Effect of protic compounds on ethylene polymerization by Hf–Ti supported catalysts

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The effect was investigated of the addition of different protic compounds, such as water, n-butanol, butanoic acid and methyl ethyl ketone, to triisobutylaluminium used as the cocatalyst for an Hf–Ti bimetallic catalyst supported on magnesium dichloride ($Ti_{1.0}Hf_{1.3}Mg_{2.0}Al_{0.85}Cl_{12.45}$) in the polymerization of ethylene. All the above compounds show a similar behaviour by decreasing catalyst activity, increasing polymer molecular weight and narrowing polymer molecular weight distribution. Minor differences are observed in the end-group unsaturations. An attempt has been made to correlate these effects to the interaction of hafnium and titanium sites with the reaction products from AlR_3 and the different protic compounds.

(Keywords: ethylene polymerization; bimetallic Ziegler–Natta catalyst; hafnium; titanium; protic modifiers)

INTRODUCTION

It is now fully accepted that the polymerization of olefins in the presence of Ziegler–Natta catalysts occurs by insertion of the monomer into a transition metal–carbon bond[1], which is the essential part of the catalytic site. Protic molecules are expected to react with this bond, resulting in the formation of inactive species and reduced activity[2,3]. However, in typical Ziegler–Natta catalysts a significant excess of the alkylaluminium derivative with respect to the transition metal is usually used and also the aluminium–carbon bonds are reactive towards protic compounds[4]. The reaction products are not necessarily inactive or inert, as shown by methylalumoxanes which are formed by reaction of AlR_3 with H_2O[5] and are excellent cocatalysts for the cyclopentadienyl derivatives of transition metals[6,7].

In industrial use, protic compounds may be introduced unwillingly as impurities with solvents, monomers and other reagents. Their presence can vary in different stocks of the feed, thus affecting the process parameters and polymer specifications[8].

Taking into account these aspects, the present paper describes the investigation of the influence exerted on the ethylene polymerization kinetics and polymer properties by different protic molecules such as water, n-butanol, butanoic acid and methyl ethyl ketone. The protic compounds were added in amounts up to equimolar with respect to AlR_3 and hence up to a twenty-fold molar excess with respect to Ti and Hf.

EXPERIMENTAL

Chemicals

Commercial grade triisobutylaluminium (TIBA) and polymerization grade ethylene were used without further purification. Research grade n-hexane was purified according to the usual procedure.

The magnesium dichloride supported catalyst having the chemical composition $Ti_{1.0}Hf_{1.3}Mg_{2.0}Al_{0.85}Cl_{12.45}$ was prepared according to a procedure similar to that previously described[9]. Titanium tetra-n-butanolate and hafnium tetra-n-butanolate were solubilized in anhydrous paraffin, then spray-dried magnesium chloride was added and the resulting slurry heated at 80°C for 4 h. On cooling the slurry to room temperature, a paraffin solution of an aluminium alkylchloride was added dropwise and the mixture heated at 80°C for 2 h. The resulting solid was washed with anhydrous paraffin and dried *in vacuo*.

Polymerization experiments

A solution of 0.6 g of TIBA in 1800 ml of n-hexane containing the protic additive was placed in a 5 l stainless steel reactor equipped with a mechanical stirrer. The mixture was heated to 75°C in about 15 min, then the reactor was loaded with hydrogen up to 8 bar and ethylene up to 11 bar in that order. Finally, a suspension of catalyst (0.077 mmol Ti and 0.10 mmol Hf) in 100 ml of anhydrous n-hexane was introduced into the reaction vessel by raising the ethylene pressure up to 12 bar. The pressure was kept constant for 2 h by a continuous ethylene feed, then the polymerization was interrupted by adding 20 ml of a 10% by weight solution of

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2,6-di-t-butyl-4-methylphenol in ethanol. The coagulated polymer was filtered and dried under vacuum to constant weight.

Polymer characterization

The melt-flow index (MI) was measured by the plastometer ATS-FAAR Mod. 10.02 013 with a load of 5.0 kg, according to ASTM-D1238.

