Activity, Stereospecificity, and Structure of Ziegler-Natta Catalysts

Kazuo SOGA

Research Laboratory of Resources Utilization,
Tokyo Institute of Technology, Nagatsuta, Midori-ku, Yokohama 227

(Received February 3, 1987)

This paper summarizes some of our recent fundamental studies of isotactic polymerization of propylene. Based on the results of propylene polymerization with several kinds of one-component catalysts, the origin of polymerization activity is first discussed. The correlation between the oxidation states of titanium and polymerization activities for various olefins is clarified reasonably well from a detailed study of homo- and copolymerizations using a simplified catalyst. The role of MgCl_2 on the enhancement of polymerization activity is also discussed in detail. The effect of internal and external donors in improving catalyst stereospecificity is then discussed; where are also presented the results of propylene polymerization using new types of highly active and isospecific catalysts originally found by Hercules Inc. and modified in our laboratory. A plausible model of isospecific catalytic center is finally proposed on the basis of these results.

1. Introduction

Over three decades have elapsed since the discovery of marvelous Ziegler-Natta catalyst. More than 15,000 papers concerning it and its related subjects have appeared. Tremendous research efforts have further been made to improve this catalyst, and the efforts have yielded new generations of Ziegler-Natta catalysts with superior activity and stereospecificity. Complexities arising from the multiplicity and heterogeneity of the catalyst system, however, have hindered understanding of the catalytic processes which take place on the catalyst surface. Nevertheless, many fundamental features of the catalyst system have now been clarified reasonably well. More recently, a highly active homogeneous catalytic system, which is capable of catalyzing even isotactic polymerization of propylene,¹⁾ has been developed. Isotactic living polymerization of propylene is also realized by using a special heterogeneous catalyst system.²⁾ These new catalytic systems will not only contribute to our understanding of the mechanism of stereospecific polymerization, but also stimulate the development of various kinds of tailored polymers having excellent physical properties. Thus, this subject will be of paramount importance in the de-

velopment of chemical and polymer sciences. The present paper summarizes some of our recent fundamental studies of isotactic polymerization of propylene, with particular attention focused on the nature of the active species in Ziegler-Natta catalysts.

2. Origin of the Polymerization Activity

Transition metal halides usually form heterogeneous active catalysts in the presence of aluminum alkyls. The alkyl-halogen exchange forms an unstable alkyl derivative of the transition metal which decomposes to yield a lower valence halogenide and an alkane-alkene mixture. The degree of reduction of the transition metal is strongly dependent on the nature and concentration of the reagent as well as on reaction time and temperature.³⁾ Thus, the study of these catalyst systems is hindered by complication and variety of the reactions taking place during the interaction of aluminum alkyls with the transition metal halides.

From this point of view, one-component catalysts, which cause polymerization without a cocatalyst, have been investigated for the study of the detailed mechanism of olefin polymerization. Brief reviews of these studies have been presented by some authors.^{4) ~ 7)} Basic types of such one-

component catalysts are (a) supported oxides, (b) organometallic compounds of transition metals, and (c) subhalides of transition metals, especially, titanium halides which are activated by ball milling, γ -irradiation or additives. Yashima et al.⁸⁾ found previously that Cr-Y zeolite catalysts initiate polymerization of ethylene.

We have found that titanium ion-exchanged Y-zeolite catalysts which were prepared by ion exchange of the Na form of Y-zeolite with Ti^{3+} or Ti^{4+} in an aqueous solution of $\text{Ti}_2(\text{SO}_4)_3$ or that of $\text{Ti}(\text{SO}_4)_2$, initiated isotactic polymerization of propylene without any additive.⁹⁾ These catalysts contain neither Ti-alkyl bonds nor Cl ligands, and therefore seem to be the simplest in composition among the one-component catalysts reported so far. The result has led to the important conclusion that only titanium ion (Ti^{3+} or Ti^{4+} in these cases) is necessary to give the activity for olefin polymerization. However, the activities of these catalysts were very low owing to the extremely small pores of Y-zeolite used as the support.¹⁰⁾ We have prepared various kinds of one-component catalysts, and the results of propylene polymerization with those catalysts are summarized in **Table 1**.¹¹⁾

The polymerization activity depends drastically on the carrier as well as on titanium compounds. For instance, the activity of the $\text{Ph}_3\text{SiOTiCl}_2/\text{SiO}_2$ catalyst is about 100 times higher than that of the $\text{TiCl}_3/\text{SiO}_2$ catalyst. It is considered that $\text{Ph}_3\text{SiOTiCl}_2$ is supported highly dispersed on SiO_2 , while the major part of the TiCl_3 remains as small particles. Such particles should be inactive because of the difficulty in coordinating an olefin monomer with the titanium ion which is sterically

disturbed by the Cl ligands. Thus, the marked difference in activity between the two catalysts may reflect the degree of dispersion of the titanium compounds on SiO_2 .

3. Correlation between Oxidation States of Titanium and Activity of Olefin Polymerization

During recent years, the copolymerization of ethylene with higher olefins (LLDPE) or with propylene (EPM) has aroused a great interest, and industrial efforts have been directed toward finding novel and more efficient catalysts for the synthesis of desired copolymers. It is well known that copolymer composition strongly depends on the transition metal component and sometimes on the metal alkyl component. This clearly indicates that variability in the active sites plays an important role in determining the composition of the copolymer. However, our fundamental knowledge of the true nature of the active sites is still imperfect due mainly to the complexity of the catalytic systems.

