CHAPTER II

LITERATURE REVIEW

2.1 Metallocene Catalysts

2.1.1 Role of Metallocene Catalysts for Olefin Polymerization

One of the biggest challenges for modern organometallic chemistry is to apply metallocene complexes with Group IV metals to new technologies and production of new materials. Metallocene compounds are becoming an important class of catalysts for the synthesis of organic molecules and polymers. Metallocene catalysts are operative in all existing industrial plants that are presently used for polyolefin manufacture revolutionize the technology for the production of these polymers (Imanishi and Naga, 2001).

Polyethylenes properties must meet customer needs and the appropriate technology must be used to produce products with the required properties. This requires detailed knowledge and know-how of relationships among processing conditions, polymer structure and polymer properties. For catalytic polymerization processes the catalyst, mostly in combination with a cocatalyst, and the polymerization process are regarded as the polymerization technology. This means that both the process and the catalyst are an integrated whole and must be well balanced in respect to each other (Xie *et al.*, 1994). The catalyst or catalyst system plays the key role, as shown on Figure 2.1, in the choice of process and product properties. The catalyst determines the polymerization behavior, the polymer structure and for heterogeneous processes the polymer powder morphology. The catalyst system must fit the polymerization process.
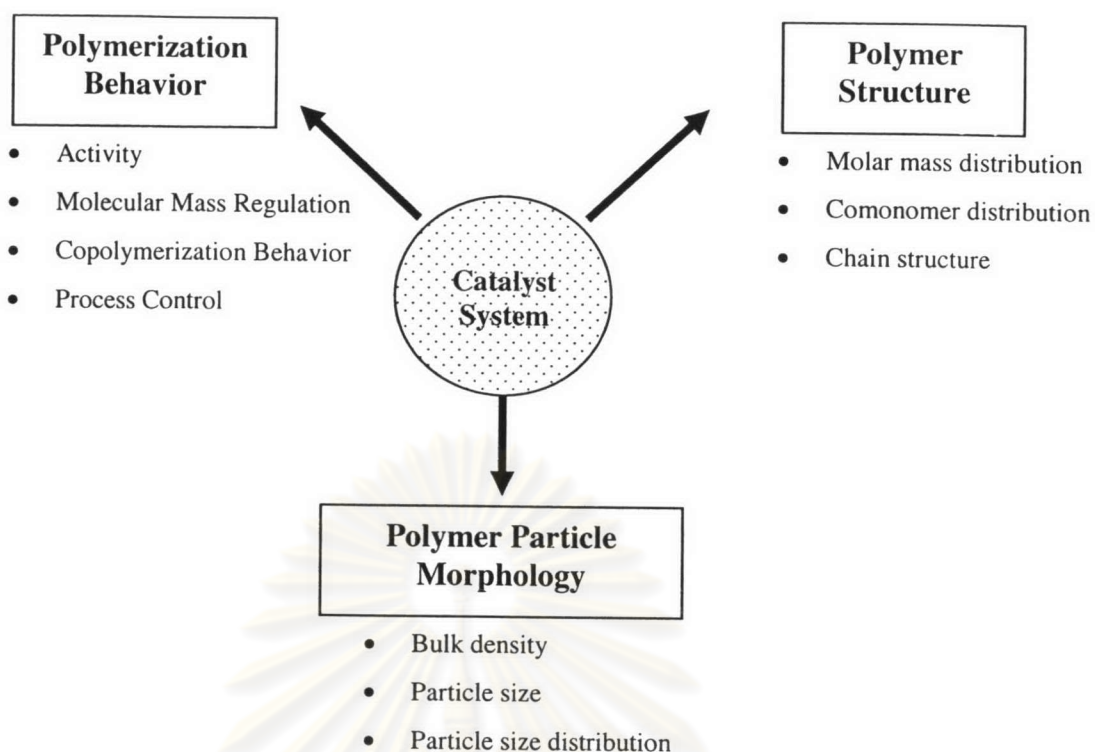
Polymerization Behavior		Polymer Structure

- Activity
- Molecular Mass Regulation
- Copolymerization Behavior
- Process Control

Catalyst System

- Molar mass distribution
- Comonomer distribution
- Chain structure

Polymer Particle Morphology

- Bulk density
- Particle size
- Particle size distribution

Figure 2.1. The key role of the catalyst system (Kaminsky, 1999)

2.1.2 History of Catalyst Systems for Olefin Polymerization

The discovery of catalysts based on titanium trichloride and diethylaluminum chloride as cocatalyst was made by Karl Ziegler, who succeeded in polymerizing ethylene into high-density polyethylene (HDPE) at standard pressure and room temperature in 1953 at the Max-Planck-Institute in Mulheim. A little later, Natta, at the Polytechnical Institute of Milan, was able to demonstrate that an appropriate catalyst system was capable of polymerizing propene into semi-crystalline polypropene. Ziegler and Natta shared a Nobel Prize for Chemistry in 1963 for their work (Kaminsky and Laban, 2001). With this so-called Ziegler-Natta catalyst.

Ziegler-Natta catalyst has been widely used in olefin polymerization; the coordination polymerization allows the catalyst geometry around the metal center to control the polymer structure. In homogeneous polymerization, the ligand of a catalyst largely controls the geometry of an active metal center on which the polymerization reaction occurs. However, the molecular structure of the polymers cannot be controlled well for conventional Ziegler-Natta catalysts because these catalysts are heterogeneous with different types of catalytic sites.

The metallocene catalyst system discovered by Kaminsky has proven to be a major breakthrough for the polyolefin industry. Metallocene catalysts show in contrast to conventional Ziegler-Natta catalytic systems, only one type of active site (single site catalyst), which produces polymers with a narrow molar mass distribution ($M_w/M_n = 2$). The molecular structure of the metallocene catalysts cöan be easily changed which allows control of the structure of polyolefin produced with these catalysts. Many metallocenes are soluble in hydrocarbons or liquid propene. These properties allow one to predict accurately the properties of the resulting polyolefins by knowing the structure of the catalyst used during their manufacture and to control the resulting molar mass and distribution, comonomer content and tacticity by careful selection of the appropriate reactor conditions. In addition, their catalytic activity is 10-100 times higher than that of the classical Ziegler-Natta systems.

Metallocenes, in combination with the conventional aluminum alkyl cocatalyst used in Ziegler systems, are indeed capable of polymerizing ethylene, but only at a very low activity. Only with the discovery and application of methylaluminoxane (MAO) by Sinn et al., 1980, was it possible to enhance the activity, surprisingly, by a factor of 10000. Therefore, MAO played a crucial part in the catalysis with metallocenes. Since this discovery of effective zirconocene-MAO catalyst systems for ethylene polymerization, improvement of the catalyst system has been conducted to achieve higher activity and to obtain higher molecular weight polyethylene. Modifications of metallocene ligand were investigated in non-bridged and bridged zirconocene catalysts (Alt and Köppl, 2000).

Polyolefins, with different microstructures and characteristics, can be custom-made just by varying the ligand of the metallocene. By combining different olefins and cycloolefins with one another, the range of characteristics can be further broadened. The production of polyolefins with tailored microstructures and of chemically uniform copolymers has not yet been achieved by conventional heterogeneous catalysts (Kaminsky and Laban, 2001). However, extensive research has been devoted towards metallocene catalyst studying modifications of the catalyst system, which leads to specific changes in catalytic activity and product characteristics (Scheirs and Kaminsky, 1999; Alt and Köppl, 2000). The development of metallocene catalysts has not yet been concluded, and studies are required to

increase the understanding of several important factors which affect catalytic performance, such as transition metal-olefin interaction, metal-alkyl bond stability, influence of other ligands, and steric effects of the other ligands.

