

Unusual product distribution in ethylene oligomerization promoted by in situ *ansa*-chloroneodymocene–dialkylmagnesium systems

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Abstract

Ethylene polymerization using in situ combinations between a chloroneodymocene precursor and a dialkylmagnesium reagent has been investigated to prepare tailor-made oligomers. Combinations of $[\text{Cp}^*_2\text{NdCl}_2\text{Li}(\text{OEt}_2)_2]$ (**1**) with 40 equiv. of *n*-butylethylmagnesium (BEM) or di(*n*-hexyl)magnesium (DHM) gave oligoethylenes with M_n up to 2500 and narrow molecular weight distributions ($M_w/M_n < 1.10$) in moderate activity ($A_{1h} = 79 \text{ kg}/(\text{mol of Nd h atm})$ at 80°C , 1 atm). Under these conditions, ethylene polymerization proceeded in a controlled fashion, with a linear growth of M_n vs monomer conversion, ascribed to an effective chain transfer between the Nd and Mg centers. Combinations of $[\text{rac}\{-\{\text{Me}_2\text{Si}(\eta^5\text{-}2\text{-SiMe}_3\text{-}4\text{-}t\text{-Bu-C}_5\text{H}_2)_2\}\text{Nd}(\mu\text{-Cl})_2\text{Li}(\text{THF})_2\}]$ (**2**) with either BEM or DHM (20–40 equiv.) showed decreased activity, suggesting possibly a different rate-determining-step for ethylene polymerization than for that of higher α -olefins. The oligoethylenes obtained from combinations based on **2** have narrow molecular weight distributions ($M_w/M_n < 1.2$) but higher contents of vinyl terminations. Monitoring of the reactions showed also a non-linear growth of M_n vs monomer conversion, especially marked when DHM was used as co-reagent. The **2**/DHM combination behaves as a “self-correcting” catalyst system that deviates from the calculated M_n values for a controlled-living polymerization in the early stage of the reaction and re-approach them progressively in the second stage.

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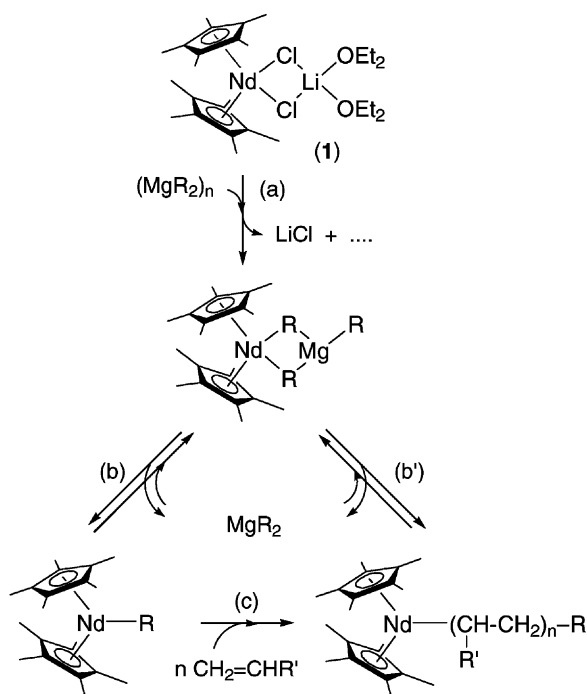
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1. Introduction

Neutral d^0 trivalent organolanthanidocenes $[\{\text{Cp}'_2\text{LnR}\}_n]$ (Cp' : substituted cyclopentadienyl ligand, typically $\text{C}_5\text{Me}_5 = \text{Cp}^*$; $\text{Ln} = \text{La}, \text{Nd}, \text{Sm}, \dots$; $\text{R} = \text{H}, \text{Me}, \text{CH}_2\text{SiMe}_3$; $n = 1, 2$) are well known for

