

CHAPTER III

THEORY

3.1 INTRODUCTION

One of the most important achievements in the field of synthetic polymer chemistry during the past 50 years has been the discovery in 1953 by Ziegler and his co-workers [3], that alkylaluminum compounds used along with many transition metal halides in an inert hydrocarbon medium could polymerize ethylene under conditions of normal temperatures and pressures to yield a solid polymer of high molecular weight and of linear structure. The developments which led to the discovery of this catalyst have been described by Ziegler [3]. For some time Ziegler's group had studied growth reaction in which ethylene undergoes oligomerization when heated with an alkylaluminum compound. Although the insertion step proceeds at temperatures of 100 - 200 °C. By accident Holzkamp, one of Ziegler's students, discovered that the displacement reaction could be catalyzed at lower temperatures by traces of colloidal nickel inadvertently left in a reactor. Subsequently, during wider investigations using other metals, Breil discovered that zirconium acetylacetonate, used with triethylaluminum, was an exceedingly active catalyst with the autoclave being filled with polyethylene. Other transition metal compounds from Groups IV to VI when used with alkylaluminum compounds gave similar results, with titanium compounds showing a high activity. Characterization studies on the polyethylenes produced by the new catalyst systems showed them to have linear unbranched structures and high molecular weights.

Ziegler and his co-workers were mainly concerned with the polymerization of ethylene and its copolymerization with α -alkenes, and it was left to Natta to extend Ziegler's discovery to α -alkenes. Natta disclosed his results to Montecatini, and it was agreed that research could be carried out on the polymerization of α -alkenes. Using a combination of titanium tetrachloride and triethylaluminum Natta and co-workers [5,15] established that propylene could be polymerized to give a product which could be separated into largely crystalline and amorphous fractions. Subsequently Natta and his co-workers extended the type of transition metal halide used to solid crystalline transition metal salts in a lower valence state, e.g. TiCl_3 ,

VCl_3 , etc. It was also established that stereoregular polymers of butene-1, styrene, dienes, etc., could be prepared.

Ziegler's discovery, together with the ensuing work into the polymerization of propylene and other α -alkenes by Natta, has given rise to the development of new classes both of catalysts and polymers. In the case of ethylene, the essential advance which was achieved was the preparation of a more linear type of polyethylene, whilst in the case of propylene and other α -alkenes, it was the control of the propagation step so as to give linear unbranched stereoregular molecules. The commercial advantage was that this control could be achieved in the polymerization of such readily available and cheap monomers as ethylene and propylene. In recognition of their contributions the 1963 Nobel Prize for Chemistry was awarded to Ziegler and to Natta.

Independent and concurrent research carried out in the USA in several industrial laboratories during the early 1950s led to the discovery of a related class of polymerization catalysts, which are formed from oxides of transition metals from Groups V-VII of the periodic table. To increase catalytic activity the transition metal oxide were supported on high area substrates such as silica, alumina, silica-alumina, etc. These catalysts constitute some of the earliest low pressure catalysts for alkene polymerization, The silica-supported chromium trioxide catalyst developed by the Phillips Petroleum Company [36] is the most important transition metal oxide catalyst of this class and is used for the polymerization of ethylene, producing linear, high density polymers, The discovery of these catalysts, their high activity, and the particular methods of their preparation have had profound effects on subsequent developments in Ziegler-Natta catalysis.

Due to their commercial and scientific importance Ziegler-Natta and related catalysts have been extensively reviewed in the scientific literature and in publications of symposia proceedings.

3.2 POLYMER STRUCTURES

Stereoregularity arises because of order in the spatial structures of polymer chains. Such ordered spatial structures are determined by two phenomena. During the polymerization step the monomer units are joined together in a regular sequence determined by the catalyst used and by the polymerization conditions. Regularity of this type cannot be altered or changed during subsequent physical treatment of the polymer. Subsequently these regularly constructed polymer chains spontaneously arrange themselves into helical structures.

If the backbone of a polymer chain is drawn in a flat zigzag form in the plane of the paper, the patterns shown in Figure 3.1 can be easily envisaged in the case of monosubstituted vinyl units. It should be noted that in (a) all the substituent R groups lie uniformly on the same side of the zigzag plane. Natta called this structure isotactic. In (b) the substituent R groups occupy positions alternatively above and below the backbone plane. Such a structure is termed syndiotactic. In (c) there is no regular arrangement of the substituent R groups and this structure is called atactic.

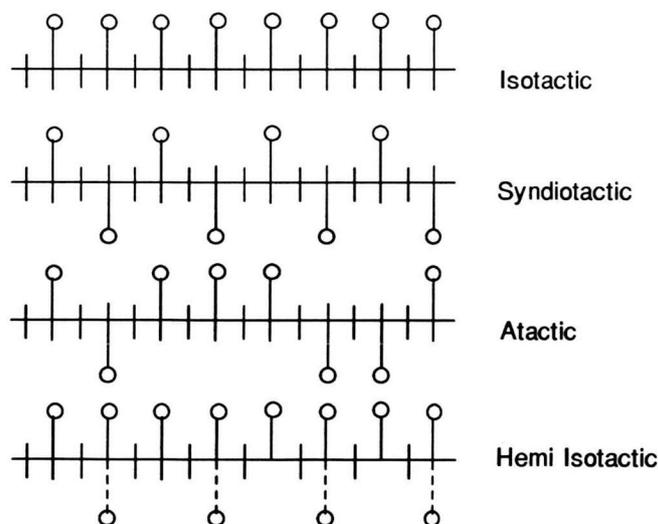


Figure 3.1 Types of olefin polymer tacticity [7]

The tertiary carbon atoms in polyalkene chains are not strictly asymmetric since two substituents are constructed from infinite monomer sequences, and are thus similar, and so the symbols of asymmetric carbon atoms, R and S, can not be usefully applied. Normally the symbols D and L are used to designate the two possible configurations of the tertiary carbon

atoms in polyalkene chains: DDDDDDD or LLLLLLL, an isotactic sequence; DLDLDDL, a syndiotactic sequence; DLDDLDDLLDLLLDDDDL, and atactic sequence.

In reality the polymer chain never adopts the flat extended forms shown in Figure 3.1 but is coiled in a helix since such a structure results in the least crowding between the hydrogen atoms. The form of the helix depends on the substituent R. Helical structures for isotactic and syndiotactic polypropylene are shown in Figure 3.2. Normally only one helical form is stable under given conditions but sometimes different helical forms can coexist depending on the melt crystallization conditions, e.g. isotactic polybutene-1.

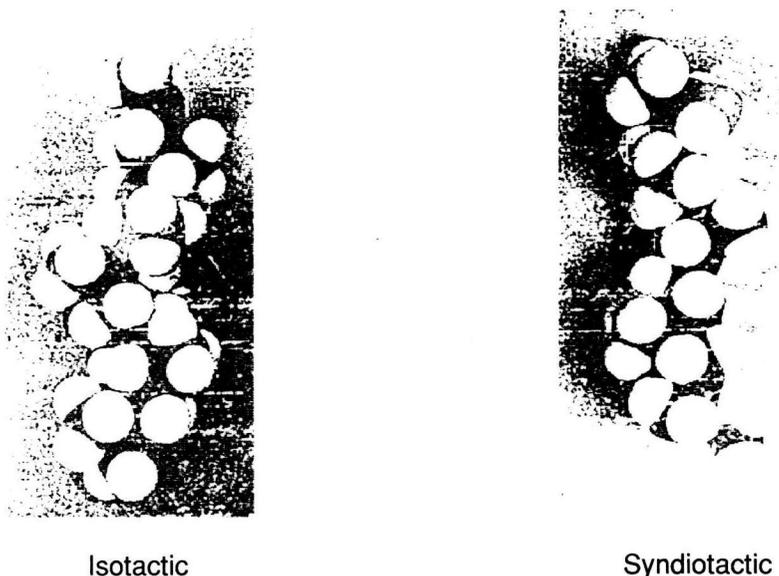


Figure 3.2 Chain models of helices of (a) isotactic and (b) syndiotactic polypropylene [47]

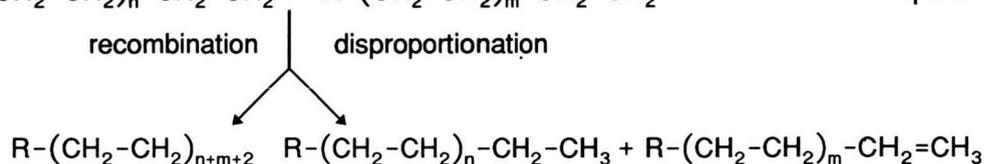
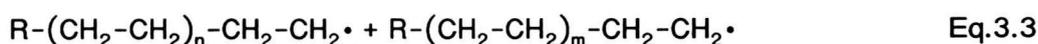
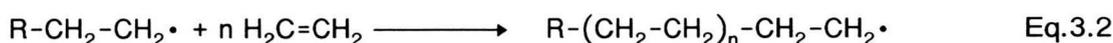
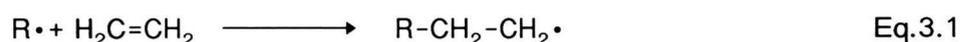
The polymerization of propylene by heterogeneous Ziegler-Natta catalysts produces a mixture of isotactic and atactic polymer, and one of the many significant contributions made by Natta and his co-workers [48] was a rapid method they devised for catalyst characterization which was based on simple stereoisometric fractionation procedures involving the use of boiling solvents, e.g. ether, heptane, xylene, etc. However, different solvents tend to extract varying fractions of lower molecular weight material, as well as removing atactic polymer. The most common procedure adopted in industrial laboratories is extraction using boiling n-heptane, and the percentage of polymer in soluble in this solvent under these conditions is normally referred to as the Isotactic Index(II). It should, however, be realized that the term atactic is used loosely since the soluble fraction may contain chains made up of blocks of isotactic or syndiotactic placements in addition to purely atactic material.

3.3 POLYETHYLENE

The polymerization of ethylene can be released by radical initiators at high pressures as well as by organometallic coordination catalysts. The polymerization can be carried out either in solution or in bulk. For pressures above 100 MPa, ethylene itself acts as a solvent. Both low- and high-molecularweight polymers up to 10^6 g/mole can be synthesized by either organometallic coordination or high pressure radical polymerization. The structure of the polyethylene differs with the two methods. Radical initiators give more-or-less branched polymer chains, whereas organometallic coordination catalysts synthesize linear molecules.

3.3.1 Radical Polymerization

Since the polymerization of ethylene develops excess heat, radical polymerization on a laboratory scale is best carried out in a discontinuous, stirred batch reactor. On a technical scale, however, column reactors are widely used. The necessary pressure is generally kept around 180 to 350 MPa and the temperature ranges from 180 to 350 °C [49]. Solvent polymerization can be performed at substantial lower pressures and at temperatures below 100 °C. The high-pressure polymerization of ethylene proceeds via a radical chain mechanism. In this case chain propagation is regulated by disproportionation or recombination.



The rate constants for chain propagation and chain termination at 130 °C and 180 MPa can be specified as follows [50].

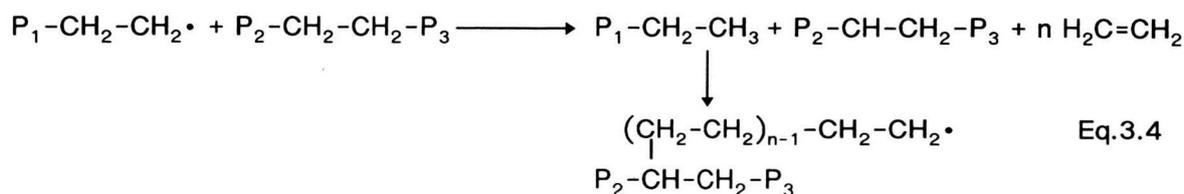
$$M_p = 5.93 \cdot 10^3 \text{ L}\cdot\text{mole}^{-1}\cdot\text{s}^{-1}$$

$$M_t = 2 \cdot 10^8 \text{ L}\cdot\text{mole}^{-1}\cdot\text{s}^{-1}$$

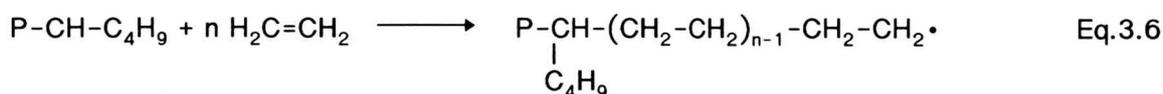
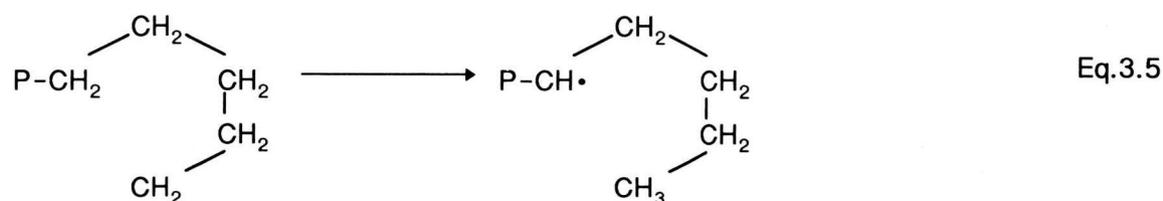
Intermolecular and intramolecular chain transfers take place simultaneously. This determines the structure of the polyethylene. Intermolecular chain transfer results in long

flexible side chains but is not as frequent as intramolecular chain transfer, from which short side chains mainly of the butyl type arise [51].

Intermolecular chain transfer:



Intramolecular chain transfer:



Radically created polyethylene typically contains a total number of 10 to 50 branches per 1000 C atoms. Of these, 10% are ethyl, 50% are butyl, and 40% are longer side chains. With the simplified equation 3.5 and 3.6, not all branches observed could be explained [52]. A high-pressure stainless steel autoclave (0.1 to 0.51 MPa) equipped with an inlet and outlet valve, temperature conductor, stirrer, and bursting disk is used for the synthesis. Best performance is obtained with an electrically heated autoclave [53].

To prevent self-degeneration, the temperature should not exceed 350 °C. Ethylene and initiator are introduced by a piston or membrane compressor. An in-built sapphire window makes it possible to observe the phase relation. After the polymerization is finished, the reaction mixture is released in two steps. Temperature increases are due to a negative Joule-Thompson effect. At 26 MPa, ethylene separates from the 250 °C hot polymer melt. After further decompression down to normal pressure, the residual ethylene is removed [54]. Reaction pressure and temperature are of great importance for the molecular weight average, molecular weight distribution, and structure of the polymer. Generally, one can say that with increasing reaction pressure the weight average increases, the distribution becomes narrower, and short- and long-chain branching both decrease.

Recently, transition metals and organometallics have gained great interest as catalysts for the polymerization of olefins [55] under high pressure. High pressure changes the properties of polyethylene in a wide range and increases the productivity of the catalysts.

Catalyst activity at temperatures higher than 150 °C is controlled primarily by polymerization and deactivation. This fact can be expressed by the practical notion of catalyst life time, which is quite similar to that use with free-radical initiators. The deactivation reaction at an alkylaluminum concentration below 5×10^{-5} mole/lit seems to be a first-order reaction [56]. Thus for various catalyst-activator systems, the approximate polymerization times needed in a continuous reactor to ensure the best use of catalyst between 150 and 300 °C are between several seconds and a few minutes. Several studies have been conducted to obtain Ziegler-Natta catalysts with good thermal stability. The major problem to be solved is the reduction of the transition metal (e.g., TiCl_3) by the cocatalyst, which may be dialkyl aluminum halide, alkylsiloxylanes [56], or aluminoxane.

Luft and colleagues [57] investigated high-pressure polymerization in the presence of heterogeneous catalysts consisting of titanium supported on magnesium dichloride or with homogeneous metallocene catalysts. With heterogeneous catalysts, a pressure of 150 MPa (80 to 210 °C) results in a productivity of 700 to 1800 $\text{kgPE} \cdot \text{g}^{-1} \cdot \text{M}$, molecular weights up to 110,000 g/mole, and a polydispersity of 5 to 10, with homogeneous catalysts, whereas the productivity is 3000 to 7000 $\text{kgPE} \cdot \text{gM}^{-1}$, molecular weight up to 70,000 g/mole, and polydispersity 2.

