NOVEL MAGNESIUM - TITANIUM CATALYST SYSTEMS FOR THE POLYMERIZATION OF UNSATURATED MONOMERS

A THESIS SUBMITTED TO THE
UNIVERSITY OF POONA FOR THE DEGREE OF

DOCTOR OF PHILOSOPHY
(IN CHEMISTRY)

BY

G. SATYANARAYANA

DIVISION OF POLYMER CHEMISTRY
NATIONAL CHEMICAL LABORATORY
PUNE 411008, INDIA.
AUGUST 1993.

DEDICATED TO MY BELOVED
LATE SISTER

ACKNOWLEDGEMENTS

Now, at the final and happy moments of my research career as a graduate student at NCL, it is my moral responsibility to thank people who helped me all the way. I extend my sincere thanks to my supervisor **Dr. S. SIVARAM** from whom I learned the most. His encouragement, criticism, advice and optimism were instrumental in the successful completion of this thesis. I hope, I have learned the art of critical analysis and enquiry of scientific data and experimental results and to have a bright imagination in science(" let one's mind leap ahead to never say something is impossible") from my supervisor.

My friend Sujata Marathe and I joined at the same time as research students in Polymer Chemistry Division of NCL. We, being the beginners of "*Inert Atmosphere Olefin Polymerization Chemistry*" at NCL, faced lot of difficulties and failures during the first two years (1988 -90). Our determination and mutual understanding made us achieve the goals. I am thankful for the cooperation and friendship she rendered to me. I am also indebted to my other laboratory colleagues Dr. B.M. Shinde, Dr. S.P. Kashikar (presently in Belgium), Mr. D.Baskaran (presently in Germany) and Dr. S. Chakrapani for their cooperation, patience and friendship. Further, I wish to thank all the members of Polymer Chemistry Division, who helped generously through out my stay at NCL.

I am much thankful to all my friends of "Saturday Group Discussion Forum" who educated me on the fundamentals of Polymer Chemistry. In fact, our discussions during and after presentations helped in improving and enhancing my appreciation of Polymer Chemistry. I shall miss these healthy discussions.

Although I can't mention the big chain of my hostel friends who made my free time most enjoyable, I would like to thank Prasad, Mani, Vivek, Ganesh, Jawhar, Anuj, Tandel, Prakash, RK, Vijay, Anand. I will miss all of them. I extend special thanks to my friends Mani, Tomal, Binod and Srinivas for proofreading and helping in formatting the thesis on Lotus Manuscript with meticulous care.

I awe my sincere gratitude for the right advice and moral support given by my *Parents, Brother, Late Grandfather* and *Uncle* at tough moments in my career.

Finally, my thanks are due to the Council of Scientific and Industrial Research; New Delhi, for the award of Research Fellowship and the Director, NCL, Pune, for the permission to submit this work in the form of a thesis.

G. Satyanarayana
(G. SATYANARAYANA)

THE WOODS ARE LOVELY, DARK AND DEEP,
BUT I HAVE PROMISES TO KEEP,
AND MILES TO GO BEFORE I SLEEP,
AND MILES TO GO BEFORE I SLEEP.....

Robert Frost

DECLARATION

Certified that the work incorporated in the thesis entitled

"NOVEL MAGNESIUM - TITANIUM CATALYST SYSTEMS FOR THE POLYMERIZATION OF UNSATURATED MONOMERS"

submitted by Mr. G. Satyanarayana was carried out by the candidate under my supervision. Such material as has been obtained from other sources has been duly acknowledged.

S. Sivaram

S. Sivaram,
Research Guide.

TABLE OF CONTENTS

CHAPTER I

MAGNESIUM - TITANIUM CATALYST SYSTEMS FOR OLEFIN POLYMERIZATION

CHAPTER II

OBJECTIVE AND APPROACHES OF PRESENT INVESTIGATION

CHAPTER III

A MAGNESIUM CHLORIDE-TETRAHYDROFURAN DERIVED SUPPORT FOR OLEFIN POLYMERIZATION CATALYSTS

CHAPTER IV

SYNTHESIS AND CHARACTERIZATION OF XYLENE SOLUBLE MAGNESIUM - TITANIUM CATALYSTS

CHAPTER V

POLYMERIZATION OF ETHYLENE USING A SOLUBLE MAGNESIUM - TITANIUM CATALYST

CHAPTER VI

SYNTHESIS AND CHARACTERIZATION OF POLYMERS OF HEXENE - 1 AND OCETNE -1 USING XYLENE SOLUBLE MAGNESIUM - TITANIUM CATALYST

CHAPTER VII

SYNTHESIS AND CHARACTERIZATION OF POLY(PHENYLACETYLENE)S USING XYLENE SOLUBLE MAGNESIUM - TITANIUM CATALYST

CHAPTER VIII

SYNTHESIS, CHARACTERIZATION AND POLYMERIZATION OF ETHYLENE USING A MAGNESIUM CHLORIDE SUPPORTED BIS(CYCLOPENTADIENYL) TITANIUM(IV)DICHLORIDE CATALYST SYSTEM

CHAPTER IX

APPENDICES

A-1

A-2

A-3

ABSTRACT

The Thesis describes investigations that elucidate the role of Magnesium Chloride support in Ziegler - Natta catalysts for the polymerization of unsaturated monomers. Two, otherwise, inefficient Ti - based polymerization catalysts, namely titanium -n-butoxide (TNB) and dicyclopentadienyl titanium(IV) chloride were chosen for this study. A novel route to the preparation of $MgCl_2.2THF$ was discovered and used as support for the synthesis of two unique catalysts systems, namely (a) a homogeneous xylene soluble Mg - Ti catalyst based on TNB (b) a heterogeneous $MgCl_2$ supported titanocene catalyst. The two catalysts were used for ethylene polymerization in conjunction with alkylaluminums as cocatalysts. The results show that $MgCl_2$ plays a significant role in converting the otherwise inefficient titanium based catalysts to efficient polymerization catalysts. The role of support in transforming the nature of active centers has been explained based on the known chemistry of Mg - Ti catalysts.

The xylene soluble Mg - Ti catalyst is also active towards the polymerization of hexene-1 and octene-1 as well as phenylacetylene. The catalyst yields the first ever narrow molecular weight distribution of poly(α-olefin)s and poly(phenylacetylene)s with significantly higher proportion of soluble fraction compared to hitherto known Ziegler - Natta catalysts for phenylacetylene.

Different techniques of characterization such as elemental analysis, UV, ^{1}H NMR, ^{13}CP-MAS NMR, FT-IR, ESR, Powder XRD, GPC and TGA have been employed for characterizing both the catalyst and polymers obtained in the present investigation.

GLOSSARY

acac : Acetyl acetonate

C_p^* : Total Concentration of Active Centers (mol/mol of Ti)

C_p^{*a} : Concentration of Atactic Active Centers (mol/mol Ti)

C_p^{*i} : Concentration of Isotactic Active Centers (mol/mol Ti)

Cp : Cyclopentadienyl

Cp^* : Pentamethyl cyclopentadienyl

DEAC : Diethylaluminumchloride

dmg : Dimethylene Glycol

EB : Ethyl Benzoate

EDTA : Ethylene Diamine Tetra Acetate Sodium Salt

ET : Ethyl

Et : Ethylene

Flur : Fluorenyl

Ind : Indenyl

$IndH^4$: Tetrahydro-1-indenyl

k_p : Polymerization Rate Constant (lit/mol/s)

k_t^M : Chain Transfer Constant to Monomer

k_t^{Al} : Chain Transfer Constant to Cocatalyst

k_t^H : Chain Transfer Constant to Hydrogen

MPT : Methyl-p-toluate

MAO : Methylaluminoxane

PES : Phenyltriethoxy silane

R_p : Rate of Polymerization (M sec^{-1})

TNB : Titanium -n- butoxide

THF : Tetrahydrofuran

TIBAL : Triisobutylaluminum

TMA : Trimethylaluminum

TEAL : Triethylaluminum

TOAL : Trioctylaluminum

TGA : Thermogravimetric Analysis

LIST OF TABLES

LIST OF FIGURES

INTRODUCTION

1.0 HISTORY OF ZIEGLER - NATTA CATALYSTS

1.1 Early History and Developments

Discoveries in the laboratories of Professor Karl Ziegler in the fall of 1953 and Professor G. Natta in the spring of 1954 created a revolution in polymer science and organometallic chemistry. Ziegler and co-workers discovered that alkylaluminum compounds in combination with transition metal halides in an inert atmosphere and solvent could polymerize ethylene under normal temperature and pressure to yield a solid polymer of high molecular weight and linear structure.

Ziegler and Holzkamp, while studying the organometallic route to the synthesis of olefins by growth reaction (Afbau reactions, equations 1.1 & 1.2),

$$AlH_3 + 3\,H_2C{=\!=}CH_2 \text{ -----------> } Al(CH_2CH_3)_3 \qquad 1.1$$

$$Al(CH_2CH_3)_3 + 3\,CH_2 == CH_2 \text{ ---------> } Al(CH_2CH_2CH_2CH_3)_3 \qquad 1.2$$

found that small traces of colloidal nickel, inadvertently left in the reactor, caused faster displacement reaction yielding butene-1[1]. This prompted them to study the effect of other metal compounds on Afbau reaction. Subsequently, Breil observed the conversion of ethylene to a white solid cake in presence of zirconium acetylacetonate and triethylaluminum. On further investigations, it was shown that transition metal compounds of Group IV - VI were active catalysts for polymerization of ethylene[2]. Characterization of poly(ethylene) obtained by this route revealed that it had a linear unbranched structure and high molecular weights.

After Ziegler's disclosure of his discovery to Montecatini in Italy, Natta working as a consultant to the company at that time, undertook investigations of this new class of catalysts within the terms of agreement between Ziegler and Montecatini[3]. This led to the discovery of stereoregular polymers of 1-alkenes such as propylene, 1-butene and styrene. Ziegler concentrated on polymerization of ethylene and its copolymerization with 1-alkene and Natta on stereospecific polymerization of α-olefins. For their unique contribution, Prof. Ziegler and Natta shared the prestigious Nobel Prize for chemistry in 1963.

Independent and simultaneous research carried out in early 1950's in industrial laboratories also generated a different class of polymerization catalysts formed from metal oxides of Group V-VII[4]. These catalysts are also low pressure ethylene polymerization catalysts. For better catalytic activity, the transition metal oxides are supported on high surface area solids such as silica, alumina, silica-alumina and clay. Silica supported chromium trioxide(CrO_3) catalyst, commonly known as Phillips catalyst, is the most successful transition metal oxide catalyst for ethylene polymerizations.

1.2 Developments Since 1965

The commercial importance of Ziegler - Natta catalyst system has stimulated enormous amount of research in scientific and industrial laboratories during the past thirty years. Development and commercialization of heterogeneous high activity supported transition metal catalysts based on reaction of specific magnesium, titanium and aluminum compounds and the recent discovery of homogeneous metallocene - methylaluminoxane catalysts showing high activity, stereo- and regiospecificity towards olefin polymerization were the major achievements during the past three decades (Table 1.1). The major objectives towards design and development of new catalysts are high activity, stereospecificty, ability to polymerize and copolymerize a wide variety of monomers, control of morphology as well as control of molecular weight distribution.

2.0 DEFINITION AND TYPES OF ZIEGLER - NATTA CATALYSTS

Both basic and commercial interest in developing newer combinations of Ziegler - Natta catalysts have prevented the emergence of a simple classification of these catalysts. Boor defined these catalyst systems as products formed from reaction involving certain transition metal compounds of Group IV - VIII, such as titanium, vanadium, chromium compounds with alkyl or aryl halides of Group I - IV[5]. Further

Table 1.1: Chronolgy of Development in Ziegler - Natta Catalysis

Year	Catalyst System	Monomer	Activity (Kg Polymer/gmetal/h)	Tacticity (%)
1953 - 55	$TiCl_4$ - Et_3Al	Ethylene	10 - 15	---
		Propylene	5 - 10	50 - 60
	$TiCl_3$ - Et_3Al	Ethylene	5 - 10	---
		Propylene	1 - 3	60 - 80
1955 - 60	$TiCl_3$ Electron Donors - Et_3Al	Propylene	1 - 10	90 - 95
1970 - Present	Supported $MgCl_2$.$TiCl_4$ - Et_3Al	Ethylene	500 - 1000	----
		Propylene	500 - 1000	50 -70
	Supported $MgCl_2$.Electron Donor.$TiCl_4$ - Et_3Al	Ethylene	500 - 1000	---
		Propylene	300 - 500	90 - 99
1980 - Present	Homogeneous Metallocene - Methylaluminoxane	Ethylene	400 - 500	---
1985 - Present	Stereorigid Metallocene - Methylaluminoxane	Propylene	150 - 170	96 - 98
	Homogeneous Aluminum Free Metallocene catalysts.	Propylene	0 - 1	97 - 98

developments like supported high activity catalysts, metallocene- methylaluminoxane and the like do not fall within the scope of the above definition. The most convenient method of classification of these catalysts is as follows,

2.1: Soluble or Homogeneous Ziegler - Natta Catalyst

2.2: Heterogeneous Ziegler - Natta Catalysts

It should be emphasized that these terms imply only the physical state of the catalysts and not the polymerization reaction as a whole.

2.1 Soluble or Homogeneous Ziegler - Natta Catalysts

Since the discovery of homogeneous bis(cyclopentadienyl) titanium(IV) dichloride (metallocene) - alkylaluminum catalyst system, homogeneous catalysts have achieved significance for mechanistic and kinetic studies[6]. The discovery of homogeneous highly- active and stereospecific metallocene - methaylaluminoxane catalysts have stimulated renewed commercial and scientific interest in homogeneous catalysts[7]. In a homogeneous catalyst system every site has equal reactivity. This causes narrowing of molecular weight distributions. Homogeneous catalysts can further be subdivided into two classes,

2.1.1 Metallocene Based Homogeneous Catalysts

2.1.2 Vanadium Based Homogeneous Catalysts

2.1.1 Metallocene Based Homogeneous Catalysts

Natta and co-workers and Breslow and Newburg studied the metallocene based catalysts for the polymerization of ethylene with alkylaluminums[8]. Later Chein established through kinetic studies, the nature of decay process which resulted in the deactivation of catalysts system[9]. This was further confirmed by Reichert[9]. These catalyst systems, therefore, were mostly used for kinetic and mechanistic studies and had little practical significance, until recently.

Sinn and Kaminsky in 1980 made a significant observation that metallocenes in toluene solution when activated with methylaluminoxane can polymerize ethylene with activities in the order of 25×10^6 g PE$(gZr)^{-1}$ h^{-1}[10]. A large excess of methylaluminoxane (high Al/Zr ratio) is generally required for high activity. Methylaluminoxanes are usually prepared from the controlled hydrolysis of trimethylaluminum with $CuSO_4.5H_2O$ or $Al_2(SO_4)_3.16H_2O$ in toluene. Propylene is also reported to be polymerized with this catalyst system but only to atactic polypropylene[11]. More recently, chiral and stereorigid metallocenes activated with methylaluminoxanes have been shown to polymerize propylene to a variety of stereostructures namely isotactic, syndiotactic and hemi-isotactic[12].

2.1.2 Vanadium Based Homogeneous Catalysts

Homogeneous vanadium catalysts based on VCl_4 - $AlEt_2Cl$ system have been extensively studied for the polymerization of propylene to yield highly syndiospecific polymer at temperatures below -50°C[13]. It is observed that as the temperature is increased the polymerization becomes non stereospecific.

Using this homogeneous and stereospecific catalyst system a large family of stereospecific homo polymers, block , random and alternating copolymers can be obtained. But the disadvantage of maintaining very low temperatures has restricted the commercial development of these catalyst systems. Homogeneous catalysts based on vanadium are also used for the synthesis of elastomeric ethylene and propylene copolymers(EPR's and EPDM's).

2.2 Heterogeneous Ziegler - Natta Catalysts

Early commercial success of heterogeneous catalysts over homogeneous catalysts stimulated substantial research efforts on such catalysts. The success of these catalysts can be traced to their high activity, stability, stereo- and regiospecificity, elimination of catalyst removal steps and control of polymer morphology. Heterogeneous Ziegler - Natta catalysts can be further subdivided into,

2.2.1 Unsupported Heterogeneous Catalysts

2.2.2 Supported Heterogeneous Catalysts

2.2.1 Unsupported Heterogeneous Catalysts

Classical δ - $TiCl_3$ as well as Solvay type δ - $TiCl_3$, and complexes of $TiCl_3$ with various additional adjuvants added to enhance the activity and stereospecificity, fall under this category[14,15]. The unsupported titanium based catalysts described in the literature are summarized in the Table 1.2 with their salient features. Low to moderate activity and high residual metal contents in the polymer are the characteristic features of the unsupported catalysts.

2.2.2 Supported Heterogeneous Catalysts

Natta and co-workers extensive research showed that less than one percent of titanium atoms present on the surface of unsupported titanium based catalysts were active in the polymerization of olefins[16]. Since then number of approaches have been adopted to increase the polymerization efficiency by increasing the concentration of active titanium centers. One of the successful methods is through supporting titanium compounds on high surface area inorganic inert carriers called supports. The success of this method is evident by the volume of published and patented catalyst systems based on different supports and active titanium compounds. Various supports such as silica, alumina, clay, chromium oxide and alkali earth metal compounds have been evaluated as carriers for titanium compounds[17,18]. Extensive studies have resulted in the identification of anhydrous magnesium chloride as the ideal support material. In fact, all magnesium compounds are well studied as supports of titanium compounds. This is believed to be due to similarities in size and shape of magnesium and titanium cations. Reactive compounds like MgH_2,$Mg(OH)Cl$, $MgSO_4$, MgO, $Mg(OR)_2$ have also been tested as supports of titanium halides. These studies generated several high efficiency catalysts for olefin polymerization. Some of these are based on the reaction between titanium and magnesium compounds such as MgH_2[19], $Mg(OH)Cl$[20], $MgSO_4$[21], MgO[22], $Mg(OR)_2$[23]. Nevertheless, the most active catalysts are based on activated anhydrous magnesium chloride(disordered crystalline structure called δ - $MgCl_2$) or

Table 1.2: Examples of Heterogeneous Unsupported Titanium Based Catalysts

Catalyst System	Monomer	Activity (Kg Polymer/g Ti/h)	Isotacticity (%)
$TiCl_3$ - Et_3Al	Ethylene	1 - 3	---
	Propylene	1 - 3	80 - 90
$TiCl_3$.1/3$AlCl_3$ - Et_3Al or Et_2AlCl	Ethylene	10 - 20	---
	Propylene	10 - 20	80 - 90
$TiCl_3$.1/3$AlCl_3$/Electron Donor - Et_3Al	Ethylene	5 - 10	----
	Propylene	3 - 7	92 - 96

reaction which would bring about its formation in situ, namely, the reaction between $TiCl_4$ and reactive magnesium compounds, such as Grignard reagents and dialkylmagnesiums[24].

These newer developments in Ziegler - Natta catalysis ushered great progress in polyethylene production technologies, making it possible to develop new processes which are conceptually simpler and more economical than the traditional ones. However, these catalysts were unsuitable for producing isotactic polypropylene. Introduction of suitable additives called stereoregulators to these catalysts led to the discovery of highly active and stereospecific magnesium chloride supported catalysts for propylene polymerization[26]. The scientific understanding of these catalysts has slowly emerged during the past two decades. In the following sections we shall discuss the synthesis, characterization and salient features of Mg - Ti catalysts with respect to ethylene and propylene polymerization chemistry.

3.0 SUPPORTED MAGNESIUM - TITANIUM CATALYSTS FOR OLEFIN POLYMERIZATION

3.1 Unique Role of Mg^{+2} Cation in Magnesium - Titanium Catalysts

It was observed that Mg^{+2} cations played a vital role in high activity magnesium chloride supported catalysts during olefin polymerization. This was attributed to the similarities in size, shape, coordination number, electronegativity and electronic structure of magnesium and titanium (Table 1.3). These similarities probably permitted an easy substitution between ions in Mg - Ti catalyst frame work. Further, it was observed that

i) Active titanium catalysts supported on anhydrous magnesium chloride as supports are characterized by high rates of polymerization possibly due to easy substitution of Mg^{+2} ions for Ti^{+4} in the crystal lattice of Mg - Ti catalysts.

ii) Active titanium centers are diluted by the presence of inert magnesium ions. This dilution influences drastically the number of active centers that tend to be isolated. Hence, the number of active centers are higher than the unsupported titanium catalysts.

Table 1.3: Similarities Between Mg^{+2} and Ti^{+4} Ions of Magnesium - Titanium Catalysts

Ion	Radius (A°)	Size/Charge	Electronegativity	Electronic Structure	Coordination Number	Geometry
Ti(IV)	0.068	0.017	1.5	$3s^2,3p^6,3d^0$	6	Octahedral
					4	Tetrahedral
					5	Distorted Trigonal Bipyramid
Mg(II)	0.65	0.033	1.3	$2s^2,2p^6$	6	Octahedral
					4	Tetrahedral

iii) It is observed that the presence of inert magnesium ions stabilize the titanium centers from deactivation process relative to soluble or heterogeneous unsupported catalysts.

iv) It is also observed that chain transfer processes are enhanced as the Mg/Ti ratio increases. Hence, number average molecular weight of polymer decreases as Mg/Ti increases.

v) Control on number average molecular weights regulates the molecular weight distribution ($\bar{M}_w/\bar{M}_n$ = 3-5). Hence, presence of Mg^{+2} cation controls to some extent molecular weight distribution of polymer.

vi) The ability of Mg^{+2} to expand its coordination number permits easy complexation of Mg^{+2} cation with stereoregulators (electron donors), such as ethers, ester etc. These donors, on complexation with active sites, control the stereospecificity of polymerization.

3.2 Comparison of Performance of Mg - Ti Catalysts with Unsupported Ti- Catalysts

Supported Mg - Ti catalyst systems are generally superior to unsupported Ti catalysts for both ethylene and propylene polymerization (Table - 1.4 & 1.5). Following are the significant advantages of the supported Mg - Ti catalysts;

i) Higher concentrations of active sites (C_p^*), typically in the range of 10 - 1 X 10^{-3} mole $(\text{moleTi})^{-1}$ for supported catalyst, whereas it is only 0.04 - 0.1 X 10^{-3} mole $(\text{moleTi})^{-1}$ for unsupported catalysts.

ii) Higher rates of polymerization (k_p), typically in the range of 5 - 20 X 10^{-2} l mole^{-1} s^{-1}, as compared to 1.1 - 0.5 X10^{-2} l mole^{-1} s^{-1} for unsupported catalysts for propylene polymerization. However, for ethylene polymerization, (k_p) does not significantly increase with supported catalysts.

iii) Supported catalysts show higher activities, namely 100 - 500 kg of polymer /g Ti/h, as compared to 1 - 5 kg of polymer/ g Ti/h for unsupported catalysts. This increase is attributed to the higher number of active centers in supported catalysts.

Table 1.4: A Comparison of Ethylene Polymerization Behavior of Supported Magnesium - Titanium and Unsupported Titanium Catalysts

Catalyst System	Method of Preparation of Catalyst	Activity (kg PE/g Ti/h)	Features
α $TiCl_3$ - AlR_3	Hydrogen reduction of $TiCl_4$	0.01	$[C^{*}_{p}] = 2 - 6.3$ $k_p = 25$
δ $TiCl_3$ - AlR_3	By reduction of $TiCl_4$ with Ti	1 - 2	$[C^{*}_{p}] = 0.36 - 1.0$ $k_p = 70$
δ $TiCl_3$ - AlR_2Cl	By reduction of $TiCl_4$ with Ti	3 - 10	$[C^{*}_{p}] = 1.4 - 2.0$ $k_p = 73$
δ$TiCl_3$/Electron Donor - AlR_3	By reduction of $TiCl_4$ with Ti	3 - 5	$[C^{*}_{p}] = 0.1 - 1.0$ $k_p = 72$
$MgCl_2.TiCl_4$ - AlR_3	Ball milling $MgCl_2$ and $TiCl_4$	400 - 500	$[C^{*}_{p}] = 5.2 - 1.8$ $k_p = 129$
$MgCl_2$/Ethyl Benzoate/$TiCl_4$ - AlR_3	Ball milling $MgCl_2$ and ethyl benzoate later on thermochemical reaction with $TiCl_4$	100 - 200	$[C^{*}_{p}] = 10 - 50$ $k_p = 121$
$Mg(OEt)_2$/$TiCl_4$ - AlR_3	Ball milling $Mg(OEt)_2$ and $TiCl_4$	50 - 70	$[C^{*}_{p}] = 10 - 20$ $k_p = 200$
$C_8H_{17}MgBr$/$TiCl_4$ - AlR_3	Grignard decomposition	10 - 20	$[C^{*}_{p}] = 10 - 30$ $k_p = 280$

Units of $[C^{*}_{p}]$: x 10^{-3} $mol(mol.Ti)^{-1}$; k_p : $dm^3mol^{-1}s^{-1}$

Table 1.5: A Comparison of Propylene Polymerization Behavior of Supported Magnesium - Titanium Catalysts and Unsupported Titanium Catalysts

Catalyst System	Method of Preparation of Catalyst	Activity (kg PP/g Ti/h)	Features
α $TiCl_3$ - AlR_2Cl	Hydrogen reduction of $TiCl_4$	0.01	$[C_p^*] = 0.33$ $k_p = 71$
δ $TiCl_3$ - AlR_2Cl	By redution of $TiCl_4$ with Ti	0.5 - 1.0	$[C_p^*] = 1.7$ $k_p = 91$
$\delta TiCl_3$/Electron Donor - AlR_2Cl	By reduction of $TiCl_4$ with Ti	3 - 5	$[C_p^*] = 0.1 - 1$ $k_p = 85$
$MgCl_2TiCl_4$ - AlR_3	Ball milling $MgCl_2$ and $TiCl_4$	25 - 50	$[C_p^{*i}] = 5.2$ $[C_p^{*a}] = 4.1$ $k_p^i = 740$ $k_p^a = 620$
$MgCl_2$/Ethyl Benzoate/ $TiCl_4$-AlR_3	Ball milling $MgCl_2$ and ethyl benzoate later a thermochemical treatment with other components	10 - 20	$[C_p^{*i}] = 2.7$ $[C_p^{*a}] = 1.3$ $k_p^i = 870$ $k_p^a = 330$
$MgCl_2$/Ethyl Benzoate/p-cresol/$TiCl_4$-AlR_3/ Electron Donor	Ball milling $MgCl_2$ and ethyl benzoate later a thermochemical treatment with other components	4.0	$[C_p^{*i}] = 6.7$ $[C_p^{*a}] = 6.3$ $k_p^i = 200$ $k_p^a = 11$
$MgCl_2$/2-Ethylhexanol-1/ Diisobutylphathalate/ $TiCl_4$-$AlEt_3$/ Electron Donor	Thermochemical reaction between 2-ethyl-hexanol solubilized $MgCl_2$ and later with $TiCl_4$	16.1	$[C_p^{i}] = 250$ $[C_p^{*a}] = 150$ $k_p^i = 206$ $k_p^a = 11$

Units of $[C^{*i}_p]$ & $[C^{*a}_p]$: $\times 10^{-3}$ mol(mol.Ti)$^{-1}$; k_p : $dm^3mol^{-1}s^{-1}$

iv) Use of stereoregulators with organoaluminum compounds enable control of polymer stereospecificity with Mg - Ti catalysts. By suitable adjustment of alkylaluminum to donor ratio, polymer isotacticity in the range of 94 - 99% can be achieved. With unsupported catalysts control of donor/Ti ratio can lead to improved isotacticity. However, the range of control is relatively narrow, namely, 90 - 94%.

v) High activity with Mg - Ti catalysts obviates the need for catalyst killing and removal of unreacted catalysts residues. Polyolefins processes involving unsupported catalysts require catalyst killing and removal to attain the specified titanium level (<5ppm) in the polymer.

vi) Control of morphology of polymer particles by regulating the morphology of catalyst particles is possible with Mg - Ti catalysts. This has led to development of polyolefin processes where the final step of extrusion and pelletization have been totally eliminated. Morphology control with unsupported catalysts has not met with such spectacular success.

Inspite of the many advantages of the Mg - Ti catalysts they still suffer from a few drawbacks. These are,

i) High ash content in the polymer contributed by the presence of $MgCl_2$.

ii) High level of chlorine content in the polymer, which requires neutralization to prevent the adverse effects of chloride ions in down stream processing equipments such as extruders.

iii) Although Mg - Ti catalysts produce relatively narrower molecular weight distribution polymer compared to unsupported catalysts, variation of molecular weight distribution with a given catalyst continues to be still a challenge.

3.3 Synthesis of Magnesium - Titanium Catalysts

Based on published and patented literature, synthesis of Mg - Ti catalysts can be broadly discussed in terms of two approaches:

3.3.1 Synthesis of Magnesium - Titanium Catalysts Based on Activation of Preformed Anhydrous Magnesium Chloride and Titanium Compounds

3.2.2 Synthesis of Magnesium - Titanium Catalysts Based on Insitu Precipitation of Mg - Ti Complexes from Reactive Reagents

3.3.1 Synthesis of Mg - Ti Catalysts Based on Activation of Preformed Anhydrous Magnesium Chloride and Titanium Compounds

Anhydrous magnesium chloride, existing in α, β or δ forms, is employed to synthesize highly active supported Mg - Ti catalysts. α form of $MgCl_2$ is obtained on reduction of $TiCl_4$ with magnesium metal[27]; β form, by dehydration of $MgCl_2.6H_2O$ with $SOCl_2$[28] and δ form, by mechanical treatment of α or β forms, or by chlorination of organic derivatives of magnesium. Preformed $MgCl_2$ is subjected to activation in two ways for the purpose of synthesis of highly active Mg - Ti catalysts.

3.3.1.1 Physical Activation

3.3.1.2 Chemical Activation

3.3.1.1 Physical Activation

Physical activation involves ball milling of anhydrous magnesium chloride with a transition metal component like $TiCl_4$, $Ti(OR)_4$ and electron donor such as ethyl benzoate as the first step, followed by thermochemical treatment (if necessary) with a transition metal component. The primary effect of the physical activation is to break the layered structure of magnesium chloride crystals to introduce structural variations associated mainly with rotational disorder of the Cl-Mg-Cl layers. This disorder promotes reduction of crystallite dimensions to <10nm along the weakly bonded layers. On prolonging the milling time, X-ray diffraction peaks of $MgCl_2$ becomes progressively broader indicating the decrease in size of crystallites. The rate of broadening of X-ray peaks of $MgCl_2$ was more rapid when milled with $TiCl_4$ or electron donor compared with milling of pure $MgCl_2$. This could be due to the diffusion of $TiCl_4$ or electron donor into the inner layers of $MgCl_2$, causing easier breaking of layers of $MgCl_2$. Further, it was confirmed that grinding affects the crystallite dimensions of (0,0,1) plane for $MgCl_2$ - $TiCl_4$ system and (1,1,0) plane for $MgCl_2$ - ethylbenozate system[29]. Also, in Mg - Ti catalysts, active titanium centers are in a high state of dispersion on $MgCl_2$; thus, when a monomer enters into the internal voids of the $MgCl_2$ substrate and polymerizes, the catalyst particle disintegrates into individual crystallities having very small dimensions, causing an increase in the activity of polymerization.

Several studies led to an understanding of the nature and performance of highly active Mg - Ti catalysts obtained by physical activation method. These studies correlated activity and performance of catalysts to the solid state structure of catalyst. The effect of ball milling on $MgCl_2$, $MgCl_2$ - $TiCl_4$ and $MgCl_2$ - electron donor systems was then correlated with activity and performance of these catalysts[30,31]. More recently, effect of ligand environment around the titanium center in Mg - Ti catalysts have also been examined.

Studies have shown that milling of anhydrous $MgCl_2$ with $TiCl_4$ or electron donor proceeds through three distinguishable stages. In the first stage (10h), the specific surface area increases very rapidly, whereas in the second stage (20-50h), it remains constant. Beyond 50h, i.e., third stage of grinding, the specific surface area decreases and essentially remains constant[33]. It is interesting to note that in ethylene polymerization the catalyst activity parallel the three stages of grinding.

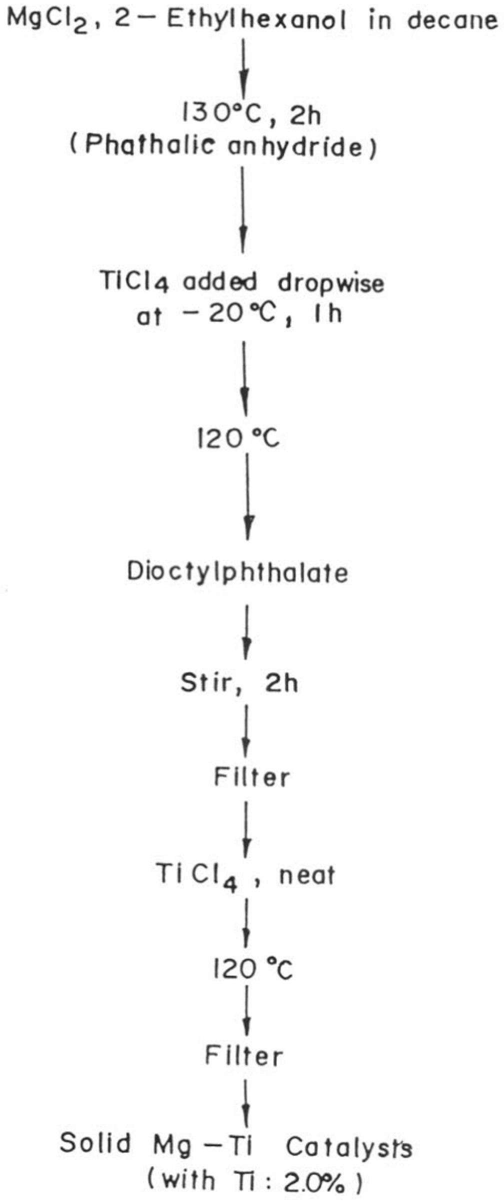
3.3.1.2 Chemical Activation

This method involves dissolution of preformed anhydrous $MgCl_2$ in a polar electron donor followed by a complex series of treatments with electron donors, titanium and other compounds to generate highly active Mg - Ti catalysts with defined structures[34,35]. These defined bimetallic complexes have high activity towards olefin polymerizations. Examples of bimetallic complexes of Mg - Ti reported in the literature are shown in Table 1.6. A typical synthesis of Mg - Ti catalyst by chemical activation process is schematically represented in Scheme - 1.1.

The formation of Mg - Ti catalyst by this method comprises of three steps. In the first step ,crystalline magnesium chloride is dissolved in polar solubilizing agent, leading to the disruption of crystalline $MgCl_2$ structure and creation of amorphous structure for

Table 1.6: Examples of Heterogeneous Magnesium - Titanium Catalysts Formed from Preformed Magnesium Chloride, Titanium Tetrachloride and an Electron Donor

Electron Donor	Catalyst System	Monomer	Polymerization Conditions	Activity (kg poly/g Ti/h)	Tacticity (%)	Reference
Ethanol	$MgCl_2/C_2H_5OH/TiCl_4$ - AlR_3	Ethylene	Pressure : 7 kg/cm^2, Temp., : 70°C, Time : 1 hour.	40 - 60	--	34
Butanol	$MgCl_2/C_4H_9OH/TiCl_4$ - AlR_3	Ethylene	Pressure : 1 kg/cm^2, Temp., : 80°C, Time : 1 hour	25 - 30	---	33
2-Ethyl-hexanol	$MgCl_2$/2-Ethyl Hexanol/Phthalic anhydride/$TiCl_4$ - $AlEt_3$/Electron Donor	Propylene	Pressure : 7 kg/cm^2, Temp., : 50°C, Time : 1 hour	15.5	96	88
Tetrahydrofuran	$MgCl_2$/Tetrahydrofuran/$TiCl_4$ - $AlEt_3$	Ethylene	Pressure : 2 kg/cm^2, Temp., : 70°C, Time : 1 hour.	150 - 200	---	35



Sche.1.1 Example of Preparation of a Solid Mg - Ti Catalyst

magnesium chloride. In this state, the Mg^{+2} cation expands the coordination number by forming well defined molecular complex. This process is accompanied by increase in BET surface area and decrease in crystallite size, indicating that the small crystallites are held together in the form of layer aggregates by complexation with alcohols. In the second stage, these complexes are further treated with silicon compounds anhydrides or alkylaluminumchloride, resulting in the removal of excess of alcohol by chemical reaction and precipitation of $MgCl_2$. In the third and final step, thermal treatment of $MgCl_2$ with $TiCl_4$ results in the fixation of Ti on the support, presumably on the exposed edges and corners of (101) faces of $MgCl_2$. This fixation provides structural bonding between Mg & Ti. These bonds are nonuniformly distributed on the surface of $MgCl_2$ and are highly active and stable when compared with physical activation methods.

3.3.2 Synthesis of Magnesium - Titanium Catalysts Based on Insitu Precipitation of Magnesium - Titanium Complexes from Reactive Reagents

Catalysts formed by the reduction of Ti - compounds with reactive magnesium reagents fall in this category. An examination of the literature reveals two general approaches,

3.3.2.1 Decomposition of Grignard Reagents

3.3.2.2 Decompositions of Soluble Bivalent Salts of Mg+2 Cations

3.3.2.1 Decomposition of Grignard Reagents

Organomagnesium compounds are known to cause reduction of titanium (IV)chlorides (Equation 1.3). This leads to the cocrystallization of a magnesium - titanium complex with disordered structure, as evidenced by X - ray diffraction. These magnesium - titanium complexes when treated with an organoaluminum compound show high polymerization activity (Table - 1.7).

$TiCl_4 + RMgCl$ -----------> $TiCl_3. MgCl_2$ + organic fragments 1.3

Haward and co-workers and more recently Munoz-Escalono co-workers have extensively studied the effect of Grignard reagents on the reduction of $TiCl_4$ in polar

Table 1.7: Examples of Magnesium - Titanium Catalysts Formed Through Decomposition of Grignard Reagents with Titanium Tetrachloride

Grignard Reagent	Catalyst System	Monomer	Polymerization Conditions	Activity (Kg poly/g Ti/h)	Tacticity	Reference
C_4H_9MgCl	$C_4H_9MgCl/TiCl_4$ - AlR_3	Ethylene	Pressure : 0 - 1 kg/cm^2, Temp., : 80°C, Time : 3 hours	78.8	--	36
C_6H_5MgCl	$C_6H_5MgCl/TiCl_4$ - AlR_3	Ethylene	Pressure : 0 - 1 kg/cm^2, Temp., : 80°C, Time : 3 hours	490.8	--	36
$C_{12}H_{25}MgBr$	$C_{12}H_{25}MgBr/TiCl_4$ - AlR_3	Ethylene	Pressure : 5 kg/cm^2, Temp., : 50°C, Time : 1 - 2 hours	749	---	37
C_4H_9MgBr	$C_4H_9MgBr/TiCl_4$ - AlR_3	Ethylene	Pressure : 5 kg/cm^2, Temp., : 50°C, Time : 1 - 2 hours	604	--	37
C_4H_9MgI	$C_4H_9MgI/TiCl_4$ - AlR_3	Ethylene	Pressure : 0 - 1 kg/cm^2, Temp., : 80°C, Time : 3 hours	462	--	36
C_4H_9MgCl	$C_4H_9MgCl/AlCl_3/CH_3Si(OC_2H_5)_3/$ $TiCl_4$ - AlR_3/Electron Donor	Propylene	Pressure : 1 kg/cm^2, Temp., : 60°C, Time : 1 hours	32.4	90.4	38
	$C_4H_9MgCl/AlCl_3/CH_3Si(OC_2H_5)_3$/Ethyl Benzoate/$TiCl_4$ - AlR_3/Electron Donor	Propylene	Pressure : 1 kg/cm^2, Temp., : 60°C, Time : 1 hours	59.4	89.0	38

and non polar solvents[36,37]. No major change in homopolymerization activities of ethylene by varying the medium or conditions on the performance of catalyst was noticed. It was also noted that no specific x- ray line of $MgCl_2$ or $TiCl_3$ are noted in Mg - Ti catalyst indicating that complexes are distinct and have very small crystallite sizes. Transmission electron micrograph also showed a very fine nodular structure with primary particle size of less than 50nm.

Recently, soluble Mg - Ti catalysts have been synthesized by reacting Grignard reagents with $TiCl_4$ in an electron donor solvents[39]. These soluble catalysts are found to be good for copolymerization of ethylene and propylene.

3.3.2.2 Decompositions of Soluble Bivalent Salts of Mg^{+2} Cations

Soluble bivalent magnesium compounds such as R_2Mg, $(RO)_2Mg$, Mg(Stearate) on treatment with Ti - compounds in presence or absence of electron donors in a nonpolar solvents yield highly active Mg - Ti catalysts[40,41,42]. Examples are shown in the Table - 1.8. It is observed that during the catalyst preparation stage, the original structure of bivalent magnesium compound is completely destroyed and new crystalline species are formed with large increase in surface area. Modification of properties of catalysts is also possible by introduction of additional elements or donors in the catalytic complexes, or by carrying out reaction in the presence of an acid halide.

3.4 Techniques of Characterization of Mg - Ti Catalysts

Detailed characterization of Mg - Ti catalysts is critical for the understanding of the mechanism of polymerization. Different analytical methods have been used to relate the catalyst activity with the structure and composition of catalysts. Most commonly used techniques are powder XRD, IR, BET, mercury intrusion porosimetry, ESR, NMR, and scanning electron microscopy. A brief description of various techniques of characterization of Mg - Ti catalysts are summarized in the following sections[43,44,45].

Table 1.8: Examples of Magnesium - Titanium Catalysts Formed Through Decomposition of Bivalent Magnesium Reagents with Titanium Tetrachloride

Bivalent Mg^{+2} Reagent	Catalyst System	Monomer	Polymerization Conditions	Activity (Kg poly/g Ti/h)	Tacticity (%)	Reference
$Mg(n\text{-}C_4H_9)_2$	$Mg(n\text{-}C_4H_9)_2$/Electron Donor/$SiCl_4$/$TiCl_4$ - AlR_3/Electron Donor	Propylene	Pressure : 1.2 kg/cm^2, Temp., : 70°C, Time : 2 hours $[H_2]$: 0.006mol.	8.3	98.5	40
$Mg(n\text{-}C_4H_9)_{1.5}$ $(n\text{-}C_8H_{17})_{0.5}$	$Mg(n\text{-}C_4H_9)_{1.5}$ $(n\text{-}C_8H_{17})_{0.5}$ Electron Donor /$SiCl_4$/$TiCl_4$ - AlR_3/Dimethoxydiphenylsilane	Propylene	Pressure : 1.2 kg/cm^2, Temp., : 70°C, Time : 2 hours $[H_2]$: 0.006mol.	8.0	98.7	40
$Mg(n\text{-}C_4H_9)_{0.75}$ $(n\text{-}C_8H_{17})_{0.25}$ $(OC_2H_5)_1$	$Mg(n\text{-}C_4H_9)_{0.75}(n\text{-}C_8H_{17})_{0.25}(OC_2H_5)_1$/ElectronDonor/$SiCl_4$/$TiCl_4$ - AlR_3/Dimethoxydiphenylsilane	Propylene	Pressure : 1.2 kg/cm^2, Temp., : 70°C, Time : 2 hours $[H_2]$: 0.006mol.	6.78	98.8	40
$C_4H_9Mg(OC_3H_7^i)MgC_{12}H_{25}Mg(OC_3H_7^i)Mg$	$C_4H_9Mg(OC_3H_7^i)Mg/TiCl_4$ - AlR_3	Ethylene	Pressure : 4.5 kg/cm^2, Temp., : 80°C, Time : 3 hours.	570	--	36

Table 1.8: Examples of Magnesium - Titanium Catalysts Formed Through Decomposition of Bivalent Magnesium Reagents with Titanium Tetrachloride

Bivalent Mg^{+2} Reagent	Catalyst System	Monomer	Polymerization Conditions	Activity (Kg poly/g Ti/h)	Tacticity (%)	Reference
$C_4H_9Mg(OC_3H_7^i)MgC_{12}H_{25}Mg(OC_3H_7^i)Mg$	$C_{12}H_{25}Mg(OC_3H_7^i)Mg/TiCl_4$ - AlR_3	Ethylene	Pressure : 4.5 kg/cm^2, Temp., : 80°C, Time : 3 hours.	604	--	36
$Mg(OEt)_2$	$Mg(OEt)_2/TiCl_4$ - AlR_3	Ethylene	Pressure : 6 kg/cm^2, Temp., : 35 - 85°C, Time : 2 hours.	50 - 70	--	41
$Mg(OEt)_2$	$Mg(OEt)_2/TiCl_4$ - AlR_3/Triethoxyphenylsilane	Propylene	Pressure : 10 kg/cm^2, Temp., : 70°C, Time : 2 hours	11.2	72.1	42
$Mg(OEt)_2$	$Mg(OEt)_2/EB/TiCl_4$ - AlR_3/Triethoxyphenylsilane	Propylene	Pressure : 10 kg/cm^2, Temp., : 70°C, Time : 2 hours	32.7	79.0	42
$Mg(OEt)_2$	$Mg(OEt)_2/ED/SiCl_4/TiCl_4$ - AlR_3/Dimethoxydiphenylsilane	Propylene	Pressure : 10 kg/cm^2, Temp., : 70°C, Time : 2 hours	1.65	86.4	42

3.4.1 Powder XRD Technique

This technique is most commonly employed to characterize and understand structural changes that occur during the various stages of preparation of Mg - Ti catalysts. It provides information on structural parameters like crystal structure and crystallite particle size. The maximum limit of crystallite size is 300A° at large angles and the limit is 100A° with medium angles by X-ray analysis. Although precise crystal dimensions and lattice parameters cannot be obtained, it is useful for understanding the changes occurring at various stages of catalyst preparation involving $MgCl_2$, $MgCl_2$ - $TiCl_4$ $MgCl_2$ - electron Donor and $MgCl_2$ - Electron Donor - $TiCl_4$.

3.4.2 BET or Mercury Porosimetry

Nitrogen adsorption technique and mercury intrusion porosimetry methods are routine techniques for characterization of Mg - Ti catalysts. Both techniques provide information regarding surface area, pore volume and pore size of heterogeneous Mg - Ti catalysts. It is well known that olefin polymerization occurs with participation of active sites present only on the surface of heterogeneous Mg - Ti catalysts. Monitoring of surface area of Mg - Ti catalyst systems at every stage of preparation of catalyst showed that higher the surface area of catalyst, better dispersion of active sites and high rates of polymerization.

3.4.3 IR Spectroscopy

FT-IR and AT FT-IR techniques have been employed for the characterization of Mg - Ti catalyst system. This technique provides information on the organic and inorganic moieties present in the catalyst system and leads to an understanding of the role of electron donor in controlling the activity and specificity of Mg - Ti catalysts. Recently, this technique has been used to predict the effect of activation methods on catalysts performance[46]. AT FT-IR is also used to quantify electron donors present in the matrix of inorganic magnesium chloride complex[47].

3.4.4 NMR Spectroscopy

^{13}CP - MAS NMR has been used as a tool for understanding the chemical interactions involved in every stage of preparation of Mg - Ti catalysts[48]. The 13CP-MAS NMR chemical shifts, on complexation of electron donors with magnesium chloride and titanium compounds, have been studied and an attempt has been made to correlate these shifts with activities of catalysts.

3.4.5 ESR Spectroscopy

This technique is employed to understand the paramagnetic behavior and oxidation states of active transition metal centers in olefin polymerization. It is well known that lower oxidation species (Ti $^{+3}$ or Ti^{+2}) are active for olefin polymerization, hence, ESR technique is employed to characterize the active Mg - Ti catalyst oxidation state, homogeneity and ligand environment during polymerization[49]. With the help of ESR, it can be shown that Ti^{+4} state is responsible for the formation of active species for ethylene and propylene[50]. A plausible structure of active species involved in Mg - Ti catalyst system has also been invoked from ESR studies.

3.4.6 Other Miscellaneous Techniques

Redox titrations[45,50], Optical microscopy[51], ESCA[52], TGA analysis,[53] Extended X-ray absorption fine structure[54] and X-ray absorption near edge structure analysis[36] are some of other techniques adopted to characterize Mg - Ti catalysts. All these techniques have been adopted to explain the unique polymerization features of Mg - Ti supported catalyst systems.

3.5 Structural Features of Magnesium - Titanium Catalysts

3.5 .1 Features of Anhydrous Magnesium Chloride

Anhydrous magnesium chloride exists in two forms, namely, α and β. The α form exhibits cubic close packing structure with stacking sequence of chlorine layers and Mg^{+2} ions at interstitial position with six fold coordination. The β form shows hexagonal close packing structure with single chlorine stacking sequence. These two forms can attain disordered active form (called δ form) on grinding or complexation with electron donors. This form is due to the rotation of Cl- Mg -Cl layers by +60°. The δ - disordered form can also be obtained by synthesizing magnesium chloride using indirect routes. There are only few reports available in the literature that describe the features of $MgCl_2$ obtained by indirect routes. A comparative crystallographic structural features of α, β and δ forms of $MgCl_2$ are shown in Table 1.9

It is observed that X - ray diffraction pattern corresponding to $2\theta = 10 - 50°$ region is the characteristic fingerprint area to understand the structural changes occurring in the formation of disordered active δ form of magnesium chloride. Hence, half peak width of (003) peak, crystallite dimensions corresponding to characteristic peaks and broadening of these characteristic peaks are commonly monitored during the process of synthesis of active magnesium chloride. The features of the active magnesium chloride can be discussed under two separate headings,

3.5.1.1 Features of Active δ - $MgCl_2$ Synthesized Through Physical Activation Methods

3.5.1.2 Features of Active δ- $MgCl_2$ Synthesized Through Chemical Activation Methods

3.5.1.1 Features of Active δ - $MgCl_2$ Synthesized Through Physical Activation

Milling is the chosen physical activation route for synthesizing active δ $MgCl_2$. It creates three different types of surface magnesium ions, namely, i) those present on lateral faces with single vacancy Mg ions having an effective charge of O_o, ii) those present on corners with single vacancy Mg ions having an effective charge of -2/3e and iii) and those present on corners with double vacancy Mg ions having an effective charge of +1/3e[55]. As crystallite size decreases the double vacancy Mg ions increases. The changes occurring during the milling process are commonly monitored by X - ray diffraction technique in terms of CCP structure. Whereas only Xiao et. al., considered

Table 1.9: Structural Features of Crystalline Forms of Anhydrous Magnesium Chloride

Crystal Parameter	α - $MgCl_2$	β - $MgCl_2$	δ - $MgCl_2$
Structure	Cubic Close Packing	Hexagonal Close Packing	A disordered structure consisting of ccp and hcp planes
Lattice Parameters (A°)	a = b = 3.63; c = 17.79.	a = b = 3.64; c = 5.93	a = b = 3.63 - 3.65;c = 5 - 6.
Crystalline Form	Rhombohedral	Rhombohedral	Disordered
Space Group	R 3m	P 3m1	--
Specific Gravity (g/cm^3)	2.33	2.32	2.33
Cation Coordination	Octahedral	Octahedral	Octahedral
Atomic Distances (A°)	Mg - Cl : 2.56	Mg - Cl : 2.5	Mg -Cl : 2.57
Distinct X - ray diffraction Planes	(104) at d : 2.56A°, (35°): (003) at d : 5.85A°, (15°)	(101) at d : 2.71A°, (32°): (110) at d : 1.82A°, (50°): (001) at d : 5.85A° (15°)	Broadening of all the characteristic peaks corresponding to other two forms

the less prominent hcp structure[56]. Formation of active δ - $MgCl_2$ from anhydrous magnesium chloride is a time consuming process. It can be hastened by resort to grinding in the presence of small quantity of electron donors such as esters, alcohols and ethers. One of the common electron donors which has been well studied is ethyl benzoate. The milling disintegrates the primary and the secondary bonds existing in the $MgCl_2$ and creates deficient sites by rotational disorder of Cl - Mg - Cl layers which yield active δ - $MgCl_2$[27]. On prolonged milling, crystallite sizes and half peak width ratio of (003) plane progressively decrease with time. The extent of decrease of crystallite size is more pronounced in the direction perpendicular to (001) plane in case of $MgCl_2$ alone and (110) plane in case of $MgCl_2$ + activators[29]. The surface area is observed also to increase with milling time , and reaches constant value with $MgCl_2$ alone but in presence of activator, it reaches faster to maximum value and decreases due to aggregation of crystallites[27,43].

Interaction of $MgCl_2$ with ethyl benzoate (on milling or unmilling) results in the formation of a new crystalline phase. Conflicting reports have appeared on the nature of changes occurring in the $MgCl_2$ crystalline structure as a result of this process. While some authors observed a modest increase in surface area[29], Sergeev et. al., reported a decrease in the surface area. Crystallite size was reported to decrease progressively with increased milling time[57]. This led Chien to suggest that the small crystallites of $MgCl_2$ are held together as an aggregate by complexation with ethyl benzoate resulting in the decrease in surface area[45].

Despite existence of little supporting data in the literature, it is worth mentioning that Xiao et. al., observed that thermal treatment of $MgCl_2$ sample under vacuum increases the particle sizes in the direction perpendicular to (110) and (001) plane and hence the ratio (001)/(110) representing the lateral to basal surface ratio $(S_l)/S_b$ increases[56] as shown in the Table 1.10. Very recently, Bart showed that extensive dry ball milling of $MgCl_2$ (200h) resulted in a moderate reduction in mean particle size and a more pronounced decrease in crystallite size in directions parallel and transverse to the hexagonal crystal axis[58]. The relative reduction in crystallite size was understood

Table1.10: Structural Changes Upon Thermal Treatment of Anhydrous Magnesium Chloride[56]

Temperature (°C)	S/S_b	Crystallite size perpendicular to (110) Plane (A°)	Crystallite size perpendicular to (001) Plane (A°)
30	1.33	---	---
180	1.50	723	1300
320	1.93	960	1570
420	1.85	---	---
500	---	1237	1570

on the basis of sliding of the Cl - Mg - Cl double layers by the action of shear. The effect was accompanied by a change from cubic or hexagonal layer structures to arrangements with lattice disorder. This can be completely reversed by annealing the sample at 250°C.

3.5.1.2 Features of Active δ- $MgCl_2$ Synthesized Through Chemical Activation Methods

Complexation of anhydrous magnesium chloride with various reagents such as ethers, esters and alcohols expands the coordination of Mg^{+2} cation thus creating a path for the formation of active magnesium chloride. Complexes formed from alcohols, ethers or esters and magnesium chloride are well documented in the literature as efficient precursors for synthesizing highly active Mg - Ti catalysts. Alcohols and phenols solubilize anhydrous magnesium chloride with the formation of well defined molecular complexes, whereas esters and ethers form defined complexes on thermal treatments. The structural changes occurring due to the complexation with alcohols were recently studied[59,60]. The following are the conclusions of this study,

i) Complexation is always accompanied by increase in BET surface area (30 - 150 m^2/g) and decrease in crystallite size (300 to 50 A°), indicating that the layer structure of $MgCl_2$ is disrupted. The smaller crystallites of $MgCl_2$ are held together in the form of layer aggregates by complexation (hydrogen bonding) with alcohols.

ii) Alcohols with higher carbon numbers and branching appear more efficient in this process. Phenols are less effective. However, ethanol may be preferred for the formation of stable crystallite agglomerates.

iii) Treatment of $MgCl_2$.alcohol complex with ethyl benzoate causes further disruption of the $MgCl_2$ structure. Ethyl benzoate does not displace the complexed alcohol. Unlike physical milling, reduction to crystallite size during chemical activation is not accompanied by reduction in surface area, indicating that crystal reaggregation may not be occurring.

iv) treatment of $MgCl_2$.alcohol complex with silicon tetrachloride or organoaluminum compound, results in the partial removal of alcohols causing further collapse of the $MgCl_2$ crystal aggregates.

3.5.2 Features of Magnesium - Titanium Catalysts

Physical or chemical activation methodology of combination of anhydrous $MgCl_2$(α, β or δ - forms), Ti - compounds and various other adjuvants such as electron donors and complexing agents yield Mg - Ti catalysts. The features of these catalysts are mainly concerned with olefin polymerization chemistry. High polymerization activity, high stereospecificity, control of morphology of polymer and elimination of deashing step are the well known polymerization features. These features have not been correlated systematically with structural feature of Mg - Ti catalysts in the literature, even though some scattered reports have appeared.

The synthetic methodologies discussed under section 3.3 yield highly stable and active Mg - Ti catalysts for olefin polymerization. The commercial importance of these catalysts has crippled systematic elucidation of structural features of these catalysts. Yet, a few scattered studies have reported the correlation of the structural features of these catalysts with polymerization behavior.

It is well understood that during catalyst preparation steps, disordered and coordinatively unsaturated Mg^{+2} cations are formed, which can adsorb transition metal components on the surface. This leads to the formation of bonds between Mg and Ti compounds. These new bonds are responsible for conferring special features to these catalysts. These structural features can be conveniently discussed under the following subheadings

3.5.2.1 Crystallographic Parameters

3.5.2.2 Surface Area and Porosity

3.5.2.3 Titanium Content

3.5.2.4 Oxidation States of Titanium

3.5.2.5 Morphology

3.5.2.6 Nature of Internal Electron Donors

3.5.2.1 Crystallographic Parameters

Crystallographic parameters such as crystallite dimensions, half peak width ratio of distinct reflections corresponding to defined crystal planes and disorder parameters are commonly monitored during the synthesis of Mg - Ti catalysts[27,61]. The changes occurring in these parameters during the synthesis of Mg - Ti catalysts are as follow,

i) synthesis of Mg - Ti catalysts disturbs cubic and hexagonal packing sequences of $MgCl_2$ crystals. It also rotates the mutual chlorine layers present in $MgCl_2$ by +60°. The probability of changes in these parameters are commonly monitored against the milling time. It is observed that the rotational disorder is more pronounced than the cubic or hexagonal sequences disorder.

ii) synthesis of Mg - Ti catalysts ruptures the crystalline planes which can be observed as broadening of sharp crystalline peaks in X - ray diffraction spectrum. The crystalline size perpendicular to plane (110) are commonly calculated against the milling time. It shows decrease of crystallite size to <50nm. The pattern of breakage of these crystallites is shown in Figure 1.1.

iii) it is observed that the path of disorder parameter is linear indicating that the structural changes occurring during the grinding follow a linear zone of path[61].

iv) Physical activation of $MgCl_2$ with electron donors promote structural changes as discussed in section 3.5.1.1. These structural changes create some high energy unsaturated Mg^{+2} sites on lateral faces, edges and corners of $MgCl_2$. These can easily adsorb catalytic titanium centers to yield nonuniformly distributed active centers on $MgCl_2$ surface[29]. The coordination of Ti occurs through chlorine bridges to coordinatively unsaturated Mg - atoms placed on $MgCl_2$ surface yielding stable Mg - Ti catalysts with similar structural defects.

v) Half peak width ratio of (003) plane is shown to decrease in a three stage process as shown in Figure 1.2. It reaches maxima in second stage and after that remains constant[33].

