

## CHAPTER II

### LITERATURE REVIEW

#### 2.1 Ziegler- Natta polymerization

The use of ionic polymerizations for the preparation of highly stereoregular polymers is restricted to specific monomers, especially polar monomers. Generally this method is not suitable for non-polar monomers because it requires stronger coordination which can be achieved with the counter-ions used in ionic polymerizations.

In 1953, Karl Ziegler reported the preparation of linear polyethylene by polymerization of ethylene using catalysts prepared from aluminium alkyl compounds and transition metal halides (cf. free radical polymerization of ethylene yields polyethylene with a large number of both short- and long-chain branches). Giulio Natta quickly recognized the potential of this new type of polymerization for the preparation of stereoregular polymers. By slightly modifying the catalysts used in Ziegler's work, he was able to prepare highly isotactic linear crystalline polymers from non-polar  $\alpha$ -olefins (e.g. propylene). The enormously academic and industrial importance of these discoveries was recognized in 1963 by the joint award to Ziegler and Natta for the Noble Prize in chemistry (Boor, 1979).

### 2.1.1 Ziegler-Natta catalysts

Usually *Ziegler-Natta catalysts* are broadly defined in terms of their preparation which involves reacting compounds (commonly halides) of groups IV-VIII transition metals (e.g. Ti, V, Cr, Zr) with organometallic compounds (e.g. alkyls or hydrides) of groups I-III metals (e.g. Al, Mg, Li). In fact, this definition is too broad since not all such reactions yield catalysts suitable for preparing stereoregular polymers. However, for each monomer there is a wide range of catalysts that are suitable.

The catalysts which are useful for the preparation of isotactic polymers are *heterogeneous*, i.e. they are insoluble in the solvent, or diluent, in which they are prepared. Their activity and stereoregulating ability are greatly affected by the components, and method, used for their preparation. For example, the  $\alpha$ -form of  $\text{TiCl}_3$  can be used to prepare catalysts suitable for synthesis of isotactic polypropylene, whereas the  $\beta$ -form yields catalysts which give no stereochemical control. If  $\alpha$ - $\text{TiCl}_3$  is reacted with  $\text{AlEt}_2\text{Cl}$  it gives a catalyst of lower activity but much higher stereospecificity than that obtained from its reaction with  $\text{AlEt}_3$ . The inclusion of electron donors, such as Lewis bases (e.g. ethers, ketones and esters) during preparation of the catalyst also can improve stereospecificity, often but not always with a loss of activity. Ball milling of the catalyst usually improves its activity, by not only increasing the surface area to be available but also inducing crystal-crystal transformations.

In the search for higher efficiency, *supported Ziegler-Natta catalysts* have been developed in which the transition metal is either bonded to or occupied lattice sites in the support material. Magnesium compounds are widely used as supports (e.g.  $\text{Mg(OH)}_2$ ,  $\text{Mg(OEt)}_2$ ,  $\text{MgCl}_2$ ) and catalysts with

both high activity and stereospecificity can be obtained from  $\text{TiCl}_4$  supported on  $\text{MgCl}_2$  which has been ball-milled in the presence of aromatic esters (Young and Lovell, 1981).

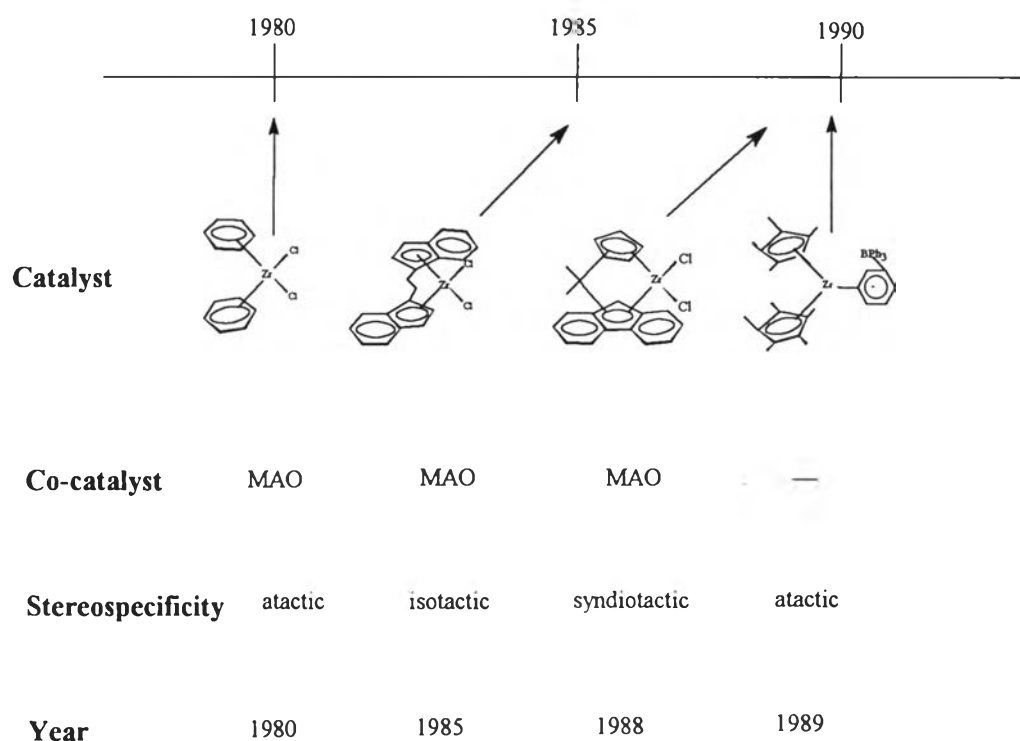
Ziegler-Natta catalysts that are soluble in the solvent in which they are prepared (i.e. *homogeneous*) are of limited use because in general they do not provide stereochemical control. Nevertheless there are some remarkable exceptions. For example, syndiotactic polypropylene can be prepared at low temperatures (e.g.  $-78^\circ\text{C}$ ) using soluble catalysts based upon vanadium compounds (e.g.  $\text{VCl}_4 + \text{AlEt}_3$ ). In addition, homogeneous catalysts prepared from benzyl derivatives of Ti and Zr have yielded isotactic polypropylene but are of low activity.

