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Ethylene polymerisation by a high activity $MgCl_2$ supported Ti catalyst in the presence of hydrogen and/or 1-octene

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This paper presents the results of slurry polymerisation of ethylene that has been initiated by an Al/Ti/Mg–alcohol supported catalyst. Special attention has been paid to the effects of hydrogen, catalyst composition and addition of an α-olefin on catalyst efficiency, molecular weight, crystallinity, and physico-mechanical properties of the final polyolefin. The efficiency of this Al/Ti/Mg catalyst, molecular weight and melting temperature of the formed High Density Polyethylene (HDPE) has been found to decrease as the partial pressure of hydrogen is increased. In parallel, crystallinity and elongation at break of HDPE increase. The composition of this Al/Ti/Mg catalyst has a marked effect on catalyst efficiency, e.g. decrease in the Ti relative content results in an improved efficiency from 86 to 7942 kg PE g^{-1} Ti h^{-1} as the Mg/Ti molar ratio is increased from 1 to 333. Copolymerisation with 1-octene has also been investigated. When ethylene polymerisation is carried out with this Al/Ti/Mg catalyst at a Mg/Ti ratio of 333, addition of the α-olefin is responsible for a decrease in the polymerisation rate, which is typical of a negative 'comonomer' effect. This effect is still more pronounced in the presence of H_2. Comparison with other catalytic systems has been made in order to understand the role played by the α-olefin and/or hydrogen on the catalyst efficiency and the physico-mechanical properties of the resulting polyolefins. © 1997 Elsevier Science Ltd.

(Keywords: polyethylene; Ziegler–Natta polymerisation; M_w control)

INTRODUCTION

Although the high activity of $TiCl_4$-based catalysts supported on anhydrous $MgCl_2$ is very well known in olefin polymerisation[1], the basic reasons for this activity are not well understood. In this respect, a patent from Dow has recently reported on Al/Ti/Mg–alcohol catalysts[2], that deserve more detailed investigation. Where catalyst efficiency is concerned, the polymerisation rate is of prime importance in relation to the Ti content. Indeed, efficiency is defined as the amount of PE produced per gram Ti and per time unit, i.e. kg PE g^{-1} Ti h^{-1}. The relative amount of Ti has thus to be optimised, and, as will be explained later, the effect of hydrogen and/or addition of an α-olefin has to be tested on both polyethylene molecular weight and catalyst efficiency. It is worth recalling that the Ziegler–Natta (Z–N) catalysts of the first and second generations ($TiCl_3$–$AlEt_2Cl$) commonly produce polyethylene (PE) with a very broad molecular weight distribution (MWD). The fraction of very high M_w chains is responsible for very difficult melt processing to the point where thermo-mechanical chain scission has been considered to increase melt flowability. Where Z–N catalysts ($MgCl_2$ supported $TiCl_4$ catalysts) of the third and fourth generations are concerned, hydrogen (H_2) is currently mixed with the monomer to control molecular weight ($\bar{M}_w$)[3] in accordance with Keii's[4] equation valid for both polyethylene and polypropylene (equation (1)):

$$(\bar{M}_w)^{-1} = a + b(P_{H_2})^{1/2} \qquad (1)$$

Hydrogen seems, however, to have a contradictory effect on the PP polymerisation rate (R_p). For instance, R_p is observed to decrease upon addition of hydrogen to the $MgCl_2$/EB/$AlCl_3$/$TiCl_4$–$AlEt_3$/EB catalyst (EB = ethylbenzoate)[5] in contrast to what happens with the $MgCl_2$/$TiCl_4$–$AlEt_3$ catalyst[6–9]. In the case of ethylene polymerisation, it is generally accepted that hydrogen decreases the polymerisation rate[5,10,11].

Addition of an α-olefin to the polymerisation medium is also a way to control the polyolefin molecular weight (M_w). This effect, usually reported as the comonomer effect, not only decreases the M_w but also the polymer crystallinity. It also increases the ethylene polymerisation rate, the extent of which depends on the catalytic system, e.g. $TiCl_4 > TiCl_4/MgO > TiCl_4/(Al_2O_3, SiO_2) > TiCl_4/MgCl_2$, and length and/or substitution of the comonomer according to the following order: 1-propylene > 1-pentene > 1-hexene > 1-heptene > 1-octene > 1-nonene > 4-methyl-1-pentene[12,13].

Although explanations have been tentatively proposed to account for these effects, kinetics of the olefin polymerisation still remain complex and not completely understood owing to the complex interplay of chemical and physical processes[12].

The addition of an α-olefin as comonomer affects not only the polymerisation kinetics, but also the polyolefin microstructure and accordingly macroscopic properties,

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such as viscoelasticity, mechanical and thermal behaviour[14]. Linear low density polyethylene (LLDPE) is a typical example of the improved mechanical properties that can be obtained by this strategy[15].

This paper aims at reporting on the effect of catalyst composition, particularly the relative Ti content, and the addition of hydrogen and α-olefin, on the ethylene polymerisation initiated by a Dow Mg-based Ti catalyst[2]. Special attention will be paid to the catalyst efficiency, molecular weight and physico-mechanical properties of the formed high density polyethylene (HDPE). The main purpose of this study will be to increase the catalyst efficiency by changing the relative Ti content of the Al/Ti/Mg catalyst and by using 1-octene as comonomer.

