Supporting Information for

Enhancing thermostability of iron ethylene polymerization catalysts through *N,N,N*-chelation of doubly fused α,α′-bis(arylimino)-2,3:5,6-bis(hexamethylene)pyridines

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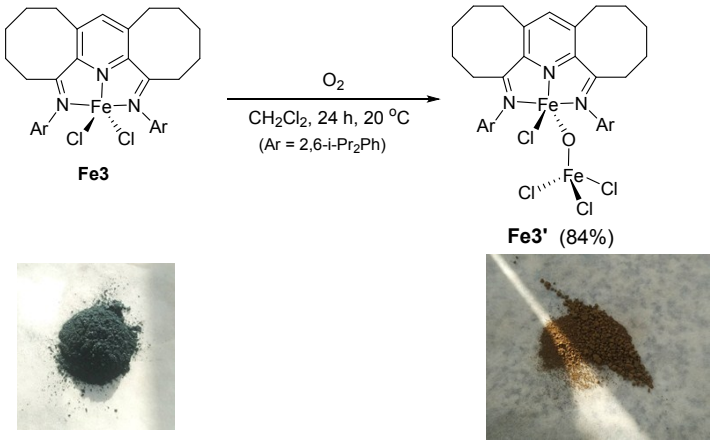
1. General considerations

All manipulations involving air- and moisture-sensitive compounds were carried out under nitrogen atmosphere using standard Schlenk techniques. Toluene was heated to reflux over sodium and distilled under nitrogen prior to use. The NMR spectra were recorded with a Bruker DMX 500 MHz and 600 MHz instrument at ambient temperature using TMS as internal standard. The melting points of the polyethylenes were measured from the fourth scanning run on a PerkinElmer TA-Q2000 differential scanning calorimeter under a nitrogen atmosphere. A sample of about 5.0 mg was heated to 160 °C at a rate of 20 °C min^{-1}, maintained for 2 min at 160 °C to remove the thermal history and then cooled to – 40 °C at a rate of 20 °C min^{-1}. ^{13}C NMR spectra of the polyethylenes were recorded with a Bruker DMX 300 MHz instrument at 135 °C in 1,1,2,2-d_2-tetrachloroethane with TMS as internal standard. The compound α,α′-dioxo-2,3:5,6-bis(hexamethylene)pyridine was prepared by the reported method.[1,2]

2. Oxidation of Fe3 to Fe3'



A sample of **Fe3** (0.35 g, 0.50 mmol) dissolved in dichloromethane (25 mL) was stirred for 24 h at 20 °C under and an atmosphere of oxygen (or 120 hours under air) resulting in a color change from blue to light green. The solvent was removed under reduced pressure and diethyl ether (20 mL) added to induce precipitation. The solid was filtered, washed with diethyl ether and dried under reduced pressure affording [2,3:5,6-{$C_5H_{10}C$=N(2,6-i-Pr_2Ph)}$_2C_5HN$] FeCl(μ-O)$FeCl_3$ (**Fe3'**) as a yellow solid (0.18 g, 84%). FT-IR (cm^{-1}): 2963 (m), 2929 (m), 2864 (w), 1677 (m, $\nu_{C=N}$) 1584 (m), 1543 (w), 1453 (s), 1385 (w), 1360 (w), 1306 (w), 1248 (m), 1188 (w), 1162 (w), 1110 (w), 1052 (w), 1009 (w), 932 (w), 844 (w, $\nu_{Fe\text{-}O\text{-}Fe}$), 799 (m), 754 (m). Anal. Calcd for $C_{41}H_{55}Cl_4Fe_2N_3O$ (859.40): C, 57.30, H, 6.45, N, 4.89; found: C, 57.22, H, 6.23, N, 4.70%.

3. Comparison of the catalytic performance of (**G**)$FeCl_2$ (**Fe1**) with previous iron catalysts bearing **A**,[3] **B**,[4] $\mathbf{D}_{Me}$ (R = Me),[5] $\mathbf{D}_{Ph}$ (R = Ph),[6] and **F**[7] at 80 °C; MAO used as activator in each case.

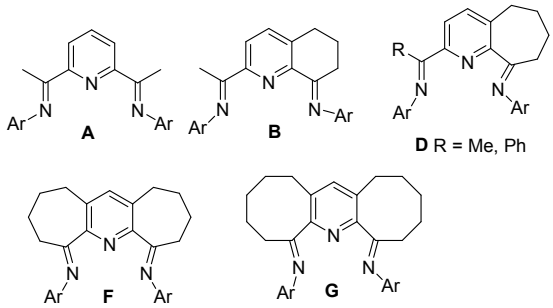


Table S1. Polymerization screening using (**A**)$FeCl_2$/MAO[a,3]

Run	Al:Fe	T (°C)	t (min)	Mass of PE (g)	Activity[b]	M_w[c]	M_w/M_n[c]	T_m (°C)[d]
1	2000	80	30	5.70	5.70	38.5	8.3	130.0

[a] Conditions: 2.0 μmol of iron complex; 100 mL toluene, 10 atm C_2H_4. [b] Values in units of 10^6 g(PE) mol^{-1} (Fe) h^{-1}.

[c] Determined by GPC, and M_w in kg mol^{-1}. [d] Determined by DSC.

Table S2. Polymerization screening using (**B**)$FeCl_2$/MAO[a,4]

Run	Al:Fe	T (°C)	t (min)	Mass of PE (g)	Activity[b]	M_w[c]	M_w/M_n[c]	T_m (°C)[d]
1	2000	80	30	10.20	6.81	18.5	4.3	127.6

[a] Conditions: 3.0 μmol of iron complex; 100 mL toluene, 10 atm C_2H_4. [b] Values in units of 10^6 g(PE) mol^{-1} (Fe) h^{-1}.

[c] Determined by GPC, and M_w in kg mol^{-1}. [d] Determined by DSC

Table S3. Polymerization screening using ($\mathbf{D}_{Me}$)$FeCl_2$/MAO[a,5]

Run	Al:Fe	T (°C)	t (min)	Mass of PE (g)	Act.[b]	M_w[c]	M_w/M_n[c]	T_m (°C)[d]
1	2500	80	30	9.30	6.20	13.7	3.8	129.0

[a] Conditions: 3.0 μmol of iron complex; 100 mL toluene, 10 atm C_2H_4. [b] Values in units of 10^6 g(PE) mol^{-1} (Fe) h^{-1}.

[c] Determined by GPC and M_w in kg mol^{-1}. [d] Determined by DSC

Table S4. Polymerization screening using ($\mathbf{D}_{Ph}$)$FeCl_2$/MAO[a,6]

Run	Al:Fe	T (°C)	t (min)	Mass of PE (g)	Activity[b]	M_w[c]	M_w/M_n[c]	T_m (°C)[d]
1	2000	80	30	10.30	6.87	4.4	2.9	126.5

[a] Conditions: 3.0 μmol of iron complex; 100 mL toluene, 10 atm C_2H_4. [b] Values in units of 10^6 g(PE) mol^{-1} (Fe) h^{-1}.

[c] Determined by GPC, and M_w in kg mol^{-1}. [d] Determined by DSC.

Table S5. Polymerization screening using (**F**)$FeCl_2$/MAO[a,7]

Run	Al:Fe	T (°C)	t (min)	Mass of PE (g)	Activity[b]	M_w[c]	M_w/M_n[c]	T_m (°C)[d]
1	2000	80	30	14.62	9.75	12.7	13.7	128.9

[a] Conditions: 3.0 μmol of iron complex; 100 mL toluene, 10 atm C_2H_4. [b] Values in units of 10^6 g(PE) mol^{-1} (Fe) h^{-1}.

[c] Determined by GPC, and M_w in kg mol^{-1}. [d] Determined by DSC.

4. X-Ray crystallographic studies

Table S6. Crystal data and structure refinement for **Fe3** and **Fe3'**

Identification code	**Fe3**·THF	**Fe3'**
Empirical formula	$C_{90}H_{122}Cl_4Fe_2N_6O_2$	$C_{41}H_{55}N_3Cl_4Fe_2O$
Formula weight	1573.43	859.41
Temperature/K	293(2)	175.15
Crystal system	monoclinic	monoclinic
Space group	$P2_1/c$	$P2_1/c$
a/Å	13.3638(3)	12.228(2)
b/Å	34.6037(6)	21.820(4)
c/Å	18.3685(4)	16.338(3)
α/°	90	90
β/°	102.600(2)	104.20(3)
γ/°	90	90
Volume/Å^3	8289.7(3)	4225.9(16)
Z	4	4
ρ_{calc}g/cm^3	1.261	1.3507
μ/mm^{-1}	0.530	0.974
F(000)	3360.0	1805.7
Crystal size/mm^3	0.355 × 0.080 × 0.035	0.355 × 0.071 × 0.063
Radiation	Mo-K_α (λ = 0.71073)	Mo-K_α (λ = 0.71073)
2Θ range for data collection/°	3.272 to 55	3.18 to 54.96
Index ranges	-15 ≤ h ≤ 17, -44 ≤ k ≤ 44, -23 ≤ l ≤ 23	-14 ≤ h ≤ 15, -28 ≤ k ≤ 28, -21 ≤ l ≤ 21
Reflections collected	77124	45762
Independent reflections	19015 [R_{int}= 0.0632, R_{sigma}= 0.0639]	9671 [R_{int} = 0.0678, R_{sigma} = 0.0522]
Data/restraints/parameters	19015/0/953	9671/36/496
Goodness-of-fit on F^2	1.094	1.038
Final R indexes [I>=2σ (I)]	R_1 = 0.1006, wR_2 = 0.2461	R_1 = 0.0840, wR_2 = 0.1395
Final R indexes [all data]	R_1 = 0.1373, wR_2 = 0.2641	R_1 = 0.0943, wR_2 = 0.1445
Largest diff. peak/hole / e Å^{-3}	2.80/-0.80	0.81/-0.85

5. DSC thermograms of the polyethylenes

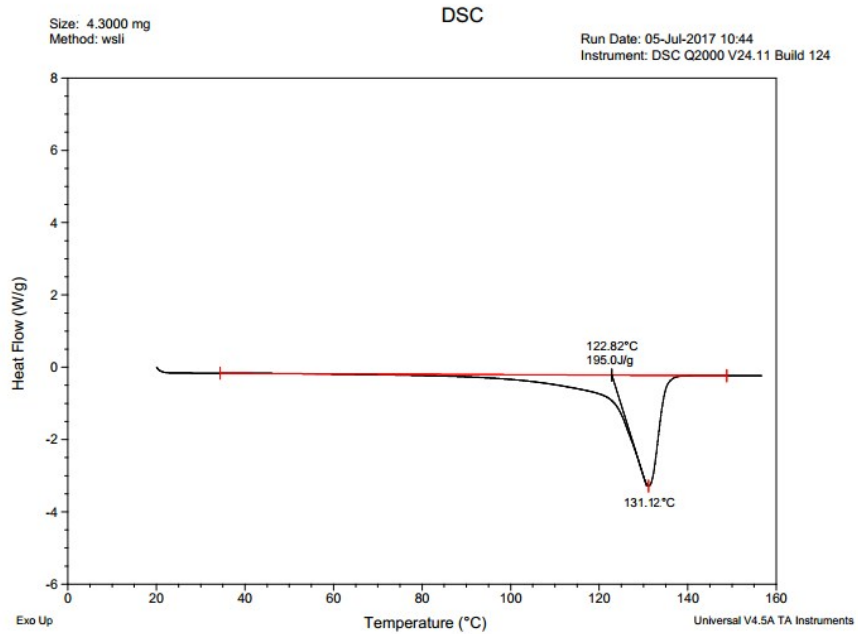


Figure S1. DSC thermogram of the polyethylene obtained using **Fe1**/MMAO at 30 °C (Al:Fe = 2000, Table 2, entry 1)

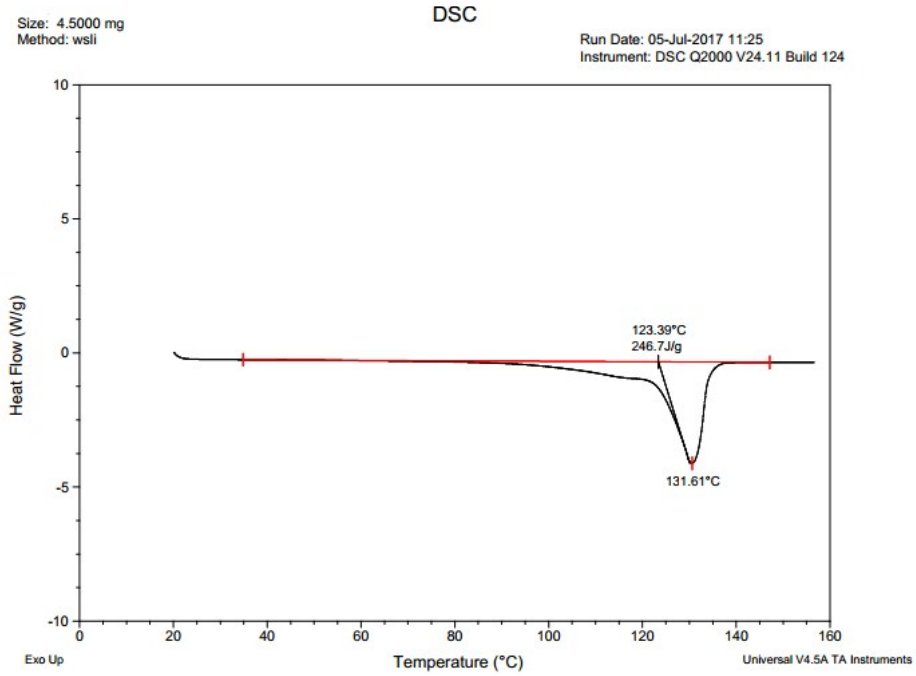


Figure S2. DSC thermogram of the polyethylene obtained using **Fe1**/MMAO at 40 °C (Al:Fe = 2000, Table 2, entry 2)

