

CHAPTER 1.

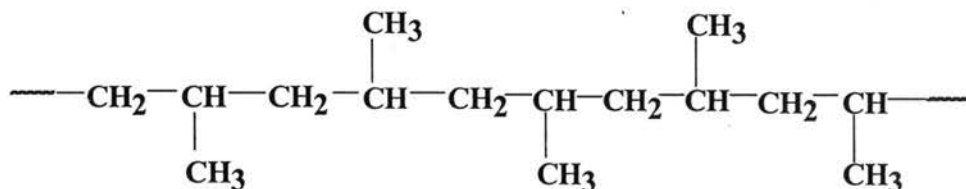
INTRODUCTION



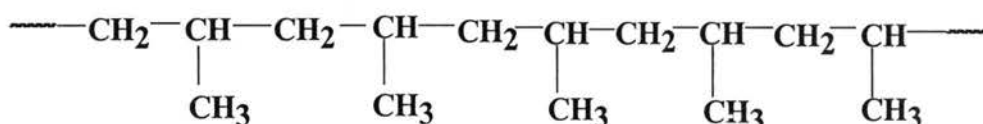
1.1 Polypropylene

Polymers are macromolecules comprised or built up of smaller units called monomer. The arrangements of these units, the various types of chains that can be synthesized, and the shapes that these chains can bend themselves into, result in a class of materials that are characterized by an enormous and intriguing range of properties. Some of these properties are unique to polymer, which is simply a consequence of their size and chain-like structure.

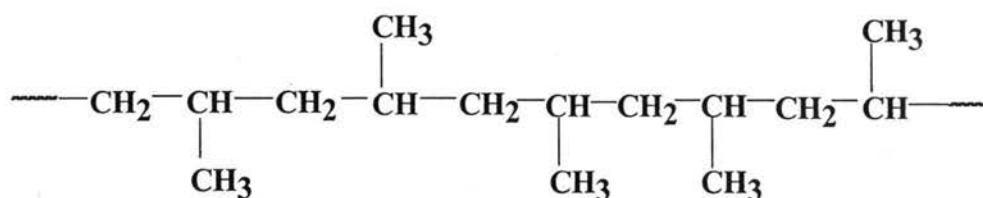
One of the very important commercial polymers is polypropylene. Polypropylene is the lightest major plastic with a density of 0.905 g/cm^3 . It has high crystallinity, high tensile strength, stiffness, and hardness. The high ratio of strength and weight gives an advantage to many applications such high resistance and good gloss, high melting point, and high tensile strength at elevated temperatures. Polypropylene has excellent electrical property and the chemical inertness as well as the moisture resistance typical of hydrocarbon polymer and is completely free from environmental stress cracking. Polypropylene can be made in isotactic, syndiotactic, and atactic forms (Figure 1.1). The isotactic polypropylene owing to its unique properties is of commercial interest. The isotactic polypropylene is an essentially linear, highly crystalline polymer, with a melting point of 165°C .



syndiotactic polypropylene



isotactic polypropylene



atactic polypropylene

Figure 1.1 The syndiotactic, isotactic, and atactic form of polypropylene.

The properties of polymer are depended on the structure of polymer. For example, the isotactic polypropylene has low density and light weight but physically hard. In the experiment, the % isotacticity represents the selectivity and the productivity and reaction time represents the reactivity. The selectivity and reactivity of polypropylene polymerization cannot be very well controlled by the Ziegler-Natta catalyst, the convention. On the other hand, the metallocene catalysts introduce by Natta and Pino in 1957 [1] can control the selectivity and the reactivity of polypropylene polymerization very well. This is done by modifying substituents on the cyclopentadienyl (Cp) rings of metallocene. These substituents have an effect on

properties of zirconocene such as charge distribution, gap aperture, obliquity, distance between Cp plane, angle between Cp plane etc. (all parameters were defined in Chapter 3). The change of properties, somehow, controls selectivity and reactivity of the catalyst.

