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ADDITIVE EFFECTS OF LEWIS BASES ON OLEFIN POLYMERIZATION WITH TITANIUM-BASED CATALYSTS

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General Introduction

In 1953 K. Ziegler found that ethylene is polymerized with the catalyst composed of $TiCl_4$ and $Al(C_2H_5)_3$ under ambient temperature and pressure$^{1)}$. G. Natta then succeeded in polymerizing propylene to isotactic crystalline polypropylene by using crystalline α-$TiCl_3$ in place of $TiCl_4$$^{2)}$. These epoch-making discoveries brought us not only one of biggest petrochemical industries but also new fields in polymer science, that is, coordination and stereospecific polymerization.

With the use of Ziegler-Natta catalysts are produced many commercial plastics and elastomers such as high density polyethylene(HDPE), linear low density polyethylene(LLDPE), isotactic polypropylene(PP), syndiotactic polybutadiene, cis-1,4 polybutadiene(BR), ethylene-propylene random copolymer (EPR) and so on. Although it has passed over thirty years since the discoveries by Ziegler and Natta, this field is still very important in petrochemical industries. In Japan, for example, the amount of polyolefin plastics produced by Ziegler-Natta catalysts in 1984 was about 2.3×10^6 ton which corresponds to a quarter of total plastics. In particular, production of isotactic polypropylene still continues to increase because of its superior properties.

Ziegler-Natta catalysts have been continueously improved to increase the activity as well as the stereospecificity of polymers. For ethylene polymerization, enhancement of activity was mainly investigated by supporting titanium compounds on solid carriers and $MgCl_2$ was found to show the highest activity among various solid carriers. This effort has yielded an economic polymerization process. The effect of $MgCl_2$ on the activity has recently been attributable to a marked increase in the propagation rate constant(k_p) and also the number of active species(C^*) as well[3-5].

On the other hand, in the case of propylene polymerization, stereospecificity should be taken into consideration. Highly efficient catalysts have been developed by two different methods. The improvement of activity was first attempted upon the $TiCl_3/Al(C_2H_5)_2Cl$ catalyst system which is well known to give highly isotactic polypropylene (I.I. > 90 %). Since polymerization takes place on the catalyst surface, it is natural that much effort has been paid to enlarge the surface area of $TiCl_3$. Grinding of $TiCl_3$ in a steel mill improved the activity to some extent[6]. Then, based on the assumption that the active species is closely related to the Cl vacancy of $TiCl_3$, porous $TiCl_3$ was prepared by extracting $AlCl_3$ by ether from the surface of aluminium reduced $TiCl_3$[7,8]. The catalyst thus prepared showed very high activity(20 kg-PP/g-Ti·h), but elimination of deashing process couldn't be realized with such type of catalysts. Therefore, improvement of the stereospecificity was attempted by using the $MgCl_2$-supported catalyst which was known to show very high activity for ethylene polymerization. The catalyst was proved to be extremely highly active also for propylene polymerization[9]. However, the isotacticity of produced polymers were too low (I.I. < 50 %).

In order to increase the stereospecificity, various kinds of electron donor compounds were added to the original catalyst (called "internal donor") and also to the polymerization system (called "external donor"). Addition of these compounds increased the stereospecificity, but usually accompanied by significant deactivation. Supprisingly, some aromatic esters like ethyl benzoate were found not to decrease but rather to increase the activity as well[10,11]. Thus, an economic process has been developed also for propylene polymerization. The role of such additives on propylene polymerization has been investigated by many researchers[12]. The complexity of the catalyst system, however, has hindered understanding of the precise mechanism of controlling the stereospecificity of catalysts.

It has recently be claimed that addition of some aromatic diesters and organosilicon compounds as internal and external donors respectively also increases the stereospecificity without decreasing the activity[13]. Replacement of aromatic esters with such organosilicon compounds as external donors seems to be recommendable since the latter is needed in less amount. However, we can not see any scientific papers about these catalyst systems.

On the other hand, hydrogen is widely used in the industrial olefin polymerization process to regulate the molecular weight of polymers. Many papers describes the polymerization kinetics in relation to hydrogen pressure[14-

[17]. The published data indicate that dependence of molecular weight on hydrogen pressure is strongly dependent upon the catalyst systems. However, most of the results are discussed based on the whole polymers, i.e., mixture of isotactic and atactic polymers. Separation of polymers into isotactic and atactic parts may give us some useful information about the difference in isotactic and atactic active species.

EPR, a random copolymer of ethylene and propylene, is one of the valuable polymers produced by using Ziegler-Natta catalysts. So far, it has been synthesyzed with vanadium based homogeneous catalysts. More recently it has been proved that EPR can also be manufactured by using the titanium based heterogeneous catalysts[18]. There are, however, some clean differences in the chemical structures of both polymers, which suggests that structure and/or the electronic nature of active species regulate the reactivity of both monomers. The correlation between the valence states of titanium and the activity for various olefins has been investigated in detail[19]. But there are still few papers which discuss the above point.

Kaminsky[20] has recently developed a new type of extremely high active homogeneous catalyst system, which is essentially composed of some transition metal compounds and methylalumoxiane, $-\!\!\left(\mathrm{Al(CH_3)-O}\right)\!\!-_{n}$. For example, the $(\eta^5\text{-}C_5H_5)_2Zr(CH_3)_2$/methylalmoxiane system shows the activity as high as 2.5×10^3 kg-polymer/g-Zr h for ethylene polymerization at 90°C and 8 bar. The catalyst also shows very high activity for propylene polymerization, but gives perfectly atactic polypropylene21). By substituting the ligand from cyclopentadienyl to ethylene-bridged indenyl or tetrahydroindenyl, highly isotactic polypropylene (isotactic triad fraction [mm] > 95%) can be obtained22,23). In addition, the use of one antipode of ethylene(bis-tetrahydroindenyl) zirconium dichloride has led to the first synthesis of optically active isotactic polypropylene24).

Living polymerization is useful to functionalize the end of polymer chain and also to synthesyze block polymers. It is known that the homogeneous catalyst systems composed of vanadium acethylacetonato derivatives and alkylaluminium halides polymerize propylene to give living syndiotactic polypropylene at low temperature25,26). More recently, $TiCl_3$ combined with bis-cylopentadienyl or alkylsubstituted cyclopentadienyl titanium dimethyl has been found to polymerize propylene to living isotactic polypropylene at around room temperature27). Under suitable conditions, for example at 0.15 atm and 45°C, the mean life time of polymer chain is over 20 h. This catalyst system seems to be most suitable to discuss the stereospecificity of Ziegler-Natta catalyst, because it shows very high stereospecificity although it contains neither internal nor external donors.

As described above, several types of new catalysts for isospecific polymerization of propylene have been developed. In particular, $MgCl_2$-supported titanium catalysts combined with adequate additives are of great importance in industry because of their high activity and high isospecificity. Contrary to the homogeneous isospecific catalyst developed by Kaminsky, however, such heterogeneous catalysts have given us limitted informations in the field of chemistry. This may be partly attributed to their complexties, but mainly owing to the fact that most of the investigations have been aimed at the development of better catalyst systems.

In this thesis, in order to clarify the role of such electron donors as well as the mechanism of isospecific polymerization, propylene polymerization and some related reactions were carried out in detail with $MgCl_2$-supported titanium catalysts in the absence or presence of several electron donors.

In Chapter 1, various $MgCl_2$-supported $TiCl_4$ catalysts containing internal donor compounds were prepared. With these catalysts propylene polymerization was conducted in the absence or presence of organosilicon compounds, and were examined the catalyst activity, stereospecificity and molecular weight distribution of the produced polymers. Based on the results obtained, the effect of internal and external donors on the polymerization of propylene was discussed.

In Chapter 2, propylene polymerization was performed with the typical $MgCl_2$-supported $TiCl_4$ catalyst in the presence of hydrogen. The polymers produced were fractionated into the isotactic and atactic parts by solvent extraction, and the correlation between the molecular weights and hydrogen pressure was investigated putting some emphasis on the difference in the structures of isospecific and aspecific species.

In Chapter 3, copolymerizations of ethylene with higher α - olefins were carried out with $MgCl_2$-supported $TiCl_4$ catalysts using ethyl benzoate and phenyltriethoxysilane as external donors. From the correlation between the monomer sequence distributions of copolymers and the amount of electron donors, the role of additives was discussed in relation to propylene polymerization.

Since a marked deactivation is usually inevitable during polymerization with highly active $MgCl_2$-supported titanium catalysts, in Chapter 4 was tried to stabilize the catalysts activity. Copolymerization of ethylene with propylene was also conducted by using the stable catalyst developed.

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Chapter 1

Effect of Internal and External Lewis Bases on Propylene Polymerization with $MgCl_2$-Supported $TiCl_4$ Catalysts

1-1 Introduction

1-1-1 Origin of Isospecific Polymerization

Before describing the origin of isospecificity, studies on active species of Ziegler-Natta catalysts are briefly reviewed. Proposed structures of Ziegler-Natta catalysts are roughly devided into two types. One is so-called "bimetallic" mechanism proposed by Natta et al.[1-3] and the other is the "monometallic" mechanism proposed by Cossee et al.[4,5]. Several experimental results have been obtained using homogeneous catalyst systems which are easier to investigate.

Fink et al.[6] investigated the $(\eta^5\text{-}C_5H_5)_2Ti(C_2H_5)Cl/Al(C_2H_5)Cl_2$ system which gives linear high density polyethylene. From ^{13}C NMR spectra complexation of $(\eta^5\text{-}C_5H_5)_2Ti(C_2H_5)Cl$ with $Al(C_2H_5)Cl_2$ and insertion of ethylene into $Ti\text{-}C_2H_5$ bond were confirmed. Recently a cationic complex, $(\eta^5\text{-}C_5H_5)_2TiCSi(CH_3)_3{=}C(CH_3)C_6H_5$, was isolated from the reaction of $Si(CH_3)_3C{\equiv}CC_6H_5$ with $(\eta^5\text{-}C_5H_5)_2TiCl_2/Al(CH_3)Cl_2$ and its structure was determined by X-ray analysis[7]. The cationic zirconium complex of $[(\eta^5\text{-}C_5H_5)_2Zr(CH_3)(THF)]^+$, structure of which was determined by X-ray analysis, was revealed to polymerize ethylene in the absence of alkylaluminium compounds[8)]. The lanthanide complex of (η^5-$C_5(CH_3)_5)_2Lu(CH_3)$(diethyl ether) was reported to polymerize ethylene and oligomerize propylene. Dissociation of the ether ligand from the complex was found to be necessary for a propylene monomer to insert into Lu-CH_3 bond[9,10)]. Lanthanide hydride complexes like $[(\eta^5$-$C_5(CH_3)_5)_2MH]_2$ (M = La, Nd, Lu) were also found to be highly active for ethylene polymerization[11)]. These results strongly suggest that olefin polymerization proceeds via a monomer insertion into transition metal-carbon bonds.

Whereas, isospecific polymerization with heterogeneous catalysts seems to be so complicated that it is impossible to obtain direct evidences of the structure of active species. However, the facts that some titanium-based catalysts free from alkylaluminium compounds can catalyze the polymerization of propylene to isotactic polymer[12,13)] indicate that transition metal-carbon bonds are also formed from the reaction between transition metal compounds and olefin monomers.

Concerning the isospecific polymerization reaction, various mechanisms have been proposed so far. Most of them are based on the assumption that olefin monomer should coordinate with the active center in a way to minimize the steric interaction. Natta[14)] suggested that the enantiomorphous bimetallic complex formed between $Al(C_2H_5)_2Cl$ and $TiCl_3$ compelled an olefin monomer to coordinate in the same configuration. Rodiguez and Van Looy[15)] proposed that the isotactic orientation was favoured because the propylene molecule could complex with the titanium center only in one configuration, that is, with its methyl group directed away from the alkyl groups of the aluminium atoms.

Cossee$^{16)}$ developed a monometallic model shown in Figure 1-(i). According to this model, the repulsion between methyl group of propylene and surrounding chlorine ligands compels the propylene monomer to coordinate only in one configuration. After the migration of alkyl group to the β-carbon of propylene, the configuration of the asymmetric carbon atom seen from the Ti becomes to be in a clockwise order, $R \rightarrow CH_3 \rightarrow H$. Figure 1-(ii) shows the coordination of the next monomer, which indicates that the asymmetric carbon newly formed by the subsequent insertion retains the same configuration. Repetition of such a process produces the isotactic polypropylene. Cossee$^{17)}$, however, corrected this model taking into consideration of the crystal structure of $TiCl_3$. According to this mechanism, the alkyl group reverts to the former position after insertion of propylene owing to the differences in repulsion between the alkyl group and the chlorine ligands. Thus, propylene monomers can be coordinated to the same site in the same configuration.

Allegra$^{18)}$ pointed out the defects of this mechanism ; 1) Considering the steric repulsion between the methyl group of propylene and the methylene group of the propagating chain end, it may be difficult for the propylene monomer to coordinate with the titanium parallel to the titanium-carbon

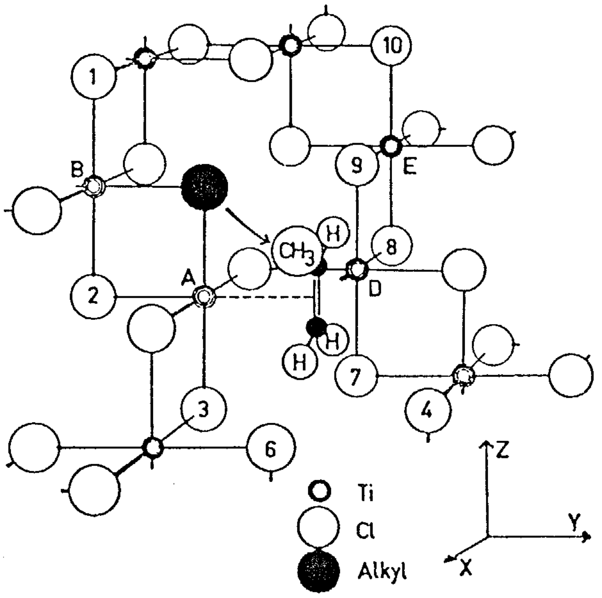


Figure 1-(i) Schematic drawing of part of the α-$TiCl_3$ lattice showing "active center" with monomer propylene-molecule in Cl-vacancy by Cossee$^{16)}$.

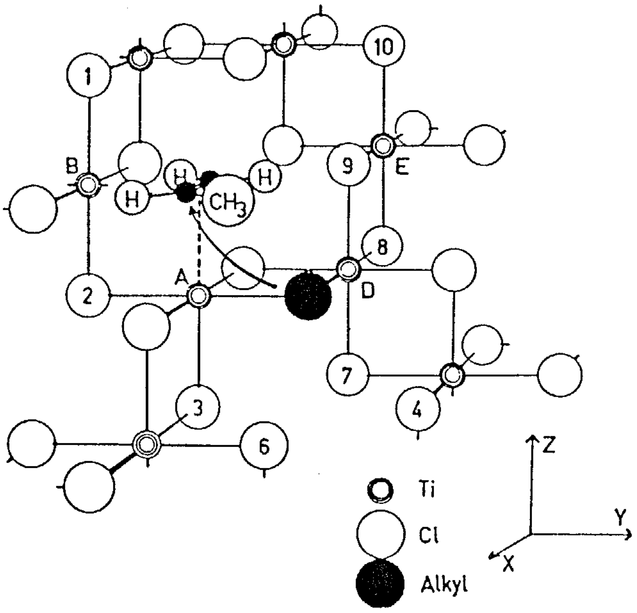


Figure 1-(ii) Schematic drawing of the situation after migration of alkyl group R according to reaction path indicated by the arrow in Figure 1-(i).

bond 2) Migration of the propagating chain might be need somewhat higher activation energy than the observed one (5 kcal/mol). He proposed the corrected mechanism from these points of view.

Using the enantiomorphic monoalkylated titanium atom having one chlorine vacancy and chlorine bridge-bonded two titanium atoms as a model of active species, Corradini et al.$^{19)}$ calculated the energy of nonbonded interaction among the propylene monomer, propagating chain end and surrounding chlorine atoms. Here he assumed that the insertion of propylene takes place according to the "least nuclear motion" principle$^{20)}$. Based on the results obtained, he proposed that the chirality of the active center might regulate the coordination of propylene as well as the chiral orientation of the first carbon-carbon bond of the propagating chain end.

From the statistical treatment of the ^{13}C NMR spectra of polypropylene prepared by various catalyst systems, Doi$^{22)}$ concluded that isospecific propagation with titanium catalysts is controlled by "catalytic site", while syndiospecific propagation with vanadium catalysts by "polymer chain end". The polypropylenes produced with the $TiCl_3$-$Al(C_2H_5)_2Cl$ and $TiCl_4$/EB/$MgCl_2$-$Al(C_2H_5)_3$ catalysts were divided into several parts by solvent extraction and the steric pentad composition of each polymer was investigated by ^{13}C NMR$^{23)}$. In the highly isotactic fraction small amount of steric defects were observed in the following relation

$$[mmmm] >> [mmmr] = [mmrr] = 2[mrrm]$$

where m and r denote a isotactic and syndiotactic diad respectively. The result suggests that the structure of isotactic polymer is

- - - mmmmmmmmmmmmrrmmmmmmmmmmmmmmmmrrmmmm - - -

, that is, steric inversion occurs accidentally in isotactic polymer chain. This confirms that the during the polymerization the driving force of the enantioselectivity is the original chirality of the active site. On the other hand, the steric pentad composition in atactic fraction shows the following relations

[mmmm] > [mmmr] > [rmmr]
[rrrr] > [rrrm] > [mrrm]

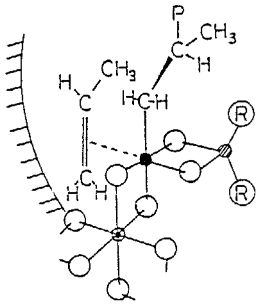
which suggest that the atactic polypropylene consists of isotactic and syndiotactic stereoblocks shown as below.

- - mmmmrrmmmmm - - rrrrrmrrr - - mmmmmrrmmm - -

Based on these results such a model shown in Figure 1-(iii) was proposed for the active species of isospecific polymerization[24).

Zambelli et al.[25) investigated the initiation reaction of isospecific polymerization with titanium halides and AlR_3, AlR_2X or ZnR_2 using the ^{13}C enriched metal alkyl compounds. The insertion of the second monomer was found to produce diastereometric end groups as below.

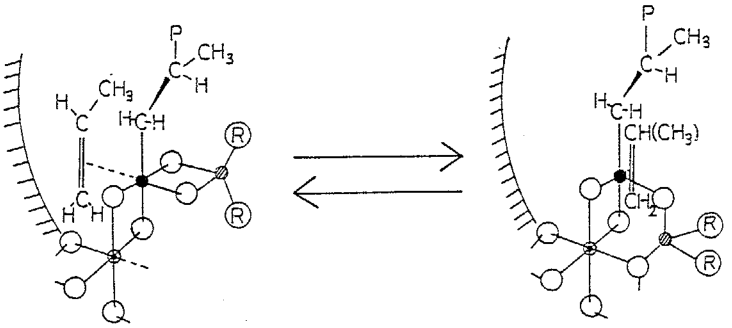
Site A (Isotactic PP)



Isotactic Propagation

● ;Ti
○ ;Cl
⊛ ;Al
⊙ ;Mg, Mn,or Ti
Surface

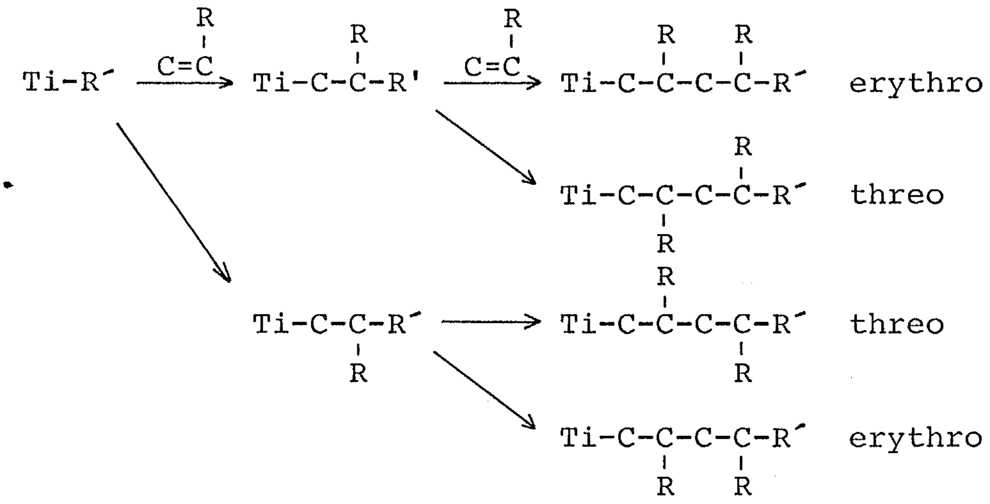
Site B (Atactic PP)



(B_6)
Isotactic Propagation

(B_5)
Syndiotactic Propagation

Figure 1-(iii) Proposed structures of the active sites A and B present in a titanium-based catalyst by Doi24).



From ^{13}C NMR spectra, the ratio of erythro/threo ([e]/[t]) were determined in the various combinations of monomers, titanium compounds and cocatalysts (Table 1-(i)). Although the stereochemical triad composition was nearly the same for all the samples, the [e]/[t] was different. In the case of $TiCl_3$-$Al(CH_3)_3$ or $Al(CH_3)_2Cl$, the content of [e] in the chain end structure was about 50 %, suggesting that the insertion of the first monomer is not enantioselective. On the other hand, the presence of iodine in the enviornment of the active species enhanced the steric control. Unless iodine was present, R must be bulkier than CH_3 for the occurrence of stereospecific initiation.

Kaminsky26) found that the homogeneous catalyst systems composed of zirconocen derivatives and methyl alumoxiane show extremely high activity for ethylene polymerization. These catalysts could polymerize also propylene, but produced perfectly atactic polypropylene. Using the rac-ethylene-bis tetrahydroindenyl (or indenyl) zirconium chloride (Figure 1-

Table 1-(i) The isospecificity of various kinds of Ti-based catalyst systems for propylene polymerization obtained by Zambelli et al.25)

Ti catalyst	Al alkyl	Zn alkyl	triad composition			[e]	P_{DD}^{*}	I_{DD}^{*}
			[mm]	[mr+rm]	[rr]			
δ-$TiCl_3$	$Al(^{13}CH_3)_2Cl$		0.76	0.12	0.12	0.50	0.92	0.50
δ-$TiCl_3$	$Al(^{13}CH_3)_3$	$Zn(^{13}CH_3)_2$	0.79	0.11	0.10	0.52	0.93	0.52
δ-$TiCl_3$	$Al(^{13}CH_3)_2I$		0.82	0.10	0.08	0.75	0.94	0.78
δ-$TiCl_3$	$Al(^{13}C_2H_5)_3$	$Zn(^{13}C_2H_5)_2$	0.91	0.05	0.04	0.79	0.97	0.80
$TiCl_4/MgCl_2$ /EB	$Al(^{13}C_2H_5)_3$	$Zn(^{13}C_2H_5)_3$	0.89	0.06	0.05	0.80	0.96	0.83

* P_{DD} and I_{DD} represent the isospecificity in propagation and initiation steps, respectively.

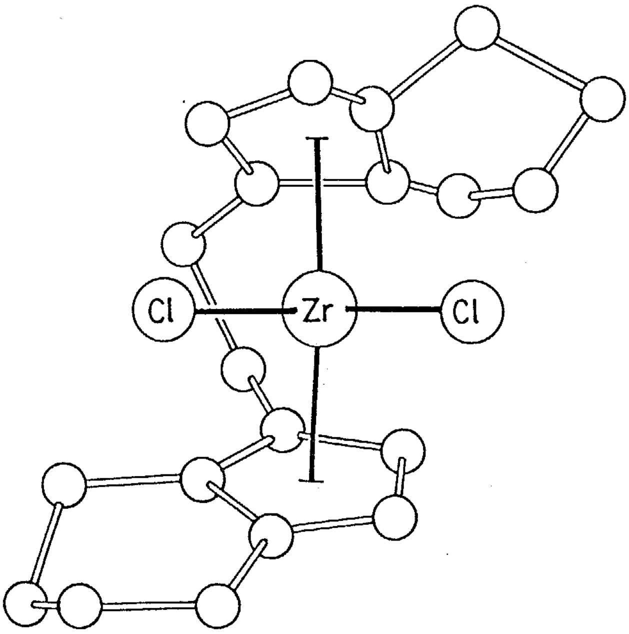


Figure 1-(iv) The strucrure of rac-ethylene bis(tetrahydroindenyl)zirconium dichloride[29].

(iv)), highly isotactic polypropylene has recently been obtained[27,28]. Further separating the racemic mixture of the zirconocen compounds into optically active pure enantiomeric forms, he also succeeded in preparing the optically active isotactic polypropylene[29].

These results strongly suggest that the enantiomeric structure of transition metal compounds might distinguish the prochiral faces of propylene and polymerize it to isotactic polymer.

1-1-2 Effect of Additives on Propylene Polymerization

Effect of additives on polymerization of α-olefins has been extensively studied not only as modifiers to increase isotacticity of polypropylene but also as the powerful diagnostic tool to prove the mechanistic features of isospecific polymerization. Boor divided the effects of such additives into the following three categories[30].

1) Additives selectively react or form complexes with metal alkyl components : The typical catalyst system is $TiCl_3$-$Al(C_2H_5)Cl_2$ that hardly polymerize olefin by itself. However, the presence of inorganic salts such as KCl and NaF increased the activity by 10 to 20 times. Zambelli et al.[31] proposed that mixing of $Al(C_2H_5)Cl_2$ and KCl produced more active $Al(C_2H_5)_2Cl$ and $AlCl_3$ KCl. While Cooper et al.[32] proposed that $Al(C_2H_5)Cl_2$ KCl was a good activator. Watt et al.[33] found that the addition of aldehyde promoted the isospecific polymerization of propylene with $TiCl_3$-$Al(C_2H_5)Cl_2$, and proposed the following mechanism for the

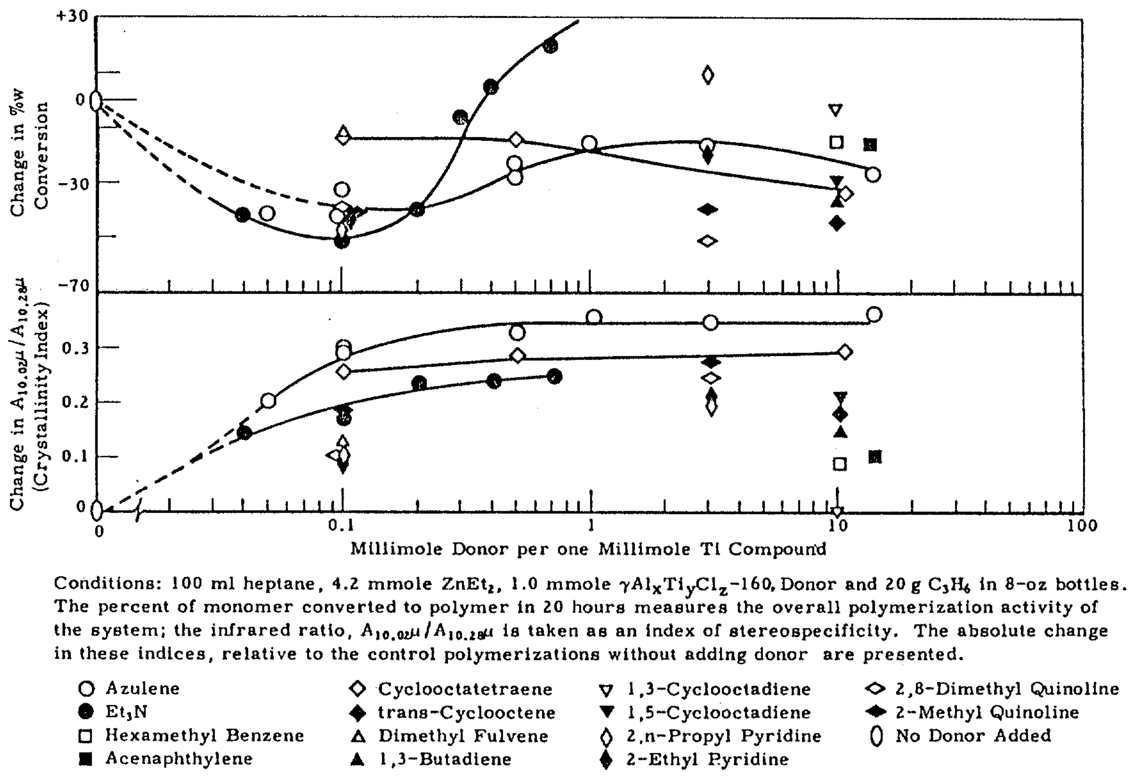
activation.

$$RCHO + R'AlCl_2 \xrightarrow{TiCl_3} TiCl_2R' + RCHO\ AlCl_3$$

As described above, in the catalyst systems where the additives preferentially react with metal alkyl compounds, additives seem to increase the ability of metal alkyl compounds or produce new metal alkyl species.

2) Additives preferentially react with transition metal salts : This type of catalysts were extensivily investigated by Boor[34]. He selected $TiCl_3$-$Zn(C_2H_5)_2$/tertiary amine, $TiCl_3$ or VCl_3-$Al(C_2H_5)_2Cl$ or $Al(C_2H_5)_3$/azulene and $TiCl_3$/tertiaryamine systems. In the propylene polymerization with $TiCl_3$-$Zn(C_2H_5)_2$, a small amount of $(C_2H_5)_3N$ significantly lowered the conversion and increase isospecificity. At a higher concentration of $(C_2H_5)_3N$, however, the conversion was increased without changing the isospecificity (Figure 1-(v)). In the case of $TiCl_3$-$Al(C_2H_5)_3$/azulene, addition of azulene hardly changed the polymer yield with increasing the isospecificity.

Boor[35] found that $TiCl_3$ combined with electron donors such as tertiary amines produced high molecular isotactic polypropylene in the presence or absence of hydrogen. Both the activity and stereospecificity strongly depended on the donor compounds. Interpreting these results, he proposed that the active centers were composed of various exposed titanium atoms which had different complexing ability and stereoregulating ability : At a low ratio of donor/$TiCl_3$,



Conditions: 100 ml heptane, 4.2 mmole $ZnEt_2$, 1.0 mmole $\gamma Al_xTi_yCl_z$-160, Donor and 20 g C_3H_6 in 8-oz bottles. The percent of monomer converted to polymer in 20 hours measures the overall polymerization activity of the system; the infrared ratio, $A_{10.02\mu}/A_{10.28\mu}$ is taken as an index of stereospecificity. The absolute change in these indices, relative to the control polymerizations without adding donor are presented.

Figure 1-(v) Effect of donors on propylene polymerization with γ-$Al_xTi_yCl_z$-$Zn(C_2H_5)_2$ obtained by Boor[35).]

Table 1-(ii) Site removal and site activation by donors at low and high donor concentration, respectively, obtained by Boor$^{34)}$.

Strong	Moderate-weak	Ineffective
	Relative Abilities of Donors to Remote Sites	
Azulene	n-$Octyl_3N$	Benzene
Et_3N	Acenaphthylene	Naphthalene
n-Pr_3N	Mesitylene	Acenaphthene
Pyridine and quinoline compounds	Durene	Anthracene
$(C_6H_6)_2Cr$	Pentamethylbenzene	Pyrene
Cyclopentadienyl compounds of V, Cr, Ni, and Co	Hexamethylbenzene	Fluorene
Butadiene	Tetramethylethylene	Hexaethylbenzene
Isoprene		1,3-Cyclooctadiene
1,4-Pentadiene		$(C_6H_5)_3N$
2-Butyne		
Cyclooctatetraene		
Dimethylfulvene		
Diphenylfulvene		
2,5-Norbornadiene		
trans-Cyclooctene		
PF_3		
1,5-Cyclooctadiene		
n-Bu_3N		
	Relative Abilities of Donors to Activate Sites	
R_3N (R = Et to n-octyl)	Azulene	
	Diphenylphosphine	Benzene
$(C_6H_5)_3P$	2-Ethylpyridine	Naphthalene
n-Bu_3P	2-Propylpyridine	Acenaphthene
	2,4,6-Trimethylpyridine	Anthracene
		Pyrene
		Fluorene
		Hexaethylbenzene
		1,3-Cyclooctadiene
		$(C_6H_5)_3N$

---

[a] Under the conditions examined in this investigation. At much higher donor concentrations different results might be obtained.

the donor preferentially forms the complexes with more exposed titanium species (less-isospecific site) to deactivate them. With an increase in the amount of donor, it adsorbs chemically on the chlorine surface, which causes the increase in activity. The activation is attributed to the following two potential mechanistic paths : (1) the electron donor, when chemisorbed on the surface near the active site, enhances the activity ; (2) the chemisorbed electron donor promotes the disruption of larger catalyst aggregates to smaller particles. Boor favored the latter although no evidence was present. Similar interpretations were made for the other two catalyst systems. He also classified these additives based on their effects (Table 1-(ii)).

3) Additives react both metal alkyl compounds and transition metal salts : Most of the industrial catalysts may contain these additives. However, the complexity of the system makes it difficult to deal the mechanistic feature of additives.

In 1959[36)], Vesley found that the addition of $(C_4H_9)_3N$ on propylene polymerization with $TiCl_3$-$Al(C_2H_5)_3$ does not affect the polymerization rate but increase the molecular weight of produced polymer. He proposed that the selective adsorption of $(C_4H_9)_3N$ on the active species prohibited the termination reaction by solvent. He successively made kinetic studies on additive effects of various sulfer, nitrogen and oxygen compounds to the same system and pointed out the decrease in the rate by the addition of ethanol was due to the decrease in the effective concentration of

$Al(C_2H_5)_3$[37).

Caunt[38) found that addition of NaCl, KCl etc. increases the activity without decreasing the isotacticity in the polymerization of propylene with the $TiCl_3$-$Al(C_2H_5)_2Cl$ catalyst system. He proposed that these compounds excluded the inactive $Al(C_2H_5)Cl_2$ which was produced by the alkylation of $TiCl_3$.

$$NaCl + Al(C_2H_5)Cl_2 \longrightarrow Na[Al(C_2H_5)Cl_3]$$

A kinetic study was made on propylene polymerization with $TiCl_3$-$Al(C_2H_5)_3$ combined with $SeOCl_2$[39). The results obtained strongly suggested that $SeOCl_2$ increased the isotacticity by decreasing the effective concentration of $Al(C_2H_5)_3$. The effects of O_2[41) and ether[42) were also studied and similar results were obtained.

Burfield et al.[43) made the kinetic study on the polymerization of 4-methyl-1-pentene with VCl_3-$Al(iso\text{-}C_4H_9)_3$ by using R_3N as a modifier. Rate equation was revealed as

$$R = k_p\theta_M[C^*], \quad \theta_M = \frac{K_M[M]}{1 + K_M[M] + K_A[Al] + K_D[D]}$$

He suggested that the effect of amine on the rate could be explained by the change in θ_M. The effects of these additives described above may be classified into the following four types.

1) selective poisoning of the aspecific sites - Boor

2) decreasing the effective concentration of alkylaluminium

compounds

3) changing the chemical property of alkylaluminium compounds by the reaction or complexation with the additives

4) scavenging the deactivative compounds

Contrary to these conventional catalyst systems, highly active $MgCl_2$-supported catalysts, usually contain such electron donors in the solid catalysts as well. For example, aromatic esters like ethyl benzoate(EB) are used in the solid catalyst (internal donor) as well as in the catalyst solution (external donor)44). The isospecificity of supported catalysts drastically increases as a result. The dependences of the activities for both isotactic and atactic parts on the amount of EB were investigated by several authors. As shown in Figure 1-(vi), the increase in the amount of EB caused a drastic decrease in the activity of atactic part, while it rather caused an increase in that of isotactic one. Based on the detailed studies Keii et al.45) proposed that the enhancement of stereospecificity might be attributed partly to the decrease in the effective concentration of $Al(C_2H_5)_3$, and partly to the selective poisoning of aspecific sites. Kashiwa et al.46) proposed that EB produces more active isospecific sites in addition to the selective poisoning of aspecific sites. The following fifth type should be added, therefore, to the above classification.

