

입체규칙도가 우수한 고허성 이에스테르 촉매에 의한 프로필렌중합에서 외부 전자공여체의 영향

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(1991년 2월 1일 접수)

The Effect of External Electron Donors on the Polymerization of Propylene over a Highly Isospecific and Active Diester Catalyst

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(Received February 1, 1991)

요약 : 이에톡시마그네슘을 사부톡시티탄, 무수프탈산 및 염화티탄과 반응시켜 내부전자공여체로서 이에스테르가 포함된 새로운 염화마그네슘 담지 염화티탄촉매를 제조하였다. 이 촉매를 삼에틸알루미늄을 공촉매로하여 프로필렌중합에 이용할 경우 활성이 대단히 높고 입체규칙도가 뛰어났다. 외부전자공여체가 촉매의 활성 및 입체규칙도에 미치는 영향을 조사하기 위하여 삼에톡시페닐실란(PTES), 에틸벤조이트(EB), 테트라히드로푸란(THF)과 같은 외부전자공여체(ED)를 촉매에 첨가하여 프로필렌 중합을 수행하였다. 또한 이들 전자공여체를 첨가하지 않았을 때와 첨가하였을 때의 활성점의 수를 일산화탄소 흡착법을 이용하여 측정하였다. 실험결과 PTES를 외부전자공여체로 사용하였을 때 입체규칙도가 우수할 뿐만 아니라 높은 활성도를 보였다. PTES를 공촉매용액에 첨가함으로써 입체적으로 불규칙한 활성점들이 입체규칙 활성점으로 전환되었으며 중합활성점들이 안정화되었다.

Abstract : A new $MgCl_2$ -supported $TiCl_4$ catalyst with a diester as an internal donor was prepared from the reactions of $Mg(OEt)_2$ with $Ti(OBu)_4$, phthalic anhydride, and $TiCl_4$. The catalyst combined with $AlEt_3$ showed very high activity and isospecificity for the propylene polymerizations. In order to investigate the effects of external donor (ED) on the productivity and the isospecificity of the catalyst, the polymerization of propylene was carried out by modifying this catalyst with various external donors such as phenyltriethoxy silane (PTES), ethyl benzoate(EB), and tetrahydrofuran (THF). The number of active sites was also determined by the CO inhibition method in the absence and presence of external donors. The results showed that PTES is the best external donor in that it produced highly isotactic polypropylene, in association with high activity of the catalyst. The addition of PTES to the coatalyst solution not only transformed atactic sites to isotactic ones, but stabilized polymerization centers so that the active sites deactivated less sharply.

INTRODUCTION

The classical Ziegler-Natta catalyst, γ -TiCl₃ 0.33 AlCl₃/DEAC, had been used during the past quarter century to manufacture polypropylene. Not until the discovery of the high-activity and high isospecificity MgCl₂ supported titanium catalyst systems in 1975 by the joint research of Mitsui Petrochemical Ind. and Montedison,^{1,2} can it be said that a major breakthrough has been achieved in the technology of commercial polypropylene production. These new generation catalyst systems are characterized by the joint use of MgCl₂ as an activity booster and Lewis bases as stereospecific improvers.^{1,2} Even though excellent catalyst performance has been already achieved using existing or newly developed commercial plants, many of the functions of the catalyst components still remain controversial.

The isospecificity of MgCl₂ supported TiCl₄ catalyst systems for propylene polymerization has been markedly improved by using Lewis bases as internal and external donors. The electron donor compounds would include such compounds as alkyl esters of aliphatic and aromatic carboxylic acids, aliphatic esters, cyclic ethers and aliphatic ketones. Among these electron donor compounds aromatic esters are the principal modifiers of the modern high activity supported catalysts.³ However, when a Lewis base was added to such catalyst system, a large increase in isospecificity resulted albeit accompanied by a detrimental decrease in productivity. The optimum performance of a catalyst can be achieved only with the appropriate Lewis base compound incorporated by particular operational procedures.⁴ The most widely used operational procedure to improve isospecificity with a minimum effect on the productivity is to incorporate the Lewis base by two steps: internal donor is incorporated in the catalyst and external donor added with a cocatalyst at the start of polymerization.

Some recent patents have shown that the combination of diesters as internal donor with alkoxy-

silanes as external donor improves catalyst stability and isospecificity much more effectively than the aromatic esters used as external donor previously.⁵ The actual mechanism by which these compounds function is not known with certainty but their interaction with the trialkyl aluminum cocatalyst is acknowledged to be important.⁶

The main purpose of this work was to study how the type of external donors influences the rate of propylene polymerization. A second purpose was to understand better the effects of external donors on the isospecific control in active centers of the catalyst.