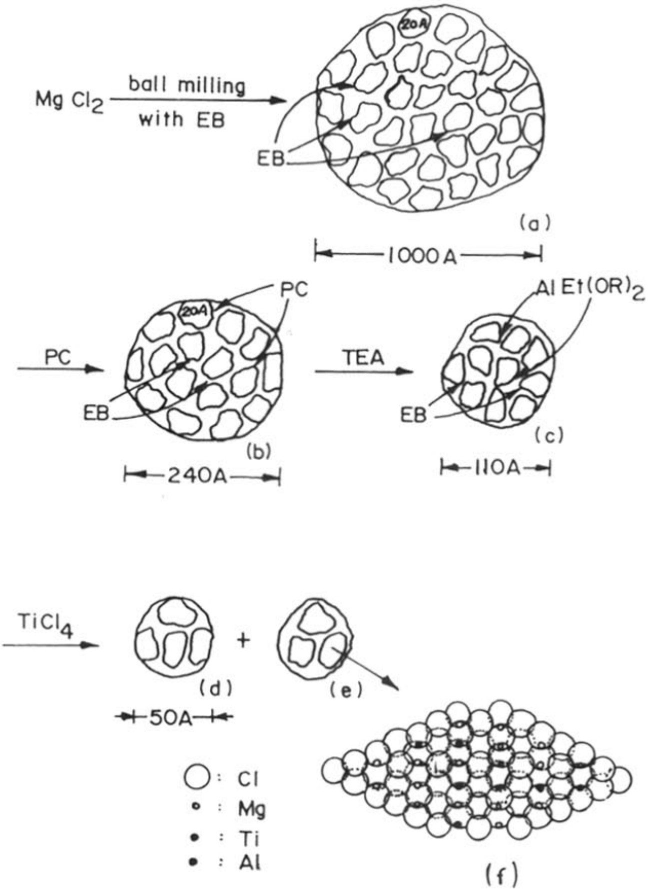


Fig.1.1 Schematic Representation of the Physicochemical Changes of Magnesium Chloride During Catalyst Preparation

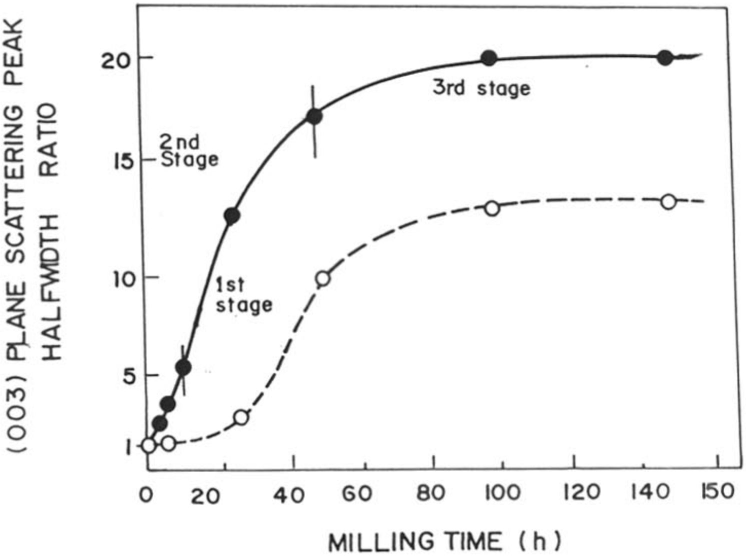


Fig.1.2 Change of Half-Width of (003) peak of $MgCl_2$ for the Milling Time : (--O--) $MgCl_2$ Along Milling; (--●--) $MgCl_2$ + 0.12 $TiCl_4$ Milling

vi) Chemical routes of synthesis with preformed $MgCl_2$ is also observed to create rotational disorder along Cl - Mg - Cl layers. Broadening of crystalline peaks and reduction of crystallite dimensions to <100nm are observed. No systematic studies are reported in the literature on the changes occurring due to this process. Recently, Chien and co-workers showed a marked difference in X - ray diffraction pattern of Mg - Ti catalysts prepared from $MgCl_2$, 2-ethylhexanol and $TiCl_4$ under different conditions[49]. These catalysts showed no changes in reflections corresponding to $2\theta = 20.3, 40.3$, and 67.8, when compared with Mg - Ti catalysts prepared by physical activation of $MgCl_2$, ethylbenozate, p-cresol and $TiCl_4$.

3.5.2.2 Surface Area and Porosity

The changes in surface area and porosity of heterogeneous Mg - Ti catalysts during the process of synthesis are also monitored as one of the important features of Mg - Ti catalysts. High surface area and low pore size lead to better exposure of edges and corners of $MgCl_2$ crystal to yield strong structural bonds between Mg & Ti centers. It is known that the catalytic centers present at edges or corners are better sites than those present at basal faces. Hence, high surface area and low pore size Mg - Ti catalysts are preferred in olefin polymerization[54,62].

Physical and chemical methods of synthesis of Mg - Ti catalysts increase the surface area, which is commonly monitored by BET N_2 adsorption or Mercury intrusion technique. In case of physical methods of synthesis of Mg - Ti catalysts, surface area is shown to increase linearly upto 70h of grinding. Later, a decrease in surface area occurs due to reaggregation of crystalline particles and no significant variation in pore size is observed[33]. It has also been showed that milling time and ratio of Ti/Mg controls the surface area of Mg - Ti catalysts. At a ratio of Ti/Mg = 1.2 a faster rate of increase of surface area is observed and at a ratio of Ti/Mg slowest is observed. The method of milling (dry ball milling or rotatory or vibratory milling) also affects the surface area[63].

3.5.2.3 Total Titanium Content

Usually, approximately 2 - 4% of titanium per gram of catalyst is bonded to $MgCl_2$ surface in the course of synthesis of Mg - Ti catalysts. Introduction of titanium by physical activation route proceeds by disrupting the crystalline $MgCl_2$ surface, whereas in chemical activation routes, it either forms directly bonds with highly unsaturated Mg^{+2} cations on thermal treatment, or displaces the complexing agents or polar adjuvants which are attached to high energy electron deficient sites on $MgCl_2$ surface, thereby creating structural bonds with catalytic Ti - centers.

Effects of percentage of titanium on structural pattern of Mg - Ti catalysts are monitored by X- ray diffraction and BET - adsorption measurements. It is observed that as the percentage of titanium bonded to the magnesium chloride surface increases, the probability of cubical, hexagonal and rotational disorder also increase[61]. This further affect the path of disorder parameter by deviating it from linear path as shown in Figure 1.3. Surface area is observed to increase with titanium at a faster rate in presence of higher amount of titanium and reaches a maximum, and then, due to reaggregation of titanium ions, it decreases. The half peak width ratio is found to increase with higher content of Ti when compared with lower content of Ti.

3.5.2.4 Oxidation States of Titanium

In Mg - Ti catalysts, titanium exists in +4, +3 and +2 oxidation states. It is well shown that while +2 state of titanium is active for only ethylene polymerization , +3 state is highly active for both ethylene and propylene polymerization. So, Ti^{+4} species is commonly reduced with cocatalysts to yield lower valent titanium species which are active for polymerization. It is of interest to understand the role, nature and percentage of different oxidation states present on Mg - Ti catalyst during olefin polymerizations. Redox titration and ESR spectroscopic techniques are adopted for determining the percentage of different oxidation states of titanium. It is found that ESR observable Ti^{+3} species concentrations is only a small fraction of the total Ti^{+3} obtained by redox titrations. This led Chein to predict that there are two types of Ti^{+3} species on Mg - Ti

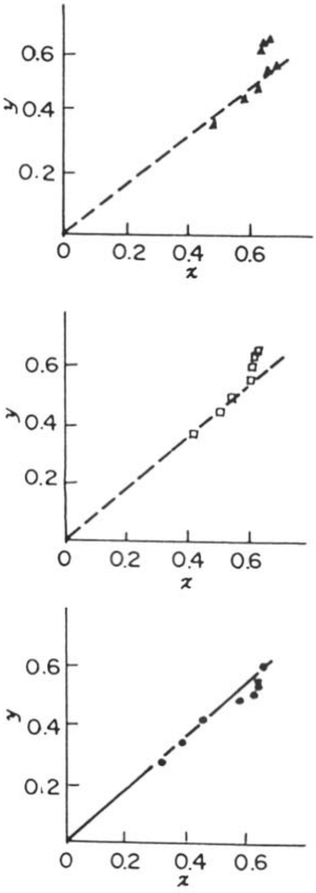


Fig.1.3 Paths of Examined Series in the Disorder parameters Space
(●) 2.0 % Ti; (□) 3.4 % Ti, (▲) 4.2% Ti

catalysts, namely, ESR silent and ESR active[64]. The concentration of ESR silent are very high when compared with ESR active species. Further an excellent agreement between $[C^*_i]$ and Ti^{+3} ESR active and between $[C^*_a]$ and Ti^3 ESR silent signals was found regardless of whether $[C^*_i] >> [C^*_a]$ or vice versa. These observations led to predict that ESR silent signals are due to the bridging of Ti^{+3} centers by chloride ions resulting in antiferromagnetism nature of Ti^{+3}.

Zakharov and co-workers studied the nature of Ti^{+3} species present on three different Mg - Ti catalyst systems and showed that the splitting factor constant, commonly designated as g -factor, for Ti^{+3} species varies between 1.80 - 1.99[65]. Based on the g - values, four principal signals (A,B,C,G), corresponding to Ti^{+3} ions with different symmetry and coordination states were shown (Table -1.11). The structure and coordination of Ti^{+3} species and ligand environment were also assigned.

3.5.2.5 Morphology

Morphology of catalyst particles play a vital role for the formation of polymer without affecting the catalysts performance. It is recognized that spherical granules having particles sizes in the range of 10 - 40μm are the most suitable in industrial applications, particularly for gas phase polymerization. High porosity, high mechanical resistance during manipulation and polymerization, capability of breaking down into particles during polymer growth; homogeneous distribution of active centers having equal activity and access to monomer are the basic morphological requirements for Ziegler - Natta catalysts[66]. It is proved beyond doubt that supporting the active species on carriers permits greater control of polymer morphology than obtained with non supported catalysts. Magnesium chloride, which constitutes the best activating support, is unusual in that it can be shaped into uniform spherical or globular particles having different sizes. Thus, under appropriate condition of catalyst preparation and polymerization, uniformly dispersed, highly compact polymer particles can be obtained, having desired size and shape since they retain the original shape of the catalyst particles[67].

Table 1.11: ESR on Titanium (III) Ions Formed in Magnesium - Titanium Catalysts of Various Compositions[65]

Signal	Value of g - factor	Coordination	Proposed composition and localization site of Ti^{+3} compounds
A	g = 1.940	Distorted octahedron	Solid solution of $TiCl_3$ in $MgCl_2$
	g = 1.89 - 190		
B	g = 1.915 - 1.925	Distorted Octahedron	Ti^{+3} ions in chlorine environment, exchanged - bonded with one another or with $TiCl_3$
C	g = 1.97	Tetrahedron	$TiCl_3$ molecules stabilized in the $Mgcl_2$ surface
G	g = 1.99	---	Ti^{+3} compounds with titanium - alkyl or titanium - hydride bonds
D	g = 1.96	---	$TiCl_3$.3Py complex
E	g = 1.90	---	Compound $Cl_xTi^{+3}OH$
F	g = 1.89	---	---

The replication studies showed that under controlled conditions for growth of spherical [polymer particles, the behavior of the polymer particle size as a function of time may be expressed by[68] as in Equation 1.4.

$$R_{t} = \sqrt[3]{\frac{3}{4\pi\delta N}\int_{0}^{t} R_p\,dt} \qquad 1.4$$

Where, R_t = Radius of polymer particles at time "t",

R_p = Total polymerization rate,

N = Number of polymer particles per unit volume and

δ = Polymer density under polymer conditions

3.5.2.6 Nature of Internal Electron donors

Aromatic mono and diesters are found to be effective internal donors for Mg - Ti catalyst systems[69]. This conclusion was reached by comparing the basic strength, steric hindrance and functionality of different Lewis bases. Among these esters the nature of ethylbenzoate (EB) as an internal electron donor is extensively studied in the literature[29]. The ability of internal electron donors to complex with the exposed planes of $MgCl_2$ when added in absence or presence of $TiCl_4$ leads to prediction of the nature of interaction of EB in Mg - Ti catalysts. Spectroscopic studies showed that EB forms two types of structural bonds namely O - Mg - Cl or Mg - Cl - Ti - O[70]. On the contrary, mono and di aromatic ester complexation with $TiCl_4$ was not detected by Terano on $MgCl_2$ surface[71]. It was then proposed that esters and $TiCl_4$ exists independently on $MgCl_2$ surface. This conclusion does include the possibility that EB is coordinated at a site adjacent to $TiCl_4$ or $MgCl_2$. It is observed that when EB is added to $MgCl_2$ in absence of $TiCl_4$, it complexes through a slow adsorption process leading to the formation of new crystalline faces. The crystalline faces have higher dimensions and lower surface areas. When EB is added with $TiCl_4$ to $MgCl_2$, it is observed that (Ti.EB) complex disappears rapidly and $MgCl_2$.EB complex is formed. This is reasoned to be due to the higher thermodynamic stability of $MgCl_2$.EB complex. It is proposed that EB blocks the aspecific active Ti^{+3} centers or rather converts them to isospecific centers by coordinating with alkylaluminum compounds during olefin polymerization.

3.6 Molecular Weight and Molecular Weight Distribution Control of Polyolefins Using Magnesium - Titanium Catalysts

Regulation of molecular weight (MW) and molecular weight distribution (MWD) still is a crucial factor in polyolefin process to achieve the ultimate properties of polymers for given end use applications. It is observed that Mg - Ti catalysts yield relatively low molecular weight and narrower molecular weight distribution polyolefins when compared to unsupported catalysts. This is due to the dilution of active centers on the inert support material, magnesium chloride. This dilution promotes considerable increase of chain transfer process such as (k_t^M k_t^{Al} k_t^H), and thereby, regulation of MW and MWD by termination of growing polymer chains. Extensive studies have revealed that the MW of polymers is controlled using appropriate chain transfer agents and MWD by varying the reaction parameters. These aspects can be discussed in terms of the following subsections.

3.6.1 Control of Molecular Weights of Polyolefins Using Magnesium - Titanium Catalysts

3.6.2 Control of Molecular Weight Distribution of Polyolefins Using Magnesium - Titanium Catalysts

3.6.1 Control of Molecular Weights of Polyolefins Using Magnesium - Titanium Catalysts

Chain transfer agents such as hydrogen and diethyl zinc are commonly employed to regulate the MW of polyolefins with Mg - Ti catalysts. Even though diethyl zinc is the effective chain regulator, hydrogen is extensively used as it is cheap and has limited effect on the activity of the catalyst[72].

It is believed that the hydrogen through a chain transfer process generates inactive polymer chains and metal hydride species which continue the insertion reaction. Use of hydrogen yields lower molecular weight polymers with Mg - Ti catalysts when compared to unsupported catalysts[73]. A decrease in activity of ethylene polymerization and enhancement in activity of propylene polymerization in particular activities of aspecific sites with $MgCl_2$ - $TiCl_4$ - $AlEt_3$, is observed. But in presence of external and/or internal donors these supported catalyst show drop in activity and stereospecificity upon increasing hydrogen concentration[74]. Further, the influence of hydrogen can be noticed in supported Mg - Ti catalysts at temperatures above 50°C only.

The molecular weight and applied hydrogen pressure are related by an (Equation 1.5)in heterogeneous Ti catalyst as shown[75],

$$Mn^{o} / Mn^{H} = 1 + k(P_{H2})^{2} \qquad 1.5$$

The value of exponent " n " is invariably 0.5 when olefin polymerization is conducted in absence of donors. In presence of donors, " n " is found to be 1.0[76].

In absence of hydrogen, at normal polymerization conditions and at normal ethylene concentrations the molecular weight is controlled predominantly by chain transfer process to monomer in Mg - Ti catalysts.

3.6.2 Control of Molecular Weight Distribution of Polyolefins Using Magnesium - Titanium Catalysts

Even though there exists different termination reactions during olefin polymerization reactions, the molecular weight distribution, popularly known as Q - factor, should be close to two according to Shultz - Flory distribution[77]. In practice Q of polyolefins are observed to be substantially broader ranging from 5 - 40. The reasons for such a large variation are explained in terms of diffusion theory and chemical theory. Both the theories explain that the heterogeneity of active sites present on the surface of Mg - Ti catalyst control the rate of propagation of polymerization, and hence, regulation in MWD distribution[78]. Bohm et. al., confirmed it by showing the broadening of MWD upon increasing the heterogeneity of Ti active sites present on a Mg - Ti catalyst[79].

Apart from heterogeneity, electron donor concentration is another major factor which regulates the MWD of polyethylene. Further more, reaction conditions such as cocatalyst concentration and chain transfer agent also play an important role in controlling the MWD of polyethylene[80].

Even though MWD factor is not a commercially significant parameter for polypropylene, the scientific studies show conflicting reports. Some researchers observed change of MWD from mono to bimodal distribution upon increasing electron donor concentration, whereas Soga and co-workers showed independence of MWD on electron donor concentrations[81,82]. These appears to be no unanimity of opinion on the role of reaction parameters such as cocatalyst concentration and hydrogen chain transfer agent on MWD of polypropylene[83].

3.7 Relation Between Structure of Magnesium - Titanium Catalysts with Performance During Polymerization

It has been observed that the structural modification that occur during the various stages of Mg - Ti catalysts preparation strongly influence the performance and specificity of catalysts during polymerization under given conditions. Surface area, crystallite dimensions, disorder parameter, concentration of titanium, internal and external electron donors affect the crystal structure of Mg - Ti catalyst and performance during the polymerization. Recently, it has been shown that the ligand environment around the titanium metal also influence the performance of catalyst for ethylene polymerization. The relation between the structure of Mg - Ti catalyst and its performance are summarized below:

i) Higher the electron releasing capacity of the ligands around titanium metal in $MgCl_2/TiCl_4$ system, higher is the polymerization activity[32]. It is observed that the activity of catalyst during polymerization increase according to the series

$X = N(C_2H_5)_2 < O(CH_2)_2CH_3 < OC_6H_5 < Cl$

namely, the reverse order of ligands electronic releasing ability. Neglecting the amide ligand scarce activity, the catalyst with aliphatic alkoxide ligands show in comparison with other types of ligands a relatively slow decay of polymerization rate as shown in Figure 1.4. It is also observed for the $MgCl_2/Ti(OR)_nCl_{4-n}$ catalyst activity increases by increasing the number of chlorine atoms from 0 - 4. In case of $MgCl_2/Ti(OR)_4$, the increase of activity along the series is given by

$R = CH_3 < C(CH_3)_3 < CH(CH_3)CH_2CH_3 < CH(CH_3)_2 < C_2H_5 < CH_2(CH)(CH_3)_2 < (CH_2)_3CH_3$

Finally, in case of aromatic titanium alkoxides with unsubstituted and in 2,4,6 - position substituted phenyl rings the catalyst activity increases in the order of

$R = CH_3 < Cl < H$

ii) Conflicting results have appeared on the relation between the performance of Mg -Ti catalyst and surface area. Galli et. al., Showed increase of surface area with activity of $MgCl_2/TiCl_4$ catalyst till 70 hours milling time followed by drop in surface area without affecting the catalyst activity[66], whereas Kashiwa showed a linear increase of surface area with activity of catalyst in $MgCl_2/TiCl_4$ catalyst[33].

iii) Lower the crystallite size dimensions, higher the activity of catalyst. It was shown that the crystallite size of 20 - 50nm are effective in forming structural bonds with titanium ions with lateral and corners of $MgCl_2$ surface. These catalytic centers are more exposed and hence, can be said to be more active[29].

iv) A close relation between structural disorder parameter and activity is obtained with Mg - Ti catalyst, indicating that there exist a well defined triplet of probability parameter which is not related to the surface area but controls the polymerization activity as shown[61] in Figure 1.5.

v) The activity of the catalyst is found to be dependent on percentage of Ti present. Higher titanium content in catalyst leads to aggregation of particles and also structural bonding with less exposed basal face of active δ - $MgCl_2$. This reduces the average activity of catalyst. So, a low percentage of titanium is preferred to achieve high activity with Mg - Ti catalyst[61].

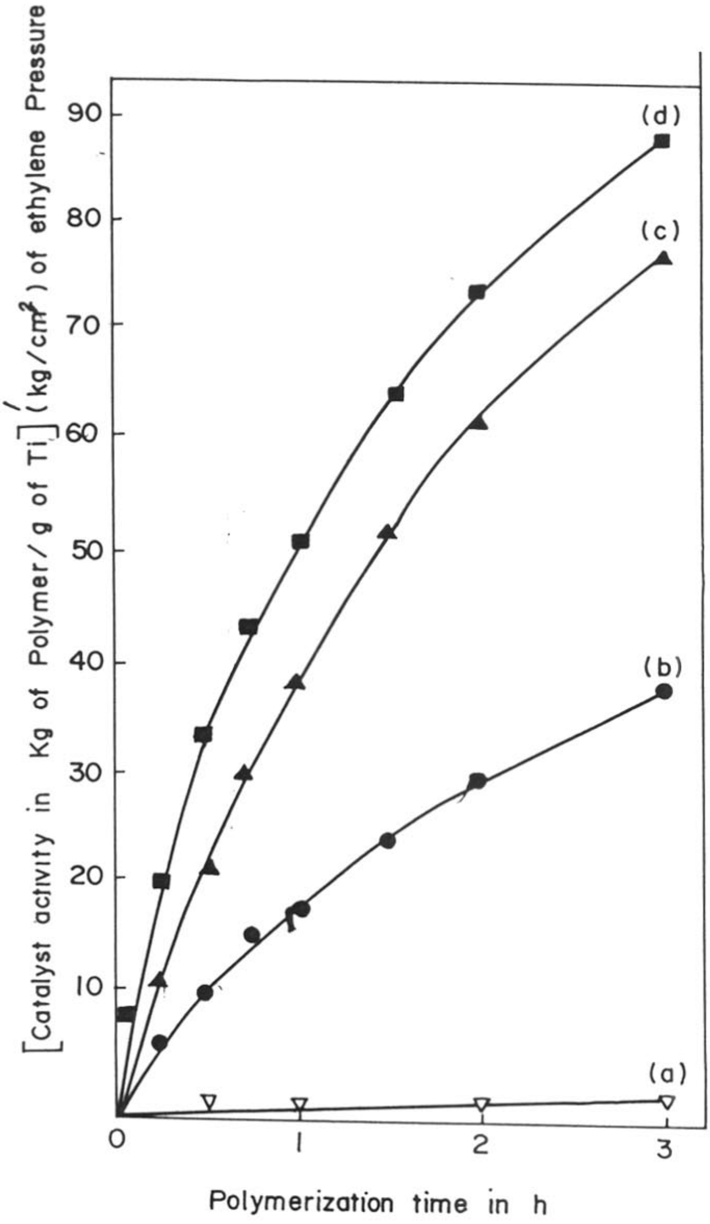


Fig.1.4 Time Dependence of Polymer Yield in the Polymerization of Ethylene with $MgCl_2/TiX_4$ - $Al[CH_2(CH_3)_2]_3$ Catalyst System for Different Type of Lignads: (a) $X = N(C_2H_5)_2$, (b) $X = O(CH_2)_3CH_3$, (c) $X = OC_6H_5$ and $X = Cl$.

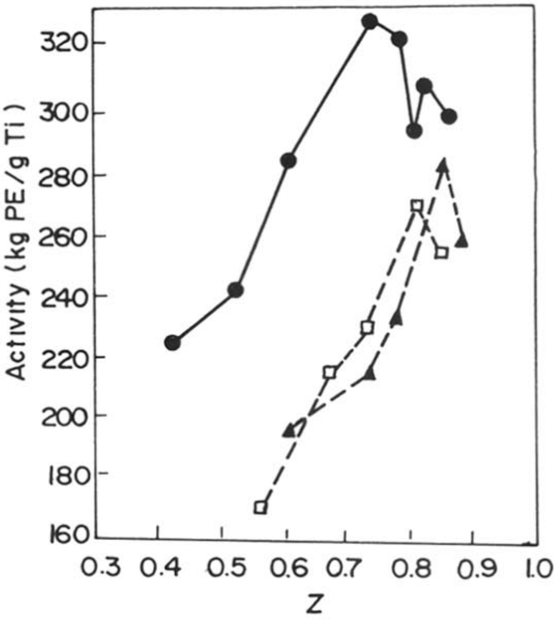


Fig.1.5 Plot of Catalytic Activites of the Examine Series Vs the Linear Zone of the Paths Described in the Disorder Parameters Space: (--O--) 2.0% Ti; (-- --) 3.4%; (-- --) 4.2% Ti.

vi) It is observed that electron donors play a major role in catalyst performance both in ethylene and propylene polymerization. These donors in ethylene polymerization decrease the activity of Mg - Ti catalysts and change the kinetic curve from stationary type to decay type[30]. In case of propylene polymerization, they affect the activity, stereospecificity and polymerization kinetics[29,30,43]. Upon reduction with alkylaluminums, Mg - Ti catalysts containing an internal donor with alkylaluminums show poor stereospecificty for propylene polymerization (60 - 70%). Further more, when these catalysts are in contact with alkylaluminum they selectively lose the internal donor and the extent of loss strongly depends on the time, aluminum/titanium ratio and temperature. However, in presence of added external donors, they show increased stereospecificity in the range of isotactic index = 95 - 99%. Studies on the effect of external donors in absence or presence of internal donors showed that the complexation of alkylaluminum with donors is necessary to achieve this dramatic result. Conflicting reports have appeared on the extent of effect of these donors on steresopecificity and activity. Different hypotheses and models are proposed to explain these results. In general, it can be said that the effect of electron donor is to selectively poison the aspecific active sites and reduce the activity, and to increase the specificity. Use of electron donors results in decay type mode of deactivation.

3.8 Kinetic Features of Magnesium - titanium Catalysts and Comparison with Unsupported Catalysts

Basic kinetic principles of heterogeneous Ziegler Natta catalysts are well discussed by Boor, Keii and Kissin[5,84,85]. The kinetic features of heterogeneous Mg - Ti catalysts have been recently reviewed in the literature[86]. Kinetic studies are important to understand the fundamental principles governing the heterogeneous catalysts. These studies provide information on activation energies, life time of catalyst, initiation, propagation and termination rate constants and a clue to understanding of the mechanism of olefin polymerization.

Extensive studies have been reported on kinetic features of different Mg-Ti supported and Ti unsupported heterogeneous catalysts. Prominent features of these studies in comparison with unsupported heterogeneous catalyst are highlighted here.

a) Supported Mg - Ti catalysts have very low or no acceleration period and reach maximum rates in short time and decay rapidly with time in comparison to unsupported catalysts where there exist three distinct kinetic stages viz., Initiation, stationary and decay stages (Figure 1.6). Many high activity supported catalysts such as $MgCl_2$/ethylbenozate/$TiCl_4$ - $AlEt_3$ show the same kinetic behavior for both ethylene and propylene. Existence of initiation period in unsupported catalysts is due to the breakage of the catalyst matrix as the polymerization or growth of polymer proceeds, thus exposing fresh titanium centers leading to the formation of new active sites. After the breakdown, a steady state rate exists for significant time and then decays with time. In case of supported catalysts, the active sites are well exposed on the surface of inert support matrix, leading to the formation of little fresh active sites during polymerization. Hence, no initiation period is observed.

Further the fast decay observed with supported catalysts in comparison to unsupported catalysts could be due to the diffusion phenomenon and chemical interactions occurring during the course of polymerization. It is believed that the polymer is formed in the pores of heterogeneous catalysts and as the polymerization proceeds the catalyst particle size becomes larger and there may be diffusion hindering of the different compounds to the catalyst system. This leads to the temperature gradient with the particle and the medium surrounding it, resulting in decay the rate of polymerization. The argument in favour of chemical change concerns the nature of donor - cocatalyst interactions which are very fast and known to degrade in a short span of time. This leads to the decay of rate of polymerization. The effect of mass transfer is also believed to play a role in decay process in supported catalysts.

b) It is observed that kinetic rate profiles of supported as well as unsupported Ti - based catalysts are very much dependent on the nature and amount of cocatalyst present during olefin polymerization. In comparison with unsupported catalysts, high amount

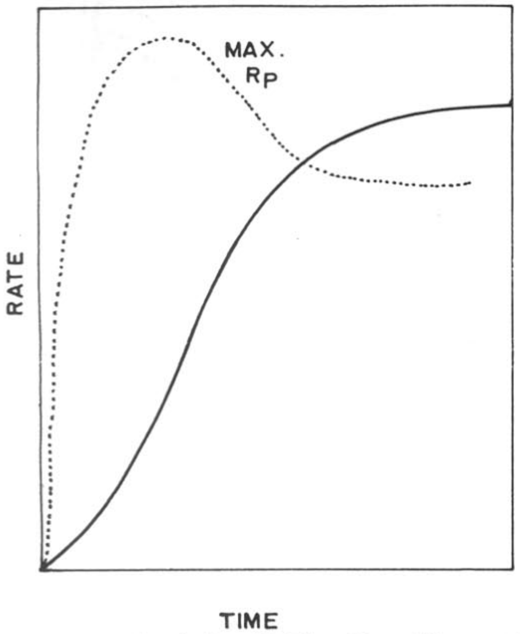


Fig. 1.6 Kinetic Rate Vs Time Plot of Supported and Unsupported Catalysts

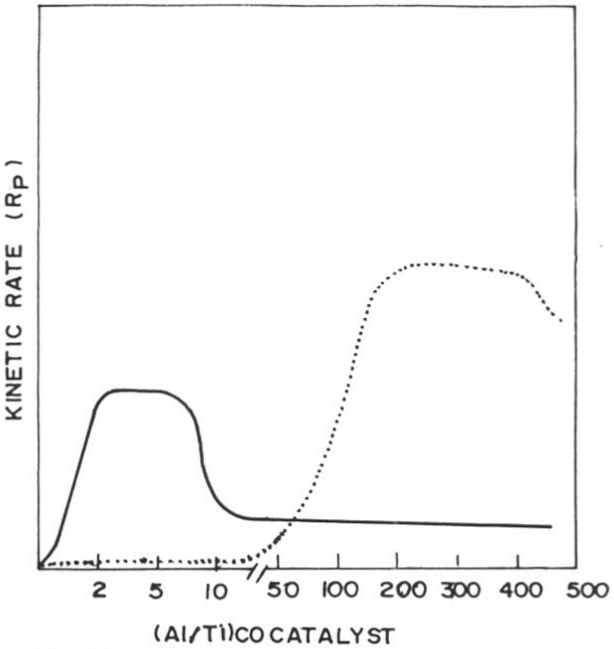


Fig.1.7 Kinetic Rate Vs Al/Ti Ratio Plot of Supported and Unsupported Catalysts

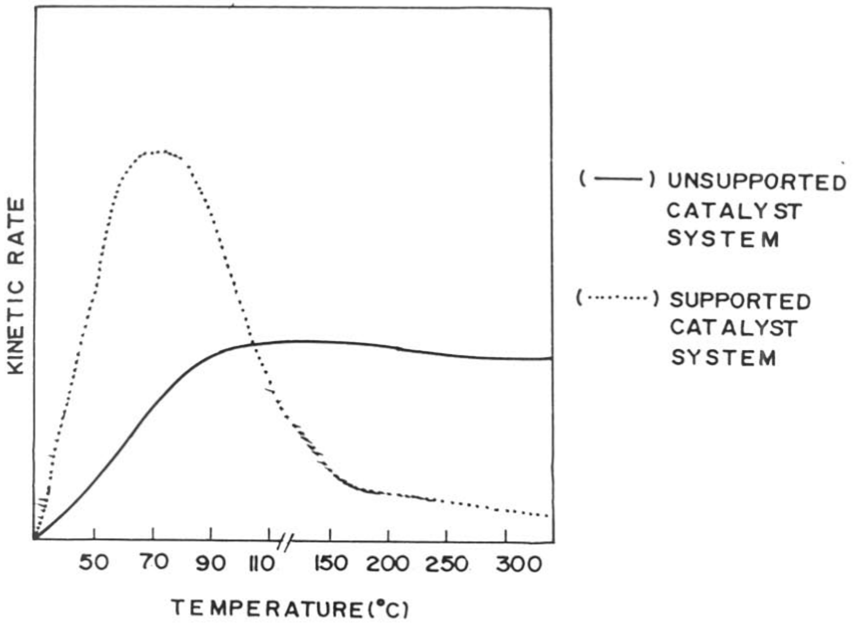


Fig.1.8 Kinetic Rate Vs Temperature Plot of Supported and Unsupported Catalysts

of alkylaluminum concentrations are required to achieve optimum activities with supported catalysts. The rate Vs Al/Ti kinetic profiles are shown in Figure 1.7 for supported and unsupported catalysts.

In case of unsupported catalysts, the rate of polymerization increases with an increase of cocatalyst concentration upto a certain limit and then becomes independent of this parameter. In contrast, the supported catalysts show a similar increase as the Al/Ti ratio increases, but later on rate is observed to decrease with Al/Ti ratios. Similar effects are noticed in presence or absence of electron donors in both the catalyst systems. Further it is observed that besides rate, the stereospecificity of obtained polymers is high with trialkylaluminums in comparison with dialkylaluminum chlorides in supported catalysts. But this effect is exactly opposite in unsupported catalysts.

c) It is observed that the rates of olefin polymerization using supported catalysts and unsupported catalysts depend on the temperature of reaction. Rates are observed to be maximum near 60 - 70°C and then decrease with increase in the temperatures of polymerization in case of supported catalyst, whereas in unsupported catalysts the rates of polymerization are linearly proportional to temperature as shown in Figure 1.8. The reason for this could be the exposure of highly active titanium sites present over inert magnesium chloride surface which generates inactive sites on reduction with alkylaluminums at high temperatures. This results in a severe drop in rates of polymerization as the temperature is increased. This hypothesis does not explain the deactivation process of catalysts system $MgCl_2$ - $TiCl_4$ above 70°C. This can be explained to be due to the highly exposed active sites present on the surface of support which shatter at high temperatures, resulting in destruction of bonds between catalytically active sites and surface.

Apart from these parameters, the kinetic rate of polymerization is also dependent on manner of addition of catalyst and cocatalyst, ageing time, pressure, poisons, activators and chain transfer agents. These variations are in fact very typical to every individual catalyst system. Further, the effects of these parameters on polymerization process is very complex.

3.9 Proposed Structural Models of Active Sites in Magnesium - Titanium Catalysts

Although many studies have been reported on the synthesis of new and better catalyst systems and effects of different parameters on polymerization efficiency using Mg - Ti catalysts, only very few studies exist regarding the elucidation of the structure of active sites in Mg - Ti catalysts. The structure of active sites are thus best discussed under the following subheadings

3.9.1 Chien's Model
3.9.2 Doi & Soga's Model
3.9.3 Kakugo's Model

3.9.1 Chien's Model

Extensive investigations of two different catalyst systems (CH and CW) based on $MgCl_2$ and $TiCl_4$ have allowed Chien to predict the structure of active species in Mg - Ti catalysts. The two catalysts are prepared by different routes. CW catalyst is made by grinding hydrochloric acid pretreated $MgCl_2$, ethyl benzoate and then treating with p - cresol, $AlEt_3$ and $TiCl_4$[88]. The second CH - catalyst is prepared by reacting phthalic anhydride and 2 - ethyl hexanol solubilized $MgCl_2$ at 130° for 2h. This mixture was further treated with $TiCl_4$ at -20°C[89].

Thorough characterization of both CH & CW catalysts on reduction with alkylaluminums in presence of external electron donors showed that there exists two types of active species, namely, atactic and isotactic Ti(III) species[89]. The atactic species are ESR silent and isotactic species are ESR active. It is therefore proposed that in atactic active species the active Ti^{+3} species is positioned between chlorine bridges which are attached to the support as shown in Figure 1.9 . These nonstereospecific sites are more Lewis acidic than stereospecific sites.

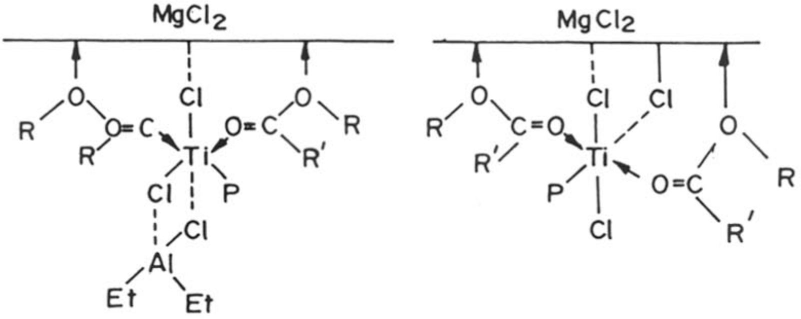


Fig.1.9 Proposed Model of Isospecific Active Site on Magnesium Chloride Surface

The isospecific site structure complexed with electron donors are shown in Figure 1.10 . In case of the CH catalyst, the monoesters in the above structures are replaced by the phthalate esters. These active sites are characterized by low Lewis acidity, low affinity, ESR activity with rhombic symmetry, chirality and long life time.

3.9.2 Doi & Soga's Model

Indirect studies of microstructure analysis of polypropylene by 13C NMR produced by various Mg - Ti catalysts led Doi and Soga to predict a model for the active centers[90]. This model also considered that there existed two types of active centers on $MgCl_2$ surface, one producing atactic polypropylene and the other predominantly isotactic polypropylene as shown Figure 1.11. The catalysts systems studied are δ - $TiCl_3$ /$AlEt_3$ and $MgCl_2$/$TiCl_4$/EB/$AlEt_3$.

In site A, the support is coordinatively saturated whereas in site B, it has a chlorine vacancy. Reversible migration of alkylaluminum compound in site B was suggested as a cause of the frequent changes in polymer structure.

3.9.3 Kakugo's Model

Recently, Kakugo et. al., studied the microtacticity distribution of polypropylene obtained by using various heterogeneous Ti - based catalyst systems[91]. The microstructure of the isotactic parts of various polypropylene were determined by ^{13}C - NMR spectroscopy. It was observed that the isotacticity of the isotactic parts as determined by the mmmm pentad sequence (micoisotacticity) increases as the stereospecificty of the catalyst (isotactic index) employed increases. On fractionation of several polypropylenes, it was concluded that two types isospecific active centers reside these Mg - Ti catalysts by analogy to β - $TiCl_3$ catalysts. They are shown in the Figure 1.12.

Further, it was proposed that the addition of electron donors convert nonstereospecific centers to highly specific centers, whereas low isospecific centers are rendered inactive.

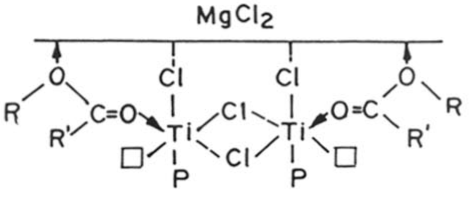
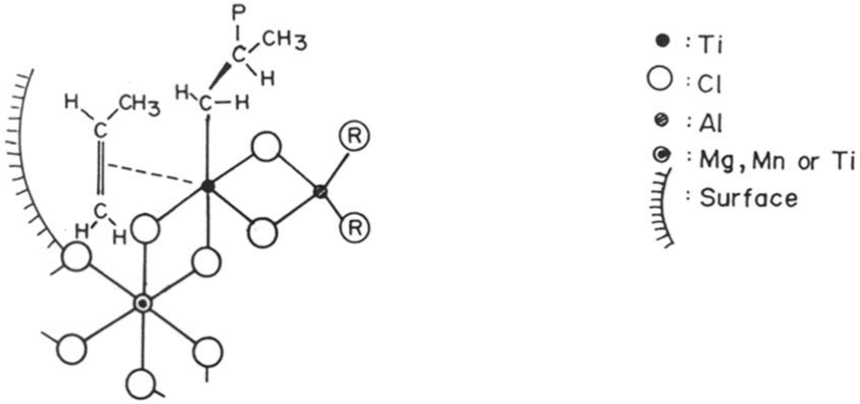


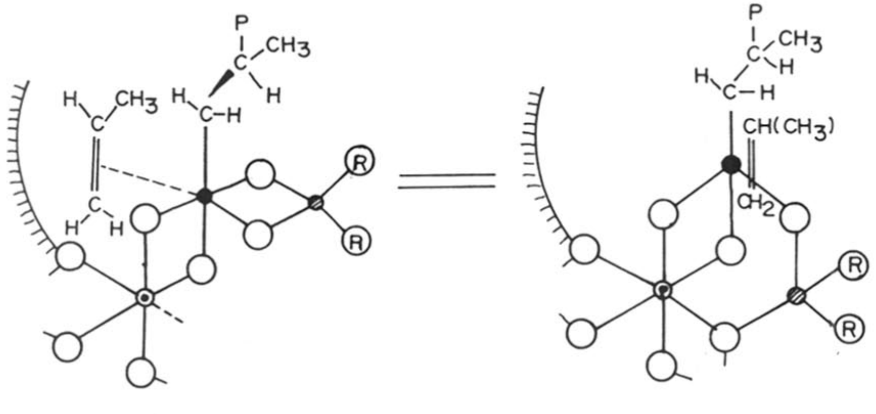
Fig.1.10 Proposed Model of Nonstereospecific Active Site on Magnesium Chloride Surface

Site A (Isotactic PP)



Isotactic Propagation

Site B (Atactic PP)



(B6)

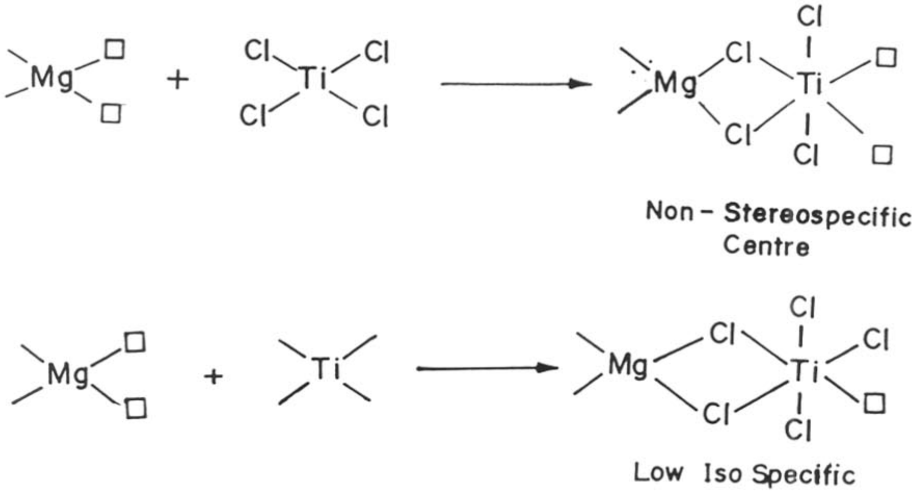
(B5)

Isotactic Propagation

Syndiotactic Propagation

Fig. 1.11 Doi and Soga's Model of Propagating Active Species on the Surface of the Support

In Absence of Donor



In Presence of Donor

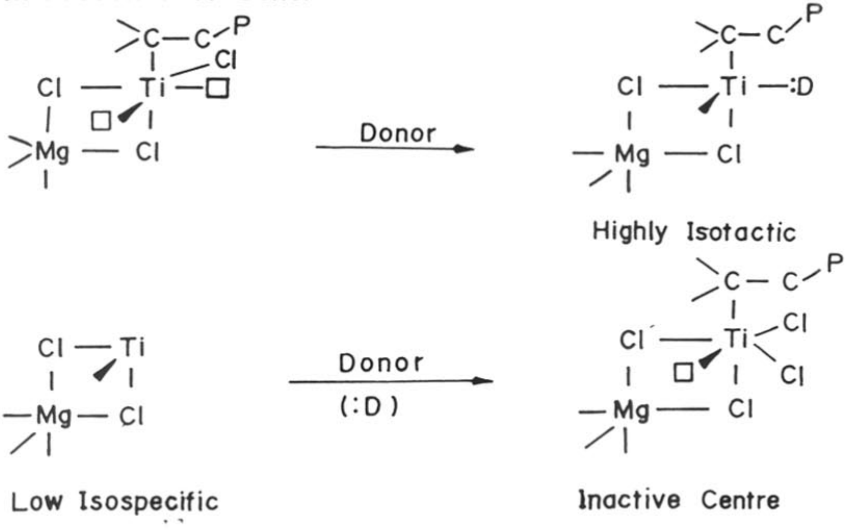


Fig.1.12 Kakugo's Model of Formation of Active Species in Absence and presence of Donor

Representative Patent Literature on Magnesium - Titanium Catalysts for Ethylene and Propylene Polymerization (1991 - 93)

Patent Number	Chem. Abstr. No	Name of Company	Monomer	Catalyst Composition	Features
Ger. Offen DE 3,936,857	115: 136985a	BASF AG	Propylene	Silica, butylhexyl magnesium, titanium tetrachloride, ethanol, esters of substituted phthalic acids, triethylaluminum and siloxane.	Yield : 9.86 kg/ g catalyst/h
Fr. Demand FR 2,628,10	112: 99484b	BP Chemie S.A.	Propylene	Dibutylmagnesiumt-butylchloride, diisoamylether, butanol, ethyl benzoate, titanium chlroide, triethylaluminum and methyl-p-toluate.	Yield : 10 kg/ g catalyst/h
PCT Int. Appl. WO 9113, 914	115: 256913x	Exxon	Ethylene and Butene-1	Butyl ethyl magnesium chloride boron trichloride, titanium chloride vanadium trichloride silica and triethylaluminum.	MWD : 5 - 12.

Patent Number	Chem. Abstr. No	Name of Company	Monomer	Catalyst Composition	Features
EP 506,074	118: 102907y	Himont Inc	Propylene	Magnesium chloride, titanium chloride, silica, 1,3-dimethoxy-2-isopentyl-2-isopropyl propane and triethylaluminum.	Yield : 12.5 kg/g catalyst/h
EP 437,263	115: 208851d	Himont Inc	Propylene	Magnesium chloride, methyl phenyl dimethoxy methyl silane, titanium tetrachloride, dibutyl phthalate and trialkylaluminum.	Yield : 1.0 kg/ g catalyst/h isotacticity : 92.7%.
EP 437,264	115: 208852e	Himont Inc	Propylene	Aluminum chloride, methyl magnesiumbromide, silica, 2-isopropyl-2-isopentyl-1,3-dimethoxy propene, titanium alkoxide, titanium chloride.	Yield : 26.4 kg/ g catalyst/h
EP 483, 523	117: 112784z	Himont Inc	Propylene	Magnesium chloride, ethanol, diisobutylphthalate, titanium trichloride and triethylaluminum	Yield : 10 kg/ g catalyst/h isotacticity : 95%.

Patent Number	Chem. Abstr. No	Name of Company	Monomer	Catalyst Composition	Features
JP 04,39,307	116: 215126v	Mitsubishi Petrochemicals	Propylene	Magnesium chloride, butoxytitanium, silicon tetrachloride , t-butylmethyl dimethoxysilane,ethylenbenzoate,Triisobutyl aluminum	Yield : 13 kg/ g catalyst/h
JP 04,20,510	117: 8687j	Mitsubishi Petrochemicals	Propylene and Norbornene	Magnesium chloride, silicontetrachloride, butoxytitanium, tungsten hexachloride and triethylaluminum.	Yield : 0.7 kg/ g catalyst/h
JP 0339,302	115: 72449u	Mitsubishi Petrochemicals	Propylene	Magnesium chloride, butoxytitanium, silicon tetrachloride, diemthyl siloxane and triethylaluminum	Yield : 14 kg/g catalyst/h isotacticity : 98.4%.
JP 03,22,9706	116: 60202r	Mitsubishi Petrochemicals	Propylene	Magnesium chloride, butoxytitanium, polysiloxane, silicontetrachloride, phthaloyl chloride, tungsten hexachloride, t-butylmethyl dimethoxysilane,Triethylaluminum	Yield : 8.8 kg/ g catalyst/h

Patent Number	Chem. Abstr. No	Name of Company	Monomer	Catalyst Composition	Features
JP 01,188,503	112: 36781a	Japan Synthetic Rubber Co., Ltd.	Ethylene and Hexene	Magnesium stearate, dibutylphthalate, titanium tetrachloride, phenyltriethoxy silane and triethylaluminum	Yield : 1 kg/ g catalyst/h
EP 500,392	117: 251994f	Nippon Oil Co. Ltd.	Butene-1	Silica, magnesium chloride, 2-methyl pentanol, ethoxytitanium, tetraethoxy silane and diethylaluminumchloride.	----
US 5,104,837	117: 86929	Phillips PetroChemicals Ltd.	Propylene	Alumina, magnesium compounds, alcohols, titanium chloride, dialkyl phthalate and triethylaluminum.	isotacticity : 97%.
US. 4,855371	112: 56986z	Shell Oil Co. Ltd.	Propylene	Magnesium chloride, methano, isoproponol, isobutylphthalate, phthaloyl chloride, phenyl diemthoxy silane and triethylaluminum	Yield : 24 kg/ g catalyst/h

Patent Number	Chem. Abstr. No	Name of Company	Monomer	Catalyst Composition	Features
US 4,870,039	112: 119606y	Shell Oil Co. Ltd.	Propylene	Magnesium alkoxides, dialkylmagnesium, titanium tetrachloride, ethylbenzoate and triethylaluminum	Yield : 27.9 kg/ g catalyst/h.
US 5,066,737	116: 42229a	Shell Oil Co. Ltd.	Propylene	Magnesium ethoxide, titanium tetrachloride, diisobutylphthalate, O-cresol, triethylaluminu and siloxane.	Yield : 20 kg/ g catalyst/h
EP 435,250	115: 72462t	Union Carbide Company	Ethylene	Magnesium chloride, titanium trichloride, aluminum trichloride, tetrahydrofuran, triethylaluminum, silica activated with trihexylaluminum	Yield : 68 kg/ g catalyst/h
EP 340,688	112: 140041v	Union Carbide Company	Ethylene	Magnesium ethoxide, titanium tetrachloride and triethylaluminum	Yield : 53 kg/ g catalyst/h

5.0 REFERENCES

1. K. Ziegler, E. Holzkamp H. Breil, and H. Martin, Angew. Chem., **67**, 541 (1955).

2. K. Ziegler, in "Advances in Organometallic Chemistry", (Eds. F.G.A. Stone and R. West), Academic Press, New York, (1979).

3. a) G. Natta, Angew. Chem., **68**, 393 (1956).
   b) G. Natta, Mod. Plastics, **34**, 169 (1956).
   c) G. Natta, Angew. Chem., **76**, 553 (1964).

4. a) E.F. Peters, A. Zletz, and B.L. Evering, Ind. Eng. Chem., **49**, 1879 (1957).
   b) A. Clark, J.P. Hogan, R.L. Banks, and W.C. Lanning, Ind. Eng. Chem., **48**, 1152 (1956).
   c) H.N. Frindlands, in "High Polymers", (Eds. R.A.V. Raff and K.W. Doak), Wiley Interscience, New York, **Vol 20**, 215 (1965).

5. J. Boor Jr, in "Ziegler - Natta Catalysts and Polymerizations", Academic Press, New York, (1979).

6. K.H. Reichert, in "Transition Metal Catalyzed Polymerizations of Alkenes and Dienes" (Ed. R.P. Quirk), Harwood Academic Publications, New York, Part B, p 465 (1981).

7. W. Kaminsky, in "Transition Metal Catalyzed Polymerization" (Ed. R.P. Quirk), MMI Press, Symposium Series Vol 4, Harwood Academic Press Publications, New York, p 225 (1985).

8. a) *D.S. Breslow and N.R.* NewBurg, J. Am. Chem. Soc, **79**, 5072 (1957).
   b) G. Natta, P. Pino, G. Mazzanti, and R. Lanzo, Chim. Ind., (Milan) **39**, 1032 (1957).
   c) G. Natta, P. Pino, G. Mazzanti, and B. Giannini, J. Inorg. Nucl. Chem., **8**, 612 (1958).

9. J.C.W. Chien, J. Am. Chem. Soc., **81**, 86 (1959).

10. H. Sinn, W. Kaminsky, H.J. Vollmer, and R. Woldt, Angew. Chem. Int. Ed. Eng., **19**, 390 (1980).

11. W. Kaminsky, Angew. Makromol Chem., **145/146**, 149 (1986).

12. a)J.A. Ewen, J. Am. Chem. Soc., **106**, 6355 (1984).
    b) F.R.W.P. Wild, L. Zsolnai, G. Huttrer, and H.H. Brintzinger, J. Organometal. Chem. **232**, 233 (1982).

13. a) G. Natta, I. Pasquon, and A. Zambelli, J. Am. Chem. Soc., **84**, 1488 (1962).
    b) Y. Doi, S. Ueki, and T. Keii, Macromolecules, **12**, 814 (1979).

14. J. Boor, J. Polym. Sci., Part B, **2**, 7 (1965).

15. J. Boor, J. Polym. Sci., Part A, **3**, 995 (1965).

16. a) G. Natta and I. Pasquon, Adv. Catal., **11**, 1 (1959).
    b) G. Natta, G. Mazzanti, D. DeLuca, U. Giannini, and F. Bandini, Makromol. Chem., **76**, 54 (1964).

17. R.P. Quirk (ed) in " Transition Metal Catalyzed Polymerizations: Alkenes and Dienes", Harwood Acdemic Publications, New York, (1983).

18. K. Gardner, I.W. Parsons, and R.N. Haward, J. Polym. Sci., Part A, **16**, 1683 (1978).

19. Belgian Patent, 735,291 to Hoechst A-G (1968).

20. British Patent, 114,0640 to Solvay (1966).

21. Belgian Patent 735,290 to Hoechst A-G (1968).

22. Belgian Patent, 650,679 to Solvay (1963).

23. Belgian Patent, 744,470 to Shell Int., (1969).

24. Belgian Patent, 743,315 to Solvay (1969).

25. Belgian Patent, 751,315 to Stamicarbon (1969).

26. German patent 264,3143 to Montedison and Mitsui Petrochemicals (1975).

27 P. Galli, P.C. Barbe, G.P. Guidetti, R. Zannetti, A. Martorana, A. Marigo, M. Bergozza and A. Fichera, Eur. Poly. J., **19**,19 (1983).

28. I.W. Bassi, F. Polato, M. Calcaterra, and J.C.J. Bart, Zeitschr. Fur. Kristallog., **159**, 297 (1982).

29. a) B. Keszler, A. Grobler, E. Takacs, and A. Simon, Polymer, **22**, 818 (1981).
b) B. Keszler, G. Bodor, and A. Simon, Polymer, **21**, 1037 (1980).

30. A. Sergeev, G.D. Bukatov, V.A. Zakharov, and M. Moroz, Makromol. Chem., **184**,2421 (1983).

31. B. Kessler and A. Simon, Polymer, **23**, 916 (1982).

32. U. Zucchini, I. Cuffiani, and G. Penniani, Makromol. Chem. Rapid Commun., **5**, 567 (1984).

33. N. Kashiwa, Polymer.J., **12**, 603 (1980).

34. a) F.J. Karol, Catal. Rev. - Sci. Eng., **26**, 557 (1984).
b) F. Massi, S. Malquori, L. Barazzoon, and R. Invernizzi, Makromol Chem. Suppl., **15**, 147 (1989).

35. I.I. Kim and S.I. Woo, Polym. Bull., **22**, 239 (1989).

36. R.N. Haward, A.N. Roper, and K.L. Fletcher, Polymer, **14**, 365 (1973).

37. A. Munoz-Escalona, H. Garcia, and A. Albornoz, J. Appl. Polym. Sci., **34**, 977 (1987).

38. T. Yano, I. Inoe, S. Ikai, M. Shimizu, Y. Koi, and M. Tamura, J. Polym. Sci. Part A, **26**, 477 (1988).

39. K. Makino, T. Tsuda, and M. Takaki, Polym. Bull, **27**, 41 (1991).

40. B.V. Johnson, N.M. Karayannis, C.R. Hoppin, and L. Ornellas, Makromol. Chem., **190**, 1997 (1989).

41. L.L. Bohm, Polymer, **19**, 553 (1978).

42. V. Jeong and D. Lee, Makromol. Chem., **191**, 1487 (1990).

43. P.C. Barbe, G. Cecchin, and L. Noristi, Adv. Polym. Sci., **81**, 1 (1986).

44. a) C. Dumas and C.C. Hsu, J. Macro. Sci. - Rev. Macromol. Chem. Phy., **C24**, 355 (1984).
b) U. Zucchini, T. Dall'Occo, and L. Resconi, Indian J. Technol., **31**, 247 (1993).

45. J.C.W. Chien, Catal. Rev. - Sci. Eng., **26**, 613 (1984).

46. G..G. Arzoumanidis and N.M. Karayannnis, Appl. Catal., **76**, 221 (1991).

4.7 V.D. Noto, M. Saccon, S. Bresadola, and R. Zannetti, Analyst, **115**, 1041 (1990).

48. L. Abis, G. Bacchilega, S. Spera, U. Zucchini, and T. Dall'Occo, Makromol. Chem., **192**, 981 (1991).

49. J.C.W. Chien in " Catalysis in Polymer Synthesis" (Eds. E.J. Vandenberg and J.C. Salamone) ACS Symposium Series **496**, p 27, (1991).

50. A.A. Baulin, Ye.I. Novikova, G.A. Mal'Kova, V.I. Maksimov, L.I. Vyshirskaya, and S.S. Ivanchev, Vysokomol. Soyed., **A22(1)**, 181 (1980).

51. J.F. Revol, W. Luk, and R.H. Marchessault, J. Cryst. Growth., **48**, 240 (1980).

52. R. Merryfield, M. McDaniel, and G. Parks, J. Catal., **77**, 348 (1982).

53. L. Latocha and H. Machiejewska, Polimery, **29**, 384 (1986).

54. Yu.I. Yermakov, B.N. Kuznetsov, and V.A. Zakharov, in " Studies in Surface Science and Catalysis" Elsevier Publications, New York, Vol 8, (1981).

55. B.L. Goodall, in "Transition Metal Catalyzed Polymerization" (Ed. R.P. Quirk), MMIPress. Symp. Ser., **4**, Harwood Academic Press Publication, New York, p355, (1983).

56. S. Xiao, C. Cai, H. Liu, S. Zhang, and L. Zhou, Ts'ui Hua Hsueh Pao, **1(4)**, 291 (1980).

57. S.A. Sergeev, G. D. Bukatov, V.A. Zakharov, and E.M. Moroz, Makromol. Chem., **184**, 2421 (1983).

58. J.C.J. Bart, J. Mater. Sci., **28(11)**, 278 (1993).

59. S. Sivaram and P.R. Srinivasan in "Advances in Polyolefins" (Eds. R. B. Seymour and T. Cheng), Plenum Press, New York and London, p283 (1987).

60. D.N.T. Magalhaes, O.Do,C. Filho, F.M.B. Coutinho, and P. Cenpes, Eur. Polym. J., **27**, 827 (1991).

61. R. Gerbasi, A. Marigo, A. Martorana, R. Zannetti, G.P. Guidetti, and G. Baruzzi, Eur. Polym. J., **20**, 967 (1984).

62. P.C. Barbe, L. Noristi, G. Baruzzi, and E. Marchetti, Makromol. Chem. Rapid Commun., **4**, 249 (1983).

63 N. Kashiwa and A. Toyota, Polym. Bull., **11(5)**, **471** (1984).

64. J.C.W. Chien and J.C. Wu, J. Poly. Sci Part A., **20**, 2461 (1982).

65. V.A. Zakharov, S.I. Makhtarulin, V.A. Polyboyarov, and V.F. Anufreenku, Makromol. Chem., **185**, **1781** (1984).

66. P. Galli, L. Luciani, and G. Cecchini, Angew. Makromol. Chem., **94**, 63 (1981).

67. a) A. Munoz-Esacalona, J.G. Hernandez, and J.A. Gallardo, J. Appl. Polym. Sci., **29**, 1187 (1984).
b) A. Maunoz-Escalona, Polymer Preprint ACS., Div. Polym. Chem., **24**, 112 (1981).

68. M.P. McDaniel, J. Polym. Sci Part A., **19**, 1967 (1981).

69. M. C. Sacchi, I. Tritto, and P. Locatelli, Prog. Polym. Sci., **16**, 331 (1991).

70. E.Rytter, S. Kvisle, O. Nirisen, M. Ystenes, and H.A. Oye, in "Transition Metal Catalyzed Polymerizations: Ziegler - Natta Metathesis Polymerizations" (Ed. R.P. Quirk), Cambridge University Press, London, p 292 (1988).

