Supporting Information for

# Ethylene Polymerization by Dinuclear Xanthene-Bridged Imino- and Aminopyridyl Nickel Complexes

Chunyong Rong,[†] Fuzhou Wang,*[,†,‡] Weimin Li[†] and Min Chen*[,†]

[†]Advanced Catalysis and Green Manufacturing Collaborative Innovation Center, School of Pertrochemical Engineering, Changzhou University, Changzhou 213164, China.
[‡]Graduate School of Engineering, Hiroshima University, Higashi-Hiroshima 739-8527, Japan

*E-mail: wangfuzhou1718@126.com (F. W); misschen@ustc.edu.cn (M. C)

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## 1. $^{1}H$ and $^{13}C$ NMR spectra of ligands L-A, L-B, L-C and L-D

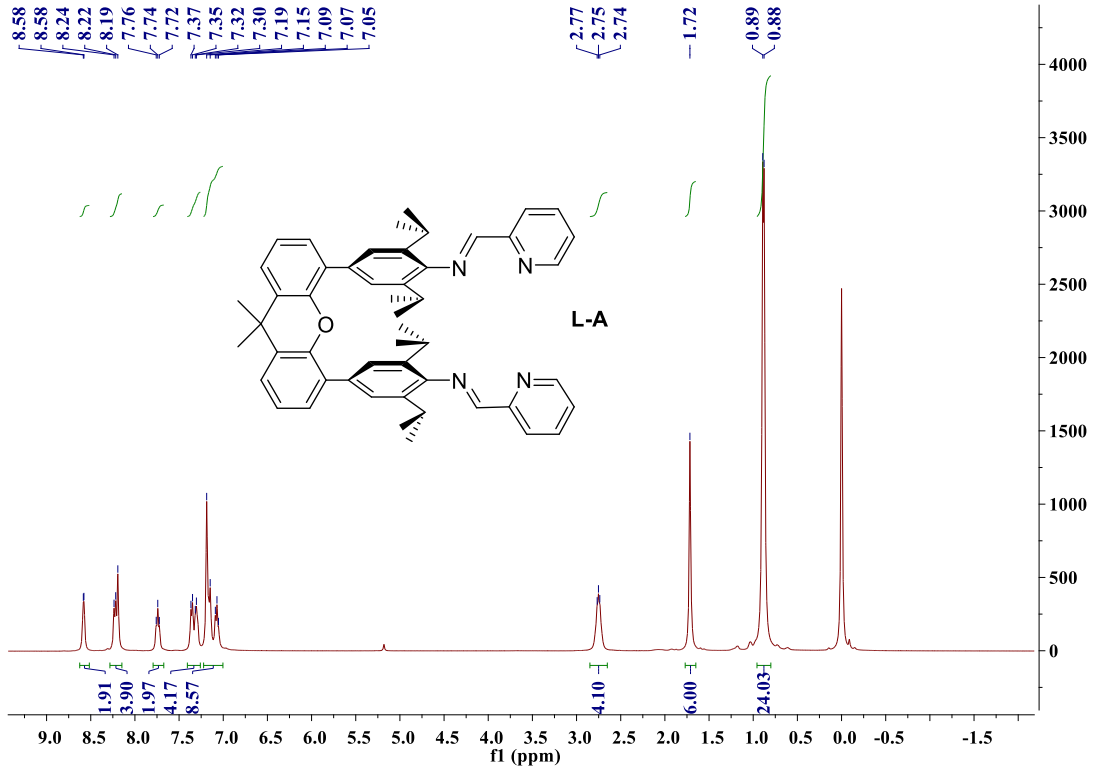


**Figure S1**. $^{1}H$ NMR spectrum (500 MHz, $CDCl_3$, ppm) of **L-A**.

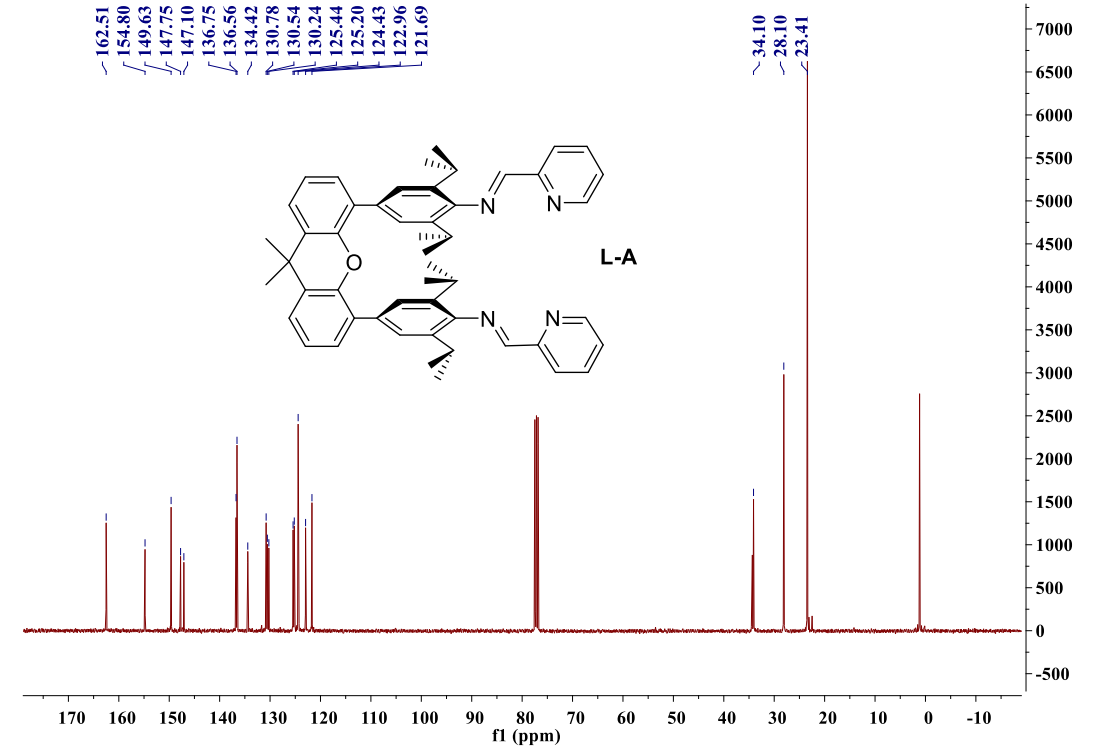


**Figure S2**. $^{13}C$ NMR spectrum (125 MHz, $CDCl_3$, ppm) of **L-A**.

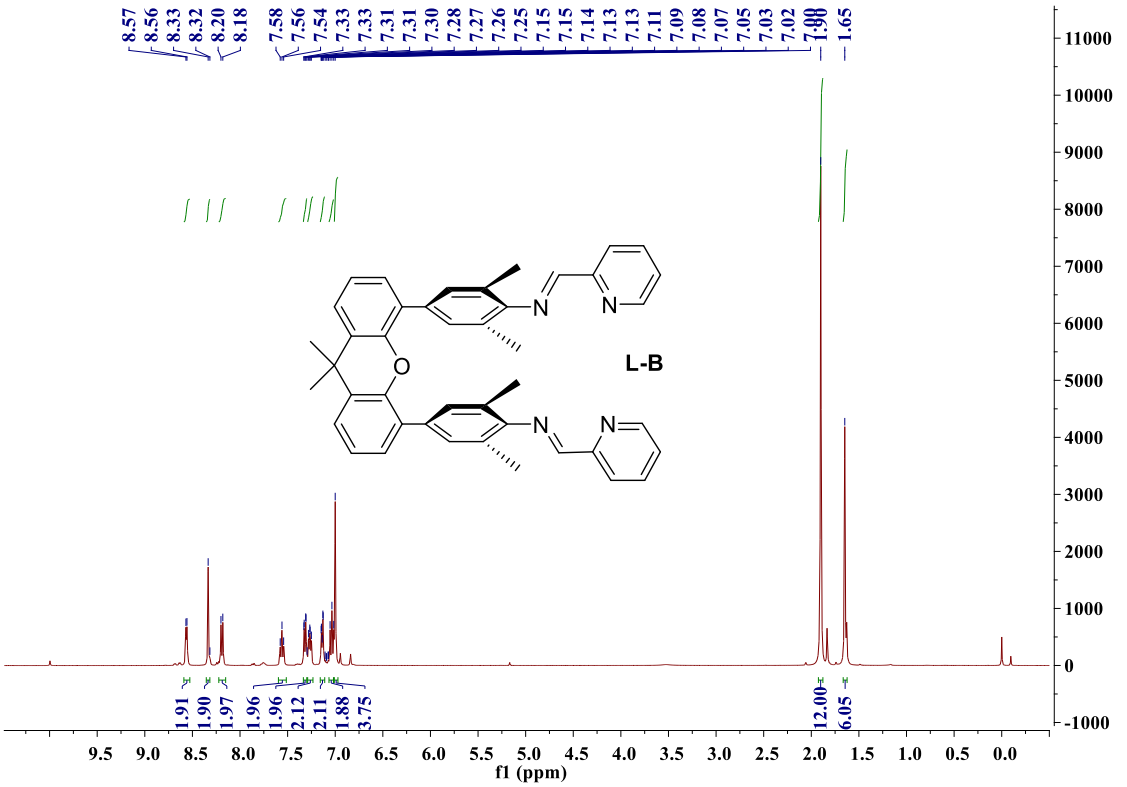


**Figure S3**. $^{1}$H NMR spectrum (500 MHz, $CDCl_3$, ppm) of **L-B**.

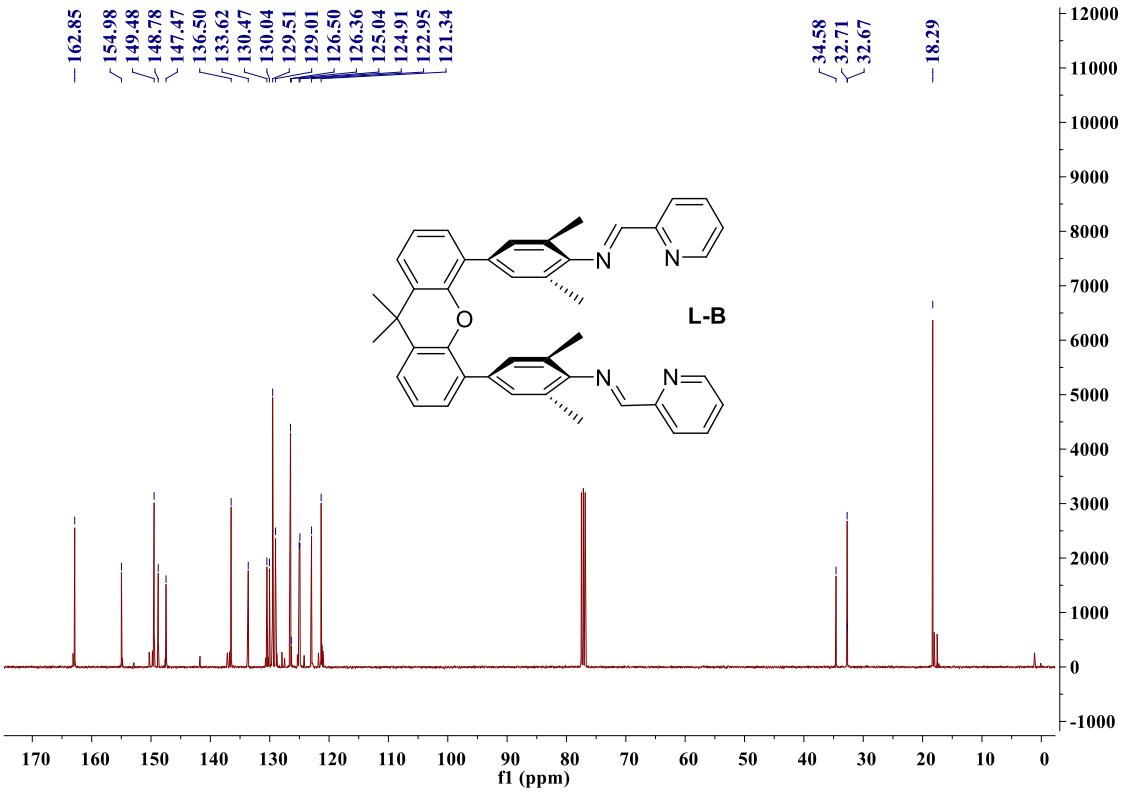


