CHAPTER II

LITERATURE REVIEWS

Two major classes of single-site catalyst (SCC) technology were recently developed for the polymerization of ethylene and α-olefins. These two catalyst systems are the metallocene catalyst and constrained geometry catalyst systems. The use of these catalyst technologies has allowed a very rapid development of olefin copolymers with a wide range of structures and related properties. This technology has initiated a major revolution for the polyolefin industry [19].

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. Metalllocene catalysts are operative in all existing industrial plants that are presently used for polyolefin manufacture revolutionize the technology for the production of these polymers [20].

Research in single-center metal-catalyzed polymerization has been explosive growth over the past two decades, advancing from questions of academic interest to solving problems in the commercial field. The variation of the aromatic ligands, the bridging of ligands and the variation in the type of metal provides an enormous number of variations to control polymerization reactions in terms of stereospecificity, long chain and short chain branching and the generation of block copolymers. Metallocene catalysts can produce tailored polyolefins for nearly every purpose and with these new materials they generate new markets, such as LLDPE (linear low density polyethylene) with new properties.

As we found in the open literature, there are many reviews on the nature of metallocene complexes, catalytic performance and its influence on polymer properties, cocatalyst for metal-catalyzed olefin polymerization, and polymerization reactions including reaction mechanisms of polymerization and chain transfer [1, 20-28].

2.1 Classification of Polyethylene

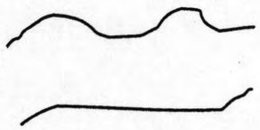
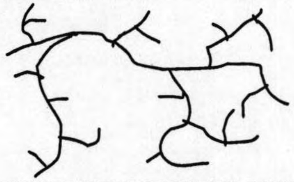
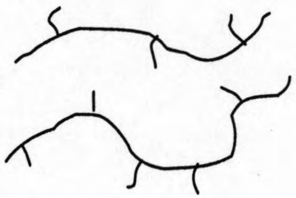
Polyethylene (PE) is the major commodity polymer worldwide; world demand exceeded 50 million tons in 2000. The consensus of numerous studies shows that the world production of polyethylene is estimated to be around 93 million tons; LDPE/LLDPE 55 million tons and HDPE 38 million tons in 2010 [1]. Such increase in production of this material is due to the outstanding versatile physical and chemical properties of PE. Conventionally polyethylene is classified into three types according to its density: high density polyethylene (HDPE), low density polyethylene (LDPE), and linear low density polyethylene (LLDPE).

Table 2.1 summarizes some characteristics of the three types of polyethylenes. It is evident that each type of PE is associated with the characteristic molecular structure, production process, density range, and applications. HDPE is a homopolymer of ethylene possessing a linear chain structure with no or very few branches, and up to 70% of the polymer can be in the crystalline phase, resulting in a high density of about 0.96 g/cm^3. LDPE is also a homopolymer of ethylene, but has a branched structure with long chain branches (LCB) and short chain branches (SCB) as depicted in Table 2.1. The branches disrupt the ordered arrangement of the macromolecular chains. A high SCB or LCB content means a large amount of crystal defects, which lead to a lower crystallinity with a lower density and melting temperature. In general, LCBs have a profound effect on solution viscosity and melt rheology because of molecular size reduction and entanglements, while SCBs are particularly critical in influencing the morphology and solid-state properties of polyethylene.

The polymer commonly known as LLDPE is a copolymer produced by copolymerization of ethylene with α-olefins such as propylene, 1-butene, 1-hexene, 1-octene, and 4-methyl-1-pentene. LLDPE possesses a linear molecular structure with SCBs distributed nonuniformly along the backbone of polyethylene chain. The amount and distribution of SCBs have a profound effect on the thermal, physical, and mechanical properties of LLDPE. The diversity of various LLDPE grades is primarily a result of variations in distributions of molar mass and short chain branches.

Polyethylene 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 process 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 [29]. 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 polymerization structure and for heterogeneous processes the polymer powder morphology. The catalyst system must fit the polymerization process.

Table 2.1 Density range, molecular structure, synthesis, and applications of various type polyethylenes

Type of PE	Density (g/cm^3)	Molecular structure	Synthesis	Common uses
HPDE	0.945-0.965		Polymerization of ethylene on Philips, Ziegler-Natta and metallocene catalyst	Gas pipe, car gas tanks, bottles rope and fertilizer bag
LDPE	0.890-0.940		Free radical polymerization of ethylene at high temperature and high pressure	Packing film, bags, wire, sheathing, pipes, waterproof membrane
LLDPE (VLDPE,ULDPE)*	0.910-0.925		Copolymerization of ethylene with α-olefins on Ziegler-Natta and metallocene catalysts	Shopping bag, stretch wrap, greenhouse film

* A family of LLDPE with density of 0.87-0.915 g/cm^3

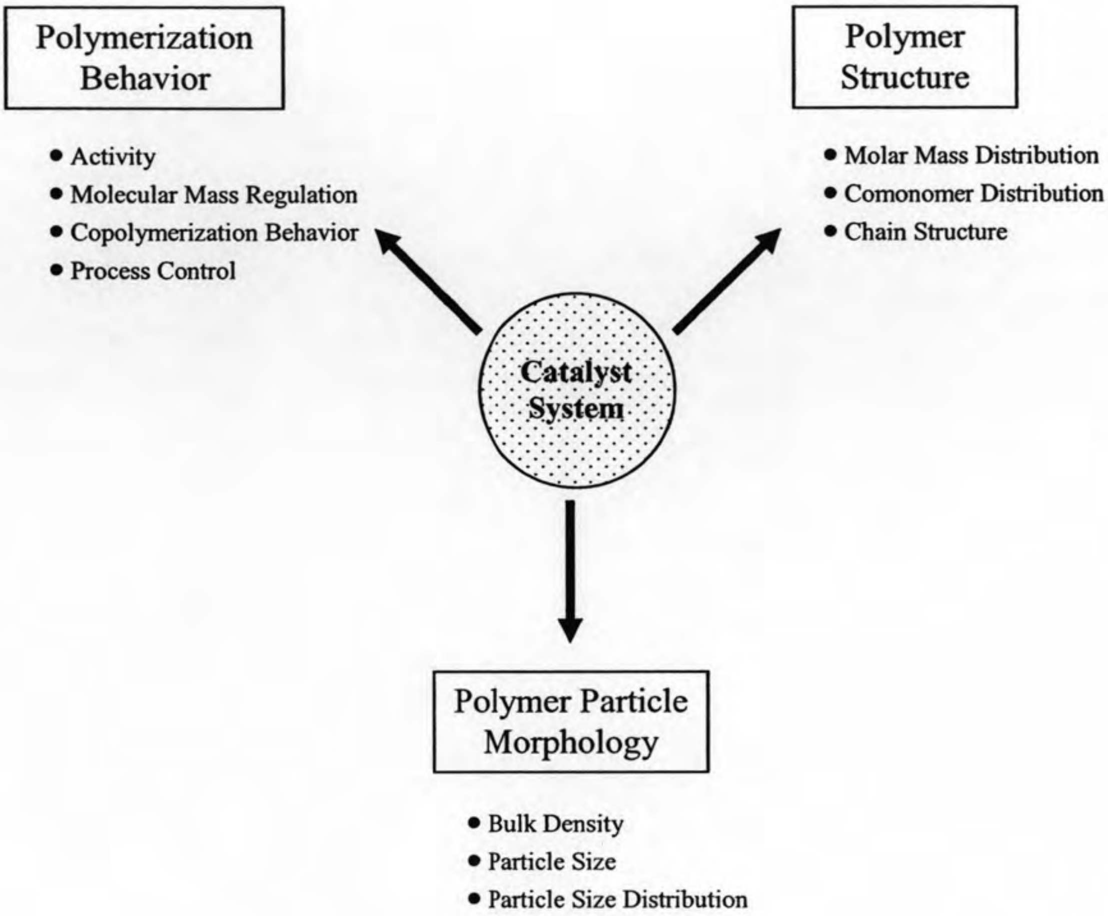


Figure 2.1 The key role of the catalyst system [22]

