CHAPTER II

LITERATURE REVIEW

The discovery of Ziegler-Natta catalyst in the early 1950's gave rise to a great deal of interest from both academic and industrial laboratories.Since the Ziegler-Natta catalyst was applied to propylene polymerization[14,15], the problem about the production of isospecific polymer has become widely interested. Most of the researches tried to approach this problem by using electron donors as the third component in polymerization reaction[4-13]. This thesis will further study in this area. Due to a wide spectrum of the Ziegler-Natta catalyst , it was very difficult to handle a summarization of all investigations here. Survey of the literatures in this review will limit to the brief history of Ziegler-Natta catalyst , the use of support and the research about the effect of both internal and external electron donors to improve stereospecificity of Ziegler-Natta catalyst in propylene polymerization.

In 1953 Ziegler [2,3] demonstrated the linear polyethylene could be obtained by using a combination of triethylaluminum and titanium tetrachloride. A year later, Natta [14,15] succeeded in using the same type of catalyst to prepare polypropylene . These catalysts were then later named Ziegler-Natta catalyst. These discoveries provoked a worldwide research and development effort that culminated in many new commercial plastics .

In 1955 Vandenberg at Hercules[16] and Ettore and Luciano at Montecatini [17] applied for patents which disclosed that molecular hydrogen acted as a true transfer agent for the Ziegler-Natta catalysts. This was a very important discovery because many of the Ziegler-Natta catalysts produced polymers with molecular weights too high for facile processing and certain product applications. The desired molecular weight was easily obtained in the presence of hydrogen.

Natta [18] determined the number of active centres in the catalyst systems, α-$TiCl_3$-$AlEt_3$ and α-$TiCl_3$-$AlEt_2Cl$, which were utilized for the polymerization of propylene. The α-$TiCl_3$ was in the powdered form and the aluminum alkyls contained radioactive C^{14}. Being treated with aluminum alkyls, complex formation occured on the surface of α-$TiCl_3$ which was at least partially irreversible. An evidence was that the $TiCl_3$ so obtained liberated C_2H_4 and C_2H_6 upon treatment with acids. The degree of reversibility was found to depend upon the temperature at which adsorption of aluminum alkyl was allowed to occur. Below 60°C, the number of alkyl (ethyl) groups found in the polymer was lower than the total number of ethyl groups adsorbed on the $TiCl_3$ (as measured by gas evolution). However, at 70°C and above, the number of ethyl groups in the polymer corresponded closely to the total number adsorbed on the $TiCl_3$ and it was therefore assumed that at 70°C and above the ethyl groups found in the polymer correspond to the number of active sites initially present on the $TiCl_3$ surface.

For the α-$TiCl_3$-$AlEt_2Cl$ system at 70° C, the number of active centres was found to be less than a value of 1% mole of $TiCl_3$ that found for the α-$TiCl_3$-$AlEt_3$ system. This result could explain the lower catalyst activity for the former system. From the number of active centres and the overall polymerization rate, the mean growth rate of the chain on each active centre could be estimated. It was also found that there was unequal activity of the various surface sites. This should lead to a broad molecular weight distribution and a mixture of atactic and tactic polymers.

Tepenitsyna and co-workers [19] had discussed stereoregular polymerization initiated by $AlEt_3$-$TiCl_4$. The interaction of these components led to an alkyltitanium halide of lower valency which was insoluble in hydrocarbons and which was capable of adsorbing the alkyls of certain metals with small ionic radius, e.g. Al, Zn, Be, Li, etc. to form unstable surface complexes with them. It was found that upon interaction of these components, the obtained solid phase consisted essentially of titanium and chlorine while the liquid phase the contained essentially of aluminium and chlorine. Neither the precipitate nor the liquid phase in itself promoted polymerization of $TiCl_4$ to the liquid phase caused active catalysts to result again. This was additional evidence that Ziegler-Natta catalysts were unstable surface complexes which resulted from the addition of AlR_3 to titanium halide.