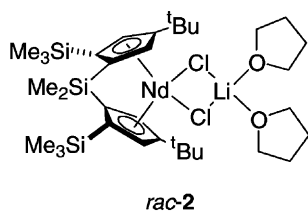
their high intrinsic activity in ethylene polymerization [1–5]. These complexes, especially the hydride complexes $[\{\text{Cp}'_2\text{LnH}\}_2]$, are, however, extremely sensitive and their synthesis as their handling is arduous. An alternative to skip this difficulty is the in situ alkylation of readily available chloro precursors, e.g. $[\text{Cp}^*_2\text{NdCl}_2\text{Li}(\text{OEt}_2)_2]$ (**1**), with a dialkylmagnesium compound. It has been shown by some of us that such a combination provides an active, stable ethylene polymerization system in which a controlled (“pseudo-living”) ethylene growth chain transfer reaction between the MgR_2 derivatives and the catalytically active lanthanidocene complexes takes place, yielding

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Scheme 1.

eventually long chain dialkylmagnesium compounds, $\text{Mg}(\text{PE})_2$, with a narrow distribution (Scheme 1) [6–9]. Recently, we have extended this methodology to trivalent chloroneodymium complexes based on bulky substituted *ansa*-bridged Cp ligands [10–15], e.g. $[\text{rac}\{-\{\text{Me}_2\text{Si}(\eta^5\text{-}2\text{-SiMe}_3\text{-}4\text{-}t\text{-Bu-C}_5\text{H}_2)_2\}\text{Nd}(\mu\text{-Cl})_2\text{Li}(\text{THF})_2\}]$ (2) (Scheme 2), to investigate the oligomerization/polymerization of higher α -olefins such as styrene and 1-octene [16,17]. Herein, we report on preliminary studies for the controlled oligomerization of ethylene using similar combinations between a dialkylmagnesium reagent and chloro precursors 1/2 and comment on the unusual peculiarities of some initiator systems.



Scheme 2.

2. Experimental

2.1. General considerations

All operations were performed under dry argon by using standard Schlenk techniques and a glove box. Solvents were distilled from sodium benzophenone ketyl (toluene) or Na/K alloy (alkanes) under nitrogen and thoroughly degassed prior to use. Ethylene (Air Liquide) was purified by passage through a moisture filter (Chrompack). *n*-Butylethylmagnesium (BEM) (Texas Alkyl) and di(*n*-hexyl)magnesium (DHM) (Akzo Nobel), both as 20 wt.% solutions in heptane, were used as received. Lanthanidocenes $[(\eta^5\text{-C}_5\text{Me}_5)_2\text{Nd}(\mu\text{-Cl})_2\text{Li}(\text{OEt}_2)_2]$ (1) [18] and $[\text{rac}\{-\{\text{Me}_2\text{Si}(\eta^5\text{-}2\text{-SiMe}_3\text{-}4\text{-}t\text{-Bu-C}_5\text{H}_2)_2\}\text{Nd}(\mu\text{-Cl})_2\text{Li}(\text{THF})_2\}]$ (2) [16] were prepared according to the literature procedures. The average molecular masses (M_n) and polydispersity (M_w/M_n) of oligo/polyethylenes were measured by size exclusion chromatography (SEC) in 1,3,5-trichlorobenzene at 135 °C¹ using a Waters 150C Plus chromatograph equipped with a refractometer and a Waters 150R Plus Retrofit viscometer, and Waters styragel columns (HT3-HT6). M_n and M_w/M_n values were calibrated from polystyrene standards using universal calibration. Consistent M_n and M_w/M_n values were obtained by analysis of some samples (Table 1, entries 3 and 6) by gas chromatography using a Varian CP-3800 chromatograph equipped with an on-column injector and a JW DB-prosteel metal column (DBHT-SIMD). ¹H (400 MHz) and ¹³C (100 MHz) NMR spectroscopy were performed in C₂D₂Cl₄ solutions at 120 °C on an AM-400 Bruker spectrometer and used to determine the nature and percentage of unsaturations in the oligomers according to literature methods [19].

2.2. Typical procedure for ethylene oligomerization

Toluene (190 ml) was introduced in a 500 ml Schlenk tube equipped with a mechanic stirrer rotating at speeds up to 1500 rpm. The reaction vessel was heated to 80 °C and toluene was saturated with

¹ It is noteworthy that some polymer samples collected after the apparition of solid materials in the reaction mixture could not be completely dissolved in 1,3,5-trichlorobenzene at 135 °C, even after prolonged times.