From such a viewpoint, we have prepared a simple catalyst and investigated the correlation between oxidation states of titanium and activities of various olefins.¹²⁾ The catalyst was prepared by reacting TiCl_4 with the surface hydroxyl groups of $\gamma\text{-Al}_2\text{O}_3$ in heptane. The fractions of (1) and (2) were 76% and 24%, respectively, estimated from the reaction of ZnEt_2 with the same $\gamma\text{-Al}_2\text{O}_3$.¹⁰⁾ As reported by Chien et al., (2) is not reduced even in the presence of an aluminum alkyl. The catalyst was then thermally reduced at 800°C for 4 h under reduced pressure to obtain (3). Catalyst (1) did not show any activity for olefin polymerization because of the difficulty of olefin

Table 1 Results of Propylene Polymerization using One-component Catalysts^{a)}

Carrier	Ti-Compound	Preparative Method	Activity (g-PP/g-Ti·h)	I. I. ^{b)} (%)
Y-Zeolite	TiCl_3	Ion exchange	0.0088	—
"	"	"	3.50 (ethylene)	—
"	$\text{Ti}_2(\text{SO}_4)_3$	"	0.0090	63
"	$\text{Ti}(\text{SO}_4)_2$	"	0.0034	54
Al_2O_3	TiCl_4	Reaction ^{c)}	12.3	56
SiO_2	TiCl_3	Co-milling	2.09	60
Al_2O_3	"	"	0.61	44
SiO_2	"	Impregnation	6.49	50
"	$\text{Ph}_3\text{SiOTiCl}_2$	"	230	63
MgCl_2	"	"	1,300	45
$\text{MgCl}(\text{OH})$	"	"	4,600	54

^{a)} Polymerization was carried out at 65°C in a 0.1 dm^3 stainless steel reactor by using 0.30 mol of propylene and 0.005 dm^3 of heptane.

^{b)} Determined by IR

^{c)} TiCl_4 was reacted with the surface OH groups of metal oxides followed by thermal reduction at 800°C for 4 h.

coordination with the titanium ion as described above. However, thermally reduced catalyst (3) initiated the polymerization of various monomers in the absence of cocatalyst. Homopolymerizations of various olefins were carried out at 40–60°C in heptane with catalyst (3) using AlEt₃ as a reducing reagent. With an increase in the concentration of the cocatalyst, the activity for propylene, 1-butene, 1-hexene, 1,3-butadiene etc. markedly decreased, whereas the activity for ethylene increased slightly. These results suggest that both the Ti³⁺ and Ti²⁺ species be active for ethylene, while only the Ti³⁺ species be active for the other olefins.

To obtain a better insight into this point, copolymerizations of ethylene with propylene, 1-hexene, and 1,3-butadiene were conducted under similar conditions, and the polymers obtained were analyzed by ¹³C NMR. Structures of the polymers were found to change drastically with increasing concentration of cocatalyst from random copolymers to polyethylene. Copolymerization of propylene and 1-butene was then examined by using the TiCl₄-Mg(C₆H₁₃)₂ catalyst.¹⁴⁾ ESR measurements were also made on the catalytic system. In Fig. 1 are summarized the results, which indicate that the activity is approximately proportional to the concentration of Ti³⁺ species (*g*-value = 1.983, which can be assigned as Ti³⁺ with alkyl groups attached¹⁵⁾), and that the composition of the copolymer remains unchanged.

It is well known that the activity of propylene polymerization usually decreases substantially during the course of polymerization. By using the activated TiCl₃ catalyst combined with AlEt₃, Ambroz et al.¹⁶⁾ found previously that a considerable amount of Cl⁻ is extracted from the TiCl₃ during polymerization and proposed a rate equation for the Cl⁻ extraction. More recently, we have come to notice that the equation is identical with the one¹⁷⁾ we have previously proposed for the

Copolymerization was conducted at 40°C for 1 h at an initial total pressure of 532 mbar using 0.20 mmol of TiCl₄ in 0.02 dm³ of heptane
 (●) ; activity, (◐) ; 1-butene content
 (○) ; relative intensity of Ti³⁺

Fig. 1 Dependences of Activity, 1-Butene Content in Copolymer and Relative Intensity of Ti³⁺ Species on the Concentration of Mg(C₆H₁₃)₂

deactivation process of propylene polymerization with the same catalyst system. The identity of the equations strongly indicates that Cl⁻ extraction from the surface of TiCl₃ causes the reduction of the active Ti³⁺ species to an inactive species of lower valence.¹⁸⁾ Kashiwa et al. have recently examined the change in the valency state of titanium in the MgCl₂-supported Ti catalyst during the course of propylene polymerization, and they have validated the above assumption.¹⁹⁾

These experimental results have led to the important conclusion that both Ti³⁺ and Ti²⁺ species are active for polymerization of ethylene, while only the Ti³⁺ species is active for polymerization of other olefins. This conclusion does not mean that Ti⁴⁺ species is inactive. In fact, in the highly active homogeneous catalysts developed by Kaminsky, it is proposed that the active species be Ti⁴⁺,¹⁾ and our zeolite catalyst containing Ti⁴⁺ actually initiated polymerizations of ethylene and propylene.⁹⁾ Besides, Eisch et al.²⁰⁾ have recently determined, for the first time, the crystal structure of the initial insertion product formed in the polymerization of trimethyl (3,3-dimethyl-1-butynyl) silane, (CH₃)₃CC≡CSi(CH₃)₃, using the Cp₂TiCl₂-CH₃AlCl₂ catalyst in chloroform, where the active titanium is demonstrated to be tetravalent, Cp₂Ti⁴⁺(IV)-CH₃···AlCl₄⁻. In the usual heterogeneous catalysts, however, most of the Ti⁴⁺ species are reduced to lower valencies, i.e., Ti³⁺ and Ti²⁺ by its reaction with the metal alkyls which are used as activators, and the Ti⁴⁺ species becomes less important.

