*Stereoregular Polymers. I. Polymerization of Styrene by Triethylaluminum-Titanium Tetrachloride Catalysts**

By Shunsuke MURAHASHI, Shun'ichi NOZAKURA, Masao SUMI
and Kōichi HATADA

(Received November 17, 1958)

Much information is now accumulating in regard to the isotactic polymerization of α-olefins. In particular, the reports of Natta and his collaborators[1] are very instructive about the mechanisms of stereospecific polymerization of propylene. These experiments, however, are mainly based on the heterogeneous catalysts composed of triethylaluminum ($AlEt_3$) and titanium trichloride ($TiCl_3$) (Natta's type). Catalysts derived from $AlEt_3$ and $TiCl_4$ (Ziegler's Type) have not been examined in detail mainly because of their poor reproducibility. Recently, Yamazaki has reported some aspects of polymerization of styrene with this type of catalysts[2].

The authors carried out the polymerization of styrene with the heterogeneous catalysts prepared from $AlEt_3$ and $TiCl_4$, and found that the stereospecificity of the catalysts varied very much with the method of preparation of catalytic mixtures.

The object of the present work is to investigate the relationship between property and stereospecificity of the catalysts.

Results and Discussion

Effect of Preparative Conditions of Triethylaluminum-Titanium Tetrachloride Catalysts upon the Stereospecificities of the Catalysts.— Even in the catalysts of the same ratio of $AlEt_3$ to $TiCl_4$ the stereospecificities of the catalytic mixtures varied intensively according to the method of mixing the two components. Some of the experimental data are listed in Table I.

When $AlEt_3$ and the monomer were charged before the introduction of $TiCl_4$, the stereospecificity was very low, and this is probably due to the cationic polymerization with $TiCl_4$. There was only a small difference between two kinds of catalysts that were prepared under the reverse orders of addition of $AlEt_3$ and $TiCl_4$. A very pronounced effect was observed when the catalysts were prepared with or without stirring. In some cases ultrasonic wave was applied in order to effect an efficient agitation. The catalyst that was prepared without stirring had an appearance of solid mass and was colored orange-brown. Such a catalyst yielded a high stereospecificity. When, on the other hand, the catalyst was prepared under mixing, it was a fine black powder and showed a poor stereospecificity. An explanation for this difference will be given later.

Influence of the Ratio of Triethylaluminum to Titanium Tetrachloride. — Preparation of catalysts and polymerization were carried out under stirring by magnetic stirrer. Yields of the atactic and the isotactic polystyrene polymerized on varying the ratios of $AlEt_3$ to $TiCl_4$ are shown in Fig. 1.

The yield of atactic polystyrene decreased rapidly up to the molar ratio (r) of unity and remained almost constant at

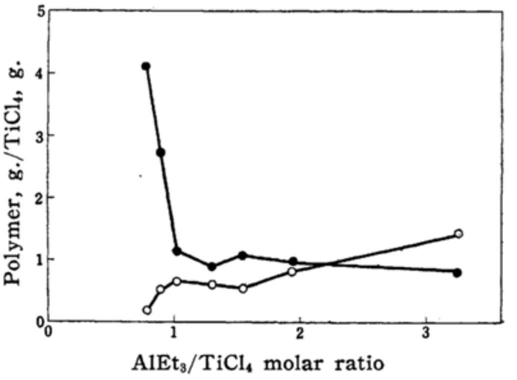


Fig. 1. Polymerization of styrene with Ziegler catalysts.
○ Isotactic polystyrene
● Atactic polystyrene

---

* Part of this work was presented at the 10th Meeting of the Chemical Society of Japan, Tokyo, April 6, 1957.

[1] G. Natta, I. Pasquon and E. Giachetti, *Angew. Chem.*, **69**, 213 (1957); *Makromol. Chem.*, **24**, 258 (1957).

[2] N. Yamazaki, *Chem. of High Polymers* (*Kōbunshi Kagaku*), **15**, 49 (1958).

TABLE I. POLYMERIZATION OF STYRENE WITH $AlEt_3$-$TiCl_4$ CATALYSTS PREPARED UNDER VARIOUS CONDITIONS

$TiCl_4$ 0.20 g., *n*-Heptane 15 ml.
$AlEt_3$ 0.36 g., Styrene 5.00 ml.

