CHAPTER I

INTRODUCTION

For the polymer industry, polyolefins are one of the largest business with worldwide production of 78 million tons a year and polyethylene alone in excess of 51 million tons. Despite this size, polyolefins are a fast growing segment with the highest amount of nearly 4 million tons a year. The production of polyolefins is estimated to be around 140 million tons in 2010 [1]. The use of metallocene catalysts has allowed a very rapid development in the field of polyolefins. These catalysts present single-site characteristics (and very high activities), and thus all the sites produce nearly the same chain architecture, leading to polymers with a narrow molecular weight distribution. In the case of copolymers with α-olefins, the side branches are randomly distributed in the polymer backbone [2].

The discovery of homogeneous catalyst systems comprising of metallocene and aluminoxane has opened up a new millennium in the polymer science [1]. Even if there are many advantages, such as high activity and stereoregularity, there are also some critical problems for the commercial applications, such as the difficulties in controlling the polymer morphology, instabilities for slurry and gas phase processes and requirement of a large amount of expensive methylaluminoxane (MAO) [3]. Moreover, these catalysts also result in lower residual metal content in final product [4]. In this regard, it is desirable to heterogenize the homogeneous catalysts for their possible industrial applications [3].

Heterogeneous metallocene systems have an advantage over homogeneous metallocene systems because of easy adaptation to use in the existing industrial polymerization processes. Other advantages when compared to homogeneous metallocene systems are: avoiding the fouling-effect, the sticking of formed polymer to the reactor wall, good controllable morphology and high bulk density of polymer products [4]. Moreover, high molecular weights and melting temperatures, narrow molecular weight distributions, improved polymer properties have been achieved for

supported catalysts [5]. Many studies were reported on the immobilization of metallocenes on metal oxide carriers (silica or alumina), $MgCl_2$, or polymer supports [2-14]. Some scientists have carried out the polymerization using the regular arranged mesoporous silica materials such as MCM-41 as the support of metallocene catalysts [2, 15].

Since their discovery in 1992 [16], MCM-41 and related mesoporous molecular sieves have attracted much attention. MCM-41 is known as a well-defined and designable mesoporous material with narrow pore size distribution, large internal surface area and hexagonal arrangement of uniformly sized cylindrical pores ($\approx$15 to 100Å) [15]. Many scientists investigated MCM-41 materials in which a catalytically active component was introduced. Several elements, such as Al [3, 5] and B [4, 17, 18] have been incorporated into the framework in order to generate potential catalytic activity. Therefore, a modification of the MCM-41 could provide an alternative strategy to obtain suitable supports to maintain high activity as in the homogeneous system for the supported metallocene catalysts.

In this thesis, it consists of two parts: part 1 investigated the effect of boron modification on MCM-41-supported dMMAO/zirconocene catalyst during ethylene/1-octene copolymerization with varied boron loading and part 2 investigated the effect of boron modification on MCM-41-supported dMMAO/zirconocene catalyst during ethylene/1-octene copolymerization on the different pore sizes of MCM-41 supports and the amounts of boron loading were also varied. The characterization of different supports was performed by means of XRD, Raman spectroscopy, SEM/EDX, TGA and XPS. The polymer obtained was further analyzed using GPC, in order to determine the effect of boron modification on molecular weight (MW) and molecular weight distribution (MWD), ^{13}C-NMR spectroscopy was performed to determine the comonomer incorporation and polymer microstructure and DSC was performed to determine the thermal properties of polymer.

1.1 Objective of the Thesis

To investigate the impact of boron-modified MCM-41-supported zirconocene catalyst via ethylene/1-octene copolymerization on the polymerization behaviors.

1.2 Scope of the Thesis

1.2.1 Preparation of MCM-41-supported with various pore sizes.

1.2.2 Modified MCM-41-supported with 1 and 5 wt% of boron loading.

1.2.3 Study and characterize effects of boron-modified MCM-41-supported with zirconocene catalyst on catalytic properties during the copolymerization of ethylene/1-octene.

1.2.4 Characterize the properties of polymers that were synthesized by the copolymerization of ethylene/1-octene with boron-modified MCM-41-support.