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EFFECT OF ELECTRON DONORS AND EXTRACTION ON ZIEGLER-NATTA
CATALYST PREPARATION FOR PROPYLENE POLYMERIZATION

Mr. Surachai Surasompop

A Thesis Submitted in Partial Fulfillment of the Requirements
for the Degree of Master of Science Program in Petrochemistry and Polymer Science
Faculty of Science
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Thesis Title	EFFECT OF ELECTRON DONORS AND EXTRACTION ON ZIEGLER-NATTA CATALYST PREPARATION FOR PROPYLENE POLYMERIZATION
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วิทยานิพนธ์หลัก: รศ. ดร. วิมลรัตน์ ตระการพฤกษ์, 87 หน้า.

งานวิจัยนี้มีเป้าหมายเพื่อปรับปรุงการสกัดในขั้นตอนการเตรียมตัวเร่งปฏิกิริยาซี
เกลอร์-นัตตาสำหรับการผลิต PP ตัวเร่งปฏิกิริยาซีเกลอร์-นัตตา $TiCl_4/MgCl_2$-SiO_2ผสมร่วมกับ
ตัวให้อิเล็กตรอนภายในชนิดบิวทิวพาทาเลท (DBP) เปรียบเทียบวิธีการสกัดแบบดีแคนต์และ
วิธีการสกัดแบบรีฟลักซ์ (ซึ่งใช้ในอุตสาหกรรม)โดยการศึกษาภาวะในการสกัดด้วยวิธีดี
แคนต์ เช่น เวลาในการสกัด จำนวนรอบการสกัด รวมทั้งปริมาณของสารสกัด ตัวเร่งปฏิกิริยาที่ได้
จะนำไปวิเคราะห์หาปริมาณ ไททาเนียม แมกนีเซียม และคลอไรด์ รวมถึงปริมาณตัวทำละลายและ
ไดบิวทิวพาธาเลทที่เหลือ เปรียบเทียบประสิทธิภาพของตัวเร่งปฏิกิริยาและสมบัติด้านสเตอรี
โอสเปกซิฟิก ผลการทดลองพบว่าตัวเร่งปฏิกิริยาที่เตรียมโดยการสกัดวิธีดีแคนต์มีปริมาณไดบิว
ทิวพาทาเลทที่เหลือมากกว่าการสกัดวิธีรีฟลักซ์ นอกจากนี้ ตัวให้อิเล็กตรอนภายนอกที่แตกต่างกัน
3 ชนิด พบว่าไซโครเฮกซิลเมทิลไดเมททอกซีไซเลน (C-donor) ให้ผลผลิตสูงสุด (24,141 g
PP/g cat.) เมื่อใช้ C-donorต่อไทเทเนียม = 5 การตรวจสอบพื้นผิวของตัวเร่งปฏิกิริยาโดยเครื่อง
สแกนนิงอิเล็กตรอนไมโครสโคป (SEM) พบว่าตัวเร่งปฏิกิริยาที่ไม่ผ่านการสกัดมีผิวค่อนข้าง
หยาบเมื่อเทียบกับตัวเร่งปฏิกิริยาที่ผ่านการสกัด ตัวเร่งปฏิกิริยาที่ผ่านการสกัดทั้งสองวิธีมีลักษณะ
ทางสัญฐานวิทยาที่ดี พอลิโพรพิลีนแสดงลักษณะจำลองรูปร่างของตัวเร่งปฏิกิริยา

สาขาวิชา   ปิโตรเคมีและวิทยาศาสตร์พอลิเมอร์   ลายมือชื่อนิสิต ....

ปีการศึกษา 2558   ลายมือชื่อ อ.ที่ปรึกษาหลัก ....

5472411923 : MAJOR PETROCHEMISTRY AND POLYMER SCIENCE
KEYWORDS: ZIEGLER-NATTA CATALYST / POLYPROPYLENE / DECANT / EXTRACTION / ELECTRON DONOR

SURACHAI SURASOMPOP: EFFECT OF ELECTRON DONORS AND EXTRACTION ON ZIEGLER-NATTA CATALYST PREPARATION FOR PROPYLENE POLYMERIZATION. ADVISOR: ASSOC. PROF. WIMONRAT TRAKARNPRUK, Ph.D., 87 pp.

This research is aimed to improve the extraction method in the preparation of Ziegler-Natta catalyst used for PP production. The $TiCl_4/MgCl_2$-SiO_2 Ziegler-Natta catalysts with added internal electron donor, dibutylphathalate (DBP), were prepared. Extraction by decant method was compared with reflux method (used in industry). The conditions of decant extraction such as time, cycle of decant, and volume of extract solvent were studied. Ti, Mg and Cl contents were analyzed as well as the residual solvent and DBP. Catalytic performance and stereospecific properties of polypropylene (PP) were compared. Experimental results show that the extraction by the decant method gave the higher residual quantity of DBP on the catalyst than that from the reflux method. In addition three different external electron donors were compared. It was found that cyclohexyl methyl dimethoxysilane (C-donor) gave best productivity (24,141 g PP/g cat.) when C-donor/Ti ratio = 5 was used. Surface of catalysts were examined by SEM. The crude catalyst shows more roughly surface than the extracted catalysts. The catalyst after extraction by both methods show good morphology. The PP polymers replicate their catalyst shape.

Field of Study: Petrochemistry and   Student's Signature ....

Polymer Science   Advisor's Signature ....

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จุฬาลงกรณ์มหาวิทยาลัย
CHULALONGKORN UNIVERSITY

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LIST OF ABBREVIATIONS

BET	Brunauer-Emmett-Teller method
$^{\circ}$C	degree Celsius
Cat	Catalyst
cm^{-1}	unit of wave number
deg	degree
EB	Ethyl benzene
ED	External electron Donor
FID	Flame Ionized Detector
FTIR	Fourrier transform infrared spectroscopy
g	gram (s)
GC	gas chromatography
h	hour (s)
I.I	Isotactic index
ICP-OES	Inductively Coupled Plasma-Optical Emission-Spectroscopy
ID	Internal electron Donor
l	liter (s)
min	minute (s)
ml	milliliter (s)
mmol	millimole
SEM	Scanning Electron Microscope
wt.	weight
XRD	X-ray diffraction
XRF	X-ray fluorescence
XS	Xylene extraction soluble

CHAPTER 1
INTRODUCTION

1.1   The purpose of the research

Polyolefins are the polymer produced from simple olefin monomer, the common is ethylene monomer. The first commercial polyolefin, low density polyethylene (LDPE) was occurred from trace of oxygen leaked into reactor when two chemists at Imperial Chemical Industries (ICI) attempted to condense ethylene and benzaldehyde at high pressure 140 Mpa at 200 $^{\circ}$C. Among the commercial polymers, polyolefins are the most preferred choice with excellent chemical and physical properties combination. The fabrication included extrusion, compression, injection and calendering all available methods for its. The superior processibility and good recyclability of polyolefins make it the most commercial polymers, PE and PP.

Polypropylene is the high desirable demand due to the outstanding in stiffness, impact resistance and transparent properties. The crystallinity is required for polypropylene production. Because propylene molecule is asymmetric molecule not like ethylene so the crystallinity of the chain in not control only by the branching effect like ethylene but the stereoregularity of polymerization is significant affect to crystallinity of polypropylene. The stereoregular polypropylene most obtained with Ziegler-Natta catalysts, isotactic PP is commercially significant. In industrial production, isotactic polypropylene production was controlled by use of internal electron or external electron donor or both in Ziegler-Natta catalyst system. The activation of $MgCl_2$ support with electron donor improves activities and stereospecificities [1].

Catalyst preparation comprises of many steps: support preparation, titanation, internal donor addition and extraction step. The extraction method used in the industry is reflux method in which the pre-catalyst in a reactor is transferred to extraction tank. Then the hot extraction mixture is flowed through catalyst from top to bottom and then passes a sieve tray. After longer time the sieve tray will plug due

to the accumulation of the extracted materials. Also some by-product will accumulate and coat on inner wall piping exchanger which causes less efficiency of heat transfer.

Therefore to solve these problems, this research is aimed to improve the extraction step in the Ziegler-Natta catalyst preparation. Extraction by decant method which is more conveniencet is proposed. Factors that affect efficiency of extraction such as extraction temperature and extraction time were studied. The prepared catalysts were characterized in terms of surface analysis, element content and quantity of internal donor and residual solvent. Then the catalysts were used for propylene polymerization. Different types of the external donors were studied. The catalytic activity and stereospecificity were determined.

1.2   Objectives

- Prepare Ziegler-Natta catalysts using two extraction methods, reflux and decant methods.
- Perform polymerization of propylene.
- Study effect of internal electron donor quantity in catalyst on polypropylene property.
- Study effect of external electron donor type on polypropylene property.

1.3   Scope of the research

1. Search and review literature.
2. Prepare Ziegler-Natta catalysts.
3. Study and compare the extraction methods, the reflux and decant methods.
4. Characterize resulting catalysts: surface analysis, element content and analysis of internal electron donor and residual solvent content.
5. Perform propylene polymerization with different types of external electron donor.
6. Analyze property of polypropylene.
7. Discuss and summarize the experimental data and write thesis.

CHAPTER 2
THEORY AND LITERATURE REVIEWS

2.1 Polypropylene (PP)

Polypropylene is homopolymer, as thermoplastic, that derived from propylene monomer by propylene polymerization. The structures of propylene and polypropylene are shown in Figure 2.1.
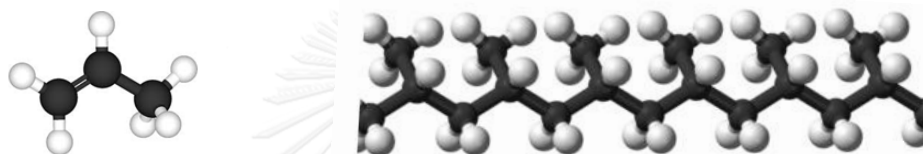
Figure 2.1 Structures of propylene (left) and polypropylene (right).

2.1.1 Tacticity or stereoregularity

The structures of commercial PP polymer are isotactic, crystalline PP homopolymers, and copolymers on random copolymer and block copolymer. The tacticity level can be varied in PP due to the effectiveness of the catalyst and polymerization process. The tacticity of 100% of stereoregular PP are ideal and often not reached in practice. Factors that control the stereo arrangement of polypropylene are:

1. The degree of branching: The linear chain will complete as the monomer insert at the chain end, branching not form. The insertion of the monomer onto the backbone causes increase in the degree of branching. The chain insertion is shown in Figure 2.2.

(A) Linear addition   (B) Branched addition
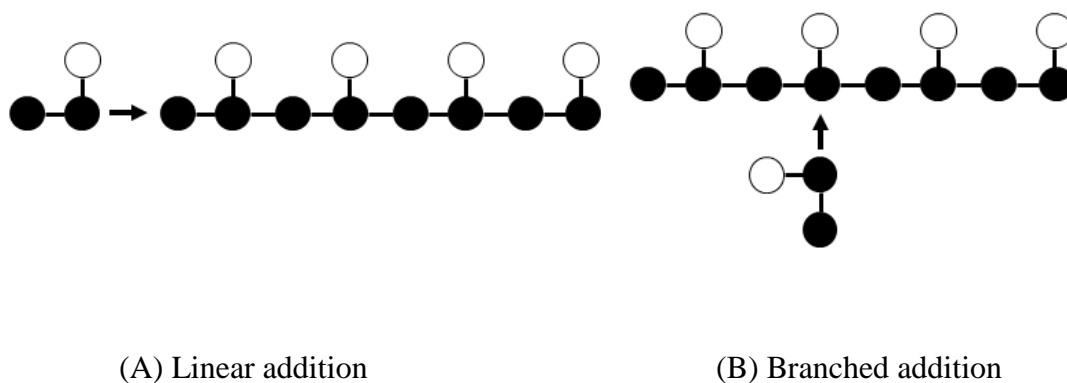
Figure 2.2 The addition of propylene monomer to the growing PP chain.

    2. The pedant methyl sequence: The incoming of next propylene monomer onto the end of growing polymer is always in head-to-tail manner (regeospecific). Sometimes head-to-head or tail-to-tail manner insertion occurs and causes inter molecular defect in the chain as shown in Figure 2.3.

(A) Head to tail

(B) Tail to tail

(C) Head to head
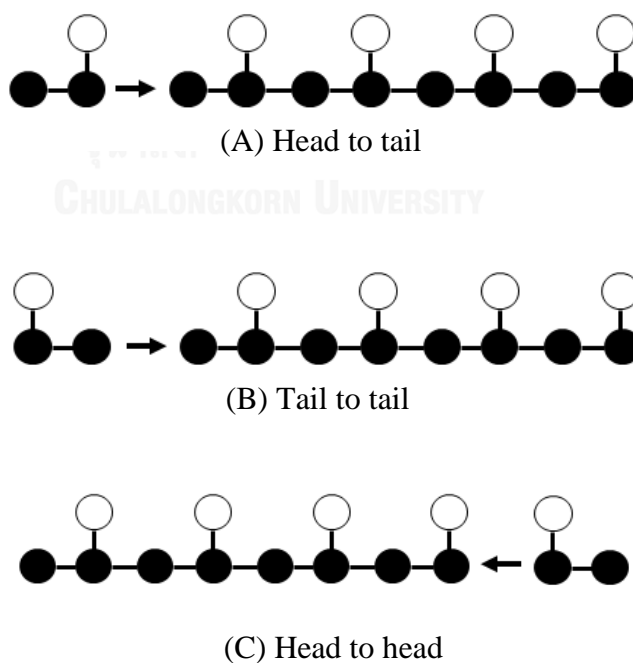
Figure 2.3 Addition of propylene monomer.

3. Stereospecificity: The monomer unit adds in same head-to-tail manner with the methyl pedant placed in the same side of backbone (isotactic) or opposite side (syndiotactic) as shown in Figure 2.4.

(A) Same hand

(B) Opposite hand
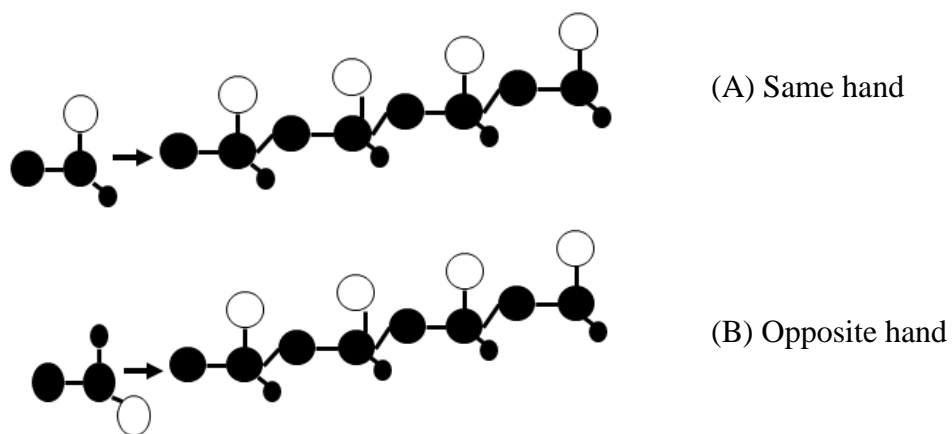
Figure 2.4 Arrangement of methyl pedant groups on the PP backbone.

The schematic of isotactic, syndiotactic and atactic of PP chains is shown in Figure 2.5.

Isotactic

Syndiotactic
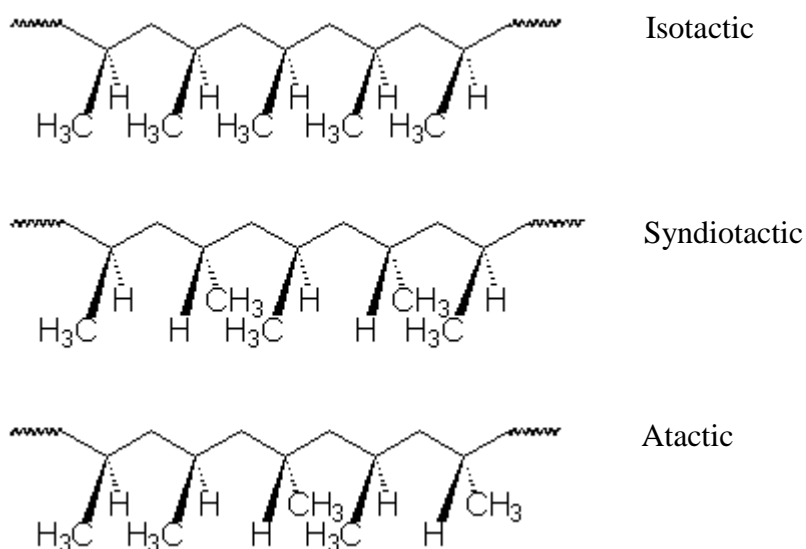
Atactic

Figure 2.5 Tacticity of polypropylene.

The isotactic regularity of chain allows it to crystalize when the chain is close nesting of chain to form lamella shape crystals. The degree of crystallinity of PP homopolymer is governed primarily by tacticity of the chain. The crystallizability of the PP chain is critical factor to morphology.