71. M. Terano, T. Katoka, M. Hosaka, and T. Keii in "Transition Metals and Organometallics as Catalysts for Olefin Polymerizations" (Eds. W. Kaminsky and H. Sinn) Springer Verlag, Berlin, p52 (1988).

72. a) G. Guastalla, and U. Giannini, Makromol. Chem. Rapid Commun., **4**. 519 (1983).
b) T. Keii, Y. Doi, F. Suzuki, K. Soga, M. Tamura, and M. Murata, Makromol. Chem., **185**, 1537 (1984).

73. L.L. Bohm, Makromol. Chem., **182**, 3291 (1981).

74. K. Soga and T. Shiono, Polym. Bull., **8**, 261 (1982).

75. a) G. Natta, G. Mazzanuti, P. Longi and F. Bernardini, Chim. Ind. (Milan) **41**, 519 (1959).
b) Italian Patent, 554,013 to Motecatini, (1957).

76. K. Soga, T. Sano, K. Yamamoto, and T. Shiono, Chem. Lett., 425 (1982).

77. a) G.V. Schulz, Z. Phys.Chem. **B30**, 379 (1935).
b) P.J. Flory, J. Am. Chem. Soc., **58**, 1877 (1936).
c) G. Henrici - Olive and S. Olive, Angew. Chem. Int. Ed. Engl., **9**, 243 (1970).

78. a) U. Zucchini and G. Cecchini, Adv. Polym. Sci., **51**, 101 (1983).
b) R. Spitz, in "Recent Advances in Mechanistic and Synthetic Aspects of Polymerizations" (Eds. M. Fontanille and A. Guyot), Reidel Publishing Company, Paris, p485 (1987).

79. a) L.L. Bohm, Polymer, **19**, 562 (1978).
b) L.L. Bohm, Polymer, **19**, 553 (1978).

80. a) P. Pino and R. Mulhaupt, in " Transition Metal Catalyzed Polymerizations" (Ed. R.P. Quirck), MMI Press, Vol A, p1 (1983).
b) P. Pino and B. Rotzinger, Makromol. Chem. Suppl., **7**, 41 (1984).

81. N. Kashiwa, in "Transition Metal Catalyzed Polymerization Unsolved Problems" MMI Press, Symposium Series 2, Midland, (1981).

82. N. Kashiwa and J. Yoshitake, Makromol Chem. Rapid Commun., **3**, 211 (1982).

83. T. Keii, Y. Doi, E. Suzuki, M. Tamura, M. Murata, and K. Soga, Makromol. Chem., **185**, 1537 (1984).

84. Y.V. Kissin, in "Isospecific Polymerization of Olefins" Springer - Verlag, New York (1985).

85. T. Keii, in "Kinetics of Ziegler - Natta Polymerization" Chapman and Hall, London, (1972).

86. K - Y. Choi and W. Harmony Ray, J. Macro. Sci. - Rev. Macromol. Chem. Phy., **C25(1)**, 1 (1985).

87 P.J.T. Tait, in "Comprehensive Polymer Science" (Eds. G. Allen and J.C. Bevington) Pergamon Press, Oxford, Vol **4**, 533 (1989).

88. J.C.W. Chien, J.C. Wu, and C.I. Kuo, J. Polym. Sci Part A., **20**, 2019 (1982).

89. Y. Hu and J.C.W. Chien, J. Polym. Sci. Pat A., **26**, 2003 (1988).

90. Y. Doi, E. Suzuki and T. Keii, in " Transition Metal Catalyzed Polymerizations: Alkene and Dienes", (Ed. R.P. Quirk), Harwood, New York, part B, p97 (1983).

91. M. Kakugo, T. Miyatake, Y. Naito, and K. Mizunuma, Macromolecules, **21**, 314 (1988).

OBJECTIVE

1.0 OBJECTIVE IN UNDERTAKING THE PRESENT WORK

Magnesium chloride supported titanium halides form the basis of successful heterogeneous supported Ziegler - Natta catalysts for olefin polymerization. High activity, stereo- and regioselectivity, control of morphology of polymer and elimination of catalyst removal step during the polymer processing are the unique features of these catalysts. The scientific and industrial importance of such catalysts can be evidenced by the large volume of published and patented literature during the last thirty years.

The most well studied catalysts are based on halides of Ti^{+4} or Ti^{+3} supported on activated magnesium chloride. The activation of magnesium chloride is generally performed either by physical milling or chemical methods. Distinct changes in physical state of magnesium chloride, such as increase in surface area, porosity and breakage of laminar layers of magnesium chloride accompany these treatments. Literature in this area has been extensively reviewed in recent years[1].

Nevertheless, many aspects of catalyst preparation and its relationship to polymer properties are still not well understood. The continuing objectives of these investigations are to improve the catalyst efficiency, to realize better understanding of the nature of active centers and to design new and novel catalysts for imparting specific properties to polymers. The key to tailoring of properties of polymers essentially rests on the design of catalysts.

The present investigation was undertaken with a view to understand some of the features of Mg - Ti catalysts as described below:

a) anhydrous magnesium chloride, a successful support material exists in three forms namely α, β or δ forms. α and β forms, with a very low surface area, exist in cubic close packing and hexagonal close packing arrangement, respectively. The α form is generally obtained as a by product in the preparation of titanium sponge from titanium tetrachloride and magnesium metal at very high temperatures (>1000°C)[2]. Thermodynamically, less stable β - form is obtained by dehydration of $MgCl_2 .6H_2O$ with thionyl chloride[3]. These two forms, being highly crystalline, lack surface defects for complexing with coordinatively unsaturated transition metal components. Hence, activation techniques like grinding and coprecipitation are adopted to generate surface defects. The coordinatively unsaturated high energy magnesium chloride thus obtained is classified as δ - form. This form is generally stabilized by complexing with Lewis bases or transition metal components. Recently, there have been attempts to synthesize δ - form of magnesium chloride insitu by chlorination of Grignard reagents. Hence, one of the objectives of the present investigation is to explore new routes for the synthesis of highly active δ - form of magnesium chloride complexed with a Lewis base at as low a temperature as possible.

b) titanium halides are the preferred transition metal components to synthesize high activity magnesium chloride supported catalysts. Extensive studies have been reported by Chien[4], Yermakov[5], Soga[6] and Kashiwa[7] on the synthesis of heterogeneous Mg - Ti catalysts and olefin polymerization using the said catalysts . However, there are only few reports in the literature on the use of non halogen containing titanium compounds as transition metal components. Recently, Zucchini[8], Kashiwa[9], Soga[10] and Yano[11] have used alkoxy - containing titanium compound to synthesize catalyst compositions for the polymerization of olefins. It has been observed that these catalysts show a relatively high activity during polymerization. Further, it is well known that titanium alkoxides promote only selective dimerization of ethylene to butene-1 in conjunction with alkylaluminums[12]. However, when supported on $MgCl_2$, they are converted to polymerization catalysts. This observation indicates that the support $MgCl_2$ is not inert and has a specific role in changing the nature of the active centers. Zuchinni and co-workers adopted a physical grinding method to prepare $MgCl_2$ - $Ti(OR)_4$ catalysts[8]. They further studied the effect of ligands around the transition metal component, and showed that the catalyst activity for ethylene polymerization is in the order of decreasing electron releasing effect of alkyl group.

R= $CH_3 < C(CH_3)_3 < CH(CH_3)CH_2CH_2 < CH(CH_3)_2 < C_2H_5 < CH_2CH(CH_3)_2 < CH(CH_2)_3CH_3$

Thus, it is observed that the catalyst activity is dependent on two factors namely, steric and electronic nature of ligands. Soga et. al., showed that a solution of $MgCl_2$ - 2 - ethylhexanol in conjunction with TNB polymerizes propylene with a steady state kinetics[10]. This feature is unusual for propylene polymerization using a Mg - Ti catalyst, which generally shows a decay type kinetics. Similarly, Yano and co-workers used a heptane solution of anhydrous magnesium chloride - 2 - ethylhexanol complex along with titanium tetrachloride or TNB as a catalyst for high temperature polymerization of ethylene[11]. In both the studies, although the precursors were hydrocarbon soluble, the active catalyst formed by addition of diethylaluminumchloride was presumably heterogeneous. More recently Makino and co-workers[13] and Zucchini and co-workers[8] reported a truly soluble Mg - Ti catalyst. Reduction of titanium tetrachloride by Grignard reagent or solubilizing anhydrous magnesium chloride with trialkylphosphate was reported to result in soluble Mg - Ti catalyst capable of copolymerizing ethylene and propylene[13]. Reaction of anhydrous magnesium chloride with titanium tetraethoxide in 2:1 stoichiometry resulted in a defined bimetallic complex which was reported to show activity for ethylene polymerization as homogeneous catalysts in toluene solution[8]. These soluble catalysts offer a greater scope to understand the catalyst systems through kinetic and analytical studies.

Hence one of the objectives of the present investigation is to synthesize and characterize aromatic hydrocarbon soluble Mg - Ti compounds using well characterized Lewis base complex of $MgCl_2$ and titanium alkoxides

c) titanium alkoxides alone in conjunction with alkylaluminums do not polymerize ethylene. They selectively dimerize ethylene to butene-1[12]. However, it is observed that these alkoxides by supporting on $MgCl_2$ polymerize ethylene with relatively high activities[8-11]. This observation led to the belief that the ligand environment of magnesium chloride influences the active titanium center and promote ethylene polymerization. Hence, we propose to examine the efficiency of hydrocarbon soluble Mg - Ti catalyst in conjunction with alkylaluminums towards polymerization of ethylene.

d) high molecular weight amorphous homopolymers of higher α - olefins such as hexene-1, octene-1 have assumed importance as rheology modifiers in a variety of end applications[14,15]. Conventionally heterogeneous titanium - aluminum or magnesium - titanium - aluminum catalysts have been used for homopolymerization of higher α - olefins. High molecular weight polymers with broad molecular weight distribution (>10) are produced using these catalysts[16]. Recently, transition metal alkoxides (Ti, Zr, Hf) supported on magnesium chloride catalysts have attracted attention as efficient catalysts for higher α olefin polymerization[17]. Therefore, another objective of the study is to examine the polymerization of higher α olefins using aromatic hydrocarbon soluble Mg - Ti in conjunction with diethylaluminum chloride.

e) polyacetylenes have been considered as speciality polymers due to the properties like chain stiffness, geometrical isomerism, chemical reactivity, color, electrical conductivity and paramagnetism. The presence of alternating double bonds along the main chain in substituted and unsubstituted polyacetylenes is responsible for these properties. Generally, polymerization of monosubstituted acetylenes have been performed by using catalyst systems based on Ti, Mo or W based catalysts[18]. The choice of catalyst as well as suitable experimental conditions strongly depend on the chemical nature and steric hindrance of the substituents. In fact, Ti based Ziegler catalysts are generally preferred with uncrowded monomers bearing aliphatic groups such as ethyl and butyl groups[19]. Similarly, aromatic monosubstituted acetylenes are preferred with Mo - based catalysts. The experimental conditions, ligand environment and acidity of active sites play a vital role during polymerization of monosubstituted acetylene. Hence, we propose to examine the efficacy of homogeneous hydrocarbon soluble Mg - Ti catalysts in conjunction with triisobutylaluminum towards polymerization monosubstituted acetylene.

f) Metallocenes have been identified as truly homogeneous hydrocarbon soluble Zielger - Natta catalyst. Breslow and Newburg were the first to show that bis(cyclopentadienyl) titanium(IV) dichloride existed as a homogeneous solution in conjunction with alkylaluminums[20]. They further showed that Cp_2TiCl_2 - Et_2AlCl catalyst system polymerized ethylene to polyethylene. Further Chien demonstrated by kinetic studies, that these catalyst underwent a rapid decay process to generate inactive trivalent species[21]. A number of attempts have been made to stabilize the active species using different approaches. These include, inter alia, a) heterogenization of homogeneous metallocene catalyst on an inert support b) modification of alkylaluminums c) development of cocatalyst free metallocenes. Sinn and co-workers showed that by modifying alkylaluminums a highly active stable and homogeneous catalyst could be obtained for olefin polymerization[22]. This has become an important discovery in the area of olefin polymerization catalysts. This system suffers from several drawback such as ambiguity of structure of modified aluminumalkyls, requirement of high concentration of aluminum to initiate polymerization and rapid decay of catalyst activity with time. Recently, cationic d^0, $14e^-$ metallocene compounds, which do not require a cocatalyst for polymerization of olefins, have been identified. Jordan and co-workers found that ethylene polymerization proceeds effectively in presence of dicyclopentadienyl zirconium alkyl complexes in absence of cocatalysts[23]. Similarly, Ewen and co-workers found that cationic zirconium complex such as $Et[Ind\ H_4]_2ZrMe^+$, $iPr[Flu(Cp)_2]ZrMe^+$ show very high activity for propylene polymerization[24]. These catalysts are not stable at high temperature and require lengthy and difficult manipulations for their preparation. These catalysts are mostly suitable for mechanistic studies of olefin polymerizations.

Relatively lesser attention has been paid to the aspects of heterogenization of homogeneous metallocene catalysts. One of the early attempts in this direction was made by Slotfeldt - Ellingsen and co-workers. Cp_2TiCl_2 was supported on silica gel and used to polymerize ethylene using Et_nAlCl_{3-n} as cocatalyst[25]. The specific catalyst activity was found to be comparable for both homogeneous and supported catalysts. Recently, Soga and co-workers studied the isospecific polymerization efficiency of propylene using supported ethylene bis($IndH_4$)zirconium(IV) dichloride in conjunction with alkylaluminums[26]. Alumina, silica and magnesium chloride and methylaluminoxane (MAO) pretreated silica were used as supports and trialkylaluminum as cocatalyst.

Al_2O_3 and $MgCl_2$ gave low molecular weight polymers with broad polydispersities. On the contrary, SiO_2 pretreated with MAO gave narrow polydispersities and lower catalyst activities[27]. MAO pretreated SiO_2 has been shown to polymerize propylene with no change of stereospecificity by Chien and co- workers and Collins and co-workers[28,29]. All these catalyst systems have been prepared by physically grinding the support and the transition metal component in a diluent such as toluene.

We, therefore, propose to examine the routes for heterogenization of homogeneous metallocene catalysts. This includes synthesis and characterization of heterogeneous bimetallic Mg and Ti catalysts based on preformed magnesium chloride and metallocenes. Further, we propose to study the polymerization efficiency of these catalysts in conjunction with alkylaluminums to elucidate the mechanism of olefin polymerization.

2.0 APPROACHES

2.1 A self Grignard decomposition route has been designed to synthesize anhydrous $MgCl_2$. The proposed route is shown below. This magnesium chloride has been shown to exist in δ active form.

$ClCH_2CH_2CL$ + Mg -----------> $MgCl_2.2THF$ + C_2H_4

2.1 A thermochemical approach for synthesis of aromatic hydrocarbon soluble Mg - Ti catalysts from δ - $MgCl_2.2THF$ complex and titanium-n-butoxide (TNB) in xylene medium is proposed

$MgCl_2.2THF$ + TNB -----------> A soluble Mg - Ti catalyst

2.1 Ethylene, higher α - olefins and phenylacetylene polymerization studies using hydrocarbon soluble catalyst are proposed.

2.1 Solubilization of magnesium chloride by Grignard decomposition and dissolution of cyclopentadienyl titanium(IV) dichloride to form a clear solution is proposed. This clear solution on coprecipitation in a nonsolvent should yield a bimetallic Mg - Ti catalyst. Synthesis, characterization and ethylene polymerization efficiency of this catalyst are proposed.

3.0 REFERENCES

1. a) P.C. Barbe, G.Cecchin, and L. Noristi, Adv. Polym. Sci., **81**, 1 (1986).
   b) J.C.W. Chien, Catal. Rev. Sci & Eng., **26**, 613 (1984).

2. P. Galli, P.C. Barbe, G. Guidetti, R. Zannatti, A. Martorana, A. Marigo, M. Bergozza, and A. Fischera, Eur. Polym. J., **19**, 19 (1983).

3. I.W. Bassi, F. Polato, M. Calcaterra, and J.C.J. Bart, Zeitschr. Fur. Kristallog., **159**, 297 (1982).

4. J.C.W. Chien, in "Catalysis in Polymer Synthesis" (Eds. E.J. Vandenberg and J.C. Salamone) ACS Symposium Series 496, Washington, (1992).

5. Y. Yermakov, B.N. Kuznetov, and V.A. Zakharov, "Catalysis by Supported Complexes" Elsevier Sci. Publ. Co., Chap.2 (1981).

6. K. Soga, Makromol. Chem. Macromol. Symp., **66**, 43 (1993).

7. N.Kashiwa, in "Transition Metal Catalyzed Polymerization: Unsolved Problems", MMI Press, Symposium Series 2, Harwood Academic Press Publications, Midland, (1981).

8. a) U. Zucchini and T Dall'Occo, in " Polymer Science Contemporary Themes" [Ed. S. Sivaram] Tata - McGraw - Hill Publ. Co., New Delhi, **1**, 221 (1991).
   b) M.Malpezzi, U.Zucchini and T. Dall'Occo, Inorg. Chem. Act., **180**, 245 (1991).

9. N.Kashiwa and A. Toyota, Polym. Bull., **11**, 471 (1984).

10. a) K. Soga, T. Shiono, Y.Y. Wu, K. Ishii, A. Nogami, and Y. Doi, Makromol Chem. Rapid Commun., **6**, 537 (1985).
    b) Y. Doi, K. Soga, M. Murate, E. Suzuki, Y. Ono, and T. Keii, Polymer, **24**, 244 (1983).

11. T. Yano, S. Ikai, M. Shimizu, and K. Washio, J. Polym. Sci Part A., **23**, 1455 (1985).

12. S. Muthukumaru Pillai, M. Ravidranathan, and S. Sivaram, Chem. Rev., **86**, 353 (1986).

13. a) K. Makino, K. Tsuda, and M. Takaki, Polym. Bull., **26**, 371 (1991).
    b) K. Makino, K. Tsuda, and M. Takaki, Polym. Bull., **27**, 41 (1991).

14. U.S.Pat., 4433123 (1984); to Conoco. Inc.

15. U.S. Pat. 4613712 (1986); to Mobil Oil Corporation Ltd.,
    Ger. Pat., 3323725 (1988); to Hoechst A.G.

16. J.C.W. Chien and T. Ang, J. Polym. Sci Part A., **24**, 2217 (1986).

17. A. Altomare, R. Solaro, F. Ciardelli, C. Barrazzoni, F. Menconi, S. Malquori, and F. Masi, Polymer, **33**, 1768 (1992).

18. M. Masuda and T. Higashimura, Adv. Polym. Sci., **81**, 121 (1986).

19. C.I. Simionescu and V. Percec, Prog. Polym. Sci., **8**, 133 (1982).

20. D.S.Breslow and N.R. Newburg, J.Am. Chem. Soc., **79**, 5072 (1957).

21. J.C.W. Chien, J. Am. Chem. Soc., **81**, 86 (1959).

22. W. Kaminsky, in " Transition Metal Catalyzed Polymerization" Ed. R.P. Quirk, Harwood Academic Publishers, New York MMI Press, Vol. 4, 225 (1983).

23. R.F. Jordan, J. Chem. Educ., **65**, 285 (1988).

24. J. A. Ewen, L. Haspeslagh, L. Atwood, and H. Zhang, J.Am. Chem. Soc., **109**, 6544 (1987).

25. D. Slotfeldt-Ellingsen, I.M. Dahl, and O.H. Ellestad, J. Mol. Catal., **9**, 423 (1980).

26. K. Soga and M. Kaminaka, Makromol Chem. Rapid Commun., **12**, 367 (1992).

27. K. Soga and M. Kaminaka, Makromol. Chem. Rapid Commun., **13**, 221 (1992).

28. J.C.W. Chien and D. He, J. Polym. Sci., Part A., **29**, 1603 (1991)

29. S. Collins, W. Mark Kelly, and D.A. Holden, Macromolecules, **25**, 1780 (1992).

A MAGNESIUM CHLORIDE - TETRAHYDROFURAN DERIVED SUPPORT FOR OLEFIN POLYMERIZATION CATALYST

1.0 INTRODUCTION TO LEWIS BASE COMPLEXES OF MAGNESIUM CHLORIDE

Magnesium chloride, Lewis bases and titanium compounds were identified as the primary precursors of high efficiency and stereospecific Mg - Ti heterogeneous catalysts for olefin polymerization. Use of such catalysts in commercial plants lead to many advantages in the manufacture of linear low density polyethylene (LLDPE) and high density polyethylene (HDPE). The primary step during the synthesis of these catalysts is the formation of active disordered δ - form of magnesium chloride. This δ - form of $MgCl_2$ is either complexed with a Lewis base or generated in situ as a complex of Lewis base to stabilize in active disordered form.

There are very few reports in the scientific literature on the synthesis and characterization of Lewis base complexes of magnesium chloride, even though these are commonly employed as precursors for the preparation of high efficiency olefin polymerization catalysts. Hence, in this section, the significance of Lewis base in Mg - Ti catalysts, the nature of Lewis bases commonly employed and the synthesis of Lewis base complexes of $MgCl_2$ will be discussed.

1.1 Significance of Lewis Base in Mg - Ti Catalysts

Lewis bases play a significant role both during the synthesis of Mg - Ti catalysts as well as during olefin polymerization. Complexation of Lewis base with $MgCl_2$ creates highly unsaturated Mg^{+2} cations in the crystal lattice. These cations expose the lateral and edges of $MgCl_2$ crystal surfaces (crystal defects), thus providing electron deficient Mg^{+2} cationic sites for complexation with catalytically active Ti centers. Hence, it can be said that the Lewis base acts as an activator or a promoter for generating highly efficient Mg - Ti catalysts. In fact, two or more Lewis bases are often employed in successive treatments to generate electron deficient sites on preformed $MgCl_2$. Typically, less than two moles of Lewis base per mole of $MgCl_2$ is used for catalyst preparation.

The specific role of Lewis base, in particular ethylbenzoate (EB) associated with $MgCl_2$, in catalysis has been extensively studied and speculated upon in the literature[1,2]. In essence, the significance of Lewis base is in the following descending order of importance:

i) Lewis base enhances the stability of surface complexes formed between $TiCl_4$ and active $MgCl_2$. The grinding of EB and $MgCl_2$, in fact, results in a new crystalline phase with total loss of crystal lattice of $MgCl_2$[3]. An EB/$MgCl_2$ 0.17 crystallite particle size is the minimum which makes it amorphous.

ii) The Lewis base prevents agglomerations of $MgCl_2$ crystallites upon grinding by complexing with high energy sites. Thus, incorporation of EB, in particular, on $MgCl_2$ decreases its surface area.

iii) Lewis base regulates the stereospecificity of polymerization. It is associated with the active center or blocks non-stereospecific centers on $MgCl_2$ - $TiCl_4$. Also, it reacts with $AlEt_3$, even if it is complexed on $MgCl_2$. Thus, it can affect stereospecificity.

iv) The activity of Mg - Ti catalyst as well as its useful life time are decreased at the cost of high stereospecificity in presence of Lewis base.

1.2 Most Commonly Employed Lewis Base Complexes of $MgCl_2$ in Mg - Ti Catalysts

Any organic compound having an "n" electron can be complexed with $MgCl_2$. The most commonly employed organic molecules are alcohols, esters and ethers. Of this, esters of benzoic acid and phthalic acid are widely used in patent and published literature. Extensive studies by Chien et. al., have shown that diesters, such as, dibutyl phthalate, dimethyl phthalate, dimethyl terephthalate etc., based Mg - Ti catalysts, yield more active and stereospecific catalyst systems in comparison to monoesters based Mg - Ti catalysts[4]. The method of preparation also plays an important role. Thus, the physical ball milling method shows very marginal variations in activity and specificity between monoester based Mg - Ti catalysts. In contrast, Mg - Ti catalysts prepared by chemical methods using monoesters as Lewis bases yield very inferior catalysts in all respects when compared to the diester Lewis base based Mg - Ti catalysts. Of the diesters, Chien et. al., found that butyl phthalate based Mg - Ti catalysts yield superior activity (16.1 KgPP/g Ti/h, II: 98.6%), in comparison to other diesters.

A thorough kinetic and spectroscopic investigation of $MgCl_2$/2-ethyl hexanol/butyl phthalate/$TiCl_4$ - $AlEt_3$/PES and $MgCl_2$/ethyl benzoate/$TiCl_4$ - $AlEt_3$/MPT showed that although both the esters are present in the isospecific environment, they interact with the nonstereospecific sites in different ways.

1.3 Synthetic Methods

Various synthetic methods adopted for complexation of Lewis base with $MgCl_2$ are be as follows:

1.3.1 Direct Complexation Routes

1.3.2 Indirect Complexation Routes

1.3.1 Direct Complexation Routes

Physical milling or thermochemical reaction constitute examples of direct complexation routes to synthesize Lewis base complexes of anhydrous $MgCl_2$. Both the reactions yield active δ form of $MgCl_2$ by disturbing the crystalline planes of $MgCl_2$. The most prominently disturbed planes are (101), (001) & (110).

Esters, in particular ethylbenzoate (EB) are the most well studied Lewis bases for complexation through physical milling. It is observed that this complexation reduces the crystallite sizes in both (110) & (001) direction. A $MgCl_2$:EB ratio of 6.0 is identified as an optimum ratio to obtain crystallites having suitable dimensions. Reaggregation of $MgCl_2$ crystals occurs upon increasing $MgCl_2$:EB ratio, which results in the reduction of surface area of $MgCl_2$. Ethers and alcohols are preferred for synthesizing $MgCl_2$ Lewis base complexes by thermochemical route[5,6]. This results in formation of well defined stoichiometric complexes and alters the crystallite sizes in the (110), (001) & (101) planes. Complexation with alcohols/ ethers also promotes solubilization of $MgCl_2$.

The extent of solubility is dependent on the Lewis base acidic strength. Accordingly, the esters cannot solubilize $MgCl_2$ upon heating, even though they can form complexes by physical milling.

The $MgCl_2$.alcohol system has been well studied. Excess of alcohols are shown to solubilize $MgCl_2$ at their boiling points[6]. Isolation in a non solvent yields regular complexes of $MgCl_2$ and alcohols. The complexing ability is dependent on the nature of alcohols. In general, complexing $MgCl_2$ with alcohols or phenols cause an increase in surface area and decrease in crystallite sizes in the direction perpendicular to (101), (001) & (110) planes.

1.3.2 Indirect Complexation Routes

Indirect routes of synthesis of $MgCl_2$.Lewis base complexes involve decomposition of active bivalent Mg^{+2} reagents or Grignard reagents insitu in the presence of Lewis base with a chlorinating agent. No systematic study has been reported on the synthesis and characterization of such $MgCl_2$ Lewis base complexes. A few scattered reports exist on $MgCl_2$ Lewis base complexes obtained by Grignard decomposition routes[7]. This method is suitable only for the ether complexes of $MgCl_2$ on account of the reactivity of Grignard reagent with esters or alcohols. Tetrahydrofuran (THF) is the preferred ether for generating these complexes (vide infra).

2.0 MAGNESIUM CHLORIDE - TETRAHYDROFURAN DERIVED SUPPORT

A series of patents issued to Union Carbide Corporation reveal that THF is the preferred Lewis base for synthesizing high efficiency catalysts for ethylene polymerization[8]. Although such catalysts are in commercial use, little details have appeared in the open literature. As disclosed in the patents, the complexes were prepared by refluxing anhydrous magnesium chloride with THF for 8 - 12 hours. More recent studies have revealed that the complex exists in three forms, namely, $MgCl_2$.1.5THF, $MgCl_2$.2THF, $MgCl_2$.4THF. The crystal and molecular structure of $MgCl_2$.4THF has been well understood[9].

2.1 Synthesis

Literature reports five synthetic routes for the preparation of $MgCl_2$ - THF complexes[9], as shown in equations 3.1 to 3.5. All these produce THF solvates of $MgCl_2$ soluble in THF.

$$MgCl_2 \xrightarrow{THF,\Delta} MgCl_2(THF)_x \tag{3.1}$$

$$Mg + HgCl_2 \xrightarrow{THF,\Delta} MgCl_2(THF)_x \tag{3.2}$$

$$Mg + CH_2{=}CHCH_2Cl \xrightarrow{THF} MgCl_2(THF)_x + CH_2{=}CHCH_2CH_2CH{=}CH_2 \tag{3.3}$$

$$C_4H_9MgCl + C_4H_9Cl \xrightarrow{THF} MgCl_2(THF)_x + C_4H_9C_4H_9 \tag{3.4}$$

$$Mg + 2HCl \xrightarrow{THF} MgCl_2(THF)_2 + H_2 \tag{3.5}$$

Even though these routes produce THF adducts of $MgCl_2$ upon isolation in a non solvent, the following drawbacks limit their general applicability:

i) The direct synthetic route as shown in Equation 3.1 suffers from low solubility of $MgCl_2$ in THF. In fact, it was observed that this route could produce only 0.02 mol L^{-1} solution of $MgCl_2$ in THF when compared to 0.5 - 0.7 mol L^{-1} solution obtained by other methods.

ii) The indirect synthetic routes as shown in Equations 3.2 - 3.5 generate considerable amount of by products or even starting materials which act as impurities in subsequent steps of catalyst preparation.

iii) The synthetic route according to Equation 3.2 produces very low yields of $MgCl_2(THF)_x$ complex. The method according to Equation 3.5 produces high yields of $MgCl_2.2THF$ complex. However, it is necessary to carefully neutralize excess hydrochloric acid (HCl) to prevent the reaction of HCl with THF.

Thus, it can be seen that none of the available methods offer a simple synthesis of $MgCl_2.2THF$ complex free of impurities that could adversely interfere in the subsequent steps of catalyst preparation.

2.2 Characterization

Solid phase - solution equilibrium studies reveal that $MgCl_2.4THF$ and $MgCl_2.2THF$ solvates exists in equilibrium with the saturated solution of $MgCl_2$ in THF[9]. The analysis of solid phase showed that upto the temperature of 28°C, $MgCl_2.4THF$ complex is in equilibrium with the saturated solution, whereas above this temperature, the composition of solid corresponds to the $MgCl_2.2THF$ solvate. This solution prefers a metastable state for a longer period at supersaturation. It was further shown that the change of $MgCl_2.4THF$ to $MgCl_2.2THF$ is connected with a deep structural change, which can be observed in XRD pattern.

Isolation of solids from $MgCl_2$ - THF solution in a non solvent such as hexane or 1,2 - dichloroethane, below 28°C yields $MgCl_2.4THF$ and above 28°C produces $MgCl_2.2THF$. The composition of these adducts were identified by elemental analysis, powder X- ray diffraction and IR - spectroscopic techniques[9]. Powder XRD patterns of the two complexes differ sufficiently in both magnitude of the diffraction angle (inter layer distances) as well as intensities of lines. They also differ from the diffraction lines of two modifications of anhydrous $MgCl_2$. The almost perfect agreement of the lattice parameters of $MgCl_2.4THF$ and $MgBr_2.4THF$, a homologous compound, obtained from the powder XRD pattern, led to the conclusion that the molecular structure of $MgCl_2.4THF$ is analogous to that of $MgBr_2.4THF$[10]. Crystals of two compound consequently constructed from isolated units of $[MgX_2.4THF]$ (X = Cl or Br) with trans - octahedral coordination around the Mg atoms. Thus $MgCl_2.4THF$ must be formulated as trans- dichloro - tetrakis(THF)Mg(II) complex. The IR spectroscopic results support this assumption.

The powder XRD of the $MgCl_2.2THF$ complex differs markedly from that of the orthorhombic $MgBr_2.2THF$. The total number of lines is higher in this case. The IR spectra of these complexes showed characteristic peaks corresponding to $\nu(COC)$ vibration bands of THF at $1037 Cm^{-1}$ and $883\ Cm^{-1}$ bonded to $MgCl_2$ and $1068\ Cm^{-1}$ and $917\ Cm^{-1}$ non bonded to $MgCl_2$ and in the regions of $1360 - 1170\ Cm^{-1}$ the vibrations corresponding to C-H and C-C bonds of THF.

2.3 Role of THF in Mg - Ti Olefin Polymerization Catalysts

Structural Studies of Sobota and co-workers confirmed that THF promotes the complexation of $MgCl_2$ & $TiCl_4$ to yield bimetallic complexes. In fact, three different complexes were obtained as shown in Equations 3.6 and 3.8 depending upon the molar ratios in which $MgCl_2.2THF$ & $TiCl_4.2THF$ were combined[11,12,13].

$$\mathrm{MgCl_2(THF)_2 + 2\ [TiCl_4(THF)_2] \;\text{-->}\; Mg(THF)_6][TiCl_5(THF)]_2} \qquad 3.6$$

$$\mathrm{Mg(THF)_6][TiCl_5(THF)]_2 + MgCl_2(THF)_2 \;\text{-->}\; [(THF)_4Mg(\mu\text{-}Cl)_2\ TiCl_4]} \qquad 3.7$$

$$\mathrm{[(THF)_4Mg(\mu\text{-}Cl)_2TiCl_4) + MgCl_2(THF)_2 \;\text{-->}\; [Mg(\mu\text{-}Cl)_3(THF)_6][TiCl_5(THF)]} \qquad 3.8$$

These complexes exist either in monomeric or dimeric forms. Alkylaluminums were unable to reduce these bimetallic complexes due to the strong association of THF with catalytically active Ti sites. Consequently, these complexes showed no polymerization activity.

Recently, Choi et. al., and Chang et. al., synthesized Mg - Ti bimetallic complexes of $MgCl_2$, $TiCl_4$ ($TiCl_3.0.33AlCl_3$) and THF and studied the polymerization activities on changing the crystallization conditions, or by thermal and chemical treatment[14,15]. It was observed that all these treatments led to decrease in the THF content present on the catalyst surface, thus exposing active Ti centers for polymerization and hence, increase in activity. It was also observed that, when these complexes were used in polymerization without any treatment to remove THF, little or no activity was observed because of strong complexation of THF with catalytically active centers.

Choi et. al., showed that homo and copolymerization activities with Mg - Ti bimetallic catalysts, obtained from a solution of $MgCl_2$ - THF - $TiCl_4$, increased with increasing crystallization temperature from 0 - 60°C[14]. It was observed that all these catalyst have considerable induction period and it decreases with increasing crystallization temperature. Further, studies on this bimetallic catalyst showed that the rate and activity of homo and copolymerization of ethylene and propylene are very much dependent on the amount of THF present on this catalyst. A systematic temperature programmed decomposition of bimetallic complex $MgCl_2/TiCl_4/THF$ (Mg/Ti = 5.2) showed that below 108°C, the ethylene polymerization activity of catalyst increased while it decrease above 140°C. However, the catalytic activity of the bimetallic complex (Mg/Ti = 16.5) decreased after thermal treatment at 80°C, indicating that the thermal stability of bimetallic complexes is low at high Mg/Ti ratios. The characterization of products obtained upon thermal treatment showed that THF and 1,4 dichlorobutane were produced during the thermal treatment. Thus, it can be concluded that removal of THF by heating exposes active Ti - centers resulting in increase in the activity. Similar observations were reported by Chang et. al., upon removal of THF by reacting with diethylaluminumchloride from the surface of bimetallic Mg - Ti catalysts obtained from $MgCl_2$, $TiCl_3$ $0.33AlCl_3$ and THF[15]. Comparison of the ESR Ti^{+3} signal and polymerization results showed that multinuclear Ti^{+3} species contribute to the increase of isotacticity and activity in propylene polymerization and for the formation of propylene blocks in ethylene - propylene copolymerization. On the other hand, isolated Ti^{+3} (due to the presence of more THF) contribute to the increase of activity in ethylene polymerization and to the random insertion of propylene into the ethylene main chain in ethylene - propylene copolymerization. In comparison, a catalyst having less THF content shows high activity in ethylene homopolymerization, high randomness of propylene unit in copolymerization and lower isotactic index of polypropylene. It was further shown that molecular weight distribution of ethylene - propylene copolymers become broader, probably due to the formation of active species of more than one type in the catalysts.

3.0 RESULTS AND DISCUSSION

To obviate the disadvantages of the earlier reported methods for preparation of $MgCl_2$.THF complex, a new and simple synthetic route was explored (equation 3.9). This method of synthesis is clean and results in 100% conversions leaving no unwanted residues that could cause subsequent interference.

$Mg + CH_2ClCH_2Cl \dashrightarrow MgCl_2 (THF)_x + CH_2{=}CH_2$ 3.1

There appears to be no precedence for this reduction in the prior literature although similar Grignard decomposition with 1,2- dibromoethane has been reported to be facile[16]. The only by product is ethylene which is a gas. The formation of $MgCl_2.(THF)_x$ proceeds in two steps, namely, (i) formation of β - chloroethylmagnesium chloride, and ii) concomitant decomposition of this intermediate to generate $MgCl_2(THF)_x$. In excess of THF, the complex was obtained as a clear solution.

The concentration of the solution thus obtained was found to be 0.6 - 0.7 mol L^{-1}. The solvate, $MgCl_2(THF)_x$, was isolated by precipitation either in a non solvent hexane or in 1,2 dichloroethane.

3.1 Characterization

Elemental analysis established the stoichiometry of the complex as $MgCl_2$.2THF. The presence of tetrahydrofuran was established by the appearance of triplets at 3.7 and 5.7ppm in proton NMR spectrum in D_2O as solvent (Figure 3.1) and bands at 1039 and 885cm^{-1} corresponding to COC linkage bonded to magnesium chloride in FT - IR spectrum (Figure 3.2). The powder XRD spectrum of $MgCl_2$2THF showed strong reflection at 2θ = 29.2, 32.4 and 40.8(Figure - 3.3). The powder XRD pattern of $MgCl_2$.2THF is in agreement with that reported in the literature, but prepared by a different route. The results show that the complex is highly crystalline. The complex had a total pore surface area of 10 m^2/g and a mean pore volume of 0.83 cm^3/g. $MgCl_2$.2THF was subjected to thermogravimetric analysis (N_2 - atmosphere, 50 - 300°C

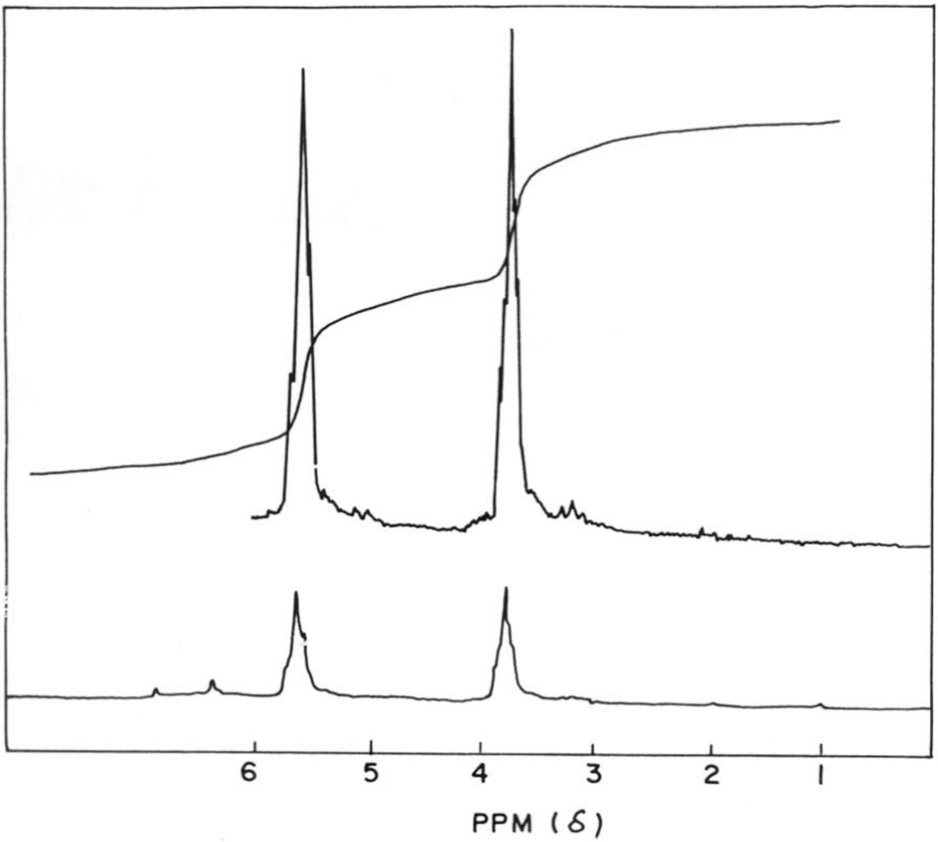


Fig.3.1 NMR Spectrum of $MgCl_2.2THF$ in D_2O

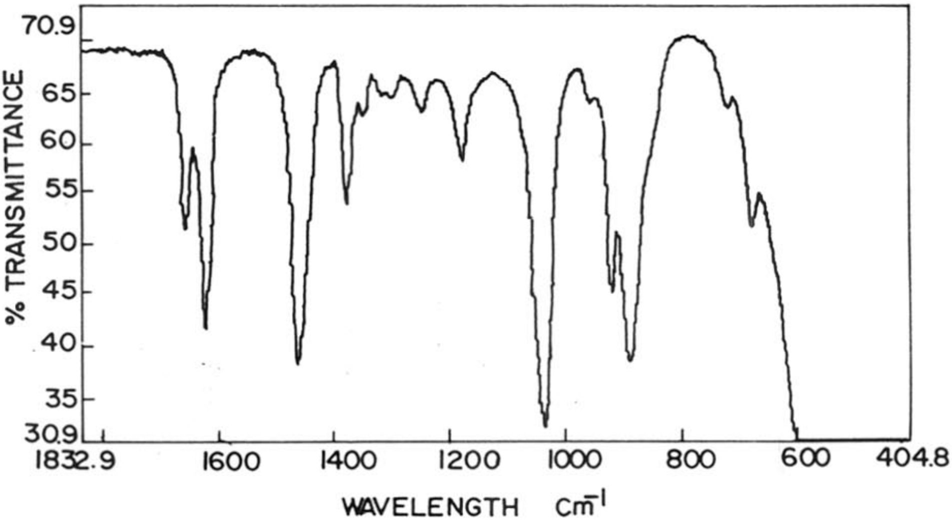


Fig.3.2 FT - IR Spectrum of $MgCl_2.2THF$ in Nujol Mull (1600 - 400 cm^{-1})

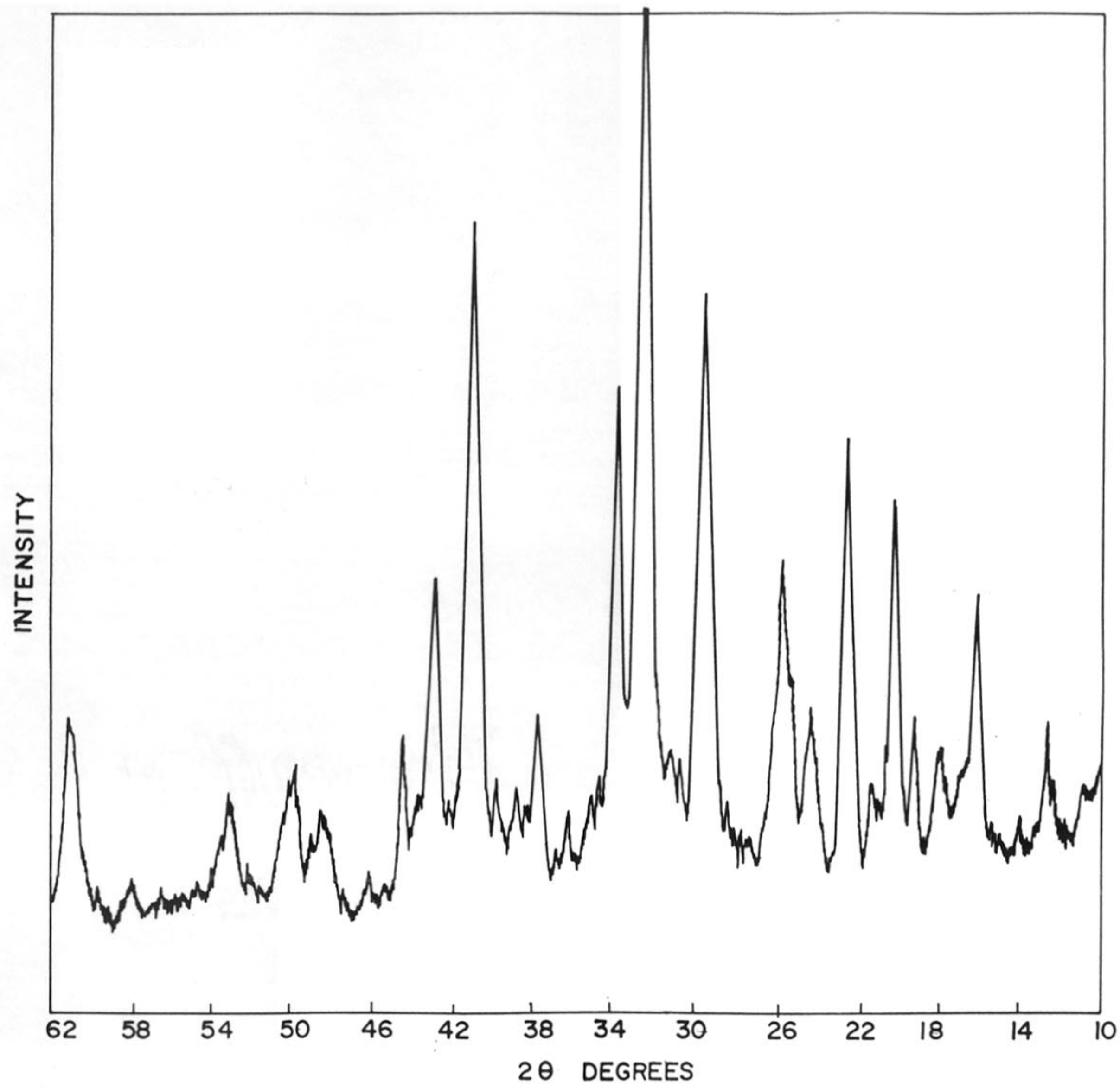


Fig.3.3 Powder X - ray Diffraction Spectra of $MgCl_2.2THF$

at a rate of 10°C/min). The results showed that the loss of THF occurred by a two stage process. The total weight loss was observed to be 74%, which corresponds to 2 moles of THF per mole of magnesium chloride(Figure 3.4).

3.2 Physical Activation of $MgCl_2.2THF$

Milling of the $MgCl_2.2THF$ complex was carried out to understand the role of the complexed Lewis base (THF). It was observed that THF promotes faster cleavage of crystalline layers in comparison with anhydrous $MgCl_2$. The structural changes occurring at every stage of grinding were monitored by observing the broadening of XRD pattern. Even after 20h of grinding, the anhydrous $MgCl_2$ showed sharp crystalline peaks (Figure 3.5) in comparison with $MgCl_2.2THF$ which showed severe reduction in peak intensities in six hours time. The changes in X- ray diffraction pattern with grinding time (0, 1, 2, 3 & 6h) are shown in Figure 3.3, 3.6, 3.7, 3.8 and 3.9. It was observed that the major peaks corresponding to 2θ = 63.2, 42.8, 41.2, 33.4, 29.6, 25.8, 22.6 20.4 & 16.0, were either absent or reduced in intensities to less than 10% of their original intensities. The major characteristic peak corresponding to 2θ = 32.4 was observed, even after 6h grinding, with decrease in intensity. These observations confirm that the THF molecule present in the crystal lattice of $MgCl_2.2THF$ facilitates rupturing of the crystalline structure and reduces the crystallite size of the compound. The presence of bonded THF, even after grinding on the crystalline surface was confirmed by NMR and elemental analysis with no change in stoichiometry upon grinding.

3.3 Chemical Activation of $MgCl_2$. 2THF

Various techniques can be adopted to remove the THF from the surface of catalyst to generate highly unsaturated Mg^{+2} sites. One of the methods is chemical treatment with alkylaluminum compounds. Alkylaluminum compounds are form complexes with THF with ease, thus facilitating the removal of THF from $MgCl_2.2THF$ surface. However, there are no reports on the nature of structural changes occurring as a consequence of such treatment. Hence, we treated $MgCl_2.2THF$ with alkylaluminum and examined the structural changes by X- ray diffraction. It was observed that all the sharp crystalline

