

Generation effects on the microstructure and product distribution in ethylene polymerization promoted by dendritic nickel catalysts†

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Carbosilane dendrimers $Gn-[(ONNMe_2)NiBr_2]_m$, containing up to sixteen terminal pyridylimine nickel complexes, have been studied as catalysts for polymerization of ethylene; the microstructure and the oligomer/polymer distribution are significantly affected by the generation of the dendritic precursor.

Late-transition metal complexes have been shown to be important catalysts in the polymerization of olefins.¹ Most relevant to our present contribution are Ni(II) N/N pyridylimine-type compounds.² These and related catalysts produce ethylene derivatives ranging from light oligomers to high molecular weight polyethylene (PE), with linear to hyperbranched, or even dendritic, microstructures as a result of the so called “chain-walking mechanism”.³ The polymer topology is precisely controlled through simple variation of the reaction conditions, or by structural steric/electronic tuning of the ancillary ligands.⁴ Encouraged by the fact that dendrimers can be used as well-defined supports for active metal centers in the homogeneous phase, their catalytic applications are being widely studied.⁵ Pioneering work on dendrimer-bound metal catalysts highlighted their possible separation from the product stream by nanofiltration methods.⁶ In addition, several positive dendritic effects on catalyst properties have been observed for dendrimers with peripheral⁷ or embedded⁸ active metal centers. So far, only a few examples of metallo-dendritic systems have been studied in oligomerization⁸ and polymerization⁹ processes. Here, we report on a nickel catalyst system, based on pyridylimine-ended carbosilane dendrimers, that exhibits a significant dendritic effect on ethylene catalysis.

The pyridylimine ligand **1** (Chart 1) is synthesized by condensation in toluene of pyridine-2-carbaldehyde with 4-amino-2,5-dimethylphenol. Subsequent silylation of the hydroxy group with chlorosilanes $Gn-(Cl)_m$, in the presence of NEt_3 , results in the formation of derivatives **2–5**. The monometallic ($n = 0$) and

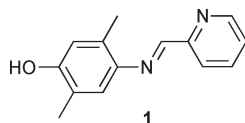


Chart 1

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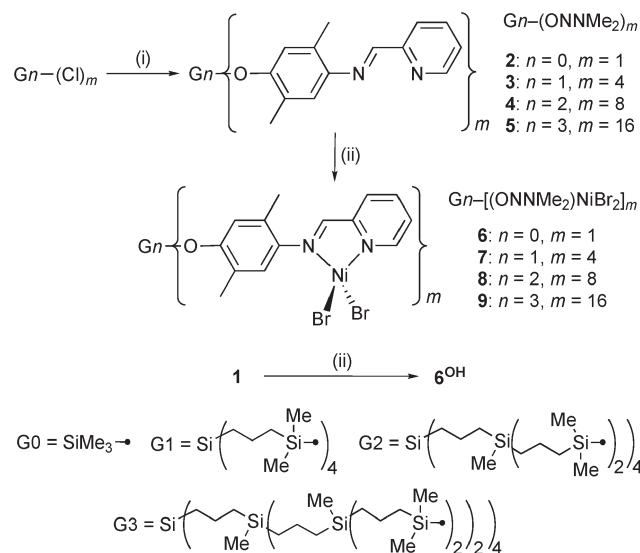
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† Electronic supplementary information (ESI) available: Synthesis and characterizing data for the new compounds, and ethylene catalytic reactions details. See <http://dx.doi.org/10.1039/b511379m>

dendritic ($n > 0$) nickel complexes **6–9**, as well the monometallic **6^{OH}**, are synthesized through the replacement of the labile ligand in $[NiBr_2(DME)]$ by the corresponding chelate ligand **2–5** in dichloromethane (Scheme 1) (see ESI†).

All of the compounds gave satisfactory elemental analyses. The complete replacement of the chloride atom in the starting $Gn-(Cl)_m$ (i.e., RMe_2Si-Cl) by pyridylimine groups in **2–5**, is confirmed by the shift of the $SiMe_2$ NMR resonances from δ 0.4 (1H) and 0.2 (^{13}C) to about 0.2 (1H) and -1.0 (^{13}C). The NMR studies of Ni(II) complexes **6–9** are not informative because of the interfering effect caused by their paramagnetism. However, their IR spectra show significant changes in the absorptions corresponding to $\nu_{C=N}$, indicating the coordination of the pyridylimine bidentate ligand to the nickel center.¹⁰ The solubility of all these compounds diminishes with the increase of dendrimer generation, and the low solubility of the nickel derivatives limits the preparation of higher generations.