**Figure S4**. $^{13}$C NMR spectrum (125 MHz, $CDCl_3$, ppm) of **L-B**.

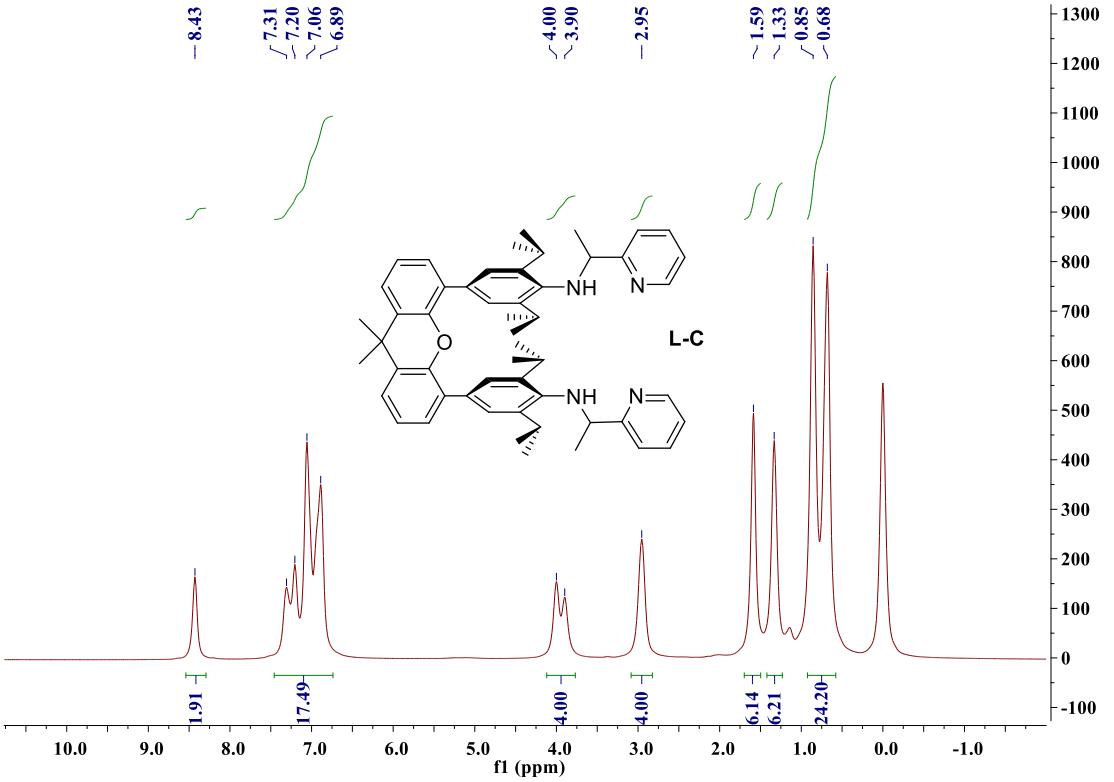


**Figure S5**. $^{1}$H NMR spectrum (500 MHz, $CDCl_3$, ppm) of **L-C**.

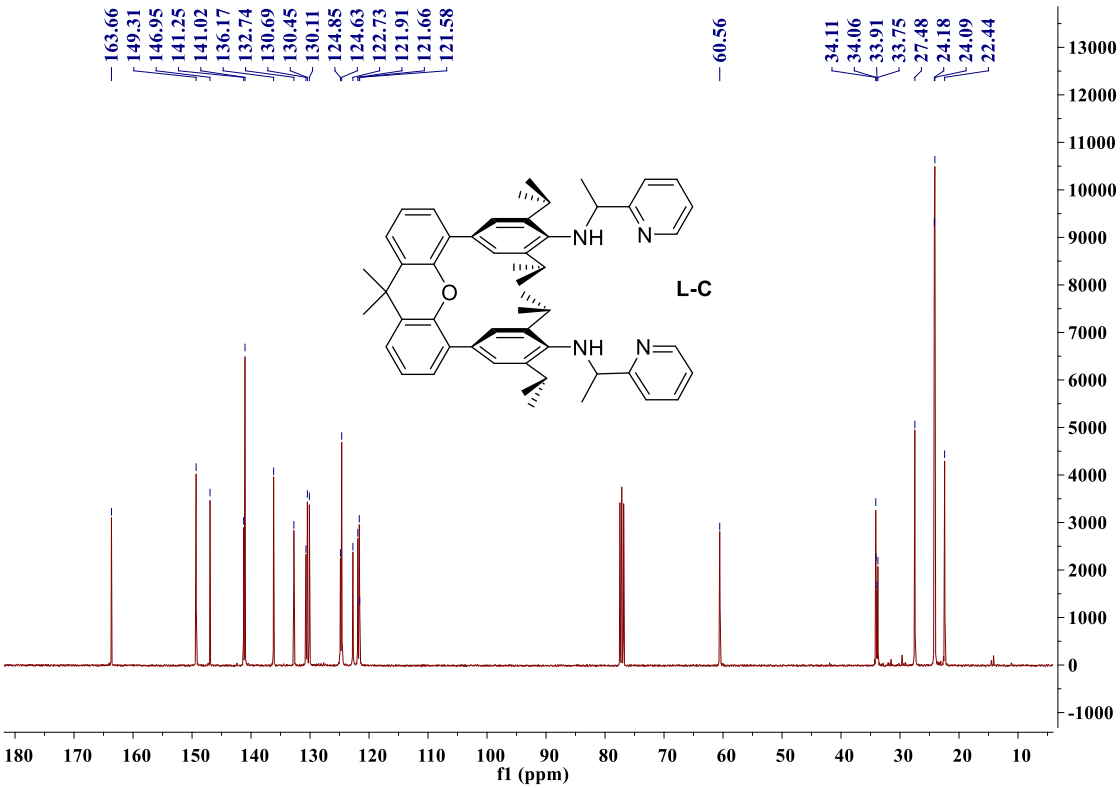


**Figure S6**. $^{13}$C NMR spectrum (125 MHz, $CDCl_3$, ppm) of **L-C**.

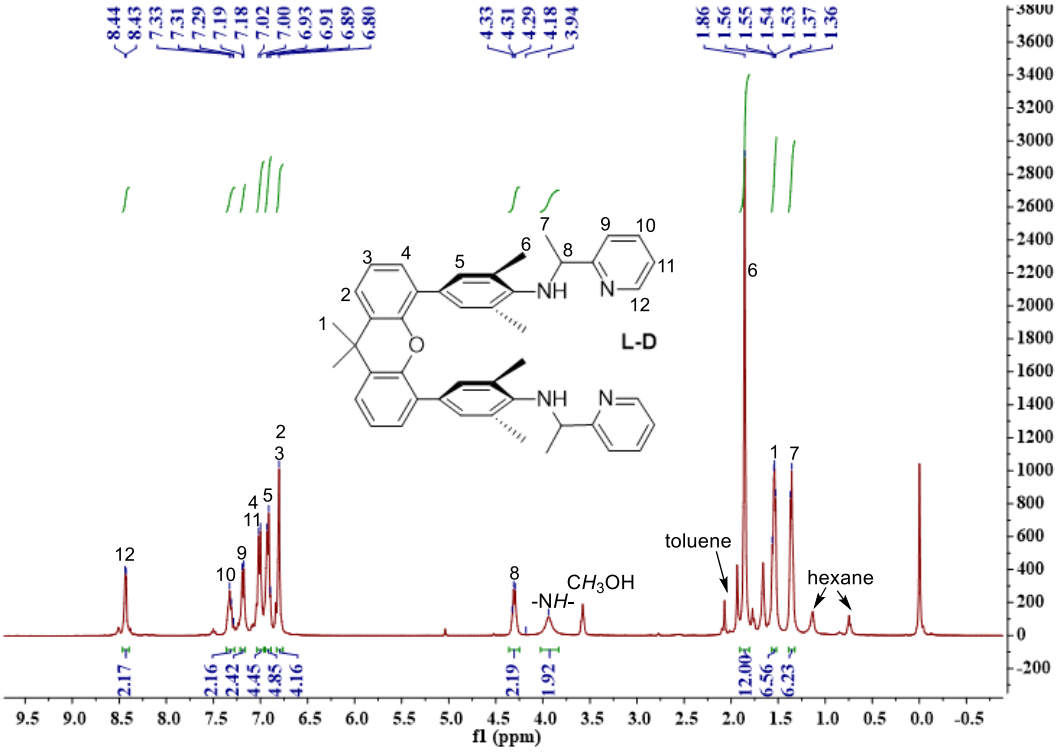


**Figure S7**. $^{1}$H NMR spectrum (500 MHz, $CDCl_3$, ppm) of **L-D**.

## 2. $^{1}$H NMR spectra of the polyethylenes

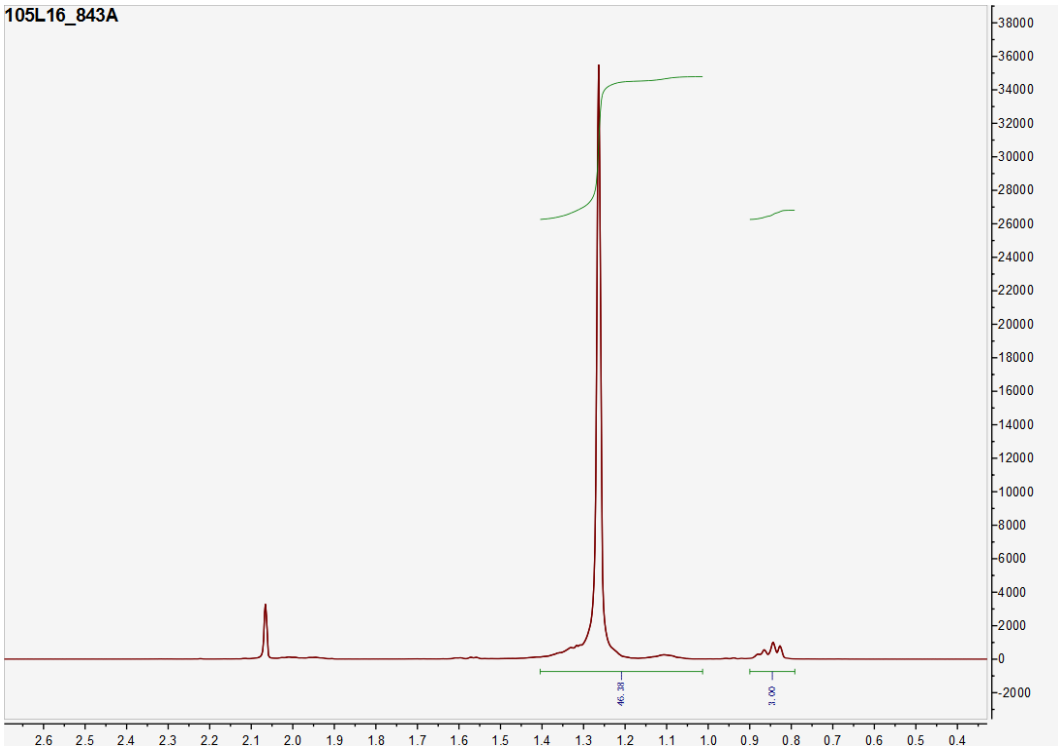


**Figure S8**. $^{1}$H NMR spectrum of polyethylene obtained by **$Ni_2$-A** from table 1, entry 1 ($C_2D_2Cl_4$, 120 $^{o}$C, B = 40).

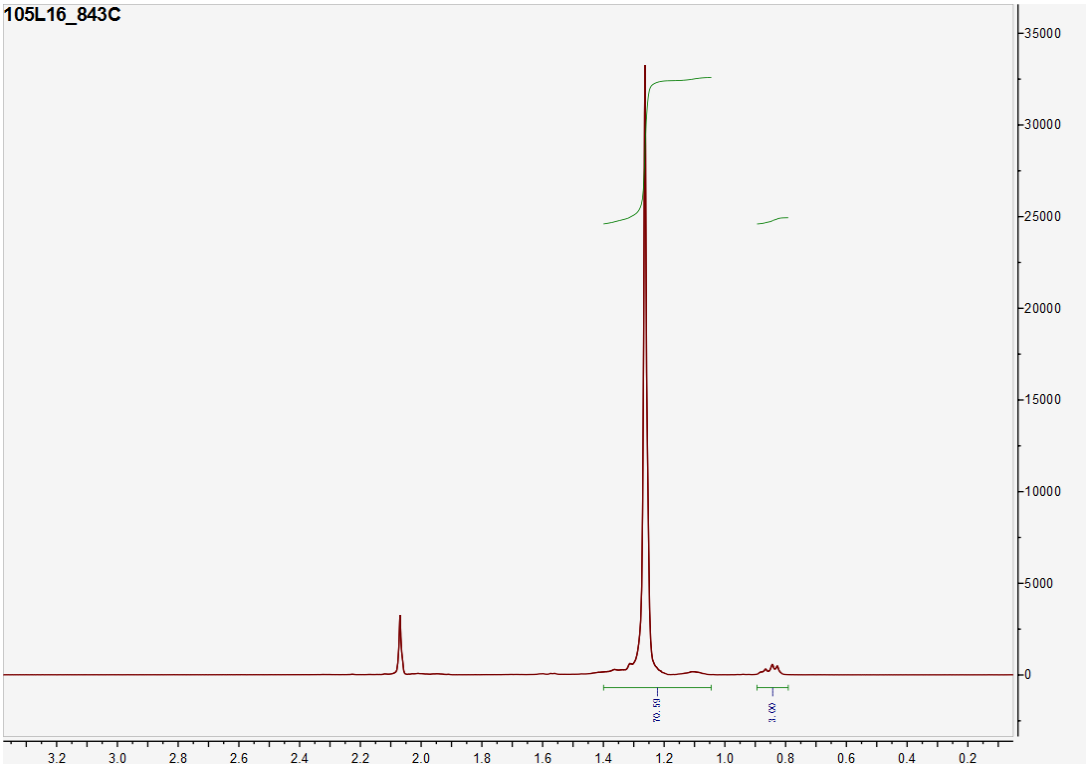


**Figure S9**. $^{1}$H NMR spectrum of polyethylene obtained by **$Ni_2$-A** from table 1, entry 4 ($C_2D_2Cl_4$, 120 $^{o}$C, B = 27).

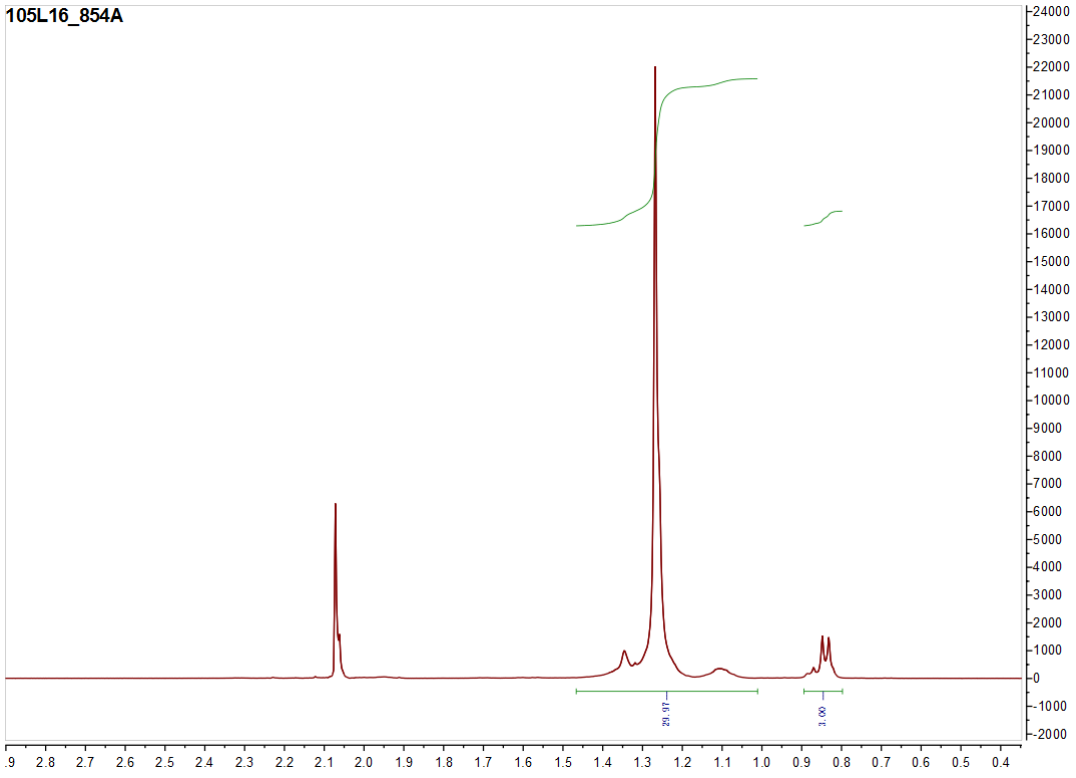


**Figure S10**. $^{1}$H NMR spectrum of polyethylene obtained by **$Ni_2$-C** from table 1, entry 7 ($C_2D_2Cl_4$, 120 $^{o}$C, B = 61).