No.	Preparation of catalysts		Temp., °C	Time, hr.	Conversion, %	Insoluble part in M.E.K., %[c]
	The order of addition	Agitation				
1	Monomer-$AlEt_3$-$TiCl_4$	Stirring[a]	70	4	27.4	23
2	$AlEt_3$-$TiCl_4$-Monomer	Without stirring	70	3	28.0	84
3	〃	Without stirring	15	3	5.2	66
4	〃	Stirring	70	4	15.8	60
5	〃	Stirring and ultrasonic wave[b]	70	4	18.4	39
6	$TiCl_4$-$AlEt_3$-Monomer	Without stirring	70	4	19.5	81
7	〃	Stirring	70	4	7.9	64
8	〃	Stirring and ultrasonic wave[b]	70	4	13.3	4.4

a) Stirring was carried out by a magnetic stirrer.

b) After mixing by a magnetic stirrer, ultrasonic wave (450 KC, ca. 2W./cm^2) was applied for about ten minutes.

c) The percentage fraction of extraction residue with hot methylethylketone in total polymer.

increasing ratios. On the other hand, the yield of isotactic polymer showed a small but gradual increase over the whole range examined.

The high content of atactic polymer that was formed in a condition $r<1$ may reasonably be ascribed to the existence of remaining $TiCl_4$. Furthermore, the appearance of a break on the atactic curve in Fig. 1 seems to indicate the disappearance of $TiCl_4$ and the appearance of another kind of catalyst which also promotes the atactic polymerization of styrene with minor activity, and this kind of catalyst may probably be soluble complex compounds containing titanium and aluminum.

Valency States of Titanium in Catalytic Mixtures.—The reaction between $AlEt_3$ and $TiCl_4$ may be considered to be analogous to that of Grignard's reagent on alkyl orthotitanate[3]. Therefore, the reaction scheme may be written in the following manner:

Alkylation (fast)

$$Et_3Al + TiCl_4 \rightarrow EtTiCl_3 + Et_2AlCl \qquad (1)$$

$$Et_3Al + EtTiCl_3 \rightarrow Et_2TiCl_2 + Et_2AlCl \qquad (2)$$

Decomposition (slow)

$$EtTiCl_3 \rightarrow Et\cdot + TiCl_3 \qquad (3)$$

$$Et_2TiCl_2 \rightarrow 2Et\cdot + TiCl_2 \qquad (4)$$

The alkylation reaction may be fast and the decomposition which yields titanium of lower valencies may be comparatively slow.

In order to elucidate the results obtained above, the distribution of the valency states of titanium in catalysts was examined. When $AlEt_3$ and $TiCl_4$ was mixed to produce a heterogeneous catalyst, a gas evolved. According to the gas chromatographic analysis, the gas consisted of a large portion of ethane and small portions of butane and hydrogen. Ethane might be derived from the disproportionation reaction of ethyl radical which occurred in reactions 3 and 4. Ethylene, which is another procuct of disproportionation, was not found. It probably had polymerized in this condition.

On the other hand, the gas, which evolved when the solid catalyst was decomposed by dilute sulfuric acid, was found to be composed mainly of ethane and hydrogen, a small amount of butane, and a trace of ethylene. Ethane might be derived from the hydrolysis of ethyl-metal bond in the catalyst mixture. Hydrogen can be assumed to evolve according to the following reaction[3]:

$$Ti^{2+} + H_2O \rightarrow Ti^{3+} + \frac{1}{2}H_2 + OH^- \qquad (5)$$

Therefore, the amount of hydrogen was measured volumetrically by absoption with colloidal palladium and one mole of hydrogen was assumed to be equivalent to two moles of divalent titanium. The total trivalent titanium in the hydrolyzate was then determined by redox titration with ceric sulfate. The results are given in Table II. As expected, the catalyst which was prepared in a condition $r=1$

---

[3] D. F. Herman, W. K. Nelson, *J. Am. Chem. Soc.*, **75**, 3877, 3882 (1952).

