# Highly Stereospecific Catalytic Systems for the Polymerization of α-Olefins to Isotactic Polymers

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## Introduction

The first highly stereospecific catalytic systems for the polymerization of α-olefins to polymers composed prevailingly of isotactic macromolecules were discovered in this Institute.[1] Since then, it had been pointed out that the best catalytic systems are prepared from a metalloorganic aluminum compound and from violet titanium trichloride.

At least three crystalline modifications of violet $TiCl_3$ ($\alpha$, $\gamma$, and $\delta$)[2-6] are now known. They are more or less pure, depending upon the preparation method. For instance, $TiCl_3$ as prepared by Ruff and Neumann[7] in 1923 by reduction of $TiCl_4$ with aluminum, contained aluminum as $AlCl_3$ in solid solution in the $TiCl_3$ lattice. The same can be said for $\gamma$-$TiCl_3$ prepared by reduction at 200°C. with trialkyl aluminum,[8] and for some types of $\delta$-$TiCl_3$ studied by us. The crystalline structure of each modification of $TiCl_3$ has been determined.[2-6]

In this paper we want to examine the possible influence exerted by the particular crystalline structure of violet $TiCl_3$ (with or without aluminum as $AlCl_3$ in solid solution) on the stereospecificity of the catalytic systems for the polymerization of α-olefins. We have therefore studied systematically the polymerization of propylene carried out with highly stereospecific catalytic systems prepared from different modifications of violet $TiCl_3$ and from different metalloorganic compounds of aluminum. It was observed that the stereospecificity of the catalytic systems is practically independent of the type of $TiCl_3$ modification (provided the samples are not altered), even if Al is present as $AlCl_3$ in solid solution with the $TiCl_3$, but that it is influenced by the type of metalloorganic compound of aluminum employed.

## I. Catalytic Systems Prepared from Violet TiCl₃ (α, γ or δ modifications) and from Al(C₂H₅)₂X (where X = Cl, Br, or I)

Tables I and II show the stereospecificity indexes (expressed as per cent of isotactic polypropylene insoluble in boiling n-heptane) of the different violet $TiCl_3$-$Al(C_2H_5)_2X$ catalytic systems used in the polymerization of propylene at 70 and 15°C. The data are compared with those obtained

TABLE I

Stereospecificity Indexes[a] of the Catalytic Systems ($\alpha$, $\gamma$, and $\delta$) Crystalline Violet $TiCl_3$ With or Without $AlCl_3$ in Solid Solution–$Al(C_2H_5)_2$ X–Toluene, in Polymerization of Propylene at 70°C. and $p(C_3H_6)$ = 2000 mm. Hg

| | $TiCl_3$ | | | | |
|---|---|---|---|---|---|
| | $\alpha$ | | | $\delta$ | |
| | Free of $AlCl_3$ | Containing $AlCl_3$[b] | $\gamma$[c] | Free of $AlCl_3$ | Containing $AlCl_3$[b] |
| $Al(C_2H_5)_2Cl$ | 92 | 91 | 93 | 93 | 94 |
| $Al(C_2H_5)_2Br$ | 95 | 95 | 96 | 96 | 96 |
| $Al(C_2H_5)_2I$ | 96 | 96 | 98 | 97 | 97 |
| $Al(C_2H_5)_3$ | 84 | 82 | 80 | 83 | 81 |

[a] As per cent of isotactic polymer, nonextractable with boiling $n$-heptane. The reported data are average values obtained from runs performed twice.

[b] Containing 4.5% Al as $AlCl_3$ in solid solution.

[c] Containing 1% Al as $AlCl_3$ in solid solution.

TABLE II

Indexes of Stereospecificity[a] of Catalytic System Prepared from ($\alpha$, $\gamma$ or $\delta$) Crystalline Violet $TiCl_3$ in Polymerization of Propylene[b]

| | Index of stereospecificity | |
|---|---|---|
| Organometallic compd. | Polym. runs at 15°C. | Polym. runs at 70°C. |
| $Al(C_2H_5)_2I$ | 99–100 | 96–98 |
| $Al(C_2H_5)_2Br$ | 97–98 | 94–96 |
| $Al(C_2H_5)_2Cl$ | 96–98 | 91–94 |
| $Al(C_2H_5)_3$ | 80–85 | 80–85 |
| $Be(C_2H_5)_2$ | 94–96 | 93–95 |

[a] As per cent of isotactic polypropylene, nonextractable with boiling $n$-heptane.

