DECLARATION

Certified that the work incorporated in the thesis “**Synthesis and Characterization of Functional Poly(olefin)s”** submitted by Mr. M.J. Yanjarappa was carried out by the candidate under my supervision. Such material as has been obtained from other sources has been duly acknowledged in the thesis.

(S. Sivaram)
Research Guide

DEDICATED

TO

SRI RAGHAVENDRA SWAMY

SYNTHESIS AND CHARACTERIZATION OF FUNCTIONAL POLY(OLEFIN)S

A thesis submitted to the
UNIVERSITY OF PUNE
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Synopsis

This thesis entitled “Synthesis and characterization of functional poly(olefin)s” consists of seven chapters and chapter 8 summarizes the work reported in the thesis.

Introduction

Poly(olefin)s are widely used in a wide range of applications since they provide an excellent combination of mechanical and chemical properties as well as processibility. Nevertheless, lack of reactive functional groups in the polymer structure have limited some of their end uses, particularly, those in which adhesion, dyeability, paintability, printability or compatibility with other functional polymers are paramount. This disadvantage can be overcome by introducing suitable functional groups in poly(olefin)s [1-4].

There are two broad approaches to the synthesis of functional poly(olefin)s, namely, "*chain end*" functionalization and "*in chain*" functionalization**.** Synthesis of functional poly(olefin)s by the first method involves either chemical reactions on preformed terminally unsaturated poly(olefin)s or through use of appropriate chain transfer agents, whereas, the second approach involves the copolymerization of olefins with precursors which do not interfere in polymerization followed by organic chemical transformations on the preformed polymers.

Functionalization of poly(olefin)s especially, poly(propylene), poly(ethylene) and poly(ethylene-co-propylene) has been extensively investigated using melt phase free radical grafting. This involves activation of the polymer by shear in presence of free radical initiators or high energy radiation which creates radical sites on the polymer backbone for reaction with acrylic monomers, maleic anhydride etc. Ionizing radiation such as X-rays, γ-rays and e-beams in the presence of air, ozone and UV radiation along with accelerators and free radical initiators (generally organic peroxides) are commonly employed for free radical grafting [5]. However melt phase free radical grafting is usually accompanied by several side reactions such as cross linking and degradation of the polymer.

Synthesis of functional poly(olefin)s using conventional Ziegler-Natta catalysts have been extensively studied [6-9]. The direct copolymerization of olefins with functional monomers has not been successful due to the incompatibility of the Ziegler-Natta catalysts towards polar functionalities as well as heteroatoms present in the functional monomers.

Metallocene and post metallocene catalysts offer significant advantages for the synthesis of functional poly(olefin)s. When olefins are polymerized using homogeneous metallocene / MAO (methyl aluminoxane) catalysts, several chain transfer reactions (such as β-hydrogen transfer etc) are found to occur. Such chain transfer reactions results in terminally unsaturated poly(olefin)s. High degree of terminal unsaturation(> 95%) and narrow molecular weight distribution (MWD = 2) are some of the distinguishing features of poly(olefin)s obtained using metallocene catalysts. There are several reports in the literature, which define synthetic strategies for poly(olefin)s bearing various terminal functional groups such as OH, COOH and NH_2 etc by utilizing the terminally unsaturated poly(olefins) [10-17].

Copolymerization of olefins with dienes can be achieved with ease using metallocene catalysts [18-25]. Such copolymerizations are difficult to accomplish with conventional Ziegler-Natta catalysts in view the low reactivity of the dienes and unwanted side reactions such as cyclo polymerization and crosslinking. Dienes can be copolymerized with olefins with high regio specificity using metallocenes. Copolymerization of olefins with dienes results in poly(olefin)s with pendant double bonds which can be further converted functional groups by organic chemical reactions. Pendant unsaturation can also act as potential 'active sites' for the synthesis of graft copolymers.

Objectives of the present work

The objectives of the present work is to explore the capabilities of metallocene based catalysts for the synthesis of functional poly(olefin)s. Two methods, namely synthesis of terminally unsaturated poly(α-olefin)s by exploiting the chain transfer reactions in metallocene catalyzed polymerization and copolymerization of α-olefins with dienes were examined. Both the methods produce poly(α-olefin)s with unsaturation, the difference being only in the production of unsaturation in the chain.

(1) To exploit the chain transfer reactions in metallocene catalyzed polymerization of 1-hexene to terminally unsaturated oligomers (Mn 500-5000) of hexene-1.

(2) To study the chain transfer reactions in metallocene catalyzed polymerization of hexene-1 and a bicyclic diene, namely, norbornadiene. Effect of experimental conditions and nature of metallocenes on the regiospecificity of insertion was studied.

(3) To establish the feasibility of alkylation of phenols with vinylidene terminated oligo(1-hexene) using BF_3OEt_2 catalyst. Characterization of the phenol terminated oligo(1-hexene) by NMR(^1H, ^{13}C, ^{31}P), FT-IR, and UV are also described.

(4) To synthesise N-poly(alkenyl) alkylamides by Ritter reaction of various nitriles with vinylidene terminated oligo(1-hexene) using acid catalyst.

(5) To synthesize carboxylic acid functionalized poly(olefin) from poly(1-hexene-co-2,5-Norbornadiene) under phase transfer conditions. Effect of various properties of copolymer such as Mn and NBD incorporation on the solubility of functionalized copolymer is also described.

Chapter 1: Recent developments in the synthesis of functional poly(olefin)s

A general literature survey on recent developments in the synthesis of functional poly(olefin)s by various methods is provided. The use of late transition metal catalysis for the synthesis of functional poly(olefin)s is described.

Chapter 2: Scope and Objectives

This chapter describes the scope and objectives of the present work.

Chapter 3: Polymerization of hexene-1 using metallocene/MAO catalyst system

Results of polymerization of hexene-1 using four catalysts, namely, dicyclopentadienylzirconium dichloride, di(n-butylcyclopentadienyl)zirconium dichloride, ethylenebis(indenyl) zirconium dichloride and dimethylsilyldicyclopentadienylzirconium dichloride are described in this chapter. Effect of catalysts concentration, temperature, Al/Zr ratio and nature of metallocene on catalyst activity, number average molecular weight(Mn) and regio errors are described.

Chapter 4: Copolymerization of hexene-1 with 2,5-norbornadiene using metallocene/MAO catalyst system

Results of copolymerization of hexene-1 and 2,5-norbornadiene using four catalysts, namely, dicyclopentadienylzirconium dichloride, di(n-butylcyclopentadienyl)zirconium dichloride, ethylenebis(indenyl) zirconium dichloride and dimethylsilyldicyclopentadienylzirconium dichloride are described. Effect of catalysts concentration, temperature, Al/Zr ratio and nature of metallocene on catalyst activity, number average molecular weight (Mn) and regio errors are described.

Chapter 5: Alkylation of phenols with terminally vinylidene unsaturated poly(hexane-1) using BF_3OEt_2 catalyst

Results of alkylation of various mono / bis-phenol and Bis-phenol-A with terminally vinylidene unsaturated oligo(1-hexene) using BF_3OEt_2 catalyst is described. Characterization of the phenol terminated oligo(hexene-1) by NMR (^{1}H, ^{13}C, and ^{31}P) FT-IR, UV etc will be discussed.

Chapter 6: Synthesis of N-poly(alkenyl) alkylamides by Ritter reaction of vinylidene terminated oligo(1-hexene) with nitriles

Results obtained from Ritter reaction of vinylidene terminated oligo(1-hexene) with nitriles namely acrylonitrile, acetonitrile and benzonitrile using H_2SO_4 catalyst are described. The mode of aggregation of N-poly(alkenyl) acrylamide via intermolecular hydrogen bonding is established by FT-IR, SEM, DSC, and WAXS.

Chapter 7: Synthesis of carboxylic acid functionalized poly(olefin)s from hexene-1-2,5-norbornadiene copolymer

This chapter describes the results of oxidation of endocyclic double bond present in hexene-1-2,5-Norbornadiene copolymer under phase transfer conditions to generate carboxylic acid functionalized copolymer.

Chapter 8: Summary and conclusions

This chapter describes briefly the salient outcomes of the present studies. Future perspectives on the synthesis of functional poly(olefin)s are described.

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Abstract

This thesis explores the capabilities of metallocene based catalysts for the synthesis of functional poly(olefin)s. Two methods, namely, synthesis of terminally unsaturated poly(α-olefin)s by exploiting the chain transfer reactions in metallocene catalyzed polymerization of α-olefins and copolymerization with dienes, were examined.

A study of bulk polymerization of hexene-1 using different metallocene/MAO catalysts was undertaken to produce terminally unsaturated poly(hexene-1) via chain transfer reactions. Poly(hexene-1) with Mn varying from 500 - 15 000 was obtained with polymerization temperature (Tp) varying from -20 to 50^0C. Highly regiospecific catalysts like Cp_2ZrCl_2, $(n\text{-}BuCp)_2ZrCl_2$ and $(CH_3)_2SiCp_2ZrCl_2$ result in vinylidene as the major end group which arise due to β-hydrogen transfer after 1,2 insertion. Both vinylidene as well as internal vinylene (arising due to β-hydrogen transfer after 2,1 insertion) end groups were observed with a poorly regiospecific catalyst like *rac* $Et(Ind)_2ZrCl_2$. Interestingly internal vinylene end group was found to increase with decrease in temperature with all the catalysts.

A study of copolymerization of hexene-1 with a symmetrical diene namely 2,5-norbornadiene using different metallocene/MAO catalysts was found to occur exclusively through one of the two equally reactive endocyclic double bonds for unbridged as well as ethylene bridged catalysts. No crosslinking occurs during copolymerization with any of the catalysts examined. The amount of incorporation of diene, catalytic activity, number average molecular weight (Mn), regio errors and end groups depend on the metallocene used and also on the experimental conditions.

A relatively facile method for the synthesis of phenol/2,6 dimethylphenol terminated poly(hexene-1) was established by alkylation of phenol/2,6 dimethylphenol with terminal vinylidene unsaturation of poly(hexene-1) using $BF_3{:}OEt_2$ catalyst. The number average degree of functionality (Fn) as high as 95 mol % was obtained for low molecular weight oligomers with >95 mol% para selectivity. The selectivity of para isomer was found to decrease with increase in number average molecular weight (Mn).

A polyolefin bearing terminal alkylamide functional group was synthesized by Ritter reaction of terminal vinylidene double bonds in poly(hexene-1) with various nitriles using an acid catalyst. This is the first example of a post polymerization functionalization of terminal vinylidene double bond in a polyolefin to alkylamide group. The number average degree of functionality (Fn) as high as 90 mol% was obtained. Among the three N-poly(alkenyl) alkylamides, N-poly(alkenyl) acrylamide was found to undergo aggregation via intermolecular hydrogen bonding as evidenced by FT-IR. *N*-poly(alkenyl) acrylamide is a useful macromonomer and can be used in the synthesis of hydrophobically modified polymers.

The pendant double bonds in hexene-1/2,5-norbornadiene copolymer were functionalized to carboxylic acid groups under mild conditions using $KMnO_4$. The functionalized copolymer was found to be insoluble in toluene with NBD incorporation more than 6 mol%. The fact that the double bond was part of a strained endocyclic [2.2.1] skeleton enabled it to be oxidized under a very mild condition.

Glossary

MAO	Methylaluminoxane
TMA	Trimethylaluminum
MWD	Molecular weight distribution
GMA	Glycidyl methacrylate
$ZnEt_2$	Diethyl zinc
Cp	Cyclopentadienyl
Cp*	Pentamethyl cyclopentadienyl
THI	Tetrahydroindenyl
Me_2Si	Dimethylsilyl
$PhSiH_3$	Phenylsilane
$(CH_3)_2SiH_2$	Dimethylsilane
9-BBN	9-borabicyclo[3.3.1]nonane
Mn	Number average molecular weight
Mw	Weight average molecular weight
THF	Tetrahydrofuran
$[HB(Mes)_2]$	Dimesitylborane
$[HB(Trip)_2]$	Bis(2,4,6-triisopropylphenyl)borane
Fn	Number average degree of functionality

$TiCl_3$	Titanium trichloride
BAZ	bis[3-(2,2,5,5 tetramethyl-1-aza-2,5 disilacyclopentyl)propyl] zinc
MMA	Methylmethacrylate
MA	Maleic anhydride
VPO	Vapour pressure osmometer
GPC	Gel permeation chromatography
FDMS	Field desorption mass spectrometry
POSS	Polyhedral oligomeric silsesquioxane
HALS	Hindered amine light stabilizers
VTMS	Vinyltrimethylsilane
ATMS	Allyltrimethylsilane
TIBAL	Tri-isobutyl aluminum
TIPS	Triisopropylsilyl
TMS	Trimethylsilyl
NBD	Bicyclo[2.2.1]hepta-2,5-diene (2,5-norbornadiene)
NB-OH	Bicyclo[2.2.1] hept-5-ene-2-methanol
MOD	7-methyl-1,6-octadiene
PHD	6-phenyl-1,5-hexadiene
ATRP	Atom transfer radical polymerization
DFT	Density functional theory

GC	Gas chromatography
Rp	Rate of polymrization
CaH_2	Calcium hydride
BF_3OEt_2	Boron trifloride etherate
BPA	Bisphenol-A
DOP	2-chloro-1,3,2-dioaphosphalane
PNIPAAM	Poly(N-isopropylacrylamide)
LCST	Lower critical solution temperature
LMOGs	Low molecular weight organic gelators
T_{gel}	Sol-gel transition temperature
DSC	Differential scanning calorimetry
WAXS	Wide angle X-ray scattering
SEM	Scanning electron microscopy
VNB	5-vinyl-2-norbornene
DCP	Dicyclopentadiene
DMSO	Dimethylsulfoxide
$KMnO_4$	Potassium permanganate
ODCB	Ortho dichloro benzene

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Chapter-1 Recent developments in the synthesis of functional poly(olefin)s

1.1 Introduction

One of the most exciting developments in the areas of catalysis, organometallic chemistry, and polymer science in recent years has been the intense exploration and commercial exploitation of new polymerization technologies based on single site metallocenes and late transition metal olefin polymerization catalysts. More than thousand patents and a large number of papers published in this area is a testament to its importance in both industrial and academic fields. Though metallocene/alkylaluminum combination has been well known since the late fifties as an active catalyst system for olefin polymerization [1], the current excitement in this area can be traced back to the seminal discovery by Kaminsky and Sinn that methylaluminoxane (MAO) is a highly active cocatalyst for metallocenes in 1980 [2].

Metallocene catalysts consist of a group IVB transition metal sandwiched between two cyclopentadienyl type ligands. The two ligands can optionally be tied up by a silicon or carbon containing bridging group. MAO, which is a partial hydrolysis product of trimethylaluminum (TMA), is oligomeric in nature having a molecular weight in the range of 800 to 1500. Though the exact structure of MAO is not known, it can be inferred from the available literature that it possesses -Al(Me)-O- repeat units, with tetra-coordinated Al. MAO is always associated with some amount of unhydrolyzed TMA .

The significance of metallocene catalysts lies in their high polymerization activity as well as in the breadth of the type and level of comonomer that can be incorporated. Proper tuning of the ligands around the metal enables the synthesis of isotactic, hemiisotactic, elastomeric, high molecular weight atactic and syndiotactic poly(propylene)s and ethylene/styrene interpolymers. The near random distribution of comonomer along the polymer chain along with narrow molecular weight distribution (MWD) is an added advantage of the metallocence based copolymers.

Unlike in conventional Ziegler-Natta catalysts, where comonomers are distributed non-uniformly among the chains, with lower molecular weight fractions having higher amounts of comonomer, the composition distribution is uniform in metallocene based copolymers [3].

Poly(olefin)s are widely used in a wide range of applications since they provide an excellent combination of mechanical and chemical properties as well as processibility. Nevertheless, deficiencies such as lack of reactive functional groups in the polymer structure have limited some of their end uses, particularly those in which adhesion, dyeability, paintability, printability or compatibility with other functional polymers is paramount. This disadvantage can be overcome by introducing suitable functional groups in poly(olefin)s [4-9].

1.2 Methods of synthesis of functional poly(olefin)s

There are two broad approaches to the synthesis of functional poly(olefin)s, namely, chain end functionalization and in chain functionalization

Synthesis of functional poly(olefin)s by the first method involves chemical reactions on preformed terminally unsaturated poly(olefin)s, whereas, the second approach involves the copolymerization of olefins with precursors which do not interfere in polymerization followed by post polymerization organic chemical transformations.

Functionalization of poly(olefin)s especially poly(propylene), poly(ethylene) and poly(ethylene-co-propylene) has been extensively investigated using melt phase free radical grafting. The synthetic technique involves activation of the polymer by shear in presence of free radical initiators or high energy radiation which creates radical sites on the polymer backbone for reaction with acrylic monomers, maleic anhydride etc. Ionizing radiation such as X-rays, γ-rays and e-beams in the presence of air, ozone and UV radiation along with accelerators and free radical initiators (generally organic peroxides) are commonly employed for free radical grafting [10].

Poly(olefin) graft copolymer is widely employed as compatibilizer for blends involving poly(olefin)s and more polar polymers such as poly(amide)s. Recently graft copolymers of glycidyl methacrylate (GMA) onto poly(ethylene), poly(propylene) and poly(ethylene-co-propylene) have been prepared by melt phase free radical polymerization [11-17]. The ability of epoxy group present in glycidyl methacrylate to react with various other functional groups like carboxyl, hydroxyl, anhydride, amine etc. renders such graft copolymers useful as compatibilizer. Melt phase free radical grafting is usually accompanied by several side reactions such as cross linking and degradation of the polymer.

Synthesis of functional poly(olefin)s using Ziegler-Natta catalysts have been extensively reviewed [18-21]. The direct copolymerization of olefins with functional monomers has not been successful due to the sensitivity of the Ziegler-Natta catalysts towards polar functionalities as well as heteroatoms present in the functional monomers. Several strategies have been devised to obviate this problem, like, protection of functional groups, reduction of nuclephilicity of the functional group etc.