2.1.3 General Structure of Metallocene Catalysts

Metallocene catalysts are organometallic coordination compounds in which one or two π-carbocylic 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 typical chemical structure of a metallocene catalyst is represented by Figure 2.2.
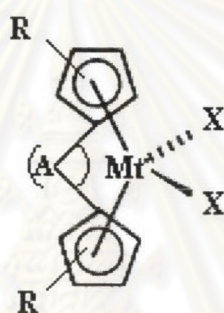
where Mt = Group 4, 5, or 6 transition metal (e.g. Zr, Ti or Hf)

A = an optional bridging unit consisting of 1-3 atoms in the backbone

R = hydrocarbyl substituents or fused ring systems (indenyl, fluorenyl and substituted derivatives)

X = chlorine or other halogens from group 17 or an alkyl group

Figure 2.2. Typical chemical structure of a metallocene catalyst (Alt, 1999)

Single site catalysts can be divided into five main symmetry categories, which influence on the polymer architectures as shown in Figure 2.3. It is assumed that the polymer rapidly equilibrates with the available coordination site for the purposes of assigning symmetry. Catalysts exhibiting C_{2v} symmetry typically produce atactic polymers or moderately stereoregular polymers by chain-end control mechanisms. C_s-symmetric catalysts that have mirror planes containing the two-diastereotopic coordination sites behave similarly. However, C_s-symmetric catalysts

that have a mirror plane reflecting two enantiotopic coordination sites frequently produce syndiotactic polymers. C_2-symmetric complexes, both racemic mixtures and enantiomerically pure ones, typically produce isotactic polymers via a site-control mechanism. Stereoselectivities of asymmetric (C_1) complexes are unpredictable and have been reported to produce polymer architectures ranging from highly isotactic, to atactic, including isotactic-atactic stereoblock and hemiisotactic. Polymer architectures relevant to this modification of ligands are shown in Figure 2.4.
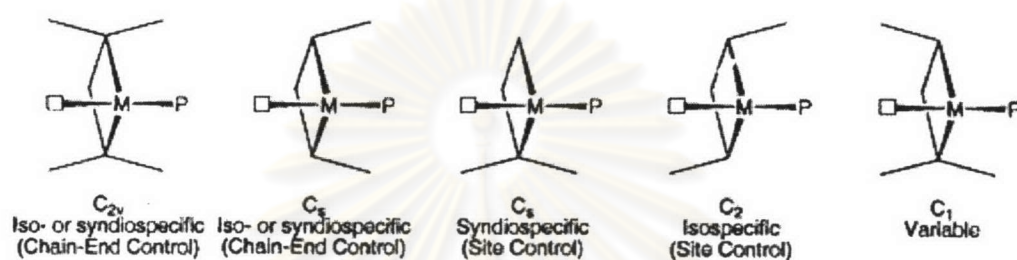
Figure 2.3. General symmetry classifications, based on ligand geometries, of catalysts and their stereoselectivities for polyolefin synthesis (Coates, 2000)
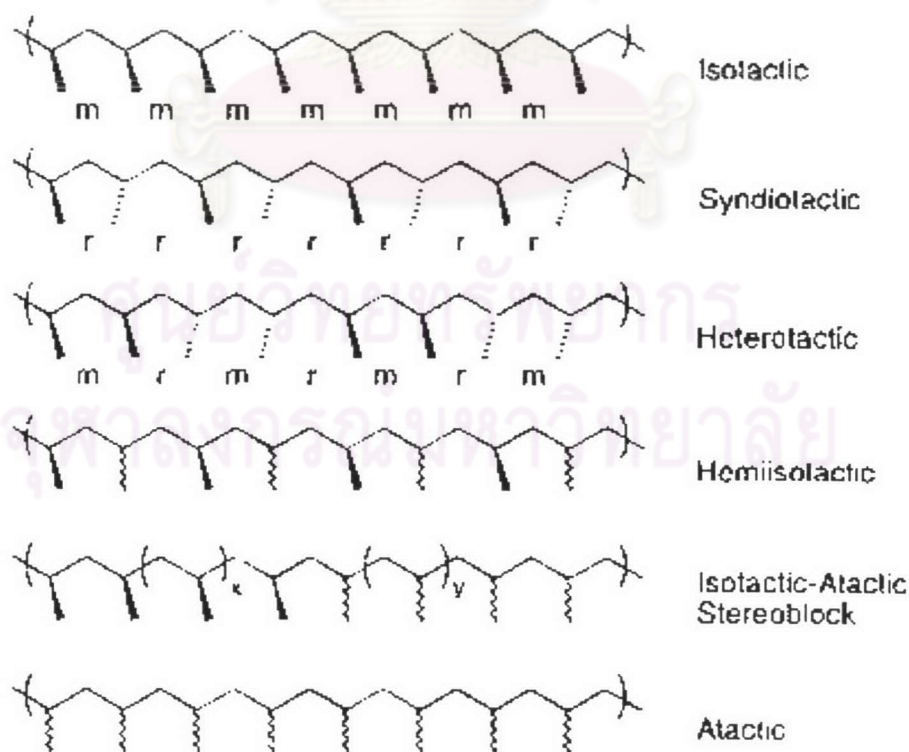

Figure 2.4. Common polymer tacticities (Coates, 2000)

### 2.1.4 'Tailoring' of metallocene catalysts (Long, 1998)

Extensive research has been devoted towards 'catalytic tailoring' with modification of the catalyst system leading to specific changes in catalytic activity and product characteristics. This requires an understanding of the physical properties involved in ligand modification and there are several important factors affecting catalytic performance:

(a) Transition metal-olefin interaction. The olefin has a basic character with respect to the metal and therefore acts as an electron donor. The σ- and π-bonds formed between the metal and olefin destabilize and activate the olefin for insertion. Olefin co-ordination also destabilizes the M-R (R=alkyl) bond. The stability of olefin co-ordination to M decreases with increasing olefin size due to steric factors and the energies of the olefin orbitals involved in bonding to the metal.

(b) Metal-alkyl bond stability. Fine adjustment of the M-R bond is possible by variation of ligand electronic effects. The M-R bond should be unstable to permit facile opening and olefin insertion to form a new metal-alkyl bond but also strong enough to favor catalytic lifetimes. The strength of this bond depends on R itself and the stability decreases in the order Me> Et> $(CH_2)_nCH_3$. Olefin co-ordination is also another method of weakening the M-R bond in preparation for migratory insertion.

(c) Influence of other ligands. Considering the Cp rings and substituents attached to them, then if the ligand system used is a good electron donor it will reduce the positive charge on the metal. This weakens the bonding between the metal and all other ligands, particularly the already unstable M-R bond, making insertion more facile. Conversely, this will also stabilize high oxidation state complexes and make co-ordination of the incoming olefin more unfavorable and so a balance must be found between these effects.

(d) Steric effects of the other ligands. Bulky ligands will aid stereospecific olefin co-ordination and polymerization. Steric effects influence the coordination of bulky monomers and selectivity towards different monomeric species in a polymerization reaction can be maintained. The coordination site can be opened or closed by controlling the angle that the cyclopentadienyl rings tilt away from each other. Shortening or lengthening the bridge in ansa-metallocenes can lead to much improved monomeric stereoselectivity.

2.2 Methylaluminoxane Cocatalyst

The importance of cocatalysts in metal-catalyzed polymerization processes can be appreciated as follows. First, to form active catalysts, catalyst precursors must be transformed into active catalysts by an effective and appropriate activating species. Second, a successful activation process requires cocatalysts which retain the nature of the catalytic site and do not have adverse effects on the polymerization kinetics and polymer properties. Finally, the cocatalyst, which becomes an anion after the activation process, is the vital part of catalytically active cation-anion pair and may significantly influence polymerization characteristics and polymer properties (Chen and Marks, 2000).