EXPERIMENTAL

Materials

All experiments were performed under nitrogen using standard inert-atmosphere polymerisation conditions. Ethylene (99.5% purity, Air Liquide) and heptane were dried on a column of 4 Å molecular sieves. Nitrogen (N55 99.9999%; 2 ppm H_2O, 0.5 ppm O_2) and hydrogen (N50 99.999%; 3 ppm H_2O, 2 ppm O_2) were purchased from Air Liquide and were used as received. 1-Octene (99%, Aldrich) was dried overnight by stirring over anhydrous CaH_2, distilled under reduced pressure and then stored over dry molecular sieves under N_2 atmosphere. Butyl-octyl magnesium (BOMAG from Witco), or $(n\text{-}C_4H_9)_{1.5}(n\text{-}C_8H_{17})_{0.5}Mg$, was used as a 15 wt% ($0.643\ \mathrm{mol\ l^{-1}}$) solution in heptane. Triethyl aluminium (TEA, Witco) was used as $1.00\ \mathrm{mol\ l^{-1}}$ or $0.10\ \mathrm{mol\ l^{-1}}$ solution in heptane. Ethylaluminium dichloride (EADC, Witco) was used as a $0.916\ \mathrm{mol\ l^{-1}}$ solution in heptane. Tetrabutyl titanate (TBT, Dynamit Nobel Chemkalien), or $(n\text{-}C_4H_9O)_4Ti$, was used as a $0.49\ \mathrm{mol\ l^{-1}}$ or $0.05\ \mathrm{mol\ l^{-1}}$ solution in heptane.

Concentrations of TEA, EADC, TBT and BOMAG solutions were measured by complexometric titration, as follows.

2 ml of the TEA (or EADC) solution in heptane were hydrolysed by HCl ($12\ \mathrm{mol\ l^{-1}}$) and heated until the complete removal of heptane. The Al-containing solution was added with 25 ml of ethylenediaminetetraacetic disodium salt (EDTA, $0.1042\ \mathrm{mol\ l^{-1}}$) and a few drops of Xylenol-Orange at room temperature. The pH was kept constant at 4.8 by addition of sodium acetate. The Al salts were back-titrated by $ZnSO_4$ ($0.1057\ \mathrm{mol\ l^{-1}}$).

2 ml of the TBT solution were added with HCl ($4\ \mathrm{mol\ l^{-1}}$) and heated until the complete removal of heptane. The aqueous solution was then added with 30 ml of EDTA ($0.1042\ \mathrm{mol\ l^{-1}}$), 5 ml of pyridine and ten drops of pyrochatechol violet (0.1%) at room temperature. The final solution was back-titrated with $ZnSO_4$ ($0.1057\ \mathrm{mol\ l^{-1}}$).

2 ml of the BOMAG solution were added with HCl ($2\ \mathrm{mol\ l^{-1}}$) and heated until heptane removal. Magnesium was titred with EDTA ($0.1042\ \mathrm{mol\ l^{-1}}$) at room temperature and at a pH of 10 (via NH_4OH addition), in the presence of Eriochrome Black T.

Catalyst preparation

A patented Al/Ti/Mg catalyst (Dow Chemical[2]) was used in this study and prepared under nitrogen as schematised by equation (2).

$$\mathrm{BOMAG} + 1/2\ \mathrm{TEA} \xrightarrow[n-\mathrm{heptane}]{\mathrm{R.T.}} \mathrm{BOMAG/0.5\ TEA}$$

$$\xrightarrow[n-\mathrm{heptane}]{3.5\ n-\mathrm{PrOH};\ 25^{\circ}C\rightarrow 40^{\circ}C}$$

$$(n-\mathrm{PrO})_2\mathrm{Mg}/(n-\mathrm{PrO})_3\mathrm{Al} \xrightarrow[n-\mathrm{heptane}]{x\ \mathrm{TBT};\ \mathrm{R.T.}} (n-\mathrm{PrO})_2\mathrm{Mg}/$$

$$(n-\mathrm{PrO})_3\mathrm{Al}/x\mathrm{TBT}$$

$$\xrightarrow[n-\mathrm{heptane;\ R.T.;\ 12\ h}]{5\ \mathrm{EADC}} \mathrm{Dow\ Al/Ti/Mg\ catalyst} \tag{2}$$

The pale yellow Al/Ti/Mg catalyst was aged for at least 12 h prior to polymerisation and then appeared as a brown catalyst slurry. The Al/Ti/Mg composition was $55/x/10$ with $x =$ 0.030 (DOW 0.03/10), 0.075 (DOW 0.075/10) and 2.000 (DOW 2.0/10). The Al content was kept unchanged at 55. An additional catalyst of composition 55/2.0/2.0 Al/Ti/Mg was also prepared and is referred to as DOW 2.0/2.

Polymerisation

Ethylene was polymerised in a batch mode, either in a 1.5 l glass Bücchi reactor or a 2 l stainless-steel Autoclave Engineers reactor. Both reactors were equipped with a magnetic coupled stirrer with variable stirring speed and with an external jacket heater that kept the temperature constant at 60°C. The stainless-steel reactor was also equipped with an internal coil in which cold water was flowing at a constant rate.

A pressure regulator was used to keep the ethylene pressure constant (4 bar). The ethylene flow was measured with a Weva thermal mass flowmeter. The dry and oxygen-free reactor was heated at 60°C and loaded with the desired amounts of pure heptane (1 l), 1-octene (3.2×10^{-3} mol) if needed and the required amount of the cocatalyst (TEA) so as to reach a final Al/Ti ratio of 200. The DOW x catalyst (e.g. 2.5 ml DOW 2.0/10, i.e. 1.2×10^{-5} mol Ti) was then added under N_2. The reactor headspace was repeatedly purged with hydrogen and the desired hydrogen pressure was set up. Polymerisation started upon ethylene feeding (equation (3)). Ethylene consumption was measured with the mass flowmeter since ethylene pressure was kept constant.

$$\mathrm{DOW\ X + TEA} \xrightarrow[n-\mathrm{heptane},\ 60^{\circ}\mathrm{C}]{(1)\ \mathrm{H_2}\ (+1-\mathrm{octene})\quad (2)\ \mathrm{C_2H_4}} \mathrm{Polyethylene} \tag{3}$$

At the end of the polymerisation, the reaction mixture was added with a small amount of methanol and cooled down. The polymer was filtered, vacuum dried at 60°C and weighed.

