

CHAPTER I

INTRODUCTION

1.1 State of Problem

Polyolefin has been one of the most important commercial polymers. The market demand of polyolefin has been increasing even in the conventional polyolefin such as high-density polyethylene (HDPE), linear-low-density polyethylene (LLDPE), and polypropylene (PP) due to their broad utility for making many kinds of material (Tullo, 2009 and Busico, 2009). Beside the conventional polyolefin, there has been alternation for synthesis of new polyolefin with specified functions (Kaminky, 1994 and Cherdron *et al.*, 1994), for example, cyclic olefin copolymers (COCs) which have optical characteristic. Since new polymers would be mostly prepared by incorporation of new comonomers in the copolymerization, it is now believed that the design of efficient transition metal complex catalysts that precisely control olefin coordination polymerization could be the key for the success (Nomura, 2009).

The development of catalysts for olefin polymerization began with the discovery of Ziegler-Natta catalyst in the early 1950s. Since then, polymerization catalysts have been improved by the aim of simplifying the production process (Kashiwa and Imuta, 1997). Although the development of highly active $MgCl_2$ supported Ti catalysts exhibited excellent catalyst performance and simplified the production process, Ziegler-Natta catalysts provided the resulting polymers with broad molecular weight distribution and wide composition distributions due to multiple active sites. Moreover, their heterogeneous nature hindered investigation of the fine reaction mechanism and impeded true rational design of new catalysts. To address this issue, the next major breakthrough in olefin polymerization catalysts is the development of homogeneous metallocene systems. The metallocene catalysts allow the production of polyolefin with more uniform comonomer incorporation and controlled molecular weight distribution due to single active species. From their homogeneous and single site feature, metallocenes lead to the true rational design of new polymerization catalysts (Camacho and Guan, 2010).

For the successful design of an efficient transition metal catalyst for ethylene (co)polymerization, the catalysts exhibiting remarkable activities with better comonomer incorporation should be desired. Bridged (*ansa*) metallocene type complexes, so called constrained geometry catalysts (CGC) show better comonomer incorporation than non-bridged analogues in ethylene/ α -olefin copolymerization. The fact has been explained as that the bridged metallocenes possess rather large coordination space compared to the nonbridged analogues, allowing better accessibility for (rather) bulky α -olefins (Brintzinger *et al.*, 1995; Kaminsky, 1996 and 1997 and Suhm *et al.*, 1998).

Non-bridged half-titanocenes containing anionic ancillary donor ligands of the type, $\text{Cp}'\text{TiX}_2(\text{Y})$ [Cp' = cyclopentadienyl group; Y = anionic donor ligand; X = halogen, alkyl], are explored as promising candidates for new efficient catalysts for precise olefin polymerization (McMecking *et al.*, 2000; Zhang *et al.*, 2000; Dias *et al.*, 2004; Martins *et al.*, 2005; Stephan, 2005 and Nomura, 2008). These complex catalysts are also demonstrated as effective catalysts for ethylene copolymerization with efficient comonomer incorporation. Even bulky olefins which are known as traditionally unreactive monomer in transition metal catalyzed coordination polymerization can be incorporated by these complexes (Stephan 200, Nomura *et al.*, 2007 and Nomura, 2009). Since the activity and the monomer reactivity are affected by Cp' and ligand employed, the modification of these two parts can lead to the efficient ethylene copolymerization. For example, the copolymerization of ethylene and vinylcyclohexane can be successfully achieved by $\text{Cp}^*\text{TiCl}_2(\text{O}-2,6\text{-}^i\text{Pr}_2\text{C}_6\text{H}_3)$, poly(ethylene-*co*-norbornene) and poly(ethylene-*co*-vinyltrimethylsilane) can be achieved by $\text{CpTiCl}_2(\text{N}=\text{C}^i\text{Bu}_2)$, while poly(ethylene-*co*-styrene) and poly(ethylene-*co*-*tert*-butylethylene) can be achieved by $(^i\text{BuC}_5\text{H}_4)\text{TiCl}_2(\text{O}-2,6\text{-}^i\text{Pr}_2\text{C}_6\text{H}_3)$ and $(\text{Me}_3\text{C}_5\text{H}_2)\text{TiCl}_2(\text{O}-2,6\text{-}^i\text{Pr}_2\text{C}_6\text{H}_3)$ (Nomura, 2009).

