

## CHAPTER II

### THEORY

#### 2.1 Ziegler-Natta Catalysts

Ziegler-Natta catalysts are the most important widely used as coordination catalysts and are complexes of a transition metal of group IV-VIII and an organometallic compound of a metal from group I-III elements. Usually transition metal halides are known as catalysts and organometallic compound of I-III group are known as co-catalysts. Catalysts like zirconium, cobalt and iron are also found useful while co-catalysts like hydrides, alkyl, aryls of Al, Li, Zn, Sn, Cd, Be and Mg are prevalent in usage. Most useful catalysts in polymerization of lower olefins are composed of ethyl (alkyl) aluminium and titanium tetra (tri) chloride. Although the polymerization is not clearly understood with these catalysts, these have still gained significance in the production of stereo regular polymers. Before polymerization with an olefin has been completed, various types of halides and alkyl metal halides are produced by the reacting catalyst as shown below [5].

Organic titanium compounds are believed to undergo reduction via homolytic bond cleavage.



The reaction continues till  $\text{TiCl}_3$  is formed. Soluble complexes of Ti and Al have tetrahedral configurations, with localized active sites on the catalyst surface. Organometallic compounds are believed to activate the sites by alkylation of the transition metal atom surface.

Ziegler–Natta catalysts have been used for the commercial manufacture of various polymeric materials since 1956. Together these polymers represent the largest commercial plastic as well as the largest commodity chemicals in the world. The resulting initiators exhibit a range of behaviors in terms of activity and stereospecificity. The term activity as used in most literature references applies exclusively to the rate of polymerization. Activity is often expressed in terms of kilograms of polymer formed per gram of initiator component. Modification of an initiator system to increase activity has often come at the expense of stereospecificity. Ziegler-Natta catalysts give polymers with a much broader molecular weight distribution and compositions vary not only from one molecule to another, but also between molecules of different molecular weight. This is because most high performance Ziegler-Natta catalysts are heterogeneous and contain many different catalyst active sites (multi active sites) with different characteristics.

The polyethylene prepared with this catalyst had physical properties completely different from the conventional high-pressure product. This process produces polyethylene by polymerization at low pressure and ambient temperature using a mixture of triethylaluminum and titanium tetrachloride as the cocatalyst.

High density polyethylene is a linear polymer that was produced by the Ziegler-Natta catalysts; it has a much lower degree of branching that results in higher crystallinity and higher crystalline melting temperature. Metallocene linear low density polyethylene is the homogenous short chain branching distribution, which is produced by single-site catalysts. In addition, it offers results such as more controlled uniform molecules with narrower molecular weight distribution and narrower composition distribution Table 2.1 shows the properties of HDPE and MLLDPE.

**Table 2.1** The properties of HDPE and MLLDPE.

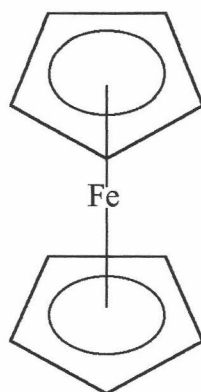
Commercial product	MLLDPE	HDPE
Density range, g/cm <sup>3</sup>	0.905 – 0.942	0.941 – 0.965
Approximate % crystallinity	54 – 63	70 – 90
Crystalline melting point, °C	120 – 130	133 – 138
Tensile strength, psi	1,900 – 4,000	3,100 – 5,500
Elongation, %	100 – 950	200 – 1,000

## 2.2 Metallocene Catalysts for Olefin Polymerization

Metallocene catalysts for the polymerization of ethylene are almost as old as the Ziegler – Natta catalyst itself. In 1957 Natta reported a soluble, crystalline and isolable complex from  $(C_5H_5)_2TiCl_2$  and  $AlEt_3$  which was polymerization active towards ethylene but much slower than a comparative heterogeneous Ziegler Catalyst, based on  $TiCl_3$  and  $TiCl_4$ . Consequently, metallocene catalyst development was dormant for 20 years, until new work sparked interest. Metallocene is a more elegant replacement for the term “iron sandwich” initially used to describe the structure of dicyclopentadienyl iron  $[(C_5H_5)_2Fe]$ .