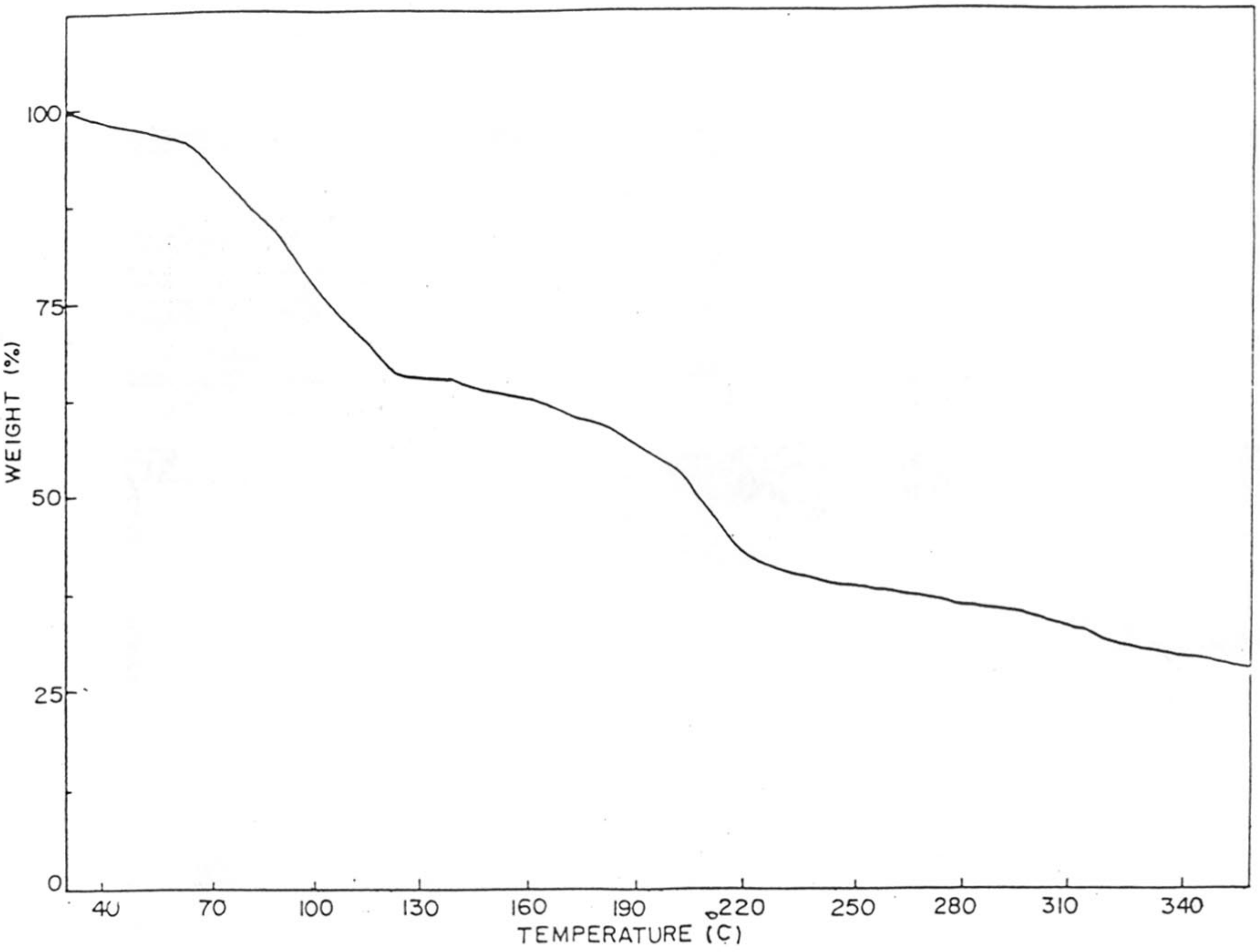


Fig.3.4 Thermogravimetric Analysis Pattern of $MgCl_2.2THF$

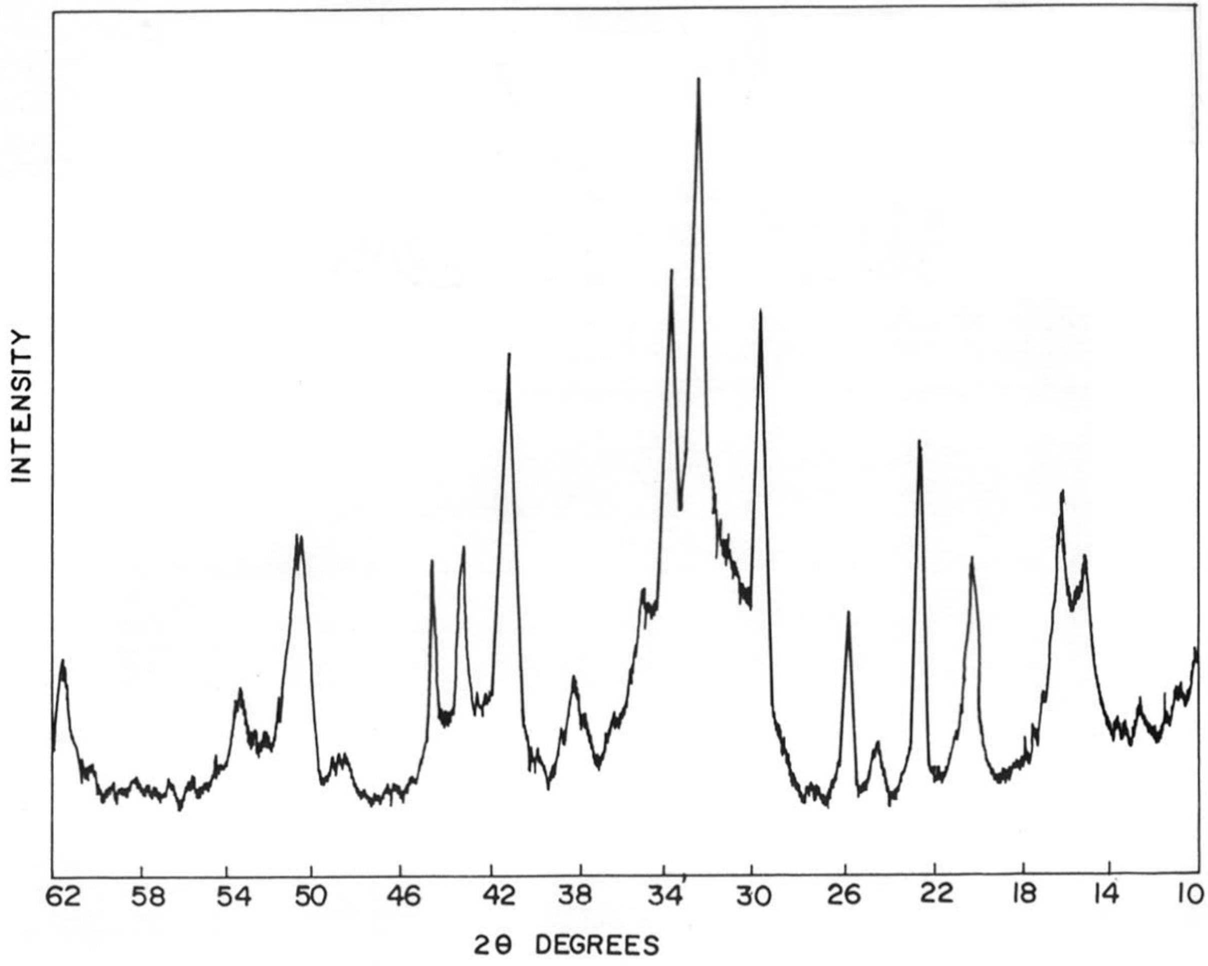


Fig.3.5 Anhydrous $MgCl_2$ (Toho) X - Ray Spectra After Ten Hours Grinding

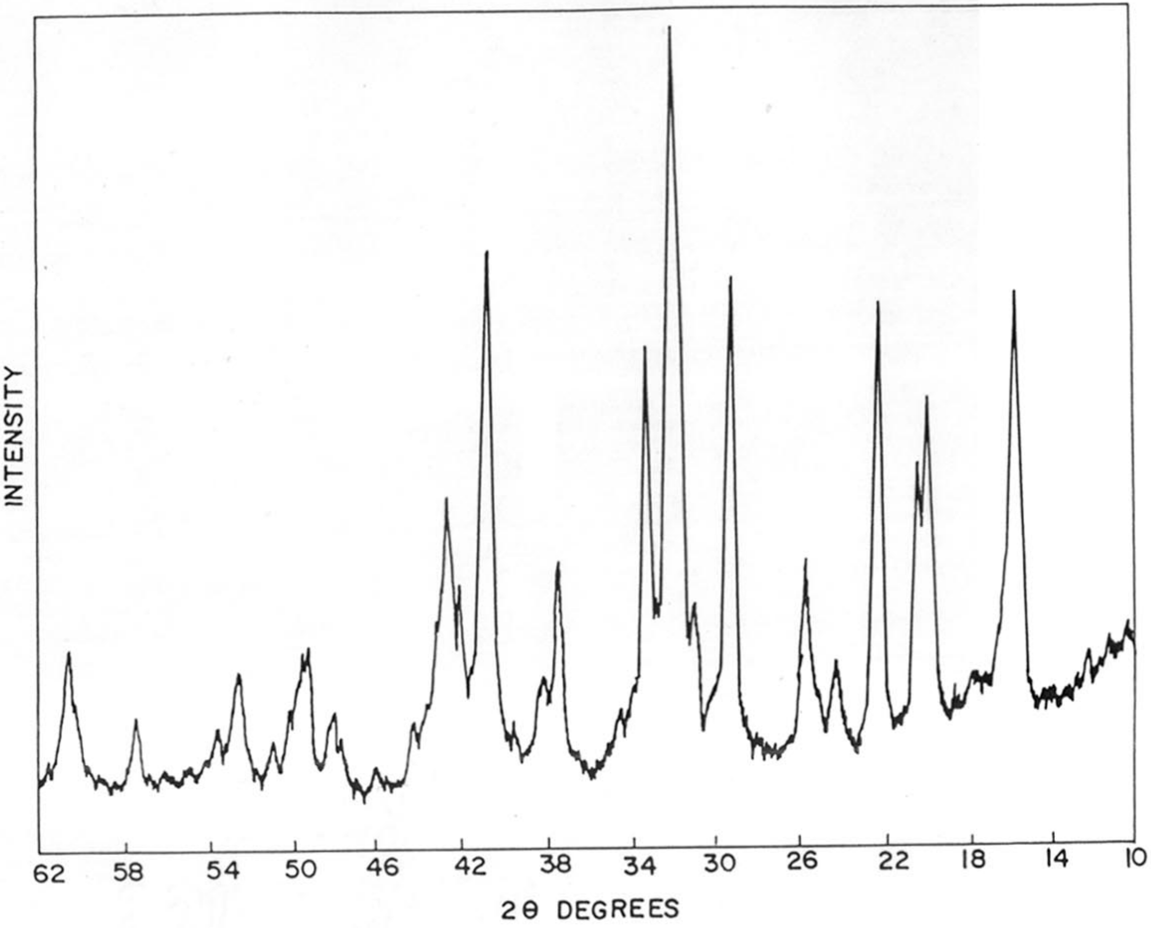


Fig.3.6 $MgCl_2.2THF$ X - Ray Spectra After One Hour Grinding

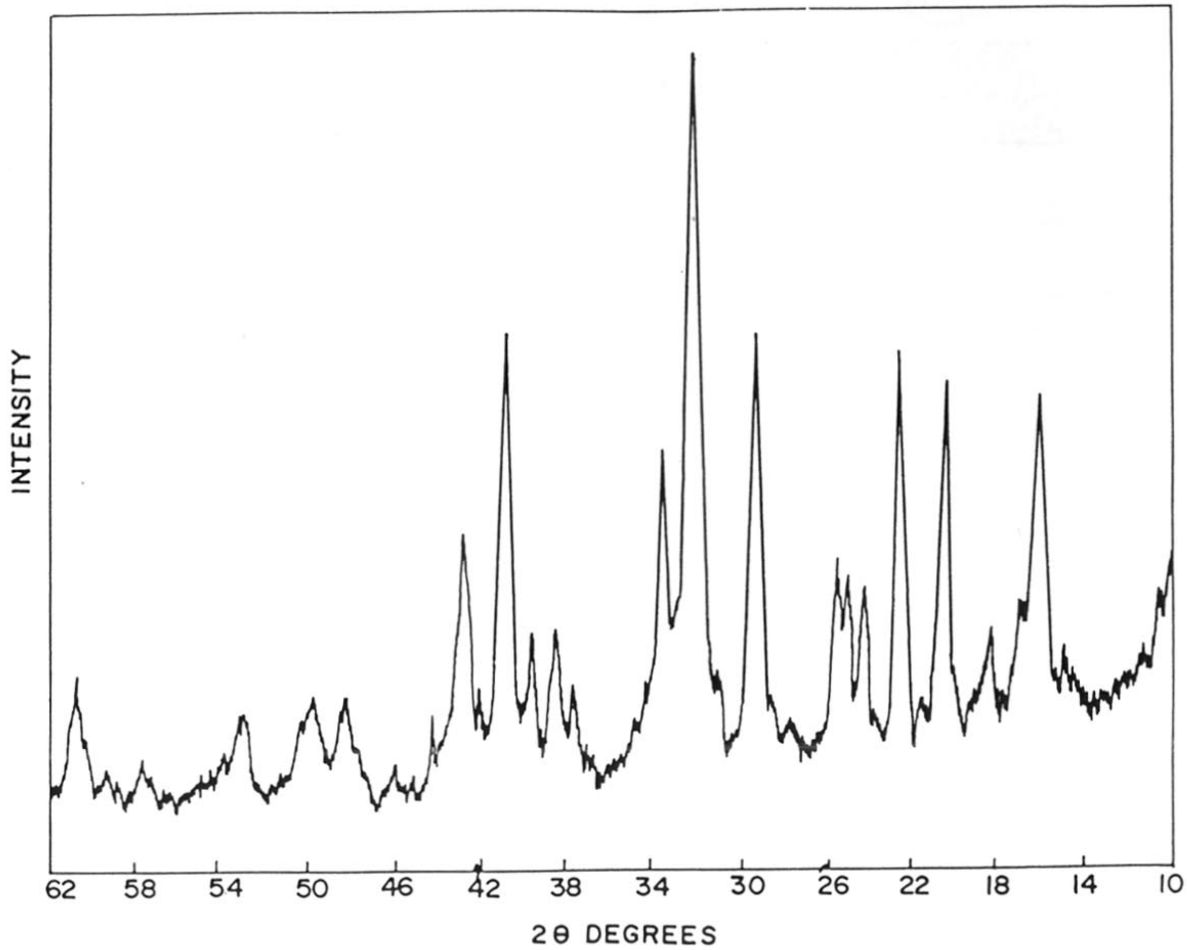


Fig.3.7 $MgCl_2.2THF$ X - Ray Spectra After Two Hour Grinding

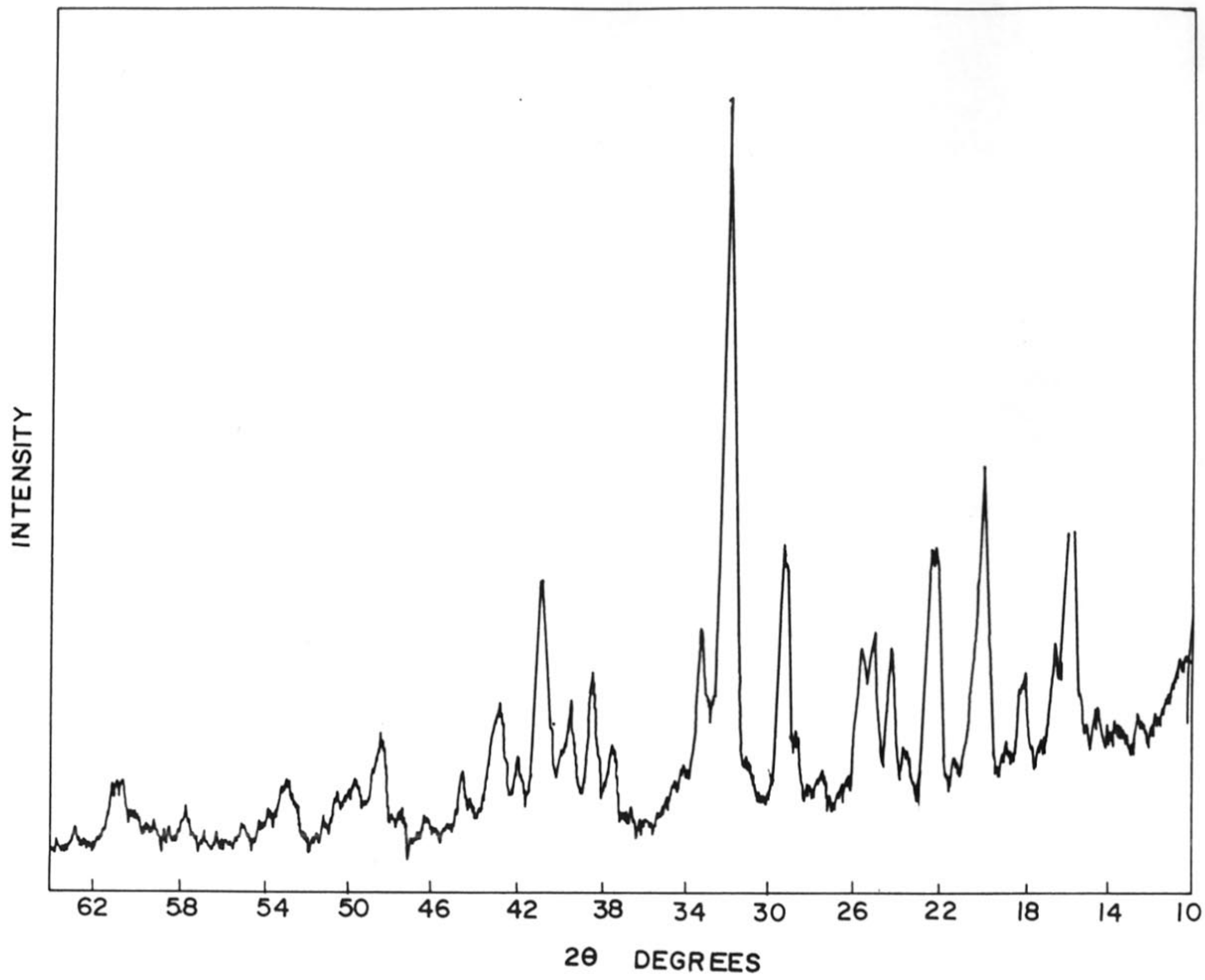


Fig.3.8 $MgCl_2$.2THF X - Ray Spectra After Three Hour Grinding

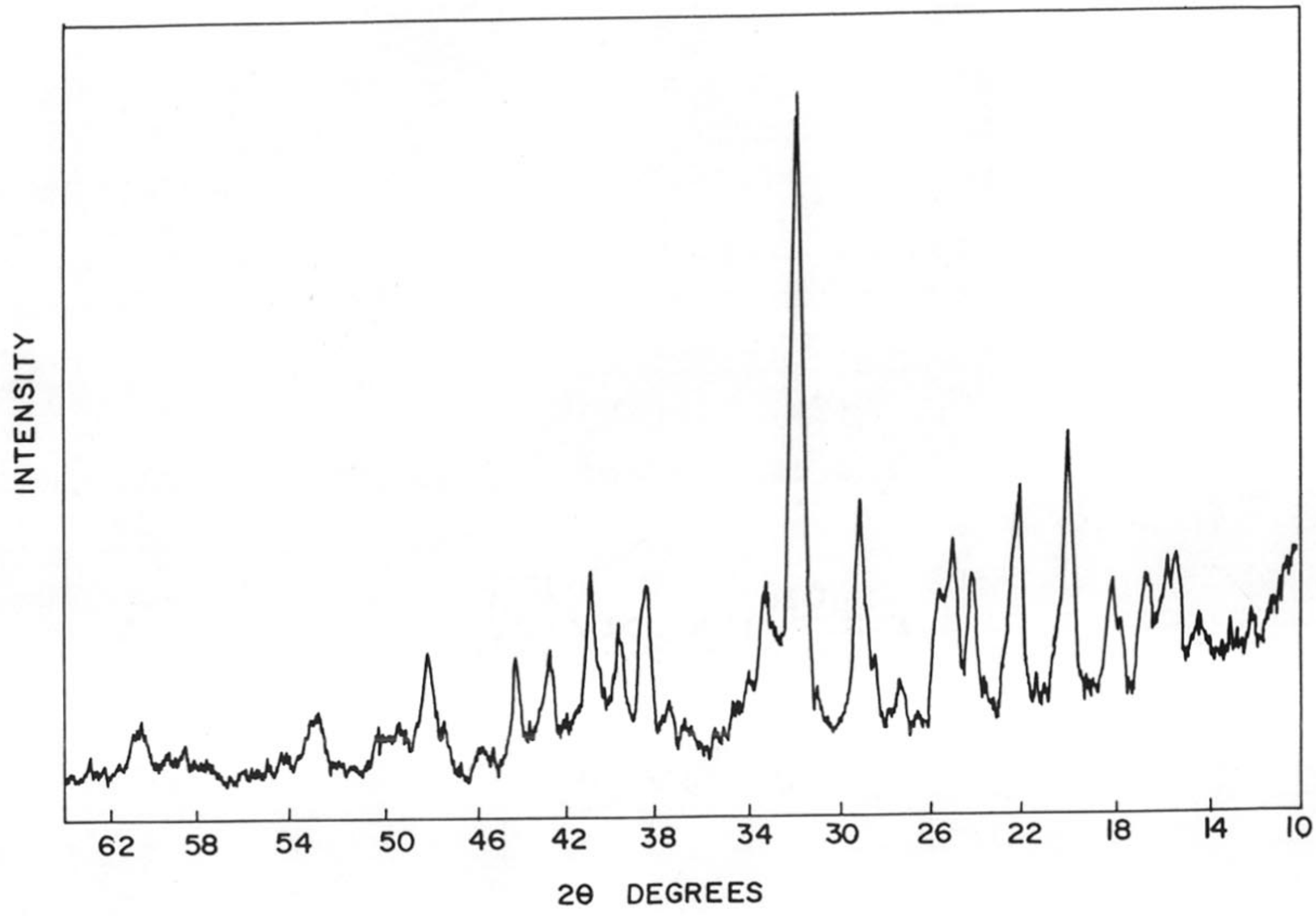


Fig.3.9 $MgCl_2.2THF$ X - Ray Spectra After Six Hour Grinding

peaks in $MgCl_2$.2THF disappeared and a haloshift was noticed. The shift was greater in the sample obtained upon treatment with diethylaluminum chloride when compared to the sample obtained on treatment with triisobutylaluminum (Figure 3.10 and 3.11).The product was shown to be free of THF by NMR and elemental analysis. This indicates that removal of THF results in vacant unsaturated Mg^{+2} cation sites.

4.0 CONCLUSION

A new and simple synthetic route was developed to prepare a tetrahydrofuran complex of magnesium chloride. The stoichiometry of the complex was confirmed to be $MgCl_2$.2THF. This complex, upon grinding, underwent faster cleavage of crystalline layers of $MgCl_2$ due to the polar Lewis base character of THF. Chemical treatment with alkylaluminum also results in the removal of THF. This was characterized by a haloshift in the region between $2\theta = 30 - 40°$, which indicate that this routes yield support containing highly unsaturated Mg^{+2} cations.

5.0 EXPERIMENTAL SECTION

All manipulations involving air sensitive compounds were performed either inside a Labconco Model 50004 inert atmosphere glove box continuously purged with high purity N_2 (<5ppm moisture) generated using N_2 generator (Spantech, Model NG 300-1, England) or under a positive pressure of high purity N_2 using standard bench top inert atmosphere techniques.

5.1 Materials

Triisobutylaluminum, diethylaluminum chloride (Schering A.G., Germany) and calcium hydride (Aldrich, USA) were used as received. Grignard grade magnesium turnings (Loba Chemical, Bombay), 1,2 - dichloroethane, hexane and tetrahydrofuran (THF) were purified as described in section 5.2. 3A° molecular sieves (S.D. Fine Chemicals, Bombay) were activated at 140°C for 24 hours and later cooled under dry nitrogen atmosphere.

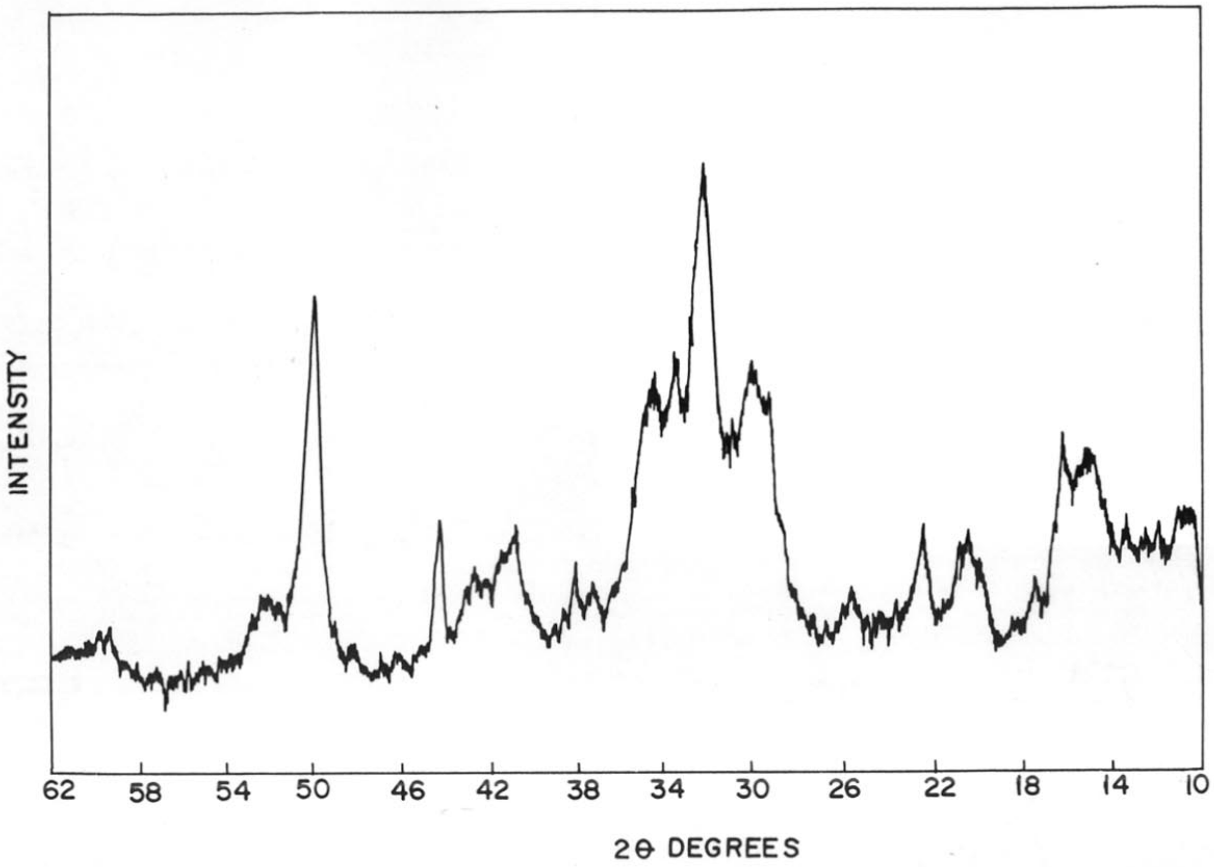


Fig.3.10 X - Ray Diffraction Pattern of Product Obtained on Treatment of $MgCl_2.2THF$ with Diethylaluminum Chloride

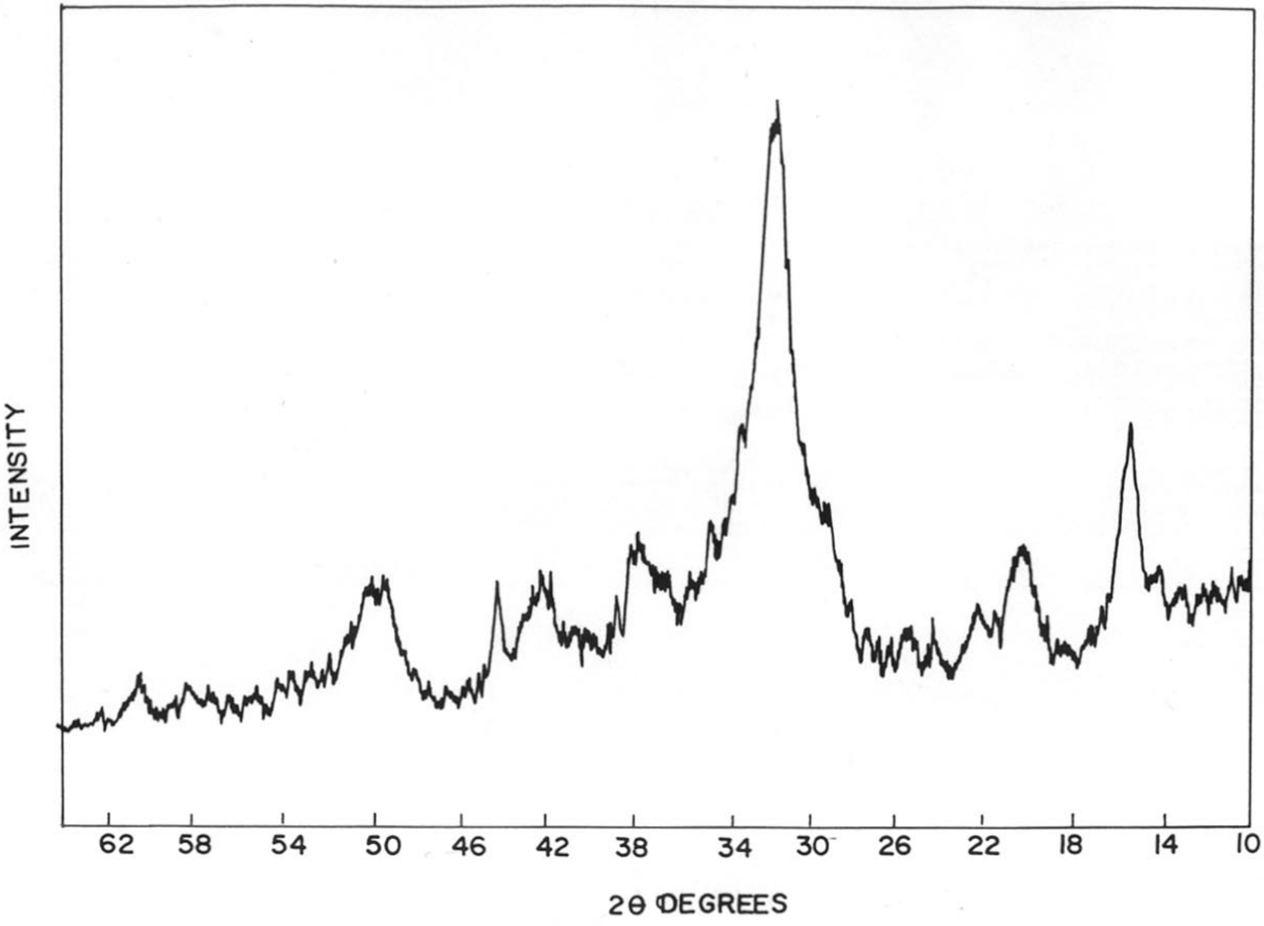


Fig.3.11 X - Ray Diffraction Pattern of Product Obtained on Treatment of $MgCl_2.2THF$ with Triisobutylaluminum

5.2 Purification

Magnesium turnings, previously dried at 120°C for 8 hours, were cooled in the glove box under N_2, washed with dilute HCl and later with distilled water to remove unwanted $Mg(OH)_2$. Further, acetone wash was given to remove the water and dried in the oven at 120°C for 8h. These shining magnesium turnings were used to conduct Grignard reaction.

All solvents were initially distilled at their boiling points prior to use. Further purification was performed under N_2 - atmosphere as described below.

Hexane and THF were distilled and refluxed over fresh sodium wire with a pinch of benzophenone in an inert atmosphere . The solvents were refluxed till the color of the benzophenone ketyl anion persisted. Freshly distilled solvents were used whenever necessary. 1,2 - Dichloroethane was stirred over calcium hydride, distilled under N - atmosphere and stored over activated 3A° molecular sieves in Aldrich sure/seal bottles

5.3 Synthesis of THF complex of $MgCl_2$

A three neck round bottom flask equipped with a magnetic bar, nitrogen inlet, addition funnel and reflux condenser was flame dried and cooled under N_2 atmosphere. Iodine activated Mg - turnings (2g) was placed in the flask and THF was added at 40°C. 1,2 dichloroethane (30mL) was added drop wise to the refluxing THF till all magnesium turnings dissolved. Evolution of ethylene indicated rapid decomposition of intermediate β - chloroethylmagnesium chloride. A clear solution was obtained. Dry hexane was added to precipitate the solid compound at room temperature. The solid was filtered and dried under vacuum for 8 hours at 30°C. The yield obtained was 16.5g.

5.4 Ball Milling of $MgCl_2.2THF$

Dry ball milling of solid $MgCl_2.2THF$ was performed in a pulverisette - 6 centrifugal ball mill (Fritsch Gmbh, Germany). The chromium - nickel - steel grinding bowl, of capacity 500mL with twenty grinding balls (10mm & 20mm diameter, 10 each), were dried at 120°C for 6 hours and cooled in the glove box. A known amount of $MgCl_2.2THF$ was charged into the bowl inside the glove box and the sample ground at constant speed for 6 hours. At regular intervals (1, 2, 3, & 6 hours), samples were removed from the grinding bowl in the dry box. The samples were then stored in the dry box for further analysis.

5.5 Chemical Activation

Chemical activation was performed using triisobutylaluminum and diethylaluminum chloride as chemical activating agents. A typical procedure is follows.

A flame dried three neck round bottom flask with stirring bar was charged with $MgCl_2$2THF (2g) in the glove box. It was then fitted with a N_2 - inlet, addition funnel and a reflux condenser. Dry hexane (40mL) was added through addition funnel at 40°C with stirring. Neat triisobutylaluminum (2ml) was charged using a hypodermic syringe via an addition funnel to the slurry of $MgCl_2$.2THF. The mixture was stirred at 60°C for 3h. The reaction mixture was cooled, washed with dry hexane and dried under vacuum at 30°C for 4h. This was used for further analysis.

5.6 Analysis

Chlorine and magnesium estimations were performed by argentimetric and EDTA titrations respectively as described in section 5.7. NMR spectrum was recorded in D_2O using a Brucker FT - 80 NMR spectrometer. IR spectrum was recorded on a Perkin - Elmer 16PC FT - IR spectrometer. Powder XRD was recorded on a Phillips PW 1730 spectrometer using Ni filtered Cuα radiation. Thermogravimetric analysis was performed on a Perkin - Elmer TGA - 7 Thermal Analysis Work Station. Surface area measurements were performed on Quantachrome Mercury Intrusion Porosimeter.

5.7 Estimation of Magnesium and Chlorine in $MgCl_2$.2THF

5.7.1 Preparation of $MgCl_2$.2THF Solution

An appropriate amount of the $MgCl_2$.2THF was dissolved in distilled water. The volume of the solution was then brought to 100 mL by adding distilled water. This solution was used for the estimation of Mg and Cl.

5.7.2 Estimation of Chloride

Silver Nitrate (0.01M) solution and sodium chloride (0.01M) solution were prepared using analytical grade samples. An indicator solution was prepared by dissolving potassium chromate (0.42g) and potassium dichromate (0.7g) in 10 mL of distilled water. Silver nitrate solution was standardized by titrating against sodium chloride (0.01N) solution using potassium chromate as indicator.

In a 250 mL capacity conical flask, $MgCl_2.2THF$ (10 mL) solution was taken to which was added indicator solution (1 mL). Further dilution was performed with distilled water (15 mL). This solution was titrated against silver nitrate solution. The addition was performed slowly under constant swirling and was continued until the red color formed by the addition of each drop begins to disappear more slowly. This was an indication that most of the chloride has been precipitated. The addition was further continued drop wise until a faint but distinct change in color occurred. This faint reddish - brown color should be persist even after brisk shaking. This was the end point. The titration was repeated two to three times to confirm the end point.

5.7.3 Estimation of Magnesium

Ethylenediamine tetraacetic acid disodium salt (EDTA) (0.01M) and zinc sulphate heptahydrate (0.01 M) solutions were prepared by dissolving the appropriate amounts of the substances in distilled water using 1000 mL volumetric flasks. An indicator solution was prepared by dissolving Eriochrome Black T (0.49g) in fresh methanol (100 mL). Further, a buffer solution of P^H 10 was also prepared by mixing 142 mL of concentrated ammonia solution (Sp. Gr. 0.88 - 0.99) with ammonium chloride (17.5g) and diluting with water to 250 mL. The EDTA solution was standardized by titrating against standard zinc sulphate solution using Erichome Black T as indicator. In a 250 mL capacity conical flask, $MgCl_2.2THF$ (10 mL) solution was taken to which was added fresh buffer solution (2 mL) and 3 - 4 drops of indicator solution (1 mL). The solution was further diluted with distilled water (15 mL). This solution was titrated with EDTA (0.01M) solution until the color changes from red to pure blue. The last traces of a reddish shade should disappear at the end point.

1 mL of 0.01 EDTA solution corresponds to 0.2432 mg of magnesium.

6.0 REFERNCES

1. M. C. Sacchi, I. Tritto, and P. Locatelli, Prog. Polym. Sci., **16**, 331 (1991).

2. P. Pino, G. Guastalla, B. Rotzinger, and R. Mulhaupt, in "Transition metal Catalyzed Polymerizations: Unsolved Problems" MMI Symposium, Harwood Publications, Midland, (1982).

3. S.A. Sergeev, G.D. Bukatov, V.A. Zakharov, and E.M. Moroz, Makromol. Chem., **184**, 2421 (1983).

4. J.C.W. Chien, in " Catalysis in Polymer Synthesis" (Eds. J. Vandengerg and J.C. Salamone) ACS Symposium Series **496**, Chap 2, p27 (1991).

5. P. Sobota, Polym - Plast. Technol. Eng., **28**, 493 (1989).

6. S. Sivaram and P.R. Srinivasan, in " Advances in Polyolefins" (Eds. B. Seymour and T. Cheng) Plenum Press, New York, p 283 (1987).

7. E. C. Ashby and R.C. Arnott, J. Organometal. Chem., **14**, 1 (1968).

8. a) US 14556 to Union Carbide (1987).
   b) US 13830 to Union Carbide, (1988).
   c) EP 340688 to Union Carbide (1990).

9. K. Handlir, J. Holecek, and Benes, Collect. Czech. Chem. Commun., **50**, 2422 (1985).

10. R. Sarma, F. Ramirez, B. Mckeever, Y. F. Chaw, J. F. Marecek, D. Nierman, and T. M. McCaffrey, J. Am. Chem. Soc., **99**, 5289 (1977).

11. P. Sobota, P. Pluzinski, and T. Lis, Z. anorg. allg. Chem., **533**, 215 (1986).

12. J.C.J. Bart, I.W. Bassi, M. Calcaterra, and E. Albizzati, Z. anorg. allg. Chem. **482,** 121 (1981).

13 P. Sobota, P. Pluzinski, and T. Lis, Bull. Acad. Pol. Sci. Ser. Sci. Chim., **33**, 491 (1985).

14 H.K. Coi, D.W. Chung, T.K. Han, and S.I. Woo, Macromolecules, **26**, 452 (1993).

15 H.S. Chang, W.-D. Song, K.-J. Chu, and S.K. Ihom, Macromolecules, **25**, 2086 (1992).

16. P. Muret and P. Alphonse, J. Organometal. Chem., **76**, 249 (1984).

SYNTHESIS AND CHARACTERIZATION OF A XYLENE SOLUBLE MAGNESIUM - TITANIUM CATALYST

1.0 INTRODUCTION

Synthesis and characterization of soluble bimetallic complexes based on magnesium and titanium is an area of current interest in Ziegler - Natta Catalysis. The interest is mainly on account of their ability to initiate homo- polymerization of ethylene and copolymerization with propylene, and the scope they offer towards the study of olefin polymerization mechanisms.

It is well known that anhydrous magnesium chloride does not dissolve in titanium halides[1]. Hence, the synthesis of soluble catalysts based on magnesium chloride and titanium halides is not possible. However, solid catalysts based on magnesium chloride and titanium halides have attracted considerable attention during the past twenty years as components of highly efficient ethylene and propylene catalysts. The synthesis and characterization of these solid catalysts are well discussed in the literature[2]. There are, however, only a few reports in the literature dealing with truly soluble magnesium - titanium catalysts. Herein we shall the discuss the synthesis and significance of these catalysts under two subsections, namely,

1.1 Examples and Significance of Soluble Magnesium - Titanium Catalysts
1.2 Synthetic Routes for Soluble Magnesium - Titanium Catalysts

1.1 Examples and Significance of Soluble Magnesium - Titanium Catalysts

Very few soluble Mg - Ti catalyst systems are reported in the literature[4-7]. Except two catalyst systems, the rest of the known soluble Mg - Ti catalyst systems consists of three components, namely, $MgCl_2$, a solubilizing agent and a Ti - compound. In the first step, solubilization of magnesium chloride was achieved, followed by addition of a Ti - compound. The catalysts reported in the prior literature are shown in Tables 4.1 and 4.2.

Table 4.1: Soluble Magnesium - Titanium Catalysts from Preformed Magnesium Chloride and Titanium Compounds

Catalyst System	Synthesis	Characterization	Reference
$MgCl_2$ - $Ti(OBu)_4$	[Anhydrous $MgCl_2$ (1mole) + $Ti(OBu)_4$]---> [125°C, dry N_2/2h]---> [filtered]---> [viscous liquid] (yield:95%).	Elemental analysis $[MgCl_2][T(OBu)_4]_{4.0}$ (Mg/Ti: 0.23)	5
$MgCl_2$ - $Ti(OEt)_4$	[Anhydrous $MgCl_2$(72mmoles) + $Ti(OEt)_4$ (17.25g)]---> [80°C, warming]---> [dry hexane(150mL)]---> [3h, 80°C]---> [filtered at 80°C]---> [cooled to room temp.,]---> [4h, at room temp.,]---> [0°C,12h]---> [solid product, filtered]---> [recrystallized from dry n- hepatne (100mL)] yield 69%).	Characterized by elemental analysis, single crystal X- ray diffraction, cryoscopic measurments, IR, UV & ^1H NMR. Found to have a molecular formula $[Ti_2(OC_2H_8)_8Cl]_2$ $Mg_2(\mu\text{-}Cl)_2$	6
$MgCl_2$ - 2-Ethyl Hexanol - $Ti(OBu)_4$	[$MgCl_2$ (7.1moles) + heptane]---> [slurry of $MgCl_2$]---> 2-Ethyl hexanol (30 or 14 moles)---> [80°C, heated]--->[solubilization of $MgCl_2$ in 2-Ethyl hexanol] ---> [$Ti(OBu)_4$ (1mole)]---> [a clear homogeneous solution].	No catalyst characterization. Except on reduction it showed Ti^{+4}: 17.4 %, Ti^{+3}: 61.2 % & Ti^{+2}: 21.4 %	8

Table 4.1: Soluble Magnesium - Titanium Catalysts from Preformed Magnesium Chloride and Titanium Compounds

Catalyst System	Synthesis	Characterization	Reference
$MgCl_2$-2Ethyl Hexanol-1/ $TiCl_4$	[$MgCl_2$ (7.1moles) + heptane]---> [slurry of $MgCl_2$]---> 2-Ethyl hexanol (30 or 14 moles)---> [80°C, heated]---> [solubilization of $MgCl_2$ in 2-Ethyl hexanol]---> [$TiCl_4$ (1mole)]---> [a clear homogeneous solution].	No catalyst characterization	8
$MgCl_2$ -Phosphate or Phosphonate - $TiCl_4$	[$MgCl_2$(1g,10.5mmoles)]---> [hexane (30mL) + phosphate or phosphonate (42mmoles)]---> [2h, agitation at room Temp.,]---> $TiCl_4$ (10.5mmoles)---> [a homogeneous light yellow solution]---> [hexane] (total: 52.2mL).	FT - IR & elemental analysis	4
Mg(OH)Cl -Phosphate or Phosphonate - $TiCl_4$	[Mg(OH)Cl (1g,13mmoles)]---> [phophonate or phosphate (35mmoles)]---> [130°C, 2h]---> [$TiCl_4$ (13mmoles), dropwise addition]---> [evolution of HCl gas and formation of clear solution]---> [130°C, 2h]---> [a brown colour solution]---> [cool to room temp.,]---> [hexane addition to make total 65mL].	Elemental analysis showed the complex has {[$TiCl_3$-O-$MgCl_2$].3[O=P(O-Bu)$_3$]}	4
$MgCl_2$/2-Ethyl Hexanol-1/ $Ti(OBu)_4$	[$MgCl_2$ (10mmol)]---> [dried, at 200 - 400°C, 5h]---. [2-Ethyl hexanol-1 (90 mmol)]---> [diluted with heptane]---> [added to $Ti(OBu)_4$/$Al(C_2H_5)_2Cl$ during the polymerization].	ESR characterization was done.	3

Unlike the conventional homogeneous catalysts, the soluble Mg - Ti catalysts show significant catalytic activity even at higher temperatures. Furthermore, the soluble bimetallic complexes of Mg - Ti are amenable to thorough characterization by a variety of methods such as X- ray, conductivity and cryoscopy.

1.2 Synthetic Routes for Soluble Magnesium - Titanium Catalysts

The synthetic routes for obtaining soluble Mg - Ti catalysts can be further subdivided into two categories, namely,

1.2.1 Synthesis from Preformed Magnesium Chloride

1.2.2 Synthesis from Reactive Magnesium Reagents

1.2.1 Synthesis from preformed Magnesium Chloride

As mentioned in the section 1.3.1 chapter - 3, dissolution of $MgCl_2$ can be achieved in organic solvents having Lewis base character. This solubilized magnesium chloride on further treatment with titanium compounds yield a soluble Mg - Ti catalyst. Thus, the reported catalyst systems $MgCl_2$ - (2-ethyl hexanol-1) - (titanium -n- butoxide) (TNB)[3] and $MgCl_2$ - (Phosphonate or phosphite) - (titanium tetrachloride)[4] (Table 4.1) fall under this category. It is observed that a minimum ratio of $MgCl_2$ to solubilizing agent is necessary to form a clear solution[4]. A molar ratio of >4 for $O{=}P(OBu)_3/(MgCl_2 + TiCl_4)$ thus yields a soluble clear yellow solution of Mg - Ti catalysts. But in $MgCl_2$ - phosphonate or phosphite - $TiCl_4$ system, disappearance of 1300 cm^{-1} band based on the P=O bond in $O{=}P(OBu)_3$ and appearance of new bands at 1220 & 1130 cm^{-1} is observed. However, the structural changes occuring during the course of preparation of $MgCl_2$ - (2-ethylhexanol-1) - (TNB or titanium tetrachloride) have also been inadequately characterized.

Recently, it is also reported that titanium alkoxides solubilize magnesium chloride at high concentration to form homogeneous solutions[5,6]. The dissolution is favoured by the complexation of the chloride ligand with the vacant coordination sites of titanium, thus forming a bimetallic soluble complexes of Mg & Ti. Thus, $MgCl_2$(TNB), a 1:2 ratio stoichiometric complex was synthesized by mixing $MgCl_2$ & TNB. This complex was

Table 4.2: Soluble Magnesium - Titanium Catalysts from Reactive Magnesium Compounds and Titanium Compounds

Catalyst System	Synthesis	Characterization	Reference
$(C_4H_9)(C_2H_5)Mg$/ 2-Ethyl Hexanol-1/$Ti(OBu)_4$	[$(C_4H_9)(C_2H_5)Mg$ (7.1mmole) + heptane]---> [a clear solution]---> [2-ethyl hexanol-1 (13.2 or 15.6 or22 moles)]---> [a clear solution with evolution of a gas indicating the formation of $Mg(OC_8H_{17})_2$]---> [$Ti(OBU)_4$ (1mole)].	No characterization was done; used for polymerization directly.	8
$(C_4H_9)(C_2H_5)Mg$/ 2-Ethyl Hexanol-1/$TiCl_4$	[BEM (7.1mmole) + heptane]---> [a clear solution]---> [2-Ethyl Hexanol-1 (22moles)---> [a clear solution with evolution of a gas indicating the formation of $Mg(OC_8H_{17})_2$]---> [$TiCl_4$ (1mole)].	No characterization was done; used for polymerization directly.	8
Magnesium octoate/$Ti(OBu)_4$	[Mineral solution of magnesium octate (a magnesium salt of 2-ethylhexanoic acid) (Mg:3.12%, H_2O: 0.54%)---> [hexane]---> [$Ti(OBu)_4$]--->[a clear solution].	No characterization	9
RMgX/$TiCl_4$/ Electron Donor	[(Dichloroethane(50mL) + $TiCl_4$(10mmoles)]---> [dibutyl ether (30mmoles), 30min, 0°C]---> [n-C_4H_9MgI, (10mmoles) in dibutyl ether]---> addition at 0°C, (over 30min, addition)---> [0°C, 1h stirring]---> [homogeneous $TiCl_3.MgX_2$.ether complex]---> [stored at 0°C in the refrigerator].	Elemental analysis	7

found to be active for selective dimerization of ethylene[5]. A systematic isolation and characterization of bimetallic complex formed on solubilizing magnesium chloride in highly concentrated titanium ethoxide (TE) has yielded a bimetallic complex with no ionic character[6]. Single crystal X-ray diffraction study of the isolated complex has shown that the reaction between TE and $MgCl_2$ in the 2:1 stoichiometric ratio yields single crystals of complex $[Ti_2(OC_2H_5)_8Cl]_2Mg_2[\mu\text{-}Cl]_2$ as shown in the Figure 4.1. The complex has monoclinic space group P2/n, with two molecules per unit cell and a: 13.9, b: 14.624 & c: 13.982A° and β : 95.05, V: $2831A^{\circ 3}$, D_{cal} : 1.292 g/cm^2. Based on these results and considering the degrees of association reported earlier in TE, a possible mechanism of formation of bimetallic complex upon the reaction of $MgCl_2$ and TE, is speculated and is shown in scheme 4.1.

1.2.2 Synthesis from Reactive Magnesium Reagents

The ability to solubilize reactive magnesium compounds such as Grignard reagents in polar or non polar solvents forms the basis of the other route to the synthesis of soluble Mg - Ti catalyst. There are only three reported soluble catalyst systems obtained from reactive magnesium reagents (Table 4.2) . They are RMgX/Lewis base/$TiCl_4$[7], $(C_4H_9)(C_2H_5)Mg$/2 - Ethyl hexanol/TNB)[8] or $TiCl_4$ and magnesium carboxylate/H_2O/TNB[9].

It is observed that the nature of solvent and Lewis base, the relative amount of Lewis base to $TiCl_4$ and the reducing temperature are important variables for synthesizing soluble Mg - Ti catalysts from reactive Grignard reagents. Generally, low temperature decomposition of Grignard reagent in presence of polar electron donor reagent is preferred. Furthermore, the molar ratio of Lewis base to Grignard reagent is also an important factor. This ratio is dependent on the nature of Lewis base and Grignard reagent. For dibutyl ether/C_4H_9MgX/$TiCl_4$ system, a molar ratio of dibutyl ether/(Ti+Mg) > 3 is required to obtain soluble Mg - Ti catalyst. On decreasing this ratio, the titanium compound precipitate out of solution. For the other two systems, no detailed studies on characterization or conditions to obtain a soluble catalyst are

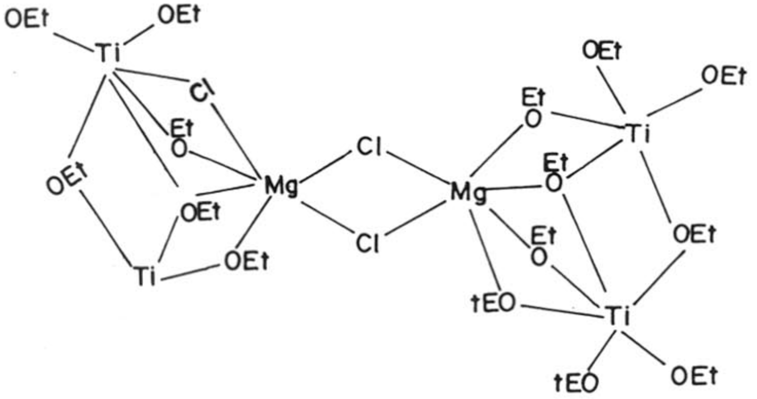
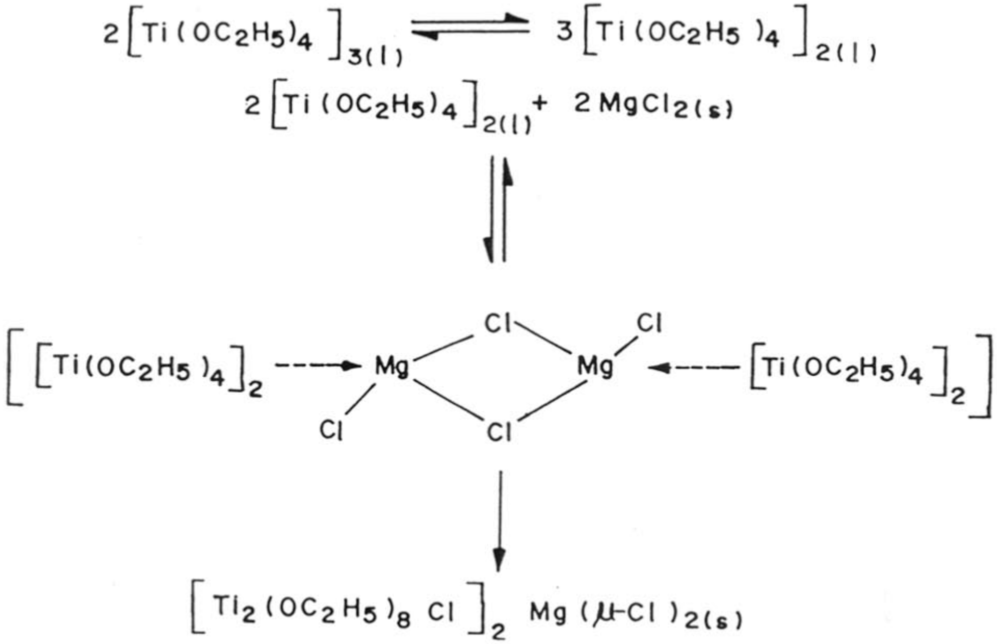


Fig.4.1 Structure of $[Ti_2(OC_2H_5)_8Cl_2Mg_2(\mu\text{-}Cl)_2]$



Sche.4.1 Mechanism of Formation of [$Ti_2(OC_2H_5)_8Cl_2Mg_2(\mu\text{-}Cl)_2$]

reported.

2.0 RESULTS AND DISCUSSION

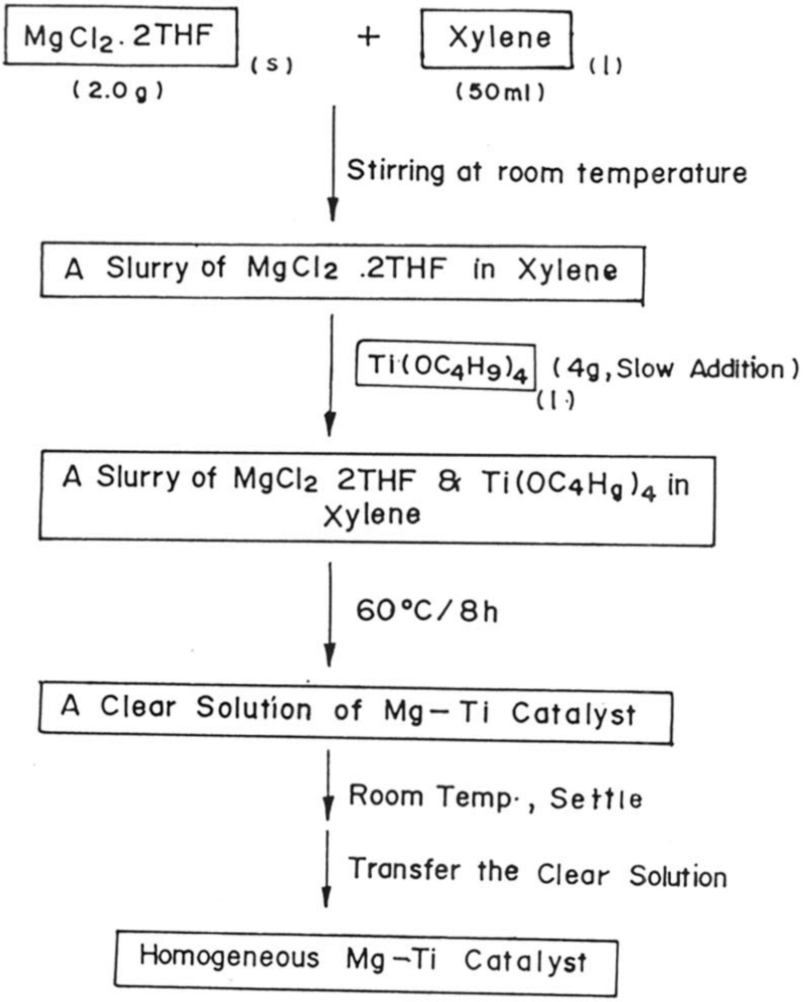
Anhydrous α or β form of crystalline magnesium chloride is commonly employed during the preparation of soluble Mg - Ti catalysts from preformed magnesium chloride and TNB. High crystallinity and absence of electron deficient coordination sites in the structure of magnesium chloride necessitates the use of excess Lewis base and high temperature for generating a soluble Mg - Ti catalyst. We, therefore, studied the synthesis of a soluble Mg - Ti catalyst starting from preformed $MgCl_2.2THF$ complex and TNB in xylene as the reaction medium (Equation 4.1).

$MgCl_2.2THF$ + TNB -------> A soluble Mg - Ti Catalyst 4.1

2.1 Synthesis and Characterization of Soluble Magnesium - Titanium Catalyst

Under defined experimental conditions, $MgCl_2.2THF$ was dissolved in TNB in xylene at 60°C over an 8 hours span of time (Scheme 4.2). $MgCl_2.2THF$ alone, in the absence of TNB is insoluble in xylene medium even at refluxing temperature.

The soluble Mg - Ti catalyst was characterized by elemental analysis, UV. and ESR spectroscopic techniques. The soluble Mg - Ti complex typically analyzed for Ti : 8.7mg/mL & Mg : 3.8mg/mL. The complex was, therefore, estimated to contain 1.5 moles of TNB per mole of $MgCl_2.2THF$. A blue shift of 5nm was observed with xylene Mg - Ti catalyst in comparison with TNB on UV - analysis. Further, the soluble Mg - Ti catalyst showed absence of ESR signal indicating that Ti existed in Ti^{+4} state in this catalyst. But upon reduction with alkylaluminum, it showed a sharp intense signal at g ; 1.94. The intensity of the signal was higher when compared to the signal obtained with TNB - alkylaluminum system (figure 4.2). The sharp intense peak without any fine structures indicates that the Mg - Ti catalyst is homogeneous in xylene even on addition of alkylaluminum.



Sche.4.2 Synthesis of Homogeneous Xylene Soluble Mg - Ti Catalyst

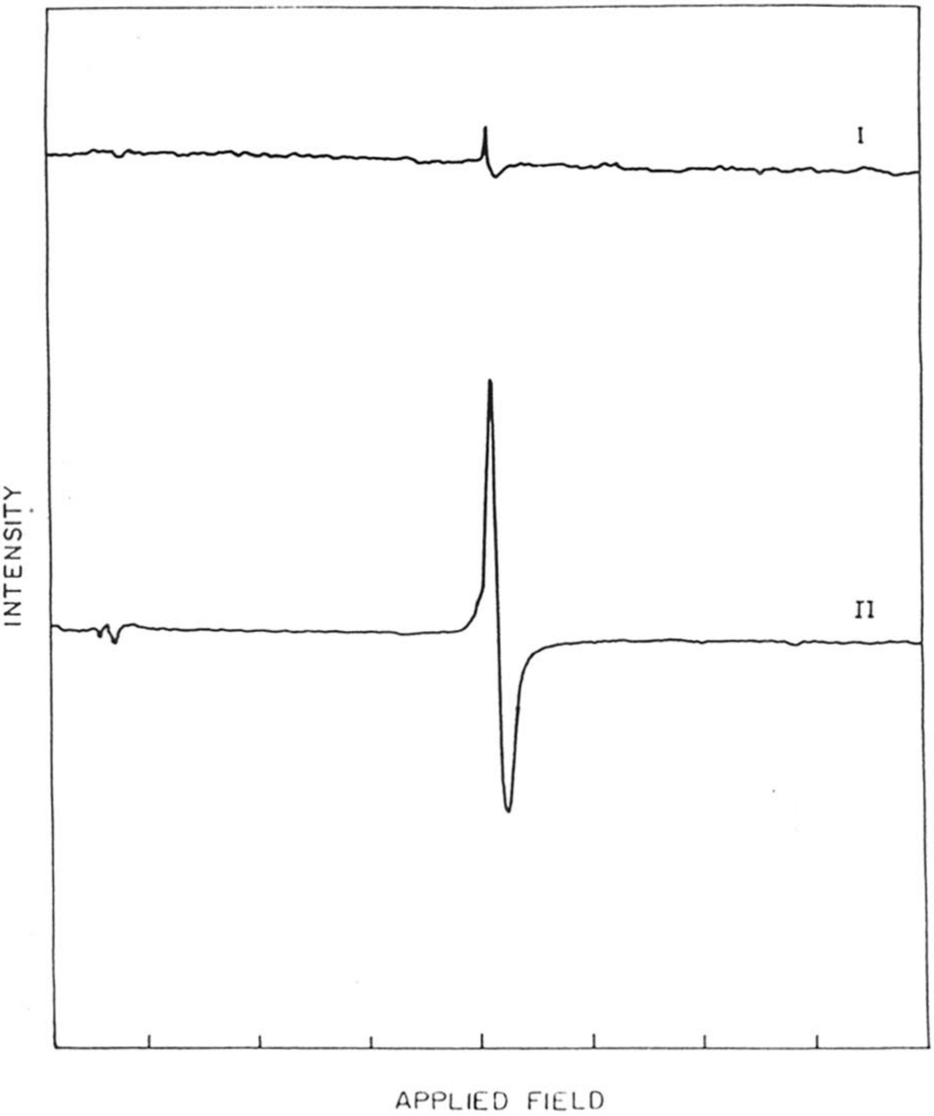


Fig.4.2 ESR Spectra of (I) TNB - TIBAL and (II) Xylene Soluble Mg - Ti - TIBAL Catalyst in Xylene

2.2 Isolation of Soluble Magnesium - Titanium Catalyst

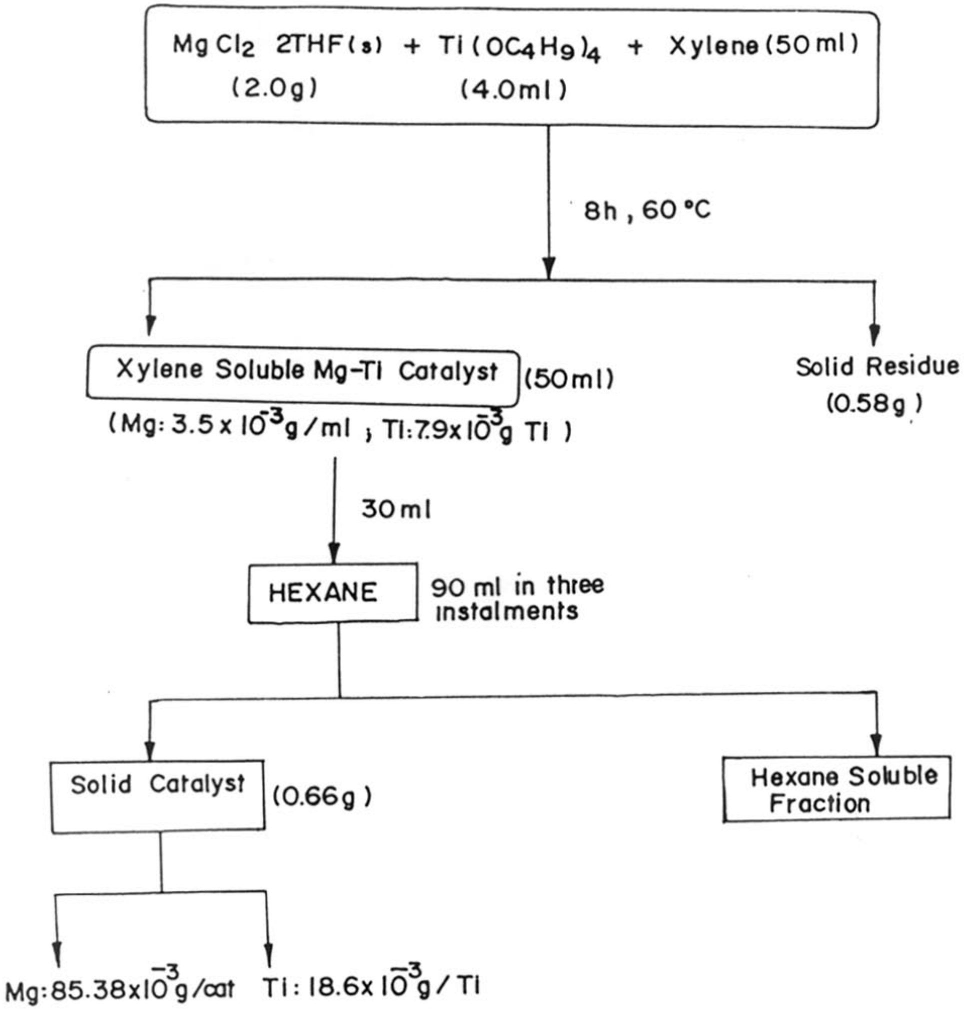
Non - solvent precipitation of a homogeneous Mg - Ti bimetallic complex was attempted. Hexane was chosen as a non solvent. During the course of addition of large excess of hexane to soluble Mg - Ti catalyst, turbidity and separation of white fluffy solid was observed. The turbidity increased when the separation was performed below 10°C. Upon settling, the fluffy solid compound settled at the bottom of flask. Thus two fractions, namely, hexane soluble fraction & insoluble solid fraction were isolated from the soluble Mg - Ti catalyst. The hexane insoluble solid fraction was found to be insoluble even in boiling xylene upon redissolution. This indicated that the composition of solid fraction and xylene soluble magnesium - titanium complex were not identical. Elemental analysis indicated that this fraction contained very low content of Ti i.e., 0.1% of Ti per gram of solid. The attempted isolation procedure is schematically shown in Scheme 4.3.

3.0 CONCLUSIONS

$MgCl_2$. 2THF dissolves in TNB in xylene at around 60°C. The soluble complex contains 1.5 mole of TNB per mole of $MgCl_2$.2THF. Attempts to isolate the bimetallic complex failed. It is observed that this soluble Mg - Ti complex is homogeneous even upon reduction with trialkylaluminums.

4.0 EXPERIMENTAL SECTION

All manipulations involving air sensitive compounds were performed either inside a Labconco Model 50004 inert atmosphere glove box continuously purged with high purity N_2 (<5ppm moisture) generated using N_2 generator (Spantech, Model NG 300-1, England), or under a positive pressure of highly purity N_2 using standard bench top inert atmosphere techniques.



Sche.4.3 Isolation of Xylene Soluble Mg - Ti Catalyst

4.1 Materials

Triisobutylaluminum (Schering A.G., Germany) was used as received. Titanium-n-butoxide (TNB) (Synthochem, India) was purified as described in section 4.2. xylene, hexane and tetrahydrofuran (THF) (S.D. Fine Chemical, Bombay) were purified as described in chapter III.

4.2 Purification of Titanium tetra-n-butoxide (TNB)

TNB was vacuum distilled twice and was further purified by adding triisobutylaluminum (2mL in 10mL of hexane) to 15mL of TNB drop wise at room temperature. The color of the solution turned black. The mixture was stirred for half an hour and distilled at 120°C/0.5mm of Hg. The distilled product was used for the preparation of catalyst.

4.3 Preparation of Soluble Catalyst

$MgCl_2.2THF$ (2g) was placed in a three neck round bottom flask fitted with a condenser, nitrogen inlet and a septum. Xylene(50mL) was added in the flask, followed by TNB (4mL) using a hypodermic syringe. The slurry was heated carefully at 60°C in an oil bath for 8 hours with stirring. It was found that the solid slowly dissolved in the xylene phase. The reaction mixture was cooled. The unreacted $MgCl_2.2THF$ was allowed to settle and the supernatent clear liquid was transferred by a cannula into an Aldrich Sure/Seal^R bottle under N_2 pressure.

4.4 Isolation of Solid Catalyst

A known amount of xylene soluble Mg - Ti catalyst(20mL) prepared as described in section 4.3 was transferred into an oven dried three neck round bottom flask equipped with N_2 - inlet, addition funnel and a septum. Dry hexane was added drop wise through a cannula till the turbidity was observed. A total of 60mL of hexane was added. The solution was cooled to 0 - 5°C for half an hour. The white solid material separated out was allowed to settle. Hexane fraction was collected into another two neck flask. The solid fraction was dried and transferred into vials inside the glove box.

4.5 Analysis

Magnesium estimation was performed by EDTA titration as described in section 4.6.1. Titanium estimation was performed by UV technique using a Hitachi Model 220 UV - Visible spectrophotometer(section 4.6.3). ESR spectrum was run on a Brucker model ER - 200D ESR spectrometer at room temperature (9.72GHz).

4.6 Estimation of Magnesium and Titanium in the Xylene Soluble Mg - Ti Catalyst

4.6.1 Preparation of Catalyst Solution

An appropriate volume of the soluble catalyst was digested with 5% H_2SO_4 solution. The volume of the solution was then brought to 100 mL by adding 5% H_2SO_4 solution. This solution was used for the estimation of magnesium titanium.

4.6.2 Estimation of Magnesium

Magnesium could not be estimated by the method described in section 5.7.3 of chapter III due to the interference of titanium in the solution. Therefore, a different method was used which includes the removal of titanium before the estimation of magnesium by EDTA method.

The catalyst solution (10 mL) was taken in a conical flask. It was diluted with distilled water (10 mL). The solution was heated to boiling with a few drops of concentrated nitric acid. A small amount or ammonium chloride was added into the solution. The titanium was precipitated by adding sufficient quantity of buffer solution. The hot mixture was filtered and washed with hot water. The solution was allowed to cool down. The P^H of solution was brought to 10 by adding 5 - 10 mL of buffer solution. A few drops of Eriochrome Black T indicator solution was added. The resultant solution was titrated against EDTA till the pink color of the solution changed to blue. The volume of EDTA consumed was noted. The percentage of magnesium was calculated by using Equation 4.2.

$$\text{Mg (\%)} = \frac{V_1 \text{ X } M \text{ X } V_2 \text{ X At. Wt. of Mg X } 100}{V_3 \text{ X mL of catalyst X } 1000}$$

Where,

V_1 : volume of EDTA solution,

V_2 : volume of catalyst solution prepared,

V_3 : volume of catalyst solution taken and

M : molarity of EDTA solution.