Measurements

As specified in the ASTM test D1238, melt index (*MI*) of polyethylene was measured with a weight of 2.16 kg (MI_2) and 10.00 kg (MI_{10}) at 190°C; the results were expressed in g per 10 min. The MI_{10}/MI_2 ratio was referred to as the melt flow ratio (MFR).

Polymer samples were kneaded on a two roll-mill in the presence of Irganox 1010 (Ciba-Geigi) at 190°C for 5 min. Samples were then compression moulded at 200°C for 3 min into 2-mm-thick plates. Tensile properties were measured at room temperature with an Instrom universal tensile tester (model DY24) in accordance with the ASTM D638 test. The gauge length was 20 mm and the crosshead speed 20 mm min^{-1}. From the stress–strain curves, the following properties (based on the average of five samples) were calculated: initial Young's modulus (E), yield strength (σ_y) and yield elongation (ϵ_y) (at the first maximum), ultimate tensile strength (σ_b) and elongation at break (ϵ_b).

Charpy impact tests were carried out at room temperature with a 4 J hammer in order to break U-notched samples in accordance with the ASTM D 256 B test procedure. The impact energy (I.E.) was the average of five samples of 50 mm length, 6 mm width, 2 mm thickness and 0.35 mm notch depth.

Molecular weight ($\bar{M}_n$, $\bar{M}_w$ and $\bar{M}_v$) and molecular weight distribution (MWD) were measured in 1.2.4-trichlorobenzene with a SEC equipment operating at 140°C and calibrated with polystyrene standards.

The melting endotherms were measured with a Dupont 2000 calorimeter. Melting temperature (T_m) and degree of crystallinity (X_c) were reported from the first heating scan (T_{m_1}, X_{c_1}) and from the second scan recorded after sample quenching in liquid nitrogen (T_{m_2}, X_{c_2}). The heating rate was 25°C min^{-1}. X_c was calculated on the basis of a melting enthalpy of 2.93×10^5 J kg^{-1} for 100% crystallinity PE[16]. T_m was reported as the temperature at the maximum of the melting endotherm.

^{13}C n.m.r. measurements were carried out with a Brucker 400 apparatus at 110°C, by using approximately 50 000 pulses with a 0.4 sec spacing. Samples were dissolved in a perdeuterobenzene–trichlorobenzene 1/5 (v/v) mixture. Deuterobenzene was used as an internal lock.

RESULTS AND DISCUSSION

Effect of hydrogen

Effect of the hydrogen partial pressure on catalyst efficiency (kg PE/g Ti·h) and the polyethylene molecular weight is shown in *Table 1* in the case of the Dow 2.0/10 catalyst used in the Bücchi glass reactor.

It can be seen from *Figure 1* that the catalyst efficiency linearly decreases with increasing H_2 partial pressure in agreement with equation (4):

$$\mathrm{Eff}^{H_2} = \mathrm{Eff}^0 - \alpha P_{H_2} \tag{4}$$

where Eff^{H_2} and Eff^0 refer to the catalyst efficiency at a well-defined H_2 pressure (P_{H_2}) and in the absence of H_2, respectively. Under the experimental conditions reported in *Table 1*, the α coefficient is 9.1 kg PE g^{-1} Ti h^{-1} bar^{-1}. This observation is at least qualitatively in agreement with the observation by U. Giannini *et al.*[5] that hydrogen significantly reduces the efficiency of the $TiCl_4/MgCl_2$/TEA catalyst in ethylene polymerisation, in contrast to what happens for the propylene polymerisation which is faster in the presence of hydrogen.

The decrease in catalyst efficiency may be ascribed to either a change in the oxidation state of the active species or a poisoning of the active sites by hydrogen. J. C. W. Chien *et al.*[17,18] have investigated the effect of H_2 on the oxidation states of Ti by double redox titration of the $MgCl_2$/EB/PC/TEA/$TiCl_4$/TEA/MMB catalyst referred to as the CW catalyst (EB = ethylbenzoate, PC = *p*-cresol, MMB = 4-methyl-methylbenzoate). The oxidation states of Ti atoms

Table 1 Effect of the H_2 partial pressure on catalyst efficiency and the polyethylene molecular weight[a]

Entry	Code	P_{H_2} (bar)	Efficiency (kg PE g^{-1} Ti h^{-1})	$\bar{M}_n$ (10^{-3})	$\bar{M}_v$ (10^{-3})	$\bar{M}_w$ (10^{-3})	MWD
1	A 38	0.0	154	30	235	300	10.2
2	A 33	1.0	145	15	175	215	12.3
3	A 53	1.5	140	45	155	195	4.3
4[b]	A 60	1.5	239	35	155	190	5.4
5	A 16	2.0	136	20	95	120	6.0

[a] Experimental conditions: catalyst is DOW 2.0/10, $P_{C_2H_4} = 4$ bar, $T = 60$°C and polymerisation time (t_p) is 50 min in the Bücchi glass reactor
[b] Further purification of H_2 and C_2H_4 as described in the Experimental section ($t_p = 30$ min)