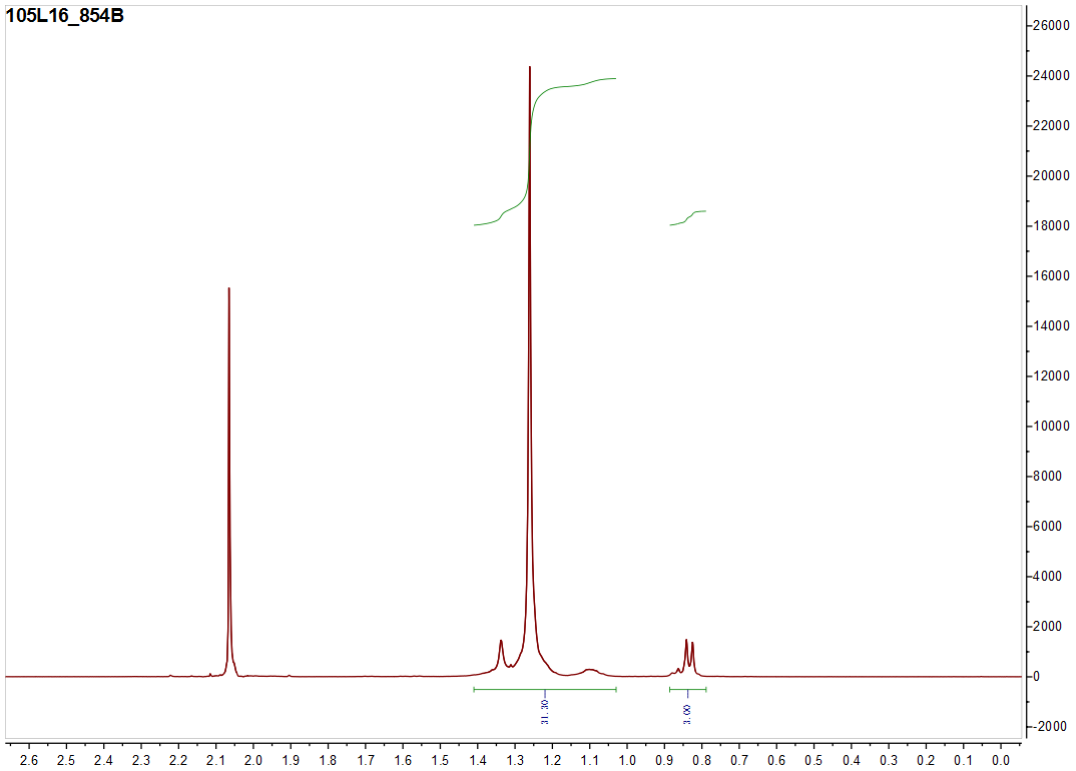


**Figure S11**. $^{1}$H NMR spectrum of polyethylene obtained by **Ni$_2$-C** from table 1, entry 10 ($C_2D_2Cl_4$, 120 $^{o}$C, B = 58).

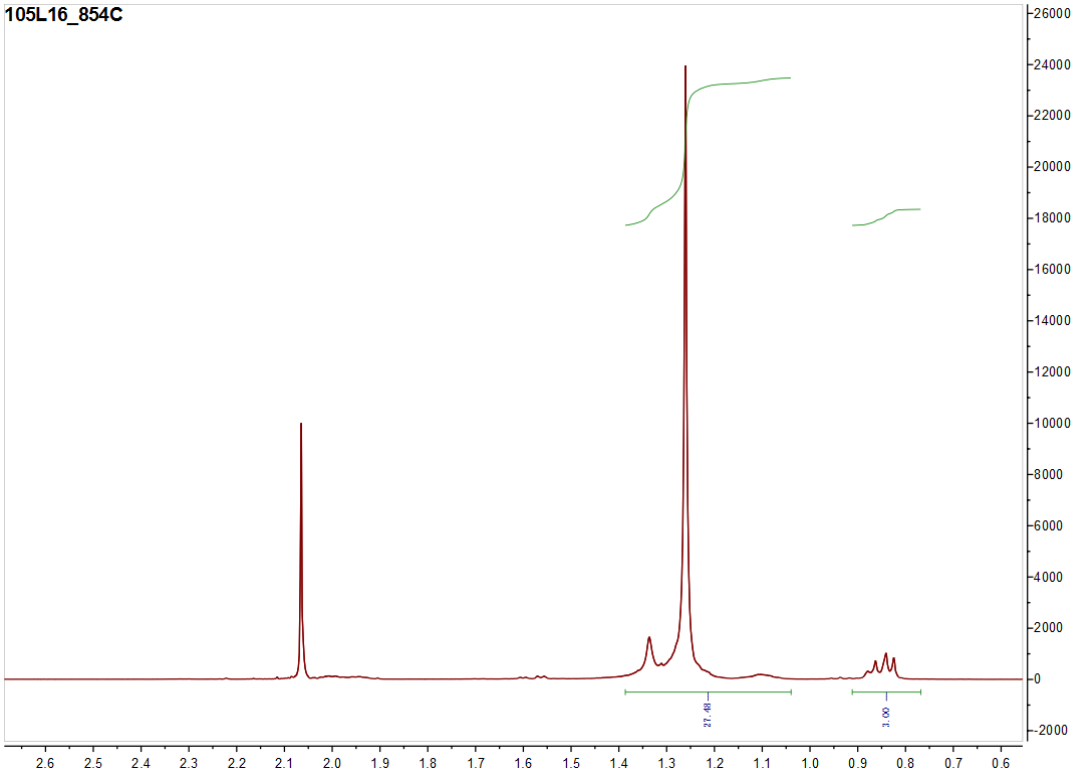


**Figure S12**. $^{1}$H NMR spectrum of polyethylene obtained by **Ni-A** from table 1, entry 13 ($C_2D_2Cl_4$, 120 $^{o}$C, B = 66).

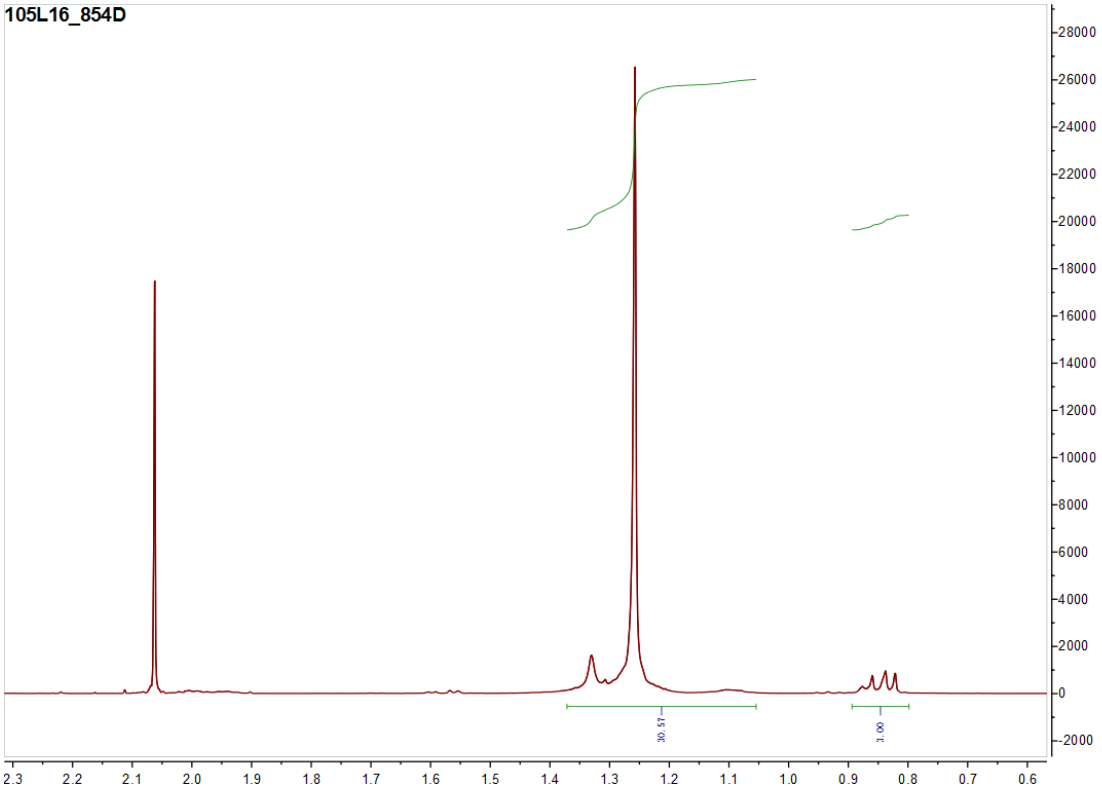


**Figure S13**. $^{1}$H NMR spectrum of polyethylene obtained by **Ni-B** from table 1, entry 16 ($C_2D_2Cl_4$, 120 $^{o}$C, B = 60).

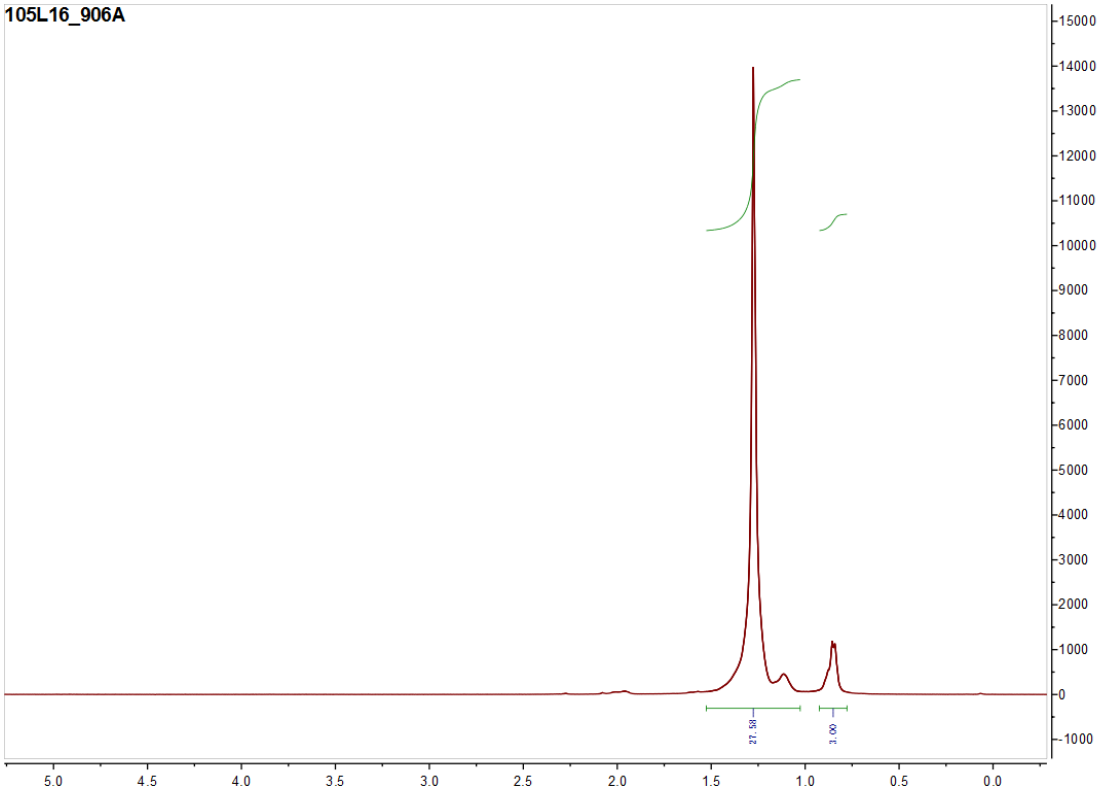


**Figure S14**. $^{1}$H NMR spectrum of polyethylene obtained by **Ni-C** from table 1, entry 19 ($C_2D_2Cl_4$, 120 $^{o}$C, B = 65).

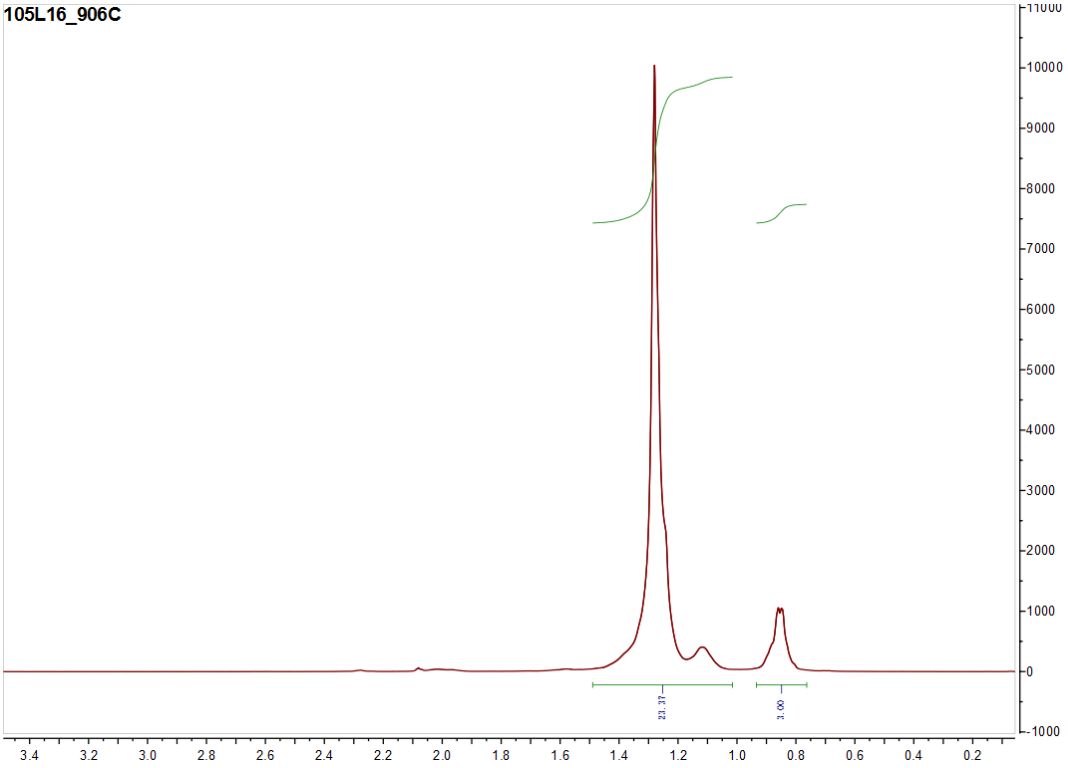


**Figure S15**. $^{1}$H NMR spectrum of polyethylene obtained by **Ni-D** from table 1, entry 22 ($C_2D_2Cl_4$, 120 $^{o}$C, B = 76).