2.1.2 Morphology of polypropylene [2]

Polypropylene is semicrystalline polymer. Macromorphology is in range millimeters, coincide with features as the gross reactor and skin core structure. The finer scale, spherulite structure is on the order of 1 to 50 micron composed of building blocks of lamellae-shaped crystals. The distance between center-to-center of lamellae (long spacing) has values in range of 100-300 Å depending on processing and thermal history. A finer scale, the lamellae are composed of crystallographically ordered region that the individual chains of lamellae are arranged with specific symmetry and unit cell dimension. The morphological scales in PP are shown in Figure 2.6.
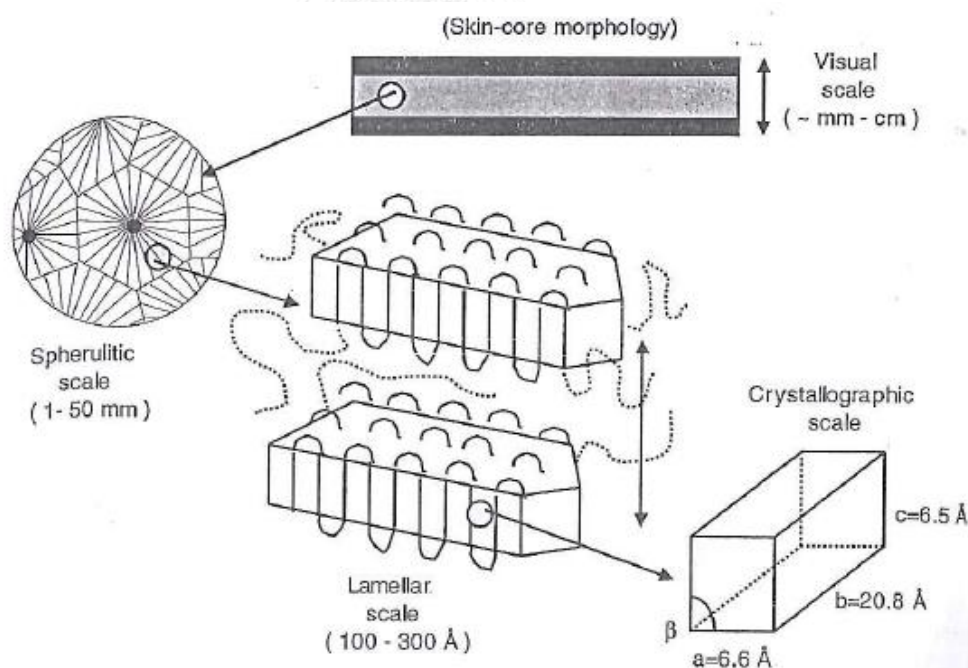
Figure 2.6 Characteristic hierarchy of morphology scales in PP.

Isotactic PP crystalize in helical form due to the steric hindrance between contiguous methyl pedant substituents. The crystalline forms of isotactic PP have several polymophic forms, α, β, γ and mesomorphic forms. These forms differ in

interchain packing, unit cell symmetry and structure disorder. The 3,1 helical conformation of isotactic PP in crystalline state is shown in Figure 2.7.
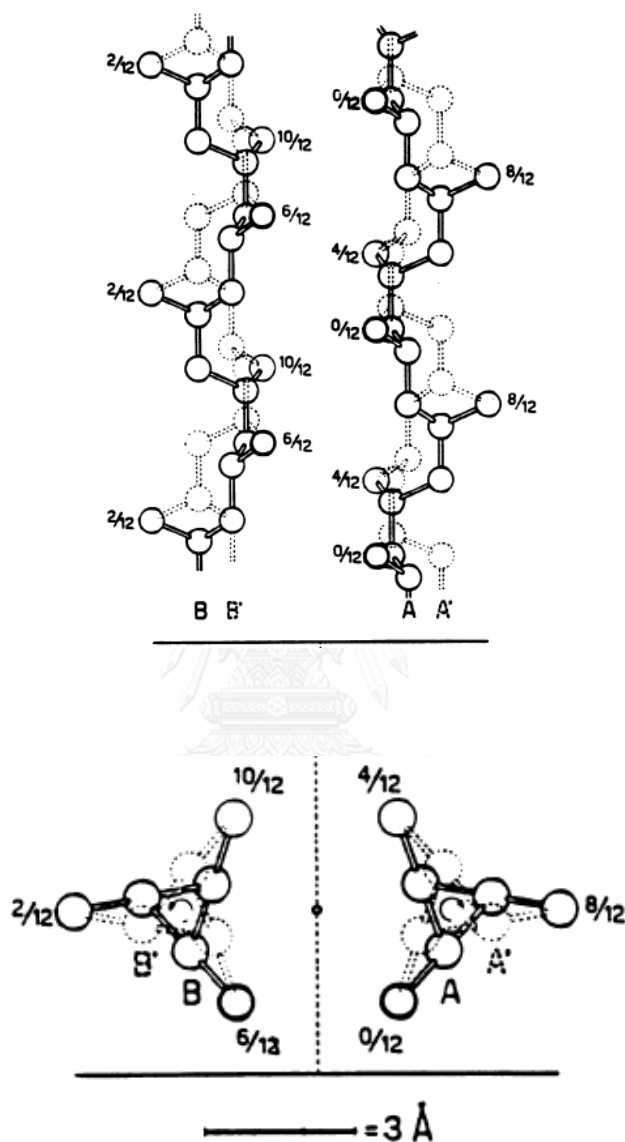
Figure 2.7 The 3,1 helical conformation of isotactic PP in crystalline state.

The isotactic and syndiotactic PPs show reflection in X-ray pattern whereas atactic PP shows no reflection, characteristic of noncrystalline material. The X-ray reflection patterns of PP are shown in Figure 2.8.
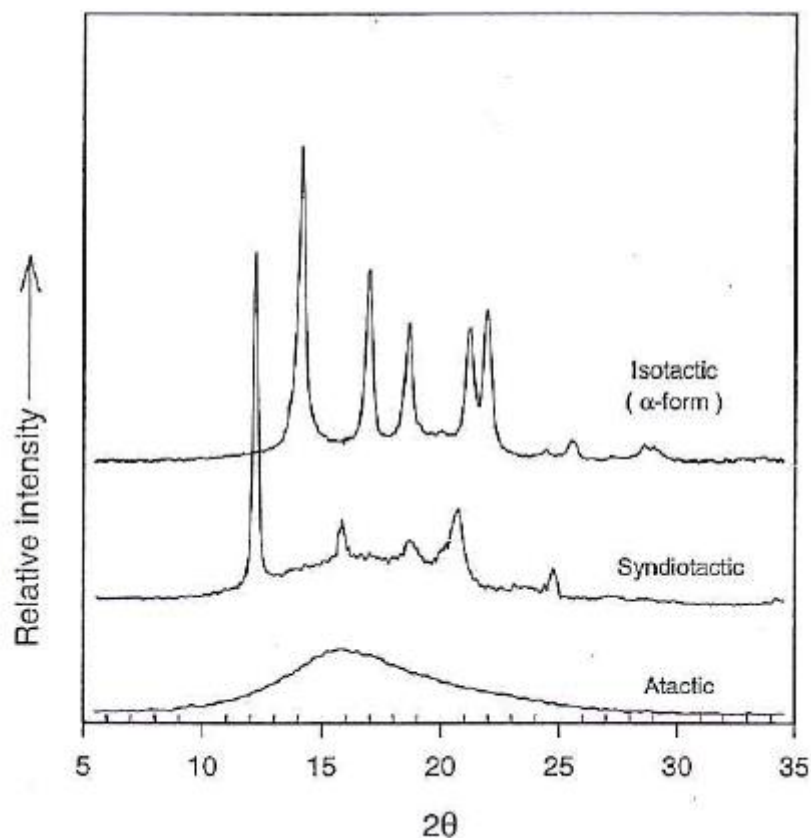
Figure 2.8 X-ray reflection patterns of isotactic, syndiotactic and atactic PP.

2.2   Ziegler-Natta catalysts[3]

Ziegler-Natta catalysts are a mixture of a metal alkyl of group I to III metal and a transition metal of group IV to VIII. In 1954, Professor Giulio Natta realized that the Ziegler catalyst is capable produce α-olefin polymers with stereoregular repeating units, such as 1-propene. Ziegler and Natta were jointly awarded the Noble Prize for Chemistry in 1963.

The first generation catalysts based on $TiCl_3/AlCl_3$ or $TiCl_3/AlEt_2Cl$ used in earlier industrial for production of PP, show only 90% isotactic and low productivity still required the separation of atactic fraction and catalytic residues. In the second generation catalysts, the productivity and stereoregularity were increased by

increasing surface area of catalysts. The drastic development started in third generation catalysts by comilling high surface supports ($MgCl_2$), $TiCl_4$ and Lewis base, usually refer to as "internal donor", combined with Al-trialkyl as cocatalyst and second Lewis base, usually call "external donor" leading to highly active and stereospecific catalysts. For fourth generation catalysts, further development was done by new type of both internal and external Lewis bases, such as diester, diether and alkoxysilane to provide the high activity and isotacticity. For fifth generation catalysts, external donor was not used

At the same time, homogeneous stereospecific catalysts, the sixth generation catalysts, offered several advantaged over the traditional Ziegler-Natta catalysts, combined metallocene ($LL´MtX_2$) with cocatalyst called methylaluminoxane (MAO) which enable control over both the molecular weight and the microstructure (tacticity, regioregularity, comonomer distribution) of polyolefins.

2.2.1 Heterogeneous Ziegler-Natta catalysts

For PP commercial production, the heterogeneous catalysts consist of $TiCl_3$ and $MgCl_2$ support. $TiCl_3$ has four different crystalline forms: α, β, γ and δ. The triple layer structure of Cl-Ti-Cl ions of the three modifications (α, γ and δ) only differ in the mode of Cl packing. The structure packing form of α form is hexagonal, γ form is cubic and δ form displays a random succession of hexagonal and cubic close packings. For industrial production of $TiCl_3$ catalysts, the most significant synthesis by reduction of $TiCl_4$ with Al or Al-alkyls in hydrocarbon solvents. In the first generation $TiCl_3$ catalysts, the surface area of solid catalysts are only in range 40-50 m^2/g by dry milling and show low productivity. The higher activity of catalysts appear in presence of co-crystallized $AlCl_3$ that affect either to electronic factors or to an increase in the catalyst surface area. The second generation $TiCl_3$ catalysts were developed in the synthesis method to obtained higher surface area (150-200 m^2/g) and catalytic activity, also isotacticity.

2.3   Catalysts based on magnesium chloride with transition metal compounds

Ziegler-Natta catalyst based on transition metal compounds, mostly titanium chloride compounds, in the first commercially ZN, $TiCl_3$/DEAC, shows low activities and poor stereospecificities with respect to i-PP production and required purification procedures, deashing, to remove catalyst residue and by product. To overcome these peripeteia driving force the development of new type catalysts.

The intensive research led to develop of $MgCl_2$-supported $TiCl_4$ catalysts with higher activity and controlled stereoselectivity using several types of electron donors. The activity can be as high as about 27 kg polypropylene per gram of catalyst and stereoregularities of PP produced by 1,3 diether as donor electron can achieved 99 % of isotactic pentad (mmmm) in the polymer [4].

In the catalyst based on $TiCl_3$ crystal, the interior encapsulated titanium atoms cannot be transformed into the active site, only minor amount titanium, outside part of crystal, can accessible to cocatalyst and monomer that responded for polymer production during polymerization. The second effect of $MgCl_2$ is significantly enhances the polymerization activity.

The typical kinetic profile of $MgCl_2$ supported catalyst has short activation period and when active site formation the $MgCl_2$ supported catalyst shows high initial activities followed by a rapid deceleration in polymerization rate shown in Figure 2.9

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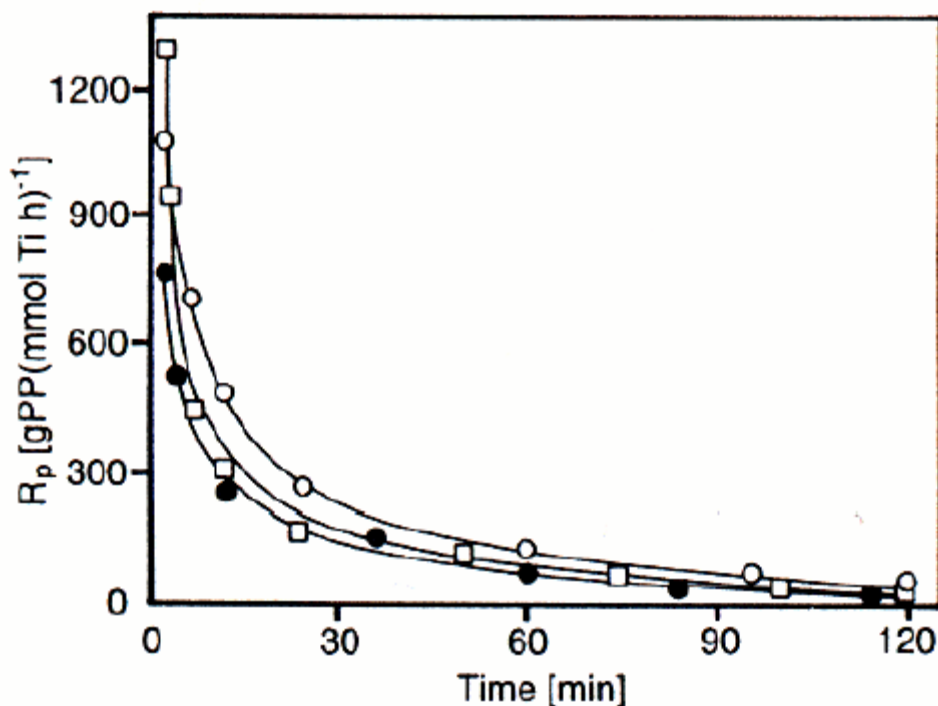
Figure 2.9 Typical decelerating kinetic profiles of MgCl$_2$ (ball milled)/EB/TiCl$_4$-TEA catalytic system in propene polymerization expressed as a plot of polymerization rate Rp vs. time. Polym. conditions:temperature 60 $^{\circ}$C; pressure 1 atm; TEA/Ti molar ratio: ● = 176, ○ = 235 and □ =588.

Several theories explain the high catalyst activity, some of researchers assumed that it is caused by stabilization of coordination of titanium and monomer occurred from MgCl$_2$ electron donating on titanium which results in an acceleration of the monomer insertion.

The reasons that explain catalyst decay during polymerization, one assume that it could be caused by limitation of monomer flux due to encapsulation of the catalyst in the polymer layer.

The interaction of catalyst with an alkylaluminium compound, titanium were reduced to lower oxidation state, mainly Ti (II) that was reported to be inactive in propylene polymerization.

The main reason for activity decay in propylene polymerization was caused from irregular (2,1) monomer insertion into the growing chain that make chain propagation slow down due to steric hindrance of methyl group close to the Ti atom (Figure 2.10).
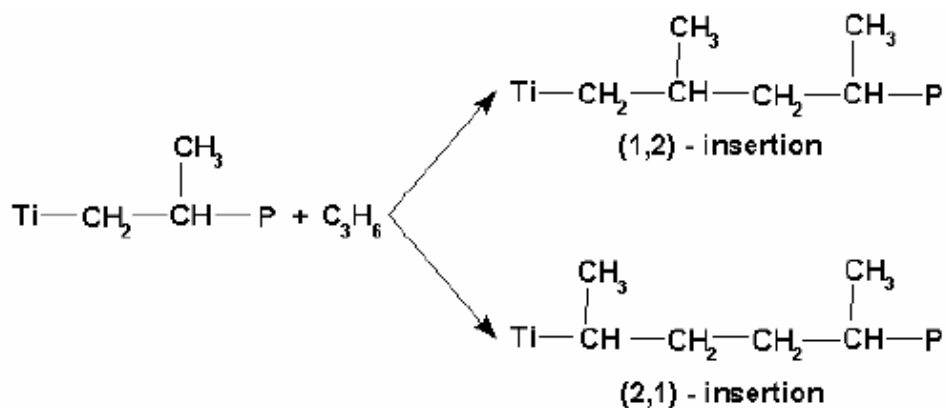
Figure 2.10 Regioregular (1,2) and regioirregular (2,1) insertion of propylene.

$MgCl_2$-supported catalysts can be prepared with variety of routes, differing either in the type of $MgCl_2$ precursor that will convert to active $MgCl_2$ or in procedure for incorporate of titanium compound and internal donor. The structure of $MgCl_2$ that dealing with the key of supporting catalyst is δ form $MgCl_2$ or activated $MgCl_2$ which exhibited a disordered structure (Figure 2.11). The activated $MgCl_2$ lateral cuts correspond to the (110) and (100) cuts which contain coordinatively unsaturated Mg^{2+} ions with coordination number 4 and 5 respectively (Figure 2.12).
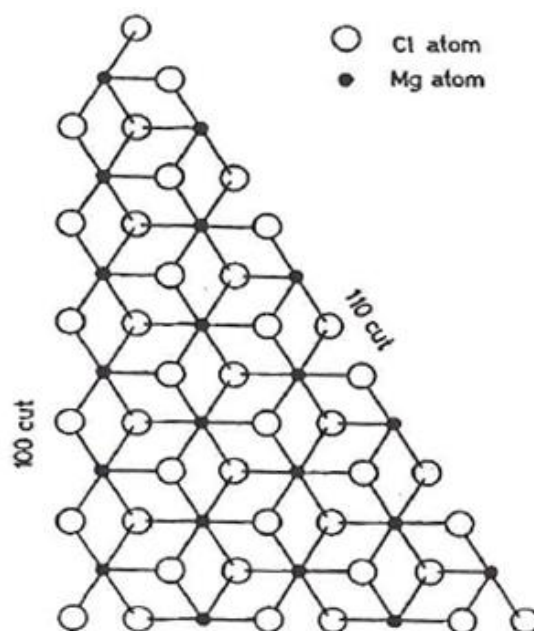
Figure 2.11 Model of MgCl$_2$ layer showing the (100) and (110) cuts.

Lateral face (100)

Lateral face (110)
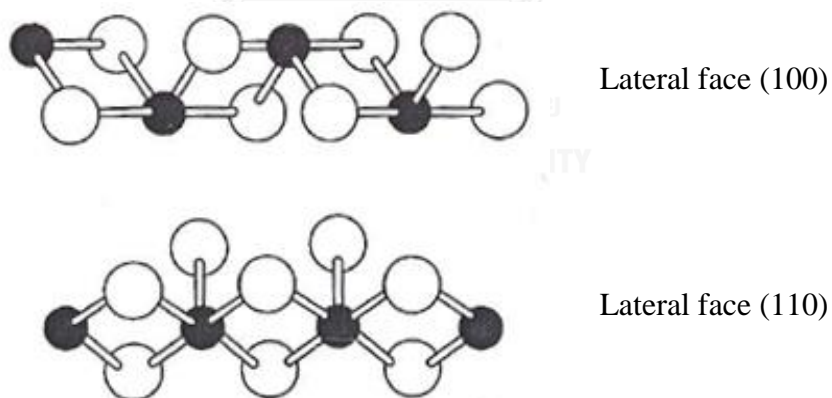
Figure 2.12 Magnesium coordination on the (100) (upper) and (110) (lower) faces of MgCl$_2$.