In heterogeneous processes (slurry or gas-phase technology) the polymerization reaction only takes place inside the polymer particles. Each of these polymer particles is a small reactor (micro reactor) with its own energy and mass balance. The polymer particles grow from the catalyst particles by polymer formation around the catalyst fragments (primary particles) [22].

2.2 History of Catalyst Systems for Olefin Polymerization

In 1953 Karl Ziegler, who succeeded in polymerizing ethylene into high-density polyethylene (HDPE) at standard pressure and room temperature, discovered of catalysts based on titanium trichloride and diethylaluminum chloride as cocatalyst, at the Max-Planck-Institute in Mulheim. A little later, Natta, at the Polytechnical Institute of Milan, was able to indicate 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 [1]. 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 conventional Ziegler-Natta catalysts the molecular structure of the polymers cannot be controlled well the molecular structure of the polymers because these catalysts have different nature types of catalytic sites.

Kaminsky discovered the metallocene catalyst system; it has proven to be a major breakthrough for the polyolefin industry. Metallocene catalysts show in opposite 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 can be easily changed which allows control of the structure of polyolefin produced with these catalysts. Many metallocene 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.

Metallocene, 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, development of the catalyst system has been conducted to achieve higher activity and to obtain higher molecular weight polyethylene [19].

2.3 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 chained to a metal central transition atom. The typical chemical structure of a metallocene catalyst is represented by Figure 2.2

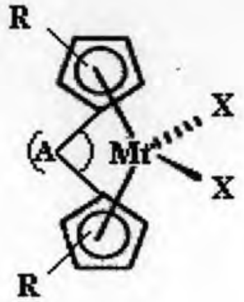


Figure 2.2 Typical chemical structure of a metallocene catalyst [30]

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 7 or an alkyl group

Single site catalysts can be separated into five main symmetry group, 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.

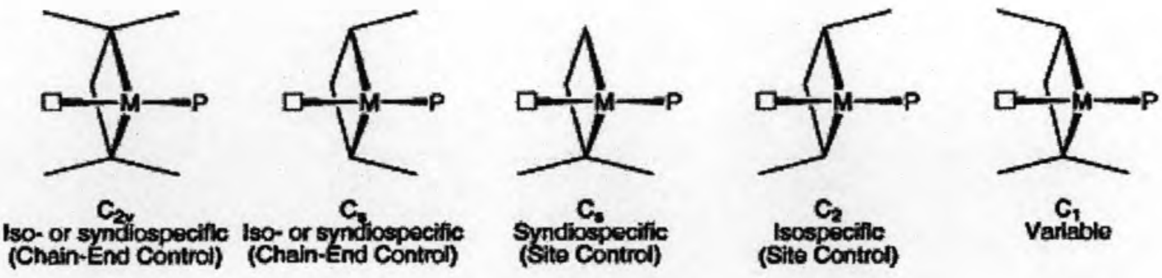


Figure 2.3 General symmetry classifications, based on ligand geometries, of catalysts and their stereoselectivities for polyolefin synthesis [31]

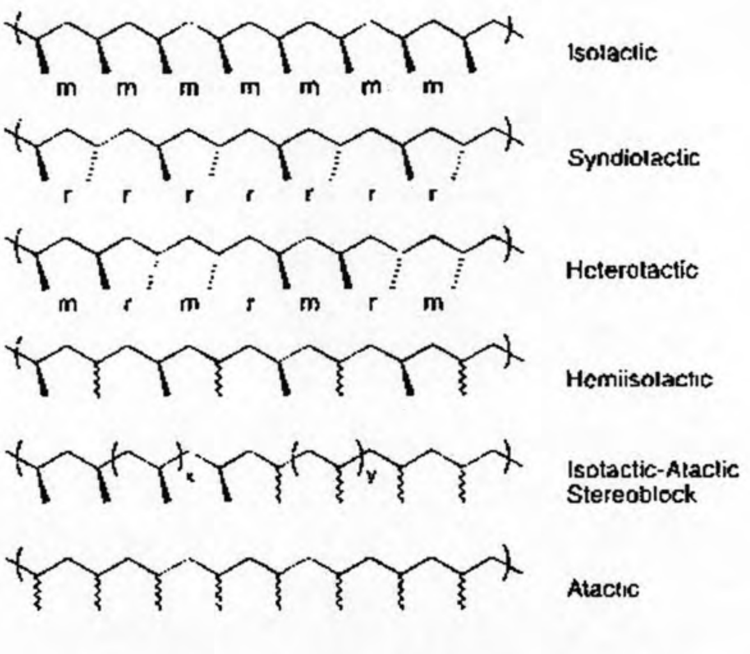
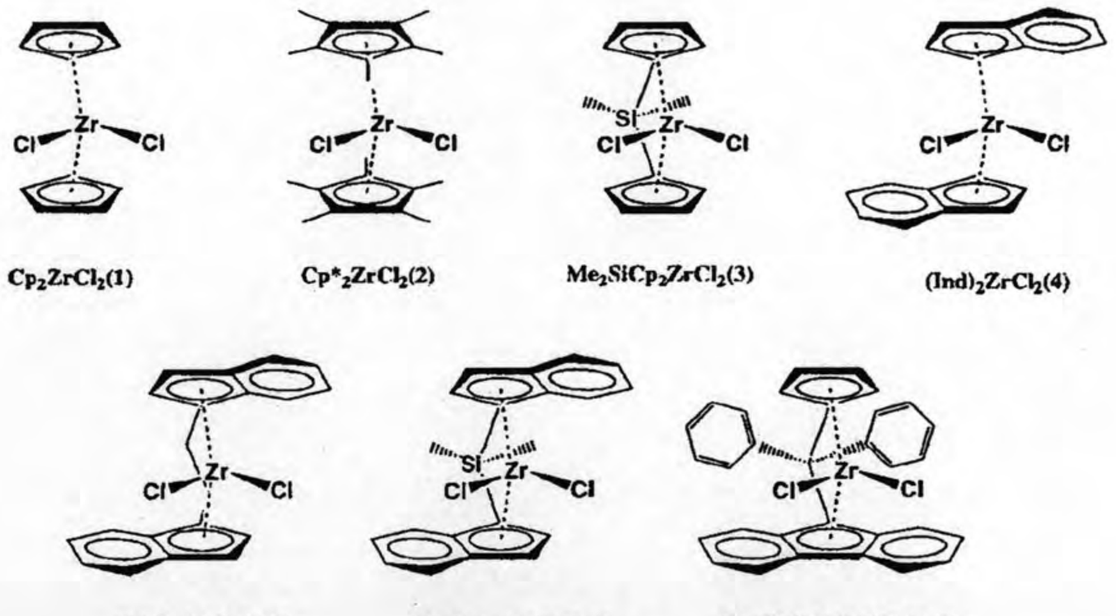


Figure 2.4 Common polymer tacticities [1]

Representative examples of each category of metallocenes and some of zirconocene catalysts are shown in Table 2.2 and Figure 2.5, respectively.

