

CHAPTER II

LITERATURE REVIEW

The award of the Nobel Prize for Chemistry to Ziegler and Natta in 1963 was intended to acknowledge their revolutionary studies which had allowed them to obtain new polymeric materials with exceptionally controlled molecular structure and excellent properties. The discoveries changed polymer chemistry forever, and provoked a worldwide research and development effort that culminated in many new commercial plastics and elastomers. Numerous patents and scientific literature were published with attention on polyolefins polymerization. The metallocene-alkylaluminum catalyst is a mixture of transition metal compounds of group IV-VIII of the periodic table with alkylaluminum. Due to a wide spectrum of the metallocene-alkylaluminum catalyst, it is very difficult to summarize all previous investigations here. Survey of the literature in this review will limit to the polymerization of low α -olefin only.

2.1 HISTORICAL ORIGIN OF ZIEGLER-NATTA CATALYST

Synthetic polyolefins were first synthesized by decomposition of diazomethane. With the exception of polyisobutylene, these polymers were essentially laboratory curiosities. They could not be produced economically. The situation changed with the discovery of the high-pressure process by Fawcett and Gibson (ICI) in 1930. Ethylene was polymerized by radical compounds [35]. To achieve a sufficient polymerization rate, a pressure of more than 100 MPa is necessary. First produced in 1931, low-density polyethylene (LDPE) was used as insulation material in cables.

Due to its low melting point of less than 100 °C, LDPE could not be applied to the production of domestic articles that would be in contact with hot water. Important progress for a broader application was made when Hogan and Banks [5] (Phillips Petroleum) and Ziegler et al. [2] found that ethylene can be polymerized by means of activated transition metal catalyst systems. In this case the high-density polyethylene (HDPE), a product consisting of highly linear polymer chains and softens above 100 °C, was produced. Hogan polymerized

ethylene using a nickel oxide catalyst and later a chromium salt on an alumina-silica support. Zletz [36] used molybdenum oxide on alumina in 1951 (Standard Oil). Fischer [37] used aluminum chloride along with titanium tetrafluoride (BASF 1953) for the production of high-density polyethylene. Ziegler et al.'s use of transition metal halogenides and aluminum organic compounds [2] and the work of Natta [3] in applying this catalyst system for the synthesis of stereoregular polyolefins were probably the two most important achievements in the area of catalysis and polymer chemistry in the last 50 years. They led to the development of a new branch of the chemical industry and to a large production volume of such crystalline polyolefins as HDPE, isotactic polypropylene, ethylene-propylene rubbers, and isotactic poly(1-butene). For their work, Ziegler and Natta were awarded the Nobel Prize in 1963. The initial research of Ziegler and Natta was followed by an explosion of scientific papers and patents covering most aspects of olefin polymerization, catalyst synthesis, and polymerization kinetics as well as the structural, chemical, physical, and technological characteristics of stereoregular polyolefins and olefin copolymers. Since that first publication, more than 15,000 papers and patents have been published on subjects related to that field. Several books and reviews giving detailed information on the subjects have been published [38-40].

The first generation of Ziegler-Natta catalysts, based on $\text{TiCl}_3/\text{AlEt}_2\text{Cl}$, was characterized by low polymerization activity. Thus a large amount of catalyst was needed, which contaminated the raw product. A washing step that increased production costs was necessary. A second generation of Ziegler-Natta catalysts followed, in which the transition metal compound is attached to a support (MgCl_2 , SiO_2 , Al_2O_3). These supported catalysts are of high activity. The polyolefin product contains only traces of residues, which may remain in the polymer. Most Ziegler-Natta catalysts are heterogeneous. More recent developments show that homogeneous catalyst systems based on metallocene-aluminoxane can also be applied to olefin polymerization. These systems are easy to handle by laboratory standards, and show the highest activities over an extended range of polymer products.