5) Increase the propagation rate of isospecific sites

However, the complexities of the catalyst system arising from the reaction of such esters with catalyst components,

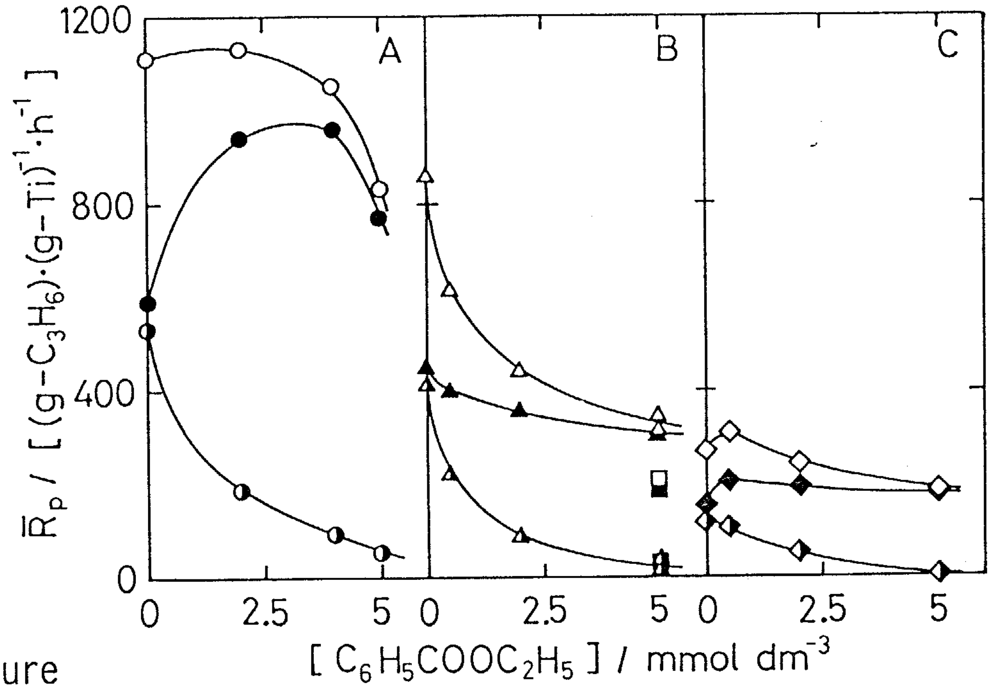


Figure 1-(vi) Average polymerization rate versus concentration of ethyl benzoate added. Figures A, B, and C are the results for polymers obtained with catalysts of Ti content 0.84, 0.69, and 4.65 wt%, respectively. ○, △, ◇, □: total polymers, ●, ▲, ◆, ■: isotactic polymers, ◑, ◭, ⬖, ◧ atactic polymers. □, ■, ◧: Ethyl benzoate and $Al(C_2H_5)_3$ were pre-mixed. Polymerization conditions: T = 41°C, [Ti] = 0.5 mmol dm^{-3}, [$Al(C_2H_5)_3$] = 20 mmol dm^{-3}, $P_{C_3H_6}$ = 660 Torr. by Keii et al.45)

Table 1-(iii) Additive effect of organosilicon compounds on propylene polymerization with $MgCl_2$-supported Ti-based catalysts

External donor	Catalyst*	Activity [kg-PP/g-Ti·h]	I.I. [%]	Polymerization** conditions	Ref.
PTES	$MgCl_2/DIBP/TiCl_4$	71.4	97.5	70°C, 7 atm	47)
PTES	$MgCl_2/Ti(OC_4H_9)_4$/ethanol/ $SiCl_4/DHepP/TiCl_4$	35.3	95.5	70°C, 6 atm	48)
PTES	$Mg(C_{17}H_{35}OO)_2/Mg(OC_2H_5)_2/$ $DPrP/TiCl_4$	195	96.1	70°C, 6 atm	49)
PTES	$Mg(OC_2H_5)_2/HSiCl_3/DIBP/$ $TiCl_4$	378	96.9	70°C, liq.propylene	50)
PTES	$MgCl_2$/2-EHA/phthalic acid/ $DIBP/TiCl_4$	265	98.4	70°C, 7 atm	51)
DPDMS	〃	329	98.9	〃	〃

* DIBP, DHepP, DPrP and 2-EHA denote di-iso-butylphthalate, diheptylphthalate, dipropylphthalate and 2-ethylhexan-1-ol, respectively.

** $Al(C_2H_5)_3$ was used as cocatalyst.

especially alkylaluminium compounds,. hindered the understanding of the precise role of them.

More recently some patents claimed that the combination of organosilicon compounds and aromatic diesters as external and internal donors respectively are more effective to improve the catalyst stability and stereospecificity as shown in Table 1-(iii). These new external donors like phenytriethoxysilane are expected to be less reactive toward the organoaluminium compounds. In this chapter, therefore, $MgCl_2$-supported $TiCl_4$ catalysts containing several kinds of esters were prepared and used for propylene polymerization combined with organosilicon compounds as external donors.

1-2 Experimental

Materials

Propylene (purity 99.9 %, major impurity being propane) supplied from Mitsubishi Petrochemical Co. was used after passing it through columns of $CaCl_2$, P_2O_5 and molecular sieve 3A.

Nitrogen of extra pure grade (99.9995 %) was obtained from Nihon Sanso Co. and used after passing it through the molecular sieve 3A column.

Heptane (pure grade, Kanto Kagaku Co.) was purified by passing through column of molecular sieve 4A followed by fractional distillation over sodium wire under nitrogen atmosphere.

Toluene (pure grade, Kanto Kagaku Co.) was purified by refluxing with calcium hydride powder for 24 h followed by fractional distillation over sodium wire under nitrogen atmosphere.

Ethyl benzoate(EB), dimethyl phthalate(DMP), diethyl phthalate(DEP) and di-n-butyl phthalate(DNBP) (extra pure grade, Tokyo Kasei Co.) were used after drying over molecular sieve 4A and deoxygenized by nitrogen.

Phenyltriethoxysilane(PTES), phenyltrimethoxysilane (PTMS), diphenyldimethoxysilane(DPDMS), tetramethoxysilane (TTMS) (extra pure grade, Tokyo Kasei Co.), $Al(C_2H_5)_3$ (Toyo Staufer Chemical Co.), anhydrous $MgCl_2$ (Toho titanium Co.) and $TiCl_4$ (pure grade, Kanto Kagaku Co.) were used without further purification.

<u>Preparation of catalysts</u>

The mixture of 30 g (315 mmol) of $MgCl_2$ and 22 mmol of each ester was ground in an 1 l stainless steel vibration mill pot with 50 balls (25 mm in diameter) under nitrogen atmosphere for 20 h at room temperature. 8 g of the resultant mixture was reacted with 40 ml of $TiCl_4$ at 120°C for 2 h with a vigorous stirring followed by filtration under a nitrogen atmosphere. The precipitate was washed 8 times with 80 ml of toluene at 60°C and dried i. vac. for 8 h at room temperature to give the catalyst.

The $MgCl_2$-supported $TiCl_4$ catalyst without ester was prepared by cogrinding 30 g (315 mmol) of $MgCl_2$ with 27 mmol of $TiCl_4$ as the same method described above, followed by the same procedures.

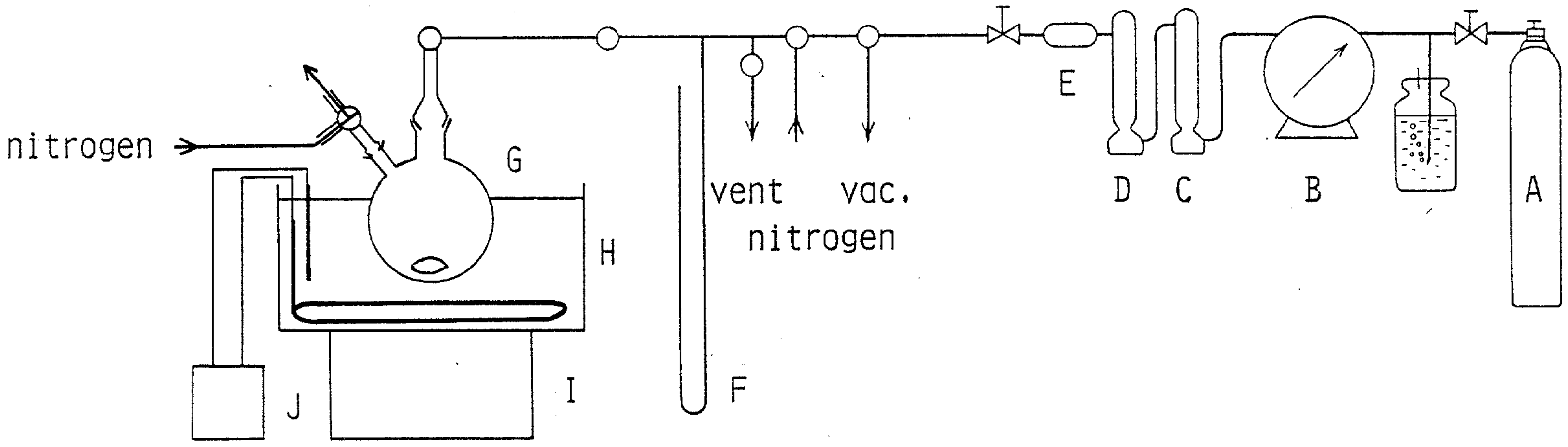
Polymerization procedures

Figure 1-1 shows an outline of the apparatus used for propylene polymerization. Polymerization of propylene was carried out in a 500 ml glass reactor equipped with a magnetic stirrer. A given amount of the catalyst and heptane as solvent were taken into the reactor under nitrogen atmosphere. After it was kept at the polymerization temperature for 20 min, nitrogen gas evacuated and propylene was introduced to saturate the solvent. Given amount of $Al(C_2H_5)_3$ and an external donor (if needed) solution was added to start the polymerization. Kinetic curves of polymerization were obtained by measuring the total volume of propylene consumed at various reaction time under constant monomer pressure. Polymerization was quenched by introducing a mixture of ethanol and hydrochloric acid to the reactor. Produced polymers were washed with ethanol and dried under vacuum at 60°C.

Analytical procedures

The amount of titanium and silicon contained in the catalysts were determined by atomic absorption spectrophotometry (Shimazu AA-610s). The contents of carbon, hydrogen and chlorine were analyzed by elemental analysis. The isotactic index, weight fraction of boiling heptane insoluble fraction, was determined by extraction with heptane for 15 h.

The gel permiation chromatograms of polymers were measured at 140°C in o-dichlorobenzene by using Shodex LC HT-



A : propylene B : flow meter C : $CaCl_2$ D : P_2O_5
E : molecular sieve 4A F : manometer G : reactor
H : water bath I : magnetic stirrer J : thermostat

Figure 1-1 Apparatus for propylene polymerization.

3 equipped with Shodex AD80M/S column. Molecular weights were determined by universal calibration technique.

^{13}C NMR (proton-decoupled natural abundance Fourier-Transformed) spectra were recorded at 125.6 MHz and 120°C. The sample solution were made up to 15 wt% in 2 ml of 1,2,4-trichlorobenzene.

1-3 Results and Discussion

1-3-1 Effect of Internal Donors

Several kinds of $MgCl_2$-supported $TiCl_4$ catalysts were prepared according to the procedures described in the experimental section. The surface areas and Ti contents of the prepared catalysts are summarized in Table 1-1. Polymerization of propylene was conducted with these catalysts in the absence or presence of phenyltriethoxysilane(PTES). The results are summarized in Table 1-2. In Figures 1-2 and 1-3 are illustrated the kinetic curves of polymerization obtained in the absence and presence of PTES as an external donor, respectively. When polymerization was conducted without using PTES, the $TiCl_4$/ethyl benzoate(EB,monoester)/$MgCl_2$ catalyst showed the highest activity among these catalyst systems. However, addition of small amount of PTES caused the activity drastically to decrease. On the other hand, in the case of the catalysts containing diesters as an internal donor, especially di-n-butyl phthalate(DNBP), the addition of PTES did not cause the profound decrease in activity.

Table 1-1 Surface area and Ti content of prepared catalysts

Ester	Surface area[a) $[m^2/g]$	Ti content [wt%]
$C_6H_5COOC_2H_5$ (EB)	144	1.8
$C_6H_4(COOCH_3)_2$ (DMP)	63	0.85
$C_6H_4(COOC_2H_5)_2$ (DEP)	121	1.5
$C_6H_4(COO\text{-}n\text{-}C_4H_9)_2$ (DNBP)	170	2.0
none	71	2.8

a) Surface area measured by the BET method of nitrogen adsorption at -196°C

Table 1-2 The results of propylene polymerization with various $MgCl_2$-supported $TiCl_4$ catalysts

Catalyst	PTES	$\bar{R}_{2h}$ a)	Iso	Ata	I.I. b)
	[mmol/l]	[kg-PP/g-Ti·h]			[%]
$TiCl_4/MgCl_2$	0	4.5	1.2	3.3	27
〃	0.25	1.4	1.0	0.4	74
$TiCl_4$/EB/$MgCl_2$	0	13.7	8.2	5.5	60
〃	0.25	3.2	2.8	0.4	88
$TiCl_4$/DMP/$MgCl_2$	0	1.5	1.1	0.4	74
〃	0.25	0.74	0.68	0.06	92
$TiCl_4$/DEP/$MgCl_2$	0	4.8	3.6	1.2	74
〃	0.25	1.3	1.2	0.1	96
$TiCl_4$/DNBP/$MgCl_2$	0	5.2	4.1	1.1	79
〃	0.25	4.9	4.6	0.3	94
$TiCl_4$·DNBP/$MgCl_2$ c)	0	4.0	3.0	1.0	76
〃	0.25	2.0	1.7	0.3	87

Polymerization conditions ; $P_{C_3'}$ = 660 Torr, $Al(C_2H_5)_3$ = 5 mmol/l, Al/Ti = 50, 40°C, 2 h, heptane = 200 ml.

a) Average rate for the initial 2 h.

b) Isotactic Index determined by solvent extraction

c) $TiCl_4$·DNBP complex was used.

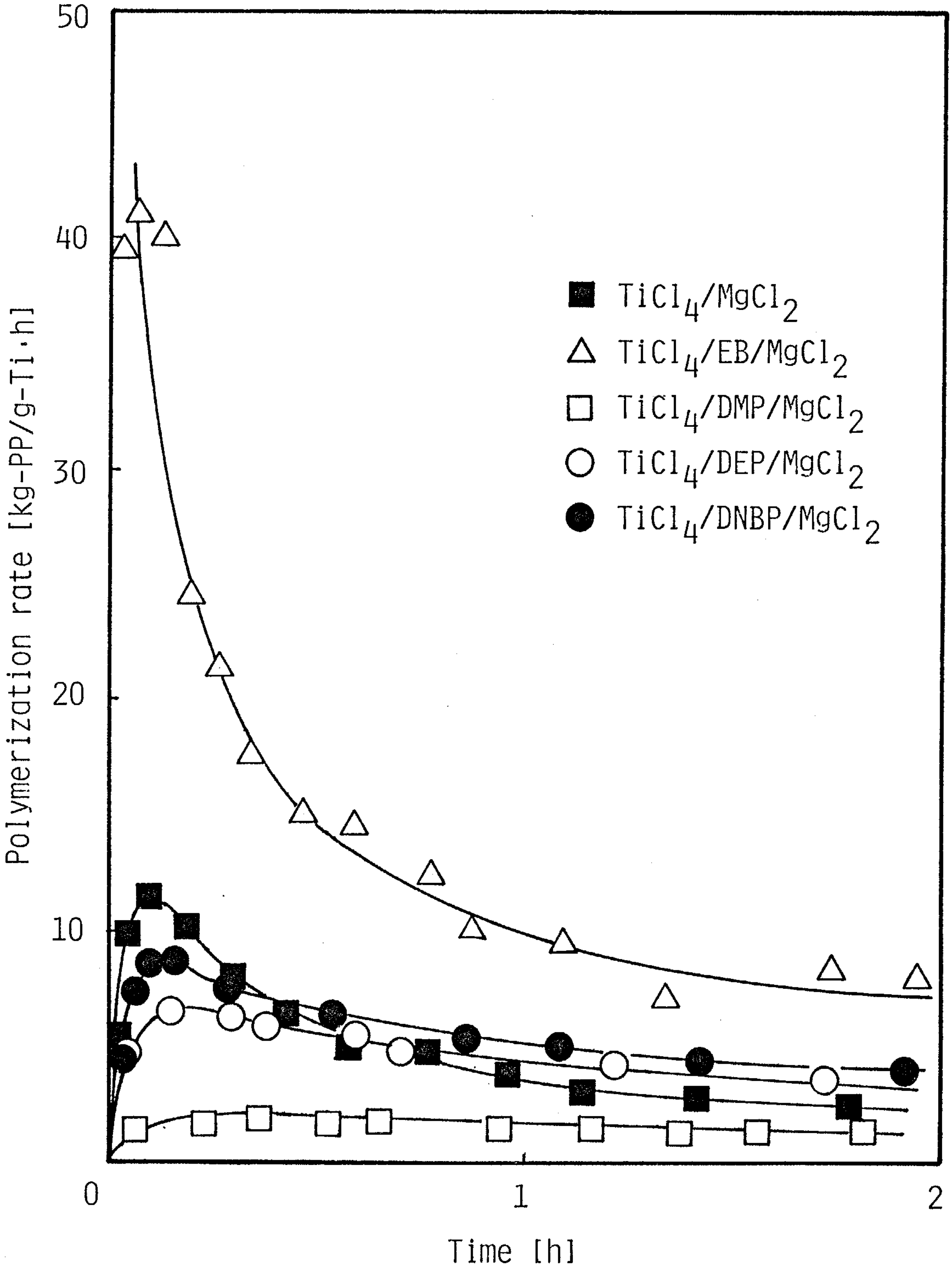


Figure 1-2 Rate-time profiles for the polymerization of propylene with various $MgCl_2$-supported $TiCl_4$ catalysts.
Polymerization conditions as indicated in Table 1-2.

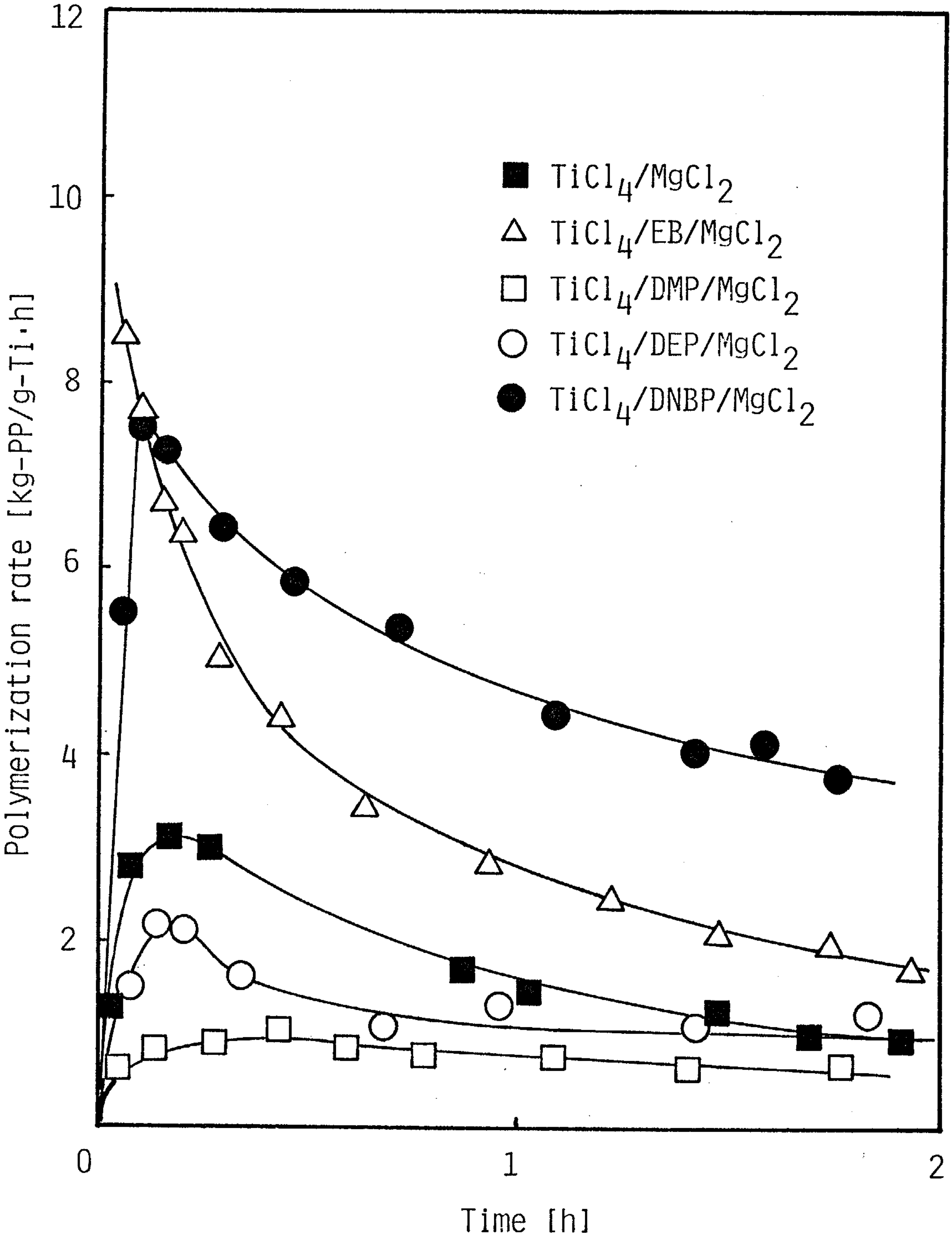


Figure 1-3 Rate-time profiles for the polymerization of propylene with various $MgCl_2$-supported $TiCl_4$ catalysts in the presence of PTES.

Polymerization conditions as indicated in Table 1-2.

In Figure 1-4 are plotted the polymerization rates in a logarithmic scale against polymerization time. It is evident from Figure 1-4 that the kinetic behaviors of polymerization are completely different between monoester and diester systems and that the addition of PTES does not change the kinetic profile. When using DNBP(diester) the rate decay obeyed the first-order kinetics rate. While in the EB(monoester) containing catalyst system, it might obey the second-order deactivation as reported previously3).

These results suggest that the active Ti species in the diester systems are supported more tightly in higher dispersion as compared with those in the EB(monoester) system.

To throw some light on this point, the following analytical experiments were carried out. Both the $TiCl_4$/EB(monoester)/$MgCl_2$ and $TiCl_4$/DNBP(diester)/$MgCl_2$ catalysts were brought into contact with an $Al(C_2H_5)_3$ solution in heptane [$Al(C_2H_5)_3$ = 40 mmol/l] at 40°C for 1 h with a vigorous stirring and the contents of the internal donors and the titanium in these catalysts were analyzed. The results shown in Table 1-3 indicate that EB(monoester) is much more removable by this treatment.

Propylene polymerization was then carried out at 40°C with these catalyst systems as well as the $TiCl_4/MgCl_2$ catalyst. In Table 1-4 are shown the activity and isotacticity of polymers obtained at different polymerization periods. In the case of the EB(monoester) system, the

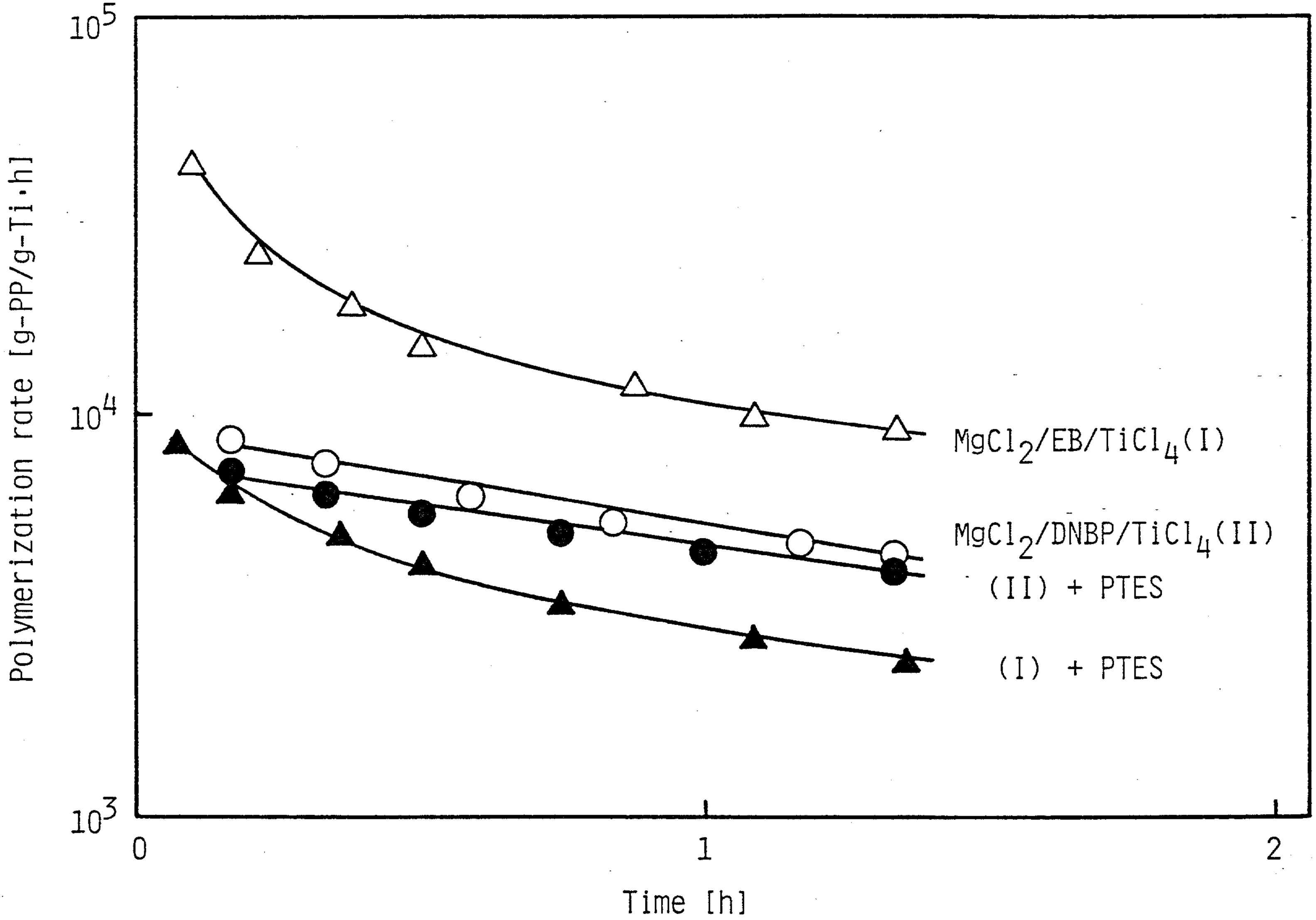


Figure 1-4 Plots of log(rate) versus time by using the results shown in Figures 1-2 and 1-3

Table 1-3 Analyses of catalysts before and after treatment with $Al(C_2H_5)_3$

	before treatment		after treatment		loss of ester
	$Ti^{a)}$ [wt%]	$C^{b)}$ [wt%]	$Ti^{a)}$ [wt%]	$C^{b)}$ [wt%]	[%]
$TiCl_4$/DNBP/$MgCl_2$	2.0	6.9	1.7	5.6	19
$TiCl_4$/EB/$MgCl_2$	1.8	4.9	1.8	2.8	43

Reaction conditions ; $Al(C_2H_5)_3$ = 40 mmol/l, Al/Ti = 20, heptane = 20 ml, 40°C, 1 h.

a) By atomic absorption spectrophotometry

b) By elemental analysis

Table 1-4 The dependence of activity and isotacticity on polymerization time

Catalyst system	Polymerization time [min]	Activity[a] [kg-pp/g-Ti·h]	I.I. [%]
$TiCl_4/MgCl_2$	8	11.1	23
〃	120	4.6	24
$TiCl_4/EB/MgCl_2$	8	44.2	53
〃〃	120	9.7	43
$TiCl_4/DNBP/MgCl_2$	8	13.1	78
〃	120	5.4	76

Polymerization conditions ; heptane = 100 ml, $Al(C_2H_5)_3$ = 10 mmol/l, Al/Ti = 100(mol/mol), $P_{C_3'}$ = 660 Torr, 40°C

a) Average rate for the polymerization time.

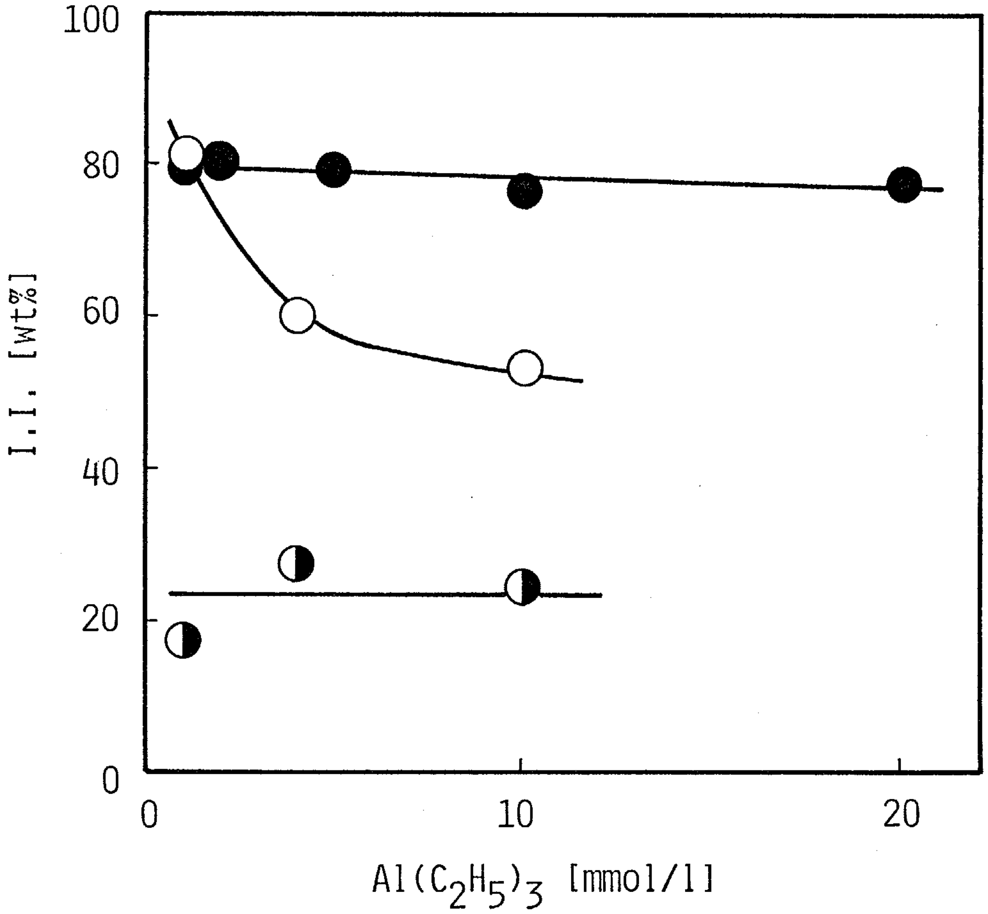


Figure 1-5 The dependence of I.I. on the concentration of $Al(C_2H_5)_3$.

◑ ; $TiCl_4/MgCl_2$, ○ ; $TiCl_4/EB/MgCl_2$, ● ; $TiCl_4/DNBP/MgCl_2$

isotacticity was decreased with increasing the polymerization time. While in the ester-free and the DNBP(diester) systems, the isotacticity remained almost unchanged. The isotacticity of polymers decreased in the following order.

DNBP > EB > ester-free

The dependences of the isotacticity on the concentration of $Al(C_2H_5)_3$ are illustrated in Figure 1-5. The increase in the $Al(C_2H_5)_3$ concentration caused a drastic decrease in the isotacticity in the case of the EB system. On the other hand, the isotacticity of polymers obtained with the ester-free and DNBP systems was almost independent upon the concentration of $Al(C_2H_5)_3$.

These results may be understood in terms of the following mechanism. Most of the Ti species formed on the $MgCl_2$ surface in the absence of internal donor may have two vacant sites to which propylene monomers can coordinate, and produce atactic polymer. When an internal donors is added, one of the vacant sites may be selectively blocked, which forces the monomer to coordinate via one vacant site, resulting in producing isotactic polymer. However, since the monoesters like EB have only one ester group to coordinate either with $MgCl_2$ or with Ti species, they can be removed from the catalyst surfaces according to the following equilibrium equation.

$$EB + [Al(C_2H_5)_3]_x \rightleftharpoons EB\cdot[Al(C_2H_5)_3]_x$$

Therefore, when polymerization is carried out with the $TiCl_4$

/EB/$MgCl_2$ catalyst without using an external EB, the number of EB-free Ti species increases markedly with increasing the polymerization time and/or the concentration of $Al(C_2H_5)_3$. Such EB-free Ti species which produce atactic polypropylene may easily interact with the neighboring EB-free Ti species to deactivate according to the second-order kinetics. On the other hand, when diesters like DNBP are used as an internal donor, it can be assumed that one of the ester group is coordinated with the Ti species and the other with $MgCl_2$ and consequently they are hardly removable from the catalyst surfaces. The profound effect of diesters on catalyst stability is considered mainly attributed to this peculiar ability to make complexes with both the Ti species and $MgCl_2$.

1-3-2 Effect of Organosilicon Compounds as an External Donors

As shown in Table 1-2, addition of phenyltriethoxysilane(PTES) remarkably increased the isotacticity of the produced polypropylene. The value of the isotactic index and the loss of activity, however, depend strongly on the catalyst systems. Among the catalyst systems investigated, the DNBP system was found most effective ; it gave highly isotactic polymer without decreasing the activity.

To get more information on this point, polymerization was conducted using various kinds of organosilicon compounds with the $TiCl_4$/DNBP/$MgCl_2$-$Al(C_2H_5)_3$ catalyst system. The results are summarized in Table 1-5. The isotacticity was found to be strongly dependent upon the organosilicon compounds :

Table 1-5 The effect of the amount and kinds of organosilicon compounds on propylene polymerization with $TiCl_4$/DNBP/$MgCl_2$.

Organosilicon compound [mmol/l]		$Al(C_2H_5)_3$ [mmol/l]	Propylene pressure [Torr]	Activity [kg-PP/g-Ti·h]			I.I. [%]
				Total	Iso	Ata	
none	—	5	660	5.2	4.1	1.1	79
PTES	0.13	〃	〃	4.7	4.4	0.3	93
〃	0.25	〃	〃	4.9	4.6	0.3	94
〃	0.50	〃	〃	3.9	3.7	0.2	95
〃	1.0	〃	〃	1.8	1.7	0.1	94
〃	1.5	〃	〃	2.8	2.7	0.1	96
none	—	10	200	1.9	1.4	0.5	72
DPDMS	0.20	〃	〃	1.6	1.3	0.3	78
〃	0.50	〃	〃	1.8	1.7	0.1	93
〃	1.0	〃	〃	1.3	1.2	0.1	93
PTES	0.5	〃	〃	1.5	1.4	0.1	93
PTMS	〃	〃	〃	1.3	1.2	0.1	91
TTMS	〃	〃	〃	0.78	0.71	0.06	91

Polymerization conditions ; catalyst = 50 mg (1 mg-Ti), 40°C, 1 h.

PTES, DPDMS, PTMS and TTMS denote phenyltriethoxysilane, diphenyldimethoxysilane, phenyltrimethoxysilane and tetramethoxysilane, respectively.

$C_6H_5Si(OC_2H_5)_3$ (PTES) $\approx$ $(C_6H_5)_2Si(OCH_3)_2$(DPDMS)
$>$ $(C_6H_5)Si(OCH_3)_3$(PTMS) $>$ $Si(OCH_3)_4$(TTMS)

The activities for isotactic (boiling heptane insoluble) and atactic (soluble) polymers are plotted in Figure 1-6 against the amount of PTES or DPDMS. Addition of a small amount of PTES or DPDMS, isotactic polymer was rather increased followed by a gradual decrease. A similar experiment was carried out by using EB as an external donor in place of PTES or DPDMS. In this case, both the isotactic and atactic polymers were monotonously decreased with increasing the amount of EB (Figure1-7). Thus, such a remarkable effect of organosilicon compounds seems to be attributed mainly to selective deactivation of aspecific sites.

The molecular weights of isotactic and atactic polymers obtained with the $TiCl_4$/DNBP/$MgCl_2$ catalyst are summarized in Table 1-6. The molecular weights of both polymers decreased gradually with increasing the concentration of $Al(C_2H_5)_3$, which implies that $Al(C_2H_5)_3$ acts as a chain transfer reagent. In Figure 1-8 is plotted $1/\bar{M}n$ versus $[Al(C_2H_5)_3]^{1/2}$ according to Eq.(1) proposed by Pasquon$^{52)}$, however, which is not fitted in this case.

$$\frac{1}{\bar{M}n} = a[Al]^{1/2} + b \qquad (1)$$

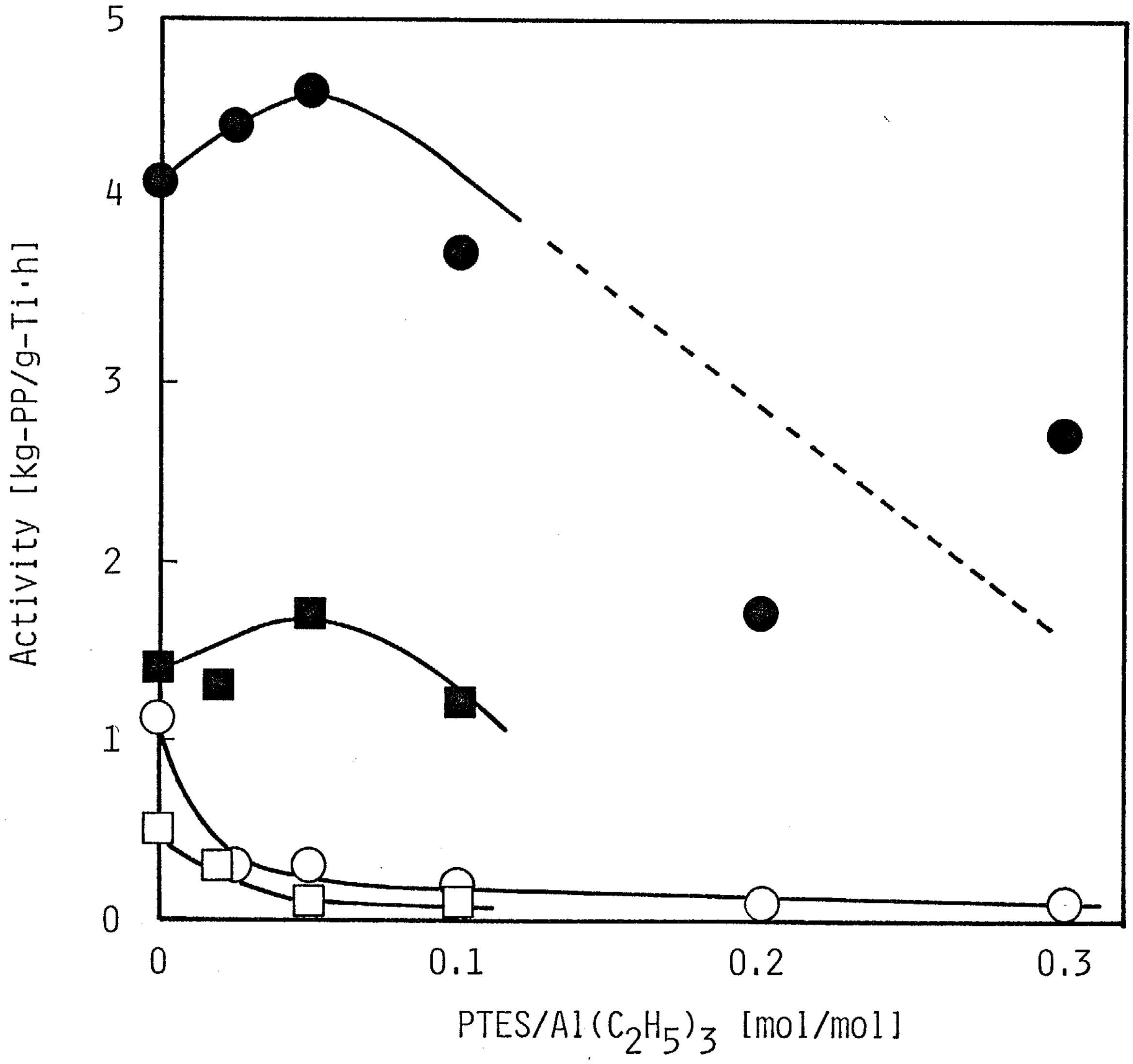


Figure 1-6 Plots of the activity versus the amount of organosilicon compounds added with $TiCl_4$/DNBP/$MgCl_2$-$Al(C_2H_5)_3$.