EXPERIMENTAL

Materials

Polymerization grade of propylene (from Korea Petrochem. Co.) and extra pure grade of CO (from Matheson Co.) were used after passing them through columns of Fisher RIDOX catalyst and molecular sieve 5A/13X. Extra pure heptane (from Tedia Co., USA) was dried over sodium and fractionally distilled before use. Chlorobenzene (BzCl, from Kanto Chemical Co., Japan) and THF (from Aldrich) were purified according to previous method.^{3(e)} Phthalic anhydride (from Aldrich), PTES (from Aldrich), magnesium diethoxide (from Strem Co.), TiCl₄ (from Korea Petrochem. Co.), Ti(OBu)₄ (from Aldrich) and AlEt₃ (TEA, from Aldrich) were used without further purification.

Preparation of catalyst

Magnesium diethoxide (50 mmol) was stirred at room temperature with 25 mmol of Ti(OBu)₄ and 13 mmol of phthalic anhydride. To this mixture 75 ml of BzCl as TiCl₄ (75ml) was added dropwise over the course of 20 min. The mixture was brought to 110°C for 180 min then filtered hot. The resulting solid was washed at room temperature with three 150 ml portions of heptane, stirred with 100 ml of TiCl₄ at 130°C for an hour, washed at room temperature with three 150 ml portions of heptane. The reddish solid was again stirred with 100 ml of TiCl₄ at 130°C for 30 min then filtered

hot. The pink colored solid was washed with seven 150 ml portion of heptane to give catalyst containing 2.8% of Ti.

Polymerization

The polymerization was carried out in a 250 ml round bottom flask equipped with a stirrer. To ensure reproducibility of the polymerizations a detailed schedule was developed: all polymerizations were done exactly in the same way, with external donor selection and donor amount as the only variations.

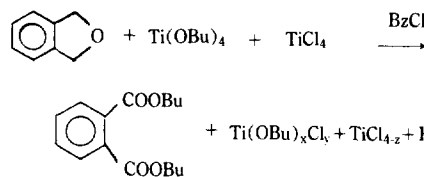
Measured amounts of TEA and an external donor were added to the reactor containing 100 ml of heptane. After raising the temperature of the mixture to 50°C, propylene was saturated to heptane. When no more absorption of propylene to heptane, a prescribed amount of catalyst slurry was added into the mixture and then the polymerization was started. The polymerization rate was measured according to the previous method.⁷ When required, prescribed amounts of carbon monoxide were added during polymerization by means of gas-tight syringe and a variation in the overall rate of polymerization was measured simultaneously in order to determine the number of active centers.^{7,8}

Characterization of Catalyst and Polymer

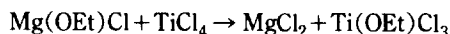
IR spectra of reactant and catalyst were recorded on a MB-100 spectrometer in a nujol capillary apparatus with KBr plates. Specific surface area of the samples was measured by a conventional BET method. The isotactic index (II) of polymer was measured by extracting the polymer with boiling heptane in a Soxhlet-type apparatus. Isotacticity (II) was defined as II in % = 100 weight of insoluble fraction/whole polymer weight.

RESULTS AND DISCUSSION

The rationale in the preparation of the present catalyst to generate dibutyl phthalate, diester internal donor, in situ from the following reaction:

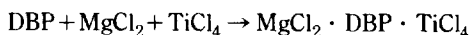


Stoichiometries are not included in the above and following equations because they are variable and unknown. The magnesium diethoxide in the catalyst medium is chlorinated by the repeated treatments with excess TiCl_4 .^{3(f),9}



Alkoxy titanium chloride generated from above reactions is negligible quantity in comparison with TiCl_4 . Nevertheless, it may be detrimental effect on the productivity of the catalyst, if it anchored onto the catalyst matrix.¹⁰ However, alkoxy titanium chloride is volatile enough to be removed by hot filtering and washing during catalyst preparation steps.¹¹

DBP generated in situ is coordinated to MgCl_2 and TiCl_4 as follows.



