STUDIES IN POLYMERIZATION OF VINYL MONOMERS USING HOMOGENEOUS TRANSITION METAL CATALYSTS

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*** synopsis**

SYNOPSIS

The thesis entitled **"Studies in polymerization of vinyl monomers using homogeneous transition metal catalysts"** consists of six chapters. Chapter 7 summarizes the work reported in the thesis.

Introduction

The discovery of transition metal catalysts in conjunction with aluminium alkyls for olefin polymerization by Ziegler and Natta in 1955 formed the foundation of today's polyolefin industry.[1] The distinctive feature of Ziegler-Natta catalyst is its extraordinary stereospecificity close to that of enzymes in some cases. Intense research in this area resulted in a series of generations of catalysts with considerable improvement in activity as well as stereospecificity.[1] However the complex and multisited nature of these heterogeneous catalysts has hindered their detailed characterization and rational modification thereby making it unsuitable candidates for mechanistic studies.

Homogeneous metallocene catalysts, which polymerize ethylene in conjunction with aluminium alkyls were known from 1957.[2,3] But these catalysts showed low activity for ethylene and were inactive for propylene polymerization. This situation changed dramatically in the early 1980s when Kaminsky and Sinn discovered that partially hydrolyzed TMA (or methyl aluminoxane, MAO) alongwith group 4 metallocenes were highly active catalysts for the polymerization of ethylene and α-olefins.[4] This discovery stimulated a renaissance in Z-N catalysis, both in industry and academics.

These uniform site metallocene catalysts have provided the opportunity to study the mechanistic and kinetic aspects of Z-N polymerization. A wide range of tailor made materials could be synthesized by proper ligand tuning. Metallocene catalysts, which can polymerize almost any monomer, now allow us to create as yet unknown materials. Narrow molecular distribution, tacticity control, uniform comonomer distribution, control over molecular weight and polymer structure are the salient features of metallocene catalyzed polymerization.[5]

In the recent past several "single site nonmetallocene catalysts" have been emerged as potential catalysts for olefin polymerization. The best known is the Brookhart catalysts, which are Ni and Pd catalysts with diimine ligands.[6] These catalysts produce *narrow polydispersity branched* (SCB and LCB) ethylene polymer from a single monomer viz. ethylene. These late transition metal catalysts are more tolerant to heteroatom functionality in monomers and have the potential for polar monomer incorporation.[7] Block copolymers are also possible with these catalysts.[8] The most important aspect of these catalysts is the control of molecular weight by changing the bulkiness of substituents in the ligand.

More recently iron and cobalt catalysts based on 2,6-bis(arylamino)pyridyl ligands have been reported which shows extremely high activity for ethylene polymerization and lead to high molecular weight poly(ethylene)s.[9,10] The iron(II) bis(imino)pyridyl catalyst produces prevailingly isotactic poly(propylene).[11] In contrast to Ni catalysts the bis(imino)pyridyl Fe(II) complexes produce *broad polydispersity linear* poly(ethylene)s. The molecular weight of the polymer can be controlled by changing the bulkiness of substituents in the ligand.

Objective of the present work

The objective of the present work was to study the homo and copolymerization of vinyl monomers using several "single site catalysts".

1 Syntheses of ethylene-styrene copolymers have been made possible only recently with metallocene catalyst.[12] Constrained geometry catalysts have been found to be extremely effective and upto 90 mol % styrene could be incorporated into poly(ethylene) chain without the formation of homopolymer impurities. Styrene incorporation is difficult due to steric as well as electronic reasons. The objective of the present work was to study the copolymerization of ethylene with styrene, allylbenzne and 4-phenyl-1-butene. Our intention was to separate the phenyl group from the olefinic bond and to study the effect of spacer on copolymerization behavior. Metallocene catalysts, Ni(diimine) catalysts and iron(II)bis(imino)pyridyl catalysts were used for copolymerization.

2 Another objective of the work was to study copolymerization of ethylene with silicon containing monomers. Since a silyl group is known as a “masked hydroxyl group” which is generated by oxidative cleavage of silicon-carbon bond, poly(ethylene) containing silyl groups may be further utilized as precursors for functional polyolefins.[13] Trimethylvinylsilane and allyltrimethylsilane were used as comonomers. Ethoxydimethylvinylsilane and vinylpentamethyldisiloxane were used as comonomers to explore the feasibility of preparing silicon functional polyethylene by direct copolymerization of ethylene with organosilicon comonomers. These functional groups can be used for crosslinking through hydrolysis. Metallocenes, Ni(diimine)catalysts and iron(II)bis(imino)pyridyl catalysts were used for copolymerization.

3 Recently highly active Fe and Co catalysts based on 2,6-bis(arylimino)pyridyl ligands have been reported which are very active for the polymerization of ethylene when activated by MAO or modified MAO (MMAO).[9,10] Iron(II)bis(imino)pyridyl catalysts produce linear poly(ethylene)s with broad molecular weight distribution. Polydispersity of polymer produced by transition metal catalyst is a consequence of its electronic state (single or multiple sites) as well as the nature of transfer reactions. Both these factors are intimately affected by the nature of the activator, namely, the organoaluminium compound. Study of effect of different cocatalysts on kinetics of ethylene polymerization as well as polymer properties was another objective of the work.

Chapter 1. Homogeneous transition metal catalysts for vinyl polymerization

A general literature survey, inclusive of patents, on olefin polymerization using homogeneous transition metal catalysts with emphasis on late transition metal catalysts and new single site catalysts has been described in this chapter.

Chapter 2. Scope and objectives

This chapter covers the scope and objectives in undertaking the present work

Chapter 3. Experimental methods

This chapter contains a description of materials, synthesis of catalysts and monomers and polymer characterization methods

Chapter 4. Copolymerization of ethylene with aromatic vinyl monomers using homogeneous transition metal catalysts

Results of copolymerization of ethylene with styrene, allyl benzene, 4-phenyl-1-butene using metallocene catalysts, viz.: Cp_2ZrCl_2, $Me_2SiCp_2ZrCl_2$ and $Me_2SiCp_2TiCl_2$, Nickel (dimine) catalysts, and Iron(II) 2,6-bis{1-[2,6(diisopropylphenyl)imino]ethyl} pyridineiron dichloride are described in this chapter. Effect of type and concentration of the comonomer, temperature, Al/M ratio on copolymerization activities, molecular weight and mol % incorporation of comonomer are reported in this chapter.

Chapter 5. Copolymerization of ethylene with silicon containing monomers using homogeneous transition metal catalysts

This chapter deals with copolymerization of ethylene with vinyltrimethylsilane, allyltrimethylsilane, ethoxydimethylvinylsilane and vinylpentamethyldisiloxane using various metallocenes, Ni (diimine) catalysts and 2,6-bis{1-[2,6(diisopropylphenyl)imino]ethyl} pyridineiron dichloride. Effects of catalyst structure, feed composition, temperature and Al/M ratio on copolymerization activity, molecular weight, copolymer composition are described in this chapter. A strategy for synthesizing crosslinkable polyethylene has been described.

Chapter 6. Ethylene polymerization using Ni(diimine) and iron(II)bis(imino)pyridyl catalysts

Results of ethylene polymerization studies using Ni and Fe catalysts in conjunction with various cocatalysts are reported in this chapter. Effects of cocatalysts on kinetic profile of ethylene polymerization, molecular weight, molecular weight distribution, branching etc are described in detail. Polymerizations were also conducted in different solvents and the results are compared.

Chapter 7. Summary and conclusions

This chapter summarizes the results and describes the salient conclusions of the work reported in the thesis. Scope for further continuation of this work is also discussed.

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GLOSSARY

ATMS	Allyltrimethylsilane
Cp	η^5-Cyclopentadienyl
Cp^*	Pentamethyl cyclopentadienyl
DABAn	[(N,N'-diisopropylbenzene)-2,3-(1,8-naphthyl)-1,4-diazabutadiene]
$DABH_2$	[(N,N'-diisopropylbenzene)-1,4-diazabutadiene]
DEAC	Diethylaluminium chloride
DME	Dimethoxyethane
DSC	Differential Scanning Calorimetry
FT-IR	Fourier Transformed Infra Red
GC	Gas Chromatography
GPC	Gel Permeation Chromatography
Ind	Indenyl
Kg	Kilo gram
M_n	Number average mol.wt
M_w	Weight average mol. wt
M^{vi}	Vinyltrimethylsilane
MM^{vi}	Trimethylsilyloxydimethylvinylsilane
MWD	Molecular weight distribution
MAO	Methylaluminoxane
MMAO	Modified Methylaluminoxane
NMR	Nuclear Magnetic Resonance
ODCB	*o*-dichlorobenzene
rac	Racemic
T_m	Melting point
Tp	Polymerization temperature
TEAL	Triethylaluminium

TIBAL	Triisobutylaluminium
TIBDAO	Tetraisobutyldialuminoxane
TMA	Trimethylaluminium
THF	Tetrahydrofuran
TOF	Turn over frequency
VEDMS	Vinylethoxydimethylsilane
wt %	Weight %
[η]	Intrinsic viscosity

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CHAPTER 1. HOMOGENEOUS TRANSITION METAL CATALYSTS FOR VINYL POLYMERIZATION

1.1 Introduction

The discovery of transition metal catalysts for olefin polymerization by Ziegler and Natta in 1955 laid the foundation of the polyolefin industry.[1,2] Today about 45 million metric tons of polyolefins are produced worldwide in a year. It is estimated that by the year 2005 this figure will go upto 65 million metric tons. About 45 % of plastics used today belongs to the family of polyolefins. As more and more applications are sought for these polymers made from inexpensive monomers, this share is forecast to increase. Polyolefins have the advantage of low weight, low energy consumption during polymerization and processing, low emission of volatiles, wide property ranges, versatility in application and ease of recycling. In view of this, significant resources has been invested in polyolefin research, both, in industry and academia. During the past fifteen years group 4 metallocenes has dominated the area of olefin polymerization catalysts. However, it is generally acknowledged that no single class of catalyst will be able to control all the macromolecular parameters relevant to a wide and varied range of polyolefinic products. The never ending search for new catalyst families with better activities and capable of producing new homo as well as copolymers with new properties is continuing.[3] In this chapter the current status of homogeneous transition metal catalysis is reviewed with special emphasis on late transition metal catalysts.

1.2 Early transition metal catalysts

1.2.1 Group 4 metallocenes

1.2.1.1 Historical background

Since the discovery of Ziegler-Natta (Z-N) catalysts in the 1950's, in regular intervals polyolefin technology has been revolutionized by new discoveries. Intense research in this area has resulted in five generation of catalysts which have found applications in industry.[4] Significant improvements in stereoselectivity for propylene polymerization with high yield have been achieved which eliminates the need for catalyst removal. However the complex and multisited nature of these heterogeneous catalysts has hindered their detailed molecular characterization and rational modification. As a result, fundamental questions regarding the mechanism of polymerization and origin of stereospecificity of Z-N catalysts remain still elusive.

Efforts were made to devise homogeneous models of the heterogeneous catalysts that would prove more amenable to mechanistic study. In 1957, Natta et al.[5] and Breslow and Newburg[6] reported that Cp_2TiCl_2 could be activated for olefin polymerization by Et_3Al or Et_2AlCl. But these catalyst systems polymerize ethylene with very low activity ($\sim 10^2$ g $mmol^{-1}h^{-1}$) and was found to be inactive for higher α-olefin polymerization. Significant increase in activity was observed when small amounts of water were added to the catalyst system of titanocenes and ethylaluminium chlorides by Reichert and Meyer.[7] But this situation changed dramatically when Kaminsky and coworkers observed that a catalyst system consisting of Cp_2TiMe_2/TMA/water is highly active for ethylene polymerization.[8] This discovery stimulated a renaissance in Z-N catalysis. Subsequent research lead to the isolation of MAO which was found to be a very effective cocatalyst for metallocene mediated olefin polymerization.[9,10] Kaminsky et al. showed that Cp_2ZrCl_2 or Cp_2ZrMe_2 in conjunction with MAO (Al/ Zr > 1000) polymerized ethylene in toluene solution at 70 °C with activity ($\sim 6 \times 10^7$ g $mol^{-1}h^{-1}$) which is 10 - 100 times higher than those used in most active Z-N catalyst systems.[11] However these catalysts are non stereospecific, producing only atactic polypropylene, because of the symmetric nature of the active centers.[10]

Ewen was the first to report the synthesis of stereoregular polypropylenes with $Cp_2Ti(Ph)_2$ and MAO at low temperatures.[12] In the early 1980's Brintzinger and coworkers synthesized C_2 symmetric rac-$Et(ind)_2ZrCl_2$, and rac-$Et(indH_4)_2ZrCl_2$ as well as its Ti analogues.[13] In 1985 Kaminsky et al. showed that these sterically rigid chiral complexes when activated with MAO, catalyzed stereoselective polymerization of propylene which is a prochiral monomer, with high activity.[14] This was for the first time isotactic PP was synthesized using homogeneous transition metal catalysts. Another significance of this discovery was that Natta's explanation for the origin of isospecificity by a "catalytic site control" or enantiomorphic site control" mechanism was proved experimentally. As predicted, achiral meso forms of these complexes produced only atactic PP.

This discovery of ansa-metallocene catalysts for stereospecific polymerization is considered to be a major breakthrough in homogeneous transition metal catalysts for olefin polymerization.

Several catalysts were made by varying the ligand structure surrounding the active center and a correlation of the catalyst structure with catalyst activity and stereospecificity have been established.[15] This led to a better understanding of the molecular mechanism of stereochemical control in α-olefin polymerization. In an another major development, syndiotactic polypropylene was synthesized by Ewen et al. in 1988 using C_s symmetric zirconocenes.[16]

Metallocene catalysts have several advantages over classical heterogeneous Ziegler-Natta catalysts. These are,

- Very high catalytic activities.
- The 'single site' nature enables these catalysts to produce extremely uniform homo and copolymers (with uniform comonomer distribution) with narrow molecular weight distributions and very small fraction of extractable oligomers.
- The polymer microstructure, both, intermolecular and intramolecular can be controlled by changing the symmetry of the metallocene. A number of new polyolefin products with better properties have been made using metallocenes which were not possible earlier.
- Metallocenes are able to polymerize a large variety of olefins which were not possible with classical Ziegler-Natta catalysts. They afford efficient copolymerization of less reactive long-chain α-olefins, sterically hindered α-olefins, cycloolefins and styrene.
- The main chain termination mechanisms operating with these catalyst systems provide unsaturated chain ends, which can be used for functionalization.
- Metallocenes give excellent control of short as well as long chain branches which affect the rheological properties and processing.

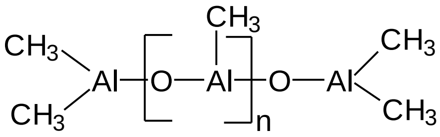
A number of reviews are available on metallocene catalyzed olefin polymerization.[17-33]

1.2.1.2 Cocatalysts

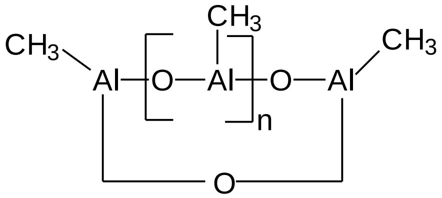
1.2.1.2.1 Methylaluminoxane

Methylaluminoxane (MAO) is the most common and important cocatalyst for metallocene based olefin polymerization. MAO is prepared by partial and controlled hydrolysis of TMA. The typical structural element is an oxygen atom joining two Al atoms that contain methyl groups

(**1,2**). The repeat unit is -[Al(CH_3)-O]-. The synthesis and characterization of MAO has been reviewed recently.[21]



1
Linear structure

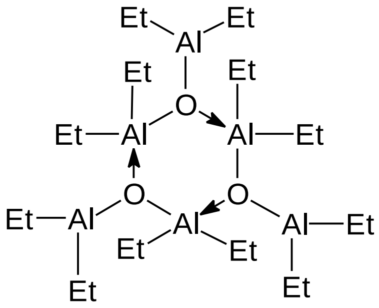


2
Cyclic structure

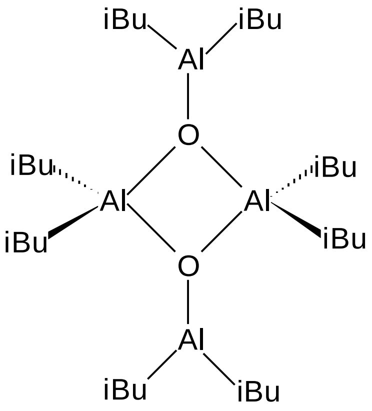
The degree of oligomerization generally varies from 5-30 and molecular weight range is 250-1700 as determined from cryoscopic measurements. Me/Al ratio varies from 1.1 to 1.6. Different structures have been proposed for MAO by various researchers: rings, clathrates, linear and cyclic structures. The structure of MAO depends upon its synthesis, isolation, solvents used etc. Despite its uniqueness as cocatalyst, MAO still remains a "black box". Its structure affects the polymerization activity and the polymer properties. Sinn et al. proposed that MAO forms an adduct with three molecules of TMA which even after distillation in the presence of cumene or complexation with THF retained one molecule of strongly associated TMA.[34]

It is reported that TMA present along with MAO acts as a chain transfer agent during olefin polymerization.[35]

1.2.1.2.2 Other aluminoxanes



3
Tetraethyldialuminoxane



4
Tetraisobutyldialuminoxane

Apart from MAO, other most commonly used aluminoxanes are ethylaluminoxane and isobutylaluminoxanes which are derived from TEAL and TIBAL respectively. Among all these aluminoxanes, MAO is the most effective. From molecular weight data (cryoscopy) ethylaluminoxane is found to be trimeric (**3**) and isobutylaluminoxane, dimeric (**4**) in nature. Based on ^{27}Al NMR studies different structures have been proposed by Sugano et al.[36]

1.2.1.2.3 Modified MAO (MMAO)

MMAO is a modifed methylaluminoxane containing 25 % tetraisobutyldialuminoxane. MMAO has the advantage of an improved shelf life, with similar activity as that of MAO. [37]

1.2.1.2.4 MAO free catalyst systems

One of the drawbacks of MAO is that a large excess is needed to activate the catalyst. Moreover it is expensive. Search for alternative catalyst systems began with the work of Jordan et al. who found that MAO free, cationic metallocene catalyst system $[Cp_2ZrMe(THF)]^+[BPh_4]^-$ can polymerize ethylene with high activity in the absence of cocatalysts. [38] Subsequently several cationic catalyst systems were developed. In principle, active homogeneous catalysts can be obtained by the reaction of dialkyl metallocene such as $Cp_2Zr(CH_3)_2$ and Bronsted acidic salts in a 1:1 ratio. The true active species produced in situ is basically a 14 electron cationic complex such as $[Cp_2ZrCH_3]^+$. Three procedures which make use of a non coordinating anion $B(C_6F_5)_4^-$ and without side reactions have been reported.

(1) $Cp_2Zr(CH_3)_2 + B(C_6F_5)_3 \rightarrow Cp_2Zr^+(CH_3) + (C_6F_5)_3B(CH_3)^-$ (Marks and coworkers[39])

(2) $Et(Ind)_2Zr(CH_3)_2 + [Ph_3NHMe_2]^+[BPh_4]^- \rightarrow Et(Ind)_2Zr(CH_3)^+ + PhNMe_3 +$
$[B(C_6F_5)_4]^- + CH_4$ (Taube and Krukowa[40])

(3) $Et(Ind)_2Zr(CH_3)_2 + [Ph_3C]^+ [B(C_6F_5)_4]^- \rightarrow Et(Ind)_2Zr(CH_3)^+ + Ph_3CCCH_3 +$
$[B(C_6F_5)_4]^-$ (Chien et al. [41])

Compared to metal methyl complexes, benzyl complexes were found to be more stable at higher temperatures.[42] Anions of the type $CB_{11}H_{12}^-$, $[M(C_2B_9H_{11})_2]^-$ (M = Fe, Cp, Ni) were also used as noncordinating anions with $[Cp_2ZrCH_3]^+$[43,44]

1.2.1.3 Polymerization mechanism

1.2.1.3.1 Nature of active species

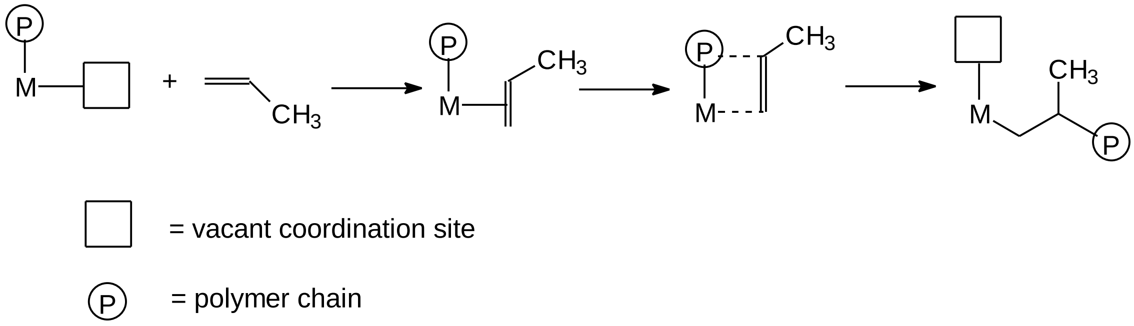
A three coordinated cationic 14 electron alkyl species Cp_2M^+R is now well established as the active species which is formed by the reaction of a metallocene dichloride and MAO.

$$Cp_2MCl_2 + MAO \rightarrow Cp_2M^+CH_3$$

Evidences towards the formation of these cationic species and cationic hydride species (such as Cp_2M^+H which are formed by β-hydride elimination of the propagating chain end) is obtained by X-ray photoelectron spectroscopy.[45] MAO serves as a supramolecular soft counteranion which hinders the recombination of zirconocene cation with Cl^- or Me group. These cationic group 4 complexes are often stabilized by other weak interactions, such as agostic interactions. Direct evidence of the formation of cationic species was reported by Marks and coworkers who studied the reaction of $Cp_2Zr(^{13}CH_3)_2$ and MAO and following ethene insertion with solid state ^{13}CPMAS-NMR.[46-50] Further confirmation was obtained when Jordan et al. isolated and characterized a cationic zirconocene species $[Cp_2ZrMe(THF)^+]$ $[BPh_4]^-$ which was found to be active for ethylene polymerization.[38] This led to the development of several cationic metallocene catalyst systems for olefin polymerization.

1.2.1.3.2 Mechanism of polymerization

The mechanism of polymerization has been the subject of many experimental and theoretical investigations. Cossee's suggestion,[51,52] originally developed for olefin polymerization with conventional Z-N catalysts, is generally accepted to be the most plausible mechanism for metallocenes also (**Scheme 1.1**).[53,54]

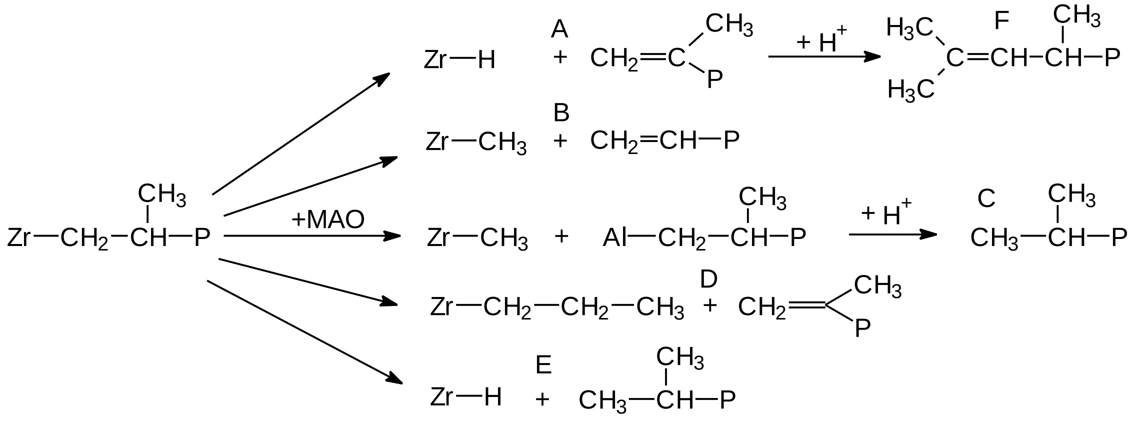


Scheme 1.1 Cossee mechanism for Ziegler-Natta polymerization

MO calculations show that once an olefin coordinates to the metallocene alkyl, the insertion of the olefin into the metal-alkyl bond occurs rapidly. The driving force of the insertion is the energy gain on transforming M-R and M-(C=C) into M-C and C-R bonds. The newly formed metal alkyl again reinserts another olefin molecule leading eventually to a polymer. During this process shifting of growing polymer chain to the position previously occupied by a coordinated monomer continues until termination of the polymer chain takes place.

1.2.1.3.3 Mechanism of chain transfer

Termination of the growing polymer chain occurs predominantly through chain transfer mechanisms involving β-hydrogen (A) or β-methyl elimination (B) (for propylene) and chain transfer to aluminium (C) or the monomer (D) (**Scheme 1.2**). H_2 can be used as transfer agent (E). The transfer mechanisms A and D results in vinylidene, B in vinyl, and C and E in 2-propyl end groups. These transfer mechanisms can be studied by ^{13}C NMR of oligomeric polypropylene. Isomerization of the vinylidene end group under the influence of some acid, used during work up might result in the formation of a vinylidene group with an internal double bond (F). The nature of the chain transfer reactions depends on the nature of metallocene, Al/M ratio, temperature and other polymer conditions.[55]



Scheme 1.2 Various termination reactions of the growing polymer chain

For example, polymerization using Cp*ZrCl $_2$/MAO proceeds with 91 % β-Me transfer, 8 % β-H transfer and 1 % chain transfer to aluminium at 50 °C while exclusive chain transfer to aluminium was found to occur at –40 °C.[56] Exclusive chain transfer by β-Me transfer was found in the case of $[Cp^*ZrMe(THF)]^+[BPh_4]^-$ over a wide range of temperatures (5 – 95 °C)[57]

1.2.1.4 Molecular weight

Molecular weight of a polymer depends on the relative rates of chain growth and chain termination reactions. Z-N based polymers are of high molecular weights about 5,00000 so that chain transfer agents like H_2 have to be utilized. But with homogeneous metallocenes low molecular weight polymers are obtained due to the effect of various chain termination and transfer reactions. Usually the Mw of polymers can be increased by sterically and/or electronically suppressing chain transfer reactions.

1.2.1.4.1 Effect of metal

Molecular weight of polymers depends on metal-C bond energy since it affects the chain transfer reactions. Molecular weight of a polymer produced with hafnocene is much higher than that produced with zirconocene or titanocene because of the higher Hf-C bond energy.

1.2.1.4.2 Steric effects

The most important chain transfer reaction is the β-H elimination. Steric effects can cause significant increase in the energy of the transition state associated with β-H elimination due to the non-bonded repulsion between the polymer chain and the ligand. So by substituting Cp with bulky Ind or Flu ligands[58] or by putting substituents at the appropriate positions of the ligands (like 2,5 positions) Mw can be increased.[59,60]

1.2.1.4.3 Electronic effects

If the Lewis acidic character of the metal can be reduced, then the thermodynamic driving for β-H elimination diminishes. This can be achieved by putting electron donating groups in the ligand. For example, the electron releasing ability increases in the order Cp<Ind<Flu.[58]

1.2.1.4.4 Temperature

Since the activation energy of chain transfer reactions is higher than insertion, lowering of Tp leads to higher molecular weight polymer. Kaminsky et al.[61] reported that at Tp below –20 °C the transfer reaction is so slow that the molecular weight of polymers is only a function of polymerization time.

1.2.1.4.5 Catalyst concentration

Average molecular wt decreases with log of increase in catalyst concentration. [62]

1.2.1.4.6 [Al/M] ratio

It has been reported that as the Al/ Zr ratio increases from 1000 to 10000, the Mw increases and further increase in the ratio does not have much effect on Mw. But at very high levels of Al/M $\approx$ 50,000 to 100000, the Mw decreases due to the transfer reactions with aluminium.

1.2.1.4.7 Effect of support

Another way of increasing the Mw is by heterogenizing the metallocene catalysts on a support. Soga and Kaminska reported that propylene polymerization with the heterogeneous catalyst system $Et(H_4Ind)_2ZrCl_2/MAO/SiO_2$ combined with TIBAL produced polypropylene with a Mw 4.5 times higher than that obtained with homogeneous $Et(H_4Ind)_2ZrCl_2/MAO$ systems under the same conditions. [63] The subject of supported metallocene has been reviewed recently. [64]

1.2.1.5 Molecular weight distribution

Molecular weight and molecular weight distribution are the important properties which affect mechanical as well as the processability of a polymer. Metallocene catalysts being "single site" produce polymers with a narrow mol.wt distribution (MWD). Typical values of Mw/Mn are 1.6 – 2.4 for polyethylenes and 1.9 – 2.6 for polypropylenes. [65] Chien and Sugimoto explained that MWD of 2 may not be due to 'single site' nature, but two or more active species with similar values for the k_p/k_{tr} ratio.[66]

1.2.1.6 Applicability to monomers

1.2.1.6.1 Propylene polymerization

In 1985 Brintzinger and coworkers synthesized pure racemic forms of ethylene-bis-indenyl as well as tetrahydroindenyl complexes of both Zr and Ti. [13] Kaminsky et al. showed that isotactic PP can be synthesized using these catalysts. [14]

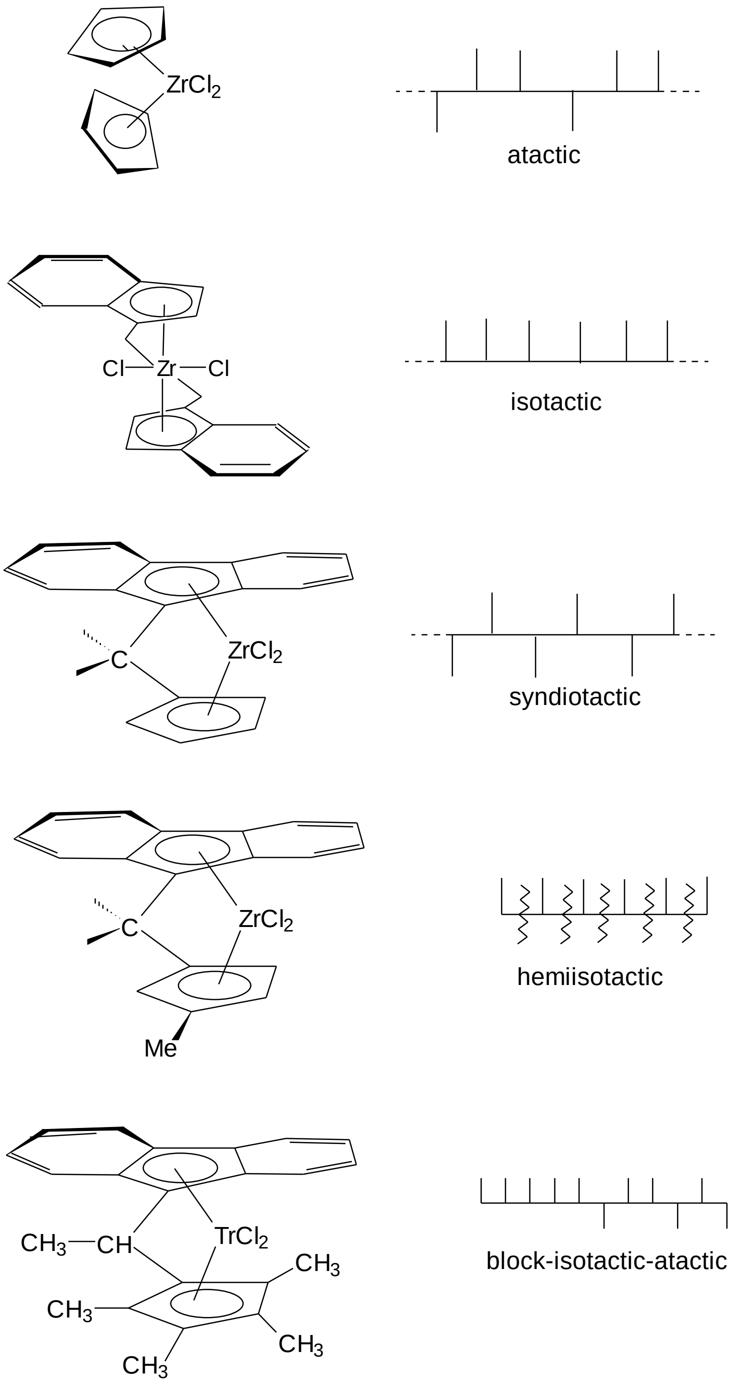


Figure 1.1 Correlation of metallocene structure to polypropylene structure

After this discovery a wide range of metallocenes with different ligands as well as different bridging groups have been synthesized. The power of "rational catalyst design" was nicely demonstrated by Spaleck et al. who systematically investigated the substitution positions in bridged bisindenylzirconocenes. [15,67] The high activities of the systems can be best explained by electronic effects, whereas, steric effects are responsible for high stereospecificities and high molecular weights of the polymers. Kaminsky has compared the polymerization of propylene with different catalysts under the same experimental conditions. [27]

Highly syndiotactic PP was prepared by Ewen et al. using a Cs symmetric $Me_2C(Cp)(Flu)ZrCl_2$.[16] The rrrr stereosequences indicate stereochemical site control with chain migratory insertions, resulting in site isomerization and occasional reversal of diastereoface selectivity.

Apart from the stereoregulation discussed, intramolecular control is also possible with specially designed metallocenes. Novel thermoplastic elastomers with flexible atactic segments containing isotactic segments for crystallization were made possible using metallocenes by Coates and Waymouth[68], Chien and coworkers[69,70] and Resconi[71] et al.

The correlation of metallocene structure to polypropylene structure is shown in the **Figure 1.1**

1.2.1.6.2 Cyclic monomers

Unlike conventional Ziegler-Natta catalysts metallocene catalysts polymerize strained cyclic alkenes such as cyclobutene, cyclopentene, norbornene, DMON or TMDM without ring opening to crystalline polymers. [72] The enchainment occurs exclusively through the endocyclic double bond without any side reactions. The homopolymers of cyclic olefins are insoluble in hydrocarbons and have melting points higher than their decomposition temperatures thereby rendering it difficult to process. Copolymerization of ethylene with these cyclic olefins represent a new class of thermoplastic amorphous materials. [73,74,75] The glass transition temperature depends on the nature of cycloolefin and its incorporation. In general bridged metallocenes are more active and favor higher incorporation of the comonomer. These cycloolefin copolymers (COC) are characterized by excellent transparency and very high, long-life service temperatures. They are solvent and chemical resistant and can be melt processed. They have very high refractive index, low birefringence, low water absorption and high stiffness. Their properties make them excellent materials for optical application, for example in compact discs, lenses, optical fibers or films. Mitsui Petrochemical and Hoechst produce ethylene- norbornene copolymers for the production of compact discs under the trade name TOPAS(Thermoplastic Olefin Polymers of

Amorphous Structure). Another advantage of COC is the low density which is about 20 % less than its competitor polycarbonate.

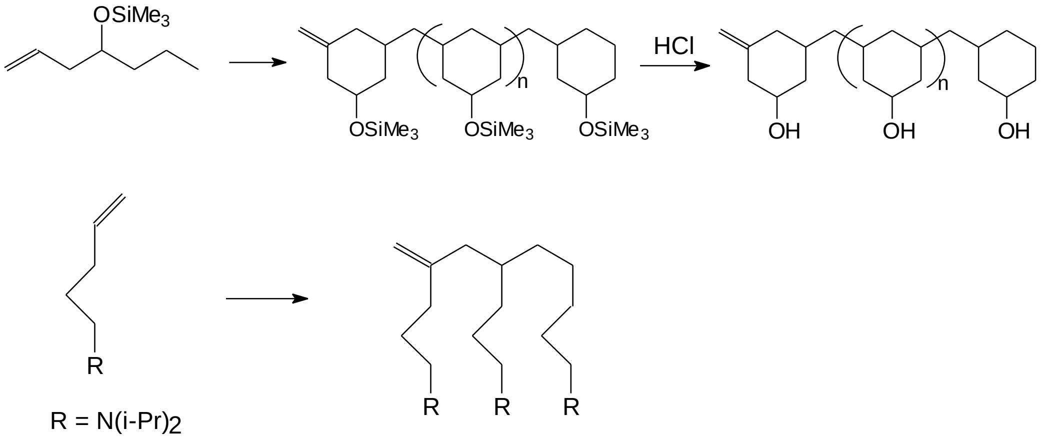
1.2.1.6.3 Syndiotactic polystyrene

Atactic polystyrene is one of the widespread polymeric materials due to its excellent properties such as stiffness, transparency and processability. Isotactic polystyrene is highly crystalline with a melting point of 240 °C. However its crystallization rate is too slow for commercial application. Ishihara et al. at Idemitsu were able to obtain syndiotactic polystyrene (SPS) by using homogeneous Ti catalysts and MAO.[76] Half sandwich complexes such as $CpTiCl_3$, Cp^*TiCl_3, Cp^*TiF_3 or tetraalkoxy complexes are highly active. SPS is a highly crystalline polymer with melting point of about 270 °C. The relatively fast crystallization rate, the low specific gravity, low dielectric constant, high modulus of elasticity and excellent resistance to chemicals make SPS a promising material for a large number of applications in the automotive, electronic and packaging industries. The development in this area has been reviewed.[77,78]

1.2.1.7.4 Functional monomers

Synthesis of functional polyolefins through direct copolymerization of functional monomers is an area of contemporary research interest. Incorporation of polar functional groups onto polymers with a hydrocarbon backbone represents an important method for modification of their chemical and physical properties including adhesion, dyeability, permeability, compatibility with additives and solid state morphology. Functional copolymers of ethylene and propylene can be made using conventional Ziegler-Natta type catalysts.[79] However, the fact that polar functional groups deactivate either the catalyst or the cocatalyst component of Ziegler catalyst has limited the synthesis of functional copolymers by Ziegler-Natta catalytic process. Different approaches have been adopted to overcome this problem, like separating the functional group from the polymerizable double bond by spacer group, by protecting the functional group either by using externally added reagent or by increasing the bulkiness around the functional group and by decreasing the nucleophilicity of the functional group.

With the discovery of metallocene/MAO catalyst system for olefin polymerizations there is a renewed interest in the area of synthesis of functional polyolefins.[80-88] Various functional monomers protected with silyl group or aluminium alkyl group have been successfully used for homo as well as copolymerizations with olefins.[89-99] Homopolymerization of olefins containing silyl protected alcohols and tertiary amines like 4-trimethylsiloxy-1 ,6-heptadiene, 5-tert-butyldimethylsiloxy-1-pentene and 5-(N,N- diisopropylamino)-1-pentene using cationic metallocene catalyst systems have been reported by Waymouth and coworkers[96,81] They were successful in synthesizing poly(methylene-3,5-(1-trimethylsiloxy) cyclohexanediyl) of Mw 1,42,600 and MWD 3.1 using $[(C_5Me_5)_2HfMe]^+[B(C_6F_5)_4]^-$ catalyst in neat monomer at -25 °C with 30 % conversion which on treatment with aq.HCl gave the polyalcohol (**Scheme 1.3**)



Scheme 1.3 Polymerization of functional monomers

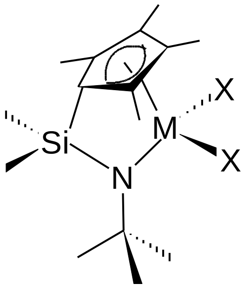
Functional polyolefin can also be made by copolymerization with a precursor monomer which can be later converted into functional groups. Two types of such monomers are reported in the literature, namely dienes [100] and ω-borane-α-olefins.[87] Marathe and Sivaram reported coversion of pendant double bonds of ethylene/VNB copolymer to epoxy and hydroxyl groups.[101] Recently Radhakrishnan and Sivaram reported a new strategy for the synthesis of functional polyolefin by copolymerization of ethylene with symmetrical dienes like norbornadiene using metallocenes. Enchainment occurs through only one of the double bonds and the other can be used for post functionalization.[102]

1.2.2 Group 4 non metallocenes

Even though metallocene based catalysts dominate the area of homogeneous Z-N catalysts, other non-metallocene based catalysts have also been developed in recent years.

1.2.2.1 Constrained geometry catalysts

This catalyst system is based on group 4B transition metals especially Ti, covalently bonded to a Cp group bridged with a hetero atom such as nitrogen (**5**). The characteristic feature of such a structure is that the bond angle between Cp, Ti and the hetero atom is less than 115°. This arrangement allows the metal center to be more open for monomer and comonomer incorporation. This type of mono Cp based homogeneous catalysts was first developed by Dow.



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A new family of ethylene-α-olefin copolymers have been developed using these catalysts by Dow under the trade name "Insite".[103] This technology allows the manufacture of both polyolefin plastomers (tradename-Affinity) and polyolefin elastomers (tradename-Engage) through the controlled incorporation of low and high comonomer concentration respectively. These polymers show excellent physical and mechanical properties due to narrow molecular weight and comonomer distribution. But in contrast to conventional homogeneous ethylene-α-olefins, POPs and POEs produced by Insite technology exhibit unusually good processability with enhanced shear thinning as a result of long chain branching (LCB) which is the subject of a recent product patent issued to Dow. The widely believed mechanism of LCB formation is the re-insertion of polymer chains that contain a vinyl chain end which are formed via β-H elimination and/or monomer chain transfer mechanism. The levels of LCB can be controlled by temperature and the concentration of chain transfer agent (H_2) in a continuous solution polymerization process.

Experimental evidence for this mechanism was obtained when Soga and coworkers copolymerized ethylene with vinyl terminated polypropylene macromonomer and oligo ethylene using a constrained geometry catalyst.[104,105]

Recently Bazan and coworkers reported the synthesis of branched polyethylene without the use of any comonomer.[106] He used a mixed catalyst system, a boratabenzene complex and a constrained geometry catalyst. The oligomer produced by the boratabenzene complex is copolymerized with ethylene by the constrained geometry catalyst.

