

## CHAPTER II

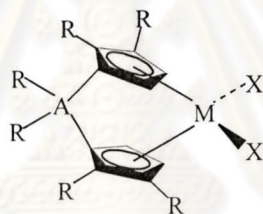
### THEORY

One of the most exciting developments in the areas of catalysis, organometallic chemistry, and polymer science in recent years has been the intense exploration and commercialization of new polymerization technologies based on metallocene coordination olefin polymerization catalysts [12, 13]. The vast number of specifically designed/synthesized transition metal complexes (catalyst precursors) and main-group organometallic compounds (cocatalysts) allows unprecedented control over polymer microstructure, the generation of new polymer architectures, and the development of new polymerization reactions. Commercialization of new generations of metallocene catalyst-based technologies has provided the multibillion pound per year polyolefins industry with the ability to deliver a wide range of new and innovative olefin-based polymers having improved properties. The intense industrial activity in the field and the challenges to our basic understanding that have come to light have in turn stimulated a burst of fundamental academic research.

#### 2.1. Metallocene

Metallocene catalysts are soluble in hydrocarbons, show only one type of active site and their chemical structures can be easily changed. 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 molecular weight and distribution, comonomer content and tacticity by careful selection of the appropriate conditions. In addition, their catalytic activity is 10-100 times higher than that of the Ziegler-Natta systems [14].

Metallocene catalysts are organometallic compounds in which one or two  $\pi$ -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. The typical chemical structure of a metallocene catalyst is represented in Figure 2.1 where M is the group 4A, 5A, or 6A transition metal, normally group 4A (Zr, Ti, Hf); A is an optional bridging atom usually Si or C atom; R is a  $\sigma$ -homoleptic hydrocarbyl such as H, alkyl, or other hydrocarbon groups; and X is chlorine or other halogens from group 7B or an alkyl group. The cyclopentadienyl ligands, halides, and  $\sigma$ -homoleptic hydrocarbyls represent the three classes of ligands of the metallocene catalysts. In case of metallocene catalyst, which have only one  $\pi$ -carbocyclic ligand with a heteroatom that is attached to the bridging atom [15].



**Figure 2.1.** Typical chemical structure of a metallocene catalyst.

## 2.2. Cocatalysts

The importance of the cocatalyst 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 many special cocatalyst features for constant catalyst precursor and kinetic/thermodynamic considerations of the reaction. Finally, the cocatalyst, which becomes an anion after the activation process, is the vital part of a catalytically active cation-anion ion pair and may significantly influence polymerization characteristics and polymer properties.

## 2.2.1. Aluminium compounds

### 2.2.1.1. Aluminium alkyls

Aluminium alkyls, including trialkylaluminums and alkylaluminum chlorides, are important components in classical heterogeneous Ziegler-Natta coordination polymerization catalysis. A wide variety of homogeneous Ziegler-Natta catalysts based on aluminum alkyls as cocatalysts were also reported for the polymerization of olefins. Breslow and Newburg at the Hercules Research Center first discovered the homogeneous catalytic system consisting of  $\text{Cp}_2\text{TiCl}_2$  in the presence of diethylaluminum chloride ( $\text{Et}_2\text{AlCl}$ ) for ethylene polymerization [16]. It has low activity because of bimolecular deactivator due to reductive metathesis [17, 18]. Sinn, Kaminsky, and co-workers subsequently investigated zirconocene complexes activated with alkylaluminum species for ethylene polymerization.

Overall, the inability of metallocenes activated by alkylaluminum halides to polymerize propylene and higher  $\alpha$ -olefins has limited their utility in this field. A number of attempts were made to improve the performance of these catalyst systems. Among these efforts, Reichert and Meyer first discovered a surprising rate enhancement in ethylene polymerization activity upon addition of water to the  $\text{Cp}_2\text{TiEtCl}/\text{AlEtCl}_2$  catalyst system. Subsequent studies by Long and Breslow on the effects of water in the otherwise inactive  $\text{Cp}_2\text{TiCl}_2/\text{AlMe}_2\text{Cl}$  system led to the suggestion that the formation of a dimeric aluminoxane, e.g.,  $\text{ClMeAl-O-AlClMe}$ , which is presumably a stronger Lewis acid than  $\text{Me}_2\text{AlCl}$  and therefore a more efficient activator, is responsible for enhancing ethylene polymerization activity.

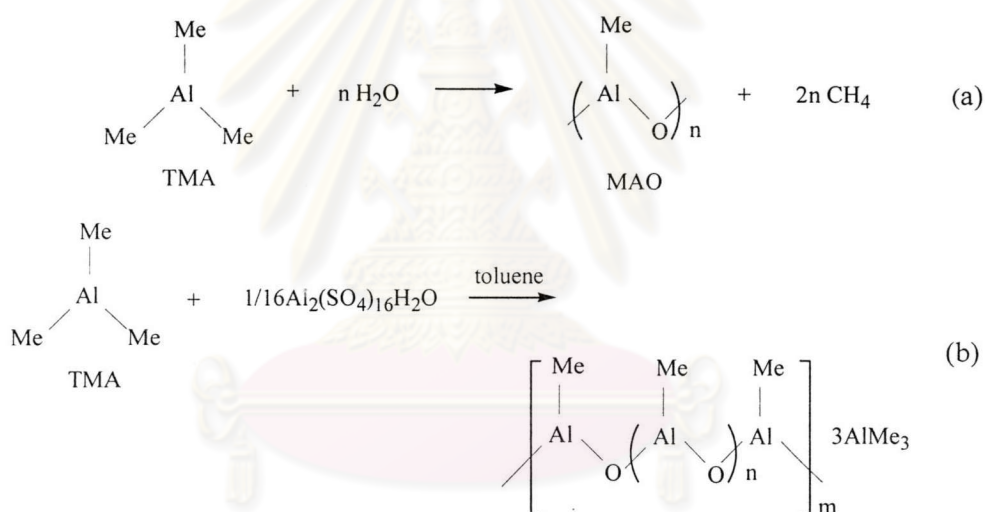
By addition of water to the halogen-free, polymerization inactive  $\text{Cp}_2\text{ZrMe}_2/\text{AlMe}_3$  system, Sinn and Kaminsky observed a surprisingly high activity for ethylene polymerization, which led to the discovery of a highly efficient activator, an oligomeric methyl aluminoxane (MAO). This discovery, rejuvenated Ziegler-Natta catalysis and, along with major advances achieved in controlling polymer



stereochemistry and architecture, began the metallocene and single site polymerization catalysis [19-26].

### 2.2.1.2. MAO

The discovery of methylaluminoxane (MAO) as an activator for metallocene catalysts for olefin polymerization has stimulated a considerable effort in unveiling the cocatalyst structure and function in the catalyst activation process [27]. The reaction of water with TMA has been found to eliminate methane and to form an aluminium-oxygen-aluminium structure (Figure 2.2a), basic formation of MAO by reaction of trimethylaluminium (TMA) with water. Alternately, hydrated aluminium salt is reacted with TMA (Figure 2.2b) [28].

