

CHAPTER I

INTRODUCTION

Polyolefins are one of the largest business for catalysis in industry with worldwide production of 78 million tone a year and polyethylene alone in excess of 51 million tone¹. Despite this size, polyolefins are a fast growing segment of the polymer industry with the highest amount of nearly 4 million tonne a year. The production of polyolefins is estimated to be around 140 million tonne in 2010 [1].

This increase is caused largely by new catalysts which are able to tailor the polymer structure and, by this, the physical properties. Some recent reviews and books give detailed information of olefin catalysis especially by metal complexes [1].

The discovery of that catalyst based on titanium tetrachloride and diethylaluminum chloride as cocatalyst was made by Kerl Ziegler, who succeeded in polymerization ethylene into high density polyethylene (HDPE) at standard pressure and room temperature in 1953 at the Max-Planck-Institute in Mulheim. A little later, Natta, at the Polytechnical Institute of Milan was able to demonstrate that an appropriate catalyst system was capable of polymerizing propylene into semi-crystalline polypropylene. Ziegler and Natta shared a Nobel Prize for Chemistry in 1963 for their work. The modern Ziegler-Natta catalysts are mixture of solid and liquid compounds, often containing $MgCl_2/TiCl_4/Al(C_2H_5)_3$ and, for propylene polymerization, different internal and external donors such as ethylbenzoate, silanes or ethers to increase the tacticity.

Natta perceived the propylene and long-chain olefins can be assembled in a stereoregular monomer, the building blocks of the resulting chain having a defined and recurring arrangement. This alignment has a considerable influence on the functional properties of the material. A statistical arrangement leads to amorphous polypropylene which flows at room temperature, whereas stereoregular polypropylene in crystalline having a melting point of 165 °C.

Metallocene catalysts show in contrast to Ziegler-Natta systems only one type of active site (single site catalysts), which produces polymers with a narrow molar mass distribution ($M_w/M_n=2$), and their structure can be easily changed. The structure of metallocenes, so called “Sandwich compounds” in which a η -bond metal atom is situated between two aromatic ring systems, was uncovered by Fisher and Wilkinson and Birmingham. They were both awarded the Nobel Prizes in 1973 for this achievement. This compound class initiated a more resourceful organometallic chemistry that did not play a role in industrial process in the past.

A further milestone was reached when Brintzinger *et al.* synthesized chiral-bridged metallocenes in 1982 at the University of Konstanz and in 1984, when Ewen, at the Exxon Company (USA), was able to demonstrate that appropriate titanocenes render partially isotactic polypropylene. Nearly at the same time, highly isotactic material was obtained with analogous zirconocenes. After this discovery, a fervent development of industrial and scientific research in the metallocene sector commenced and until today it has not been concluded.

This work focused on the effects of polymerization conditions on the isotacticity of polypropylene comparison between 2 types of the most widely used catalysts : Ziegler-Natta and Metallocene catalysts.

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