APPLIED ORGANOMETALLIC CHEMISTRY, VOL. 6, 493–500 (1992)

Ethylalumoxanes and ethylchloroalumoxanes as components of catalyst for propylene polymerization

S Pasynkiewicz and B Mańk
Warsaw Technical University (Politechnika), Faulty of Chemistry, 00-661 Warszawa, Koszykowa 75, Poland

Ethylalumoxanes and ethylchloroalumoxanes as components of Ziegler–Natta catalysts for polymerization of propylene have been studied. The influence of the degree of hydrolysis of triethyl aluminium (Et_3Al) and diethylaluminium chlorilp ($Et_2AlCl)_2$] in the range 0.5–1.5:1 on the activity and the stereospecificity of the catalytic systems was determined (the degree of hydrolysis is defined as the molar ratio H_2O/organoaluminium compound). It was found that the activity of the catalytic system ethylalumoxane–$TiCl_4$ is a little higher than the activity of the Et_2AlCl–$TiCl_4$ system. The ethylchloroalumoxane–$TiCl_4$ system is about six times more active than the classical Ziegler–Natta system. Our studies showed that alumoxanes react with $TiCl_4$ as follows: (a) to form compounds of the Al—O—$TiCl_3$ type; (b) to exchange alkyl groups for chlorine; (c) to form donor–acceptor complexes. Reactions of types (b) and (c) occur mainly in the cases of alumoxanes of low degree of hydrolysis (0.5–0.7). In cases of alumoxanes of a degree of hydrolysis equal to 0.7–1.0, reactions of all three types occur, and for alumoxanes of degree of hydrolysis > 1.0 reactions of types (a) and (c) are preferred.

Keywords: Titanium, aluminium, polymerization, propylene

INTRODUCTION

Alumoxanes, compounds possessing oxygen bridges linking two aluminium atoms, Al—O—Al, are formed by hydrolysis of simple organoaluminium compounds. They are used as components of homogeneous and heterogeneous catalysts for olefin polymerization. Heterogeneous catalysts based on alumoxanes were mainly used for polymerization of ethylene. Catalytic systems of $(Et_2Al)_2O$, $(EtClAl)_2O$ $(i\text{-}Bu_2Al)_2O$, chloroalumoxane with titanium chlorides[1-4] and $(R_2Al_2)O$ with $VOCl_3$[5,6] have been studied. These catalysts are more active than classical Ziegler–Natta systems. There are only patent reports on polymerization of propylene on catalytic systems containing alumoxanes. Catalysts with activity of about 46 kg product per mol titanium per hour were prepared using an excess of $(Et_2Al)_2O$. Polypropylene obtained on these catalysts had an isotacticity index (II) of about 70%.[7-12]

Kaminsky[13] obtained highly active homogeneous systems for polymerization of ethylene using methylalumoxanes (MAO) and Cp_2MCl_2 ($M = Ti$, Zr). In the cases of polyproplyene and higher olefins (because of stereospecificity requirements), catalytic systems where the transition metal compound has bulky substituents or/and a chiral centre[14-19] were used. Polypropylene of isotacticity over 99% was obtained with an MAO/racemic system of a stereoisomer of ethylenebis(indenyl)zirconium dichloride or ethylenebis(tetrahydroindenyl)zirconium dichloride,[20] but with an MAO/tetrabenzylzirconium system, polypropylene of isotacticity about 60 % was formed. A change of methylalumoxane for ethyl alumoxane or isobutylalumoxane causes a drastic decrease of yield and stereospecifity.[21-23]

The purpose of our work was to study alumoxanes obtained from ethyl- and chloroethylaluminium compounds as components of catalysts for propylene polymerization. Determination of the influence of degree of hydrolysis of the alumoxane and of molar ratio alumoxane /titanium tetrachloride on yield and tacticity of the polypropylene product were the main tasks of this work.

EXPERIMENTAL

All reactions were carried out in an atmosphere of dried and deoxygenated nitrogen.