Functional monomers bearing carboxyl groups have been well studied using Ziegler-Natta catalysts, where the carboxyl group is first converted to an ester group followed by complexing with an aluminum alkyl [22, 23]. The ester groups can be further transformed to carboxylic acids or imidazolids etc [22]. Another method for preparing functional poly(olefin)s by Ziegler-Natta catalysts is through intermediacy of organoboranes. This method has been extensively studied and reviewed by Chung [24, 25]. One of the drawbacks of Ziegler-Natta catalysts for such copolymerization is the poor reactivity of comonomer and, consequently, non-uniform copolymer composition distribution.

Metallocene and post metallocene catalysts offer significant advantages for the synthesis of functional poly(olefin)s as described below.

1.2.1 Chain end functionalization

1.2.2 Methods of generating chain end unsaturation

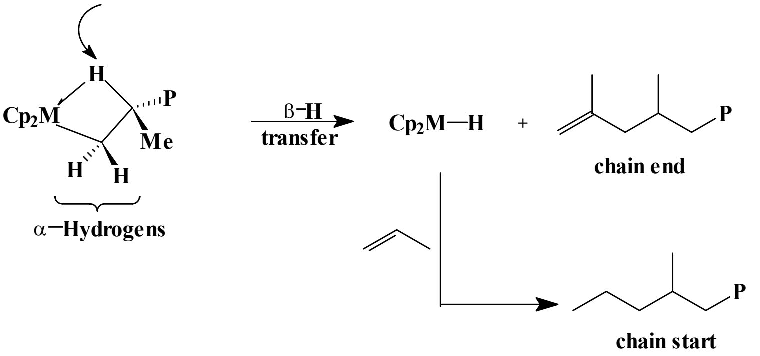
When olefins are polymerized using homogeneous metallocene / MAO (methyl aluminoxane) catalysts, several chain transfer reactions are found to occur. These are discussed below.

1.2.2.1 β-Hydrogen elimination

This is further divided into three types depending on the reaction conditions and the catalyst. They are,

a. β-Hydrogen transfer to metal (unimolecular β-hydrogen transfer)

It occurs when the metal abstracts a H atom bonded to the β-C of the growing polymer chain, forming a M-H bond (M-transition metal) and resulting in a polymer with a vinylidene unsaturated end group **(scheme-1.1).**

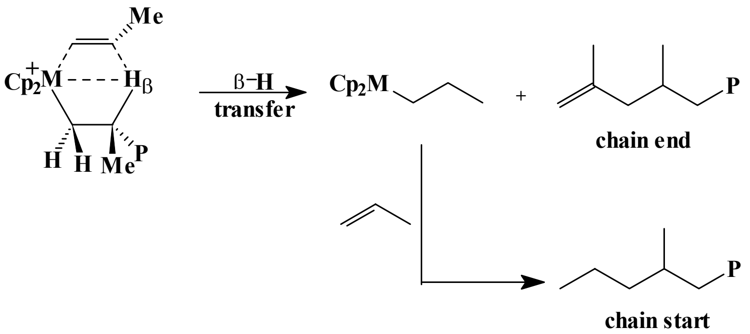


Scheme-1.1 β-Hydrogen transfer to metal

Experimental investigations by Bercaw[26, 27], and Jordan[28, 29] have confirmed that both neutral group 3 metallocene alkyl, and cationic group 4 metallocene alkyl complexes readily undergo spontaneous β-hydride transfer to the corresponding metal hydrides and alkenes.

b. β-Hydrogen transfer to monomer (bimolecular β-hydrogen transfer)

This occurs when β-H elimination and olefin monomer insertion at the active center takes place simultaneously without forming the M-H bond after a primary insertion and resulting in vinylidene terminated poly(propylene), as shown below **(scheme-1.2**). The reaction is first order in the concentration of propylene.

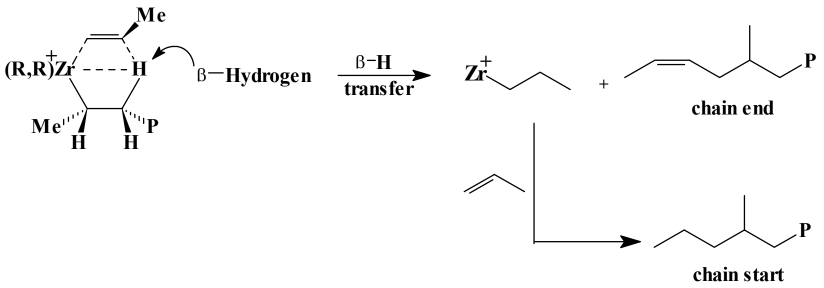


Scheme-1.2 β-Hydrogen transfer to monomer

This mechanism, has been identified as the predominant chain transfer pathway for the polymerization of propylene with heterogeneous catalysts [30-33]. It is also reported to be a preferred pathway by Tsutsui and coworkers in the copolymerization of propylene with ethylene using Cp_2ZrCl_2/MAO catalyst [34].

c. β-Hydrogen transfer after a secondary propylene insertion

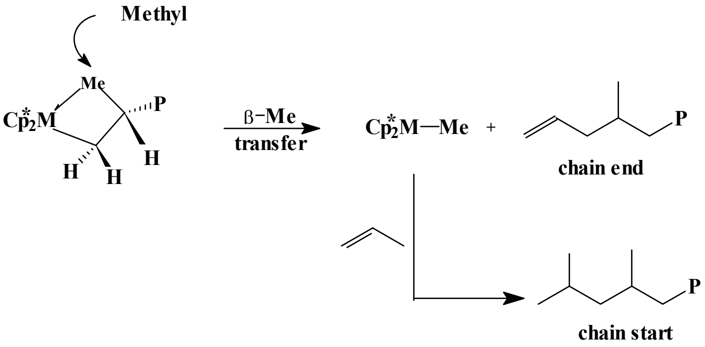
It can be either unimolecular (β-H transfer to metal) or bimolecular (β-H transfer to monomer), producing a M-H initiating species, and poly(propylene) chain terminated with either a 4-butenyl (H transfer from terminal CH_3) or a 2-butenyl (H transfer from CH_2) end group **(scheme-1.3).** In practice, only the internal vinylene unsaturation has been observed [35-38].



Scheme-1.3 β-Hydrogen transfer after a secondary propylene insertion

1.2.2.2 β-Methyl transfer

This is a newly discovered chain transfer mechanism in the polymerization of propylene. The metal center abstracts a CH_3 group, instead of an H atom at the β-Carbon of the growing chain, thus forming a M-CH_3 bond at the active center and leaving the polymer with a vinyl end group **(scheme-1.4)**. This was first observed by Watson in the oligomerization of propylene with the Cp*$_2$LuMe catalyst [39].

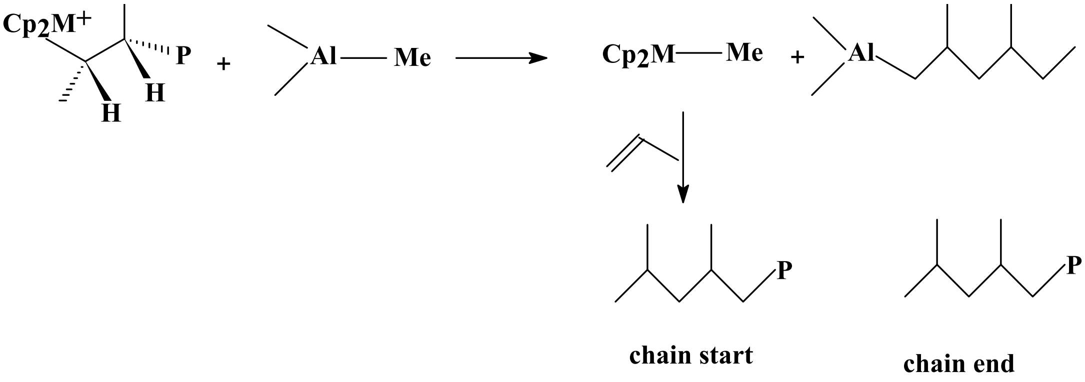


Scheme-1.4 β-Methyl transfer

This process has been reported by Jordan [29] and Bercaw [27] to be unimolecular (β-CH_3 transfer to metal). This is a remarkable example of C-C bond activation at early transition metal centers [40-44]. Hence it can be observed only for growing chains having CH_3 group in the β-position.

1.2.2.3 Chain transfer to Aluminum

This is a transalkylation reaction, and produces a polymer with saturated end groups at both ends. The growing polymer chain attached to an active center exchanges with the methyl group of methylaluminoxane molecule, if MAO is used to activate the catalyst, forming M-CH_3 bond at the active center and the Al terminated polymer chain **(scheme-1.5)**. Propylene with MAO cocatalyst produces isobutyl end groups on both sides. This transfer reaction is common with heterogeneous catalysts [45]. It also occurs with metallocenes at high Al/Zr ratios and under the conditions where the catalyst exhibits low productivity [46-50].



Scheme-1.5 Chain transfer to Al

1.2.2.4 Chain transfer to an added transfer agent

The most commonly used chain transfer agents in heterogeneous Ziegler-Natta catalysts are molecular hydrogen [51-53] and $ZnEt_2$ [54]. Marks and coworkers studied silanes as efficient chain transfer agents in olefin polymerization using homogeneous catalysts[55, 56]. Xu and Chung [57, 58] demonstrated that organoboranes containing a B-H group are efficient chain transfer agents. Hessen and coworkers studied thiophene as a chain transfer agent in ethylene polymerization using neutral lanthanum catalyst system [59, 60]. More recently Chung and Dong reported the consecutive chain transfer to p-methylstyrene in presence of hydrogen during metallocene catalyzed copolymerization of propylene and p-methylstyrene [61].

1.2.3 Effect of catalyst structure and reaction parameters on chain transfer reactions

All chain transfer reactions are influenced by the nature of the metallocene (steric/electronic factors) and the polymerization conditions (temperature/pressure).

1.2.3.1 Steric effects

Steric effects around the metal atom can cause a 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 periphery of the bulky ligand. In order to attain the transition state for β-H elimination, it is necessary to rotate the polymer chain about the $C_{(\alpha)}$-$C_{(\beta)}$ bond, so that the filled $C_{(\beta)}$-H_{σ} orbital overlaps with one of the vacant orbitals on the group 4B transition metal atom [62].

1.2.3.2 Electronic effects

If the ligands around electron deficient (Zr or Hf, Ti) become more electron releasing, then the thermodynamic driving force for β-H elimination diminishes. The electron releasing ability increases in the order Cp < Ind < Flu [62].

The influence of the substitution pattern of the Cp π ligands on poly(propylene) molecular weight is shown in **table-1.1** for a series of metallocenes of various symmetry and ligands. It clearly shows that β-H transfer after primary insertion is the most recurring transfer for aspecific zirconocenes with unsubstituted Cp ligands and for some of the first generation chiral zirconocenes. β-Me transfer becomes predominant in the case of highly substituted zirconocenes such as bis (pentamethyl cyclopentadienyl)$ZrCl_2$ or tetramethyl substituted Cp ligands.

1.2.3.3 Effect of Temperature

The chain transfer reactions have higher activation energy than insertion, consequently a change in temperature strongly affects the rate of chain transfer, which in turn affects the molecular weight. Kaminsky [63] reported that at polymerization temperature below -20^{0}C the transfer reaction is so slow that the molecular weight of polymers is only a function of polymerization time.

1.2.3.4 Effect of pressure

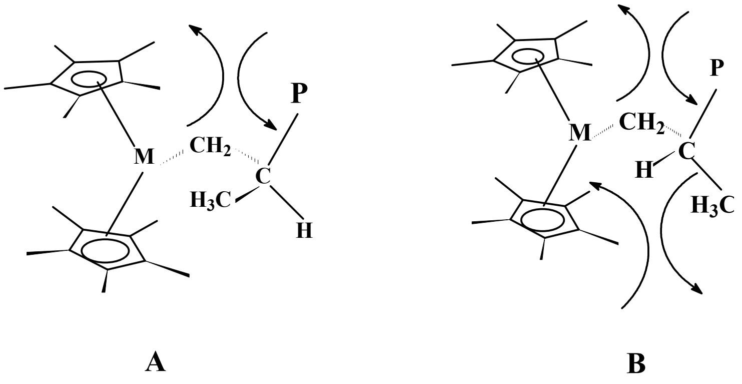
Throshang et al [64] studied the polymerization of ethylene using Cp_2ZrCl_2/MAO at 50^{0}C in the range of 0.38-8.95 bar ethylene pressure. They concluded that the trans vinylene unsaturation content increases as the pressure decreases, whereas the molecular weight remained constant. They proposed termination by β-H transfer to the coordinated monomer.

1.2.4 Chain transfer reactions in higher α-olefin polymerization

β-hydrogen transfer and chain transfer to aluminum are the most abundant chain transfer reactions in the polymerization of higher α-olefins such as 1-butene [65, 67], and 1-hexene [68, 69]. Even though β - Me elimination is a known chain transfer reaction in propylene polymerization with Cp^*_2 $ZrCl_2$/ MAO ($Cp^* = Me_5Cp$) catalyst system, the same is not true in the case of 1- butene polymerization. Polymerization of 1-butene with Cp^*_2 $ZrCl_2$/ MAO [70] shows only β-H elimination (instead of β-ethyl elimination) as with unsubstituted (Cp_2ZrCl_2) metallocenes. Chain transfer to Al becomes predominant at lower temperature [66].

In the case of propylene polymerization, β-Me transfer require the overlap of σ C-C orbital with an empty d orbital on metal. For this to occur the first two carbons of the polymer chain and the Me group must lie in the equatorial plane containing the metal, in between the two Cp rings as shown in **scheme-1.6**.

The lower steric hindrance in transition state A favors β-Me elimination as compared to B which favors β-H elimination. The presence of additional non bonded interactions in transition state B disfavor it. However, in the case of higher α - olefins such as 1- butene or 1- hexene, the ethyl or butyl group is not easily accommodated in the reaction plane between two $Cp^{*'s}$.



Scheme-1.6 Transition states associated with β-H & β-Me transfer

Table-1.1: Effect of ligand on chain transfer reactions in propylene polymerization

Metallocene	Symmetry	Type of polymer	Chain transfer reaction	P_n
Cp_2ZrCl_2	C_{2v}	Liquid oligomers	$(ß\text{-}H)_p$	17
Cp_2HfCl_2	C_{2v}	a-PP(viscous oil)	$(ß\text{-}H)_p$	140
$Cp^*_2ZrCl_2$	C_{2v}	Liquid oligomers	ß-Me	4.5
$Cp^*_2HfCl_2$	C_{2v}	Liquid oligomers	ß-Me	3.4
$(MeCp)_2ZrCl_2$	Ps-C_{2v}	a-PP(viscous oil)	$(ß\text{-}H)_p$	35
Ind_2ZrCl_2	Ps-C_{2v}	a-PP(viscous oil)	$(ß\text{-}H)_p$	100
$(2\text{-}MeInd)_2ZrCl_2$	Ps-C_{2v}	a-PP(sticky glue)	$(ß\text{-}H)_p$	220
$(4,7\text{-}Me_2Ind)_2ZrCl_2$	Ps-C_{2v}	a-PP(sticky glue)	$(ß\text{-}H)_p$	370
rac-$C_2H_4(Ind)_2ZrCl_2$	C_2	i-PP	ß-H	400
meso-$Et(Ind)_2ZrCl_2$	C_s	a-PP(viscous oil)	ß-H	75
rac-$C_2H_4(4,7\text{-}Me_2\text{-}Ind)_2ZrCl_2$	C_2	i-PP	$(ß\text{-}H)_s$	140
rac-$Me_2\,Si(Ind)_2ZrCl_2$	C_2	i-PP	ß-H	705
rac-$Me_2\,Si(2\text{-}Me\text{-}Ind)_2ZrCl_2$	C_2	i-PP	ß-H	2,750
$Me_2C(Cp)(9\text{-}Flu)ZrCl_2$	C_s	s-PP	$(ß\text{-}H)_p$	1,190
$C_2H_4(9\text{-}Flu)_2ZrCl_2$	C_{2v}	a-PP	ß-Me	1,700
$Me_2Si(9\text{-}Flu)_2ZrCl_2$	C_{2v}	a-PP	ß-Me	4,900

Polymerization conditions: liquid propylene, 50^0C, 1h, MAO cocatalyst.

P_n = number-average polymerization degree from ^{1}H NMR (assuming 1 double bond for chain) or intrinsic viscosity (assuming $M_v = M_w = 0.5M_n$). $(ß\text{-}H)_p$ = ß-hydride transfer from a primary growing chain. $(ß\text{-}H)_s$ = ß-hydride transfer from the methylene of a secondary growing chain.

1.3 Terminal functionalization of polymers

There are three methods to introduce functional end groups on polymers obtained by chain growth reactions, namely, end capping, functional initiation and chain transfer method.

The end capping method is applicable in principle only if the polymerization is of the living type. If the polymerization is initiated with a monofunctional initiator, end capping leads to a polymer with one functionalized end group. Ditelechelic polymers can be obtained by using a bifunctional initiator system.

In the functional initiation method, the functional initiator must form a stable bond with the polymer chain in addition to performing the initiating function. By this method one chain end is functionalized and, therefore, the telechelicity of the end product will be determined by the nature of the termination reaction.

The chain transfer reactions lead to polymers with end groups determined by the nature of the transfer agent. Monofunctional as well as telechelic polymers may be obtained.

In the following sections different methods for the synthesis of terminally functionalized poly(olefin)s are summarized.

