CHAPTER I

INTRODUCTION

The metal catalyzed production of polyolefins such as high density polyethylene(HDPE), linear low density polyethylene(LLDPE) and polypropylene(PP) has grown into an enormous industry. Heterogeneous transition metal catalysts are used for the vast majority of PE and all of the PP production. One of the distinguished characteristics of polyolefins made with heterogeneous Ziegler-Natta catalysts is that they have MWDs which are much broader than Flory's most probable distribution expected for ionic chain growth homo- and copolymerization. It is now generally accepted that these broad distributions are caused by the presence of several types of active sites on the catalyst, although mass and heat transfer resistance can further broaden these distributions under certain polymerization conditions.

One of the most exciting developments in the polyolefins industry in recent years was centered on the development of commercial homogeneous single-site catalysts. These single-site catalysts produce olefin polymers with properties different from traditional thermoplastic polyolefins. They permit the synthesis of polyolefins with narrow and well-controlled molecular weight distributions. Additionally, they can be adapted to existing polyolefin-manufacture industrial plants with only minor modifications.

Homogeneous Ziegler catalysts were examined in detail in the late 1950s by Breslow and Newburg (1959) for ethylene polymerization using bis (cyclopentadienyl)titanium dichloride (titanocene) plus organoaluminum chlorides. This has low activity because of bimolecular deactivation due to reductive metathesis. Much work has consequently been done to interpret the mechanism and measure the kinetics of this and related systems. It has been

found that if co-catalysts (AlEt₃ of AlEt₂Cl) are treated with water, both productivity and molecular weight (MW) of PE increase dramatically.

During the past 15 years, Kaminsky and collaborators (Kaminsky and Duch, 1996) discovered that the zirconium metallocene combined with methylaluminoxane (MAO, $[MeAlO]_n$) co-catalyst polymerized α-olefins with extremely high polymerization rate.

Active center and cocatalysts

The bis-cyclopentadienyl-based, or metallocene, single-site catalysts are generally activated with MAO in a relatively large molar amount. The catalytic activity increases with increasing Al:M ratio. Typically, at least 500 - 1000 molar equivalents of aluminum are required for acceptable activity. The role of aluminoxanes as co-catalysts is not completely understood although many functions have been attributed to these compounds. They have been proposed as being responsible for the alkylation of the catalyst, stabilization of the cationic metallocene alkyl by acting as a counter-ion, and prevention of bimolecular reduction of the catalyst. Aluminoxane also scavenges impurities such as water and oxygen from the reaction media. It has also been proposed that the most important function of aluminoxane is in the creation of active species.

The high level of MAO is a problem commercially due to the relatively high cost of MAO. In addition, very high level of MAO leaves a large amount of aluminum containing "ash" in the polymer which can affect the product properties (Stevens, 1996).

MAO-free cationic metallocene catalysts coupled with strong Lewis acid, e.g., $[Me_2SiInd_2ZrR] + [RB(C_6F_5)_3]$, are also active catalysts. The use of $B(C_6F_5)_3$ as a cocatalyst is particularly useful for solution polymerization for many reasons. Firstly, this cocatalyst is a 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 solublility in the hydrocarbon polymerization solvent. Finally, the boron center is surrounded by highly electronegative, chemically robust (i.e., resistant to electrophilic attack) functional groups having only nonpolar, minimally coordinating fluoro substituents. Furthermore, the catalytic activity is also a function of the transition metal. In general, the order of activity is $Zr > Hf > Ti$. Polymer molecular weight is also a function of the transition metal, generally following the order $Hf > Ti > Zr$.

Despite their numerous advantages, several technical problems still need to be solved before metallocene catalysts can be used widely in industry.

Two of the main problems observed are: (1) the difficulty in controlling polymer morphology with soluble homogeneous catalysts and, consequently, their inability to be used in slurry and gas-phase processes, moreover, significant reactor fouling takes place when using homogeneous systems, and (2) the very large amount of methylaluminoxane (MAO) needed to achieve maximum metallocene catalytic activity.

The olefin polymerization with aluminoxane–free cocatalyst was studied in this work. The system selected for this study is ethylene polymerization using bis(cyclopentadienyl)zirconium dichloride (Cp_2ZrCl_2)/trimethylaluminum or TMA $(Al(CH_3)_3)$/Tris(pentafluorophenyl) borane or TPFPB $(B(C_6F_5)_3)$. The objectives of this research work are: (1) to make polyethylene using bis(cyclopentadienyl) zirconium dichloride (Cp_2ZrCl_2) with tris(pentafluorophenyl)borane $(B(C_6F_5)_3)$ as cocatalyst; (2) to study the effect of different catalyst systems and the order of catalyst injection on the activity of each system.