

## CHAPTER I INTRODUCTION



Plastics have an influence on life at nearly every level in society today. Their resistance to corrosion and tremendous technological flexibility has enabled them to replace metals in the construction of many household tools and create comforts. Thus the demand for the plastics increase in huge quantities every year. One of the most common plastics, called polyethylene, is the world's largest volume bulk plastic [1]. This polyolefin accounts for one-third of the global thermoplastics [2]. On the other hand, polypropylene is the third-ranked bulk plastic (after PVC). These polyolefins are used for packing material, receptacles, pipes, foils and fibers etc.

The first polymerization of ethylene to form polyethylene can be performed by a free radical initiation of high pressure process, then low pressure process was invented using metal alkyls as catalysts [3]. Ziegler-Natta catalyst, discovered by Karl Ziegler and Giulio Natta in 1953, was the first generation of the catalyst [4]. This catalyst is a complex formed by reaction of a transition metal compound (halide, alkoxide, alkyl or aryl derivative) of group IV–VII transition metals as the catalyst with a metal alkyl or alkyl halide of group I-III base metals as the cocatalyst.  $MgCl_2$  and/or donor supported Ziegler-Natta transition catalyst system was the second-generation, which was at least 100 times more active.

The new technology that may change the polyolefins industry was the introduction of metallocene catalysts. These catalysts consist of a transition metal group IV (Zr, Ti and Hf) which was sandwiched between parallel planar two organic molecules such as cyclopentadienyl groups (Cp;  $C_5H_5$ ), including those having substituted Cp groups (indene and fluorene), and those with only one Cp group [1]. The first metallocene catalyst was discovered by Giulio Natta and Ronald Breslow [4] in 1957. The catalyst was bis(cyclopentadienyl)titanium dichloride ( $Cp_2TiCl_2$ ) activated by alkylaluminum chloride ( $AlR_2Cl$ ). However, this catalyst exhibited a low polymerization activity for ethylene until Water Kaminsky and coworkers took up the problem in 1980. They discovered that small amounts of water greatly

increased the metallocene catalyst with trimethylaluminum (TMA) as the cocatalyst. This activity resulted from the formation of methylaluminoxane (MAO) which was the hydrolysis product of TMA.

The main difference between these metallocene catalysts and conventional Ziegler-Natta catalysts was in the distribution of active sites. The Ziegler-Natta catalysts were heterogeneous and have many active sites or called multi-site catalysts [3]. Only some of these sites were stereospecific and some were more accessible to monomers for coordination and subsequent polymerization than others. On the other hand, the metallocene catalysts were believed to be homogeneous. Each catalyst molecule has the same activity and each has essentially the same accessibility to the monomer. Therefore, these metallocene catalysts were referred to as single site catalysts and offered potential advantages over traditional multi-site Ziegler-Natta catalysts. The most importance of the metallocene catalysts was the ability to control polymer structure and properties by variation of the catalyst structure. Moreover, these catalysts were able to polymerize several olefins with high activities into high molecular weight polymers and copolymers, characterized by a narrow molecular weight distribution ( $\approx 2$ ) and homogeneous chemical composition [2].

However, despite their numerous advantages, several problems still need to be solved before the metallocene catalysts can be used widely in industry. This can be observed two main problems: first, the difficulty in controlling polymer morphology with soluble homogeneous catalysts, their inability to be used in slurry and gas-phase processes, and reactor fouling; second, the very large amount of MAO as the cocatalyst for achieving maximum activity. The high levels of MAO were a problem commercially, due to relatively high cost of MAO. In addition, the very high level of MAO left a large amount of aluminum-containing ash in the polymer, which can effect the product properties [5].

One route developed to overcome these problems was the immobilization of the metallocene compounds on inorganic supports such as magnesium chloride, alumina, and silica. These supported metallocene catalysts will enable them to use in

gas- and slurry-phase processes, permit the use of less MAO to prevent the reactor-fouling problem, reduce Al/Zr ratio to obtain the maximum activity from several thousands to the range of 50-400, activate some supported metallocene systems by common alkylaluminums such as trimethylaluminum, triethylaluminum and triisobutylaluminum in the absence of any MAO and offer facile control of the polymer properties by ligand variation [4,6].

At present, many studies have been paid in the supported metallocene catalyst to reduction of the high cost of cocatalyst, control of the polymer morphology and adaptation of the catalysts for use in existing polymerization plants. Many points remain broadly open for research and development to use for the polyolefin industry in the future.

This thesis involves the preparation of supported metallocene catalyst which consists of bis(cyclopentadienyl)zirconium dichloride attached on silica support. Afterwards, ethylene polymerization is carried out on the prepared catalyst and the parameters which influence the catalytic activity on the polymerization are studied.

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## **1.1 Objective of the Thesis**

To prepare silica supported zirconocene catalyst and to study its catalytic activity on ethylene polymerization.

## **1.2 Scope of the Thesis**

1.2.1 Prepare and study the zirconocene catalyst on silica support modified with silane compounds.

1.2.2 Investigate the optimum conditions in the polymerization of ethylene:

1.2.2.1 Examine the effect of mole ratio of cocatalyst and catalyst on catalytic activity.

1.2.2.2 Determine the effect of catalyst concentration on catalytic activity.

1.2.2.3 Verify the effect of polymerization temperature on catalytic activity.

1.2.3 Study the effect of types of silanes used to modify silica support.

1.2.4 Characterize polyethylene obtained with conventional spectroscopic techniques: Infrared Spectrophotometry (IR), Scanning Electron Microscopy (SEM), Differential Scanning Calorimetry (DSC), and Gel Permeation Chromatography (GPC).