Bier and co-workers [20,21] investigated the preparation of a Ziegler-Natta type of catalyst which behaved in a manner different from that of a usual Natta catalyst. In the past time, Natta [22] prepared $TiCl_3$ by treatment of $TiCl_4$ with aluminium or aluminium compounds under specific conditions (The specific conditions employed were not disclosed.). The resulting catalyst gave macromolecules with a longer growth period than obtained with Natta-type catalysts. This resulted in a polymer of much higher molecular weight than that obtained by Natta. The longer life was attributed to the occurrence of fewer chain transfer processes than that for the Natta catalyst.

Catalyst composition strongly influences the broadness of the molecular weight distribution. Davis and Tobias [23] found that in propylene polymerization catalyst systems based on $TiCl_3$ yielded polymers with Mw/Mn ratios about twice as high as those found for polymers obtained under corresponding conditions with catalyst system based on VCl_3. Hirooka et al.[24] investigated different additives, such as amines and sulfer compounds, with respect to their influence on the molecular weight distribution of polypropylene. From experimental results it was concluded that as long as the same combination of organometallic compound and transition metal halide was used, the Mw/Mn value of the polymers remained unchanged. In ethylene polymerization it was reported by Wesslau [25] that somewhat narrower molecular weight distributions could be obtained if some of the halogen atoms of the catalyst components were replacesd by alkoxy groups.

Arlman and co-workers [26] studied the composition and the magnetic susceptibility of the violet and brown forms of $TiCl_3$ which were prepared from $AlEt_3$ and $TiCl_4$ at an Ti/Al ratio of 183 at 70 and 80°C, respectively. They found that these precipitates did not consist of $TiCl_3$ alone but also contained aluminium atom, one titanium ion in six was replaced by aluminium, and a small percentage of the chlorine was substituted by ethyl. The magnetic susceptibility study showed the different behavior between the brown β-$TiCl_3$ and violet α-$TiCl_3$ while chemical analysis showed almost the same composition for the two forms. The γ form of $TiCl_3$ was also studied; the similarity of the magnetic behavior and chemical analysis to the α form was expectable. These results showed the different in structural and physical properties between the brown and the violet forms of $TiCl_3$.

Boor [27] investigated the effects of the addition of compound containing lone-pair electrons to a given catalyst on isotacticity, polymerization rate, and molecular weight. Addition of Et_3N to a $ZnEt_2$-$TiCl_3$-based increased propylene polymerization activity. At the same time the isotacticity of the polymer increased. The author claimed that there existed isolated reaction sites on the surface of the $TiCl_3$ crystals which showed different capacities to coordinate electron donor compounds such as amines and olefins. Only exposed titaniums along the edges of the crystals favored stereospecific growth. The sites that were complexed most readily during the initial addition of amine had the fewest steric requirements. When they were complexed with amines they were dead and the net steric purity of the polymer rised while the overall activity of the catalysts fell.

A maximum value for the dependence of the catalyst activity on Al/Ti ratio was found by Schnecko et al.[28] employing an $AlEt_3$-$TiCl_4$ system. The catalyst activity was expressed by the volume of ethylene consumed in one hour. The Al/Ti ratio at which the maximum activity occured decreased as the polymerization temperature was increased. Another alkylating agent, ethylaluminum dichloride, was investigated to show no maximum resulting from no reduction of titanium beyond its trivalent state and the same type of the resulting curve as obtained by direct use of $TiCl_3$. This result strongly indicated that the lower activity was caused by the reduction of the titanium beyond its optimum valence state at higher Al/Ti ratios, an effect that was emphasized at higher reaction temperatures.

A series attempts were made to support the $TiCl_4$ on different carrier materials. The first attempt was made with the classical large-surface supports used in heterogeneous catalysis, i.e. SiO_2 [29] or $MgCl_2$ [30]. However no significant success was obtained along these until activated $MgCl_2$ was used as support [31-34].

Floyd et al. [35] studied the polymerization rate behavior of the growing polymer of ethylene and propylene in slurry process. The degree of mass transfer limitation in Ziegler-Natta system was dependent on both the catalyst particle size and the size of primary crystallites. The significant concentration gradients in the macroparticles existed at short time in slurry polymerization, even for catalysts of relatively low activity. For large particles of high activity catalyst, intraparticle mass transfer resistance could be rate limiting over longer periods. The rate limitation resulted from mass transfer of both cocatalyst and monomer.