The main general procedure for incorporation ingredient catalyst, titanium compound and internal donor can be divided in following three techniques: purely

mechanical (usually ball milling), mechanical plus chemical (ball milling following by chemical reaction) and entirely chemical technique.

Although $MgCl_2$ has been known as a preferred support for the polymerization of olefins but with frailty feature of $MgCl_2$ during preparation is still a problem for controlling the morphology of catalyst when used in olefin polymerization. To overcome the problem, $MgCl_2$-SiO_2-bisupported titanium catalyst is preferred, especially when used in a gas phase polymerization [5-7].

2.4   Reaction and mechanism of Ziegler-Natta catalysts [8-9]

Triethylaluminium activates the solid catalyst, the active center was formed in two steps. Ti is reduced by cocatalyst to lower oxidation state in first step and followed by alkylation by alkyl group of cocatalyst substitute chloride on surface catalyst.   Active center Ti of activated catalyst and incoming propylene monomer share the π-bond electrons in the double bond of propylene in coordination step according to the Cossee-Arlman's mechanism (Arlman and Cosee, 1964) [10] as shown in Figure 2.13.
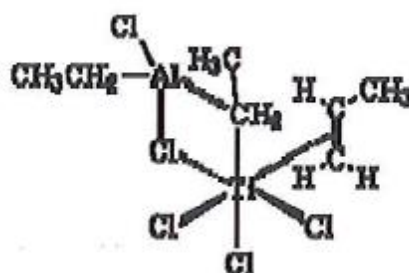
Figure 2.13 Complexation of catalyst, cocatalyst and propylene monomer.

The incoming propylene monomer shared the π-bond electrons in the double bond with the titanium atom during the coordination step. The double bond breaks during the insertion step. The one carbon of monomer molecule bond with Ti site and other one bond with the growing chain, restoring the vacant coordination site for further coordination and insertion steps as illustrated in Figure 2.14.
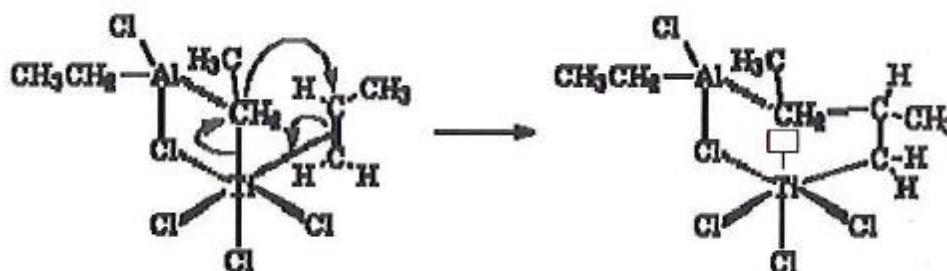
Figure 2.14 New vacant site formed in transition state.

In accordance with Cossee model of monometallic active center, the octahedral complex Ti (III) is located on a lateral face of $TiCl_3$ crystal. The monomer coordination to the active center is based on the interactions of the p-binding orbital of monomer molecules with free d-orbital of the active site transition metal at its vacant position. The mechanism presented consists of two main steps: the coordination of the monomer at the vacant octahedral coordination site with the double bond parallel to the active metal-polymer bond, and the chain migratory insertion of coordinated monomer with migration of the growing chain to the position previously occupied by the coordinated monomer. The transition state is assumed to be a four membered ring of Ti, the last carbon atom of the growing chain and the two carbon atoms forming the double bond of the monomer (Figure 2.15).
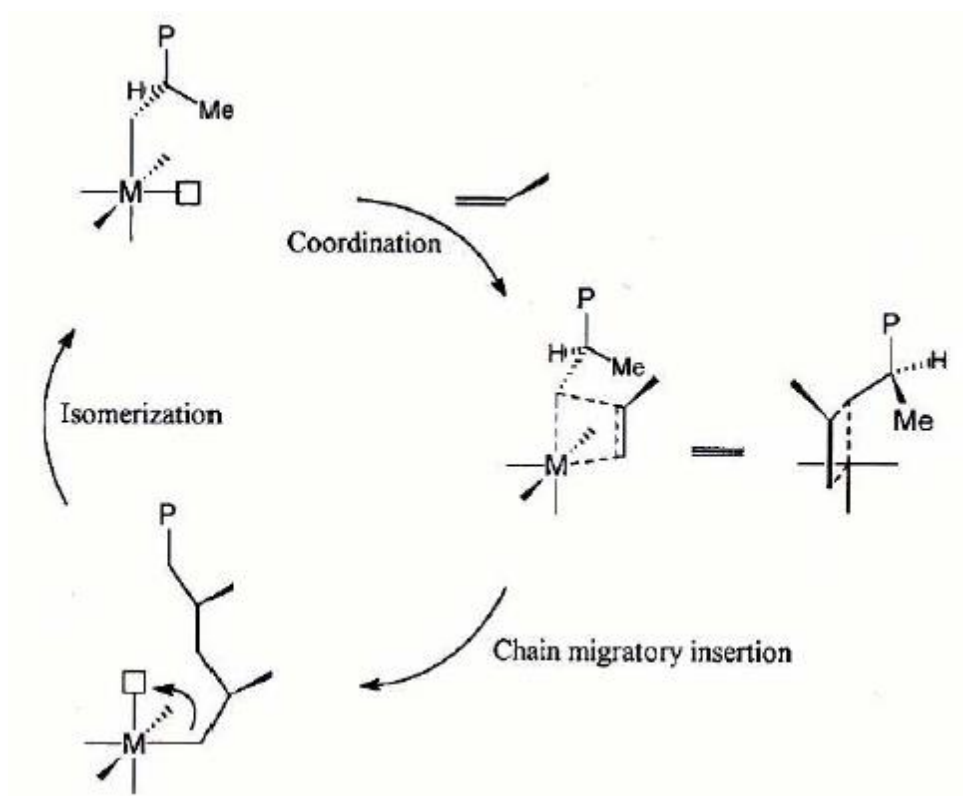
Figure 2.15 Monometallic Cossee mechanism of polymerization.

Similar to the monometallic mechanism of Cossee model, bimetallic mechanism proposed by Rodriguez and van Looy by assuming that the alkylaluminium cocatalyst is a part of an active catalytic complex, where a ligand (Cl or alkyl group) and the last carbon atom of the growing chain link Ti and Al through a double. The double bridge represents the driving force to shift back at its initial position of the bridged alkyl group (the growing chain) after the migratory insertion step. The evidence about existence of bimetallic complex has given by experiment of Lately Kohara et al. [11] (Figure 2.16).
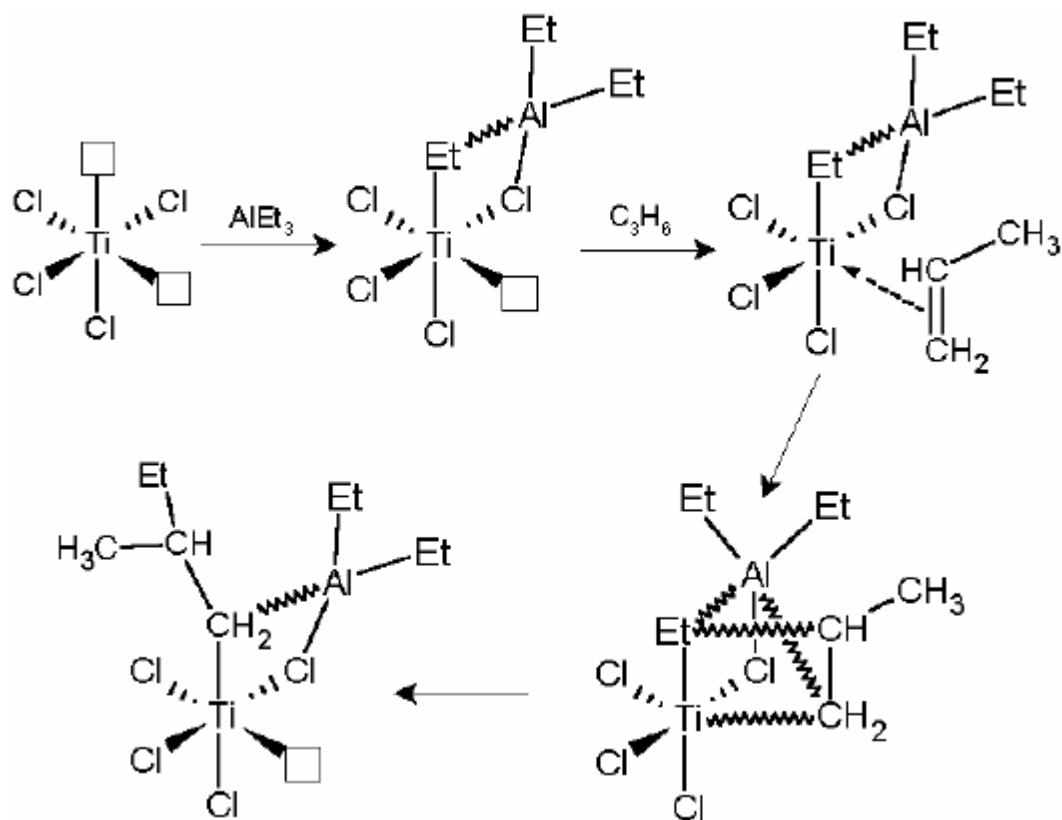
Figure 2.16 Mechanism of coordination polymerization on the bimetallic active
center.

Active site model

For isotactic polypropylene production, geometry of catalyst is very important
to ensure that the methyl group in the propylene molecule is aligned in the same
plane. Three site of molecular structure models for γ-TiCl$_3$ proposed by Kakugo et al.
[12], highly isotactic, low isotactic, and atactic shown as Figure 2.17.
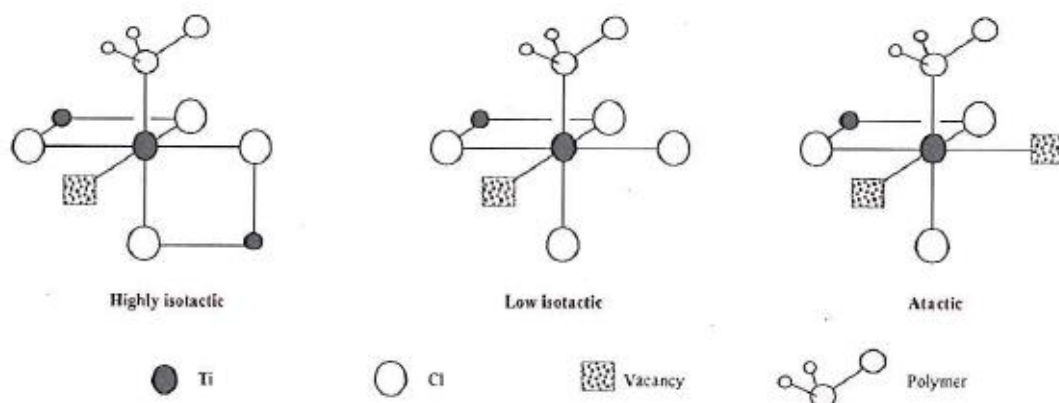
Figure 2.17 Molecular structural models for γ-TiCl$_3$ (Kakugo et al.,1988).

The highly isotactic site has one coordination vacant site and is bonded to the alkyl-polymer chain and four Cl atoms. Due to the vacant site is symmetrical site, stereo- and regioregular insertions are favored. The low isotactic site has only one coordination vacancy also but two Cl atoms not bonded to Ti atoms. The stereo- and/or regio-defects, may occur during insertion due to the vacant site are not symmetrical. Finally, the atactic site has two coordination vacancies allow for the random coordination of propylene molecules and the formation of atactic polypropylene chains.

When TiCl$_4$ is supported on MgCl$_2$, the resulting structure is similar to that of β-TiCl$_3$. An electron donor molecule block low isotactic site by complex with the Ti atom resulting the site inactive for polymerization, shown as Figure 2.18. On the other hand, an electron donor molecule may complex with one of two vacancies of atactic site and transform the atactic site to highly isotactic site. In this case, the bulkiness of the electron donor provides steric hindrance, rendering the site isospecificity, shown as Figure 2.19. It is interesting to notice that some donors, esters derived from aromatic carboxylic acids, may reduce activity of catalyst or kill the catalyst when used in excess, this phenomenon is called self extinction. However, not all donors are able to reduce the polymerization activity, even if an excess amount is added to the polymerization reactor, such as alkoxysilanes.
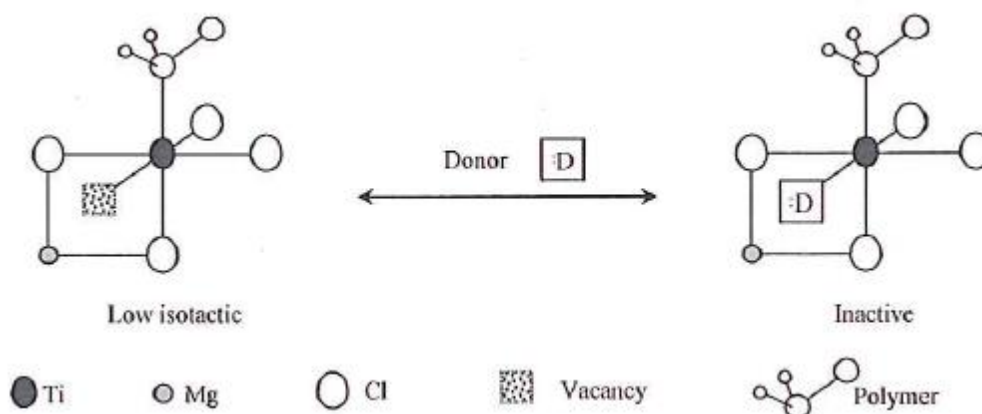
Figure 2.18 Donor addition to low isotactic site on $TiCl_4/MgCl_2$.
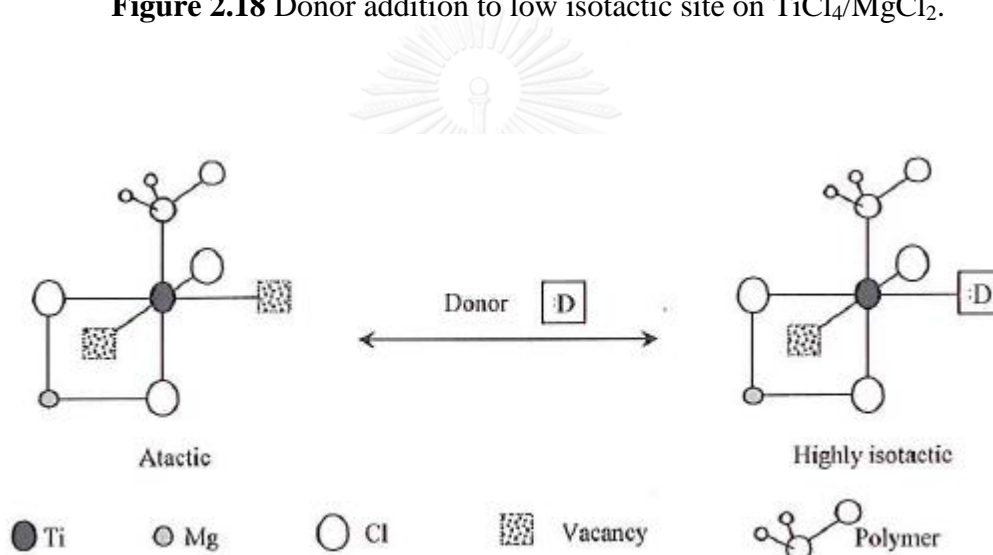
Figure 2.19 Donor addition to atactic site on $TiCl_4/MgCl_2$.

2.5   Effect of catalyst composition and structure [13]

Ziegler-Natta catalysts have been many different components of transition metal and metal groups I-III, together with and added electron donor.   Transition metal titanium was most widely studied in term of structure form and oxidation states. The structure of β-$TiCl_3$ that consists of bunch of linear $TiCl_3$ results in surface in which half the titanium atoms have two vacant sites and other half have one vacant site. This exactly opposite to other form $TiCl_3$ that all contain a layered structure made these have one vacancy per site and configuration of all chlorides and polymer

chain end ligand have fixed position on titanium site result to more stereopecificity. Oxidation state of transition titanium active site dependent on amount of group I-III metal component, usually AlR_3 or AlR_2Cl. Because of $TiCl_4$ is a liquid and more conveniently handled so it typically use for preparation by combination with cocatalyst, reducing agent. But extensive reduction of tetravalent to divalent titanium significant decreases stereopecificity For $MgCl_2$ supported catalyst the optimum Al/Ti ratio ranges 10-100. For propylene polymerization by combination with triethylaluminium, isotacticity order as $TiCl_4 > TiCl_2(OC_4H_9)_2 > Ti(OC_4H_9)_4$

Alkyl aluminium compounds are most often used in industrial polypropylene production due to their ready availability and easy to handling in solution. The size of alkyl group of group I-III metal compound affects selectivity. Replacement of one halogen ligand in AlR_3 affects stereopecificity, activity follows the orders I > Br > Cl.

Electron donors in various types have been added to enhance stereopecificity and activity [14]. Both internal and external electron donors to improve stereoselective site, decrease the reactivity of less stereopecificity and increasing the number of stereoselective sites by assisting in their site stabilize and/or disperse on support. The structure of the internal donor appears to be factor that determines the type and need for external donor. Internal and external electron donor were used the same base, an aromatic ester such as diisobutyl phatalate, in previous recipes. Recently aromatic ester or dieter was used be internal electron donor and alkoxysilane, such as $RSi(OCH_3)_3$, as the external electron donor. Adding the external donors is needed because internal electron donor due to can removed and loss by extraction of alkylaluminium compound, especially if ester as internal electron donor. The loss of diether in the catalyst preparation is much less so external electron donor is not needed.