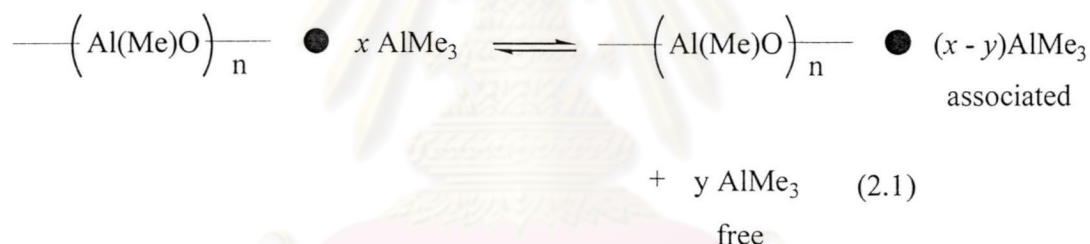


**Figure 2.2.** Formation of methylaluminoxane (MAO).

The reaction of water with alkylaluminium is extremely rapid and highly exothermic and careful synthetic routes are necessary for its controlled and safe formation. In the laboratory, often the hydrated salt method is utilized for formation of aluminoxane, which consists of reacting a hydrated salt such as hydrated aluminium, copper, or iron sulfate with TMA or other trialkylaluminiums. Several other methods for synthesizing aluminoxanes have been reported which generally involve either a wet solvent and/or gas to control the aluminoxane formation. However, there are several

disadvantages with these methods including long reaction time with hydrated salts, low yields (50% or lower), poor reproducibility, etc. Due to these disadvantages, these methods are not favoured industrially and various other methods are employed, such as directly contacting trialkylaluminium with water vapour or atomized water vapour under carefully controlled conditions.

Despite its unique effectiveness as a cocatalyst, MAO still remains a "black box". Depending on the nature of the hydrated salt (the H<sub>2</sub>O 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 equilibrium present in MAO solutions, and residual trimethylaluminum in MAO solution appears to participate in equilibrium that interconverts various MAO oligomers [29]. There are two types of TMA present in typical MAO solutions: "free" TMA and "associated" TMA.

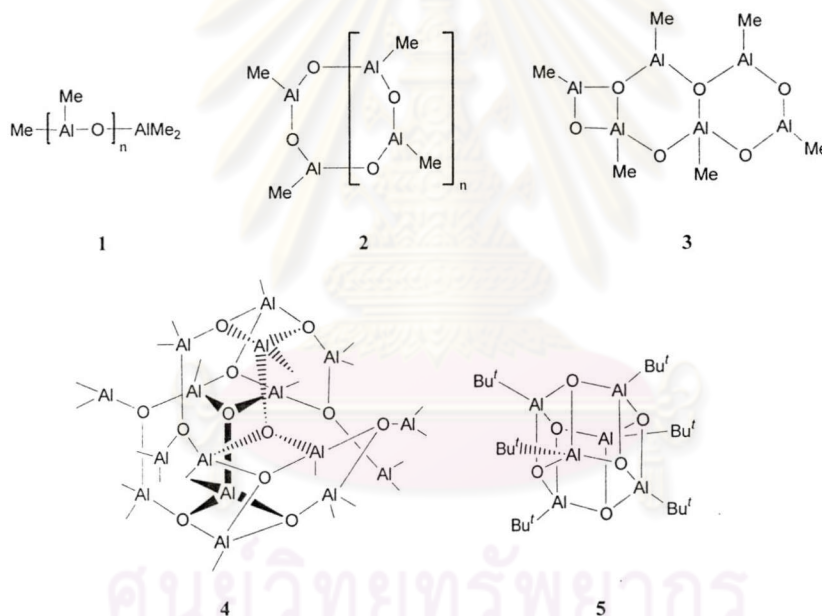


It is difficult to reduce the Me:Al ratio to less than 1.5 by evaporation of volatile components because vacuum-drying removes only the free TMA, while the associated TMA can only be removed chemically. Tritto *et al.* found that cryoscopic MAO molecular weights linearly decrease after AlMe<sub>3</sub> addition according to a linear relationships, which is caused by disproportionation reactions.

All of the synthetic techniques to produce aluminoxanes inevitably produce aluminoxanes with different structures, different degrees of oligomerization, and different amounts of unreacted TMA. Both cyclic and linear oligomers have been proposed to be produced in the formation of aluminoxanes with a degree of oligomerization between 10 and 20. More recently, 3-D cage structures with four-coordinate aluminium centers have been demonstrated for aluminoxanes produced from Al(*t*-Bu)<sub>3</sub> with similar structures

demonstrated for methylaluminoxanes. These cage structures are believed to be involved in the interaction between aluminoxane and transition metal in an active catalyst site, with the aluminoxane involved in more than just catalyst activation. By  $^{13}\text{C}$  NMR spectroscopy, Tritto *et al.* [30] found that TMA is most likely bound to MAO, bridging two or more MAO chains together and that the amount of TMA influences the active cationic metallocene concentration.

The proposed structures for MAO include one-dimensional linear chains (1) or cyclic rings (2) which contain three-coordinate Al centers (Figure 2.3). The caged structures with the general formula  $(\text{AlOMe})_n(\text{TMA})_m$ , have  $n$  ranging between 6 and 30 and  $m$  between 0 and 4, depending upon the topology of the parent cage [31-32].



**Figure 2.3.** Structures of MAO.

Despite the success of MAO in promoting high activity metallocene mediated olefin polymerization, it also exhibits disadvantageous features. High MAO: catalyst precursor ratios (100 to 10000) are generally required for obtaining acceptable polymerization activity and relatively stable kinetic profiles, which raises issues of the high cost of this cocatalyst and the high ash content ( $\text{Al}_2\text{O}_3$ ) of the product polymer. Finally, the intrinsically complicated structural features of MAO as well as the large



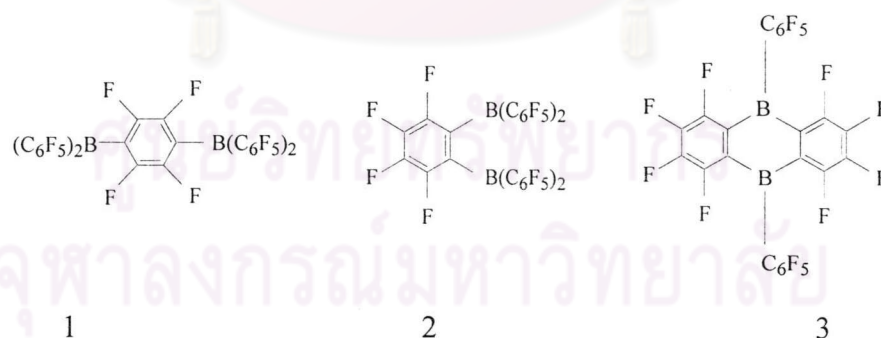
excess amount of MAO required in the activation process prevent full characterization of the catalytically active species. Consequently, there is a great need to develop new cocatalyst systems which can provide equivalent or even greater catalytic activity and, at the same time, allow isolation and characterization of the active species for a better fundamental understanding of cationic transition metal mediated coordination polymerization.

## 2.2.2. Boron compounds

### 2.2.2.1. Borane

The synthesis of tris(pentafluorophenyl)borane,  $B(C_6F_5)_3$ , was first reported in 1964 by Massey and Park. In early 1990s when Marks and Ewen discovered that, in combination with group 4A metallocene alkyls, strongly Lewis acidic  $B(C_6F_5)_3$  promotes highly efficient olefin polymerizations and allows isolation of crystallographically characterizable cationic metallocene complexes [33-34].