Table 2.2 Representative Examples of Metallocenes [21]

Category of metallocenes	Metallocene Catalysts
[A] Nonstereorigid metallocenes	1) Cp_2MCl_2 (M = Ti, Zr, Hf) 2) Cp_2ZrR_2 (M = Me, Ph, CH_2Ph, CH_2SiMe_3) 3) $(Ind)_2ZrMe_2$
[B] Nonstereorigid ring-substituted metallocenes	1) $(Me_5C_5)_2MCl_2$ (M = Ti, Zr, Hf) 2) $(Me_3SiCp)_2ZrCl_2$
[C] Stereorigid metallocenes	1) $Et(Ind)_2ZrCl_2$ 2) $Et(Ind)_2ZrMe_2$ 3) $Et(IndH_4)_2ZrCl_2$
[D] Cationic metallocenes	1) $Cp_2MR(L)^+[BPh_4]^-$ (M = Ti, Zr) 2) $[Et(Ind)_2ZrMe]^+[B(C_6F_5)_4]^-$ 3) $[Cp_2ZrMe]^+[(C_2B_9H_{11})_2M]^-$ (M = Co)
[E] Supported metallocenes	1) Al_2O_3-$Et(IndH_4)_2ZrCl_2$ 2) $MgCl_2.Cp_2ZrCl_2$ 3) $SiO_2.Et(Ind)_2ZrCl_2$



Cp_2ZrCl_2(1) $Cp^*{}_2ZrCl_2$(2) $Me_2SiCp_2ZrCl_2$(3) $(Ind)_2ZrCl_2$(4)

$Et(Ind)_2ZrCl_2$(5) $Me_2Si(Ind)_2ZrCl_2$(6) $Ph_2C(Cp)(Flu)ZrCl_2$(7)

Figure 2.5 Some of zirconocene catalysts structure [20]

2.4 Polymerization Mechanism

The mechanism of catalyst activation is not clearly understood. However, alkylation and reduction of the metal site by a cocatalyst (generally alkyl aluminum or alkyl aluminoxane) is believed to generate the cationic active catalyst species.

First, in the polymerization, the initial mechanism started with formation of cationic species catalyst that is shown below.

Initiation

$$Et(Ind)_2ZrCl_2 + Al(CH_3)_3 \longrightarrow Et(Ind)_2ZrClMe + Al(CH_3)_2Cl$$

Propagation proceeds by coordination and insertion of new monomer unit in the metal carbon bond. Cossee mechanism is still one of the most generally accepted polymerization mechanism (Figure 2.6) [32]. In the first step, monomer forms a complex with the vacant coordination site at the active catalyst center. Then through a four-centered transition state, bond between monomer and metal center and between monomer and polymer chain are formed, increasing the length of the polymer chain by one monomer unit and generating another vacant site.

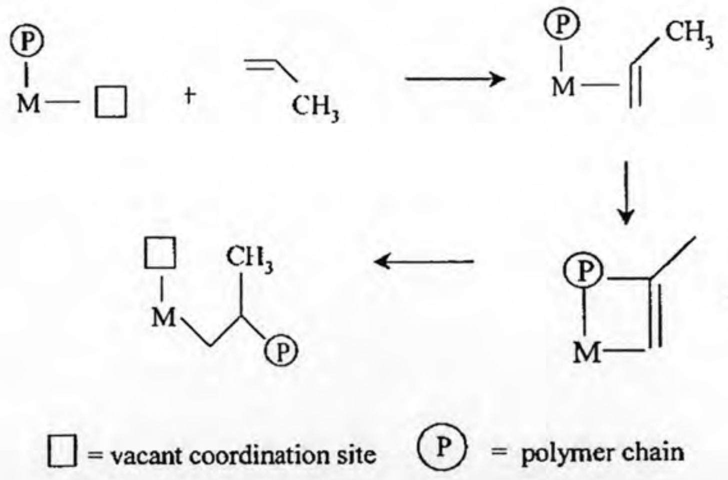


Figure 2.6 Cossee mechanism for Ziegler-Natta olefin polymerization [32].

The trigger mechanism has been proposed for the polymerization of α-olefin with Ziegler-Natta catalysts [33]. In this mechanism, two monomers interact with one active catalytic center in the transition state. A second monomer is required to form a new complex with the existing catalyst-monomer complex, thus trigger a chain propagation step. No vacant site is involved in this model. The trigger mechanism has been used to explain the rate enhancement effect observed when ethylene is copolymerized with α-olefins.

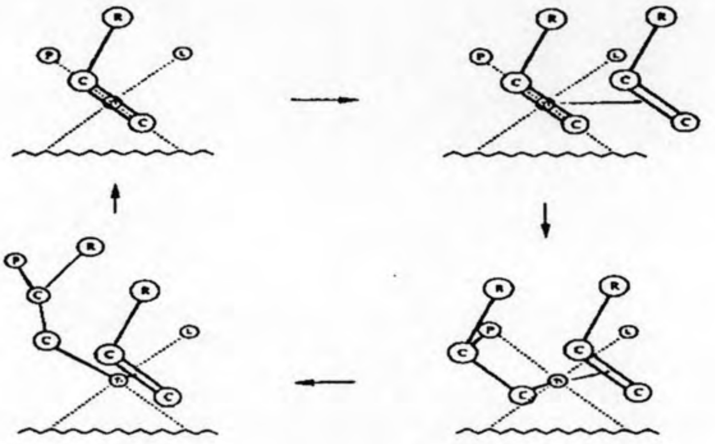


Figure 2.7 The propagation step according to the trigger mechanism [33].

After that , the propagation mechanism in polymerization shown in Figure 2.8.

Propagation

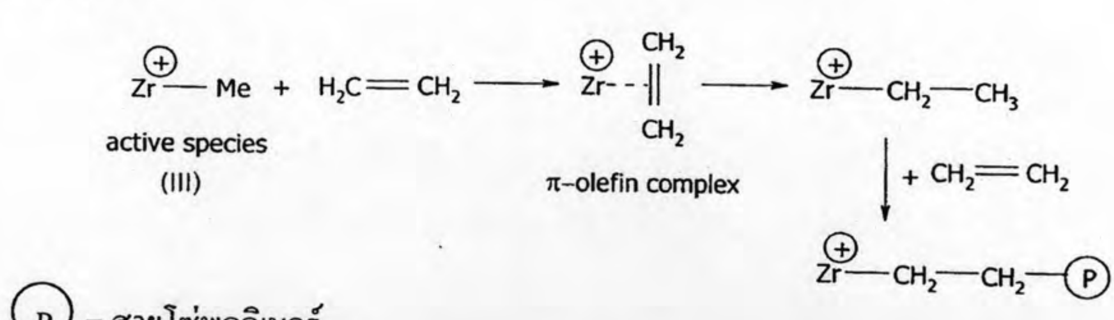


Figure 2.8 Propagation mechanism in polymerization

Finally, the termination of polymer chains can be formed by 1) chain transfer via β-H elimination, 2) chain transfer via β-Me elimination, 3) chain transfer to aluminum, 4) chain transfer to monomer, and 5) chain transfer to hydrogen (Figure 2.9-2.13)[21]. The first two transfer reactions form the polymer chains containing terminal double bonds.