TABLE II. VALENCY STATES OF TITANIUM IN SOLID CATALYSTS

The catalysts were prepared at 70°C in 15 ml. of *n*-heptane from 0.37 g. of $\mathrm{AlEt_3}$ and the appropriate amount of $\mathrm{TiCl_4}$.

$\mathrm{AlEt_3/TiCl_4}$ molar ratio	Preparation of catalyst	Gas evolved		Ti(IV) %	Ti(III) %	Ti(II) %
		When catalyst was prepared, ml.	When catalyst was decomposed, ml.[c]			
1.09	Stirring[a]	41	65	2	98	0
2.44	Stirring[a]	30	116	0	35	65
2.74	Stirring[a]	30	113	0	23	77
2.51	Without stirring[b]	13	133	4	80	16

a) $\mathrm{TiCl_4}$ and $\mathrm{AlEt_3}$ were added in this order under stirring by a magnetic stirrer.

b) Catalyst components were added in the order of $\mathrm{AlEt_3}$ and $\mathrm{TiCl_4}$ without stirring.

c) Decomposition was carried out about half an hour after preparation of the catalyst, when evolution of gas had almost entirely ended.

TABLE III. POLYMERIZATION AFTER WASHING THE SOLID CATALYSTS

Styrene (5.00 ml.) was polymerized for 3.0 hr. at 70°C without stirring.

No.	Preparation of catalyst[a]			$\mathrm{AlEt_3}$ added after washing, g.	Conversion, %	Insoluble part in M.E.K. %
	$\mathrm{TiCl_4}$, g.	$\mathrm{AlEt_3}$, g.	Temp., °C			
1	0.44	0.33	70	0.33	28.7	91
2[b]	0.45	0.33	b. p. of *n*-heptane	0.34	33.3	90
3	0.45	0.13	b. p. of xylene[c]	0.33	27.3	92
4	0.40	0.33	b. p. of *n*-heptane	0	79.4	Trace
5	0.23	0.33	b. p. of *n*-heptane	0	45.5	17
6[d]	0.44	0.32 0.32	b. p. of *n*-heptane	Without washing	32.7	86
7[e]	0.44	0.67	70	0.32	2.4	65

a) Generally heterogeneous catalysts were prepared in 15 ml. of *n*-heptane under stirring by a magnetic stirrer. $\mathrm{TiCl_4}$ and $\mathrm{AlEt_3}$ were added in this order.

b) Polymerization time was 3.2 hr.

c) Xylene wae used as solvent for preparing the catalyst. The catalyst was washed with *n*-heptane as usual, and then the polymerization was carried out in *n*-heptane.

d) $\mathrm{AlEt_3}$ (0.32 g.) was added dropwise into the solution of $\mathrm{TiCl_4}$ at the boiling temperature of *n*-heptane and the mixture was refluxed for ten minutes and kept for one hour at room temperature, and then the remaining half (0.32 g.) of $\mathrm{AlEt_3}$ and monomer was added at 70°C.

e) The order of adding two components was reversed. Into 0.67 g. of $\mathrm{AlEt_3}$ was added $\mathrm{TiCl_4}$ rapidly under stirring at 70°C and the black, fine precipitate was washed with *n*-heptane and the polymerization was carried out as usual with the secondary addition of $\mathrm{AlEt_3}$ and monomer.

contained a small amount of tetravalent titanium, which is responsible for a relatively large amount of atactic polymer. The catalyst, in which r is more than unity, was found to be mainly composed of divalent and trivalent titanium. The reduction of titanium over trivalent state does not seem to have a marked effect upon stereospecificity. In fact, the catalyst that was prepared without agitation, although it included a certain amount of tetravalent titanium and a large amount of trivalent titanium, showed a good stereospecificity and a good catalytic activity.

Influence of Washing the Solid Catalyst.—In order to remove the soluble catalysts which were considered to be responsible for the atactic polymerization, catalyst mixtures were washed with *n*-heptane by decantation and then polymerizations were carried out with or without addition of further $AlEt_3$. Experimental data are summarized in Table III.