[b] Tests carried out at different pressures (1–10 atm.) with different concentrations of reactant ($TiCl_3$ 5–30 mmole/l., organometallic compound, 10–30 mmole/l.)

with the use of violet $TiCl_3$–$Al(C_2H_5)_3$ and violet $TiCl_3$–$Be(C_2H_5)_2$ catalytic systems.

The data reported in Table II were obtained from several runs carried out for each organometallic compound with the $\alpha$, $\gamma$, and $\delta$ crystalline modifications of violet $TiCl_3$, with or without Al. We have compared:

*Two types of $\alpha$-$TiCl_3$*: one obtained by reduction of $TiCl_4$ with $H_2$ at high temperature,[2] and the other one obtained by reduction of $TiCl_4$ with aluminum at high temperature[7] and containing 4.5% aluminum in solid solution.

*One type of $\gamma$-$TiCl_3$*: obtained by reduction at 200°C.[8] of $TiCl_4$ with $AlR_3$ containing 1% aluminum.

*Two types of $\delta$-$TiCl_3$*: one obtained by grinding $\alpha$-$TiCl_3$ containing 4.5% aluminum, and the other, free of aluminum, obtained by grinding $\alpha$-$TiCl_3$ free of aluminum.

From the reported data it is possible to conclude as follows: (*1*) The different crystalline ($\alpha$, $\gamma$, or $\delta$) modifications of violet $TiCl_3$ that did or did not contain Al as $AlCl_3$ in solid solution give rise to catalytic sytems whose stereospecificity practically depends only on the organometallic compound used for preparing the catalyst, and does not depend on the particular modification of violet $TiCl_3$. (*2*) The stereospecificity of the catalytic systems examined depends on the metalloorganic compound of aluminum. (*3*) For the catalytic systems prepared from violet $TiCl_3$ ($\alpha$, $\gamma$, or $\delta$) with or without Al, and for the organometallic compounds examined, it is possible to establish the following scale of stereospecificity:

$$Al(C_2H_5)_2I > Al(C_2H_5)_2Br > Be(C_2H_5)_2 \simeq Al(C_2H_5)_2Cl > Al(C_2H_5)_3$$
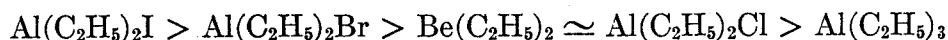
## II. Behavior of the Violet $\gamma$-$TiCl_3$–$Al(C_2H_5)_2I$ Catalytic Systems

### (*1*) Stereospecificity

We have observed that the most stereospecific catalytic systems (among those we examined) are the systems prepared from $Al(C_2H_5)_2I$. Figure 1 shows the results obtained in polymerization of propylene using the $\gamma$-$TiCl_3$–$Al(C_2H_5)_2I$ catalytic system. Stereospecificity increases with decreasing temperature to values that give, at temperatures below about 50°C., crude polypropylenes that are completely nonextractable with boiling $n$-heptane.
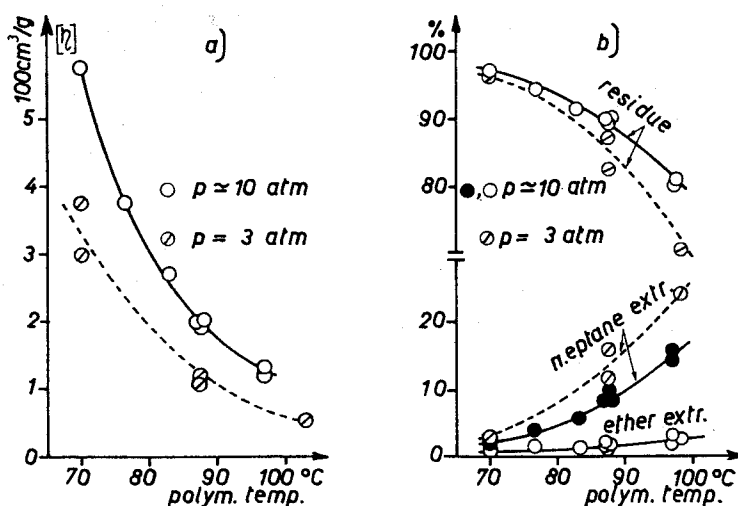


Fig. 1. (*a*) Intrinsic viscosity and (*b*) extraction data of polypropylene obtained at different temperatures with $\gamma$-$TiCl_3$–$Al(C_2H_5)_2I$–toluene catalytic system. $\gamma$-$TiCl_3$ = 13 mmole/l. $Al(C_2H_5)_2$ I = 30 mmole/l.