The formation of this complex can be demonstrated by IR spectra. IR spectra of $\text{Mg}(\text{OEt})_2$, DBP, and the resultant catalyst is recorded in Fig. 1. The C=O band of DBP at 1735 cm^{-1} appears at 1690 cm^{-1} for $\text{MgCl}_2 \cdot \text{DBP} \cdot \text{TiCl}_4$ complex. This shift pattern of the C=O band is agreed with the previous results.^{3(f),6(a),9} In addition two characteristic bands of $\text{Mg}(\text{OEt})_2$ at 1048 and 1069 cm^{-1} which have been assigned to symmetric (C-O) Mg and asymmetric (C-O)Mg stretching vibrations,¹⁴ respectively, are completely disappeared. The result shows that the chlorination of $\text{Mg}(\text{OEt})_2$ is complete.

Chemical change of $\text{Mg}(\text{OEt})_2$ was also accompanied by the structural change. The surface area of the catalyst, 252 m^2/g was 10-fold greater than

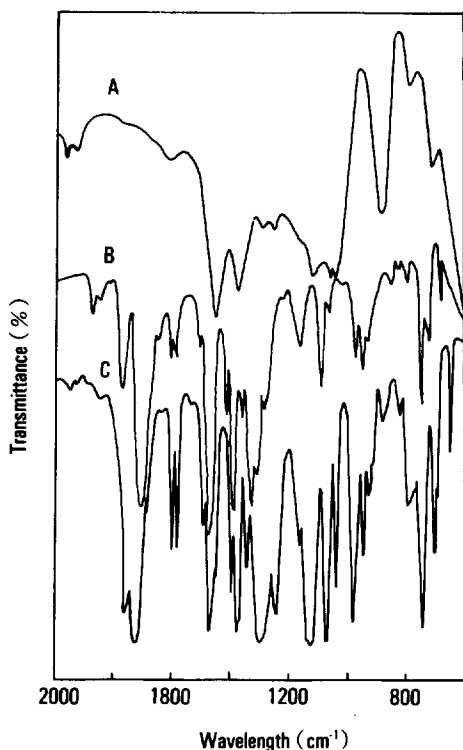


Fig. 1. FTIR spectra : (a) $Mg(OEt)_2$, (b) $MgCl_2/DBP/TiCl_4$ catalyst, and (c) diisobutyl phthalate.

that of $Mg(OEt)_2$, $25\text{ m}^2/\text{g}$. The sharp increase in the surface area can be an indirect indication of the formation of bimetallic high surface area catalyst and is deeply related to the superactivity of the catalyst. The supports with $133\text{ m}^2/\text{g}$ of surface area and with 3.3% of loaded Ti are known to be enough to achieve a monomolecular layer distribution of $TiCl_4$.¹² The 2.8% of Ti content and $252\text{ m}^2/\text{g}$ of surface area of the present catalyst are sufficient to form a monomolecular layer distribution of $TiCl_4$ so that the active sites can be uniformly distributed.

In order to estimate the performance of the catalyst and to get a better understanding of the activation procedure by external donors polymerization of propylene was conducted with this catalyst in the absence and presence of three different electron donors, PTES, EB, and THF. Fig. 2 illustrates the kinetic curves of polymerization obtained

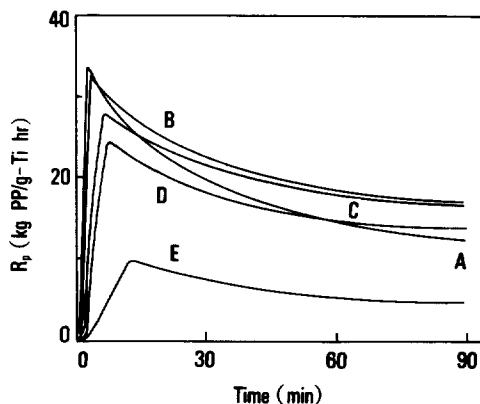
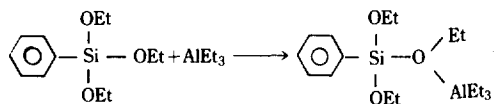


Fig. 2. Rate profiles of propylene polymerization at $[Ti]=4.24 \times 10^{-4}\text{ g}$, $[propylene]=0.43\text{ mol/l}$, $[AlEt_3]=8.9\text{ mmol/l}$, and various $[PTES]$ of : (A) $[PTES]/[TEA]=0$, (B) 0.05, (C) 0.1, (D) 0.2, (E) 0.8.