1.2 Ziegler-Natta Catalyst

In 1869, Berthelot [1] polymerized propylene by reaction with concentrated sulphuric acid. The viscous oil was obtained at room temperature that did not exhibit any interesting properties for industrial applications. In 1955, Karl Ziegler and Giulio Natta [1] discovered the transition metal catalyst, which yielded the stereo selective polymerized product of α -olefin. The Ziegler-Natta catalysts is based on titanium and aluminum (TiCl_3 and $\text{Al}(\text{C}_2\text{H}_5)_2\text{Cl}$, or TiCl_4 with $\text{Al}(\text{C}_2\text{H}_5)_3$) and is the only commercial catalyst for olefin polymerization until now. However, the Ziegler-Natta catalyst cannot controlled the molecular weight, gives low yield products with selectivity, and is very corrosive, the properties, which are still not fully satisfied. Many researchers have investigated the relationship between the properties of a particular catalyst and the coordination geometry of its reaction centers for developments of the activity and selectivity of catalyst. In 1957, patents publications by Breslow and Newburg [2] at the Hercules Research Center and by Natta, Pino, and their co-worker [3] reported that homogeneous reaction mixtures of dicyclopentadienyltitanium dichloride (Cp_2TiCl_2) and diethylaluminium chloride (Et_2AlCl) catalyzed the formation of polyethene under conditions similar to those used with heterogeneous Ziegler-Natta catalysts. These early metallocene studies contributed to the ideas of Cossee in which the mechanism for polymerization of ethylene was proposed (Figure 1.2) [4-5].

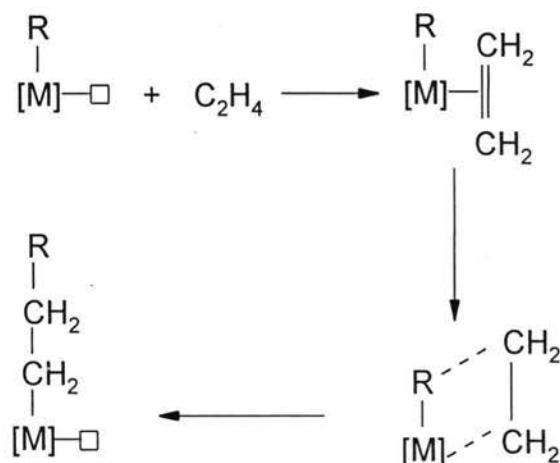


Figure 1.2 Direct insertion mechanism as proposed by Cossee and Arlman [5].

The mechanism of olefin insertion is separated into 3 steps. The first step is olefin coordination to a vacant site of metal. In the second step, olefin inserts into the M-C bond through a four-membered cyclic transition state. Finally, the alkylmetal species reinitiates olefin coordination and thus the propagation step.

1.3 Metallocene Catalyst

While studying halogen-free systems such as $\text{Cp}_2\text{ZrMe}_2/\text{AlMe}_3$, Sinn and Kaminsky [3] observed that an interaction between Cp_2ZrMe_2 and AlMe_3 occurred only when water had been added. The metallocene catalysts activated by aluminum halide capable of polymerizing propene and higher olefins [3]. The spectroscopic studies [6,7] indicated the formation of a cation $[\text{Cp}_2\text{ZrR}]^+$, which is stabilized by coordinative contact with its $\text{CH}_3\text{-MAO}^-$ counter ion. Even for large and weakly coordinating anions such as $(\text{C}_6\text{H}_5)_4\text{B}^-$ and $\text{C}_2\text{B}_9\text{H}_{12}^-$, fairly strong interactions have been observed with cationic (alkyl)zirconocene species [8]. These system and other carborane anions polymerize propane only at low rate [8]. The metallocene cation obtained which abstraction of CH_3^- form Cp_2ZrMe_2 complex by the powerful Lewis

acid $B(C_6F_5)_3$ that have the higher olefins at high rates. The mechanism of metallocene catalyst, which based on mechanism of Ziegler-Natta catalyst in olefin polymerization is proposed by Cossee-Arlman (Figure 1.3). However, the significance of the co-catalysts still needs further investigation.