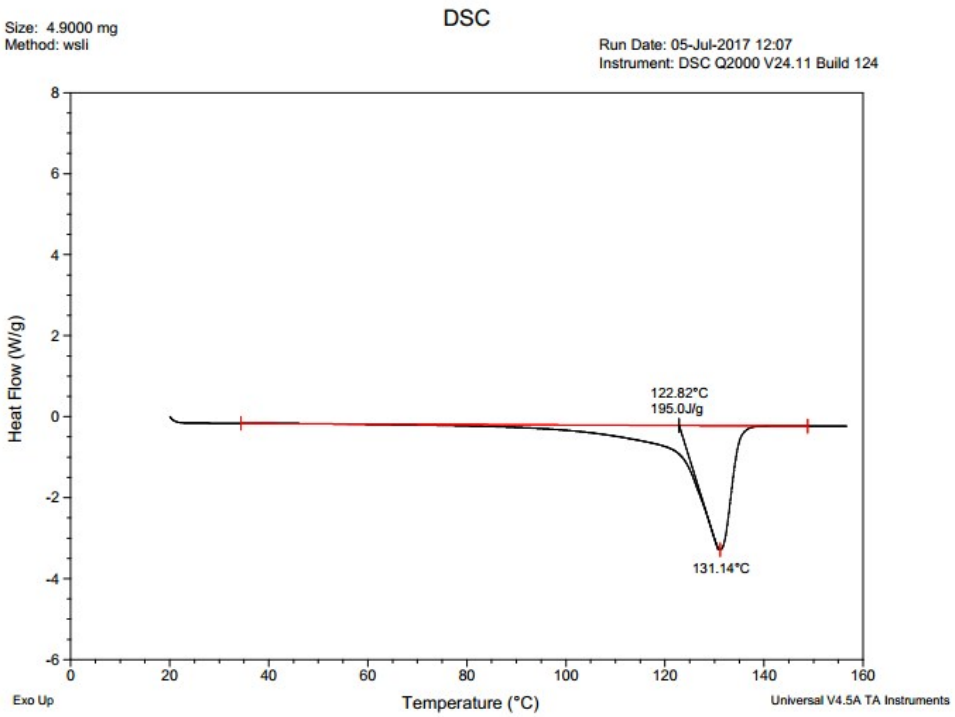


Figure S3. DSC thermogram of the polyethylene obtained using **Fe1**/MMAO at 50 °C (Al:Fe = 2000, Table 2, entry 3)

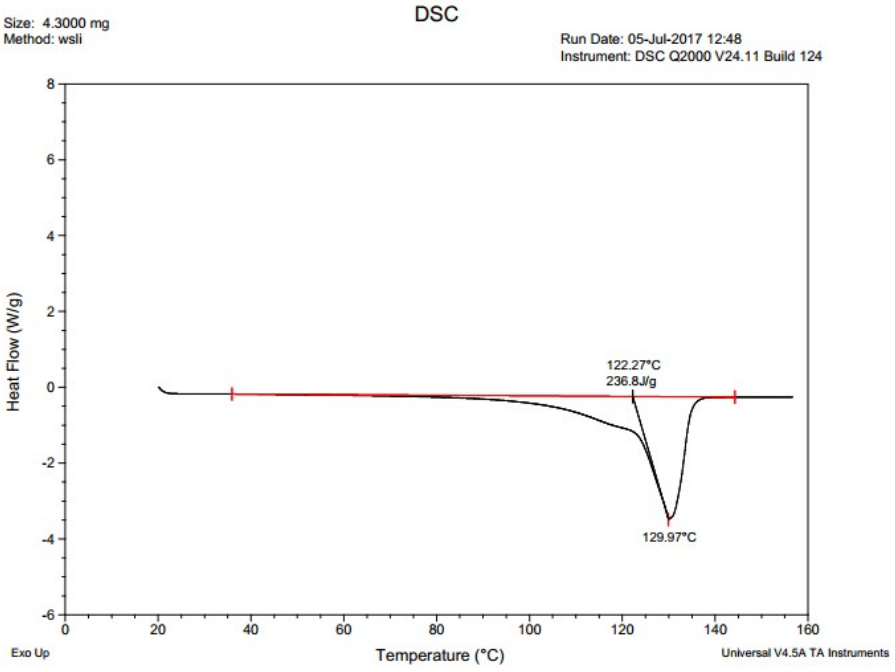


Figure S4. DSC thermogram of the polyethylene obtained using **Fe1**/MMAO at 60 °C (Al:Fe = 2000, Table 2, entry 4)

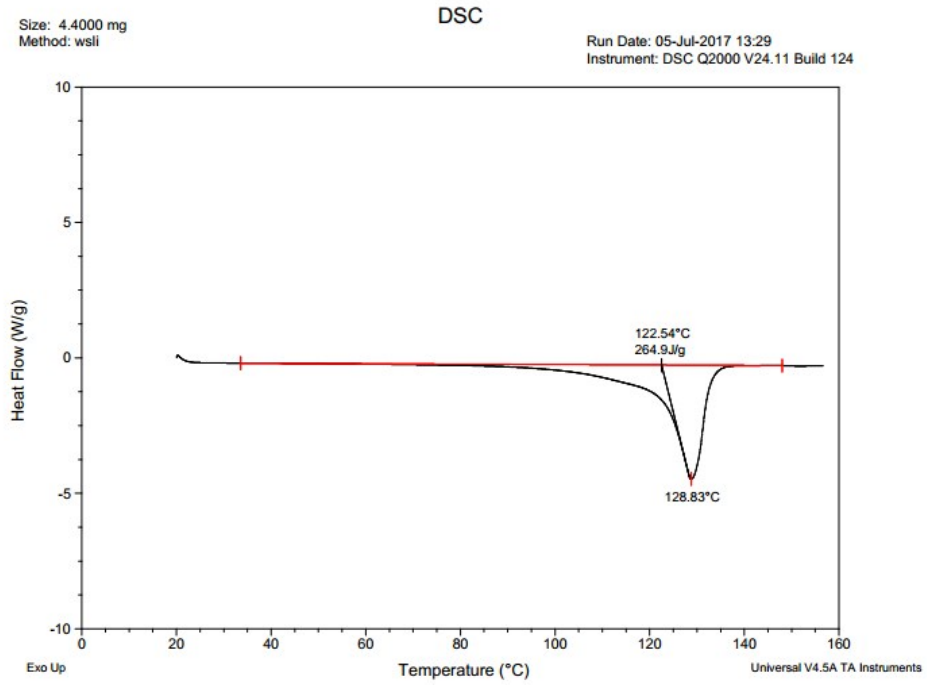


Figure S5. DSC thermogram of the polyethylene obtained using **Fe1**/MMAO at 70 °C (Al:Fe = 2000, Table 2, entry 5)

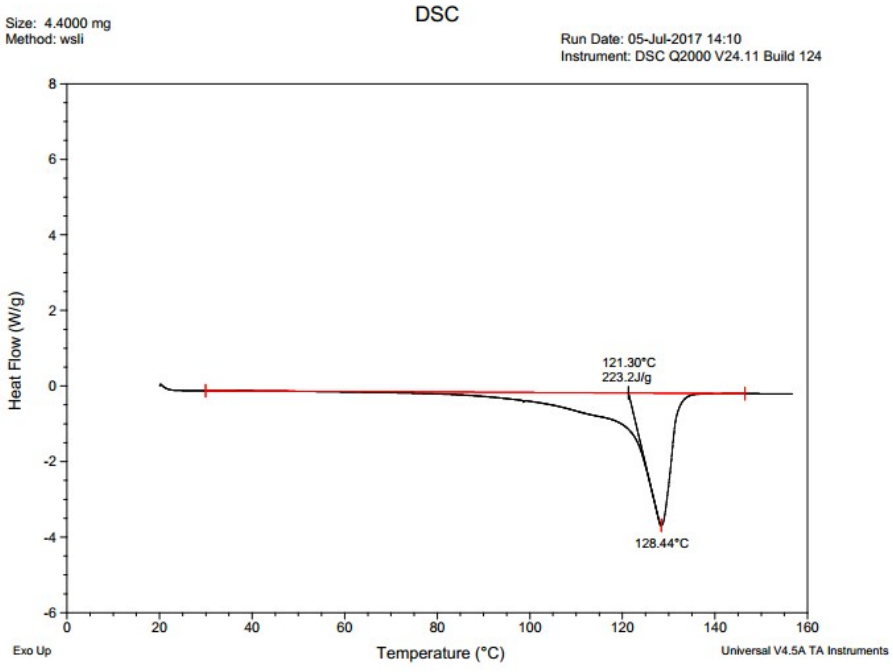


Figure S6. DSC thermogram of the polyethylene obtained using **Fe1**/MMAO at 80 °C (Al:Fe = 2000, Table 2, entry 6)

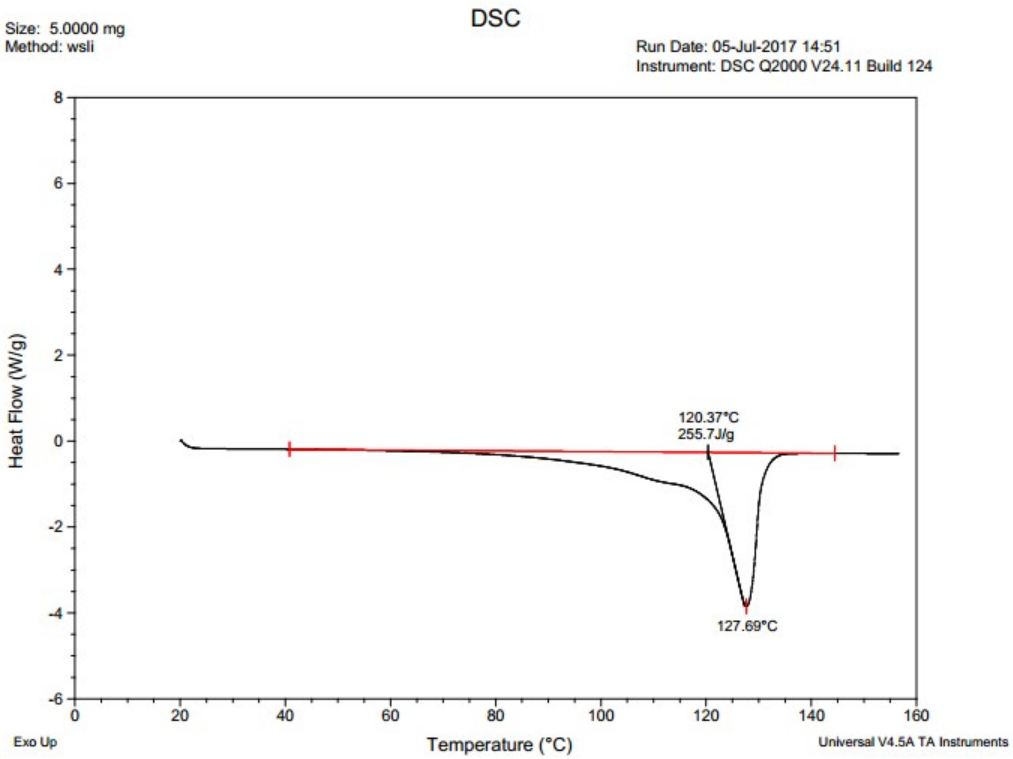


Figure S7. DSC thermogram of the polyethylene obtained using **Fe1**/MMAO at 90 °C (Al:Fe = 2000, Table 2, entry 7)

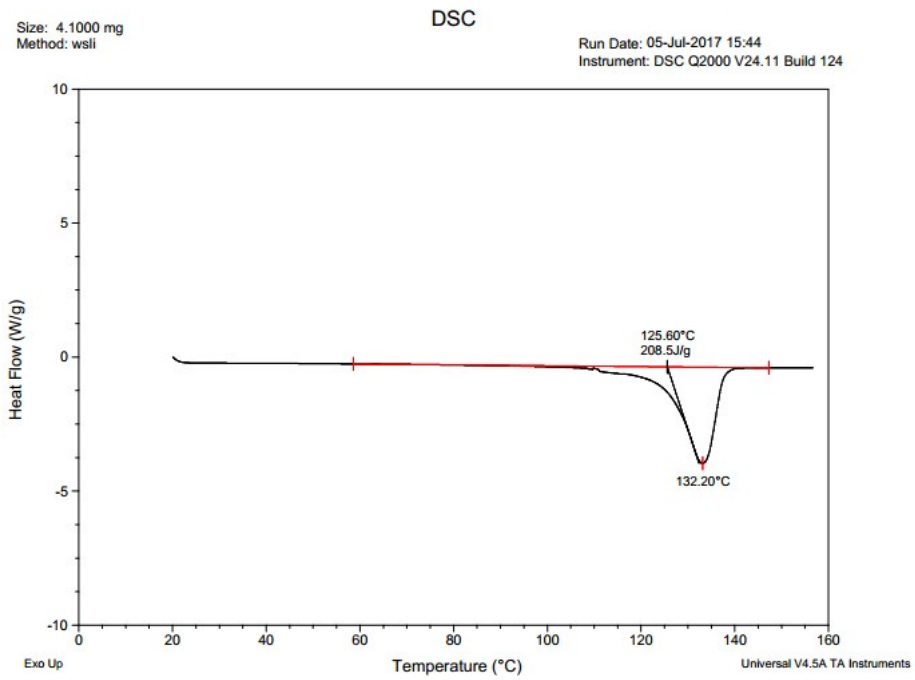


Figure S8. DSC thermogram of the polyethylene obtained using **Fe1**/MMAO at Al:Fe = 1500 (50 °C, Table 2, entry 8)

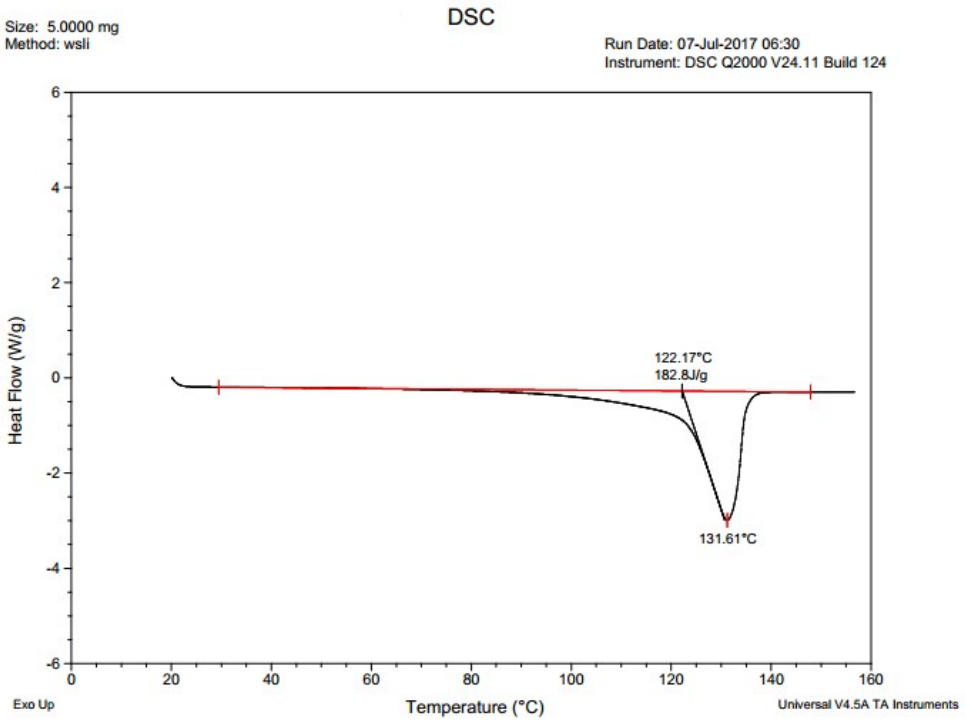


Figure S9. DSC thermogram of the polyethylene obtained using **Fe1**/MMAO at Al:Fe = 1750 (50 °C, Table 2, entry 9)