4. Activation of Catalysts

The activity of Ziegler - Natta catalysts for olefin polymerization has been markedly increased by using supported catalysts. A variety of metal halides have been reported as carriers, MgCl_2 being the most common. The first example of such a supported TiCl_4 catalyst dates back to 1955, although the patent gives examples only of ethylene polymerization.²¹⁾ Early Shell patent applications filed in this area in 1960 include the first MgCl_2 - supported TiCl_4 catalyst for propylene polymerization.²²⁾ After these initial patents many other patents followed in the 1960's describing MgCl_2 - supported TiCl_4 catalysts for olefin polymerization. The marked improvement in the polymerization activity by MgCl_2 has been recently clarified by attributing it to the remarkable increase in the propagation rate constant (k_p) as well as to the considerable increase in the number of active species (C^*).^{23) ~ 28)} However, it is still quite open to discussion why MgCl_2 causes peculiarly such a marked increase in k_p .

In considering possible explanation of this effect, it is important to appreciate the variation in k_p with different kinds of carriers. Homogeneous catalytic systems seem to be convenient to appreciate the relative k_p values, since C^* evaluation is very easy. Thus we have carried out propylene polymerization at approximately 40°C in heptane using soluble catalytic systems of $\text{Ti}(\text{OBu})_4$ - AlEt_2Cl - MCl_x ($\text{MCl}_x = \text{MgCl}_2, \text{MnCl}_2, \text{CoCl}_2, \text{NiCl}_2, \text{FeCl}_2, \text{CuCl}_2, \text{AlCl}_3, \text{TiCl}_3, \text{GaCl}_3, \text{HfCl}_4, \text{ZrCl}_4, \text{TaCl}_5$ and NbCl_5 , $[\text{MCl}_x]/[\text{Ti}(\text{OBu})_4] = 6$).²⁹⁾ These catalytic systems gave stationary polymerization rates after a short induction period. The stationary rates changed drastically depending on the electrogenativity (X_i) of the metal ion involved in MCl_x . Generally speaking, the chlorides of metal ions with X_i smaller than that of Ti^{3+} (10.5) acted as accelerators, whereas those with X_i larger than 10.5 functioned as inhibitors.

Similar results were also obtained in the polymerization of ethylene conducted at 30°C in toluene by using the homogeneous catalytic systems of $\text{Cr}(\text{CH}_3\text{COO})_3$ - AlEt_2Cl - MCl_x ,³⁰⁾ $\text{Cr}(\text{C}_{17}\text{H}_{35}\text{COO})_3$ - AlEt_2Cl - MCl_x ,³¹⁾ and $\text{Cr}(\text{OBu})_4$ - AlEt_2Cl - MCl_x .³²⁾

XPS spectra were then recorded on various MCl_x systems as well as on several $\text{TiCl}_4/\text{MCl}_x$ systems, and the results are shown in **Tables 2** and **3**.³³⁾

Table 2 XPS Analysis of MCl_x

Metal Chloride	Binding Energy of Cl_{2p} (ev)	X_i
MgCl_2	200.1	6.0
MnCl_2	200.1	7.5
CoCl_2	200.1	9.0
TiCl_3	200.6	10.5
AlCl_3	200.8	10.5
HfCl_4	200.4	11.7
ZrCl_4	200.8	12.6
TaCl_5	200.5	16.5

Table 3 XPS Analysis of $\text{TiCl}_4/\text{MCl}_x$ Catalyst

Catalyst	Binding Energy of Ti (ev)		X_i
	$\text{Ti}_{2p3/2}$	$\text{Ti}_{2p1/2}$	
$\text{TiCl}_4/\text{MgCl}_2$	459.8	465.4	6.0
$\text{TiCl}_4/\text{MnCl}_2$	459.5	465.3	7.5
$\text{TiCl}_4/\text{AlCl}_3$	460.5	466.0	10.5
$\text{TiCl}_4/\text{ZrCl}_4$	460.5	466.2	12.6

The electron density of $\text{Cl}(2p)$ in MCl_x of $X_i < 10.5$ seems to be considerably richer compared with that of $X_i > 10.5$. Additionally, electron densities of $\text{Ti}(2p)$ of $\text{TiCl}_4/\text{MgCl}_2$ and $\text{TiCl}_4/\text{MnCl}_2$ are also somewhat richer in comparison with those of $\text{TiCl}_4/\text{AlCl}_3$ and $\text{TiCl}_4/\text{ZrCl}_4$.

