CHAPTER III
THEORY

The catalyst system always plays the key role in olefin oligomerization and polymerization processes. Metallocene compounds are becoming an important catalyst for the synthesis of organic molecules and polymers. Especially, group 4 metallocene catalyst are considered to be the most versatile transition metal catalyst for the polymerization. These catalyst systems show high performance for olefin polymerization and allow tailor making of polymers due to better control over the structure of metallocene and polymerization conditions. Furthermore, there are other process advantages such as ease of handling of metallocene systems and the favorable conditions from a commercial viewpoint. Now, an enormous amount of industrial and academic works are significantly interested in developing these catalysts to be available with a suitable performance level in polyolefin manufactures.

3. 1 Categories of Metallocene Catalyst Systems

Metallocene catalyst systems can be classified into three categories. In the first category, an aluminoxane, an alkylaluminum or a combination of aluminoxanes and alkylaluminums are used to activate the metallocene catalyst. In general these metallocenes have poor or no activity when used alone. In the second category, an ion exchange compound is combined with the metallocene catalyst, forming what is generally called a cationic metallocene catalyst. It is now generally accepted that the catalytic active species for metallocene/aluminoxane/alkylaluminum systems is also cationic. In the last category, the metallocene compounds are immobilized on inorganic supports such as silica, alumina or magnesium chloride to control the morphology of the polymer and prevent reaction fouling [29].

3.1.1 Metallocene Catalyst Systems Containing Aluminoxane Compound

Breslow and Newberg were among the first researchers to apply metallocene catalysts for polymerization [30,31]. They used soluble bis

(cyclopentadienyl)titanium derivatives and alkylaluminums for ethylene polymerization. Several other researchers followed this original work, using the same catalytic system or modifications of that system, including Natta [32]. However, these catalytic systems had low activities and stabilities for the polymerization of ethylene and produced only low molecular weight polymers. Additionally, they were not active for propylene polymerization [33]. A breakthrough occurred when Kaminsky and his co-workers noticed that the addition of water to the trialkyl aluminum in molar ratio 1:1 during ethylene polymerization significantly improved the catalyst activity [34,35].

It was already known that trialkyl aluminum reacts with water to produce alkyl aluminoxane [36]. Therefore, Kaminsky and his group decided to use alkyl aluminoxane oligomeric product as the cocatalyst with the metallocene catalyst. This combination made the breakthrough in the development of metallocene/aluminoxane catalyst systems for olefin polymerization [34,35]. It produced a metallocene catalyst system whose activity is significantly higher than that of conventional Ziegler-Natta catalyst and is capable of producing stereoregular polyolefin with very narrow molecular weight distribution.

3.1.1.1 Metallocene

Metallocene catalysts are organometallic coordination compounds in which one or two π-carbocyclic ligands such as cyclopentadienyl ring, substituted cyclopentadienyl ring, or derivative of cyclopentadienyl ring (such as fluorenyl, indenyl etc.) are bonded to a central transition metal atom. The cyclopentadienyl ring of metallocene which is singly bonded to the ring-metal bond is not centered on any one of the five carbon atoms in the ring but equally on all of them [37]. The typical chemical structure of a metallocene catalyst is represented by Figure 3.1 where M is the group 4B, 5B, or 6B transition metal, normally group 4B (Zr, Ti, and Hf); A is an optional bridging atom usually Si or C atom; R is a σ-homoleptic hydrocarbyl such as H, alkyl, or other hydrocarbon groups; and X is chlorine or other halogens from group 7A or an alkyl group. The cyclopentadienyl ligands, halides, and σ-homoleptic hydrocarbyls represent the three classes of ligands of the

metallocene catalysts and variation of, and/or substitutions within, some of these ligands could result in variation of the catalytic activity, polymer stereoregularity, and average molecular mass. In case of metallocene catalysts, which have only one π-carbocyclic ligand with a hetero atom that is attached to the bridging atom [38-42].
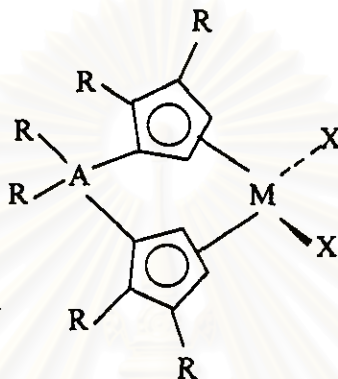
Figure 3.1 Typical chemical structure of a metallocene catalyst (where M is the transition metal, normally from Group 4B, namely Zr, Ti, and Hf; A is an optional bridging atom, usually Si or C atom; R is a σ-homoleptic hydrocarbyl such as H, alkyl, or other hydrocarbon groups; and X is chlorine or other halogens from Group 7A or an alkyl group)

Compositions and types of metallocene have several varieties. When the two cyclopentadienyl (Cp) rings on either side of the transition metal are unbridged, the metallocene is nonstereorigid and it is characterized by C_{2v} symmetry. The Cp_2M (M = metal) fragment is bent back with the centroid-metal-centroid angle θ about 140° due to an interaction with the other two σ bonding ligands [43]. When the Cp rings are bridged (two Cp rings arranged in a chiral array and connected together with chemical bonds by a bridging group), the stereorigid metallocene, called ansa-metallocene, could be characterized by either a C_1, C_2 or C_s symmetry depending upon the substituents on two Cp rings and the structure of the bridging unit as schematically illustrated [6] in Figure 3.2. A nonexhaustive list of the C_{2v}-, C_2-, and C_s-symmetric metallocenes is presented in Tables 3.1, 3.2 and 3.3, respectively. Two

examples of C_1-symmetric metallocenes are as follows: i-Pr[(3-MeCp)(Flu)]ZrCl$_2$ and Me$_2$C(3-MeCp)(Flu)ZrCl$_2$ [44,45].
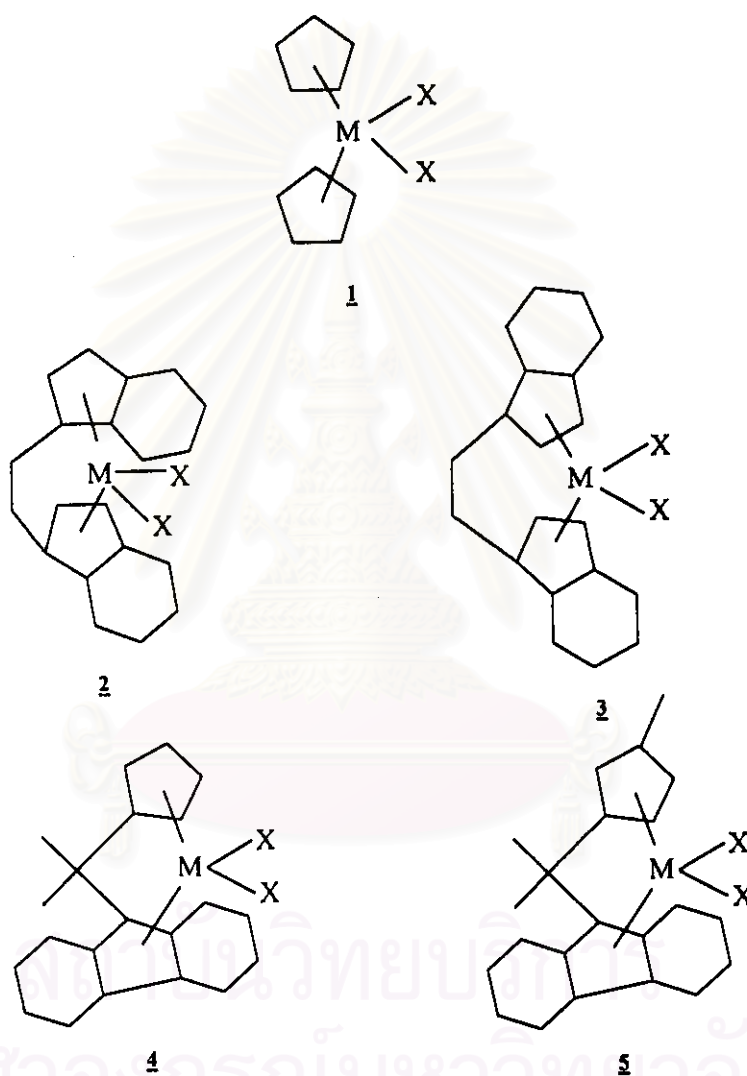
Figure 3.2 Schematic representations of metallocene symmetry [6,46]

Type 1 is C$_{2v}$-symmetric

Type 2 is C$_2$-symmetric

Type 3 is C$_s$-symmetric

Type 4 is C$_s$-symmetric

Type 5 is C$_1$-symmetric

Table 3.1 Selected List of C_{2v}-Symmetric Metallocenes

Metallocenes	References
Zirconocenes (with indenyl ligands)	
Ind_2ZrCl_2	47, 48, 49
Ind_2ZrMe_2	33, 50, 51
Ind_2ZrBz_2	52
Zirconocenes (with cyclopentadienyl ligands)	
Cp_2ZrCl_2	47, 48, 49, 50, 51,53-57
$CpZrCl_3$	53
Cp_2ZrMe_2	33, 34, 48-50, 58-62
$(SiMe_3Cp)_2ZrMe_2$	62
$Me_2Si(Cp)_2ZrCl_2$	64, 65
Titanocenes (with cyclopentadienyl ligands)	
Cp^*TiCl_3	8, 10, 13, 66, 67
$CpTiCl_3$	8, 10, 13, 66, 67
Cp_2TiCl_2	29, 67-70
Cp_2TiMe_2	61
Hafnocenes (with cyclopentadienyl ligands)	
Cp_2HfCl_2	29, 48, 49
Cp_2HfMe_2	33

Table 3.2 Selected List of C_2-Symmetric Metallocenes

Metallocenes	Pentad (%)	References
Zirconocenes (with indenyl ligands)	mmmm %	
En(Ind)$_2$ZrCl$_2$	57-93	29, 48, 54, 62-64
Me$_2$Si(Ind)$_2$ZrCl$_2$	82.2-95	48, 54, 55, 62, 65-67
Me$_2$Si(2-MeBenzInd)$_2$ZrCl$_2$	92,93	65, 68
Me$_2$Si(2-MeInd)$_2$ZrCl$_2$	88.5-90	65, 68, 69
Me$_2$Si(2Me-4Naph-Ind)$_2$ZrCl$_2$	99.1	69
i-Pr(Ind)$_2$ZrCl$_2$	na	63, 70-72
Zirconocenes (with cyclopentadienyl ligands)		
En(Cp)$_2$ZrMe$_2$	na	48, 73
Me$_2$Si(2-Me-4-t-Bu-Cp)$_2$ZrCl$_2$	94-96	63, 65, 68, 69, 74, 75
Me$_2$Si(2,4-Me$_2$-Cp)$_2$ZrCl$_2$	89.2	69
Zirconocenes (with fluorenyl ligands)		
PhEn(1,2-Flu)$_2$ZrCl$_2$	31.2-64.1	76
Hafnocenes (with indenyl ligands)		
En(Ind)$_2$HfCl$_2$	68-94	49, 62, 63, 77-79
Me$_2$Si(Ind)$_2$HfCl$_2$	83.1	63, 77-79
Hafnocenes (with cyclopentadienyl ligands)		
Me$_2$Si(2,4-Me$_2$Cp)$_2$HfCl$_2$	96.8	63, 77-79
Titanocenes (with indenyl ligands)		
En(4,5,6,7-IndH$_4$)$_2$TiCl$_2$	na	44, 80
rac-(C$_5$H$_4$MePh)$_2$ZrCl$_2$	na	6, 46

En = ethylene

na = not available.