## 3. DSC data of the polyethylenes

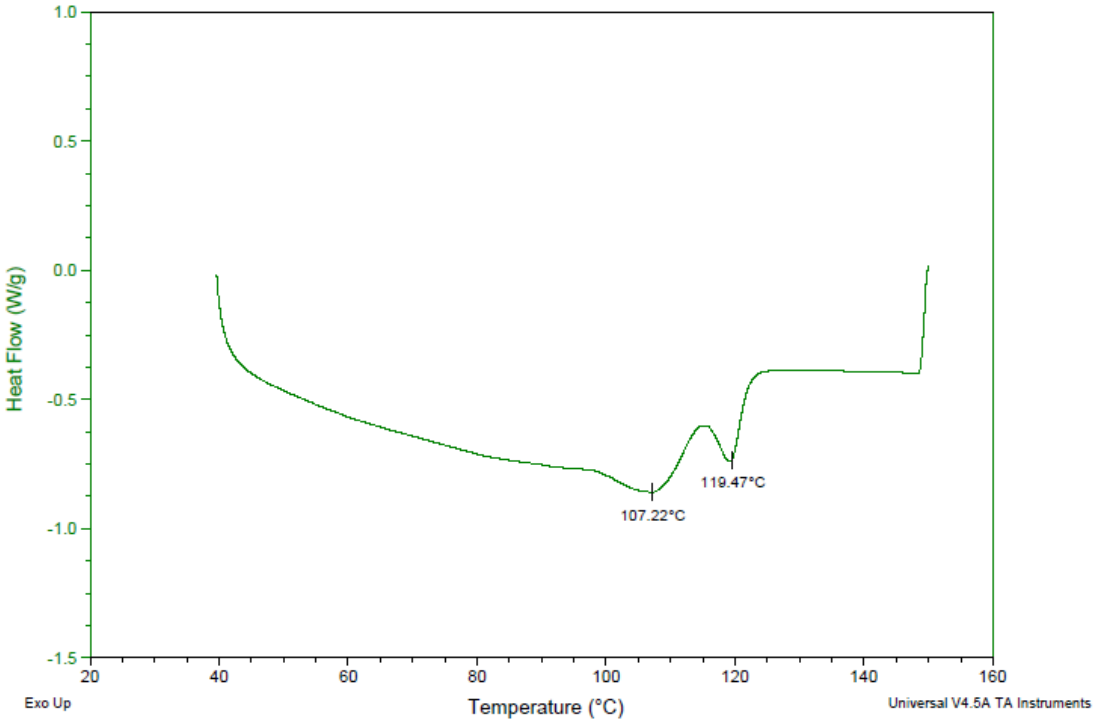


**Figure S16**. DSC data of the polyethylene from table 1, entry 1.

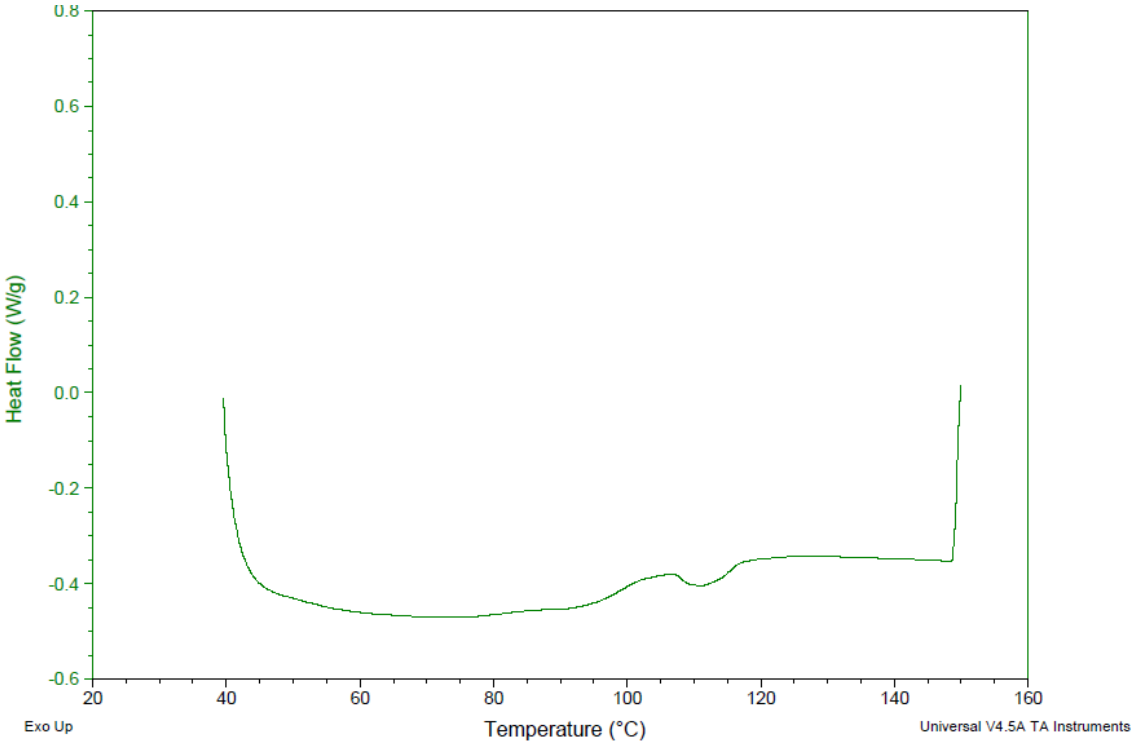


**Figure S1**7. DSC data of the polyethylene from table 1, entry 2.

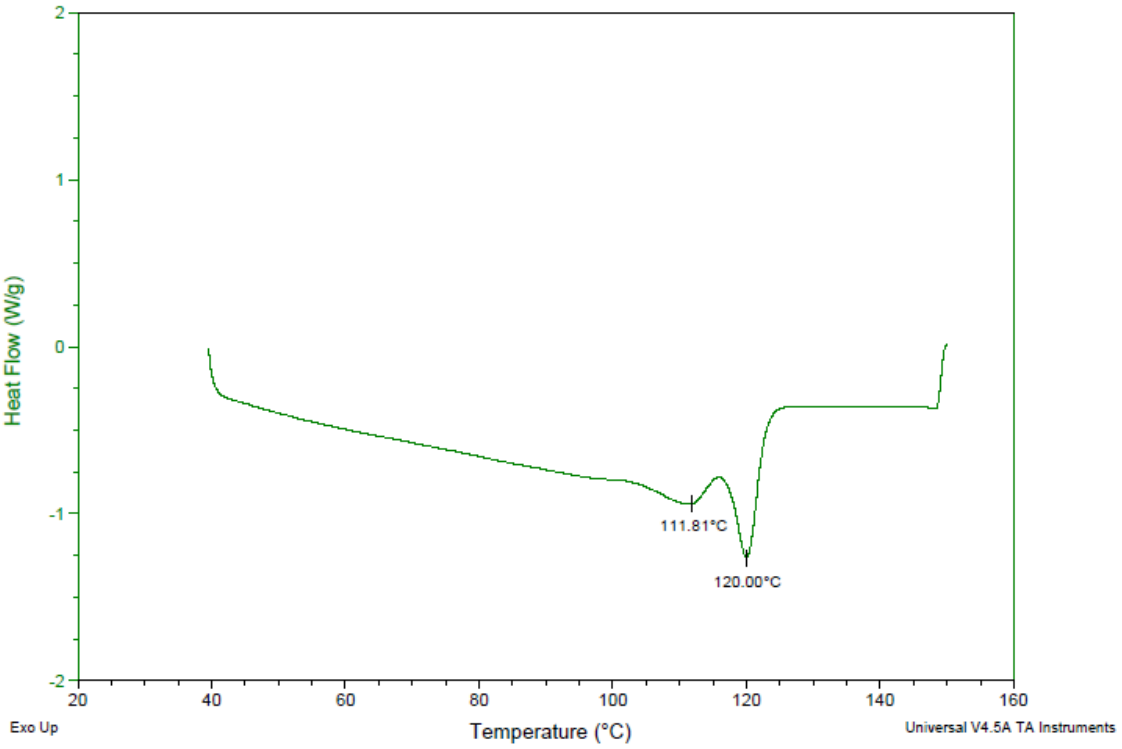


**Figure S18**. DSC data of the polyethylene from table 1, entry 4.

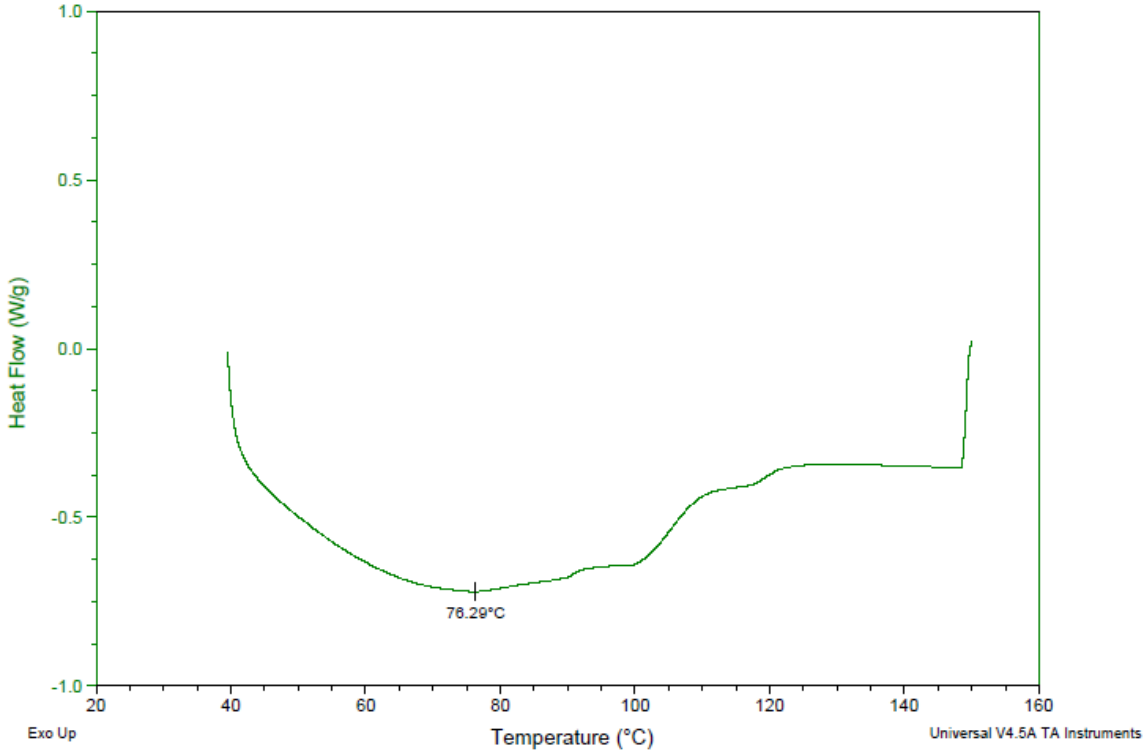


**Figure S19**. DSC data of the polyethylene from table 1, entry 5.

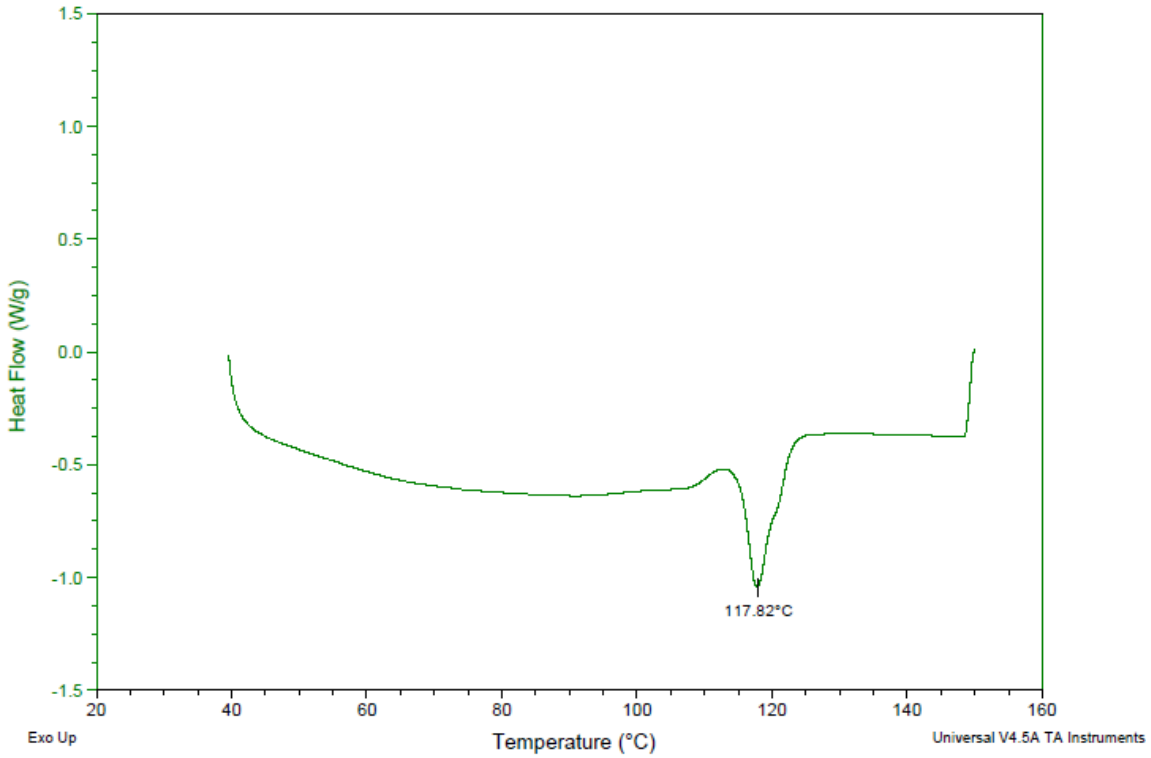


**Figure S20**. DSC data of the polyethylene from table 1, entry 6.

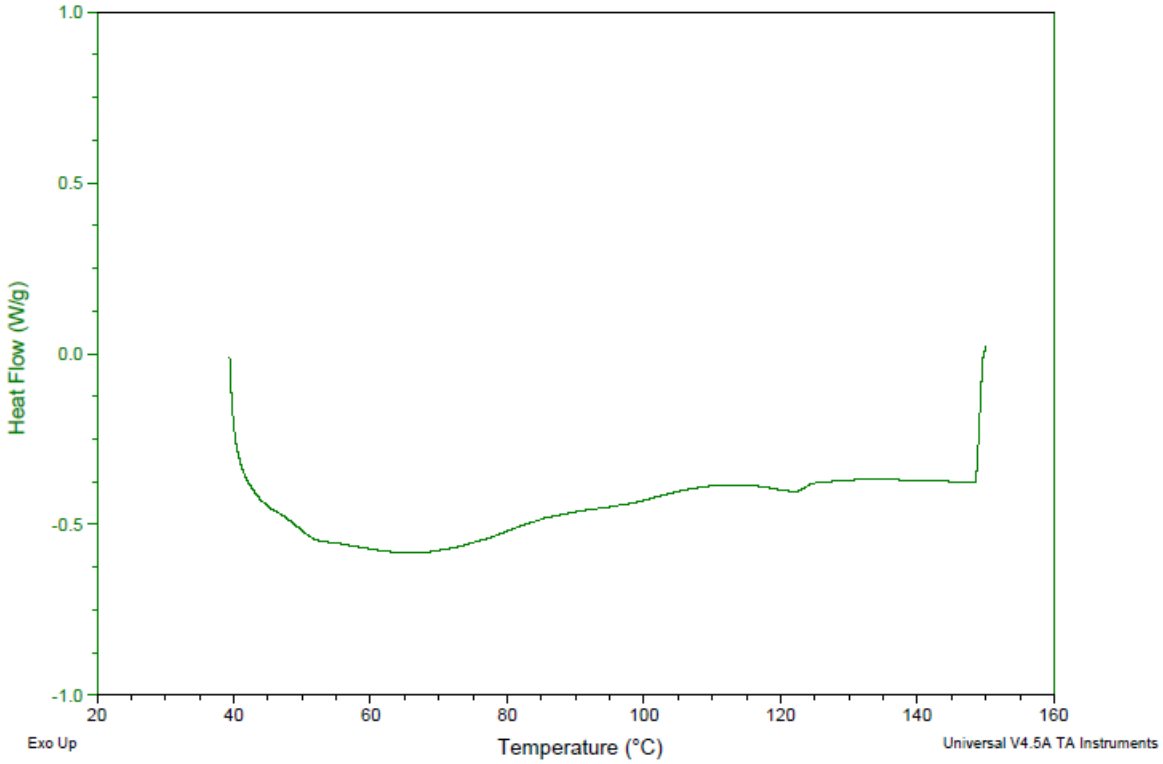


**Figure S21**. DSC data of the polyethylene from table 1, entry 7.

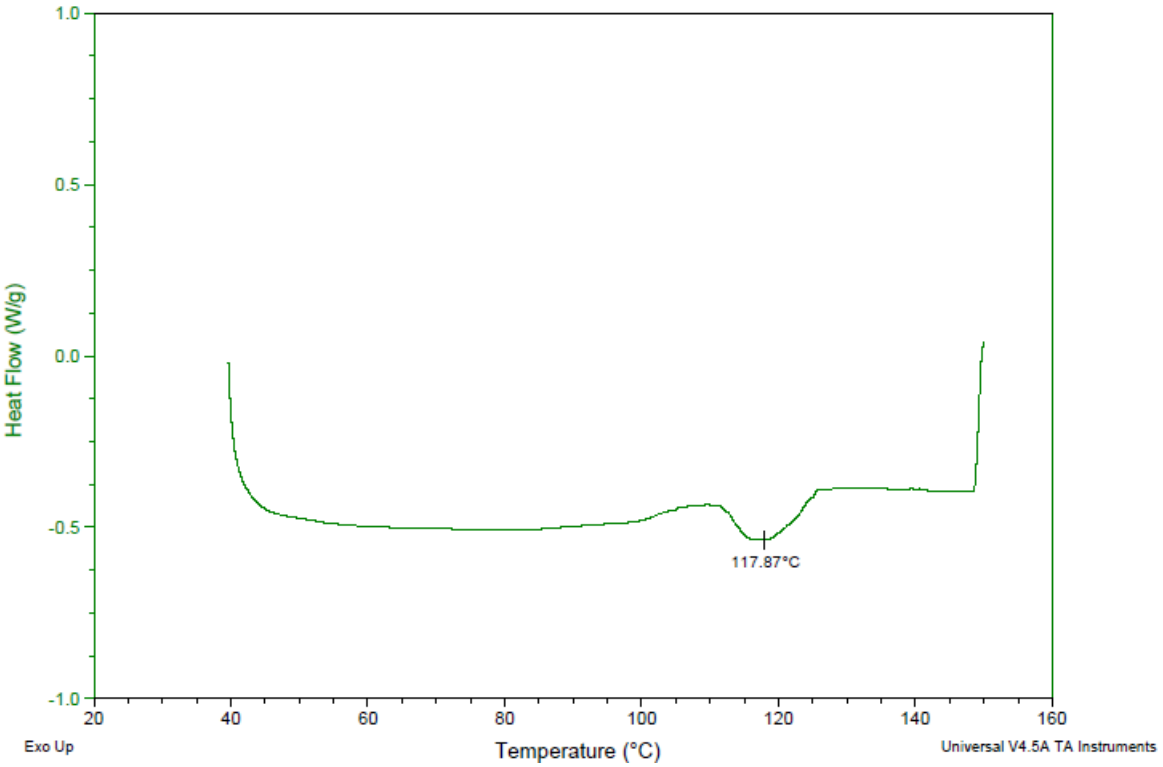


**Figure S22**. DSC data of the polyethylene from table 1, entry 10.

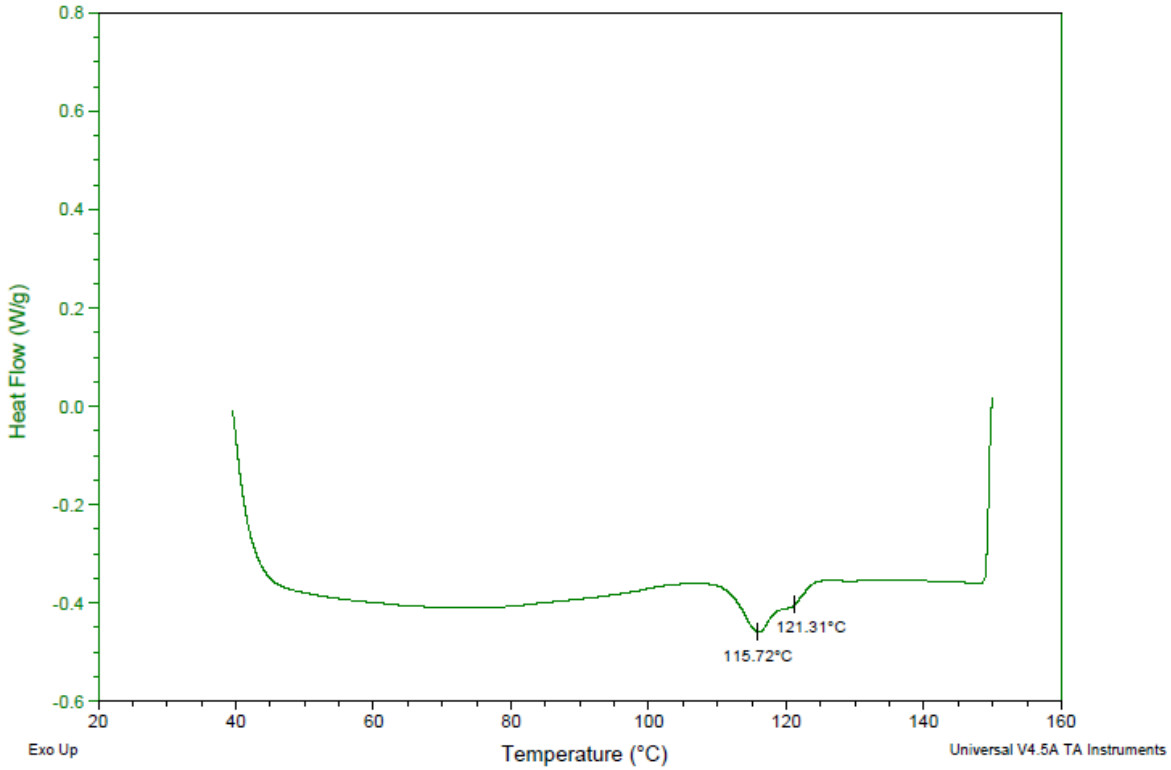


