CHAPTER II

LITERATURE REVIEW

The discovery of Ziegler-Natta catalysts in the early 1950's gave rise to a great deal of interest from both academic and industrial laboratories. Numerous patents and scientific literature were investigated to pay attention to polyolefins polymerization. The Ziegler-Natta catalyst is a mixture of transition metal compounds of group IV-VIII with metal alkyl, aryl or hydrides of group I-IV of the periodic table. Due to a wide spectrum of the Ziegler-Natta catalyst, it is very difficult to a summarization of all investigation here. Survey of the literature in this review will limit to the polymerization of lower α-olefin

2.1 HISTORICAL ORIGINS OF ZIEGLER-NATTA CATALYST

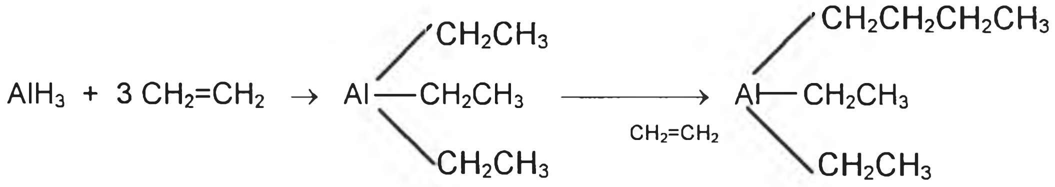
During the period of 1900-1953 a number of research groups were actively or sporadically investigating organometallic chemistry, particularly the reaction of dienes, ethylene, and substituted ethylene.

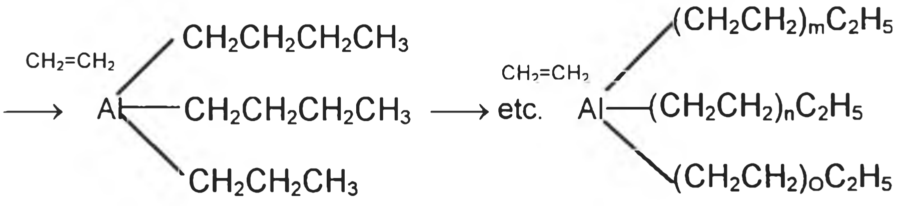
In 1930, Frederick and Marvel produce polyethylene, by the accidental polymerization of ethylene in the presence of alkyl lithium [1] Ziegler and co-worker extended this finding by investigating the mechanism by which alkali metal alkyls initiated the polymerization of conjugated dienes [2]. No work was done on ethylene until after 1945. Du Pont workers reported that ethylene at high temperature could be polymerized with a lithium-copper powder catalyst [3] and with lithium alkyl and aryl compounds [4]. Only low molecular weight compounds were obtain.

Following World War II, Ziegler reinitiated to polymerized ethylene with lithiumalkyks to synthesize higher molecular weight polymer chains. However, it was proved to be an unsuitable initiator because the growing alkyl polymer was prematurely eliminated with precipitation of lithium hydride.

$$LiR + nC_2H_4 \rightarrow Li(CH_2\text{-}CH_2)_nR \rightarrow LiH\downarrow + CH_2{=}CH\text{-}((CH_2\text{-}CH_2)_{n-1}R \qquad \text{Eq. 2.1}$$

This problem became the next important innovation. They found that it was promoted by ether to improve this reaction. They, however, speculate that the ether-soluble $LiAlH_4$ could also serve as a source of lithium alkyl, and this led them to the next advance[5]. They demonstrated that $LiAlH_4$ reacted with ethylene to form $LiAlEt_4$. At first they thought that ethylene would polymerize only on the LiEt portion and not $AlEt_3$, this turned out to be wrong - $AlEt_3$ polymerized ethylene even more efficiently. Ziegler and Gellert switch to $AlEt_3$ because of experimental advantages. The equilibrium between metal alkyl and metal alkyl hydride with olefin components could now be established since all of the metal alkyl and metal alkyl hydride components remain soluble. This feature made it possible for Ziegler and Gellert to study the organometallic synthesis of olefins by following steps.





