

POLYMERIZATION OF PROPYLENE WITH TITANIUM TRICHLORIDE AND ALKYL-ALKOXY- ALUMINIUM CHLORIDES

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Abstract—A description is given of the polymerization of propylene in the presence of catalysts prepared from titanium trichloride and alkyl-alkoxy-aluminium chlorides. These catalyst systems are very active in the propylene polymerization only in the presence of aluminium chloride, which may be present as a solid solution in TiCl_3 . $\text{Al}(\text{C}_2\text{H}_5)_2\text{Cl}$ was isolated from the mixture of reaction products of AlCl_3 and $\text{C}_2\text{H}_5\text{Al}(\text{Cl})\text{OC}_2\text{H}_5$. The results lead to the conclusion that the polymerization-active organometallic compound of aluminium is probably aluminium diethylchloride.

INTRODUCTION

SEVERAL papers published on the polymerization of propylene by Ziegler-Natta catalysts concern the influence of different organometallic compounds of aluminium and their mixtures on the activity and stereospecificity of the catalysts. From such work, it is seen that the nature of the organometallic compound used for the preparation of the catalyst influences the overall polymerization rate (which in turn depends on the number of active centres) and the stereospecificity of the catalyst.

The organometallic compound causes a surface alkylation of the transition metal salt and it co-ordinates, on the basis of its associative properties, with the surface compound of the transition metal. The different organometallic compounds employed for the preparation of the catalyst influence its activity and stereospecificity because of this two-fold action.⁽¹⁾ The non-associated organometallic compounds exhibit a higher alkylating power because they only alkylate, on the surface, the transition metal salt.⁽²⁾ It can be argued that non-associated forms, which are in equilibrium in solution with the dimeric or polymeric forms, are the active species of the organometallic compounds participating in the formation of the catalyst. On this basis, the high degree of association was considered to be responsible for the lack of catalytic activity of $\text{Al}(\text{C}_2\text{H}_5)_2\text{OC}_6\text{H}_5$ in the polymerization of propylene, in the presence of violet titanium trichloride obtained by reduction of TiCl_4 with H_2 .⁽³⁾ Therefore, it was a surprising observation that alkyl-alkoxy aluminium chlorides, although possessing a lower alkylating power than aluminium dialkylmonoalcoholates and presenting a high degree of association, can form effective catalysts for the polymerization of propylene in the presence of a particular type of titanium trichloride. It was thought interesting to study thoroughly this particular catalyst system.

Polymerization of propylene by violet TiCl_3 and ethyl-alkoxy-aluminium chlorides

As shown from the data of Table 1, the catalyst systems obtained by reaction of $\text{C}_2\text{H}_5\text{Al}(\text{Cl})\text{OC}_2\text{H}_5$ or $\text{C}_2\text{H}_5\text{Al}(\text{Cl})\text{OC}_6\text{H}_5$ with TiCl_3 ARA, supplied by Stauffer Co. ($\text{TiCl}_3\delta$ containing Al (4.6%) as AlCl_3 in a solid solution) are very active and stereospecific in the polymerization of propylene.

TABLE 1. POLYMERIZATION OF PROPYLENE BY TiCl_3 ARA* AND ALUMINIUM ALKYLs
Polymerization conditions: $\text{TiCl}_3 = 7.1 \cdot 10^{-3}$ mole/l.; pressure $C_3 = 5$ atm;
 $T = 75^\circ\text{C}$; time = 5 hr; n-heptane = 300 cm^3 .