A metallocene catalyst precursor can be activated with organoalumoxanes, especially methylaluminoxane (MAO), which provides maximum activity. Methylaluminoxane is a compound in which aluminum and oxygen atoms are arranged alternately and free valances are saturated by methyl substitutions. It is prepared by carefully controlled partial hydrolysis of trimethylaluminum (TMA) and according to investigations by Sinn, 1995; Barron et al., 1996 and Ystenes et al., 2000. The hydrolysis of AlR_3 (R = Me, Et, iBu) has been shown to proceed via the formation of an alkylaluminum water complex shown in Equation 2.1 (Barron, 1993), which subsequently eliminates an alkane to form a dialkylaluminum hydroxide complex. This rapidly associates to give dimers or larger oligomers in solution as shown in Equation 2.2.

$$AlR_3 + H_2O \longrightarrow AlR_3(H_2O) \tag{2.1}$$

$$AlR_3(H_2O) \longrightarrow 1/n\,[R_2Al(OH)]_n + RH \tag{2.2}$$
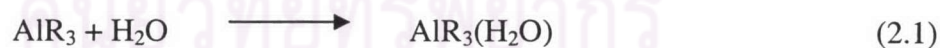
The structure of MAO consists mainly of units of the basic structure $[Al_4O_3Me_6]$, which contains four aluminum, three oxygen atoms and six methyl groups. Although very extensive research has been carried out in both academia and industry, the exact composition and structure of MAO are still not entirely clear or well understood.

The proposed structures for MAO in the open literature shown in Figure 2.5 include: (1) one-dimensional linear chains; (2) cyclic rings, which contain three-coordinate Al centers; (3) two-dimensional structures and (4) three-dimensional

clusters. The three-dimensional structure (4) proposed by Sinn, 1995 is based on structural similarities with *tert*-butylaluminoxanes, which form isoluable and X-ray crystallographically characterizable cage structures (5).
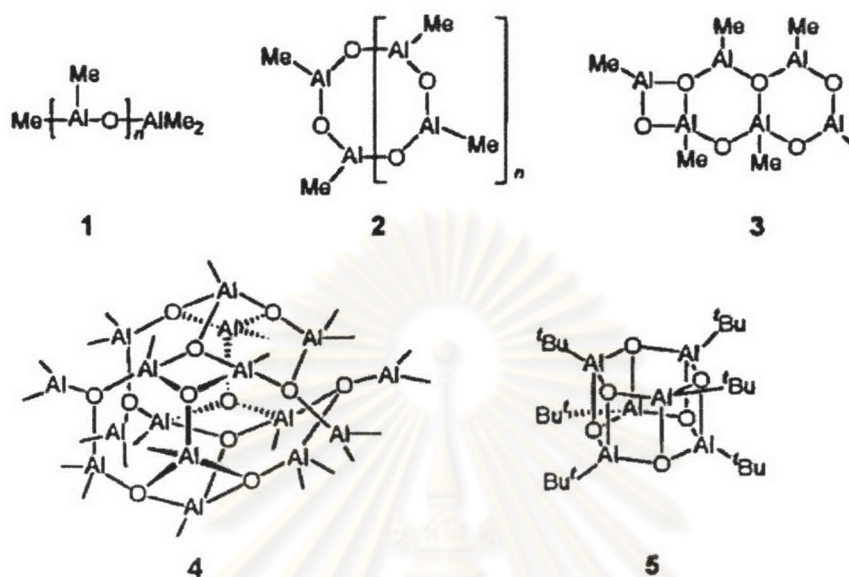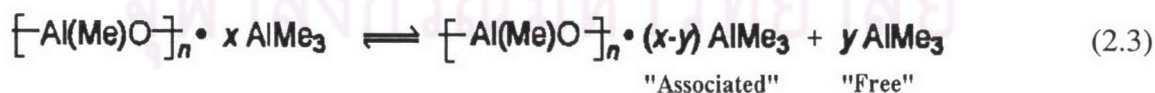

Figure 2.5. The general proposed structure of MAO (Chen and Marks, 2000)

Depending on the nature of the hydrated salt (the H_2O source) used for the MAO synthesis and the exact MAO synthetic reaction conditions, MAO-activated metallocenes may exhibit widely differing activities in olefin polymerization. The MAO structure can hardly be elucidated directly because of the multiple equilibria present in MAO solutions, and residual trimethylaluminum in MAO solutions appears to participate in equilibria that interconvert various MAO oligomers (Giannetti *et al.*, 1985; Resconi *et al.*, 1990). There are two types of TMA present in typical MAO solutions: "free" TMA and "associated" TMA shown in Equation 2.3

$$\left[Al(Me)O \right]_n \bullet \, x\, AlMe_3 \rightleftharpoons \left[Al(Me)O \right]_n \bullet (x\text{-}y)\, AlMe_3 + y\, AlMe_3 \qquad (2.3)$$

$$\text{"Associated"} \qquad \text{"Free"}$$

Tritto *et al.* (1997) found that cryoscopic MAO molecular weight decrease after $AlMe_3$ addition according to a linear relationship, which is caused by disproportionation reactions. However, recent in-situ FTIR spectroscopy investigations do not indicate any obvious reaction between TMA and MAO (Kaminsky, 1999). Nevertheless, in light of its complicated, unresolved structural

features, MAO is usually represented for the sake of simplicity as having linear chain or cyclic ring structures [-Al(Me)-O-]$_n$, containing three-coordinate aluminum centers.

Up to now the most favorable proposal for the active MAO species is to assume a cage built from six-membered rings, which consist of MeAlO building blocks. In such cages there are monomeric AlMe$_3$ molecules that have the following functionalities: alkylation of the metallocene dichloride complex and the formal abstraction of a methyl anion from the transition metal to give a metallocene monomethyl cation that is stabilized by a bulky MAO anion Figure 2.6 (Alt and Köppl, 2000).
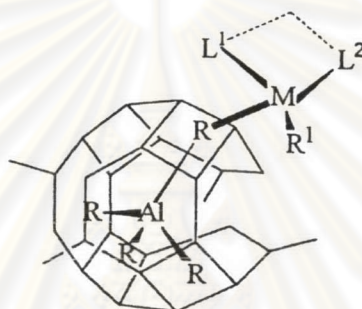
Figure 2.6. Model for an MAO cage stabilizing an activated metallocene complex
(Alt and Köppl, 2000)

Since these discoveries, MAO has become a very important cocatalyst for metal-catalyzed olefin polymerization. However, the disadvantage of this class of cocatalysts is their high price and the incorporation of fluorine into the polymer, which can cause problems when polyolefins are thermally decomposed (Alt and Köppl, 2000).

Recently, the modification by evacuated MAO was studied. Ioku et al. (2002); they found that dried methylaluminoxane (MAO) which was free of Me$_3$Al, was more active than the standard MAO system, resulting in a steady polymerization rate and giving higher M$_w$ polypropylenes. Additive effects of trialkylaluminum on the dried MAO system showed that the polymer yield was increased by the addition of i-Bu$_3$Al and Oct$_3$Al and decrease by Me$_3$Al and Et$_3$Al.