● ; PTES-boiling heptane insoluble, ○ ; soluble

■ ; DPDMS-boiling heptane insoluble, □ ; soluble

Polymerization conditions as indicated in Table 1-5.

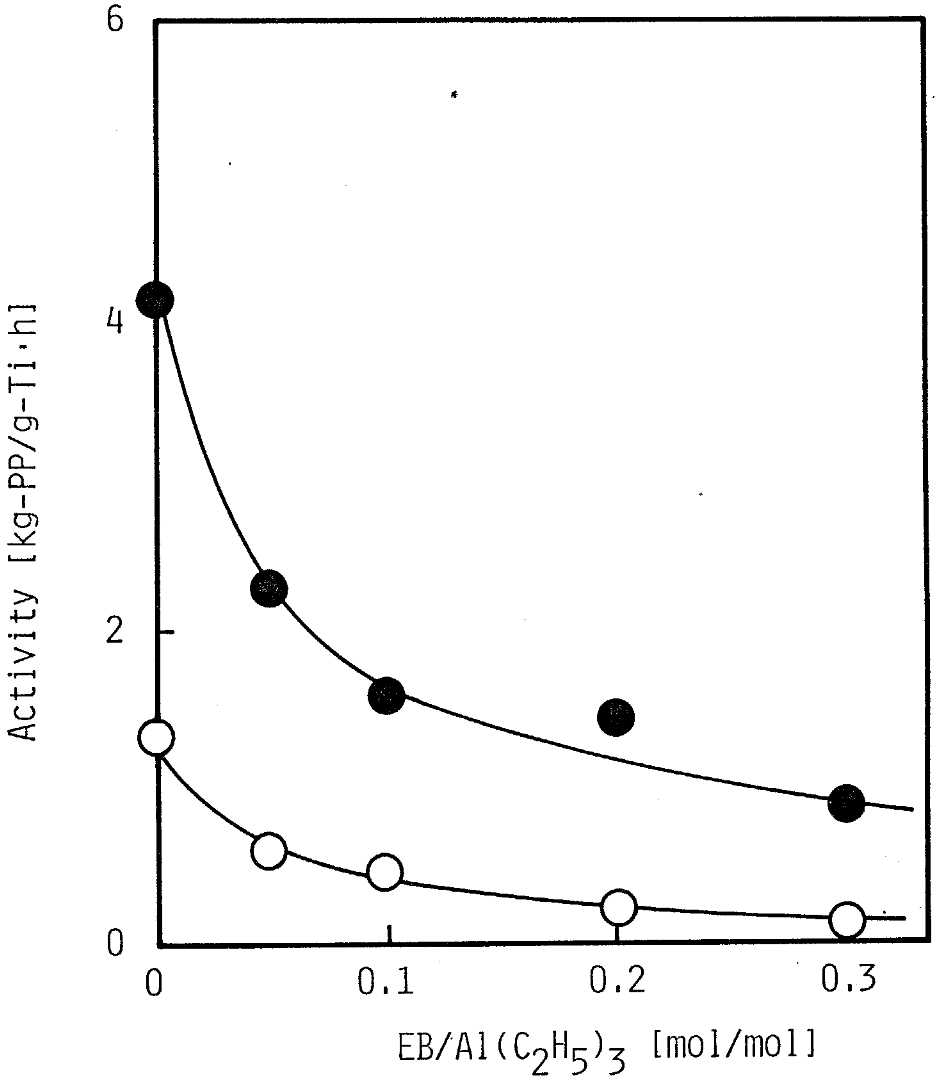


Figure 1-7 Plots of the activity versus the amount of EB added with $TiCl_4/DNBP/MgCl_2-Al(C_2H_5)_3$.

○ ; boiling heptane soluble

● ; boiling heptane insoluble

Polymerization conditions as indicated in Table 1-2.

Table 1-6 The effect of concentrations of $Al(C_2H_5)_3$ and PTES on number-average molucular weights of polypropylene obtained with $TiCl_4/DNBP/MgCl_2$.

$Al(C_2H_5)_3$ [mmol/l]	PTES [mmol/l]	heptane insoluble Mn x 10^{-4}	heptane insoluble Mw/Mn	heptane soluble Mn x 10^{-4}	heptane soluble Mw/Mn
1	0	13.0	5.4	1.5	9.6
2	0	8.3	5.8	1.4	7.1
5	0	6.8	5.8	1.2	6.2
20	0	6.0	6.3	1.1	7.3
5	0.13	9.5	3.9	0.90	7.5
5	0.25	8.7	5.8	0.88	8.0
5	0.50	8.2	7.6	0.73	9.0
5	1.0	8.2	8.3	0.69	10.0
5	1.5	7.4	8.4	0.65	13.7

Polymerization conditions as indicated in Table 1-5.

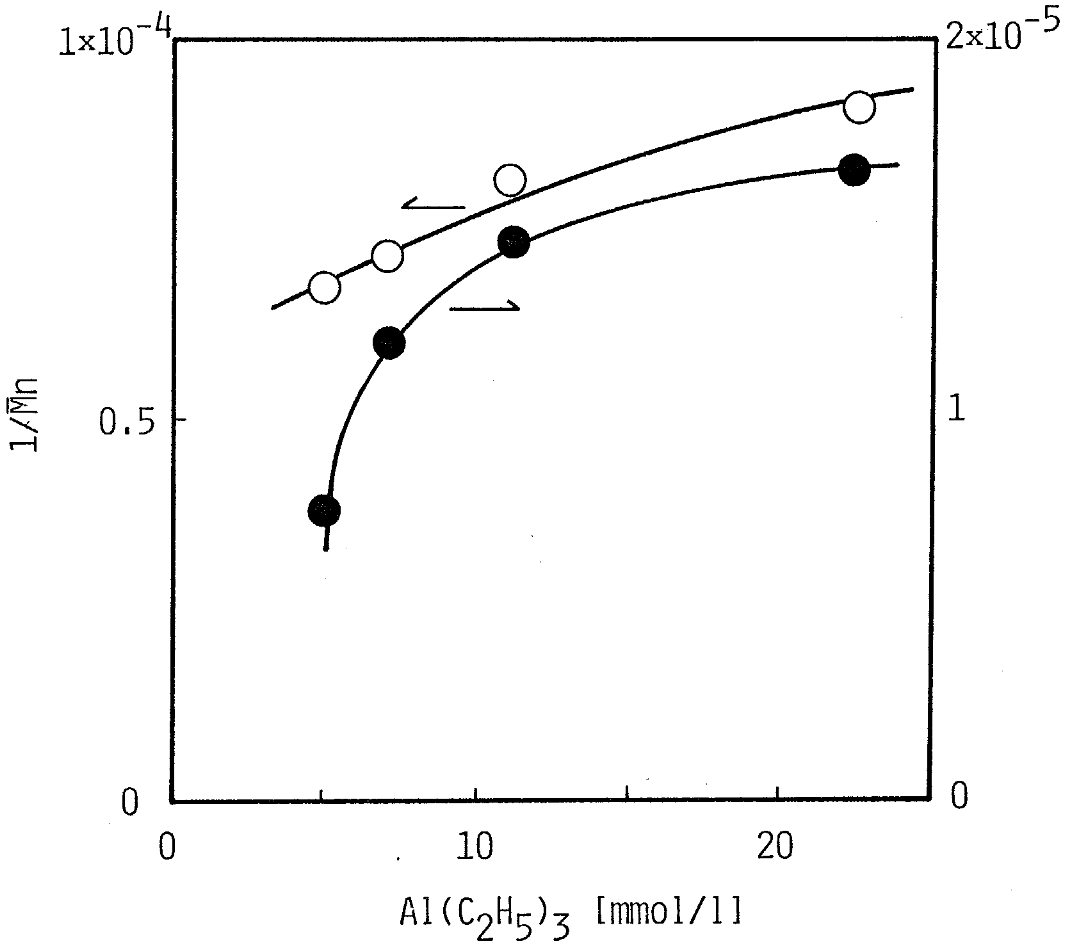


Figure 1-8 Plots of 1/$\bar{M}$n versus [Al(C$_2$H$_5$)$_3$].

●; boiling heptane insoluble, ○; soluble

Polymerization conditions as indicated in Table 1-6.

If the adsorbed $Al(C_2H_5)_3$ on the catalyst surface takes part in the transfer reaction, Eq.(2) may be applied.

$$\frac{1}{\overline{Mn}} = k \frac{K_A[Al]}{1 + K_A[Al]} + c \tag{2}$$

Since we cannot evaluate the c value in Eq.(2), it is very difficult to check the validity of Eq.(2).

On the other hand, with increasing the amount of PTES, the number-average molecular weight of atactic fraction monotonously decreased and that of isotactic fraction increased drastically followed by a slight decrease.

If it is assumed that the PTES acts as a chain transfer or termination reagent on the aspecific sites, the number-average degrees of polymerization in the presence($\overline{P}n$) and absence($\overline{P}n_0$) of PTES should be given as,

$$\overline{P}n = \frac{\int k_p[C^*][M]dt}{[C^*]_0 + \int \Sigma k'_{tr}[C^*][X]dt + \int (k_t+k_{tr})[C^*][PTES]^n dt} \tag{3}$$

$$\overline{P}n_0 = \frac{\int k_p[C^*][M]dt}{[C^*]_0 + \int \Sigma k'_{tr}[C^*][X]dt} \tag{4}$$

where k_p, k_{tr}, k_{tr} and k_t are rate constants of propagations, chain transfer by X, chain transfer and chain termination by PTES, respectively. In the $MgCl_2$-supported $TiCl_4$ catalyst, the average chain life time is extremely short$^{52)}$. Under such conditions, Eqs.(3) and (4) are simplified to Eqs.(5) and (6).

$$\overline{P}n = \frac{\int k_p[C^*][M]dt}{\int \Sigma k'_{tr}[C^*][X]dt + \int (k_t+k_{tr})[C^*][PTES]^n dt}$$

$$= \frac{k_p[M]\int[C^*]dt}{\Sigma k'_{tr}[X]\int[C^*]dt + (k_t+k_{tr})[PTES]^n\int[C^*]dt}$$

$$= \frac{k_p[M]}{\Sigma k'_{tr}[X] + (k_t+k_{tr})[PTES]^n} \qquad (5)$$

$$\overline{P}n_0 = \frac{\int k_p[C^*][M]dt}{\int \Sigma k'_{tr}[C^*][X]dt}$$

$$= \frac{k_p[M]}{\Sigma k'_{tr}[X]} \qquad (6)$$

The addition of PTES causes the decrease in atactic fraction. However, Eqs.(5) and (6) do not include [C*] and give the following equation,

$$\frac{\overline{P}n_0}{\overline{P}n} = \frac{\overline{M}n_0}{\overline{M}n} = \frac{\Sigma k'_{tr}[X] + (k_t+k_{tr})[PTES]^n}{\Sigma k'_{tr}[X]}$$

$$= 1 + \frac{(k_t+k_{tr})[PTES]^n}{\Sigma k'_{tr}[X]} \qquad (7)$$

where $\overline{M}n$ and $\overline{M}n_0$ are the number-average molecular weights with and without PTES, respectively. In Figure 1-9 are plotted $\log(\overline{M}n_0/\overline{M}n - 1)$ versus the concentration of PTES. The value of n was estimated to be 0.33 from Figure 1-9 which might suggest that the adsorbed PTES does also act as a chain transfer and/or termination reagent against the aspecific sites.

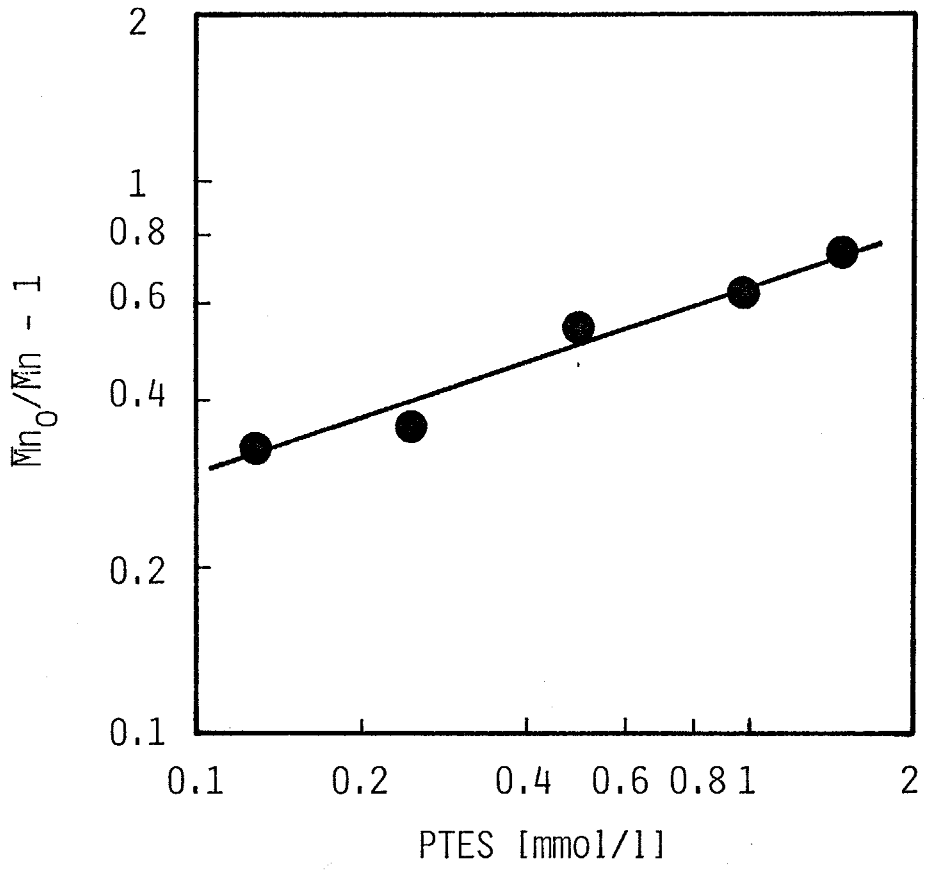


Figure 1-9 The effect of PTES on the number average molecular weight of boiling heptane insoluble fraction

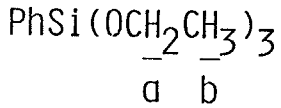
To get more information about the interactions among the catalyst components, ^1H NMR spectra were measured in d_8-toluene at room temperature. The results obtained are shown in Table 1-7. It may be said that there is no interaction between PTES and DNBP. Although the chemical shifts of protons indicate the existence of somewhat strong interaction of PTES and $Al(C_2H_5)_3$, any complex could not be isolated. Addition of DNBP to a $TiCl_4$ solution in heptane yielded a precipitate which was identified to be the 1:1 complex of DNBP and $TiCl_4$ by the elemental analysis (Table 1-8). When DNBP is added to an $Al(C_2H_5)_3$ solution in heptane, it is easily supposed that a complex is instantaneously formed between them which decomposes via chemical reactions at an elevated temperature as reported in the case of EB[53,54]. But in the actual catalyst systems the interaction between the two compounds may be not so important since DNBP is strongly coordinated with the Ti species and/or $MgCl_2$ as discussed above.

The reaction between $TiCl_4$ and organosilicon compounds have been widely investigated by Bradly et al.[55]. For example, the following reaction takes place rapidly when $TiCl_4$ and $Si(OC_2H_5)_4$ are brought into contact in hydrocarbon solvent.

$$\begin{aligned}&2\ TiCl_4 + Si(OC_2H_5)_4 \\ &\qquad \longrightarrow\ 2\ TiCl_3(C_2H_5) + SiCl_2(OC_2H_5)_2 \qquad (8)\end{aligned}$$

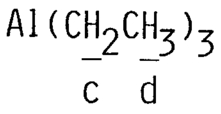
As shown in Table 1-8, such an exchange reaction acutually

Table 1-7 The data of ^{1}H-NMR spectra of catalyst components



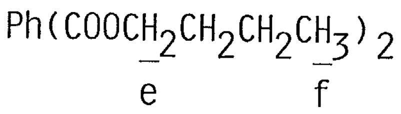
$\mathrm{PhSi(O\underset{a}{\underline{C}H_2}\underset{b}{\underline{C}H_3})_3}$

(PTES)



$\mathrm{Al(\underset{c}{\underline{C}H_2}\underset{d}{\underline{C}H_3})_3}$

(TEA)



$\mathrm{Ph(COO\underset{e}{\underline{C}H_2}CH_2CH_2\underset{f}{\underline{C}H_3})_2}$

(DNBP)

Component	Chemical shift [ppm from TMS] a	b	c	d	e	f
PTES	3.84	1.17	–	–	–	–
TEA	–	–	0.29	1.09	–	–
DNBP	–	–	–	–	4.19	0.80
PTES + TEA	3.79	1.09	0.22	1.39	–	–
PTES + $TiCl_4^*$	(3.88	0.86)	–	–	–	–
PTES + DNBP	3.84	1.18	–	–	4.19	0.81
DNBP + $TiCl_4^*$	–	–	–	–	(4.51	0.80)

Solvent ; d^8-toluene

* Products formed in heptane

Table 1-8 The results of analyses of products

	C [wt%]	H [wt%]	Cl [wt%]	Ti [wt%]	Si [wt%]	C_2H_5OH [mmol/g]
PTES + $TiCl_4$ [a] (precipitate)	11.9	2.9	50.8	24.5	n.d.	6.2
Caluculated as $C_2H_5OTiCl_3$	12.0	2.5	53.4	24.0	0	5.0
DNBP + $TiCl_4$ [b] (precipitate)	40.9	4.7	27.5	-	-	-
Calculated as DNBP·$TiCl_4$	41.0	4.7	30.3	10.3	-	-
DNBP·$TiCl_4$ + PTES [c]	42.1	5.1	26.0	-	-	-

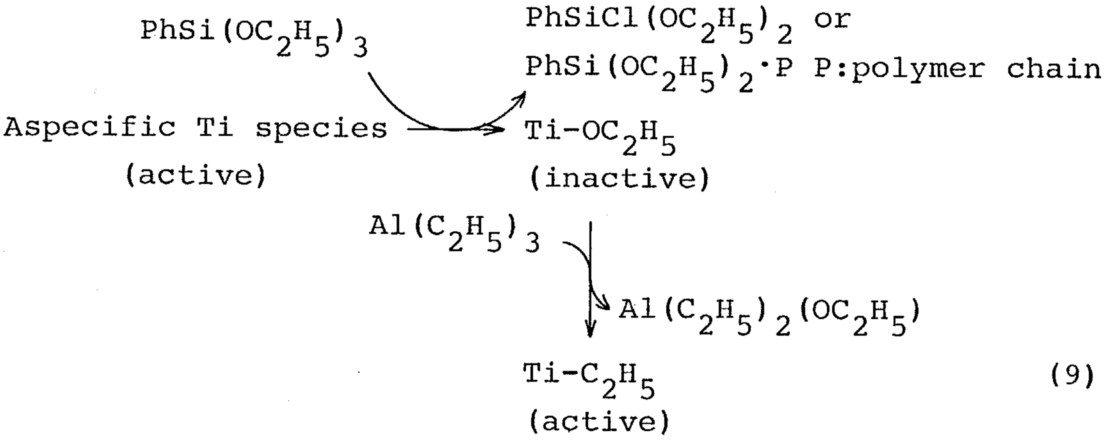
Reaction conditions ;

a) $TiCl_4$ = 14.6 mmol, PTES = 9.1 mmol, r.t.

b) $TiCl_4$ = 7.5 mmol, DNBP = 7.5 mmol, heptane = 10 ml, r.t.

c) DNBP·$TiCl_4$ = 1.1 mmol, PTES = 1.1 mmol, heptana = 22 ml, r.t.

proceeded also between $TiCl_4$ and PTES. Whereas, $TiCl_4$ DNBP complex hardly reacted with PTES, which might be attributed to the steric hindrance around the Ti species.
Considering these facts, it seems to be very easy for PTES to get access to the aspecific species which are free from the internal donor. Thus, a similar ligand exchange reaction can proceed between PTES and the aspecific Ti species, resulting in killing the activities. In actual polymerization systems, however, a ligand exchange reaction shown in Eq. (9) may occur between the deactivated species and $Al(C_2H_5)_3$ to regenerate the aspecific species which again produce atactic polymer.



(9)

Thus, there may exist an equilibrium between active and inactive species, which may be the main reason why this catalyst system also produces a small amount of atactic polymer.

The effect of PTES on the molecular weight of isotactic fraction is somewhat complicated. As shown in Table 1-5, the addition of PTES caused a drastic increase in the molecular weight, followed by a slight decrease and the MWD curves remained almost unchanged (Figure 1-10). This phenomenon strongly suggests that PTES might interact with isospecific sites as well.

For reference, Figure 1-11 displays the MWD curves for isotactic fractions obtained Kashiwa with the $TiCl_4/MgCl_2-Al(C_2H_5)_3/EB$ catalyst system[46]. The MWD curves in this case only partially shift to the higher molecular weight range by adding the external EB. In Figures 1-12 and 1-13 are illustrated the MWD curves of isotactic fractions obtained with the $TiCl_4/EB/MgCl_2-Al(C_2H_5)_3/EB$ under various concentrations of $Al(C_2H_5)_3$ and EB, respectively. In this case MWD curves gradually shifted to the higher molecular weight range with increasing the amount of EB added or decreasing the concentration of $Al(C_2H_5)_3$. Thus, the effect of PTES on MWD is different from that of EB. However, it is not clear why the MWD curve shifts to the higher molecular weight range by the addition of such external donors.

To get better insight into this point, polymers obtained in the absence and presence of PTES were again fractionated into several parts by solvent extraction. Weight fraction and steric pentad composition of each fraction determined by the methyl carbon intensities of ^{13}C NMR spectra (Figure 1-14) are shown in Table 1-9. In Figure 1-15 are illustrated normalized MWD curves for the fractionated polymers. The addition of PTES caused a drastic decrease in the amount of heptane soluble fraction as well as that of heptane insoluble -octane soluble fraction. On the contrary, octane insoluble

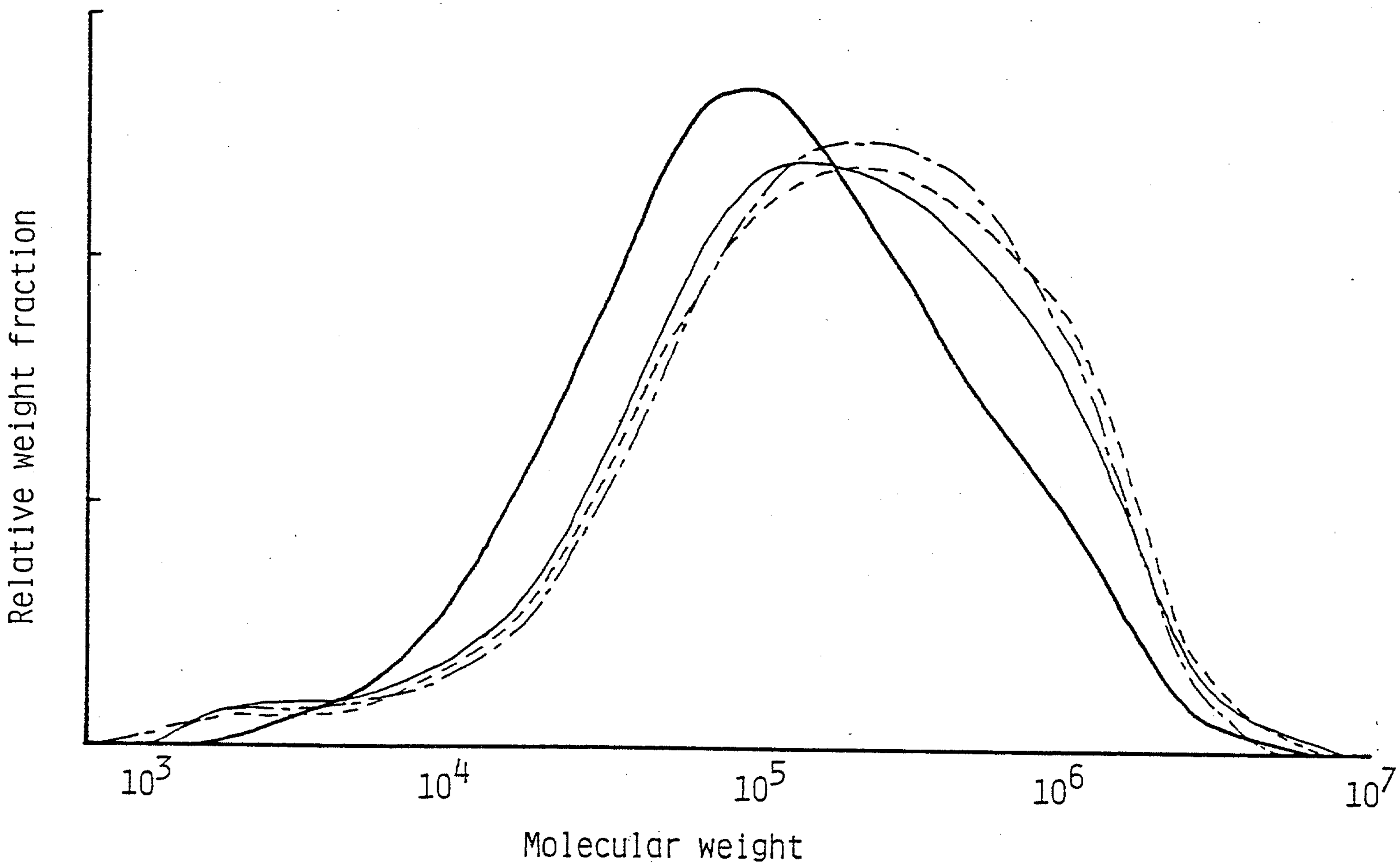


Figure 1-10 The effect of PTES on the MWD curves for the isotactic fractions obtained with $TiCl_4$/DNBP/$MgCl_2$-$Al(C_2H_5)_3$.

PTES[mmol/l] = ━; 0, ─; 0.25, ----; 0.50, —·—; 1.0

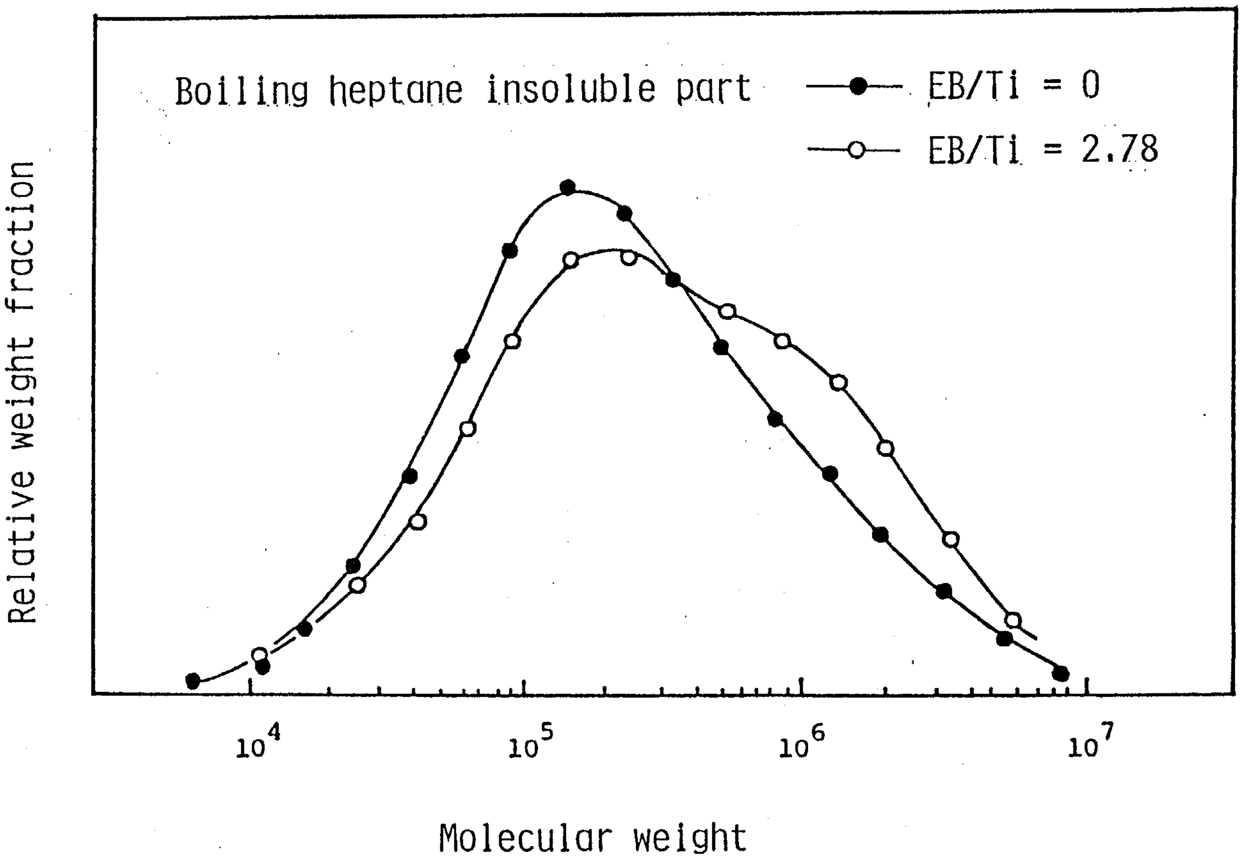


Figure 1-11 The molecular distribution curves for boiling heptane insoluble fractions obtained with $TiCl_4/EB/MgCl_2-Al(C_2H_5)_3$ in the absence or presence of external EB by Kashiwa.

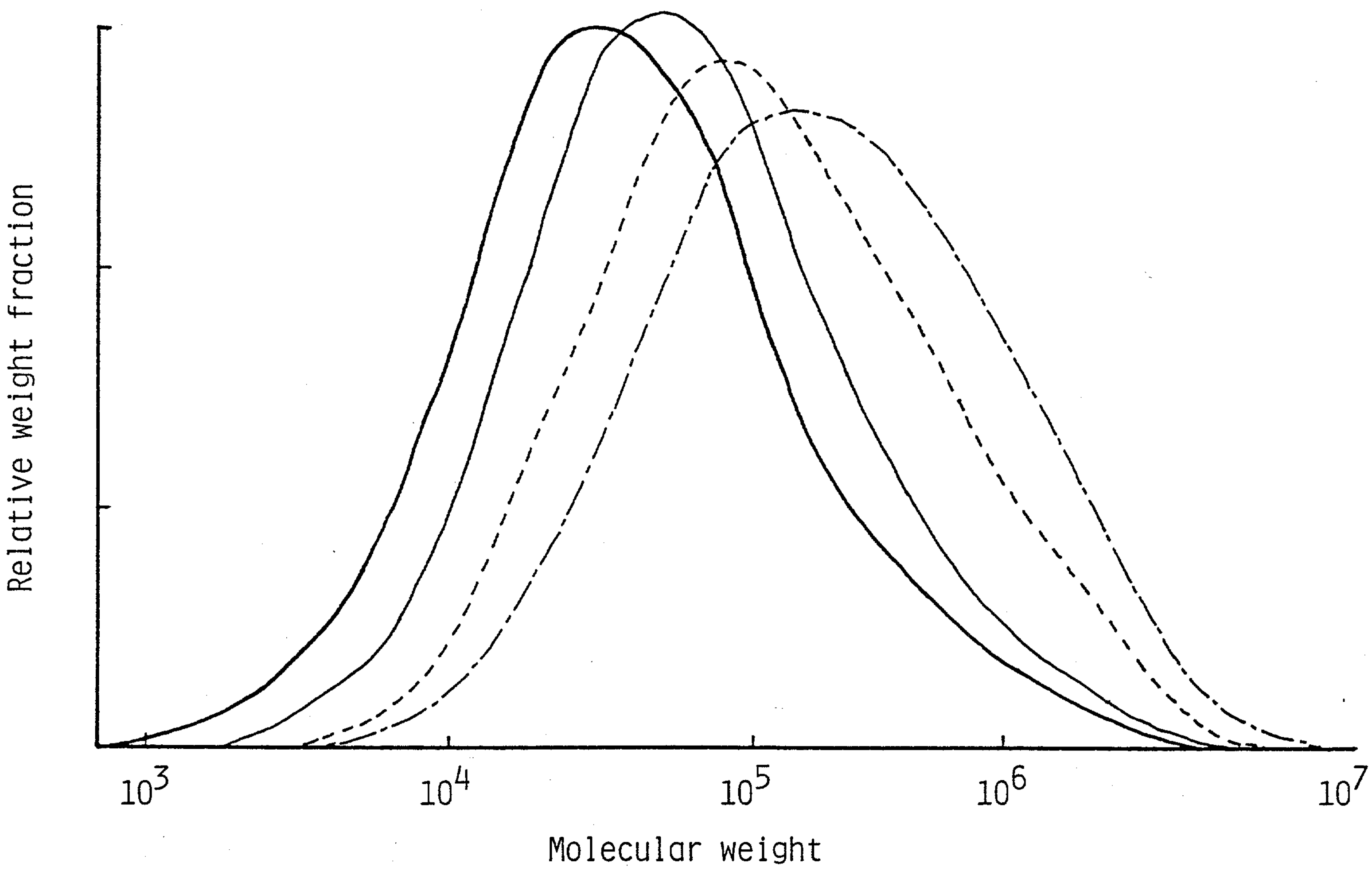


Figure 1-12 The effect of concentration of $Al(C_2H_5)_3$ on the MWD curves for isotactic fractions obtained with $TiCl_4$/EB/$MgCl_2$-$Al(C_2H_5)_3$.

Polymerization conditions ; $Al(C_2H_5)_3$ = ━━;30.0, ──;10.0, - - - -;2.5, —·—;0.25 mmol/l, $P_{C_3'}$ = 660 Torr, heptane = 100 ml, TEA/Ti = 150, 40°C, 30 min.

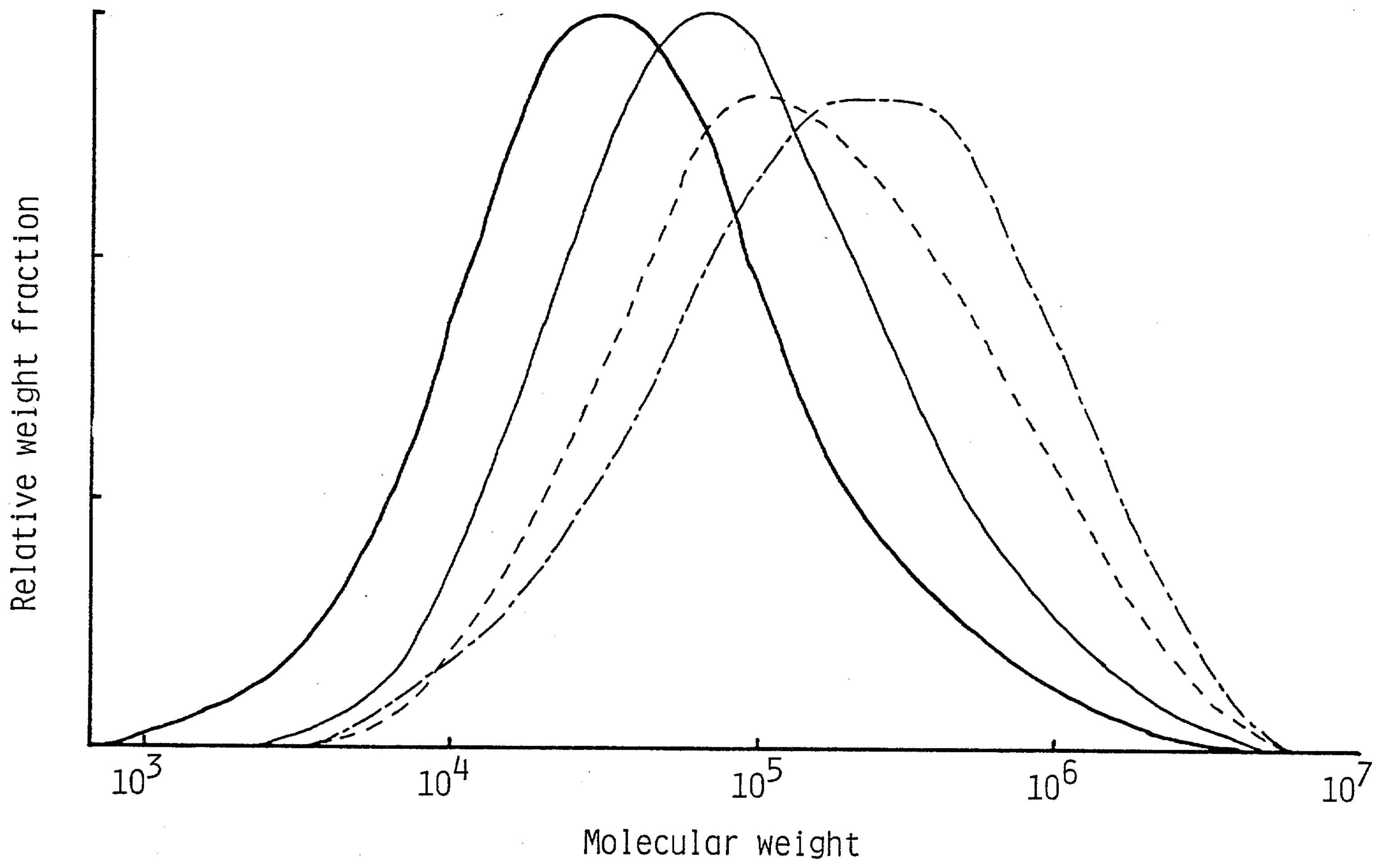


Figure 1-13 The effect of concentration of EB on the MWD curves for the isotactic fractions obtained with $TiCl_4/EB/MgCl_2-Al(C_2H_5)_3/EB$.
Polymerization conditions ; EB = ━━;0, ──;5.0, ----;10.0, -·-;15.0 mmol/l, $Al(C_2H_5)_3$ = 30 mmol/l. Other conditions as indicated in Figure 1-13.