0268-2605/92/060493-08 $09.00

Received 5 July 1991
Accepted 15 February 1992

Table 1 Elemental analysis of ethylchloroalumoxanes and ethylchloroalumoxanes

No. Alumoxane	Degree of hydrolysis[a]	Analysis (wt %) Al	C	H	Cl	Al/Cl (mol/mol)
1. Ethylalumoxane	0.5	29.0	51.6	10.6	—	
	0.6	30.4	48.5	10.0	—	
	0.7	31.6	45.7	9.6	—	
	0.8	33.1	42.4	8.9	—	
	0.9	34.6	39.0	7.9	—	
	1.0	35.7	35.5	7.5	—	
	1.25	38.9	26.5	5.7	—	
	1.50	43.6	14.4	3.3	—	
2. Ethylchloroalumoxane	0.5	27.1	24.1	5.3	35.7	0.998
	0.6	28.3	20.2	4.2	37.2	1.000
	0.75	30.2	13.9	2.9	39.7	1.000
	0.85	31.5	9.3	2.1	41.4	1.000
	1.00	30.9	8.1	2.0	40.6	1.001
	1.25	28.7	10.3	3.4	37.7	1.001
	1.50	26.7	10.2	3.5	35.2	0.997

[a] Water/organoaluminium compound, molar ratio.

IR spectra of alumoxanes and the products of their reactions with $TiCl_4$ were recorded in Nujol on a Specord M80 spectrometer.

Hexane, toluene and THF were deoxygenated and dried with a sodium–benzophenone complex.

Synthesis of alumoxanes

Hydrolysis reactions of Et_3Al and Et_2AlCl were carried out at the molar ratios given in Table 1.

For the molar ratio $Et_3Al/H_2O = 1:1$ the reaction was carried out in a 500-cm^3 three-necked flask equipped with a magnetic stirrer and dry-ice cooling bath. Vapour of a water–toluene azeotrope [100 cm^3 of toluene containing 1.962 g (0.109 mol) of water] were introduced slowly (within 2 h) to a vigorously stirred solution, cooled to −78 °C, of Et_3Al (15 cm^3; 0.109 mol) in 150 cm^3 toluene. The reaction mixture was warmed to room temperature and stirred for 24 h. Then it was refluxed for 6 h. The solvent was distilled off under reduced pressure and the powder obtained was dried at 100 °C under oil-pump vacuum.

Hydrolyses of Et_3Al and Et_2AlCl in other molar ratios (H_2O/organoaluminium compound) were carried out as above.

Full stoichiometric characterization of the alumoxanes obtained was not attempted for these polymerization reactions.

Reactions of alumoxanes with $TiCl_4$

Reactions of alumoxanes with $TiCl_4$ were carried out at various molar ratios alumoxane/$TiCl_4$ using an excess of $TiCl_4$ over alumoxane as well as, alternatively, an excess of alumoxane over $TiCl_4$.

Reaction with excess of $TiCl_4$

Alumoxane prepared at the molar ratio $H_2O/Et_3Al = 0.5:1$ (1 g containing 0.012 mol Al) and hexane (10 cm^3) were placed in a 100-cm^3 Schlenk tube and cooled to −78°C. A solution of $TiCl_4$ (11.384 g; 0.060 mol) in hexane (50 cm^3) was then added dropwise to this vigorously stirred solution during 0.5 h. The reaction mixture was stirred for 1 h at room temperature and then refluxed for further 2 h. The brown powder obtained was isolated by filtration and the remaining $TiCl_4$ was carefully washed out with hexane. The solid was dried at 60 °C for 12 h at oil-pump vacuum.

Reaction of $TiCl_4$ with alumoxanes prepared at other H_2O/Et_3Al molar ratios was carried out as above, changing the amounts of added $TiCl_4$ to obtained a fivefold excess of $TiCl_4$ over the calculated amount of aluminium in alumoxane.

In the case of ethylchloroalumoxanes, the reactions were carried out in two stages. In the first stage the reactions were carried out as described for ethylalumoxanes using a twofold excess of

$TiCl_4$ over aluminium contents in the products of Et_2AlCl hydrolysis. In the second stage the powder obtained was added to freshly distilled $TiCl_4$ and heated at the boiling point of $TiCl_4$ until a change of colour to violet. The solid was then isolated by filtration and the excess of $TiCl_4$ was carefully washed out. The powder obtained was dried at 100 °C for 12 h under oil-pump vacuum.

