



## CHAPTER II

### LITERATURE REVIEW

As indicated in chapter I, many patents and scientific literatures were written to give attention to Ziegler-Natta polymerizations. The Ziegler-Natta catalyst is a mixture of a metal alkyl of base metal alkyl of groups I to III and a transition metal salt of metals of groups IV to VIII. Not all of the possible combinations are effective, and many of these combinations are active only for certain monomers or under certain conditions [4]. Due to a wide spectrum of the Ziegler-Natta catalyst, it was very difficult to include the conclusions of all investigations here. Survey of the literatures in this review will limit to the polymerization of lower  $\alpha$ -olefin with titanium-based Ziegler-Natta catalysts in order to show the relationship of catalyst nature to catalytic activity and property of the polymer.

The earliest work in this field was that of Hall and Nash [5] who found that a mixture of aluminium and aluminum chloride treated with ethylene produced alkylaluminum chloride and low molecular weight ethylene polymer. Next, Kraus [6] used a combination of metal alkyls and inorganic halide salts to produce low molecular weight polymers from  $\alpha$ -olefins such as 1-butene. A catalyst containing titanium chloride was firstly reported by Fisher [7] who used a combination of aluminium, aluminium chloride and titanium tetrachloride to prepare polyethylene.

In the early 1950's Ziegler [8] demonstrated that linear polyethylene could be obtained by using a combination of triethylaluminum and titanium tetrachloride, while Natta [9] succeeded in using the same type of catalyst to prepare polypropylene. Since that time significant advances in Ziegler-Natta polymerization of  $\alpha$ -olefin have been made.

In 1955 Vandenberg at Hercules[10] and Ettore and Luciano at Montecatini [11] 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.



Badin [12] worked with a similar catalyst system  $(i\text{-Bu})_3\text{Al-TiCl}_4$ , at atmospheric pressure and temperature between 10 and 70 °C to study the rate of polymerization of polyolefin. The polymerization rate change was found to be proportional to an increase in the concentration of either the aluminium compound or the titanium compound when one or the other component was held constant. The titanium compound exerted the most pronounced effect on the rate. With excess ethylene in the system, the rate of polymerization was found to remain constant for a short period of about 30 min.

Boocock and co-worker [13] attempted to study quantitatively the effect of mass transfer processes on the polymerization of ethylene. Particular attention was paid to the effect of catalyst concentration on the rate of polymerization under controlled stirring conditions. By using a conventional mass transfer treatment it was possible to predict a relationship of the following type :

$$\frac{1}{(\text{polymerization rate})} = \frac{(\text{constant})}{[\text{Ti}]C_0} + \frac{(\text{constant})}{XC_0}$$

where  $[\text{Ti}]$  is the concentration of  $\text{TiCl}_3$  catalyst and  $C_0$  is the equilibrium solubility of the ethylene in the reaction diluent;  $X$  represents the agitation factor and is taken as a constant at a particular level of stirring.

The polymerization of propylene with a catalyst system  $\text{TiCl}_3\text{-AlEt}_3$  was followed dilatometrically by Ambroz and Vesely[14], but these authors could not observe any adjustment period (or initial period in the rate of polymerization curve) for the rate of polymerization. A plot of  $\ln([m_0]/[m])$  versus time yielded a straight line from the very beginning of the polymerization. In the presence of basic impurities, agglomeration of the  $\text{TiCl}_3$  crystals occurred which was subdued by a slow complex formation between the impurity and the aluminum alkyl, accompanied by an increase in the polymerization rate. If a system containing basic impurities was heated sufficiently long with the aluminum alkyl prior to the addition of the  $\text{TiCl}_3$ , no adjustment period in the rate of polymerization was found.

