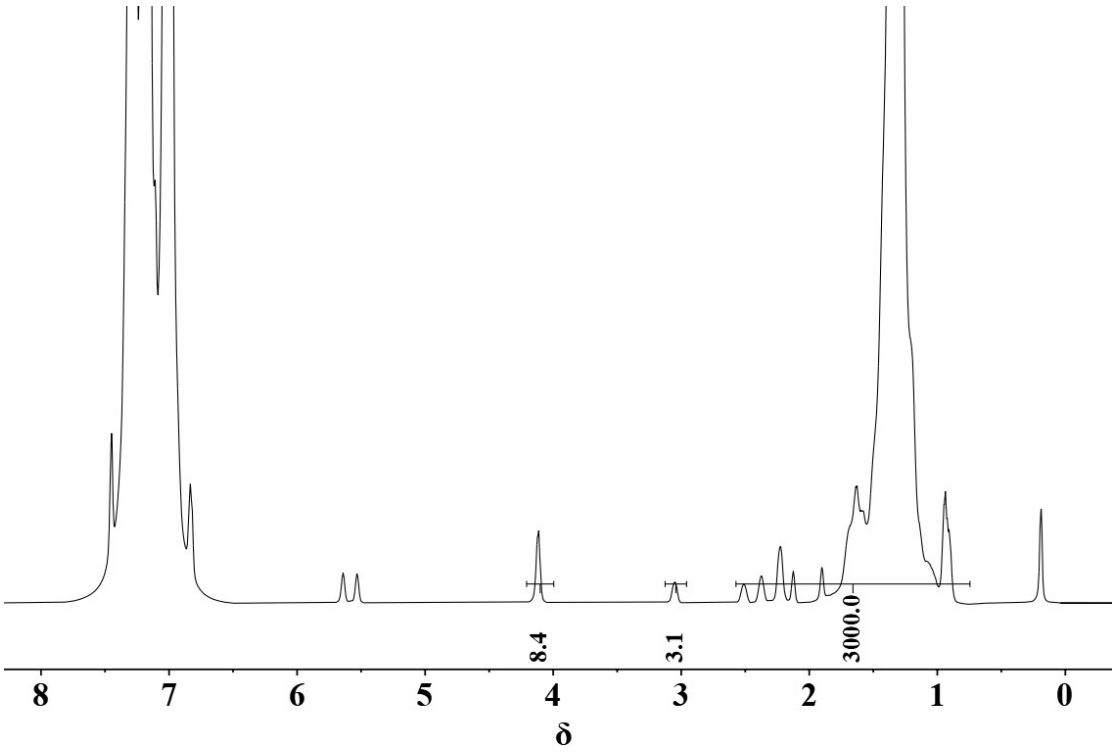
^{1}H NMR spectrum of polymer in Entry 12, Table3



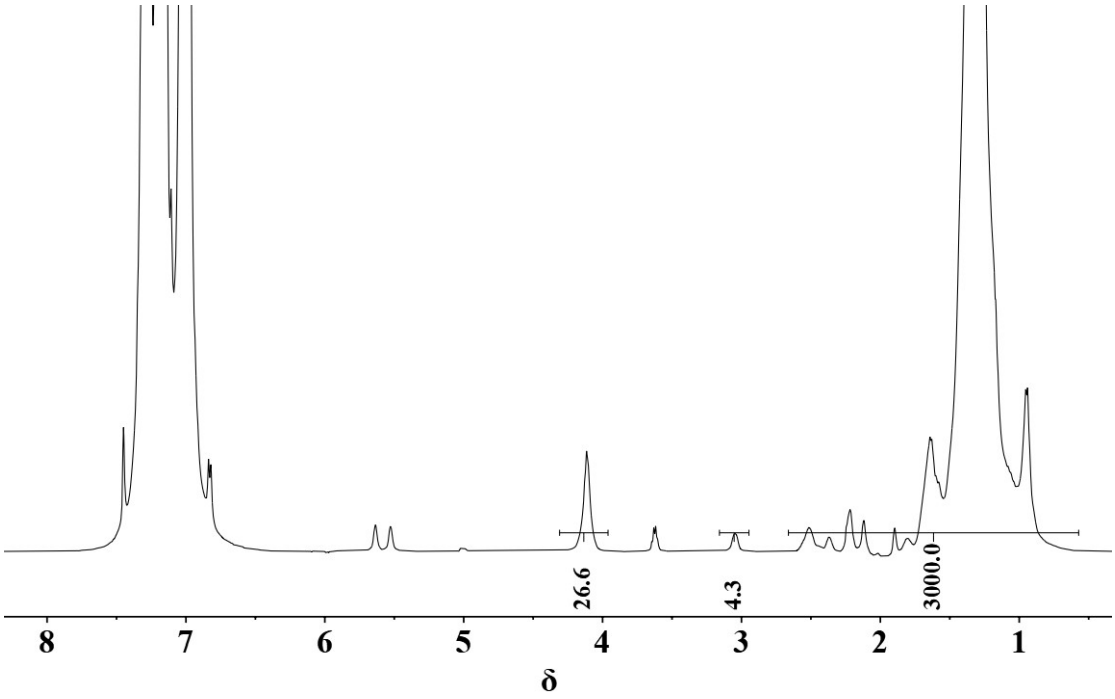
^{1}H NMR spectrum of polymer in Entry 13, Table3



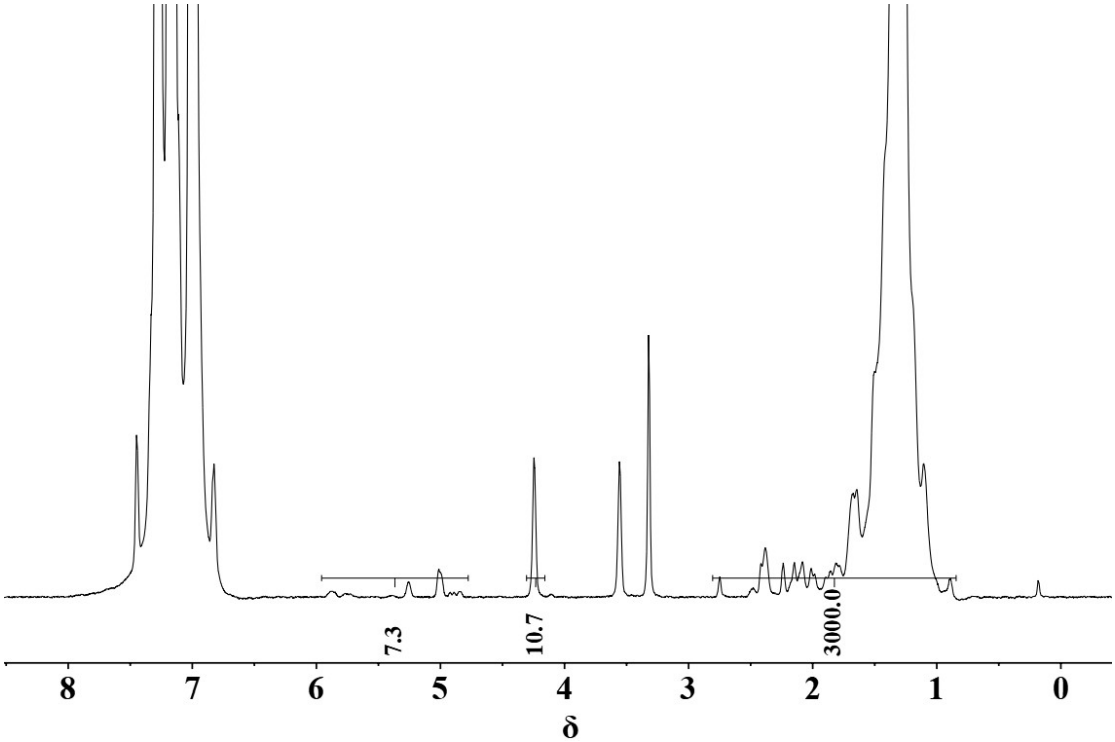
^{1}H NMR spectrum of polymer in Entry 14, Table3



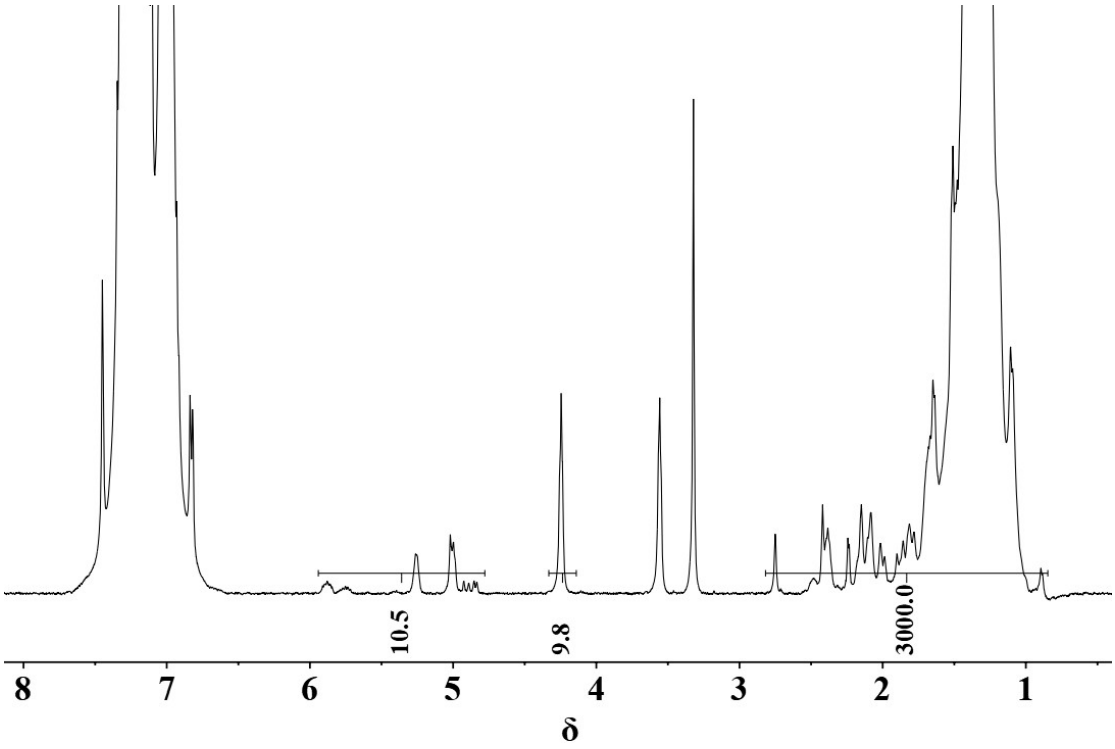
^{1}H NMR spectrum of polymer in Entry 15, Table3



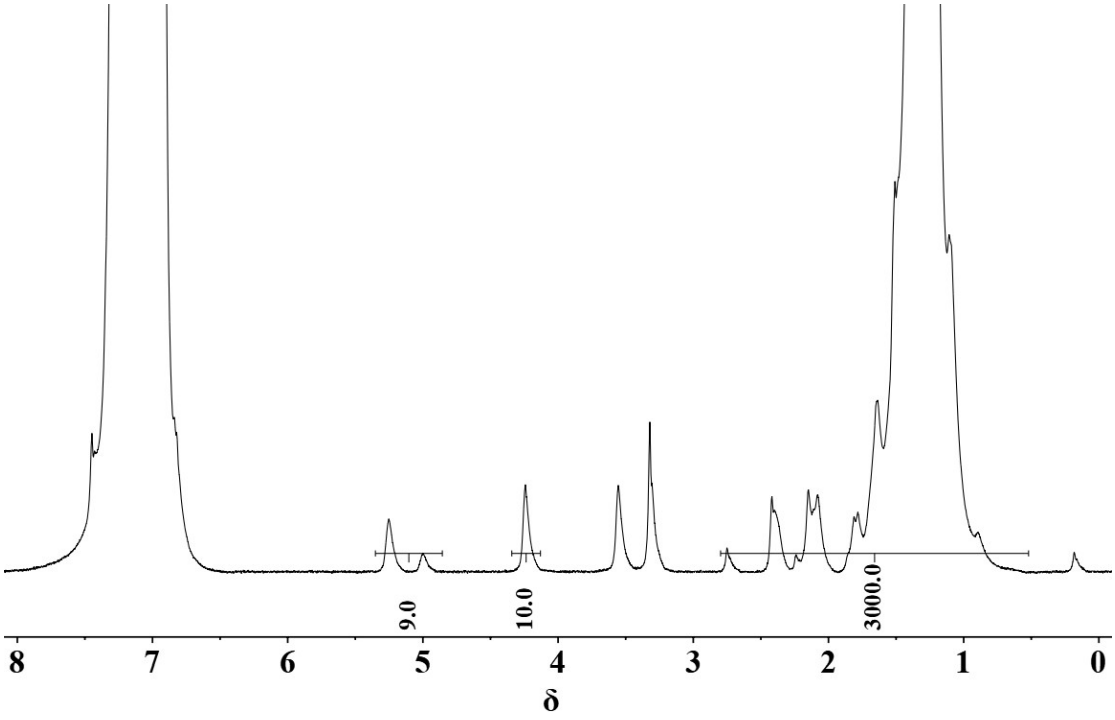
^{1}H NMR spectrum of polymer in Entry 16, Table3



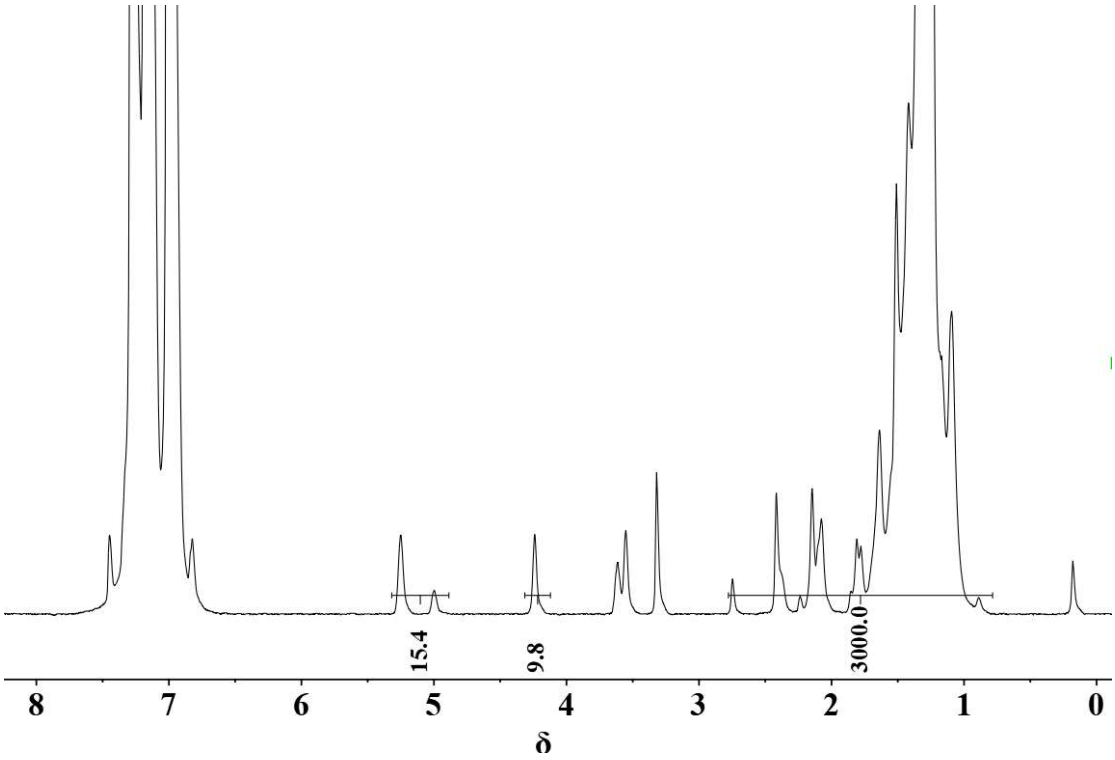
^{1}H NMR spectrum of polymer in Entry 18, Table3



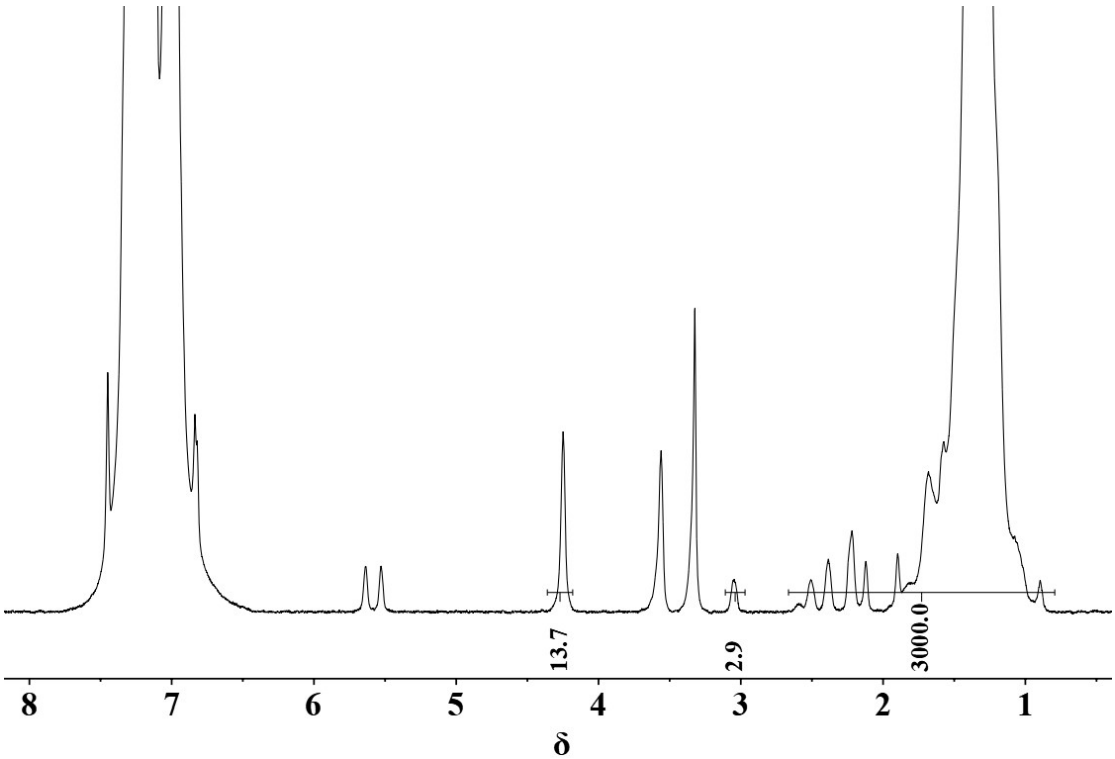
^{1}H NMR spectrum of polymer in Entry 19, Table3



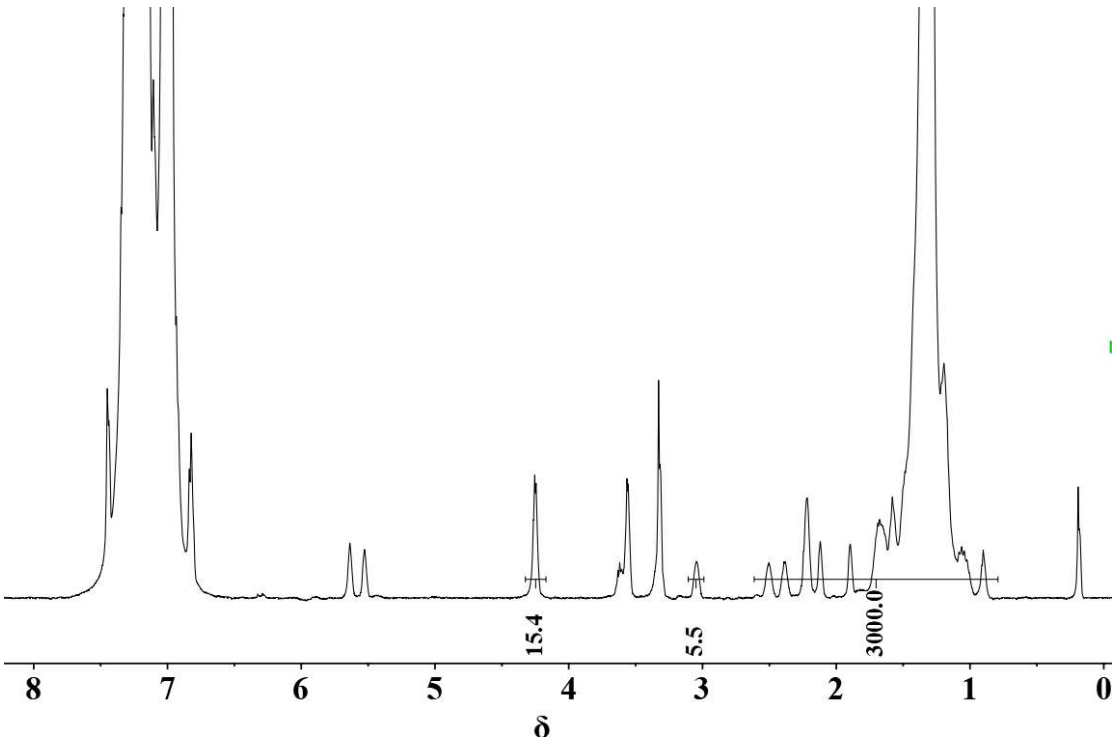
^{1}H NMR spectrum of polymer in Entry 20, Table3



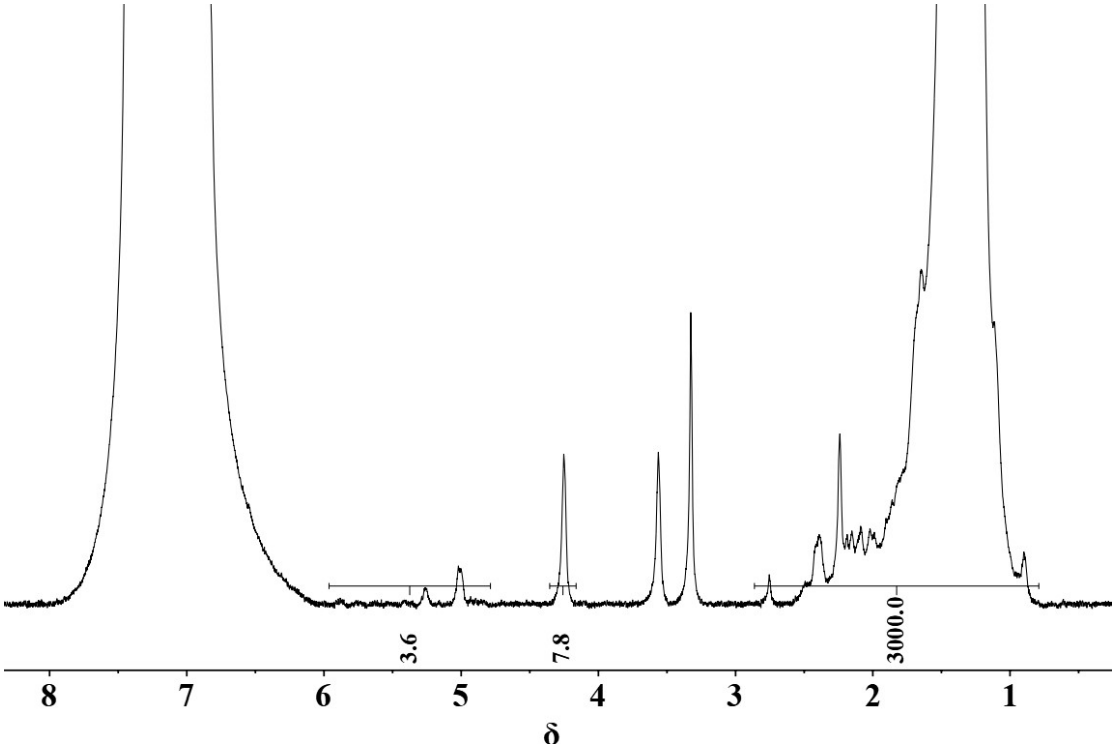
^{1}H NMR spectrum of polymer in Entry 21, Table3



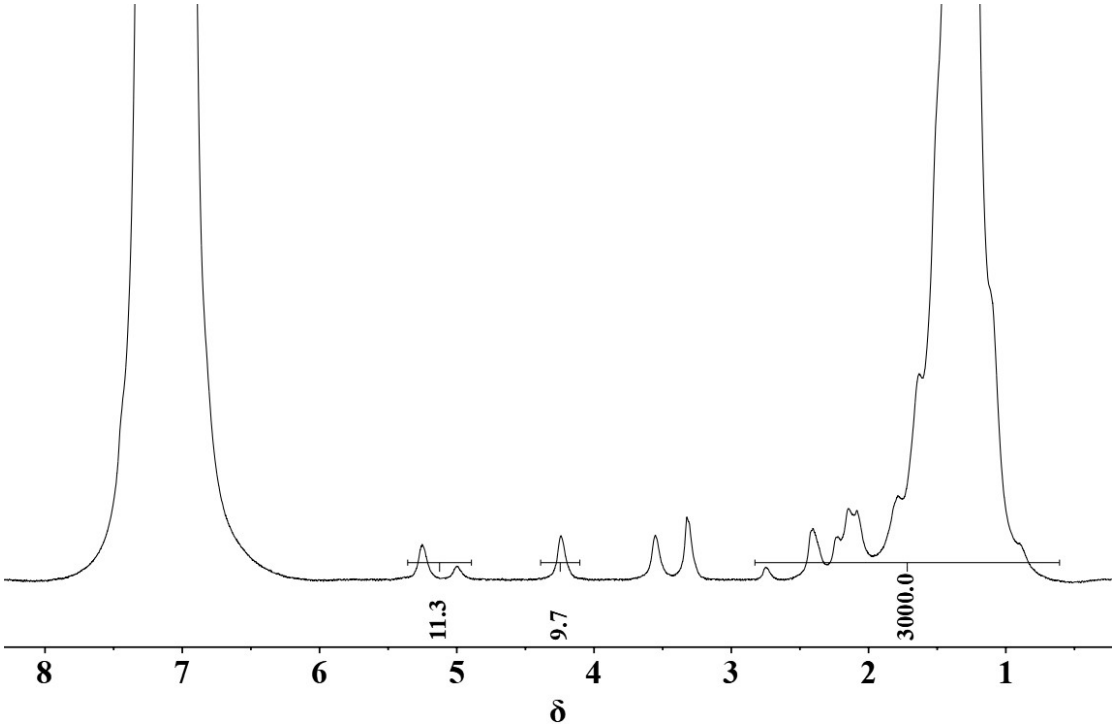
^{1}H NMR spectrum of polymer in Entry 22, Table3



