

CHAPTER I

INTRODUCTION

Polyolefins form the fastest growing family of materials within the plastic spectrum, and include some of the oldest plastics around. They are used in almost every field - from food packaging to sophisticated engineering. And although polyolefins are an established product field, the market for polyethylene (PE) has been growing constantly since its large-scale introduction in the 1960s. At the heart of corporate secrets in the plastics industry, you'll find catalyst recipes. Some companies are reluctant to release this information to their own employees unless it is absolutely necessary. Polyolefin is prepared by polymerising an olefin as the sole monomer, and at least 50 per cent of the resulting resin must be olefin. Ethylene and propylene are the most common of these olefins.

Although polyolefins have been around for some time, the area has not stood still technologically. The arrival of the metallocene catalysts in the 1980s caused a great stir and only now are the improved products, obtained via the metallocene processes becoming available commercially. Incidentally, metallocene-type catalysts have been known since Wilkinson and Fischer reported their work on ferrocene in 1952. This was before Zeigler first announced his work on what would become Zeigler-Natta catalysis the following year.

Metallocene catalysts are becoming increasingly popular in the plastics industry, and have been studied extensively with regard to polyolefin chemistry. Compared with other olefin polymerization catalysts, the metallocene catalysts have higher activity and greater versatility for controlling the microstructure and properties of polymers. There has been a great effort to introduce these catalysts into several commercial processes to obtain high performance polyolefins. However, polyolefins are traditionally obtained using a Ziegler-Natta catalyst, and most of the current polyolefin production uses these. Other developments include the mono-Cp constrained geometry catalysts which have been primarily developed by Dow and Exxon. However, it is found that the homogeneous metallocene catalytic system has

two major disadvantages; the lack of morphology control of polymer causing the reactor fouling and the limitation of being able to use only in the solution process whereas the existing technologies are mainly based on the gas phase and slurry processes. Therefore, binding these metallocene catalysts onto suitable inorganic supports can provide a promising way to overcome those drawbacks.

The role of a support material is to prevent the occurrence of sintering processes by providing a large surface area onto which the particles of active phase can become anchored. Because of the anchoring process the small particles of active phase become stabilized and will resist sintering much more strongly. There is a wide variety of support materials onto which active phases can be stabilised. The most common support materials are simple metal oxides, such as aluminas, silicas and titanias, although zirconias and cerias also find application. [1]

Nevertheless one of the key features of a support material is to exhibit a large specific surface area onto which the catalytically active phase is present with a very high dispersion. As a result, reports in 1992 about the discovery of a new class of silica-based mesoporous materials by researchers of Mobil Company [2, 3] have boosted research into the application of active phases inside the mesopores of these materials. These materials are known by their abbreviations, *viz.* MCM-41 and MCM-48. MCM denotes Mobil Composition of Matter, whereas the numbers 41 and 48 are merely batch numbers.

The best-known mesoporous support material is MCM-41. The structure of MCM-41 consists of uniform cylindrical pores arranged in a hexagonal array. The pore dimensions can be tailored in the range of 1.5-10 nm depending on synthesis chemicals and conditions. The BET surface area is usually greater than 1000 m²/g with high sorption capacities of 0.7 ml/g. [4] From a fundamental point of view MCM-41 is extremely well-suited to serve as a model support material, so MCM-41 has been studied as a catalyst support for research.

In general, the surface areas mainly control the dispersion of supported metal. As a matter of fact, too large surface area (small pore diameter) results in poor diffusion efficiency of reactant and products in the intra-pellet structure whereas a catalyst having too large pore diameter exhibits a small surface area leading to low metal dispersion and low catalytic activity. A support with a distinct bimodal structure has excellent advantages for solving the contradiction as mentioned before. In particular, the large pores provide rapid transportation of reactant and product molecules whereas the small pores render a large surface area. Moreover, the geometrical shape of the nano-channels of support can serve as polymerization reactors to affect the pattern and activity of monomer insertion. Thus, the arrangement of polymer chain and polymer morphology can be controlled. Many researchers are interested in obtaining bimodal polyethylene using bicomponent catalyst or support [5-7].

The objectives of this investigation was synthesis of various MCM-41 supports having different pore size distribution such as unimodal and bimodal and investigate on catalytic activities during the copolymerization of ethylene with α -olefins such as 1-hexene, 1-octene, 1-decene using various MCM-41 supported MMAO with zirconocene catalysts

This thesis was divided into five chapters. Chapter I involved an overview of the use of metallocene catalyst for the polyolefin industry. In Chapter II, knowledge and open literature dealing with metallocene catalysis for olefin polymerization were presented. The literature review was accentuated metallocene catalyst system used for copolymerization of ethylene with α -olefins. The experimental procedure as well as the instrument and techniques used for characterizing the resulting polymers were also described in Chapter III.

In Chapter IV, the results on ethylene and α -olefins copolymerization using various unimodal and bimodal MCM-41-supported zirconocene/dMMAO catalysts. were presented. The influences of various pore structures of MCM-41 on the catalytic activity and polymer properties were investigated. The characteristics support and

catalyst precursors using N_2 physisorption, X-ray diffraction (XRD), Thermogravimetric analysis (TGA), Raman spectroscopy, X-ray photoelectron spectroscopy (XPS), Scanning electron microscopy (SEM), and Energy-dispersive x-ray spectrometer (EDX) and obtained copolymer using Differential scanning calorimetry (DSC), Gel permeation chromatography (GPC) and ^{13}C -nuclear magnetic resonance (^{13}C -NMR).

Finally, conclusions of this work and some recommendations for future research work were provided in Chapter V.