Eq. 2.2

Where m, n, o are small number

Higher molecular weight polymer was not formed because a displacement reaction also took place at these high temperatures.

$$>Al-(CH_2CH_2)_mC_2H_5 \longrightarrow Al-H + CH_2{=}CH-(CH_2CH_2)_mC_2H_5 \qquad \text{Eq. 2.3}$$

In an attempt to prepare hexyl and octyl aluminum by heating $AlEt_3$ with ethylene at 100 °C and 100 atm in the autoclave, there was obtained instead a qualitative yield of 1-butene and $AlEt_3$. This was an entirely unexpected development. Investigations were subsequently carried out to discover the reason for this unexpected behavior, and it was found that autoclave contained small amounts of nickel phosphate, which had been reduced by $AlEt_3$. A series of transition metal salts was next examined by Ziegler and Breil in combination with $AlEt_3$ in an effort to find other displacement catalysts. The possibilities of adding nickel or cobalt to a polymerization system involving α-olefins were exploited[6,7], and it was also hope that by eliminating all traces of nickel a polymer of ethylene could result. During the systematic addition of various transition metal compounds, cobalt and platinum were found to act as cocatalyst, and the use of zirconium acetyl acetonate as cocatalyst resulted in a high yield of polyethylene.

They now synthesized high molecular weight polyethylene at low olefin pressure[8,9]. Subsequently, it was show that compounds of transition element of group IV, V and VI gave similar results. Experiments with alkylaluminums and cocatalysts were modified by carrying out the reaction in solvent. Polyethylene precipitated as a white powder and could be easily separated by filtration. Further work indicated that the most effective catalyst system consisted of alkylaluminum and $TiCl_4$ at 1 atm pressure.

Early in 1954, Natta group[10] succeeded in synthesizing crystalline polymer. Their first experiments were with Mulheim catalyst ($AlEt_3 + TiCl_4$) which they found to produce a mixture of amorphous and crystalline fraction polypropylene. When other titanium chloride (especially α $TiCl_3$ made by reducing $TiCl_4$ with H_2 at high temperature) were used in place of $TiCl_4$ the polymer obtained were much more crystalline. In this way, high crystalline polymers from propylene, 1-butene and styrene were easily synthesized for the first time.

In 1955 Vandenberg, Ettore and Luciano[11] applied for patents which disclose that molecular hydrogen acted as a true transfer agent for the Ziegler-Natta catalyst. This was a very important discovery because many of the Ziegler-Natta catalyst produce polymers whose molecular weights were too high for facile processing and certain product application. The desired molecular weight was easily obtained in the presence of hydrogen.

In 1963, the Royal academy of Science of Sweden awarded Nobel Prize for chemistry to Professors K. Ziegler and G. Natta

2.2 RELATED PAPER

Breslow and Newbury [12] studied a mixture of bis-(cyclopentadienyl)-titanium dichloride and diethylaluminium chloride, as the blue complex. The color changes in the latter case indicated quite definitely that the oxygen was functioning to form a tetravalent titanium compound. Thus, ethylene containing 0.003% oxygen was pass into a solutions of 5 milimoles of bis-(cyclopentadienyl)-titanium dichloride and 10 milimoles of diethylaluminum chloride in a liter of toluene at 15-20 °C. The blue solution turned green, and 13 g of polyethylene was formed in an hour.

Chien [13] investigated the kinetic of ethylene polymerization catalyzed by bis-(cyclopentadienyl)-titanium dichloride dimethylaluminum chloride. Initiation was followed by using C^{14}-labeled $(CH_3)_2AlCl$. Instantaneous concentration of propagating metal alkyl complex ,[C], was obtained by quenching aliquots of polymerization mixture with I_2. The propagation step was first order in a monomer and [C] with an activation energy of 12.2 kcalmol^{-1}; k_p at 30 °C was 13.6 ± 1.4 liter mol^{-1}sec^{-1}. Termination was second order with respect to metal alkyl complex with an activation energy of 16.4 kcal mol^{-1}; k_t at 30 °C, and an Al to Ti ratio of 2.5 was 9.07 ± 0.58 liter mol^{-1}sec^{-1}, which decreased with increase of the ratio. Each polymer molecule was found to contain 1.07 ± 0.27 $C^{14}H_3$ groups, thus eliminating a number of transfer processes. These kinetic data were used to calculate number-average molecular weight, $\overline{M}_n$, which agreed well with the ones obtained by fractionation of polymer.

Long [14] found that the interactions of bis-(cyclopentadienyl)-titanium dichloride with aluminum chloride and methylaluminum dichloride had been followed spectrophotometrically. In each two complexes were formed, the first at a ratio of one Al per Ti and the second at a higher ratio. Only acid-catalyzed polymerization was observed with $(C_5H_5)_2TiCl_2$ and aluminum chloride, whereas linear polyethylene was obtain with methylaluminum dichloride. The initial rate of polymerization paralleled the spectroscopic concentration of the first complex.