Table 1
Ethylene oligomerization using chloroneodymocene–MgR₂ combinations^a

Run	Catalyst system ^b	Temperature (°C)	C ₂ H ₄ consumed (g) ^c	M _n	M _w /M _n	Vinyl ^d /1000C	Internal olefines ^d /1000C
1	1/40 equiv. DHM toluene	80	8.2	340	1.24	0.8	0.0
			12.3	600	1.11	0.8	0.0
			24.6	1200	1.08	1.0	0.0
			32.8	1770	1.06	1.3	0.0
			49.2 (47.0)	2250	1.06	1.2	0.0
2	2/40 equiv. DHM toluene	80	2.1	670	1.67	3.0	0.2
			4.1	1220	1.06	2.9	0.1
			8.2	1710	1.06	2.9	0.2
			16.4	1720	1.08	3.0	0.1
			29.5 (29.2)	1830	1.04	3.9	0.2
3	2/40 equiv. BEM toluene	80	8.2	600	1.08	3.6	0.2
			16.4	970	1.13	3.7	0.2
			20.5	1170	1.03	5.3	0.3
			24.6	1600	1.05	4.3 (4.9) ^e	0.3
			44.1 (42.4)	2370	1.11	4.1 (3.8) ^e	0.6
4	2/40 equiv. DHM toluene	60	4.7	470	1.1	1.7	0.1
			6.7	490	1.1	1.3	0.1
			11.2	580	1.1	2.0	0.2
			17.6	580 ^f	1.5 ^f	1.8	0.1
			23.3 (22.8)	760 ^f	9.8 ^f	2.1	0.2
5	2/40 equiv. DHM hexane	60	4.9	460	1.1	1.8	0.1
			8.9	480	1.1	1.5	0.1
			10.8	480	1.1	1.4	0.1
			12.9 (13.0)	470 ^f	2.3 ^f	Nd	Nd
6	2/40 equiv. DHM toluene	100	7.2	570	1.1	4.7	0.3
			10.0	660	1.1	6.5	0.7
			17.5	790	1.06	9.4	1.0
			25.4	910	1.10	9.3	1.1
			40.7 (41.0)	1200	1.26	5.6	2.0
7	2/40 equiv. DHM isododecane	115	4.1	630	1.1	10.5	1.0
			8.2	740	1.04	10.3	1.4
			16.4	840	1.11	10.2	2.3
			32.8	940	1.32	6.0	2.9
			49.2	1250	1.46	4.3	3.2
			54.3 (50.9)	1170 ^f	1.62 ^f	4.1 (4.0) ^g	3.3
8	2/20 equiv. DHM toluene	80	2.1	1040	1.1	nd	nd
			4.3	1120	1.1	nd	nd
			8.3	1380	1.1	nd	nd
			20.9	2110	1.1	nd	nd
			28.1 (29.5)	3420	1.1	nd	nd

^a Unless otherwise stated reactions were conducted using 0.25 mmol of neodymium precursor in 200 ml of toluene under 1.1 atm of ethylene.

^b DHM: di(*n*-hexyl)magnesium; BEM: *n*-butylethylmagnesium.

^c Amount of ethylene consumed; the numbers into parentheses correspond to the weight (g) of dried polyethylene collected after neutralization of the reaction mixture.

^d Number of vinyl and internal olefin moieties per 1000 carbons as determined by ¹H NMR and, for numbers into parentheses, by ¹³C NMR; no vinylidene signals were detected.

^e ¹³C NMR analysis revealed 0.3 ± 0.1 tertiary carbons per 1000 carbons.

^f M_n value of the low-molecular weight fraction; the M_w/M_n value reflects the presence of high-molecular weight polyethylene (M_n > 1,000,000).

^g ¹³C NMR analysis revealed 1.3 ± 0.1 tertiary carbons per 1000 carbons.

ethylene (1.1 atm, kept constant via a back-pressure regulator). At the same time, a mixture of chloroneodymocene (0.25 mmol; i.e. 160 mg of **1** or 202 mg of **2**) and DHM (10.0 mmol, 9.75 g of a 20 wt.% solution in heptane) in toluene (10 ml) was stirred for 1 h at 23 °C. The resulting clear solution (blue from **1** and green from **2**) was then transferred via syringe into the reactor under stirring. The ethylene flow rate was monitored using a mass flowmeter (Aalborg, GFM17) connected to a totalling controller (KEP), which acts as a flow rate integrator. During the reaction course, some aliquots (2.0 ml) were regularly sampled from the mixture (according to the ethylene flow rate) via syringe for analytical purposes. After the desired time, the reaction was quenched by the addition of 1 l of a 5% HCl methanol solution to the mixture. The resulting precipitate was filtered, washed with methanol and dried under vacuum.