The shear sensitivity (SS) was evaluated as the ratio of the MI values at 21.6 kg and 5.0 kg.

Density measurements were carried out in a density-gradient column according to the ASTM-D2839 procedure.

Intrinsic viscosity measurements were carried out on an Ubbelohde viscometer at 135°C in 1,2,4-trichlorobenzene solution.

Fractionation with boiling n-heptane was carried out for 18 h in Kumagawa extractors.

Gel permeation chromatography (g.p.c.) analyses were performed on a Waters 150-C ALC/GPC instrument equipped with ultrastyragel columns (nominal pore diameters 500, 10^3, 10^4, 10^5 and 10^6 Å) and connected to a Waters Data Station. Calibration was performed by universal calibration[10–12].

The numbers of vinyl and vinylidene end-groups per 1000 carbon atoms were evaluated by a Philips PU 9800 *F*Ti.r. spectrometer according to the procedure reported by Haslam and Willis[13].

RESULTS

Polymerization experiments

Varying amounts of water (WA), n-butanol (BAL), butanoic acid (BAC) and methyl ethyl ketone (MEK) were mixed with the polymerization solvent (n-hexane). To this solution, triisobutylaluminium (TIBA) and the catalyst ($Ti_{1.0}Hf_{1.3}Mg_{2.0}Al_{0.85}Cl_{12.45}$)[9] were added in that order.

Ethylene was used as the sole monomer in the presence of hydrogen to control the polymer molecular weight[14,15]; the polymerization processes were performed by varying both the type of protic compound (PC) and its ratio with respect to the catalyst components.

The kinetics of the polymerization were followed during the first two hours and then the polymerization was stopped. In addition to monitoring the specific activity (SA) with time, the melt-flow index (MI), shear sensitivity (SS), density, content of terminal unsaturations and amount of n-heptane extractable polymer were determined (*Table 1*). The molecular weight (*MW*) and molecular weight distribution (*MWD*) of the obtained polyethylene were also evaluated.

Influence of protic compounds on the polymerization kinetics

The effect of different amounts (with respect to the catalyst components) of protic additives on the ethylene polymerization rate in the first two hours of polymerization

Table 1 Ethylene polymerization in the presence of different protic compounds (PC)[a]

Run	PC Type	PC (mmol)	PC/AlR_3 (mol mol^{-1})	SA[b]	MI (g per 10 min)	SS	Density (g ml^{-1})	Unsaturation[c]	Extraction[d] (%)
1	None	0	0	910	0.28	31	0.9581	0.15	3.4
18	WA	0.28	0.09	890	0.32	32	0.9593		
20	WA	1.13	0.38	970	0.27	29	0.9581		
19	WA	1.85	0.62	360	0.11	18	0.9521	0.02	1.2
21[e]	WA	2.29	0.38	1010	0.30	28	0.9589		
5	BAL	1.73	0.58	960	0.34	29	0.9574		
7	BAL	2.37	0.79	530	0.25	17	0.9537	0.13	11.4
6	BAL	3.45	1.15	0	–	–	–		
8[e]	BAL	3.45	0.58	930	0.42	29	0.9581		
29	BAC	0.71	0.24	1080	0.33	27	0.9579		
28	BAC	1.43	0.48	910	0.57	24	0.9596		
53	BAC	2.18	0.73	960	0.31	27	0.9586		
56	BAC	2.45	0.82	850	0.28	25	0.9566		
55	BAC	2.72	0.91	170	0.08	19	0.9538	0.01	1.1
31[e]	BAC	1.74	0.29	1100	0.28	29	0.9574		
12	MEK	1.51	0.50	960	0.29	23	0.9585		
10	MEK	2.16	0.72	660	0.25	19	0.9567	0.12	2.3
11[e]	MEK	3.02	0.50	1080	0.30	28	0.9585		
80[f]	None	0	0	530	24.0	12	–[g]	0.18	6.0