Investigations of the reaction products of ethylalumoxane and ethylchloroalumoxanes with an excess of $TiCl_4$

The product formed in the reduction of alumoxane (degree of hydrolysis =0.5–1.0) and excess of $TiCl_4$ (1 g) and THF (10 cm^3) was refluxed in a 50-cm^3 Schlenk tube for 20 min and then filtered at 60 °C. $TiCl_3$. 3THF crystallizes from the filtrate at 0 °C.

Product data were as follows IR (CH_2Cl_2): 1038, 986, 862, 368 cm^{-1}. Analysis: found, Ti 12.89, Cl 28.72; C 38.91; H 6.49; calcd for $C_{12}H_{24}Cl_3O_3Ti$: Ti 12.93; Cl 28.75; C 38.88; H 6.48 %. The product was obtained in the solid state, as described previously above.

Reactions with an excess of alumoxane

Into a vigorously stirred suspension of ethylchloroalumoxane (0.1 g containing 1.1 mmol aluminium—degree of hydrolysis = 1) in hexane (1 cm^3) a solution of $TiCl_4$ in hexane (0.23 cm^3 containing 0.011 mmol $TiCl_4$) was added dropwise within 5 min. The reaction mixture was then stirred at room temperature for 24 h. The product was used for catalyst synthesis without isolation.

In case of other alumoxanes the procedure was as described above, changing the amount of $TiCl_4$ to obtain aluminium/$TiCl_4$ ratios of 10, 20, 50, 100 and 200:1.

Catalyst synthesis

Catalysts were synthesized in the same reactor in which propylene polymerization was carried out. This was a 200-cm^3 steel reactor equipped with a magnetic stirrer. Hexane (40 cm^3) and a 1.0 mol dm^{-3} solution of Et_3Al in hexane (the volume being calculated to obtain the Et_3Al/titanium ratios given in Table 2) were placed in the reactor and the product of the reaction of alumoxane with $TiCl_4$ was added (the amount being calculated to produce a titanium content 0.01–1.0 mmol). The mixture was stirred at room temperature for 20 min and used for polymerization without isolation.

Polymerization

Propylene was introduced at 7 atm to the reactor described above containing the prepared catalyst. Polymerization was carried out for 1 h at room temperature under a pressure of propylene of 7 atm. Polymerization was then stopped by addition of a solution of conc. hydrochloric acid in methanol (1:50, v/v). The solvent was filtered off and the polypropylene product was dried at 60 °C until constant weight was achieved. The Isotacticity Index was determined by Soxhlet extraction with heptane.

RESULTS AND DISCUSSION

Ethylalumoxanes or ethylchloroalumoxanes are formed in reactions of water with Et_3Al or Et_2AlCl respectively. Formation of a trimer of tetraethylalumoxane $[(Et_4Al_2O)_3]$ in the reaction of water with Et_3Al at a molar ratio 1:2 was postulated previously.[24–28] Increasing the molar ratio to 1:1 led to the formation of $(EtAlO)_n$ (Eqn[1]):

$$n(Et_3Al)_2 \xrightarrow{nH_2O} n(Et_2Al)_2O$$

$$+2nEtH \xrightarrow{nH_2O} 2(EtAlO)_n + nEtH \quad [1]$$

Formation of a pentamer of ethylchloroalumoxane was postulated in the reaction of water

Table 2 Influence of molar ratio Et_3Al/titanium on activity of catalysts prepared from ethylchloroalumoxane of degree of hydrolysis 1.0

No.	Catalyst[a]	Et_3Al/Ti (mol/mol)	Yield (kg product per mol Ti per h)	II (wt %)
1	I	10	47.9	91.2
		90	578.5	90.5
		100	60.0	89.7
		200	61.2	79.3
2	II	1	152.1	50.2
		10	174.3	49.3
		30	206.0	48.5
		50	208.9	42.4
		100	213.6	38.7

[a] I, Catalysts obtained with an excess of $TiCl_4$ over aluminium; II, catalysts obtained with an excess of ethylchloroalumoxane over $TiCl_4$ (molar ratio aluminium/$TiCl_4$ = 100:1).

with Et_2AlCl at a molar ratio of 1:2 and $(EtClAl)_2O.H_2O$ was formed at a molar ratio of 1:1.[29] Further increase in the degree of hydrolysis led to the formation of $Al(OH)_2Cl$ (Eqn [2]).