It was observed that the residue obtained after 48 hr. of extraction with ethylbenzene melts at 177 ± 0.5°C. (Table III). This is the highest value measured for isotactic polypropylene.[5,9] (Measurements of the melting point with a polarized light microscope were made through the courtesy of Dr. Moraglio.)

TABLE III

Characteristics of Polypropylene Obtained at Low Temperature Using Highly Stereo-specific Catalytic Systems Prepared from $\gamma$-TiCl$_3$-Al(C$_2$H$_5$)$_2$I-Toluene[a] at 15°C. and a Pressure of 5 Atm.

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| | | | | Al/Ti = 1.5 | | | |
| | | n-Oc- | Residue of | | Crude polymer | | Melt. temp. of res. obtd. after 48 |
| Ether ext., % | Heptane ext., % | tane ext., % | n-octane extn., % | $[\eta]$[b] | Crystal-linity[c] | Melt. temp., °C. | hr. extn. with ethylbenzene |
| — | Traces | 4% | 96 | >10 | 75% | 174 ± 0.5 | 177 ± 0.5 |

[a] $\gamma$-TiCl$_3$ contained 1% Al.
[b] Measured in tetralin at 135°C.
[c] Measured by x-rays on a sample annealed at 150°C.

In contrast to other systems the catalytic systems prepared from Al-(C$_2$H$_5$)$_2$I are highly stereospecific even if used in polymerizations at temperatures higher than 80°C. Actually (Fig. 1) the polymers obtained in polymerization runs at 100°C. also contain less than 3% boiling ethyl ether-extractable product, even if the intrinsic viscosity of the crude polymer is lower than 1.

TABLE IV

Characteristics of Polypropylene Obtained at High Temperature Using Highly Stereo-specific Catalytic Systems Prepared from Violet TiCl$_3$-Al(C$_2$H$_5$)$_2$I-Toluene at a Pressure of 1760 mm. Hg

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| | | | Al/Ti = 1.5 | | | | |
| | | | Characteristics of polymer obtained | | | | |
| | | | | | Residue of heptane extn. | | |
| | | | Ether extract | | | Crystal-linity under x-rays | $[\eta]$ of crude polymer |
| TiCl$_3$ | Polym. temp., °C. | % | $[\eta]$[c] | Crystallinity under x-ray | % | | |
| $\alpha$[a] | 76 | 1.5 | <0.3 | ~15% | 94 | 79% | 2.3 |
| $\gamma$[b] | 97 | 2 | <0.12 | ~40% | 70.5 | 78% | 0.7 |

[a] Free from aluminum.
[b] Containing 1% aluminum as AlCl$_3$ in solid solution.
[c] Measured in tetraline at 135°C.

The high stereospecificity of the catalytic systems under study is further emphasized by the fact that the boiling ethyl ether-extractable fraction of propylene obtained from runs carried out at temperatures higher than 75°C. also exhibits the crystallinity of isotactic polypropylene (see Table IV). Solubility in ethyl ether of these partially crystalline polymers is due to their very low molecular weight which has been observed in all the fractions obtained in polymerization runs effected at high temperatures, where

the polymeric chain termination process depending on $Al(C_2H_5)_2I$ concentration prevails.

## (2) Dependence of MW on Concentration of $Al(C_2H_5)_2I$

From runs carried out using the $\gamma$-$TiCl_3$–$Al(C_2H_5)_2I$–toluene catalytic system, we have observed that, when increasing the alkyl aluminum concentration in the reacting system, the molecular weight of the polypropylene obtained decreases (see Table V). In analogy with what has been observed

TABLE V

Influence of Alkyl Aluminum-Concentration on MW. of Polypropylene Obtained with $\gamma$-$TiCl_3$–$Al(C_2H_5)_2I$ Catalytic System[a]

$\gamma$-$TiCl_3$ = 13 mmoles/l.    $t$ = 86 ± 1°C.    $p(C_3H_6)$ = 2.5 atm.    Diluting agent = toluene.    Polymerization time = 2 hr.

| $Al(C_2H_5)_2I$, mmoles/l. | Polymer obtained, g./l. | $[\eta]$ of crude polymer[b] | MW of crude polymer | Ether ext., % | Heptane ext., % | Residue, % |
|---|---|---|---|---|---|---|
| 12 | 46.0 | 1.86 | 276,000 | 2 | 14 | 84 |
| 30 | 50.0 | 1.27 | 165,000 | 1.5 | 11 | 87.5 |
| 91 | 44.8 | 1.00 | 119,000 | 2 | 19 | 79 |
| 120 | 47.2 | 0.96 | 113,000 | 2 | 17.5 | 80.5 |

[a] $\gamma$-$TiCl_3$ contained 1% Al.