**Figure S23**. DSC data of the polyethylene from table 1, entry 12.

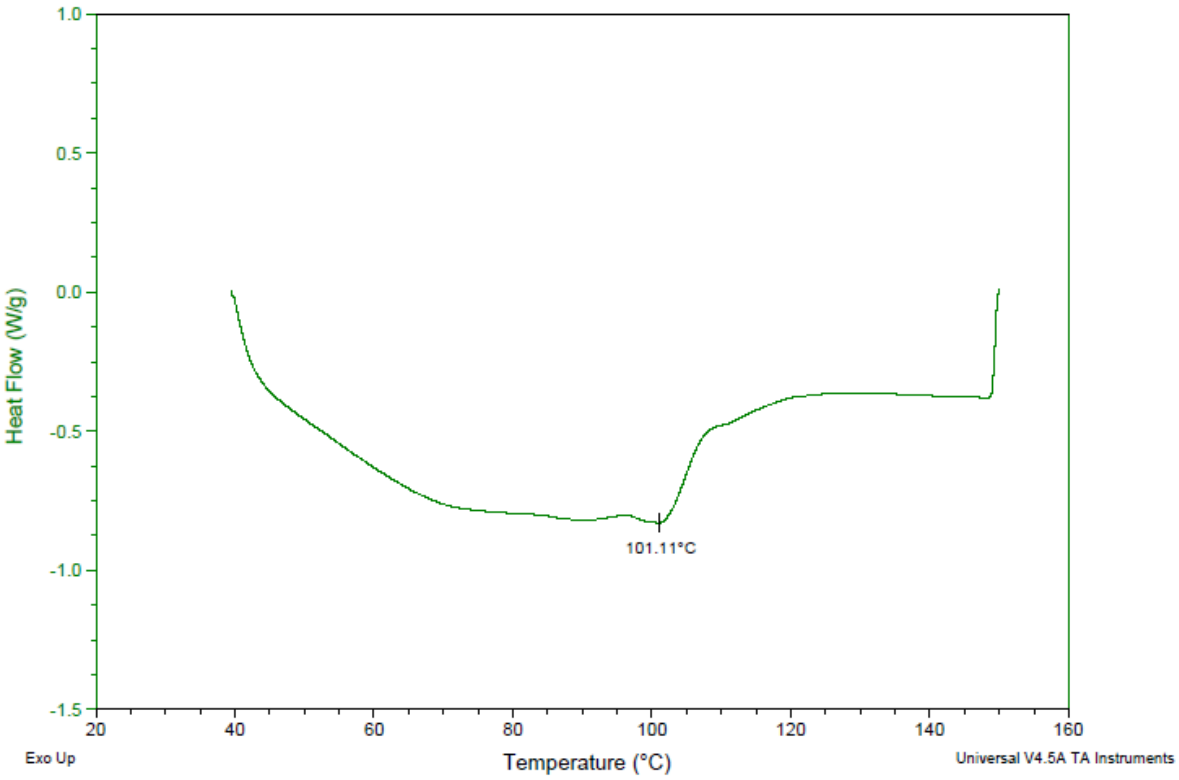


**Figure S24**. DSC data of the polyethylene from table 1, entry 13.

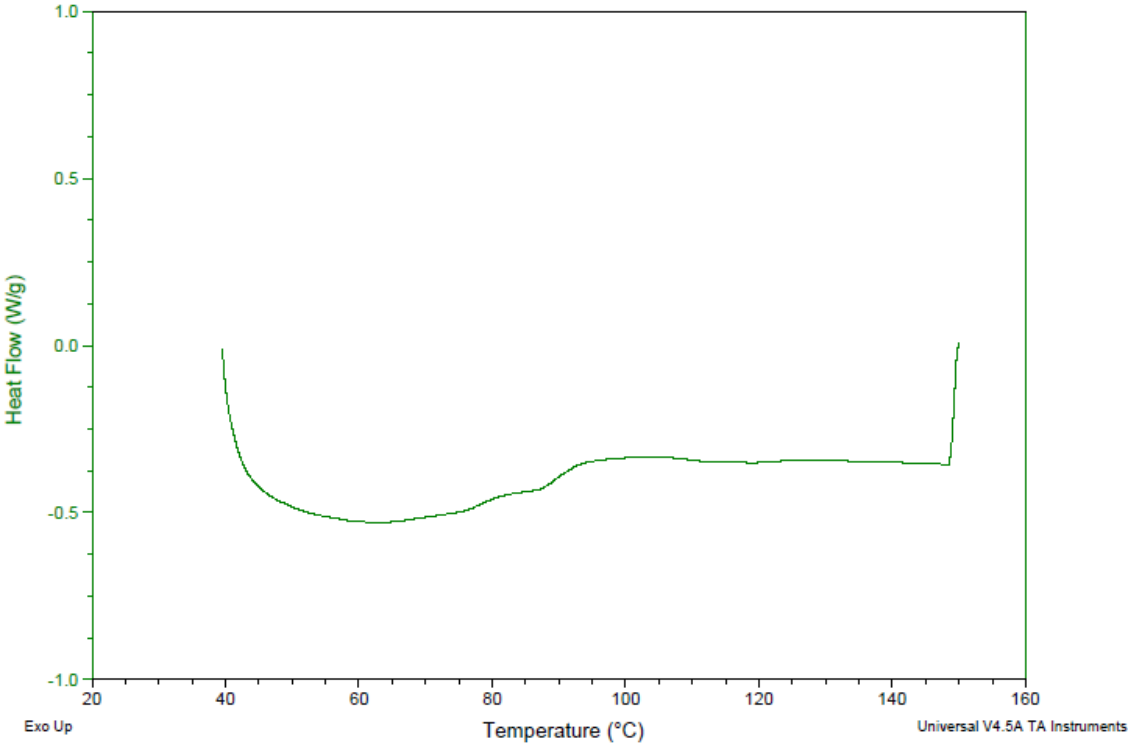


**Figure S25**. DSC data of the polyethylene from table 1, entry 14.

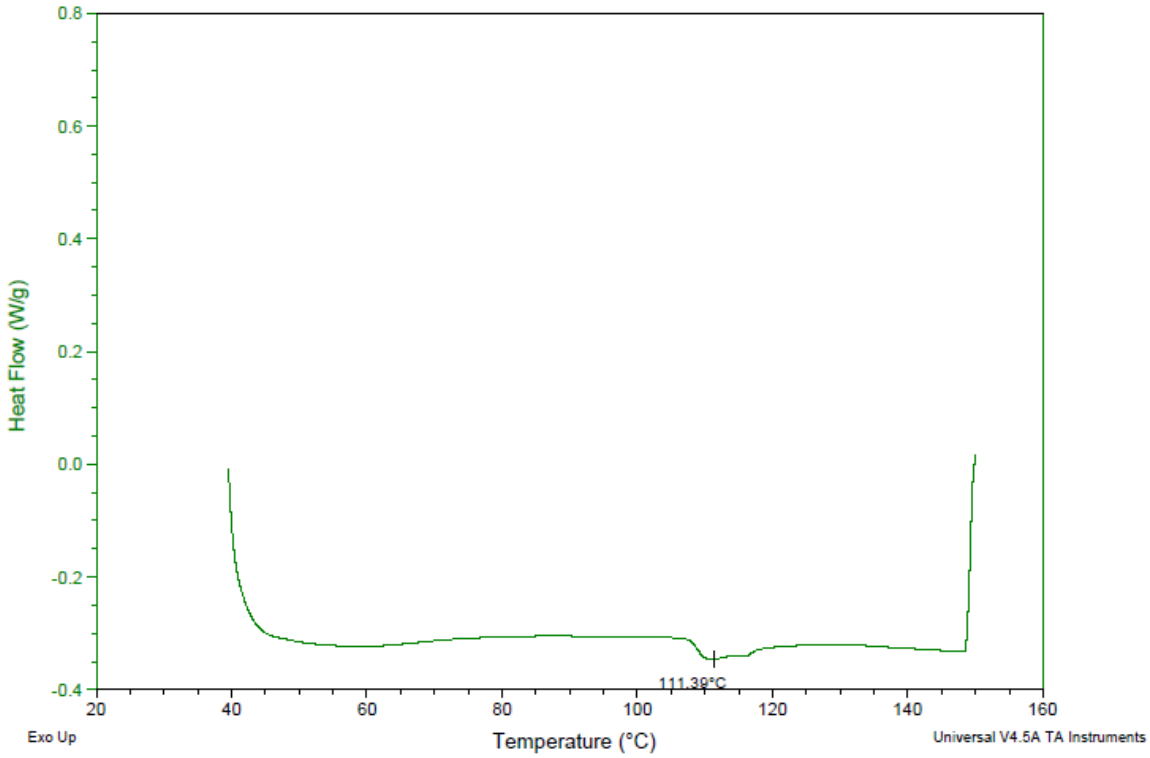


**Figure S26**. DSC data of the polyethylene from table 1, entry 15.

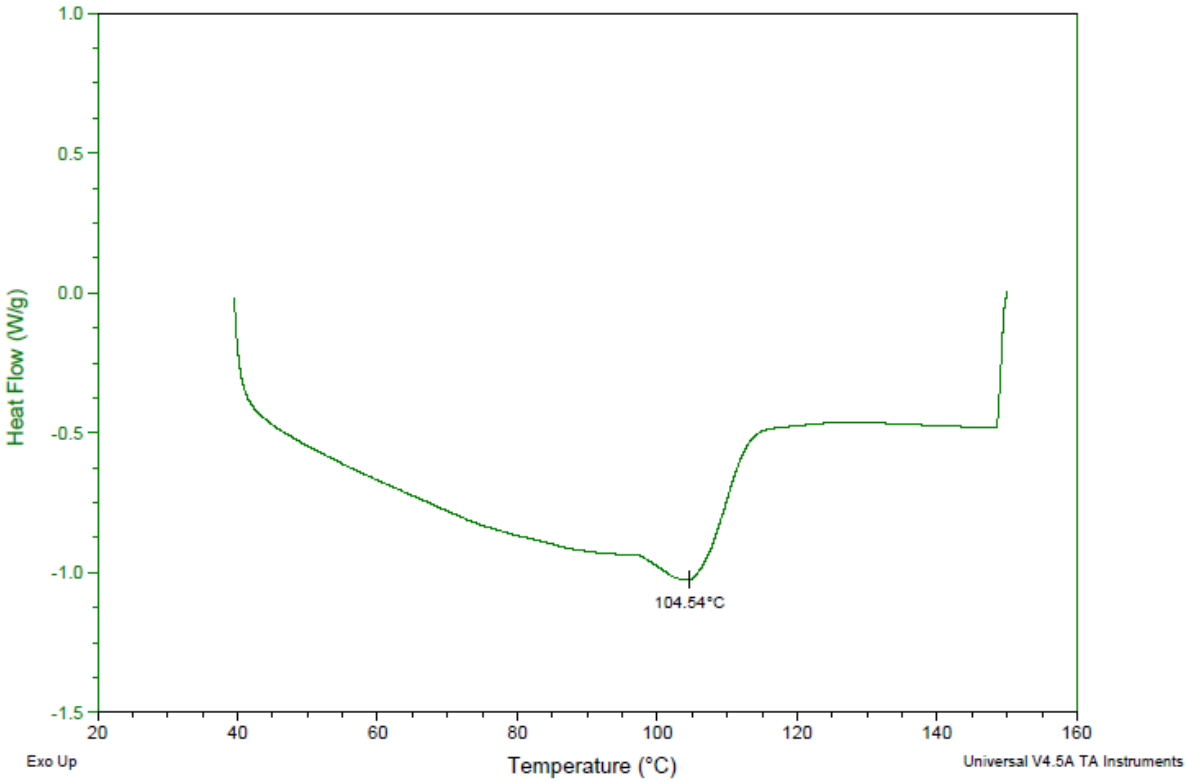


**Figure S27**. DSC data of the polyethylene from table 1, entry 16.

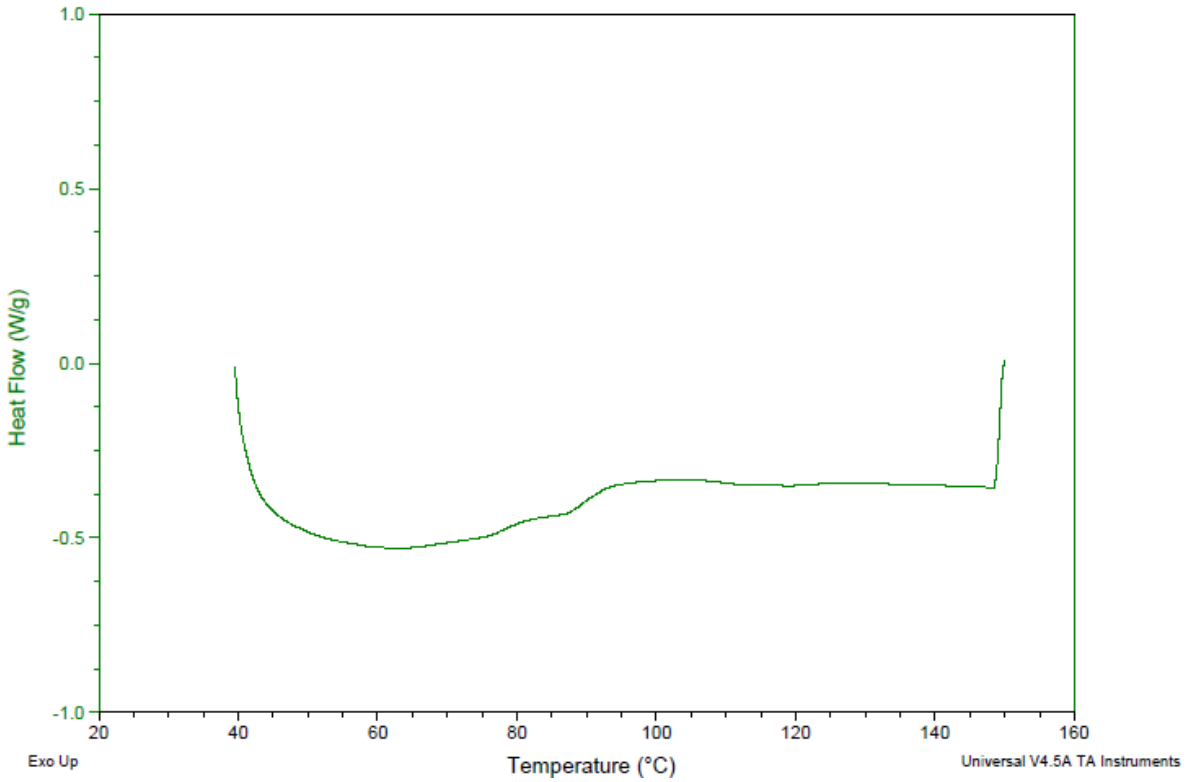


**Figure S28**. DSC data of the polyethylene from table 1, entry 17.

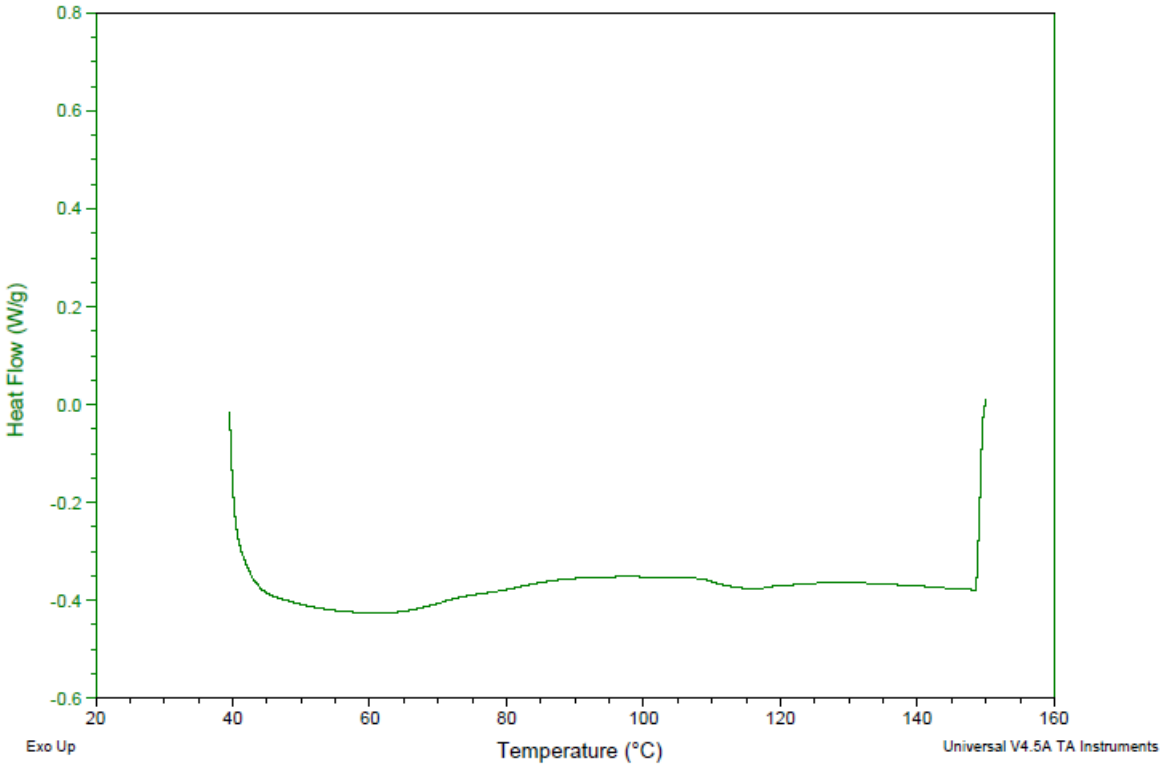


**Figure S29**. DSC data of the polyethylene from table 1, entry 18.

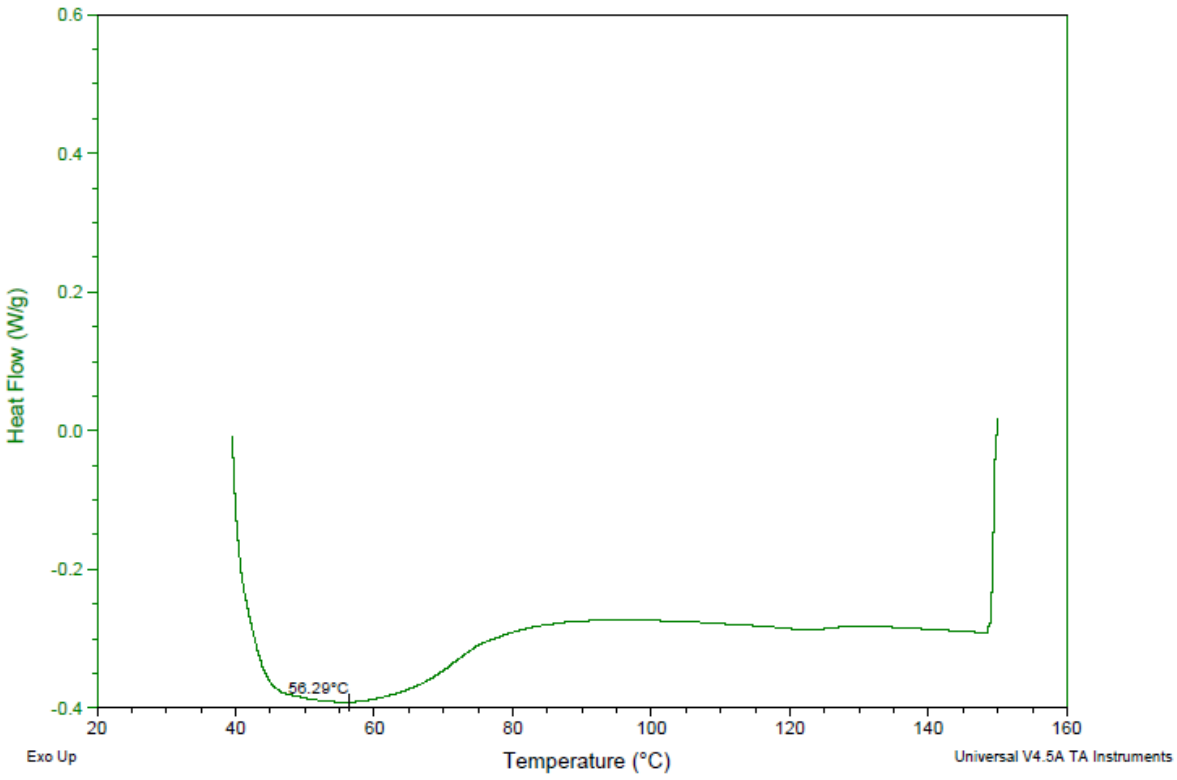


**Figure S30**. DSC data of the polyethylene from table 1, entry 19.

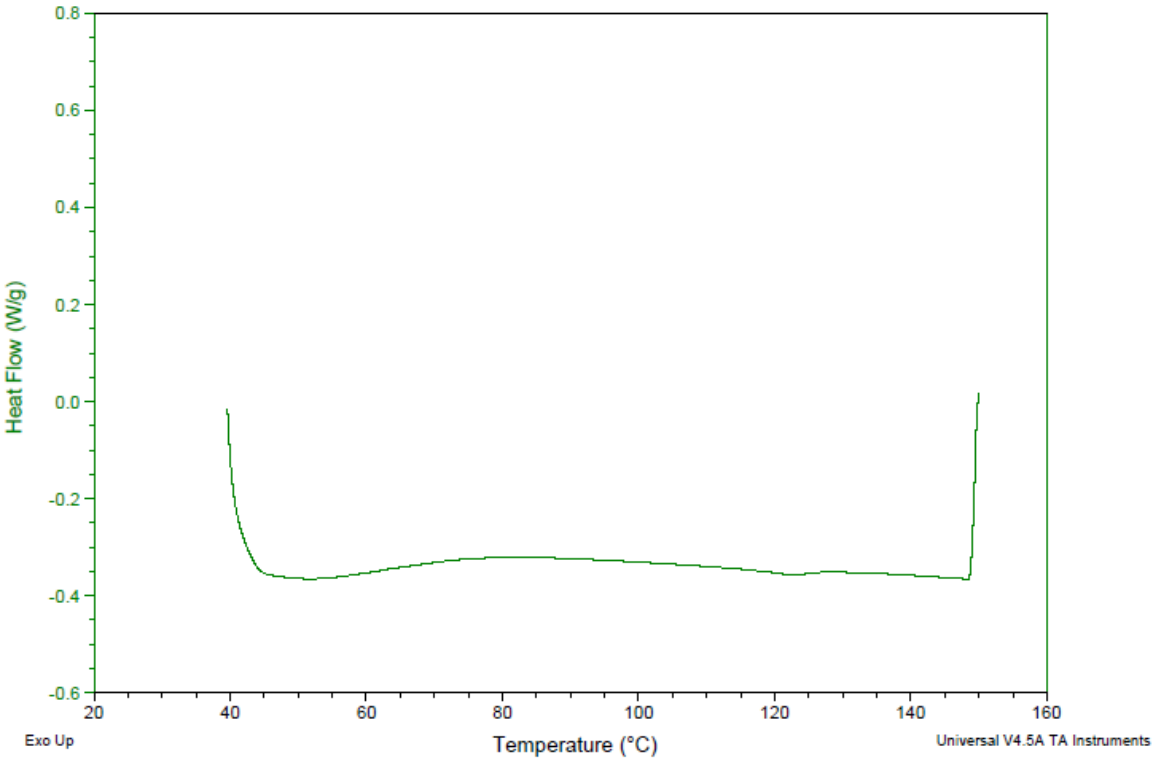