Table 3.1 Polymerization Conditions and Product Properties of high-pressure Processed Polyethylene (LDPE) [58]

Pressure (MPa)	Temp. (°C)	Regulator (propane:wt%)	Density (g/cm^3)	Molecular weight MFI	Distribution
165	235	1.6	0.919	1.3	20
205	290	1.0	0.915	17.0	10
300	250	3.9	0.925	2.0	10

3.3.2 Coordination Catalysts

Ethylene polymerization by the use of catalysts based on transition metals gives a polymer exhibiting a greater density and crystallinity than the polymer obtained via radical polymerization. Coordination catalysts for the polymerization of ethylene can be of very different nature. They all contain a transition metal that is soluble or insoluble in hydrocarbon, supported by silica, alumina, or magnesium chloride [2]. In most cases cocatalysts are used as activators. These are organometallic or hydride compounds of group I to III elements: for

example, AlEt_3 , AlEt_2Cl , $\text{Al}(\text{i-Bu})_3$, GaEt_3 , ZnEt_2 , $n\text{-BuLi}$, amyl Na . Three groups are used for catalysis:

1. Catalysts based on titanium or zirconium halogenides or hydrides in connection with aluminum organic compounds (**Ziegler-Natta catalysts**)
2. Catalysts based on chromium supported by silica or alumina without a coactivator (**Phillips catalysts**)
3. Homogeneous catalysts based on metallocenes in connection with aluminoxane or on nickel

3.3.2.1 Titanium Chloride-Based Catalysts (Ziegler-Natta catalysts)

The first catalyst used by Ziegler et al. [2] for the polymerization of ethylene was a mixture of TiCl_4 and $\text{Al}(\text{C}_2\text{H}_5)_3$, each of which is soluble in hydrocarbons. In combination they form an olive-colored insoluble complex that is very unstable. Its behavior is very sensitive to a number of experimental parameters, such as the Al/Ti ratio, temperature and time of mixing of all components, and absolute and relative concentrations of reactants. After complexation, TiCl_4 with alkylaluminum molecules followed by a dealkylation reduction to a trivalent state:



Under drastic conditions, TiCl_3 can be reduced to TiCl_2 in a similar way. The actual TiCl_3 product is a compound alloyed with small amounts of AlCl_3 and probably some chemisorbed AlEt_2Cl . The mechanistic process is very complex and not well understood.

Instead of $\text{Al}(\text{C}_2\text{H}_5)_3$, also $\text{Al}(\text{C}_2\text{H}_5)_2\text{Cl}$, $\text{Al}_2(\text{C}_2\text{H}_5)_3\text{Cl}_3$, or $\text{Al}(\text{i-Bu})_3$ could be used. These systems, called first-generation catalysts, are used for the classic process of olefin polymerization. In practice, however, the low activity made it necessary to deactivate the catalyst after polymerization, remove the diluent, and then remove the residues of catalyst with HCl and alcohols. This treatment is followed by washing the polyethylene with water and drying it with steam. Purification of the diluent recovered and feedback of the monomer after a purification step involved further complications. The costs of these steps reduced the advantage of the low-pressure polymerization process. therefore, it was one of the main tasks of polyolefin research to develop new catalysts (second generation catalysts) that are more active, and can therefore remain in the polymer without any disadvantage to the

properties (Table 4) [59]. The process is adjust as sensitive to perturbation, it is cheaper, and energy consumption as well as environmental loading are lower. It is also possible to return to the polymerization vessel diluent containing a high amount of the alkylaluminum. The second generation is based on TiCl_3 compounds or supported catalysts $\text{MgCl}_2/\text{TiCl}_4/\text{Al}(\text{C}_2\text{H}_5)_3$ or $\text{CrO}_3(\text{SiO}_2)$ (Phillips).

Table 3.2 Comparison of Various Catalyst Processes for Ethylene Polymerization [59]

First generation	Second generation
Catalyst preparation	Catalyst preparation
Polymerization	Polymerization
Limited influence to molecular weight and weight distribution	Great variation of molecular weight and weight distribution
Catalyst deactivation with alcohol	
Filtration	Filtration
Washing with water (HCl), wastewater treatment, purification, and drying of diluent	Feedback of diluent
Drying of PE	Drying of PE
Finishing	Finishing
Thermal degradation of molecular weight, blending	
Stabilization	Stabilization

a) Unsupported Titanium Catalysts

There are a very large number of different combinations of alkylaluminum and titanium salts to make high-mileage catalysts for ethylene polymerization, such as $\alpha\text{-TiCl}_3 + \text{AlEt}_3$, AlEt_2Cl , $\text{Al}(\text{i-Bu})_3$, and $\text{Ti}(\text{III})$ alkanolate-chloride + $\text{Al}(\text{i-hexyl})_3$. TiCl_3 exists in four crystalline modifications, the α , β , γ and δ forms [60]. The composition of these TiCl_3 's can be as simple as one Ti for as many as tree Cl, or they can have a more complex structure whereby a second metal is cocrystallized as an alloy in the TiCl_3 . The particular method of reduction determines both composition and crystalline modification. $\alpha\text{-TiCl}_3$ can be synthesized by reduction of TiCl_4 with H_2 at elevated temperatures (500 to 800 °C) [60] or with aluminum powder at lower temperatures (about 250 °C); in this case the $\alpha\text{-TiCl}_3$ contains Al cation. More active are γ - and $\delta\text{-TiCl}_3$ modifications. They are formed by heating the $\beta\text{-TiCl}_3$ to 100 or 200 °C. The preferred β -

TiCl_3 contains Al and is synthesized by reducing TiCl_4 with about 1/3 part AlEt_3 or 1 part AlEt_2Cl . A modern TiCl_3 catalyst has a density of 2.065 g/cm^3 , a bulk density of 0.82, a specific surface area (BET) of $29 \text{ m}^2/\text{g}$, and a particle size of 10 to 100 μm . The polymerization activity is in the vicinity of $500 \text{ L} \cdot \text{mole}^{-1} \cdot \text{s}^{-1}$ [61].

b) Supported Catalysts

$\text{MgCl}_2/\text{TiCl}_4$ catalysts. Good progress in increasing the polymerization activity was made with the discovery of $\text{MgCl}_2/\text{TiCl}_4$ -based catalysts [62]. Instead of MgCl_2 , $\text{Mg}(\text{OH})\text{Cl}$, MgRCl , or MgR_2 [63] can be used. The polymerization activity goes up to $10,000 \text{ L} \cdot \text{mole}^{-1} \cdot \text{s}^{-1}$. At this high activity the catalyst can remain in the polyethylene. For example, the bulk density of the catalyst is 0.226 g/m^3 , the density is 1.335 g/cm^3 , and the specific volume (BET) is $60 \text{ m}^2/\text{g}$. The high activity is accomplished by increasing the ethylene pressure. The dependence is not linear as it was for first-generation catalysts, and the morphology is also different. The polyethylene has a cobweb-like structure, whereas first-generation catalysts produced a worm-like structure. The cobweb structure is caused by the fact that polymerization begins at the surface of the catalyst particle. The particle is held together by the polymer. While polymerization is in progress, the particle grows rapidly and parts of it break. Cobweb structures are formed by this fast stretching process of the polyethylene.

It is known that in the case of these supported catalysts the higher activity is linked to a higher concentration of active titanium. In contrast to first-generation catalysts, in which only 0.1 to 1% of all titanium atoms form active sites, in supported catalysts 20 to 80% of them are involved in the formation of active sites [64].

Solvay workers [65] have investigated extensively the supported $\text{Mg}(\text{OH})\text{Cl}/\text{TiCl}_4/\text{AlEt}_3$ catalyst and related systems, including MgSO_4 , MgOSiO_2 , and MgO . It is not clear whether all of the Ti centers in the supported catalysts are isolated. The high activity suggests the incorporation of small TiCl_3 crystallites into the $\text{Mg}(\text{OH})\text{Cl}$. Fink and Kinkelin [66] prepared a high-activity catalyst by combination of MgH_2 and TiCl_4 . The MgH_2 has a much greater surface area ($90 \text{ m}^2/\text{g}$). It reacts with the TiCl_4 under the evolution of hydrogen. By 30 °C and 2 bar ethylene pressure, 110 kg. of PE per gram of Ti could be obtained.

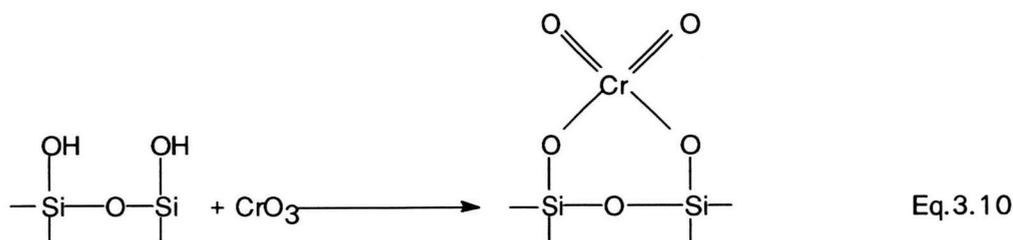
3.3.2.2 Phillips Catalysts

The widely investigated Phillips catalyst, which is alkyl free, can be prepared by impregnating a silica-alumina (87:13 composition [5]) or a silica support with

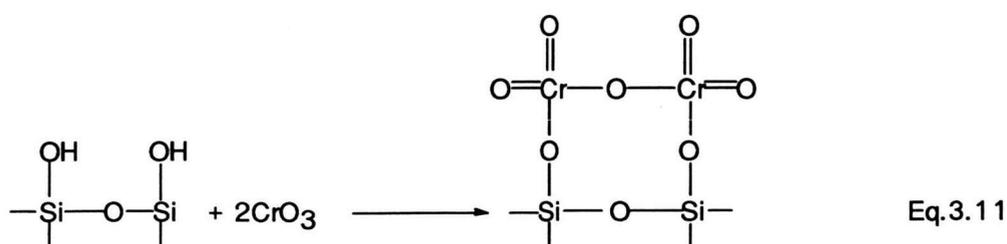
an aqueous solution of CrO_3 . High surface supports with about 400 to 600 g/m^2 are used. After the water is removed, the powdery catalyst is fluidized and activated by a stream of dry air at temperatures of 400 to $800 \text{ }^\circ\text{C}$ to remove the bound water. The impregnated catalysts contain 1 to $5 \text{ wt}\%$ chromium oxides. When this catalyst is heated in the presence of carbon monoxide, a more active catalyst is obtained. The Phillips catalyst specifically catalyzes the polymerization of ethylene to high-density polyethylene. To obtain polyethylene of lower crystallinity, copolymers with known amounts of an α -olefin, usually several percent of 1-butene, can be synthesized. The polymerization can be carried out by a solution, slurry, or gas-phase (vapor phase) process.

The chromium oxide-silica is inactive for polymerizing ethylene at low temperatures but becomes active as the temperature is increased from $196 \text{ }^\circ\text{C}$ (the melting point for CrO_3) to $400 \text{ }^\circ\text{C}$. Interactions of chromium oxide with SiO_2 and Al_2O_3 take place.

Hogan [67] calculated that for a silica support of $600 \text{ m}^2/\text{g}$ and about 5% Cr(VI) , the average distance between adjacent Cr atoms is 10 \AA . This corresponds to the accepted population of silanol groups on silica after calcination. The structures Eq.3.10 and Eq.3.11



or



It has been calculated that between 0.1 and $0.4 \text{ wt}\%$ of the total chromium forms active centers. A difficult question relates to the valences of chromium in the active sites. Valences of II, III, IV, V, and VI have been established [68]. Because of the small number of total chromium atoms that are active centers, it has not been possible to unequivocally assign the active valence. Krauss and Jums [69] concluded that the reduction of hexavalent chromium centers linked to support produced coordinatively unsaturated Cr(II)

surface compounds. A specialty of the Phillips catalyst is that there is no influence of hydrogen to control the molecular weight of the polyethylene. Only by higher activation temperatures can the molecular weight be lowered.

3.3.2.3 Homogeneous Catalysts

Homogeneous catalysts consisting of cyclopentadienyls of titanium with alkylaluminum were found active for ethylene polymerization [70]. These systems were investigated to understand the mechanistic aspects of olefin polymerization which were difficult to comprehend employing titanium tetrachloride-based heterogeneous catalysts. A general feature of these homogeneous catalysts is their relatively low activity, viz., $1 \cdot 10^3$ to $4.2 \cdot 10^3$ gPE*(gTi)⁻¹*h⁻¹*atm⁻¹. However, the addition of small amounts of water was found to increase the activity of these catalyst systems significantly.

In the 1980s Kaminsky, and coworkers [71] found that metallocenes such as Cp₂ZrCl₂ and Cp₂ZrMe₂ in conjunction with methyl aluminoxane polymerize ethylene with activities in excess of $25 \cdot 10^6$ gPE*(gZr)⁻¹. These catalysts polymerize propylene to produce atactic polypropylene. In 1985 Kaminsky, Brintzinger, et al. [72] examined the activities of stereorigid metallocenes for propylene polymerization. They found that rac-[ethylene (bis-tetrahydroindenyl)]zirconium dichloride in conjunction with methyl aluminoxane produces isotactic polypropylene. This observation led researchers to examine the potential of a number of stereorigid metallocene compounds for stereospecific polymerization of α -olefins.

a) Metallocene

Metallocenes are a class of compounds in which cyclopentadienyl or substituted cyclopentadienyl ligands are π -bonded to the metal atom. Various types of metallocenes have been synthesized and characterized by physicochemical methods. The number of known complexes is so large that it restricts the inclusion of synthetic and characterization aspects of metallocenes in this review. Representative examples of each category of metallocenes are shown in Table 3.3. In recent years, a great deal of attention has been directed at the synthesis of new metallocenes including a variety of cationic types and metallocenes incorporated on inorganic supports such as τ -alumina, MgCl₂, and silica [73-74].

b) Aluminoxane

Aluminoxanes are synthesized by controlled hydrolysis of alkylaluminum [75]. Simple synthetic routes to methyl aluminoxanes are not available due to the high reactivity of trimethylaluminum with water. Many inorganic hydrated compounds are

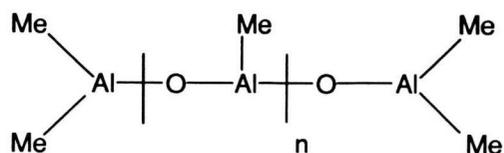
used as a source of water for preparing aluminoxane from alkylaluminum [40]. Hydrating compounds such as $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ and $\text{Al}_2(\text{SO}_4)_3 \cdot 6\text{H}_2\text{O}$ are employed. Various physicochemical data, such as compositional analysis, molecular weight determination, mass spectra, x-ray powder diffraction, infrared, and NMR spectroscopy, are used for the characterization of aluminoxane [76]. In spite of these measurements, the structures of the alkylaluminoxane are not unambiguously known. Methyl aluminoxane (MAO) is considered to be the oligomeric (cyclic or linear, Fig.3.3) mixture of $-\text{AlMeO}-$ units [71] containing possibly clusterlike of supramolecular aggregates [40,76]. In metallocene-based catalyst systems, the aluminoxanes appear to have a combination (depending on the nature of the catalyst and the polymerization conditions) of the following functions:

1. Aluminoxane alkylates the metallocene compound and scavenges the impurities [15].
2. Aluminoxane interacts with metallocene to generate cationic metallocene alkyl species.

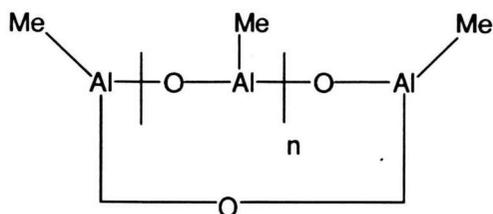
Table 3.3 Metallocene Catalyst Systems^a [77]

Catalyst	Cocatalyst	Remark
1. Chlorocyclopentadienyl derivative of titanium: e.g., Cp_2TiCl_2	Dialkylaluminum chloride	Active for ethylene but inactive for propylene polymerization
2. Metallocene catalyst systems containing aluminoxane compounds 2.1. Nonstereorigid metallocenes, e.g., Cp_2MX_2 2.2. Stereorigid metallocenes, e.g., $\text{Et}(\text{Ind})_2\text{MCl}_2$ 2.3. Supported metallocene catalysts, e.g., $\text{SiO}_2-\text{Et}(\text{Ind})_2\text{MCl}_2$	Aluminoxane Aluminoxane Aluminoxane / alkylaluminum	a) High activity for ethylene polymerization b) Active for propylene polymerization (atactic polymer) Active for regio- and stereospecific polymerization of propylene Active for ethylene and propylene polymerization
3. Metallocene catalysts systems containing nonaluminoxane compounds 3.1. Ionic metallocenes, e.g., $[\text{Cp}_2\text{MR}(\text{L})]^+ [\text{BPh}_4]^-$	-	Active for ethylene and propylene polymerization

^a M = Ti, Zr, Hf.