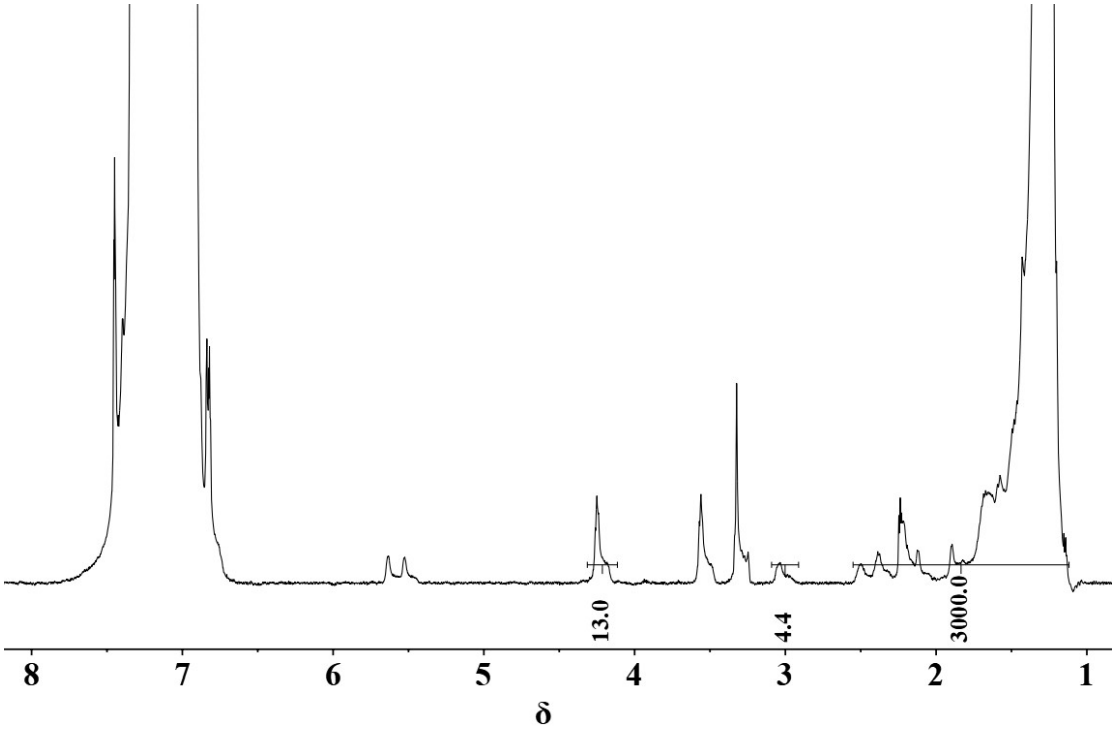
^{1}H NMR spectrum of polymer in Entry 23, Table3



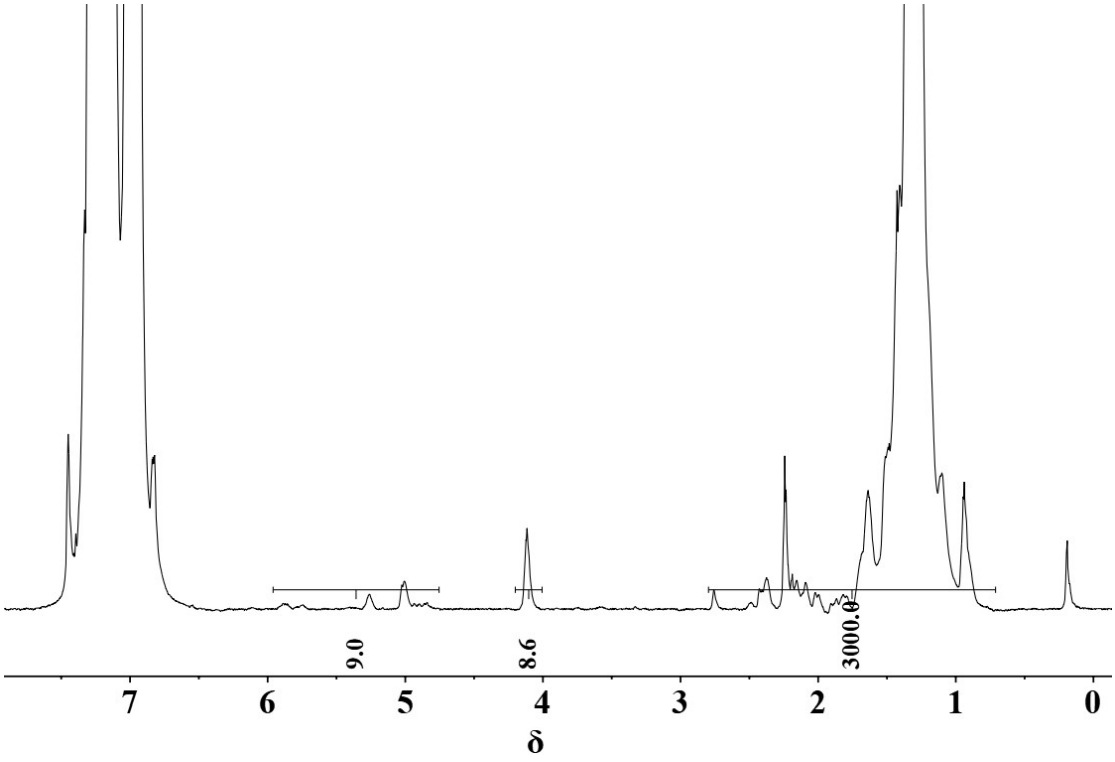
^{1}H NMR spectrum of polymer in Entry 24, Table3



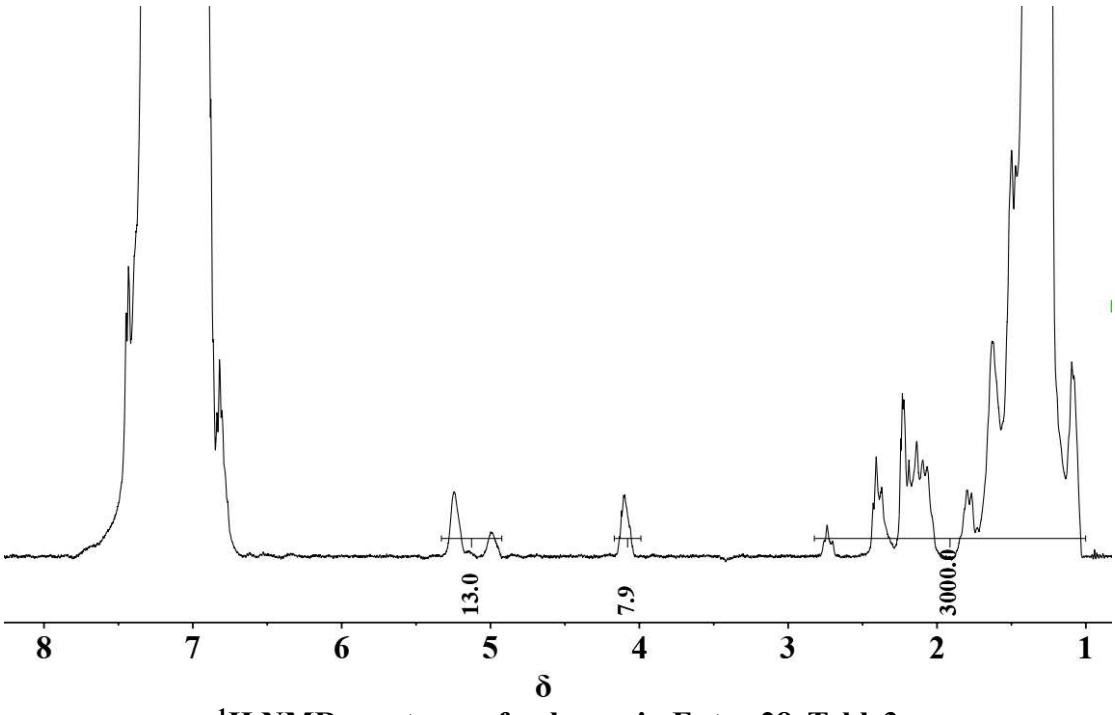
^{1}H NMR spectrum of polymer in Entry 25, Table3



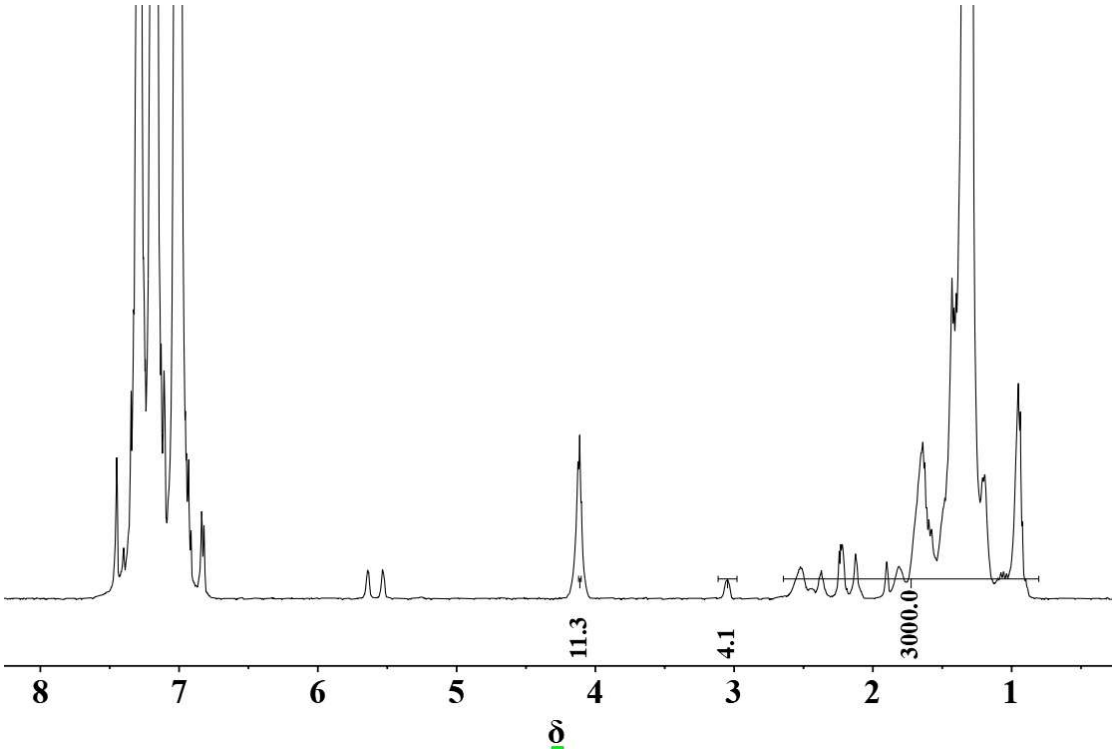
^{1}H NMR spectrum of polymer in Entry 26, Table3