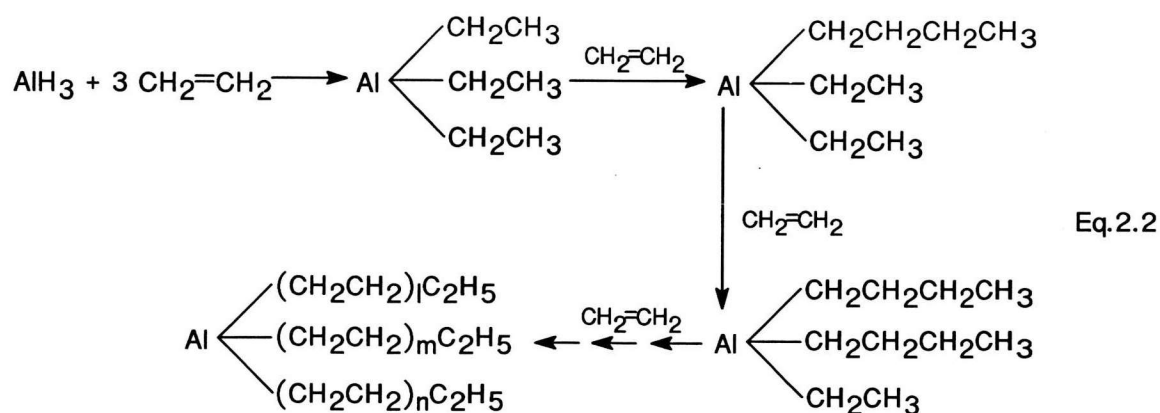
In 1930, Frederick and Marvel [41] produced polyethylene by the accidental polymerization of ethylene in the presence of alkyl lithium. Ziegler and co-worker extended this finding by investigating the mechanism by which alkali metal alkyls initiated the polymerization of conjugated dienes. No work was done on ethylene until after 1945. Du Pont workers [42] reported that ethylene at high temperature could be polymerized with a lithium-

copper powder catalyst and with lithium alkyl and aryl compounds. Only low molecular weight compounds were obtained.

Following World War II, Ziegler reinitiated the polymerization of ethylene with lithium alkyls 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 (see eq.2.1).

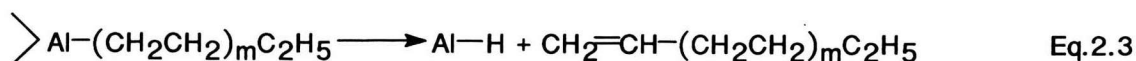


This problem became the next important innovation. They found that it was promoted by ether to improve this reaction. They, however, speculate that the ether-soluble LiAlH_4 could also serve as a source of lithium alkyl, and this led them to the next advance [43]. They demonstrated that LiAlH_4 reacted 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 explain the organometallic synthesis of olefins by following steps.



Where l, m and n are small number

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



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 [44], 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 [2]. Subsequently, it was shown 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 [45] succeeded in synthesizing crystalline polymer. Their first experiments were with Mulheim catalyst ($\text{AlEt}_3 + \text{TiCl}_4$) 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 Van Denberg, Ettore and Luciano [46] 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 HISTORICAL ORIGINS OF METALLOCENE CATALYST AND RELATED PAPER

The first homogeneous Ziegler-Natta catalyst or metallocene catalyst was discovered independently by Breslow and Newbury in 1957 [4]. The catalyst, bis(cyclopentadienyl) titanium dichloride (Cp_2TiCl_2 , $\text{Cp} = \eta^5\text{-cyclopentadienyl}$) activated with alkylaluminum chloride (AlR_2Cl) exhibited a low polymerization activity (A) for ethylene, ca. $A \approx 10^4$ gPE/(moleTi*h*atm), and none for propylene. The mixture of bis(cyclopentadienyl)titanium dichloride and diethylaluminum 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.

Long [12] 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 $(\text{C}_5\text{H}_5)_2\text{TiCl}_2$ and aluminum chloride, whereas linear polyethylene was obtain with methylaluminum dichloride. The initial rate of polymerization paralleled the spectroscopic concentration of the first complex.

Herwing and Kaminsky [13] found that a soluble, halogen-free Ziegler-catalyst could be obtained when using bis(cyclopentadienyl)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.

Giannetti, Nicoletti and Mazzocchi [9] examined homogeneous Ziegler-Natta systems for the ethylene polymerization, deriving from $\text{R}_2\text{R}'_2\text{M}$ complexes ($\text{R} = \text{cyclopentadienyl}$; $\text{R}' = \text{alkyl, aryl}$; $\text{M} = \text{Ti, Zr, Hf}$) and oligomeric oxoalane compounds. Further results

concerning the methylaluminoxane 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 methylaluminoxane, 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.

Mallin, Rausch and Chien [14] 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.

Chien and Wang [15] verified that ethylene was polymerized by $Cp_2ZrCl_2/$ methylaluminoxane (MAO) catalyst where a portion of the MAO was replaced with trimethylaluminum. 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 [16] 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 less 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 $[MAO]$ at a constant $[Zr] = 1.5 \mu M$ and proportional to $[Zr]^{-1.2}$ at a constant $[MAO] = 64.5 \text{ mM}$. At very large $[MAO]/[Zr]$, the catalyst had

extremely high activity ; $k_p = 5 \cdot 10^3 \text{ (Ms)}^{-1}$ at 50 °C. There was also facile chain transfer to aluminum, $k_{tr}^A = 0.14 \text{ s}^{-1}$ 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.

