

STUDIES ON THE EFFECTS OF EXTERNAL ELECTRON DONOR IN PROPYLENE POLYMERIZATION

Sang-Yun Lim, Suk-Jin Choung[†] and Kyung-Ho Song*

Department of Chemical Engineering, College of Engineering, Kyung Hee University, Suwon 449-701, Korea

*Ho Nam Oil Co., Research Center, Seoul 150-010, Korea

(Received 13 February 1995 • accepted 22 August 1995)

Abstract—In order to investigate effects of an electron donor in propylene polymerization (in gas and slurry phase reactions each) by using a 3rd generation Ziegler-Natta catalyst, the catalytic activities were measured before and after the addition of an electron donor. And physical properties of produced polymer were estimated. Polymerization rate was decreased with increasing EB/Al mole ratio because atactic sites on catalyst were selectively poisoned by the addition of the electron donor, and consequently total number of active sites were diminished. It was found that the overall reaction order was the 2nd order, and a reaction rate form was suggested by using a CO inhibition technique. Catalyst deactivation was due to the formation of dense isotactic polypropylene on the catalyst at the beginning of polymerization so that monomers had the difficulties in diffusion into catalyst surface through the dense polymer. From the measurements of polymer physical properties, probability of active site transitions from atactic→low isotactic→high isotactic sites could be considered, which may be due to the formation of a complex between co-catalyst and electron donor.

Key words: Ziegler-Natta Catalyst, External Electron Donor, Gas Phase Polymerization, CO Inhibition Method, Isotactic Site, Co-catalyst

INTRODUCTION

Remarkable research and development in olefin polymerization catalyst have been progressed since the first olefin polymerization catalyst was developed by Ziegler and Natta in early 1950's. Since then polymerization of propylene in gas phase was successful at BASF company in Germany at the beginning of 1960's. In 1980's, most of the commercial propylene polymerization process employs the gas phase process [Lee, 1987; Choung, 1994; Koura, 1993].

Such gas phase polymerization method has a benefit of simplicity in process design and operation compared with other method (slurry or bulk phase process), and has other advantages such as the production of wide range of polymer grades and economical benefits by reducing steps for APP (Atactic Polypropylene) and catalyst residue removal [Kang, 1988]. In order to keep pace with the world wide trends, all the propylene polymerization process of newly established or expanded by Korean industries employ the gas phase process [Kim, 1991].

Although a lot of development in propylene polymerization process were made, there are still some problems to solve in this area, such as understanding of reaction mechanisms in polymer chain growth, thermal stability of reactor, structure of catalyst active site, reaction behavior in gas phase reactors, effects of reaction parameters on reaction rate, yield and polymer physical properties and so on. From these parameters, the external electron donor addition effects seem to be the most effective in changing polypropylene physical properties, though no clear results were shown when effects of EB/Al mole ratio change on reaction rate, yield and polymer physical properties were studied. Keii et al. [1983] reported that external electron donor poisons the atactic

sites selectively resulting an increase of the relative isotactic index, and polymer molecular weight increase because co-catalyst amount is decreased by formation of complexes with electron donor. Kashiwa [1983], however, reported that there is no atactic site poisoning, instead site conversion to isotactic site occurs so that polymerization rate is increased on the isotactic site. Pino et al. [1983] also reported that low isotactic site is converted into high isotactic site regardless of atactic site, and thus polymerization rate is decreased. On the other hand, Soga and Park [1990] insisted that atactic site is converted to isotactic site without affecting reaction rate. And Härkönen et al. [1990] reported that electron donor poison the atactic sites with formation of new isotactic sites. Besides these results, various tendencies of the role of electron donor were reported [Spitz, 1983; Langer, 1983; Miyatake, 1990; Okano, 1990; Kakugo, 1988; Sacchi, 1990; Sugano, 1990].

As discussed above, there was no consistency in the external electron donor addition effects on catalyst in all the results obtained from slurry phase polymerization. In addition, no experimental results were obtained from gas phase polymerization.

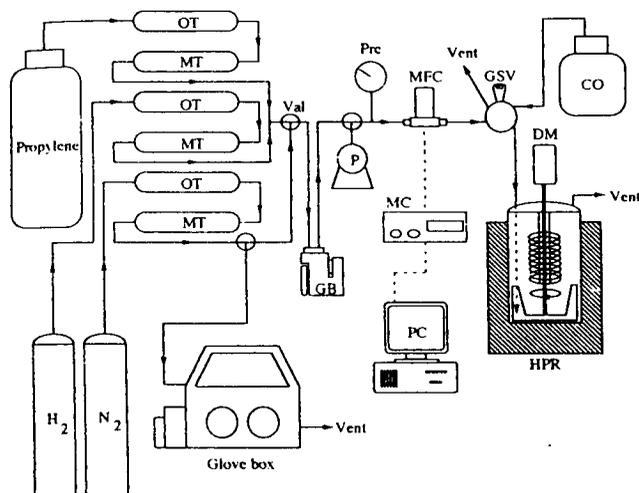
It was thought that there might be some differences in the effects of electron donor addition on catalyst with the polymerization types.

Therefore, in this study it was concentrated on the electron donor addition effects on catalyst surfaces in both reaction types, say, slurry and gas phase polymerizations each. The objectives of this study were set as follows: First, both of gas and slurry phase polymerizations were carried out to investigate into the differences in catalytic activity behavior depending upon the change in reaction types. Second, in order to suggest the reaction rate form of propylene polymerization with the addition of electron donor at any reaction time, CO inhibition method was carried

[†]To whom all correspondence should be addressed.

Table 1. List of catalyst and reagents used in this study

Materials	Remarks
3rd Generation Ziegler-Natta cat.	-
Triethylaluminum (TEAL)	Co-catalyst
Paraethoxyethylbenzoate (PEEB)	Electron donor
Propylene	Monomer (polymer grade)
CO	Active site poisoning material (He balance)
n-Hexane	Catalyst washing, solvent for slurry reaction
Xylene	Polymer extraction
Methanol	Polymerization quenching agent
Sodium	Solvent purification
Benzophenone	Solvent purification

**Fig. 1. Schematic diagram of propylene polymerization system.**

OT : Oxygen trap	MC : MFC controller
MT : Moisture trap	PC : Personal computer
Val : 3-way valve	GSV : 6-port gas sampling valve
GB : Gas booster	DM : DC motor driver
P : Vacuum pump	HSP : High pressure syringe pump
Pre : Pressure gauge	
MFC : Mass flow controller	HPR : High pressure reactor