4.6.3 Estimation of Titanium

The estimation of titanium was based on the application of Beer's law. For titanium, the plot of absorbance Vs concentration of titanium at 420 nm (wave length) gives a straight line passing through the origin. The Beer's law was confirmed to be applicable up to 50 ppm of titanium in solution.

(a) Preparation of Standard Sample and Standard Plot of Absorbance Vs Titanium Content: A mixture of potassium titanium oxalate (0.3162 g) and ammonium sulphate (1.26 g) were taken in 100 mL beaker. The mixture was heated to boiling with 30 mL of 50% H_2SO_4 solution for 15 minutes. After cooling the mixture was poured slowly into 750 mL of distilled water. The reaction was diluted to 1000 mL (1 mL = 4.2 mg Ti).

The UV - Visible spectrophotometer was calibrated with a reference solution prepared by mixing 2 mL of 30% H_2O_2 and 98 mL of 1:9 H_2SO_4 solution. The measure volume of (0.5 mL, 1.0 mL, 1.5 mL, 2.0 mL and 2.5 mL) of stock potassium titanium oxalate solutions were taken in 10 mL volumetric flasks. A one mL of 30% of H_2O_2 was added to all the flasks. The solution was allowed for 15 minutes for complex formation. The solution was then diluted to 10 mL with distilled water. The absorbance value of each prepared solution was noted at 420 nm using the UV - Visible spectrophotometer. A plot of absorbance Vs titanium content gave a straight line passing though origin. This plot was used as standard for estimating the percentage of titanium in the unknown sample.

(c) Estimation of Percentage of Titanium in the Unknown Sample: In 10 mL standard volumetric flasks, 0.2 mL, 0.5 mL, 1.0 mL and 2.0 mL catalyst solution with one mL of 30% H_2O_2 solution were taken. They were allowed to stand 15 minutes to ensure complete complex formation. The solution was made up to 10 mL with distilled water. The absorbance of the solution was recorded at 420 nm by using spectrophotometer. The amount of the titanium in the sample corresponding to the observed absorbance was obtained from the standard plot of absorbance Vs concentration of titanium.

5.0 REFERENCES

1. N. Kashiwa, Polym. J., **12**, 603 (1980).
2. P.C. Barbe, G.Cecchin, and L. Noristi, Adv. Polym. Sci., **81**, 1 (1986).
3. Y. Doi, K. Soga, M. Murate, E. Suzuki, Y. Ono, and T. Keii, Polym. Commun., **24** 244 (1983).
4. K. Makino, K. Tsuda, and M. Takaki, Polym. Bull., **27**, 41 (1991)
5. S. Sivaram, Shashikant, and V.K. Gupta., Preprints, Div., Petroleum Chem. Inc., (ACS) **34**, 595 (1989).
6. a) U. Zucchini and T Dall'Occo, in " Polymer Science Contemporary Themes" [Ed. S. Sivaram] Tata - McGraw - Hill Publ. Co., New Delhi, **1**, 221 (1991)
   b) M.Malpezzi, U.Zucchini, and T. Dall'Occo, Inorg. Chem. Act., **180** 245, (1990).
   c) L. Abis, G. Bacchilega, S. Spera, U. Zucchini, and T. Dall'Occo, Makromol Chem., **192**, 981 (1991).
7. K. Makino, K. Tsuda, and M. Takaki, Polym. Bull., **26**, 371 (1991).
8. T. Yano, S. Ikai, M. Shimizu, and K. Washio, J. Polym. Sci., Part A., **23**, 1455 (1985).
9. T. Yano, S. Ikai, and K. Washio, J. Polym. Sci., Part A., **23**, 3069 (1985).

POLYMERIZATION OF ETHYLENE USING A SOLUBLE MAGNESIUM - TITANIUM CATALYST

1.0 INTRODUCTION TO MAGNESIUM - TITANIUM CATALYSTS FOR OLEFIN POLYMERIZATION

Titanium compounds especially, titanium halides in conjunction with alkylaluminum compounds, are known to be good catalysts for ethylene and propylene polymerization. The activities of these catalysts are dramatically enhanced by supporting them on anhydrous magnesium chloride. The physical and chemical properties of the support, and its role in determining the activities of these catalysts have been extensively studied in the literature[1,2].

Nevertheless, many aspects, such as, the role of magnesium chloride, electron (internal/external) donors, chain transfer agent, morphology and physical state of catalyst and their relationship to the kinetics and mechanism of olefin polymerization as well as final polymer properties are still not well understood. It is generally believed that the role of magnesium chloride is to function as an inert support in these catalyst systems, allowing a better dispersion of the catalytically active titanium centers. However, evidences have recently accumulated which indicate the magnesium chloride plays a more active role in determining the nature of active center. It is well known that titanium alkoxides, in conjunction with organoaluminum compounds, promote only the dimerization of ethylene to selectively butene-1[3]. However, they are transformed to polymerization catalysts when supported on magnesium chloride.

In this chapter, we shall discuss the nature and behavior of $MgCl_2$ - $Ti(OR)_4$ catalyst systems for olefin polymerization. It is observed from the literature that two types of catalysts are generally employed for olefin polymerization based on $MgCl_2$ and $Ti(OR)_4$. These are,

1.1 Solid Mg - Ti Catalysts Based on $MgCl_2$ and $Ti(OR)_4$

1.2 Soluble Mg - Ti Catalysts Based on $MgCl_2$ and $Ti(OR)_4$

1.1 Solid Mg - Ti Catalysts Based on $MgCl_2$ and $Ti(OR)_4$

Both physical and chemical activation methods are adopted to synthesize heterogeneous Mg - Ti catalysts using preformed magnesium chloride and titanium alkoxides. In the physical activation method, magnesium chloride is either ground in presence or absence of electron donor with titanium alkoxides[4,5,6]. No details on the structural changes occurring during the course of preparation have been reported. In the chemical activation method precomplexation of anhydrous $MgCl_2$ with an electron donor, followed by a thermochemical reaction with electron donors is adopted for the preparation of solid Mg - Ti catalysts[7]. These catalysts have also not been adequately characterized in the reported literature. It is believed that physical and chemical activation methods of synthesis of Mg - Ti catalyst based on $MgCl_2$ and $Ti(OR)_4$ promote similar structural changes that are observed with Mg - Ti catalyst synthesized from $MgCl_2$ and $TiCl_4$ as discussed in chapter - I.

Ethylene and propylene polymerization studies with these catalysts showed that the activities are relatively lower, when compared with $MgCl_2$ - $TiCl_4$ based catalysts[5]. Further, it was observed that the electron releasing ability of ligands present on Ti center and their bulkiness control the polymerization activity. In case of $MgCl_2/Ti(OR)_4$ prepared by mechanical grinding of anhydrous $MgCl_2$ with $Ti(OR)_4$ system, the catalyst activities were observed to increase in the order

$R = CH_3 < C(CH_3)_3 < CH(CH_3)CH_2CH_3 < CH(CH_3)_2 < C_2H_5 < CH_2CH(CH_3)_2 < (CH_2)_3CH_3)$

Aliphatic alkoxides gave more active catalysts compared to aromatic alkoxides (Table 5.1). Furthermore, in 2,4,6 - substituted aromatic alkoxides the activity increased in the order

$R = CH_3 < Cl < H$

The propylene polymerization activities with these catalysts were very low when compared to $MgCl_4$- $TiCl_4$ system. However, the striking feature of this catalyst was the observed steady state kinetic behavior for propylene polymerization[4] (Figure 5.1).

Table 5.1: Heterogeneous Magnesium - Titanium Catalysts Based on Magnesium Chloride and Titanium Alkoxides for Ethylene Polymerization

Catalyst System	Polymerization Conditions	Activity (KgPE/gTi/h)	Reference
$MgCl_2/Ti[OCH_3]_4$ - $Al(i\text{-}C_4H_9)_3$	Pressure : 13.5 kg/cm^2, Temp., : 70°C, Time : 3 hours.	10.0	5
$MgCl_2/Ti[OC_2H_5]_4$ - $Al(i\text{-}C_4H_9)_3$	Pressure : 13.5 kg/cm^2, Temp., : 70°C, Time : 3 hours.	75.33	5
$MgCl_2/Ti[OC_2H_5]_4$ - $Al(C_2H_5)_3$	Pressure :8 kg/cm^2, Temp., : 80°C, Time : 2 hours.	74.53	6
$MgCl_2/Ti[OCH(CH_3)_2]_4$ - $Al(i\text{-}C_4H_9)_3$	Pressure : 13.5kg/cm^2, Temp., : 70°C, Time : 3 hours.	53.3	5
$MgCl_2/Ti[O(CH_2)_3CH_3]_4$ - $Al(i\text{-}C_4H_9)_3$	Pressure : 13.5kg/cm^2, Temp., :70°C, Time : 3 hours.	128.67	5
$MgCl_2/Ti[O(CH_2)_3CH_3]_4$ - $Al(C_2H_5)_3$	Pressure : 1.0kg/cm^2, Temp., : 30°C, Time : 2 hours.	0.11	11
$MgCl_2.xEtOH/Ti[O(CH_2)_3CH_3]_4$ - $(C_2H_5)_2AlCl$	Pressure : 12kg/cm^2, Temp., : 85°C, Time : 2 hours, Butene : 3 g.	17.8	7
$MgCl_2.xEtOH$/Ethyl Benzoate/ $Ti[O(CH_2)_3CH_3]_4$ - $(C_2H_5)_2AlCl$	Pressure : 12kg/cm^2, Temp., : 85°C, Time : 2 hours, Butene : 3 g.	13.7	7

Table 5.1: Heterogeneous Magnesium - Titanium Catalysts Based on Magnesium Chloride and Titanium Alkoxides for Ethylene Polymerization

Catalyst System	Polymerization Conditions	Activity (KgPE/gTi/h)	Reference
$MgCl_2/Ti[OCH(CH_3)CH_2CH_3]_4$ $- Al(i\text{-}C_4H_9)_3$	Pressure : 13.5kg/cm^2, Temp., : 70°C, Time : 3 hours.	22..67	5
$MgCl_2 - Ti[OCH_2CH(CH_3)_2]_4$ $/Al(i\text{-}C_4H_9)_3$	Pressure : 13.5kg/cm^2, Temp., : 70°C, Time : 3 hours.	89.00	5
$MgCl_2/Ti[OC(CH_3)_3]_4 - Al(i\text{-}C_4H_9)_3$	Pressure : 13.5kg/cm^2, Temp., : 70°C, Time : 3 hours.	13.33	5
$MgCl_2/Ti[OC_6H_5]_4 - Al(i\text{-}C_4H_9)_3$	Pressure : 13.5kg/cm^2, Temp., : 70°C, Time : 3 hours.	260.0	5
$MgCl_2/Ti[OC_6H_2(CH_3)_3]_4 - Al(i\text{-}C_4H_9)_3$	Pressure : 13.5kg/cm^2, Temp., : 70°C, Time : 3 hours.	96.00	5
$MgCl_2/Ti[OC_6H_2(Cl)_3]_4 - Al(i\text{-}C_4H_9)_3$	Pressure : 13.5kg/cm^2, Temp., : 70°C, Time : 3 hours.	164.33	5

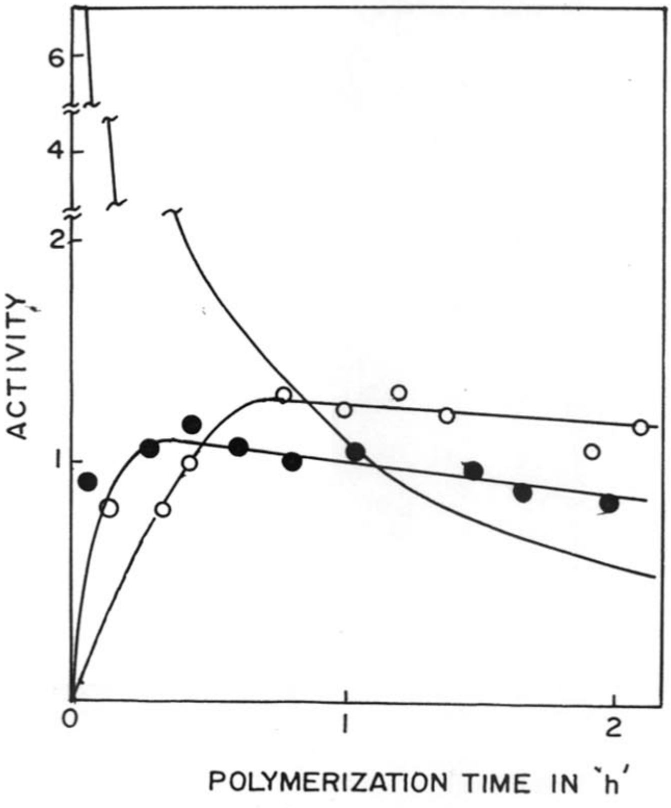


Fig.5.1 Time Courses of Propylene Polymerization with TNB/MgCl$_2$/Et$_3$Al, (○) TNB/EB/MgCl$_2$/Et$_3$Al (●) and TiCl$_4$/EB/MgCl$_2$/Et$_3$Al (—)

Further, it was observed. That a pretreatment with diethylaluminumchloride (DEAC) is required to promote ligand interaction between $Ti(OR)_4$ and DEAC for the formation of active complex, which can be easily alkylated to generate active species for propylene polymerization. When catalyst pretreatment is performed with trialkylaluminum it showed low activity (0.2kg/gTi/h) and low specificity (45% isotacticity). Thus, these results indicate that pretreament step with DEAC promotes ligand exchange reaction between $Ti(OBu)_4$ and DEAC on $MgCl_2$ surface. This, on further treatment with alkylaluminum generates the active center for polymerization. Based on this observation, it was proposed that a chlorine ligand is important for the active titanium center to undergo alkylation. The formation of active species is shown in scheme 5.1.

1.2 Soluble Mg - Ti Catalysts Based on $MgCl_2$ and $Ti(OR)_4$

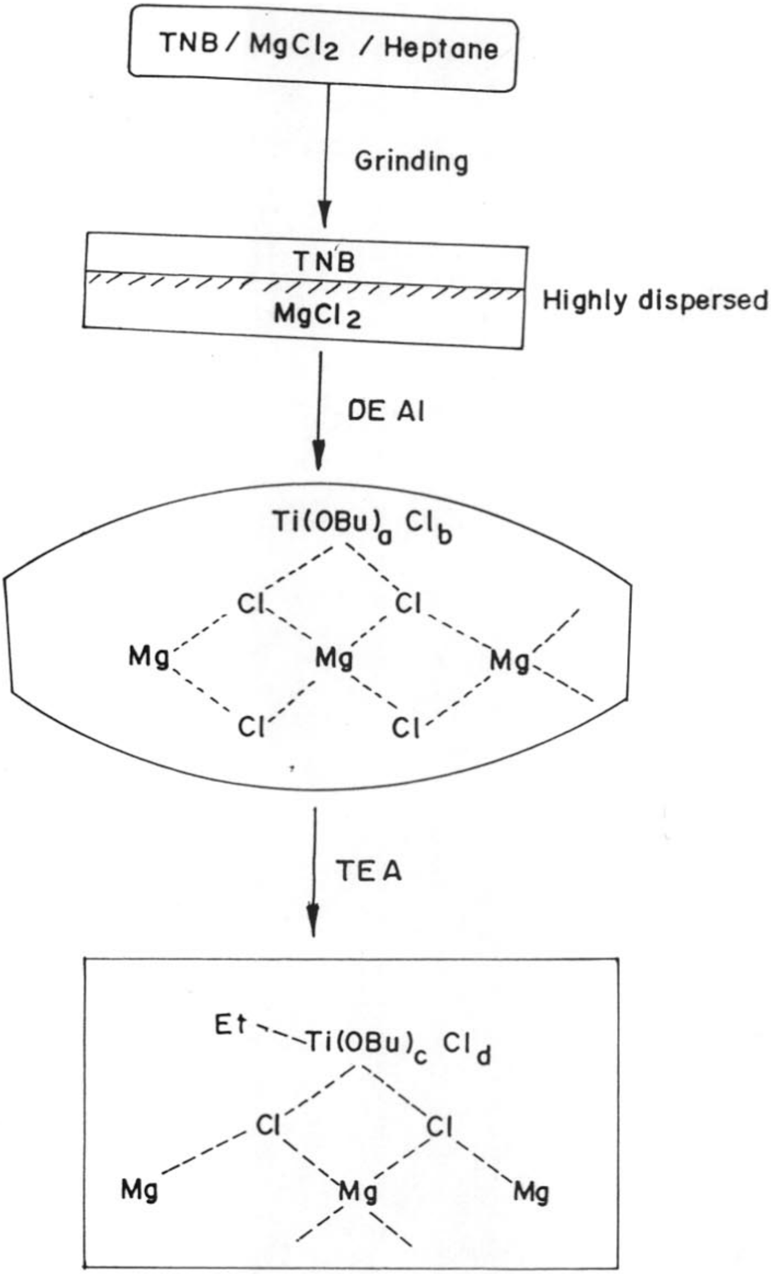
As discussed in Chapter - III, soluble Mg - Ti catalysts based on $MgCl_2$ & $Ti(OR)_4$ can be prepared in the presence or absence of electron donors. The polymerization efficiency of these soluble catalysts have been studied under different conditions. Thus, the polymerization behavior of these catalysts can be discussed under two subheadings, namely,

1.2.1 Polymerization Behavior of $MgCl_2$ - Electron Donor - $Ti(OR)_4$ Catalyst System

1.2.2 Polymerization Behavior of $MgCl_2$ - $Ti(OR)_4$ Catalyst System

1.2.1 Polymerization Behavior of $MgCl_2$ - Electron Donor - $Ti(OR)_4$ Catalyst System

The polymerization behavior of these catalyst systems are shown in Table 5.2. In general, these catalysts are active upon reduction with diethylaluminum chloride only. They show no activity on reduction with trialkylaluminum. Improved catalyst stabilities at higher temperatures, development of heterogenity on reduction with alkylaluminum compounds and steady state kinetic behavior during propylene polymerization are some of the salient features of these catalyst systems.



Sche.5.1 Soga's Model of Formation of Active Center in Heterogeneous $MgCl_2$/TNB Catalyst

Table 5.2: Soluble Magnesium - Titanium Catalysts Based on Magnesium Chloride and Titanium Alkoxides for Ethylene Polymerization

Catalyst System	Monomer	Conditions	Activity (Kgpolymer/g Ti/h)	Reference
$(C_4H_9)(C_2H_5)Mg$/2-Ethyl Hexanol-1/$Ti(OC_4H_9)_4$ - $(C_2H_5)_2AlCl$	Ethylene	$Mg{:}C_8H_{17}OH{:}Ti$:: 7.1:15.6:1 (mole) Pressure : 10kg/cm^2 Temp., : 200°C, Time : 20 minutes.	39.9	8
Magnesium octate/H_2O/ $Ti(OC_4H_9)_4$ - $(C_2H_5)_2AlCl$	Ethylene	$MO{:}H_2O{:}Ti$ :: 14:1.7:1 Pressure : 10kg/cm^2 Temp : 200°C Time : 1 -3 minutes.	600 - 800	10
$MgCl_2$/2-Ethyl Hexanol-1/$Ti(OC_4H_9)_4$ - $(C_2H_5)_2AlCl$	Ethylene	$Mg{:}C_8H_{17}OH{:}Ti$ :: 7.1:30:1 Pressure : 10 kg/cm^2 Temp., : 200°C Time : 20 minutes.	21.03	8
$MgCl_2$/2-Ethyl Hexanol-1/$Ti(OC_4H_9)_4$ - $(C_2H_5)_2AlCl$	Ethylene	$MgCl_2$: 10 mmol, $C_8H_{17}OH$: 90 mmoles $Ti(OC_4H_9)_4$: 0.085 mmoles Pressure : 0.6 kg/cm^2 Temp : 41°C Time : ---	0.5 - 1.0	9

With $MgCl_2$ - $Ti(OR)_4$, catalysts the catalyst activity is critically dependent on Mg/Ti ratios for different monomer. Yano et. al., reported high catalyst activities for ethylene polymerization (20 - 24 kg/gTi/h) at a Mg/Ti ratio of >15 with $(C_2H_5)(C_4H_9)Mg$ - (2-ethyl hexanol-1) - TNB catalyst system[8]. In contrast, Doi et. al., showed high activities for propylene polymerization with steady state kinetic behavior at molar ratios of >4 using $MgCl_2$/2EHA/TNB catalyst system[9]. The difference is on account of both, the nature of monomers and different polymerization conditions adopted, as shown in Table 5.2.

Further Yano et. al[10]., studied the effect of solubilizing agent [in case of $(C_2H_5)C_4H_9)Mg$ - 2-ethyl hexanol-1 - TNB catalyst system, 2 - ethyl hexanol - 1] concentration on ethylene polymerization activity and in Mg(octoate)/H_2O/TNB catalyst system, concentration of H_2O] on polymerization activity[8,10]. Even though the solubilizing agents effect on polymerization is not uniform, it can be said that at high concentration they decrease the activity of catalyst systems. Similarly, with Mg(octoate)/H_2O/TNB system Yano et. al., studied the effect of ageing temperature, order of addition at different temperatures and also the reaction condition on polymerization activity of ethylene using Mg(octoate)/H_2O/TNB catalyst system.

Based on these results, it can be said that the polymerization behavior of these Mg - Ti catalysts are similar and are dependent on the polymerization conditions and catalyst components. Thus, titanium alkoxides are converted to polymerization catalyst in presence of magnesium chloride. This observation raises doubts over the inert role of magnesium chloride in Mg - Ti catalysts.

1.2.2 Polymerization Behavior of $MgCl_2$ - $Ti(OR)_4$ Catalyst System

The ability to use $Ti(OR)_4$ itself as a solubilizing agent to synthesize Mg - Ti soluble catalysts as described in chapter - III, has further paved the way towards understanding the role of magnesium chloride in olefin polymerization catalysts. It is well known that titanium alkoxides promote selective dimerization of ethylene to butene-1 in conjunction with trialkylaluminums[3]. But Zucchini et. al., observed that under homogeneous conditions $MgCl_2$ - $Ti(OEt)_4$ catalyst shows ethylene polymerization activity (49.9 g

PE/gTi/h) and conversion to 70 - 90%[11]. In contrast Sivaram, et. al., showed that $MgCl_2$ - TNB forms a soluble complex having stoichiometric composition $MgCl_2[TNB]_4$[11]. This catalyst showed dimerization and oligomerization activity with ethylene, but no polymerization activity in conjunction with trialkylaluminums. In contrast to heterogeneous $MgCl_2$/TNB catalyst, the soluble analog shows dimerization, oligomerization and polymerization activity. The reason for this could be due to the higher concentration of titanium alkoxide and low molar ratio of Mg/Ti.

2.0 RESULTS AND DISCUSSION

It is observed that heterogeneous Mg - Ti catalysts having very high content of Mg show ethylene polymerization behavior, whereas homogeneous Mg - Ti catalysts based on $MgCl_2$ - $Ti(OR)_4$ do show dimerization, oligomerization and polymerization behavior, depending on ratio of magnesium and titanium. To delineate further the nature of these catalysts, polymerization of ethylene was studied with the xylene soluble Mg - Ti obtained from $MgCl_2.2THF$ and $Ti(OBu)_4$.

2.1 Ethylene Polymerization Using Xylene Soluble Mg - Ti Catalyst

Polymerization of ethylene was performed with xylene soluble Mg - Ti catalyst at different Al/Ti ratios and at different temperatures in xylene and hexane as reaction medium at a total ethylene pressure of one atmosphere. In a typical experiment, appropriate amount of catalyst, followed by cocatalyst was injected into a constant known volume of ethylene saturated xylene or hexane. After the addition, the color of the solution changed from brown to black depending on the polymerization temperature. The polymerization reaction was followed as a function of time for 30 min. The percentage of conversion of ethylene to polyethylene and activities at different Al/Ti ratios and temperatures in xylene and hexane medium are shown in Table - 5.3, 5.4 and 5.5. It can be observed that the catalyst activities and conversions were high with DEAC when compared with trialkylaluminums. Further, with DEAC as cocatalysts, conversions to polymer increased with temperature and catalyst activity increased with Al/Ti ratio. The catalyst activities were relatively poorer with trialkylaluminums. No

Table 5.3: Polymerization of Ethylene Using Xylene

Soluble Magnesium - Titanium Catalyst in Xylene: Effect of Al/Ti Ratio[a]

Entry	Cocatalyst	Al/Ti (Wt.ratio)	Temperature (°C)	Conversion (%)	Activity (gPE/gTi/h)	$[\eta]^b$ (dl/g)
1	DEAC	12	70	78	397	3.2
2	DEAC	50	70	80	522	2.5
3	DEAC	100	70	80	633	1.4
4	DEAC	50	50	60	355	2.3
5	DEAC	50	30	50	231	2.5
6	TIBAL	100	70	72	35	2.9
7	TIBAL	200	70	72	35	3.1
8	TIBAL	200	70	65	30	2.8
9	TIBAL	200	50	68	39	2.7
10	TIBAL	200	70	70	40	3.1

a) All polymerizations were performed at a total pressure of one atmosphere for 30 minutes.

b) Intrinsic viscosities were determined in o-dichlorobenzene at 135°C.

Table 5.4: Polymerization of Ethylene Using Xylene Soluble Magnesium - Titanium Catalyst in Xylene: Effect of Cocatalyst[a]

Entry	Cocatalyst	Al/Ti (Wt.ratio)	Temperature (°C)	Conversion (%)	Activity (gPE/gTi/h)	$[\eta]^b$ (dl/g)
1	DEAC	100	70	80	633	1.4
2	TMAL	100	70	78	68	2.4
3	TEAL	100	70	75	50	2.2
4	TIBAL	100	70	72	35	2.4
5	TOAL	100	70	NO POLYMERIZATION ACTIVITY		

a) All polymerizations were performed at a total pressure of one atmosphere for 30 minutes.

b) Intrinsic viscosities were determined in o-dichlorobenzene at 135°C.

Table 5.5: Polymerization of Ethylene Using Xylene Soluble Magnesium - Titanium Catalyst in Hexane Medium[a]

Entry	Al/Ti (Wt.ratio)	Cocatalyst	Temperature (°C)	Conversion (%)	Activity (gPE/gTi/h)	$[\eta]^b$ (dl/g)
1	12	DEAC	30	82	235	4.5
2	50	DEAC	30	80	275	4.3
3	100	DEAC	30	90	310	4.0
4	100	TIBAL	30	78	224	3.9
5	200	TIBAL	30	85	210	4.2

a) All polymerizations were performed at a total pressure of one atmosphere for 30 minutes.

b) Intrinsic viscosities were determined in o-dichlorobenzene at 135°C.

ethylene absorption was observed below an Al/Ti ratio 100. Furthermore, polymerization activity decreased as alkyl length in organoaluminum compound increased (Table 5.4). In hexane medium, the catalyst precipitated in the form of fluffy white material which also polymerized ethylene, but with reduced activity (Table - 5.5).

A kinetic investigation of ethylene polymerization on xylene soluble Ng - Ti catalyst was conducted. The millimoles of ethylene uptake in the reaction was plotted against time for purposes of calculating the rate of polymerization of ethylene. A kinetic plot of R_p versus time showed a steady kinetic curve at low Al/Ti ratios or temperatures up to 50°C in xylene medium. At temperatures higher than 50°C & Al/Ti > 50, a decay type kinetic curve was observed indicating competing deactivation process (Figure 5.2). The Arrhenius plot of R_p versus time was linear with an overall activation energy of 3 - 4 kcal/ mole (Figure 5.3). This value is similar to that observed for homogeneous catalysts based on Group - IV metallocene - aluminoxane catalyst system.

2.2 Characterization of Polyethylene

The polyethylene obtained was characterized for molecular weights by intrinsic viscosity measurements (Tables 5.3, 5.4 and 5.5), crystallinity from XRD and melting temperature from DSC. The polymers showed high molecular weights and a T_m 135 - 140°C with percentage of X-ray crystallinity varying between 60 - 70%.

3.0 CONCLUSIONS

These results show that the xylene soluble Mg - Ti catalyst exists as a homogeneous phase even on reduction with alkylaluminums. Furthermore, during the initial stages of polymerizations (up to 10 minutes), it shows homogeneity in xylene medium due to the solubility of polyethylene having molecular weights between 50,000-1,00,000 at 70°C. The low activation energies for polymerization is further indicative of the homogeneous nature of the catalyst.

It is well known that TNB in conjunction with organoaluminum compounds selectively promotes dimerization of ethylene to butene-1[3]. It has been also previously reported that the soluble $MgCl_2$.TNB catalyst (Mg/Ti mole ratio: 0.23), obtained on a

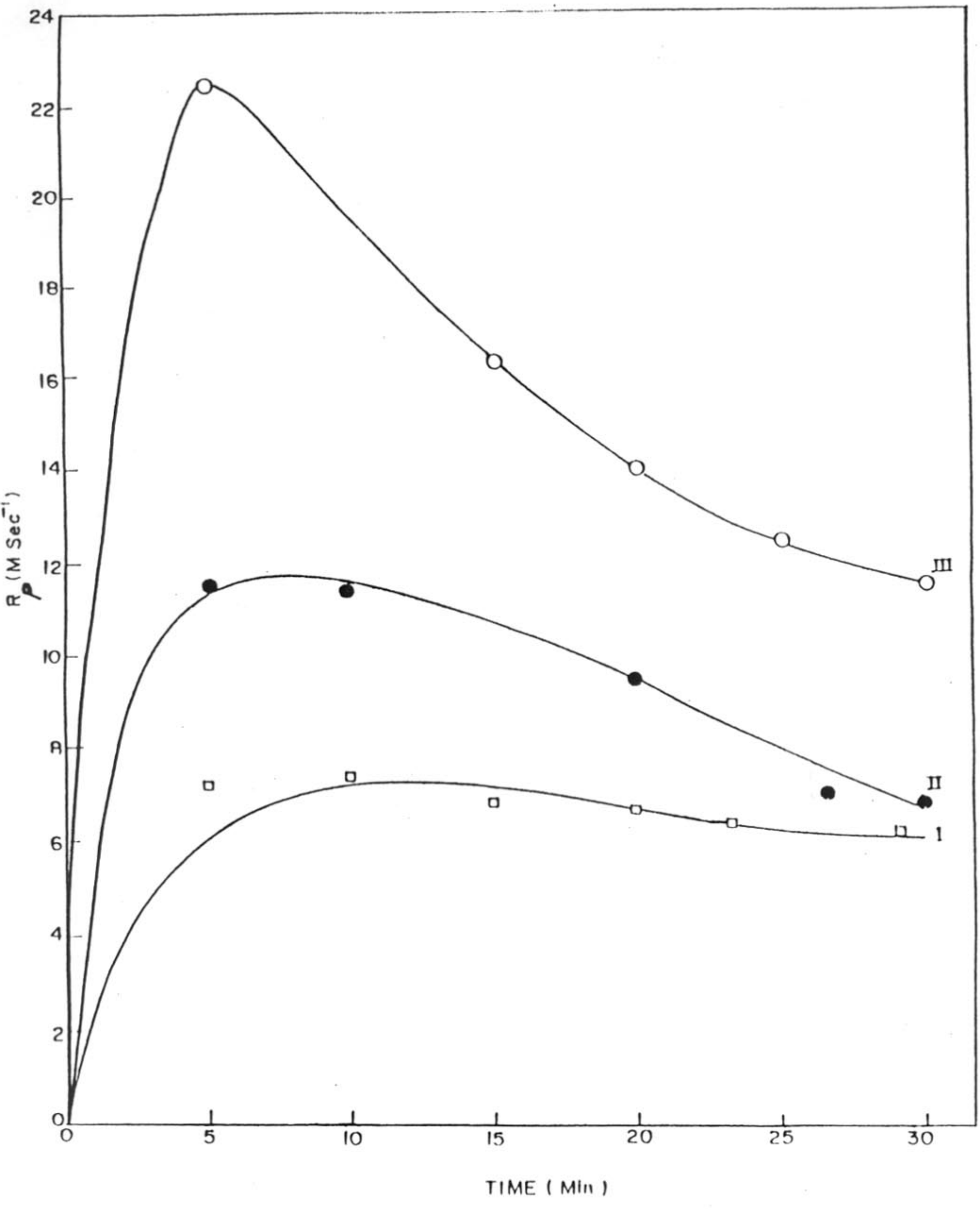


Fig.5.2 Plot of Rate of Polymerization Vs Time for Soluble Mg - Ti - DEAC Catalyst System at 60°; (I) Al/Ti = 50, (II) Al/Ti = 100 (III) = 200.

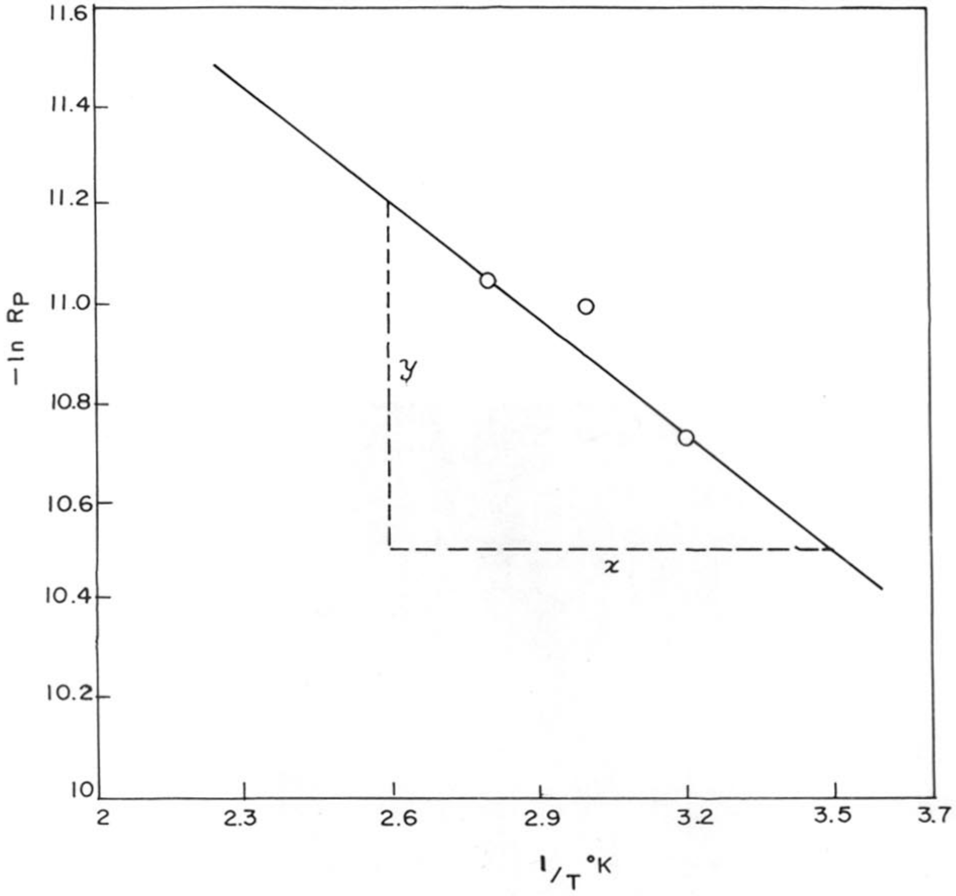


Fig.5.3 Activation Energy Plot

thermochemical reaction of TNB and anhydrous $MgCl_2$, promotes selective dimerization of ethylene[3]. In contrast, the present xylene soluble Mg - Ti catalyst (Mg/Ti:0.38) promotes ethylene polymerization to high molecular weight linear polyethylenes. The results can best be understood in terms of bimetallic species formed by the cleavage of distorted orthorhombic structure of $MgCl_2.2THF$[12] by the tetrameric TNB. The chlorine ligands of magnesium chloride thus contribute to the stability of the **[Ti-C]** bond resulting in the polymerization activity. Thus, in these catalysts, magnesium chloride exerts a subtle, yet significant, influence on the nature of titanium active center in transforming it from a dimerization to polymerization catalyst.

4.0 EXPERIMENTAL SECTION

All manipulations involving air sensitive compounds were performed either inside a Labconco Model 50004 inert atmosphere glove box continuously purged with high purity N_2 (<5ppm moisture) generated using N_2 generator (Spantech, Model NG 300-1, England) or under a positive pressure of high purity N_2 using standard bench top inert atmosphere techniques.

4.1 Materials

Triisobutylaluminum (TIBAL), diethylaluminum chloride (DEAC), triethylaluminum (TEAL), trimethylaluminum (TMA) and trioctylaluminum (TOAL) (Schering A.G., Germany) were used as received. Xylene soluble Mg - Ti catalyst synthesized as described in section 3.3 of chapter III was used for polymerization studies. Polymer grade ethylene was obtained from the Maharashtra Gas Cracker Complex of Indian Petrochemical Corporation Limited at Nagothane, India. It had a moisture content of <4ppm (Shaw model SHA - TR moisture analyzer) and oxygen content of <3ppm (Braun oxygen analyzer). Xylene and hexane (S.D. Fine Chemical, Bombay) were purified as described in chapter III. Freshly distilled methanol (S.D. Fine Chemical, Bombay) was used.

4.2 Description of Apparatus used for Ethylene Polymerization Studies under Atmospheric Pressures (Figure 5.4)

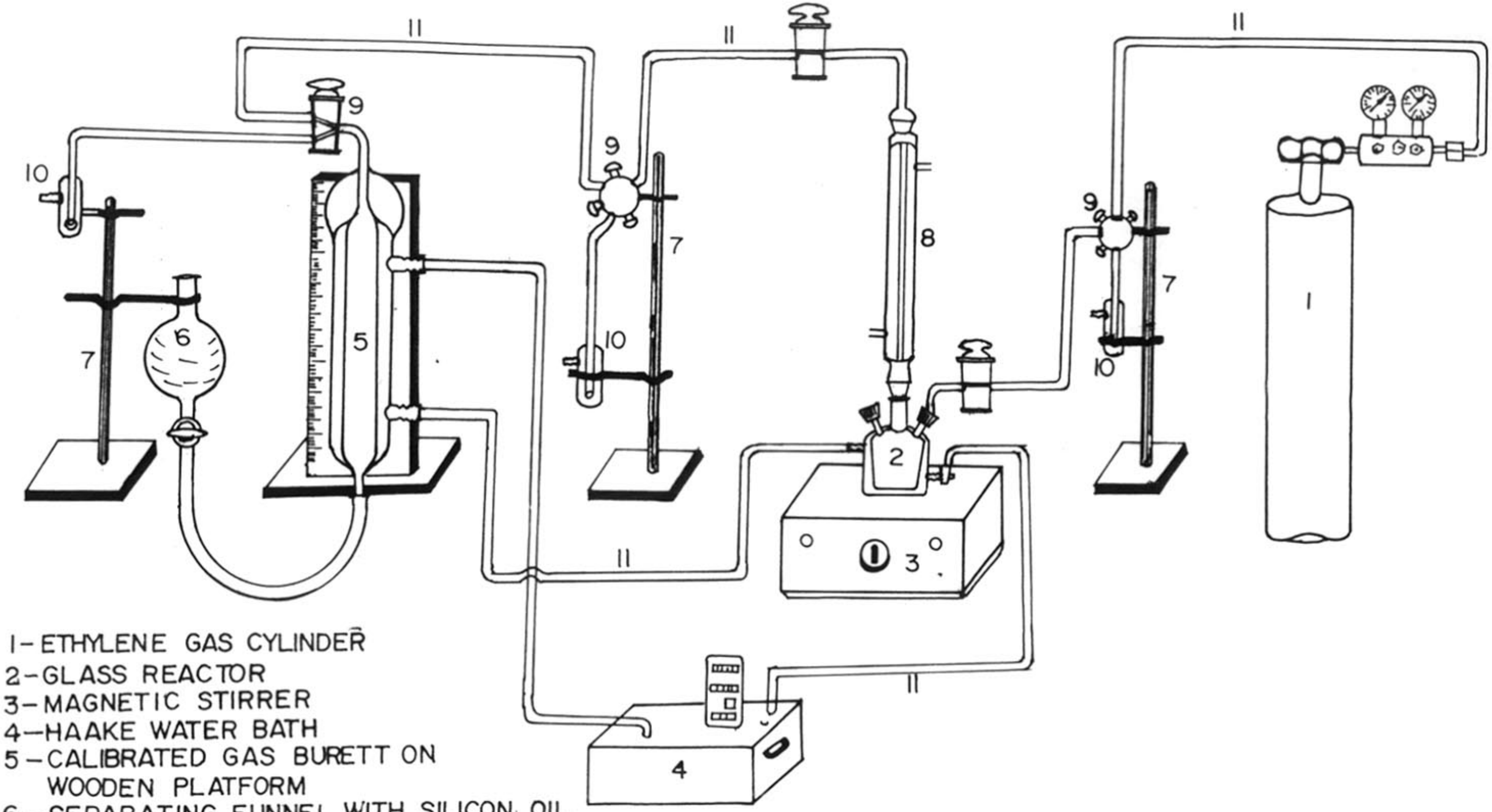
A glass tube (inner diameter:1.648cm & length : 117cm) was fabricated with a glass jacket, a three way stop cock and a supporting parallel glass tube of length 120 cm. The fabricated unit was mounted on a wooden platform of length 150 cm. Graph sheets were pasted on the wooden frame neatly to calibrate the fabricated glass apparatus. Upon calibration, it was found that one unit on graph sheet corresponds to 8.55 cm^3 of volume, at STP in the glass tube. The calibrated glass tube was used as a gas burette for measuring the difference in displacement of volume of ethylene during the polymerization. A three neck flat bottomed glass jacketed vessel of capacity 70 - 100 mL was used as the polymerization cell.

A separating funnel of capacity 1000 mL filled with silicone oil (800 mL) was connected through a rubber tubing to the gas burette. The reaction cell was mounted on a magnetic stirrer, which was connected to the gas burette via a T - shaped stopcock using a pressure tubing. Two paraffin bubblers were also connected for evacuation purpose to the reaction assembly and gas burette. The reaction cells were dried at 120°C for 12 hours and thoroughly checked for leaks by running a blank experiment under one atmosphere pressure for 2 hours. The silicone oil was presaturated with ethylene gas before the start of experiment.

4.3 Polymerization of Ethylene

Polymerization was performed with the assembly described in section 4.3 at one atmosphere pressure of ethylene in xylene and hexane as diluents. A gas burette with a reservoir containing silicone oil saturated with ethylene was used to feed ethylene continuously to the cell. Solvent was introduced into the cell using a hypodermic syringe followed by 0.2mL of the soluble Mg - Ti catalyst. The xylene in the cell was saturated with ethylene. Polymerization was commenced immediately upon addition of required amount of organoaluminum compound. Reaction temperature was maintained by circulating water from a thermostat through the jacket of the cell and the gas burette.

FIG. 5.4 ETHYLENE POLYERIZATION ASSEMBLY



1- ETHYLENE GAS CYLINDER
2- GLASS REACTOR
3- MAGNETIC STIRRER
4- HAAKE WATER BATH
5- CALIBRATED GAS BURETT ON WOODEN PLATFORM
6- SEPARATING FUNNEL WITH SILICON OIL
7- IRON STAND
8- GLASS CONDENSER
9- THREE WAY STOP COCKS
10- SILICON OIL BUBBLER
11- POLYETHYLENE PRESSURE TUBING

Ethylene uptake was measured as function of time. Reaction was terminated after 30 minutes by addition of acidified methanol. The polymer was filtered and dried at 40°C under vacuum and weighed. The gas volume measured was corrected for STP to calculate percentage of conversions.

4.4 Analysis

Powder XRD was recorded on a Phillips PW 1730 spectrometer using Ni filtered CuKα radiation. Differential scanning calorimetric analysis of polyethylene was performed on a Perkin- Elmer DSC - 7 Thermal analysis Work Station.

5.0 REFERENCES

1. P.C. Barbe, G.Cecchin, and L. Noristi, Adv. Polym. Sci., **81**, 1 (1986).

2. J.C.W. Chien, Catal. Rev. Sci & Eng., **26**, 613 (1984).

3. S. Muthukumaru Pillai, M. Ravidranathan, and S. Sivaram, Chem. Rev., **86**, 353 (1986).

4. K. Soga, T. Shiono, Y.Y. Wu, K. Ishii, A. Nogami, and Y. Doi, Makromol. Chem. Rapid Commun., **6**, 537 (1985).

5. U. Zucchini, I. Cuffiani, and G. Pennini, Makromol. Chem. Rapid Commun., **5**, 567 (1984).

6. N. Kashiwa and A. Toyota, Polym. Bull., **11**, 471 (1984).

7. F. Masi, S. Malquori, L. Barazzoni, C. Ferrero, A. Moalli, F. Menconi, and R. Invernizzi, Makromol. Chem. Suppl., **15**, 147 (1989).

8. T. Yano, S. Ikai, M. Shimizu, and K. Washio, J. Polym. Sci., Part A., **23**, 1455 (1985).

9. Y. Doi, K. Soga, M. Murate, E. Suzuki, Y. Ono, and T. Keii, Polym. Commun., **24** 244 (1983).

10. T. Yano, S. Ikai, and K. Washio, J. Polym. Sci., Part A., **23**, 3069 (1985).

11. S. Sivaram, Shashikant, and V.K. Gupta, Preprints, Div. Petroleum Chem. Inc., (ACS) **34**, 595 (1989).

12 R. Sarma, F. Raminez, B. Mekeever, Y.F. Chew, J.F. Marecek, D. Nierman, and T.M. McCaffrey, J. Am. Chem. Soc., **99**, 5289 (1977).

SYNTHESIS AND CHARACTERIZATION OF POLYMERS OF HEXENE-1 AND OCTENE-1 USING XYLENE SOLUBLE MAGNESIUM - TITANIUM CATALYST

1.0 INTRODUCTION

Among the series of linear α - olefins, propylene and butene-1 are extensively studied monomers using Ziegler - Natta catalysts. Higher α - olefins have been far less investigated. It is reported that ethylene is 10 to 50 and even up to 100 times more reactive than propylene, depending on the catalyst system. In contrast, propylene is about three times more active than butene-1. The decrease in drop in activity becomes progressively less when increasing the size of the alkyl group α- to the unsaturation and only small changes in polymerization activity are reported while going from pentene-1 to dodecene-1.

Polymers of higher α - olefins such as hexene-1 and octene-1 have assumed importance as rheology modifiers in a variety of end applications[1,2]. High molecular weight polymers of higher α - olefins with very broad molecular weight distribution can be produced using heterogeneous Ziegler - Natta catalysts[3]. We shall briefly review the polymerization of higher α - olefins using heterogeneous magnesium - titanium catalysts and their characterization.

2.0 HIGHER α - OLEFIN POLYMERIZATION USING HETEROGENEOUS MAGNESIUM - TITANIUM CATALYSTS

Very few reports exist in the literature dealing with higher α - olefin polymerization studies using magnesium - titanium catalysts (Table 6.1). This is due to their low reactivity towards these catalysts. Mostly the higher α - olefins polymerization studies were performed to understand the effect of monomer diffusion phenomenon in catalyst deactivation process and the effect of catalyst disintegration during polymerization of ethylene and propylene monomers. Thus, Chien et. al., by comparing the polymerization profiles of propylene and decene-1 by a CW - catalyst based on $MgCl_2$ & $TiCl_4$, have shown that the rate constant of propagation is about eight times greater for propylene, while the rate constant of termination, i.e., decay of R_p (rate of polymerization), is comparable for the two monomers[4]. Based on these results, it is concluded that the diffusion of monomer plays a very minor role in the deactivation of polymerization active

Table 6.1: Heterogeneous Magnesium - Titanium Catalysts for the Polymerization of Higher α - Olefins

Catalyst System	Monomer	Polymerization Conditions	Activity (Kg Polym/g Ti/h)	Features	Reference
$MgCl_2/Ti(OBu)_4$ - $Al(i\text{-}C_4H_9)_3$	Hexene-1	Temp., : 50°C, Time : 2 hours Al/Ti : 10 - 500, [M] : ---, Solvent: Heptane.	13.7	Isotactic Index : 91%., [η] : 3.4 dl/g (at 135°C)	6
$MgCl_2/Ti(OBu)_4$ - $Al(i\text{-}C_4H_9)_3$	Octene-1	Temp., : 50°C, Time : 2 hours Al/Ti : 10 - 500, [M] : ---, Solvent: Heptane.	18.1	Isotactic Index : 91%., [η] : 3.4 dl/g (at 135°C)	6
$MgCl_2/Hf(OBu)_4$ - $Al(i\text{-}C_4H_9)_3$	Hexene-1	Temp., : 50°C, Time : 2 hours Al/Ti : 10 - 500, [M] : ---, Solvent: Heptane.	0.32	Isotactic Index : 90%., [η] : 9.8 dl/g (at 135°C)	6

Table 6.1: Heterogeneous Magnesium - Titanium Catalysts for the Polymerization of Higher α - Olefins

Catalyst System	Monomer	Polymerization Conditions	Activity Kg Polym/g Ti/h	Features	Reference
$MgCl_2/Hf(OBu)_4$ - $Al(i\text{-}C_4H_9)_3$	Octene-1	Temp., : 50°C, Time : 2 hours Al/Ti : 10 - 500, [M] : ---, Solvent: Heptane.	0.41	Isotactic Index : 93%, $[\eta]$: 8.4 dl/g (at 135°C)	6
$MgCl_2/TiCl_4$ - $Al(i\text{-}C_4H_9)_3$	Decene-1	Temp., : 70°C, Time : 1 hour, [M] : ---, Al/Ti : 55 Solvent: Heptane	1890	Isotactic Index : 43%, $[\eta]$: 0.36 dl/g, (in THF 25°C) $\bar{M}_v$: 0.97 X 10^5	7
$MgCl_2$/Dibutylphthalate/ $TiCl_4$ - $Al(i\text{-}C_4H_9)_3$	Decene-1	Temp., : 70°C, Time : 1 hour, [M] : ---, Al/Ti : 55 Solvent: Heptane	521	Isotactic Index : 78%, $[\eta]$: 0.36 dl/g, (in THF 25°C) $\bar{M}_v$: 1.04 X 10^5	7

Table 6.1: Heterogeneous Magnesium - Titanium Catalysts for the Polymerization of Higher α - Olefins

Catalyst System	Monomer	Polymerization Conditions	Activity Kg Polym/g Ti/h	Features	Reference
$MgCl_2$/Dibutylphthalate/ $TiCl_4$ - $Al(i\text{-}C_4H_9)_3$/External Donor	Decene-1	Temp., : 70°C, Time : 1 hour, [M] : ---, Al/Ti : 55 Solvent: Heptane	236	Isotactic Index : 100%, [η] : 0.67 dl/g, (in THF 25°C) M_v : 2.18 X 10^5	7
$Mg(OEt)_2/TiCl_4$ - $Al(C_2H_5)_3$	Octene-1	Temp., : 80°C, Time : 1 - 3.5 hours, [M] : 1 - 3 M, Al/Ti : 10, Solvent: Cyclohexane or Toluene.	5.0 - 8.4	Aim of the study is to understand the effect of ethylene monomer diffusion during polymerization.	5
$Mg(OEt)_2/TiCl_4$ - $Al(C_2H_5)_3$	Hexene-1	Temp., : 60°C, Time : 0.3 hours, [M] : 1 M, Al/Ti : 30, Solvent: Cyclohexane or Toluene.	0.5 - 3.0	Aim of the study is to understand the effect of ethylene monomer diffusion during polymerization.	5
$MgCl_2$/Ethyl Benzoate/p-cresol/ $TiCl_4$ - $AlEt_3$/methyl-p-toluate	Decene-1	Temp., : 50°C, Time : 0 - 1 hour, [M] : 0.65 M, Al/Ti : 167 Solvent : Heptane.	0.1	Aim of the study is to understand the effect of propylene monomer doffusion on polymerization.	4

sites. Similarly, studies by Franz et. al., on ethylene and octene monomers using $Mg(OC_2H_5)$ - $TiCl_4$ catalyst, supported to Chien's conclusions[5]. The molecular weight distribution of polymers are were found to be very broad indicating that the mass transport of monomers or diffusion of monomer does not play a major role by deactivation process.

More recently, interest is evident in the literature towards the understanding of the role of transition metal component and donors in polymerization of higher α - olefins using magnesium chloride supported catalysts. Thus, Group IV metal alkoxide supported on magnesium chloride have been synthesized and tested for the efficiency of homopolymerization of higher α - olefins[6]. It is observed that titanium based catalysts are highly active and hafnium based catalysts produce polymers with higher molecular weight in comparison with titanium based catalysts. Further, it was observed that internal and external donors reduce the activity and increase the molecular weight of poly(decene-1), but the stereoregularity was found to increase from 43% to 78% in Mg - Ti catalysts[7]1.

2.1 Characterization

Characterization of poly higher α - olefins are mostly performed using 13C - NMR technique following the nomenclature proposed by Lindeman and Adams[11] and recently Randall[12]. DSC for T_m and GPC for MWD are also employed to characterize poly(α - olefin)s.

3.0 RESULTS AND DISCUSSION

Insoluble magnesium-titanium-aluminum and titanium-aluminum catalysts possesses active centers which are a consequence of the different valence states of the transition metal, differing steric requirements of the site and sites having different acidic characters. Consequently, polymers with differing kinetic chain lengths are produced on these heterogeneous catalysts, leading to broad molecular weight distributions. On the contrary, soluble catalysts such as metallocene - methylaluminoxane systems possess a single active site and therefore produce narrow molecular weight distribution polymers[8]. However, metallocene based catalysts are quite inefficient for the synthesis of homopolymers of higher α - olefins. Only low molecular weight liquid oligomers could be produced from 4-methyl-pentene-1 and hexene-1 using dicyclopentadienyl zirconium dichloride - methylaluminoxane catalyst system[9,10]. Using a chiral stereorigid metallocene, Asanuma and co-workers have recently reported that poly(hexene-1) with a $\bar{M}_n$: 6000 and polydispersity of 1.7 can be produced[10]. Therefore we extended the study of xylene soluble Mg - Ti catalyst to the polymerization of hexene-1 and octene-1 using diethylaluminumchloride as cocatalyst.

3.1 Hexene-1 and Octene-1 Polymerization Using Soluble Magnesium - Titanium Catalyst

Polymerization of hexene-1 and octene-1 were performed with the soluble Mg - Ti catalyst in bulk and in solution at various Al/Ti ratios and temperature using diethylaluminumchloride as cocatalysts. The results are summarized in Table 6.2. In general, bulk polymerization gave better conversions and higher catalyst productivity. The intrinsic viscosities are in the range of 1.2 - 4 for poly(hexene-1) and 0.5 - 3.0 for poly(octene-1). Conversions and activities for hexene-1 polymerization are higher than that of octene-1 polymerization.

Based on the above observations a systematic study on bulk polymerization of hexene-1 under different experimental conditions was performed. The effect of Al/Ti ratio, absolute Ti and time on conversion and activity were studied (Tables 6.3, 6.4 and 6.5). It is observed that as Al - content increased, the activity, conversion and molecular weight of polymer decreased. In contrast, higher the absolute Ti content, higher conversion and activity but lower molecular weights were obtained. It was also observed that the reaction time has no effect on conversion and molecular weight of poly(hexene-1).

Table 6.2: Polymerization of Higher α - Olefins with Soluble Magnesium - Titanium Catalyst and Diethylaluminum Chloride[a]

S.No.	Monomer	Xylene	Al/Ti (Wt. ratio)	Temp., (°C)	Time (min)	Conversion (%)	Activity (g polym/g Ti/h)	$[\eta]$[b] (dl/g)	M.W.D.
MONOMER: HEXENE - 1									
1	5.0	--	25	40	90	35	256	3.0	2.1
2	5.0	--	50	40	90	10	71	2.9	--
3	5.0	10	25	25	120	13	69	1.3	2.7
4	5.0	25	25	40	420	20	15	3.1	2.0
5	5.0	25	25	40	420	20	16	5.0	2.1
MONOMER: OCTENE - 1									
6	5.0	--	25	40	60	20	222	0.8	2.1
7	5.0	--	25	25	120	7	18	1.3	2.9
8	5.0	25	40	40	420	14	10	1.9	3.1
9	5.0	25	25	40	420	12	9	3.5	---

a) [Ti] : 0.04mmoles in bulk reaction, [Ti] : 0.19 mmoles in solution

b) Intrinsic viscosity was determined at 135°C in decalin as a solvent for poly(hexene-1) and 0-dichloro benzene for poly(octene-1)

Table 6.3: Bulk Polymerization of Hexene - 1 with Soluble Magnesium - Titanium Catalyst and Diethylaluminum Chloride: Effect of Absolute Titanium[a]

S.No.	Absolute Ti (10^5 moles)	Conversion (%)	Activity (g polym/g Ti/ h)	$[\eta]^b$ (dl / g)
1	4.3	40.0	485	2.9
2	5.15	58.0	281	2.0
3	10.30	75.0	189	1.8

a) Polymerization Conditions: [Monomer] : 0.594 moles; Al/Ti: 25, Time: 2h and Temp., : 40°C.

b) Intrinsic viscosities of Poly(hexene-1) were determined at 135°C in Decalin.

Table 6.4: Bulk Polymerization of Hexene - 1 with Soluble Magnesium - Titanium Catalyst and Diethylaluminum Chloride: Effect of Al/Ti Ratio[a]

S.No.	Al/Ti (Wt . ratio)	Conversion (%)	Activity (g Polym/g Ti/h)	$[\eta]^b$ (dl/g)
1	25	40	485	2.9
2	50	21.4	259	2.1
3	100	9.4	114	1.3
4	200	5.4	65	1.2

a) Polymerization Conditions: [Ti] : 0.043 mmoles; Time : 2h; Temp.,: 40°C.

b) Intrinsic viscosities of Poly(hexene-1) were determined at 135°C in Decalin.

Table 6.5: Bulk Polymerization of Hexene - 1 with Soluble Magnesium - Titanium Catalyst and Diethylaluminum Chloride: Effect of Time[a]

S.No.	Reaction Time (hours)	Conversion (%)	Activity (g Polym/g Ti/ h)	$[\eta]$[b] (dl/g)
1	0.5	50.3	978	2.2
2	1.0	53.4	518	2.2
3	2.0	53.4	257	2.2

a) Polymerization Condtions: [Ti] : 0.101 mmoles; Al/Ti : 25; Temp., : 40°C.

b) Intrinsic viscosities of Poly(hexene-1) were determined at 135°C in Decalin.

3.2 Characterization

Poly(hexene-1) and poly(octene-1) were characterized using GPC, 13C - NMR, and TGA techniques. GPC results showed relatively narrow MWD ranging between 2 - 3 for poly(hexene-1) and poly(octene-1) samples (Figure 6.1 and 6.2) and are compared with a poly(hexene-1) prepared using a heterogeneous Mg - Ti catalyst, prepared in our laboratory. This indicates that the active titanium centers responsible for polymerization are more uniform. In our opinion this is the first example of a high molecular weight relatively narrow molecular weight distribution poly(hexene-1) and poly(octene-1).

Carbon - 13 NMR characterization of poly(hexene-1) and poly(octene-1) were performed. It was inferred from the spectrum that the polymers are atactic in nature. The spectra of poly(hexene-1) and poly(octene-1) and INEPT spectra of poly(octene-1) are shown in Figures 6.3, 6.4 & 6.5. Following the Lindeman and Adams method, the chemical shifts of Poly(hexene-1) and poly(octene-1) were calculated and compared with experimental results. A very good agreement with experimental values was observed (Tables 6.6 & 6.7). Thermogravimetric analysis in N_2 of these polymers showed an initial decomposition temperature difference of 20°C between poly(hexene-1) and poly(octene-1) (Figure 6.6 and 6.7). For poly(hexene-1), initial decomposition temperature (IDT) was 291°C and final decomposition temperature (FDT) was 440.4°C, whereas for poly(octene-1), IDT was 269.7°C and FDT was 440.4°C indicating that poly(hexene-1) is more thermally stable compared to poly(octene-1).

