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Japan Advanced Institute of Science and Technology

Doctoral Dissertation

Structure-performance relationship of alkoxysilanes as external donors in various propylene polymerizations using Ziegler-Natta catalyst

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Chapter 1

General Introduction

Since 1950s, after crystalline polypropylene has been invented by Giulio Natta, there were several commercial producers delivering PP products into several rapidly expanding applications. Now there are many innovative product applications with the elegant processes developing in each year. For this matter, it made the researchers' passion and process engineers' commitment enabled substantial improvements of the early technology (catalyst, process and products) to substitute traditional materials to the new polymer such as polyolefins. Nowadays, the combined production of polypropylene and polyethylene was already reached to around 120 million tons and is expected to grow to over 150 million tons in 2015. This increasing demand of the polyolefins production comes from low costs and excellent material properties. So that is why there are continuous improvements to the properties window of the polyolefins. This chapter describes the present understanding and the developments of Ziegler-Natta catalysts in propylene polymerization in the viewpoints of academic and industrial aspects.

1.1 Polypropylene

Polypropylene (PP), also known as polypropene, is a thermoplastic polymer used in a wide variety of applications with excellent polymer properties. An addition polymer made from the propene monomer. Most commercial polypropylene is isotactic and has an intermediate level of crystallinity between that of low-density polyethylene (LDPE) and high-density polyethylene (HDPE). Polypropylene is normally tough and flexible, especially when copolymerized with ethylene. This allows polypropylene to be used as an engineering plastic. The melting point of polypropylene occurs at a range, so a melting point is determined by finding the highest temperature of a differential scanning calorimetry chart. Perfectly isotacticity PP has a melting point of 171 ^{0}C. Commercial isotactic PP has a melting point that ranges from 160 to 166 ^{0}C, depending on atactic portion and crystallinity. The melt flow rate (MFR) or melt flow index (MFI) is a measure of molecular weight of polypropylene which varied with the wide range of applications. There are three general types of polypropylene; homopolymer, random copolymer and block copolymer. The comonomer which is typically used is ethylene which impact strength properties can be improved. There are many industrial processes which widely used for polypropylene production as shown in Table 1.1. The advantages of each process are also shown in Table 1.2.

Polypropylene is widely used in many applications with excellent mechanical properties such as high chemical resistance, high strength, etc. These excellent properties made it idea not only for exposure to hostile environments but also for applications requiring compliance with FDA regulations, such as food packaging and medical delivery systems. It can be copolymerized with other monomers or alloyed with other polymers to yield final products custom-designed for specific applications. This section illustrates the versatility of PP by highlighting many of the applications for which it has become the selected resin such as fibers, injection moldings, industrial applications, automotive, film, etc.

Table 1.1 Various PP industrial processes[1]

Process	Reactor type	Mode of operation	Reactor temperature (℃)	Reactor pressure (bar)	Residence time (h)
Slurry	Series of stirred autoclaves	Slurry	65 - 75	8 - 12	up to 5
Unipol	Fluidized bed gas phase	Condensed gas phase	60 - 70	25 - 30	1
Spheripol	Loop	Liquid pool (bulk)	65 - 75	30 - 35	2
Hypol	Autoclaves	Liquid pool (bulk)	65 - 75	30 - 35	2
NTH	Vertical stirred bed gas phase	Non-condensed gas phase	80 - 85	30 - 35	1
Innovene Amoco Chisso SABIC	Horizontal stirred bed gas phase	Non-condensed gas phase	60 - 70	25- 30	1

Table 1.2 Advantages and disadvantages of each industrial processes [1]

Reactor configuration	Advantages	Disadvantages
Stirred autoclave	Low capital cost	- Low heat transfer area - Low space time yield
Loop	- Low capital cost - High heat removal - High space time yield	Limited flexibility
Fluidized gas phase	- High heat removal - High space time yield	Difficult to operate
Horizontal stirred gas phase	Allow for fast production grade transfer	More complex reactor design, higher capital cost
Circulating bed	- Better polymer properties control - Different reacting zone allows production of product which not possible with traditional reactors	- Complex reactor design, high capital cost - Still unproven technology

1.2 Ziegler-Natta (ZN) catalyst

Ziegler-Natta catalyst was invented in 1953 by Karl Ziegler and Giulio Natta. Series of improvements have been carried out in last six decades and now it is one of the most important industrial catalysts responsible for olefin polymerization.[2-4] . Since it was invented, there were several developments of ZN catalysts as follows;

First generation of ZN catalyst

It is the early stage of the catalyst which used in the PP industrial processes with $TiCl_3/AlEt_2Cl$ and showed the low productivity and also stereospecificity. That is the reason why the deashing unit and atactic removal unit are needed in the PP processes. Several researches came in action to develop the catalyst performance by prolonging ball milling time or Al-reduced $TiCl_3$.[5-7]

Second generation of ZN catalyst

Second generation is important for the $TiCl_3$ catalyst which has the basic information for the synthesis as followings; First, the preparation of a reduced solid by reducing $TiCl_4$ in hydrocarbon solvent and introduce DEAC at low temperature. The catalyst has very low surface area as well as catalytic activity.[8] Second, the treatment of reduced solid with i-amyl ether which almost all the Al is removed from the solid, while some ether remains complexed. This product, referred to as ‘treated solid’, also shows low surface area and catalyst activity.[9] Third, the solid system was treated with excess $TiCl_4$. A ‘catalytic complex’ is obtained with high surface area and porosity and very high catalytic activity.

Compared with the earlier generation, both the productivity and the isotacticity re considerably higher and the morphology much improved. The polymer MWD appears boarder than with supported catalysts but somewhat narrower than with AA-$TiCl_3$ owing to the absence of $AlCl_3$.

Third generation of ZN catalyst

In this generation, conventional high surface supports with surface functional groups were used. But it was not successful in PP production due to the low activity. Then the catalysts based on activated $MgCl_2$ were used with the addition of appropriate Lewis bases which made it possible to obtain highly active and stereospecific catalysts by comilling $MgCl_2$, $TiCl_4$, and a Lewis base (LB) which called “Internal donor”(InD) , combined with an Al-trialkyl as cocatalyst and a second Lewis base called “External donor” (ExD). Even these catalysts system can avoid the need for deashing unit, these catalysts still required the unit for atactic removal. So the improvement in this generation was mainly about the combination of electron donors led to the high active and stereospecific catalysts. [10-11]

Fourth generation of ZN catalyst

Further research led to highly active and stereospecific catalysts, called by the inventors’ super high activity catalysts, which still making use of benzoic acid esters as electron donors, were claimed to display a superior productivity and isotacticity.[12-14] The letter resulted, in the early 80s in the discovery of a new combination of electron donors, namely alkylphthalate as internal donor and alkoxysilane as external donor, able to afford a much better productivity/isotacticity balance than benzoic esters.[15] The above catalyst system are currently used in most of the modern industrial processes for PP manufacturing.

Fifth generation of ZN catalyst

In this generation, new type of electron donors was discovered (1,3-diether). This new electron donor type can give high catalyst activity and stereospecificity when used as internal donor without the use of external donors.[16] Now, this catalyst system is still continuously improving in the new class. The summary of Ziegler-Natta catalyst performance in the different system was shown in Table 1.3.

Table 1.3 Summary of different Ziegler-Natta Catalysts performance[1]

Catalysts system	Productivity (kg-PP/gcat)	II (%)	mmmm (%)	M_w/M_n	Hydrogen response
δ-$TiCl_3 \bullet 0.33AlCl_3 + AlEt_2Cl$	2 - 4	90 - 94			Low
δ-$TiCl_3 + AlEt_2Cl$	10 - 15	94 - 97			Low
$MgCl_2/TiCl_4 + AlR_3$	15	40	50 - 60		
$MgCl_2/TiCl_4$/Benzoate + AlR_3/benzoate	15 - 30	95 - 97	90 - 94	8 - 10	Low
$MgCl_2/TiCl_4$/Phthalate + AlR_3/Silane	40 - 70	95 - 99	94 - 99	6.5 - 8	Medium
$MgCl_2/TiCl_4$/Diether + AlR_3	100 - 130	95 - 98	95 - 97	5 - 5.5	Very high
$MgCl_2/TiCl_4$/Diether + AlR_3/Silane	70 - 100	98 - 99	97 - 99	4.5 - 5	High
$MgCl_2/TiCl_4$/Succinate + AlR_3/Silane	40 - 70	95 - 99	95 - 99	10 - 15	Medium

1.3 Ziegler-Natta catalyst preparation procedure

The synthesis of the active form of $MgCl_2$ can be performed according two different approaches; either using a mechanical treatment (usually ball milling) or a chemical reaction during which the other catalyst ingredients, either the titanium derivative or/and the Lewis Base (LB), can be directly incorporated. The synthetic procedures for catalyst preparation can thus be divided into three main classes: mechanical routes, chemical routes, and mixed mechanical- chemical routes.

Mechanical routes

This approach is directly derived from the methods used for the activation of the early $TiCl_3$-based catalysts it consists of a step in which the catalyst components are milled together for several hours. A ball mill is usually employed. $MgCl_2$ can also be generated during the milling process by reacting a magnesium compound with a chlorinating agent. This milling method makes higher amount of surface leading to the higher initial catalyst activity which suitable for the very short time polymerization study.[10,17]

Mechanical Plus Chemical Routes

There are two different approaches belonging to this type of catalyst synthesis. First, Co-milling of $MgCl_2$ or a $MgCl_2$-precursor and, optionally, a Lewis base or internal donor. The resulting solid is then separately treated with an excess of $TiCl_4$. The treatment with $TiCl_4$ has the roles of binding itself on the $MgCl_2$ surface and the vacant Mg coordinates sites, displacing part of the internal donor. The other role is the removal from the catalyst surface all the undesired by-product formed during the reaction. Second, the co-milling of all the catalyst component, as described in the pure mechanical approach, followed by one or more washings with halogenated or aromatic solvents. This type of post-treatment of the solid increases the activity and the stereospecificity of the final catalyst.

Chemical routes

In the case of preparation method, both the formation of the active form of $MgCl_2$ and the incorporation of the other components are carried out by means of a chemical reaction. The most common synthetic procedures can be divided in to four categories according to both types of reagents and reactions involved. Some parameters are critical for the control and, in particular, for the improvement of the catalyst performances in polymerization. In the case of catalysts obtained from mechanical or mixed (mechanical plus chemical) routes, the main factors affecting the catalyst performances are the time and the efficiency of milling and the ratio between the components. For example, a longer milling time brings about an increase of catalyst activity. For catalysts obtained from chemical routes, the purity of reagents, their ratio, the order of mixing, the reaction time, and the treatment temperature are the main factors to be optimized in order to obtain high-performance catalyst. An important distinction between the former preparation method based on the milling of catalyst components and the pure chemical routes, is the difference in the physical status of the solid catalyst precursor.[10,18,19]

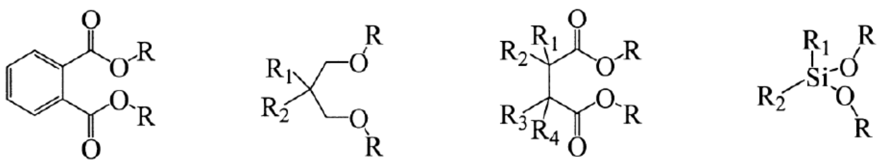
1.4 Donors

The catalyst activity and stereo-specificity (for PP) have been developed throughout this development era due to increasing demand of PP which comes from wide variety of product properties such as excellent mechanical properties, chemical resistance, etc. Ziegler-Natta catalyst system contains solid catalyst system (activated $MgCl_2$ support, $TiCl_4$) activator (organo-aluminum compound) and electron donors. Electron donors are Lewis bases which can be divided into two types; internal donors are introduced during catalyst preparation and external donors are additional component which are externally introduced during polymerization.[20] It is known that electron donors have played the important roles in regulating the stereospecificity and activity of $MgCl_2$-supported Ziegler-Natta catalysts. Catalytic properties of Ziegler-Natta catalysts are strongly influenced by the combination of different internal and external donor. Recent developments aim at the finding of new donors to give boarder molecular weight distribution (MWD) and higher hydrogen response for the control of molecular weight. Therefore, it is important to investigate the effects of donors on the polymer properties for the further improvement of catalyst system.

Table 1.4 Revolution of electron donors incorporating with Ziegler-Natta catalyst [20]

Year	Electron donors		Productivity	II	mmmm
	Internal	External	(kg-PP/gcat)	(%)	(%)
1971	benzoate	benzoate	15 - 30	95 - 97	90 - 94
1980	phthalate	silane	40 - 70	95 - 99	94 -99
1988	diether		100 - 130	95 - 98	95 - 97
	diether	silane	70 - 100	98 - 99	97 - 99
1999	succinate	silane	40 - 70	95 - 99	95 - 99

Some aromatic esters such as ethyl benzoate were found to increase not only stereospecficity but also catalyst activity.[21] During the revolution of ZN catalysts, there are several developments to find the good combination of internal and external donor. Due to the most commercially used 4th generation ZN catalyst, the good combination between phthalate and alkoxysilane was found to be efficient.[22-25] Moreover, some hindered diethers were claimed to provide the excellent performance without the necessity of external donor.



Phthalate Diether Succinate Silane

Figure 1.1. General formula of internal and external donor.

In all system, the polymer properties also appear to depend on the amount of external donor. For instance, the average molecular weight of the obtained polymer, especially that of the isotactic fraction increases with the ED/Al ratio in both EB/MPT and the phthalate/silane systems in the absence of hydrogen. The structure of external donor also plays the important role to improve the catalyst performance. As previously mentioned, among the monoester system, the most effectively used external donors are methyl- or ethylbenzoate bearing in para position with an electron-releasing group (CH_3, OCH_3, OEt, t-Bu, etc.) to decrease their reactivity toward the Al-akyl. Guyot *et al*.[26] reported some polymerization results obtained with a $TiCl_4$/EB/$MgCl_2$ catalyst combined with TEA and EB, EA, EPT as external donors. It was found that EB, EA and EPT provided the similar stereospecificity improvement, whereas the productivity is higher in the case of EPT. On the other hand, higher steric hindrance that limits the ability to form complex with TEA, work as the good stereoregulating agent. In the previous research, MPT shows the superior performance over EB as external donor by Kashiwa *et al*.[27]. More results are also available for the effects of alkoxysilane structure in phthalate/alkoxysilane system. The performance of alkoxysilane is affected by the number and size of alkoxy group as well as size of alkyl group[28-30]. Two or three alkoxy group with small bulkiness of alkyl is believed to provide the excellent catalyst performances.

1.5 Catalyst chemistry

It is well known that neither $TiCl_4$ nor the internal donor can be easily removed from the catalyst unless severe treatments or strongly coordinating solvents are applied. Thus, it seems that the catalyst components lose their identity and become strongly linked together, forming new complexes. A considerably amount of work has been done aiming at the elucidation of the bonding nature by means of spectroscopic observations (IR, NMR) and thermogravimetric (TG) analyses carried out on both the true catalyst and model combinations of its components (called “model catalyst”). A great results of IR data is available for catalysts containing ethylbenzoate (EB) as internal donor[5,31,32] for which a shift of the C=O stretching frequency from 1725 cm^{-1} in the free ester to 1680 cm^{-1} to 1700 cm^{-1} is the most commonly observed in both the catalyst and the co-milled EB/$MgCl_2$ mixtures. This result has been indicated that a complexation of EB through the carbonyl oxygen taking place to Mg.

Solid state CP MAS (cross polarization with magic angle spinning) ^{13}C NMR investigations on both the catalyst[33-34] and model $TiCl_4{\cdot}EB$ complex or EB·$MgCl_2$ comilled mixtures also led to the conclusion that EB is prevailingly complexed to $MgCl_2$. Possible structures for EB complexed to the {100} and {110} faces of $MgCl_2$ have been proposed by Chien *et. al.* [33] and are shown in Figure 1.2.

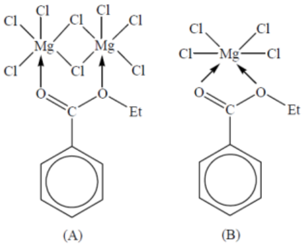


Figure 1.2. Possible model for EB coordination on the {100} (A) and {110} (B) faces of $MgCl_2$ [33]

According to some researchers[35,36], a slight difference can be noticed in the infrared C=O absorption frequency of the catalyst (1680 cm^{-1}) and that of the EB/$MgCl_2$ mixture (1690 cm^{-1}). This is suggested that EB possible to get complexation with both Mg and Ti. On the other hand, from electron spin resonance (ESR) analysis of the catalyst after interaction with TEA, some evidence for the presence of small amounts of EB or phthalates complexed to Ti^{3+} has been reported as well.[37,38] The information concerning bifunctional donors (phthalates, diethers) is not as abundant. From all evidences, it seems that both monofunctional and bifunctional donors are essentially complexed to Mg rather than to Ti. The structure of complexes could be different depending on the donor types. Moreover, bifunctional Lewis bases could form either 1:1 chelate complexes with tetracoordinated Mg ions on the {100} face.[39] As far as the $TiCl_4$ bonding is concerned, the most widely accepted models supported by energy calculations, are those based on epitaxial adsorption on the different $MgCl_2$ faces. According to Corradini and his group[40-41], the {100} lateral cut is more basic than {110} one as far as $TiCl_4$ coordination is concerned. The calculations suggest that $TiCl_4$ coordination as a Ti_2Cl_8 dimer on the former face and perform as a monomer on the latter are energetically preferred. Similar models were also proposed by Chien[42]. It was assumed that the presence of tetracoordinated rather hexacoordinated monomeric species on the {110} face, both in clusters and in isolated form. As a consequence of the presence of $TiCl_4$ to coordinate on the {100} face. The catalyst before and after reduction with Al-alkyl can be roughly represented as in Figure 1.3, with the {100} face being prevailingly occupied by Ti_2Cl_8 dimers and the {110} face by the Lewis base.

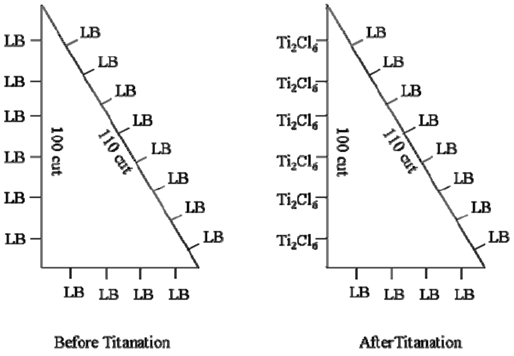


Figure 1.3. Schemetic drawing of the Lewis base and Ti halide distribution on the {110} and {100} cuts $MgCl_2$: (left) support, (right) catalyst activated with Al-alkyl [43]

However, recent spectroscopic studies using FT-raman have provided evidence for strong adsorption of $TiCl_4$ on the {110} lateral cut of $MgCl_2$, giving a monomeric species with octahedrally coordinated titanium, which can be the precursor for active and stereospecific sites [44-45] as shown in Figure 1.4.

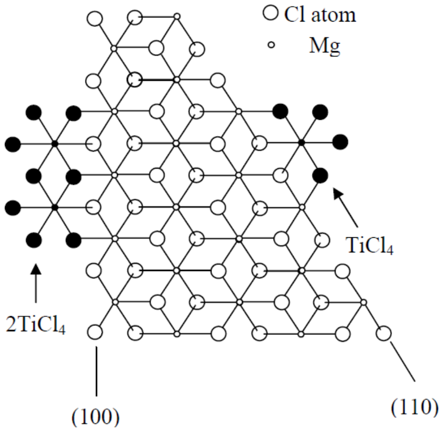


Figure 1.4. Epitaxial binding of $TiCl_4$ on the surface of δ-$MgCl_2$

1.6 Cocatalyst chemistry

Various types of cocatalyst are used with ZN catalysts, such as Al-trialkyls, triethylaluminum (TEA) and triisobutylaluminum (TiBA). Al-alkyl-Cl affords a much poorer performance and can be used only in combination with trialkyls [46]. On the other hand, the external donor which can be used appears to be dependent on the types of internal donor. If internal donor is an aromatic monoesterm esters of the same type are normally required, such as methyl-p-tolulate (MPT), wthylanisate (EA), whereas alkoxysilanes are required for the phthalates /or diethers. Hindered piperidines, such as 2,2,6,6-tetramethylpiperidines (TMP) seems to work well with diethers but give the inverse response with monoesters. However, depending on its basic nature and acidic nature of the AlR_3, a more or less complex interaction between the two components takes place. According to the most widely used information, the interaction involves the first formation of an acid-base complex through the carbonyl oxygen. The complex is most often assumed to exist in a 1:1 ratio. But, from the spectroscopic evidence and calorimetric studies[47], complexes involving two moles of AlR_3 per mole of external donor also have been hypothesized. Structures such as those represented in Figure 1.5 have been proposed by Spitz *et al.*[48], which is similar to those whose proposed by Chien *et al.*[49] and Tashiro *et al.*[50]. The complex formation is very fast even at low temperature and in diluted solutions.

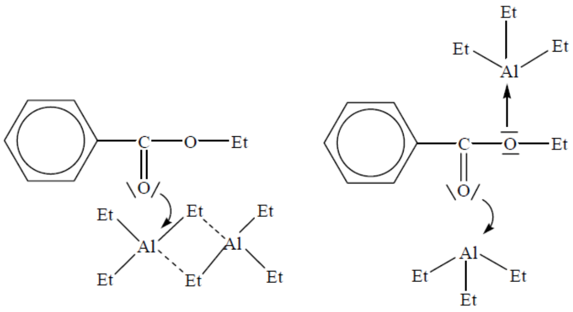


Figure 1.5. Possible structures of 1:2 EB/TEA complexes [48]

As mentioned earlier, the formation of a 1:1 complex between TEA and phenyltriethoxysilane (PTES) has been indicated by means of ^{13}C NMR spectroscopy[51]. The complex seems to involve the O atom from the only one alkoxy group, irrespective of the number of alkoxy groups attached to Si atom. This complex can undergo a further reaction, especially in the presence of excess AlR_3 as is usual for polymerization. In the case of aromatic monoesters, such as EB, a nucleophilic attack the free AlR_3 on the carbonyl group complexed with AlR_3 has been postulated. The reaction leas finally to the formation of two moles of dialkylaluminum alkoxide per one mole of ester, according to the Figure 1.6.[46]

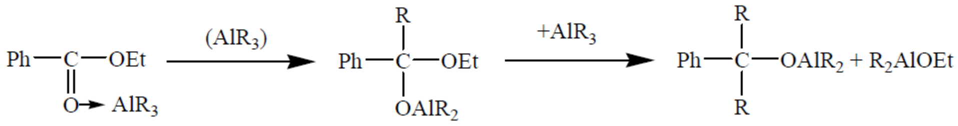


Figure 1.6. Formation of EB and AlR_3 complexation[46]

The reaction rate is higher for TEA than TiBA even at the mild conditions used in polymerization and in the presence of monomer. However, the reaction proceeds to a considerable extent. Alkoxysilane can undergo an exchange reaction with Al-alkyl, with the formation of alkylated silylethers and dialkyl-Al-alkoxides. The reaction rate is appreciable for silanes containing three or four alkoxy groups and at high concentrations of the Al-alky. Starting from $PhSi(OMe)_3$ and TEA, the reaction can proceed due to the formation of $PhEt_2SiOMe$, according to the Figure 1.7.

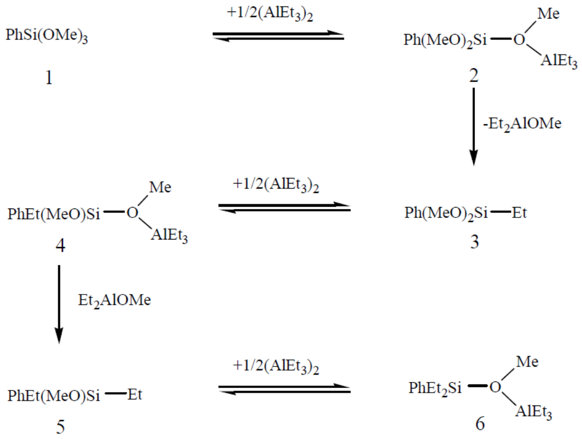


Figure 1.7. Pathway of the reaction between TEA and alkoxysilane [51].

The reaction is slower in the absence of dialkoxysilane and practically will be absent for all monoalkoxysilane structure.[51] In the case of troalkoxysilanes, the main product besides the Al-alkoxide is a dialkoxysilane derivative which different from the aromatic derivatives, still works as a good stereoregulating agent. It can be concluded that all types of external donor can easily form complexes with the AlR_3 cocatalyst. These complexes are rather stable for alkoxysilane, in the case of aromatic esters.

1.7 Mechanism of propylene polymerization

The coordination of the monomer to the transition metal before the insertion step is generally assumed. The mechanism is supported by the following experimental evidence;

1. C_6H_5 chain end groups were found in PP obtained by $TiCl_4$-$Al(C_6H_5)_3$ catalyst
2. ^{13}C NMR analysis of *i*PP, prepared in the presence of δ-$TiCl_3$ or $MgCl_2$-supported catalysts and ^{13}C-enriched $Al(CH_3)_3$, shows the presence of isobutyl chain-end groups formed in the first step of the polyinsertion reaction.
3. The presence of radioactivity in the polymer obtained by quenching with ^{14}CO the polymerization of olefins with heterogeneous and homogeneous catalysts suggests that a transition metal-carbon bond is active in polymerization, since CO does not react with Al-C bonds
4. The insertion of ethylene into a Ti-C bond has been proven for the catalytic system
5. Many catalysts are active in olefin polymerization even in the absence of main group metal alkyl. Therefore there is no doubt that polymerization occurs by insertion of the olefinic double bond into a transition metal-carbon bond.

The insertion of an α-olefin in the metal-carbon may take place in two different ways; 1,2 primary insertion or 2,1 secondary insertion. Regioregularity is extremely high in isotactic polymers obtained by heterogeneous catalysts; head-to-head and tail-to-tail enchainments are sufficiently few as to be almost undetectable by IR and NMR spectroscopy, except in weakly tactic polymer fractions. However, n-butyl end groups have been detected in propylene oligomers obtained with a δ-$TiCl_3$/Et_2AlCl catalyst at high hydrogen concentration and in oligomers and higher molecular weight PP prepared, in the presence of hydrogen, with the $MgCl_2/TiCl_4$/dialkylphthalate -$AlEt_3$-alkoxysilane catalyst system. The n-butyl end-groups arise from chain transfer with hydrogen after a 2,1 insertion, as opposed to an isobutyl end group when hain transfer with hydrogen takes pace after the normal 1,2-insertion. The knowledge of the way the metal atom of the active site,bearing the growing chain, and the last carbon atom of the chain add synchronously to the double bond of the incoming monomer is essential to investigate the mechanism of stereospecific polymerization. In all the cases investigated, isospecific polymerization and syndiospecific polymerization, the stereochemistry of the insertion has been shown to be *cis* type as shown in the three-site model which proposed by Busico et.al.[52] as shown in Figure 1.8.