2.6   Industrial catalyst production

For propylene polymerization typically use Ziegler-Natta catalyst consists of $MgCl_2$-supported $TiCl_4$ combined with an alkyl aluminium compound such as triethyl aluminium, and system need to be added electron donor, internal and external donor

such as phthalate and alkoxysilane to improve stereo specificity of catalyst. A variety of metal halides and oxides have been reported as suitable supports for the catalysts. The best support is $MgCl_2$ due to the fact that Mg and Ti have similar atomic size and shape. Moreover, $MgCl_2$ has a similar crystalline structure to that of $TiCl_3$. Since the excellent properties of $MgCl_2$ supported Ziegler-Natta catalysts for production of polyolefins were discovered, many studies on treating methods of $MgCl_2$ have been carried out in order to improve the yield of catalysts through the increase of the surface area and through a better interaction between $MgCl_2$ and $TiCl_4$.

Three mainly general procedures to prepare catalysts can be described as follows [2]:

1 Mechanical technique that usually a stage of comilling, ball mill the catalyst components ($MgCl_2$, $TiCl_4$ and a Lewis base) with suitable ratios for several hours.

2 Mechanical plus chemical technique, mill the $MgCl_2$ or $MgCl_2$ precursor with Lewis base. $TiCl_4$ in solvent was added to react at temperature above $80\ ^{\circ}C$. $TiCl_4$ unreacted and some of Lewis base that was replaced by $TiCl_4$ is removed by hydrocarbon solvent.

3 Chemical technique, both $MgCl_2$ generation and Ti compound with Lewis base incorporation are done by chemical routes. The solid $Mg(OR)_2$ is treated with internal electron donor and excess $TiCl_4$ solution. Ti-alkoxides byproducts were eliminated during treatment and subsequent washing.

2.7   Literature Reviews

In 1989 Spitz et al. [15] studied the effect of triethylaluminium and triethoxyphenylsilane concentration and Al/Si mole ratio on $MgCl_2$/dibutylphthalate/$TiCl_4$. It was found that at increasing silane content, the activity increased up to a maximum and then decreased. The rate of isotactic polymer production had the same behavior and the production of atactic polymer continuously decreased.

In 1997 H.Mori et al. [16] studied interaction of internal donor and TiC_4 on supported $MgCl_2$ Ziegler-Natta catalysts with two types of internal donor, ethylbenzoate (EB) and di-n-butylphathalate. Results of experiment show that the internal donor and $TiCl_4$ interact independently with $MgCl_2$. The Zeigler-Natta catalysts with internal donor show higher yield of polypropylene with high molecular weight distribution and isotacticity than the internal donor free- Zeigler-Natta catalysts.

In 1997 Eini Puhakka et al. [17] studied the alkylation reaction of the $MgCl_2$-supported $TiCl_4$, catalyst. They indicated that the $Al(CH_3)_3$ co-catalyst inserts into the coordination sphere of the titanium atom of the catalyst so that a methyl group of $Al(CH_3)_3$ interacts with the titanium. They also tested the effect of alkylaluminium complex with the external electron donors. Results of energy reaction indicated that the external electron donor promotes the alkylation reaction of the $MgCl_2$-supported $TiCl_4$ catalyst.

In 2001 T. Nitta et al. [18] studied Ziegler-Natta catalysts, $TiCl_4$/DBP/$Mg(0Et)_2$ and transformation of stereospecific active site when induced by a short time reaction with triethylaluminium (TEA) cocatalyst. The formation of active sites of catalyst with highest isospecificity strongly depends on the interaction between the catalyst and TEA cocatalyst in the presence of internal donor. The extraction of internal donor DBP from catalyst by TEA in pretreatment procedure shows slight transformation of isospecific active sites into aspecific sites.

In 2005 X. Jiang et al. [19] studied influence of comilling NaCl in $MgCl_2$/NaCl/DBP/$TiCl_4$ supported catalyst. The free Cl^- of NaCl-doped catalyst can occupy vacancies on surface of catalyst and selectively deactivated a part of the active centers. Some of the active centers may be deactivated reversibly that make the doped catalyst changes in the active center distribution (ACD). The NaCl-doped catalyst change stereochemical structure of polypropylene to higher isotacticity.

In 2005 A. G. Potapov et al. [20] studied the internal donors in supported Ziegler-Natta catalysts. The surface complex of DBP on the $MgCl_2$ support formed 4-coordinated Mg ions and $TiCl_4$ competed with DBP for the same surface adsorption sites but did not affect the distribution of DBP complex on $MgCl_2$ support. The presence of $TiCl_4$ resulted in a drastic decrease of the total content of DBP in the catalyst.

In 2005 N.M. Ostrovskii et al. [21] studied about mechanism and model of deactivation of Ziegler–Natta catalysts. They indicated that the main reason for decreasing catalyst activity is the poisoning by $C_2H_5AlCl_2$ (EADC), which is the product of interaction of catalyst ($TiCl_3$, $TiCl_4$) with cocatalyst $(C_2H_5)_2AlCl$ (DEAC) and $Al(C_2H_5)_3$ (TEA). This phenomenon is the gradual elimination of chlorine from the catalyst. The reaction with TEA (triethylaluminium) for a long time induces the almost complete reduction of the original Ti^{4+}.

In 2008 A. Andoni et al. [22] studied the role of electron donors on lateral surfaces of $MgCl_2$-supported Ziegler–Natta catalysts. The effects of diether and ester donors in the controlled growth of $MgCl_2$ crystallites showed that diether is effective in promoting the formation of the (110) surface. In contrast, the use of a monoester or diester as internal donor generates crystallites of both the (110) and the (104) edge surfaces of $MgCl_2$. The high activity and relatively uniform nature of the active species in catalysts of type $MgCl_2/TiCl_4$/diether is likely to be due to preferential formation of the (110) face of $MgCl_2$ when using a diether as internal donor.

In 2009 D. V. Stukalov et al. [23] studied surface species formed upon interaction of internal donor with TiCl4 on the supported $MgCl_2$ by DRIFT (diffuse reflectance infrared spectroscopy) and XRD (X-ray diffraction). They found that activated $MgCl_2$ contains 5-coordinated Mg cation surface (104) ca. 90% and 4-coordinated Mg cation surface (110) ca. 10%. The adsorption order of internal donor and $TiCl_4$ is first order. The $TiCl_4$ occupies the adsorption sites on the inaccessible for the internal donor because of steric ligand of internal donor which internal donor act the matrix for incoming of $TiCl_4$ to adsorb on activated $MgCl_2$

In 2009 M. Fatima et al. [24] studied effect of new internal donors and external donors on $MgCl_2$ supported Ziegler-Natta catalyst, $MgCl_2/DI/TiCl_4/ED/AlR_3$. (DI = internal donor , ED = external donor)The prepared catalyst with diethyl cyclobutane-1-1 dicarboxylate (DECBDC) as an internal donor and can produce high isotactic index polypropylene up to 98% compared to the conventional butyl phthalate (BP) that shows 92 % isotactic index under same polymerization condition and same external donor, dimethoxy diphenylsilane.

In 2010 A. G. Potapov et al. [25] studied interaction of the internal donor with $AlEt_3$ cocatalyst in $TiCl_4/DBP/MgCl_2$ catalysts. The results showed that $AlEt_3$ cocatalyst can remove more weak DBP complexs and $AlEt_3$ being adsorbed on the $MgCl_2$ surface in place of the removed DBP. The removed internal donor can readsorb forming complexes with alkylaluminium chloride. The external donor alkylalkoxysilane does not influence the removal of DBP complexes from the catalyst surface.

In 2011 S. Nichapat et al. [26] studied about the catalytic behaviors of $MgCl_2$-$SiO_2/TiCl_4/THF$ Ziegler-Natta (ZN) catalysts with fumed SiO_2 treated with silane compounds. They found that the surface concentrations for Ti in the treated catalysts with low steric hindrance silane compounds were remarkably high. The large amounts of Ti located on the surface promoted these catalysts to exhibit very high activities. The high activity of the Ziegler-Natta catalysts can be attributed to the large amounts of Ti content on surface, not in the bulk of catalysts.

CHAPTER 3
EXPERIMENTAL

3.1   Materials and instruments

Table 3.1 List of chemicals

Chemical	Supplier
Hexane (commercial grade)	IRPC Public Company
Ethylbenzene (commercial grade)	IRPC Public Company
Titanium tetrachloride (commercial grade)	IRPC Public Company
Heptane (commercial grade)	IRPC Public Company
n-Heptane (AR grade)	RCI Labscan
Methyl alcohol (commercial grade)	IRPC Public Company
Tetrachloroethylene (A.R. grade, purity 99.8%)	RCI Labscan
Sulfuric acid (A.R. grade, purity 95.0-98.0%)	RCI Labscan
Hydrogen peroxide (L.R. grade, purity >30%)	Fisher Scientific
Nitric acid (A.R. grade, purity 70%)	Carlo Erba
ICP multi-element standards	Merck
Triethylaluminium (TEA), (commercial grade)	IRPC Public Company
di-n-butyl phthalate (DBP), (commercial grade)	IRPC Public Company
Isobutyl isopropyl dimethoxysilane (commercial grade)	IRPC Public Company
Cyclohexyl methyl dimethoxysilane (commercial grade)	IRPC Public Company
Dicyclopentyl dimethoxysilane (commercial grade)	IRPC Public Company
n-Nonane (GC grade)	Merck
Na_2SO_4 (anhydrous)	Carlo Erba

Table 3.2 List of instruments

Instruments	Supplier
20 liter stainless autoclave	Buchi
Inductive Couple Plasma-Optical Emission Spectroscopy	Spectro Acros
Scanning Electron Microscope (SEM)	JEOL JSM 5410LV
FT-IR spectrometer model Tensor 27	Bruker
Differential scanning calorimeter (DSC)	Metlter Toledo International
Gas chromatographer model Clarus 500 AS	Perkin Elmer
Reflux apparatus set and rotary evaporator for xylene soluble	Heidolph
Glass reactor for catalyst extraction 1.5 liter	Buchi
Drying oven model FED 200	Binder
Compression machine	Local brand
Automatic titrator	Metrohm

3.2   Preparation of catalysts

Crude catalyst

SiO_2, $MgCl_2$ in ethylbenzene medium was heated up and refluxed in a reactor with stirred agitator at 95 $^{\circ}$C for 30 minutes and cool down to room temperature and filled with ethanol, then refluxed at 50 $^{\circ}$C 30 minutes, after that $TiCl_4$ was filled and heated up to 60 $^{\circ}$C, internal donor added and reheated to 100 $^{\circ}$C for 1 h. The mixture was transferred to next drying step.

Apparatus for catalyst preparation composed with double wall 1.5 liter glass reactor with speed control agitator. The electric heating and cooling for control reactor temperature. Inert N_2 gas system for blanket and purge reaction system. The preparation of catalyst was shown in step reaction as below.

1. Support preparation
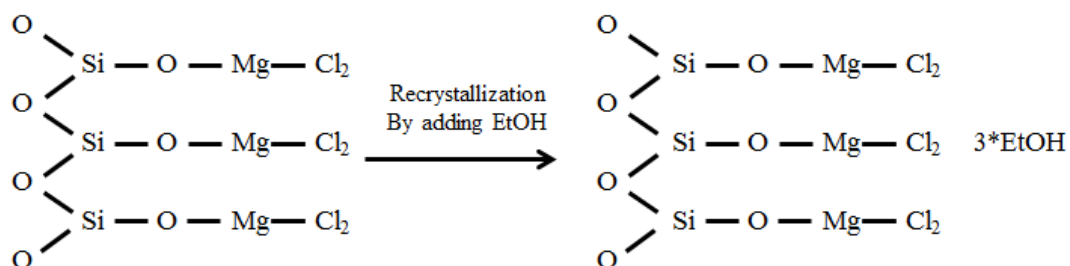
2.Titanation
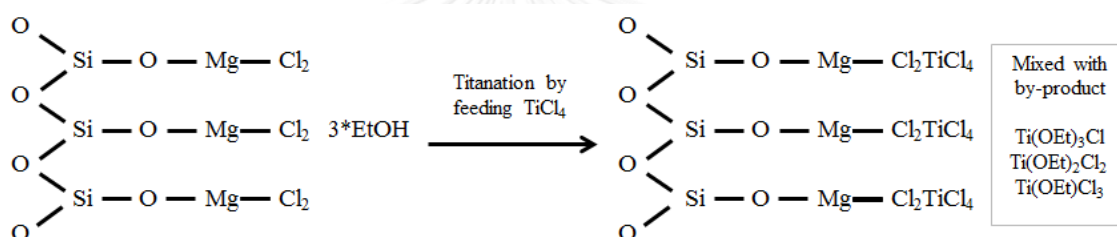
3.Coupling Ti with DBP
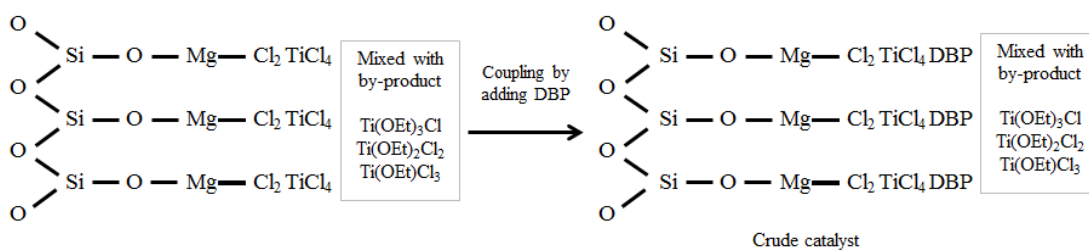
Drying of crude catalyst

Crude catalyst was washed with hexane (500 ml) then purged with N_2 until dry (1.5 h). The dried catalyst was transferred to a stock flask for next extraction step.

Extraction step

Extraction step was done as shown in below scheme.
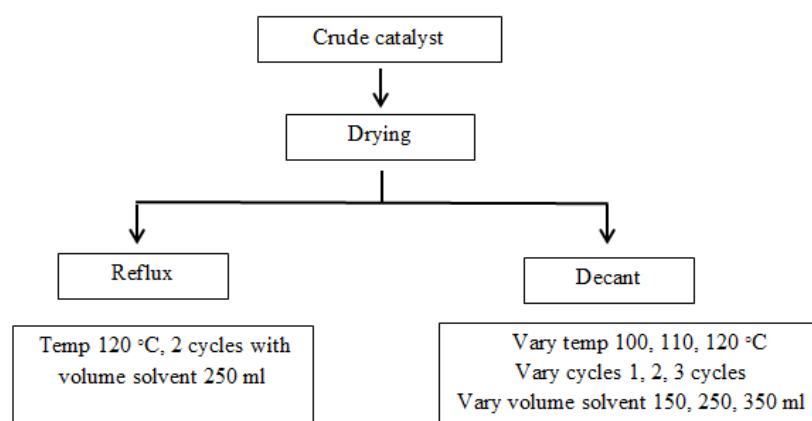
Figure 3.1 Scheme of extraction method.

1. Refluxing method

The dried catalyst was transferred to an extraction chamber. The extraction mixture (10% $TiCl_4$ in EB) 500 ml was heated up to 120 $^\circ$C and refluxed for 3 h. The extracted catalyst was filtered, dried and collected in the flask under N_2.
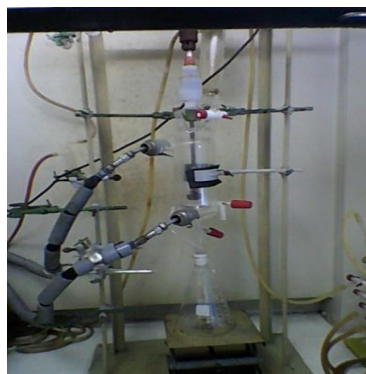
Figure 3.2 Apparatus for reflux extraction.

2. Decantation method

The dried catalyst was filled with extraction mixture (10% $TiCl_4$ in EB) 150 ml in the extraction chamber. It was stirred at 400 rpm, and then the catalyst was decanted. The extracted catalyst was dried and collected in the flask under nitrogen atmosphere.

Figure 3.3 Apparatus for decant extraction.

The $TiCl_4$ was added in extraction mixture transform all titanium alkoxyhalide by-product to titanium trialkoxychloride that can be dissolved in the extraction mixture.

Temperature for the extraction was varied: 100, 110, and 120°C with other parameters were fixed. Then appropriate temperature was then used for 1-3 extraction loops and volume of extraction mixture solution was varied: 100, 125, and 150 ml.

3.3   Characterization of catalyst

The catalysts from extraction step was analyzed as following scheme.
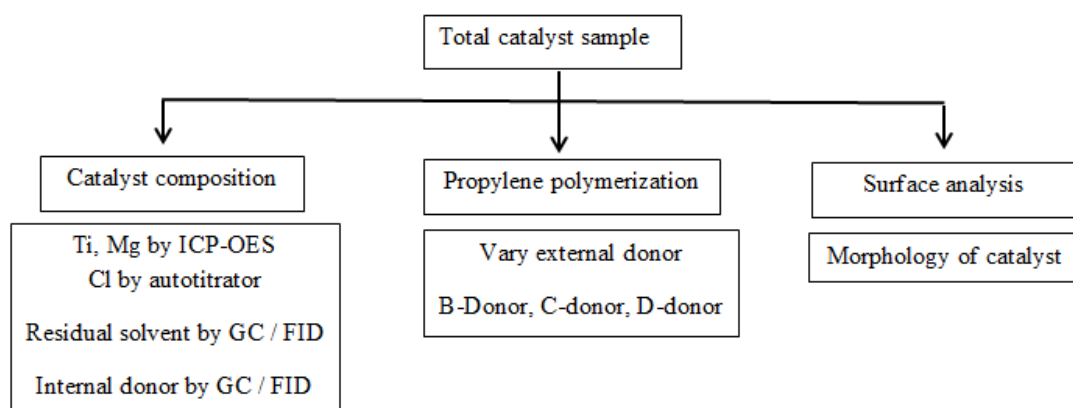
Figure 3.4 Scheme of catalyst analysis.