2.2.1 Interaction of Metallocene with Aluminoxanes and Nature of Active Species

The interaction of metallocene with aluminoxanes has been studied in detail. Metallocene dichloride reacts with methylaluminoxane to yield a methylated compound (Figure 2.7) It undergoes either methyl or chloride abstraction to generate metallocene methyl cation (Giannetti *et al.*,1985; Chien *et al.*,1988). The research work reported by Marks, Bochmann, Jordan and others gave synthetic and spectroscopic evidence that cationic metallocene $[(Cp_2MR)]^+$ are the active species (Yang *et al.*,1991; Hlatky *et al.*,1989). The interaction of dichlorozirconocene, methylchlorozirconocene and dimethylzirconocene with MAO has been studied by x-ray photoelectron spectroscopy (Gassman and Callstrom, 1987). The results indicated 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.*, 1992 who studied the reaction $Cp_2Zr(^{13}CH_3)_2$ 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.*, 1990 employed solution ^{13}C-NMR spectroscope to demonstrate that dimethyl metallocene such as $Cp_2Zr(^{13}CH_3)_2$, $(MeCp)_2Zr(^{13}CH_3)_2$, $(Indenyl)_2Zr(^{13}CH_3)_2$, $Me_2Si(C_5H_4)_2Zr(^{13}CH_3)_2$ and $Cp_2Hf(^{13}CH_3)_2$ undergo degenerate methyl exchange with methyl acceptor compounds such as Me_6Al_2 and $(MeAlO)_x$ (see equation 2.4). 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.
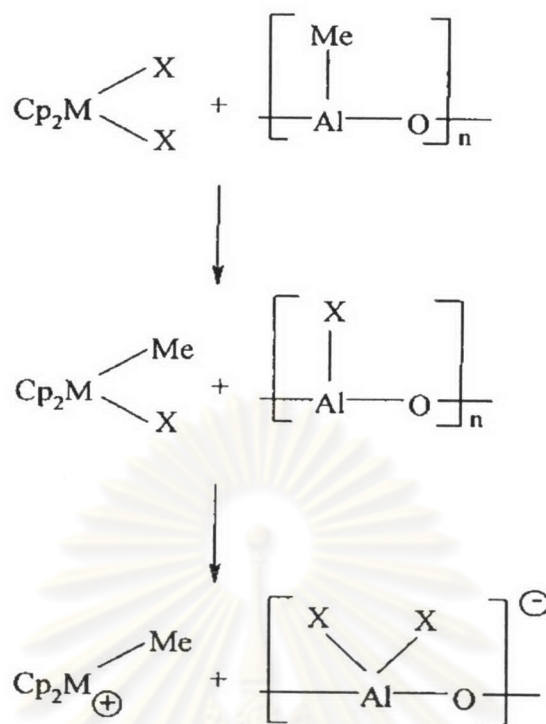
$$Cp_2Zr(^{13}CH_3)_2 + Me_3Al \longrightarrow Cp_2Zr^{13}CH_3^{(+)}AlMe_4^{(-)} \qquad (2.4)$$

Figure 2.7. Postulated mechanism of formation of the active species in the reaction between metallocene and methylaluminoxane (Zucchini *et al.*, 1993)

2.3 Polymerization Mechanism

The mechanism of the polymerization of olefins by zirconocene catalysts has been many theoretical investigations such as Cossee mechanism and the Trigger mechanism. However, alkylation and reduction of the metal site by cocatalyst (generally alkylaluminum or alkylaluminoxane) is believed to generate the active catalyst species, cationic metallocene species.

In the cationic metallocene species, the metal atom is coordinated with the π-ligands and alkyl group (growing polymer chain). During polymerization, the monomer is coordinated with a highly electrophillic 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 and the formation of the metal-carbon bond occur in concert through a four-center transition state. These results in the reaction 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. The proposed mechanism of metallocene-catalyzed polymerization is illustrated in Figure 2.8.
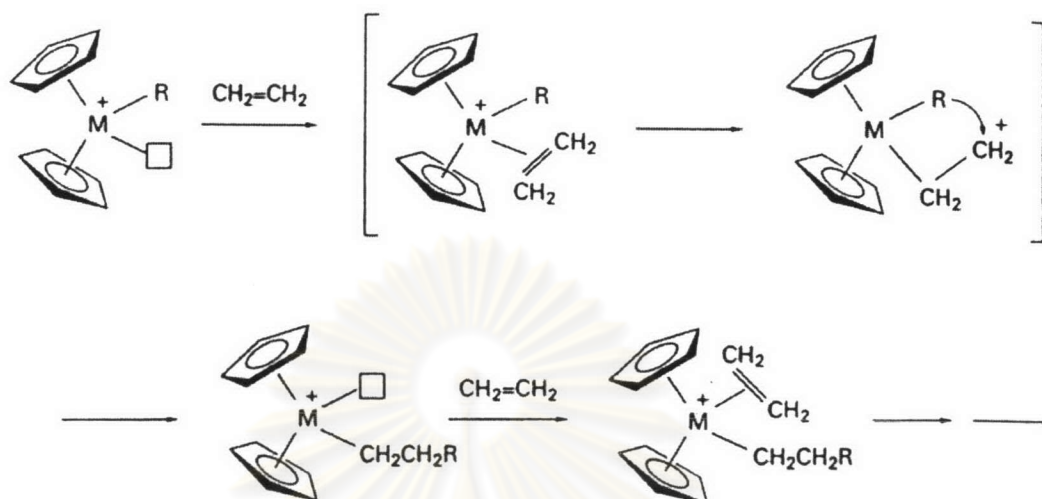

Figure 2.8. The mechanism of olefin polymerization using metallocene catalysts. (Long, 1998)

2.4 Chain Termination and Transfer

Chain termination and transfer mechanisms can have tremendous influences on the nature of the polymer. In metallocene-catalyzed olefin polymerization (Gupta et al., 1994), the termination of polymer chain occurs through a chain transfer involving β-H elimination, β-Me elimination, chain transfer to aluminum or chain transfer to monomer or chain transfer to hydrogen were demonstrated in Figure 2.9-2.13 respectively. All of the mechanisms proposed above are dependent on the nature of the metallocene, aluminoxane, and the polymerization conditions. Resconi et al. (1992) 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 ^{1}H-and ^{13}C-NMR analyses of the products show the presence of unsaturated and saturated end groups. The unsaturated end groups contain vinylidine and alkyl 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$_3$ and β-H elimination.
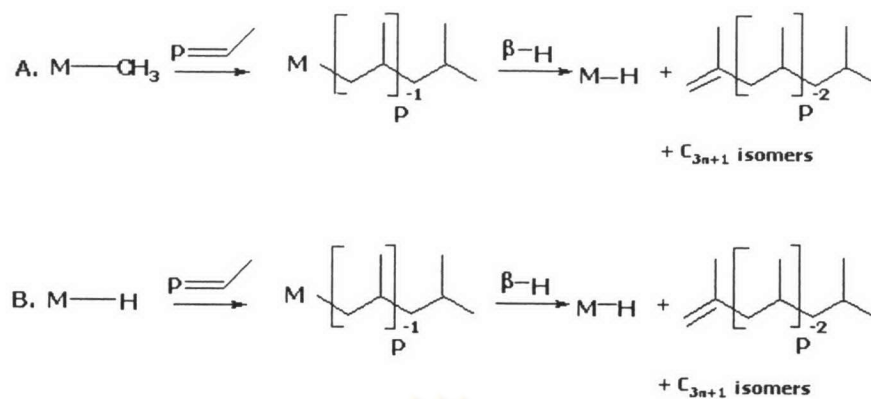
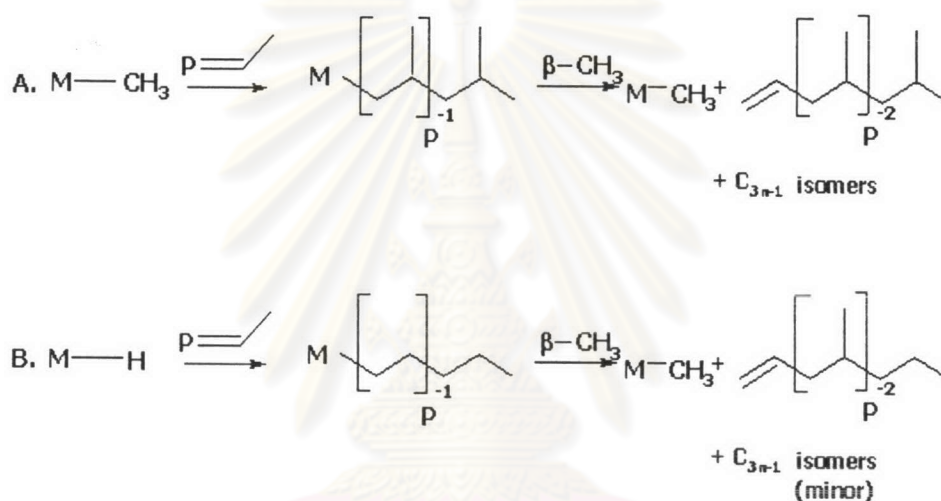**Figure 2.9.** Chain transfer via β-H elimination (Resconi et al., 1992)