3. Results and discussion

To investigate the influence of the structure of the chloroneodymocene precursor and of the dialkylmagnesium co-reagent in ethylene polymerization,

different combinations were studied based on the usual Cp* precursor **1** and the *ansa*-silylene bridged complex **2**, and either *n*-BEM or DHM. MgR₂/Nd ratios in the range 20–40 were used to produce soluble oligomers. Representative polymerization data are summarized in Table 1. The corresponding ethylene flow rates are depicted in Fig. 1 and selected plots of the average molecular weight (M_n) vs monomer conversion are depicted in Figs. 2 and 3, respectively.

3.1. General features of non-bridged lanthanidocene–dialkylmagnesium systems

The combination of **1** with DHM (40 equiv.) at 80 °C led to a catalyst system that shows the polymerization behavior usually observed with these systems [9]. This corresponds to a relatively steady catalyst activity in the first stages of the reaction (average activity over the first hour, $A_{1h} = 79 \text{ kg}/(\text{mol of Nd h atm})$), till the gradual precipitation of high-molecular weight dialkylmagnesium derivatives after 2.5 h which is accompanied by a fast deactivation (Fig. 1) (vide infra). Monitoring of the reaction showed the formation of oligomers with a narrow molecular weight distribution ($M_w/M_n < 1.10$) and a linear relationship

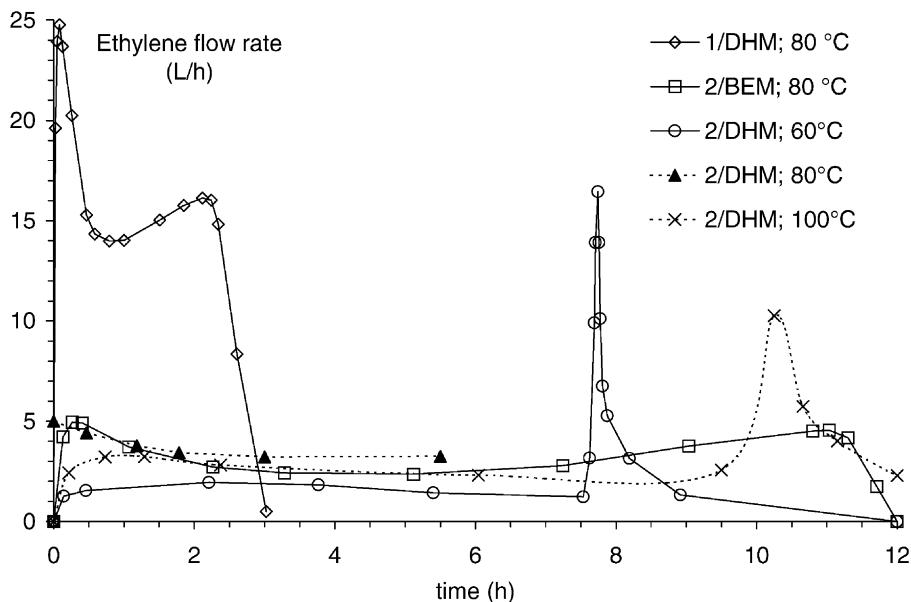


Fig. 1. Ethylene flow rates for chloroneodymocene–dialkylmagnesium systems (toluene, Mg/Nd = 40; see Table 1 for other reaction conditions).