Giannetti, Nicoletti and Mazzocchi [15] examined homogeneous Ziegler-Natta systems for the ethylene polymerization, deriving from $R_2R'_2M$ complexes (R = cyclopentadienyl; R′ = alkyl, aryl; M = Ti,Zr,Hf) and oligomeric oxoalane compounds. Further results concerning the methyl aluminoxane synthesis and the reacted chemistry were report. Results from polymerization experiments show that the highest productivity were obtained only by oxoalane cocatalyst having a high degree of oligomerization. The catalytic activity of the system under investigation was strongly affected also by changing both the σ-alkyl and the π -cyclopentadienyl ligands. Furthermore, it was found that in the presence of methyl aluminoxane, the homoleptic σ-alkyl derivatives of IVB transition metals such as $Zr(CH_2C_6H_5)_4$ were also able to polymerize ethylene with a family high productivity. Active species containing Zr-O-Al bonds had been postulated.

Kaminsky and Miri [16] found that EPDM terpolymers with ethylidene norbornene as diene monomer could be prepared by means of a soluble

Ziegler catalyst formed from bis-(cyclopentadienyl)-zirconium dimethyl and methylaluminoxane. The overall activities lay between 100 and 1000 kg EPDM (mol Zr-h-bar)$^{-1}$, obtainable at zirconium concentrations as low as $5*10^{-7}$ mol/L. After an induction period (0.5-5 h) the polymerization rates increased and then leveled to a value which was constant for several days. From copolymerization kinetics reactivity ratio $r_{12} = 31.5$, $r_{21} = 5*10^{-3}$ and $r_{13} = 3.1$ could be derived, and by C^{13} NMR spectroscopy $r_{12}*r_{21} = 0.3$ was found(1 = ethylene, 2 = propylene, 3 = ethylidene norbornene). The regiospecifity of the catalyst toward propylene led exclusively to the formation of head-to-tail enchainments. The diene polymerized via vinyl polymerization of the cyclic double bond, and the tendency to branching was low. The Molecular weight distribution of 1.7 was remarkably narrow. Glass transition temperature of -60 to -50 °C could be observed.

Chien and Wang [17] verified that ethylene was polymerized by Cp_2ZrCl_2 -methylaluminoxane (MAO) catalyst where a portion of the MAO was replaced with trimethyl aluminum. At a total Al to Zr ratio of 1070, there was neither appreciable loss of productivity nor change in polymerization profile for TMA/MAO $\leq$ 10. The productivity was reduced only by two-to three -fold for TMA / MAO $\leq$ 100 accompanied by a 10 min induction period. Aging of this catalyst did not affect the induction period, but improves its productivity. The kinetic isotope effect for radio labeling with tritiated methanol was 2.0. About 40% of the Zr was active for the catalyst with { 99[TMA] + 1[MAO] } to Zr ratio of 100. The rate constants for propagation and chain transfer were obtained. The mechanisms for the mixed TMA and MAO cocatalyst system were discussed.

Chien and Razavi [18] investigated the bis(neomenthyl cyclopentadienyl) zirconium dichloride/methylaluminoxane (η^5-$(NMCp)_2ZrCl_2$/MAO) catalyst for ethylene polymerization. About 51 % of Zr formed active sites more or loss instantaneously according to quenching with tritiated methanol. There was an initial drop of rate polymerization, R_P, of about 30% which remained constant thereafter. The catalytic activity increased monotonically with temperature, it was proportional to $[MAO]^{1.75}$ at a constant [Zr] = 1.5 μM and proportional to $[Zr]^{-1.2}$ at a constant [MAO] = 64.5 mM. At very large [MAO] / [Zr] , the catalyst had extremely high activity ; $k_p = 5*10^3$ $(Ms)^{-1}$ at 50 °C. There was also facile chain transfer to aluminum, $k_{tr}{}^A = 0.14$ s^{-1} at 50 °C, Both k_p and $k_{tr}{}^A$ were about 30 times greater than the corresponding rate constants for $MgCl_2$ supported $TiCl_3$ catalyst.

Chien and Wang [19] studied the ethylene polymerization by bis (cyclopentadienyl)- zirconium dichliride/methyl aluminoxane, (Cp_2ZrCl_2/MAO) , and cyclopentadienyl zirconium trichloride/methyl aluminoxane, ($CpZrCl_3$/MAO). The M_w and PD ($=M_w/M_n$) of polymers obtained after 2.5-60 min were the same, which indicate short chain lifetime. The values of rate constants for Cp_2ZrCl_2 at 70 °C were : K_p = 168-1670 $(Ms)^{-1}$ and $k_{tr}{}^A$ = 0.012-0.81 s^{-1} depending upon [Zr] and [MAO] , $k_{tr}{}^{\beta} = 0.28$ s^{-1} and $k_{tr}{}^H = 0.2$ M^{-1} $torr^{-1/2}$ s^{-1}. These chain transfer rate constant values were two to three order of magnitude greater than the corresponding values found for $MgCl_2$ supported titanium catalysts. One significant difference between the heterogeneous and homogeneous catalysts was that former decay according to an apparent second order kinetics, whereas the latter decay is simple first order at 0 °C and biphasic first order at higher temprature. The productivity of the catalysts depended weakly on temperature while the M_w decreased strongly with increase of temperature above 30 °C. All the active species were formed upon mixing Cp_2ZrCl_2 with MAO while it took up to 20 min for the $CpZrCl_3$ / MAO system. The productivity of the former increased more strongly with decrease of [Zr] than the latter. Otherwise, the two catalyst systems had all their kinetic parameters differing less than a factor of two.