The fortuitous discovery of the ferrocene  $[(C_5H_5)_2Fe]$  was a milestone in chemistry. The recognition and explanation of the remarkable structural and bond theoretical properties of ferrocene and the metallocenes at large by Fischer, Wilkinson, Woodward and Dunitz culminated in the award of the 1973 Nobel prize. Its structure was described by Fischer and Wilkinson (Figure 2.1) as comprising an iron atom (Fe) sandwiched between parallel planar cyclopentadienyl group, and the name is now applied generally to similar organometallic structure.

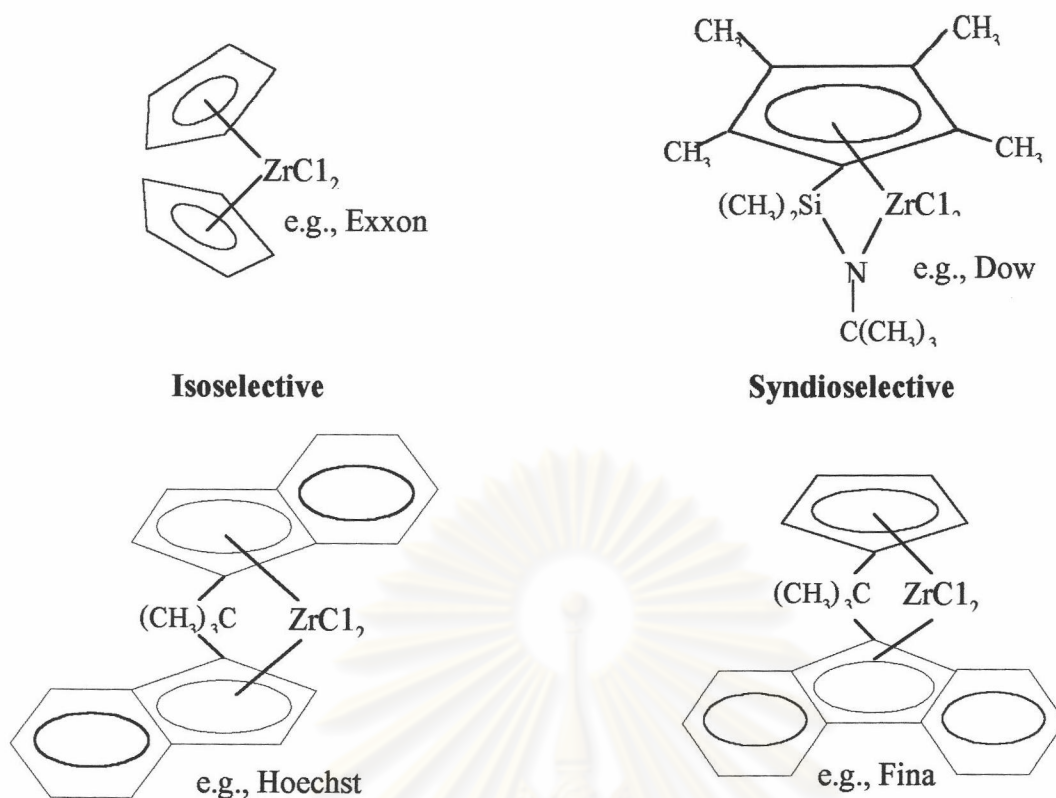




**Figure 2.1** The iron sandwich, the first metallocene dicyclopentadienyl iron  $(C_5H_5)_2Fe$

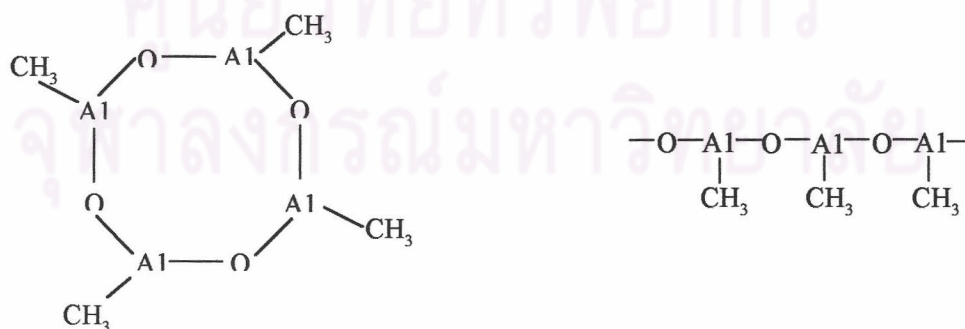
The level of industry research activity is tremendous and more than 50 metallocene catalyst families [6] have been discovered. Among these, the four basic metallocenes shown in Figure 2.2 appear to be the foundations for many other families. The upper two structures are stereoselective while the lower two structures exemplify the nonstereoselective families. The latter are known as “bridged metallocene” because the two cyclopentadienyl ligands are joined by a covalent bridge, in this case a methylene-center or isopropyl bridge. The bridge makes the structure rigid and enables the development of stereoselective catalysts. The left-hand system is isoselective and yields products, for example, that are similar to conventional isotactic polypropylene (PP). The other is syndioselective and is the first system developed that can produce highly syndiotactic (96-98 %) PP, a new form of PP with several very interesting performance characteristics.

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**Figure 2.2** Primary metallocene catalysts.

The dichloride derivatives of the most common metallocene complexes are typically crystalline solids, stable in dry air, slowly hydrolyzed in moist air, and moderately soluble in toluene and polar organic solvents. They are not polymerization catalysts in themselves and must be activated with a cocatalyst. The most common cocatalysts are methyl aluminoxane (MAO), which are oligomeric compounds containing Al-O-Al linkages (Figure 2.3) prepared by the hydrolysis of trimethyl aluminum (TMAL).



