

## Supporting Information

# Cocatalyst effect in Hf-catalysed olefin polymerization: taking well-defined Al-alkyl borate salts into account

Gaia Urciuoli,<sup>a,b,c</sup> Francesco Zaccaria,<sup>a,c,\*</sup> Cristiano Zuccaccia,<sup>b,c,\*</sup> Roberta Cipullo,<sup>a,c,\*</sup> Peter H. M. Budzelaar,<sup>a</sup> Antonio Vittoria,<sup>a</sup> Christian Ehm,<sup>a,c</sup> Alceo Macchioni,<sup>b,c</sup> Vincenzo Busico<sup>a,c</sup>

a) Dipartimento di Scienze Chimiche, Università di Napoli Federico II, 80126 Napoli, Italy.

b) Dipartimento di Chimica, Biologia e Biotecnologie and CIRCC, Università di Perugia, 06123 Perugia, Italy.

c) DPI, P.O. Box 902, 5600 AX Eindhoven, the Netherlands.

## Table of content

<b>Detailed polymerization procedure</b> .....	2
<b>Table S1.</b> Full polymerization results .....	4
<b>Figure S1.</b> Representative monomer uptake vs. time profiles .....	6
<b>Figure S2.</b> Representative GPC traces .....	7
<b>Figure S3.</b> Representative <sup>13</sup> C NMR spectra of PP .....	8

## Detailed polymerization procedure

Prior to the execution of a polymerization library, the PPR48 modules undergo 'bake-and-purge' cycles overnight (8 h at 90-140°C with intermittent dry N<sub>2</sub> flow), to remove any contaminants and left-overs from previous experiments. After cooling to glovebox temperature, the module stir tops are taken off, and the 48 cells are fitted with disposable 10 mL glass inserts (pre-weighed in a Mettler-Toledo Bohdan Balance Automator) and polyether ether ketone (PEEK) stir paddles. The stir tops are then set back in place, and N<sub>2</sub> in the reactors is replaced with ethene (ambient pressure).

The cells are then loaded with the appropriate amounts of toluene, containing TIBA, MAO or MAO/BHT as a scavenger where appropriate (see Table 1). The system is then thermostated at the reaction temperature and pressurized with 2 bar (30 psi) partial pressure of propene. At this point, the catalyst injection sequence is started; aliquots of (a) a toluene 'chaser', (b) a toluene solution of catalyst, (c) a toluene solution of the proper activator, and (d) a toluene 'buffer', all separated by nitrogen gaps, are uploaded into the needle and subsequently injected into the cell of destination in reverse order, thus starting the reaction. This is left to proceed under stirring (800 rpm) at constant temperature and pressure with feed of propene on demand until the desired monomer consumption has been reached, and quenched by over-pressurizing the cell with 3.4 bar (50 psi) of dry air (preferred over other possible catalyst quenchers because in case of cell or quench line leakage oxygen is promptly detected by the dedicated glove-box sensor).

Once all cells have been quenched, the modules are cooled down to glovebox temperature and vented, the stir-tops are removed, and the glass inserts containing the reaction phases are taken out and transferred to a centrifugal evaporator (Genevac EZ-2 Plus or Martin Christ RVC 2-33 CDplus), where all volatiles are removed, and the polymers are thoroughly dried overnight. Reaction yields are double-checked against on-line monomer conversion measurements by robotically weighing the dry polymers while still in the reaction vials, subtracting the pre-recorded tare. Polymer aliquots are then sent to characterization.

All polymers were characterized by means of high-temperature gel permeation chromatography (GPC) and <sup>13</sup>C NMR spectroscopy. GPC curves were recorded with a Freeslate Rapid GPC setup, equipped with a set of two mixed-bed Agilent PLgel 10 μm columns and a Polymer Char IR4 detector. Calibration was performed with the universal method, using 10 monodisperse polystyrene samples (*M<sub>n</sub>* between 1.3 and 3,700 kDa). Quantitative <sup>13</sup>C NMR spectra were recorded by using a Bruker Avance III 400 spectrometer equipped with a high-temperature cryoprobe for 5-mm OD tubes, on 45-mg mL<sup>-1</sup> polymer solutions in tetrachloroethane-*d*<sub>2</sub> (with