Conventional Z-N catalysts incorporate only traces of styrene during copolymerization with olefins.[107] In contrast, even though homopolymerization of styrene is not possible, constrained geometry catalysts incorporate a large amount of styrene into polyethylene as well as ethylene/1-olefin copolymers.[108,109] The elastomeric properties can be controlled by styrene and 1-olefin comonomer content. In the case of ethylene-styrene copolymers the polymers with larger amounts of styrene have semi-glassy characteristics, those with equal amounts of ethylene and styrene have elastomeric characteristics and those with more ethylene have semi-crystalline characteristics.

A systematic study of the copolymerization behaviour using these catalysts was done by Mulhaupt and coworkers.[110] $Me_2Si(Me_2Cp)(N\text{-tert-butyl})TiCl_2$ in conjunction with MAO shows extremely high activity (1000 to 9200 Kg copolymer/ molTi.h.mol/L total comonomer conc.) compared to other catalysts known to copolymerize ethylene and styrene. In the experimental conditions they studied, a maximum of 34 .6 mol % styrene incorporation was achieved. It seems that high incorporation of styrene is difficult with these catalysts since polymerization activity decreases with increasing styrene concentration in the feed. Another important aspect is that at higher concentration of styrene considerably less styrene incorporation is achieved. The reactivity parameters which were calculated from Finemann – Ross method ($r_E = 23.4$, $r_S = 0.015$ with $r_E.r_S = 0.35$) shows that styrene does not prefer multiple insertion whereas ethylene does. A detailed study of the ^{13}C NMR spectra of the copolymer shows that only tail-to-tail coupling occurs and no more than two styrene monomers follow each other.

Sernetz et al. studied the copolymerization behavior of different constrained geometry catalysts by varying the substituents on the cyclopentadienyl ring and the substituents on the amide.[111] It was found that high electron density at the metal center accounts for the higher activity of the catalyst. Bulky substituents on the Cp ring results in steric hindrance, leading to lower incorporation of styrene. However, the long-term activity of the catalyst increases.

1.2.2.2 Alkoxides

Kakugo and coworkers reported that Ti alkoxides in combination with MAO are highly active catalysts for ethylene and propylene polymerization.[112] The Ti complexes with a bidentate 2,2'-thiobis(6-tert-butyl-4-methylphenoxy) ligand produce stereoirregular PP with very high molecular weight (>6 x 10^6) and highly syndiotactic polystyrene. These are also active towards both conjugated and nonconjugated dienes. Schaverien and coworkers have reported olefin polymerization using a variety of Zr and Ti sterically hindered chelating alkoxide complexes.[113] For polymerization of ethylene, activity upto 4740 kg PE $mol^{-1}h^{-1}$ has been achieved but with broad molecular weight distribution indicating more than one active species. In contrast narrow molecular weight distribution was observed in the case of poly(1-hexene).

The most important aspect of these catalysts is their ability to copolymerize ethylene with styrene. An ethylene-styrene copolymer with significant amount of styrene incorporation was first reported by Kakugo et al.[114] An alternating ethylene-styrene copolymer together with syndiotactic polystyrene was obtained by using 2,2-thiobis(4-methyl-6-tert-butylphenoxy)titanium isopropoxide (SBP) or dichloride activated with MAO.

A more systematic study of copolymerizations using these type of phenoxy compounds was conducted by Sernetz et al. by varying the bridging unit between both phenolate moieties of the ligand.[115] In contrast to Kakugo's conclusions they found that the sulphur bridge is not required for the formation of poly(ethylene-co-styrene). In fact the ethylene bridged catalyst is found to favor higher incorporation of styrene. The catalyst activity and styrene incorporation can be explained on the basis of electronic and steric factors respectively. In comparison to the ethylene-styrene copolymers obtained with amido-monocyclopentadienyl complexes the decay of crystallinity was much less pronounced. With constrained geometry catalysts the Tm of E-S copolymer was found to decrease to 89 ^oC for 6 mol % styrene incorporation and in the case of SBP it was 109 ^oC for a copolymer containing 35 mol % styrene. This may be due to the stereoirregular arrangement of styrene units in the copolymers obtained with amido-Cp complexes because of exclusive tail to tail arrangement of styrene which is absent in the case of SBP. Their results do not support Kakugo's hypothesis that the catalyst consists of two active centers. Moreover they could not observe the formation of alternating copolymer also. They found that these catalysts are typical multicenter catalysts similar to conventional Z-N catalysts.

Mono-aryloxy or mono-alkoxy zirconium complexes/MAO catalysts were reported for ethylene polymerization. It was found that the bulkiness around the zirconium atom in the complex is significant to achieve high activity of polymerization. [116]

1.2.2.3. Chelating Diamide complexes

McConville and coworkers[117,118] have synthesized chelating diamide complexes $[ArN(CH_2)_3NAr]\text{-}TiR_2$ (Ar = 2,6-$iPr_2C_6H_3$; R = Me, CH_2Ph) and found them to polymerize 1-hexene with an activity of 350,000 g poly(hexene)/mol Ti. In this system chain transfer to Al is the exclusive chain transfer mechanism. The titanium dimethyl complex when activated with $B(C_6F_5)_3$ catalyze the living aspecific polymerization of α-olefins at room temperature.[119] This is the first example of a living polymerization of an aliphatic α-olefin. However the Zr analogs of these complexes were found to be inactive for olefin polymerization.

1.2.2.4 Other catalyst systems

A wide variety of non-metallocene complexes have been reported for olefin polymerization. The recent developments in this area have been reviewed. [3]

1.2.3 Other early transition metal catalysts

Neutral group 3 metallocene alkyls or hydrides are 14 electron species and show an isolobal and isoelectronic analogy to cationic group 4 metallocene species. Many catalysts are reported to be active for olefin polymerization. [120-134] One of the important advantages of group 3 catalysts is that they are single-component catalysts; no cocatalyst is required. Living polymerizations of acrylates were made possible using several lanthanide complexes. The topic of living polymerization of polar and nonpolar monomers using rare earth metal complexes has been reviewed recently.[135-137]

Vanadium based Ziegler catalysts have been used for a long time for olefin polymerization. Based on isolobal and isoelectronic relationships with cationic metallocene alkyl complexes of group 4 metals, several 14 electron cationic species of group 5 metals have been developed and reported to be active for olefin polymerization.[138-146] A good account of the developments in this area can be found in a recent review. [32]

One third of HDPE production is based on heterogeneous Cr_2O_3/SiO_2 which is popularly known as the Phillips catalyst. Another well known Cr catalyst is the silica supported chromocene developed at Union Carbide. Several Cr catalysts have been studied as homogeneous models for these heterogeneous catalysts. This subject has been reviewed recently.[147,148]

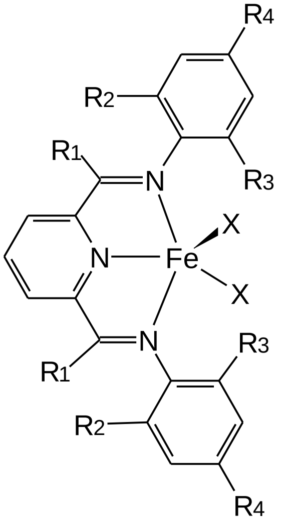
1.3 Late transition metal catalysts

Late transition metal catalysts are best known for oligomerization of olefins. These metals prefer β-hydride elimination followed by reductive elimination. Even though there were few examples of olefin polymerization, the real breakthrough came when Brookhart and coworkers developed Ni and Pd (diimine) based catalysts which showed high activities. The steric bulk around the metal retard the rate of associative olefin exchange leading to high molecular weight polymers.

1.3.1 Group 8 metal catalysts

Brookhart and coworkers[149] and Gibson and coworkers[150] developed the first iron based homogeneous ethylene polymerization catalysts based on neutral tridentate pyridine bis-imine ligands in which the imine moieties are bulky *ortho*-substituted aryl imines. The complex (**6**) when activated with MAO or MMAO (MMAO is MAO containing 25% tetraisobutyl dialuminoxane) polymerize ethylene with exceptionally high activities comparable to the most active Ziegler-Natta systems; turn over frequencies (TOF) of greater than 10^7/h can be achieved at 60 °C and 600 psig ethylene which corresponds to 3.3×10^5 kg PE/mol Fe.h. Poly(ethylene)s produced are highly linear (Tm 133-139 °C) with very high crystallinity.

These complexes show a pseudo square pyramidal geometry in the crystal structure. The aryl groups on the imine nitrogen are perpendicular to the square plane and the bulky ortho substituents provide the necessary steric protection around the metal in order to get high molecular weight polymers. The polymer molecular weights vary with modifications in ligand; increasing the steric bulk of the ortho aryl substituents increase the molecular weight. Aryl substituents with only one small ortho substituent give highly active oligomerization catalysts with exceptionally high selectivities for the production of α-olefins.[37] These iron catalysts produce broad polydispersity linear poly(ethylene)s. Depending on the experimental conditions poly(ethylene) prepared by Fe catalyst has even bimodal distribution. ^{13}C NMR analysis of these polymers reveal saturated end groups in addition to the low levels of vinyl unsaturation. The broad MWD is explained as due to chain transfer to aluminium cocatalyst.



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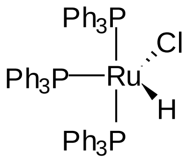
R^1 = H, Me
R^2 = R^3 = iPr, R^4 = H
R^2 = R^3 = Me, R^4 = H, Me
R^2 = R^4 = Me, R^3 = H

Small and Brookhart[151] as well as Pellecchia et al.[152] have reported isospecific polymerization of propylene. The chain growth proceeds by a 2,1 insertion and the microstructure is controlled by a "chain end" control mechanism, both of which are unprecedented for isospecific polymerization of propylene. In contrast to poly(ethylene)s, the poly(propylene)s synthesized were found to have narrow molecular weight distribution. By NMR studies both the groups established that Fe-CH_2-CH_2-CH_3 is the key intermediate in the catalytic cycle. Brookhart found that alkyl transfer does not occur in secondary Fe-alkyls and the presence of n- propyl and 3-methylbutyl end groups is due to the transfer reactions which Fe- propyl complex undergoes with TEAL and TIBAL or TIBDAO(from MMAO). The methyl groups from MMAO are found to be not involved in these exchange reactions since *sec*-butyl end groups were not observed. The alkyl chain transfer processes are significant only in ethylene polymerization since primary Fe-alkyl bonds are present. This might be the reason for the narrow molecular weight distribution observed in the case of propylene polymerization. He concluded from his study that the effectiveness of the transfer reactions decrease in the order TEAL> TIBDAO(from MMAO) ≈ TIBAL >>>Al-CH_3. In contrast using ^{13}C enriched TMA Pellecchia observed the presence of ^{13}C enriched end groups which are formed from 1,2 or 2,1 insertion of propylene into the Fe- $^{13}CH_3$.[152]

One of the major advantages with these type of catalysts is the simplicity of the preparation of ligands, whereas in the case of metallocenes ligand synthesis can prove to be challenging. Active research is in progress in Dupont and BP Chemicals for the commercial exploitation of these types of catalysts.[153,154]

The ruthenium complex(**7**) produce a branched poly(ethylene) with very low activity.[155] Iron and ruthenium complexes have been reported to polymerize functionalized vinyl monomers.[156-158] The Ru Complex (**8**) rapidly polymerize acrylonitrile.[158] But it is not active for ethylene polymerization. The Fe complex (**9**) is reported to polymerize a range of monomers including methyl methacrylate, acrolein, methyl vinyl ketone, and acrylonitrile.[156]



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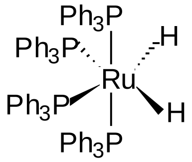

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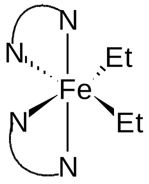
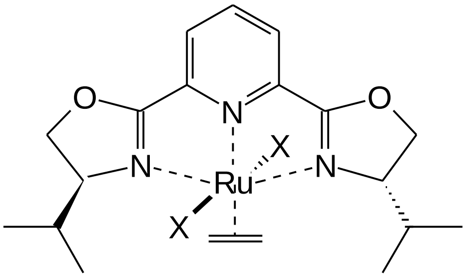


9

= 2,2'-bipyridyl

Recently a Ru complex (2,6-bis[(4S)-isopropyl-2-oxazolin-2-yl]pyridine)RuX_2(ethylene) (**10**) was reported for ethylene polymerization when activated with MAO.[159]



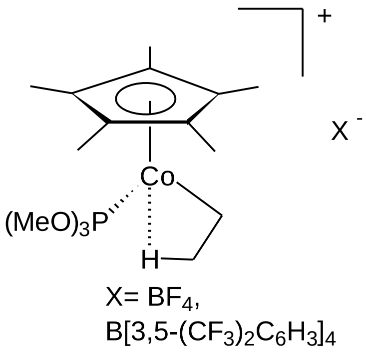
X = Cl or I

10

The maximum activity was about 2 Kg PE/mol Ru.h. In contrast to the analogous Fe catalysts poly(ethylene) produced is of narrow molecular weight distribution presumably due to the use of MAO with reduced amount of TMA which reduced the extent of chain transfer reactions. Furthermore, **10** is active for copolymerization of ethylene with 1-hexene, probably, due to the more open space around the metal center. About 27 mol % hexene incorporation was reported.

1.3.2 Group 9 metal catalysts

Brookhart and coworkers reported a living ethylene polymerization system based on a cobalt complex.[160,161] A cobalt olefin complex (**11**), $(C_5Me_5)Co\{P(MeO)_3\}(H_2C{=}CHAr)$ (Ar = Ph, *p*-C_6H_4Cl, *p*-C_6H_4OAc, *p*-$C_6H_4CF_3$, C_6F_5), with $HB\{C_6H_3(CF_3)_2\text{-}3,5\}_4$ polymerize ethylene with an activity 3.8 kg PE $mol^{-1}h^{-1}atm^{-1}$, $M_n = 1.48 \times 10^4$, $M_w/M_n = 1.11$. Higher α-olefins are only oligomerized, but end functionalized polyethylene materials have been synthesized with this system.



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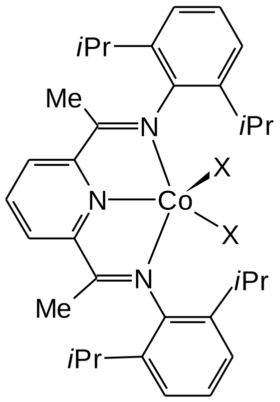

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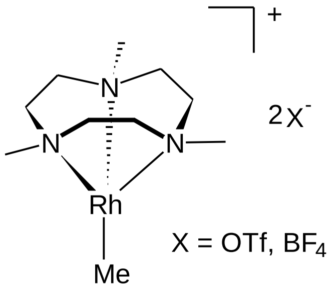

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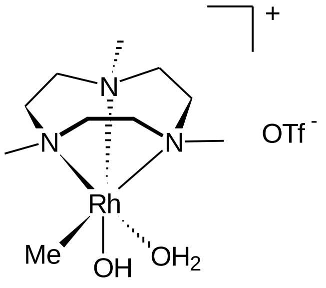

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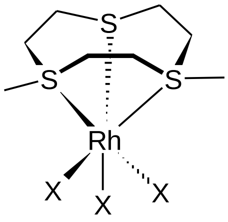

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Cobalt complexes were also made with tridentate pyridinebis(imine) ligands [149,150] The complex (**12**) shows an activity of 460 g $mmol^{-1}h^{-1}bar^{-1}$ when activated with MAO. The cobalt complexes generally exhibit activities that are an order of magnitude lower than their iron analogs. Moreover the molecular weights of the polymers are also lower compared to that synthesized by iron analogs.

Recently Longo et al. reported that cobaltocene is active for ethylene polymerization when activated with MAO to give polyethylene with narrow molecular weight distribution (1.59) and a melting point of 136 °C.[162]

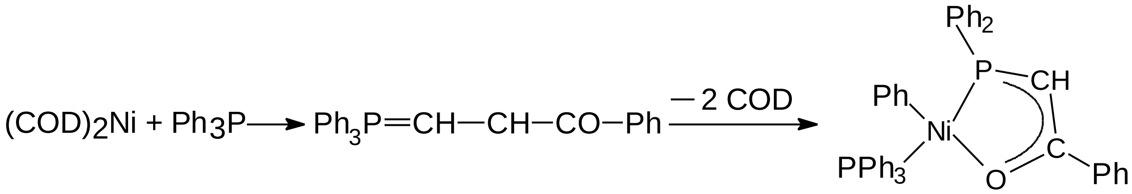
The dicationic rhodium(III) complex (**13**) with a triazacyclononane ligand is reported to be active for ethylene polymerization.[163] Polymerization of ethylene in water is reported for this catalyst.[164] The active species is believed to be **14.** The activity is very low, corresponding to only one turnover per day at 60 bar. Nevertheless this is the first report of ethylene polymerization using a Rh catalyst and also ethylene polymerization in aqueous medium by any catalyst.

Related trithiacyclononane derivative (**15**) has been synthesized which when activated with MAO shows low activity for ethylene polymerization.[165]

1.3.3 Group 10 metal catalysts

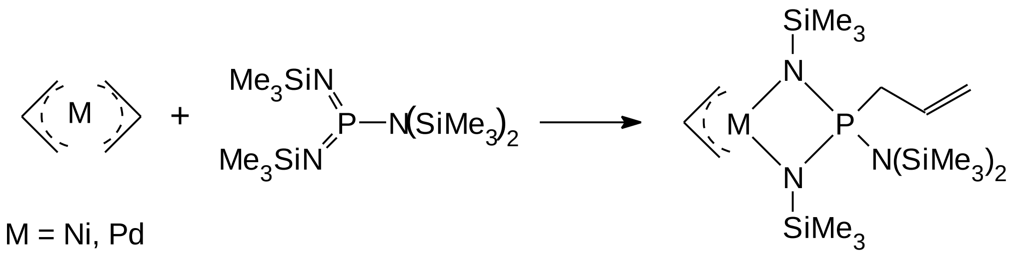
Group 10 metal catalysts are known to dimerize or oligomerize ethylene and higher α-olefins. There have been relatively few reports on polymerization. The Shell Higher Olefin Process (SHOP) is a commercial process for the synthesis of α-olefins ranging from C_6-C_{20} using homogeneous nickel catalyst discovered by Peuckert and Keim. The SHOP process catalyst (η^3-C_8H_{13}) (($C_6H_5)_2PCH_2COO$)Ni, at 75 °C, 10-80 bar, oligomerize ethylene in toluene to linear (99 +%) α-olefins (93-99%) at turnovers of 3600.[166] No cooligomerization was found when 1-hexene or propylene was added. The dimerization or oligomerization of propylene and higher α-olefins was not achieved using these catalysts. The activities of the catalysts are lower than the early transition metal catalysts. A comprehensive review is available on the subject of C_2, C_3 and higher α-olefin oligomerization using various transition metal catalysts.[167]

A single component compound prepared by reacting Ph_3P=CH-CO-Ph with $Ni(PPh_3)_4$ or $Ni(COD)_2/Ph_3P$ in toluene was found to convert ethylene to α-olefins (98%).[168](**Scheme 1.4**)



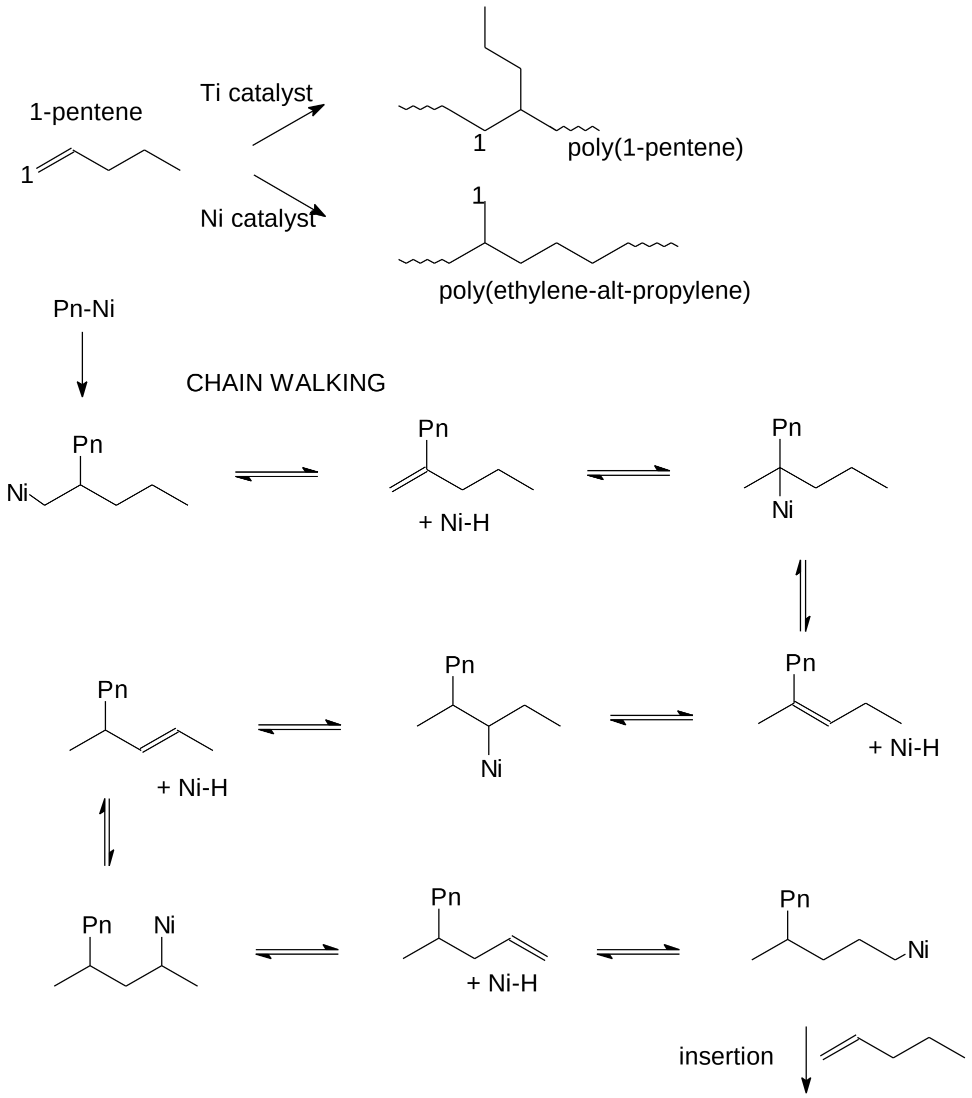
Scheme 1.4 Oligomerization /polymerization catalyst

At 50 bar ethylene pressure and 50 °C an activity of 6000 mol ethylene per mol of the complex was reported. Interestingly a high molecular weight linear polyethylene was obtained when the reaction was conducted in hexane as suspension medium. Novel Ni and Pd complexes containing aminobis(imino)phosphorane as chelate ligand have been reported by Keim et al. (**Scheme 1.5**).[169] In situ reaction of Ni(COD)$_2$ or bis-(η^3-allyl) nickel with the aminobis(imino) phosphorane in toluene yields a catalyst which polymerizes ethylene to polyethylene which has short chain branches. The physical properties of these polymers lie between those of high pressure PE and EPDM (ethylene-propylene-diene monomer) due to the branching nature of these polymers. However, complete characterization of the polymer has not been reported. At 70 °C and 50 bar the activity was 1000 mol C$_2$/mol Ni. The corresponding Pd complex was inactive.



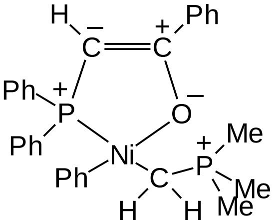
Scheme 1.5 Ni and Pd catalysts with aminobis(imino)phosphorane ligand

Following this work, Mohring and Fink reported the polymerization of α-olefins using the same catalyst.[170] The degree of polymerization for the oligomerization of higher α-olefins dropped off with an increase in chain length. The most important aspect of these polymerizations is the structure of the poly(α-olefin)s obtained. Thus, the polymer of a linear α-olefin was found to contain only methyl branches, regularly spaced along the chain with a separation corresponding to the chain length of the monomers. For α-olefin with n CH$_2$ groups the distance between two methyl groups is (n+1) CH_2. Thus polymerization of 1-pentene leads to a perfectly alternating copolymer of ethylene and propylene.[171] This unexpected branching reaction is attributed to the migration of the transition metal alkyl along the olefin between two insertions. During this "migration" transfer reactions to monomer can occur but not insertions. Monomer inserts only into a CH_2-Ni bond at the end of the growing chain. Fink's "2, ω-polymerization" is also known as polymerization according to the 'chain walking" or "chain running" mechanism (**Scheme 1.6**). Ni(II)acetylacetonate can also be used in combination with the phosphorane and $AlEt_3$ as cocatalyst for this kind of 2, ω polymerization.



Scheme 1.6 Chain walking mechanism

Reaction of $Ni(COD)_2$ with benzoylmethylenetriphenylphosphorane and trimethylmethylenephosphorane yields an active homogeneous ethylene polymerization catalyst (**16**) which at 10 bar pressure and 90 °C shows an activity of 5×10^4 mol C_2/mol Ni. But the polymers are of low molecular weights with melting points around 116 °C.[172] Keim et al. reported that 1,3-diphospha nickel allyl complexes(**17**) are also active for ethylene polymerization.[173] Reaction of $Ni(COD)_2$ with 1,3-diphosphapropene in toluene affords a catalyst **18** which at 70-100 °C and 30 bar pressure shows activity > 100 mol C_2/ mol Ni.h.



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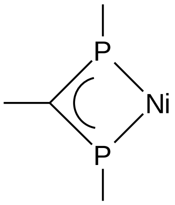

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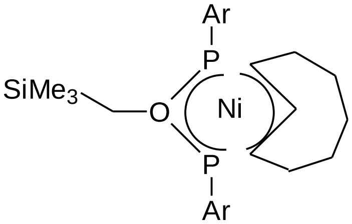

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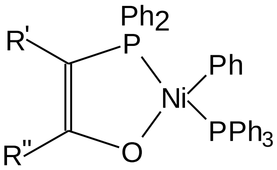
Klabunde reported that single component catalysts for olefin polymerization can be obtained from shell type catalysts $Ni[Ph_2PCH=C(Ph)O](Ph)(PPh_3)]$ of the structure **19** which are known to oligomerize ethylene, either by removing phosphine ligand or by replacing it with a weakly coordinated pyridine.[174] Phosphine acceptors such as Rh(acetylacetonate)$(C_2H_4)_2$ or $Ni(COD)_2$ are found to be most effective. Complex without phosphine ligand exists as a dimer **20.**



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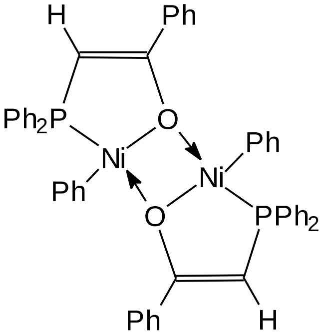

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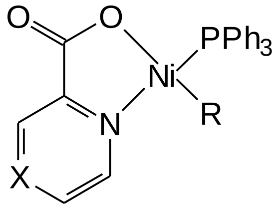
These active homogeneous catalysts can be tuned to give either low or high molecular weight, linear low or high density poly(ethylene). The poly(ethylene)s produced were found to have broad molecular weight distribution of 10-25 suggesting the presence of multiple species. Substituents on P-O chelate part was found to influence the product distribution and molecular weights.[175] These catalysts are active even at high temperatures as high as 150 °C. The most noticeable observation was that the polymerization could be run in oxygenated solvents such as alcohols and ketones, even though hydrocarbon solvents are preferred. This observation has the obvious advantage of operating polymerization process using lower purity, less expensive ethylene.

Copolymerizations of ethylene with α-olefins as well as polar monomers were also reported with these catalysts.[176] Copolymerization of ethylene with polar monomers where the functional group is in conjugation with olefinic bond was not successful. This was explained as due to the blocking of vacant coordination site by a chelation mechanism. But copolymerizations were possible for monomers in which vinyl unsaturation and the functional group were separated by a spacer of two or more methylene units.

Heterogenization of SHOP type catalysts on organic polymers was found to yield high molecular weight poly(ethylene)s with high activity. [177] But the polymers were found to have broad MWD indicating the presence of different active species.

Binuclear nickel – ylide complexes in the presence of phosphine scavengers were also found to be active ethylene polymerization catalysts with activities higher than that of mononuclear complexes. Polymerizations using these complexes in polar solvents such as acetone, tetrahydrofuran, methanol and alcohol/water mixtures were reported . [178,179]

Complex **21**, based on mixed N,O donor chelates, shows low polymerization activity. [180] Use of electron withdrawing substituents or pyrazine donors is essential for polymerization to occur.

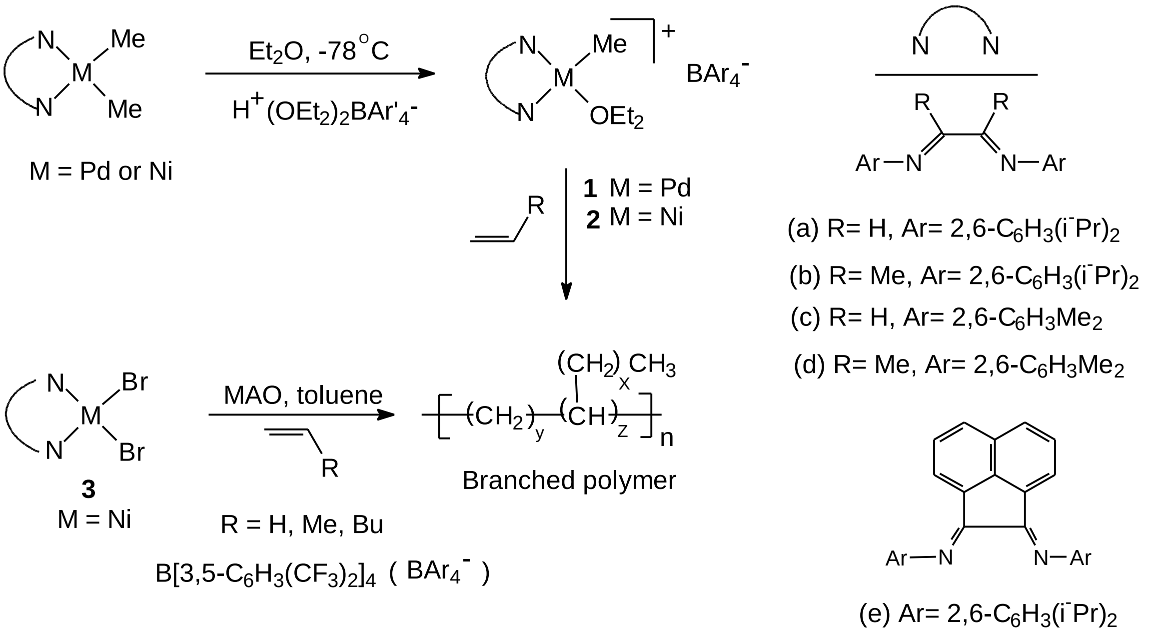


21

X = N, C-NO_2

R = *o*-$CH_3C_6H_4$

But a real breakthrough in the area of Ni and Pd catalyzed olefin polymerization came when Brookhart and coworkers in collaboration with Dupont developed Pd(II) and Ni(II) catalyst systems with bulky diimine ligands for olefin polymerization. Square planar Pd(II) and Ni(II) catalyst systems with 1,4-diazabutadiene derivatives and weakly coordinating anion $[B(C_6H_3\text{-}3,5\text{-}(CF_3)_4]^-$ have been reported for olefin polymerization (**Scheme 1.7**)[181]



Scheme 1.7 Ni and Pd diimine complexes for olefin polymerization

These catalyst systems polymerize ethylene, propylene and other higher α-olefins to high molecular weight polymers.

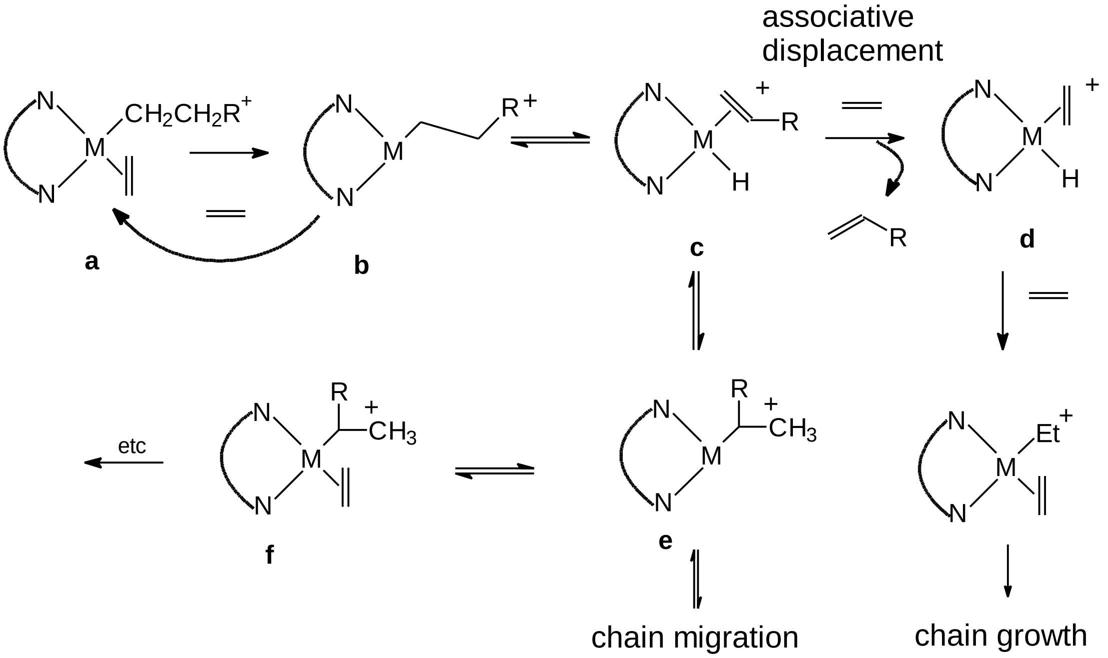
Ethylene polymerizations using these Pd catalysts afford extremely branched poly(ethylene)s. For example, initiator 1b yields polyethylene with 103 branches /1000 carbon atoms.

Active Ni systems can also be obtained by activation of Ni(diimine) dibromide complexes with MAO (Al/Ni ≈1000) which polymerize ethylene, propylene and higher α-olefins. Polyethylene produced by these catalysts range from highly linear to highly branched polymers depending on temperature, pressure and the catalyst structure. Increase in temperature leads to increased branching whereas pressure has an opposite effect. Degree of branching increases with increase of the steric bulk of the substituents on either the aromatic rings of the ligand or the bridge of the two imine moieties.[182,183] Branching tendencies were also found to depend on the cocatalysts. For example, DEAC and TMA activated catalysts generally afford more branched polymers.

The activities of Ni catalysts are very high, comparable to highly active metallocene systems. 3a + MAO shows an activity of 11,000 kg PE/mol Ni.h.atm. Propylene is polymerized by 3e +

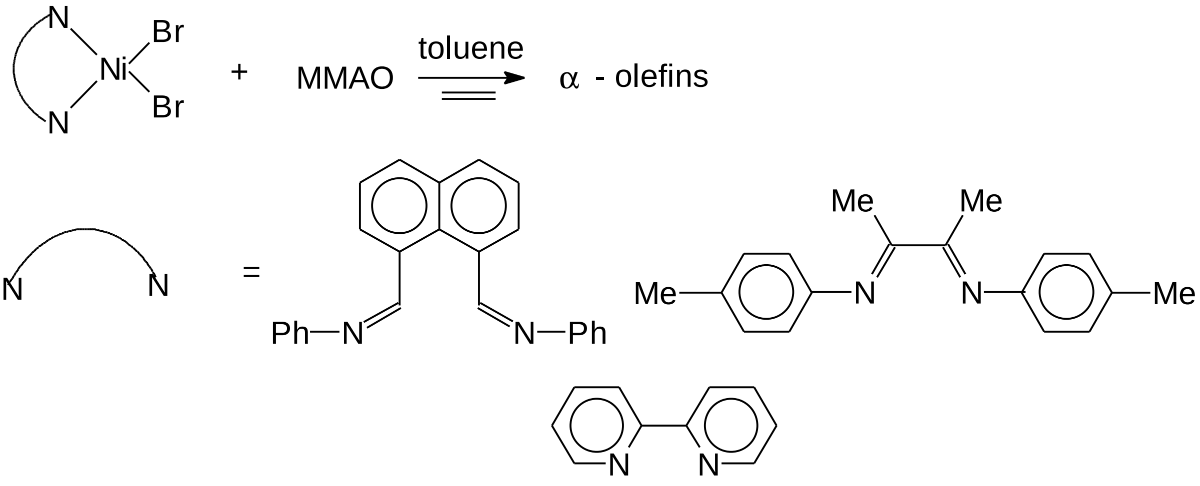
MAO at 0 °C in toluene to produce amorphous polypropylene (126 kg PP/mol Ni.h.atm) while for hexene, 3a + MAO shows a productivity of 176 kg polymer/mol Ni.h. These are the first examples of late transition metal catalysts for the polymerization of propylene and higher α-olefins to high molecular weight polymers.

A polymerization mechanism has been proposed from NMR as well as the kinetics of polymerization (**Scheme 1.8**).



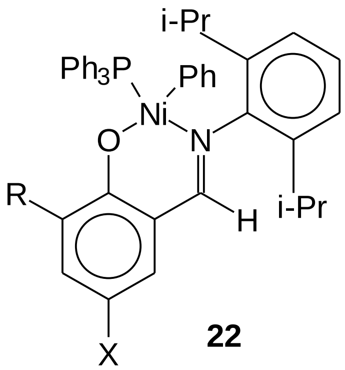
Scheme 1.8 Mechanism of ethylene polymerization

The catalyst resting state is established as an alkyl olefin complex **a**. Rate limiting migratory insertion results in the formation of **b**. Complex **b** can either revert back to **a** following a trapping by ethylene or form an olefin hydride complex **c** after β-hydride elimination. Now the species **c** can reinsert the olefin either 1,2 (giving again **b**) or with the opposite regiochemistry (2,1) generating **e** which if trapped by ethylene followed by insertion would introduce a methyl branch in the growing polymer chain. If this does not happen and chain migration continues via a series of β-hydride elimination and reinsertion steps, longer branches (eg. ethyl, propyl etc) will result. The chain transfer process in these systems is believed to occur by associative exchange of olefin with free ethylene from the species **c** or by alkyl exchange with the Al cocatalyst. The molecular weight of the growing polymer chain is decided by the relative rate of chain propagation against chain transfer. Unlike in most late transition metal systems which normally oligomerize olefins, the rate of associative displacement and chain transfer are greatly retarded by the extreme steric bulk of the diimine ligand. The aryl groups lie roughly perpendicular to the square of the plane of the complex and the bulky ortho substituents restrict the approach of ethylene.



Scheme 1.9 Oligomerization of ethylene using Ni (diimine) complexes

Consistent with this mechanism, complexes with unsubstituted and para substituted aryl α-diimine ligands, resulted in oligomerization of ethylene and dimerization of propylene (**Scheme 1.9**). The activities of these complexes were much higher than SHOP catalysts and α-olefins in C_4-C_{26} range with selectivities as high as 94 % with Shultz – Flory distribution were reported.[184,185]



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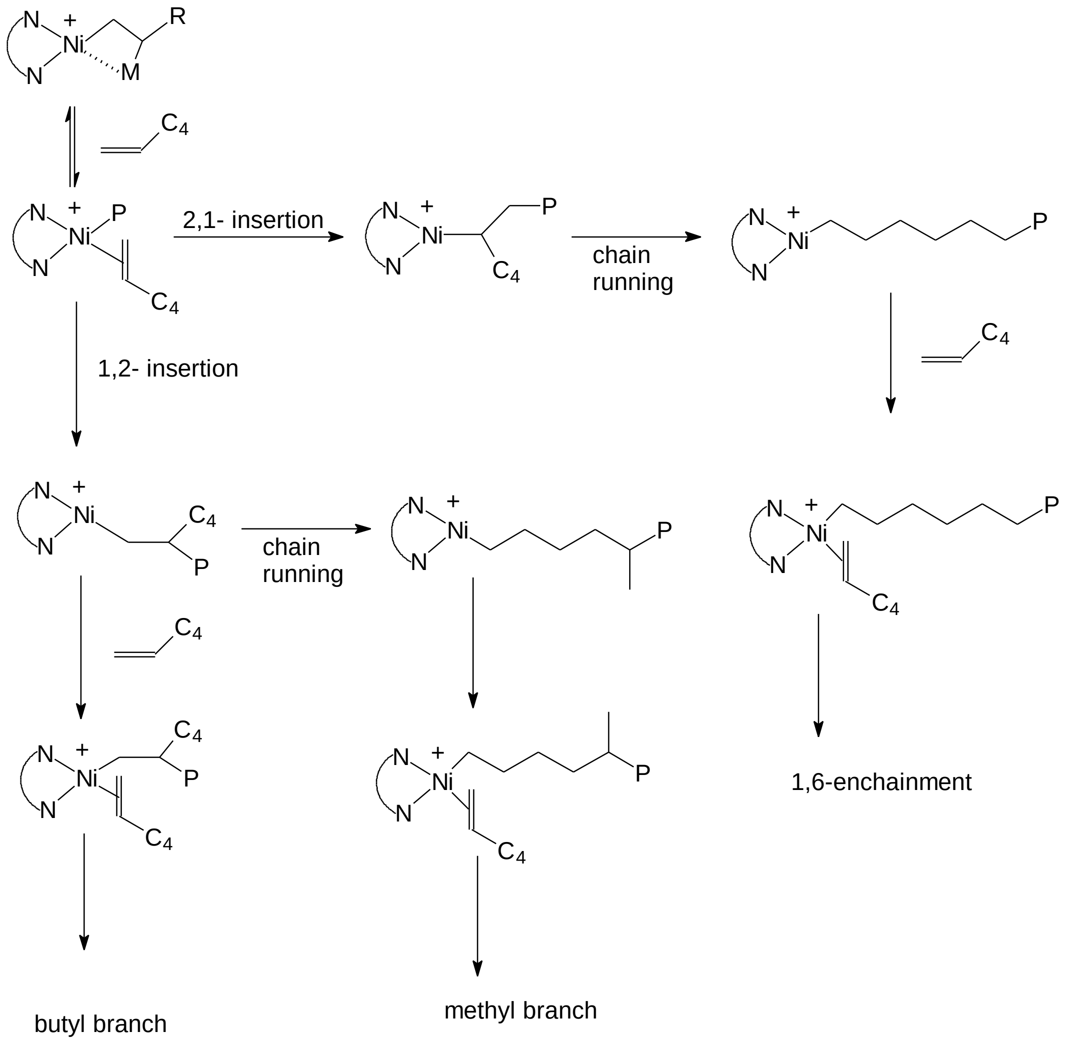
More recently Grubbs and coworkers reported several neutral Ni(II) based catalysts like **22** which were found to be active catalysts for ethylene polymerization in the presence of phosphine scavenger such as $Ni(COD)_2$ or $B(C_6F_5)_3$.[186]

It has been found that complexes with a bulky substituent in the 3-position of the salicylaldiminato ring gave higher molecular weight polyethylene with Mw values 11400 to 54000 and decreased branching. This is explained in the light of mechanism given by Brookhart. The bulky substituent retard the chain migratory processes (which control branching) and the rate of associative displacement (which control molecular weight). As expected at lower temperatures higher molecular weight and decreased branching are observed for the polymers. An electron withdrawing group at 5-position of the salicylaldiminato ring was found to increase the catalyst activity as well as molecular weight. A long induction period was observed suggesting that phophine abstraction is the rate limiting step since an electron withdrawing ligand strengthens the $Ni-PPh_3$ bond. But a broad molecular weight distribution was observed in this case. The activity of the catalyst depends on the electrophilicity of the metal. The neutral Ni(II) complexes may be particularly useful for polymerization of functional monomers compared to more oxophilic cationic metal complexes.