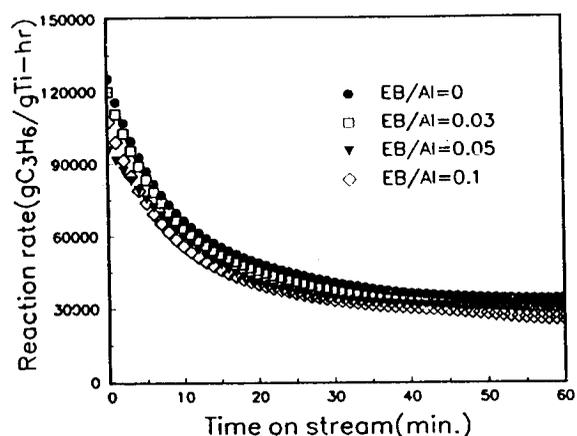
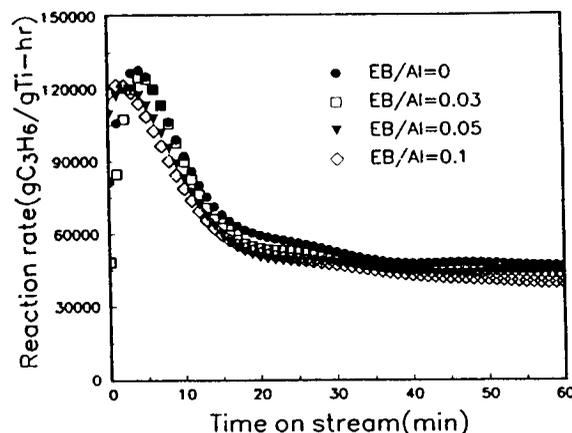
out to determine the active site concentration and propagation rate constant. Third, a monomer diffusion model was examined in order to explain the reason why reaction rate decreases with increasing time, and the effects of the monomer diffusion resistance during polymerization. Forth, various polymer characterization techniques (xylene extraction, DSC, GPC, FTIR, UV) were employed, and the effects of external electron donor were investigated systematically. From these studies, the effects of external electron donor addition explained systematically.

EXPERIMENTAL

1. Catalyst and Reagents

Catalyst used was the 3rd generation Ziegler-Natta catalyst, and triethylaluminum (TEAL) and paraethoxyethylbenzoate (PEEB) were used as a co-catalyst and electron donor. Other materials are summarized in Table 1.

2. Activity Measurements

**(a) Gas phase polymerization****(b) Slurry phase polymerization****Fig. 2. Comparison of kinetic curves with external electron donor addition.**

Temp. = 40°C, Press. = 100 psi, Al/Ti mole ratio = 100, Electron donor = PEEB

Fig. 1 shows the polymerization system used in this experiment. In order to estimate the reactivity of each condition, a high pressure semi-batch type reactor which has volume of 600 ml was used. All used gases were purified by using molecular sieve 5A and Ridox (Fischer Co.) traps which remove catalyst poisoning materials such as H₂O and O₂.

Reaction rate was measured by mass flow controller (MFC) connected to PC with A/D converter, and expressed as gC₃H₆/gTi-hr. In order to maintain the reaction pressure (100 psi), gas booster was used. All materials used were treated in a glove box, and reaction conditions in this experiment for gas phase and slurry phase were as follows: reaction temperature = 40°C, reaction pressure = 100 psi, Al/Ti mole ratio = 100 and EB/Al mole ratio = 0-0.1 (divided by 4 steps). And 300 ml of purified n-hexane was pre-filled in reactor for slurry reaction.

3. Measurements of Polymer Physical Properties

A melting point of obtained polymers was measured by using DSC (Perkin Elmer DSC7), and GPC (Waters 150C) was used for determining molecular weight and distributions of polymers. In order to investigate the possibility of complex formation between TEAL and PEEB, FTIR (Perkin Elmer system 2000) and UV-VIS (Hitachi) were used. The isotactic index of polymer was

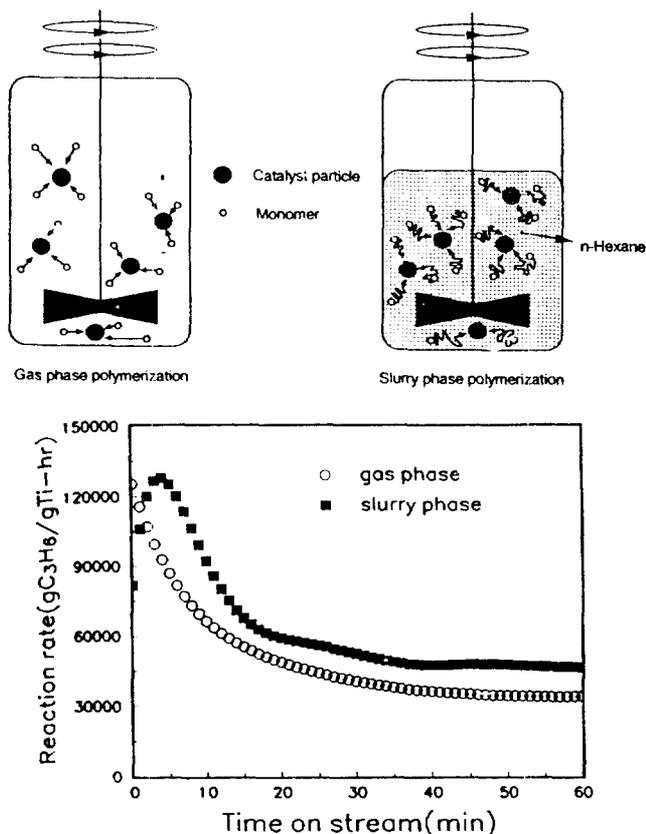


Fig. 3. Comparison of kinetic curve patterns between gas and slurry phase polymerization.

Temp.=40°C, Press.=100 psi, Al/Ti mole ratio=100, EB/Al mole ratio=0.03

determined with xylene extraction method introduced by Chadwick [1992] in order to gain more reasonable results in comparison with the boiling heptane method.

RESULTS AND DISCUSSION

1. Results of Activity Measurement

Gas and slurry phase propylene polymerization was carried out to investigate reaction rate changes before and after the addition of external electron donor.