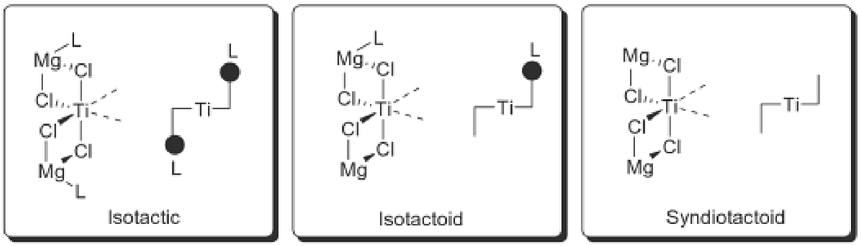


Figure 1.8. three-site model proposed by Busico et.al.[52]

Catalysts are very useful in the industrial development of the reaction but have made limited contribution to the understanding of the mechanism of polymerization. The heterogeneous nature of the catalyst, the presence on its surface of different types of active centers, the activity decay during the polymerization, the chemical medication of the components of the catalyst during the time, and the influence of the procedure of contact of catalyst components on the rate and stereospecificity of the polymerization make it difficult to study the kinetics of polymerization with these catalysts. The polymerization kinetics are affected by the process variables, catalyst, activator, monomer and hydrogen concentration, temperature, and polymerization time. Quantitative data on the number of active sites and on their reactivity in the propagating reaction are very useful for the formation of reaction mechanisms, for explaining the effect of process variables on reaction kinetics, and for interpreting the increased activity of $MgCl_2$-supported catalysts in comparison with traditional ones. Different techniques, generally based on kinetics and radio-tagging methods such as tritiated alcohol RO^3H and ^{14}CO as quenching agent, have been used for quantitative determination of the number of active sites and of the propagation rate constant. However, none of the radio tagging methods is completely reliable, as indicated by differences in the results obtained by different author. While, for kinetic method performed in the conventional laboratory scale slurry polymerization using semi-batch reactor, the shortest polymerization time of kinetics measurement would be several seconds because of disturbance of the system at the time of starting of polymerization. Even the very short time of polymerization, chain transfer reaction as side-reaction cannot be inhibited completely, so that the obtained the value of [C*] and k_p are not reliable.

1.8 Stopped-flow polymerization

There are number of researches regarding enhancement of catalytic efficiency in terms of catalyst activity, H_2 response and stereospecificity by optimizing the combination of internal and external donors by usual polymerization.[53-55] But it has been known through the elegant studies by Terano et al. that most of significant phenomena occur in the very initial stage of polymerization and these phenomena directly affects and controls the catalyst efficiency. Such phenomena can be investigated by Stopped-flow (SF) polymerization method. It was first invented by Keii and Terano in 1987 [56] to elucidate the kinetic parameters and to understand the nature and the state of active sites in olefin polymerization by $MgCl_2$-supported Ziegler-Natta catalyst in 2-vessel system of catalyst slurry and activator solution which flows through a junction point and polymerization is carried out for a very short period, then reaction was quenched by ethanol and hydrochloric acid. Due to the quasi-living polymerization characteristics of stopped-flow system (ca. 0.05-0.2 s), it is an effective way to investigate not only kinetic parameters, but also relationships between the states of active sites and polymer microstructures[57] because in quasi living stage of polymerization the unfavorable side reactions such as chain transfer, fragmentation can be neglected and it is one of the most important feature of stopped-flow system. Series of improvements have been carried out in SF since its invention but major improvement in SF has been carried out by Taniike et al. and termed the new technique as large scale stopped flow technique which works on the same principal but offers better flow rate of solution, facilitates better polymerization quenching through homogenizer and the yields can be scaled up by flowing larger volume of catalyst and activator solutions. [58]

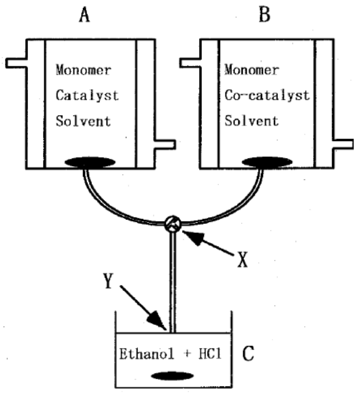


Figure 1.9. Illustration of stopped-flow polymerization [56]

There are some aspects which have already been investigated by using stopped-flow polymerization.[57] There is still an unsolved question about the board molecular weight distribution of polyolefins produced with heterogeneous Ziegler catalysts. There are three explanations that already suggested about this matter, (i) a change in the rate constants for propagation and transfer reactions at different polymer chain lengths,(ii) the existence of polymer layers leading to monomer diffusion limitation, and (iii) the existence of various active sites having different properties. From stopped-flow polymerization with $MgCl_2$-supported Ziegler catalyst, in which transfer reaction is negligible and the existence of the polymer layer can be ignored, the molecular weight distribution in the initial stage of polymerization can be determined in term of the (iii) explanation. By assuming the existence of non-uniform surface sites, Keii proposed the theory to explain the behavior of molecular weight distribution, which is the time- and temperature-dependence of polydispersity, as well as the large values of polydispersity in the initial stage of polymerization.

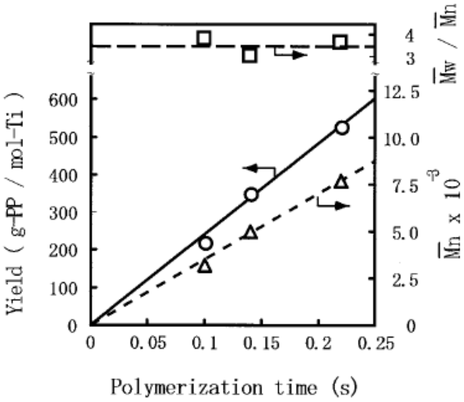


Figure 1.10. Dependence of yield, molecular weight on polymerization time[56]

The determination of the kinetic parameters is one of the useful methods to elucidate how the polymerization proceeds on the active sites formed by reaction between catalyst and cocatalyst. The rate constants of propagation (k_p) and transfer (k_{tr}) and the concentration of the polymerization centers ([C*]) were determined by the following relations;

$$\overline{M}_n = M_0 \cdot \frac{k_p \cdot [M][C^*] \cdot t}{[C^*] + k_{tr} \cdot [C^*] \cdot t}$$

$$Y = k_p \cdot [M] \cdot [C^*] \cdot t$$

Where M_0, M_n, t,Y and [M] are molecular weight of monomer, number-average molecular weight, polymerization time, polymer yield, and monomer concentration, respectively. It was shown that the polymer yield is proportional to polymerization time up to ca. 0.2 s. When rearranging the above equation, the following equation is achieved.

$$\frac{1}{\overline{P}_n} = \frac{M_0}{\overline{M}_n} = \frac{k_{tr}}{k_p \cdot [M]} + \frac{1}{k_p \cdot [M]} \cdot \frac{1}{t}$$

From the tangent and the intercept of the plot of $1/P_n$ vs $1/t$, k_p and k_{tr} were obtained. The polymerization time in the stopped-flow method is much shorter than the average lifetime of the growing polymer chains. From the Figure 1.10, the curves show a linear relationship of molecular weight versus polymerization time through the original point, meaning chain transfer reactions can be neglected. The difference of the kinetic parameters is thought to be mainly governed by the gap between the polymerization stages: the stopped-flow technique gives the information on the active sites at the very beginning, while other methods deal with the later stage of the polymerization, where the catalyst deactivation, various types of chain transfer reactions and fragmentation of catalyst particles occur simultaneously with the propagation reaction. The kinetic parameters obtained by other methods are given by superimposing the above-mentioned individual factors generated during the polymerization. From some previous study, stopped-flow polymerization method seems to reflect the intrinsic properties of the active sites just after their formation in the initial stage of polymerization.

Even a stopped-flow polymerization has given a variety of important information on active sites of heterogeneous Ziegler-Natta catalysts but absolutely short polymerization time gives a poor polymer yield and therefore it is not sufficient amount for getting precise ^{13}C NMR analysis or any other polymer fractionation which has limited its experimental applicability. So one of the approaches to increase the polymer yield per batch is to develop a large-scale stopped-flow (LSF) polymerization apparatus which invented by Taniike *et.al.*[58]. From this, polymer yield can be scaled up by the flow volume without changing any polymerization conditions. The LSF apparatus developed is illustrated in Figure 1.11. Vessels A and B were replaced by commercial three-way flasks, soaked in a circulating heat bath. For the homogeneous agitation of the catalyst slurry, a mechanical stirrer was used in the catalyst flask. The catalyst slurry and alkylaluminum solution were simultaneously transferred by a tubing pump, whose pumping rate can be adjusted from 0 – 600 rpm. Since the viscosity of the polymerization slurry linearly increases with the polymerization time, it is essential to choose a sufficiently large inner diameter in order to keep a constant transfer rate.

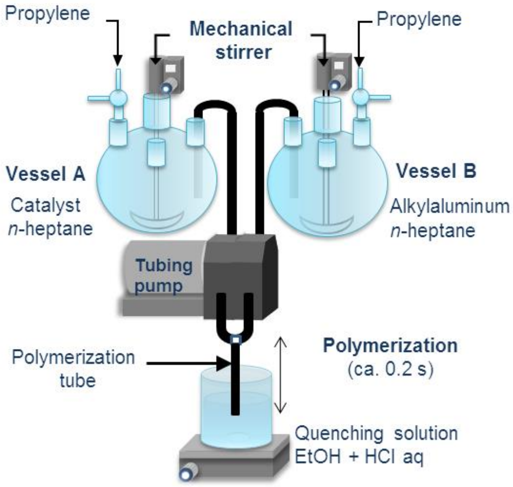


Figure 1.11. Illustration of large-scale stopped-flow system[58]

1.9 Principle of temperature rising elution fractionation (TREF) analysis

Temperature rising elution fractionation (TREF) is a separation technique for fractionating crystallizable polymers based on crystallinity. The wide application of TREF in polyolefins is related to the following features of polyolefins as (1) Most polyolefins are crystalizable , (2) polyolefins dissolve in solvents (such as xylene, trichlorobenzene and *o*-dichlorobenzene at high temperature, (3) inhomogeneous structures including board molecular weight distribution, composition distribution and tacticity distribution of polyolefins prepared with conventional Ziegler-Natta catalysts permit that polymer fractions be eluted in a wide temperature range and make them suitable for TREF analysis. When polymer fractions obtained with TREF are analyzed with ^{13}C-NMR and other methods, it is possible to obtain very detailed information about polymer microstructure and the nature of catalyst active sites.

The fractionation mechanism of TREF can be depicted as shown in Figure 1.12.[59] The operation of TREF is divided into two steps. In the first step, the dilute solution of a polymer is mixed with inert support and this mixture is slowly cooled own to room temperature. Since the decreased crystallinity will be reflected in a lower dissolution temperature, the polymer fractions precipitate from the solution and coat the support in layers of different crystallinity when the temperature decreases gradually. The most easily crystallizable fraction precipitates first and deposits on the support in the innermost layer. On the contrary, the fraction with least crystallinity precipitates last and deposits on the outermost layer. This process is of great importance and a slow cooling rate is key, since it ensures that polymer fractions precipitate orderly according to the crystallinity. A fast cooling rate may lead to cocrystallization of fractions with different crystallinity. The slow cooling rate also provides an optimal crystallizability separation which is free from significant influence of molecular weight. In the second step, the precipitated polymer is eluted with solvent at increasing temperature (continuously or stepwise). At lower temperatures,the fractions with less crystallinity (outermost layer) dissolve. With increasing elution temperature, the fractions of higher crystallinity dissolve.

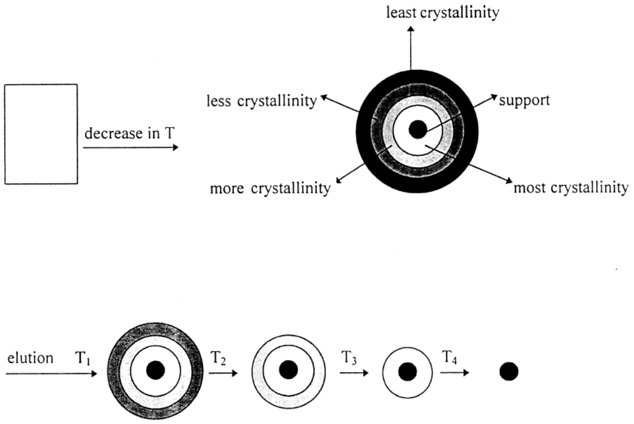


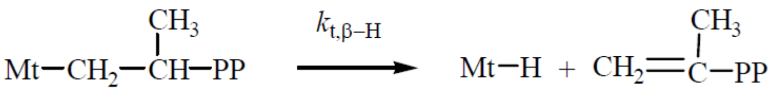
Figure 1.12. Schematic separation mechanism of TREF[59]

There are two kinds of experimental TREF apparatus: analytical and preparative TREF. Analytical TREF is generally automated. It is connected with other analytical instruments such as IR and GPC, and the structure of polymer fractions can be determined on-line. Preparative TREF is used to obtain a large amount of polymer fractions and the polymer fractions can be characterized off line by NMR and/or DSC. Preparative TREF is time-consuming, but it usually provides more information than analytical TREF and is frequently used for polypropylene. The crystallinity of polypropylene is mainly dependent on stereoregularity and regioregularity, and almost independent of molecular weight, thus the TREF curves reflect tacticity distribution of PP. Kakugo *et al.*[60] fractionated PP prepared with various Ti-based catalysts and found that the isotacticity of fractions increased with elution temperature and two peaks were observed above 100 °C. They concluded that there existed two kinds of isospecific active sites. In the PP fractions prepared with $MgCl_2$-supported catalysts, four types of different structures were identified: atactic PP containing some stereoblock structures (room temperature), PP of low isotacticity with *rr* and long *r* sequences (80 °C), PP with small amount of *rr* defects (103 °C), and high isotactic PP with no stereodefects (115 °C). These fractions were believed to be produced by different active sites.

1.10 Chain transfer reactions

Polymer chain termination occurs mostly through the following reactions: where center metal (M) and PP denote the transition metal and polymer chain, respectively. Reaction 1 and 4 are followed by a rapid insertion of the olefin into the M-H bond. All the above reported reactions are well-known in organometallic chemistry. The relative importance of the different chain transfer reactions depends on the catalyst system which is used and the process conditions. Chain transfer by β-hydride elimination is not considered important in propylene polymerization with traditional $MgCl_2$-supported catalyst at normal polymerization temperature[61-63]. This reaction becomes a significant chain transfer process in most metallocene-based catalyst system[64]. In the absence of hydrogen and under normal polymerization conditions, chain transfer to Alkyl-Al is the most important chain termination process. Chain transfer to hydrogen is the most efficient chain termination process. A half-order dependence of the chain transfer rate with respect to hydrogen has been generally found for $TiCl_3$ [65-66] and $MgCl_2$-supported catalysts [67-68]. The chain transfer reactions are shown as follows;

1. B-hydride elimination

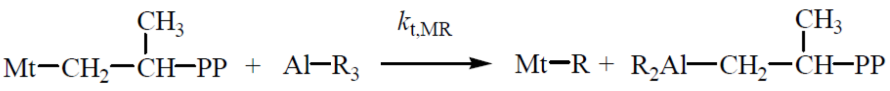


$$Mt-CH_2-\overset{CH_3}{CH}-PP \xrightarrow{k_{t,\beta-H}} Mt-H + CH_2=\overset{CH_3}{C}-PP$$

2. Transfer to monomer

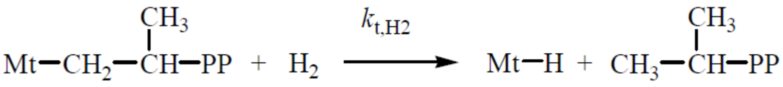
$$Mt-CH_2-\overset{CH_3}{CH}-PP \xrightarrow{k_{t,M}} Mt-CH_2-\overset{CH_3}{CH_2} + \overset{CH_3}{CH}=CH-PP$$

3. Transfer to cocatalyst



$$Mt-CH_2-\overset{CH_3}{CH}-PP + Al-R_3 \xrightarrow{k_{t,MR}} Mt-R + R_2Al-CH_2-\overset{CH_3}{CH}-PP$$

4. Transfer to hydrogen



$$Mt-CH_2-\overset{CH_3}{CH}-PP + H_2 \xrightarrow{k_{t,H2}} Mt-H + CH_3-\overset{CH_3}{CH}-PP$$

1.11 Effects of hydrogen

Hydrogen is considered to be the most active transfer agent commonly used as a standard molecular weight modifier in commercial polyolefin production plants. Several researchers [69-72] demonstrated that the addition of hydrogen in propylene polymerization caused a significant activity increase, but on the contrary, substantially reduces the activity in ethylene polymerization. It was proven that the hydrogen did not affect the propagation rate constant and did not lead to the formation of new active sites [72]. The experimental results indicate that the hydrogen activation effect in the propylene polymerization corresponds to the regeneration of the dormant sites by the transfer reactions with hydrogen

[73-76]. These inactive dormant sites originate from the irregular 2,1-insertion [77-79]. Kojoh *et al.* [80] applied ^{13}C-NMR for the detection of polymer chain ends in the PP production in the presence of hydrogen. It was found that the hydrogen addition leads not only the conversion of the 2,1-dormant sites into the active sites, but also to a decrease in the frequency of 2,1- insertions. Terano *et al.* [81-83] used the stopped-flow method, observed no effect of hydrogen in the initial stage of polymerization. Further studies showed that the chain transfer with hydrogen occurs only with dissociated atomic hydrogen[81,84]. They applied $PdCl_2$ for enhancing hydrogen production by dissociation of hydrogen molecules. Consequently, the atomic hydrogen induced a chain transfer in the initial stage of propylene polymerization. Kissin *et al.* [85-87] proposed a plausible explanation for the ethylene polymerization activity decrease after the introduction of hydrogen. It was assumed that the $Ti-C_2H_5$ bond is unusually stable due to the strong β-agostic interaction between the hydrogen atom of the methyl group and the Ti atom. The introduction of hydrogen causes the more frequent generation of Ti-H bonds, leading to the formation of stabilized $Ti-C_2H_5$ bonds and a deceleration of polymerization. Moreover, the extensive investigation of the hydrogen effect on MWD was performed by Al-haj Ali[88-89] indicating that the dependence of average molecular weight on hydrogen could be described by the model based on dormant sites over the wide range of hydrogen concentrations.

1.12 Effects of comonomer

Isotactic polypropylene is widely used in various applications such as fibers and injections molding. The relatively high melting point employs its interesting properties in wide temperature range. But in some viewpoints, homopolypropylene is high stiffness but it is too rigid and the transparency is poor. Some applications require a higher flexibility and clarity with a lower melting point combined with the good stiffness. Propylene copolymerization is the objective to achieve these required properties. As far as PP toughening is concerned, it is known that a material constituted of an elastomeric poly(propylene-co-ethylene) copolymer, well dispersed in a homopolymer matrix, shows an improved low temperature impact resistance together with an sufficient stiffness.

There are two possible copolymer structures obtained from propylene-ethylene copolymerization, random and sequential copolymer. Random copolymer is obtained when copolymer content is up to 7%. For, sequential copolymer or impact copolymer, ethylene molecules are linked among propylene chain. Thus, the polymer structure is contained with segmented polyethylene and polypropylene. The characteristics of polypropylene are summarized in Table 1.5.[90]

Table 1.5. Characteristics of polypropylene.

Type of polypropylene(a)	Comonomer content (wt%)	Impact resistance	Film Clarity	Tensile strength
Homopolymer	0	Poor	Poor	Good
Random copolymer	1-7	Medium	Good	Medium
Impact copolymer	5-25	Good	-	Poor

(a) Densities of all types are in the range of 0.89 – 0.91 g/mL

1.13 Coadsorption energies

The performance of $MgCl_2$-supported ZN catalysts for propylene polymerization is strongly dependent on the molecular structure of donors. Atomic-level understanding of the catalyst components and their interactions would provide valuable information regarding further development of the polymerization process. Due to the complexity of the whole system, computational and modeling techniques have been exploited to address the binding of $TiCl_4$ and electron donors to $MgCl_2$ support.[91-94] Coadsorption of $TiCl_4$ and electron donors has been shown to provide several effects. Donors present in excessive amounts may lead to effective poisoning of the polymerization active sites via direct binding to the Ti atom, therefore affecting molecular weights of the polymeric products.[95-96] Besides, donors bound to the $MgCl_2$ surfaces in the proximity of the Ti species may alter their steric environment and improve stereospecificity.[97-98] Moreover, donors bound to the adjacent sites may provide the active sites with the electron density transmitted through the $MgCl_2$ support.[99-100] There are several researches trying to apply the Density functional calculations based on coadsorption model examining the molecular behavior of donor coadsorbed with an active Ti species during the propylene insertion. Taniike *et al.* [99-100] examined the molecular behavior of ethylbenzoate and found that the suitable confinement of the flexibility was proposed to be essential for active and isospecific propylene insertion, which might be achieved by steric interference between EB molecules adsorbed close to each other on the $MgCl_2$ surface. In the recent study, Taniike also propose the coadsorption model for first-principle description of roles of donor to clarify mechanism for donors exerting steric and electronics influences on propylene polymerization.[101] From this coadsorption model, it believed to be useful for the prediction of new donor structures after determination with a variety of experimentally known facts.

1.14 Objectives of this study

Polypropylene is an interesting polyolefin, which the production rate has been increasing annually. Because of its excellent properties, it has been used in many applications. The development of technology and the research in polyolefin also expand range of usage and make polypropylene more and more advanced material. To develop the new PP applications, improving the catalyst performance is one of the most effective approaches. Due to the importance of donors which is already explained earlier, it makes the development of new donor system interesting for the target to provide a wide range of tailor-made product properties. A development of new external donor is the effective approaches due to the unnecessity changes in solid catalyst system. Although several researches have already tried attempt to understand the effects of alkoxysilane external donor on the catalyst performances. But the systematic investigation is still required.

In this dissertation, the author intensively investigated the structure-performance relationship of alkoxysilane on the catalyst performance in terms of catalyst activity, stereospecificity, comonomer incorporation and hydrogen response. The study was divided into four chapters.

Chapter 2: Structure-performance relationship of dimethoxysilane in propylene homopolymerization. In this chapter, the correlation between dialkyldimethoxysilane and catalyst performance in terms of catalyst activity and stereospecificity was explored.

Chapter 3: Structure-performance relationship of triethoxysilane in propylene homopolymerization. The other type of alkoxysilane was applied as an external donor to verify the effects on the catalyst performance, aiming at the generalization of SPR through various types of alkoxysilane.

Chapter 4: Effects of alkoxysilane structures on propylene copolymerization. In this chapter, it was explained the relationship of alkoxysilane on the other catalyst performance which is not verified yet. Comonomer incorporation efficiency was determined with the different alkoxysilane structures used as external donor.

Chapter 5: Effects of alkoxysilane structures on propylene polymerization in the presence of hydrogen. Because external donor can regulate the hydrogen response which is also the important performance for PP production, the effects of alkoxysilane structure on the hydrogen response was investigated in this chapter.

The summary and general conclusion were be reported in Chapter 6.

References

1. E. Albizzati, U. Giannini, G. Collina, L. Noristi, L. Resconi, *Propylene Handbook*, E. P. Moore, Ed., Hanser, New York **1996**, Chapter 2.

2. G. Morini, E. Albizzati, G. Balbontin, I. Mingozzi, *Macromolecules* **1996**, *29*, 5770.

3. E. Magni, G.A. Somorjai, *J.Phy.Chem*. **1998**, *102*, 8788.

4. B. Liu, T. Nitta, H. Nakatani, M. Terano, *Macromol. Chem. Phys*. **2003**, *204*, 395.

5. P. Galli, *Structural order in polymers*, F. Ciardelli, P.Giusti, Ed., Pergamon Press **1981**, p.63

6. W. Erik, J. Arthur, W. Langer, N. J. Watchung, *U.S. Patent 3130003*, **1964**, Esso Research and Engineering Company.

7. W. Erik, J. Arthur, W. Langer, N. J. Watchung, *U.S. Patent 3032510*, **1962**, Esso Research and Engineering Company.

8. *German Patent 2213086*, **1972**, Solvay & CIE.

9. J. P. Hermans, S. Bever, P. Heuriulle, *U.S. Patent 3769233*, **1973**, Solvay & CIE.

10. *British Patent 1286867*, **1968**, Montedison.

11. I. Pasquon, U. Giannini, *Catalysis Science and Technology,* J. R. Anderson, M. Boudart, Eds., Springer Verlag, Berlin **1984**, Vol.6.

12. B. L. Goodall, A. A. Nat, W. Sjardijn, *U. S. Patent 4414132*, **1979**, Shell Oil.

13. B. L. Goodall, A. A. Nat, W. Sjardijn, *U. S. Patent 4393182*, **1979**, Shell Oil.

14. B. L. Goodall, *Transition metal Catalyzed polymerizations*, R. P. Quirk, Ed., Harwood Academic Publishers, New york **1983**, p.355.

15. *European Patent 45977*, **1982**, Motedison.

16. E. Albizzati, P. C. Barbé, L. Noristi, *Angew. Makromol. Chem. 120*, **1980**, 73

17. *Belgian Patent 845593*, **1975**.

18. *Belgian Patent 745325,* **1969,** Solvay & CIE.

19. *U. S. Patent 4829037,* **1989**, Toho Titanium Co.

20. E. Albizzati, U. Giannini, G. Collina, L. Noristi, L. Resconi, *Propylene Handbook*, E. P. Moore, Ed., Hanser, New York **1996**, Chapter 3.

21. L. Luciani, N. Kashiwa, P.C. Barbé, A. Toyama, *German Patent 2643143,* **1977**.

22. S. Parodi, R. Nocci, U. Giannini. P. C. Barbé, U. Scata, *European Patent 45976*, **1981**.

23. M. Kioka, A. Toyama, N. Kashiwa, *European Patent 115195,* **1983**.

24. T. Yamamoto, H. Furuhashi, M. Imai, H. Ueno, N. Inaba, *European Patent 147053*, **1984**.

25. P. C. Barbé, E. Albizzati, U. Giannini, G. Baruzzi, L. Noristi, *European Patent 276573*, **1987**.

26. A. Guyot, C. Bobichon, R. Spitz, L. Duranel, J. L. Lacombe, *Transition metals and organometallics as catalysts for olefin polymerization*, W. Kaminsky, H. Sinn, Eds. Springer Verlag, Berlin **1988**, p.13.

27. N. Kashiwa, S. Kojoh, *Makromol. Chem.***1995**, *89*, 27.

28. J. V. Seppälä, M. Härkönen, L. Luciani, *Makromol. Chem*. **1989**, *190*, 2535.

29. J. V. Seppälä, M. Härkönen, *Makromol. Chem*. **1991**, *192*, 2857.

30. M. Härkönen, J. V. Seppälä and T. Väänänen, *Makromol. Chem*. **1991**, *192*, 721.

31. T. Yano, T. Inoue, S. Ikai, M. Shimizu, Y. Kai, M. Tamaura, *J. Polym. Sci. Part A: Polym. Chem.***1988**, *26*, 477.