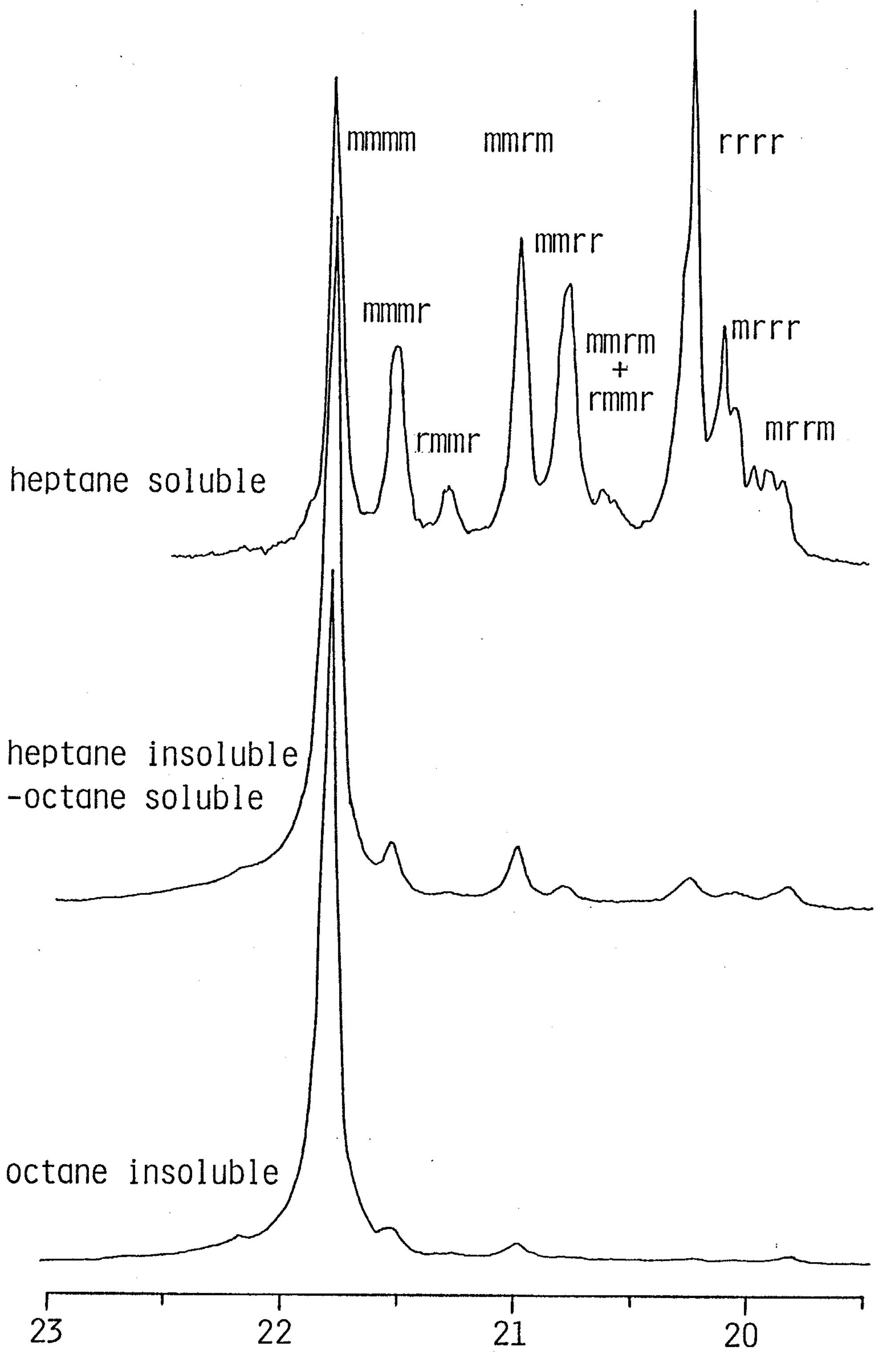


Figure 1-14 Methyl carbon regions in ^{13}C NMR spectra of fractionated polypropylene obtained with $TiCl_4$/DNBP/$MgCl_2$-$Al(C_2H_5)_3$/PTES

Table 1-9 The steric pentad compositions of fractionated parts by solvent extraction

PTES [mmol/l]	Extracted fraction	[%]	[mmmm]	[mmmr]	[rmmr]	[mmrr]	[mmrm] [rmrr]	[rmrm]	[rrrr]	[mrrr]	[mrrm]
0	S.7	21	21	11	2	13	13	2	17	13	7
	I.7-S.8	38	82	3	1	5	2	-	3	2	3
	I.8	41	95	2	-	2	-	-	-	-	1
0.5	S.7	5	19	9	2	12	14	2	20	13	5
	I.7-S.8	14	82	5	-	3	3	-	2	2	3
	I.8	81	95	2	-	2	-	-	-	-	1

S.7, I.7-S.8 and I.8 denote boiling heptane soluble, boiling heptane insoluble-boiling octane soluble and boiling octane insoluble parts, respectively.

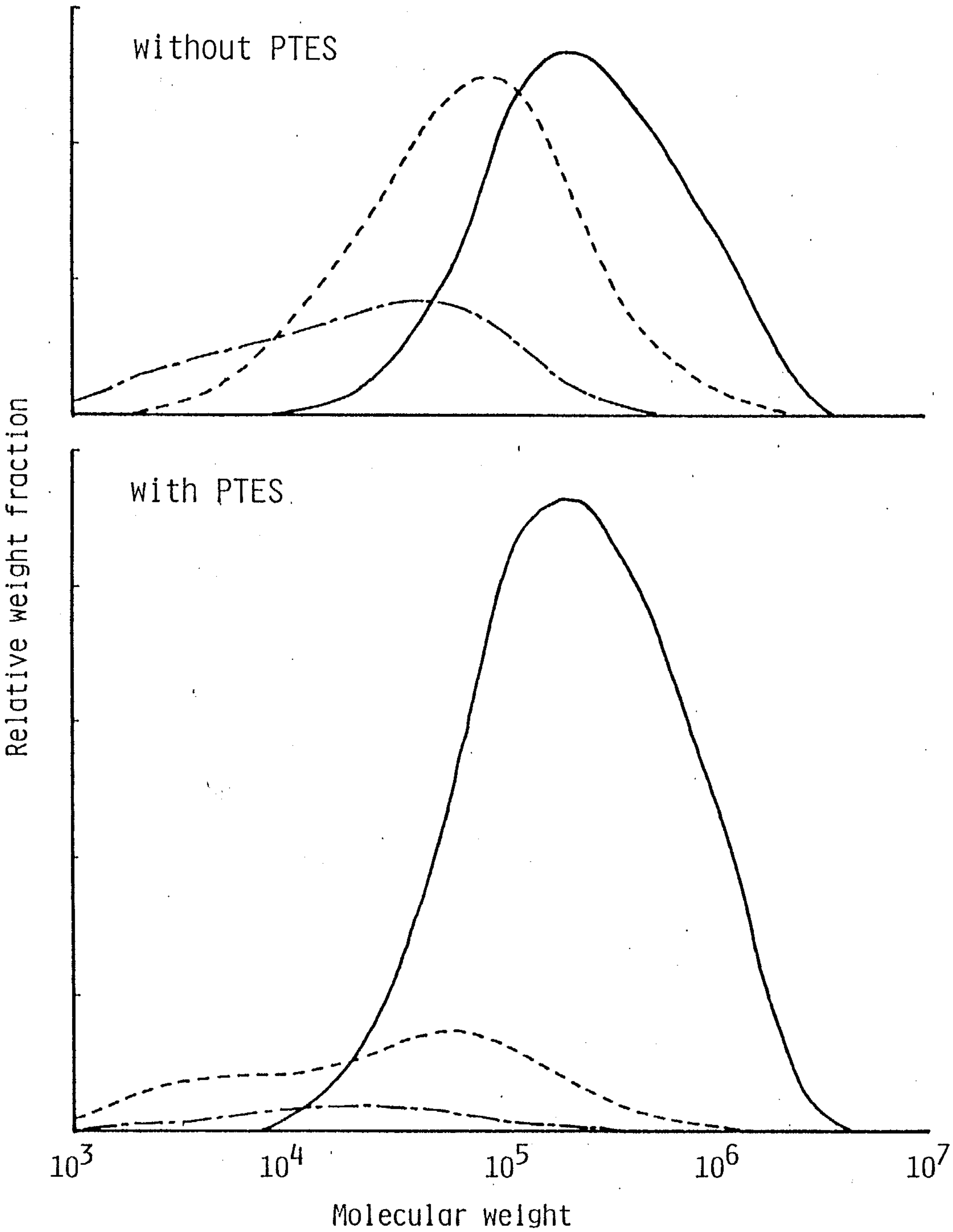


Figure 1-15 The MWD curves of fractionated polymers obtained in the presence and absence of PTES

—·—·—; nC_7 Sol. - - - - -; nC_7 Insol.-nC_8 Sol.

———; nC_8 Insol

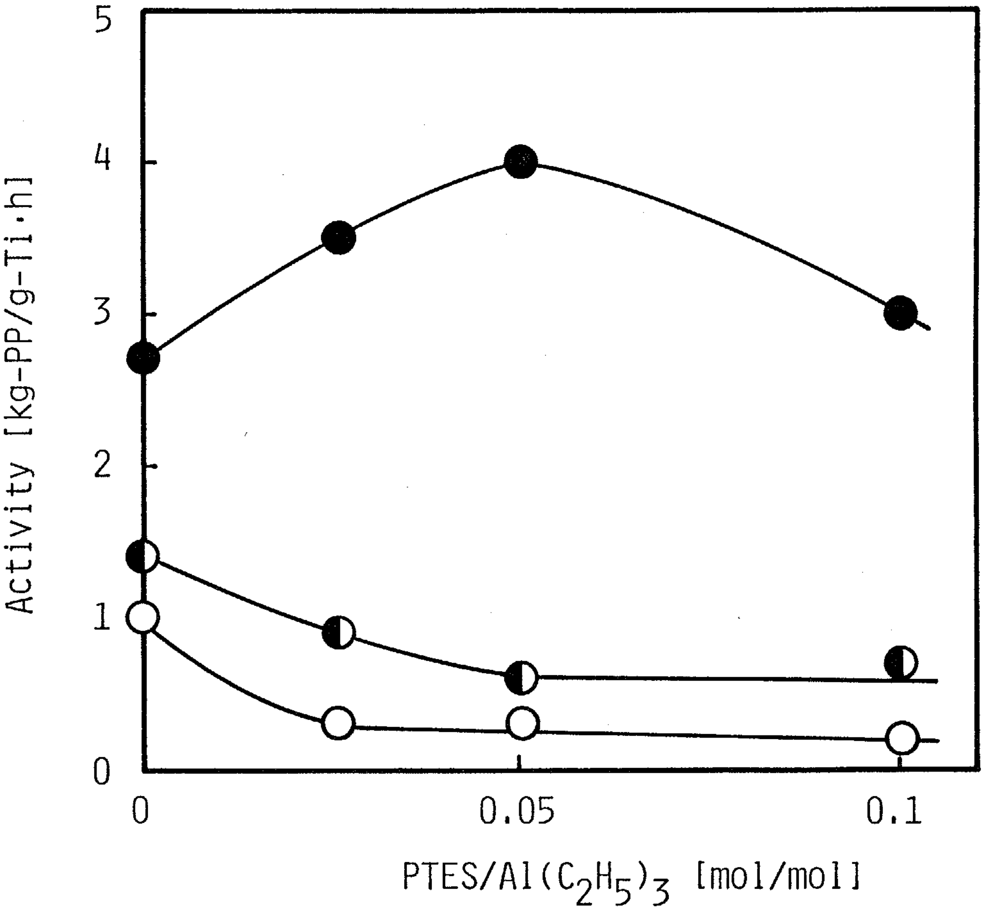


Figure 1-16 Plots of the activity versus the amount of PTES added with $TiCl_4$/DNBP/$MgCl_2$-$Al(C_2H_5)_3$.

○ ; boiling heptane soluble

◐ ; boiling heptane insoluble - boiling octane soluble

● ; boiling octane insoluble

fraction increased significantly without changing the MWD curve. In Figure 1-16 are plotted the amounts of these fractions against the amount of PTES added, which indicates that the addition of PTES causes a marked increase in the octane insoluble polymer.

The steric pentad compositions of these fractions have the following relations :

for octane insoluble polymer :

$$[mmmm] \gg [mmmr] = [mmrr] = 2[mrrm]$$

for heptane insoluble-octane soluble polymer :

$$[mmmm] \gg [mmmr] \approx [mmrr] \approx [rrrr] \approx$$
$$[mrrr] \approx [mrrm] \gg [rmrm] \approx [rmmr] \approx 0$$

These results clearly indicate that the octane insoluble polymer is highly isotactic containing few steric defects, whereas the octane soluble polymer contains appreciable amount of syndiotactic stereoblocks in the chain. This may be interpreted as follows. As mentioned in Section 1-3-1, DNBP may selectively coordinate with one of two vacant sites of the Ti species formed on the $MgCl_2$ surface, resulting in the isospecific Ti species. However, since the $MgCl_2$ surface is not uniform, it can be assumed that at least two types of isospecific species exist on the $MgCl_2$ surface which differ from each other in the ability to coordinate with the ligand (internal donor and/or chlorine atom). One, which is strongly coordinated with the ligands (Site-I), may produce highly isotactic, octane insoluble polymer. Whereas, the interaction between the other (Site-I') and the ligands is not so strong that the ligands can be mobile during polymerization. Accordingly the Site-I' may be sometimes coordinated with the ligand and sometimes free from it, resulting in producing the stereoblock, octane soluble polymer.

The change in the structure of the Site-I' may rapidly occur, but polymerization might stop during this interval. Taking into consideration that the mean life time of the living polymer is usually very short56), such a short pause should cause a significant decrease in the molecular weight. Another plausible model is that the propagation rate constant for syndiotactic propagation is smaller than that for isotactic or the chain trasfer rate constant for the former is larger than that of the latter, resulting in shortening the chain length.

Then the main effect of PTES on the isospecific sites is assumed to change the Site-I' into the Site-I by forcing the ligand to strongly coordinate with the Site-I'. Because of the hindered steric environment around the isospecific sites, it seems impossible for such large molecules as PTES to have sufficient access to them. Therefore, PTES is considered only to form fairly stable complexes with the Site-I'. In Figure 1-15, a small quantity of lower molecular weight polymer is observed in the heptane insoluble-octane soluble fraction in the presence of PTES. The precise reason for producing such polymer is not clear.

Busico et al.[57) have recently reported that three kinds of Ti species exist on the $MgCl_2$ surface shown in Figure 1-17. The highly isospecific(Site-I), isospecific(Site-II) and aspecific species(Site-II) which we propose here may correlate with them. However, the detailed structures for those active species are not clear at the present stage.

On the basis of above results and proposed mechanism, the effects of esters and organosilicon compounds on the isospecificity are discussed. The addition of PTES caused a significant increase in the isospecificity even in the DMP and DEP systems, but the amount of isotactic fractions decreased to a great extent in these systems. On the contrary, in the DNBP system, $Si(OCH_3)_4$ was less effective than PTES or DPDMS. Therefore, when less hindered diesters and organosilicon compounds are used as internal and external donors, the organosilicon compounds can get enough access access also to the isospecific Ti species. Thus, the isospecific Ti species are also partly deactivated. Recent patent literature[47) claims that meta- and para-derivatives of dialkylphthalates are less effective as compared with ortho-derivatives, which may be attributed to their poor ability to coordinate with the Ti species and/or $MgCl_2$.

In the case of monoesters like EB, a considerable amount of EB are removed from the catalyst surface as discussed in Section 1-3-1. This is based on the fact that the interaction between EB and $Al(C_2H_5)_3$ is not negligible. The resulting ester-free Ti species can easily react with PTES, and therefore PTES does not improve the stereospeci-

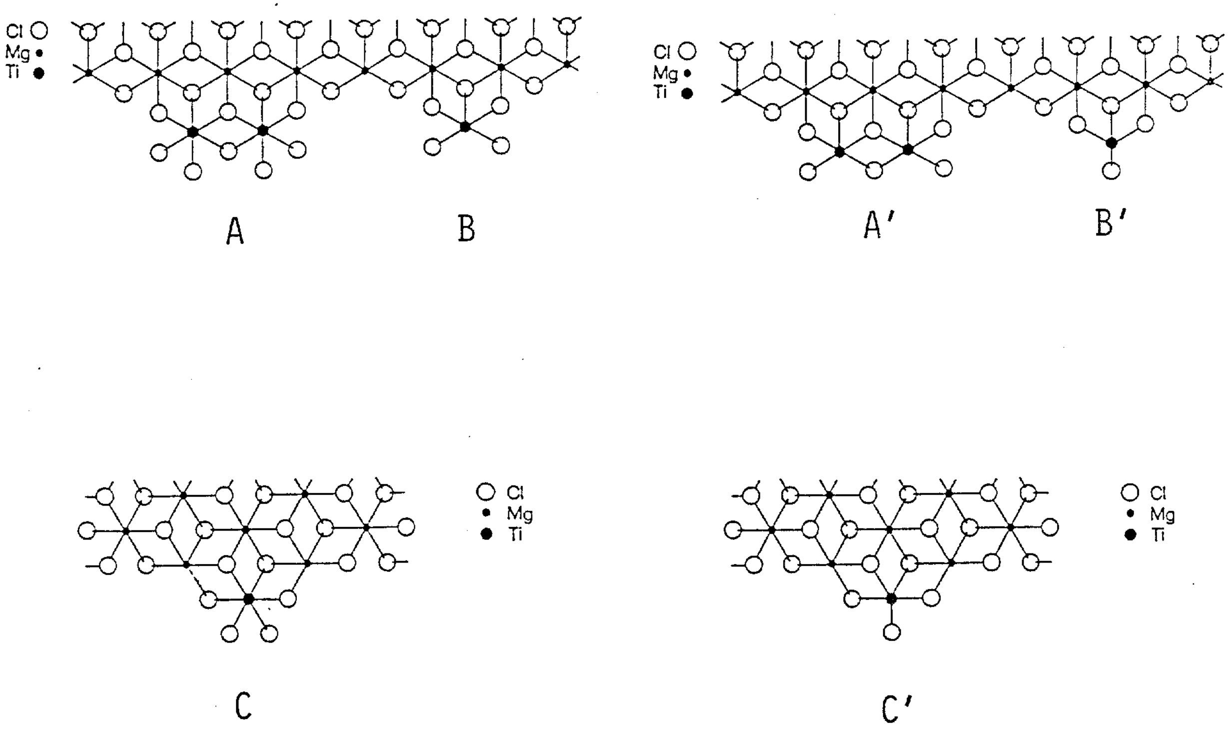


Figure 1-17 Possible models of Ti(IV) complexes coordinated epitactically to the (100) cuts (A and B), (110) cuts of $MgCl_2$; the same after activation by the alkylaluminium(catalytic sites A′, B′ and C′, respectively). The position of the non-bridged chlorine atoms is only indicative. Proposed by Busico et al.[56).]

ficity of the catalyst, but mainly deactivates the active species. An appreciable amounts of the external EB must, therefore, be added to prevent the removal of EB from the catalyst surface. While in the case of diesters like DNBP, which are already bound firmly to the catalyst, external EB acts only as adsorptive reagent to deactivate. On the contrary, PTES selectively interacts with the Ti species, which may be the main reason why the addition of a small amount of PTES markedly improves the stereospecificity of the catalyst.

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Chapter 2

Effect of Hydrogen on Propylene Polymerization with Isospecific Catalysts

2-1 Introduction

Hydrogen is one of the most efficient chain transfer agents in Ziegler-Natta catalyst systems and widely used in industrial plants. The mechanism of chain transfer with hydrogen is proposed as follows.

$$[\mathrm{Cat}]\text{-P} + \mathrm{H_2} \longrightarrow [\mathrm{Cat}]\text{-H} + \text{H-P} \qquad (1)$$

$$[\mathrm{Cat}]\text{-H} + \mathrm{CH_2{=}CHCH_3} \longrightarrow [\mathrm{Cat}]\text{-}\mathrm{CH_2CH_2CH_3} \qquad (2)$$

The dependence of the molecular weight on hydrogen pressure has been investigated by several authors. Natta$^{1)}$ has reported that the decrease in molecular weights(PM) of polyethylene and polypropylene obtained with α-$\mathrm{TiCl_3}$-$\mathrm{Al(C_2H_5)_3}$ catalyst system follows Eq.(3).

$$\mathrm{PM} = 1/K_1 + K_2 P_H{}^{1/2} \qquad (3)$$

Keii et al.$^{2)}$ found that the viscosity-average molecular weight of polypropylene obtained with the $\mathrm{TiCl_3}$-$\mathrm{Al(C_2H_5)_3}$ catalyst system decreases with increasing the hydrogen pressure according to the following equation, where $\bar{M}_\infty^{0}$ and $\bar{M}_\infty^{H}$ are viscosity-average molecular weights of polymers obtained in the absence and presence of hydrogen, respectively.

$$\frac{\bar{M}_\infty^0}{\bar{M}_\infty^H} = 1 + \beta \cdot P_{H_2}^{1/2} \qquad (4)$$

The effect of hydrogen on propylene polymerization with the $MgCl_2$-supported $TiCl_4$ catalyst have also been reported by several authors. Keii et al.[3) have studied the propylene polymerization with the $TiCl_4/EB/MgCl_2-Al(C_2H_5)_3$ catalyst system and found the following correlation between the number-average molecular weight, $\bar{M}n$, and hydrogen pressure.

$$\frac{1}{\bar{M}n} = a + b \cdot P_{H_2}^{1/2} \qquad (5)$$

Gastalla and Giannini[4) have investigated both ethylene and propylene polymerizations with the $TiCl_4/MgCl_4-Al(C_2H_5)_3$ catalyst system. They found that the dependence of the viscosity-average molecular weight of the heptane insoluble polypropylene on the hydrogen pressure also obeys Eq.(4).

These results strongly suggest that transfer reactions mainly occur by using the adsorbed hydrogen atoms. The effect of hydrogen on the molecular weight has also been studied with homogeneous catalyst systems. For example, Doi et al.[5) have employed the $V(acac)_3-Al(C_2H_5)_2Cl$ catalyst system for the syndiospecific polymerization of propylene and obtained Eq.(6).

$$\frac{1}{\bar{M}n} = a + b \cdot P_{H_2} \tag{6}$$

Kaminsky[6)] has studied the polymerization of ethylene with $(\eta^5\text{-}C_5H_5)_2ZrCl_2$ methylalumoxiane catalyst system and found a linear relationship between $\bar{M}v_0/\bar{M}v_H$ and $\log(P_{H_2}/P_{C_2H_4})$, where P_{H_2} and $P_{C_2H_4}$ denote the partial pressures of hydrogen and ethylene.

Schindler [7,8)] has studied ethylene polymerization using the conventional Ziegler-Natta catalysts in the presence of molecular deuterium and found that the deuterium in gas phase exchanges with the hydrogen atoms attached to the β-carbon of the growing polymer chain(β-hydrogen). At high Al/Ti ratios, deutrated ethanes were also found[9)]. From these comprehensive studies, Schindler[10)] proposed the following mechanism.

The exchange reaction between the adsorbed deuterium and β-hydrogen of the growing polymer chain preferentially occurs with Ti(IV) species,

$$\begin{array}{ccc} \text{Cat-}CH_2\text{-}CH_2\text{-R} & \text{Cat-}CH_2\text{-CHD-R} & \text{Cat-}CH_2\text{-}CD_2\text{-R} \\ + & + & + \\ \text{D - D} & \text{H - D} & \text{H - H} \end{array}$$

and only a transfer reaction proceeds with Ti(III) species.

$$\text{Cat-}CH_2\text{-}CH_2\text{-R} + H_2 \longrightarrow \text{Cat-H} + CH_3\text{-}CH_2\text{-R}$$

whereas, Ti(II) species, which become predominant at high

Al/Ti ratios, catalyze the following reactions,

$$\text{Cat-H} \xrightarrow{CH_2=CH_2} \text{Cat-}CH_2CH_3 \xrightarrow{D_2} \text{Cat-D} + CH_3CH_2D$$

$$\text{Cat-D} + CH_2=CH_2 \longrightarrow \text{Cat-}CH_2\text{-}CH_2D \longrightarrow \text{Cat-H} + CH_2=CHD$$

Kojima et al.[11)] have investigated the H_2/D_2 exchange reactions over $TiCl_3$ combined with various organometallic compounds. They observed that the rates of the exchange reactions are strongly dependent on the organometallic compounds used,

$$Al(C_2H_5)_3 > Al(CH_3)_3 > Zn(C_2H_5)_2 > Al(C_2H_5)_2Cl \gg Al(C_2H_5)Cl_2$$

From the fact that this order is in good accordance with that of the reduction ability, they suggested that the titanium species with lower valency states are active for the exchange reactions.

On the other hand, as described in Chapter 1, there may exist more than two types of active species. In order to investigate the nature of active species, both propylene and isoprene polymerizations were conducted under similar conditions with the $TiCl_4$-$Al(C_2H_5)_3$ and the $TiCl_4/MgCl_2$-$Al(C_2H_5)_3$ catalysts in the presence of external donors like EB[12)]. From the analyses of the microstructures of produced polymers, it was found that the increase in the external donors improves the isotacticity of polypropylene and, at the same time, decreases in cis-1,4 content of polyisoprene. On the basis of these results, we proposed that atactic polypropylene and cis-1,4 polyisoprene are produced by Ti species having two chlorine vacancies, while isotactic polypropylene and trans-1,4(or 3,4) polyisoprene by one vacancy sites.

It is expected that hydrogen molecules should react in different ways over these two kinds of species : Since hydrogen molecules can be adsorbed in atomic forms over the Ti species having two chlorine vacancies, transfer reactions over this kind of species may proceed by taking the reactive, atomic hydrogens, while it is impossible for the hydrogen molecules to be desociatively adsorbed on the other Ti species and molecular hydrogen may take part in the transfer reactions over such species.

Therefore, in this chapter, H_2/D_2 exchange reactions were carried out with $TiCl_4/MgCl_2-Al(C_2H_5)_3$ catalyst system in the presence of various amount of EB and were investigated the kinetic features of transfer reactions.

In addition, propylene polymerization was also carried out with highly isospecific catalysts ($TiCl_3-Al(C_2H_5)_2I$ and $TiCl_4/EB/MgCl_2-Al(C_2H_5)_3/EB$), followed by fractionation of polymers into isotactic and atactic, and dependence of the molecular weight on hydrogen pressure was investigated for both fractions.

2-2 Experimental

Materials

Hydrogen(99.99999 %) of ultra high purity was obtained from Nihon Sanso Co. and used after passing through the molecular sieve 3A column. Deuterium(99.75 atom-%) obtained from Takachiho Chemical Co. was used without further purification.

Ti-reduced, activated $TiCl_3$ (from Toho Titanium Co.), $Al(C_2H_5)_2I$ (from Nippon Alkylaluminium Co.), γ-Al_2O_3 (from Nishio Industry Co., 80~100 mesh) and $MnCl_2$ (from Kanto Kagaku Co., extra pure grade) were used without further purification.

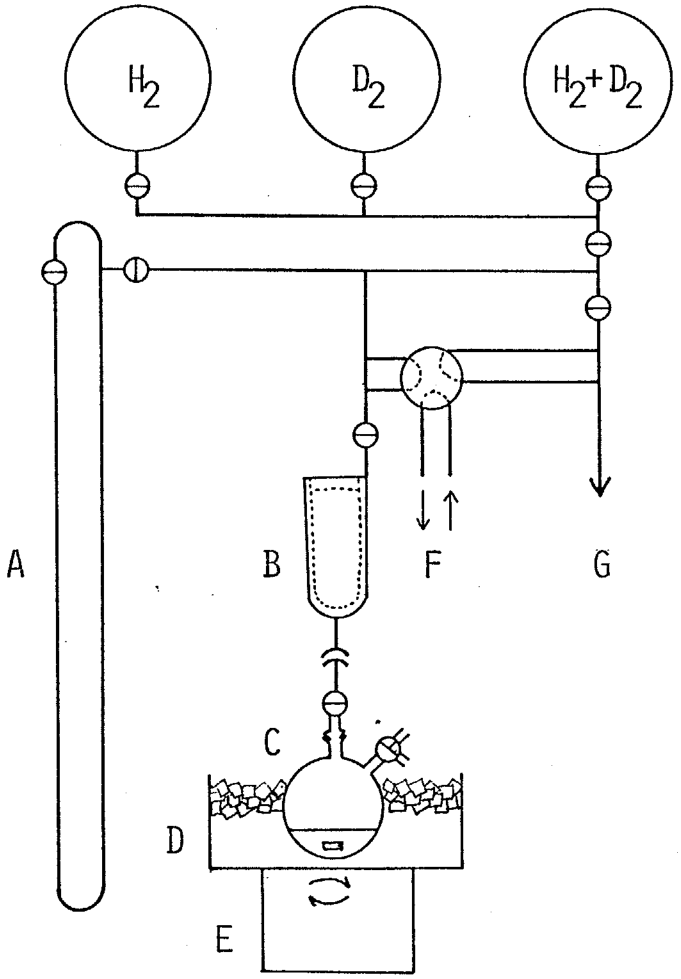
For the purification methods of the other chemicals to see the previous chapters.

Preparation of catalysts

The $TiCl_4/MgCl_2$ catalyst was prepared by cogrinding the mixture of 20 g of $MgCl_2$ and 10.4 g of $TiCl_4$. The catalyst was found to contain 8.6×10^{-2} g-Ti/g-cat. The $TiCl_4$/EB/$MgCl_2$ catalyst was obtained from the Research Center, Mitsui Petrochemical Industries, Co. Ltd.(3.2×10^{-2} g-Ti/g-cat).

H_2/D_2 exchange reaction

The exchange reactions between H_2 and D_2 were carried out in a conventional gas circulating system(Figure 2-1). Given amounts of heptane, $TiCl_4/MgCl_2$ catalyst, EB(if needed) and $Al(C_2H_5)_3$ were taken into the 50 ml Schlenk tube reactor. The reactor was then attached to the circulation system



A : manometer B : condencer(-78°C) C : reactor

D : ice-water bath E : magnetic stirrer

F : gas chromatography G : vacuum pump

Figure 2-1 Apparatus for H_2/D_2 exchange reactions.

having a dead space of about 5.0 l including the reactor, cooled by liquid nitrogen and evacuated. After the mixtures were kept at 0°C for 20 min, the exchange reactions were started by introducing the mixtures of H_2 and D_2.

Propylene polymerization

For comparison, propylene polymerization was carried out under similar conditions. Polymerization was conducted with the semi-batch system as described in Chapter 1.

Propylene polymerization in the presence of hydrogen

The polymerization of propylene was carried out at 40°C by using a semi-batch reactor system(300 ml) equipped with a dropping funnel and a magnetic stirrer. Given amounts of heptane, catalyst and EB (if needed) were placed in the reactor, while the cocatalyst was separately put in the dropping funnel under nitrogen atmosphere. After the reactor was kept at polymerization temperature, the nitrogen in it was completely pumped out. Then given amounts of propylene, hydrogen and nitrogen were introduced into the reactor so that the total pressure became an atmospheric pressure. Polymerization was started by adding the cocatalyst from the dropping funnel.

Analytical procedures

Hydrogen isotopes in gas phase were analyzed by a gas chromatograph13) connected with the circulating system.

Molecular weight distributions of polymers were measured according to the same procedures as described in Chapter 1.

The isotacticity of polypropylene was determined by the methods of Luongo[14) with IR or of solvent extraction as described in Chapter 1.

2-3 Results and Discussion

2-3-1 H_2/D_2 Exchange Reactions

H_2/D_2 exchange reactions were carried out with the $TiCl_4/MgCl_2$-$Al(C_2H_5)_3$ catalyst in the presence of various amounts of EB. In Figure 2-2 are plotted the contents of HD in gas phase against reaction time. Within the experimental conditions, the HD content increased linearly with the reaction time. The rate of HD formation calculated from the slopes in Figure 2-2 are shown in Table 2-1. With increasing the concentration of EB, the rate of HD formation decreased significantly. This results may be interpreted as follows. The $TiCl_4/MgCl_2$-$Al(C_2H_5)_3$ catalyst has two types of active Ti species ; one having one chlorine vacancy(I) and the other having two chlorine vacancies(II). It may be plausible to consider that the hydrogen molecules can be dessociatively adsorbed over the latter Ti species, while it cannot over the former species. Therefore, the H_2/D_2 exchange reactions may proceed much faster over the latter species. The decrease in the rate of exchange reactions by the addition of EB might be attributed to the selective poisoning of the latter species. As mentioned in Section 2-1, however, Kojima et al.9) have reported that the rate of H_2/D_2 exchange reactions strongly

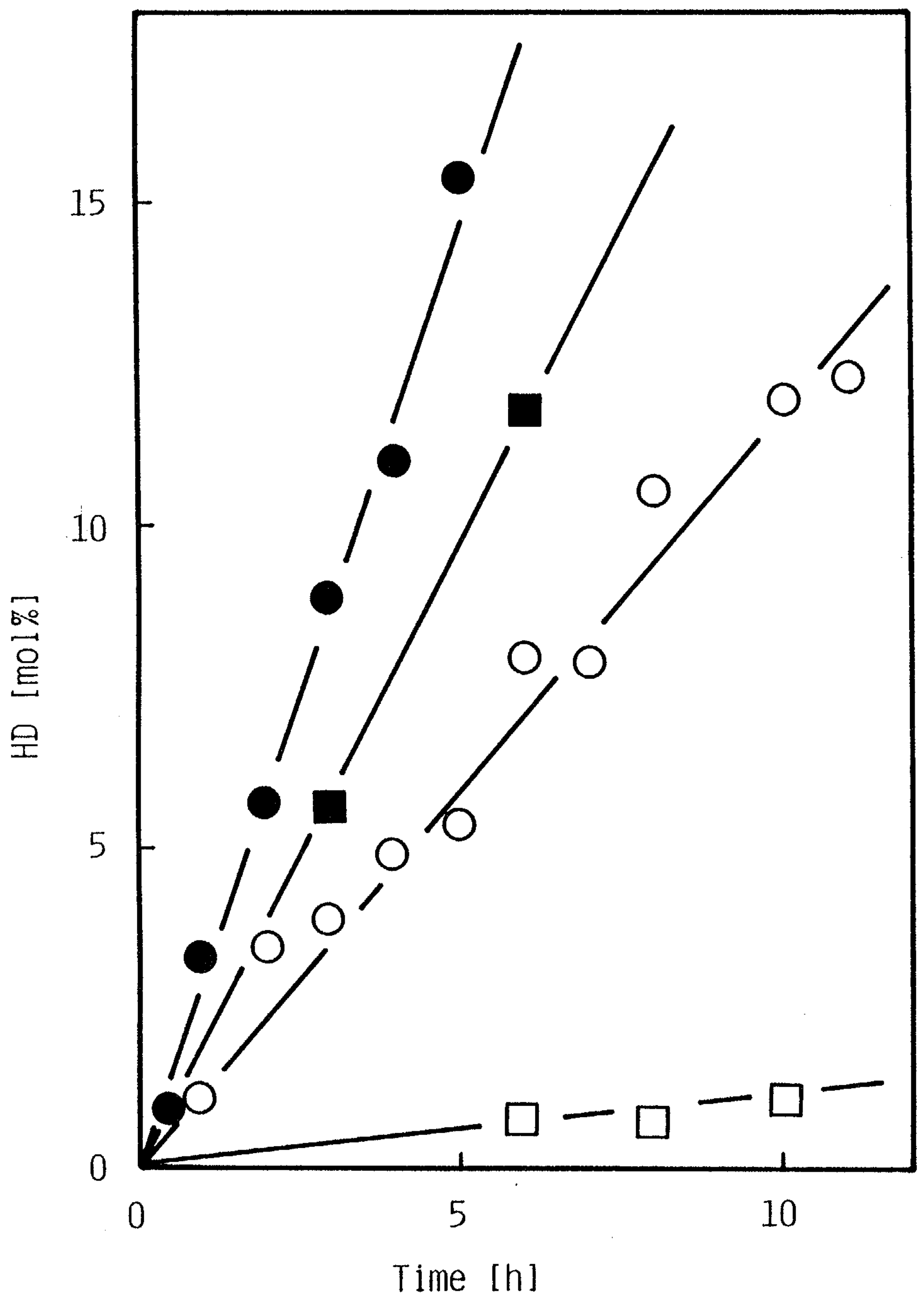


Figure 2-2 Mole fraction of HD in gas phase versus reaction time.

[EB] = ●; 0, ■; 8, ○; 14, □; 80 mmol/l

Reaction conditions as indicated in Table 2-1.

Table 2-1 Results of H_2/D_2 exchange reaction with $TiCl_4/MgCl_2$-$Al(C_2H_5)_3$ in the presence of EB.

Run no.	EB [mmol/l]	Time [h]	HD content (gas phase) [%]	Activity [mmol-HD/g-Ti·h]
1	0	5	14.5	5.2
2	8	5	9.8	3.6
3	14	5	6.0	2.1
4	60	5	0.6	0.22

Reaction conditions: $TiCl_4/MgCl_2$ = 0.2 g (0.4 mmol-Ti), $Al(C_2H_5)_3$ = 80 mmol/l, heptane = 5 ml, H_2/D_2 = 1.0 (molar ratio), Total pressure = 130 Torr, Temp. = 0°C.

Table 2-2 Results of propylene polymerization with $TiCl_4/MgCl_2-Al(C_2H_5)_3$ in the presence of EB.

Run no.	EB [mmol/l]	Time [min]	Activity [kg-PP/g-Ti·h] Iso.	Activity [kg-PP/g-Ti·h] Ata.	I.I.[a) [%]
1	0	4	0.69	0.42	62
2	8	4	0.71	0.21	77
3	14	8	0.41	0.10	81
4	57	8	0.01	0.00	90

Polymerization conditions: $TiCl_4/MgCl_2$ = 0.4 g (0.8 mmol-Ti), $Al(C_2H_5)_3$ = 80 mmol/l, heptane = 10 ml, $P_{C_3'}$ = 660 Torr, Temp. = 0°C.

a) Determined by IR.