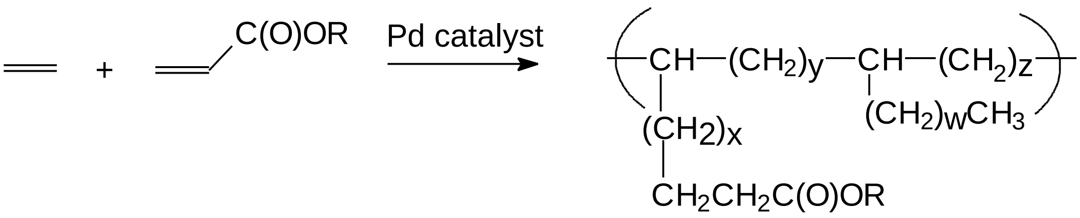
Living polymerization of α-olefins are also possible with Ni(diimine) catalysts.[187] The molecular weight distribution decreases at lower polymerization temperatures. At –10 °C polydispersity of 1.1 was observed suggesting a living polymerization. Block polymers (di and triblock) were also synthesized. A-B-A triblock copolymers of 1-octadecene-propylene-octadecene are elastomeric in nature. The microstructures of these α-olefin polymers are unique in the sense that they have fewer branches than expected from normal 1,2 insertions, and linear unbranched segments are incorporated along the main chain resulting in crystalline domains. The proposed mechanism for α-olefin polymerization is shown in **Scheme 1.10**. During polymerization, a significant fraction of α-olefin insertions occur in a 2,1 fashion. Metal migration to the terminal carbon and subsequent insertion results in enchainment of α-olefins in a 1, ω fashion.

The length of the linear segments increases with the chain length of the α-olefins. The 1,2 versus 2,1 insertion depends on the structure of the catalyst. At low temperature, propylene is polymerized to syndiotactic polypropylene by chain-end control.[188,189] The ^{13}C analysis of the end groups suggests that the regiospecificity of propylene insertion during propagation is prevailingly 1,2.[190]



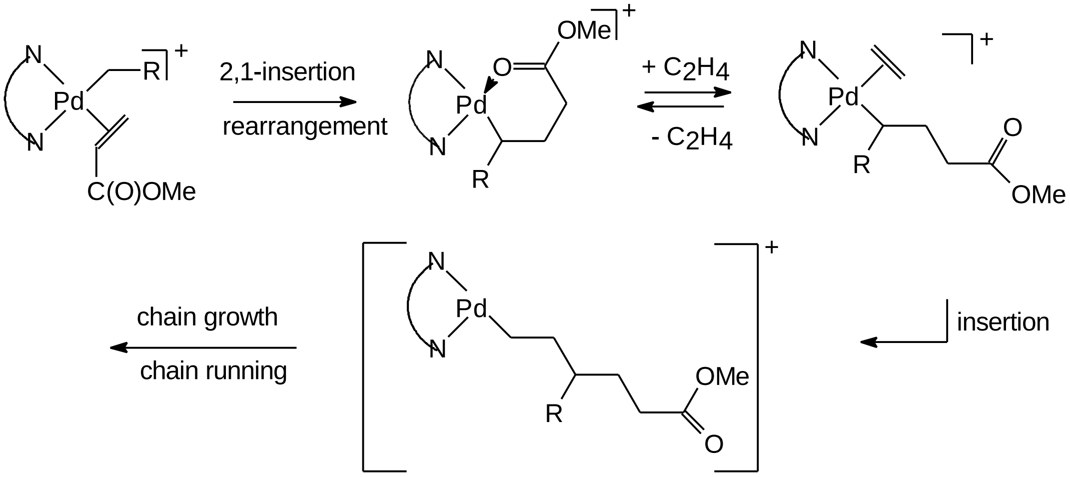
Scheme 1. 10 Mechanism of 1,w polymerization of a-olefins

The coordination copolymerization of α-olefins with readily available and cheap acrylic monomers and carbon monoxide is one of the challenging problems in polymer synthesis. For the early transition metal catalysts these monomers are well known poisons. Late transition metal catalysts are less oxophilic and are expected to be tolerant to hetero atom functional groups in the monomer. Copolymerization of non polar olefins like ethylene and propylene with functional monomers like alkyl acrylates and methyl vinyl ketones have been reported using Pd (diimine) catalysts (**Scheme 1.11**)[191-194]



Scheme 1.11 Copolymerization of ethylene with functional monomers

The copolymers are highly branched, and the acrylate comonomer being incorporated predominantly at the ends of branches as –CH_2CH_2COOMe groups.[193] The NMR studies and the structure of the copolymers support the mechanistic pathway depicted in **Scheme 1.12**



R = polymer chain

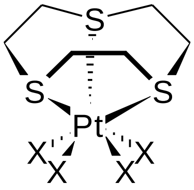
Scheme 1.12 Mechanistic pathway for the formation of poly(ethylene-co-acrylates)

During the copolymerization, a six membered chelate is formed after insertion of MA. Chain grows after coordination and insertion of ethylene.

Copolymers of carbon monoxide with α-olefins have several advantages. First, carbon monoxide is inexpensive and available in plenty. Second, these polymers will be biodegradable due to the presence of keto group in the polymer chain. Third, since the carbonyl group can be chemically modified polyketones can be used as precursors for other functional polymers. First alternating copolymer of ethylene with carbon monoxide was synthesized using Ni catalysts. Sen and coworkers discovered that some cationic palladium compounds catalyze this alternative copolymerization, giving polyketones.[195-197] But the breakthrough in this field came when Drent and Budzelaar found that Pd complexes with bidentate tertiary phosphine chelating ligands are highly active for this type of copolymerization.[198] This subject has been extensively reviewed recently.[199,200] Ethylene-CO copolymers are white crystalline solids with high melting points (Tm ≈ 260 °C) which are difficult to process. Terpolymers containing small amounts of propylene (about 6 %) show reduced melting transition (Tm ≈ 225 °C) and a much favorable behavior in blow molding or in extrusion applications. This new group of semicrystalline thermoplastics which exhibits polyamide 6-like properties are supplied by SHELL under the trade name Carilon and by BP under the trade name Ketonex. A higher content of α-olefins leads to elastomeric polyketone.[200] Optically active alternating copolymer of α-olefin and carbon monoxide can be obtained by using chiral palladium complexes as catalysts.[201,202]

Theoretical studies have been performed on these diimine catalysts.[203-210] The results corroborate the crucial role of axial steric protection in the formation of high molecular weight polymers. The development of these catalysts, both in terms of ligand modification and new activation pathways, continues apace.[211,212,213]

Recently Longo et al. examined simple Ni complexes and found them to be active for polymerization.[214] Cp_2Ni was found to be highly active producing high molecular weight polyethylene. $Ni(acac)_2$ was also found to be moderately active. One example of a platinum(IV) catalysts has been reported.[215] Trithiacyclononane-supported complex (**23**) shows a moderate activity of 12 g $mmol^{-1}h^{-1}bar^{-1}$ for the polymerization of ethylene when activated with MAO. But the details have not been reported.



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1.3.4 Patent literature

The Ni and Pd diimine catalysts have been developed by Dupont in collaboration with the University of North Carolina, and a number of patents have been granted to them. Dupont is actively pursuing the commercial exploitation of these catalysts (Versipol). The iron and cobalt catalysts have been developed simultaneously by Dupont and BP chemicals (in collaboration with Imperial College, London). **Table 1.1** summarizes the representative patents concerning these classes of late transition metal catalysts.

1.4 Conclusion

The last 15 years has witnessed tremendous technology advancement in the area of single site catalysts for olefin polymerization. Metallocenes based on group 4 metals dominated the area of olefin polymerization catalysis and commercial exploitation of these catalysts has just begun. However, the search for new catalyst systems is far from over. Some of the recent developments have occurred with late transition metal systems. The catalyst systems based on late transition metals provide an opportunity to synthesize functional polymers due to their lower electrophilicity. In conclusion, the search for new catalyst systems with higher activities and capable of producing new polymers with better properties is continuing.

Table 1.1 Description of new generation late transition metal catalysts in the Patent literature

CA. No. and Year	Patent No. and Company Name	Olefin/Comonomer	Catalyst/Cocatalyst	Features
(1999)	US 5,866,663 Dupont / UNC	Ethylene/ cyclopentene/CO/ acrylates/vinyl ketone/ pentenoates/norbornene/	Metal = Ni, Pd, Ti,Zr,Sc,Cr,V,Co,Fe Ligand = diimines, allyl anions etc/ Cocatalyst =MAO	Linear and branched polyethylene; block copolymer; poly(cyclopentene) with 1,3-linkage;synthesis of polyketones; functional polyolefins
130:237997 (1999)	US 5,880,241 Dupont / UNC	Ethylene/cyclic and acyclic olefins/functional monomers	Numerous catalysts are disclosed. Ni(II) diimine derivatives with unsubstituted aryl groups	Branched polyolefins; Oligomerization of ethylene to C_{4-40} linear α-olefins; living polymerizations
(1999)	US 5,880,323 Dupont	Ethylene	Ni and Pd diimine complexes	Control of degree and type of branching; oligomerization of ethylene to α-olefins
(1999)	US 5,916,989 Dupont / UNC	Ethylene/α-olefins/cyclic olefins/olefinic esters and carboxylic acids	Ni(diimine) complexes	Oligomerization; synthesis of block copolymers; functional polyolefins
(1999)	US 5,891,963 Dupont/UNC	Ethylene/α-olefins/olefinic esters	Ni and Pd diimine complexes	Branched polyethylene; copolymers of ethylene with olefinic esters (incorporation upto 40 mol %)
(1999)	US 5,886,224 Dupont/UNC	Ethylene/cyclic olefins/olefinic esters	Ni complexes	Copolymerization of ethylene with various comonomers; Synthesis of linear α-olefins

(1999)	WO 99/30822 Exxon Research and Engineering Company, US		Group 11 metal complexes with nitrogen containing bidentate ligands	Co,Ag,Au metal complexes for olefin polymerization
130: 82010 (1999)	US 5852145 Dupont	Ethylene/ α-olefin/ cyclopentene	Ni and Pd diimine complexes	In situ synthesis of catalysts
130: 252793 (1999)	WO 99/12981 BP Chemicals Limited, UK	Ethylene	Fe and Ru bis(imino)pyridyl catalysts/MAO	Activity 480g/mmol.h.
130:197106 (1999)	WO 99/10391 Dupont	Ethylene	Ni(diimine) and group 4 metallocene/MAO	Broad molecular weight distributed polyethylene
130: 282493 (1999)	WO 99/15569 Phillips Petroleum Company,USA	Ethylene/ α-olefins	Ni(0)diimine/MAO	Slurry polymerization; High molecular weight polyolefin
130:297124 (1999)	JP 11092521 Idemitsu Petrochemical Corporation Ltd,Japan	Ethylene	Ni N,N'-bis(2,6-diisopropylphenyl)ethanediimine complex dibromide/ $Me_2AlOAlMeOAlMe_2$	IV = 2.8 dL/g;Tm = 131; activity = 53.7 Kg PE/g Ni.h
130:325487 (1999)	JP 11106424 Idemitsu	Ethylene	Ni N,N'-bis(2,6-diisopropylphenyl)ethanediimine complex dibromide/ $[C_6H_5NH(CH_3)_2]B(C_6F_5)_4$/ TMA	IV = 2.75 dL/g;Tm = 123 °C; Mw = 19.7×10^4; activity = 100.8 kg PE /g Ni
128:90888 (1998)	US 5,811,379 EP 906348	Olefins (C_{3-20})	Ni and Pd catalysts	Polyolefins with average ethylene sequence length of 1-3, at least 5

	WO 97/48741 Exxon Chemical Patents. Inc.			branches/1000 C, and terminal unsaturation; lubricant and fuel oil additives
126:199931 (1998)	US 5,714,556 EP 835269 WO 97/02298 Dupont	Ethylene/norbornenes/ styrenes	Various Ni complexes	Styrene-norbornene copolymer; syndiotactic rich polystyrene
129:331168 (1998)	WO 98/47933 Eastman Chemical Company	Ethylene/propylene	Ni,Pd,Co or Fe metal complexes with bidentate ligands	Novel catalysts are disclosed
129:261037 (1998)	WO 98/40420 Eastman Chemical Company			Novel ligands for catalyst synthesis
129:261023 (1998)	WO 98/40374 Eastman Chemical Company	Ethylene/propylene/olefinic esters/vinyl ethyl carbonate	Ni complexes with bidentate ligands	Functional polyolefins; copolymerization of ethylene with α-olefins; low Mw resins as waxes
129:149362 (1998)	WO 98/30609 Dupont	Ethylene/propylene/styrene/ norbornene/functional olefins	Ni(II) complexes with monoanionic ligands	Synthesis of novel ligands are described; isotactic rich polystyrene
129:149375 (1998)	WO 98/30612 Dupont UNC	Propylene	Fe bis(imino)pyridyl catalysts/MAO	TOF = 1.1×10^3/h; MWD = 1.4; Isotactic rich PP
129:217041 (1998)	WO 98 37110 Eastman Chemical Company	Polar monomers like 2,2-dimethyl-4-vinyldioxolane, vinylethylene carbonate	Pd (diimine) catalysts	Homo and copolymerization of polar monomers with ethylene and propylene

129:149363 (1998)	WO 98/30610 Dupont/UNC	Ethylene	Ni(II) complexes with phosphine containing alkyl sulphonamides	Low molecular weight polyethylene
	WO 98/27124 Dupont	Ethylene	Fe,Co bis(imino)pyridyl catalysts/MAO	Broad molecular weight distributed and highly crystalline polyethylene
130:4185 (1998)	WO 98/49208 BP Chemicals Ltd, UK	Ethylene	Ni or Pd catalysts	-
128:141183 (1998)	WO 98/03559 EP 914354 Dupont	Ethylene, α-olefins, cylcopentene	Ni and Pd diimine complexes	Branched polyolefins; poly(cyclopentene)
128:141181 (1998)	WO 98/03521 EP 920436 Symyx Tech.,USA	Ethylene	Libraries of supported and unsupported Ni(diimine) complexes	Combinatorial synthesis
130:66907 (1998)	WO 98/56832 Dupont	Ethylene	Preformed Ni(dimine) catalysts	Solid catalysts for gas phase polymerization
129:331169 (1998)	WO 98/47934 UNC	Ethylene/α-olefins/ styrene/norbornene	Ni complexes with t-butyl substituted phosphine	Branched polyethylene;copolymers of ethylene with styrene(8.3 mol %),norbornene(8-85 mol %) and norbornene diester
130:82005 (1998)	JP 10330415 Mitsui	Hexene	Ni(diimine) and Ti amide complexes/MAO	IV = 0.78 dL/g; MWD = 4.6 Broad MWD
129:122982	JP 10182679	Ethylene	Ni(diimine) catalysts/MAO	Rubber like polymer; activity = 136 kg PE/mol Ni.h; Mw = 44,000

(1998)	Mitsui			
129:136645 (1998)	JP 10195128 Mitsui	Ethylene	Ni(dimine) catalysts/TEAL	Polymn. activity 122 kg PE/mol Ni.h.
129:261401 (1998)	JP 10245455 Sumitomo Chemical Corporation Ltd, Japan	Ethylene	Ni(diimine)/MAO	Blend of polypropylene and branched polyethylene prepared with Ni catalysts for better properties and processability
128:217753 (1998)	JP 10060045 Asahi Chemical Industry Co., Ltd., Japan	Ethylene	N,N'-bis(o-triisopropylsilylphenyl)(1,8-naphthylene)-1,4-diaza-1,3-butadienenickel dibromide/MAO	Branched polyethylene; catalytic activity 1.3×10^7 g PE/mol Ni.h, and Mw/Mn = 2.4
128:61919 (1997)	JP 09302019 Mitsui	Ethylene	Ni(diimine)/MAO	Activity = 1290 Kg PE/molNi.h
128:61920 (1997)	JP 09302021 Mitsui	Ethylene	Silica/Ni(diimine)/MAO	Activity = 5120 Kg PE/molNi.h
128:61918 (1997)	JP 09302020 Mitsui	Ethylene	Ni(diimine)/TIBAL/MAO	Activity = 4800 g PE/mmolNi.h
127:359236 (1997)	JP 09272709 Mitsui	Ethylene/propylene	[1-octene, Ni(dimine),MAO]/ MAO	Method for storage of Ni catalyst with reduced loss of catalyst activity.
127:176850 (1997)	JP 09194525 Ube Industries, Ltd., Japan	Ethylene	Dibromo(2,9-dimethyl-1,10-phenanthroline)nickel/MAO	6.85 kg PE/mmol Ni.h.atm; Mw = 53,000 and MWD = 2.8.
125: 222773	WO 96/23010	Ethylene/acyclic/cyclic	Ni and Pd diimine	Polymerization;oligomerization;living

(1996)	Dupont / University of North Carolina (UNC)	olefins/various functional monomers	complexes/MAO	polymerization; functional polyolefins; branched polyethylene; Largest patent ever with 562 claims!!
128:89234 (1997)	WO 97/48735 EP 906343 Exxon Chemical Patents Inc.	Ethylene	Ni(diimine) and metallocene/MAO	Polyethylenes with bimodal distribution
128:89236 (1997)	WO 97/48737 Exxon Chemical Patents, Inc.	Ethylene	Ni(diimine)/MAO	Supercritical phase polymerization at high pressure; Branched polyethylene
127:319388 (1997)	WO 97/38024 Mitsui Petrochemical Industries Ltd. Japan	Ethylene	Group 4 metallocene or Mg-Ti catalyst and Ni,Pd catalysts	Broad molecular weight distributed polyolefins

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CHAPTER 2. SCOPE AND OBJECTIVES

2.1 Introduction

The discovery of transition metal catalysts in conjunction with aluminium alkyls for olefin polymerization by Ziegler and Natta in 1955 laid the foundation for today's polyolefin industry.[1] The distinctive feature of Ziegler-Natta (Z-N) catalyst is its extraordinary stereospecificity close to that of enzymes in some cases. Intense research in this area resulted in a series of generations of catalysts with considerable improvement in activity as well as stereospecificity.[1] However, the complex and multisited nature of these heterogeneous catalysts hindered their detailed molecular characterization as well as rational modifications.

Homogeneous metallocene catalysts, which polymerize ethylene in conjunction with aluminium alkyls were known from 1957.[2,3] But these catalysts showed poor activity for ethylene and were inactive for propylene polymerization. This situation changed dramatically in the early 1980's when Kaminsky and Sinn discovered that partially hydrolyzed TMA (or methyl aluminoxane, MAO) alongwith group 4 metallocenes were highly active catalysts for the polymerization of ethylene and α-olefins.[4] This discovery stimulated a renaissance in Z-N catalysis, both in industry and academics.

These uniform site metallocene catalysts have provided new insights into the mechanistic and kinetic aspects of Z-N polymerization. A wide range of tailor-made materials could be synthesized by appropriate ligand tuning. Metallocene catalysts, which polymerize most vinyl monomers, now allow creation of new materials with improved properties. Narrow molecular weight distribution, tacticity control, uniform comonomer distribution, control over molecular weight and polymer structure are the salient features of metallocene catalyzed polymerization.[5]

In the recent past several "single site nonmetallocene catalysts" have emerged as potential catalysts for olefin polymerization. The best known is the Brookhart catalysts, which are Ni and Pd catalysts with diimine ligands.[6] These catalysts produce *narrow polydispersity branched* (SCB and LCB) ethylene polymer from a single monomer viz. ethylene. These late transition metal catalysts are more tolerant to heteroatom functionality in monomers and have the potential for polar monomer incorporation.[7] Block copolymers are also possible with these catalysts.[8] The most important aspect of these catalysts is the control of molecular weight by changing the bulkiness of substituents in the ligand.

More recently iron and cobalt catalysts based on 2,6-bis(arylimino) pyridyl ligands have been reported which shows extremely high activity for ethylene polymerization and lead to high molecular weight poly(ethylene)s.[9,10] The iron(II) bis(imino) pyridyl catalyst produces prevailingly isotactic poly(propylene) with narrow molecular weight distribution.[11,12] In contrast to Ni catalysts the bis(imino) pyridyl Fe(II) complexes produce *broad polydispersity linear* poly(ethylene)s. The molecular weight of the polymer can be controlled by changing the bulkiness of substituents in the ligand.

2.2 Objective of the present work

The objective of the present work was to study the homo and copolymerization of vinyl monomers using several "single site catalysts".

1 Syntheses of ethylene-styrene copolymers have been made possible only recently with metallocene catalyst.[13] Among the various catalysts Constrained Geometry Catalysts have been found to be extremely effective and upto 90 mol % styrene could be incorporated into poly(ethylene) chain without the formation of homopolymer impurities. Due to its more nucleophilic character, styrene strongly coordinates with the catalytic site and furthermore its rate of insertion is slow, presumably, on account of steric hindrance. The objective of the present work was to study the copolymerization of ethylene with styrene, allylbenzene and 4-phenyl-1-butene. Our intention was to separate the bulky phenyl group from the double bond and study the effect of methylene spacer on its copolymerization behavior with ethylene. Metallocene catalysts, Ni(diimine) catalysts and iron(II)bis(imino) pyridyl catalysts were used for copolymerization.

2 Silicon containing polymers are important due to their special properties. Another objective of the work was to explore the copolymerization of ethylene with various silicon containing monomers. Trimethylvinylsilane and allyltrimethylsilane were

used as comonomers. Since a silyl group is known as a "masked hydroxyl group" which can be generated by oxidative cleavage of silicon-carbon bond, poly(ethylene) containing silyl groups may be considered as precursors for functional polyolefins. [14] Ethoxydimethylvinylsilane and vinylpentamethyldisiloxane were also used as comonomers to explore the feasibility of direct copolymerization of ethylene with monomers containing silyloxy group with Si-O-Si linkage. Apart from metallocenes, late transition metal catalysts based on Ni(diimine)catalysts and iron(II)bis(imino) pyridyl catalysts were used for copolymerization.

3 Iron(II)bis(imino) pyridyl catalysts have been reported to produce linear poly(ethylene)s with broad molecular weight distribution and poly(propylene)s with narrow molecular weight distribution, when activated with MAO or modified MAO. [9] Polydispersity of polymers produced by transition metal catalysts is a consequence of its electronic state (single or multiple sites) as well as the nature of transfer reactions. Both these factors are intimately affected by the nature of the activator, namely, the organoaluminium compound. Study of the effect of different cocatalysts on kinetics of ethylene polymerization as well as polymer properties with special emphasis on molecular weight distribution is another objective of the work. Effect of cocatalyst and solvent on ethylene polymerization using a Ni(diimine) catalyst is also another objective.

2.3 References

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CHAPTER 3. EXPERIMENTAL METHODS

3.1 Introduction

All the catalysts used viz., metallocenes, nickel (diimine) and iron bis(imino) pyridyl catalysts are sensitive to air and/or moisture and the active centers in Ziegler-Natta polymerizations are susceptible to termination by protic sources. Hence, all the reagents and solvents should be carefully purified and dried prior to use. All manipulations of air- and/or moisture-sensitive compounds were performed using high vacuum or Schlenk techniques. All manipulations involving solid, air and moisture sensitive compounds were performed inside an inert atmosphere glove box (Labconco model 50004 and M. Braun/labmaster 100) continuously purged with high purity nitrogen from a generator (Spantech model NG 300-1, England). Argon and nitrogen were purified by passage through columns of 4 Å and 3 Å molecular sieves.

In this chapter, materials used, purification and drying of reagents, synthesis of catalysts, polymerization methods and polymer characterization techniques used in the present study are discussed.

3.2 Materials used

Table 3.1 List of chemicals

Name of chemical	Formula/Abbreviation	Grade/purity	Source
Acenaphthenequinone		Tech.	Aldrich, USA
Acetone	CH_3COCH_3	AR	S.d.fine.chem.Ltd. India.
Allyl benzene	$CH_2=CHCH_2C_6H_5$	98 %	Aldrich
Allyl bromide	$CH_2=CHCH_2Br$	99 %	Aldrich
Allyltrimethylsilane	$CH_2=CHCH_2Si(CH_3)_3$	99 %	Aldrich
Benzophenone	$(C_6H_5)_2CO$	99 %	Aldrich
Benzyl bromide	$C_6H_5CH_2Br$	98 %	Aldrich

Bis(n-butyl) cyclopentadienyl zirconium dichloride	$(n\text{-}BuCp)_2ZrCl_2$		Witco Gmbh, Germany.
rac - ethylene bis(indenyl)zirconium dichloride	*rac*-$Et(Ind)_2ZrCl_2$		Witco
Bromobenzene	C_6H_5Br	99+ %	Aldrich
n-Butylchloride	$CH_3CH_2CH_2CH_2Cl$	99 %	Aldrich
Calcium hydride	CaH_2	95%	Aldrich
Chloroform	$CHCl_3$	LR	S.d.fine.chem.Ltd. India.
Dicyclopentadiene			Aldrich
Decalin	$C_{10}H_{16}$	99+%, anhydrous	Aldrich
2,6-diacetylpyridine		>98%	Fluka A. G., Switzerland
1,2-dichlorobenzene	$C_6H_4Cl_2$	ExtrapureAR	SISCO, India.
Dichlorodimethylsilane	$(CH_3)_2SiCl_2$	99 %	Aldrich
Dichloromethane	CH_2Cl_2	LR	Merck, India.
Diethylaluminiumchloride	$(C_2H_5)_2AlCl$ or DEAC		Schering A-G, Germany.
Diethylether	$(C_2H_5)_2O$	LR	S.d.fine.chem.Ltd. India.
2,6-diisopropylaniline		90%	Aldrich

1,2-dimethoxyethane	$C_2H_4(OCH3)_2$/DME	99+ %	Aldrich
Dimethyl ethoxy vinyl silane	$CH_2=CHSi(CH_3)_2(OEt)$	98 %	Aldrich
Ethanol	C_2H_5OH	Commercial	S.d.fine.chem.Ltd. India.
Ethylene	$CH_2=CH_2$	Polymerizn. Grade. H_2O content < 4ppm O_2 content < 3 ppm	C_2-C_3 Gas Cracker unit of Indian Petrochemical Corp.Ltd., Nagothane, Maharashtra, India
Glyoxal (40% aq.soln)	OHC-CHO	LR	S.d.fine.chem.Ltd. India.
Formic acid	HCOOH	97%	Indian Drugs & Petrochemicals Ltd. India.
Hexane	$CH_3(CH_2)_4CH_3$	AR	S.d.fine.chem.Ltd.India.
Hydrochloric acid	HCl	LR	Ranbaxy, India
Irganox 1010		antioxidant	Ciba-Giegy
Iron(II)Chloride	$FeCl_2$	> 99 % anhydrous	Fluka
Isopropanol	$(CH_3)_2CHOH$	LR	Ranbaxy, India.
Lithium Metal	Li	Rod, 99.9 %	Aldrich
Magnesium turnings	Mg	98 %	Aldrich

Methanol	CH_3OH	AR	S.d.fine.chem.Ltd. India.
Methylaluminoxane	MAO	30 wt % solution in toluene. Me/Al = 1.7 free TMA = 31 wt %. Al content = 10.9 %	Witco GmbH, Germany.
Molecular Sieves(4Å and 3 Å)			S.d.fine.chem.Ltd. India.
Nickel(II)Bromide	$NiBr_2$	Anhydrous, 99.99+ %	Aldrich
Norbornene		99 %	Aldrich
Pentane	$CH_3(CH_2)_3CH_3$	LR	S.d.fine.chem.Ltd. India.
Petroleum Ether		Synthesis	Merck
Phosphorus pentoxide	P_2O_5	AR	S.d.fine.chem.Ltd. India.
Sodium metal	Na	LR	S.d.fine.chem.Ltd. India.
Sodium sulfate	Na_2SO_4	Anhydrous LR	S.d.fine.chem.Ltd. India.
Styrene	$C_6H_5CH=CH_2$	Polymerization grade	Thermax Ltd, Pune, India.

Tetrahydrofuran	THF	Synthesis grade	Merck, India.
Tetraisobutyl dialuminoxane	TIBDAO	20 wt % solution in heptane	Schering A.-G., Germany.
Titanium Tetrachloride	$TiCl_4$	99.995+ %	Aldrich
Toluene	$C_6H_5CH_3$	Sulfur free, LR	S.d.fine.chem.Ltd. India.
1,2,4-Trichlorobenzene	$C_6H_3Cl_3$	Spectrophotometric grade	Merck, India.
Triisobutylaluminium	TIBAL		Witco GmbH, Germany.
Trimethylaluminium	TMA		Schering A.-G., Germany.
Vinylpentamethyl disiloxane	$C_7H_{18}OSi_2$		Gelest, Inc. USA.
Vinyltrimethylsilane	$CH_2=CH\text{-}Si(CH_3)_3$		Gelest, Inc. USA.
Zirconium (IV) chloride	$ZrCl_4$	99.9+ %	Aldrich
Zirconocene Dichloride	Cp_2ZrCl_2	98+ %	Aldrich

3.3 Purification and Drying

All solvents and reagents were purified and dried under dry nitrogen atmosphere by standard procedures.[1] Toluene, n-hexane, n-pentane, diethylether and tetrahydrofuran were distilled from sodium benzophenone ketyl radical. Dichloromethane was dried and distilled from phosphorus pentoxide. 1,2-dichlorobenzene was dried and distilled from calcium hydride and stored over 4 Å molecular sieves.

3.4. Synthesis of Catalysts

3.4.1. Synthesis of $Me_2SiCp_2ZrCl_2$[2]

3.4.1.1. Synthesis of sodium sand

2.3g (0.1 mol) of sodium metal was melted in 45 mL of toluene by refluxing and vigorous stirring for 15 min. After the formation of the sodium sand, toluene was siphoned off using a cannula under nitrogen pressure. The sodium sand was dried under vacuum for 30 min.

3.4.1.2. Synthesis of sodium cyclopentadienylide

130 mL of freshly distilled tetrahydrofuran was added into the sodium sand and 35 mL (0.28 mol) of cyclopentadiene was directly distilled into it over a period of 45 min. The mixture was stirred till all the sodium was dissolved. THF was removed under vacuum to obtain a slightly yellow colored sodium cyclopentadienylide. Sodium cyclopentadienylide is very sensitive to moisture and light. Therefore, the next step was carried out immediately.

3.4.1.3. Synthesis of Lithium salt of dimethylsilylcyclopentadiene

100 mL of freshly distilled dry THF was added to sodium cyclopentadienylide followed by dropwise addition of 6.4 mL (0.05 mol) of dichlorodimethylsilane at –78 ºC. The reaction mixture was vigorously stirred for 1 h, allowed to warm to room temperature and stirred for 4 h. The flask was again cooled to –78 ºC and 50 mL (0.1 mol) of 2 M n-butyllithium in hexane was added dropwise. The reaction mixture was allowed to warm to room temperature and was stirred for 3 hours.

3.4.1.4. Synthesis of $ZrCl_4$.THF adduct

12.03 g (0.05 mol) of $ZrCl_4$ was taken in a 100 mL round bottomed flask and 100 mL of THF was added dropwise at –78 ºC. The temperature was then allowed to rise slowly to 0 ºC and the reaction mixture was stirred for 1 h.

3.4.1.5. Synthesis of the metallocene

The lithium salt was transferred to the $ZrCl_4$.THF adduct through a cannula over a period of one hour. The reddish brown solution thus obtained was stirred overnight and then heated at 50 ºC for 2 h. The solvent was then removed by vacuum. A reddish brown mass was obtained to which

50 mL of dry pentane was added and stirred for 1 h. The pentane was syringed out and the residual mass was vacuum dried. It was then soxhlet extracted with dichloromethane. The yellow colored solution was concentrated and then cooled in refrigerator to get pale green crystals. It was purified by recrystallization from dichloromethane. The yield was 10 % based on $ZrCl_4$.

^1H NMR ($CDCl_3$) 6.97 (s, 4H, $-C_5H_4$), 5.97 (s, 4H, $-C_5H_4$) and 0.75 (s, 6H, $(CH_3)_2Si$).

Elemental anal. calculated for $C_{12}H_{14}SiZrCl_2$: C, 41.36; H, 4.05. Found: C, 41.11; H, 4.23

3.4.2. Synthesis of $Me_2SiCp_2TiCl_2$[2]

3.4.2.1. Synthesis of $TiCl_4$.THF adduct

10.05 g(0.053 mol) of $TiCl_4$ was taken in a 500 mL three-neck, round bottomed flask and 100 mL of THF was added dropwise at –78 ºC. The temperature was then allowed to rise to 0 ºC and the reaction mixture was stirred for 1 h.

3.4.2.2. Synthesis of the metallocene

The dilithiosalt (prepared according the procedure mentioned in **Section 3.4.1**) was slowly added to the $TiCl_4$.THF adduct through a cannula over a period of 1 h. The reddish brown solution was stirred overnight at room temperature and then refluxed for 1 h. The solvent was removed by vacuum. The reddish brown residue was washed twice with 30 mL portions of dry pentane and stirred for 1 h. The pentane-insoluble product was dried and extracted with chloroform. Large dark red-brown crystals of $Me_2SiCp_2TiCl_2$ were obtained by recrystallization from dichloromethane. The yield was 22 % based on $TiCl_4$.

Elemental anal. calculated for $C_{12}H_{14}SiTiCl_2$: C, 47.24; H, 4.59. Found: C, 46.97; H, 4.84

3.4.3. Synthesis of 2,6-bis[1-(2,6-diisopropylphenylimino)ethyl]pyridine Iron(II)chloride[3]

3.4.3.1. Synthesis of 2,6-bis[1-(2,6-diisopropylphenylimino)ethyl pyridine

In a round bottomed flask, 3.0 g (18.4 mmol) of 2,6-diacetylpyridine and excess of 2,6-diisopropylaniline were dissolved in 50 mL of dichloromethane. To this, sodium sulfate and five drops of 97% formic acid were added and the solution was stirred for two days. The solvent was removed by vacuum. The solid residue was redissolved in dichloromethane and recrystallized by slow evaporation to give a yellow solid. Yield was about 60 %.

^{1}H NMR. 8.5 (d, 2, Py-Hm), 7.95 (t, 1, Py-Hp), 7.1 (m, 6, H aryl), 2.75 (septet, 4, **H**Me$_2$), 2.25 (s, 6, N=CMe), 1.1 (d, 24, CH**(CH$_3$)**$_2$).

Elemental analysis calculated for $C_{33}H_{43}N_3$: C, 82.33; H, 8.93; N, 8.73. Found: C, 82.36; H, 9.41; N, 8.53.

3.4.3.2. Synthesis of the catalyst

The above ligand (1.05eq) and anhydrous iron(II)chloride were weighed into a Schlenk flask inside the drybox and charged with THF. The reaction mixture was stirred for several hours until there were no detectable unreacted salts in the flask. On adding diethylether to the reaction mixture, a dark blue colored complex was precipitated. It was filtered in air, washed successively with diethylether and pentane and dried in vacuum. Yield was 90 %.

Elemental analysis calculated for $C_{33}H_{43}N_3FeCl_2$: C, 65.14; H, 7.12; N, 6.91. Found: C, 64.75; H, 7.61; N, 6.07.

3.4.4. Synthesis of [(N, N'- diisopropylbenzene)-1,4-diazabutadiene]dibromonickel catalyst[4]

3.4.4.1. Synthesis of (N, N'- diisopropylbenzene)-1,4-diazabutadiene

In a 100 mL round bottomed flask, 20mL of methanol and a few drops of formic acid were added. 7 mL (34.5 mmol) of 2,6-diisopropylaniline was added to it and the flask was cooled to 0 ºC. To this, 2.5 mL (17.25mol) of glyoxal (40% aqueous solution) was added dropwise. After 5-10 min, a yellow precipitate was formed and the reaction mixture turned yellow. It was stirred overnight. The precipitate was filtered and washed with cold methanol. The compound was recrystallized from hexane/methanol mixture and redissolved in hexane to which methanol was added and kept in a freezer. Crystals of the compound were collected in a Buchner funnel and washed with cold methanol and dried. Yield, 62 %; Melting point 107 ºC (literature[5] mp 104 ºC)

^{1}H NMR. 8.1 (s, 2, CH=N), 7.2 (m, 6, H aryl), 2.9 (m, 4, CHPh), 1.25 (d, 24, CH(C**H**$_3$)$_2$)

Elemental analysis calculated for $C_{26}H_{36}N_2$: C, 82.97; H, 9.57; N, 7.45. Found: C, 83.30; H, 10.17; N, 7.33.

3.4.4.2. Synthesis of Dibromo(1,2-dimethoxyethane)nickel(II)

In a 100 mL round bottomed flask, 2 g of nickel(II)bromide and 20 mL of anhydrous ethanol were added. The homogenous green solution was stirred under reflux for 2 hours. The anhydrous ethanol solution was evaporated to the stage of incipient crystallization at the boiling point and diluted with 15 mL of 1,2-dimethoxyethane (dried over lithium aluminium hydride). A pink colored precipitate formed, was collected and washed successively with anhydrous 1,2-dimethoxyethane and dried under vacuum.

3.4.4.3. Synthesis of the catalyst

0.787 g (2.55 mmol) of $(DME)NiBr_2$ complex was taken in a round bottomed flask. 20 mL of dichloromethane was added through a cannula. The dried DAB ligand (980 mg, 2.61 mmol) dissolved in dichloromethane was transferred into the flask through a cannula. A reddish brown mixture formed, which was stirred for 24 hours. The solvent was removed by vacuum and the reddish brown mass was washed with 10 mL each of hexane three times. The complex was dried under vacuum and stored in dry box. Yield was 75 %.

Elemental analysis calculated for $C_{26}H_{36}N_2NiBr_2$: C, 52.47; H, 6.1; N, 4.7; Ni, 9.75; Br, 26.85. Found: C, 51.92; H, 6.28; N, 4.49.

3.4.5. Synthesis of [(N, N'- diisopropylbenzene)-2,3-(1,8-naphthyl)-1,4-diazabutadiene) dibromonickel catalyst[4]

3.4.5.1. Synthesis of [(N, N'- diisopropylbenzene)-2,3-(1,8-naphthyl)-1,4-diazabutadiene]

4 mL (21 mmol) of 2,6-diisopropylaniline and 20 mL of methanol were taken in a 100 mL round bottomed flask. 3 g (16.5 mol) of acenaphthenequinone was added slowly to it and was stirred overnight. The reaction mixture was filtered, washed several times with methanol. The solid mass was recrystallized from chloroform-hexane mixture.

^{1}HNMR. 7.9 (d, 2, naphthyl), 7.4 (t, 2, naphthyl), 7.25 (s, 6, H aryl), 6.15 (d, 2, naphthyl), 3.05 (septet, 4, $C\mathbf{H}(Me)_2$), 1.25 (d, 12, $CH(C\mathbf{H}_3)_2$, 1.0 (d, 12, $CH(C\mathbf{H}_3)_2$)

Elemental analysis calculated for $C_{36}H_{40}N_2$: C, 86.4; H, 8.00; N, 5.6. Found: C, 86.54; H, 7.99; N, 5.42.

3.4.5.2. Synthesis of the catalyst

0.750 g (1.5 mmol) of the ligand and 0.440 g (1.43 mmol) of $NiBr_2$(DME) were weighed into a flame-dried Schlenk flask inside a dry box. 20 mL of dichloromethane was added to this mixture. An orange colored solution was formed, which was stirred for 18 hours to obtain a reddish brown suspension. The reaction mixture was allowed to settle and some amount of dichloromethane was removed by means of a cannula. To the resulting mass, dichloromethane was added, stirred for sometime and filtered through a cannula. Thus the product was washed with dichloromethane and the reddish brown complex was dried *in vacuo*. Yield was 700 mg (65 %)

Elemental analysis calculated for $C_{36}H_{40}N_2NiBr_2$: C, 60.12; H, 5.61; N, 3.89. Found C, 59.73; H, 5.35; N, 3.66.

3.5. Polymerization Techniques

3.5.1. Apparatus used for ethylene homopolymerization at one atmosphere pressure

A glass tube of 3 L capacity with a glass jacket, a three-way stopcock and a supporting glass tube was fabricated. The fabricated unit was mounted on a wooden platform. In order to calibrate the fabricated glass apparatus, graph sheets were pasted on the wooden frame. Upon calibration, it was found that one unit on the graph sheet corresponds to 30 mL of ethylene. The calibrated glass tube was used as a gas burette for measuring the differences in displacement of volume of ethylene during the polymerization. A three-neck flat-bottomed jacketed vessel of capacity 100-150 mL was used as the polymerization reactor.