Run No.	Aluminium alkyl	Al/Ti	Polymer obtained		
			(g)	index of isotacticity (%)†	$[\eta]$ (100 ml/g)‡
1	$\text{C}_2\text{H}_5\text{Al}(\text{Cl})\text{OC}_2\text{H}_5$	1.2	5.1	90.3	3.82
2	$\text{C}_2\text{H}_5\text{Al}(\text{Cl})\text{OC}_2\text{H}_5$	4	15.6	91.3	5.73
3	$\text{C}_2\text{H}_5\text{Al}(\text{Cl})\text{OC}_2\text{H}_5$	6	23.5	86	6.1
4	$\text{C}_2\text{H}_5\text{Al}(\text{Cl})\text{OC}_2\text{H}_5$	8	109	85	4.9
5	$\text{C}_2\text{H}_5\text{Al}(\text{Cl})\text{OC}_6\text{H}_5$	4	16.8	77.73	4.1
6	$\text{C}_2\text{H}_5\text{Al}(\text{Cl})\text{OC}_6\text{H}_5$	8	37.6	75	4.11
7	$\text{Al}(\text{C}_2\text{H}_5)_2\text{Cl}$	4	110	93.9	4.6

* $\delta\text{-TiCl}_3$ containing AlCl_3 (22.3% by weight) in solid solution.

† Expressed as % of boiling n-heptane non-extractable polymer.

‡ Intrinsic viscosity of the residue after the heptane extraction, measured in tetralin at 135° .

A more detailed study of these catalyst systems revealed that the ratio of organo-metallic compound to titanium salt has a considerable effect on activity in the polymerization (Fig. 1). The polymerization rate increases with increasing this ratio until, for an Al/Ti ratio of 8, it is very close to that for the $\text{Al}(\text{C}_2\text{H}_5)_2\text{Cl}\text{-TiCl}_3$ ARA catalyst system under the same conditions.

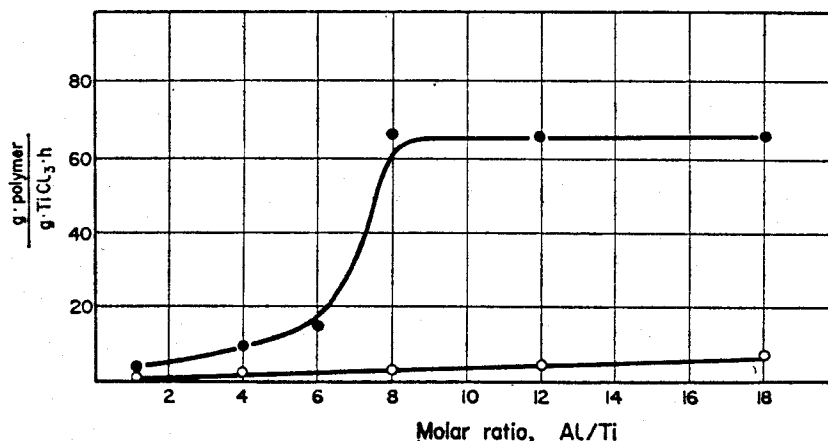


FIG. 1. Influence of the Al/Ti ratio on the rate of polymerization of propylene by the catalyst systems $\text{C}_2\text{H}_5\text{Al}(\text{Cl})\text{OC}_2\text{H}_5\text{-TiCl}_3$ ARA (●) and $\text{C}_2\text{H}_5\text{Al}(\text{Cl})\text{OC}_2\text{H}_5\text{-TiCl}_3$ HRA (○). Polymerization conditions: $\text{TiCl}_3 = 7.1 \cdot 10^{-3}$ mole/l.; pressure $C_3 = 5$ atm; $T = 75^\circ$; time: 5 hr; n-heptane = 300 cm^3 .

The catalyst activity increases with increasing the Al/Ti ratio because of the absolute amount and not because of the higher concentration of the organometallic compound of aluminium. In fact, no increase in polymerization rate was observed by repeating run (2) of Table 1 with the amount of solvent decreased to $\frac{1}{3}$ while all other conditions were kept constant. These results cannot be easily interpreted by considering that the reaction between the organometallic compound of aluminium and titanium trichloride takes place heterogeneously. No appreciable dependence of the polymerization rate on the Al/Ti ratio has ever been observed, when $\text{Al/Ti} > 1$, in all the catalyst systems based on the organometallic compounds of aluminium [$\text{Al}(\text{C}_2\text{H}_5)_3$, $\text{Al}(\text{C}_2\text{H}_5)_2\text{Cl}$, $\text{Al}_2\text{Cl}_3(\text{C}_2\text{H}_5)_3$ ⁽⁴⁾] so far studied.

