# *Supporting Information for*

## Lewis Acid-Induced Homo- and Heterogeneous Nickel Catalysts for Ethylene Polymerization and Copolymerization with Polar Monomers

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# 1. Experimental Section

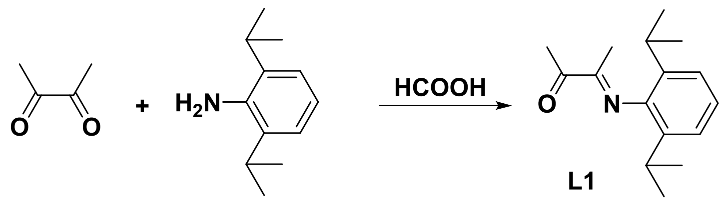
## 1.1. General Considerations

All manipulations, unless otherwise mentioned, were carried out under a dry nitrogen atmosphere using standard Schlenk techniques or in a glovebox. Deuterated solvents used for NMR spectroscopy were dried and distilled prior to use. $^{1}H$, $^{13}C$, and H-H COSY spectra were recorded on a Bruker Ascend Tm 400 MHz spectrometer at ambient temperature unless otherwise stated. The chemical shifts of the $^{1}H$, $^{13}C$, and H-H COSY spectra were referenced to tetramethylsilane. X-ray diffraction data were collected at 298(2) K on a Bruker Smart CCD area detector with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å) radiation at room temperature. Gel permeation chromatography (GPC) analyses of the molecular weight and molecular weight distribution of the (co)polymers at 150°C were performed on a high temperature chromatograph, PL-GPC 220 instrument equipped with a triple detection array, including a differential refractive index (RI) detector, a two-angle light scattering (LS) detector, and a four-bridge capillary viscometer. The system was calibrated with a polystyrene standard and chromatograms were corrected for linear polyethylene through universal calibration using the Mark-Houwink parameters of Rudin: $K = 1.75 \times 10^{-2}$ $cm^3/g$ and $R = 0.67$ for polystyrene, and $K = 5.90 \times 10^{-2}$ $cm^3/g$ and $R = 0.69$ for polyethylene. Differential scanning calorimetry (DSC) was performed by a DSC Q20 from TA Instruments. Samples were quickly heated to 150°C and kept for 5 min to remove thermal history, then cooled to 40°C at a rate of 10 K/min, and finally reheated to 160°C at the same rate under a nitrogen flow (50 mL/min). The maximum point endotherm (heating scan) was taken as the melting temperature ($T_m$). Toluene, *n*-hexane, *n*-heptane, Chlorobenzene, $CDCl_3$ and $CH_2Cl_2$ were purified over 4 Å molecular sieves or $CaH_2$. All the other reagents were used as received from commercial sources.

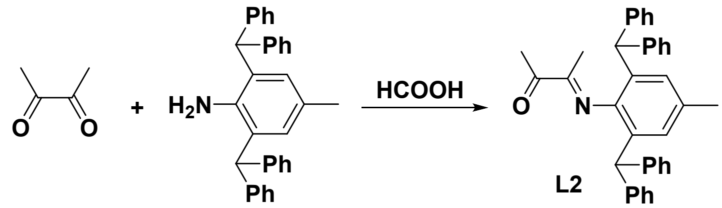
**Computational Methods.** All the DFT studies were performed by using the Gaussian 16 program. For geometry optimizations, the B3LYP hybrid exchange-correlation functional and the dispersion-corrected density functional theory (B3LYP-D3BJ) were used. The 6-31G (d, p) basis set was used for H, C, B, F, O and N atoms. Ni atoms were treated by the LANL2DZ basis set. In the single point energy calculations, the dispersion-corrected density functional theory B3LYP-D3(BJ) and a larger basis set BSII were used. In the BSII, 6-311G (d, p) was used for H, C, B, F, O and N atoms, and Ni atoms were treated by the SDD basis set. In these single-point calculations, solvation effects were considered with the SMD model. The toluene was employed as a solvent in the SMD solvation calculations. Full NBO population analyses were also done at the B3LYP-D3(BJ)/6-311G (d, p)/SMD level of theory, and were performed at the same time as the initial geometry optimization. Normal modes of all structures were examined. No imaginary frequency was observed.

**Stress-Strain Curves.** 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°C above their melting point to obtain the dog-bone-shaped tensile-test specimens. The test specimens showed 12 mm gauge length, 2 mm width, and thickness of 0.5 mm. Stress/strain experiments were performed at 10 mm/min using a Universal Test Machine (UTM2502) at room temperature. At least three specimens of each copolymer were tested.

### 1.2. Preparation of Ligand L1-L2 and Nickel Complexes

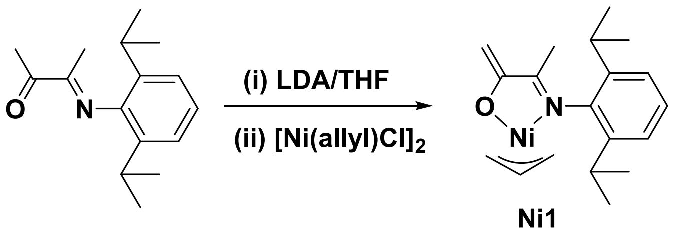



**Preparation of L1.** To the mixture of 2, 6-diisopropylaniline (10 mmol, 1.78 g) in methanol (50 mL) was added 2, 3-butanedione (25 mmol, 2.15 g) and formic acid (several drops), heat at 80°C for 12 h until the completion of reaction check by TLC. After the completion of reaction, rotary evaporate the solvent and purified the crude oil by reduce pressure distillation to give the yellow liquid **L1** (2.25 g, 92%). $^1$H NMR (400 MHz, Chloroform-*d*) δ 7.19-7.13 (m, 2H), 7.13-7.07 (m, 1H), 2.59 (s, 2H), 2.57 (d, $J$ = 10.5 Hz, 5H), 1.82 (s, 3H), 1.14 (dd, $J$ = 6.9, 5.2 Hz, 12H).



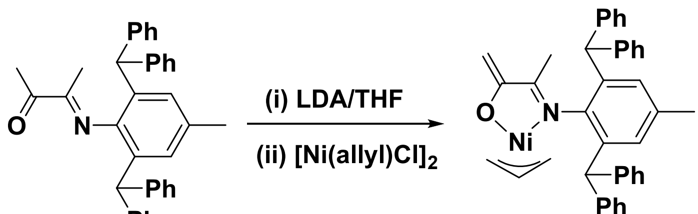

**Preparation of L2.** Similar procedure as **L1** was employed except 2, 6-dibenzhydryl-4-methylaniline (10 mmol, 4.39 g) was used. **L2** was obtained through recrystallization as the yellow powder (4.56 g, 90%). $^1$H NMR (400 MHz, Chloroform-*d*) δ 7.31-7.08 (m, 14H), 7.07-6.93 (m, 8H), 6.65 (s, 2H), 5.10 (s, 2H), 2.32 (s, 3H), 2.14 (s, 3H), 0.67 (s, 3H).

**General method for the Preparation of Nickel Catalysts.**



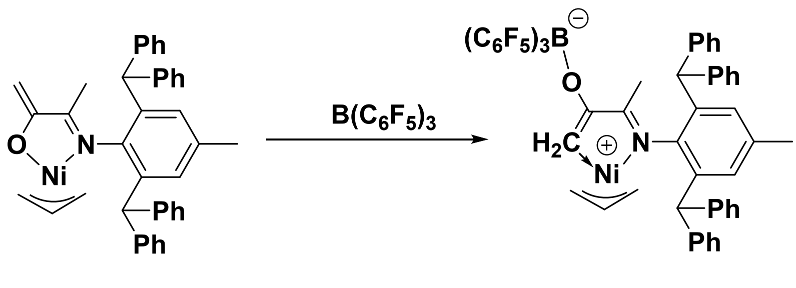

Ni1

**Preparation of Ni1.** A Schlenk flask was charged with **L1** (1 mmol, 0.25 g), anhydrous THF (20 mL) under nitrogen and cooled to -78°C. LDA (1 M in hexane, 1.1 mL, 1.1 mmol) was added dropwise and the resulting solution was stirred for 1.0 h. Then the solution was filtered through celite and the solvent was removed under reduced pressure to generate the corresponding lithium salt. The above lithium salt (1 mmol) and $[Ni(allyl)Cl]_2$ (0.53 mmol, 0.14 g) were dissolved in DCM (20 mL) stirring overnight at room temperature. The dark yellow solution was filtered through celite and the solvent was evaporated. The crude solid was washed three times with *n*-hexane to give the yellow powder **Ni1** (0.30 g, 88%), and the $^1$H NMR spectrum showed the broad peaks within the ranging zone.




Ni2

**Preparation of Ni2.** Similar procedure as catalyst **Ni1** was employed except **L2** (0.5 mmol, 0.51 g) was used. **Ni2** was obtained as the yellow powder (0.55 g, 92%). $^1$H NMR (400 MHz, Chloroform-*d*) δ 7.32 (m, 7H), 7.25-7.07 (m, 12H), 7.03 (s, 3H), 6.81 (s, 1H), 6.72 (s, 1H), 5.88 (s, 1H), 5.57 (s, 1H), 5.14 (m, 1H), 4.69 (s, 1H), 4.28 (s, 1H), 3.10 (d, $J$ = 5.0 Hz, 1H), 2.21 (s, 3H), 1.98 (d, $J$ = 13.1 Hz, 1H), 1.59 (d, $J$ = 6.7 Hz, 1H), 0.88 (d, $J$ = 12.8 Hz, 1H), 0.74 (s, 3H). $^{13}$C NMR (101 MHz, Chloroform-d) δ 183.20, 167.06, 144.93, 142.14, 142.05, 141.99, 141.82, 135.66, 134.96, 134.92, 130.03, 129.89, 129.86, 129.57, 129.09, 128.99, 128.74, 128.67, 128.63, 126.77, 126.66, 126.60, 110.77, 95.03, 52.37, 52.30, 52.25, 51.19, 21.50, 15.84. MALDI-TOF-MS (m/z) for $C_{37}H_{32}NNiO$: 565.1069 [M-Allyl]. Anal. Calcd for $C_{40}H_{37}NNiO$: C, 79.22; H, 6.15; N, 2.31; Found: C, 79.26; H, 6.12; N, 2.28.




**Preparation of Ni2-BCF.** A Schlenk flask was charged with **Ni2** (20 μmol, 12 mg), $B(C_6F_5)_3$ (2 eq., 10.2 mg) and $CDCl_3$ (0.5 mL). The resulting solution was stirred for 1.0 h at room temperature to generate the dark-red **Ni2-BCF** solution. $^1$H NMR (400 MHz, Chloroform-*d*) δ 7.40-7.36 (m, 2H), 7.22-7.18 (m, 4H), 7.12-7.06 (m, 5H), 6.98-6.89 (m, 8H), 6.84-6.79 (m, 2H), 6.63-6.58 (m, 1H), 5.45 (s, 1H), 5.16 (s, 1H), 5.06 (s, 1H), 4.99 (m, 1H), 3.26 (br, 1H), 2.98 (br, 1H), 2.16 (s, 3H), 1.91 (br, 1H), 1.66 (d, $J$ = 12.1 Hz, 1H), 1.37 (d, $J$ = 12.5 Hz, 1H), 1.24 (s, 3H). $^{19}$F NMR (376 MHz, Chloroform-*d*) δ -133.35, -158.66, -164.46.

### 1.3. Preparation of Supported Nickel Catalysts

**Preparation of Supported Catalysts Ni-BCF/SiO$_2$.** Nano $SiO_2$ (2.0 g, was thermally pretreated under vacuum at 500°C for 4 h) and $B(C_6F_5)_3$ (3.2 g, 6.3 mmol) were combined in a Schlenk tube under $N_2$, to which was added a mixture of toluene (100 mL) and deionized water (10 μL). Then the slurry was stirred at 100°C for 3 d. The solid product was collected and washed with dried toluene (3 × 10 mL). The powder was transferred to a Schlenk tube and dried at 100°C under vacuum for 3 h to give a solid (**BCF/SiO$_2$**). Then the mixture of nickel complex with Lewis Acid-modified $SiO_2$ (**BCF/SiO$_2$)** in toluene was stirred for 3 h, filtrated and washed with toluene to generated the supported catalyst (**Ni-BCF/SiO$_2$**). The maximum catalyst supporting capacity was ca. 5 $\mu$mol **Ni2** per 100 mg of $SiO_2$.

**Preparation of Supported Catalysts Ni-MAO/SiO$_2$.** The preparation of **Ni-MAO/SiO$_2$** was similar to procedure of **Ni-BCF/SiO$_2$**, except the **MAO/SiO$_2$** was used. **MAO/SiO$_2$** was synthesized starting from the nano $SiO_2$ (2.0 g) and MAO (2 g, 34.4 mmol) in toluene, which was stirred overnight at room temperature, filtrated and dried.

## 1.4. Procedure for Ethylene Polymerization

**Procedure for Lewis Acid-induced Ethylene Homogeneous Polymerization.** A 250 mL pressure flask was charged with 10 eq. of $B(C_6F_5)_3$ or 100 eq. of MAO and 28 mL of dried heptane along with a magnetic bar in the glove box. Then 5 $\mu$mol nickel complex in 2 mL DCM was injected into the pressure flask. The flask was attached with the ethylene line. The vessel was warmed to the desired temperature and allowed to equilibrate for 15 minutes. With rapid stirring, the reactor was pressurized and maintained at 8 atm of ethylene. After for 0.5 h, the polymerization was quenched with addition of 5% acidic methanol (150 mL) and the polymer was precipitated. After filtration, the polymer was obtained and dried at 50 °C for 24 h under vacuum.

**Procedure for Lewis Acid-induced Ethylene Heterogeneous Polymerization.** A 250 mL pressure flask was charged with 5 $\mu$mol **Ni-BCF/SiO$_2$** or **Ni-MAO/SiO$_2$** in 30 mL of dried heptane and a magnetic bar in the glove box. The flask was attached with the ethylene line. The vessel was warmed to desired temperature and allowed to equilibrate for 15 minutes. With rapid stirring, the reactor was pressurized and maintained at 8 atm of ethylene. After for 0.5 h, the polymerization was quenched with addition of 5% acidic methanol (150 mL) and the polymer was precipitated. After filtration, the polymer was obtained and dried at 50 °C for 24 h under vacuum.

## 1.5. Procedure for Ethylene Copolymerization

**Procedure for Ethylene-Polar Monomer Copolymerization.** In a typical experiment, a 350 mL glass thick-walled pressure vessel was charged with dried heptane and polar monomer (0.5 M) in total 18 mL, a magnetic stir bar in the glovebox. The pressure vessel was connected to a high-pressure line and the solution was degassed. The vessel was warmed to desired temperature using an oil bath and allowed to equilibrate for 15 min. 10 $\mu$mol of Ni catalysts and Lewis Acid (10 eq. of $B(C_6F_5)_3$ or 100 eq. of MAO) in 2 mL $CH_2Cl_2$ was injected into the polymerization system via syringe. With rapid stirring, the reactor was pressurized and maintained at 8 atm of ethylene. After 1 h, the polymerization was quenched with addition of 5% acidic methanol (150 mL) and the polymer was precipitated. After filtration, the polymer was obtained and dried at 50 °C for 24 h under vacuum.

**Procedure for Ethylene-Polar Monomer Heterogeneous Copolymerization.** In a typical experiment, a 350 mL glass thick-walled pressure vessel was charged with 10

$\mu$mol **Ni-BCF/SiO$_2$** or **Ni-MAO/SiO$_2$**, dried heptane and polar monomer (0.5 M) in total 20 mL, and a magnetic stir bar in the glovebox. The pressure vessel was connected to a high-pressure line and the solution was degassed. The vessel was warmed to desired temperature using an oil bath. With rapid stirring, the reactor was pressurized and maintained at 8 atm of ethylene. After 1 h, the polymerization was quenched with addition of 5% acidic methanol (150 mL) and the polymer was precipitated. After filtration, the polymer was obtained and dried at 50 °C for 24 h under vacuum.