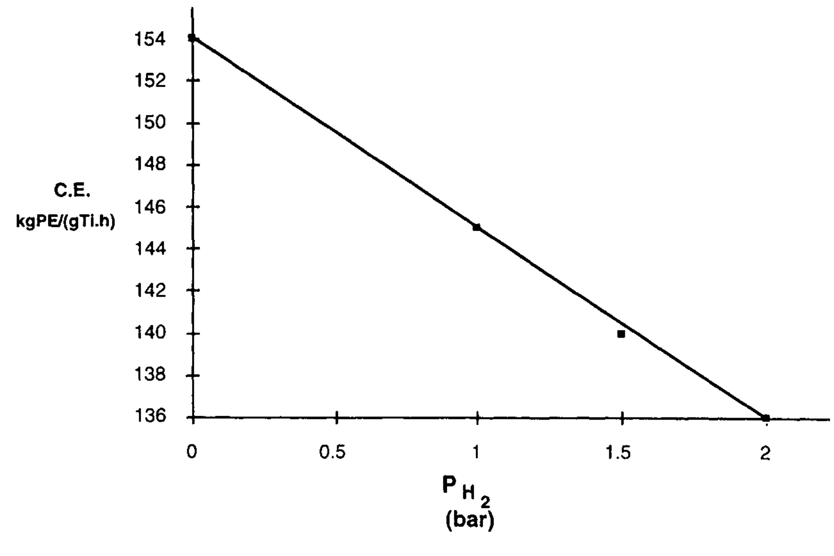


Figure 1 Dependence of the catalyst efficiency on the hydrogen partial pressure (experimental conditions, see *Table 1*)

Table 2 Effect of the H_2 partial pressure on melt index, melting temperature and crystallinity of polyethylene

Entry	P_{H_2} (bar)	MI_2 (g/10 min)	MI_{10} (g/10 min)	MFR	T_{m_1} [b] (°C)	T_{m_2} [c] (°C)	X_{c_1} [b] (%)	X_{c_2} [c] (%)
1	0.0	–[a]	–[a]	–	139	139	32	33
2	1.0	0.06	0.7	10.8	137	137	61	58
3	1.5	0.10	1.7	17.0	136	135	62	62
4	2.0	2.11	20.5	9.8	132	133	73	80

[a] No polymer was flowing under the test conditions
[b] First scan
[c] Second scan after quenching in liquid nitrogen

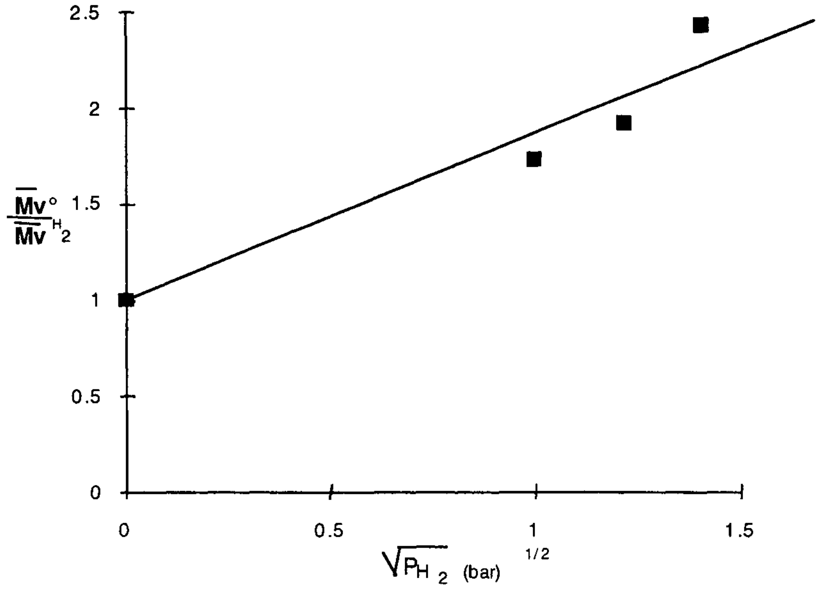


Figure 2 Dependence of the viscosity average molecular weight ($\bar{M}_v$) on the H_2 partial pressure (experimental conditions, see *Table 1*)

in decene polymerisation initiated by the CW catalyst were measured as a function of the polymerisation time (t_p). In the absence of H_2, concentration of each Ti type, $[Ti^{+n}]$ with $n = 2, 3, 4$, was kept constant throughout the polymerisation. In the presence of H_2 and within a 5 min period, $[Ti^{+2}]$ decreased by *ca.* 15% of the total $[Ti^{+n}]$, in favour of $[Ti^{+3}]$ that increased by the same ratio. $[Ti^{+4}]$ was observed to remain unchanged. This oxidative process was held responsible for the rate enhancement of PP polymerisation, in relation to the increased number of Ti^{+3} active sites[19]. According to Soga *et al.*[34,35] Ti^{+3} can polymerise both ethylene and propylene, although Ti^{+2} is only active in ethylene polymerisation. Therefore, in the case of ethylene polymerisation, modification in the oxidation states should not noticeably interfere with the polymerisation rate since both Ti^{+3} and Ti^{+2} are active species. This conclusion, which assumes that Ti^{+3} and Ti^{+2} are of a comparable activity, might be crude since Chien *et al.*[20,21] have confirmed the depressive effect of hydrogen on the catalyst efficiency although at the very beginning of the ethylene polymerisation, R_p is significantly increased by H_2. The qualitative agreement on the effects of hydrogen on the efficiency of the CW-catalyst and the DOW 2.0/10 catalyst suggests some similarity in their oxidative behaviour. In addition to a decrease in catalyst efficiency, hydrogen also has an effect on M_w (*Table 1*), melting temperature and degree of crystallinity of HDPE (*Table 2*).