Table 3.3 Selected List of C_s-Symmetric Metallocenes

| Metallocenes	Pentad (%)	References
Zirconocenes	rrrr %	
[1-(9-Flu)-2-(1-Ind)En]ZrCl$_2$	na	76
[1-(9-Flu)-1(R)-Ph-2-(1(R)-Ind)En]ZrCl$_2$	na	76
[1-(9-Flu)-1(R)-Ph-2-(1(S)-Ind)En]ZrCl$_2$	na	76
i-Pr[(MeCp)(Ind)]ZrCl$_2$	mmmm, 54%	80, 78-79
i-Pr[(3-t-BuCp)(Flu)]ZrCl$_2$	mmmm, na	63, 64, 68
Me$_2$Si(3-t-BuCp)(Flu)]ZrCl$_2$	mmmm, na	63, 64, 68
Me$_2$C(MeCp)(Ind)ZrCl$_2$	mmmm, na	80
Me$_2$C(Cp)(2,7-t-Bu$_2$-Flu)ZrCl$_2$	mmmm, na	74
t-BuCH(3-t-Bu-Cp)(Flu)ZrCl$_2$	mmmm, na	63, 64, 66
En(4,5,6,7-IndH$_4$)$_2$ZrCl$_2$	atactic	81

En = ethylene

na = not available.

3.1.1.2 Aluminoxane

Aluminoxane, especially methylaluminoxane (MAO) is the most important cocatalyst, which activates the group 4B metallocenes in homogeneous Ziegler-Natta polymerization. Before the discovery of the MAO cocatalyst, the homogeneous Ziegler-Natta catalyst Cp$_2$TiCl$_2$ was activated with alkylaluminum chloride, which led to poor catalyst activity. The use of MAO *cocatalyst raised the catalyst activity by several orders of magnitude.* There are some other aluminoxanes which can also activate the metallocenes, such as ethylaluminoxane (EAO) and isobutylaluminoxane (iBAO), but MAO is much more effective than its ethyl and isobutyl analogues and is most preferred in practice [50].

Aluminoxanes were prepared by controlled hydrolysis of alkylaluminums [82-89]. Many inorganic hydrated compounds, such as CuSO$_4$.5H$_2$O were used as a source of water for preparing aluminoxane from alkylaluminum [90-92]. Later, Al$_2$(SO$_4$)$_3$ hydrates were chosen as the water source for the reaction, in

order to prevent the combination of MAO from Cu(I) alkyl compounds [33,58]. In recent years, some patents claimed that MAO could be made through the reaction of TMA with dimethyltin-oxide (Me$_2$SnO) [93]. The most commonly used alkylaluminums for the synthesis of aluminoxanes are triisobutylaluminum (TIBA), triethylaluminum (TEA) and trimethylaluminum (TMA).

The simplest representative of the aluminoxane was μ-oxo bisalkylaluminum or tetra-alkyl-dialuminoxide, respectively. Various physico-chemical data, such as compositional analysis, molecular weight determination, mass spectra, X-ray powder diffraction, infrared, and NMR spectroscopy, were used for the characterization of aluminoxanes [94-96]. In spite of these measurements, the structures of the alkyl aluminoxane were not unambiguously known. Methylaluminoxane was considered to be the oligomeric (cyclic or linear, Figure 3.3) mixture of -AlMeO- units [94] containing possibly clusterlike or supramolecular aggregates [95-96]. The preferred aluminoxanes for olefin polymerization catalysts contained approximately 4-30 of repeating units.
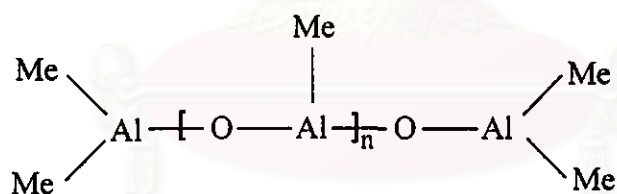

(A) Linear structure
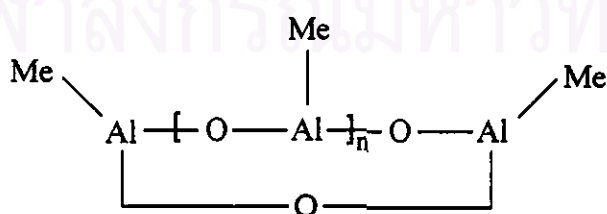
(B) Cyclic structure

Figure 3.3 Plausible structure of methylaluminoxane (MAO) [97]

However, base on ^{27}Al NMR spectroscopic studies, some researchers recently indicated that there appears to be no logical structure for MAO with n > 4, in which all aluminum atom simultaneously achieve a coordination number of 4. A possible structure was shown in Figure 3.4 as proposed by Sugano *et al.* [98]. The presence of some three-coordinate aluminum sites was to be expected and their Lewis acidity will be enhanced by electronegative effect of adjacent oxygen atoms (see Fig.3.4) [99].
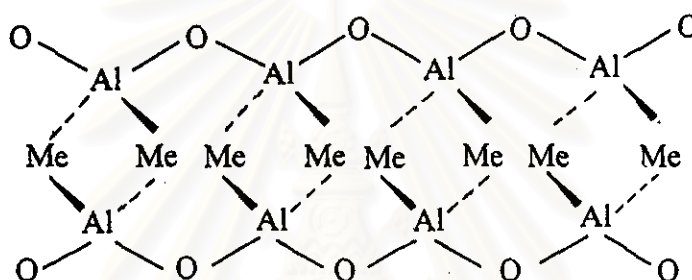
Figure 3.4 A proposed structure of MAO with a coordination number of 4 [98]

In metallocene-based catalyst systems, the aluminoxanes appeared to have a combination (depending on the nature of the catalyst and polymerization conditions) of the following functions:

1. Aluminoxane alkylated the metallocene compound and scavenged the impurities [100].
2. Aluminoxane interacted with metallocene to generate cationic metallocene alkyl species.

The aluminoxanes not only produced the cations but also stabilized them [101-102]. This view has been gaining support due to isolation of the cationic species [33,103]. Resconi *et al.* [96] 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.

3.1.2 Cationic Metallocene Catalyst Systems

Active homogeneous catalysts can be obtained, in the absence of MAO, by using cationic-metallocene-based single component catalysts. Cationic metallocene are catalysts in which the transition metal atom is positively charged. The metallocene complex is therefore a cation associated with a stable anion. There is now enough experimental evidence to support the hypothesis that all active center types operative with metallocenes are cationic.

Cationic metallocenes are prepared by combining at least two components. The first is a metallocene and the second is an ion exchange compound comprising a cation and a non-coordinating anion. The latter component is the new class of non-aluminum activators or co-catalysts based on boranes. The cation reacts irreversibly with at least one of the first component's ligands. The anion must be capable of stabilizing the transition metal cation complex and must be labile enough to be displaced by the polymerization monomer. The relationship of the counterion to the bridged structure controls monomer insertion and isomerization [104].

The metallocene-borane catalyst systems demonstrate polymerization activity for both ethylene and propylene. Table 3.4 shows details of ethylene polymerization using the metallocene-borane catalyst systems.

Non-aluminum activators such as $B(C_6F_5)_3$ or $[Ct][B(C_6F_5)_4]$ (Ct^+ = alkyl- or hydride-abstracting cation) may obviate many of the disadvantages of MAO as an activator for metallocene catalysts. Many cations have been developed for the $[B(C_6F_5)_4]^-$ anion, most recently silylium salts, prepared by metathesis of $Li[B(C_6F_5)_4]$ with R_3SiCl [105]. Besides, tris(pentafluorophenyl)boron is a widely used activator for converting metallocene dihydrides and dialkyls to cationic catalysts. It has been prepared by reaction of C_6F_5MgBr (from C_6H_5Br and alkylmagnesium halides) with BF_3 etherate [106].

These cationic metallocene catalysts exhibit the same activity as MAO-activated catalysts. Unfortunately, the metallocene catalysts activated with the boron compounds are very sensitive to impurities during the polymerization process. A careful consideration is therefore needed before applying to industrial scale production [107].

Table 3.4 Polymerization Features of Ethylene Using Cationic Metallocene-Based Single Component Catalysts

Catalyst	Co-catalyst	Polymerization conditions	Activity (kg-PE/mol-metal.h)	Ref.
$Cp_2Zr(CH_3)_2$	$B(C_6F_5)_3$	P= 100kPa T= 25°C Time= 40-150s	450	103
$(Cp^*)_2Zr(CH_3)_2$	$[Bu_3NH][B(C_6H_4R)_4]$	P= 600kPa T= 80°C	375	108
$(Cp^*)_2Zr(CH_3)_2$	$C_2B_9H_{13}$	P= 1630kPa T= 40°C	265	108
$Cp_2ZrMe(THF)^+$	BPh_3	P=100-400kPa T= 25°C	12	102

3.1.3 Supported Metallocene Catalyst

Since the discovery of metallocene catalysts by Sinn and Kaminsky in 1980, they have caught the interest of the polymer industries due to their potential in producing tailor-made polymers. Metallocene catalysts have many advantages over conventional Ziegler-Natta or chromium catalysts used in industry. They are well defined organometallic transition metals compounds with only one active site for the polymerization reaction (single-site catalysts), while conventional catalysts are formed by complex chemical reactions leading to the forming of chemically ill-defined multiple active centers, each of them with its own ability for (co)

polymerization, transfer and termination rates, producing polymers with heterogeneous molecular and chemical composition. In contrast, single-site catalysts produce very homogeneous polymers with narrow molar weight distribution (MWD) (polydispersity of about 2) as well as chemical composition distribution (CCD)

Although original homogeneous metallocene catalysts exhibit several advantages for olefin polymerization as previous mentioned, control of the size and shape of produced polymers is very difficult. Additionally, due to the high cost of MAO as well as the disadvantage for slurry and gas phase processes, further practical application of homogeneous metallocene catalyst seems to be limited. Attempt to overcome those unsolved problems have led to a rapid development of heterogeneous metallocene catalysts during the last ten years. The special features of supported metallocene catalysts can be summarized as follows [109].