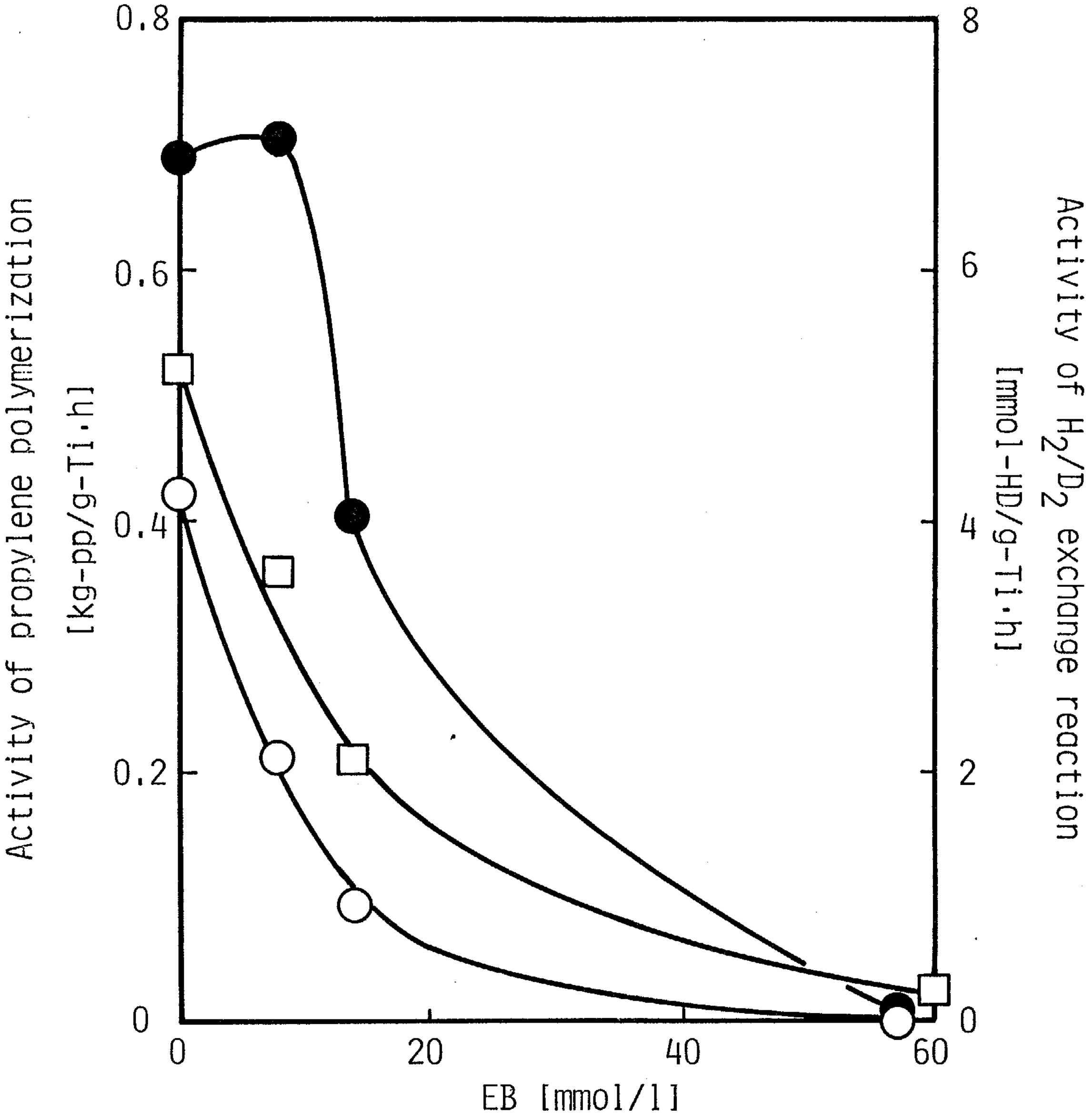


Figure 2-3 Effect of EB on activity of both propylene polymerization and H_2/D_2 exchange reaction.

● ; activity of heptane insoluble fraction

○ ; activity of heptane soluble fraction

☐ ; activity of H_2/D_2 exchange reaction depend upon the reducing ability of organometallic compounds. It is well known that $Al(C_2H_5)_3$ forms a complex with EB. Therefore, the concentration of $Al(C_2H_5)_3$ decreases in the presence of EB, resulting in the decrease in the reducing ability. This may be the other plausible mechanism.

To get further information on this point, propylene polymerization was carried out under similar conditions. The results are summarized in Table 2-2. The addition of EB caused the drastic decrease in the production of atactic polymer. Both the activites of propylene polymerization and of the exchange reactions are plotted against the concentration of EB. The activity of producing atactic polypropylene correlates closely with that of the exchange reactions.

These results support the following hypotheses : 1) Atactic and isotactic polymers are produced by the two vacancy Ti species and one vacancy Ti species, respectively ; 2) Addition of small amount of EB selectively deactivates the two vacancy Ti species.

2-3-2 Effect of Hydrogen on Propylene Polymerization

The results in 2-3-1 strongly suggest that hydrogen molecules can be dessociatively adsorbed only on the aspecific Ti species. Thus, the chain transfer reactions of atactic polymer may mainly take place by atomic hydrogens, while those of isotactic polymer by molecular hydrogens.

To confirm this point, propylene polymerization was carried out with the $TiCl_4/EB/MgCl_2-Al(C_2H_5)_3/EB$ catalyst in the presence of hydrogen gas. In Table 2-3 are summarized the polymerization results. The insoluble fraction in boiling heptane gradually decreased with an increase in the pressure of hydrogen. The isotactic index of the whole polymers determined by IR, however, remained almost unchanged. Such a decrease in the insoluble fraction is considered to be attributed to the decrease in the molecular weight. In fact, the IR spectra of the soluble fractions indicate that a considerable amount of isotactic polypropylene is contained in the soluble fractions (Table 2-3).

Propylene polymerization was also conducted with the $TiCl_3$-$Al(C_2H_5)_2I$ catalyst system in the presence of hydrogen and was obtained similar results (Table 2-4).

The number-average molecular weights of fractionated polymers are summarized in Table 2-5. Based on these data, the kinetic analyses were carried out.

Growth of a polymer chain at the metal-carbon bond center can be terminated not only by hydrogen but by $Al(C_2H_5)_3$, propylene and so on. Since the present polymerizations were carried out under the same conditions except for the partial pressure of hydrogen, the rate of the chain transfer reactions, r_{tr}, may be represented by Eq.(7).

$$r_{tr} = k_H P_{H_2}^{n} [C^*] + \alpha \ (= \sum_i k_i [X_i][C^*]) \tag{7}$$

where k_H , P_H and $[C^*]$ are the rate constant of the chain transfer reactions by hydrogen, the partial pressure of hydrogen and the concentration of the growing polymer chains, and n and α are constants.

The number-average degree of polymerization($\bar{P}_n$) of the total polymer is generally given by Eq.(8).

$$\bar{P}n = \frac{\int_0^t r_p dt}{[C^*] + \int_0^t r_t dt + \int_0^t r_{rt} dt} \qquad (8)$$

where r_p and r_t represent the rates of polymerization and termination, respectively. In the case of propylene polymerization with $MgCl_2$-supported $TiCl_4$ catalysts, it is well established that the propagation rate is extremely high and that $\bar{P}_n$ is independent of the polymerization time[3]. This fact strongly implies that $\int_0^t r_{tr} dt$ is far greater than $[C^*] + \int_0^t r_t dt$. Thus, Eq.(8) can be simplified as

$$\bar{P}n = \frac{\int_0^t r_p dt}{\int_0^t r_{tr} dt} = \frac{r_p}{r_{tr}} = \frac{k_p[M][C^*]}{k_H P_{H_2}^n [C^*] + \Sigma k_i [X_i][C^*]}$$

$$= \frac{k_p[M]}{k_H P_{H_2}^n + \sum_t k_i [X_i]} \qquad (9)$$

On the other hand, Ingberman et al.[15] have found that neither chain transfer nor termination reactions proceed with the $TiCl_3$-$Al(C_2H_5)_2Cl$ catalyst system. Under such conditions, therefore, transfer reactions take place only by hydrogen. The kinetic features of propylene polymerization with the $TiCl_3$-$Al(C_2H_5)_2I$ system may be considered to be very similar. Thus Eq.(10) can be used for this system.

$$\overline{P}n = \frac{\int_0^t r_p dt}{[C^*] + \int_0^t r_{tr} dt} = \frac{k_p[M][C^*]}{[C^*] + k_H P_{H_2}^n [C^*]}$$

$$= \frac{k_p[M]}{1 + k_H P_{H_2}^n} \quad (10)$$

As can be seen in Table 2-3 and 2-4, the rates of polymerization gradually decreases with increase in the partial pressure of hydrogen with these two types of catalyst systems. This may be attributed to the decrease in [C*], which is caused by the slow recovery of the inactive metal-hydride bond formed as a result of the chain transfer by hydrogen(Eq.(11)).

$$\text{Cat-H} \xrightarrow[\text{slow}]{C_3H_6} \text{Cat-R} \ (R = C_3H_7) \quad (11)$$

Eqs.(9) and (10) are, however, free from [C*], and hence we have the following relations between $\overline{P}n_0$ and $\overline{P}n_H$ for both catalyst systems.

In the case of $TiCl_4/EB/MgCl_2$-$Al(C_2H_5)_3/EB$,

$$\frac{\overline{P}n_0}{\overline{P}n_H} = \frac{\overline{M}n_0}{\overline{M}n_H} = \frac{\sum_i k_i[X_i] + k_H P_{H_2}^n}{\sum_i k_i[X_i]} = \frac{\alpha + k_H P_{H_2}^n}{\alpha}$$

$$= 1 + \frac{k_H}{\alpha} P_{H_2}^n \quad (12)$$

and in the case of $TiCl_3-Al(C_2H_5)_2I$,

$$\frac{\bar{P}n_0}{\bar{P}n_H} = \frac{\bar{M}n_0}{\bar{M}n_H} = 1 + k_H P_{H_2}^{\ n} \tag{13}$$

where $\bar{P}n_0$ and $\bar{P}n_H$ are the number-average degrees of polymerization without and with hydrogen, and $\bar{M}n_0$ and $\bar{M}n_H$ the number-average molecular weights without and with hydrogen, respectively. Eqs.(12) and (13) indicate that the dependence of molecular weight on hydrogen pressure can be estimated from the slope of the plot of $\log(\bar{M}n_0/\bar{M}n_H - 1)$ against P_{H_2} (Figures 2-4 and 2-5). The values of n obtained with the $TiCl_4/EB/MgCl_2-Al(C_2H_5)_3/EB$ catalyst system (Figure 2-4) were 0.8 for heptane insoluble fraction and 0.7 for heptane soluble fraction. Whereas, the values obtained with the $TiCl_3-Al(C_2H_5)_2I$ catalyst system were 0.7 and 0.2, respectively. However, the value(0.2) for the heptane soluble fraction obtained with the latter system seems to be incredible, since their molecular weights are too low ($\bar{M}n$ = 500~800) to be determined by GPC under our operation conditions.

In general, the molecular weights of the present polymers are considerably low. Thus, the discrepancy between the observed and expected n values (n = 1 for isotactic and n = 0.5 for atactic) may partially owe to the fact that the soluble fraction also contains a considerable amount of isotactic polypropylene. But there should probably be other important reasons which are closely related to the catalyst.

Table 2-3 Results of propylene polymerization with $TiCl_4/EB/MgCl_2-Al(C_2H_5)_3$ in the presence of hydrogen

Run no.	Partial press. of hydrogen [Torr]	Yield [g]	Activity [kg-PP/g-Ti·h]	I.I.[a] [%]	I.I.[b] [%]	I.I.[c] [%]
5	0	1.45	3.02	90	94	61
6	10	1.22	2.55	86	94	-
7	41	1.40	2.93	87	95	70
8	92	1.00	2.09	86	92	-
9	147	0.75	1.57	84	94	73
10	251	0.68	1.42	83	96	-

Polymerization conditions: $TiCl_4/EB/MgCl_2$ = 30 mg (0.02 mmol-Ti), EB = 10 mmol/l, $Al(C_2H_5)_3$ = 30 mmol/l, $P_{C_3'}$ = 350 Torr, 40°C, 30 min.

a) Isotactic index of the whole polymer determined by extraction.

b) Isotactic index of the whole polymer determined with IR.

c) Isotactic index of the polymer soluble in boiling heptane determined with IR.

Table 2-4 Results of propylene polymerization with $TiCl_3$-$Al(C_2H_5)_2I$ in the presence of hydrogen.

Run no.	Partial press. of hydrogen [Torr]	Yield [g]	Activity [g-PP/g-Ti·h]	I.I.[a] [%]	I.I.[b] [%]
11	0	1.31	4.28	97	94
12	12	1.04	3.63	95	95
13	42	1.01	2.91	93	94
14	114	0.90	3.10	89	96
15	162	0.65	2.14	87	95
16	251	0.52	1.60	83	93

Polymerization conditions: $TiCl_3$ = 0.5 g, $Al(C_2H_5)_2I$ = 20 mmol/l, heptane = 100 ml, $P_{C_3'}$ = 340 Torr, 40°C, 2 h.

Table 2-5 Number-average molucular weights of fractionated polymers shown in Tables 2-3 and 2-4.

Run no.	$\bar{M}n \times 10^{-3}$		$\bar{M}w/\bar{M}n$		$\bar{M}n_0/\bar{M}n_H$	
	Insol.	Sol.	Insol.	Sol.	Insol.	Sol.
5	26.2	4.1	6.1	5.6	1.0	1.0
6	20.8	3.6	6.1	4.7	1.3	1.1
7	15.5	3.0	4.4	3.6	1.7	1.4
8	10.3	2.4	4.6	2.5	2.5	1.7
9	8.0	2.2	4.7	2.5	3.3	1.8
10	6.2	1.8	4.3	2.8	4.3	2.3
11	24.3	0.77	7.8	5.6	1.0	1.0
12	17.8	0.58	9.0	2.8	1.7	1.3
13	9.3	0.57	11.0	1.8	2.6	1.4
14	5.7	0.57	12.9	1.4	5.3	1.4
15	5.5	0.52	11.0	1.3	5.5	1.5
16	5.0	0.46	10.7	1.6	6.0	1.6

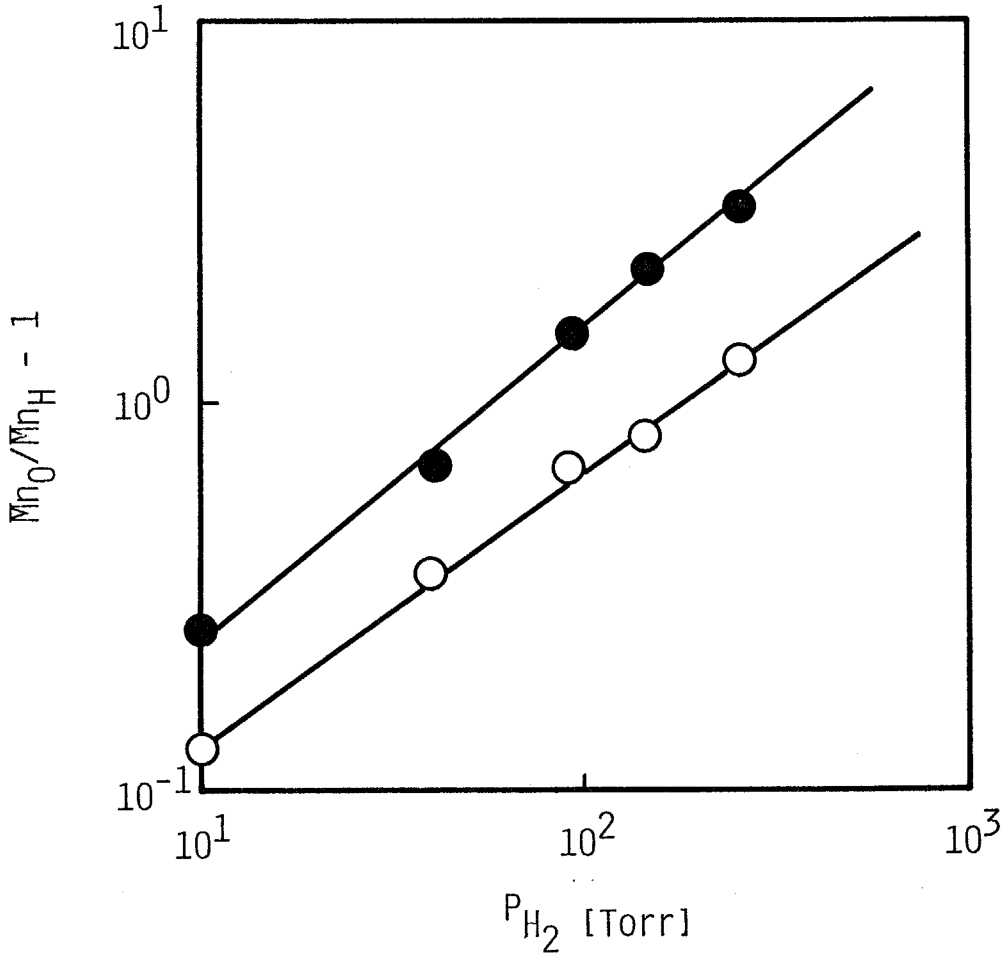


Figure 2-4 Plots of ($\overline{M}n_0/\overline{M}n_H$ - 1) against the hydrogen pressure in propylene polymerization with $TiCl_4$/EB/$MgCl_2$-$Al(C_2H_5)_3$/EB.

○ ; Polymer soluble in boiling heptane

● ; Polymer insoluble in boiling heptane

Polymerization conditions as indicated in Table 2-3.

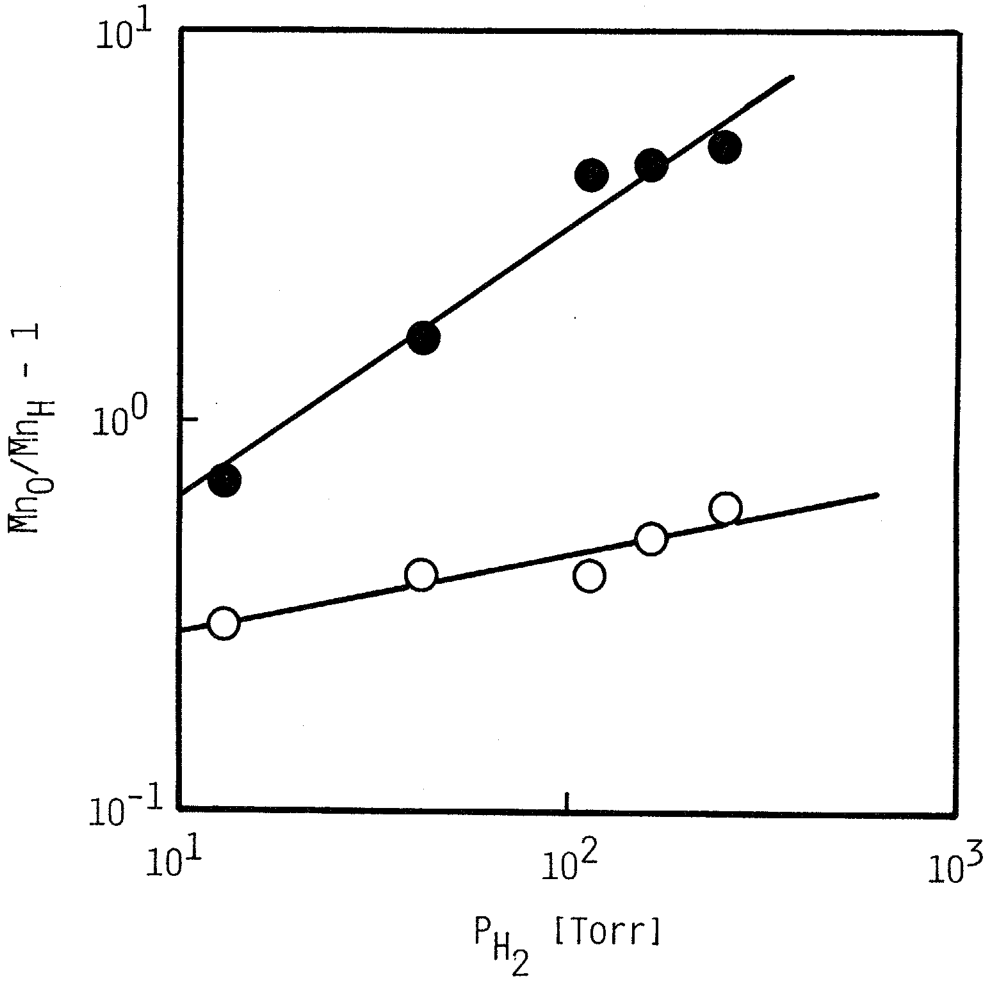


Figure 2-5 Plots of ($\overline{M}n_0/\overline{M}n_H$ - 1) against the hydrogen pressure in propylene polymerization with $TiCl_3$-$Al(C_2H_5)_2I$.

○ ; Polymer soluble in boiling heptane

● ; Polymer insoluble in boiling heptane

Polymerization conditions as indicated in Table 2-4.

As mentioned in Section 2-1, generally speaking, the molecular weights of polypropylenes produced with heterogeneous catalyst systems reported so far are approximately proportional to the square root of hydrogen pressure. However, most of the experiments have been carried out with the use of less isospecific catalysts. For example, Keii et al.3) and Guastalla et al.4) have conducted propylene polymerization with $MgCl_2$-supported $TiCl_4$ catalysts which do not contain any external donors and produce polypropylene with very low isotacticity (I.I. < 50 %).

In the polymerization of propylene with the $TiCl_4/MgCl_2$-$Al(C_2H_5)_3$ catalyst, Kashiwa et al.16) have estimated the concentration of both aspecific and isospecific sites and reported that the concentration of aspecific sites is more than ten times higher than that of isospecific sites. Under such conditions, therefore, most of Ti species on the catalyst surface might be aspecific. Thus hydrogen molecules can easily be adsorbed on them as atomic forms, and consequently the transfer reactions of isotactic polymers should also proceed by dessociatively adsorbed atomic hydrogens. Such a phenomenon(spillover)* is well known in many reactions which take place over solid catalysts. If the active species are highly dispersed(isolated form) on the catalyst surface, however, such a spillover might not proceed. The transfer reaction over such active species should take place, therefore, with the use of molecular hydrogens.

To confirm this point, propylene polymerization was carried out with the $TiCl_4/MgCl_2$-$Al(C_2H_5)_3$ catalyst system in the presence of hydrogen under similar conditions. The results of propylene polymerization as well as the molecular weight of heptane insoluble fraction are shown in Table 2-6. In Figure 2-6 are plotted the values of $\log(\bar{M}n_0/\bar{M}n_H - 1)$ against the P_{H_2} using the data shown in Table 2-6, which gives n = 0.5. This result strongly supports above speculation.

From this point of view, we have analyzed the data reported by Keii et al.[17,18) using the catalyst systems of $TiCl_3$-$Al(C_2H_5)_3$ and $TiCl_3$-$Al(C_2H_5)_2Cl$ (Table 2-7). The analytical results are shown in Figure 2-7, which gives n = 0.9 for the highly isotactic(94 %) polymers obtained with $Al(C_2H_5)_2Cl$ and n = 0.5 for the low isotactic(64 %) polymers obtained with $Al(C_2H_5)_3$.

These results also support the previous mechanism that the isospecific Ti species in highly isospecific catalysts are isolated from the neighbouring species and the transfer reactions over them take place mainly by using molecular hydrogens, whereas the aspecific Ti species as well as the isospecific Ti species in less isospecific catalysts form some clusters and the transfer reactions proceed by reactive atomic hydrogens (spillover). In fact, we have observed that the hydrogen gas are hardly effective to control the molecular weight of polypropylene in the highly isospecific $TiCl_3/(\eta$-$C_5H_5)_2Ti(CH_3)_2$ catalyst system (I.I. > 99 %)[19).

Table 2-6 Effect of hydrogen on heptane insoluble fractions obtained with $TiCl_4$/$MgCl_2$-$Al(C_2H_5)_3$.

Run no.	Partial press. of hydrogen [Torr]	Activity [kg-PP/g-Ti·h]	I.I.[a] [%]	$\overline{M}n \times 10^{-3}$	$\overline{M}w/\overline{M}n$	$\overline{M}n_0/\overline{M}n_H$
17	0	0.59	31	36.9	4.4	1.0
18	12	0.57	32	28.4	3.7	1.3
19	39	0.58	35	22.9	6.3	1.6
20	93	0.59	33	19.9	2.7	1.9
21	168	0.54	36	16.1	2.9	2.3
22	249	0.54	29	16.5	3.2	2.2

Polymerization conditions: $TiCl_4/MgCl_2$ = 0.42 g, $Al(C_2H_5)_3$ = 20 mmol/l, heptane = 80 ml, 40 C, 15 min.

a) Weight fraction of boiling heptane insoluble fraction.

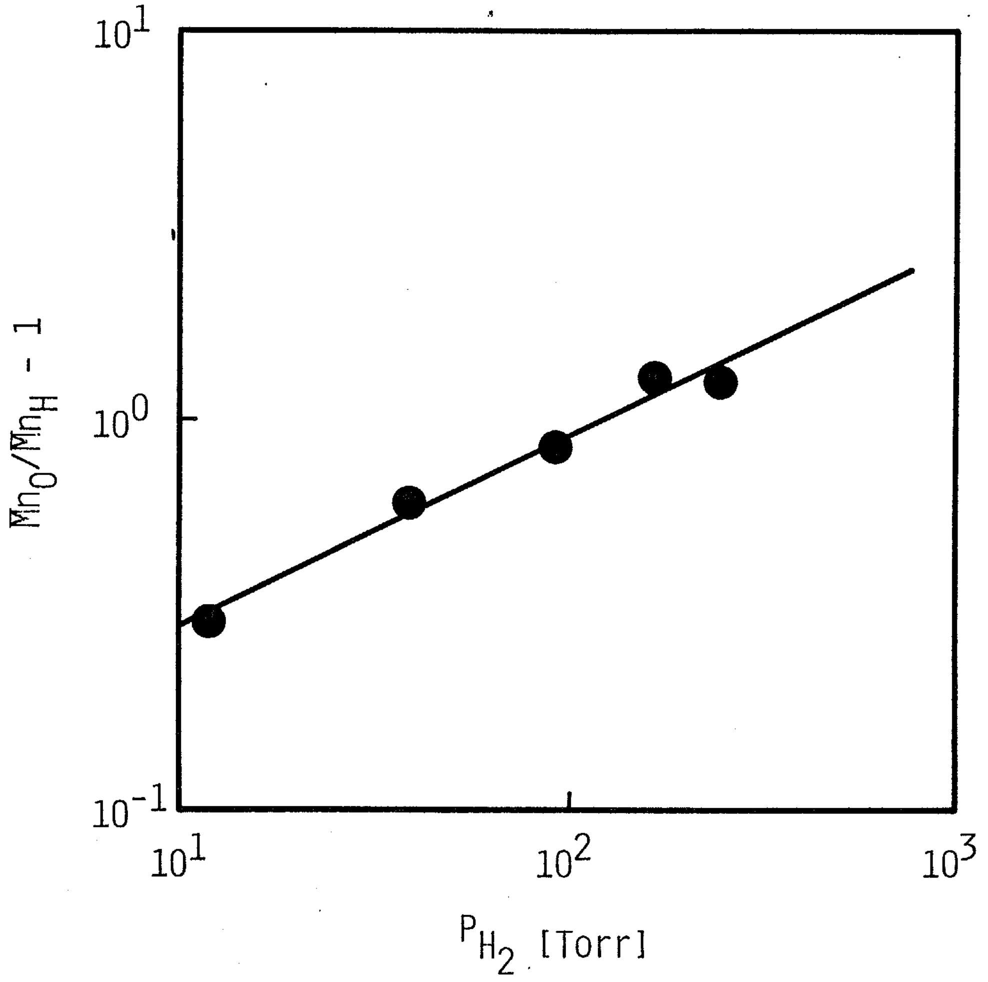


Figure 2-6 Plot of ($\overline{M}n_0/\overline{M}n_H$ - 1) against the hydrogen pressure in propylene polymerization with $TiCl_4/MgCl_2$-$Al(C_2H_5)_3$.
Polymerization conditions as indicated in Table 2-6.

Table 2-7 Results of propylene polymerization with $TiCl_3$-alkyl aluminium systems in the presence of hydrogen obtained by Keii et al.[17,18)]

Catalyst system	Partial press. of hydrogen [Torr]	$\bar{M}v \times 10^{-4}$	$\bar{M}v_0/\bar{M}v_H$
$TiCl_3$-$Al(C_2H_5)_3$	0	42.8	1.0
〃	8	22.5	1.9
〃	30	15.9	2.7
〃	50	12.7	3.4
〃	290	7.5	5.7
$TiCl_3$-$Al(C_2H_5)_2Cl$	0	50.0	1.0
〃	17	33.0	1.5
〃	65	16.8	3.0
〃	130	12.3	4.1
〃	168	10.0	5.0

Polymerization conditions: $TiCl_3$-$Al(C_2H_5)_3$; $TiCl_3$ = 1 mmol, $Al(C_2H_5)_3$ = 1 mmol, toluene = 150 ml, $P_{C_3'}$ = 400 Torr, 43°C. $TiCl_3$-$Al(C_2H_5)_2Cl$; $TiCl_3$ = 3.3 mmol, $Al(C_2H_5)_2Cl$ = 4 mmol, heptane = 250 ml, $P_{C_3'}$ = 400 Torr, 45°C.

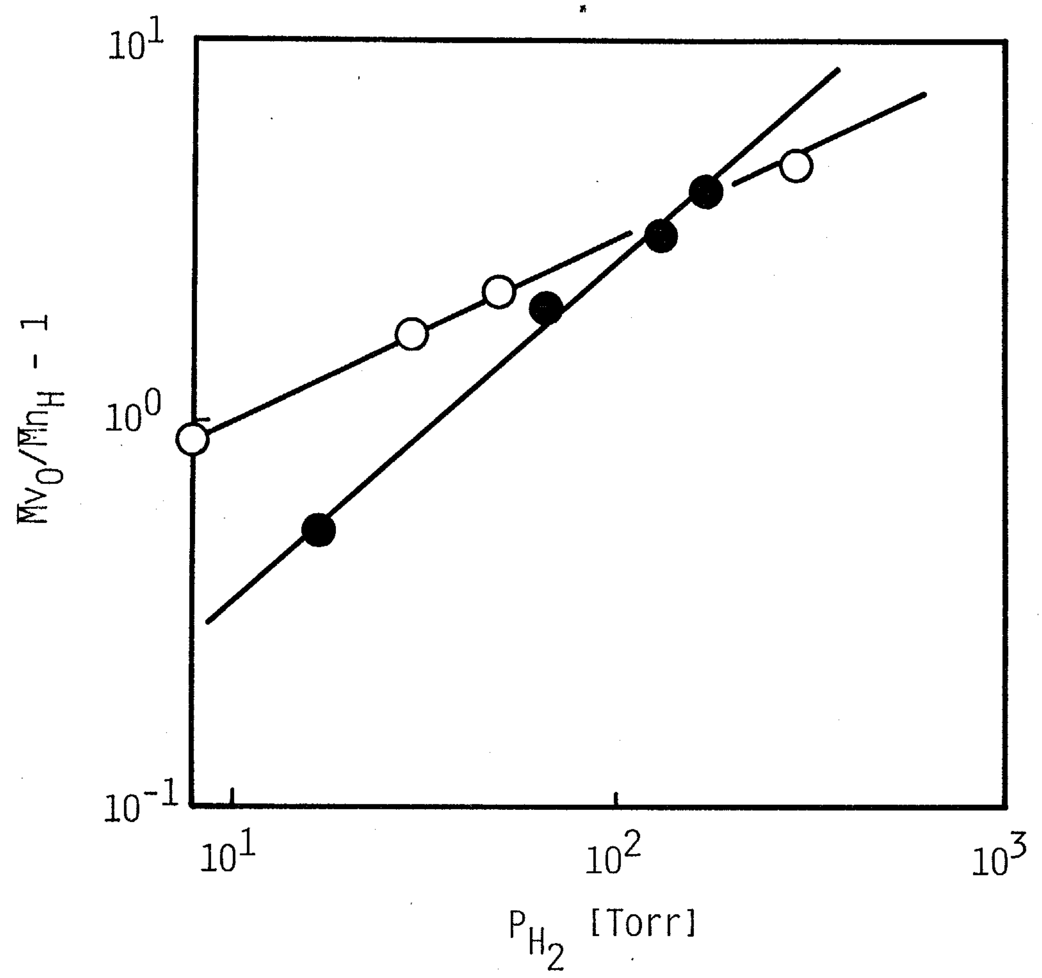


Figure 2-7 Plots of ($\bar{M}v_0/\bar{M}v_H$ - 1) against the hydrogen pressure based on the data obtained by Keii et al.[17,18]

○ ; Whole polymer obtained with $TiCl_3$-$Al(C_2H_5)_3$

● ; Whole polymer obtained with $TiCl_3$-$Al(C_2H_5)_2Cl$

Polymerization conditions as indicated in Table 2-7.

* NOTE

"Spillover" is a phenomenon that adsorbed atoms on supported catalysts easily spill over onto the support or the cocatalysts by diffusion. Spillover can be observed on condition that the adsorbed atoms don't make irreversible strong bonds with the active species and the mass of the adsorbed atom is preferred to be light for transfer. Therefore, a large number of examples reported so far are hydrogen - metal supported catalyst systems. The center of spillover is the transition metal which can dissociate and adsorb hydrogen molecules like Pt and Pd, and carbon, alumina, silica, zeolite, metal oxides, metal sulfides and organic high polymers are known as supports.

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Chapter 3

Effect of Electron Donor Compounds on Copolymerization of Ethylene with Higher α-Olefins

3-1 Introduction

By copolymerization of ethylene with higher α-olefins, several important commercial polymers are produced. Linear low density polyethylene(LLDPE) is synthesyzed with titanium-based catalyst systems under mild conditions, which is now taking place of low density polyethylene(LDPE) produced by high pressure radical process. Ethylene-propylene random copolymer(EPR) is one of the most important technical polymers and is widely used as irreplaceable products in various industries. Commercial EPR has long been synthesized with the vanadium-based catalysts. From such viewpoints, the industrial and scientific researches have been chiefly forcused on such catalyst systems.

In the meantime, Soga et al. investigated the homopolymerization of various α-olefins as well as copolymerizations among then with the use of γ-Al_2O_3- or SiO_2-supported $TiCl_4$ catalyst in detail$^{1)}$. The results strongly suggested that Ti(II) is active only for ethylene, while Ti(III) is active not only for ethylene but other α-olefins such as propylene, 1-hexene and 1,3-butadiene. On the basis of this information he prospected the possibility of synthesyzing EPR using titanium-based catalysts by controlling the oxidation state of the Ti species.

As described in previous chapters, there should exist two kinds of the Ti(III) species which catalyze propylene polymerization. One is the aspecific Ti(III) species having two vacant sites, and the other isospecific species having only one vacant site. In the copolymerization of ethylene and various α-olefins with titanium-based catalysts it is generally recognized that the copolymer composition strongly depends on the catalyst systems, polymerization conditions, etc. This may be mainly attributed to the oxidation states of the Ti species, but may partly reflect the distribution of these two Ti(III) species.

From such viewpoints, in this chapter was carried out the copolymerization of ethylene and α-olefin (propylene or 1-butene) with the catalyst systems of $TiCl_4$/(ester)/$MgCl_2$-$Al(C_2H_5)_3$, and was examined the effect of the additives, ethylbenzoate(EB) and phenyltriethoxysilane(PTES), on the copolymer compositions.

3-2 Experimental

Materials

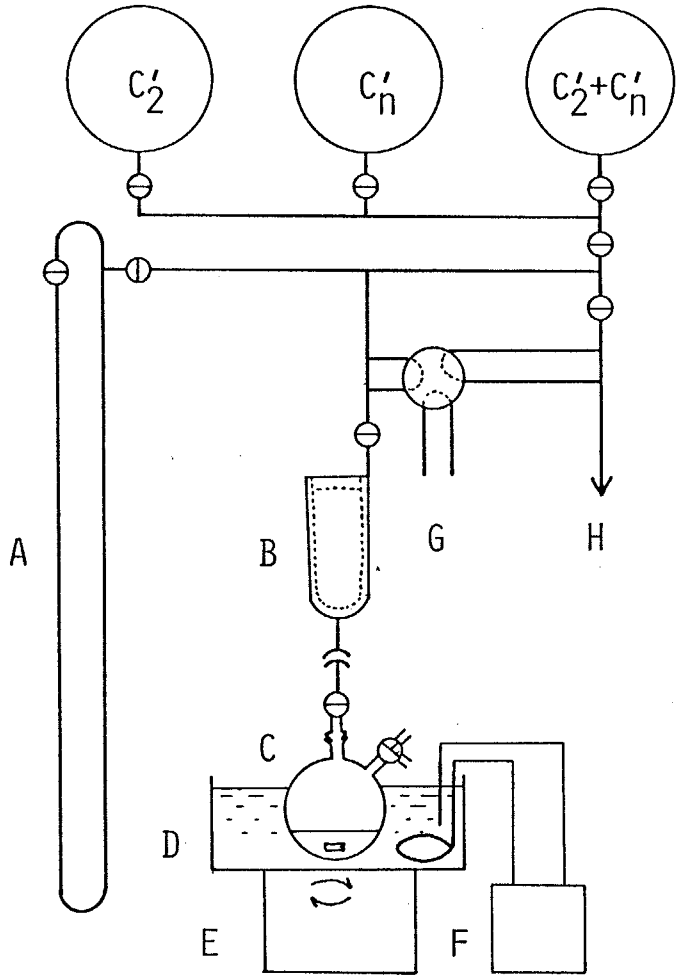
Research grade ethylene, propylene and 1-butene were purified by trap-to-trap distillation with dry ice-ethanol to liquid nitrogen bath and admitted into the gas holders. The preparative method of the $TiCl_4/MgCl_2$ and $TiCl_4$/ethylbenzoate

(EB)/$MgCl_2$ catalysts were shown in Chapter 2, and that of the $TiCl_4$/di-n-butylphthalate(DNBP)/$MgCl_2$ catalyst in Chapter 1. For the purification methods of other chemicals to see the previous chapters.