A separating funnel of 4 L capacity filled with paraffin oil was connected to the gas burette through a PVC tubing. The reaction cell was mounted on a magnetic stirrer, which was connected to the gas burette through a T-shaped stopcock using pressure tubing. Two paraffin bubblers were also connected for purging purpose to the reaction assembly and gas burette as shown in the diagram. The reaction cell was dried at 200 °C overnight and thoroughly checked for leaks by running a blank experiment under one atmosphere pressure for 2-3 hours. The paraffin oil was saturated with ethylene gas before starting the experiment.

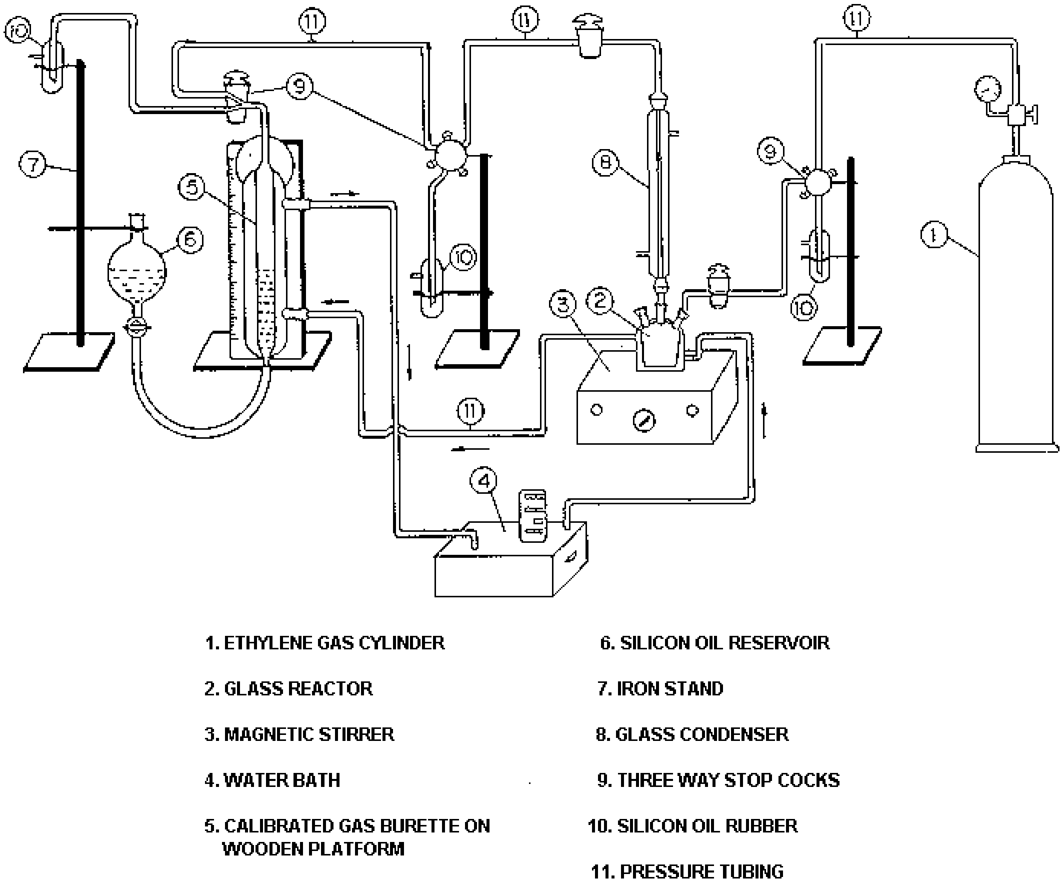

Figure 3.1 Ethylene polymerization set-up at one atmosphere pressure

3.5.2. Homopolymerization of ethylene

Polymerization was performed with the assembly described previously at one atmosphere pressure in toluene, 1,2-dichlorobenzene and dichloromethane. Ethylene was continuously fed to the cell using a gas burette with a reservoir containing paraffin oil. The reaction cell, pre dried at 200 ºC overnight was cooled under ethylene. The gas burette was flushed 2-3 times by passing ethylene. Solvent was introduced into the cell using a hypodermic syringe and saturated with ethylene. Toluene solution of the cocatalyst (MAO, TMA, TIBDAO, TIBAL, DEAC as the case may be) was added. Polymerization was initiated by the addition of the catalyst dissolved in a suitable solvent (toluene was used in the case of metallocenes, and 1,2-dichlorobenzene in the case of iron and nickel based catalysts). The polymerization temperature was maintained by circulating water from a thermostat through the jacket of the cell and the gas burette. Ethylene uptake was measured as a function of time from the gas burette. The reaction was terminated by the addition of acidified methanol (methanol containing 10 % HCl). The polymer was precipitated by the addition of acetone, filtered, washed with acetone and dried at 60 ºC under vacuum.

3.5.3. Copolymerization of ethylene with other comonomers

Copolymerization of ethylene with other monomers was carried out using toluene as diluent at one atmosphere pressure. The polymerization cell was dried at 200 ºC and cooled under ethylene. Ethylene was fed continuously to the cell using the gas burette with a reservoir containing paraffin oil. The burette was flushed 2-3 times by passing ethylene. Solvent was introduced into the cell using a hypodermic syringe. Required amount of the comonomer was then added using a syringe. Toluene solution of the cocatalyst was added and the polymerization was initiated by the addition of the catalyst dissolved in the suitable solvent. The temperature of the polymerization was maintained by circulating water from a thermostat through the jacket of the cell and the gas burette. Ethylene uptake was noted as a function of time using the gas burette. The reaction was terminated by the addition of acidified methanol. The polymer was precipitated by adding acetone, filtered, washed with methanol and dried at 60 ºC under vacuum.

3.6. Characterization techniques

3.6.1. Gel Permeation Chromatography (GPC)

The molecular weights and molecular weight distributions of the polymer samples were determined by high temperature GPC analysis. A GPC instrument, Waters 150C ALC/GPC, equipped with a refractive index detector was employed using μ-styragel columns (10^6, 10^5, 10^4, 10^3, 500Å) and 1,2,4-trichlorobenzene as the solvent at 135 ºC with a flow rate of 1mL/min. Universal calibration method was used for analysis. 1,2,4-trichlorobenzene used was of spectrophotometric grade purchased from Merck. This grade was also prepared in the laboratory by double distillation under vacuum and filtering it through 0.45 μ membrane (Millipore) thrice.

3.6.2. Differential Scanning Calorimetry (DSC)

DSC of the homo- and copolymers were recorded on a Perkin Elmer DSC 7 instrument. The sample was initially heated upto 150 ºC at a heating rate of 10 ºC/min and then rapidly cooled to 50 ºC at a rate of 100 ºC/min. Finally it is again heated at a rate of 10 ºC/min. The melting points reported were that observed in the second heating.

3.6.3. Intrinsic viscosity

Intrinsic viscosities of the polymer samples were determined in decalin at 135 ºC using an Ubbelohde viscometer.

3.6.4. Infra Red Spectra

The IR spectra were recorded on a Perkin Elmer 16PC FT-IR Spectrometer.

3.6.5. NMR Spectra

^{1}H NMR spectra were recorded using a 200 MHz Bruker NMR spectrometer. Deuterated solvents like $CDCl_3$, 1,1,2,2-tetrachlorodideuterioethane were used.

^{13}C NMR spectra were recorded at 120 ºC on a Bruker MSL 300 model spectrometer operating at 75.5 MHz for ^{13}C nuclei. The solution for analysis were prepared by dissolving 150 mg of the polymer in 2 mL of 1,2,4-trichlorobenzene in a 10-mm-o.d. tube containing about 20 % by volume of deuterated benzene for internal lock. The spectra were obtained under conditions permitting quantitative analysis.

3.7 References

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CHAPTER 4. COPOLYMERIZATION OF ETHYLENE WITH AROMATIC VINYL MONOMERS USING HOMOGENEOUS TRANSITION METAL CATALYSTS

CHAPTER 4. COPOLYMERIZATION OF ETHYLENE WITH AROMATIC VINYL MONOMERS USING HOMOGENEOUS TRANSITION METAL CATALYSTS

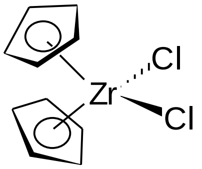
4.1 Introduction

Copolymerization of ethylene with styrene has been achieved recently using homogeneous catalysts, consisting of Ti or Zr compounds.[1-22] Conventional Ziegler-Natta catalysts which efficiently homopolymerize ethylene and styrene, however, provide copolymers with little incorporation of styrene or a mixture of homopolymer and block copolymer products.[23] Styrene incorporation is difficult due to steric and electronic factors.

Several reports on ethylene-styrene copolymerization indicate that depending upon the catalyst structure and polymerization conditions alternating, block, and pseudo random copolymers are formed. Kakugo et al.[1] reported that an alternating ethylene-styrene copolymer could be obtained by using a catalyst based on 2,2’-thiobis (4-methyl-6-tert-butyl-phenoxy)titanium dichloride and MAO. A systematic study of copolymerizations using phenoxy compounds was conducted by Sernetz et al.[2] by varying the bridging unit between the two phenolate moieties of the ligand. In contrast to Kakugo’s conclusions they found that the sulphur bridge is not required for the formation of poly (ethylene-co-styrene). Moreover, they did not observe the formation of alternating copolymer. Oliva et al.[3] reported that cyclopentadienyl titanium trichloride activated by MAO promotes the copolymerization of the two monomers along with mixture of homopolymers. But contrary results were reported by Aaltonen and Seppala.[4] They obtained only a mixture of homopolymers of ethylene and styrene. It has been found that Ti^{3+} leads to the formation of syndiotactic polystyrene and Ti^{4+} is responsible for the copolymerization of ethylene and styrene. The residual TMA present in MAO, in turn, affects the relative concentration of these oxidation states.[5] This may be the reason for the contradictory results reported from different laboratories, as the TMA content varies in different MAO samples.

Later in patents issued to Dow[6] and Exxon several constrained geometry Ti and Zr compounds were claimed to copolymerize ethylene and styrene to give “pseudorandom copolymers”. While Inoue et al.[7] and Jane Ren and Hatfield et al.[8] reported that pseudorandom E-S copolymers can also be obtained using ansa-zirconocene based catalysts such as [isopropylidene(1-

cyclopentadienyl)(9-fluorenyl)]zirconium dichloride-MAO. Synthesis of crystalline alternating copolymer with isotactic structure using C_2 symmetric *rac*-ethylenebis(indenyl)zirconium dichloride has been reported by Oliva et al.[9] A kinetic study was reported later.[10] Similar copolymers were also reported using a cationic compound $[(\eta^1:\eta^5\text{-}C_{13}H_8SiMe_2NCMe_3)TiMe]^+[B(C_6F_5)_4]^-$.[11] Pellecchia et al. reported alternating E-S copolymer with atactic structure using a MAO free half titanocene catalyst.[12] A random ethylene-styrene copolymer of 10-52 mol % styrene content having head to tail styrene chain structure and a highly isotactic ethylene-styrene copolymer structure has been reported recently using bridged zirconocene catalysts.[13]



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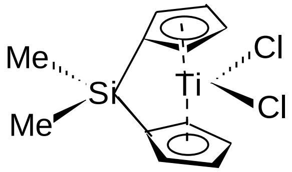

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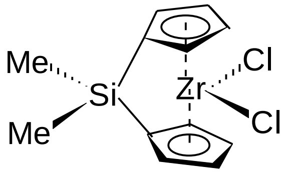

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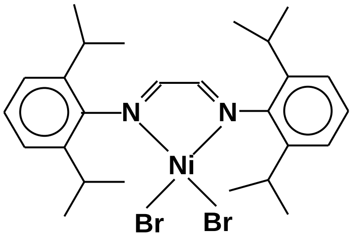

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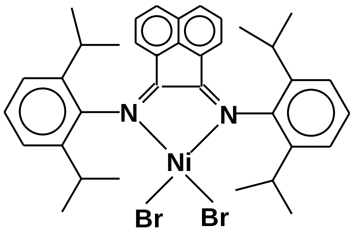

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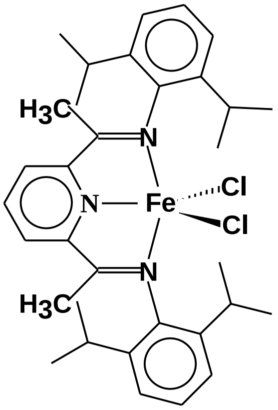

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The results obtained so far suggest that the active species responsible for the copolymerization is different from that responsible for the homopolymerizations of ethylene and styrene. The composition, microstructure, molecular weight and catalytic activity are strongly dependent upon the reaction conditions like comonomer feed ratio, polymerization temperature, catalyst/MAO ratio, TMA content in MAO and the structure of MAO. Due to its more nucleophilic character, styrene strongly coordinates with the catalytic site. Furthermore the rate of insertion is slow, presumably, on account of steric hindrance.

In this chapter we describe the copolymerization behavior of ethylene with styrene, allyl benzene and 4-phenyl-1-butene using different coordination polymerization catalysts. The objective is to separate the bulky phenyl group from the double bond and study its effect on the copolymerization behavior with ethylene. It has been reported earlier that higher styrene incorporation is difficult even with constrained geometry catalysts as the catalyst activity decreases drastically when the comonomer concentration in the feed increases.[14] Another objective of the present study was to find out the behavior of allyl benzene and 4-phenyl-1-butene in this aspect. The following three metallocenes, namely, Cp_2ZrCl_2 (**1**), $Me_2SiCp_2TiCl_2$ (**2**), and $Me_2SiCp_2ZrCl_2$ (**3**) and the recently reported Ni(diimine)[24] (**4** and **5**) and Fe(II)bis(imino) pyridyl catalysts[25] (**6**) were selected for the present study.

4.2 Experimental part

4.2.1 materials

Styrene was purified by vacuum distillation over CaH_2 under argon atmosphere just prior to use. Allyl benzene was prepared from the coupling reaction of allyl bromide and phenyl magnesium bromide. 4-phenyl-1-butene was prepared from the reaction of benzyl magnesium chloride and allyl bromide. Both the comonomers were characterized by ^1H NMR. The procedure for the synthesis of catalysts is given in **chapter 3.**

4.2.2 polymerization

The detailed polymerization procedure and the work up are given in **chapter 3.**

4.2.3 characterization

The molecular weight distributions were determined using a Waters Gel Permeation Chromatograph model GPC/ALC 150C instrument equipped with a refractive index detector and μ-styragel columns (10^6, 10^5, 10^4, 10^3 and 500^oA) at 135 °C and 1,2,4-trichlorobenzene as solvent with 1 mL/min flow rate.

4.3 Results and discussion

4.3.1 metallocenes

4.3.1.1 influence of the type of comonomer

There are a few reports of homopolymerization of allyl benzene, where it is reported to proceed partly via isomerization by cationic and coordination polymerization catalysts. [26,27] Allyl benzene isomerizes to β-methylstyrene under the conditions of polymerization resulting in polymers containing both the units. The FT-IR spectrum of polyallylbenzene prepared with Cp_2ZrCl_2/MAO system is shown in the **Figure 4.1.**

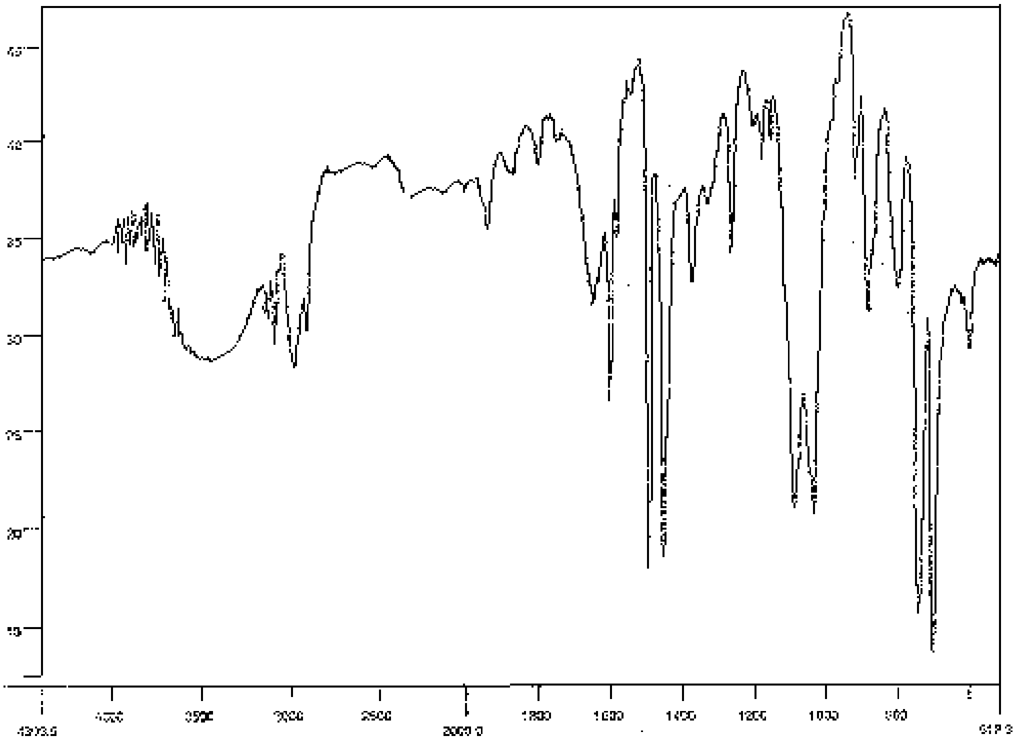


Figure 4.1 IR spectrum of polyallylbenzene prepared with Cp_2ZrCl_2/MAO

It shows the characteristic peaks of poly(allylbenzene) at 3024, 1494, 1452, 738 and 698 cm^{-1}. The peaks corresponding to the methyl group of β-methylstyrene at 2960, 2878 and 1380 cm^{-1}

were absent which indicated that the polymerization of allylbenzene proceeded without isomerization. Moreover the GC analysis of the recovered monomer from polymerization showed the presence of allyl benzene only. A similar conclusion has also been reported in a recent paper.[28]

In order to study the effect of spacer between the double bond and the aromatic ring, copolymerization of ethylene was studied with styrene, allyl benzene, and 4-phenyl-1-butene under identical experimental conditions. The results are shown in **Table 4.1**. The kinetic profiles of ethylene polymerization using different catalysts in the presence of comonomers are shown in **Figures 4.2, 4.3, and 4.4.** The catalyst activity decreases in the presence of the comonomer for all the catalysts. It is observed that the activity is very low in the case of styrene as compared to allyl benzene and 4-phenyl-1-butene. However, in the case of Cp_2ZrCl_2 the initial rate of polymerization is very high when styrene is the comonomer (**Figure 4.2**). In this case the rate of catalyst deactivation is also higher. The high initial rate of polymerization may be due to the difficulty in the accessibility of styrene to the active center since the catalyst is unbridged and, therefore, less open compared to bridged metallocene. Under these conditions, no incorporation of styrene was observed. Similar deactivation has been reported for many catalysts in the copolymerization of ethylene with styrene.[14] Furthermore, it should be noted that allyl benzene and 4-phenyl-1-butene presumably behave as normal α-olefins with a 1,2 insertion, whereas, styrene favors 2,1 insertion.

The IR spectra **(Figure 4.5)** of the copolymers of ethylene with allyl benzene and 4-phenyl-1-butene show the presence of aromatic groups in the polymer (1600 - 1604 and 1492 - 1496 cm^{-1}). The comonomer content in the polymer was analyzed by ^1H NMR spectroscopy. The ^1H NMR spectra of ethylene-4-phenyl-1-butene and ethylene-allyl benzene copolymers are shown in **Figures 4.6 and 4.7** respectively. The extent of incorporation varies in the order 4-phenyl-1-butene > allyl benzene > styrene. From this it is clear that the proximity of the phenyl group to the olefinic bond has an adverse effect on the insertion. Higher incorporation of allyl benzene and 4-phenyl-1-butene is observed when the bridged metallocenes were used, indicating that α-olefin insertion is controlled by the access of the comonomer to the active center. The stereo rigid bridged metallocenes produce a higher coordination angle of the ligands along the Zr-Cl vector.[29]

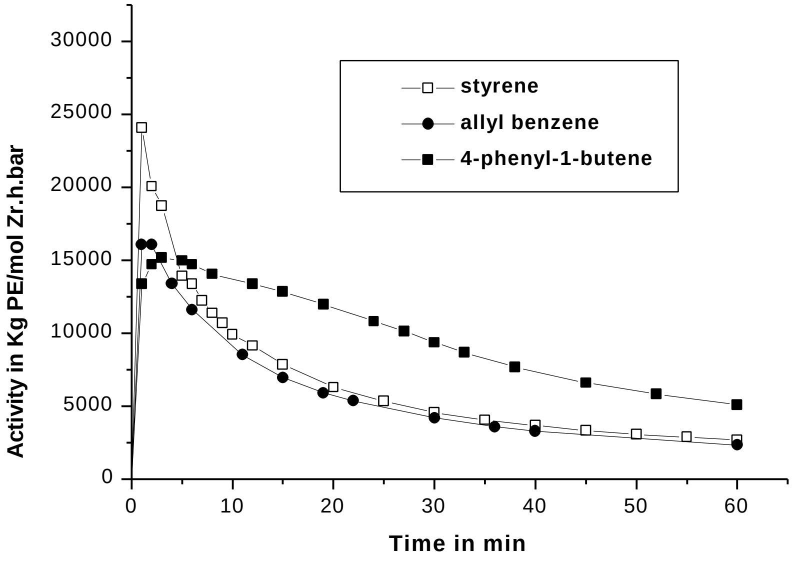


Figure 4.2 Kinetic profile of ethylene polymerization using Cp_2ZrCl_2 in the presence of different comonomers

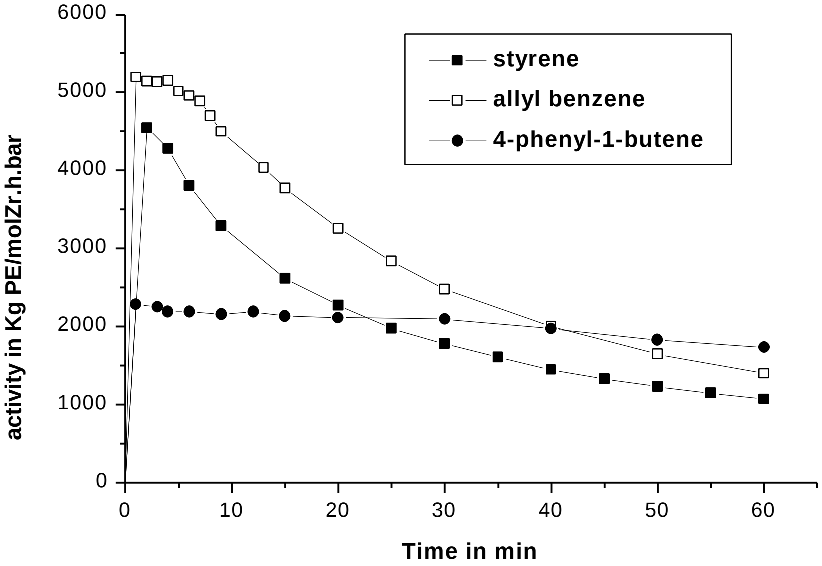


Figure 4.3 Kinetic profile of ethylene polymerization using $Me_2SiCp_2ZrCl_2$ in the presence of different comonomers

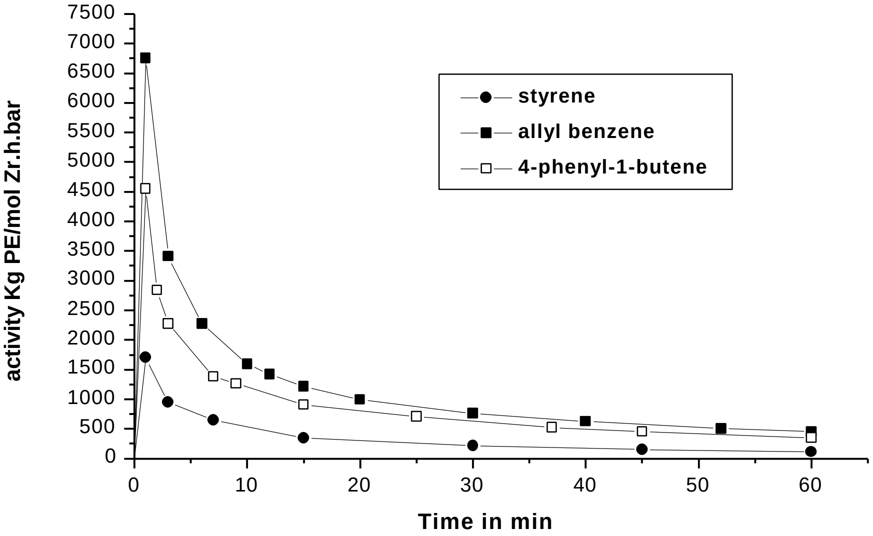


Figure 4.4 Kinetic profile of ethylene polymerization using $Me_2SiCp_2TiCl_2$ in the presence of different comonomers

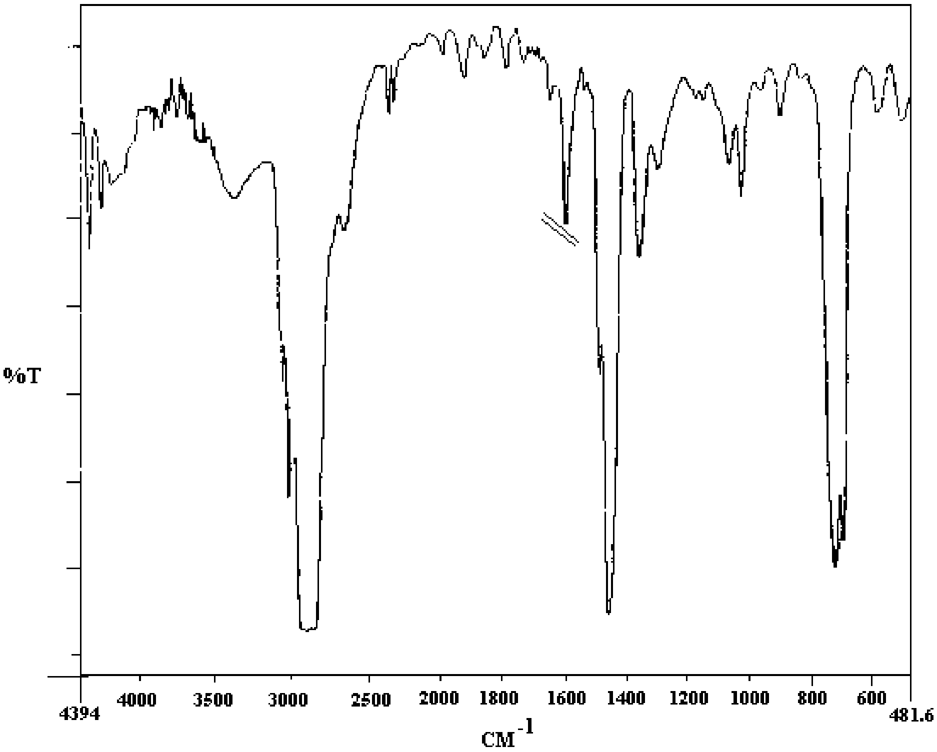


Figure 4.5 IR spectrum of ethylene-allyl benzene copolymer

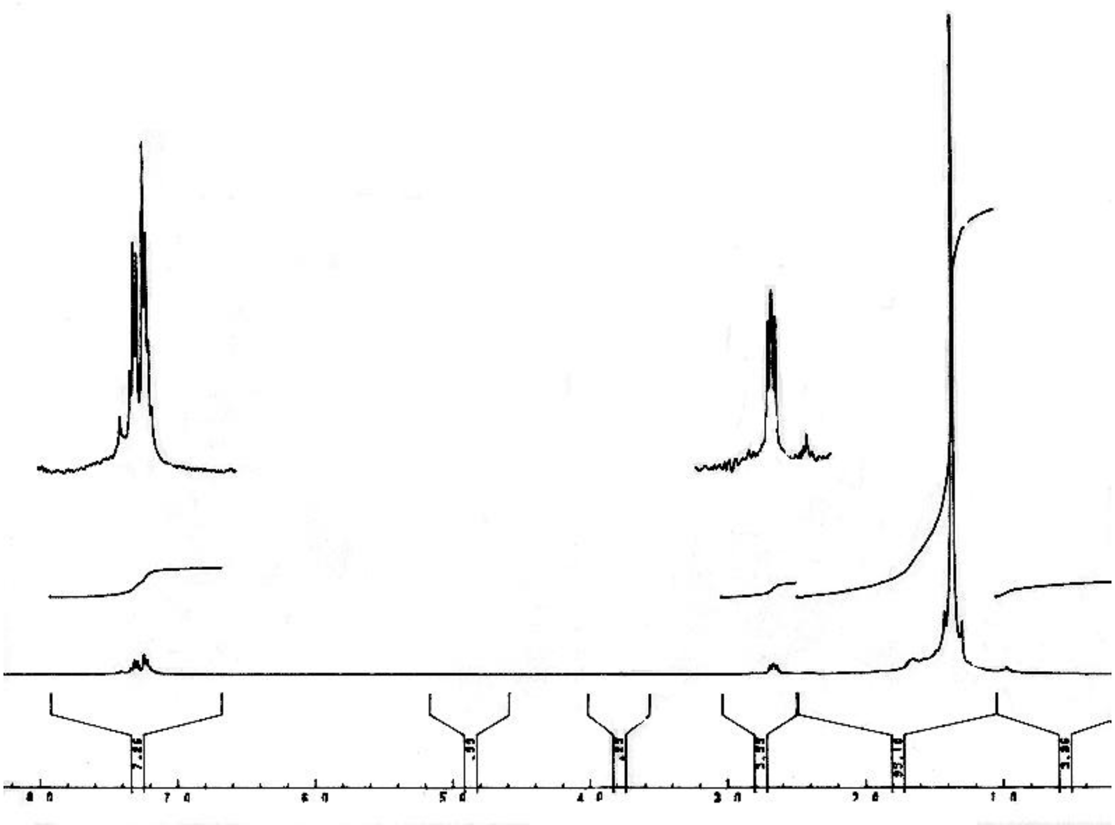


Figure 4.6 ^{1}H NMR spectrum of ethylene-4-phenyl-1-butene copolymer

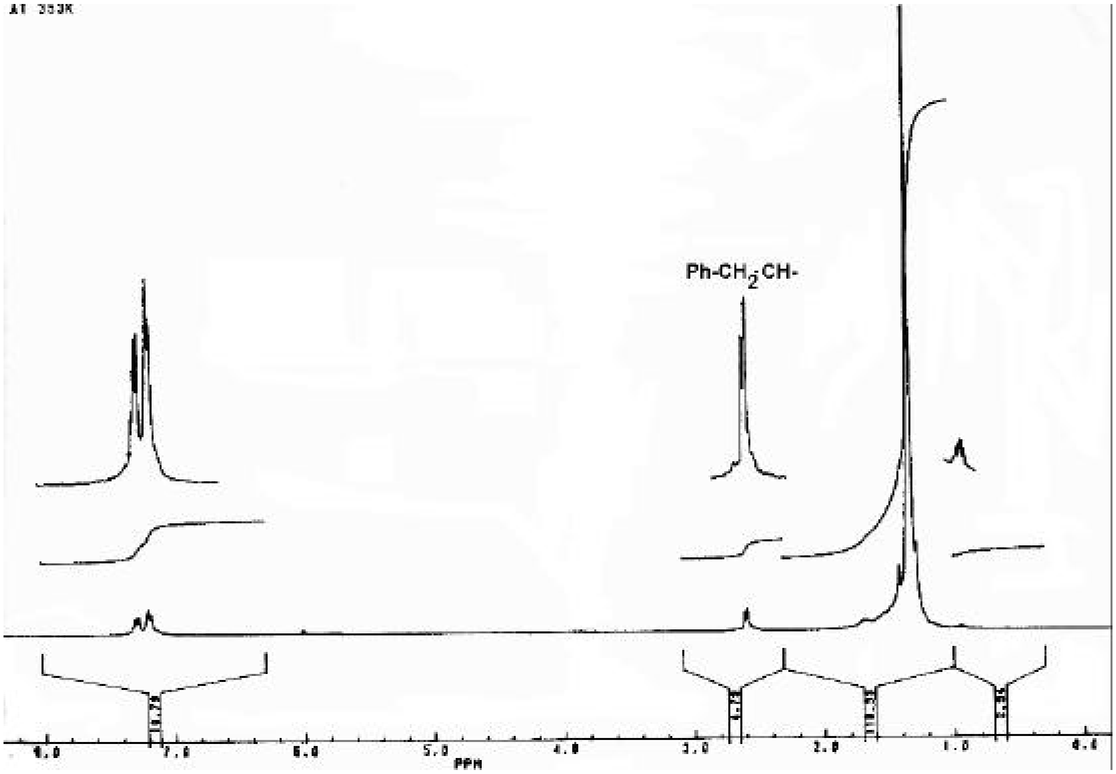


Figure 4.7 ^{1}H NMR spectrum of ethylene-allylbenzene copolymer

Table 4.1 Effect of type of comonomer on catalytic activity and polymer properties[a]

Entry	catalyst[b]	comonomer	Activity[c] $\times 10^{-2}$	[comonomer] in copolymer (mol %)	T_m[d] °C	[h] dL/g	M_n[e]
1	Cp_2ZrCl_2	Styrene	26.7	0.0	129	2.02	
2		Allyl benzene	23.2	1.1	115	1.41	
3		4-phenyl-1-butene	33.8	2.7	104	1.27	
4	$Me_2SiCp_2ZrCl_2$	styrene	10.9	0.7	127	1.01	
5		allyl benzene	17.1	3.0	122, 107	0.57	
6		4-phenyl-1-butene	18.4	5.5	117	0.33	
7[g]	$Me_2SiCp_2TiCl_2$	styrene	1.1	n. d.[h]	130	n. d.	
8		allyl benzene	4.8	1.7	116	1.69	
9		4-phenyl-1-butene	3.9	3.4	106	0.92	

[a] Reaction conditions: [catalyst] = 1.2×10^{-5} mol/L; [comonomer] = 0.25 mol/L; [Al]/[M] = 10,000; temperature

$P_{ethylene}$ = 1 bar. [b] Cp = η^5 -cyclopentadienyl. [c] Activity in Kg copolymer/ mol Zr.h.bar. [d] By DSC. [e] Number-av

[f] Molecular weight distribution. [g] Traces of polymer were obtained. [h] Not determined.

The molecular weights of the copolymers decrease in the order styrene > allylbenzene > 4-phenyl-1-butene for similar concentration of comonomer in the feed. Since the incorporation shows an opposite trend it seems that the chain termination by β-H elimination is favored once the comonomer is inserted in to the metal - carbon bond.

The values obtained for the molecular weight distribution are those expected for single site catalysts. But in the case of $Me_2SiCp_2ZrCl_2$ broader distributions were observed. Moreover for ethylene-allylbenzene copolymer prepared with this catalyst two melting points were observed indicating multiple active species. But only one melting point was observed for ethylene-4-phenyl-1-butene copolymer.

4.3.1.2 Effect of comonomer concentration

Copolymerization of ethylene with allyl benzene and 4-phenyl-1-butene were studied using Cp_2ZrCl_2, $Me_2SiCp_2ZrCl_2$ and $Me_2SiCp_2ZrCl_2$ by varying the comonomer concentration in the feed. The results are given in the **Table 4.2 and 4.3.** The results of the catalyst activities for ethylene polymerization as a function of comonomer concentration is shown in **Figures 4.8 to 4.10.**

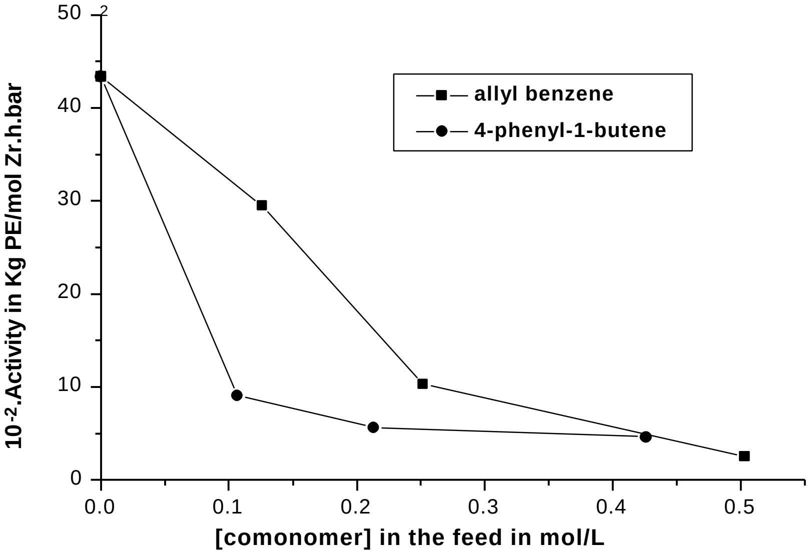


Figure 4.8 Effect of comonomer concentration on catalyst activities for ethylene polymerization (catalyst system Cp_2ZrCl_2/MAO)

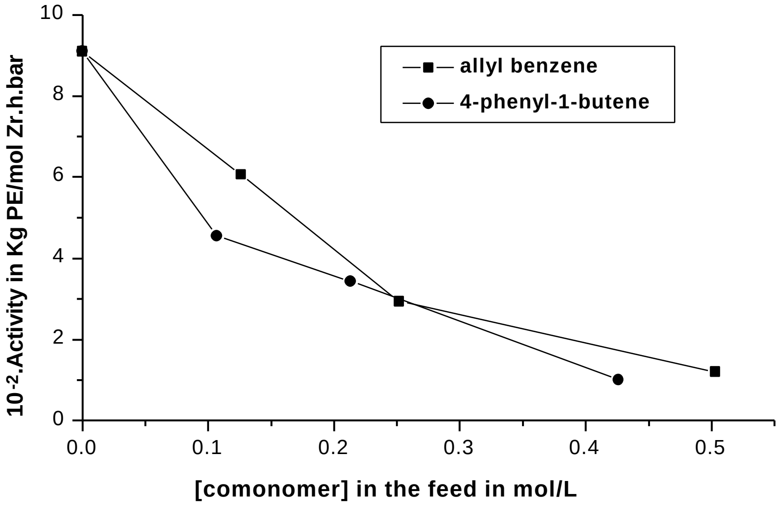


Figure 4.9 Effect of comonomer concentration on catalyst activities for ethylene polymerization (catalyst system $Me_2SiCp_2ZrCl_2$/MAO)

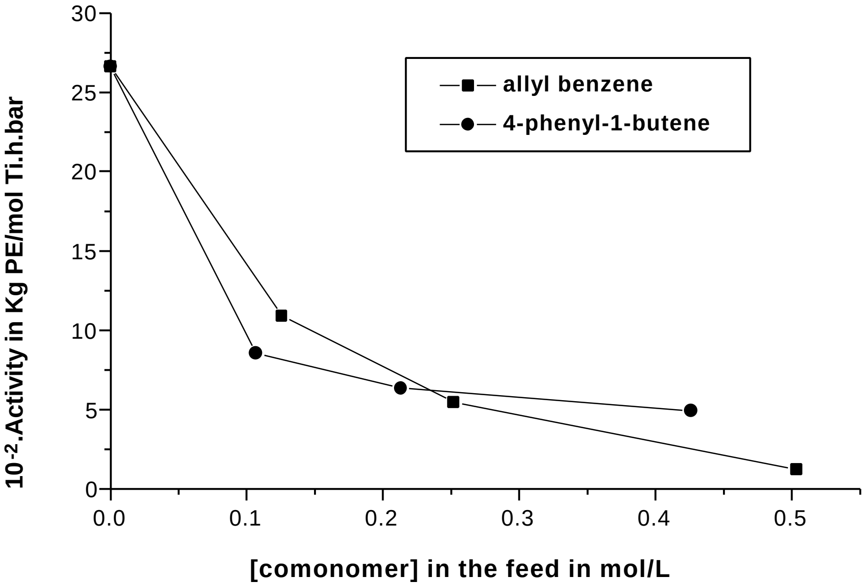


Figure 4.10 Effect of comonomer concentration on catalyst activities for ethylene polymerization (catalyst system $Me_2SiCp_2TiCl_2$/MAO)

The catalyst activity decreases in the presence of the comonomer for all the catalysts. It is observed that the decrease in catalyst activity is larger with allyl benzene compared to 4-phenyl-1-butene, especially, when the comonomer concentration is high. This implies that rate of polymerization of allyl benzene is slow compared to 4-phenyl-1-butene. The proximity of the aromatic ring closer to the olefinic bond, in the case of allyl benzene, may be responsible for this observation.

The catalyst activities for titanium metallocene were found to be higher than the Zr analogue when the polymerization temperature was 30 °C (**Table 4.2 and 4.3**). However, at higher temperatures (50 °C) the catalyst activities were lower, presumably, due to the reduction of the metal (compare entries 7 ,11 in **Table 4.2** with 5 and 8 in **Table 4.1**). In case of Ti metallocene the activities were high in the initial stages followed by a rapid deactivation (Figure 4.4). Severe deactivation was also observed in the case of styrene. This may be due to the reduction of the metal in the presence of styrene.[30]

The comonomer incorporation increases with increase in concentration of the comonomer in the feed. Under the experimental conditions employed, a maximum of 6 .7 mol % incorporation of 4-phenyl-1-butene was achieved using the catalyst system $Me_2SiCp_2ZrCl_2$/MAO. Higher comonomer incorporation is difficult to achieve as the catalyst activity decreases drastically with increase in comonomer feed. No incorporation of styrene was found except in the case of $Me_2SiCp_2ZrCl_2$ where less than one mol % incorporation was observed.