4.0 CONCLUSIONS

Xylene soluble Mg - Ti catalysts polymerizes hexene-1 and octene-1 to high molecular weight poly(α- olefins). The homogeneous nature of the catalyst as well as the reaction even upon reduction with organoaluminum compound is responsible for the production of polymers with relatively narrow molecular weight polymers. High molecular weight poly(α- olefins) with such narrow molecular weight distribution is presently unknown in the literature.

Table 6.6: Experimental and Calculated Chemical Shifts of the ^{13}C NMR Spectrum of the Poly(hexene-1) Prepared with Xylene Soluble Magnesium - Titanium Catalyst

Carbon	Expected (Without Standard Error)	Expected (With Standard Error)	Observed
α	39.48	40.95	40.67
br	32.91	34.91	32.64
4B	34.72	35.85	34.90
3B	29.96	30.76	28.39
2B	22.61	23.12	23.39
1B	13.92	15.71	14.12

Table 6.7: Experimental and Calculated Chemical Shifts of the ^{13}C NMR Spectrum of the Poly(octene-1) Prepared with Xylene Soluble Magnesium - Titanium Catalyst

Carbon	Expected (Without Standard Error)	Expected (With Standard Error)	Observed
α	39.48	40.95	41.60
br	32.91	34.91	33.77
6B	34.72	35.85	36.23
5B	27.52	28.50	27.72
4B	29.96	30.76	31.14
3B	32.4	32.31	33.14
2B	22.61	23.12	23.85
1B	13.92	15.71	14.99

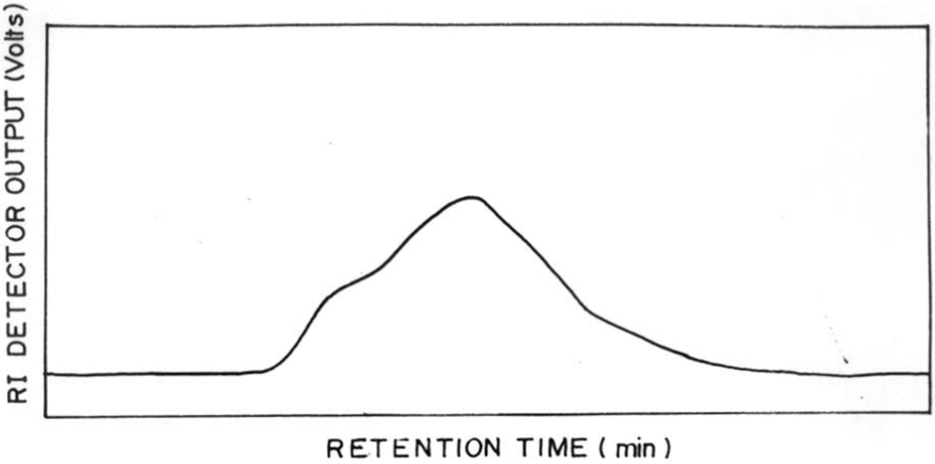


Fig.6.1a GPC Chromatogram of Poly(hexene-1) Obtained with Homogeneous Mg - Ti Catalyst

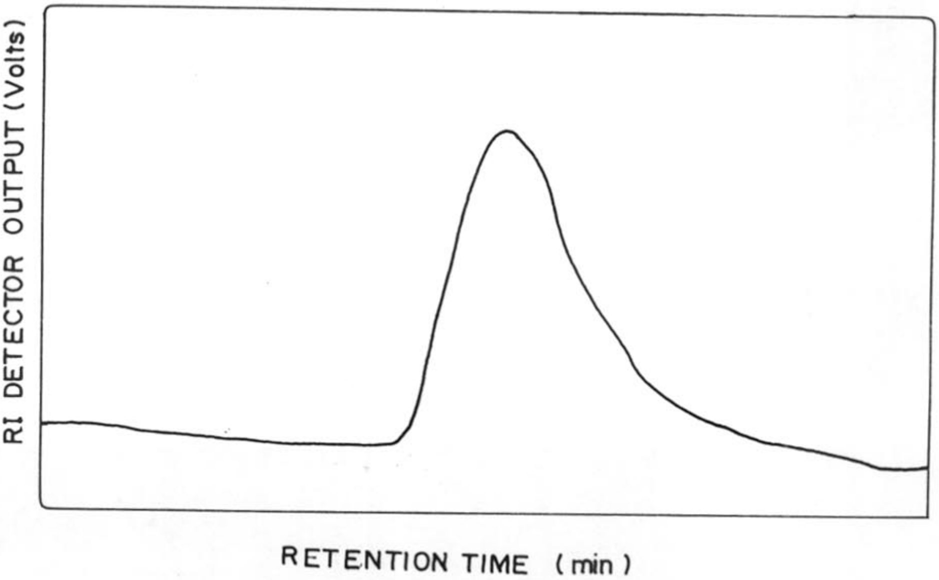


Fig.6.1b GPC Chromatogram of Poly(hexene-1) Obtained with Heterogeneous Mg - Ti Catalyst

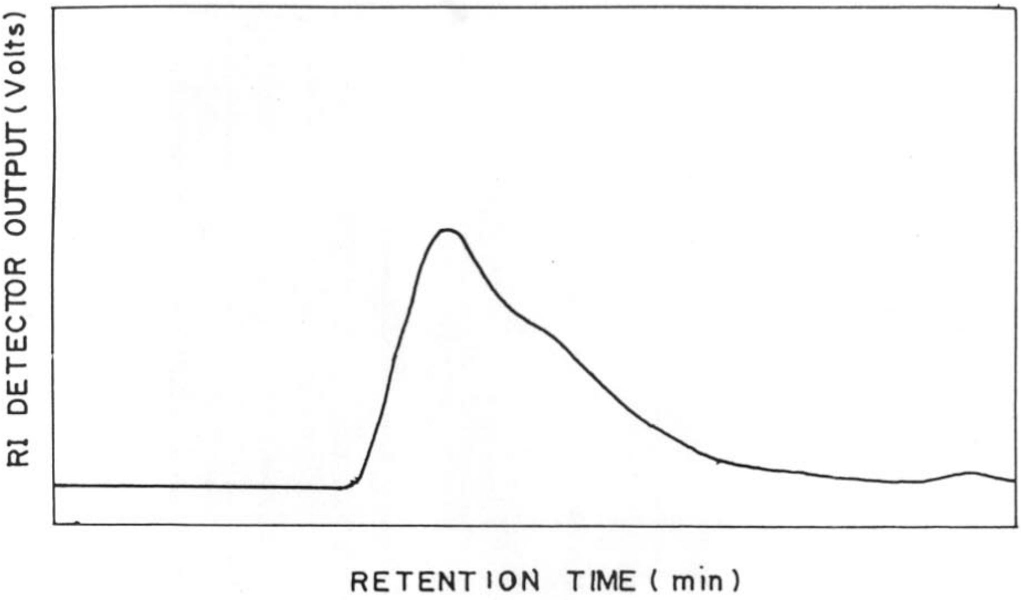


Fig.6.2 GPC Chromatogram of Poly(octene-1) Obtained with Homogeneous Mg - Ti Catalyst

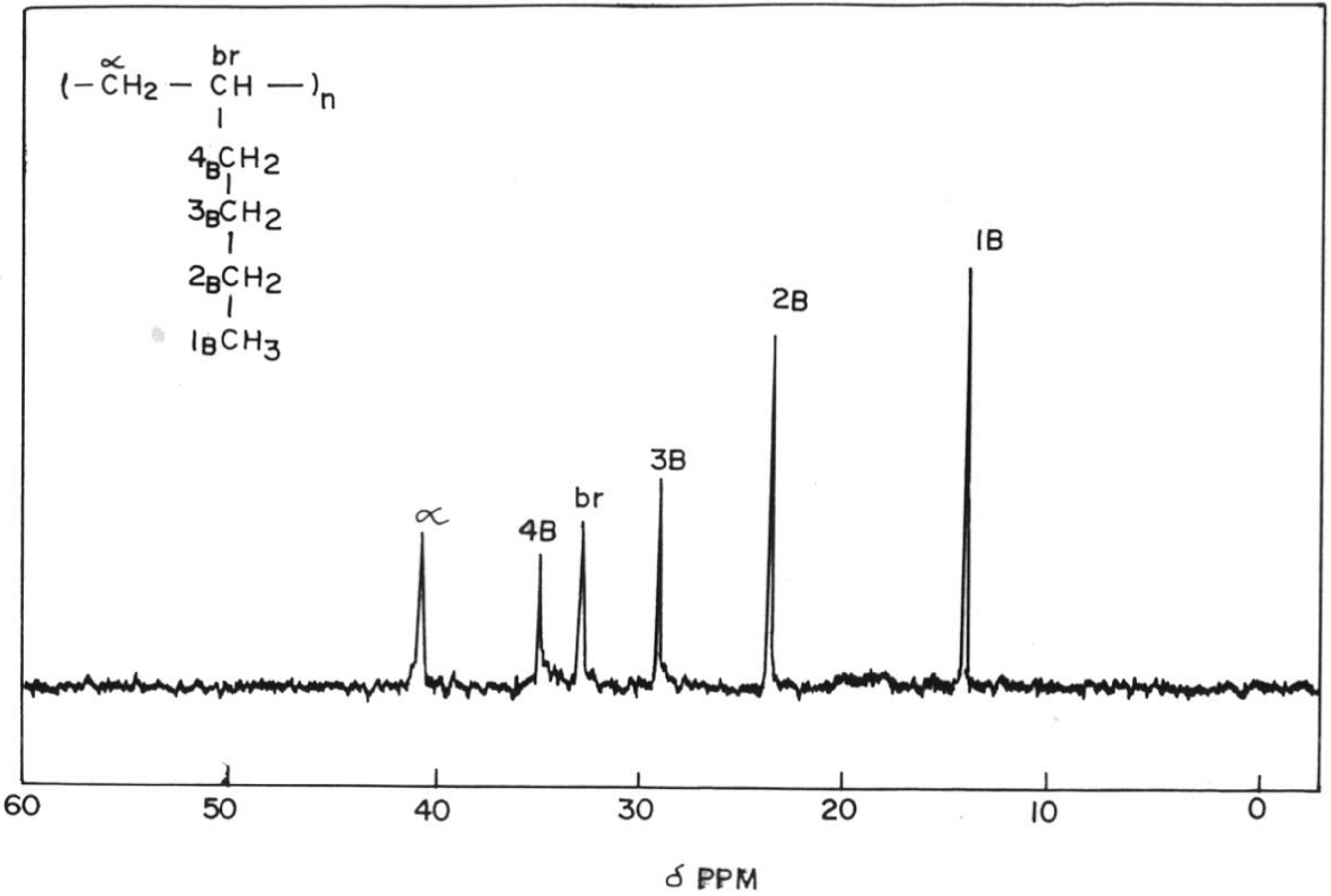


Fig.6.3 ^{13}C - NMR Spectra of Poly(hexene-1)

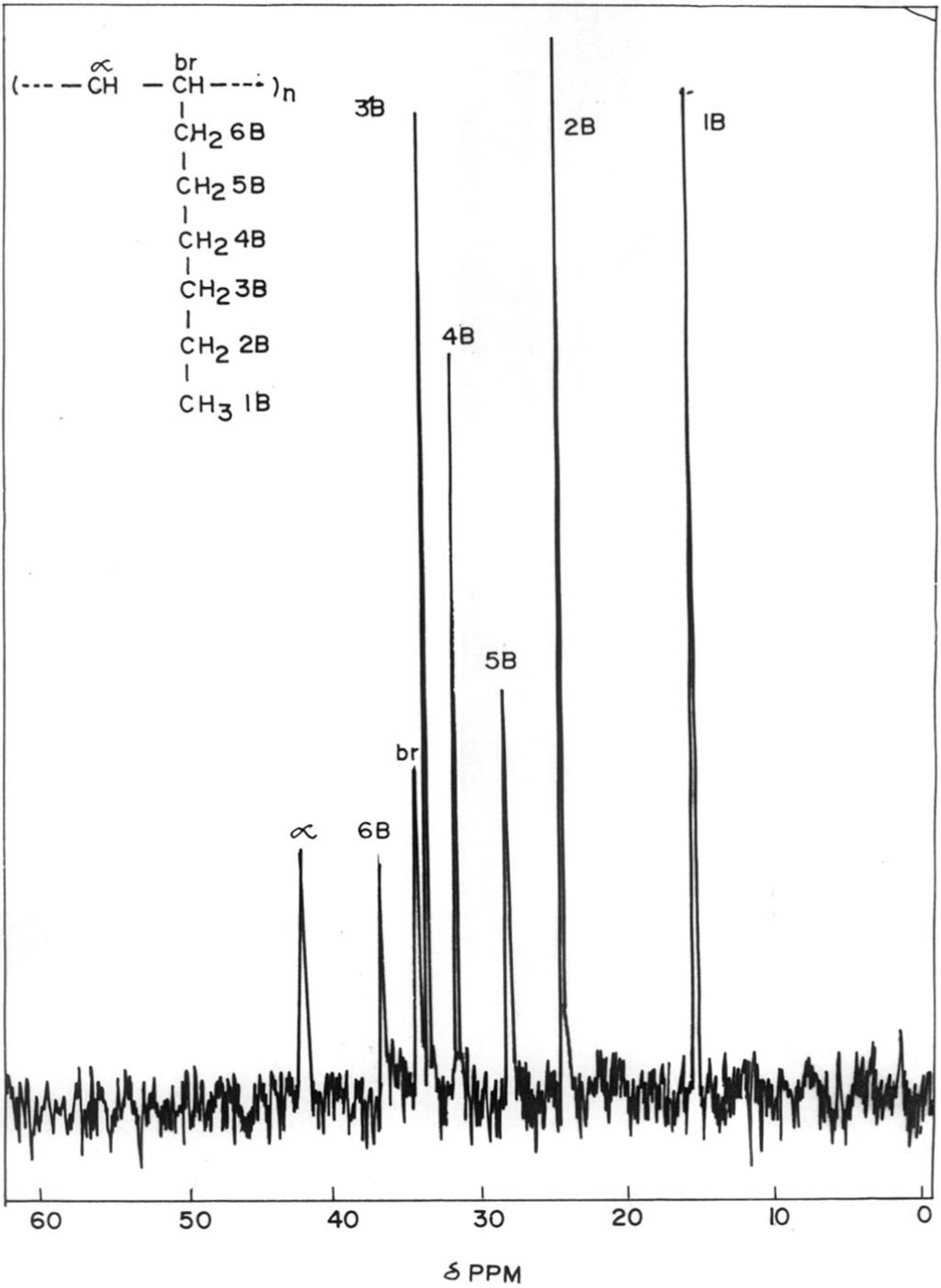


Fig.6.4 ^{13}C - NMR Spectra of Poly(octene-1)

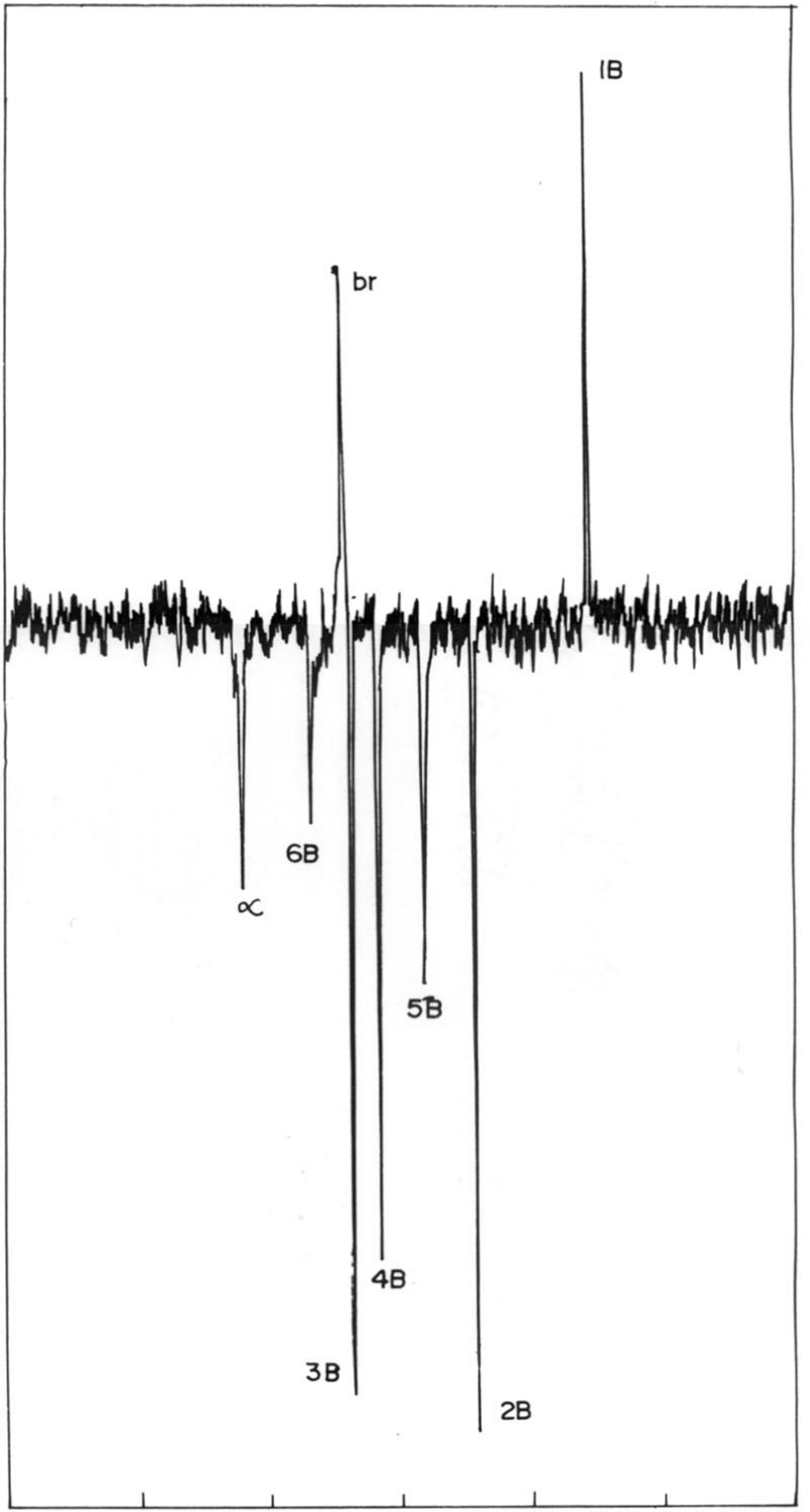


Fig.6.5 INEPT ^{13}C - NMR Spectra of Poly(octene-1)

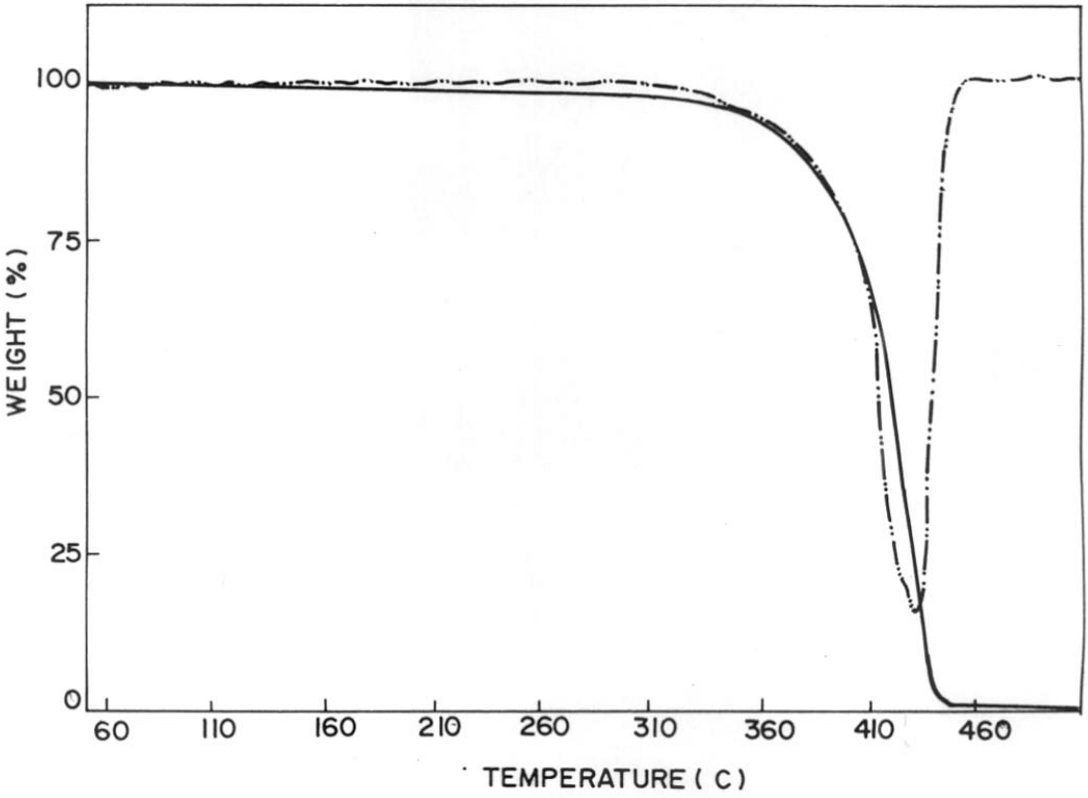


Fig.6.6 Thermogravimetric Analysis of Poly(hexene-1)

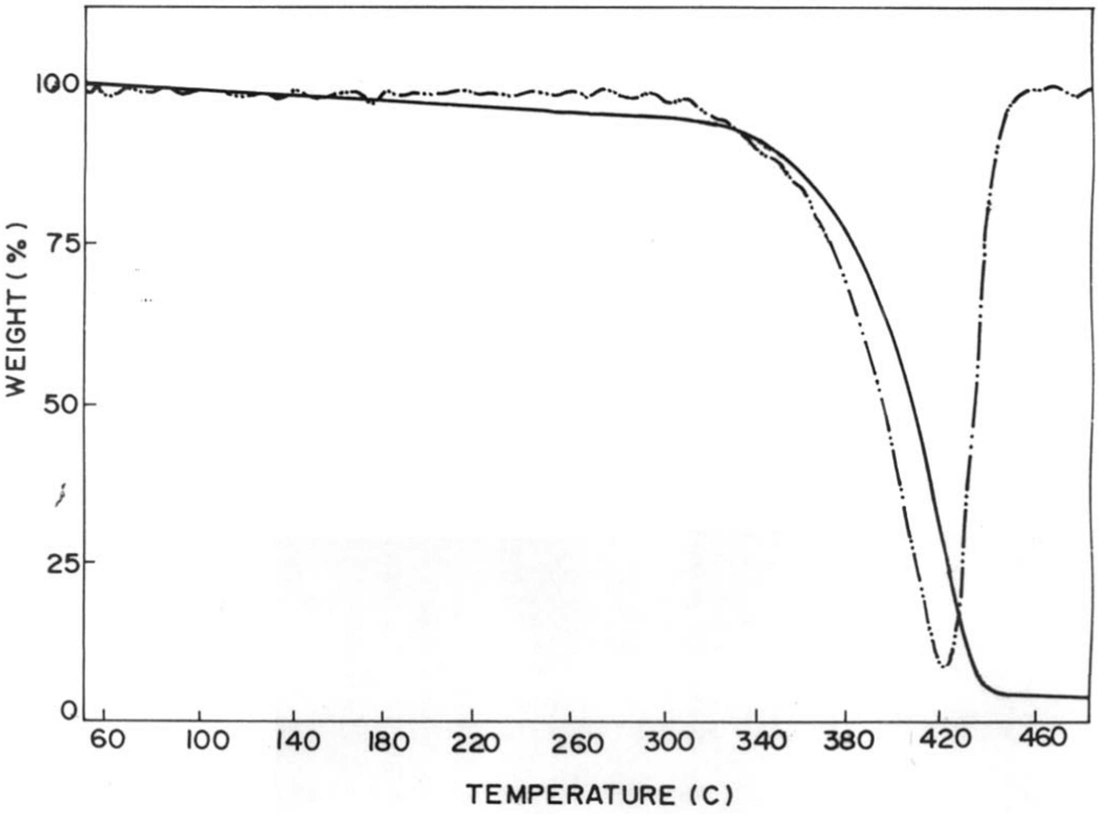


Fig.6.7 Thermogravimetric Analysis of Poly(octene-1)

5.0 EXPERIMENTAL SECTION

All manipulations involving air sensitive compounds were performed either inside a Labconco Model 50004 inert atmosphere glove box continuously purged with high purity N_2 (<5ppm moisture) generated using N_2 generator (Spantech, Model NG 300-1, England) or under a positive pressure of high purity N_2 using standard bench top inert atmosphere techniques.

5.1 Materials

Diethylaluminumchloride (Schering A. G., Germany) was used as received. Hexene-1 (97%) and octene-1 (97%) (Aldrich Chemical Co., USA) were purified as described below. Purified xylene and hexane (S.D. Fine Chemicals, Bombay) as described in chapter - 3 were used.

5.2 Purification of hexene-1 and octene-1

These monomers were stored over CaH_2 for 12 hours and then distilled under vacuum. Aldrich Sure/Seal^R bottles baked overnight at 140°C were cooled under high purity N_2. Freshly distilled hexene-1 and octene-1 were transferred into these bottles by cannula under N_2 pressure and then stored by crimping a crown cap on these bottles.

5.3 Polymerization

All polymerizations were performed in a three neck 75mL capacity glass jacketed polymerization cell equipped with a magnetic stirring bar, nitrogen inlet, septum and an outlet. The polymerization temperature was maintained by circulating water using a constant temperature circulating water bath. A typical polymerization procedure is as follows:

The glass reactor was charged with xylene soluble Mg - Ti catalysts (0.38mmole) and neat DEAC (1.77mmole) under N_2 atmosphere using a hypodermic syringe at 30°C. The temperature was slowly raised to 70°C and maintained at that temperature for 90 minutes. Subsequently, the temperature was cooled to the desired polymerization temperature. Freshly distilled neat hexene-1 (5g) was added to the Mg-Ti-Al catalyst mixture using hypodermic syringe. After the desired polymerization time, 30 - 50 mL of hexane or THF was injected into the reactor and the solution stirred for few minutes. The reaction mixture was transferred into a 1000mL beaker and the catalyst destroyed by the addition of 20 mL of 5% acidified methanol. Further addition of freshly distilled methanol caused the polymer to precipitate. The polymer was filtered and dried in a vacuum oven at 30°C for six hours. Yield : 1.39g (28% conversion).

5.4 Analysis

Estimation of magnesium and titanium was performed as described in chapter - IV. Molecular weight distributions were performed by gel permeation chromatography (GPC) on a Waters Model No: GPC II using styragel columns (10^5, 10^4, 10^3 and 500 A°; concentration : 0.2 - 0.3w/v; flow rate 1.0 mL/min; temperature :25°C) using tetrahydrofuran as mobile phase. Intrinsic viscosities of polymers were measured using as Ubbelohde viscometer and decalin or o-dichlorobenzene as solvents at 135°C.

6.0 REFERENCES

1. US 4433123 (1984) to Conoco.

2. a) US 4613712 (1986) to Mobil Oil Corporation.

   b) Ger. Pat. 3323725 (1985) to Hoechst A-G.

3. J.C.W. Chien and T. Ang, J. Polym. Sci., Part A., **24**, 353 (1986).

4. J.C.W. Chien, C.I. Kuo, and T. Ang, J. Polym. Sci., Part A., **23**, 723 (1985).

5. H. Franz, H. Meyer, and K.H. Reichert, Polymer, **22**, 226 (1981).

6. A. Altomare, R. Solaro, F. Ciardelli, L. Barazzoni, F. Menconi, S. Malquori, and F. Masi, Polymer, **33**, 1768 (1992).

7. B. Pena and J.A. Delgado, Makromol. Chem. Rapid Commun., **12**, 353 (1991).

8. W. Kaminsky and Buschernohle, in "Recent Advances in Mechanistic and Synthetic Aspects of Polymerization" (Eds. M. Fontanille and A. Guyot), Reidel Publishing Co., Holland, p503 (1987).

9. EP 328609 (1990) to Mitsui Petrochemical Ltd.

10. a)T. Asanuma, Y. Nishimori, M. Ito, N. Uchikawa and T. Shiomura, Poly. Bull., **25**, 567 (1991).

    b)S. Sivaram and S. Marathe, unpublished results.

11. L.P. Lindeman and J.Q. Adams, Anal. Chem., **43**, 1245 (1971).

12. J. C. Randall, J. Macromol. Sci. Rev - Macromol. Chem. Phy., **29**, 201 (1989).

SYNTHESIS AND CHARACTERIZATION OF POLY(PHENYLACETYLENE)S USING XYLENE SOLUBLE MAGNESIUM - TITANIUM CATALYST

1.0 INTRODUCTION

Radical and ionic initiators have been frequently employed for the polymerization of substituted acetylenic monomers. In most of these cases, the products are linear oligomers whose molecular weights are a few thousands. Subsequently, the Ziegler - Natta catalysts were extended to the polymerization of substituted acetylenes[1,2,3]. It was observed that aromatic or hetero atom containing monosubstituted acetylenes produce mostly insoluble polymers and/or oligomers. Among monosubstituted acetylenes, phenylacetylene is has been well studied. Whereas radical or ionic initiation produce only oligomers, Ziegler - Natta catalysts produce relatively high molecular weight polymers having a large fraction of insoluble polymers. We discuss below the different Ziegler - Natta catalyst systems reported in the literature for the polymerization of phenylacetylene, their limitations and the characterization of poly(phenylacetylene)s.

2.0 ZIEGLER - NATTA CATALYST SYSTEMS FOR THE POLYMERIZATION OF PHENYLACETYLENE

Since the first reports of Natta et. al., in 1955 on phenylacetylene polymerization using coordination catalysts there has been continuous efforts to test different combination of transition metal catalysts and cocatalyst systems for the polymerization phenylacetylene[4,5,6]. These catalysts systems are shown in Table 7.1. Corresponding of poly(phenylacetylene)s and trimerization of phenylacetylene are commonly encountered during polymerizations of phenylacetylene using Ziegler - Natta catalysts. Presumably, high acidity of the catalyst is responsible for generating low molecular weight or insoluble polymers and for causing trimerization of phenylacetylene. For example, the catalysts system $TiCl_4/AlEt_2Cl$ leads only to cyclic trimers which is independent of the reaction conditions[7]. In contrast, the reaction conditions play an important role in generating soluble poly(phenylacetylene)s with the $AlEt_3/TiCl_4$ catalyst system[8]. Thus, at 10°C, no cyclic trimer or linear polymer of phenylacetylene can be

Table 7.1: Literature on Phenylacetylene Polymerization Using Ziegler - Natta Catalysts

Catalyst System	Polymerization Conditions	Conversion (%)	Polymer Features	Reference
$TiCl_4$ - $Al(C_2H_5)_3$	Temp., : 10°C, Time : 1 hour, Monomer : 0.91 M, Solvent : Benzene (50mL) Catalyst : 2.27 mmoles Al/Ti : 1 - 20	20 - 40	At low Al/Ti ratios either 7 oligomerization or no polymerization; but at higher Al/Ti(>10), polymerizations. Polymer color : Orange, Polymer structure : Trans - Cisoidal.	7
$TiCl_4$ - $Al(C_2H_5)_2Cl$	Temp., : 5°C, Time : 1 hour, Monomer : 0.91 M, Solvent : Benzene (50 mL), Catalyst : 3 mmoles,	20 - 80	Only oligomerization at all 8 the ratios leading to formation of 1,24 or 1,3,6 - triphenylbenzene	8
$Ti(OBu)_4$ - $Al(C_2H_5)_3$	Temp., : 60°C, Time : 6 hours, Monomer : 0.91 M, Solvent : Toluene (11 mL), Catalyst : 0.61 mmoles.	10 - 40	No major oligomerization. 9 Polymer color : Red brown, Polymer structure : Trans - Cisoidal.	9
$(C_5H_5)_2TiCl_2$ - $(C_2H_5)_2AlCl$	Temp., : 80°C, Time : 2 hours, Monomer : 9.1 M, Solvent : Benzene (5 mL), Catalyst : 1.67 mmoles	100	Polymer yield : 90 %, at low reaction temperatures oligomerization was observed.	14

Table 7.1: Literature on Phenylacetylene Polymerization Using Ziegler - Natta Catalysts

Catalyst System	Polymerization Conditions	Conversion (%)	Polymer Features	Reference
$(C_5H_5)_2HfCl_2$ - $(C_2H_5)_2AlCl$	Temp., : -78°C, Time : 1 hour, Monomer : 1.5 M, Solvent : Dichloroethane (25 mL), Catalyst : 2 mmoles	75	Polymer Yield : 50%, $\bar{M}_n$: 700	15
$(C_5H_5)_2HfCl_2$ - $(C_2H_5)_2AlCl$	Temp., : 70°C, Time : 6 hour, Monomer : 1.5 M, Solvent :Toluene (25 mL), Catalyst : 2 mmoles	91.6	Polymer Yield : 67%, $\bar{M}_n$: 600	15
$(C_5H_5)_2HfCl_2$ - $(C_2H_5)_3Al_2Cl_3$	Temp., : 60°c, Time : 24 hours, Monomer : 1 M, Solvent : Toluene (50 mL) Catalyst : 2 mmoles	20 - 100	Yield : 79%, Polymer Structure : Trans - Cisoidal, $\bar{M}_n$: 1130 - 900, $\bar{M}_w$ 3380 -1400, M.W.D. : 1 - 2.	13

obtained when Al/Ti < 1. At high Al/Ti ratios, 1,3,5 - triphenylbenzene and 1,2,4 - triphenylbenzene are obtained, and for Al/Ti > 7 and no cyclic products are obtained except a soluble phenylacetylene.

Soluble Ziegler - Natta catalysts such as $AlEt_3/Fe(acac)_3$, $AlEt_3/V(acac)_3$ and $AlEt_3/VO(acac)_2$, $AlEt_3/Ti(OR)_4$ have also been examined for the polymerization of phenylacetylene[9,10,12]. It is reported that $AlEt_3/Ni(dmg)_2$, $AlEt_3/Co(dmg)_2$, $AlEt_3/Fe(dmg)_2$, and $AlEt_3/Fe(dmg)_2.2NH_3$ are the most efficient catalysts with maximum efficiency at Al/Fe = 10. The catalyst activity decreases in the following order: $Fe(dmg)_2$ >> $Fe(dmg)_2.2Py$ > $Fe(dmg)_2.2NH_3$

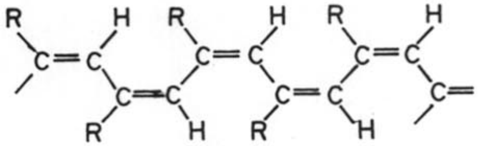
Conversions higher than 90% are obtained in a maximum of one hour and molecular weight reaches 8900.

Recently, group IV metallocenes in combination with alkylaluminum compounds have been studied for the polymerization of phenylacetylene[13,14,15]. These catalyst systems also yielded low molecular weight polymers with low conversions. It was shown that the polymerization proceeds through successive (2+2) cycloadditions with an active cationic species.

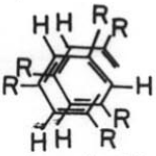
2.1 Characterization of Poly(phenylacetylene)s

Based on theoretical studies, it has been shown that poly(phenylacetylene)s exists in four configurations as shown in Figure 7.1, namely cis- transoidal, cis- cisoidal, trans- trnasoidal and trans- cisoidal[16]. Both cis and trans poly(phenylacetylene)s can be synthesized using Ziegler - Natta catalysts. It is observed that the same catalyst can produce cis and trans poly(phenylacetylene)s under different operating conditions. This is due to the rapid isomerization of cis and trans poly(phenylacetylene)s.

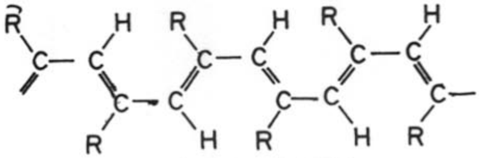
Extensive studies with the help of different analytical tools on cis - trnas isomerization have shown that in general, the cis opening of triple bond occurs at any polymerization temperature with all Ziegler type catalysts. Thus, trans double bonds are formed by the isomerization of cis double bonds in the course of reaction. The rate of isomerization is very low at room temperature, but it increases with temperature.



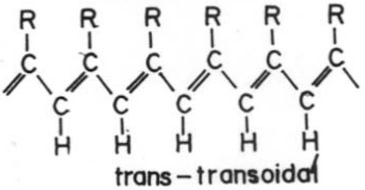
cis-transoidal



cis-cisoidal



trans-cisoidal



trans-transoidal

Fig.7.1 Configuration of Poly(phenylacetylene)s

Thus, with Ziegler catalysts, the heat of the reaction during polymerization and the thermal effect which accompanies the work up of the polymer promote the isomerization leading to the formation of trans poly(phenylacetylene)s.

Characterization of poly(phenylacetylene)s is frequently performed with IR and NMR techniques[17,18]. The cis - cisoidal and cis - transoidal structures of poly(phenylacetylene)s show identical IR spectra with characteristic peaks at 740, 870 and 1380 cm^{-1}, while the IR spectra of trans - cisoidal and trans - transoidal is devoid of these bands, but have characteristic bands at 910, 970 and 1265 cm^{-1}. High resolution NMR studies at elevated temperatures are normally carried out to determine the configuration of poly(phenylacetylene)s by NMR. The best resolution for cis - transoidal structure of poly(phenylacetylene)s can be obtained at 70°C having three protonic resonances centered at δ : 6.7 ppm, δ : 6.85 ppm and δ : 6 - 8.5 ppm. The NMR spectrum of trans - cisoidal poly(phenylacetylene)s presents at δ : 2 - 4.5 ppm the methinic protons resonance of 1,3 and 1,4 - cyclohexadiene structures between δ :4.5 - 6 ppm and the resonance of double bond protons from cyclohexadiene structures at δ: 6 - 7.6 ppm the resonance of aromatic monosubstitued protons and of trans - polyenic protons at δ : 7.6 - 8.4 ppm.

A typical NMR of the soluble fraction corresponds to cis - transoidal structure with cis rich (90%) shows three proton resonances centered at 5 .82 ppm (one olefin proton), 6.7 ppm (one aromatic proton) and 6.85 ppm (four aromatic protons). The best spectral resolution is obtained at 70°C. The insoluble polymer obtained with Ziegler Natta catalyst has a cis - cisoidal structure which is highly crystalline and can be regarded as the homologue of the isotactic α - vinylic polymers. Similarly, the trans - cisoidal poly(phenylacetylene)s obtained by cationic polymerization shows trans - polyenic protons at 6.2 - 7.2 ppm.

Powder X - ray diffraction pattern of poly(phenylacetylene)s has broad peaks probably because of the small crystalline peaks[19]. It is observed that the X- ray diffraction spectrum of cis - transoidal structure shows an amorphous halo shift at 2θ : 19° and a crystalline maximum at 2θ : 8.25°. The trans - cisoidal shows only amorphous halo shift at 2θ : 19°[20].

Additional characterization studies involving ESR, Raman spectroscopy, Electron absorption spectra and UV - visible spectra are reported in the literature[21,13].

3.0 RESULTS AND DISCUSSION

High Lewis acidity of Ziegler - Natta catalysts is believed to promote side reactions during the phenylacetyelene polymerization. Consequently, polymers which are insoluble and trimers are commonly produced. On the contrary, soluble catalysts based on metallocenes are observed to promote phenylacetylene polymerization with high conversions. It was therefore of interest to examine the polymerization of phenylacetylene using the xylene soluble Mg - Ti catalyst in conjunction with trisisobutylaluminum. This catalyst system presumably has low Lewis acidity.

3.1 Phenylacetylene Polymerization

Polymerization of phenylacetylene was performed with the soluble Mg - Ti catalyst in solution by varying temperature, monomer concentration and Al/Ti ratios. The results are shown in Tables 7.2, 7.3 and 7.4. In general, it was observed that xylene soluble Mg - Ti catalyst shows activities and conversions comparable to metallocene catalyst system. Further, increase of activity and conversion were observed with xylene soluble Mg - Ti catalyst by increasing Al/Ti ratio, temperature and monomer concentration.

The solubilities of isolated poly(phenylacetylene)s were tested using THF as a solvent. It was observed that the polymers were soluble in THF and solubilities ranges between 50 - 70% in contrast to 90 - 100% solubility of poly(phenylacetylene)s obtained by using metallocene catalyst system.

3.2 Characterization

Soluble poly(phenylacetylene)s was characterized by FT - IR, Powder XRD and ESR techniques. The IR spectra of all the soluble poly(phenylacetylene)s samples were virtually identical and similar to those obtained by Sisko et. al., and Trumbo and

Table 7.2: Phenylacetylene Polymerization Using Xylene Soluble Magnesium - Titanium Catalyst: Effect of Al/Ti[a]

S. No.	Al/Ti (Wt . Ratio)	Conversion (%)	Activity (Kg Polymer/g Ti/h)	Solubility (in THF %)
1	10	48	0.7	68
2	25	69	1.0	60
3	50	72	1.0	52

a) Polymerization Conditions: [Ti] : 1.53×10^{-3} M; [M] : 0.54M; Time : 30 min and Temp., : 60°C.

Table 7.3: Phenylacetylene Polymerization Using Xylene Soluble Magnesium - Titanium Catalyst: Effect of Monomer Concentration[a]

S. No.	[M] (mol L^{-1})	Conversion (%)	Activity (Kg Polymer/g Ti/h)	Solubility (THF %)
1	0.182	21	0.1	--
2	0.364	43	0.4	59
3	0.546	71	0.78	60

Polymerization Conditions: [Ti] : 1.53 X 10-3 M;
Al/Ti : 25; Time : 30 min and Temp., : 60oC.

Table 7.4: Phenylacetylene Polymerization Using Xylene Soluble Magnesium - Titanium Catalyst: Effect of Temperature[a]

S. No.	Temperature (°C)	Conversion (%)	Activity (Kg Polymer/g Ti/h)	Solubility (% THF)
1	40	33.0	0.5	-
2	50	52.4	0.8	55
3	60	70.0	1.1	58

Polymerization Conditions: [Ti] : 1.53 X 10^{-3} M;
[M] : 0.54 M; Time : 30 min and Al/Ti : 25.

Marvel[22,23] (figure 7.2). The spectra obtained in this study showed absorbances which are characteristic of a polyconjuagated system (15770 - 1600 cm^{-1}) of trans - cisoidal structure 9910 - 915 cm^{-1}). Further, the powder XRD spectrum showed a halo amorphous shift at 2θ : 19 - 20°. Thus confirming the trans - cisoidal structure (Figure 7.3).

The ESR spectrum of poly(phenylacetylene)s obtained in the present investigation showed a symmetrical single line with a g - factor value of 2.26. Thus, it shows radical character which is due the presence of π - delocalized bonds in the polymeric chains (figure 7.4).

4.0 CONCLUSIONS

It is observed that xylene soluble Mg - Ti catalyst in conjunction with triisobutylaluminum promotes clean phenylacetylene polymerization. On characterization the polymer, it was shown to have trans - cisoidal structure.

5.0 EXPERIMENTAL SECTION

All manipulations involving air sensitive compounds were performed either inside a Labconco Model 50004 inert atmosphere glove box continuously purged with high purity N_2 (<5ppm moisture) generated using N_2 generator (Spantech, Model NG 300-1, England) or under a positive pressure of high purity N_2 using standard bench top inert atmosphere techniques.

5.1 Materials

Trisisobutylaluminum (Schering A. G., Germany) was used as received. Phenylacetylene (Aldrich Chemical Co., USA) was purified as described below. Purified xylene (S.D. Fine Chemicals, Bomaby) as described in Chapter - III was used.

5.2 Purification of Phenylacetylene

Phenylacetylene was stored over CaH_2 for 12 hours and then distilled under vacuum. Aldrich Sure/Seal^R bottles baked overnight at 140°C was cooled under high purity N_2. Freshly distilled phenylacetylene was transferred into these bottles by cannula

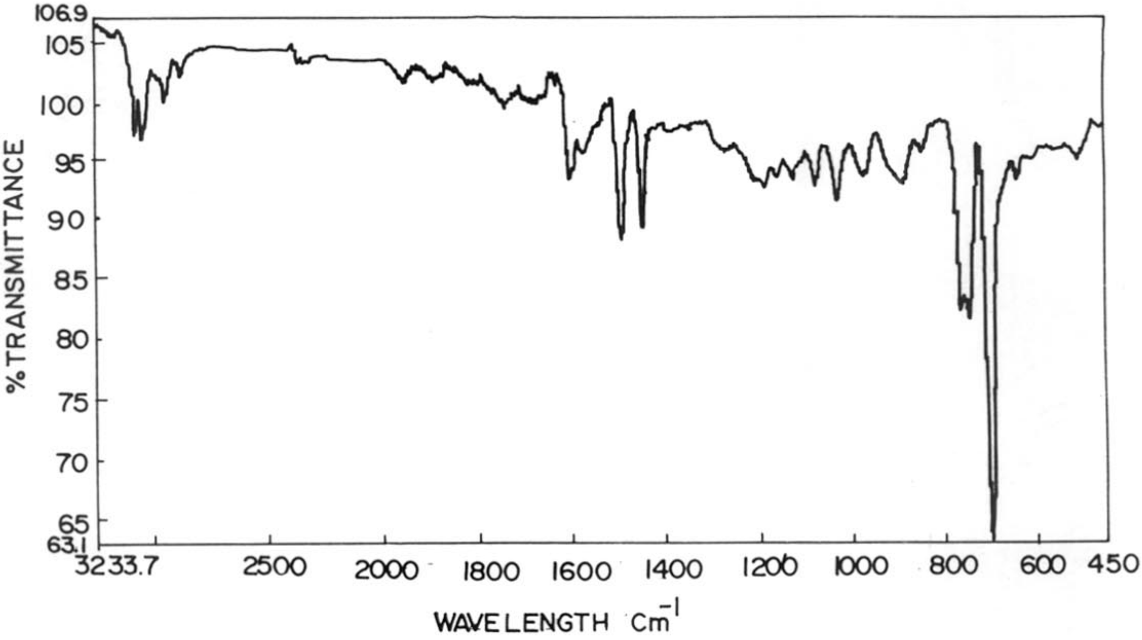


Fig.7.2 FT - IR Spectra of Poly(phenylacetylene)s

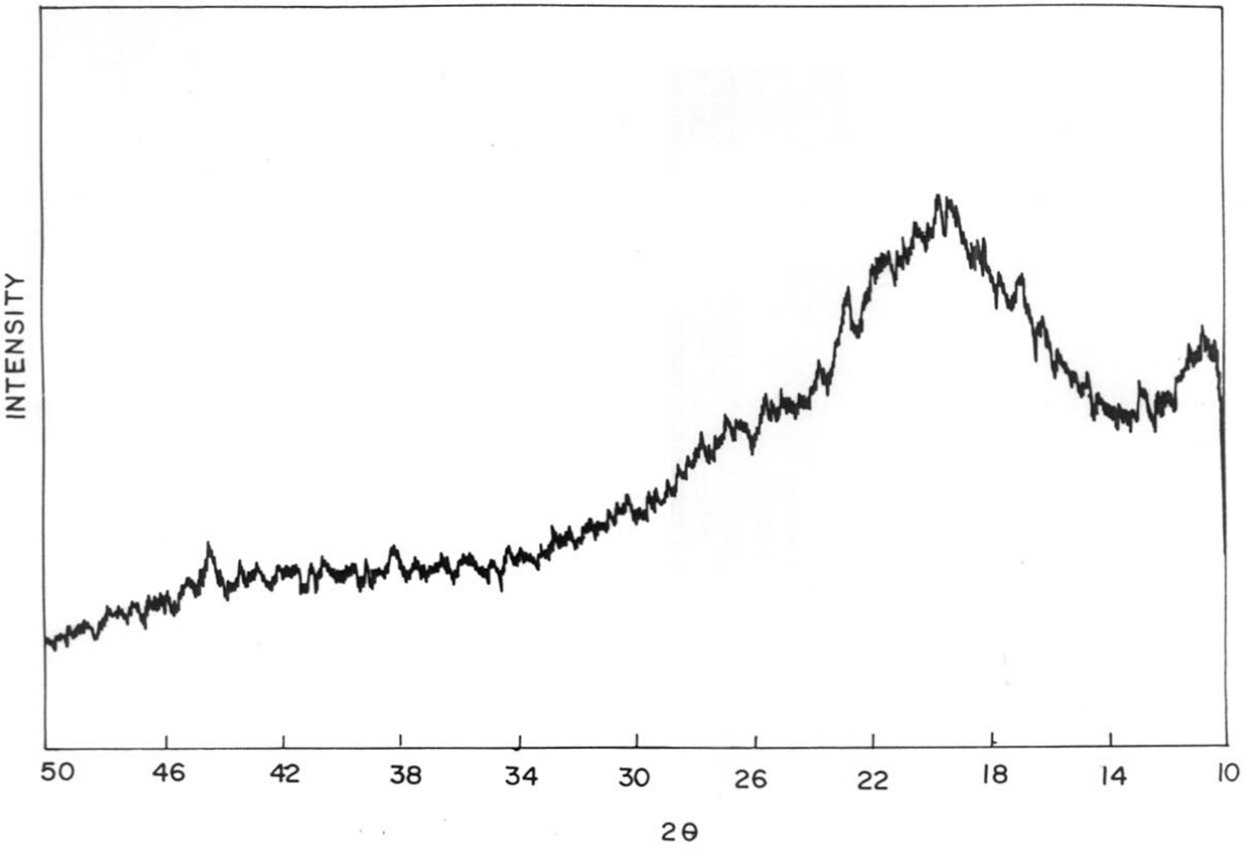


Fig.7.3 Powder X - Ray Diffraction Pattern of Poly(phenylacetylene)s

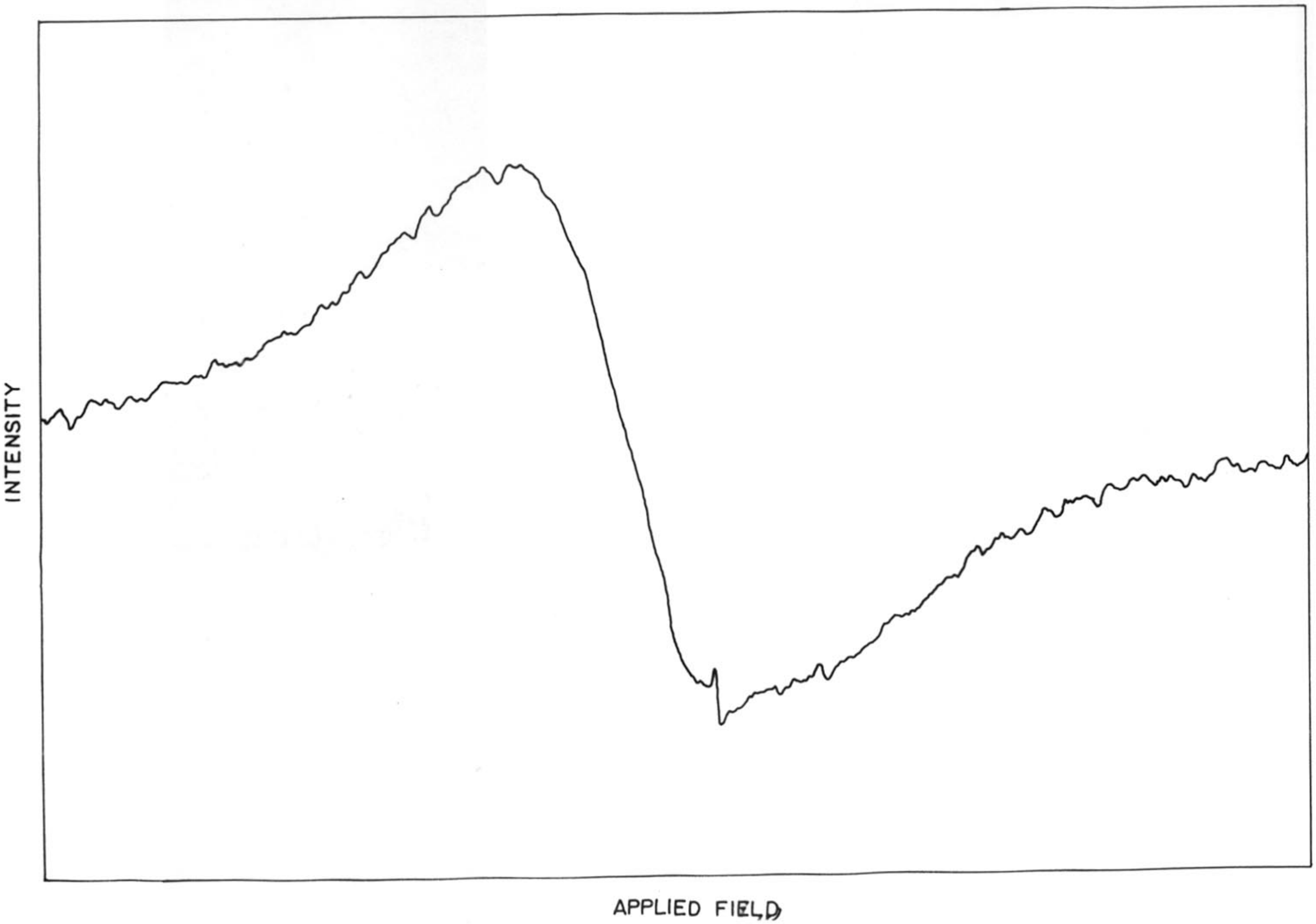


Fig.7.4 ESR Spectra of Poly(phenylacetylene)s

under N_2 pressure and then stored by crimping a crown cap on this bottle. Further, a stock solution of concentration 4.5 moles/lit was prepared in xylene by dissolving 10 mL of phenylacetylene in 10 mL of xylene.

5.4 Polymerization

All the polymerizations were performed in a three neck 75 mL capacity glass jacketed polymerization cell equipped with a magnetic stirring bar, nitrogen inlet, septum and an outlet. The polymerization temperature was maintained by circulating water using a constant temperature circulating water bath. A typical polymerization procedure is follows:

The glass reactor was charged with required amount of solvent xylene (22 mL), neat triisobutylaluminum (3.06×10^{-1} moles), xylene soluble Mg - Ti catalyst (1.53×10^{-3} moles of Ti) and finally the stock solution of monomer (0.54 moles/lit) at the polymerization temperature. After the desired polymerization time (30 minuets), the reaction mixture was terminated by adding acidified methanol at room temperature. Further addition of fresh methanol caused the polymer to precipitate. The polymer was filtered and dried and determined the yield. The solubility of the polymer was checked in refluxing tetrahydrofuran (THF). The percentage solubility was determined by isolating the insoluble polymer.

5.5 Analysis

Estimation of magnesium and titanium of soluble catalyst were performed as described in chapter - IV. Infrared spectra were recorded on a Perkin - Elmer 16PC FT - IR using KBr pellets. Powder XRD of polymer was recorded on a Phillips PW 1730 spectrometer using nickel filtered CuKα radiation. The ESR spectra were recorded on a Brucker model ER - 200D ESR spectrometer at room temperature (9.72 GHz).

6.0 REFERENCES

1. C.I. Simionescu and V. Percec, Prog. Polym. Sci., **8**, 133 (1982).
2. A. Bolognesi, M. Catellani, and S. Destri, in "Comprehensive Polymer Science" (Eds. G. Allen and J.C. Bevington) Pergamon Press, Oxford, **Vol 4**, 143 (1989).
3. G. Costa, in "Comprehensive Polymer Science" (Eds. G. Allen and J.C. Bevington) Pergamon Press, Oxford, **Vol 4**, 155 (1989).
4. Ital. 530 753 (1958).
5. M.G. Chauser, Y.M. Rodionov, V.M. Misin, and M.I. Cherkashin, U. Khim, **45**, 695 (1979); Russ. Chem. Rev., **45**, 348 (1976).
6. M.J. Benes, M. Janic, and J. Perska, Chem. Listy., **64**, 1094 (1970).
7. A. Furlani, E. Cervone, and M.A. Biancifiori, Rec. Trav. Chim., **81**, 585 (1962).
8. A. Furlani, G. Moretti, and A. Guedorieri, J. Polym. Sci., **B,5**, 523 (1967).
9. V.C. Simionescu and S. Dumitrescu, Makromol. Chem., **136**, 47 (1970).
10. H. Noguchi and S. Kambara, J. Polym. Sci., **B,1**, 553 (1963).
11. R.J. Kern, Polymer Preprints(ACS), **9**, 59 (1968).
12. R.J. Kern, J. Polym. Sci., Part A, **7**, 621 (1969).
13. M.G. Sisko, E.P. Bokaris, A.K. Zarkadis, and G. Kyriakakou, Eur. Polym. J., **28**, 1127 (1992).
14. A. Familli and M.F. Farona, Polym. Bull., **8**, 429 (1982).
15. S. Sabade and M.F. Farona, Polym. Bull., **8**, (1987).
16. C.I. Simionescu, S.V. Dumitrescu, and V. Percec, J. Polym. Sci., Polym. Symp., **64**, 209 (1978).
17. C.I. Simionescu and V. Percec, J. Polym. Sci., Polym. Symp., **67**, 43 (1980).
18. C.I. Simionescu, V. Percec, and S.V. Dumitrescu, J. Polym. Sci., Part A., **15**, 2497 (1977).
19. a) P. Ehrlich, R.J. Kern, E.D. Pieron, and T. Provder, J. Polym. Sci., Polym. Lett., **5**, 911 (1967).
20. M.I. Kushnerev, G.I. Bautzisev, M.I. Cerkashin, and A.A. Berlin, Izv. Akad. Nauk. SSSR, Ser. Chim., **10**, 2291 (1971).
21. H. Shirakawa, T.Ito, and S. Ikeda, Polym. J., **4**, 460 (1973).
22. D. L. Trumbo and C.S. Marvel, J. Polym. Sci., Part A., **25**, 1027 (1987).
23. V.S. Kambara and H. Noguchi, Makromol. Chem., **73**, 244 (1964).

SYNTHESIS, CHARACTERIZATION AND POLYMERIZATION OF ETHYLENE USING A MAGNESIUM CHLORIDE SUPPORTED BIS(CYCLOPENTADIENYL)TITANIUM(IV) DICHLORIDE CATALYST SYSTEM

1.0 INTRODUCTION TO METALLOCENE BASED CATALYST SYSTEMS

Metallocenes of Group - IV A transition metals with ligands such as cyclopentadienyl, indenyl, fluorenyl etc., in combination with alkylaluminum compounds, have been known in the literature as inefficient catalyst systems for ethylene polymerization. Breslow was the first to study cyclopentadienyl titanium(IV) compounds, which are soluble in hydrocarbon solvents, together with alkylaluminums to polymerize ethylene[1]. He found that the polymerization reaction is short lived with very fast decay of catalyst activity. Subsequently, Chien established by kinetic studies that the tetravalent titanium center is the active species in such catalysts which undergoes a rapid bimolecular decay process by disproportionation to generate inactive trivalent species[2]. Analogous zirconium(IV) compounds showed no polymerization activity[3]. The basic kinetic and mechanistic features of these homogeneous metallocenes catalysts in combination with alkylaluminums have been reviewed adequately in the literature[4]. The distinguishing features of these catalysts are rapid decay as well as loss of activity within minutes of start of polymerization reaction and at temperatures higher than 30°C.