[b] Measured in tetralin at 135°C.

in previous runs carried out using the $\alpha$-$TiCl_3$–$Al(C_2H_5)_3$–$n$-heptane catalytic system,[10,11] the rate of the process giving rise to the lowering of the molecular weight seems to be, also in this case, of $^1/_2$ order with respect to
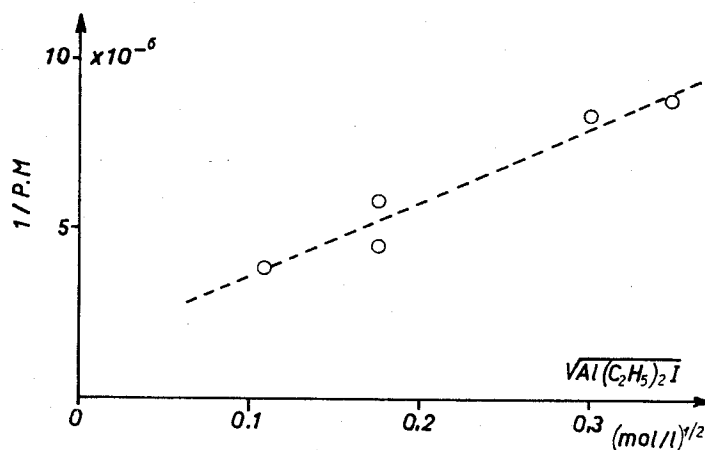


Fig. 2. Dependence of reciprocal molecular weight of polypropylene on square root of aluminum alkyl concentration. Polymerization conditions are listed in Table V.

the concentration of the organic aluminum compound (see Fig. 2). In the case of $Al(C_2H_5)_3$, such a lowering had been attributed to an exchange of alkyls between triethylaluminum and the polymeric growing chains.

### (3) Polymerization of 1-Butene

The catalytic systems prepared from violet $TiCl_3$ and from $Al(C_2H_5)_2I$ are also highly stereospecific in the polymerization of 1-butene. Actually, polybutene obtained at temperatures of 70°C. with the catalytic system $\gamma$-$TiCl_3$-$Al(C_2H_5)_2I$ is 98% nonextractable by boiling ethyl ether (Table VI). The mechanical properties (e.g., tensile strength, hardness, etc.)

TABLE VI
Polymerization of 1-Butene Using the $\gamma$-$TiCl_3$-$Al(C_2H_5)_2I$-$n$-Heptane Catalytic System[a]

| | |
|---|---|
| $\gamma$-$TiCl_3$ = 23 mmoles/l. | $CH_2Cl_2$ extract = traces. |
| $Al(C_2H_5)_2I$ = 30 mmoles/l. | $[\eta]$ of crude polymer = 2.88. |
| Butene = 88 g. | Density = 0.924–0.925.[b] |
| $t$ = 70°C. | M.P. = 136°C. ± 0.5.[b] |
| Time = 20 hr. | Hardness, Shore D = 68–70. |
| Polymer obtained = 70 g. | Tensile strength = 280–360 kg./cm.[2]. |
| Ether extract = 2%. | Yield stress = 210–220 kg./cm.[2]. |

[a] We wish to thank Dr. Crespi for making the mechanical measurements.

[b] The density and melting point were determined by dilatometric means, through the courtesy of Dr. Moraglio.

of polybutene obtained using these catalytic systems are better than those of polymers prepared with less stereospecific catalytic systems. For instance, the yield stress of the crude product is about double that of a polymer, residual to the ether extraction, obtained with the violet $TiCl_3$-$Al(C_2H_5)_3$ catalytic systems.