**Figure 2.3** Cyclic and linear methyl aluminoxane (MAO).

The behavior of a metallocene catalyst system is extremely sensitive to the geometry of the catalytic site at the transition metal, and thus to the chemical composition of the metallocene. For example, substitution of a particular hydrogen atom on the metallocene may change the catalyst from being highly stereoselective to having zero stereoselectivity, or from being highly active toward propylene polymerization to being almost totally inactive to propylene (but not to ethylene). This sensitivity to the molecular geometry of a single component of the catalyst system, the geometry of the catalytic site, can be designed to assemble precisely tailored polymer molecules from the appropriate reaction system.

Nowadays, metallocene catalysts can be defined as a compound consisting of a transition metal atom such as titanium and zirconium sandwiched between ring structures to form a sterically hindered site. It is the presence of these stereoselective catalytic sites that enable polymerization of almost any monomer even beyond the traditional  $C_3$  to  $C_8$   $\alpha$ -olefins in a precise manner. By the selection of proper metallocene catalysts, polymer molecular weight distribution and content, and tacticity can be independently controlled, which otherwise was thought to be beyond control [7]. If one (high purity) metallocene composition is used, all the active polymerization sites are the same and each polymer molecule is therefore the same (within the limits allowed by the reactor configuration).

Metallocene catalysts have initiated a new era in polymer synthesis. These well defined catalysts now allow producers to design polymers with exact properties and to create as yet unknown materials. Metallocene catalysts have proven to control properties such as polymer molecular weight, molecular weight distribution, comonomer distribution and content, and tacticity of the polyolefins in an efficient manner as compared to conventional catalysts. They tend to have



features such as increased impact strength and toughness; better melt characteristics and improved clarity and higher puncture resistance in film.

With the metallocene catalysts currently used for some production, polymerization takes place in a very defined pattern. It produces materials with narrow molecular weight distributions, and therefore a uniform co-monomer distribution from one polymer chain to another resulting in a more specific set of properties. One benefit of this single site catalyst process is that the outcome of polymerization is much more predictable, which enables known effects to be more likely to be repeated, and therefore form the basis of a more reliable modeling procedure.