[a] In 2 l n-hexane at 75°C for 2 h, $p(H_2) = 8$ kg cm^{-2}, p(total) = 11 kg cm^{-2}, 3 mmol TIBA, molar ratio Al/(Ti + Hf) = 17; WA = water, BAL = n-butanol, BAC = butanoic acid, MEK = methyl ethyl ketone

[b] Average specific activity, evaluated as kg of polyethylene per mol of transition metals per h

[c] Number of double bonds per 1000 carbon atoms

[d] Fraction extracted in boiling n-heptane

[e] Run carried out in the presence of 6 mmol TIBA

[f] Run carried out in the presence of a Ti–Mg catalyst

[g] Not determined

was evaluated in comparison with standard polymerization runs where no protic additive was present. The relevant kinetic curves are shown in *Figures 1* to *4* for water, n-butanol, butanoic acid and methyl ethyl ketone, respectively.

The four protic compounds show a substantially similar effect on the polymerization kinetics. In all cases, the polymerization rate is very little affected or slightly increased up to a protic compound/AlR_3 molar ratio of about 0.5. Such an increase may be considered to be within the limits of experimental error, as indicated by several standard experiments carried out in the absence of protic compounds (*Table 2*). At higher contents of protic additives, the activity markedly decreases and practically no polymer is obtained at PC/AlR_3 molar ratios larger than 1 (*Table 1*). The effect of PC on the instantaneous polymerization rate is particularly evident during the initial period of polymerization. Accordingly, ethylene absorption, which is a good measure of the polymerization rate, decreases in the first 40 min when the PC/AlR_3 ratio is lower than 0.5, whereas at higher ratios an almost constant value is observed during the entire polymerization time (*Figures 1* to *4*).

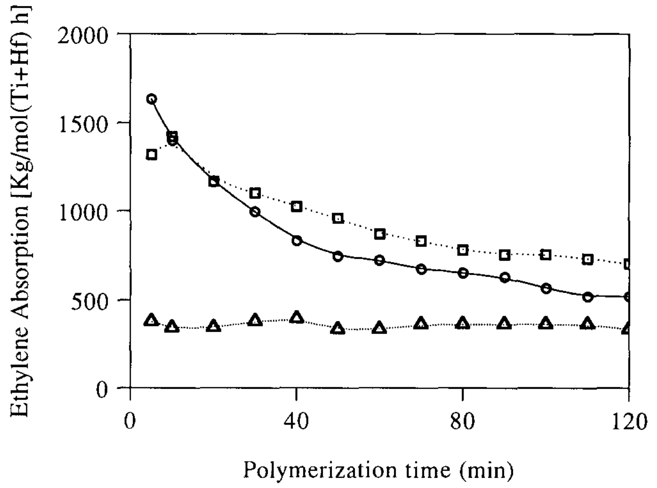


Figure 1 Dependence of polymer productivity on the amount of water (WA) added to the polymerization solvent. Molar ratios WA/AlR_3: (○) 0; (□) 0.38; (△) 0.62

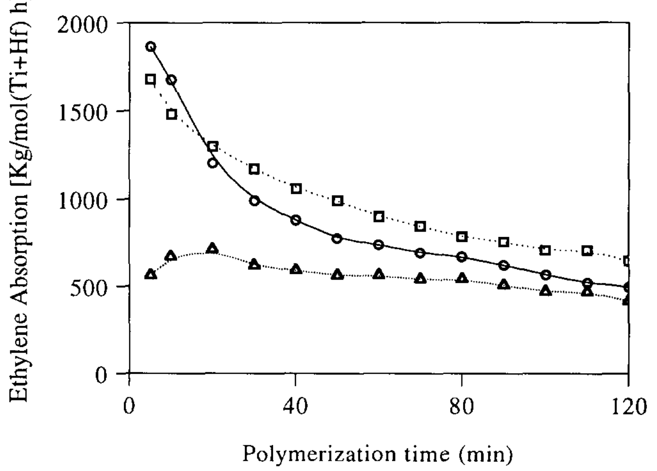


Figure 2 Dependence of polymer productivity on the amount of n-butanol (BAL) added to the polymerization solvent. Molar ratios BAL/AlR_3: (○) 0; (□) 0.58; (△) 0.79