^{1}H NMR spectrum of polymer in Entry 27, Table3

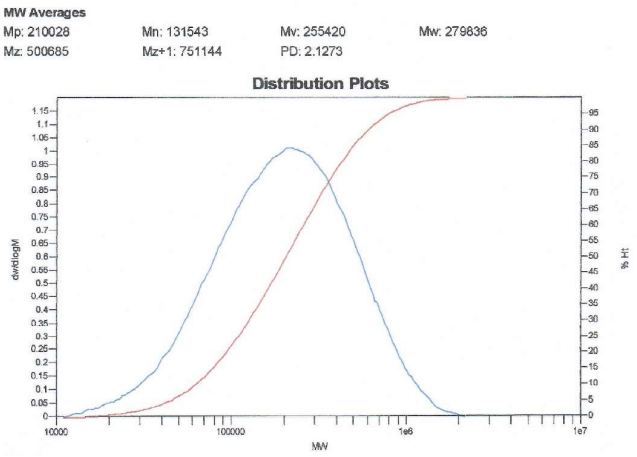


^{1}H NMR spectrum of polymer in Entry 28, Table3

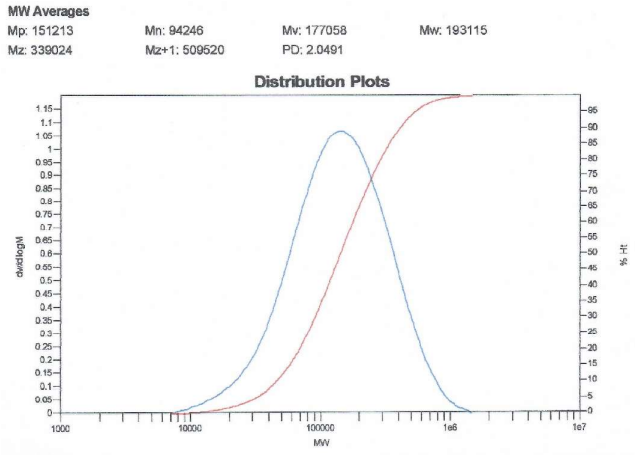


^{1}H NMR spectrum of polymer in Entry 29, Table3

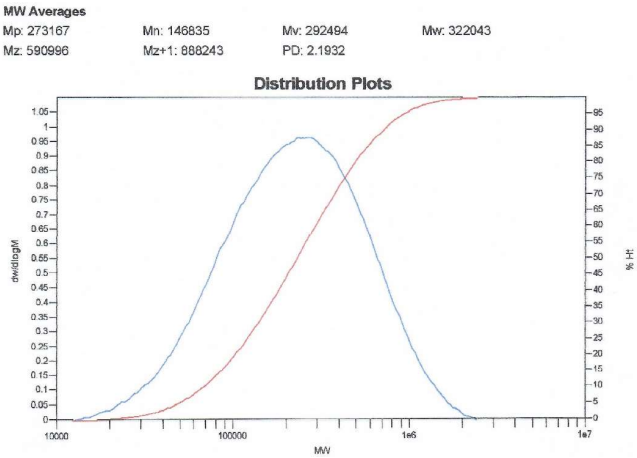
GPC spectra of polymers



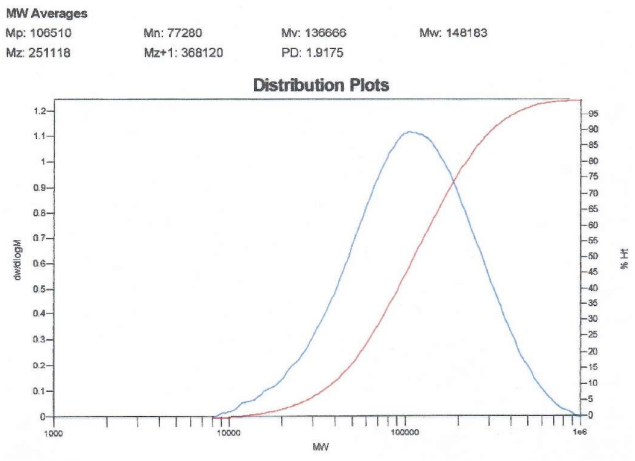
GPC spectrum of PE in Entry 2, Table 1



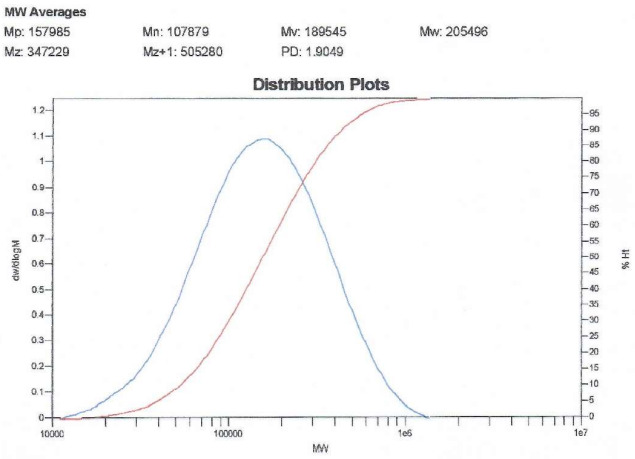
GPC spectrum of PE in Entry 3, Table 1



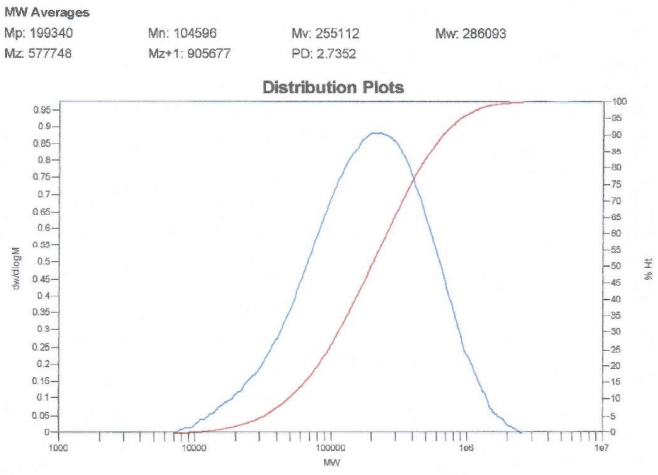
GPC spectrum of PE in Entry 4, Table 1



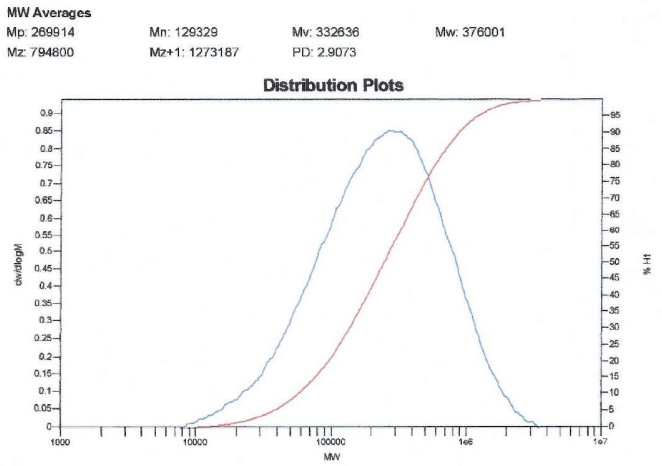
GPC spectrum of PE in Entry 5, Table 1



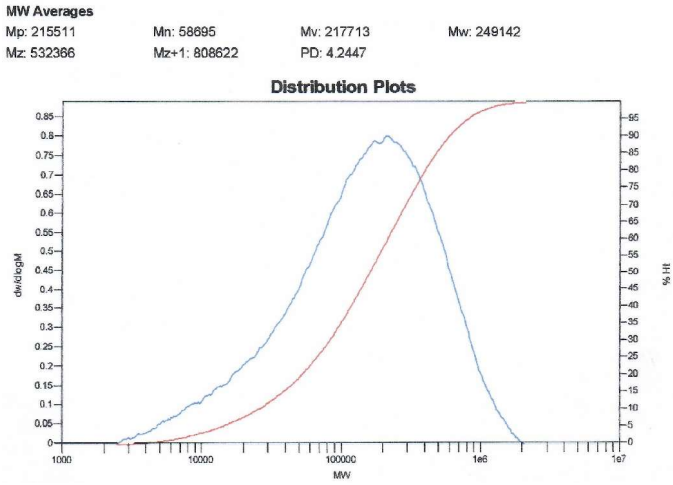
GPC spectrum of PE in Entry 6, Table 1



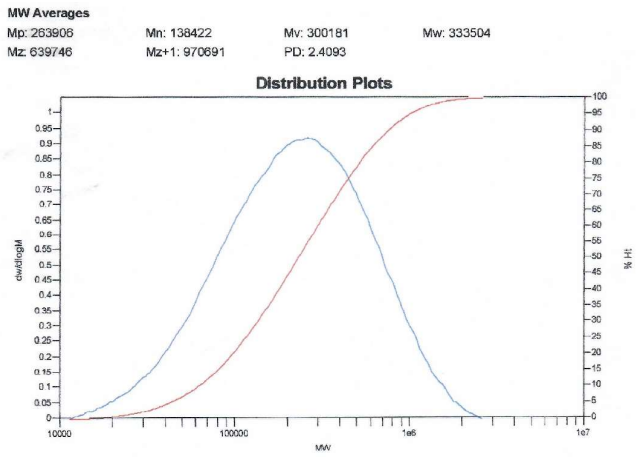
GPC spectrum of PE in Entry 7, Table 1



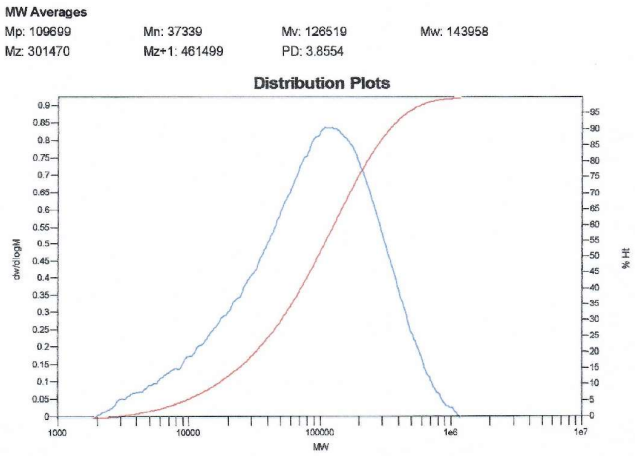
GPC spectrum of PE in Entry 8, Table 1



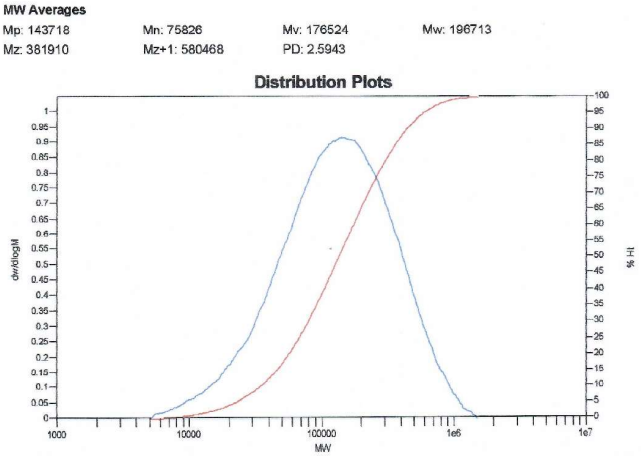
GPC spectrum of PE in Entry 9, Table 1



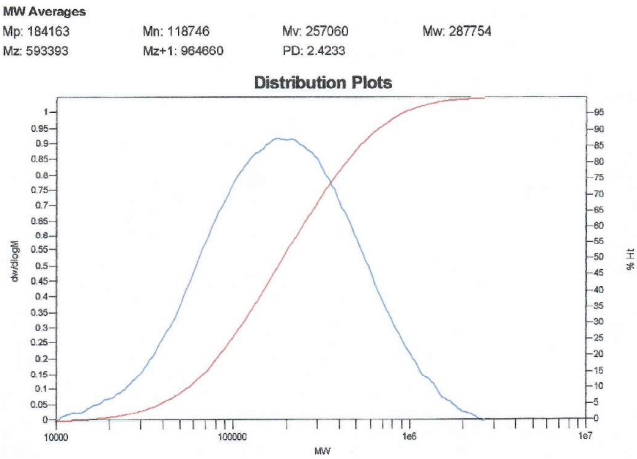
GPC spectrum of PE in Entry 10, Table 1



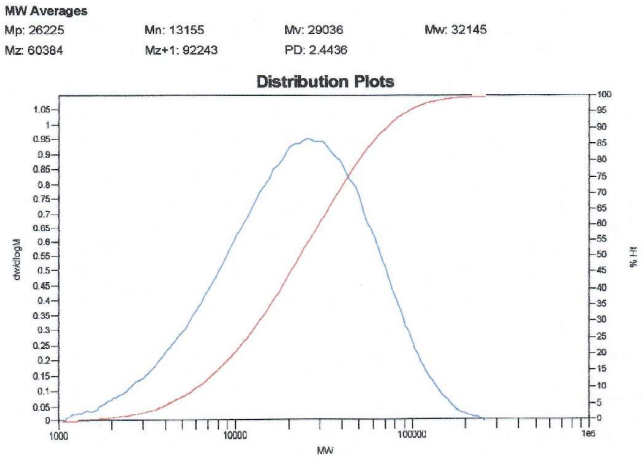
GPC spectrum of PE in Entry 11, Table 1



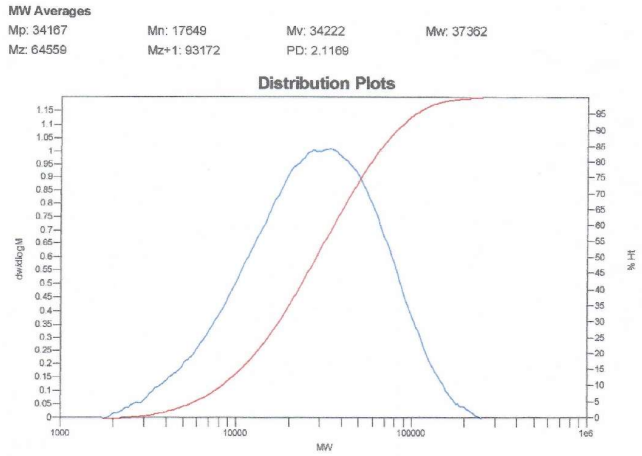
GPC spectrum of PE in Entry 12, Table 1



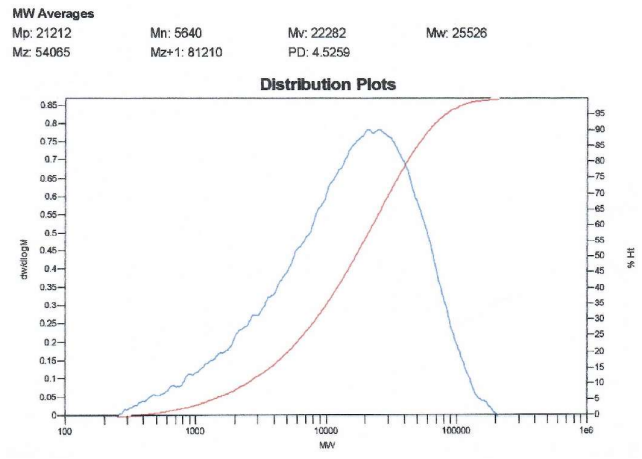
GPC spectrum of PE in Entry 1, Table 1



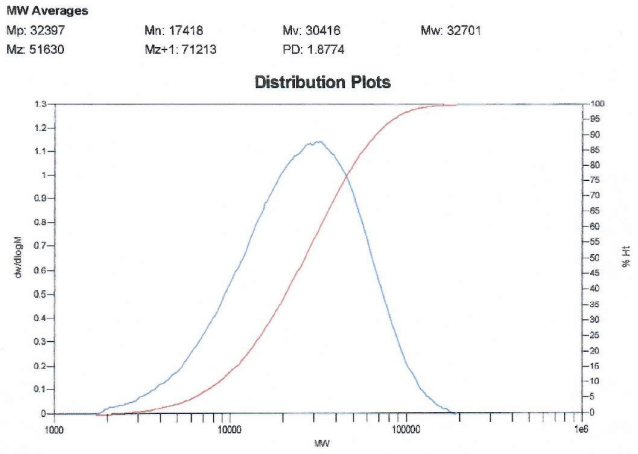
GPC spectrum of PE in Entry 13, Table 1



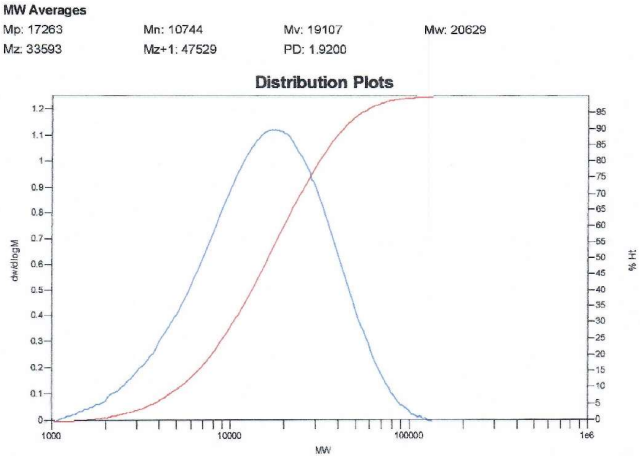
GPC spectrum of PE in Entry 14, Table 1



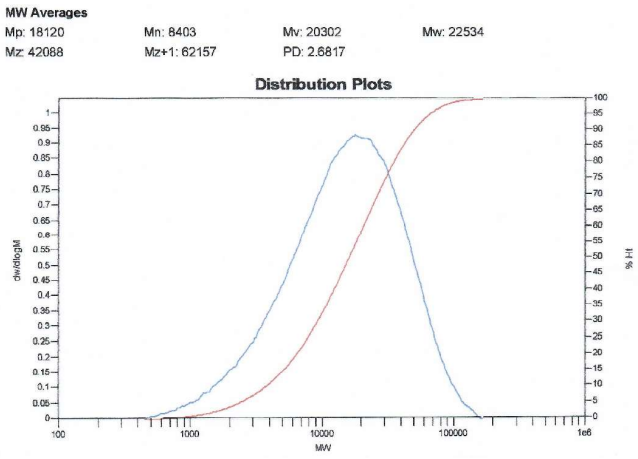
GPC spectrum of PE in Entry 15, Table 1



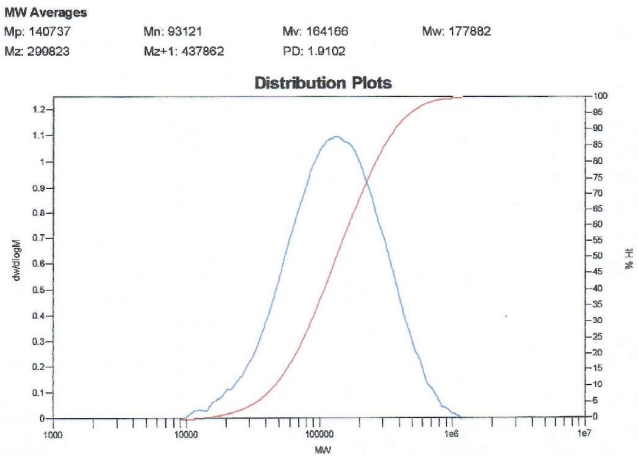
GPC spectrum of PE in Entry 16, Table 1



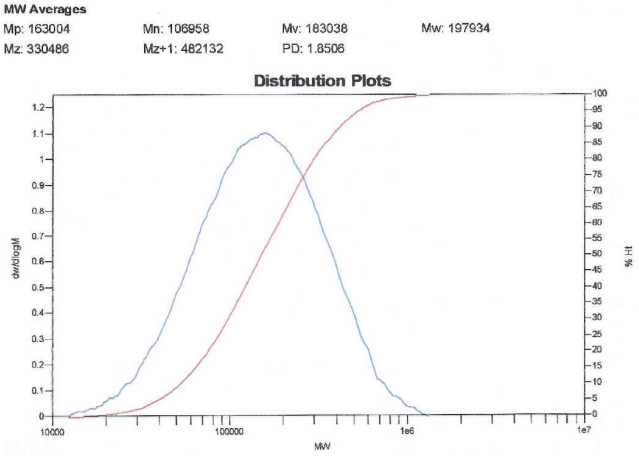
GPC spectrum of PE in Entry 17, Table 1



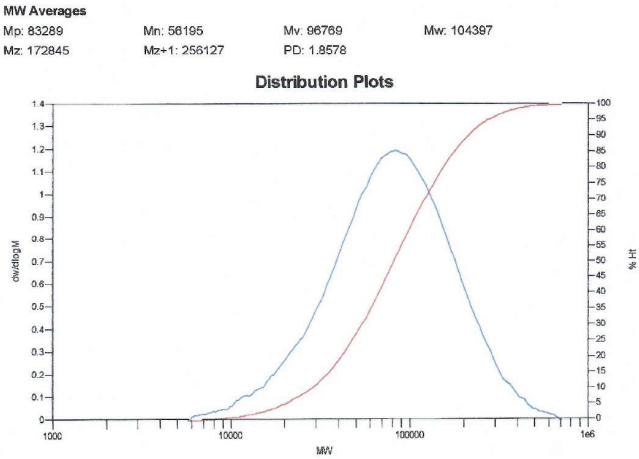
GPC spectrum of PE in Entry 18, Table 1



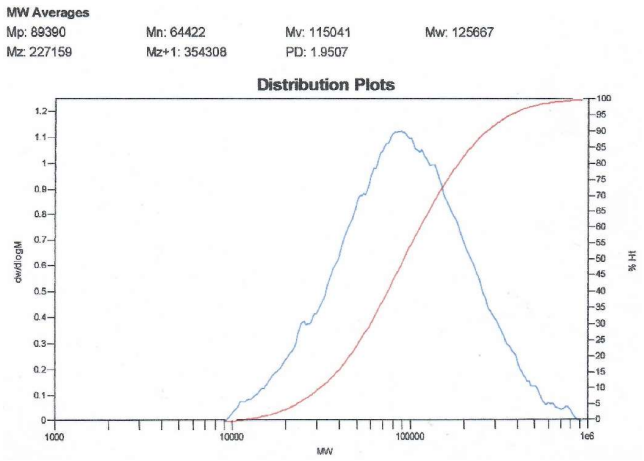
GPC spectrum of PE in Entry 19, Table 1



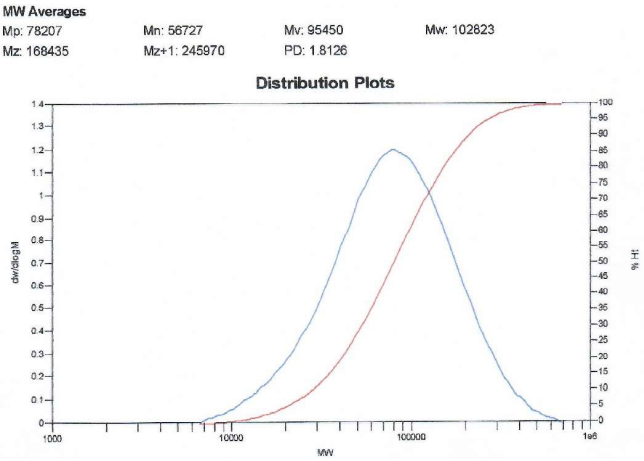
GPC spectrum of PE in Entry 20, Table 1



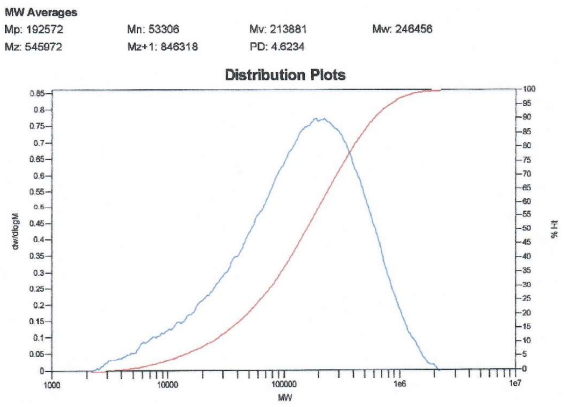
GPC spectrum of PE in Entry 21, Table 1



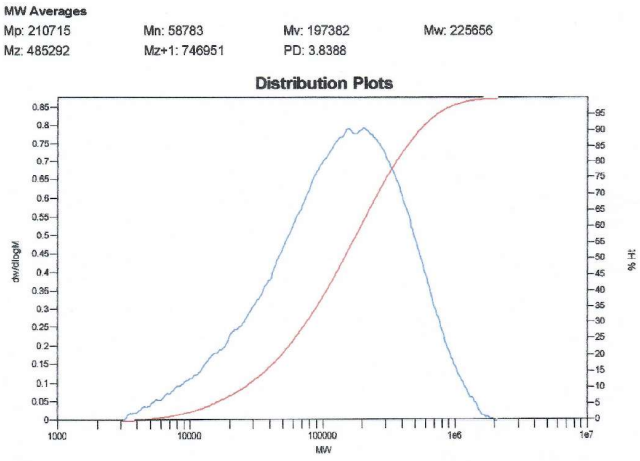
GPC spectrum of PE in Entry 23, Table 1



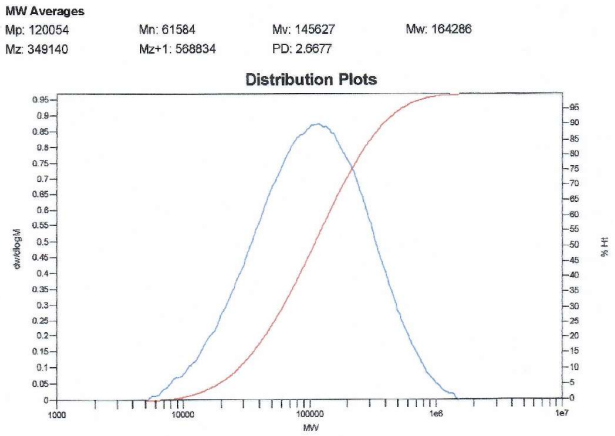
GPC spectrum of PE in Entry 24, Table 1



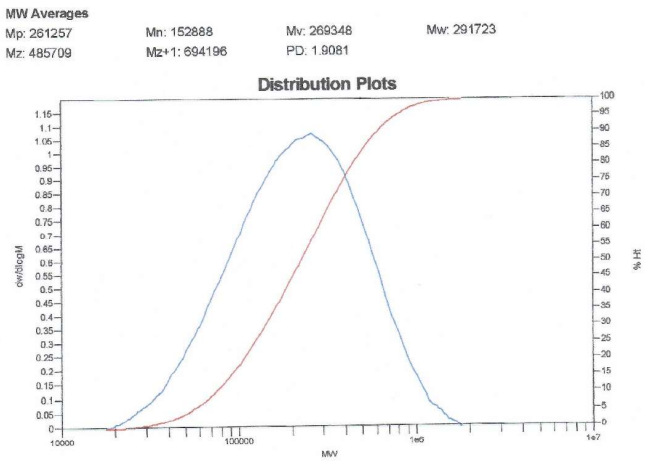
GPC spectrum of PE in Entry 25, Table 1



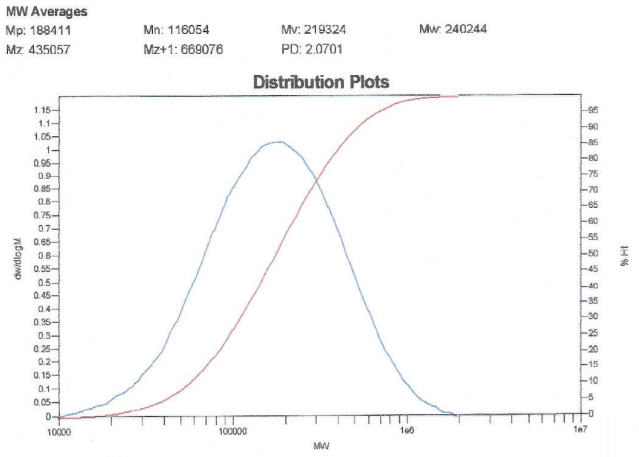
GPC spectrum of PE in Entry 26, Table 1



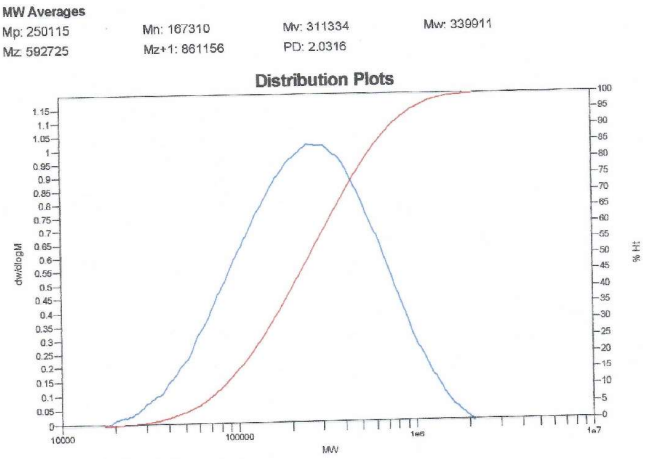
GPC spectrum of PE in Entry 27, Table 1



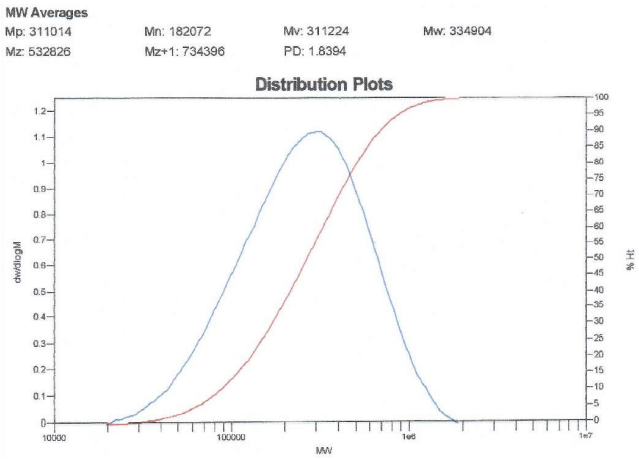
GPC spectrum of polymer in Entry 1, Table 2



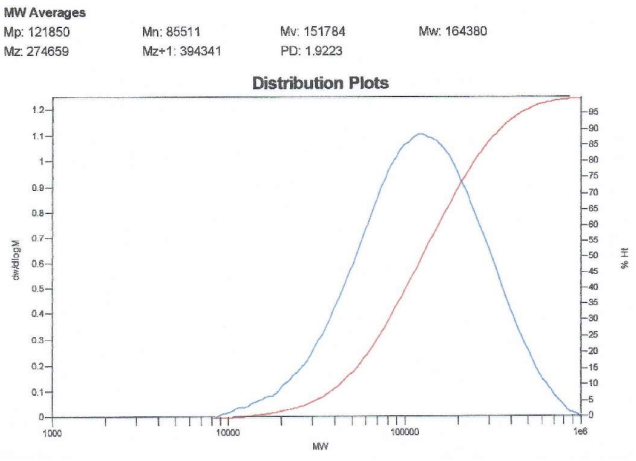
GPC spectrum of polymer in Entry 2, Table 2



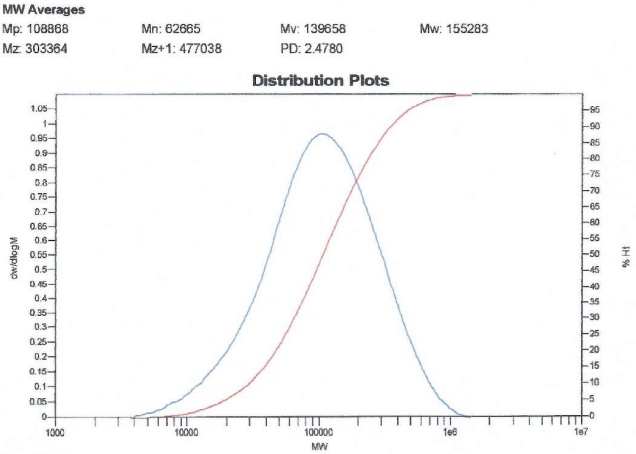
GPC spectrum of polymer in Entry 3, Table 2



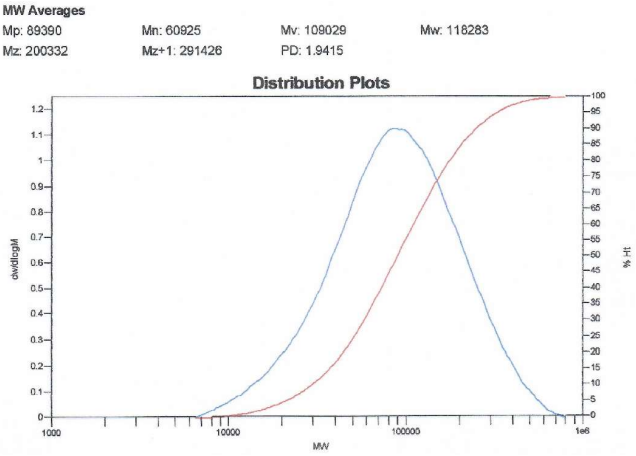
GPC spectrum of polymer in Entry 4, Table 2



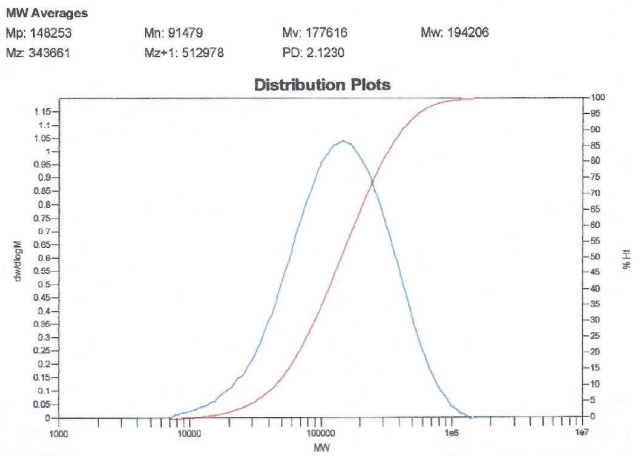
GPC spectrum of polymer in Entry 5, Table 2



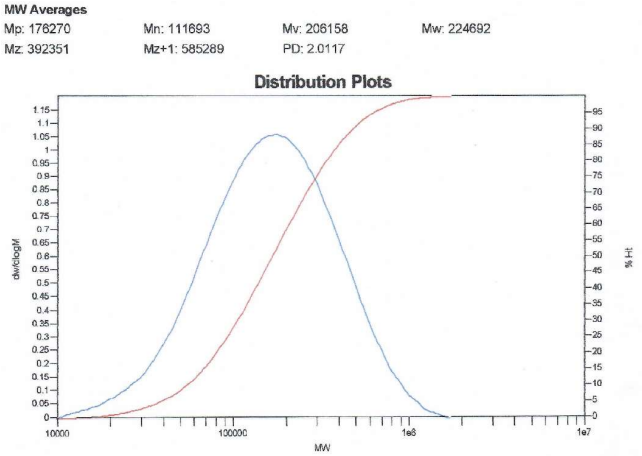
GPC spectrum of polymer in Entry 6, Table 2



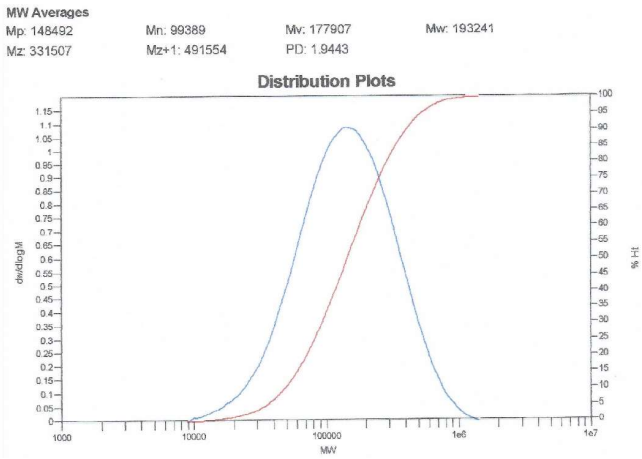
GPC spectrum of polymer in Entry 7, Table 2



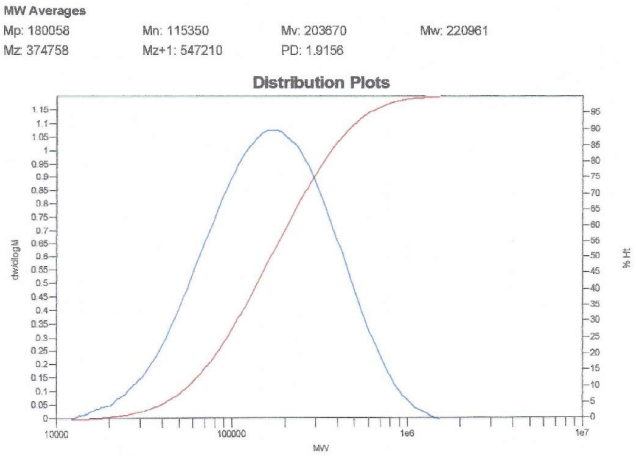
GPC spectrum of polymer in Entry 8, Table 2



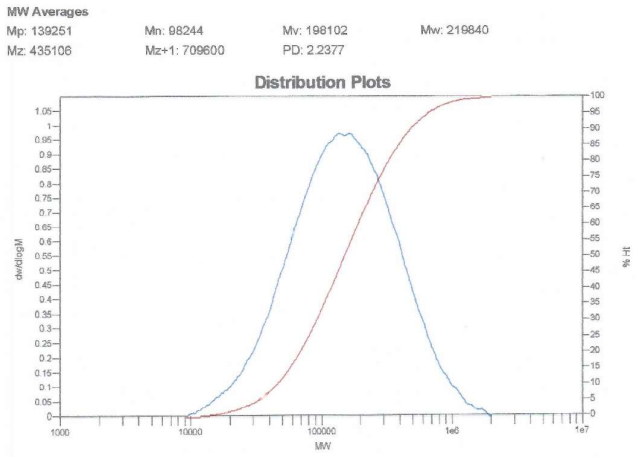
GPC spectrum of polymer in Entry 10, Table 2



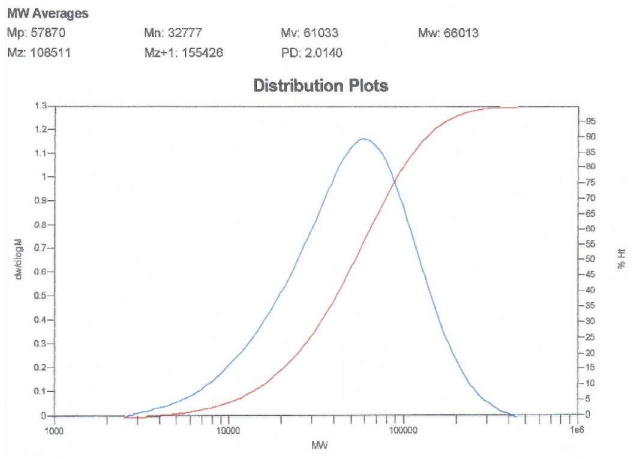
GPC spectrum of polymer in Entry 11, Table 2



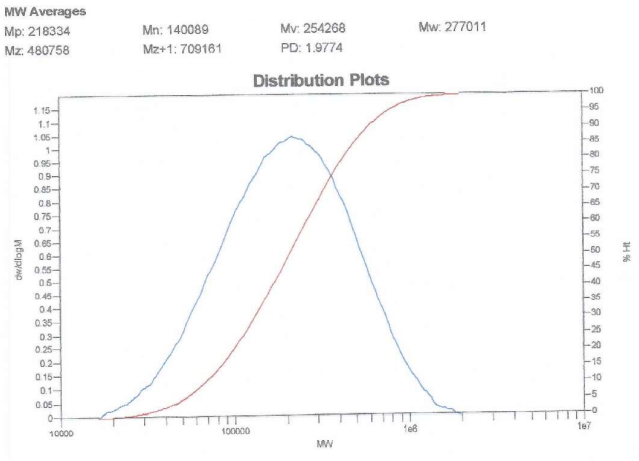
GPC spectrum of polymer in Entry 12, Table 2



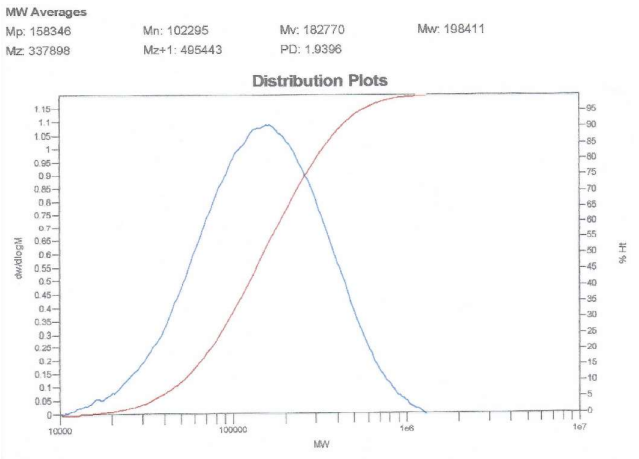
GPC spectrum of polymer in Entry 13, Table 2



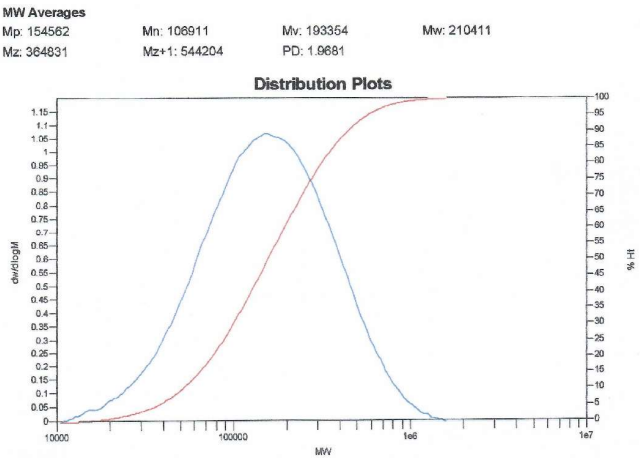
GPC spectrum of polymer in Entry 14, Table 2



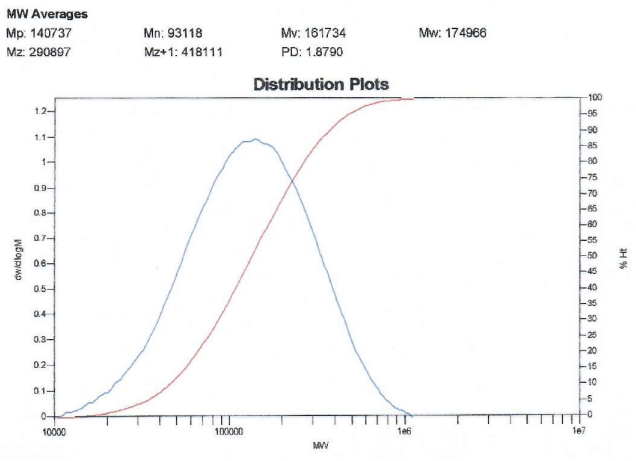
GPC spectrum of polymer in Entry 15, Table 2



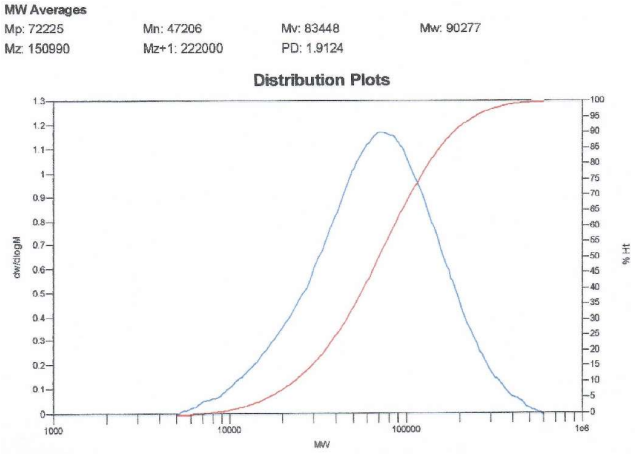
GPC spectrum of polymer in Entry 16, Table 2



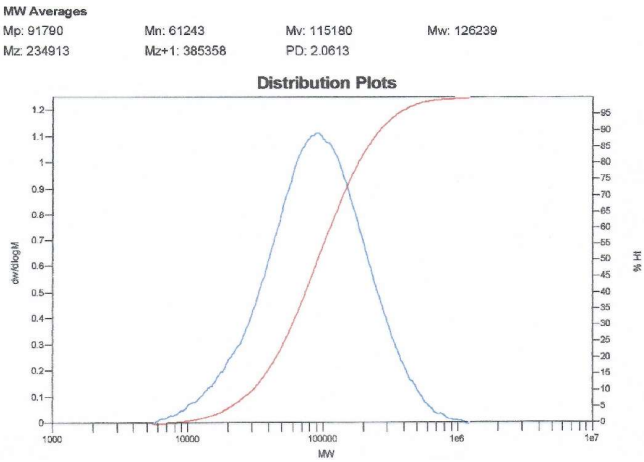
GPC spectrum of polymer in Entry 17, Table 2



