Quasi-living character of ethylene polymerization by hafnium alkoxide catalysts

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Ethylene was polymerized in the presence of soluble catalysts prepared from hafnium alkoxides and an equimolar mixture of triethylaluminium and diethylmonochloroaluminium. These systems show lower productivity than analogous systems based on titanium, but give polymer with high molecular weight, increasing with time and conversion. The kinetic analysis carried out according to the traditional steady-state kinetic model indicates the partial living character of the polymerization. This behaviour is more evident with the bidentate 1,1′-bis-2-naphtholate ligand, which further stabilizes the transition metal–carbon bond towards chain transfer.

(Keywords: ethylene polymerization; hafnium alkoxides; living polymerization; 1,1′-bis-2-naphtholate ligand)

INTRODUCTION

Hafnium is a relative newcomer to the class of Ziegler–Natta catalysts and has recently been used for olefin polymerization supported on $MgCl_2$ in combination with aluminium alkyls[1] and in the form of hafniocene soluble complexes in combination with methylalumoxane[2–4]. In the papers mentioned some distinctive differences were reported between hafnium and conventional titanium catalysts, thus stimulating investigation aimed at better characterization of hafnium-based catalysts.

In this context hafnium tetrabutanolate, $(BuO)_4Hf$, and hafnium 1,1′-bis-2-naphtholate-dibutanolate, $(BnfO)(BuO)_2Hf$, were used in combination with trialkylaluminium and dialkylmonochloroaluminium for the homogeneous polymerization of ethylene in order to understand the features of these systems in the basic polymerization steps. In particular, the dependence of conversion and chain length on polymerization time was examined and related to catalyst structure and number of active species. For the sake of comparison a similar titanium-based system was also studied.

By using classical kinetics schemes for insertion polymerization (see Appendix), some characteristic parameters of the polymerization process, such as number of chains *versus* transition metal (N') and mean growing chain lifetime ($\bar{L}$), were calculated. On this basis number of active sites, chain propagation rate and chain length were correlated with nature of the transition metal and alcoholate ligand in the starting complex.

EXPERIMENTAL

Triethylaluminium ($AlEt_3$) and diethylmonochloroaluminium ($AlEt_2Cl$) (Schering) and hafnium tetrabutanolate (Tioxide) were commercial products. Hafnium and titanium 1,1′-bis-2-naphtholate-dibutanolates were prepared as previously described[1].

Polymerization experiments

Hafnium 1,1′-bis-2-naphtholate-dibutanolate, $(BnfO)(BuO)_2Hf$. Stock solutions of $(BnfO)(BuO)_2Hf$ (0.95 $mol\,l^{-1}$, toluene) and $AlEt_3/AlEt_2Cl$ (0.073/0.079 $mol\,l^{-1}$, toluene) were used in the ratio of 5 ml to 200 ml to give $[AlEt_3 + AlEt_2Cl]/[(BnfO)(BuO)_2Hf] = 6.4$.

Both solutions were introduced into a Büchi 2 litre glass autoclave with ethylene stream. The polymerization was then started by working at 7 bar ethylene pressure (P_E) and $T = 35°C$. Seven runs were carried out under the same conditions by changing the polymerization time from 0.58 to 7.78 h (*Table 1*).

Hafnium tetrabutanolate, $(BuO)_4Hf$. Seven runs with duration from 0.55 to 5.00 h were carried out as described in the previous paragraph for $(BnfO)(BuO)_2Hf$, with $[AlEt_3 + AlEt_2Cl]/[(BuO)_4Hf] = 6.7$, at $P_E = 7$ bar and $T = 28°C$ (*Table 2*).

Titanium 1,1′-bis-2-naphtholate-dibutanolate, $(BnfO)(BuO)_2Ti$. Nine runs were carried out as above, with $[AlEt_3 + AlEt_2Cl]/[(BnfO)(BuO)_2Ti] = 11.6$, at $P_E = 2$ bar and $T = 26–27°C$ (*Table 3*).

Intrinsic viscosity

Determinations of the intrinsic viscosity $[\eta]$ were carried out in 1,2,4-trichlorobenzene at 135°C. The viscosity-average molecular weight $\bar{M}_v$ was calculated by the equation:

$$[\eta] = 4.06 \times 10^{-4} \bar{M}_v^{0.725}$$

reported in the literature[5].