### III. ($\alpha$, $\gamma$ or $\delta$) Violet $TiCl_3$-Y+2$AlC_2H_5X_2$ Catalytic Systems (where Y = Electron Donor Substance or an "Onium" Salt and X = Cl, Br or I

Aluminum monoalkyl dihalides used in the presence of violet $TiCl_3$, do not provide stereospecific catalytic systems for the polymerization of $\alpha$-olefins. However, these compounds, if reacted with one-half molecule of a suitable electron donor substance or with "onium" salts, allow the preparation of highly stereospecific catalytic systems for the polymerization of $\alpha$-olefins to isotactic polymers. The stereospecificity of some of these catalytic systems employed at 70°C. is one of the highest known (Table VII). Also in this case, in analogy with what was reported above for the systems prepared from $Al(C_2H_5)_2X$, stereospecificity does not depend on the particular ($\alpha$, $\gamma$, or $\delta$) modification or violet crystalline $TiCl_3$ used for preparing the catalyst, or on the possible presence of Al as $AlCl_3$ in solid solution in the $TiCl_3$ lattice.

*Kinetic Behavior of the Catalytic Systems: ($\alpha$, $\gamma$, or $\delta$) Violet TiCl₃–Organometallic Compounds of Aluminum or of Beryllium*

The catalytic activity of the systems examined in the stereospecific polymerization of propylene depends not only on the metalloorganic compound used for the preparation of the catalyst, but, contrary to what

TABLE VII

Stereospecificity of the ($\alpha$, $\gamma$ or $\delta$) Crystalline Violet $TiCl_3$–Y + $2AlC_2H_5X_2$ Catalytic
Systems in Polymerization of Propylene at 70°C. and $p(C_3H_6)$ = 3500 mm. Hg

| Catalytic system | | | Fractionation of crude polymer | | |
|---|---|---|---|---|---|
| $TiCl_3$ modif. | Y + $2AlC_2H_5X_2$[a] | Diluting agent | Ether ext., % | Heptane ext., % | Residue of ext., % |
| $\gamma$[b] | $Py+2AlEtBr_2$ | Toluene | <0.5 | 1 | >98.5 |
| $\gamma$[b] | $NEt_3+2AlEtCl_2$ | $n$-Heptane | 2 | 3 | 95 |
| $\delta$[c] | $NHEt_2+2AlEtCl_2$ | Toluene | 2 | 5 | 93 |
| $\alpha$[d] | $NHEt_2+2AlEtCl_2$ | " | 2 | 5 | 93 |
| $\alpha$[d] | $NBu_4I+2AlEtCl_2$ | " | 0.5 | 1.5 | 98 |
| $\gamma$[b] | $NBu_4I+2AlEtCl_2$ | " | 0.5 | 1.5 | 98 |
| $\delta$[c] | $NBu_4I+2AlEtCl_2$ | " | 0.5 | 2.5 | 97 |
| $\gamma$[b] | $NBu_4I+2AlEtBr_2$ | " | Traces | <1 | >99 |
| $\delta$[c] | $NBu_4Br+2AlEtBr_2$ | " | 1 | 3.5 | 95.5 |
| $\gamma$[b] | $NBu_4Br+2AlEtCl_2$ | " | 1 | 3 | 96 |

[a] Py = pyridine, Et = $-C_2H_5$, Bu = $n$-$C_4H_9$.
[b] Containing 1% Al.
[c] Containing 4.5% Al.
[d] Free from Al.

happens with stereospecificity, also on the origin, and particularly on the modification, of the $TiCl_3$ used.

The polymerization rate, in particular the initial rate, is strongly influenced by the degree of subdivision of the $TiCl_3$ crystals. Since the various types and modifications of $TiCl_3$ examined by us were prepared by reduction of $TiCl_4$, both operating conditions and methods employed being different, it is clear that the size of crystals is different each time. We believe that this, in addition to the existence of lattice imperfections, the number of which differ in the different cases, is one of the most important causes of the varying catalytic activity of the several types of $TiCl_3$. In general, it has been observed that the catalytic systems prepared from $AlR_2X$ or from $Y+2AlRX_2$ show, for all the modifications of $TiCl_3$ a catalytic activity lower than that of the systems prepared from $AlR_3$ or from $BeR_2$. Furthermore, with a given metalloorganic compound, and with the types of $TiCl_3$ examined by us, the highest overall polymerization rate was observed for the most subdivided $\delta$-$TiCl_3$ samples containing Al.

In Table VIII, we report the approximate mean values of the polymerization rate obtained with the use of some very stereospecific catalytic systems. It must be observed that only with the use of some systems, e.g., with particular types of $\alpha$-$TiCl_3$, and operating under suitable conditions is the polymerization rate constant with time.[10,12] In other cases, for some types of $TiCl_3$ the polymerization rate increases with time to a constant value, and for other types it has a very high value at the beginning of polymerization which decreases more or less slowly. The latter behavior is particularly observed in very subdivided $TiCl_3$.[10,13] For these reasons, the mean values of the polymerization rates shown in Table VIII also

TABLE VIII

Behavior of Some Highly Stereospecific Catalytic Systems in Polymerization
Propylene at 70°C.