As shown in Fig. 2, reaction rate is decreased with increasing the amount of electron donor. It is well known that the addition of electron donor generally decreases the reaction rate, and these phenomena are well explained by Keii [1983], that is, atactic sites on the catalyst are selectively poisoned by the electron donor so that total numbers of active sites are diminished. It was also found that sudden deactivation is progressed as soon as reaching a maximum reaction rate. This can be explained by chemical phenomena such as reducing of active component from Ti^{+4} to Ti^{+3} or Ti^{+2} by co-catalyst. However, physical effects must not be ignored to explain this tendency of deactivation. That is, a polymer shell is formed around the catalyst particle with reaction time, and then monomers have difficulties in diffusion to the catalyst surface through the polymer shell [Floyd et al., 1986a, 1986b, 1987]. The same phenomena were found in slurry phase polymerization. Meanwhile, there were some differences between gas and slurry phase polymerizations in comparing to reaction rate

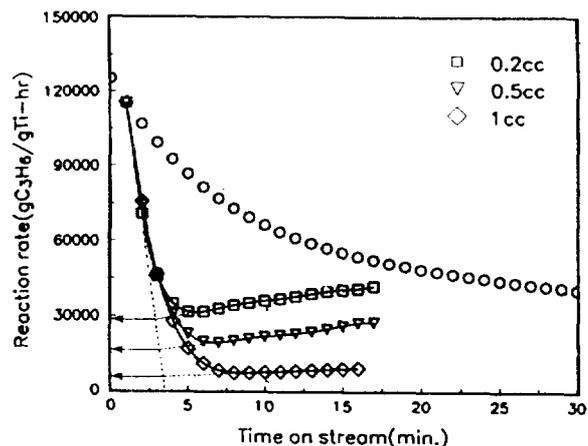


Fig. 4. Polymerization rate changes with CO addition in gas phase.

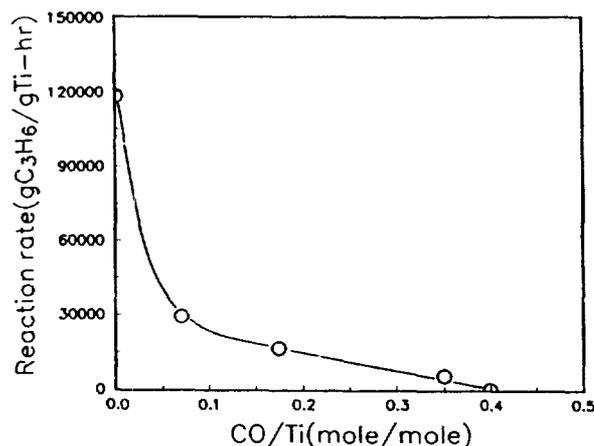


Fig. 5. Correlation between polymerization rate and CO/Ti mole ratio in gas phase.

appearances as shown in Fig. 3. Time of reaching at the maximum reaction rate in slurry phase is longer than that in gas phase. This phenomenon can be explained as follows: as shown in Fig. 3, there is no intermediate in gas phase between catalysts, co-catalysts and monomers so that direct polymerization and catalyst activation by co-catalyst are progressed. However, in slurry phase, there exist intermediates of n-hexane between catalysts, co-catalysts and monomers as solvent molecules so that monomer and co-catalyst diffusions have difficulty of passing through the solvent to the catalyst surface [Choi, 1985].

2. Determination of Catalyst Active Site Concentration

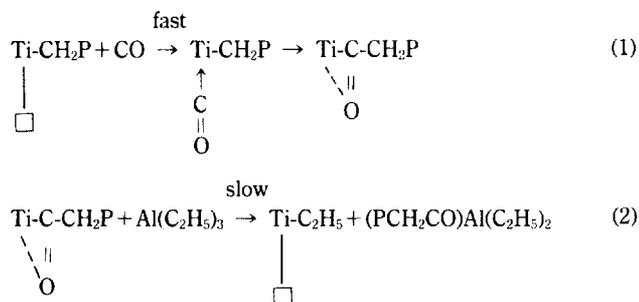
In order to determine concentration of the catalyst active site and a propagation rate constant before and after the addition of a electron donor, the CO inhibition method was used which was introduced by Doi et al. [1982].

The theory of CO inhibition is as follows: if CO is introduced into a reactor in the course of polymerization, it is inserted between Ti of catalyst active sites and a growing polymer chain on an active site as shown in Eq. (1) and then reaction rate decreases very fast as shown in Fig. 4. However, pre-existing co-catalyst (TEAL) converts the CO poisoned active site to fresh one which has a free vacant site, and then reaction rate is recovered slowly [See Eq. (2) and Fig. 4].

Table 2. Results of CO poisoning experiment in gas phase

EB/Al mole ratio	C* (mole/mole Ti)	K _p * (l/mole sec)
0	0.4	131.876
0.03	0.33	166.807
0.05	0.29	262.45
0.1	0.28	305.053

* $R_p = k_p(C^*)(M)$ where R_p = reaction rate
 k_p = reaction rate constant
 (C^*) = active site concentration
 (M) = monomer concentration



Where, \square = Free coordination site
 $-\text{CH}_2\text{P}$ = Polymer chain

At this moment, the tangents of declining and recovering curves are drawn, and then, the catalyst active site concentration can be determined when the reaction rate at the intersection point of two tangents are co-plotted with the amount of CO introduced and extrapolation as shown in Fig. 5, and the results are shown in Table 2.

3. Kinetic Study

In order to suggest the reaction rate form with the addition of electron donor at any reaction time, a kinetic study was carried out before and after the addition of electron donor. It was thought that reaction rate was proportional to monomer and active site concentration as shown in Eq. (3), and it was assumed that catalyst deactivation followed 1st, 1.5th and 2nd order reaction [e.g., in case of 2nd order-Eq. (4)] [Brockmeier and Rogan, 1985]. In each case, the changes of active site concentration with time on stream were gained with 4th order Runge-Kutta method, and then inserted into reaction rate form of Eq. (3). Fortunately, there were good agreements between the experimental data and the calculated results in the case of 2nd order reaction as shown in Fig. 6. There-