Figure 2 is in agreement with the equation proposed by G. Guastalla (equation (5))[5], according to which the viscosity average molecular weight decreases with increasing hydrogen pressure.

$$\frac{\overline{M}_v^0}{\overline{M}_v^{H_2}} = 1 + K(P_{H_2})^{\frac{1}{2}} \qquad (5)$$

where $\overline{M}_v^0$ and $\overline{M}_v^{H_2}$ are the experimental viscosity average $\overline{M}_v$ in the absence and in the presence of H_2, respectively, (*Table 1*). K is a constant that depends on the catalyst composition and polymerisation condition. In this case, $K = 0.86\ \text{bar}^{-0.5}$. As a rule, H_2 tends to decrease the average chain length which might be compatible with a chain transfer activity. At very low hydrogen partial pressure, very high molecular weight polyethylene chains are formed and are removed by filtration prior to SEC analysis. This leads to an asymmetrical elution peak and the molecular weight parameters so measured are inaccurate and result in a larger molecular weight distribution (*ca.* 10, entries 1 and 2 of *Table 1*). At higher hydrogen partial pressure, a symmetrical elution peak is observed and smaller (narrower) molecular weight distribution is obtained, *ca.* 5 (entries 3–5 in *Table 1*).

The polymer melt flow index, particularly the MI_2 melt index, was also measured as the signature of the HDPE molecular weight and its effect on rheology. Although the melt index is an empirical measurement, it has been inversely related to $\bar{M}_n$ of the polymer[22,23] (equation (6)):

$$\bar{M}_n = k\,(MI_2)^{-0.28} \qquad (6)$$

The few data in *Tables 1 and 2* do not confirm this relationship, although there is an expected increase in MI_2 (from 0 to 2.1) and in MI_{10} (from 0 to 20.5) as $\bar{M}_v$ decreases (from 235 000 to 95 000). The melt flow index ratio (MFR) is a measure of the relative change in viscosity with shear stress, that increases with both $\bar{M}_w$ and MWD[24]. Indeed, MI_2 increases with the H_2. The MFR values show a parallel modification compared with the MWD as shown from entries 2 and 5 in *Tables 1 and 2*. The melting range and degree of crystallinity of polyethylene prepared from the DOW 2.0/10 catalyst are also dependent on the H_2 partial pressure, as reported in *Table 2*.

The degree of crystallinity (X_c) increases linearly with increasing H_2 pressure (X_{c_2} from 33 to 80%, *Figure 3*), in contrast to the melting temperature, which decreases (*Figure 4*). These variations fit the following equations:

$$X_c^{H_2} = X_c^0 + \beta P_{H_2} \tag{7}$$

$$T_m^{H_2} = T_m^0 + \gamma P_{H_2} \tag{8}$$

where $X_c^{H_2}$ and $T_m^{H_2}$ are the degree of crystallinity and the melting temperature (as measured during the second scan), respectively, at a given H_2 pressure. X_c^0 and T_m^0 are the values measured in the absence of H_2. Under the experimental conditions in this study, β and γ are 22.34 bar^{-1} and 2.97°C bar^{-1}, respectively.

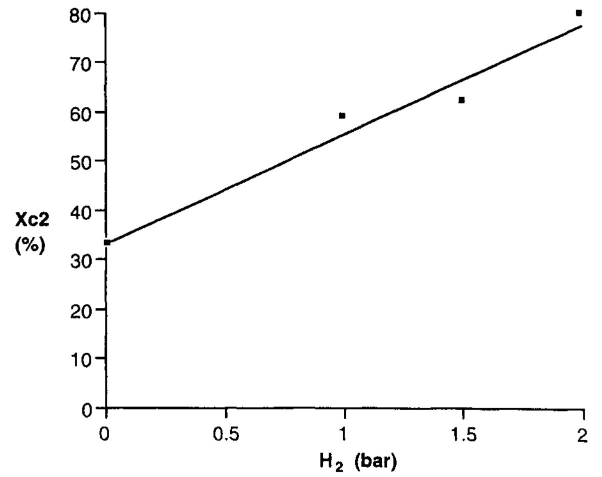


Figure 3 Dependence of the degree of crystallinity on the hydrogen partial pressure (X_c measured during the second heating scan; *Table 2*)

Under the same crystallisation conditions[25–27] it appears that the crystallinity degree decreases for a M_w higher than *ca.* 10^5 due to the formation of irregular polyethylene spherulites (entry 1, *Table 2*)[28]. In parallel, the melt temperature decreases with the reduction in molecular weight, i.e. increasing number of chain ends which act as crystallisation impurities.

In addition to the effect on polymerisation kinetics and polymer molecular weight, hydrogen pressure also influences the mechanical properties of the final polyolefin. Tensile measurements show that elongation at break (ϵ_b) directly depends on $\bar{M}_w$ and is thus inversely proportional to the H_2 pressure (from 233% at $P_{H_2} = 1$ bar down to 80–90% at $P_{H_2} = 2$ bar), while strength at the yield point (σ_y) and impact energy (I.E.) remain essentially unaffected (*Table 3*). The unexpectedly low values of elongation and impact strength of the A38 sample (entry 1, *Table 3*) might be accounted for by a processing problem due to an exceedingly high melt flow viscosity (*Table 1*). Indeed, this polymer (A38) does not flow so has to be processed at a higher temperature (220°C) at which the PE chains start to be degraded.

The hydrogen effect may be summarised as follows. The molecular weight of PE is controlled by hydrogen which apparently behaves as a convenient transfer agent. An increase in the hydrogen partial pressure leads to a decrease of catalyst efficiency, M_w, T_m, ϵ_b and to an increase of X_c, MI_2 and MI_{10}, while σ_y and I.E. remain unchanged.