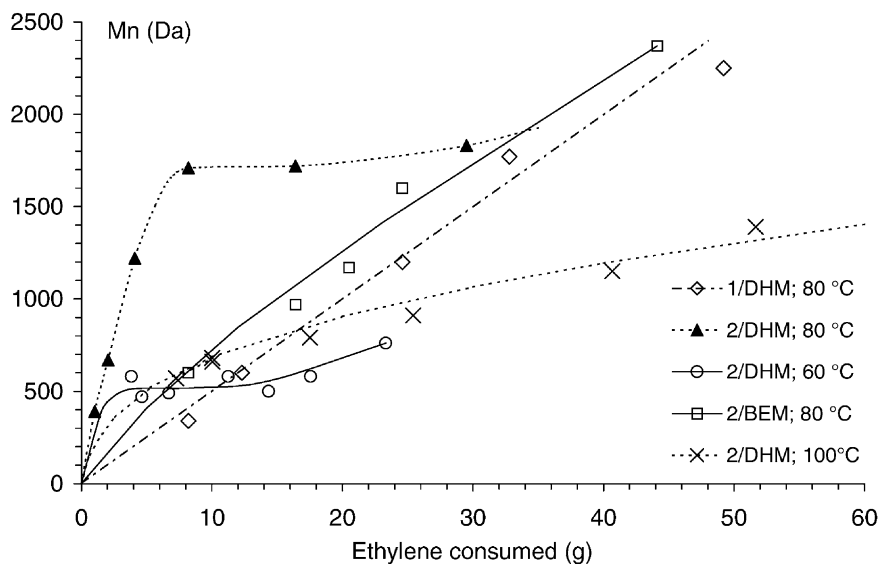


Fig. 2. Plots of average molecular weight (M_n) vs monomer conversion (toluene, Mg/Nd = 40; see Table 1 for other reaction conditions).

between the average molecular weight (M_n) and the amount of ethylene consumed (Fig. 2). The molecular weights obtained approach within 20% the theoretical values calculated assuming a fast interchange between the growing chain at the Nd center and both

of the alkyl chains at the Mg center (Table 1, entry 1: $M_{n,th} = 495, 905, 1315, 1725$ and 2545 g mol^{-1} , respectively). This is consistent with the controlled polymerization mechanism outlined in Scheme 1. The presence of a few unsaturations in the oligomers,

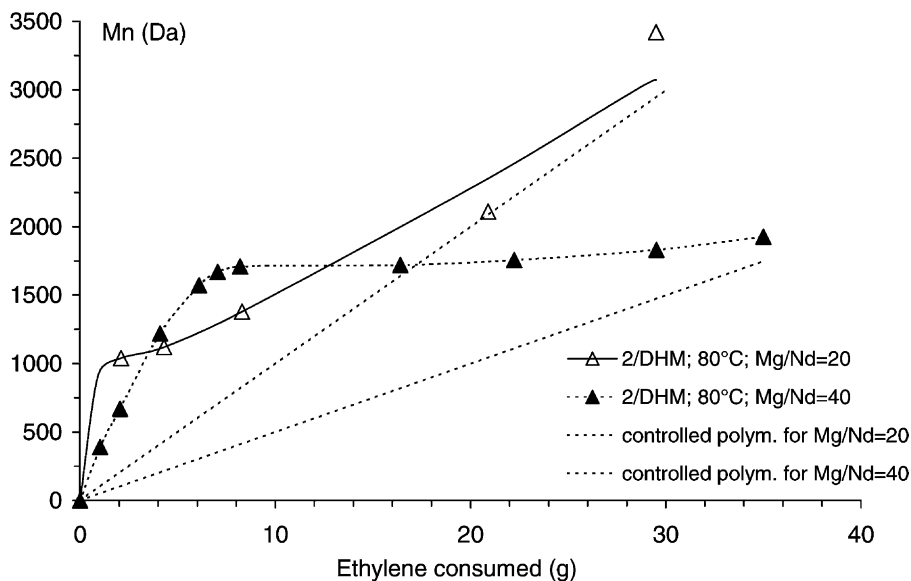


Fig. 3. Plots of experimental (symbols) and calculated (lines) molecular weight (M_n) vs monomer conversion (see Table 1 for reaction conditions).

essentially of vinyl type according to ^1H NMR spectroscopy, reveals the existence of another minor transfer process. β -Hydrogen elimination from $[\text{Cp}'_2\text{NdR}]$ species and subsequent ethylene insertion in the resulting hydrido-lanthanocene species is the classical chain transfer to monomer process that accounts for the formation of vinyl-terminated polymers. Here, due to the formation of low-molecular mass oligomers, this minor process does not affect the linearity of the relationship between M_n and the amount of ethylene consumed within experimental uncertainty.