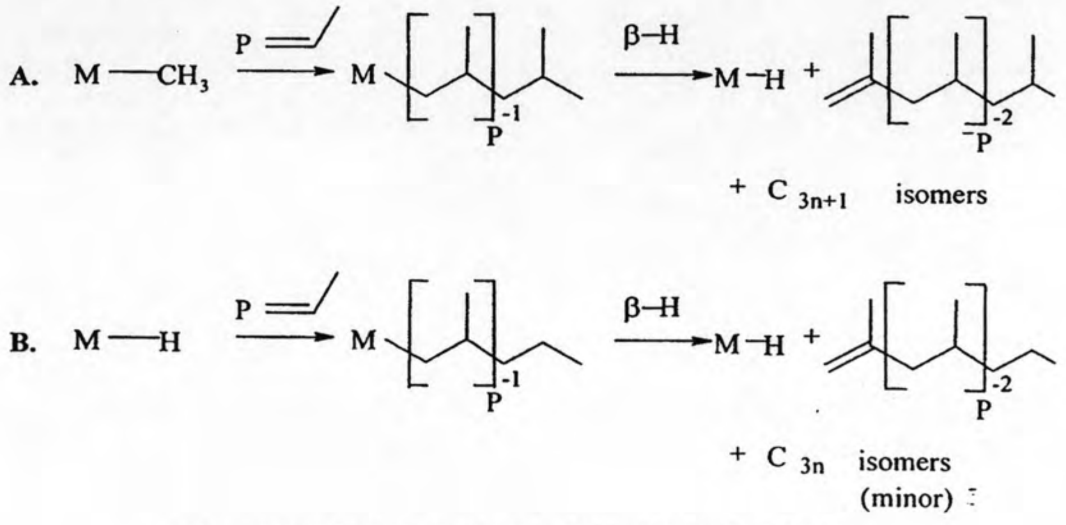


Figure 2.9 Chain transfer via β-H elimination [21]

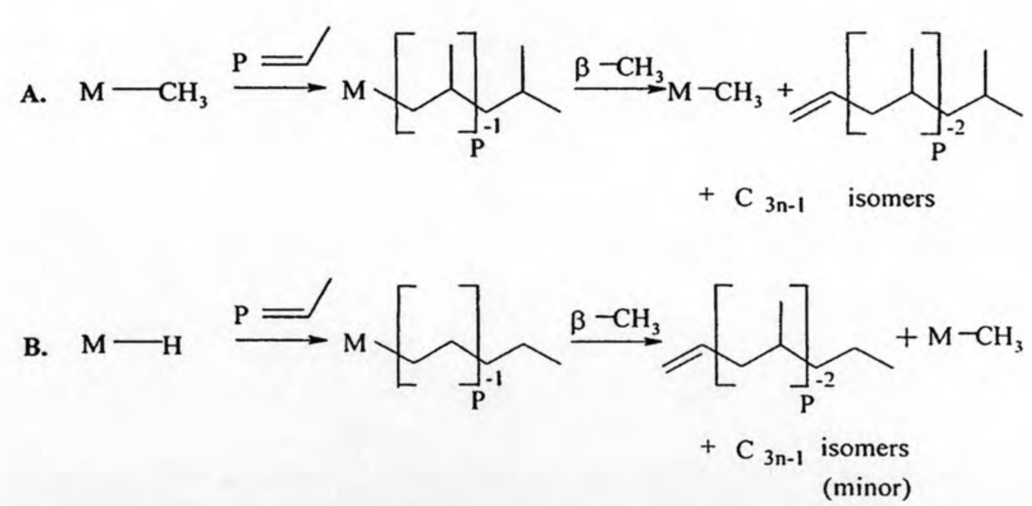


Figure 2.10 Chain transfer via β-CH_3 elimination [21]

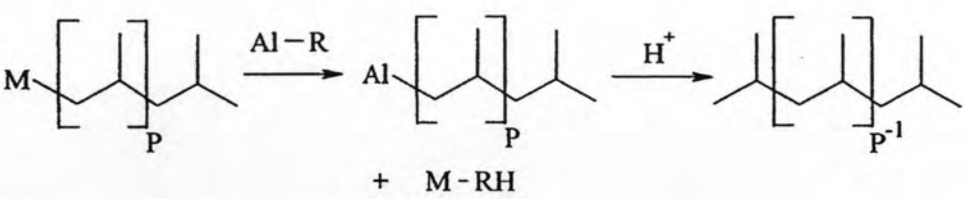


Figure 2.11 Chain transfer to aluminum [21]

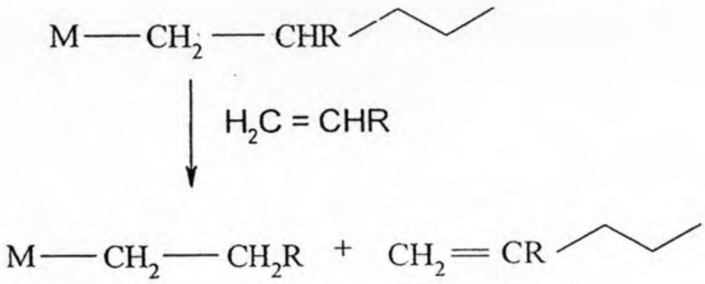


Figure 2.12 Chain transfer to monomer [21]

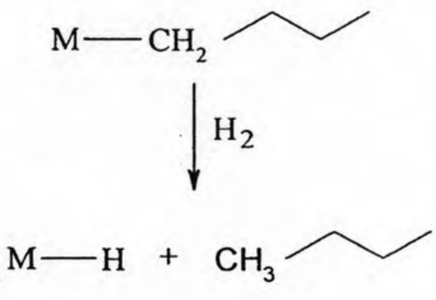
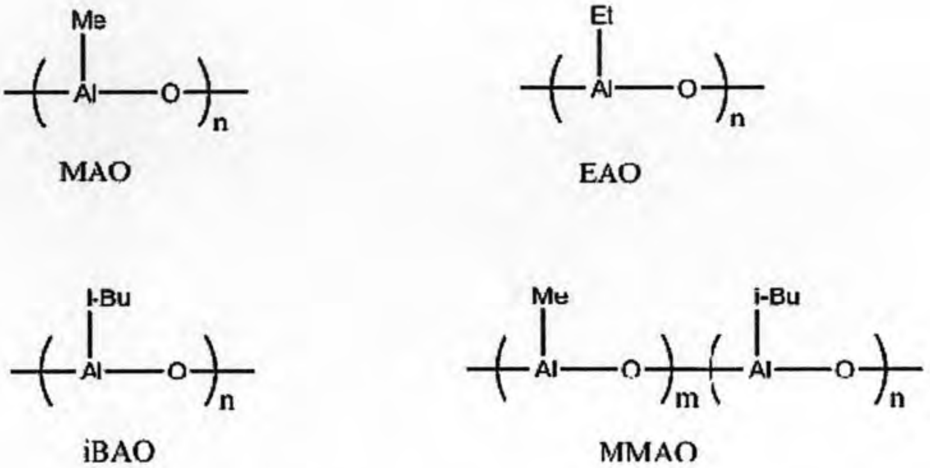


