

CHAPTER I

INTRODUCTION

The extensive use and production of polyolefins using heterogeneous group IV transition metal catalyst which was discovered by K. Ziegler and G. Natta in the early 1950s has become a giant industry. These catalyst systems are products formed from reactions involving certain transition metal compounds from group IV and group VIII such as Ti, V or Cr compounds with alkyl halides of group I to group III metals. They can be used to polymerize ethylene to high molecular weight polyethylene. Early polyethylenes such as linear low density polyethylene (LLDPE) and high density polyethylene (HDPE) consist of a broad array of molecular weights because the catalysts used had low activity and low stereo specificity. Hence it has become a major objective to develop catalysts with high efficiency and high stereospecificity. Highly efficient homogeneous metallocene/aluminoxane catalyst systems, which give high activities, narrow molecular weight distributions, and good stereochemical control, are some of the major achievements in recent years.

Metallocene catalysts, also known as single site catalysts, initiate polymerization through only one type of catalytic site. They are compounds obtained as cyclopentadienyl derivatives of a transition metal or metal halide. The transition metal is usually zirconium, but other group IV metals are sometimes used. Metallocene compounds are not active enough to polymerize olefins so aluminoxane compounds are normally added as powerful activators. One of the widely used activators or cocatalyst due to its high catalytic activity is methylaluminoxane (MAO). This metallocene/MAO catalyst system generally offers several potential advantages over traditional multi-site Ziegler catalyst. Polyolefins produced with metallocene catalysts are expected not

only to compete with the polyolefins made with Ziegler-Natta catalyst but also to open entirely new markets for polyolefin resins. However homogeneous metallocene/MAO catalyst system also have some disadvantages. They cannot be use in gas phase or slurry process, control of morphology is poor and they require a large amount of MAO to realize the maximum catalytic activity which may impair its value in commercial applications. Because of this, the attention in recent years has been focused on the way to overcome these drawbacks and at the same time to lower the amount of MAO used in polymerization.

One strategy to address this problem is based on the hypothesis that, if the role of the cocatalyst is indeed to promote the formation of unsaturated “cation-like” active centers, it might then be possible to devise other potent Lewis acids which are as effective as cocatalyst but which can form isolable and characterizable catalyst with group IV metallocenes. Tris(pentafluorophenyl)borane, $(B(C_6F_5)_3)$, is one such alternative. The borane have several advantages. Firstly, it is a relatively strong molecular Lewis acid (acidity between BCl_3 and BF_3) and has been shown to form a variety of characterizable Lewis base adducts. Secondly, it has good solubility in nonpolar, noncoordinating solvents. Thirdly, the boron center is surrounded by highly electronegative, chemically robust, functional groups having only nonpolar, minimally coordinating, fluorosubstituents. Using this borane a variety of cationic zirconocene alkyl and hydrido complexes have been isolated. These are highly active catalysts for the polymerization of ethylene and α -olefins. A large body of precise diffraction structural information has also been obtained. It has been found that only a stoichiometric amount of the cocatalyst is required to achieve the maximum catalytic activity. However the borane cannot scavenge impurities present in the system. Therefore to overcome this problem alkylaluminum compounds are usually added to accomplish this task. In this research work ethylene polymerization by

$\text{Cp}_2\text{ZrCl}_2\text{-B}(\text{C}_6\text{F}_5)_3$ catalyst with two different aluminum compounds, triethylaluminum (TEA) and tributylaluminum (TBA), were studied. The properties of polyethylene prepared from the above catalytic systems were also determined.