RESULTS AND DISCUSSION

The homogeneous system $(BnfO)(BuO)_2Hf/AlEt_3/AlEt_2Cl$ was tested in toluene at $P_E = 7$ bar ethylene pressure and $T = 35°C$ in a series of polymerization experiments at different reaction times, keeping constant all other reaction parameters (i.e. P_E, T, [Hf], [cocatalyst], total volume of the polymerizing mixture,

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Table 1 Polymerization of ethylene in the presence of (BnfO)(BuO)$_2$Hf/AlEt$_3$/AlEt$_2$Cl catalyst[a]

Run	Time (h)	$\bar{M}_v$ ($\times 10^{-6}$)	Yield ((g PE/mol Hf) h^{-1} bar^{-1})	N'[b] ($\times 10^5$)	L[c] (h)
1	0.58	0.062	n.d.	n.d.	0.18
2	1.13	0.214	0.5	2.0	0.66
3	1.50	0.300	0.9	3.2	0.91
4	2.40	0.496	1.2	4.0	0.91
5	3.53	1.130	2.8	7.6	3.44
6	5.82	2.415	4.3	8.8	7.36
7	7.78	3.534	6.8	10.4	10.70

[a] (BnfO)(BuO)$_2$Hf = 0.475 mmol, AlEt$_3$ = 14.6 mmol and AlEt$_2$Cl = 15.8 mmol in 205 ml toluene solution; $P_E = 7.0$ bar, $T = 35°C$, stirring 500 rev min^{-1}

[b] N' = number of chains per Hf atom

[c] Mean growing chain lifetime (see Appendix)

Table 2 Polymerization of ethylene in the presence of (BuO)$_4$Hf/AlEt$_3$/AlEt$_2$Cl catalyst[a]

Run	Time (h)	$\bar{M}_v$ ($\times 10^{-6}$)	Yield ((g PE/mol Hf) h^{-1} bar^{-1})	N'[b] ($\times 10^3$)	L[c] (h)
1	0.55	1.078	23.9	0.4	0.23
2	1.08	1.638	42.1	0.8	0.35
3	1.50	2.300	146.5	3.3	0.49
4	2.08	n.d.	239.0	n.d.	n.d.
5	3.00	3.491	458.7	13.6	0.75
6	4.25	3.598	775.7	31.7	0.78
7	5.00	4.239	1015	41.5	0.91

[a] (BuO)$_4$Hf = 1.82 mmol, AlEt$_3$ = 5.86 mmol and AlEt$_2$Cl = 6.26 mmol in 202 ml toluene solution; $P_E = 7.0$ bar, $T = 28°C$, stirring 500 rev min^{-1}

[b] and [c] See *Table 1*

Table 3 Polymerization of ethylene in the presence of (BnfO)(BuO)$_2$Ti/AlEt$_3$/AlEt$_2$Cl catalyst[a]

Run	Time (h)	$\bar{M}_v$ ($\times 10^{-6}$)	Yield ((g PE/mol Hf) h^{-1} bar^{-1})	N'[b] ($\times 10^3$)
1	0.50	0.035	6.7	0.2
2	1.00	0.041	13.4	0.6
3	1.58	0.048	46.4	3.0
4	2.50	n.d.	287.4	n.d.
5	3.00	0.051	738.6	87.7
6	3.50	n.d.	718.5	n.d.
7	4.50	0.042	564.2	119.0
8	5.50	0.044	468.0	115.0
9	6.50	0.046	401.0	112.0

[a] (BnfO)(BuO)$_2$Ti = 1.50 mmol, AlEt$_3$ = 8.8 mmol and AlEt$_2$Cl = 9.2 mmol in 202 ml toluene solution; $P_E = 2$ bar, $T = 26°C$, stirring 200 rev min^{-1}

[b] N' = number of chains per atom of Ti

stirring and geometry of the polymerization vessel) (*Table 1*).

For the different polyethylene (PE) samples, intrinsic viscosity was measured and the corresponding $\bar{M}_v$ was determined. Also the overall yield of high-molecular-weight product and the normalized productivity obtained were determined. Approximate values the number of polymer chains per hafnium atom (N') were calculated by using $\bar{M}_v$.

The yield (grams of PE) in the presence of the (BnfO)(BuO)$_2$Hf-based system increases non-linearly on increasing the polymerization time. Although a non-linear fit of the data was not performed, a more realistic expression representing the yield dependence on time appears to be a quadratic equation of the type $y = at^2 - bt$, where y is the amount of polyethylene obtained, and a and b are constants. By dividing the right-hand side of the former equation by t, the expression:

$$y' = at - b \tag{1}$$

can be assumed, where y' ($= y/t$) is the normalized productivity. This last expression corresponds to a linear growth of y' with time, as experimentally observed (*Figure 1a*).