When employing TiCl_3HRA ($\delta\text{-TiCl}_3$ obtained by reduction of TiCl_4 with hydrogen and activated by grinding) instead of TiCl_3ARA in the polymerization of propylene with $\text{C}_2\text{H}_5\text{Al}(\text{Cl})\text{OC}_2\text{H}_5$, a catalytic system is obtained which exhibits a negligible activity (Table 2).

TABLE 2. POLYMERIZATION OF PROPYLENE BY $\text{TiCl}_3\text{HRA}^*$ AND ALUMINIUM ALKYL

Polymerization conditions: $\text{TiCl}_3 = 7.1 \cdot 10^{-3}$ mole/l.; pressure $\text{C}_3 = 5$ atm;
 $T = 75^\circ$; time = 5 hr; n-heptane = 300 cm^3 .

Aluminium alkyl	Al/Ti	Polymer obtained		
		(g)	index of isotacticity† (%)	$[\eta]$ (100 ml/g)‡
$\text{C}_2\text{H}_5\text{Al}(\text{Cl})\text{OC}_2\text{H}_5$	4	0.15	—	—
$\text{C}_2\text{H}_5\text{Al}(\text{Cl})\text{OC}_2\text{H}_5$	8	0.5	—	—
$\text{C}_2\text{H}_5\text{Al}(\text{Cl})\text{OC}_2\text{H}_5$	16	3.4	91.6	4.9
$\text{Al}(\text{C}_2\text{H}_5)_2\text{Cl}$	4	73	91.4	5.45

* $\delta\text{-TiCl}_3$.

† Expressed as % of boiling n-heptane insoluble polymer.

‡ Intrinsic viscosity of the residue after the heptane extraction, measured in tetralin at 135° .

Also when increasing the Al/Ti ratio, the catalyst activity is far lower than that shown, under the same conditions, by the catalyst based on TiCl_3ARA and $\text{C}_2\text{H}_5\text{Al}(\text{Cl})\text{OC}_2\text{H}_5$ (Fig. 1). Such a difference in the behaviour of the two types of TiCl_3 is quite anomalous, considering that, in the presence of other organometallic compounds of aluminium [e.g. $\text{Al}(\text{C}_2\text{H}_5)_2\text{Cl}$], the catalytic activity of TiCl_3ARA is only slightly higher than that of TiCl_3HRA . Therefore, we concluded that such a difference in catalytic activity of the two types of titanium trichloride is due to the presence of AlCl_3 in TiCl_3ARA . In fact, by adding small amounts of aluminium chloride to the $\text{C}_2\text{H}_5\text{Al}(\text{Cl})\text{OC}_2\text{H}_5\text{-TiCl}_3\text{HRA}$ catalyst system, the polymerization rate markedly increase (Table 3) until reaching a value very close to that shown, under the same conditions, by $\text{Al}(\text{C}_2\text{H}_5)_2\text{Cl-TiCl}_3\text{HRA}$. It is interesting to observe that no large difference in polymerization rate is observed when varying, over a fairly wide range, the ratio of organometallic compound of aluminium to aluminium chloride.