32. J. C. W. Chien, J. C. Wu, C. I. Kuo, *J. Polym. Sci. Part A: Polym. Chem.***1983**, *21*, 725.

33. J. C. W. Chien, C. L. Dickinson, J. Vizzini, *J. Polym. Sci. Part A: Polym. Chem***,1990**, *28*, 232.

34. M. Terano, M. Saito, T. Kataoka, *Makromol. Chem*. **1992**, *13*, 103.

35. J. A. Ewan, R. L. Jones, A. Razavi, J. D. Ferrara, *J. Am. Chem. Soc*. **1988**, *110*, 6255.

36. A. Guyot, R. Spitz, L. Duranel, J. L. Lacombe, *Catalytic polymerizaiton of olefins*, T. Keii, K. Soga, Eds., Kodansha Elsevier, Tokyo **1986**, p. 147.

37. S. A. Sergeev, V. A. Polabayarov, V. A. Zakharov, V. F. Anufrienko, G. D. Bukatov, *Makromol. Chem*. **1985**, 186, 243.

38. J. C. W. Chien, Y. Hu, *J. Polym. Sci. Part A: Polym. Chem.***1989**, *27*, 897.

39. E. Albizzi, U. Giannini, G. Morini, C. A. Smith, R. Ziegler, *Ziegler Catalysts*, G. Fink, R. Mulhaupt, H. Brintzinger, Eds., Springer Verlag **1995**, p. 413.

40. V. Busico, P. Corradini, A. Ferraro, A. Proto, V. Savino, E. Albizzati, *Makromol. Chem*. **1985**, *186*, 1279.

41. V. Busico, P. Corradini, A. Ferraro, A. Proto., *Makromol. Chem*. **1986**, *187*, 1125.

42. J. C. W. Chien, S. Weber, Y. Hu, *J. Polym. Sci. Part A: Polym. Chem*. **1989**, *27*, 1499.

43. J. C. W. Chien, S. Weber, Y. Hu, *J. Polym. Sci. Part A: Polym. Chem.* **1989**, *27*, 1480.

44. L. Brambilla, G. Zerbi, S. Nascetti, F. Piemontesi, G. Morini, *Macromol. Symp.* **2004**, *213*, 287.

45. L. Brambilla, G. Zerbi, S. Nascetti, F. Piemontesi, G. Morini, *J. Mol. Catal. A: Chem.* **2007**, *263*, 103.

46. P. C. Barbe, G. Cecchin, L. Noristi, *Adv. Polym. Sci*. **1986**, *81*, 1.

47. E. Albizzati, M. Galimberti, U. Giannini, G. Morini, *Macromol. Symp.* **1991**, *48*, 223.

48. R. Spitz, J. L. Lacombe, M. Primet, *J. Polym. Sci., Part A: Polym. Chem*. **1984**, *22*, 2611.

49. J. C. W. Chien, J. C. Wu, *J. Polym. Sci., Part A: Polym. Chem.* **1982**, *20*, 2445.

50. K. Tashiro, M. Yokohama, T. Sugano, K. Kato, *Contemporary Topics in Polymer Science*, **1984**, *4*, 647.

51. E. Vähäsärja, T. T. Pakkanen, T. A. Pakkanen, E. Iiskola, P.Sormunen, *J. Polym. Sci., Part A: Polym. Chem.* **1987**, *25*, 324.

52. V. Busico, R. Cipullo, G. Monaco, G. Talarico, M. Vacatello, J. C. Chadwick, A. L. Segre, O. Sudmeijer, *Macromolecules* **1999**, *32*, 4173.

53. K. Soga, T.Shiono, Y. Doi, *Makromol.Chem.***1988**, *189*, 1531

54. A. Proto, L. Oliva, C. Pellecchia, A. J. Sivak, L. A. Cullo, *Macromolecules* **1990**, *23*, 2904.

55. M. C. Sacchi, F. Forlini, I. Tritto, R. Mendichi, G. Zannoni, *Macromolecules* **1992**, *25*, 5914.

56. T. Keii, M. Terano, K. Kimura, K. Ishii, *Macromol. Rapid Commun*. **1987**, *8*, 583.

57. B. Liu, H. Matsuoka, M. *Terano, Macromol. Rapid Commun*. **2001**, *22,* 1.

58. T. Taniike, S. Sano, M. Ikeya, V.Q. Thang, M. Terano. *Macromol. React. Eng*. **2012**, *6*, 275.

59. J. Xu, L. *Feng, European Polymer Journal* **2000**, *36*, 867.

60. M. Kakugo, H. Sadatoshi, J. Sakai, M. Yokoyama, *Macromolecules* **1989**, *22*, 3172.

61. V. Zakkharov, G. Bukatov, Y. Yermakov, *Industrial developments* **1983**, p. 61.

62. P. Pinp, B. Rotzinger, E. V. Achenbach, *Makromol. Chem*. **1985**, *25*, 461.

63. A. A. Baulin, A. G. Radionov, S. S. Ivanchev, N. N. Domreva, *Eur. Polym. J*. **1980**, *25*, 461.

64. J. C. W. Chien, B. P. Wang, *J. Polym. Sci., Part A: Polym. Chem*. **1990**, *28,* 15.

65. T. Keii, *Kinetics of Ziegler-Natta Polymerization*, Kodansha, Tokyo **1972**, p. 89.

66. T. Keii, *Hetereogeneous Kinetics*, Kodansha Springer, Tokyo **2004**.

67. T. Keii, Y. Doi, E. Suzuki, M. Tamaura, M. Murata, K. Soga, *Makromol. Chem*. **1984**, *185*, 1537.

68. G. Guastalla, U. Giannini, *Makromol. Chem., Rapid Commun*. **1983**, *4*, 519.

69. J. C. Chadwick, A. Miedema, O. Sudmeijer, *Macromol. Chem. Phys*. **1994**, *195*, 167.

70. G. Guastalla, U. Giannini, *Makromol. Chem., Rapid Commun*., **1983**, *4*, 519.

71. Y. V. Kissin, *Makromol. Chem., Macromol. Symp*. **1993**, *66*, 83.

72. H. Mori, E. Endo, K. Tashino, M. Terano, *J. Mol. Catal. A, Chem*. **1999**, *145*, 153.

73. J. C. Chadwick, A. Miedema, O. Sudmeijer, *Macromol. Chem. Phys.* **1994**, *195*, 167.

74. J. C. Chadwick, G. M. M. vanKessel, O. Sudmeijer, *Macromol. Chem. Phys*. **1995**, *196*, 1431.

75. G. D. Bukatov, V. S. Goncharov, V. A. Zakharov, *Macromol. Chem. Phys*. **1995**, *196*, 1751.

76. S. Kojoh, M. Kioka, N. Kashiwa, M. Itoh, A. Mizuno, *Polymer* **1995**, *36*, 5015.

77. T. Tsutui, N. Kashiwa, A. Mizuno, *Makromol. Chem., Rapid Commun.* **1990**, *11*, 565.

78. P. Corradini, V. Busico, R. Cipullo, *Catalyst Design for Tailor-made Polyolefins,* Eds., K. Soga, M. Terano, Kodansha-Elsevier, Amsterdam London New York Tokyo **1994**, Vol. 89, p. 21.

79. V. Busico, R. Cipullo, P. Corradini, *Makromol. Chem., Rapid Commun*. **1992**, *13*,15.

80. S. Kojoh, M. Kioka, N. Kashiwa, M. Itoh, A. Mizuno, *Polymer* **1998**, *39*, 6309.

81. B. Liu, H. Matsuoka, M. Terano, *Macromol. Rapid Commun.* **2001**, *22*, 1.

82. B. Liu, H. Matsuoka, M. Terano, *Macromol. Symp.* **2001**, *165*, 3.

83. H. Mori, K. Tahino, M. Terano, *Macromol. Rapid Commun*.**1995**, *16*, 651.

84. H. Mori, K. Tahino, M. Terano, *Macromol. Chem. Phys*.**1996**, *197*, 895.

85. Y. V. Kissin, R. I. Mink, T. E. Nowlin, *J. Polm. Sci., Part A, Polym. Chem*. **1999**, *37*, 4255.

86. Y. V. Kissin, A. J. Brandolini, *J. Polm. Sci., Part A*, *Polym. Chem*. **1999**, *37*, 4273.

87. Y. V. Kissin, R. I. Mink, T. E. Nowlin, *J. Polm. Sci., Part A, Polym. Chem*. **1999**, *37*, 4281.

88. M. Al-haj Ali, Ph.D. Thesis, University of Twante, 2006.

89. M. Al-haj Ali, B. Betlem, B. Roffel, G. Weickert, *AIChE Journal*, **2006**, *52*, 1866.

90. D. B. Malpass, E. Band, *Introduction to Industrial Polypropylene: Properties, Catalysts Processes,* Wiley-Scrivener, Massachusetts, United States of America.

91. N. Bahri-Laleh, A. Correa, S. Mehdipur-Ataei, H. Arabi, M. N. Haghigli, G. Zohuri, L. Cavallo, *Macromolecules* **2011**, *44*, 778.

92. D. V. Stukalov, V. A. Zakharov, *J. Phys. Chem.* **2009**, *113*, 21376.

93. A. Turunen, M. Linnolahti, V. A. Karttunen, T. A. Pakkanen, P. Denifl, T. Leinonen, *J. Mol. Catal. A: Chem*. **2011**, *334*, 103.

94. R. Credendino, J. T. M. Peter, A. Correa, G. Morini, L. Cavallo, *J. Phys. Chem. C* **2011**, *115*, 13322.

95. M. Seth, T. Ziegler, *Macromolecules* **2003**, *36*, 6613.

96. H. Weiss, M. Boero, M. Parrinello, *Macromol. Symp.* **2001**, *173*, 137.

97. A. Correa, R. Credendino, J. T. M. Peter, G. Morini, L Cavallo, *Macromolecules* **2012**, *45*, 3695.

98. A. Correa, F. Piemontesi, G. Morini, L. Cavallo, *Macromolecules* **2007**, *40*, 9181.

99. T. Taniike, M. Terano, *Macromol. Rapid Commun*. **2007**, *28*, 1918.

100. T. Taniike, M. Terano, *Macromol. Symp*. **2007**, *260*, 98.

101. T. Taniike, M. Terano, *J. Catal.* **2012**, *293*, 39.

Chapter 2

Structure-performance relationship of dialkoxysilane external donor in propylene polymerization

1. Introduction

For propylene polymerization with $MgCl_2$-supported Ziegler-Natta (ZN) catalysts, Lewis bases called donors are key additives to improve the catalyst performance.[1,2] Donors are classified into two types: Internal donors are introduced during catalyst preparation and external donors are additional components which are externally introduced during polymerization. It can be seen that donors are important for the improvement of catalyst performance including the catalyst activity, stereospecificity, hydrogen response, comonomer incorporation efficiency, polymer molecular weight distribution, and etc. During the revolution of ZN catalyst system, there is the development of the combination between internal and external donor to update the ZN catalyst. These are benzoate/benzoate, phthalate/alkoxysilane, 1,3-diether/(alkoxysilane) and succinate/alkoxysilane. Due to the unnecessity to change the existing solid catalyst system, it made the external donor more preferable for the development of donor system, especially alkoxysilanes since the 4th generation which is the most commercially used.[3]

Since internal donors (except 1,3-diether) are gradually removed from catalyst surfaces during polymerization to cause performance deterioration,[1] external donors are usually added in order to augment advantages of internal donors. On the other hand, the usage of external donors in the absence of internal donors is not able to improve the catalyst performance as much as a level achieved by combination usage. It is believed that internal donors have a specific role to structure catalyst surfaces in catalyst preparation, while external donors fill vacant spaces formed after the removal of internal donors from the surfaces. Nonetheless, mechanisms for external donors to improve the catalyst stereospecificity have been discussed on the same ground with those for internal donors. A number of hypotheses have been proposed in previous numerous studies such as poisoning of non-stereospecific centers, increase in the propagation rate constant (k_p) for stereospecific centers, conversion of non-stereospecific or isospecific sites into highly isospecific sites.[4,5,6,7] Representatively, Busico et al. and Terano et al. proposed a three-site model as a general active site model in Ziegler-Natta catalysts, where donor molecules coadsorb in the vicinity of a Ti site to sterically improve its stereospecificity.[8,9] Taniike et al. proposed a coadsorption model by means of systematic density functional theory (DFT) calculations in close comparison with experimentally known facts. They proposed that aspecific Ti mononuclear species located on $MgCl_2$ (110) surfaces is converted into an isospecific site as a result of random coadsorption of donors: Donors improve the stereospecificity, regiospecificity, and the tendency for chain growth in a way to form an active site, whose structure and performance are sensitive to the molecular structure of donors.[10]

As is known, the catalyst performance greatly depends on the type and structure of donors.[11] To enable systematic development of new donor structure, the understanding of relationships between the molecular structure of donors and resultant olefin polymerization performance is essential. There have been several studies reported for effects of alkoxysilane structure on catalyst performance,[12-18] among which a research by Seppälä et al. can be regarded as the most comprehensive one. They found that the catalyst performance including the activity, stereospecificity, molecular weight and molecular weight distribution strongly depends on the number and size of alkoxy groups as well as on the size of hydrocarbon groups attached to the silicon atom.[14] Yao et al. applied quantitative structure-activity relationship (QSAR) in order to establish statistical relationships between molecular properties of nitrogen-containing alkoxysilanes and the catalyst performance (activity and molecular weight distribution of polypropylene).[15] Sacchi et. al. explained that the activation of isospecific sites and the poisoning of non-stereospecific sites can be modulated by varying the number and relative bulkiness of both hydrocarbon and alkoxy substituent.[17] Gupta et. al. use trialkoxysilane to observe the increase of the bulkiness of alkyl group leads to the increase of melt flow rate and the decay kinetic constant of propylene polymerization.[18]

In this way, effects of molecular structure of alkoxysilanes have been more or less understood in an empirical or qualitative way. However, it is still unclear how alkoxysilanes with different structures affect the catalyst performance at the level of active sites, and it is also difficult to predict new structure without knowing such a molecular mechanism.

In this chapter, three types of polymerization: stopped-flow (SF) polymerization, slurry polymerization and pressurized polymerization were carried out in order to elucidate the structure-performance relationship of dimethoxysilane in the different polymerization conditions. The SF technique, which was invented by Keii and Terano,[19] enables the precise control of polymerization time at a time scale much shorter than typical lifetime of active sites for transformation and deactivation.[20] Then, SF technique was employed in combination with temperature rising elution fractionation (TREF) which active site distribution can be analysed from the obtained polymer. Moreover, DFT calculations based on the coadsorption model was also applied to investigate the correlation between experimental results and calculated parameters. From the results, it was found that an alkoxysilane which adsorbed more strongly on $MgCl_2$ surfaces tended to give a higher polymer yield, while simulated stereospecificity well correlated with the experimental stereoregularity of polypropylene, where the conformation detail around active sites played a key role.

2. Experimental Section

2.1. Raw Materials

Propylene (donated by Japan Polypropylene Corporation), $MgCl_2$ (65.1 m^2g^{-1}, donated by Toho Titanium Co., Ltd.), triisobutylaluminum (TiBA, donated by Tosoh Finechem Corporation), and $TiCl_4$ were used as delivered. Heptane was used after passing through a column of 4Å molecular sieves and bubbling with dry nitrogen for 2 h. Ethanol / hydrochloric acid (90/10 v/v) was used for quenching. The dimethoxysilanes were used as external donors as shown in Table 2.1 and Figure 2.1.

Table 2.1. List of dimethoxysilane external donors used in propylene polymerization

Name	Alkoxysilane
DMDMS	dimethyldimethoxysilane
DiPDMS	di-i-propyldimethoxysilane
DnBDMS	di-n-butyldimethoxysilane
DiBuDMS	di-i-butyldimethoxysilane
DCPDMS	dicyclopentyldimethoxysilane
DPDMS	diphenyldimethoxysilane
DCHDMS	dicyclohexyldimethoxysilane

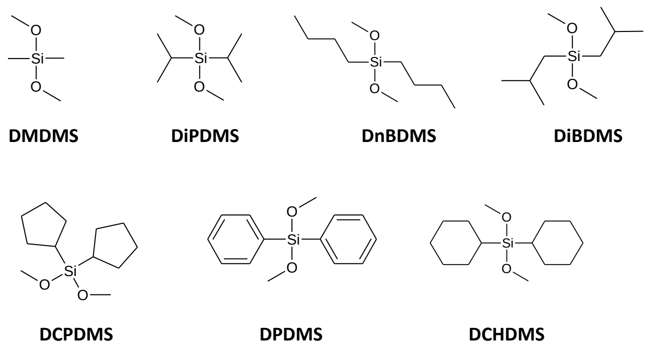


Figure 2.1. Dimethoxysilane external donors

2.2. Catalyst Preparation

In this study, two types of catalyst: internal donor-free ($TiCl_4/MgCl_2$) catalyst and internal donor-contained catalyst ($TiCl_4$/DiBP/$MgCl_2$) catalyst were used to investigate the effects of alkoxysilane external donor in the absence and presence of internal donor.

2.2.1 Internal donor-free catalyst

An internal donor-free catalyst was prepared by the following procedure.[7] 36 g of $MgCl_2$ and 100 mL of $TiCl_4$ were transferred into a 1.2 L stainless steel vibration mill pot with 55 stainless balls (25 mm diameter) and ground for 30 h at room temperature under nitrogen atmosphere. After that, the ground product was reacted with 150 mL of $TiCl_4$ in a 1 L stirred flask for 2 h at 90 °C under nitrogen. Thus obtained catalyst was repeatedly washed with heptane and kept as slurry in heptane under nitrogen. The Ti content was measure by UV-Vis spectroscopy (JASCO V670) as 1.8 wt%.

2.2.2 Internal donor-contained catalyst

A $TiCl_4/DiBP/MgCl_2$ catalyst was prepared from Mg(OEt)2 based on patent[29] with the minor modification[30]. The Ti and DiBP contents in the catalyst were determined as 3.4 and 12 wt%, respectively.

2.3. Polymerization Procedures

In this study, three types of polymerization were carried out for comparison: slurry polymerization, two-vessel SF polymerization and three-vessel SF polymerization. Their details are described as follows.

2.3.1. Slurry Polymerization

Propylene polymerization was carried out in a stirred flask containing 200 mL of heptane and 2 mmol of TiBA (at the Al/Ti molar ratio of 30). After propylene saturation at 1 atm and 30 °C, 0.3 mmol of an external donor was added followed by the addition of 0.17 g of the catalyst. The polymerization was continued under continuous supply of propylene at 1 atm and 30 °C for 10 min. The polymerization was terminated by adding acidic ethanol. The polymer was reprecipitated by ethanol and dried in vacuum for 6 h at 60 °C.

2.3.2. Two-Vessel SF Polymerization

A large-scale stopped-flow apparatus was used in this study, whose detail had been described in our previous paper.[19] 1 L of catalyst slurry in heptane containing 4.67 mmol of Ti and 1 L of TiBA solution in heptane containing 140 mmol of Al were respectively charged into stirred flasks under nitrogen. After propylene saturation at 1 atm and 30 °C, the catalyst slurry and the TiBA solution were respectively transferred with a tubing pump at the flow rate of 10 mL s^{-1}. The polymerization was initiated at the T junction, where the catalyst slurry and the TiBA solution were mixed. The polymerization time was fixed at 0.4 s. The polymerization slurry was quenched in acidic ethanol, which was vigorously stirred with a homogenizer to instantaneously quench the polymerization. The obtained polymer was washed with distilled water, followed by reprecipitation with xylene/ethanol. Then the polymer was dried in vacuum for 2 h at 60 °C.

2.3.3. Pressurized polymerization

Propylene homopolymerization was performed in a 1 L autoclave equipped with a mechanical stirrer rotating at 350 rpm. 500 ml of *n*-heptane was introduced into the reactor. TEA ([Al] = 10 mmol/L) and alkoxysilanes (Al/Si = 5) were introduced into the reactor, and the solution was saturated with 0.5 MPa of monomer at 50°C. 30 mg of a catalyst was injected into the reactor to initiate the polymerization. The polymerization was conducted for 60 min with a continuous supply of monomer gas at 0.5 MPa. After 60 min, propylene was vented and the polymer slurry was filtered immediately after mixing with quenching solution.

2.4. Polymer Analyses

2.4.1. Solvent Fractionation

100 mg of a PP sample was once dissolved in *o*-dichlorobenzene (ODCB) at 150 °C and naturally cooled down to room temperature for precipitating the insoluble fraction. After filtration and vacuum drying, the weight percentage of the insoluble fraction was measured.

2.4.2. Temperature Rising Elution Fractionation (TREF)

The isotacticity distribution of PP samples was determined by TREF (Senshu SSC-7300) with ODCB as an extraction solvent, which contained 0.03 wt% of 2, 6-di-tert-butyl-4-methyphenol as an antioxidant. 100 mg of a PP sample was dissolved in 10 mL of ODCB at 150 °C for 3 h. A part of solution was passed through the fraction column, which was then gradually cooled down from 140 °C to room temperature. Then the column was heated gradually up to 140 °C. The eluted PP solution was analyzed by an IR detector to obtain the TREF profile.

2.4.3. ^{13}C NMR spectroscopy for mesopentad fraction

Mesopentad fraction of PP samples were determined by ^{13}C NMR (Bruker 400 MHz) at 120 °C using 1,2,4-trichlorobenzene as a diluent and 1,1,2,2-tetrachloroethane-*d2* as an internal lock and reference.

2.5. Density Functional Theory (DFT) Calculations

All the DFT calculations were implemented according to the coadsorption model as described in our previous literature.[10] Briefly, the exchange-correlation functional of Perdew-Burke-Ernzerhof (PBE)[22] and the basis set of DNP plus effective core potentials[21] were employed within the program of DMOL3.[24] The active sites at the {110} edge on the {104} surface of $MgCl_2$ were regarded as the most plausible active sites for the coadsorption of alkoxysilanes.[25] The adsorption energy of each alkoxsysilane on the {110} edge at the proximity of mononuclear $TiCl_4$ was calculated as ΔE_{ad}, while the stereospecificity ($\Delta\Delta E_{stereo}$) was given as a differential activation energy of two propylene 1,2-insertion pathways with *re* and *si* prochiral faces. The transition state for each insertion pathway was approximated by the structure obtained at 2.2 Å of the distance between the propylene C_2 carbon and the C_α carbon of an isobutyl group bound to the Ti center. Further details are found in literature [10,25].

3. Results and Discussion

3.1. Effects of Alkoxysilane Structure

To study effects of the alkoxysilane structure on the catalyst performance, three types of polymerization were carried out. In the case of slurry polymerization and SF polymerization, an internal donor-free catalyst was used. An internal donor-contained catalyst was applied only in pressurized polymerization. The yields of the obtained polymer are summarized in Table 2.2.

Table 2.2. Yields of propylene polymerization for various dimethoxysilanes

Alkoxysilanes	slurry polymerization[a)] [g-PP/mol-Ti]	SF polymerization[b)] [g-PP/mmol-Ti]	Pressurized polymerization[c)] [g-PP/mmol-Ti·h·atm]
DMDMS	40	17	31
DIPDMS	30	10	19
DiBuDMS	25	8.0	11
DnBDMS	28	9.0	17
DCPDMS	35	16	30
DCHDMS	22	7.5	15
DPDMS	28	9.5	17

[a)] polymerization conditions: $TiCl_4/MgCl_2$ catalyst, 20 min, 30 °C, Al = 2 mmol, Al/Ti = 30, Al/Si = 6

[b)] polymerization conditions: $TiCl_4/MgCl_2$ catalyst, 0.4 s, 30 °C, [Al] = 140 mmol/L, Al/Ti = 30, Al/Si = 6

[c)] polymerization conditions: $TiCl_4$/DiBP/$MgCl_2$ catalyst, 60 min, 50 °C, Al = 5 mmol, Al/Si = 5

In all of the cases, the addition of an external donor accompanied decreases in the polymer yield. This phenomenon is usual when an external donor is added to an internal donor-free catalyst, and can be explained by the reduction in [C*] due to poisoning of active sites.[26] The order of the yields was found to follow similar tendency irrespective of the polymerization procedures (i.e. the polymerization time, pressure, temperature, the presence of internal donor): No external donor > DMDMS ~ DCPDMS > DIPDMS > DPDMS > DnBDMS > DiBuDMS > DCHDMS, with no clear dependence on the bulkiness of the alkyl groups.

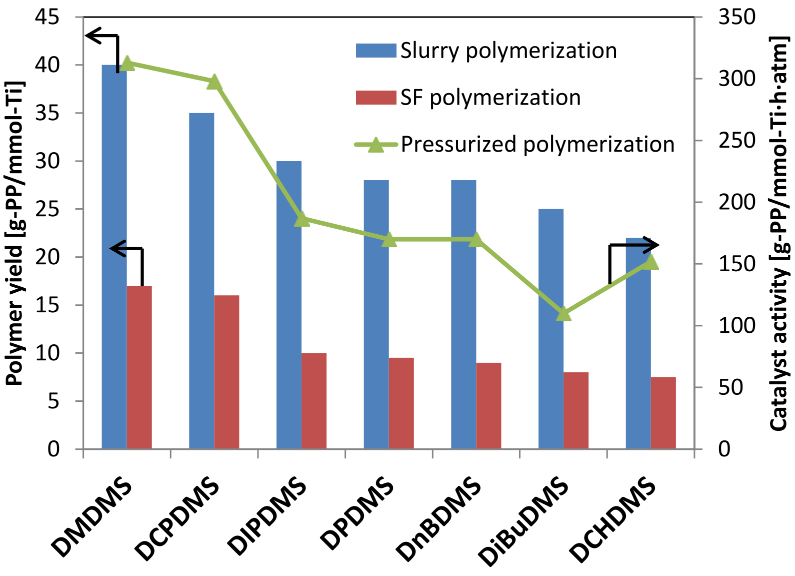


Figure 2.2. Yields of propylene polymerization for various dimethoxysilanes

It was thought that influences of alkoxysilanes on the catalyst performance result from complicated interplay between structural and electronic factors, which affect how they interact with other components such as active sites, alkylaluminum and $MgCl_2$ surfaces. Since it was not clear how alkoxysilanes poison active sites, it was rather difficult to explain and reproduce the obtained tendency. However, an empirical trial to find a potential correlation with any of calculated parameters based on the coadsorption model let us identify a plausible correlation between the experimental yields and calculated adsorption energies (ΔE_{ad}) of alkoxysilanes in the vicinity of active sites. The order of ΔE_{ad} was not simply correlated with the bulkiness of the alkoxy groups, but decided as a result of a subtle balance among structural propensity for chelete adsorption, structural interference with the proximiate $TiCl_4$, and the electron donation ability of methoxy groups. As shown in Figure 2.3, the yields tended to be greater when ΔE_{ad} became smaller with an exception of DCHDMS and DPDMS. The mechanistic origin of the tendency was unclear, but it would be possible that an alkoxysilane which tends to reside more stably around active sites might form “coadsorbed” active sites more efficiently. However, as can be judged from the exception of DCHDMS and DPDMS, the given explanation would be only one of factors which can affect the catalyst activity. The exception of DCHDMS and DPDMS may come from the cyclic group which the conformation detail around active site needs to be considered. But the correlation could be that alkoxysilane providing greater adsorption energies tended to enhance polymer yield.