In accordance with the proposed expression, the system has an induction period probably related to the relatively slow kinetics of formation of the active sites. After this period, $\bar{M}_v$ increases almost linearly with time and reaches very high values ($>3 \times 10^6$) in a few hours (*Figure 1b*).

A similar trend was observed (*Table 2*) in the case of the (BuO)$_4$Hf-based system under similar experimental conditions (*Figure 2*), but some distinctive features deserve consideration.

Indeed $\bar{M}_v$ also increases with polymerization time in this last case to reach values of the order of millions, but a larger deviation from linearity is observed after 2.5 h (*Figure 2b*).

Moreover the normalized productivities are higher than for the (BnfO)(BuO)$_2$Hf system. Under the assumption reported in the Appendix, the number of chains per atom of transition metal (N') can be calculated from productivity and molecular-weight values.

The N' values relative to both the (BnfO)(BuO)$_2$Hf and (BuO)$_4$Hf systems are not constant, as expected for a classical living polymerization. These values are very low (especially in the case of (BnfO)(BuO)$_2$Hf), indicating that only a small fraction of the hafnium atoms are active for the catalysis (*Tables 1* and *2*).

The growth of molecular weight with time under the hypothesis of constant propagation rate constant (K_p = const) is consistent with a modest contribution of transfer reactions but cannot account for the linear increase of the normalized productivity, which should be

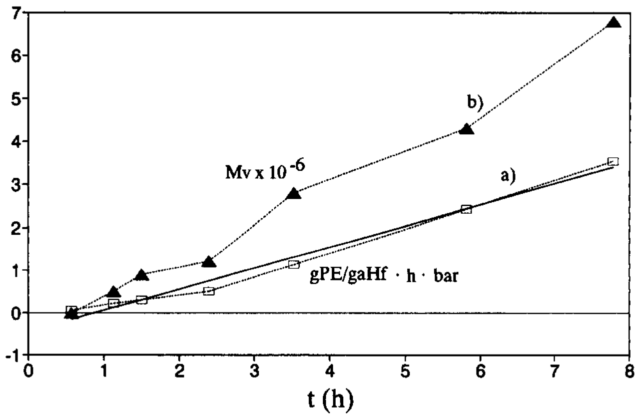

Figure 1 Time dependences of (a) normalized productivity (□, experimental data; ———, best-fitting straight line) and (b) viscosity-average molecular weight for ethylene polymerization in the presence of (BnfO)(BuO)$_2$Hf catalyst (from *Table 1*)

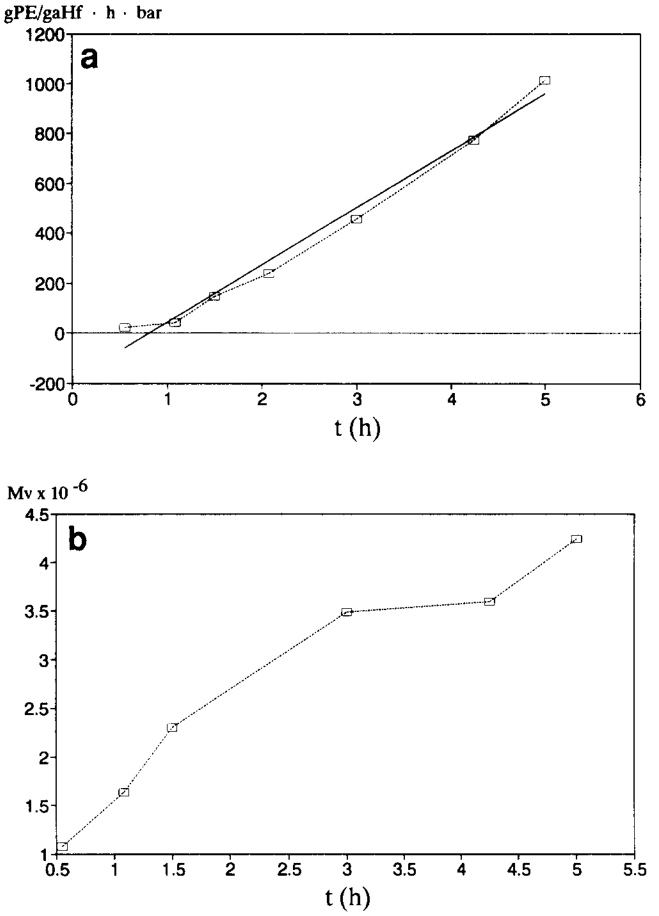

Figure 2 Polymerization of ethylene in the presence of $(BuO)_4Hf$ catalyst (from *Table 2*): (a) time dependence of normalized productivity (□, experimental data; ———, best-fitting straight line); (b) time dependence of molecular weight

constant when polymer yield increases linearly with time[6–9].