## 2. NMR Spectra of Ligand L1-L2 and Nickel Complexes Ni1-Ni2

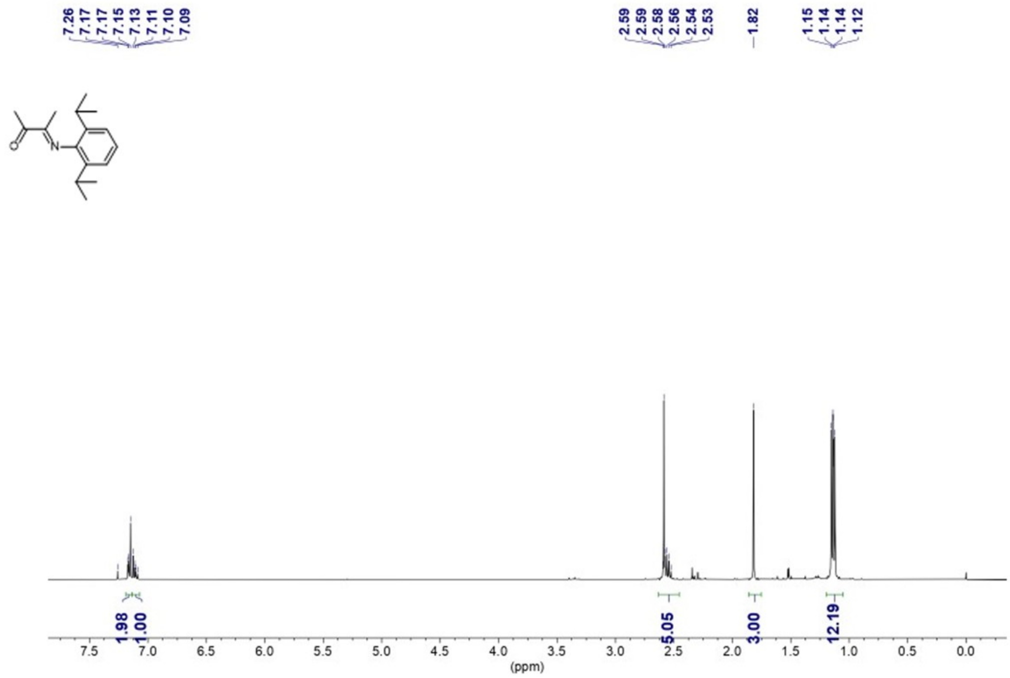



**Figure S1.** $^1$H NMR spectrum (400 MHz, $CDCl_3$) of **L1**.

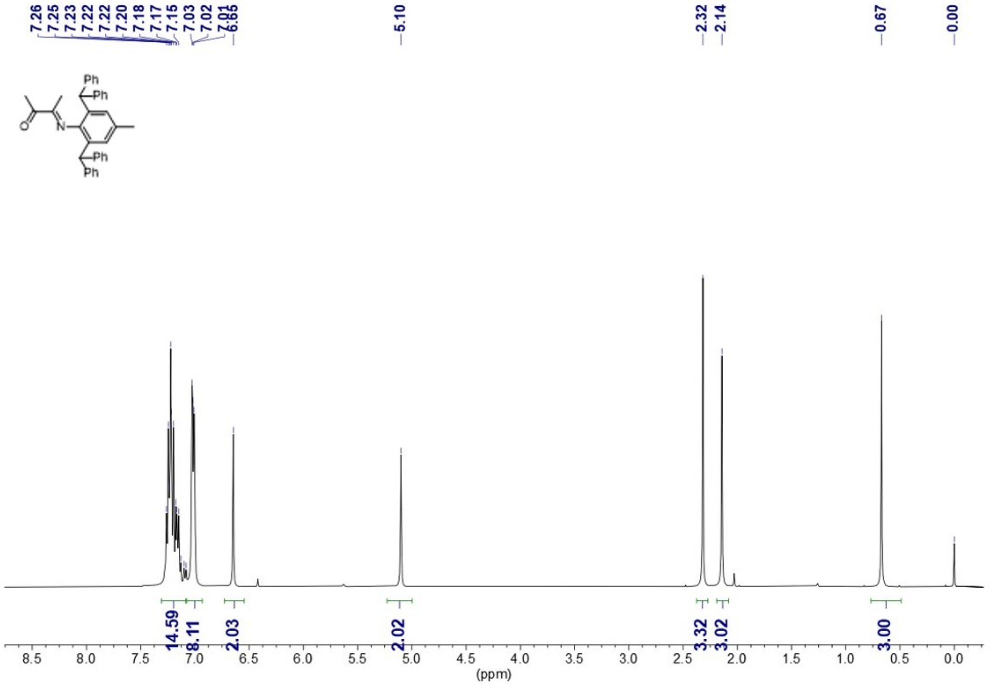



**Figure S2.** $^{1}$H NMR spectrum (400 MHz, $CDCl_3$) of **L2**.

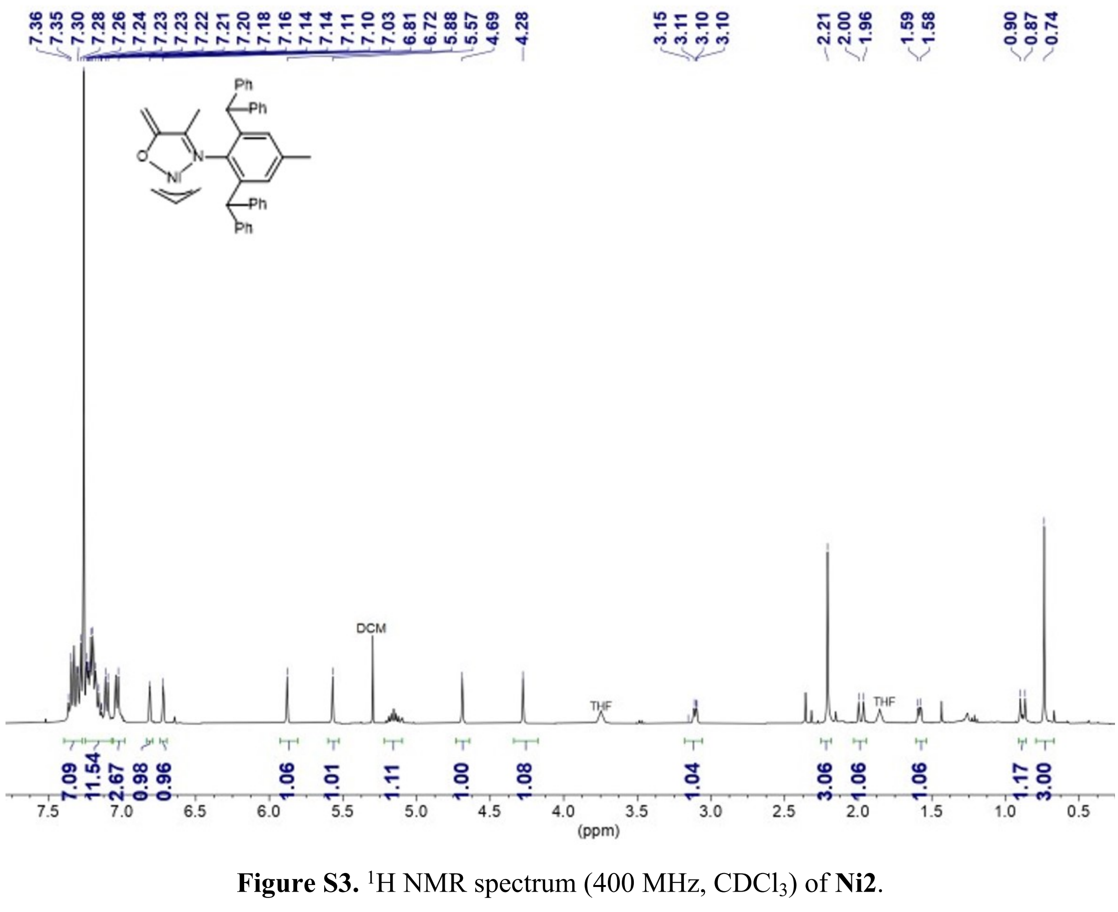



**Figure S3.** $^{1}$H NMR spectrum (400 MHz, $CDCl_3$) of **Ni2**.

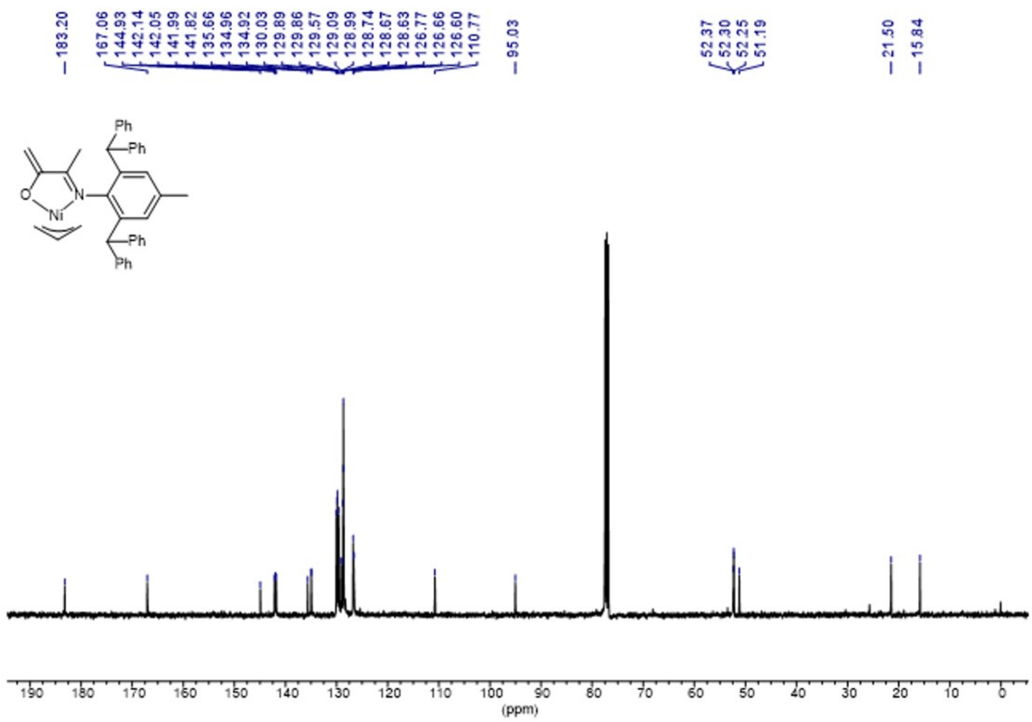



**Figure S4.** $^{13}$C NMR spectrum (101 MHz, $CDCl_3$) of **Ni2**.

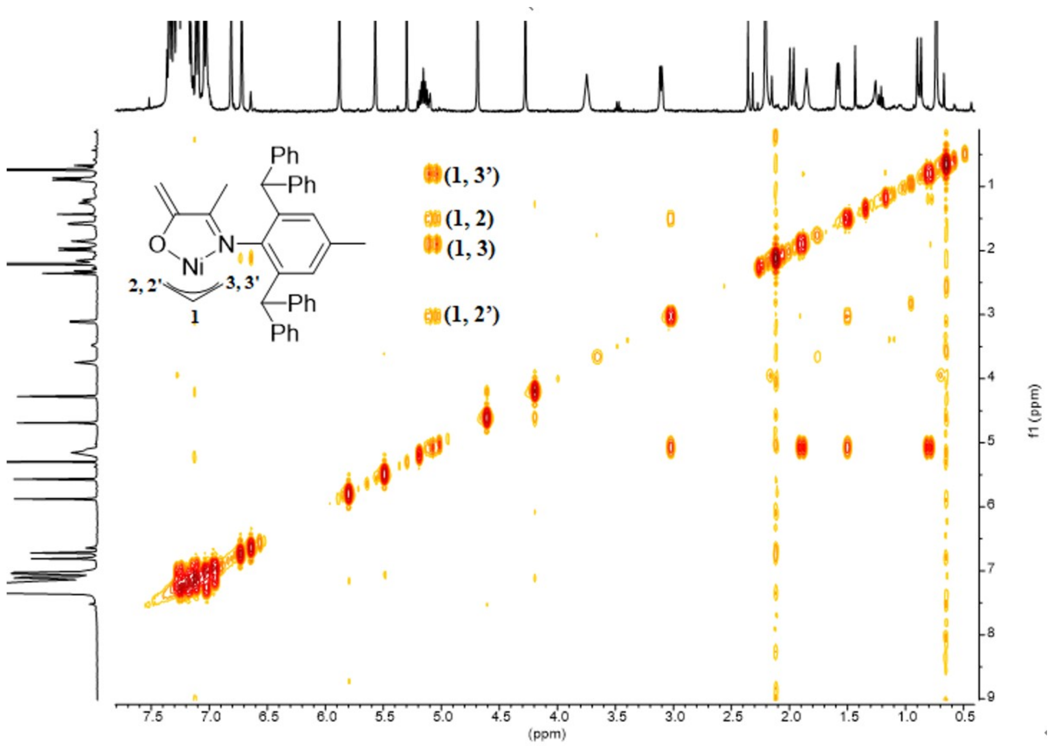



**Figure S5.** H-H COSY NMR spectrum (400 MHz, $CDCl_3$) of **Ni2**.

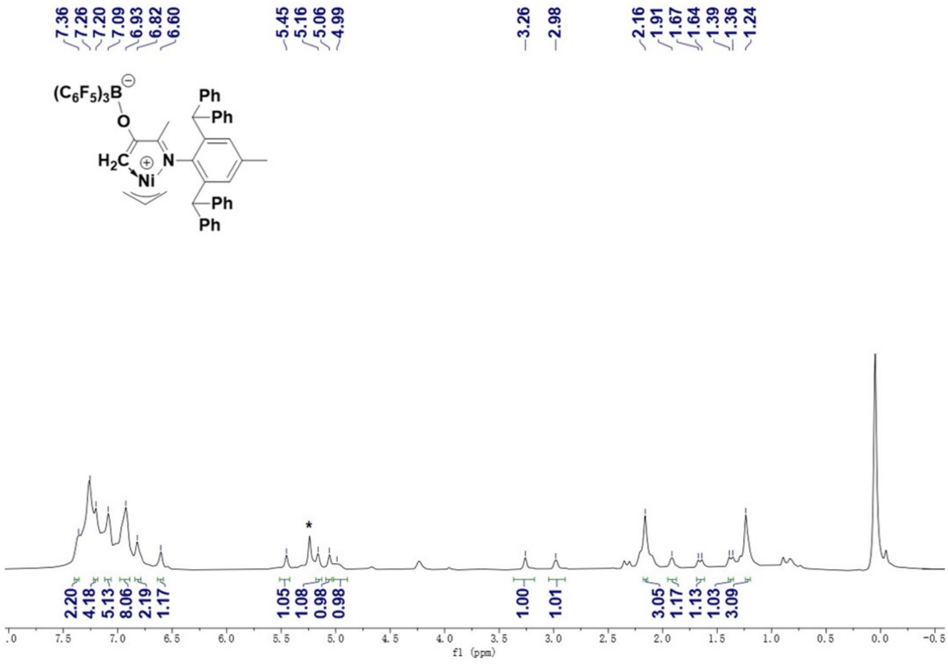


**Figure S6.** $^{1}H$ NMR spectrum (400 MHz, $CDCl_3$) of **Ni2-BCF** (* is $CH_2Cl_2$).

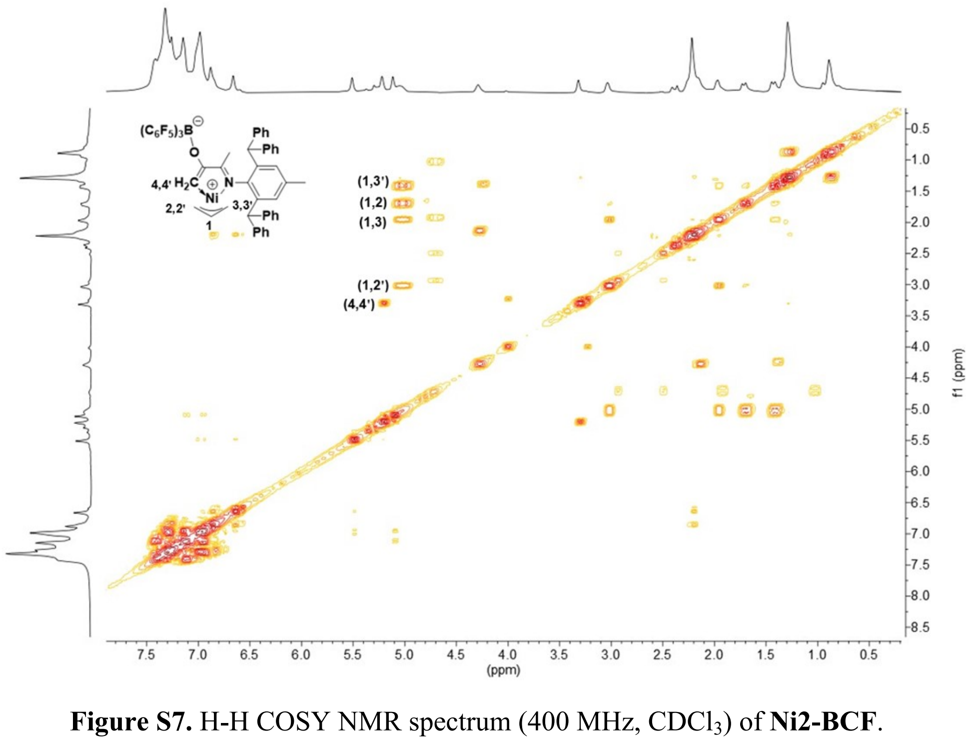


**Figure S7.** H-H COSY NMR spectrum (400 MHz, $CDCl_3$) of **Ni2-BCF**.

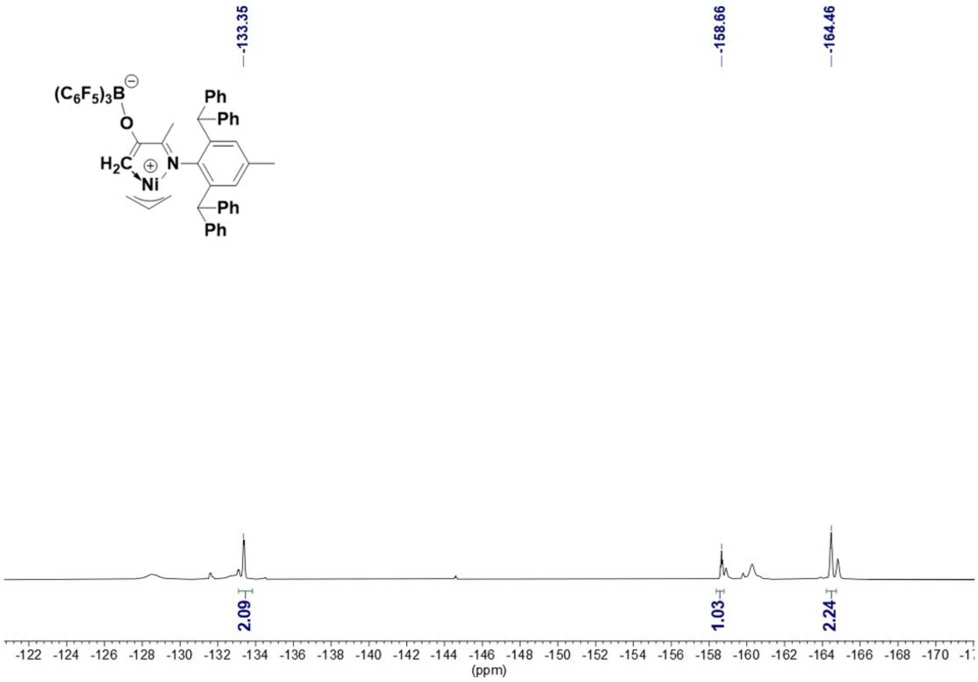



**Figure S8.** $^{1}$F NMR spectrum (376 MHz, $CDCl_3$) of **Ni2-BCF**.

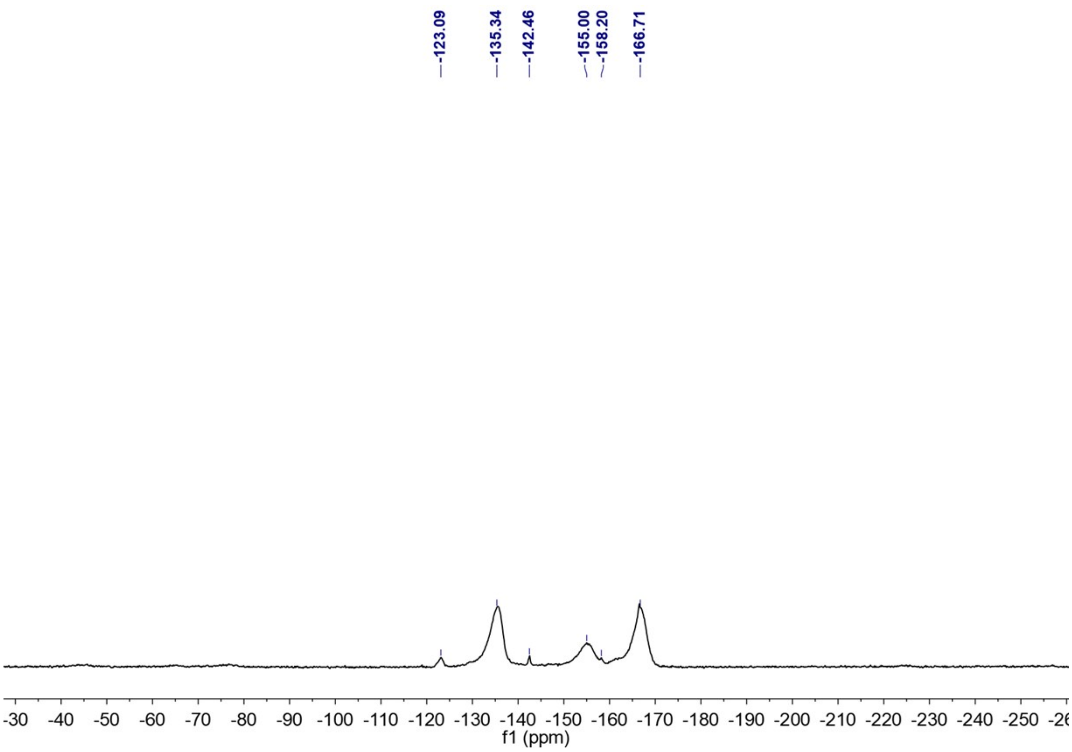



**Figure S9.** Solid-state $^{19}$F MAS NMR spectra of **Ni2-BCF/SiO$_2$**.

## 3. NMR Spectra of the Polyethylenes and Copolymers

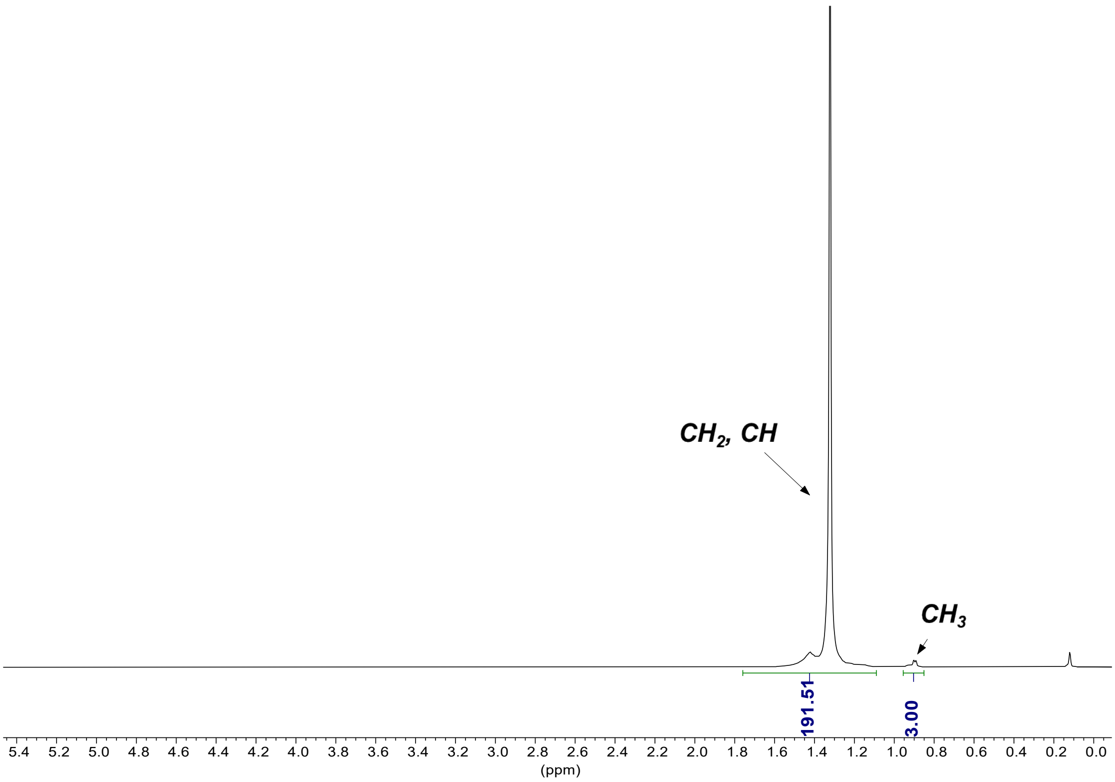



**Figure S10.** $^{1}$H NMR spectrum ($C_2D_2Cl_4$, 120$^{o}$C) of the polymer from Table 1, Entry 3.

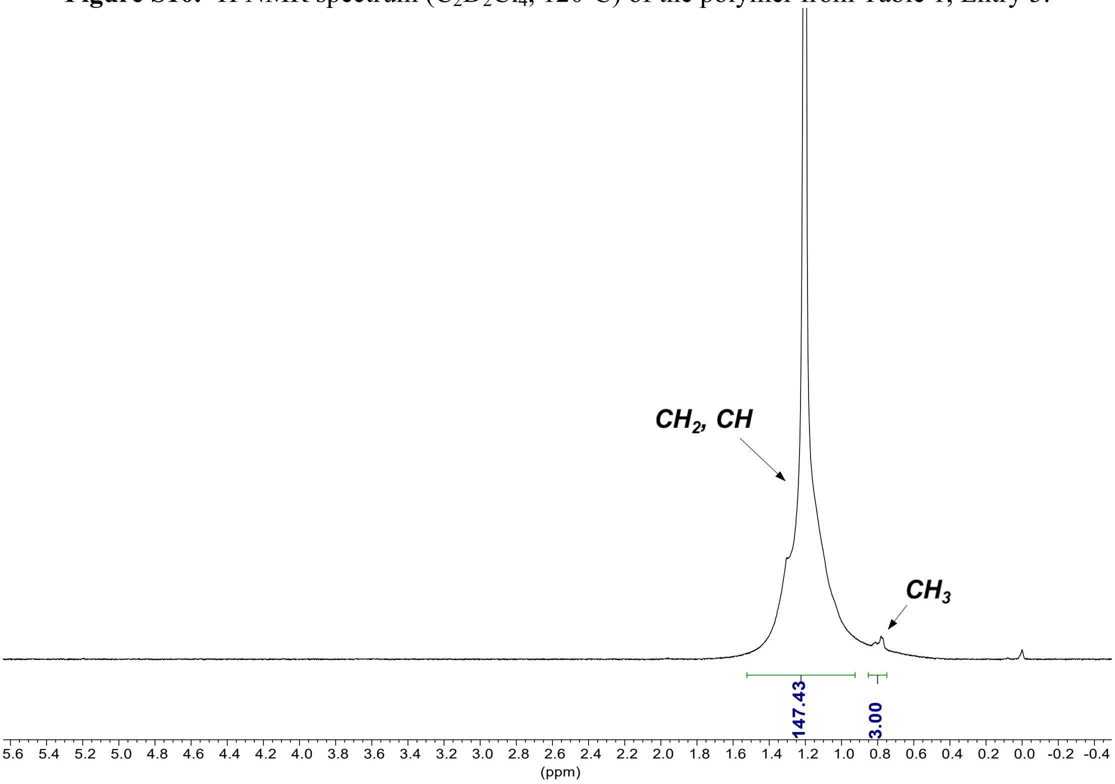



**Figure S11.** $^{1}$H NMR spectrum ($C_2D_2Cl_4$, 120$^{o}$C) of the polymer from Table 1, Entry 4.

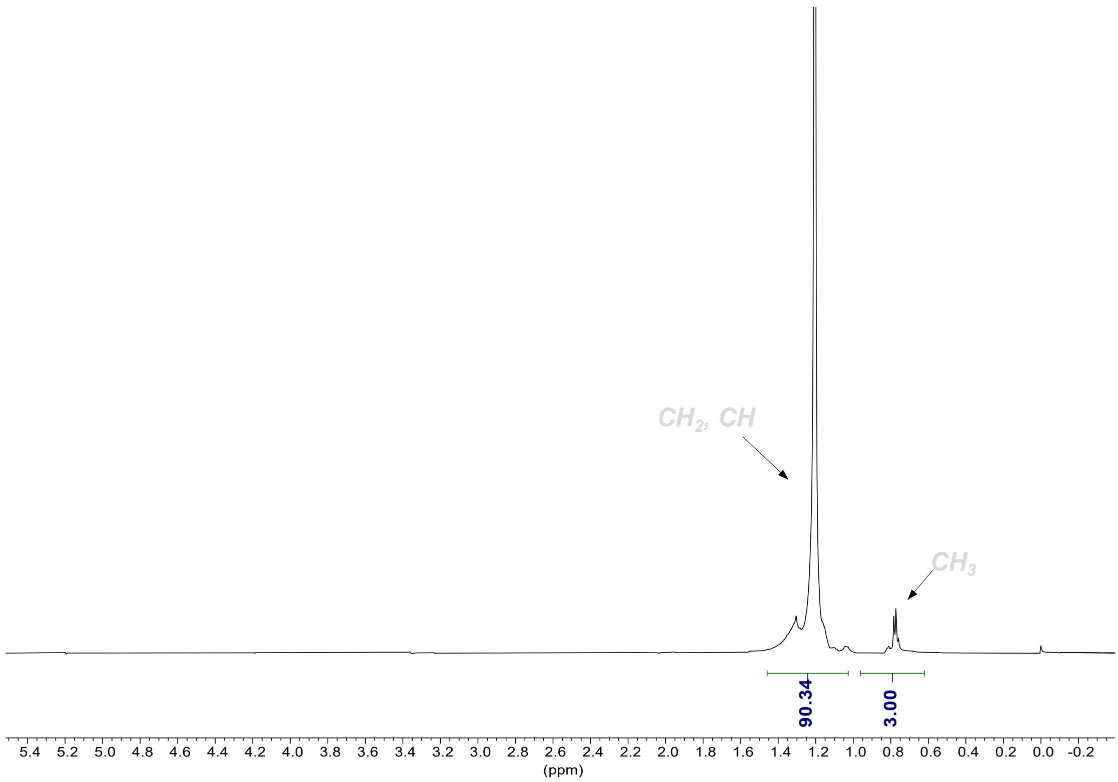



**Figure S12.** $^1$H NMR spectrum ($C_2D_2Cl_4$, 120$^o$C) of the polymer from Table 1, Entry 5.

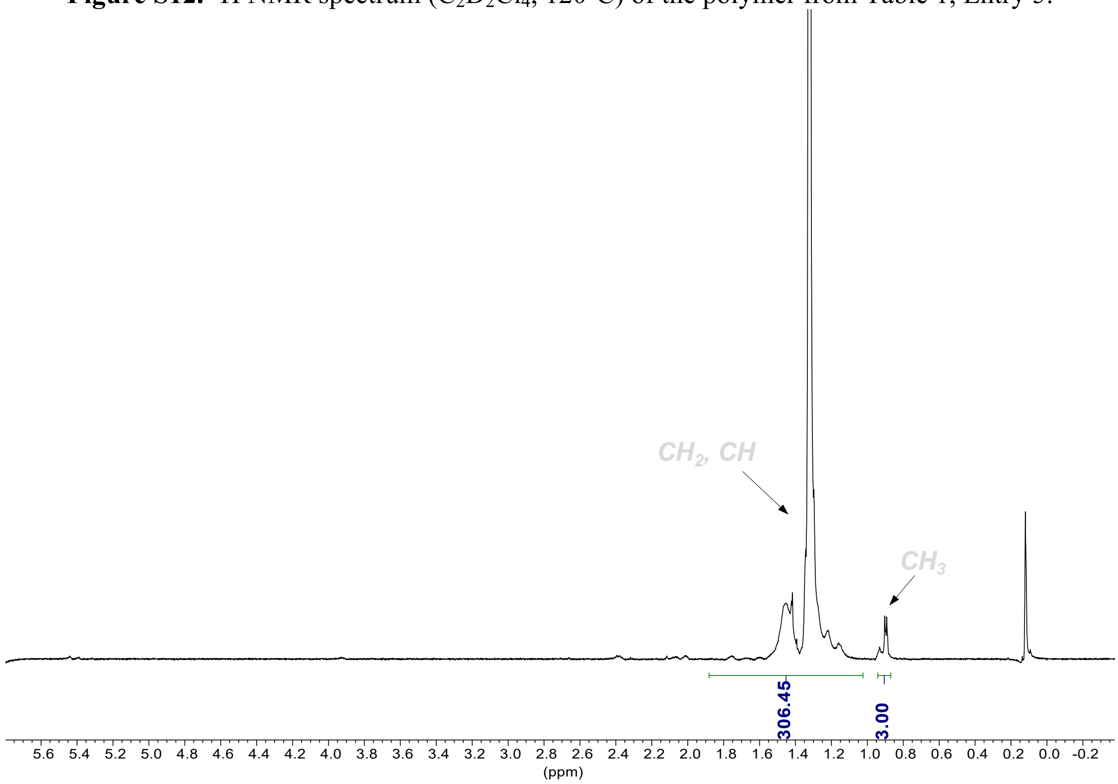



**Figure S13.** $^1$H NMR spectrum ($C_2D_2Cl_4$, 120$^o$C) of the polymer from Table 1, Entry 6.

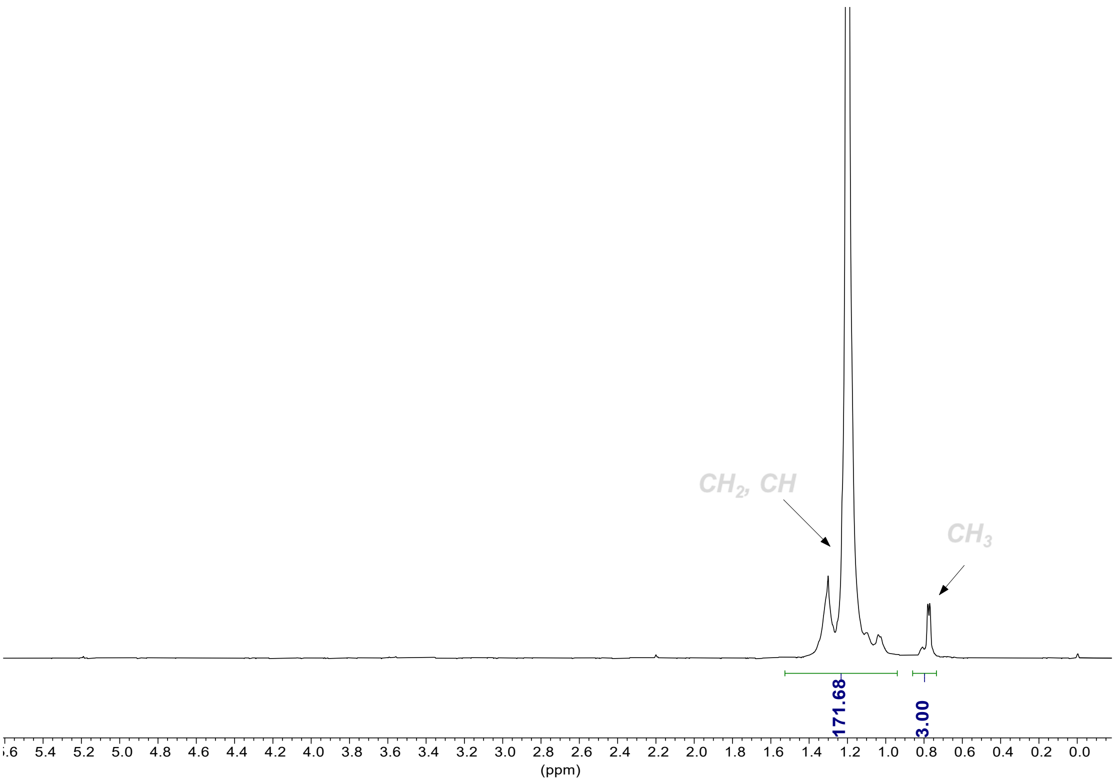