### 2.1.2 Feature of metallocene-catalyzed polyolefins

Since the catalyst system of biscyclopentadienyl zirconium dichloride ( $\text{Cp}_2\text{ZrCl}_2$ ) and methylaluminoxane (MAO) produces high activity, and was found by Sinn and Kaminsky (Sinn and Kaminsky, 1980), metallocene catalyst system is in the limelight as a new type of catalyst system. Recently, plans for the commercialization of metallocene catalyzed polyolefins have been announced and some of them has been already on market. For example, EXXON Chemical Co. marketed linear low density polyethylene (LLDPE) made by high pressure process. Furthermore, syndiotactic polypropylene and syndiotactic polystyrene are now in the stage of market testing.

The historical current of highly active metallocene catalyst system (Figure 2.1) started from finding the combination of  $\text{Cp}_2\text{ZrCl}_2$  and MAO by Sinn and Kaminsky in 1980 as described above. After five years, Kaminsky and Brintzinger et al. (Kaminsky et al., 1985) found isospecific

catalyst such as rac-ethylenebisindenyl zirconium dichloride [ $\text{rac-Et(Ind)}_2\text{ZrCl}_2$ ].



**Figure 2.1** History of metallocene catalysts.

In 1988, Ewen succeeded to synthesize the syndiotactic polypropylene using isopropylidene(cyclopentadienyl-9-fluorenyl)zirconium dichloride. Further, MAO free catalyst system by employing boron compound, such as triphenylcarbeniumtetrakis (pentafluorophenyl) boron,  $[\text{Cph}_3] [\text{B}(\text{C}_6\text{F}_5)_4]$ , instead of MAO was found. After that, by modifying the ligand of metallocene etc., the catalyst performance is further improved and the polymer with unique characteristics appears. Today, by metallocene catalyst technology, polyolefin industry is in the transition stage of the breakthrough (Kashiwa, 1988).

### 2.1.3 Metallocene-based polypropylene

The development of the first metallocenes for isospecific polymerization of propene described by Britzinger and Ewen to technologically attractive catalysts took about 10 years. The reason that metallocene-based polypropylene is being commercialized a few years later than metallocene-based polyethylene is especially due to the problem of isospecificity. EXXON started up the first commercial plant for LLDPE in 1991, and DOW entered two years later. In this area new polyolefin materials for special applications have been commercialized. The commercialization of the first metallocene-based PP-types has been announced in late 1995.

Today, the catalytic properties of metallocenes refer to isospecificity, average molecular weight, productivity and incorporation of comonomers. Their advantages offer market potential in field of fibres, specialty of films with exceptional heat sealing performance, high modulus, high service temperature, as well as in the field of injection molding with an outstanding balance between stiffness and toughness (Aulbach et al., 1995).

### 2.1.4 Catalyst and co-catalyst

Many types of soluble initiators, such as di- $\eta^5$ -cyclopentadienyl titanium and tetrabenzyl zirconium, are active but unspecific initiators. However, the combination of some of these soluble initiators with methylaluminumoxane are partially effective for initiating isospecific polymerization.

Methylaluminumoxane apparently interacts with the transition metal compound to form an initiator with a considerable tendency to

isospecific polymerization. However, polymerization at higher temperature yields atactic structure.

Chiral initiators, such as cyclopentadienyl-indenylmethyl zirconium chloride, are active but still not exceptionally high in isospecificity. A major breakthrough occurred with the preparation of rigid chiral metallocene initiators, such as racemic 1,1-ethylene bisindenyl zirconium dichloride the racemic 1,1-ethylene bis-4,5,6,7-tetrahydroindenyl compounds (Kaminsky et al., 1985 ; Reiger et al., 1990 ; Reddy et al., 1993)

These metallocenes are rigid, as a result of a bridge between the two-5-membered rings. (Similar metallocenes have been synthesized with dimethylsilyl ,  $\text{Si}(\text{CH}_3)_2$  , bridges between the two rings.)

## 2.2 Objective

To determine the relationship between polymerization parameters and polypropylene properties.

## 2.3 Scope of research work

To study the effect of the following conditions on polypropylene properties:

- Temperature
- Zirconium and aluminium concentrations at constant Al:Zr ratio
- Al (of MAO) : Zr ( of rac-Et(Ind)<sub>2</sub>ZrCl<sub>2</sub>)
- Monomer concentration

## 2.4 Catalyst system

In this research,  $\text{rac-Et(Ind)}_2\text{ZrCl}_2$  and methylaluminoxane were the metallocene catalyst system whose products were studied.