Gas purity and catalyst composition

To improve catalyst efficiency (kg PE g^{-1} Ti h^{-1}), the amount of Ti in the catalyst has been tentatively reduced, whereas traces of moisture able to poison the catalyst have been further eliminated by the additional purification of the reagents. Indeed, up to now, ethylene and hydrogen have been used as received, which might be harmful to the high activity of the Al/Ti/Mg catalysts. Purification of ethylene by passing through a column of molecular sieves has triggered a sizeable improvement in catalyst efficiency from

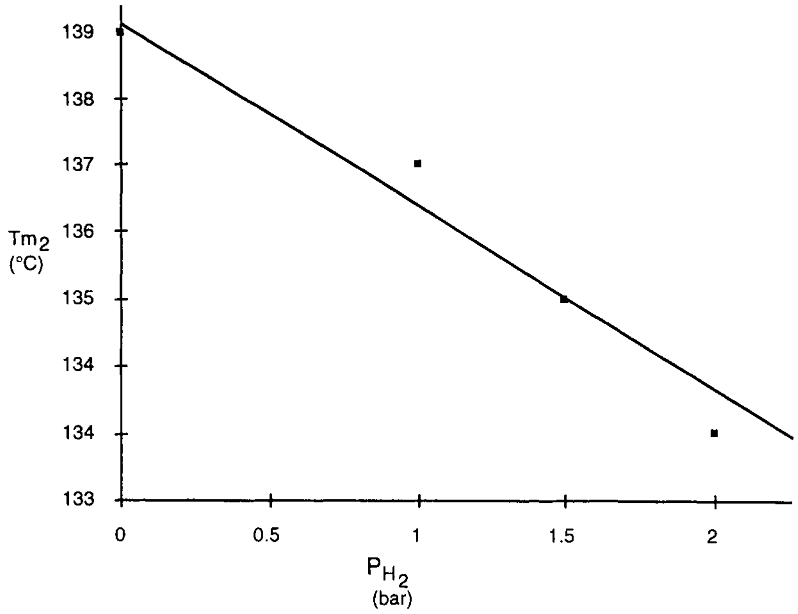


Figure 4 Dependence of the melting temperature on the hydrogen partial pressure (T_m measured during the second heating scan; *Table 2*)

Table 3 Effect of H_2 partial pressure on tensile and impact properties of polyethylene

Entry	Code[a]	P_{H_2} (bar)	σ_y (MPa)	σ_b (MPa)	ϵ_b (%)	I.E. (kJ m^{-2})
1	A 38[b]	0.0	24	12	38	48
2	A 33	1.0	25	25	233	62
3	A 60	1.5	25	12	84	19[c]
4	A 16	2.0	25	12	98	60

[a] See *Table 1*

[b] Specimen moulded at 220°C and partly degraded

[c] Underestimated value since the sample did not completely break under the test conditions

Table 4 Effect of catalyst composition on catalyst efficiency (at various polymerisation times, t_p), melting temperature and crystallinity of polyethylene. Polymerisation conditions: $P_{H_2} = 1.5$ bar, total $t_p = 30$ min for Dow 2.0/10 and Dow 2.0/2, $t_p = 90$ min for Dow 0.075/10, and $t_p = 350$ min for Dow 0.03/10

	Catalyst			
	DOW 2.0/2.0	DOW 2.0/10	DOW 0.075/10	DOW 0.03/10
	B 108[a]	A 60	B 25	B 27
	55/2.0/2.0[b]	55/2.0/10	55/0.075/10	55/0.03/10
	1[c]	5	133	333
Efficiency (kg PE g^{-1} Ti h^{-1})				
$t_p = 30$ min	87	239	3223	7942
$t_p = 50$ min	–	–	2563	6243
$t_p = 90$ min	–	–	1919	4655
$t_p = 350$ min	–	–	–	2579
D.s.c.[d]				
T_{m_1} (°C)	137	136	139	137
T_{m_2} (°C)	136	136	135	132
X_{c_1} (%)	51	62	67	60
X_{c_2} (%)	47	64	65	50

[a] Code

[b] Al/Ti/Mg ratio

[c] Mg/Ti ratio

[d] Determined at highest t_p value

140 to 239 kg PE g^{-1} Ti h^{-1} under the same H_2 partial pressure (*Table 1*, entry 3 *vs.* entry 4). In parallel to this enhanced catalyst efficiency, no significant modification in molecular weight has been observed (entries 3 and 4 from *Table 1*).

Under these conditions of improved gas purity, ethylene has been polymerised using two new Al/Ti/Mg catalysts of lower Ti content, i.e. $x = 0.075$ and 0.03 (see Experimental section). Knowing that only a few percentage of the Ti atoms taking part of the catalyst composition are effectively active sites, a reduction in the amount of Ti might not lead to a drastic reduction of the number of active sites. Consequently, an increase in catalyst efficiency is expected as it is expressed as the ratio between the amount of PE produced per hour and the grams of Ti considered in the catalyst composition.

For the sake of comparison, the efficiency of the different catalysts (DOW 2.0/10, DOW 0.075/10 and DOW 0.03/10, *Table 4*) have been estimated at different polymerisation times (t_p). It is clear that, in the presence of H_2, the DOW 0.03/10 catalyst is the most active one with an efficiency of *ca.* 8 t PE g^{-1} Ti for the first 30 min of reaction. This efficiency remains remarkably high even for extremely long polymerisation time, e.g. 2600 kg PE g^{-1} Ti h^{-1} after 6 h.

Catalyst efficiency has also been observed to depend on the magnesium content. A reduction in magnesium content by a factor of 5 (Al/Ti/Mg: 55/2.0/2.0 *vs.* 55/2.0/10, *Table 4*) results in a decrease in catalyst efficiency by a factor of 3. This confirms the beneficial effect of the constitutive magnesium components on the number of active sites.

Although the thermal characteristics (T_m and X_c) of the PE chains remain essentially unaffected (*Table 4*), decrease in the Ti content slightly improves the tensile properties of the final polymer, as shown in *Table 5*. The tensile curves show an increase in modulus at the end of the tensile test, which is the signature of crystallisation under extension ($\sigma_b > \sigma_y$). Measurement of the Charpy impact strength has currently been a problem since the samples bend rather than break.