Monometallic (**6**, **6^{OH}**) and dendritic (**7–9**) nickel complexes combined with MAO become readily soluble in toluene, and are active in ethylene catalysis.‡ They give a mixture of a toluene-soluble fraction of oligomers together with solid polyethylene (PE), with low to moderate activities according to Gibson's classification (Table 1).¹¹ The catalytic activities are maximal at the beginning of the reaction and steadily decrease over the time. The oligomeric oily products are composed of even olefins up to C_{34} . The number average molecular weight of these oligomers is in the range



Scheme 1 Reagents: m equiv. of: (i) $1/NEt_3$ in THF, (ii) $[NiBr_2(DME)]$ in CH_2Cl_2 .

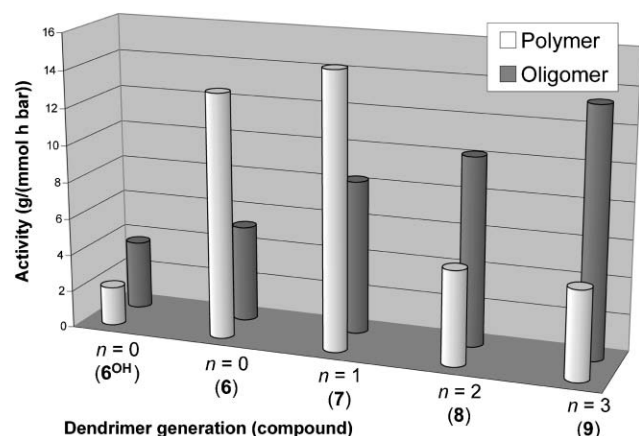
Table 1 Ethylene oligomerization/polymerization catalyzed by precursors **6**–**9**^a

Precatalyst	Generation	Oligomers				Polymer		C _n branches/1000 C ⁱ			
		Activity ^{b,c}	α ^{d,e}	M _n ^f	Branches/ 100 C ^{f,g}	Activity ^b	T _m ^h /°C	n = 1/2–5/≥6	Total	10 ⁻³ M _w ^j	PDI ⁱ
6 ^{OH}	Monometallic	3.70	0.65	341.1	4	2.09	121.4	10/18/48	76	5.88	6.61
6	Monometallic	5.21	0.70	265.8	3	13.21	117.1	12/36/97	145	1.64	3.58
7	First	8.32	0.60	284.5	3	14.88	120.5	17/22/62	101	2.16	2.77
8	Second	10.21	0.51	342.5	3	5.12	123.2	13/11/38	62	10.62	11.25
9	Third	13.40	0.45	327.6	3	4.82	124.7	12/10/36	58	17.07	14.06

^a Conditions: 50 ml toluene; n(Ni) = 14 μmol; Al/Ni = 1000; τ_p = 24 h; T_p = 20 °C; p_{CH₄} = 2 bar; activities ± 7%. ^b Activity: g/(mmol_{Ni} h bar). ^c Corrected to consider the lower olefin lost during work-up. ^d Schulz–Flory parameter α . ^e Determined by GC. ^f Determined by ¹H NMR. ^g Total number of methyl per 100 C. ^h Determined by DSC (second heating run). ⁱ Determined by ¹³C NMR. ^j Determined by GPC.

M_n = 265–340, and they are characterized by Schulz–Flory chain length distributions with α values from 0.45 to 0.70. A relatively low branching is observed by ¹H NMR (three branches per 100 C, for C₄ to C₃₄ oligomers).¹² In contrast, a higher degree of branching is found in the solid polymers that makes some of them to be considered hyperbranched.⁴ T_m values of all the samples are in agreement with their level of chain branching, and are lower than those typically found for HDPE (≥ 135 °C).^{13a} Analysis by GPC of the solid materials shows that weight average molecular weights of the polymers are low (M_w = 1600–17 000) with wide distributions (PDI = 3–14). The quantitative ¹³C NMR analyses of the polymers formed show branching densities in the range of 60–170 total branches per 1000 main-chain carbons and an abundant amount of branches are relatively long (≥ 6 C).¹³ These findings imply that polymerization active species walk along the chain much further than the oligomerization ones.