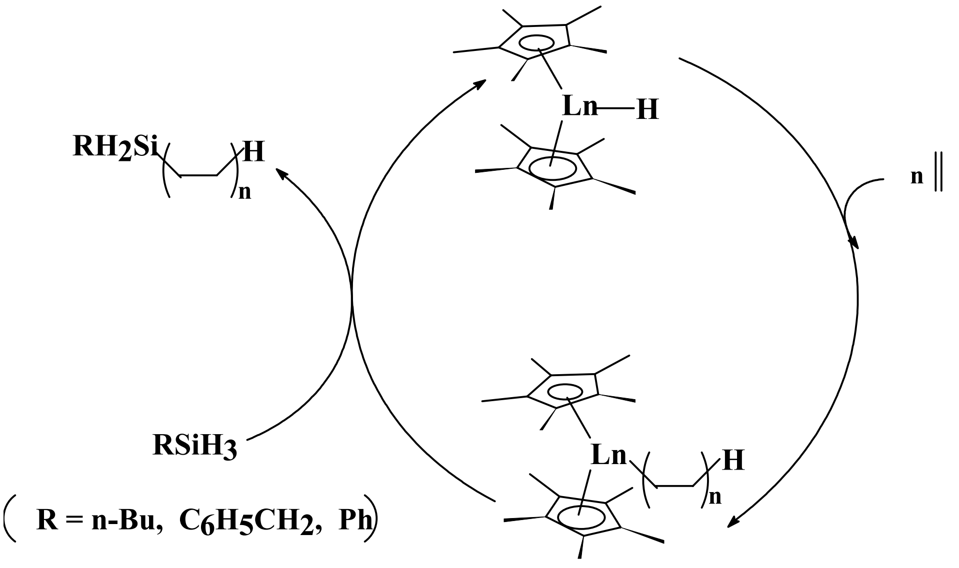
1.3.1 Functional poly(olefin)s through use of chain transfer agents

1.3.1.1 Functional poly(olefin)s using silanes as chain transfer agents

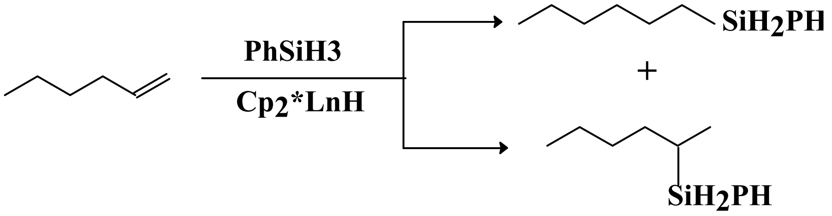
Marks [55, 71] and coworkers reported that primary silanes act as efficient chain transfer agents in ethylene homo and ethylene α- olefin copolymerisation to yield silyl capped poly(olefin)s **(scheme-1.7).** The fact that the gradual decrease in molecular weight with increase in silane concentration reveals their efficiency to act as chain transfer agents.

Lanthanocene are known to be good catalysts for hydrosilylation of α-olefins [72, 73]. The hydrosilylation mechanism involves rapid, and irreversible olefin insertion into Ln-H bond, followed by a turn over limiting Si-H / Ln-H transposition [74]. The important aspect of this reaction pathway is that the organic fragment appended to the metal center is transferred stereospecifically to silicon.

The competence of lanthanide complexes for olefin polymerization along with the above hydrosilylation reaction have demonstrated that such catalysts can be used for polymerization of olefins in presence of silanes as chain transfer agents. The end groups associated with conventional chain transfer processes (eg. β-H transfer) are not detectable. The regio chemistry of the obtained product clearly indicates that the silylation arises from the direct chain transfer rather than from hydrosilylation of a β-H elimination product, since the same organo lanthanide catalysts and $PhSiH_3$ under similar conditions yield mixed 1,2 and 2,1 regio products in α olefin hydrosilylation [74] as shown **in scheme-1.8.**



Scheme-1.7 Catalytic cycle for silyl capped poly(olefin) s

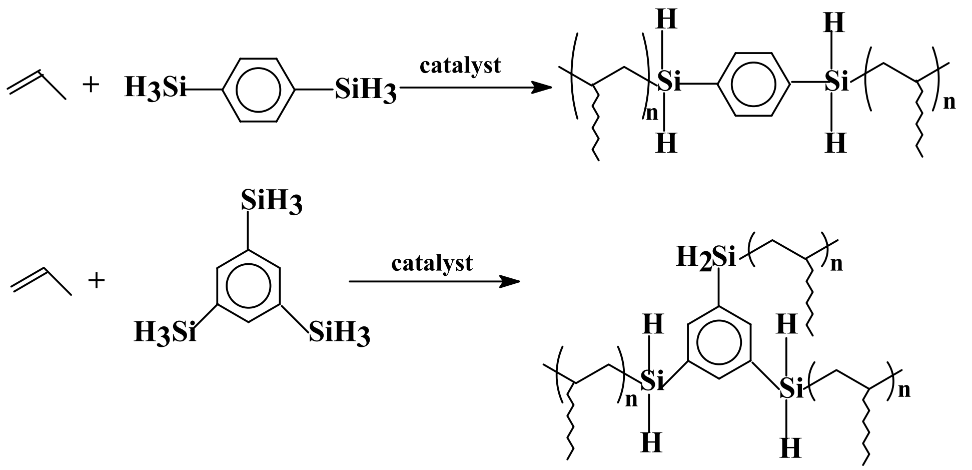


Scheme-1.8 Hydrosilylation of hexene-1 with $PhSiH_3$ using lanthanide initiators

Propylene was also polymerized using single – site cationic group IV metallocene catalyst such as $[Me_2Si(Me_4C_5)t\text{-}BuN]Ti\ Me^+B(C_6F_5)^-$ in presence of $PhSiH_3$ [75] as chain transfer agent. The silyl functionality was delivered selectively to one terminus of the atactic poly(propylene). The dependence of poly(propylene) molecular weight on concentration of $PhSiH_3$ was similar to that of the organolanthanide mediated ethylene polymerization. Secondary silanes such as $(C_2H_5)_2SiH_2$ or $(CH_3)_2SiH_2$ result in increased molecular weight of silyl capped poly(propylene) when compared to primary silanes, indicating that the secondary silanes are less reactive chain transfer agents [76].

Diblock and star block copolymers were also reported by silanolytic chain transfer processes [75]. Propylene polymerization in the presence of multifunctional chain transfer agents such as 1,4-disilabenzene and 1,3,5-trisilabenzene with $[Me_2Si(Me_4C_5)t\text{-}BuN]Ti\ Me^+B(C_6F_5)^-$ catalyst results in A-A and starlike block copolymers **(scheme-**

1.9). The block copolymers were characterized by NMR (^{1}H, ^{13}C, ^{29}Si) and compared with authentic samples prepared by hydrosilylation of the corresponding silanes with terminally unsaturated polyolefins with comparable molecular weight. Good agreement between the two methods reveals that the block copolymers are true diblock and star like block copolymers in nature.



catalyst = $[Me_2Si(Me_4C_5)t\text{-}BuN]Ti\ Me^+\ B(C_6F_5)^-$

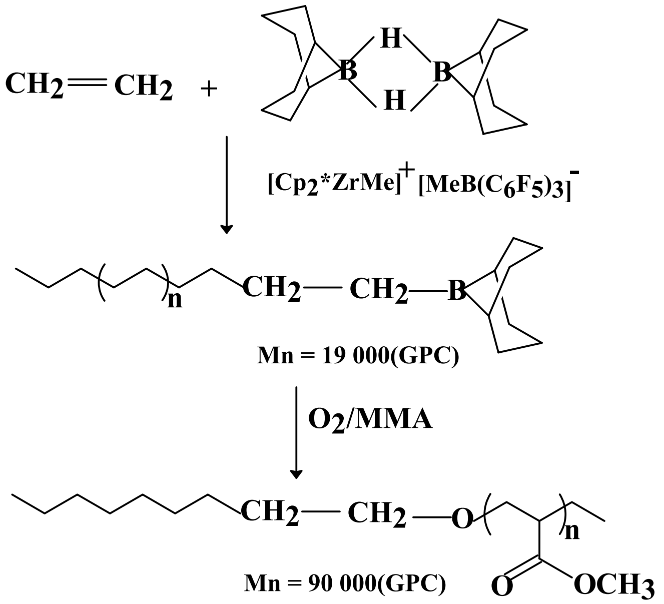
Scheme-1.9 Synthesis of star block copolymers by silanolytic chain transfer

Silanolytic chain transfer reactions were also studied using silica supported single site metallocene catalysts [77] in presence of three different silanes namely n-hexylsilane, diethysilane and arylsilane. Among the four catalysts studied, the silica supported Cp_2ZrCl_2 was reported to produce silyl capped poly(ethylene) in presence of n-hexyl silane and arylsilane as evidenced by NMR (^{1}H, ^{13}C and ^{29}Si) and IR. The number average degree of functionality (Fn) determined by ^{1}H NMR revealed that Fn decreases from 62 to 9% with increase in silane concentration from 0.2 to 1.43 M. It was attributed to the increase in H_2 concentration, which is generated as a byproduct in-situ as a result of dehydrogenative silane coupling.

1.3.1.2 Functional poly(olefin)s using borane as chain transfer agent

Xu and Chung have successfully utilized borane such as 9-borabicyclo[3.3.1]nonane (9-BBN) dimer as a chain transfer agent in metallocene catalyzed polymerization of olefins [57 ,58]. It was reasoned that the dimer of 9-BBN, which is more stable than the monomer could prevent the hydroboration of olefins and acts as a chain transfer agent. The fact that molecular weight (Mn) of the poly(ethylene) decreased from 85200 to 3700 with increase of 9-BBN concentration from 0 to 23.4 mM demonstrated the ability of borane to act as chain transfer agents. The borane terminated poly(ethylene) was utilized for the preparation of poly(ethylene)-block-poly(methyl methacrylate) **(scheme-1.10**).

Selective oxidation of borane terminated poly(ethylene) by oxygen forms stable polymeric alkoxy radical. These polymeric alkoxy radicals are highly reactive and initiate the copolymerization with monomers such as methyl methacrylate, maleic anhydride etc.



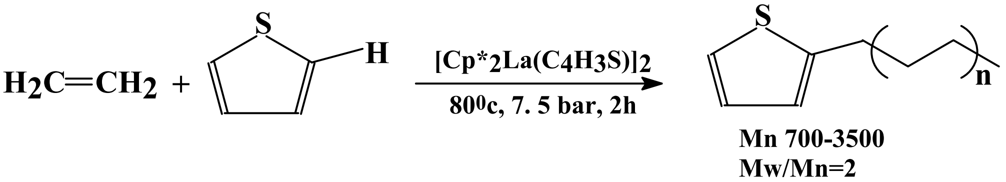
Scheme-1.10 Synthesis of block copolymers via borane terminated polyolefin

Poly(methyl methacrylate) homopolymer (about 10%) from the mixture was removed by Soxhlet extraction using boiling THF. The formation of poly(methyl methacrylate) homopolymer was attributed to the initiation of methylmethacrylate by a bicyclic radical which is formed due to non selective oxidation reaction of alkyl-9-BBN. The molecular weight (Mn) of the final block copolymer increased from 19,400 (borane terminated PE) to 90,300. The molecular weight of poly(ethylene) and poly(methyl methacrylate) segments were further confirmed by ^{1}H NMR spectroscopy.

A comparative study of the ability of other dialkyl boranes such as dimesitylborane [HB(Mes)$_2$] and bis(2,4,6-triisopropylphenyl)borane [HB(Trip)$_2$] with 9-BBN in polymerization of ethylene/propylene using various metallocene/borate catalyst systems was also reported by Chung et al [78]. Dimesitylborane was found to a better chain transfer agent, exhibiting high catalyst activity and good control of molecular weight during polymerization. However no polymer was obtained with [HB(Trip)$_2$] due to its complex formation with olefins. The fact that the π-electron delocalization from aryl group to boron in dimesitylborane, which not only strengthens aryl-B bonds also reduces the acidity of borane moiety was found to affect the chain transfer reaction between B-H and C-M moieties.

1.3.1.3 Functional poly(olefin)s using thiophene as chain transfer agent

The ability of lanthanide metallocenes to perform ethylene polymerization as well as hydrocarbon C-H activation was utilized to prepare terminally functionalized poly(ethylene) [59, 60]. Polymerization of ethylene was studied in presence of various hydrocarbons containing hetero atoms with activated C-H bonds as chain transfer agents using $[Cp^*_2LaH]_2$ catalyst. Among the various hetero compounds studied thiophene was successfully utilized as a chain transfer agent **(scheme-1.11)**.



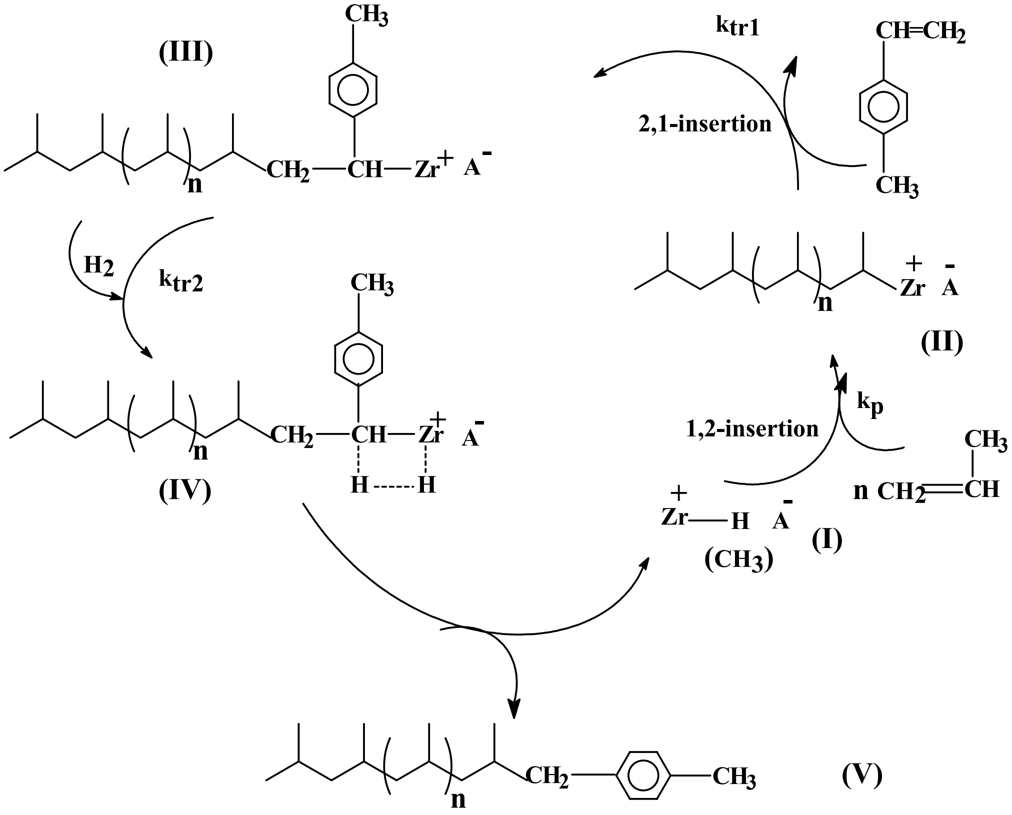
Scheme-1.11 Synthesis of thiophene terminated poly(ethylene)

The sulfur in thiophene is less Lewis basic compared to the other hetero atoms in pyridene, furan, THF etc. Hence, the ortho C-H bond can be readily activated by $[Cp^*_2LaH]_2$ to give $[Cp^*_2La(C_4H_3S)]_2$. The molecular weight and catalyst activities were found to increase with decrease in thiophene concentration. Polymerization in neat thiophene gave low molecular weight (Mn=700) oligomers. Characterization of the polymer by ^1H NMR (integral ratio between α-CH_2 protons and methyl end groups) established that the functionality (Fn) was as high as 98%.

1.3.1.4 Functional poly(olefin)s using p-methyl styrene as chain transfer agent

Recently Chung and Dong reported [61, 79] a new insitu chain transfer reaction in metallocene catalyzed copolymerization of propylene with p-methyl styrene. During the copolymerization of propylene with p-methyl styrene using *rac*-$SiMe_2[2\text{-}Me\text{-}4\text{-}Ph.(Ind)]_2ZrCl_2$/MAO, the polymerization reaction was found to be completely inhibited in the beginning. It was attributed to the secondary insertion of p-methyl styrene subsequent to primary insertion of propylene **(site -III in scheme-1.12)**. The combination of unfavorable primary insertion of propylene and lack of p-methyl styrene homopolymerization at the propagating site III drastically reduces the catalyst activity.

But the insertion of ethylene is observed at the dormant site III as evidenced by increase in activity by the addition of small amount of ethylene.



Scheme-1.12 Synthesis of p-Me styrene terminated poly(propylene)

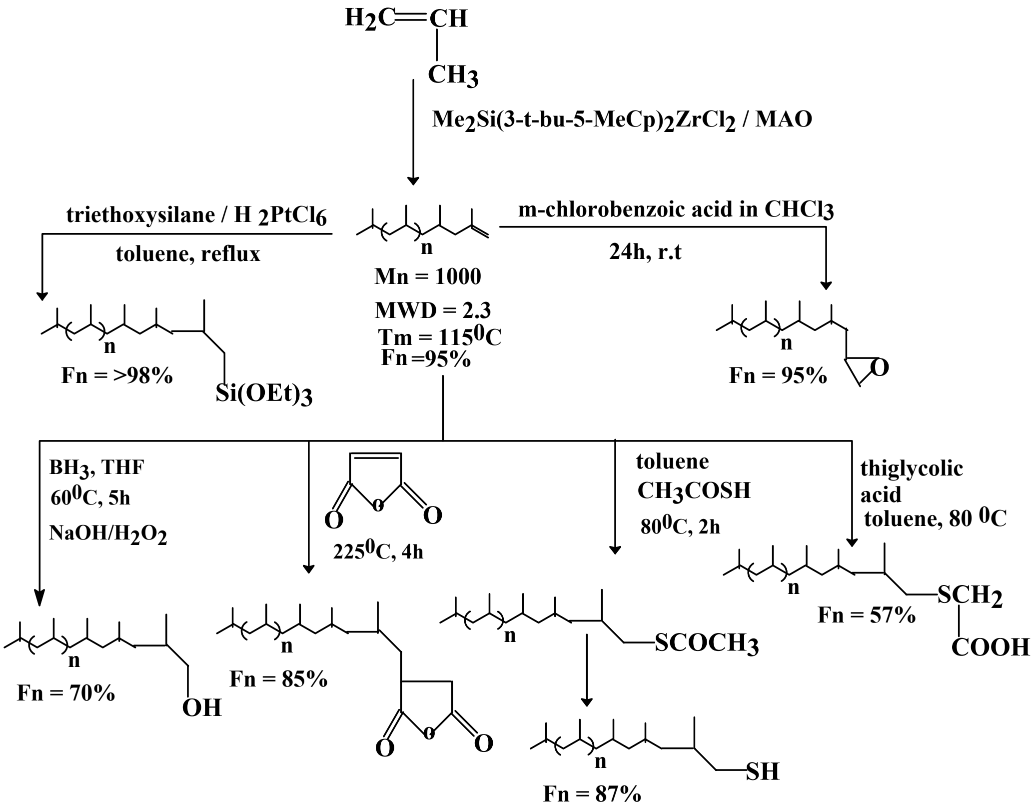
When the dormant site(**III**) reacts with hydrogen, it not only regenerates the active Zr-H site but also results in poly(propylene) terminated with a p-methylaryl group. The molecular weight of poly(propylene) was found to decrease with increase in p-methyl styrene concentration, but independent of hydrogen concentration. A linear relation was found between catalyst activity and hydrogen concentration. Poly(propylene) with Mn ranging from 1800 - 77 600 were prepared with MWD 1.4 - 2.0. Characterization of the polymer by NMR (^{1}H and ^{13}C) did not show any terminal unsaturation, which arises due to conventional chain transfer reactions. The existence of terminal p-methyl aryl functional group in poly(propylene) was further confirmed by block copolymer preparation. The terminal p-methylaryl group was selectively lithiated by s-BuLi and utilized as an initiator for anionic polymerization of styrene. The block copolymer was purified by Soxhlet extraction in boiling THF to remove homo poly(styrene) and characterized by NMR and GPC. The fact that the molecular weight of the block copolymer increases with polymerization time indicates the true living nature of lithiated poly(propylene).