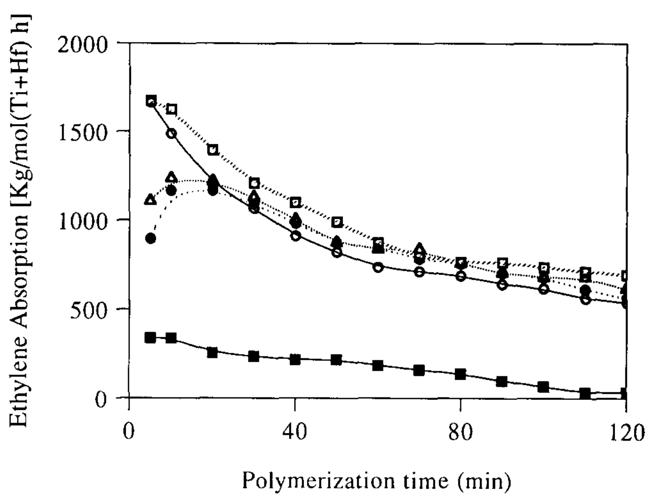


Figure 3 Dependence of polymer productivity on the amount of butanoic acid (BAC) added to the polymerization solvent. Molar ratios BAC/AlR_3: (○) 0; (□) 0.24; (△) 0.48; (●) 0.73; (■) 0.91

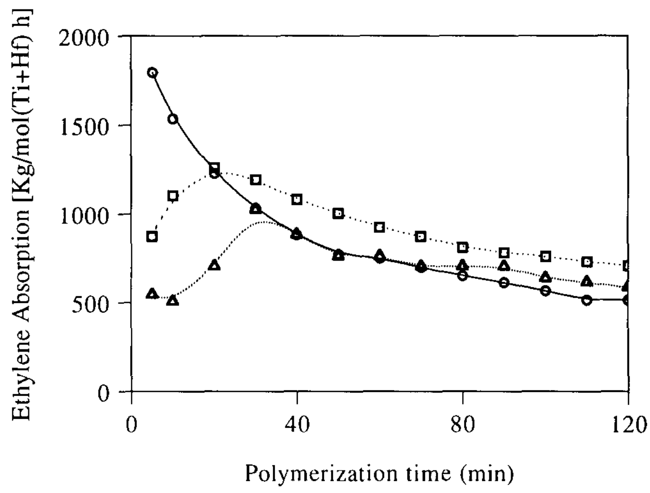


Figure 4 Dependence of polymer productivity on the amount of methyl ethyl ketone (MEK) added to the polymerization solvent. Molar ratios MEK/AlR_3: (○) 0; (□) 0.50; (△) 0.72

Table 2 Ethylene polymerization in the absence of protic additives[a]

Run	SA[b]	MI (g per 10 min)	SS	Density (g ml^{-1})
1	880	0.28	31	0.9581
2	940	0.29	31	0.9588
9	910	0.32	30	0.9588
18	890	0.32	32	0.9593
25	1040	0.33	29	0.9592
30	960	0.26	31	0.9586
Mean	936±56	0.30±0.03	30.5±0.83	0.9588

[a] Molar ratio Al/(Ti+Hf) = 17

[b] Average specific activity, evaluated as kg of polyethylene per mol of transition metals per h

This trend is confirmed by the values of the average specific activity during the first 120 min of the polymerization. As a consequence of the effect of protic compound addition on the instantaneous polymerization rate discussed above, the average specific activity (SA) is also moderately affected by the addition of the PC up to a 0.5 molar ratio with respect to AlR_3. A larger amount of PC produces a sharp reduction of the SA and no polymer is formed when $PC/AlR_3 \geq 1$ (*Table 1*). It is of interest to note that the amount of PC employed was always in a large molar excess as compared to that of Ti and Hf, as in all the experiments a molar ratio $AlR_3/(Ti+Hf)$ of 17 was used.