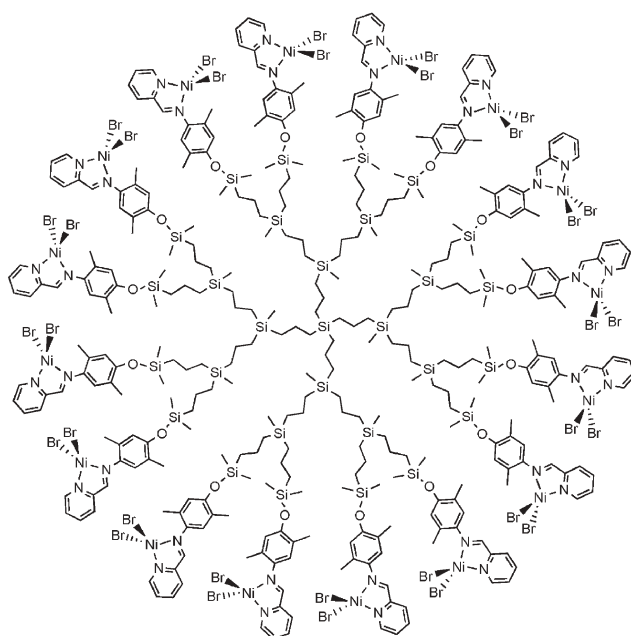
Several trends arise when analyzing the data in Table 1 with regard to the metallic nuclearity or generation of the precursors. The activity leading to oligomers slightly increases whereas the activity producing polymer diminishes for higher generations (Fig. 1). Monometallic compound **6** is superior yielding PE than oligomer, while the contrary is observed for polynuclear dendrimer **9**, with sixteen Ni centers (Fig. 2). The Schulz–Flory parameter (α) also decreases with increasing nuclearity. Conversely, higher molecular weights (and PDIs) are observed for the polymers produced by higher generations. The branching degree of the polymers is also generation-dependent and decreases progressively on going from the monometallic complex **6** to the G3 dendrimer **9**;

**Fig. 1** Activities by precursors **6**^{OH} and G_n-[(ONNMe₂)NiBr₂]_n.

this reduction in the number of branches is larger for the longest branches than for the methyl ones.

The production of oligomers and polymers by eventual formation of mononuclear nickel species by the split of the Si–O bond after the addition of the cocatalyst, is excluded because of the observed performance of compound **6**^{OH} (Table 1), which behaves differently than the reference compound **6** and related dendrimers. Therefore, protection at the phenolic oxygen, even with a very simple carbosilane group (Me₃Si–), seems to be positive in terms of polymerization activity (compare the performance of **6**^{OH} vs. **6**).

Although, the cooperative effect of other metal centers in close proximity to the active site could play an important role, these results might be interpreted as a consequence of the combination of the “steric pressure” on the growing chains and “microenvironment protection” of higher generation dendrimers on the polymerization species. Their bulkiness enhances chain transfer processes, and favors the performance of the oligomerization species, as reflected by lowering in α parameter and increasing in activity, respectively. A larger size also affects the polymerization active species encumbering the catalyst chain walking process from going too deep into the coiled polymer chain, leading to less

**Fig. 2** Metallodendrimer G₃-[(ONNMe₂)NiBr₂]₁₆ (**9**).

branched polymers. At the same time, the polymers are probably produced by more protected active centers in larger dendrimers, with lower activity, but higher M_w (and PDI). For instance, the later is reasonable if back-folding of terminal active species into the dendrimer matrix becomes significant at higher generation.

In summary, we have shown an example in which the size of the dendrimer regulates the production of ethylene insertion products (oligomer vs. polymer), the oligomer chain-length distribution (α), and the branching density, molecular weight, and polydispersity of the polymers. It is noteworthy that such dendritic effect has been obtained with peripheral metal dendrimers when core- or focal-point-dendrimers are *a priori* more suited systems for these purposes.

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Notes and references

‡ We found the starting material $[\text{NiBr}_2(\text{DME})]$ to be totally inactive under the same reaction conditions.

§ Schulz-Flory parameter $\alpha = k_p/(k_p + k_{ct}) = \text{mol of } C_{n+2}/\text{mol of } C_n$; k_p = rate of propagation, k_{ct} = rate of chain transfer.

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