Figure 2.13 Chain transfer to hydrogen [21]

2.5 Cocatalysts

Aluminoxane, especially methylaluminoxane (MAO) plays the very important role to activate metallocene catalyst. Before the MAO was discovered, in Ziegler-Natta catalyst alkylaluminumchloride was used to activate Cp_2TiCl_2 but it exhibited the very poor activity. Using of MAO as cocatalyst can promote the productivity of polymerization by several order of magnitude. Otherwise using of MAO, the other aluminoxanes such as, ethylaluminoxane (EAO) or iso-buthylaluminoxane (iBAO) or modified methylaluminoxane was employed to use as cocatalyst too. (Structure of MAO, EAO, iBAO and MMAO was shown in figure 2.14)



MAO EAO

iBAO MMAO

Figure 2.14 Several kinds of MAO

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 [34]. 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 1 [19], 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.

$$AlR_3 + H_2O \longrightarrow AlR_3(H_2O) \qquad (1)$$

$$AlR_3(H_2O) \longrightarrow 1/n\ [R_2Al(OH)]_n + RH \qquad (2)$$

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 2.15 include: (1) one-dimensional linear chains; (2) cyclic rings, which contain three-coordinate Al centers; (3) two-dimensional structures and (4) three-dimensional clusters is based on structural similarities with *tert*-butylaluminoxanes, which form isoluable and X-ray crystallographically characterizable cage structures

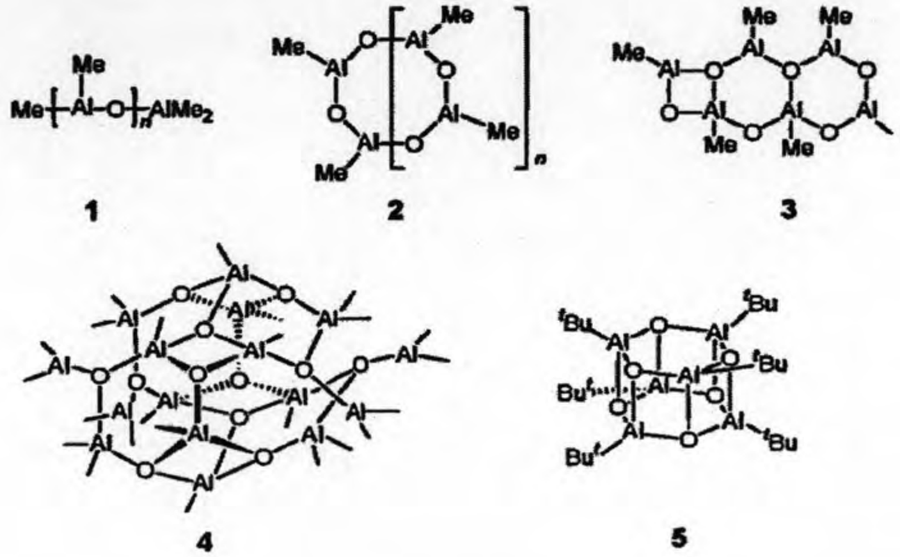


Figure 2.15 The general proposed structure of MAO [35]

The interaction of metallocene with aluminoxanes has been studied in detail. Metallocene dichloride reacts with methylaluminoxane to yield a methylated compound (Figure 2.16) It undergoes either methyl or chloride abstraction to generate metallocene methyl cation.

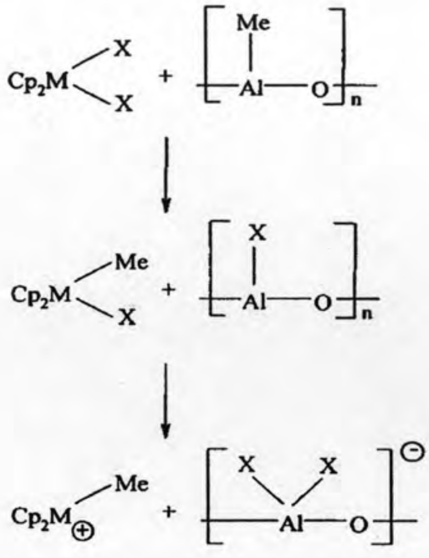


Figure 2.16 Postulated mechanism of formation of the active species in the reaction between metallocene and methylaluminoxane

In the case of rac-Et(Ind)$_2$ZrMe$_2$ as precursor, the extracted methyl ligands do not yield any modification in the structure and reactivity of the MAO counter-anion, thus allowing zirconium coordination site available for olefin that presented in Figure 2.17 [36].

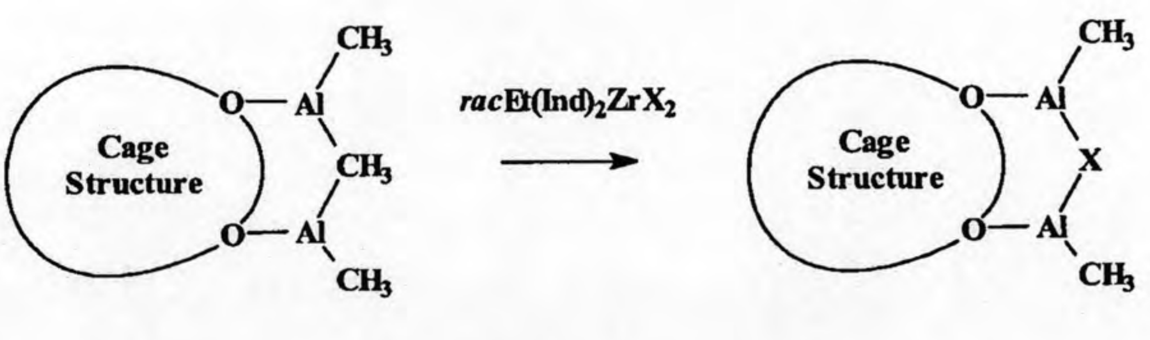


Figure 2.17 Representation of MAO showing the substitution of one bridging methyl group by X ligand extracted from racEt(Ind)$_2$ZrCl$_2$ (X = Cl, NMe$_2$, CH$_2$Ph) [36].

Cam and Giannini [37] investigated the role of TMA present in MAO by a direct analysis of Cp$_2$ZrCl$_2$/MAO solution in toluene-d$_8$ using ^{1}H-NMR. Their observation indicated that TMA might be the major alkylating agent and that MAO acted mainly as a polarization agent. However, in general it is believed that MAO is the key cocatalyst in polymerizations involving metallocene catalysts. The role of MAO included 1) alkylation of metallocene, thus forming catalyst active species, 2) scavenging impurities, 3) stabilizing the cationic center by ion-pair interaction and 4) preventing bimetallic deactivation of the active species.