Catalyst composition (Ti, Mg, Cl content)

Approximate100 mg catalyst was digested in 20% HNO_3 (5 ml) and make up volume to100 ml in a volumetric flask. The Ti, Mg contents were analyzed by ICP-OES technique.

Approximate 0.1 g catalyst was digested in 20% HNO_3 (5 ml) and make up volume to150 ml. The solution was analyzed for Cl content by autometric titrator (Metrohm model 848, Ag/AgCl electrode for measurement).

Determination of residual solvent in catalyst

1.5-2.0 g catalyst was hydrolyzed with 20% H_2SO_4 (10 ml) and added tetrachloroethylene to extract the EB. The EB in organic phase was transfer to a vial, dried with anhydrous Na_2SO_4. This was added n-nonane as an internal standard and analyzed by GC-FID.

Determination of dibutyl phthalate (DBP), internal donor in catalyst

200 mg catalyst was hydrolyzed with 20% H_2SO_4 (10 ml) and n-heptane was added to extract the DBP to heptane phase. This heptane phase was transfer to a vial, dried with anhydrous Na_2SO_4. This was added n-nonane as an internal standard and analyzed by GC-FID.

Morphology analysis

The morphology of catalyst was determined by using scanning electron microscope (SEM). Precautions were taken to avoid the expose of the sample to air, nitrogen glove box was used. The container top was sealed with parafilm. The samples were transferred quickly to the gold coating machine operated in vacuum. After sample was coated with the layer of gold, the sample was analyzed by SEM.

3.4 Propylene polymerization

The 20 liter reactor was filled with hexane while purged with N_2. PP powder 300 g was added into the reactor to be powder base for catalyst dispersing. The reactor was filled with catalyst around100 mg, cocatalyst and external donor then H_2 was filled (10 bar). Adjust the agitator speed to 350 rpm. Then feed the propylene to the reactor while temperature of the reactor was raised up and maintained to 70 $^{\circ}$C, propylene was fed in 1.5 h and the total pressure was kept at 28 bar. The unreacted propylene was released from the reactor together while the system was cooled down to room temperature and then the polymer powder was drained out from the reactor and weighed. It was characterized.

3.5   Characterization of polypropylene

Isotactic Index (I.I.) by FTIR

The PP powder was compressed at $170\,^{\circ}$C to produce 50 μm thin film samples. The FTIR scans were performed at an ambient temperature in the range of 400 to 4,000 cm^{-1}. The determination of Isotactic Index (I.I) was through the relation between the absorbance ratio (A_{999} / A_{973}).The 998 cm^{-1}band is assigned to CH_3 rocking + CH_2 wagging + CH bending vibrations, whereas 973 cm^{-1} band belongs to coupled CH_3 rocking + C-C chain stretching vibrations. The 998 cm^{-1}absorption band is usually assigned to the crystalline phase, whereas 973 cm^{-1}band is assigned to both the crystalline and the amorphous chains in helical conformations. Isotactic Index was calculated by using the below equation [27]:

$$\frac{A998}{A973} = 1.08\,(I.I)\,-0.15$$

Crystallinity by differential scanning calorimeter (DSC)

5 mg. of sample was heated from 30 to $200\,^{\circ}$C, held at $200\,^{\circ}$C for 5 min to erase the thermal history, and then cooled to $30\,^{\circ}$C and re melted over the same temperature of 30 to $200\,^{\circ}$C for the second scan. The heating and cooling were performed at a rate $10\,^{\circ}$C/min. The crystallization and melting parameters were recorded from the cooling and reheating scans. The degree of crystallinity (X_c) was calculated by comparison the melting heat of crystalline in sample (ΔH^a_m) with the melting heat (ΔH^{100}_m) of perfectly crystalline polypropylene, i.e., 209J/g [28], according to the below equation.

$$X_c = \left(\frac{\Delta H^a_m}{\Delta H^{100}_m}\right) \times 100$$

<u>Xylene soluble extraction : ASTM D 5492 – 06 (Gravimetric method)</u>

Xylene extraction method involves extracting soluble atactic fraction after boiling polypropylene in xylene solvent where the remaining matter is insoluble isotactic polypropylene. A weighed amount of sample was refluxed in xylene. The solution was cooled and crystallization of the insoluble fraction took place. The insoluble portion precipitated and was isolated by filtration. The xylene was evaporated, leaving the soluble fraction in the residue. This was weighed. Mass percent of the soluble fraction was calculated using below equation:

% Xylene soluble = (mass of soluble fraction /mass of PP sample) * 100

CHAPTER 4
RESULTS AND DISCUSSION

The catalyst was prepared by refluxing SiO_2 and $MgCl_2$ in ethylbenzene medium solution. The solution was heated to 70 $^{\circ}$C then the ethanol was added and solution was refluxed at temp around 90 $^{\circ}$C for 4 h. The solution was cooled to   20 $^{\circ}$C then add $TiCl_4$ for titanation. The DBP was added when solution was heated up until reach 60 $^{\circ}$C after that keep at 100 $^{\circ}$C for 1 h. The crude catalyst was filtered and washed with ethylbenzene.

The crude catalyst was dried with N_2. In order to make sure the catalyst was dried completely, the residual solvent was determined. The dried crude catalyst was used to prepare final catalyst with different extraction step. Crude catalyst and all final catalysts were characterized. The catalyst sample names were displayed in Table 4.1.

Table 4.1 Description of catalyst samples

Sample code	Description
Crude	Dried crude catalyst before extraction
R120	Final catalyst prepared with reflux extraction at temp 120 $^{\circ}$C, solvent volume 500 ml, reflux time 3 h.
D100-2 D110-2 D120-2	Final catalyst prepared with decant extraction at temp 100 , 110 and 120 $^{\circ}$C, solvent volume 250 ml, 2 cycles, decant 1 h.

The parameters influencing the preparation of catalyst were studied and the results are described as following.

4.1   Effect of extraction temperature

In the reflux extraction method, the reflux temperature was 120 °C and extracted solvent 500 ml. In the decant method, the dried crude catalyst was immersed in 250 ml solvent, 2 cycles with varying temperature as 100, 110 and 120 °C. Dried crude catalyst and decant catalyst were analyzed for Ti, Mg and Cl contents, the results are shown in Figure 4.1 and residual solvent is showed in Table 4.2.
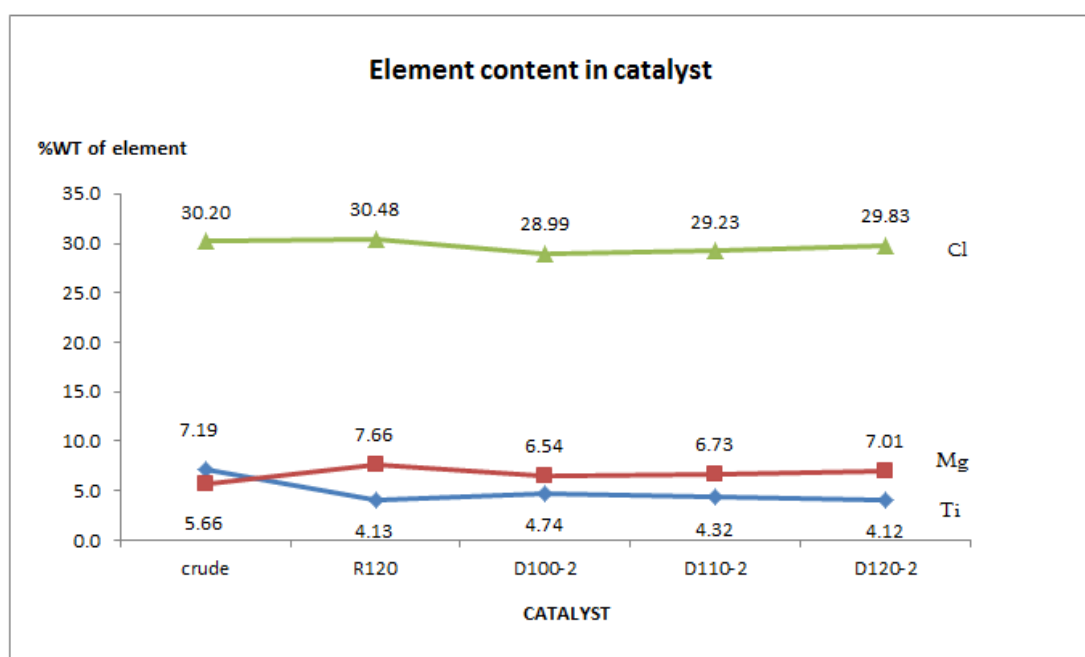
Figure 4.1 Results of elements content of catalyst.

The crude catalyst shows Ti = 7.19 %, after extraction with reflux or decant method Ti content decreases which means that the by-product was removed. In the decant method, Ti content was decreased when decant temperature was increased.

Table 4.2 Residual solvent on catalyst

Sample	% residual solvent
Crude	0.3
R120	0.4
D100-2	0.4
D110-2	0.5
D120-2	0.4

All dried catalyst sample has low residual solvent in range 0.3 to 0.5 %, so the catalyst was dried completely and the weight of catalyst can be used as weight of the catalyst after the drying step.

Internal electron donor residual on catalyst after extraction with varying temperature was determined. In Table 4.3, the internal donor DBP decreased with increasing decantation temperature (6.51 % at decant temp 100 $^\circ$C to 3.85 % at decant 120 $^\circ$C). However, DBP quantity by decantation method is 1.6% higher than that by reflux method. Higher extreme condition of extraction will elute or remove DBP internal donor from the catalyst. With the decant method the DBP that was removed from catalyst to solvent still was in the extracted solvent, so it can recombine on catalyst. But in the reflux method the removed DBP was in reservoir tank that was not evaporated at 120 $^\circ$C because DBP has higher boiling point (340 $^\circ$C) than extraction mixture (10% $TiCl_4$ in ethylbenzene: BP 136 $^\circ$C).The performance of all catalysts are shown in Table 4.3.

Table 4.3 Performance and property of catalysts and polymer

Sample	DBP %	Productivity* (g PP/g cat.)	I.I	XS %	Crystallinity %
Crude	12.71	7,751	0.91	4.8	46.8
R120	2.26	22,008	0.91	2.8	46.9
D100-2	6.51	17,485	0.91	2.2	47.4
D110-2	5.03	18,867	0.92	2.1	47.5
D120-2	3.85	17,904	0.91	2.2	47.8

* Polymerization condition : Pressure 28 bar, temperature 70 $^{\circ}$C, ratio TEA/Ti = 200, TEA/ED = 100, ED/Ti = 2, time 1.5 h (TEA = Triethyl aluminium, ED = isobutyl isopropyl dimethoxy silane (B-donor))

The activity results of catalyst relate with purity of catalyst, the crude catalyst shows very low activity (7,751 g PP/g cat.) due to by-product was not removed. All catalysts were prepared with decant method show low activity in range 17,485-18,867 g PP/g cat. compared with the reflux catalyst shows the highest productivity is 22,008 g PP/g cat.. The reflux method is good to extract by-product compared with decant method.

Crude catalyst shows xylene soluble value higher than all extracted catalysts. The catalyst still shows high DBP at 12.71 %. With more DBP quantity of all decant catalysts (3.85-6.51%) so the decant catalyst exhibited better stereospecific control than that from the reflux catalyst. PP catalyzed with decant catalyst show lower XS value, 2.1-2.1%. The PP catalyzed with reflux catalyst show 2.8 %XS and has low DBP quantity, 2.26 %. The D110-2 catalyst is selected for further study since it showed the best productivity with average Ti and DBP quantity value.

For isotactic index and % crystallinity, they are not different. All of catalysts give I.I = 0.91-0.92 and % crystallinity = 46.8-47.8.

4.2   Effect of external donor

Catalyst D110-2 with the highest productivity was used to study effect of external donor. Three types of alkoxysilanes: isobutyl isopropyl dimethoxysilane, cyclohexyl methyl dimethoxysilane and dicyclopentyl dimethoxysilane were used as external electron donor. Their influence on the catalytic activity and stereospecificity on PP were compared. Xylene insoluble fraction, isotactic index and crystallinity of the PP were determined.

Structure of external donor; isobutyl isopropyl dimethoxysilane (B-donor), cyclohexyl methyl dimethoxysilane (C-donor) and dicyclopentyl dimethoxysilane (D-donor) as Figure 4.2.

B-donor   C-donor   D-donor
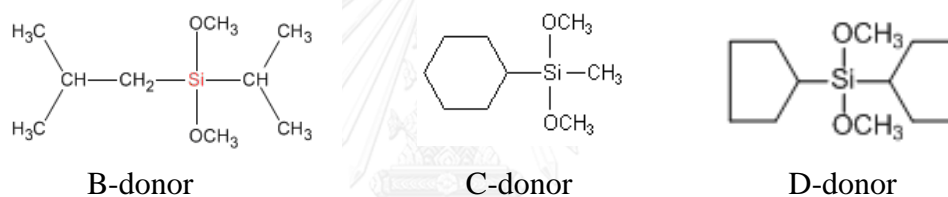
Figure 4.2 Structure of external electron B-donor, C-donor and D-donor.

Table 4.4 Productivity and PP properties of D110-2 catalyst with different external electron donors

External donor	Productivity*	XS	I.I	Crystallinity
	g PP/g cat	%	-	%
B-donor (isobutyl isopropyl dimethoxysilane)	18,867	2.1	0.92	47.5
C-donor (Cyclohexyl methyl dimethoxysilane)	19,004	4.5	0.88	45.2
D-donor (Dicyclopentyl dimethoxysilane)	20,785	1.5	ND	47.8

* Polymerization condition: Pressure 28 bar, temperature 70 $^{\circ}$C, ratio TEA /Ti = 200, TEA/ED = 100, ED/Ti = 2, time 1.5 h

ND = not determined

The catalyst with dicyclopentyl dimethoxysilane, D-donor shows the highest activity (20,785 g PP/g cat). Order of electron donor performance is: D > C > B. D-donor is also good for stereospecific control. The XS value is lowest (1.5 %). Order of stereospecificity control of electron donor is: D > B > C. However D-donor is more expensive than C-donor so C-donor was chosen to further study for varying ratio of ED/Ti.

To study effect of the stereospecificity control of C-donor, ED/Ti ratio was varied = 1, 2, 5, 10, 15 and 20. The activity of catalyst and the PP properties were shown in Table 4.5.

Table 4.5 Productivity and PP properties of D110-2 catalyst with varying C-donor/Ti ratios

C-donor*/Ti	Productivity**	I.I	Crystallinity	XS
	g PP/g cat.	-	%	%
1	22,409	0.92	43.7	5.6
2	23,254	0.90	45.1	3.7
5	24,141	0.93	45.4	2.9
10	19,460	0.94	46.5	1.7
15	19,021	0.92	47.8	1.1
20	19,811	0.92	47.5	0.8

* C-donor vary 0.09-1.7 mmole

** Polymerization condition: Pressure 28 bar, temperature 70 $^{\circ}$C, time 1.5 h

The productivity of catalyst was affected by varying ratio of C-donor/Ti, the activity of catalyst was increased when increased the quantity of C donor. The best productivity is 24,141 g PP/g cat. occurred at C-donor/Ti ratio= 5, after that the activity decreased.

Isotactic index value of polymer analyzed by IR technique show all polymer has isotactic index range 0.90 - 0.94.

The crystallinity of PP polymer is proportional to increasing quantity of C-donor. The crystallinity is 47 % when ratio C-donor/Ti is 15-20.

The XS results correspond with % crystallinity value. The high crystallinity polymer gives the low XS value. When electron donor amount is low, some active site catalyst lacks of stereospecific control and will give more atactic polypropylene so it shows high XS.

4.3   Effect of parameters of decantation

The catalyst was extracted at optimum temperature 110 $^{\circ}$C was selected to study other decant parameters, time of decant, number of decant cycle and volume of decant solvent.

4.3.1   Time of decantation

The decant time was varied in range of 30-90 min with 2 cycles using D110-2 catalyst. The activity of catalysts and properties of PP polymer was investigated, as shown in Tables 4.6 and 4.7.

Table 4.6 Results of catalysts D110-2 properties with varying decant time
(Decant 2 cycles with solvent volume 250 ml/cycle)

Decant time	Ti	Mg	Cl	Ti/Mg mole ratio	DBP
	%wt	%wt	%wt	-	%
30 min	4.69	7.86	30.1	1.2	6.1
60 min	3.94	9.26	32.2	0.8	5.2
90 min	4.24	8.06	29.6	1.0	3.6

Table 4.7 Productivity and properties of PP with varying decant time
(Decant 2 cycles with solvent volume 250 ml/cycle)

Decant time	Productivity*	Crystallinity	XS
	g PP/g cat	%	%
30 min	15,488	44.7	5.6
60 min	22,067	45.7	3.0
90 min	21,687	44.4	3.7

* Polymerization condition : Pressure 28 bar, temperature 70 $^\circ$C, ratio TEA /Ti = 200, TEA/ED = 100, ED/Ti = 2, time 1.5 h

With 30 min of decant time the efficiency of extracting is not sufficient to remove by-product, $Ti(OEt)_3Cl$, $Ti(OEt)_2Cl_2$ or $Ti(OEt)Cl_3$, or impurities in the process. The quantity of   Ti by-product results in poor activity. The DBP internal donor is high 6.1 % . The by-product on catalyst may block the DBP fixing on or near the active site Ti to be isospecific active site. This can be seen from high XS value (5.6 %).

The longer decant time increases the efficiency of catalyst. Catalyst activity increased to 21,687 g PP/g cat and 22,067 g PP/g cat. Longer decant time removed more DBP, resulting in higher amount of atactic fraction PP. The good activity and stereospecific control was found at 60 min decant time.