On the basis of these results we might deduce that the active organometallic compound is not $\text{C}_2\text{H}_5\text{Al}(\text{Cl})\text{OC}_2\text{H}_5$, but another compound of aluminium formed in the reaction

TABLE 3. POLYMERIZATION OF PROPYLENE WITH TiCl_3 HRA*, $\text{C}_2\text{H}_5\text{Al}(\text{Cl})\text{OC}_2\text{H}_5$ AND AlCl_3

Polymerization conditions: $\text{TiCl}_3 = 7.1 \cdot 10^{-3}$ mole/l.;
 $\text{C}_2\text{H}_5\text{Al}(\text{Cl})\text{OC}_2\text{H}_5 = 56.8 \cdot 10^{-3}$ mole/l.; pressure $\text{C}_3 = 5$ atm;
 $T = 75^\circ$; time = 5 hr; n-heptane = 300 cm^3 .

AlCl_3 (m.moles)	$\text{C}_2\text{H}_5\text{Al}(\text{Cl})\text{OC}_2\text{H}_5$	Polymer obtained (g)
	AlCl_3	
0		0.5
0.568	30	65
2.12	8	64
4.26	4	33

* $\delta\text{-TiCl}_3$.

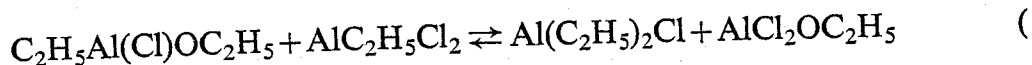
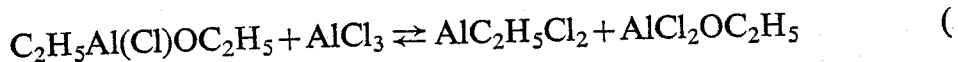
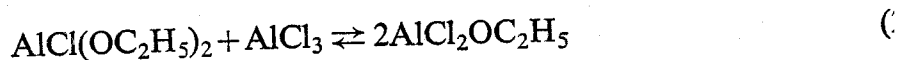
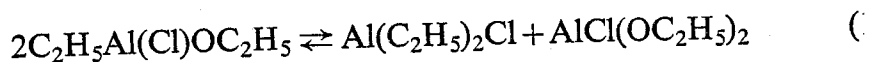
between $\text{C}_2\text{H}_5\text{Al}(\text{Cl})\text{OC}_2\text{H}_5$ and aluminium chloride. Therefore we thought it interesting to isolate the products obtained from the reaction between ethyl-ethoxy-aluminium chloride and aluminium chloride.

Study of the reaction between AlCl_3 and $\text{C}_2\text{H}_5\text{Al}(\text{Cl})\text{OC}_2\text{H}_5$

$\text{C}_2\text{H}_5\text{Al}(\text{Cl})\text{OC}_2\text{H}_5$ was caused to react with AlCl_3 in a molar ratio 8:1 at the same temperature as that employed in the polymerization. The reaction mixture was then subjected to fractionation under high vacuum (10^{-4} – 10^{-5} mm Hg) by heating the distillation flask to 75° .

A fraction was obtained containing about 5.5% of the total aluminium, in which the ratio $\text{Al}:\text{Cl}:-\text{C}_2\text{H}_5$ is 1:1.3:1.4. The distillate mostly consisted of a mixture of aluminium diethylmonochloride and aluminium ethylsesquichloride.

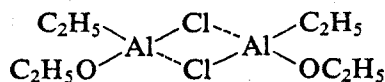
It is known that a mixture of the two components in such proportions is active in the polymerization of propylene in the presence of violet TiCl_3 .⁽⁵⁾ The formation of $\text{Al}(\text{C}_2\text{H}_5)_2\text{Cl}$ by reaction between $\text{C}_2\text{H}_5\text{Al}(\text{Cl})\text{OC}_2\text{H}_5$ and AlCl_3 can occur through the following equilibrium reactions:



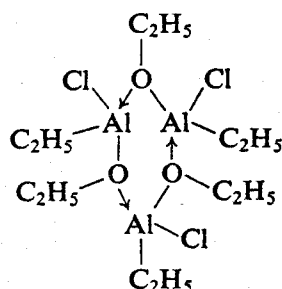
The possibility of occurrence of the disproportionation reaction (1) was evidenced by subjecting $\text{C}_2\text{H}_5\text{Al}(\text{Cl})\text{OC}_2\text{H}_5$ to careful fractionation at 0.5 mm at 120° . It was then possible to separate a fraction consisting almost exclusively of $\text{Al}(\text{C}_2\text{H}_5)_2\text{Cl}$ and of a distillation residue in which organometallic bonds are nearly absent. At a low temperature (75°), it was impossible to isolate a distillate containing $\text{Al}(\text{C}_2\text{H}_5)_2\text{Cl}$. Probably at that temperature the equilibrium (1) is shifted towards $\text{C}_2\text{H}_5\text{Al}(\text{Cl})\text{OC}_2\text{H}_5$.

The view was put forward by some authors,⁽⁶⁾ on the basis of spectroscopic data and cryoscopic determinations of the molecular weight, that $\text{C}_2\text{H}_5\text{Al}(\text{Cl})\text{OC}_2\text{H}_5$ can ex-

in two associated forms, viz. a dimer in which the association between two Al atoms takes place by chlorine bridges



and a trimer in which the association between aluminium atoms takes place through the oxygen atoms:



For each temperature, an equilibrium should exist between the two association forms; with increasing temperature, it should shift in favour of the dimeric form with chlorine bridges.

Evidently, at 120° , in addition to the equilibrium suggested by the above authors, another equilibrium exists between $\text{C}_2\text{H}_5\text{Al}(\text{Cl})\text{OC}_2\text{H}_5$ and its disproportionation products,



When the aluminium diethylmonochloride is removed by distillation, the equilibrium is effectively shifted toward the right.

The interpretation of these results led us to conclude that, in the system $\text{C}_2\text{H}_5\text{Al}(\text{Cl})\text{OC}_2\text{H}_5\text{--TiCl}_3$ ARA, the polymerization-active organometallic compound of Al is probably aluminium diethylmonochloride, formed in the reaction between $\text{C}_2\text{H}_5\text{Al}(\text{OC}_2\text{H}_5)\text{Cl}$ and the aluminium chloride contained, as a solid solution, in TiCl_3 ARA. The amount of $\text{Al}(\text{C}_2\text{H}_5)_2\text{Cl}$ produced is relatively small with respect to $\text{C}_2\text{H}_5\text{AlOC}_2\text{H}_5\text{Cl}$ but is enough to account for the catalytic activity.

In fact, the rate of the polymerization of propylene by the system $\text{TiCl}_3\text{--Al}(\text{C}_2\text{H}_5)_2\text{Cl}$ is very high also for low ratios of organometallic compound to titanium salt, when the polymerization is carried out in the absence of impurities interacting with the active centres.

The experimental conditions adopted are never such as to exclude the presence of traces of impurities. Among all organometallic compounds present in the catalytic system, aluminium diethyl monochloride is the most sensitive to impurities; if the amount of $\text{Al}(\text{C}_2\text{H}_5)_2\text{Cl}$ produced is very low, the polymerization rate depends on the concentration of aluminium diethylmonochloride.

In the light of these remarks, we can try to interpret the influence of the ratio of $\text{C}_2\text{H}_5\text{AlOC}_2\text{H}_5\text{Cl}$ to TiCl_3 ARA on the polymerization rate. With increasing the amount of $(\text{C}_2\text{H}_5)_2\text{Al}(\text{Cl})(\text{OC}_2\text{H}_5)$ present in the system, the concentration of $\text{Al}(\text{C}_2\text{H}_5)_2\text{Cl}$ increases and consequently the polymerization rate rises. Thus for an

amount of $C_2H_5Al(Cl)OC_2H_5$ higher than that for the run with a ratio Al/Ti=8, the concentration of aluminium diethylmonochloride formed is such that the polymerization rate becomes independent of a further increase of it.