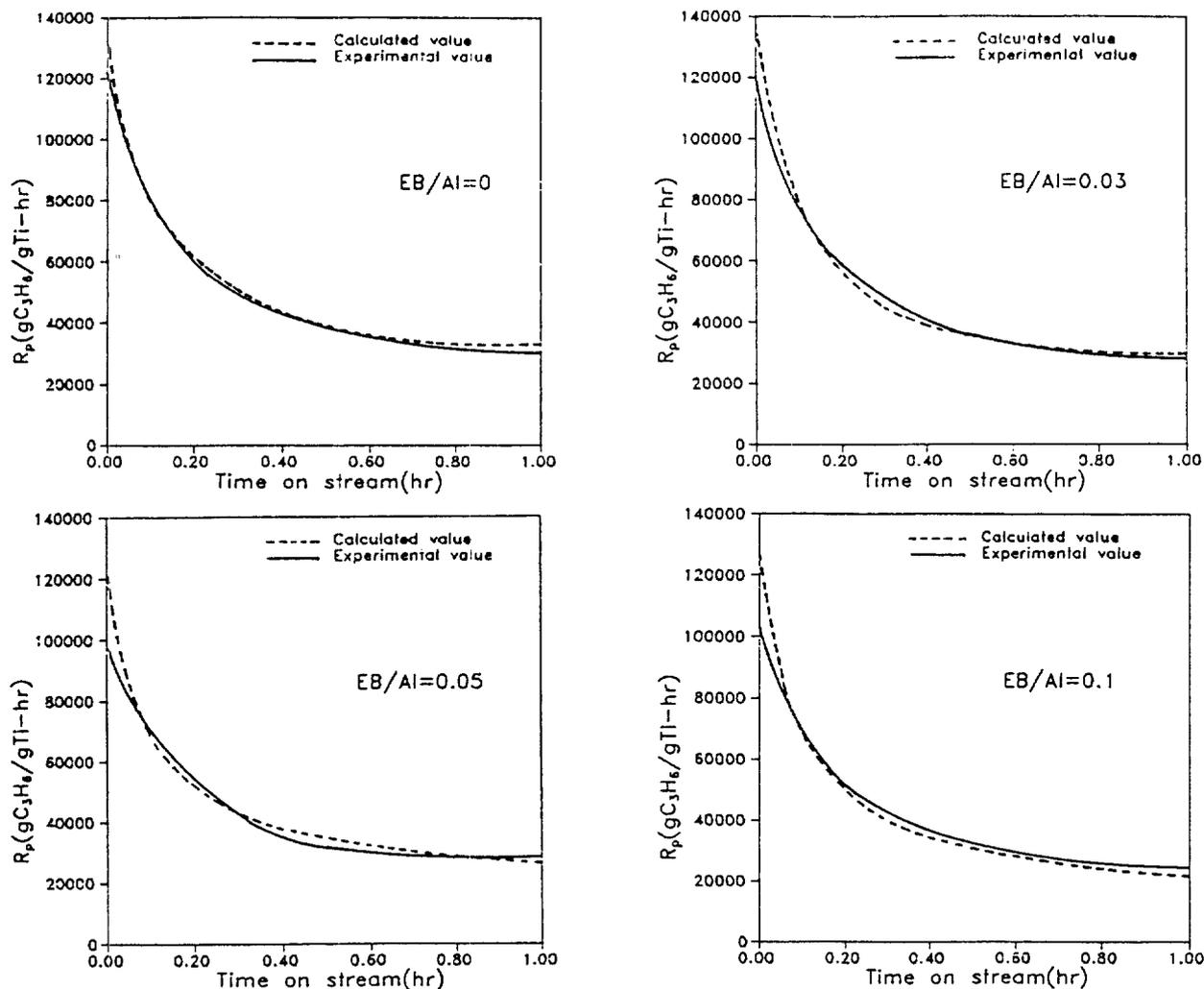


Fig. 6. Kinetic study results of deactivation rate.

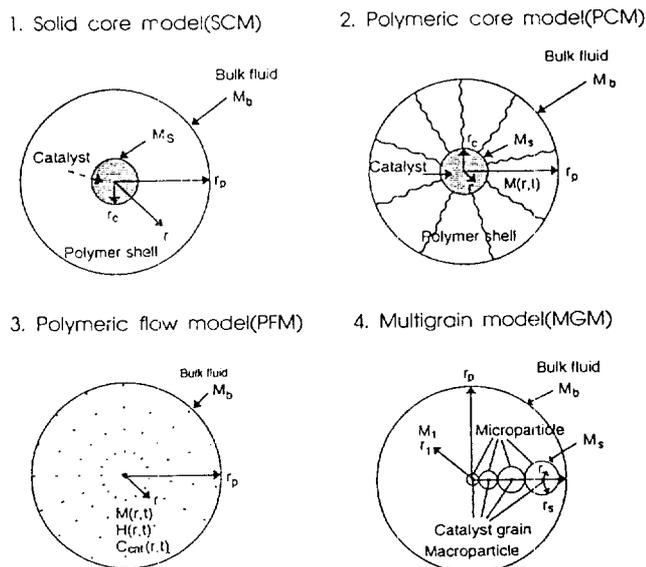


Fig. 7. Monomer diffusion models.

fore, the polymerization reaction rate form which predicts the reaction rate at any time on stream (in this study, the elapsed time from the moment the impeller break the capsule which contains the catalyst so as to distribute it within a reactor) can be proposed.

$$R_p = k_p [M] [C^*], \quad (3)$$

$$-d[C^*]/dt = k_d [C^*]^2 \quad (4)$$

4. Modeling of Monomer Diffusion Phenomena

Meanwhile, as shown the previous results, it was found that reaction rate was decreased abruptly after reaching a maximum rate at the beginning of polymerization because of monomer diffusion resistances. In order to explain these phenomena quantitatively, a monomer diffusion model was introduced in this study.

In general, there are 4 types of monomer diffusion models. (See Fig. 7) as follows: Solid Core Model (SCM) such as simple polymer growing around catalyst; Polymeric Core Model (PCM) such as dispersion of a polymer particle and catalyst broken into pieces in the center of growing polymer; Polymeric Flow Model (PFM) such as diffusion out of a polymer particle and catalyst broken into pieces with polymerization; and Multi Grain Model (MGM) such that a catalyst is broken into pieces with polymerization forming microparticles and then as polymers grow around each broken catalyst particles, and then they flock together to form a macroparticle [Taylor et al., 1983]. In this study, MGM model is adopted because it is thought to be similar to the practical reaction.

Fig. 8 shows more detailed expression of MGM model. That is, as mentioned previously, microparticles are formed with polymers which grow around broken catalyst particles into pieces as polymerization is progressed, and then, they form a macroparticle. At this moment, it is assumed that microparticles located at the same distances from the center of the polymer particle have perfect sphere shape of the same size. In MGM, it must be considered about macro- and microparticle, however, the conception of macroparticle was excepted because monomer diffusion resistance in macroparticle is not excessive comparing to that of microparti-