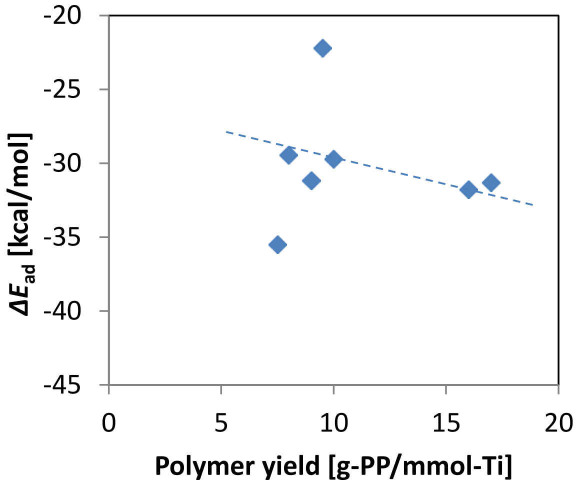


Figure 2.3. Correlation between experimental yields and calculated adsorption energy (ΔE_{ad}) of alkoxysilanes.

Table 2.3 summarizes effects of the alkoxysilane structure on the insoluble fraction. The addition of alkoxysilanes more or less increased the insoluble fraction, where DCPDMS and DMDMS gave the highest and the lowest values, respectively. The order of the insoluble fraction became as follows, again irrespective of the polymerization procedures: DCPDMS > DIPDMS > DnBDMS > DiBuDMS > DCHDMS > DPDMS > DMDMS > No external donor. It seemed that the presence of internal donor did not affect the stereoregularity improvement. The ability to regulate the stereospecificity by alkoxysilane external donor was not depends on the adsorption of external donor after extracting the internal donor by alkylaluminum.

Table 2.3. Insoluble fractions of polypropylene for various dialkyldimethoxysilanes

Alkoxysilanes	Insoluble fraction[a)] [%wt]	Insoluble fraction[b)] [%wt]	%mmmm[c)] [mol%]
DMDMS	39.2	38.5	88.8
DIPDMS	45.7	43.5	95.7
DiBuDMS	41.5	41.2	92.5
DnBDMS	42.0	41.1	93.0
DCPDMS	46.3	45.0	94.8
DCHDMS	41.1	40.2	93.0
DPDMS	40.0	39.1	94.5

a)obtained polymer from slurry polymerization

b)obtained polymer from SF polymerization

c)obtained polymer from pressurized polymerization

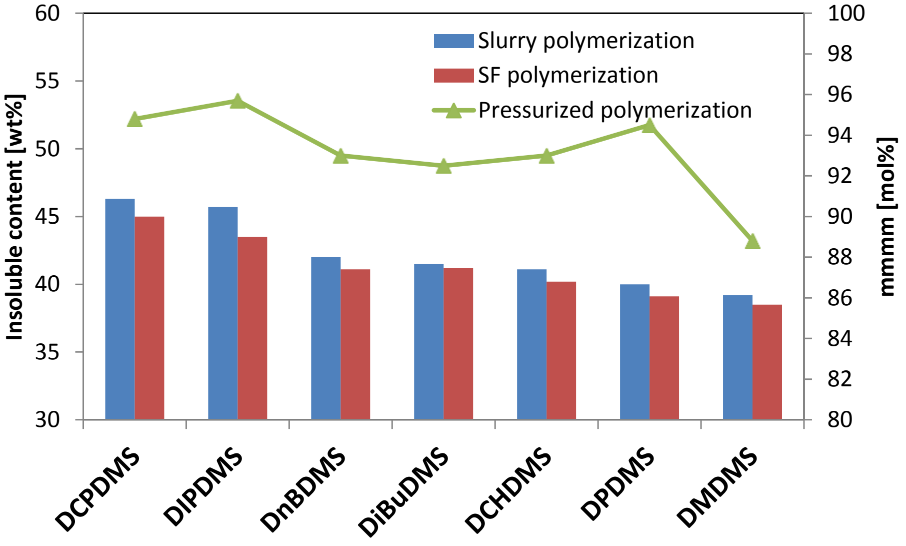


Figure 2.4. Stereoregularity of polymer from various dimethoxysilanes

TREF diagrams were acquired for polymer obtained from the two-vessel SF polymerization with some of dimethoxysilane external donors in order to investigate the distribution of the stereospecificity of active sites just after the formation (Figure 2.5).[27] In the absence of donors, the diagram showed an elution peak centered at around 105 °C. The addition of alkoxysilanes (more or less) shifted the elution peaks to higher temperature than for the donor-free case. This fact was regarded as the formation of new active sites with higher isospecificity by the addition of alkoxysilanes. The location and breadth of the elution peaks seemed to be dependent on the alkoxysilane structure: DCPDMS gave an elution peak at the highest temperature, while DPDMS gave at the lowest. The temperature for the elution peaks showed the same order with the insoluble fractions (Table 2.3).

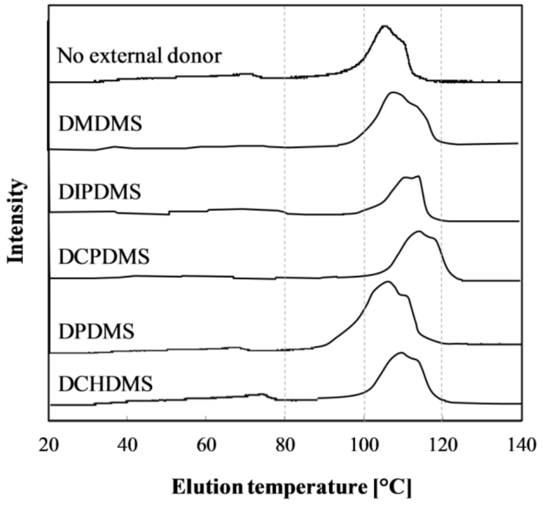


Figure 2.5. TREF diagrams for polypropylene obtained by two-vessel SF polymerization in the absence or presence of various alkoxysilanes.

In general, it is known that larger steric hindrance around active sites tends to give larger stereospecificity, and that branches at the C_{α} carbons of dialkyl groups are especially important for alkoxysilanes to improve the stereospecificity.[28] On the other hand, as was exemplified by a disorder between DIPDMS and DCHDMS, the obtained experimental tendency did not simply follow either the bulkiness of the alkyl groups or the presence of branches at the C_{α} carbons. A detailed steric environment around active sites must be considered. Thus calculated $\Delta\Delta E_{\text{stereo}}$ values within the framework of the coadsorption model were compared with the experimental insoluble fractions. As shown in Figure 2.6, $\Delta\Delta E_{\text{stereo}}$ showed almost perfect correlations with the insoluble fractions. For example, the order of $\Delta\Delta E_{\text{stereo}}$ became DCPDCM > DCHDMS > DPDMS among dimethoxysilanes with cyclic alkyl groups, which can be understood by visualizing the conformations of coadsorbed alkoxysilanes (Figure 2.7). The dicyclopentyl groups of DCPDMS possess a planar conformation orientating toward the Ti center, which imposed the greatest hindrance. On the other hand, the planar phenyl groups of DPDMS oriented vertically to the Ti center, leading to the smallest steric congestion. In the case of DCHDMS, the cyclohexyl groups at the chair conformation were obliquely oriented to the Ti center, i.e. intermediate hindrance between DCPDMS and DPDMS.

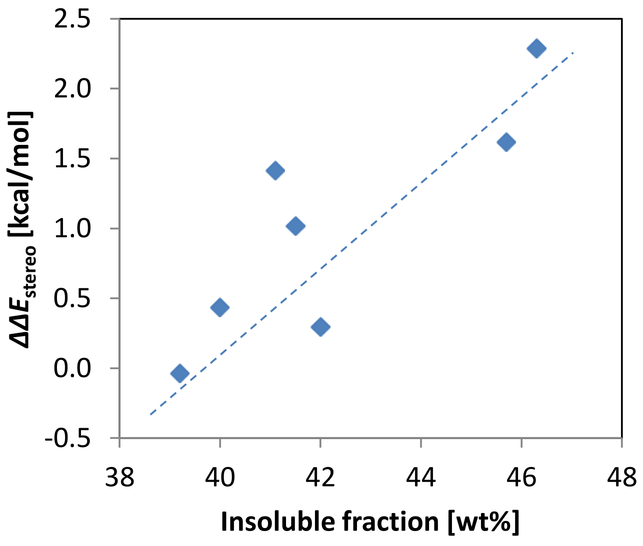


Figure 2.6. Correlation between experimental insoluble fractions and calculated stereospecificity of active sites ($\Delta\Delta E_{\text{stereo}}$).

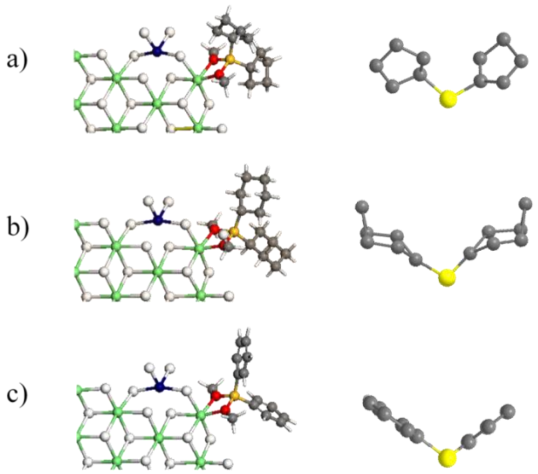


Figure 2.7. Conformation of (a) DCPDMS, (b) DCHDMS, (c) DPDMS coadsorbed with mononuclear $TiCl_4$ on a $MgCl_2$ surface

In summary, impacts of the molecular structure of alkoxysilanes on the polymerization performance of a Ziegler-Natta catalyst could not be explained simply by the bulkiness, but molecular simulation based on the coadsorption model more or less explained the obtained experimental tendencies: stronger adsorption of alkoxysilanes tended to enhance the yield, while the stereoregularity of obtained polypropylene was accounted by the calculated stereospecificity of active sites coadsorbed with alkoxysilanes.

4. Conclusion

The structure-performance relationship was examined for dialkyldimethoxysilane external donors in heterogeneous Ziegler-Natta propylene polymerization. It was found that an alkoxysilane which adsorbed more strongly on $MgCl_2$ surfaces in DFT calculations tended to give a higher polymer yield. Though the branching at the C_α carbons was a prerequisite for higher isospecificity, the conformation detail around active sites was also important. The calculated stereospecificity based on the coadsorption model successfully explained the experimentally observed stereoregularity of polymer. Various pretreatment conditions were used to understand interaction of alkoxysilane external donors with a catalyst. The formation of new isospecific sites plays a major role in improving the catalyst stereospecificity, while poisoning to cause an activity decrement occurred rather non-selectively. This study illustrates first successful combination of the stopped-flow polymerization and DFT-based coadsorption model as a powerful tool to explore active-site-level structure-performance relationships in Ziegler-Natta catalysis.

References

102. E. Albizzati, U. Giannini, G. Collina, L. Noristi, L. Resconi, *Propylene Handbook*, E. P. Moore, Ed., Hanser, New York **1996**, Chapter 2.

103. Q. Wang, N. Murayama, B. Liu, M. Terano, *Macromol. Chem. Phys*. **2005**, *206*, 961.

104. T. Taniike, M. Terano, *Polyolefins: 50 years after Ziegler and Natta I*, W. Kaminsky, Ed., Springer, New York **2013**, p.82.

105. S. Y. Kim, Y. Hiraoka, T. Taniike, M. Terano, *Macromol. Symp*. **2009**, *285*, 115.

106. T. Wondimagegn, T. Ziegler, *J. Phys. Chem*. **2012**, *116*, 1027.

107. H. Matsuoka, B. Liu, H. Nakatani, M. Terano, *Macromol. Rapid. Commun*. **2001**, *22*, 326.

108. H. Mori, H. Saito, M. Terano, *Macromol. Chem. Phys*. **1998**, *199*, 55.

109. V. Busico, R. Cipullo, G. Monaco, G. Talarico, M. Vacatello, J. C. Chadwick, A. L. Segre, O. Sudmeijer, *Macromolecules* **1999**, *32*, 4173.

110. B. Liu, T. Nitta, H. Nakatani, M. Terano, *Macromol. Chem. Phys*. **2003**, *204*, 395.

111. T. Taniike, M. Terano, *J. Catal*. **2012**, *293*, 39.

112. H. Mori, H. Saito, M. Yamahiro, H. Kono, M. Terano, *Macromol. Chem. Phys.* **1998**, *199*, 613.

113. J. C. Chadwick, G. M. M. van Kessel, O. Sudmeijer, *Macromol. Chem. Phys*. **1995**, *196*, 1431.

114. J. C. Chadwick, G. Morrini, G. Balbontin, I. Camurati, J. J. R. Heere, I. Mingozzi, F. Testoni, *Macromol. Chem. Phys.* **2001**, *202*, 1995.

115. J. V. Seppälä, M. Härkonen, *Makromol. Chem.* **1989**, *190*, 2535.

116. S. Yao, Y. Tanaka, *Macromol. Theory Simul*. **2001**, *10*, 850.

117. M. Härkonen, L. Kuutti, J. V. Seppälä, *Makromol. Chem*. **1992**, *193*, 1413.

118. M. C. Sacchi, F. Forlini, I. Tritto, R. Mendichi, G. Zannoni, L. Noristi, *Macromolecules* **1992**, *25*, 5914.

119. P. B. Vyas, S. Kaur, H. R. Patil, V. K. Gupta, *Polym. PPlast. Tech. Eng*, **2012**, *51*, 466.

120. T. Keii, M. Terano, K. Kimura, K. Ishii, *Makromol. Chem., Rapid Commun*. **1987**, *8*, 583.

121. B. Liu, H. Matsuoka, M. Terano, *Macromol. Rapid. Commun*. **2001**, *22*, 1.

122. T. Taniike, S. Sano, M. Ikeya, V.Q. Thang, M. Terano, *Macromol. React. Eng*. **2012**, *6*, 275.

123. J. P. Perdew, K. Burke, M. Ernzerhof, *Phys. Rev. Lett.* **1996**, *77*, 3865.

124. a) M. Dolg, U. Wedig, H. Stoll, H. Preuss, *J. Chem. Phys*. **1987**, *86*, 866, b) A. Bergner, M. Dolg, W. Kuechle, H. Stoll, H. Preuss, *Mol. Phys*. **1993**, *80*, 1431.

125. B. Delley, *J. Chem. Phys*. **1990**, *92*, 508.

126. T. Taniike, M. Terano, *Next Generation Polyolefins*, Sankeisha, Tokyo **2010**, p. 63.

127. I. Nishiyama, B. Liu, H. Matsuoka, H. Nakatani, M. Terano, *Macromol. Symp.* **2003**, *193*, 71.

128. B. Liu, T. Nitta, H. Nakatani, M. Terano, *Macromol. Symp.* **2004**, *213*, 7.

129. M. Toto, G. Morini, G. Guerra, P. Corradini, L. Cavallo, *Macromolecules*, **2000**,*33*, 1134.

130. M. Terano, K. Kimura, A. Murai, M. Inoue, M. Miyoshi, *JP patent* S62-158704, **1987.**

131. A. Dashti, A. Ramazani, Y. Hiraoka, S. Y. Kim, T. Taniike, M. Terano, *Polym. Int.* **2008**, *58*, 40.

Chapter 3

Structure-performance relationship of triethoxysilane external donor in propylene polymerization

3.1 Introduction

During the past 60 years of Ziegler-Natta (ZN) catalyst improvements, the catalyst activity and stereospecificity for polypropylene (PP) have been developed throughout this development era due to the increasing demand. For propylene polymerization with ZN catalysts, electron donors are the key factor to improve catalyst performance. Electron donors are Lewis bases which can be divided into two types; internal donors are introduced during catalyst preparation and external donors are additional component which externally introduced during polymerization.[1] Although internal donor is also playing the important role for the stereoregularity improvement of catalyst, external donor is possible to directly be applied to the industrial scale without any changes in the existing catalyst platform.

From the previous researches, Terano et al. stated that the formation of active site with highest stereospecificity strongly depends upon the interaction of catalyst and activator without any monomer as a pretreatment by classifying the active sites into aspecific and three kinds of isospefic sites in the Ziegler-Natta catalysts.[2] The isospecificity of active sites strongly depends upon the bulkiness of the ligand positions for construction of asymmetry and chirality of active sites and steric hindrance.[3] Busico et al. and Terano et al. proposed a three-site model to simulate the active site of Ziegler-Natta catalysts, where donor molecules coadsorb and improve their stereospecificities with their steric-hindered structures.[4,5] Furthermore, coadsorption model which implemented by using density functional theory (DFT) calculations was also propose by Taniike et. al., that aspecific active species is converted into an isospecific site as a result of random coadsorption of donors. The stereospecificity, regiospecificity improvements are sensitive to the molecular structure of donors.[6] It is necessary to understand the effects of molecular structure of alkoxysilanes more precisely. So, structure-performance relationship (SPR) is essentially required for the development of new donor structures.

Due to the importance of alkoxysilane structure that leading to the catalyst performance, there are several studies trying to explain how the structure effects to the catalyst performance.[7-11] Seppälä et al. studied the influence of alkoxysilane structure on the propylene polymerization by varying the number and size of alkyl/alkoxy groups. It was found that effect of external donor strongly depends on the number and size of alkoxy groups as well as on size of alkyl groups attached to silicon atom, such as alkoxysilanes with 2-3 alkoxy groups with large hydrocarbon substituents causes high activity and high isotacticity which give the best performance.[9,11] Yao et.al used

Quantitative Structure-Activity Relationship (QSAR) with molecular dynamics and molecular mechanics calculation to simulate the effects of catalyst activity and molecular weight distribution of polypropylene by changing R-group of alkoxysilanes. It was found that catalyst activity is mainly getting affected by the interaction energy between active site and external donor.[10] However, the systematic investigation of structure-performance relationship (SPR) of alkoxysilanes has been rarely explored. Previous chapter has already explained the SPR using the different types of dimethoxysilane in propylene polymerization.[12] The calculated adsorption energies and stereospecificities from density functional theory (DFT) calculations were also used to correlate the experimental results. It was found that an alkoxysilane adsorbed stronger on $MgCl_2$ surfaces tended to give a higher polymer yield. Moreover, the conformation detail around active sites has also played a key role to improve stereospecificity. In this chapter, the SPR investigation was extended to triethoxysilane with provides three alkoxy groups with various alkyl structures, aiming at generalization of SPR for different types of alkoxysilanes.

To achieve this target, stopped-flow (SF), slurry polymerization and pressurized polymerization were performed using various types of triethoxysilane as an external donor. SF polymerization was used to apply the advantages of the investigation of effects on catalyst performance at the level of active sites. [13] The level of stereospecificity improvement was also investigated using the amount of insoluble fraction in the case of slurry and SF polymerization,while %mmmm was used in the case of polymer from pressurized polymerization. All experimental data was discussed with the calculated parameters by DFT calculations based on coadsorption energies to determine the correlation between alkoxysilane structure and catalyst performance.

From the results in this chapter, it was found that order of polymer yield from SF and slurry polymerization is same, but there is no clear tendency between bulkiness of alkoxysilane structures and polymer yields. On the other hand, the order of polymer yield in the case of pressurized polymerization was found to be different. Considering the calculated value from DFT calculations, alkoxysilane adsorbed stronger on the $MgCl_2$ surface based on coadsorption model tends to give a higher polymer yield in SF and slurry polymerization while no tendency was found in pressurized polymerization. In the case of stereospecificity, the order was found to be same for all polymerization types. It seemed that the branches at the C_α carbons, representing larger steric hindrance around active sites, tended to give the improvement of stereospecificity. The generalization of structure-performance relationship (SPR) for stereospecificity could be achieved for both di- and trialkoxysilanes in all types of propylene polymerization system.

3.2. Experimental

3.2.1 Materials

Propylene (donated by Mitsui Chemicals, Inc.), $MgCl_2$ (65.1 m^2/g, donated by Toho Titanium Co., Ltd.), triisobutylaluminum (TiBA, donated by Tosoh Finechem Corporation), and $TiCl_4$ were used as delivered. Heptane was used after passing through a column of 4Å molecular sieves and bubbling with dry nitrogen for 2 h. Ethanol / hydrochloric acid (90/10 v/v) was used for quenching. Alkoxysilanes which used in this study are as shown in Table 3.1 and Figure 3.1.

Table 3.1. List of triethoxysilane external donors used in propylene polymerization

Name	Alkoxysilane
MTES	metyltriethoxysilane
ETES	ethyltriethoxysilane
iBuTES	i-butyltriethoxysilane
CPTES	cyclopentyltriethoxysilane
VTES	vinyltriethoxysilane
ATES	allyltriethoxysilane

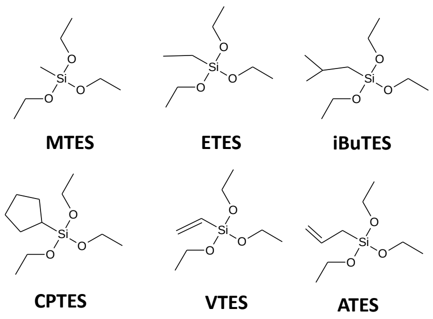


Figure 3.1. Triethoxysilane structure

3.2.2 Catalyst Preparation

3.2.2.1 Internal donor-free catalyst

An internal donor-free catalyst was prepared by the following procedure.[5] 36 g of $MgCl_2$ and 100 mL of $TiCl_4$ were transferred into a 1.2 L stainless steel vibration mill pot with 55 stainless balls (25 mm diameter) and ground for 30 h at room temperature under nitrogen atmosphere. After that, the ground product was reacted with 150 mL of $TiCl_4$ in a 1 L stirred flask for 2 h at 90 °C under nitrogen. Thus obtained catalyst was repeatedly washed with heptane and kept as slurry in heptane under nitrogen. The Ti content was measure by UV-Vis spectroscopy (JASCO V670) as 1.8 wt%.

3.2.2.2 Internal donor-contained catalyst

A $TiCl_4$/DiBP/$MgCl_2$ catalyst was prepared from $Mg(OEt)_2$ based on patent[14] with the minor modification[15]. The Ti and DiBP contents in the catalyst were determined as 3.4 and 12 wt%, respectively.

3.2.3 Polymerization Procedures

In this study, three types of polymerization were carried out for comparison: slurry polymerization, two-vessel SF polymerization and three-vessel SF polymerization. Their details are described as follows.

3.2.3.1 Slurry Polymerization

Propylene polymerization was carried out in a stirred flask containing 200 mL of heptane and 2 mmol of TiBA (at the Al/Ti molar ratio of 30). After propylene saturation at 1 atm and 30 °C, 0.3 mmol of an external donor was added followed by the addition of 0.17 g of the catalyst. The polymerization was continued under continuous supply of propylene at 1 atm and 30 °C for 10 min. The polymerization was terminated by adding acidic ethanol. The polymer was reprecipitated by ethanol and dried in vacuum for 6 h at 60 °C.

3.2.3.2 Two-Vessel SF Polymerization

A large-scale stopped-flow apparatus was used in this study, whose detail had been described in our previous paper.[16] 1 L of catalyst slurry in heptane containing 4.67 mmol of Ti and 1 L of TiBA solution in heptane containing 140 mmol of Al were respectively charged into stirred flasks under nitrogen. After propylene saturation at 1 atm and 30 °C, the catalyst slurry and the TiBA solution were respectively transferred with a tubing pump at the flow rate of 10 mL/s. The polymerization was initiated at the T junction, where the catalyst slurry and the TiBA solution were mixed. The polymerization time was fixed at 0.4 s. The polymerization slurry was quenched into acidic ethanol, which was vigorously stirred with a homogenizer to instantaneously quench the polymerization. The obtained polymer was washed with distilled water, followed by reprecipitation with xylene/ethanol. Then the polymer was dried in vacuum for 2 h at 60 °C.

3.2.3.3 Pressurized polymerization

Propylene homopolymerization was performed in a 1 L autoclave equipped with a mechanical stirrer rotating at 350 rpm. 500 ml of *n*-heptane was introduced into the reactor. TEA ([Al] = 10 mmol/L) and alkoxysilanes (Al/Si = 5) were introduced into the reactor, and the solution was saturated with 0.5 MPa of monomer at 50°C. 30 mg of a catalyst was injected into the reactor to initiate the polymerization. The polymerization was conducted for 60 min with a continuous supply of monomer gas at 0.5 MPa. After 60 min, propylene was vented and the polymer slurry was filtered immediately after mixing with quenching solution.

3.2.4 Polymer Analyses

3.2.4.1 Solvent fractionation

100 mg of a PP sample was dissolved in *o*-dichlorobenzene (ODCB) at 150 ^{0}C and gradually cooled down to room temperature using temperature controller. The insoluble

fraction was precipitated. After filtration and vacuum drying, the weight percentage of the insoluble fraction was measured and reported as insoluble fraction in wt%.

3.2.4.2 ^{13}C NMR spectroscopy for mesopentad fraction

The mesopentad fraction of PP samples were determined by ^{13}C NMR (Bruker 400 MHz) at 120 °C using 1,2,4-trichlorobenzene as a diluent and 1,1,2,2-tetrachloroethane-*d2* as an internal lock and reference.

3.2.5. Density Functional Theory (DFT) Calculations

All the DFT calculations were implemented according to the coadsorption model as described in our previous literature.[6] Briefly, the exchange-correlation functional of Perdew-Burke-Ernzerhof (PBE)[17] and the basis set of DNP plus effective core potentials[18] were employed within the program of DMOL3.[19] $MgCl_2$ surfaces were expressed as a slab model, where active sites at the {110} edge on the {104} surface were regarded as the most plausible active sites for the coadsorption of alkoxysilanes.[20] The adsorption energy of each alkoxsysilane on the {110} edge at the proximity of mononuclear $TiCl_4$ was calculated as ΔE_{ad}, while the stereospecificity ($\Delta\Delta E_{\mathrm{stereo}}$) was given as a differential activation energy of two propylene 1,2-insertion pathways with *re* and *si* prochiral faces. The transition state for each insertion pathway was approximated by the structure obtained at 2.2 Å of the distance between the propylene C_2 carbon and the C_α carbon of an isobutyl group bound to the Ti center. Further details are found in literature [6,20].