**Figure S31**. DSC data of the polyethylene from table 1, entry 20.

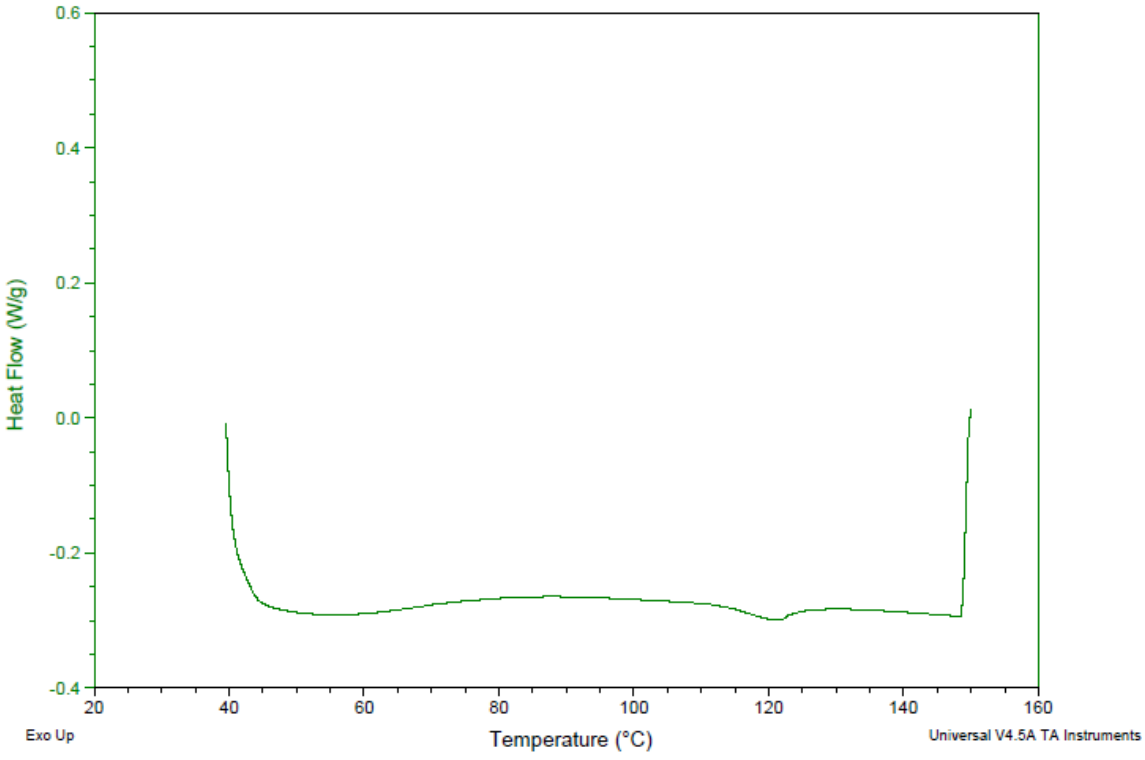


**Figure S32**. DSC data of the polyethylene from table 1, entry 21.

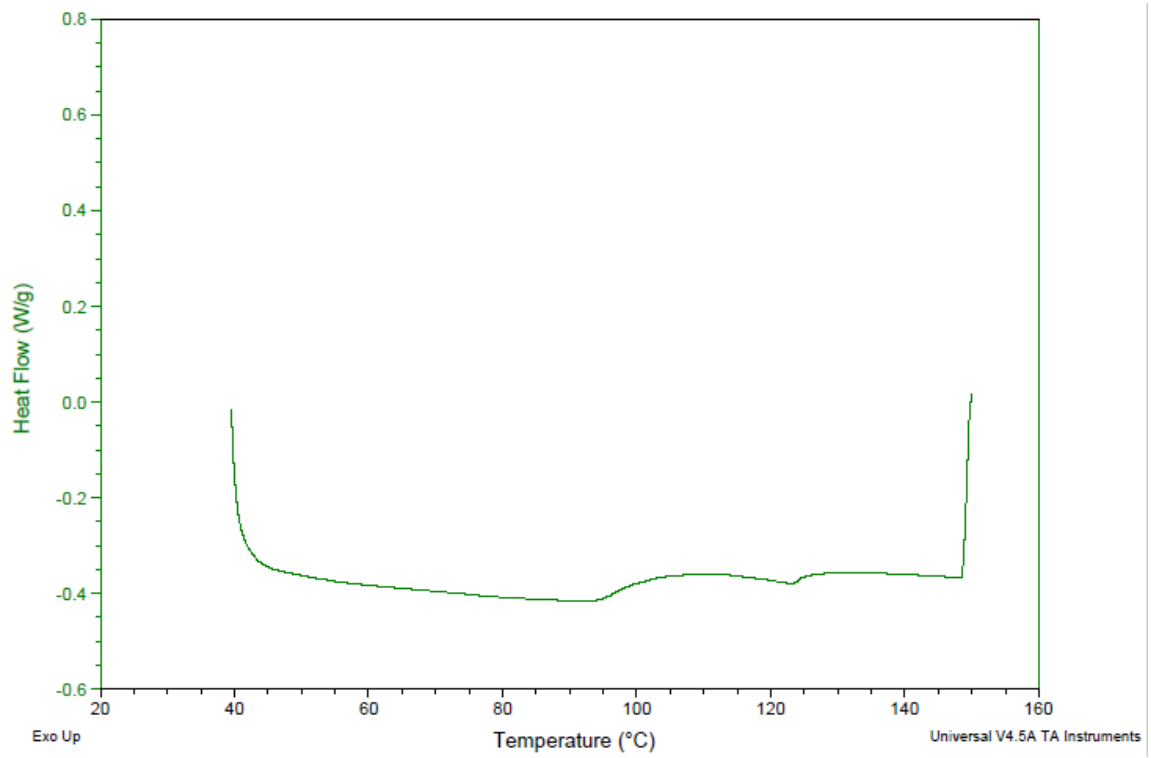


**Figure S33**. DSC data of the polyethylene from table 1, entry 22.

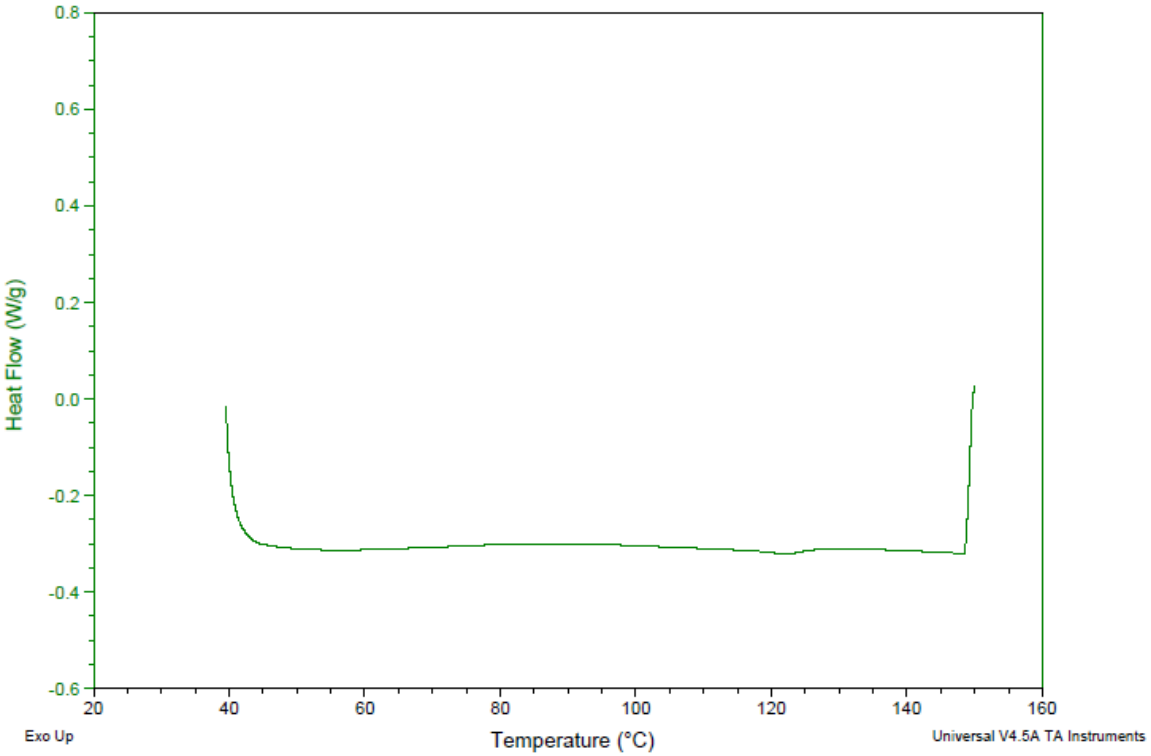


**Figure S34**. DSC data of the polyethylene from table 1, entry 23.

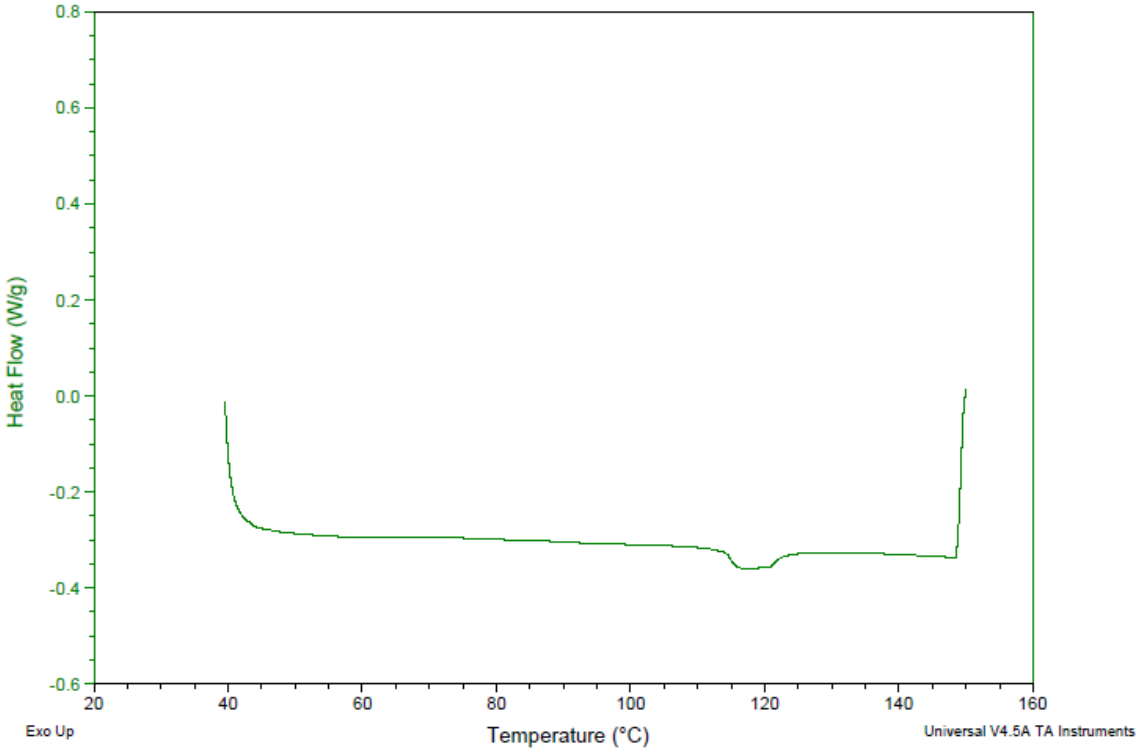


**Figure S35**. DSC data of the polyethylene from table 1, entry 24.

## 4. X-ray Crystallography

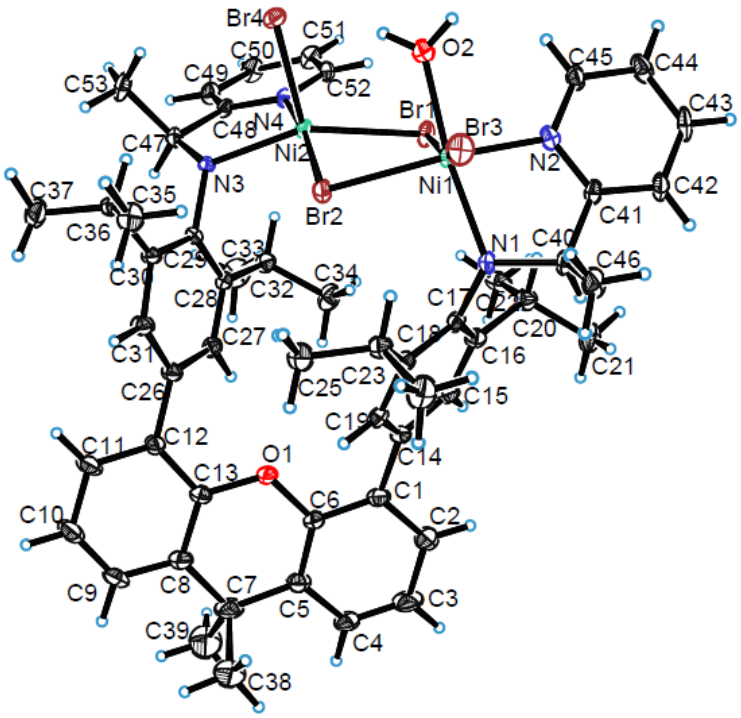


**Figure S36**. Molecular structure of **$Ni_2$-C′**. Thermal ellipsoids are shown at the 30% probability level.

The molecular structure of **$Ni_2$-C′** was confirmed by single-crystal X-ray diffraction and the corresponding ORTEP diagram is shown in **Figure S8**. Data collections were performed at 296(2) K on a Bruker SMART APEX diffractometer with a charge-coupled device (CCD) area detector, using graphite monochromated MoKa radiation ($\lambda$ = 0.71073 Å). The determination of crystal class and unit cell parameters was carried out using the SMART program package. The raw frame data were processed using SAINT and SADABS to yield the reflection data file. The structures were solved by using the SHELXTL program. Refinement was performed on $F^2$ anisotropically for all nonhydrogen atoms by the full-matrix least-squares method. The hydrogen atoms were placed at the calculated positions and were included in the structure calculation without further refinement of the parameters. Crystal data, data collection, and refinement parameters are listed in **Table S1**. Bond distances and angles are summarized in **Table S2** and **S3**.