**Figure S14.** $^1$H NMR spectrum ($C_2D_2Cl_4$, 120$^o$C) of the polymer from Table 1, Entry 7.

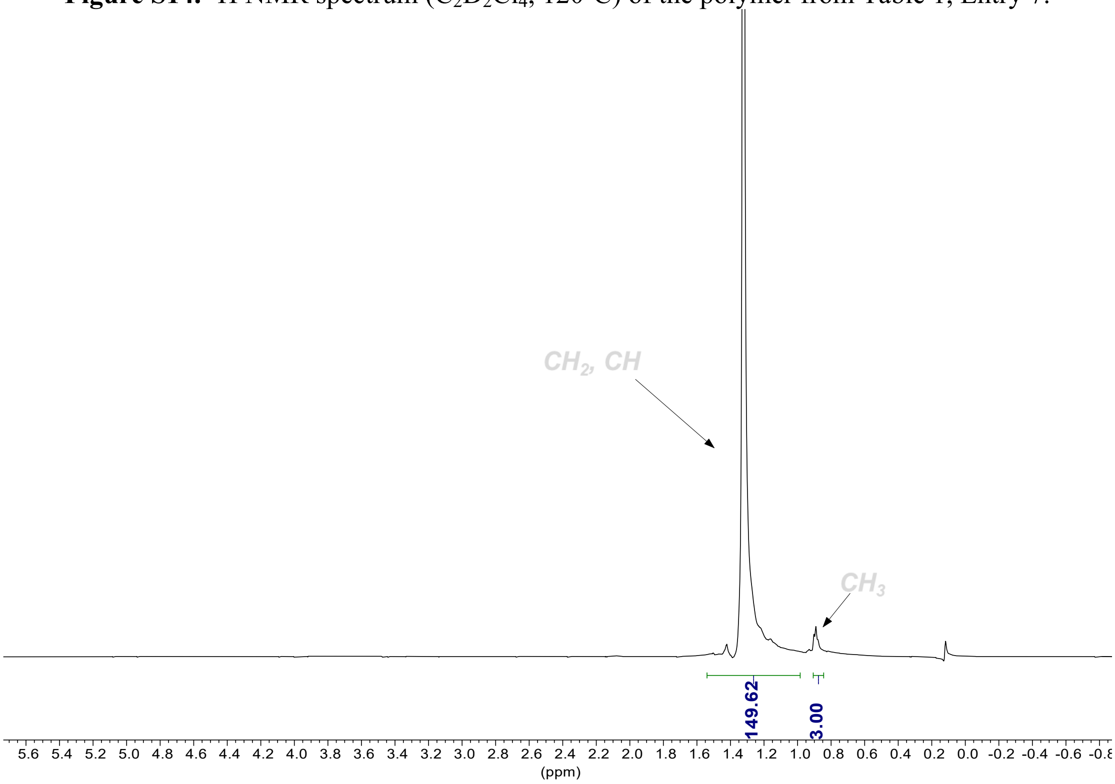



**Figure S15.** $^1$H NMR spectrum ($C_2D_2Cl_4$, 120$^o$C) of the polymer from Table 1, Entry 8.

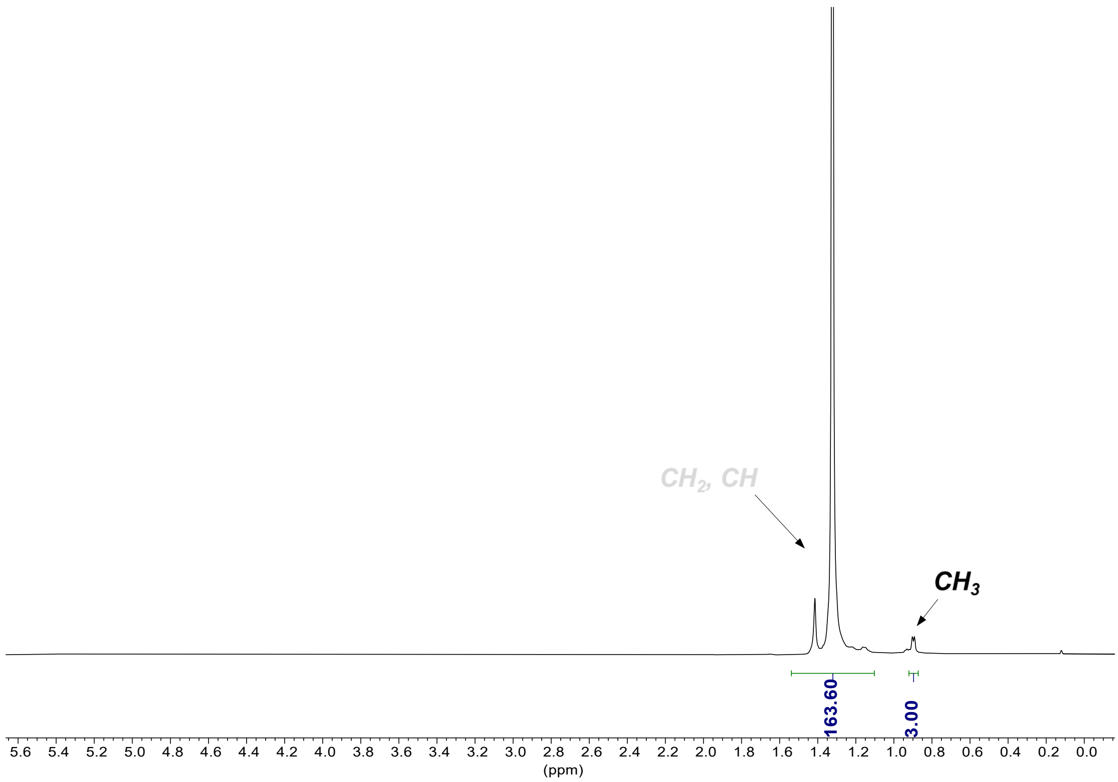


**Figure S16.** [1]H NMR spectrum ($C_2D_2Cl_4$, 120$^o$C) of the polymer from Table 1, Entry 9.

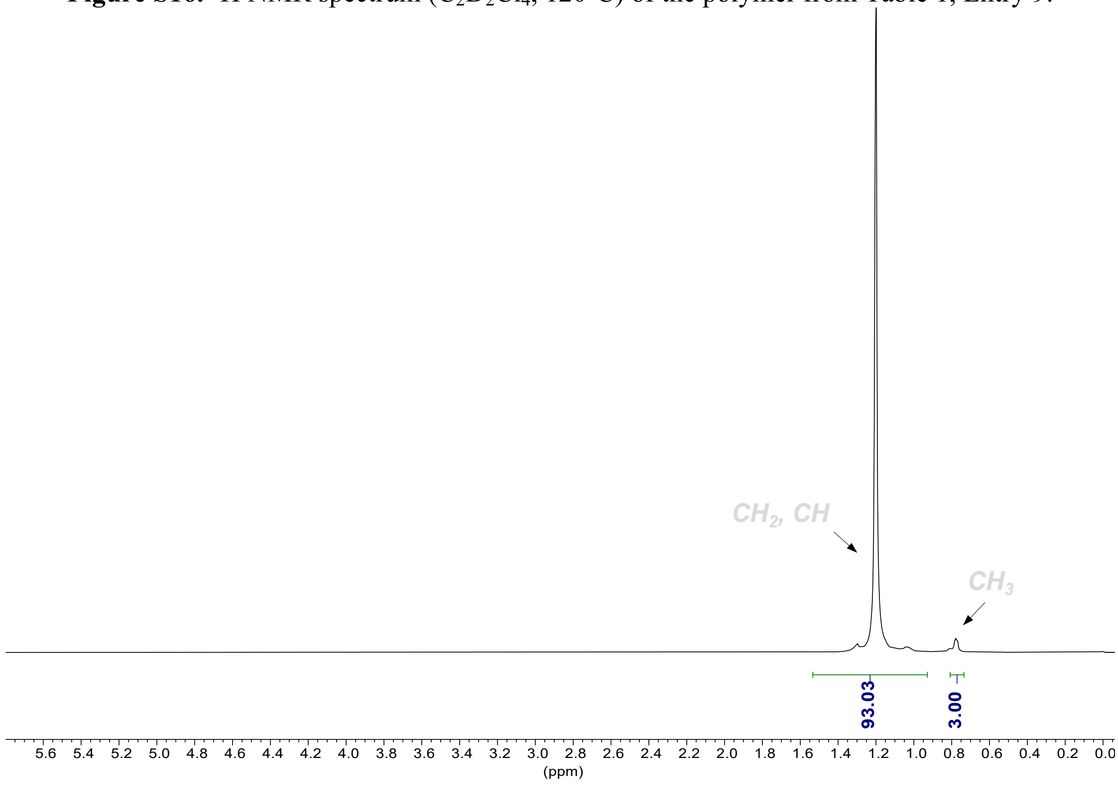


**Figure S17.** [1]H NMR spectrum ($C_2D_2Cl_4$, 120$^o$C) of the polymer from Table 1, Entry 10.

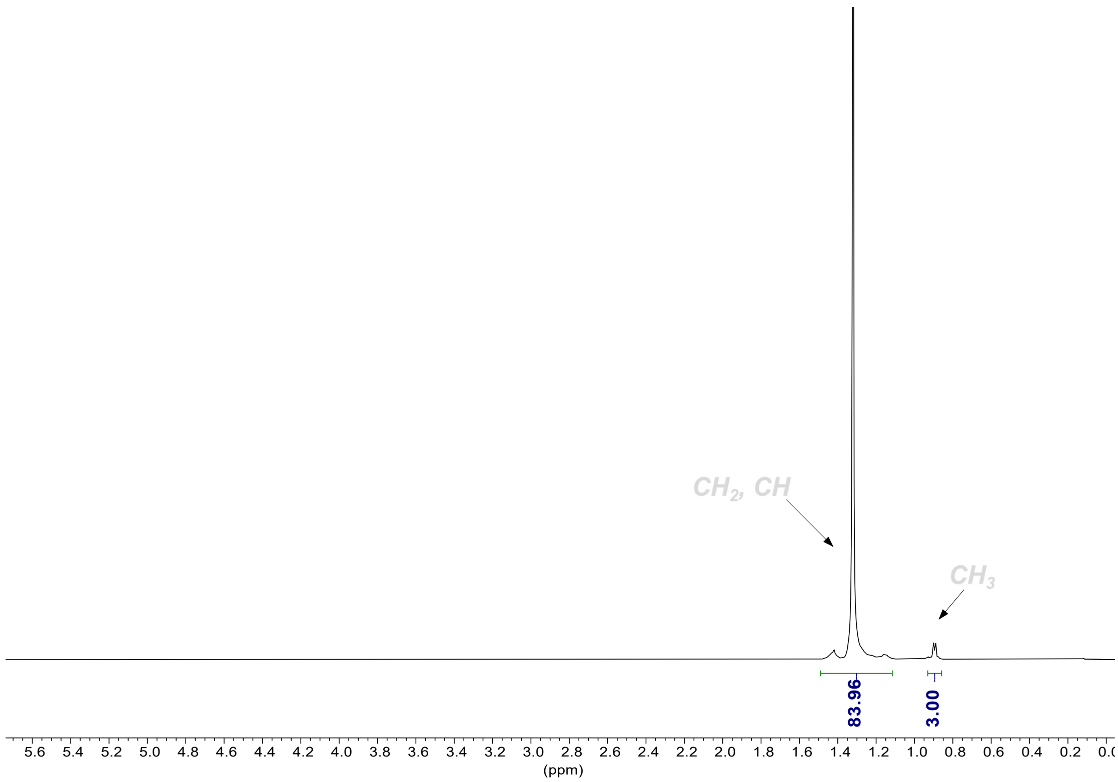



**Figure S18.** $^1$H NMR spectrum ($C_2D_2Cl_4$, 120$^o$C) of the polymer from Table 1, Entry 11.

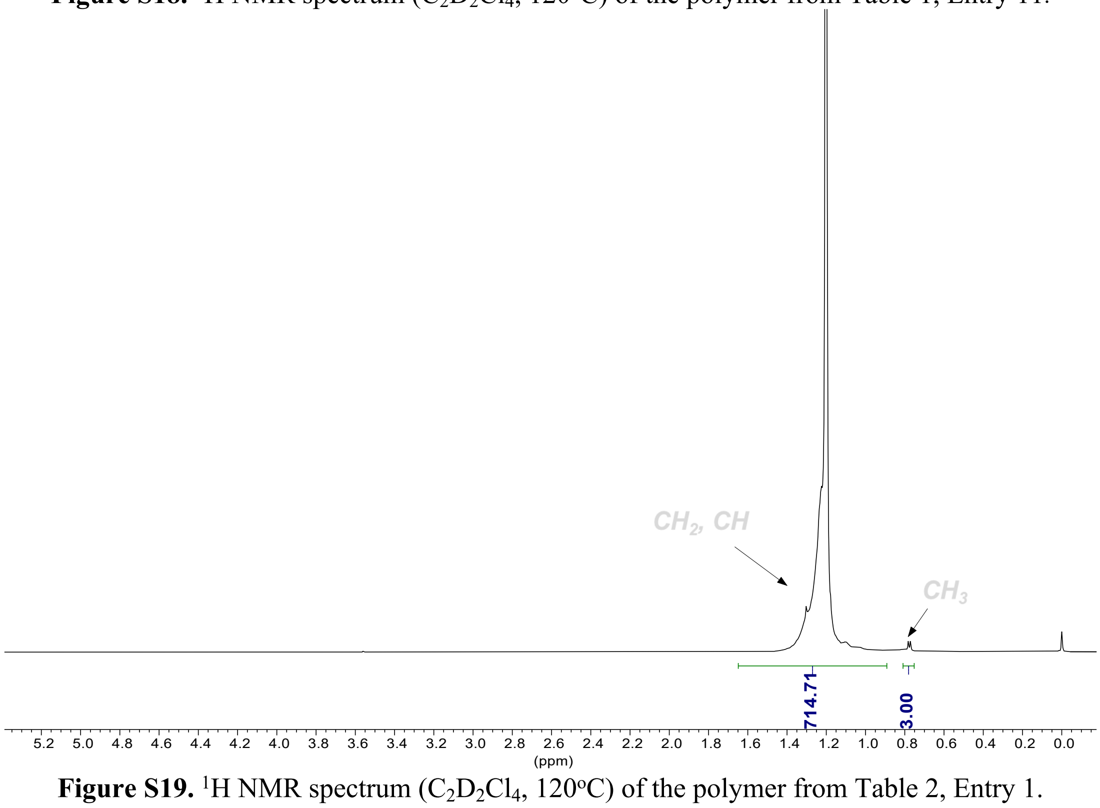



**Figure S19.** $^1$H NMR spectrum ($C_2D_2Cl_4$, 120$^o$C) of the polymer from Table 2, Entry 1.

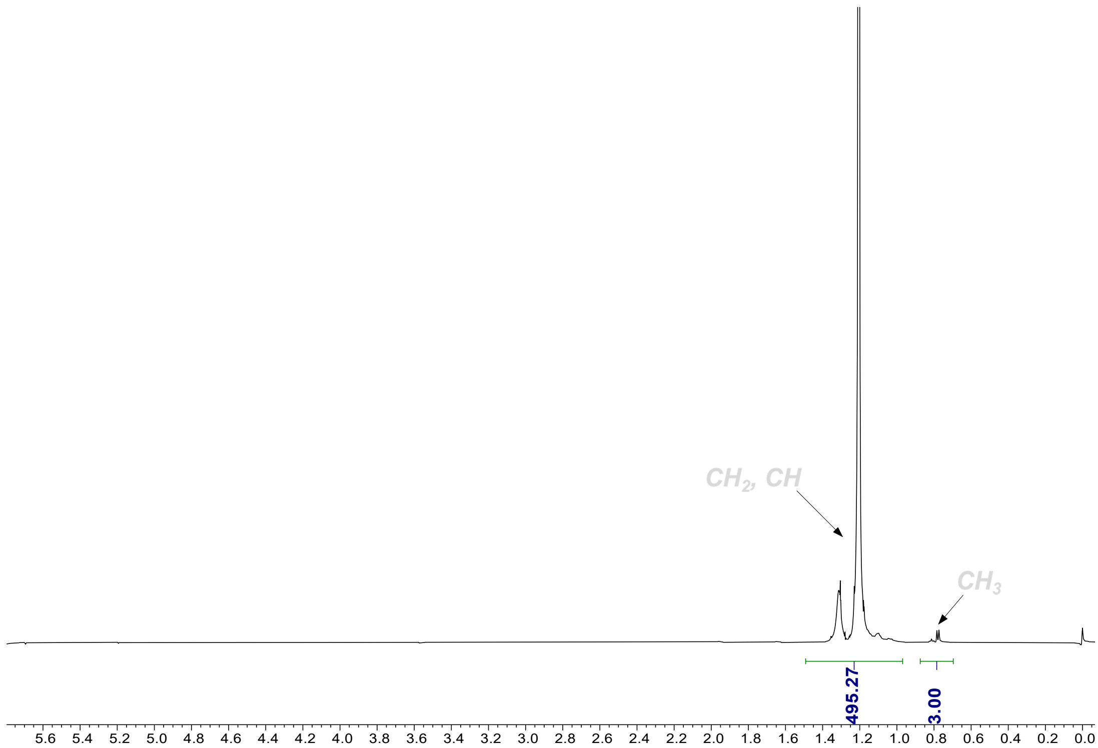



**Figure S20.** [1]H NMR spectrum ($C_2D_2Cl_4$, 120°C) of the polymer from Table 2 Entry 2.

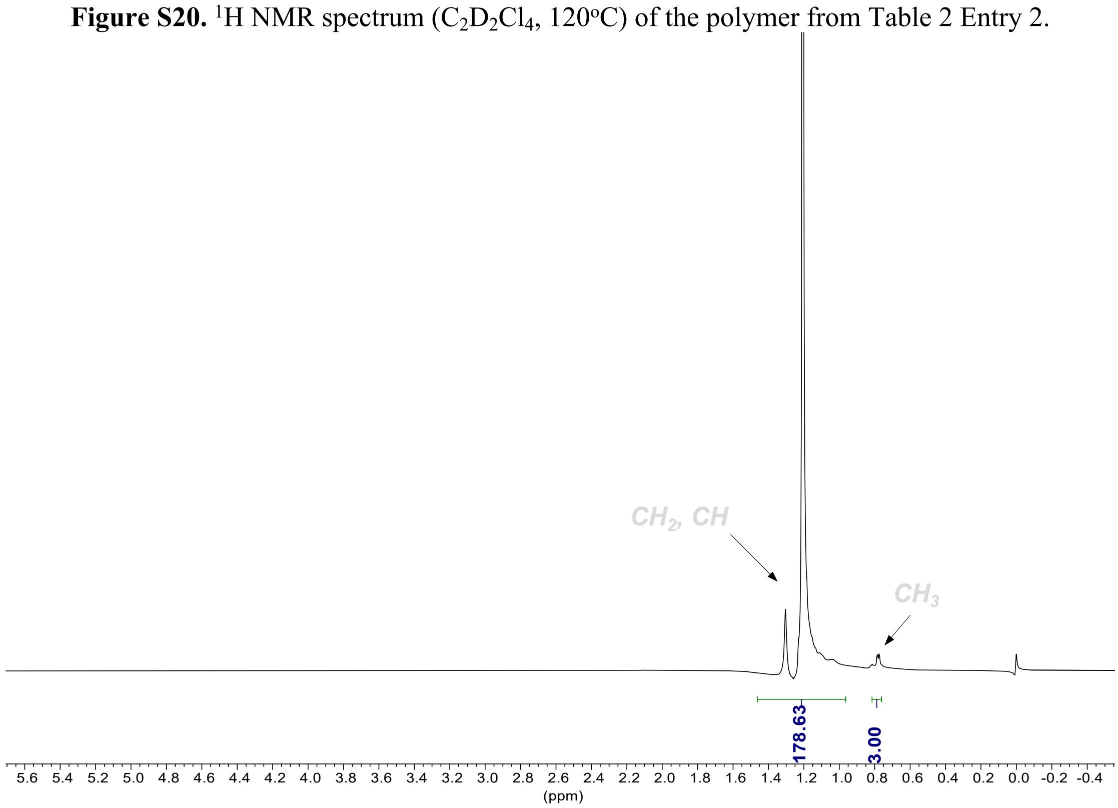



**Figure S21.** [1]H NMR spectrum ($C_2D_2Cl_4$, 120°C) of the polymer from Table 2, Entry 3.

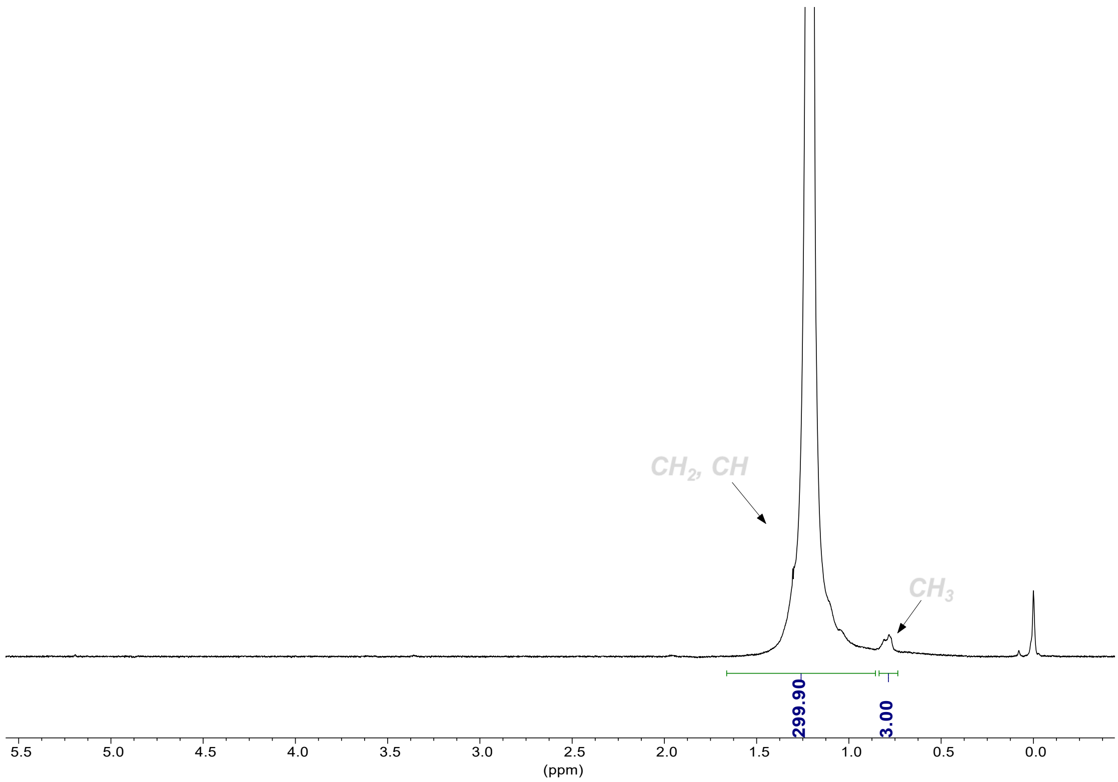



**Figure S22.** [1]H NMR spectrum ($C_2D_2Cl_4$, 120°C) of the polymer from Table 2, Entry 4.

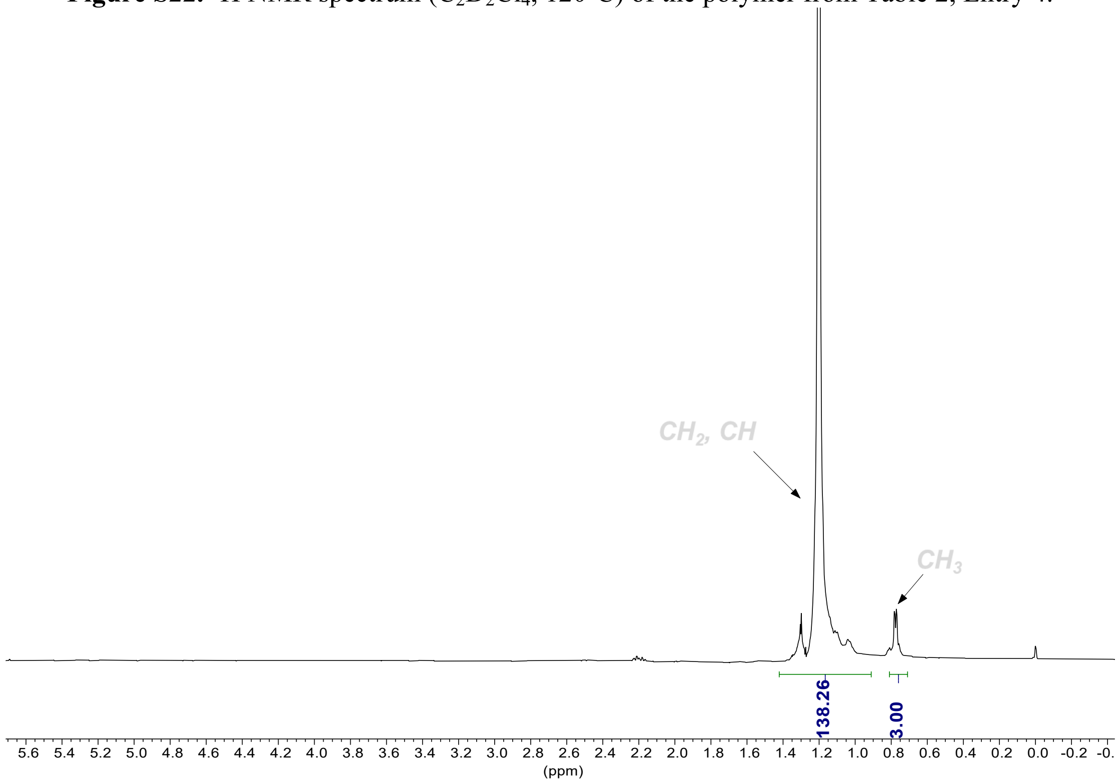



**Figure S23.** [1]H NMR spectrum ($C_2D_2Cl_4$, 120°C) of the polymer from Table 2, Entry 5.

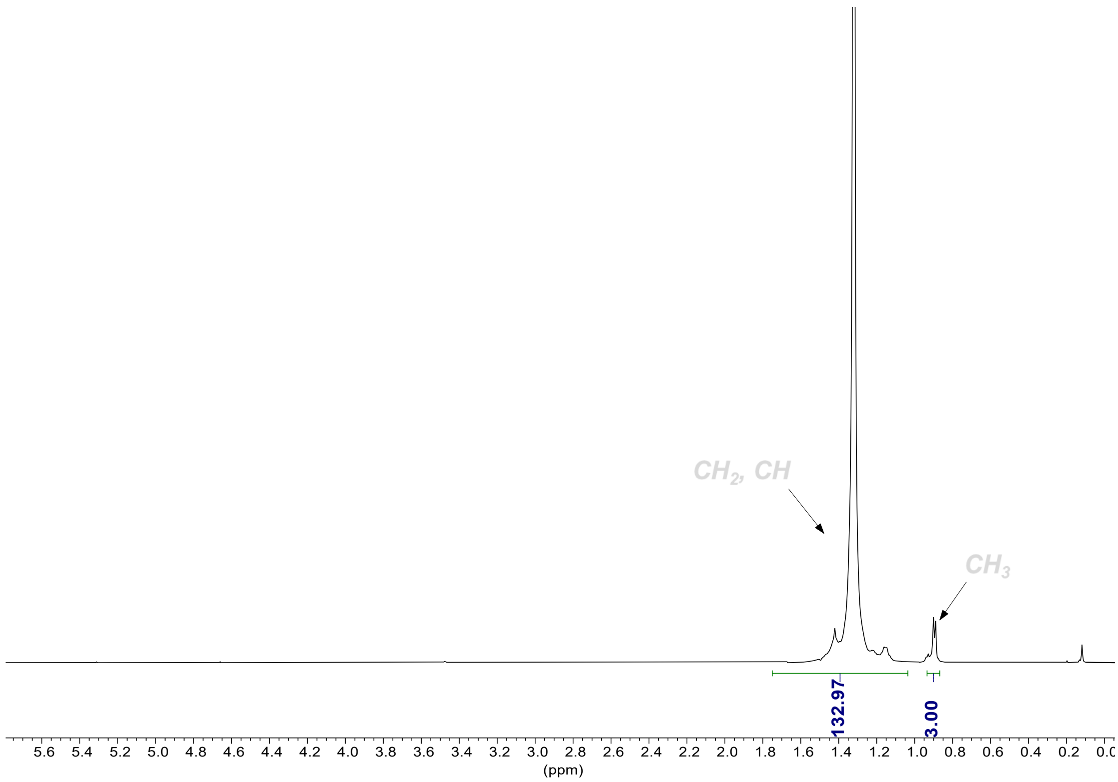


**Figure S24.** $^{1}H$ NMR spectrum ($C_2D_2Cl_4$, 120$^{o}$C) of the polymer from Table 2, Entry 6.

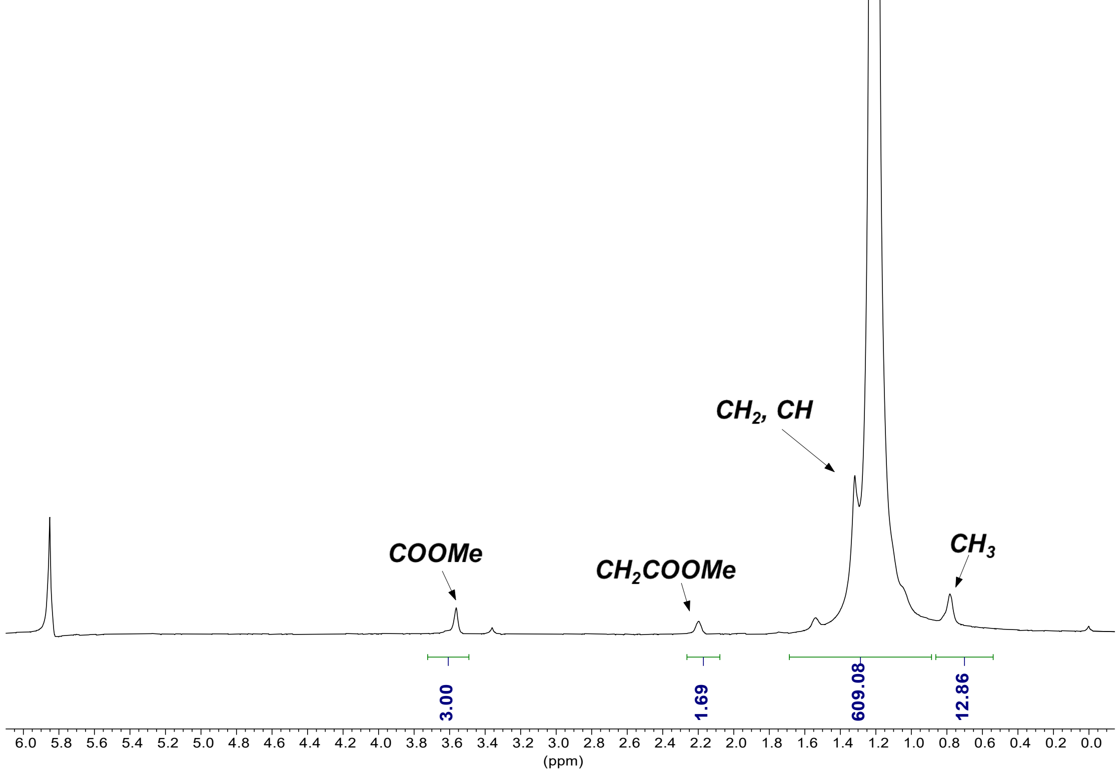


**Figure S25.** $^{1}H$ NMR spectrum ($C_2D_2Cl_4$, 120$^{o}$C) of the polymer from Table 3, Entry 1.

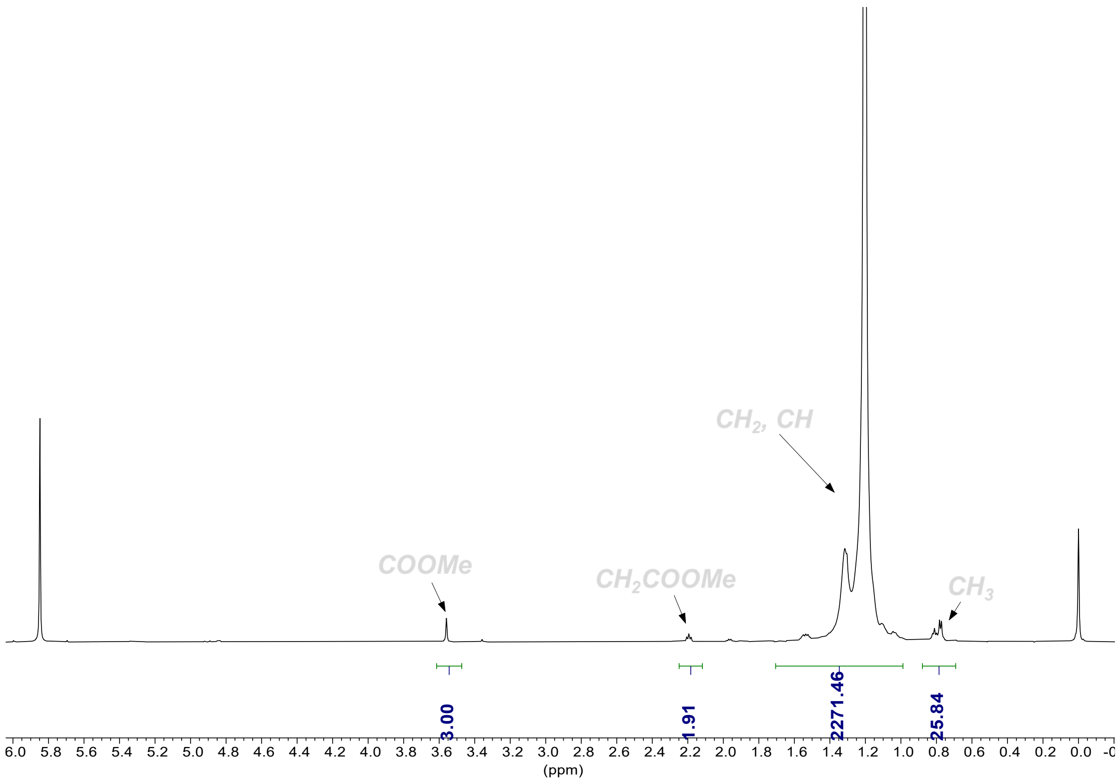