The use of supports in the heterogeneous catalysis was well understood by 1950 and was highlighted by the discovery in 1958 by Hogan and Banks [36] of highly active chromium trioxide catalysts supported on silica which could polymerize ethylene under mild conditions of temperature and pressure to produce predominantly linear, high density polyethylene. At about the same time Natta and co-workers [18] demonstrated that only a small percentage of the titanium atoms (<1%mol.) in first generation α-$TiCl_3$ / $AlEt_2Cl$ catalysts was active. It was evident that higher catalyst activities were likely to be achieved through the use of transition metal compounds supported on appropriate matrices. Over the years a wide range of supported catalysts have been successfully developed and used for the commercial production of polyethylene, and more recently of polypropylene also.

"Activated" $MgCl_2$, a key ingredient of these catalyst systems, has been known for some time, being mentioned by Bryce-Smith [37] in 1959, and described by Kaminski [38] in 1967. A number of preparation methods are available and include; (i) treatment of $MgCl_2$ with activating agents such as electron donors; (ii) ballmilling $MgCl_2$; and (iii) reaction of compounds such

Grignard reagents with chlorinating agents. All three procedures have been found useful in catalyst preparation for olefin polymerization.

Some of the most promising catalysts, especially for propylene polymerization, have resulted from the use of magnesium chloride as supports. An early patent in 1960 described the use of ground $MgCl_2$ with electron donors in propylene polymerization . However, it was the discoveries by Montecatini-Edison Co. [4] and Mitsui Petrochemicals Ind.[5] that catalysts, prepared from $MgCl_2$, $TiCl_4$ and electron donors and activated by a mixture of trialkylaluminum and an electron donor, could polymerize propylene with a high yield [>50kg $PP(gTi)^{-1}$] and with good sterospecificity (isotactic index >90%), that have set the scene for much of the present explosion in catalyst development.

Doi[39] studied the influence of metal chloride supports on polymerization activity in the polymer[illegible]tion of propylene with the soluble $Ti(OC_4H_9)_4/Al(C_2H_5)_2Cl/MCl_x$ catalyst system. The polymerization activity was in the order :

$CoCl_2>MgCl_2>MnCl_2>NiCl_2>TiCl_3>FeCl_2>HfCl_4>CuCl_2\text{-}AlCl_3\text{-}GaCl_3\text{-}NbCl_5\text{-}TaCl_5>ZrCl_4$

. Yoon el al. [40] investigated ethylene-propylene copolymerizations by using conventional and high activity supported Ziegler-Natta catalysts to examine the reduction of Ti(III) to Ti(II) by aluminium alkyls, which has been considered as amain reason for the catalytic activity decay in propylene polymerization. For the catalyst system cocatalyzed with DEAC, the reduction was neligible regardless of the catalyst types while an irreversible catalyst modification such as the reduction reaction occured significantly for the catalyst with $AlEt_3$.

Both the homopolymerization of ethylene, propylene, 1-hexene and 1,3-butadiene and the copolymerization of ethylene with these monomers were conducted over the SiO_2-supported $TiCl_4$ catalyst using $AlEt_2Cl$ or $AlEt_3$ as a reducing reagent [41]. With an increase in the concentration of $AlEt_3$, the polymerization activities except for ethylene markedly decreased and the strucures of the copolymers drastically changed to polyethylene. A relation was established between the oxidation states of titinium and the polymerization activities.

Chien and Hu [6] studied the functions of external lewis base , methyl-p-toluate, MPT for catalyst system, $MgCl_2/EB/PC/AlEt_3/TiCl_4$ - $AlEt_3/MPT$ (EB was ethylbenzoate and PC was p-cresol) . They found that the action of external Lewis base was highly stereospecific. The isotacticity index of polypropylene was >95% in the presence of external electron donor but <68% without it .

Sacchi and co-workers [7] studied the effect of Et_3N and 2,2,6,6-tetramethyl-piperidine (TMPip) as donor additive on the catalyst $MgCl_2/TiCl_4/AlEt_3$, δ-$TiCl_3/AlEt_3$ and δ-$TiCl_3/ZnEt_2$ for propylene polymerization. They found that amines exerted at least two different and concurrent effects (i) poisoning of both the isotactic and the atactic sites ; (ii) activation of isotactic sites.