The homogeneous metallocene catalyst cannot be activated by common trialkylaluminum only. However, Soga *et al.*[38] were able to produce polyethylene with modified homogeneous Cp_2ZrCl_2 activated by common trialkylaluminum in the presence of $Si(CH_3)_3OH$. Their results show that for an “optimum” yield aging of the catalyst and $Si(CH_3)_3OH$ mixture for four hours is required. However, MWD of the produced polymers is bimodal although the polymers obtained in the presence of MAO have narrow MWD.

Ethylene/α-olefins copolymers with bimodal CCD were produced with homogeneous Cp_2ZrCl_2 with different cocatalysts such as MAO and mixture of TEA/borate or TIBA/borate [39]. It seemed that the active species generated with different cocatalysts have different activities and produce polymers with different molecular weights.

2.6 Catalyst Activity

The ethylene polymerization rate of the copolymerization reaction with the catalyst system SiO_2/MAO/rac-Me_2Si [2-Me-4-Ph-Ind]$_2ZrCl_2$ was studied by Fink *et al.* [40]. The temperature was varied from 40 to 57°C. Small amount of hexene in the reaction solution increased the polymerization rate. The extent of the "comonomer effect" depended on the polymerization temperature. At 57°C the maximum activity of the ethylene/hexene copolymerization was 8 times higher than the homopolymerization under the same conditions. At 40°C the highest reaction rate for the copolymerization is only 5 times higher than that for the ethylene homopolymerization. For the polymer properties of the ethylene/α-olefin copolymerization, the molecular weights of the polymers decreased with increasing comonomer incorporation. Ethylene/hexene copolymers produced by a metallocene catalyst also have the same melting point and glass transition temperature.

Series of ethylene copolymerization with 1-hexene or 1-hexadecene over four different siloxy-substituted ansa-metallocene/methylaluminoxane (MAO) catalyst systems were studied by Seppala *et al.* [41]. Metallocene catalysts rac-Et[2-(t-$BuMe_2SiO$)Ind]$_2ZrCl_2$ (1), rac-Et[l-(t-$BuMe_2SiO$)Ind]$_2ZrCl_2$ (2), rac-Et[2-(i-Pr_3SiO)Ind]$_2ZrCl_2$ (3) and rac-Et[l-(i-Pr_3SiO)Ind]$_2ZrCl_2$ (4) were used. The effects of minor changes in the catalyst structure, more precisely changes in the ligand substitution pattern were studied. They found that series of polymerization with siloxy-substituted bis(indenyl) ansa-metallocene are highly active catalyst precursors for ethylene-α-olefins copolymerizations. The comonomer response of all four catalyst precursors was good. Under the same conditions the order of copolymerization ability of the catalyst was rac-Et[2-(i-Pr_3SiO)Ind]$_2ZrCl_2$ > rac-Et[2-(t-$BuMe_2SiO$)Ind]$_2ZrCl_2$ and rac-Et[l-(i-Pr_3SiO)Ind]$_2ZrCl_2$ > rac-Et[l-(t-$BuMe_2SiO$)Ind]$_2ZrCl_2$. These catalysts are able to produce high molecular weight copolymers.

2.7 Copolymerization

By adding a small amount of comonomer to the polymerization reactor, the final polymer characteristics can be dramatically changed. For example, the Unipol process for linear low density polyethylene (LLDPE) uses hexene and the British Petroleum process (BP) uses 4-methylpentene to produce high-performance copolymers [42]. The comonomer can be affected the overall crystallinity, melting point, softening range, transparency and also structural, thermochemical, and rheological properties of the formed polymer. Copolymers can also be used to enhance mechanical properties by improving the miscibility in polymer blending [43].

Ethylene is copolymerized with α-olefin to produce polymers with lower densities. It is commonly observed that the addition of a comonomer generally increases the polymerization rate significantly. This comonomer effect is sometimes linked to the reduction of diffusion limitations by producing a lower crystallinity polymer or to the activation of catalytic sites by the comonomer. The polymer molecular weight often decreases with comonomer addition, possibly because of a transfer to comonomer reactions. Heterogeneous polymerization tends to be less sensitive to changes in the aluminum/transition metal ratio. Chain transfer to aluminum is also favored at high aluminum concentrations. This increase in chain transfer would presumably produce a lower molecular weight polymer. In addition, some researchers observed the decrease, and some observed no change in the molecular weight with increasing aluminum concentration [44].

The effect of polymerization conditions and molecular structure of the catalyst on ethylene/α-olefin copolymerization have been investigated extensively. Pietikainen and Seppala [45] investigated the effect of polymerization temperature on catalyst activity and viscosity average molecular weights for low molecular weight ethylene/propylene copolymers produced with homogeneous Cp_2ZrCl_2. Soga and Kaminaka [46] compared copolymerizations (ethylene/propylene, ethylene/1-hexene, and propylene/l-hexene) with $Et(H_4Ind)_2ZrCl_2$ supported on SiO_2, Al_2O_3 or $MgCl_2$. Broadness of MWD was found to be related to the combination of support types and types of monomers. The effect of silica and magnesium supports on copolymerization characteristics was also investigated by Nowlin *et al.* [47]. Their results indicated that comonomer incorporation was significantly affected by the way that support was treated based on the reactivity ratio estimation calculated with simplified Finemann Ross method. However, it should be noted that Finemann Ross method could be misleading due to linear estimation of nonlinear system.

Copolymer based on ethylene with different incorporation of 1-hexene,1-octene, and 1-decene were investigated by Quijada [48]. The type and the concentration of the comonomer in the feed do not have a strong influence on the catalytic activity of the system, but the presence of the comonomer increases the activity compared with that in the absence of it. From ^{13}C-NMR it was found that the size of the lateral chain influences the percentage of comonomer incorporated, 1-hexene being the highest one incorporated. The molecular weight of the copolymers obtained was found to be dependent on the comonomer concentration in the feed, showing that there is a transfer reaction with the comonomer. The polydispersity (Mw/Mn) of the copolymers is rather narrow and dependent on the concentration of the comonomer incorporation.

Soga *et al.* [49] noted that some metallocene catalysts produce two-different types of copolymers in terms of crystallinity. They copolymerized ethylene and 1-alkenes using

6 different catalysts such as Cp_2ZrCl_2, Cp_2TiCl_2, Cp_2HfCl_2, $Cp_2Zr(CH_3)_2$, Et(Ind $H_4)_2ZrCl_2$ and i-Pr(Cp)(Flu)$ZrCl_2$. Polymers with bimodal crystallinity distribution (as measured by TREF-GPC analysis) were produced with some catalytic systems. Only Cp_2TiCl_2-MAO and Et(H_4Ind)$_2ZrCl_2$-MAO produced polymers that have unimodal crystallinity distribution. The results seem to indicate that more than one active site type are present in some of these catalysts. However, it is also possible that unsteady-state polymerization conditions might have caused the broad distributions since the polymerization times were very short (5 minutes for most cases).