Mallin, Rausch and Chien [20] compared the ethylene polymerization by Cp_2ZrCl_2 / MAO and Cp_2HfCl_2 / MAO. The Hf catalyst had about two-thirds the activity of the Zr catalysts. This difference may be attributed to the greater number of active centers presents in the Zr catalyst . The Hf catalyst showed a smaller dependence of : i) polymer M_w on temperature and ii) polymerization activity on transition metal concentration than the Zr catalyst.

Herwing and Kaminsky [21] found that a soluble, halogen-free Ziegler-catalyst could be obtained when using bis (cyclopenadienyl) dimethyl titanium together with methylaluminoxane. It was possible to polymerized both ethylene as well as propylene with high activities. The so formed polypropylene was 100 % atactic. Polymerization activities in dependence upon Al and Ti-concentrations and polymerization rates of ethylene and propylene were show.

Rieger and Chien [22] studied propene polymerization with ethylene bis (1-indenyl)dichloridezirconium ($Et(Ind)_2ZrCl_2$) and methylaluminoxane (MAO) at 70 °C . The polymer was fractionated by solvent extraction; there was no hexane insoluble material. The pentane insoluble , hexane soluble (C_{5i} - C_{6s})

fraction contained 67 % mmmm pentads. It had x-ray crystallinity of 59 % comprised of 93 % γ-phase , and no NMR detectable misinsertions. However, 1,3-insertion was found in the more stable fractions.

Asanuma, Nishimori, Ito et al. [23] studied polyolefins having syndiotactic by using 1-methyl-1-ethylidene-(cyclopentadienyl-1'fluorenyl) zirconium dichloride and methylaluminoxane as a catalyst. 1-Butene and 4-methyl-1-pentene gave crystalline polymer having syndiotactic structure, while 1-pentene, 1-hexane and 1-octane gave noncrystalline polymer having syndiotactic structure. The identification of syndiotactic and isotactic polyolefins were made by ^{13}C-NMR, X-ray diffraction, and differential scanning calorimetry.

Chien , Rieger and Martin [24] showed that polypropylenes obtained with the homogeneous racemic ethylene bis (indenyl) zirconium dichloride / methylaluminoxane catalyst were fractionated by solvent extraction . The IR absorbance ratios A_{998}/A_{973} and A_{841}/A_{973} , were found that to vary linearly with the homosteric sequence population , [mmmm] and [mm]. These results were compared with the results of a similar study by Burfield and Loi on commercial and laboratory polypropylenes of conventional type.

Chien and He [25] had compared for ethylene/propylene copolymerization to find relationship between the polymerization activity, copolymer structure and copolymerization reactivity ratio with the catalyst structures. Stereorigid racemic ethylene bis (indenyl) zirconium dichloride and tetrahydro derivative exhibited very high activity of 10^7 g (mole Zr h bar)$^{-1}$, giving copolymers having comonomer compositions about the same as the feed composition, molecular weights increasing with the increase of ethylene in the feed, random incorporation of comonomer, and narrow molecular weight distribution indicative of a single catalytic species. Nonbridged bis (indenyl) zirconium behaved differently, favoring the incorporation of ethylene over propylene, producing copolymer whose molecular weight decreases with the increase of ethylene in the feed, broad molecular weight distribution , and methanol soluble fraction. Simple metallocene catalysts had much lower polymerization activities. Cp_2TiCl_2 / MAO produced copolymer with tendency toward alternation, whereas Cp_2HfCl_2 / MAO gave copolymer containing short blocks of monomer.

Longo , Proto , Grassi et al. [26] had investigated syndiotactic and isotactic polypropylene in the presence of the catalytic system isopropyl (cyclopentadienyl) (1-fluorenyl) zirconium dichloride/methylaluminoxane and rac-ethylene bis (1-indenyl) zirconium dichloride/methylaluminoxane. C^{13}-enriched $Al(CH_3)_3$ had been added to the catalysts in order to observe the stereospecificity of initiation on metal-CH_3 bonds. C^{13}-NMR analysis of the enriched end groups showed the contribution to the enantioselectivity of direct interaction of the incoming monomer with the ligands of the transition metal of the true catalytic species.