The analogous combination of **1** with BEM (40 equiv.) gave essentially the same results in terms of catalytic activity and characteristics of the produced oligomers.

3.2. Polymerization activity of lanthanidocene–dialkylmagnesium systems

The use of the *ansa*-silylene bridged complex **2** resulted systematically in lower polymerization activities than with systems based on the above non-bridged lanthanidocene (Fig. 1). At 80°C , the combinations of **2** with BEM and DHM (40 equiv.) proved strictly equivalent in this regard ($A_{1\text{h}} = 20\text{ kg}/(\text{mol of Nd h atm})$; Table 1, entries 2 and 3). At 60°C , the average activity of the **2**/DHM (1:40) combination ($A_{1\text{h}} = 9\text{ kg}/(\text{mol of Nd h atm})$) was nearly the half of that at 80°C (Table 1, entry 4). Under these conditions, concomitant with the apparition of precipitated materials in the reaction medium, a sudden although brief increase in the ethylene flow rate was observed after 7.5 h (i.e. after 14 g of ethylene were consumed) (Fig. 1). Similar observations were reproducibly made when the polymerization was performed under different conditions; e.g. at 80°C with a Mg to Nd ratio of 20 (Table 1, entry 8; $A_{1\text{h}} = 14\text{ kg}/(\text{mol of Nd h atm})$; precipitation and peak consumption at 4 h, i.e. after 14.5 g of ethylene were consumed), at 60°C using hexane as the solvent in place of toluene (Table 1, entry 5; $A_{1\text{h}} = 4\text{ kg}/(\text{mol of Nd h atm})$; precipitation and peak consumption at 13 h, i.e. after ca 13 g of ethylene were consumed) and at 40°C in toluene ($A_{1\text{h}} = 0.5\text{ kg}/(\text{mol of Nd h atm})$; precipitation and peak consumption at 9 h, i.e. for ca 9 g of ethylene consumed). These data show that the sudden increase in the ethylene flow rate is directly related to the precipitation of the higher dialkylmagnesium compounds

produced. Considering the basic mechanism depicted in Scheme 1, one may consider that once the solubility limit of the dialkylmagnesium compounds has been reached (i.e. for a definite degree of polymerization according to the temperature and the solvent used), the concentration of the latter in solution decreases rapidly; therefore the dissociation equilibrium (b) between inactive bimetallic species $[\text{Cp}'_2\text{NdR}-\text{MgR}_2]$ and active $[\text{Cp}'_2\text{NdR}]$ species is shifted to the profit of the latter. This results temporarily in a high polymerization activity to give high-molecular weight polyethylene; however, because the $[\text{Cp}'_2\text{NdR}]$ species are not stabilized any longer by the dialkylmagnesium species, a rapid catalyst deactivation is observed as usually when organolanthanidocenes are used as single-component catalysts [1–5]. This general scheme is supported by the following observations: (i) For all of the catalyst systems investigated [6–9] and as evidenced in the present study with the DHM/**2** combination at 80°C (Table 1, entries 2 and 8), the higher the MgR_2 -chlorolanthanidocene ratio, the lower the polymerization activity, the later the precipitation and peak consumption. (ii) Simultaneous to the sudden increase in the ethylene flow rate and to the heavy precipitation of solids, high-molecular weight polyethylene ($M_n > 1,000,000$) forms resulting in a dramatic increase in the molecular weight distribution (see for instance Table 1, entries 4–7).

The global decrease in activity going from **1** to **2** is likely to result from a complex balance of electronic and steric, direct and indirect effects onto the catalytically active Nd center as well as interactions between the latter and dialkylmagnesium species. Because of the different equilibria that take place in the in situ systems and the exact structure of some of the (bimetallic) intermediates that remain to be clarified, these are obviously issues difficult to address into details [16,17]. A partial explanation to this trend can be proposed considering only structural parameters of the chloroneodymocene precursors: one may point out that the silylene bridge in *ansa*-complex **2** enforces a $\text{Cp}'(\text{centroid})-\text{Nd}-\text{Cp}'(\text{centroid})$ bite angle (118.9°) that is significantly lower to that of non-bridged complex **1** (ca $134^\circ-136^\circ$) [16]. Despite the presence of bulky *tert*-butyl groups, such a decrease of the bite angle induces, via a “scissoring effect”, an increase of the vacant space around neodymium [13–15]; this

factor has been claimed to account for the observed polymerization activity of some *ansa*-lanthanidocenes towards higher α -olefins vs the inactivity of non-bridged systems, considering the coordination of the incoming olefin for chain propagation as the rate-determining step [15]. The lower ethylene polymerization activity of combinations based on **2** (with respect to those based on **1**) might suggest therefore that, in this case, coordination of the olefin monomer to the active metal center is not the rate-determining step of the process; this is not unexpected in view of the small size of ethylene.

