CHAPTER I

INTRODUCTION

Since the discovery of metallocene catalysts by Sinn and Kaminsky in 1980 (Sin and Kaminsky,1980), the manufacture of polyolefins by metallocene catalysts represents a revolution in polymer industry. Polymerization of olefin monomers with single-site metallocene catalysts allows the production of polyolefins, such as polyethylene and polypropylene with a highly defined structure and superior properties.

Metallocene polymerization catalysts generally have a constrained transition metal (usually a group 4b metal, such as Ti, Zr or Hf) which is sandwiched between cyclopentadienyl ring structure to form a sterically hindered site. Variation in this theme includes ring functionalization with various alkyl or aromatic groups, ring bridging with either a Si or C atom and metal coordination to either an alkyl group or halogen atom.

The term metallocene classically describes compounds with a π-bound cyclopentadienyl ring structure. Today's catalysts are better described as single-site catalyst. They differ from traditional olefin polymerization catalysts by the fact that the catalytically active metal atom is generally in a constrained environment and thereby only permits single access by monomers. By limiting the polymerization reaction to a single site instead of the conventional multiple sites, these types of catalysts allow close control over comonomer placement, side chain length and branching. Such single-site catalysts give precise control over polymer design because the polymer grows by a single mechanism rather than multiple routes. This new catalyst technology has been commercialized and it advantageously combines high activity with the possibility to tailor polymer properties such as, molecular weight, molecular weight distribution, comonomer insertion and distribution, as well as stereoregularity of α-olefin polymers through a rational ligand design at the transition metal center.

Olefin polymerization by metallocene catalysts is believed to occur via Cossee-Arlman mechanism like traditional Ziegler-Natta catalyst (Daniel, 2000). A significant amount of experimental and theoretical evidence suggest that a cationic alkyl-metallocene complex is the active species in polymerization (Petitjean *et. al,* 1999). Typically, metallocene catalysts are generated by activating metallocene halides with methylaluminoxane (MAO) (Janiak *et al.*, 1993). However, in order to achieve the high activities, extremely high molar Al to transitional metal ratios (Al:M) of between 1000-15 000 :1 were required (Marks and Chen, 1997). Such ratios are commercially unacceptable in terms of cost and the amount of residues in the resulting polymer. A significant effort has been put into reducing the amount of MAO and this has led to the development of many alternative systems. Metallocene catalysts may be generated in the absence of MAO by treating metallocene alkyl with a cation generating agents such as, $[HNR_3][B(C_6F_5)_4]$, $[CPh_3][B(C_6F_5)_4]$ or $B(C_6F_5)_3$ to obtain an equilibrium concentration of catalytically active species $[Cp_2MR]^+$. The activity and stability of such MAO-free cationic catalysts are strongly dependent on the weakly coordinating nature of counterion with $[B(C_6F_5)_4]^-$ and $[RB(C_6F_5)_3]^-$ being particularly successful.

Tris(pentafluorophenyl)borane, $B(C_6F_5)_3$, is selected to be an alternative cocatalyst in this research work. The borane is a relatively strong molecular Lewis acid (acidity between BCl_3 and BF_3) and it has good solubility in nonpolar, noncoordinating solvents. Consequently, this highly active cocatalyst is suitable for the polymerization of ethylene and α-olefins. 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 introduced to accomplish this task. Ethylene polymerization with aluminoxane-free catalyst was studied in this work by using bis(cyclopentadienyl)zirconocene dichloride (Cp_2ZrCl_2)/tris(pentafluorophenyl)borane $B(C_6F_5)_3$)/triethylalumiuum (TEA) catalyst system. The effects of catalyst concentration, ethylene pressure and ethylene consumption profile, polymerization temperature on productivity, molecular weight, molecular weight distribution, crystallinity and melting temperature of polyethylene obtained were studied.