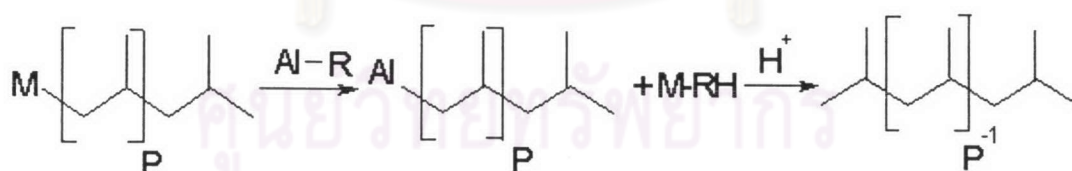**Figure 2.10.** Chain transfer via β-Me elimination (Resconi et al., 1992)

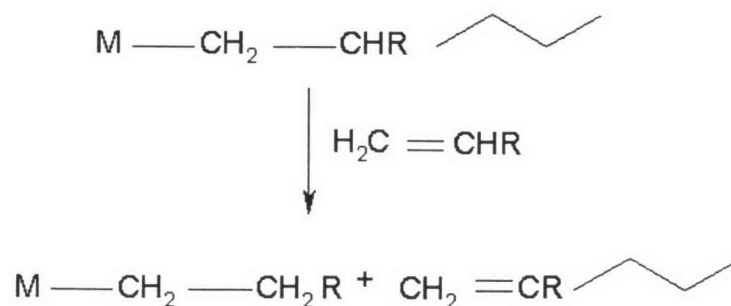**Figure 2.11.** Chain transfer to aluminum (Resconi et al., 1992)

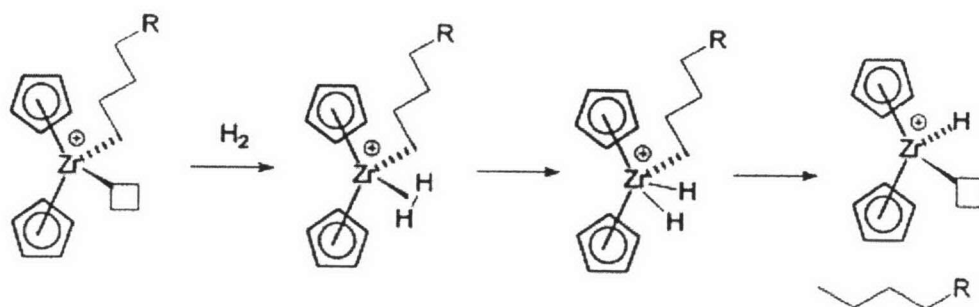**Figure 2.12.** Chain transfer to monomer (Gupta et al., 1994)

**Figure 2.13.** Chain transfer to hydrogen (Alt and Köppl, 2000)

2.5 Deactivation Processes

An important deactivation process for MAO-activated catalytic systems is α-hydrogen transfer, which leads to the production of methane (Kaminsky, 1996). The methane production is much more rapid with MAO than with less Lewis acidic TMA. The deactivation of the metallocenium alkyl + MAO might be attributed to the formation of inactive species with Zr-CH_2-Al or Zr-CH_2-Zr structures in Equation 2.5. Although these inactive species can be reactivated by a transmetallation reaction with MAO and lost Al-CH_2-Al structure at excess MAO, forming $L_2Zr(CH_3)^+$ and Al-CH_2-Al structures in Equation 2.6.
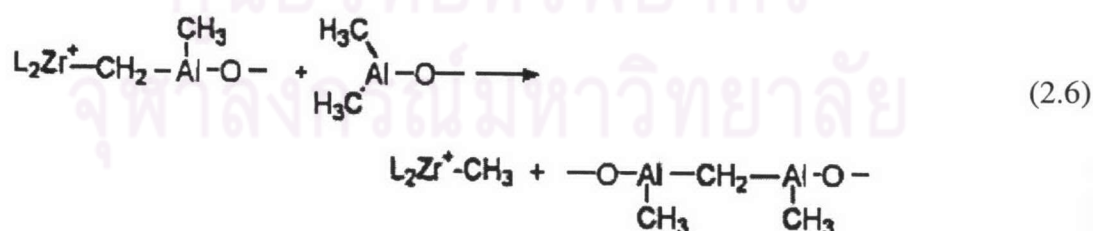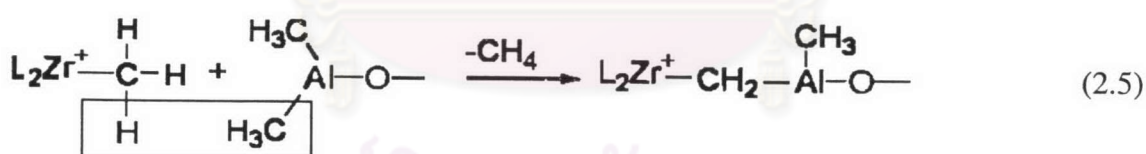
Fischer et al. (1993) found that there is another type of deactivation, which is fast and second-order relative to the active site concentration, in the Cp_2ZrCl_2/MAO catalyst system and subsequently proposed a reversible + irreversible deactivation process kinetic scheme to fit the decay of the polymerization rate as a function of time (Equation 2.7). The mechanism involves reversible second-order deactivation

combined with a slower irreversible deactivation of the active and/or dormant zirconium sites, which may involve interactions between active as well as inactive Zr sites (binuclear processes). The reversible conversion of active cationic zirconium sites into dormant neutral zirconium sites is shown in Figure 2.14.

$$2\,C^* \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} C_1 \xrightarrow{k_2} C_2 \qquad (2.7)$$

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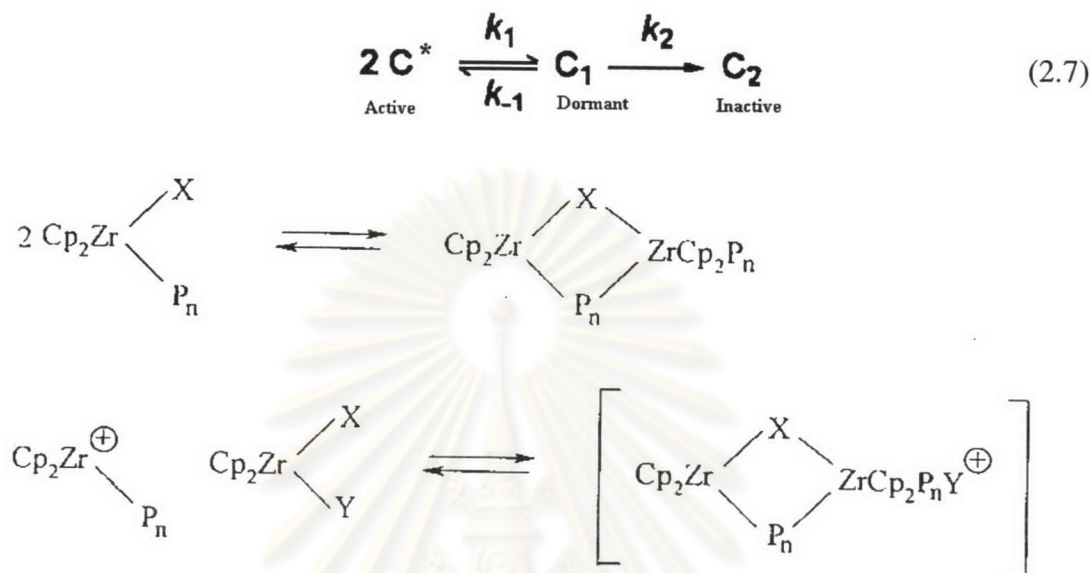
X, Y : Me, Cl, O-AlMe-MAO; P : polymer

Figure 2.14. Mechanism of reversible second-order deactivation

2.6 Cyclic Olefin Copolymers (COCs)

A few years after the discovery of the Ziegler-Natta catalysts, attempts were made to polymerize cycloolefins. The processes, developed prior to 1984 and based on heterogeneous Ti or V catalysts, had many disadvantages. These disadvantages included low activities and varying product properties that were difficult to control. A breakthrough was finally achieved with metallocene/methylaluminoxane (MAO) catalysts (Ruchatz and Fink, 1998).