1.3.2 Functional polyolefins using terminal unsaturation

The chain transfer reactions in metallocene catalyzed polymerization lead to terminal double bonds which are amenable to further chemical reactions.

Mulhaupt et al [80] reported the synthesis of low molecular weight isotactic poly(propylene) (Mn = 1000) having at least one vinylidene end group per chain using dimethylsilyl bis(3-t-bu-5-methyl cyclopentadienyl)$ZrCl_2$/MAO catalyst system. The resulting terminal double bonds were converted to various functional groups using organic chemical transformation reactions **(scheme-1.13).**

The number average degree of functionality (Fn) was estimated by titration. Among the addition reactions at vinylidene end groups, quantitative conversions have been achieved with silanes and boranes. Triethoxysilane terminated isotactic polypropylenes are interesting adhesion promoters and dispersing agents to enhance the filler dispersion in the poly(propylene) matrix.

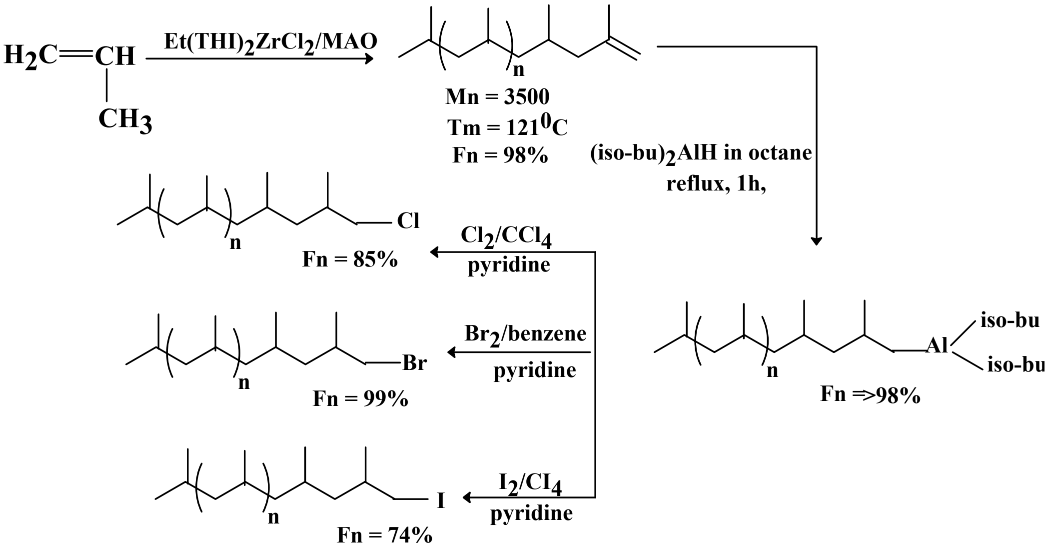


Scheme-1.13 Synthesis of terminally functionalized poly(propylene)

Halogenation

Shino et al [81] prepared a series of terminally halogenated poly(propylene)s in fairly good yields by halogenolysis of Al terminated poly(propylene)s. The latter can be obtained by hydroalumination of terminal vinylidene groups with di-isobutyl aluminumhydride [83] **(scheme-1.14).**

Hydroxy terminated poly(propylene) with Fn 80% was also reported by reacting Al terminated poly(propylene) with oxygen [84]. The functionality (Fn) was determined by NMR (^{1}H & ^{13}C). Chlorination of Al-polymer bonds was carried out according to the patent literature [82].

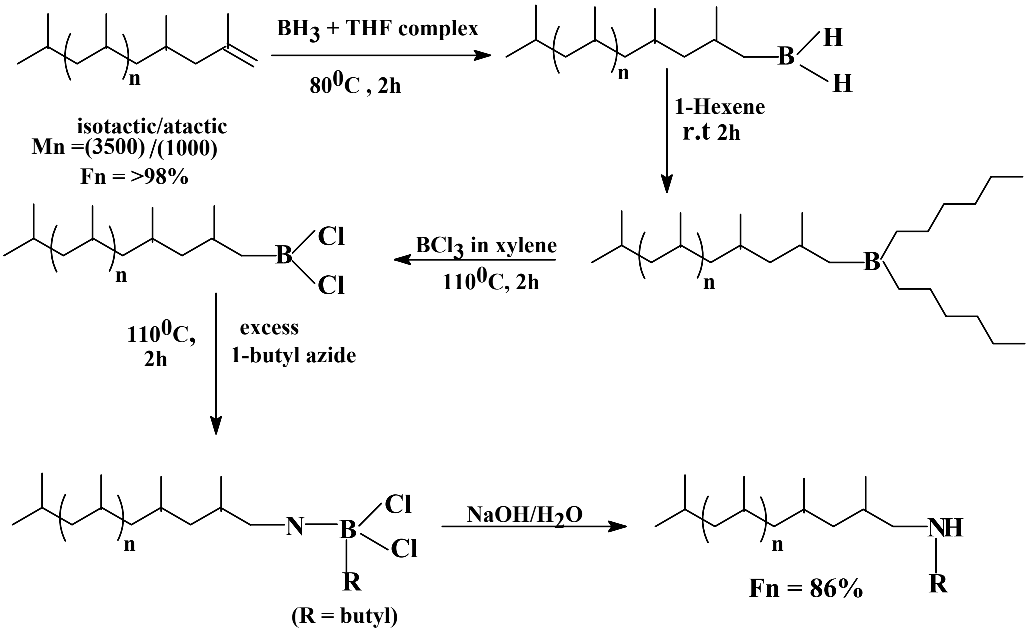


Scheme-1.14 Synthesis of terminally halogenated poly(propylene)

Amination

Amongst the various terminal functional groups, amino groups are desirable due to their high reactivity, and affinity to other compounds. Terminally aminated polymers are commercially utilized in elastomers to improve the dispersity of fillers [85]. Shiono et al [86] prepared secondary amine terminated polypropylene using borane chemistry **(scheme-1.15)**. Poly(propylene) (isotactic/atactic) with vinylidene terminal unsaturation was treated with an excess of borane in benzene followed by treatment with an excess of 1-hexene to give trialkylboranes. The resulting trialkylboranes were disproportionated with BCl_3 to obtain alkyldichloroboranes which on further treatment with n-butylazide results in poly(propylene) having a n-butylamino group at the chain end.

Hydroboration of disubstituted terminal olefins (similar to vinylidene terminated poly(propylene) have been reported [87] to take place quantitatively to give trialkyl boranes. The disproportionation of trialkylboranes with boron trichloride [88] yields alkyldichloroboranes.

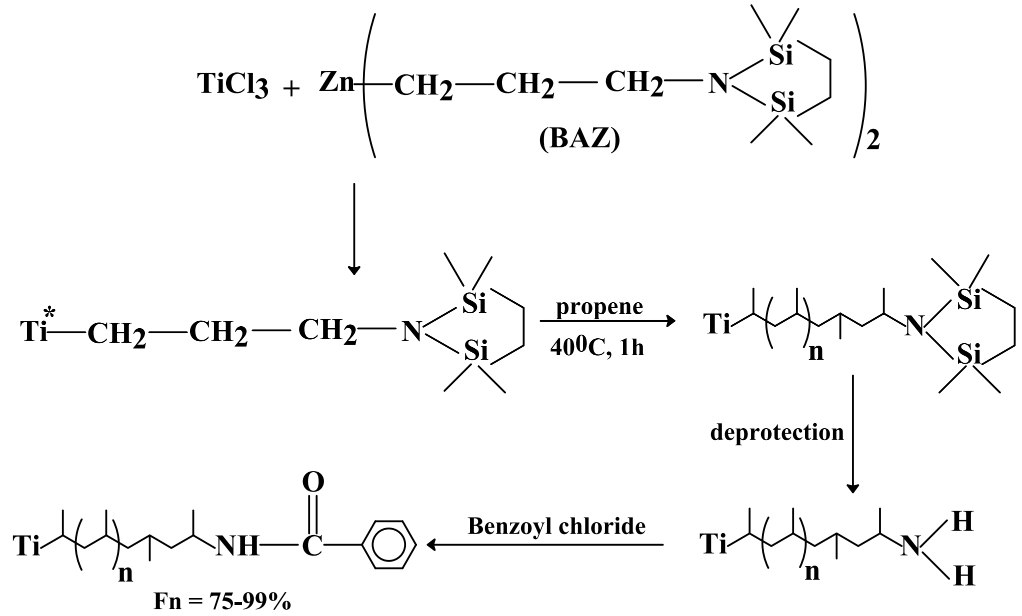


Scheme-1.15 Synthesis of secondary amino terminated poly(propylene)

Trialkylboranes react with a variety of organic azides in refluxing xylene [89], which upon basic hydrolysis results in secondary amine. Unfortunately the reaction is relatively slow and very sensitive to steric requirements. Even though use of dialkylchloroboranes circumvent these problems [90, 91], it still suffers from a significant disadvantage that only one of the two alkyl groups on boron is utilized in the synthesis. The number average degree of functionality (Fn) was determined by NMR (^{1}H, ^{13}C), and IR for atactic and derivatization method for amine terminated isotactic poly(propylene). In derivatization method the amine terminated isotactic poly(propylene) was amidated by reacting with benzoyl chloride at 140^{0}C for for 6h.

Poly(propylene) having primary amine group at the initiation end [92] was prepared by conventional Z-N catalyst $TiCl_3$ and a dialkylzinc compound with alkylsilyl protected primary amino groups as a cocatalyst **(sceme-1.16).**

Thus, propylene was polymerized using $TiCl_3$ as catalyst and bis[3-(2,2,5,5 tetramethyl-1-aza-2,5 disilacyclopentyl)propyl] zinc (BAZ) as cocatalyst. The authors proposed that neither the polymer yield nor the Mn depend on the concentration of BAZ. Hence BAZ does not act as a chain transfer agent, but only as a true cocatalyst. BAZ has been chosen as cocatalyst based on the fact that the olefin polymerization with Z-N catalysts is initiated by alkylation of transition metal with cocatalyst, followed by successive monomer insertion. Therefore, one can expect to obtain a poly(olefin) with a functional group at the initiation end and a metal-carbon bond at the termination end.



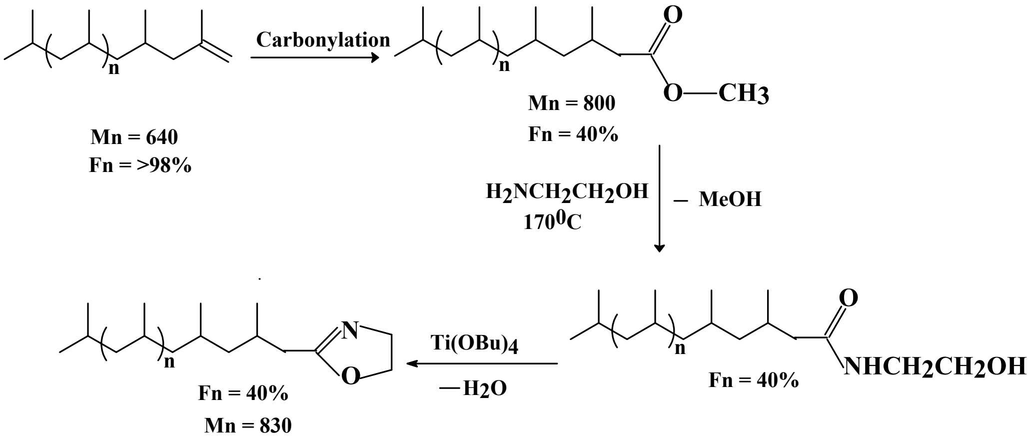
Scheme-1.16 Synthesis of poly(propylene) with primary amine end group

Amine terminated poly(propylene) with molecular weight (Mn) ranging from 13 000 - 2,10,000 were obtained with Fn (measured by FT/IR) varying from 75 - 99%. The higher catalyst activity was found when diethyl aluminum chloride was used as a cocatalyst with comparable isospecificity.

Oxazoline terminated poly(propylene)

Mono (1,3-oxazolin-2yl) terminated poly(propylene)s have been reported by Mulhaupt et al [93]. Vinylidene terminated poly(propene) with Mn 640-800 is converted into monomethyl ester terminated via carbonylation reaction. The monomethyl ester terminated poly(propene) reacts with two fold molar excess of 2- amino ethanol at 170° C gives the corresponding N-(2-hydroxy ethyl) amide, which on cyclisation reaction in presence of Ti $(OC_4H_9)_4$ yields mono(1,3-oxazolin-2 yl) terminated poly(propylene) **(scheme-1.17).**

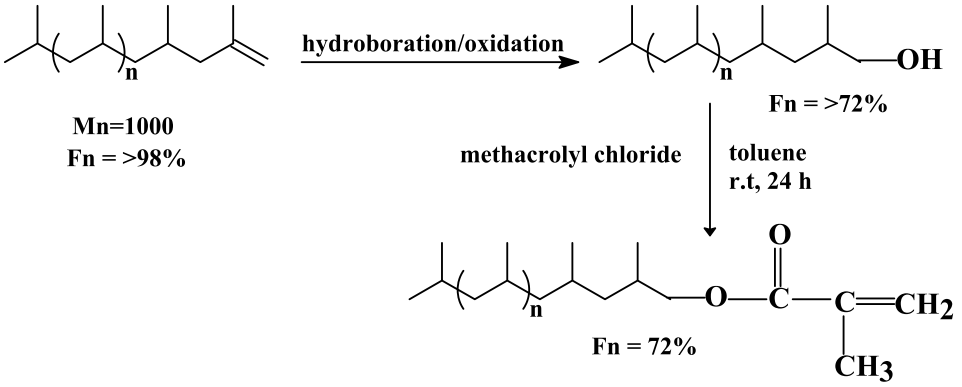
The unreacted vinylidene terminated poly(propylene) and other side products were separated from the oxazoline terminated poly(propylene) using a deactivated silica column. The oxazoline functionality (Fn) calculated from NMR was found to be 40%. Oxazoline terminated poly(propylene)s are highly reactive intermediates which can be used as macromonomers to produce N-acylated poly(ethyleneimine)s containing oligopropene side chains.



Scheme-1.17 Synthesis of oxazoline terminated poly(propylene)

Methacrylate terminated PP

Methacrylate terminated poly(propylene) was [94] obtained by the esterification of hydroxy terminated poly(propylene) with methacryloyl chloride **(scheme-1.18).** Hydroxy terminated poly(propylene) was obtained by hydroboration followed by oxidation of the terminally vinylidene unsaturated poly(propylene) (Mn= 1000). The hydroxyl group were estimated by titration and showed 72% conversion of the double bond. The functional poly(propylene) was converted to a methacrolyl terminated poly(propylene) by reaction with methacrolyl chloride.

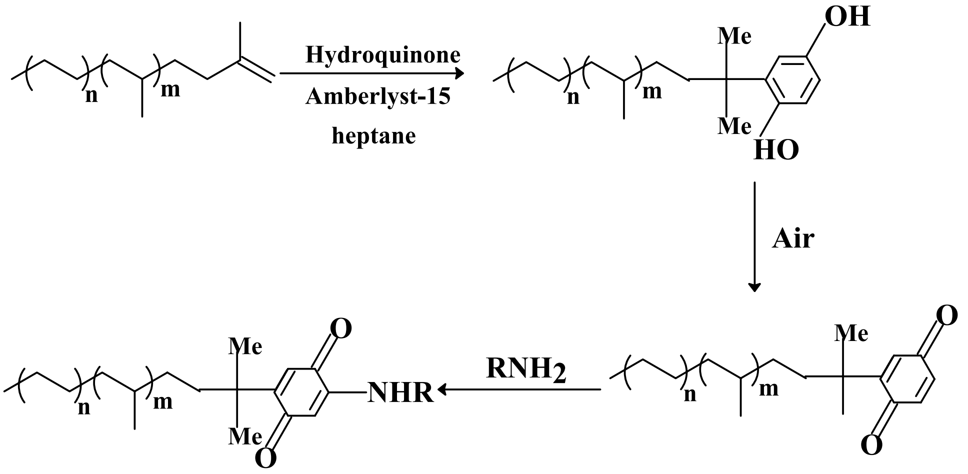


Scheme-1.18 Synthesis of methacrylate terminated poly(propylene)

Methacrolyl terminated poly(propylene) macromonomers have been copolymerised with methyl methacrylate by free radical initiators to give poly(methyl methacrylate)-g-poly(propylene).