- The morphology of polymers can be precisely controlled through replica process.

- Most metallocene catalyst in solution produces polyolefins of a very low molecular weight (MW) especially at high polymerization temperature (Tp). The supported catalyst should produce higher MW polymers at high Tp.

- Metallocene catalyst in solution give polymers with narrow MW distribution (MWD), and consequently with a poor processibility-physicomechanical property balance. The supported metallocene should have the capability of producing polymers having a desired broad or bimodal MWD for good rheological and physical properties.

- The active species in case of supported metallocene catalyst are much more stabilized. Consequently, their thermal stability and longevity are markedly enhanced.

- The steric control of metallocene catalysts is determined by molecular structure. It would be advantageous if this can be controlled or even altered by the support.

To apply the metallocene catalyst existing polymerization reactors in slurry or gas phase processes, single site catalysts need to be supported on appropriate carriers. Silica is one the most widely used inorganic carrier for polyolefin, especially ethylene polymerization since it leads to good morphological features for polymer particles [107,110]. In addition, other materials such as alumina (Al_2O_3) or magnesium chloride ($MgCl_2$) are also main supports used. Some other materials have been investigated such as zeolites, MgO, MgF_2, CaF_2, AlF_3, etc; but they are not yet of commercial consequence [109].

The main preparatory route for supported metallocene can be varied as follows:

Method 1. The first method involves direct impregnation of metallocene on the support (modified with heating or chemical reagent by previous treatment or not). This can be done either (a) with mild impregnation conditions or (b) at high temperatures and long impregnation time (refined route).

This method involves physical mixing of metallocene and support, and it was one of first preparatory routes used. In the method, the dry support is reacted first with the metallocene compound in a solvent such as toluene. The solid part is then recovered by filtration and washed with hydrocarbon. The mixing temperature and the contact time are important parameters since they influence both the catalytic performances and final properties of the polymer [110].

Method 2. The second method involves immobilization of MAO on the support followed by reaction with the metallocene compound. A modified version of this method involves the replacement of MAO by an aluminium alkyl [110].

Method 3. Precontacting metallocene and MAO complex may be added to support [11].

Method 4. The metallocene can be chemically bonded directly to support by a spacer and an anchor group. This method involves direct synthesis of metallocene on support (mainly modified SiO_2) by immobilization of aryl ligand on the support followed by addition of metal salt such as zirconium halide, recently, titanium and neodymium halides to form the attached metallocene [110-111].

Among them, the most investigated method are based on the direct adsorption of metallocene on the support materials (method 1) or the initial adsorption of MAO on the support (method 2) [12,23,29,112-114]. The other methods (methods 3 and 4) have been less employed [22,26,115-116]. All procedures afford different catalysts and these in turn produce polyolefins with different properties.

3.2 Mechanism

3.2.1 Interaction of Metallocene with Aluminoxanes and Nature of Active Species

The interaction of metallocene with aluminoxanes has been studied in detail [33,100,117-119]. Metallocene dichloride reacts with methyl aluminoxane to yield a methylated compound (Figure 3.5). It undergoes either methyl or chloride abstraction to generate metallocene methyl cations [33,100]. The research work reported by Marks, Bochmann, Jordan, and others gave synthetic and spectroscopic evidence that cationic metallocene [(Cp_2MR)]$^+$ are the active species [103,108]. The interaction of dichlorozirconocene, methylchlorozirconocene, and dimethylzirconocene with MAO has been studied by x-ray photoelectron spectroscopy [118]. 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.* [117] who studied the reaction of Cp_2Zr ($^{13}CH_3$)$_2$ with MAO. The solid-state $^{13}CPMAS$-NMR study at different Al/Zr ratios indicated the formation of a cation like the $Cp_2ZrCH_3^+$ species. The data also indicate that the Al:Zr stoichiometry required to form this cation is considerably lower than that in a typical catalyst reaction. Siedle *et al.*, [119] employed solution ^{13}C-NMR

spectroscopy to demonstrate that dimethyl metallocenes such as $Cp_2Zr(^{13}CH_3)_2$, $(Me_5Cp)_2Zr(^{13}CH_3)_2$, $(Indenyl)_2Zr(^{13}CH_3)_2$, $Me_2Si(C_5H_4)_2Zr(^{13}CH_3)_2$, and Cp_2Hf $(^{13}CH_3)_2$ undergo degenerate methyl exchange with methyl acceptor compounds such as Me_6Al_2 and $(MeAlO)_x$ (equation 3.1). The kinetics of degenerate methyl exchange indicates that steric effects are important determinants of the free energy of activation as compared to electronic effects in the formation of cationic species.

$$Cp_2Zr(^{13}CH_3)_2 + Me_3Al \longrightarrow Cp_2Zr^{13}CH_3^{(+)}AlMe_4^{(-)} \qquad (3.1)$$
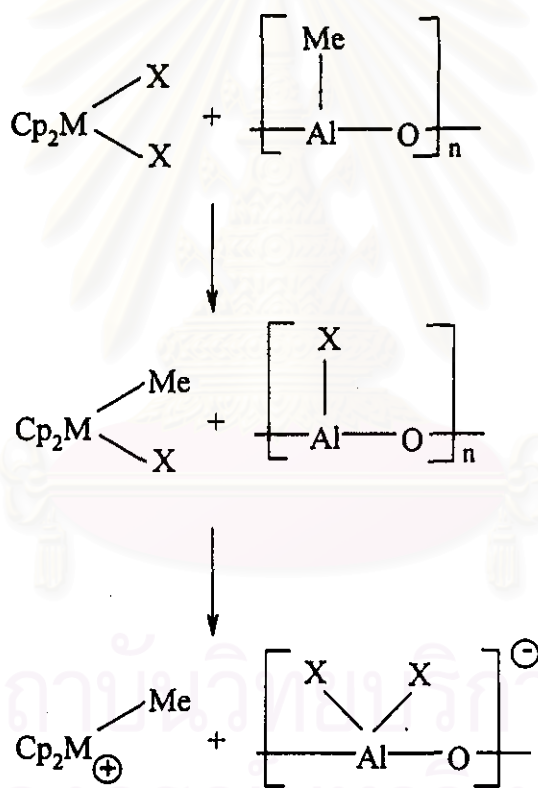
Figure 3.5 Postulated mechanism of formation of the active species in the reaction between metallocenes and methyl alumoxane [46]

3.2.2 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 [45,78,81,121-128]. These studies have shown that the Cossee mechanism of polymerization is indeed viable (Figure 3.6) for metallocene catalysts [128-130]. 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. These 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-agostic hydrogen interaction has also been suggested [51,131]. Brintzinger *et al.* provided experimental evidence for such an α-agostic hydrogen interaction in zirconocene-catalyzed polymerization of olefin [132].

☐ = Vacant coordination site, Ⓟ = Polymer chain
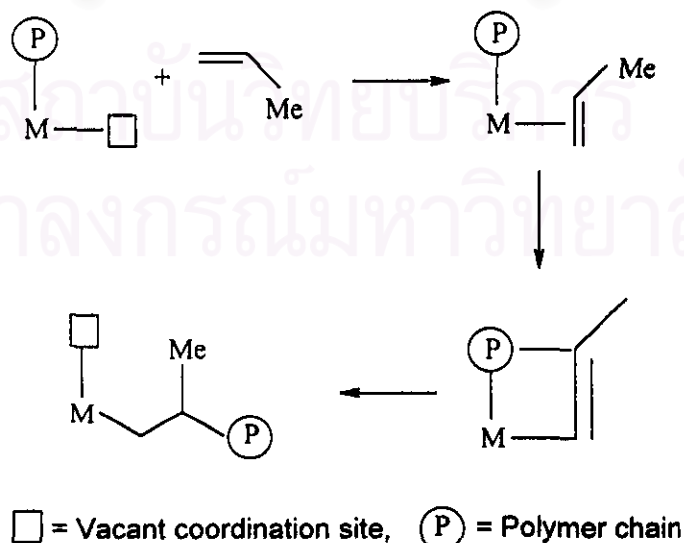
Figure 3.6 Cossee mechanism for Ziegler-Natta olefin polymerization [81]

Stereoregulation in α-olefin polymerization is one of the most important capabilities of metallocene catalyst systems. Propylene polymerization produces four types of polypropylene: isotactic, syndiotactic, atactic, and hemiisotactic [45,81] (Figure 3.7). 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 [133] that chiral, nonbridged rac-(C_5H_4CHMePh)_2ZrCl_2/MAO produces isotactic polypropylene through both chain end control and the enantiomorphic site control mechanisms. The polymer obtained (Figure 3.8) consists of 35% isotactic PP of type 1 (enantiomorphic site control) and 65% of type 2 (chain end control) [133]. A number of other studies [45,78,125] 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.

3.3.5 Effect of Time

The variation of molecular weight of poly(ethylene)s with polymerization time has been studied for different catalyst systems. With increase in polymerization time and decrease in catalyst concentration, the molecular weight is reported to be increased. The literature data is summarized in Table 3.9.

Chien and Wang [53] have studied the variation of polyethylene molecular weight with polymerization time for the catalysts Cp_2ZrCl_2 at [Zr] of $4.8x10^{-5}$ M and $3.8x10^{-6}$ M and $CpZrCl_3$ catalysts at a [Zr] of $3.8x10^{-6}$ M. The polymer obtained after 5 min. of polymerization had a Mn 4000, which increases by 43% to a value of 5700 after 40 min. for Cp_2ZrCl_2 at [Zr] = $4.8x10^{-5}$ M. The molecular weight distribution Mw/Mn is approximately 3 for all the polymers. The polyethylene obtained at the lower [Zr] is reported to have a higher Mn of 21,000 and a narrower molecular weight distribution of 2.2. For $CpZrCl_3$-initiated polymerizations, it was observed that there was a slight dip of Mn during the first 10 min., after which Mn increases with time. This decrease of molecular weight with time during the early stages of polymerization was related to the slow activation of the $CpZrCl_3$ system as compared to the Cp_2ZrCl_2 system.