$p(C_3H_6)$ = 2000 mm. Hg.  Diluting agent = toluene.  Al/Ti = 1.5–2.
Polymerization time 3 hr.

| TiCl₃ Modif. | Metalloorg. compd. | Mean polym. rate, g. polymer/hr. ———————— g. TiCl₃·atm. C₃H₆ | [η] of crude polymer | Extractions | | |
|---|---|---|---|---|---|---|
| | | | | Ether ext., % | Heptane ext., % | Res., % |
| $\gamma$ | $Al(C_2H_5)_2I$ | ~1 | 3.5 | 1 | 1 | 98 |
| $\gamma$ | $Al(C_2H_5)Br$ | ~1 | 4.5 | 2.5 | 2 | 95.5 |
| $\gamma$ | $Al(C_2H_5)_2Cl$ | ~1 | 4.3 | 3 | 4 | 93 |
| $\gamma$ | $N(C_4H_9)_4I$ + $2AlC_2H_5Cl_2$ | ~2 | 5.2 | 0.5 | 1.5 | 98 |
| $\delta$ | $Al(C_2H_5)_2I$ | ~2.5 | 3.1 | 2 | 1 | 97 |
| $\delta$ | $Al(C_2H_5)_2Br$ | ~11.5 | 4.5 | 2 | 2 | 96 |
| $\delta$ | $Al(C_2H_5)_2Cl$ | ~11 | 3.5 | 2 | 4 | 94 |
| $\delta$ | $N(C_4H_9)_4I$ + $2AlC_2H_5Cl_2$ | ~6 | 3.5 | 0.5 | 2.5 | 97 |
| $\delta$ | $NH(C_2H_5)_2$ + $2AlC_2H_5Cl_2$ | ~4 | 4.1 | 2 | 5 | 93 |
| $\delta$ | $N(C_4H_9)_4Br$ + $2AlC_2H_5Cl_2$ | ~3 | 4.5 | 1 | 4 | 95 |
| $\alpha$ | $Be(C_2H_5)_2$ | ~22 | 3.0 | 2.5 | 3.5 | 94 |

$\delta$-TiCl₃ contains 4.5% Al present as AlCl₃ in solid solution.
$\gamma$-TiCl₃ contains 1% Al present as AlCl₃ in solid solution.
$\alpha$-TiCl₃ does not contain Al.

depend on polymerization time; the values reported are therefore only indicative.

## Interpretation of Results

The results obtained when comparing the different modifications of TiCl₃ with or without AlCl₃ in solid solution, may be interpreted on the basis of the results obtained by x-ray examination, as carried out in this Institute[5] and described in more detail in another article in this issue.[6] We found that actually all the violet TiCl₃ forms show lattice layers of the same type, the Ti atoms having a coordination number of 6. All violet TiCl₃ modifications are different from brown TiCl₃ ($\beta$-modification), which can be considered as a linear polymer of TiCl₃. The differences among the various violet modifications are due to the mode of packing of bidimensional layers in the tridimensional lattice. AlCl₃, at least in the concentrations that correspond to those observed in the samples examined by us, is present in a solid solution with TiCl₃; it causes only a contraction of the lattice constants, without other alterations of the lattice structure. This occurs in all three ($\alpha$, $\gamma$, and $\delta$) violet modifications of TiCl₃ studied by us.

We have thus confirmed the hypothesis of previous[10,14] papers—that the active centers are prevailingly formed on the borders of each layer. These layers, considered in themselves, are identical in all three violet modifications: it follows that all the active centers are of the same type. This structural identity of layers in the case of chemisorption of the same metalloorganic compound gives active centers of the same type having, in practice, the same stereospecificity, whereas stereospecificity changes in the same way for all the violet modifications when varying the chemisorbed metalloorganic compound.

In previous papers it was observed that this adsorption caused by the coordinating properties of the transition metal gives rise to phenomena of epitaxy, owing to which the metal of the metalloorganic compound, e.g., Al, is placed in positions structurally equivalent to those assumed by Ti in the layer lattice.