Recently, several bifunctional perfluoroarylboranes, *para*-phenylenediborane(1), *ortho*-phenylenediborane(2), and octafluoro-9,10-bis(pentafluorophenyl)-9,10-diboraanthracene(3) have been prepared (Figure 2.4) [35].



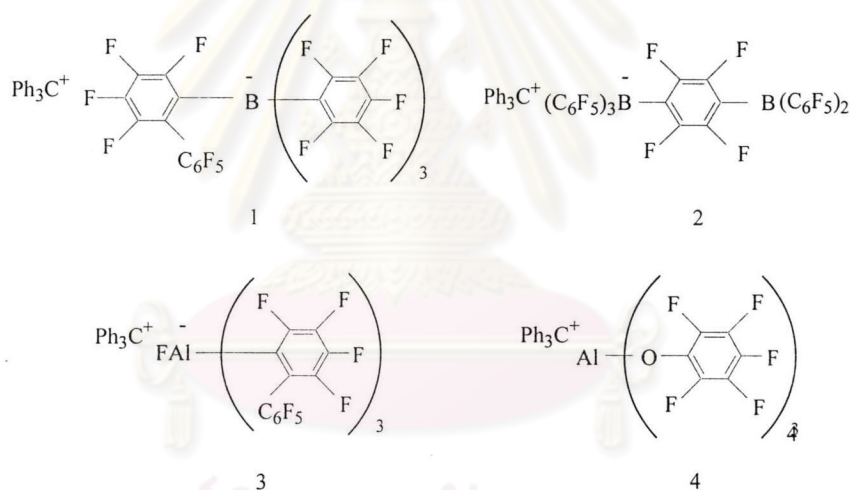
**Figure 2.4.** Structures of bifunctional perfluoroarylboranes.

The diborane is expected to exhibit very high Lewis acidity because the nearly perpendicular conformation of the two  $C_6F_5$  rings prevents significant electron density transfer to the B center, of which exhibit a strong electron withdrawing effect. Indeed,

when combined with group 4A metallocene and other single-site precatalysts, cationic active species have higher olefin polymerization efficiency (up to 20 times) than those based on  $B(C_6F_5)_3$ .

### 2.2.2.2. Borate

The trityl cation  $Ph_3C^+$  is a powerful alkide and hydride-abstrating (and oxidizing) reagent, and ammonium cations of the formula  $HNR_2^+$  can readily cleave M-R bonds via facile protonolysis. In combination with  $M(C_6F_5)_4^-$  ( $M = B, Al$ ) noncoordinating/weakly coordinating anions, borate and aluminate activators,  $[Ph_3C]^+[B(C_6F_5)_4]^-$  [36],  $[HNR_2]^+[B(C_6F_5)_4]^-$  [37],  $[Ph_3C]^+[Al(C_6F_5)_4]^-$ , have been developed as effective cocatalysts for activating metallocene and related metal alkyls, thereby yielding highly efficient olefin polymerization catalysts. Examples are shown in Figure 2.5.



**Figure 2.5.** Structures of borate cocatalysts.

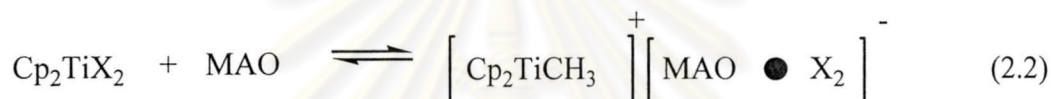
## 2.3. Polymerization mechanisms

Catalysts for the syndiospecific polymerization of styrene are typically Group 4A metal compound, especially titanium compounds, with MAO or borate derivatives as the cocatalyst. Several studies have been carried out to clarify the nature of the active center and to explain the mechanisms of polymerization and of stereochemical control [38, 39].



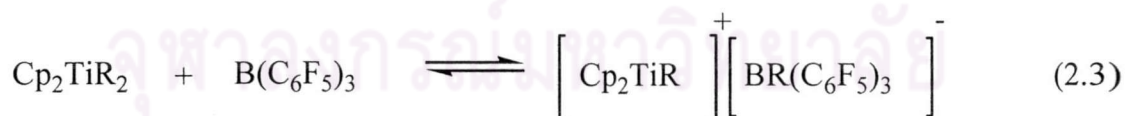
### 2.3.1. Initiation step: active species

Group 4A metal compounds show high activities in syndiospecific styrene polymerization. Zirconium derivatives have lower activity than that of titanium homologues,  $\text{CpTiX}_n$  or  $\text{Cp}^*\text{TiX}_n$  compounds ( $n = 2, 3$ ;  $X = \text{alkyl, alkoxyde, halide}$ ) [40]. Cyclopentadienyl anion is regarded as a "fixed" ligand, while  $X$  are "mobile" ligands. A cocatalyst must be added to the polymerization mixture to generate active species. The nature and the formation of the true active catalytic species are not yet fully elucidated. For olefin polymerization, it is generally accepted that homogeneous catalysts based on group 4A metallocene/MAO consist of cationic complexes formed by reaction of a metallocene with methylalumoxane, according to the following equilibrium.



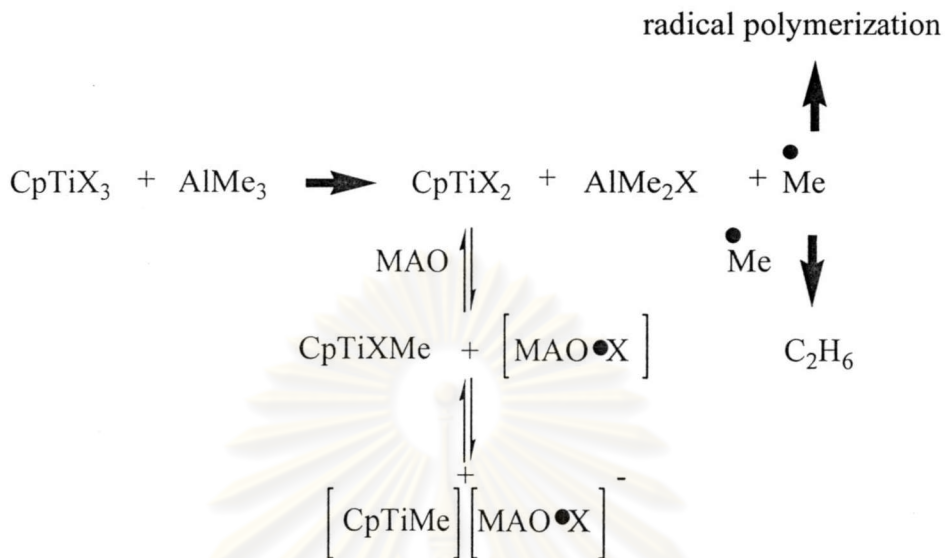
Methylation and ligand abstraction by MAO are possible due to its pronounced Lewis acidity. Due to the low value of the equilibrium constant, the use of a large excess of MAO is often required.

Active syndiospecific catalysts can be obtained not only by reaction of the metallocene with MAO as cocatalyst, but also by allowing to react in hydrocarbon medium, e.g.  $\text{CpTiMe}_3$  and  $\text{B}(\text{C}_6\text{F}_5)_3$  or  $[\text{NR}_3\text{H}]^+\text{B}[\text{C}_6\text{F}_5]_4^-$  in 1/1 molar ratio. It is known that  $\text{B}(\text{C}_6\text{F}_5)_3$  [41],  $[\text{NR}_3\text{H}]^+\text{B}[\text{C}_6\text{F}_5]_4^-$ ,  $[\text{Ph}_3\text{C}]^+[\text{B}(\text{C}_6\text{F}_5)_4]^-$ , as well as MAO, cationize group 4A alkyl metallocenes providing cations together with noncoordinating anion (Equation 2.3).