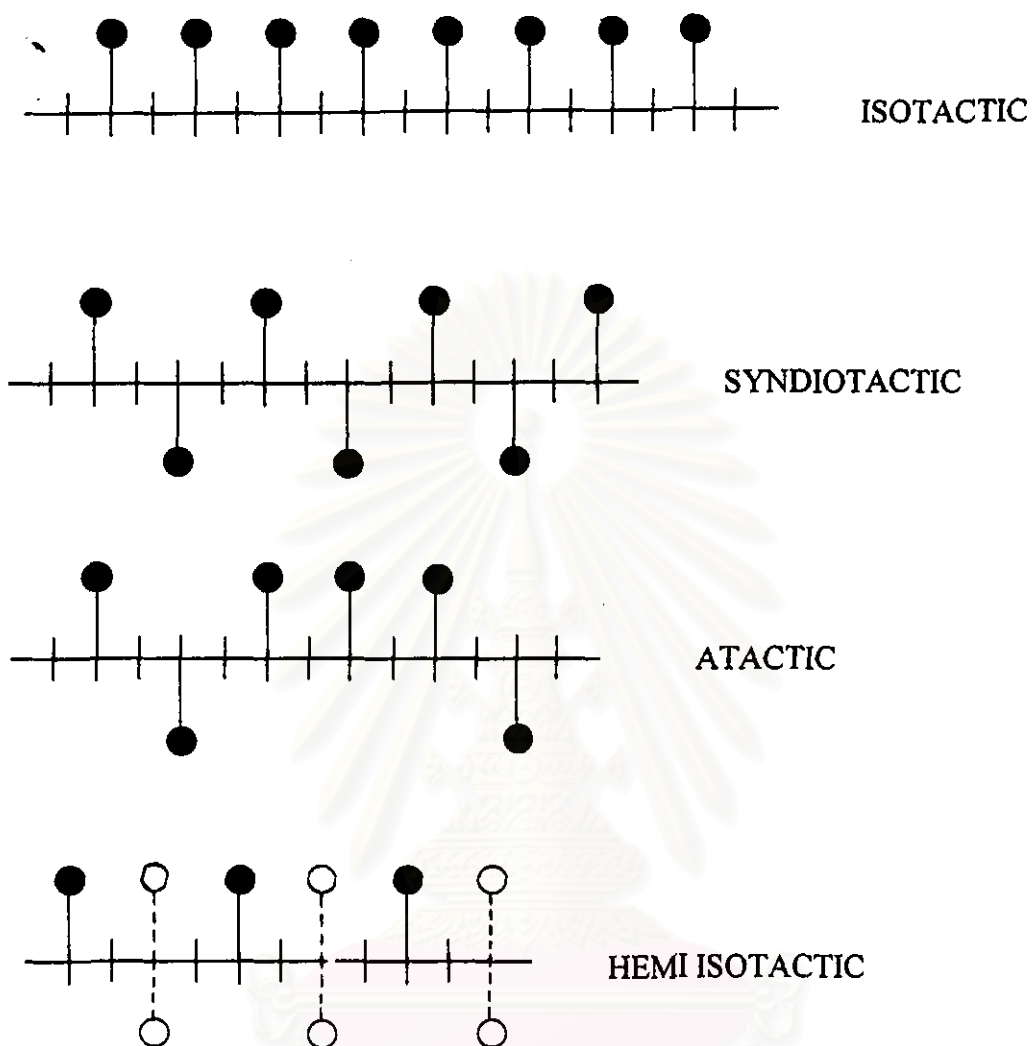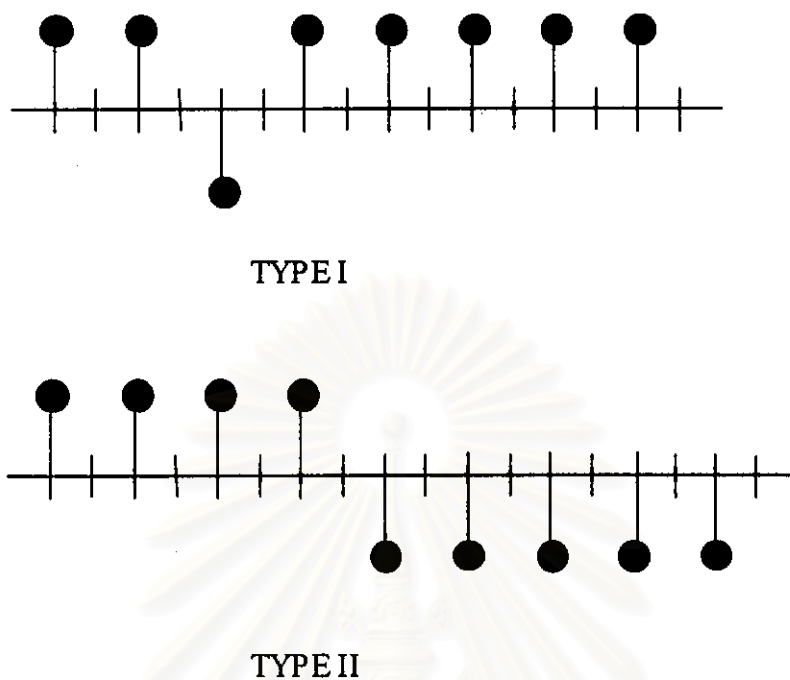Figure 3.7 Types of olefin polymer tacticity [45,81]

TYPE I

TYPE II

Figure 3.8 Isotactic polypropylene: Type1, enantiomorphic site-controlled mechanism; Type 2, chain-end-controlled mechanism [133]

3.2.2.1 Enantiomorphic-Site Controlled Stereoregulation

The stereorigid ligand environment around the metal is required for the enantiomorphic 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 rac-Et(IndH$_4$)$_2$ZrCl$_2$ and rac-Et (Ind)$_2$ZrCl$_2$ with C$_2$ symmetry yield an isotactic polymer. The configuration of the catalytic complex is ideally the same during isotactic polymerization [81] (Figure 3.9). Defects also occur during the synthesis of isotactic polymer (Figure 3.10). 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 [81] of propylene has a regular alternate configuration at adjacent chiral center along the polymer chain (Figure 3.11). A metallocene with C$_s$ symmetry, such as isopropyl-(Cp-1-fluorenyl)ZrCl$_2$/MAO, produces syndiotactic polypropylene. The enantiomorphic site-controlled mechanism has been extended to catalytic complexes yielding hemiisotactic polymer [45, 134]. The mechanism of polymerization additionally involves an isomerization step either with or without

monomer coordination. The metallocene ^{i}Pr[3MeCpFlu)ZrCl$_2$]/MAO [45] with C$_1$ symmetry generates hemiisotactic polypropylene.
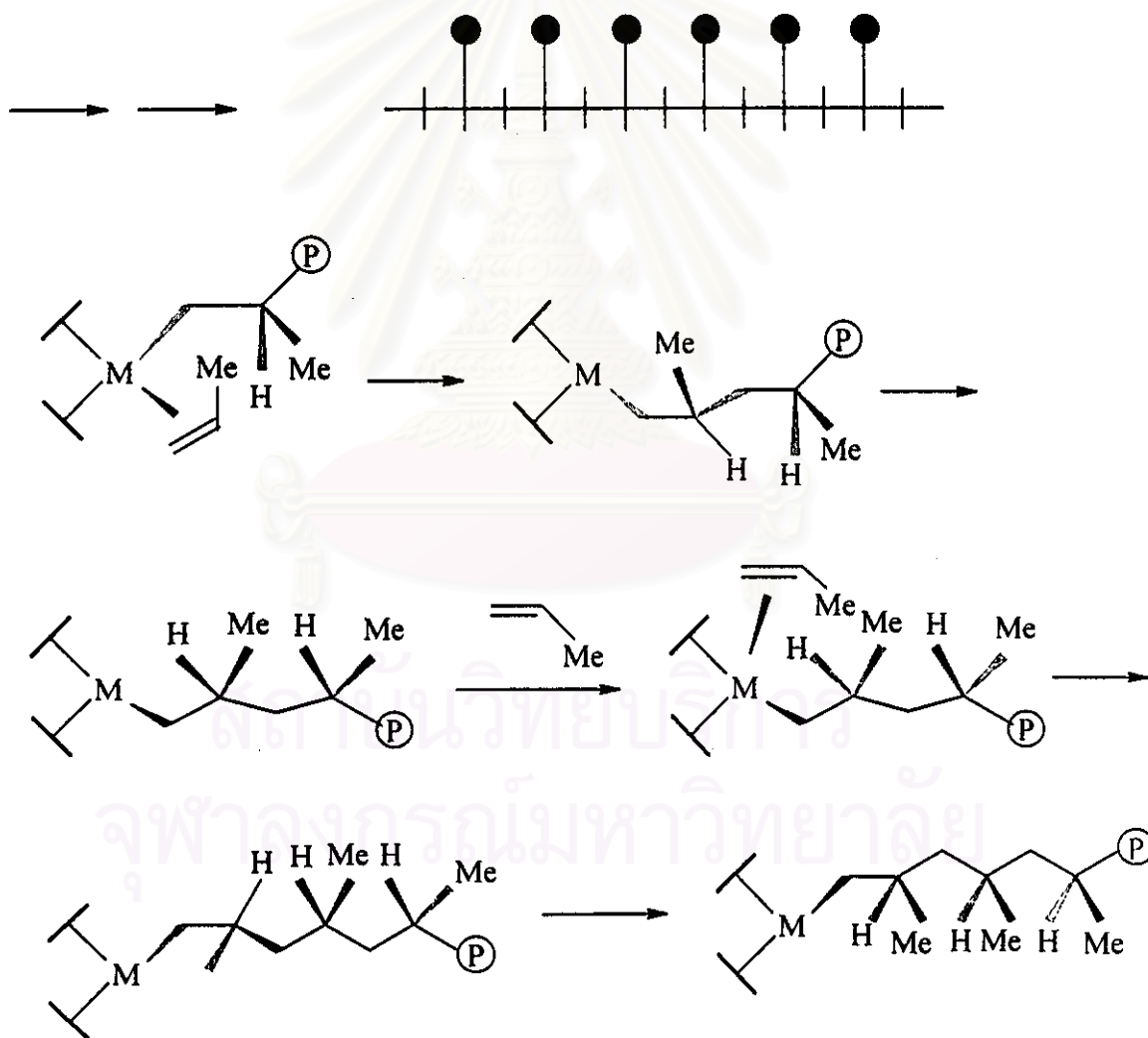
Figure 3.9 Isotactic propylene polymerization by enantiomorphic site-controlled mechanism [81]

and HT5) with a 1×10^7 exclusion limit for polystyrene. The columns were calibrated with standard narrow molar mass distribution polystyrenes and linear low density polyethylenes and polystyrenes.

