Electronic Supplementary Information for Dalton Transactions


# Vanadium-based imido-alkoxide procatalysts bearing bisphenolate ligands for ethylene and ε-caprolactone polymerisation.

**Supplementary Material**

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**Supplementary ethylene polymerisation data for pro-catalysts 1 – 11**

*General conditions*

*Data for pro-catalysts **1** – **11***

**Supplementary ethylene polymerisation data for pro-catalysts 1 – 11**

*General Conditions*

Unless otherwise stated, the ethylene polymerisations were run as follow. Ethylene polymerisations were performed in a flame-dried glass flask (250 mL) equipped with a magnetic stirrer bar. The flask was evacuated and filled with ethylene gas at 1 bar pressure, which was maintained throughout the polymerisation. Dry and degassed toluene (50 mL) was added by using a dry glass syringe. The reactivating agent ETA was added (0.1 mL, 0.72 mmol) if applicable, and the solution was stirred for 10 min, allowing ethylene saturation and the correct temperature (45 °C, unless otherwise stated) to be acquired by the use of a water bath. After saturation, the co-catalyst was added (DMAC, 2 mL, 40 000 equivalents with respect to the vanadium pro-catalyst). The pro-catalyst was injected as a toluene solution (a stock solution of 0.5 μmol per mL of pro-catalyst in toluene was prepared and pro-catalyst loadings of 0.05 μmol were employed). The polymerisation time was taken from pro-catalyst injection. The polymerisation was quenched upon the injection of methanol (5 mL). The resultant polymer solution was transferred into a 500 mL beaker containing acidified methanol and the solid polyethylene was collected by filtration and dried *in vacuo* at 70 °C overnight.

*Data for pro-catalysts **1** – **11***

**Table S1.** Supplementary ethylene polymerisation data for pro-catalysts **1** – **3**.

| Run | Pro-catalyst | Time | Polymer yield (g) | Activity (g PE/mmol[V].h.bar) | Mn (g/mol) | PDI |
|---|---|---|---|---|---|---|
| 1 | **1** | 5 | 0.20 | 48 000 | - | - |
| 2 | **1** | 10 | 0.32 | 38 400 | - | - |
| 3 | **1** | 20 | 0.60 | 36 000 | - | - |
| 4 | **1** | 30 | 0.94 | 37 600 | 115 000 | 2.6 |
| 5 | **2** | 5 | 0.28 | 66 560 | - | - |
| 6 | **2** | 10 | 0.16 | 19 015 | - | - |
| 7 | **2** | 20 | 0.40 | 23 770 | - | - |
| 8 | **2** | 30 | 0.40 | 15 850 | 58 000 | 4.0 |
| 9 | **3** | 5 | 0.37 | 88 800 | - | - |
| 10 | **3** | 10 | 0.72 | 86 400 | 121 000 | 4.1 |
| 11 | **3** | 20 | 1.24 | 74 400 | 186 000 | 2.8 |
| 12 | **3** | 30 | 1.17 | 46 800 | 146 000 | 4.1 |

**Table S2.** Supplementary ethylene polymerisation data for pro-catalyst **4**.

| Run | Time | Cocatalyst | Polymer yield (g) | Activity (g PE/mmol[V].h.bar) | Mn (g/mol) | PDI |
|---|---|---|---|---|---|---|
| 1 [a] | 15 | DMAC | 0.48 | 38 400 | 165 000 | 4.7 |
| 2 [a] | 15 | DMAC | 0.02 | 1 600 | 165 000 | 4.1 |
| 3 [a] | 15 | MAO | 0 | - | - | - |
| 4 [a] | 15 | MAO | 0 | - | - | - |
| 5 [a] | 15 | TMA | 0 | - | - | - |
| 6 [a] | 15 | TMA | 0 | - | - | - |
| 7 | 5 | DMAC | 0.27 | 64 800 | 115 000 | 2.3 |
| 8 | 10 | DMAC | 0.46 | 55 200 | 146 000 | 2.2 |
| 9 | 20 | DMAC | 0.97 | 58 200 | 177 000 | 2.4 |
| 10 | 30 | DMAC | 0.97 | 38 800 | 165 000 | 2.2 |

[a] 25 °C.