4.3.2   Cycle of decantation

Using catalyst D110, decant   time 60 min and 250 ml solvent each cycle, decant cycle was varied from 1 to 3 cycles. The activity of catalysts and stereospecificity properties of PP polymer were investigated and shown in Tables 4.8 and 4.9.

Table 4.8 Results of catalysts D110 properties with varying no. of decant cycle
(Decant time 60 min/cycle and solvent volume 250 ml/cycle)

No. of decant cycle	Ti	Mg	Cl	Ti/Mg mole ratio	DBP
	%wt	%wt	%wt	-	%
1	5.46	7.17	29.5	1.5	6.7
2	3.94	9.26	32.2	0.8	5.2
3	4.09	7.07	29.9	1.1	4.1

Table 4.9 Stereospecific properties of PP with catalyst D-110
(Decant time 60 min/cycle and solvent volume 250 ml/cycle)

No. of decant cycle	Productivity*	Crystallinity	XS
	g PP/g cat	%	%
1	13,895	45.1	5.5
2	22,067	45.7	3.0
3	17,909	48.7	2.2

* Polymerization condition : Pressure 28 bar, temperature 70 $^\circ$C, ratio TEA /Ti = 200,
TEA/ED = 100, ED/Ti = 2, time 1.5 h

Effect of the number of decant cycle shows the same result as the effect of decant time. The 1 cycle-decant shows higher Ti and residual DBP content because not all by-products is removed from the catalyst. Efficiency of extraction was increased at 2 cycle- decant, the Ti content is 3.94. However at the 3 cycle-decant, the catalyst gave low productivity than that from the 2-cycle decant, this might be due to some catalyst decomposition.

4.3.3   Volume of solvent of decantation

Catalyst D110 with condition 2 cycles of 60 min decant, with varying the solvent volume each cycle is 150 ml, 250 ml and 350 ml. The activity of catalysts and stereospecificity properties of PP polymer were investigated.

Table 4.10 Results of decant catalysts D110 with varying volume of decant solvent (Decant 2 cycles with decant time 60 min/cycle)

Solvent volume	Ti	Mg	Cl	Ti/Mg mole ratio	DBP
	%wt	%wt	%wt	-	%
150	5.04	7.38	29.7	1.3	5.7
250	3.94	9.26	32.2	0.8	5.2
350	4.54	8.12	29.8	1.1	3.7

Table 4.11 Stereospecific properties of PP with varying volume of decant solvent (Decant 2 cycles with decant time 60 min/cycle)

Solvent volume	Productivity*	Crystallinity	XS
	g PP/g cat	%	%
150	15,879	45.1	4.4
250	22,067	45.7	3.0
350	18,690	45.3	3.4

* Polymerization condition : Pressure 28 bar, temperature 70 $^{\circ}$C, ratio TEA /Ti = 200, TEA/ED = 100, ED/Ti = 2, time 1.5 h

The 2 cycle extraction and decant time of 60 min, in 150 ml solvent could not remove all by-products so that activity is low, only 15,879 g PP/g cat. Using more solvent can increase the efficiency of extraction by removing by-product and DBP. Productivity of decant catalyst with solvent volume 350 ml is, however, lower (18,600 g PP/g cat). This might due to the excess $TiCl_4$ in extraction mixture solvent which can recombine on the catalyst.

Crystallinity of polymer using different solvent volume is not different. For the XS value, it decreased when using more solvent volume.

4.4   Morphology of catalyst and polymer

Surface of catalysts were examined by SEM (in Figure 4.3). The crude catalyst shows more roughly surface than the catalysts after extraction. Both catalysts after extraction show similar shape and size. This reveals that extraction at high temperature used in this work did not affect the catalyst morphology. The decant extraction method with stirring does not affect to catalyst shape.
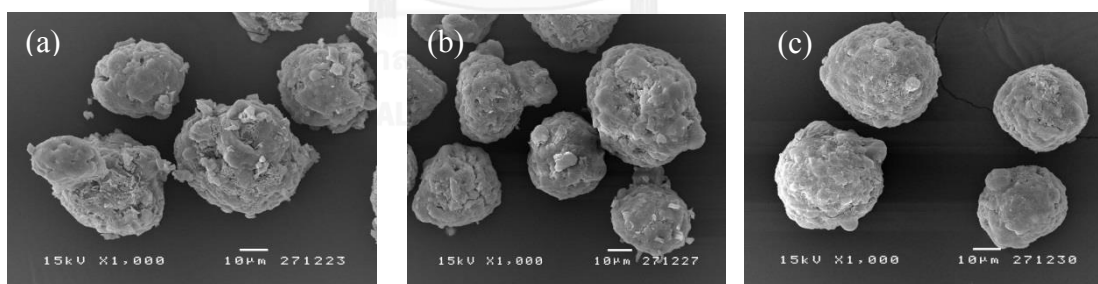
Figure 4.3 SEM analysis of catalysts: (a) crude catalyst, (b) reflux catalyst and (c) decant catalyst.

Figure 4.4 shows morphology and surface of the PP polymer produced from the crude catalyst and the catalysts after extraction. All show quite sphere shape, indicating replica phenomenon.
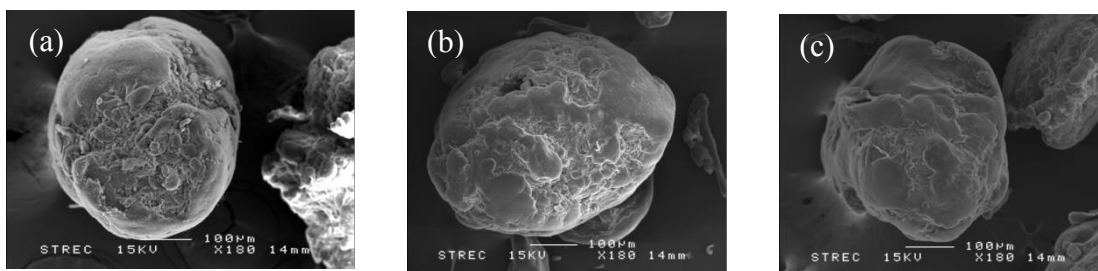
Figure 4.4 SEM analysis of PP: (a) from crude catalyst, (b) from reflux catalyst and (c) from decant catalyst.
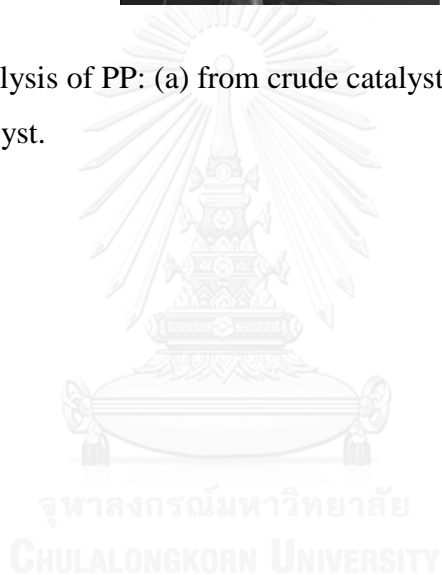
CHAPTER 5
CONCLUSION AND SUGGESTION

5.1   Conclusions

The Ziegler-Natta catalysts, $MgCl_2$-SiO_2/$TiCl_4$/DBP, were purified by two different extraction methods (reflux and decant). They have higher productivity than the crude catalyst. With decant method extraction, the decant catalyst (D110) at 110 $^\circ$C shows highest productivity. However the decant catalysts show lower productivity when compared with reflux method. Increasing the decant temperature the Ti content of catalysts decreased.

All catalysts prepared by decant method have more residual DBP content than the reflux catalyst. The decant catalyst produces PP with lower XS value.

The D-donor (dicyclopentyl dimethoxysilane) shows the highest activity. Order of electron donor performance is: D (Dicyclopentyl dimethoxysilane) > C (cyclohexyl methyl dimethoxysilane) > B (isobutyl isopropyl dimethoxysilane). Due to higher cost of D-donor, the C-donor was used and activity of catalyst was increased when increased the quantity of C donor.

Order of stereospecificity control of electron donor is: D > B > C. The crystallinity of PP polymer is proportional to increasing quantity of C-donor. The best productivity is 24,141 g PP/g cat. with C-donor/Ti ratio = 5.

The crude catalyst shows more roughly surface than the extracted catalysts. The catalyst after extraction method show good morphology. The PP polymers replicate their catalyst.

In summary the decantation method can be used for catalyst preparation. The decant catalyst with C-donor (cyclohexyl methyl dimethoxysilane) can produce PP polymer with low xylene soluble property, applied in industrial production.

5.2 Suggestions for the future work

A future work will compare performance of catalyst prepared with and without SiO_2 support: SiO_2 together with $MgCl_2$ is used as the support (bi-supported catalysts system) to enhance strength. Another way is reducing cost by not using SiO_2, this needs an additional method to increase the productivity.

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APPENDICES

APPENDIX A

Summarize table of Ti, Mg content of catalysts analyzed by ICP-OES

Table A-1 Data of Ti and Mg content of crude, reflux and decant catalysts analyzed by ICP-OES

Catalyst	Sample no.	Element	Tube no.	Sample wt. (mg)	Result (mg/L)	%wt. in sample	AVE (%)	
crude	1	Mg	1	68.9	39.00	5.66	5.66	Mg=5.66
			2	70.9	40.06	5.65		Ti=7.19
		Ti	1	68.9	50.43	7.32	7.19	
			2	70.9	50.06	7.06		
reflux	1	Mg	1	50.8	39.01	7.68	7.59	
			2	49.0	36.70	7.49		
		Ti	1	50.8	21.79	4.29	4.25	
			2	49.0	20.58	4.20		
	2	Mg	1	46.1	34.94	7.58	7.59	Mg=7.66
			2	53.7	40.76	7.59		Ti =4.13
		Ti	1	46.1	18.90	4.10	4.10	
			2	53.7	22.02	4.10		
	3	Mg	1	47.5	35.58	7.49	7.80	
			2	45.6	36.94	8.10		
		Ti	1	47.5	18.53	3.90	4.04	
			2	45.6	19.02	4.17		
100-2	1	Mg	1	72.8	47.25	6.49	6.41	
			2	58.6	37.09	6.33		
		Ti	1	72.8	37.20	5.11	5.04	
			2	58.6	29.07	4.96		
	2	Mg	1	62.8	41.39	6.59	6.56	Mg=6.54
			2	57.4	37.42	6.52		Ti =4.74
		Ti	1	62.8	30.21	4.81	4.64	
			2	57.4	25.66	4.47		
	3	Mg	1	64.7	42.25	6.53	6.66	
			2	65.3	44.27	6.78		
		Ti	1	64.7	31.06	4.80	4.55	
			2	65.3	29.25	4.48		

Table A-1 Data of Ti and Mg content of crude, reflux and decant catalysts analyzed by ICP-OES (Continued)

Catalyst	Sample no.	Element	Tube no.	Sample wt. (mg)	Result (mg/L)	%wt. in sample	AVE (%)	
110-2	1	Mg	1	56.2	39.06	6.95	6.89	Mg=6.73 Ti =4.32
			2	59.9	40.85	6.82		
		Ti	1	56.2	23.10	4.11	4.15	
			2	59.9	25.10	4.19		
	2	Mg	1	52.6	33.82	6.43	6.56	
			2	60.7	40.55	6.68		
		Ti	1	52.6	22.88	4.35	4.32	
			2	60.7	26.04	4.29		
	3	Mg	1	52.6	34.45	6.55	6.74	
			2	60.7	42.00	6.92		
		Ti	1	52.6	22.88	4.35	4.48	
			2	60.7	26.04	4.29		
120-2	1	Mg	1	57.0	38.82	6.81	6.85	Mg=7.01 Ti =4.12
			2	54.2	37.29	6.88		
		Ti	1	57.0	22.91	4.02	4.08	
			2	54.2	22.44	4.14		
	2	Mg	1	56.1	39.44	7.03	7.04	
			2	52.7	37.10	7.04		
		Ti	1	56.1	23.51	4.19	4.24	
			2	52.7	22.56	4.28		
	3	Mg	1	62.0	46.00	7.42	7.16	
			2	58.1	40.03	6.89		
		Ti	1	62.0	26.35	4.25	4.05	
			2	58.1	22.37	3.85		

Table A-2 Data of Ti, Mg content of D110-2 catalysts with varying decant time analyzed by ICP-OES

Decant time (min)	Sample no.	Element	Tube no.	Sample wt. (mg)	Result (mg/L)	%wt. in sample	AVE (%)	
30	1	Mg	1	62.1	48.56	7.82	7.78	Mg=7.86 Ti =4.69
			2	58.4	45.20	7.74		
		Ti	1	62.1	27.39	4.41	4.58	
			2	58.4	27.74	4.75		
	2	Mg	1	58.8	46.33	7.88	7.94	
			2	66.9	53.52	8.00		
		Ti	1	58.8	27.69	4.71	4.80	
			2	66.9	32.71	4.89		
60	1	Mg	1	67.6	62.26	9.21	9.14	Mg=9.26 Ti =3.94
			2	59.4	53.88	9.07		
		Ti	1	67.6	28.19	4.17	4.08	
			2	59.4	23.70	3.99		
	2	Mg	1	63.5	59.82	9.42	9.38	
			2	62.2	58.09	9.34		
		Ti	1	63.5	24.32	3.83	3.80	
			2	62.2	23.45	3.77		
90	1	Mg	1	54.2	45.09	8.32	8.21	Mg=8.06 Ti =4.24
			2	61.8	50.06	8.10		
		Ti	1	54.2	23.09	4.26	4.11	
			2	61.8	24.47	3.96		
	2	Mg	1	65.0	50.64	7.79	7.91	
			2	68.2	54.76	8.03		
		Ti	1	65.0	29.12	4.48	4.37	
			2	68.2	29.05	4.26		

Table A-3 Data of Ti and Mg content of D110-2 catalysts with varying cycle of decant analyzed by ICP-OES

No. of cycle	Sample no.	Element	Tube no.	Sample wt. (mg)	Result (mg/L)	%wt. in sample	AVE (%)	
1	1	Mg	1	57.3	48.56	7.23	7.25	Mg=7.17 Ti =5.46
			2	59.4	45.20	7.27		
		Ti	1	57.3	27.39	5.36	5.41	
			2	59.4	27.74	5.46		
	2	Mg	1	58.2	46.33	7.88	7.09	
			2	63.7	53.52	6.30		
		Ti	1	58.2	27.69	4.86	5.51	
			2	63.7	32.71	6.16		
2	1	Mg	1	67.6	62.26	9.21	9.14	Mg=9.26 Ti =3.94
			2	59.4	53.88	9.07		
		Ti	1	67.6	28.19	4.17	4.08	
			2	59.4	23.70	3.99		
	2	Mg	1	63.5	59.82	9.42	9.38	
			2	62.2	58.09	9.34		
		Ti	1	63.5	24.32	3.83	3.80	
			2	62.2	23.45	3.77		
3	1	Mg	1	63.7	45.09	8.32	6.96	Mg=7.07 Ti =4.09
			2	58.4	50.06	5.60		
		Ti	1	63.7	23.09	4.26	4.13	
			2	58.4	24.47	4.00		
	2	Mg	1	64.2	50.64	7.79	7.18	
			2	63.2	54.76	6.57		
		Ti	1	64.2	29.12	4.48	4.05	
			2	63.2	29.05	3.62		

Table A-4 Data of Ti and Mg content of D110-2 catalysts with varying volume of solvent analyzed by ICP-OES

Volume Solvent (ml)	Sample no.	Element	Tube no.	Sample wt. (mg)	Result (mg/L)	%wt. in sample	AVE (%)	
150	1	Mg	1	66.7	48.56	7.23	7.19	Mg=7.38 Ti =5.04
			2	64.3	45.20	7.15		
		Ti	1	66.7	27.39	5.12	4.98	
			2	64.3	27.74	4.84		
	2	Mg	1	63.8	46.33	7.48	7.57	
			2	59.5	53.52	7.66		
		Ti	1	63.8	27.69	5.14	5.10	
			2	59.5	32.71	5.06		
250	1	Mg	1	67.6	62.26	9.21	9.14	Mg=9.26 Ti =3.94
			2	59.4	53.88	9.07		
		Ti	1	67.6	28.19	4.17	4.08	
			2	59.4	23.70	3.99		
	2	Mg	1	63.5	59.82	9.42	9.38	
			2	62.2	58.09	9.34		
		Ti	1	63.5	24.32	3.83	3.80	
			2	62.2	23.45	3.77		
350	1	Mg	1	56.1	45.09	7.95	8.08	Mg=8.12 Ti =4.54
			2	57.2	50.06	8.21		
		Ti	1	56.1	23.09	4.60	4.62	
			2	57.2	24.47	4.64		
	2	Mg	1	65.9	50.64	7.87	8.16	
			2	71.2	54.76	8.45		
		Ti	1	65.9	29.12	4.41	4.46	
			2	71.2	29.05	4.51		

Summarize table of Cl content of catalysts analyzed by autotitrator

Table A-5 Data of Cl content of crude, reflux and decant catalysts analyzed by autotitrator

Catalyst	Test no.	Flask no.	wt. cat (mg)	%wt. Cl	AVE Cl (%wt.)	
Crude	1	1	0.1204	30.24	30.20	30.20
		2	0.1142	29.97		
		3	0.1223	30.39		
Reflux	1	1	0.1113	29.31	29.25	30.48
		2	0.1218	29.01		
		3	0.1288	29.44		
	2	1	0.0905	30.73	30.90	
		2	0.0970	31.04		
		3	0.1005	30.94		
	3	1	0.0901	31.22	31.30	
		2	0.0956	31.34		
		3	0.0928	31.33		
D100-2	1	1	0.1024	28.79	28.68	28.99
		2	0.1024	28.51		
		3	0.1038	28.74		
	2	1	0.1094	29.01	29.20	
		2	0.1130	29.22		
		3	0.1270	29.38		
	3	1	0.1082	29.08	29.10	
		2	0.1243	29.03		
		3	0.1222	29.20		
D110-2	1	1	0.1012	28.59	28.55	29.23
		2	0.1074	28.24		
		3	0.1240	28.82		
	2	1	0.0969	28.58	28.55	
		2	0.1101	28.76		
		3	0.1110	28.31		
	3	1	0.0969	30.59	30.60	
		2	0.1101	30.82		
		3	0.1110	30.38		