**Figure S26.** $^{1}H$ NMR spectrum ($C_2D_2Cl_4$, 120°C) of the polymer from Table 3, Entry 2.

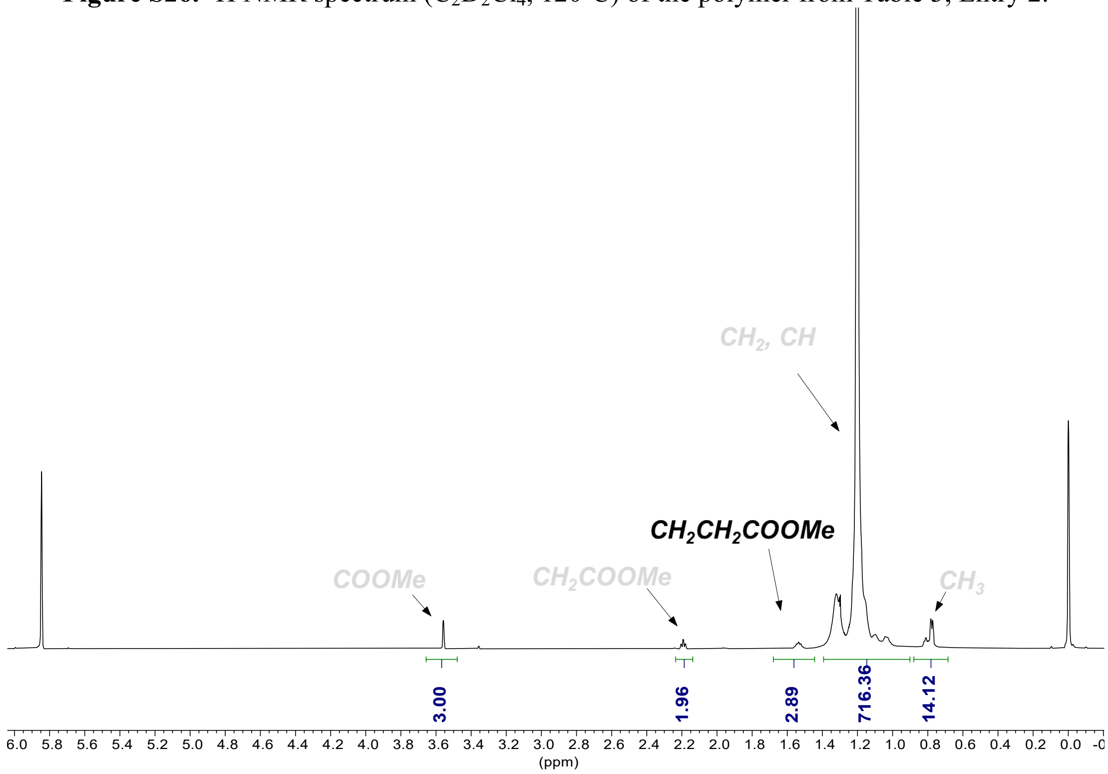



**Figure S27.** $^{1}H$ NMR spectrum ($C_2D_2Cl_4$, 120°C) of the polymer from Table 3, Entry 3.

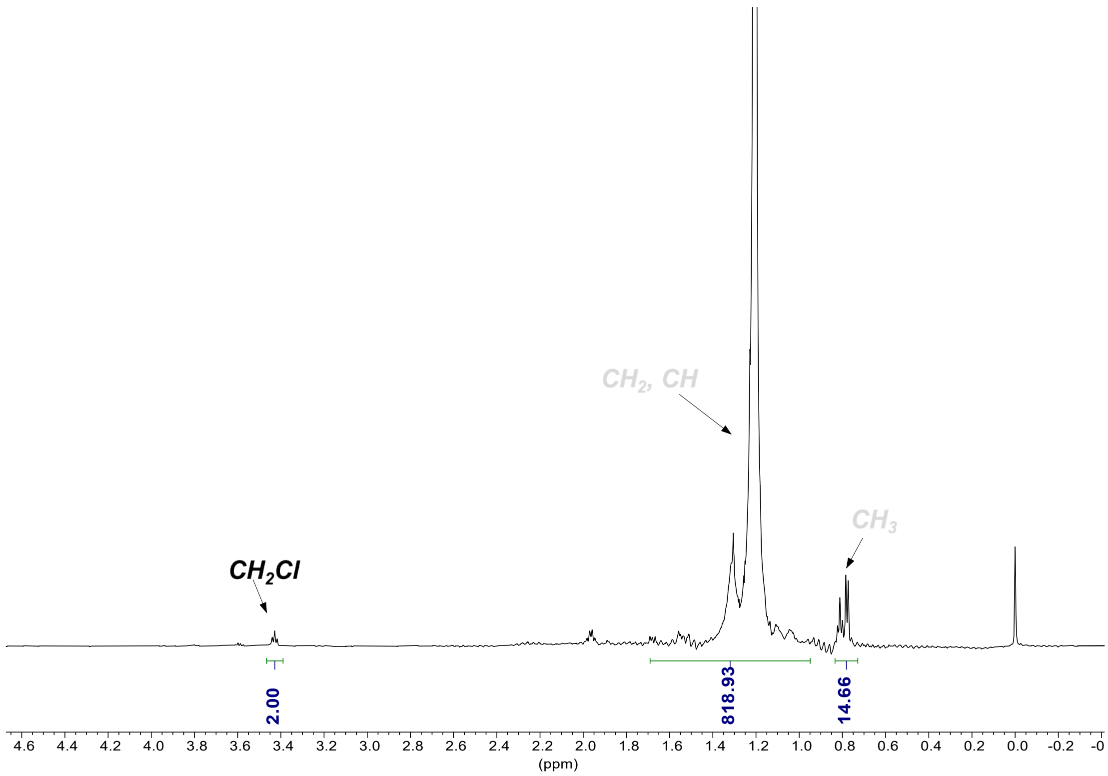



**Figure S28.** $^1$H NMR spectrum ($C_2D_2Cl_4$, 120$^o$C) of the polymer from Table 3, Entry 5.

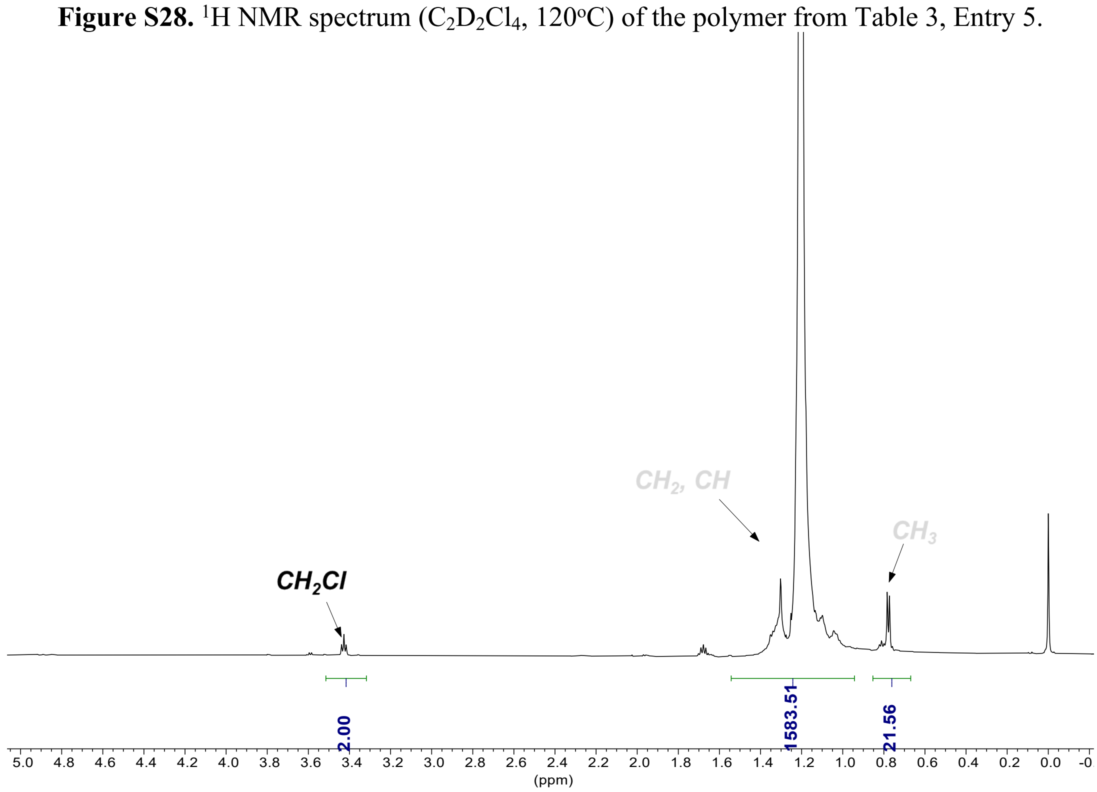



**Figure S29.** $^1$H NMR spectrum ($C_2D_2Cl_4$, 120$^o$C) of the polymer from Table 3, Entry 6.

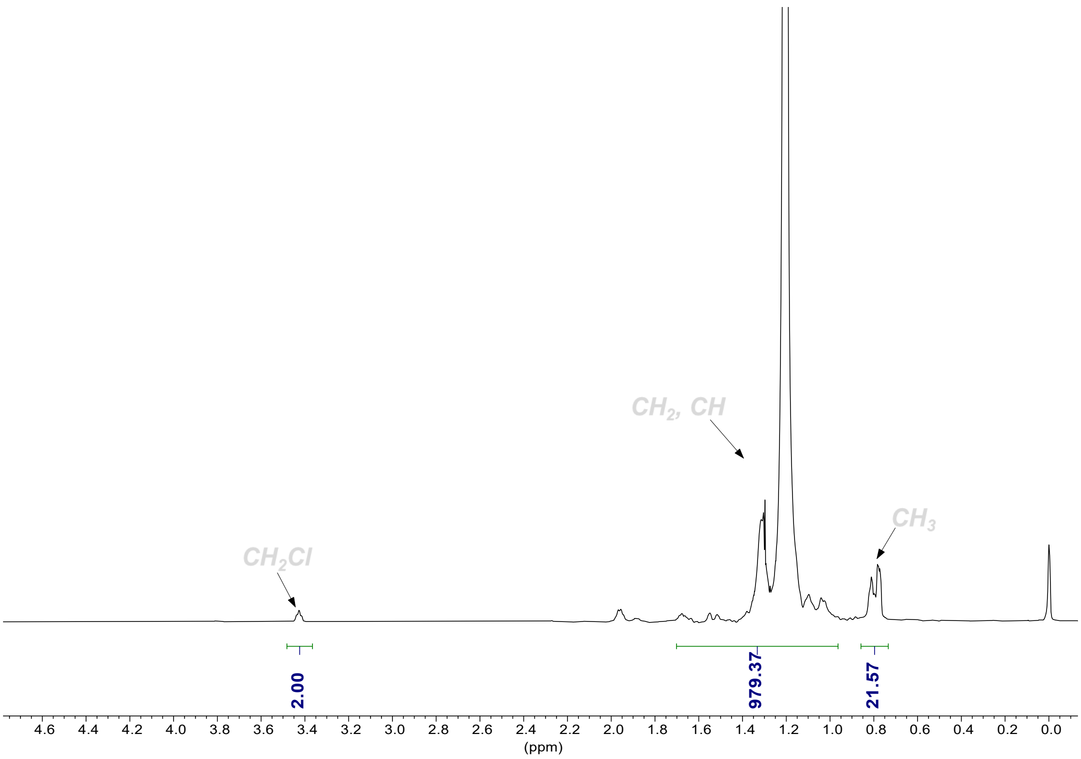
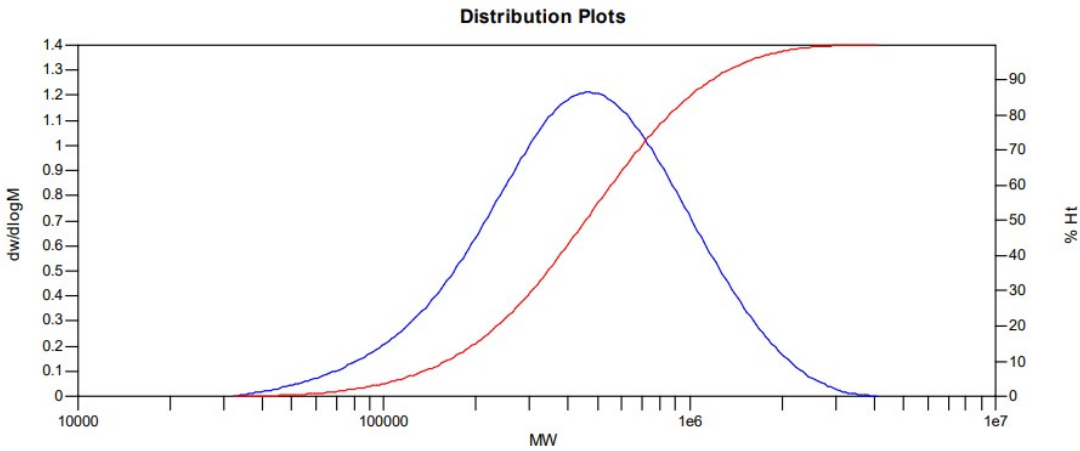



**Figure S30.** $^1$H NMR spectrum ($C_2D_2Cl_4$, 120°C) of the polymer from Table 3, Entry 7.

## 4. GPC Curves of the (Co)Polymers



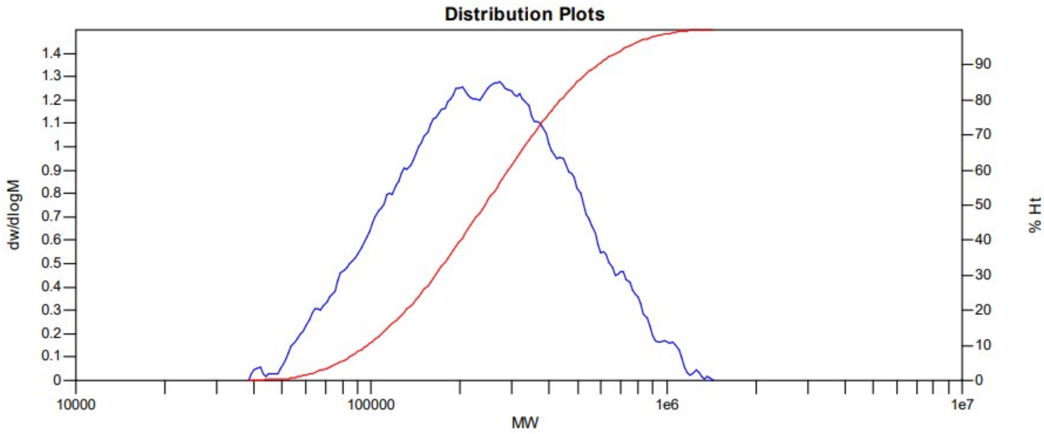

**MW Averages**

| Peak No | Mp | Mn | Mw | Mz | Mz+1 | Mv | PD |
|---|---|---|---|---|---|---|---|
| 1 | 458912 | 319725 | 576973 | 929626 | 1334015 | 531595 | 1.80459 |

**Processed Peaks**

| Peak No | Name | Start RT (mins) | Max RT (mins) | End RT (mins) | Pk Height (mV) | % Height | Area (mV.secs) | % Area |
|---|---|---|---|---|---|---|---|---|
| 1 | | 10.37 | 11.93 | 13.83 | -132.904 | 0 | 10850.9 | 100 |

**Figure S31.** GPC of the polymer from Table 1, Entry 3.



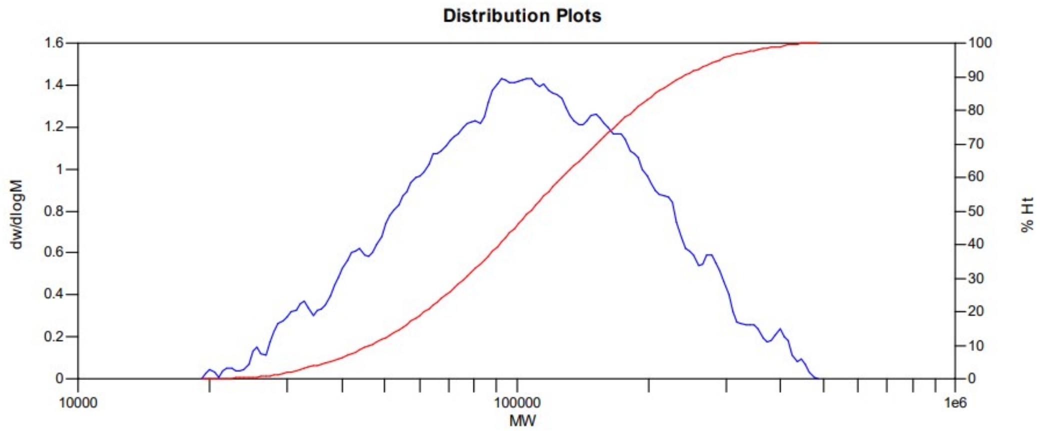

**MW Averages**

| Peak No | Mp | Mn | Mw | Mz | Mz+1 | Mv | PD |
|---|---|---|---|---|---|---|---|
| 1 | 271707 | 189485 | 295830 | 438283 | 588415 | 276740 | 1.56123 |

**Processed Peaks**

| Peak No | Name | Start RT (mins) | Max RT (mins) | End RT (mins) | Pk Height (mV) | % Height | Area (mV.secs) | % Area |
|---|---|---|---|---|---|---|---|---|
| 1 | | 11.53 | 12.77 | 14.22 | -4.0308 | 0 | 322.639 | 100 |