$$(Et_2ClAl)_2 \xrightarrow{H_2O} (EtClAl)_2O + 2EtH \xrightarrow{2H_2O} (EtClAl)_2O.H_2O \xrightarrow{2H_2O} 2Al(OH)_2Cl + 2EtH \quad [2]$$

Ethylalumoxanes and ethylchloroalumoxanes obtained at molar ratios (H_2O/organoaluminium compounds) in the range 0.50–0.60 were liquids and those obtained at molar ratios of 0.70–1.50 were amorphous powders. A broad band at 760–790 cm^{-1}, assigned to stretching vibrations of Al—O—Al,[24–28] were observed in the IR spectra of the liquid products. In alumoxanes of degree of hyrolysis 0.70 and higher, a broad band at 3100–3550 cm^{-1}, characteristic for associated hydroxyl groups, was observed additionally. Ethylochloroalumoxanes showed also a strong absorption at 430–470 cm^{-1} probably due to vibrations of Al—Cl bridges.

Results of elemental analysis (Table 1) of alumoxanes of degree of hydrolysis 0.50 and 0.60 correspond to hypothetical compositions $[(Et_{2x}Cl_xAl)_2O]_n$ and $(Et_{1.8-x}Cl_xAlO_{0.6})_n$ where $x = 0$ or 1. IR spectra and results of elemental analysis show in alumoxanes of degree of hydrolysis 0.5 and 0.6 the presence of Al—Et and Al—O—Al fragments (in ethylchloroalumoxanes, Al—Cl also) and in alumoxanes of higher degree of hydrolysis the presence of Al—OH fragments as well. The presence of ethyl groups was observed even in the product of hydrolysis of Et_2AlCl at molar ratio water/Et_2AlCl = 1.5:1. This could be caused by an extended structure of alumoxane association resulting from the inaccessibility of some ethyl and hydroxyl groups.

As shown in Table 1 the molar ratio Al/Cl does not depend on the degree of hydrolysis (Al/Cl = 1:1). This indicates that the Al—Cl bond in $(Et_2AlCl)_2$ does not hydrolyse at the molar ratios studied. This phenomenon was also observed by Bolesiawski.[30]

The alumoxanes obtained gave in the reactions with $TiCl_4$, products used as components of catalysts for propylene polymerization. The main parameters influencing catalytic activity of these products obtained from alumoxanes and $TiCl_4$ are the degree of hydrolysis of alumoxane and the molar ratio, aluminium/$TiCl_4$. Reactions of alumoxanes with $TiCl_4$ were carried out for various values of this molar ratio, calculated from the percentage of aluminium in alumoxane (Table 1):

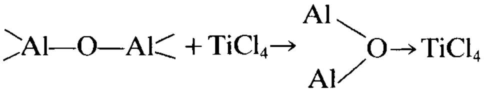
(1) at an excess of $TiCl_4$ over aluminium;
(2) at an excess of aluminium over $TiCl_4$.

Reactions of alumoxane with $TiCl_4$

The presence of Al—OH, Al—Et and Al—O—Al bonds causes the possibility of occurrence of various reactions between $TiCl_4$ and alumoxane (Eqns [3]–[5]).

$$>Al—OH + TiCl_4 \rightarrow >Al—O—TiCl_3 + HCl \quad [3]$$

$$>Al—Et + TiCl_4 \xrightarrow{red.} >Al—Cl + TiCl_3 \xrightarrow{THF} TiCl_3.3HF + alumoxane \quad [4]$$



$$>Al—O—Al< + TiCl_4 \rightarrow \begin{matrix} Al \\ Al \end{matrix}> O \rightarrow TiCl_4 \quad [5]$$

Strong broad bands at 750–780 and 722 cm^{-1}, assigned to Al—O—Al and Al—O—Ti vibrations, were observed in IR spectra of the reaction products of $TiCl_4$ and alumoxanes of degree of hydrolysis 0.5–1. No absorption was observed in the region characteristic for hydroxyl groups. Strong absorptions, probably due to Al–Cl and Ti–Cl vibrations, were observed at 368, 380, 406 and 440 cm^{-1}. The absence of absorptions in the hydroxyl group region and the appearance of additional bands in the region characteristic for M—O—M vibrations[31–36] confirm that the reaction occurred according to the Eqn [3].

