

# CHAPTER I

## INTRODUCTION

Polyolefin plastics are nowadays in their mature phase, with a consumption of about 40 million tons per year, and could therefore be appropriately defined as “commodity”. These materials have been discovered and now produced all over the world. Polymer-based materials such as plastic, fibers, elastomers were consumed. In the portion of markets, polyolefins is majority. The production and consumption of polyolefins will proportionally increase with the increasing population number.

Such an exceptional expansion is mainly due to the following factors:

1. A great versatility in terms of properties, that makes them suitable to the most diverse application;
2. The environmental aspects (polyolefins are absolutely non-toxic and friendly to the environment);
3. The superior saving in energy costs, both at production and application levels with respect to other conventional materials;
4. The low costs due to the plentiful availability of raw materials;
5. The possibility of adopting low cost, very versatile and non-polluting processes.<sup>[1]</sup>

Metallocene-based catalysts, including the so-called “single-site” catalysts has become an important technology for the global polymer industry. Although it is true that free radical initiated high pressure polyethylene polymerization was the foundation for the polyolefins industry, advances in coordination Ziegler-Natta catalysis during the past 40 or so years has been responsible for most of the growth in production volume in polyolefin plastics. It is very likely that with the emergence of the metallocene-type catalysts, coordination catalysts will become of even greater importance to the polyolefin industry.

While polyethylene and polypropylene dominate in terms of production volumes in the polyalkene industry, polymers of higher  $\alpha$ -alkenes find use due to their special physical properties. In catalytic alkene polymerization the molecular weights of the produced polyalkenes and reaction rates decrease in order propylene > 1-butene > 1-pentene > 1-hexene.<sup>[2]</sup>

The polymerization of 1-olefin, particularly of propylene, allows to highlight some of the most important features of metallocene based catalyst such as their versatility, demonstrated by the capability to produce atactic, isotactic, syndiotactic, hemiisotactic and thermoplastic-elastomeric polypropylene.

The impact of plastics and polymers on modern society continues to spur the exploration of transition metal complexes for single-site olefin polymerization catalysts. These efforts have resulted in the evolution from metallocenes to non-metallocenes. In general the organo-early transition metal complexes have partially ionic metal-carbon bonds and show  $\alpha$ -agostic hydrogen interaction that stabilizes the catalytically active species by providing electrons at a vacant site on the metal. The organo-late transition metal complexes generally show  $\beta$ -hydrogen elimination and reductive elimination, which leads to oligomerization rather than polymerization of the olefins.

Although the late transition metal systems are not good catalysts for polymerization, an important advance in late transition metal polymerization catalyst technology was described by Brookhart and co-workers<sup>[64]</sup>, who showed that Ni(II) and Pd(II) complexes incorporating bulky  $\alpha$ -diimine ligands are capable of polymerizing ethylene and  $\alpha$ -olefins to high molar mass polymers. These catalyst systems also incorporate polar monomers such as methyl acrylate into ethylene and propylene copolymers, but with relatively low productivities.

DuPont has reported highly active ethylene polymerization catalysts based on Fe(II) and Co(II) bearing 2,6-bis(imino)pyridyl ligands.<sup>[3]</sup> LePichon synthesized iron phosphinimide and phosphinimine complexes and used as catalyst precursors for ethylene polymerization.<sup>[4]</sup>

The idea that late transition metal chelate complexes could polymerize  $\alpha$ -olefins has stimulated a search for other late-transition metal polymerization catalysts. This thesis was attracted by the potential of iron as a polymerization active center due to its low cost and ready availability. Iron complexes with neutral bidentate and tridentate ligands such as 2,6-diaminopyridyl ligand and Schiff base were studied because bis-chelation with substituents in the ortho position on aryl groups was observed for sterically undemanding ligands and produced the desired chelation and an active ethylene polymerization catalyst.<sup>[5-10]</sup>



ศูนย์วิทยทรัพยากร  
จุฬาลงกรณ์มหาวิทยาลัย

## 1.1 The objective of the thesis

- 1.1.1 To synthesize iron - based non - metallocene catalysts for use in 1-hexene polymerization.
- 1.1.2 To study the influence of the iron-based non-metallocene catalysts with boron cocatalyst on catalytic yields and activity.
- 1.1.3 To investigate the product structure and determine the optimum conditions for 1-hexene polymerization.

## 1.2 The scope of the thesis

- 1.2.1 To synthesize and characterize iron-based non-metallocene catalysts.
- 1.2.2 To polymerize 1-hexene monomer using the synthesized iron-based non-metallocene catalyst.
- 1.2.3 To investigate the corresponding parameters affecting the 1-hexene polymerization :
  - 1.2.3.1 Polymerization temperature
  - 1.2.3.2 Adding solvent
  - 1.2.3.3 Concentration of the catalyst
  - 1.2.3.4 Types of alkylating agents
  - 1.2.3.5 Types of cocatalysts
- 1.2.4 To characterize the product.