The different behavior of brown $TiCl_3$ ($\beta$-modification) from violet $TiCl_3$ is due to its different structure, which is not a layer structure. In previous works carried out in this Institute,[6,15] in fact, it was demonstrated that brown $TiCl_3$ may be considered as a linear inorganic polymer in which the coordination of the Ti atoms along the chain axis is assured by three chlorine atoms. This emphasizes the importance of the nature of the crystalline sublayer, constituting the catalytic system, on stereospecificity in the polymerization of $\alpha$-olefins to isotactic polymers.

## EXPERIMENTAL

### Apparatus and Procedures

Polymerization runs were carried out in autoclaves operating at constant temperature and pressure, with the aid of apparatus and procedures already described in other papers.[10,12]

### Reagents

*Solvents.* The hydrocarbon solvents used as diluting agents were pure commercial products, which were dehydrated by refluxing on sodium for 24 hr. The products thus treated were subsequently distilled.

*Monomers.* Propylene and 1-butene were furnished by Montecatini. The propylene was over 98% pure and 1-butene over 95% pure. Impurities were substantially propane in propylene and *n*-butane and 2-butene in the 1-butene. Appreciable amounts of acetylene or allene hydrocarbons were not present.

*Titanium trichloride—$\alpha$-$TiCl_3$.* We used two types of violet titanium trichloride ($\alpha$-modification). The samples of the first type, supplied by Stauffer Co. and by Montecatini, were obtained by reduction of $TiCl_4$ with $H_2$ at high temperature; some samples were tested after grinding. The samples of the second type (Montecatini) were obtained by reduction of $TiCl_4$ with Al at high temperature, following the method of Ruff and Neu-

mann. These samples of $\alpha$-TiCl$_3$ contained 4.5% aluminum present as AlCl$_3$ in solid solution.

Before use, $\alpha$-TiCl$_3$ was washed under nitrogen atmosphere by extraction in a Kumagawa extractor with anhydrous toluene. To the toluene in the extractor were added amounts of triethylaluminum sufficient to fix the soluble impurities (substantially chloride and oxychloride of tetravalent titanium, contained as impurity in stored TiCl$_3$). TiCl$_3$ was considered clean when it did not color toluene yellow.

*$\gamma$-TiCl$_3$.* We prepared $\gamma$-TiCl$_3$[8] by reducing TiCl$_4$ at 180–200°C. by means of Al(C$_2$H$_5$)$_3$, and operating with Al/Ti = 1 ratios, in petroleum oil as diluting agent. The reaction product, after cooling, was diluted in anhydrous toluene, and the whole product was filtered on a porous plate. The precipitate, comprised, substantially, of TiCl$_3$ and AlCl$_3$ in solid solution, was thoroughly washed with anhydrous toluene, then rapidly washed with absolute ethyl ether, then with toluene again, and finally with petroleum ether. Then a first drying under vacuum was performed on the porous plate; subsequently the dry TiCl$_3$ was placed in a large test tube, and a more accurate drying under the vacuum at 120–140°C. was performed. $\gamma$-TiCl$_3$ thus obtained was stocked in anhydrous toluene under nitrogen atmosphere. All the samples contained at least 1% aluminum.

*$\delta$-TiCl$_3$.* Montecatini and Stauffer furnished samples of $\delta$-TiCl$_3$ that did and did not contain Al. Samples with Al contained $\sim$4.5% Al as AlCl$_3$ in solid solution. The product, before being employed, was washed by us with anhydrous toluene.

*Metal alkyls.* Triethylaluminum was obtained by exchange between triisobutylaluminum and ethylene in the presence of nickel.[16] The other aluminum alkyls (mono-/or dihalides) were obtained by dissolution at 70–80°C. of stoichiometric amounts of the corresponding anhydrous trihalides of aluminum in triethylaluminum, and subsequent distillation of the product. The purity of the starting triethylaluminum (used in the preparation of aluminum halides) measured by potentiometric analysis[17] was more than 92%. Aluminum monoethyl dichloride was obtained in the crystalline state.

The reaction of monoalkyl dihalides of aluminum with electron donor substances or with "onium" salts was carried out each time by placing the reagents into direct contact with each other or in the presence of a small quantity of solvent, in suitable stoichiometric ratios, and subsequently heating to 50°C.

Beryllium diethyl was prepared by exchange between diethyl magnesium bromide and beryllium chloride in ether.[18]

### Fractionation of Polymers and Determinations of Molecular Weights

The fractionation of polymers was carried out by extractions with solvents at the boiling temperature, in Kumagawa extractor, maintained in nitrogen atmosphere. The extraction with each solvent was made on about 5 g. of polymer and carried on until exhaustion.