Alkylation

Alkylation of hydroquinone with vinylidene terminated EP copolymer (Mn = 870) was studied using amberlyst-15 catalyst [95-97]. The hydroquinone functional group was transformed to corresponding aminoquinone functional group by reacting with amine under mild conditions as shown below **(scheme-1.19).**



Scheme-1.19 Synthesis of hydroquinone terminated poly(ethylene-co-propylene)

Hydroquinone oxidizes to corresponding quinone at room temperature. Quinones are known to react with amines to give amonoquinones. Characterization of the hydroquinone terminated EP copolymer by NMR, IR and GPC coupled with RI and UV detector showed the functionality to be as high as 95%. Such aminoquinone terminated poly(olefin)s were found to be effective lubricant dispersants.

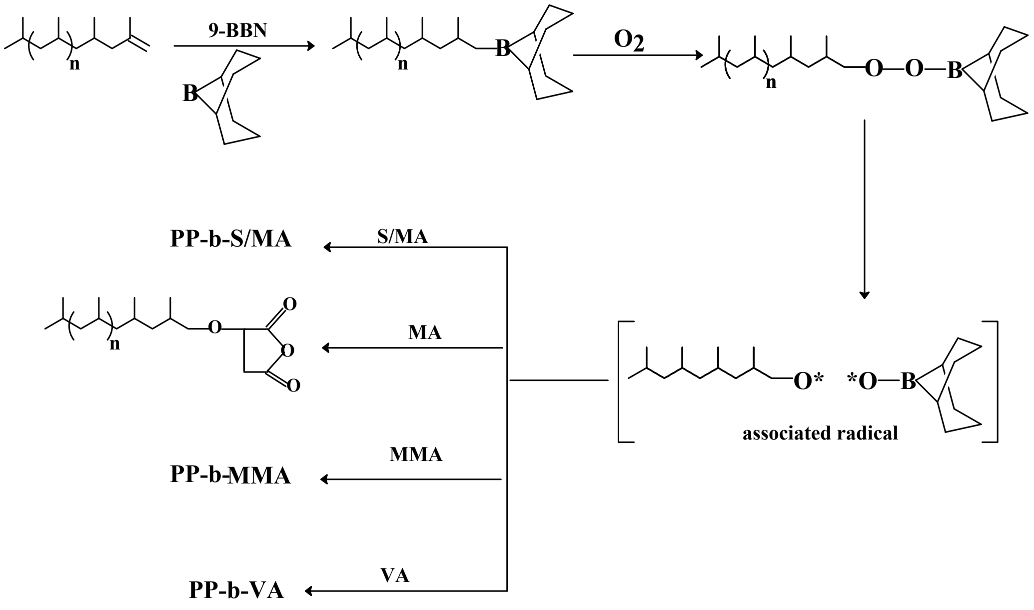
1.3.3 Block copolymer preparation

Poly(propylene)-b-poly(styrene) and poly(propylene-b-styrene-co-acrylonitile) copolymers have been reported [80] using thiol terminated polypropylene as a chain transfer agent and AIBN as radical initiator. As the content of thiol terminated poly(propylene) increases up to 50 wt%, the molecular weight of the corresponding styrene homo and copolymer decreases drastically indicating the capability of thiol functionalized polypropylene to function as chain transfer agent.

Poly(propylene) block copolymers have also been prepared using borane chemistry. Poly(propylene)-b-maleic anhydride, poly(propylene) -b-poly(styrene-maleic anhydride) [99] and poly(propylene)-b-poly(methylmethacrylate) [100], poly(propylene)-b-poly(ethylmethacrylate), poly(propylene)-b-poly(vinyl acetate), poly(propylene)-b-poly(butyl acrylate), poly(propylene)-b-poly(styrene) [101] have been reported by Chung et al. Poly(propylene) with terminal unsaturation was hydroborated with 9-BBN which upon selective oxidation by oxygen forms stable polymeric alkoxy radical. These polymeric alkoxy radicals are highly reactive and initiate the copolymerization with monomers such as MMA , MA, etc.

In the case of maleic anhydride [99] a very low concentration of MA was incorporated (probably only one MA unit at the end), because of its low tendency of homopolymerization. On the other hand the presence of styrene in poly(propylene)/MA mixture enhances the formation of diblock copolymer poly(propylene) -b-poly(styrene-maleic anhydride).

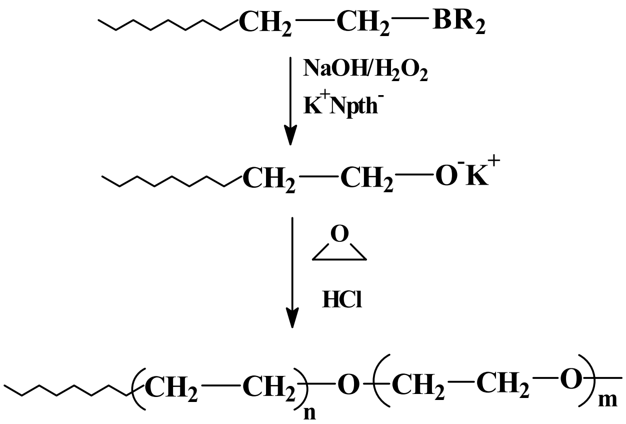
The oxidation of 9-BBN terminated poly(propylene) usually takes place slowly. The unfavorable increase in ring strain (occurs due to insertion of oxygen into C-B bonds in the bicyclic ring of 9-BBN) destroys the stable double chair form structure. Hence, the oxidation reaction selectively takes place at C-B bond [102, 103] in the linear alkyl group to produce peroxy borane(C-O-O-B) **(scheme-1.20).**



Scheme-1.20 Synthesis of poly(propylene) block copolymers by borane approach

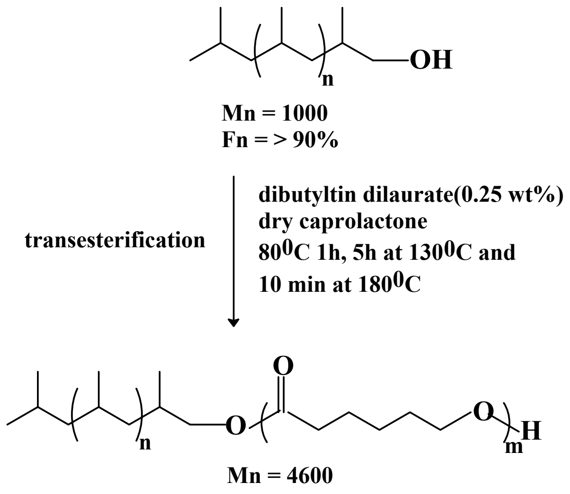
The peroxy borane behaves very differently from regular benzoyl peroxide and consequently decomposes homolytically by itself even at ambient temperature to form an alkoxy radical(C-O*) and a borinate radical(B-O*). The alkoxy radical is very reactive and can be used for the initiation of radical polymerization [104]. But the borinate relatively stable due to the back donation of electron density to the empty p-orbital of boron; hence it may not initiate polymerization.

Recently Lu et al reported the synthesis of amphiphilic poly(olefin)-b-poly(ethylene oxide) copolymers by converting borane terminated poly(olefin) to anionic macro initiator (-O^-K^+) for ring opening polymerization of ethylene oxide [120]. Copolymers having broad composition with controlled molecular weight and molecular weight distribution were obtained **(scheme-1.21).** The block copolymers were also found to be effective compatibilizer for the blends of corresponding homopolymers.



Scheme-1.21 Synthesis of poly(olefin)-b-poly(ethylene oxide) copolymers

Mulhaupt et al [105, 106] reported the synthesis of poly(propylene)-b-poly(caprolactone) and poly(propylene)-b-poly(amide)-66 block copolymers. Hydroxy terminated poly(propylene) was used as an initiator in caprolactone polymerization to form poly(propylene)-b-poly(caprolactone) **Scheme-1.22**

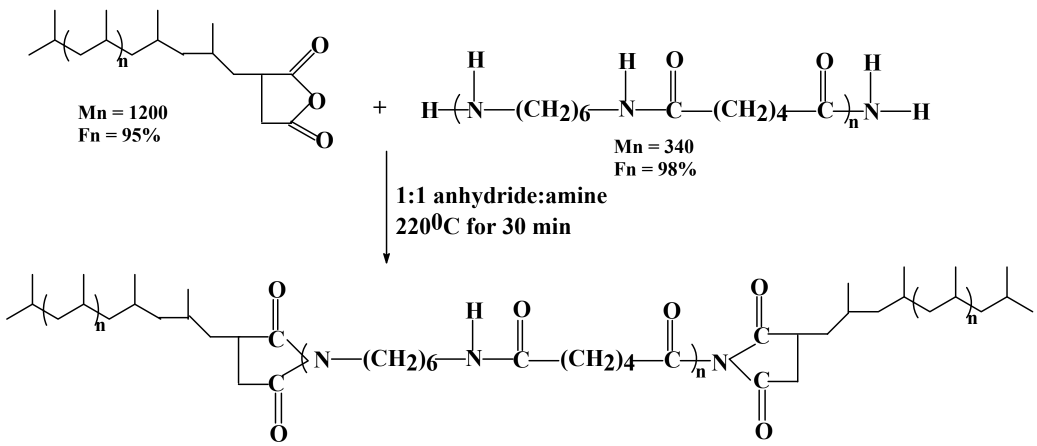


Scheme-1.22 Synthesis of poly(propylene)-b-poly(caprolactone)

The block copolymer was purified by precipitating from a THF solution in methanol and the copolymers were found to be insoluble in boiling n-pentane. The characterization of the block copolymers by NMR, VPO and GPC showed that the efficiency of block formation was as high as 70%. Such poly(olefin)-b-poly(caprolactone) copolymers were also reported by utilizing hydroxy terminated poly(4-methyl 1-pentene) as a macro initiator [98, 107].

Succinic anhydride terminated poly(propylene) react with oligomeric diamine terminated polyamide-66 at an amine to anhydride ratio of 1:1 in the melt to yield poly(propylene)-b-poly(amide)-66-b- poly(propylene) triblock copolymers **(scheme-1.23)**. Despite the small molecular weight (Mn 2800), such triblock copolymers were found to be insoluble in all the solvents typically used for poly(propylene) and poly(amide)-6,6.

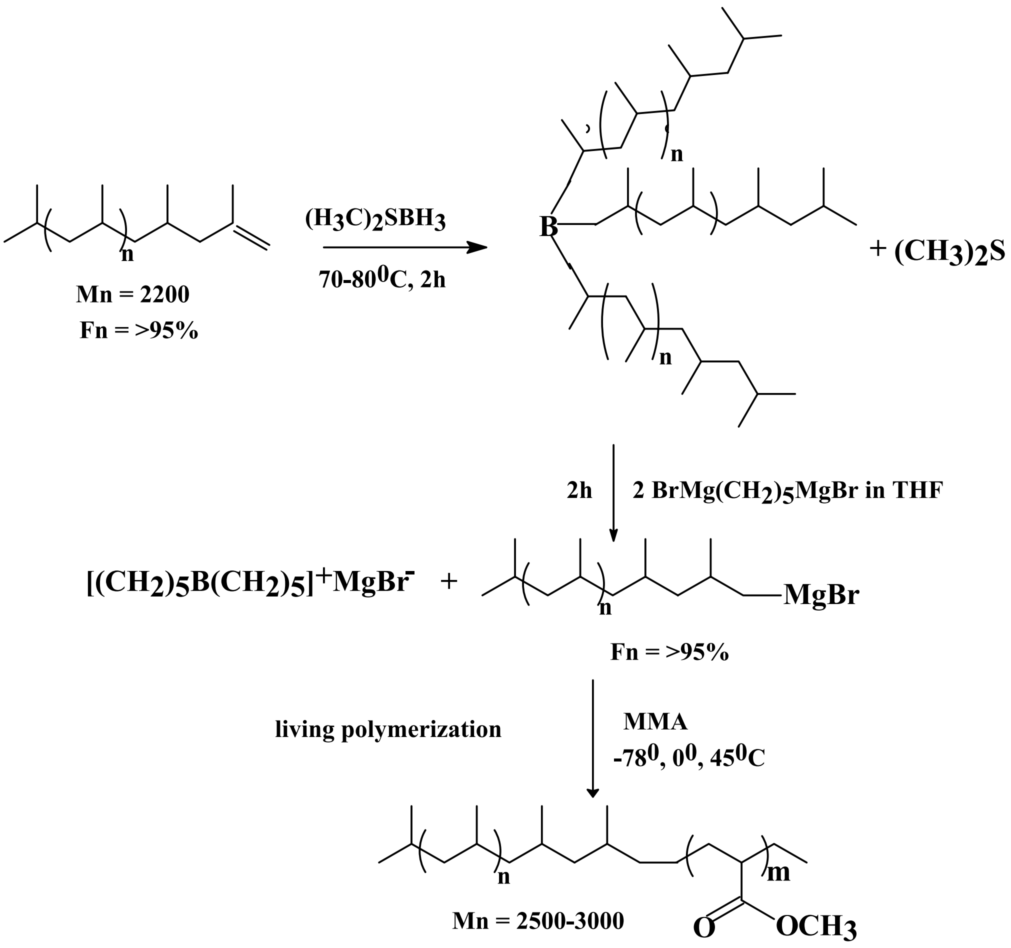
Characterization of the block copolymers by IR showed the absence of anhydride end group and presence of cyclic imide groups. Poly(propylene)-b-poly(amide)-6 diblock copolymers were also prepared by reacting succinic anhydride terminated poly(propylene) with amine terminated poly(amide)-6 [106]. Such block copolymers were successfully utilized as compatibilizers of poly(propylene)-b-poly(amide)-6 blends.



Scheme-1.23 Synthesis of poly(propylene)-b-pol(yamide)-6,6-b-poly(propylene) triblock copolymer

Isotactic poly(propylene)-b-poly(methyl methacrylate) copolymers were also reported [108] by using MgBr terminated poly(propylene) as an anionic initiator for methyl methacrylate copolymerization **(scheme-1.24)**. Poly(propylene) with terminal vinylidene unsaturation was hydroborated by a borane-dimethylsulphide complex [109].

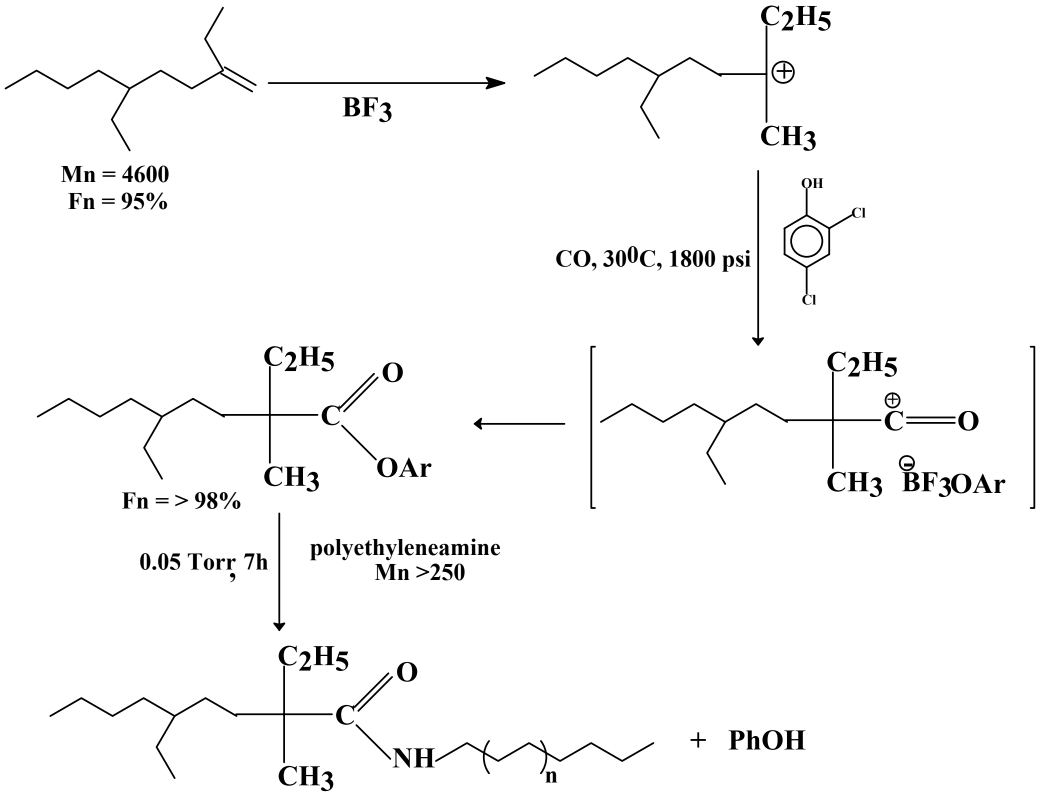
Trialkylboranes can be quantitatively converted to the corresponding Grignard reagent by reacting with pentane-1,5-diyl di(MgBr) in benzene or toluene [110]. The formation of relatively stable bicyclic borate causes a shift of the equilibrium to the right. Hence the MgBr terminated poly(propylene) prepared using the above principle was subjected to polymerization of methyl methacrylate as an anionic initiator.



Scheme-1.24 Synthesis of poly(propylene)-b-poly(methylmethacrylate)

The block copolymer was extracted with boiling acetone to remove any homo poly(methyl methacrylate). Characterization of the block copolymers by GPC at different intervals of time showed that the methylmethacrylate content in the copolymer increased with increase in polymerization time. The structure of the block copolymer was further confirmed by NMR (^{1}H and ^{13}C).

Recently Emert et al reported a new block copolymer of poly(olefin)-b-polyamine for motor oil additives [111]. The synthesis involves two steps in which poly(olefin) segment consists of ethylene-butene copolymer with greater than 95 mol% terminal vinylidene unsaturation were prepared using $(CH_3)_2Si(THI)_2ZrCl_2$/MAO catalyst.



Scheme1.25 Synthesis of carboaryloxy terminated EB copolymer

The terminal vinylidene double bonds were converted to carboaryloxy group using Koch-Haaf functionalization reaction (**scheme-1.25**). The linking of of polyethyleneamine with carboaryloxy terminated poly(ethylene-co-butene) was accomplished by ester aminolysis. It is more facile with phenyl esters with aromatic ring containing an electron attracting group.