It has been established that, in the ammonia synthesis reaction, transition metals are activated by alloying them with electropositive metals. For example, Raney Ru prepared from Ru - Al alloy is more active than pure Ru and the alloy is further activated by addition of an alkali metals. Ozaki et al. have developed a theory of promotion in which the activation of Ru is attributed mainly to the increase in electron concentration which simultaneously strengthens the Ru - N bond and weakens the $\text{N}\equiv\text{N}$ bond.³⁴⁾

Our present results may be interpreted in terms of a similar mechanism as described in the following. The MCl_x involved in the active species influences the electronic structure of the active transition metal ion by inductive effects. The use of MCl_x with a smaller X_i causes an increase in the electron density of the active transition metal ion, which stabilizes the coordination of an olefin monomer by the back - donation of electron, resulting in an acceleration of a subsequent insertion of the coordinated monomer into an active transition metal ion - polymer chain bond. In contrast, the electron - withdrawing capability of MCl_x with a larger X_i causes an unfavorable effect on the chain propagation. A possible model³³⁾ is illustrated in **Fig. 2**.

The majority of highly active catalysts reported

Fig. 2 Plausible Model of MCl₄-promotion of Ti³⁺

so far has been prepared by supporting the titanium species on the surface of MgCl₂. Union Carbide Corp., on the other hand, has developed a new type of catalyst containing smaller amounts of chloride by supporting both titanium compound and MgCl₂ on a solid carrier.³⁵⁾ Besides the industrial importance of eliminating the catalyst-removal process, the catalyst seems to give us useful information as to why MgCl₂ markedly accelerates *k_p*.

In this connection, we have prepared similar catalysts with varying molar ratios of Mg to Ti³⁶⁾ and examined the difference in the activity for propylene polymerization. The catalysts were prepared according to the following procedures. TiCl₄ was reacted with SiO₂ in heptane at approximately 98°C to obtain a SiO₂-supported TiCl₄ catalyst containing 66% of (4) and 34% of (5).

Then certain measured amounts of MgCl₂ (THF)₂ and AlEt₂Cl were added to the catalyst in heptane, and the resulting mixtures were kept standing with vigorous stirring at r.t. for 20 h. The precipitates were separated by filtration, washed with heptane and dried under vacuum at r.t.. The final catalysts obtained displayed green color, indicating the formation of a complex of MgCl₂ and titanium species.

Typical results of propylene polymerization obtained by using the catalysts thus prepared combined with AlEt₃ are shown in **Table 4**.

With increase in the molar ratio of Mg to Ti, the polymerization activity drastically increased to a constant value at the ratio of about 2. Thus, it may be concluded that the activity is markedly improved by co-existing of only a small amount of MgCl₂. Accordingly, it is not essential to use MgCl₂ as a carrier for preparing highly active supported catalysts. Most of the MgCl₂ was removed by washing the TiCl₄/MgCl₂/SiO₂ catalyst with

Table 4 Results of Propylene Polymerization^{a)}

Run No.	Catalyst	Mg/Ti	Activity (kg-pp/g-Ti·h)
1	TiCl ₄ /SiO ₂	0	0.73
2	TiCl ₄ /MgCl ₂ /SiO ₂	1.2	4.09
3	"	1.8	14.8
4	"	2.2	11.9
5	"	3.1	12.5
6	"	4.2	13.9
7	"	4.6	10.6

^{a)} Polymerization was conducted in a 0.1 dm³ of stainless steel reactor at 65°C for 15 min by using 0.1 mmol of AlEt₃, 0.01 dm³ of heptane and 0.26 mol of propylene. Ti supported: 0.51 matom/g-cat.

Fig. 3 Plausible Mechanism for the Formation of Active Species with TiCl₄/MgCl₂/SiO₂

THF, indicating a weak complexation between MgCl₂ and titanium species. A plausible scheme for the formation of the active species is shown in **Fig. 3**.

The other catalyst, which was prepared by coprecipitation using TiCl₃·3C₅H₅N, MgCl₂(THF)₂ and SiO₂ in the presence of AlEt₂Cl in heptane, also showed similar results.³⁷⁾

5. Control of Stereospecificity of Catalysts

The stereospecificity of Ziegler-Natta catalysts has been markedly improved by using suitable Lewis bases as internal and external donors. The effect of such Lewis bases, especially ethylbenzoate (EB) and 2,2,6,6-tetramethylpiperidine (TMP), in enhancing catalyst stereospecificity has been discussed in some detail by many authors.^{27),28),38)~43)}

By increasing the concentration of the Lewis base, a drastic decrease in the atactic fraction takes place, while the amount of isotactic polymer decreases but a little or sometimes even increases to some extent, indicating that catalytic centers having different stereospecificities exist in the catalytic system. Some authors have proposed a mechanism in which stereospecificity is controlled by the number of vacant sites in the catalytic centers. However, it is not easy to confirm the validity of such a model.

On the other hand, in the polymerization of dienes catalyzed by transition metal compounds, Teyssie et al. have suggested that *cis*-1,4-polymer is obtained from *s-cis*-coordinated monomer while *trans*-1,4-structure results from monomer coordination involving only one double bond with the molecule in its *s-trans*-form.⁴⁴⁾ From the polymerization of 1,3-butadiene using the $\text{TiCl}_3/n\text{AlEt}_3$ -THF catalyst, Tornquist et al. have also proposed a similar model that *cis*-1,4-forming species have two vacant sites to which the diene monomer can coordinate in the *cisoid* form, while one of the vacant sites is blocked by THF addition, which forces the monomer to coordinate via one double bond and to add in the *transoid* conformation to give *trans*-1,4-polybutadiene as a result.⁴⁵⁾

From these standpoints, we have carried out polymerization of propylene as well as that of isoprene under similar conditions with TiCl_4 - AlEt_3 and $\text{TiCl}_4/\text{MgCl}_2$ - AlEt_3 catalyst systems by using typical Lewis bases, EB and TMP.⁴⁶⁾ The isotacticity of the polypropylene and the microstructure of polyisoprene determined by IR and ^1H NMR, respectively, are shown in **Figs. 4** and **5**.