Ethylene/1-octene copolymerisation

Since the DOW catalyst has proved to be active in olefin copolymerisation[2], copolymerisation of ethylene with an α-olefin has been investigated by using the catalyst of the highest efficiency (DOW 0.03/10). 1-Octene is a very attractive comonomer, that may lead to linear low density polyethylene (LLDPE) known for its good mechanical properties[15]. Clearly, the addition of 1-octene decreases the efficiency of the DOW 0.03/10 catalyst, leading to a negative comonomer effect (*Table 6*, entry 2 *vs. Table 4*). This effect is, however, less important in the absence of H_2 (*Table 6*, entry 1). Nevertheless, the polyethylene accordingly formed is prohibitively viscous at 190°C under a high load since $MI_{21} = 0$.

The scientific literature usually reports on a positive 'comonomer effect', although a negative effect has been mentioned very recently[29,30], for instance in case of the ethylene polymerisation initiated by the soluble Cp_2ZrCl_2/MAO catalyst in the presence of hexene. Chien *et al.*[30] have reported that all Zr atoms are efficient in initiating ethylene

Table 5 Effect of catalyst composition on tensile and impact properties

Entry	Catalyst Dow	E (MPa)	σ_y (MPa)	ϵ_y (%)	σ_b (MPa)	ϵ_b (%)	I.E. (kJ m^{-2})
1	2.0/10	–[a]	25	8.4	25	233	62.1
2	0.075/10	890	24	9.2	27	346	–[b]
3	0.03/10	810	23	10.0	31	318	–[b]

[a] Could not be measured

[b] The sample did not break under test conditions

Table 6 Effect of 1-octene and H_2 on catalyst activity. Polymerisation conditions: 1-octene = 3.2×10^{-3} mol, $P_{C_2H_4} = 4$ bar, $T = 60°C$, high purity gases

Entry	Catalyst Dow	Code	P_{H_2} (bar)	Efficiency (kg PE g^{-1} Ti h^{-1})	t_p (min)
1	0.03/10	B 53	0.0	744	35
2	0.03/10	B 54	1.5	313	65
3	2.0/2	B 112	0.0	82	34

Table 7 Hypothesis for the comonomer effect on the enhancement of the ethylene polymerisation rate

	Hypothesis	Ref.
1	Physical disintegration of catalyst matrix particles	30
2	Diffusion of ethylene and/or increased aluminium alkyl by encapsulation of active centres with low crystallinity PE	12,33–35
3	Displacement of adsorbed or complexed molecules	36
4	Activation of dormant or potential centres by comonomer	14,33,37
5	Formation of new active centres by reactions involving α-olefin molecules	12,32,36,38,39
6	'Triggering' effect increase of propagation rate constant	34,38
7	Change of the distribution of transition metal oxidation states	30,35,40
8	Alteration of association state of transition metal	30

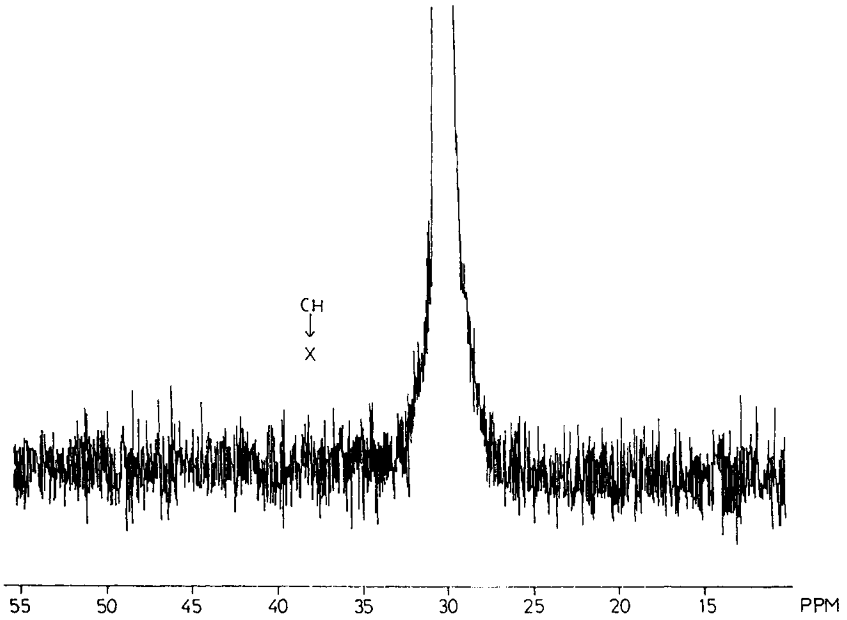


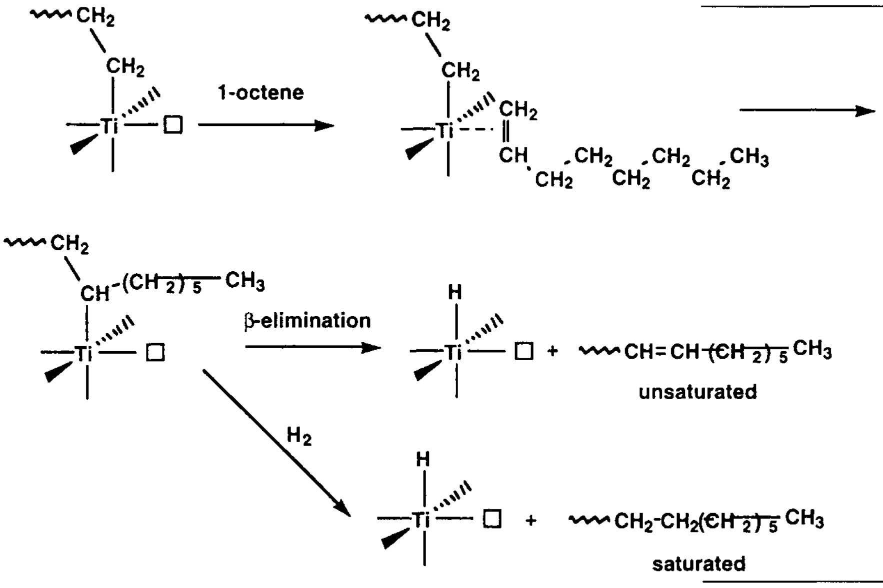
Figure 5 ^{13}C n.m.r. spectrum of the B112 sample polymerised in the presence of 3.2×10^{-3} mol of 1-octene (Al/Ti/Mg = 55/2.02.0)