In all cases (runs 21, 8, 31 and 11, *Table 1*), the use of a larger amount of AlR_3 in order to give a PC/AlR_3 molar ratio equal to or smaller than 0.5 restores the original value of the SA.

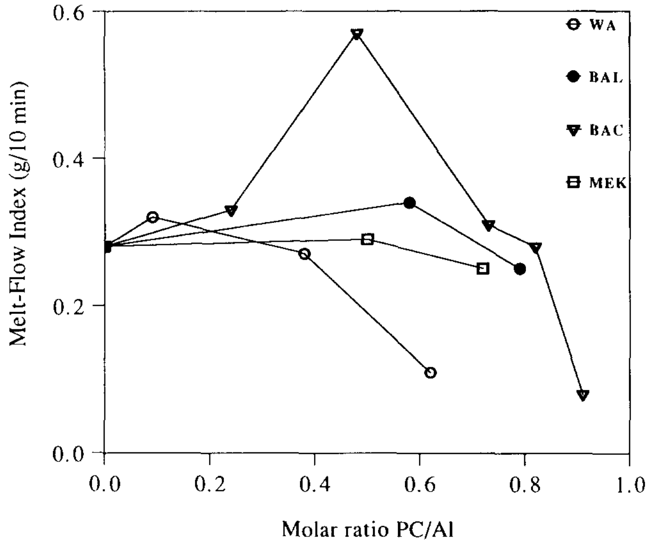


Figure 5 Dependence of melt-flow index (MI) on the amount and type of protic compound (PC) added to the polymerization solvent

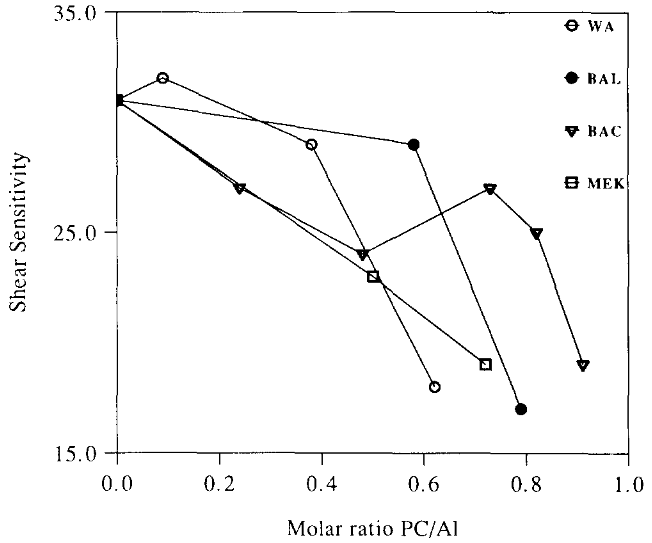


Figure 6 Dependence of shear sensitivity (SS) on the amount and type of protic compound (PC) added to the polymerization solvent

Influence of protic compounds on polymer products

The melt-flow index, shear sensitivity and density of the polyethylene recovered after 120 min polymerization carried out in the presence of water, n-butanol, butanoic acid and methyl ethyl ketone (*Table 1*) are lower than in the absence of the PC. This decrease becomes more evident when the PC/AlR_3 molar ratios are larger than 0.5. This tendency is shown graphically in *Figures 5* and *6*, where MI and SS, respectively, are plotted *versus* the molar ratio PC/AlR_3. The total content of unsaturated end-groups in the polymer is strongly reduced when water or butanoic acid are present, while n-butanol and methyl ethyl ketone give almost the same values as in the absence of the PC. In the presence of n-butanol ($BAL/AlR_3 = 0.79$) at different polymerization times (10 and 120 min), the decrease in the MI and SS as compared to the process carried out in the absence of n-butanol becomes more marked at longer polymerization times (*Table 3*).

G.p.c. analysis of polyethylene samples obtained after 120 min polymerization time shows in all cases the narrowing of the molecular weight distribution accompanied by an increase of the average molecular weight (*Table 4*) due to the absence of low-molecular-weight macromolecules (*Figure 7*).