Zambelli, Longo and Grassi [17] 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.

Chien and Wang [18] studied the ethylene polymerization by bis (cyclopentadienyl)-zirconium dichloride/methylaluminoxane, ($\text{Cp}_2\text{ZrCl}_2/\text{MAO}$), and cyclopentadienyl zirconium trichloride/methylaluminoxane, ($\text{CpZrCl}_3/\text{MAO}$). 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 : $K_p = 168\text{--}1670 \text{ (Ms)}^{-1}$ and $k_{tr}^A = 0.012\text{--}0.81 \text{ s}^{-1}$ depending upon $[\text{Zr}]$ and $[\text{MAO}]$, $k_{tr}^\beta = 0.28 \text{ s}^{-1}$ and $k_{tr}^H = 0.2 \text{ M}^{-1} \text{ torr}^{-1/2} \text{ s}^{-1}$. 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 temperature. 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 $\text{CpZrCl}_3/\text{MAO}$ system. The productivity of the former increased more strongly with decrease of $[\text{Zr}]$ than the latter. Otherwise, the two catalyst systems had all their kinetic parameters differing less than a factor of two.

Riegler, Mu, Mallin et al. [19] 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 $1.6 \cdot 10^4$. 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 enchainments. In addition, there was tail –to – tail enchainments in polypropylene obtained at a low MAO to Zr ratio. The results

indicated variations of degrees of stereochemical and regiochemical control by the $\text{rac-Et[Ind]}_2\text{ZrCl}_2\text{-MAO}$ catalyst with polymerization temperature and catalyst composition.

Chien and He studied [20] a number of metallocene/methylaluminoxane (MAO) catalysts have been compared for ethylene/propylene copolymerizations to find relationship between the polymerization activities, copolymer structures, and copolymerization reactivity ratio with the catalyst structures. Stereorigid racemic ethylene bis(indenyl)zirconium dichloride and the tetrahydro derivative exhibit very high activity of $10^7 \text{ g}^*(\text{moleZr}^*\text{h}^*\text{bar})^{-1}$, 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 comonomers, 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 copolymers whose molecular weight decreases with the increase of ethylene in the feed, broad molecular weight distribution, and a methanol soluble fraction. This catalyst system contains two or more active species. Simple metallocene catalysts have much lower polymerization activities. $\text{CpTiCl}_2/\text{MAO}$ produced copolymers with tendency toward alternation, whereas $\text{Cp}_2\text{HfCl}_2/\text{MAO}$ gave copolymer containing short blocks of monomers.

Tsutsui and Kashiwa [21] studied polymerization of propylene in the gas phase was carried out with a solid Zr complex catalyst obtained from ethylenebis(1-indenyl)zirconium dichloride ($\text{Et(Ind)}_2\text{ZrCl}_2$) and methylaluminoxane (MAO). The resulting polymer had structurally similar features to that obtained in toluene liquid-phase polymerization with a soluble Zr catalyst composed of $\text{Et(Ind)}_2\text{ZrCl}_2$ and MAO, suggesting that the solid Zr complex catalyst in the gas-phase polymerization system maintains the nature of active centres in the soluble Zr catalyst system.

Kolthammer, Mangold and Gifford [22] studied the kinetic parameters have been measured for octene-1 solution polymerization at 120°C catalyzed by zirconocene with the cocatalyst methylaluminoxane. The polymerizations were performed in an attenuated total reflectance (ATR) reaction cell. The progress of the reactions were followed by observing the disappearance of octene-1 using the 910 cm^{-1} band measured by FT-IR spectroscopy. The dependence of the reaction rate (R_p) on catalyst concentration and cocatalyst/catalyst ratio was examined. The catalyst deactivation mechanism was studied by fitting the experimental

data to mathematical models involving second-order propagation and either first or second order catalyst deactivation. Second-order catalyst deactivation provided a much better fit. The calculated deactivation rate constant, $k_d = 21 \text{ (M*s)}^{-1}$. This model is used to determine the propagation rate constant for $\text{Al/Zr} = 4 \times 10^3$ as $k(p) = 19.9 \text{ (M*s)}^{-1}$. A decrease in $\text{Al/Zr} = 3 \times 10^2$ lowered the propagation rate constant, $k(p)$, to 9.6 (M*s)^{-1} indicating that less than 50% of the initial Zr is active at this Al/Zr ratio.