The former effect is due to the interaction between the uncomplexed base and active sites on the heterogeneous catalytic surface, the selection of the process depending on the steric hindrance of the base. The latter effect is connected with the presence in solution of the sufficient base-alkyl metal complex. Also the extent of the activation depends on the structure of the base.

Kashiwa, Yoshitake and Toyota [8] studied the polypropylene produced by highly active $MgCl_2$ supported $TiCl_4$ in conjunction with Et_3Al and ethylbenzoate (EB). The obtained polypropylene sample was separated into four fractions by successive extraction with pentane, heptane and trichloroethylene(trichlene). Yield, M_n, T_m and microtacticity of each fraction were determined,
and the effects of the concentration of EB on these items of results were investigated. It has been found that EB enhances yield, M_n and stereospecificity of trichlene insoluble (the most stereospecific) fraction, and in contrast, it decreases rapidly yields of other three fractions without changing the character of the polymers.

Sugano [9] has found that the electron donor compound, diphenyl dimethoxymethane (DPDMM), is useful for the stereospecific polymerization of propylene. He studied the kinetic reaction of DPDMM with alkylaluminum, the reaction atmosphere influence on the reaction rate and the reaction products. The stereospecificity of polypropylene depends on the concentration of DPDMM .

Terano [10] applied t.g.-d.t.a. (thermalgravimetry differential thermal analysis) in combination with infrared (i.r.) spectroscopy to study the state of EB and $TiCl_4$ in $MgCl_2$-supported catalyst for propylene polymerization, and found that :

(i) $TiCl_4$-EB complex decomposes by grinding with $MgCl_2$, on which $TiCl_4$ and EB are supported independently.

(ii) $TiCl_4$ directly coordinated by EB can barely form active sites.

(iii) increase of activity with grinding time is caused by an increase in active sites.

Seppälä and Härkönen [11] used nineteen silane compounds of the structure $R_nSi(OR')_{4-n}$, where n = 1-4, R = C_6H_5, alkyl or H : R' = C_{1-3} alkyl as external donors. The effect of the external alkoxysilane donor on the polymerization strongly depended on the number and size of alkoxy groups and the size of hydrocarbon groups attached to the silicon atom. Two major effects were observed : selective deactivation of atactic active centers and the increased production of high-molecular-weight isotactic polypropylene. Evidently, at least on free non-hindered alkoxy group in the complex between alkoxysilane and $AlEt_3$ is required for the selective deactivation.

Kokta and Raj[12] correlated the interaction occuring between the catalytic components of a Ziegler-Natta stereospecific system formed by $TiCl_3$ and $AlEt_3$ in heptane and the polymerization process. Titanium trichloride was prepared by the reduction of titanium tetrachloride with hydrogen on tungsten spiral. The addition of electron donor (e.g. pyridine) to the catalyst system formed by non-activated $TiCl_3$ and $AlEt_3$ can either increase or inhibit the rate of polymerization.

Kokta and Raj [42] characterized the reaction between the catalytic components of a Ziegler-Natta stereospecific system formed by $TiCl_3$ and $AlEt_3$ in heptane by IR spectroscopy. The IR spectroscopy can be used to follow $AlEt_2Cl$ formation during the interactions of catalytic components in Ziegler-Natta catalytic system.

They had clarified that the formation and decay of the active centers are independent. The interaction of the catalyst components, influences the rate of polymerization. They also showed later that the rate of propylene polymerization is influenced by the rate of the interaction, activation energy, and the efficiency of interaction.[43]

Tasuya Miyatake et al.[13] studied the effect of phenyltrimethoxysilane (PTMS) as an external electron donor on the microtacticity distribution of the isotactic parts of polypropylene prepared with $MgCl_2$-supported Ti catalyst-$AlEt_3$ system by programmed temperature column fractionation (PTCF) technique. PTMS deactivated nonstereospecific and low isospecific sites and enhanced stereoregulating ability of highly isospecific sites.