1.3.4 Vinyl terminated polypropylene as a macromonomer

Vinyl terminated poly(propylene) has been used as a macromonomer in ethylene copolymerization to give comb shaped poly(ethylene) with pendant poly(propylene) branches.

Polymerization of propylene using $Cp^*_2ZrCl_2$/MAO (Cp^* = Me_5Cp) catalyst results in atacic poly(propylene) having exclusively vinyl end groups. Such vinyl terminated poly(propylene) (Mn = 710) was copolymerized with ethylene [112] using (t-butylamido) dimethyl(tetramethyl-η^5-cyclopentadienyl)silane titanium dichloride (CGC-Ti), $Et(THI)_2ZrCl_2$, Cp_2ZrCl_2 and Cp_2TiCl_2/MAO catalysts. The structure of the resulting copolymer confirmed that the macromonomer was copolymerized with ethylene. The addition of the macromonomer resulted a marked increase in the activity with the constrained geometry catalyst, whereas, the activity of the other metallocene catalysts decreased. The maximum incorporation of the macromonomer was 1 mol % in the copolymer using a mono Cp constrained geometry catalyst [113].

It was found that the rate enhancement observed at 40^0C is due to an increase in the solubility of the polymer by copolymerization, which decreases diffusion resistance of ethylene to the active centers and/or increases the number of effective active centers.

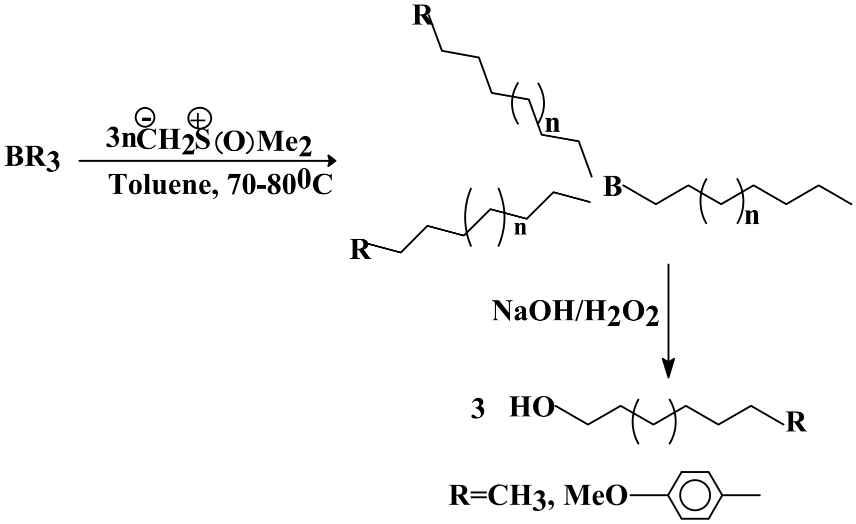
Vinyl terminated poly(propylene) macromonomer (Mn=630) was also copolymerized with propylene [114] using *rac* $Me_2Si(2\text{-}MeBenz[e]Ind)_2ZrCl_2/MAO$ catalyst to give isotactic PP with atactic side chains. The maximum incorporation of poly(propylene) macromonomer was found to be 3.8 mol % in the copolymer.

Macromonomers can also incorporated in to polyolefin backbone by "insitu" process without sequential addition as discussed above by use of mixed metallocene catalysts [115]. In mixed metallocenes, one catalyst is responsible for the generation of macromonomer followed by the incorporation of macromonomer by second catalyst.

1.3.5 Terminal functional poly(olefin)s by polyhomologation

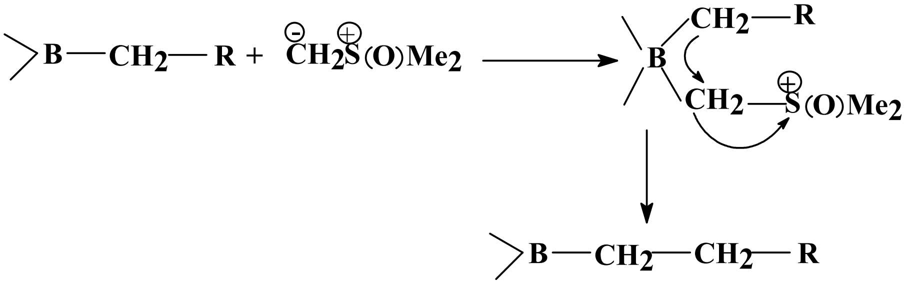
Recently Shea et al reported a new polymerization reaction for the synthesis of terminally functionalized poly(methylene) known as polyhomologation [116]. It is a living polymerization in which ylides such as dimethyl sulfoxonium methylide serve as a source of monomer and alkyl boranes function as initiator or catalyst **(scheme-1.26)**. The molecular weight of the polymethylene is controlled by the molar ratio of the ylide to alkyl borane.

The homologation involves the initial attack of ylide on the alkylborane. The borate complex undergoes a 1,2- migration of the alkyl group to produce the homologated alkylborane and a molecule of dimethyl sulfoxide. The propagation involves the reaction of homologated alkylborane with additional ylide **(scheme-1.27).** The reaction continues as long as the ylide is available. Hydroxy terminated poly(methylene) with Mn ranging from 700 - 3300 were reported. Polydispersity as low as 1.01 has been obtained at lower molecular weight, where as higher polydispersity was obtained at higher molecular weight. This was attributed to the competing precipitation of poly(methylene) during polyhomologation.



Scheme-1.26 Synthesis of terminally functionalized poly(methylene) by polyhomologation

Hydroxy terminated poly(methylene) was characterized by field desorption spectrometry (FDMS), GPC and NMR. The number average molecular weights (Mn) by NMR end group analysis were consistent with those calculated from the ratio of alkylborane to ylide by assuming equal probability of migration of all three alkyl groups. However GPC and FDMS analysis indicated slightly higher polydispersities. This is an elegant approach to make terminally functionalized poly(ethylene) with high functionality (Fn > 99%) and low polydispersity.



Scheme-1.27 Mechanism of polyhomologation

Polyhomologation is also amenable for the synthesis of telechelic polymethylene, AB and ABA block copolymers of poly(ethylene glycol)-b-poly(methylene) and poly(dimethylsiloxane)-b-poly(methylene) [117-119]. Telechelics such as α-(p-methoxyphenyl)-ω-hydroxypoly(methylene) was prepared by reacting the ylide with tris[(p-methoxyphenyl)ethyl]borane. Allyl terminated poly(ethylene glycol) (DP = 12) was hydroborated with borane to give trialkyl borane. Addition of such alkyl boranes to ylides followed by oxidative cleavage yields poly(ethylene glycol-b-methylene).

1.4 In chain functionalization

There are four different methods adopted for the synthesis of functional polyolefins by "in chain functionalization". These are described in the following paragraph.

1.4.1 Direct Copolymerization

The direct method for the synthesis of functionalized poly(olefin)s involves the copolymerization of an olefin with comonomers having the desired functional group. This method is limited by the ability of many functional groups to co-ordinate with the catalyst/co-catalyst components, thus, causing catalyst deactivation.

Different strategies have been adopted to obviate this problem. These include separating the functional group from the polymerizable double bond by spacer groups, masking the functional group by the use of suitable protecting agents, increase of bulk-steric around the functional group and decreasing the nucleophilicity of the functional group.

1.4.1.1 Copolymerization of ethylene with ω-chloro-α-olefins

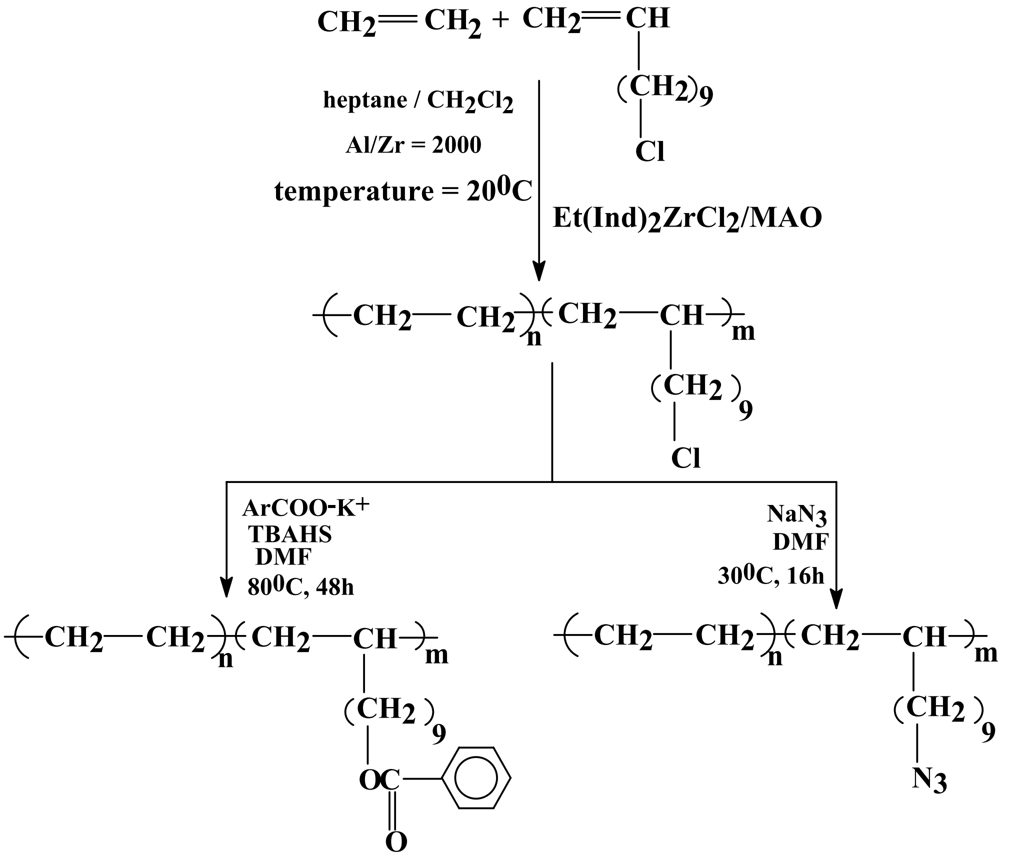
Bruzaud et al.[121, 122] reported the copolymerization of ethyelene with ω-chloro-α-olefins using $Et(ind)_2ZrCl_2/MAO$ in heptane medium **(Scheme-1.28)** followed by functionalization of pendant chloro end groups to aromatic ester, hydroxyl and azide groups. Copolymerization in toluene resulted in copolymers having aromatic rings, most probably due to Friedel-Crafts reaction between chloro end groups and toluene assisted by the Lewis acidic MAO.

Characterization of the functionalized copolymers by NMR revealed greater than 95% conversion of chlorine to corresponding functional group.

1.4.1.2 Copolymerization of olefins with amine functionalized olefins

Tertiary amine functionalized olefins can be polymerized with group IV metallocene catalysts, provided sufficient steric hindrance is present around the nitrogen atom. Amines, such as diisopropyl and diphenyl derivatives can be polymerized without the necessity of protection by Lewis-acid complexation.

Waymouth [123] et al carried out homopolymerization of amine functionalized olefins using $Cp^*_2ZrMe_2$/Borate catalyst. The catalyst activity was lower for 5-(*N,*N-dimethylamino)- and 5-(*N,N*-diethylamino)-1-pentene compared to the bulkier diisopropylamino and diphenylamino derivatives. Steric considerations indicate that the bulkiness of the amine substituents is more important in determining compatibility with the catalysts than electronic factors.



Scheme-1.28 Copolymerization of ethylene with ω-chloro-α-olefins

Waymouth et al. also prepared atactic and isotactic copolymers of 5-(*N,*N diisopropylamino)-1-pentene with 1-hexene and 4-methyl-1-pentene [124] using an $Et(THI)_2ZrMe$ catalyst. The copolymerization of the amino monomer with 1-hexene was almost ideal (r_1r_2) = 0.99), allowing polymers with a wide range of compositions to be prepared.

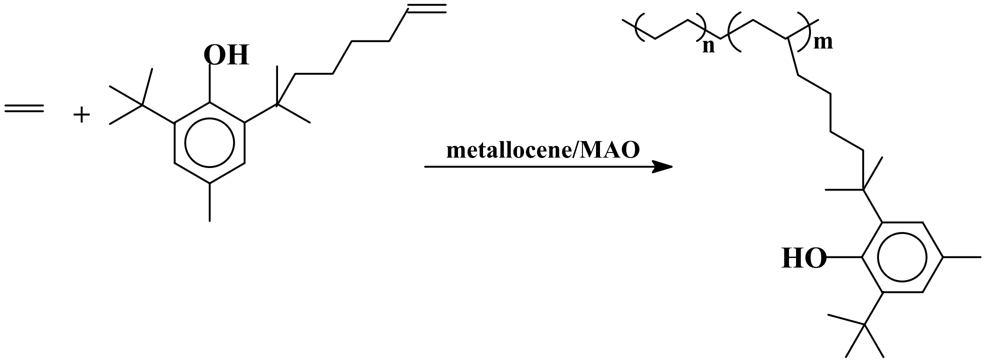
1.4.1.3 Copolymerization of ethylene with monovinyl functional silsequioxane

Synthesis of polyethylene having pendant cubic silsequioxane groups have been reported by Tsuchida et al [125] by the copolymerization of ethylene with a novel monovinyl functional silsequioxane cage 1-(9-decenyl)-3,5,7,9,11,13,15-hepta-ethylpentacyclo[9.5.1.1^{3,9}.1^{5,15}.1^{7,13}]octasiloxane using metallocene/MAO catalyst system. A maximum incorporation of 1.2 mol % has been reported. These copolymers exhibit superior thermal stability.

Recently Zheng et al reported the synthesis of a novel poly(olefin) nanocomposite by the copolymerization of ethylene/propylene with norbornylene substituted polyhedral oligomeric silsesquioxane (POSS) namely 1-[2-(5-norbornen-2-yl)ethyl]-3,5,7,9,11,13,15-heptacyclopentylpentacyclo$[9.5.1.1.^{3.9}1.^{5.15}1.^{7.13}]$ octasiloxane macromonomer using *rac* $Et(Ind)_2ZrCl_2$/MAO catalyst [126]. The maximum comonomer incorporation of 3.4 and 10.4 mol% have been reported with ethylene and propylene respectively. Thermogravimetric analysis of the Poly(ethylene-co-POSS) copolymers under air have shown a 90^0C improvement.

1.4.1.4 Copolymerization of ethylene with vinyl monomer bearing anti oxidant group

Antioxidants have been incorporated into polyolefin backbone by copolymerizing ethylene with a functional monomer namely 6-tert-butyl-2-(1,1-dimethylhept-6-enyl)-4-methyl phenol [127, 128]. The activity was improved when $Me_2Si(IndH_4)_2ZrCl_2$ was employed as as catalyst **(scheme-1.29).**

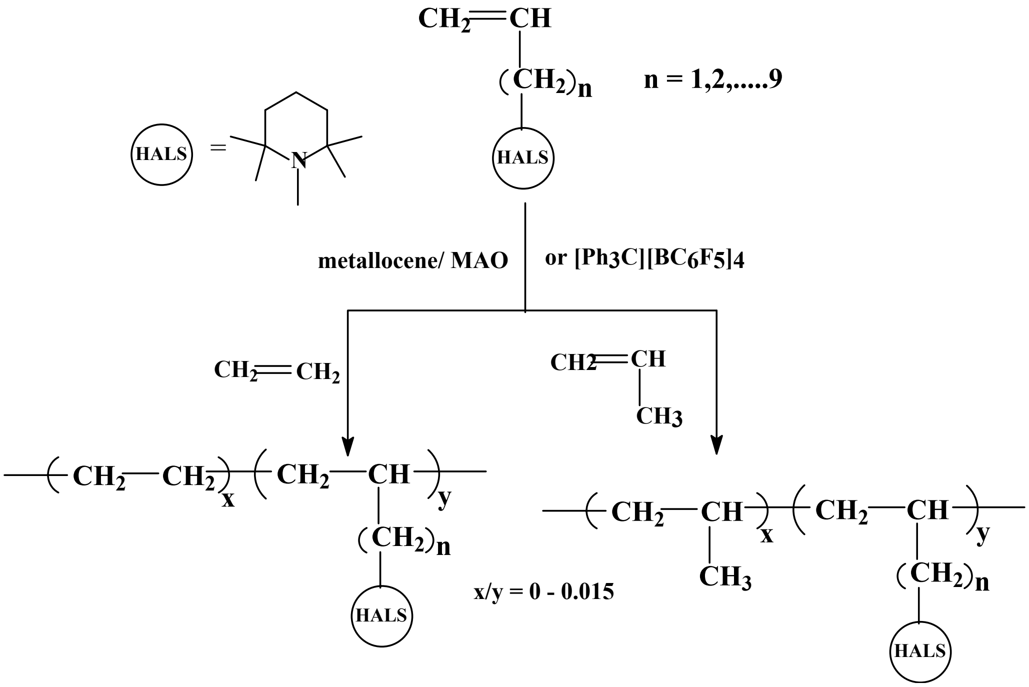


Scheme 1.29 Copolymerization of ethylene 6-tert-butyl-2-(1,1-dimethylhept-6-enyl)-methyl phenol

The maximum comonomer incorporation was found to be 6.7 wt%. The copolymerization activities were not influenced by the variation of Al/phenol ratio between 1.2 to 4.8 at the temperature range of 20-30°C. But at 80°C, no activity was found for an Al/phenol ratio of 2.2, indicating that at higher temperature, the catalytic sites are more sensitive to donor interactions.