A marked increase in the isotacticity of polypropylene was accompanied with a remarkable decrease in the *cis*-1,4-content of polyisoprene with both catalyst systems. The results clearly indicate that there exist actually two types of active species: the species having two vacant sites may give the atactic polypropylene and *cis*-1,4-polyisoprene, while the other species having only one vacant site may give the isotactic polypropylene and *trans*-1,4-polyisoprene. When a Lewis base like EB or TMP is added, one of the vacant sites of the aspecific species may be blocked, and consequently the species may become inactive or may turn into the isospecific species depending on the nature of the Lewis base. If the vacant site of the isospecific species is blocked, the species become inactive. Usually, it is observed that isospecific species are

Polymerization was conducted at 65°C by using 0.5 mmol of TiCl_4 and 0.5 mmol of AlEt_3 in 0.01 dm^3 of heptane.

① no additives, ② 0.025 mmol of EB, ③ 0.25 mmol of EB, ④ 0.40 mmol of EB, ⑤ 0.50 mmol of EB, ⑥ 0.10 mmol of TMP, ⑦ 0.25 mmol of TMP, ⑧ 0.50 mmol of TMP.

Fig. 4 Relation between the Isotacticity and *cis*-1,4-Content with the TiCl_4 - AlEt_3 Catalyst

Polymerization was conducted at 65°C by using 0.10 g of the $\text{TiCl}_4/\text{MgCl}_2$ catalyst and 0.2 mmol of AlEt_3 in 0.01 dm^3 of heptane.

⑨ no additives, ⑩ 0.01 mmol of EB, ⑪ 0.04 mmol of EB, ⑫ 0.04 mmol of TMP, ⑬ 0.11 mmol of EB, ⑭ 0.15 mmol of EB.

Fig. 5 Relation between the Isotacticity and *cis*-1,4-Content with the $\text{TiCl}_4/\text{MgCl}_2$ - AlEt_3 Catalyst

less affected by Lewis bases; such observation may be attributed to the difference in acidity between the two species.

Some recent patents indicate that the combination of diester and organosilicon compounds as internal and external bases, respectively, improves the catalyst stereospecificity effectively.¹⁷⁾ We studied propylene polymerization in detail with the

TiCl₄/MgCl₂ - AlEt₃ catalytic system by using EB or di-*n*-buthyl phthalate (DNBP) and EB or phenyltriethoxysilane (PTES) as internal and external donors, and investigated the effects of the additives on the catalyst stereospecificity. The results obtained have led to the following conclusions.⁴⁸⁾

- (1) The interaction between EB and Ti species is not very strong. Thus, a large amount of EB is removed by formation of a complex with the AlEt₃ on addition of AlEt₃ thereby generating uncomplexed aspecific Ti species.
- (2) Removal of DNBP by AlEt₃ is suppressed because of a strong interaction between DNBP and Ti species and/or MgCl₂.
- (3) PTES interacts strongly with the Ti species, and hence the catalyst stereospecificity is markedly improved by addition of a small amount of PTES.
- (4) PTES coordinates with the potentially isospecific Ti species, which are surrounded by DNBP to give highly active isospecific Ti species, whereas it reacts with the aspecific Ti species to chemically inactivate this group. Accordingly, the TiCl₄/DNBP/MgCl₂ - AlEt₃/PTES catalyst may be explained in terms of the following model.

Thus, the effect of Lewis bases in enhancing catalyst stereospecificity has now been reasonably clarified. However, complexities arising from multiplicity and heterogeneity of the catalytic systems

still hinder complete understanding of the precise role of such bases. From such a viewpoint, Gianini et al. prepared a single crystal of TiMgCl₆(CH₃COOC₂H₅)₄ from the reaction of TiCl₄, MgCl₂, and ethylacetate and determined the structure of the complex.⁴⁹⁾ Unfortunately, the complex did not show any activity for propylene polymerization, and it rapidly decomposed on adding AlEt₃.

Recently, Hercules Inc. has reported that the catalyst system composed of TiCl₃ and (RCp)₂TiMe₂ (R = H, Me) could catalyze the isotactic living polymerization of propylene in the absence of any additives.²⁾ There is no doubt that this simple catalyst system will not only contribute to our understanding of the detailed mechanism of stereoregulation, but it will stimulate the development of new types of highly isospecific catalysts.

We have, therefore, prepared various kinds of similar catalysts and carried out propylene polymerization with them. The kinetic behavior of the polymerization was found strongly dependent on the solid catalyst used, indicating that the active species formed between the solid catalyst and (RCp)₂TiMe₂ is located on the surface of the solid catalyst.⁵⁰⁾ In **Table 5** the results of polymerization activity as well as those of the isotactic index of the polymer are summarized.