A similar mechanism which leads to a  $[\text{CpTiMe}]^+$  cation can be advanced for styrene syndiospecific catalyst (Figure 2.6). Ti(IV) is reduced to Ti(III). Reduction is probably caused by the free trimethylaluminium contained in MAO, since aluminium alkyls are better reducing agents than aluminoxanes. Methyl radicals formed as a consequence of  $\text{AlMe}_3$  oxidation could initiate the radical polymerization of styrene to an

atactic polymer, although it is known that primary radicals have short life times and are poor initiators.

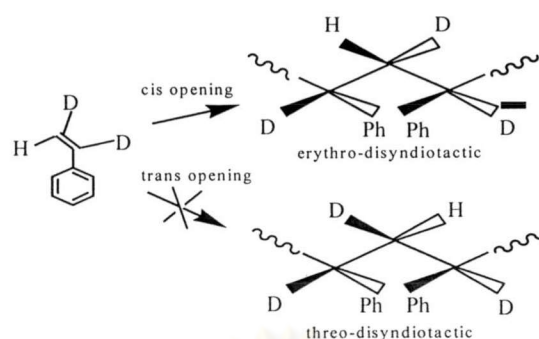


**Figure 2.6.** Formation of initiating species by CpTiX<sub>3</sub>/MAO catalytic system.

The titanium oxidation state in the active catalytic species is (III) in CpTiX<sub>3</sub>/MAO system [42]. CpTi(OC<sub>4</sub>H<sub>9</sub>)<sub>3</sub>/MAO systems redox titrations were carried out to establish the metal oxidation state, the formation of such hydridotitanium (III) complexes is almost quantitative. Ti(IV):Ti(III):Ti(II) ratios depend strongly on the titanium concentration. Experiments carried out in toluene using an electro dialysis polymerization apparatus did not afford syndiotactic polymer, suggesting that the catalytic species has little or no ionic mobility.

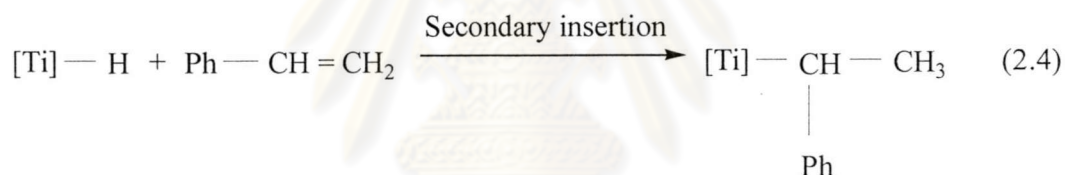
### 2.3.2. Propagation step

By polymerizing deuterium labelled styrene and analyzing the <sup>1</sup>H NMR spectra, Longo et al. detected the exclusive presence of erythro-disyndiotactic conformer and demonstrated that the insertion of styrene on Ti-C bond proceeds through cis opening of the double bond (Figure 2.7) [43-44].

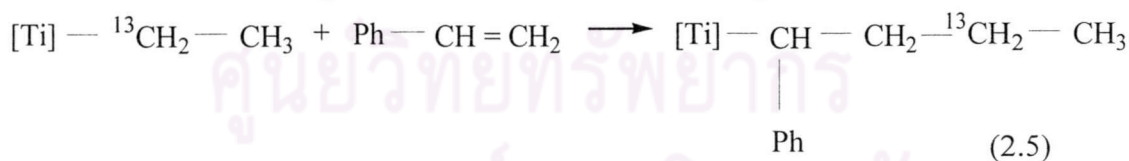


**Figure 2.7.** Stereochemistry of double bond opening of cis-styrene- $\beta$ -d by syndiospecific catalysts for styrene polymerization.

Syndiotactic polystyrene is very regioregular and there is no evidence of either head-to-head or tail-to-tail arranged units. The mode of the insertion of the monomer into the metal-carbon bond of the active species is secondary and was demonstrated the polymer end group by using  $^{13}\text{C}$  NMR [45].



The enriched end groups expected from secondary insertion were also detected when performing polymerization in the presence of  $\text{Al}(\text{C}_2\text{H}_5)_3$  enriched with  $^{13}\text{C}$  on the methylenes [46].



### 2.3.3. Chain transfer and termination steps

If the polymerization mechanism was a true living process, molecular weight distribution (MWD) value of 1 and an increase in molecular weight with reaction time would be observed.



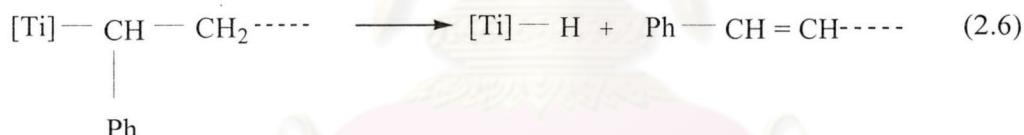
Actually, a limiting molecular weight is reached with some initiating systems, depending on reaction conditions (temperature, diluent), while with other initiating systems the molecular weight continues to increase during the entire reaction [47, 48].

Three main factors may contribute to MWD broadening:

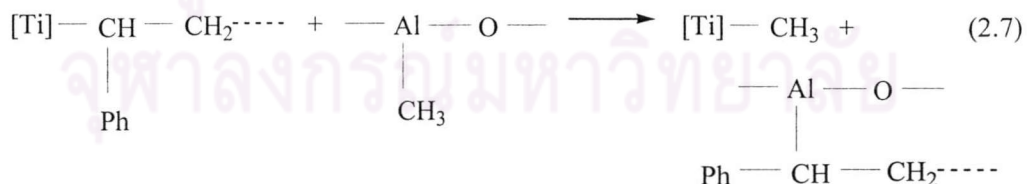
1. existence of different catalytic centers.
2. existence of chain-transfer or termination reactions.
3. formation of some atactic PS due to spurious radical or ionic initiation.

As far as atactic impurities are concerned, after atactic PS extraction, a narrowing of MWD is also observed. MWD values of 1.7-2.4 are obtained in most cases, suggesting that chain transfer is present.

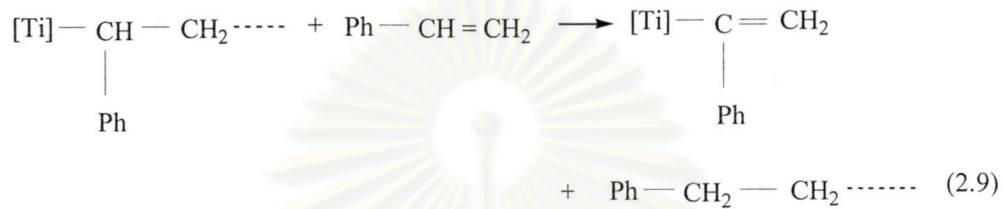
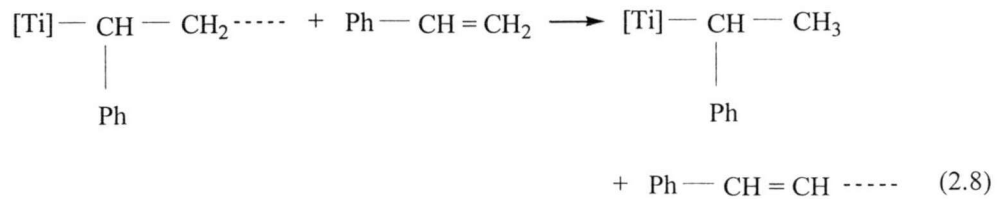
As previously mentioned, strong experimental evidence for  $\beta$ -hydrido abstraction exists (transfer rate constant =  $k_\beta$ ). The so formed hydridotitanium species is able to re-initiate a new polymer chain.