in the absence and presence of PTES. The catalyst shows very high activity, $18\text{ kg PP/g-Ti hr atm}$, in the absence of external donor. Even in the presence of PTES, $PTES/AlEt_3=0.05\sim 0.2$ mole ratio, the kinetic profiles do not change so much and the rate-time profiles obeyed first-order deactivation. Even though the maximum rates slightly decrease as the amount of PTES increases, the average rate of polymerization for 90 min are increased to 23, 21, and $19\text{ kg PP/g-Ti hr atm}$ in case of $PTES/AlEt_3=0.05, 0.1$, and 0.2 , respectively. This demonstrates that the PTES as an external donor stabilizes the active sites. This kind of kinetic profile is in line with that obtained by $MgCl_2/DBP/TiCl_4-AlEt_3$ PTES system in which DBP was anchored into the $MgCl_2$ matrix directly by ball milling.¹⁰ However, catalyst activity was under $10\text{ kg PP/g-Ti hr atm}$ for the latter catalyst system. Addition of excess amount of PTES, $PTES/AlEt_3=0.8$ severely decreases the activity of the catalyst, remaining the pattern of the kinetic profile. It is also interesting to observe the time to reach maximum rate. As the amount of PTES increases, the time to reach maximum rate is delayed. It is well known that the formation of Ti active sites is through the adsorption cocatalyst.^{7,13} The bulky solution complex¹⁴ formed from the following reac-

tion may be difficult to diffuse and adsorb onto the Ti sites anchored on $MgCl_2$ matrix.



As the amount of PTES in polymerization medium increases, the amount of above bulky complex increases, so that the formation of initial active sites is delayed.

Similar kinetic profiles were recorded when EB was used as an external donor. As shown in Fig. 3 the addition of small amount of EB, $[EB]/[AlEt_3]=0.05-0.1$, stabilizes the active sites so that the polymerization rates can be deactivated less severely. However, as in the case of the polymerization by using PTES as an external donor, excess amount of EB, $[EB]/[AlEt_3]=0.5$, reduces the polymerization rate by about 6-fold. In addition the time to reach maximum rates is delayed as the amount of EB increases in the polymerization medium. The formation of bulky solution complex between EB and $AlEt_3$ has already been studied by Spitz et al.¹⁵

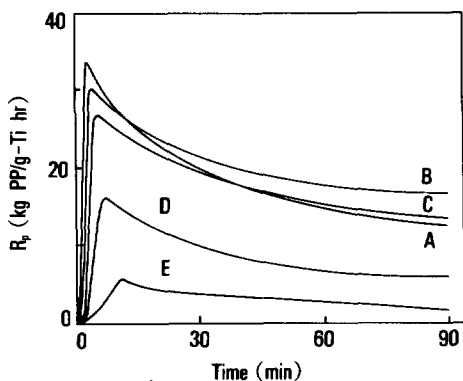
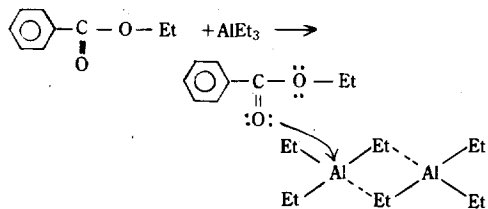


Fig. 3. Rate profiles of propylene polymerization at $[Ti]=4.24 \times 10^{-4}$ g, $[propylene]=0.43$ mol/l, $[AlEt_3]=8.9$ mmol/l, and various $[EB]$ of : (A) $[EB]/[TEA]=0$, (B) 0.05, (C) 0.1, (D) 0.2, (E) 0.5.



THF, a good solvent of metal chlorides and strong electron donor, has also been applied as an external electron donor for the propylene polymerization. Fig. 4 shows the rate-time profiles when using THF. While they obey first-order deactivation, the addition of even small amount of THF brings about a significant decrease in activity and in the end to a negligible degree at $[THF]/[AlEt_3]=0.5$. The sharp decrease in activity and the slow-down of the time to reach maximum rate by the addition of THF might be ascribed to the formation of strong complex between THF and $AlEt_3$.¹⁶

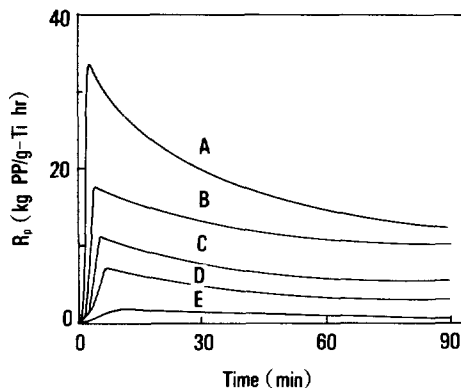
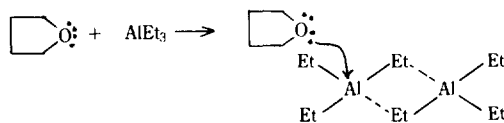