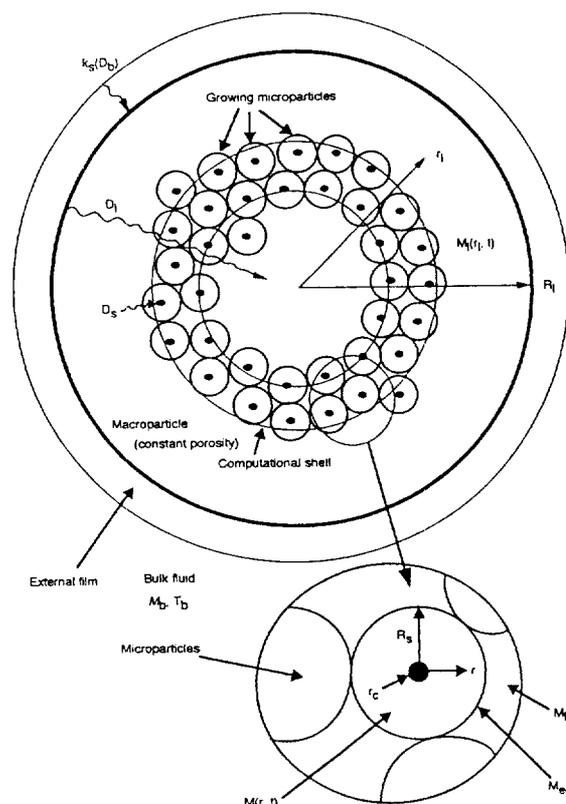


Fig. 8. Multi Grain Model (MGM).

cle. From this assumption, a material balance of monomer around a shell was obtained as follows;

$$\epsilon_s \frac{\partial M}{\partial t} = \frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 D_s \frac{\partial M}{\partial r} \right) \quad (5)$$

Initial and boundary conditions of Eq. (5)

$$\textcircled{1} \quad r = r_c \rightarrow 4\pi r_c^2 D_s \frac{\partial M}{\partial r} = \frac{4}{3} \pi r_c^3 R_{cs}$$

$$\text{where, } R_{cs} = \sum_{i=1}^N k_{pi} C^* M_i = k_p C^* M_c$$

$$\textcircled{2} \quad r = R_s \rightarrow M = M_{eq}, \quad M_{eq}(M_i) \leq M_i$$

$$\textcircled{3} \quad t = 0 \rightarrow M = M_{so}$$

When Eq. (5) was solved by QSSA (Quasi-steady-state approximation) using above initial and boundary conditions, concentration gradient of Eq. (6) is obtained which is expressed with monomer concentration at catalyst surface (M_c) and polymer surface (M_{eq}).

$$M_c = \frac{M_{eq}}{1 + \frac{r_c^2 k_p C^*}{3D_s} \left(\frac{R_s - r_c}{R_s} \right)} \quad (6)$$

Meanwhile, a definition of effectiveness factor (η_s) is introduced as Eq. (7) which is expressed with the ratio of reaction rate between with diffusion resistance and without diffusion resistance. Then, Eq. (8) is obtained by insertion of Eq. (6) into Eq. (7). In order to employ the results of this study, catalyst active site concentration and propagation rate constant are used which was obtained by CO inhibition method in the previous study, and results are shown in Fig. 9.

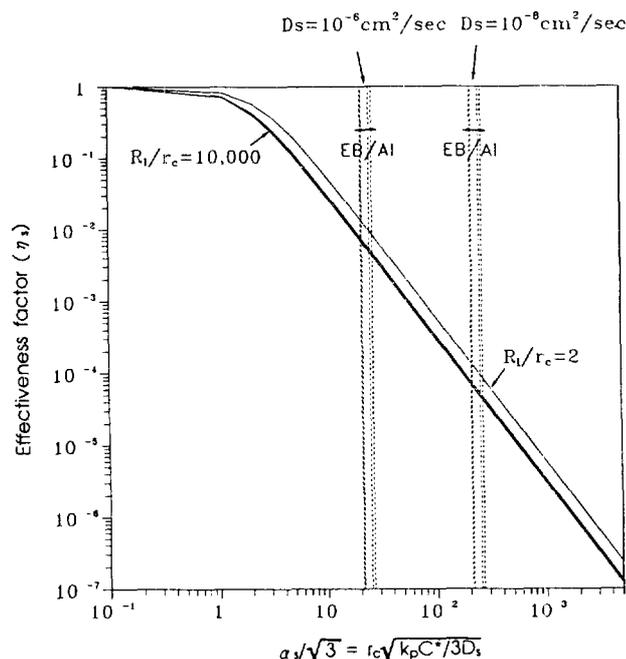


Fig. 9. Microparticle effectiveness factor vs. thiele modulus for growth factor.

$$R_s/r_c = \text{particle growth factor} = \Phi_g$$

$$D_s = \text{diffusivity}$$

$$\alpha_s = \text{thiele modulus} = r_c(k_p C^*/D_s)^{1/2}$$

Table 3. Isotactic index changes with polymerization time in gas phase

Time on stream (min)	Isotactic index (%)
1	82.4
2	93.2
5	95.1
10	95.2
15	95.1
20	95.1

$$\eta_s = \frac{\text{Observed reaction rate with diffusion resistance}}{\text{Surface reaction rate without diffusion resistance}}$$

$$= \frac{k_p C^* M_c}{k_p C^* M_{eq}} = \frac{M_c}{M_{eq}} \quad (7)$$

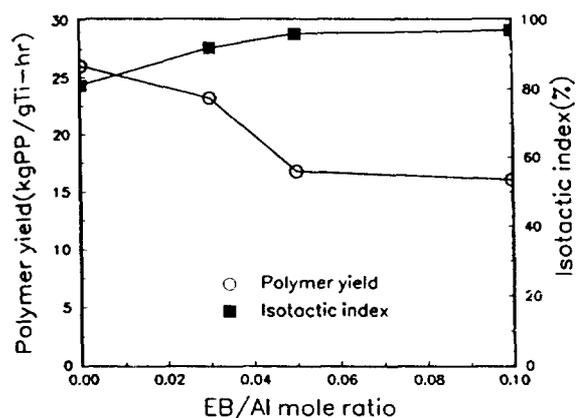
$$= \frac{1}{1 + \frac{1}{3} \alpha_s^2 (\Phi_g - 1) / \Phi_g} \quad (8)$$

$$\text{where, } \alpha_s = \text{Thiele modulus} = r_c(k_p C^*/D_s)^{1/2}$$

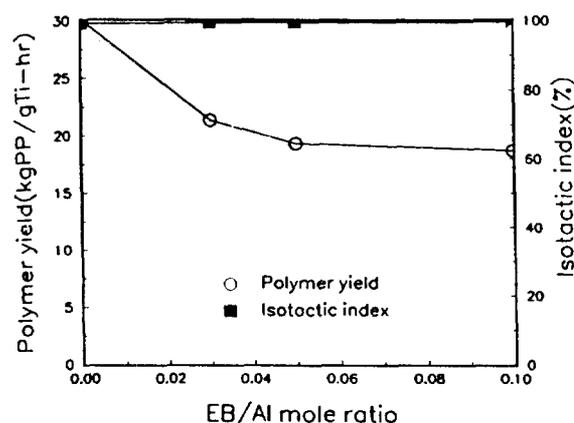
$$\Phi_g = \text{Particle growth factor} = R_s/r_c$$

Since diffusion coefficient (D_s) can not be determined at this time, industrial data of gas phase process are used [Floyd et al., 1986a].