Metallocene catalysts are effective not only for polymerization of common olefins, such as ethylene and propylene, but for polymerization of cycloolefins. Key for high activites is the selection of the right cocatalyst. Methylaluminoxane (MAO) activates most of the transition metal complexes in an extremely way. Meanwhile also other bulky cocatalysts such as perfluorinated phenylboranes and

aluminosilicates can be used. Metallocene/methylaluminoxane (MAO) catalyst can be used to polymerize and copolymerize strained cyclic olefins such as cyclopentene, norbornene, DMON and substituted norbornenes (Figure 2.15). While polymerization of cyclic olefins by Ziegler-Natta catalysts is accompanied by ring opening, homogeneous metallocene, nickel palladium catalysts achieve exclusive double bond opening polymerization (Kaminsky and Laban, 2001).
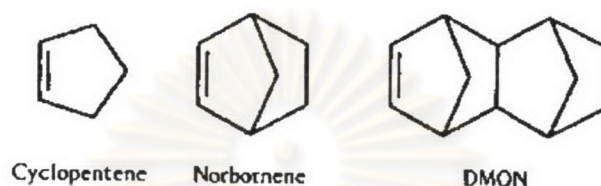

Cyclopentene   Norbornene   DMON

Figure 2.15. Cycloolefins used for the polymerization by metallocenes (Kaminsky, 2000)

Homopolymerization of cyclic olefins via ring opening polymerization by means of metathesis (ROMP) results in elastomeric materials. The metallocene homopolymers feature two chiral centers per monomer unit therefore are ditactic. The cycloolefins may be divided into achiral, monocyclic and prochiral, polycyclic types. Polymerization of both types by chiral metalocenes may yield tactic, crystalline homopolymer. A tactic homopolymers of cyclic olefins are produced by non-chiral metallocenes such as Cp_2ZrCl_2. They have a high glass transition temperature and are not elastic. While the atactic polymers can be dissolved in hydrocarbon solvents at least to some extent, tactic polymers are hardly soluble.

Tactic poly(cycloolefins) are not processable due to their high melting points but by copolymerization of these cyclic olefins with ethylene or α-olefins COCs can be produced, representing a new class of thermoplastic amorphous material (Kaminsky and Noll, 1993). Early attempts to produce such copolymers were made using heterogeneous $TiCl_4/AlEt_2Cl$ or vanadium catalysts, but first significant progress was made by utilizing metallocene catalysts for this propose. They are bout 10 times more active than vanadium systems and by care choice of the metallocene, the comonomer distribution may be varied from statistical to alternating. Furthermore, the glass transition temperature can be varied over a wide range by selection of the appropriate cycloolefin and its degree of incorporation into the polymer chain.

Statistical copolymers become amorphous at comonomer incorporations beyond 10-15 mol% cycloolefin.

The first metallocene-based COC material was synthesized from ethylene and cyclopentene (Kaminsky and Spiehl, 1989). While homopolymerization of cyclopentene results in 1,3-enchainment of the monomer units (Collins and Kelly, 1992), isolated cyclopentene units are incorporated into the ethylene-cyclopentene copolymer chain by 1,2-insertion. Ethylene is able to compensate the steric hindrance at the α-carbon of the growing chain after and before the insertion of cyclopentene. Main industrial interest is paid to ethylene-norbornene copolymer.

Cyclic olefin copolymers (COCs) are characterized by excellent transparency and very high, long-life service temperatures. They are soluble, chemically resistant and can be melt-processed. Due to their high carbon/hydrogen ratio, these polymers feature a high refractive index, e.g. 1.53 for ethylene-norbornene copolymer at 50 mol% norbornene incorporation. Their stability against hydrolysis and chemical degradation, in combination with their stiffness lets them become desirable materials for optical applications, e.g. for compact discs, lenses, optical fibers and films (Cherdron et $al.$, 1994).

2.6.1 Copolymerization of Ethylene and Norbornene

The structure of biscyclo[2.2.1]hept-2-ene, better known by its trivial name norbornene is shown in Figure 2.16 and its derivatives can be polymerized in three different ways are illustrated in Figure 2.17. It is important to note that each route leads to its own polymer type which is different in structure and properties from the other two.
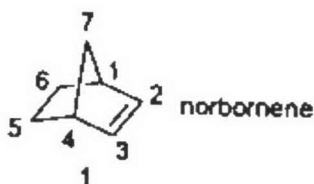
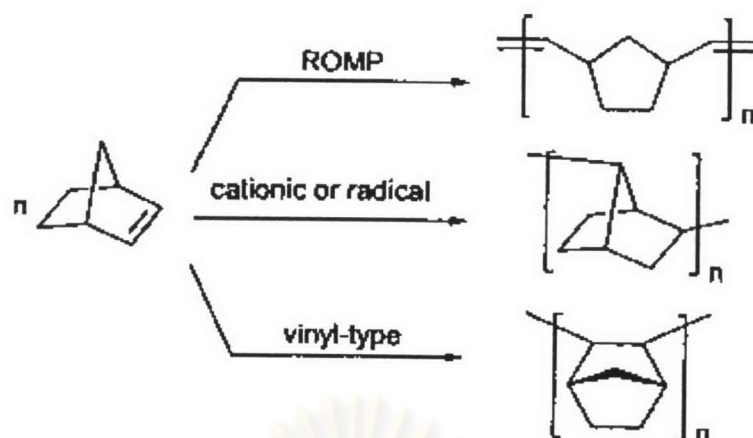**Figure 2.16.** The structure of norbornene (Janiak and Lassahn, 2001)

Figure 2.17. Schematic representation of the three different types of polymerization for norbornene (Janiak and Lassahn, 2001)

The best known polymerization of norbornene is the ring-opening metathesis polymerization (ROMP). The reaction is technically applied in the Norsorex process. The polymer thus, obtained is a polyalkenamer which still contains double bonds in the polymer backbone. Through the double bonds the polymer chains can be crosslinked or vulcanized.

It is also possible to polymerize norbornene and to leave the bicyclic structure unit intact, i.e. to open only the double bond of the π-component. The product does not contain anymore double bonds. The vinyl polymerization of norbornene can take place as a homo- or as a copolymerization. Occasionally the vinyl polymerization of norbornene is also termed "addition polymerization".

Of interest is the vinyl copolymerization of cyclic and acyclic (especially ethylene and propylene) olefins. Cycloolefin copolymers (COC) are produced by copolymerization of these cyclic olefins with ethylene or α-olefins. Such as copolymerization can be carried out with metallocene and half-sandwich/MAO-catalysts (Ruchatz and Fink, 1998; Kaminsky and Noll, 1993; Kaminsky and Spiehl, 1989). The COC's can be melt-processed. The materials can be extruded to foil, tubes, pipes, fibers, etc. Their high transparency makes them ideally suited for optical applications. Cycloolefin copolymers have high refractive indices close to crown

glass. Thus, cycloolefin copolymers can be applied as a glass substitute in lenses, prisms, carrier plates and foils for optical data storage, video and compacts disks. They are envisioned as cover and focusing plates for solar cells or in glass fiber optics. Hoechst and Mitsui Sekka have jointly developed a highly transparent technical plastic: a thermoplastic olefin polymer of amorphous structure (TOPAS). TOPAS is a copolymer from norbornene and ethylene made through metallocene catalysis (Janiak and Lassahn, 2001).

