Supporting information

Highly Branched Unsaturated Polyethylenes Achievable Using Strained Imino-cyclopenta*[b]*pyridyl-nickel Precatalysts

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Ethylene Polymerization in the Presence of MMAO

Using MMAO as co-catalyst, **Ni3** was investigated in the first instance as the test precatalyst in order to determine the optimum polymerization parameters. Typically the Al/Ni molar ratio, reaction temperature and reaction time were systematically varied. The results, tabulated in Table

S1, reveal similar activities and slightly lower molecular weights to those seen with MAO as the co-catalyst, but the resultant polyethylenes exhibit slightly broader polydispersities.

Employing different molar ratios of Al/Ni led to notable variations in the catalytic activity; higher activities were observed as the Al/Ni molar ratio was increased from 1500 to 2000 (entries 1 − 3, Table S1). The catalyst system with a Al/Ni ratio of 2000 showed the best activity up to 4.66 × 10^6g(PE)·mol^{-1}(Ni)·h^{-1}. However, on further increasing the Al/Ni molar ratio to 2250 and 2500 (entries 4 and 5, Table S1), the catalytic activities slightly decreased. Their GPC curves are shown in Fig. S2.

In a similar manner, the temperature of the polymerization run was varied but in this case keeping the Al/Ni ratio and reaction duration constant. With the polymerization conducted over 30 minutes and the Al/Ni ratio set at 2000, the temperature was varied from 20 to 60 °C (entries 3, 6 – 9, Table S1). The data confirmed that the optimal temperature was 30 °C (entry 3, Table S1), and that the higher the reaction temperature, the lower the molecular weight of the resultant polyethylene; the functional active species sharply decreased from 5614 to 698 h^{-1}. Their GPC curves are shown in Fig. S2.

With the ethylene pressure maintained at 10 atmospheres, the Al/Ni molar ratio at 2000 and the temperature at 30 °C, the run time was varied by quenching the polymerization after different reaction periods (entries 3, 10 – 14, Table S1); the aim was to explore the lifetime of the active species. The highest activity was observed within 10 minutes (entry 11, Table S1); on extending the reaction time (entries 3, 12 − 14, Table S1), the activities gradually decreased. Compared with **Ni3**/MAO system, the induction period became less.

Table S1 Polymerization of ethylene in the presence of MMAO[a]

Entry	Precat.	Al/Ni	*T*/°C	*t*/min	PE/g	Activity[b]	T_m[c]/°C	M_w[d]/Kg·mol^{-1}	M_w/M_n[d]	*N*[e]/h^{-1}
1	**Ni3**	1500	30	30	11.02	4.41	79.1	0.80	1.68	5510
2	**Ni3**	1750	30	30	11.51	4.60	76.5	0.78	1.70	5903
3	**Ni3**	2000	30	30	11.65	4.66	87.0	0.83	1.51	5614
4	**Ni3**	2250	30	30	10.30	4.12	89.1	0.89	1.70	4630
5	**Ni3**	2500	30	30	9.35	3.74	79.8	0.82	1.71	4560
6	**Ni3**	2000	20	30	9.80	3.92	93.3	1.34	2.15	2925
7	**Ni3**	2000	40	30	9.55	3.82	70.0	0.76	1.70	5026
8	**Ni3**	2000	50	30	3.15	1.26	66.8	0.75	1.63	1680
9	**Ni3**	2000	60	30	1.10	0.44	66.8	0.63	1.51	698

10	**Ni3**	2000	30	5	1.37	3.29	79.5	1.05	1.63	3131
11	**Ni3**	2000	30	10	4.41	5.28	78.3	0.99	1.82	5345
12	**Ni3**	2000	30	15	5.63	4.51	73.3	1.07	1.67	4209
13	**Ni3**	2000	30	45	12.38	3.30	74.5	1.08	1.83	3058
14	**Ni3**	2000	30	60	14.85	2.97	79.1	1.48	1.88	2008
15	**Ni1**	2000	30	30	9.83	3.93	61.8	0.67	1.41	5869
16	**Ni2**	2000	30	30	6.78	2.71	60.4	0.98	1.34	2767
17	**Ni4**	2000	30	30	9.45	3.78	56.7	0.57	1.47	6632
18[f]	**Ni3**	2000	30	30	3.13	1.25	65.8	0.77	1.33	1626

[a] Reaction conditions: 5 μmol of Ni, 10 atm of ethylene, 100 mL total volume of toluene; [b] 10^6 g(PE)·mol^{-1}(Ni)·h^{-1}; [c] Determined by DSC; [d] Determined by GPC; [e] N (active species) = molecular number of polymer/molecular number of Ni; [f] Conditions: 5 atm of ethylene.