In spite of using the catalyst active site concentration and propagation rate constant at the beginning of polymerization, considerable diffusion resistances are found for both cases ($D_s = 10^{-6} \text{ cm}^2/\text{sec}$, $10^{-8} \text{ cm}^2/\text{sec}$), though any remarkable differences are not observed with EB/Al mole ratio. From these results, it can be considered that the most reasonable reason of catalyst deacti-



(a) Gas phase polymerization



(b) Slurry phase polymerization

Fig. 10. Correlation of polymer yield and isotactic index with EB/Al mole ratio.

Temp. = 40°C , Press. = 100 psi, Al/Ti mole ratio = 100, Electron donor = PEEB

vation at the beginning of polymerization is monomer diffusion resistance. It can be also found that there are no large differences in effectiveness factor with particle growth factor (Φ_g) changes from 2 to 10,000. This means that monomer diffusion resistance is not concerned with quantitative aspect of how much polymer formed around catalyst, but with qualitative aspect. Therefore, in order to prove these phenomena indirectly, isotactic index of polymer with time on stream was measured, and the results are shown in Table 3. It shows high isotactic index of 82.4% after 1 minute of polymerization, and above 90% after more than 2 minutes. That is, most polymer produced at the beginning of polymerization is dense isotactic polypropylene. Therefore, it is thought that dense isotactic polypropylene is formed at the beginning of polymerization around catalyst particle instead of atactic polypropylene with loose structure so that monomers have difficulties in diffusion into catalyst surface through dense polymer. And it is thought that this phenomena will be more severe with increasing of EB/Al mole ratio.

5. Polymer Yield and Isotactic Index

In order to investigate the effect of electron donor on the polymer physical properties during polymerization, various characterization techniques were employed to newly produced polypropylene.

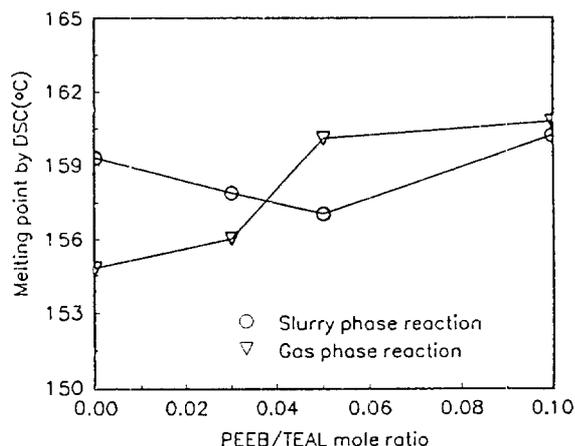
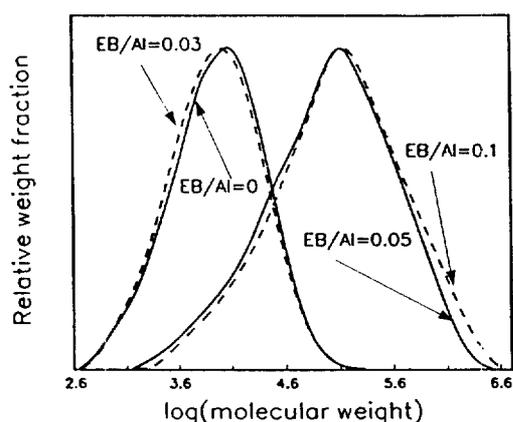
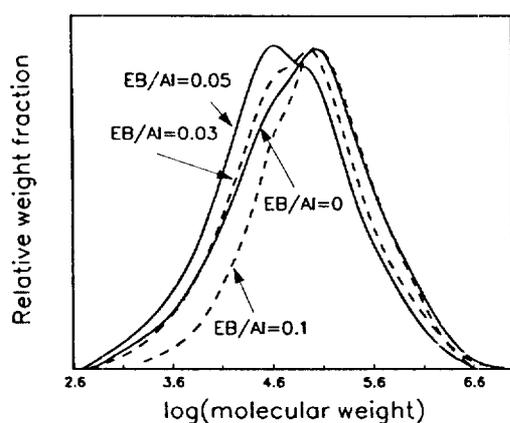


Fig. 11. Melting point changes of IPP with EB/Al mole ratio.



(a) In case of gas phase



(b) In case of slurry phase

Fig. 12. GPC curve patterns of IPP with EB/Al mole ratio.

First of all, as shown in Fig. 10, isotactic index and polymer yield in gas phase polymerization are compared to those in slurry phase polymerization.

Polymer yield in gas phase decreases with increasing of EB/Al mole ratio while isotactic index increases. This result can be explained by using the theory proposed by Keii [1983] temporarily. Atactic sites on catalyst are selectively poisoned by electron donor so that relative isotactic index is increased. On the other hand,

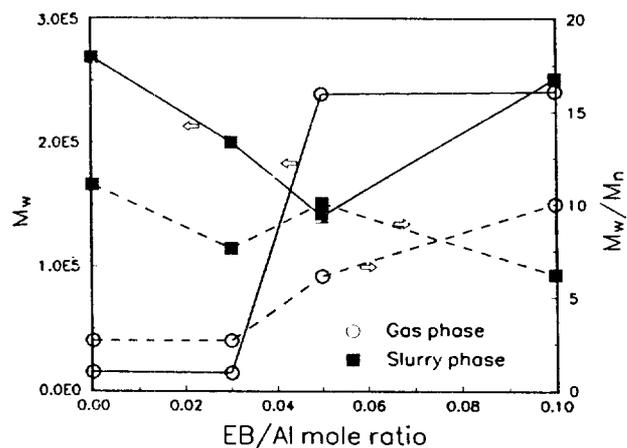


Fig. 13. Weight average molecular weight and molecular weight distribution of gas and slurry phase polymerized IPP with EB/Al mole ratio.

in slurry phase, polymer yield shows the same pattern as in the gas phase, whereas isotactic index pattern is different in the gas phase. That is, as shown in (b) of Fig. 10, severe changes of isotactic index are not found with EB/Al mole ratio, and all cases show very high isotactic index of above 99%. This phenomena could be a result of that atactic polymer of low molecular weight was dissolved in solvent of n-hexane as soon as produced, so that all polypropylene obtained become isotactic polymers. Thus, it is thought that there is little effect of addition of electron donor in slurry phase. Practically, it is well known that additional atactic polymer recovering process is necessary in industrial plants [Brockmeier, 1983].