An absorption at 3150–3500 cm^{-1} was observed in the products of reactions of $TiCl_4$ with alumoxanes of degree of hydrolysis higher than one. This is probably caused by the presence of hydroxyl groups inaccessible to an attack of $TiCl_4$.

The reduction of $TiCl_4$ by alumoxane of degree of hydrolysis 0.5–1.0 was confirmed by the isolation of titanium trichloride in the form of a complex $TiCl_3.3THF$ from the products of reaction [4].

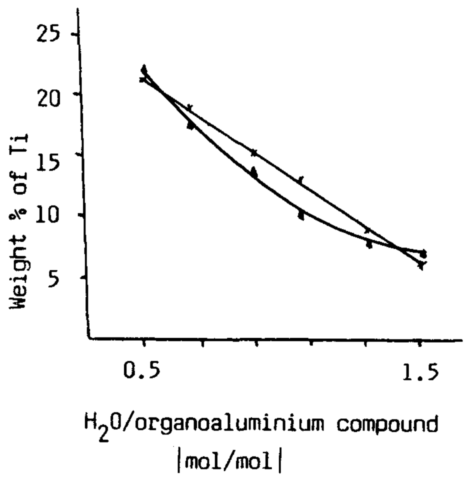


Figure 1 Dependence of percentage of titanium in catalyst precursor on degee of hydrolysis of alumoxane: ▲, ethylalumoxane; ×, ethylchloroalumoxane.

Catalysts obtained in an excess of $TiCl_4$

Catalysts for propylene polymerization were prepared according to Scheme 1.

An excess of $TiCl_4$ was added to the alumoxane; the mixture was heated and the remaining $TiCl_4$ was washed out from the catalyst precursor. Ethylalumoxanes react with $TiCl_4$ more easily than do ethylchloroalumoxanes (ethylalumoxanes of degree of hydrolysis 0.5–1.0 react with $TiCl_4$ at room temperature; this was not observed for ethylchloroalumoxanes).

$$\text{Alumoxane} \xrightarrow[60\text{–}130\,^{\circ}\text{C}]{TiCl_4} \text{catalyst precursor} \xrightarrow[\text{room temp.}]{Et_3Al} \text{catalyst}$$

Scheme 1

The dependence of the percentage of titanium in the catalyst precursor on the degree of hydrolysis of alumoxane is shown in Fig. 1. It was found that the highest percentages of titanium were obtained in the reactions of alumoxanes of degree of hydrolysis 0.5. A substantial decrease of the amount of titanium in the reaction products was observed for alumoxanes obtained at molar ratios (water/Et_3Al) of 0.5–1.0. Further increase of degree of hydrolysis causes only a minor decrease of titanium content (Fig. 1). For ethylchloroalumoxanes a steady decrease of titanium content with an increase of degree of hydrolysis was observed. The highest content of titanium was 22.1 wt% for ethylalumoxane and 19.2 wt% for ethylchloroalumoxane, and the lowest was 7.3 and 6.3 wt% respectively. The lowest content of titanium was in both cases for alumoxanes of degree of hydrolysis 1.50.

2.1. Ethylalumoxanes as catalyst components (degree of hydrolysis 0.5 and 0.6)

Catalysts obtained from ethylalumoxanes and $TiCl_4$ are more active than Ziegler–Natta catalysts (Et_3Al–$TiCl_4$). For example, 29.5 kg product per mol titanium per hour (II = 42.8 %) and 25.6 kg product per mol titanium per hour (II = 36.6%) were obtained from catalysts formed from ethylalumoxanes of degree of hydrolysis equal to 0.50 and 0.60 respectively, while for the Ziegler system ($Et_3Al/TiCl_4$) prepared by the same method only 23 kg product per mol titanium per hour (II = 47.8 %) was obtained. Further increase of the degree of hydrolysis of ethylalumoxane causes a decrease of activity of the prepared catalysts (Fig. 2). The system prepared for alumoxane of degree of hydrolysis 1.5 was completely inactive.