(a) Linear Structure



(b) Cyclic Structure

Figure 3.3 Plausible structure of methyl aluminoxane [76].**Table 3.4** Representative Examples of Metallocenes [77].**[A] Nonstereorigid metallocenes:**

- 1) Cp_2MCl_2 (M = Ti, Zr, Hf)
- 2) Cp_2ZrR_2 (R = Me, Ph, CH_2Ph , CH_2SiMe_3)
- 3) $(\text{Ind})_2\text{ZrMe}_2$

[B] Nonstereorigid ring-substituted metallocenes:

- 1) $(\text{Me}_5\text{C}_5)_2\text{MCl}_2$ (M = Ti, Zr, Hf)
- 2) $(\text{Me}_3\text{SiCp})_2\text{ZrCl}_2$

[C] Stereorigid metallocenes:

- 1) $\text{Et}(\text{Ind})_2\text{ZrCl}_2$
- 2) $\text{Et}(\text{Ind})_2\text{ZrMe}_2$
- 3) $\text{Et}(\text{IndH}_4)_2\text{ZrCl}_2$

[D] Cationic metallocenes:

- 1) $\text{Cp}_2\text{MR}(\text{L})^+ [\text{BPh}_4]^-$ (M = Ti, Zr, Hf)
- 2) $[\text{Et}(\text{Ind})_2\text{ZrMe}]^+ [\text{B}(\text{C}_6\text{F}_5)_4]^-$
- 3) $[\text{Cp}_2\text{ZrMe}]^+ [\text{C}_2\text{B}_9\text{H}_{11}]_2\text{M}^-$ (M = Co)

[E] Supported metallocenes:

- 1) $\text{Al}_2\text{O}_3 \cdot \text{Et}[\text{IndH}_4]_2\text{ZrCl}_2$
- 2) $\text{MgCl}_2 \cdot \text{Cp}_2\text{ZrCl}_2$
- 3) $\text{SiO}_2 \cdot \text{Et}[\text{Ind}]_2\text{ZrCl}_2$

The aluminoxane not only produces the cations but also stabilizes them. This view has been gaining support due to isolation of the cationic species [9]. Resconi et al. [76] proposed that trimethylaluminum is the actual cocatalyst in Cp_2ZrR_2 -MAO- Me_3Al systems, while MAO acts as a soluble carrier-activator of the ion pair formed upon reaction of the metallocene with trimethylaluminum.

3.4 MECHANISMS OF METALLOCENE-ALUMINOXANE FOR MONOOLEFINS POLYMERIZATION

3.4.1 *Interaction of Metallocene with Aluminoxanes and Nature of Active Species*

The interaction of metallocene with aluminoxanes has been studied in detail [9,23]. Metallocene dichloride reacts with methyl aluminoxane to yield a methylated compound (Fig.3.4). It undergoes either methyl or chloride abstraction to generate metallocene methyl cations [9]. The research work reported by Marks, Bochmann, Jordan, and others gave synthetic and spectroscopic evidence that cationic metallocens $[(\text{Cp}_2\text{MR})]^+$ are the active species [78]. The interaction of dichlorozirconocene, methylchlorozirconocene, and dimethylzirconocene with MAO has been studied by X-ray photoelectron spectroscopy. The results indicate the formation of cationic metallocene with MAO as the counteranion. Spectroscopic evidence for the formation of cationic species is also reported by Marks et al. who studied the reaction of $\text{Cp}_2\text{Zr}(\text{}^{13}\text{CH}_3)_2$ with MAO. The solid-state ^{13}C PMAS-NMR study at different Al/Zr ratios indicated the formation of a cation like the $\text{Cp}_2\text{ZrCH}_3^+$ species. The data also indicate that the Al:Zr stoichiometry required to form this cation is considerably lower than that employed in a typical catalyst reaction. Siedle et al., [79] employed solution ^{13}C -NMR spectroscopy to demonstrate that dimethyl metallocenes such as $\text{Cp}_2\text{Zr}(\text{}^{13}\text{CH}_3)_2$, $(\text{Me}_5\text{Cp})_2\text{Zr}(\text{}^{13}\text{CH}_3)_2$, $(\text{Indenyl})_2\text{Zr}(\text{}^{13}\text{CH}_3)_2$, $\text{Me}_2\text{Si}(\text{C}_5\text{H}_4)_2\text{Zr}(\text{}^{13}\text{CH}_3)_2$, and $\text{Cp}_2\text{Hf}(\text{}^{13}\text{CH}_3)_2$ undergo degenerate methyl exchange with methyl acceptor compounds such as Me_6Al_2 and $(\text{MeAlO})_x$ (Eq.3.12). The kinetics of degenerate methyl exchange indicate that steric effects are important determinants of the free energy of activation as compared to electronic effects in the formation of cationic species.

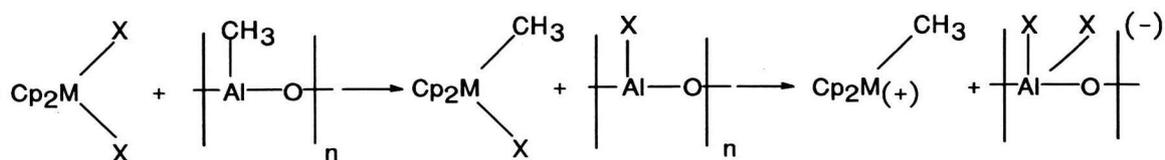
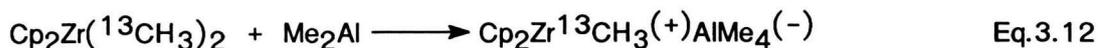


Figure 3.4 Postulated mechanism of formation of the active species in the reaction between metallocenes and methyl aluminoxane [80]

3.4.2 Mechanism of Polymerization

The mechanism of monoolefin polymerization catalyzed by a highly active metallocene–aluminoxane system has been the subject of many experimental and theoretical investigations [7,80–83]. These studies have shown that the Cossee mechanism of polymerization is indeed viable (Fig.3.5) for metallocene catalysts. In the cationic metallocene species, the metal atom is coordinated with the π -ligands and an alkyl group (growing polymer chain). During polymerization, the monomer is coordinated with a highly electrophilic and coordinatively unsaturated cationic complex. It is followed by insertion of a monomer in the metal–carbon bond to produce a polymer chain. The migration of the polymer chain, P, and the formation of the metal–carbon bond occur in concert through a four-center transition state. This results in the recreation of a vacant coordination site at the site originally occupied by the polymer chain. This process involving shifting of the growing chain to the position previously occupied by a coordinated monomer continues until termination of the polymer chain. Modification in the Cossee mechanism by α -agnostic hydrogen interaction has also been suggested [83]. Brintzinger et al. provided experimental evidence for such an α -agnostic hydrogen interaction in zirconocene–catalyzed polymerization of olefin.

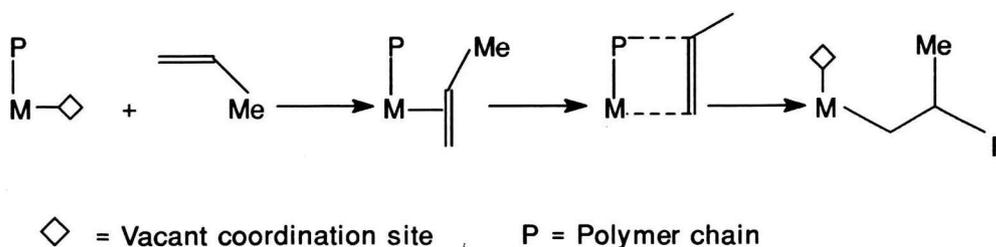


Figure 3.5 Cossee mechanism for Ziegler–Natta olefin polymerization [7].

Stereoregulation in α -olefin polymerization is one of the most important capabilities of metallocene catalyst systems. Propylene polymerization produced four types of polypropylene: isotactic, syndiotactic, atactic, and hemiisotactic [7] (Fig.3.1). There are two types of stereocontrol mechanisms operating: stereochemical control due to chirality of the catalyst (enantiomorphic site control) and stereochemical control due to configuration (chirality) of the last inserted monomer unit (chain end control). These stereocontrol mechanisms do not operate independently in all metallocene catalyst systems. Erker et al. reported [81] that chiral, nonbridged $\text{rac}-(\text{C}_5\text{H}_4\text{CHMePh})_2\text{ZrCl}_2/\text{MAO}$ produces isotactic polypropylene through both chain end control and the enantiomorphic site control mechanism. The polymer obtained (Fig.3.6) consists of 35% isotactic PP of type 1 (enantiomorphic site control) and 65% of type 2 (chain end control) [81]. A number of other studies have revealed that symmetry of the metallocene mostly affects the tacticity of the polymer. A relationship has also been observed among the stereochemistry of the starting metallocene, the stereocontrol mechanism, and the polymer stereoregularity (Table 3.5).

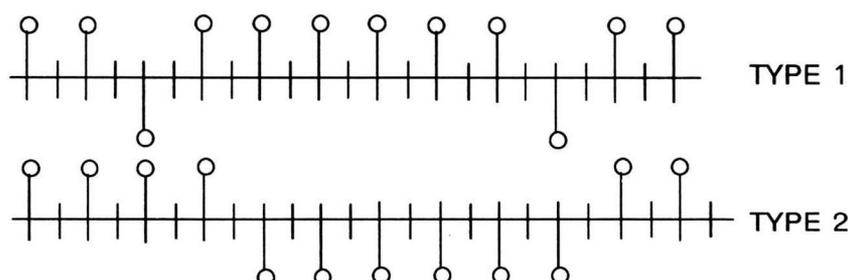


Figure 3.6 Isotactic polypropylene: Type 1, enantiomorphic site-controlled mechanism; Type 2, chain-end-controlled mechanism [81].

Table 3.5 Relationship between Stereochemistry of the Metallocene and Polymer Microstructure

Metallocene system	Symmetry of metallocene	Polymer	Microstructure	Stereocontrol mechanism	Ref.
$\text{rac-Et}(\text{IndH}_4)\text{ZrCl}_2/\text{MAO}$	C_2	PP	Isotactic	Enantiomorphic site controlled	7
$\text{meso-Et}(\text{IndH}_4)\text{ZrCl}_2/\text{MAO}$	C_s	PP	Atactic	Enantiomorphic site controlled	7
$\text{Isopropyl}(\text{Cp}-1\text{-flu})\text{ZrCl}_2/\text{MAO}$	C_s	PP	Syndiotactic	Enantiomorphic site controlled	7
$\text{rac}(\text{C}_5\text{H}_4\text{CHMePh})_2\text{ZrCl}_2/\text{MAO}$	C_2 chiral	PP	Isotactic	Enantiomorphic site controlled	81
$\text{Cp}_2\text{TiCl}_2/\text{MAO}$	C_{2v} achiral	PP	Atactic	Chain end controlled	82
$\text{Cp}_2\text{TiPh}_2/\text{MAO}$	C_{2v} achiral	PP	Isotactic	Chain end controlled	82

3.4.2.1 Enantiomorph-Site Controlled Stereoregulation

The stereorigid ligand environment around the metal is required for the enantiomorph site-controlled mechanism. It helps in distinguishing the enantiofaces of the prochiral monomer and controlling the orientation of monomer insertion into the M-C bond. Metallocenes such as $\text{rac-Et(IndH}_4)_2\text{ZrCl}_2$ and $\text{rac-Et(Ind)}_2\text{ZrCl}_2$ with C_2 symmetry yield an isotactic polymer. The configuration of the catalytic complex is ideally the same during isotactic polymerization [7] (Fig.3.7). Defects also occur during the synthesis of isotactic polymer (Fig.3.8). A syndio-type defect takes place when propylene reacts from the opposite prochiral face, whereas secondary defects produce a polymer with two adjacent methine units. Syndiotactic polymerization [7] of propylene has a regular alternate configuration at adjacent chiral center along the polymer chain (Fig.3.9). A metallocene with C_s symmetry, such as isopropyl-(Cp-1-fluorenyl)ZrCl₂/MAO, produces syndiotactic polypropylene. The enantiomorph site-controlled mechanism has been extended to catalytic complexes yielding

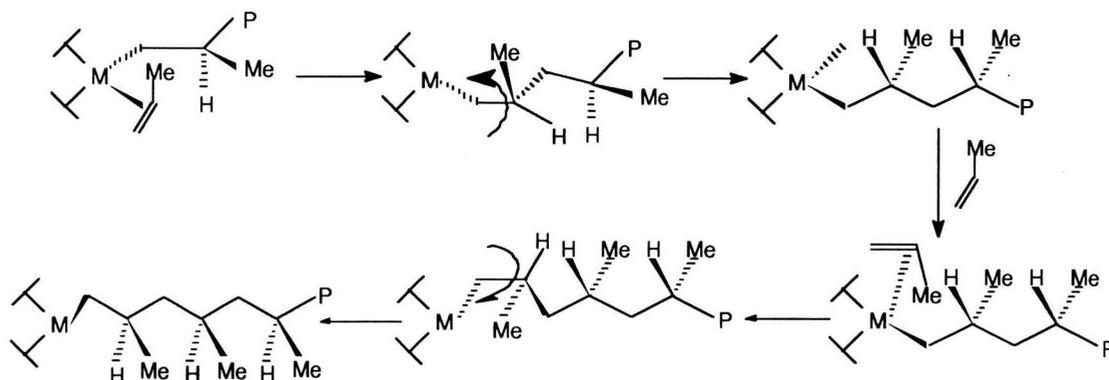


Figure 3.7 Isotactic propylene polymerization by enantiomorph site-controlled mechanism [7].

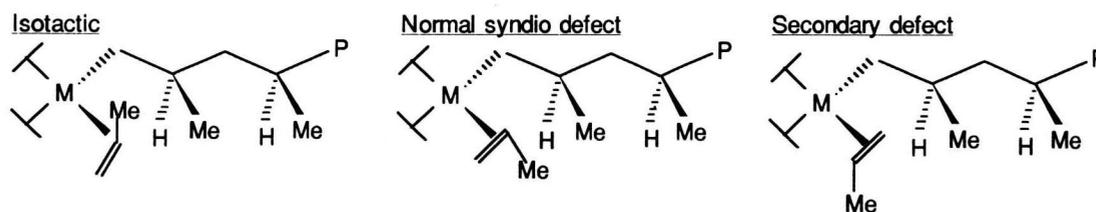


Figure 3.8 Stereodefects in an isotactic polymer chain [7].

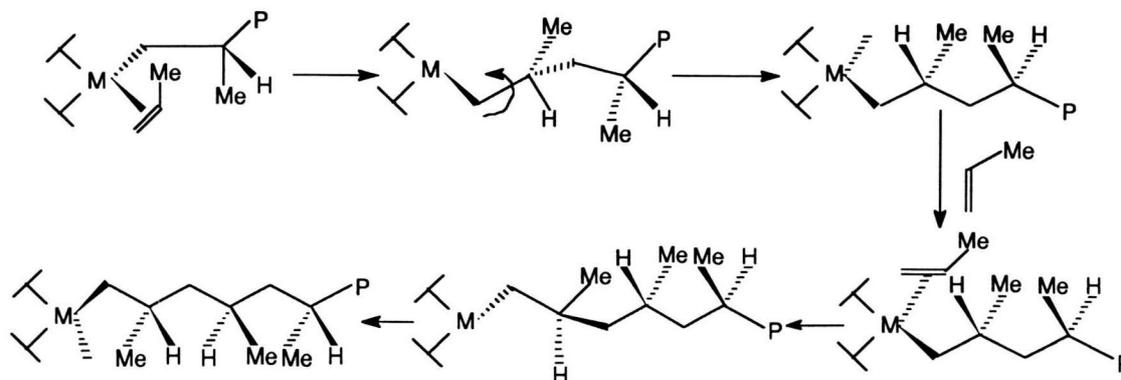


Figure 3.9 Stereoregulation for syndiotactic propylene polymerization by enantiomorphic site-controlled mechanism [7].

hemiisotactic polymer. The mechanism of polymerization additionally involves an isomerization step either with or without monomer coordination. The metallocene $^i\text{Pr}[(3\text{MeCpFlu})\text{ZrCl}_2]/\text{MAO}$ with C_1 symmetry generates hemiisotactic polypropylene.