6. Polymer Melting Point

To investigate the physical properties of polymer produced indirectly, measurement of melting point for each isotactic polymer was carried out. As shown in Fig. 11, sudden increasing of melting point at EB/Al=0.03 is found in gas phase. In slurry phase, slow declining of melting point is progressed until EB/Al=0.05 and increases again above of EB/Al=0.05. From these results, it is thought that there may be severe changes in polymer molecular weight because of the intimate relations between molecular weight and melting point.

7. Results of GPC Analysis

In practice, when molecular weight of isotactic polymer was measured by GPC, it was found that there were severe changes in patterns of molecular weight distribution curves of isotactic polypropylene with the changes of EB/Al mole ratio as shown in Fig. 12. In case of gas phase, molecular weight of EB/Al=0.03 is shifted to a little lower part than that of EB/Al=0, however, there is large shift to higher molecular weight above of EB/Al=0.03. These phenomena can not be explained by the theory of Keii [1983], that is, atactic sites are selectively poisoned by the addition of electron donor and molecular weight is increased by decreasing of co-catalyst amount which has the role of chain transfer. Therefore, it could be explained by active site transition phenomena. That is, when external electron donor is added on catalyst, atactic sites are preferentially converted into low isotactic sites to a certain extent of added amount, and then converted into high isotactic sites above that amount. These phenomena are more definite in slurry phase as shown in (b) of Fig. 12. Molecular weight is shifted to lower part until EB/Al=0.05, and then

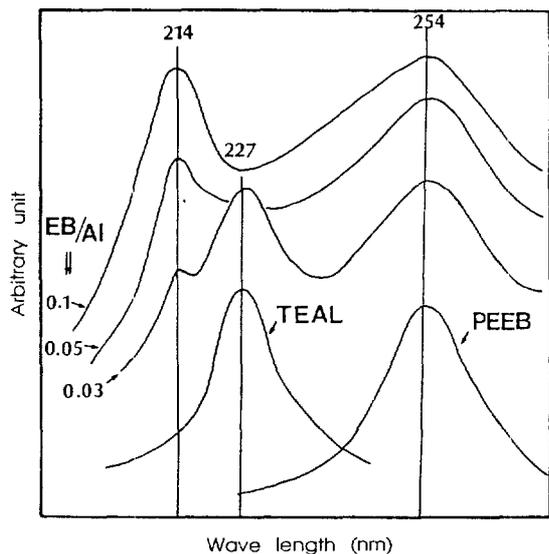


Fig. 14. UV-VIS spectra of PEEB, TEAL and PEEB-TEAL mixture with the change of EB/Al mole ratio.

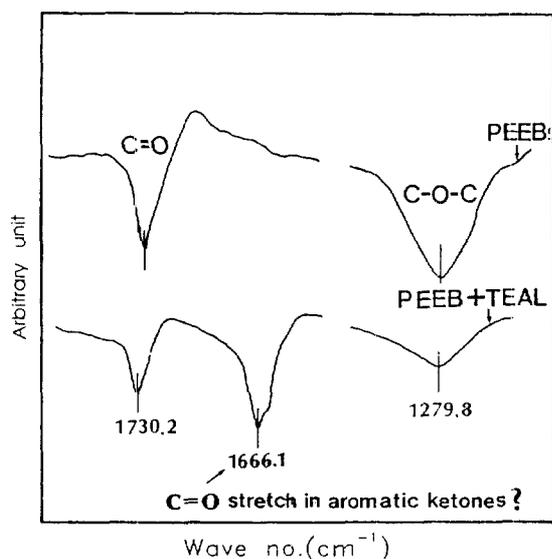


Fig. 15. FTIR spectra of PEEB and PEEB-TEAL mixture.

shifted to higher part again above of EB/Al=0.05. From these results, it could be considered that if external electron donor is added into catalyst, first, atactic sites are converted into low isotactic sites which produce low molecular weight isotactic polymer. Second, low isotactic sites are converted into high isotactic sites which produce high molecular weight isotactic polymer.

The weight average molecular weight and molecular weight distribution (MWD) of isotactic polypropylene are compared between gas and slurry phase reaction as shown in Fig. 13.

As previously mentioned on the GPC curves, weight average molecular weight is increased remarkably over EB/Al=0.03 in gas phase. In case of slurry phase, molecular weight of isotactic polypropylene is decreased until EB/Al=0.05 because of atactic site conversion into low isotactic site, producing low molecular weight isotactic polymer. However, it increases again when EB/Al mole ratio overs the value of 0.05. If atactic sites are selectively poisoned by electron donor, molecular weight distribution of iso-

tactic polypropylene produced on the catalyst must not be changed because any changes do not happen on isotactic sites. However, the molecular weight distributions of isotactic polypropylene produced by both reactions have changed very severely with EB/Al mole ratio. This means that various active sites on catalyst must exist, and therefore it strongly supports the active site transition phenomena.

8. Results of UV-VIS and FTIR Analysis

In order to investigate the reason of active site conversion phenomena, UV analysis study was carried out for co-catalyst and electron donor which were additives on polymerization except for catalyst.

As shown in Fig. 14, a peak at 254 nm corresponds to electron donor and at 227 nm to co-catalyst. However, in case of a mixture of them, a new peak at 214 nm appears. With increasing the EB/Al mole ratio, the 214 nm peak is growing at the expense of the co-catalyst peak at 227 nm. From this result, it is found that a new complex is formed by mixing co-catalyst and electron donor, and all the co-catalyst is consumed to make up this complex. Therefore, it can be considered that this new complex has an ability of catalyst active site conversion from atactic site to isotactic site.

In another method to confirm the presence of this new complex, IR analysis was carried out and results are shown in Fig. 15. Except for two peaks 1730.2 and 1279.8 cm^{-1} corresponding to electron donor, a new peak at 1666.1 cm^{-1} is found which is considered as a complex between co-catalyst and electron donor. Though it is difficult to assign this peak correctly, it may be a result of a C=O stretching mode in aromatic ketones.

CONCLUSIONS

In order to investigate the addition effect of electron donor on the 3rd generation Ziegler-Natta catalyst in gas and slurry phase polymerization, catalytic activities and polymer physical properties were measured. Following results are obtained:

1. From catalytic activity measurement, it was found that reaction rate was decreased with increasing of EB/Al mole ratio because atactic sites on catalyst were selectively poisoned by added electron donor so that total number of active sites were diminished.

2. Through the kinetic study, it could be found that the overall reaction rate was followed the 2nd order, and a reaction rate form which could predict the reaction rate at any time could be suggested.