Natta [15] determined the number of active centers in the catalyst systems,  $\alpha\text{-TiCl}_3\text{-AlEt}_3$  and  $\alpha\text{-TiCl}_3\text{-AlEt}_2\text{Cl}$ , which were utilized for the polymerization of propylene. The  $\alpha\text{-TiCl}_3$  was in a powdered form and the aluminum alkyls contained radioactive  $\text{C}^{14}$ . Being treated with aluminum alkyls, complex formation occurred on the surface of  $\alpha\text{-TiCl}_3$  which was at least partially irreversible. An evidence was that the  $\text{TiCl}_3$  so obtained liberated  $\text{C}_2\text{H}_4$  and  $\text{C}_2\text{H}_6$  upon treatment with acid. The degree of reversibility was found to depend upon the temperature at which adsorption of aluminum alkyl was allowed to occur. Below  $60^\circ\text{C}$ , the number of alkyl (ethyl) groups found in the polymer was lower than the total number of ethyl groups adsorbed on the  $\text{TiCl}_3$  (as measured by gas evolution). However, at  $70^\circ\text{C}$  and above, the number of ethyl groups in the polymer corresponded closely to the total number adsorbed on the  $\text{TiCl}_3$  and it was therefore assumed that at  $70^\circ\text{C}$  and above the ethyl groups found in the polymer correspond to the number of active sites initially present on the  $\text{TiCl}_3$  surface.

For the  $\alpha\text{-TiCl}_3\text{-AlEt}_2\text{Cl}$  system at  $70^\circ\text{C}$ , the number of active centers was found to be less than a value of 1% mole of  $\text{TiCl}_3$  that found for the  $\alpha\text{-TiCl}_3\text{-AlEt}_3$  system. This result could explain the lower catalyst activity for the former system. From the number of active centers and the overall polymerization rate, the mean growth rate of the chain on each active center 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.

Raha [16] estimated that only about 1% of the alkyl which remained as  $\text{AlR}_3$  after the reduction step were catalytically active, based on the changes in intrinsic viscosity with conversion for the system  $\text{AlR}_3\text{-TiCl}_4\text{-isoprene}$ . Provided that each active site contained only one titanium atom, the only 0.5% of the titanium participates in active complexes. From a good comparison between the theoretical calculated and experimental curve for the change in polymer viscosity with conversion, only very small fractions of the Ziegler-Natta components reacted were involved in effective catalysis.

Ludlum et al. [17] studied the polymerization of ethylene with catalyst systems based on  $\text{TiCl}_4$  and different alkylaluminum and alkyllithium compounds. The solvent employed was decalin, the main temperature investigated was  $100^\circ\text{C}$ . The rate of polymerization was found to decrease in nearly all cases from the



beginning of the reaction. The actual shape of the rate curves was not analyzed, but the decrease in rate was attributed to occlusion of catalyst sites by the polymer formed and not to a decrease in catalyst concentration. It was postulated that a true termination reaction was absent in this system and the polymerization reaction was catalytic. In order to compare different catalyst preparations, the volume of ethylene polymerized after two hours was chosen as a characteristic rate value. In the pressure range 1.0-1.5 atm, the rates were found to be proportional to the pressure. A first-order dependence of the rate was also observed with respect to the concentration of the transition metal. From the amount of ethane released in the reaction between  $\text{TiCl}_4$  and  $\text{AlEt}_3$ , the maximum catalytic activity corresponded to an average oxidation state of the titanium of about 2.5.

Tepenitsyna and co-workers [18] had discussed stereoregular polymerization initiated by  $\text{AlEt}_3\text{-TiCl}_4$ . 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 contained essentially aluminium and chlorine. Neither the precipitate nor the liquid phase in itself promoted polymerization of  $\text{TiCl}_4$  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  $\text{AlR}_3$  to titanium halide.

Havinga and Tan [19] used amylsodium as a reducing agent for  $\text{TiCl}_4$ . At ratios of Na/Ti below 1, practically no polymer was formed, but above this limiting ratio the amount of ethylene converted during 30 min. increased linearly with the catalyst ratio, the titanium concentration being kept constant. The constancy of the intrinsic viscosities of the polymers indicated that the nature of the catalyst sites was not changed. It was proposed that the active sites were formed by alkylation of the initially formed  $\text{TiCl}_3$  by the surplus amylsodium.

Bier and co-workers [20-22] 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 [23] prepared  $\text{TiCl}_3$  by treatment of  $\text{TiCl}_4$  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 [24] found that in propylene polymerization catalyst systems based on  $\text{TiCl}_3$  yielded polymers with  $M_w/M_n$  ratios about twice as high as those found for polymers obtained under corresponding conditions with catalyst system based on  $\text{VCl}_3$ . Hirooka et al. [21] investigated different additives, such as amines and sulfur 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  $M_w/M_n$  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 replaced by alkoxy groups.