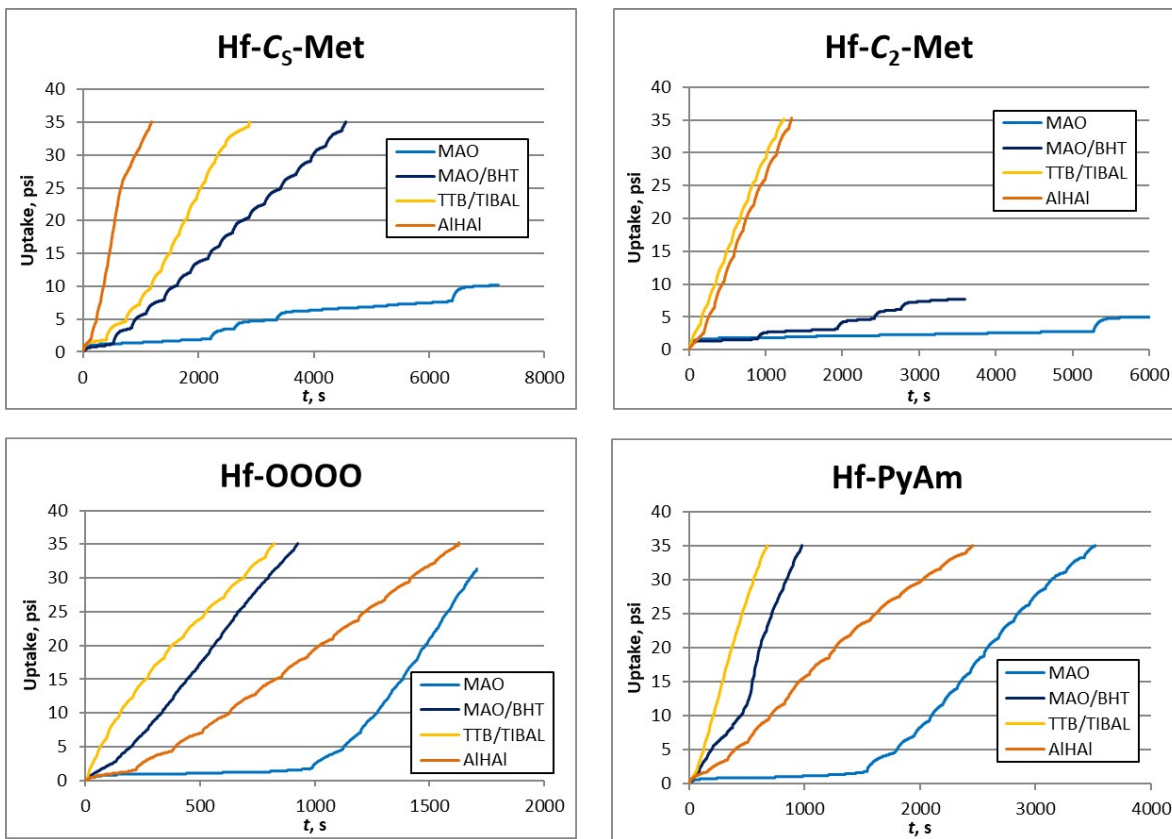
BHT added as a stabilizer, [BHT] = 0.4 mg mL<sup>-1</sup>). Acquisition conditions were: 45° pulse; acquisition time, 2.7 s; relaxation delay, 5.0 s; 2 K transients. Broadband proton decoupling was achieved with a modified WALTZ16 sequence (BI\_WALTZ16\_32 by Bruker).