3.3 Results and Discussion

From chapter 2, some level of structure-performance relationship (SPR) of dimethoxysilane was explored. In this chapter, triethoxysilane was used as external donor aiming at the generalization of SPR to the other types of alkoxysilane with the different number of alkoxy groups. Similar as the described in chapter 2, three types of polymerization were carried out with various triethoxysilane external donors in the absence and presence of internal donor. Stopped-flow polymerization was also used in this study to investigate how alkoxysilanes with different structures affect the catalyst performance in the level of active sites. The other two polymerization types were conducted to observe the effects of polymerization time, pressure, the presence of internal donor, etc. Then, the results of stereospecificity improvement by triethoxysilane were reported as insoluble content and mesopentad fraction in obtained polymer samples. To achieve the target, the experimental results from dimethoxysilane and triethoxysilane were investigated the overall correlations to observe the SPR of alkoxysilane on catalyst activity and stereospecificity. The discussions were categorized as follows;

3.3.1 Effects of trialkoxysilane structure on polymer yield

From the previous study about the effect of dimethoxysilane as an external donor on the catalyst performances, alkoxysilane structure also affects the polymer yield. In this time, the polymerization results of triethoxysilanes were also reported as shown in Table 3.2 and Figure 3.2.

Table 3.2. Yields of propylene polymerization for various triethoxysilanes

Alkoxysilanes	slurry polymerization[a)] [g-PP/mol-Ti]	SF polymerization[b)] [g-PP/mmol-Ti]	Pressurized polymerization[c)] [g-PP/mmol-Ti·h·atm]
no ExD	48	19	410
MTES	33	15	100
ETES	32	15	140
VTES	26	11	83.0
ATES	30	14	97.7
iBuTES	28	12	160
CPTES	36	17	170

[a)] polymerization conditions: $TiCl_4/MgCl_2$ catalyst, 20 min, 30 °C, Al = 2 mmol, Al/Ti = 30, Al/Si = 6

[b)] polymerization conditions: $TiCl_4/MgCl_2$ catalyst, 0.4 s, 30 °C, [Al] = 140 mmol/L, Al/Ti = 30, Al/Si = 6

[c)] polymerization conditions: $TiCl_4$/DiBP/$MgCl_2$ catalyst, 60 min, 50 °C, Al = 5 mmol, Al/Si = 5

From the above results in Table 3.2, it was shown that the additional of external donor decreases the polymer yield in all cases of alkoxysilanes. The reason which also found from the chapter 2 is due to the reduction in the active site concentration ([C*]) from the selective poisoning of active sites. Considering only dimethoxysilane structures, the order of the polymer yield was similar in both types of polymerization (SF polymerization and slurry polymerization) which can be interpreted that polymerization time did not affect the influence of alkoxysilanes. In the case of dimethoxysilane, there is no clear tendency between bulkiness of alkyl structure and polymer yield. Considering among triethoxysilane structures, polymer yields were also decreased with the introduction of external donors. The order of polymer yield: CPTES > MTES ~ ETES > ATES > iBuTES > VTES, with no clear tendency with the bulkiness of alkoxysilanes as shown in Figure 3.2. In contrast, the different order was found in the case of pressurized polymerization. The assumption can be explained by the presence of internal donor. The vacant space for replacement of external donor may provide the different effect to the poisoning of active site leading to the decreasing degree of polymer yield compared to in the absence of internal donor.

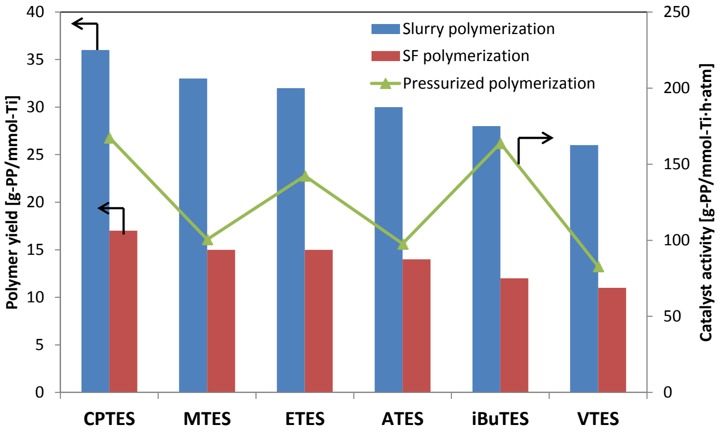


Figure 3.2. Yields of propylene polymerization for various triethoxysilanes

Comparing between dimethoxysilane and triethoxysilane with the same alkyl structure, the yields of methyl, cyclopentyl and *i*-butyl group were shown in Figure 3.3. The reverse order was found between two types of polymerization. In the case of SF polymerization which also referred to slurry polymerization, triethoxysilane tended to provide greater polymer yield in the case of bulky dimethoxysilane is used as external donor. But the result was found to be opposite in the case of pressurized polymerization which possibly came from the presence of internal donor provide the different effects.

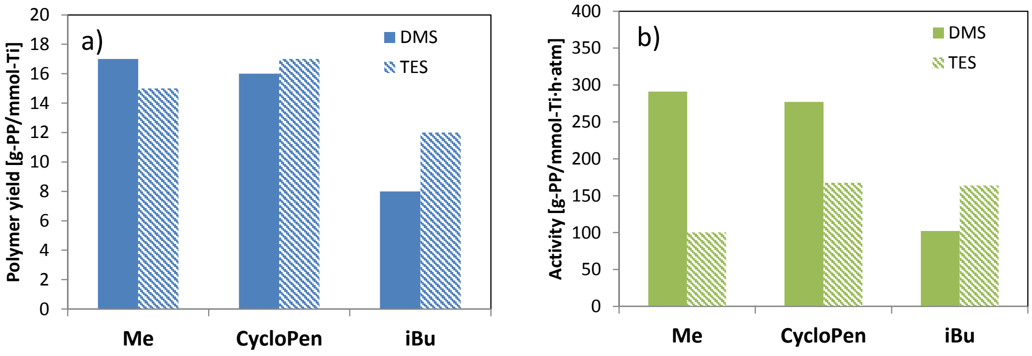


Figure 3.3. Yields compared between dimethoxysilane (DMS) and triethoxysilane (TES) from; a) SF polymerization, b) pressurized polymerization

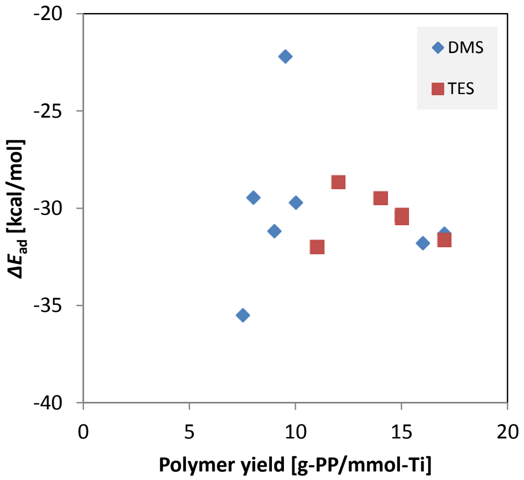


Figure 3.4. Correlation between experimental polymer yields and calculated adsorption energies (ΔE_{ad})

As shown in the correlation between experimental polymer yields and calculated adsorption energies in Figure 3.4, the correlation became clearer after the introduction of results from triethoxysilanes. It still showed that the alkoxysilane which adsorbed more strongly on $MgCl_2$ surface enhanced the polymer yield due to the stability on donor on the catalyst surface. But it can explain only for the effect from the catalyst in the absence of internal donor.

3.3.2 Effects of trialkoxysilane structures on stereospecificity

As known from the previous study that alkoxysilane structure plays the important role for the stereoregularity improvement of catalyst. In this chapter, to achieve the target of structure-performance relationship generalization for all alkoxysilanes, the stereoregularity of polymer samples from three polymerization types were considered as shown in Table 3.3. It summarized effects of alkoxysilane structures on the stereospecificity in term of insoluble and mesopentad fraction. The addition of triethoxysilane external donors more or less increased the insoluble fraction, where ETES gave the greatest stereospecificity improvement. The order of the insoluble fraction became as follows; ETES > ATES ~ VTES > MTES > CPTES > iBuTES > no external donor as shown in Figure 3.5.

Table 3.3. Polymer stereoregularity using various triethoxysilane external donors

Alkoxysilanes	Insoluble fraction [%wt]	Insoluble fraction [%wt]	%mmmm [mol%]
no donor	38.7	36.4	86.4
MTES	42.1	41.4	95.2
ETES	48.1	46.5	96.3
VTES	47.0	45.0	95.7
ATES	48.0	45.0	95.2
iBuTES	41.4	40.1	93.1
CPTES	42.0	40.2	93.8

[a)] obtained polymer from slurry polymerization

[b)] obtained polymer from SF polymerization

[c)] obtained polymer from pressurized polymerization

Similarly as dimethoxysilane structures, the introduction of triethoxysilane external donor improved the catalyst stereospecificity probably due to the increase of steric hindrance around active sites. The enhancement of polymer stereoregularity can be well-explained of these results. The differences of insoluble fraction and mesopentad fraction showed that the structures of triethoxysilane also affected the stereospecificity of active sites. Comparing the results in each polymerization types, it was shown that the similar tendencies of stereospecificity were obtained. It can be implied that the effects of alkoxysilane structure on the stereospecificity improvement is irrespective to the polymerization method and the presence of internal donor.

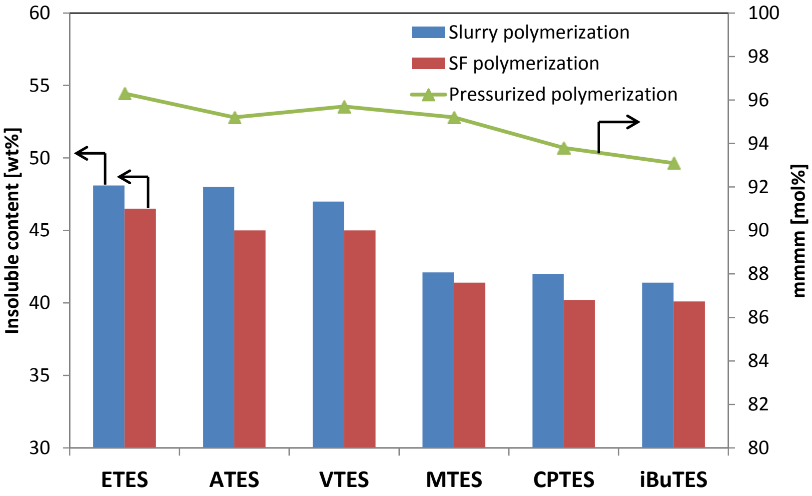


Figure 3.5. Polymer stereoregularity using various triethoxysilane external donors

Although the polymer samples from slurry polymerization and SF polymerization were analyzed by using insoluble fractionation, results were slightly different. The SF polymerization may produce the polymer with less molecular weight compared to slurry polymerization, leading to the possibility that some isotactic polymer may dissolved together with the soluble fraction. From the results in chapter 2 which only dimethoxysilanes were considered, there is strong correlation between experimental and calculated stereospecificities. It seemed that the branches at the C_α carbons, representing larger stereic hindrance around active sites, tended to give improvement of stereospecificity. Triethoxysilane with less bulkiness at C_α carbon seemed to provide greater isotacticity, in contrast to the results of dimehoxysilane. This probably came from the effect of free alkoxy group is more predominant for the hindrance around active site more than alkyl structure in the case of triethoxysilane.

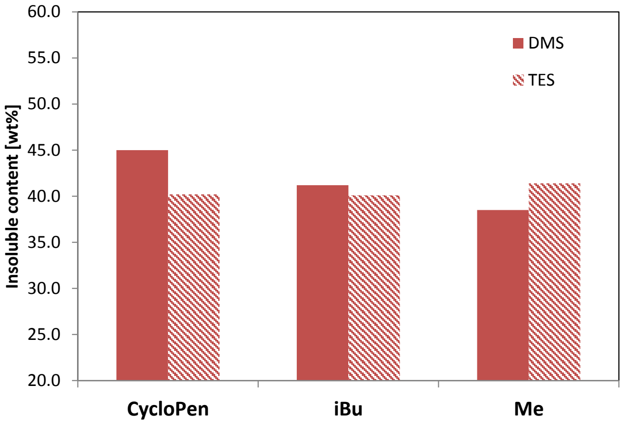


Figure 3.6. Comparison of insoluble fraction between dimethoxysilane (DMS) and triethoxysilane (TES) with the various alkyl structures

Figure 3.6 shows the results of comparison between insoluble content between dimethoxysilane and triethoxysilane with the same alkyl structure. The results show some tendencies that dimethoxysilane provided the better improvement of stereospecificity except in the case of methyl group or small bulkiness of alkyl structure. The possibility that in the case of small bulky alkyl group, the other alkoxy group of triethoxysilane play the important role to improve the stereospecificity rather than small alkyl group.

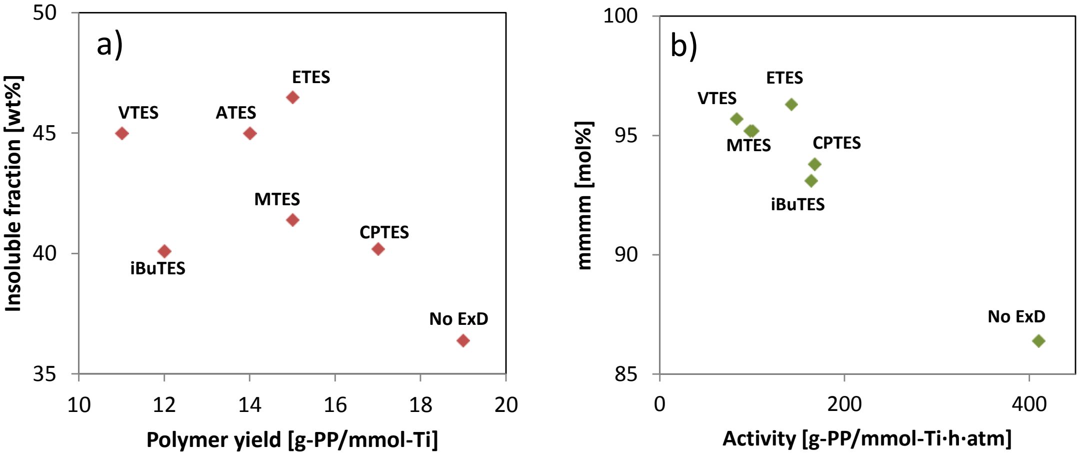


Figure 3.7. the comparison between polymer yield and stereospecificity from; a) SF polymerization, b) pressurized polymerization

From the previous assumption that alkoxysilane which gives greater polymer yield, provides less stereospecificity improvement due to the hindered structure of alkyl group. The correlation between polymer yield and stereospecificity was determined in Figure 3.7. It was found that there is no correlation between these two parameters. It can be implied that the alkoxysilane which gives the lower polymer yield due to the selective poisoning of active sites but it was not transformed to the highly isospecificity active sites. It just make a decrease of active site concentration ([C*]). Moreover, there are the other parameters relating to the enhancement of stereospecificity rather than the bulkiness of alkyl structure. From the previous chapter determining the effects of dimethoxysilane structure on stereospecificity, not only the bulkiness of alkyl structure but also the conformation detail around active site toward the Ti active centers plays the important role to regulate the stereospecficity improvement. So, the correlation between calculated stereospecificity ($\Delta\Delta E_{\text{stereo}}$) and experimental stereospecificity from alkoxysilane (dimethoxysilane and triethyoxysilane) was investigated which shown in Figure 3.8. The correlation shows that both dimethoxysilane and triethoxysilane have shared the same correlation between experimental and calculated stereospecificity.

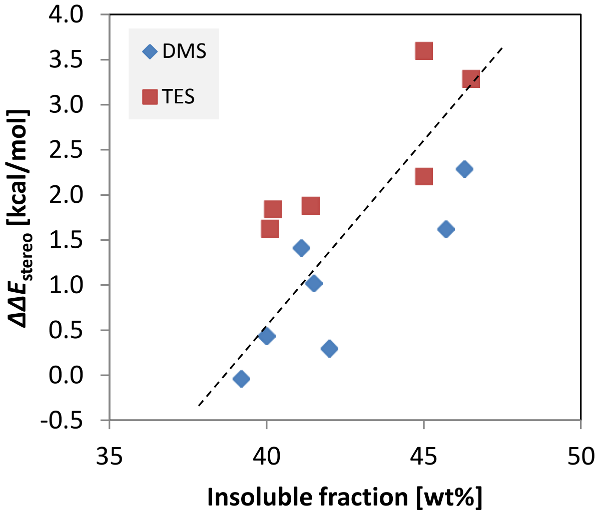


Figure 3.8. Correlation between experimental insoluble fractions from SF polymerization and calculated stereospecificity of active sites ($\Delta\Delta E_{\text{stereo}}$)

3.4 Conclusion

The structure-performance relationship was examined for alkyltrialkoxysilane external donors in heterogeneous Ziegler-Natta propylene polymerization. Similar as dimethoxysilane, an alkoxysilane adsorbed stronger on the $MgCl_2$ surface based on coadsorption model tends to give a higher polymer yield in SF and slurry polymerization while no tendency was found in pressurized polymerization. Moreover, the relationship between insoluble fraction and stereospecificity calculated based on coadsorption model remained valid with the addition of triethoxysilane structures.

References

132. E. Albizzati, U. Giannini, G. Collina, L. Noristi, L. Resconi, *Propylene Handbook*, E. P. Moore, Ed., Hanser, New York **1996**, Chapter 2.

133. H. Mori, H. Saito, M. Terano, *Macromol. Chem. Phys*. **1998**, *199*, 55.

134. H. Matsuoka, B. Liu, H. Nakatani, M. Terano, *Macromol. Rapid. Commun*. **2001**, *22*, 326.

135. V. Busico, R. Cipullo, G. Monaco, G. Talarico, M. Vacatello, J. C. Chadwick, A. L. Segre, O. Sudmeijer, *Macromolecules* **1999**, *32*, 4173.

136. B. Liu, T. Nitta, H. Nakatani, M. Terano, *Macromol. Chem. Phys*. **2003**, *204*, 395.

137. T. Taniike, M. Terano, *J. Catal*. **2012**, *293*, 39.

138. J. C. Chadwick, G. M. M. van Kessel, O. Sudmeijer, *Macromol. Chem. Phys*. **1995**, *196*, 1431.

139. J. C. Chadwick, G. Morrini, G. Balbontin, I. Camurati, J. J. R. Heere, I. Mingozzi, F. Testoni, *Macromol. Chem. Phys.* **2001**, *202*, 1995.

140. J. V. Seppälä, M. Härkonen, *Makromol. Chem.* **1989**, *190*, 2535.

141. S. Yao, Y. Tanaka, *Macromol. Theory Simul*. **2001**, *10*, 850.

142. M. Härkonen, L. Kuutti, J. V. Seppälä, *Makromol. Chem*. **1992**, *193*, 1413.

143. S. Poonpong, S. Dwevedi, T. Taniike, M. Terano *Macromol. Chem. Phys*. **2014**, *215*, 1721.

144. T. Keii, M. Terano, K. Kimura, K. Ishii, *Makromol. Chem., Rapid Commun*. **1987**, *8*, 583.

145. M. Terano, K. Kimura, A. Murai, M. Inoue, M. Miyoshi, *JP patent* S62-158704, **1987.**

146. A. Dashti, A. Ramazani, Y. Hiraoka, S. Y. Kim, T. Taniike, M. Terano, *Polym. Int.* **2008**, *58*, 40.

147. T. Taniike, S. Sano, M. Ikeya, V.Q. Thang, M. Terano, *Macromol. React. Eng*. **2012**, *6*, 275.

148. J. P. Perdew, K. Burke, M. Ernzerhof, *Phys. Rev. Lett.* **1996**, *77*, 3865.

149. a) M. Dolg, U. Wedig, H. Stoll, H. Preuss, *J. Chem. Phys*. **1987**, *86*, 866, b) A. Bergner, M. Dolg, W. Kuechle, H. Stoll, H. Preuss, *Mol. Phys*. **1993**, *80*, 1431.

150. B. Delley, *J. Chem. Phys*. **1990**, *92*, 508.

151. T. Taniike, M. Terano, *Next Generation Polyolefins*, Sankeisha, Tokyo **2010**, p. 63.

Chapter 4

Influence of alkoxysilane structure on comonomer incorporation in propylene copolymerization

4.1 Introduction

Due to the importance of external donor for the development of catalyst system, there are several researchers trying attempts to understand the roles of donors more clearly. It is known that the roles of external donor involve poisoning of non-stereospecific active site, increasing the propagation rate (k_p) for stereospecific active centers and transformation into highly isospecific active sites.[1-3] Several researches tried to understand the fundamental factors determining the performance of $MgCl_2$-supported catalysts in relation to the roles of electron donors. An effective model was proposed by Busico et al. which explained that the strongly co-ordinating donors give polymers with stereoregularity in which highly isotactoid sequences predominate.[4] Terano et al. established that the formation of active site with highest stereospecificity strongly depends upon the interaction of catalyst and activator without any monomer as a pretreatment by classifying the active sites into aspecific and three kinds of isospecific sites in the ZN catalysts.[5] The isospecificity improvement of active sites depends on the bulkiness of the ligand conformation of asymmetry and chirality of active sites and steric hindrance.[6] Taniike et al. proposed a coadsorption model using density functional theory (DFT) calculations to explain that a specific Ti mononuclear species located on the $MgCl_2$ (110) surface is converted into an isospecific site from the random coadsorption of donors. Donors improve stereospecificity and regiospecificity and performance correlates to the molecular structure of donors.[7]

As mentioned above, the catalyst performance depends on the structure and type of donors.[8] The study of structure-performance relationship (SPR) is essentially required for the development of new donor system. A number of researches have reported the effects of alkoxysilane structure on catalyst performance. Especially, Seppälä et al. found that the catalyst performance including the activity, stereospecificity, molecular weight and its distribution strongly depends on the number and size of alkoxy group as well as on the size of alkyl groups attached to the silicon atom.[9-10] Sacchi et al. explained how alkoxysilanes activate isospecific sites, affecting both microstructure and molecular weight of polypropylene (PP). They also found that the size of hydrocarbon group mainly affects the copolymerization yield. Also, the number of alkoxy groups affect the fraction distribution.[11-12] Although there are several studies which attempted to explain the effects of alkoxysilane systematically on the catalyst performance, but it is still ambiguous that how alkoxysilanes with the different structures affect the other catalyst performances than catalyst activity and stereospecificity. The other catalyst performances are also important to improve the PP properties such as hydrogen response, comonomer incorporation, molecular weight and its distribution, etc.

In this chapter, to generalize the structure-performance relationship of alkoxysilane external donor, the investigation of the effects on propylene copolymerization is required. Propylene-ethylene and propylene-1-octene copolymerizations were carried out with the various dimethoxysilane structures as external donors. The condition of propylene-ethylene copolymerization was optimized in order to prevent the insufficient amount of dissolved ethylene in heptane medium by considering the appropriate catalyst activity and solubility of ethylene in heptane. Also, 1-octene, less reactive comonomer was used in propylene copolymerization. The resulted comonomer contents were analyzed by using ^{13}C NMR spectroscopy, which can represent the comonomer incorporation efficiency depending on the alkoxysilane structure. From the results, it was found that dimethoxysilane which accounts greater isotacticity, provides lower comonomer incorporation. This tendency is similar for both ethylene and 1-octene which irrespective to types of comonomer.

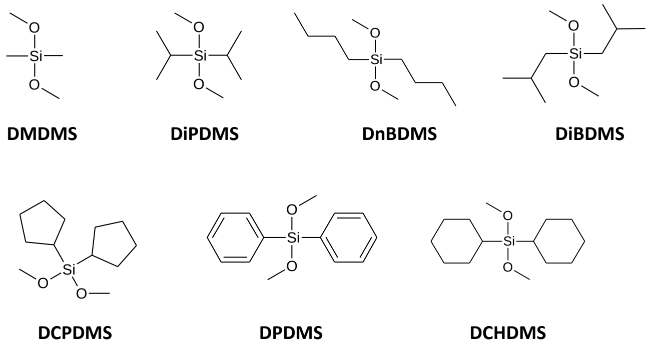
4.2 Experimental

4.2.1 Materials

Propylene (donated by Mitsui Chemicals, Inc.) and triethylaluminum (TEA, donated by Tosoh Finechem Corporation) were used as received. Heptane was used after passing through a column of 4Å molecular sieves and bubbling with dry nitrogen for 2 h. Ethanol/hydrochloric acid (90/10 v/v) was used for quenching. Alkoxysilanes which used in this study are as shown in Table 4.1 and Figure 4.1.

Table 4.1. List of dimethoxysilane external donors used in propylene copolymerization

Name	Alkoxysilane
DMDMS	dimethyldimethoxysilane
DiPDMS	di-i-propyldimethoxysilane
DnBDMS	di-n-butyldimethoxysilane
DiBuDMS	di-i-butyldimethoxysilane
DCPDMS	dicyclopentyldimethoxysilane
DPDMS	diphenyldimethoxysilane
DCHDMS	dicyclohexyldimethoxysilane



DMDMS DiPDMS DnBDMS DiBDMS

DCPDMS DPDMS DCHDMS

Figure 4.1. Dimethoxysilane external donors

4.2.2 Catalyst Preparation

A $TiCl_4$/DiBP/$MgCl_2$ catalyst preparation was performed from the method in patent[13] with the minor modification[14]. The Ti content and diisobutylphthalate (DiBP) content in the catalyst were analyzed as 3.4 and 12 wt%, respectively.

4.2.3 Pressurized polymerization

Propylene homopolymerization was performed in a 1-L autoclave equipped with a mechanical stirrer rotating at 350 rpm. 500 ml of *n*-heptane was introduced into the reactor. TEA ([Al] = 10 mmol/L) and alkoxysilanes (Al/Si = 5) were introduced into the reactor, and the solution was saturated with 0.5 MPa of the mixture between propylene and ethylene (or 1-octene) at 50°C. A catalyst was injected into the reactor to initiate the polymerization. When polymerization was finished, propylene was vented and the polymer slurry was filtrated immediately after mixing with acidic ethanol as quenching solution.