Arlman and co-workers [26] studied the composition and the magnetic susceptibility of the violet and the brown forms of  $\text{TiCl}_3$  which were prepared from  $\text{AlEt}_3$  and  $\text{TiCl}_4$  at an Al/Ti ratio of 183 at 170 and 80 °C, respectively. They found that these precipitates did not consist of  $\text{TiCl}_3$  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  $\beta\text{-TiCl}_3$  and violet  $\alpha\text{-TiCl}_3$  while chemical analysis showed almost the same composition for the two forms. The  $\gamma$  form of  $\text{TiCl}_3$  was also studied; the similarity of the magnetic behavior and chemical analysis to the  $\alpha$  form was expectable. These results showed the different in structural and physical properties between the brown and violet forms of  $\text{TiCl}_3$ .

Korotkov and Tsun-Chan [27] studied changes in structure and catalytic properties of  $\text{TiCl}_3$  by thermal treatment. When  $\beta\text{-TiCl}_3$  was heated at 200 °C for 20 hr., a portion of the sample recrystallized into hexagonal plates of larger

dimensions. At 300°C for 2 hr. hexagonal prisms and small crystals, still larger than the original needle-like crystals, were formed. At 400°C, the resulting crystals were much larger and had a more regular structure. At still higher temperatures, disproportionation of the  $\text{TiCl}_3$  into  $\text{TiCl}_4$  and  $\text{TiCl}_2$  occurred. The X-ray diagrams indicated that thermally treated  $\beta\text{-TiCl}_3$  possessed the same structure as  $\alpha\text{-TiCl}_3$ . Polymerizations of propylene were carried out using thermally treated  $\beta\text{-TiCl}_3$  and  $\text{AlEt}_3$ . The content of isotactic structure increased with higher concentrations of  $\alpha\text{-TiCl}_3$ . The  $\text{TiCl}_3$  heated at 400° C was less effective because of its disproportionation into  $\text{TiCl}_2$ . The specific surface of  $\alpha\text{-TiCl}_3$  was found to be 1/10 to 1/20 that of  $\alpha\text{-TiCl}_3$  prepared by thermal treatment of  $\beta\text{-TiCl}_3$ , and therefore the catalytic activity of the latter should be greater. When lower temperatures were used to prepare  $\beta\text{-TiCl}_3$  (from  $\text{TiCl}_4 + \text{AlEt}_3$ ), the resulting crystals were more dispersed, had less regular structure, and the catalyst prepared from them possessed greater activity. It was found that the stereospecificity was not affected by the disperseness, but the specificity of  $\text{AlEt}_3$   $\beta\text{-TiCl}_3$  catalyst can be increased by treating the  $\beta\text{-TiCl}_3$  with  $\text{AlEt}_3$  solution.

Keii [28] studied the kinetics of the adjustment period until a steady rate of polymerization was reached. This period showed two adverse types of behaviors with respect to the change in the rate of polymerization : the decay type which was observed with ground  $\text{TiCl}_3$  catalyst ( $\leq 2$  microns) and the build-up type observed with unground catalyst (1-100 microns) . In his system the rates of propylene polymerization were studied at different temperatures and pressures as a function of the polymerization time. Analysis of these results led Keii to a kinetic expression for the adjustment period of Natta's propylene polymerization as follows :

$$\frac{dr}{dt} = -k(r-r_\infty)$$

where  $r$  and  $r_\infty$  denote the instantaneous and stationary rates of polymerization and  $k$  which denote the constant depends on the type of phenomenon occurring.

Boor [29] investigated the effects of the addition of compound containing lone-pair electrons to a given catalyst on isotacticity, polymerization rate, and molecular weight. Additions of  $\text{Et}_3\text{N}$  to a  $\text{ZnEt}_2\text{-TiCl}_3$ -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  $\text{TiCl}_3$  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. [30] employing an  $\text{AlEt}_3$ - $\text{TiCl}_4$  catalyst system. The catalyst activity was expressed by the volume of ethylene consumed in one hour. The Al/Ti ratio at which the maximum activity occurred 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  $\text{TiCl}_3$ . 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 which was emphasized at higher reaction temperatures.