**Table S1.** Full polymerization results.<sup>[a]</sup>

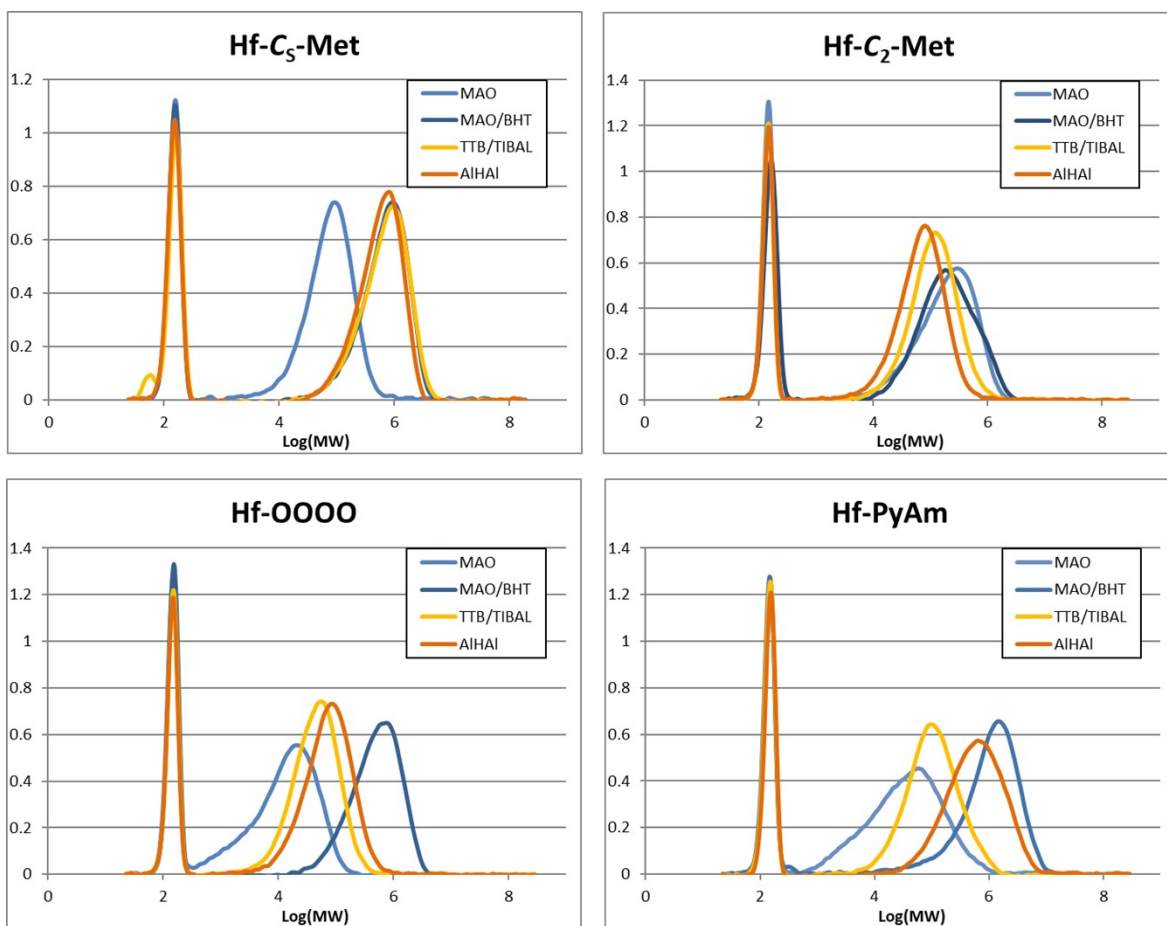
Entry	Catalyst	[Hf] (10 <sup>-6</sup> M)	Cocatalyst	[Al]/[Hf]	t <sub>p</sub> (s)	Yield (mg)	R <sub>p</sub> , (kg <sub>PP</sub> ·mmol <sub>Cat</sub> <sup>-1</sup> ·h <sup>-1</sup> )	M <sub>n</sub> <sup>[b]</sup> (kDa)	M <sub>w</sub> <sup>[b]</sup> (kDa)	PDI	σ <sup>[c]</sup>
1	<b>C<sub>S</sub>-Met</b>	20	MAO	500	7201	26.1	0.13	50	107	2.2	0.96
2	<b>C<sub>S</sub>-Met</b>	20	MAO	500	7200	21.5	0.11	59	113	1.9	0.96
3	<b>C<sub>S</sub>-Met</b>	20	MAO	500	3943	10.4	0.09	53	109	2.1	0.96
4	<b>C<sub>S</sub>-Met</b>	20	MAO/BHT	500	2990	132.9	1.6	410	914	2.2	0.95
5	<b>C<sub>S</sub>-Met</b>	20	MAO/BHT	500	3735	134.9	1.3	392	856	2.2	0.95
6	<b>C<sub>S</sub>-Met</b>	20	MAO/BHT	500	4556	139.2	1.1	395	862	2.2	0.95
7	<b>C<sub>S</sub>-Met</b>	20	TTB/TIBAL	50	1660	92.2	2.0	422	970	2.3	0.96
8	<b>C<sub>S</sub>-Met</b>	20	TTB/TIBAL	50	1926	74.9	1.4	410	970	2.4	0.96
9	<b>C<sub>S</sub>-Met</b>	20	TTB/TIBAL	50	2893	112.5	1.4	400	971	2.4	0.96
10	<b>C<sub>S</sub>-Met</b>	20	<b>AIHAI</b>	10	627	121.4	7.0	372	814	2.2	0.95
11	<b>C<sub>S</sub>-Met</b>	20	<b>AIHAI</b>	10	1187	165.1	5.0	290	721	2.5	0.95
12	<b>C<sub>S</sub>-Met</b>	20	<b>AIHAI</b>	10	754	96.8	4.6	354	743	2.1	0.95
13	<b>C<sub>2</sub>-Met</b>	30	MAO	333	7123	20.5	0.06	90	279	3.1	0.999
14	<b>C<sub>2</sub>-Met</b>	30	MAO	333	10048	13.4	0.03	100	314	3.2	0.998
15	<b>C<sub>2</sub>-Met</b>	30	MAO	333	7202	12.0	0.03	83	213	2.6	0.999
16	<b>C<sub>2</sub>-Met</b>	30	MAO/BHT	333	3601	19.1	0.13	129	413	3.2	0.998
17	<b>C<sub>2</sub>-Met</b>	30	MAO/BHT	333	7202	46.3	0.15	140	406	2.9	0.997
18	<b>C<sub>2</sub>-Met</b>	30	MAO/BHT	333	2925	10.9	0.10	138	373	2.7	0.997
19	<b>C<sub>2</sub>-Met</b>	12	TTB/TIBAL	100	1470	92.7	3.8	79	178	2.2	0.995
20	<b>C<sub>2</sub>-Met</b>	12	TTB/TIBAL	100	1602	67.3	2.5	73	170	2.3	0.995
21	<b>C<sub>2</sub>-Met</b>	12	TTB/TIBAL	100	1237	72.9	3.5	68	155	2.3	0.995
22	<b>C<sub>2</sub>-Met</b>	12	<b>AIHAI</b>	20	1630	75.2	2.8	61	140	2.3	0.993
23	<b>C<sub>2</sub>-Met</b>	12	<b>AIHAI</b>	20	1405	82	3.5	51	113	2.2	0.993
24	<b>C<sub>2</sub>-Met</b>	12	<b>AIHAI</b>	20	1336	80.8	3.6	44	98	2.2	0.993