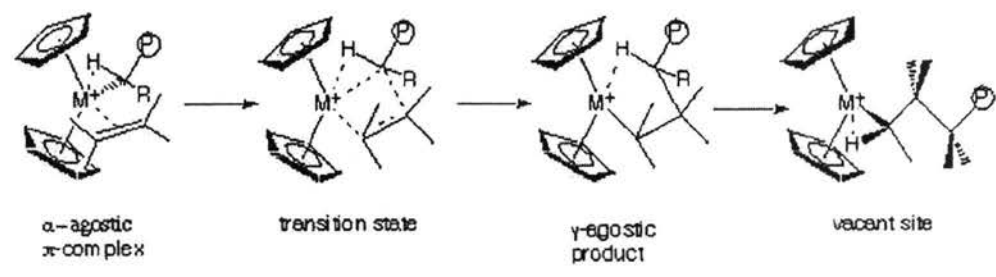


Figure 1.3 The Cossee-Arlman mechanism.

The theoretical study by Morokuma *et al.* [9] which based on Cossee-Arlman mechanism suggested that for olefin polymerization the α -agostic π -complex formation is the rate determining step. This step has the barrier height (activation energy) of 12 kcal/mol for propylene and 6.5 kcal/mol for ethylene.

1.3.1 The Stereoselectivity of Propylene from Metallocene Catalysts.

1.3.1.1 Definition of % isotacticity

The ^{13}C NMR signals of polymer are related to its microstructure by stereochemical notation developed by Bovey [10]. The relative configurations of neighboring units are designated as *m* (*meso*) for equally and *r* (*racemo*) for unequally positioned substituents in a Fischer-type projection of the polymer chain. In polypropylene, the ^{13}C NMR shift of each CH_3 group is determined by the configurations of two neighboring repeat units on either side, each CH_3 signal is thus assignable to particular *pentad* pattern, represented by the four consecutive *m* or *r* designators framing the CH_3 group under consideration (Figure 1.4).

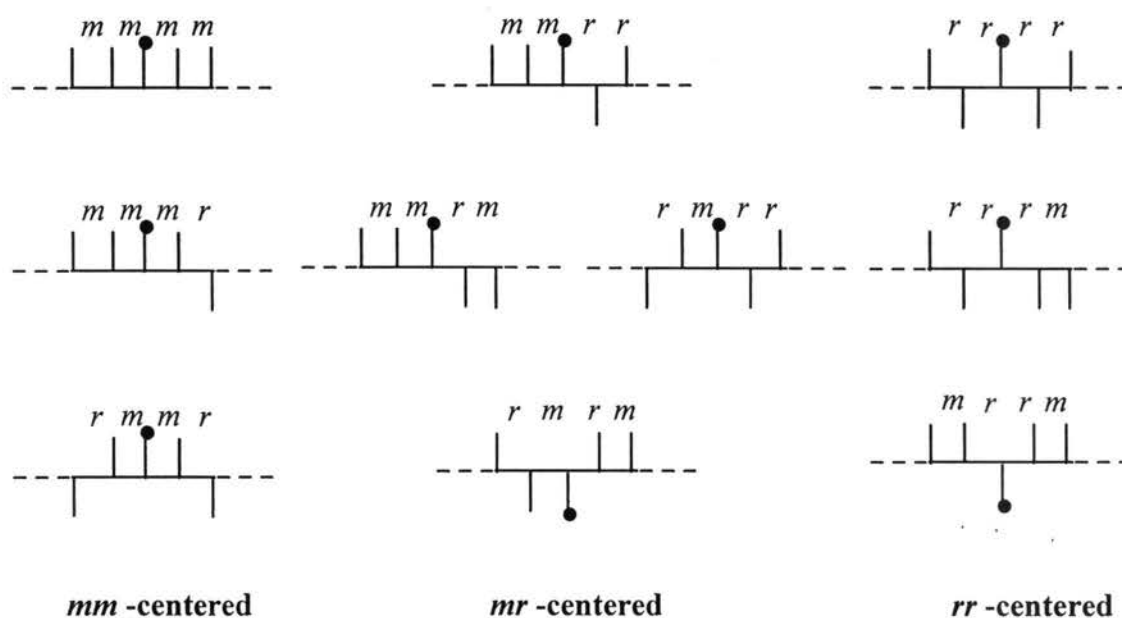


Figure 1.4 The ten possible stereochemical pentads of a polyolefin [10-13].

All ten possible pentad signals are observed for the random configuration repeat units of atactic polypropylene. Isotactic polypropylene is ideally characterized by a single ^{13}C NMR signal for *mmmm* pentads, since its repeat units have identical configuration over long segments of the polymer chain. The degree of isotacticity of such a polymer is usually expressed as the ratio of the *mmmm* pentad integral to the integral sum of all pentad signals observed.