Polymerization procedures

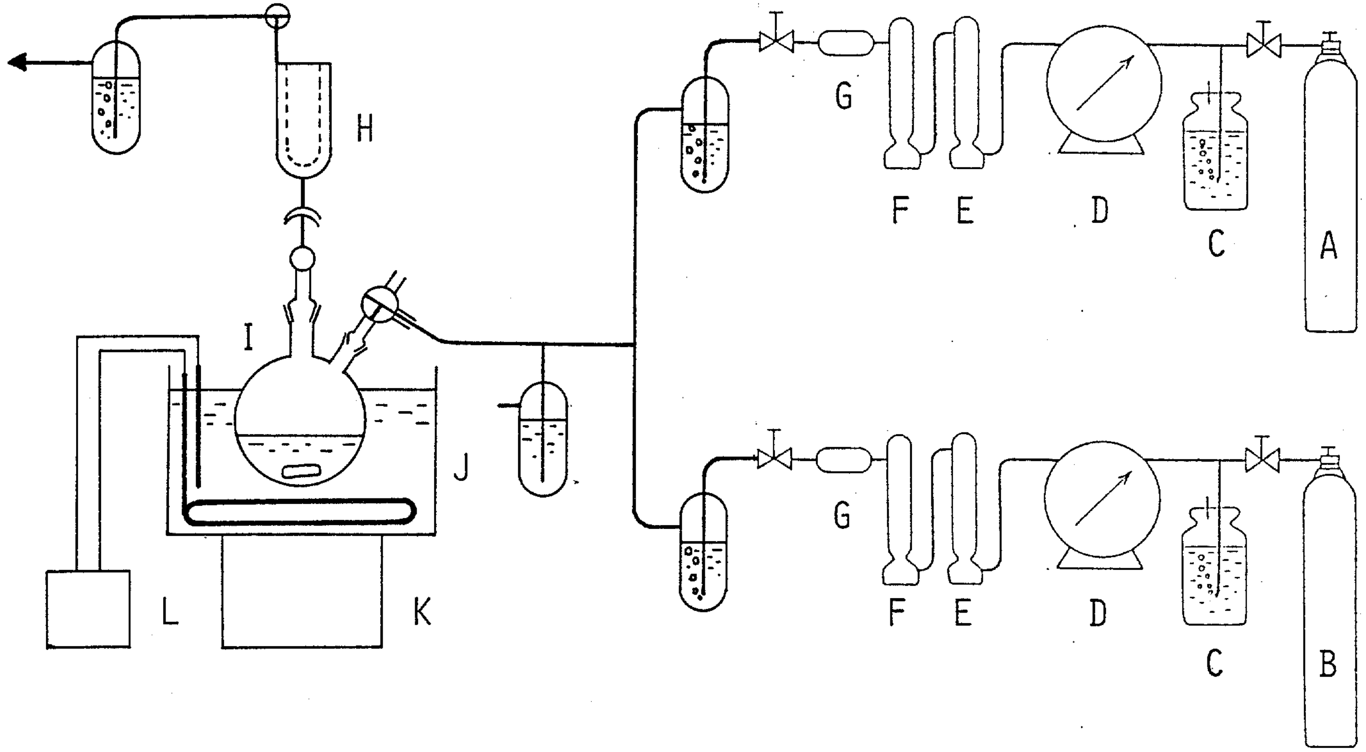
Procedure A : Copolymerization of ethylene with α-olefins (propylene, or 1-butene) was carried out in a conventional gas circulation system. It has a dead space of about 5.0 l including the reactor(50 ml) and is equipped with a condencer and a magnetic stirrer as shown in Figure 3-1. Given amounts of n-heptane, catalyst, electron donor compound (if needed) and $Al(C_2H_5)_3$ were taken into the reactor. The reactor was then attached to the circulation system, cooled by liquid nitrogen, and evacuated. After it was kept at the polymerization temparature for 5 min, the copolymerization was started by introducing the mixture of ethylene and α-olefin.

Procedure B : The outline of the copolymerization procedure of ethylene with propylene is shown in Figure 3-2. Copolymerization was carried out in a 200 ml glass reactor equipped with a condenser(-20°C) and a magnetic stirrer. A known weight of the catalyst was suspended in heptane under nitrogen atmosphere. After it was raised up to the polymerization temperature, the mixture of ethylene and propylene was introduced into the reactor and copolymerization was started by introducing the alkylaluminium compound. Both the mole ratio of ethylene to propylene and the flow rate of



A : manometer　B : condencer (-20°C)　C : reactor
D : water bath　E : magnetic stirrer　F : thermostat
G : gas chromatography　H : vacuum pump

Figure 3-1 The gas circulation system for copolymerization of ethylene and higher α-olefins.



A : ethylene
B : propylene
C : manostat
D : flow meter
E : $CaCl_2$
F : P_2O_5
G : molecular sieve 3A
H : condenser(-20°C)
I : reactor
J : water bath
K : magnetic stirrer
L : thermstat

Figure 3-2 Apparatus for copolymerization of ethylene and propylene the mixed gas were kept constant during the copolymerization. In above both procedures, copolymerization was terminated by adding the ethanol into the reactor. The resultant copolymer was precipitated in acidic ethanol followed by washing with plenty of ethanol and dried i. vac at r.t. for 8 h.

Propylene polymerization was conducted with the same procedure as indicated in Chapter 1.

Analytical procedures

The composition of monomers in gas phase was determined by gas chromatography. The compositions of ethylene-propylene and ethylene-1-butene copolymers were determined by ^{13}C NMR spectra according to the methods reported by Ray et al.$^{2)}$ and Hsieh et al.$^{3)}$, respectively. ^{13}C NMR spectra were recorded on a JEOL FX-100 spectrometer operating at 25.14 MHz or JEOL GX-270 spectrometer operating at 67.20 MHz under proton decoupling in the Fourier Transform (FT) mode. Instrument conditions were $\pi/4$ pulse of 9.0 μs, 8.0 s repetition time. Sample solution of copolymers were made up as described in Chapter 1.

3-3 Results and Discussion

The colymerization of ethylene and propylene was carried out with the three types of $MgCl_2$-supported $TiCl_4$ catalysts using $Al(C_2H_5)_3$ as cocatalyst. The copolymerization with the gas circulation system was terminated at low conversion, less

Table 3-1 The results of ethylene-propylene copolymerization with $MgCl_2$-supported $TiCl_4$ catalyst systems

Run no.	Catalyst	Electron donor [mmol/l]		$Al(C_2H_5)_3$ [mmol/l]	Time[a)] [min]	C_3' in feed[b)] [mol%]	C_3' in copolymer [mol%]	I.I.[c)] [%]
1	$TiCl_4/EB/MgCl_2$	EB	0	30	14	76	44	72
2	〃	〃	5	〃	90	〃	38	91
3	〃	〃	10	〃	330	〃	29	95
4	$TiCl_4/DNBP/MgCl_2$	PTES	0	5	22	85	55	79
5	〃	〃	0.25	〃	36	84	48	94
6	〃	〃	0.50	〃	50	85	45	95
7	$TiCl_4/MgCl_2$	EB	0	20	38	85	56	56
8	〃	〃	4	〃	160	〃	52	70

Polymerization conditions ; [Ti] = 0.10(Run no. 1-3), 0.20(Run no. 4-6) and 0.18(Run no. 7,8) mmol, respectively. Total pressure = 450 Torr, heptane = 10 ml, 40°C.

a) The time required to reach 10 % conversion, b) in liquid phase, c) Run no. 1-3,7 and 8 were determined by IR. Run no. 4-6 were determined by sohxlet extraction with heptane.

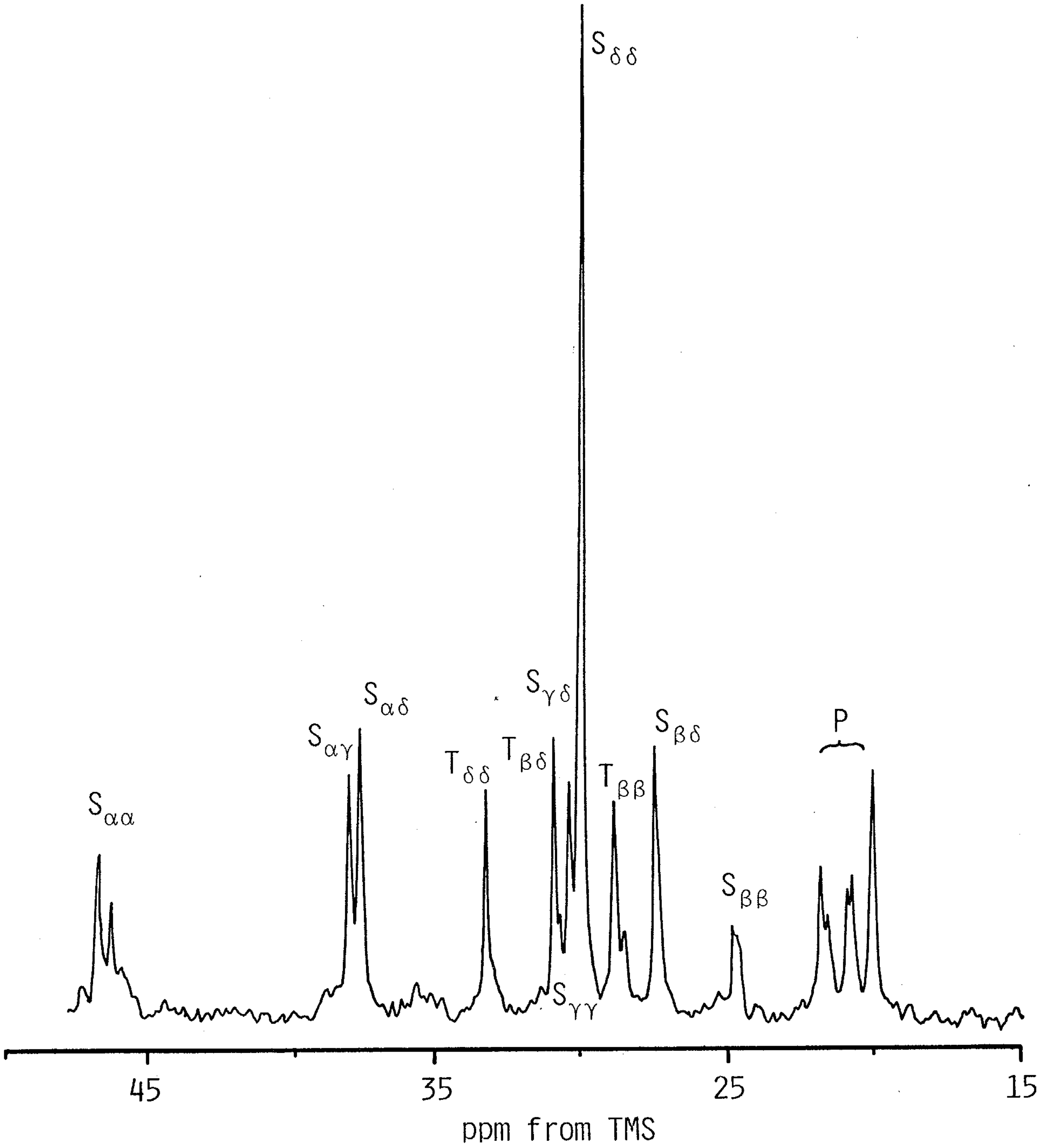
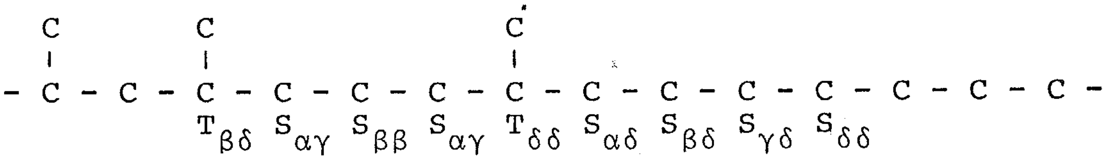


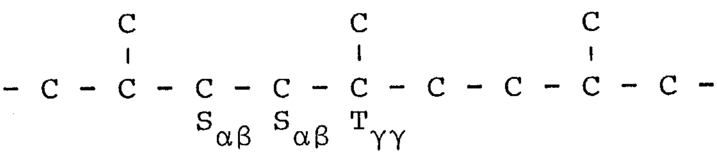
Figure 3-3 ^{13}C NMR spectrum of ethylene-propylene copolymer of Sample 1.

than 10 %, in order to keep the monomer composition unchanged. Table 3-1 shows the correlation between the monomer composition of copolymers and the isotacticity of polypropylene which were obtained under similar conditions. In Figure 3-3 are illustrated a typical ^{13}C NMR spectrum of copolymer (Run no. 1) with the assignment reported by Carman et al.4) Tertiary and secondary carbon atoms are denoted as T and S with two Greek subscripts indicating the position relative to the nearest tertiary carbon atoms in both directions along the copolymer chain as below. The letter δ indicates that a secondary or tertiary carbon is in the δ or further position relative to a tertiary carbon, which are not resolved spectroscopically.



$$\begin{array}{cccccccccccccc}
C & & C & & & & C & & & & & & & \\
| & & | & & & & | & & & & & & & \\
-C- & C- & C- & C- & C- & C- & C- & C- & C- & C- & C- & C- & C- & C- \\
 & & T_{\beta\delta} & S_{\alpha\gamma} & S_{\beta\beta} & S_{\alpha\gamma} & T_{\delta\delta} & S_{\alpha\delta} & S_{\beta\delta} & S_{\gamma\delta} & S_{\delta\delta} & & &
\end{array}$$

All the primary carbon atoms are represented by P since both monomer sequence distribution and configuration of propylene unit inseparably affected the chemical shift of methyl groups. In the copolymerization of ethylene and propylene with vanadium-based catalysts, inversion of propylene units frequently occurs to give the following structures.



$$\begin{array}{ccccccccc}
 & C & & & C & & & C & \\
 & | & & & | & & & | & \\
-C- & C- & C- & C- & C- & C- & C- & C- & C- \\
 & & S_{\alpha\beta} & S_{\alpha\beta} & T_{\gamma\gamma} & & & &
\end{array}$$

In the spectra of the present copolymers, however, intensities of the peaks at 34.9 ppm($S_{\alpha\beta}$), 33.6 ppm($T_{\gamma\gamma}$) and 27.9 ppm($S_{\beta\gamma}$) were negligible, which may be due to a high regioselectivity of $MgCl_2$-supported $TiCl_4$ catalyst as reported by Doi⁵⁾. Therefore, the present copolymerization can be analyzed as a binary copolymerization of ethylene(E) and propylene(P). Table 3-2 are summarized the areas of the resonance peaks together with the ^{13}C NMR chemical shift assignment. The dyad and triad sequence distributions in the copolymers were determined from the peak areas by using the following equations.

$$[PP] = I(S_{\alpha\alpha}) \tag{1}$$

$$[PE] = I(S_{\alpha\gamma}) + I(S_{\alpha\delta}) \tag{2}$$

$$[EE] = 1/2[I(S_{\beta\delta}) + I(S_{\delta\delta})] + 1/4\, I(S_{\gamma\delta}) \tag{3}$$

$$[PPP] = I(T_{\beta\beta}) \tag{4}$$

$$[PPE] = I(T_{\beta\delta}) \tag{5}$$

$$[EPE] = I(T_{\delta\delta}) \tag{6}$$

$$[PEP] = I(S_{\beta\beta}) = 1/2\, I(S_{\alpha\gamma}) \tag{7}$$

$$[PEE] = I(S_{\alpha\delta}) = I(S_{\beta\delta}) \tag{8}$$

$$[EEE] = 1/2\, I(S_{\delta\delta}) + 1/4\, I(S_{\gamma\delta}) \tag{9}$$

The monomer compositions were calculated from both the dyad and triad sequence distributions using Eqs.(10) and (11).

$$[P] = [PP] + 1/2[PE] = [PPP] + [PPE] + [EPE] \tag{10}$$

$$[E] = [EE] + 1/2[PE] = [EEE] + [EEP] + [PEP] \tag{11}$$

In Table 3-3 are shown the monomer content as well as the

Table 3-2 ^{13}C NMR area data for ethylene-propylene copolymer samples 1 through 8.

Carbon type	Monomer sequence	1	2	3	4	5	6	7	8
$S_{\alpha\alpha}$	PP	10.4	9.6	7.1	14.0	13.7	12.4	16.1	14.5
$S_{\alpha\gamma}$	2PEP	6.7	6.4	4.8	10.3	6.2	6.9	7.7	6.8
$S_{\alpha\delta}$	$PEE_n(n\geq1)$	6.7	6.8	7.1	6.0	6.2	6.0	5.2	6.8
$S_{\gamma\gamma}$	PEEP	0.6	0.8	0.6	1.5	0.4	0.6	0.6	0.8
$S_{\gamma\delta}$	$PEEE_n(n\geq1)$	4.9	4.4	4.2	3.0	3.4	2.8	3.2	1.9
$S_{\delta\delta}$	$EEE_n(n\geq1)$	21.4	29.9	41.7	13.0	22.6	25.3	14.2	18.4
$S_{\beta\delta}$	$PEE_n(n\geq1)$	6.7	6.8	7.1	6.0	6.2	6.0	5.2	6.8
$S_{\beta\beta}$	PEP	3.4	3.2	2.4	5.2	2.7	3.4	3.9	3.4
$T_{\delta\delta}$	EPE	5.5	3.6	3.6	5.0	3.4	3.2	2.9	2.9
$T_{\beta\delta}$	PPE	8.0	7.2	5.4	8.0	8.5	7.2	6.8	5.8
$T_{\beta\beta}$	PPP	6.1	5.2	4.2	9.0	9.6	9.2	12.3	11.6
P	–	19.6	16.1	11.9	19.0	17.1	17.0	21.9	20.3

Table 3-3 Copolymer compositions and sequence distributions in each sample.

Run no.	1	2	3	4	5	6	7	8
P	0.44	0.38	0.29	0.55	0.48	0.45	0.56	0.52
E	0.56	0.62	0.71	0.45	0.52	0.55	0.44	0.48
PP	0.26	0.23	0.16	0.35	0.33	0.30	0.40	0.35
EP	0.34	0.31	0.27	0.40	0.30	0.31	0.33	0.33
PP	0.39	0.46	0.57	0.25	0.37	0.39	0.27	0.32
PPP	0.15	0.12	0.09	0.22	0.22	0.22	0.23	0.30
PPE	0.19	0.17	0.12	0.20	0.20	0.17	0.17	0.14
EPE	0.13	0.09	0.08	0.12	0.08	0.08	0.07	0.07
PEP	0.08	0.08	0.05	0.13	0.07	0.08	0.10	0.08
EEP	0.16	0.16	0.16	0.15	0.14	0.14	0.13	0.17
EEE	0.29	0.38	0.50	0.18	0.29	0.31	0.20	0.24

dyad and triad fractions calculated from these equations. The observed monomer sequence distributions of copolymers may be interpreted in terms of a first-order Markovian process of a binary copolymerization involing the following four equations.

$$\text{---E-Ti} + C_2H_4 \xrightarrow{k_{EE}} \text{---EE-Ti} \quad (12)$$

$$\text{---E-Ti} + C_3H_6 \xrightarrow{k_{EP}} \text{---EP-Ti} \quad (13)$$

$$\text{---P-Ti} + C_2H_4 \xrightarrow{k_{PE}} \text{---PE-Ti} \quad (14)$$

$$\text{---P-Ti} + C_3H_6 \xrightarrow{k_{PP}} \text{---PP-Ti} \quad (15)$$

Here k_{ij} is the rate constant of step ij, and the subscripts E and P denote ethylene and propylene, respectively. Assuming a statistical statioary condition in the copolymerization, the relation between the dyad fractions can be represented as follows.

$$\frac{[EE]}{[PE]} = \frac{k_{EE}[C_E^*][C_2H_4]}{k_{EP}[C_E^*][C_3H_6] + k_{PE}[C_P^*][C_2H_4]} = \frac{k_{EE}[C_2H_4]}{2k_{EP}[C_3H_6]} \quad (16)$$

$$\frac{[PP]}{[PE]} = \frac{k_{PP}[C_P^*][C_3H_6]}{k_{EP}[C_E^*][C_3H_6] + k_{PE}[C_P^*][C_2H_4]} = \frac{k_{PP}[C_3H_6]}{2k_{PE}[C_2H_4]} \quad (17)$$

Then we can calculate the monomer reactivity ratios r_E and r_P using Eqs.(18) and (19) which are derived from Eqs.(16) and (17).

$$r_E = \frac{k_{EE}}{k_{EP}} = \frac{2[EE]}{[PE]X} \tag{18}$$

$$r_P = \frac{k_{PP}}{k_{PE}} = \frac{2[PP]X}{[PE]} \tag{19}$$

where X is the concentration ratio of ethylene to propylene in the feed.

In Table 3-4 are summarized the results obtained. By using r_E, r_P and X, we can get four conditional probabilities, p_{ij}, for copolymerization of ethylene and propylene.

$$\begin{aligned} P_{EE} &= \frac{k_{EE}[C_E^*][C_2H_4]}{k_{EE}[C_E^*][C_2H_4] + k_{EP}[C_E^*][C_3H_6]} \\ &= \frac{r_E X}{r_E X + 1} \end{aligned} \tag{20}$$

$$P_{EP} = 1 - P_{EE} = \frac{1}{r_E X + 1} \tag{21}$$

$$\begin{aligned} P_{PE} &= \frac{k_{PE}[C_P^*][C_2H_4]}{k_{PE}[C_P^*][C_2H_4] + k_{PP}[C_P^*][C_3H_6]} \\ &= \frac{1}{1 + r_P/X} \end{aligned} \tag{22}$$

$$P_{PP} = 1 - P_{PE} = \frac{r_P/X}{1 + r_P/X} \tag{23}$$

In the first-order Markovian statistics, monomer fraction in copolymer, [E] and [P] are given as

$$[E] = \frac{p_{PE}}{p_{EP} + p_{PE}} \tag{24}$$

$$[P] = \frac{p_{EP}}{p_{EP} + p_{PE}} \tag{25}$$

Using the above relations, triad sequence distributions can be represented with four conditional probabilities.

$$[PPP] = \frac{p_{EP}p_{PP}p_{PP}}{p_{EP} + p_{PE}} \tag{26}$$

$$[PPE] = [EPP] = \frac{p_{EP}p_{PP}p_{PE}}{p_{EP} + p_{PE}} \tag{27}$$

$$[EPE] = \frac{p_{PE}p_{EP}p_{PE}}{p_{EP} + p_{PE}} \tag{28}$$

$$[PEP] = \frac{p_{EP}p_{PE}p_{EP}}{p_{EP} + p_{PE}} \tag{29}$$

$$[EEP] = [PEE] = \frac{p_{PE}p_{EE}p_{EP}}{p_{EP} + p_{PE}} \tag{30}$$

$$[EEE] = \frac{p_{PE}p_{EE}p_{EE}}{p_{EP} + p_{PE}} \tag{31}$$

Then we can compare the triad sequence distributions calculated and observed. These values are shown in Table 3-5. The discrepancy between observed triad distributions and calculated ones are significantly large in the absence of external donors. Whereas addition of EB or PTES to the $TiCl_4/EB/MgCl_2$ and $TiCl_4/DNBP/MgCl_2$ catalysts considerably

Table 3-4 Reactivity ratios r_E, r_P and the product $r_E r_P$ in the copolymerization of ethylene and propylene.

Run no.	1	2	3	4	5	6	7	8
r_E	7.4	9.2	13.4	7.1	14.0	14.3	9.3	11.0
r_P	0.48	0.46	0.38	0.31	0.39	0.34	0.43	0.37
$r_E r_P$	3.5	4.2	5.1	2.2	5.5	4.9	4.0	4.1

Table 3-5 Comparison of observed and calculated triad sequence distributions in each sample.

Run no.	1 obs.	1 calc.	1 dev.	2 obs.	2 calc.	2 dev.	3 obs.	3 calc.	3 dev.	4 obs.	4 calc.	4 dev.
PPP	15	16	+1	12	13	+1	9	9	+1	22	22	0
PPE	19	21	+2	17	19	+2	12	15	+3	20	25	+5
EPE	13	7	-6	9	6	-3	8	6	-2	12	7	-5
PEP	8	5	-3	8	4	-4	5	3	-2	13	8	-4
EEP	16	24	+8	16	23	+6	16	21	+5	15	22	+8
EEE	29	28	-1	38	34	-4	50	46	-4	18	13	-5
Run no.		5			6			7			8	
PPP	22	23	+1	22	20	-2	32	29	-3	29	24	-5
PPE	20	21	+1	17	20	+3	17	23	+6	14	22	+8
EPE	8	5	-3	7	5	-2	7	5	-2	7	5	-2
PEP	7	4	-3	8	4	-4	10	6	-4	8	6	-2
EEP	14	22	+8	15	22	+7	13	20	+7	17	22	+5
EEE	29	25	-3	31	29	-2	20	17	-3	24	21	-3

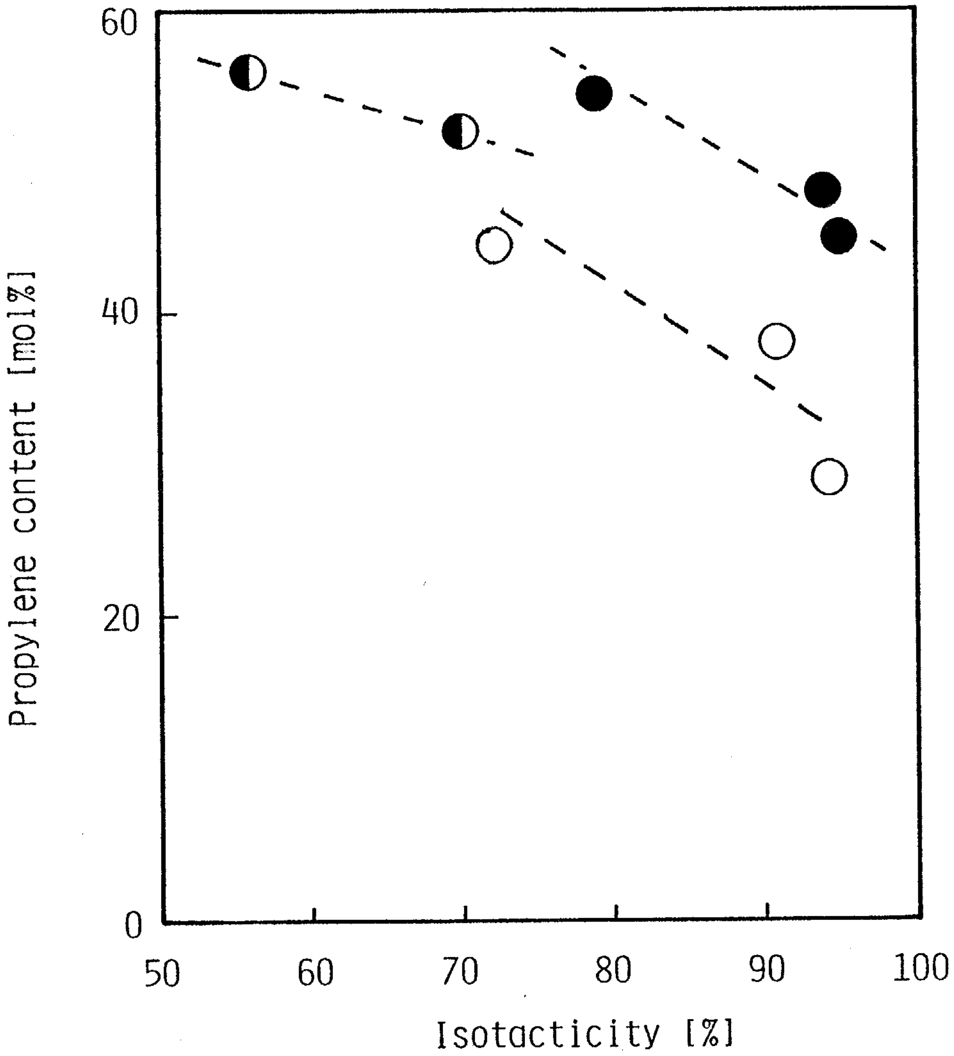


Figure 3-4 Relations between the comonomer contents in the copolymer and the isotacticity of polypropylene.

◐ ;$\mathrm{TiCl_4/MgCl_2{-}Al(C_2H_5)_3/EB}$

○ ;$\mathrm{TiCl_4/EB/MgCl_2{-}Al(C_2H_5)_3/EB}$

● ;$\mathrm{TiCl_4/DNBP/MgCl_2{-}Al(C_2H_5)_3/PTES}$

reduced the discrepancy. On the other hand, addition of EB(external donor) to the internal donor free $TiCl_4/MgCl_2$ catalyst hardly reduced the discrepancy.

Figure 3-4 shows the correlation between the content of propylene units in copolymer and the isotacticity of polypropylene, which clearly indicates that increase in the isotacticity is followed by decrease in the propylene content.

These results can be interpreted as follows : There exist at least two different species as mentioned in Chapter 1. One is Ti(III) having one chlorine vacancy(Site-I) which produces isotactic polypropylene and the other is Ti(III) having two chlorine vacancies(Site-II) which produces atactic one. These two Ti(III) species are active also for ethylene polymerization and hence give copolymers of ethylene and α-olefins when the mixtures are brought into contact. It is natural to consider that Site-I and Site-II should give different monomer reactivity ratios, r_E and r_P. Judging from the fact that addition of external donors causes a significant decrease in propylene content in copolymer, the r_E value over Site-I is considered somewhat larger than that over Site-II, while the r_P value over Site-I smaller than that over Site-II. Therefore, the discrepancy between the observed and calculated triad values may reflect the distribution of Site-I and Site-II. If the catalyst contains only one species, either Site-I or Site-II, there should be no discrepancy. Actually, when external donors like EB and PTES were added to the internal donor containing catalysts (highly isospecific catalysts), the discrepancy was reduced to some extent(to see the results of sample 3, 5 and 6). However, when the catalyst contains both Site-I and site-II, copolymerization systems can not be represented by a simple binary first-Markovian process with four elementary reactions. This may be the main reason why such a discrepancy appears.

To get better insight into this point, copolymerization was conducted with the $TiCl_4/DNBP/MgCl_4-Al(C_2H_5)_3/PTES$ catalyst system using the apparatus as shown in Figure 3-2. The copolymers obtained were fractionated into three parts, diethyl ether soluble, heptane soluble and heptane insoluble fractions by solvent extraction. The results obtained are summarized in Table 3-6. In Figure 3-5 is illustrated the correlation between each polymer yield and the concentration of PTES. With increasing the concentration of PTES, the yield of ether soluble polymer decreased drastically, while that of heptane insoluble polymer remained almost unchanged. Then, the comonomer compositions and sequence distributions for these fractions were estimated from ^{13}C NMR spectra (Tables 3-7 and 3-8), and monomer reactivity ratios of each polymer were determined by using dyad compositions and the ratio of comonomers in the feed (Table 3-9). In Table 3-9 are also shown the calculated triad sequence distributions as well as the deviations from the observed ones. The discrepancies between the calculated and observed triad sequence distributions in Table 3-9 are considerably smaller than those in Table 3-5. These results strongly support the above speculation ; there exist at least two types of Ti species, one producing the ethylene-propylene copolymer with higher propylene content and the other producing the copolymer containing less amount of propylene. The ether insoluble-heptane soluble polymer might be produced by the intermediate Ti species which was previously proposed in Chapter 1.

Copolymerization of ethylene and 1-butene was also carried out with the $TiCl_4/MgCl_2-Al(C_2H_5)_3$ catalyst system in the presence of EB as an external donor. The ^{13}C NMR spectrum of a typical copolymer(Run No. 12) together with the assignment is illustrated in Figure 3-6. In Table 3-10 are shown the results of copolymerization as well as the isotacticity of polypropylene produced under similar conditions. The content of 1-butene unit decreased with an increase in the amount of EB also in this case. In Table 3-6 are also shown the propylene content in ethylene-propylene copolymer obtained under similar polymerization conditions. In spite of higher comonomer content in feed(1-butene/ethylene = 4.0 and propylene/ethylene = 0.85 in gas phase), for example, the content of 1-butene(23%) was much smaller than that of propylene(56%) in the absence of EB. This also suggests that the steric interaction between the active species and the monomer should affect the polymerization activity in this catalyst system.

Table 3-6 Effect of PTES on copolymerization of ethylene and propylene with $TiCl_4$/DNBP/$MgCl_2$-$Al(C_2H_5)_3$.

Run no.	PTES [mmol/l]	C_3' in feed [mol%]	Yield [g]	Weight of solvent exracted fraction [g]		
				Ether sol.	Heptane sol.	Heptane insol.
9	0	85	0.99	0.52	0.18	0.29
10	0.25	84	0.70	0.29	0.13	0.28
11	0.50	85	0.62	0.24	0.13	0.25

Polymerization conditions: $Al(C_2H_5)_3$ = 10 mmol/l, Al/Ti = 50, heptane = 100 ml, Total pressure = 760 Torr, 40°C, 20 min.

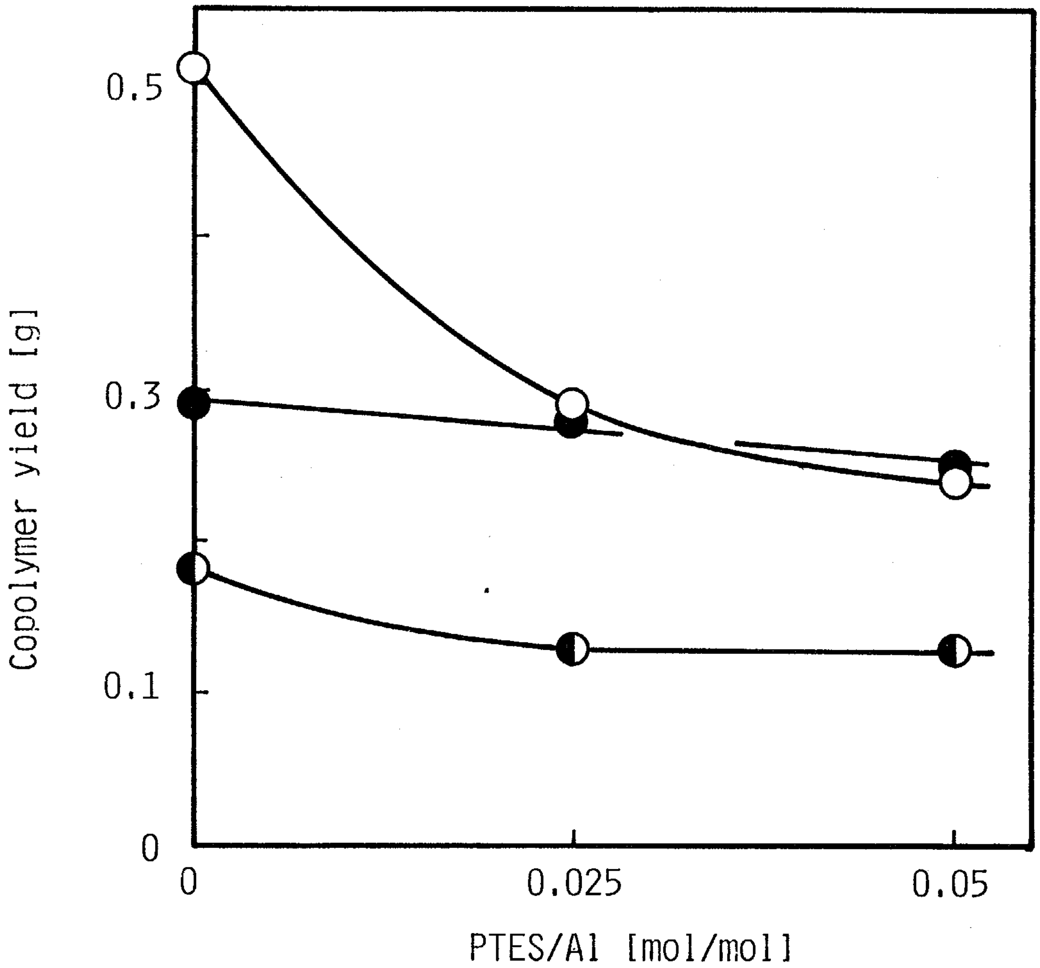


Figure 3-5 Effect of PTES on the copolymerization of ethylene and propylene with $TiCl_4$/DNBP/$MgCl_2$-$Al(C_2H_5)_3$.

○ ; ether soluble fraction

◐ ; heptane soluble fraction

● ; heptane insoluble fraction

Table 3-7 ^{13}C NMR area data for each solvent extracted fraction

Carbon type	Monomer sequence	Ether sol.			Heptane sol.			Heptane insol.		
		9	10	11	9	10	11	9	10	11
$S_{\alpha\alpha}$	PP	11.4	11.2	13.3	8.1	8.3	10.1	1.5	1.5	2.0
$S_{\alpha\gamma}$	2PEP	9.4	10.0	8.9	4.7	6.3	6.8	1.5	1.9	2.3
$S_{\alpha\delta}$	$PEE_n(n>1)$	10.0	7.6	7.8	9.3	8.9	8.8	7.0	5.9	6.0
$S_{\gamma\gamma}$	PEEP	1.7	1.5	1.8	1.7	1.6	1.4	0.7	0.5	0.3
$S_{\gamma\delta}$	$PEEE_n(n>1)$	4.7	4.7	3.9	4.7	5.2	6.1	5.7	4.1	5.8
$S_{\delta\delta}$	$EEE_n(n>1)$	10.7	10.0	10.3	26.2	22.5	20.9	64.0	68.6	66.5
$S_{\beta\delta}$	$PEE_n(n>1)$	8.1	7.6	7.8	8.7	8.9	8.8	6.8	6.0	6.0
$S_{\beta\beta}$	PEP	4.0	4.3	3.9	2.3	3.7	3.4	0.8	0.9	1.0
$T_{\delta\delta}$	EPE	4.7	3.8	3.9	5.8	4.7	4.7	3.3	3.1	3.1
$T_{\beta\delta}$	PPE	10.1	11.1	10.0	8.1	6.3	8.1	2.0	1.2	1.0
$T_{\beta\beta}$	PPP	5.4	7.1	7.8	4.0	6.3	4.1	0.9	0.7	0.5
P	–	19.5	21.1	20.6	16.3	17.3	16.8	5.8	5.7	5.5

Table 3-8 Copolymer compositions and sequence distributions in each fraction.