Without the secondary addition of $AlEt_3$ after washing only amorphous polystyrene was obtained, while with its addition the catalyst acquired a very high stereospecificity and also good catalytic activity. However, when $TiCl_4$ was reduced gradually by an equivalent amount of $AlEt_3$ and then an additional equivalent amount of $AlEt_3$ and styrene was added, a good result was obtained (Table III, No. 6).

The catalyst which was prepared by adding $TiCl_4$ to 2.5 times on molar base of $AlEt_3$ under stirring showed a very poor catalytic activity even after washing (Table III, No. 7).

The results seem to suggest the importance of the physical nature of solid catalyst. This subject will be discussed in detail in the later part of this paper.

Recently similar experiments were described in a patent publication where the catalyst was filtered through a glass filter and the effect of filtration was explained there to be due to the removal of the finely dispersed parts of the catalyst[4].

X-ray Study of Solid Catalysts.—The solid catalysts, which were prepared in similar manners to those of Tables I and II, were washed with *n*-heptane and sealed in a small ampoule with a thin wall (Fig. 2), and then exposed to X-ray. It was found in general that the more stereospecific and active catalyst showed the sharper diffraction pattern. X-ray photographs of the catalysts prepared under various conditions are shown in Fig. 3. In the case of the catalyst that was prepared by dropping $TiCl_4$ quickly into the solution of 2.5 mol. equivalents of $AlEt_3$ at 70°C under agitation, there was found no crystalline reflection but a diffuse halo. Such a catalyst had a poor stereospecificity and catalytic activity.

Fig. 2. A capillary ampoule for the X-ray study.

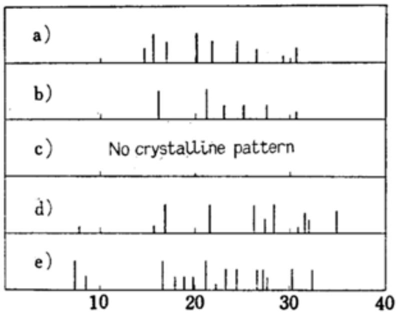


Fig. 3. X-ray powder patterns of catalytic masses (CuKα radiation).
a) $TiCl_4$ (1 mol. equivalent) was added into $AlEt_3$ (2.3 mol. equivalents) at 70°C without agitation.
b) $AlEt_3$ (1 mol. equivalents) was added to $TiCl_4$ 1 mol. equivalent) at 70°C under agitation.
c) $AlEt_3$ (2.3 mol. equivalents) was added quickly into $TiCl_4$ (1 mol. equivalent) at 70°C under agitation.
d) $TiCl_3$, the product of Stauffer Chem. Co.
e) $TiCl_2$[6].

On the contrary, when either (a) 1 mol. equivalent of $TiCl_4$ was added into 2.4 mol. equivalents of $AlEt_3$ without agitation or (b) 1 mol. equivalent of $AlEt_3$ into the solution of 1 mol. equivalent of $TiCl_4$ under agitation, the solid mass showed moderately crystalline reflections. These reflections are rather diffuse as compared with that of commercial $TiCl_3$, indicating an imperfect growth of the crystals. The reflections coincide with neither that of $TiCl_3$[5] nor that of $TiCl_2$[6]. This fact might suggest the existence of some crystalline complex compound containing Al and Ti or another modification of $TiCl_3$ and $TiCl_2$[7].

The solid mass prepared by method a showed a good stereospecificity and catalytic activity. But in the case of the catalyst b, also good results were obtained