However, the stereoselectivity of metallocene catalysts depends on the structure of the complex, in particular on different bridging units and substituent patterns. This has been the subject of comparative studies in several research groups.

Around 1980 [3], the chiral metallocene suitable for stereoselectivity purpose are ethylene-bridged ligands. Brintzinger obtained ethylenebis(indenyl)- and ethylenebis(tetrahydroindenyl)titanium complexes which could be expected to be retained even under catalysis condition. Ewen used *rac*-(en)(thind)₂TiCl₂/MAO [3]

and Kaminsky and Külper used *rac*-(en)(thind)₂ZrCl₂/MAO [3] to polymerize propylene and other α -olefins and obtained highly isotactic polymers. Erker and co-workers [15-16] using unbridged zirconocenes with substituents containing an asymmetric C atom, also obtained isotactic polypropylene with $[mmmm] \approx 0.4 - 0.8$ at the polymerization temperature of -50°C or lower. It was observed that chirally substituted *ansa*-zirconocene catalysts with α -CH₃ groups at each cyclopentadienyl ring has very high stereoselectivity [17].

The effects of the β -substituents of cyclopentadienyl ring are very interesting. The β -substituents are in close proximity to the coordination sites at which the growing polymer chain and the α -olefin substrate are bound. If the β -substituents are very bulky, as in Me₂Si(2-Me-4-*t*Bu-C₅H₂)₂ZrCl₂ [17] or Spaleck's Me₂Si(2-Me-4-aryl-1-indenyl)₂ZrCl₂, polypropylene with stereoregularities of $[mmmm] > 0.95$ are obtained. Brintzinger proposed that steric relationship in a metallocene complex can be described by the coordination gap aperture, which the largest possible angle spanned by two planes through the metal center which touch the van der Waals surfaces of β -substituents at the cyclopentadienyl ring ligands [18]. Using the integrated Molecular Orbital and Molecular Mechanics (IMOMM) methods, Morokuma *et al.* [19] studied isotacticity control in propylene polymerization with silylene-bridged zirconocene catalyst. They found that the isotacticity of polypropylene is controlled by the steric at the transition state. This steric interaction can be divided into 2 terms, the direct term, which is steric energy due to the catalyst-olefin interaction and the indirect term, which is steric energy due to the catalyst-polymer and polymer-olefin interaction. The possibility of propylene attack to zirconium center can be separate into 4 configurations as shown in Figure 1.5. To attain good stereoregulation, the substituents at the 2- and 4-positions of the indenyl-based metallocene are very important.