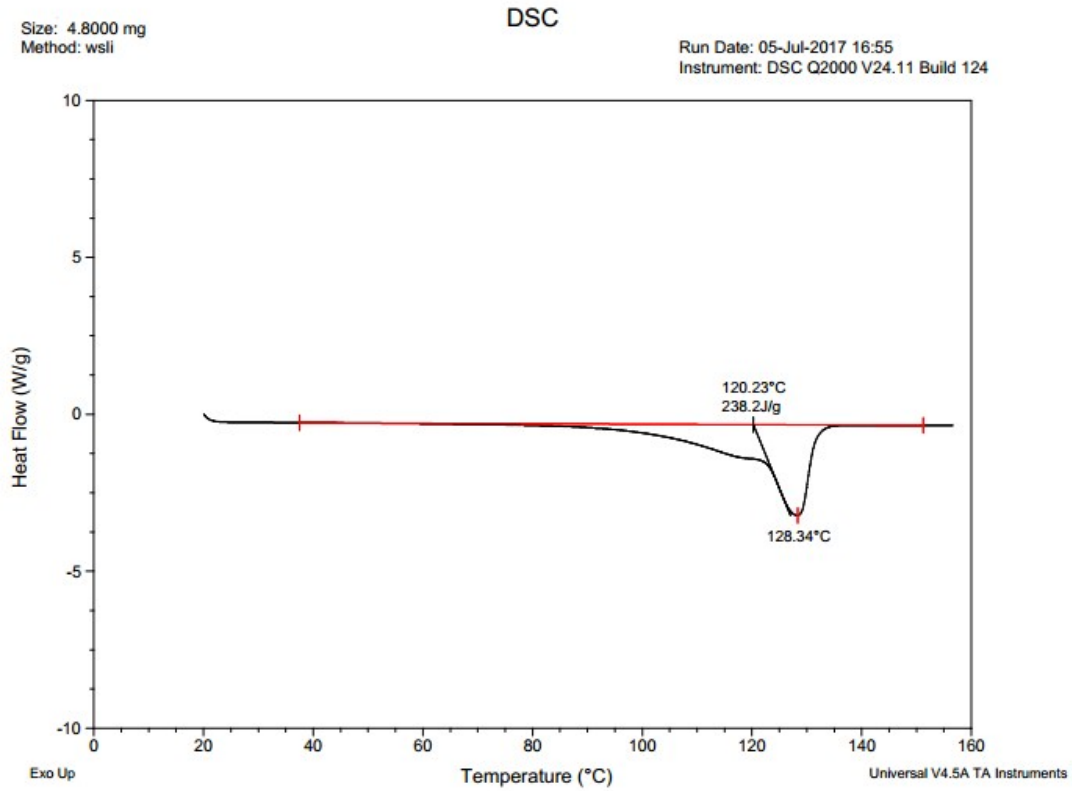


Figure S10. DSC thermogram of the polyethylene obtained using **Fe1**/MMAO at Al:Fe = 2250 (50 °C, Table 2, entry 10)

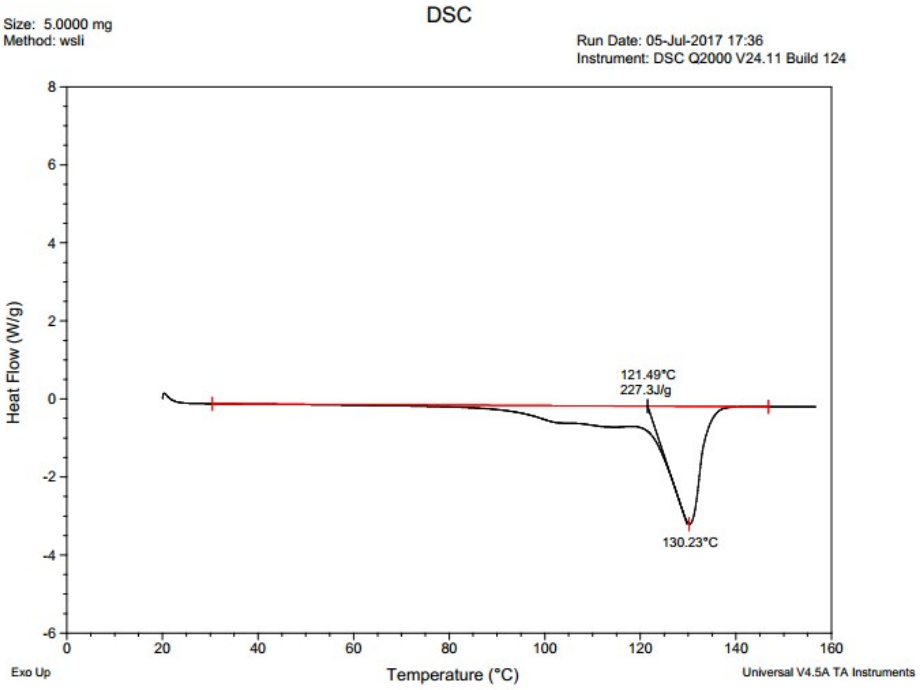


Figure S11. DSC thermogram of the polyethylene obtained using **Fe1**/MMAO at Al:Fe = 2500 (50 °C, Table 2, entry 11)

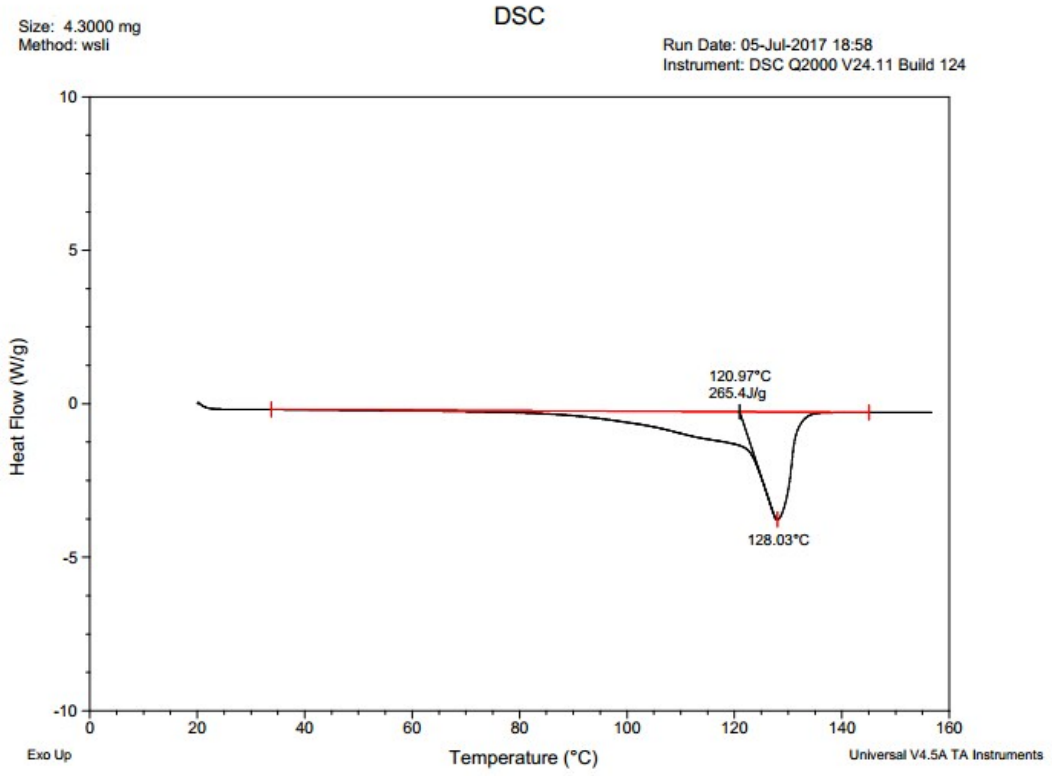


Figure S12. DSC thermogram of the polyethylene obtained using **Fe1**/MMAO after 5 minutes (Al:Fe = 2000, 50 °C, Table 2, entry 12)

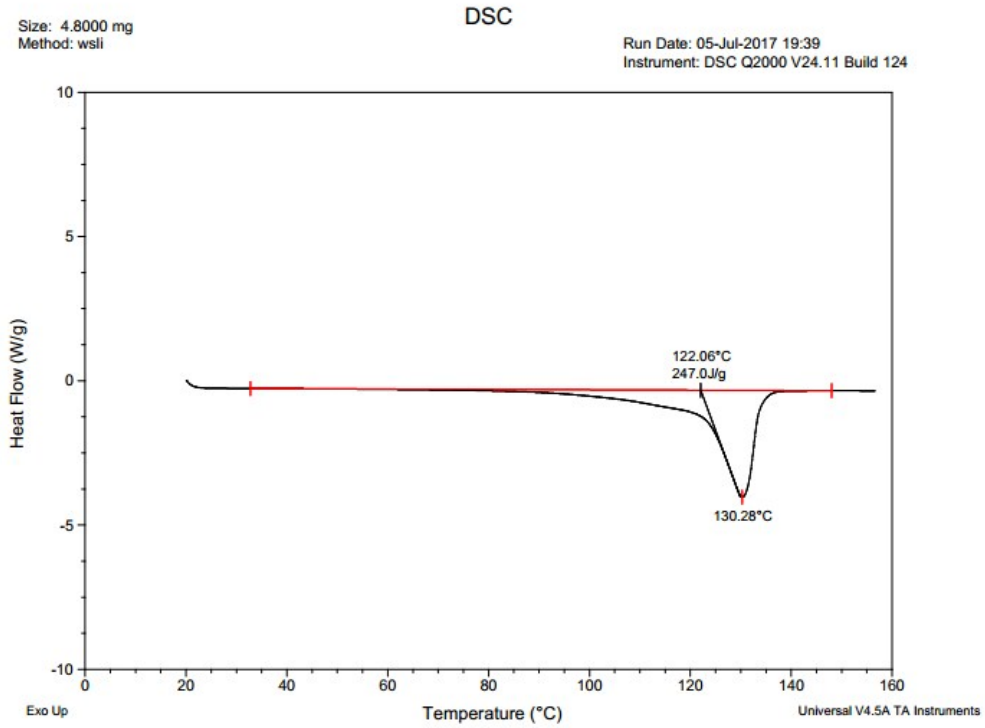


Figure S13. DSC thermogram of the polyethylene obtained using **Fe1**/MMAO after 15 minutes (Al:Fe = 2000, 50 °C, Table 2, entry 13)

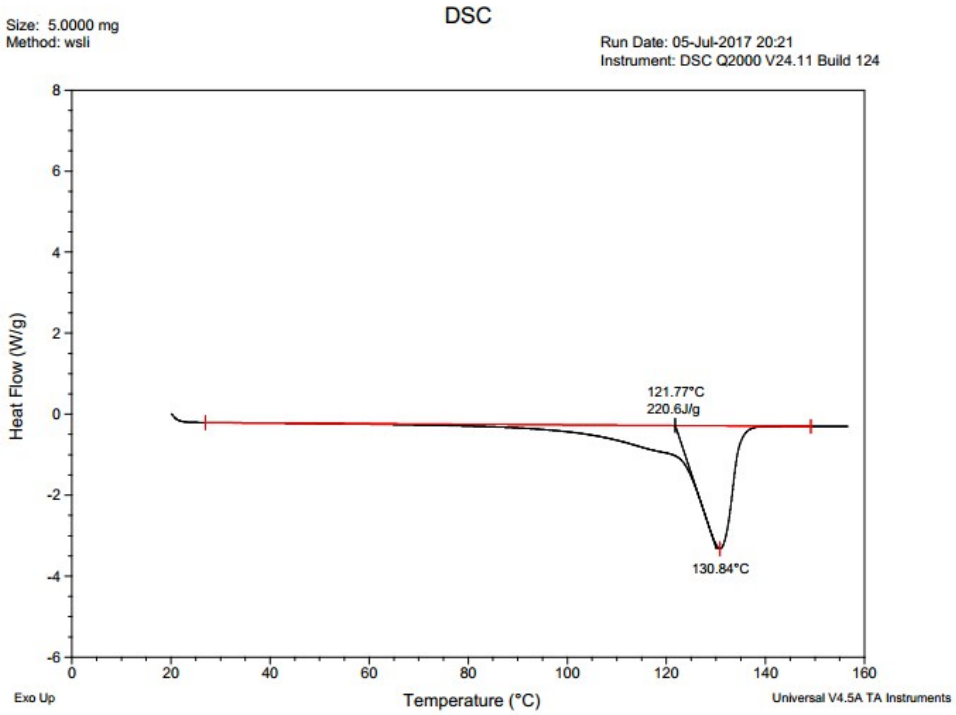


Figure S14. DSC thermogram of the polyethylene obtained using **Fe1**/MMAO after 45 minutes (Al:Fe = 2000, 50 °C, Table 2, entry 14)