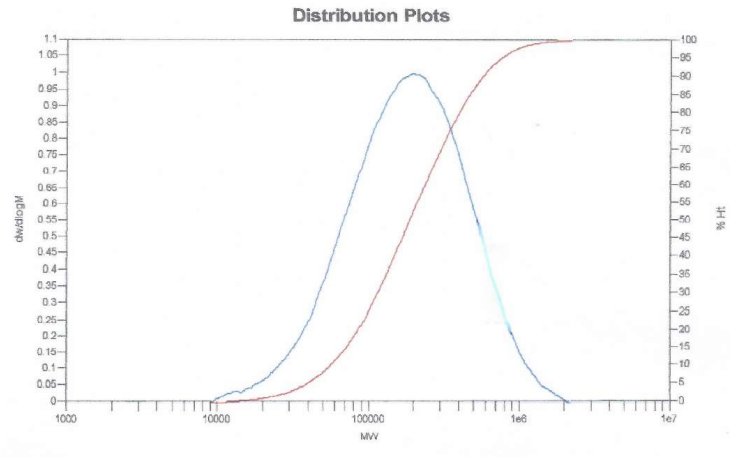
GPC spectrum of polymer in Entry 18, Table 2



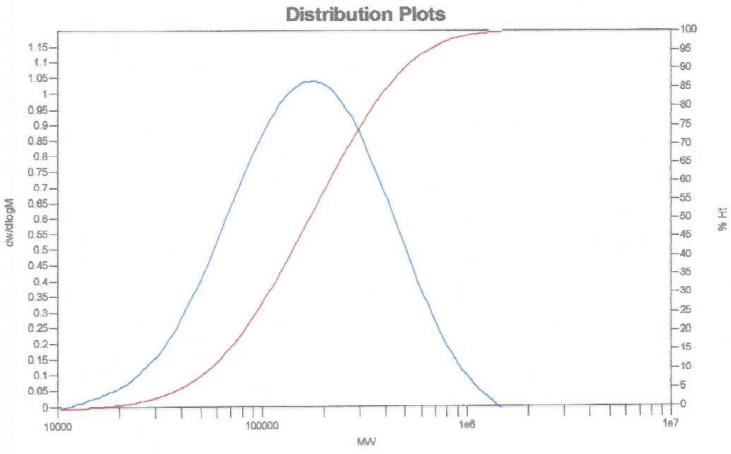
GPC spectrum of polymer in Entry 19, Table 2



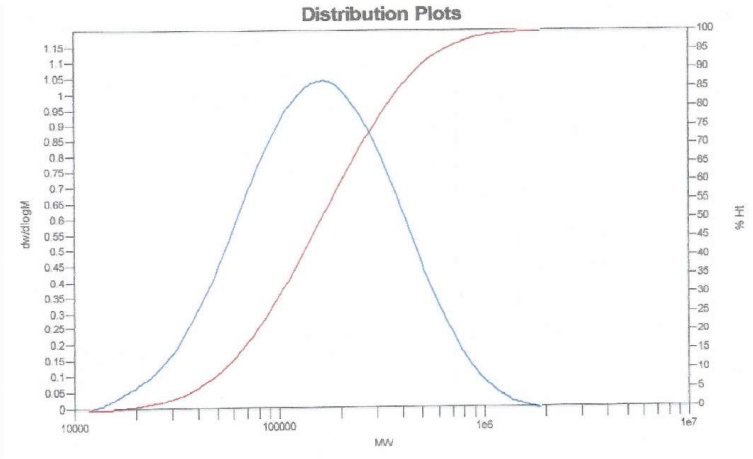
GPC spectrum of polymer in Entry 20, Table 2



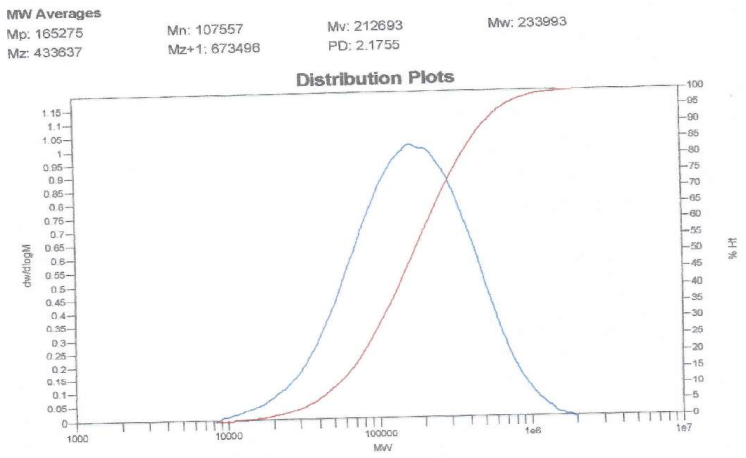
GPC spectrum of polymer in Entry 1, Table 3



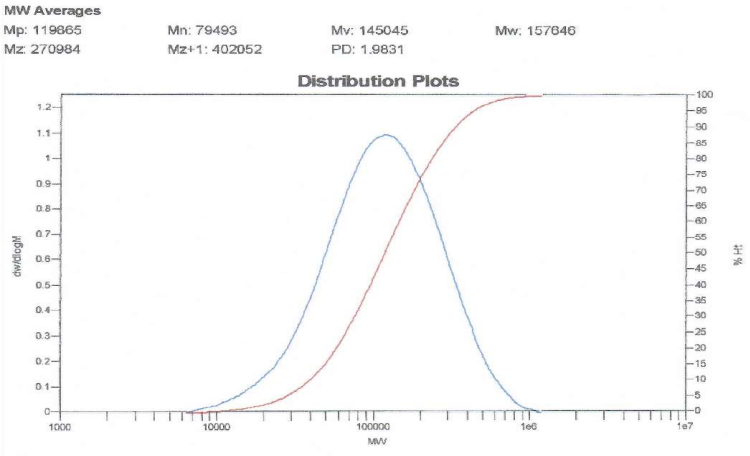
GPC spectrum of polymer in Entry 2, Table 3



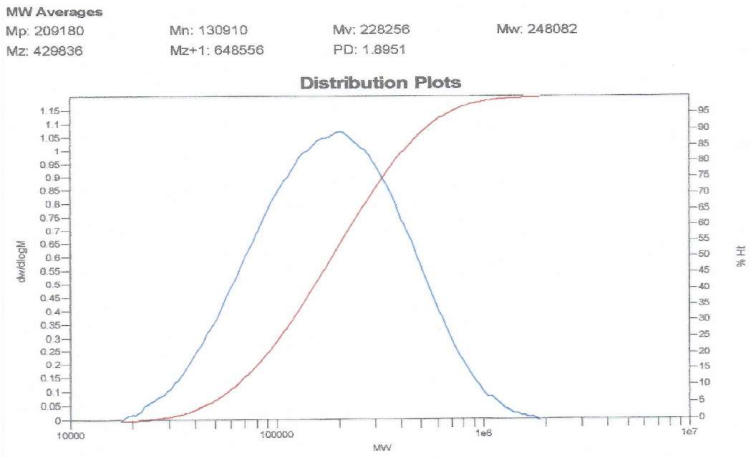
GPC spectrum of polymer in Entry 3, Table 3



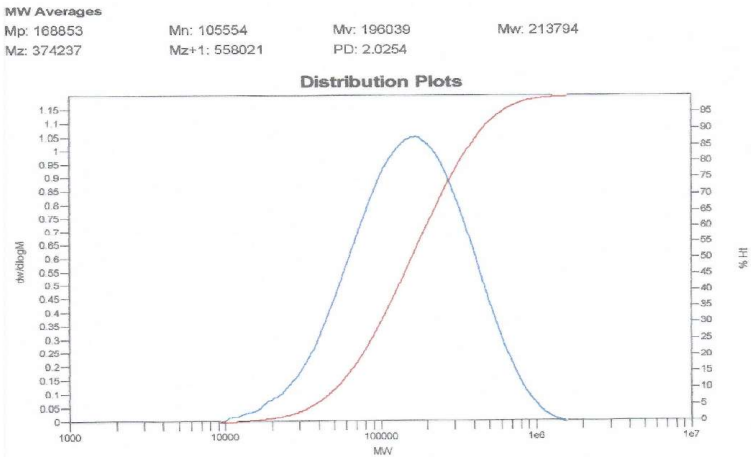
GPC spectrum of polymer in Entry 4, Table 3



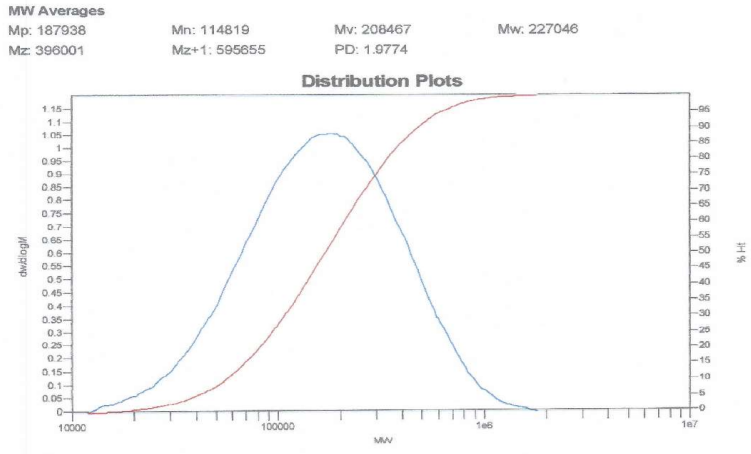
GPC spectrum of polymer in Entry 5, Table 3



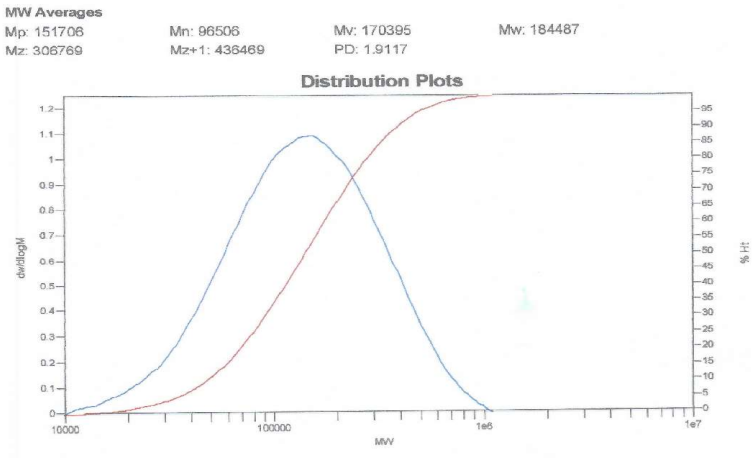
GPC spectrum of polymer in Entry 6, Table 3



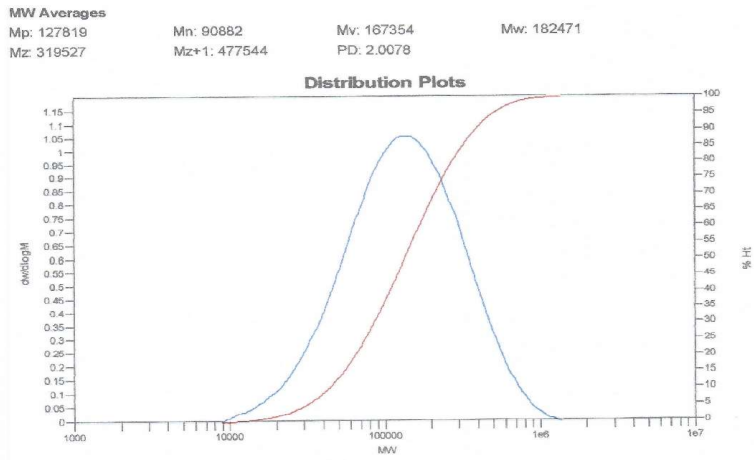
GPC spectrum of polymer in Entry 7, Table 3



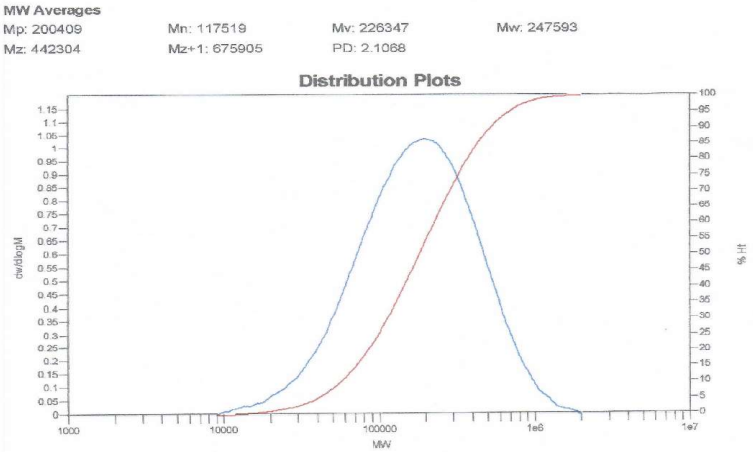
GPC spectrum of polymer in Entry 8, Table 3



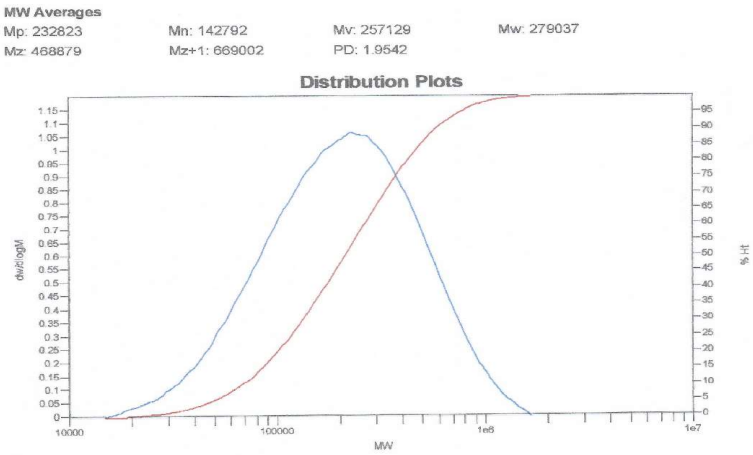
GPC spectrum of polymer in Entry 9, Table 3



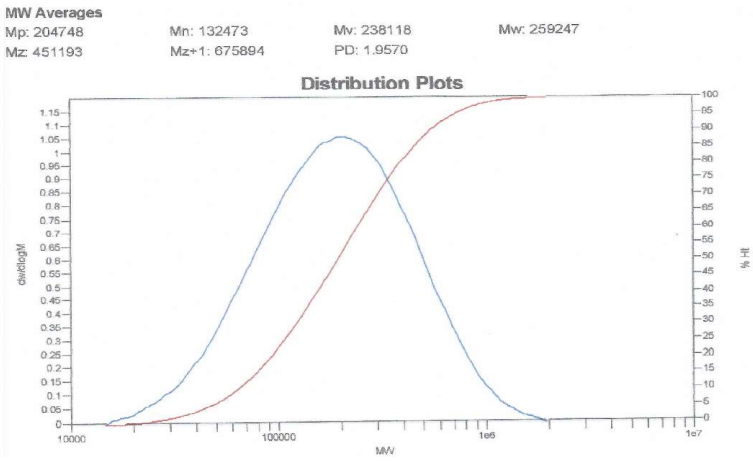
GPC spectrum of polymer in Entry 10, Table 3



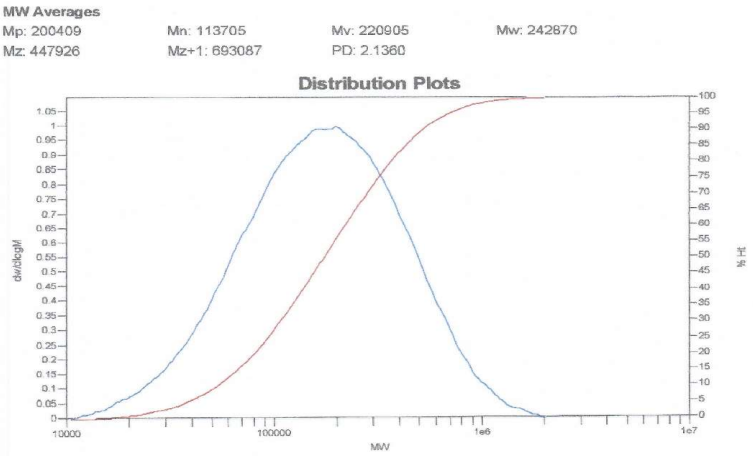
GPC spectrum of polymer in Entry 10, Table 3



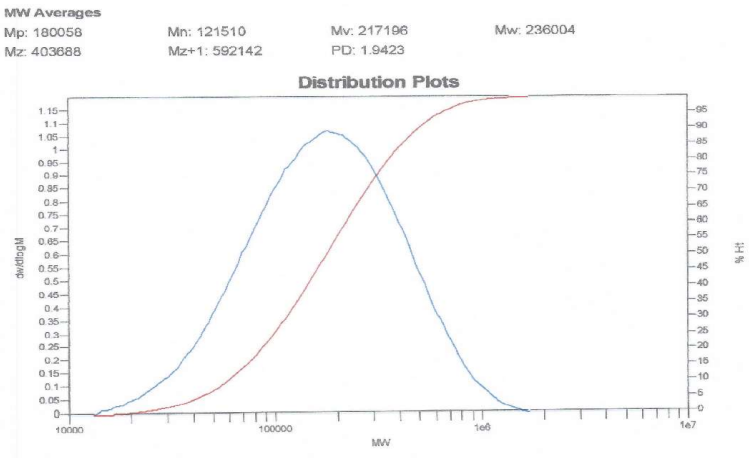
GPC spectrum of polymer in Entry 12, Table 3



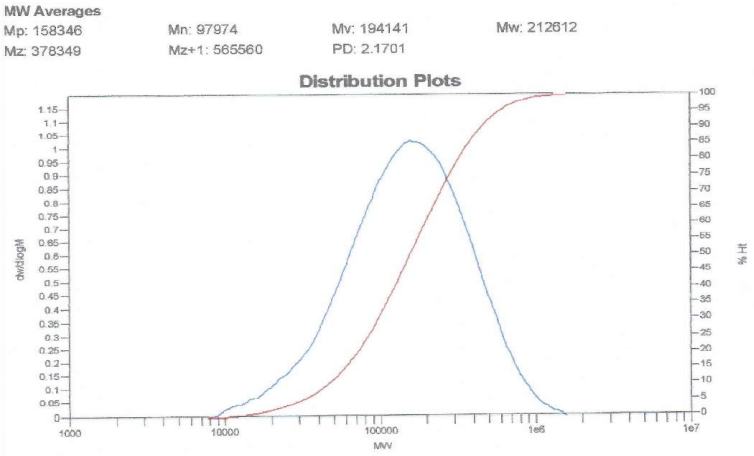
GPC spectrum of polymer in Entry 13, Table 3



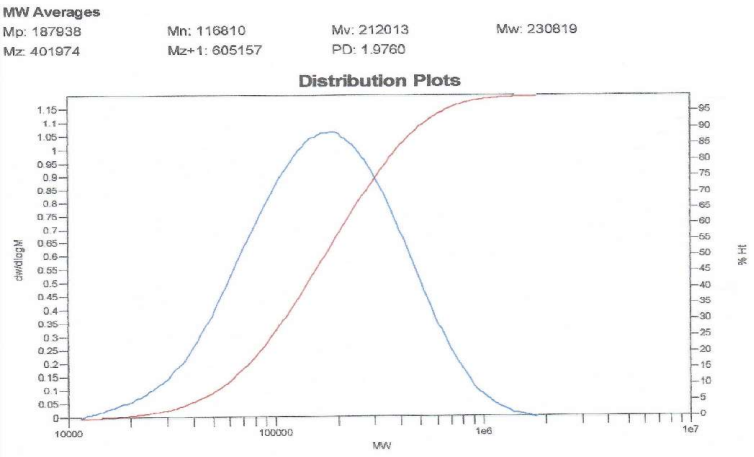
GPC spectrum of polymer in Entry 14, Table 3



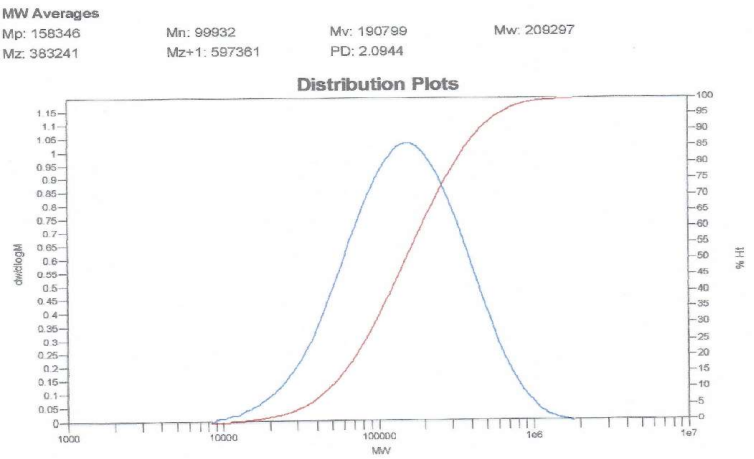
GPC spectrum of polymer in Entry 15, Table 3



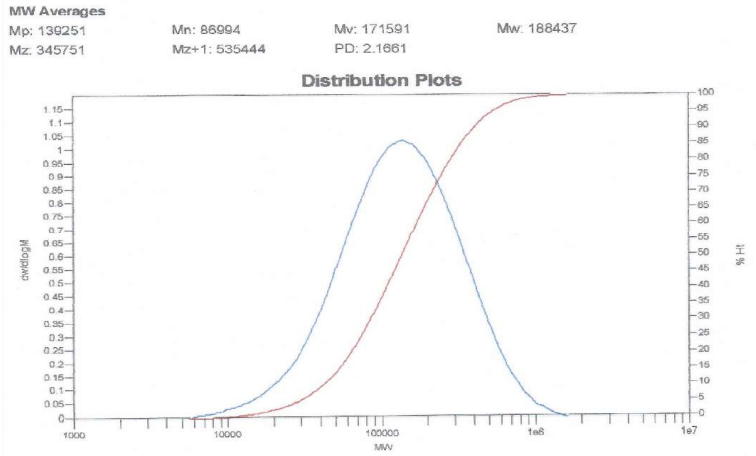
GPC spectrum of polymer in Entry 16, Table 3



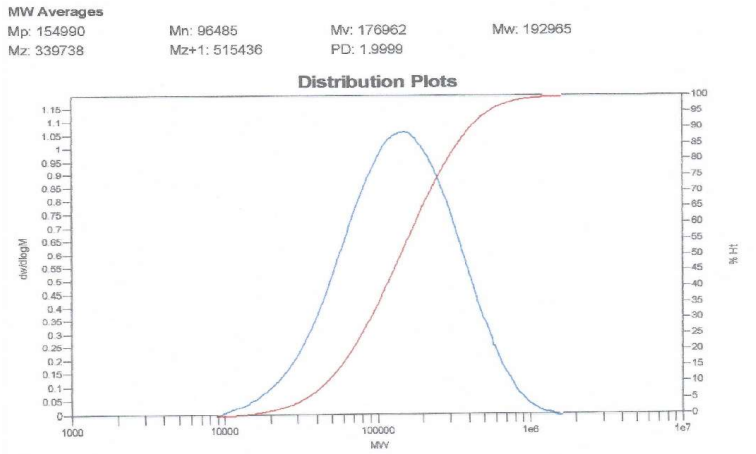
GPC spectrum of polymer in Entry 17, Table 3



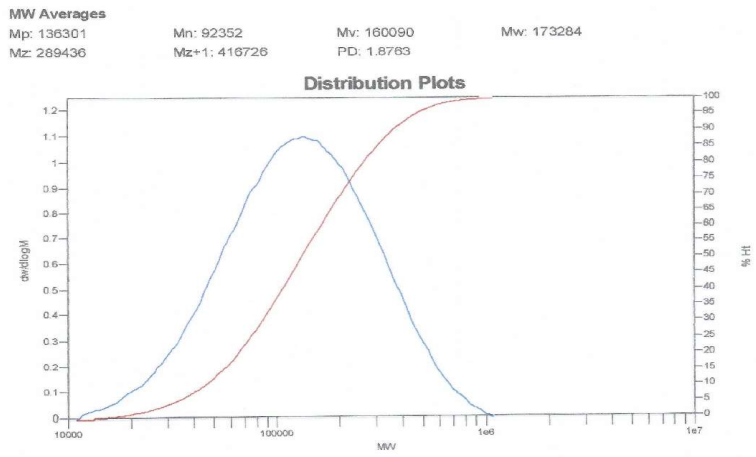
GPC spectrum of polymer in Entry 18, Table 3



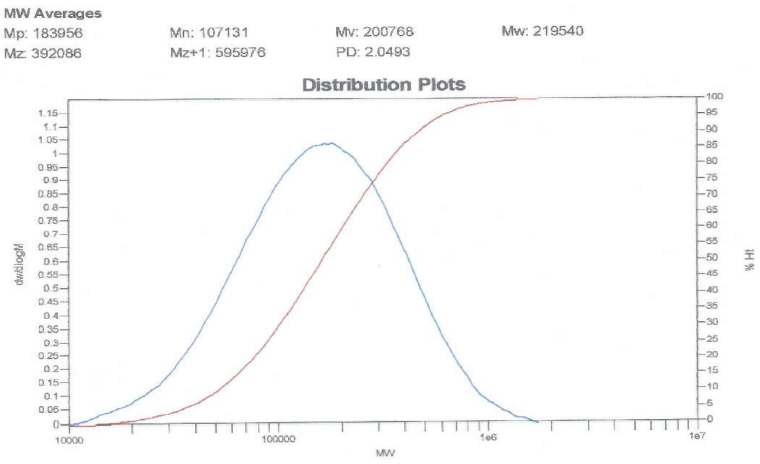
GPC spectrum of polymer in Entry 19, Table 3



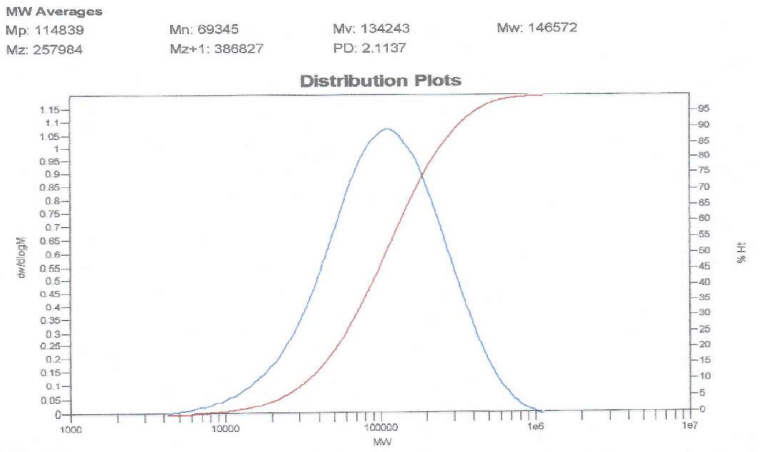
GPC spectrum of polymer in Entry 20, Table 3