3.4.2.2 Chain-End Controlled Stereoregulation

In the case of achiral metallocene, the selection between the two faces of the prochiral monomer is dictated predominantly by the configuration of the asymmetric center of the last inserted monomer unit. The catalyst system $\text{Cp}_2\text{TiPh}_2/\text{MAO}$ produces isotactic polypropylene by a chain-end-controlled mechanism (Fig.3.10) [82]. The isotactic polypropylene produced by a chain-end stereocontrol involves an occasional change in the configuration of the last inserted monomer unit which tends to be perpetuated (Fig.3.6). The $\text{Cp}_2\text{MCl}_2/\text{MAO}$ catalyst system polymerizes 1-butene to a predominantly syndiotactic poly(1-butene). This is the first example of a syndiospecific chain-end control (Fig.3.10) mechanism for a metallocene catalyst system.

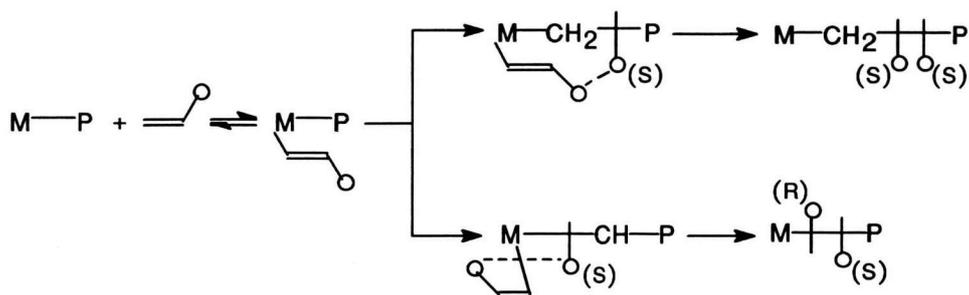


Figure 3.10 Stereochemical chain-end-controlled syndio- and isotactic propylene polymerization [82].

3.4.3 Chain Transfer Mechanism

In metallocene-catalyzed olefin polymerization, the termination of polymer chain occurs through a chain transfer involving β -H elimination (Fig.3.11) [84] and β -Me elimination (Fig.3.12). The termination of a polymer chain may also occur due to chain transfer to aluminum (Fig.3.13) [18,76], monomer (Fig.3.14) [85], or hydrogen (Fig.3.15). All of the mechanisms proposed above are dependent on the nature of the metallocene, aluminoxane, and the polymerization conditions. Resconi et al. [84] studied the contribution of various chain transfer processes in the propylene polymerization reaction due to the different metallocenes and reaction conditions (Table 3.6). $\text{Cp}^*_2\text{MCl}_2/\text{MAO}$ (Cp^* = pentamethylcyclopentadienyl; $\text{M} = \text{Zr, Hf}$) gives atactic propylene oligomers and low molecular weight polymers. The GC-MS and ^1H and ^{13}C -NMR analyses of the products show the presence of unsaturated and saturated end groups. The unsaturated end groups contain vinylidene and allyl groups. Product analysis shows that both $\text{M}-\text{CH}_3$ and $\text{M}-\text{H}$ bonded active species are involved in the chain termination step involving β - CH_3 or β -H elimination.

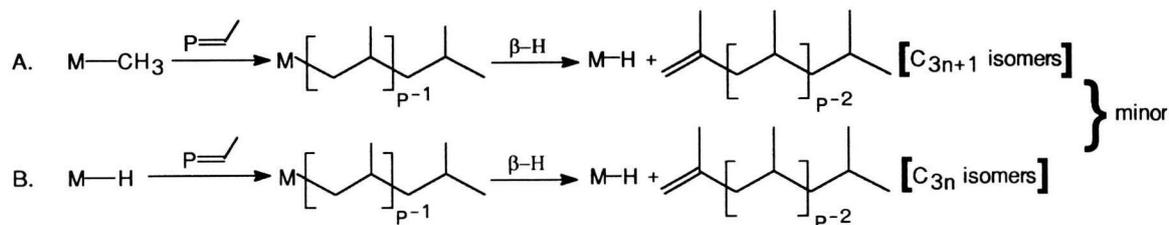


Figure 3.11 Chain transfer via β -H elimination [84].

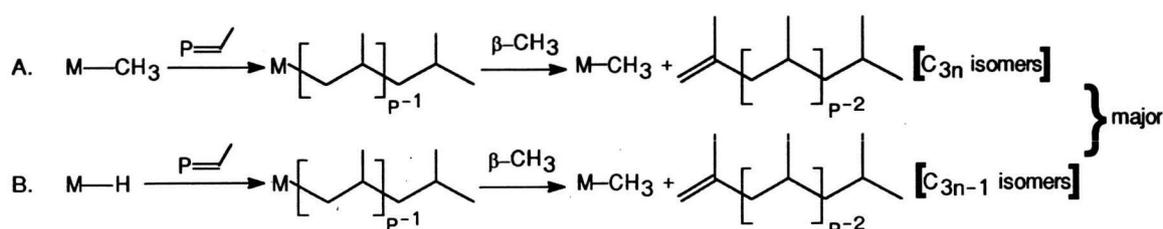


Figure 3.12 Chain transfer via β -Me elimination [84].

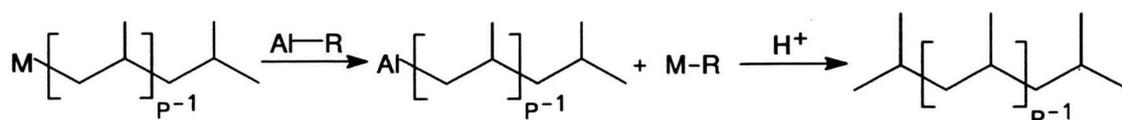


Figure 3.13 Chain transfer via aluminum [84].

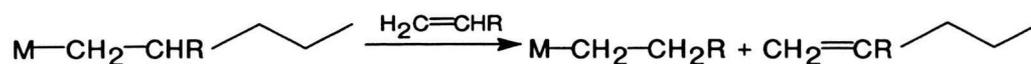


Figure 3.14 Chain transfer to monomer [84].

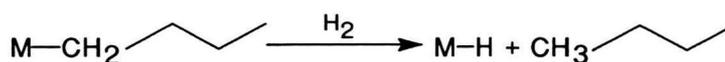


Figure 3.15 Chain transfer to hydrogen [84].

Table 3.6 Percentage of Chain Transfer Mechanisms in Polypropylene Samples^a [84].

Metallocene	T _p (°C)	β-H	β-Me	Al-tr
Cp ₂ ZrCl ₂	50	100	-	-
Cp ₂ ZrCl ₂	0	100	-	-
Cp ₂ HfCl ₂	50	100	-	-
Cp* ₂ ZrCl ₂	50	7.9	91.1	1.0
Cp* ₂ ZrCl ₂	0	7.1	81.8	11.1
Cp* ₂ ZrCl ₂	-40	-	-	100
Cp* ₂ HfCl ₂	50	2.0	98.0	Traces
Cp* ₂ HfCl ₂	0	2.0	62.7	35.3

^aCp = cyclopentadienyl; Cp* = pentamethylcyclopentadienyl.

Percentages calculated from the relative intensities of different end groups; β-H = vinylidene;

β-Me = allyl; Al-tr = (isobutyl alkyl)/2

3.5 POLYMERIZATION GROWTH SITES AND ACTIVE CENTRE

MODELS

Numerous proposals have been made for the structure of the transition metal centres responsible for polymerization. Some of the more important models will be described here.

3.5.1 The Active Centre in TiCl₃-based Catalysts

A determinant factor in the formulation of such structure is the actual locus of polymerization on the TiCl₃ surface. For example, in the mechanism of Cossee and Arlman [85] polymerization is suggested to occur at exposed titanium atoms present on the lateral

faces of TiCl_3 crystals formed by the edges of the close-packed anion planes. Evidence for such a hypothesis comes from electron microscopy studies which have clearly demonstrated polymer growth occurring along spiral dislocations and on surface defects of the $\alpha\text{-TiCl}_3$ crystal. The geometry of the Cossee-Arlman active site is shown in Figure 3.16; the alkyl ligand and three of the chlorines around the titanium atom are square coplanar, the plane through them forming an angle of 55° to the close-packed anion planes. The environments of the alkyl ligand and coordination vacancy are not equivalent, necessitating the 'back-jump' step of the Cossee-Arlman mechanism.

Theoretical calculations have also supported polymerization occurring at edge sites. Layer edges are present in all of the layer forms of TiCl_3 , and an appreciable amount of titanium atoms are located at edge sites in high surface area catalysts.

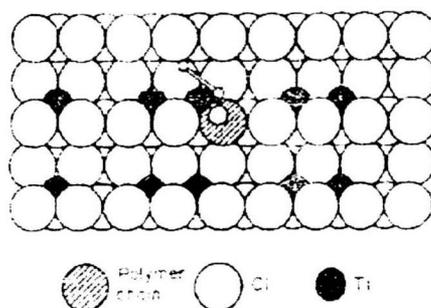


Figure 3.16 Geometry of the active centre in the Cossee-Arlman mechanism [85].

Kissin et al. [86] have proposed a monometallic active centre present in heterogeneous catalysts having two vacant coordination positions and which is located on the basal planes of the lattice crystals. The centres are produced by removal of chlorine atoms from the basal surfaces of the transition metal halide by alkylation reactions, and thus contain metal-carbon bonds. The active site model is shown in Figure 3.17

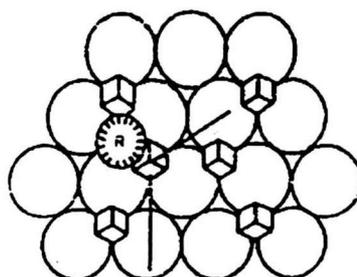


Figure 3.17 Model of active centre for Ziegler-Natta polymerization according to Kissin and Chirkov. R is an alkyl group of small volume; the arrows correspond to the direction of monomer approach [86].

Evidence for the Kissin model was provided by active centre concentration determinations using a methanol inhibition technique. The value obtained for the polymerization of propylene by $\alpha\text{-TiCl}_3\text{-AlEt}_3$ was 3×10^{18} sites m^{-2} and suggested that the active sites practically cover the whole surface of the catalyst. Since the basal planes account for some 95% of the total surface area then the majority of catalytic centres must be located on these planes. It should be noted that the Kissin theory relies on the validity of the methanol inhibition method and furthermore takes no account of catalyst modification and disintegration during polymerization.

Fuji [87] has studied three different catalyst systems for the polymerization of ethylene: (i) TiCl_4 reduced by AlEt_2Cl ; (ii) TiCl_4 reduced by AlEt_2Cl and TiCl_4 added as cocatalyst; and (iii) TiCl_4 reduced by AlEt_2Cl and AlEt_2Cl added as cocatalyst.

The titanium present in all three catalysts was in the Ti^{III} state. However, differences in polymerization rates and the numbers of branches and double bonds in the polymer formed were attributed to the physical state around the titanium atoms. Investigations of concentrations of alkyl groups unstable to heat treatment at 140°C , assumed to be Ti-R linkages, and those that were thermally stable, assumed to be either bonded Al-R or $\text{Ti}\text{---}\text{R}\text{---}\text{Al}$, led Fuji to propose the structures shown in Figure 3.18 for the active centres present in catalysts (i), (ii) and (iii).

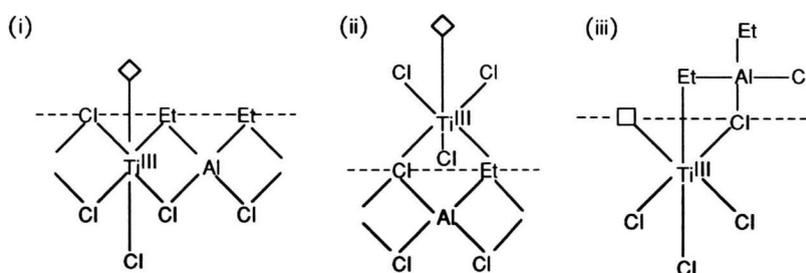


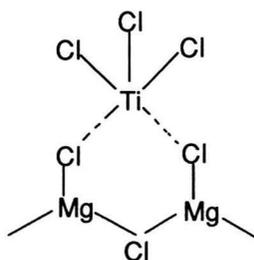
Figure 3.18 Structures proposed for the active centres present in the catalyst systems described by Fuji [87].

3.5.2 Models for Active Centre in Magnesium Chloride Supported Catalysts

Commercially important catalysts for the polymerization of propylene have been developed which are based on the use of magnesium chloride as a support. In a typical preparation anhydrous magnesium chloride is ball-milled in the presence of an electron donor and then reacted with a titanium compound such as TiCl_4 . Although many studies have been made concerning such parameters as the effect of ball-milling on the support, interactions

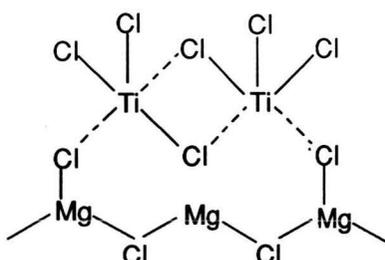
with the electron donor, etc., few models have been proposed for the active centres present in these complex systems.

Chien et al. [88] have made an extensive study of a “high mileage” catalyst prepared by ball-milling magnesium chloride, pre-treated with HCl, in the presence of ethyl benzoate and then treating with p-cresol, AlEt₃ and TiCl₄. The oxidation states of the titanium atoms present were reported as Ti^{II} (8%), Ti^{III} (38%) and Ti^{IV} (54%). Electron paramagnetic studies on the final catalyst revealed a single observable Ti^{III} species which was strongly attached to the catalyst surface (structure 1). This Ti^{III} species is coordinately unsaturated; the vacant coordination position may be occupied by a weak ligand or solvent molecule.



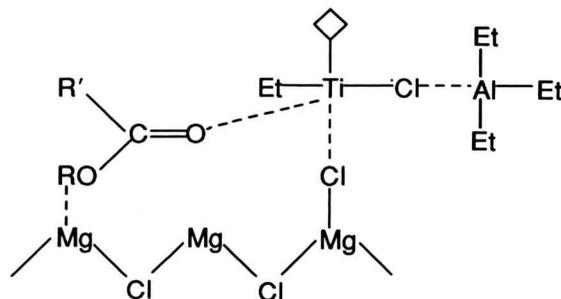
Structure 1

Only approximately 20% of the Ti^{III} present was attributed to the EPR observable species. It was concluded that the remainder of the Ti^{III} had adjacent sites occupied by one or more Ti^{III} ions. Chlorine bridge structures such as that shown in structure 2 were suggested as being responsible for the EPR silence.



Structure 2

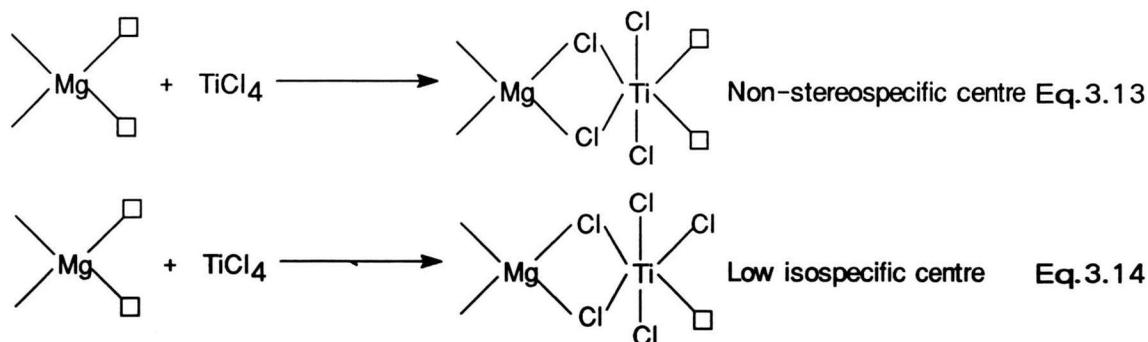
Activation of the catalyst with a mixture of AlEt₃ and methyl p-toluate (3:1) leads to a reduction of 90% of the Ti^{IV} to lower oxidation states. Furthermore, a single Ti^{III} species with rhombic symmetry is produced with a structure believed to be that shown in structure 3. The species was found to be unstable, and on ageing was converted to a Ti^{III} species with axial symmetry.



Structure 3

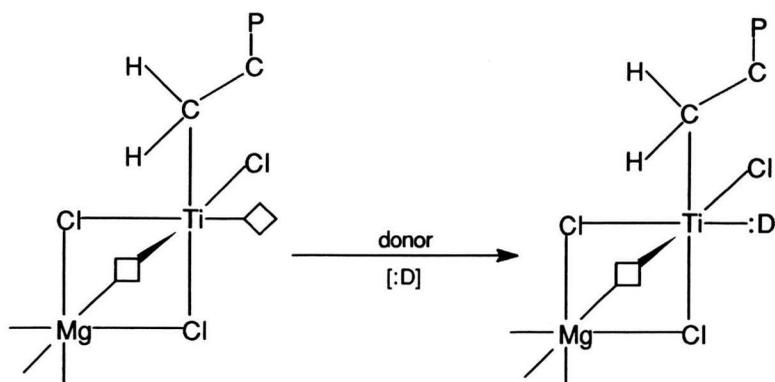
Structure 3 is coordinately unsaturated and contains a Ti^{III} atom with a vacant site and an asymmetric field, and thus fulfills the requirements of a site capable of stereospecific polymerization.