**Figure S32.** GPC of the polymer from Table 1, Entry 4.



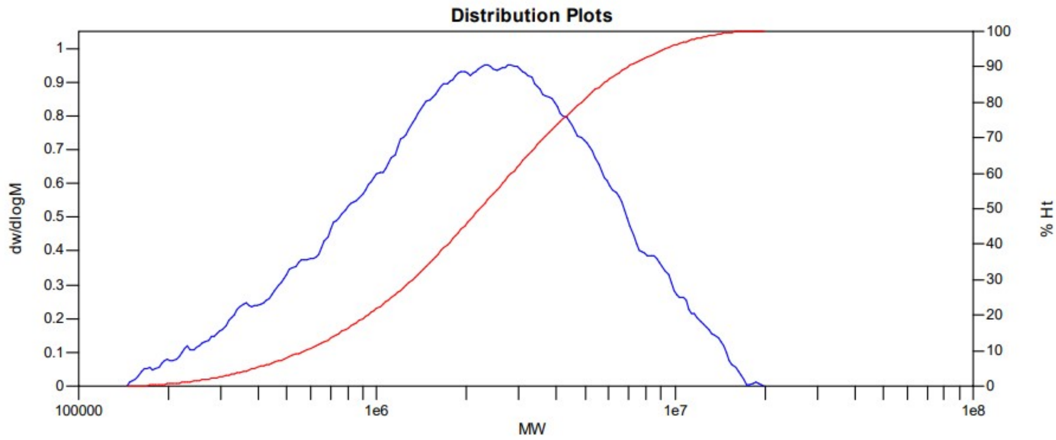

**MW Averages**

| Peak No | Mp | Mn | Mw | Mz | Mz+1 | Mv | PD |
|---|---|---|---|---|---|---|---|
| 1 | 105638 | 87147 | 126735 | 175968 | 226301 | 119897 | 1.45427 |

**Processed Peaks**

| Peak No | Name | Start RT (mins) | Max RT (mins) | End RT (mins) | Pk Height (mV) | % Height | Area (mV.secs) | % Area |
|---|---|---|---|---|---|---|---|---|
| 1 | | 12.33 | 13.57 | 14.73 | -2.6553 | 0 | 189.994 | 100 |

**Figure S33.** GPC of the polymer from Table 1, Entry 5.



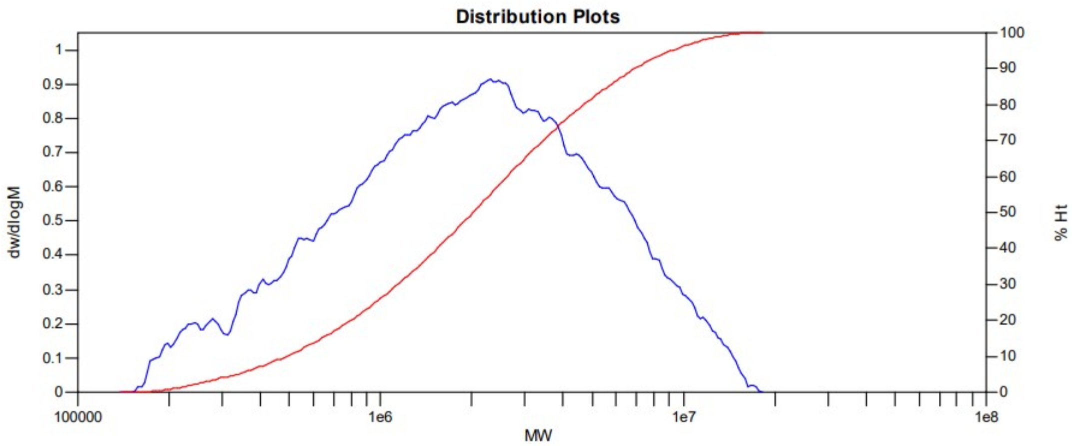

**MW Averages**

| Peak No | Mp | Mn | Mw | Mz | Mz+1 | Mv | PD |
|---|---|---|---|---|---|---|---|
| 1 | 2755865 | 1308206 | 3091338 | 5662897 | 8161525 | 2760245 | 2.36304 |

**Processed Peaks**

| Peak No | Name | Start RT (mins) | Max RT (mins) | End RT (mins) | Pk Height (mV) | % Height | Area (mV.secs) | % Area |
|---|---|---|---|---|---|---|---|---|
| 1 | | 9.58 | 11.18 | 13.23 | -6.72501 | 0 | 724.867 | 100 |

**Figure S34.** GPC of the polymer from Table 1, Entry 6.



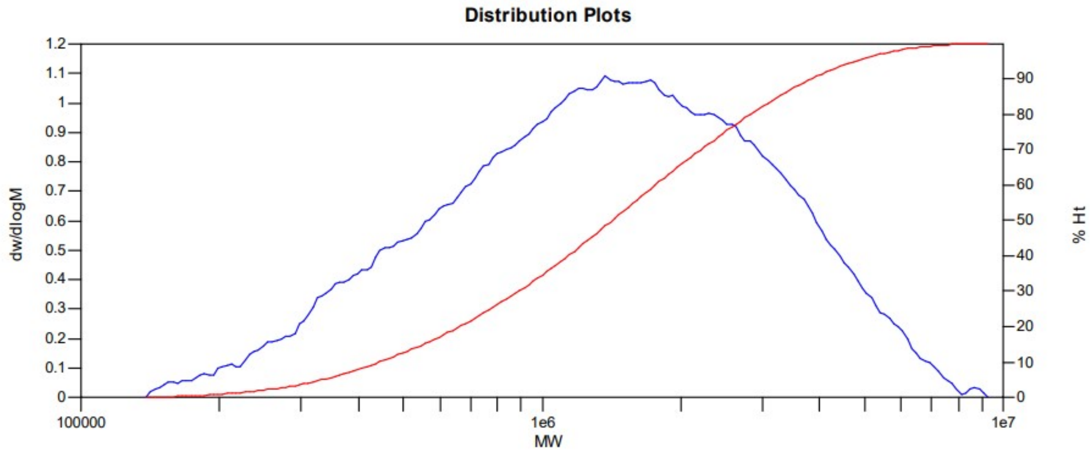

**MW Averages**

| Peak No | Mp | Mn | Mw | Mz | Mz+1 | Mv | PD |
|---|---|---|---|---|---|---|---|
| 1 | 2302024 | 1155237 | 2939337 | 5629987 | 8115864 | 2595284 | 2.54436 |

**Processed Peaks**

| Peak No | Name | Start RT (mins) | Max RT (mins) | End RT (mins) | Pk Height (mV) | % Height | Area (mV.secs) | % Area |
|---|---|---|---|---|---|---|---|---|
| 1 | | 9.65 | 11.18 | 13.27 | -4.96734 | 0 | 556.92 | 100 |

**Figure S35.** GPC of the polymer from Table 1, Entry 7.



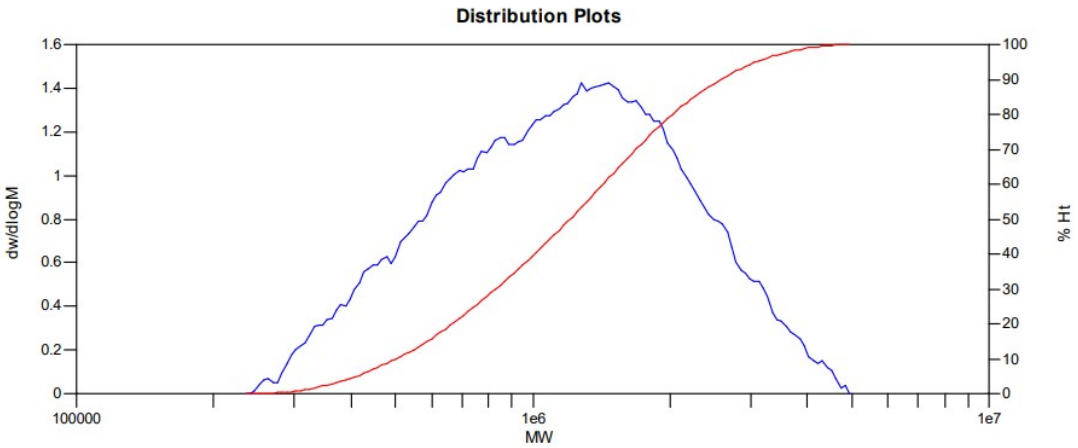

**MW Averages**

| Peak No | Mp | Mn | Mw | Mz | Mz+1 | Mv | PD |
|---|---|---|---|---|---|---|---|
| 1 | 1372252 | 960313 | 1806379 | 2886482 | 3902569 | 1657857 | 1.88103 |

**Processed Peaks**

| Peak No | Name | Start RT (mins) | Max RT (mins) | End RT (mins) | Pk Height (mV) | % Height | Area (mV.secs) | % Area |
|---|---|---|---|---|---|---|---|---|
| 1 | | 10.15 | 11.57 | 13.27 | -5.28152 | 0 | 495.702 | 100 |

**Figure S36.** GPC of the polymer from Table 1, Entry 8.



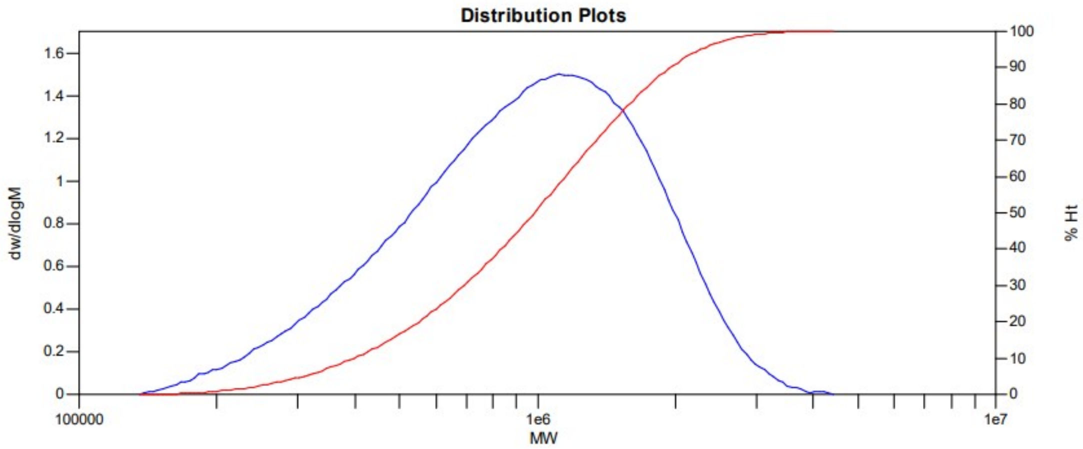

**MW Averages**

| Peak No | Mp | Mn | Mw | Mz | Mz+1 | Mv | PD |
|---|---|---|---|---|---|---|---|
| 1 | 1469691 | 958122 | 1381162 | 1880884 | 2363345 | 1309630 | 1.44153 |

**Processed Peaks**

| Peak No | Name | Start RT (mins) | Max RT (mins) | End RT (mins) | Pk Height (mV) | % Height | Area (mV.secs) | % Area |
|---|---|---|---|---|---|---|---|---|
| 1 | | 10.55 | 11.53 | 12.77 | -1.08814 | 100 | 76.8903 | 100 |

**Figure S37.** GPC of the polymer from Table 1, Entry 9.



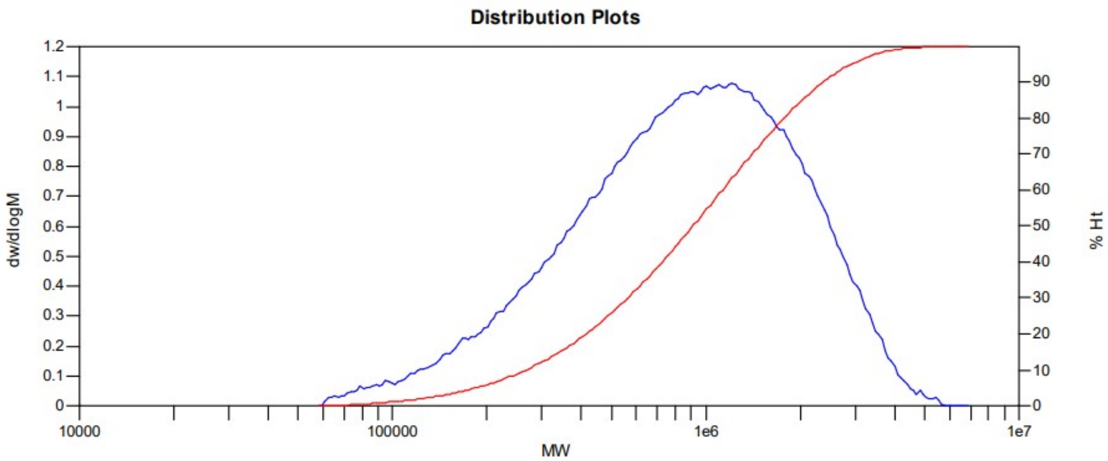

**MW Averages**

| Peak No | Mp | Mn | Mw | Mz | Mz+1 | Mv | PD |
|---|---|---|---|---|---|---|---|
| 1 | 1116325 | 754378 | 1085022 | 1429563 | 1750066 | 1033429 | 1.4383 |

**Processed Peaks**

| Peak No | Name | Start RT (mins) | Max RT (mins) | End RT (mins) | Pk Height (mV) | % Height | Area (mV.secs) | % Area |
|---|---|---|---|---|---|---|---|---|
| 1 | | 10.63 | 11.63 | 13.17 | -4.43771 | 100 | 297.501 | 100 |

**Figure S38.** GPC of the polymer from Table 1, Entry 10.



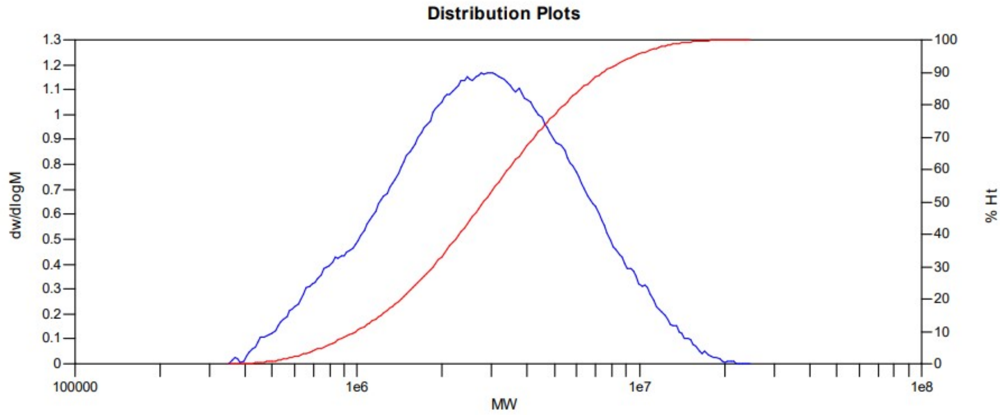

**MW Averages**

| Peak No | Mp | Mn | Mw | Mz | Mz+1 | Mv | PD |
|---|---|---|---|---|---|---|---|
| 1 | 1214911 | 567540 | 1128835 | 1779069 | 2371207 | 1036392 | 1.989 |

**Processed Peaks**

| Peak No | Name | Start RT (mins) | Max RT (mins) | End RT (mins) | Pk Height (mV) | % Height | Area (mV.secs) | % Area |
|---|---|---|---|---|---|---|---|---|
| 1 | | 10.47 | 11.70 | 13.87 | -1.54917 | 0 | 141.828 | 100 |

**Figure S39.** GPC of the polymer from Table 1, Entry 11.



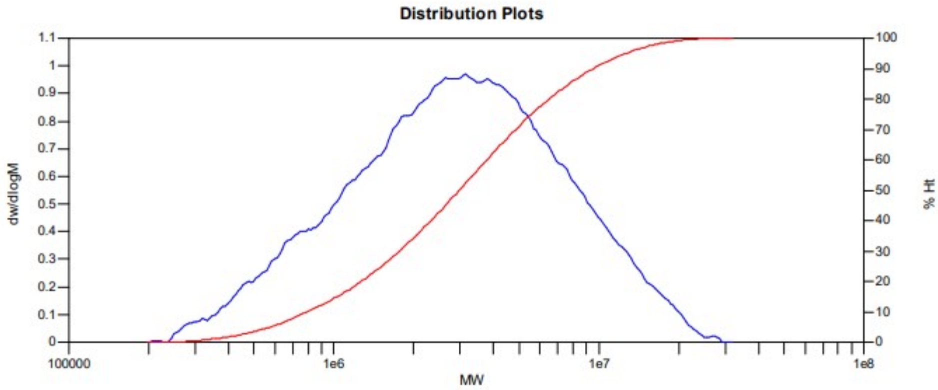

**MW Averages**

| Peak No | Mp | Mn | Mw | Mz | Mz+1 | Mv | PD |
|---|---|---|---|---|---|---|---|
| 1 | 3024013 | 2053223 | 3609907 | 5839957 | 8286149 | 3322856 | 1.75817 |

**Processed Peaks**

| Peak No | Name | Start RT (mins) | Max RT (mins) | End RT (mins) | Pk Height (mV) | % Height | Area (mV.secs) | % Area |
|---|---|---|---|---|---|---|---|---|
| 1 | | 9.55 | 11.20 | 12.58 | -1.63985 | 0 | 140.364 | 100 |

**Figure S40.** GPC of the polymer from Table 2, Entry 1.



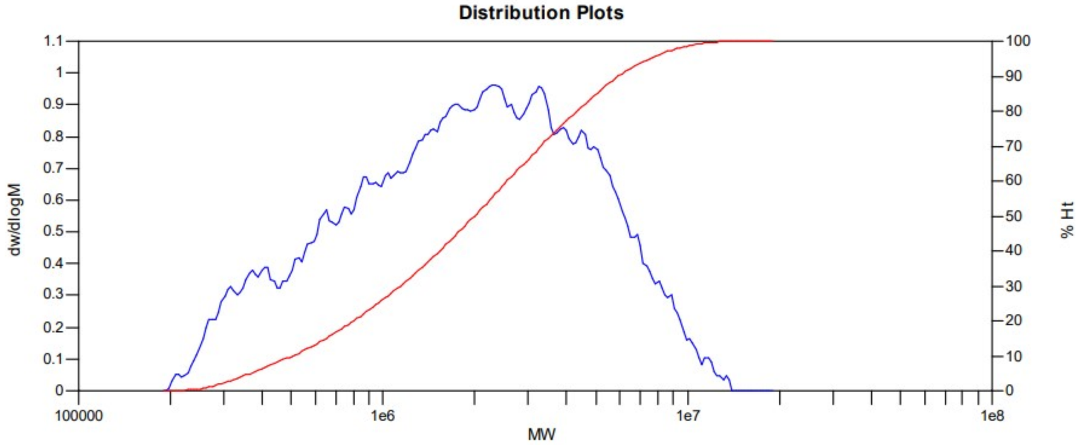

**MW Averages**

| Peak No | Mp | Mn | Mw | Mz | Mz+1 | Mv | PD |
|---|---|---|---|---|---|---|---|
| 1 | 3154054 | 1838435 | 4208580 | 7888188 | 11705017 | 3751599 | 2.28922 |

**Processed Peaks**

| Peak No | Name | Start RT (mins) | Max RT (mins) | End RT (mins) | Pk Height (mV) | % Height | Area (mV.secs) | % Area |
|---|---|---|---|---|---|---|---|---|
| 1 | | 9.23 | 10.95 | 13.00 | -7.74507 | 100 | 818.516 | 100 |

**Figure S41.** GPC of the polymer from Table 2, Entry 2.



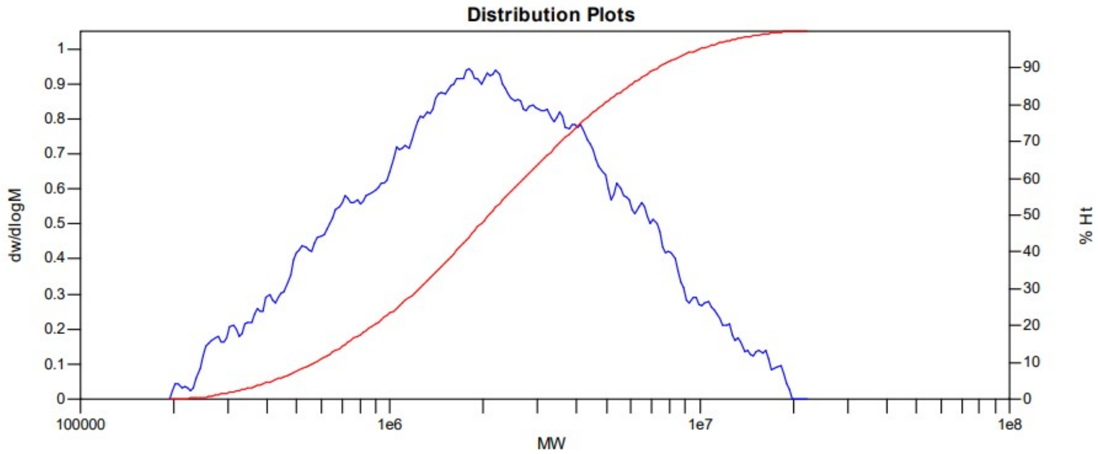

**MW Averages**

| Peak No | Mp | Mn | Mw | Mz | Mz+1 | Mv | PD |
|---|---|---|---|---|---|---|---|
| 1 | 2286556 | 1208126 | 2671623 | 4620168 | 6353474 | 2405191 | 2.21138 |

**Processed Peaks**

| Peak No | Name | Start RT (mins) | Max RT (mins) | End RT (mins) | Pk Height (mV) | % Height | Area (mV.secs) | % Area |
|---|---|---|---|---|---|---|---|---|
| 1 | | 9.27 | 10.78 | 12.57 | -2.16747 | 0 | 222.72 | 100 |

**Figure S42.** GPC of the polymer from Table 2, Entry 3.



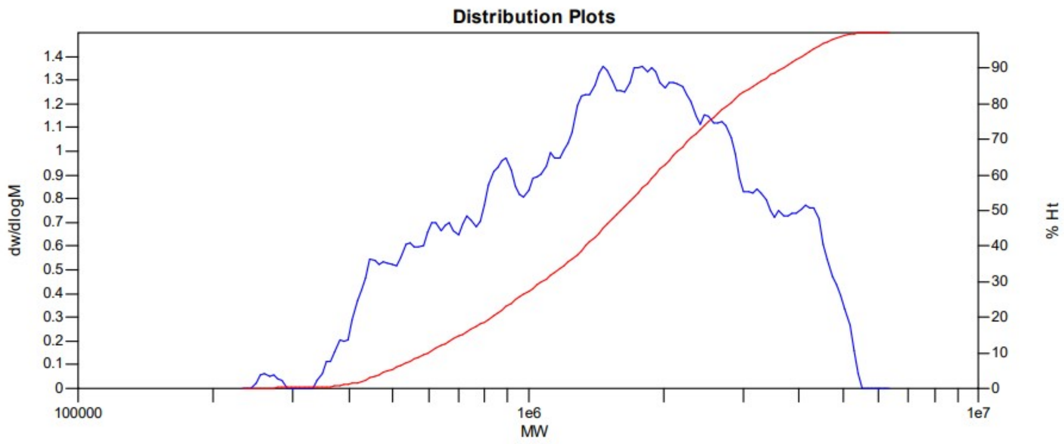

**MW Averages**

| Peak No | Mp | Mn | Mw | Mz | Mz+1 | Mv | PD |
|---|---|---|---|---|---|---|---|
| 1 | 1797447 | 1325029 | 3145617 | 6243567 | 9425934 | 2774284 | 2.374 |

**Processed Peaks**

| Peak No | Name | Start RT (mins) | Max RT (mins) | End RT (mins) | Pk Height (mV) | % Height | Area (mV.secs) | % Area |
|---|---|---|---|---|---|---|---|---|
| 1 | | 9.50 | 11.37 | 13.02 | -2.98765 | 0 | 324.558 | 100 |

**Figure S43.** GPC of the polymer from Table 2, Entry 4.



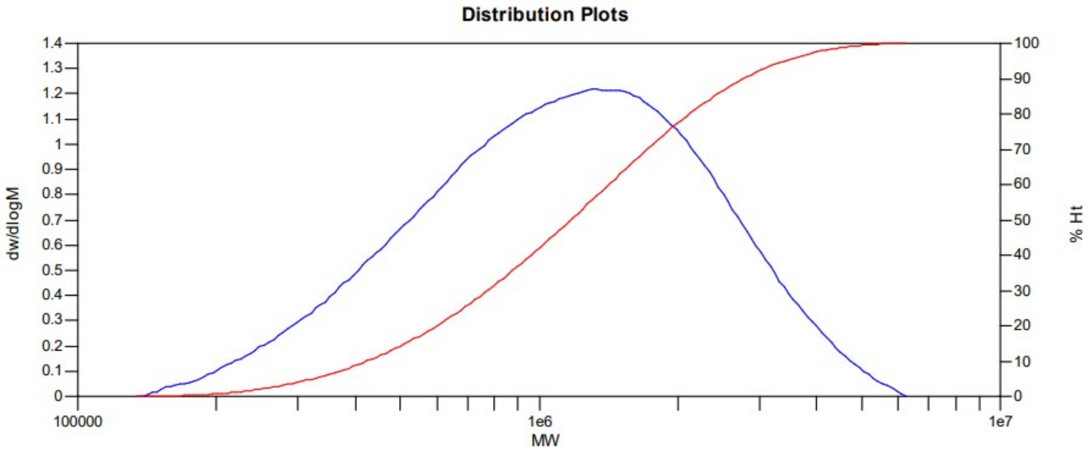

**MW Averages**

| Peak No | Mp | Mn | Mw | Mz | Mz+1 | Mv | PD |
|---|---|---|---|---|---|---|---|
| 1 | 1468046 | 1217711 | 1850155 | 2555228 | 3154741 | 1745439 | 1.51937 |

**Processed Peaks**

| Peak No | Name | Start RT (mins) | Max RT (mins) | End RT (mins) | Pk Height (mV) | % Height | Area (mV.secs) | % Area |
|---|---|---|---|---|---|---|---|---|
| 1 | | 10.43 | 11.52 | 12.88 | -1.6458 | 0 | 123.836 | 100 |