**Table S1.** Crystal data and structure refinements of **$Ni_2$-C′**.

| | |
|---|---|
| Empirical Formula | $C_{53}H_{62}Br_4N_4Ni_2O_2$ |
| Formula mass | 1224.12 |
| Temperature (*K*) | 291(2) |
| Wavelength (*Å*) | 0.71073 |
| Crystal size ($mm^3$) | 0.33 × 0.31 × 0.25 |
| Crystal system | Orthorhombic |
| Space group | $P2_12_12_1$ |
| *a* (Å) | 12.9028(4) |
| *b* (Å) | 16.4766(6) |
| *c* (Å) | 30.5902(16) |
| *V* ($Å^3$) | 6503.3(5) |
| *Z* | 4 |
| Density (calcd.) ($mg/cm^3$) | 1.250 |
| Absorption coefficient ($mm^{-1}$) | 3.071 |
| *F* (000) | 2480.0 |
| Theta range for data collec. (°) | 6.016 to 52.744 |
| Limiting indices | $-16 \le h \le 15$, $-20 \le k \le 20$, $-38 \le l \le 38$ |
| Reflections collected | 30275 |
| Independent reflections | 12921 |
| $R_{int}$ | 0.0516 |
| Final *R* indices [$I > 2\sigma(I)$] | $R_1$ = 0.0588, $wR_2$ = 0.1365 |
| *R* indices (all data) | $R_1$ = 0.0882, $wR_2$ = 0.1500 |
| Refinement method | Full-matrix least-squares on $F^2$ |
| Goodness-of-fit on $F^2$ | 1.083 |
| Largest diff. peak and hole ($e.Å^{-3}$) | 0.54 and –0.40 |
| Flack parameter | 0.003(6) |

**Table S2**. Bond lengths (Å) for of **$Ni_2$-C′**.

| Atom | Atom | Length/Å | Atom | Atom | Length/Å |
|---|---|---|---|---|---|
| Br4 | Ni2 | 2.4643(17) | C16 | C15 | 1.382(16) |
| Br2 | Ni2 | 2.4873(14) | C16 | C20 | 1.538(15) |
| Br2 | Ni1 | 2.5222(15) | C31 | C26 | 1.390(14) |
| Ni2 | Br1 | 2.5038(15) | C31 | C30 | 1.395(14) |
| Ni2 | N3 | 2.105(8) | N4 | C48 | 1.345(12) |
| Ni2 | N4 | 2.062(8) | C32 | C33 | 1.493(17) |
| Br3 | Ni1 | 2.5780(16) | C32 | C34 | 1.521(15) |
| Br1 | Ni1 | 2.6319(15) | C43 | C42 | 1.372(18) |
| Ni1 | N2 | 2.041(8) | C43 | C44 | 1.365(19) |
| Ni1 | N1 | 2.195(9) | C50 | C49 | 1.333(15) |
| Ni1 | O2 | 2.087(8) | C50 | C51 | 1.378(16) |
| O1 | C6 | 1.374(13) | C26 | C12 | 1.491(14) |
| O1 | C13 | 1.388(13) | C23 | C18 | 1.530(15) |
| C28 | C29 | 1.389(13) | C23 | C25 | 1.517(17) |
| C28 | C27 | 1.387(14) | C23 | C24 | 1.536(15) |
| C28 | C32 | 1.501(14) | C13 | C8 | 1.386(16) |
| N2 | C41 | 1.342(13) | C13 | C12 | 1.397(15) |
| N2 | C45 | 1.319(14) | C36 | C30 | 1.526(14) |
| N3 | C29 | 1.474(12) | C36 | C35 | 1.524(15) |
| N3 | C47 | 1.522(12) | C36 | C37 | 1.517(16) |
| C17 | C16 | 1.410(15) | C48 | C49 | 1.389(13) |
| C17 | N1 | 1.476(14) | C44 | C45 | 1.368(16) |
| C17 | C18 | 1.414(15) | C20 | C22 | 1.564(17) |
| C40 | C41 | 1.536(15) | C20 | C21 | 1.539(17) |
| C40 | N1 | 1.490(12) | C1 | C2 | 1.389(17) |
| C40 | C46 | 1.507(14) | C5 | C7 | 1.51(2) |
| C14 | C19 | 1.402(15) | C5 | C4 | 1.391(16) |
| C14 | C15 | 1.366(15) | C11 | C12 | 1.380(16) |
| C14 | C1 | 1.484(15) | C11 | C10 | 1.367(18) |
| C52 | N4 | 1.347(12) | C8 | C9 | 1.366(17) |
| C52 | C51 | 1.379(14) | C8 | C7 | 1.53(2) |
| C29 | C30 | 1.430(13) | C2 | C3 | 1.44(2) |
| C47 | C48 | 1.527(14) | C9 | C10 | 1.36(2) |
| C47 | C53 | 1.529(16) | C7 | C39 | 1.44(4) |
| C41 | C42 | 1.355(14) | C7 | C38 | 1.64(4) |
| C27 | C26 | 1.407(14) | C7 | C38' | 1.40(4) |
| C6 | C1 | 1.392(16) | C7 | C39' | 1.83(4) |

| | | | | | |
|---|---|---|---|---|---|
| C6 | C5 | 1.388(15) | C3 | C4 | 1.33(2) |
| C19 | C18 | 1.388(15) | | | |

**Table S3.** Bond angles (º) for **$Ni_2$-C′**.

| Atom | Atom | Atom | Angle/° | Atom | Atom | Atom | Angle/° |
|---|---|---|---|---|---|---|---|
| Ni2 | Br2 | Ni1 | 93.38(5) | C14 | C15 | C16 | 126.4(11) |
| Br4 | Ni2 | Br2 | 96.17(5) | C28 | C32 | C34 | 109.5(9) |
| Br4 | Ni2 | Br1 | 108.61(6) | C33 | C32 | C28 | 114.6(10) |
| Br2 | Ni2 | Br1 | 86.35(5) | C33 | C32 | C34 | 110.6(11) |
| N3 | Ni2 | Br4 | 96.7(2) | C44 | C43 | C42 | 119.8(11) |
| N3 | Ni2 | Br2 | 91.8(2) | C41 | C42 | C43 | 118.5(12) |
| N3 | Ni2 | Br1 | 154.7(2) | C49 | C50 | C51 | 118.9(9) |
| N4 | Ni2 | Br4 | 93.6(2) | C27 | C26 | C12 | 121.5(9) |
| N4 | Ni2 | Br2 | 168.9(3) | C31 | C26 | C27 | 117.3(10) |
| N4 | Ni2 | Br1 | 95.6(2) | C31 | C26 | C12 | 120.9(9) |
| N4 | Ni2 | N3 | 81.8(3) | C18 | C23 | C24 | 111.2(9) |
| Ni2 | Br1 | Ni1 | 90.40(5) | C25 | C23 | C18 | 112.5(9) |
| Br2 | Ni1 | Br3 | 95.98(5) | C25 | C23 | C24 | 111.1(10) |
| Br2 | Ni1 | Br1 | 82.97(5) | O1 | C13 | C12 | 116.2(9) |
| Br3 | Ni1 | Br1 | 166.47(7) | C8 | C13 | O1 | 122.1(10) |
| N2 | Ni1 | Br2 | 170.5(2) | C8 | C13 | C12 | 121.6(11) |
| N2 | Ni1 | Br3 | 92.3(2) | C35 | C36 | C30 | 110.8(10) |
| N2 | Ni1 | Br1 | 90.1(2) | C37 | C36 | C30 | 109.9(10) |
| N2 | Ni1 | N1 | 80.4(3) | C37 | C36 | C35 | 112.1(11) |
| N2 | Ni1 | O2 | 94.0(3) | N4 | C48 | C47 | 119.1(8) |
| N1 | Ni1 | Br2 | 95.4(2) | N4 | C48 | C49 | 119.8(9) |
| N1 | Ni1 | Br3 | 86.1(3) | C49 | C48 | C47 | 121.2(9) |
| N1 | Ni1 | Br1 | 107.4(3) | C29 | C30 | C36 | 124.5(9) |
| O2 | Ni1 | Br2 | 92.0(2) | C31 | C30 | C29 | 117.1(9) |
| O2 | Ni1 | Br3 | 81.2(2) | C31 | C30 | C36 | 118.4(9) |
| O2 | Ni1 | Br1 | 85.4(2) | C17 | N1 | Ni1 | 124.9(6) |
| O2 | Ni1 | N1 | 165.9(3) | C17 | N1 | C40 | 115.1(9) |
| C6 | O1 | C13 | 120.0(8) | C40 | N1 | Ni1 | 110.6(7) |
| C29 | C28 | C32 | 124.0(9) | C17 | C18 | C23 | 123.3(10) |
| C27 | C28 | C29 | 117.8(9) | C19 | C18 | C17 | 118.8(11) |
| C27 | C28 | C32 | 118.2(9) | C19 | C18 | C23 | 117.8(10) |
| C41 | N2 | Ni1 | 117.6(7) | C43 | C44 | C45 | 118.2(12) |
| C45 | N2 | Ni1 | 124.0(8) | C16 | C20 | C22 | 112.8(10) |
| C45 | N2 | C41 | 118.3(9) | C16 | C20 | C21 | 111.8(10) |

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|---|---|---|---|---|---|---|---|
| C29 | N3 | Ni2 | 118.7(6) | C21 | C20 | C22 | 108.7(11) |
| C29 | N3 | C47 | 113.5(8) | C50 | C49 | C48 | 121.6(11) |
| C47 | N3 | Ni2 | 111.8(6) | C6 | C1 | C14 | 124.3(10) |
| C16 | C17 | N1 | 121.7(10) | C2 | C1 | C14 | 117.6(11) |
| C16 | C17 | C18 | 120.7(10) | C2 | C1 | C6 | 117.6(11) |
| C18 | C17 | N1 | 117.6(10) | C6 | C5 | C7 | 120.4(12) |
| N1 | C40 | C41 | 111.0(8) | C6 | C5 | C4 | 120.1(12) |
| N1 | C40 | C46 | 111.6(9) | C4 | C5 | C7 | 119.5(12) |
| C46 | C40 | C41 | 109.9(10) | C10 | C11 | C12 | 121.4(14) |
| C19 | C14 | C1 | 120.2(10) | C13 | C8 | C7 | 120.1(12) |
| C15 | C14 | C19 | 115.9(11) | C9 | C8 | C13 | 119.0(12) |
| C15 | C14 | C1 | 123.5(11) | C9 | C8 | C7 | 120.8(12) |
| N4 | C52 | C51 | 121.9(11) | C13 | C12 | C26 | 122.8(10) |
| C28 | C29 | N3 | 120.4(8) | C11 | C12 | C26 | 120.3(10) |
| C28 | C29 | C30 | 121.9(9) | C11 | C12 | C13 | 116.7(11) |
| C30 | C29 | N3 | 117.6(8) | C50 | C51 | C52 | 118.8(11) |
| N3 | C47 | C48 | 110.1(8) | C1 | C2 | C3 | 119.3(14) |
| N3 | C47 | C53 | 111.5(9) | C10 | C9 | C8 | 120.1(13) |
| C48 | C47 | C53 | 109.2(9) | C5 | C7 | C8 | 113.0(11) |
| N2 | C41 | C40 | 118.3(9) | C5 | C7 | C38 | 106.4(17) |
| N2 | C41 | C42 | 122.4(11) | C5 | C7 | C39' | 97.1(19) |
| C42 | C41 | C40 | 119.3(10) | C8 | C7 | C38 | 104.1(19) |
| C28 | C27 | C26 | 123.0(10) | C8 | C7 | C39' | 100.9(17) |
| O1 | C6 | C1 | 115.3(9) | C39 | C7 | C5 | 118(2) |
| O1 | C6 | C5 | 122.9(10) | C39 | C7 | C8 | 115(2) |
| C5 | C6 | C1 | 121.7(11) | C39 | C7 | C38 | 97(2) |
| C18 | C19 | C14 | 122.1(11) | C38' | C7 | C5 | 121(2) |
| C17 | C16 | C20 | 124.9(11) | C38' | C7 | C8 | 122(2) |
| C15 | C16 | C17 | 115.9(10) | C38' | C7 | C39' | 93(2) |
| C15 | C16 | C20 | 119.1(10) | N2 | C45 | C44 | 122.8(12) |
| C26 | C31 | C30 | 122.8(10) | C4 | C3 | C2 | 121.8(14) |
| C52 | N4 | Ni2 | 125.5(7) | C9 | C10 | C11 | 120.8(14) |
| C48 | N4 | Ni2 | 115.5(6) | C3 | C4 | C5 | 119.3(13) |
| C48 | N4 | C52 | 119.0(8) | | | | |