4.4 Catalyst Preparation Procedure

All reactions were carried out under argon atmosphere using Schlenk techniques and glove bag.

4.4.1 Preparation of the Modified Silica Gel

To a suspension of 940 mg of calcined SiO_2 in 10 ml of toluene was added 10 ml of a toluene solution containing 1 mmol of $Cl_2Si(CH_3)_2$ under argon atmosphere. The reaction mixture was refluxed for 7 hours under stirring with a magnetic stirrer. The resulting silica gel was filtered and washed five times with 20 ml of toluene, and then to the silica gel in 20 ml of toluene was added 1.8×10^{-2} ml of 1.5 N aqueous sodium hydrogencarbonate solution under argon atmosphere. The mixture was kept standing at room temperature for 7 hours with rigorous stirring. The solid part was separated by filtration, washed five times with 20 ml of toluene and dried in vacuo at room temperature to obtain the modified silica gel.

### 4.4.2 Preparation of the Catalyst Precursor

The modified silica gel prepared above was reacted with 16 mmol of MAO in 10 ml of toluene at room temperature for 30 minutes. The solid part was separated by filtration and washed five times with 20 ml of toluene, followed by drying in vacuo at room temperature to obtain the catalyst precursor.

4.4.3 Ethylene Polymerization Procedure

The ethylene polymerization reactions were carried out in a 100 ml stainless steel autoclave equipped with a magnetic stirrer. The autoclave and magnetic bar were dried in oven at $110^{\circ}C$ for 30 minutes and purged with argon 5 times in glove bag before used in the polymerization of ethylene. Toluene, 100 mg of the catalyst precursor, and mixture of a prescribed amount of Cp_2ZrCl_2 and TMA
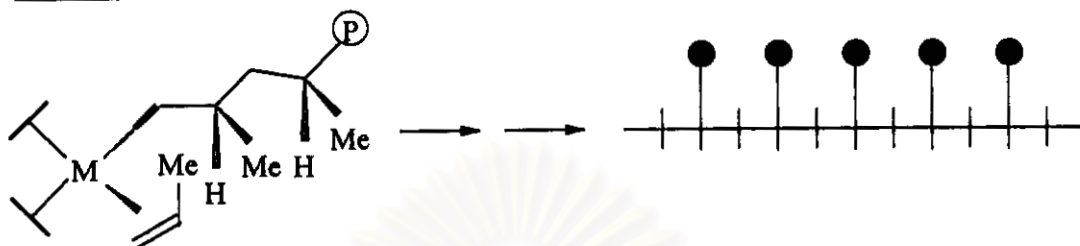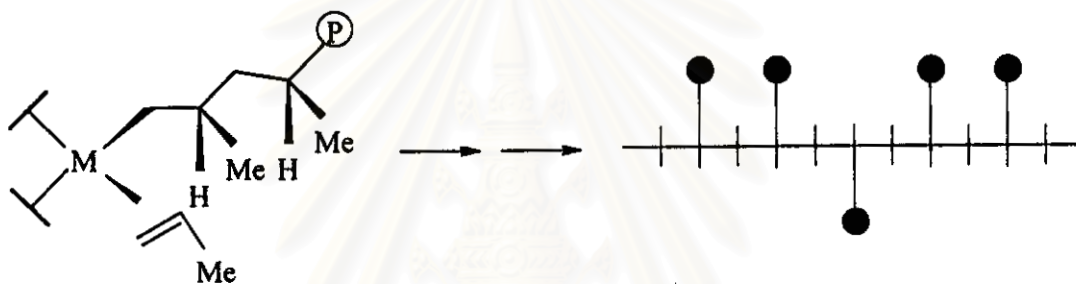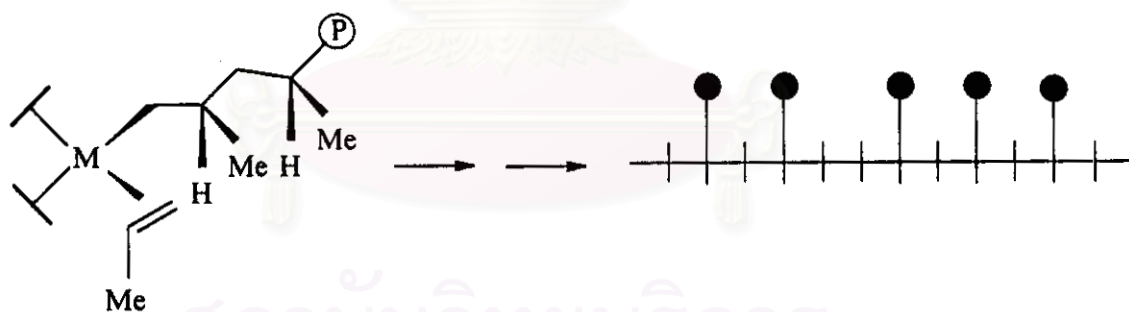
**Figure 3.10** Stereodefects in an isotactic polymer chain [81]
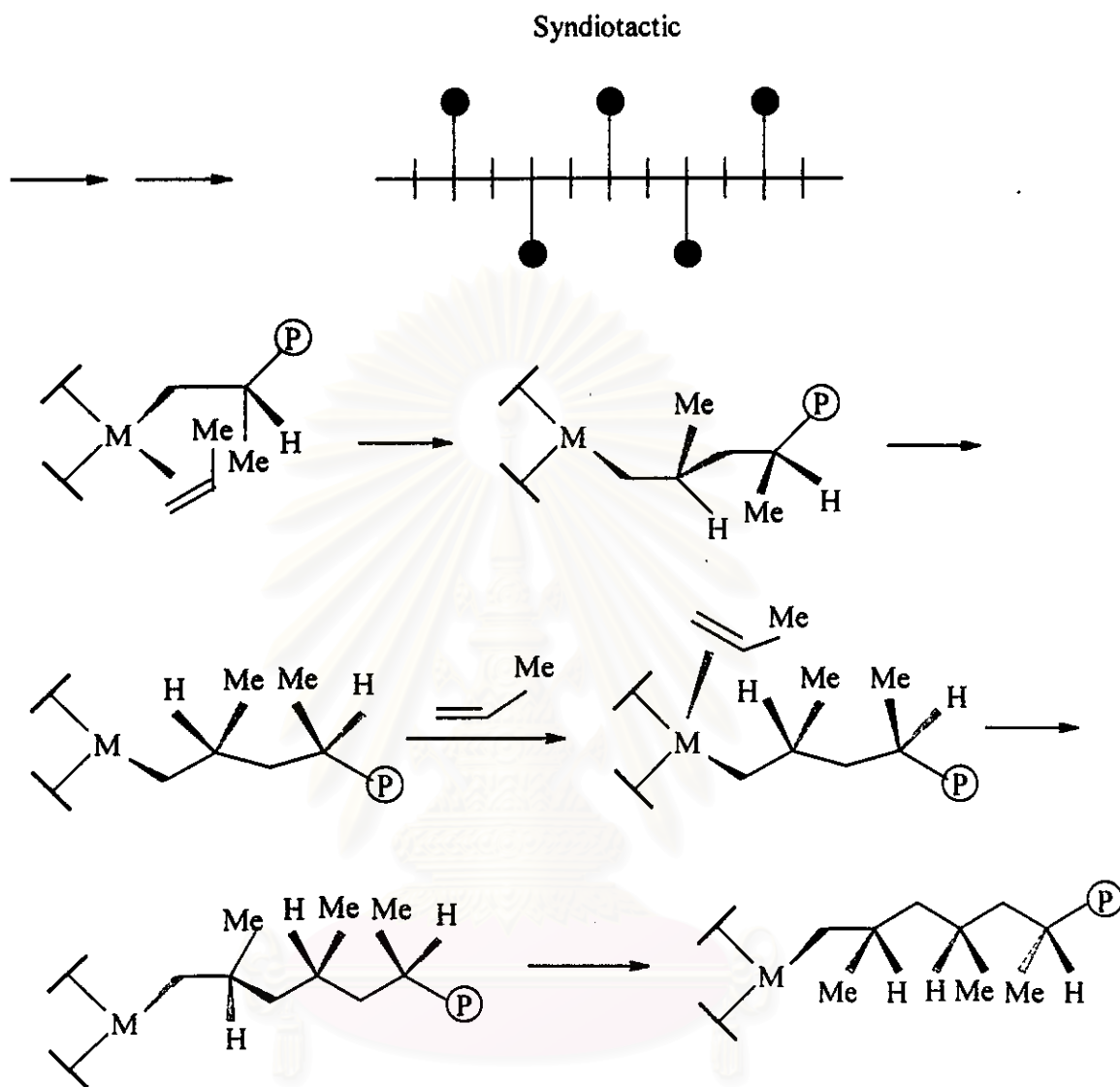
Figure 3.11 Stereoregulation for syndiotactic propylene polymerization by enantiomorphic site-controlled mechanism [81]