Therefore a probably linear increase (see Appendix) of the number of active sites [C*] could be hypothesized, while an acceleration of the polyinsertion process seems less probable.

According to the former hypothesis N' values should increase with time. Indeed in the case of the $(BnfO)(BuO)_2Hf$-based system, N' growth with time is roughly linear in the first 4 h whereas a certain deviation from linearity towards a limiting value is observed for longer polymerization times. In the case of $(BuO)_4Hf$, N' values are larger and increase continuously but non-linearly over the examined reaction times.

As reported in the Appendix, the values of $\bar{M}_v$ at different reaction times allow the evaluation of growing chain average lifetime $\bar{L}$ at least with the approximations reported.

The $\bar{L}$ values calculated at different reaction times and for different molecular weights are reported in *Tables 1* and *2*, respectively, for the two hafnium complexes.

The $\bar{L}$ values calculated in the case of $(BnfO)(BuO)_2Hf$ for longer polymerization times are affected by large experimental errors. The other values increase with polymerization time, thus suggesting a certain living character of the system; they are longer than the values estimated for the $(BuO)_4Hf$ catalyst (*Table 2*). In accordance with what has previously been suggested, this observation supports the viewpoint that, in the tetra-alkoxy system, the transfer processes are relatively faster than for $(BnfO)(BuO)_2Hf$. These values are in any case larger than the ones reported for heterogeneous $TiCl_3$ conventional systems, which are in the region of about 15 min[10–13].

The observed differences, under the similar experimental conditions adopted, can reasonably be considered to be due to the presence of the bidentate BnfO ligand. On the one hand, this seems to decrease the activity of hafnium; and on the other, to increase the ratio $\sum R_p/\sum R_t$ as the rate of the transfer processes is reduced by the stabilization of the growing chain end.

A very different behaviour has been observed for the soluble titanium system $(BnfO)(BuO)_2Ti/AlEt_3/AlEt_2Cl$ (*Table 3*). Indeed the polymer yield (grams of PE) does not increase monotonically with time but, after a short induction time, increases to a constant value that does not change even for longer lasting runs. This effect corresponds to substantial deactivation of the catalyst.

The $\bar{M}_v$ values are practically constant and in the range of ≈50 000. Hence titanium confirms its tendency[1,3] to give lower-molecular-weight chains than hafnium under similar coordination and experimental conditions.

Although yield grows after ~3 h from the beginning of the polymerization reaction, the $\bar{M}_v$ values stabilize quite early, in agreement with effective transfer processes.

The N' parameter increase with time much more sharply than for the previous hafnium system. Also in this case the fraction of active sites with respect to the whole number of atoms present in the reacting system is very low, but in any case higher than for similar hafnium systems.

CONCLUSIONS

The results obtained in the present work allow us to make the following remarks:

Polymer productivity and chain length are markedly affected by both the nature of the transition-metal atom and the ligands around it.

Hafnium-based alcoholate systems when activated with aluminium alkyls provide higher molecular weight than analogous titanium systems, but lower activity. These data fit perfectly with what has been observed in homogeneous phase systems with hafniocene and titanocene systems activated with alumoxane[3]. They are also consistent with the behaviour of hafnium in bimetallic systems (Hf/Ti) supported on $MgCl_2$ (ref. 1).

The bidentate 1,1'-bis-2-naphtholate ligand is very important in stabilizing the Me–C bonds against transfer reactions. Indeed, in the case of Ti, only ethylene oligomers are obtained with titanium tetrabutanolate[14]. This effect should be mainly attributed to the higher electron releasing ability of this bidentate aromatic ligand[15]. Steric effects probably do play a certain role also, as shown by the better stereospecificity of $(BnfO)HfCl_2$ in propylene and 4-methyl-1-pentene polymerization[16].

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APPENDIX

In steady-state kinetics, where active site concentration $[C^*]$, sum of propagation rates ($\sum R_p$) and sum of transfer reactions ($\sum R_t$) are constant, a linear relationship between $1/\bar{M}_v$ and $1/t$ is expected provided $\bar{M}_w/\bar{M}_n(Q)$ is constant during the polymerization process[13]. Under our hypothesized conditions, $[C^*] = At$, transfer reactions ($\sum R_t$) are negligible and the sum of propagation rates ($\sum R_p$) is given by the equation:

$$\sum R_p = k_p'[C^*] \tag{A1}$$

where k_p' is a pseudo-first-order propagation kinetic rate constant containing the monomer concentration, which was kept constant. The general expression:

$$\overline{DP}_{n,t} = \frac{\int_0^t \sum R_p \, dt}{[C^*]_t + \int_0^t \sum R_t \, dt} \tag{A2}$$

where $\overline{DP}_{n,t}$ is the number-average polymerization degree, can then be rewritten as:

$$\overline{DP}_{n,t} = \frac{\int_0^t K_p' A t \, dt}{At} \tag{A3}$$

Under the hypothesis that $Q = \bar{M}_v/\bar{M}_n = \overline{DP}_v/\overline{DP}_n$ is constant during the polymerization, from this one obtains:

$$\frac{d(1/\overline{DP}_v)}{d(1/t)} = \frac{2}{Qk_p'} = \text{constant} \tag{A4}$$