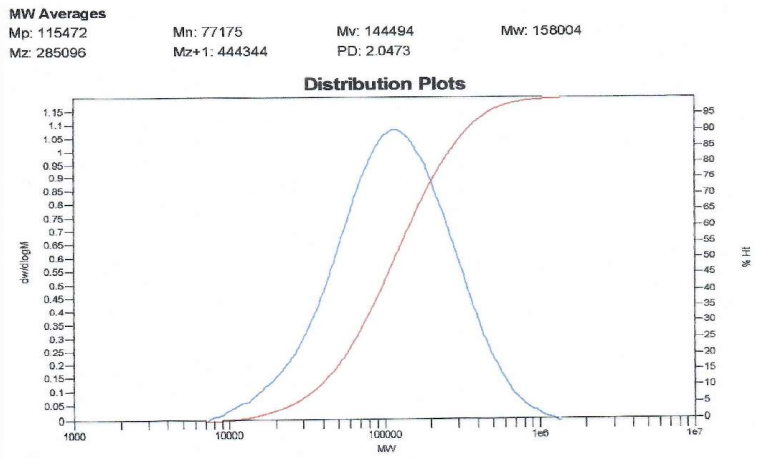
GPC spectrum of polymer in Entry 21, Table 3



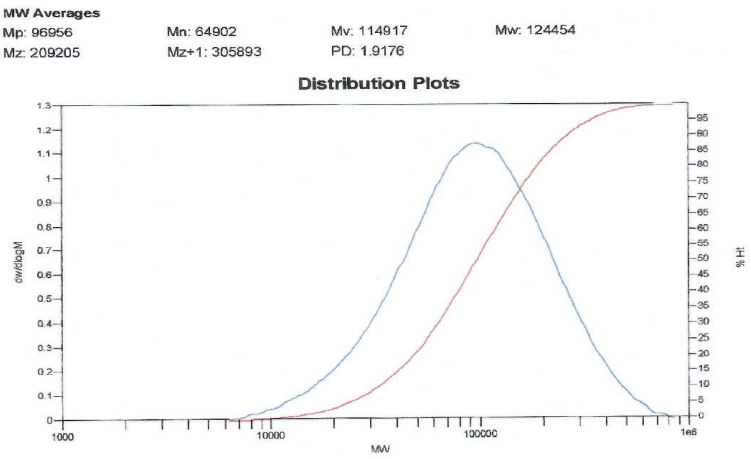
GPC spectrum of polymer in Entry 22, Table 3



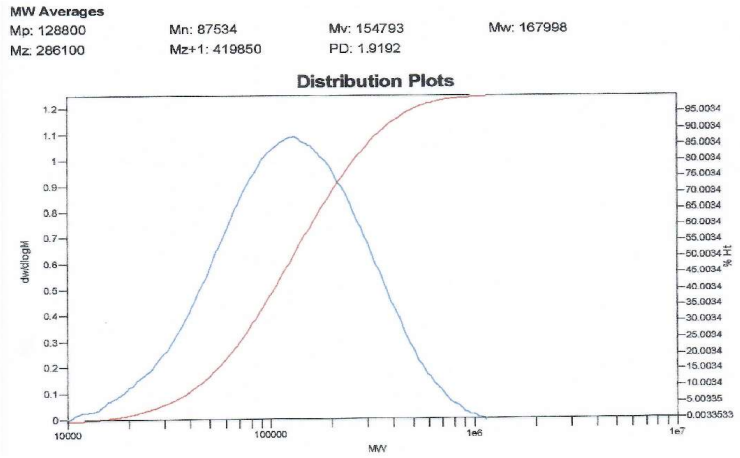
GPC spectrum of polymer in Entry 23, Table 3



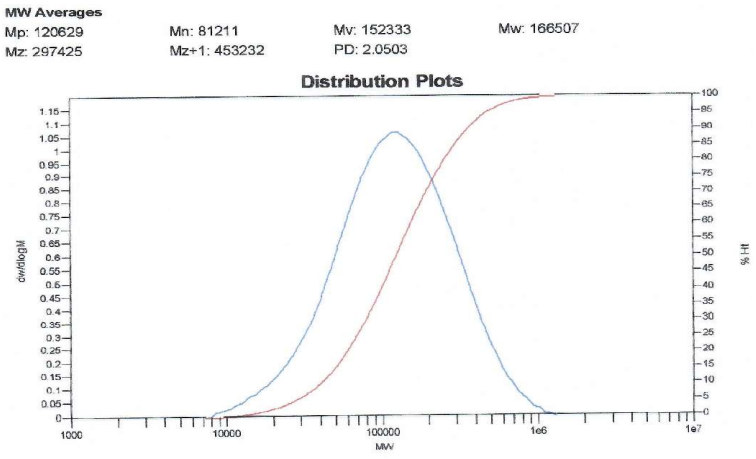
GPC spectrum of polymer in Entry 24, Table 3



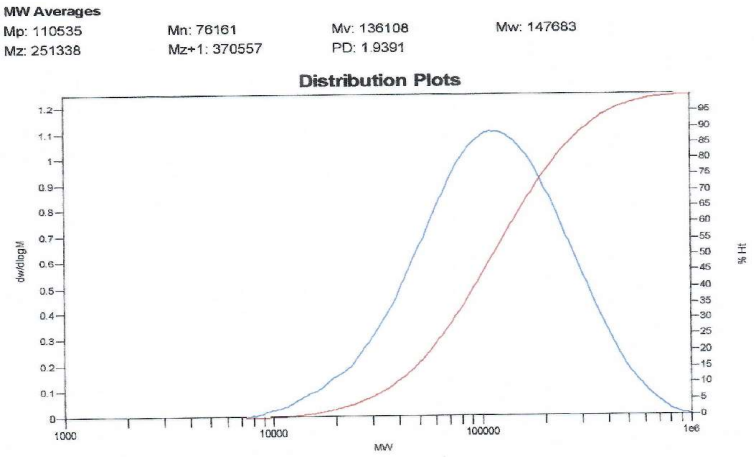
GPC spectrum of polymer in Entry 25, Table 3



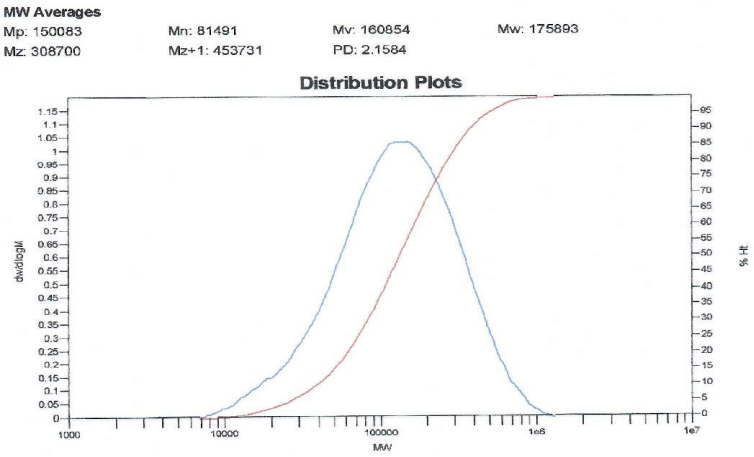
GPC spectrum of polymer in Entry 26, Table 3