Sacchi [44] used ^{13}C NMR to study the effect of the Lewis base on high yield supported Ziegler-Natta catalysts for isotactic propylene polymerization. They found that the roles of the internal base are as follows:

(i) The base, $MgCl_2$ and $TiCl_4$ formed a three-component complex, which was the real active center; thus the base had a direct function to catalyze.

(ii) The two-component complex $MgCl_2$-$TiCl_4$ was the true polymerization center; thus, the base had an indirect function, for instance, of controlling the titanium fixation on $MgCl_2$.

Coutinho and Santa Maria[45] studied the effect of di-n-butyl ether(DBE) in the synthesis of a highly active propylene polymerization catalyst. Electron-donors having ester and phosphate groups (ethyl benzoate-EB, diisobutyl phthalate-DIBP, tri-n-butyl phosphate-TBP) were added as second internal bases (IB_2) in the catalysts prepared by the reduction of TiCl4 with $AlClEt_2$ (DEAC) in the presence of DBE as a first internal base (IB_1). The crystalline forms were examined for all catalyst samples by X-ray method. β-$TiCl_3$ is brown with a fiber-shaped structure. α-, γ- and δ-$TiCl_3$ are violet with a lamellar structure. The catalyst system based on the β-modification of $TiCl_3$ and organoaluminium compounds exhibited low stereospecificity and activity in the propylene polymerization. The violet modifications based on $TiCl_3$, specially the δmodification, produced highly active and highly stereospecific catalyst systems for propylene polymerization.

Yang and Hsu [46] studied the effects of four different external Lewis bases namely ethylbenzoate (EB), dimethoxydiphenyl silane (DMDPS) , 2,2,6,6-tetramethylpiperidine (TMPip) and t-butylmethylether (TBME) on propylene polymerization using the $MgCl_2$ - supported $TiCl_4$ catalyst. The internal Lewis base used in this study was dioctylphthalate (POC). With ethyl benzoate as the external donor no change in activity was observed, but the interaction between ethyl benzoate and $MgCl_2$-phthaloyl chloride complex resulted in a decrease of isotacticity . Increasing the bulkiness of the external Lewis base hindered the monomer coordination. It was found that the relative amount of the phthaloyl chloride complex to other complexes played an important role in the formation of active sites.

San-Yun Lim et al. [47] studied the effect of an electron in propylene polymerization (in gas and slurry phase reactions each) by using the third generation Ziegler-Natta catalyst. The kinetic study suggested that the overall reaction rate was followed the second order. From the measurements of polymer physical properties, it was found that a new complex was formed with mixing of cocatalyst and electron donor, which converted atactic site to isotactic site. At this moment, the site transition path could be considered as "atactic site →low isotactic site → high isotactic site". It could be also thought that high isotactic site was formed over EB/Al = 0.03 in gas phase and EB/Al = 0.05 in slurry phase. These difference were considered to be a result of a difference in reaction type.

Alain Guyot et al.[48] studied the system comprising dibutyl phthalate which is a diester as an internal Lewis base and a silane which is phenyltriethoxysilane as an external Lewis base. High isotacticity was obtained with a low ratio Ai/Lewis base, the stereospecificity was stable with temperature and time. When dibutyl phthalate was used as an internal lewis base but an external lewis base was not phenyltriethoxysilane the activity and tacticity remain poor.

Kokka et.al. [49] claimed in U.S. Patent 4,952,649 about the process for producing olefin polymers and catalyst components used for polymerization. A solid titanium catalyst component of a catalyst system useful in the polymerization of olefins or copolymerization of two or more olefins or one or more olefins and a diene was prepared by contacting a liquid hydrocarbon solution of (I) a magnesium compound, such as magnesium chloride, with (ii) a liquid titanium compound, such as $TiCl_4$, or a solution of a titanium compound in a hydrocarbon solvent, to form a solid product. The solid product was formed in the presence of an electron donor. The polymerization or copolymerization of the olefin was carried out in the presence of the solid titanium catalyst and an organometallic compound of a group I to III metal and an organic silicon compound having an Si-O-C bond. Granulal or spherical polyethylene, polypropylene, etc. were produced in high yield, with good flowability, high bulk density, and narrow particle size distribution. The polymers can be produced over a wide range of melt index values without reduction in stereospecificity.