Prepared catalysts are characterized by low isotacticity index (II), e.g. with a maximum of 42.8 % for the system prepared from ethylalu-

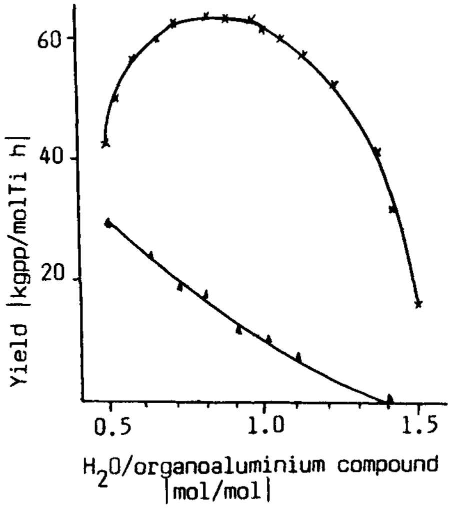


Figure 2 Dependence of catalytic activity on degree of hydrolysis of alumoxane. Catalysts were prepared from the products of reactions of alumoxanes with an excess of $TiCl_4$: ▲, ethylalumoxane; ×, ethylchloroalumoxane. Yield is in kg product per mol Ti per hour.

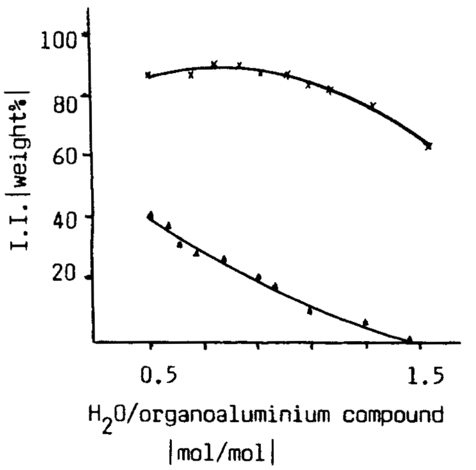


Figure 3 Dependence of isotacticity index of polypropylene on degree of hydrolysis of alumoxane. Catalysts were prepared from the products of reactions of alumoxanes with an excess of $TiCl_4$: ▲, ethylalumoxane; ×, ethylchloroalumoxane.

moxane of degree of hydrolysis 0.50. An increase of the degree of hydrolysis of ethylalumoxanes causes a decrease of the stereospecificity of prepared catalysts (Fig. 3).

Ethylchloroalumoxanes as catalyst components
Catalysts obtained from ethylchloroalumoxanes of degree of hydrolysis 0.5–1.0 were much more active than Ziegler systems (Et_2AlCl–$TiCl_4$). The highest yield of 63.5 kg product per mol titanium per hour (II = 90.3 %) was obtained for a catalyst prepared from ethylchloroalumoxane of degree of hydrolysis 0.85, while for an Et_2AlCl–$TiCl_4$ system prepared by the same method, a yield of 31.5 kg product per mol titanium per hour (II = 87.6 %) was obtained.

An increase of degree of hydrolysis over 1.0 causes a rapid decrease of activity of prepared catalysts (a catalyst prepared for water Et_2AlCl = 1.5:1 had activity of 15.4 kg product per mol titanium per hour II = 63.2 %) (Fig. 2).