GPC spectrum of polymer in Entry 27, Table 3

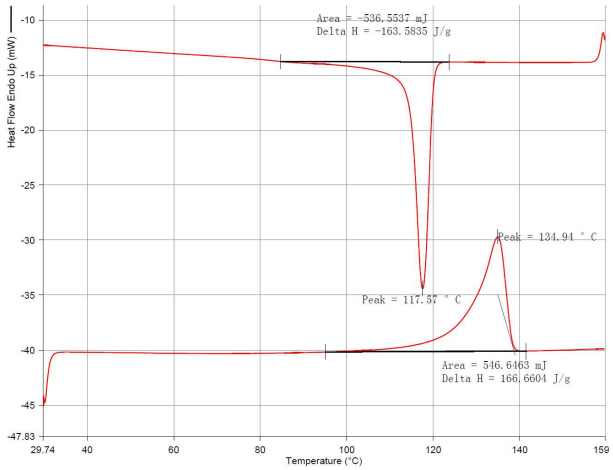


GPC spectrum of polymer in Entry 28, Table 3

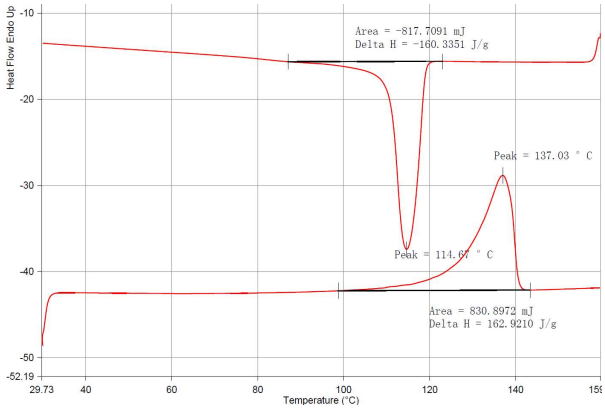


GPC spectrum of polymer in Entry 29, Table 3

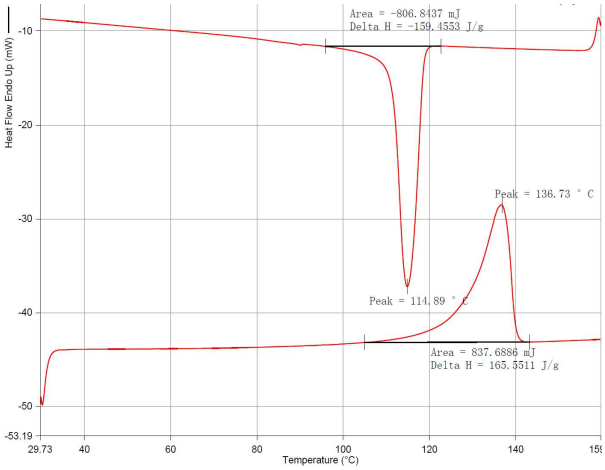
DSC spectra of polymers



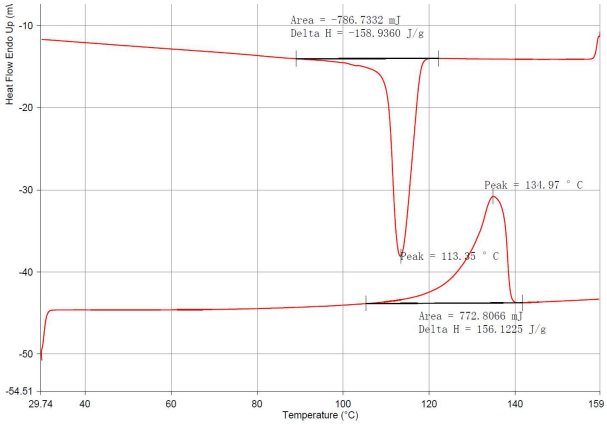
DSC spectrum of PE in Entry 1, Table 1



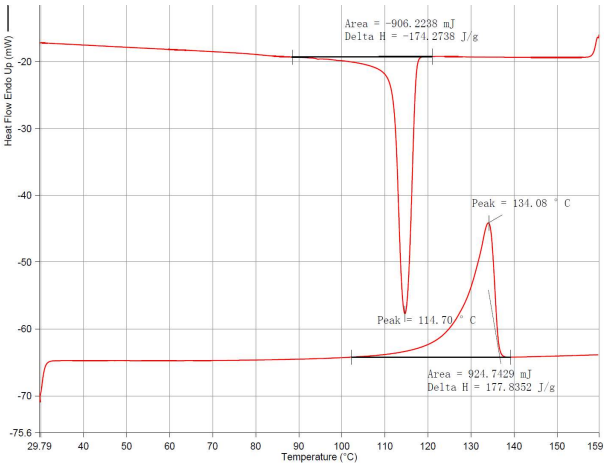
DSC spectrum of PE in Entry 2, Table 1



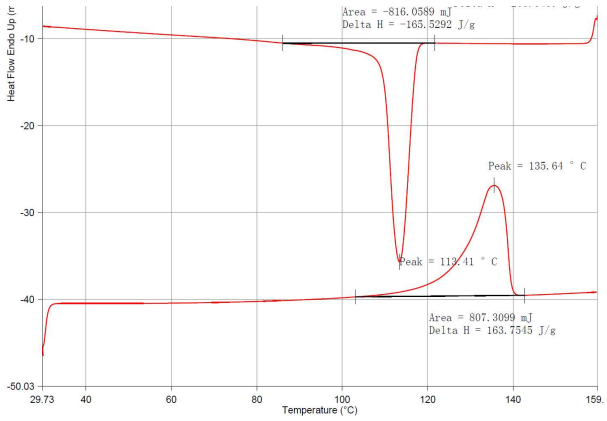
DSC spectrum of PE in Entry 3, Table 1



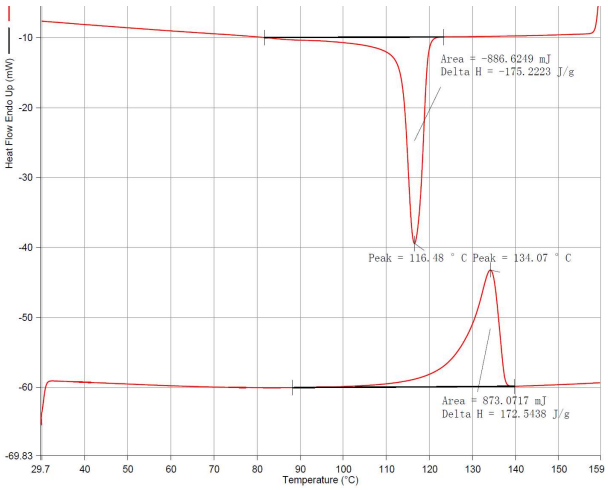
GPC spectrum of PE in Entry4, Table 1



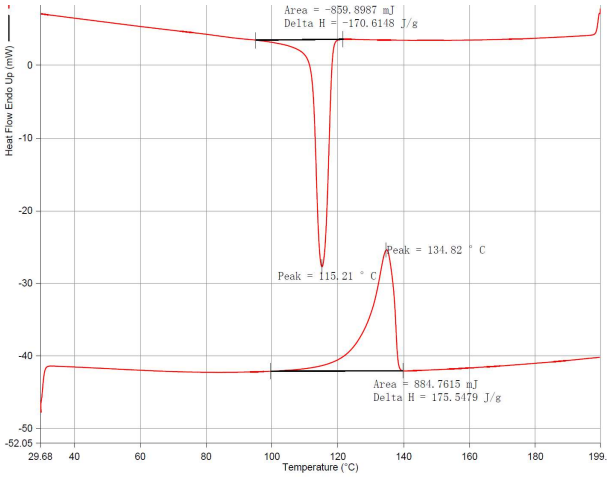
DSC spectrum of PE in Entry 5, Table 1



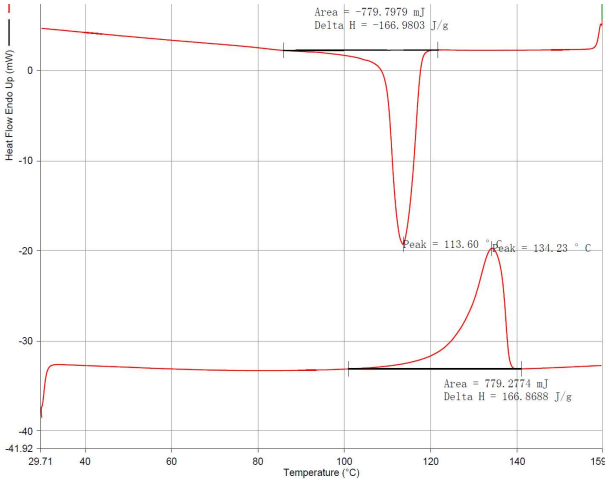
DSC spectrum of PE in Entry 6, Table 1



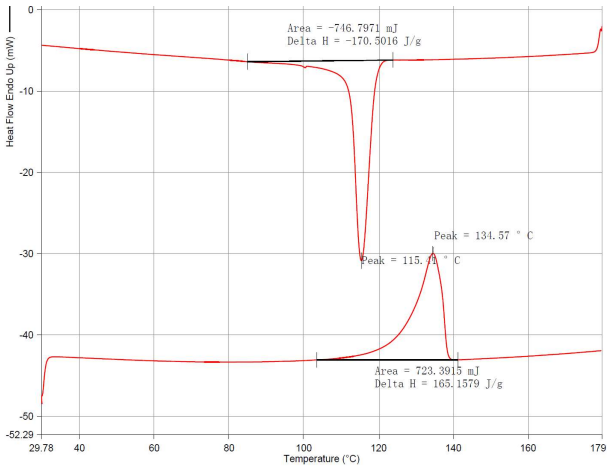
DSC spectrum of PE in Entry 7, Table 1



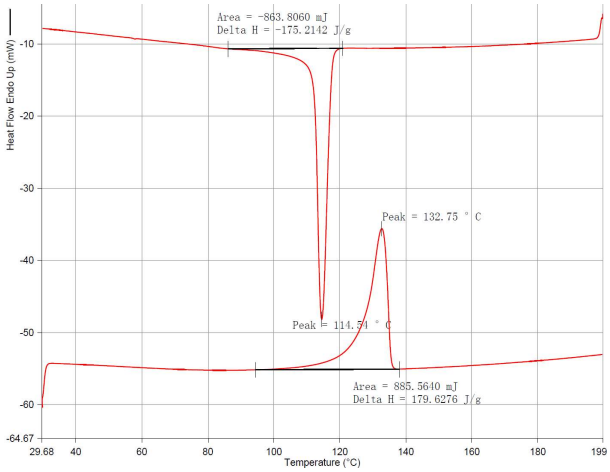
DSC spectrum of PE in Entry 8, Table 1



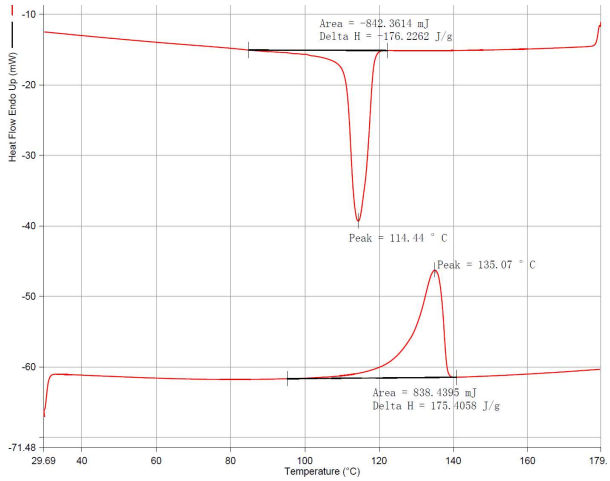
DSC spectrum of PE in Entry 9, Table 1



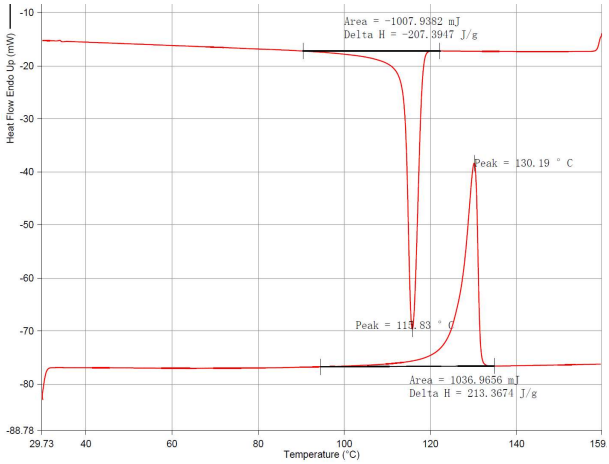
DSC spectrum of PE in Entry 10, Table 1



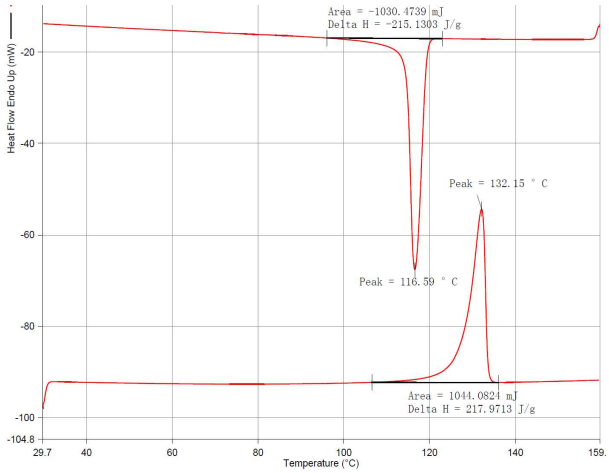
DSC spectrum of PE in Entry 11, Table 1



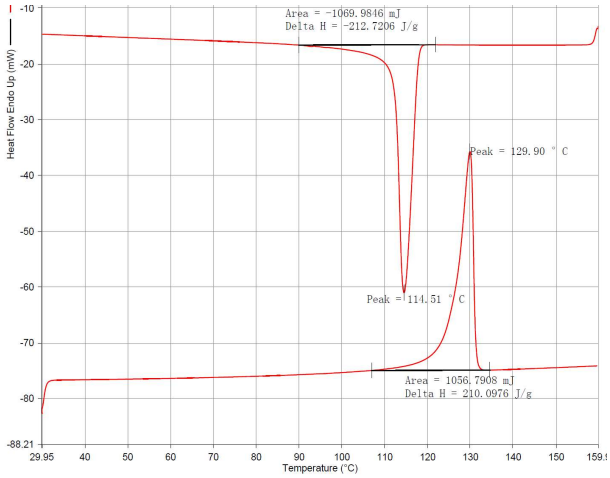
DSC spectrum of PE in Entry 12, Table 1



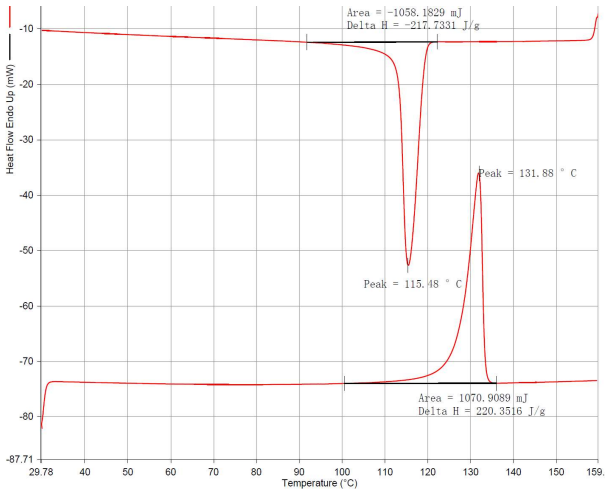
DSC spectrum of PE in Entry 13, Table 1



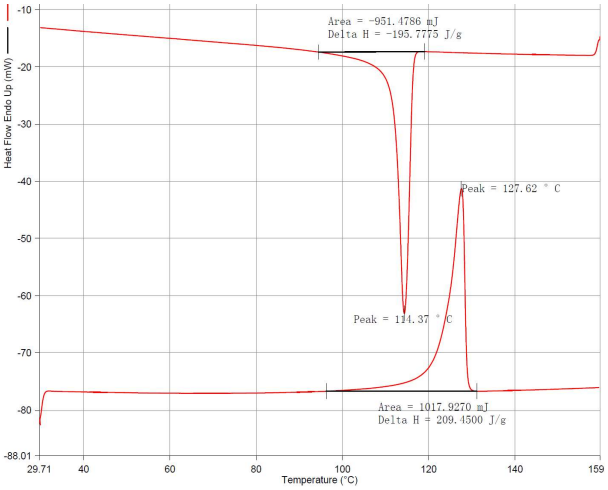
DSC spectrum of PE in Entry 14, Table 1



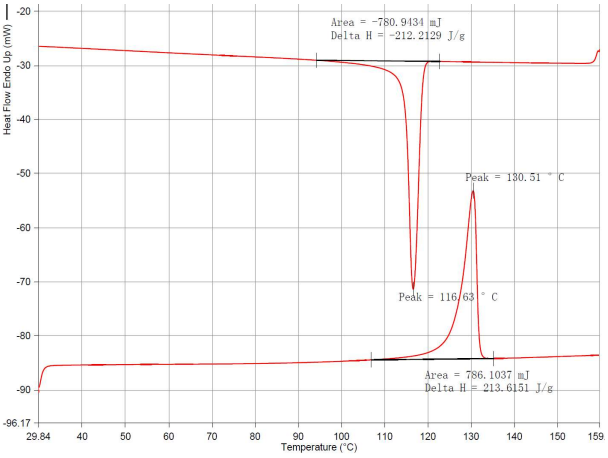
DSC spectrum of PE in Entry 15, Table 1



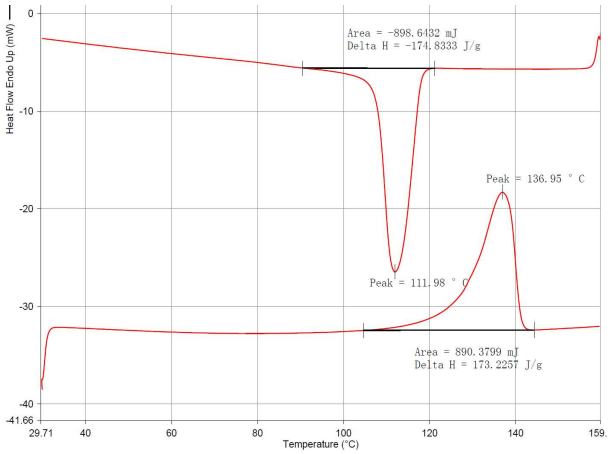
DSC spectrum of PE in Entry 16, Table 1



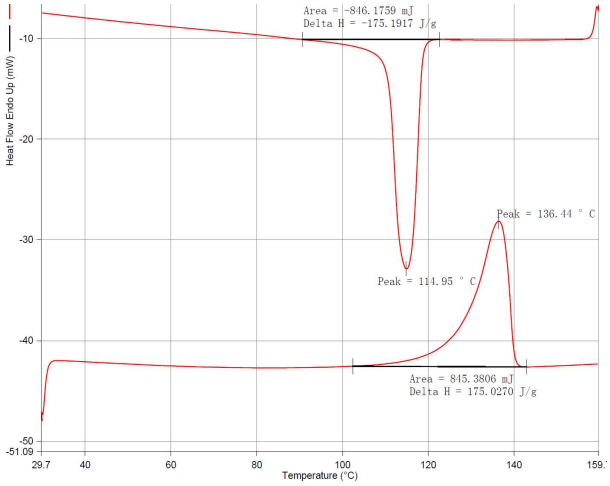
DSC spectrum of PE in Entry 17, Table 1



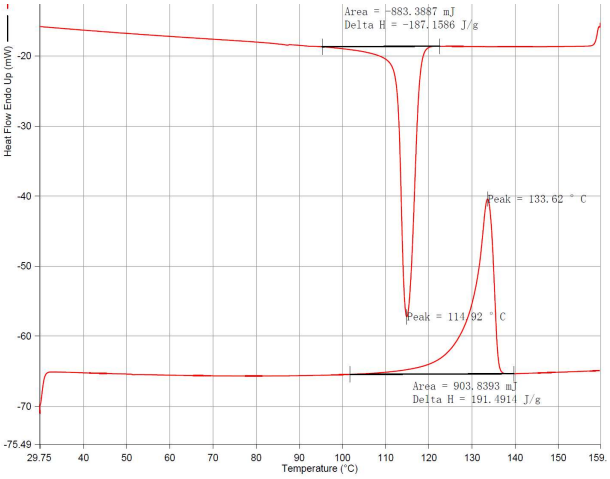
DSC spectrum of PE in Entry 18, Table 1



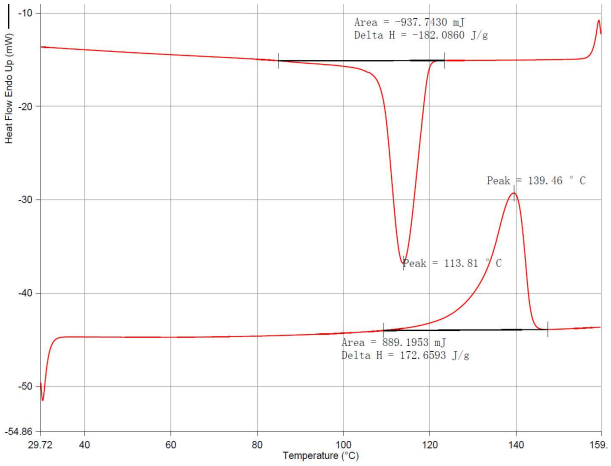
DSC spectrum of PE in Entry 19, Table 1



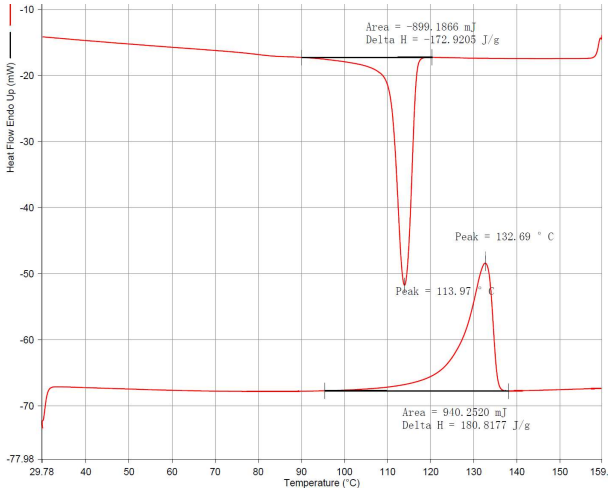
DSC spectrum of PE in Entry 20, Table 1



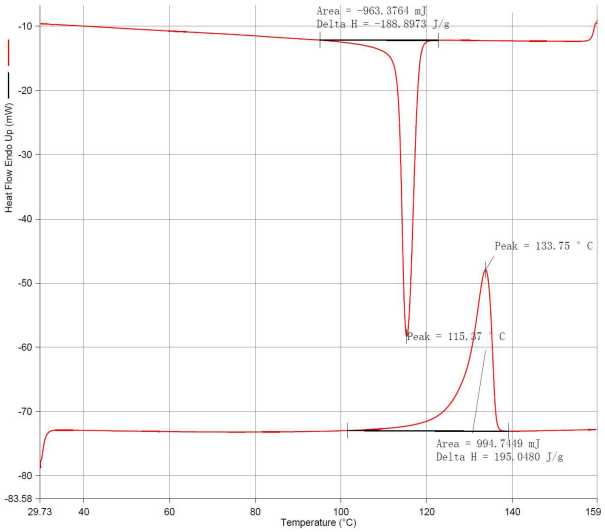
DSC spectrum of PE in Entry 21, Table 1



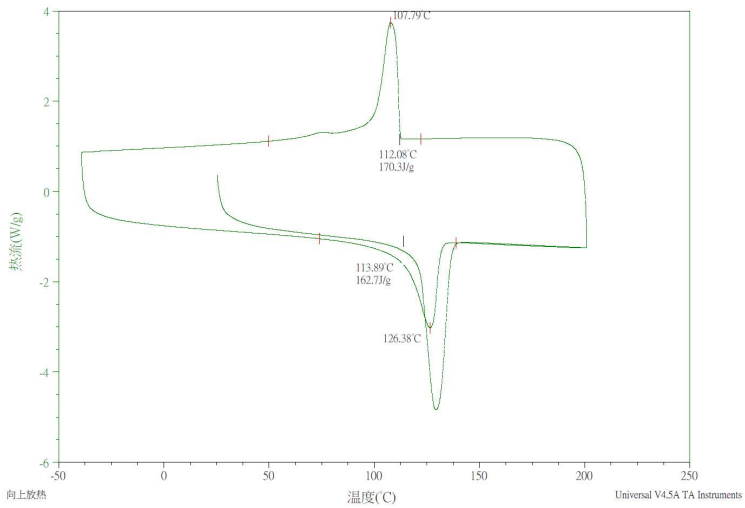
DSC spectrum of PE in Entry 22, Table 1



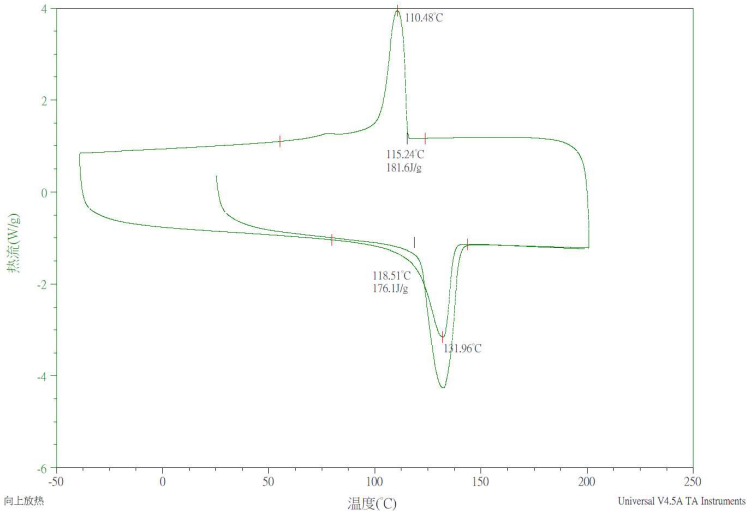
DSC spectrum of PE in Entry 23, Table 1



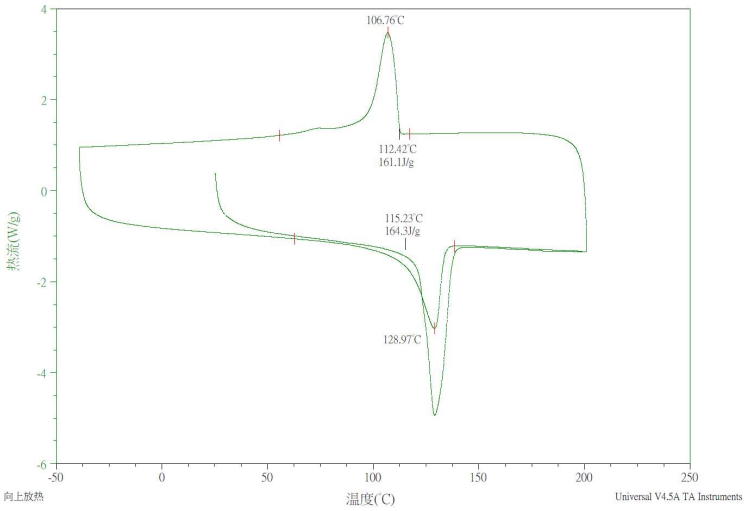
DSC spectrum of PE in Entry 24, Table 1



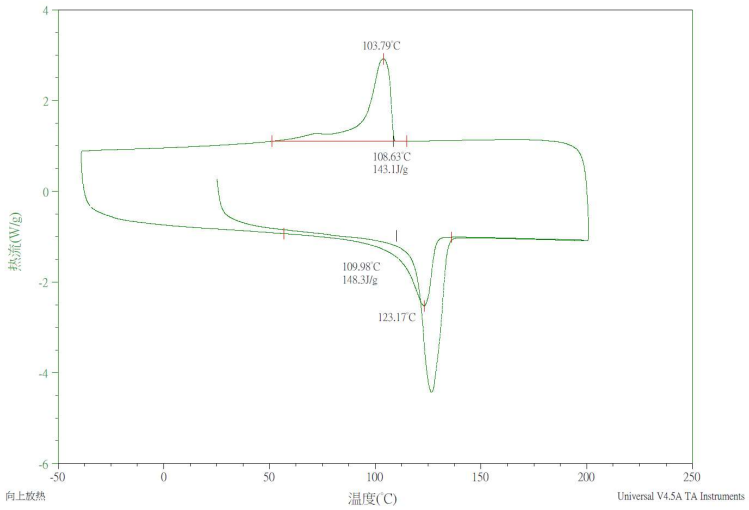
DSC spectrum of polymer in Entry 1, Table 2



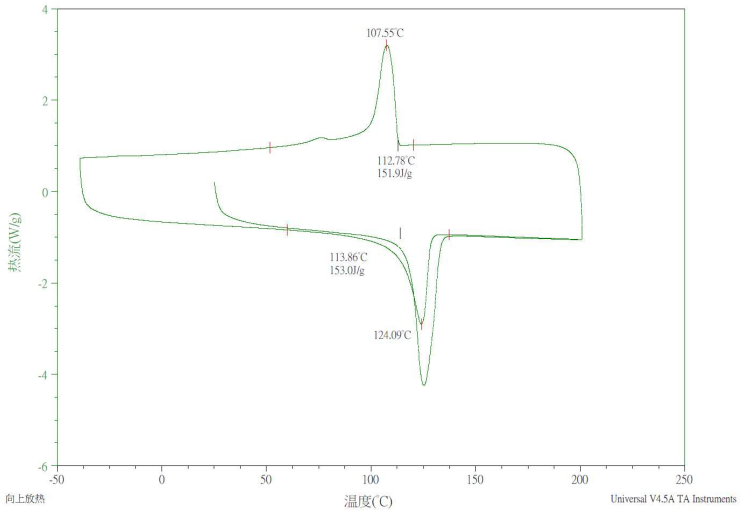
DSC spectrum of polymer in Entry 2, Table 2



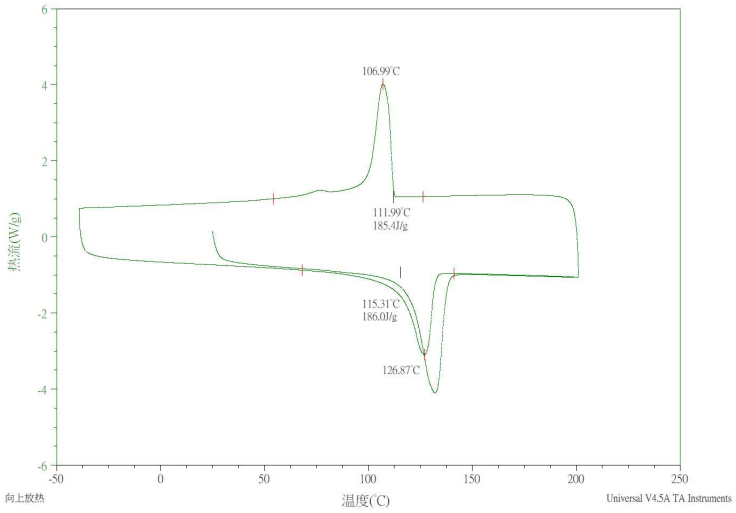
DSC spectrum of polymer in Entry 3, Table 2



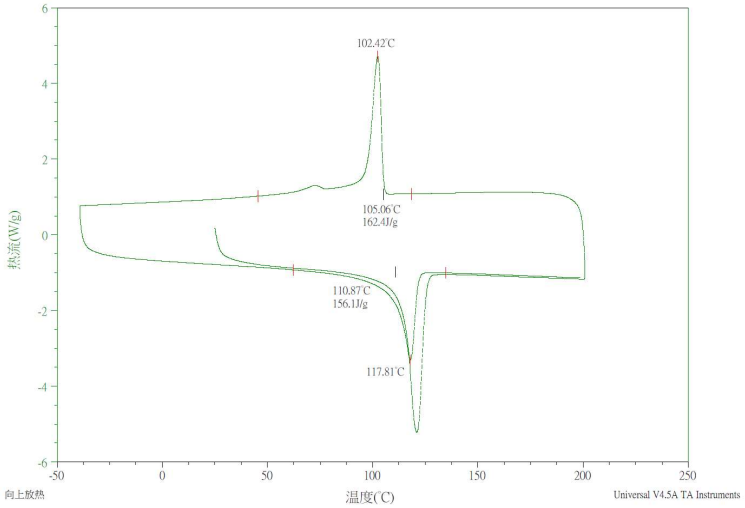
DSC spectrum of polymer in Entry 4, Table 2



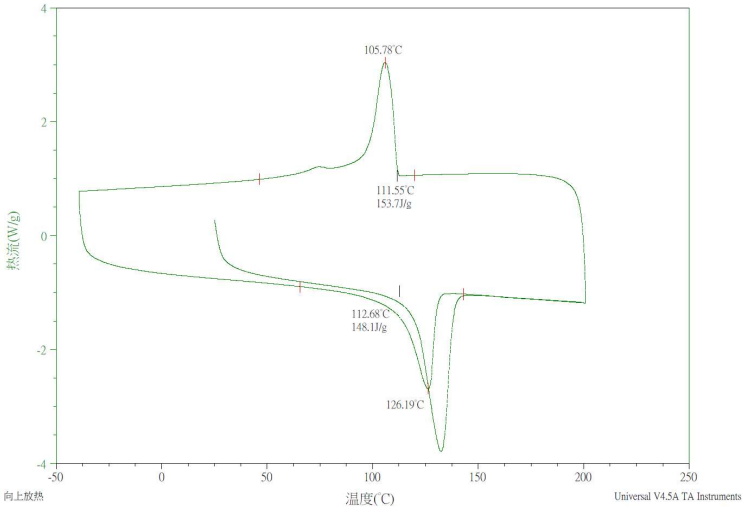
DSC spectrum of polymer in Entry 5, Table 2



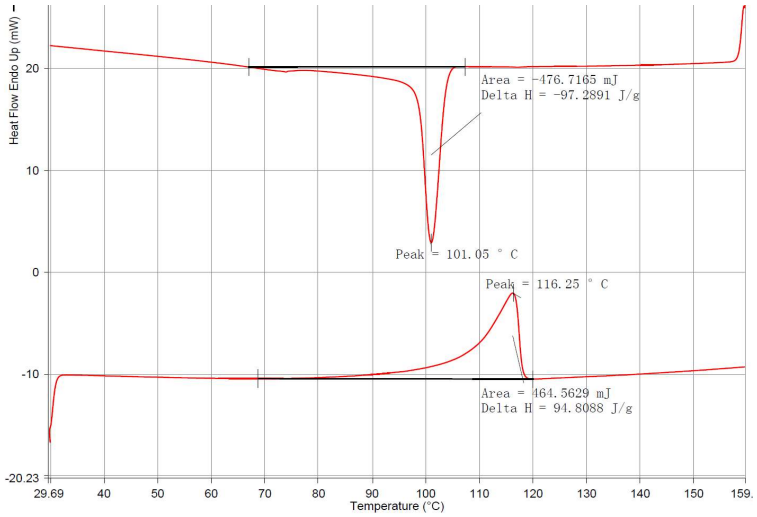
DSC spectrum of polymer in Entry 6, Table 2



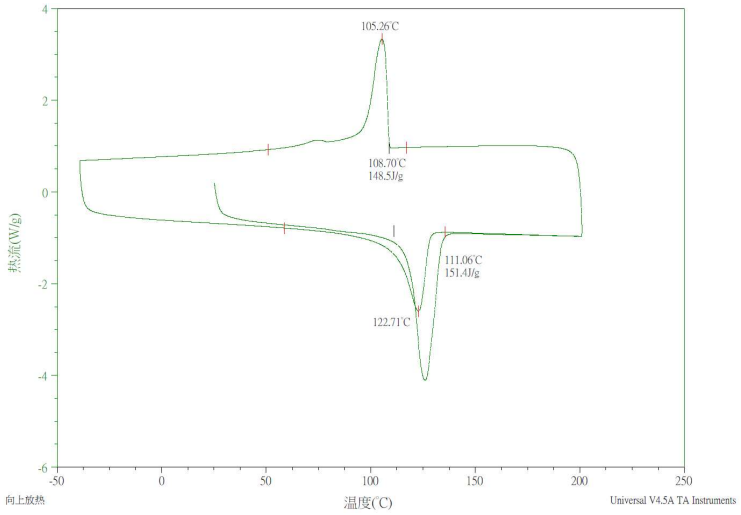
DSC spectrum of polymer in Entry 7, Table 2



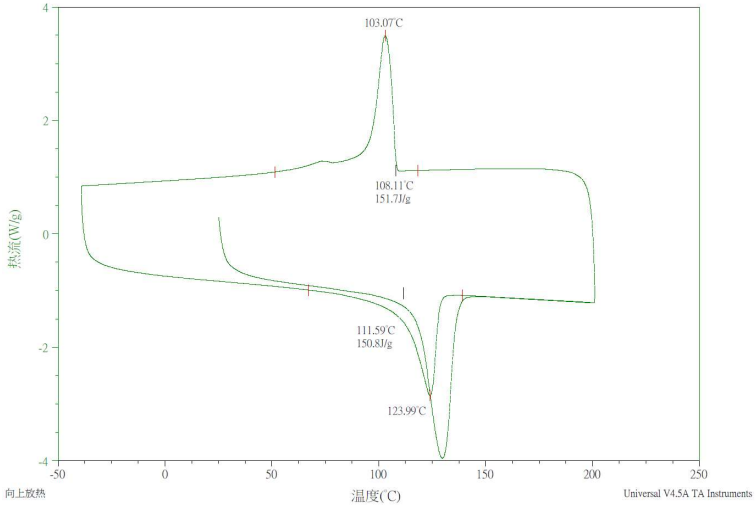
DSC spectrum of polymer in Entry 8, Table 2



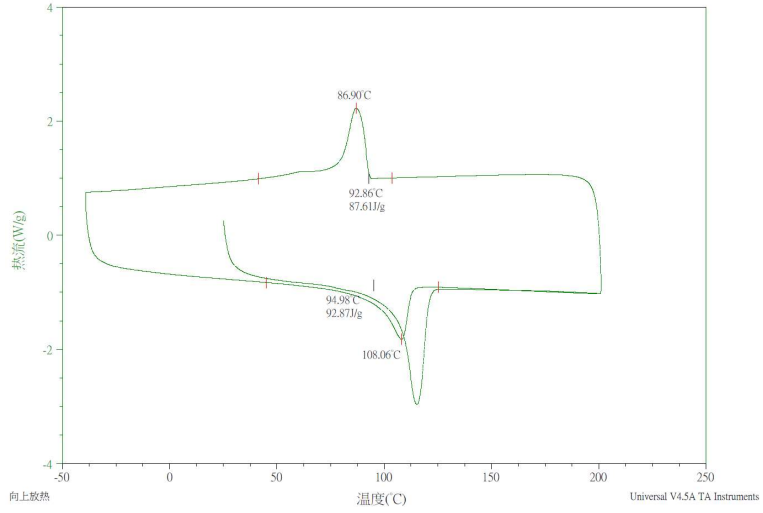
DSC spectrum of polymer in Entry 10, Table 2



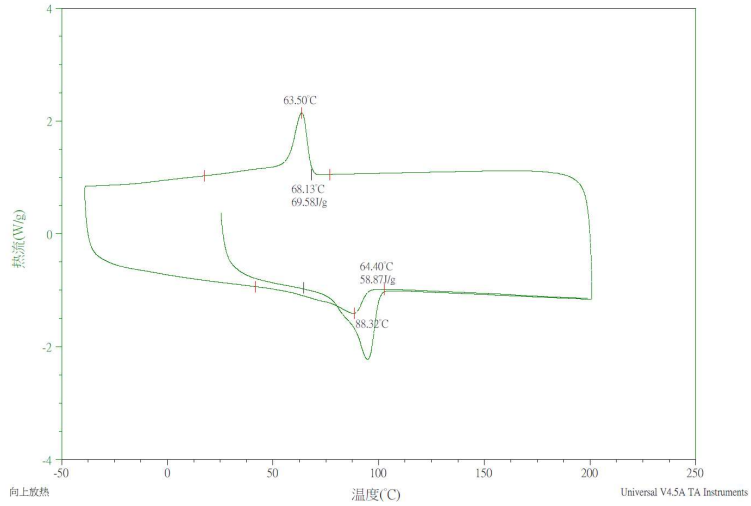
DSC spectrum of polymer in Entry 11, Table 2



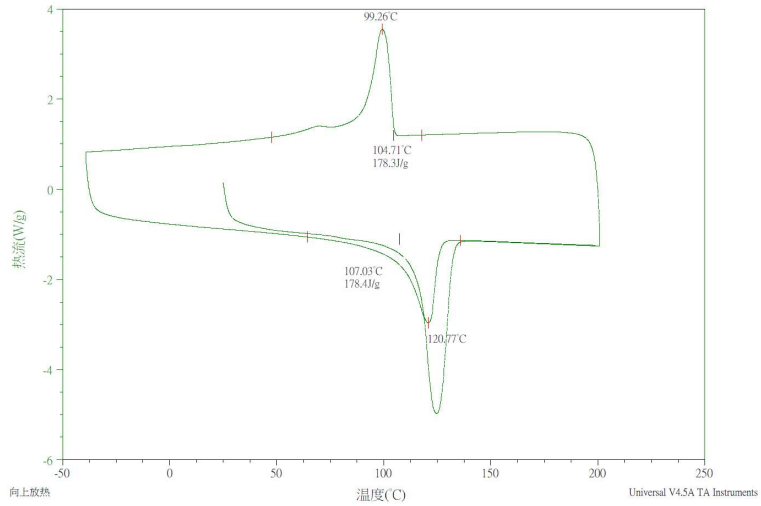
DSC spectrum of polymer in Entry 12, Table 2



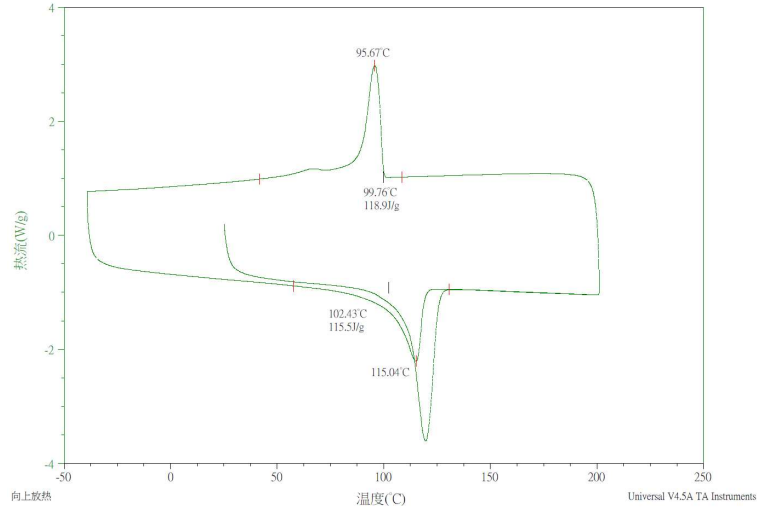
DSC spectrum of polymer in Entry 13, Table 2



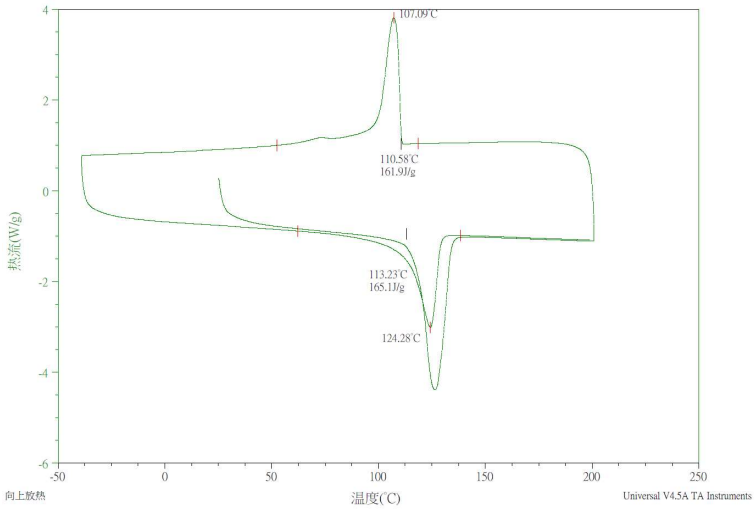
DSC spectrum of polymer in Entry 14, Table 2



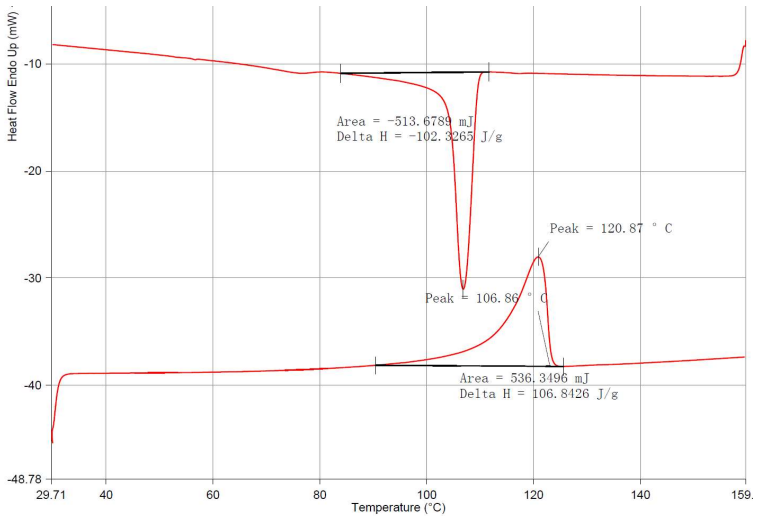
DSC spectrum of polymer in Entry 15, Table 2



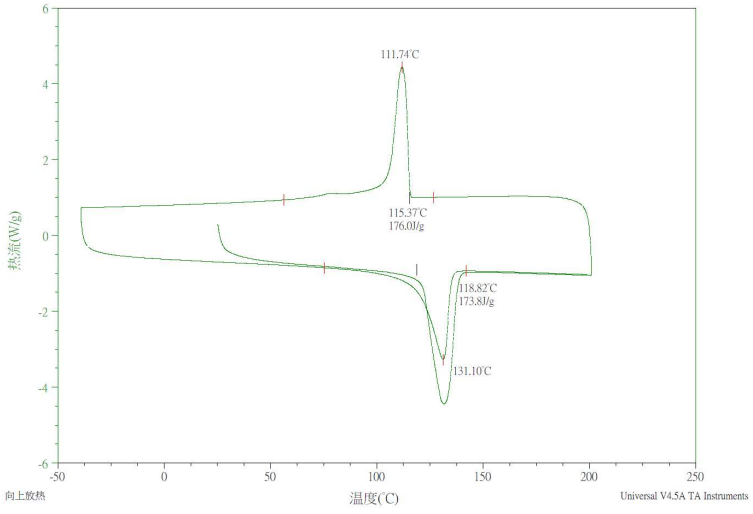
DSC spectrum of polymer in Entry 16, Table 2