**Figure S44.** GPC of the polymer from Table 2, Entry 5.



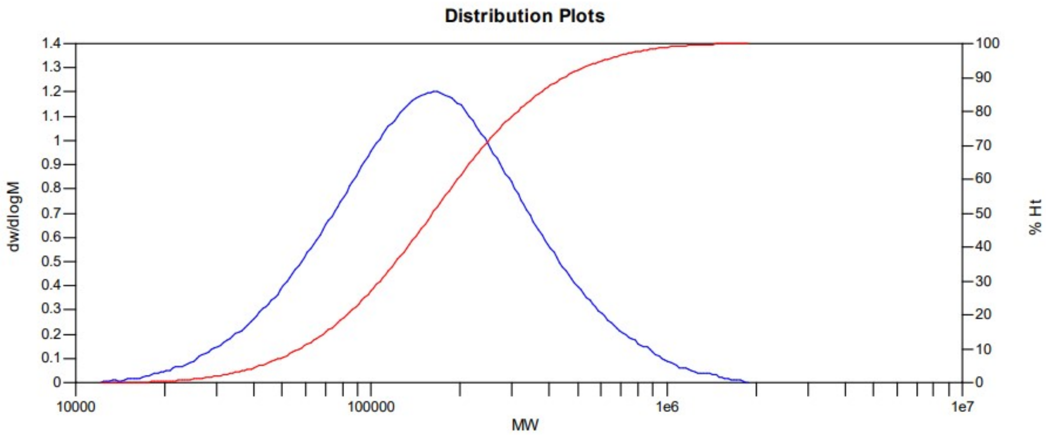

**MW Averages**

| Peak No | Mp | Mn | Mw | Mz | Mz+1 | Mv | PD |
|---|---|---|---|---|---|---|---|
| 1 | 1334025 | 854878 | 1403682 | 2068214 | 2713981 | 1310505 | 1.64197 |

**Processed Peaks**

| Peak No | Name | Start RT (mins) | Max RT (mins) | End RT (mins) | Pk Height (mV) | % Height | Area (mV.secs) | % Area |
|---|---|---|---|---|---|---|---|---|
| 1 | | 10.53 | 11.63 | 13.27 | -6.54621 | 100 | 528.858 | 100 |

**Figure S45.** GPC of the polymer from Table 2, Entry 6.



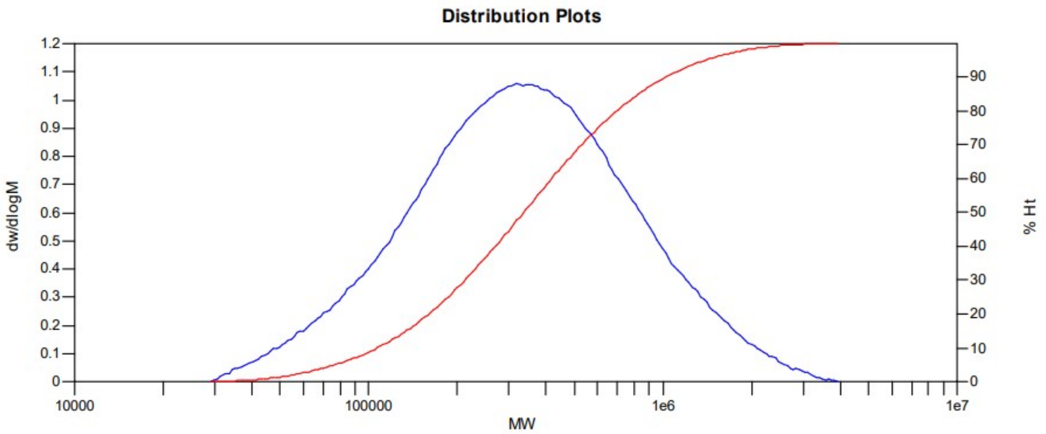

**MW Averages**

| Peak No | Mp | Mn | Mw | Mz | Mz+1 | Mv | PD |
|---|---|---|---|---|---|---|---|
| 1 | 162640 | 115677 | 217301 | 394031 | 639531 | 197328 | 1.87852 |

**Processed Peaks**

| Peak No | Name | Start RT (mins) | Max RT (mins) | End RT (mins) | Pk Height (mV) | % Height | Area (mV.secs) | % Area |
|---|---|---|---|---|---|---|---|---|
| 1 | | 11.38 | 13.13 | 14.98 | -5.50793 | 0 | 451.264 | 100 |

**Figure S46.** GPC of the polymer from Table 3, Entry 1.



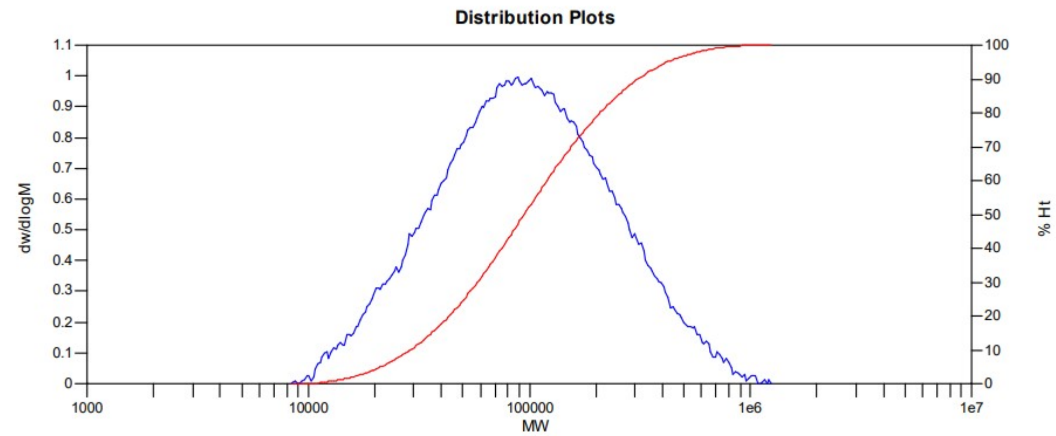

**MW Averages**

| Peak No | Mp | Mn | Mw | Mz | Mz+1 | Mv | PD |
|---|---|---|---|---|---|---|---|
| 1 | 318872 | 227695 | 470410 | 885606 | 1398536 | 423788 | 2.06597 |

**Processed Peaks**

| Peak No | Name | Start RT (mins) | Max RT (mins) | End RT (mins) | Pk Height (mV) | % Height | Area (mV.secs) | % Area |
|---|---|---|---|---|---|---|---|---|
| 1 | | 10.80 | 12.60 | 14.32 | -3.76624 | 0 | 352.021 | 100 |

**Figure S47.** GPC of the polymer from Table 3, Entry 2.



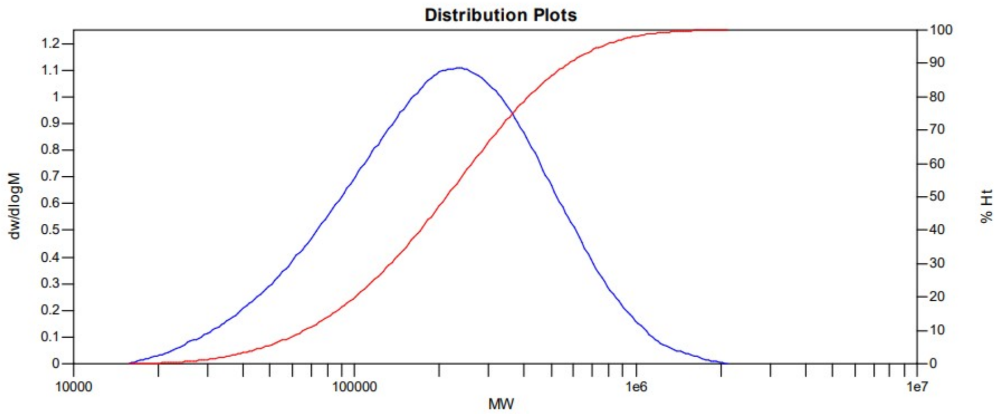

**MW Averages**

| Peak No | Mp | Mn | Mw | Mz | Mz+1 | Mv | PD |
|---|---|---|---|---|---|---|---|
| 1 | 88552 | 63954 | 138933 | 273604 | 436111 | 123531 | 2.17239 |

**Processed Peaks**

| Peak No | Name | Start RT (mins) | Max RT (mins) | End RT (mins) | Pk Height (mV) | % Height | Area (mV.secs) | % Area |
|---|---|---|---|---|---|---|---|---|
| 1 | | 11.68 | 13.57 | 15.25 | -0.842176 | 0 | 83.0909 | 100 |

**Figure S48.** GPC of the polymer from Table 3, Entry 3.



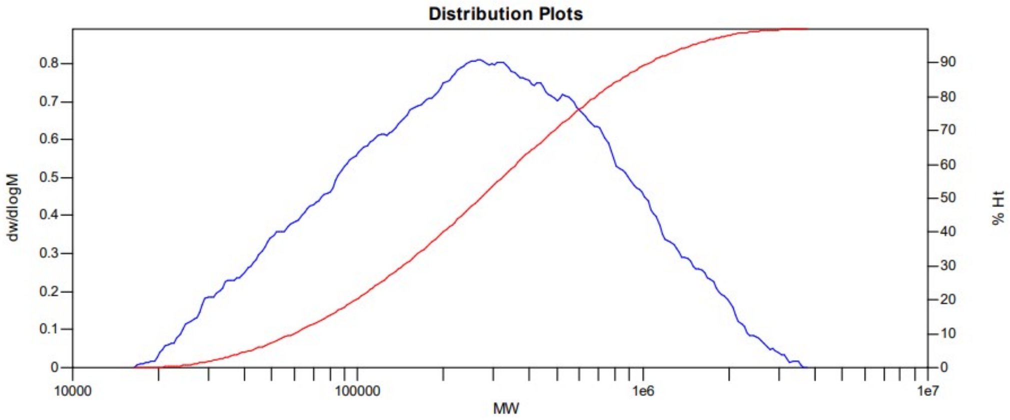

**MW Averages**

| Peak No | Mp | Mn | Mw | Mz | Mz+1 | Mv | PD |
|---|---|---|---|---|---|---|---|
| 1 | 234957 | 140689 | 276046 | 474036 | 708730 | 251311 | 1.9621 |

**Processed Peaks**

| Peak No | Name | Start RT (mins) | Max RT (mins) | End RT (mins) | Pk Height (mV) | % Height | Area (mV.secs) | % Area |
|---|---|---|---|---|---|---|---|---|
| 1 | | 11.17 | 12.77 | 14.73 | -45.8558 | 0 | 4152.55 | 100 |

**Figure S49.** GPC of the polymer from Table 3, Entry 4.



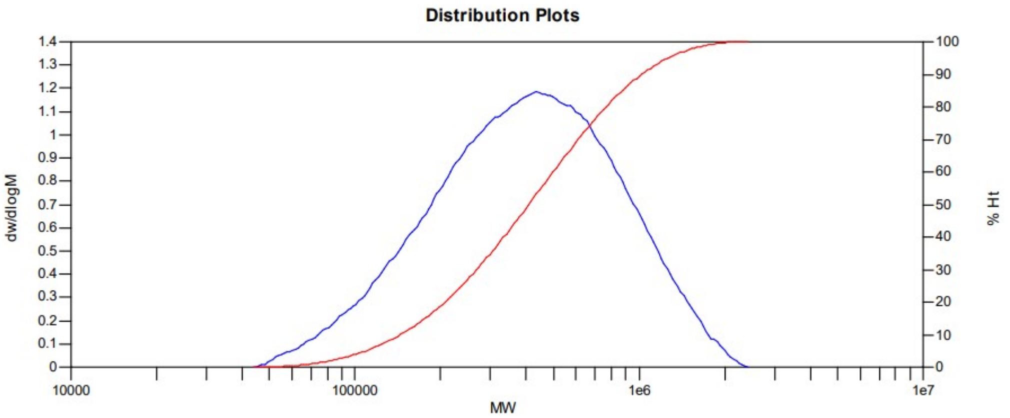

**MW Averages**

| Peak No | Mp | Mn | Mw | Mz | Mz+1 | Mv | PD |
|---|---|---|---|---|---|---|---|
| 1 | 269592 | 147147 | 434690 | 956333 | 1488920 | 373916 | 2.95412 |

**Processed Peaks**

| Peak No | Name | Start RT (mins) | Max RT (mins) | End RT (mins) | Pk Height (mV) | % Height | Area (mV.secs) | % Area |
|---|---|---|---|---|---|---|---|---|
| 1 | | 10.75 | 12.68 | 14.70 | -7.41099 | 0 | 920.079 | 100 |

**Figure S50.** GPC of the polymer from Table 3, Entry 5.



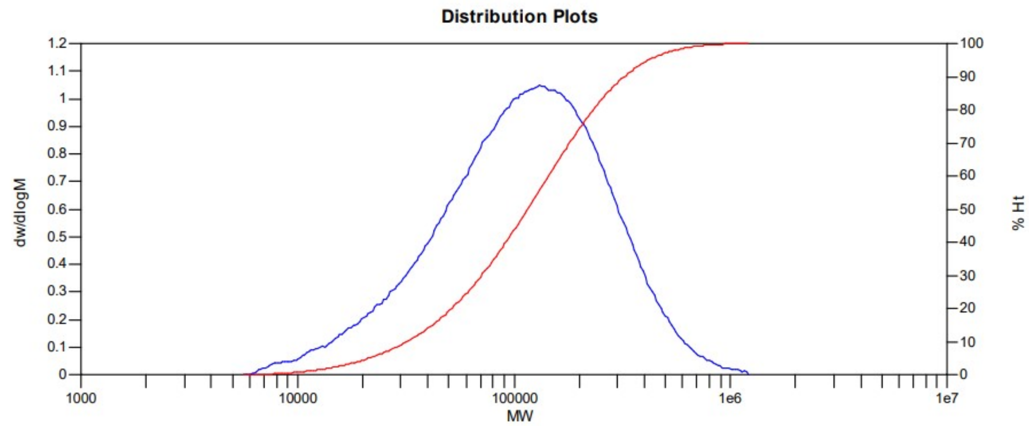

**MW Averages**

| Peak No | Mp | Mn | Mw | Mz | Mz+1 | Mv | PD |
|---|---|---|---|---|---|---|---|
| 1 | 435752 | 294812 | 503542 | 766043 | 1023724 | 467403 | 1.70801 |

**Processed Peaks**

| Peak No | Name | Start RT (mins) | Max RT (mins) | End RT (mins) | Pk Height (mV) | % Height | Area (mV.secs) | % Area |
|---|---|---|---|---|---|---|---|---|
| 1 | | 11.15 | 12.42 | 14.12 | -15.7874 | 0 | 1365.92 | 100 |

**Figure S51.** GPC of the polymer from Table 3, Entry 6.



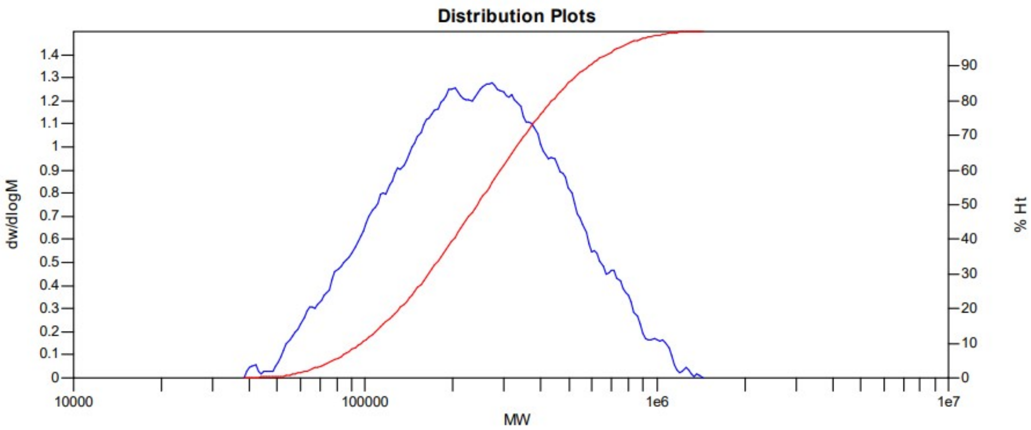

**MW Averages**

| Peak No | Mp | Mn | Mw | Mz | Mz+1 | Mv | PD |
|---|---|---|---|---|---|---|---|
| 1 | 131775 | 69176 | 152769 | 271980 | 414436 | 137875 | 2.20841 |

**Processed Peaks**

| Peak No | Name | Start RT (mins) | Max RT (mins) | End RT (mins) | Pk Height (mV) | % Height | Area (mV.secs) | % Area |
|---|---|---|---|---|---|---|---|---|
| 1 | | 11.70 | 13.28 | 15.53 | -2.97479 | 0 | 279.753 | 100 |

**Figure S52.** GPC of the polymer from Table 3, Entry 7.




**MW Averages**

| Peak No | Mp | Mn | Mw | Mz | Mz+1 | Mv | PD |
|---|---|---|---|---|---|---|---|
| 1 | 271707 | 189485 | 295830 | 438283 | 588415 | 276740 | 1.56123 |

**Processed Peaks**

| Peak No | Name | Start RT (mins) | Max RT (mins) | End RT (mins) | Pk Height (mV) | % Height | Area (mV.secs) | % Area |
|---|---|---|---|---|---|---|---|---|
| 1 | | 11.53 | 12.77 | 14.22 | -4.0308 | 0 | 322.639 | 100 |