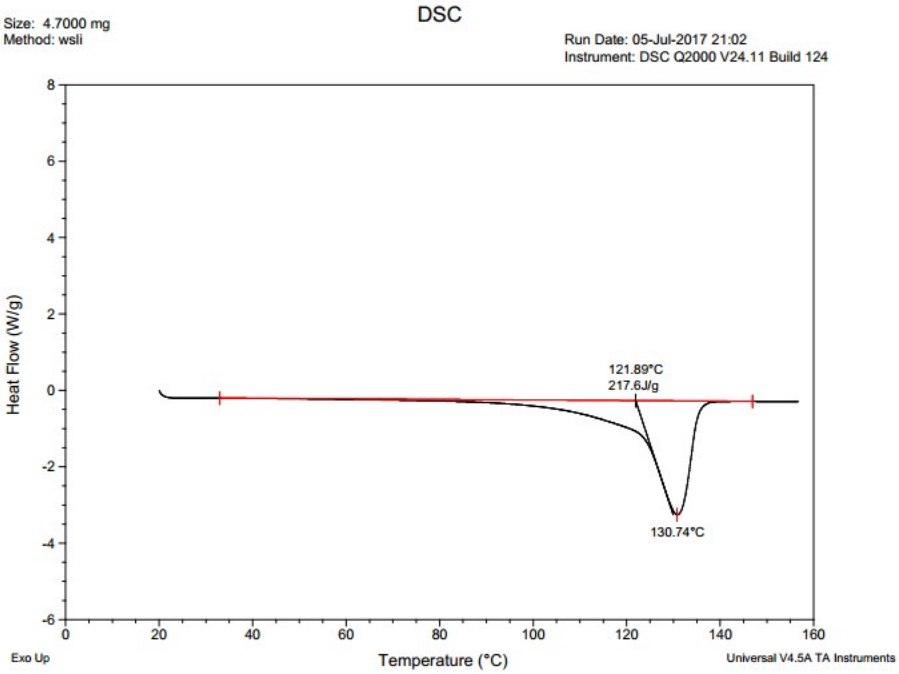


Figure S15. DSC thermogram of the polyethylene obtained using **Fe1**/MMAO after 60 minutes (Al:Fe = 2000, 50 °C, Table 2, entry 15)

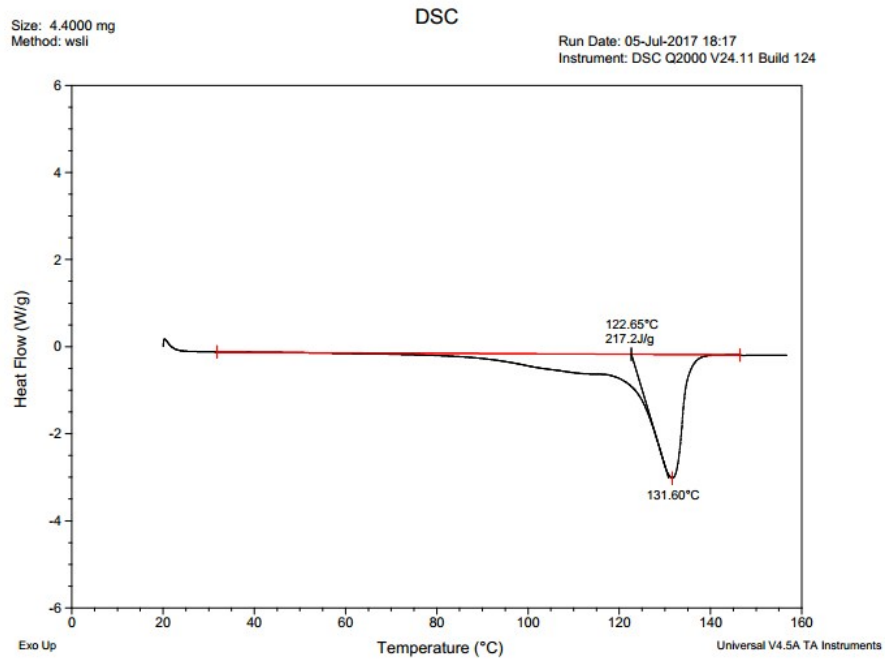


Figure S16. DSC thermogram of the polyethylene obtained using **Fe1**/MMAO at 5 atm ethylene (Al:Fe = 2000, 50 °C, Table 2, entry 16)

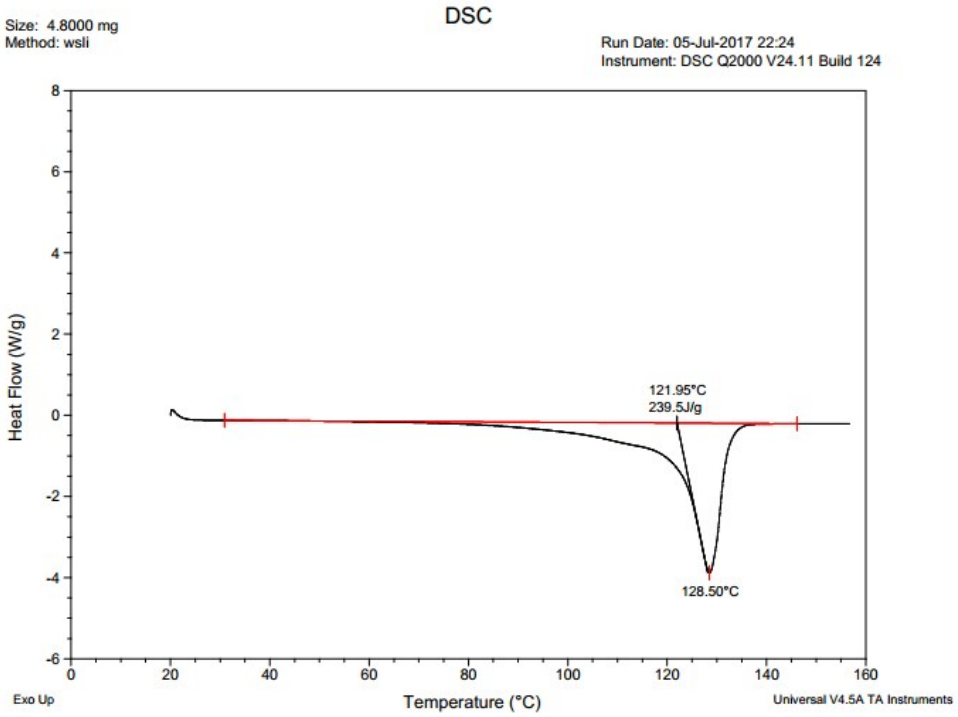


Figure S17. DSC thermogram of the polyethylene obtained using **Fe1**/MMAO at 1 atm ethylene (Al:Fe = 2000, 50 °C, Table 2, entry 17)

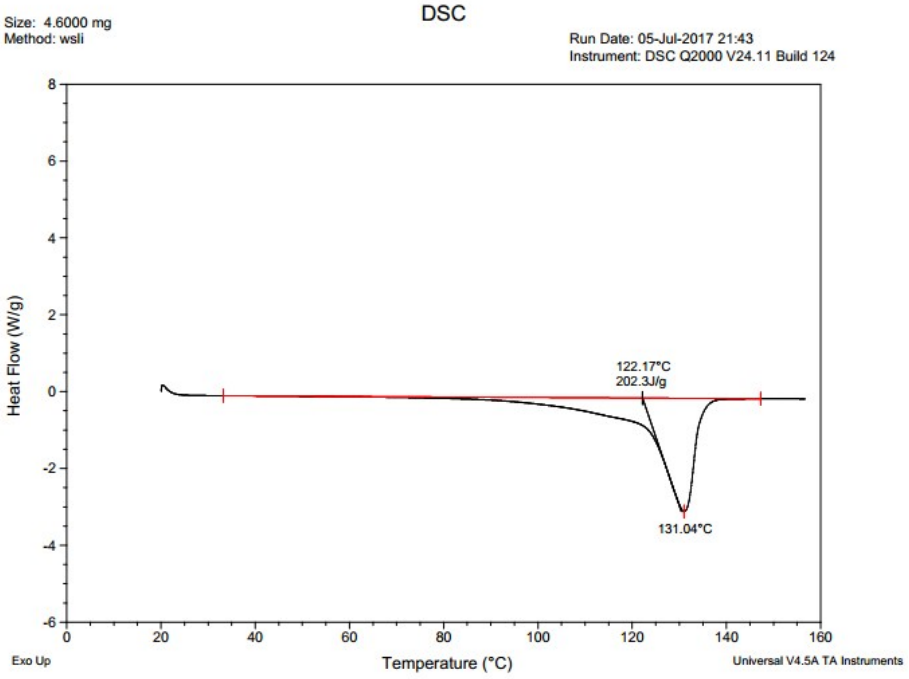


Figure S18. DSC thermogram of the polyethylene obtained using **Fe2**/MMAO at 10 atm ethylene (Al:Fe = 2000, 50 °C, 30 min, Table 3, entry 2)

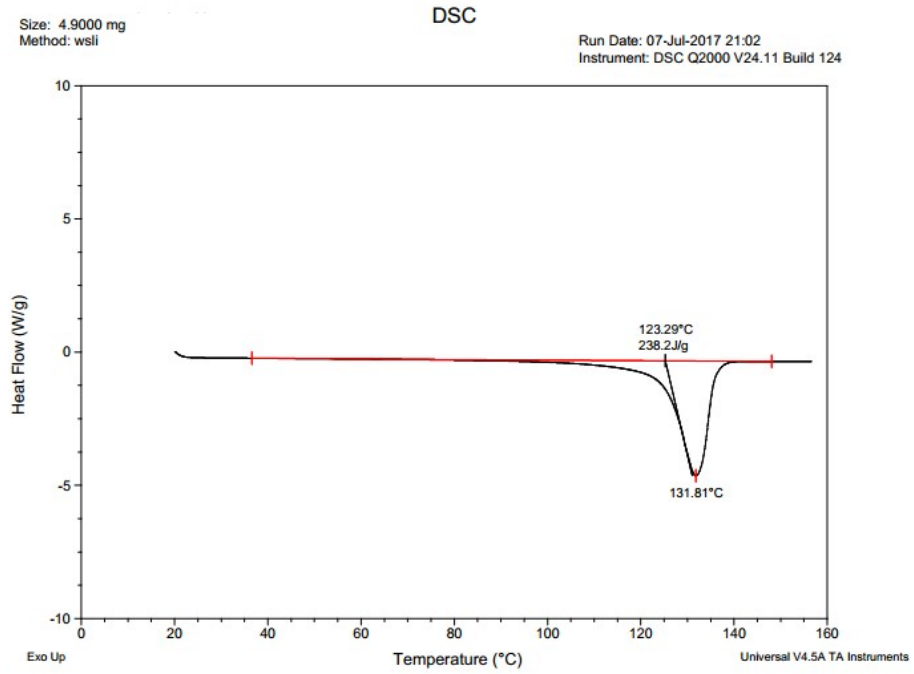


Figure S19. DSC thermogram of the polyethylene obtained using **Fe3**/MMAO at 10 atm ethylene (Al:Fe = 2000, 50 °C, 30 min, Table 3, entry 3)

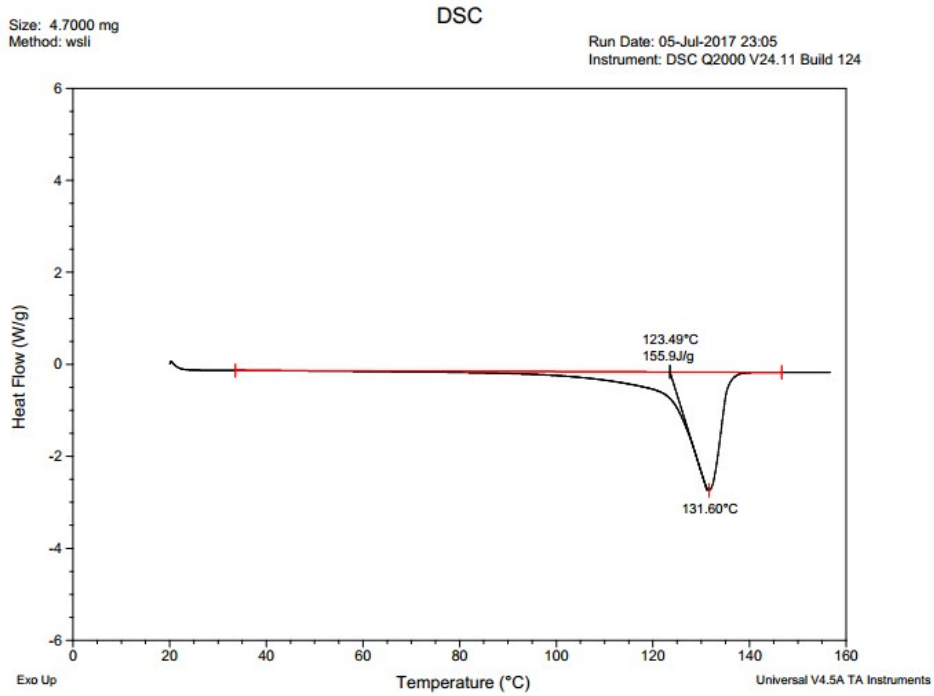


Figure S20. DSC thermogram of the polyethylene obtained using **Fe4**/MMAO at 10 atm ethylene (Al:Fe = 2000, 50 °C, 30 min, Table 3, entry 4)

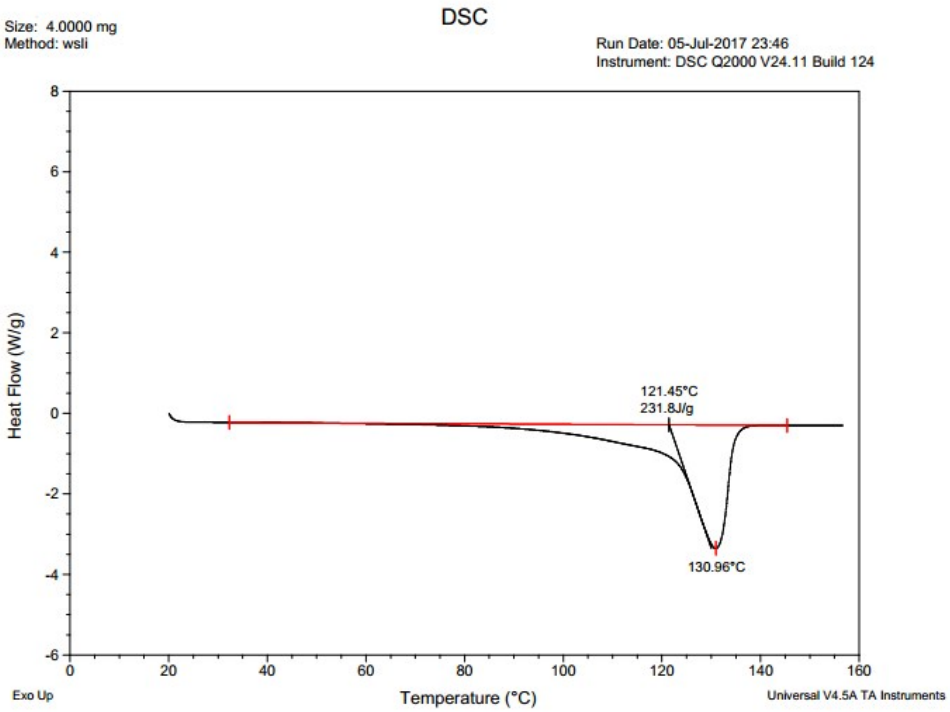


Figure S21. DSC thermogram of the polyethylene obtained using **Fe5**/MMAO at 10 atm ethylene (Al:Fe = 2000, 50 °C, 30 min, Table 3, entry 5)