Fig. 4. Rate profiles of propylene polymerization at $[Ti]=4.24 \times 10^{-4}$ g, $[propylene]=0.43$ mol/l, $[AlEt_3]=8.9$ mmol/l, and various $[THF]$ of : (A) $[THF]/[TEA]=0$, (B) 0.05, (C) 0.1, (D) 0.2 ; (E) 0.5.

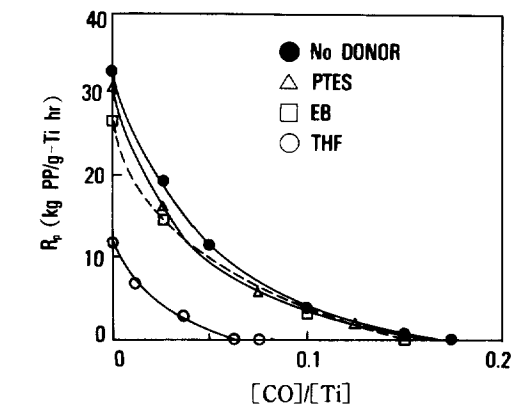
Table 1. Effect of Different External Donors on the Catalyst Productivity and Isospecificity

External Donor	[ED]	Activity (kg PP/g-Ti hr atm)	Isotactic Index(%)
	[AlEt ₃]		
None	0.0	18	73
PTES	0.05	23	84
	0.1	21	97
	0.2	19	96
	0.8	6	98
EB	0.05	21	78
	0.1	19	82
	0.2	9	92
	0.5	3	94
THF	0.05	13	75
	0.1	8	74
	0.2	4	74
	0.5	1	76

In order to throw light on the effectiveness of control of isospecificity, boiling heptane-insoluble fraction (II) of the polymers has been investigated. Table 1 shows the variation of average polymerization rate as well as II according to the change in the amount of various external donors. The highest isospecificity is obtained by PTES especially on the condition of $[\text{PTES}]/[\text{AlEt}_3]=0.8$, while the productivity is significantly lowered. The addition of controlled amount of PTES, $[\text{PTES}]/[\text{AlEt}_3]=0.1\sim 0.2$, not only improves the isospecificity to an acceptable degree, but increases the average polymerization rate. But in the case of EB over 90% of II can be obtained at the considerable sacrifice of the productivity. Other than above two cases no acceptable II is obtained when using THF as an external donor regardless of the amount of addition. Only the decrease of productivity can be characterized by the addition THF.

The effect of the addition of external donor to the cocatalyst solution on the productivity and isospecificity has been studied by many research groups.^{3,5,6,9~15} The proposals can be summarized as follows:¹⁷

(1) Selective poisoning of atactic centers :


Fig. 5. Relation between the polymerization rate and the amount of CO added. Polymerization conditions : $[\text{Ti}]=4.24 \times 10^{-4}$ g, $[\text{propylene}]=0.43$ mol/l, $[\text{AlEt}_3]=8.9$ mmol/l, and $[\text{ED}]/[\text{AlEt}_3]=0.1$.

(2) Transformation of atactic centers to isotactic ones :

(3) Increase in the propagation rate constant of isotactic centers :

(4) Stabilization of the active center structure and chirality.

In order to get a better understanding on this controversy the number of active sites was measured by CO inhibition method,^{3(e),7,8} in the absence and presence of external donors(ED), $[\text{ED}]/[\text{AlEt}_3]=0.1$. The results are shown in Fig. 5 and Table 2 with reference data. The prescribed amounts of CO were injected after the polymerization rates reached maximum. The rate constant for chain propagation, k_p , was calculated from the relation that the overall polymerization rate, R_p , is given by the simplistic equation, $R_p=k_p C^*[\text{M}]$, with the observed values of C^* .