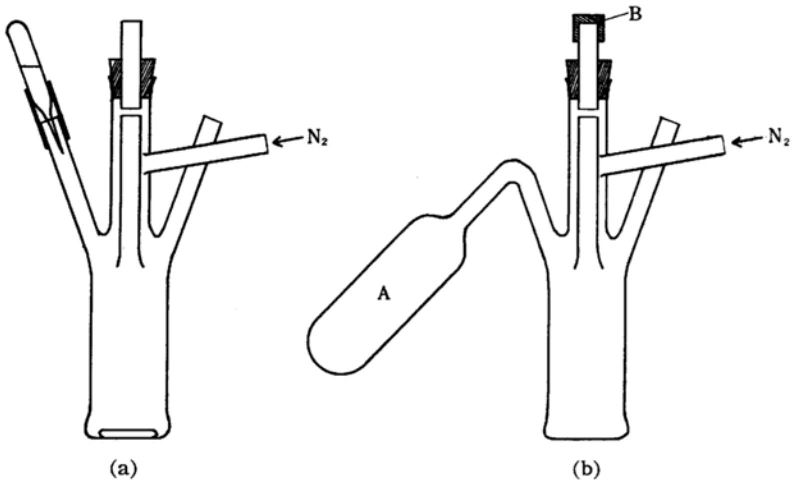
---

[4] S. G. Montecatini and K. Ziegler, Irish Pat., 66,855 (1955).

[5] W. Klemm and E. Krose, *Z. anorg. u. allgem. Chem.*, **253**, 218 (1947).

[6] M. Farber, A. J. Darnell and F. Brown, *J. Chem. Phys.*, **23**, 1556 (1955).

[7] F. Böck and L. Moser, *Monatsch.*, **34**, 1825 (1913). The existence of two modifications of $TiCl_3$ was first suggested by Böck and Moser in the study of the heat of solution. Two kinds of $TiCl_3$ were described by them to be violet colored and brown. The violet is the one that is obtaind by reduction of $TiCl_4$ at high temperture and is now available commercially.



(a) (b)

Fig. 4. Vessels for the polymerization.

by washing with *n*-heptane. (Table III, No. 1—3). Although both the catalysts (a and b) gave the crystalline patterns, they showed some differences in details of X-ray diagram. Further study of this point would be necessary, but was not pursued.

Conclusion

Titanium tetrachloride, ethylaluminum chlorides, soluble aluminum-titanium complex compounds, and amorphous insoluble solid are conceivable for the formation of atactic polymer. Titanium tetrachloride is the one that remained unreacted when the molar ratio of $AlEt_3$ to $TiCl_4$ did not exceed unity. The others are considered to be formed by the reaction between $AlEt_3$ and $TiCl_4$. Although the first three can be removed by washing with *n*-heptane, the last one can not.

The content of the crystalline component in solid mass depends upon the condition of reaction between $AlEt_3$ and $TiCl_4$. If the alkylation of $TiCl_4$ proceeded beyond the stage of $EtTiCl_3$ (or Et_2TiCl_2), the sufficient growth of the crystallites of the compound containing $TiCl_3$ (or $TiCl_2$) could not be expected. Moreover, it is a factor to be considered that some amorphous titanium compound would be produced if the alkylation of the unstable compound containing titanium chlorides occurred preferentially before the sufficient growth of crystallites was permitted.

In order to prepare a crystalline catalytic mass, therefore, it is preferable to use $AlEt_3$ in an amount not more than an equivalent of $TiCl_4$. As shown in the experiments, it may be a convenient method for obtaining a crystalline catalytic mass to combine the solutions of two reactants without agitation.

It is noteworthy that the crystalline component of the effective solid catalyst is neither $TiCl_3$ nor $TiCl_2$, and is probably some complex compound containing Al and Ti or the other modification of $TiCl_3$ (or $TiCl_2$). The fact seems to be one of the important differences between catalysts of Ziegler's type (i. e., $AlEt_3$ and $TiCl_4$) and Natta's type (i. e., $AlEt_3$ and $TiCl_3$).

Experimental

Meterials. — Commercial styrene was washed with 10% solution of sodium hydroxide and water, dried over calcium chloride, and distilled in a nitrogen stream before use[8].

n-Heptane was shaken with fuming sulfuric acid, washed with water and dilute alkali, dried over calcium chloride, distilled and stored over sodium chips.

$AlEt_3$ was the product of Mitsui Chem. Ind. Co. and was used as 30% solution in *n*-heptane. Concentration was checked by the amount of ethane evolved when the solution was hydrolyzed.

$TiCl_4$ was the product of Osaka Titanium Co. and used as 21% solution in *n*-heptane. The concentration was checked by determining titanium by redox titration with ceric solution after reduction with zinc amalgam.