The increase in the concentration of $Al(C_2H_5)_2Cl$ with increasing the amount of $C_2H_5Al(Cl)(OC_2H_5)$ can be explained simply by consideration of equilibria (2), (3) and (4). Another hypothesis is that aluminium chloride can react only with the dimeric form (having chlorine bridges) or a hypothetical non-associated form of $C_2H_5Al(Cl)(OC_2H_5)$, both being in equilibrium with the more stable trimeric form. This hypothesis could account for the considerable increase in the polymerization rate observed with decreasing the time elapsing between the distillation of the organometallic compound and its use in the polymerization of propylene in the presence of $TiCl_3$ ARA, also for low ratios of Al to Ti (Table 4).

TABLE 4. POLYMERIZATION OF PROPYLENE BY $TiCl_3$ ARA* AND $C_2H_5Al(Cl)OC_2H_5$

Polymerization conditions: $TiCl_3 = 7.1 \cdot 10^{-3}$ mole/l.;
 $C_2H_5Al(Cl)OC_2H_5 = 28.4 \cdot 10^{-3}$ mole/l.; pressure $C_3 = 5$ atm;
 $T = 75^\circ$; time = 5 hr; n-heptane = 300 cm³.

Time of ageing†	Polymer obtained		
	(g)	Index of isotacticity‡	$[\eta]$ (100 ml/g)§
0	54.7	88.1	5.9
1 hr	21	89.6	5.6
2 days	15	91.3	5.73

* 8- $TiCl_3$ containing $AlCl_3$ (22.3%) in solid solution.

† Time between distillation of $C_2H_5Al(Cl)OC_2H_5$ and its use in the polymerization.

‡ Expressed as percentage of boiling n-heptane non-extractable polymer.

§ Intrinsic viscosity of the residue after the heptane extraction measured in tetralin at 135° .

It was actually demonstrated that freshly distilled $C_2H_5Al(Cl)OC_2H_5$ exists in an unstable dimeric form (with chlorine bridges), which changes into a more stable trimeric form.⁽⁶⁾ The freshly distilled $C_2H_5Al(Cl)OC_2H_5$ does not, however, contain noticeable amounts of $Al(C_2H_5)_2Cl$. As a matter of fact, when $TiCl_3$ HRA is caused to react with freshly distilled $C_2H_5Al(Cl)OC_2H_5$, the observed rate of polymerization of propylene is equal to that for the catalyst system obtained from $TiCl_3$ HRA and aged $C_2H_5Al(Cl)OC_2H_5$.

EXPERIMENTAL

Reagents

$C_2H_5Al(Cl)OC_2H_5$ was prepared as described by U. Giannini and S. Cesca.⁽⁷⁾ The distilled product was further purified by crystallization from n-heptane at low temperature. $C_2H_5Al(Cl)OC_6H_5$ was prepared by reaction between $Al(C_2H_5)_2Cl$ and phenol in equimolecular amounts in benzene solution and isolated by precipitation with n-heptane. The product separated as a white crystalline precipitate was further purified by precipitation with n-heptane from benzene solution. The compound melts at $102-103^\circ$, reacts with alcohols, evolving the calculated amount of ethane and by analysis has given the following results:

found %: Al 14.64; Cl 18.8

for $\text{C}_2\text{H}_5\text{Al}(\text{Cl})\text{OC}_2\text{H}_5$ calc. %: Al 14.61; Cl 19.21.

TiCl_3 HRA and TiCl_3 ARA were commercial products supplied by Stauffer Chemical Co. and purified by treatment with hot hydrocarbons to remove possible traces of TiCl_4 .

Polymerizations were carried out in 1000 ml rocking autoclaves.