A series of attempts were made to support the  $\text{TiCl}_4$  on different carrier materials. The first attempt was made with the classical large-surface supports used in heterogeneous catalysis, i.e.  $\text{SiO}_2$  [31] or  $\text{MgCl}_2$  [32]. However, no significant success was obtained along these until activated  $\text{MgCl}_2$  was used as support [33-36].

Ambroz et al. [37] demonstrated that in the presence of an excess of aluminum trialkyl, chlorine atoms were removed from the  $\text{TiCl}_3$  leaving a catalyst of changed composition and little activity. In this process the brown  $\beta$ -form or purple  $\gamma$ -form of  $\text{TiCl}_3$  visibly darken and tend to the brownish black color typical of the lower chloride of titanium. However, at lower temperatures the rate of chlorine abstraction was reduced, so that the fall in polymerization rate with time was not as marked.

Orzechowski [38] investigated the catalyst system  $\text{TiCl}_4$ - $\text{Al}(\text{i-Bu})_3$  and measured the activity of the catalyst by comparing the yields in polyethylene after

given polymerization times. The activity of a catalyst prepared at 50 °C at a Al/Ti ratio of 2.8 dropped to half of its value after aging for a few minutes and became very low after 30 minutes. The activity of the aged catalyst could not be restored by the addition of fresh aluminum alkyl, thus indicating that the catalyst surface had deteriorated irreversibly during aging. A possible explanation for the decreased activity could be the assumption of coagulation of catalyst particles whereby the available surface was decreased.

Boucher et al. [39] investigated the polymerization of ethylene using magnesium reduced titanium trichloride catalysts together with the usual aluminum alkyl activator. The activity constant of this type of catalyst was reported at 50°C and 1 atm pressure to be a value of  $3.4 \cdot 10^6 \text{ g dm}^3 (\text{mol TiCl}_3)^{-1} \text{ h}^{-1}$  which was  $10^2$  times larger than for a conventional aluminium reduced  $\text{TiCl}_3$ . On the other hand the viscosity-molecular weight-time (or conversion) relation was not very different from those given by conventional catalysts. Analysis of the result suggested that a high portion (e.g 50%) of the titanium atoms in the magnesium reduced  $\text{TiCl}_3$  played as active sites.

Balazs and co-worker [40] investigated an intermediate coordination complex,  $[\text{CH}_3\text{TiCl}_4(\text{C}_2\text{H}_4)]^{n=0,-2}$ , in Ziegler-Natta polymerization reaction in SCF-X $\alpha$ -SW molecular-orbital calculation to study a possible reaction path for Ziegler-Natta catalysis. A series of calculations for  $\text{CH}_3\text{TiCl}_4(\text{C}_2\text{H}_4)$  disagreed with the Cossee mechanism [ ] for the propagation step.

Doi studied [41] studied the influence of metal chlorides on polymerization activity in the polymerization of propylene with the soluble  $\text{Ti}(\text{OC}_4\text{H}_9)_4/\text{Al}(\text{C}_2\text{H}_5)_2\text{Cl}/\text{MCl}_x$  catalyst system. The enhanced polymerization activity decreased in the order :

$\text{CoCl}_2 > \text{MgCl}_2 > \text{MnCl}_2 > \text{NiCl}_2 > \text{TiCl}_3 > \text{FeCl}_2 > \text{HfCl}_4 > \text{CuCl}_2 - \text{AlCl}_3 - \text{GaCl}_3 - \text{NbCl}_5 - \text{TaCl}_5 > \text{ZrCl}_4$

Galvan and co-worker [42] developed a model and used to predict degree of polymerization and polydispersity, using concept from monomer mass transfer and multiplicity of sites. For the cases evaluated it was shown that the broad MWD was not due to restrictions in monomer availability but was a consequence of the presence of difference type of sites.



