

# CHAPTER I

## INTRODUCTION

Polyolefins are among the most important polymers in terms of production. In 1995, 47 million tons of polyethylene and 24 million tons of polypropylene were produced in the industrial nations [1]. These products are used for packing material, receptacles, pipes, domestic articles, foils, and fibers. Polyolefins consist of carbon and hydrogen atoms only. Considering environmental aspects, clean disposal can be achieved by burning or pyrolysis, for instance. Burning involves conversion to CO<sub>2</sub> and H<sub>2</sub>O, exclusively.

Ethylene can be polymerized radically or by means of organometallic catalysts [2]. The existence of several types of polyethylene as well as blends of these polymers provides the designer with an unusual versatility in resin specifications. Thus polyethylene technology has progressed from its dependence on one low-density polymer to numerous linear polymers, copolymers, and blends that will extend the use of polyethylene to many previously unacceptable applications.

One of the most important achievements in the field of synthetic polymer chemistry during the past 50 years has been the discovery in 1953 by Ziegler and his co-workers [2] that aluminum alkyl compounds used along with many transition metal halides in an inert hydrocarbon medium could polymerize ethylene under conditions of normal temperatures and pressures to yield a solid polymer of high molecular weight and of linear structure. The developments which led to the discovery of this catalyst have been described by Ziegler [2]. For some time Ziegler's group had studied the 'aufbau' or growth reaction in which ethylene undergoes oligomerization when heated with an aluminum alkyl compound. Although the insertion step proceeds at temperatures of 100–120 °C, the displacement reaction requires temperatures of greater than 120 °C. By accident Holzkamp, one of Ziegler's students, discovered that the displacement reaction could be catalyzed at lower temperatures by traces of colloidal nickel inadvertently left in a reactor. Subsequently, during wider investigations using other metals, Breil discovered that zirconium acetylacetonate, used with aluminum-triethyl, was an exceedingly active catalyst with the autoclave being filled with polyethylene.

Other transition metal compounds from Groups IV to VI when used with aluminum alkyl compounds gave similar results, with titanium compounds showing a high activity. Characterization studies on the polyethylenes produced by the new catalyst systems showed them to have linear unbranched structures and high molecular weights.

Ziegler and his co-workers were mainly concerned with the polymerization of ethylene, and it was left to Natta to extend Ziegler's discovery to other  $\alpha$ -olefins. Natta disclosed his results to Montecatini, and it was agreed that research could be carried out on the polymerization of  $\alpha$ -olefins. Using a combination of titanium tetrachloride and aluminum-triethyl Natta and co-workers [3] established that propylene could be polymerized to give a product which could be separated into largely crystalline and amorphous fractions. Subsequently, Natta and his co-workers extended the type of transition metal halide by using the supported transition metal salts in a lower valence state, e.g.  $TiCl_3$ ,  $VCl_3$ , etc. It was also established that stereoregular polymers of butene-1, styrene, dienes, etc., could be prepared [3].

Ziegler's discovery, together with the ensuing work into the polymerization of propylene and other  $\alpha$ -olefins by Natta, has given rise to the development of new classes both of catalysts and polymers. In the case of ethylene, the essential advance which was achieved was the preparation of a more linear type of polyethylene, whilst in the case of propylene and other  $\alpha$ -olefins, it was the control of the propagation step so as to give linear unbranched stereoregular molecules [2,4]. The commercial advantage was that this control could be achieved in the polymerization of such readily available and cheap monomers as ethylene and propylene. In recognition of their contributions the 1963 Nobel Prize for Chemistry was awarded to Ziegler and to Natta.

Independent and concurrent researches carried out in the USA in several industrial laboratories during the early 1950s led to the discovery of a related class of polymerization catalysts, which are formed from oxides of transition metals from Groups V-VII of the periodic table. To increase catalytic activity the transition metal oxides were supported on high area substrates such as silica, alumina, silica-alumina, etc. These catalysts constitute some of the earliest low pressure catalysts for alkene polymerization. The silica-supported chromium trioxide catalyst developed by the Phillips Petroleum Company [5] is the most important transition metal oxide catalyst of this class and is used for the polymerization of ethylene,

producing linear, high density polymers. The discovery of these catalysts, their high activity, and the particular methods of their preparation have had profound effects on subsequent developments in Ziegler–Natta catalysis.

Metallocene compounds are becoming an important class of catalyst for the synthesis of organic molecules and polymers [6]. These complexes also have good potential to act as catalysts or catalyst precursors for a number of organic reactions. The discovery of Group IV metallocene–aluminoxane systems as catalysts for polymerization reactions has opened up a new frontier in the area of organometallic chemistry and polymer synthesis. The polymerization of mono–olefins by metallocenes in comparison to conventional Ziegler–Natta systems offers a versatile possibility to polymer synthesis. The broader flexibility of electronic and steric variations in the cyclopentadienyl (Cp) type ligands allows greater maneuvering in the design of catalyst systems. Such modifications govern the polymerization leading to regio- and stereoregular polyolefins. Scientific understandings in this area have reached a level where full commercial realization is a possibility.