4.2.4 Polymer Characterization

The comonomer content of propylene copolymer were determined by ^{13}C NMR (Bruker 400 MHz) at 120 °C using 1,2,4-trichlorobenzene as a diluent and 1,1,2,2-tetrachloroethane-*d2* as an internal lock and reference. In the case of propylene-ethylene copolymerization, resulted ethylene content of obtained copolymer from ^{13}C NMR was compared with the ratio of peak height from ATR-IR to establish the calibration curve as shown in Figure 4.2. The value of P-733/P-1044 is the ratio between peak height of absorbance band of statistical ethylene band at 733 cm^{-1} and peak height of absorbance band at 1044 cm^{-1}

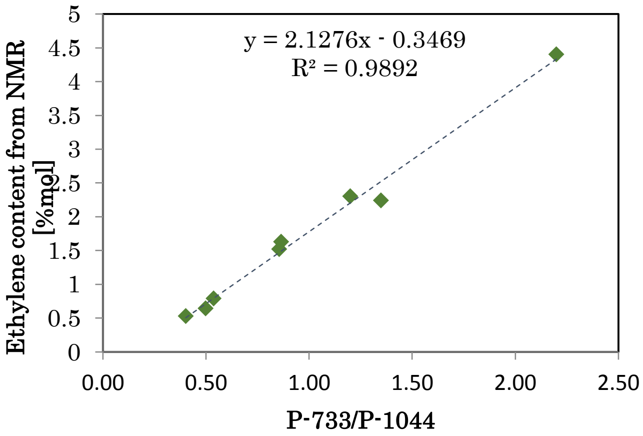


Figure 4.2. Calibration curve using the information of ^{13}C NMR and ATR-IR for the interpolation in the C_2 content range of 0.5 – 5.0%

4.3 Results and Discussion

4.3.1 Optimization of propylene-ethylene copolymerization conditions

As mentioned in the introduction part, to investigate the effects of alkoxysilane structures on the comonomer incorporation efficiency, ethylene was used as comonomer for propylene copolymerization. It is known that the problem of propylene-ethylene copolymerization is the insufficient amount of ethylene in the polymerization system. The problem was due to the less dissolubility in heptane medium and more reactive for polymerization than propylene. So, it is necessary to optimize the polymerization conditions to prevent the shortage of ethylene in the reactor system. The approaches were to increase the dissolubility of ethylene in solution by increasing pressure, or increasing the heptane amount in the reactor, or reducing polymerization rate by adjustment of polymerization conditions (time, temperature, catalyst amount). Table 4.2 shows the optimization results by reducing the polymerization rate by decreasing catalyst amount and polymerization time to keep ethylene consumption less than 10%.

Table 4.2. Copolymerization results with the various amounts of catalyst and polymerization time

Run	Catalyst amount [mg]	Polymerization time [min]	Polymer yield [g-PP]	Ethylene content [mol%]	Ethylene consumption [%]
1	5.0	30	3.2	0.79	10
2	10	30	9.3	0.64	24
3	15	30	18.9	0.57	44
4	20	30	14.9	0.50	31
5	0.5	10	0.09	1.37	0.5
6	1.0	10	0.15	1.45	0.9
7	2.0	10	0.22	1.29	1.2
8	3.0	10	0.40	1.30	1.5

Polymerization conditions : $TiCl_4/DiBP/MgCl_2$ catalysts, polymerization temperature 50 °C, [Al] = 10 mmol/L, volume 500 mL in heptane, ethylene/propylene feed mol ratio = 1/50

It was found that ethylene consumption was higher than 10% with low resulted ethylene content in the case of high reaction rate (Run 1-4). The appropiate amount of ethylene for the copolymerization without the problem of ethylene insufficient was optimized. Table 4.3 shows the copolymerization results with various ethylene feed amount. It was found that in the case of ethylene/propylene feed ratio 1/50 (ethylene dissolved in heptane = 0.012 mol/500 mL) and 1/33 (ethylene dissolved in heptane = 0.016 mol/500 mL), less than 10% of ethylene consumption can be achieved. So, these two conditions

(Run 9 and 10) were selected to be the optimum conditions for the propylene-ethylene copolymerization in this study.

Table 4.3. Propylene-ethylene polymerization results with various ethylene Concentrations

Run	Ethylene feed [L/min]	Propylene feed [L/min]	C_2/C_3 feed ratio	Polymer yield [g-PP]	Ethylene content [mol%]	Ethylene consumption [%]
9	0.18	9.0	1/50	0.4	1.30	1.5
10	0.27	9.0	1/33	1.3	2.24	4.8
11	0.36	9.0	1/25	1.8	3.95	14
12	0.45	9.0	1/20	1.5	7.29	18

Polymerization conditions: catalyst 3 mg, [Al] = 8 mmol/L, 50 °C, 10 min, 0.5 MPa

Considering the dissolubility of ethylene in heptane, the correlation between ethylene solubilities and resulted ethylene contents from obtained copolymer samples was made as shown in Figure 4.3. Left one shows the correlation in the case 10 mg of catalyst was copolymerized while right one shows the correlation when 3 mg of catalyst was used. It was found that when ethylene was insufficient, linear correlation cannot be obtained. Even ethylene is more reactive comparing with propylene but the solubility in heptane was 1/70 times compared with propylene. When lower the catalyst amount to reduce polymerization yield, linear correlation can be obtained as shown in the right one.

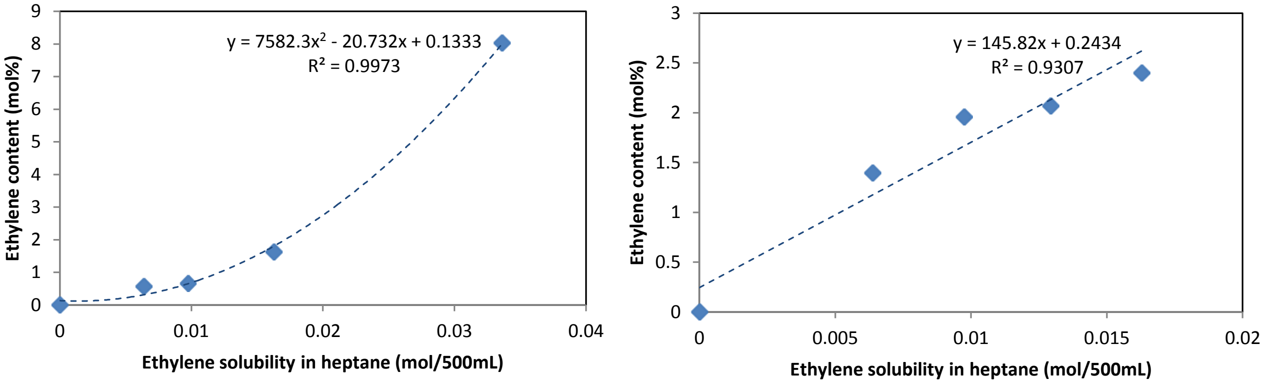


Figure 4.3. Correlation between solubility of ethylene in heptane and resulted ethylene content; Polymerization time 10 min, catalyst amount more than 10 mg (left), catalyst amount 3 mg (right)

4.3.2 Results of propylene-ethylene copolymerization with the different alkoxysilane structures

As mentioned earlier that to investigate the structure-performance relationship between alkoxysilane structures and catalyst performances, the understanding of effects on comonomer incorporation efficiency is also required to fulfill the information of SPR. The propylene-ethylene copolymerizations with different types of alkoxysilanes were carried out which their resutls are shown in Table 4.4.

Table 4.4. Propylene-ethylene copolymerization results

Alkoxysilanes	Polymer yield [g-PP]			Ethylene content [mol%]	
	no C_2	C_2 = 0.012 mol	C_2 = 0.016 mol	C_2 = 0.012 mol	C_2 = 0.016 mol
no ExD	0.9	1.4	1.8	2.26	2.73
DMDMS	0.8	1.3	1.7	2.13	2.67
DiPDMS	0.5	1.1	1.2	1.92	2.30
DnBDMS	0.6	0.9	1.2	2.12	2.56
DiBDMS	0.6	0.9	1.1	1.98	2.47
DCPDMS	0.8	1.2	1.5	1.82	2.04
DPDMS	0.3	0.6	0.9	1.84	2.40
DCHDMS	0.4	0.6	0.8	1.75	2.27

Polymerization conditions: catalyst 3 mg, [Al] = 8 mmol/L, 50 °C, 10 min, 0.5 MPa

Dissolved ethylene in heptane = mol/500 mL

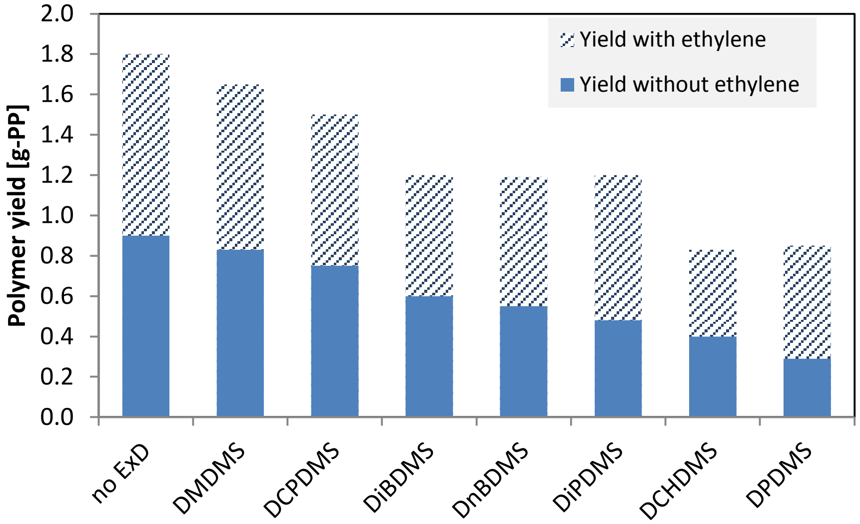


Figure 4.4 Yields in the absence/presence of ethylene in propylene-ethylene polymerization with various dimethoxysilane external donors

From the results in Table 4.4 and Figure 4.4, it was found that ethylene enhanced higher polymer yield in all cases. This came from the comonomer effects where comonomer makes the acceleration of monomer diffusions through less-crystalline polymer from the comonomer incorporation. And from the previous researches, it also showed the results that copolymerization accelerated the fragmentation of catalyst particles. All these phenomena might enhance diffusion of alkylaluminum through polymer. The resulted ethylene contents were represented the efficiency of comonomer incorporation. The dimethoxysilane which give higher ethylene content seem to have higher incorporation efficiencies among the other alkoxysilane structures.

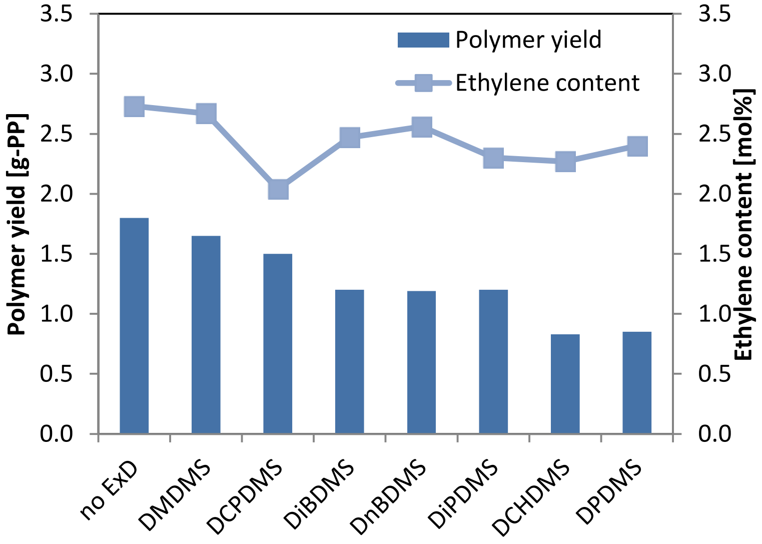


Figure 4.5 Yields and resulted ethylene contents from various dimethoxysilane external donors

Figure 4.5 shows the results of polymer yield in the presence of ethylene and resulted ethylene content in propylene-ethylene copolymerization. It was found the tendency of polymer yield enhancement is not inline with the resulted ethylene content. It can be implied that after the introduction of ethylene, it diffused into the polymer and made the less-crystalline portion which enhanced more propylene for polymerization. To confirm this effect, less reactive comonomer as 1-octene was used in the propylene-1-octene copolymerization.

4.3.3 Results of propylene-1-octene copolymerization with the different alkoxysilane structures

From the above results of propylene-ethylene copolymerization, ethylene incorporation efficiency did not show direct correlation with the structure of alkoxysilanes which coordinated to the active sites. To confirm this phenomena, 1-octene which is the less reactive comonomer was used in propylene-1-octene copolymerization as shown in Table 4.5.

Table 4.5. Propylene 1-octene copolymerization results

Alkoxysilanes	Polymer yield [g-PP]		1-octene in copolymer [mol%]
	no 1-octene	1-octene = 0.04 mol	
no ExD	6.4	10	1.30
DMDMS	5.2	7.8	1.17
DiPDMS	4.0	8.3	0.80
DnBDMS	4.2	7.4	1.05
DiBDMS	3.8	5.4	0.90
DCPDMS	4.1	7.2	0.73
DPDMS	3.0	5.8	0.85
DCHDMS	3.7	5.7	0.80

Polymerization conditions: 30 mg of $TiCl_4$/DiBP/$MgCl_2$ catalyst, [Al] = 10 mmol/L, Al/Si = 5, 1-octene in the feed = 4 mol, 50 °C, 0.5 MPa, 30 min

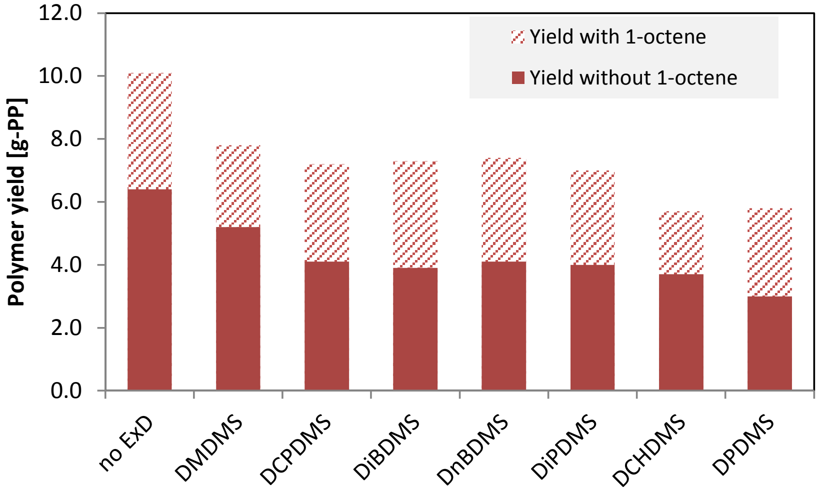


Figure 4.6 Yields in the absence/presence of 1-octene in propylene-1-octene polymerization with various dimethoxysilane external donors

From the results as shown in Table 4.5 and Figure 4.6, it was found that 1-octene also enhanced polymer yield in all cases of alkoxysilane structures. Considering with the results from propylene-ethylene polymerization, the order of polymer yield was similar as in the case of 1-octene used as comonomer. An alkoxysilane giving greater polymer yield by ethylene, also enhances greater polymer yield in the case of 1-octene, irrespective to the types of comonomer.

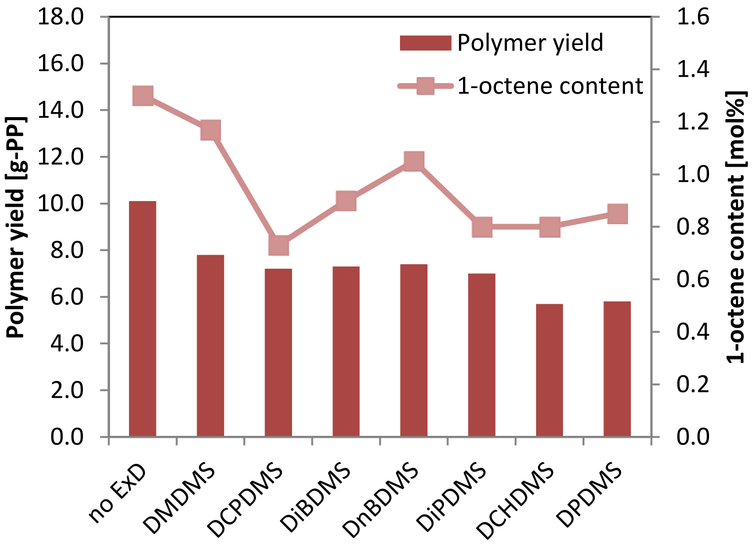


Figure 4.7 Yields and resulted 1-octene contents in propylene-1-octene copolymerization with various dimethoxysilane external donors

Figure 4.7 shows the results of both polymer yield and resulted 1-octene content in PP copolymer. It was shown that there is no correlation between polymer yield in 1-octene content. An alkoxysilane giving greater polymer yield from the comonomer enhancement did not provide the better comonomer incorporation as resulted in the comonomer content. The correlation between comonomer content and stereospecificity was shown in Figure 4.8 for both ethylene and 1-octene. It was suggested that comonomer content was well-correlated with stereospecificity with the same order of alkoxysilane, irrespective to the types of comonomer. Although there is no clear tendency between bulkiness of alkyl structure and comonomer incorporation, cyclic alkyl structure of dimethoxysilane tended to provide low comonomer incorporation.

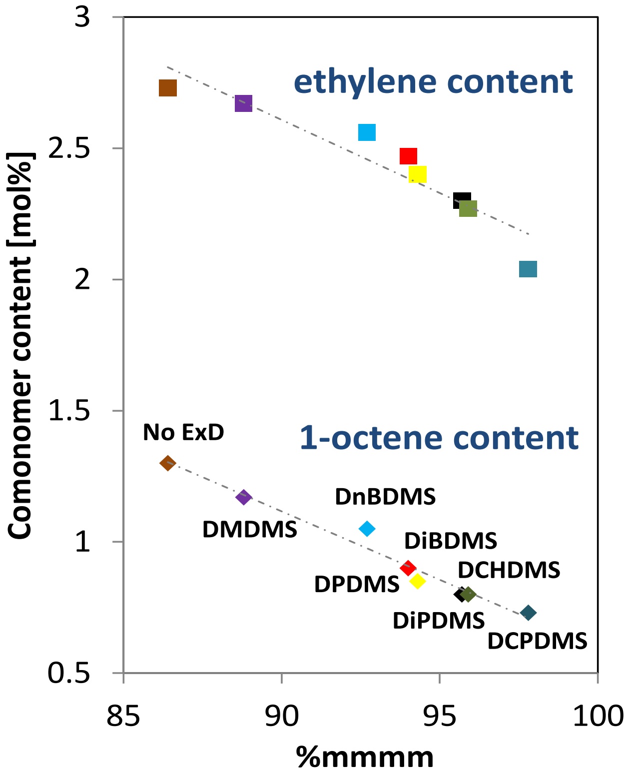


Figure 4.8 Correlations between resulted comonomer content in PP copolymer and mesopentad fraction of homopolymer

4. Conclusion

The relationship of alkoxysilane structure with comonomer incorporation was explored in this chapter. The results showed that ethylene enhances polymer yield in all dimethoxysilane structures as the comonomer effects where ethylene accelerates the monomer diffusion through the less-isotactic polymer. The polymer yield enhancement also can be obtained in the case of propylene-1-octene copolymerization. Dimethoxysilane with a higher in ethylene incorporation gave a higher 1-octene incorporation too. It was also found that the isotacticity of polymer played a key role for the commoner incorporation which can be explained from the different k_p depending on the alkoxysilane structures.

References

1. S. Y. Kim, Y. Hiraoka, T. Taniike, M. Terano, *Macrocol. Symp.* **2009**, *285*, 115.
2. H. Matsuoka, B. Liu, H. Nakatani, M. Terano, *Macromol Rapid Commun.* **2001**, *22*, 326.
3. H. Mori, H. Saito, M. Terano, *Macromol. Chem. Phys*. **1998**, *199*, 55.
4. V. Busico, P. Corradini, R. De Biasio, L. Landriani, A. L. Segre, *Macromol*. **1994**, *27*, 4521.
5. B. Liu, T. Nitta, H. Nakatani, M. Terano, *Macromol. Chem. Phys*. **2002**, *203*, 2412.
6. T. Nitta, B. Liu, H. Nakatani, M. Terano, *J. Mol. Catal. A: Chem*. **2002**, *180*, 25.
7. T. Taniike, M. Terano, *J. Catal*. **2012**, *293*, 39.
8. H. Mori, H. Saito, M. Yamahiro, H. Kono, M. Terano, *Macromol. Chem. Phys*. **1998**, *199*, 613.
9. J. V. Seppälä, M. Härkonen, *Makromol. Chem.* **1989**, *190*, 2535.
10. M. Härkonen, L. Kuutti, J. V. Seppälä, *Makromol. Chem*. **1992**, *193*, 1413.
11. M. C. Sacchi, C. Shan, P. Locatelli, I. Tritto, *Macromolecules,***1990**, *23*, 383
12. M. C. Sacchi, Z. Q. Fan, F. Forlini, I. Tritto, *Macromol. Chem. Phys*. **1994**, *195*, 2805.

13. M. Terano, K. Kimura, A. Murai, M. Inoue, M. Miyoshi, *JP patent* S62-158704, **1987.**

14. A. Dashti, A. Ramazani, Y. Hiraoka, S. Y. Kim, T. Taniike, M. Terano, *Polym. Int.* **2008**, *58*, 40.

Chapter 5

Influence of alkoxysilane structure on hydrogen response in propylene polymerization

5.1 Introduction

For propylene polymerization, electron donors are the key factor to improve catalyst performance. Electron donors are Lewis bases which can be divided into two types; internal donors are introduced during catalyst preparation and external donors are additional component which externally introduced during polymerization.[1] The development of good combination between internal and external donor has been carried out to improve the catalyst performance.

Recently significant advances have been made in understanding the fundamental factors determining the performance of state-of-the-art $MgCl_2$-supported catalysts in relation to the role of electron donors. Most interestingly studies by Busico et al. have shown that the chain irregularities in isotactic polypropylene prepared using heterogeneous catalysts are not randomly distributed along the chain but are clustered.[2] The chain can therefore contain sequences, which can be attributed to weakly isotactic (isotactoid) and to syndiotactic blocks, in addition to highly isotactic blocks. This implies that active site can isomerize very rapidly (during the growth time of single polymer chain, i.e., in less than a second between three propagating species. The polymer can therefore be considered to have stereo-block structure in which highly isotactic sequence alternate with defective isotactic and with syndiotactoid sequences. A mechanistic model was proposed by Busico et al. and explains about the strongly co-ordinating stereorigid donors typically give stereo-regular polymers in which highly isotactoid sequences predominate.[3] Terano et al. established that the steric hindrance need not always arise from a donor molecule by using Busico model to propose structures for stereospecific active sites in the donor free Ziegler-Natta catalyst system, where high stereospecificity can arise by co-ordination of the Al alkyl adjacent to the active Ti. Terano et al. stated that the formation of active site with highest stereospecificity strongly depends upon the interaction of catalyst and activator without any monomer as a pretreatment by classifying the active sites into aspecific and three kinds of isospefic sites in the Ziegler-Natta catalysts.[4] The isospecificity of active sites strongly depends upon the bulkiness of the ligand positions for construction of asymmetry and chirality of active sites and steric hindrance.[5] In Ziegler-Natta catalysts external electron donors are used to improve the stereospecificity of the catalysts. Even after much understanding on the effects of electron donors in academia as well as in industry, the specific mechanism is still unclassified. Such as how the donor and the potential active sites are getting affected before and after interaction with alkyl aluminium activator. Although both donors are important to regulate the catalyst performance, external donor is more preferable to develop the effective catalyst system due to the unnecessity change of solid catalyst platform. Up to now, alkoxysilane is the most commercially used external donor in industrial scale.

Because the catalyst performance strongly depends on the structure and type of donors[6-10], the study of structure-performance relationship (SPR) is essentially required for the development of new donor system. A number of researches have reported the effects of alkoxysilane structure on catalyst performance. Especially, Seppälä et al. found that the catalyst performance including the activity, stereospecificity, molecular weight and molecular weight distribution strongly depends on the number and size of alkoxy group as well as on the size of alkyl groups attached to the silicon atom.[7-8] Sacchi et al. explained how alkoxysilanes activate isospecific sites, affecting both microstructure and molecular weight of polypropylene (PP). They also found that in copolymerization, the size of hydrocarbon group mainly affects the yield, while the number of alkoxy groups has a greater influence on the fraction distribution.[9-10] Although there are several researches trying to explain the structure-performance relationship of alkoxysilane, only the effects on catalyst activity and stereospecificity have been investigated. Hydrogen response is also one of the most important catalyst performances, which can regulate the molecular weight of PP to the wide range of required applications. Hydrogen is the effective chain transfer agent which also reactivates the dormant sites to enhance the catalyst activity. The Catalyst providing low hydrogen response, will lead to the problematic process control. Moreover, external donor can adjust the hydrogen response of the catalyst. So, the investigation of alkoxysilane effects on the hydrogen response is also essentially required for the further development of donor system.

In this chapter, propylene polymerization in the presence of hydrogen was carried out to investigate the effects on polymer yield and molecular weight. Hydrogen response was also applied to be the representative of the ability of the catalyst to utilize the hydrogen and regulate the molecular weight. From the results, it was found that the effect of hydrogen on polymer molecular weight is independent on the nature of the alkoxysilane used as external donor in polymerization. Although there is no clear correlation of the hydrogen response with stereospecificity, cyclic alkyldimethoxysilane and triethoxysilane tended to provide greater hydrogen response.

5.2 Experimental

5.2.1 Materials

Propylene (donated by Mitsui Chemicals, Inc.) and triethylaluminum (TEA, donated by Tosoh Finechem Corporation) were used as received. Heptane was used after passing through a column of 4Å molecular sieves and bubbling with dry nitrogen for 2 h. Ethanol/hydrochloric acid (90/10 v/v) was used for quenching. Alkoxysilanes which used in this chapter are as shown in Table 5.1 and Figure 5.1.

Table 5.1 List of alkoxysilane external donors used in propylene polymerization

Name	Alkoxysiane
DMDMS	dimethyldimethoxysilane
DIPDMS	di-i-propyldimethoxysilane
DiBuDMS	d-i-butyldimethoxysilane
DnBDMS	d-n-butyldimethoxysilane
DCPDMS	dicyclopentyldimethoxysilane
DCHDMS	dicyclohexyldimethoxysilane
DPDMS	diphenyldimethoxysilane
MTES	methyltriethoxysilane
ETES	ethyltriethoxysilane
iBuTES	i-butyltriethoxysilane
CPTES	cyclopentyltriethoxysilane
VTES	vinyltriethoxysilane
ATES	allyltriethoxysilane

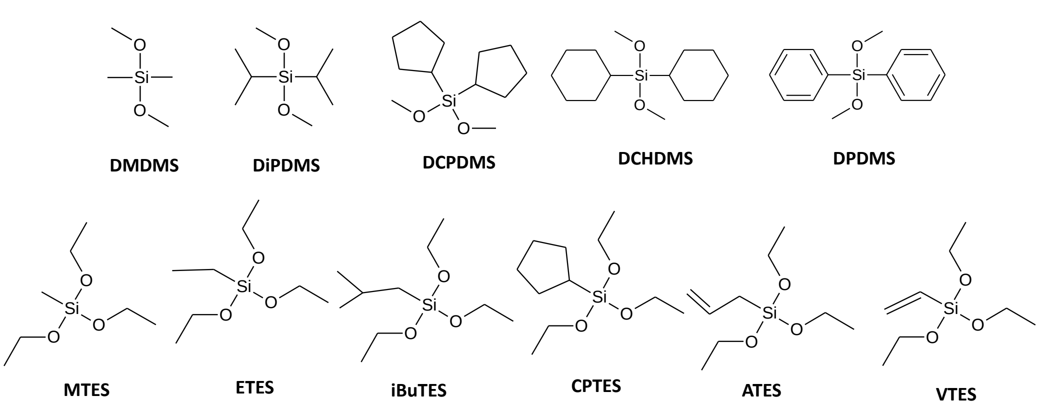


Figure 5.1. Structures of alkoxysilane external donors

5.2.2 Catalyst Preparation

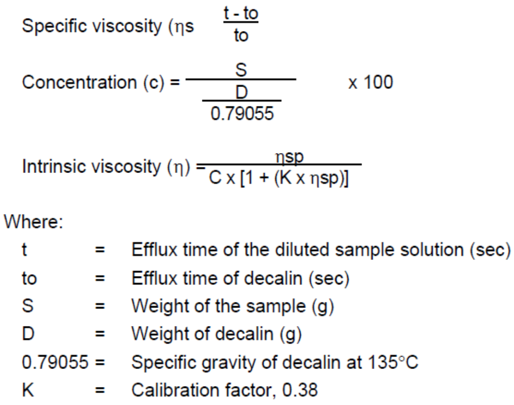
A $TiCl_4$/DiBP/$MgCl_2$ catalyst was prepared from $Mg(OEt)_2$ based on patent[11] with the minor modification[12]. The Ti and diisobutylphthalate (DiBP) contents in the catalyst were determined as 3.4 and 12 wt%, respectively.