Reichert et al. [43] investigated the semicontinuous polymerization of ethylene in slurry with supported Ziegler-Natta catalyst to determine the kinetic parameter in the three phase system by applying the model of resistance in series mass transfer. The diffusion of ethylene within porous catalyst and polymer particles was indicated to play a certain role. Width in molecular weight distribution depended to some extent on cocatalyst and hydrogen concentration.

Floyd et al. [44] 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.

Yoon et al. [45] 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 aluminum alkyls, which has been considered as a main reason for the catalytic activity decay in propylene polymerization. For the catalyst system cocatalyzed with DEAC, the reduction was negligible regardless of the catalyst types while an irreversible catalyst modification such as the reduction reaction occurred significantly for the catalyst with  $\text{AlEt}_3$ .

Both the homopolymerization of ethylene, propylene, 1-hexene and 1,3-butadiene and the copolymerization of ethylene with these monomers were conducted over the  $\text{SiO}_2$ -supported  $\text{TiCl}_4$  catalyst using  $\text{AlEt}_2\text{Cl}$  or  $\text{AlEt}_3$  as a reducing reagent [46]. With an increase in the concentration of  $\text{AlEt}_3$ , the polymerization activities except for ethylene markedly decreased and the structures of the copolymers drastically changed to polyethylene. A relation was established between the oxidation states of titanium and the polymerization activities.

Sugano[47] had found that the ketal compound, diphenyl dimethoxymethane (DPDMM), was useful for the stereospecific polymerization of propylene. He studied the kinetic reaction of DPDMM with alkylaluminum. The reaction atmosphere influenced the reaction rate and the reaction products. The

stereospecificity of polypropylene depended on the concentration of DPDMM at that time.

Kokta and Raj [48] correlated the interaction occurring between the catalytic components of a Ziegler-Natta stereospecific system formed by  $\text{TiCl}_3$  and  $\text{AlEt}_3$  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  $\text{TiCl}_3$  and  $\text{AlEt}_3$  could either increase or inhibit the rate of polymerization

Kokta and Raj [49] characterized the interaction between the catalytic components of a Ziegler-Natta stereospecific system formed by  $\text{TiCl}_3$  and  $\text{AlEt}_3$  in heptane by IR spectroscopy. The IR spectroscopy can be used to follow  $\text{AlEt}_2\text{Cl}$  formation during the interaction of catalytic components in Ziegler-Natta catalytic system.

Kokta and Raj [50] had clarified that the formation and decay of the active centers were independent. The interaction of the catalyst components, influenced the rate of polymerization. They had also showed that the rate of propylene polymerization was influenced by the rate of the interaction, activation energy, and the efficiency of interaction[51].

Tasuya Miyatake et al. [52] studied the effect of phenyltrimethoxysilane (PTMS) as an external electron donor on the microtacticity distribution of the isotactic parts of polypropylene prepared with  $\text{MgCl}_2$ -supported Ti catalyst- $\text{AlEt}_3$  system by programmed temperature column fractionation (PTCF) technique. PTMS deactivated nonstereospecific and low isospecific sites and enhanced stereoregulating ability of highly isospecific sites.

Coutinho and Maria [53] 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 base ( $\text{IB}_2$ ) in the catalysts prepared by the reduction of  $\text{TiCl}_4$  with  $\text{AlClEt}_2$ (DEAC) in the presence of DBE as a first internal base ( $\text{IB}_1$ ). The crystalline forms were examined for all catalyst samples by X-ray method.  $\beta$ - $\text{TiCl}_3$  was brown with a fiber-shaped

structure.  $\alpha$ ,  $\gamma$  and  $\delta$ - $\text{TiCl}_3$  were violet with a lamellar structure. The catalyst system based on the  $\beta$ -modification of  $\text{TiCl}_3$  and organoaluminium compounds exhibited low stereo specificity and activity in the propylene polymerization. The violet modifications based on  $\text{TiCl}_3$ , specially the  $\delta$ -modification, produced highly active and highly stereospecific catalyst systems for propylene polymerization.

At the present time, most developments concerning relatively high activity and stereoregularity of this catalyst have paid attention to conventional Ziegler-Natta modified by compounds of alkoxy silane group as third component in system. Notably, the other alkoxy silane group modifications existed only as a few part in Ziegler-Natta catalyst development.