Half-titanocenes containing imidazolin-2-iminato ligands, $\text{Cp}'\text{TiCl}_2[1,3\text{-R}_2(\text{CHN})_2\text{C}=\text{N}]$ [Cp' = Cp (**1**), $^i\text{BuC}_5\text{H}_4$ (**2**); R = ^iBu (1,3-di-*tert*-butylimidazolin-2-imide, **a**), 2,6- $^i\text{Pr}_2\text{C}_6\text{H}_3$ (1,3-diisopropylphenyl-imidazolin-2-imide, **b**)], are known to exhibit high catalytic activities for ethylene polymerization in the presence of methylaluminoxane (MAO), affording ultrahigh molecular weight polymers (Tamm *et al.*, 2004, 2006 and Stelzig, 2008). Using ligands of this type is promising, because

these ligands have been widely used for the preparation of early transition metal complexes due to their unique ability to act as a strong $2\sigma,4\pi$ -electron donors toward early transition metals and/or metals in a higher oxidation state (Beer et al., 2007-2009; Panda et al., 2007, 2009-2010 and Trabitás, 2010-2011). Thus, it is interesting to further explore the performance of this type of complex in ethylene copolymerization.

Not only investigation for promising catalysts in olefin copolymerization, synthesis of new polymer is also another important issue. Since the properties of the polymers can be adjusted by polymerization of ethylene with the interest comonomer, the resulting copolymer with improved properties can thus be obtained. As mentioned above that half-titanocene complexes can efficiently incorporate the bulky monomer, such as vinyltrimethylsilane and *tert*-butylethylene, it is very interesting to perform the polymerization with other comonomers to achieve the new polymers with special properties. In this work, half-titanocenes containing anionic ancillary donor ligands were employed in ethylene copolymerization.

1.2 Objectives

The main objective of this study was to explore the effect of ligands in nonbridged half-titanocenes in ethylene/ α -olefin copolymerization and to investigate new polymers with special properties. The overall objectives of this work were as follows:

1. To study the effect of ligands in nonbridged half-titanocenes in ethylene/ α -olefin copolymerization.
2. To synthesize polyolefin with high transparent properties.
3. To introduce functionality to polyolefin by grafting polymers

1.3 Scope of Work

To explore the effect of Cp' and ligands on the catalytic activity and comonomer incorporation, half-titanocenes containing imidazolin-2-iminato ligands,

$\text{Cp}'\text{TiCl}_2[1,3\text{-R}_2(\text{CHN})_2\text{C}=\text{N}]$ [$\text{Cp}' = \text{Cp}$ (1), Cp^* (2), $\text{'BuC}_5\text{H}_4$ (3); $\text{R} = \text{'Bu}$ (a), 2,6- $\text{'Pr}_2\text{C}_6\text{H}_3$ (b), 2,6- $\text{Me}_2\text{C}_6\text{H}_3$ (c)] were used in the presence of MAO for ethylene polymerization and ethylene/ α -olefin (1-hexene, 1-dodecene) copolymerization. The effect of MAO loading in ethylene polymerization was also studied to investigate the appropriate condition.

Ethylene/norbornene copolymerization by $\text{CpTiCl}_2[1,3\text{-'Bu}_2(\text{CHN})_2\text{C}=\text{N}]$ -MAO catalyst system was conducted and compared with the previous reports prepared by the other complex. The effect of catalyst on catalytic activity, monomer incorporation and molecular weight as well as molecular weight distribution was studied. Glass transition temperature, which can be controlled by norbornene content in the copolymer, was also observed.

Terpolymerization of ethylene with styrene and α -olefin (1-hexene, 1-decene) was conducted by $\text{Cp}^*\text{TiCl}_2(\text{O}-2,6\text{-'Pr}_2\text{C}_6\text{H}_3)$ - MAO catalyst system. The monomer feed concentration was varied to study the effect on catalytic activity and monomer incorporation. The polymerization was also conducted by using *p*-methylstyrene in place of styrene in $\text{Cp}^*\text{TiCl}_2(\text{O}-2,6\text{-'Pr}_2\text{C}_6\text{H}_3)$ - borate/alkyl aluminum catalyst systems.

Introduction of vinyl group into polymer chain was achieved by terpolymerization of ethylene with styrene and 3,3-divinylbiphenyl using $\text{Cp}'\text{TiCl}_2(\text{O}-2,6\text{-'Pr}_2\text{C}_6\text{H}_3)$ [$\text{Cp}' = \text{Cp}^*$ (1), $\text{'BuC}_5\text{H}_4$, (2), 1,2,4- C_5H_2 (3)] in the presence of MAO. The post-polymerization of the resulting copolymer with styrene initiated by *n*-BuLi was also investigated in this study.