The melting points and crystallinities of the copolymers decrease with increase in comonomer content. The melting point decreased upto 103 °C for a copolymer containing 3.6 mol % of 4-phenyl-1-butene. Similar melting point depressions have been observed in the case of random copolymers of ethylene and styrene synthesized using constrained geometry catalyst. A melting point of 103.9 °C was reported for a copolymer containing 3.5 mol % styrene.[14] Broad melting transitions were reported for ethylene-styrene copolymers with less than 20 mol % styrene incorporations, synthesized using *rac*-ethylenebis(indenyl)zirconium dichloride/MAO system.[21] The melting point was found to increase upon further increase in styrene incorporation due to crystallization of alternating E-S sequences. In the case of bis(phenolate) complexes about 35 mol % of styrene was needed to decrease the melting point of the copolymer to 109 °C.[2] For copolymers containing the same amount of comonomer, the effect of 4-phenyl-1-butene on the crystallinity is more pronounced than allyl benzene.

In general, it was observed that for comparable comonomer content in the copolymer, the $Me_2SiCp_2TiCl_2$ catalyst gave consistently higher molecular weights than $Me_2SiCp_2ZrCl_2$ catalyst (**Table 4.2**). Similar observations have been previously reported for Ti and Zr unbridged metallocenes for ethylene polymerizations.[31] But at higher temperatures the molecular weights decrease drastically compared to zirconocene (compare **Table 4.1** with **4.2 and 4.3**). This may be due to the occurrence of catalyst deactivation reactions at higher temperatures.

Table 4. 2 Effect of concentration of allyl benzene in the feed on catalyst activity and polymer properti

Entry	catalyst	[Comonomer] mol/L	Activity[b] $\times 10^{-2}$	[comonomer] in copolymer (mol %)	T_m[c] °C	$[h]$ dL/g	M_n[d]
1	Cp_2ZrCl_2	0	43.4	0	130	2.25	
2		0.126	29.7	0.6	124	1.30	
3		0.252	10.4	0.8	121	1.24	
4		0.503	2.7	3.6	119	n. d.	
5	$Me_2SiCp_2ZrCl_2$	0	9.1	0	129	1.72	
6		0.126	6.4	2.4	115	1.25	
7		0.252	3.2	3.6	100,113, 119	1.00	
8		0.503	1.4	7.2	110,116	0.42	
9	$Me_2SiCp_2TiCl_2$	0	26.6	0	132	3.82	1
10		0.126	11.1	0.6	121	3.50	1
11		0.252	5.7	1.2	117	2.36	
12[e]		0.503	1.2	n. d.	109	n. d.	r

[a] Reaction conditions: [catalyst] = 1.2×10^{-5} mol/L; [Al]/[M] = 10,000; temperature = 30 °C; polymerization time

[b] Activity in Kg copolymer/mol Zr.h.bar. [c] By DSC. [d] Number average molecular weight. [e] Only traces of poly

Table 4.3 Effect of concentration of 4-phenyl-1-butene in the feed on catalyst activity and polymer pro

Entry	catalyst	[Comonomer] mol/L	Activity[b] $\times 10^{-2}$	[comonomer] in copolymer (mol %)	T_m[c] °C	$[h]$ dL/g	M_n[d]
1	Cp_2ZrCl_2	0	43.4	0	130	2.25	
2		0.107	10.1	0.7	120	2.35	
3		0.213	5.9	1.5	114	1.11	
4		0.426	4.9	2.9	105	0.72	
5	$Me_2SiCp_2ZrCl_2$	0	9.1	0	129	1.72	
6		0.107	4.9	3.6	103	0.83	
7		0.213	3.6	6.7	83	0.56	
8[e)]		0.426	1.0	n. d.	n. d.	n. d.	
9	$Me_2SiCp_2TiCl_2$	0	26.6	0	132	3.82	
10		0.107	8.6	1.1	118	2.51	
11		0.213	6.5	2.2	110	1.23	
12		0.426	5.2	3.7	99	1.07	

[a] Reaction conditions: [catalyst] = 1.2×10^{-5} mol/L; [Al]/[M] = 10,000; temperature = 30 °C; polymerization time

[b] Activity in Kg copolymer/mol Zr.h.bar. [c] By DSC. [d] Number average molecular weight. [e] Only traces of poly

With the catalyst $Me_2SiCp_2ZrCl_2$ and at higher concentration of allyl benzene more than one melting point is observed for the copolymers. This indicates the presence of more than one catalytically active species. Broader molecular weight distribution was observed for poly(ethylene) prepared by this catalyst. In the case of 4-phenyl-1-butene only one melting point and narrow MWD are observed.

The intrinsic viscosities of the copolymers decrease with increase in concentration of comonomer in the feed as shown in the **Figures 4.11 and 4.12.** This indicates transfer reactions with the comonomer.[32] The low molecular weights obtained with the catalyst $Me_2SiCp_2ZrCl_2$ is an indication that the termination reactions are facile as compared to that of unbridged ones. The presence of a bridge favors an increase of comonomer incorporation, which facilitates transfer reactions, thus, reducing the molecular weight of the polymers.[33] In a recent report on copolymerization of ethylene with allyl benzene using *rac*-ethylenebis(indenyl)zirconium dichloride/MAO chain transfer to aluminium was established as the major chain breaking reaction which is induced by the allyl benzene unit incorporated in the propagating chain end.[34]

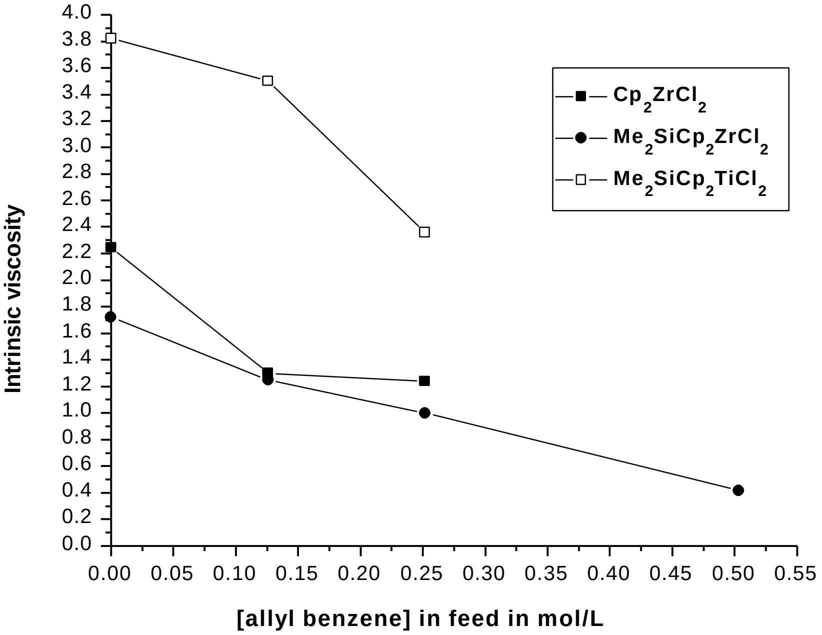


Figure 4.11 Intrinsic viscosity of copolymers as a function of allyl benzene concentration in the feed

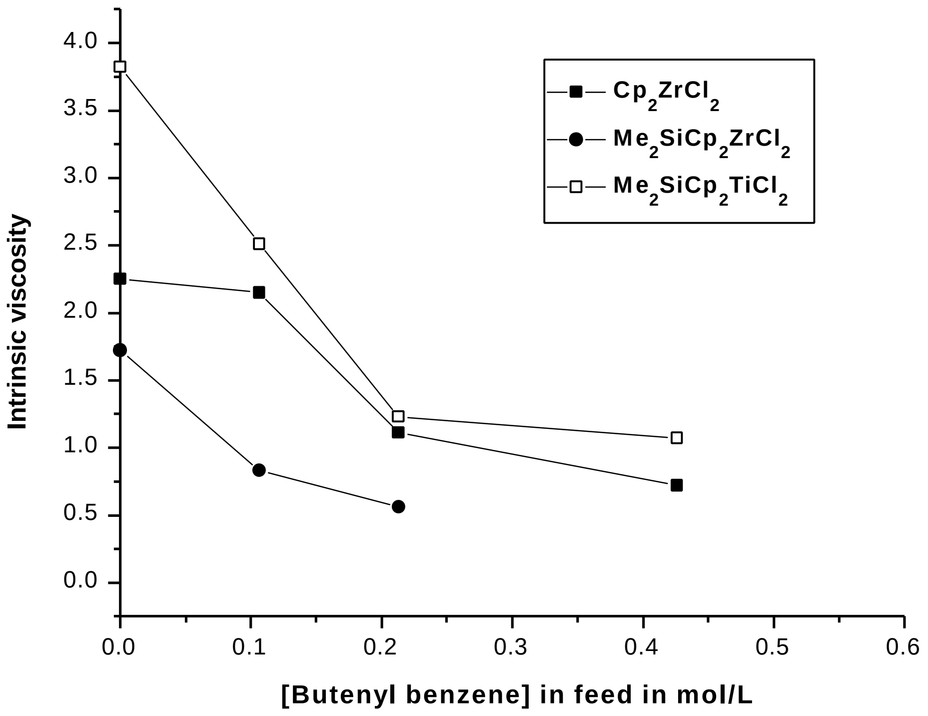


Figure 4.12 Intrinsic viscosity of copolymers as a function of 4-phenyl-1-butene concentration in the feed

4.3.1.3 Effect of temperature

Copolymerization of ethylene with 4-phenyl-1-butene was conducted at different temperatures using the catalyst system $Me_2SiCp_2ZrCl_2$/MAO. The results are given in **Table 4.4.** The comonomer incorporation was independent of temperature in the range 30 - 70 °C. Since the polymer yield was higher at higher temperatures, it indicates higher conversion of comonomer at higher temperatures. As expected, the intrinsic viscosities and molecular weights of the polymers decrease as the polymerization temperature increases.

Table 4.4 Effect of temperature on the copolymerization of ethylene with 4-phenyl-1-butene using $Me_2SiCp_2ZrCl_2$/MAO^a

Entry	temp °C	Activity^b $\times 10^{-2}$	[comonomer] in copolymer (mol %)	T_m^{c} °C	$[h]$ dL/g	M_n^{d} $\times 10^{-4}$	MWD
1	30	3.4	6.7	83	0.56	0.6	2.0
2	50	18.8	6.5	117	0.33	0.2	3.0
3	70	25.5	6.2	No T_m	0.13	0.1	2.6

[a)] Reaction conditions: [catalyst] = 1.2×10^{-5} mol/L; [4-phenyl-1-butene] = 0.213 mol/L ; Al/Zr = 10000; polymerization time = 1 h; P_{ethylene} = 1 bar.

[b)] Activity in Kg copolymer/mol Zr.h.bar. [c)] By DSC

[d)] Number average molecular weight

4.3.1.4 Effect of Al/Zr ratio

Effect of Al/Zr ratio on copolymerization of ethylene with 4-phenyl-1-butene was conducted using the catalyst system $Me_2SiCp_2ZrCl_2$/MAO. The results are given **Table 4.5.** In all the copolymerizations Al/Zr ratio of 10000 was required to get a reasonable activity. At a ratio of 1000, the activity was very less and only traces of polymer were obtained. Al/Zr ratio was found to have no influence on comonomer incorporation. The molecular weight of the polymer prepared at Al/Zr ratio of 5000 was found to be lower with a broader molecular weight distribution.

Table 4.5 Effect of Al/Zr ratio on the copolymerization of ethylene with 4-phenyl-1-butene using $Me_2SiCp_2ZrCl_2$ / MAO catalyst.[a]

Entry	Al/Zr	Activity[b] $\times 10^{-2}$	[comonomer] in copolymer (mol %)	T_m[c] °C	[h] dL/g	M_n[d] $\times 10^{-4}$	MWD
1	10000	3.4	6.7	83	0.56	0.6	2.0
2	5000	2.4	6.7	No T_m	n. d.	0.2	3.3
3[e]	1000	0.5	n. d.	n. d.	n. d.	n. d.	n. d.

[a] Reaction conditions: [catalyst] = 1.2×10^{-5} mol/L; [4-phenyl-1-butene] = 0.213 mol/L; temperature = 30 °C; polymerization time = 1 h; $P_{ethylene}$ = 1 bar.

[b] Activity in Kg copolymer /mol Zr.h.bar. [c] by DSC

[d] Number average molecular weight [e] Only traces of polymer were obtained

4.3.2 Late transition metal catalysts

Late transition metal catalysts are best known to oligomerize ethylene and dimerize propylene and higher α-olefins and there were only few reports of olefin polymerization using Ni based catalysts.[35-40] These metals prefer β-hydride elimination followed by reductive elimination. Discovery of olefin polymerization catalysts based on Ni(II) and Pd(II) diimine derivatives by Brookhart et al. is considered as a major breakthrough in coordination polymerization. [24] In these systems the bulky substituents on the aryl groups of the diimine ligand block associative olefin exchange thereby retarding the chain transfer, leading to high molecular weight polymers. These catalyst systems can afford poly(ethylene)s ranging from substantially linear to highly branched polymers, depending on polymerization temperature, monomer pressure and pre-catalyst structure. Late transition metal catalysts are less oxophilic in nature and are expected to be more tolerant of functional groups compared to early transition metal catalysts. The α,β-diimine Pd catalysts were reported to copolymerize ethylene with acrylic monomers and methyl vinyl ketone with modest comonomer incorporation.[41,42]

Recently Brookhart et al.[25] and Gibson et al.[43] reported iron and cobalt catalysts based on tridentate pyridine bis-imine ligands in which the imine moieties are bulky *ortho*-substituted aryl imines. The Fe based catalysts are highly active for ethylene polymerization.

Ni catalysts are known to polymerize styrene.[44-46] Accordingly, these catalysts were used for the copolymerization of ethylene with styrene. Prior to copolymerization experiments the homopolymerization of styrene using Ni(diimine) catalysts as well as the Fe catalyst was studied. [(N,N'-isopropylbenzene)-1,4-diazabutadiene] dibromonickel (**4**), [(N,N'-isopropylbenzene)-2,3-(1,8-naphthyl)-1,4-diazabutadiene] dibromonickel (**5**) and 2,6-bis{1-[2,6(diisopropylphenyl) imino]ethyl}pyridine iron dichloride (**6**) were used. The results are given in **Table 4.6.**

Table 4.6 Homopolymerization of styrene using late transition metal catalysts

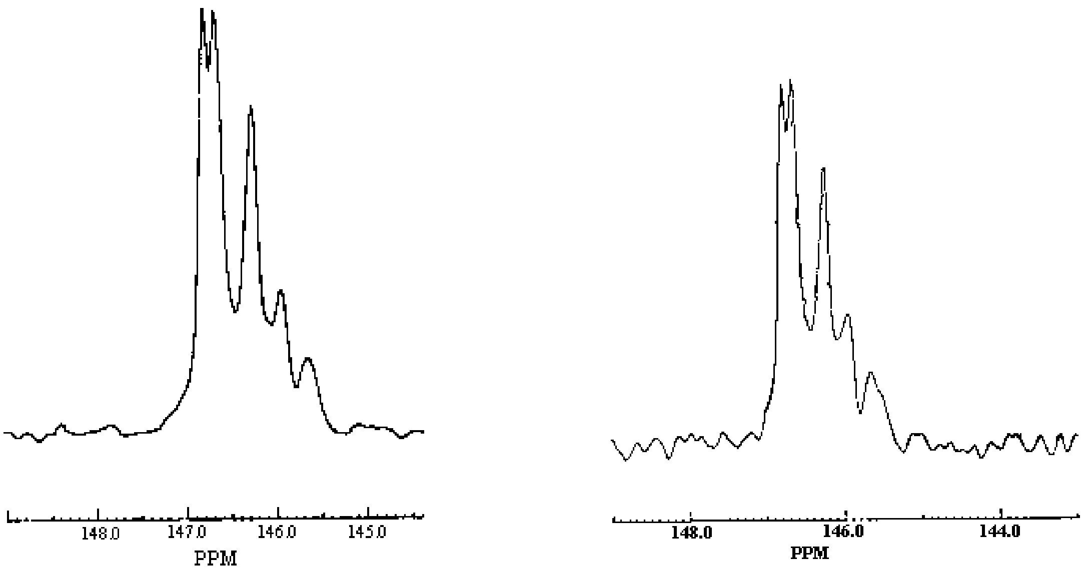
Entry	catalyst	Yield (g)	Conversion (%)
1	**4**	1.0	22
2	**5**	4.5	100
3	**6**	Traces of polymer were obtained	

Reaction conditions: catalyst = 8.4×10^{-6}; [Al/Ni] = 500; [styrene] = 4.2×10^{-3} moles; toluene 10 mL; temperature = 30 °C; polymerization time = 4 h.

The catalyst **5** is found to be more active than **4**. The ^{13}C analysis of the polymers shows that the polymers obtained are partially isotactic rich. The spectra are shown in **Figures 4. 13.** Only traces of polymer were obtained in the case of the Fe catalyst.

Several copolymerization runs of ethylene with styrene, allyl benzene and 4-phenyl-1-butene were carried out. It was found that the catalyst loses its activity in the presence of any of these aromatic vinyl monomers. The colour of the reaction mixture after mixing the catalyst and cocatalyst in the presence of comonomer was dark blue whereas in the case of ethylene homopolymerization the colour was purple. The ethylene consumption ceased immediately when any of these comonomers were added after initiating ethylene polymerization.

These results show that the active species for ethylene polymerization is different from that of styrene polymerization.



Catalyst 4

Catalyst 5

Figure 4.13 ^{13}C spectra of partially isotactic rich polystyrene

The Fe catalyst **6** was also employed for copolymerization of ethylene with aromatic vinyl monomers, namely, styrene, allyl benzene and 4-phenyl-1-butene. The experimental conditions employed are given in **Table 4.7**. The catalyst activity was substantially diminished. The FT-IR analysis of these polymers showed the absence of characteristic peaks of the aromatic monomers. This catalyst seems to be highly selective for ethylene polymerization.

Table 4.7 Copolymerization of ethylene with aromatic vinyl monomers using iron(II)bis(imino)pyridyl catalyst

Entry	Comonomer	Activity (Kg polymer/mol Fe.h)	Tm °C
1	-	750	139
2	Styrene	360	136
3	Allyl benzene	440	136
4	4-phenyl-1-butene	480	134

Exptal conditons: Toluene = 30 mL; catalyst = 2.5×10^{-6} mol; MAO/Fe = 1000; comonomer = 2 mL; Time = 60 min

4.4 Conclusion

The proximity of the phenyl group to olefinic bond is found to have adverse effect on insertion as the extent of incorporation decreases in the order 4-phenyl-1-butene > allyl benzene > styrene. The incorporation achieved were less than 10 mol %. Higher incorporation is difficult as the increased comonomer concentration in the feed leads to drastic reduction in catalyst activity, presumably due to β-hydrogen elimination once the comonomer is incorporated into the polymer.

The Ni(diimine) and Fe catalysts were found to be inactive for the copolymerization of ethylene with the various aromatic vinyl monomers examined.

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CHAPTER 5. COPOLYMERIZATION OF ETHYLENE WITH SILICON CONTAINING MONOMERS USING HOMOGENEOUS TRANSITION METAL CATALYSTS

5.1 Introduction

Synthesis of functional polyolefins through direct copolymerization of functional monomers is an area of contemporary research interest. Functional copolymers of ethylene and propylene can be made using conventional Ziegler-Natta type catalysts.[1] However, the fact that polar functional groups deactivate either the catalyst or the cocatalyst component of Ziegler catalyst has limited the synthesis of functional copolymers by Ziegler-Natta catalytic process. Different approaches have been adopted to overcome this problem, like separating the functional group from the polymerizable double bond by spacer group, by protecting the functional group either by using externally added reagent or by increasing the bulkiness around the functional group and by decreasing the nucleophilicity of the functional group.

With the discovery of metallocene/MAO catalyst system for olefin polymerizations there is a renewed interest in the area of synthesis of functional and heteroatom containing polyolefins.[2-10] Functional monomers protected with silyl group or aluminum alkyl group have been successfully used for homo as well as copolymerizations with olefins.[11-20] Copolymerization of styrene and 4-tert-butyldimethylsilyloxystyrene using IndTiCl$_3$ has been reported recently, as a method for the synthesis of hydroxyl functionalized syndiotactic polystyrene.[21]

Silicon containing vinyl monomers have received far less attention. There are a few reports on coordination polymerization of vinyl monomers like allylsilane, allyltrimethylsilane, 5-trimethylsilyl-1-pentene to isotactic polymers utilizing Ziegler catalysts as the initiators.[22-24] In contrast, polymerizability of vinyl silanes, such as, vinylethylsilane or trimethylvinylsilane is poor on account of the steric effect caused by the silyl substitution at olefinic carbon.[25] Coordination polymerization of vinylsilane has been reported recently.[26]

Crystalline alkenyl silane-olefin random copolymers have been synthesized using Ziegler catalysts as well as metallocene catalysts and are found to have applications such as nucleating agents, adhesive and surface coating agents.[27] A detailed study of structure and tacticity of allyltrimethylsilane has been reported. [28] Using appropriate metallocene/MAO catalysts, atactic, isotactic and syndiotactic poly(allyltrimethylsilane) were synthesized.

Polymers with Si-H bonds can be easily crosslinked by the action of oxygen at higher temperatures or by the action of alkali/alcohol mixtures through the formation of Si-O-Si bonds. [29] These kind of polymers can also be crosslinked by irradiation due to the coupling of silyl radical of vinylsilane unit with the carbon radical. [30] Polymers containing silyl groups can be considered as precursors for functional polyolefins since it can be transformed into a hydroxyl group by the oxidative cleavage of silicon-carbon bond. [31-36]

There appears to be practically no study on the polymerizability of monomers containing silyloxy group with Si-O-Si linkage. Presence of this polar group may interfere with the catalyst. But the nucleophilicity of the oxygen atom may be less due to the dπ-pπ back bonding. Synthesis of polyethylene having pendant cubic silsesquioxane groups have been reported by Tsuchida et al. [37] by the copolymerization of ethylene with a novel monovinyl functional silsesquioxane cage 1-(9-decenyl)-3,5,7,9,11,13,15-hepta-ethylpentacyclo octasiloxane using metallocene/MAO system.

The present study was undertaken with a view to explore the copolymerization of ethylene with various silicon containing monomers. Silicon bearing monomers viz. trimethylvinylsilane, allyltrimethylvinylsilane, trimethylsilyloxydimethylvinylsilane, vinylethoxydimethylsilane were used for the study. Apart from metallocenes, late transition metal catalysts based on Ni(diimine) derivatives and an iron based catalyst, 2,6-bis{1-[2,6(diisopropylphenyl) imino]ethyl} pyridineiron dichloride were also used for the study.

5.2 Experimental part

5.2.1 Materials

Vinyltrimethylsilane , and trimethylsilyloxydimethylvinylsilane were purchased from Gelest Inc. and purified by fractional distillation. Allyltrimethylsilane and vinylethoxydimethylsilane were purchased from Aldrich and purified by fractional distillation. All the comonomers were dried over CaH_2 and vacuum transferred before use.

5.2.2 Polymerization

The detailed polymerization procedure and work up is given in **chapter 3**. In the case of copolymerizations where trimethylsilyloxydimethylvinylsilane was used as the comonomer the polymerization mixture was passed through a column filled with neutral alumina to remove the catalyst residues and the eluted solution was poured into acetone to precipitate the polymer. This step is necessary due to the fact that the silyloxy group reacts with moisture and HCl slowly.

5.2.3 Characterization

The various characterization methods are given in **chapter 3**. Molecular weight and molecular weight distribution (MWD) of the polymers were determined using a Waters gel-permeation chromatograph (GPC/ALC 150C) equipped with a refractive index detector and μ-styragel columns (HT-3, 4, 5, 6E), based on polystyrene standards and universal calibration methods, at 140 °C using 1,2,4-trichlorobenzene as eluent with 1mL/min flow rate.

5.3 Results and Discussion

5.3.1 Metallocenes

5.3.1.1 Homopolymerization of vinyltrimethylsilane

Homopolymerization of allyltrimethylsilane has been reported using various metallocenes. [38,28] Polymerization of vinyltrimethylsilane (abbreviated as M^{vi}) was attempted using various metallocenes like $(n\text{-}BuCp)_2ZrCl_2$, $Et(Ind)_2ZrCl_2$, $Me_2SiCp_2ZrCl_2$, Cp_2ZrCl_2 etc in conjunction with MAO. Under the various conditions tried, no polymerization was observed. The experimental conditions employed are given in **Table 5.1**. For all the reactions toluene was used as the solvent and an Al/ Zr ratio of 1000 was used. The poor polymerizability of this monomer may be due to the bulky trimethyl substituent at the olefinic carbon. Homopolymerization of vinylsilane with 48 % yield has however, been reported in a patent using Cp_2ZrCl_2 as the catalyst.[39]

Table 5.1 Homopolymerization of vinyltrimethylsilane

Entry	M^{vi} (mL)	Toluene (mL)	catalyst	catalyst mol × 10^{-7}	Temp °C	Time tp (h)	results
1	2	5	$(n\text{-}buCp)_2ZrCl_2$	10	30	7	No polymn
2	2	5	$(n\text{-}buCp)_2ZrCl_2$	10	30	7	No polymn
3	5	15	$(n\text{-}buCp)_2ZrCl_2$	23	60	22	No polymn
4	2	5	$Me_2SiCp_2ZrCl_2$	9.2	30	22	No polymn
5	5	15	$Me_2SiCp_2ZrCl_2$	23	60	22	No polymn
6	2	5	Cp_2ZrCl_2	9.2	70	6	No polymn
7	2	4	$Me_2SiCp_2ZrCl_2$	9.2	70	6	No polymn
8	2	5	$Et(Ind)_2ZrCl_2$	9.2	50	16	No polymn

5.3.1.2 Copolymerization of ethylene with M^{vi} and ATMS

5.3.1.2.1 Effect of type of comonomer

Copolymerization of ethylene with M^{vi}, and allyltrimethylsilane (ATMS) was studied with the catalyst systems $Et(Ind)_2ZrCl_2$/MAO and $Me_2SiCp_2ZrCl_2$ at one atmosphere pressure of ethylene in toluene. All the polymerizations were generally conducted upto one hour except in some cases where difficulty was observed for stirring due to the high amount of polymer formed.

The kinetic profile of ethylene polymerization in the presence of these comonomers is shown in **Figure 5.1** and **5.2**. The concentration of comonomer was 0.32 M. The experimental data is presented in **Table 5.2** and **5.3**. It can be seen that the catalyst activity decreases in the presence of both the comonomers and the ethylene polymerization rate for both the catalysts are much higher for ATMS than that for M^{vi} under the experimental conditions used. It can also be seen that there is a drastic decay in activity for ethylene homopolymerization compared to the copolymerization. This is due to the high initial rate of ethylene polymerization and the decreased diffusion of monomer to the active site as the reaction progresses. In the case of copolymerizations the ethylene consumption rate does not decrease much from the initial rate due to the better solubility of the copolymer.

The FT-IR spectrum **(Figure 5.3)** of all the copolymers shows the presence of characteristic peaks of $Si\text{-}CH_3$ bonds at 1248 cm^{-1} and 834 cm^{-1}. The comonomer incorporation was found out from ^1H NMR spectrum. Typical spectra of copolymers with M^{vi} and ATMS as comonomers are shown in the **Figure 5.4** and **5.5** respectively.

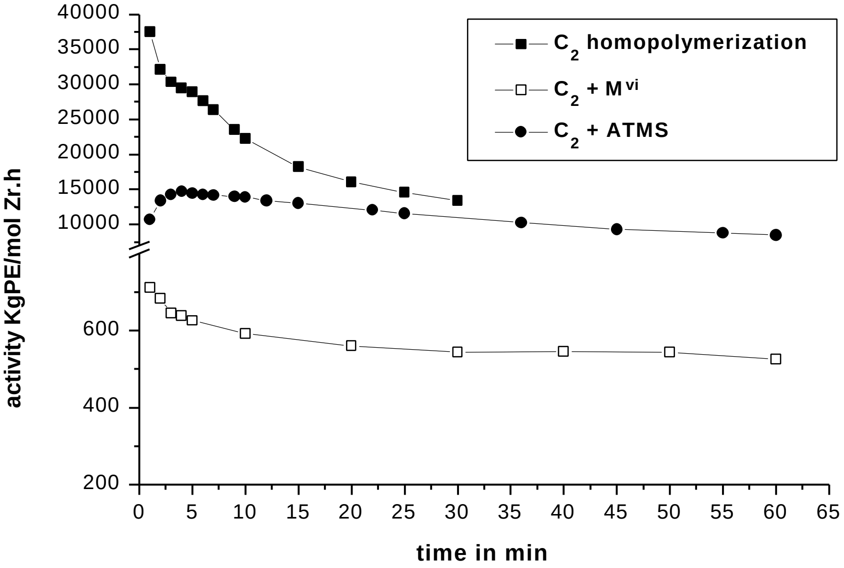


Figure 5.1 Kinetic profile of ethylene polymerization using the catalyst system $Et(Ind)_2ZrCl_2$/MAO in the presence of comonomers

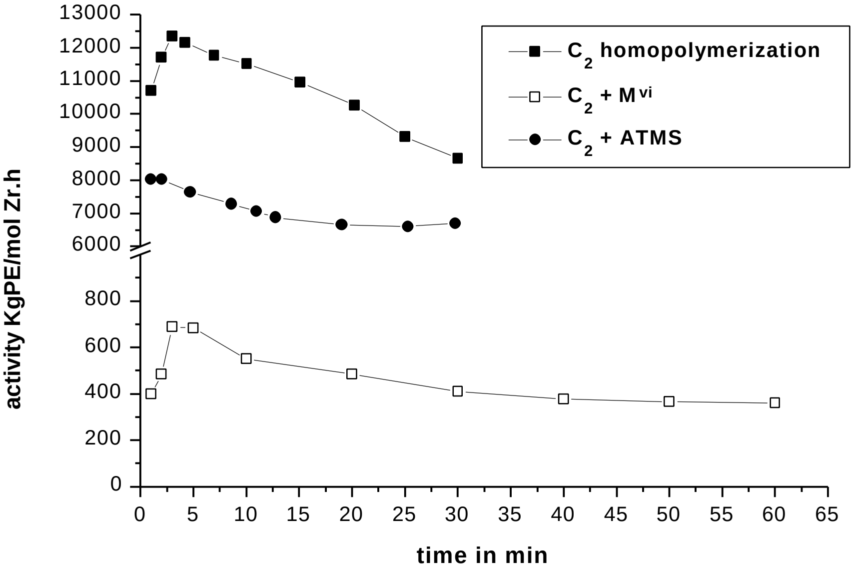


Figure 5.2 Kinetic profile of ethylene polymerization using the catalyst system $Me_2SiCp_2ZrCl_2$/MAO in the presence of comonomers

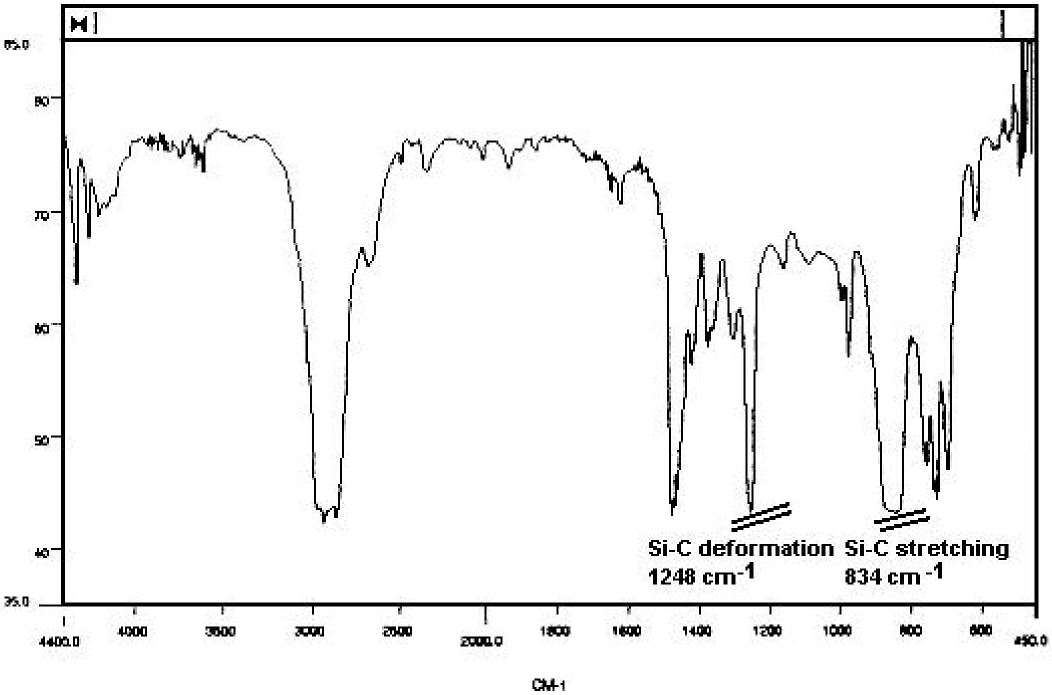


Figure 5.3 IR spectrum of ethylene-vinyltrimethylsilane copolymer

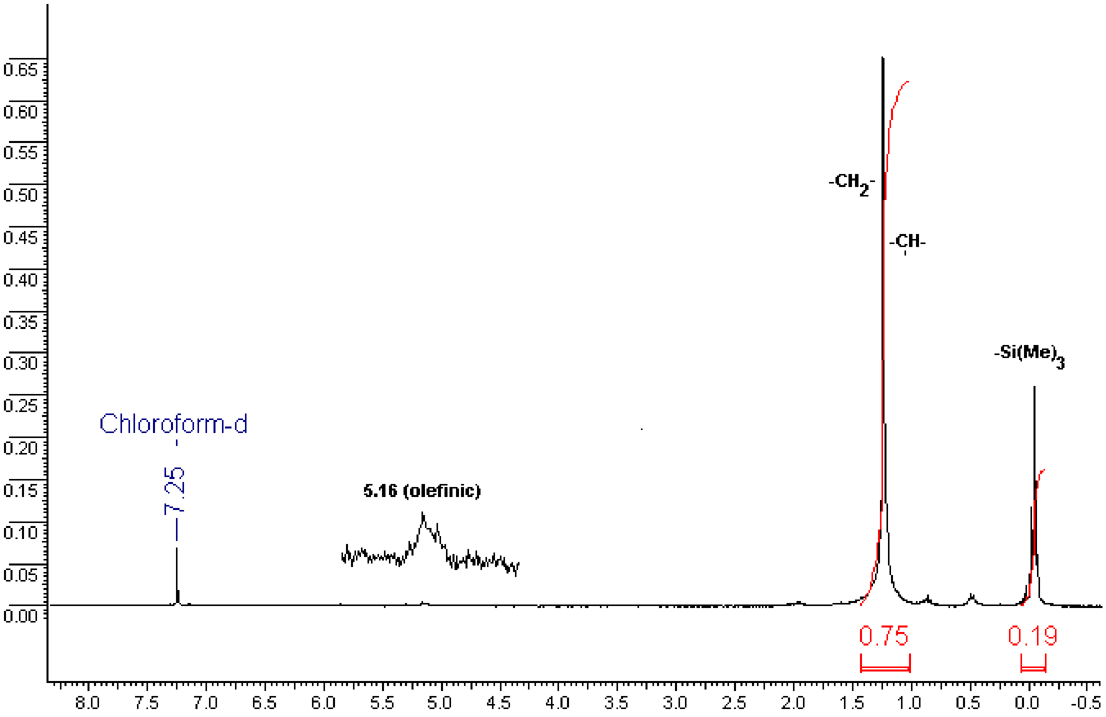


Figure 5.4 ^{1}H NMR spectrum of ethylene-M^{vi} copolymer synthesized with metallocene (Table 5.2 Entry 8)

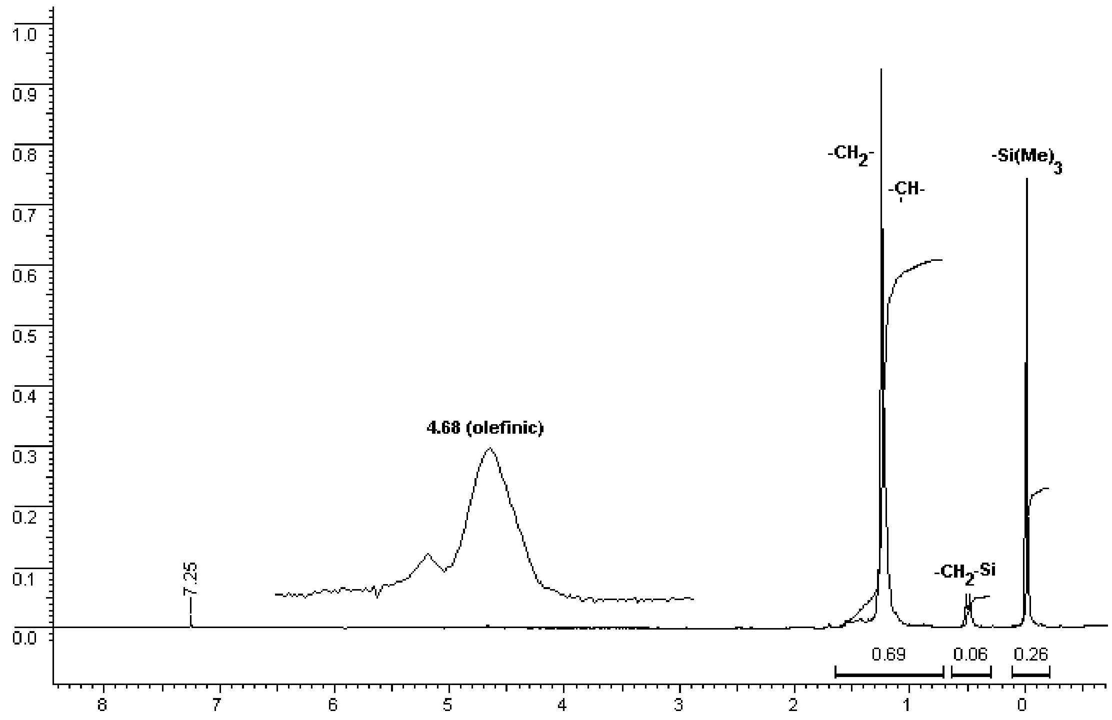


Figure 5.5 ^{1}H NMR spectrum of ethylene-ATMS copolymer synthesized with metallocene (Table 5.3 Entry 4)

5.3.1.2.2 Effect of comonomer concentration

The copolymerizations were conducted using the two metallocenes, Et(Ind)$_2$ZrCl$_2$ and Me$_2$SiCp$_2$ZrCl$_2$ by varying the comonomer feed and the results are shown in **Table 5.2** and **5.3**. The catalyst activity decreases with increase in comonomer feed for both the comonomers. Catalyst activities are one order of magnitude higher in the case of ATMS than M ^{vi}. This may be due to the fact that the active species [R-M^{vi}-cat] inserts a new monomer (ethylene or M^{vi}) much slower than [R-ATMS-cat] due to steric effects.

In terms of incorporation Et(Ind)$_2$ZrCl$_2$ and Me$_2$SiCp$_2$ZrCl$_2$ catalysts behaved differently. Higher incorporation was observed for ATMS than M^{vi} in the case of Et(Ind)$_2$ZrCl$_2$. For Me$_2$SiCp$_2$ZrCl$_2$ catalyst M^{vi} incorporation was found to be higher. But for both the catalysts the comonomer conversion was much higher in the case of ATMS due to the higher copolymerization activity.

Comonomer incorporation was found to increase with increase in comonomer feed. Copolymers upto 16 mol % ATMS incorporation was prepared. In the case of M^{vi} maximum incorporation achieved was 10 mol % under the experimental conditions used. The crystallinities and melting points of the copolymers decrease with increase in comonomer incorporation. Copolymers with more than 10 mol % comonomer incorporation were found to be amorphous in nature.