1.4.1.5 Copolymerization of ethylene with vinyl monomer bearing HALS

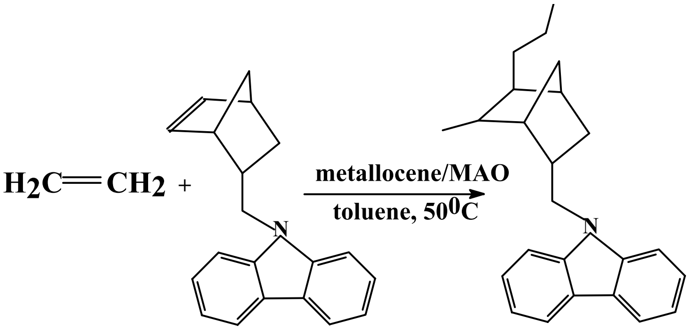
Vinyl monomers bearing hindered amine light stabilizers (HALS) have also been copolymerized with ethylene or propylene [129]. The catalyst *rac*$[(CH_3)_2Si(Ind)_2ZrCl_2)$/triethyl aluminum/trityl tetra(perfluorophenyl)borate affords the best results amongst eight homogeneous metallocene/MAO catalysts studied **(scheme-1.30)**. The maximum incorporation of functional comonomer was 14 wt% with Mn in the range of 6000 to 18 000. The copolymers exhibited superior UV and thermooxidative stability over poly(ethylene).



Scheme-1.30 Copolymerization of ethylene vinyl monomers bearing HAS

1.4.1.6 Copolymerization of ethylene with vinyl monomer bearing carbazole group

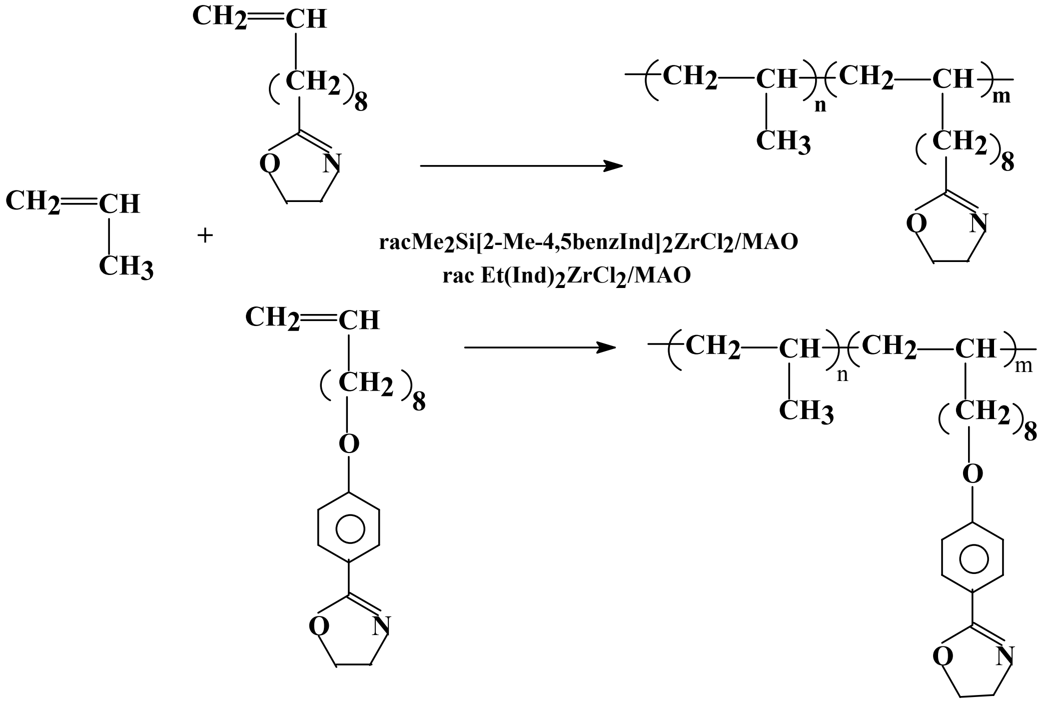
Recently Mustonen [130] et al reported the copolymerization of ethylene with a carbazole based comonomer namely 9-(bicyclo-[2.2.1.]hept-5-en-2yl-methyl)-9H carbazole using [$Ph_2C(Flu)(Cp)ZrCl_2$] and [$Ph_2C(Ind)(Cp)ZrCl_2$]/MAO catalysts **(Scheme-1.31).** The maximum comonomer incorporation was 4.6 mol% with Mw 70200. Such functional polymers may find applications as photorefractive materials.



Scheme 31 Copolymerization of ethylene with 9-(bicyclo-[2.2.1.]hept-5-en-2ylmethyl)-9H carbazole

1.4.1.7 Copolymerization of propylene with with vinyl monomer bearing oxazoline group

Copolymerization of propylene with 2-(9-decene)-1,3-oxazoline and 2-(4-(10-undecene-1-oxo)phenyl)-1,3-oxazoline was carried out by Kaya et al [131] using *rac*-Et[Ind]$_2$ZrCl$_2$ and *rac*-Me$_2$Si[2-Me-4,5-BenzInd]$_2$ZrCl$_2$/MAO catalyst **(scheme-1.32).**



Scheme-1.32 Copolymerization of propylene with 2-(9-decene)-1,3-oxazoline (1), and 2-(4-(10-undecene-1-oxo)phenyl)-1,3-oxazoline

Under similar conditions, the catalyst deactivation was more pronounced in case of 2-(4-(10-undecene-1-oxo)phenyl)-1,3-oxazoline compared to 2-(9-decene)-1,3-oxazoline. It was attributed due to the additional polar phenoxy moiety in the spacer between oxazoline and vinyl double bond in 2-(4-(10-undecene-1-oxo)phenyl)-1,3-oxazoline. The maximum comonomer incorporation was 0.53 mol% with mmmm pentad 85% and Mn was 8000. Oxazoline ring opening was observed when the copolymers were extracted from hydrochloric acid solution. These copolymers are of interest especially for reactive blending with carboxylic acid functionalized polymers.

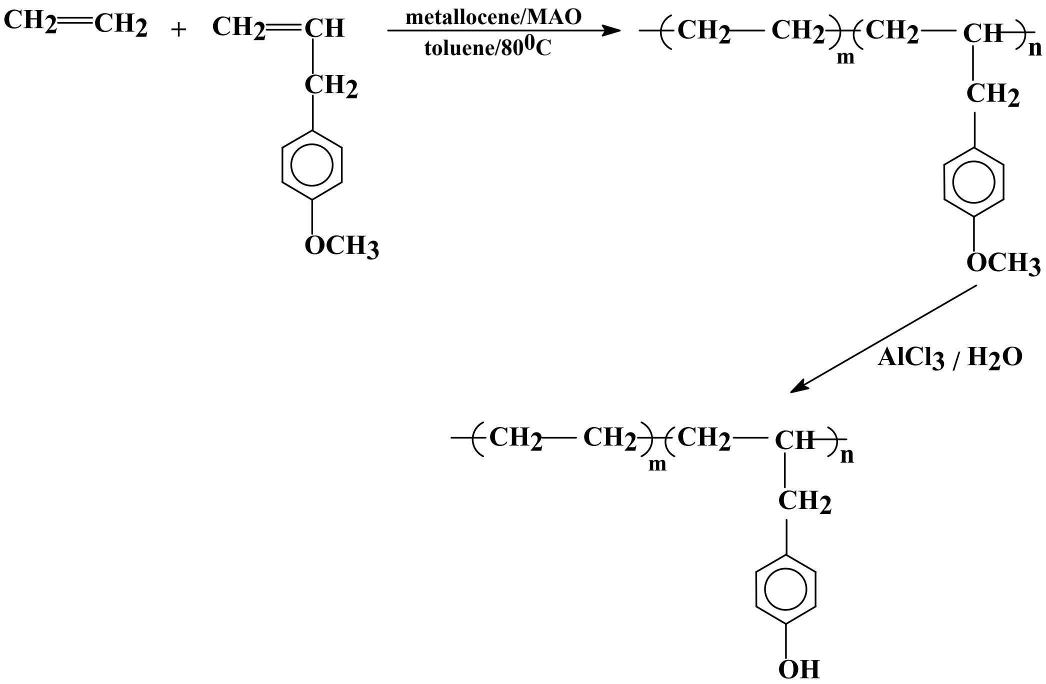
Copolymerization of propylene with more sterically hindered oxazoline namely 2-(9-decen-1-yl)-4,4-dimethyl-1,3-oxazoline and 10-undecenoylchloride was also reported by kaya et al [132]. Under identical conditions the higher activity was found with sterically hindered oxazoline compared to the above two oxazolines. Propylene copolymers with

10-undecenoylchloride are of interest for the synthesis of various other functional group containing poly(propylene).

1.4.1.8 Copolymerization of ethylene with allylanisole

Byun et al adopted a two step approach for the preparation of phenol containing polyethylene [133]. First ethylene was copolymerized with allylanisole using metallocene/MAO catalyst systems followed by the transformation of corresponding methoxy groups to hydroxy group **(scheme-1.33).**

Among the catalysts studied, bridged and less substituted catalysts exhibited higher comonomer incorporation (maximum 6.4 mol%), whereas, the substituted catalysts showed higher activity and Mw (34,000) with lower comonomer incorporation. Pretreatment of allylanisole with MAO did not show any significant change either in activity or comonomer incorporation regardless of the pretreatment time. The comonomer incorporation exhibited an inverse relation with Al concentration, which was attributed to the interaction of allylanisole with MAO (or free TMA in MAO). The allylanisole coordinated with MAO becomes less accessible to the active metal center due to steric hindrance.



Scheme-1.33 Copolymerization of ethylene with allylanisole

1.4.1.9 Copolymerization of ethylene with silicon containing monomers

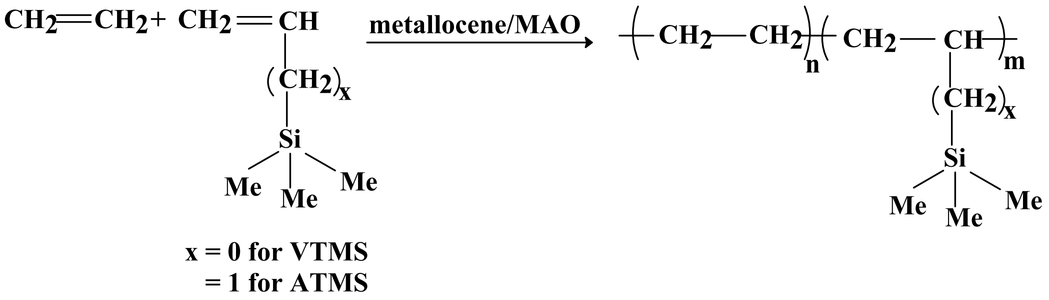
Copolymerization or homopolymerization of silicon containing vinyl monomers have received far less attention. There are a few reports on coordination polymerization of vinyl monomers like allylsilane, allyltrimethylsilane, 5-trimethylsilyl-1-pentene to isotactic polymers utilizing Ziegler catalysts as the initiators [134-136]. 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 [137]. Coordination polymerization of vinylsilane has been reported recently [138].

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 [139]. A detailed study of structure and tacticity of allyltrimethylsilane has been reported [140]. 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 [141]. These kind of polymers can also be crosslinked by irradiation due to the coupling of silyl radical of vinylsilane unit with the carbon radical [142]. 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 [143-148].

There appears to be practically no study on the polymerizability of monomers containing silyloxy group with Si-O-Si linkage except the copolymerization of ethylene with cubic silsesquioxane by Tsuchida et al [125]. Presence of siloxane polar group may interfere with the catalyst. But the nucleophilicity of the oxygen atom may be less due to the dπ-pπ back bonding.

The copolymerization of ethylene with various silicon containing monomers namely Vinyltrimethylsilane (VTMS), allyltrimethylsilane (ATMS), trimethylsilyloxydimethylvinylsilane, and vinylethoxydimethylsilane using various metallocene catalysts [149] have been studied in our laboratory **(scheme-1.34)**.



Scheme-1.34 Copolymerization of ethylene with vinyl silanes

The overall catalyst activity decreases in the presence of both TMVS and ATMS. The rate of ethylene polymerization is higher for ATMS than for VTMS.

Higher comonomer incorporation was observed for allyltrimethylsilane than vinyltrimethylsilane when $Et(Ind)_2ZrCl_2$ was employed as the catalyst. The crystallinity 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.

No polymerization activity was observed for copolymerization of ethylene with trimethylsilyloxydimethylvinylsilane and vinylethoxydimethylsilane with various metallocene catalysts. The active center is deactivated due to the presence of ethoxy and silyloxy groups. Similar deactivation of the catalyst has been observed by Fink et al. when hydroxyl group containing vinyl monomers were used for copolymerization with ethylene after protecting the hydroxyl group with trimethylsilyl group [162].

Recently Seppala et al reported the copolymerization of ethylene with 7-octenyldimethylphenylsilane using $[Me_2Si(Me\text{-}2\text{-}Ind)_2ZrCl_2$ and $Et(Ind)_2ZrCl_2/MAO$ catalysts [150]. The comonomer incorporation as high as 2.6 mol% was obtained with Mw varying from 300 – $600X10^3$. No deactivation of the catalyst was observed in presence of comonomer. Higher activities were observed in copolymerization compared to ethylene homopolymerization due to comonomer effect.

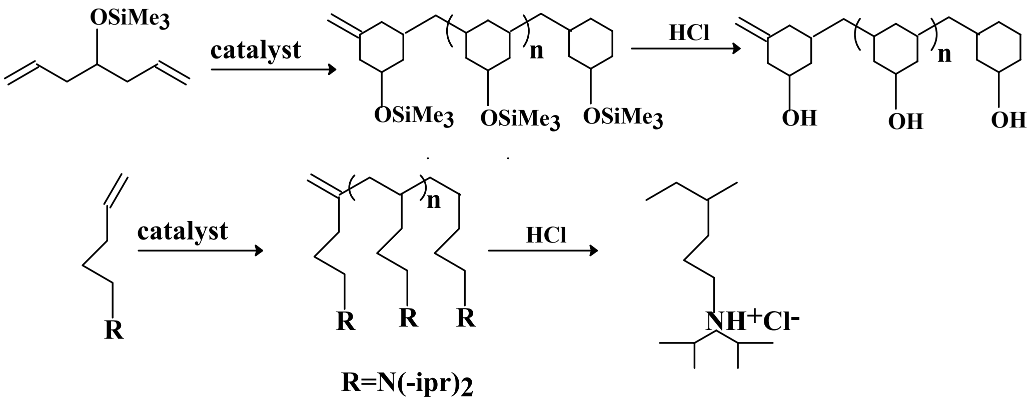
Although, the above methods discuss about the copolymerization of various polar monomers with olefins, but the engineering aspects of functionalized poly(olefin)s such as adhesion strength, hardness etc have not been discussed. Recently Santos et al studied the adhesive properties of poly(ethylene-co-10-undecenoic acid) and poly(ethylene-co-5,7-dimethylocta-1,6-diene) which inturn were prepared by Cp_2ZrCl_2 and $(Me_4Cp)SiMe_2(N\text{-}t\text{-}Bu)TiCl_2/MAO$ catalyst respectively, with various substrates such as glass, PVC and steel [151]. Poly(ethylene-co-10-undecenoic acid) with 1.6 mol% of comonomer incorporation has shown a five fold increase in adhesion strength compared to high density poly(ethylene).

1.4.2. Protection of functional groups

Many functional groups containing monomers require protection-deprotection strategies for use in copolymerization. The most commonly employed reactions involve the use of organoaluminum, organoboron, and organosilicon chemistry. Organoaluminum compounds are advantageous because of its ubiquitous existence in polymerization reactions.

Homopolymerization of olefins containing silyl protected alcohols and tertiary amines like 4-trimethyl siloxy-1,6-heptadiene, 5-tert-butyldimethylsiloxy-1-pentene and 5-(N,N-diisopropyl amino)-1-pentene using cationic metallocene catalyst systems have been reported by Waymouth et al.[152]. They successfully synthesized 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 $^{-}25^{0}$ C with 30 % conversion which on treatment with aq.HCl gives the polyalcohol **(Scheme-1.35).**

Copolymerization of ethylene with 10-undecen-1-ol with $(n\text{-}buCp)_2ZrCl_2/MAO$ catalyst system, with a maximum incorporation of 1.7 mol %, have been reported by Aaltonen et al [153]. A comparative study of ethylene/10-undecen-1-ol copolymerizations over a series of unbridged, ethylene bridged and silylene bridged metallocenes showed that the silylene bridged metallocenes showed the best performance, with the highest incorporation of 3 mol % using the metallocene $Me_2Si[2\text{-}Me\text{-}4,5\text{-}Benzo\ Ind]_2ZrCl_2$ [154].



Scheme-1.35 Polymerization of silyl protected alcohol

Copolymerization of ethylene with 5-hexen-1-ol and 10-undecen-1-ol using (n-buCp)$_2$ZrCl$_2$/MAO catalyst system under identical conditions showed that increasing the length of the spacer group between the polymerizable double bond and the functional group do not have any effect on copolymerization activity. However, longer the spacer group higher was the incorporation [155]. Though hydroxyl group do have a poisonous effect on catalyst system if present in the polymerization medium, the effect varies with the extent of incorporation of the comonomer. Higher the incorporation, higher is the deleterious effect. Otherwise, no polymerization should have been observed with the comonomer 2-methyl-3-buten-2-ol at such a high concentration where 5-hexen-1-ol or 10-undecen-1-ol copolymerizations failed to produce a polymer [155].

Introduction of hydroxyl group considerably increases the melt index of the polymer, thus improving its processability. The MWD of the copolymers increased with increase of alcohol content in feed. At higher alcohol levels, even bimodal MWDs were observed.

Pretreatment of 10-undecen-1-ol with MAO or increase in Al/Zr ratio increased the copolymerization activity, but marginally decreased the comonomer content [154] as well as molecular weight [153]. It can be presumed that the alcohol reacts with MAO 'in situ' to form alcoholate which underwent copolymerization. The reaction of MAO with hydroxyl group, with the release of methane gas, will lower the Me/Al ratio which itself is a decisive factor in polymerization [156]. Copolymerization with carboxylic acid or ester containing functional monomers reduced the copolymerization activity as well as incorporation by one half of that for the hydroxyl functional analogue [155]. Since the ketone functionality undergoes weaker interaction with an aluminum-based protecting agent, the strategies described above for alcohols have not been successfully studied to any extent. Hakkala et al [157] attempted the copolymerization of 2,2-dimethyl-11-dodecen-3-one with propylene using zirconocene/MAO catalyst but found that the ketone comonomer completely suppressed polymerization.