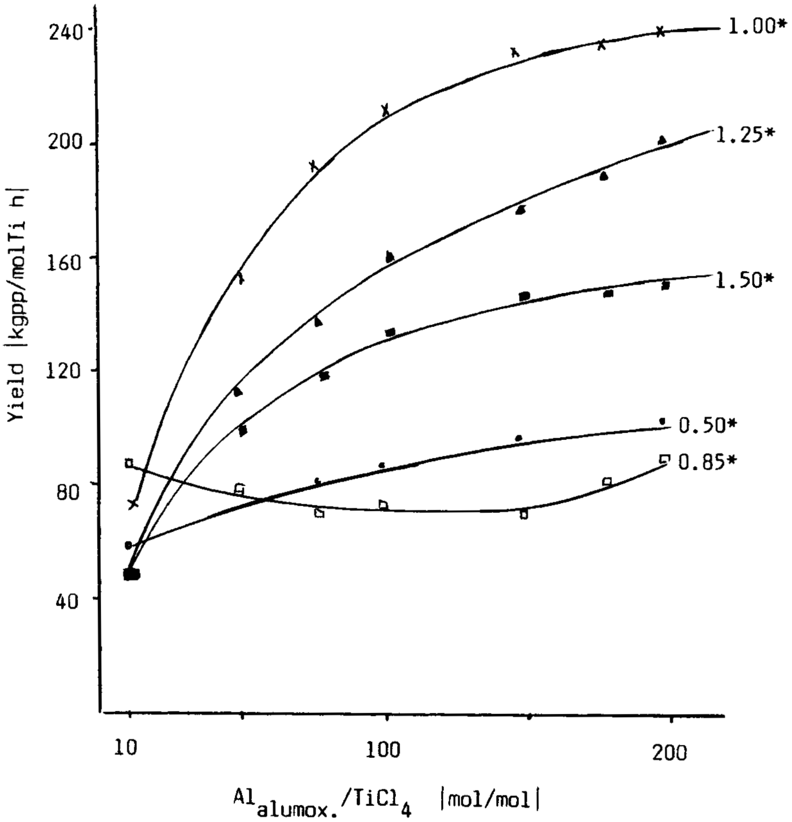


Figure 4 Influence of molar ratio, aluminium/$TiCl_4$, on activity of catalysts prepared from ethylchloroalumoxanes of various degrees of hydrolysis, as indicated on each curve (*). Yield is in kg product per mol Ti per hour.

Catalysts obtained from ethylchloroalumoxanes are characterized by high stereospecificity. The isotacticity index (II) polypropylene was about 90 % for catalytic systems based on ethylchloroalumoxanes of degree of hydrolysis 0.5–1.0 (Fig. 3). An increase of degree of hydrolysis over 1.0 causes a decrease of isotacticity index.

Catalysts obtained with an excess of alumoxane (aluminium/$TiCl_4$ = 10, 20, 50, 100 and 200:1)

An increase of the molar ratio of aluminium/$TiCl_4$ has various influences on activity of catalysts prepared from ethylalumoxanes and ethylchloroalumoxanes. A small increase of activity together with a substantial decrease of isotacticity index of the polypropylene was observed for ethylalumoxanes. For example, 33.7 kg product per mol titanium per hour (II = 18.34 %) was obtained with a catalyst prepared from ethylalumoxane of degree of hydrolysis 0.5 (aluminium/$TiCl_4$ = 10:1). An increase of degree of hydrolysis leads to a loss of catalytic activity.

A severalfold increase of activity together with, in contrast, a decrease of isotacticity index was obtained for catalysts prepared from ethylchloroalumoxanes.

A yield of 206 kg product per mol titanium per hour (II = 50.79 %) was obtained for ethylchloroalumoxane of degree of hydrolysis 1.0 and molar ratio aluminium/$TiCl_4$ = 100:1 (Fig. 4). Molar ratios (aluminium/$TiCl_4$) have a substantial influence on catalyst activity. It was found that an optimum molar ratio, aluminium/$TiCl_4$, was about 100:1 (Fig. 4). No rapid decrease of catalyst actvitiy was observed with an increase of degree of hydrolysis over 1.0.

Catalysts prepared from alumoxanes of degree of hydrolysis 1.25 and 1.50 were more active than catalysts prepared from alumoxanes of degree of hydrolysis 0.50–0.85, but a decrease of isotacticity index of the polypropylene was observed. For example, 56.7 kg product per mol titanium per hour (II = 51.2 %) was obtained for ethylchloroalumoxane of degree of hydrolysis 0.85 and 128.4kg product per mol titanium per hour (II 42.3 %) was obtained for ethylchloroalumoxane of degree of hydrolysis 1.50.

A substantial influence on a catalytic activity was the amount of Et_3Al used in the catalyst preparation reaction (Scheme 1).

For ethylchloroalumoxane, an optimum molar ratio (Et_3Al/titanium in precursor) was about 100:1 in the case of an excess of $TiCl_4$ and about 30:1 in cases of an excess of alumoxane (Table 2) (content of titanium in the catalyst precursor are shown in Fig. 1). Further increase of the amount of Et_3Al leads to a small increase of yield with a simultaneous substantial decrease of isotacticity index.