Table A-5 Data of Cl content of crude, reflux and decant catalysts analyzed by autotitrator (continued)

Catalyst	Test no.	Flask no.	wt.cat (mg)	%wt. Cl	AVE Cl (%wt.)	
D120-2	1	1	0.0830	29.71	29.81	29.83
		2	0.0868	30.55		
		3	0.0916	29.18		
	2	1	0.0916	31.12	30.39	
		2	0.0976	30.40		
		3	0.1063	29.65		
	3	1	0.1125	28.99	29.30	
		2	0.1163	29.32		
		3	0.1226	29.58		

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Table A-6 Data of Cl content of D110-2 catalysts with varying decant time analyzed by autotitrator

Decant time (min)	Test no.	Flask no.	wt.cat (mg)	%wt. Cl	AVE Cl (%wt.)	
30	1	1	0.1142	29.65	29.96	30.1
		2	0.1033	30.11		
		3	0.1128	30.12		
	2	1	0.1223	30.02	30.24	
		2	0.1371	29.43		
		3	0.1420	31.27		
60	1	1	0.1022	31.13	31.65	32.2
		2	0.1045	31.22		
		3	0.1173	32.60		
	2	1	0.0922	31.69	32.75	
		2	0.1321	33.28		
		3	0.1062	33.28		
90	1	1	0.0967	29.92	29.72	29.6
		2	0.1098	30.52		
		3	0.1192	28.72		
	2	1	0.1178	29.53	29.48	
		2	0.1346	29.66		
		3	0.1232	29.25		

Table A-7 Data of Cl content of D110-2 catalysts with varying cycle of decant analyzed by autotitrator

No. of cycle	Test no.	Flask no.	wt.cat (mg)	%wt. Cl	AVE Cl (%wt.)	
1	1	1	0.1221	29.45	30.12	29.5
		2	0.1382	30.21		
		3	0.1036	30.70		
	2	1	0.1199	28.89	28.88	
		2	0.1032	29.24		
		3	0.1216	28.51		
2	1	1	0.1022	31.13	31.65	32.2
		2	0.1045	31.22		
		3	0.1173	32.60		
	2	1	0.0922	31.69	32.75	
		2	0.1321	33.28		
		3	0.1062	33.28		
3	1	1	0.1025	30.16	30.86	29.9
		2	0.0959	30.93		
		3	0.1043	31.49		
	2	1	0.1228	29.21	28.94	
		2	0.1783	29.07		
		3	0.1098	28.54		

Table A-8 Data of Cl content of D110-2 catalysts with varying volume of solvent analyzed by autotitrator

Volume solvent (ml)	Test no.	Flask no.	wt.cat (mg)	%wt. Cl	AVE Cl (%wt.)	
150	1	1	0.1034	30.13	30.21	29.7
		2	0.1129	30.24		
		3	0.1094	30.26		
	2	1	0.1221	29.09	29.19	
		2	0.1218	29.34		
		3	0.1150	29.14		
250	1	1	0.1022	31.13	31.65	32.2
		2	0.1045	31.22		
		3	0.1173	32.60		
	2	1	0.0922	31.69	32.75	
		2	0.1321	33.28		
		3	0.1062	33.28		
350	1	1	0.1171	29.78	29.89	29.8
		2	0.1099	29.98		
		3	0.1232	29.91		
	2	1	0.1224	29.87	29.71	
		2	0.1189	29.64		
		3	0.1155	29.62		

Summarize table of residual solvent content of catalysts analyzed by GC

Table A-9 Data of residual solvent content of crude, reflux and decant catalysts
analyzed by GC

Catalyst	Vial no.	Injection no.	Solvent content (%wt.)	AVE (%wt.)	
Crude	1	1	0.36	0.34	0.34
		2	0.33		
		3	0.34		
Reflux	1	1	0.43	0.44	0.44
		2	0.45		
		3	-		
D100-2	1	1	0.43	0.42	0.38
		2	0.43		
		3	0.40		
	2	1	0.34	0.35	
		2	0.36		
		3	0.34		
D110-2	1	1	0.43	0.42	0.52
		2	0.41		
		3	-		
	2	1	0.61	0.62	
		2	0.63		
		3	-		
D120-2	1	1	0.47	0.49	0.47
		2	0.50		
		3	-		
	2	1	0.46	0.45	
		2	0.46		
		3	0.44		

Summarize table of DBP content of catalysts analyzed by GC

Table A-10 Data of DBP content of crude, reflux and decant catalysts analyzed by GC

Catalyst	Sample no.	Vial no.	Injection no.	DBP (%wt.)	AVE (%wt.)		
Crude	1	1	1	12.82	12.86	12.71	12.71
			2	12.91			
			3	12.84			
		2	1	12.54	12.57		
			2	12.56			
			3	12.61			
Reflux	1	1	1	2.24	2.24	2.29	2.26
			2	2.26			
			3	2.21			
		2	1	2.19	2.34		
			2	2.63			
			3	2.19			
	2	1	1	2.32	2.24	2.23	
			2	2.21			
			3	2.20			
		2	1	2.23	2.22		
			2	2.21			
			3	2.22			

Table A-10 Data of DBP content of crude, reflux and decant catalysts analyzed by GC (continued)

Catalyst	Sample no.	Vial no.	Injection no.	DBP (%wt.)	AVE (%wt.)		
D100-2	1	1	1	6.48	6.54	6.54	6.51
			2	6.56			
			3	6.58			
		2	1	6.53	6.53		
			2	6.57			
			3	6.49			
	2	1	1	6.48	6.46	6.48	
			2	6.45			
			3	6.45			
		2	1	6.46	6.49		
			2	6.52			
			3	6.49			
D110-2	1	1	1	4.98	5.04	5.08	5.03
			2	5.13			
			3	5.02			
		2	1	5.13	5.11		
			2	5.08			
			3	5.12			
	2	1	1	5.08	5.02	4.97	
			2	4.96			
			3	5.02			
		2	1	4.91	4.93		
			2	4.89			
			3	4.98			

Table A-10 Data of DBP content of crude, reflux and decant catalysts analyzed by GC (continued)

Catalyst	Sample no.	Vial no.	Injection no.	DBP (%wt.)	AVE (%wt.)		
D120-2	1	1	1	3.91	3.90	3.78	3.85
			2	3.90			
			3	3.90			
		2	1	3.65	3.65		
			2	3.67			
			3	3.63			
	2	1	1	3.94	3.90	3.92	
			2	3.88			
			3	3.89			
		2	1	3.94	3.94		
			2	3.93			
			3	3.96			

Table A-11 Data of DBP content of D110-2 catalysts with varying decant time analyzed by GC

Decant time (min)	Vial no.	Injection no.	DBP (%wt.)	AVE (%wt.)	DBP (%wt.)
30	1	1	6.66	6.67	6.73
		2	6.61		
		3	6.74		
	2	1	6.81	6.79	
		2	6.74		
		3	6.82		
60	1	1	5.17	5.13	5.24
		2	5.18		
		3	5.04		
	2	1	5.37	5.35	
		2	5.32		
		3	5.36		
90	1	1	4.32	4.21	4.08
		2	4.21		
		3	4.10		
	2	1	3.92	3.95	
		2	4.09		
		3	3.84		

Table A-12 Data of DBP content of D110-2 catalysts with varying cycle of decant analyzed by GC

No. of cycle	Vial no.	Injection no.	DBP (%wt.)	AVE (%wt.)	DBP (%wt.)
1	1	1	6.66	6.67	6.73
		2	6.61		
		3	6.74		
	2	1	6.81	6.79	
		2	6.74		
		3	6.82		
2	1	1	5.17	5.13	5.24
		2	5.18		
		3	5.04		
	2	1	5.37	5.35	
		2	5.32		
		3	5.36		
3	1	1	4.32	4.21	4.08
		2	4.21		
		3	4.10		
	2	1	3.92	3.95	
		2	4.09		
		3	3.84		

Table A-13 Data of DBP content of D110-2 catalysts with varying volume of solvent analyzed by GC

Volume solvent (ml)	Vial no.	Injection no.	DBP (%wt.)	AVE (%wt.)	DBP (%wt.)
150	1	1	5.74	5.82	5.72
		2	5.81		
		3	5.91		
	2	1	5.58	5.62	
		2	5.72		
		3	5.56		
250	1	1	5.17	5.13	5.24
		2	5.18		
		3	5.04		
	2	1	5.37	5.35	
		2	5.32		
		3	5.36		
350	1	1	3.90	3.86	3.74
		2	3.82		
		3	3.86		
	2	1	3.55	3.62	
		2	3.68		
		3	3.63		

APPENDIX B

Summarize table of XS content of PP analyzed by gravimetric method

Table B-1 Data of XS content of PP catalyzed by crude, reflux and decant catalysts analyzed by gravimetric method

Catalyst	Sample no.	wt. sample (g)	wt. of soluble fraction (g)	% XS	AVE XS (%wt.)
Crude	1	2.0574	0.0996	4.84	4.8
Reflux	1	2.1286	0.0622	2.92	2.8
	2	2.2098	0.0572	2.59	
	3	2.1978	0.0618	2.81	
100-2	1	2.3221	0.0512	2.20	2.2
	2	2.0492	0.0471	2.30	
	3	2.1533	0.0461	2.14	
110-2	1	2.0449	0.0431	2.11	2.1
	2	2.0843	0.0447	2.14	
	3	2.1325	0.0466	2.19	
120-2	1	2.1738	0.0529	2.44	2.2
	2	2.2197	0.0466	2.10	
	3	2.0465	0.0443	2.17	

Table B-2 Data of XS content of PP catalyzed by D110-2 catalyst with different external donor analyzed by gravimetric method

External donor	Sample no.	wt. sample (g)	wt. of soluble fraction (g)	% XS	AVE XS (%wt.)
B donor	1	2.0449	0.0431	2.11	2.1
	2	2.0843	0.0447	2.14	
	3	2.1325	0.0466	2.19	
C donor	1	2.0449	0.0906	4.43	4.5
	2	2.0843	0.0970	4.66	
	3	2.1325	0.0957	4.49	
D donor	1	2.1738	0.0355	1.63	1.5
	2	2.2197	0.0330	1.49	
	3	2.0465	0.0302	1.48	

Table B-3 Data of XS content of PP catalyzed by D110-2 catalyst with varying C-donor/Ti ratio analyzed by gravimetric method

C-donor/Ti ratio	Sample no.	wt. sample (g)	wt. of soluble fraction (g)	% XS	AVE XS (%wt.)
1	1	2.1271	0.1328	6.24	5.61
	2	2.0935	0.1041	4.97	
2	1	2.0812	0.0810	3.89	3.72
	2	2.1116	0.0751	3.55	
5	1	2.0983	0.0580	2.76	2.89
	2	2.2321	0.0674	3.02	
10	1	1.9894	0.0357	1.80	1.68
	2	2.1328	0.0334	1.56	
15	1	2.4772	0.0315	1.27	1.08
	2	2.1548	0.0192	0.89	
20	1	2.1832	0.0187	0.86	0.79
	2	2.2088	0.0161	0.73	

Table B-4 Data of XS content of PP catalyzed by D110-2 catalyst with varying decant time analyzed by gravimetric method

Decant time (min)	Sample no.	wt. sample (g)	wt. of soluble fraction (g)	% XS	AVE XS (%wt.)
30	1	2.0177	0.1154	5.72	5.64
	2	2.2112	0.1229	5.56	
60	1	2.1486	0.0692	3.22	3.03
	2	2.2015	0.0625	2.84	
90	1	2.3217	0.0833	3.59	3.68
	2	2.0854	0.0786	3.77	

Table B-5 Data of XS content of PP catalyzed by D110-2 catalyst with varying decant cycle analyzed by gravimetric method

No. of cycle	Sample no.	wt. sample (g)	wt. of soluble fraction (g)	% XS	AVE XS (%wt.)
1	1	2.2594	0.1252	5.54	5.49
	2	2.2241	0.1210	5.44	
2	1	2.1486	0.0692	3.22	3.03
	2	2.2015	0.0625	2.84	
3	1	2.0287	0.0461	2.27	2.23
	2	2.1012	0.0460	2.19	

Table B-6 Data of XS content of PP catalyzed by D110-2 catalyst with varying volume solvent analyzed by gravimetric method.

Volume solvent (ml)	Sample no.	wt. sample (g)	wt. of soluble fraction (g)	% XS	AVE XS (%wt.)
150	1	2.2881	0.0979	4.28	4.37
	2	2.2756	0.1015	4.46	
250	1	2.1486	0.0692	3.22	3.03
	2	2.2015	0.0625	2.84	
350	1	2.0949	0.0737	3.52	3.38
	2	2.1548	0.0698	3.24	

Summarize table of %crystallinity of PP analyzed by DSC

Table B-7 Data of % crystallinity of PP catalyzed by crude, reflux and decant catalysts analyzed by DSC

Catalyst	Sample no.	% Crystallinity	% Crystallinity (AVE)
crude	1	46.8	46.8
Reflux	1	48.2	46.9
	2	47.7	
	3	44.7	
100-2	1	44.9	47.4
	2	49.2	
	3	48.0	
110-2	1	45.8	47.5
	2	49.0	
	3	47.8	
120-2	1	47.5	47.8
	2	47.6	
	3	48.2	

Table B-8 Data of % crystallinity of PP catalyzed by D110-2 catalyst with different external donor analyzed by DSC

Sample	Sample no.	% Crystallinity	% Crystallinity (AVE)
B-donor	1	45.8	47.5
	2	49.0	
	3	47.8	
C-donor	1	45.2	45.2
	2	44.2	
	3	46.3	
D-Donor	1	47.5	47.8
	2	48.6	
	3	47.2	

Table B-9 Data of % crystallinity of PP catalyzed by D110-2 catalyst with varying C-donor/Ti ratio analyzed by DSC

C-donor/Ti ratio	Sample no.	% Crystallinity	% Crystallinity (AVE)
1	1	44.7	43.7
	2	42.7	
2	1	45.6	45.1
	2	44.5	
5	1	44.8	45.4
	2	45.9	
10	1	46.3	46.5
	2	46.6	
15	1	46.9	47.8
	2	48.7	
20	1	47.3	47.5
	2	47.6	

Table B-10 Data of %crystallinity of PP catalyzed by D110-2 catalyst with varying decant time analyzed by DSC

Decant time (min)	Sample no.	% Crystallinity	% Crystallinity (AVE)
30	1	45.3	44.7
	2	44.1	
60	1	44.9	45.7
	2	46.5	
90	1	44.6	44.4
	2	44.1	

Table B-11 Data of %crystallinity of PP catalyzed by D110-2 catalyst with varying decant cycle analyzed by DSC

No. of cycle	Sample no.	% Crystallinity	% Crystallinity (AVE)
1	1	45.2	45.1
	2	45.0	
2	1	44.9	45.7
	2	46.5	
3	1	49.1	48.7
	2	48.3	

Table B-12 Data of % crystallinity of PP catalyzed by D110-2 catalyst with varying volume solvent analyzed by DSC

Volume solvent (ml)	Sample no.	% Crystallinity	% Crystallinity (AVE)
150	1	45.1	45.1
	2	45.1	
250	1	44.9	45.7
	2	46.5	
350	1	44.9	45.3
	2	45.7	

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Summarize table of I.I (Isotactic Index) of PP analyzed by FTIR

Table B-13 Data of I.I of PP catalyzed by crude, reflux and decant catalysts analyzed by FTIR

Catalyst	Sample no.	I.I	AVE I.I
crude	1	0.91	0.91
Reflux	1	0.93	0.91
	2	0.90	
	3	0.91	
100-2	1	0.91	0.91
	2	0.90	
	3	0.92	
110-2	1	0.94	0.92
	2	0.90	
	3	0.92	
120-2	1	0.92	0.91
	2	0.89	
	3	0.92	

Table B-14 Data of I.I of PP catalyzed by D110-2 catalyst with different external donor analyzed by FTIR

Sample	Sample no.	I.I	AVE I.I
Crude	1	0.91	0.91
B donor	1	0.94	0.92
	2	0.90	
	3	0.92	
C-donor	1	0.89	0.88
	2	0.88	
	3	0.88	

Table B-15 Data of I.I of PP catalyzed by D110-2 catalyst with varying C-donor/Ti ratio analyzed by DSC

C-donor/Ti ratio	Sample no.	I.I	AVE I.I
1	1	0.91	0.92
	2	0.92	
2	1	0.90	0.90
	2	0.89	
5	1	0.92	0.93
	2	0.94	
10	1	0.93	0.94
	2	0.94	
15	1	0.90	0.92
	2	0.93	
20	1	0.92	0.92
	2	0.93	

APPENDIX C

Summarize table of propylene polymerization at pressure 28 bar, Temperature 70°C

Table C-1 Data of polymerization of propylene catalyzed by crude, reflux and decant catalysts

Catalyst	Sample no.	wt. cat (mg)	%Ti	mmol Ti	mmol TEA	mmol ED	Productivity (g PP/g cat)	AVE (g PP/g cat)
crude	1	114.7	7.19	0.172	34.458	0.345	7,751	7,751
Reflux	1	95.9	4.25	0.085	17.029	0.17	22,158	22,008
	2	101.1	4.10	0.087	17.319	0.173	20,138	
	3	99.8	4.04	0.084	16.880	0.169	23,727	
D100-2	1	107	5.04	0.113	22.532	0.225	18,963	17,485
	2	107.3	4.64	0.104	20.802	0.208	16,608	
	3	100.4	4.55	0.095	19.087	0.191	16,885	
D110-2	1	99.2	4.15	0.086	17.201	0.172	19,049	18,867
	2	103.4	4.32	0.093	18.664	0.187	18,922	
	3	102.7	4.48	0.096	19.224	0.192	18,630	
D120-2	1	99.4	4.08	0.085	16.945	0.169	18,032	17,904
	2	94.4	4.24	0.084	16.724	0.167	17,712	
	3	94.7	4.05	0.080	16.025	0.160	17,968	

Polymerization: TEA:Ti=200, ED/Ti=2

TEA concentration 0.332 mol/l, ED concentration=19.7 %wt.