The isotactic index of the polymer obtained by using AlEt₃ in place of (RCp)₂TiMe₂ is also shown as a reference. Polymerization carried out in an autoclave at 40°C using some Tebbe type compounds resulted in activities higher than 60 kg-polypolypropylene/g-Ti.⁵¹⁾ It should be noted that the present catalytic systems show very high isotactic index even in the absence of any additives. In **Fig. 6** is shown a plausible model of the isospecific sites in the present catalysts according to the

Table 5 Results of Propylene Polymerization with Various Solid Catalysts and (RCp)₂TiMe₂^{a)}

Solid Catalyst	Alkyl Titanium Compound [mg]	[mmol]	Polym. Temp. [°C]	Activity ^{f)} [g-PP/g-Ti·h]	I. I. ^{g)} [%]	I. I. ^{h)} [%]
TiCl ₃ ^{b)}	110 Cp ₂ TiMe ₂	0.3	25	20	93	65
TiCl ₃ ^{b)}	110 (MeCp) ₂ TiMe ₂	0.6	40	47	98	65
TiCl ₄ /PhCO ₂ Et/MgCl ₂ ^{c)}	100 Cp ₂ TiMe ₂	0.3	25	280	95	60
TiCl ₄ /PhCO ₂ Et/MgCl ₂ ^{c)}	100 (MeCp) ₂ TiMe ₂	0.5	40	920	96	60
TiCl ₄ /PhCO ₂ Et/MgCl ₂ ^{c)}	80 (MeCp) ₂ TiCH ₂ (CH ₃)AlMe ₂	0.4	40	1,850	93	60
TiCl ₄ /MgCl ₂ ^{d)}	100 (MeCp) ₂ TiMe ₂	0.6	40	120	90	27
Ti(OBu) ₄ /MgCl ₂ /AlEt ₃ Cl ^{e)}	170 (MeCp) ₂ TiMe ₂	0.7	40	180	91	28
—	(MeCp) ₂ TiMe ₂	0.7	40	none	—	—
MgCl ₂	500 (MeCp) ₂ TiMe ₂	0.2	40	none	—	—

- a) Polymerizations were carried out in a 0.2 dm³ glass reactor using 1 atm. of propylene and 0.1 dm³ of heptane as solvent for 2 h. b) Prepared by reducing TiCl₄ with Ti. c) Ti cont. = 2.3 wt%. d) Ti cont. = 2.8 wt%. e) Ti cont. = 0.9 wt%. f) Average activity for the initial 2 h. g) Determined by fractionation with boiling heptane. h) Polymerizations were carried out under similar conditions by using 0.5 mmol of AlEt₃.

Fig. 6 Plausible Model of Isospecific Catalytic Center

mechanism proposed by Henrici-Olive and Olive.⁵²⁾

An inactive intermediate complex (7) may be first formed between $(\text{RCp})_2\text{TiMe}_2$ and the surface Ti species (6) having two Cl vacancies, followed by exchange between Cl and Me to give an active isospecific species (8). Neither the mixture of $(\text{RCp})_2\text{TiMe}_2$ and MgCl_2 nor that of $(\text{RCp})_2\text{TiMe}_2$ and $\text{AlEt}_n\text{Cl}_{3-n}$ showed any polymerization activity, indicating that the isotactic living polymerization of propylene proceeds with the Ti^+ species, which is similar to the active species in the usual Ziegler-Natta catalysts. The ability of the present catalyst systems to give highly isotactic, living polypropylene may, therefore, be attributed to the unusual stability of the active species (8). Additional and more comprehensive investigations are being carried out, and further details will be published elsewhere.

On the other hand, Kaminsky has recently developed highly active soluble catalyst systems based on transition metal compounds and polymeric methylaluminoxanes. If some special compounds like rac-ethylene (bisindenyl) zirconiumdichloride are used as a transition metal compound, propylene is polymerized to highly isotactic polypropylene. Separation of the racemic mixture of the zirconocene compound into optically active pure enantiomeric forms can be performed, leading for the first time to optically active polypropylene. The helix (3/1) thus formed remains stable, unless treated at higher temperatures or dissolved completely. Molecular weight distributions of these polymers are very narrow ($\text{Mw/Mn} = 2 \sim 2.5$), and that narrowness is a characteristic of homogeneous catalysts with only one type of active species.^{1-c)} Therefore, further detailed studies of these catalyst systems will undoubtedly contribute to our complete understanding of the polymerization mechanism including the active species as well

as stereospecificity of Ziegler-Natta catalysts.

6. Models of Catalytic Centers

Various models of catalytic centers and monomeric unit addition mechanism have been proposed to interpret the isotactic polymerization of olefins with Ziegler-Natta catalyst systems. One of the most complete presentations has been made by Pino et al.³⁸⁾ However, as pointed out by Pasquon et al.³⁾, the catalytic centers especially in heterogeneous catalysts are likely to have much greater complexity than described by the various models proposed; and more research is likely to be required to fully investigate their structures.

An outline of our recent fundamental studies on isotactic polymerization of propylene is presented, and particular attention is being paid to the nature of the active species in Ziegler-Natta catalysts. Our knowledge of the true nature, especially, of heterogeneous polymerization catalyst surfaces is still imperfect requiring greater attention. We await the development of better methods for characterization of catalyst surfaces.

Acknowledgements

The author wishes to express his sincere gratitude to Professor emeritus Tominaga Keii for his fruitful suggestions and encouragement throughout the course of this work. The author wish to acknowledge the help and assistance of Professor Y. Doi, Dr. K. Izumi, Dr. T. Sano, Dr. M. Terano, Dr. R. Ohnishi, Dr. K. Yamamoto, Dr. S. I. Chen, Mr. T. Shiono, and Mr. H. Yanagihara whose research works have been referred to in the preparation of this paper. The author also acknowledges the contribution of Dr. N. Tomotsu of Petrochemical Research Division, Idemitsu Kosan Co. Ltd. for obtaining the XPS spectra.