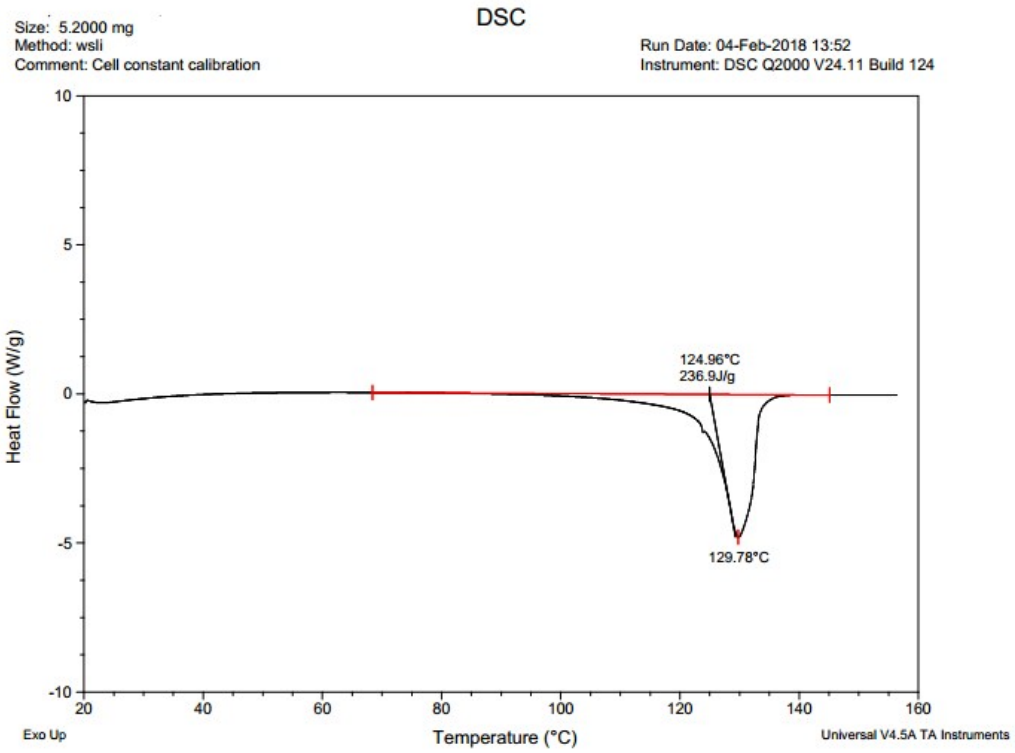


Figure S22. DSC thermogram of the polyethylene obtained using **Fe3'**/MMAO at 10 atm ethylene (Al:Fe = 2000, 50 °C, 30 min, Table 3, entry 6)

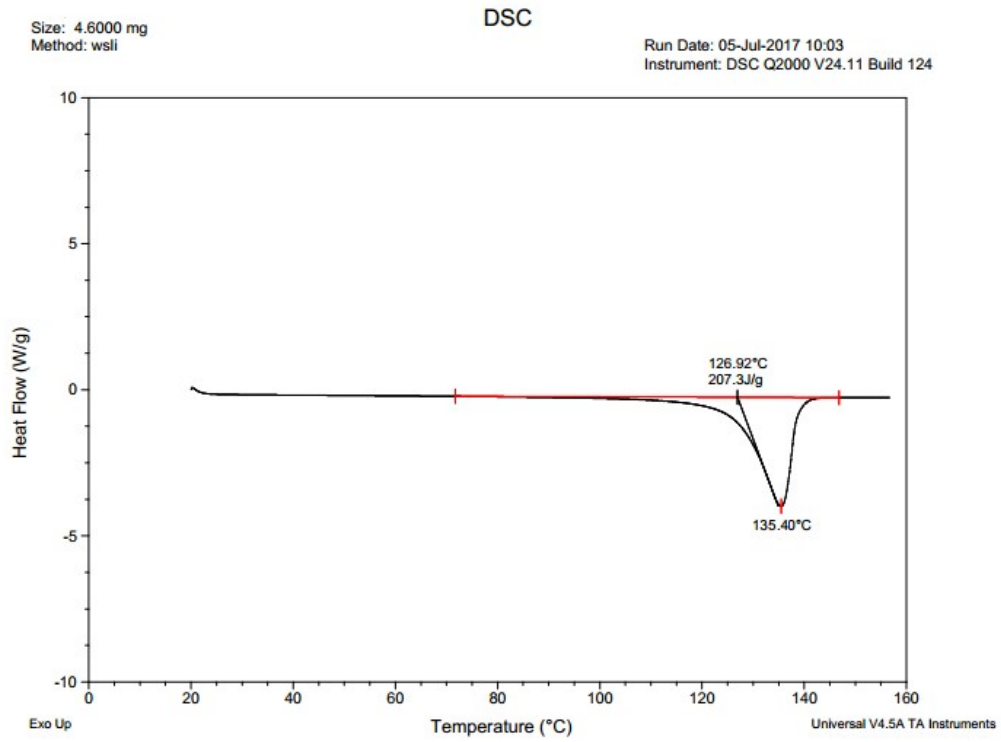


Figure S23. DSC thermogram of the polyethylene obtained using **Fe1**/MAO at 30 °C (Al:Fe = 2000, Table 4, entry 1)

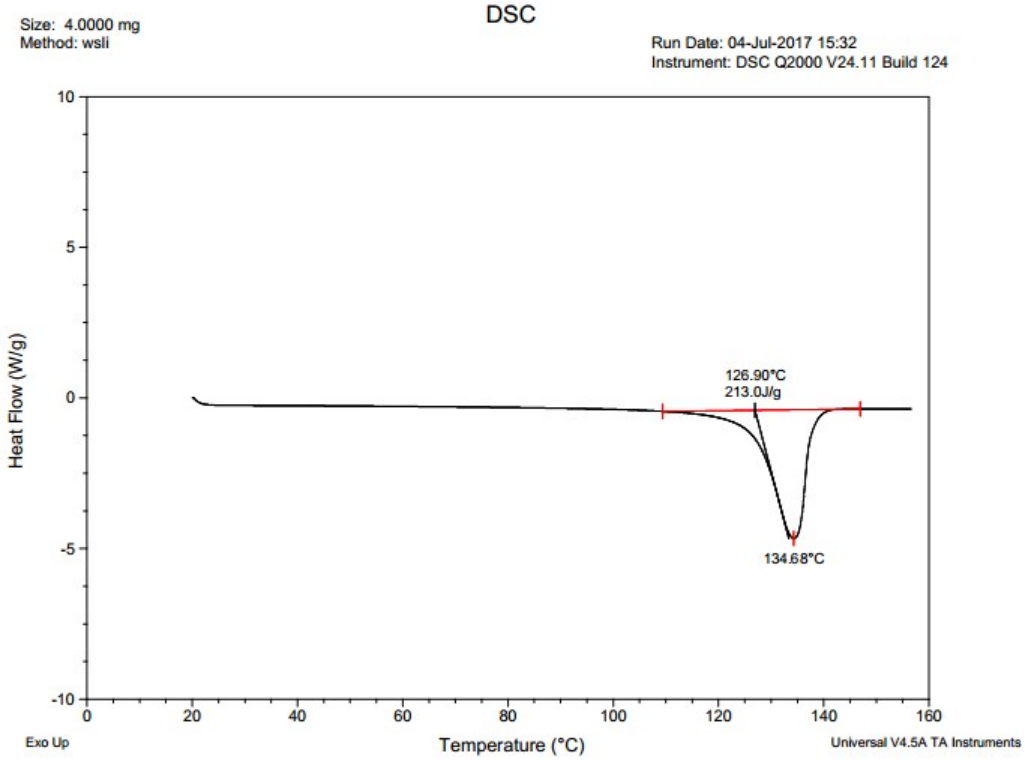


Figure S24. DSC thermogram of the polyethylene obtained using **Fe1**/MAO at 40 °C (Al:Fe = 2000, Table 4, entry 2)

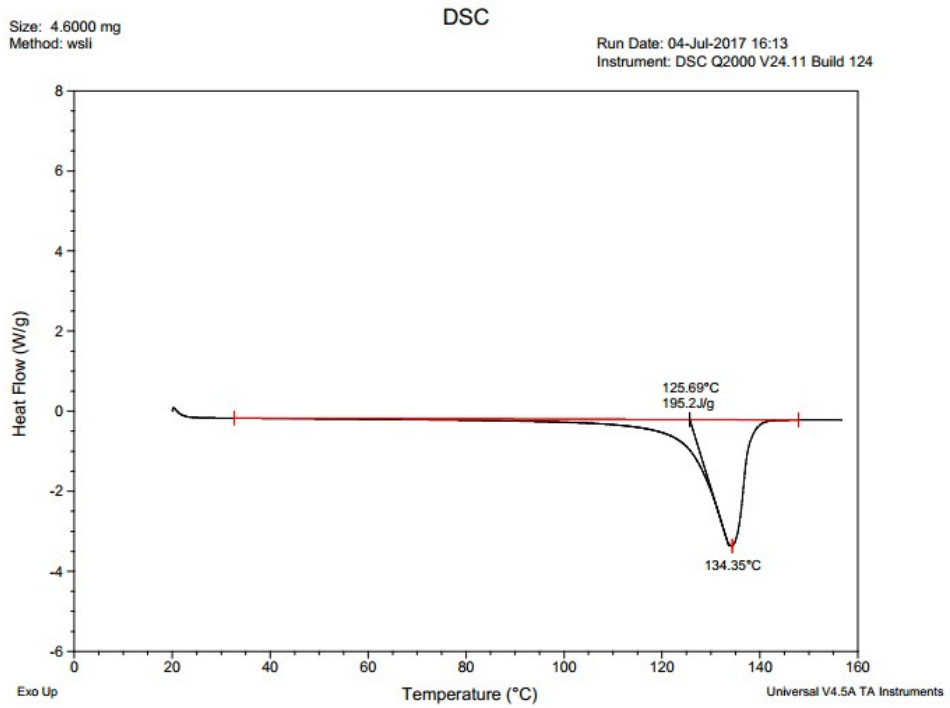


Figure S25. DSC thermogram of the polyethylene obtained using **Fe1**/MAO at 50 °C (Al:Fe = 2000, Table 4, entry 3)

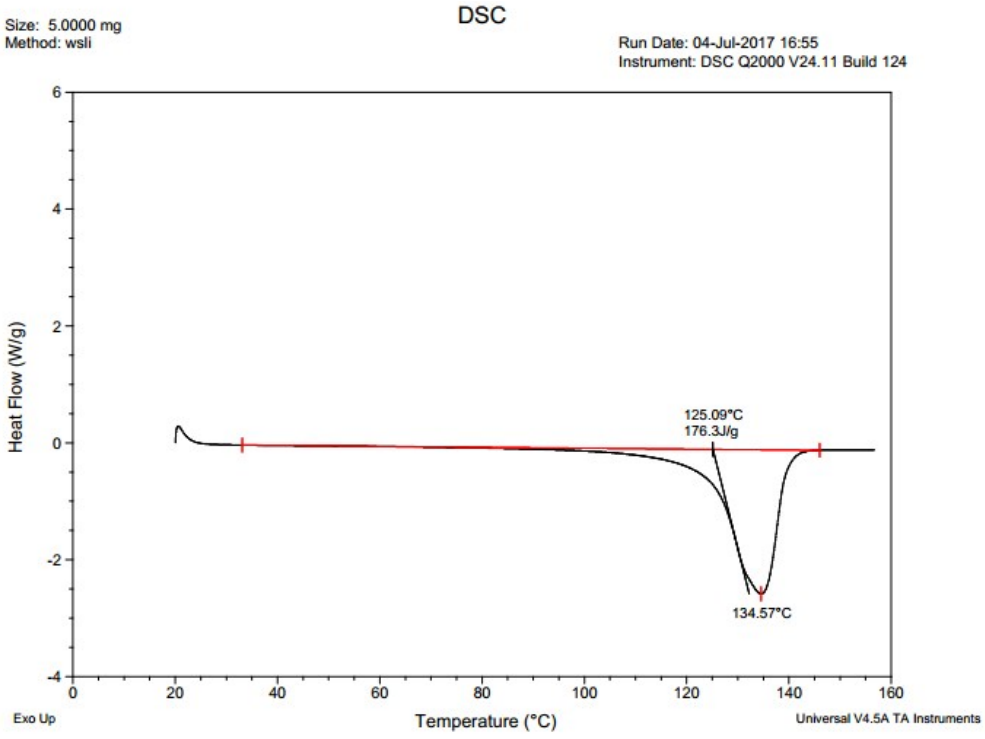


Figure S26. DSC thermogram of the polyethylene obtained using **Fe1**/MAO at 60 °C (Al:Fe = 2000, Table 3, entry 4)

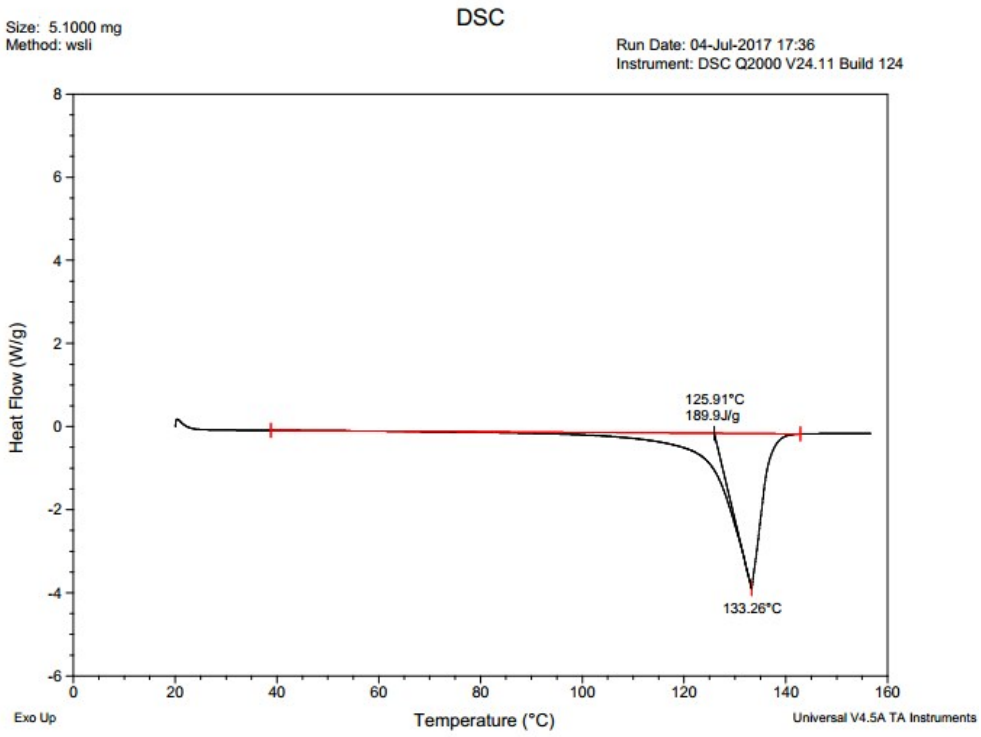


Figure S27. DSC thermogram of the polyethylene obtained using **Fe1**/MAO at 70 °C (Al:Fe = 2000, Table 4, entry 5)