25	<b>OOOO</b>	10	MAO	1000	2461	96.9	2.8	5	17	3.5	0.87
26	<b>OOOO</b>	10	MAO	1000	1706	83.9	3.5	5	23	4.2	0.87
27	<b>OOOO</b>	10	MAO	1000	1550	95.6	4.4	7	25	3.8	0.87
28	<b>OOOO</b>	10	MAO/BHT	1000	1244	135.2	7.8	309	725	2.3	0.87
29	<b>OOOO</b>	10	MAO/BHT	1000	924	104.5	8.1	258	579	2.2	0.87
30	<b>OOOO</b>	10	MAO/BHT	1000	978	125.2	9.2	331	802	2.4	0.87
31	<b>OOOO</b>	10	TTB/TIBAL	100	1542	76.1	3.6	31	64	2.1	0.89
32	<b>OOOO</b>	10	TTB/TIBAL	100	1556	79.3	3.7	33	72	2.2	0.89
33	<b>OOOO</b>	10	TTB/TIBAL	100	824	54.5	4.8	29	64	2.2	0.89
34	<b>OOOO</b>	10	<b>AIHAI</b>	20	2040	79	2.8	52	117	2.2	0.88
35	<b>OOOO</b>	10	<b>AIHAI</b>	20	1787	75.5	3.0	49	107	2.2	0.88
36	<b>OOOO</b>	10	<b>AIHAI</b>	20	1627	76.7	3.4	65	150	2.3	0.88
37	<b>PyAm</b>	4	MAO	750	4002	64	2.9	14	86	6.1	0.994
38	<b>PyAm</b>	4	MAO	750	3513	69.3	3.6	13	80	6.4	0.994
39	<b>PyAm</b>	4	MAO	750	2745	86.7	5.7	6	33	5.7	0.995
40	<b>PyAm</b>	4	MAO/BHT	750	862	95.7	20	732	1930	2.6	0.994
41	<b>PyAm</b>	4	MAO/BHT	750	981	113.6	21	812	1829	2.3	0.994
42	<b>PyAm</b>	4	MAO/BHT	750	371	81.6	40	860	2073	2.4	0.994
43	<b>PyAm</b>	4	MAO/BHT	2250	805	65.5	15	442	1098	2.5	0.994
44	<b>PyAm</b>	4	MAO/BHT	2250	800	99.6	22	931	1925	2.1	0.994
45	<b>PyAm</b>	4	MAO/BHT	2250	573	110.9	35	662	1734	2.6	0.994
46	<b>PyAm</b>	4	TTB/TIBAL	250	528	71.9	24	62	203	3.3	0.994
47	<b>PyAm</b>	4	TTB/TIBAL	250	677	87.4	23	60	172	2.8	0.994
48	<b>PyAm</b>	4	TTB/TIBAL	250	564	75.7	24	57	152	2.7	0.994
49	<b>PyAm</b>	4	<b>AIHAI</b>	50	2811	69.7	4.5	310	929	3.0	0.995
50	<b>PyAm</b>	4	<b>AIHAI</b>	50	2459	76.8	5.6	221	760	3.4	0.995
51	<b>PyAm</b>	4	<b>AIHAI</b>	50	1888	81.4	7.8	358	1151	3.2	0.995