Kakugo et al. [89] have studied the microstructure of polypropylenes produced by TiCl_3 -based and MgCl_2 -supported catalysts using ^{13}C -NMR spectroscopy. Two types of isospecific centres were identified in the catalysts studied which produced polymer with high and low stereospecificities. By analogy with TiCl_3 -based systems, Eq.3.13 and Eq. 3.14 was proposed for the formation of active centres in MgCl_2 -supported catalysts.



Kakugo et al. [89] proposed that the addition of electron donors converts the non-stereospecific centres to ones of high isospecificity, whereas the low isospecific centres are rendered inactive as shown in Eq.3.15 and Eq.3.16

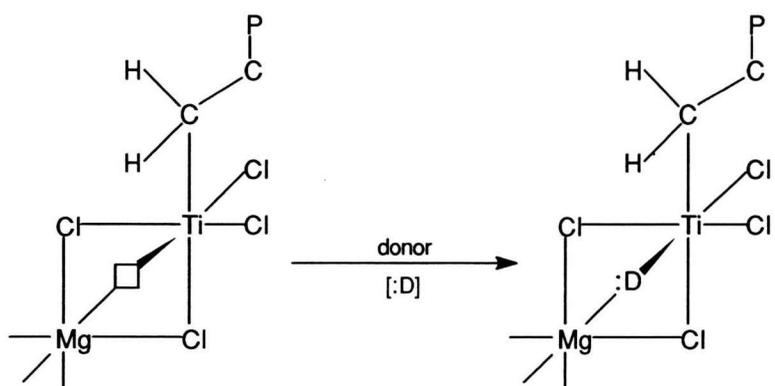
Doi et al. [90] have carried out similar ^{13}C -NMR studies on the structures of polypropylenes produced by various catalyst systems, including $\text{TiCl}_4/\text{AlEt}_3$, $\delta\text{-TiCl}_3/\text{AlEt}_3$, $\text{MgCl}_2/\text{TiCl}_4/\text{ethylbenzoate-AlEt}_3$ and $\text{TiCl}_4/\text{MnCl}_2/\text{ethyl benzoate-AlEt}_3$. Two types of active centre were proposed, one producing highly isotactic polypropylene and the other producing atactic polymer composed of isotactic and syndiotactic stereoblocks of short sequence length.



Eq.3.15

Atactic

Highly isotactic



Eq.3.16

Low isotactic

Inactive

The structures of the centres are shown in Figure 3.19. In site A the surface metal (Mg, Mn or Ti) is coordinatively saturated, whereas in site B it has a chlorine vacancy. Reversible migration of the alkylaluminum compound in site B was suggested as the cause of the frequent changes in polymer structure.

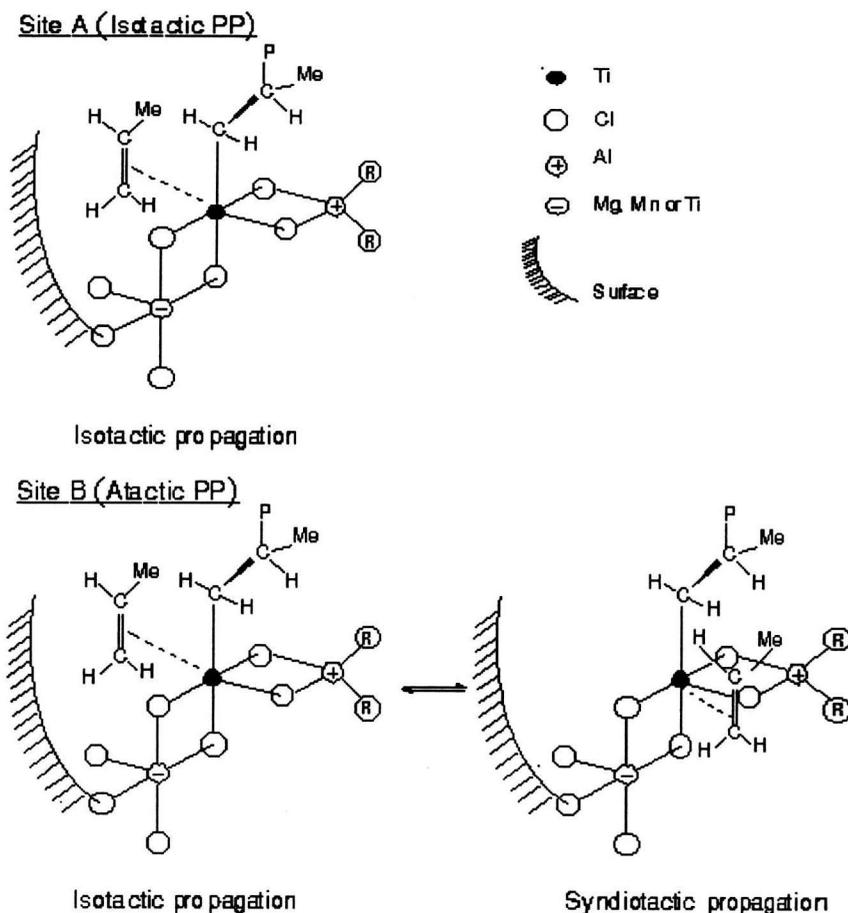


Figure 3.19 Structures for active centres proposed by Doi et al., site A producing highly isotactic polypropylene, site B producing atactic polypropylene [90].

3.5.3 Models for Active Centre in the Phillips Catalysts

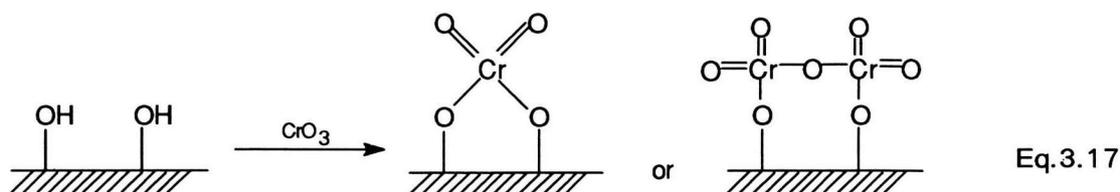
An important catalyst for the commercial polymerization of HDPE is the Phillips Cr/silica catalyst.

The Phillips system comprises an oxide support, usually silica or alumina-silica, impregnated with chromium(VI) oxide to a loading of 0.5–5.0% chromium, typically 1%. Supports are often modified by compounds such as titania.

The catalysts produce high polymerization rates and in contrast to true Ziegler–Natta systems do not require an activator or cocatalyst compound.

The support plays an important role in the stabilization of the Cr^{VI} species; a high temperature treatment is required to activate the catalyst and to remove any moisture from the surface. Heating of unsupported CrO_3 in the range 473–703 K leads to decomposition to Cr^{III} with the evolution of oxygen. However, the use of a support such as silica stabilizes the Cr^{VI} and prevents reduction to Cr^{III} during the heat treatment.

The stabilization of Cr is believed to be due to the interaction of CrO_3 with hydroxyl groups on the support surface. Hogan [67] showed that a $\text{CrO}_3/\text{SiO}_2\text{-Al}_2\text{O}_3$ catalyst containing 2.49 wt% Cr contains 96% as Cr^{VI} after calcination at 813 K in dry air, and he concluded that the stabilization was due to the formation of surface chromate and dichromate species (Eq.3.17)

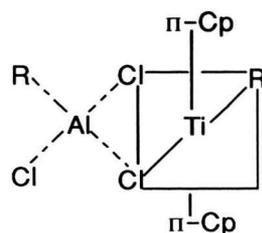


The valence state of Cr during polymerization has been the subject of considerable dispute; every valence state between Cr^{II} and Cr^{VI} has in fact been proposed as the active species. Although some early workers proposed that Cr^{V} was responsible for the polymerization of ethylene, few workers now believe that higher oxidation states are the active species. Most researchers at the present time believe that the active species is Cr^{II} or Cr^{III} , or perhaps a combination of both. However, it is also possible that the coordinative unsaturation of the Cr is as important as its valency.

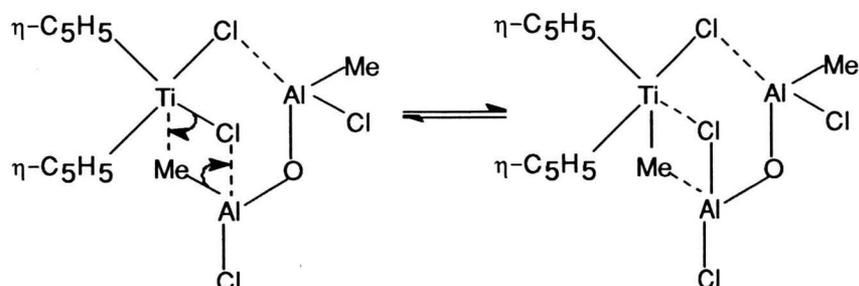
3.5.4 Active Centre in Soluble Catalyst Systems

Much work has been performed using homogeneous Ziegler-Natta catalyst or metallocene-alkylaluminum catalyst systems with the aim of establishing a general mechanistic scheme; such systems are easier to study than heterogeneous systems in that each metal atom is supposed to form an active centre. The studies of Natta using the Cp_2TiCl_2 catalyst for the polymerization of propylene has been described earlier; the model for the active centres of the catalyst $\text{Cp}_2\text{TiCl}_2\text{-AlEtCl}_2$ proposed by Henrici-Olive was shown in structure 4.

More recently a fascinating discovery has been made whereby a very highly active catalyst for the polymerization of ethylene can be prepared by pre-treating AlEt_3 with water and adding to dialkylbis(cyclopentadienyl)titanium(IV) catalysts. Earlier work had shown that the addition of water to homogeneous chloride-containing systems based on bis(cyclopentadienyl)titanium(IV) catalysts increased the activity. Cihlar et al. [91] proposed the stabilized complexes shown in Eq.3.18 from similar studies.

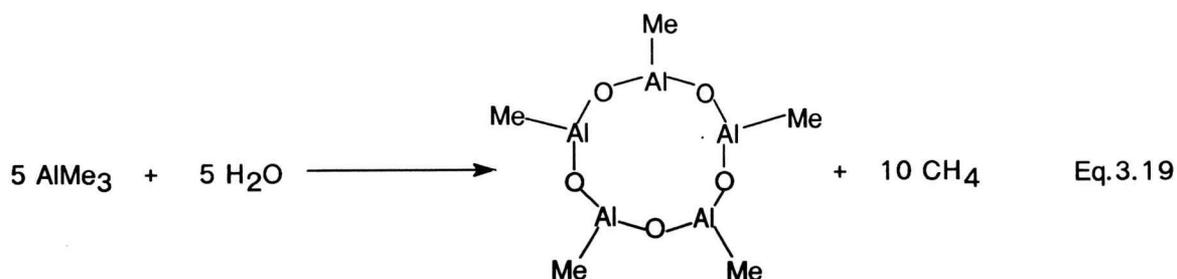


Structure 4



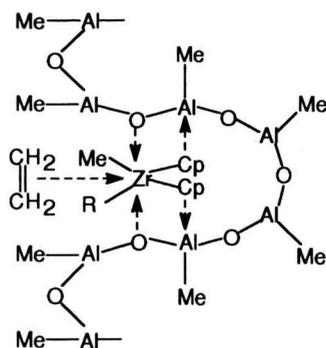
Eq.3.18

The addition of water to AlMe_3 leads to the formation of an oligomeric aluminoxane with the structure $[-\text{OAl}(\text{Me})-]_n$. Further condensation with elimination of AlMe_3 is believed to give rise to cyclic structures of the type suggested by Kaminsky and Sinn [92], shown in Eq.3.19.



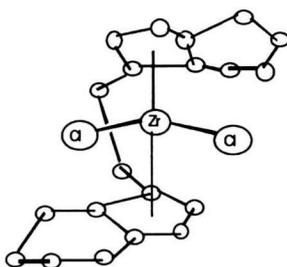
Eq.3.19

Kaminsky et al. [93] have shown that cyclopentadienyl derivatives of zirconium [e.g. bis(cyclopentadienyl)dimethylzirconium] in conjunction with alkylaluminoxanes produce exceptionally active catalysts for ethylene polymerization, $> 10^8$ gPE/gZr. A large excess of aluminoxanes was required and the rate was found to be proportional to the Zr concentration and to depend quadratically on that of the aluminoxane. The polymerization rate increased after an induction period to a maximum value and thereafter remained constant, indicating a 'living' polymerization system. The complex shown in structure 5 was proposed. The system could also polymerize propylene to atactic polymer and copolymers ethylene and propylene.



Structure 5

In later papers, however, Kaminsky et al. have reported that highly isotactic polypropylene can be prepared using stereorigid chiral zirconocenes such as a racemic mixture of ethylenebis(indenyl)zirconium dichloride or ethylene(tetrahydroindenyl)zirconium dichloride together with methylaluminoxane cocatalyst. *rac*-Ethylene bis(tetrahydroindenyl)zirconium dichloride is shown in structure 6.



Structure 6

A separation of racemic mixtures of the zirconocene compounds has been performed to yield an optically pure enantiomer. The use of such a compound has led to the first ever preparation of optically active polypropylene, since the growing polymer chain is formed predominantly in only one screw sense.

3.6 FACTORS DETERMINING CATALYTIC BEHAVIOR

The metallocene–aluminoxane catalyst systems are used for homo-, co-, and terpolymerization of ethylene. However, major attention has been paid to homopolymerization. The natures of metallocene, cocatalyst, and reaction parameters are put to advantage for achieving high productivity. Published and patent literature reveal that both nonstereorigid and stereorigid metallocenes are used for the homopolymerization of ethylene (Table 3.7). These

studies demonstrate that the natures of metal and the ligand of metallocenes highly influence the polymerization reaction [9,18,94-101]. Giannetti et al. [9] studied the effects of the change of sigma ligand around the zirconium atom in Cp_2ZrR_2 on polymer productivity. The productivity increases in the order of $\text{R} = \text{Me} < \text{Ph} < \text{CH}_2\text{Ph} < \text{CH}_2\text{SiMe}_3$. It was also observed that a change of metal in CpMPh_2 increases the productivity of the system in the order of $\text{Zr} > \text{Ti} > \text{Hf}$. The productivity of metallocene having an alkylated cyclopentadienyl ligand is dependent [16,98] on the nature of the alkyl group. Effects of various alkyl groups in catalysts, viz., $(\text{MeCp})_2\text{ZrCl}_2$, $(\text{EtCp})_2\text{ZrCl}_2$, and $(\text{NmCp})_2\text{ZrCl}_2$ (Nm = neomenthyl-cyclopentadienyl), on the productivity demonstrated that the monoalkyl substituent increases the catalytic productivity in the following order $\text{Me} > \text{Et} > \text{Nm}$. Polysubstituted derivatives like pentamethyl have significantly lower productivity. Such observations indicate that electron-donating groups enhance the productivity whereas steric crowding lowers it. Thus, a judicious balance of steric and electronic properties is necessary for designing metallocenes of high productivity. Chien et al. [18] compared the effect of the number of cyclopentadienyl ligands bonded to zirconium, viz., Cp_2ZrCl_2 and CpZrCl_3 , on their productivity. It was observed that Cp_2ZrCl_2 has better activity than CpZrCl_3 . The kinetic parameters in these systems differ by less than a factor of 2 from each other. The nature of metallocenes is found to influence the molecular weight of the polyethylene produced [9]. Ewen et al. [102] studied the effects of a substituent in the cyclopentadienyl ring on the molecular weight of polyethylene. A catalyst possessing a methyl substituent in the cyclopentadienyl ligand is more active and gives a higher molecular weight polymer than catalysts having ethyl-substituted or unsubstituted cyclopentadienyl ligands. The ethylene-bridged metallocene compared to the analogous unbridged metallocene produces a lower molecular weight polyethylene despite possessing similar productivity [100]. The molecular weights/MWD of polyethylenes obtained [95] with mixed metallocenes, viz., Cp_2ZrCl_2 - Cp_2HfCl_2 , Cp_2ZrCl_2 - $\text{Et}(\text{Ind})_2\text{ZrCl}_2$, $(\text{Ind})_2\text{ZrCl}_2$ - $\text{Et}(\text{Ind})_2\text{ZrCl}_2$, and Cp_2HfCl_2 - $\text{Et}(\text{Ind})_2\text{ZrCl}_2$ have been examined. It was observed that the mean molecular weights of the polymers differ from each other by a factor of 3 to 10. The molecular weight distributions vary from 2.5 to 10. Polyethylenes produced with $(\text{Ind})_2\text{ZrCl}_2$ - $\text{Et}(\text{Ind})_2\text{ZrCl}_2$ / MAO and Cp_2HfCl_2 - $\text{Et}(\text{Ind})_2\text{ZrCl}_2$ / MAO give bimodal distributions

