CHAPTER I

INTRODUCTION

Polyolefins are one of the largest business for catalysis in industry with worldwide production of 78 million tons a year and polyethylene alone in excess of 51 million tons. Despite this size, polyolefins are a fast growing segment of the polymer industry with the highest amount of nearly 4 million tons a year. The production of polyolefins is estimated to be around 140 million tons in 2010 (Kaminsky and Laban, 2001). This increase is caused largely by new catalysts especially by metallocene and other metal complexes which are able to tailor the polymer structure and, by this, the physical properties.

The metallocene catalyst system discovered by Kaminsky has proven to be a major breakthrough for the polyolefin industry. Metallocene and conventional Ziegler-Natta catalyst differ in their coordination environments. As a heterogeneous catalyst, the environment of the active metal center of a Ziegler-Natta catalyst varies with the nature of the support material. However, a homogeneous metallocene catalyst has a uniform environment of the active metal center. Consequently, the polydispersity indices of metallocene catalysts are smaller than those of the Ziegler-Natta catalysts. The physical properties of the polymer product when using a homogeneous metallocene catalyst system can thus be modified by modifying the catalyst structure. Metallocenes are soluble in hydrocarbons or liquid propene. These properties allow one to predict accurately the properties of the resulting polyolefins by knowing the structure of the catalyst used during their manufacture and to control the resulting molar mass and distribution, comonomer content and tacticity by careful selection of the appropriate reactor conditions. In addition, their catalytic activity is 10-100 times higher than that of the classical Ziegler-Natta systems.

Metallocenes, in combination with the conventional aluminumalkyl cocatalyst used in Ziegler systems, are indeed capable of polymerizing ethylene but only at a very low activity. Only with the discovery and application of methylaluminoxane (MAO) by Kaminsky, was it possible to enhance the activity, surprisingly, by factor of 10000. The enormous interest in the scientific community as well as in industry in

metallocene catalysts is due to their high activity in the presence of MAO and the well-defined nature of the active sites (Scheirs and Kaminsky, 1999). However, despite their numerous advantages, several problems still need to be solved before metallocene catalysts can be used widely in industry for the commercial production of polyolefins. There are two main problems : One, reactor operating problems, that is, the difficulty in controlling polymer morphology with soluble homogeneous catalysts limits their use in slurry and gas-phase processes due to reactor fouling, and two, the high level of MAO as the cocatalyst required with homogeneous metallocenes to achieve high activities which 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.

Metallocene catalysts are effective not only for polymerization of common olefins, such as ethylene and propylene but also for polymerization of cycloolefins. These cycloolefins polymerized without ring opening occurring and when copolymerized with ethylene or propylene low incorporations decreased the crystallinity until amorphous elastomeric copolymers were obtained.

Cyclic olefin copolymers (COCs) belong to a family of olefinic copolymers are engineering thermoplastics in which a cycloolefin such as cyclobutene, cyclopentene, norbornene and dimethanooctahydronapthalene is incorporated into the polymer backbone. The COCs produced by metallocene catalysts can be noted as metallocene cyclic olefin copolymer (mCOC). Copolymerization of ethylene with norbornene without ring opening, using single site metallocene catalysts, has produced an amorphous polymer with glass-like transparency, high heat deflection temperature, excellent electrical properties and chemical resistance. They possess low density and are stiff, strong, hard and dimensionally stable, that can be processed by injection molding, extrusion, blow molding and other methods. For these reasons, the ethylene-norbornene copolymers belong to a new class of technical thermoplastics for high-quality applications such as digital data storage devices, CD-ROM, packaging, medical equipment, optics, capacitors, toner binder for printers and other applications (B.-G. Jeong *et al.*,2003;M.-J. Yong *et al.*,2003). These norbornene-ethylene copolymers were recently introduced on the market under the tradenames APEL and TOPAS. They are expected to completed mainly with polycarbonate (PC),

acrylonitrile-butadiene-styrene (ABS) and PC/ABS blends in technical, nonoptical applications and with PC and other COCs in optical applications.

The properties of ethylene-norbornene copolymers can be tailor-made by changing the polymerization conditions or metallocene catalyst. Here, metallocene catalysts must show good activity for norbornene and produce copolymer with uniform comonomer distribution. Generally the catalyst activity, comonomer incorporation and distribution, tacticity and molecular weights of the polymer depend heavily on the ligand structures of the metallocene catalysts. Therefore, the intention of the present study is to increase our standing of the main parameters when copolymerizing norbornene and ethylene using *ansa*-metallocene catalysts and methylaluminoxane (MAO) as a cocatalyst.

The objective of this investigation was to study the influence of the polymerization parameters on the catalytic activity ,norbornene content in the copolymer, thermal characteristics and morphology of ethylene and norbornene copolymer produced using metallocene catalyst and MAO. The main parameters are the type of metallocene catalyst, the norbornene concentration and the polymerization temperature. The effects of catalyst concentration, Al/Zr ratio and polymerization time were also studied.

This thesis is divided into five chapters. Chapter I provides an overview of the use of metallocene catalyst for the polyolefin industry. In Chapter II, knowledge and open literature dealing with metallocene catalysis for olefin polymerization are presented. The literature review is emphasized metallocene catalyst system used for copolymerization of ethylene and cycloolefin. The experimental procedure as well as the instrument and techniques used for characterizing the resulting polymers are described in Chapter III.

In Chapter IV, the results on ethylene and norbornene copolymerization are presented. Effects of various polymerization conditions on catalytic activities, norbornene content in the copolymer, thermal characteristics and morphology of copolymer are summarized. The polymer characteristics were determined by Scanning Electron Microscope (SEM), Differential Scanning Calorimetry (DSC), ^{13}C-

Nuclear Magnetic Resonance (^{13}C-NMR) and Fourier Transform Infrared Spectroscopy (FT-IR).

Finally, conclusions of this work and some recommendations for future research work are provided in Chapter V.