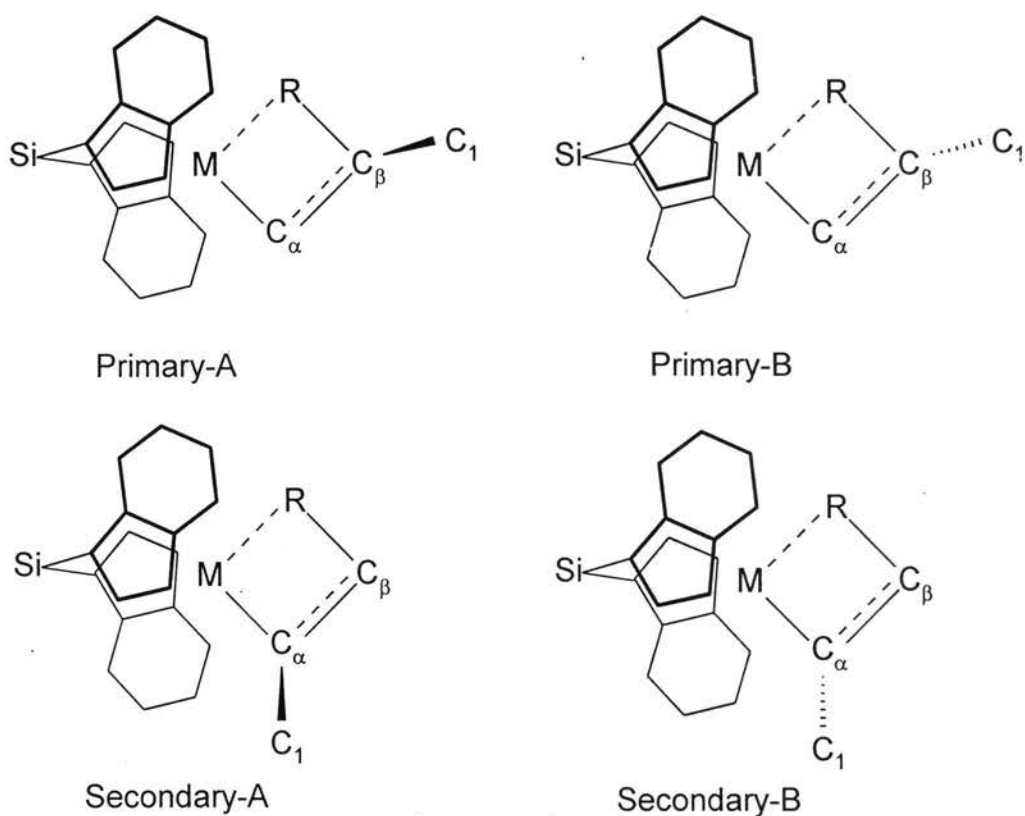


Figure 1.5 The 4 possibilities of propylene attack to metallocene catalyst [19].

The primary-A has the lowest energy at the transition state following by the primary-B, the secondary-A, and the secondary-B. The energy difference between the primary-A and other configurations must be large enough to ensure very good stereoselectivity.

1.3.2 Activities of Metallocene Catalysts.

Normally, the rate of reaction is expected to decrease when the stereoselective increases by imposing steric restrictions on some of its possible reaction modes. For example, strongly congested chiral catalyst such as *rac*-Me₂Si(2-Me-4-*t*Bu-(C₅H₂)₂ZrCl₂/MAO produces polypropylene at higher rates than Cp₂ZrCl₂/MAO system [17]. These show the important effect of bridging ligand that

linking the cyclopentadienyl rings. The zirconocene with the one atom bridge such as Me_2Si is more reactive than that with two-atom bridge such as ethylene. The zirconocene with three-atom or four-atom bridge have been found to be inactive in the MAO system. Activities of zirconocene catalysts are depending on MAO concentrations. Increasing activation occurs at Al:Zr ratios of up to 1-5000:1, whereas inhibition is also observed at still higher Al:Zr ratios [20].

In the last few years, a large number of studies have been devoted to transformation of soluble metallocene complexes into heterogeneous catalyst by supporting them on inorganic or organic carriers. Inorganic oxide, finely divided polymers or other high surface area materials have been used as supports. The main inorganic supports used are silica, alumina and magnesium compounds. Soga *et al.* [21] studied the zirconocene catalysts supported on poly(bisindenylsiloxane) and poly(bisfluorenylsiloxane) that give the highest activities for the ethylene and propylene polymerization, respectively. A modified SiO_2 was prepared by reacting SiO_2 with $\text{Cl}_2\text{Si}(\text{CH}_3)_2$ in toluene, on which methylaluminoxane (MAO) was supported to obtain a catalyst precursor. The mixture of the precursor and Cp_2ZrCl_2 gave polyethylene in a high yield even by using common trialkylaluminiums as co-catalyst [22]. Helmut *et al.* [23] observed the average molecular weights of the obtained polymers differ from polymethylsiloxane micro gels of the corresponding homogeneous catalysts as from silica supported systems.

Goal of this study

In this study, the structure-property relationships between structural parameters such as distance between Cp planes, angle between Cp planes, gap aperture, obliquity, twisted angle, cavity distance, cavity angle and atomic charges and catalytic properties such as % isotacticity and productivity of zirconocene catalysts in propylene polymerization were sought using various quantum chemical calculations techniques. The relationship between structural properties with %

isotacticity and productivity was plotted. The statistic interpretation, which leads to Quantitative Structure-Property Relationship (QSPR) study, cannot be used for this case because only 4 zirconocenes were studied. This study aims to gain the understanding of the relation between structural properties and the selectivity and reactivity of catalyst and the effect of substituents on the cyclopentadienyl ring opening. Furthermore, this understanding would probably guide to the suggestion of the new zirconocene catalyst.