Table 3.7 Representative Examples of Metallocene-Aluminoxane Catalyst Systems for Ethylene Polymerization

No.	Catalyst	Co-catalyst	Reaction conditions	Yield	Ref.
1	Cp_2ZrMe_2	MAO	$3.07 \cdot 10^{-7}$ mole/l Zr, $4.34 \cdot 10^{-3}$ mole/l Al, $\text{Pc}_2 = 3 \text{ kg/cm}^2$, 30 min	$32.1 \cdot 10^1$ kgPE/gZr/h	9
2	$\text{Cp}_2\text{Zr}(\text{CH}_2\text{SiMe}_3)_2$	MAO	$3.18 \cdot 10^1$ mole/l Zr, $4.48 \cdot 10^{-3}$ mole/l Al, $\text{Pc}_2 = 3 \text{ kg/cm}^2$, 30 min	$170.0 \cdot 10^4$ kgPE/gZr/h	9
3	Cp_2ZrPh_2	MAO	$2.85 \cdot 10^{-7}$ mole/l Zr, $5.11 \cdot 10^{-3}$ mole/l Al, $\text{Pc}_2 = 3 \text{ kg/cm}^2$, 30 min	$98.4 \cdot 10^1$ kgPE/gZr/h	9
4	$\text{Cp}_2\text{Zr}(\text{CH}_2\text{C}_6\text{H}_5)_2$	MAO	50°C , $\text{Pc}_2 = 3 \text{ kg/cm}^2$, 30 min, $2.96 \cdot 10^{-7}$ mole/l Zr, $4.32 \cdot 10^{-3}$ mole/l Al	$5.51 \cdot 10^1$ kgPE/gZr/h	9
5	$(\text{Ind})_2\text{ZrMe}_2$	MAO	50°C , $\text{Pc}_2 = \text{kg/cm}^2$, 30 min, $2.62 \cdot 10^{-7}$ mole/l Zr, $5.85 \cdot 10^{-3}$ mole/l Al	$217.6 \cdot 10^1$ kgPE/gZr/h	9
6	Cp_2HfPh_2	MAO	$3.0 \cdot 10^{-7}$ mole/l Hf, $3.7 \cdot 10^{-3}$ mole/l Al, $\text{Pc}_2 = 3 \text{ kg/cm}^2$, 30 min	$4185 \cdot 10^1$ kgPE/gHf/h	9
7	Cp_2TiPh_2	MAO	$2.62 \cdot 10^{-7}$ mole/l Ti, $4.86 \cdot 10^{-3}$ mole/l Al, $\text{Pc}_2 = 3 \text{ kg/cm}^2$, 30 min	$35.7 \cdot 10^1$ kgPE/gTi/h	9
8	Cp_2HfMe_2	MAO	$3.0 \cdot 10^{-7}$ mole/l Hf, $4.52 \cdot 10^{-3}$ mole/l Al, $\text{Pc}_2 = 3 \text{ kg/cm}^2$, 30 min	$0.50 \cdot 10^4$ kgPE/gHf/h	9
9	Bis(neomenthylcyclopentadienyl)ZrCl ₂	MAO	$\text{PC}_2\text{H}_4 = 8 \text{ bar}$, $[\text{Zr}] = 0.35 \mu\text{M}$, $[\text{Al}] = 64.6 \text{ mM}$, 90°C	$87 \cdot 10^1$ kgPE/(g compound \cdot h \cdot atm)	16
10	Cp_2ZrCl_2	Hexaisobutyl tetraaluminoxane - Me ₃ Al	85°C , 9 kg/cm^2 , 2 h, heptane-hexane	Polymer	94
11	$\text{Cp}_2\text{HfCl}_2/\text{Cp}_2\text{ZrCl}_2$	MAO	60°C , $\text{Pc}_2 = 5 \text{ bar}$, 330 mL toluene, MAO = $1.5 \cdot 10^{-2}$ mole, Hf = $10 \cdot 10^{-7}$ mole/l, Zr = $1.0 \cdot 10^{-7}$ mole/l	0.009 kgPE	95

(continued)

No.	Catalyst	Co-catalyst	Reaction conditions	Yield	Ref.
12	$\text{Et}(\text{Ind})_2\text{ZrCl}_2/\text{Cp}_2\text{HfCl}_2$	MAO	$\text{Hf} = 1.0 \cdot 10^{-7}$ mole/l, $T = 60^\circ\text{C}$, $\text{Pc}_2 = 5$ bar, MAO = $1.5 \cdot 10^{-2}$ mole/l, 330 mL toluene	0.006 kgPE	95
13	$\text{Et}(\text{Ind})_2\text{ZrCl}_2/\text{Cp}_2\text{HfCl}_2$	MAO	$\text{IndZr} = 1.0 \cdot 10^{-7}$ mole/l, 60°C $\text{CpZr} = 1.0 \cdot 10^{-7}$ mole/l, $\text{Pc}_2 = 5$ bar MAO = $1.5 \cdot 10^{-2}$ mole/l,	0.003 kgPE	95
14	$\text{Et}(\text{Ind})_2\text{ZrCl}_2/\text{Ind}_2\text{HfCl}_2$	MAO	$\text{IndZr} = 1.0 \cdot 10^{-7}$ mole/l, 60°C $\text{CpZr} = 1.0 \cdot 10^{-7}$ mole/l, $\text{Pc}_2 = 5$ bar MAO = $1.5 \cdot 10^{-2}$ mole/l,	0.009 kgPE	95
15	$\text{Cp}_2\text{TiPh}_2/\text{Cp}_2\text{ZrMe}_2$	MAO	$\text{Ti} = 0.906$ mg, $\text{Zr} = 0.102$ mg	0.02 kgPE	95
16	Cp_2ZrCl_2	MAO	60°C , 3 bar	82,800 kgPE/(moleZr ^h *bar)	95
17	$\text{Et}(\text{Ind})_2\text{ZrCl}_2$	MAO	60°C , 3 bar	98,760 kgPE/(moleZr ^h *bar)	95
18	$(\text{Ind})_2\text{ZrCl}_2$	MAO	60°C , 3 bar	61,920 kgPE(moleZr ^h *bar)	95
19	Cp_2HfCl_2	MAO	60°C , 3 bar	7,320 kgPE/(moleHf ^h *bar)	95
20	Cp_2ZrMe_2	MAO	90°C , 8 bar	$24.8 \cdot 10^3$ kgPE/(moleZr ^h *bar)	96
21	Cp_2TiMe_2	MAO	20°C , 8 bar, $5 \cdot 10^{-3}$ mole [Al]	0.5 kgPE/(gTi ^h *bar)	97
22	Cp_2TiMeCl	MAO	20°C , 8 bar, $5 \cdot 10^{-3}$ mole [Al]	50 kgPE/(gTi ^h *bar)	97
23	Cp_2TiCl_2	MAO	20°C , 8 bar, $5 \cdot 10^{-3}$ mole [Al]	90 kgPE/(gTi ^h *bar)	97
24	Cp_2HfMe_2	MAO	70°C , 8 bar, $5 \cdot 10^{-3}$ mole [Al]	60 kgPE/(gHf ^h *bar)	97
25	Cp_2ZrCl_2	Ethylaluminoxane	60°C , 8 bar, $5 \cdot 10^{-3}$ mole [Al]	23 kgPE/(gZr ^h *bar)	97
26	Cp_2ZrMe_2	Tetraisobutyldialuminoxane	70°C , 8 bar, $5 \cdot 10^{-3}$ mole [Al]	175 kgPE/(gZr ^h *bar)	97
27	$(\text{MeCp}_2)_2\text{ZrCl}_2$	Ethylaluminoxane	70°C , 10 bar, 45 min	$1.7 \cdot 10^2$ kgPE/(moleZr ^h)	98
28	$(\text{EtCp}_2)_2\text{ZrCl}_2$	Ethylaluminoxane	70°C , 10 bar, 45 min	$4.8 \cdot 10^2$ kgPE/(moleZr ^h)	98
29	$(\text{i-PrCp})_2\text{ZrCl}_2$	Ethylaluminoxane	70°C , 10 bar, 45 min	$3.2 \cdot 10^2$ kgPE/(moleZr ^h)	98
30	$(\text{t-BuCp})_2\text{ZrCl}_2$	Ethylaluminoxanel	70°C , 10 bar, 45 min	$8.6 \cdot 10^2$ kgPE/(moleZr ^h)	98
31	$(\text{Me}_3\text{SiCp})_2\text{ZrCl}_2$	Ethylaluminoxane	70°C , 10 bar, 45 min	$4.9 \cdot 10^2$ kgPE/(moleZr ^h)	98

(continued)

No.	Catalyst	Co-catalyst	Reaction conditions	Yield	Ref.
32	(PhMe ₂ Ccp) ₂ ZrCl ₂	Ethylaluminoxane	70 °C, 10 bar, 45 min	1.7*10 ² kgPE/(moleZr*h)	98
33	(Me ₃ Cp)CpZrCl ₂	MAO	70 °C, [Zr] = 1 μM, [Al] = 15.0 mm	0.57*10 ⁴ kgPE/(g compound*h*atm)	99
34	(Me ₃ Cp) ₂ ZrCl ₂	MAO	70 °C, [Zr] = 1 μM, [Al] = 15.0 mm	0.38*10 ⁴ kgPE/(g compound*h*atm)	99
35	Bis(5,6-dimethylindenyl)-ZrCl ₂	MAO	25 °C, 0.75 bar C ₂ H ₄ , [Al]:[Zr] = 2000:1	25,200 kgPE/(moleZr*h)	100
36	Bis(4,7-dimethylindenyl)-ZrCl ₂	MAO	25 °C, 0.75 bar C ₂ H ₄ , [Al]:[Zr] = 2000:1	13,800 kgPE/(moleZr*h)	100
37	Bis(5,6-dimethylindenyl)-ZrCl ₂	MAO	25 °C, 0.75 bar C ₂ H ₄ , [Al]:[Zr] = 2000:1	122 kgPE/(moleZr*h)	100
38	Et(Ind) ₂ ZrCl ₂	MAO	2 bar C ₂ H ₄ , 6.25*10 ⁻⁶ mole metallocene	10,000 kgPE/(moleZr*h)	100
39	Et(Me ₂ Ind) ₂ ZrCl ₂	MAO	2 bar C ₂ H ₄ , 6.25*10 ⁻⁶ mole metallocene	22,200 kgPE/(moleZr*h)	100
40	Et(MeOInd) ₂ ZrCl ₂	MAO	2 bar C ₂ H ₄ , 6.25*10 ⁻⁶ mole metallocene	120 kgPE/(moleZr*h)	100
41	rac[Me ₂ Si(Ind) ₂]ZrCl ₂	MAO	2 bar C ₂ H ₄ , 6.25*10 ⁻⁶ mole metallocene	36,900 kgPE/(mole metallocene*h)	101
42	rac[Ph ₂ Si(Ind) ₂]ZrCl ₂	MAO	2 bar C ₂ H ₄ , 6.25*10 ⁻⁶ mole metallocene	20,000 kgPE/(mole metallocene*h)	101
43	rac[Bz ₂ Si(Ind) ₂]ZrCl ₂	MAO	2 bar C ₂ H ₄ , 6.25*10 ⁻⁶ mole metallocene	12,200 kgPE/(mole metallocene*h)	101
44	rac[Me ₂ C(Ind)(MeCp)]ZrCl ₂	MAO	2 bar C ₂ H ₄ , 6.25*10 ⁻⁶ mole metallocene	2,700 kgPE/(mole metallocene*h)	101
45	rac[Et(IndH ₄) ₂]ZrCl ₂	MAO	2 bar C ₂ H ₄ , 6.25*10 ⁻⁶ mole metallocene	22,200 kgPE/(mole metallocene*h)	101
46	[Me ₂ C(Fluo)(Cp)]ZrCl ₂	MAO	2 bar C ₂ H ₄ , 6.25*10 ⁻⁶ mole metallocene	2,000 kgPE/(mole metallocene*h)	101

with MWD = 5.5 to 10. The bimodal distribution becomes monomodal by changing the zirconium-hafnium ratio in the $\text{Cp}_2\text{HfCl}_2\text{-Et(Ind)}_2\text{ZrCl}_2\text{-MAO}$ system.

The composition of cocatalyst in terms of free Me_3Al and MAO governs the overall performance of metallocene systems toward ethylene polymerization. It was observed [9] that an excess of free trimethylaluminum in methylaluminoxane decreases the productivity for both $(\text{Ind})_2\text{ZrMe}_2$ and $\text{Cp}_2\text{Zr}(\text{CH}_2\text{-C}_6\text{H}_5)_2$ systems. The former complex seems less sensitive than the latter one to the cocatalyst composition. The effect of the replacement of MAO with trimethylaluminum on the productivity of Cp_2ZrCl_2 was studied [15]. There is little effect on ethylene polymerization by replacement of 90% MAO with trimethylaluminum. The rate of polymerization and yield are reduced by a factor of 3 to 4 when 99% of methylaluminoxane is replaced with trimethylaluminum. The molecular weight of polyethylene produced by the $\text{Cp}_2\text{ZrCl}_2\text{-MAO-Me}_3\text{Al}$ system is decreased by increasing ratio of Me_3Al to MAO from 2 to 10. At $[\text{Me}_3\text{Al}]/[\text{MAO}] < 2$, the molecular weight remains unaffected whereas at 10 it is reduced by 40%.

The concentrations of catalyst and cocatalyst in metallocene-aluminoxane systems influence the polymerization productivity and molecular weight of the polyethylene produced. A detailed investigation was reported for $\text{CpZrCl}_3/\text{MAO}$, $\text{Cp}_2\text{ZrCl}_2/\text{MAO}$, and $(\text{NmCp})_2\text{ZrCl}_2/\text{MAO}$ catalyst systems [15-16,18]. The productivity of the $\text{Cp}_2\text{ZrCl}_2\text{-MAO}$ system was found to increase proportionately with an increase of Al/Zr ratios at constant MAO concentration. Cocatalyst concentration-dependent studies of the $(\text{NmCp})_2\text{ZrCl}_3/\text{MAO}$ catalyst system show that a threshold value of $[\text{Al}]/[\text{Zr}]$, i.e., 3×10^3 , is necessary for the activity of the catalyst. The polymerization is inhibited below this concentration. Furthermore, the ratio of $[\text{MAO}]/[\text{Zr}]$ should be greater than $n[(\text{O-AlMe})_n]$ to avoid deactivation of active species.

The performance of metallocene catalysts as a function of time [15-16,18] were investigated for $\text{Cp}_2\text{ZrCl}_2/\text{MAO}$, $\text{CpZrCl}_3/\text{MAO}$, and $(\text{NmCp})_2\text{ZrCl}_2/\text{MAO}$ systems. The kinetic profile of these systems indicates that the rate of polymerization is initially fast, followed by a steady state, and then decreases within a few minutes. The kinetic profile is found to depend on the polymerization temperature and concentration of zirconocenes. The decay in the rate of polymerization is less at a higher ratio of MAO to metallocene. At the same $[\text{Al}]/[\text{Zr}]$ ratio, the deactivation process is retarded by bulky substituents on the

cyclopentadienyl ring. Kinetic studies on $^i\text{Pr}[\text{FluCp}]\text{ZrCl}_2/\text{MAO}$ and $\text{Me}_2\text{Si}[\text{Ind}]_2\text{ZrCl}_2/\text{MAO}$ systems indicate a first order dependence on the concentration of zirconium [103]. Tsutsui et al. [104] examined short-time kinetic studies on the $\text{Cp}_2\text{ZrCl}_2/\text{MAO}$ catalyst system. The concentration of active centers and the polymerization rate constant in toluene were found to be 1 mole/mole Zr and $1700 \text{ L}(\text{mole}\cdot\text{s})^{-1}$, respectively. Kinetic analysis of $\text{Cp}_2\text{ZrCl}_2/\text{MAO} + \text{Me}_3\text{Al}$ indicated that the Me/Al ratio in MAO needs to be suitably adjusted to produce a catalyst of high activity and long kinetic life. Studies on the $\text{Cp}_2\text{ZrCl}_2/\text{MAO}$ system revealed that the kinetic profile of the system [105] does not vary with changing monomer concentration whereas it affects the molecular weight of the polyethylene and the activity of the system.