References

- 1) a) Sinn, H., Kaminsky, W., *Adv. Organomet. Chem.*, **18**, 99 (1980).
b) Kaminsky, W., 189th ACS Meeting, Miami, April (1985).
c) Kaminsky, W., Külper, K., Brintzinger, H. H., Wild, F. R. W. P., *Angew. Chem.*, **97**, 507 (1985).
- 2) a) Hercules Inc., U. S. Pat., 4408019 (1983).
b) Hercules Inc., Japan Pat. (Open), 57-111307 (1982).
c) Lock, G. A., International Symposium on Recent Advances in polyolefins, Chicago, September (1985).
- 3) Pasquon, I., Giannini, U., "Catalytic Olefin Polymerization, in Catalysis, Science and Technology", Vol. 6, Anderson, J. R., Boudart, M., (Eds.), pp. 74 (1984), Springer-Verlag.
- 4) Boor, J., *Macromol. Rev.*, **2**, 115 (1967).
- 5) Clark, A., *Catal. Rev.*, **3**, 145 (1969).
- 6) Ballard, D. G. H., *Adv. Catal.*, **23**, 267 (1973).
- 7) Yermakov, Yu., Zakharov, V., *Adv. Catal.*, **24**, 173 (1976).
- 8) Yashima, T., Ebisawa, M., Hara, N., *Chem. Letters*, **1972**, 473.
- 9) Soga, K., Sano, T., Ikeda, S., *Polym. Bull.*, **1**, 665 (1979).
- 10) Soga, K., Izumi, K., Terano, M., Ikeda, S., *Makromol. Chem.*, **181**, 657 (1980).
- 11) a) Soga, K., Sano, T., Ikeda, S., *Polym. Bull.*, **2**, 817 (1980).
b) Soga, K., Sano, T., *Hyomen*, **19**, 613 (1981).
- 12) Soga, K., Sano, T., Ohnishi, R., *Polym. Bull.*, **4**, 157 (1981). Soga, K., Chen, S. I., Ohnishi, R., *Polym. Bull.*, **8**, 473 (1982).
- 13) Chien, J. C. W., *J. Catal.*, **23**, 71 (1971).
- 14) Soga, K., Ohtake, M., Ohnishi, R., Doi, Y., *Makromol. Chem.*, **186**, 1129 (1985).
- 15) Okura, I., Sendoda, Y., Keii, T., *Kogyo Kagaku Zasshi*, **10**, 276 (1970).
- 16) Ambroz, J., Osecky, P., Mejzlik, J., Hamerik, O., *J. Polym. Sci.*, **C16**, 423 (1967).
- 17) Keii, T., Soga, K., Saiki, N., *J. Polym. Sci.*, **C16**, 1507 (1967).
- 18) Soga, K., Shiono, T., Wu, Y. Y., Ishii, K., Nogami, A., Doi, Y., *Makromol. Chem., Rapid Commun.*, **6**, 537 (1985).
- 19) Kashiwa, N., Yoshitake, J., *Makromol. Chem.*, **185**, 1133 (1984).
- 20) Eisch, J. J., Piotrowski, A. M., Brownstein, S. K., Gabe, E. J., Lee, F. L., *J. Am. Chem. Soc.*, **107**, 7219 (1985).
- 21) Petrochemicals Ltd., Brit. Pat., 841822 (1955).
- 22) Shell, Brit. Pat., 904510 (1960).
- 23) Giannini, Y., *Makromol. Chem. Suppl.*, **5**, 216 (1981).
- 24) Keii, T., Suzuki, E., Tamura, T., Murata, M., Doi, Y., *Makromol. Chem.*, **183**, 2285 (1982).
- 25) Kashiwa, N., Yoshitake, J., *Makromol. Chem., Rapid Commun.*, **4**, 41 (1983).
- 26) Bukatov, G. D., Shepelev, S. H., Zakharov, V. A., Sergeev, S. A., Yermakov, Yu. I., *Makromol. Chem.*, **183**, 2657 (1982).
- 27) Chien, J. C. W., Kuo, C. I., *J. Polym. Sci. Polym. Chem. Ed.*, **23**, 761 (1985).
- 28) Tait, P. J. T., "Catalytic Polymerization of Olefins", Keii, T., Soga, K., (Eds.), pp. 305 (1986), Kodansha & Elsevier.
- 29) Doi, Y., Soga, K., Murata, M., Suzuki, E., Ono, Y., Keii, T., *Polym. Commun.*, **24**, 244 (1983).
- 30) Soga, K., Chen, S. I., Shiono, T., Doi, Y., *Polymer*, **26**, 1891 (1985).
- 31) Soga, K., Chen, S. I., Shiono, T., Doi, Y., *Makromol. Chem.*, **187**, 351 (1986).
- 32) Soga, K., Chen, S. I., Doi, Y., Shiono, T., *Macromolecules*, in press.
- 33) Soga, K., "History of Polyolefins", Seymour, R. B., Cheng, T., (Eds.), pp. 243 (1986), D. Reidel Publishing Co., Dordrecht.
- 34) Ozaki, A., Aika, K., "Catalysis, Science and Technology", Anderson, J. R., Boudart, M., (Eds.), Vol. 1, pp. 87 (1981), Springer-Verlag, Berlin.
- 35) Karol, F. J., (Union Carbide Co. Ltd.), Japan Pat. (Open), 55-148093, 154488 etc.
- 36) Soga, K., Ohnishi, R., Doi, Y., *Polym. Bull.*, **9**, 299 (1983).
- 37) Soga, K., Terano, M., *Polym. Bull.*, **4**, 39 (1981).
- 38) Pino, P., Mulhapt, R., *Angew. Chem., Int. Ed. Engl.*, **19**, 857 (1980).
- 39) Langer, A. W., Burkhard, T. J., Steger, J. J., "Transition Metal Catalyzed Polymerizations", Quirk, R. P., (Ed.), pp. 421 (1983), Harwood Academic Publishers, New York.
- 40) Kashiwa, N., *ibid*, pp. 379.
- 41) Keii, T., *ibid*, pp. 97.
- 42) Pino, P., Rotzinger, B., Achenbach, E. V., "Catalytic Polymerization of Olefins", Keii, T., Soga, K., (Eds.), pp. 461 (1986), Kodansha & Elsevier.
- 43) Terano, M., Kataoka, T., *ibid.*, pp. 407.
- 44) Dawans, F., Teyssie, P., Organic Coatings and Plastics, Chemistry Division, ACS/CIC Meeting, Tronto, 1970, Vol. 30, pp. 208.
- 45) Tornquist, E., Cozewith, C., Libby, W. F., IUPAC International Symposium on Macromolecules, Florence, 1980, Vol. 2, pp. 79.
- 46) Soga, K., Sano, T., Yamamoto, K., Shiono, T., *Chem. Letters*, **1982**, 425.
- 47) a) Montedison, Japan Pat. (Open), 57-63310.
b) Mitsui Petrochemical Industries Co. Ltd., Japan Pat. (Open), 58-83006.
c) Mitsubishi Petrochemical Co. Ltd., Japan Pat. (Open), 59-149905.
d) Toho Titanium Co. Ltd., Japan pat. (Open), 60-23404.
e) Toa Nenryo Kogyo Co. Ltd., Japan Pat. (Open), 60-115603.
- 48) Soga, K., Shiono, T., International Symposium on Transition Metal Catalyzed Polymerization, Akron, June, 1986.
- 49) Albizzati, E., Bart, J. C. J., Giannini, U., Parodi, S., IUPAC International Symposium on Macromolecules, Florence, 1980, Vol. 2, pp. 40.
- 50) Soga, K., Shiono, T., Yanagihara, H., *Makromol. Chem. Rapid Commun.*, **7**, 719 (1986).
- 51) Soga, K., Yanagihara, H., *Makromol. Chem. Rapid Commun.*, submitted.
- 52) Henrici-Olive, G., Olive, S., *Fortschr. Hochpolym-Forsch.*, **6**, 421 (1969).