In analogy with  $\alpha$ -olefin polymerization with  $\text{Cp}_2\text{MCl}_2/\text{MAO}$  ( $\text{M} = \text{Zr}, \text{Hf}$ ) catalysts, transfer to aluminium would lead to the formation of aluminium-polymer bonds (transfer rate constant =  $k_m$ ):



Chain transfer with monomer has transfer rate constant =  $k_S$  :



## 2.4. Supported metallocene catalyst

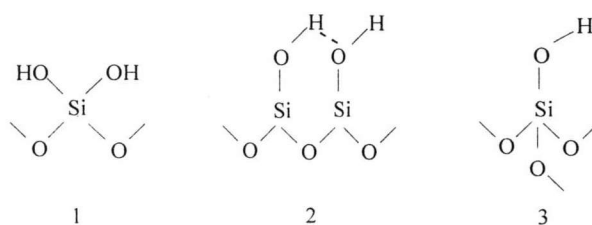
A large proportion of commercial polyolefin production is currently achieved by large scale slurry and gas phase polymerization processes, which require the polymerization catalysts to be anchored on solid supports. Although supported catalysts are generally less active than homogeneous catalysts, they often offer advantages in producing polymeric products with good morphology and high bulk density. Supported catalysts also enable the use of highly active polymerization systems with less reactor fouling than in conventional homogeneous processes.

### 2.4.1. Supported materials

#### 2.4.1.1. Silica

Silica, the most commonly used support for heterogeneous catalysts, contains Si-OH groups of varying structures and concentrations depending on the dehydration temperature. These Si-OH groups may be geminal (undehydrated silica) (1, Figure 2.8), hydrogen bonded (dehydrated at temperatures up to 600°C) (2, Figure 2.8), or isolated (dehydrated above 600°C) (3, Figure 2.8). These can react with metal dichloride to form

Si-O-M functionalities which can be converted to active catalysts when a cocatalyst is added.



**Figure 2.8.** Different Si-OH group.

These surface hydroxyl groups can be removed by treatment with a variety of agents. An IR spectroscopic study of the action of  $\text{AlMe}_3$  and  $\text{AlMe}_3$ -rich and -lean MAO on  $400^\circ\text{C}$  dried silica showed that the silanol groups reacted preferentially with  $\text{AlMe}_3$  and less rapidly with the aluminoxane oligomer. The  $\text{Et}(\text{Ind})_2\text{ZrCl}_2\text{-SiO}_2$  ( $\text{Al}_2\text{O}_3$ )-MAO combination polymerizes propylene with much improved activity when partially dehydroxylated silica or alumina is first treated with  $\text{AlMe}_3$ .  $\text{AlMe}_2\text{Cl}$  has also been used as the passivating agent. The activity of a  $\text{Me}_2\text{Si}(2\text{-Me-4-PhInd})_2\text{ZrCl}_2$  -MAO catalyst increased from 67 to 242 kg/g of metallocene.h and the melting point increases from  $156$  to  $160^\circ\text{C}$  when the silica is treated with  $\text{AlMe}_3$  before supporting the catalyst.

At  $\text{Al/Zr} = 200$ , a variety of metallocene-MAO catalysts were supported on silicas dried at various temperatures (Table 2.1). Supports dried at lower temperatures afford catalysts of higher activities. Analysis of the distribution of aluminium and silicon indicates a very even distribution of cocatalyst on the support.



**Table 2.1.** Polymerization performance of metallocene catalysts based on support dehydration temperature

Metallocene	Dehydration temp (°C)	Productivity (g/g of cat.h.100 psi)	Melt index
$(n\text{-BuCp})_2\text{ZrCl}_2$	20	2300	18.7
$(n\text{-BuCp})_2\text{ZrCl}_2$	110	2700	1.16
$(n\text{-BuCp})_2\text{ZrCl}_2$	300	2500	1.19
$(n\text{-BuCp})_2\text{ZrCl}_2$	600	1300	0.72
$\text{Cp}^*_2\text{ZrCl}_2$	200	300	1.8
$\text{Cp}^*_2\text{ZrCl}_2$	600	150	2.0
$(\text{Ind})_2\text{ZrCl}_2$	200	1700	6.5
$(\text{Ind})_2\text{ZrCl}_2$	600	1500	5.5
$(\text{MeCp})_2\text{ZrCl}_2$	200	600	0.4
$(\text{MeCp})_2\text{ZrCl}_2$	600	500	0.8

#### 2.4.1.2. Magnesium chloride

Magnesium chloride, a widely used support in conventional Ziegler-Natta catalysts, has been studied far less extensively than silica as a carrier for single site catalysts. Reaction of dibutylmagnesium tert-butyl chloride in a diisoamyl ether-hexane mixture produces  $\text{MgCl}_2$  with very narrow particle size distribution.

Metallocene complex  $\text{Cl}_2\text{Si}(\text{Ind})_2\text{ZrCl}_2$  [49] on  $\text{MgCl}_2$ , activated by MAO or  $\text{Al}(i\text{-Bu})_3$ , polymerizes propylene to isotactic polypropylene, but with an activity about 100 times less than of  $\text{Me}_2\text{Si}(\text{Ind})_2\text{ZrCl}_2$ -MAO. The  $\text{Me}_2\text{C}(\text{Cp})(\text{Flu})\text{ZrCl}_2$ -MAO- $\text{MgCl}_2$  catalyst was also used in the syndiospecific polymerization of propylene at 20°C; in this case, the catalyst activity was higher than that of the homogeneous catalyst.

### 2.4.1.3. Zeolites

Zeolites have begun to attract more interest as supports for single site catalysts. The copolymerization of ethylene with 1-olefins catalyzed by zirconocenes-MAO supported on HY zeolite shows a loss in activity on heterogenization, an increase in molecular weight, and a decrease in comonomer incorporation (Table 2.2).