Molecular weight was determined in a solution of tetralin at 135°C. by means of a Desreux-Bischoff viscometer, applying the formula[19]:

$$[\eta] = 1.75 \times 10^{-4} \times \overline{MW}^{0.74}$$

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## Synopsis

The highly stereospecific catalytic systems for the polymerization of α-olefins have been compared. These are obtained starting either from the α, γ, or δ modifications of violet TiCl₃ with or without AlCl₃ present in solid solution, and from aluminum diethyl monohalides, or from metalloorganic products obtained by reacting two molecules of aluminum monoalkyl dihalide with one molecule of particular electron donor compounds. The catalytic systems considered polymerize propylene, giving rise to crude polymers containing 90 to 100% isotatic propylene (nonextractable in boiling n-heptane) for a wide range of polymerization temperatures. By fractionation of crude polymers prepared with the use of these catalytic systems, highly isotactic polypropylenes, having a melting temperature up to 177°C., have been separated. The results, correlated with those obtained in x-ray determinations of the structure of the modification of TiCl₃ used, demonstrate that the stereospecificity of all the catalytic systems examined is independent of the particular type of violet modification (α, γ, or δ), whether or not these contain aluminum as AlCl₃ in solid solution. This proves that the single active centers are substantially of the same type; a variation in their number causes only a variation of the overall polymerization rate.

## Résumé

On a comparé entr'eux les systèmes catalytiques hautement spécifiques pour la polymérisation des α-oléfines. Ceux-ci sont obtenus au départ des variétés α, γ ou δ du TiCl₃ violet avec ou sans AlCl₃ présent dans la solution solide, et au départ de diéthylhalogénoaluminium, ou au départ de produits organométalliques obtenus par réaction de deux molécules d'alcoyl-dihalogéno-aluminium avec une molécule d'un composé électrodonneur particulier. Les systèmes catalytiques considérés polymérisent le propylène en donnant des polymères bruts contenant de 90 à 100% de polypropylène isotactique (non-extractible à l'heptane-n bouillant) et cela sur une large échelle de température de polymérisation. Par fractionnement des polymères bruts préparés au moyen de ces systèmes, on a pu isoler un polypropylène hautement isotactique, fondant à 177°C. Ces résultats, mis en corrélation avec ceux obtenus au dépens des déterminations au rayons-X concernant la structure de la variété du TiCl₃ utilisé, démontrent que la stéréospécificité de tous ces systèmes catalytiques est indépendante du type particulier de la variété violette (α, γ ou δ), ou de ce qu'elle contient ou ne contient pas d'aluminium tel AlCl₃ dans la solution solide. Ceci prouve que les centres actifs sont en substance du même type; une variation de leur nombre entraine uniquement une modification de la vitesse de polymérisation globale.

## Zusammenfassung

Ein Vergleich der hochgradig stereospezifischen Katalysatorsysteme für die Polymerisation von α-Olefinen wurde durchgeführt, die entweder ausgehend von der α, γ oder δ-Modifikation des violetten TiCl₃ mit oder ohne in fester Lösung vorhandenem AlCl₃ und von Aluminiumdialkylmonohaliden oder ausgehend von metallorganischen Produkten aus der Reaktion zweier Moleküle Aluminiummonoalkyldihalid mit einem Molekül spezieller Elektronendonorverbindungen erhalten wurden. Diese katalytischen Systeme polymerisieren Propylen und ergeben in einem grossen Temperaturbereich Rohpolymere mit einem Gehalt von 90 bis 100% isotaktischem Propylen (in kochendem n-Heptan nicht extrahierbar). Durch Fraktionierung des so hergestellten Rohpolymeren wurde hochgradig isotaktisches Polypropylen mit einer Schmelztemperatur bis zu 177°C erhalten. Diese Ergebnisse zeigen in Verbindung mit den bei der röntgenologischen Strukturbestimmung der verwendeten TiCl₃-Modifikation erhaltenen, dass die Stereospezifität aller untersuchten katalytischen Systeme unabhängig vom speziellen Typ der violetten Modifikation (α, γ oder δ) ist, gleichgültig, ob sie Aluminium als AlCl₃ in fester Lösung enthalten oder nicht. Dies beweist, dass die einzelnen aktiven Zentren im wesentlichen von gleichem Typ sind; Änderung ihrer Anzahl verursacht lediglich eine Änderung der Bruttopolymerisationsgeschwindigkeit.