要 旨

チグラー・ナッタ触媒の活性，立体規制および構造

曾我 和雄

東京工業大学資源化学研究所，227 横浜市緑区長津田町 4259

プロピレンのアイソタクチック重合に関する最近の著者らの研究結果をまとめて示した。

まず，幾つかの一元系触媒による重合結果から，重合活性の起源について述べた。すなわち，通常のイオン交換法により調製した Ti^{3+} -Y ゼオライト触媒が単独でプロピレンのアイソタクチック重合能を示すことから，重合活性の発現にはチタン-アルキル結合やハロゲンは必ずしも必要でなく，チタンイオンのみで十分であることを述べ，種々の方法で調製した一元系触媒による重合結果から，チタン種のみを含む一元系触媒でも従来のチグラー・ナッタ触媒とほぼ同程度の活性が得られることを示した。

ついで，このような観点から調製した単純化触媒を用い，各種オレフィンの単独および共重合を詳細に検討した。チタンが3価から2価に還元されるに伴い，エチレンの重合活性は微増するが，他のオレフィンの重合活性は著しく低下し，またエチレンとの共重合においては，ランダム共重合体からポリエチレンへと構造が変化するなどの結果から，つぎの結論を得た。「エチレンの重合に対しては， Ti^{3+} ， Ti^{2+} が共に活性を示すが，他のオレフィンに対しては Ti^{3+} のみが活性である」

触媒の高性能化についても，重合活性，立体特異性の両面か

ら議論した。

まず，幾つかの均一および不均一系触媒を調製し，これに種々の金属塩化物 (MCl_n) を添加した系でプロピレンの重合活性を調べた。その結果，重合活性と MCl_n 中に含まれる M^{n+} の電気陰性度 $X(M^{n+})$ との間に興味ある相関が認められた。すなわち， $X(M^{n+})$ が活性種である Ti^{3+} の電気陰性度より小さい場合に限って重合活性は向上することがわかった。同様の現象はクロム系触媒においても観測された。これら金属塩化物および担持触媒の XPS の測定結果をも総合して，重合活性に及ぼす $MgCl_2$ の作用機構について述べた。

ついで，触媒の立体選択能を向上させる目的で使用される内部および外部ドナーの効果について検討した。最近注目されているジエステル（内部ドナー）-ケイ素化合物（外部ドナー）系についても触れた。また，ハーキュリーズ社で開発されたプロピレンのアイソタクチック・リビング重合触媒 ($(RCp)_2TiMe_2-TiCl_3$) が，この問題を議論する上できわめて有用なことを述べ，著者らがこれを改良して得た高活性，高立体特異性触媒を用いて行ったプロピレンの重合結果をも併せて示した。これらの結果から想定される立体特異性触媒の活性種の構造を提案した。

Keywords

Complex catalyst, Olefin, Polymerization, Reaction mechanism, Stereospecificity, Ziegler-Natta catalyst