Marques *et al.*[50] investigated copolymerization of ethylene and 1-octene by using the homogeneous catalyst system based on Et(Flu)$_2ZrCl_2$/MAO. A study was performed to compare this system with that of Cp_2ZrCl_2/MAO. The influence of different support materials for the Cp_2ZrCl_2 was also evaluated, using silica, $MgCl_2$, and the zeolite sodic mordenite NaM. The copolymer produced by the Et(Ind)$_2ZrCl_2$/MAO system showed higher molecular weight and narrower molecular weight distribution, compared with that produced by Cp_2ZrCl_2/MAO system. Because of the extremely congested environment of the fluorenyl rings surrounding the transition metal, which hinders the beta hydrogen interaction, and therefore, the chain transference. Moreover, the most active catalyst was the one supported on SiO_2, whereas the zeolite sodic mordenite support resulted in a catalyst that produced copolymer with higher molecular weight and narrower molecular weight distribution. Both homogeneous catalytic systems showed the comonomer effect, considering that a significant increase was observed in the activity with the addition of a larger comonomer in the reaction medium.

The effect of different catalyst support treatments in the 1-hexene/ethylene copolymerization with supported metallocene catalyst was investigated by Soares *et al.* [51]. The catalysts in the study were supported catalysts containing SiO_2, commercial MAO supported on silica (SMAO) and MAO pretreated silica (MAO/silica) with Cp_2HfCl_2, Et(Ind)$_2HfCl_2$, Cp_2ZrCl_2 and Et(Ind)$_2ZrCl_2$. All the investigated supported catalysts showed good activities for the ethylene polymerization (400-3000 kg polymer/mol metal.h). Non-bridged catalysts tend to produce polymers with higher molecular weight when supported on to SMAO and narrow polydispersity. The polymer produced with Cp_2HfCl_2 supported on silica has only a single low crystallinity peak. On the other hand, Cp_2HfCl_2 supported on SMAO and MAO/silica produced ethylene/1-

hexene copolymers having bimodal CCDs. For the case of Cp_2ZrCl_2 and $Et(Ind)_2ZrCl_2$, only unimodal CCDs were obtained. It seems that silica-MAO-metallocene and silica-metallocene site differ slightly in their ability to incorporate comonomer into the growing polymer chain, but not enough to form bimodals CCDs.

Soares *et al.* [52] studied copolymerization of ethylene and 1-hexene. It was carried out with different catalyst systems (homogeneous $Et(Ind)_2ZrCl_2$, supported $Et(Ind)_2ZrCl_2$ and in-situ supported $Et(Ind)_2ZrCl_2$). Supported $Et(Ind)_2ZrCl_2$: an $Et(Ind)_2ZrCl_2$ solution was supported on SMAO. It was used for polymerization of ethylene and 1-hexene. In-situ supported $Et(Ind)_2ZrCl_2$: an $Et(Ind)_2ZrCl_2$ solution was directly added to SMAO in the polymerization reactor, in the absence of soluble MAO. Homogeneous $Et(Ind)_2ZrCl_2$ showed higher catalytic activity than the corresponding supported and in-situ supported metallocene catalysts. The relative reactivity of 1-hexene increased in the following order: supported metallocene ≈ in-situ supported metallocene < homogeneous metallocene catalysts. The MWD and short chain branching distribution (SCBD) of the copolymer made with the in-situ supported metallocene were broader than those made with homogeneous and supported metallocene catalysts. They concluded that there are at least two different active species on the in-situ supported metallocene catalyst for the copolymerization of ethylene and 1-hexene.

Soares *et al.* [53] investigated copolymerization of ethylene and 1-hexene with different catalysts: homogeneous $Et(Ind)_2ZrCl_2$, Cp_2HfCl_2 and $[(C_5Me_4)SiMe_2N(tert\text{-}Bu)]TiCl_2$, the corresponding in-situ supported metallocene and combined in-situ supported metallocene catalyst (mixture of $Et(Ind)_2ZrCl_2$ and Cp_2HfCl_2 and mixture of $[(C_5Me_4)SiMe_2N(tert\text{-}Bu)]TiCl_2$. They studied properties of copolymers by using ^{13}C-NMR, gel permeation chromatography (GPC) and crystallization analysis fractionation (CRYSTAF) and compared with the corresponding homogeneous metallocene. The in-situ supported metallocene produced polymers having different 1-hexene fractions, SCBD and MDW. It was also demonstrated that polymers with broader MWD and SCBD can be produced by combining two different in-situ supported metallocenes.

In addition, Soares *et al.* [54] studied copolymerization of ethylene and 1-hexene with an in-situ supported metallocene catalysts. Copolymer was produced with alkylaluminum activator and effect on MWD and SCBD was examined. They found that TMA exhibited the highest activity while TEA and TIBA had significantly lower activities. Molecular weight distributions of copolymers produced by using the different activator types were unimodal and narrow, however, short chain branching distributions were very different. Each activator exhibited unique comonomer incorporation characteristics that can produce bimodal SCBD with the use of a single activator. They used individual and mixed activator system for controlling the SCBDs of the resulting copolymers while maintaining narrow MWDs.

2.8 Heterogeneous Metallocene Catalysts

Since Kaminsky discovered the high activity Cp_2ZrCl_2/MAO ethylene polymerization system, metallocene catalysts have slowly evolved as procedures push to commercialize the technology. In order to achieve the high activities, the metallocene catalyst required excessive molar Al to transition metal ratio (Al:M) of between 1000-15000 : 1. Such ratio are commercially unacceptable in terms of the cost and the amount of residues left in the polymer. A significant effort has been put into reducing the amount of MAO required and this has led to the development of many systems with non-aluminum cocatalysts. Significant effort has also gone into heterogenizing the catalyst system by supporting the metallocene and cocatalyst onto an inorganic support such as silica, alumina, magnesium chloride, starch, zeolite, cyclodextrin and polymers [55].

Therefore, heterogeneous catalysts offer several additional advantages important to industry, they improved product morphology and the ability to be used in gas and/or slurry phase synthesis methods more than their corresponding homogeneous metallocene systems. To overcome the preparation complexities of traditionally supported metallocene catalysts, metallocene can be supported in situ, which eliminates the need for a supporting step before polymerization. These systems have a good catalytic activity, produce polymers with a good morphology and high bulk density and do not cause reactor fouling [56].

2.8.1 Types of Supports

Many materials have been used as catalyst support to improve the catalytic efficiency and product morphology. The supports used include silica, alumina, magnesium chloride, starch, zeolites, cyclodextrin, polymers, and mesoporous molecular sieves. The most commonly used supported are spherical amorphous silica, alumina, and magnesium chloride. Mesoporous molecular sieve have recently been used for olefin polymerization and proposed as support for metallocene catalyst to synthesize the polymers having controlled molecular weight and narrow polydispersity. These characteristics of these catalysts are of both fundamental interest and practical importance.

2.8.1.1 Silica and Mesoporous Molecular sieves as Supporting Materials

The right choices of supporting materials as well as the choice of suitable properties (pore size, specific surface area, chemical surface composition) are important factors influencing the immobilization of the metallocene catalyst and the fragmentation of the support during polymerization. Commercially used porous silica gels are prepared by neutralization of aqueous alkali metal silicate with acid. The pore structure and pore size distribution can be controlled by the type of chemical reaction and experimental conditions. The pore size distribution is relatively narrow; pore diameter range from 1 to 20 nm; i.e. the silicas contain micropores (pore diameter ≤ 2 nm) and mesopores (pore diameters 2 to 50 nm). These small pores are responsible for high specific surface area, which ranges from 250 to 1000 m^2/g, depending on whether micro- or mesopores are dominant.