polymerisation, thus preventing the formation of additional active sites, consequently, proposals (4), (5) and (7) listed in *Table 7* can be eliminated. Furthermore, since the metallocene complexes are soluble and form individual molecular species, proposals (1), (2) and (8) can also be rejected. There is no reason why ethylene and α-olefin would be chemically different from each other to the point where proposals (3) and (6) are feasible. The experimentally observed negative 'comonomer' effect has been ascribed to competition between hexene and ethylene for a p-complex formation with metallocene.

In case of the modified $Et(Ind)_2ZrCl_2$/MAO catalyst, a similar behaviour is reported for a low hexene content (0.13 molar fraction), whereas at a high hexene content (0.83 molar fraction), the catalyst efficiency is increased, more slightly due to the very fast hexene homopolymerisation[30]. J. V. Seppala *et al.*[31] have confirmed the negative 'comonomer' effect at a temperature (95°C) where the polymer formed by Cp_2ZrCl_2 catalyst is soluble in the reaction mixture. In contrast, at a lower temperature (50°C), such that the polymer is insoluble, the ethylene polymerisation is activated by a factor of 2.5 upon the comonomer addition. This effect has been attributed to the easier monomer diffusion through the insoluble copolymer of a low crystallinity (proposal 2 in *Table 7*). In agreement with this proposal, the observed activation is smaller when the comonomer is added some time after the ethylene polymerisation has been initiated. Seppala *et al.*[32] have suggested that the comonomer could be bound to the metallocene active centre in such a way that the activation energy for the monomer insertion is decreased, making propagation and chain transfer reactions easier (proposal 6 in *Table 7*).

A very recent study[29] dealing with the ethylene polymerisation initiated by the supported $MgCl_2$/THF/$TiCl_4$ catalyst, has concluded that 1-octene increases or decreases R_p depending on the Mg/Ti ratio in the catalyst composition. Indeed, a positive comonomer effect has been observed at low Mg/Ti ratios which switches over a negative effect at Mg/Ti ratios higher than 2.5.

When the copolymerisation is initiated by the Al/Ti/Mg Dow catalyst, the negative comonomer effect is still observed even at Mg/Ti ratios lower than 2.5 (DOW 2.0/2, *Table 6*, entry 3). The drop in the catalyst efficiency which is promoted by the comonomer might be accounted for by either a competitive coordination of ethylene and the α-olefin onto the active centre or to the potential of the comonomer to act as a transfer agent as shown in equation (9):



(9)

The latter assumption is mainly supported by ^{13}C n.m.r. spectroscopy which shows no signal at 38 ppm, characteristic of branched methine[41–43] (*Figure 5*). A transfer activity should induce a reduction of the molecular weight of the polyethylene produced in the presence of 1-octene. Nevertheless, the M_w measurement could not be achieved by SEC due to the presence of ultra high molecular polyethylene. Furthermore, no comonomer insertion nor the presence of unsaturations resulting from the β-elimination of the growing chain (equation (9)) was supported by the thin film infra-red analysis. Thus, no ethylene/1-octene copolymerisation occurs when Dow catalysts of an Al/Ti/Mg composition of 55/2/2 and 55/0.03/10 are used and the observed negative comonomer effect is rather attributed to the formation of inactive site resulting from the irreversible complexation of the 1-octene to the active site. This observation is in sharp contrast to the claims in the Dow patent[2] that copolymerisation is possible for a catalyst composition of 120/1/10. The Al/Ti/Mg composition and particularly the Ti/Mg ratio is of the utmost importance for the catalyst ability to copolymerise ethylene with an α-olefin. This key parameter deserves special attention in the future in order to clear up the copolymerisation mechanism.

CONCLUSIONS

The activity of the Dow Al/Ti/Mg catalysts towards the ethylene polymerisation has been investigated. It appears that hydrogen is efficient in decreasing the PE molecular weight control in agreement with Keii's law. The decrease in molecular weight—proportional to $P_{H_2}^{0.5}$—parallels a linear reduction in both catalyst efficiency and the polymer melting temperature and to an increase in crystallinity, melt indices (MI_2 and MI_{10}) and elongation at break of PE. The catalyst efficiency is strongly enhanced (from 239 to 7950 kg PE g^{-1} Ti h^{-1}) by a decrease in the transition metal content of the catalyst (Al/Ti/Mg from 55/2/10 to 55/0.03/10). The main physico-mechanical properties of PE are largely independent of the catalyst composition. Copolymerisation of ethylene with 1-octene has been investigated using the Dow catalyst of the highest efficiency (DOW 0.03 Al/Ti/Mg: 55/0.03/10) and with a catalyst of Mg/Ti ratio smaller than 2.5 (DOW 2.0/2.0, Al/Ti/Mg: 55/2.0/2.0). This composition was known for a positive 'comonomer effect' in the case of a catalyst of the general $MgCl_2$/THF/$TiCl_4$ composition[29]. A negative 'comonomer effect' has been observed for the two catalysts under investigation. This drop in the catalyst efficiency has been tentatively explained by a competition of ethylene and 1-octene for coordination onto the catalyst active centres to the role of transfer agent of the comonomer.

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