The molecular weights of the polymers decrease with increase in comonomer feed as evidenced from the intrinsic viscosity values. This may be due to the chain transfer reactions with the comonomer or due to the enhanced chain termination by β-hydrogen elimination after the comonomer is inserted in to the metal-carbon bond. Since the comonomer incorporation increases with increase in comonomer feed with lowering of polymerization activity, it can be inferred that the rate of polymerization of the comonomers is low. This should result in end groups formed after the comonomer is inserted. ^{1}H-NMR spectrum of a ethylene-ATMS copolymer **(Figure 5.5)** shows the presence of olefinic protons of the vinylidene end group structure derived from β-hydrogen elimination. The peak at 4.68 is due to the geminal protons in the $RR'C=CH_2$ end group where R is the polymer chain and R' is the -CH2-SiMe3 group.[28]

Table 5.2 Copolymerization of ethylene with vinyltrimethylsilane[a]

Entry	catalyst	[comonomer] (mol/L)	Activity[d]	[comonomer] in copolymer (mol %)	Tm °C[e]	[η] dL/g
1[b]	$Et(Ind)_2ZrCl_2$	-	13400	-	136	3.4
2		0.11	1550	1.0	120	0.57
3		0.22	975	2.2	115	0.46
4		0.32	525	3.7	107	0.18
5[c]	$Me_2SiCp_2ZrCl_2$	-	8700	-	129	1.08
6		0.22	1120	4.7	95	0.15
7		0.32	360	6.7	90	0.12
8		0.43	240	11.5	No Tm	n.d

[a] Reaction conditions: toluene = 30 mL; [Zr] = 2.4×10^{-5} mol/L; Al/ Zr = 10000; temp = 50 °C; time = 60 min; [b] [Zr] = 1.2×10^{-5} mol/L; time 30 = min; [c] time = 30 min

[d] activity expressed in Kg copolymer/mol Zr.h; [e] by DSC

Table 5.3 copolymerization of ethylene with allyltrimethylsilane[a]

Entry	catalyst	[comonomer] mol/L	Activity[d]	[comonomer] in copolymer (mol %)	Tm °C	[η] dL/g
1	$Et(Ind)_2ZrCl_2$[b]	-	13400	-	136	3.4
2		0.22	12225	3.7	124	0.6
3		0.32	10420	7.5	111	0.4
4		0.43	3950	16.1	NoTm	0.1
5	$Me_2SiCp_2ZrCl_2$[c]	0.22	7900	3.5	112	0.10
6		0.32	6760	4.8	106	0.05
7		0.43	5070	7.1	109	0.04

[a] Toluene = 30 mL; Al/Zr = 10000; temp = 50°C; time = 60 min; [b] $[Zr] = 1.2 \times 10^{-5}$ mol/L; [c] $[Zr] = 2.4 \times 10^{-5}$ mol/L; time = 30 min; [d] activity expressed in Kg copolymer/mol Zr.h

5.3.1.2.3 Effect of temperature

Copolymerization of ethylene with M^{vi} and ATMS were conducted at different temperatures using the catalyst systems $Et(Ind)_2ZrCl_2$/MAO and $Me_2SiCp_2ZrCl_2$/MAO. The results are given in the **Tables 5.4** and **5.5.**

Table 5.4. Effect of temperature on copolymerization of ethylene with vinyltrimethylsilane[a]

Entry	catalyst	Temperature °C	Activity[b]	[comonomer] in copolymer (mol %)	Tm °C	[η] dL/g
1	$Et(Ind)_2ZrCl_2$	25	80	3.0	108	0.35
2		50	480	3.4	107	0.18

[a] Reaction conditions: toluene = 30 mL; $[Zr] = 2.4 \times 10^{-5}$ mol/L; $[M^{vi}] = 0.32$ mol/L; Al/Zr = 10000; time = 60 min; [b] activity expressed in Kg copolymer/mol Zr.h

Table 5.5. Effect of temperature on copolymerization of ethylene with ATMS[a]

Entry	catalyst	Temperature °C	Activity[d]	[comonomer] in copolymer (mol %)	Tm °C	[η] dL/g
1	$Et(Ind)_2ZrCl_2$[b]	25	4225	12.0	No Tm	0.25
2		50	10420	7.5	111	0.40
3		70	7042	12.3	No Tm	0.20
4	$Me_2SiCp_2ZrCl_2$[c]	25	2520	9.7	No Tm	0.06
5		50	6760	4.8	106	0.05
6		70	7825	3.8	120	0.10

[a] Reaction conditions: toluene = 30 mL; [ATMS] = 0.32 mol/L; Al/ Zr = 10000; time = 60 min; [b] [Zr] = 1.2 × 10^{-5} mol/L; [c] [Zr] = 2.4 × 10^{-5} mol/L; time = 30 min;

[d] activity expressed in Kg copolymer/mol Zr.h

From **Table 5.4,** it can be seen that the copolymerization activity increases drastically when the polymerization temperature was increased from 25 to 50 ºC. This is due to the increased rate of propagation observed in the case of zirconocene catalysts. Eventhough the incorporation of M^{vi} is almost similar , the conversion of the comonomer is higher at higher temperatures. The molecular weight of the polymers decreases at higher temperatures as expected.

In the case of ATMS also, the polymerization activity increases as the temperature increases. But the comonomer incorporation decreases at higher temperatures **(Table 5.5)**. Higher temperature favors polymerization of ethylene over the comonomer. But in all the cases the conversion of the comonomer was found to increase as the polymerization temperature increases. In the case of $Et(Ind)_2ZrCl_2$ catalyst ethylene polymerization was found to decrease at 70 ºC. Because of this, higher comonomer incorporation was achieved. The molecular weights of the copolymers depend on polymerization temperature as well as on the extent of comonomer incorporation.

5.3.1.3 Copolymerization of ethylene with MM^{vi} and VEDMS

Two functional monomers trimethylsilyloxydimethylvinylsilane abbreviated as MM^{vi} and vinylethoxydimethylsilane abbreviated as VEDMS were used for copolymerization with ethylene. These monomers can be considered as derivatives of vinyltrimethylsilane in which one of the CH_3 groups is replaced by -O-CH_2CH_3 and -O-$SiMe_3$ groups respectively. It was observed that in the presence of these comonomers, there was no polymerization activity for the various metallocene systems tried. In some experiments these comonomers were added after initiating the ethylene polymerization and the immediate ceasing of ethylene consumption was observed. It seems that deactivation of the active species occurs due to these functional monomers. The close proximity of the oxygen atom to the olefinic bond may be one of the reasons for this. Similar deactivation of the catalyst has been observed and reported by Fink et al. when hydroxyl group containing vinyl monomers were used for copolymerization with ethylene after protecting the hydroxyl group with trimethylsilyl group.[11] They found that good catalyst activities and comonomer incorporation can be obtained with the corresponding triisopropyl silyl protected monomers.

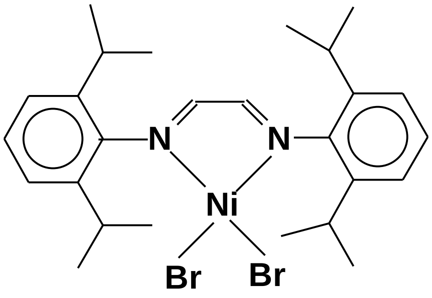
5.3.2 Ni(diimine) catalysts

Late transition metal catalysts are best known to oligomerize ethylene and dimerize propylene and higher α-olefins and there were only few reports of olefin polymerization using Ni based catalysts.[40--45] These metals prefer β-hydride elimination followed by reductive elimination. Discovery of olefin polymerization catalysts based on Ni(II) and Pd(II) diimine derivatives by Brookhart et al. is considered as a major breakthrough in coordination polymerization.[46] In these systems the bulky substituents on the aryl groups of the diimine ligand block associative olefin exchange thereby retarding the chain transfer leading to high molecular weight polymers. These catalyst systems can afford poly(ethylene)s ranging from substantially linear to highly branched polymers, depending on polymerization temperature, monomer pressure and pre-catalyst structure. Late transition metal catalysts are less oxophilic in nature and are expected to be more tolerant to functional groups compared to early transition metal catalysts. The α,β-diimine Pd catalysts were reported to copolymerize ethylene with acrylic monomers and methyl vinyl ketone with modest comonomer incorporation.[47,48]

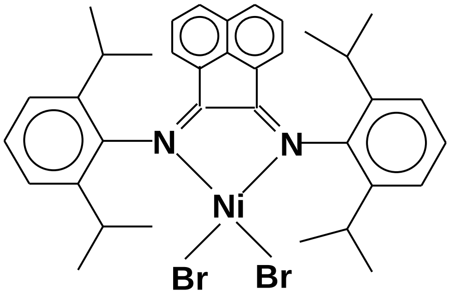
5.3.2.1 Copolymerization

5.3.2.1.1 Effect of type of comonomer

Copolymerization of ethylene with vinyltrimethylsilane (M^{vi}), allyltrimethylsilane (ATMS), Trimethylsilyloxydimethylvinylsilane (MM^{vi}) and vinylethoxydimethylsilane (VEDMS) were studied using two Ni(diimine) catalysts **1** and **2** in conjunction with MAO.



DABH$_2$NiBr$_2$ (1)



DABAnNiBr $_2$(2)

Like metallocenes, Ni(diimine) catalysts are also active for the copolymerization of ethylene with M^{vi} and ATMS. But these catalysts are also found to be active when trimethylsilyloxydimethylvinylsilane was used as the comonomer. No polymerization occurred for the comonomer vinylethoxydimethylsilane. The close proximity of the oxygen atom to the olefinic bond and the lack of steric protection may be the reason for this. The compatibility of MM^{vi} with the catalytic species may be due to the fact that the oxygen atom is surrounded by two bulky groups. Futhermore, this oxygen is less nucleophilic because of d π -pπ interaction with two silicon atoms.

The catalyst activity decreases in presence of the comonomers (**Table 5.6**). The kinetic profile of ethylene polymerization is shown in the **Figure 5.6.** The activities are similar in the case of M^{vi} and MM^{vi}. The better tolerance towards this functional monomer is due to the less oxophilic nature of late transition metal catalysts. In contrast to the metallocene catalysts, the ethylene consumption rate is lower in the case of ATMS than M^{vi}.

Table 5.6 Copolymerization of ethylene with silicon containing monomers using Ni(diimine) catalyst(2)[a]

Entry	comonomer	Activity[b]	[comonomer] in copolymer (mol %)	[η] dL/g	Tm	Mw × 10^{-4}	MWD
1	-	630	-	3.1	45	21	1.7
2	M^{vi}	105	0.3	2.3	36	11	2.3
3	MM^{vi}	120	0.4	1.8	41	10	1.7
4	ATMS	50	3.5	1.3	No Tm	6.4	1.8

[a] Experimental conditions: toluene = 50 mL; [Ni] = 5 × 10^{-5} mol/L; Al/Ni = 1000; temp = 25 °C; [comonomer] = 0.21 mol/l; time = 60 min;

[b] activity expressed in Kg copolymer/mol Zr.h

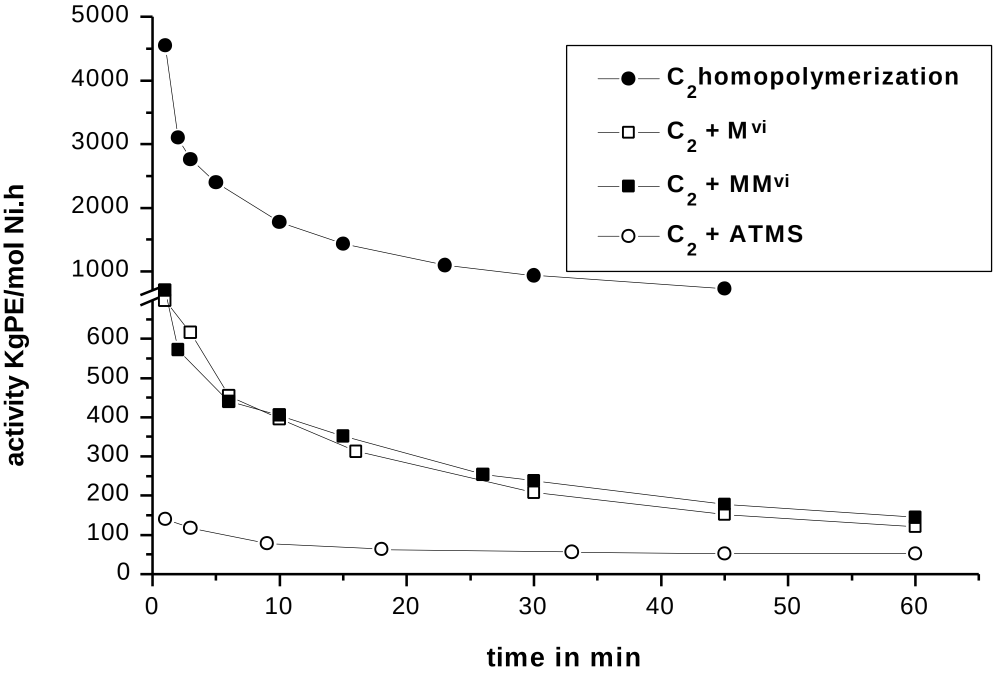


Figure 5.6 Kinetic profile of ethylene polymerization using the catalyst system DABAnNiBr$_2$/MAO in the presence of comonomers

The FT-IR spectrum **(Figure 5.7)** of the copolymers of ethylene with MM^{vi} shows a characteristic band at 1058 cm^{-1} attributed to Si-O bond apart from the peaks of Si-CH_3 bond observed at 1252 and 842 cm^{-1}. The comonomer incorporation was determined from ^{1}H NMR. Very small amounts of M^{vi} and MM^{vi} are found to be incorporated into the copolymer. But ATMS incorporation is much higher. The ^{1}H NMR also shows that the polymers are highly branched. A typical ^{1}H NMR spectrum of a copolymer is shown in the **Figure 5.8**. The molecular weights of the copolymers are less than that of the homopolymer prepared under identical conditions. The molecular weight decreases with increase in comonomer incorporation.

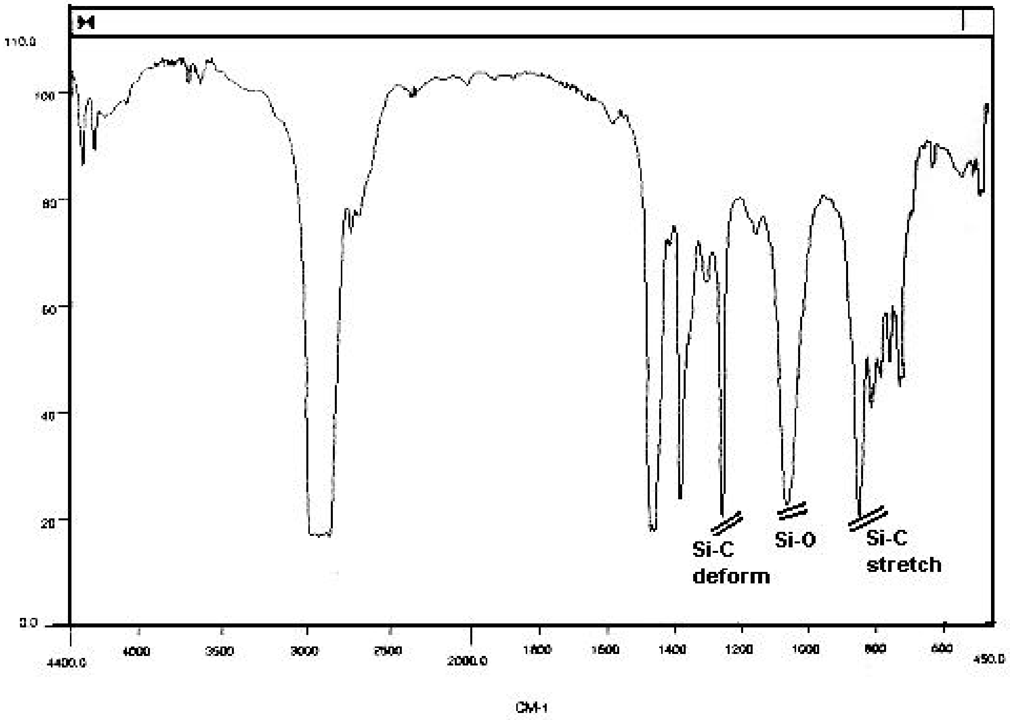


Figure 5.7 IR spectrum of ethylene-MM^{vi} copolymer

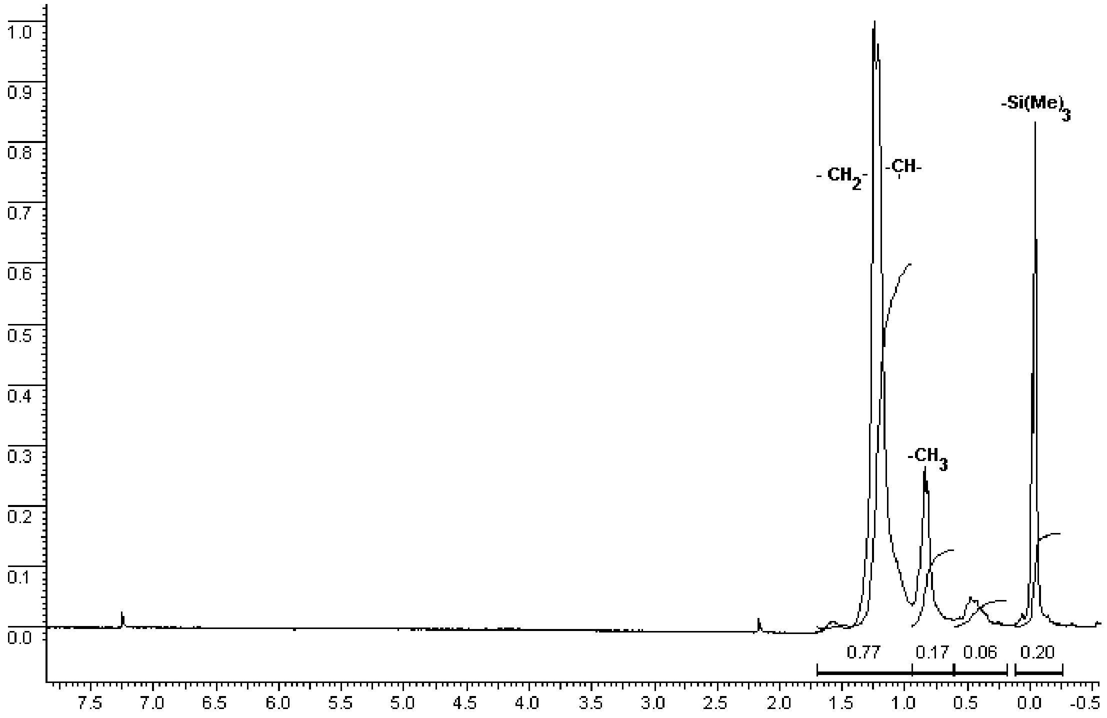


Figure 5.8 ^{1}H NMR spectrum of copolymer of ethylene with ATMS (Table 5.8; Entry 9)

5.3.2.1.2 Effect of comonomer concentration

Copolymerization of ethylene with these monomers were carried out by changing the comonomer feed and the results are given in **Table 5.7.** The ethylene polymerization rate decreases as the comonomer concentration in the feed increases for all the comonomers. The comonomer incorporation in the polymer also increases as its concentration in the feed increases. The dependence of comonomer feed concentration on comonomer incorporation into the polymer is shown in **Figure 5.9**. It clearly shows that the reactivity of M^{vi} and MM^{vi} is very poor. For M^{vi} and MM^{vi} the extent of incorporation was below 1 %.

The molecular weights of the copolymers decrease with increase in comonomer concentration in the feed. The MWDs of the copolymers are in the region 1.6 - 2.0 indicating the single site nature of the catalyst sites. The DSC chromatogram of the copolymers show that they are amorphous in nature. The 1st and 2nd runs of the DSC analysis of a copolymer of ethylene with ATMS is shown in the **Figure 5.10.**

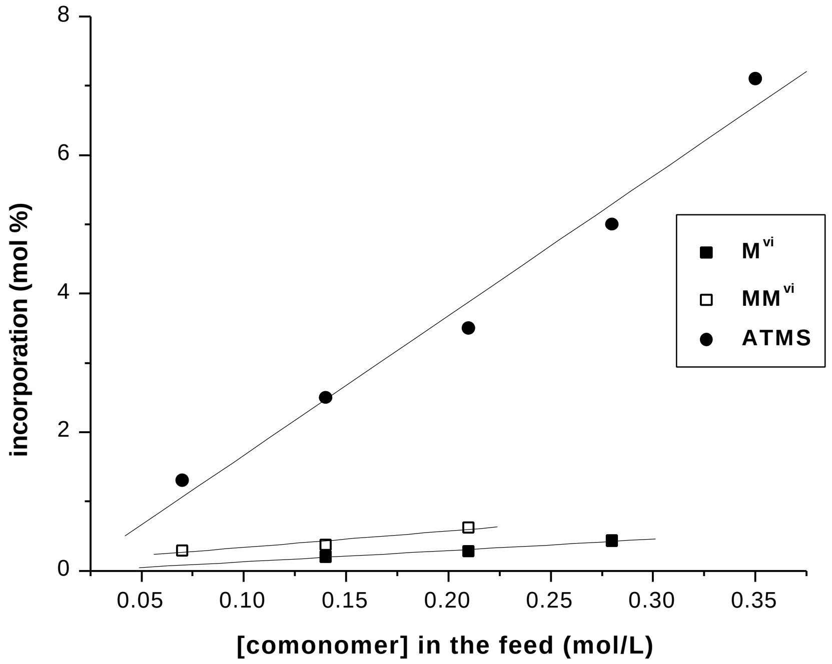


Figure 5.9 Effect of comonomer feed on copolymer composition

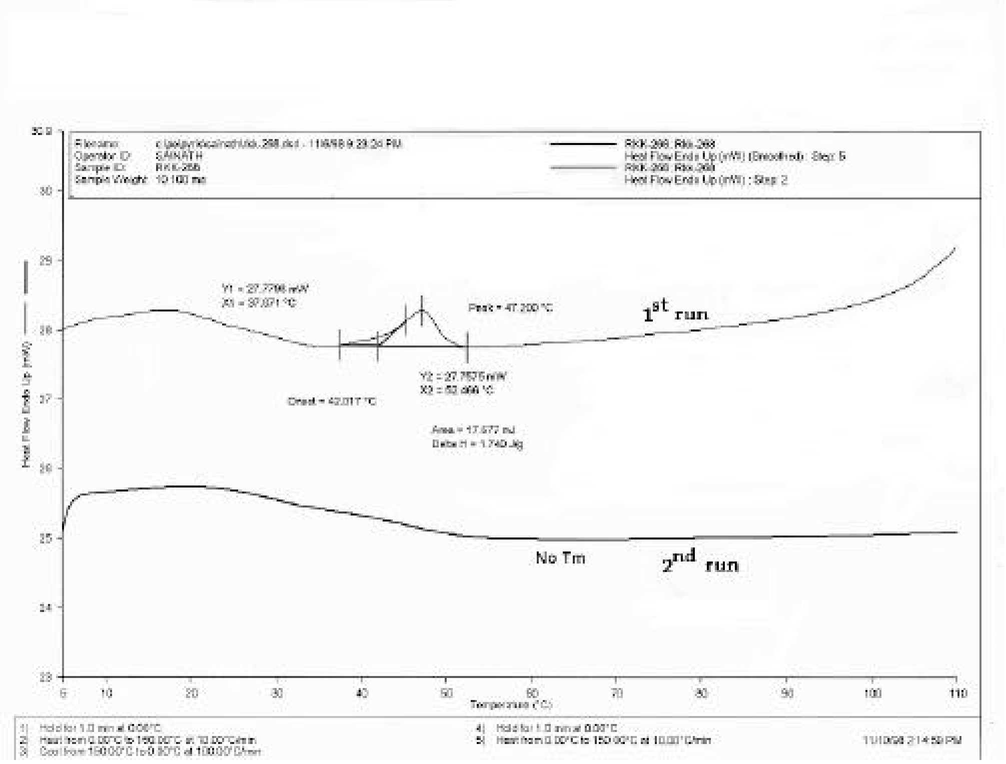


Figure 5.10 DSC chromatogram of a copolymer of ethylene with ATMS synthesized using DABAnNiBr$_2$

Table 5.7 Effect of comonomer feed on copolymerization using DABAnNiBr$_2$[a]

Entry	Comonomer	[comonomer] (mol/L)	Activity[b]	[comonomer] in copolymer (mol %)	Tm °C	[η] dL/g	Mw × 10^{-4}	MWD
1	-	-	635	-	45	3.2	21	1.7
2	M[vi]	0.07	312	nd	42	3.2	20	1.7
3		0.14	135	0.2	42	2.8	15	1.7
4		0.21	106	0.3	36	2.3	11	2.0
5		0.28	68	0.4	36	1.9	10	1.8
6[c]		0.52	44	0.9	30	1.4	6.2	2.0
7	MM[vi]	0.07	367	0.3	34	1.9	12	1.7
8		0.14	117	0.4	41	1.8	10	1.7
9		0.21	131	0.6	44	1.7	8.6	1.7
10		0.28	88	0.8	39	1.6	7.1	1.7
11	ATMS	0.07	253	1.3	No Tm	1.9	14	1.8
12		0.14	120	2.5	No Tm	1.8	11	1.6
13		0.21	50	3.5	No Tm	1.3	6.4	1.8
14[d]		0.28	27	5.0	No Tm	0.8	4.6	1.8
15[e]		0.35	46	7.1	No Tm	0.7	4.4	1.6

[a] Experimental conditions: Toluene = 50 mL; [Ni] = 5 × 10^{-5} mol/L; Al/Ni = 1000; time = 60 min; temp = 25 °C

[b] activity Kg copolymer/mol Ni.h; [c] [Ni] = 15 × 10^{-5} mol/L

[d] time = 180 min; [e] [Ni] = 1.5 × 10^{-4} mol/L

5.3.2.1.3 Effect of temperature

The effect of temperature on catalyst activity and polymer properties was studied. The ethylene polymerization rate decreased with increase in temperature. But slight improvement in the comonomer incorporation was observed in the case of MM^{vi} compared to M^{vi}. Substantial improvement in comonomer incorporation was observed in the case of ATMS. This may be either due to the enhanced reactivity of ATMS or due to the decreased ethylene concentration at high temperatures.

The copolymers prepared at higher temperatures are amorphous in nature due to increased methyl branching. Molecular weight of the copolymers decrease at higher temperatures as expected. The values for MWD are similar to that expected for single site catalysts.

Table 5.8 Effect of temperature on copolymerization using DABAnNiBr$_2$[a]

Entry	Comono-mer	Temp. °C	Activity[b]	[comonomer] in copolymer (mol %)	Tm °C	[η] dL/g	Mw × 10^{-4}	MWD
1	M^{vi}	25	106	0.3	36	2.3	11	2.3
2		35	105	0.25	No Tm	2.0	7.6	1.9
3		45	76	0.5	No Tm	1.4	6.7	1.7
4	MM^{vi}	25	117	0.4	41	1.8	10	1.7
5		50	235	0.7	No Tm	1.4	8.2	1.7
6		70	112	1.0	No Tm	1.0	5.2	1.8
7	ATMS	25	61	3.2	No Tm	1.4	7.8	1.6
8		50	80	4.8	No Tm	0.8	4.5	1.7
9		70	65	8.8	No Tm	0.2	nd	nd

[a] Experimental conditions: toluene = 50 mL; [Ni] = 5 × 10^{-5} mol/L; Al/Ni = 1000; time = 60 min; [comonomer] = 0.21 mol/L

[b] activity Kg copolymer/mol Ni.h

From **Table 5.7** and **5.8** it can be seen that unlike in the case of metallocene systems the extent of incorporation of the comonomers M^{vi} and MM^{vi} in the polymer is less than 1 mol % under the experimental conditions employed. In contrast, considerable amount of ATMS was incorporated.

This indicates the significance of methylene spacer group between the olefinic bond and the silyl group. Similar difference in reactivities due to spacer groups were observed and reported by Klabunde et al. using nickel catalysts which are modified SHOP catalysts. [43] He reported that copolymerization of ethylene with methyl methacrylate or vinyl acetate was unsuccessful since the strongly activating effect of the ester group on the vinyl group caused it to react with the nickel center, binding in an irreversible manner and blocking any further addition of olefins. But copolymerization of ethylene with functionalized monomers in which the vinyl unsaturation and the functional group are separated by a spacer of two or more methylene units was successful. Similarly all our attempts to copolymerize ethylene with allyl alcohol, allyl amine, methyl methacrylate, acrylonitrile etc using these Ni(diimine) catalysts were unsuccessful. However it was found that considerable amount of 5-hexenol (in excess of 15 mol %) can be incorporated in to the polyethylene chain using these catalysts. [49]

5.3.2.1.4 Effect of catalyst structure

The catalysts $DABAnNiBr_2$ and $DABH_2NiBr_2$ were used for the copolymerization studies under identical conditions to find out the effect of steric nature of the ligand on copolymerization. The results are given in **Table 5.9 and 5.10.**

Table 5.9 Effect of catalyst structure on the copolymerization behavior of MM^{vi} with ethylene[a]

Entry	Catalyst	Activity[b]	[comonomer] in copolymer (mol %)	[η] dL/g	Tm °C	Mw × 10^{-5}	MWD
1	$DABAnNiBr_2$	331	1.0	1.8	No Tm	11	1.8
2	$DABH_2NiBr_2$	105	2.0	0.7	91	2.4	2.3

a) Experimental conditions; toluene = 50 mL; [Ni] = 2.7×10^{-4} mol/L; Al/Ni = 1000; time = 60 min; temp = 25 °C; [MM^{vi}] = 0.39 mol/L

b activity Kg copolymer/mol Ni.h

Table 5.10 Effect of catalyst structure on the copolymerization behavior of ATMS with ethylene[a]

Entry	catalyst	Activity[b]	[comonomer] in copolymer (mol %)	[η] dL/g	Tm °C	Mw × 10^{-4}	MWD
1	$DABAnNiBr_2$	62	4.2	1.2	No Tm	6.9	1.6
2	$DABH_2NiBr_2$	40	5.2	0.3	75	1.1	2.1

[a] Experimental conditions; toluene = 50 mL; [Ni] = 1.5 × 10^{-4} mol/L; Al/Ni = 1000; time = 60 min; temp = 25 °C; [ATMS] = 0.2 mol/L

[b] activity Kg copolymer/mol Ni.h

As can be seen from the **Tables 5.9** and **5.10**, the catalyst $DABH_2NiBr_2$ incorporates higher amount of comonomer as compared to $DABAnNiBr_2$. This may be due to the fact that the catalyst $DABH_2NiBr_2$ is less sterically crowded and allows easy approach of bulky comonomers. The molecular weights of the copolymers are also lower in the case of $DABH_2NiBr_2$. The polymer prepared with this catalyst is less branched and more crystalline compared to that prepared with $DABAnNiBr_2$. The DSC chromatogram of the copolymers of ethylene with ATMS synthesized using $DABAnNiBr_2$ and $DABH_2NiBr_2$ are shown in **Figure 5.10** and **5.11** repectively. Eventhough the copolymer synthesized with $DABH_2NiBr_2$ has higher comonomer incorporation as well as lower molecular weight, it shows some crystallinity in the DSC chromatogram (second run).

Since $DABH_2NiBr_2$ was found to give better incorporation of the comonomer several copolymerization experiments were conducted in order to improve the incorporation of MM[vi]. But after work up the polymers were found to be insoluble, even in *o*-dichlorobenzene at 150 ºC. This indicates crosslinking through inadvertent hydrolysis of the siloxy functional groups.

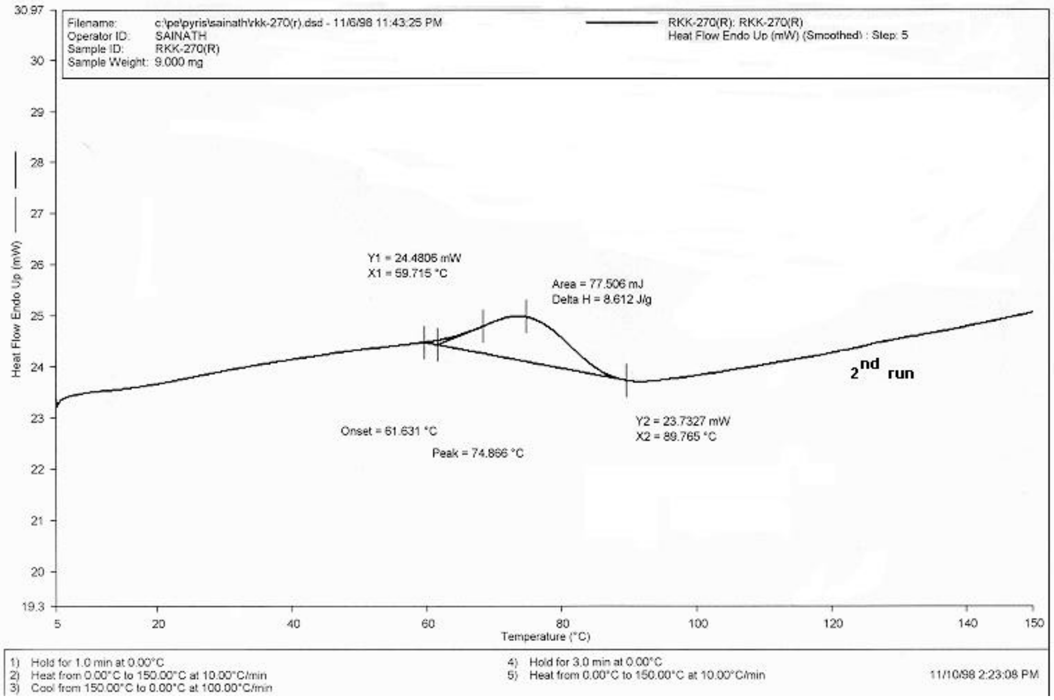
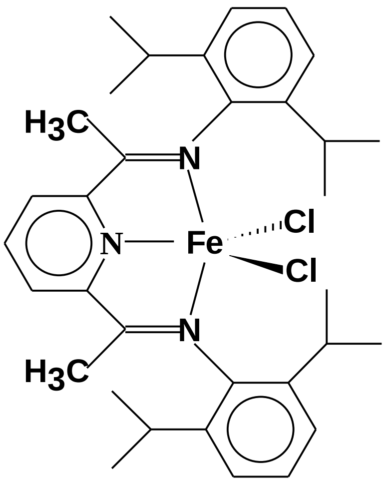


Figure 5.11 DSC Chromatogram of a copolymer of ethylene with ATMS synthesized using $DABH_2NiBr_2$

5.3.3 Iron(II)bis(imino)pyridyl catalyst

Recently Brookhart et al.[50] and Gibson et al.[51] developed iron and cobalt catalysts based on tridentate pyridine bis-imine ligands in which the imine moieties are bulky *ortho*-substituted aryl imines. The Fe based catalysts are highly active for ethylene polymerization. The iron(II)bis(imino)pyridyl catalysts have been reported to produce prevailingly isotactic poly(propylene).[52,53] Whereas Ni(II) based catalysts result in narrow polydispersity branched poly(ethylene)s, the bis(imino)pyridyl Fe(II) complexes produce broad polydispersity linear poly(ethylene)s when activated with either methylaluminoxane or modified methylaluminoxane (MMAO is MAO containing 25% isobutyl aluminoxane).



(3)

5.3.3.1 copolymerization

These catalysts could be even less electrophilic and oxophilic than the Ni based catalysts. Therefore copolymerization of ethylene with M^{vi}, MM^{vi}, ATMS, and VEDMS were studied. The reaction conditions and the catalyst activities are given in the **Table 5.11.**

Table 5.11 Copolymerization of ethylene with silicon containing monomers using Fe catalyst

Entry	[Fe] × 10^5 (mol/L)	comonomer	[comonomer] (mol/L)	Activity (Kg PE/mol Fe.h)	Tm °C
1	2.5	-	-	2600	139
2	5	M^{vi}	0.4	1600	131
3	5	M^{vi}	0.5	1940	133
4	2.5	M^{vi}	0.5	2400	137
5	2.5	ATMS	0.4	1027	134
6	5	MM^{vi}	0.4	1720	135
7	5	VEDMS	0.4	1100	134

Experimental conditions: toluene = 50 mL; [Al]/[Fe] = 1000; Time = 30 min;

In the case of Fe catalyst also the catalyst activity is decreased in the presence of comonomers. The IR and ^{1}H NMR analysis of the polymers show the absence of incorporation of comonomers.

It seems that this catalyst is highly selective for ethylene polymerization. The ^{1}H NMR spectra of copolymers of ethylene with M^{vi} and ATMS are shown in the **Figures 5.12** and **5.13** respectively.

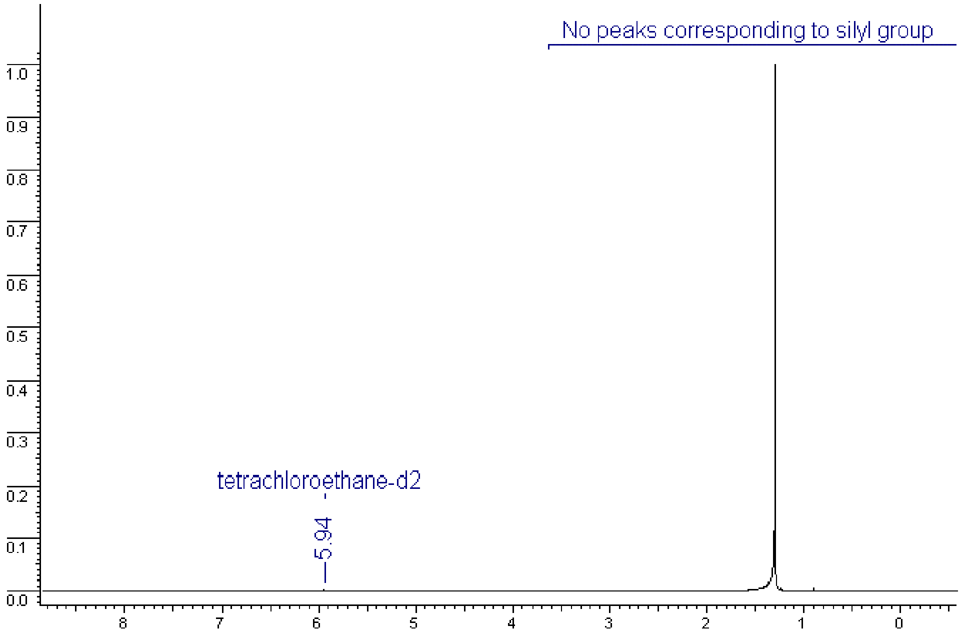


Figure 5.12 ^{1}H NMR spectrum of a copolymer of ethylene with M^{vi} (Table 5.11 Entry 4)

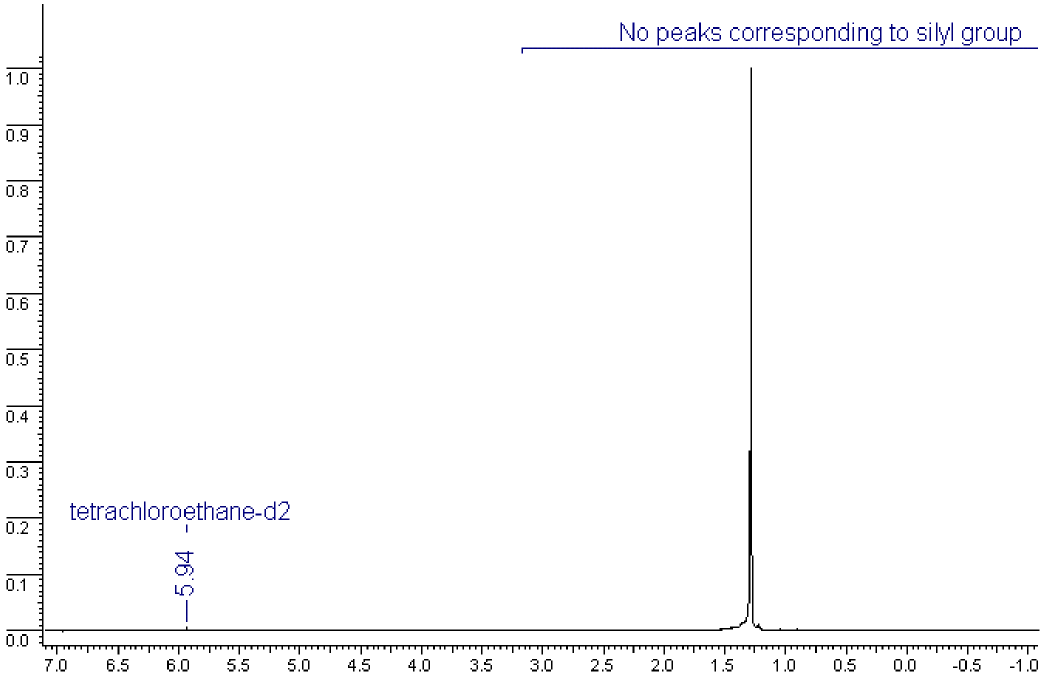


Figure 5. 13 ^{1}H NMR spectrum of a copolymer of ethylene with ATMS (Table 5.11 Entry 5)

5.4 Conclusions

Successful copolymerizations of ethylene with various silicon containing monomers have been described. The results indicate the sensitivity of coordination catalysts towards functional monomers. Ni based catalysts are more compatible with heteroatom functionality owing to their less oxophilic nature.

Copolymers of ethylene with MM^{vi} were prepared with Ni catalysts. This strategy can be applied for the synthesis of poly(ethylene) with crosslinkable functional sites.

Significant difference in reactivity was observed when the functional group is separated from the double bond by a methylene group. Since metallocene catalysts are reported to copolymerize ethylene with monomers containing Si-O bond, the deactivation may be due to the close proximity of Si-O bond to the double bond. The Fe based catalyst is found to be a poor catalyst for copolymerization. It is exclusively an ethylene polymerization catalyst.

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CHAPTER 6. ETHYLENE POLYMERIZATION USING NICKEL (DIIMINE) AND IRON(II)BIS(IMINO)PYRIDYL CATALYSTS

6.1 Introduction

Four decades after Ziegler and Natta's invention of transition metal catalysts for the polymerization of olefins, we are witness to the evolution of new generations of single site catalysts and polyolefin materials, which is revolutionizing the plastics industry. [1-3] In this aspect group 4 metallocenes and half-sandwich titanium amide complexes (constrained geometry catalysts) have dominated both academic and industrial research in the last 15 years. [4-18] However, it is generally acknowledged that no single class of catalyst will be able to control all the macromolecular parameters relevant to a wide and varied range of polyolefinic products. The never ending search for new catalyst families with better activities and capable of producing new homo as well as copolymers with new properties is continuing. A number of new discoveries have been made in this area and several new non-metallocene single site catalysts have appeared which show useful potential as catalysts for polyolefins. [19] In this aspect discovery of late transition metal catalysts based on Ni(II) and Pd(II) diimine derivatives can be considered as a major landmark. [20-23]

The late transition metal catalysts are best known to oligomerize ethylene and dimerize propylene and higher α-olefins and there are only few reports of olefin polymerization using Ni based catalysts.[24-29] Brookhart et al. reported a living ethylene polymerization system based on a cobalt complex.[30,31] A cobalt olefin complex, $(C_5Me_5)Co\{P(MeO)_3\}(H_2C{=}CHAr)$ (Ar = Ph, p-C_6H_4Cl, p-C_6H_4OAc, p-$C_6H_4CF_3$, C_6F_5), with $HB\{C_6H_3(CF_3)_2\text{-}3,5\}_4$ polymerize ethylene with an activity 3.8 kg PE $mol^{-1}h^{-1}atm^{-1}$, Mn = 1.48×10^4, $M_w/M_n = 1.11$.