Metallocene catalyst systems require a large amount of methylaluminoxane for achieving higher productivity. The high cost of the cocatalyst stimulated the search for new families of metallocenes which can perform in the absence of aluminoxane. In recent years this has led to the synthesis of a number of cationic metallocenes [6]. Attention is now being paid to incorporate metallocene on inorganic supports such as  $\text{MgCl}_2$  and  $\text{SiO}_2$  to control the morphology of the polymer and prevent reactor fouling.

The mechanism of metallocene catalyst in polymerization of  $\alpha$ -olefins is not known in detail. A two–step mechanism is commonly accepted [7]. First, the monomer is adsorbed at the transition metal. During this step the monomer may be activated by the configuration established in the active complex. Second, the activated monomer is inserted into the metal–carbon bond. In this sequence the metal–organic polymerization resembles what nature accomplishes with enzymes.

Metallocene catalysts are highly sensitive to oxygen, moisture, and a large number of chemical compounds. Therefore, very stringent requirements of reagent purity and utmost care in all manipulations of catalysts and polymerization reactions themselves are mandatory for achieving experimental reproducibility and reliability. Special care must be taken to ensure that

solvents and monomers are extremely pure. Alkanes and aromatic compounds have no substantial effect on the polymerization and can therefore be used as solvents. Secondary alkenes usually have a negative effect on polymerization rates, and alkynes, alkenes (e.g. 1,2-butadiene), and conjugated dienes are known to act as catalyst poisons, as they tend to form stable complexes [8].

The methylaluminoxane has a complex structure, which moreover drastically varies with its preparation mode [9]. Methylaluminoxanes may be prepared by adding an extremely finely divided water, such as in the form of a humid solvent, to a solution of methylaluminum in toluene or other aromatic hydrocarbons. The production of an methylaluminoxane by such procedure requires the use of explosion-proof equipment and very close control of the reaction conditions in order to reduce potential fire and explosion hazards. For this reason, it has been preferred to produce methylaluminoxane by reacting an trimethylaluminum with a hydrated salt, such as hydrated copper sulfate. In either of the above described methods, only trimethylaluminum (TMA) forms aluminoxane with good catalytic activity [10].

The various reaction parameters which may influence the cocatalytic efficiency of MAO in the metallocene activation process for olefin polymerization has been investigated [11]. This study involved in the ethylene polymerization in the presence of bis(cyclopentadienyl) zirconium dichloride/MAO as catalyst. The preparative method of the methylaluminoxanes, together with the analytical data of hydrated salts and produced polymers are also presented.

The metallocene catalysts have been investigated for a long time since 1980's and attempts have been put to improve its productivity [12-34]. The significant technological advances based on new and improved catalysts have been made, but the comprehensive knowledge of the metallocene catalysts is still weak. The study of ethylene polymerization by the high activity metallocene catalyst is one important area. The results of this study will increase our knowledge on the technology of the high activity metallocene catalytic polymerization of ethylene.

## **1.1 THE OBJECTIVES OF THE THESIS**

1.1.1 To investigate the techniques and steps of ethylene polymerization by metallocene–methylaluminoxane catalyst.

1.1.2 To determine the suitable condition for ethylene polymerization by metallocene–methylaluminoxane catalyst.

1.1.3 To observe the effects of metallocene–methylaluminoxane catalyst on the rate of polymerization, catalytic activity, and physical properties of the polymer.

1.1.4 To characterize polymer which obtained from metallocene–methylaluminoxane catalyst.

## **1.2 THE SCOPE OF THE THESIS**

1.2.1 Study the condition of preparation technique of metallocene catalysts. The resulting method was applied to slurry ethylene polymerization process.

1.2.2 Examine the effect of preparation time for methylaluminoxane cocatalyst on rate of polymerization and catalytic activity by varying the time between 10 – 80 hours.

1.2.3 Verify the effect of the type of hydrated salts to supply the water for preparing methylaluminoxane cocatalyst on rate of polymerization and catalytic activity.

1.2.4 Verify the effect of concentration of catalyst on rate of polymerization and catalytic activity.

1.2.5 Examine the effect of catalyst mole ratio on rate of polymerization and catalytic activity by varying the catalyst ratio between 500 – 8000.

1.2.6 Examine the effect of pressure on rate of polymerization and catalytic activity by varying the pressure between 10 – 80 psi.

1.2.7 Examine the effect of temperature on rate of polymerization and catalytic activity by varying the temperature between 300 - 363 K.

This thesis is consisted of 6 chapters. The introduction, the objectives, and the scope of the thesis are described in Chapter I. The related articles and patents are summarized in Chapter II. General considerations of chemistry of metallocene-alkylaluminumoxane catalyst, models of active species formation and some aspects of catalytic behavior are mentioned in Chapter III. And the concepts of polymerization, mechanisms, and factors that control polymer properties are also included. In Chapter IV, the details about chemicals, equipment, procedures, characterization methods used in this thesis are described. Result and discussion are reported in Chapter V. Conclusion with recommendation are given in Chapter VI.