**Figure S53.** GPC of the polymer from Table 3, Entry 8.

## 5. DSC Data of the (Co)Polymers

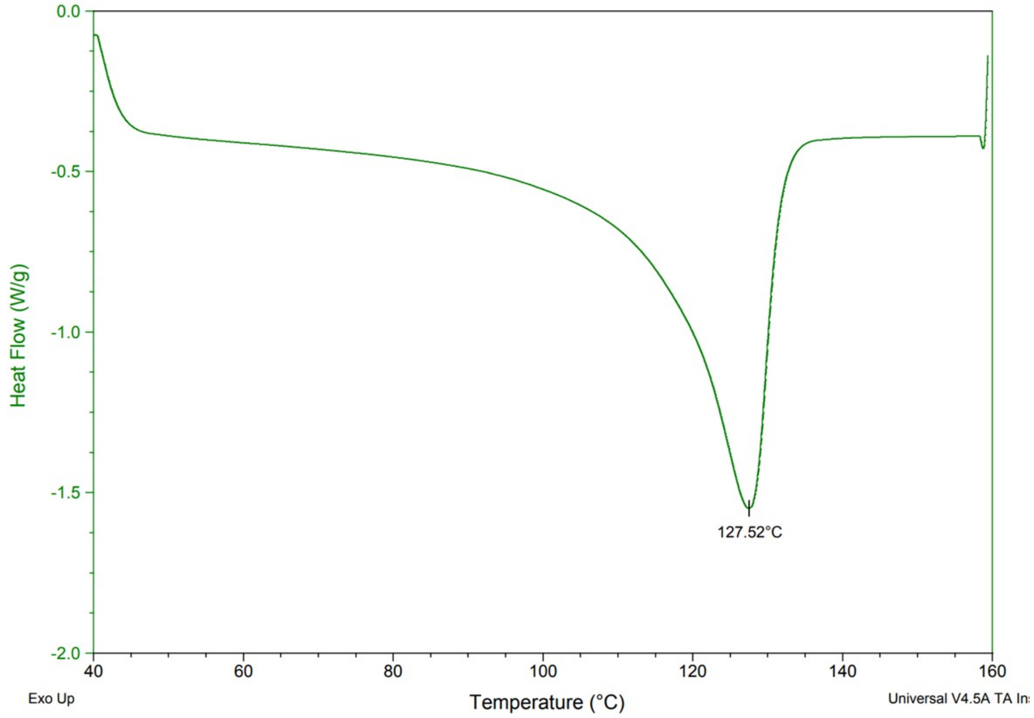



**Figure S54.** DSC of the polymer from Table 1, Entry 3.

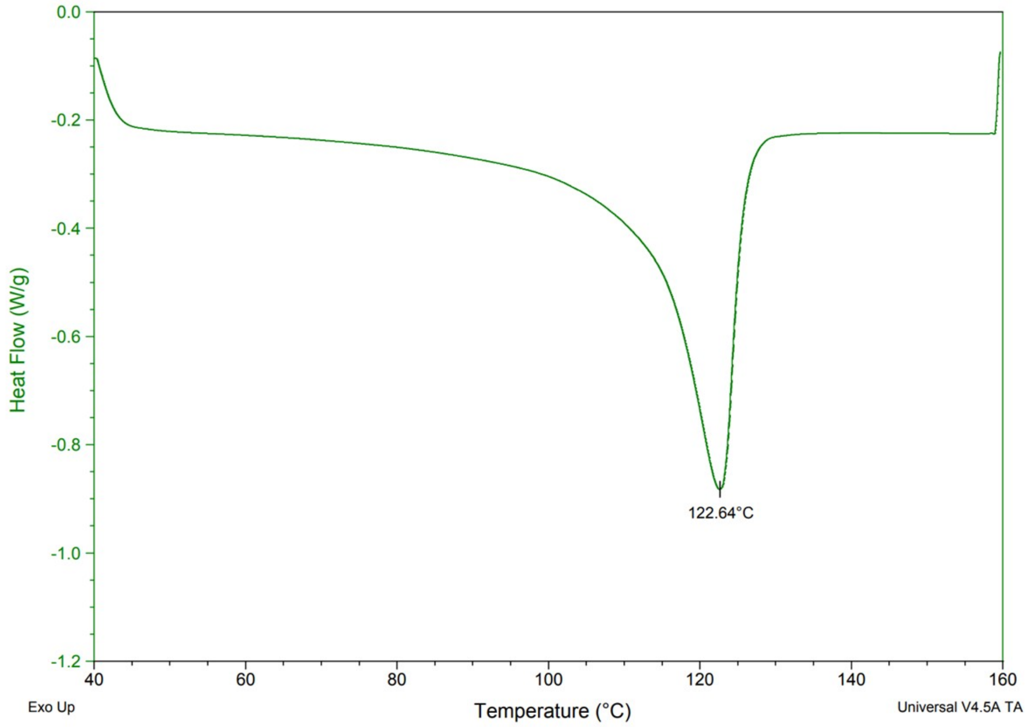



**Figure S55.** DSC of the polymer from Table 1, Entry 4.

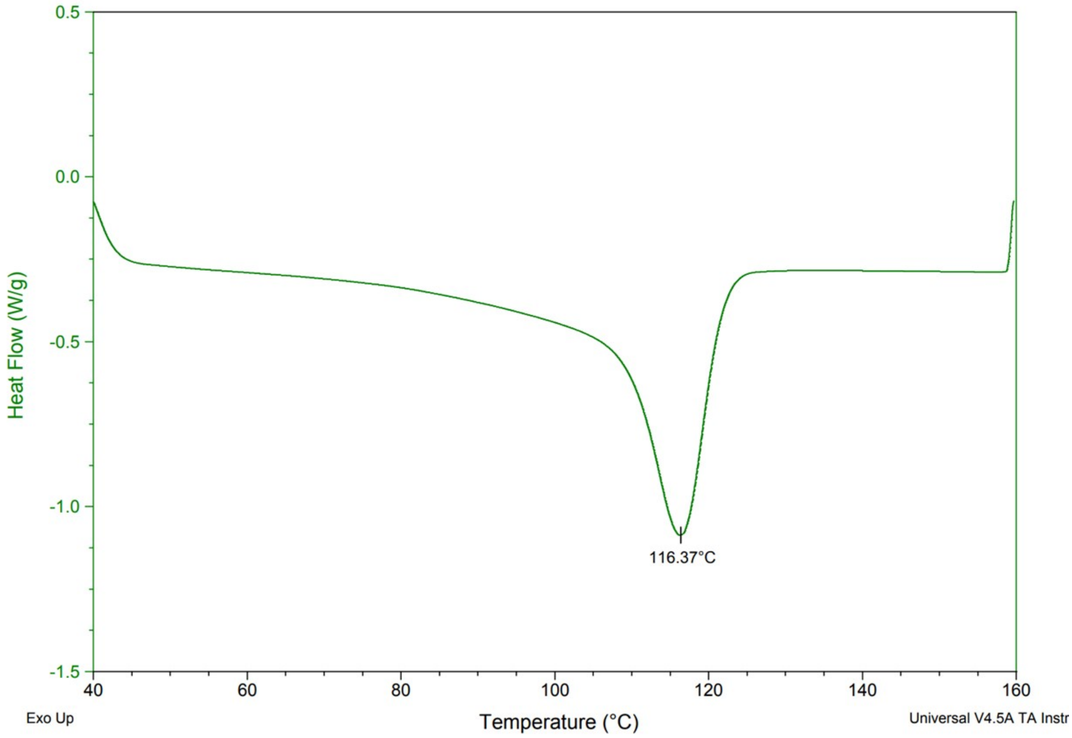



**Figure S56.** DSC of the polymer from Table 1, Entry 5.

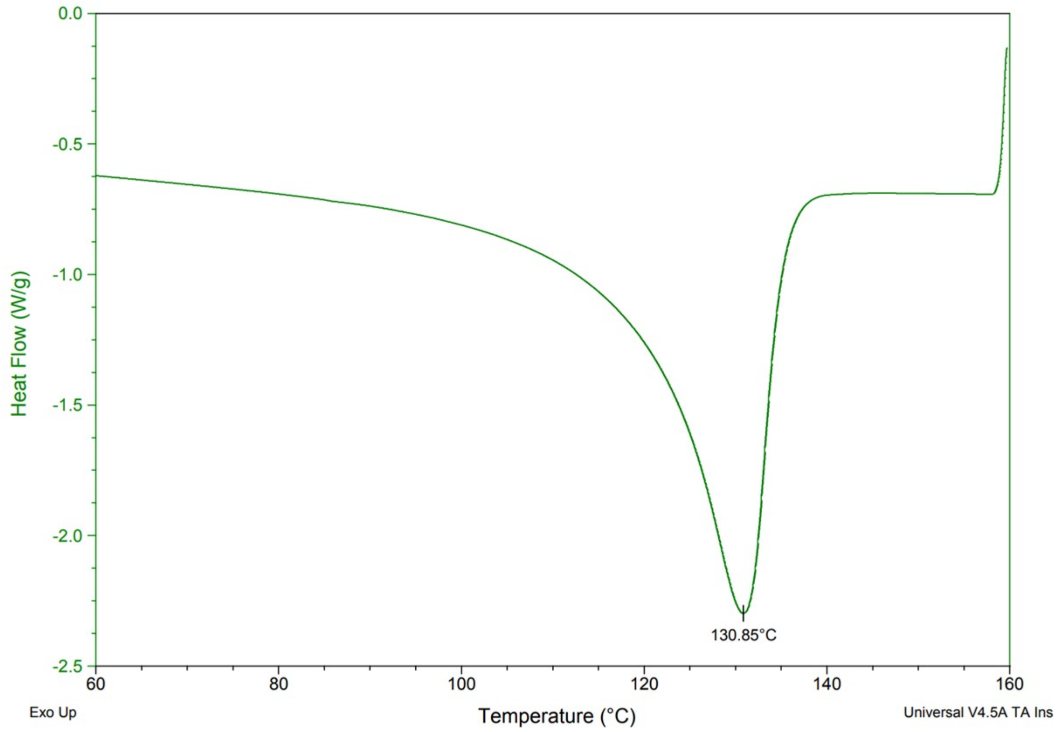



**Figure S57.** DSC of the polymer from Table 1, Entry 6.

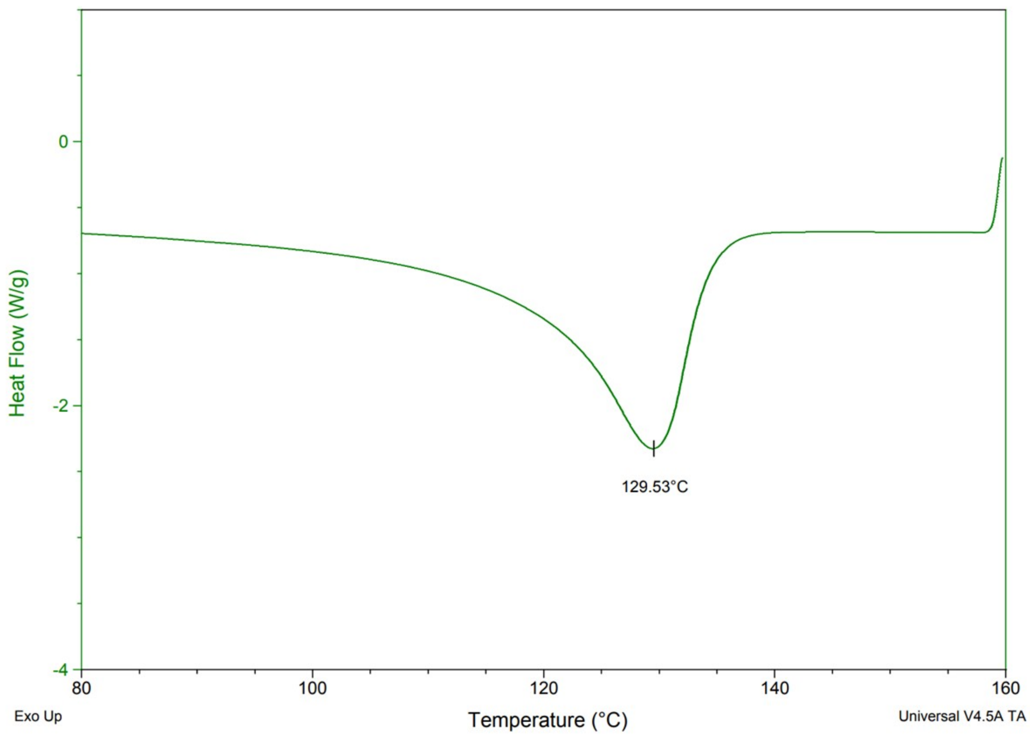



**Figure S58.** DSC of the polymer from Table 1, Entry 7.

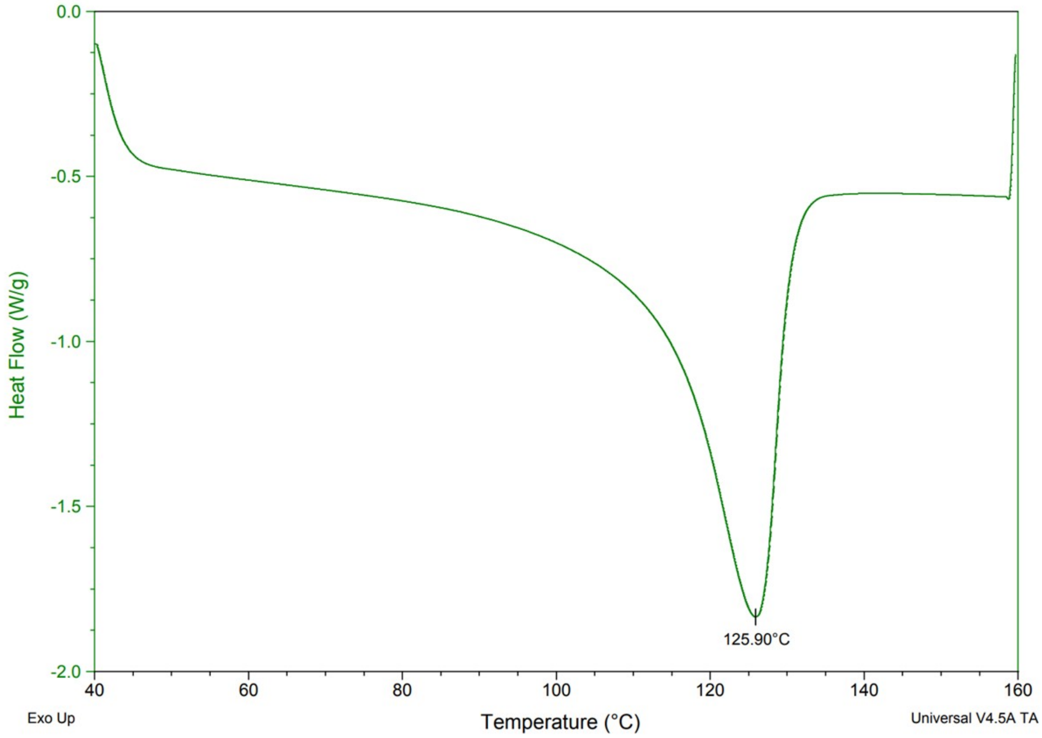



**Figure S59.** DSC of the polymer from Table 1, Entry 8.

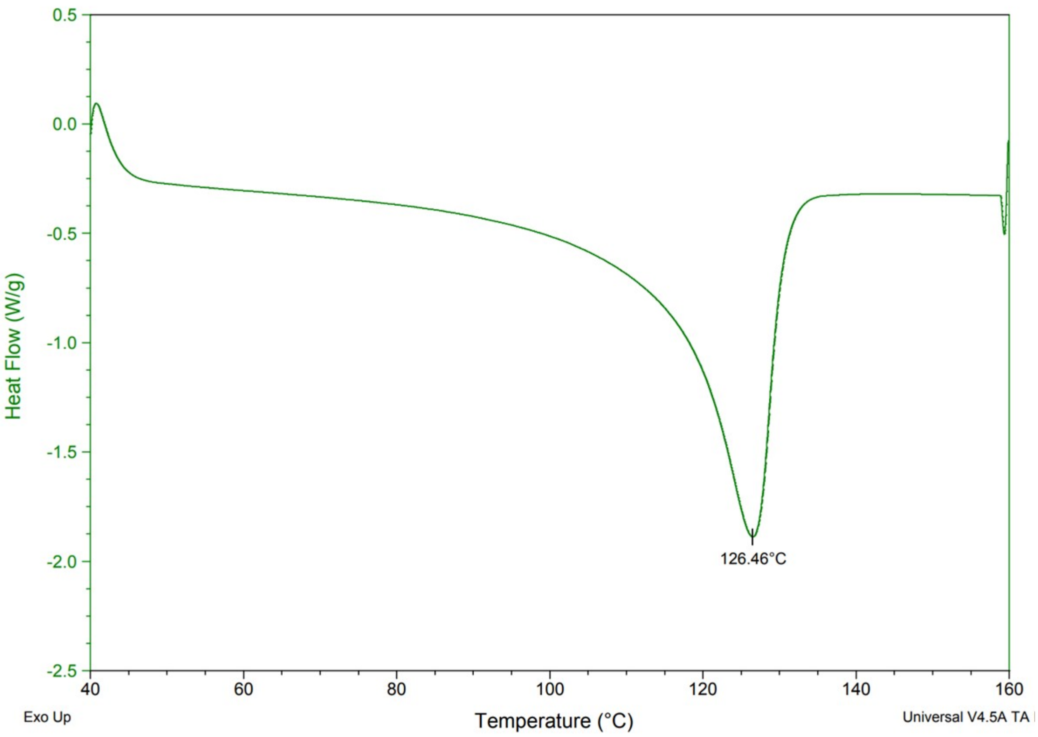



**Figure S60.** DSC of the polymer from Table 1, Entry 9.

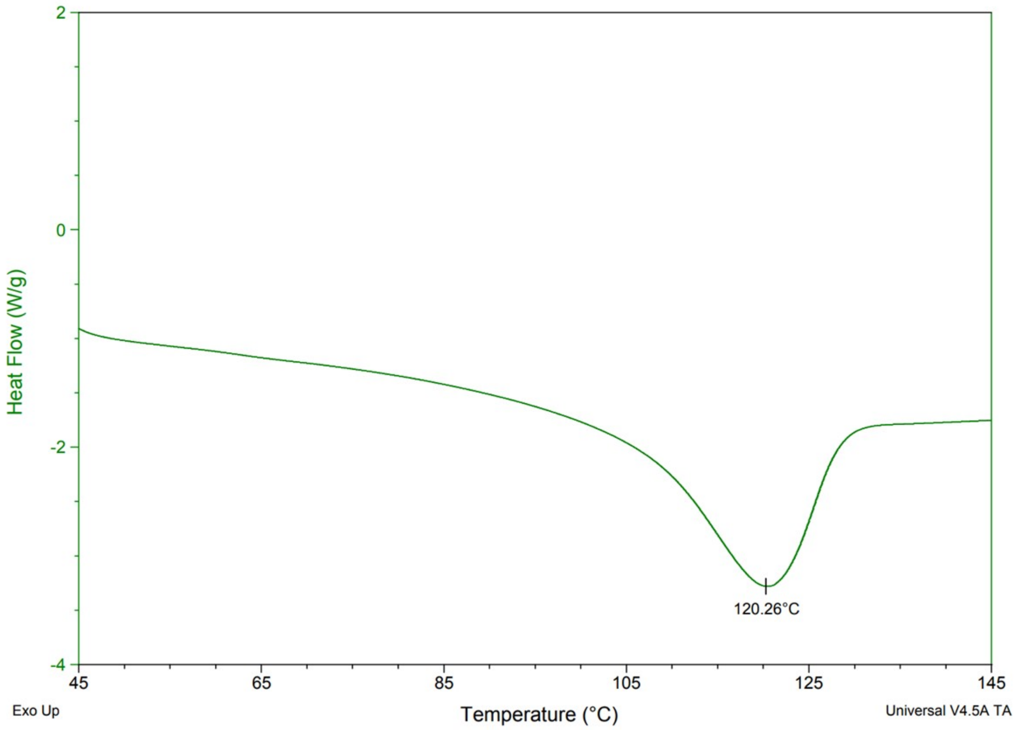



**Figure S61.** DSC of the polymer from Table 1, Entry 10.

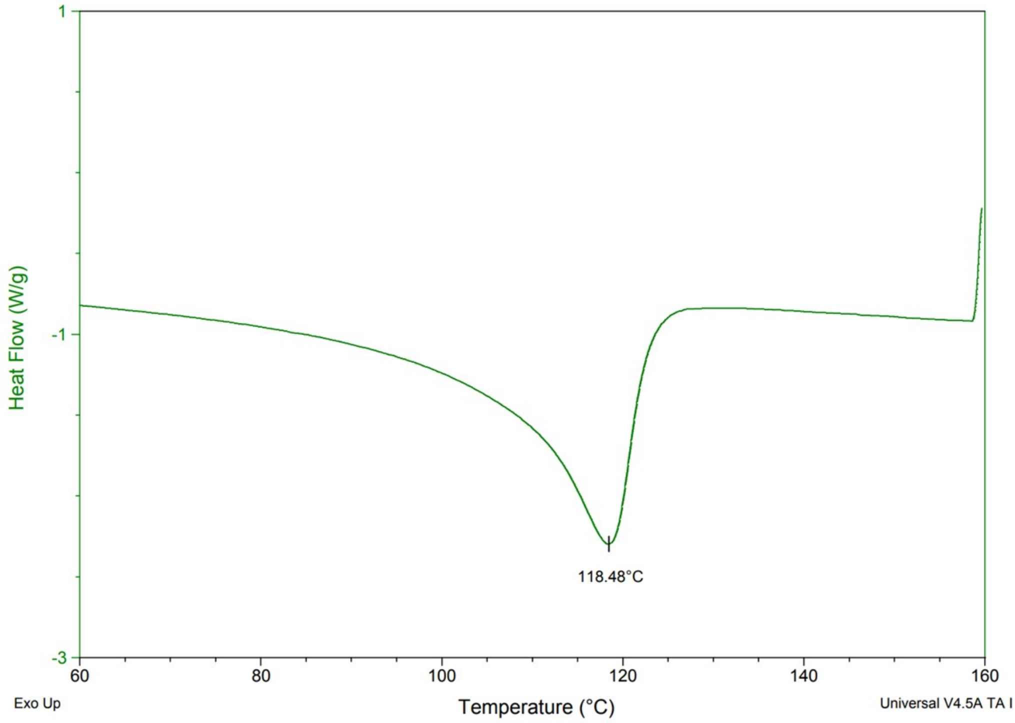



**Figure S62.** DSC of the polymer from Table 1, Entry 11.

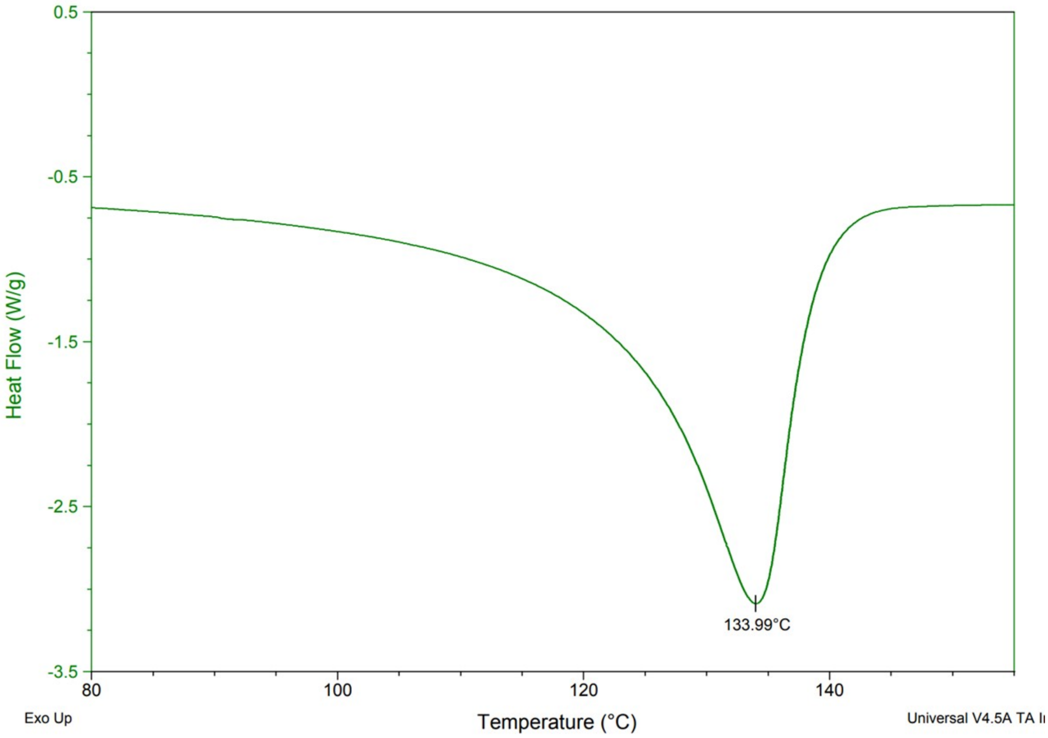



**Figure S63.** DSC of the polymer from Table 2, Entry 1.

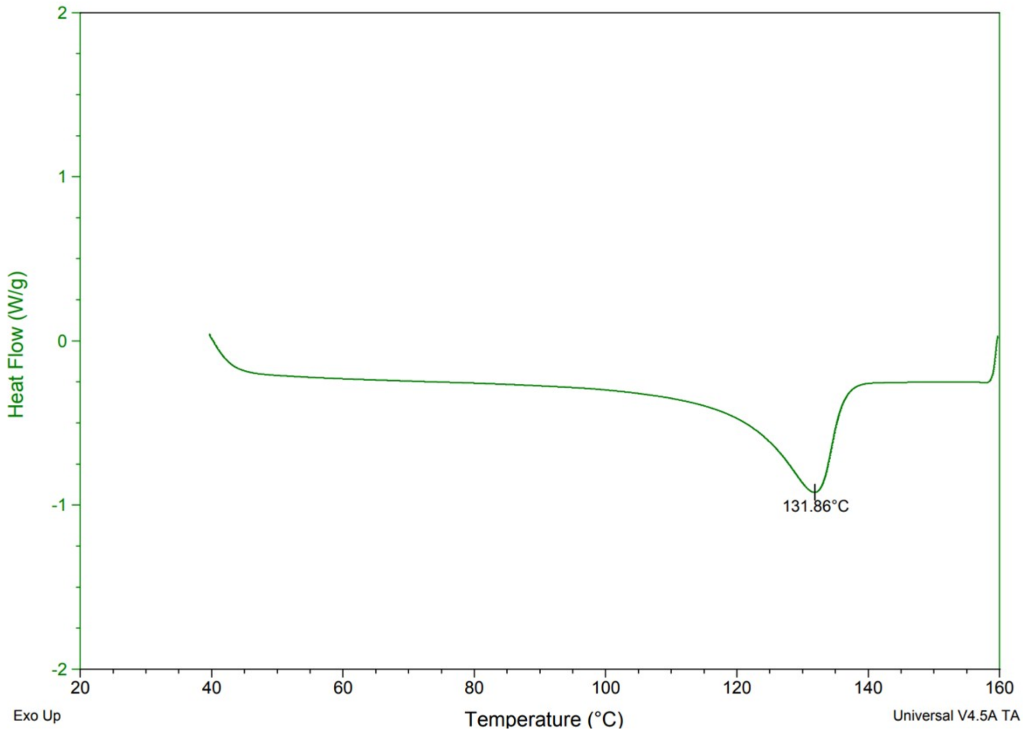



**Figure S64.** DSC of the polymer from Table 2, Entry 2.

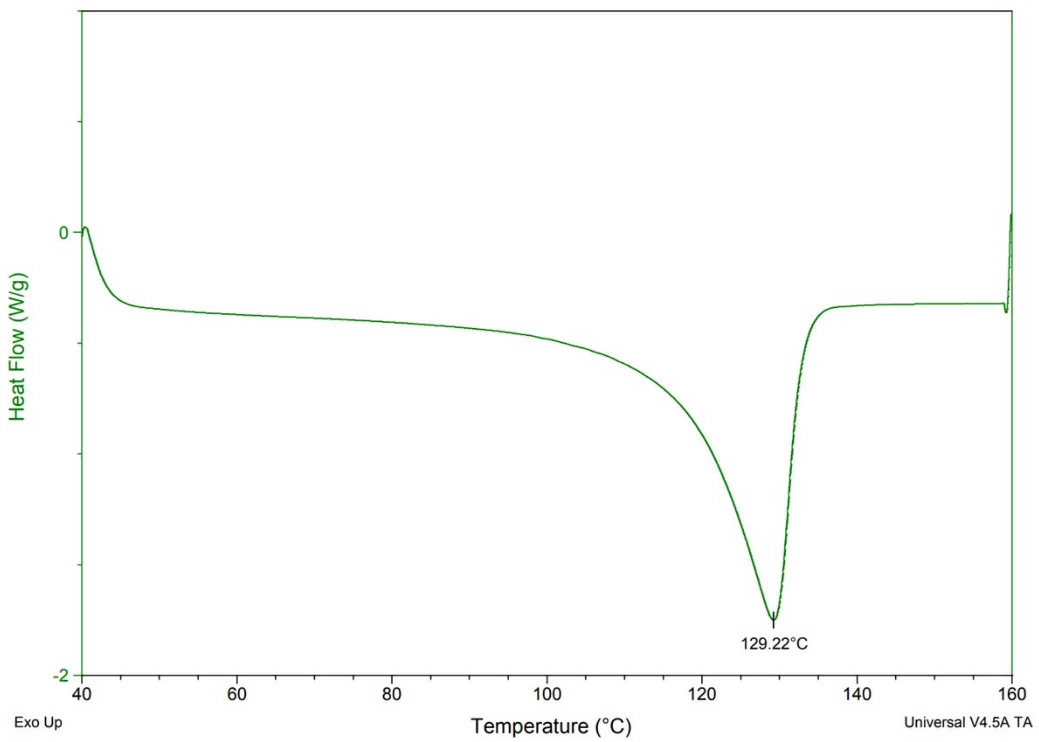



**Figure S65.** DSC of the polymer from Table 2, Entry 3.

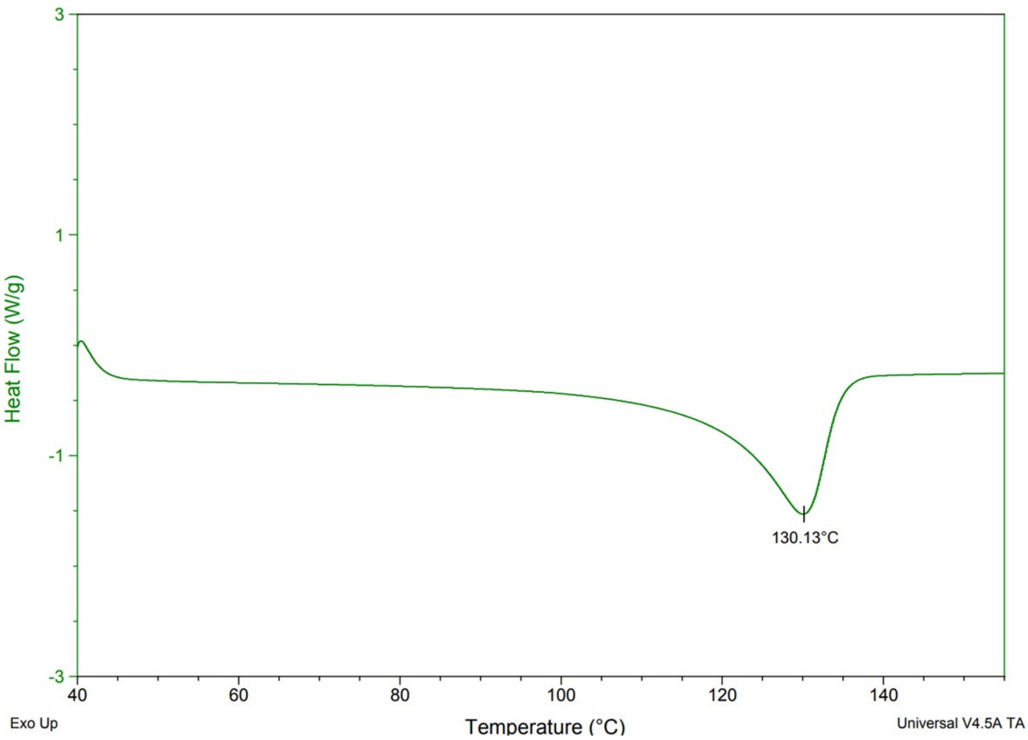



**Figure S66.** DSC of the polymer from Table 2, Entry 4.

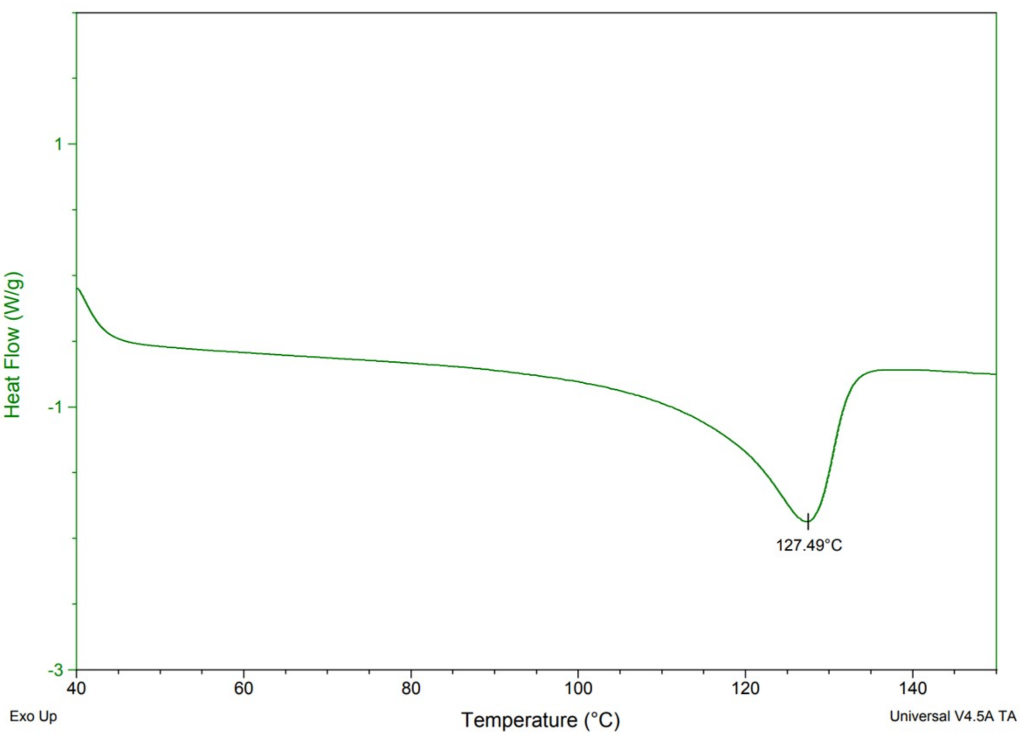



**Figure S67.** DSC of the polymer from Table 2, Entry 5.

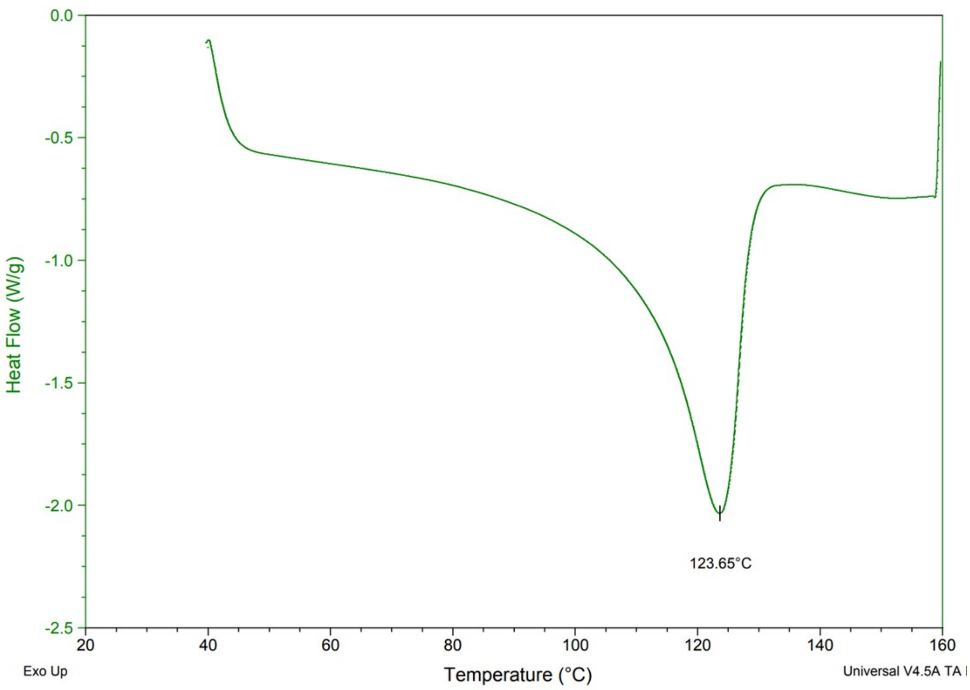



**Figure S68.** DSC of the polymer from Table 2, Entry 6.

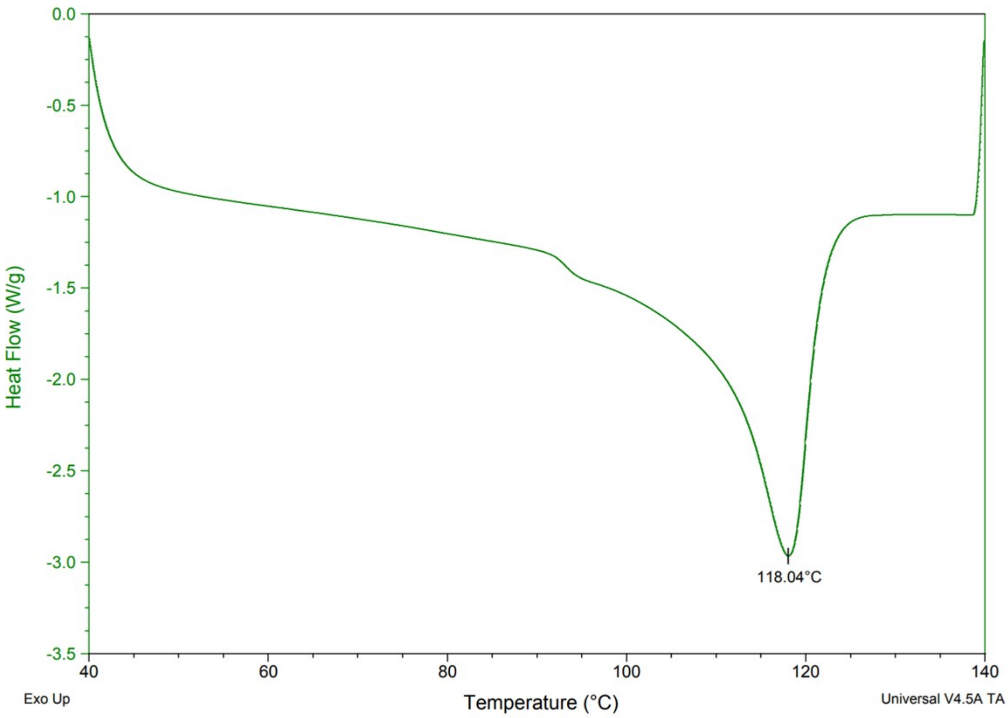



**Figure S69.** DSC of the polymer from Table 3, Entry 1.

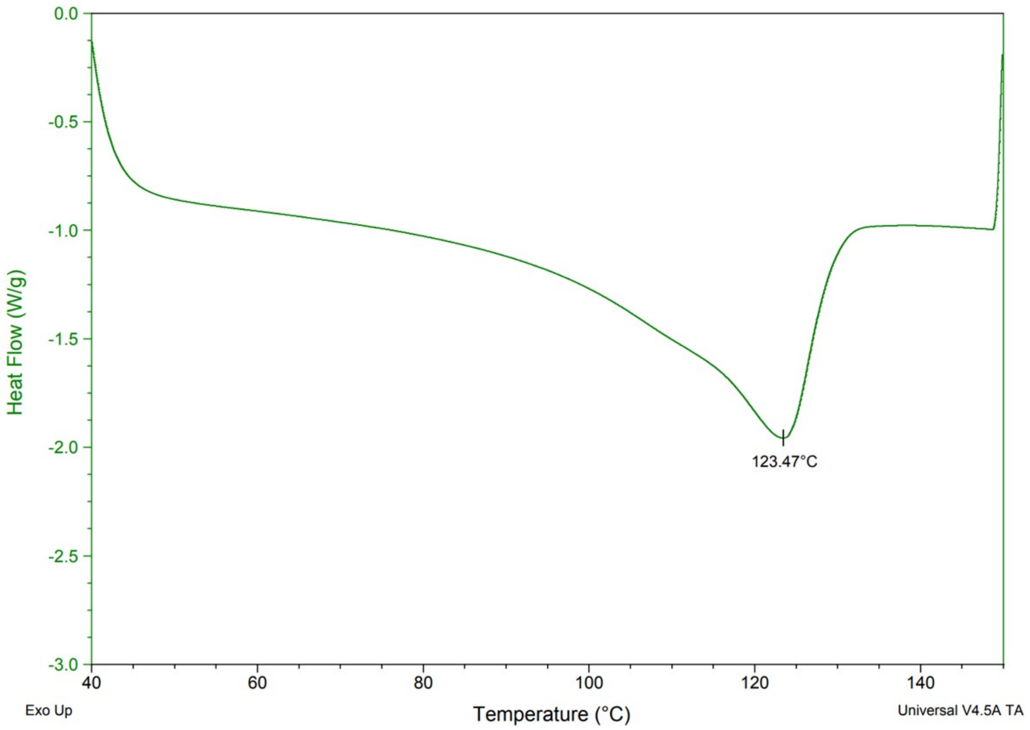



**Figure S70**. DSC of the polymer from Table 3, Entry 2.

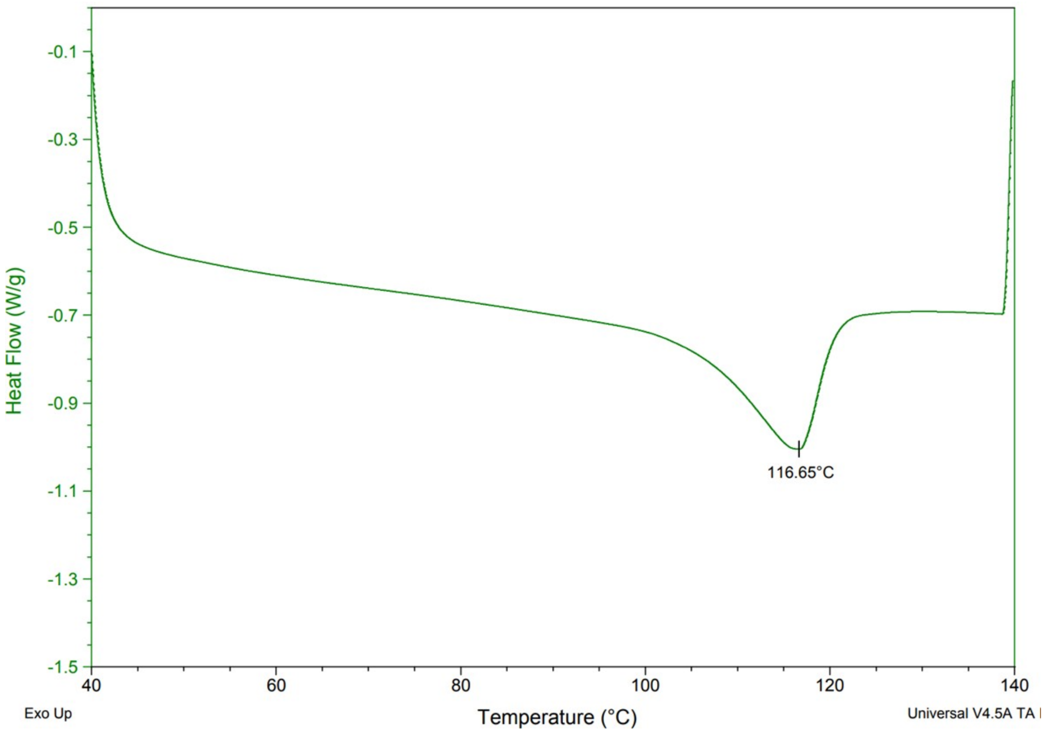