5.2.3 Pressurized polymerization

Propylene homopolymerization was performed in a 1-L autoclave equipped with a mechanical stirrer rotating at 350 rpm. 500 ml of *n*-heptane was introduced into the reactor. TEA ([Al] = 10 mmol/L) and alkoxysilanes (Al/Si = 5) were introduced into the reactor, and the solution was saturated with 0.5 MPa of monomer at 50°C. 30 mg of a catalyst was injected into the reactor to initiate the polymerization. The polymerization was conducted for 30 min with a continuous supply of monomer gas at 0.5 MPa and hydrogen as the various feeds (2, 4, 8 and 16 mmol). After 30 min, propylene was vented and the polymer slurry was filtered immediately after mixing with acidic ethanol as quenching solution.

5.2.4 Polymer Analyses

Electromagnetically spinning viscometer (EMS) was used to determine the viscosity of diluted polypropylene as the conditions referred to ASTM D1601 which decalin is used as solvent at the temperature 135 ˚C. Then, the intrinsic viscosity (IV) and viscosity average molecular weight (M_v) can be obtained from the below equations.



$$\text{Specific viscosity } (\eta s \quad \frac{t - to}{to}$$

$$\text{Concentration (c)} = \frac{S}{\frac{D}{0.79055}} \quad \text{x } 100$$

$$\text{Intrinsic viscosity } (\eta) = \frac{\eta sp}{C \text{ x } [1 + (K \text{ x } \eta sp)]}$$

Where:

t = Efflux time of the diluted sample solution (sec)
to = Efflux time of decalin (sec)
S = Weight of the sample (g)
D = Weight of decalin (g)
0.79055 = Specific gravity of decalin at 135°C
K = Calibration factor, 0.38

And the below equation was used to calculate the M_v (Mark-Houwink equation)

$$\text{Intrinsic viscosity (IV)} = KM_v^{\alpha} \quad (\text{When } K = 0.0001580 \text{ dL/g}, \alpha = 0.770)$$

5.3 Results and Discussion

From the results in chapter 4, Figure 4.7 shows the ethylene incorporation efficiency correlates with the stereospecificity of polymer. It was mentioned earlier that the higher stereospecificity polymer tends to provide lower ethylene content. This came from the high isotactic polymer makes the low comonomer incorporation due to low k_p. In this chapter, the correlation between hydrogen response and stereospecificity was observed.

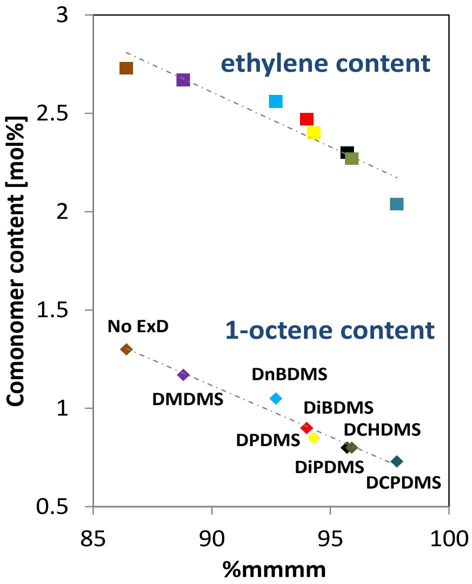


Figure 4.7. Correlation between ethylene content and stereospecificity of polymer

The effects of hydrogen with different structures of alkoxysilane external donors with $TiCl_4/DiBP/MgCl_2$ catalyst in propylene polymerization were investigated in this report. Propylene polymerizations in the presence of hydrogen were conducted. EMS viscometer was used to determine the viscosity of diluted polypropylene, and then intrinsic viscosity and molecular weight of obtained polymer were analysed. The relationship between alkoxysilane structure and hydrogen response can be obtained for the further discussion.

In propylene polymerization with $MgCl_2$-supported catalysts, the effect of hydrogen on catalyst activity and polymer molecular weight is dependent on the type of internal donors and external donors applied in catalyst system. The effect on polymer yield comes from the hydrogen activation effect which can be ascribed to the regeneration of active sites via chain transfer at dormant (2,1-insertion) sites. It can be assumed that the different of alkoxysilane structures used as external donors can regulate different results depending on their structures. The results of polymer yield from the propylene polymerization carried out at different hydrogen concentrations in the presence of various alkoxysilane structures are shown in Table 5.2. It is apparent that, in all cases, catalyst activity increased with increasing hydrogen concentration. The polymer yield at high hydrogen concentration were 2-3 times higher than those obtained in the absence of hydrogen. Moreover, the order of polymer yields was not similar in each given hydrogen concentration. There was also no tendency between polymer yield and the bulkiness of alkoxysilane structures.

Table 5.2. Results of polymer yield in the different ranges of hydrogen concentration

	Polymer yield [g-PP]				
Alkoxysilanes	no H_2	H_2 2 mmol	H_2 4 mmol	H_2 8 mmol	H_2 16 mmol
no donor	9.6	11	15	20	23
DMDMS	6.5	7.4	9.8	15	17
DiPDMS	4.5	5.8	7.8	11	12
DiBuDMS	3.6	5.1	6.8	8.9	9.5
DnBDMS	4.2	5.6	7.8	9.0	9.3
DCPDMS	7.2	10	13	19	21
DCHDMS	4.5	5.7	7.1	10	13
DPDMS	5.5	7.8	10.5	13	15
MTES	5.2	5.8	6.4	7.5	7.7
ETES	4.2	5.8	6.8	8.2	8.6
iBuTES	2.8	4.0	4.8	7.3	8.9
CPTES	2.1	5.8	8.3	10.1	11
PTES	2.0	3.4	4.6	6.1	7.4
VTES	1.5	3.9	4.3	6.0	7.0
ATES	2.5	3.5	6.2	7.5	8.2

Polymerization conditions: 30 mg of $TiCl_4$/DiBP/$MgCl_2$ catalyst, [Al] = 10 mmol/L, Al/Si = 5, 50 °C, 0.5 MPa, time 30 min

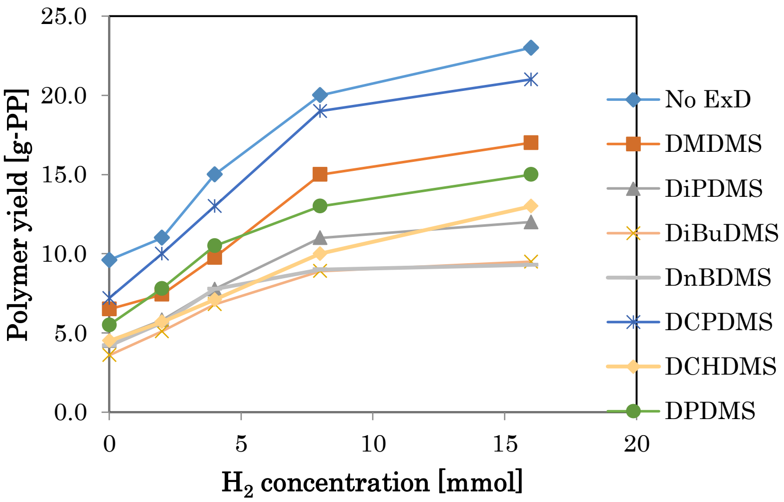


Figure 5.2. Correlation between H_2 concentration and polymer yield using dimethoxysilane as external donor

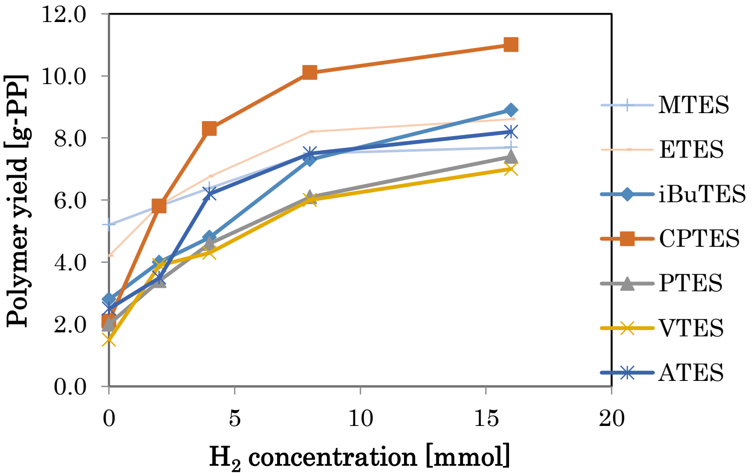


Figure 5.3. Correlation between H_2 concentration and polymer yield using triethoxysilane as external donor

In propylene polymerization using $MgCl_2$-supported catalysts, the molecular weight of the polymer is controlled by the use of hydrogen as a transfer agent. So it is necessary to understand the effect of alkoxysilane structures on the hydrogen response. The hydrogen response of a catalyst is the sensitivity of chain transfer with hydrogen, which is known to be dependent on both regio- and stereoselectivity. Considering the effects on hydrogen response, the results of intrinsic viscosity and molecular weight of polymer are shown as in Table 5.2. The results show that hydrogen gave the lower molecular weight for all alkoxysilane structures. These alkoxysilanes differ considerably in their effects on polymer molecular weight in propylene polymerizations carried out in the presence of hydrogen as shown in the increasing degree of polymer yield in Figure 5.2 and Figure 5.3.

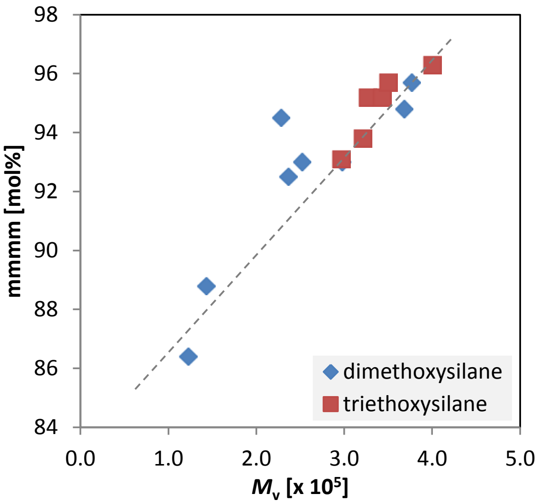


Figure 5.4. Correlation between molecular weight of polymer in the absence of hydrogen with mesopentad fraction

Table 5.3. Results of intrinsic viscosity and molecular weight in various hydrogen feed ranges

	Intrinsic viscosity [dL/g]					M_v (x 10^5)				
Alkoxysilanes	no H_2	H_2 2 mmol	H_2 4 mmol	H_2 8 mmol	H_2 16 mmol	no H_2	H_2 2 mmol	H_2 4 mmol	H_2 8 mmol	H_2 16 mmol
no donor	1.31	1.01	0.70	0.34	0.17	1.23	0.87	0.55	0.21	0.09
DMDMS	1.47	1.02	0.82	0.37	0.16	1.43	0.89	0.67	0.24	0.08
DiPDMS	3.11	2.43	2.11	1.65	1.02	3.77	2.74	2.27	1.66	0.88
DiBuDMS	2.17	1.64	1.09	1.02	0.89	2.36	1.65	0.97	0.88	0.74
DnBDMS	2.28	2.01	1.80	1.48	1.12	2.52	2.14	1.86	1.44	1.00
DCPDMS	3.05	1.43	1.10	0.63	0.28	3.68	1.38	0.98	0.47	0.16
DCHDMS	2.59	1.45	1.38	1.21	1.05	2.97	1.41	1.32	1.10	0.92
DPDMS	2.11	1.15	0.87	0.67	0.42	2.28	1.03	0.73	0.52	0.28
MTES	2.78	1.60	1.19	0.69	0.68	3.26	1.59	1.08	0.53	0.53
ETES	3.25	2.19	1.40	0.54	0.51	4.00	2.39	1.33	0.39	0.36
iBuTES	2.58	1.89	1.64	1.38	0.96	2.97	1.97	1.65	1.31	0.82
CPTES	2.75	1.90	1.62	1.46	1.10	3.21	1.98	1.62	1.42	0.98
PTES	2.86	2.07	1.92	1.33	1.07	3.38	2.22	2.02	1.25	0.95
VTES	2.89	1.51	1.09	0.87	0.75	3.43	1.47	0.96	0.72	0.59
ATES	2.93	2.17	1.80	1.50	1.10	3.50	2.36	1.85	1.46	0.98

Polymerization conditions: 30 mg of $TiCl_4/DiBP/MgCl_2$ catalyst, [Al] = 10 mmol/L, Al/Si = 5, 50 °C, 0.5 MPa, time 30 min

Table 5.4. Viscosity average molecular weight (M_v) of obtained polymer in the absence of hydrogen compared with the stereospecificity of polymer

Alkoxysilanes	M_v (x 10^5)	%mmmm[a)]
no donor	1.20	86.4
DMDMS	1.43	88.8
DiPDMS	3.77	95.7
DiBuDMS	2.40	92.5
DnBDMS	2.53	93.0
DCPDMS	3.68	94.8
DCHDMS	3.00	94.5
DPDMS	2.30	93.0
MTES	3.26	95.2
ETES	4.00	96.3
iBuTES	2.95	93.1
CPTES	3.20	93.8
PTES	3.38	94.7
VTES	3.43	95.7
ATES	3.50	95.2

[a)] %mol (determined by ^{13}C NMR spectroscopy)

In the absence of hydrogen, the results in Table 5.4 showed that alkoxysilanes giving high stereospecificity also gave high molecular weight polypropylene. So, in the absence of hydrogen, the molecular weight was well-correlated with the stereospecificity of polymer as shown in Figure 5.4. It can be seen that molecular weight was lower in all cases of alkoxysilane structures in the presence of hydrogen. The molecular weight was decreased when increasing the hydrogen concentration. The slope of the molecular weight decrement was found in the hydrogen concentration of 2-4 mmol is steeper comparing with those from the hydrogen concentration of 8 and 16 mmol (Figure 5.2 and 5.3). It seems that hydrogen became saturated after hydrogen concentration more than 8 mmol which cannot be used for the investigation of hydrogen response. Although the molecular weight are decreased but it is also not similar order for each given hydrogen concentration. It may come from the different of hydrogen responses depending on the structure of alkoxysilanes.

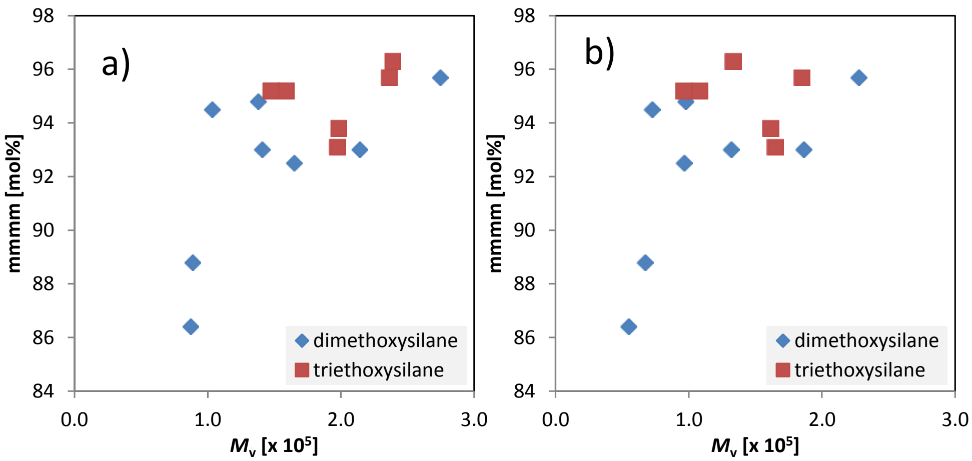


Figure 5.5. Correlation between molecular weight of polymer in the presence of hydrogen with mesopentad fraction; a) P_{H2} = 1 atm, b) P_{H2} = 2 atm

Considering the hydrogen response depending upon the alkoxysilane structures, Table 5.5 and Figure 5.6 showed the results of the decrement rate of molecular weight at 2 mmol and 4 mmol. It was found that triethoxysilane seemed to provide the slightly better hydrogen response comparing with the dimethoxysilanes. But DiBuDMS also provided the best hydrogen response among the other dimethoxysilanes.

Table 5.5. Results of hydrogen response

	Hydrogen response	
Alkoxysilanes	1	2
no donor	1.41	2.24
DMDMS	1.62	2.13
DiPDMS	1.37	1.66
DiBuDMS	1.43	2.44
DnBDMS	1.18	1.35
DCPDMS	2.67	3.77
DCHDMS	2.12	2.25
DPDMS	2.21	3.14
MTES	2.06	3.02
ETES	1.68	3.00
iBuTES	1.50	1.80
CPTES	1.62	1.99
PTES	1.53	1.67
VTES	2.33	3.57
ATES	1.48	1.89

*H_2 response 1 = M_v of no H_2/M_v of H_2 2 mmol, H_2 response 2 = M_v of no H_2/M_v of H_2 4 mmol

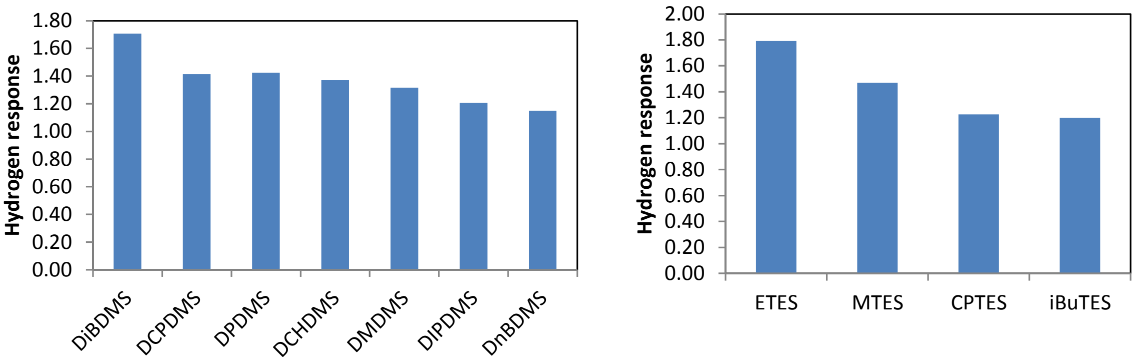


Figure 5.6. Hydrogen response with different alkoxysilane structures

The effect of hydrogen on polymer molecular weight is dependent on the nature of alkoxysilanes used as external donors in polymerization. At a given hydrogen concentration, methoxysilanes typically provide higher molecular weight polymer than ethoxysilanes.[10] But there are also differences between among methoxysilane structures, depending on the type of alkyl substituents. In the case of triethoxysilanes, VTES provides the best while iBuTES gives the worst hydrogen response. Considering the structure of alkyl substituents, there is no tendency between hydrogen response and the bulkiness of alkyl structures. Moreover, there is also no correlation between stereospecificity of polymer and hydrogen response. It means that the universal correlation of sterospecificity related to k_p which affected by alkoxysilane structure, cannot be applied to the polymerization in the presence of hydrogen. It can be applied for the explanation in the case of comonomer incorporation and the molecular weight enhancement in the absence of hydrogen with the introduction of alkoxsilane external donor. It is known that regio- and stereoregular can be restored by chain transfer with hydrogen, means that the effects of both regio- and stereoirrugular insertion should be condsidered in relation to hydrogen activation. The combined effects of regio- and stereoirregular insertion were already explained in the previous study[19] that the ratio *n*-Bu/*i*-Bu chain ends increases with increasing stereospecificity of the system. Considering the correlation in Figure 5.5 shows that the correlation between molecular weight and stereospecificity which found to be occurred in the absence of hydrogen, was disappeared. It can be concluded that we cannot explain the effects of alkoxysilane structure on hydrogen response with only stereospecificity of polymer from each alkoxysilane used as external donor.

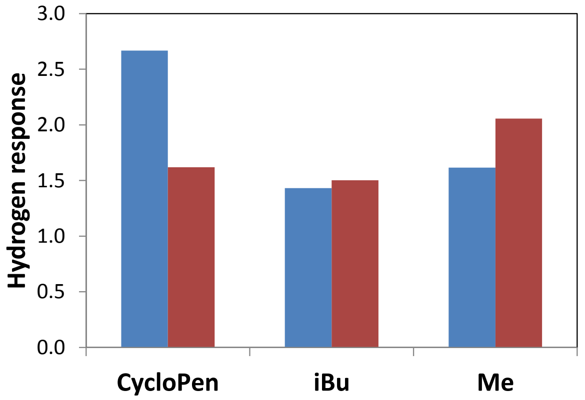


Figure 5.7. Hydrogen response compared between; dimethoxysilane (blue), triethoxysilane (red) with same alkyl structure

From the comparison between hydrogen response of dimethoxysilane and triethoxysilane, it was found that triethoxysilane seemed to provide better hydrogen response compared to dimethoxysilane except cycloalkyl alkoxysilane.

5.4 Conclusion

In this chapter, the influence of alkoxysilane structure on hydrogen response in propylene polymerization was investigated. Dimethoxysilane tended to provide greater polymer yield as compared to triethoxysilane where a higher polymer yield in the absence of hydrogen accompanied a higher yield in the presence of hydrogen too. Di- and trialkoxysilane shared the same correlation between molecular weight and stereospecificity which cannot explain in the case of in the presence of hydrogen. The hydrogen response made the effects of alkoxysilane structure changed which cannot be explained by the k_p. It also can be suggested that dialkoxysilane with cycloalkyl and triethoxysilane with small alkyl group seemed to provide good hydrogen response.

References

1. E. Albizzati, U. Giannini, G. Collina, L. Noristi, L. Resconi, *Propylene Handbook*, E. P. Moore, Ed., Hanser, New York **1996**, Chapter 2.
2. V. Busico, R. Cipullo, G. Talarico, A. L. Segre, J. C. Chadwick, *Macromolecules* **1997**, *30*, 4786.
3. V. Busico, P. Corradini, R. D. Biasio, L. Landriani, A. L. Segre, *Macromolecules* **1994**, *27*, 4521.
4. B. Liu, T. Nitta, H. Nakatani, M. Terano, *Macromol. Chem. Phys*. **2003**, *204*, 395.
5. T. Nitta, B. Liu, H. Nakatani, M. Terano, *J.Mol.Catal. A:Chem***., 2002**, *180*, 25.
6. H. Mori, H. Saito, M. Yamahiro, H. Kono, M. Terano, *Macromol. Chem. Phys.* **1998**, *199*, 613.
7. J. V. Seppälä, M. Härkonen, *Makromol. Chem.* **1989**, *190*, 2535.
8. M. Härkonen, L. Kuutti, J. V. Seppälä, *Makromol. Chem*. **1992**, *193*, 1413.
9. M. C. Sacchi, F. Forlini, I. Tritto, R. Mendichi, G. Zannoni, L. Noristi, *Macromolecules* **1992**, *25*, 5914.
10. M. C. Sacchi, Z. Q. Fan, F. Forlini, I. Tritto, P. Locatelli, *Macromol. Chem. Phys*. **1994**, *195*, 2805.
11. M. Terano, K. Kimura, A. Murai, M. Inoue, M. Miyoshi, *JP patent* S62-158704, 1987.
12. A. Dashti, A. Ramazani, Y. Hiraoka, S. Y. Kim, T. Taniike, M. Terano, *Polym. Int.* 2008, *58*, 40.

Chapter 6

General Conclusion

6.1 General summary

In this dissertation, the structure-performance relationship of alkoxysilane as external donor in propylene polymerization was discussed. The results were categorized for discussion into 5 chapters as follows;

In chapter 1, general introductions introduced the importance of Ziegler-Natta catalyst system, the development of ZN catalysts, the importance of alkoxysilane external donor and the existing structure-performance relationship of alkoxysilane, the calculations based on coadsorption energies, which was applied in the correlation, aiming to achieve the information based on the objectives of this dissertion.

In chapter 2, structure-performance relationship of dimethoxysilane in propylene polymerization was elucidated. Three types of polymerization were carried out in the absence/presence of internal donor to observe the effects on the catalyst performances in terms of catalyst activity and stereospecificity.

In chapter 3, structure-performance relationship of triethoxysilane in propylene polymerization was also elucidated with three polymerization conditions. This chapter is aiming at the generalization of SPR to the other types of alkoxysilane structures.

In chapter 4, the effects of alkoxysilane structures on propylene copolymerization was investigated due to the importance of comonomer for polypropylene. Pressurized polymerization was conducted with different structures of dimethoxysilane as external donor. The resulted comonomer contents were applied to determine the SPR on the catalyst performance in term of comonomer incorporation efficiency.

In chapter 5, propylene polymerization in the presence of hydrogen was carried out to investigate the effects of alkoxysilane structure on the hydrogen response.

6.2 Conclusion

The development of donor system has been researched over decades since the discovery of Ziegler-Natta catalyst. It is known that the structures of donor affect the catalyst performances in terms of catalyst activity, stereospecificity, comonomer incorporation, molecular weight and its distribution, etc. Several researches tried to explain the relationship between structure of alkoxysilane external donor and catalyst performance. However, the systematic understanding was not explored yet. To develop new donor system, structure-performance relationship of alkoxysilane is essentially required. In Chapter 2 and 3, the generalization of structure-performance relationship for alkoxysilane was achieved in terms of catalyst activity and stereospecificity. The catalyst stereospecificities from all types of alkoxysilane provide the universal correlation with the DFT calculations based on coadsorption energies, which is useful for the development of new donor structure. To consider about the other catalyst performances which are also important, Chapter 4 and 5 discussed about the influence of alkoxysilane structure on the comonomer incorporation and hydrogen response. It was found that selection of appropriate alkoxysilane external donors, the balance of comonomer content and stereospecficity is needed to be considered. These results can provide the information for the catalyst users to improve the catalyst performance leading to the required product properties.