The late transition metal based catalysts prefer β-hydride elimination followed by reductive elimination. But the use of bulky substituents on the aryl groups of the diimine ligand block associative olefin exchange, thereby, retarding the chain transfer leading to high molecular weight polymers. Using this as a hypothesis research groups of Brookhart [32,33] and Gibson[34] developed iron and cobalt catalysts based on tridentate pyridine bis-imine ligands in which the imine moieties are bulky *ortho*-substituted aryl imines. An iron(II)bis(imino)pyridyl catalyst has also been reported to produce prevailingly isotactic poly(propylene). [35,36]

Whereas Ni(II) based catalysts containing bulky diimine ligands result in narrow polydispersity branched poly(ethylene)s, the bis(imino)pyridyl Fe(II) complexes produce broad polydispersity linear poly(ethylene)s when activated with either methylaluminoxane or modified methylaluminoxane (MMAO is MAO containing 25% tetraisobutyl dialuminoxane). Depending on the experimental conditions poly(ethylene) prepared by Fe catalyst has even bimodal distribution. This behavior in the case of Fe catalyst was explained as due to chain transfer to aluminium in the cocatalyst, MAO. [32] But poly(propylene)s synthesized using this catalyst were of narrow molecular distributions with a polydispersity of 2.0.[36]

Polydispersity in poly(ethylene)s produced by transition metal catalyst is a consequence of its electronic state (single or multiple sites) as well as the nature of transfer reactions. Both these factors are intimately affected by the nature of the activator, namely, the organoaluminum compound.

The objective of the present work is to study the effect of employing different cocatalysts on ethylene polymerization and polymer properties. An iron(II) based catalyst 2,6-bis{1-[2,6(diisopropylphenyl)imino]ethyl}pyridine iron dichloride was used for the study. A Ni diimine catalyst [(N,N′-diisopropylbenzene)-2,3-(1,8-naphthyl)-1,4-diazabutadiene] dibromo nickel has also been used in conjunction with various organoaluminum compounds.

6.2 Experimental

6.2.1 Materials

Procedures for the preparation of 2,6-bis[1-(2,6-diisopropylphenylimino)ethyl]pyridineiron(II) chloride and [(N,N′-diisopropylbenzene)-2,3-(1,8-naphthyl)-1,4-diazabutadiene] dibromo nickel are described in **chapter 2.**

6.2.2 Polymerization

The detailed polymerization procedure and work up is given in **chapter 3.** All the polymerizations were done in the presence of solvents (total volume 50 mL) and at 25 °C unless indicated otherwise.

6.2.3 Analysis

The molecular weight distributions were determined using a Waters Gel Permeation Chromatograph mode GPC/ALC 150C instrument equipped with a refractive index detector and μ-styragel columns (HT-3, 4, 5, 6E) at 140 °C and 1,2,4-trichlorobenzene as solvent with 1 mL/min flow rate. The data was processed using *PSSwinGPC scientific software.* The GPC analysis of those samples whose intrinsic viscosity (η) values exceed 3 dL/g were not performed.

6.3 Results and Discussion

6.3.1 iron(II) catalyst

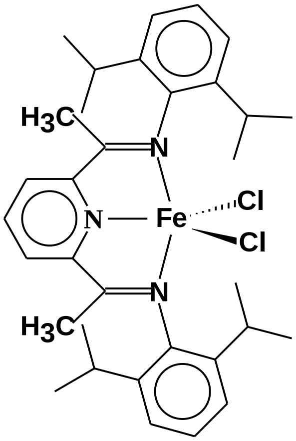

Figure 6.1 Structure of the iron(II)bis(imino) pyridyl catalyst

6.3.1.1 Effect of cocatalysts

All the polymerizations were done under identical experimental conditions. Cocatalysts viz. MAO, TIBDAO, TIBAL, TMA and DEAC were used. Al/Fe ratio of 1000 had been used even though the catalyst is active at lower ratios also. The results are summarized in **Table 6.1.** Like MAO and TIBDAO, other simple aluminium alkyls like TIBAL and TMA are also effective cocatalysts for ethylene polymerization. However, under the various conditions tried, DEAC was found to be a non-activator for the iron catalyst.

The rate profiles **(Figure 6.2)** exhibited typical decay type kinetics, i.e., very high initial rate followed by a rapid decay, reminiscent of zirconocene based homogeneous catalysts.[37] For all the cocatalysts, the catalyst activity was found to be very high in the initial stage i.e. upto 10 min followed by a rapid decay. This suggests that the lifetime of the catalyst is very short, may be due to some degradation of the catalyst. The catalyst activity as well as its lifetime was superior in the case of TIBDAO compared to MAO. But under these identical conditions the highest activity was observed when TMA was used as the cocatalyst and its kinetic profile was of build up type in nature. The activities were found to decrease in the order TMA>TIBDAO>MAO>TIBAL.

Table 6.1 Effect of cocatalyst on catalyst activity and polymer properties

Entry	Cocatalyst	Yield (g)	Catalyst activity[a]	Mw	Mw/Mn	[η] dL/g	Tm °C
1	MAO	1.05	950	146 000	bimodal	2.5	139
2	TIBDAO	1.58	1440	108 000	2.2	2.2	136
3	TIBAL	0.84	765	117 000	2.1	1.9	135
4	TMA	1.75	1600	128 000	bimodal	2.3	131

Exptl conditions: toluene = 50 mL; Fe = 1.1 $\times 10^{-6}$ mol; Al/Fe = 1000; temp. = 25 °C; [a]Activity is expressed as Kg PE/mol Fe.h

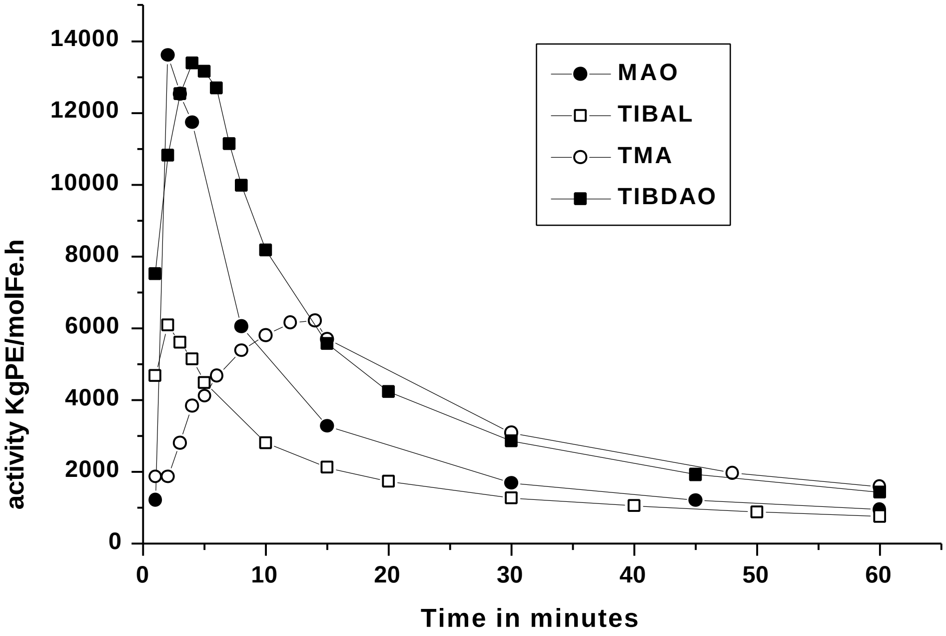

Figure 6.2 Kinetic profile of ethylene polymerization using different cocatalysts

In all the cases linear poly(ethylene)s (Tm 130-140 °C) were produced (Figure 6.3). The molecular weights are high with intrinsic viscosities ranging from 2 to 2.5 dL/g.

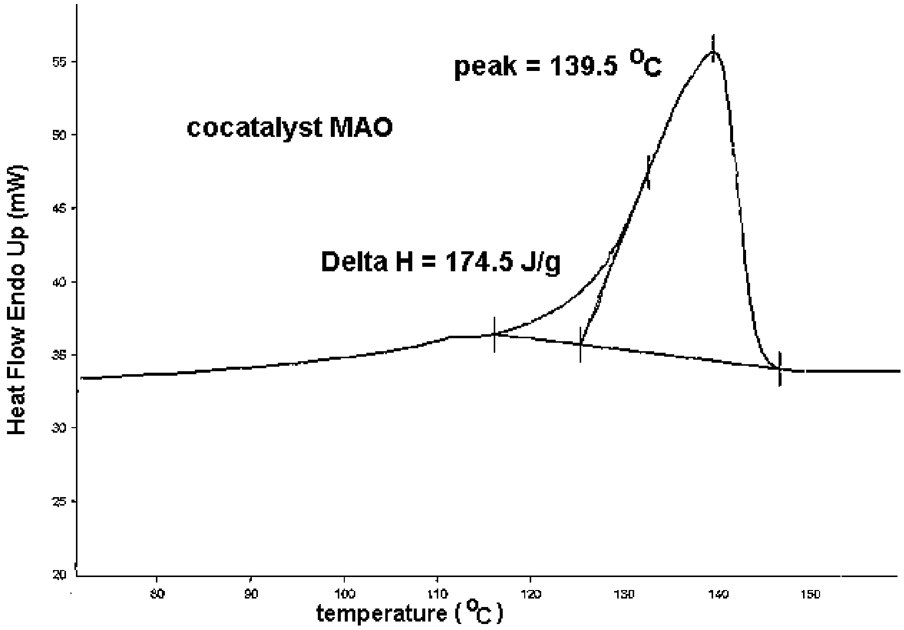

Figure 6.3 DSC thermogram of poly(ethylene) synthesized using the iron catalyst

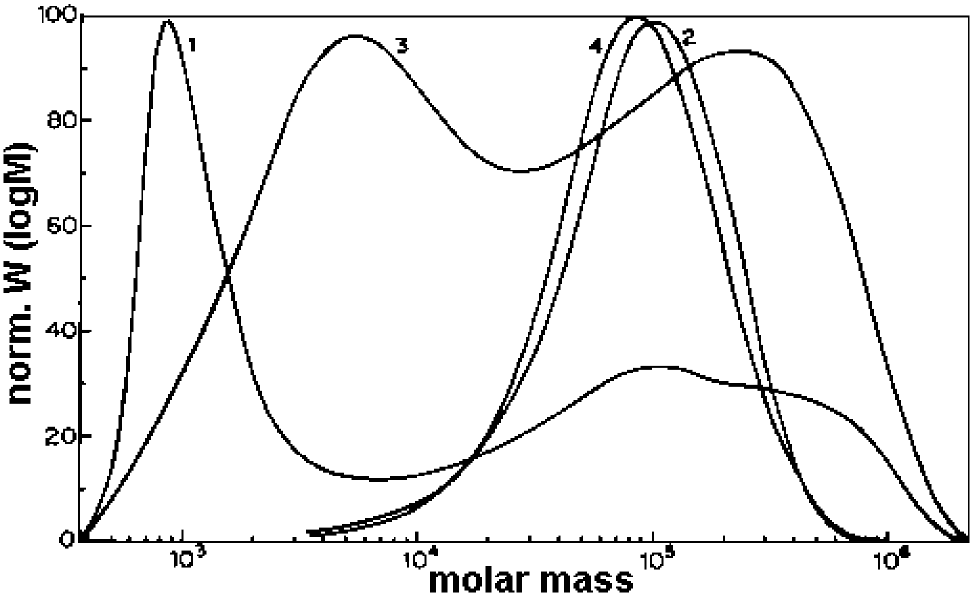

Figure 6.4 GPC curves of poly(ethylene)s synthesized using different cocatalysts, (1) TMA, (2) TIBAL, (3) MAO, (4) TIBDAO

However, the most unexpected observation was with respect to polydispersity (**Figure 6.4**). Whereas MAO and TMA gave broad and bimodal distribution of molecular weights, TIBDAO and TIBAL gave a narrow distribution of molecular weights, (Mw/Mn ≈ 2) similar to what is generally observed in homogeneous early transition metal (metallocene) catalysts. In the case of TMA, a distinct low molecular weight fraction was observed.

Brookhart and coworkers also reported a broad and bimodal polydispersity with the same catalyst, but using modified MAO (MMAO) as the activator.[32] MMAO is MAO modified by 25 % TIBDAO. Whereas no polydispersity data was reported by Gibson and coworkers, they used MAO as an activator and TIBAL as a scavenger.[34] Based on the observation that the end groups of the low molecular weight fraction was saturated, Brookhart and coworkers ruled out the possibility of multiple active sites as being the cause of broad polydispersity. The low molecular weight fraction was ascribed to a chain transfer process to the organoaluminium compound.

The observation that TIBAL and TIBDAO produce narrow polydispersity poly(ethylene)s is indicative that with these activators, the catalyst behaves as a “true single site” catalyst unlike in the case of MAO or MMAO as an activator. It is to be noted that TIBDAO is a more discrete and structurally pure aluminoxane as compared to MAO. The latter is always associated with variable quantities of TMA (commercial MAO contains about 30% of TMA bound to it).

Small and Brookhart[36] and Pellecchia and coworkers[35] have reported isospecific polymerization of propylene using this catalyst. Based on NMR studies both the groups established that Fe-CH_2-CH_2-CH_3 is the key intermediate in the catalytic cycle. Brookhart reported that alkyl transfer does not occur in the secondary Fe-alkyls. The presence of n- propyl and 3-methylbutyl end groups was attributed to the transfer reactions which Fe- propyl complex undergoes with TEAL and TIBAL or TIBDAO (from MMAO). The methyl groups from MMAO are found to be not involved in these exchange reactions since sec-butyl end groups were not observed. The alkyl chain transfer processes are significant only in ethylene polymerization since primary Fe-alkyl bonds are present. This might be the reason for the narrow molecular weight distribution observed in the case of propylene polymerization. He concluded from his study that the effectiveness of the transfer reactions decrease in the order TEAL> TIBDAO(from MMAO) ≈ TIBAL >>>Al-CH_3. In contrast, using ^{13}C enriched TMA, Pellecchia et al. observed the presence of ^{13}C enriched end groups which are formed from 1,2 or 2,1 insertion of propylene into the Fe- $^{13}CH_3$. Our results are not in agreement with the conclusions of Brookhart since narrow molecular weight distributions are obtained when TIBDAO and TIBAL are used as cocatalysts and excessive transfer reactions with MAO or TMA. A detailed end group analysis is needed to arrive at a definitive conclusion.

The effect of different reaction parameters for different cocatalysts employed are discussed in the following sections.

6.3.1.2 Effect of Al/Fe ratio

For all the cocatalysts the overall activities were found to increase with increase in Al/Fe ratios **(Figure 6.5)**. In the case of TIBDAO at an Al/Fe ratio of 3000 the activity was found to be lower compared to that at 1500. For other cocatalysts this kind of optimal level is not reached under the conditions used.

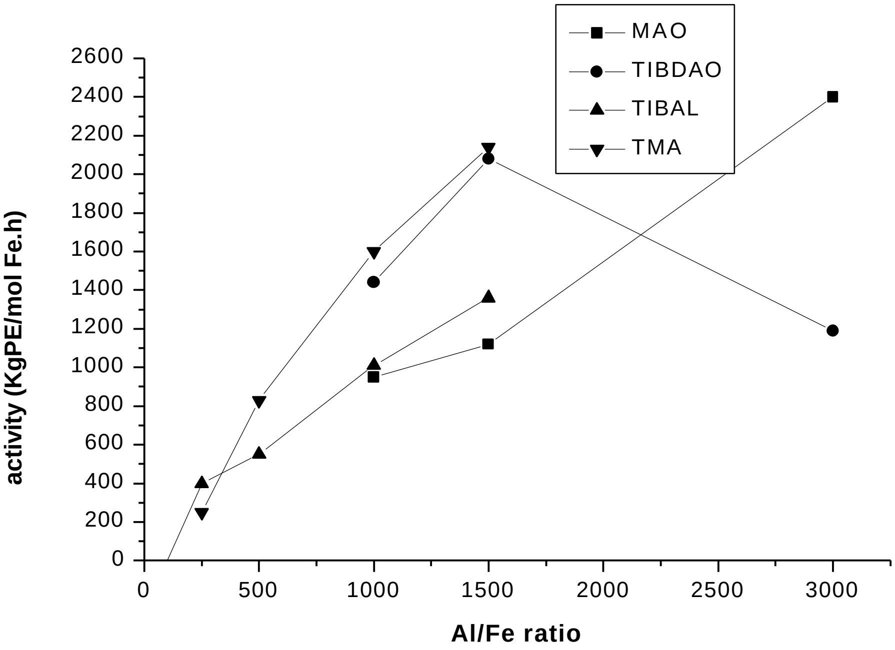

Figure 6.5 Effect of Al/Fe ratio on catalyst activity

The kinetic profile of ethylene polymerization at different Al/Fe ratios is shown in the **Figures 6.6, 6.7, 6.8** and **6.9**. For all the cocatalysts the catalyst deactivation is faster at lower ratios of Al/Fe, even though the initial activity is higher. This can be attributed to the formation of inactive species with a M-CH_2-Al structure.[38] The observed increase in life time may be due to the reactivation of this inactive species by excess cocatalyst. The results are summarized in the **Table 6.2**.

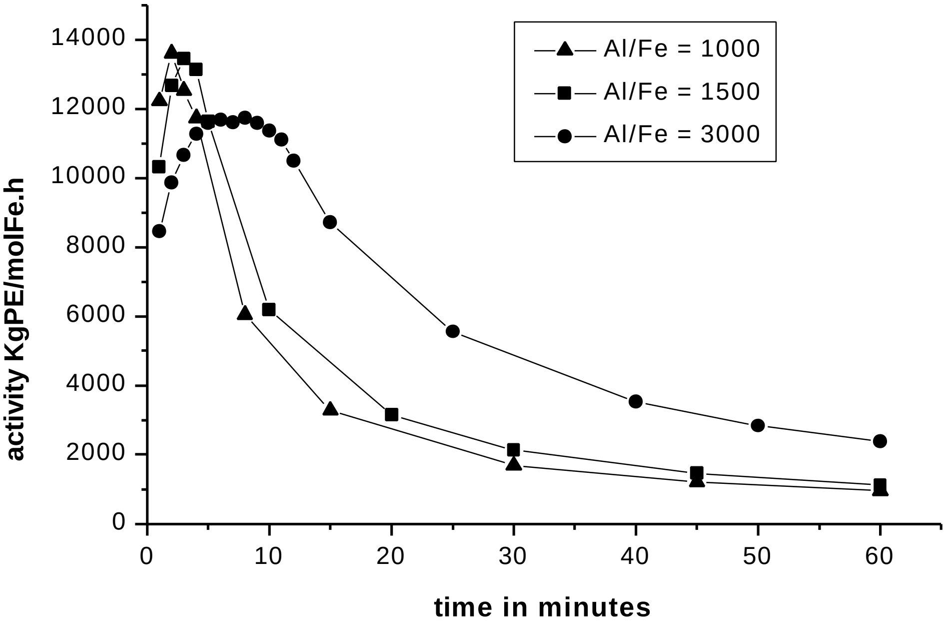

Figure 6.6 Kinetic profile of ethylene polymerization at different [MAO]/[Fe] ratios

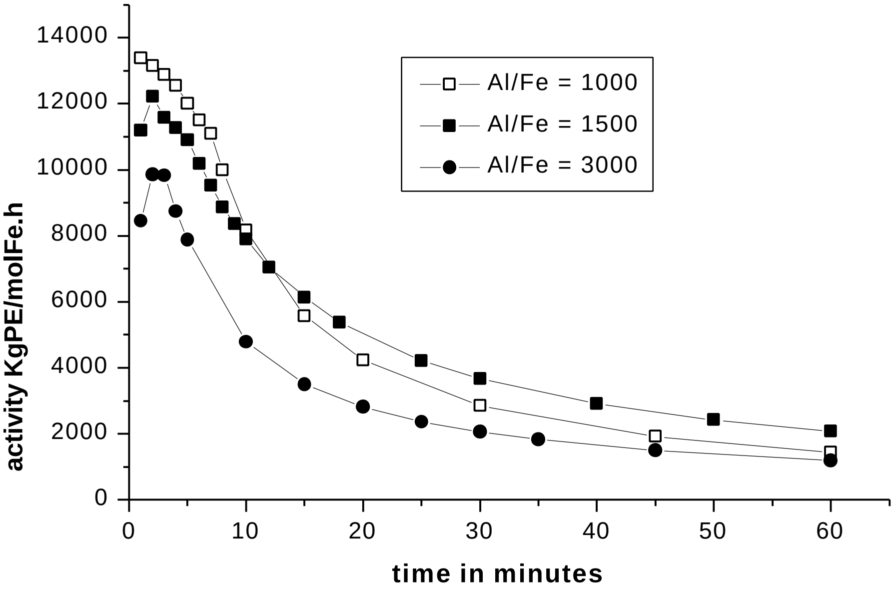

Figure 6.7 Kinetic profile of ethylene polymerization at different [TIBDAO]/[Fe] ratios

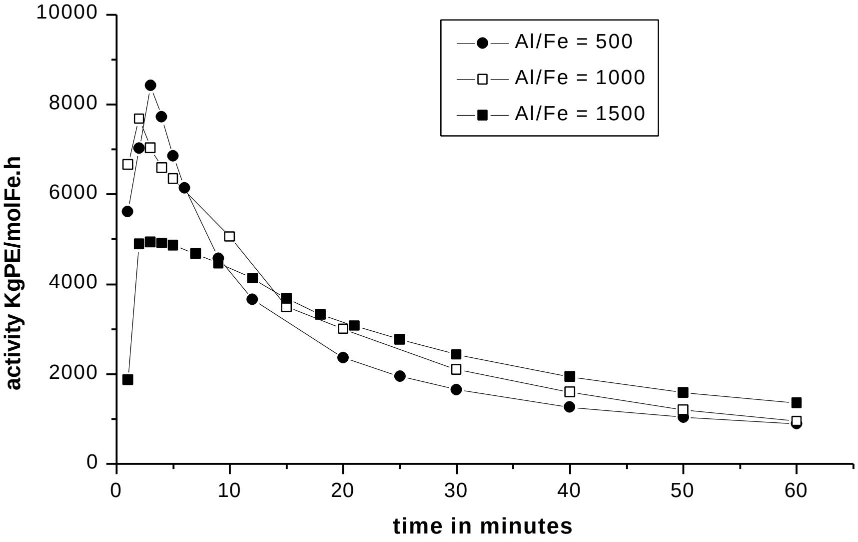

Figure 6.8 Kinetic profile of ethylene polymerization at different [TIBAL]/[Fe] ratios

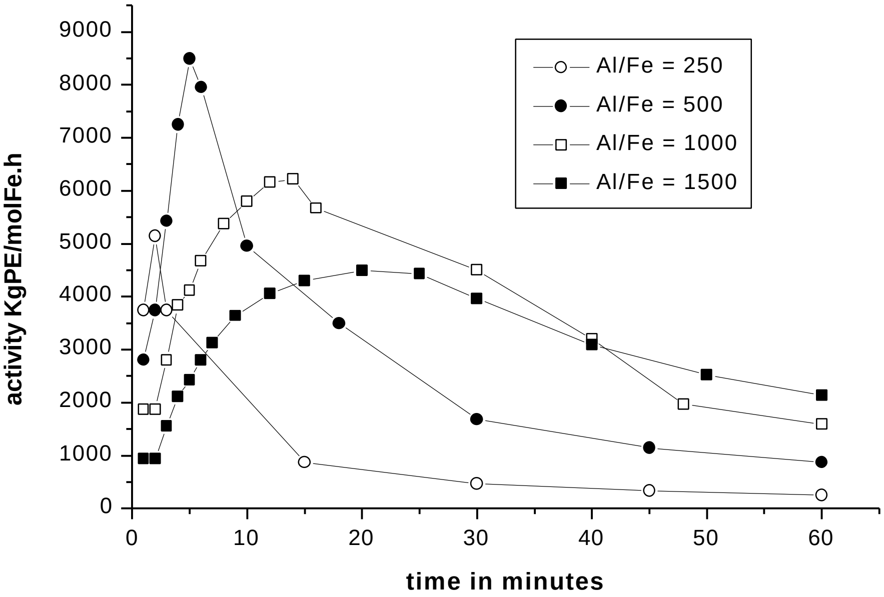

Figure 6.9 Kinetic profile of ethylene polymerization at different [TMA]/[Fe] ratios

Table 6.2 Effect of Al/Fe ratio on catalyst activity and polymer properties[a]

Entry	Cocatalyst	Al/Fe	Activity[b]	$Mw \times 10^{-4}$	Mw/Mn	[η] dL/g
1	MAO	1000	950	14.6	24, BM	2.5
2	MAO	1500	1120	10.0	25, BM	2.1
3	MAO	3000	2400	9.5	30, BM	1.9
4	TIBDAO	1000	1440	10.8	2.2	2.2
5	TIBDAO	1500	2080	9.2	2.5	2.1
6	TIBDAO	3000	1190	nd	nd	1.8
7	TIBAL	25	No polymerization			
8	TIBAL	100	No polymerization			
9	TIBAL	250	1110	nd	nd	3.4
10	TIBAL	500	990	nd	nd	3.1
11	TIBAL	1000	1010	11.7	2.1	1.9
12	TIBAL	1500	1360	9.5	2.7	1.5
13	TMA	250	250	4.0	13, broad	1.0
14	TMA	500	830	8.2	32, BM	1.5
15	TMA	1000	1600	12.8	59, BM	2.3
16	TMA	1500	2140	nd	nd	3.2

[a] Experimental conditions: Fe = 1.1×10^{-6} mol; Temperature = 30 °C. [b] activity expressed as Kg PE/mol Fe.h

In the case of MAO, TIBDAO, TIBAL the molecular weight of the polymers was found to decrease as the Al/Fe ratio increases. This may be due to the chain transfer reactions with cocatalyst. This kind of behavior is observed in the case of metallocene catalyzed olefin polymerization also. In the case of MAO, it can be observed from the GPC traces of the polymers that the higher molecular weight fraction decreases at higher ratios of Al/Fe **(Figure 6.10)** and the nature of the curve becomes similar to that in the case of TMA based polymerization **(Figure 6.12)**. It indicates that chain transfer reactions become predominant when TMA is used.

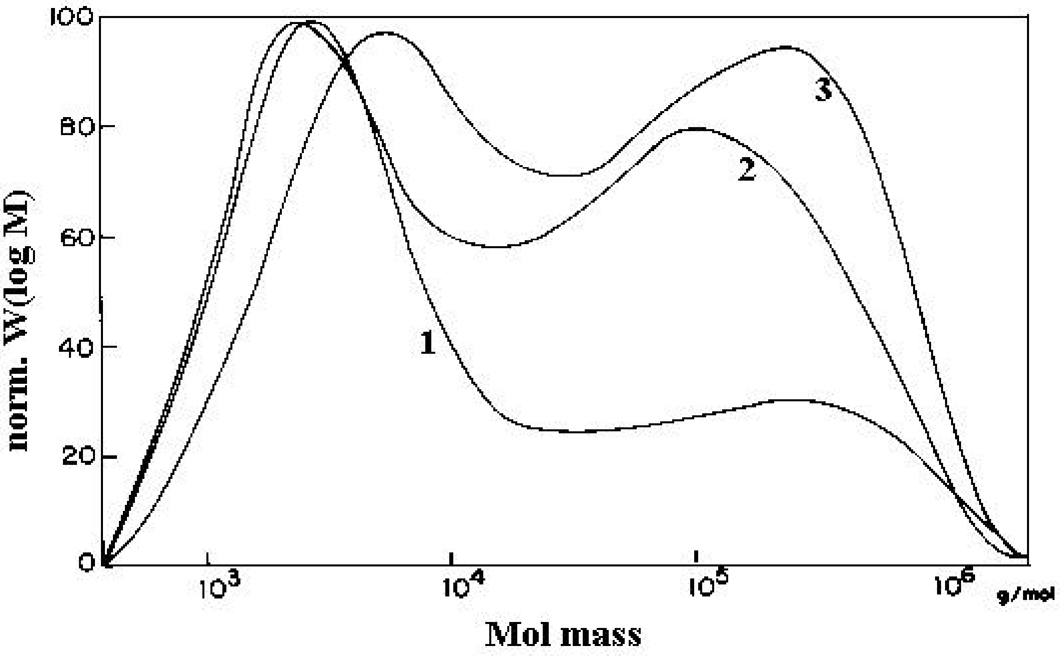

Figure 6.10 GPC curves of poly(ethylene)s synthesized using different MAO/Fe ratios (1) 3000, (2) 1500 and (3) 1000

Apart from reduction in the molecular weight values, a little broadening of the molecular weights was also observed in the case of TIBAL **(Figure 6.11).** The MWD increases from 2.0 to 2.7 when Al/Fe increased from 1000 to 1500. But in contrast the average molecular weights and the intrinsic viscosities increase when higher ratios of TMA were used. From the GPC curve **(Figure 6.12)** it can be seen that at higher ratios the lower molecular weight fraction is becoming more sharper and narrower in distribution.

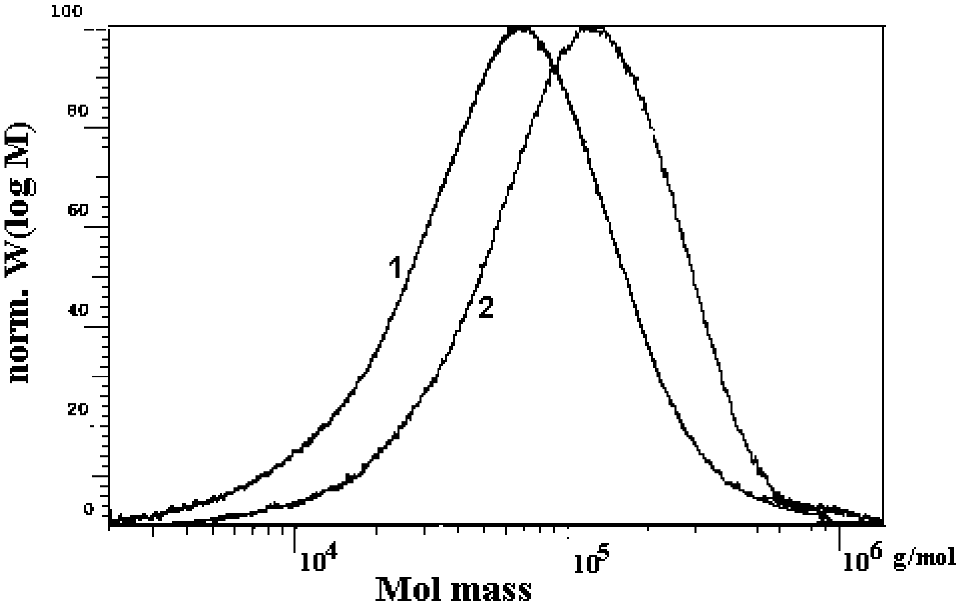

Figure 6.11 GPC curves of poly (ethylene)s synthesized using different TIBAL/Fe ratios (1) 1500 and (2) 1000

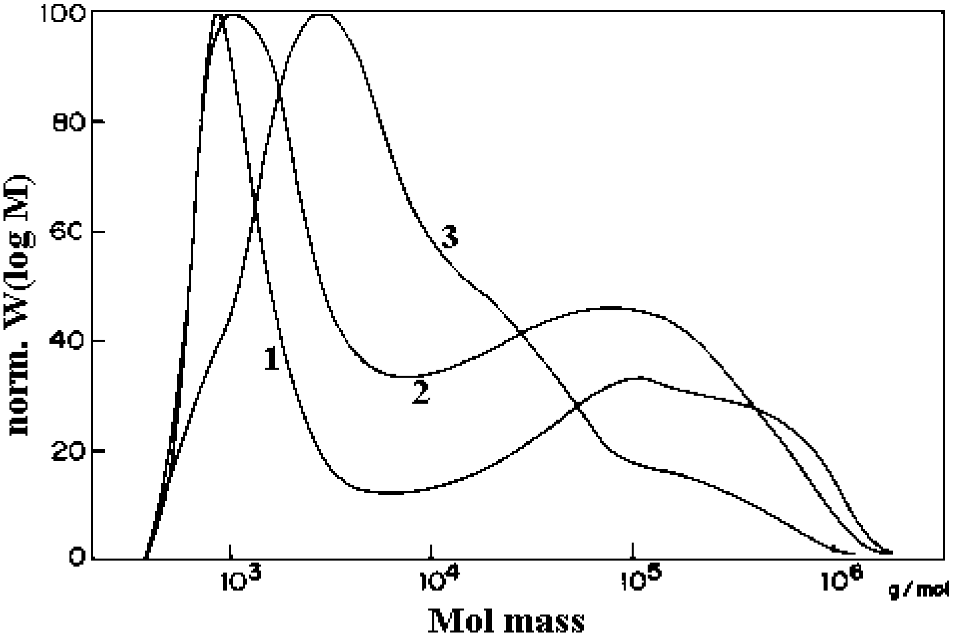

Figure 6.12 GPC curves of poly (ethylene)s synthesized using different TMA/Fe ratios (1) 1000, (2) 500 and (3) 250

6.3.1.3 Effect of catalyst concentration

Polymerizations can also be initiated with lower Al/Fe ratios when higher catalyst concentrations are used. This is due to the higher amount of aluminum alkyl used that takes care of the impurities, which becomes otherwise critical. The kinetic profile of the ethylene polymerization using different catalyst concentrations using MAO as cocatalyst **(Figure 6.13)** indicate that the catalyst life time is longer at higher concentrations of catalyst.

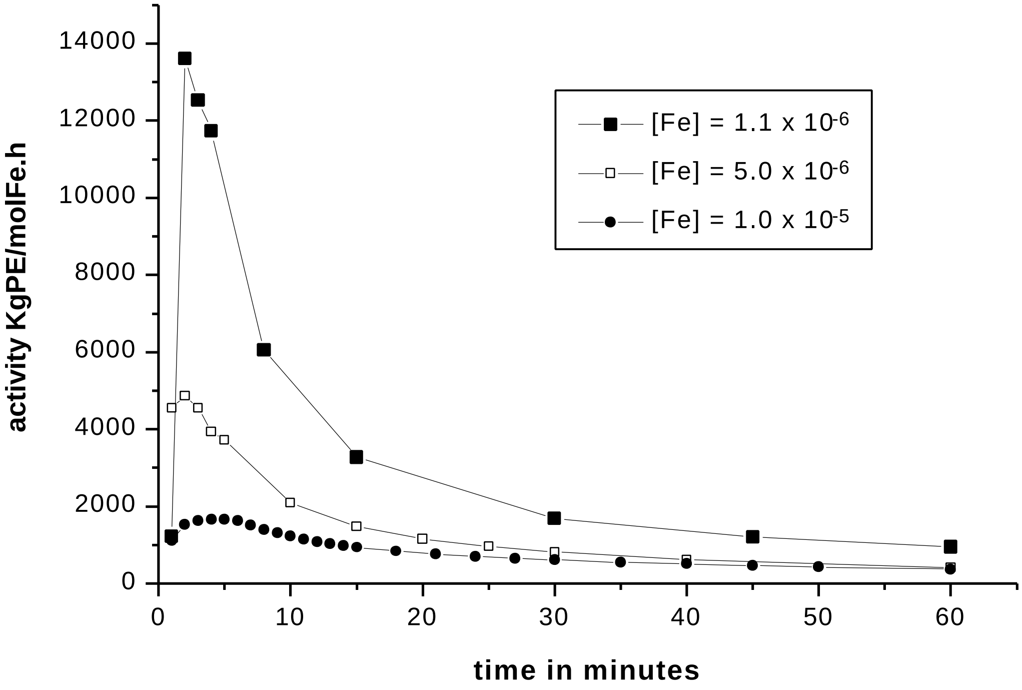

Figure 6.13 Kinetic profile of ethylene polymerization at different catalyst concentrations

A rapid decay is observed when lower concentrations of catalyst are used. This indicates deactivation of the catalyst during polymerization. The effect of catalyst concentration on activity and polymer properties has been studied and the results are summarized in **Table 6.3**.

Table 6.3 Effect of catalyst concentration on catalyst activity and polymer properties

Entry	Mol Catalyst $\times 10^6$	Cocatalyst	Al/Fe	Catalyst activity[a]	Mw $\times 10^{-4}$	Mw/Mn	[η] dL/g
1	1.1	MAO	1000	950	14.6	24, BM	2.5
2	5	MAO	1000	420	5.3	30, BM	2.0
3	10	MAO	1000	370	7.5	52, BM	1.8
4	1.1	TIBAL	100	No polymerization			
5	5	TIBAL	100	255	10.8	2.1	2.0
6	10	TIBAL	100	280	5.7	14, UM	1.2
7	1.1	TMA	250	250	4.0	13, broad	1.0
8	5	TMA	250	300	7.6	46, BM	1.4
9	10	TMA	250	650	nd	nd	4.5

[a] activity expressed in Kg PE/mol Fe.h

At higher catalyst concentrations the three cocatalysts behaved differently. Whereas in the case of MAO, the activity decreased at higher concentrations, there was no significant difference in the case of TIBAL. But an increase in activity was observed at higher catalyst concentrations when TMA was used as the cocatalyst. Unlike with other cocatalysts the kinetic profiles of ethylene polymerization for the TMA activated systems were found to be build-up type in nature. This indicates that the rate of formation of the active species is slower when TMA is used as an activator. The decrease in activity with increase of catalyst concentration was observed by many researchers in the case of metallocene catalysts. [39,40] The number of active sites [C*] lies between 75 and 100%, and therefore the activity should be independent of [Zr].[39] The increase in activity with decrease of catalyst concentration is explained as due to increase of kp(rate constant of propagation). The catalyst activity is proportional to $[Cp_2ZrCl_2]^{-0.77}$ when log activity versus $[Cp_2ZrCl_2]$ is plotted. This indicates faster propagation at lower concentrations of catalyst.

The molecular weights of the polymers were found to decrease at higher catalyst concentrations (**Figure 6.14**) in the case of MAO and TIBAL, but it was found to increase in the case of TMA

(Figure 6.15). It can be seen from the GPC traces that the low molecular weight fraction is becoming more distinct and lower in molecular weight.

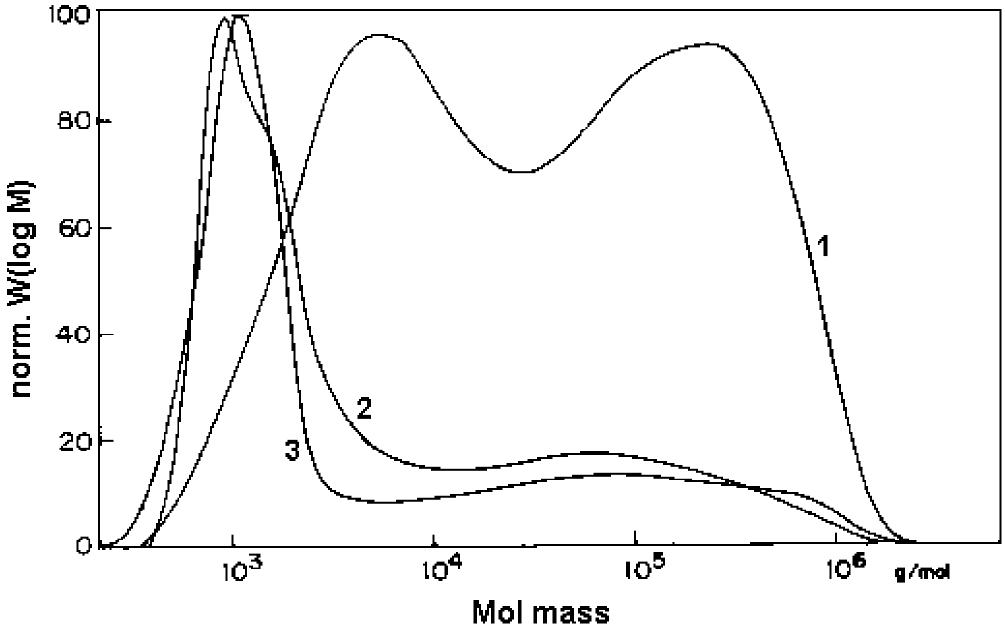

Figure 6.14 GPC curves of poly(ethylene)s synthesized using different catalyst concentrations / (MAO); (1) 1.1×10^{-6}, (2) 5×10^{-6} and (3) 10×10^{-6}

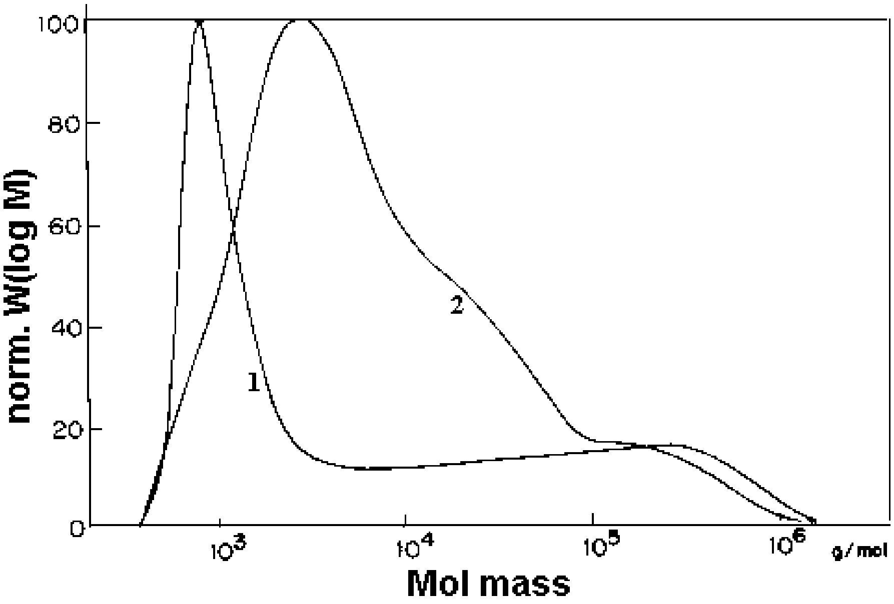

Figure 6.15 GPC curves of poly(ethylene)s synthesized using different catalyst concentrations (TMA); (1) 5×10^{-6} and (2) 1.1×10^{-6}

At the same time the higher molecular weight fraction also increases, thereby, increasing the average molecular weight of the polymer. In all the cases broadening of molecular weights were observed as the catalyst concentration were increased. The MWD distribution increased from 2.1 to 14 when the catalyst concentration was increased (Entries 5 and 6 in **Table 6.3**)

6.3.1.4 Effect of temperature on catalyst activity and polymer properties

In the case of metallocene based olefin polymerization the catalyst activities increase monotonously with temperature. A detailed study of the effect of polymerization temperature (Tp) on catalyst activity was reported by Chien and Sugimoto.[41] The strong dependence of the catalytic activity of zirconocene/MAO system on Tp may be due to either the rate of propagation or the rate of formation of active species. Since zirconocene cation has a low energy of activation for propagation, this was explained as due to the shift in equilibrium between free active species and MAO-coordinated species. The free catalytic species is more active than the complexed one. At high temperatures the solubility of ethylene in the reaction medium decreases and the concentration of the monomer available to the active species is actually less.