3.3. Interchange of the growing polymer chain between neodymium and magnesium centers

Contrary to catalyst systems based on simple chloroneodymocene **1**, ethylene polymerizations do not exhibit a linear relationship between M_n and the amount of ethylene consumed when performed with combinations using the bridged precursor **2**. Despite the narrow molecular weight distributions observed up to 115 °C for the oligoethylenes, the M_n values deviate all from the theoretical values calculated assuming a fast interchange of the growing polyethylene chain between the Nd and Mg centers. Systems based on **2** feature different behaviors upon the nature of the dialkylmagnesium derivative used. With *n*-BEM, at 80 °C, the M_n values increase monotonously with monomer conversion and the overall plot deviates slightly from the ideal straight line (Fig. 2).

The most unexpected peculiarities are observed upon using DHM (Figs. 2 and 3). With the **2**/DHM (1:40) combination, at 80 °C, the plot of M_n vs monomer conversion consists in two nearly linear domains: in the first stage, the deviation between the experimental and the ideal M_n values increases, while in the second stage it progressively diminishes to approach ultimately the theoretical straight line. Till this point, the second stage features apparently constant M_n and M_w/M_n values although the amount of ethylene polymerized has been tripled! On using the same combination at a lower Mg to Nd ratio (20), a similar behavior is observed but the first stage is much shorter than the second one, i.e. the formation of relatively high-molecular weight oligomers (with respect to calculated values for a controlled-living

polymerization) is faster. The **2**/DHM catalyst system behaves basically in the same way at 60² and 100 °C. Nevertheless, in the later case, M_n values are limited by the significant extent of transfer/ β -H elimination. Noteworthy are the narrow molecular weight distributions ($M_w/M_n = 1.1$ – 1.2) at this high temperature even though chain transfer to monomer competes with transfer to magnesium. These results do not follow the statistical Schultz–Flory law, which predicts that formation of α -olefins induces an increase of polydispersity ($1.3 < M_w/M_n < 2$).

To the best of our knowledge, this surprising “self-correcting” behavior of the [*rac*-{Me₂Si(η ⁵-2-Si-Me₃-4-*t*-Bu-C₅H₂)₂}Nd(μ -Cl)₂Li(THF)₂]/DHM combination, which features a two-stage variation of the molecular weight of the formed oligomers and enables a significant production of vinyl-terminated oligomers while maintaining a low-molecular weight distribution, is an unprecedented phenomenon. The formation of relatively high-molecular weight oligomers in the first stage of the process may be regarded as an evidence for the inefficiency of the interchange between the growing chain at the Nd center and the alkyl chains at the Mg center. However, the reasons for the selective restoring of this initial default in the second stage of the process still remain to be clarified. The marked influence of the nature of the dialkylmagnesium used indicates that intrinsic characteristics of these co-reagents, e.g. their degree of association in hydrocarbon solutions [20–25], could be a determining factor. Also, the singular behavior of the *rac*-**2** complex precursor suggests that steric interactions between the Nd center and the dialkylmagnesium species (i.e. the ones initially introduced and/or the ones formed; vide supra) may play an important role. Thorough investigations in these directions are currently under way.

² The plot of M_n vs monomer conversion at 60 °C crosses the theoretical straight line for a controlled-living polymerization (Fig. 2). As indicated by the minimal amount of olefins contained in these oligomers, this does not stem from transfer reactions. In fact, at such a relatively low temperature, early precipitation takes place (7.5 h, 14 g of ethylene), so that the amount of ethylene consumed over this point does not account only for the highly soluble oligomers of which the M_n values are plotted but also for high-molecular weight polyethylene (see footnote f in Table 1). A “correct” plot could be obtained by taking into account either the average molecular weight of oligomers and polyethylene, or the exact amount of ethylene transformed into oligomers.