Metallocene complexes of various metals, including Zr and Ti which are known to be very active catalysts for olefin polymerizations, can be attached onto the inner surface of mesoporous molecular sieves.

A new class of mesoporous molecular sieve materials designated as MCM-41 was first reported in 1992 by the researchers of the Mobil Oil Corporation, USA. After the discovery of MCM-41, the researcher interest focused on the following main subjects:

(1) characterization [16]; (2) the mechanism of formation [16]; (3) the synthesis of new materials based on the MCM-41 synthesis concept [16]; (4) morphology control; and (5) the technical applications of MCM-41 and related mesoporous materials [16].

J.S.Beck *et al.* (1992) [16] have synthesized a new synthetic composition of ultra-large pore crystalline material. This material is called M41S family. Different mesostructures have been named as MCM-41 (hexagonal), MCM-48 (cubic), and MCM-50 (lamellar). Furthermore they proposed two possible mechanistic pathways for MCM-41 formation: (1) a liquid crystal templating mechanism, where the MCM-41 structure is formed around micelles existing as single cylindrical aggregates; (2)a mechanism where the addition of the silicate results in the ordering of the subsequent silicate-encaged surfactant micelles. A schematic of this formation mechanism is shown in Figure 2.18

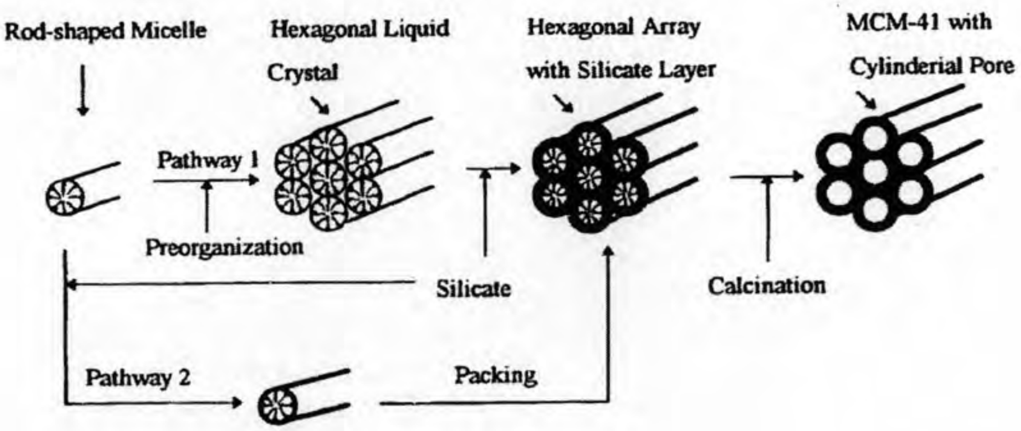


Figure 2.18 Schematic model of liquid crystal templating mechanism via two possible pathways [16]

Xiu S.Zhao *et al.* (1996) [57] presented a comprehensive overview of recent advances in the field of MCM-41. Beginning with the chemistry of surfactant/silicate solutions, progresses made in design and synthesis, characterization, and physiochemical property evaluation of MCM-41 are enumerated. Proposed formation mechanisms are presented, discussed, and identified. Potential applications are reviewed and projected.

A.Corma (1997) [58] studied the synthesis procedures and synthesis mechanisms, heteroatom insertion, characterization, adsorption, and catalytic properties, rapidly occurs. It would be highly desirable to produce high thermal and hydrothermal stability materials. The importance of the adsorption of the adsorption and diffusion of reactants and products in micro- and mesoporous catalysts on their activity and decay, especially when working in liquid phase have been reported. He suggested that it is of much interest in catalysis to prepare good mesoporous with different pore size, since in this case a high dispersion of Pt, Pd, Pt-Re, and Ni-Mo could be achieved and this could generate such new and highly active hydrogenation, re-forming, and HDS catalysts.

2.8.2 Supported Metallocene Catalyst Procedure

The performance for ethylene and propylene polymerizations of various supported metallocene systems and final polymer properties are compared and discussed on the basis of the different catalyst preparations and polymerization conditions. According to these comprehensive reviews, the different methods of heterogenization are possible and can be mainly divided into three general methods according to Kaminsky and Laban (2001) [1]. These three methods are conceptually described and illustrated in Figure 2.19

(1) In the method of direct heterogenization, the metallocene or a mixture of the metallocene and MAO is anchored via physisorption or chemisorption onto the support. In this first class, the metallocene must be activated by external MAO.

(2) The metallocene can be supported by covalent bonding of its ligand environment to the support followed by activation with external MAO. The metallocene can be synthesized gradually as a covalent bonded species direct on the supporting material.

(3) Initial impregnation of MAO onto supports followed by adsorption and simultaneous activation of the metallocene (indirect heterogenization). In analogy to the homogeneous metallocene catalysis, the bonding between the active species $[Cp_2ZrCH_3]^+$ and the supported MAO is ionic. When performing the method indirect heterogenization, no further MAO has to be added.

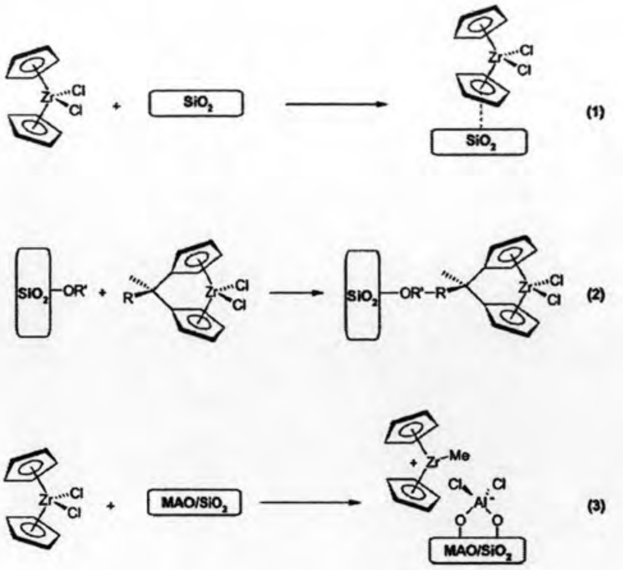


Figure 2.19 Supporting methods of metallocene: (1) direct heterogenization, (2) covalent bonding on the support, (3) indirect heterogenization [1]

2.9 Modified Supports System

Commercial Grace silica, mesoporous silicate, MCM-41, and aluminium-modified MCM-41 were used as support for catalyst activity in ethylene polymerization. The effect of the structure and surface properties of support material on metallocene (zirconocene chloride) adsorption and catalyst activity was studied. Rahiala et al. [5] reported that the highest amount of zirconocene dichloride was adsorbed on Al-modified MCM-41 (Si/Al=32), providing the most reactive sites for attachment of the active component on the support surface. The ^{13}C-CPMAS NMR studies proved that the Cp_2ZrCl_2 is bound to the support surface. Also the highest in ethane polymerization was obtained using this support [5].

Activities of ethylene/α-olefin copolymerization were found to increase with silane-modified silica-supported MAO using ansa-zirconocene catalyst. Silane modification resulted in the narrower molecular weight distribution of polymers suggesting that the system is more homogeneous-like [9].