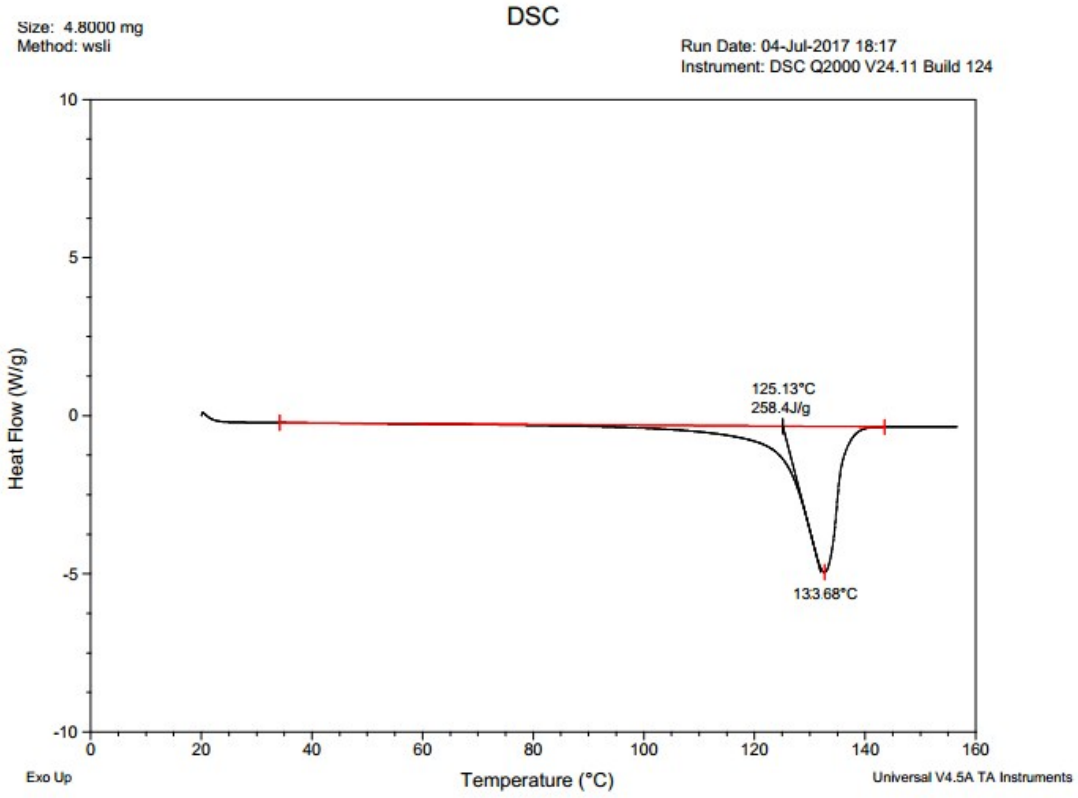


Figure S28. DSC thermogram of the polyethylene obtained using **Fe1**/MAO at 80 °C (Al:Fe = 2000, Table 4, entry 6)

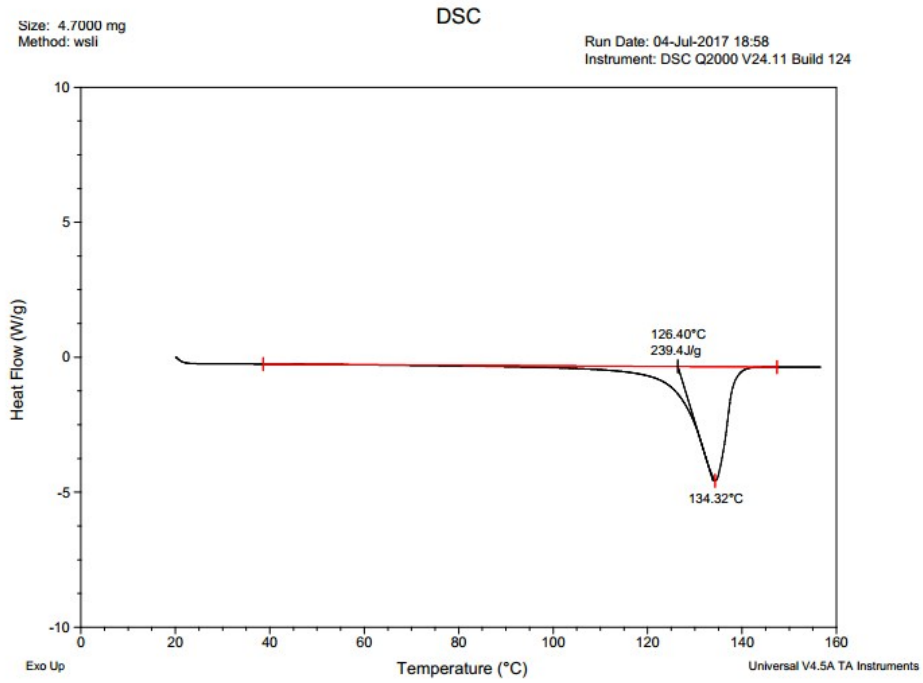


Figure S29. DSC thermogram of the polyethylene obtained using **Fe1**/MAO at 90 °C (Al:Fe = 2000, Table 4, entry 7)

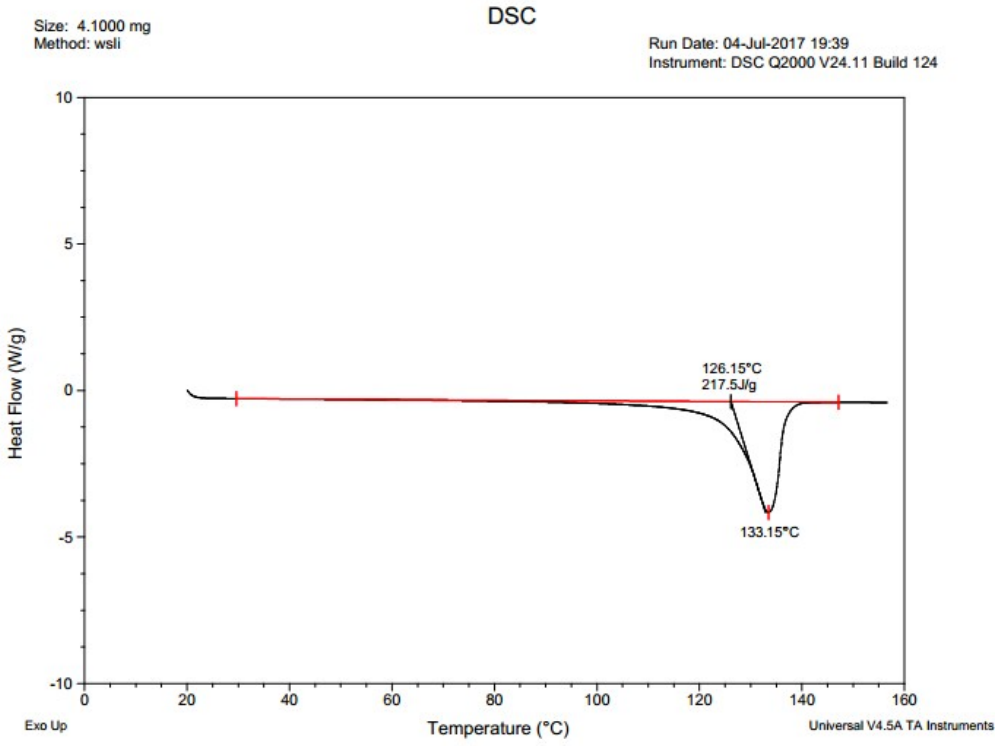


Figure S30. DSC thermogram of the polyethylene obtained using **Fe1**/MAO at Al:Fe = 1500 (80 °C, Table 4, entry 8)

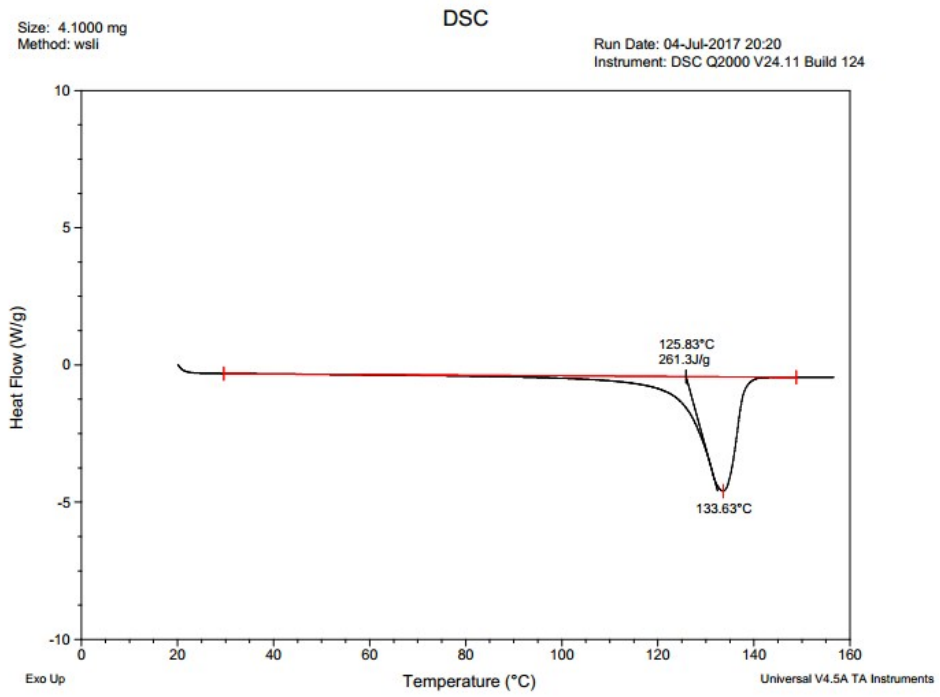


Figure S31. DSC thermogram of the polyethylene obtained using **Fe1**/MAO at Al:Fe = 1750 (80 °C, Table 4, entry 9)

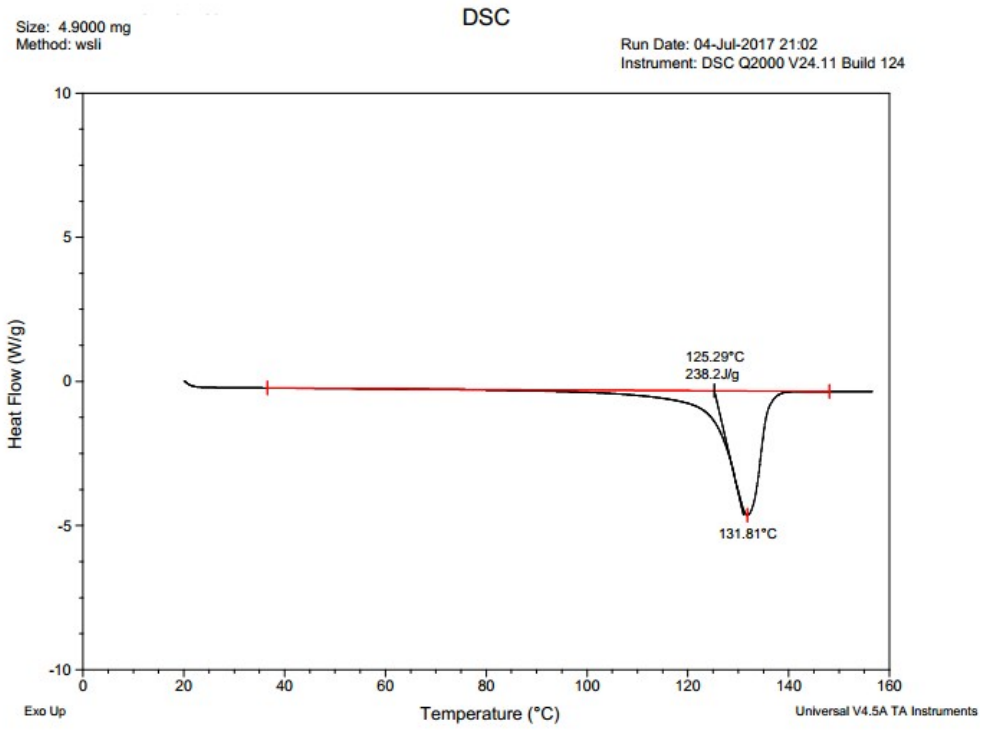


Figure S32. DSC thermogram of the polyethylene obtained using **Fe1**/MAO at Al:Fe = 2250 (80 °C, Table 4, entry 10)