3.2.2.2 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 [127]. The catalyst system Cp_2TiPh_2/MAO produces isotactic polypropylene by a chain-end-controlled mechanism (Figure 3.12) [122]. 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 (Figure 3.8). The $Cp_2{}^*MCl_2/MAO$

catalyst system polymerizes 1-butene to a predominantly syndiotactic poly(1-butene) [123]. This is the first example of a syndiospecific chain-end control (Figure 3.12) mechanism for a metallocene catalyst system.
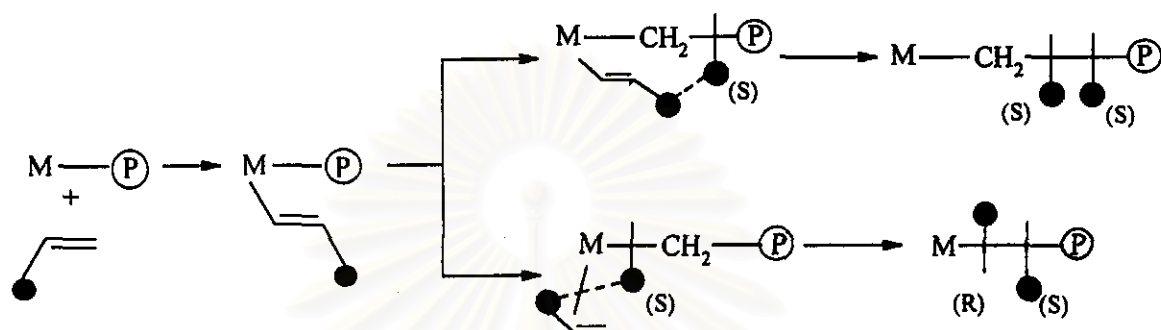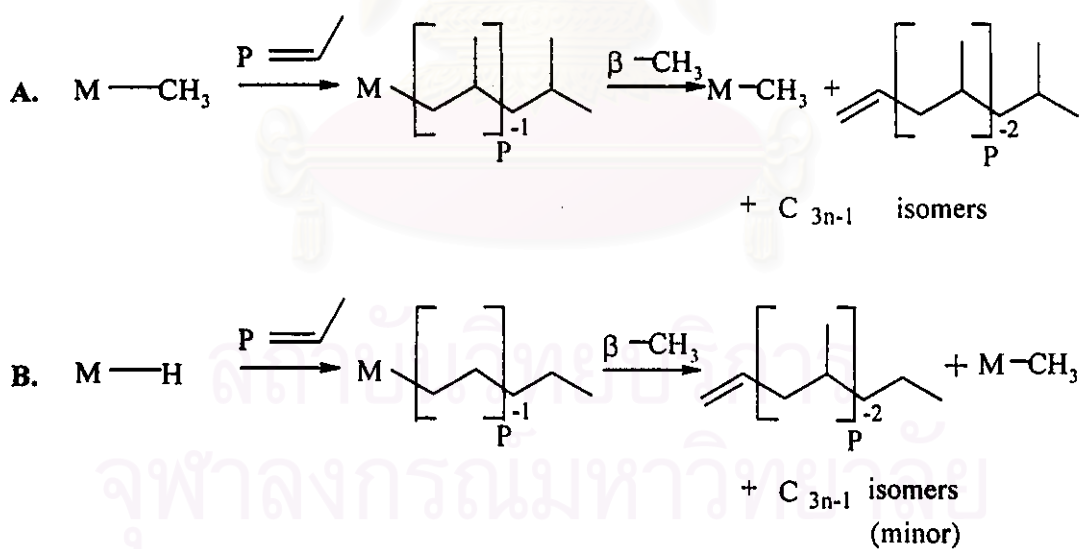

Figure 3.12 Stereochemical chain-end-controlled syndio- and isotactic propylene polymerization [81]

3.2.3 Chain Transfer Mechanism

In metallocene-catalyzed olefin polymerization, the termination of polymer chain [135-136] occurs through a chain transfer involving β-H elimination (Figure 3.13) [137] and β-Me elimination (Figure 3.14) [138]. The termination of a polymer chain may also occur due to chain transfer to aluminum (Figure 13.15) [53, 96], monomer (Figure 13.16) [139-140], or hydrogen (Figure 13.17) [140]. All of the mechanisms proposed above are dependent on the nature of the metallocene, aluminoxane, and the polymerization conditions. Resconi *et al.* [135] studied the contribution of various chain transfer processes in the propylene polymerization reaction due to the different metallocenes and reaction conditions. $Cp_2^*MCl_2/MAO$ (Cp^* = pentamethylcyclopentadienyl; M = Zr, Hf) gives atactic propylene oligomers and low molecular weight polymer. 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 vinylidine and allyl groups. Product analysis shows that both M-CH$_3$ and M-H bonded active species are involved in the chain termination step involving β-CH$_3$ or β-H elimination.
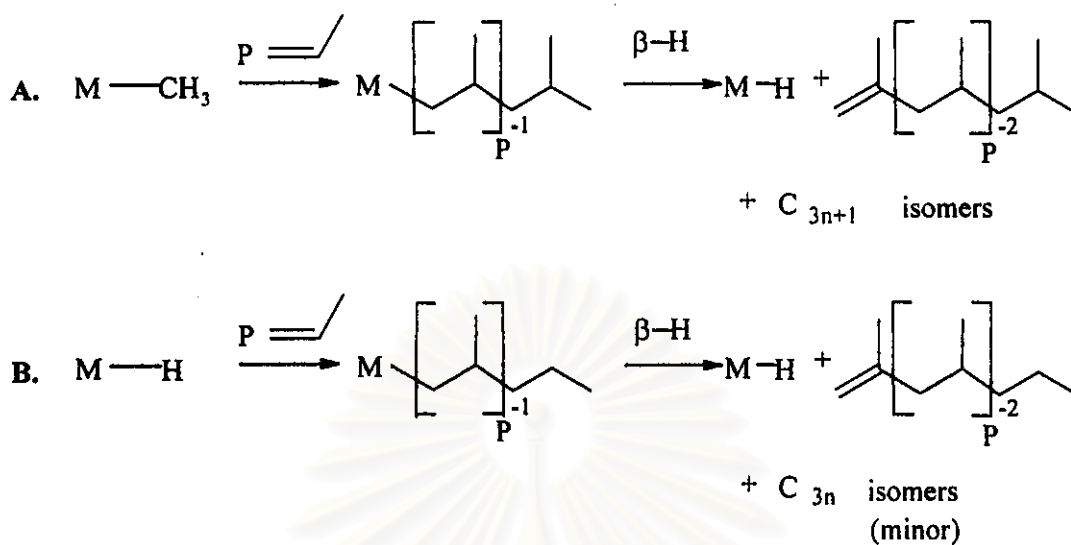
Figure 3.13 Chain transfer via β-H elimination [135]

Figure 3.14 Chain transfer via β-Me elimination [135]

Figure 3.15 Chain transfer to aluminum [135]

Figure 3.16 Chain transfer to monomer


Figure 3.17 Chain transfer to hydrogen

3.2.4 Mechanism of Catalyst Deactivation

A slow catalyst deactivation was observed in almost all polymerizations with metallocene/MAO catalysts. The deactivation might be attributed to the formation of inactive species with a M-CH$_2$-Al structure shown by evolution of methane (Figure 3.18) [141]. Although these inactive species can be reactivated by a transmetallation reaction with MAO and lost Al-CH$_2$-Al structure at high [MAO] – as MAO is consumed during the polymerization by side reactions, by impurities, by chain transfer and by recreating active sites – the regeneration of the active sites will decrease at lower [MAO], and it may not compensate for the loss of the active sites. Thus a polymerization rate decay occurs.
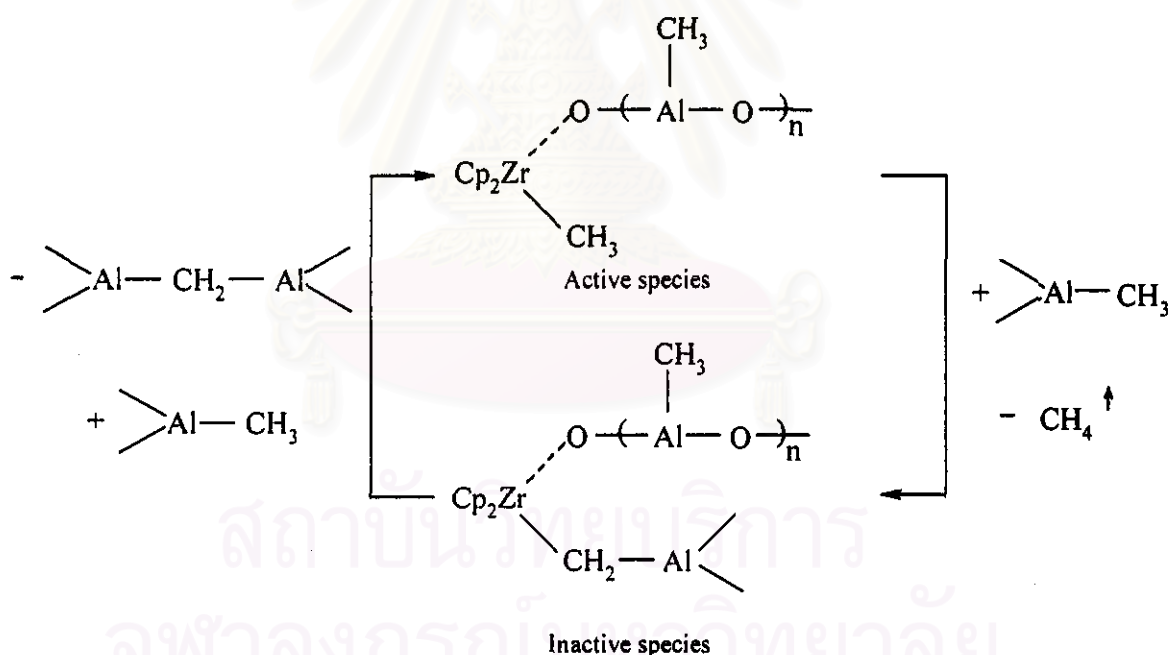
Figure 3.18 Mechanism showing the deactivation of the active center for the Cp$_2$ZrCl$_2$-MAO catalyst system

Mulhaupt *et al.* [57] found that there is another type of deactivation, which is fast and second-order relative to the active site concentration, in the Cp$_2$ZrCl$_2$/MAO system. The catalyst activation is completed within a few seconds after contacting zirconocene with MAO. After the maximum rate is reached, the