Reaction between $\text{C}_2\text{H}_5\text{Al}(\text{Cl})\text{OC}_2\text{H}_5$ and AlCl_3

$\text{C}_2\text{H}_5\text{Al}(\text{Cl})\text{OC}_2\text{H}_5$ (40.95 g; 0.3 moles) was allowed to react at 75° with AlCl_3 (5 g; 0.0375 moles). Aluminium chloride reacts rapidly and passes into solution. The solution was stirred magnetically at 75° and was subjected to fractional distillation at a pressure of $5 \cdot 10^{-5}$ mmHg. After 24 hr, a colourless liquid (3 g) was obtained; it had the analysis

Al = 21.7%

Cl = 37.2%

The product (0.2 g) after treatment with ethylhexyl alcohol evolved 50.4 ml of ethane, corresponding to 32.7% of ethyl groups. Therefore, the ratio Al: C_2H_5 :Cl is equal to 1:1.4:1.3.

Thermal disproportionation of $\text{C}_2\text{H}_5\text{Al}(\text{Cl})\text{OC}_2\text{H}_5$

$\text{C}_2\text{H}_5\text{Al}(\text{Cl})\text{OC}_2\text{H}_5$ (63.6 g) was subjected to distillation in a fractionating column at a pressure of 0.05 mmHg.

By heating the distillation flask to 115 – 120° , a colourless liquid (39 g) was distilled between 39° and 55° ; it contained about 90 per cent of the Al—C bonds initially present in $\text{C}_2\text{H}_5\text{Al}(\text{Cl})\text{OC}_2\text{H}_5$. Analysis of the residue after distillation gave the following results: Al = 20.50%; Cl = 31.3%. 1 g of product with ethylhexyl alcohol evolved 19 N cm³ of ethane corresponding to 2.46% ethyl groups.

By re-fractionation of the distillate, a product (15 g) was obtained, distilling at 39 – 40° (0.05 mmHg); 90% of it corresponded to $\text{Al}(\text{C}_2\text{H}_5)_2\text{Cl}$.

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Résumé—On a étudié la polymérisation du propylène amorcée par des systèmes catalytiques à base de TiCl_3 et d'alcooates d'alcoyle-halogéno-aluminium. Les systèmes catalytiques examinés ne sont actifs pour la polymérisation du propylène qu'en présence de AlCl_3 qui peut également être introduit sous forme de solution solide dans le TiCl_3 . Parmi les produits de la réaction du TiCl_3 avec $\text{C}_2\text{H}_5\text{Al}(\text{Cl})\text{OC}_2\text{H}_5$ on a isolé du $\text{Al}(\text{C}_2\text{H}_5)_2\text{Cl}$. Les résultats montrent que c'est $\text{Al}(\text{C}_2\text{H}_5)_2\text{Cl}$ qui est le composé organométallique actif dans la catalyse.

Sommario—Viene descritta la polimerizzazione del propilene in presenza di tricloruro di titanio e alchil-alcoossiluminio cloruri. La polimerizzazione ha luogo con elevata velocità soltanto in presenza di alluminio tricloruro libero o presente in soluzione solida nel tricloruro di titanio. Tra i prodotti della reazione tra cloruro di alluminio anidro ed etil-etossiluminio cloruro è stato isolato l'alluminio dietilmonocloruro. Questi risultati dimostrano che verosimilmente il composto metallorganico di alluminio attivo nella catalisi è l'alluminio dietilmonocloruro.

Zusammenfassung—Es wird die Polymerisation von Propylen in Gegenwart von, aus Titantrichlorid und Alkyl-alkoxy-aluminiumchloriden bereiteten, Katalysatorsystemen beschrieben.

Diese katalytischen Systeme polymerisieren Propylen mit hoher Geschwindigkeit nur in Gegenwart von AlCl_3 , das auch in fester Lösung im TiCl_3 enthalten sein kann. Diäthylaluminiumchlorid wurde aus den Reaktionsprodukten von wasserfreiem Aluminiumchlorid und Äthyl-äthoxy-aluminiumchlorid isoliert.

Diese Ergebnisse zeigen, dass wahrscheinlich die einzige katalytisch wirksame aluminium-organische Verbindung das $\text{Al}(\text{C}_2\text{H}_5)_2\text{Cl}$ ist.