Cam and Giannini [23] studied the interaction of zirconocene dichloride (Cp_2ZrCl_2) with methylaluminoxane (MAO), the two components of homogeneous catalyst for olefin polymerization, was studied by H-1 NMR spectroscopy. It was found that Cp_2ZrCl_2 is monoalkylated by $\text{Al}_2(\text{CH}_3)_6$ present in MAO. The trimethylaluminum contained in MAO appears to be the active species in the alkylation of the zirconocene dichloride. The $\text{Cp}_2\text{ZrCH}_3\text{Cl}$ likely forms, with an excess of MAO, highly polarized species. These are decomposed by a complexing agent of MAO such as KCl.

Kucht et al. [24] have been synthesized and characterized (η^5 -tetramethylcyclopentadienyl)-, (η^5 -tetraphenylcyclopentadienyl)-, (η^5 -(diphenylphosphino)tetramethylcyclopentadienyl)-, and (η^5 -(trimethylsilyl)tetramethylcyclopentadienyl)titanium triisopropoxide. Their catalytic activities for syndiospecific styrene polymerization have been compared with the reference compound (η^5 -cyclopentadienyl)titanium triisopropoxide. (η^5 -Tetramethylcyclopentadienyl)titanium triisopropoxide is the best catalyst precursor, giving rise to catalysts having the highest activity to produce polystyrene with the highest syndiotactic yield and molecular weight.

Kaminsky and Noll [25] investigated the norbornene/ethylene copolymerization was investigated by using two C_s -symmetric ($[\text{Me}_2\text{C}(\text{Flu})(\text{Cp})]\text{ZrCl}_2$ III, $[\text{Ph}_2\text{C}(\text{Flu})(\text{Cp})]\text{ZrCl}_2$ IV) and two C_2 -symmetric ($[\text{Me}_2\text{Si}(\text{Ind})_2]\text{ZrCl}_2$ I, $[\text{Ph}_2\text{Si}(\text{Ind})_2]\text{ZrCl}_2$ II) catalysts with methylaluminoxane (MAO) as cocatalyst. This investigation focused not only on the different polymerization behavior, like catalyst activity, but also considers the material properties of the synthesized copolymers. It was found, that the C_s -symmetric catalysts are very well suitable to yield amorphous copolymers with glass transition temperatures above 180°C and molecular weights $> 100.000 \text{ g/mole}$. These copolymers could be used as potential starting materials for optical discs and fibers.

Kim and Meria Eur [26] studied 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 aging 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 Hamielec [27] studied modeling of ethylene polymerization with $\text{Cp}_2\text{ZrCl}_2/\text{MAO}$ 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.

Rieger [28] studied propene polymerization by methylaluminoxane (MAO)-activated $\text{rac-[1,2-bis-(}\eta^5\text{-}(9\text{-fluorenyl))\text{-1-phenyl-ethane}]}$ zirconium dichloride at 30, 50, and 70 °C and constant monomer concentration. The polypropylene products were isotactic with stereoregularities depending on the polymerization temperature.

Rieger and Janiak [29] studied a quantitative was carried out on the homogeneous zirconocene dichloride/methylaluminoxane/trimethylaluminum ($\text{Cp}_2\text{ZrCl}_2/\text{MAO}/\text{TMA}$) catalyst system in ethylene polymerization. The effects of variation of the Al(MAO)/Zr ratio, absolute Zr concentration, and addition of TMA on ethylene polymerization activity and polymer properties were investigated. The polymerization profiles for small Al(MAO)/Zr ratios and the changes with the Zr concentration are explained with a complexation equilibrium for the active homogeneous complex and with the change to a heterogeneous catalyst upon polymer precipitation. Good polymer productivities can be achieved at Al(MAO)/Zr < 1 000 when

working at Zr concentrations between 10^{-4} and 10^{-5} mole/lit with addition of TMA ($\text{Al(MAO)}/\text{Al(TMA)}$ almost = 1.4).