second-order decay starts. It is fast as compared to the very slow subsequent decay. Mulhaupt proposed a kinetic Figure 3.19 as shown below:
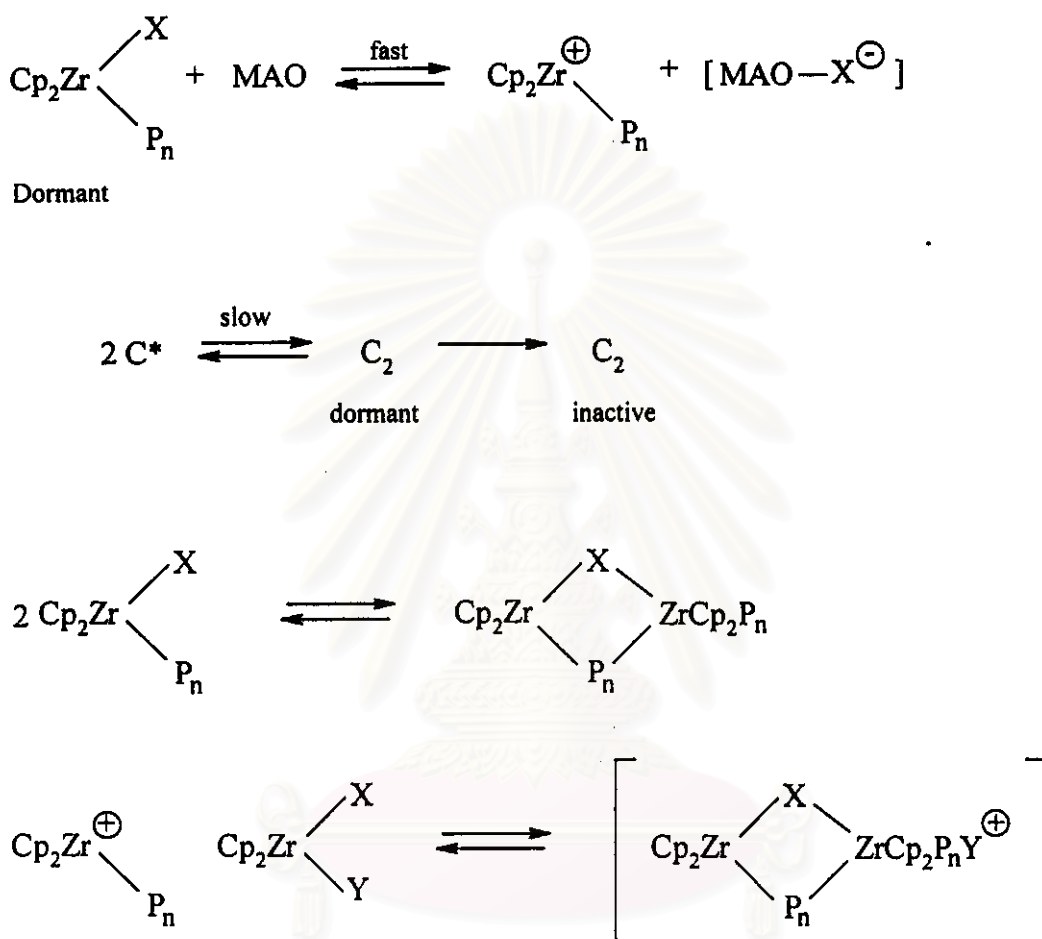
Dormant

X, Y : Me, Cl, O-AlMe-MAO; P: polymer

Figure 3.19 Mechanism of reversible second-order deactivation

The mechanism involves reversible second-order deactivation combined with a slower irreversible deactivation of the active and/or dormant zirconium sites. The reversible conversion of active cationic zirconium sites into dormant neutral zirconium sites is shown in Figure 3.19. Most likely, the reversible second-order deactivation results from zirconocene dimerization.

3.3 The Operational Factors Affecting Catalyst Activity for Ethylene Polymerization

Titanocene, when activated by organoaluminum halides, was first demonstrated by Breslow and Newburg to function as a homogeneous olefin polymerization catalyst [30]. A bimetallic complex having tetra-valent titanium was believed to be the active species. The catalyst underwent rapid deactivation by bimolecular reductive disproportionation [142]. The inactive trivalent titanium species could be reactivated by oxidation with oxygen. Sinn, Kaminsky and co-workers subsequently investigated zirconocene dichloride for ethylene polymerization [34, 143]. These titanium and zirconium catalyst systems exhibit only modest activity in the case of polyethylene, polymer product of relatively low molecular weight and do not polymerize higher olefins.

3.3.1 Effect of Transition Metal

Ti, Zr and Hf are the most commonly used transition metals for the polymerization of ethylene. Metallocenes based on different Group IVA transition metals have varying activity for ethylene polymerization. Literature data showing the effect of transition metals on ethylene polymerization are summarized in Table 3.5.

Table 3.5 Effect of transition Metals on Ethylene Polymerization Using Metallocene/ MAO Catalyst System

Catalyst system	Polymerization conditions	Activity (kg-PE/g-metal.h.MPa)	Features	Ref.
Cp_2TiCl_2	[Ti]=$3x10^{-6}$M, 20°C	900	$Mv = 4.3x10^5$	144
Cp_2ZrCl_2	[Zr]=$4.8x10^{-6}$M, Al/Zr=11,700, 70°C, 170 kPa	1,540	$Mv = 0.27x10^5$	145
Cp_2HfCl_2	[Hf]=$4.8x10^{-6}$M, Al/Hf=11,700, 70°C, 170 kPa	420	$Mv = 0.45x10^5$	145
$Cp_2Ti(CH_3)_2$	[Ti]=$3x10^{-6}$M, 20°C	50	$Mv = 5.2 x10^5$	144
$Cp_2Zr(CH_3)_2$	[Zr]=$3x10^{-7}$M, Al/Zr=14,000, 50°C, 300 kPa	1,070	$Mv = 3.31x10^5$, MWD = 1.8	146
$Cp_2Hf(CH_3)_2$	[Hf]=$3x10^{-7}$M, Al/Hf=15,000, 50°C, 300 kPa	180	$Mv = 3.6x10^5$	146
$Cp_2Ti(C_6H_5)_2$	[Ti]=$3x10^{-7}$M, Al/Ti=17,000, 50°C, 300kPa	630	$Mv = 5.7x10^5$, MWD = 1.73	146
$Cp_2Zr(C_6H_5)_2$	[Zr]=$3x10^{-7}$M, Al/Zr=18,000, 50°C, 300 kPa	3,280	$Mv = 2.9 x 10^5$	146
$Cp_2Hf(C_6H_5)_2$	[Hf]=$3x10^{-7}$M, Al/Hf=12,000, 50°C, 300 kPa	320	$Mv = 3.8 x 10^5$	146

Kaminsky *et al.* have stated that for ethylene polymerizations employing $Cp_2M(CH_3)_2$/MAO (M = Ti, Zr, Hf), the zirconium catalyst is more active than the titanium or hafnium catalysts, especially at temperatures over 50°C [61]. Gianetti *et al.* also reported highest catalyst activities with Zr-based system [146]. Considerably lower activities were achieved by the hafnium metallocenes. Ethylene polymerizations were studied by Chien *et al.* [53] using Cp_2ZrCl_2/MAO and Cp_2HfCl_2/MAO at 170 kPa of ethylene pressure. The Hf catalysts demonstrated approximately two thirds the activity of the Zr catalyst. This difference may be attributed to the greater number of active centers present in the Zr catalyst ($C^* = 52\%$ for Cp_2HfCl_2 and $C^* = 80\%$ for Cp_2ZrCl_2). The activity of the Cp_2ZrCl_2/MAO catalyst has been found to be inversely proportional to the Zr concentration. This was interpreted as due to a decrease of bimolecular deactivation. In contrast, variation of activity with Hf concentration is less pronounced [53].

The Hf catalyst shows a smaller dependence of polymer molecular weight on temperature. Depending upon the polymerization conditions (concentration of transition metal and MAO and temperature), the polymer obtained with the Hf catalyst can have higher molecular weight (>50°C) or lower molecular weight (<50°C) than the polymer obtained with the Zr catalyst. Titanium-based catalysts are more active at lower temperature. These catalysts show low polymerization activity as compared to Zr and high polymerization activity as compared to Hf-based catalysts. Due to these reasons, Zr-based metallocenes have assumed generally greater importance.

3.3.2 Effect of Ligands around the Transition Metal

The data available in the literature on the effect of ligands around the transition metal for polymerization of ethylene are summarized in Table 3.6. Bis (cyclopentadienyl)titanium(IV) and bis(cyclopentadienyl)zirconium(IV) compounds together with MAO have shown to be the most useful homogeneous Ziegler-Natta catalysts for ethylene polymerization. Ring-substituted zirconocene dichlorides, especially bis(pentamethylcyclopentadienyl)zirconium dichloride, $(CpMe_5)_2ZrCl_2$,

have been used as catalysts for polymerization of ethylene. $(CpMe_5)_2ZrCl_2$ shows a lower activity (by a factor of 5-10) compared to bis(cyclopentadienyl)zirconium dichloride. However, the molecular weight of the poly(ethylene)s produced by the former was twice that of the latter. With $(CpMe_5)_2ZrCl_2$, the highest reported molecular weight of 1,500,000 (Mn) has been achieved. However, the polydispersity was between 6 and 15, which is much broader than that obtained with Cp_2ZrCl_2. This has been attributed to the presence of two active centers with widely varying reaction rates as well as ability for monomer insertion.

Gianetti *et al.* achieved high catalyst activities with the $Cp_2Zr(C_6H_5)_2$, $Cp_2Zr(CH_2C_6H_5)_2$ and $Cp_2Zr[CH_2Si(CH_3)_3]_2$ complexes. A remarkably high activity, compared to that of $Cp_2Zr(CH_3)_2$, was achieved by the related π-indenyl complex $(Ind)_2Zr(CH_3)_2$. When the bis (π-fluorenyl) analog was employed as a catalyst component, only traces of polymer were recovered [146]. It has been proposed that reactive intermediates for soluble Ziegler-Natta catalyst are cationic alkyls [147]. Due to the steric effect or electron-donating power of ligands, the resulting cationic species may get stabilized or destabilized and result in an increase or decrease in catalyst activity. Due to steric effects, the fundamental steps involved in the polymerization process, such as alkyl migration or olefin insertion, may be either retarded or accelerated. The effect of substituents on the cyclopentadienyl rings $(\eta^5-RC_5H_4)_2ZrCl_2$ (where R = H, Me, n-Pr and t-bu) was studied in detail by Tait [148] and coworkers. Increase in rate and k_p for ethylene polymerization was observed according to the order t-Bu < H < i-Pr < n-Pr < Me. Active center concentration, C^*, remained more or less constant for all the catalyst systems.

The inductive and hyperconjugative effects of alkyl substituents will increase the electron density of the η^5-cyclopentadienyl ligand leading to increased electron density at the zirconium atom, which in turn leads to an increased rate of polymerization. This increase in polymerization rate may be due to a lowering of the stability of the η^2-alkene-zirconium bond resulting in a more weakly coordinated monomer, facilitating insertion into the growing polymer chain. Alternatively, or, in

addition, a higher electron density at the zirconium atom may weaken the zirconium-carbon σ-bond of the growing polymer chain, which could also facilitate insertion of the monomer and hence lead to an increased rate of polymerization.

Opposing these effects, an increase in the steric bulk of the alkyl substituent may hinder the approach of the incoming monomer and decrease the rate of polymerization. Thus, the observed rates of polymerization and activities may then reflect a combination of the steric and electronic effects and may reach a maximum when R = Me.

3.3.3 Effect of Cocatalyst/Catalyst (Al/Metal) Ratio

Effect of Al/metal ratio mainly influences catalyst activity, molecular weight of polymer and kinetic profile of polymerization. The effect of Al/metal ratio on ethylene polymerization is summarized in Table 3.7.