Kim and Meria Eur studied [27] polymerization of ethylene and propylene with catalysts based on titanium compounds ($TiCl_4$ or $CpTiCl_3$) modified by trimethylsilanol (TMS). The convenient conditions of catalyst preparation and polymerization were investigated such as ageing time, Si/Ti mole ratio, catalyst concentration, type of alkylaluminum compound used as cocatalyst and Al/Ti mole ratio. The influence of these parameters on the homopolymerization of ethylene and propylene was then described in detail. The polymerization activities were found to be strongly dependent upon catalyst preparation and polymerization conditions. Electron paramagnetic resonance (EPR) analyses were conducted with different Al/Ti mole ratios for elucidating the influence of the Ti oxidation state on the catalyst properties.

Estrada and Hamielee [28] studied modeling of ethylene polymerization with Cp_2ZrCl_2 /MAO catalyst. A full, two-level factorial experimental design with temperature and concentrations of zirconocene dichloride and methylaluminoxane as variables was employed to study the polymerization of ethylene. Rate of polymerization and molecular weight data were used to develop a kinetic model and estimate the kinetic parameters. The polymerization rate was continuously recorded from a semi-batch reactor and molecular weights were measured at the end of each experimental run. The analysis of the data suggests the presence of two kinds of active species. One kind of species was produced from the other via a pseudo-first-order reaction.

Shiono, Ohyizawa and Soga [29] had investigate the reaction between carbon monoxide and Ti-polyethylene. Ethylene polymerization was conducted with a typical homogenous Cp_2TiCl_2 / methylaluminoxane catalyst. The Ti-terminted polymers were introduce into toluene saturated with carbon monoxide or containing ^{13}C-enriched carbon monoxide at -78 °C. The mixture was gradually heated up to room temperature, and a small portion of the reaction mixture was taken out -78 , 0 °C and room temperature to analyze the structure of each polymer by F.T.IR., GPC., ^{1}H and ^{13}C NMR. It was found from these analyzes that carbon monoxide was incorporated into the polymer mainly as a ketone carbonyl.

Rieger [30] studied propene polymerization by methylaluminoxane (MAO)-activated rac-[1,2-bis-(η^5-(9-fluorenyl))-1-phenyl-ethane] zirconium dichloride at 30, 50, and 70 °C and constant monomer concentration. The polypropylene products were isotactic with stereoregularities dpending on the polymerization temperature.

Resconi, Abis and Franciscono [31] found that $Cp^*_2MCl_2$ /MAO catalyst (Cp^* = pentamethylcyclopentadienyl; M = Zr, Hf; MAO = methylaluminoxane) polymerized 1-butene to a low molecular weight, predominantly syndiotactic poly(1- butene) with 68% (Zr) and 77% (Hf) rr triads -20 °C. The mechanism of stereocontrol was shown to be syndiospecific chain end control in primary (head-to- tail) polyinsertion.

Riegler, Mu, Mallin et al. [32] verified that polypropylene had been obtained with racemic ethylenebis(indenyl)zirconium dichloride-methylaluminoxane (MAO) catalyst from -55 to 80 °C and Al/Zr ratios between 10^3 and $1.6*10^4$. As the polymerization temperature increases, the polymer produced had progressively lower melting transition temperature, lower homosteric pentad sequence population, and higher solubility in low-boiling solvents, indicating frequent stereochemical inversion in monomer enchainment. In addition, there was tail -to- tail enchainment in polypropylene obtained at a low MAO to Zr ratio. The results indicated variations of degrees of stereochemical and regiochemical control by the rac-Et[Ind]$_2$ZrCl$_2$-MAO catalyst with polymerization temperature and catalyst composition.

Zambelli, Longo and Grassi [33] studied propylene polymerization in the presence of stereospecific homogeneous catalyst systems consisting of group 4 metallocenes and mixtures of trimethylaluminum and dimethylaluminum fluoride. The polymer obtained were isotactic with a molecular structure very much like that of the polymer prepared in the presence of the same group 4 metallocenes and methylaluminoxane.

Fierro, Chien and Rausch [34] found that rac-isopropylidene (1-η^5-cyclopentadienyl)(1-η^5-indenyl)zirconium dichloride and 3-methylindenyl derivative had been synthesized and characterized. These precursors activated with methylaluminoxane produced polypropylene with hemiisotactic microstructures.