**Table 2.2.** Copolymerization ethylene with 1-olefins using zirconocenes supported on HY zeolite

Catalyst	Comonomer	Activity (kg/mol.h.bar)	Mol wt	% Olefin
$\text{Cp}_2\text{ZrCl}_2\text{-MAO}$	1-hexene	652	7000	20
$\text{Cp}_2\text{ZrCl}_2\text{-MAO-HY}$	1-hexene	228	63000	8
$\text{Cp}_2\text{ZrCl}_2\text{-MAO}$	4-MP-1	1160	3000	8
$\text{Cp}_2\text{ZrCl}_2\text{-MAO-HY}$	4-MP-1	270	25000	2
$\text{Cp}_2\text{ZrCl}_2\text{-MAO}$	1-octene	616	9000	16
$\text{Cp}_2\text{ZrCl}_2\text{-MAO-HY}$	1-octene	218	59000	7
$\text{Cp}_2\text{ZrCl}_2\text{-MAO}$	1-dodecene	578	10000	13
$\text{Cp}_2\text{ZrCl}_2\text{-MAO-HY}$	1-dodecene	196	68000	5
$(\text{Ind})_2\text{ZrCl}_2\text{-MAO}$	1-hexene	450	21000	4
$(\text{Ind})_2\text{ZrCl}_2\text{-MAO-HY}$	1-hexene	196	40000	<1
$\text{Et}(\text{Ind})_2\text{ZrCl}_2\text{-MAO}$	1-hexene	468	15000	36
$\text{Et}(\text{Ind})_2\text{ZrCl}_2\text{-MAO-HY}$	1-hexene	278	22000	36
$\text{Et}(\text{Ind})_2\text{HfCl}_2\text{-MAO}$	1-hexene	36	81000	16
$\text{Et}(\text{Ind})_2\text{HfCl}_2\text{-MAO-HY}$	1-hexene	17	132000	16

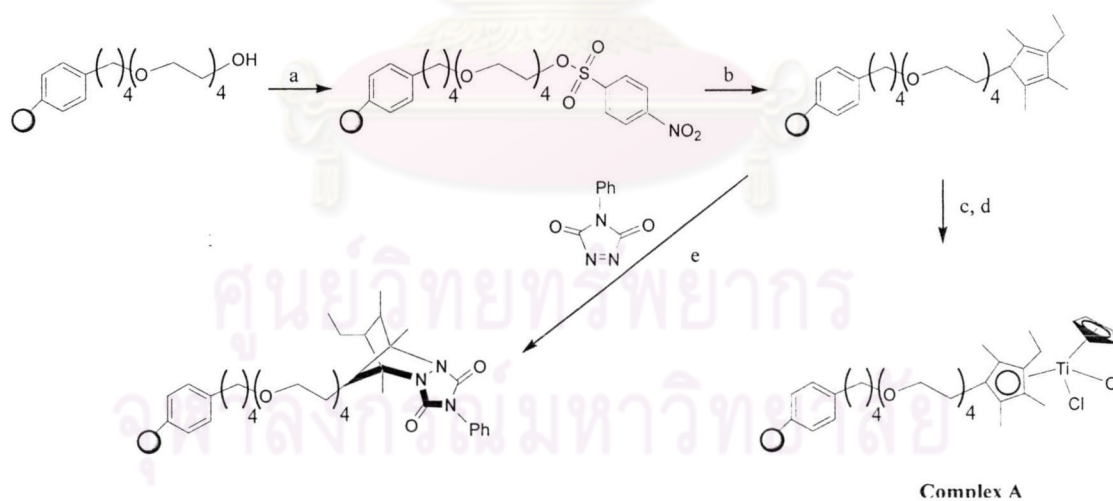
4-MP-1 = 4-methyl-1-pentene.

The  $\text{Et}(\text{Ind})_2\text{MCl}_2$  ( $\text{M} = \text{Zr}, \text{Hf}$ ) displayed no attenuation of comonomer incorporation, it was hypothesized that the smaller metallocenes are in the pores of the zeolite, into which diffusion of the comonomer is difficult, and the ansa-metallocenes, not adsorbed inside the pores, are located on the exterior and are therefore more accessible to comonomer.

#### 2.4.1.4. Polymers

Since 1996, there have been a number of reports of polystyrene-supported cyclopentadienyl metal complexes, used as heterogeneous single-site catalysts for olefin polymerization [50].

Barrett and de Miguel have prepared an immobilized  $\text{Cp}_2\text{TiCl}_2$  complex (A) (Figure 2.9). The ligand bearing a spacer group between the polymer matrix and the Ti complex has the objective of optimizing the accessibility of the metal centers. It was used as a catalyst for ethylene polymerization, but activity was not as high as expected. This may be due to poor swelling of the supported catalyst and therefore limited accessibility of the metal centers.



Reagents and conditions: (a)  $2 \times p\text{-O}_2\text{NPhSO}_2\text{Cl}$ , pyridine,  $\text{CH}_2\text{Cl}_2$ .

(b)  $\text{NaCpMe}_3\text{Et}$ , THF.

(c)  $\text{MeLi}$ , THF.

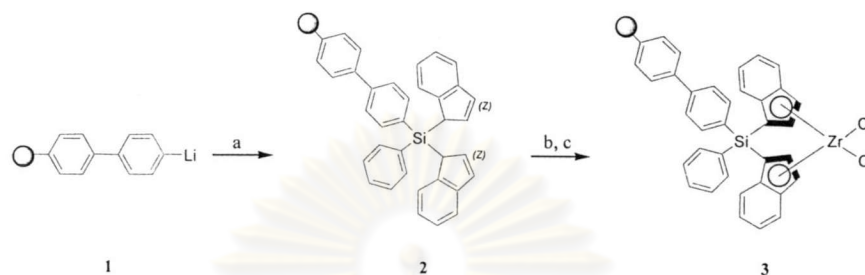
(d)  $\text{CpTiCl}_3$ , toluene.

(e)  $-78^\circ\text{C}$ ,  $\text{CH}_2\text{Cl}_2$ .

**Figure 2.9.** Preparation of polymer-supported  $\text{Cp}_2\text{TiCl}_2$  complex(A).



In Figure 2.10, lithiation of the polystyrene, treatment with 1,4-dibromobenzene, and further lithiation gave complex(1), which was treated with  $\text{PhSi(Ind)}_2\text{Cl}$  to give the supported ligand complex(2). The metal complex (3) was formed by treatment of this with  $\text{ZrCl}_4$ . The complex (3) was used for ethylene polymerization.



Reagents and conditions: (a)  $\text{PhSi(Ind)}_2\text{Cl}$ , toluene,  $40^\circ\text{C}$ , 8 h.

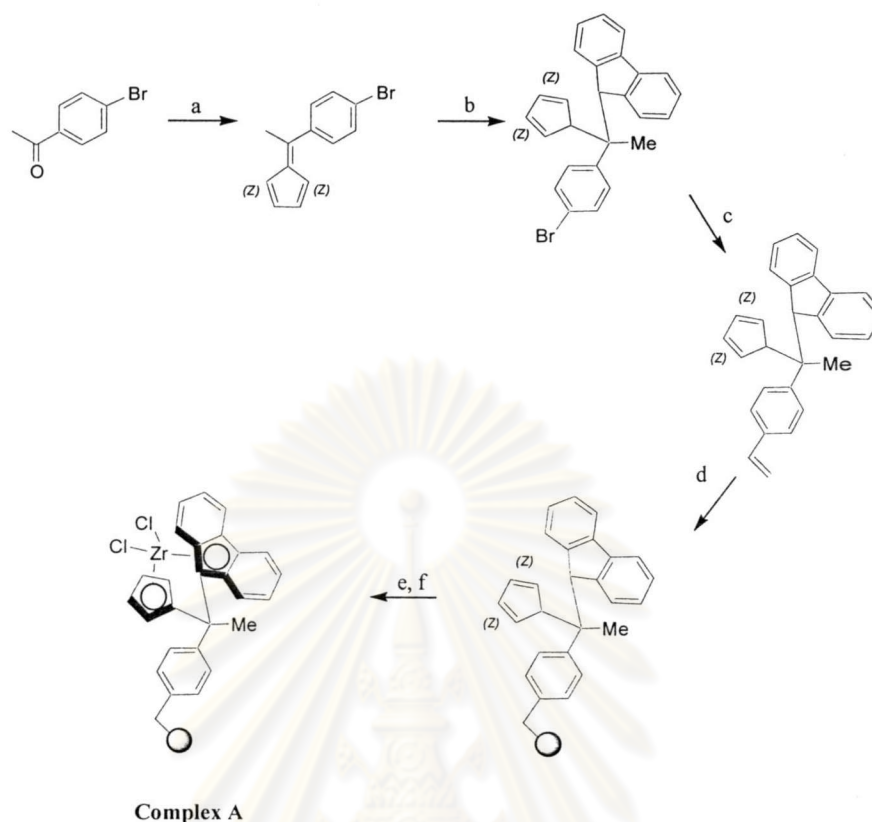
(b)  $\text{BuLi}$ , THF,  $0^\circ\text{C} \rightarrow \text{rt}$ , 6 h.