Subsequently, considerable efforts were invested in developing practical homogeneous catalysts for olefin polymerization. Various approaches were adopted of which the most successful are:

1.1 Modification of Alkylaluminums

1.2 Development of Alkylaluminum Free Catalyst Systems

1.3 Heterogenization of Homogeneous Metallocene Based Catalyst Systems

1.1 Modification of Alkylaluminums

Addition of trace quantities of water or oxygen to homogeneous metallocene catalysts resulted in a sudden increase in activity of ethylene polymerization and corresponding decrease in the process leading to catalyst deactivation[5]. (Table 8.1). The polymerization activity increases as the mole percent of water is increased up to

Table 8.1: Effect of Water on Polymerization of Ethylene Using the Catalyst System $(Cp_2)_2Ti(CH_3)_2/Al(CH_3)_3$[3]

[Titanium] (mol L^{-1})	[Aluminum] (mol L^{-1})	[Water] (mol L^{-1})	Activity (gPE/gTi/h)
7.1×10^{-4}	1.5×10^{-2}	---	0
7.1×10^{-4}	1.5×10^{-2}	$< 10^{-5}$	15
7.1×10^{-4}	1.5×10^{-2}	4.6×10^{-3}	800
7.1×10^{-5}	1.5×10^{-2}	7.4×10^{-3}	7,000
7.1×10^{-4}	1.5×10^{-2}	9.1×10^{-3}	900

certain level, followed by a decrease in activity. Similar studies with zirconium based metallocenes also showed a dramatic improvement in the polymerization activity. Based on these observations, Sinn and Kaminsky concluded a that the product of controlled hydrolysis of trialkylaluminum, namely oligomeric aluminoxanes, is the active cocatalyst in these polymerizations[6]. The reaction of water with trimethylaluminum eliminates methane and forms an aluminum - oxygen - aluminum oligomeric structure called methylaluminoxanes (MAO). Use of MAO instead of alkylaluminums with metallocenes results in high catalyst activities (1 - 10 X 10^3 kg/mole metal/ h). Such catalysts have been well reviewed in recent literature[7].

The salient features of these catalysts are high catalyst activities even at relatively high temperatures, ability to synthesize high molecular weight polymers with narrow molecular weight distribution due to homogeneous nature of catalyst and ability to copolymerize ethylene with higher alpha olefins with control of insertion sequences. Furthermore, MAO, when used in conjunction with stereorigid metallocenes, promote stereospecific polymerization of α - olefins[8].

However, inspite of these significant merits, the metallocene - MAO catalyst suffer from some major disadvantages. They are:

i) Use of expensive and structurally uncharacterized MAO as cocatalyst

ii) Need to use very high Al/Zr ratios, requiring steps such as catalyst destruction, removal etc., to destroy the excess cocatalyst

iii) Inability to adopt the catalyst system to gas phase polymerization process.

Nevertheless, commercial application of such catalysts to polyolefin process are now emerging.

1.2 Development of Aluminum Free Metallocene Based Catalyst Systems

Extensive research on metallocene /AlR_3 or metallocene/MAO catalyst has implicated the unsaturated "Cation - like " metal center [Cp_2MR^+] as the active centre during polymerization[9]. Even though indirect studies such electrodialysis[10], chemical trapping[11], XPS[12],NMR[13] and theoretical studies[14] have supported this hypothesis, only recently success been achieved in isolation and characterization of such aluminum free cationic metallocene compounds. A new class of activators based on boranes are shown to polymerize ethylene and propylene in presence of metallocenes with activities comparable with zirconocene/MAO catalyst system(Table - II). Thus, group IV metallocene dialkyls (Cp_2ZrR_2), upon reaction with a stiochiometric (or near stiochiometric) amount of an activator such as $[C_6H_5(CH_3)_2NH^+][B(C_6F_5)_3]$[15], $[(C_6H_5)_3C^+][B(C_6H_5)_4]$[16] or $[B(C_6H_5)_3]$[17], generate stable, isolable, and crystallographically characterizable highly active "cation - like " zirconium polymerization catalysts.

These studies have demonstrated the role of Lewis acid (activator) in the stoichiometric conversion of a zirconocene dialkyl to the corresponding "cation - like" zirconocene monoalkyl. This monoalkyl species is observed to show high polymerization activity (Table 8.2).

In another approach, "cation - like" metallocenes complexed with strong Lewis bases such as THF, CH_3CN have been isolated[18]. These cation - like complexes have been reported to show olefin polymerization. The cationic $Cp_2Zr(R)(L)^+$ complexes (L = THF, CH_3CN) are formed in high yields by the reaction of neutral dialkyl complexes $Cp_2Zr(R)_2$ with $Ag(BPh)_4$ in CH_3CN or with $Cp_2Fe(BPh)_4$ in a variety of solvents. These reactions are believed to proceed by one electron oxidation d^o $Cp_2Zr(R)_2$ which occurs with loss of $R^{\cdot}$radical and formation of $Cp_2Zr(R)^+(L)$. The anions such as BPh_4,PF_6^- $AlCl_4^-$ coordinate strongly or react with $Cp_2Zr(R)^+(L)$ cations to form adducts of the type $[Cp_2Zr(R)(THF)][BPh_4]$. These discrete base coordinated adducts polymerize ethylene at a very slow rate due to the presence of a Lewis base (Table 8.2).

Even though the above studies were aimed towards an understanding of the basic structure of the active catalytic center, they do provide a hope that a practical catalyst free of MAO and capable of yielding high catalyst activities are feasible in near future.

Table 8.2: Efficiency of Ethylene and Propylene Polymerization Using Metallocene - Aluminum Free Catalyst System

Catalyst	Cocatalyst	Monomer	Polymerization Conditions	Activity (Kg/mole metal/h)	Features	Reference
$Cp_2Zr(CH_3)_2$	$B(C_6F_5)_3$	Ethylene	Pressure : 1 kg/cm^2, Temp., : 25°C, Time : 40-150 sec.	450	Very linear, $\bar{M}_w$: 124000, $\bar{M}_n$: 61200	17(b)
$Cp_2Zr(CH_3)_2$	$B(C_6F_5)_3$	Propylene	Pressure : 1-5 kg/cm^2, Temp., : 25°C, Time : 0.5 hours.	4.3	$\bar{M}_w$: 15600 $\bar{M}_n$: 3000	17(b)
$(Cp')_2Zr(CH_3)_2$	$[Bu_3NH]\ [B(C_6H_4R)_4]$	Ethylene	Pressure : 6 kg/cm^2, Temp., : 80°C, Time : --.	375	---	15(a)
$(Cp')_2Zr(CH_3)_2$	$C_2B_9H_{13}$	Ethylene	Pressure : 16.3 kg/cm^2, Temp., : 40°C, Time : --.	265	---	15(a)
$C_2H_4[Ind]_2ZrMe_2$	$[PhNMe_2H]\ [BPh_4]$	Propylene	Pressure : 6 kg/cm^2, Temp., : 15°C Time : 1.9 hours.	12.97	$\bar{M}_n$: 25,500, $\bar{M}_w$: 45,600 $\bar{M}$.W.D.:1.8 T_m:142°C	17(c)
$C_2H_4[IndH_4]_2ZrMe_2$	$[PhNMe_2H]\ [BPh_4]$	Propylene	Pressure : 6 kg/cm^2, Temp., : 15°C Time : 2.6 hours.	19.0	$\bar{M}_n$: 10,900 $\bar{M}_w$: 28,600 $\bar{M}$.W.D.: 2.6 T_m: 143_oC	17(c)
$Cp_2ZrMe(THF)^+$	$B(Ph)_4$	Ethylene	Pressure : 1-4 kg/cm^2, Temp., : 25°C, Time : ---.	12	---	18

1.3 Heterogenization of Homogeneous Metallocene Based Catalyst Systems

Relatively little interest is evident in the literature on supported metallocene based catalyst systems. Slotfeldt - Ellingsen and co-workers were the first to use heterogenized cyclopentadienyl titanium (IV) dichloride (Cp_2TiCl_2) as an ethylene polymerization catalyst[19]. The recent successes in homogeneous metallocene based catalysts have generated a renewed interest in the area of heterogeneous metallocene catalysts for olefin polymerization studies. This is evident from the recent patent and published literature. The patent literature available to date is summarized in Table 8.3. It can be observed that adsorption of an appropriate metallocene compound, with or without an alkylaluminum on silica, alumina, magnesium chloride or other high surface area supports, is the commonly adopted synthetic route in the heterogenization process. Thus, the olefin polymerization efficiency of these catalysts have been studied with alkylaluminums or aluminoxanes. However, the published literature has used only the techniques of physical mixing of the support and metallocene for heterogenization. We shall briefly discuss herein the synthesis, characterization and polymerization studies of such supported metallocene catalysts under two sub sections, namely,

1.3.1 Synthesis and Characterization of Supported Heterogeneous Metallocene Catalysts

1.3.2 Polymerization Behaviour of Supported Metallocene Catalysts

1.3.1 Synthesis and Characterization of Supported Heterogeneous Metallocene Catalysts

Magnesium chloride, alumina, silica and trialkylaluminum or aluminoxane pretreated silica or alumina are reported as supports for the synthesis of supported metallocene catalysts. Physical mixing of support and metallocene is the only preparative route employed to synthesize these catalysts. No detailed characterization studies have been performed during the synthesis of these catalysts (Table 8.4).

Kaminaka and Soga were the first to screen systematically the efficiency of different supports by preparing supported $Et[IndH_4]_2ZrCl_2$ catalyst towards propylene polymerization[20]. These catalyst were prepared by physical mixing route as shown

Table 8.3: Recent Patent Literature on Heterogeneous Metallocene Catalysts

Patent Number	Chem. Abstr. No	Name of Company	Monomer	Catalyst Composition	Features
EP 435, 514	115: 160013c	BP Chemicals Ltd.	Ethylene	Magnesium chloride, diisoamyl ether, zirconocene and methylaluminoxane.	Yield : 100 Kg/Zr/h M.W.D. : 2.3.
EP 436, 326	115: 72464v	BP Chemicals Ltd.	Ethylene	Dibutyl magnesium, t-butyl chloride, diisoamylether, zirconocene and methylaluminoxane.	Yield : 100 Kg/g Zr/h, Density : 0.947 g/cm^3 M.W.D. : 2.2
US 506, 500	115: 30117d	Exxon	Ethylene	Silica, triisobutylaluminum, trimethylaluminum and di(n-butylcyclopentadienyl) zirconium dichloride.	Yield : 0.1 kg/g Zr/h,
PCT Int.Appl. WO. 89 09, 237	112: 99482z	Exxon	Ethylene and Butene-1	Aqueous silica gel, zirconocene, trimethylaluminum	Density : 0.936 g/cm^3 MFI : 1.7 g/m.

Table 8.3: Recent Patent Literature on Heterogeneous Metallocene Catalysts

Patent Number	Chem. Abstr. No	Name of Company	Monomer	Catalyst Composition	Features
EP 439,964	115:208861g	Mitsui Petrochemicals	Ethylene and 4-methyl pentene-1	Magnesium chloride, zirconocene, titanium tetrachloride, and diethylaluminum chloride	MFI : 0.49 g/10 m, Density : 0.914 g/cm^3 M.W.D. : 10.9
EP 442,725	115: 233129g	Mitsui Petrochemicals	Ethylene	Silica, trimethylaluminum, triisobutylaluminum and bis(methylcyclopentadienyl) zirconium dichloride.	No Data Provided
EP 516,458	118: 169792a	Mitsui Petrochemicals	Ethylene and Butene-1	Silica, methylaluminoxane, bis(butylcyclopentadienyl) zirconium dichloride and triisobutylaluminum.	No Data Provided.
JP 03,131,608	115: 23316m	Mitsui Petrochemicals	Propylene	Silica, isopropyl(cyclopentadienyl 1-1-fluorenyl) zirconium dichloride and methylaluminoxane.	[η] : 1.18 dl/g, isotacticity : 94.8 %.

Table 8.3: Recent Patent Literature on Heterogeneous Metallocene Catalysts

Patent Number	Chem. Abstr. No	Name of Company	Monomer	Catalyst Composition	Features
JP 04,11,604	116: 174977c	Mitsui Petrochemicals	Ethylene	Methylaluminoxane activated silica, zirconocene and triisobutylaluminum	Yield : 1.8 kg/ g Zr/h
JP 03,234,709	116: 60207w	Mitsui Petrochemicals	Ethylene	Silica, zirconocene and tributylammonium tetra(p-tolyl) borate.	Yield : 1.2 Kg/ g Zr/h Density : 0.39 g/cm^3 M.W.D. : 2.7.
JP 04,08,704	116: 195079b	Mitsui Petrochemicals	Ethylene	Silica, bis(η - butylcyclopentadienyl) zirconium dichloride and triisobutylaluminum.	Yield : ---, Density : 0.4 g/cm^3, MFI : 0.539 g/10 min.
JP 01,217,013	116: 56981u	Mitsui Petrochemicals	Propylene	Magnesium chloride, ethyl benzoate, trimethylaluminum, bis(methylcyclopentadienyl) titanium dichloride and methylaluminoxane	Yield : 0.96 Kg/ g Ti/h, Isotacticity : 90.6 %.
JP 04,224,808	118: 148230a	Mitsui Petrochemicals	Propylene	Methylaluminoxane, hydrated magnesium chloride isopropylidene cylcopentadienyl-1-fluorenyl zirconium dichloride and methylaluminoxane.	Syndiotacticiy : 79.8 %.

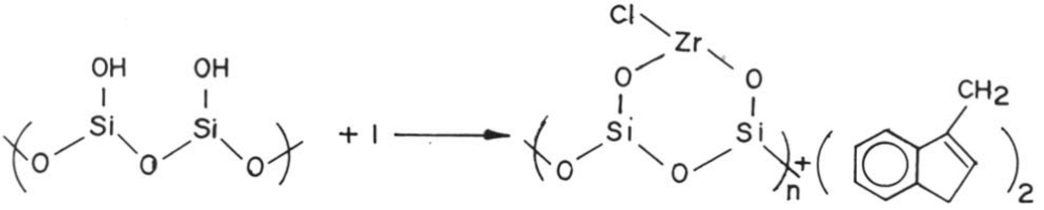
Table 8.4: Synthesis and Characterization Features of Supported Metallocene Catalysts

Support	Catalyst	Preparation	Characterization	Reference
SiO_2	Cp_2TiCl_2	Method - A: [Et_nAlCl_{3-n}(n:1-3)] --->[heptane solution of Et_nAlCl_{3-n}] --->[silica] --->[2h,room temp.,] --->[washing with heptane] --->[dried silica] ---> [SiO_2.Et_nAlCl_{3-n} (Al:2.5, 1.4, & 2.8 Al per m^2 Silica for n: 1, 2 & 3 respectively)]---> [$CpTiCl_2$ (Al/Ti>1)] --->[a solid slurry]. Method - B: [Cp_2TiCl_2] --->[dissolve in methylene chloride] ---->[silica gel] ---> [boiling temp., 8 days] ---> [extraction, 2 days] ---> [drying, 4 days] --->[solid catlyst] (Ti: 0.5 g/m^2 silica & Cl/Ti: 1.0.	ESR studies were performed. It was shown heterogneization leads to splitting of ESR signal of Ti^{+3} signal. Further, Al.Ti complexes bound to the silica surface by Si-O-Al bonds were predicted responsible for heterogenization of catalyst	19
$MgCl_2$, Al_2O_3 or SiO_2	*ansa* - $Et[IndH_4]_2ZrCl_2$ or $iPr[Flur][Cp] ZrCl_2$ or $[Cp]_2ZrCl_2$	[Al_2O_3 (20g)] ---> [ground at room temp., with 30 balls (15 of 12 mm and 15 of 9 mm diameter), 48 h] ---> [toluene (15 mL), $Al(CH_3)_3$ or $Al(C_2H_5)_3$] --->[stirred 10 min, room temp.,.] ---> [separated solid & washed with toluene (20mL)] ---> [dried] ---> [solid catalyst].	No characterization except elemental analysis	20,21

Table 8.4: Synthesis and Characterization Features of Supported Metallocene Catalysts

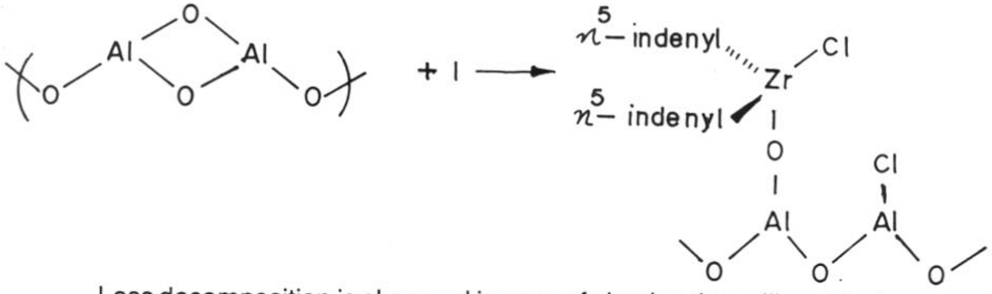
Support	Catalyst	Preparation	Characterization	Reference
SiO_2	*ansa* - Et$[IndH_4]_2$ $ZrCl_2$	[SiO_2 (940mg) in toluene(10mL)] ---> [MAO (22 mmol)] ---> [stirred at room temp., 30 min] ---> [filtered] ---> [washed with toluene (20 mL, 5 times)] ---> [Et$[IndH_4]ZrCl_2$ in toluene (0.1 mmole)] ---> [stirring room temp., 30 min] ---> [filtered, washed with toluene] ---> [solid catalyst].	No characterization except elemental analysis	21(a)
SiO_2	*ansa* - Et$[Ind]_2ZrCl_2$	[Silica (5g)] ---> [heated for 18h at 350°C in argon] ---> [200°C in vacuum for 4h] ---> [suspended in MAO solution (1.74gof MAO in 100 mL of toluene)] ---> [50°C, 4h] ---> [filtered, washed to MAO/SiO_2 (Al:8.57%)] ---> [Et$[IndH_4]ZrCl_2$ (0.1g in 100 mL toluene)] ---> [stirred over night, washed 5 times with toluene, dried in vaccum] ---> [supported SiO_2/Zr catalyst]	No characterization except elemental analysis	23
SiO_2 or Al_2O_3 [Fully hydroxylated, partially dehydroxylated and dehydroxylated supports]	*Ansa* - Et$[Ind]_2ZrCl_2$ or *ansa* - Et$[IndH_4]_2ZrCl_2$	[*ansa* - Et$[Ind]_2ZrCl_2$ (160 mg)] ---> [toluene(112mL)] ---> [partially dehydroxylated alumina(1.3g)] ---> [stirred in dark for 24h at room temp.,] ---> [filtered, washed with toluene] ---> [dried] ---> [a solid catalyst]	No characterization except elemental analysis	22

schematically in Scheme 8.1. It is observed that pretreated silica or alumina are the suitable supports based on the efficiency of olefin polymerization[21]. Recently, Collins et. Al., have studied the interactions between silica and alumina and metallocenes { Et[IndH$_4$]$_2$ZrCl$_2$ (1) and Et[IndH$_4$]$_2$ZrCl$_2$ (2)}[22]. It is observed that hydroxyl groups, present on the surface of silica or alumina, play a major role in the formation of complexes. Fully hydroxylated, partially dehydroxylated and dehydroxylated silica and alumina are reacted with 1 & 2. It is observed that compound 1 is adsorbed in significantly higher amounts than compound 2 on all the supports due to the low van der waals surface area of compound 1. Adsorption of 1 is accompanied by significant decomposition on partially dehydroxylated and fully dehydroxylated support. The decomposed product is bis(indenyl) ethane which was confirmed by ^{1}H NMR studies (equation 8.1).



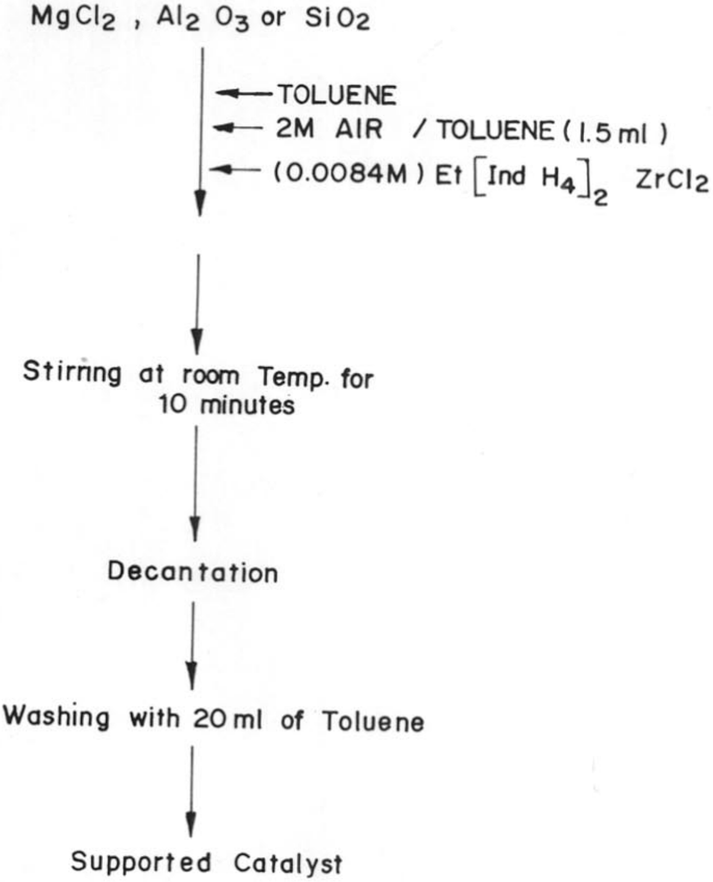
8.1

In case of alumina, there are additional pathways for the metallocene decomposition as the surface is progressively dehydroxylated. It is possible that the high Lewis acidity of alumina facilitates the formation of Al-Cl bonds and Zr-O bonded species when the metallocene compound is adsorbed at these sites as shown in equation 8.2.



8.2

Less decomposition is observed in case of alumina than silica. No decomposition of metallocene is observed with trimethylaluminum pretreated supports. In this case the amount of metallocene adsorbed is very much lower.



Sche.8.1 Soga's Method of Synthesis of Supported Metallocene Catalyst

Independently Chien and He, while studying the polymerization efficiency of methylaluminoxane pretreated silica supported Et[Ind]$_2$ZrCl$_2$ catalyst, have proposed a scheme for the formation of supported catalyst[23](scheme 8.2). It is proposed that MAO reacts with surface hydroxyl present on the silica and forms stable Si - O - Al bonds. These supports, upon reaction with Et[Ind]$_2$ZrCl$_2$, remove a chloride and produce cationic zirconocene methyl species. These ionic species are postulated to be trapped and stabilized as multicoordinate "crown" aluminoxane complex. These complexes are quite stable against dissociation. Further, it is observed that free MAO cannot extract the cationic zirconocene species from the surface of silica.

1.3.2 Polymerization Behaviour of Supported Metallocene Catalysts

Homo and copolymerization studies were performed with magnesium chloride, silica and aluminum supported metallocene catalysts (Table 8.5, 8.6, 8.7). The following features of these catalyst systems emerge from these studies:

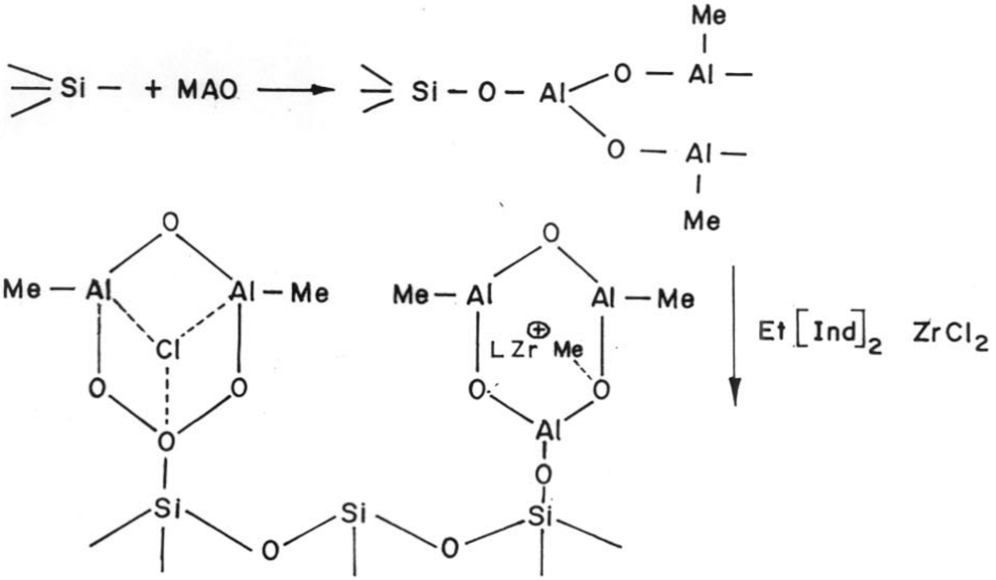
(i) Supported metallocene catalysts showed higher activities and longer life time during polymerization in comparison to unsupported catalysts when used in conjunction with alkylaluminums.

(ii) Broadening of MWD of polyethylene, and comparable activities of ethylene polymerization were observed with silica supported Cp$_2$TiCl$_2$ - Et$_2$AlCl catalyst system when compared with homogeneous Cp$_2$TiCl$_2$ - Et$_2$AlCl catalyst system.

(iii) By screening the different supported catalyst during olefin polymerization, it was concluded that AlR$_3$ or MAO pretreated silica and alumina provide highly active supported catalysts in conjunction with alkylaluminums or MAO.

(iv) Cocatalyst treatment step is necessary to generate active cationic species in all the supported metallocene catalysts.

(v) Iso-, syndio- and atactic polypropylenes are obtained with supported metallocene - alkylaluminum catalyst system. When MAO is used as cocatalyst, the stereoregularity of homogeneous metallocene is not altered upon heterogenization.



Sche.8.2 Chien's Model of Supported *ansa* Zirconocene Catalyst

Table 8.5: Propylene Polymerization Studies Using Magnesium Chloride Supported Metallocene Catalysts[20]

Catalyst System	Polymerization Conditions	Activity, (Kg PP /mole Zr/h/atm)	Features
$MgCl_2/Al(CH_3)_3/Et[IndH_4]_2ZrCl_2$	Pressure : 1 kg/cm^2, Temp., : 40°C, Time : 18 hours.	-	---
$MgCl_2/Al(CH_3)_3/Et[IndH_4]_2ZrCl_2$ - $Al(CH_3)_3$	Pressure : 1 kg/cm^2, Temp., : 40°C, Time : 18 hours.	19.7	$\bar{M}_n$: 1590, MWD: 4.2
$MgCl_2/Al(C_2H_5)_3/Et[IndH_4]_2ZrCl_2$ - $Al(C_2H_5)_3$	Pressure : 1 kg/cm^2, Temp., : 40°C, Time : 18 hours.	8.4	$\bar{M}_n$:2130, MWD:4.8
$MgCl_2/AlMe_3/iPr(Flu)(Cp)ZrCl_2$ - $AlMe_3$	Pressure : 1 kg/cm^2, Temp., : 40°C, Time : 18 hours.	8.4	$\bar{M}_n$:10700,MWD: 3.3, T_m:134°, Syndio:81%..
$MgCl_2/AlMe_3/iPr(Flu)(Cp)ZrCl_2$ - $AlMe_3$	Pressure : 1 kg/cm^2, Temp., : 40°C, Time : 18 hours.	9.6	$\bar{M}_n$:370

Table 8.6: Propylene Polymerization Studies Using Alumina Supported Metallocene Catalysts

Catalyst System	Polymerization Conditions	Activity, (Kg PP /mole Zr/h/atm)	Features	Reference
$Al_2O_3/Al(CH_3)_3/Et[IndH_4]_2ZrCl_2$	Pressure : 1 kg/cm^2, Temp., : 40°C, Time : 18 hours.	18.6	-----	20
$Al_2O_3/Al(CH_3)_3/Et[IndH_4]_2ZrCl_2$ - $Al(CH_3)_3$	Pressure : 1 kg/cm^2, Temp., : 40°C, Time : 18 hours.	14.4	$\bar{M}_n$: 1730, MWD: 2.4	20
$Al_2O_3/Al(C_2H_5)_3/Et[IndH_4]_2ZrCl_2$ - $Al(C_2H_5)_3$	Pressure : 1 kg/cm^2, Temp., : 40°C, Time : 18 hours.	8.8	$\bar{M}_n$:3200, MWD: 2.4	20
$Al_2O_3/AlMe_3/iPr(Flu)(Cp)ZrCl_2$ - $AlMe_3$	Pressure : 1 kg/cm^2, Temp., : 40°C, Time : 18 hours.	9.2	$\bar{M}_n$:4600,MWD:2.0 Syndiotacticity: 86%.	21(b)
$Al_2O_3/AlMe_3/Cp_2ZrCl_2$	Pressure : 1 kg/cm^2, Temp., : 40°C, Time : 18 hours.	2.6	$\bar{M}_n$: 370	21(b)
100% Hydroxylated alumina / $Et[Ind]_2ZrCl_2$ - MAO	Pressure : 5 kg/cm^2, Temp., : 25 - 40°C, Time : 1.5 hours.	Zero activity	-----	22
Dehydroxylated alumina /$Et[Ind]_2ZrCl_2$ - MAO	Pressure : 5 kg/cm^2, Temp., : 25 - 40°C, Time : 1.5 hours.	0.08	-----	22
$Al(Me)_3$/partially dehydroxylated alumina/$Et[Ind]_2ZrCl_2$ - MAO	Pressure : 5 kg/cm^2, Temp., : 300 °C, Time : 1.5 hours.	0.6	T_m:143°C, $\bar{M}_n$:19500, MWD:1.61, Cryst:45.8 %, Syndiotacticity:89.7%	22

Table 8.7: Propylene Polymerization Studies Using the Silica Supported Metallocene Catalysts

Catalyst System	Polymerization Conditions	Activity, (kg PP /mole Zr/h/atm)	Features	Reference
$SiO_2/Al(CH_3)_3/Et[IndH_4]_2ZrCl_2$-$Al(CH_3)_3$	Pressure : 1 kg/cm², Temp., : 40°C, Time : 18 hours.	No activity	---	20
$MAO/SiO_2/Et[IndH_4]_2ZrCl_2$	Pressure : 1 kg/cm², Temp., : 40°C, Time : 18 hours.	No activity	---	21(a)
$MAO/SiO_2/Et[IndH_4]_2ZrCl_2$-$Al(CH_3)_3$	Pressure : 1 kg/cm², Temp., : 40°C, Time : 18 hours.	20.6	T_m:139°C, $\bar{M}_n$:6400, MWD:2.3, II :89 %.	21(a)
$MAO/SiO_2/Et[IndH_4]_2ZrCl_2$-$Al(C_2H_5)_3$	Pressure : 1 kg/cm², Temp., : 40°C, Time : 1 hour.	43.3	T_m:140°C, $\bar{M}_n$:5300, MWD: 2.5, II :90 %.	21(a)
$MAO/SiO_2/Et[IndH_4]_2ZrCl_2$-$Al(i\text{-}C_4H_9)_3$	Pressure : 1 kg/cm², Temp., : 40°C, Time : 1 hour.	8.3	T_m:127°C, $\bar{M}_n$:4000, MWD:2.5, II :85 %.	21(b)
$(C_2H_5)_nAlCl_{3-n}$[**]/SiO_2/Cp_2TiCl_2-$(C_2H_5)_nAlCl_{3-n}$	Pressure : 1 kg/cm², Temp., : 20°C, Time : 0.5 hours.	Activity value is not reported	No data is reported but brodening of MWD by GPC observed	19
$MAO/SiO_2/Et[Ind]_2ZrCl_2$	Pressure : 0.9 kg/cm², Temp., : 50°C, Time : 2 hours.	No activity[*]	----	21(b)
$MAO/SiO_2/Et[Ind]_2ZrCl_2$-MAO	Pressure : 0.9 kg/cm², Temp., : 50°C, Time : 2 hours.	Very low activity[*]	Product is a gel. $[\eta]$: 0.88 dl/g	21(b)

[*] Printing Confusion in the Reported Data.

[**] Ethylene is used as monomer.

Table 8.7: Propylene Polymerization Studies Using Silica Supported Metallocene Catalysts

Catalyst System	Polymerization Conditions	Activity, kg P /mole Zr/h/atm	Features	Reference
$MAO/SiO_2/Et[Ind]_2ZrCl_2$ - $(i\text{-}C_4H_9)_3Al$	Pressure : 0.7 kg/cm^2, Temp., : 50°C, Time : 2 hours.	8700*	Product is Gel. $[\eta]$: 1.08 dl/g.	21(b)
$MAO/SiO_2/Et[Ind]_2ZrCl_2$ - $(i\text{-}C_4H_9)_3Al$	Pressure : 0.7 kg/cm^2, Temp., : 50°C, Time : 2 hours.	910*	Product is Solid, $[\eta]$: 1.05 dl/g.	21(b)
$MAO/SiO_2/Et[Ind]_2ZrCl_2$ - $(CH_3)_3Al$	Pressure : 0.7 kg/cm^2, Temp., : 50°C, Time : 2 hours.	960*	Product is Solid, $[\eta]$: 1.26 dl/g	21(b)
100% Hydroxylated silica / $Et[Ind]_2ZrCl_2$ - MAO	Pressure : 5 kg/cm^2, Temp., : 25 - 40°C, Time : 1.5 hours.	Zero Activity	------	22
Dehydroxylated silica/ $Et[Ind]_2ZrCl_2$ - MAO	Pressure : 5 kg/cm^2, Temp., : 25 - 40°C, Time :1.5 hours.	0.18	-----	22
$Al(Me)_3$/partially dehydroxylated silica/$Et[Ind]_2ZrCl_2$ - MAO	Pressure : 5 kg/cm^2, Temp., : 25 - 40°C, Time :1.5 hours.	0.66	T_m:143°C, $\bar{M}_n$:19000, MWD:1.68, Cryst:42.3 % Syndiotactcity:89.0%	22
$Al(Me)_3$/partially dehydroxylated silica/$Et[IndH_4]_2ZrCl_2$- MAO	Pressure : 5 kg/cm^2, Temp., : 25 - 40°C, Time :1.5 hours.	1.0	T_m:139°C, $\bar{M}_n$:6800, MWD:2.8, Cryst:37 % Syndiotactcity:91.8%	22

---

* Printing Confusion in the Reported Data.

** Ethylene is used as monomer.

(vi) Copolymerization activities of supported metallocene catalysts are comparable with unsupported metallocene when used with MAO.

(vii) Fully hydroxylated or partially hydroxylated silica supported metallocene catalyst show no activity toward propylene monomer. This is due to the destruction of metallocene upon heterogenization.

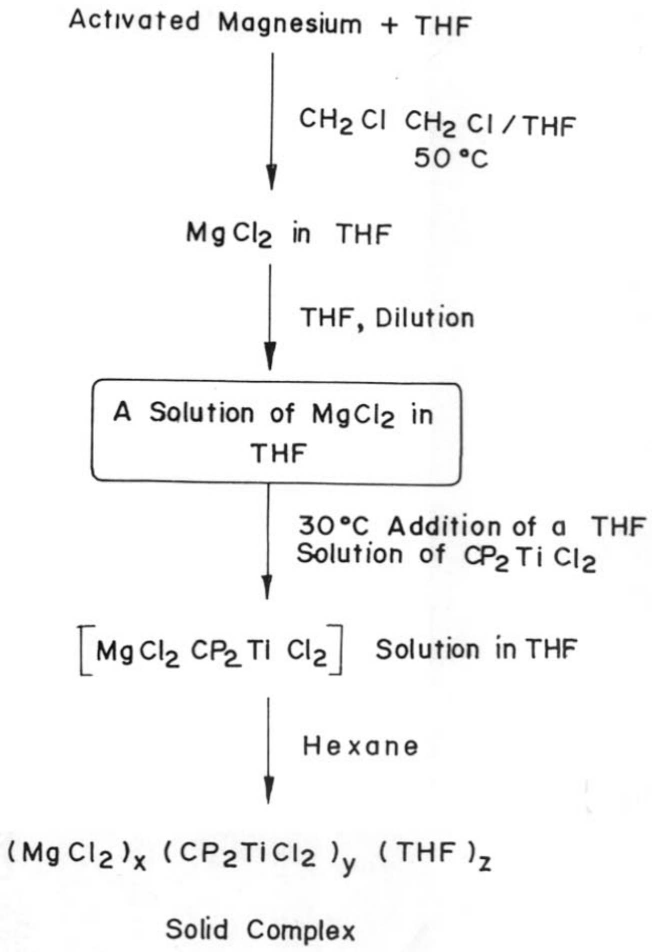
2.0 RESULTS AND DISCUSSION

2.1 Synthesis of Magnesium Chloride Supported Bis(cylcopentadienyl) Titanium (IV) Dichloride Catalysts:

Chemical methods of synthesis of high activity Mg - Ti catalysts based on magnesium chloride and titanium chloride are well known in the literature, However, such methods are not reported for synthesizing heterogeneous supported metallocene catalysts. Recently, Stephan has reported a simple synthetic route for the preparation of bimetallic complexes of magnesium and titanium based on magnesium turnings and cyclopentadienyl/ titanium (IV) dichloride. Upon reacting activated magnesium metal with Cp_2TiCl_2 in THF, complexes of formula $[Cp_2Ti(\mu\text{-}Cl)_2]_2[Mg(THF)_2]$ (I) and $[Cp_2Ti(\mu\text{-}Cl)_2Mg(THF)_2]_2$ (II) were isolated[24]. The single crystal X - ray studies showed that I exists as monoclinic space group and II in tetragonal space group. Further characterization by ESR showed that the titanium in these complexes exists in +3 oxidation state. Thus, it can be inferred that reduction of Cp_2TiCl_2 with magnesium turnings led to the formation of these complexes.

To avoid this reduction process and to synthesize bimetallic complexes useful as catalysts for ethylene polymerization, we explored a simple synthetic route for the preparation of magnesium chloride supported bis(cyclopentadienyl)titanium(IV) dichloride catalyst system (Scheme 8.3).

Thus, solubilization of magnesium turnings was achieved by reaction with 1,2 - dichloroethane in tetrahydrofuran(THF) as described in chapter III. Excess THF was added to obtain a clear solution of $MgCl_2.2THF$. The easy solubility of Cp_2TiCl_2 in THF enabled formation of a homogeneous mixture of Cp_2TiCl_2 and $MgCl_2.THF$ in THF.



Sche.8.3 Synthesis of Supported $MgCl_2.Cp_2TiCl_2$ Catalyst

Addition of known amounts of Cp_2TiCl_2 to THF, yielded a clear red colour solutions which was added to a stock solution of $MgCl_2$ - THF (A & B). Thorough stirring of the mixture at room temperature for three hours yielded a clear homogeneous red color solution (A&B). These solutions upon isolation by precipitation using a nonsolvent yielded a lightish - pink color solid (A&B).

2.2 Characterization of Magnesium Chloride Supported bis[cylcopentadienyl] Titanium (IV) Dichloride Catalysts

Supported heterogeneous Mg - Ti catalysts (A&B) synthesized as above had an empirical formula $MgTi_{0.05}Cl_{2.0}Cp_{0.1}(THF)_{0.5}$ and $MgTi_{0.15}Cl_{2.09}Cp_{0.3}(THF)_{1.2}$ as calculated from elemental analysis. Presence of THF and cyclopentadienyl ligands were confirmed by FT - IR and CP- MAS NMR studies (Figure 8.1 and 8.2). The FT- IR spectrum of the solid catalysts showed distinct bands at 1460 cm^{-1} and 820 cm^{-1}, characteristic of C- C stretching bands of cyclopentadienyl ring[25]. It also showed bands at 1036 cm^{-1} and 888 cm^{-1}, characteristic vibration bands of "THF" bound to the solid surface[26] (Figure 8.1). Further CP - MAS NMR showed a signal at 120.96 ppm corresponding to the cyclopentadienyl ligand attached to titanium, and signals at 25.77 and 68.96 ppm which correspond to the THF moiety present on the solid catalyst (Figure 8.2).

Powder XRD pattern of the Mg - Ti catalyst showed sharp peaks, indicating that the complex is highly crystalline (Figure 8.3). When compared with highly crystalline powder XRD pattern of Cp_2TiCl_2 (Figure 8.4), the XRD of the complex showed the absence of strong reflection at 2θ : 34.4° and a reduction in the intensity of reflection at 2θ : 20°. Further, a new reflection at 2θ: 32° appeared in the Mg - Ti catalysts. This reflection corresponds to that of THF complex of $MgCl_2$. Thermogravimetric analysis of the complex was different from that of $MgCl_2.2THF$ and Cp_2TiCl_2. The complete decomposition of the structure occurred in three stages as shown in Figure 8.5. This indicates that the complex has a deformed structure with moieties filled with THF at different places. The complex showed no ESR signal, indicating that the titanium is in

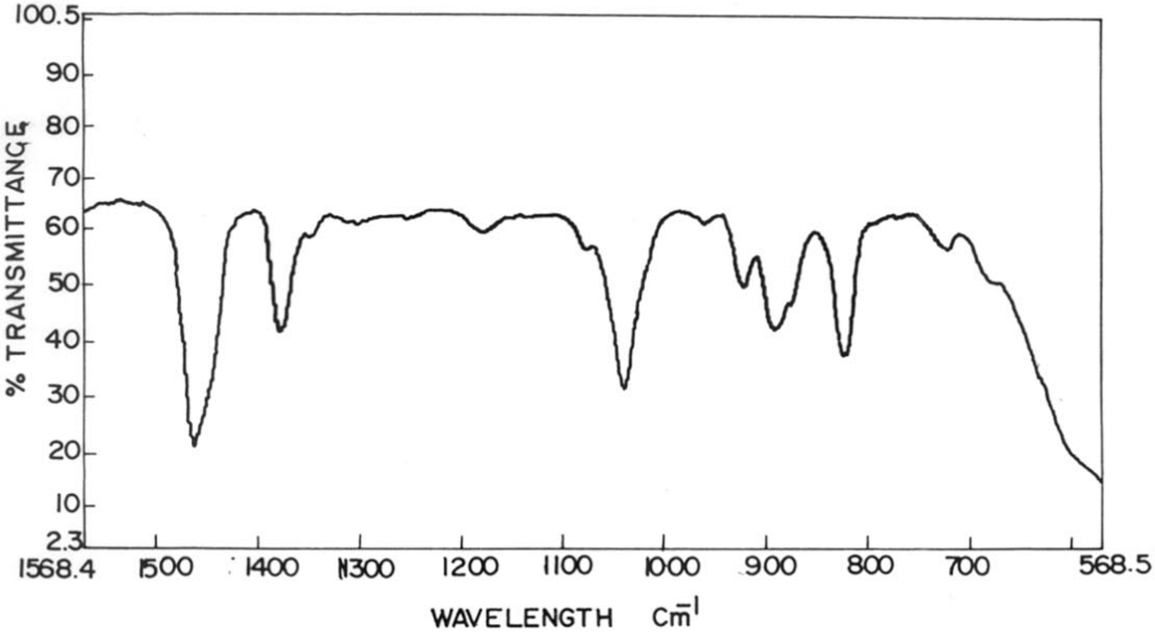


Fig.8.1 FT- IR Spectra of Supported Catalyst

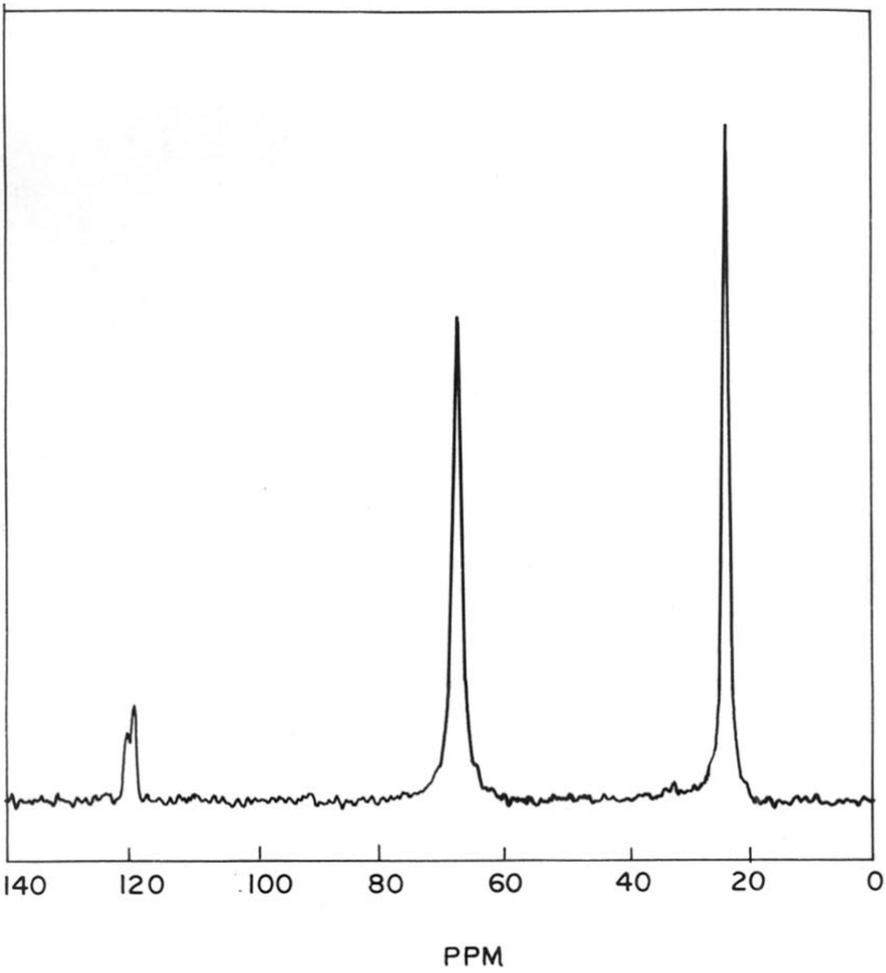


Fig.8.2 CP - MAS Spectra of Supported $Cp_2TiCl_2/MgCl_2$ Catalyst

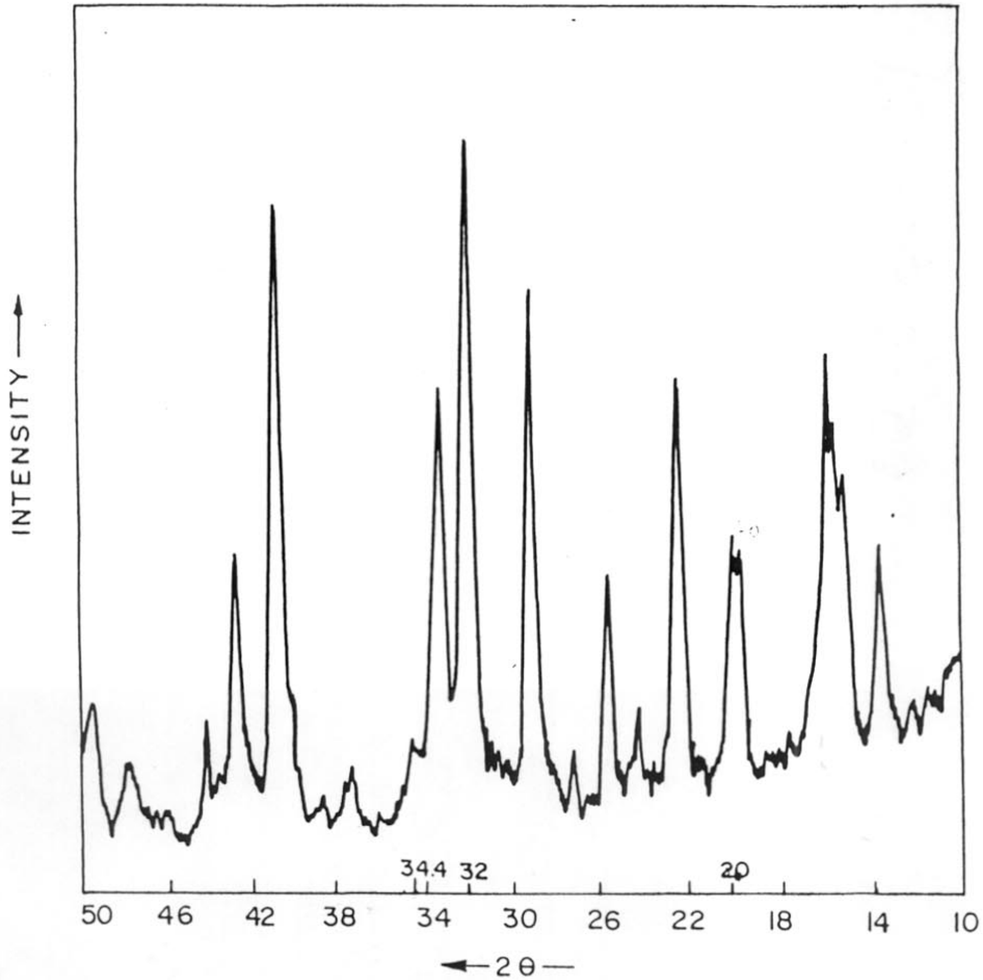


Fig.8.3 X - Ray Diffraction Spectra of Supported Catalyst

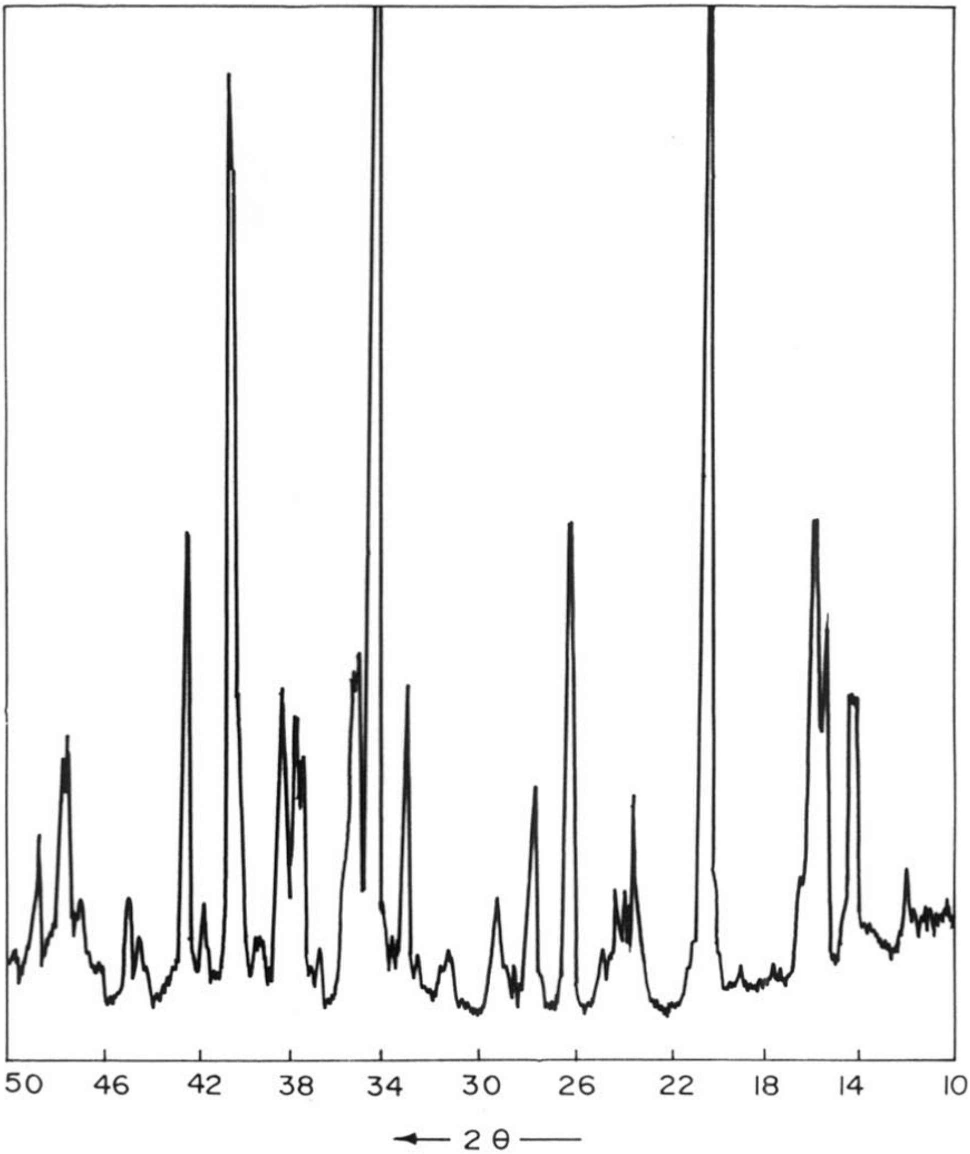


Fig.8.4 X - Ray Diffraction Spectra of Cp_2TiCl_2

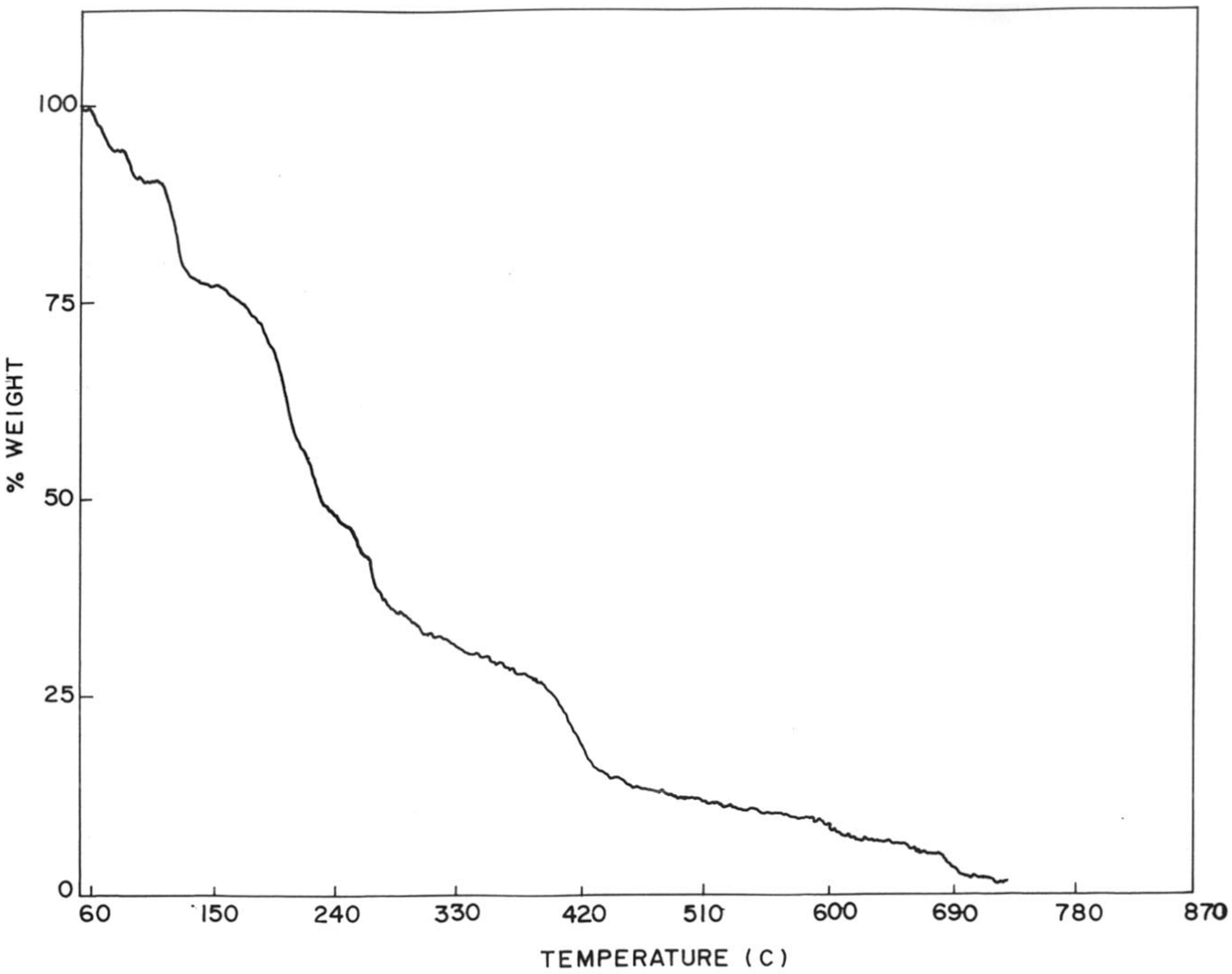


Fig.8.5 Thermogravimetric Analyses of Supported $Cp_2TiCl_2/MgCl_2$ Catalyst

the +4 oxidation state. Upon reduction with TIBAL, the complex showed a spectrum with fine splittings, in contrast to a sharp signal peak at g : 1.98 for Cp_2TiCl_2 (Figure 8.6). This indicates that the metallocene is heterogenized on the support.

2.3 Polymerization of Ethylene Using Magnesium Chloride Supported Bis(cyclopentadienyl) Titanium(IV) Dichloride Catalysts

Ethylene was polymerized using the two heterogeneous Mg -Ti catalysts (A&B). The study was aimed to provide an understanding of the effect of heterogenization of homogeneous metallocene catalysts on polymerization of ethylene.

it is well known that the homogeneous titanocene catalyst in conjunction with trialkylaluminum is inactive for ethylene polymerization. However, with dialkylaluminum halides ethylene can be polymerized using titanocenes. The active species, however is short lived and ethylene absorption ceases with in ten minutes of mixing of catalyst and cocatalyst components. In contrast, magnesium chloride supported titanocene catalyst show significant polymerization activity even with TIBAL and a three fold increase in activity with DEAC. The catalyst system was observed to show steady state build up type kinetic behaviour over a period of 60 minutes (Table 8.8). Increase in molecular weight, catalyst activity and rate of polymerization can be observed with supported catalyst when compared to homogeneous catalyst.