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References

- [1] D.G.H. Ballard, A. Courtis, J. Holton, J. McMeeking, R. Pearce, *J. Chem. Soc., Chem. Commun.* (1978) 994–995.
- [2] P.L. Watson, G.W. Parshall, *Acc. Chem. Res.* 18 (1985) 51–56.
- [3] G. Jeske, L.E. Schock, P.N. Swepston, H. Schumann, T.J. Marks, *J. Am. Chem. Soc.* 107 (1985) 8103–8110.
- [4] G. Jeske, H. Lauke, P.N. Swepston, H. Schumann, T.J. Marks, *J. Am. Chem. Soc.* 107 (1985) 8091–8103.
- [5] B.J. Burger, M.E. Thompson, D.W. Cotter, J.E. Bercaw, *J. Am. Chem. Soc.* 112 (1990) 1566–1577.
- [6] X. Olonde, A. Mortreux, F. Petit, K. Bujadoux, *J. Mol. Catal.* 82 (1993) 75–82.
- [7] Patent WO 93/07180 A1 to ECP Enichem Polymeres France; *Chem. Abstr.* 119 (1993) 271958s.
- [8] J.-F. Pelletier, A. Mortreux, X. Olonde, K. Bujadoux, *Angew. Chem., Int. Ed. Engl.* 35 (1996) 1854–1856.
- [9] K. Bujadoux, T. Chenal, C. Fouga, X. Olonde, J.-F. Pelletier, A. Mortreux, in: W. Kaminsky (Ed.), *Metalorganic Catalysts for Synthesis and Polymerization*, Springer, Berlin, 1999, pp. 590–600.
- [10] E.B. Coughlin, J.E. Bercaw, *J. Am. Chem. Soc.* 114 (1992) 7606–7607.
- [11] P.J. Shapiro, W.D. Cotter, W.P. Schaefer, J.A. Labinger, J.E. Bercaw, *J. Am. Chem. Soc.* 116 (1994) 4623–4640.
- [12] J.P. Mitchell, S. Hajela, S.K. Brookhart, K.I. Hardcastle, L.M. Henling, J.E. Bercaw, *J. Am. Chem. Soc.* 118 (1996) 1045–1053.
- [13] E. Ihara, H. Yasuda, *Tetrahedron* 51 (1995) 4563–4570.
- [14] E. Ihara, M. Nodono, H. Yasuda, N. Kanehisa, Y. Kai, *Macromol. Chem. Phys.* 197 (1996) 1909–1917.
- [15] E. Ihara, S. Yoshioka, M. Furo, K. Katsura, H. Yasuda, S. Mohri, N. Kanehisa, Y. Kai, *Organometallics* 20 (2001) 1752–1761.
- [16] S. Bogaert, J.-F. Carpentier, T. Chenal, A. Mortreux, G. Ricart, *Macromol. Chem. Phys.* 201 (2000) 1813–1822.
- [17] S. Bogaert, T. Chenal, A. Mortreux, G. Nowogrocki, C.W. Lehmann, J.-F. Carpentier, *Organometallics* 20 (2001) 199–205.
- [18] T.D. Tilley, R.A. Andersen, *Inorg. Chem.* 20 (1981) 3267–3270.
- [19] J.C. Randall, *J. Macromol. Sci. Rev. Macromol. Chem. Phys.* C 29 (1989) 201–317.
- [20] E. Weiss, *J. Organometall. Chem.* 2 (1964) 314–321.
- [21] E. Weiss, *J. Organometall. Chem.* 4 (1965) 101–108.
- [22] C.W. Kaminsky, J.F. Eastmann, *J. Org. Chem.* 34 (1969) 1116–1121.
- [23] D.B. Malpass, L.W. Fannin, *J. Organometall. Chem.* 93 (1975) 1–6.
- [24] D.B. Malpass, L.W. Fannin, J.J. Ligi, in *Kirk-Othmer Encyclopedia of Chemical Technology*, third ed., Vol. 16, Wiley, New York, 1981, p. 555.
- [25] R.A. Andersen, G. Wilkinson, *J. Chem. Soc., Dalton Trans.* (1977) 809–811.