Fraction	Ether sol. 9	Ether sol. 10	Ether sol. 11	Heptane sol. 9	Heptane sol. 10	Heptane sol. 11	Heptane insol. 9	Heptane insol. 10	Heptane insol. 11
P	0.52	0.53	0.54	0.37	0.39	0.42	0.11	0.11	0.12
E	0.48	0.47	0.46	0.63	0.61	0.58	0.89	0.89	0.88
PP	0.28	0.29	0.33	0.20	0.20	0.24	0.03	0.03	0.04
PE	0.47	0.45	0.42	0.34	0.38	0.37	0.18	0.16	0.17
EE	0.26	0.26	0.25	0.46	0.42	0.39	0.79	0.81	0.79
PPP	0.13	0.18	0.19	0.09	0.15	0.10	0.02	0.01	0.01
PPE	0.25	0.27	0.25	0.19	0.15	0.20	0.04	0.03	0.02
EPE	0.11	0.09	0.10	0.13	0.11	0.11	0.07	0.07	0.07
EPE	0.11	0.12	0.11	0.05	0.08	0.08	0.02	0.02	0.02
EEP	0.24	0.19	0.19	0.21	0.21	0.21	0.14	0.13	0.13
EEE	0.16	0.15	0.15	0.33	0.30	0.29	0.71	0.75	0.75

Table 3-9 Reactivity ratios r_E, r_P, the products r_Er_P and the calculated triad compositio compositions in each solvent exracted fraction.

	Ether sol.			Heptane sol.			Heptane insol.		
	9	10	11	9	10	11	9	10	11
r_E	6.2	6.1	6.8	15	12	12	49	54	53
r_P	0.21	0.24	0.28	0.21	0.20	0.23	0.060	0.071	0.082
r_Er_P	1.3	1.5	1.9	3.1	2.4	2.8	2.9	3.8	4.4
PPP	15(+2)	16(-2)	21(+2)	11(+2)	10(-5)	14(+4)	1(-1)	1 (0)	1 (0)
PPE	25 (0)	25(-2)	26(+6)	18(-1)	19(+4)	21(+1)	4 (0)	4(+1)	5(+3)
EPE	11 (0)	10(+1)	8(-2)	8(-5)	9(-2)	8(-3)	7 (0)	6(-1)	6(-1)
PEP	11 (0)	11(-1)	10(-2)	5 (0)	6(-2)	6(-2)	1(-1)	1(-1)	1(-1)
EEP	24 (0)	24(+5)	23(+4)	25(+4)	26(+5)	25(+4)	16(+2)	14(+1)	15(+2)
EEE	14(-2)	14(-1)	13(-2)	33 (0)	30 (0)	26(-3)	71 (0)	74(-1)	72(-3)

- The values in ( ) show the difference between the calculated and observed triad.

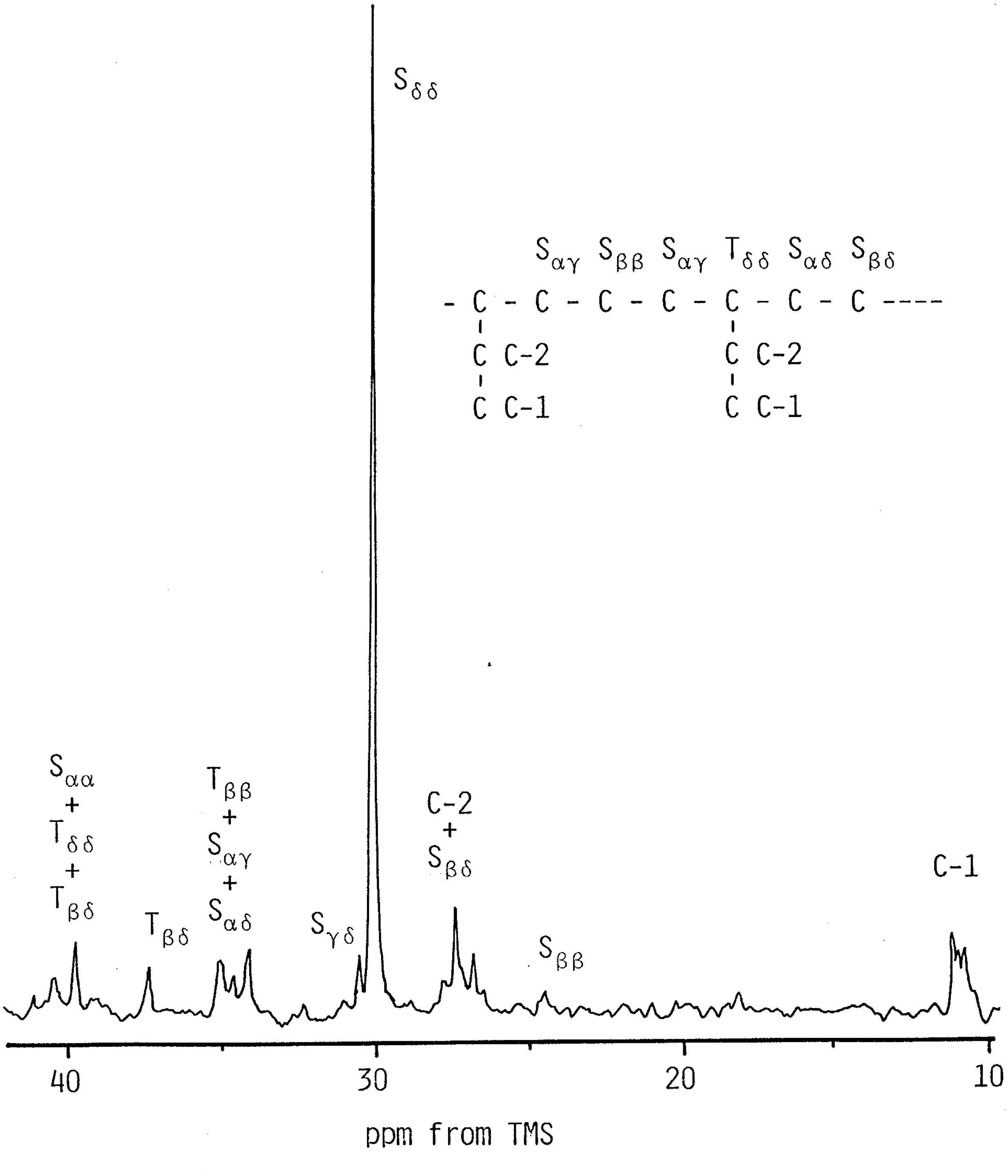


Figure 3-6 ^{13}C NMR spectrum of ethylene-1-butene copolymer of Sample 12.

Table 3-10 Results of copolymerization of ethylene and 1-butene with $TiCl_4$/$MgCl_2$-$Al(C_2H_5)_3$ in the presence of EB.

Run no.	EB [mmol/l]	Time [min]	C_4' in copolymer [mol%]	I.I. of PP[a)] [%]	C_3' in copolymer[b)] [mol%]
12	0	3.5	22	56	56
13	4	3.0	19	70	52
14	11	7.0	16	79	-
15	15	13.0	7.4	85	-

Polymerization conditions: $TiCl_4/MgCl_2$ = 80 mg, $Al(C_2H_5)_3$ = 20 mmol/l, heptane = 10 ml, ethylene/1-butene = 4.0(molar ratio, gas phase), Total pressure = 530 Torr, 40°C.

a) Determined with IR.

b) The results shown in Table 3-1.

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Chapter 4

Preparation of a Stable $MgCl_2$-Supported Titanium-Based Catalyst for Olefin Polymerization

4-1 Introduction

By supporting the Ti species on a magnesium-based support, most often $MgCl_2$, polymerization activities of ethylene and propylene significantly increase. In the polymerization of propylene with these supported catalysts, however, the polymerization rate usually decays rapidly with an increase in the polymerization time. For example, over the $MgCl_2$-supported $TiCl_4$ catalysts with and without ethyl benzoate(EB), the decrease of polymerization rate is fitted by Eq.(1)$^{1)}$.

$$-\frac{dR}{dt} = k_d \cdot R^2 \qquad (1)$$

On the other hand, as mentioned in Chapter 1, over the $MgCl_2$-supported $TiCl_4$ catalysts containing diesters like di-n-butyl phthalate(DNBP) deactivation occurs according to the first order kinetics and addition of electron donors like EB and phenyltriethoxysilane(PTES) does not affected the rate profile.

It has reportd that the deactivation occurs similarly even in the absence of monomer$^{1)}$. Therefore deactivation should not be due to the monomer diffusion through the polymer layer produced on the catalyst particles, but might owe to overreduction of Ti(III) to Ti(II), which is active only for ethylene polymerization. Kashiwa et al. reported that the treatment of the deactivated catalyst with oxdizing reagents like Cl_2, tert-C_4H_9Cl and so on regenerates the activity[2].

The rate of propylene polymerization with activated $TiCl_3$ combined with $Al(C_2H_5)_3$ also deactivated according to Eq.(2),

$$\frac{R_t - R_\infty}{R_0 - R_\infty} = e^{-kt} \tag{2}$$

where R_0, R_t and R_∞ are the rate of polymerization at t = 0, t and ∞, and k is a constant. By differentiating Eq.(2), we obtain

$$-\frac{dR}{dt} = k(R_t - R_\infty) \tag{3}$$

Ambroz et al.[3] examined the same catalyst system ($TiCl_3$-$Al(C_2H_5)_3$) and found that a considerable amount of Cl is extracted from the $TiCl_3$ contacted with $Al(C_2H_5)_3$. The rate of Cl extraction is given by Eq.(4).

$$-\frac{d[Cl^-]}{dt} = k'([Cl^-]_t - [Cl^-]_\infty) \tag{4}$$

The identity of Eqs.(3) and (4) strongly implies that the deactivation process in the $TiCl_3$-$Al(C_2H_5)_3$ catalyst system results from the extraction of Cl ligand (over-reduction of Ti(III) proceeds as a result).

On the other hand, there are some catalyst systems which show stationary rates of polymerization. One of the typical catalysts is the $TiCl_3$ combined with $Al(C_2H_2)_2Cl$. Some soluble catalysts like $Ti(OC_4H_9)_4$/2-ethyl-hexan-1-ol/$MgCl_2$-$Al(C_2H_5)_2Cl$ also show stationary rates for propylene polymerization, but to give atactic polypropylene.

These catalyst systems, however, have some induction period. Considering that the polymerization is initiated by the alkylation of Ti species with alkyl aluminium compounds, such an alkylation in these systems seems to be less easy as compared with those in the $TiCl_3$-$Al(C_2H_5)_3$ and $TiCl_4$/$MgCl_2$-$Al(C_2H_5)_3$ systems. It may be considered that the alkylated Ti species are reduced according to the following scheme.

$$2\ Ti^{n+}\text{-}R \longrightarrow 2\ Ti^{(n-1)+} + R\text{-}R$$

$$\text{or}\quad Ti^{n+}\text{-}R \longrightarrow Ti^{(n-1)+} + R$$

$$\text{or}\quad Ti^{n+}\text{-}R_2 \longrightarrow Ti_{(n-2)+} + R\text{-}R$$

The reduction of Ti species may be affected by the feasibility of alkylation of Ti species as well as the stability of alkylated Ti species. Therefore the following two points should be most important to obtain stable $MgCl_2$-supported titanium-based catalysts for propylene polymerization. One is how to choose the adequate alkylating reagents which do not cause overalkylation. The other is how to choose the ligands which stabilize the titanium-alkyl species.

Anyway, usual catalysts either deactivate during the course of polymerization (reduction ; $Ti^{3+} \longrightarrow Ti^{2+}$) or show induction periods. The analysis of the copolymerization results obtained over these catalysts seems to be much complicated.

From these points of view, new type of catalysts were tried to prepare by supporting alkoxy titanium compounds on $MgCl_2$. The resulting catalysts were found to show very stable activites from the initial stage of polymerization. Copolymerization of ethylene and propylene was therefore carried out with them.

4-2 Experimental

Materials

n-butanol(extra pure grade, Kanto Kagaku Co.) was dried over calucium hydride, followed by fractional distillation.

$Ti(OC_4H_9)_4$(pure grade, Kanto Kagaku Co.) was used without further purification.

$Ti(OC_4H_9)Cl_3$, $Ti(OC_4H_9)_2Cl_2$ and $Ti(OC_4H_9)_3Cl$ were prepared by the reactions between $TiCl_4$ and n-butanol/or $Ti(OC_4H_9)_4$[4].

$Al(C_2H_5)Cl_2$, $Al_2(C_2H_5)_3Cl_3$, $Al(C_2H_5)_2Cl$, $Al(C_2H_5)_3$ and $Al(iso\text{-}C_4H_9)_3$ were supplied from Toyo Staufer Co. and used without further purification.

Other chemicals are obtained and purified as the same procedures described in previous Chapters.

Preparation of catalysts

Method A : The mixture of 5.5 mmol of $Ti(OC_4H_9)_4$, 5 g of $MgCl_2$, 25 ml of heptane and 11 mmol of EB (if needed) was ground in a 200 ml stainless steel ball mill at 20°C for 24 h under nitrogen atmosphere, followed by washing with plenty of heptane. The resultant mixture was treated with several kinds of organoaluminium compounds under various conditions, washed throughly with heptane and dried i. vac. at 20°C to give the catalyst.

Method B : The mixture of 11 mmol of $Ti(OC_4H_9)_xCl_{4-x}$ and 30 g of $MgCl_2$ in the absence or presence of 11 mmol of DNBP was ground in a 1 l stainless steel vibration mill at 20°C for 20 h under nitrogen atmosphere. The resultant mixture was used as catalyst.

Polymerization procedures

Homopolymerization of propylene was conducted with the same procedures as described in Chapter 1.

Copolymerization of ethylene and propylene was conducted with the procedure B as described in Chapter 3.

Analytical procedures

The isotacticity of produced polypropylene was determined by extraction with boiling heptane as described in Chapter 1. The comonomer contents in copolymer were determined by ^{13}C NMR spectra as described in Chapter 3 or IR spectra[5]. The amount of supported Ti was determined by atomic absorption spectrophotometry. The molecular weight distribution was measured as described in Chapter 1.

4-3 Results and Discussion

4-3-1 Propylene Polymerization

In Figure 4-1 are illustrated the rate-time profiles of propylene polymerization with $Ti(OC_4H_9)_4/MgCl_2$ and $Ti(OC_4H_9)_4/MgCl_2$ treated with $Al_2(C_2H_5)_3Cl_3$. Hereafter $Ti(OC_4H_9)_4/MgCl_2$ treated with alkylaluminium compounds ($Al_x(C_2H_5)_yCl_z$) are represented as $Ti(OC_4H_9)_4/MgCl_2/Al_x(C_2H_5)_yCl_z$. Although $Ti(OC_4H_9)_4/MgCl_2$ combined with $Al(C_2H_5)_3$ showed a stationary rate, the activity was very low. Treatment of the catalyst with $Al_2(C_2H_5)_3Cl_3$ caused a significant increase in the polymerization rate. Deactivation during the polymerization strongly depended on the concentration of $Al_2(C_2H_5)_3Cl_3$ treated. In Figure 4-2 are plotted the correlation between ln(rate) versus polymerization time, which suggest that deactivation obeys the first-order kinetics with respect to the polymerization rate.

$$-\frac{dR}{dt} = k_d \cdot R \qquad (5)$$

Therefore the deactivation rates over these catalysts can be evaluated by the first-order rate constant, k_d.

In Table 4-1 are summarized the catalyst preparation

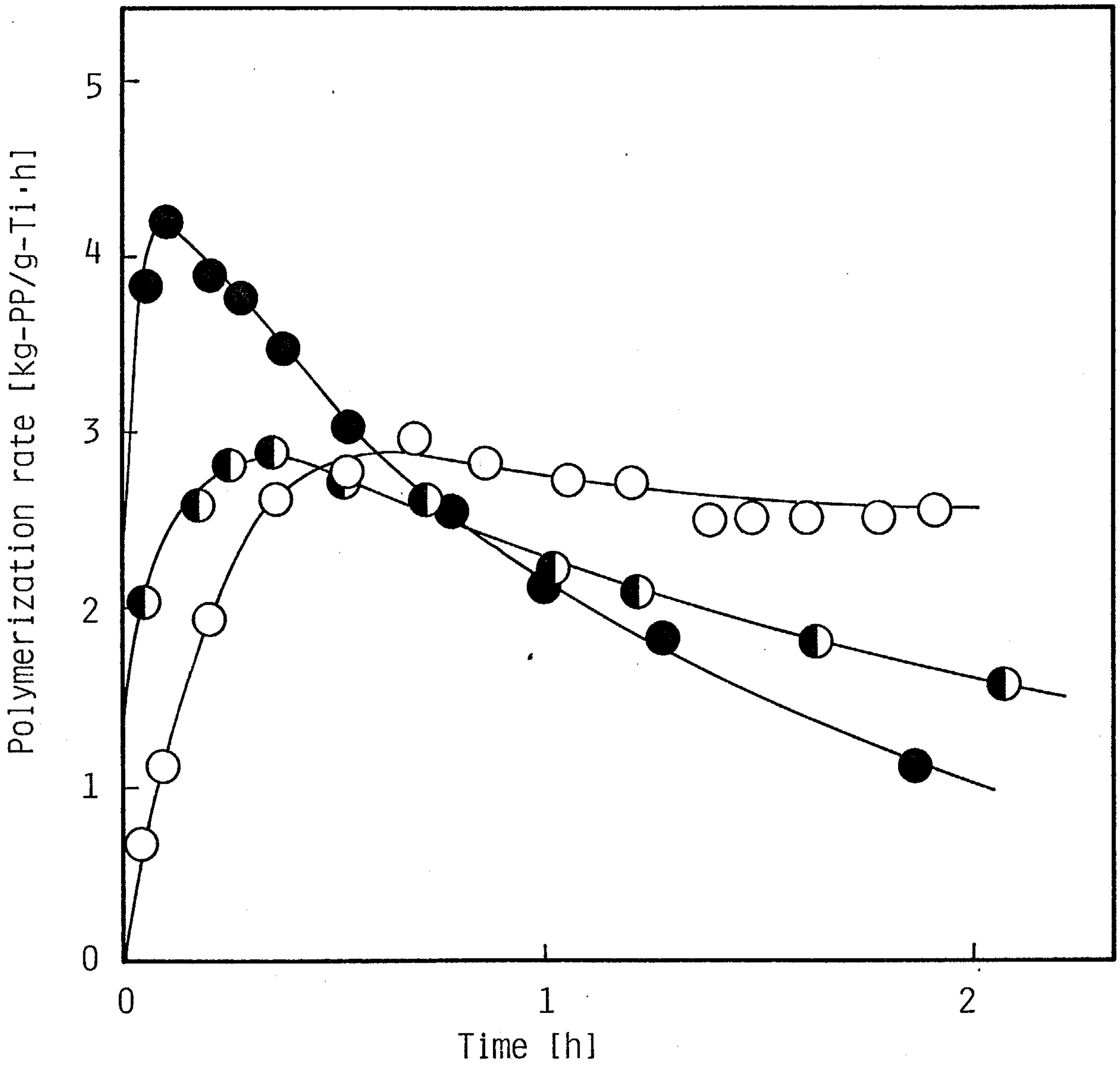


Figure 4-1 Rate-time profiles of propylene polymerization with $MgCl_2$-supported $Ti(OC_4H_9)_4$-based catalysts.
$Al_2(C_2H_5)_3Cl_3$ = 12 mmol/l(○), 50 mmol/l(◐) and 100 mmol/l(●).
Polymerization conditions as indicated in Table 4-1.

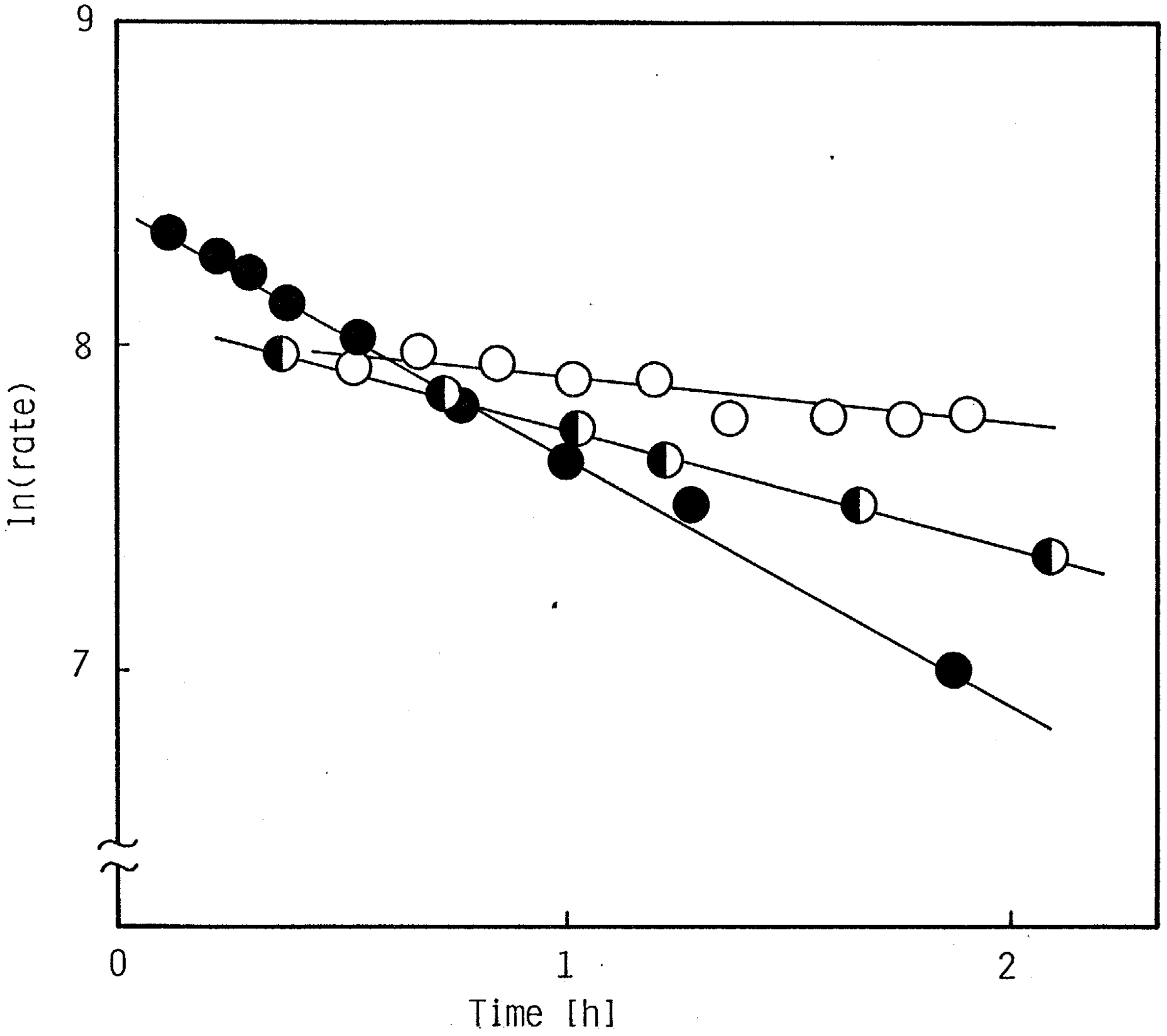


Figure 4-2 Semi-logarithmic plots of polymerization rate versus polymerization time shown in Figure 4-2.

conditions, activities and constants of deactivation. Increase in the $Al_2(C_2H_5)_3Cl_3$ concentration gave rise to the higher initial activity and rapid deactivation.

Then the effect of alkylaluminium compounds used in the catalyst preparation was investigated. In Figure 4-3 are illustrated the rate-time profiles of propylene polymerization. Treatment with chlorine containing alkylaluminiums increased the catalyst activity as well as stability. The activity decreased in the following order.

$$Al_2(C_2H_5)_3Cl_3 > Al(C_2H_5)Cl_2 > Al(C_2H_5)_2Cl$$

The effect of such a treatment may be considered as follows.

As is well known, the $Ti(OC_4H_9)_4$-$Al(C_2H_5)_3$ system catalyzes neither ethylene nor propylene polymerization even in the presence of $MgCl_2$. By using $Al(C_2H_5)_2Cl$ in place of $Al(C_2H_5)_3$, however, propylene polymerization proceeds with a stationary rate and addition of $MgCl_2$ to this system causes a considerable increase in the activity6). On the other hand, it is proposed that the role of $MgCl_2$ on the improvement of activity (propagation rate constant, k_p) is mainly attributed to the increase in the electron density of the active Ti, since the electron density of Mg^{2+} is lower than that of Ti^{3+}. Such an interaction , however, does not occur in the absence of chlorine bridges between the Ti species and $MgCl_2$7). When the $Al_x(C_2H_5)_yCl_z$ is used in the catalyst preparation, ligand exchange reactions might occur between $Ti(OC_4H_9)_4$ and $Al_x(C_2H_5)_yCl_z$ to produce $Ti(OC_4H_9)_nCl_{4-n}$, which may be capable of interacting with

Table 4-1 Treatment conditions of catalysts and the results of propylene polymerization

Chlorine containing compound	Al [mmol/l]	Temp. [°C]	Time [h]	Ti [wt%]	Surface area [m^2/g]	Activity [kg-PP/g-Ti·h]	kd [h^{-1}]
$Al_2(C_2H_5)_3Cl_3$	100	20	0.5	0.90	-	2.4	0.87
〃	50	〃	〃	0.95	-	2.1	0.36
〃	12	〃	〃	0.65	54	2.5	0.12
$Al(C_2H_5)_2Cl$	80	〃	〃	0.71	-	0.97	0.09
〃	12	〃	〃	0.65	55	0.91	0.20
$Al(C_2H_5)Cl_2$	12	〃	〃	0.43	48	2.0	0.01
$TiCl_4$	neat	120	3	2.3	-	0.96	0.27

Polymerization conditions ; Heptane = 200 ml, $Al(C_2H_5)_3$ = 6 mmol/l, $P_{C_3'}$= 660 Torr, 40°C, 2 h, [Ti] = 0.1 mmol/l.

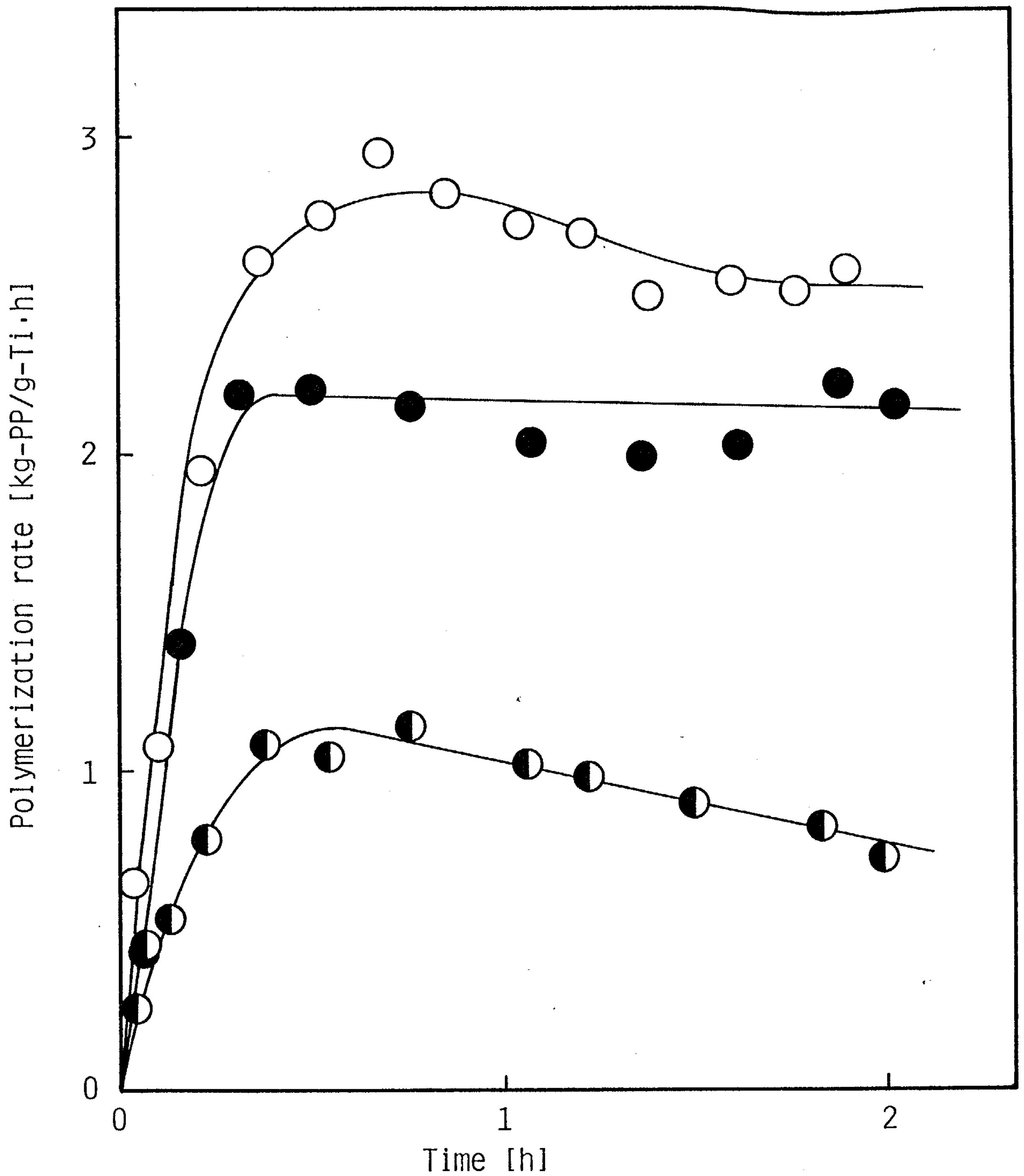


Figure 4-3 The effect of treatment with various organoaluminium compounds on propylene polymerization.

◐; $Al(C_2H_5)_2Cl$, ○; $Al_2(C_2H_5)_3Cl_3$, ●; $Al(C_2H_5)Cl_2$

Polymerization conditions as indicated in Table 4-1.

$MgCl_2$.

To throw light on this point, $Ti(OC_4H_9)_nCl_{4-n}$ was used in place of $Ti(OC_4H_9)_4$. The catalyst prepared from $Ti(OC_4H_9)Cl_3$ and $MgCl_2$ actually showed a similar rate-time profile as shown in Figure 4-4. When $Ti(OC_4H_9)_2Cl_2$ or $Ti(OC_4H_9)_3Cl$ was used, the rate-time profiles were somewhat different ; with an increase in the polymerization time, the rate was increased gradually. In addition, the polymerization rates over these catalysts were about one tenth lower than that over the $Ti(OC_4H_9)Cl_3$. From these results, formation of the active species in these catalyst systems may be speculated as Scheme 4-1.

Then the effect of external donor on the isospecificity was investigated. In Figure 4-5 are illustrated the rate-time profiles for propylene polymerization with the $Ti(OC_4H_9)_4/MgCl_2/Al(C_2H_5)Cl_2-Al(C_2H_5)_3$/ethylbenzoate(EB) system. Addition of EB did not change the kinetic feature. In Figure 4-6 are plotted the activity for both isotactic and atactic fractions against the concentration of EB. Addition of only small amount of EB caused a drastic decrease in the atactic fraction keeping in the isotactic fraction almost unchanged, which is similar to that obtained by Kashiwa with the use of the $TiCl_4/MgCl_2$ catalyst (Figure 4-7)$^{8)}$. When EB was used as internal and external donor, the isotacticity was improved to a great extent (Table 4-3).

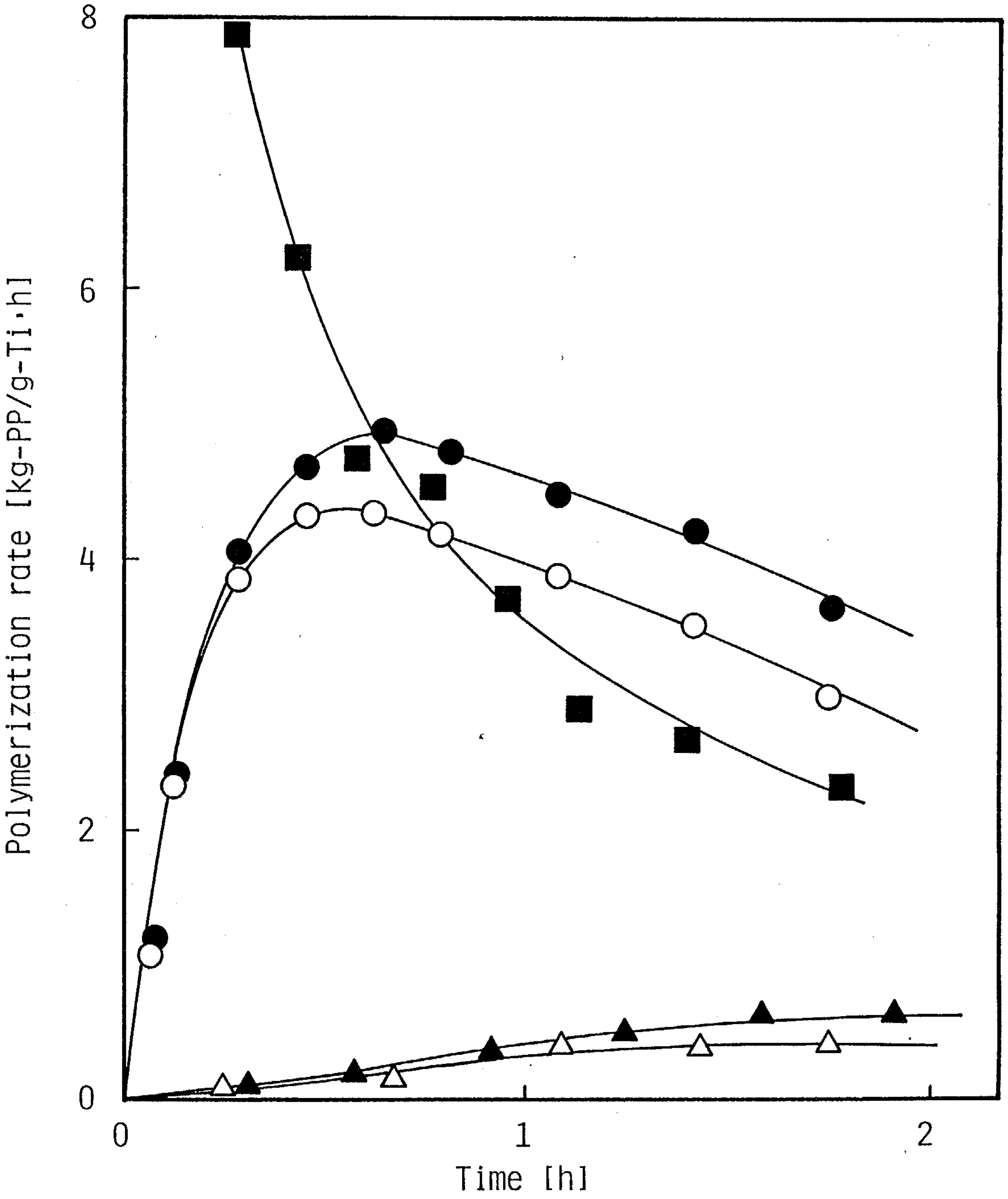


Figure 4-4 Rate time profiles of propylene polymerization with $Ti(OC_4H_9)_xCl_{4-x}/(DNBP)/MgCl_2-Al(C_2H_5)_3$.

○; $Ti(OC_4H_9)Cl_3/MgCl_2$, ●; $Ti(OC_4H_9)Cl_3/DNBP/MgCl_2$,

△; $Ti(OC_4H_9)_2Cl_2/DNBP/MgCl_2$, ▲; $Ti(OC_4H_9)_3Cl/DNBP/MgCl_2$,

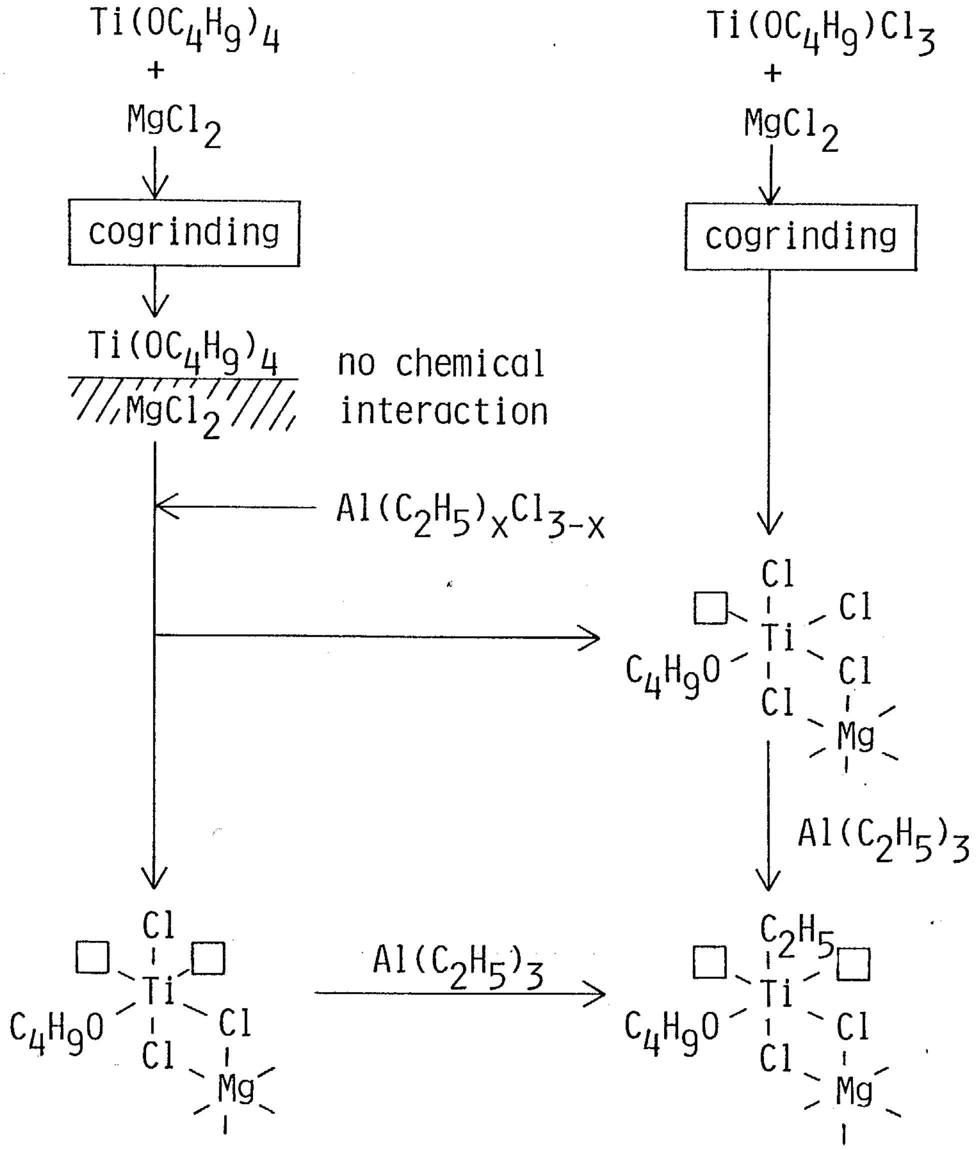
■; $TiCl_4/MgCl_2$

Polymerization conditions as indicated in Table 4-2.