(c)  $\text{ZrCl}_4$ , THF,  $0^\circ\text{C} \rightarrow \text{rt}$ , 12 h.

**Figure 2.10.** Preparation of polymer-supported Zr-di-Ind complex.

A supported Cp/fluorene ligand was prepared by AIBN-initiated polymerization of a styrene-derivatized monomer, complex A, with styrene (Figure 2.11). Complex A was found to be active for the polymerization of propylene, the activity is very low compared to that of the homogeneous analogue [51].

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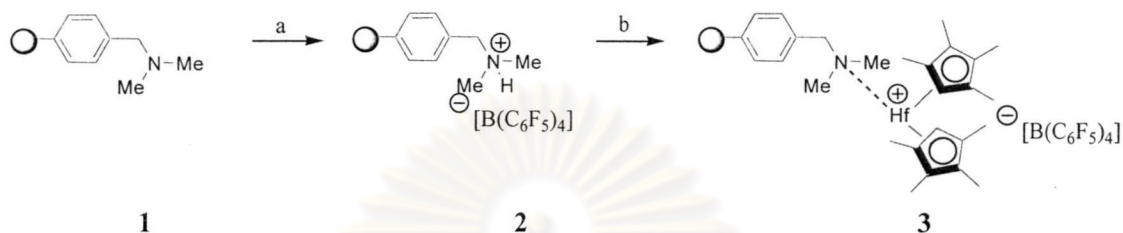


Reagents and conditions: (a) CpLi, THF, 0° C → reflux, 3 h.  
 (b) FluLi, Et<sub>2</sub>O, 0° C → rt, 8 h.  
 (c) vinyltributyltin, Pd(PPh<sub>3</sub>)<sub>4</sub>, toluene, reflux, 8 h.  
 (d) styrene, AIBN, toluene, 60° C, 12 h.  
 (e) BuLi, THF, 0° C → rt, 6 h.  
 (f) ZrCl<sub>4</sub>, THF, 0° C → rt, 12 h.

**Figure 2.11.** Preparation of polymer-supported Cp/fluorene ligand (complex A).

As well as immobilizing metallocenes via supported Cp or Ind functionalities, there have been reports of other methods of attachment (Figure 2.12). Frechet *et al.* have immobilized metal cyclopentadienyl complexes on a noninteracting polystyrene support. The supported catalysts were prepared by first treating lightly cross-linked Merrifield resin with dimethylamine to form the corresponding supported amine (complex 1). This was then treated with [PhNMe<sub>2</sub>H]<sup>+</sup>[B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>]<sup>-</sup>, which protonates the basic support and binds the perfluorinated borate anion to the support by ion pairing, giving complex 2. The active catalyst (complex 3) is formed by reacting the borated support with the neutral

dialkylmetallocene  $[(C_5HMe_4)_2HfMe_2]$ . The metal complex is bound to the support through a weakly coordinating interaction between the Hf and the N of the supported amine. The catalyst proves to be very active in ethene/1-hexene copolymerization, the weak coordination between metallocene and this support being strong enough to retain the metal complex on the support during the course of the reaction.

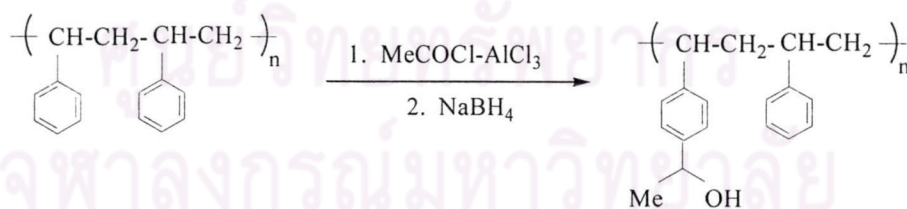


Reagents and conditions: (a)  $[PhNMe_2H][B(C_6F_5)_4]$ ,  $CH_2Cl_2$ , rt, 1.5 h.

(b)  $(Me_4C_5H)_2HfMe_2$ , toluene, rt, 1 h.

**Figure 2.12.** Immobilized metal cyclopentadienyl complex on a noninteracting polystyrene support.

Polymer with polar groups can also be used as supports for single site catalysts. Crosslinked polystyrene which has been chloromethylated, or acylated with  $CH_2COCl-AlCl_3$  then reduced with  $NaBH_4$  (Figure 2.13), functions as a support for  $Et(Ind)_2ZrCl_2-MAO$  catalysts. Unfunctionalized polystyrene or functionalized polystyrene with insufficient crosslinking gave inferior activities and extensive reactor fouling.



**Figure 2.13.** Polymer-supported zirconocene catalyst with polar group.

With a  $Cp_2ZrCl_2-MAO$  catalyst, the nature of the functional group had a profound influence on the molecular weight of the ethylene-1-hexene polymer produced, ranging



from a melting index. When the metal component is  $(n\text{-BuCp})\text{ZrCl}_2$ , the dramatic differences in molecular weight are largely moderated.

**Table 2.3.** Ethylene polymerization by zirconocene supported on crosslinked polystyrenes

Metallocene	Support	Activity (g/g of cat.h.100 psi)	Melt index
$\text{Cp}_2\text{ZrCl}_2$	crosslinked PS	810	1.9
$\text{Cp}_2\text{ZrCl}_2$	hydroxy-PS	490	430
$\text{Cp}_2\text{ZrCl}_2$	acetoxy-PS	560	1500
$\text{Cp}_2\text{ZrCl}_2$	silica	500	34
$(n\text{-BuCp})_2\text{ZrCl}_2$	acetoxy-PS	1000	1.0
$(n\text{-BuCp})_2\text{ZrCl}_2$	crosslinked PS	920	0.52
$(n\text{-BuCp})_2\text{ZrCl}_2$	silica	310	0.38

## 2.4.2. Supported catalysts activator

### 2.4.2.1. Trialkylaluminums

Silica supported  $\text{Cp}_2\text{TiCl}_2\text{-AlEt}_n\text{Cl}_{3-n}$  catalysts afford quite different polyethylene products depending on the preparation procedure. When the alkylaluminum is contacted with silica prior to reacting with the titanocene, the polyethylene formed has a higher molecular weight and broader molecular weight distribution than that produced from the homogeneous catalyst.  $\text{Cp}_2\text{TiCl}_2$  supported on silica and reacting with alkylaluminum gives polyethylene with a bimodal distribution, one component of which has a molecular weight similar to that produced from the soluble catalyst, which might be due to desorption of active catalyst from the support to the solution.