Effect of Al/Ti ratio at constant temperature on ethylene polymerization was studied using the heterogeneous magnesium chloride supported catalysts (A&B) in conjunction with triisobutylaluminum (Table 8.9). It was observed that the catalyst activity increased with Al/Ti ratio. Lower activities were observed with catalysts containing lower content of titanium. Polymer molecular weights increased with increasing Al/Ti ratios and titanium content in the catalyst. Rate of polymerization increased with increasing Al/Ti ratios. Increase of temperature at constant Al/Ti ratio showed a decrease in conversion and activities of ethylene polymerization (Table 8.10). Catalyst with high titanium content

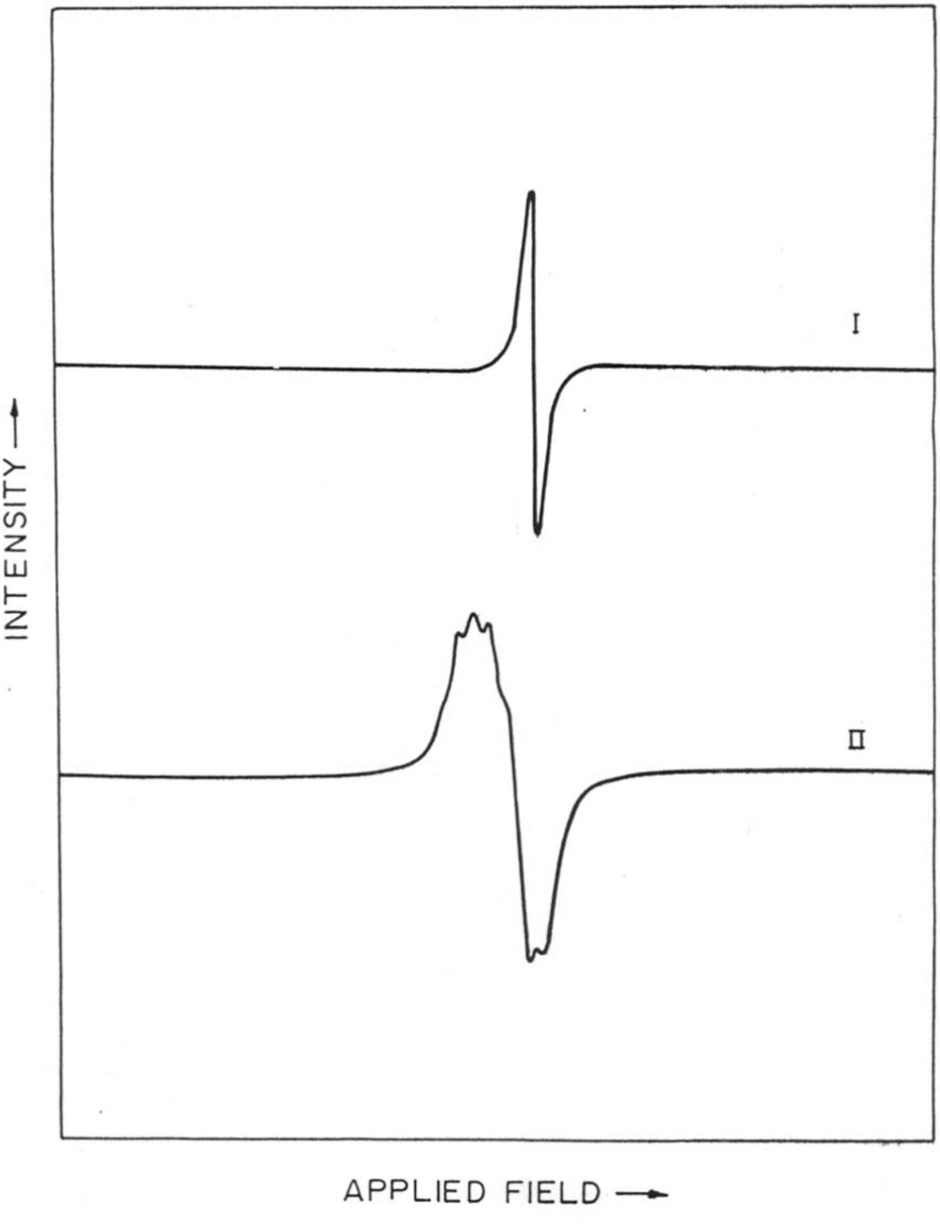


Fig. 8.6 : ESR Spectra of (I) Cp_2TiCl_2-TIBAL (II) Cp_2TiCl_2/$MgCl_2$-TIBAL in Xylene at 25°C Ti : 1.25×10^{-4} mole, Al/Ti = 50

Table 8.8: Ethylene polymerization with Unsupported and Supported Titanocene Catalysts[a]

S.No.	Catalyst	Cocatalyst	Time (h)	PE (g)	Conv., (%)	R_p (M sec^{-1})	Activity (KgPE/moleTi)	$[\eta]^c$ (dl/g)
1	Cp_2TiCl_2	TIBAL	60	NO POLYMERIZATION ACTIVITY				
2[b]	Cp_2TiCl_2	DEAC	10	0.30	100	1.37	0.9	0.3
3	Cat -A	TIBAL	60	0.48	100	0.39	2.4	3.5
4	Cat -B	TIBAL	60	0.61	100	1.69	6.4	0.9

a) All polymerizations were performed at 40° in xylene medium at Al/Ti: 50 at a total pressure of one atmosphere. b) Ethylene absorption ceased after a lapse of ten minutes. c) Intrinsic viscositites were determined in o-dichlorobenzene at 135°C.

showed more severe drop in activity and conversion compared to catalyst with lower titanium content. The molecular weights of polyethylene was also reduced at higher temperatures.

A brief kinetic study was performed using the supported metallocene catalysts at one atmosphere pressure of ethylene. The millimoles of ethylene uptake was plotted against the time to calculate the rate of ethylene polymerization from the initial slope of the linear graphs. The rates thus obtained are shown in Tables 8.7 to 8.10. It is observed that the initial rates of polymerization(R_p) increased with increase of temperature and Al/Ti. Further, the rates were lower for the catalyst containing lower Ti content. A plot of R_p versus Al/Ti ratio shows that at higher Al/Ti ratio, a decay type kinetic curve is observed in the system (Figure 8.7). The deactivation process is slow at lower Al/Ti ratios and with lower Ti content. The activation energy of these catalysts as calculated from the Arrhenius plot (Figure 8.8) is 7.0 kcal/mole K, indicating the heterogeneous nature of catalyst system.

These results imply that magnesium chloride confers unusual stability to an otherwise unstable active centre. Dramatic enhancement in catalytic activity has been reported for $Cp'_2Th(CH_3)_2/MgCl_2$ for propylene hydrogenation[27]. Based on ^{13}C CP - MAS NMR study of $Cp'_2Th(CH_3)_2/MgCl_2$, it was concluded that the active center was a "cation-like" complex formed by the transfer of methide anion from the actinide center to the Lewis acidic sites on the surface of $MgCl_2$[28]. A similar mechanism can be proposed to explain the unusual activity as well as stability of the $Cp_2TiCl_2/MgCl_2$ - trialkylaluminum catalyst systems for ethylene polymerization. Thus, the active site is a *"cation like"* complex of Cp_2TiR^+ adsorbed on magnesium chloride as shown in the Figure 8.9. It can be observed that the reactive sites are isolated on the support, thereby stabilizing the coordinatively unsaturated monomeric titanium species. Matrix isolation of catalytically active sites in the case of Cp_2TiCl_2 chemically anchored to rigid polymeric support has been shown to be responsible for higher rates of olefin hydrogenation observed with supported Cp_2TiCl_2compared to Cp_2TiCl_2 in solution[29].

Table 8.9: Effect of Al/Ti Ratio on Ethylene Polymerization with Supported Magnesium - Titanium and Triisobutylaluminum Catalyst Systems[a]

S.No.	Ti (Wt.ratio)	Al/Ti	Conversion (%)	R_p (M Sec^{-1})	Activity (Kg/mole Ti)	$[\eta]^b$ (dl/g)
1	3.3	50	95	0.39	2.5	2.6
2	3.3	100	97	0.51	2.5	3.6
3	3.3	200	99	0.68	2.0	4.7
4	1.8	50	99	0.18	0.8	2.2
5	1.8	100	98	0.48	1.0	3.4
6	1.8	200	98	0.61	2.0	4.0

a) All polymerizations were performed at 40°C for 60 min in xylene at a total pressure of one atmosphere.

b) Intrinsic viscosities were determined in o-dichlororbenzene at 135°C.

Table 8.10: Effect of Temperature on Ethylene Polymerization with Supported Magnesium - Titanium and Triisobutylaluminum Catalyst Systems[a]

S.No.	Ti (Wt.ratio)	Temperature (°C)	Conversion (%)	Polyethylene (g)	R_p (M Sec^{-1})	Activity (Kg/mole Ti/h)	$[\eta]^b$ (dl/g)
1	3.3	40	93.6	0.25	0.51	2.5	3.52
2	3.3	60	33.3	0.16	0.76	2	1.37
3	3.3	70	22.2	0.08	1.29	0.7	0.79
4	1.8	40	99.0	0.18	0.18	0.7	3.42
5	1.8	60	60.0	0.08	0.19	0.5	2.20
6	1.8	70	50.0	0.07	0.33	0.4	1.40

a) All polymerizations were performed at Al/Ti =100 ratio in xylene for 60min at a total pressure of one atmosphere.

b) Intrinsic viscositites were determined in o-dichlorobenzene at 135°C.

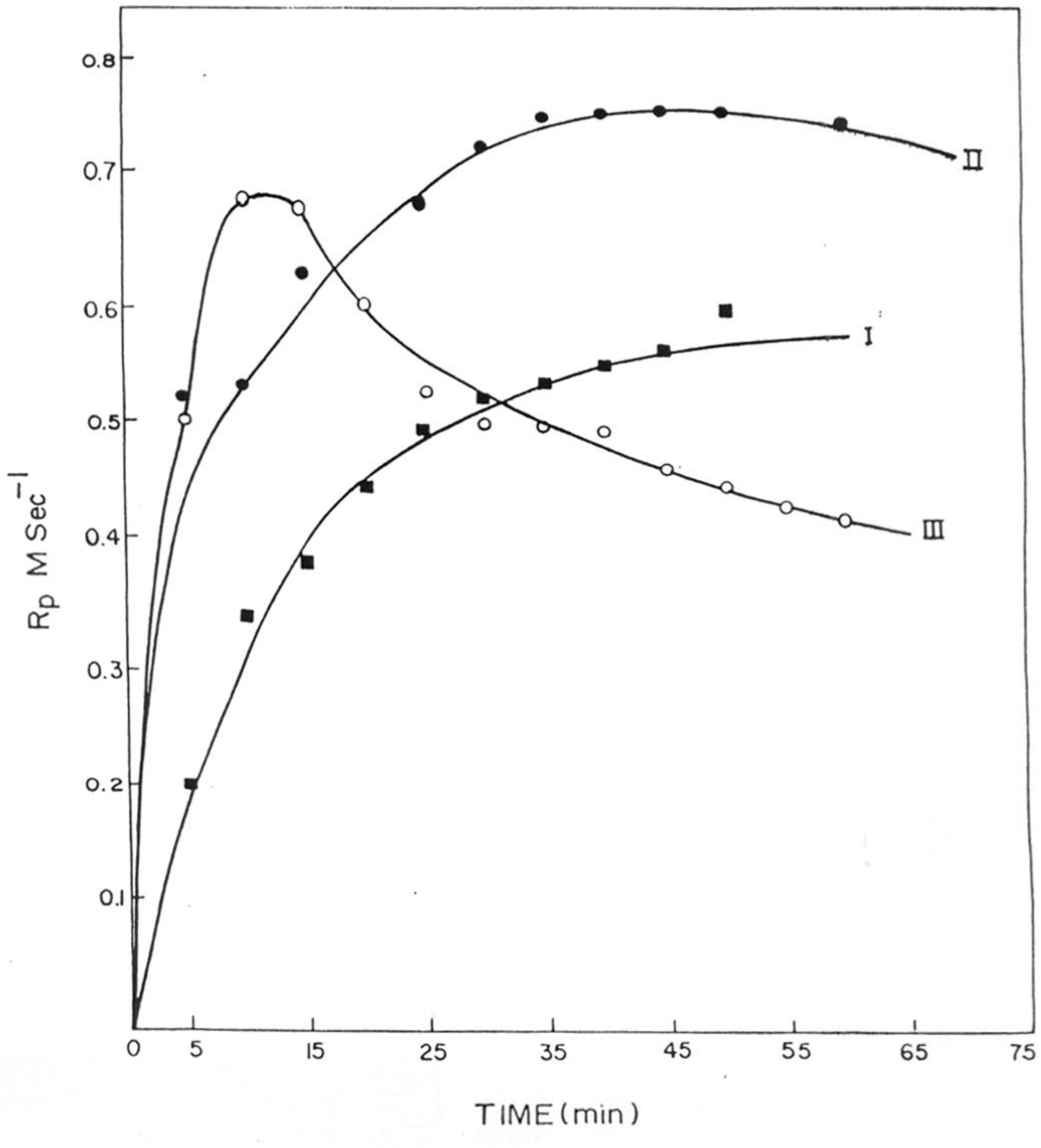


Fig.8.7 Plot of Rate of Polymerization Vs Time for Supported Catalyst at 40°C: (I) Al/Ti = 50, (II) Al/Ti = 100 and (III) = 200.

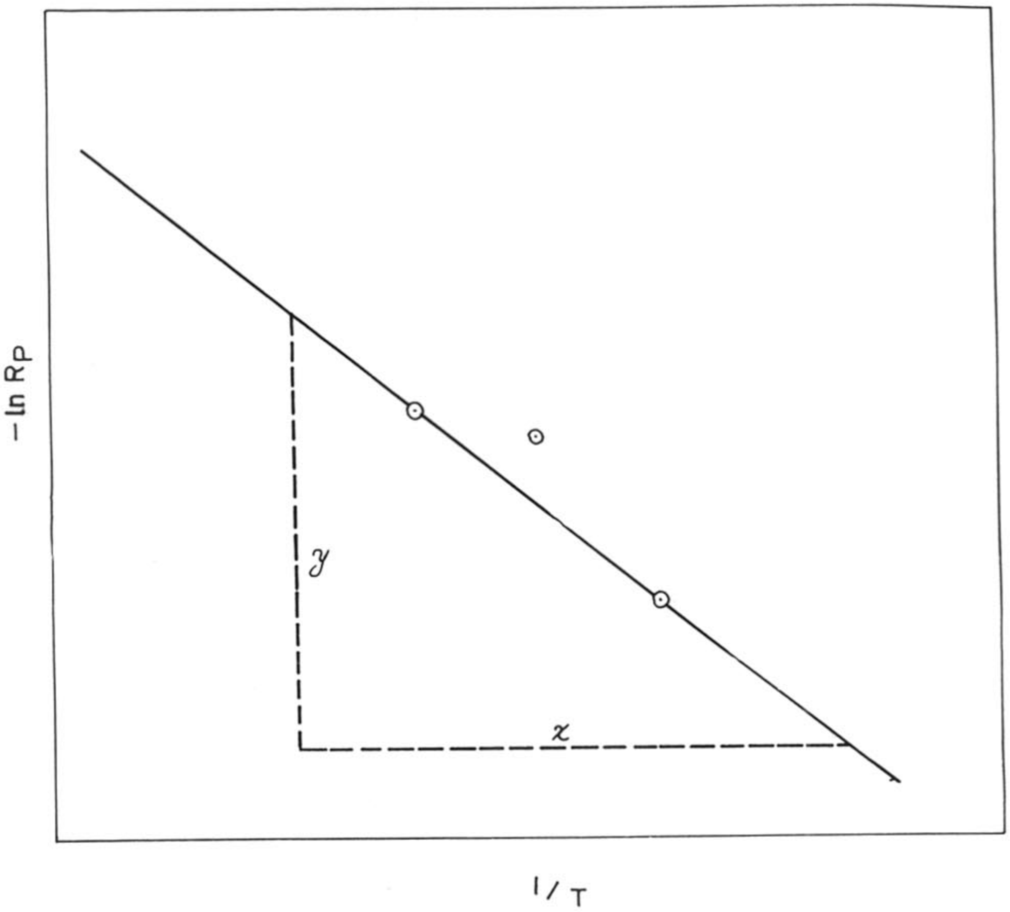


Fig.8.8 Activation Energy Plot

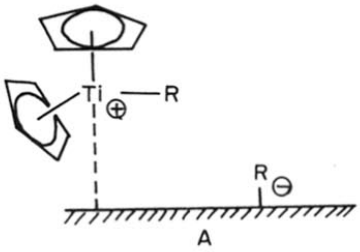


Fig.8.9 Structure of "***Cation Like***" Active Species

3.0 CONCLUSION

A simple and efficient synthetic route for the heterogenization of homogeneous metallocene catalysts on $MgCl_2$ was demonstrated. The method yielded a bimetallic complex of magnesium chloride and bis(cyclopentadienyl) titanium(IV) dichloride with THF. Characterization of the complex confirmed the presence of THF and cyclopentadienyl ligand on the solid catalyst. The complex showed appreciable polymerization activity towards ethylene in conjunction with trialkylaluminum. The unusual stability of the active centre has been explained on the basis of formation of a ***"cation like"*** structure for the active species on the support.

4.0 EXPERIMENTAL SECTION

All manipulations involving air sensitive compounds were performed either inside a Labconco Model 50004 inert atmosphere glove box continuously purged with high purity N_2 (<5ppm moisture) generated using N_2 generator (Spantech, Model NG 300-1, England) or under a positive pressure of high purity N_2 using standard bench top inert atmosphere techniques.

4.1 Materials

Bis(cyclopentadienyl)titanium(IV)dichloride (Cp_2TiCl_2) (Aldrich, USA), triisobutlyaluminum(TIBAL) and diethylaluminumchloride (DEAC) (Schering A.G., Germany) were used as received. Magnesium turnings (Loba Chemicals Ltd., Bombay), 1,2 dichloroethane, THF, hexane, Xylene (S.D. Fine Chemical, Bombay) were purified as described in earlier chapters. Polymer grade ethylene was obtained from the Maharastra Gas Cracker complex of Indian Petrochemical Corporation Limited at Nagothane, India. It had a moisture content of <4ppm (Shaw model SHA-TR moisture Analyzer) and oxygen content of <3ppm (Braun Oxygen analyzer).

4.2 Synthesis of Catalysts

Two supported Cp_2TiCl_2 catalysts having 1.8% and 3.3 percent by weight of titanium, were used in this study (Catalyst A and B respectively). A typical procedure for synthesis of catalyst is as follows.

A three neck round bottom flask equipped with a magnetic stirring bar, N_2 - inlet, addition funnel and a reflux condenser was flame dried and cooled under N_2 atmosphere. Iodine(5mg) activated magnesium turnings(0.4g) were placed in the flask and THF(30mL) was added. The slurry was stirred for 30 minutes at 40°C. A mixture of 1,2 - dichloroethane and THF (1:!) (40mL) was transferred into the addition funnel using a cannula and added dropwise at 40 - 50°C. It was observed that all the Mg turnings slowly dissolved in THF with the formation of a clear solution. Steady evolution of ethylene gas was observed indicating decomposition of the intermediate, β - chloroethylmagnesium chloride to a complex of $MgCl_2$ and THF and its dissolution in THF. The clear solution was further diluted by addition of 20mL of THF, separated from traces of unreacted magnesium and transferred into another flame dried three neck flask equipped with a magnetic stirring bar, N_2 - inlet, addition funnel and a septum.

Cp_2TiCl_2(3.36mmole) was dissolved in THF in a flame dried round bottom flask. The clear dark red color solution was then transferred into an addition funnel using a cannula. The Cp_2TiCl_2 - THF solution was added dropwise into the $MgCl_2$ - THF solution. It was observed that no separation of layers or any solid material occurred. This red color solution was then added slowly to 300mL of dry hexane. A solid precipitate having a whitish pink color separated out. The solid was dried under vacuum at 40°C. The dried solid was transferred into vials and stored in the glove box. Yield: 4.2g

4.3 Polymerization

Ethylene polymerization was performed in a stirred glass reactor at one atmosphere pressure in xylene using about 100 to 120mg of solid catalyst in conjunction with cocatalyst. The reactor assembly and manner of conducting polymerization are described in chapter V.

4.3 Analysis

Titanium estimation was performed using Hitachi model 220 UV - Visible spectrophotometer. Magnesium estimation was performed by EDTA titration as described in chapter 4. Similarly, chlorine estimation was performed at neutral P^H by following the method described in chapter 3. ESR spectra was run on a Brucker model ER - 200D ESR spectrometer at room temperature(9.72GHz). Powder XRD was recorded on a Phillips PW 1730 spectrometer using nickel filtered $CuK\alpha$ radiation. FT - IR spectra was run on a Perkin - Elmer 16PC Ft - IR in Nujol mull using NaCl cells(1600 - 400 Cm^{-1}). Viscosities of the polymer samples were determined using an Ubbelohde viscometer in o - dichlorobenzene as solvent at 135°C.

5.0 REFERENCES

1. a) D.S.Breslow and N.R. Newburg, J. Am. Chem. Soc., **79**, 5072 (1957).
   b) D.S. Breslow and N.R. Newburg, J. Am. Chem. Soc., **81**, 81 (1959).

2. J.C.W. Chien, J. Am. Chem. Soc., **81**, 86 (1959).

3. W. Kaminsky, in "Transition Metal Catalyzed Polymerization " (Ed. R.P. Quirk) MMI, Press, Harwood Academic Publishers, New York , Vol. 4, p225 (1983).

4. K.H. Reichert, in "Transition Metal Catalyzed Polymerization of Alkenes and Dienes" (Ed. R.P. Quirk), Harwood Academic Publications, USA, Part B, p465 (1981).

5. K.H. Reichert and K.R. Meyer, Makromol. Chem., **169**, 163 (1973).

6. H. Sinn and W. Kaminsky, Adv. Organomet. Chem, **18**, 99 (1980).

7. a) R.P. Quirk, in "Transition Metal Catalyzed polymerizations" Cambridge University Press, Cambridge (1988).
   b) W. Kaminsky and H. Sinn, in "Transition Metals and Organometallics as Catalysts for Olefin Polymerization" Springer, New York, (1988).

8. J.A. Ewen, L. Haspeslagh, J.L. Atwood and H. Zhang., J. Am. Chem. Soc., **109**, 6544 (1987).

9. a) F.S. Dyachkovskii, A.K. Shilov, and A.Y. Shilov, J. Polym. Sci., Part C., **16**, 2333 (1967).

10. J.J. Eisch, A.M. Piotrowski, S.K. Brownstein, E.J. Gabe, and F.L. Lew, J. Am. Chem. Soc., **107**, 7219 (1985).

11. P.J. Watson, and G.W. Parshall, Acc. Chem. Res., **18**, 51 (1985).

12 P.G. Gassman and M.R. Callstrom, J. Am. Chem. Soc., **109**, 7875 (1987).

13. C. Sishta, R.M. Hathorn, and T.J. Marks, J. Am. Chem. Soc., **114**, 1112 (1992).

14. a) C.A. Jolly and D.S. Marynick , J. Am. Chem. Soc., **111**, 7968 (1989).
    b) J.w. Lauher and R. Hoffmann, J. Am. Chem. Soc., **98**, 1729 (1976).

15. a) G.G. Hlatky, H.W. Turner, and R.R. Eckmann, J. Am. Chem. Soc., **111**, 2728 (1989)
    b) H.A. Turner, EP 277004 (1988).

16. a) J.A. Ewen and M.J. Elder, EP 426638 (1991),
    b) J.C.W. Chien, W.M. Tsai, and M.D. Rausch, J. Am. Chem. Soc., **113**, 8570 (1991).

17. a) J.A. Ewen and M.J. Elder, EP 427697 (1991),
    b) X. Yang, C.L. Stern, and T.J. Marks, J. Am. Chem. Soc., **113**, 3623 (1991).
    c) A.D. Horton and J.H.G. Frijns, Angew. Chem. Int. Ed. Engl., **30**, 1152 (1991).

18. R.F. Jordan, J. Chem. Educ., **65**, 285 (1988).

19. D. Slotfeldt-Ellingsen, I.M. Dahl, and O.H. Ellestad, J. Mol. Catal., **9**, 423 (1980).

20. K. Soga and M. Kaminaka, Makromol. Chem. Rapid Commun., **12**, 367 (1992).

21. a) K. Soga and M. Kaminaka, Makromol. Chem. Rapid Commun., **13**, 221 (1992).
b) K. Soga and M. Kaminaka, Polymer, **33**, 1102 (1992).

22. S. Collins, W. M. Kelly, and A. Holden, Macromolecules, **25**, 1780 (1992)

23. J.C.W. Chien and D. He, J. Polym. Sci., Part A., **29**, 1603 (1991).

24. D.W. Stephan, Organometalics, **11**, 996 (1992).

25. H.P. Fritz, Adv. Organometal. Chem., **1**, 262 (1964).

26. K. Handlir, J. Holecek, and Benes, Collect. Czech. Commun., **50**, 2422 (1985).

27. a) T. J. Marks, Acc. Chem. Res., **25**, 57 (1992),
b) R.D. Gillespie, R.L. Burwell Jr, and T.J. Marks, Langmuir, **6**, 1465 (1990).

28. W.C. Finch, R.D. Gillespie, D. Hedden, and T.J. Marks, J. Am. Chem. Soc., **112**, 6221 (1990).

29. R.H. Grubbs, C. Gibbons, T.C. Kroll, W.D. Bonds Jr, and C.H. Brubaker, J. Am. Chem. Soc., **95**, 2373 (1973).

CONCLUSIONS

The research embodied in this Thesis has lead to the following results and conclusions.

1. A novel insitu Grignard decomposition has been discovered for the preparation of magnesium chloride - tetrahydrofuran complex which is crystalline in nature. The reaction is clean and is free of organic byproducts. The $MgCl_2.2THF$ complex can be either isolated as a solid or a THF solution and used for the synthesis of novel $MgCl_2$ supported titanium based homogeneous and heterogeneous catalysts.

2. Using $MgCl_2.2THF$, a xylene soluble Mg - Ti catalyst can be prepared using titanium -n- butoxide (TNB). The hydrocarbon soluble Mg - Ti catalyst stays homogeneous even upon reduction with TIBAL or DEAC.

3. TNB in conjunction with trialkylaluminum is a catalyst for selective dimerization of ethylene to butene-1. However, the xylene soluble Mg - Ti catalyzed polymerization of ethylene yields linear polyethylene in 70-90% conversion. These results show that TNB is converted to a polymerization catalyst in presence of $MgCl_2$. The homogeneous nature of the catalyst is also confirmed by the overall activation energy of polymerization (3 - 4 K Cal mole^{-1}). It is proposed that the ligands of $MgCl_2$ take part in stabilization of the **[Ti - C]** bond thereby increasing the relative rate of propagation over that of chain transfer due to β - hydrogen elimination.

4. The xylene soluble Mg - Ti catalyst also promotes homopolymerization of hexene-1 and octene-1 to high molecular weight poly(α - olefin)s. The significant feature of this catalyst is that it produces relatively polymers with narrow MWD compared to heterogeneous Mg - Ti catalysts. This indicates that the active sites in the soluble Mg - Ti catalysts are homogeneous.

5. The relatively low Lewis acidity of the xylene soluble catalyst makes it very suitable for the synthesis of poly(phenylacetylene)s with higher soluble fraction compared to Ziegler - Natta catalysts hitherto reported. Interestingly, the conversions and configuration obtained using the soluble Mg - Ti catalysts are identical to those reported recently for the metallocene catalyzed polymerizatin of phenylacetylene.

6. A new approach to heterogenize a homogeneous titanocene catalyst has been discovered by exploiting the solubility of $MgCl_2.2THF$ in THF. The titanocene supported magnesium chloride has been completely characterized. This catalyst polymerize ethylene in conjunction with TIBAL with significant activity to high molecular weight polyethylene. In contrast, the titanocene shows no polymerization activity under similar conditions. These observations provide rare insight into the role of $MgCl_2$ in stabilizing the active center by isolating them on a solid matrix thereby preventing rapid deactivation. Heterogenization of metallocene is also evident from the values of the overall activation energy of polymerization (approximately 7 K Cal mole^{-1}).

In conclusion, the results in this Thesis presented testifies to the multifarious role of the familiar $MgCl_2$ support in supported Ziegler - Natta catalyst for the polymerization of unsaturated monomers. They stabilize the active center, alter the ligand environment around titanium, function as a Lewis acid in accepting a ligand from titanium and provide matrix isolation to lower valent titanium species, thus preventing it from undergoing a rapid decay process and consequent deactivation of the catalyst.

APPENDICES

A COMPARATIVE STUDY OF THERMOCHEMICAL REACTION OF ANHYDROUS MAGNESIUM CHLORIDE AND TITANIUM -n- BUTOXIDE AND THE TERAHYDROFURAN COMPLEX OF MAGNESIUM CHLORIDE AND TITANIUM -n- BUTOXIDE

INTRODUCTION

Synthesis, characterization and polymerization efficiency of bimetallic complexes of magnesium and titanium have assumed importance in the last ten years[1,2]. Magnesium chloride, titanium tetrachloride and various donors are normally employed to synthesize these complexes. Thermochemical route is normally adopted to synthesize these bimetallic magnesium - titanium complexes. It is well known that magnesium chloride cannot form a bimetallic complex with titanium tetrachloride in absence of electron donor by thermochemical route[3]· But recently, a different class of titanium compound, namely titanium alkoxides, are shown to form structurally characterizable bimetallic complexes in absence of electron donors[4]. Generally, a large excess of titanium alkoxide is used to solublize magnesium chloride through thermochemical reaction and later the bimetallic complex is isolated.

We undertook a study of a similar thermochemical reaction of titanium -n- butoxide (TNB), with anhydrous magnesium chloride and magnesium chloride-2.tetrahydrofuran(THF) complex. The objective of the study was to examine the extent of fixation of titanium on the two supports, one containing no THF and the other containing THF.

EXPERIMENTAL SECTION

Materials:

Anhydrous magnesium chloride (Toho Titanium Co., Japan, Mg = 25.53%, Cl = 74.36% , Surface area = 86 m^2/g). $MgCl_2$.2THF(Prepared as described in Chapter 3), TNB(Synthochem, India) (purified as described in Chapter 4) were used in this study.

Synthesis of Solid Mg - Ti Complex:

A known amount of anhydrous magnesium chloride or $MgCl_2$.2THF(2 g) was charged into a flame dried three necked round bottom flask inside the glove box. It was later connected to N_2, - inlet, condenser and thermowell. Dry xylene (50mL) and TNB (4g) were added by means of a hypodermic syringes, and stirred at room temperature for half an hour. Subsequently, the reaction mixture was heated to 140°C and xylene allowed to reflux for 12 hours under stirring. The flask was removed and cooled to room temperature. A known amount of dry n-hexane (30 mL) was added and the mixture stirred for one hour. After the solid had settled the top layer was syringed out. This step was repeated and the solid was washed serval times with dry hexane to remove any free TNB as indicated by the absence of color formation with hydrogen peroxide. The solid was filtered and dried for three hours at 40 - 60° under vacuum. The isolated solid was transferred into a bottle in the glove box and analyzed for Mg and Ti.

Analysis:

Magnesium and titanium analysis of solid were determined by EDTA and UV - Spectrophotometric analysis as described in Chapter - 4.

RESULTS AND DISCUSSION

With a given amount of anhydrous magnesium chloride and $MgCl_2.2THF$, the thermochemical reaction of TNB at different concentrations were studied using xylene as the reaction medium. The results are tabulated in Table A-1 and A-2. It was observed that, in case of anhydrous $MgCl_2$, the percentage of fixation of titanium was independent of the concentration of TNB in the reaction medium. However, in case of $MgCl_2.2THF$, the fixation of titanium was dependent on the amount of TNB, solvent and temperature. Titanium fixation increased with the concentration of TNB and amount of solvent.

These results show that, unlike the $MgCl_2$ - $TiCl_4$ system, titanium alkoxides can be supported on anhydrous $MgCl_2$ by a thermochemical route. Presence of THF complexed with $MgCl_2$ renders such fixation more facile. Presumably the coordinatively unsaturated Mg^{+2} sites complexed to THF are made available for Ti^{+4} complexation.

Table A.1: Preparation of Solid Magnesium - Titanium Catalysts from Anhydrous Magnesium Chloride and Titanium -n- Butoxide in Xylene

S.No.	$MgCl_2$ (g)	TNB (g)	Xylene (mL)	%Ti fixation (estimated)	Fraction of Ti incorporated
1	3.0	6.0	30.0	4.2	0.15
2	3.3	3.3	33.0	4.1	0.29
3	3.4	1.2	35.0	1.6	0.35

Conditions: Temp., : 135°C and Time: 8h under N_2 atmosphere

Table A.2: Preparation of Solid Magnesium - Titanium Catalysts from Tetrahydrofuran Adduct of Magnesium Chloride and Titanium -n- Butoxide in Xylene.

S.No.	$MgCl_2.2THF$ (g)	TNB (g)	Xylene (mL)	%Ti fixation (estimated)	Fraction of Ti incorporated
1	2.1	4.0	20	8.8	0.32
2	2.3	2.3	23	6.1	0.44
3	1.9	0.9	19	5.9	0.88
4	2.3	0.6	23	3.7	1.00
5	1.8	3.7	20	7.8	0.22
6	2.3	4.7	48	11.5	0.40
7	2.5	5.0	63	12.6	0.45
8*	1.8	2.0	20	2.3	0.18

Conditions: Temp., : 135°C (* 60°C) and Time: 8h under N_2 atmosphere

REFERENCES

1. F.J. Karol, Catal. Rev. - Sci. Eng., **26(3&4)**, 557 (1984).

2. J.C.W. Chien, in " Catalysis in Polymer Synthesis" (Eds. E.J.Vandengerg and J.C. Salamone) ACS Symposium Series **496**, p 27 (1991).

3. N. Kashiwa, Polym. J., **12**, 603 (1982).

4. a) U. Zucchini and T Dall'Occo, in " Polymer Science Contemporary Themes" [Ed. S. Sivaram] Tata - McGraw - Hill Publ. Co., New Delhi, **1**, 221 (1991)
   b) M.Malpezzi, U.Zucchini and T. Dall'Occo, Inorg. Chem. Act., **180**, 245 (1990).
   c) L. Abis, G. Bacchilega, S. Spera, U. Zucchini, and T. Dall'Occo., Makromol. Chem., **192**, 981 (1991).

SYNTHESIS OF SYNDIOSPECIFIC POLYSTYRENE USING XYLENE SOLUBLE MAGNESIUM - TITANIUM CATALYST SYSTEM

INTRODUCTION

Polystyrene is one of the few polymers which can be synthesized by free radical, anionic and coordination polymerization techniques. The coordination polymerization of styrene with Ziegler - Natta catalysts is known to produce atactic and isotactic polystyrene. Synthesis of syndiotactic polystyrene using Ziegler - Natta catalysts is a recent development which has attracted considerable attention in the literature.

Synthesis and Characterization of Syndiospecific Polystyrene

Syndiospecific polymerization of styrene can be promoted by homogeneous catalytic systems consisting of methylaluminoxane and soluble compounds of titanium or zirconium such as tetrabenzyltitanium, tetrabenzylzirconium, Bis(cyclopentadienyl) titanium trichloride, titanium or zirconium alkoxides[1,2,3] etc., Among them, titanium alkoxides in particular titanium -n- butoxide (TNB), in combination with MAO has been studied extensively as a syndiospecific polymerization catalyst[4]. It is observed that homogeneous medium is a prerequisite for promoting syndiospecific polymerization of styrene. The titanium alkoxide based catalyst systems, in general , have shown low activity (20 - 50 kg/mole Ti/mole styrene/h) and low conversion (2 - 4%)[5]. It has been reported that heterogenization of TNB on anhydrous magnesium chloride gave a catalyst which in conjunction with MAO gave isospecific polymerization of styrene[5]. On the contrary, a homogeneous complex of anhydrous $MgCl_2$ and $Ti(OEt)_4$ polymerized styrene to syndiotactic polystyrene in conjunction with MAO, but with reduced activity and conversions[6] (Table B.1). Dramatic enhancement in catalyst activity with high syndiospecificity can be achieved by using homogeneous monocyclopentadienyl titanium tributoxide in conjunction with MAO[7].

Different analytical techniques such as ^{13}C NMR, ^{1}H NMR, FT - IR, DSC, X - ray analysis and insolubility in methylethyl ketone or acetone are employed to characterize syndiotactic polystyrene in literature. ^{13}C NMR spectrum of syndiotactic polystyrene shows a characteristic chemical shift at δ : 145.13ppm in comparison to a sharp peak at lower magnetic field δ : 146.24 ppm for isotactic polystyrene[8]. Similarly, DSC shows

Table B.1: A Comparative Picture of Syndiospecific Polymerization of Styrene Using Titanium Alkoxides Based Catalyst in Conjuction with Methylaluminoxane.

Catalyst	Conversion (%)	Activity (g PS/molTi/mol M/h X10-3)	Syndiotacticity (%)]	Reference
HOMOGENEOUS				
Ti(OBu)4	2.4	27	83	4
Ti(OEt)4	3.1	20	96	6
CpTi(OBu)3	94.0	3,800	82	7
[Ti2(OEt)8Cl2]Mg2Cl2	1.6	5	95	6
Ti(OBu)4	2.8	29	78	THIS WORK
Soluble Mg-Ti	1.0	9	73	THIS WORK
HETEROGENEOUS				
SiO2/Ti(OBu)4	2.3	8	100	5
Mg(OH)2/Ti(OBu)4	4.4	0.3	100	
MgCl2/Ti(OBu)4	4.4	78	12	5

a T_m of 260 - 270°C for syndiotactic polystyrene[8]. Similarly, FT - IR spectrum also shows marked difference between syndio and isotactic polystyrene[6]. We therefore undertook a brief study of styrene polymerization using xylene soluble Mg - Ti catalyst.

EXPERIMENTAL SECTION

Materials

Methylaluminoxane (Schering Company A.G., Germany) was used as received. It contains 5.8% wt of aluminum with an average molecular weight of 850 in toluene and methyl to aluminum ratio of 1.22. Double distilled styrene was stirred over calcium hydride for 12 hours in inert atmosphere. This was distilled under reduced pressure over CaH_2 before use. Xylene soluble Mg - Ti catalyst was prepared as reported in chapter 4.

Polymerization of Styrene

All polymerizations were performed in 75 mL capacity glass jacketed polymerization cells equipped with a magnetic stirring bar, nitrogen inlet, septum and an outlet. The polymerization temperature was maintained by circulating water using a constant temperature circulating bath. A typical procedure is as follows:

Freshly distilled xylene (30 mL), methylaluminoxane (MAO) (84 moles/liter of Al), xylene soluble Mg - Ti catalyst (0.84 moles/liter of Ti) and styrene (2.9 moles /liter) were added in this order to polymerization cell equipped with magnetic stirring bar, N_2 inlet and a septum. After performing the polymerization at desired temperature for four hours, the reaction was terminated by addition of 10 % of acidified methanol (10mL). Further addition of methanol caused the polymer to precipitate. The polymer thus isolated was filtered and dried in vacuum at 30°C for two hours.

RESULTS AND DISCUSSION

Polymerization of styrene was performed using xylene soluble Mg - Ti catalyst in conjunction with methylaluminoxane (MAO). The results are shown in the Table B.2, B.3 and B.4. For the sake of comparison, styrene polymerization using TNB - MAO was also conducted (Table B.5). All polymers were isolated and were characterized by

Table B.2: Syndiospecific Polymerization of Styrene Using Xylene Mg - Ti Catalyst and Methylaluminoxane: Effect of Cocatalyst[a]

S.No.	[MAO]/Catalyst (moles)	Conversion (%)	Activity (g PS/mol Ti/mol M/h X 10-3)	Syndiotacticity (%)
1.	50	1.0	8.5	73.0
2.	100	2.0	23.9	66.0
3	200	3.0	31.0	65.0

a) Conditions: [Ti]: 0.84M, [M]: 2.9M, Temperature: 75°C, Time: 4h.

Table B.3: Syndiospecific Polymerization of Styrene Using Xylene Mg - Ti Catalyst and Methylaluminoxane: Effect of Temperature

S.No.	Temperature (°C)	Conversion (%)	Activity (g PS/mol Ti/mol M/h X 10-3)	Syndiotacticity (%)
1.	90	2.6	26.4	65.6
2.	75	2.0	22.2	65.9
3	60	2.2	27.8	53.0

Conditions: [Ti]: 0.84M, [MAO/CAT]: 100, [M]: 2.9M.

Table B.4: Syndiospecific Polymerization of Styrene Using Xylene Mg - Ti Catalyst and Methylaluminoxane: Effect of Monomer Concentration.

S.No.	[Monomer] (M)	Conversion (%)	Activity (g PS/mol Ti/mol M/h X 10-3)	Syndiotacticity (%)
1	4.36	2.0	20.3	72.0
2	2.91	2.0	22.2	66.0
3	1.45	1.3	13.6	65.0

Conditions: Al/Ti: 100, Temperature: 75°C, [Ti]: 0.84M, Time: 4h.

Table B.5: Syndiospecific Polymerization of Styrene Using Titanium -n- Butoxide and Methylaluminoxane[a].

S.No.	Temperature (°C)	Conversion (%)	Activity (g PS/mol Ti/mol M/h X 10-3)	Syndiotacticity (%)
1	90	2.7	39.0	70
2.	75	2.8	29.0	73
3	60	0.5	15.0	56

a) Conditions:Al/Ti: 50, [M]: 3.27M, [Ti]: 0.48M, Time: 4h.

extraction in boiling methylethylketone and DSC melting point. All polymers showed a T_m of 260 - 270°C. The results indicate that activity and conversions are reduced in presence of magnesium chloride. However, syndiospecificity did not change. The effect of monomer and cocatalyst concentration and temperature on styrene polymerization showed that at higher monomer concentration and at higher temperature syndiospecificity is higher. Similarly, the syndiospecificity was higher at lower catalyst concentration.

Thus, homogeneous Mg - Ti catalysts promote syndiospecific polymerization of styrene whereas the heterogeneous Mg - Ti catalysts promote isospecific polymerization.

REFERENCES

1. a) N. Ishihara, M. Kuramoto, and M. Uoi, EP. 210615 (1987).
   b) N. Ishihara, T. Seimiya, M. Kuramoto, and M. Uei, Macromolecules, **19**, 2464 (1986).
2. A. Grassi, C. Pellecchia, P. Longo, and A. Zambelli, Gazz. Chim. Ital., **19**, 2465 (1987).
3. C. Pellecchi, P. Longo, A. Grassi, P. Ammendola, and M. Zambelli, Makromol. Chem. Rapid Commun., **8**, 277 (1984).
4. L. Oliva, C. Pellecchia, P. Cinquinam, and A. Zambelli, Macromolecules, **22**, 1642 (1989).
5. K. Soga, and H. Nakatani, Macromolecules, **23**, 957 (1990).
6. T. Dall'Occo, F. Saartori, G. Vecellio, and U. Zucchini, Makromol. Chem., **194**, 151 (1993).
7. J.C.W. Chien and Z. Salajka, J. Polym. Sci., Part A., **29**, 1253 (1991).
8. A. Grassi, P. Longo, A. Proto and A. Zambelli, Macromolecules, **22**, 104 (1989).

SYNTHESIS OF ESTERS OF CARBOXYLIC ACIDS FROM ALKYL OR ARYL HALIDES

INTRODUCTION

Synthesis of carboxylic acid esters from alkyl or aryl halides generally requires two steps, namely carboxylation of the Grignard reagent followed by esterification with alcohols. We have found that under controlled experimental conditions Grignard reagents undergo facile reaction with dialkyl and diaryl carbonate in tetrahydrofuran , to yield in a single step, carboxylic acid esters in good yields. The reaction is very selective in the sense that no ketone or alcohol is detectable.

There is a growing interest in the application of dialkylcarbonates in synthetic organic chemistry. They are useful alkylating agents[1] (replacement for toxic dimethyl sulfate) and convenient substitute for phosgene[2] (highly toxic, undesirable by products such as hydrogen chloride). However, but for a solitary reference[3], no reaction of dialkyl or diaryl carbonate with Grignard reagent have reported in the prior literature. It has been reported that the reaction of three moles of ethyl magnesium bromide with diethyl carbonate led to triethyl carbinol.

The reaction of Grignard reagent with carbonates is general and occurs with aryl, arylakyl and alkyl Grignards. Dialkyl, diaryl and cyclic carbonates can be used resulting in alkyl, aryl or hydroxyalkyl esters (Table C.1). The reverse addition of Grignard to the carbonate was found necessary for obtaining the esters in high selectivities.

RMgBr + R'O-C-OR' -------> R-C-OR'

From a viewpoint of simple operation, good yields, high product purities and easy availability of reagents, the present reaction may provide a useful method for the synthesis of carboxylic acid esters in one step from the corresponding halides.

EXPERIMENTAL SECTION

General Procedure

In a two necked round bottom flask equipped with an addition funnel and a N_2 inlet was placed 3.4 mL (38 mmoles) of dimethyl carbonate in 10 mL of dry THF. Phenylmagnesium bromide (19 mmoles) in 40 mL of dry THF was added drop wise under agitation to dimethyl carbonate at 0 - 5°C. The reaction mixture was maintained

Table C.1: Preparation of Carboxylic Acid Esters from Alkyl or Aryl Halides

R	R'	Yield[a] (%)	BP(°C)[b]/mmHg	Lit[c]. data	IR (neat)[d] μ - (cm^{-1})	^1H NMR ($CDCl_3$)[e]
C_6H_5-	CH_3	87	195/760	199.5	1710(C=O); 1600;1450 (C-O)	3.7 (δ,3H);7.6 (δ,5H)
p-$CH_3C_6H_5$-	CH_3	85	110/15	113/15	1710 (C=O); 1600; 1440 (C-O)	2.1 (δ, 3H); 3.7(δ -3H); 7.2 (δ, 5H)
C_6H_5-CH_2-	CH_3	80	135/30	220/760	1740 (C=O); 1600; 1500 (C-O)	3.5 (δ - , 3H); 3.6 (δ, 2H); 7.2 (m, 5H)
C_4H_9	CH_3	80	125/760	127.3/760	1745 (C=O); 1430, 1260 (C-O)	0.9 - 2 (m, 4H); 2.3 (t, 2H); 7.5 (m,5H)
C_6H_5	CH_2-CH_2-OH	88	145/760	--	1820 (C=O); 1740; 1600(C-O); 3400(OH)	3.6 (t, 2H); 4.3 (t, 2H); 7.5 (m, 5H)
C_2H_5	C_6H_5	80	135/760	--	1750 (C=O); 1610;1500 (C-O)	1.2 (t, 3H); 2.5 (q, 2H); 7.5 (m, 5H)

a) Isolated yield based on RX; b) Uncorrected boiling points; c) CRC Hand Book of Chemistry and Physics, 61st Edition, 1980 - 81; d) Recorded on a Perkin Elmer IR Spectrophotometer and e)Recorded on a Bruker WH 90 MHZ NMR spectrophotometer.

at 10°C for one hour followed by one hour at 25 - 26°C. The reaction mixture is then poured into aqueous dilute hydrochloric acid and extracted by pet ether. The extract is dried over anhydrous sodium sulphate and the solvent is evaporated. The product is distilled to yield 2.3g (87%) of methyl benzoate.

REFERENCES

1. M. Lissel, A. R. Rohani-Dezfuli, and G. Vogt, J. Chem. Research (s), 312 (1989); F. Merger, F. Towae, and L. Schroff, Ger. Offen. 2,729,031 (1979); CA 90: 137482m.
2. G. Illuminati, R. Ugo, and T. Tesei, Ger. Offen. 2,528,412 (1976).
3. Reagents for Organic Synthesis, L. F. Fieser and M. Fieser, Vol.1, John Wiley & Sons, New York, p.420 (1967).

SYNOPSIS

INTRODUCTION

Magnesium chloride supported titanium compounds form the basis of the successful second and third generation " Ziegler - Natta " catalysts for the polymerization of ethylene and higher α - olefins. High activity, stereo- and regioselectivity, control of morphology and elimination of deashing steps are the salient features of these new generation catalysts. The scientific and industrial importance of this class of catalysts can be evidenced by a large volume of published and patented literature during the last thirty years.

The most well studied Mg - Ti catalyst systems are based on supporting Ti^{+3} halides on activated magnesium chloride as supports. The activation of magnesium chloride is performed either by physical milling or chemical treatment. Fixation of titanium on magnesium is generally performed by cogrinding or liquid treatment. Distinct changes in the physical state of magnesium chloride such as increase in surface area and porosity accompany such treatment. Literature in this area has been exhaustively reviewed in recent years[1,2].

Inspite of extensive literature, many aspects of catalyst preparation and its relationship to polymer properties are still not well understood. The continuing goals of these investigations are to improve the catalyst efficacy, realize better understanding of nature of active centers and to design new and novel catalysts for imparting specific properties to polymers. The key to tailoring of properties of polymers essentially rests with the " designing of catalysts".

OBJECTIVE OF PRESENT INVESTIGATION

The objectives of the present investigation are to:

(a) examine routes to prepare active support such as magnesium chloride at temperatures below 100°C. The aim is to synthesize and characterize tetrahydrofuran adducts of magnesium chloride by a Grignard decomposition route;

(b) examine the use of titanium alkoxides as components of high efficiency Mg - Ti catalysts for the polymerization of unsaturated monomers. It is well known that titanium alkoxides, in particular, titanium -n -butoxide(TNB) do not polymerize ethylene, or higher α - olefins[3,4]. It has been reported that cogrinding $MgCl_2$ - TNB (Ti 2 - 3%) results in a catalyst which shows activity for ethylene or higher α - olefin polymerization[5,6]. Independently, Soga et al., observed that a solution of $MgCl_2$ - 2-ethylhexanol in conjunction with TNB and diethylaluminumchloride polymerizes propylene with a steady state kinetics[7]. This feature is unusual for propylene polymerization by Mg - Ti catalysts which generally show a decay type kinetics. These results raise serious questions about the role of support (magnesium chloride) in determining the activity and kinetic behavior of Mg - Ti catalysts. Direct characterization of Mg - Ti catalysts for the purpose of elucidating the role of support has been complicated by their heterogeneous multicomponent composition and the low concentration of active sites on the support. It has been generally assumed that the support plays the role of an inert high surface area carrier in Ziegler - Natta catalyst systems. Hence one of the objectives of the present investigation is to synthesize and characterize aromatic hydrocarbon soluble Mg - Ti compounds using well characterized tetrahydrofuran adduct of magnesium chloride and TNB by thermochemical reaction and their evaluation as catalysts for the polymerization of ethylene, hexene-1, octene-1, decene-1 and phenylacetylene;

(c) examine routes to heterogenize a homogeneous metallocene catalyst system and study its polymerization behavior towards ethylene polymerization. Homogeneous metallocene catalysts in combination with aluminumalkyls form inefficient and short lived catalysts due to rapid decay of active tetravalent titanium species to inactive trivalent species[8,9]. Recently, silica, magnesium chloride and alumina have been studied as supports to heterogenize homogeneous metallocene catalysts[10,11]. Methylaluminoxane pretreated silica is found to be a better support[12]. Hence, it was proposed to examine the activity of *insitu* synthesized magnesium chloride as a support of bis(cyclopentadienyl)titanium(IV) dichloride towards ethylene polymerization.

These studies were undertaken with a view to elucidate the role of inorganic support on the kinetics, stability of active centers and mechanism of Ziegler - Natta polymerization of ethylene and higher α - olefins.

OUTLINE OF THESIS

The present thesis entitled **"NOVEL MAGNESIUM - TITANIUM CATALYST SYSTEMS FOR POLYMERIZATION OF UNSATURATED MONOMERS"** is divided into nine chapters.

CHAPTER I

This chapter provides a historical background to the Ziegler - Natta catalyst systems and a detailed literature pertaining to the magnesium - titanium catalyst systems and their applications to olefin polymerization.

CHAPTER II

The objective and scope of the present investigation is described in this chapter.

CHAPTER III

This chapter deals with a new and general method of synthesis of $MgCl_2.2THF$ using a Grignard decomposition route as shown below

$$ClCH_2\text{--}CH_2Cl + Mg(I_2 \text{ activated}) \text{ ----------->} MgCl_2.2THF + C_2H_4$$

The advantages of this new synthetic route are highlighted. The $MgCl_2.2THF$ obtained has been characterized by using spectroscopic and other analytical techniques. Additional activation techniques have been studied to improve the properties of the support.

CHAPTER IV

In this chapter the chemical reaction of $MgCl_2.2THF$ and $MgCl_2$(anhydrous) with TNB in xylene medium is described . $TiCl_4$ cannot be supported on magnesium chloride(anhydrous) by a purely chemical process. However, using $MgCl_2.2THF$, TNB could be chemically fixed on the $MgCl_2$. Further it is shown that adsorption of Ti is dependent on the concentration of TNB, solvent and temperature. This study lead to a novel method of synthesis of a soluble Mg - Ti catalyst capable of imparting unique properties to different polymers which are explained in detail in subsequent chapters.

CHAPTER V

It is well known that TNB promotes selective dimerization of ethylene to butene-1 in conjunction with aluminumalkyls[3]. However, it was found that soluble $MgCl_2$.TNB complex can polymerize ethylene in conjunction with aluminumalkyls. This indicates that $MgCl_2$ plays subtle and significant role in changing the ligand environment around titanium, thereby, converting a dimerization active center to a polymerization active center.

The kinetics of ethylene polymerization was carried out with the soluble Mg- Ti catalyst. Experimental setup to study kinetics of ethylene polymerization in slurry medium is described in this chapter. Effect of different cocatalysts, namely, triisobutylaluminum, diethylaluminumchloride, triethylaluminum and trioctylaluminum in conjunction with the soluble Mg - Ti catalyst on ethylene polymerization was explored. Effect of Al/Ti ratio and temperature on the two catalyst systems i.e., soluble Mg - Ti/DEAC and soluble Mg -Ti /TIBAL was studied. This study indicates an activation energy of 3 - 4 kcalmole^{-1} for the soluble Mg - Ti catalyst which is similar to homogeneous Group IV metallocene - methylaluminoxane catalyst system[13].

The synthesized polyethylenes were characterized by GPC, FT -IR, NMR, DSC, Powder XRD and intrinsic viscosity techniques.

CHAPTER VI

Titanium alkoxides are inefficient catalysts in conjunction with aluminumalkyls for the polymerization of higher α-olefins[4]. However, it is observed that soluble Mg - Ti catalyst described in chapter IV is active and produces high molecular weight amorphous and relatively narrow molecular weight distribution polymers of higher α - olefins. The salient features of these higher poly(α - olefin)s are highlighted in this chapter with a brief comparison with high molecular weight amorphous polymers of higher α - olefins obtained using heterogeneous Mg - Ti catalyst. The efficacy of the soluble Mg - Ti catalyst in conjunction with diethyaluminumchloride was screened towards higher α - olefins, namely, hexene-1, octene-1, and decene-1. Bulk and solution polymerization techniques were adopted. Effect of absolute [Ti], temperature and Al/Ti ratios on polymerization activity was studied.

Poly (α - olefin)s were characterized by GPC, NMR, FT -IR, TGA and intrinsic viscosity techniques.

CHAPTER VII

This chapter describes the results of polymerization of phenylacetylene with soluble Mg - Ti catalyst. In general, Ziegler type catalysts promote undesirable reactions such as dimerization, crosslinking and oligomerization leading to dark red colored insoluble poly(phenylacetylene)s[14]. These reactions are due to the high Lewis acidity of Ziegler - Natta catalysts and high cationic reactivity of monomer. It has been found that soluble Mg - Ti catalyst derived from TNB in conjunction with trialkylaluminum promotes clean polymerization without any of the attendant side reactions.

Poly(phenylacetylene)s were characterized by NMR, FT - IR, TGA and intrinsic viscosity techniques

CHAPTER VIII

This chapter deals with a new synthetic method for heterogenization of a homogeneous metallocene catalyst. The novelty of synthetic route and catalyst system are highlighted in this chapter. The efficacy of insouble bis(cyclopentadienyl)titanium(IV) dichloride towards ethylene polymerization was examined. The kinetics of polymerization was compared with soluble metallocene catalyst in conjunction with aluminumalkyls and effect of temperature as well as Al/Ti ratios were studied. Based on the results it is proposed that the magnesium chloride assists in the creation of the active center, namely, the cationic titanium center, and stabilizes it by isolating the active centers on the matrix.

CHAPTER IX

This chapter summarizes the results and describes the salient conclusions of this study. Additional thoughts for further research are indicated. The research has resulted in a soluble magnesium - titanium catalyst for polymerization of ethylene, higher α- olefins, and phenylacetylene.The soluble Mg-Ti catalyst shows some novel properties, distinct from conventional Ziegler-Natta catalysts. A novel supported metallocene catalyst with unusual stability and activity for ethylene polymerization has been synthesized and characterized.

The research presented in this thesis testifies to the multifarious role of the familiar magnesium chloride support in Ziegler-Natta catalysts. They stabilize active centers, alter the ligand environment around titanium, function as a Lewis acid in accepting a ligand from titanium and provide matrix isolation to lower valent titanium, thus preventing it from a rapid decay process.

REFERENCES

1. a) P.C. Barbe, G. Cecchin and L. Noristi, Adv. Poly. Sci., **81**, 1, 1986.
   b) J.C.W. Chien, Catal. Rev - Sci. Eng., **26**, 613, 1984.
2. a) British Patent 1.286.867 to Montedison, Chem. Abstr:73:35929(u).
   b) Belgian Patent 743.325 to Solvay, Chem. Abstr: 94:175869(h).
   c) Belgian Patent 744,470 to Shell, Chem. Abstr: 73: 77817(m).
3. S. Muthukumaru Pillai, M. Ravidranthan and S. Sivaram, Chem Rev., **86**, 353, 1986.
4. J. Skupinska, Chem. Rev.,**91**, 613, 1991.
5. U. Zucchini and T. Dall'Occo in "Polymer Science Contemporary Themes"[Ed. S. Sivaram] Tata - McGraw - Hill Pub. Co., New Delhi, **1**, 221, 1991: M. Malpezzi, U. Zucchini and T. Dall'Occo, Inorg. Chem. Acta. **180**, 245, 1990: L. Abis, G. Bacchilega, S. Spera U. Zucchini andT. Dall'Occo, Makromol. Chem. **192**, 981, 1991.
6. A. Altomara, R. Solaro, F. Ciardelli, L. Barazzoni, F. Menconi and S. Malquori, F. Masi, Polymer **33**, 1768, 1992: A. Altomare, R. Malquori and F. Masi, J. Organometal. Chem. **417**, 29, 1991.
7. K. Soga. T. Shiono, Y.Y. Wu, K. Ishii, A. Nogami and Y. Doi, Makromol. Chem. Rapid. Commun. **6**, 537, 1985.
8. D.S. Breslow and N.R. Newburg, J. Am. Chem. Soc., **79**, 5072, 1957.
9. J.C.W. Chien, J.Am.Chem. Soc., **81**, 86, 1959.
10. M. Kaminaka and K. Soga, Makromol. Chem. Rapid Commun., **12**, 367, 1991.
11. M. Kaminaka and K. Soga, Makromol.Chem. Rapid Commun., **13**, 1105, 1992.
12. J.C.W. Chien and D. He J. Poly. Sci. Polym. A-1., **29**, 1603, 1991.
13. J.C.W. Chien and B. Wang, J. Poly. Sci. Polym. A-1., **27**, 1539, 1989.
14. C.I. Simionescu and V.Percec, Prog. Poly. Sci.Polym.A-1., **8**, 133, 1983.

LIST OF PUBLICATIONS / PATENTS

1 G. Satyanarayana & S. Sivaram
A Convenient One Pot Synthesis of Esters of Carboxylic Acids from Alkyl or Aryl Halides,
Synth. Commun., **20**, 3273, 1990.

2 G. Satyanarayana & S. Sivaram
Novel Soluble Magnesium - Titanium Catalyst for Ethylene Polymerization,
Polym. Mater. Sci. Eng., **67,** 57, 1992.

3 G. Satyanrayana & S. Sivaram
An Unusually Stable Supported Bis(cyclopentadienyl)titanium(IV) dichloride - Trialkylaluminum Catalyst for Ethylene Polymerization,
Macromolecules **26**, 0000, 1993.

4 G. Satyanarayana & S. Sivaram
Synthesis, Characterization and Polymerization of Ethylene Using a Novel Soluble Magnesium - Titanium Catalyst,
Polymer [Accepted, 1993]

5 G. Satyanarayana & S. Sivaram
Synthesis of Syndiotactic polystyrene Using a Novel Soluble Magnesium - Titanium Catalyst,
A poster presented at the Indo - French Symposium on "New Trends in Tailored Polymers: Science and Engineering" held at National Chemical Laboratory, Pune, India, April 1993.

6 G. Satyanarayana & S. Sivaram
A Soluble Titanium Catalyst for the Polymerization of Higher α- Olefins : Poly(hexene-1) and Poly(octene-1) with Narrow Polydispersities,
Makromol Chem. Rapid Commun., [Submitted, 1993]

7 G. Satyanarayana & S. Sivaram
Heterogeneous Magnesium - Titanium Catalyst Systems for Olefin Polymerization: Techniques of Characterization,
Catal. Rev - Sci. Eng.,[IN PREPARATION]

8 G. Satyanarayana & S. Sivaram
An Improved Magnesium - Titanium Catalyst for the Polymerization of Higher α - Olefins
Indian Patent, Application. No.997/DEL/92

9 G. Satyanarayana & S. Sivaram
An Improved Process for the Preparation of Poly(α - olefins) Using Soluble Magnesium - Titanium Catalyst
Indian Patent, Application. No. 998/DEL/92