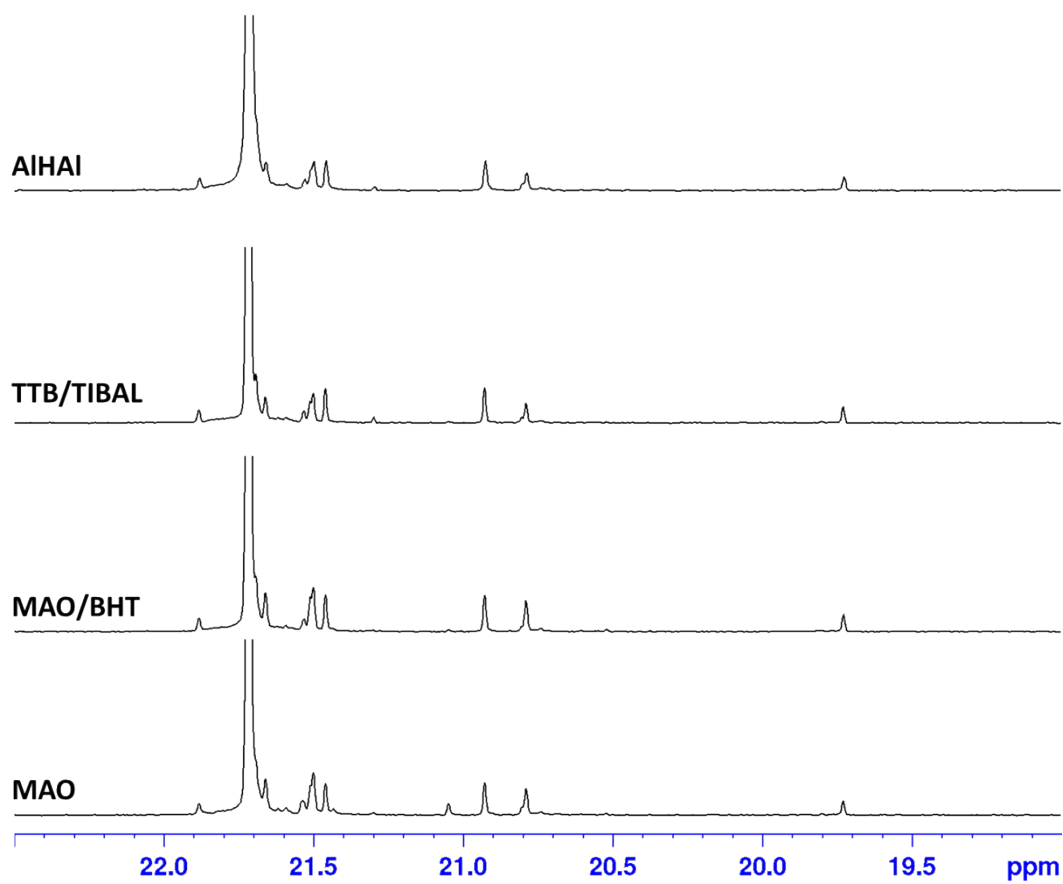
<sup>[a]</sup> in toluene (5 mL), 60 °C,  $p_{\text{propene}} = 2$  bar (30 psi); [Al] = 10 mM for MAO and MAO/BHT, 1 mM for TIBAL or 0.1 mM for **AIHAI**; [B]/[Hf] = 5 for dichloride precatalysts **Hf-C<sub>s</sub>-Met** and **Hf-C<sub>2</sub>-Met**,<sup>[31,42]</sup> 1 for **Hf-OOOO**<sup>[34]</sup> or 2 for **Hf-PyAm**,<sup>[60,61]</sup> according to previously optimized procedures. <sup>[b]</sup> As determined by GPC. <sup>[c]</sup> Probability of inserting propene with the favoured enantioface at each of the two enantiotopic sites.



**Figure S1.** Representative monomer uptake vs. time profiles obtained with the four catalysts studied.



**Figure S2.** Representative GPC traces of polymers obtained with the four catalysts studied. The sharp peak at  $\log(\text{MW}) \sim 2$  is due to the stabilizer.



**Figure S3.** Representative  $^{13}\text{C}$  NMR spectra (tetrachloroethane- $d_2$ , 393 K; methyl region) of PP obtained with Hf-PyAm.