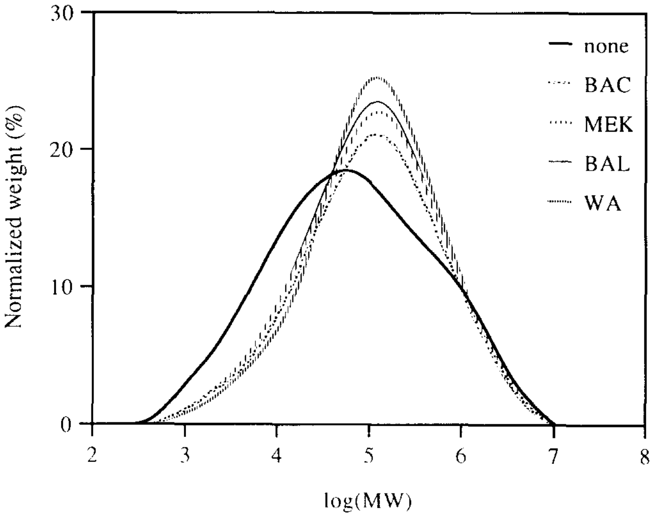


Figure 7 G.p.c. traces of polyethylene samples obtained in the presence of added protic compounds. Molar ratios PC/AlR_3: (none) 0; (BAC) 0.48; (MEK) 0.72; (BAL) 0.79; (WA) 0.62

Table 3 Kinetics of ethylene polymerization[a]

Run	PC		PC/AlR_3 (mol mol^{-1})	Time (min)	SA[b]	MI (g per 10 min)	SS	Unsaturation[c]
	Type	(mmol)						
73	None	-	0	10	1380	0.39	32	0.14
65				120	820	0.44	30	0.15
79	BAL	2.37	0.79	10	690	0.33	30	0.09
7				120	530	0.25	17	0.13

[a] In 2 l n-hexane at 75°C, $p(H_2) = 8$ kg cm^{-2}, p(total) = 11 kg cm^{-2}, 3 mmol TIBA, molar ratio Al/(Ti + Hf) = 17; BAL = n-butanol
[b] Average specific activity, evaluated as kg of polyethylene per mol of transition metals per h
[c] Number of double bonds per 1000 carbon atoms

Table 4 Influence of protic compounds on molecular weight and molecular weight distribution of polyethylene[a]

Run	PC Type	 (mmol)	PC/AlR_3 (mol mol^{-1})	$\bar{M}_n$[b]	$\bar{M}_w$[b]	$\bar{M}_w/\bar{M}_n$[b]
1	None	–	0	12600	328000	26.0
19	WA	1.85	0.62	31600	368000	11.6
28	BAC	1.43	0.48	14000	268000	19.1
7	BAL	2.37	0.79	23100	333000	14.4
10	MEK	2.16	0.72	19700	330000	16.8

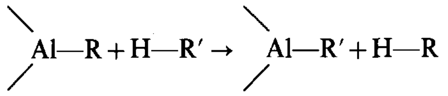
[a] In 2 l n-hexane at 75°C, $p(H_2)=8$ kg cm^{-2}, $p(\text{total})=11$ kg cm^{-2}, 3 mmol TIBA, molar ratio $Al/(Ti+Hf)=17$

[b] By g.p.c. analysis

DISCUSSION

Taking into account that the PCs were added to AlR_3 and the resulting mixture was then reacted with the catalyst, the process can be interpreted by considering that the observed effects are connected with the interaction of the transition metal complex in the active site with the reaction products from AlR_3 and the PC. Even if the reaction products are different, their effects are substantially similar in many regards, even though a few distinctive aspects have been indicated. When the PC is in defect with respect to AlR_3, the obtained results can be explained by assuming that the process is mainly governed by the reaction of the unmodified AlR_3 with Ti and Hf. However, some influence from the interaction of the PC with AlR_3 appears to occur at a PC/AlR_3 ratio lower than 1.