### **2.3 Metallocene Linear Low Density Polyethylene (MLLDPE)**

Since 1991, Exxon has launched the production of a range of ethylene- $\alpha$ -olefin copolymers named EXACT and there is also AFFINITY from DOW, which introduced the material as a plastomer. Commercial grades of metallocene linear low density polyethylene (MLLDPE) have been available for some time now, mostly in the US. Producers of polymer resins based on metallocene catalysts are pinning their hopes on the packaging industry. Applications for MLLDPE are varied, packaging film should benefit from the material improvement. It seems to be agreed by resin producers that the special properties of these resins could revolutionize the packaging industry.

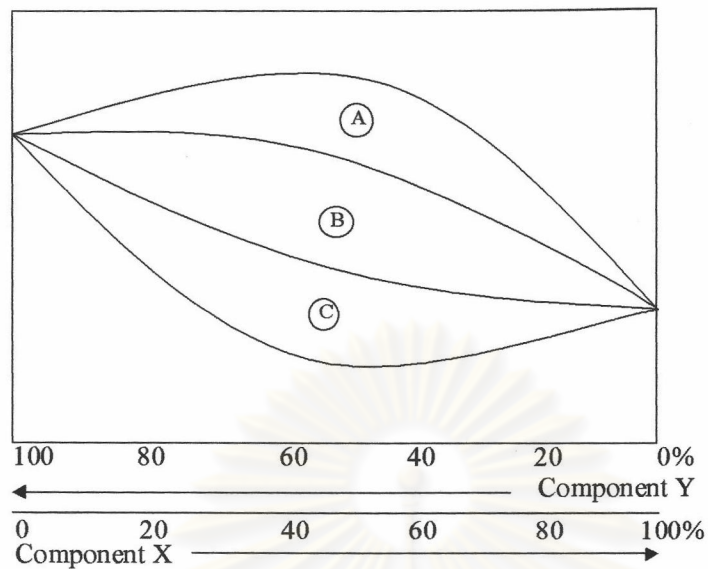
MLLDPE differs from Ziegler-Natta linear low density polyethylene (Z-NLLDPE) in cooling and crystallization in which firstly the crystal nuclei are formed, and then the crystals grow around these nuclei. Consequently, since the lamella thickness is determined by the high-density component, the lamellas are thick. In contrast, in the case of MLLDPE, these do not have a high-density

component so uniform crystal nuclei form and grow, thus yielding thin lamella [8]. MLLDPE has an impact strength and tear strength two to three times greater than Z-NLLDPE. MLLDPE has excellent optical properties, especially in haze and gloss of the film, a lower melting point and offers a film that can be heat sealed at low temperature due to the thin lamella. Because MLLDPE has a lower content of low-molecular-weight/low-density polymers than Z-NLLDPE, MLLDPE has excellent anti-blocking properties. However, one major concern is the processability of MLLDPE. Due to its very narrow molecular weight distribution, MLLDPE is difficult to process. By comparison, a rating of processability by rule of thumb has been set from easiest to the most difficult, as follows, LDPE ranks 10, bimodal HDPE 8, LLDPE 4, typical MLLDPE 1. Terms of the processability debate changed in 1993 when Dow won a composition of matter patent on placing long chain branches in MLLDPE [9].

## **2.4 Polymer Blend**

Mixing two or more polymers together to produce blends is a well-established strategy for achieving a specified portfolio of physical properties, without the need to synthesis specialized polymer systems [10]. The various types of property response of polymer A and B, when blended, are seen schematically in Figure 2.4. Incompatible blends produce lower than expected property response. Completely immiscible polymers represent the second category. When these polymer components are mixed in any proportion, the blend separates into distinct domains or phases, each containing an individual polymer. One polymer acts as the continuous phase and the other is the discrete phase.





**Figure 2.4** Schematic of the relative effects of blending polymer.

Region A represents synergism in properties. Region B represents simple property addition. Region C represents incompatibility in properties. Miscibility of blends. It is important to realize that the mixing of two polymers to a homogeneous level in most cases is quite difficult, depending on their miscibility and compatibility [11]. It is most common for compatibilisation to be achieved by the addition of a third component, called a compatibiliser, which usually increases the interfacial adhesion between the two polymers blend.

