CHAPTER I
INTRODUCTION

More than 40 years after the discovery of Ziegler-Natta catalysts these catalysts have not lost their fascination and utility. Karl Ziegler first reported the preparation of linear polyethylene by polymerization of ethylene over catalysts prepared from transition metal halides and aluminum alkyl compounds in 1953. Giulio Natta recognized the potential of this new type of polymerization for preparation of stereoregular polymers. By slightly modifying the catalyst used in Ziegler's work, he was able to prepare highly isotactic linear crystalline polymers from other α-olefins (e.g., propylene). This work has sparked further development of this unique catalyst both in industrial and academic research. To recognize their contribution in this area, both Ziegler and Natta were awarded the Nobel prize in Chemistry in 1963.

Usually Ziegler-Natta catalysts are broadly defined as the catalysts formed from groups IV-VIII transition metals (e.g.,Ti,V,Cr,Zr) with organometallic compounds (e.g., alkyls or hydrides) of group I-III metals (e.g., Al, Mg, Li). The first generation of Ziegler-Natta catalysts (e.g., $TiCl_3$-based catalyst) had only low activities. In search for higher efficiency, supported Ziegler-Natta catalysts have been developed with magnesium compounds widely used as supports (e.g., $MgCl_2$, $Mg(OH)_2$, $Mg(OEt)_2$). The latest directions for olefin polymerization have been towards soluble transition metal compounds with aluminoxane, Metallocene catalyst system, which have even higher activities. However, research in recent years have concentrated on $MgCl_2$-supported catalysts which are the most common commercial catalysts

used at this time. Thus, highly active $MgCl_2$-supported catalyst will be studied in this research.

The kinetics of olefin polymerization with Ziegler-Natta catalyst has been intensively investigated for many years. The basic principles of kinetics and the mechanism of this process were suggested by Natta. Furthermore a number of works had appeared on the studies of the polymerization kinetics, concerning both physical processes of heat and mass transfer inside the catalyst-polymer particles and the mechanism of active site formation and deactivation. Although to a great extent there is a technical application for these catalysts, so far the nature of the active centers and many reaction mechanisms are not completely known.

It is known that the activity of homogeneous vanadium catalysts generally used in the preparation of EPDM (ethylene/propylene/diene terpolymer), can be increased by means of certain organic compounds often called "activators" or "promoters". The use of halogenated compounds as activators have been described by several works. But in the case of Ziegler-Natta catalysts for ethylene polymerization, little work has been conducted.

In this research, we will examine the effect of chlorinated compounds (e.g., $CHCl_3$, CH_3CCl_3 and $C_6H_5CH_2Cl$) on the activity, productivity and the mechanism of the polymerization in the presence of these compounds. Furthermore, the synthesized polyethylene will be characterized for their molecular weights and molecular weight distributions.