3. Monomer diffusion phenomena was suggested using a mathematical expression. Based on this expression, it could be considered that catalyst deactivation was due to the formation of dense isotactic polypropylene around catalyst at the beginning of polymerization resulting that monomers had difficulties in diffusion into catalyst surface through the dense polymer.

4. From the measurements of polymer physical properties, it was found that a new complex was formed with mixing of co-catalyst and electron donor, which converted atactic site to isotactic site. At this moment, the site transition path could be considered as "atactic site \rightarrow low isotactic site \rightarrow high isotactic site." It could be also thought that high isotactic site was formed over EB/Al=0.03 in gas phase and EB/Al=0.05 in slurry phase. These differences were considered to be a result of a difference in reaction type.

ACKNOWLEDGEMENT

The author would like to acknowledge the Korea Catalyst Research Association for the support.

REFERENCES

- Brockmeier, N. F. and Rogan, J. B., "Propylene Polymerization Kinetics in a Semi-Batch Reactor by Use of a Supported Catalyst", *Ind. Eng. Chem. Prod. Res. Dev.*, **24**(2), 278 (1985).
- Brockmeier, N. F., "Latest Commercial Technology for Propylene Polymerization", Transition Metal Catalyzed Polymerizations, Alkenes and Dienes, B.: Harwood Academic Publishers, New York (1983).
- Chadwick, J. C., "Effects of Pro-Catalyst Composition on the Stereospecificity of a Ziegler-Natta Catalyst System", *Makromol. Chem.*, **193**, 1463 (1992).
- Choi, K. Y., "Polymerization of Olefins through Heterogeneous Catalysis. II. Kinetics of Gas Phase Polymerization with Ziegler-Natta Catalysts", *J. of Appl. Polym. Sci.*, **30**, 1065 (1985).
- Choung, S. J., Technical Report of "PO Polymerization Catalyst Research", 2nd Year (1994).
- Doi, Y., Murata, M., Yano, K. and Keii, T., "Gas-Phase Polymerization of Propene with the Supported Ziegler Catalyst: $TiCl_4/MgCl_2/C_2H_5COOC_2H_5/Al(C_2H_5)_3$ ", *Ind. Eng. Chem. Pro. Res. Dev.*, **21**, 580 (1982).
- Floyd, S., Choi, K. Y., Taylor, T. W. and Ray, W. H., "Polymerization of Olefins through Heterogeneous Catalysis, III. Polymer Particle Modeling with an Analysis Intraparticle Heat and Mass Transfer Effects", *J. of Appl. Polym. Sci.*, **32**, 2935 (1986a).
- Floyd, S., Choi, K. Y., Taylor, T. W. and Ray, W. H., "Modeling of Heat and Mass Transfer Resistance in the Polymer Particle", *J. of Appl. Polym. Sci.*, **31**, 2231 (1986b).
- Floyd, S., Heiskanen, T., Taylor, T. W., Mann, G. E. and Ray, W. H., "Effect of Heat and Mass Transfer Polymerization Behavior and Polymer Properties", *J. of Appl. Polym. Sci.*, **33**, 1021 (1987).
- Härkönen, M., Seppälä, J. V. and Väänänen, T., "Effect of the Structure of External Alkoxy Silane Donor in High Activity Ziegler-Natta Catalyst on the Microstructure of Polypropylene", *Studies in Surface Science and Catalysis*, **56**, 87 (1990).
- Kang, S. C., "The Present Status of Olefin Polymerization Catalyst and Manufacturing Technique", *Catalysis*, **4**(1), 51 (1988).
- Kakugo, M., "Microtacticity Distribution of Polypropylenes Prepared with Heterogeneous Ziegler-Natta Catalysts", *Macromolecules*, **21**, 314 (1988).
- Kashiwa, N., "The Role of Ester in High Activity and High Stereoselectivity Catalyst", Transition Metal Catalyzed Polymerizations, Alkenes and Dienes, A.: Harwood Academic Publishers, New York (1983).
- Keii, T., Suzuki, E., Tamura, M. and Doi, Y., "A Kinetic Study on the Role of Ethyl Benzoate Additive Durint Propene Polymerization with Magnesium Chloride Supported Ziegler-Catalyst", Transition Metal Catalyzed Polymerizations, Alkenes and Dienes, A.: Harwood Academic Publishers, New York (1983).
- Kim, H. K., "Polypropylene(I)", *Honam Oil*, **1**, 14 (1991).
- Koura, H., "Process of Propylene Polymerization and Catalyst Development", *Shokubai*, **35**(1), 40 (1993).
- Langer, A. W., "Effect of Hindered Amines on Supported Catalysts for Polypropylene", Transition Metal Catalyzed Polymerizations, Alkenes and Dienes, A.: Harwood Academic Publishers, New York (1983).
- Lee, C. S., "Producing Process of Polypropylene", *Honam Oil*, **3**, 14 (1987).
- Miyatake, T., "Microtacticity Distribution of Polypropylenes Prepared with $MgCl_2$ Supported Ti Catalyst System", *Studies in Surface Science and Catalysis*, **56**, 155 (1990).
- Okano, T., "Effect Silane Compounds on Catalyst Isospecificity-A Plausible Model Based on MO Calculation", *Studies in Surface Science and Catalysis*, **56**, 177 (1990).
- Pino, P., Guastalla, G., Rotzinger, B. and Mülhaupt, R., "Stereospecific Polymerization of Propylene: An Outlook 25 Years after its Discovery", Transition Metal Catalyzed Polymerizations, Alkenes and Dienes, A.: Harwood Academic Publishers, New York (1983).
- Soga, K. and Park, J. R., "Easy Convection of Aspecific into Isospecific Sites", *Studies in Surface Science and Catalysis*, **56**, 131 (1990).
- Spitz, R., "The Function of Ethyl Benzoate (EB) in Stereospecific Catalysts for Polymerization of Propene Supported on $MgCl_2$ ", Transition Metal Catalyzed Polymerizations, Alkenes and Dienes, A.: Harwood Academic Publishers, New York (1983).
- Sacchi, M. C., " ^{13}C NMR Investigation on Lewis Base Activation Effect in High Yield Supported Ziegler-Natta Catalysts", *Studies in Surface Science and Catalysis*, **56**, 185 (1990).
- Sugano, T., "A New Electron Donor for the Stereospecific Polymerization of Propylene", *Studies in Surface Science and Catalysis*, **56**, 201 (1990).
- Taylor, T. W., Choi, K. Y., Yuan, H. and Ray, W. H., "Physico-chemical Kinetics of Liquid Phase Propylene Polymerization", Transition Metal Catalyzed Polymerizations, Alkenes and Dienes, A.: Harwood Academic Publishers, New York (1983).