The main reaction of AlR_3 with the PC can be shown as



$$\rangle Al{-}R + H{-}R' \rightarrow \rangle Al{-}R' + H{-}R \qquad (1)$$

where $R' = OH$ (WA), OC_4H_9 (BAL), $OCOC_3H_7$ (BAC) and $OC(CH_3){=}CHCH_3$ (MEK).

In the case of water this reaction can produce some alumoxane structures which are known to play a cocatalytic role in the case of Ti and Hf soluble complexes[5,16]; the possible action towards Hf and Ti supported species is not known. In any case, when the content of water is such that free AlR_3 is no longer present, the catalytic activity tends to disappear. It is worth noting that in all cases the formation of products according to equation (1) is accompanied not only by a reduction of polymer productivity but also by an increase of the molecular weight (*MW*) and a narrowing of the molecular weight distribution (*MWD*) due to the disappearance of the lowest molecular weight fractions (*Figure 7*).

Considering that Hf supported catalysts are less active but give higher molecular weights than Ti catalysts[9], the above effects could be associated with the deactivation of relatively short-lived Ti sites which give low-molecular-weight chains[17,18].

The addition of water also gives rise to a remarkable reduction in the number of terminal unsaturations, thus indicating that the chain-termination process by β-hydride extraction is strongly reduced[18]. The occurrence of such a reaction depends on the type of transition metal to which the chain is attached and is normally favoured for Ti rather than Hf[2,19]. Similar explanations can be valid for butanoic acid, for which the main product of the reaction in equation (1) is the aluminium carboxylate[20]. Clearly the reduction in the number of unsaturated end-groups could be ascribed to the more efficient occurrence of processes such as hydrogenolysis and chain transfer to alkylaluminium, thus giving saturated end-groups. However, the general increase in *MW* strongly supports a significantly reduced probability of β-hydrogen transfer.

The general increase in molecular weight and the narrowing of the *MWD* account for the lower amount of n-heptane extractable low-molecular-weight polyethylenes, thus supporting the hypothesis of the deactivation of species which are more prone to β-chain transfer and which very probably contain Ti in the case of WA and BAC. By contrast, BAL and MEK, which by reaction with AlR_3 give the dialkyl aluminium monoalcoholates[21], appear to be able to reduce to a similar extent all the chain-termination processes, as the molecular weight increases but the percentage unsaturation remains unaffected. In these last two cases the increase in *MW* could be mainly attributed to the lower capacity of the reaction products of AlR_3 with MEK or BAL to give chain-transfer reactions.

FINAL REMARKS

At present, a detailed explanation of the above results and a complete understanding of the related mechanism are not possible. The present work was limited to the modulability of the macroscopic effects exerted by different protic compounds on the polymerization kinetics and on the properties of polyethylene. These effects can be summarized as follows.

1. Addition of protic compounds up to a molar ratio of 1 for PC/AlR_3 to AlR_3 used as a cocatalyst for $MgCl_2$-supported Hf–Ti bimetallic catalysts gives rise to a reduction in catalytic activity and an increase in polyethylene *MW* accompanied by a narrowing of the *MWD*.
2. *FT*i.r. analysis of the polymers indicates that with the more acidic compounds (water and carboxylic acids) the above effects are accompanied by a remarkable reduction in the number of unsaturated end-groups and an attenuation of the β-hydrogen shift termination process.
3. Particularly in the case of water and butanoic acid, the results can be tentatively explained by assuming that these protic compounds, or their reaction products with AlR_3, deactivate the active sites that give low-molecular-weight fractions, probably based

on Ti. On the other hand, Hf sites do not seem to be significantly affected.

4. The experiments described in this work cover the main aspects concerning the possible effects of protic compounds present in the polymer solvent. However, in order to clarify further the mechanisms responsible for the observed behaviour, it would be necessary to investigate the influence of the addition order and the relative concentrations of the various compounds as well as their effects on model catalysts based on either Hf or Ti as the sole transition metal.

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