**Table S3.** Supplementary ethylene polymerisation data for pro-catalyst **5**.

| Run | Time | Polymer yield (g) | Activity (g PE/mmol[V].h.bar) | Mn (g/mol) | PDI |
|---|---|---|---|---|---|
| 1 | 5 | 0.17 | 40 800 | - | - |
| 2 | 10 | 0.33 | 39 600 | - | - |
| 3 | 20 | 0.68 | 40 800 | - | - |
| 4 | 30 | 1.27 | 50 800 | 196 000 | 2.4 |

**Table S4.** Supplementary ethylene polymerisation data for pro-catalyst **6**.

| Run | Time | Polymer yield (g) | Activity (g PE/mmol[V].h.bar) | Mn (g/mol) | PDI |
|---|---|---|---|---|---|
| 1 | 5 | 0.17 | 40 800 | - | - |
| 2 | 10 | 0.37 | 44 400 | - | - |
| 3 | 20 | 0.87 | 52 200 | - | - |
| 4 | 30 | 1.36 | 54 400 | 200 000 | 2.3 |

**Table S5.** Supplementary ethylene polymerisation data for pro-catalyst **7**.

| Run | Time | Polymer yield (g) | Activity (g PE/mmol[V].h.bar) | Mn (g/mol) | PDI |
|---|---|---|---|---|---|
| 1 | 5 | 0.30 | 72 000 | 175 000 | 2.3 |
| 2 | 10 | 0.54 | 64 800 | 194 000 | 2.4 |
| 3 | 20 | 1.14 | 68 400 | 144 000 | 2.3 |
| 4 | 30 | 1.20 | 48 000 | 160 000 | 2.4 |

**Table S6.** Supplementary ethylene polymerisation data for pro-catalyst **8**.

| Run | Time | Polymer yield (g) | Activity (g PE/mmol[V].h.bar) | Mn (g/mol) | PDI |
|---|---|---|---|---|---|
| 1 | 5 | 0.48 | 115 200 | 141 000 | 2.5 |
| 2 | 10 | 0.68 | 81 600 | 140 000 | 2.5 |
| 3 | 20 | 1.35 | 81 00 | 215 000 | 2.6 |
| 4 | 30 | 1.88 | 75 200 | 162 000 | 2.6 |

**Table S7.** Supplementary ethylene polymerisation data for pro-catalyst **9**.

| Run | Time | Polymer yield (g) | Activity (g PE/mmol[V].h.bar) | Mn (g/mol) | PDI |
|---|---|---|---|---|---|
| 1 | 5 | 0.063 | 15 120 | - | - |
| 2 | 10 | 0.19 | 23 160 | - | - |
| 3 | 20 | 0.43 | 25 800 | - | - |
| 4 | 30 | 0.68 | 27 200 | 78 300 | 2.6 |

**Table S8.** Supplementary ethylene polymerisation data for pro-catalyst **10**.

| Run | Time | Polymer yield (g) | Activity (g PE/mmol[V].h.bar) | Mn (g/mol) | PDI |
|---|---|---|---|---|---|
| 1 | 5 | 0.06 | 14 400 | - | - |
| 2 | 10 | 0.12 | 14 400 | - | - |
| 3 | 20 | 0.26 | 15 600 | - | - |
| 4 | 30 | 0.42 | 16 800 | 161 000 | 2.2 |

**Table S9.** Supplementary ethylene polymerisation data for pro-catalyst **11**.

| Run | Time | Polymer yield (g) | Activity (g PE/mmol[V].h.bar) | Mn (g/mol) | PDI |
|---|---|---|---|---|---|
| 1 | 5 | 0.57 | 136 800 | 139 000 | 2.4 |
| 2 | 10 | 0.80 | 96 000 | 160 000 | 2.3 |
| 3 | 20 | 1.13 | 67 800 | 145 000 | 2.3 |
| 4 | 30 | 1.52 | 60 800 | 137 000 | 2.4 |