Chien and Wang have explored the effect of Al/metal ratio for the polymerization of ethylene using Cp_2ZrCl_2 and $CpZrCl_3$ systems [53]. The effects of [metallocene] and [MAO] were investigated by holding the former constant while varying the latter and vice versa. In the case of Cp_2ZrCl_2/MAO catalyst system, both the shape of polymerization rate profile and activity are only slightly dependent on [MAO] (Table 3.7). A large increase of activity of $CpZrCl_3$/MAO system is more dependent on [MAO] than in the case of Cp_2ZrCl_2/MAO; a five-fold increase of [MAO] raises activity by a factor or two.

It has been reported that the number of active sites [C*] is between 75 and 100% of the number of Zr atoms. Therefore activity should be independent of [Zr] [53]. But reality, activity is found to increase with decrease of catalyst concentration.

Table 3.6 Effect of Ligands around the Transition Metal for Ethylene Polymerization Using Metallocene/MAO Catalyst System

Catalyst system	Polymerization Conditions	Activity (kg-PE/g-Zr.h.MPa)	Features	Ref.
Cp_2ZrCl_2	$[Zr]=1\times10^{-6}M$, $Al/Zr=15000$, $70°C$, $600-800$ kPa	3230	$Mv=1.2\times10^5$	61
$Cp(CpMe_5)ZrCl_2$	$[Zr]=1\times10^{-6}M$, $Al/Zr=1000$, $70°C$, $600-800$kPa	630	$Mv=7.7\times10^5$	61
$(CpMe_5)_2ZrCl_2$	$[Zr]=1\times10^{-6}M$, $Al/Zr=15000$, $70°C$, $600-800$kPa	420	$Mv=2.7\times10^5$, $MWD=6-15$	61
$Cp_2Zr(CH_3)_2$	$[Zr]=3\times10^{-7}M$, $Al/Zr=140000$, $50°C, 300$kPa	1070	$Mv=3.31\times10^5$, $MWD=1.8$	146
$Cp_2Zr(C_6H_5)_2$	$[Zr]=3\times10^{-7}M$, $Al/Zr=18000$, $50°C, 300$kPa	3280	$Mv=2.87\times10^5$, $MWD=1.7$	146
$Cp_2Zr(CH_2SiMe_3)_2$	$[Zr]=3\times10^{-7}M$, $Al/Zr=14000$, $50°C, 300$kPa	5670	$Mv=3.22\times10^5$, $MWD=2.3$	146
Ind_2ZrMe_2	$[Zr]=3\times10^{-7}M$, $Al/Zr=22000$, $50°C, 300$kPa	7260	$Mv=3.95\times10^5$, $MWD=2.2$	146
$(\eta^5-RC_5H_4)_2ZrCl_2$				
R = H	$[Zr]=2.4\times10^{-5}M$, $Al/Zr=1000$, $60°C, 100$kPa	1000	$C^*=0.94$mol/mol.Zr, $Rp=9.1$kg.PE/mmol.Zr.h	148
R = Me	$[Zr]=2.4\times10^{-5}M$, $Al/Zr=1000$, $60°C, 100$kPa	1110	$C^*=0.98$mol/mol.Zr, $Rp=10$kg.PE/mmol.Zr.h	148

Table 3.7 Effect of Al/Metal Ratio on Ethylene Polymerization Using Metallocene/ MAO Catalyst System

Catalyst system	Al/Metal	Polymerization conditions	Activity (kg-PE/g-Zr.h.Mpa)	Ref.
Cp$_2$ZrCl$_2$	521	[Zr]=4.8x10^{-5}M, 70°C, 140kPa	166	53
Cp$_2$ZrCl$_2$	1071	[Zr]=4.8x10^{-5}M, 70°C, 140kPa	200	53
Cp$_2$ZrCl$_2$	2125	[Zr]=4.8x10^{-5}M, 70°C, 140kPa	230	53
Cp$_2$ZrCl$_2$	22,730	[Zr]=1.1x10^{-5}M, 70°C, 140kPa	3280	53
Cp$_2$ZrCl$_2$	46,730	[Zr]=1.1x10^{-5}M, 70°C, 140kPa	3940	53
Cp$_2$ZrCl$_2$	92,730	[Zr]=1.1x10^{-5}M, 70°C, 140kPa	4900	53
CpZrCl$_3$	1060	[Zr]=4.8x10^{-5}M, 50°C, 140kPa	66	53
CpZrCl$_3$	2710	[Zr]=4.8x10^{-5}M, 50°C, 140kPa	152	53
CpZrCl$_3$	5340	[Zr]=4.8x10^{-5}M, 50°C, 140kPa	343	53

3.3.4 Effect of Temperature

Temperature influences mainly the molecular weight of the polymer, but also the polymerization activity. It is a common characteristic of Ziegler-Natta catalysis that there is an optimum temperature range for maximum activity, below or above which catalyst activity decreases. The variation of catalytic activity and molecular weight with temperature is shown in Table 3.8. When temperature is

plotted against catalyst activity, there is a broad regime where the activity is relatively constant; it decreases at lower temperatures. The molecular weight of the polymer decreases monotonically with increasing temperature. The activation energy was found to be 34 kJ/mol for the Cp_2ZrCl_2/MAO catalyst system. These results may be attributed to increase in the rates of both propagation and deactivation with increasing temperature. Chien and Wang have speculated on the possible mechanism for deactivation [149]. One possibility is a slow dissociation of complexed MAO (equation 3.2).

$$C_i^* - P \longrightarrow C_{i-n}^* - P + n\,MAO \qquad (3.2)$$

Where $C_i^* = C^*$ with 'i' number of MAO complexed with it.

The C_{i-1}^* is less protected by MAO than C_i^* and in fact if $i - n = 0$, rapid bimolecular deactivation occurs. A second possible deactivation mechanism is by β-hydride elimination to give metallocene hydride, which has very low propensity for monomer insertion.

At optimum temperature, the catalysts show relatively high rates of propagation and relatively low rates of deactivation, due to which the high activity is observed. Above the optimum temperature, rates of propagation as well as deactivation increase and below the optimum temperature rates of propagation as well as deactivation decrease and as a net result, low activities will be observed. At low temperature, the chain transfer rate is low, on account of which high molecular weight polymers are produced.

Table 3.8 Effect of Temperature on Ethylene Polymerization Using Metallocene/ MAO Catalyst System

Catalyst system	Temp. (^{o}C)	Polymerization conditions	Activity (kg-PE/g-Zr.h.MPa)	Features	Ref.
Cp_2ZrCl_2	0	$[Zr]=4.75 \times 10^{-5}M$, Al/Zr=1070, 150kPa	40	$Mv=460 \times 10^3$	100
Cp_2ZrCl_2	30	$[Zr]=4.75 \times 10^{-5}M$, Al/Zr=1070, 150kPa	170	$Mv=200 \times 10^3$	100
Cp_2ZrCl_2	50	$[Zr]=4.75 \times 10^{-5}M$, Al/Zr=1070, 150kPa	160	$Mv=65 \times 10^3$	100
Cp_2ZrCl_2	70	$[Zr]=4.75 \times 10^{-5}M$, Al/Zr=1070, 150kPa	190	$Mv=11 \times 10^3$	100
Cp_2ZrCl_2	80	$[Zr]=4.75 \times 10^{-5}M$, Al/Zr=1070, 150kPa	160	$Mv=12 \times 10^3$	100
Cp_2ZrCl_2	90	$[Zr]=4.75 \times 10^{-5}M$, Al/Zr=1070, 150kPa	-	$Mv=6 \times 10^3$	100
$(CpMe_5)_2ZrCl_2$	20	$[Zr]=1 \times 10^{-6}M$, Al/Zr=15,000, 600-800kPa	90.4	$Mv= >1500$	100
$(CpMe_5)_2ZrCl_2$	70	$[Zr]=1 \times 10^{-6}M$, Al/Zr=15,000, 600-800kPa	416	$Mv=270$	100

Table 3.9 Effect of Time on Ethylene Polymerization Using Metallocene/MAO Catalyst System

Catalyst system	Time (min.)	Polymerization conditions	Features	Ref.
Cp_2ZrCl_2	5	$[Zr]=4.8 \times 10^{-5}M$, Al/Zr=1070, 70°C, 140kPa	Mn=0.04×10^5, MWD=3.2	53
Cp_2ZrCl_2	40	$[Zr]=4.8 \times 10^{-5}M$, Al/Zr=1070, 70°C, 140kPa	Mn=0.06×10^4, MWD=3.1	53
Cp_2ZrCl_2	5	$[Zr]=3.8 \times 10^{-6}M$, Al/Zr=10,790, 70°C, 140kPa	Mn=0.21×10^5, MWD=2.2	53
Cp_2ZrCl_2	20	$[Zr]=3.8 \times 10^{-6}M$, Al/Zr=10,790, 70°C, 140kPa	Mn=0.18×10^5, MWD=2.2	53
Cp_2ZrCl_2	40	$[Zr]=3.8 \times 10^{-6}M$, Al/Zr=10,790, 70°C, 140kPa	Mn=0.21×10^5, MWD=2.1	53
$CpZrCl_3$	5	$[Zr]=4.8 \times 10^{-5}M$, Al/Zr=1070, 70°C, 140kPa	Mw=0.3×10^5, Mn=0.11×10^5, MWD=2.7	53
$CpZrCl_3$	10	$[Zr]=4.8 \times 10^{-5}M$, Al/Zr=1070, 70°C, 140kPa	Mw=0.26×10^5, Mn=0.10×10^5, MWD=2.6	53
$CpZrCl_3$	60	$[Zr]=4.8 \times 10^{-5}M$, Al/Zr=1070, 70°C, 140kPa	Mw=0.3×10^5, Mn=0.11×10^5, MWD=2.7	53
$CpZrCl_3$	5	$[Zr]=3.8 \times 10^{-6}M$, Al/Zr=10,790, 70°C, 140kPa	Mw=1.1×10^5, Mn=0.46×10^5, MWD=2.4	53
$CpZrCl_3$	10	$[Zr]=3.8 \times 10^{-6}M$, Al/Zr=10,790, 70°C, 140kPa	Mw=0.7×10^5, Mn=0.78×10^5, MWD=2.5	53
$CpZrCl_3$	50	$[Zr]=3.8 \times 10^{-6}M$, Al/Zr=10,790, 70°C, 140kPa	Mw=1.01×10^5, Mn=0.46×10^5, MWD=2.2	53