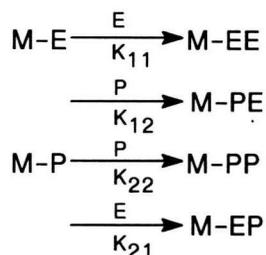
The effect of temperature on productivity was studied for $\text{Cp}_2\text{ZrCl}_2/\text{MAO}$ [15,18], $(\text{NmCp})_2\text{ZrCl}_2/\text{MAO}$ [16], $\text{CpZrCl}_3/\text{MAO}$ [18], $\text{Cp}_2\text{ZrPh}_2/\text{MAO}$ [9], $(\text{Ind})_2\text{ZrMe}_2/\text{MAO}$ [9], $\text{Et}(\text{Ind})_2\text{ZrCl}_2/\text{MAO}$ [106], and $\text{Et}(\text{Ind})_2\text{HfCl}_2/\text{MAO}$ [106] systems. In the case of Cp_2ZrCl_2 , $(\text{Ind})_2\text{ZrMe}_2$, and Cp_2ZrPh_2 , it was observed that there is an optimum temperature for maximum productivity. The productivity was found to increase monotonically with a rise of temperature for $(\text{NmCp})_2\text{ZrCl}_2/\text{MAO}$. The Arrhenius plot shows no deviation from linearity between 0 to 40 °C, and it shows an activation energy of $7.4 \text{ Kcal}\cdot\text{mole}^{-1}$ for propagation. A decrease in polymerization temperature lowers the number of active metallocene sites [107]. A higher temperature is reported to decrease the molecular weight in systems like $\text{Et}(\text{Ind})_2\text{ZrCl}_2$ and $\text{Et}(\text{Ind})_2\text{HfCl}_2$ [106]. In the case of $(\text{NmCp})_2\text{ZrCl}_2$ [16], it was observed that MW is higher at lower polymerization temperatures. The temperature affects the modality pattern of polyethylene as revealed from an investigation on the $(\text{Ind})_2\text{ZrCl}_2$ - $\text{Et}(\text{Ind})_2\text{ZrCl}_2$ -MAO system [95]. A GPC study showed that an increase of temperature from 40 to 60 °C leads to a bimodal distribution instead of a plateau.

Hydrogen was used in combination with a metallocene-methylaluminoxane system to govern the molecular weight of the polymer [18,96]. Variation in the concentration of hydrogen changes the kinetic profile of the $\text{Cp}_2\text{ZrCl}_2/\text{MAO}$ system [18]. It was observed that productivity decreases by 40–50% in the presence of hydrogen. Furthermore, the molecular weight of the polymer decreases with increasing hydrogen concentration.

The nature of the solvent influences the catalytic activity of metallocene catalyst systems for ethylene polymerization [104]. A change of solvent from toluene to n-decane

reduces the productivity of $\text{Cp}_2\text{ZrCl}_2/\text{MAO}$ to one-tenth. Similarly in the case of $(\text{Ind})_2\text{ZrMe}_2/\text{MAO}$, a change of solvent from toluene to heptane significantly lowers the productivity.

Very limited studies have been carried out in the area of copolymerization of ethylene with α -olefins (Table 3.8). The copolymerization behavior of a few metallocenes were reported using propylene as a comonomer [102,104,108-111]. The change in the kinetic profile is linked with a variation in the nature of the substituent bonded to the zirconocene, and the productivities are in the following order: $\text{Et}(\text{Ind})_2\text{ZrCl}_2 > (\text{Ind})_2\text{ZrCl}_2 > \text{Et}(\text{Ind})_2\text{ZrMe}_2$. Radio-labeling experiments indicated [109] that about 80% of zirconium in the $\text{Et}(\text{Ind})_2\text{ZrCl}_2/\text{MAO}$ system is catalytically active. The productivity in other types of metallocene is found to have the following decreasing order: $\text{Cp}_2\text{ZrCl}_2 > \text{Cp}_2\text{ZrMe}_2 > \text{Cp}_2\text{HfCl}_2 > \text{Cp}_2\text{TiCl}_2$. The metallocene chemical structure governs the reactivity ratios [108] of ethylene-propylene copolymerization (Table 3.9). A scheme is proposed for binary copolymerization where $r_1 = K_{11}/K_{12}$ and $r_2 = K_{22}/K_{21}$.



where M = metal, P = Propene, and E = Ethylene.

A regular trend of decrease in r_1 values from 60 to 1 is observed with a change in the symmetry properties of metallocene from C_{2v} to C_2 to C_s . The numerical values of the product of $r_1 r_2$ are close to 1 for C_2 precursors and lower than 1 for the C_s . These values are rationalized in terms of nonbonded interactions of the incoming monomer with the same carbon atom of the growing chain. The copolymerization performance of the $\text{Et}(\text{Ind})_2\text{ZrCl}_2/\text{MAO}$ system is affected by the variation of Al/Zr ratio, temperature, and catalyst

Table 3.8 Representative Examples of Metallocene-Aluminoxane Catalyst Systems for the Copolymerization of Ethylene with α -Olefins.

No.	Catalyst systems	Monomer/comonomer	Reaction conditions	Polymer yield	Ref.
1	rac-Et(Ind) ₂ ZrCl ₂ /MAO	Ethylene/1-butene	30 °C, 5 bar, 0.54 mole butene-1	LLDPE	106
2	rac-Et(Ind) ₂ HfCl ₂ /MAO	Ethylene/1-butene	30 °C, 5 bar, 0.54 mole butene-1	LLDPE	106
3	Isopropylidene(cyclopentadienyl)(fluorenyl) zirconium dichloride/MAO	Ethylene/propylene	Zr = 1.39-1.75 mole, Al/Zr = 820-1290, time = 30-60 min	1.8-4.0 kg polymer/mmole catalyst	108
4	Cp ₂ HfCl ₂ /MAO	Ethylene/propylene	Zr = 1.0 mm, 10 psig, 50 °C	3.0*10 ³ kg polymer/mole metallocene/h/bar	103
5	Cp ₂ ZrCl ₂ /MAO	Ethylene/1-butene	70 °C, Al/Zr = 10 ³ , 1 h, C ₆ 25 mM	1.71*10 ² kg polymer/(gZr*[C ₂]h)	108
6	Et(Ind) ₂ ZrCl ₂ /MAO	Ethylene/1-butene	70 °C, Al/Zr = 10 ³ , 1 h, C ₆ 25 mM	2.16*10 ² kg polymer/(gZr*[C ₂]h)	110
7	(MeCp) ₂ ZrCl ₂ /MAO + Bu ₃ Al	Ethylene/4-methyl-1-pentene	-	0.04 kg polymer	111
8	(Me ₃ Cp) ₂ ZrCl ₂ /aluminoxane	Ethylene/propylene	5*10 ⁻⁴ mmoleZr compound, C ₂ H ₄ 40 L/h, C ₃ H ₆ 60 L/h, 30 min	Polymer	111

concentratio. The addition of a Lewis base to the catalyst retards the rate of copolymerization as well as the productivity. All of these variations in the above-mentioned reaction parameters change the molecular weight and ethylene content of the copolymer. The substitution of MAO by trimethylaluminum decreases the rate of polymerization for the $\text{Et}(\text{Ind})_2\text{ZrCl}_2/\text{MAO}$ system. It appears that the alkylating nature, complexing behavior, and degree of oligomerization of the cocatalyst ($\text{Me}_3\text{Al} + \text{MAO}$) may individually or in combination act to reduce productivity.

Table 3.9 Reactivity Ratios r_1 and r_2 in the Copolymerization of Ethylene (1) and Propylene (2) Performed in the Presence of Different Metallocene/Methyl Aluminoxane Catalyst System [108].

Metallocene ^a	Symmetry	Temperature (°C)	r_1	r_2	r_1r_2
$(\text{Me}_5\text{Cp})_2\text{ZrCl}_2$	C_{2v}	50	250.0	0.002	0.50
$(\text{MeCp})_2\text{ZrCl}_2$	C_{2v}	50	60.0	-	-
Cp_2ZrCl_2	C_{2v}	50	48.0	0.015	0.72
Cp_2ZrMe_2	C_{2v}	60	31.5	0.005	0.25
$(\text{Me}_2\text{Si})\text{Cp}_2\text{ZrCl}_2$	C_{2v}	50	24.0	0.029	0.70
Cp_2TiPh_2	C_{2v}	50	19.5	0.015	0.29
Cp_2TiMe_2	C_{2v}	36	10.6	0.0032	0.60
$\text{Et}(\text{Ind})_2\text{ZrCl}_2$	C_2	50	6.61	0.06	0.40
$\text{Et}(\text{Ind})_2\text{ZrCl}_2$	C_2	25	6.26	0.11	0.69
$\text{Et}(\text{Ind})_2\text{ZrCl}_2$	C_2	0	5.20	0.14	0.73
$\text{Me}_2\text{C}(\text{Cp})(\text{Glu})\text{ZrCl}_2$	C_s	25	1.3	0.20	0.26

^a Me = CH_3 , Cp = cyclopentadienyl. Ph = C_6H_5 , Et = C_2H_5 , Ind = indenyl, Flu = fluorenyl.

Studies of ethylene copolymerization with 1-butene using the $\text{Cp}_2\text{ZrCl}_2/\text{MAO}$ system indicated a decrease in the rate of polymerization with increasing comonomer concentration. The reactivity ratios determined as a function of temperature [112] were found to be $r_1 = 65$ and $r_2 = 0.005$. The activation energy for K_{22} . The molecular weight distributions of the ethylene-1-butene copolymer were found to be narrow ($Q = 2-3$). $\text{Et}(\text{Ind})_2\text{ZrCl}_2$ shows a lower productivity than the analogous hafnium compound [106]. It is remarkable that the hafnium analogue has a much higher capability of incorporating the comonomer (1-butene)

on the zirconium catalyst. Furthermore, polymers obtained with the hafnium catalyst have average molar masses 10 times higher than those synthesized with the zirconium compound.

The performances of $\text{Cp}_2\text{ZrCl}_2/\text{MAO}$ [104] and $\text{Et}(\text{Ind})_2\text{ZrCl}_2/\text{MAO}$ [110] systems have been investigated for ethylene-1-hexene copolymerization. The activation energy is high (47.5 KJ/mole) as compared to ethylene-1-butene copolymerization. The reactivity ratios were found to be $r_1 = 55$ and $r_2 = 0.005$ and nearly independent of temperature in the range of 20 to 60 °C. The reactivity ratios product (r_1r_2) of less than 1 suggests an alternating sequence for the insertion of the monomer. The observation of about a twofold increase in the rate of ethylene consumption by the addition of 1-hexene is due to the increase of K_p [104]. The order of reaction with respect to aluminum is 0.8, which is considerably higher than that of homopolymerization. Variation in the metallocene concentration does not significantly change the incorporation of 1-hexene in the copolymer. $\text{Et}(\text{Ind})_2\text{ZrCl}_2/\text{MAO}$ is more active than the $\text{Cp}_2\text{ZrCl}_2/\text{MAO}$ system [110]. The copolymer shows a narrow distribution of molecular weights (MWD = 2).

Terpolymerization of ethylene-propylene-ethylidene norbornene (Table 3.10) was investigated using the Cp_2ZrMe_2 and $\text{Et}(\text{Ind})_2\text{ZrCl}_2$ catalyst systems [113]. It was reported that a soluble catalyst formed from Cp_2ZrMe_2 and MAO produces terpolymers of EPDM. The overall productivities lie between 100 and 1000 kg EPDM/(moleZr*h*bar). The polymerization rate increases after an induction period and then levels at a value which remains constant for several days. The change in the mole ratio of ethylene/propylene influences the productivity of the catalyst. The $\text{Et}(\text{Ind})_2\text{ZrCl}_2/\text{MAO}$ system [113] is 2 times more productive than $\text{Cp}_2\text{ZrMe}_2/\text{MAO}$. The diene content of the terpolymer is controlled in both Cp_2ZrMe_2 and $\text{Et}(\text{Ind})_2\text{ZrCl}_2$ systems by changing the concentration of diene during polymerization. The polymer contains 3 to 22 wt% of diene. A narrow distribution of molecular weights of the terpolymer is observed with $\text{Cp}_2\text{ZrMe}_2/\text{MAO}$ (MWD = 1.7) and $\text{Et}(\text{Ind})_2\text{ZrCl}_2/\text{MAO}$ (MWD = 1.97-2.26) systems. The observance of narrow molecular weight distribution is in contrast to the known heterogeneous zirconium and titanium catalysts which give a broad molecular weight distribution product. Microstructure examination of the terpolymer synthesized by the $\text{Cp}_2\text{ZrMe}_2/\text{MAO}$ system indicates the absence of head-to-head sequences of propylene. Thus, the regiospecific nature of the metallocene catalyst toward propylene polymerization leads to exclusive formation of head-to-tail enchainments of propylene in the terpolymer.

The terpolymerization of ethylene-propylene-1,5-hexadiene (Table 3.10) was studied by using the $\text{Et}(\text{Ind})_2\text{ZrCl}_2/\text{MAO}$ system [113-115]. The polymerization activity varies with a change in the ethylene/propylene mole ratio and the concentration of 1,5-hexadiene. The polymerization time and concentration of 1,5-hexadiene control the average molecular weight and molecular weight distribution of the terpolymer. With systems like $\text{Cp}_2\text{ZrX}_2/\text{MAO}$, the incorporation of longer chain dienes in the polymer has not been observed [112].

The metallocene catalyst systems discussed above produce polyethylene with a fluff morphology. In order to control the morphology, silica and magnesium compounds have been used as supports for anchoring the metallocenes. Such supported metallocenes in conjunction with aluminoxanes show good activity for homo-, co-, and terpolymerizations of ethylene (Table 3.11) [105,109,116-123]. MgCl_2 supported Cp_2TiCl_2 shows good activity for ethylene polymerization in the presence of trialkylaluminum [123]. Kinetic studies revealed a distinctly different behavior as compared to that of an unsupported Cp_2TiCl_2 catalyst. It is postulated that the active site is a cationlike complex of Cp_2TiR^+ adsorbed on MgCl_2 . Silica-supported $\text{Et}(\text{Ind})_2\text{ZrCl}_2$ was examined for ethylene-propylene copolymerization. A truly random behavior for copolymerization was observed at an Al/Zr ratio of 670. Compared to supported metallocene, corresponding unsupported catalysts like $\text{Et}(\text{Ind})_2\text{ZrCl}_2/\text{MAO}$ require a severalfold excess of MAO. This difference in behavior is attributed to the immobilization of zirconocene on the support which prevents deactivation by bimolecular interaction processes. The copolymerization reaction is independent of the catalyst concentration. Cocatalysts used with zirconocene, such as *i*-butylaluminum, tri-*i*-butylaluminum, and trimethylaluminum, showed less productivity than MAO. The copolymer produced has a high ethylene content and is crystalline.