Table 4-2 The results of propylene polymerization with the catalysts prepared by cogrinding $Ti(OC_4H_9)_xCl_{4-x}$ with $MgCl_2$

Ti compound	Ester	Activity [kg-PP/g-Ti·h]	I.I. [%]
$TiCl_4$	-	4.5	24
$Ti(OC_4H_9)Cl_3$	-	3.2	23
〃	DNBP	3.8	48
$Ti(OC_4H_9)_2Cl_2$	〃	0.35	-
$Ti(OC_4H_9)_3Cl$	〃	0.33	-
$Ti(OC_4H_9)_4$	-	0.05	-

Polymerization conditions ; heptane = 100 ml, $Al(C_2H_5)_3$ = 10 mmol/l, $P_{C_3^{'}}$ = 660 Torr, 40°C, 2 h, [Ti] = 0.3 mmol/l.


Ti(OC4H9)4
+
MgCl2
cogrinding
Ti(OC4H9)4
MgCl2
no chemical interaction
Al(C2H5)xCl3-x
Ti(OC4H9)Cl3
+
MgCl2
cogrinding
Cl
Ti
C4H9O
Mg
Al(C2H5)3
C2H5

Scheme 4-1

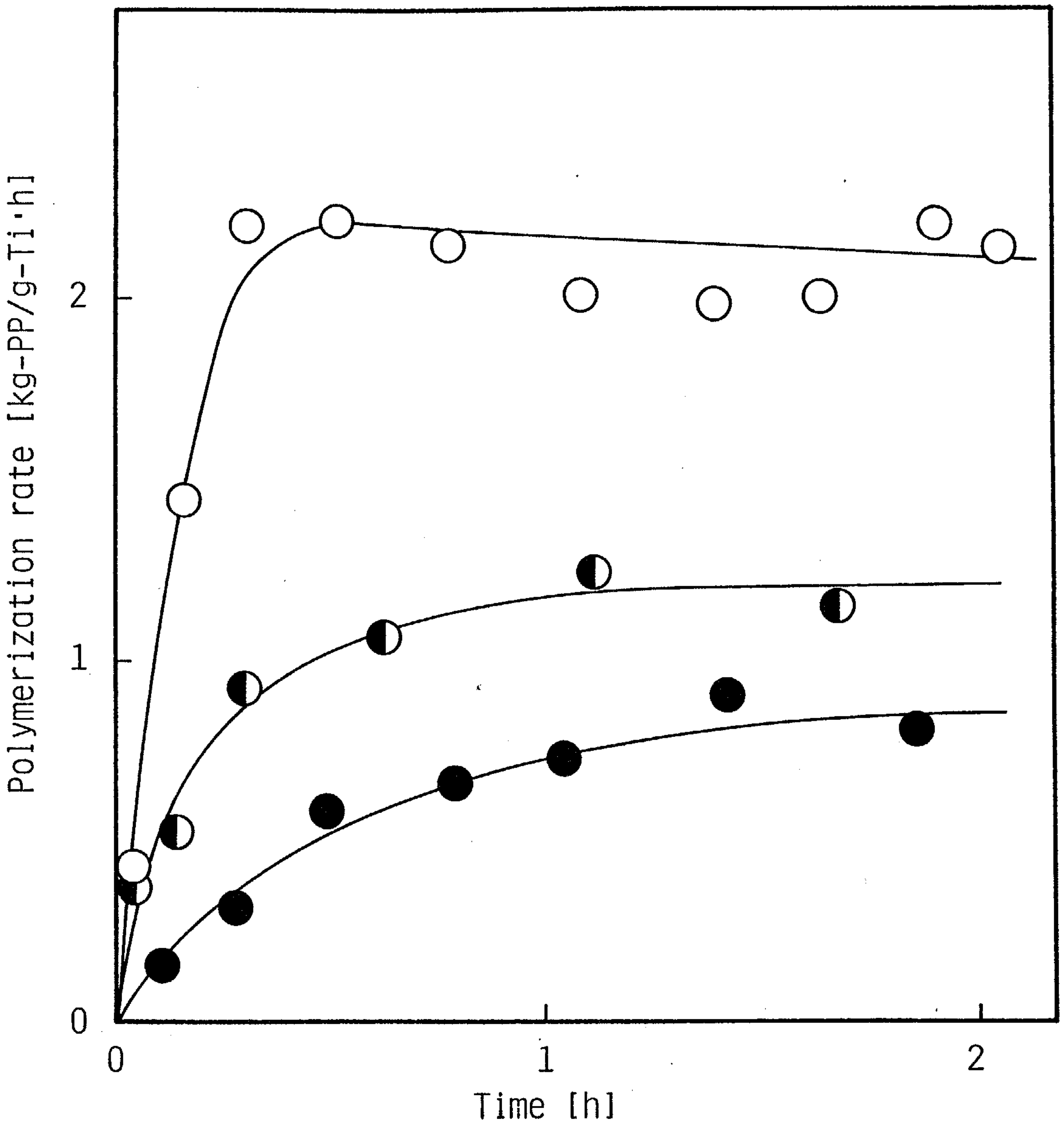


Figure 4-5 Additive effect of EB on the rate time profile of propylene polymerization with $Ti(C_4H_9)_4/MgCl_2/Al(C_2H_5)Cl_2-Al(C_2H_5)_3$.

EB = 0 (○), 0.35 (◐) and 0.75 (●) mmol/l

Polymerization conditions as indicated in Table 4-3.

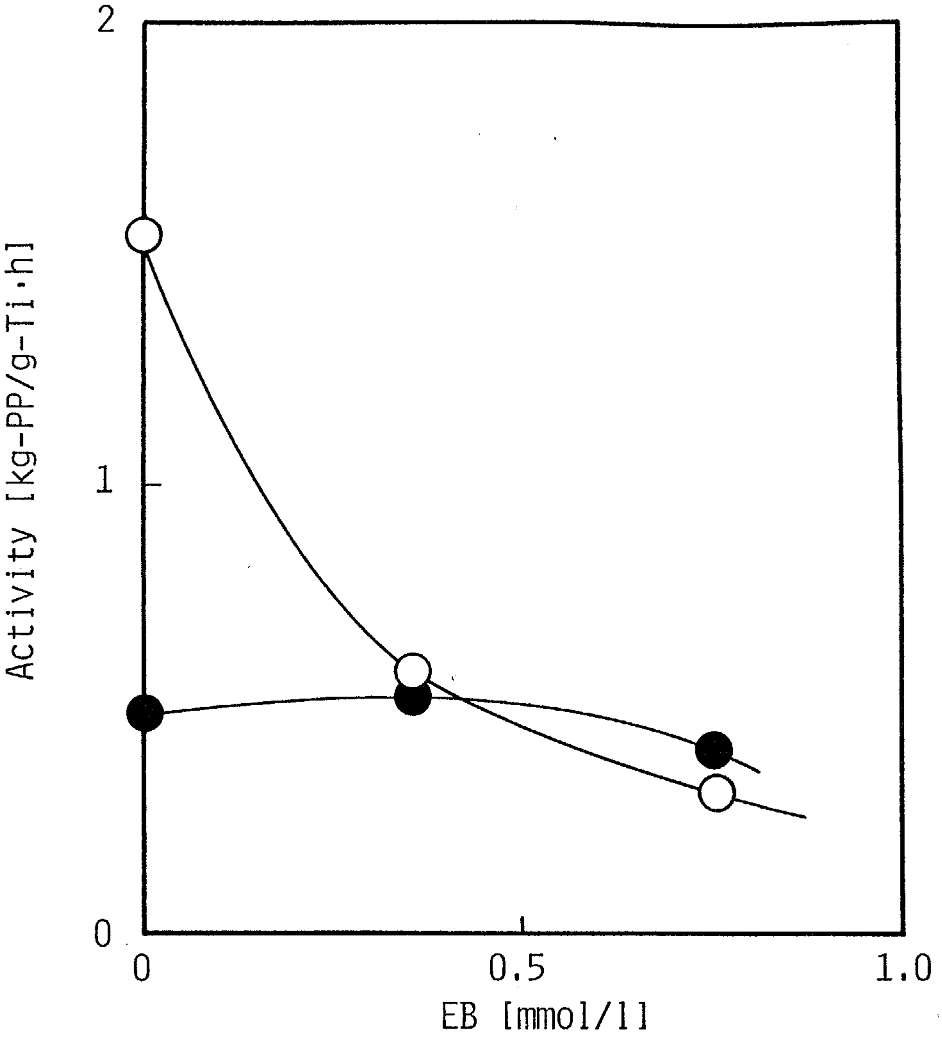


Figure 4-6 Plots of the activity versus the concentration of EB with $Ti(OC_4H_9)_4/MgCl_2/Al(C_2H_5)Cl_2-Al(C_2H_5)_3$.

●; boiling heptane insoluble fraction

○; boiling heptane soluble fraction

Polymerization conditions as indicated in Table 4-3.

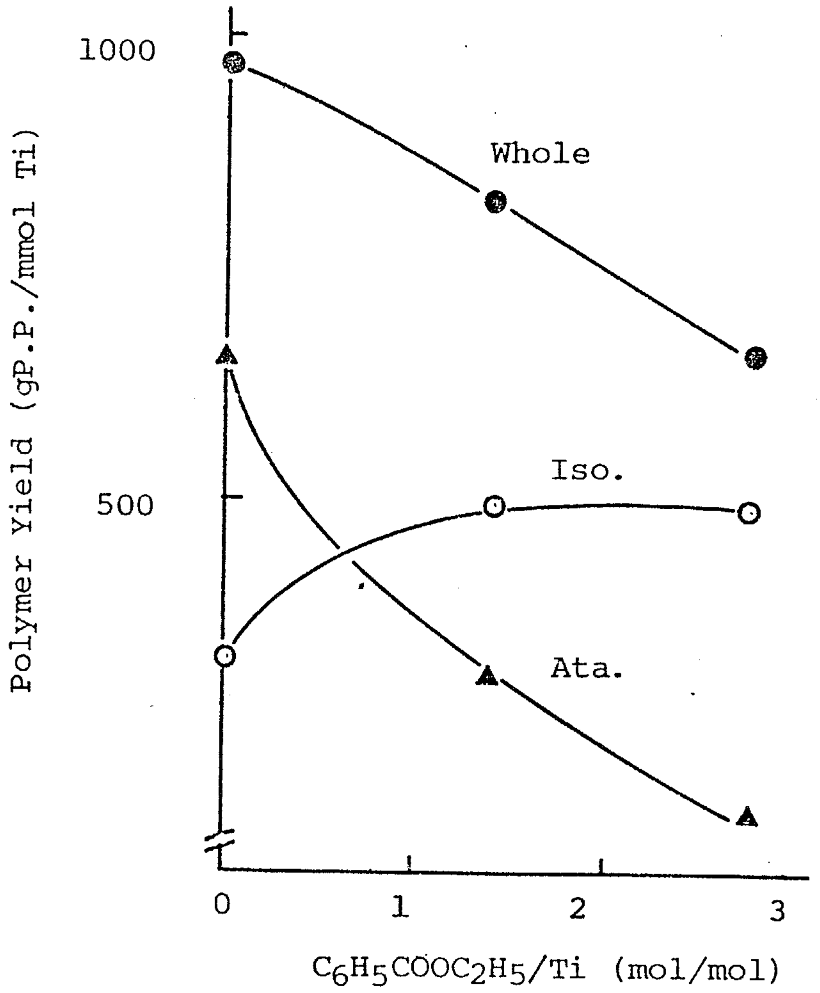


Figure 4-7 Change of polymer yield obtained with $TiCl_4/MgCl_2-Al(C_2H_5)_3$ by addition of EB.

●; whole polymer

○; boiling heptane insoluble fraction

▲; boiling heptane soluble fraction

Table 4-3 Additive effect of EB on propylene polymerization with $Ti(OC_4H_9)_4$ -based $MgCl_2$-supported catalysts

Catalyst	$Al(C_2H_5)_3$ [mmol/l]	EB [mmol/l]	Activity [kg-PP/g-Ti·h]	I.I. [%]
$Ti(OC_4H_9)_4/MgCl_2/Al(C_2H_5)Cl_2$	6	0	2.0	24
〃	〃	0.35	1.1	48
〃	〃	0.75	0.7	55
$Ti(OC_4H_9)_4/MgCl_2/EB/Al(C_2H_5)_3$	〃	0	1.0	55
〃	〃	0.90	0.3	94

Polymerization conditions as indicated in Table 4-1.

4-3-2 Copolymerization of Ethylene and Propylene

As mentioned in Chapter 3, control of valence states of Ti species is of very importance in the copolymerization of ethylene with higher -olefins to supress the by-production of homopolyethylene. As shown in Section 4-3-1, the $MgCl_2$-supported $Ti(OC_4H_9)_4$ catalysts show stable activity for propylene polymerization, which seem to be suitable for such copolymerizations. From this point of view, copolymerization of ethylene and propylene was carried out with these catalyst systems to synthesize ethylene-propylene random copolymer (EPR).

In Table 4-4 are shown the results of the copolymerization conducted at 30°C using the $Ti(OC_4H_9)_4/MgCl_2/Al(C_2H_5)_2Cl$ catalyst combined with various alkylaluminium compounds. So far as the polymerization activity is concerned, trialkylaluminium compounds like $Al(C_2H_5)_3$ and $Al(iso\text{-}C_4H_9)_3$ were found to be most effective cocatalysts. The IR spectra of copolymers obtained by using these cocatalysts are shown in Figure 4-8. The copolymer obtained by using $Al(C_2H_5)_3$ shows a weak absorption at 721 cm^{-1} attributable to the crystalline polyethylene structure, while such a peak cannot be observed in the IR spectrum of the copolymer obtained by using $Al(iso\text{-}C_4H_9)_3$. This suggests that a small amount of Ti(II) species, which are active only for ethylene polymerization, are formed when using $Al(C_2H_5)_3$ as cocatalyst. Therefore, $Al(iso\text{-}C_4H_9)_3$ was hereafter used as cocatalyst for the copolymerization.

In Table 4-5 are summarized the results of copolymeri-

Table 4-4 Polymerization results over the $Ti(OC_4H_9)_4/MgCl_2/Al(C_2H_5)_2Cl$ catalyst

Cocatalyst [mmol/l]		Ti [mmol/l]	Polymer yield [g]	Activity [kg/g-Ti·h]	Propylene contnt* [mol%]
$Al(i\text{-}C_4H_9)_3$	7.7	0.16	1.19	3.20	32
$Al(C_2H_5)_3$	6.7	0.13	1.06	3.28	33
$Al(C_2H_5)_2Cl$	4.1	0.08	0.01	0.04	-
$Al_2(C_2H_5)_3Cl_3$	7.3	0.31	0.04	0.06	-

Polymerization conditions ; 30°C, 1 h, ethylene/propylene = 2/3(mol/mol, gas phase), heptane = 50 ml.

* Determined by IR.

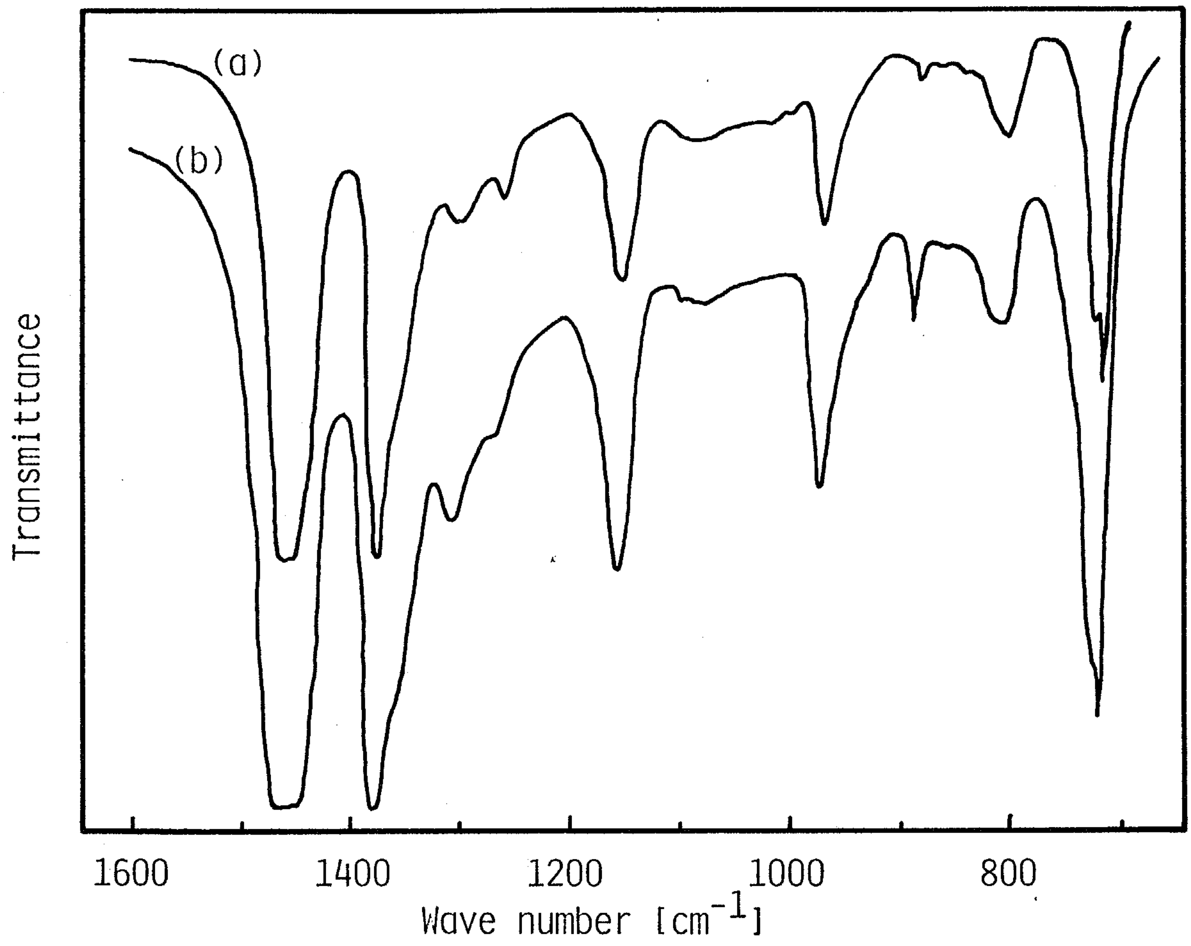


Figure 4-8 IR spectra of ethylene-propylene copolymer obtained with $Ti(OC_4H_9)_4/MgCl_2/Al(C_2H_5)_2Cl$.

(a) $Al(C_2H_5)_3$

(b) $Al(iso\text{-}C_4H_9)_3$

Table 4-5 Polymerization results over the $Ti(OC_4H_9)_4/MgCl_2/Al(C_2H_5)_2Cl$-$Al(iso\text{-}C_4H_9)_3$ cataltst

Run no.	Cocatalyst [mmol/l]	Temp. [°C]	Time [min]	Activity [kg/g-Ti·h]	Propylene content* [mol%]
1	1	30	60	5.4	31
2	3	"	"	5.3	36
3	5	"	"	11.3	48
4	10	"	"	10.3	43
5	50	"	"	9.3	42
6	5	30	10	14.9	43
7	"	"	30	12.4	46
3	"	"	60	11.3	48
8	5	0	60	7.9	36
9	"	10	"	9.1	41
10	"	20	"	10.7	41
3	"	30	"	11.3	48
11	"	40	"	10.1	41

Polymerization conditions ; [Ti] = 0.1 mmol/l, ethylene/propylene = 2/3 (mol/mol,gas phase), Total pressure = 760 Torr, heptane = 50 ml.

* Determined by IR.

zation obtained under various conditions. The results of Run no. 1 ~ 5 show that the activity of the copolymerization increased initially followed by a slight decrease with an increase in the concentration of Al(iso-$C_4H_9)_3$. The maximum value was obtained with the use of 5 mmol/l of Al(iso-$C_4H_9)_3$. The results of Run no. 3, 6 and 7, suggest that activity of the copolymerization is also very stable. From the copolymerization by changing the temperature, it may be said that both the activity and the content of propylene in copolymers are highest at around 30°C.

Then the copolymer obtained at 30°C with the use of 5 mmol/l of Al(iso-$C_4H_9)_3$(Sample 3) was analyzed. In Figures 4-9 and 4-10 are shown the IR spectrum and DSC curve, respectively. The IR spectrum shows a weak absorption at 995 cm^{-1} attributable to the isotactic polypropylene sequences, while the DSC curve does not display an absorption at around 135°C attributable to long propylene sequences. In addition, neither the absorption at 721 cm^{-1} in IR spectrum nor the absorption at around 120°C in DSC curve attributable to long ethylene sequences can be observed.

In ^{13}C NMR spectrum of Sample 3 (Figure 4-11) is, hardly observed the resonances at 34.9 ppm($S_{\alpha\beta}$), 33.6 ppm($T_{\gamma\gamma}$) and 27.9 ppm($S_{\beta\gamma}$) which are derived from the inverted propylene structure. Therefore, the present copolymerization can also be analyzed as the usual binary copolymerization with four schemes previously used in Chapter 3. Monomer compositions, sequence distributions and reactivity ratios determined from

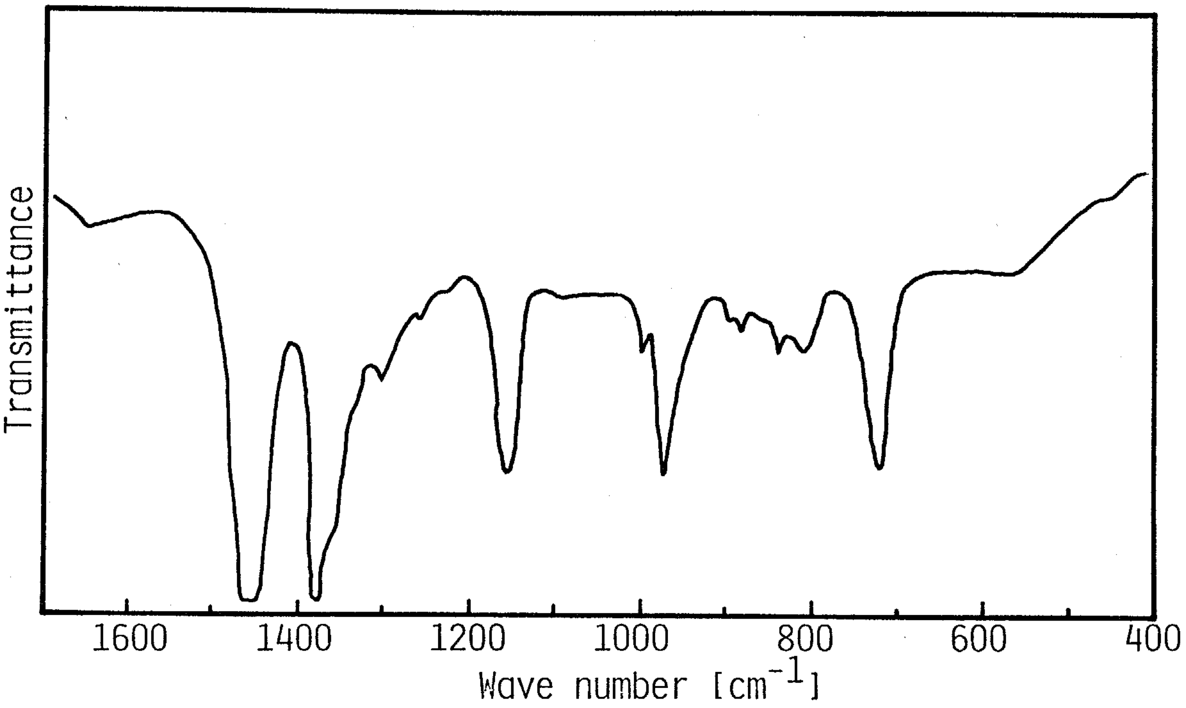


Figure 4-9 IR spectrum of Sample 3.

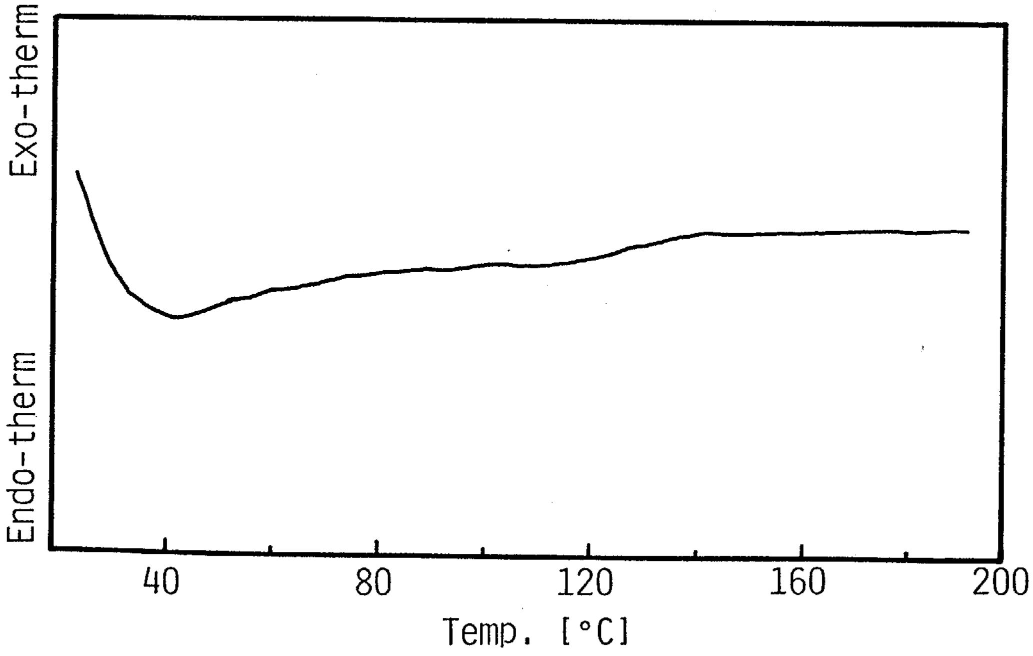


Figure 4-10 DSC curve of Sample 3.

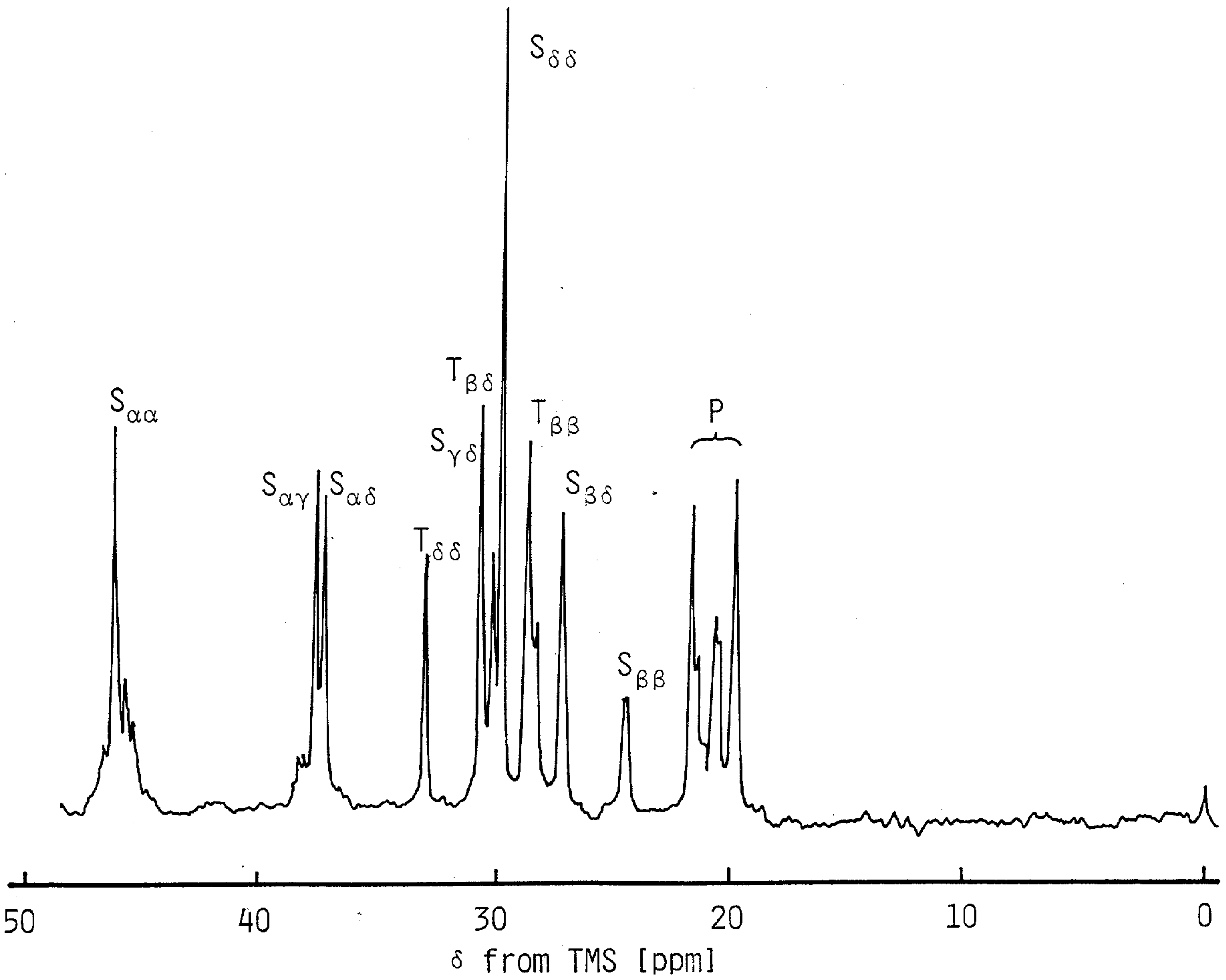


Figure 4-11 ^{13}C NMR spectrum of Sample 3.

Table 4-6 Monomer composition, sequence distributuin and reactivity ratio of Sample 3

P	0.56
E	0.44
PP	0.32
PE	0.48
EE	0.20
PPP	0.26
PPE	0.21
EPE	0.11
PEP	0.10
EEP	0.14
EEE	0.18
r_E	5.3
r_P	0.21
$r_E \cdot r_P$	1.1

the ^{13}C NMR spectrum are shown in Table 4-6. The product of the monomer reactivity ratios, $r_E r_P$, was obtained approximately to be 1, which means that random copolymerization of ethylene and propylene proceeds over this catalyst.

In conclusion, it was found that random copolymer of ethylene and propylene can be synthesyzed even by using titanium-based catalysts.

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Summary and Conclusion

In Chapter 1, to clarify the role of internal and external donors, several kinds of $MgCl_2$-supported $TiCl_4$ catalysts were prepared using both monoesters and diesters as an internal donor and were carried out propylene polymerization over these catalysts. The kinetic behavior of polymerization and the isotacticity of produced polymers were found strongly to depend on the catalyst systems. The catalysts containing diesters deactivated according to first order, while the deactivation of the catalysts free from internal donors or containing monoesters approximately obeyed the second order kinetics. On the other hand, the tacticity of produced polymers decreased in following order; diester > monoester > ester-free. When monoester was used, the isotacticity decreased significantly during polymerization time, which mainly attributed to the extraction of monoester by $Al(C_2H_5)_3$. Such a phenomenon was hardly observed with the use of diester.

The effect of phenyltriethoxysilane(PTES) on propylene polymerization was then investigated. Generally speaking, addition of PTES caused an increase in the isospecificity of all catalyst systems. However, the effect of PTES strongly depended on the catalyst systems ; in the case of diester system, addition of PTES caused a marked decrease only in the atactic polymer yield, while in the case of monoester system, it caused a significant decrease also in the isotactic polymer yield. The polymers obtained in the diester system containing different amounts of PTES were fractionated into three parts by extraction with boiling heptane and octane. From the precise analyses of those polymers, it was found that isotactic polypropylene is actually composed of two kinds of polymers which differ in structure as well as molecular weight. One, which is soluble in octane but insoluble heptane, has lower molecular weight and contains appreciable amounts of syndiotactic stereoblocks. Addition of PTES did not change the molecular weights of these isotactic polymers, but it drastically caused to change the amount of each fraction : the latter type of polymer was selectively obtained in the presence of PTES. On the basis of these results, the following assumptions were proposed. There exist three kinds of active Ti species which differ in the stereospecificity : active Ti having one chlorine vacancy(Site-I), two chlorine vacancies(Site-II) and one chlorine vacancy with a mobile ligand(Site-I'). Site-I, II and I' produce highly isotactic atactic and lower isotactic polymers, respectively. PTES kills the aspecific Site-II, and converts the lower isospecific Site-I' to the higher isospecific Site-I by prohibiting the ligand migration.

In Chapter 2, H_2/D_2 exchange reactions were carried out with the $TiCl_4/MgCl_2-Al(C_2H_5)_3$ catalyst system in the presence of monoester. A good correlation was found between the activity of exchange reactions and the amount of atactic polymer produced. The effect of hydrogen on the molecular weights were investigated for isotactic as well as atactic polypropylene. In highly isospecific catalyst systems like $TiCl_4$/monoester/$MgCl_2$-$Al(C_2H_5)_3$/monoester and $TiCl_3$-$Al(C_2H_5)_2I$, the molecular weight of the isotactic polymer decreased almost proportionally to the hydrogen pressure, whereas that of atactic polymer decreased proportionally to the square root of the hydrogen pressure. These results could be understood in terms of the above assumptions ; the highly isospecific Ti species having only one chlorine vacancy(Site-I) cannot adsorb hydrogen dissociatively, and hence chain transfer reactions proceed by molecular hydrogens, while the aspecific species having two chlorine vacancies(Site-II) can adsorb hydrogen dissociatively and hydrogen atoms participate in the chain transfer reactions. The fact that the molecular weight of the isotactic polymer obtained with lower isospecific catalyst like $TiCl_4$/$MgCl_2$-$Al(C_2H_5)_3$ decreased proportionally to the square root of hydrogen pressure may be understood in terms of the spillover phenomenon.

In Chapter 3, copolymerization of ethylene and propylene was carried out by using the $TiCl_4$/$MgCl_2$, $TiCl_4$/monoester/$MgCl_4$ and $TiCl_4$/diester/$MgCl_2$ catalysts in the presence of electron donor compounds. In all the catalyst systems, addition of electron donors caused a significant decrease in the content of propylene units in the copolymer. From the comparison of the observed sequence distributions with the calculated ones, it was suggested that there exist different kinds of active species also for the copolymerization.

Copolymerization of ethylene and propylene was then conducted with the diester system by adding different amounts of PTES, and the copolymer obtained were separated into three fractions by extracting with boiling ether and boiling heptane. The content of propylene in the copolymer decreased in the following order ; ether soluble > ether insoluble-heptane soluble > heptane insoluble. With an increase in the concentration of PTES, the yields of ether soluble and ether insoluble-heptane soluble fractions decreased drastically and slightly, respectively. Whereas, that of heptane insoluble fraction remained almost unchanged. Therefore, the ether soluble copolymer, which contains a larger amount of propylene units, produced with the aspecific site(Site-II). Although a marked increase was not observed in heptane insoluble fraction, heptane insoluble and soluble fractions might correlate with Site-I and Site-I', respectively.

In Chapter 4, a stable supported catalyst was prepared by supporting $Ti(OC_4H_9)_4$ on $MgCl_2$ followed by treatment with chlorine containing alkylaluminium, and polymerization of propylene copolymerization of ethylene and propylene was conducted over the catalyst. This catalyst was too stable to deactivate during polymerization, which may be resulted from the stability of Ti(III) species. Although the original catalyst showed very low isospecificity, it was improved as high as over 90 % by using ethyl benzoate as internal and external donor. The copolymerization of ethylene and propylene over this catalyst, on the other hand, gave a random copolymer as expected.

As described above, the $MgCl_2$-supported $TiCl_4$ catalysts usually contain at least three kinds of active Ti(III) species which differ in stereospecificity. The main factor controlling the stereospecificity may be the number of vacant sites surrounding the Ti(III) species, in other words, the number of ligands which are coordinated to the Ti(III) species. The major effect of Lewis bases is, therefore, to block the unnecessary vacant sites. If the blocking is not complete, the residual aspecific Ti(III) species can be chemically killed by using special Lewis bases as external donor. Based on these conclusions, one may suppose it very simple to design ideal isospecific catalysts. Because of the coexistenece of excess amount of Lewis acidic $Al(C_2H_5)_3$, however, these Lewis bases chemically interact not only with the Ti(III) species but $Al(C_2H_5)_3$ as well, which makes the catalyst system very complicated. More recently, simplified catalysts which contain neither $Al(C_2H_5)_3$ nor Lewis bases have been developed in our laboratory. A detailed study of propylene polymerization using these catalysts will undoubtedly contribute to our complete understanding of the effect of Lewis bases. So far, however, the present conclusions seem to agree with the results obtained with these new catalysts.

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