Table C-2 Data of polymerization of propylene catalyzed by D110-2 catalyst with different external donor

Sample	Test no.	Wt. cat (mg)	%Ti	mmol Ti	mmol TEA	mmol Silane	Productivity (g PP/g cat)	AVE (g PP/g cat)
B-donor	1	99.2	4.15	0.086	17.201	0.172	18,607	18,867
	2	103.4	4.32	0.093	18.664	0.187	18,487	
	3	102.7	4.48	0.096	19.224	0.192	19,506	
C-donor	1	100.2	4.15	0.087	17.374	0.174	18,638	19,004
	2	96.7	4.32	0.087	17.454	0.175	19,372	
	3	97.6	4.48	0.091	18.269	0.183	19,003	
D-donor	1	96.9	4.15	0.084	16.802	0.168	21,116	20,785
	2	99.0	4.32	0.089	17.870	0.179	20,456	
	3	99.8	4.48	0.093	18.681	0.187	20,784	

Polymerization: TEA:Ti=200, ED/Ti=2

Sample B-donor: TEA concentration 0.332 mol/l, ED concentration=19.7 %wt.

Sample C-donor and D-donor: TEA concentration 0.332 mol/l, ED concentration=2.5 %wt.

Table C-3 Data of polymerization of propylene catalyzed by D110-2 catalyst with varying C-donor/Ti ratio

C-donor/Ti ratio	Test no.	wt. cat (mg)	%Ti	mmol Ti	mmol TEA	mmol Silane	productivity (g PP/g cat)	AVE (g PP/g cat)
1	1	98.2	4.20	0.086	17.233	0.086	21,990	22,409
	2	101.7	4.20	0.089	17.847	0.089	22,828	
2	1	99.4	4.20	0.087	17.443	0.174	23,174	23,254
	2	98.5	4.20	0.086	17.285	0.173	23,335	
5	1	107.6	4.20	0.094	18.882	0.472	23,848	24,141
	2	103.4	4.20	0.091	18.145	0.454	24,434	
10	1	99.3	4.20	0.087	17.426	0.871	19,658	19,460
	2	97.8	4.20	0.086	17.263	0.858	19,263	
15	1	104.3	4.20	0.092	18.303	1.373	19,217	19,021
	2	101.8	4.20	0.089	17.864	1.340	18,825	
20	1	99.1	4.20	0.087	17.391	1.739	19,936	19,811
	2	98.7	4.20	0.087	17.320	1.732	19,686	

Polymerization: TEA:Ti=200, ED/Ti= 1 up to 20

TEA concentration 0.309 mol/l, ED concentration=2.5 %wt.

Table C-4 Data of polymerization of propylene catalyzed by D110-2 catalyst with varying decant time

| Decant time (min)	Test no.	wt. cat (mg)	%Ti	mmol Ti	mmol TEA	mmol Silane	Productivity (g PP/g cat)	AVE (g PP/g cat)
30	1	110.4	4.58	0.106	21.127	0.211	16,344	15,488
	2	108.2	4.80	0.109	21.700	0.217	14,632	
60	1	97.5	4.08	0.083	16.621	0.166	22,293	22,067
	2	98.5	3.80	0.078	15.639	0.156	21,841	
90	1	101.4	4.11	0.087	17.413	0.174	22,068	21,687
	2	103.6	4.37	0.095	18.916	0.189	21,306	

Polymerization: TEA:Ti=200, ED/Ti=2

Sample B-donor: TEA concentration 0.304 mol/l, ED concentration=19.7 %wt.

Table C-5 Data of polymerization of propylene catalyzed by D110-2 catalyst with varying decant cycle

No. of cycle	Test no.	wt. cat (mg)	%Ti	mmol Ti	mmol TEA	mmol Silane	productivity (g PP/g cat)	AVE (g PP/g cat)
1	1	98.3	5.41	0.111	22.220	0.222	14,135	13,895
	2	93.7	5.51	0.108	21.572	0.216	13,655	
2	1	97.5	4.08	0.083	16.621	0.166	22,293	22,067
	2	98.5	3.80	0.078	15.639	0.156	21,841	
3	1	103.7	4.13	0.089	17.895	0.179	18,296	17,909
	2	99.2	4.05	0.084	16.787	0.168	17,522	

Polymerization: TEA:Ti=200, ED/Ti=2

Sample B-donor: TEA concentration 0.304 mol/l, ED concentration=19.7 %wt.

Table C-6 Data of polymerization of propylene catalyzed by D110-2 catalyst with varying volume solvent

Volume solvent (ml)	Test no.	wt. cat (mg)	%Ti	mmol Ti	mmol TEA	mmol Silane	productivity (g PP/g cat)	AVE (g PP/g cat)
150	1	102.4	4.98	0.107	17.328	0.173	16,312	15,879
	2	107.7	5.10	0.115	22.950	0.229	15,446	
250	1	97.5	4.08	0.083	16.621	0.166	22,293	22,067
	2	98.5	3.80	0.078	15.639	0.156	21,841	
350	1	98.6	4.62	0.095	19.033	0.19	17,985	18,690
	2	101.5	4.46	0.095	18.914	0.189	19,395	

Polymerization: TEA:Ti=200, ED/Ti=2

Sample B-donor: TEA concentration 0.304 mol/l, ED concentration=19.7 %wt.
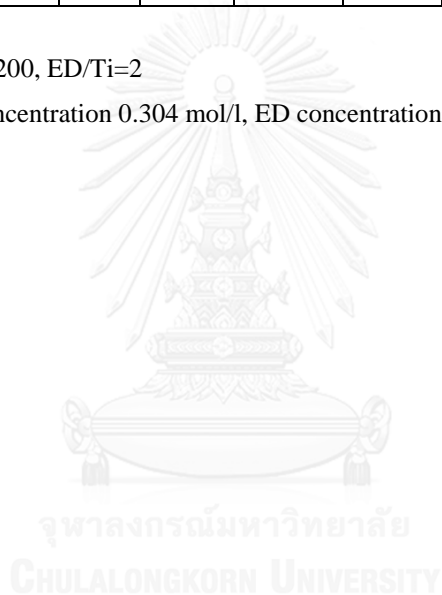
APPENDIX D
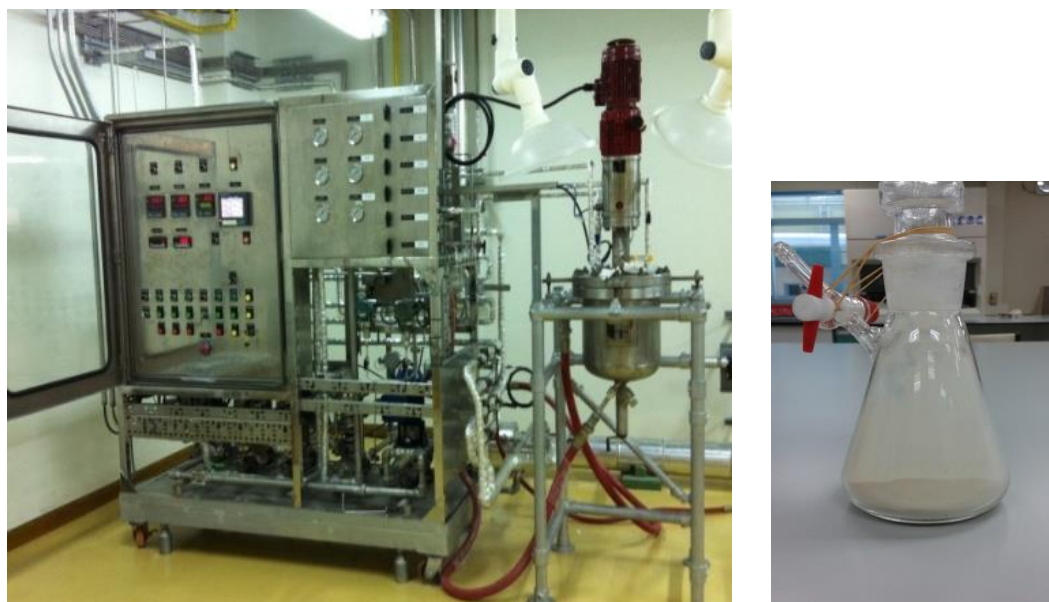
Figure D-1 Test polymerization unit 20 Liter reactor with control system**.**

Set point condition of polymerization: Reactor: Temp 70 $^\circ$C, Pressure 28 bar

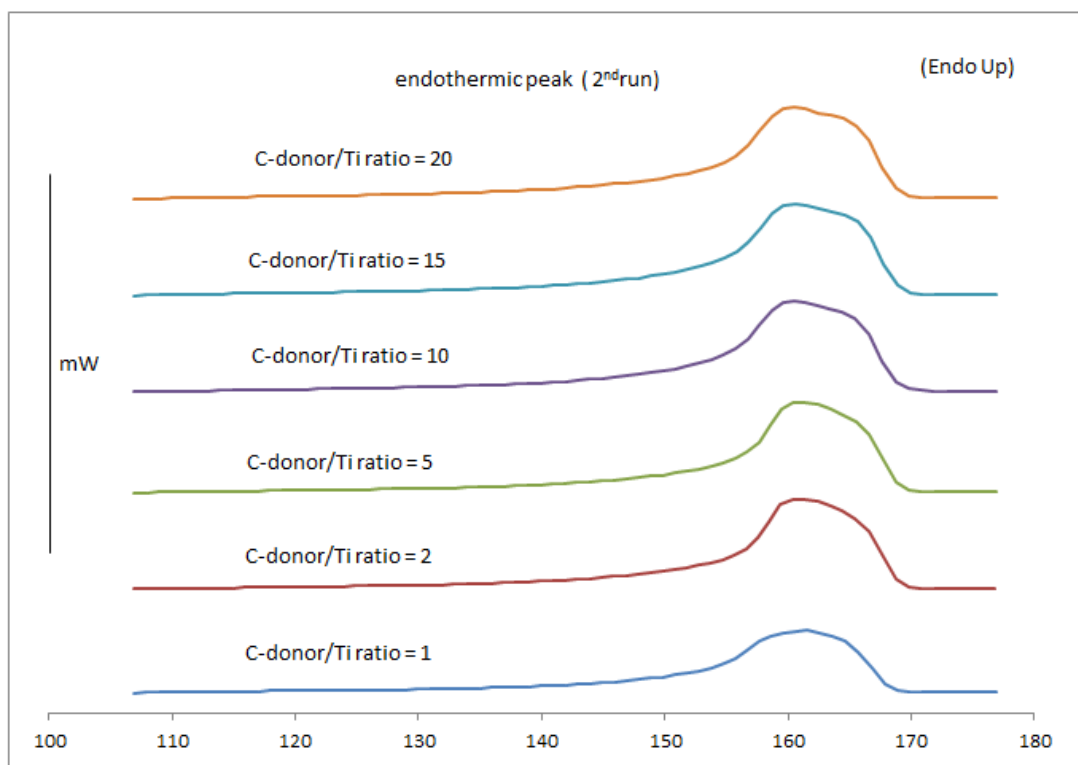Speed agitator 350 rpm.

Test period 90 min

Figure D-2 Endothermic peak overlay of PP polymerized with varying C-donor/Ti ratios analyzed by DCS. Peak area represent to % crystallinity of PP, large peak area is high crystallinity PP.
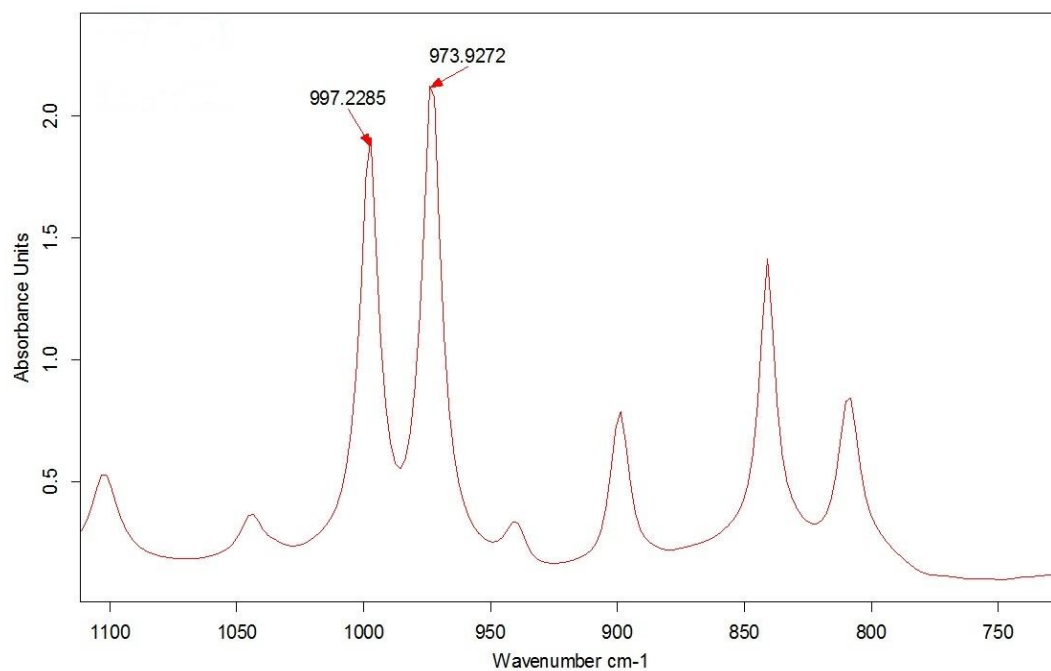
Figure D-3 Spectrum of PP analyzed by FTIR.

Isotactic Index (I.I) was through the relation between the absorbance ratio (A999 / A973).with equation:

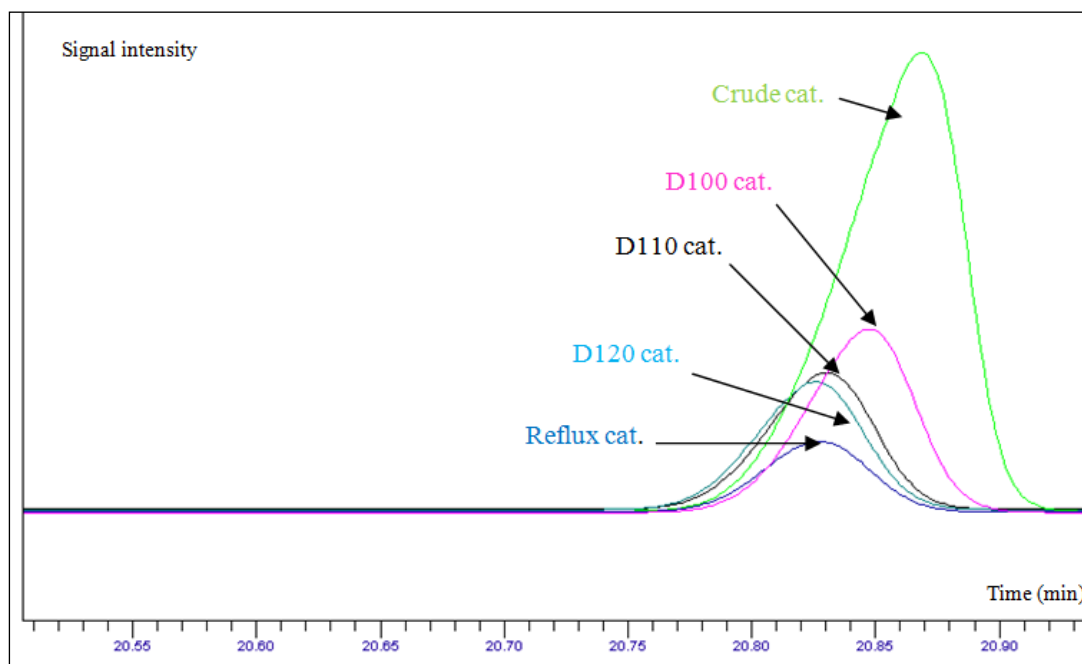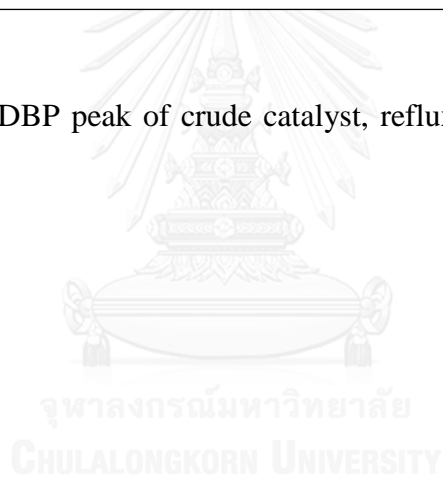$$\frac{A998}{A973} = 1.08 \, (I.I) - 0.15$$

Figure D-4 Overlay DBP peak of crude catalyst, reflux catalyst and decant catalyst analyzed by GC.

VITA

Surachai Surasompop was born on Sep 15, 1973 in Rayong, Thailand. He received a Bachelor Degree of Science in Chemistry from Kasetsart University in March, 1997. He has joined the IRPC Public Co., Ltd. as a chemist in Analytical lab and Equipment Division since July, 1997. He pursued a postgraduate study in the Master Degree Program in Petrochemistry and Polymer Science, Faculty of Science, Chulalongkorn University in 2011-2015.

Presentations at the national conference

2014 "Effect of electron donors and extraction on Ziegler-Natta catalyst preparation for propylene polymerization", March 20-21, 2014, The 4th Polymer Conference of Thailand, Bangkok, Thailand.