REFERENCES

1. Sakharovskaya, G B and Korneev, N N *Zh. Obshch. Khim.*, 1969, 39: 788
2. Nowakowska, M, Woźna, B and Niemczyk, E *Polimery*, 1986, 31: 398
3. Nowakowska, M, Czaja, K and Kruczala, Z *Zesz. Nauk.—Wyższa Szkoła Pedagog. w Opolu, Chem.*, 1985, 7: 85
4. Polish Patent 116 247 (1982).
5. Mieszkowa, J N and Uszakowa, T M *Wysokomol. Sojedin., Ser. B*, 1977, 19: 849
6. Mieszkowa, J N and Uszakowa, T M *Katalizatory Sodierżaszczije Naniesiennyje Kompleksy*, 1977, 103; *Ref. Z. Chim.*, 1977, 23S178
7. Japanese Patent 71 34 978 (1971); *Chem. Abstr.*, 76: 73062a
8. Japanese Patent 71 34 980 (1971); *Chem. Abstr.*, 76: 73063b
9. Japanese Patent 71 34 981 (1971); *Chem. Abstr.*, 76: 73063c
10. Japanese Patent 71 43 887 (1971); *Chem. Abstr.*, 77: 20414f
11. Japanese Patent 72 14 449 (1972); *Chem. Abstr.*, 77: 115117a
12. Japanese Patent 72 14 448 (1972); *Chem. Abstr.*, 77: 115119c
13. Sinn, H and Kaminsky, W *Adv. Organomet. Chem.*, 1980, 18: 99
14. Ewen, J A *J. Am. Chem. Soc.*, 1984, 106: 6355
15. Reger, B, Mu, X, Mallin, D T, Rausch, M D and Chien, J C W *Macromolecules*, 1990, 23: 3559
16. Mallin, D T, Rausch, M D, Lin, Y G, Dong, S and Chien, J C W *J. Am. Chem. Soc.*, 1990, 112: 2030
17. Röll, V, Brintzinger, H H, Rieger, B and Zolk, R *Angew. Chem.*, 1990, 102: 339
18. Kaminsky, W *Coordination Chemistry and Catalysis*, Proc. 11th Summer School, Karpacz 87, Ziółkowski, J J (ed), World Scientific Publ. Co., Singapore, 1988, pp 212–225
19 Oliva, L, Longo, P and Pellecchia, C *Makromol. Chem., Rapid Commun.*, 1988, 9: 51
20. Kaminsky, W, Klüper, K, Brintzinger, H H and Wild, F R W P *Angew. Chem.*, 1985, 97: 507
21. Kaminsky, W, Miri, M, Sinn, H and Woldt, R *Makromol. Chem., Rapid Commun.*, 1983, 4: 464
22. Dutschke, J, Kaminsky, W and Lüker, H *Polymer Reaction Engineering,* Reichert, K H and Geiseler, W (eds), Hanser Publ., Munich, 1983, p 207

23. Kaminsky, W and Herwig, J *Polym. Bull.*, 1983, 9: 464

24. Pasynkiewicz, S, Sadownik, A and Kunicki, A *J. Organomet. Chem.*, 1977, 124: 265

25. Bolesławski, M, Pasynkiewicz, S, Kunicki, A and Serwatowski, J *J. Organomet. Chem.*, 1976, 116: 285

26. Storr, A, Jones, K and Laubengayer, A W *J. Am. Chem. Soc.*, 1961, 90: 3173

27. Bolesławski, M Serwatowski, J *J. Organomet. Chem.*, 1983, 254: 159

28. Bolesławski, M Reakcje związków glinoorganicznych ze związkami ołowiu oraz chemia tworzących się ubocznie alumoksanów. In: *Prace Naukowe, Chemia*, nr 18, Politechnika Warszawska, Warszawa, 1977

29. Piotrowski, A Praca doktorska, Politechnika Warszawska, Warszawa, 1979

30. Bolesławski, M Sergiejczyk, L and Synoradzki, L *Przem. Chem.*, 1986, 65(4): 141

31. Bradley, D C and Westalake, A H *Nature (London)*, 1961, 191: 273

32. Poller, R C *J. Inorg. Nucl. Chem.*, 1962, 24: 593

33. Reid, A F and Wailes, P. C. *Aust. J. Chem.*, 1965, 18: 173

34. Cousins, M and Green, M L H *J. Chem. Soc.*, 1964: 1567

35. Barraclongh, G G, Lewis J and Nyholm, R S *J. Chem. Soc.*, 1959: 3352

36. Cotton, F A and Wing, R M *Inorg. Chem.*, 1965, 4: 867