For polymer blends a distinction must be made between miscible blends and immiscible blends, consequently, the thermodynamic condition for miscibility is  $\Delta G_{\text{mix}} = \Delta H_{\text{m}} \leq 0$ , where  $\Delta G_{\text{mix}}$  is the Gibbs free energy of mixing and  $\Delta H_{\text{m}}$  is the enthalpy of mixing. Miscible polymer blend has a single phase while, in contrast immiscible blend polymer is a polymer mixture in which polymer-A forms a separate phase from polymer-B. The thermodynamically immiscible blend is associated with the positive value of the Gibb's free energy of mixing i.e.,  $\Delta G_{\text{m}} \cong \Delta H_{\text{m}} \geq 0$ . The compatibility of a polymer-polymer system determines a

polymer system properties. In general, compatible polymer blends are a homogeneous polymer mixture with particular physical properties. Polymer blends that are heterogeneous on a macroscopic level are called incompatible polymer blends.

## 2.5 Determination the Compatibility of Polymer/Polymer Blend

There are several methods that can determine the compatibility of a polymer blend, each method has a useful range limit. A variety of experimental techniques have been used to determine the compatibility of polymer blends. Some techniques, such as calorimetry, thermomechanical, dynamic mechanical procedures, are based on the determination of the number and the location of the glass-transition temperature ( $T_g$ ). Other techniques are based on scattering or microscopic techniques.

## 2.6 Literature Reviews

Polyolefin blends are increasingly interesting in terms of processability, producibility, production cost. The binary blend of high density polyethylene (HDPE) and linear low density polyethylene (LLDPE) in the range of composition from 100% HDPE to 100% LLDPE has been investigated for mechanical properties and the morphology by various works. However, most of those works used Z-NLLDPE and using the injection mold or compression mold to prepare the specimen for physical property testing.

A.K. Gupta *et al.* [12, 13, 14, 15] who used preformed HDPE/Z-NLLDPE blend and investigated their mechanical properties such as flexural, impact and tensile, etc. including the morphology. They found that the properties of HDPE and Z-NLLDPE are distinguished by three-regions of blend composition, via (i) 0-30% Z-NLLDPE content (i.e., HDPE rich blend), (ii) 70-100% Z-NLLDPE content (i.e., Z-NLLDPE rich blend), and (iii) the middle zone. The cocrystallization

of HDPE and Z-NLLDPE occurs at all compositions of their blend prepared by melt mixing in a single screw extruder. Mechanical properties of the HDPE/Z-NLLDPE blend vary with the blending ratio and the variations are linear and nonlinear. Hoseok [16] suggested that HDPE/Z-NLLDPE system was miscible blend in the crystalline and amorphous phase the same as A.K. Gupta's was reported.

Y.M. Kim *et al.* [17] had considered the mechanical properties of blown HDPE film due to its most widely use. The most important mechanical properties of blown HDPE film are impact strength and tensile property. Blown films having a broad range of morphology were produced under several processing conditions. The mechanical properties of blown HDPE films are highly associated with their morphological feature, which are dependent on the overall characteristics of HDPE resins. Some correlation was found between the anisotropy of the tear and tensile properties of blown HDPE films and the state of orientation of the crystalline molecular chain axes and lamella stacks at the film plan.

T. Yu *et al.* [18, 19] studied the influence of molecular weight distribution and extrusion processing variables on the morphological feature and orientation of HDPE uniaxially tubular films. The results show that the final morphological structure and molecular weight distribution are very important parameters in HDPE extruded film in influencing their properties. There has been a lot of research on the morphology or properties of MLLDPE.

P. Starck [20] studied the amount and distribution of branching and compared with Z-NLLDPE by using DMA. It was found that MLLDPE gave the highest tan delta intensity value which demonstrated in the case of incorporating higher comonomer amounts in the case of single site polymer.