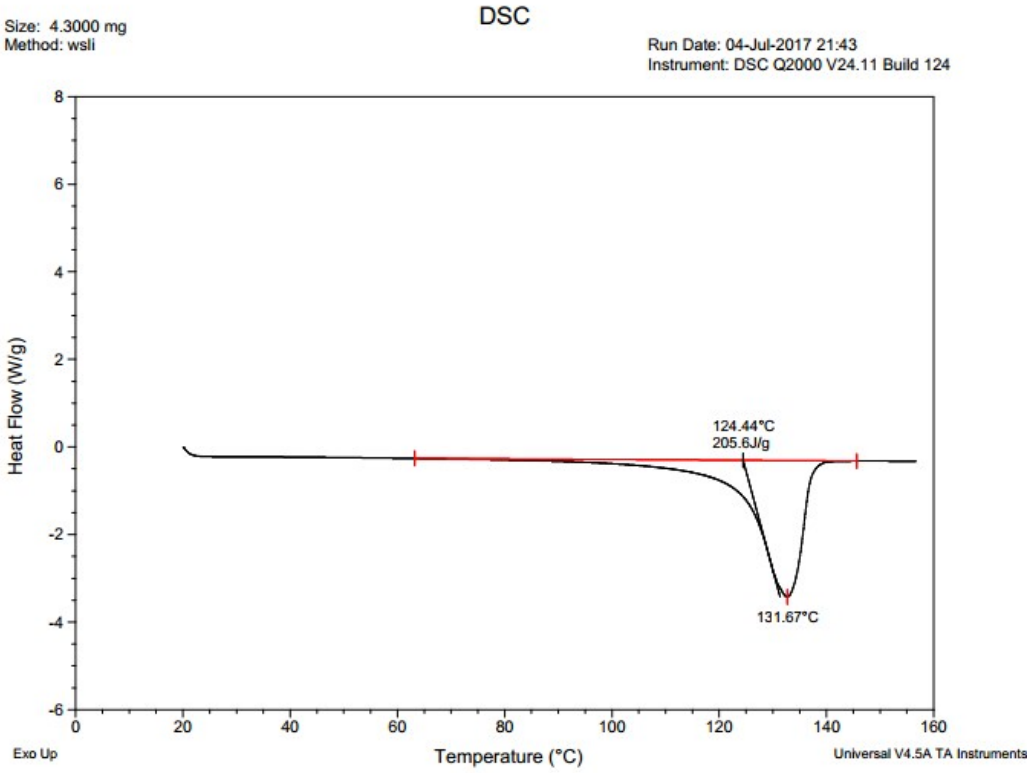


Figure S33. DSC thermogram of the polyethylene obtained using **Fe1**/MAO at Al:Fe = 2500 (80 °C, Table 4, entry 11)

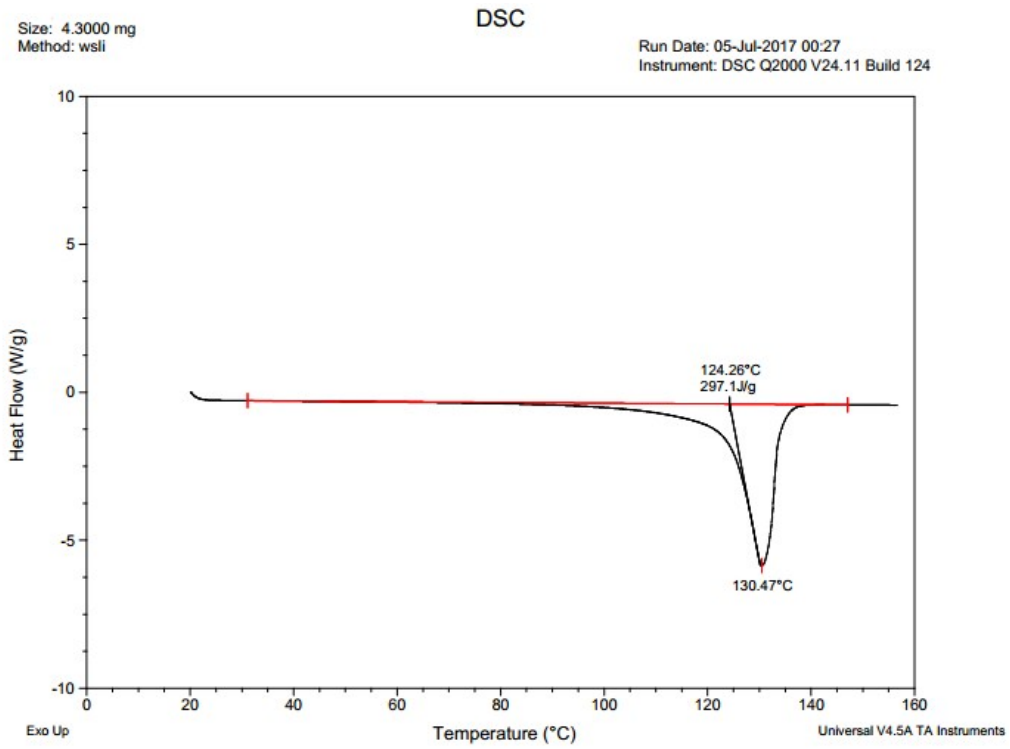


Figure S34. DSC thermogram of the polyethylene obtained using **Fe1**/MAO after 5 minutes (Al:Fe = 2250, 80 °C, Table 4, entry 12)

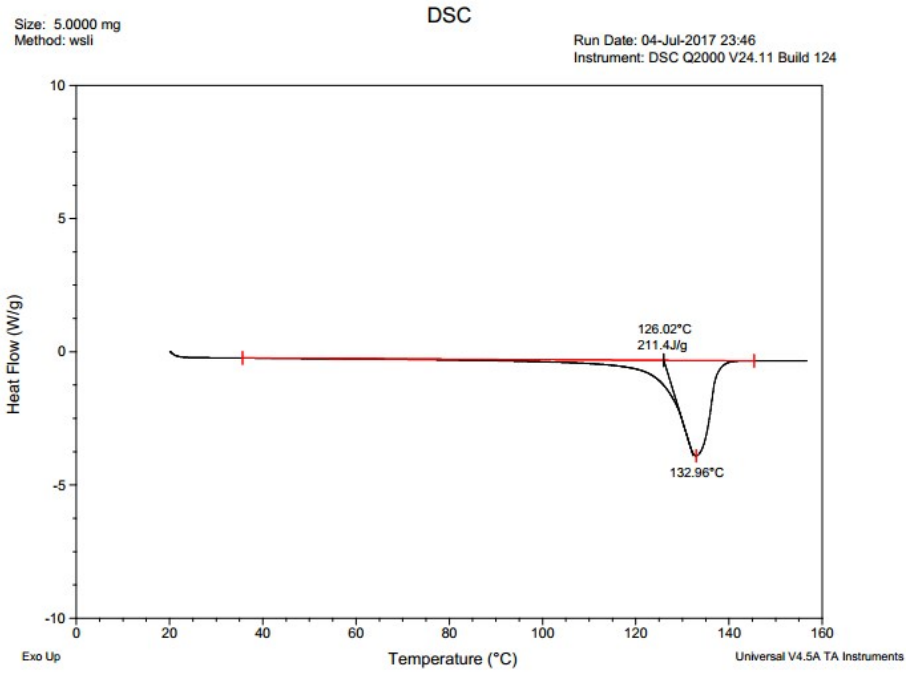


Figure S35. DSC thermogram of the polyethylene obtained using **Fe1**/MAO after 15 minutes (Al:Fe = 2250, 80 °C, Table 4, entry 13)

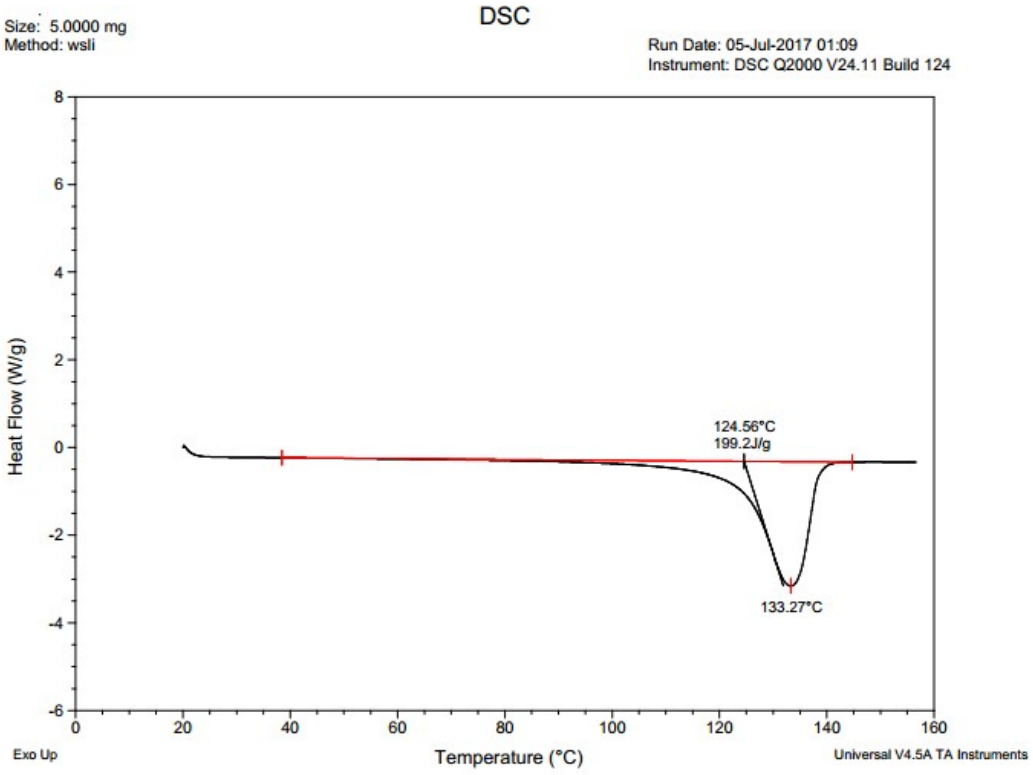


Figure S36. DSC thermogram of the polyethylene obtained using **Fe1**/MAO after 45 minutes (Al:Fe = 2250, 80 °C, Table 4, entry 14)

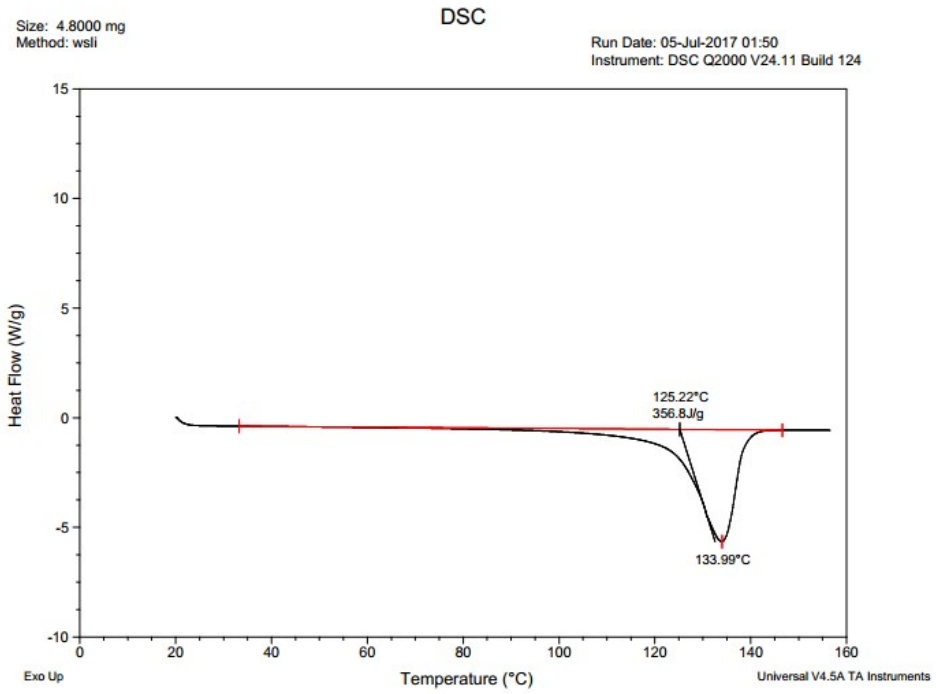


Figure S37. DSC thermogram of the polyethylene obtained using **Fe1**/MAO after 60 minutes (Al:Fe = 2250, 80 °C, Table 4, entry 15)

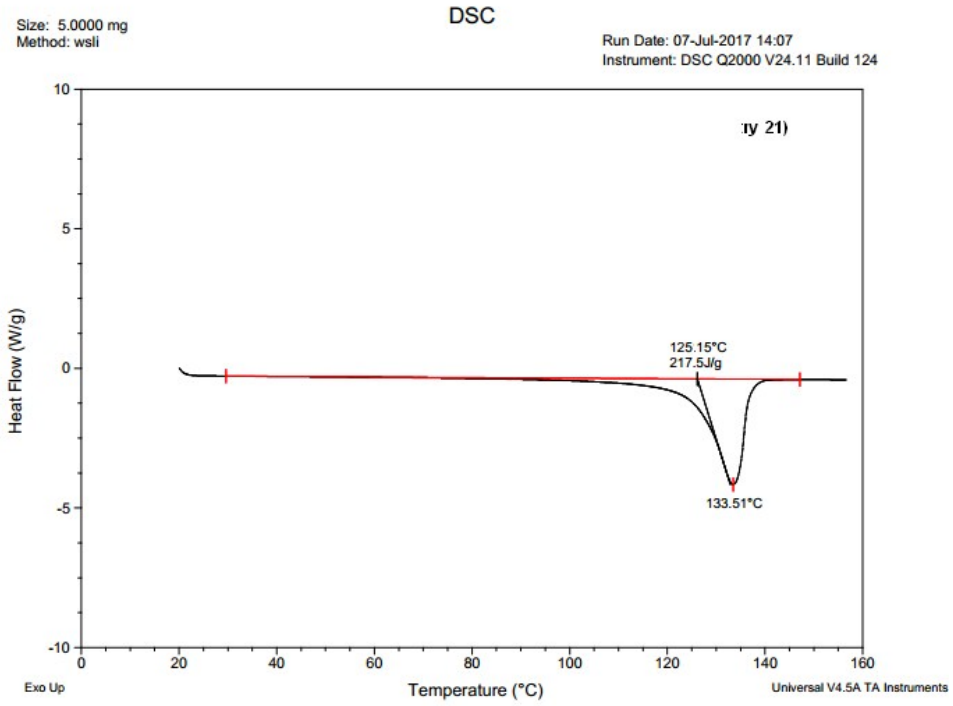


Figure S38. DSC thermogram of the polyethylene obtained using **Fe1**/MAO at 5 atm ethylene (Al:Fe = 2250, 80 °C, Table 4, entry 16)

