

CHAPTER I

INTRODUCTION

Polyolefins represented by polyethylene (PE) and polypropylene (PP) are among the world's most widely used synthetic commodity polymers owing to their excellence features and extreme versatility. They possess a combination of properties including flexibility, strength, lightness, stability, impermeability, easy processability and are moreover well-suited to recycling and re-use. Since 1950 polymer materials have experienced a rapid development from cheap, low-quality surrogates to materials that allow for new applications or replace established materials such as metal, wood or glass due to their better properties. Therefore, the worldwide production volume of polyolefins has grown to more than 80 million tons per year until now and is predicted to rise continuously to exceed 140 million tons in 2010 [1], allowing us to use them in our daily lives in such applications as packing materials, containers, films, sheets, pipes, automobile parts, electric and electronic parts, medical and sanitary products, toys, kitchen helpers, construction materials, and agricultural materials.

The early history of polyolefin started with the discovery of low density polyethylene (LDPE) by ICI. The obtained polymer has a highly branched structure and is produced radically at ethylene pressures of 1000-3000 bar. In contrast to the free radical ethylene polymerization, the discovery of the catalyst based on the activation of transition metal compounds with aluminium alkyls in 1953 by Karl Ziegler led to the formation of high density polyethylene (HDPE) [2]. A year later, Giulio Natta was able to demonstrate that an appropriate catalyst system was capable of polymerizing propylene into semi-crystalline polypropylene [3]. Since then numerous generations of catalysts and processes have been introduced on the commercial scale to produce a large variety of materials ranging from commodity thermoplastics to rubbers, e.g., high density polyethylene (HDPE), linear low density polyethylene (LLDPE), isotactic polypropylene, ethylene-propylene rubber (EPR), ethylene-propylene-diene monomer rubber (EPDM), polybutadiene and polyisoprene.

Forty years after Ziegler's discovery, transition metal catalyzed olefin and diolefin polymerization continues to represent one of the most active and exciting areas of research in academic and industrial laboratories. In the late 1960's, outstanding scientific achievement, innovation and process improvements have revolutionized polyolefin technology through the new generations of supported Ziegler-Natta catalysts which give unprecedented control of both polymer microstructures and polymer morphologies [4] and the successive discovery of electron donors (Lewis base) are capable of increasing the stereospecificity of the catalyst so that highly isotactic polypropylene could be obtained [5].

In modern Ziegler-Natta catalysts, the structure of the external electron donor is fundamental to promote the polymerization of α -olefin with a high control of stereoregularity. The first catalyst systems contained ethylbenzoate as internal donor and second aromatic ester as external donor [6], while nowadays the catalysts most widely used in polypropylene manufacture contain a diester (e.g. diisobutylphthalate) as internal donor and are used in combination with an alkoxysilane external donor of type $RR'Si(OMe)_2$ or $RSi(OMe)_3$ [7]. Following the development of these third- and fourth-generation catalysts, which have largely displaced the first and second generation $TiCl_3$ catalysts, a fifth generation of catalysts is recently being introduced. These catalysts contain a diether (typically a 2,2-disubstituted-1,3-dimethoxypropane) and have high stereospecificity even in the absence of an external donor [8]. In addition, the catalyst performance has improved substantially with each generation.

The objectives of this study were twofold: first was to elucidate the effects of metal oxide and modified metal oxide as a third component on the catalyst performances for conducting propylene polymerization and the second was to investigate the poisoning effects of low hindered-structure Lewis base on the nature of active site through kinetic study.

This dissertation consists of the following 7 chapters: Chapter I is the general introduction to lead the objective of this research. Chapter II is an introduction to Ziegler-Natta catalyst with a brief review on catalyst history and development. We also address the basic chemical principles on both catalysis and polymerization. Chapter III reports the chemical employed, catalyst preparation, polymerization

procedure and characterization technique. The influences of the incorporated CaO during *in situ* propylene polymerization on catalytic activity, catalyst stereospecificity as well as the properties and morphology of polymer obtained are presented in Chapter IV. Chapter V describes the modification of SiO₂ with various MAOs compounds and discusses its impact as co-activator on polymerization activity and polymer features. Chapter VI is concerned mainly with the effects of poisoning materials on Ziegler-Natta catalyst. The kinetic investigation was also carried out via a combination of stopped-flow technique and GPC method to determine its influence on catalyst concentration ($[C^*]$) and chain propagation rate constant (k_p). Finally, conclusion of the work and suggestions are presented in Chapter VII.