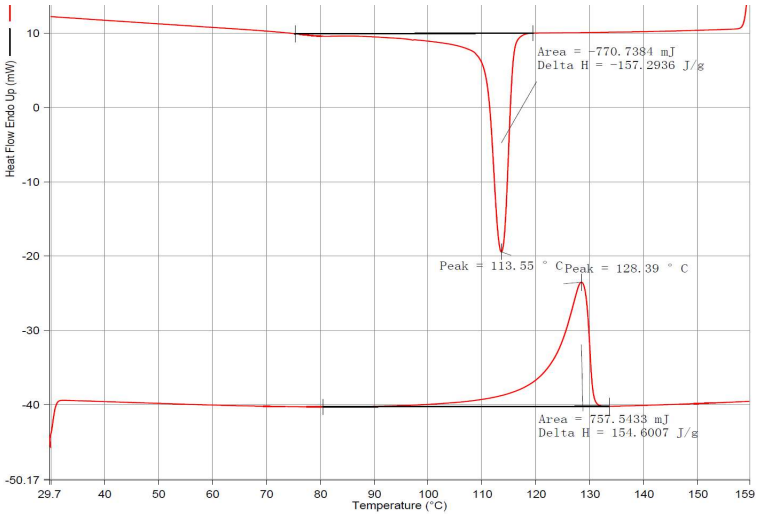
DSC spectrum of polymer in Entry 17, Table 2



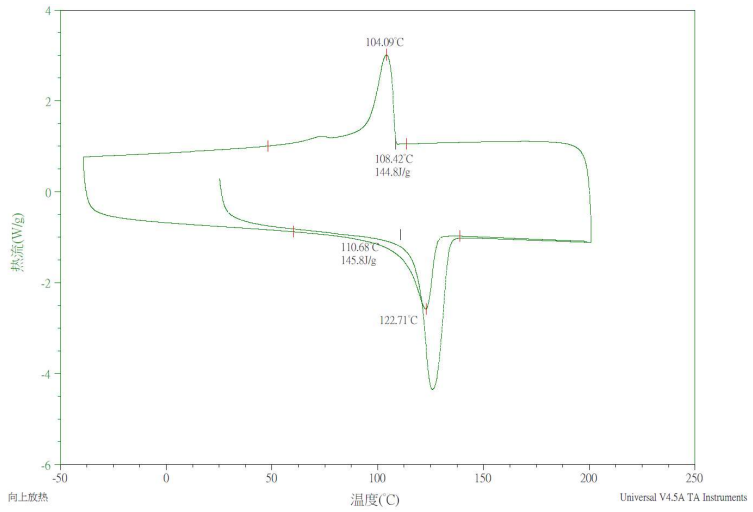
DSC spectrum of polymer in Entry 18, Table 2



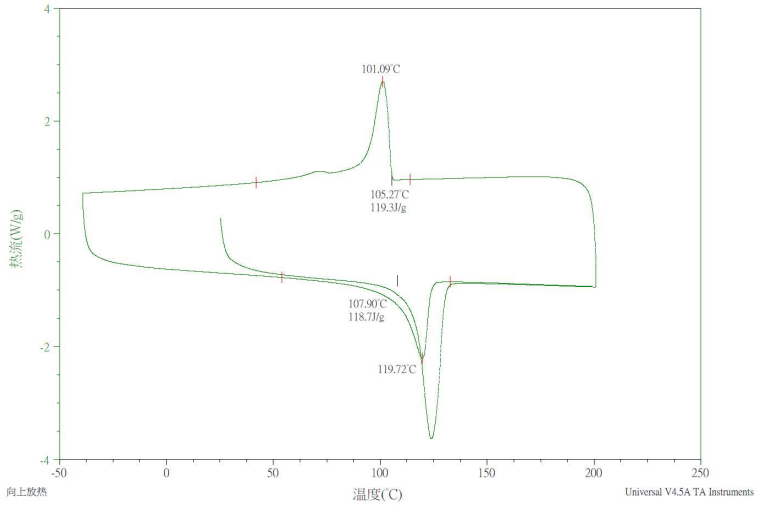
DSC spectrum of polymer in Entry 19, Table 2



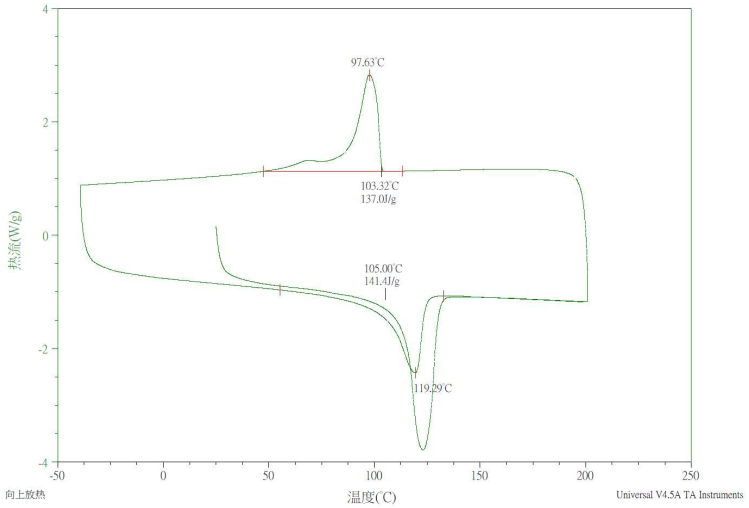
DSC spectrum of polymer in Entry 20, Table 2



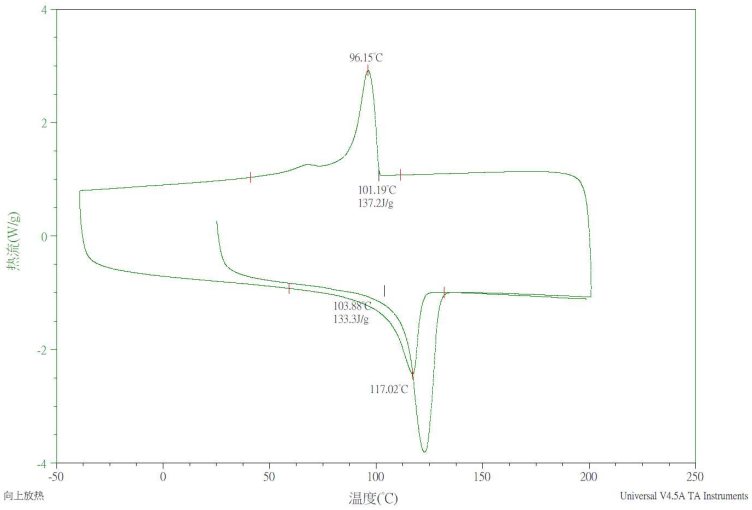
DSC spectrum of polymer in Entry 1, Table 3



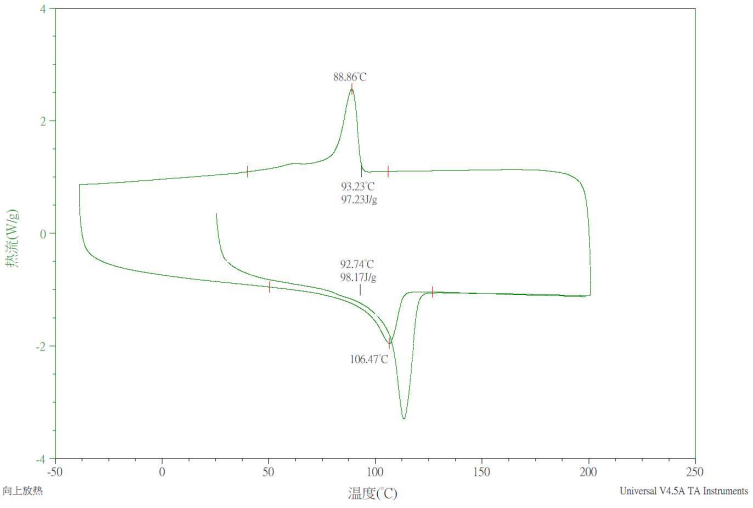
DSC spectrum of polymer in Entry 2, Table 3



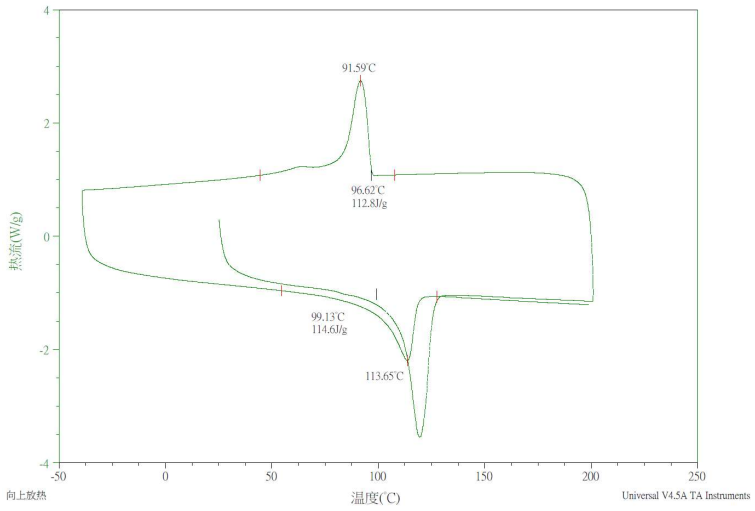
DSC spectrum of polymer in Entry 3, Table 3



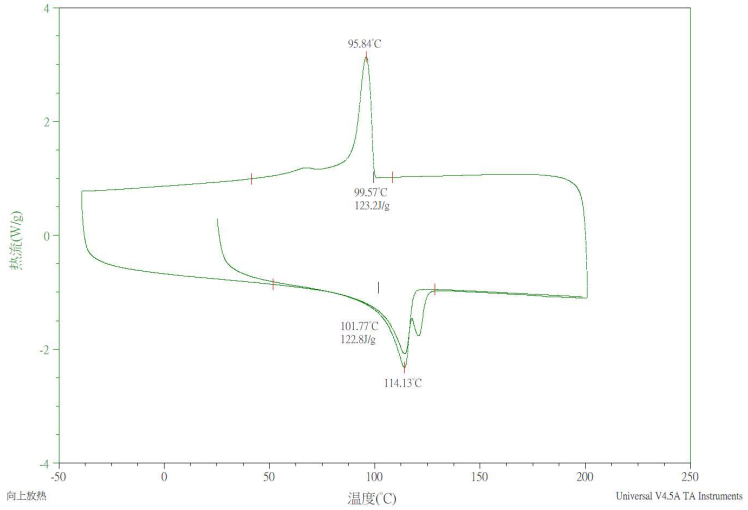
DSC spectrum of polymer in Entry 4, Table 3



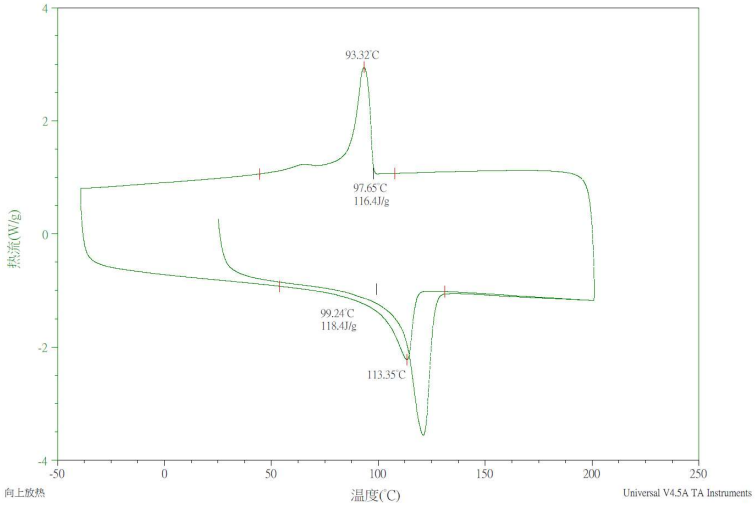
DSC spectrum of polymer in Entry 5, Table 3



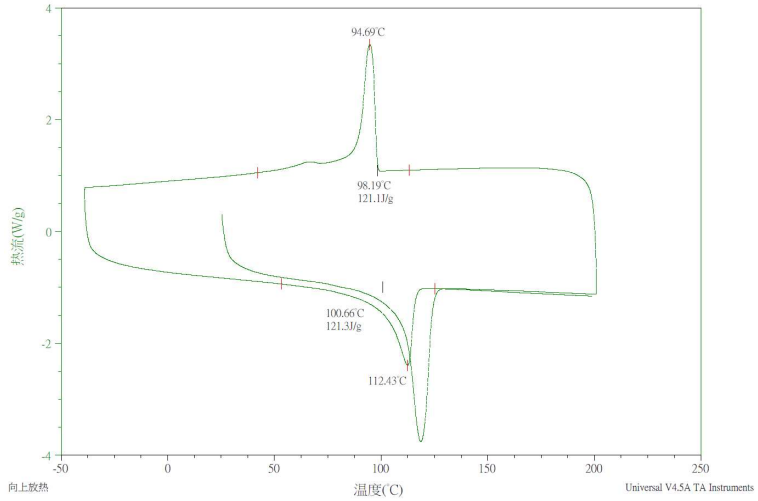
DSC spectrum of polymer in Entry 6, Table 3



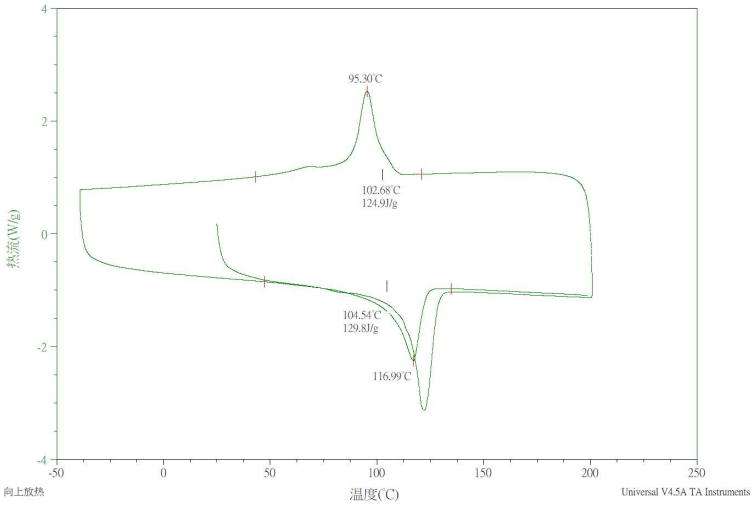
DSC spectrum of polymer in Entry 7, Table 3



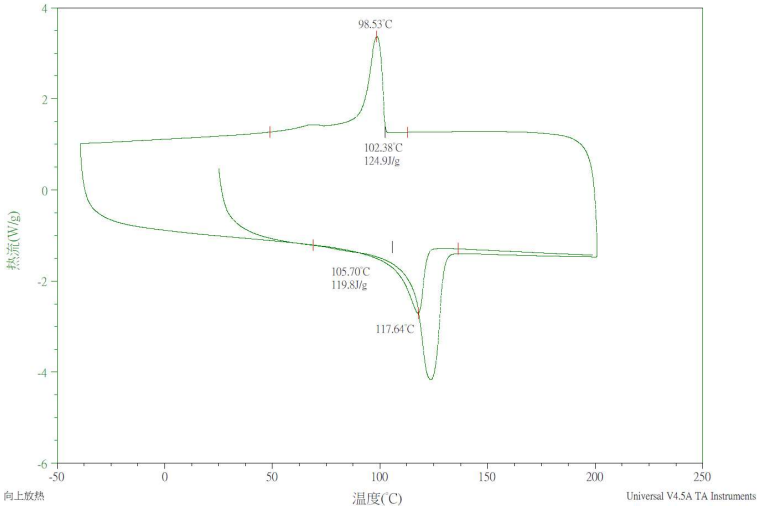
DSC spectrum of polymer in Entry 8, Table 3



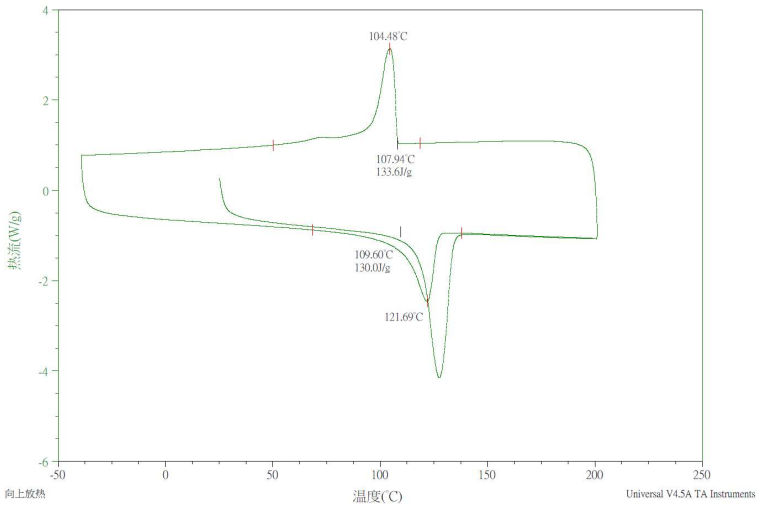
DSC spectrum of polymer in Entry 9, Table 3



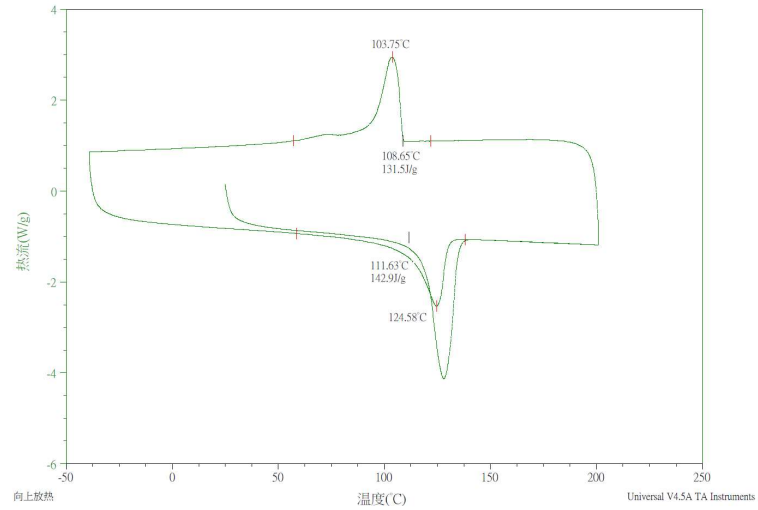
DSC spectrum of polymer in Entry 10, Table 3



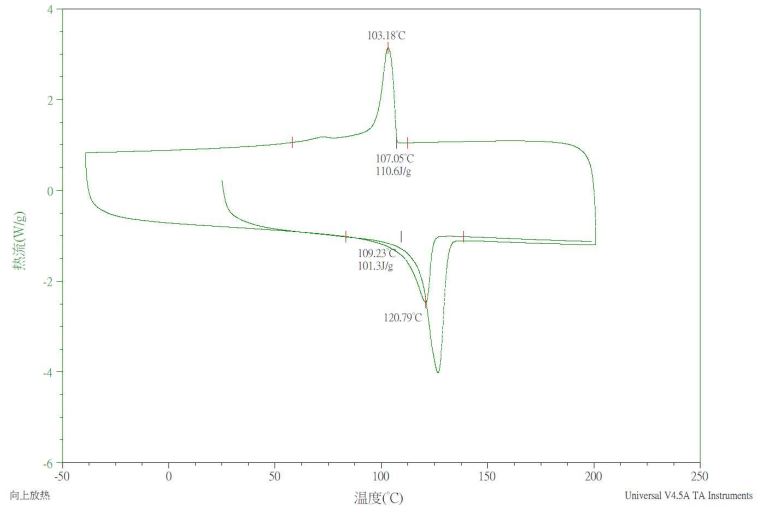
DSC spectrum of polymer in Entry 11, Table 3



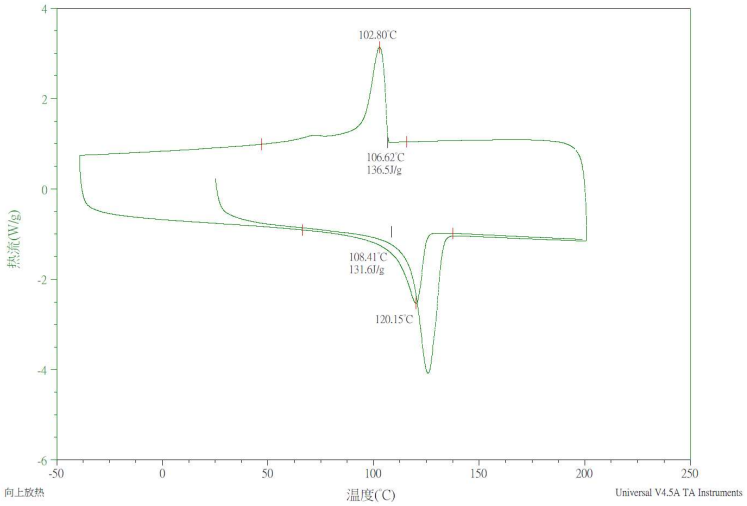
DSC spectrum of polymer in Entry 12, Table 3



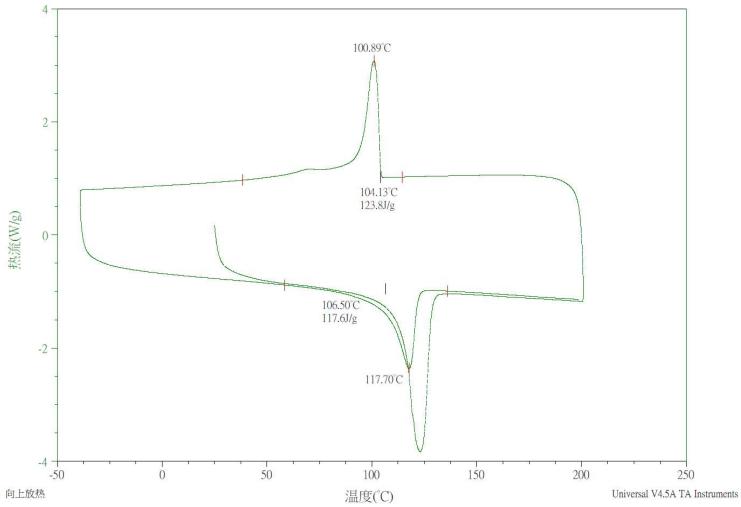
DSC spectrum of polymer in Entry 13, Table 3



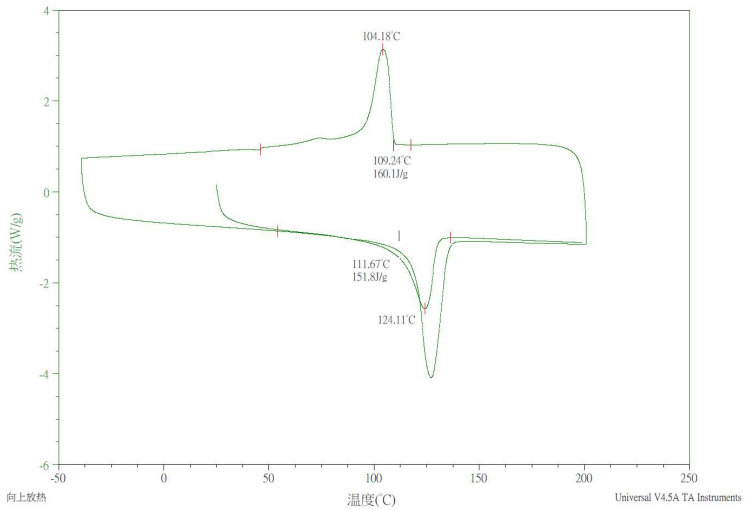
DSC spectrum of polymer in Entry 14, Table 3



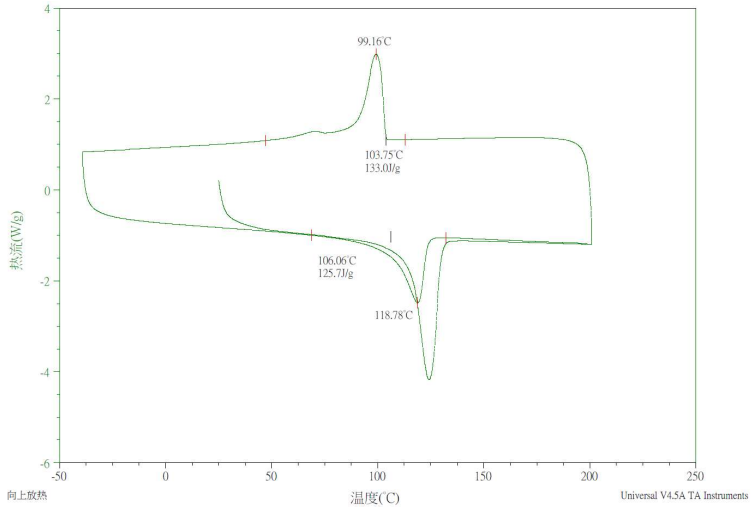
DSC spectrum of polymer in Entry 15, Table 3



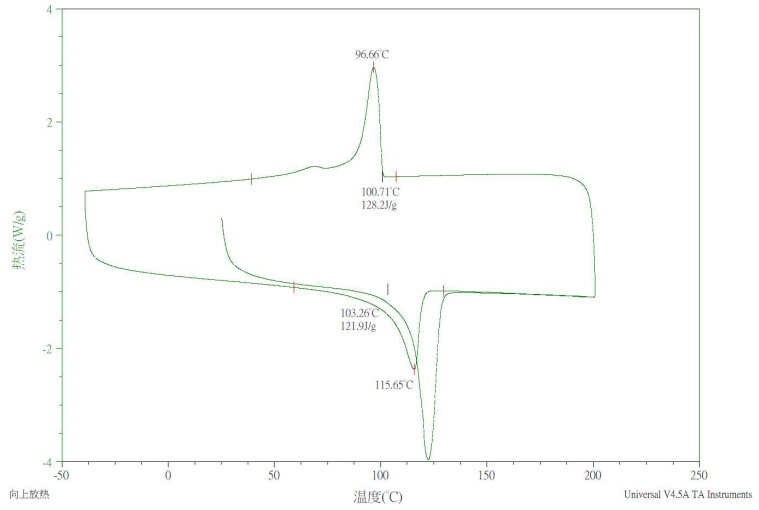
DSC spectrum of polymer in Entry 16, Table 3



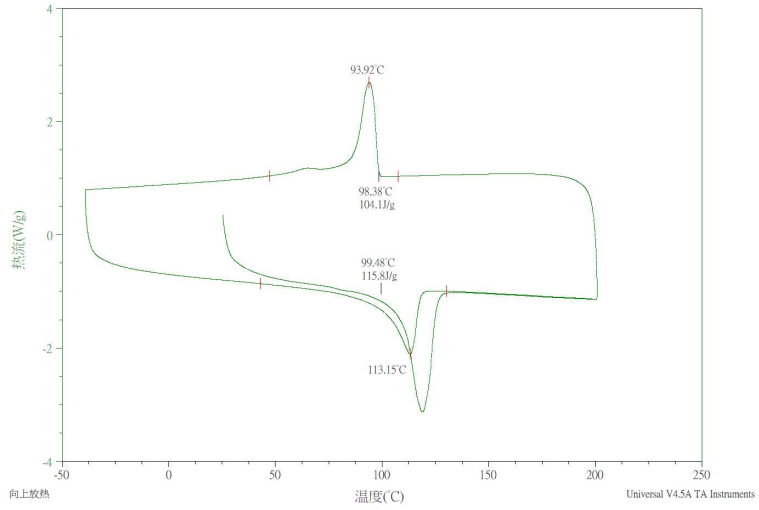
DSC spectrum of polymer in Entry 17, Table 3