The results show that the number of active centers of the catalyst when using PTES or EB as an external donor is higher than that of $\text{TiCl}_3/\text{AlEt}_3$ and $\text{TiCl}_4/\text{EB}/\text{MgCl}_2/\text{AlEt}_3$ by one order of magnitude, and that the values of k_p are of the same order with that of MgCl_2 supported catalyst and $\text{Mg}(\text{OEt})_2/\text{BzCOCl}/\text{TiCl}_4\text{-AlEt}_3$, and higher than that of TiCl_3 by one order of magnitude. It must be noted that the isospecificity increases from 73% to 97

Table 2. The Number of Active Sites (C^*) and the Average Propagation Rate Constant (k_p) in the Propylene Polymerization with Different Catalyst Systems

Catalyst System	External Donor	$C^* \times 10^2$ (mol/mol Ti)	k_p (1/mol s)	Ref.
MgCl ₂ /DBP/ TiCl ₄	—	17	451	
MgCl ₂ /DBP/ TiCl ₄	PTES	16	451	
MgCl ₂ /DBP/ TiCl ₄	EB	14	449	
MgCl ₂ /DBP/ TiCl ₄	THF	7	400	
TiCl ₄ /EB/ MgCl ₂	—	1.6	320	13
TiCl ₃ /AlEt ₃	—	1.5	31	13
TiCl ₃ /AlEt ₂ Cl	—	0.8	32	13
Mg(OEt) ₂ / BzCOCl/TiCl ₄	—	26	332	3(e)

%, remaining C^* and k_p unchanged within the experimental error, when PTES is added as an external donor. It indicates that atactic centers are transformed to isotactic ones by the adsorption of bulky AlEt₃-PTES complex onto Ti sites. In addition unexpected increase of average polymerization rate for 90 min from 18 to 23 kg PP/g-Ti hr atm suggests that the polymerization centers formed by the adsorption of AlEt₃-PTES complex should be more stable than those formed by the adsorption of AlEt₃ alone due to the unknown structure and chirality. However, the addition of excess amount of PTES, [PTES]/[AlEt₃]=0.8, not only transforms the atactic sites, but deactivates the isotactic sites severely. This fact can be distinguished from the change in productivity, from 18 to 6 kg PP/g-Ti hr atm, and isospecificity, from 73 to 98%.

The mechanism of action of EB as an external donor was somewhat different from that of PTES. The less sharp increase in isotacticity, from 73 to 82%, are achieved at the sacrifice of C^* , from 0.17 to 0.13 mol/mol Ti. It demonstrates that the improvement in the isotacticity is accompanied by the selective poisoning of atactic sites. This explana-

tion may be emphasized in the case of [EB]/[AlEt₃]=0.2. Even if relatively high degree of II (92%) is obtained, the productivity is decreased to 9 kg PP/g-Ti hr atm.

Other than PTES or EB, THF as an external donor showed completely different effect on the isospecificity and productivity of catalyst. The addition of THF, [THF]/[AlEt₃]=0.1, to the cocatalyst solution decreases the C^* to 0.07 mol/mol Ti, remaining II unchanged within experimental error (Table 1 and 2). These experimental results show that THF is poor external donor in that it poisons any active sites without differentiation of isospecific sites from atactic sites.

The external donors studied above could roughly be divided into three groups on the basis of performance. The best donor, PTES, produced highly isospecific PP, in association with high activity of the catalyst. The second group, EB, produced high isospecificity but the activity was severely lowered. The third group, THF, was characterized by low productivity and poor isotacticity.

CONCLUSION

In view of what has been studied with a new catalyst, following conclusions are drawn :

1. In spite of the complicated operational procedure starting with Mg(OEt)₂, Ti(OBu)₄, phthalic anhydride, and TiCl₄, highly active and isospecific catalyst which can be simplified to MgCl₂ · DBP · TiCl₄ complex was obtained.

2. Comparison of various external Lewis bases demonstrated that PTES exhibits much better performance as modifiers compared to EB and THF when diester is incorporated in the catalyst. This behavior could be explained by the ability of PTES (or the products of its reaction with AlEt₃) to transform atactic sites to isospecific sites and to stabilize the existing or the newly formed active sites. On the other hand the improvement of II using EB as an external donor was achieved by the selective poisoning of atactic sites.

3. The addition of excess amount of external do-

nors to the cocatalyst solution deactivated the isospecific sites as well as the atactic sites, so that the productivity of catalyst was severely lowered.

Acknowledgements : This research was funded by Ministry of Science and Technology (NO 2410, NO 3710 and NO 4900, 1986~1989). The author would like to acknowledge Honam Oil Refinery Co. for providing chemicals and helping analysis of catalyst.

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