Since $\overline{DP}_n = \bar{L} \sum R_p/[C^*]$, where $\bar{L}$ is the mean growing chain lifetime, from equation (A1) is obtained the equation:

$$\overline{DP}_n = \bar{L} k_p' \tag{A5}$$

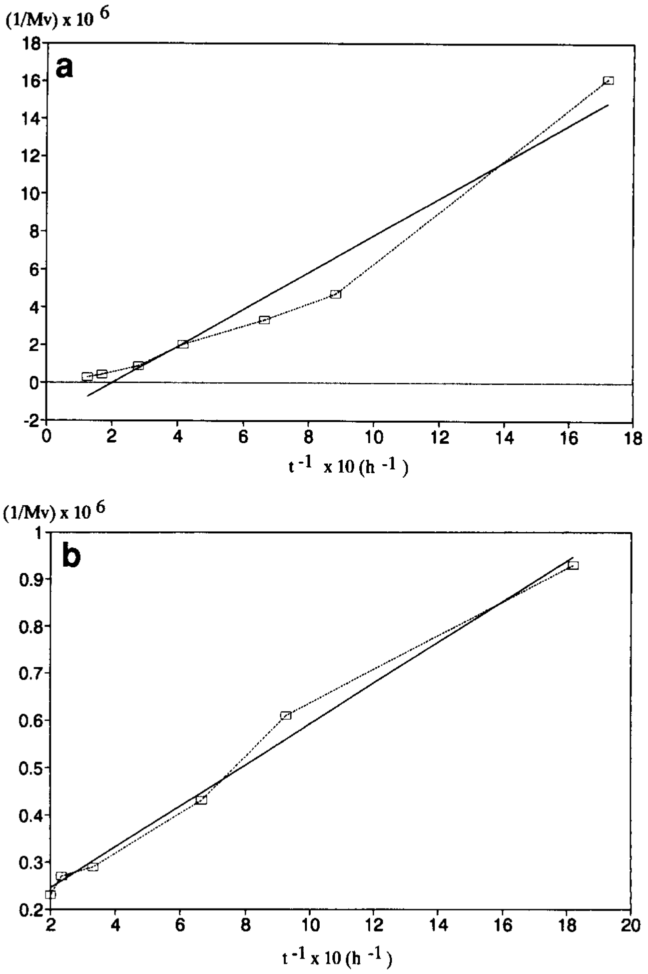

Figure 3 Plots of reciprocal viscosity-average molecular weight *versus* reciprocal time for ethylene polymerization with (a) $(BnfO)(BuO)_2Hf$ and (b) $(BuO)_4Hf$ catalysts (□, experimental data; ———, best-fitting straight line)

That is:

$$\bar{L} = \frac{\overline{DP}_n}{k_p'} = \frac{1}{2}\overline{DP}_v \frac{d(1/\overline{DP}_v)}{d(1/t)} \tag{A6}$$

The ratio $d(1/\overline{DP}_v)/d(1/t)$ can be evaluated by plotting $1/\bar{M}_v$ *versus* $1/t$ (*Figure 3*) in the case of the two hafnium catalysts for which $\bar{M}_v$ increases with time.

The data for $(BnfO)(BuO)_2Hf$ are in good agreement (*Figure 3a*) (with the exception of the values at 0.58 h) with a linear relationship, whereas those concerning $(BuO)_4Hf$ are more dispersed around a tentative straight line (*Figure 3b*). The last result suggests a more consistent contribution by transfer processes for the tetrabutanolate with respect to the complex containing the bidentate 1,1'-bis-2-naphtholate ligand. In both cases the induction period is responsible for the fact that the lines do not go through the origin.

From the above data $\bar{L}$ values have been tentatively calculated with equation (A6) and the results are reported in *Tables 1* and *2*. This type of calculation was clearly not possible for $(BnfO)(BuO)_2Ti$, as with this system $\bar{M}_v$ is constant with polymerization time (*Table 3*).