Supported zirconocenes activated by simple alkylaluminum compounds were extensively studied. In solution, alkylaluminums are ineffective activators for

zirconocenes, but when supported on alumina or  $\text{MgCl}_2$  activity improves dramatically in propylene polymerization, though it is still less than the homogeneous MAO-activated variant (Table 2.4) [52]. Trialkylaluminums work well, but chlorine containing compounds such as  $\text{AlEt}_2\text{Cl}$  and  $\text{AlEtCl}_2$  suppress activity completely. Silica, the most commonly used support for heterogenized single site catalysts, is a poor choice as a carrier when trialkylaluminums are to be used as cocatalysts; only by pretreating the silica with a small amount of MAO does activity improve.

**Table 2.4.** Propylene polymerization with supported zirconocene catalysts activated by simple alkylaluminums

Metallocene	Support	Cocatalyst	Activity (kg of PP/mol Zr)
$\text{Cp}_2\text{ZrCl}_2$	$\text{Al}_2\text{O}_3$	$\text{AlMe}_3$	47
$\text{Cp}_2\text{ZrCl}_2$	$\text{MgCl}_2$	$\text{AlMe}_3$	172
$\text{Cp}_2\text{ZrCl}_2$	None	MAO	132
$\text{Et}(\text{H}_4\text{-Ind})_2\text{ZrCl}_2$	$\text{Al}_2\text{O}_3$	$\text{AlMe}_3$	259
$\text{Et}(\text{H}_4\text{-Ind})_2\text{ZrCl}_2$	None	MAO	2,070
$\text{Et}(\text{H}_4\text{-Ind})_2\text{ZrCl}_2$	$\text{Al}_2\text{O}_3$	$\text{AlEt}_3$	158
$\text{Et}(\text{H}_4\text{-Ind})_2\text{ZrCl}_2$	$\text{Al}_2\text{O}_3$	$\text{AlMe}_2\text{Cl}$	negligible
$\text{Et}(\text{H}_4\text{-Ind})_2\text{ZrCl}_2$	$\text{MgCl}_2$	$\text{AlMe}_3$	139
$\text{Et}(\text{H}_4\text{-Ind})_2\text{ZrCl}_2$	$\text{MgCl}_2$	$\text{Al}(i\text{-Bu})_3$	138
$\text{Et}(\text{H}_4\text{-Ind})_2\text{ZrCl}_2$	$\text{MgF}_2$	$\text{AlMe}_3$	264
$\text{Et}(\text{H}_4\text{-Ind})_2\text{ZrCl}_2$	Silica	$\text{AlMe}_3$	negligible
$i\text{-Pr}(\text{Cp})(\text{Flu})\text{ZrCl}_2$	$\text{Al}_2\text{O}_3$	$\text{AlMe}_3$	52
$i\text{-Pr}(\text{Cp})(\text{Flu})\text{ZrCl}_2$	$\text{MgF}_2$	$\text{AlMe}_3$	61
$i\text{-Pr}(\text{Cp})(\text{Flu})\text{ZrCl}_2$	$\text{MgCl}_2$	$\text{AlMe}_3$	51
$i\text{-Pr}(\text{Cp})(\text{Flu})\text{ZrCl}_2$	$\text{SiO}_2$	$\text{AlMe}_3$	negligible
$i\text{-Pr}(\text{Cp})(\text{Flu})\text{ZrCl}_2$	$\text{MgO}$	$\text{AlMe}_3$	negligible
$i\text{-Pr}(\text{Cp})(\text{Flu})\text{ZrCl}_2$	None	MAO	758

### 2.4.2.2. Aluminoxanes

Metallocene catalysts in dissolved form are in most cases unsuitable for the production on an industrial scale. In order to use them in existing technical processes (drop-in technology) by exchanging the conventional Ziegler-Natta catalysts, metallocenes have to be supported. Different methods are possible by using MAO as cocatalyst [53, 54].

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 the first case, 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 directly on the supporting material.
3. Initial impregnation of MAO onto the support followed by adsorption and simultaneous activation of the metallocene (indirect heterogenization). In analogy to the homogeneous metallocene catalysis, the bonding between the active species and the supported MAO is ionic. When performing the method of indirect heterogenization, no further MAO has to be added.

### 2.4.2.3. Boron compounds

Supporting single site catalysts activated by non aluminum agents, principally borate anions such as  $[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$ ,  $[\text{PhNMe}_2\text{H}][\text{B}(\text{C}_6\text{F}_5)_4]$  or  $\text{B}(\text{C}_6\text{F}_5)_3$ , is far more problematic than supporting those activated by aluminoxane based analogues. These systems are highly prone to be deactivated by impurities. The metal halide is alkylated *in situ* using common trialkylaluminums, then converted to the cation by contacting with  $[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$ ,  $[\text{PhNMe}_2\text{H}][\text{B}(\text{C}_6\text{F}_5)_4]$  or  $\text{B}(\text{C}_6\text{F}_5)_3$ . This technique has been used



widely in the preparation of supported single site catalysts. For example,  $\text{Cp}^*\text{TiCl}_3$  complex supported on silica is catalytically inert when combined with  $\text{AlMe}_3$ , but addition of  $[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$  or  $\text{B}(\text{C}_6\text{F}_5)_3$ . Activates the metal complex to form a catalyst for the atactic polymerization of propylene.

## 2.5. Comparison of homogeneous and heterogeneous catalysts

The molecular characteristics of the products produced from heterogeneous single site catalysts resemble as closely as possible those of their homogeneous counterparts, mirroring the narrow molecular weight distribution, random distribution of comonomer and, in the case of stereospecific polymerization, high stereoregular and melting point.

The most notable difference between the two families is catalyst activity. With few exceptions [55], the activity of the supported catalyst is half to a tenth that of the soluble catalyst, which may be the result of fewer active centers present in the heterogeneous system. Catalyst centers could be deactivated when supported, or may not be generated in the metal cocatalyst interaction. The molecular weight of the polymer is unaffected or somewhat higher when a single site catalyst is supported. This suggests that the lower activity of the catalyst is due to a reduced number of active centers.

An extensive study of the effect of temperature on propylene polymerization using homogeneous and supported  $\text{Me}_2\text{Si}(\text{2-Me-4,5-BenzoInd})_2\text{ZrCl}_2\text{-MAO}$  catalysts shows that changes in activity, molecular weight, isotacticity, and polymer bulk density were more moderate for the supported catalyst than the solution catalyst. The melting point of *i*-PP from this metallocene is  $147^\circ\text{C}$  for the homogeneous catalyst, declining to  $144^\circ\text{C}$  when supported. Substituting  $[\text{PhNMe}_2\text{H}][\text{B}(\text{C}_6\text{F}_5)_4]$  as the activator affords polymer with the same melting point as the homogeneous catalyst. Although the molecular weight of the polypropylene from *rac*- $\text{Me}_2\text{Si}(\text{2,4-Me}_2\text{-Cp})(\text{3}',\text{5}'\text{-Me}_2\text{Cp})\text{ZrCl}_2\text{-MAO}$  catalyst increased when supported on silica (93,000 to 190,100), the melting point of the polymer is unaffected.