Polycycloolefins produces with metallocene catalysts show no melting point. They cannot be processed like thermoplastic polymers and therefore they are of no commercial interest. Ethylene-cycloolefin copolymers, however, do show thermoplastic behavior together with other interesting properties. Ethylene-norbornene copolymers are amorphous, highly transparent, and chemically resistant. The copolymerization of ethylene and norbornene were carried out with metallocene/MAO catalysts were shown in Figure 2.18.
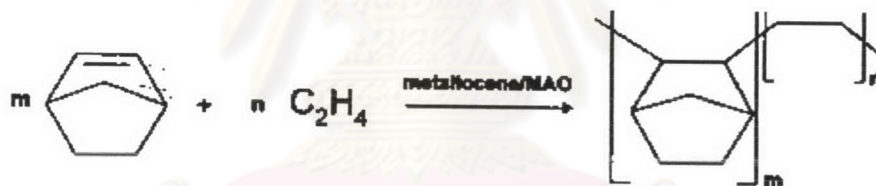

Figure 2.18. Ethylene-norbornene polymerization with metallocene/MAO catalyst (Ruchatz and Fink, 1998)

The main advantage of these copolymers lies in their wide-ranging glass transition temperatures, which can be set from 20 to 260°C by varying the norbornene content in the copolymer. Furthermore, the distribution of the monomers in the copolymer can be controlled from statistical to alternating. The insertion of norbornene units into the growing polymer chain is very easy. As seen by the copolymerization parameter r_1, which is between 2.0 and 3.4 and shows how much faster ethylene is inserted than norbornene when the previous insertion was ethylene. The copolymerization parameters r_1 and r_2 of ethylene and various cycloolefin copolymerizations with different metallocene/MAO catalysts are summarized in Table 2.1.

Table 2.1 Copolymerization parameters r_1 and r_2 of ethylene and cycloolefin copolymerizations with different metallocene/MAO catalysts (Kaminsky, 2000)

Cycloolefin	Catalyst	Temperature(°C)	r_1	r_2	r_1r_2
Cyclopentene	[En(IndH$_4$)$_2$]ZrCl$_2$	0	1.9	<1	~1
Cyclopentene	[En(IndH$_4$)$_2$]ZrCl$_2$	25	2.2	<1	~1
Norbornene	[Me$_2$Si(Ind)$_2$]ZrCl$_2$	30	2.6	<2	~1
Norbornene	[Me$_2$C(Fluo)(Cp)]ZrCl$_2$	30	3.4	0.06	0.2
Norbornene	[Ph$_2$C(Fluo)(Cp)]ZrCl$_2$	0	2.0	0.05	0.1
Norbornene	[Ph$_2$C(Fluo)(Cp)]ZrCl$_2$	30	3.0	0.05	0.15
Norbornene	[Me$_2$C(Fluo)(t-BuCp)]ZrCl$_2$	30	3.1	0	0
DMON	[Ph$_2$C(Fluo)(Cp)]ZrCl$_2$	50	7.0	0.02	0.14
DMON	[Ph$_2$C(Ind)(Cp)]ZrCl$_2$	50	6.4	0.10	0.64
DMON	[Ph$_2$C(Fluo)(Cp)]HfCl$_2$	50	7.1	0.04	0.28

2.6.2 Activity and Molecular Properties of Metallocene and Cyclic Olefin from Various Types of Metallocene

Kaminsky and Noll (1993) carried out copolymerization of norbornene and ethylene with the C_s-symmetrical complexes [Me$_2$C(Fluo)(Cp)]ZrCl$_2$ and [Ph$_2$C(Fluo)(Cp)]ZrCl$_2$ together with the C_2-symmetrical pre-catalysts [Me$_2$Si(Ind)$_2$]ZrCl$_2$ and [Ph$_2$Si(Ind)$_2$]ZrCl$_2$ (see Figure 2.19) were activated by using MAO as cocatalyst. It become clear that the polymerization rates were quite different for the two type of catalysts. The C_2-symmetrical catalyst/MAO were highly active in the ethylene polymerization. In both cases the activities dropped rapidly with an increasing norbornene-ethylene ratio. Whereas the C_s-symmetrical catalysts had a completely different copolymerization behavior. Both compounds showed a slight maximum in activity as a function of monomer ratio $c_{norb} : c_{ethylene}$.

The reaction behavior clearly indicated better sterical prerequisites of the C_s-symmetrical catalysts for the insertion of bulky olefins. The shorter bridge of the C_s-catalysts results in a wider opening angle of the ring ligands around zirconium, thus, creating a larger coordination gap (Herfert et al., 1993). The catalyst symmetry could also be correlated with the stereochemistry of the polymer chain.
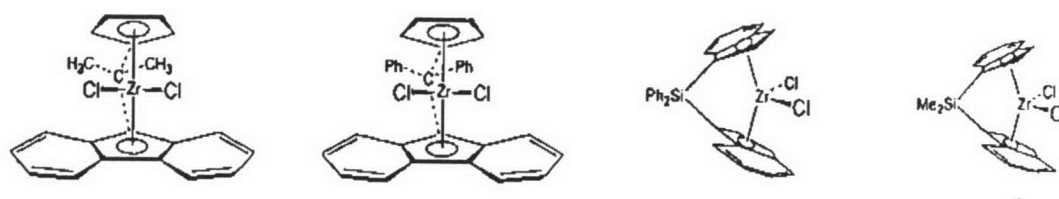
Figure 2.19. Structure of the metallocene used in ethylene and norbornene copolymerization Kaminsky *et al.* (1993)

Furthermore, Kaminsky and Laban (2001) compared activities and incorporation of norbornene in ethylene-norbornene copolymer for different catalysts. The result were displayed in Table 2.2 and show that under the chosen conditions $[En(Ind)_2]ZrCl_2$ develops the highest activity while the highest comonomer incorporation is achieved by $[Ph_2C(Ind)(Cp)]ZrCl_2$. Due to different incorporation ratios of the cyclic olefin into the copolymer, the glass transition temperature of the random copolymers can vary over a wide range which is basically independent of the applied catalyst.

Table 2.2 Copolymerization of norbornene and ethylene by different metallocene/MAO catalyst at 30°C

Catalyst	Time (min)	Activity (kg mol^{-1}h^{-1})	Incorporation of norbornene (wt.%)
Cp_2ZrCl_2	30	1200	21.4
rac-$[En(Ind)_2]ZrCl_2$	10	9120	26.1
rac-$[Me_2Si(Ind)_2]ZrCl_2$	15	2320	28.4
rac-$[En(IndH_4)_2]ZrCl_2$	40	480	28.1
$[Me_2C(Flu)(Cp)]ZrCl_2$	10	7200	28.9
$[Ph_2C(Flu)(Cp)]ZrCl_2$	10	6000	27.3
$[Ph_2C(Ind)(Cp)]ZrCl_2$	15	2950	33.3
$[Me_2C(Flu)(tert\text{-}BuCp)]ZrCl_2$	30	1133	28.0

Bergström *et al.* (1997) compared $Me_2Si(Ind)_2ZrCl_2$ and *rac*-$Et(Ind)_2ZrCl_2$ as the catalysts were used in ethylene and norbornene copolymerization. For $Me_2Si(Ind)_2ZrCl_2$ could see more block sequences but less alternating sequences in obtained copolymer than *rac*-$Et(Ind)_2ZrCl_2$, which seems to have had a decreasing effect on the T_g. Also the yields and activities were lower for $Me_2Si(Ind)_2ZrCl_2$.

B.-G. Jeong *et al.* (2003) found that $2,2'$-$CH_2(1,3\text{-}Me_2Cp)_2ZrCl_2$ catalyst (A) showed much higher activity in ethylene and norbornene copolymerization and norbornene incorporation ability than *rac*-$Et(Ind)_2ZrCl_2$ catalyst (B), due to the electronic effect and the less steric nature of the ligand structure and the absence to any substituent on the β-carbons of the cyclopentadienyl ring in the metallocene complex (Lee *et al.*,2002). Thus, the nature of no steric hindrance on the reaction site of Catalyst A results in an easy approach of a bulky norbornene. Relative lower molecular weight copolymer were produced by Catalyst A than Catalyst B.