6.3 Achievements

Publications

- S. Poonpong, S. Dwevedi, T. Taniike and M. Terano (2014). Structure-performance relationship for dialkyldimethoxysilane as an external donor in stopped-flow polymerization using a Ziegler-Natta catalyst, *Macromolecular Chemistry and Physics, 215*, 1721 – 1727.

- A. Thakur, S. Poonpong, M. Terano and T. Taniike (2014). New quenching method for improving large-scale stopped-flow technique, *Macromolecular Reaction Engineering, 8,* 766-770.

Domestic conferences

- S. Poonpong, T. Taniike and M. Terano, The investigation of structure-performance relationship of dialkoxysilanes in the initial stage of propylene polymerization in the absence/presence of internal donors. The 44th Asahikawa JPI Conference (旭川大会: 第 44 回石油・石油化学討論会), Hokkaido, Japan, 16 – 19 October 2014. *(Oral Presentation)*

- S. Poonpong, P. Chammingkwan, T. Taniike and M. Terano, Structure-performance relationship for alkoxysilanes as an external donor in propylene-ethylene polymerization using Ziegler-Natta catalyst. The SPSJ 64th symposium on Macromolecules, Sendai, Miyagi, Japan, 15-17 September 2015. *(Poster Presentation)*

- S. Poonpong, P. Chammingkwan, T. Taniike and M. Terano, Study of trialkoxysilane structure-performance relationship using stopped-flow propylene polymerization, The SPSJ 65th Annual meeting, Kobe, Hyogo, Japan, 25 – 27 May 2016. *(Poster Presentation)*

- S. Poonpong, P. Chammingkwan, T. Taniike and M. Terano, Effects of structure of dimethoxysilane external donors on the propylene copolymerization using Ziegler-Natta catalysts, The 65th Symposium Macromolecules, Yokohama, Kanagawa, Japan, 14-16 Sep 2016. (Poster Presentation)

- S. Poonpong, P. Chammingkwan, T. Taniike and M. Terano, Hydrogen and comonomer effects on ZN catalyzed propylene polymerization using different types of alkoxysilane external donor, The 46th Petroleum-Petrochemical Symposium of JPI (京都大会: 第46回石油・石油化学討論会), Kyoto, Japan, 16 - 17 Nov 2016. (Oral Presentation)

International conferences

- S. Poonpong, P. Chammingkwan, T. Taniike and M. Terano, The elucidation of structure-performance relationship for various types of di- and tri- alkoxysilane used as an external donor in propylene polymerization. The World Polyolefin Congress 2015 (WPOC 2015), Tokyo, Japan, 23 – 27 November 2015. *(Poster Presentation)*

- S. Poonpong, P. Chammingkwan, T. Taniike and M. Terano, The investigation of structure-performance relationship for alkoxysilane structure using different types of propylene polymerization, The 4th Blue Sky Conference on catalytic olefin polymerization, Sorrento, Japan, 27 June – 1 July 2016. *(Poster Presentation)*

Effects of pretreatment and prepolymerization with

alkoxysilanes on propylene polymerization using Parallel Pressure Reactor

By

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1. **Introduction**

Ziegler-Natta (ZN) catalysts comprising $TiCl_4/MgCl_2$ is one of the most important industrial catalysts contributing to more than 90% of polyolefins production in the world.[1] During the past six decades, several ZN catalyst systems have been established to satisfy process and product requirements. In ZN catalyst system, it consists of solid catalyst ($MgCl_2/TiCl_4$), activator (alkylaluminum) and electron donors. The significant advances have been made to understand the fundamental factors determining the performance of state-of-the-art $MgCl_2$-supported catalysts in relation to the role of electron donors. Most interestingly studies by Busico et al. have shown that the chain irregularities in isotactic polypropylene prepared using heterogeneous catalysts are not randomly distributed along the chain but are clustered.[2] The chain can therefore contain sequences, which can be attributed to weakly isotactic (isotactoid) and to syndiotactic blocks, in addition to highly isotactic blocks. This implies that active site can isomerize very rapidly (during the growth time of single polymer chain, i.e., in less than a second between three propagating species. The polymer can therefore be considered to have stereo-block structure in which highly isotactic sequence alternate with defective isotactic and with syndiotactoid sequences. A mechanistic model was proposed by Busico et al. and explains about the strongly co-ordinating stereorigid donors typically give stereo-regular polymers in which highly isotactoid sequences predominate.[3] Terano et al. also established that the steric hindrance need not always arise from a donor molecule by using Busico model to propose structures for stereospecific active sites in the donor free Ziegler-Natta catalyst system, where high stereospecificity can arise by co-ordination of the Al alkyl adjacent to the active Ti. Terano et al. stated that the formation of active site with highest stereospecificity strongly depends upon the interaction of catalyst and activator without any monomer as a pretreatment by classifying the active sites into aspecific and three kinds of isospefic sites in the Ziegler-Natta catalysts.[4] The isospecificity of active sites strongly depends upon the bulkiness of the ligand positions for construction of asymmetry and chirality of active sites and steric hindrance.[5]

Electron donors can be categorized into two types; internal donor which introduced during catalyst preparation and external donor which applied in the polymerization stage. Both of donors are playing the important roles to improve the catalyst stereospecificity. But external donors are more interesting for the improvement because of their applications which can directly be introduced to the process without changing of existing solid catalyst platform and possible to regulate the hydrogen response of the catalyst. Even after much understanding on the effects of electron donors in academia as well as in industry, the specific mechanism is still unclassified. Such as how the donor and the potential active sites are getting affected before and after interaction with alkyl aluminium activator. Considering the external donors, alkoxysilane is occupying the major portion in polypropylene production. Several studies have tried attempts to understand the effects of alkoxysilane on the catalyst performance more clearly. Although some information of alkoxysilane effects has already been obtained, there is still margin for the improvement of catalyst performance by using alkoxysilanes prior the polymerization period, such as catalyst pretreatment and prepolymerization step.

In the recent study, how alkoxysilane interact with active sites using stopped-flow polymerization combined with the TREF analysis was investigated.[6] It was found that selective poisoning of aspecific sites is not a main factor for alkoxysilanes to improve the catalyst stereospecificity, but the formation of new isospecific active sites is regarded as more important. Moreover, it was believed that the way how alkoxysilanes are contacted with a catalyst does not affect the kind of isospecific active sites newly formed by their additions, but affects the efficiency of their formation. It is interesting to determine how alkoxysilane affects the catalyst performance during its introduction in the catalyst pretreatment step.

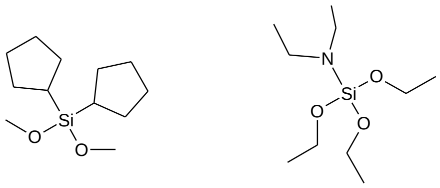
As known that prepolymerization step was described to be the polymerization in a slow polymerization rate with mild conditions at low temperature and low monomer concentration. The main objective of prepolymerization is to improve the morphology of catalysts because it is important to determine its behavior in the reactor, especially in gas phase reactor. Also, the distribution of rubber part in the production of high impact polypropylene can be improved. It can eliminate the problem of the presence of fine particles which make reactor fouling. From the previous studies of prepolymerization, it was found that comparing with only one-step polymerization (main polymerization), prepolymerization catalyst gave higher productivity with the same polymer properties in both conditions. This higher productivity comes from the increment of active sites. But in fact, propagation rate and transfer reaction rate remain unchanged which mean that there is no change in the chemical nature of active sites. So it is challenge to explore the way that we can improve active sites since in the initial polymerization step as prepolymerization.

To investigate the effects of alkoxysilanes on the catalyst performance, it needs to gather for great amount of information for screening which alkoxysilane structure can provide the significant effects. High throughput experiment using Parallel Pressure Reactor (PPR) which was invented by Busico et.al., was used to investigate the effects more carefully within a short period. So, this study is aiming to investigate the effects of alkoxysilane external donor which is introduced in pretreatment and prepolymerization step on the catalyst performance. This information will provide the results of catalyst performances in terms of polymer yield, hydrogen response and polymer microstructure for the further development of the polypropylene production using alkoxysilane external donors.

2. Experimental

2.1 Catalyst pretreatment

Catalyst pretreatment was carried out in stirred flask containing 200 mL of heptane and 2.0 mmol of TEA (at the Al/Ti ratio 0.2 by weight) and 0.3 mmol of an alkoxysilane external donor with 5.0 g of $TiCl_4$/DiBP/$MgCl_2$ catalyst. After 30 min, catalyst was washed with heptane for several times. Then, pretreated catalyst was dried under vacuum pressure. Ti content of obtained catalyst was measured by UV-vis spectroscopy. Alkoxysilane external donors used in these experiments were dicyclopentyldimethoxysilane (D-donor) and diethylaminotriethoxysilane (U-donor) which their structures are shown in Figure 1.



D-donor U-donor

Figure 1. Chemical structures of alkoxysilane external donors

2.2 Prepolymerization

Propylene prepolymerization was carried out in stirred flask containing 200 mL of heptane and 2.0 mmol of TEA (at the Al/Ti ratio of 0.2 by weight) and 0.3 mmol of alkoxysilane external donor. After 30 min of propylene saturation, 5.0 g of $TiCl_4$/DiBP/$MgCl_2$ catalyst was added under the continuous feed of propylene at 1 atm and 30 ^{0}C. The prepolymerization was carried out for 2 – 4 hours to achieve the prepolymer yield at 1 g-PP/g-cat and 7 g-PP/g-cat. The prepolymer was washed with purified heptane for several times to remove the catalyst residue. Then prepolymer was dried and kept under nitrogen atmosphere.

2.3 Parallel Pressure Polymerization (PPR)

Propylene polymerization was carried out in a 6-mL stainless steel reactor. Heptane with TEA as scavenger (total volume 5.0 mL) was introduced into the reactor in the glovebox operating under nitrogen atmosphere and then propylene gas and hydrogen gas were introduced to saturate the liquid phase to reach final pressure of 80 psi with temperature 70 ^{0}C. After propylene saturation; catalyst, TEA as activator and external donor were injected to each reactor in the Al/Si/Ti molar ratio of 140/28/1. Propylene was continuously supplied to keep constant pressure during polymerization. Polymerization was terminated after 30 – 90 min using high pressure air.

2.4 Polymer Characterization

The molecular weight and molecular weight distribution of polymer samples were characterized by Gel Permeation Chromatography (GPC). The stereostructure of polypropylene was determined by ^{13}C NMR (Bruker 400 MHz) at 120^{0}C using 1,1,2,2-tetrachloroethane-d_2 as a solvent and internal lock. Selected polymer samples were also characterized by Crystallization Elution Fractionation (CEF), using Polymer Char set up with *o*-dichlorobenzene (ODCB) as a solvent.

3 Results and Discussion

As is known, alkoxysilanes are used as external donors which are introduced during the polymerization to improve the catalyst performance in terms of catalyst activity, stereospecificity, molecular weight and its distribution. From the previous studies, the pretreatment of catalyst with external donor can improve the stereospecificity with the loss of catalyst activity from the selective poisoning of active sites. Prepolymerization is also used in the industrial process to improve the catalyst performance. So, it is still interesting to investigate the effects of alkoxysilane on the pretreatment and prepolymerization step. So, in this study, the effects of alkoxysilane used prior the polymerization were investigated. The results and discussion are separated into 2 topics; 1) the pretreatment effects with alkoxysilanes, 2) the prepolymerization effects with alkoxysilanes.

3.1 Pretreatment effects

The objective of this research is aiming at the investigation of the effects of alkoxysilanes by the catalyst pretreatment in the presence of alkoxysilane external donor. Due to the long contact time of catalyst and alkylaluminum in the case of pretreatment, catalyst may be deactivated. Because the obtained polymer from pretreated catalyst used in propylene polymerization by PPR experiments is less, the confirmation of catalyst activity by preliminary polymerization using autoclave reactor is required. Hydrogen was also introduced to observe the activity enhancement during polymerization, which can reactivate the dormant site from the deactivation. Non-pretreat cat is the

$TiCl_4/DiBP/MgCl_2$ catalyst without any pretreatment. Pretreat cat-D is the $TiCl_4/DiBP/MgCl_2$ catalyst which was pretreated in the presence of dicyclopentyldimethoxysilane (D-donor). The polymerization conditions were also described in Table 1.

Table 1. Polymerization results using batch-wise autoclave reactor

Batch no.	**Catalysts**	**External donor**	**H_2 pressure [bar]**	**Al/Si [mol/mol]**	**Polymerization time [min]**	**Catalyst activity [g-PP/mg-Ti·h·bar]**
1	Non-pretreat cat	N/A	0	0	60	20
2	Pretreat cat-D	N/A	0	0	60	11
3	Pretreat cat-D	D-donor	0	5	60	12
4	Pretreat cat-D	D-donor	0.2	5	60	30

Polymerization conditions : Propylene polymerization, TEA 2.0 mmol, pressure 3.5 bar, temperature 70 °C, time 60 min

From Table 1, it was shown that the pretreated catalyst still kept activating and can be used in the second step polymerization. Considering the polymer yield quantitatively, pretreated catalyst also provides less catalyst activity compared to non-pretreated catalyst from the poisoning of active sites. This result is corresponded to the result of previous studies.[6] In Batch 3, D-donor was also introduced during polymerization. As is known, from the former researches, polymer yield is decreased in the absence of external donor. But in this experiment using pretreated catalyst, catalyst activity is still kept similar without any reduction (Batch 2 and 3). For hydrogen, the results show that the greater catalyst activity can be obtained in the case of hydrogen addition. This may come from the following reasons; increasing of propagation rate, formation of new active sites or reactivation of dormant sites. From these results, there is the possibility of using pretreated catalyst in high throughput experiment using PPR reactors.

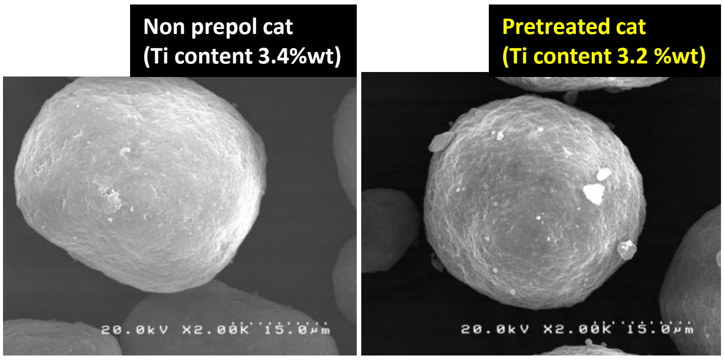


Figure 2. SEM images of non-pretreated catalyst and pretreated catalyst with D-donor

Table 2. Ti content of various catalysts

Catalyst system		Ti content [wt%]
1.	Non-pretreat cat	3.4
2.	Pretreated cat – no donor	3.2
3.	Pretreated cat – U donor	2.9
4.	Pretreated cat – D donor	3.3

Figure 2 shows the morphology of the catalysts after the pretreatment with alkylaluminum and alkoxysilane D-donor. It was found that there is no change of catalyst morphology after pretreatment in terms of size and surface of the catalyst. It can be implied that there is no physical change during the catalyst pretreatment which can lead to the change of active site concentration. Considering the Ti content which results are shown in Table 2, no significant difference of Ti content of each pretreated catalyst can be observed. This can be assumed that the prior contact of alkylaluminum and the catalyst does not make any changes of the amount of Ti in catalyst. But the obtained active site concentration can be determined in the polymerization step.

To investigate the effects of alkoxysilane external donor in pretreated catalyst on catalyst performance, different pretreated catalysts were used in propylene polymerization by PPR. The polymerization results were shown in Table 3 and Figure 3.

Table 3. Results of catalyst activity using various catalysts in propylene polymerization

	Catalyst activity [g-PP/h·mg-Ti·bar]					
Catalysts	**no H_2 no ED**	**H_2/C_3 = 0.7 no ED**	**H_2/C_3 = 2.3 no ED**	**no H_2 with ED**	**H_2/C_3 = 0.7 with ED**	**H_2/C_3 = 2.3 with ED**
Non-pretreat cat	11.1	4.5	14.3	11.6	8.3	22.9
Pretreat/no donor	6.2	6.6	20.6	4.6	6.3	19.5
Pretreat/U donor	1.4	1.6	3.5	1.1	0.7	2.8
Pretreat/D donor	5.9	9.2	21.9	5.1	7.6	16.8

Polymerization conditions: Propylene polymerization, Al/Si/Ti molar ratio = 140/28/1, temperature 70 °C, pressure 80 psi

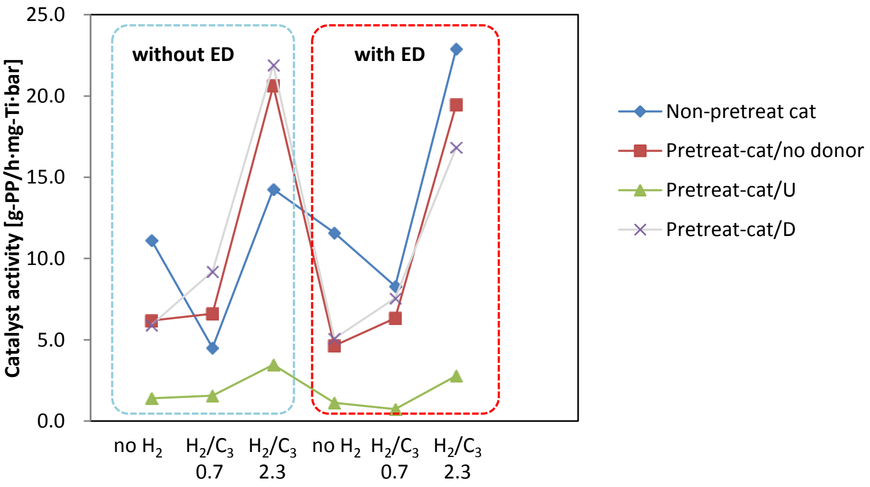


Figure 3. Catalyst activity using various catalysts

From the above results, propylene polymerizations were carried out using the different pretreated catalysts. The pretreated catalysts are varied by the introduction of alkoxysilane external donors during the pretreatment step. The effective PPR experiments were conducted to investigate the effects of alkoxysilane in the pretreatment step compared to the effects on polymerization performance using catalyst without any pretreatment. The results from PPR experiments can help us to search for the interesting conditions that further observation is required. From the previous assumption, during the contact of alkylaluminum and catalyst, active sites are activated and internal donor is leached out following by the replacement of alkoxysilane external donor. Comparing between absence and presence of external donor (D-donor) during main polymerization step, polymer yield was decreased in all cases of catalysts. This is due to the selective poisoning of active sites from the introduction of external donor, similar to the results of previous studies. Considering for the pretreatment, all pretreated catalyst provided lower catalyst activity compared to the Non-pretreat catalyst. This is plausibly due to the deactivation of some active sites during the long contact time of catalyst and alkylaluminum. Effects of alkoxysilane types, pretreat-cat/U gave the significant lower of catalyst activity and longer induction time before the activity reaches the highest catalyst activity. But pretreat-cat/no donor and pretreat-cat/D gave similar catalyst activity. Hydrogen increases catalyst activity in all catalyst types, especially in the case of pretreat-cat/no donor and pretreat-cat/D. Moreover, the results of molecular weight also show that pretreat-cat/no donor and pretreat-cat/D provide the better hydrogen response than pretreat-cat/U as shown in Table 4.

Table 4. Results of molecular weight and hydrogen response

	M_w [kDa]			**M_w [kDa]**		
Catalysts	**$H_2/C_3 = 2.3$ no ED**	**$H_2/C_3 = 0.7$ no ED**	**Hydrogen response**	**$H_2/C_3 = 2.3$ with ED**	**$H_2/C_3 = 0.7$ with ED**	**Hydrogen response**
Non-pretreat cat	98	135	1.38	227	309	1.36
Pretreat-cat/no donor	146	250	1.71	181	282	1.56
Pretreat-cat/U	172	247	1.44	201	275	1.37
Pretreat-cat/D donor	165	264	1.60	176	278	1.58

*Hydrogen response is calculated from (M_w at $H_2/C_3 = 0.7$)/(M_w at $H_2/C_3 = 2.3$)

3.2 The prepolymerization effects with alkoxysilanes

Generally, prepolymerization in the industrial scale is carried out at mild conditions to improve the catalyst morphology prior to the high-temperature polymerization. This will make the catalyst strengthen preventing the catalyst breakage and improve the catalyst morphology physically. From the previous studies, it was found that the increase of catalyst activity is plausibly due to the formation of new active sites and/or the activation of dormant sites by α-olefin. Moreover, the reduction of diffusion mass transfer resistance of the co-catalyst and monomer through the polymeric layer surrounding the active sites as a result of decrease in crystallinity of the polymer layer conveying the catalyst. This is similar effect as the introduction of comonomer in propylene copolymerization. The different of crystallinity can also be obtained from the alkoxysilane external donor. So it is interesting to investigate the effect of alkoxysilane external donor during the prepolymerization process. The prepolymer used as catalyst for polymerization, was prepared by the propylene polymerization at low pressure and temperature in the absence/or presence of alkoxysilane external donor. The prepolymers were prepared at 1 and 7 g-PP/g-cat to determine the influence of alkoxysilane types in prepolymerization performance.

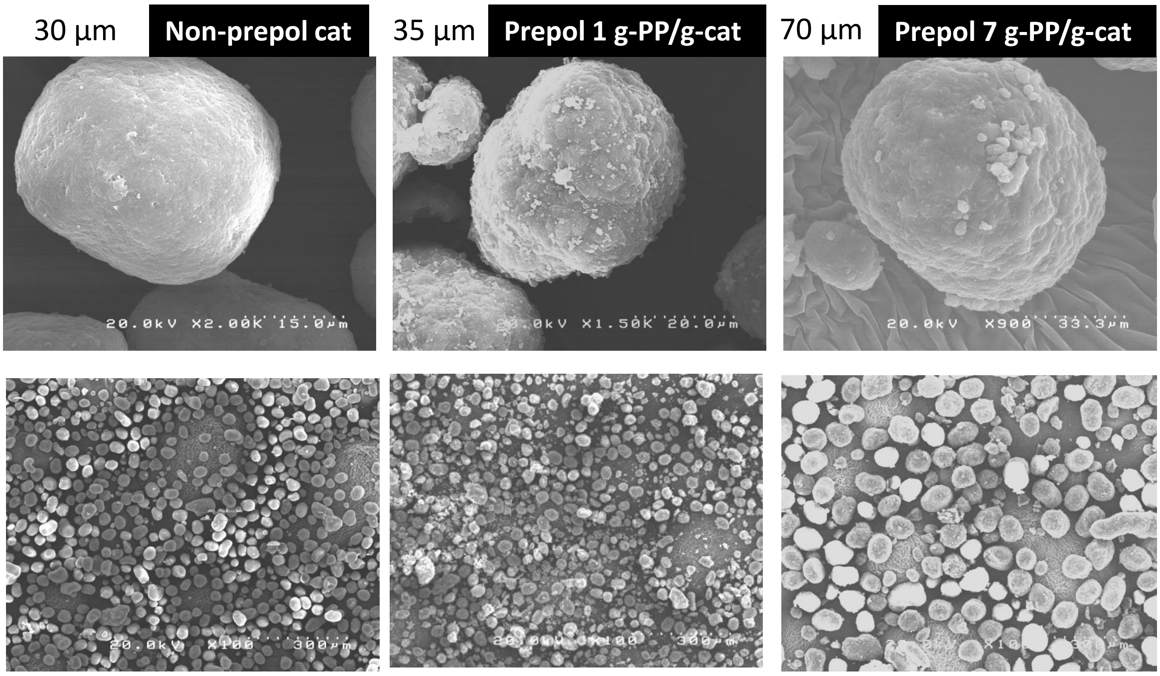


Figure 5. SEM images of prepolymer samples

Figure 5 shows the results of prepolymer morphology compared with the catalyst without the prepolymerization process. It can be observed that the prepolymer also replicate the catalyst morphology without the fine catalyst particles.

Table 5. Polymerization results with various prepolymerized catalysts

Run	**donor**	**Prepolymer yield [g-PP/g-cat]**	**Catalyst activity [g-PP/mg-Ti·h·bar]**	**mmmm [%mol]**
1	-	0	12.5	93.4
2	no donor	1	15.2	95.3
3	D-donor	1	17.6	96.2
4	U-donor	1	16.0	96.1
5	no donor	7	14.3	95.8
6	D-donor	7	15.3	97.0
7	U-donor	7	13.2	97.1

Polymerization conditions : Propylene polymerization, TEA 2.0 mmol, pressure 3.5 bar, 70 °C, time 1 h, in the presence of D-donor

Then, the results of polymerization using prepolymerized catalysts were described in Table 5. It was suggested that prepolymerized catalysts increase the catalyst activity in all cases of catalysts compared to the non-prepolymerized catalyst. Prepolymerization in the presence of alkoxysilane also enhance the catalyst activity. It is plausibly due to the formation of new active sites from fragmentation during prepolymerization and the increase of propagation rate is increased from the introduction of alkoxysilanes. Considering the amount of prepolymer yield, higher prepolymer yield gave greater total polymer yield in main polymerization. It can be implied that more polymer layer of the prepolymerized catalyst increases more active site with more catalyst strength. Comparing among the alkoxysilanes, prepolymerization with D-donor provide greater catalyst activity then with U-donor. As known, D-donor provide greater polymer yield due to more stability of cyclopentyl structure adsorbed on $MgCl_2$ surface. In the case of stereospecificity, D-donor also gave the higher stereoepecificity compared to U-donor. Furthermore, the introduction of alkoxysilane during prepolymerization process improves catalyst performances in terms of catalyst activity and stereospecificity.

4 Conclusion

In this study, a high-throughput experimental approach was applied to be the powerful tool to understand the effects of alkoxysilane in pretreatment and prepolymerization by using Parallel Pressure Reactor. Pretreatment with alkoxysilanes makes the active sites deactivation which can highly activate in the presence of hydrogen with greater polymer yield. Pretreatment process, more or less, increases the propagation rate in the presence of hydrogen compared to the non-pretreatment. Prepolymerization with alkoxysilane external donor can improve the stereospecificity of catalyst which D-donor provides the better isotacticity compared to U-donor.

5 Future plan

Additional PPR experiment with various polymerization conditions to investigate the effects of prepolymerization with alkoxysilanes

6 References

[1] E. P. Moore, Propylene *Handbook*, **1996**, Chapter 2.

[2] Busico et al., *Macromolecules* **1997**, *30*, 4786.

[3] Busico et al., *Macromolecules* **1994**, *27*, 4521.

[4] Terano et al. *Macromol.Chem.Phys*. **2002**, *203*, 2412.

[5] T. Nitta et al., *J.Mol.Catal. A:Chem*.**,** **2002**, *180*, 25.

[6] S. Poonpong et. al., *Macromol.Chem. Phys*. **2014**, *215*, 1721.

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