Polymerization.—The polymerization vessel is shown in Fig. 4a. *n*-Heptane was placed in the vessel of about 100 ml. capacity and the ampoules of monomer, $TiCl_4$, $AlEt_3$, and a thermometer if necessary were mounted on it through rubber tubings. The air in the apparatus was replaced by dry nitrogen by repeated evacuation and introduction of nitrogen. Then the lower half

---

[8] E. R. Blout and H. Mark, "Monomers", Interscience Publishers, Inc., New York (1949).

of the apparatus was immersed in the thermostat and the contents of the ampoules were dropped in by breaking the top of the ampoule which was previously scratched at the capillar part in order to ease the breaking.

Polymerization was stopped by the introduction of 2 ml. of methanol and 0.3 ml. of concentrated hydrochloric acid and then all the contents were poured onto a large amount of methanol. After standing overnight, the polymer was collected and washed with methanol, and dried.

If the washing of the solid catalyst with *n*-heptane was needed the vessel shown in Fig. 4b was used. The supernatant liquid was decanted into the side flask (A) and 15 ml. of *n*-heptane was injected through a silicone rubber cap (B). The decantation and the injection were repeated three times. The ampoule of $AlEt_3$ now emptied was exchanged with another one in the stream of nitrogen and charged, and then the monomer was dropped in.

Extraction of the Atactic Polymer from the Crude Polymer.—About 0.4 g. of polymer was refluxed with 40 ml. of methylethylketone for several hours. After standing overnight at room temperature, the remaining isotactic polymer was collected, washed with methylethylketone, dried in vacuo at 100°C.

Valency States of Titanium in Catalytic Mixtures.—A gas buret was connected to the reaction vessel of Fig. 4a and an ampoule containing 8 ml. of 10% sulfuric acid was mounted in place of styrene. After the mixing of the catalyst components, 30 to 40 min. was required for almost complete evolution of gas. The reaction vessel was cooled to 0°C and the gas in the vessel was replaced by nitrogen by repeated evacuation and filling. Then the catalyst mixture was hydrolyzed by dropping the aqueous sulfuric acid and the amount of the gas evolved was measured by the gas buret.

An aliquot of the mixed gas was analyzed for hydrogen using colloidal palladium as absorbent.

The hydrolyzed aqueous layer was separated from the organic layer in an atmosphere of carbon dioxide and analyzed for Ti(III) by titration with ceric standard solution using diphenylamine as an indicator. The amount of Ti(III) thus measured was taken as the sum of Ti(II) and Ti(III) in the catalyst mixture. Some of the results are given in Table III.

X-ray Study of Solid Catalyst—The solid catalytic mass was washed with *n*-heptane by decantation, and the slurry of catalyst was brought into a small thin-walled ampoule made of Terex glass (Fig. 2). All the operations were carried out in a nitrogen atmosphere. The ampoule was sealed at A. The solid powder was packed down to the bottom by a centrifuge and exposed to X-ray.

Summary

Styrene was polymerized by the heterogeneous catalysts of Ziegler's type which were prepared under various conditions. The important factors which have pronounced effects on the stereospecificity and the catalytic activity of the mixture are concluded to be the existence of the remaining titanium tetrachloride, ethylaluminum chlorides and some soluble aluminum-titanium complex compounds, and the crystalline nature of the solid catalytic mass. The first three are considered to be responsible for the atactic polymerization of styrene and can be removed by washing with *n*-heptane. The crystallinity of the solid catalyst seems to be necessary for its high stereospecificity and catalytic activity.

The solid catalyst was examined by X-ray. It was found that the crystalline component of the catalyst did not correspond to $TiCl_3$ or $TiCl_2$, and thus it was suggested that some crystalline complex compounds containing Al and Ti or some other modifications of $TiCl_3$ (or $TiCl_2$) would be responsible for the effective catalytic component of Ziegler catalyst. The authors also suggested that the fact might be one of the important differences between the heterogeneous catalysts of Ziegler's type and Natta's type.

The authors wish to thank Mitsui Chem. Ind. Co. for the generous supply of triethylaluminum and Osaka Titanium Co. for titanium tetrachloride. We are also very grateful to Mr. Y. Chatani of Nitta Laboratory who helped us in the experiment of X-ray.

Department of Chemistry
Faculty of Science
Osaka University
Nakanoshima, Osaka