Ruchatz and Fink (1998) summarized the results of the detailed ^{13}C – NMR analysis of the different ethane-norbornene copolymers. The catalysts can be classified into three main groups as shown in Figure 2.20. The reason for this different reaction behavior is a results of different steric effect. The existence and the origin of difference in the ^{13}C-NMR spectra arising from *meso/racemic* sequences were demonstrated in Figure 2.21.
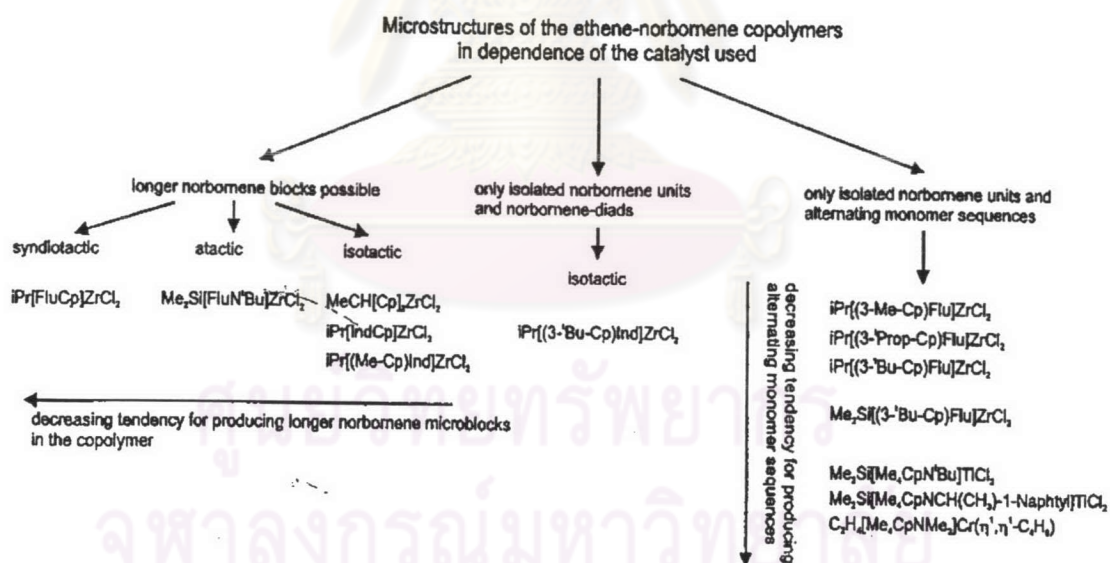

Figure 2.20. Microstructure of ethen-norbornene copolymers independence of the catalyst used
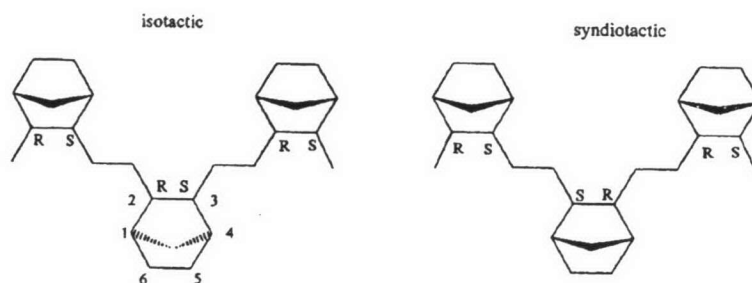
isotactic   syndiotactic

Figure 2.21. Segments of isotactic and syndiotactic alternating ethylene-norbornene copolymers (Tritto *et al.*, 2001)

2.6.3 Effect of Polymerization Condition

Bergström and Seppälä (1997) copolymerized norbornene and ethylene using *rac*-Et(Ind)$_2$ZrCl$_2$ and MAO. They showed that there is an optimum temperature and optimum ethylene pressure that should be used in order to obtain high incorporations of a cyclic comonomer and increased glass transition temperatures and that these properties can be further increased by increasing the catalyst concentration, the Al/Zr ratio, and the comonomer content in the reaction mixture.

Bergström *et al.* (1997) investigated the influence of polymerization conditions on microstructure of norbornene-ethylene copolymers by using *rac*-Et(Ind)$_2$ZrCl$_2$/MAO and Me$_2$Si(Ind)$_2$ZrCl$_2$/MAO catalyst systems. ^{13}C-NMR was used for characterization of the microstructure of obtained copolymers. For both catalysts the highest amounts of block sequences were obtained for high norbornene concentrations, medium to high Al/Zr ratios, and low polymerization temperature. There were also more alternating sequences for high norbornene concentrations and high polymerization temperatures. Three basic sequence possibilities for norbornene in addition polymerization were shown in Figure 2.22.
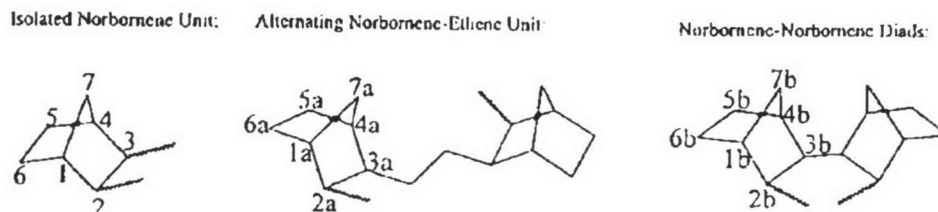
Isolated Norbornene Unit: Alternating Norbornene-Ethene Unit   Norbornene-Norbornene Diads:

Figure 2.22.   Three basic sequence possibilities for norbornene in addition polymerization (Bergström *et al.*, 1998)

Later in 2000 they copolymerized phenylnorbornene (PN) or indanylnorbornene (IN) with ethylene using the same catalyst systems, T_g increased linearly with increasing comonomer incorporation. When copolymerizing PN with *rac*-Et(Ind)$_2$ZrCl$_2$ the exo/endo ratios in the copolymers were higher than in the monomer and the exo/endo ratios increased with increasing polymerization time and ethylene pressure. When using Me$_2$Si(Ind)$_2$ZrCl$_2$ or IN, however, the exo/endo ratios were about the same in the copolymers as in the comonomers. For longer polymerization times showed broader molecular weight distributions, higher exo/endo ratios and higher Charpy impact strengths. Three basic enchainment possibilities for norbornene in addition polymerization were illustrated in Figure 2.23.
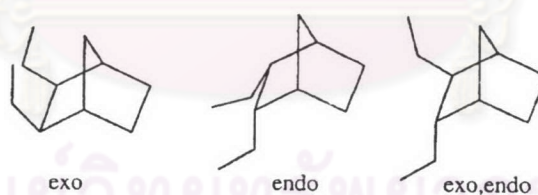
exo   endo   exo,endo

Figure 2.23.   Three basic enchainment possibilities for norbornene in addition polymerization (Bergström *et al.*, 1998)

M.-J. Young *et al.*,(2003) studied the effect of reaction condition on the molecular weight, polymer yield, and polymer structure of metallocene cyclic olefin copolymer (mCOC) and proposed polymerization kinetic model to accurately predict the reaction results. Both the catalyst activity and polymer yield decreases at elevated reaction temperature. Catalyst concentration possesses an optimal operation value for

catalyst activity. Both the glass transition temperature and the number average molecular weight of copolymer product are affected by ethylene operation pressures.

B.-G. Jeong *et al.* (2003) demonstrated the influences of the polymerization temperature and ethylene pressure on catalyst activity and the properties of ethylene and norbornene copolymers produce by 2,2'-CH_2(1,3-$Me_2Cp)_2ZrCl_2$ and *rac*-$Et(Ind)_2ZrCl_2$ in the present of MAO as a cocatalyst. The glass transition temperature of the copolymer increased with increasing temperature or decreasing ethylene pressure and mainly depended on the norbornene/ethylene ratio.

Arndt and Beulich (1998) investigated the mechanism of the alternating ethylene/norbornene copolymerization using [MeC(3-[tert]BuCp)(Flu)]$ZrCl_2$ with MAO as catalyst. The results show that process parameters, especially the temperature of reaction, may influence the mechanism and thereby the microstructure of the polymer produced. The metallocene with heterotopic sides are not only interesting for mechanistic studies but have potential for tailoring the microstructure of copolymers.

Ekizoglou *et al.* (2003) synthesized ethylene-norbornene copolymer using $Me_2Si(Me_4Cp)(NtBu)TiCl_2$ and MAO. The increase of the T_g values of ethylene-norbornene copolymers according to the norbornene content. However, it seems there are also structural factors influencing the T_g value. The values of the T_g for the same norbornene content increased significantly to a limit of M_n about 6×10^4 g/mol then T_g remains practically constant.