**Figure S71.** DSC of the polymer from Table 3, Entry 3.

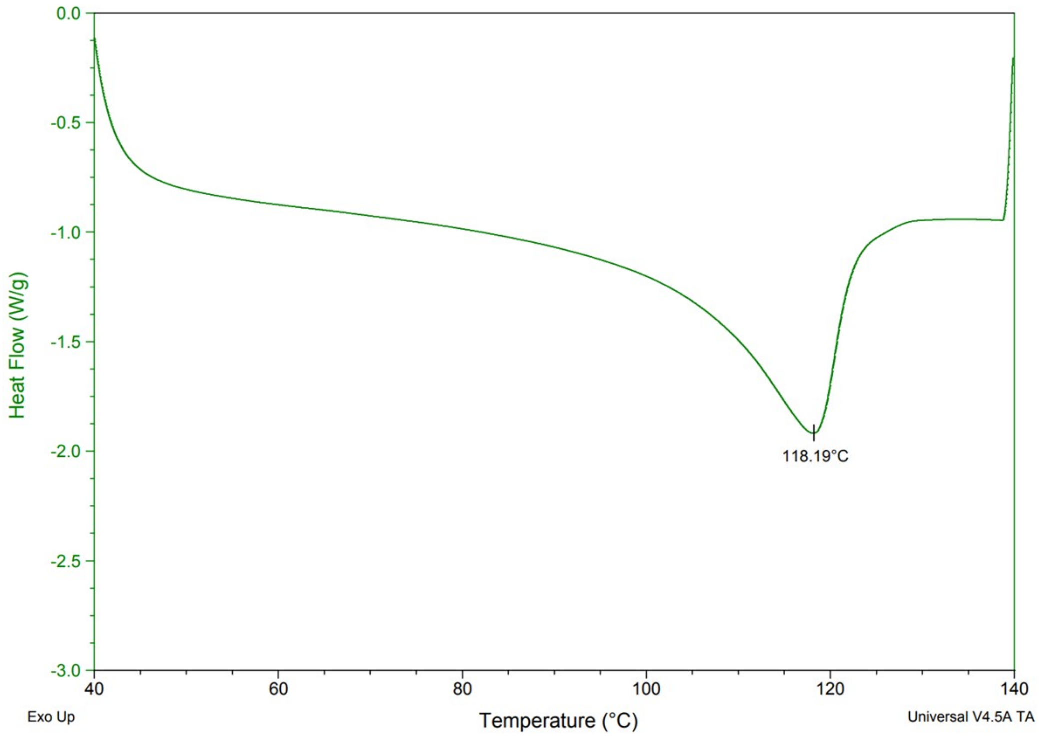



**Figure S72.** DSC of the polymer from Table 3, Entry 4.

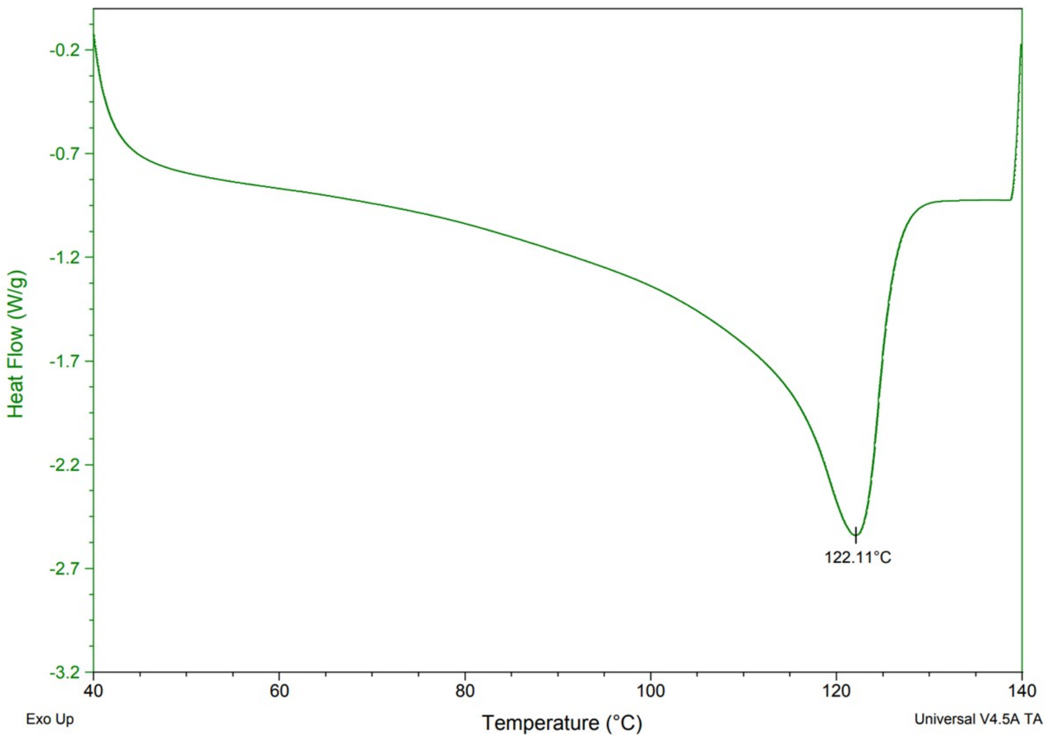



**Figure S73.** DSC of the polymer from Table 3, Entry 5.

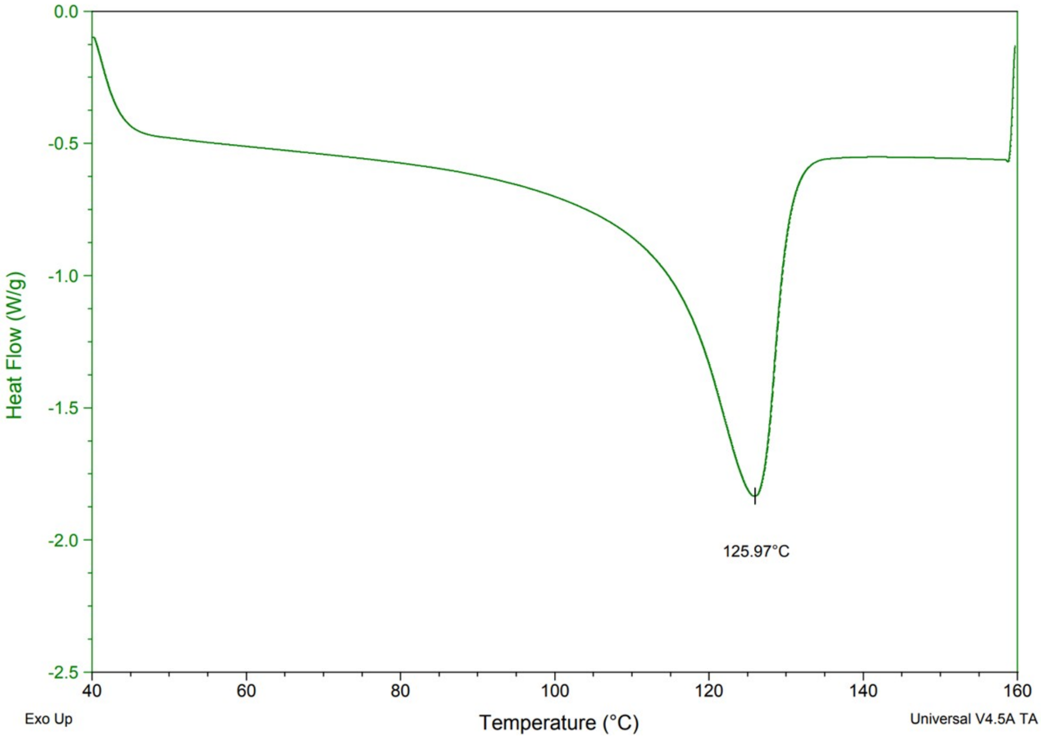



**Figure S74.** DSC of the polymer from Table 3, Entry 6.

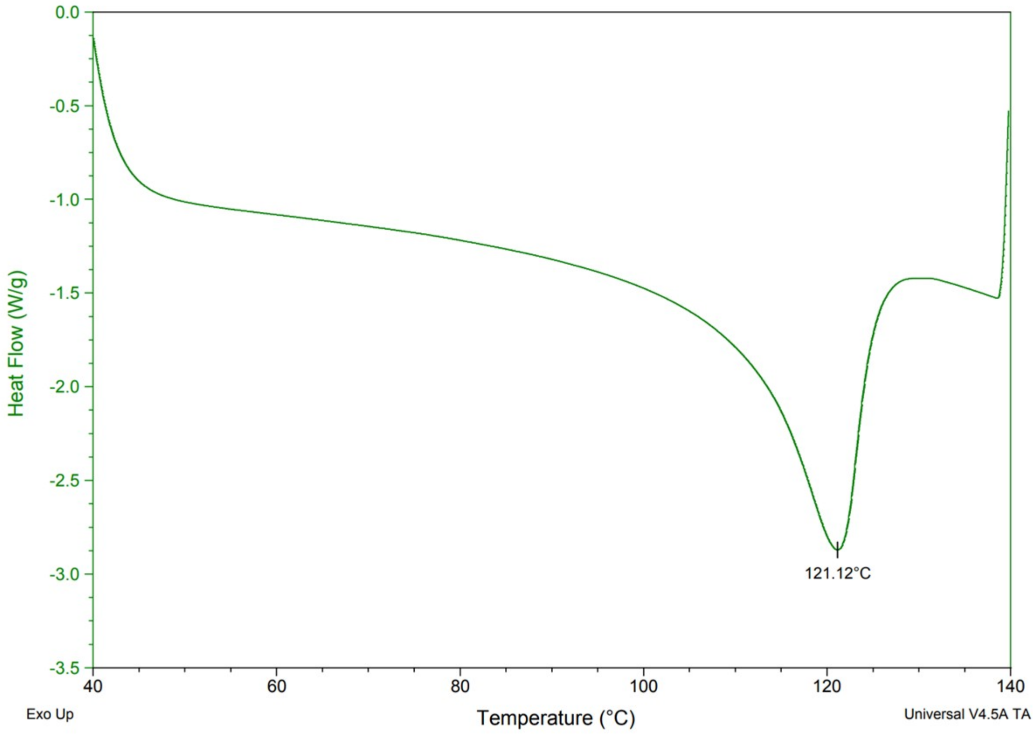



**Figure S75.** DSC of the polymer from Table 3, Entry 7.

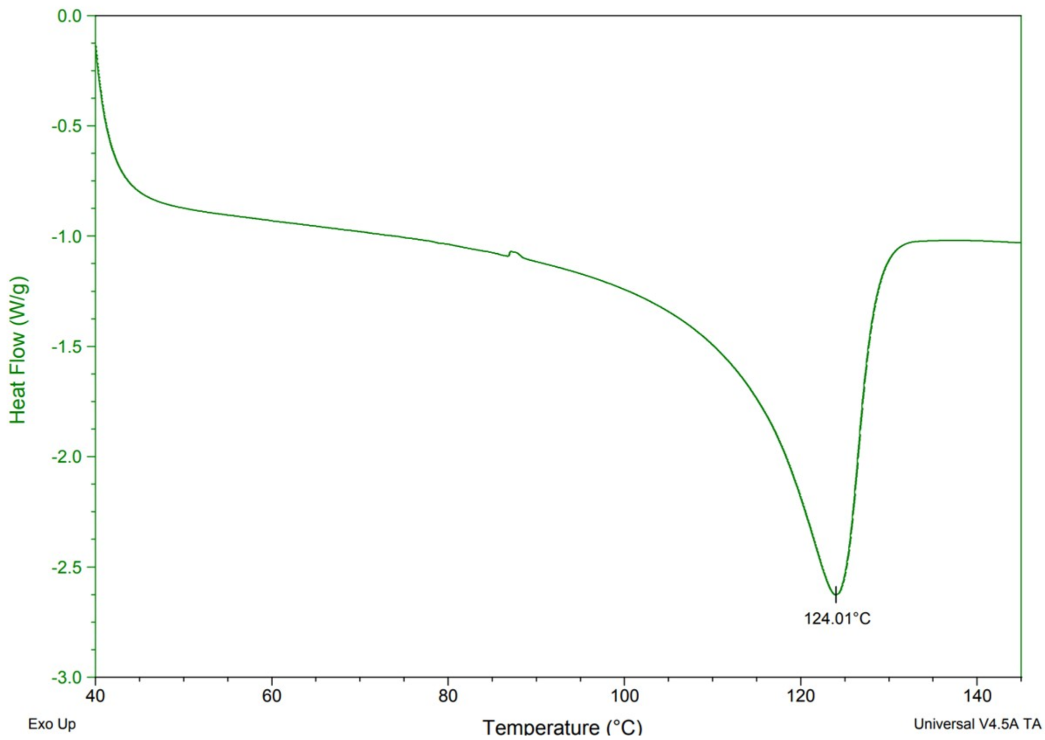



**Figure S76.** DSC of the polymer from Table 3, Entry 8.

# 6. Tensile stress-strain curves

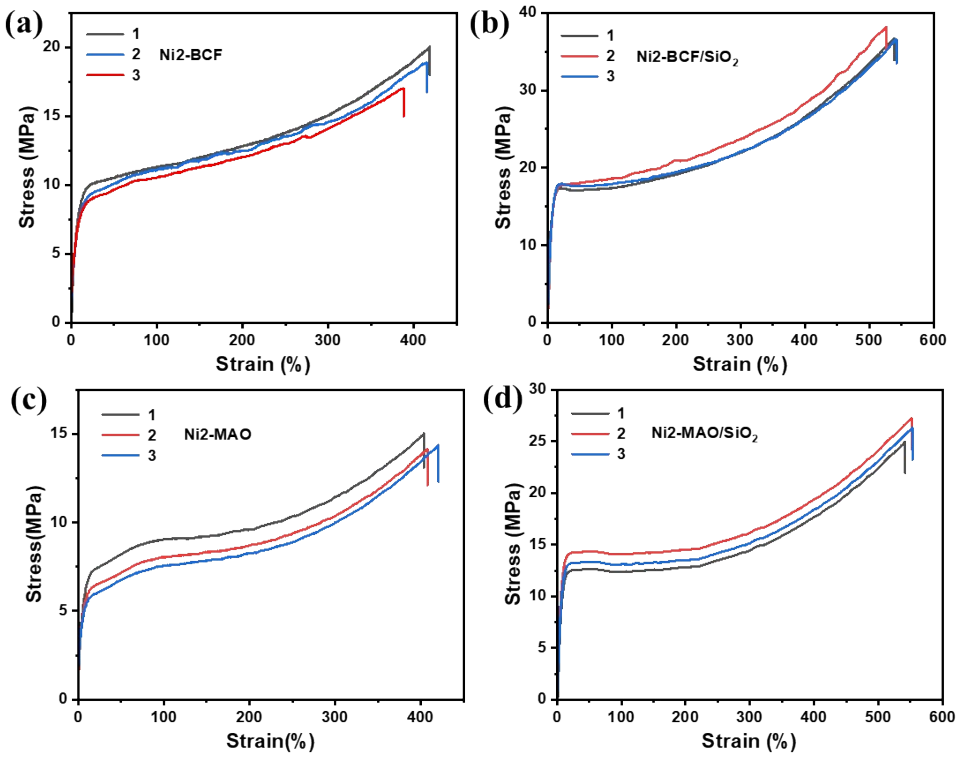



**Figure S77.** Repeated stress-strain curves of polyethylene samples prepared from **Ni2-BCF, Ni2-BCF/SiO$_2$, Ni2-MAO** and **Ni2-MAO/SiO$_2$** at 50°C.

## 7. X-Ray Crystallography

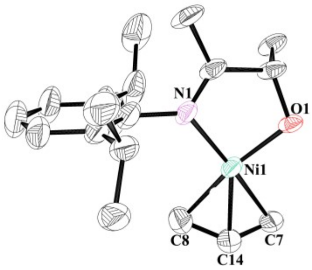



**Table S1. Crystal data and structure refinement for Ni1.**

| | |
|---|---|
| Identification code | **Ni1** |
| Empirical formula | C19 H26 N1 Ni1 O1 |
| Formula weight | 343.12 |
| Temperature/K | 170.0 |
| Crystal system | tetragonal |
| Space group | $I4_1/a$ |
| a/Å | 32.828(3) |
| b/Å | 32.828(3) |
| c/Å | 17.2912(17) |
| α/° | 90 |
| β/° | 90 |
| γ/° | 90 |
| Volume/Å$^3$ | 18634(4) |
| Z | 32 |
| $\rho_{calc}$g/cm$^3$ | 0978 |
| μ/mm$^{-1}$ | 0.834 |
| F(000) | 5856.0 |
| Crystal size/mm$^3$ | 0.5 × 0.4 × 0.3 |
| Radiation | MoKa (λ = 0.71073) |
| 2Θ range for data | 5.056 to 50.044 |
| Index ranges | -39≤h≤38, -19≤k≤20, - |
| Reflections collected | 88307 |
| Independent reflections | 8128 [$R_{int}$ = 0.0996, $R_{sigma}$ = |
| Data/restraints/paramete | 8128/270/403 |
| Goodness-of-fit on F$^2$ | 1.015 |
| Final R indexes [I>=2σ | R1 = 0.0761, wR2 = 0.1774 |
| Final R indexes [all | R1 = 0.1118, wR2 = 0.1992 |