Based on the optimum conditions for **Ni3**/MMAO [Al/Ni = 2000, temperature = 30 °C, run time = 30 minutes], **Ni1**, **Ni2** and **Ni4** were also investigated in combination with MMAO for their ability to mediate ethylene polymerization (entries 15 – 17, Table S1). All systems were found to perform with good activities; the trend in catalytic performance for **Ni1** – **Ni5**/MMAO systems being very similar to that seen for **Ni1** – **Ni5**/MAO. Hence, **Ni3** [2,4,6-tri(Me)] > **Ni1** [2,6-di(Me)] > **Ni4** [2,6-di(Et)-4-Me] > **Ni2** [2,6-di(Et)].

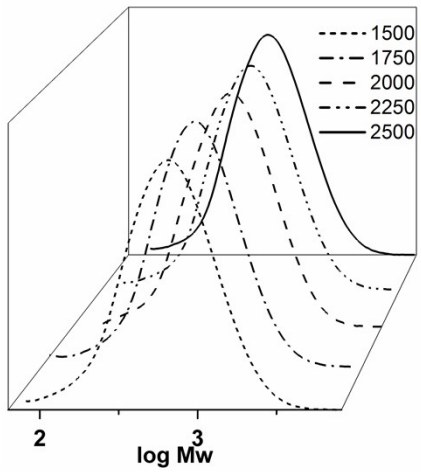

Fig. S1 GPC curves for the polyethylenes obtained using **Ni3**/MMAO system with various Al/Ni ratios (entries 1 – 5, Table S1).

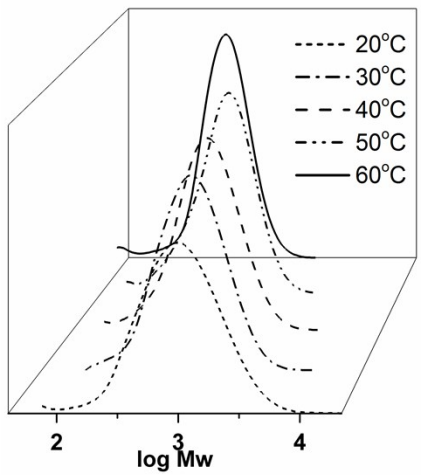

Fig. S2 GPC curves for the polyethylenes obtained using **Ni3**/MMAO at different temperatures (entries 3, 6 – 9, Table S1).

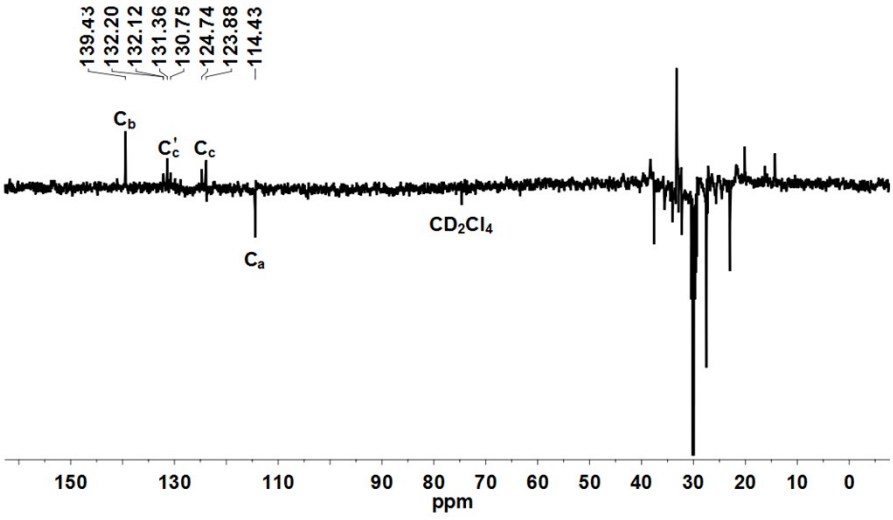

Fig. S3 DEPT135 ^{13}C NMR spectrum of the polyethylene obtained using **Ni3**/MMAO at 30 °C (entry 3, Table S1)

Calculation of the number of active species

$$N = N_p/N_{[Ni]} = n_p/n_{[Ni]} = W_p/(M_p \cdot n_{[Ni]}) \quad (1)$$

Where, N = the number of active species,

N_p = number of molecules of polyethylene,

$N_{[Ni]}$ = number of molecules of Ni,

n_p = number of moles of polyethylene,

$n_{[Ni]}$ = number of moles of Ni,

W_p = Total weight of the polyethylene,

M_p = Molecular weight of polyethylene.

Based on the equation in (**1**), the number of active species was calculated and expressed per unit time; the results are presented in Table 3 (main article) and Table S1.

For example:

For entry 1 in Table 3: W_p = 9.68 g, M_p= 1.22 Kg·mol^{-1} and $n_{[Ni]}$ = 5 μmol,

Therefore, the number of active species, N = 9.68/(1220·5·10^{-6}) = 1587,

As the polymerization run was performed over 30 min, then N h^{-1} = **3174 h^{-1}.**