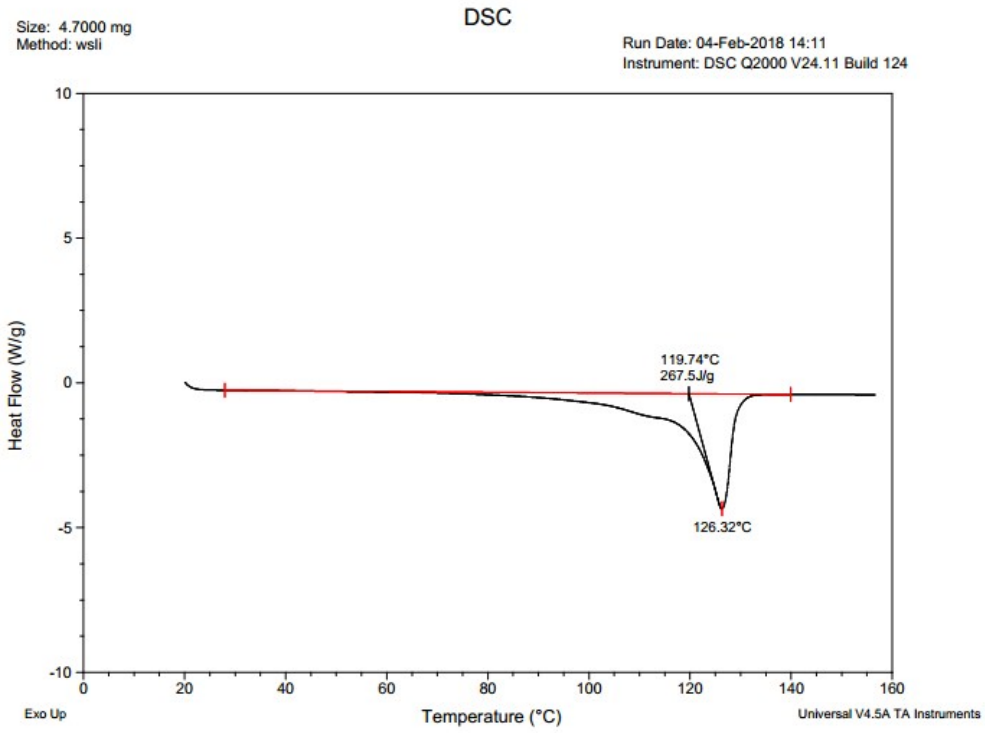


Figure S39. DSC thermogram of the polyethylene obtained using **Fe1**/MAO at 1 atm ethylene (Al:Fe = 2250, 80 °C, Table 4, entry 17)

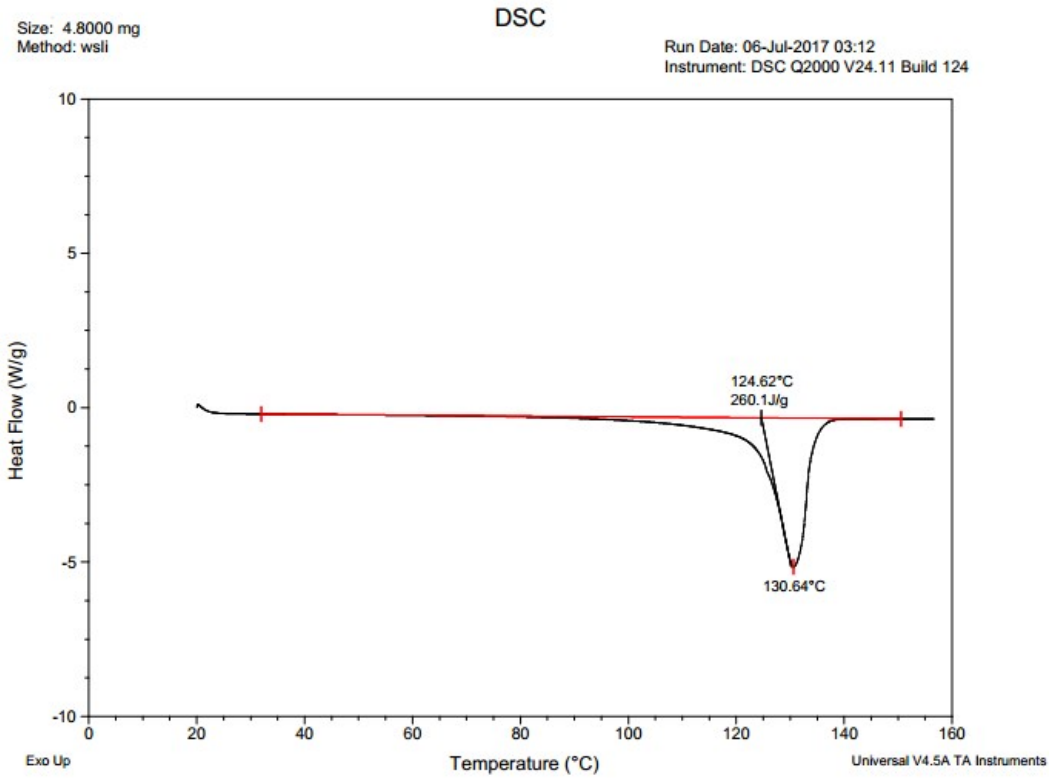


Figure S40. DSC thermogram of the polyethylene obtained using **Fe2**/MAO at 10 atm ethylene (Al:Fe = 2250, 80 °C, 30 min, Table 5, entry 2)

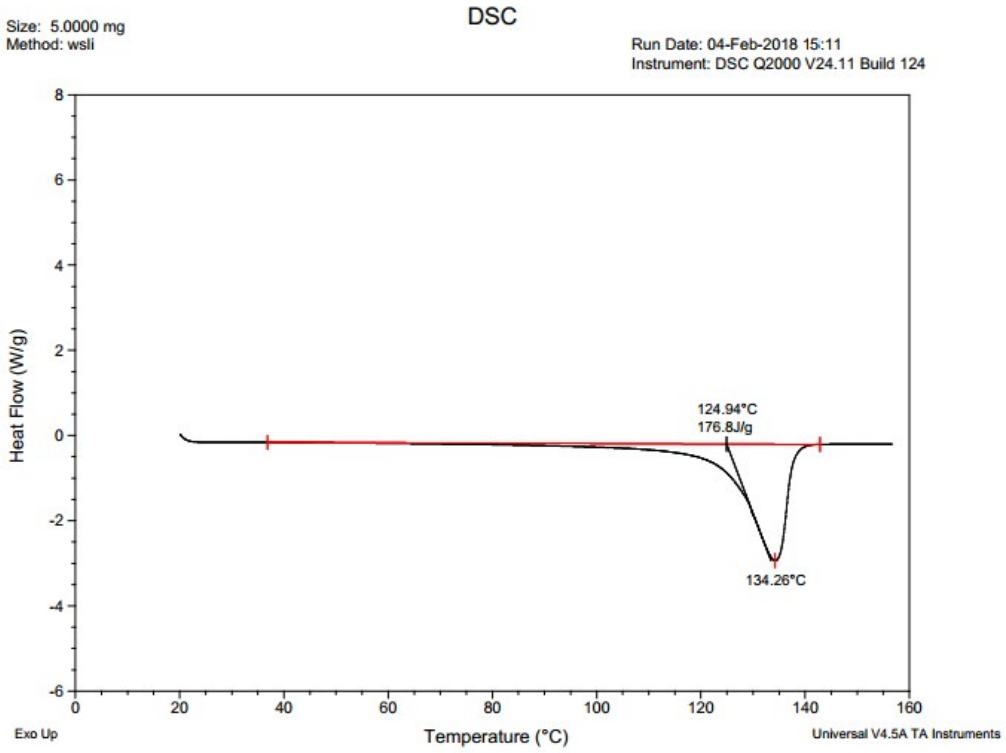


Figure S41. DSC thermogram of the polyethylene obtained using **Fe3**/MAO at 10 atm ethylene (Al:Fe = 2250, 80 °C, 30 min, Table 5, entry 3)

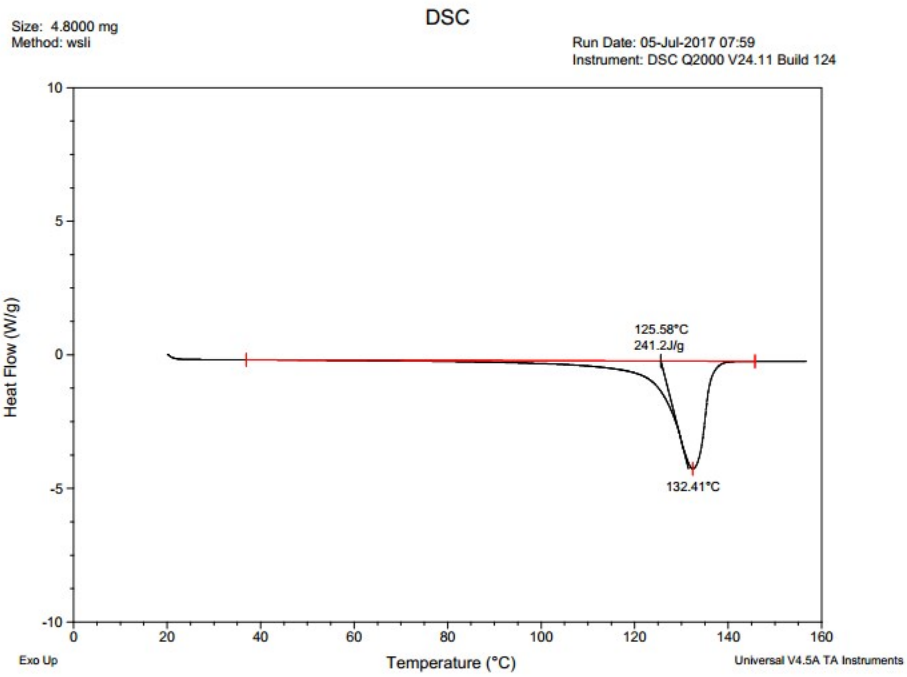


Figure S42. DSC thermogram of the polyethylene obtained using **Fe4**/MAO at 10 atm ethylene (Al:Fe = 2250, 80 °C, 30 min, Table 5, entry 4)

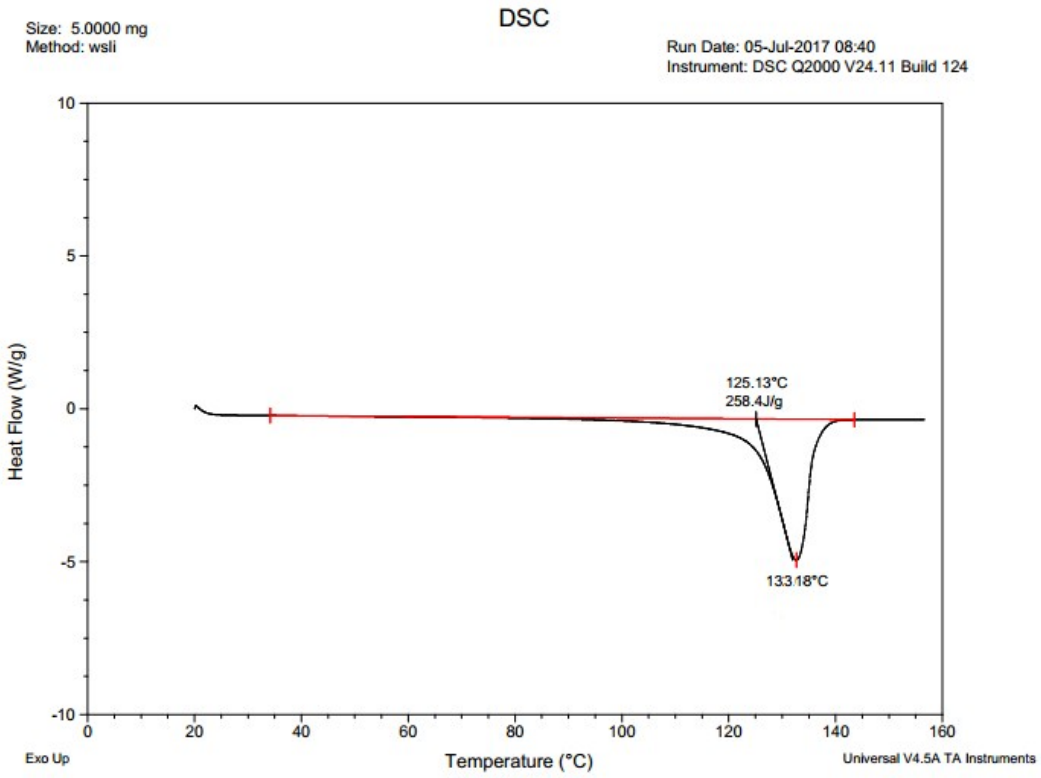


Figure S43. DSC thermogram of the polyethylene obtained using **Fe5**/MAO at 10 atm ethylene (Al:Fe = 2250, 80 °C, 30 min, Table 5, entry 5)

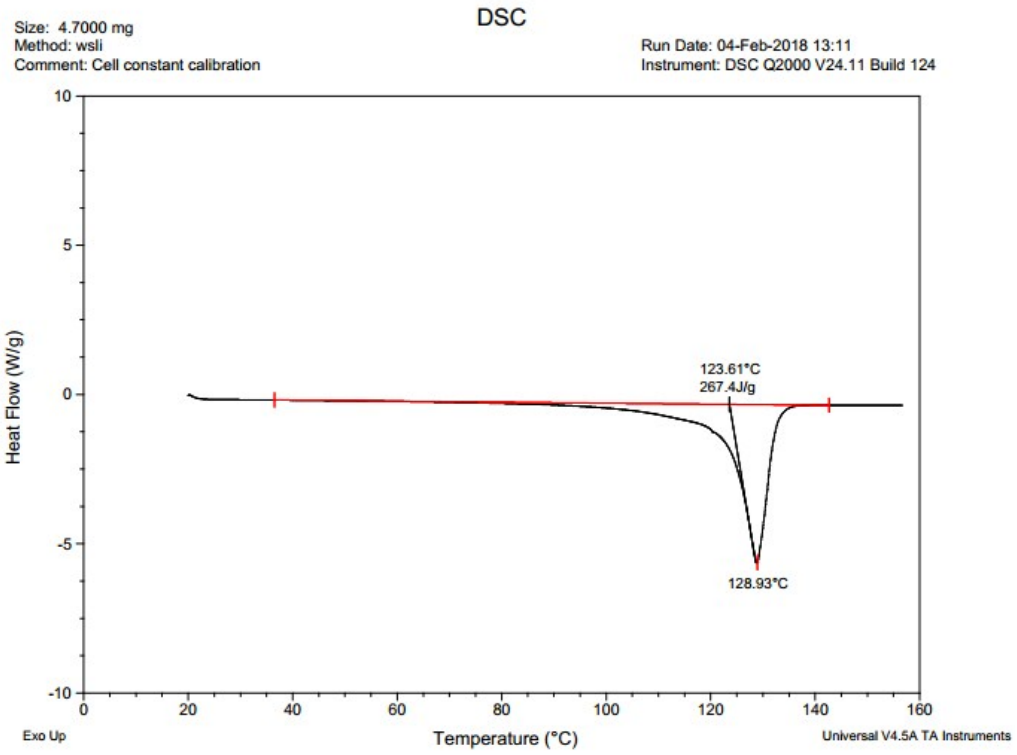


Figure S44. DSC thermogram of the polyethylene obtained using **Fe3'**/MAO at 10 atm ethylene (Al:Fe = 2250, 80 °C, 30 min, Table 5, entry 6)

6. References

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