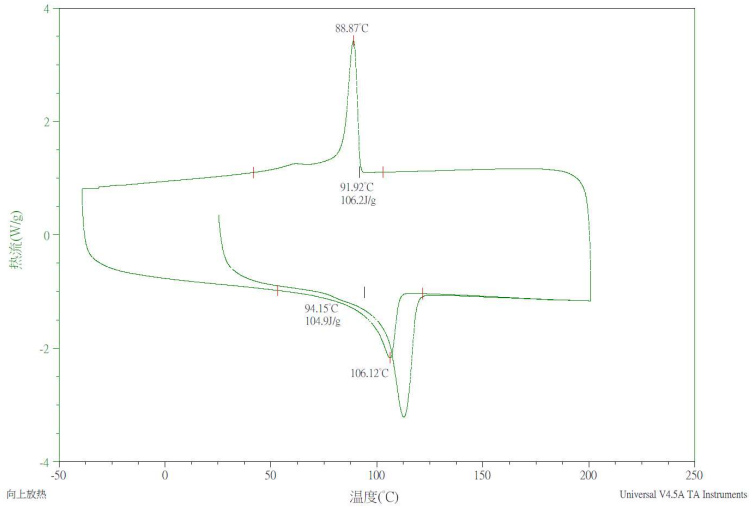
DSC spectrum of polymer in Entry 18, Table 3



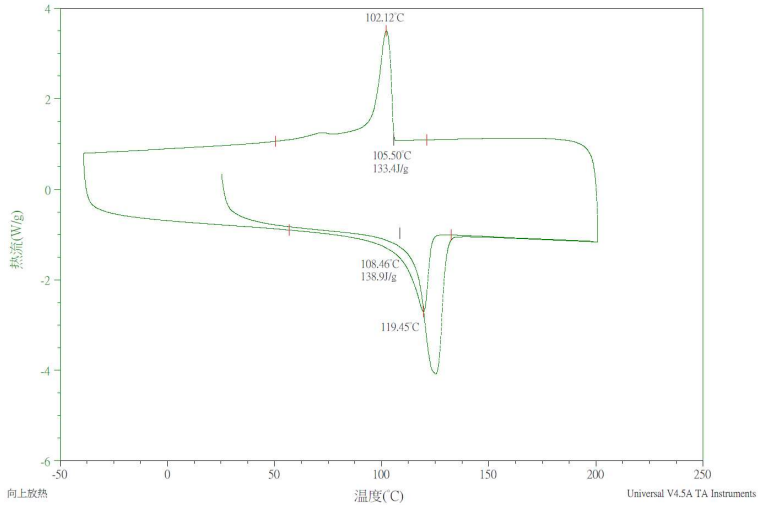
DSC spectrum of polymer in Entry 19, Table 3



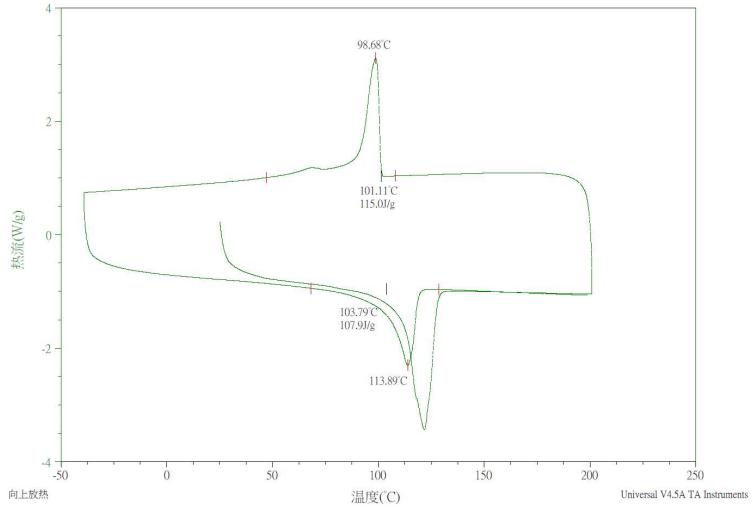
DSC spectrum of polymer in Entry 20, Table 3



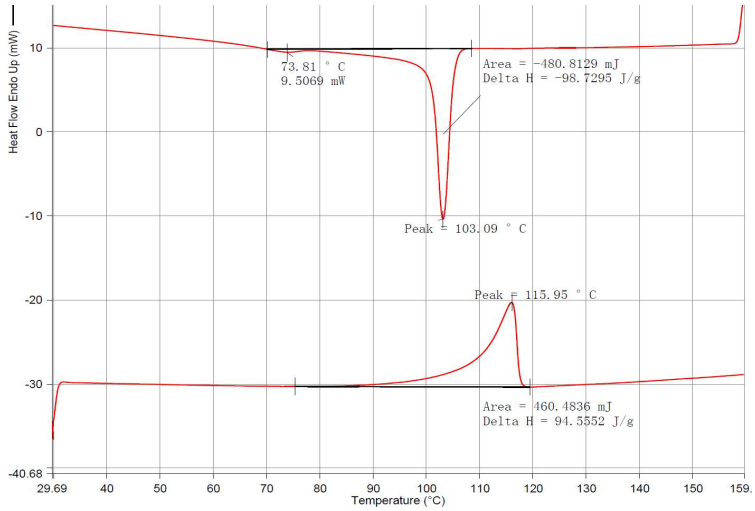
DSC spectrum of polymer in Entry 21, Table 3



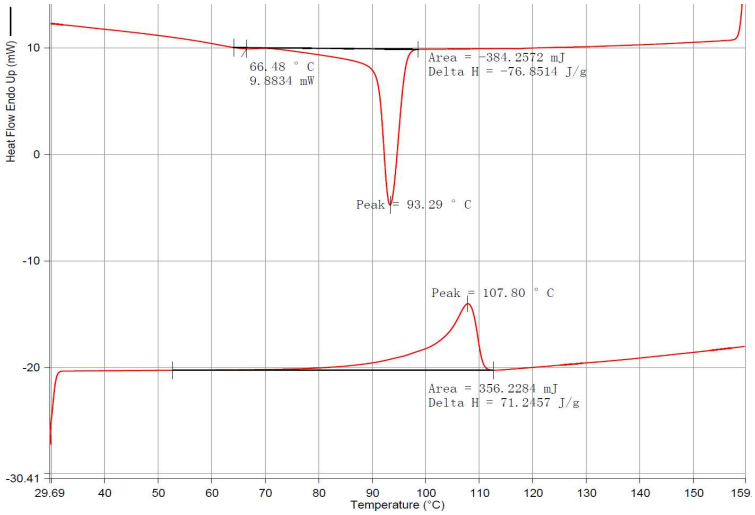
DSC spectrum of polymer in Entry 22, Table 3



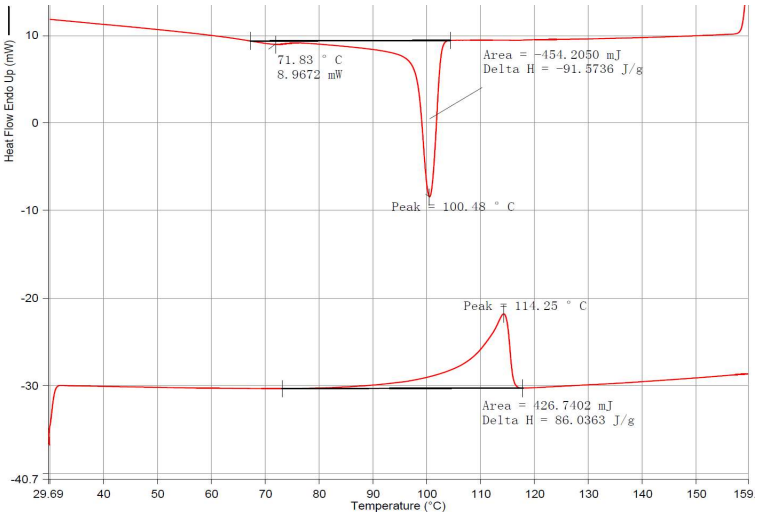
DSC spectrum of polymer in Entry 23, Table 3



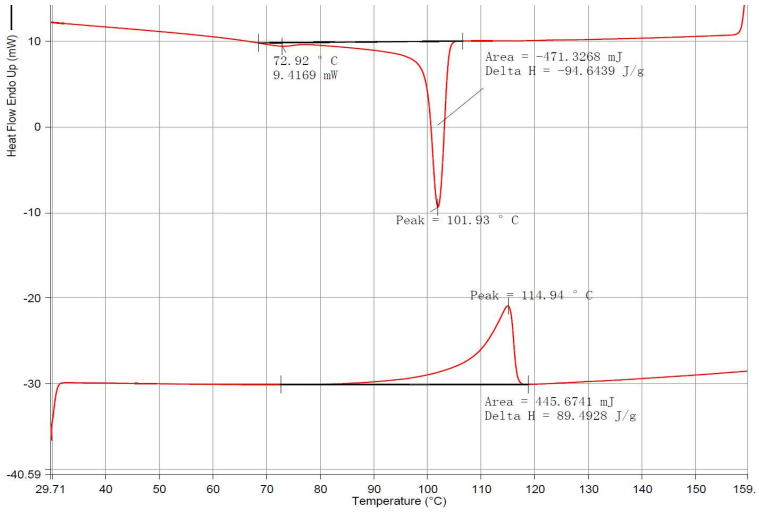
DSC spectrum of polymer in Entry 24, Table 3



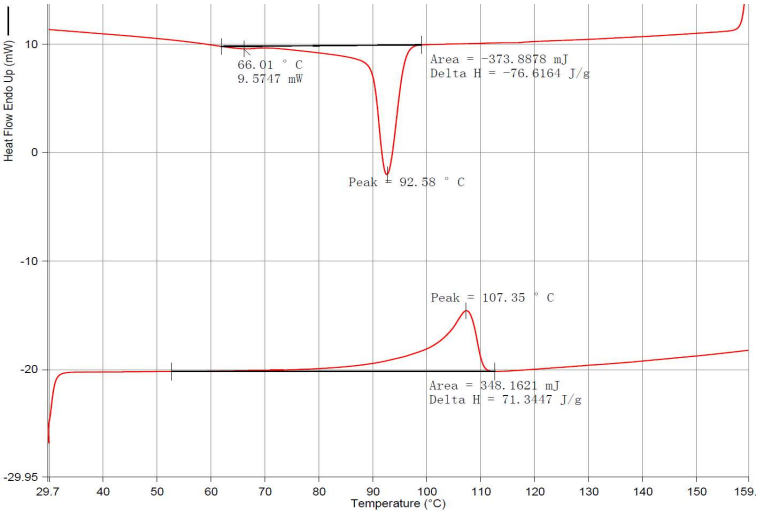
DSC spectrum of polymer in Entry 25, Table 3



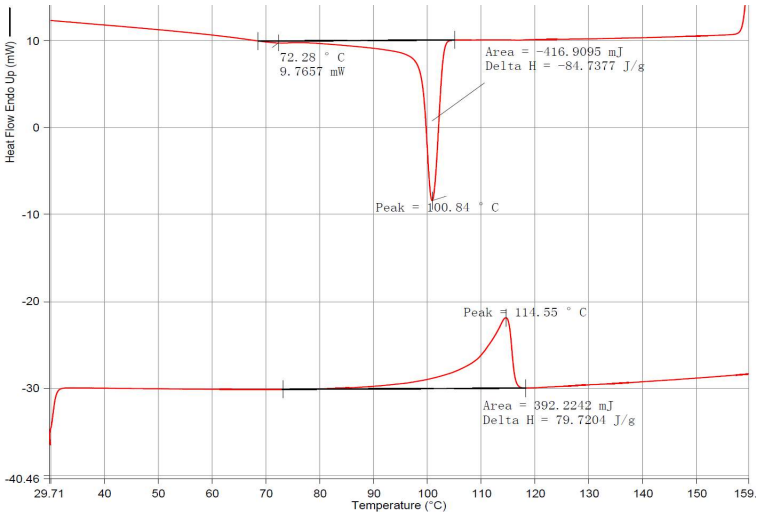
DSC spectrum of polymer in Entry 26, Table 3



DSC spectrum of polymer in Entry 27, Table 3



DSC spectrum of polymer in Entry 28, Table 3



DSC spectrum of polymer in Entry 29, Table 3

WCAs of polymers

E-Entry T-Table

PE
E6T1

106°

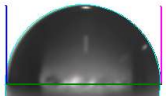
E-BA
E1T2

91°

E17T2

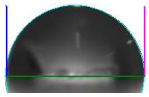
90°

E18T2



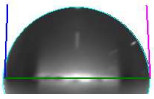
90°

E6T2



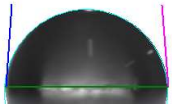
90°

E-EGMA
E11T2



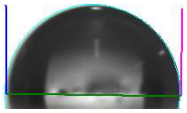
87°

E12T2



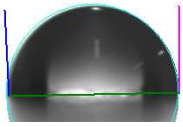
86°

E-ENB
E14T2



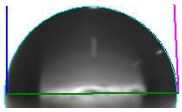
90°

E-VNB
E13T2



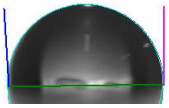
91°

E-DCPD
E16T2



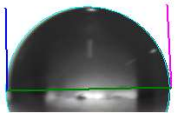
88°

E-BA-ENB
E6T3



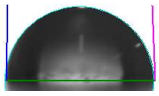
92°

E7T3



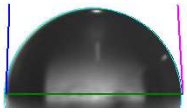
89°

E8T3



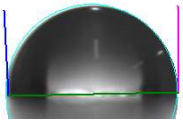
88°

E8T3



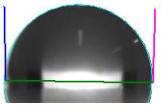
87°

E10T3



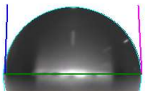
91°

E-BA-VNB
E1T3



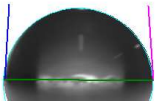
92°

E2T3



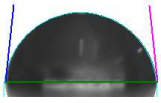
87°

E3T3



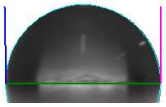
86°

E4T3



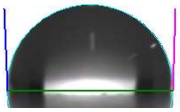
84°

E-BA-DCPD
E13T3



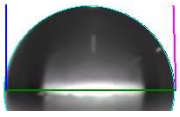
91°

E12T3



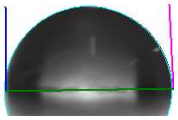
92°

E15T3



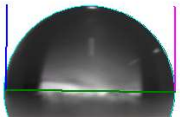
89°

E14T3



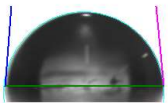
89°

E16T3



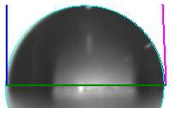
89°

E-EGMA-ENB
E21T3



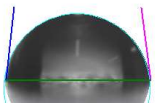
85°

E20T3



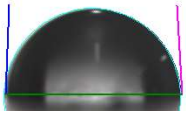
89°

E-EGMA-VNB
E19T3



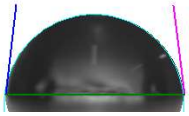
83°

E18T3



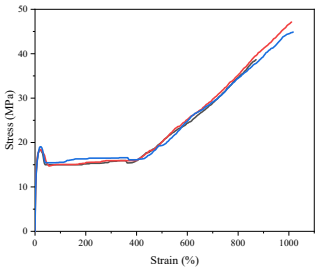
87°

E-EGMA-DCPD
E23T3

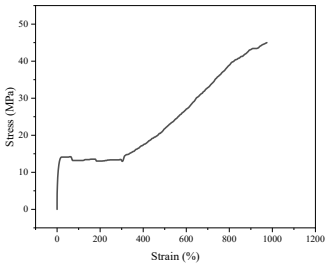


83°

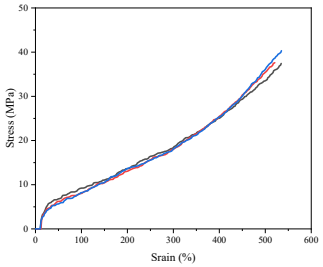
Strain-stress curves of polymers



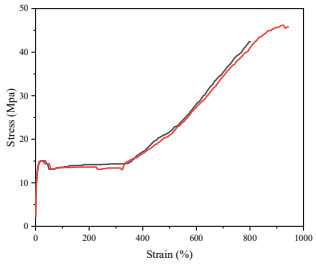
Entry 18, Table 2



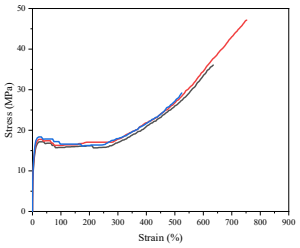
Entry 12, Table 2



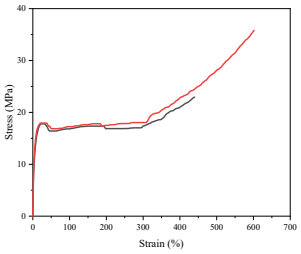
Entry 14, Table 2



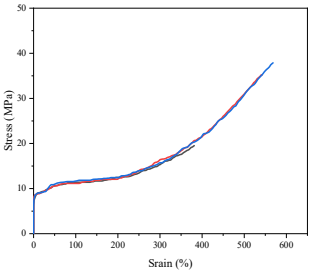
Entry 6, Table 2



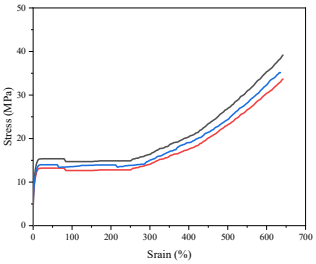
Entry 1, Table 2



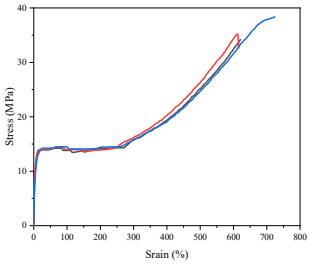
Entry 3, Table 2



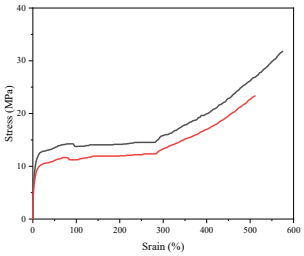
Entry 6, Table 3



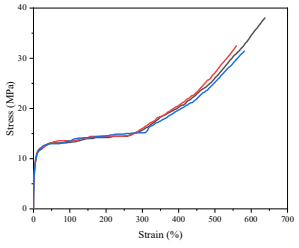
Entry 14, Table 3



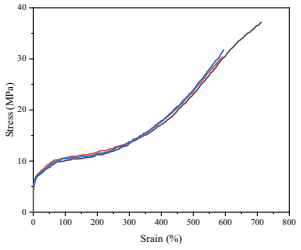
Entry 3, Table 3



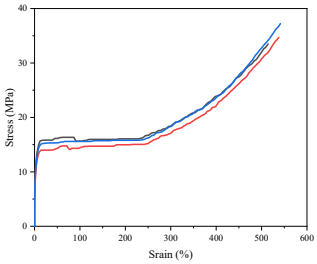
Entry 23, Table 3



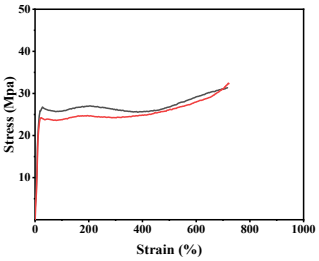
Entry 9, Table 3



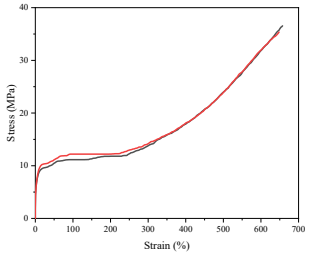
Entry 18, Table 3



Entry 15, Table 2

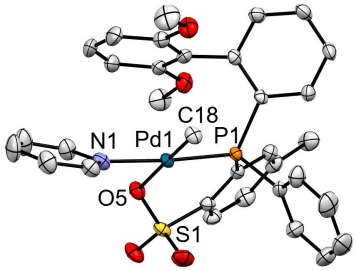


Entry 6, Table 1



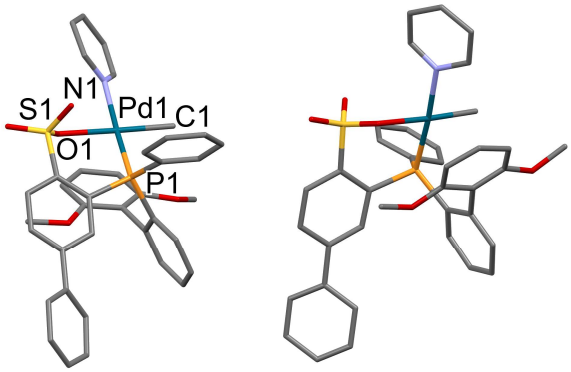
Entry 21, Table 3

X-ray Crystallography



Crystal data and structure refinement for **Pd1**

Empirical formula	C33 H32 N O5 P Pd S	
Formula weight	692.02	
Temperature [K]	193(2) K	
Wavelength	1.34139 Å	
Crystal system	Orthorhombic	
Space group	$P2_12_12_1$	
Unit cell dimensions	a = 11.0896(6) Å	α= 90°.
	b = 12.0006(7) Å	β= 90°.
	c = 22.7952(13) Å	γ = 90°.
Volume	3033.6(3) $Å^3$	
Z	4	
Absorption coefficient	4.324 mm^{-1}	
F(000)	1416	
Crystal size	0.20 x 0.16 x 0.10 mm^3	
Theta range for data collection	3.621 to 52.094°.	
Reflections collected	23824	
Independent reflections	4771 [R(int) = 0.0338]	
Completeness to theta = 52.094°	96.4 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.649 and 0.458	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4771 / 0 / 384	
Goodness-of-fit on F^2	1.093	
Final R indices [I>2sigma(I)]	R1 = 0.0215, wR2 = 0.0567	
R indices (all data)	R1 = 0.0215, wR2 = 0.0568	
Absolute structure parameter	0.875(10)	
Largest diff. peak and hole	0.518 and -0.507 $e.Å^{-3}$	



Crystal data and structure refinement for **Pd2**

Empirical formula	$C_{76}H_{69}N_2O_{10}P_2Pd_2S_2$
Formula weight	1509.19
Temperature [K]	193.00
Crystal system	monoclinic
Space group (number)	$P2_1/c$ (14)
a [Å]	17.077(3)
b [Å]	19.687(4)
c [Å]	20.582(4)
α [°]	90.00(3)
β [°]	91.10(3)
γ [°]	90.00(3)
Volume [Å^3]	6918(2)
Z	4
ρ_{calc} [gcm^{-3}]	1.449
μ [mm^{-1}]	0.687
F(000)	3092
Radiation	MoK_α (λ=0.71073 Å)
2θ range [°]	3.70 to 54.03 (0.78 Å)
Index ranges	−21 ≤ h ≤ 21
	−25 ≤ k ≤ 25
	−26 ≤ l ≤ 26
Reflections collected	129338
Independent reflections	15116
	R_{int} = 0.1963
	R_{sigma} = 0.1011
Completeness to θ = 25.242°	100.0 %
Data / Restraints / Parameters	15116/0/853
Absorption correction	0.6224/0.7455
T_{min}/T_{max} (method)	(none)
Goodness-of-fit on F^2	1.438
Final *R* indexes	R_1 = 0.1906
[$I \geq 2\sigma(I)$]	wR_2 = 0.3829
Final *R* indexes	R_1 = 0.3259
[all data]	wR_2 = 0.4786
Largest peak/hole [eÅ^{-3}]	13.88/−1.60

References

[1] De Graaf, W.; Boersma, J.; Smeets, W. J. J.; Spek, A. L.; Van Koten, G. Organometallics **1989**, 8, 2907-2917.
[2] Biscoe, M. R.; Fors, B. P.; Buchwald, S. L. Journal of the American Chemical Society **2008**, 130, 6686-6687.
[3] de Graaf, W.; Boersma, J.; Grove, D.; Spek, A. L.; van Koten, G. Recueil des Travaux Chimiques des Pays-Bas **1988**, 107, 299-301.
[4] Vela, J.; Lief, G. R.; Shen, Z.; Jordan, R. F. Organometallics **2007**, 26, 6624-6635.
[5] Becht, J.-M.; Ngouela, S.; Wagner, A.; Mioskowski, C. Tetrahedron **2004**, 60, 6853-6857.
[6] Wada, S.; Jordan, R. F. Angew. Chem. Int. Ed. **2017**, 56, 1820-1824.
[7] Neuwald, B.; Caporaso, L.; Cavallo, L.; Mecking, S. J. Am. Chem. Soc. **2013**, 135, 1026-1036.
[8] Perrotin, P.; McCahill, J. S. J.; Wu, G.; Scott, S. L. Chemical Communications **2011**, 47, 6948-6950.
[9] M. J. Frisch, G. W. T., H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox: Gaussian 09, Revision B.01. Gaussian, Inc.: Wallingford CT, 2010.
[10] (a) C. Lee, W. Yang, R. G. Parr, Physical Review B 1988, 37, 785-789. (b) B. Miehlich, A. Savin, H. Stoll, H. Preuss, Chemical Physics Letters 1989, 157, 200-206; cA. D. Becke, The Journal of Chemical Physics 1993, 98, 5648-5652.
[11] S. Grimme, J. Antony, S. Ehrlich, H. Krieg, The Journal of Chemical Physics 2010, 132, 154104.
[12] P. J. Hay, W. R. Wadt, The Journal of Chemical Physics 1985, 82, 270-283.
[13] (a) R. Ditchfield, W. J. Hehre, J. A. Pople, The Journal of Chemical Physics 1971, 54, 724-728. (b) W. J. Hehre, R. Ditchfield, J. A. Pople, The Journal of Chemical Physics 1972, 56, 2257-2261.
[14] Dunning T. H. Jr.; Hay, P. J. in Modern Theoretical Chemistry, Ed. H. F. Schaefer III, Vol. 3 (Plenum, New York, 1977) 128.
[15] (a) G. W. Spitznagel, T. Clark, J. Chandrasekhar, P. V. R. Schleyer, Journal of

Computational Chemistry 1982, 3, 363-371. (b) B. J. Lynch, Y. Zhao, D. G. Truhlar, The Journal of Physical Chemistry A 2003, 107, 1384-1388. (c) L. Goodman, R. R. Sauers, Journal of Computational Chemistry 2007, 28, 269-275.
[16] Marenich, A. V.; Cramer, C. J.; Truhlar, D. G. J. Phys. Chem. B 2009, 113, 4538−4543.
[17] Lu, T.; Chen, F. J. Comput. Chem. 2012, 33, 580−592.
[18] Humphrey, W.; Dalke, A.; Schulten, K. J. Mol. Graphics 1996, 14,33−38.
[19] Falivene, L.; Cao, Z.; Petta, A.; Serra, L.; Poater, A.; Oliva, R.; Scarano, V.; Cavallo, L. Nature Chemistry 2019, 11 (10), 872-879.
[20] Wucher, P.; Goldbach, V.; Mecking, S. Organometallics **2013**, 32, 4516-4522.
[21] Jian, Z. B.; Wucher, P.; Mecking, S. Organometallics **2014**, 33, 2879-2888.
[22] Ye, J. H.; Mu, H. L.; Wang, Z.; Jian, Z. B. Organometallics **2019**, 38, 2990-2997.
[23] Hu, X.; Zhang, Y.; Li, B.; Jian, Z. Chinese Journal of Chemistry **2021**, 39, 2829-2836.
[24] Hu, X.; Zhang, Y.; Li, B.; Jian, Z. Chem. Eur. J. **2021**, 27, 11935-11942.
[25] Zhang, Y.; Kang, X.; Jian, Z. Nat. Commun. **2022**, 13, 725.
[26] Li, K.; Ye, J.; Wang, Z.; Mu, H.; Jian, Z. Polym. Chem. **2020**, 11, 2740-2748.
[27] Vela, J.; Lief, G. R.; Shen, Z.; Jordan, R. F. Organometallics **2007**, 26, 6624-6635.