Ethylene polymerizations using the Fe catalyst with various activators were studied at various temperatures. The results are summarized in **Table 6.4.**

In the case of MAO and TIBDAO activated systems, the catalyst activity decreases at higher temperatures. This may be either due to catalyst deactivation or due to decreased monomer concentration. Since the catalyst has been reported to be stable even at high temperatures (as high as 125 °C) reduction in catalyst activity may be mainly due to the low ethylene concentration in the reaction medium.[32] The kinetic profile of polymerization in the case of MAO is shown in the **Figure 6.16.**

But in the case of TIBAL and TMA there was no significant change in the activity in the temperature range 25 – 40 °C. So there may be some rate enhancement processes which offset the effect of decreased monomer concentration. Moreover it has been observed that at 40 °C there is a slight increase in overall activity compared to that at 25 °C due to longer catalyst life. There was no reduction in activity at 60 °C in the case of TIBAL. However, in case of TMA the catalyst activity decreased upon increase of temperature. The catalyst was inactive at 60 °C.

Table 6.4 Effect of polymerization temperature (Tp) on catalyst activity and polymer properties

Entry	Mol catalyst $\times 10^6$	Cocatalyst	Al/Fe	Tp °C	Catalyst activity[a]	Mw $\times 10^{-4}$	Mw/Mn	[η] dL/g
1	1.1	MAO	1000	25	950	14.6	24, BM	2.5
2	1.1	MAO	1000	40	700	7.2	17, BM	1.2
3	1.1	MAO	1000	60	420	3.1	8.4,BM	0.5
4	1.1	MAO	1000	80	200	nd	nd	0.3
5	1.1	TIBADAO	1000	25	1040	10.8	2.2	2.2
6	1.1	TIBADAO	1000	40	690	10.5	2.2	2.0
7	1.1	TIBADAO	1000	60	380	4.2	1.9	0.9
8	5	TIBAL	100	25	255	10.8	2.1	2.0
9	5	TIBAL	100	40	285	6.6	6.9	1.2
10	5	TIBAL	100	60	260	3.6	6.4	0.7
11	5	TMA	250	25	300	7.6	46, BM	1.4
12	5	TMA	250	40	370	8.7	51, BM	1.7
13	5	TMA	250	50	350	2.8	30, BM	0.9
14	5	TMA	250	60	No polymerization			

[a] activity expressed in Kg PE/mol Fe.h

The molecular weights of the polymers are expected to decrease as the polymerization temperature increases. This is due to the increase in rate of chain transfer and termination reactions which has higher activation energy than the rate of propagation. This is found to be the case in all the polymerizations irrespective of the cocatalyst.

Temperature was found to have substantial influence on the distribution of molecular weights, especially, in the case of MAO and TIBAL activated systems. In the case of MAO, as the polymerization temperature increases the distribution of molecular weights was found to become narrower. From the GPC curves **(Figure 6.17)** it can be seen that the higher molecular weight fraction decreases drastically compared to the low molecular weight factions at higher Tp.

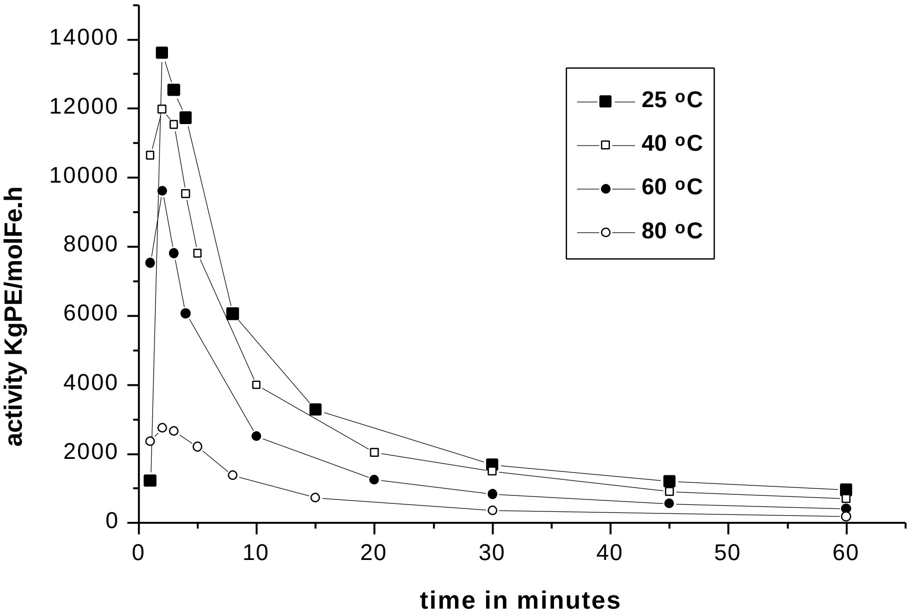

Figure 6.16 Effect of temperature on the kinetic profile of ethylene polymerization in the case of MAO.

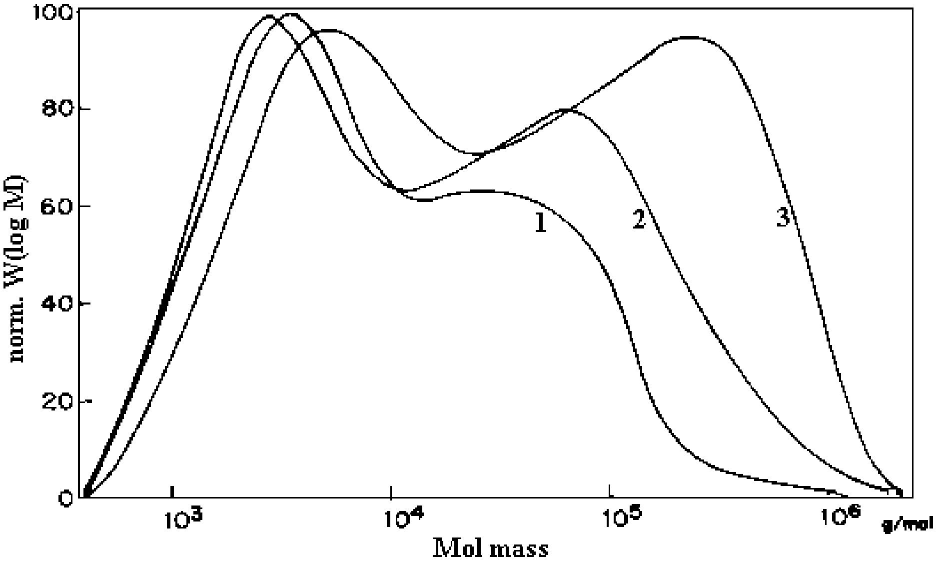

Figure 6.17 GPC curves of poly(ethylene)s synthesized at different temperatures (MAO) (1) 60 °C, (2) 40 °C and (3) 25 °C

For TIBDAO also the molecular weight distribution becomes narrower and a MWD of 1.9 was observed at a Tp of 60 °C. **(Figure 6.18)** But the most significant observation was found in the case of TIBAL. Even though a MWD of 2 .1 was found at a Tp of 25 °C it was found to broaden with the increase of the polymerization temperature. At Tp of 40 °C and 60 °C the MWD increases upto 6 - 7. This indicates that transfer reactions become more prominent at higher temperatures above 25 °C. Significant changes were not observed in the case of TMA even though the lower molecular weight fraction was found to become narrower at higher polymerization temperatures.

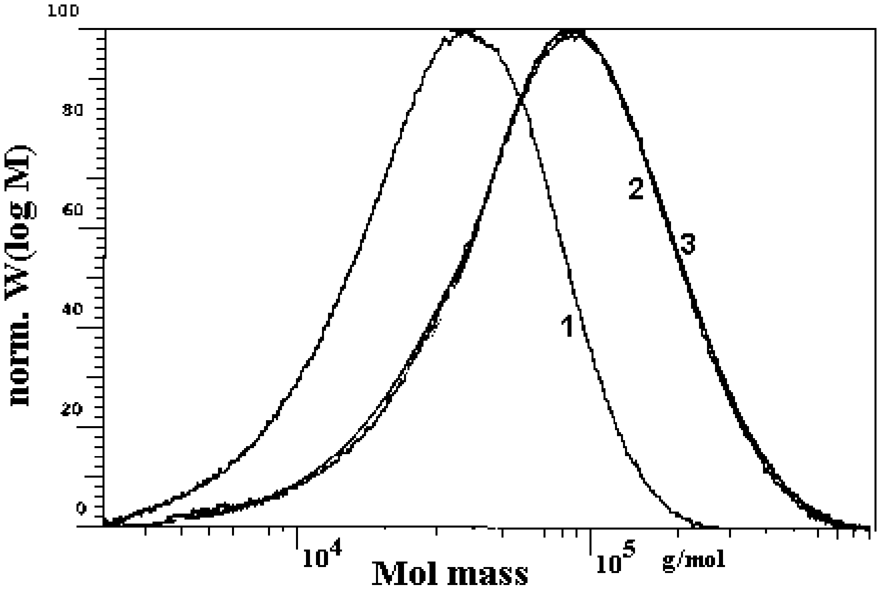

Figure 6.18 GPC curves of poly(ethylene)s synthesized at different temperatures (TIBDAO) (1) 60 °C, (2) 40 °C and (3) 25 °C

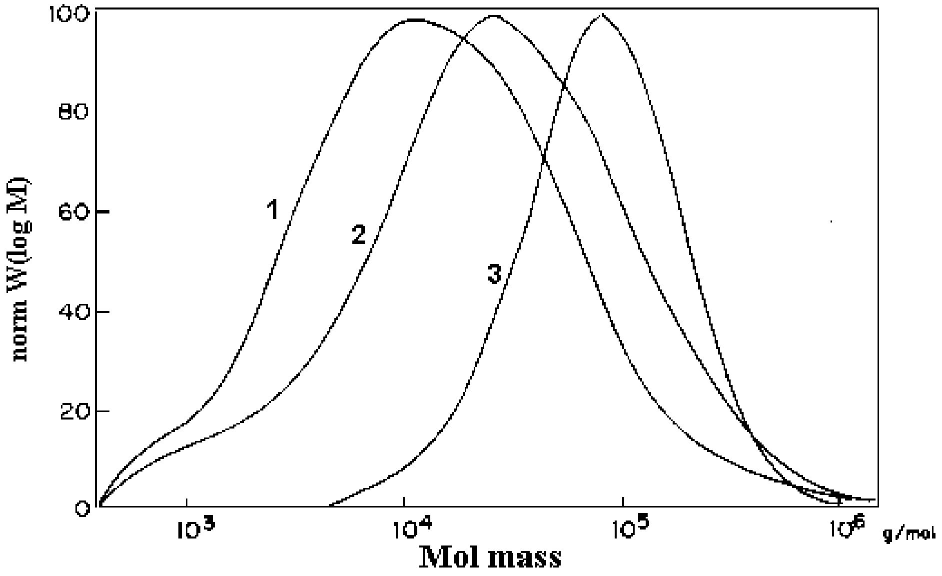

Figure 6.19 GPC curves of poly(ethylene)s synthesized at different temperatures (TIBAL) (1) 60 °C, (2) 40 °C and (3) 25 °C

6.2.1.5 Effect of solvents

Solvent affects catalyst activity in two ways: (1) by changing the monomer concentration since solubility of monomer depends on solvent; and (2) by appropriate solvation of the active centers. Ethylene polymerizations were conducted in different solvents using MAO as cocatalyst under identical conditions. Results are shown in the **Table 6.5**. The catalyst activity was found to be less in polar solvent like *o*-dichlorobenzene (ODCB) and there was little activity in methylene chloride. This reduction in activity may be due to the lower solubility of ethylene in ODCB and CH_2Cl_2 as compared to toluene.

Table 6.5 Effect of solvent on polymerization and polymer properties

Entry	solvent	Catalyst activity[a]	Mw × 10^{-4}	Mw/Mn	[η] dL/g
1	toluene	950	14.6	24, BM	2.5
2	ODCB	708	nd	nd	2.2
3	CH_2Cl_2	No polymerization			

Exptl conditions: Fe = 1.1 × 10^{-6} mol; Al/Fe = 1000; Temp. = 30 °C; [a]Activity is expressed as Kg PE/mol Fe.h

6.3.2 Ni(diimine) catalyst

It has been reported recently that the polymerization of ethylene using Ni(diimine) catalyst depends on the nature of cocatalysts.[42] Branching was found to be influenced by the catalyst structure as well as the nature of cocatalyst. DEAC-activated catalysts generally afford more branched polymers than the corresponding MAO-activated ones suggesting the possible influence of cation-anion interactions on the reaction pathway. Alkylated nickel compound (ArN=CH-CH=NAr)NiMe$_2$ (Ar = 2,6-C_6H_3(i-pr)$_2$) was activated with different cocatalysts and it was found that higher branching resulted when TMA was used as the cocatalyst (used in 1:1 mole ratio with Ni). But the exact nature of the cocatalyst influence is not clear at present.

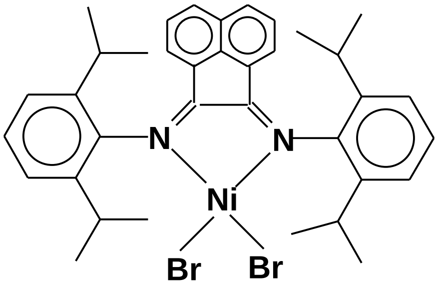

Figure 6.20 Structure of the Ni(diimine) catalyst, (DABAn)NiBr$_2$

6.3.2.1 Effect of cocatalysts

We have investigated the effect of employing different cocatalysts for ethylene polymerization using (DABAn)NiBr$_2$ and the results are summarized in **Table 6.6.** Effect of solvent on polymerization behaviour was also studied.

A typical ^{1}H NMR spectrum of poly(ethylene) prepared with the Ni catalyst is shown in **Figure 6.21**. The degree of branching can be calculated from the integration of the methyl, methylene, and methine groups as shown below.

Area of peak at 0.84 ppm due to 3 methyl protons = X

Area of peak at 1.26 ppm due to methylene and methine protons = Y

Area corresponding to methyl group = X/3 = A

Area corresponding to methine group = X/3 = A

Area corresponding to methylene group = $\frac{Y - (X/3)}{2}$ = B

Branches per 1000 C atoms = $\frac{A \times 1000}{2A + B}$

Table 6.6 Effect of cocatalyst on catalyst activity and polymer properties

Entry	Mol catalyst $\times 10^7$	cocatalyst	Al/Fe	Catalyst activity[a]	Branching[b]
1	8.3	MAO	1000	1490	96
2	16.6	TIBDAO	1000	260	92
3	16.6	TIBAL	500	165	84
4	16.6	DEAC	500	1600	106
5	16.6	TMA	500	985	89

Temp. = 30 °C. [a] activity in KgPE/molNi.h; [b] branching expressed in number of CH_3 in 1000 C atoms

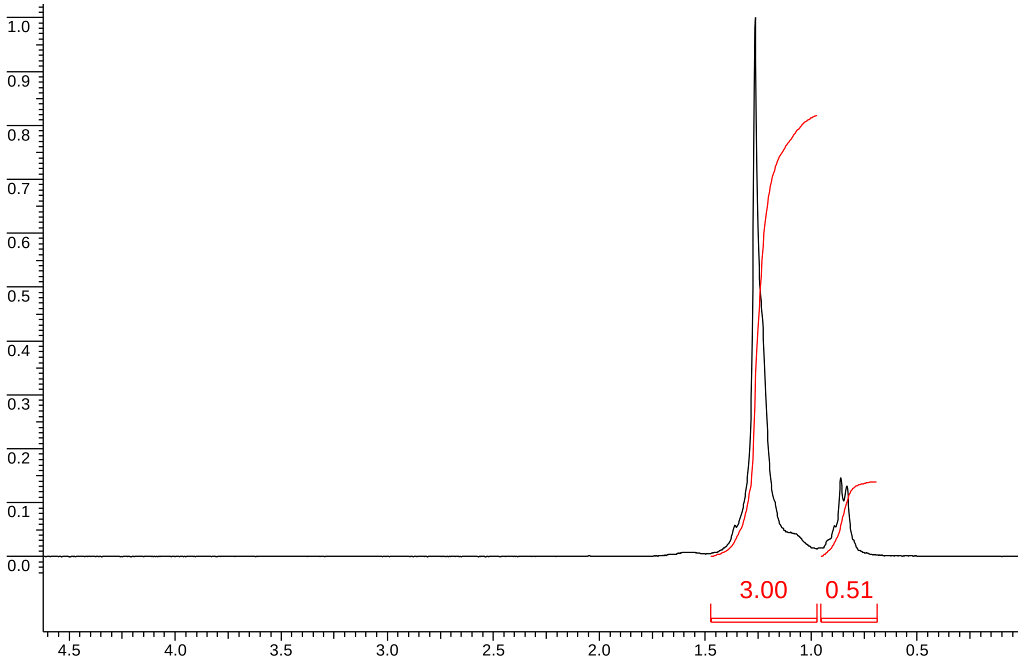

Figure 6.21 ^{1}H NMR spectrum of poly(ethylene): (DABAn)NiBr$_2$/DEAC (Table 6.7, Entry 11)

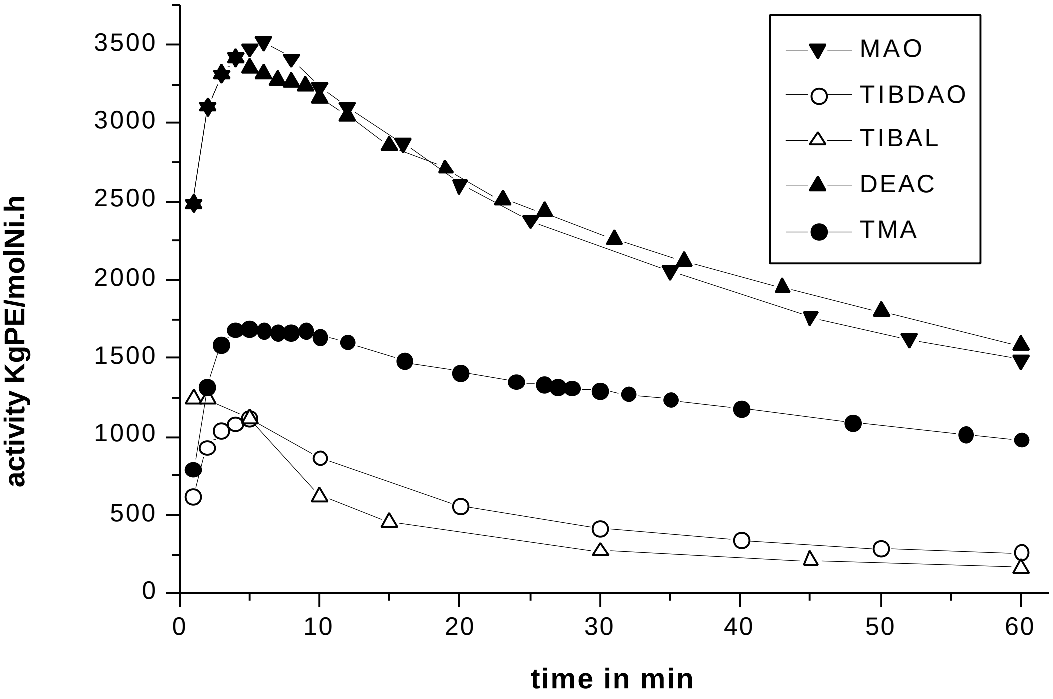

Figure 6.22 Kinetic profile of ethylene polymerization using the Ni(diimine) catalyst

All the cocatalysts used were found to activate the nickel catalyst for polymerization. The cocatalyst efficiency was in the order DEAC>MAO>TMA>TIBDAO>TIBAL under the experimental conditions mentioned above. MAO and DEAC are found to be better activators compared to other simple aluminium alkyls. It is to be noted that DEAC is a non activator for the Fe catalyst. The kinetic profiles of polymerization are shown in the **Figure 6.22**. The polymers are highly branched and the extent of branching is found to depend on cocatalyst. Branching was higher for the DEAC based polymers.

6.3.2.2 Effect of Al/ Ni ratio

Polymerizations were conducted employing different Al/ Ni ratios for each cocatalyst and the results are shown in **Table 6.7.** It can be seen from the table that the efficiency of the cocatalyst is in the order MAO>DEAC>TMA>TIBDAO>TIBAL. For all the cocatalysts the overall activities were found to increase with increase in Al/Fe ratios **(Figure 6.23)**.

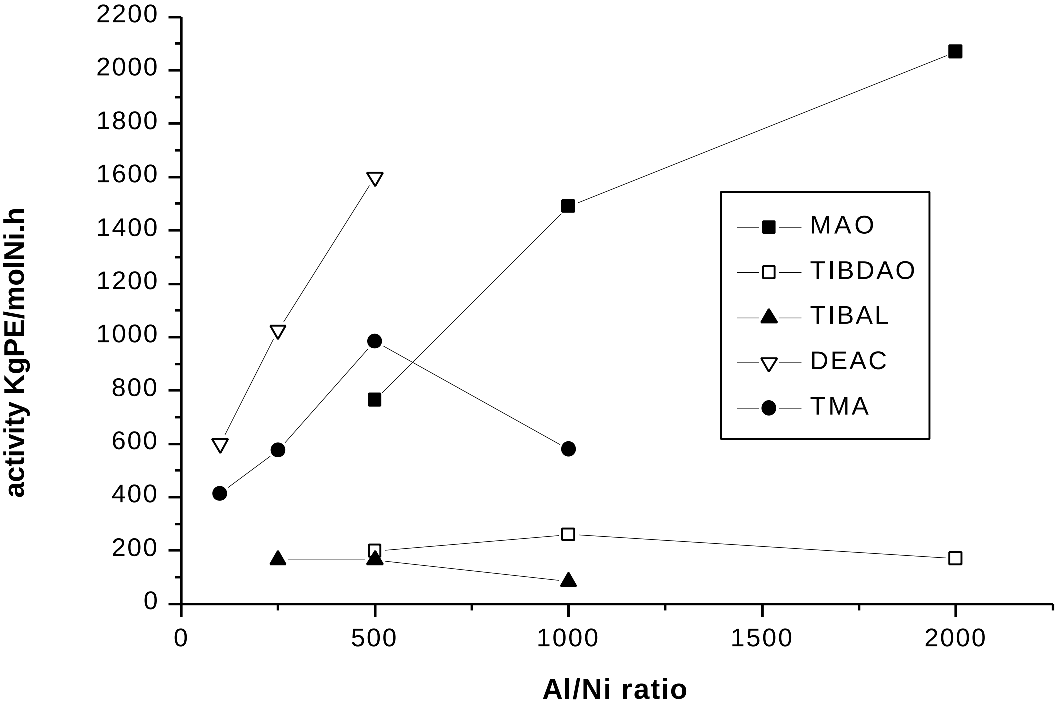

Figure 6.23 Effect of Al/Ni ratio on activity of ethylene polymerization

It has also been observed that in the case of TMA, TIBAL, TIBDAO, the activity is found to decrease after a particular Al/Ni ratio. For MAO and DEAC this kind of optimal level is not reached upto an Al/Ni ratio of 2000.

The methyl branching is found to depend not only on the type of cocatalyst but also on the Al/Ni ratio. Branching increases initially with increase in Al/ Ni ratio and decreases with further increase of Al/Ni ratio **(Figure 6.24)**

Kinetic profile of ethylene polymerization using all these cocatalysts showed typical decay type kinetics. Kinetic profile of ethylene polymerization using MAO as cocatalyst at different Al/Ni ratios is shown in **Figure 6.25.** It can be seen that at lower ratios there is a rapid decay of activity. The same kind of behaviour is observed in the case of other cocatalysts also. It is noted that the colour of the polymerization medium after mixing the catalyst and cocatalyst is generally blue coloured which turns violet and then to pink coloured solution. Consumption of ethylene occurs as long as the solution is pink. It is observed that at lower ratios the colour becomes either yellow or colourless after some time of polymerization. This indicates faster decomposition of the active species at lower ratios of Al/Ni. At higher ratios of Al/ Ni, the colour persists even after 60 minutes and the ethylene consumption continues. In the case of TIBDAO, TIBAL and TMA there is an enhanced decay at ratios above a certain value thereby decreasing the overall activities. This kind of behavior is observed in the case of metallocene based polymerizations also.

Table 6.7 Effect of Al/Ni ratio on ethylene polymerization

Entry	Cocatalyst	Al/Ni	Catalyst activity	Branching [a]
1	MAO	500	770	86
2	MAO	1000	1490	96
3	MAO	2000	2070	80
4	TIBDAO	500	200	89
5	TIBDAO	1000	260	92
6	TIBDAO	2000	170	83
7	TIBAL	250	165	86
8	TIBAL	500	165	84
9	TIBAL	1000	85	77
10	DEAC	100	600	90
11	DEAC	250	1025	99
12	DEAC	500	1600	106
13	TMA	100	415	90
14	TMA	250	575	97
15	TMA	500	985	89
16	TMA	1000	580	83

Experimental conditions: Ni = 1.66×10^{-7} mol ; in the case of MAO, Ni = 8.3×10^{-7} mol; Temp. = 30 °C. activity in KgPE/molNi.h; [a] number of branches per 1000 C atoms

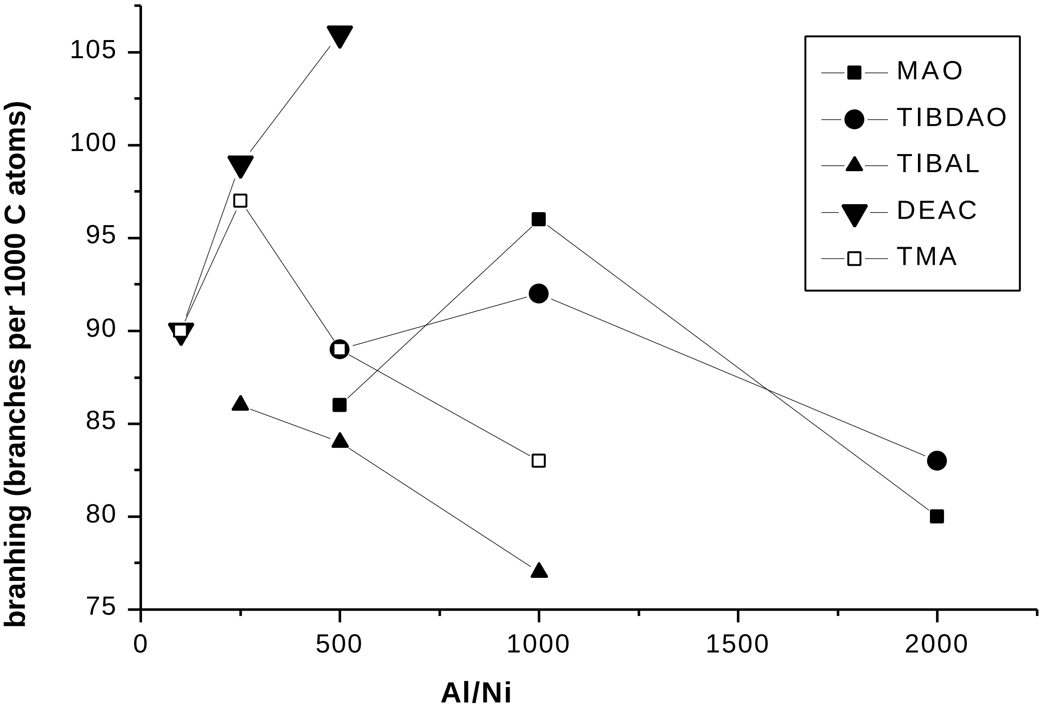

Figure 6.24 Effect of Al/Ni ratio on branching

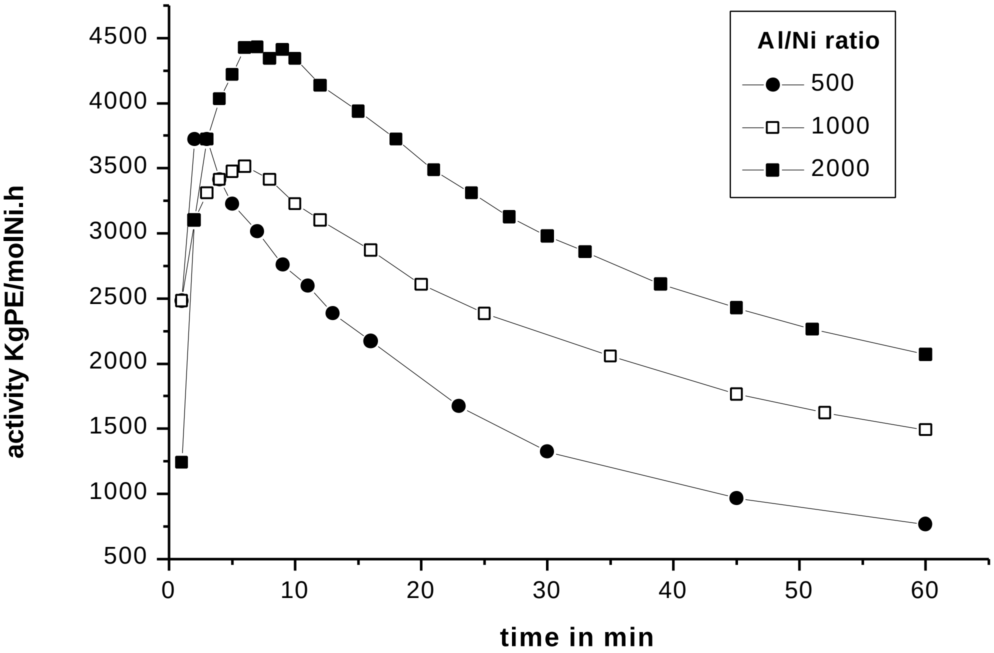

Figure 6.25 Kinetic profile of ethylene polymerization at different MAO/Ni ratios

Kinetic profile of ethylene polymerization at different ratios of TMA/Ni is shown in the **Figure 6.26.** In contrast to other cocatalysts the kinetic profile is found to be of build-up in nature especially at lower ratios. Reduced activities are observed at Al/Ni ratio of 1000.

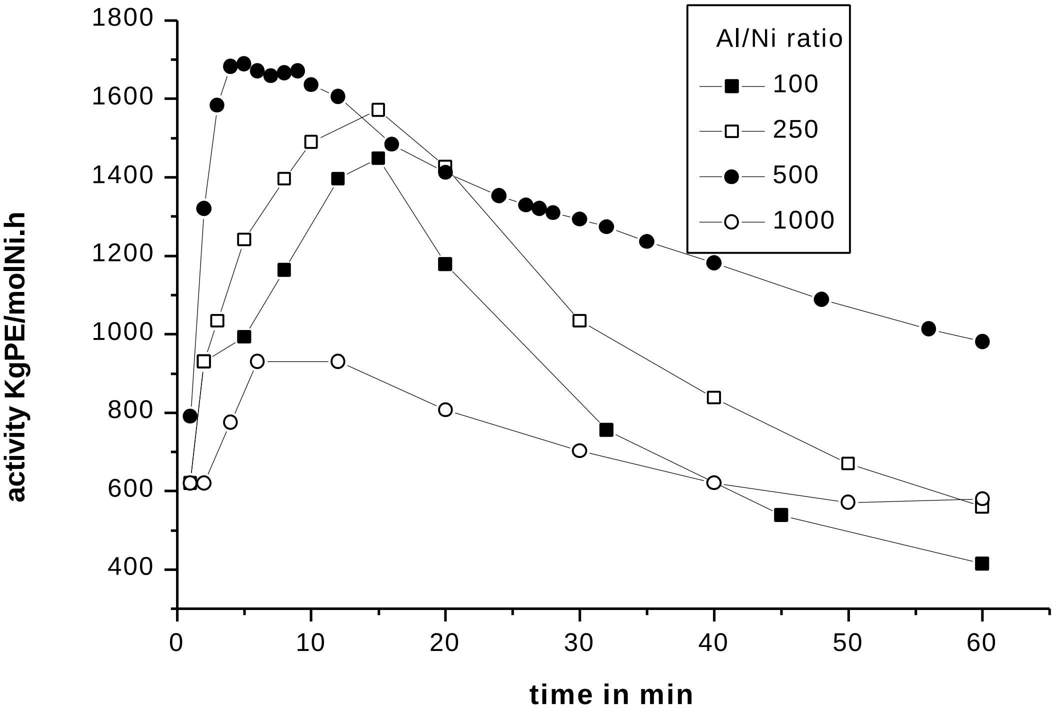

Figure 6.26 Kinetic profile of ethylene polymerization at different TMA/Ni ratios

6.3.2.3 Effect of solvent

Ethylene polymerization was conducted in a polar solvent like o- dichlorobenzene using MAO(Al/Ni = 2000) as cocatalyst and a slight increase in activity was observed. This is in contrast to the behaviour of Fe catalyst where decrease in activity was observed. The comparative kinetic profile is shown in the **Figure 6.27**. It can be seen that the active species is much more stable in ODCB. Furthermore, it was also found that increased branching (95 compared to 80 in toluene) occurs in polar solvents like ODCB. These observations are in support of the involvement of cation-anion interaction in the reaction pathway. In contrast to reactions in toluene the polymerization mixture was rose in colour and the colour persisted even after 60 minutes.

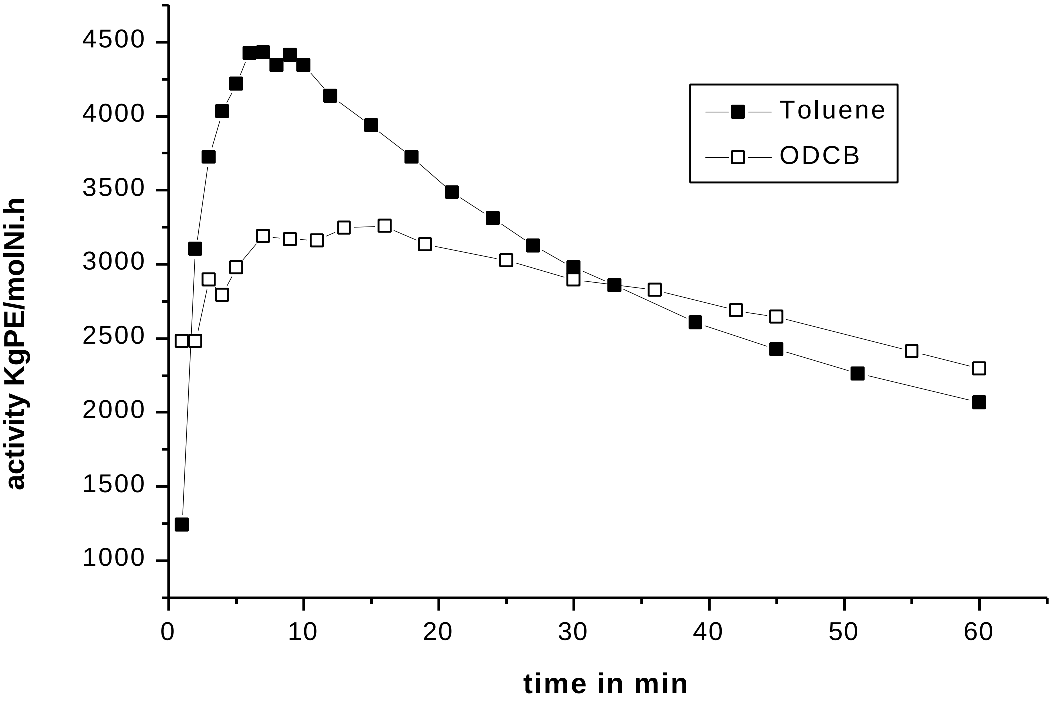

Figure 6.27 Kinetic profile of ethylene polymerization using different solvents

6.4 Conclusion and Outlook

The present study indicates that the cocatalysts play an important role in the nature of transfer and termination reactions. The polymer molecular weights and its distribution can be controlled by changing the cocatalysts and by the experimental conditions. Eventhough broad molecular weight distribution polyethylene is reported for the iron catalyst, this study indicates that narrow molecular weight distribution polyethylene can also be prepared using this catalyst.

One of the reasons for the broad MWD observed when MAO or TMA is used as cocatalyst is speculated as the presence of multiple active species. Even though direct evidence for this is not available at present, an indirect evidence can be obtained from a study of ethylene polymerization using Fe(III) based catalyst which would lead to broader MWD compared to Fe(II) based systems due to the multiplicity of the active species.

The low molecular weight fraction observed in the case of MAO or TMA activated ethylene polymerizations is due to chain transfer reactions with the cocatalyst. This can be confirmed by the use of boron based cocatalysts where the alkyl transfer reactions are absent.

Since a "mixture of cocatalysts" have been used in the earlier studies further information regarding the broad MWD can be obtained from a study of ethylene polymerization using MAOs with variable amount of TMA. The fact that the nature of GPC traces of poly(ethylene)s prepared at higher ratios of MAO and TMA resemble each other, shows that TMA actually plays a prominent role in the transfer reactions.

The present study establishes the versatility of the Fe(II) catalyst to produce narrow and broad polydispersity poly(ethylene)s, depending on the choice of the activator. In this aspect they are superior to the homogeneous zirconocene/MAO catalyst systems.

The present study reveals that the lifetime of the Fe catalyst is short. Heterogenization of the catalyst may lead to longer catalyst life. This kind of enhancement is known in the case of group 4 metallocenes.

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CHAPTER 7. SUMMARY AND CONCLUSIONS

After Ziegler and Natta's invention of transition metal catalysts for the polymerization of olefins, the evolution of new generations of homogeneous single site catalysts in the last 15 years has revolutionized the plastics industry. But no single class of catalysts can polymerize all the vinyl monomers or control all the macromolecular properties of homo as well as copolymers. Therefore, the search for new catalyst families with better activities and capable of producing new homo and copolymers with improved properties is continuing.

In this thesis the application of various homogeneous catalysts viz. metallocenes, Ni(diimine) catalysts, iron(II)bis(imino)pyridyl catalysts for the synthesis of homo as well as copolymers of various vinyl monomers is described.

Synthesis of copolymers of ethylene and styrene was achieved recently using homogenous catalysts. Styrene incorporation is difficult due to steric as well as electronic reasons. Copolymerization of ethylene with styrene, allyl benzene and 4-phenyl-1-butene was studied using metallocenes, Ni(diimine) and Fe(II)bis(imino)pyridyl catalysts. The objective was to study the effect of methylene spacer between phenyl group and the olefinic bond. The extent of incorporation was found to be in the order 4-phenyl-1-butene > allyl benzene > styrene when metallocene/MAO systems were used. Under the experimental conditions employed a maximum of 7 mol % 4-phenyl-1-butene was achieved. Further incorporation was found to be difficult as the catalyst activity decreases with increase in comonomer in the feed. No incorporation was achieved for styrene. The molecular weights of the copolymers were found to decrease with increase in comonomer incorporation. Even though the Ni(diimine) catalysts were found to polymerize styrene to partially isotactic rich polystyrene, there was no copolymerization activity with ethylene. The catalyst was found to lose its activity in the presence of the above mentioned aromatic vinyl monomers. The results show that the active species for ethylene polymerization is different from that of styrene polymerization. The Fe catalyst showed ethylene polymerization activity in the presence of these comonomers, but no incorporation was observed. This catalyst seems to be highly selective for ethylene polymerization.

Copolymerization of ethylene with various silicon containing monomers was studied. The metallocenes and the Ni(diimine) catalysts were found to be active for the copolymerization of vinyltrimethylsilane(M^{vi}) and allyltrimethylsilane (ATMS). A maximum of 16 mol % incorporation of ATMS was achieved using rac-Et(ind)$_2$ZrCl$_2$/MAO system. The molecular weights of the copolymers decrease with comonomer incorporation and vinylidene end groups were detected in ^{1}H NMR. The incorporation of M^{vi} was less than 1mol % when Ni(diimine) catalysts were used. Two functional monomers trimethylsilyloxydimethylvinylsilane (MM^{vi}) and vinylethoxydimethylsilane (VEDMS) were also used for copolymerization. The metallocenes were found to be inactive in the presence of these comonomers. But the less oxophilic Ni catalysts were found to be active for the copolymerization of ethylene with MM^{vi} eventhough the extent of incorporation was less than 2 %. Most of the copolymers of ethylene with MM^{vi} were found to be insoluble after work up presumably due to crosslinking. This method can be used for the preparation of low density polyethylene with crosslinkable functional sites by direct copolymerization of ethylene with functional comonomers. No activity was observed when VEDMS was used. No incorporation of any of these comonomers were observed when Fe catalyst was used.

Fe(II) catalysts are reported to produce broad polydispersity poly(ethylene)s when activated with MMAO due to transfer reactions with Al. The polydispersity produced by transition metal catalyst is a consequence of its electronic state as well as the nature of transfer reactions. Since both these factors are sensitive to the nature of the cocatalyst, a study of polymerization of ethylene using the iron(II)bis(imino)pyridyl catalyst employing different cocatalysts was conducted. Like MAO and TIBDAO, TIBAL and TMA are also effective cocatalysts for ethylene polymerization. Under the experimental conditions employed, DEAC was found to be a non-activator. The catalyst life time was found to be short. But the most unexpected observation was with respect to polydispersity. Whereas MAO and TMA gave broad and bimodal distribution of molecular weight, TIBDAO and TIBAL gave narrow distribution of molecular weights, (MWD ≈ 2). This study establishes the versatility of the Fe(II) catalyst to produce narrow and broad polydispersity poly(ethylene)s, depending on the choice of the activator. In this aspect they are superior to metallocene systems.