Table 3.10 Representative Examples of Metallocene-Aluminoxane Catalyst Systems for the Terpolymerization of Ethylene-Propylene-Diene

No.	Catalyst system	Monomer/comonomer/termonomer	Reaction conditions	Yield	Ref.
1	Et(Ind) ₂ ZrCl ₂ /MAO	Ethylene/propylene/ethylidene norbornene	20 min, Zr = 10 ⁻¹ mole, Al/Zr = 2500, 50 °C, pressure = 10 psig, 100 ml solvent	0.05 kg polymer/moleZr/h/bar, 3.2 wt% diene	113
2	CpZrMe ₂ /MAO	Ethylene/propylene/ethylidene norbornene	MAO = 1.9*10 ² mole/l, solvent = toluene, 20 °C, diene = 0.1 mole/l, Zr = 5*10 ⁻⁷ , time = 11 h, C ₂ H ₄ /C ₃ H ₆ = 43/57	10.6 kg polymer/moleZr/h/bar	114
3	Et(Ind) ₂ ZrCl ₂ /MAO	Ethylene/propylene/1,5-hexadiene	25 °C, Zr = 0.4*10 ⁻⁶ mole/l, MAO = 7*10 ⁻³ mole MeAlO units/l, C ₂ H ₄ /C ₃ H ₆ = 50/50, hexadiene = 10 mole	1500 mole/moleZr*s	114
4	CpZrCl ₂ /MAO	Ethylene/propylene/1,3-butadiene	Catalyst = 1.5*10 ⁻³ mmole, Al/Zr mole ratio = 530, C ₂ = 1.1 atm, C ₃ = 2.9 atm, diene = 57.4 mmole, time = 60 min, 40 °C, 40 ml toluene	2.6 kg polymer/mole catal	115
5	Et(IndH ₄) ₂ ZrCl ₂ /MAO	Ethylene/propylene/1,3-butadiene	Catalyst = 1.4*10 ⁻³ mmole, Al/Zr mole ratio = 580, C ₂ = 1.1 atm, C ₃ = 2.9 atm, diene = 57.4 mmole, time = 60 min, 40 °C, 40 ml toluene	0.07 kg polymer/mole catalys	115

Table 3.1.1 Representative Examples of Supported Metallocene Systems for the Polymerization of Ethylene

No.	Catalyst	Co-catalyst	Monomer-comonomer	Reaction conditions	Yield	Ref.
1	MgBu ₂ + Cp ₂ TiCl ₂	Et ₂ AlCl	ethylene	60 °C, 3 h, 180 psig	PE	105
2	SiO ₂ + Et(Ind) ₂ ZrCl ₂	MAO	ethylene/propylene	Zr = 5.7 mole, Al/Zr = 130	0.24*10 ³ kg polymer/moleZr/h/bar	109
3	MgCl ₂ + Cp ₂ TiCl ₂	MAO+ Al(OEt) ₃	ethylene/1-butene	60 °C, 9 kg/cm ² , 2h	65 kg polymer/gTi	116
4	Bu ₂ Mg + silica + TiCl ₄ + Cp ₂ ZrCl ₂	MAO + Me ₃ Al	ethylene/1-butene	1 h, 85 °C, H ₂ pressure	0.11 kg polymer, bimodal distribution	117
5	Al ₂ O ₃ + bis(2,4-dimethylpentadienyl)TiCl ₂	MAO	ethylene	567 g isobutane, 96 °C, 565 psig	PE	118
6	SiO ₂ + bis(n-butylcyclopentadienyl)ZrCl ₂	Bu ₃ Al + MAO	ethylene	85 °C, 8 kg/cm ²	PE	119
7	Silica gel + Cp ₂ TiCl ₂	MAO + Al(OPr) ₃	ethylene/1-butene	-	Copolymer	120
8	Silica gel + MgCl ₂ + bis(methylcyclopentadienyl)ZrCl ₂	AlMe ₃	ethylene	85 °C, 8 kg/cm ² , 1 h	PE	121
9	Silica gel + CpTiCl ₃	MAO	ethylene/propylene	[Ti] = 0.01 mmole, 20 ml toluene, 40 °C, 15 min	16.6 kg polymer/g/h	122
10	Silica gel + (Ind) ₂ ZrCl ₂	MAO	ethylene/1-butene/1,4-hexadiene	63 °C, 300 psig	Polymer	123
11	MgCl ₂ + Cp ₂ TiCl ₂ + THF	Bu ₃ Al	ethylene	40 °C, Al/Ti = 50, 1 atm, xylene	2.4 kgPE/moleTi	123
12	MgCl ₂ + Cp ₂ TiCl ₂ + THF	Et ₂ AlCl	ethylene	40 °C, Al/Ti = 50, 1 atm, xylene	6.4 kgPE/moleTi	123

3.7 POLYMERIZATION PROCESS

Three types of polymerization processes are used today for low pressure polymerization: i) liquid slurry polymerization, ii) solution polymerization, iii) gas-phase polymerization.

3.7.1 *Liquid Slurry Polymerization*

The liquid slurry polymerization process encompasses by far the largest group of HDPE technologies. In most cases this process utilizes a catalyst of activity such that catalyst deashing is not required. Excellent temperature control is major attraction of the liquid slurry process. Currently, long jacketed loop reactors and continuous stirred tank reactors (CSTR) are most widely used in slurry polymerization.

The loop reactors, which are recycle tubular reactors, are used by the Philips Petroleum Co. and the Solvay et Cie. The Philips process is characterized by use of a light hydrocarbon diluent such as isopentane or isobutane in loop reactors which consist of four jacketed vertical pipes. Figure 3.20 shows the schematic flow diagram for the Philips loop reactor polyethylene process. The use of high activity supported chromium oxide catalyst eliminates the need to deash the product. This reactor is carried out at about 35 atm. and 85–110 °C with an average polymer residence time of 1.5 hours. The Philips process relies on polymerization temperature for average molecular weight control, while the MWD is controlled by the type of catalyst employed and certain proprietary operational adjustments which alter MWD.

Continuous stirred tank reactors are also widely used for hexane slurry ethylene polymerization by many manufacturers. In the Hoechst process, the reaction is carried out in four CSTRs arranged in series such that the slurry phase and the vapor phase move in concurrent flow. Polymerization occurs at 100 psig and 85 °C with 98% conversion of ethylene. The residence time in the reactor is about 2.7 hr. The product slurry is pumped into centrifuges, which separate the bulk of the hydrocarbon diluent liquid from the polymer fluff.

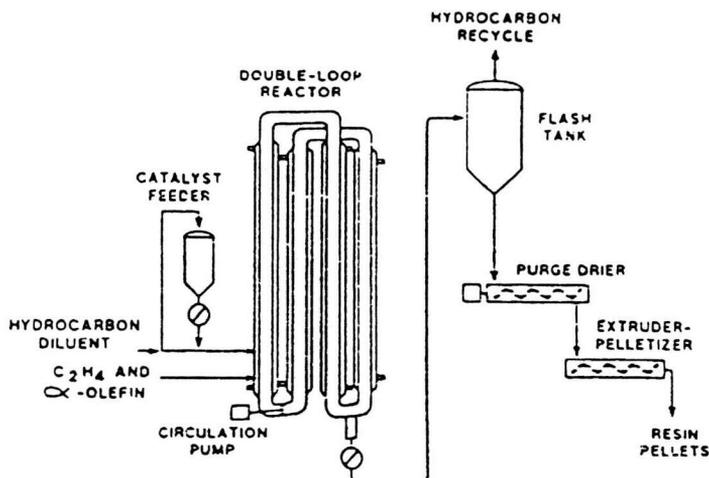


Figure 3.20 Phillips loop reactor.

3.7.2 Solution Polymerization

Solution process have some unique advantages over slurry process in that the MWD can be controlled better, and process variables are also more easily controlled because the polymerization occurs in homogenous phase. The high polymerization temperature (130–150 °C) also leads to high reaction rates and high polymer throughput from the reactor. However, very high molecular weight polymer cannot be produced easily at these high temperature, and since the solid content is relative low compared with the slurry process, greater diluent recovery may be required. Figure 3.21 shows the Du Pont solution polymerization process. The catalyst components, cyclohexane, ethylene, octene-1, and hydrogen, are charged continuously to a CSTR operating at a temperature in excess of 150 °C and a pressure about 80 atm. Because of the short residence time (5–10 min) and high polymer concentration (35%), relatively small reactors maybe used either in series or parallel to alter the MWD of the product.

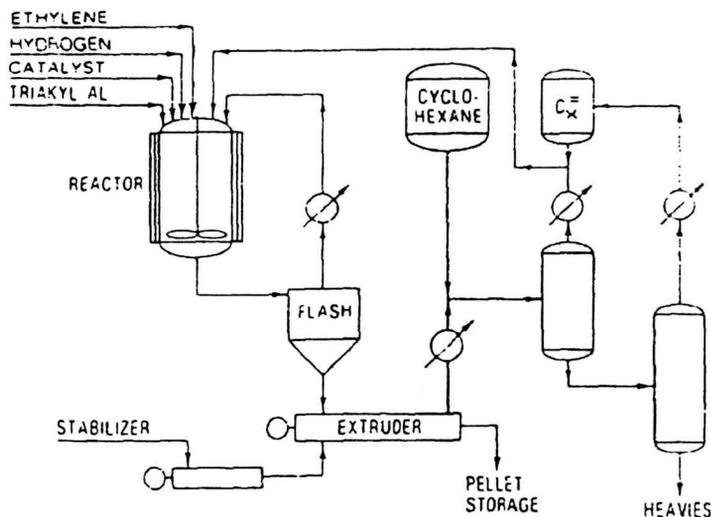


Figure 3.21 Du Pont solution process

3.7.3 Gas Phase Polymerization

The successful development of such process represents one great technological successes in this field. A gas phase, fluidized bed process(Unipol) was developed during 1960s by the Union Carbide Co. for the production of HDPE and first commercialized in 1968, as shown in Figure 3.22. The process was based initially on the use of chromium-type silica supported catalysts but may also be used with other types of high activity supported catalyst including those of a $\text{SiO}_2/\text{MgCl}_2/\text{TiCl}_4/\text{donor}$ type. The process operates at a nominal reaction pressure of 18 atm and at temperature between 85 and 100 °C. A full range of HDPE polymers can be prepared. A versatility of the original process led to a new gas phase fluidized bed process for the commercial production of LLDPE in 1975 by copolymerizing ethylene with α -olefin such as butene-1. The essential key to this new process is the development of new high activity catalyst that operate at low temperature and at pressure of only 7-20 atm. Molecular weight is controlled by polymerization temperature and the use of hydrogen.

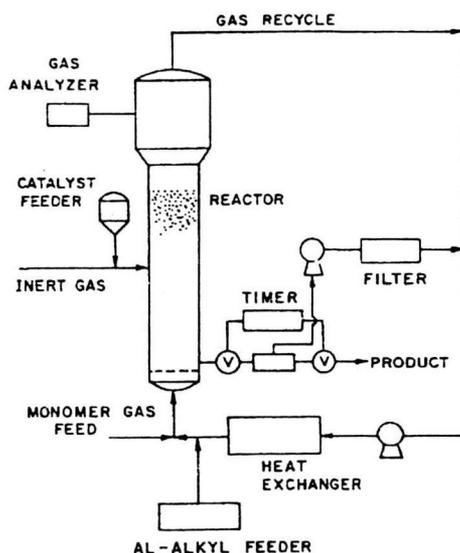


Figure 3.22 Union Carbide gas phase process

In the BP Chemicals gas phase process polymerization is carried out under mild conditions of temperature and pressure between 1.5 and 30 bar, in a fluid bed reactor. The growing polymer particles are maintained in a fluidized condition by means of a gas stream containing ethylene, the α -alkene (in copolymerization) and hydrogen (for molecular weight control). The gas stream from the top of the reactor is cooled in a heat exchanger and then recycle through a compressor. Polyethylene granules leave the reactor as a free-flowing powder. Homogeneity in the fluid bed and temperature control are ensured by the use of high activity titanium and magnesium catalysts. The process has a high degree of flexibility and can produce a broad range of products, using the same catalyst. A diagrammatic representation of the process is shown in Figure 3.23 [124].

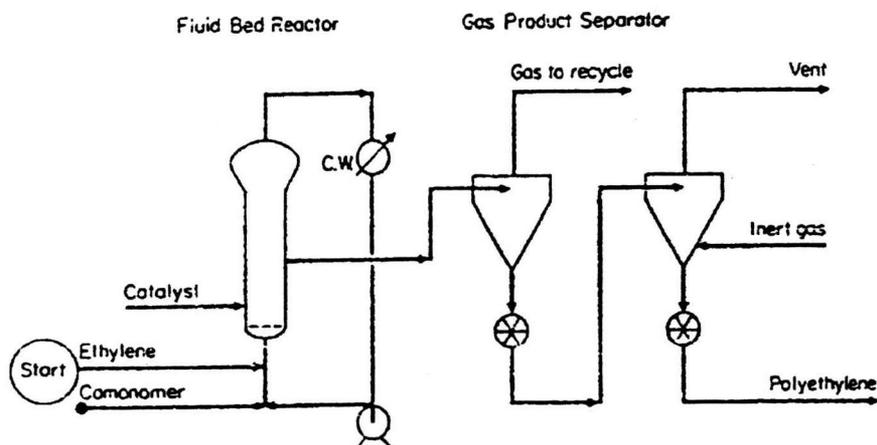


Figure 3.23 BP gas phase process

BASF uses a continuous stirred-bed reactor (CSBR) for gas phase ethylene polymerization as shown in Figure 3.24. The reactor is operated at a higher pressure and temperature (500 psig, 100–110 °C) than employed in Union Carbide's fluidized-bed process. A fairly uniform temperature of about 110 °C is maintained in the bed, and the unreact ethylene gas leaves the top of the reactor at 105 °C. About 9% of the ethylene recycle leaves the reactor with effluent polyethylene powder and is separated from the polymer at 40 psig. The recycle ethylene is compressed to 1500 psig and cooled to 32 °C before being reintroduced to the reactor.

In the Amoco (Standard Oil of Indiana) process, a compartment horizontal reactor depicted in Figure 3.25 is used. The compartments permit variation in temperature and hydrogen pressure in the reactor as a means of controlling polymerization rate and molecular weight distribution.

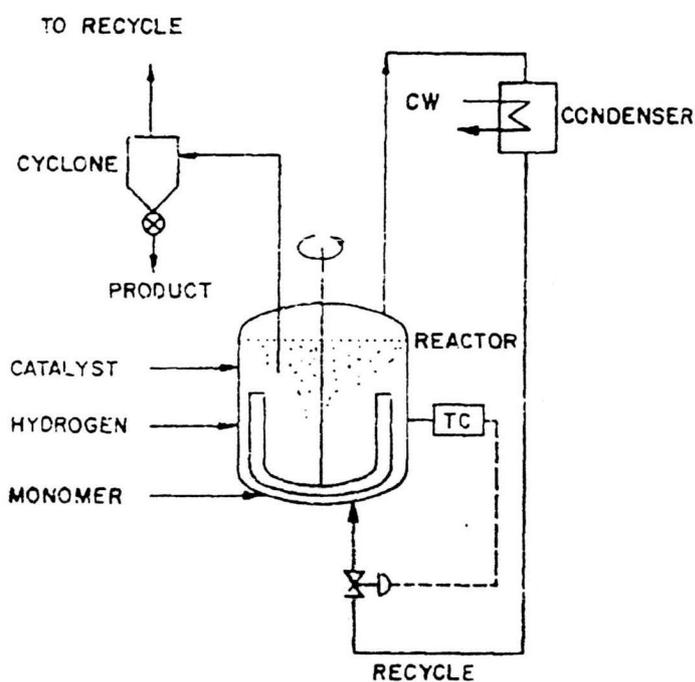


Figure 3.24 BASF gas phase process

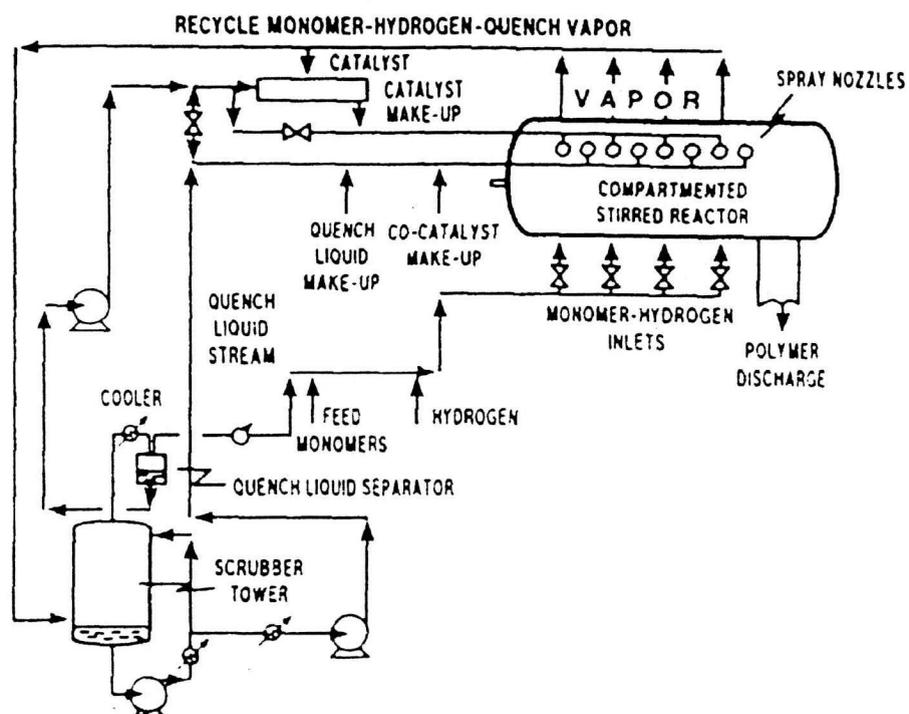


Figure 3.25 Amoco gas phase process