Aaltonen and Seppala [30] studied the copolymerization of styrene and ethylene was attempted in the presence of the catalytic system $\text{CpTiCl}_3/\text{MAO}$. Polymerizations were carried out at different polymerization temperatures and Al/Ti mole ratios. The structure of the polymer was investigated with FT-IR, DSC, GPC, and C^{13} -NMR techniques. The polymerization product was composed of polyethylene and syndiotactic polystyrene. No ethylene-styrene copolymer was detected. The composition of the product was dependent on the polymerization conditions. The catalyst activity was highest at polymerization temperature 30°C and Al/Ti ratio 1500. Styrene concentration of the product was highest at polymerization temperature 50°C and Al/Ti ratio 1500. The melting temperature of the polyethylene fraction was dependent on the styrene content of the product, suggesting some interaction between the monomers in the polymerization reaction. The formation of separate polymer fractions may indicate a different polymerization mechanism for the two monomers, or the presence of more than one active species in the catalyst, one producing polyethylene and the other syndiotactic polystyrene.

Sacchi et al. [31] studied propylene polymerized in the presence of the isospecific $\text{Et(Ind)}_2\text{ZrCl}_2$ (Et: ethylene, Ind: indenyl) and the specific $(\text{Ind})_2\text{ZrCl}_2$ complexes in solution and anchored to SiO_2 and SiO_2/MAO (MAO: methylaluminoxane) supports. From the stereochemical analysis of the polypropylene samples obtained it can be deduced that i) the same active species is formed when a metallocene is in solution and when it is anchored to the SiO_2/MAO support and ii) a completely different active species is formed when the metallocene is anchored to the silica. The fact that both systems $\text{Et(Ind)}_2\text{ZrCl}_2\text{-SiO}_2$ and $(\text{Ind})_2\text{ZrCl}_2\text{-SiO}_2$ produce the same prevailing isospecific polymer suggests that only isospecific centers are formed in this case, independently of the metallocene stereochemical structure.

Woo et al. [32] studied metallocene catalysts entrapped inside the supercages of NaY zeolite were prepared by reacting NaY with methylaluminoxane (MAO) or trimethylaluminium (TMA) and then with Cp_2ZrCl_2 (Cp: cyclopentadienyl) or Cp_2TiCl_2 . NaY/MAO/ Cp_2ZrCl_2 and NaY/MAO/ Cp_2TiCl_2 catalysts could polymerize ethylene. The amount of additional MAO for the polymerization was lowered to a mole ratio of Al/Zr of 186.

Molecular weights and melting points of polyethylene polymerized with NaY-supported catalysts were higher than those of polyethylene obtained with homogeneous metallocene catalysts. It could be confirmed by extraction experiments that the metallocene catalyst was confined securely inside the supercage of the NaY zeolite.

Eskelinen and Seppala [33] studied the effect of polymerization temperature on catalyst activity and polymer properties in the polymerization of ethylene was studied. The catalyst system was a homogeneous metallocene catalyst Cp_2ZrCl_2 with methylaluminoxane (MAO) as a cocatalyst. The polymerizations were carried out in n-heptane at temperatures from -20 to 90 °C and the polymer properties determined were molecular weight, molecular weight distribution, melting point, crystallinity, and density. The catalyst activity increased 2.3-fold between 70 °C and 80 °C, evidently due to the improved solubility of polyethylene in n-heptane at elevated temperatures. Above 30 °C the molecular weight began to decrease significantly, causing the crystallinity and density to increase and the melting point to decrease. The molecular weight distribution of the polyethylene was tailored by using stepwise polymerization procedure. The MWDs varied from 2.4 to 20.2 when the polymerization was performed at two different temperatures.

Yu et al. [34] prepared and characterized poly(styrene-co-acrylamide) (PSAm)-titanium complexes (PSAm:Ti). It is found that the coordination number of acrylamide (Am) to Ti in the complexes is strongly dependent on Am content in PSAm, but not on $[\text{Am}]/[\text{Ti}]$ ratio in the feed. The infrared and x-ray photoelectron spectra suggest that the polymer-supported complexes possess the structure [GRAPHICS] The catalytic behavior of the complexes in styrene polymerization is described. The catalytic activity is markedly affected by $[\text{Al}]/[\text{Ti}]$ ratio in the complexes. C^{13} -NMR, IR, and DSC data indicate that the polystyrene obtained with PSAm. Ti/MAO (MAO = methylaluminoxane) is highly syndiotactic. Use of Et_3Al and $i\text{-Bu}_3\text{Al}$ in place of MAO gives atactic polystyrene. The activities of the various aluminum compounds used as the cocatalysts decrease in the order: $\text{MAO} > \text{Et}_3\text{Al} > i\text{-Bu}_3\text{Al}$. The polymer-supported complexes show relatively high activity even after the complexes had been exposed to air for 19 hours or higher polymerization temperature.