Ether containing functional monomers also undergo only weak complexation to aluminum cocatalysts for protection purposes and have not been extensively studied. Waymouth et al. reported the failure of diallyl ether to polymerize with zirconocene/borane initiating systems [152]. Recently Hakkala et al [158] reported the copolymerization of ethylene with 10-undecenyl methyl ether and 10-undecenyl trimethyl silyl ether using *rac* Et(Ind)$_2$ZrCl$_2$/MAO catalyst system. The analysis of the copolymers revealed that the functional groups in the copolymer of trimethyl silylether was hydroxyl, where as the methyl ether group remained untouched in the copolymer. It reveals that the protection of the oxygen atom via aluminum alkoxide formation is not necessary for comonomer incorporation.

Copolymerization of acrylonitrile and methyl acrylate with propylene resulted in only homopolymer of propylene with zero incorporation of either of the monomers. Complexation of the polar monomers with Lewis acids like diethylaluminum chloride or trimethylaluminum did not make any significant change [159].

If the functional group is "prereacted" with an aluminum alkyl resulting in the formation of -CH_2-O-Al- bond the deleterious reaction with MAO can be prevented.

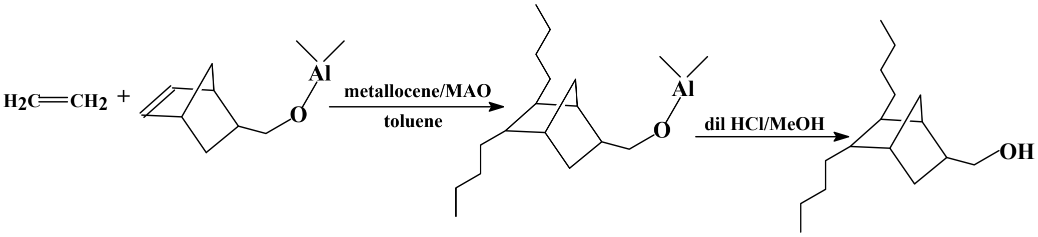
JP patent 6,172,447 [160] describes a method for the synthesis of ethylene/10-undecenoic acid copolymer using a bridged metallocene/aluminoxane catalyst system. The functional monomer was pretreated with one equivalent of an aluminum alkyl; tri-isobutyl aluminum (TIBAL) being the most preferred one. With $Me_2Si(indH_4)_2ZrCl_2$/methyl isobutyl aluminoxane catalyst system, a copolymer having a Tm of 118^{o}C and 1.87 mol % of the functional monomer have been synthesized.

JP patent 4,45,108 [161] describes a method for the synthesis of ethylene/ethyl acrylate copolymer using metallocene/MAO catalyst system containing upto 8.6 mol % ethyl acrylate. However, no decrease in Tm was observed as the copolymer with 8.6 mol % of ethyl acrylate and having a Mw of 18,000 and MWD of 2.4 has a Tm of 129^{o}C.

Imuta et al used a new stereorigid bridged metallocene having an indenyl and flurenyl ligand (IF catalyst) for copolymerization of ethylene with TMA protected allyl alcohol and 1-hydroxy-10-undecene [162, 163].

Recently Radhakrishnan and Sivaram [164] reported the synthesis of hydroxyl functional polyethylene via the copolymerization of ethylene with bicyclo[2.2.1] hept-5-ene-2-methanol (NB-OH) prereacted with trimethylaluminium (TMA) using various metallocene catalysts (**scheme-1.36**). Addition of TMA to bicyclo[2.2.1] hept-5-ene-2-methanol (NB-OH) results in dimeric dimethylaluminum-5-norbornene-2-methoxide.

The dimethylaluminum-5-norbornene-2-methoxide undergoes copolymerization with ethylene efficiently. Copolymerization activity, comonomer incorporation and molecular weight were found to depend primarily on the nature of the metallocene and on the experimental conditions used for copolymerization. No post polymerization treatment of the copolymer was required to remove the aluminum attached to the alcohol as the dilute hydrochloric acid/methanol mixture used for the precipitation as well as removal of catalyst/cocatalyst hydrolyzes the oxygen-aluminum bond in copolymer also.



Scheme-1.36 Copolymerization of ethylene with dimethylaluminum-5-norbornene-2-methoxide using various metallocenes/MAO catalyst

Goretzki and Fink [165-167] studied the copolymerization of ethylene with trimethylsilyl (TMS), triisopropylsilyl (TIPS) and tri-isobutylaluminum (TIBAL) protected 5-norbornene-2-methanol using iPr(CpInd)$ZrCl_2$/MAO catalyst and the corresponding silica supported catalyst. The comonomer incorporation as high as 24 mol % was achieved using TIBAL as the protecting group. The trimethylsilyl (TMS) protecting group could not prevent the catalyst deactivation caused by the addition of the polar comonomer. In contrast, good catalyst activities and comonomer contents were obtained with the triisopropylsilyl (TIPS) protected monomers.

Terpolymerizations of norbornene derivatives containing different functional substituents were carried out with ethylene and norbornene using iPr[CpInd]$ZrCl_2$/MAO catalyst system [168]. The norbornene derivatives 5-norbornene-2-methanol and 5-norbornene-2-carboxylic acid were prereacted with tri-isobutylaluminum. The incorporation of functional comonomer was 5 –12 mol% with homogeneous composition.

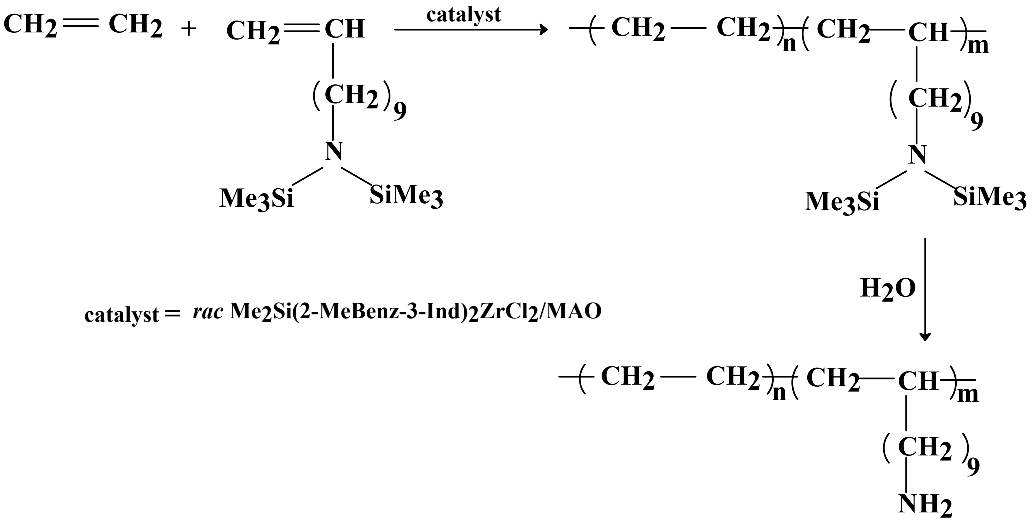
Terpolymerization of hexen-1-ol, 10-undecen-1-ol and 10-undecen-oic acid with ethylene and propylene was carried out by rac $Et(Ind)_2ZrCl_2$, $Cp^*Si(Me)_2N$-t-$BuTiCl_2$ and $(Benzind)_2ZrCl_2$/MAO [169] catalysts. Trimethylaluminum (TMA) was employed as the protecting group. Several mixing strategies were employed, and the comparisons indicate that the complexing with TMA is far more effective than complexing using MAO. The target terpolymers could be prepared with substantial decreases in catalyst activity.

Recently Hagihara et al [170] carried out the copolymerization of ethylene with 5-hexen-1-ol prereacted with TMA using Et(1-Ind)(9-Flu)$ZrCl_2$/MAO catalyst. The copolymers containing as high as 50 mol% 5-hexen-1-ol with almost alternating structure (by NMR) are reported.

Mulhaupt et al [171] reported the copolymerization of ethylene with *N,N*-bis(trimethylsilyl)-1-amino-10-undecene using *rac*$Me_2Si(2\text{-MeBenz-3-Ind})_2ZrCl_2$/MAO catalyst **(scheme-1.37).** The protecting TMS groups were cleaved during workup with aqueous HCl followed by alkali wash. The maximum comonomer incorporation of 19 wt% was reported. The copolymers even at low comonomer incorporation were found to be insoluble in solvents normally used for poly(olefin)s.

Recently Shiono et al reported the copolymerization of propylene with 7-octenyldiisobutylaluminum using $Me_2Si[2\text{-Me(Ind)}_2ZrCl_2$ and $Ph_2C[(Cp)((Flu)]ZrCl_2$ catalysts [172]. No cocatalyst was used as the comonomer itself was found to act as a cocatalyst.

Hakkala et al [173] carried the copolymerization of various long chain amide and amine functional alkenes with ethylene and propylene using *rac* $Et(Ind)_2ZrCl_2$ and *rac* $(CH_3)_2Si(2\text{-MeInd})_2ZrCl_2$/MAO catalysts. The maximum comonomer incorporation was 1.3 and 0.9 mol% with ethylene and propylene respectively.



Scheme-1.37 Synthesis of amino functionalized branched poly(ethylene)

1.4.3 Post polymerization functionalization

The most suitable way for the synthesis of functional groups is by the copolymerization with precursor monomer, which can be later converted into functional groups. Such functionalization reactions result in poly(olefin)s having pendant functional groups.

Synthesis of polyolefins having pendant functional groups

In this method, three types of precursor monomers are reported in the literature, namely dienes, ω-borane-α-olefins and para-methyl styrene which can be effectively used for the synthesis of functional polyolefins. Copolymerization with such precursor monomers result in copolymers having pendant double bonds, borane moiety and p-methylstyrene respectively, which can be later functionalized.

Synthesis of functional polyolefins by post polymerization functionalization of pendant double bonds

One of the emerging areas in metallocene based polymerizations is the copolymerization of olefins with dienes. Such copolymerizations using conventional Ziegler-Natta catalysts are limited by the low reactivity of the diene and unwanted side reactions. Higher incorporation of diene and regiospecificity are some of the highlights of copolymerization using metallocene catalysts. Copolymerization of olefins with dienes achieves either of the following two objectives.

(1) The synthesis of copolymers which are not accessible by direct copolymerizations. For instance, introduction of cyclopentane rings onto poly(olefin) backbone by direct copolymerization is difficult due to the lack or low reactivity of cyclopentene, but can be easily achieved by copolymerization with 1,3-butadiene or 1,5-hexadiene.

(2) The synthesis of functional poly(olefin)s, where the pendant double bonds in the copolymer are converted into functional groups by standard organic chemical reactions. These functional groups can act as potential 'active sites' for the synthesis of graft copolymers.

Another field where dienes are used is in the synthesis of ethylene/propylene elastomers where small amount of diene is added to get a terpolymer, popularly known as EPDM rubber. The pendant double bonds are used for crosslinking while processing.

But copolymerization with dienes is complicated by the occurrence of crosslinking reaction, particularly, if the diene is a symmetrical one.

1.4.3.1 Copolymerization with symmetrical dienes

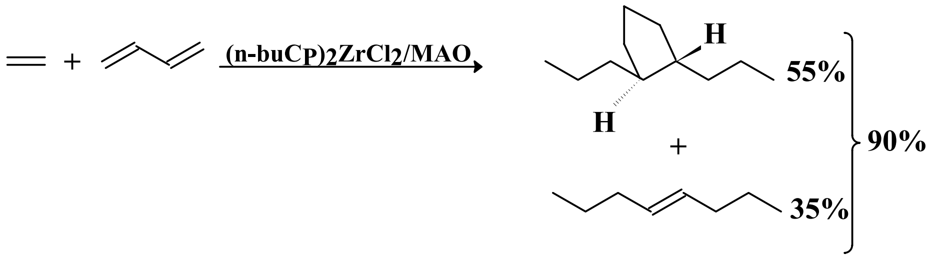
Copolymerization of olefins with symmetrical dienes usually results in copolymers having novel structures. The pendant double bond on the polymer chain formed after the insertion of one of the equally reactive double bonds of the diene gets enchained in the same polymer, generating cyclic structure on the polymer backbone. Such polymerizations are generally termed as *cyclopolymeriztion*.

In ethylene/1,3-butadiene copolymerization, comonomer can undergo enchainment either by cis 1,4, trans 1,4 or by 1,2 insertion due to the conjugated nature of the double bonds. Over 55 % of the butadiene incorporated in the copolymer synthesized with $(n\text{-}buCp)_2ZrCl_2$/MAO catalyst system was found to have undergone cyclopolymerization [174] (**Scheme-1.38)**, With $Et(indH_4)_2ZrCl_2$, enchainment was found to occur exclusively in 1,4-trans configuration with around 50 % as trans cyclopentane rings [175,176]. No cis 1,4 and 1,2 insertion products could be detected by ^{13}C NMR or IR. Such copolymers have a cluster index value of about 5 [174]. Cluster index, which indicates the randomness in which the comonomer is distributed in the copolymer, is defined by the equation,

$$\text{Cluster index} = 10 \times \frac{(X) - (EXE)}{2(X)^2 - (X)^3}$$

Where X is the mol % of comonomer and EXE is the triad sequence. A cluster index value of zero means completely isolated comonomer insertion and a value of 10 means exactly random (Bernoullian) and, thus, containing a predictable amount of continuous comonomer sequences.

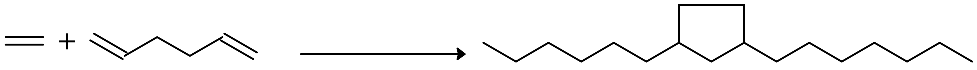
Copolymerization of ethylene with 1,5-hexadiene was reported to occur through cyclopolymerization resulting in cyclopentane units along the polymer backbone [177] **(Scheme-1.39).** However, the cyclopolymerization can be reduced to larger extent by using higher dienes like 1,9-decadiene [178].



trans 1,4 insertion products

Tm = 115^{0}C
Mw = 152.6x10^3
MWD = 4.7
cluster index = 5.0

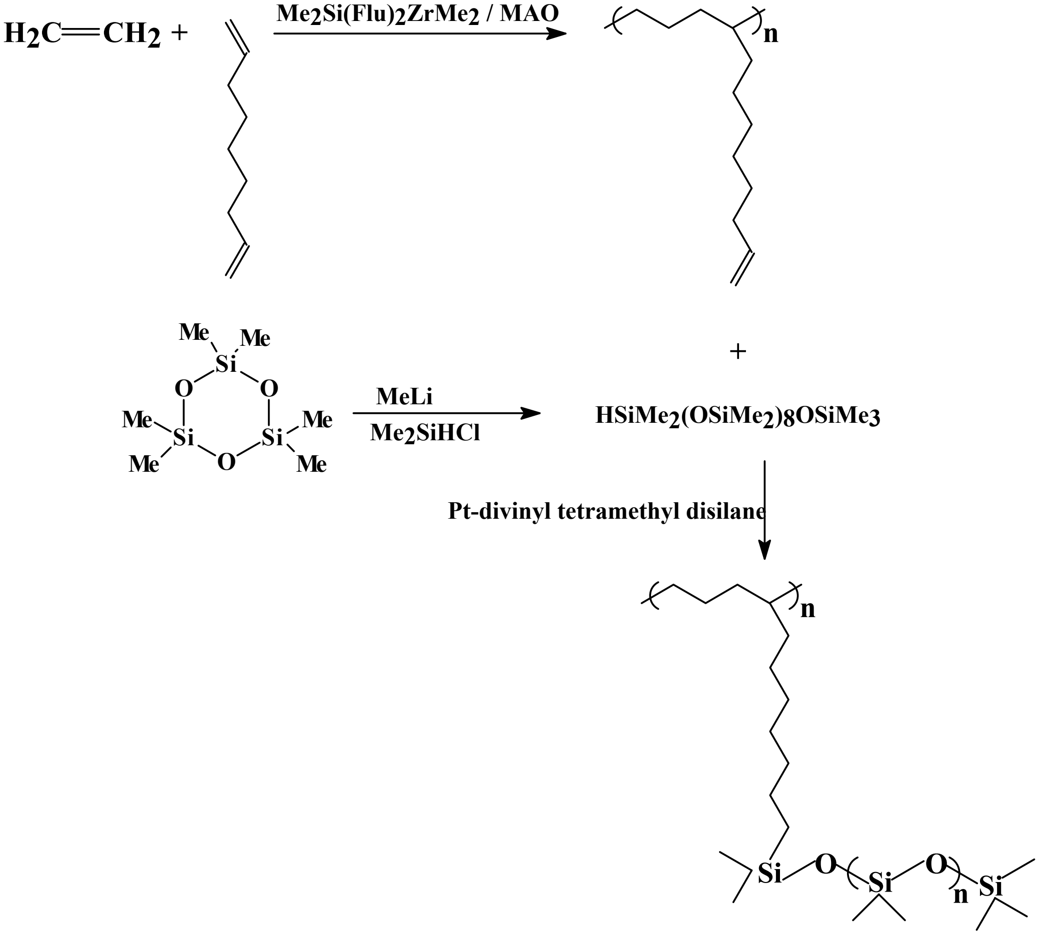
Scheme-1.38 Copolymerization of ethylene with 1,3-butadiene



10 mol% comonomer
Mw = 120x10^3
MWD = 2.6
Tm = 103.6^{0}C

Scheme-1.39 Copolymerizaton of ethylene with 1,5-hexadiene

Recently Soga et al [179] reported the alternating copolymerization of ethylene and 1,9-decadiene using $Me_2Si(Flu)_2ZrMe_2$-MAO catalyst (which was reported to produce alternating copolymers of ethylene with 1-decene) **(scheme-1.40)**. It was presumed that the side reactions such as cyclization and crosslinking could be completely suppressed due to the consecutive insertion of vinyl double bonds in diene. Characterization of the parent copolymer by NMR showed 98.2% of [ED] dyad fraction and a Tg of -66^{0}C which is comparable to poly(ethylene-alt-1-decene).

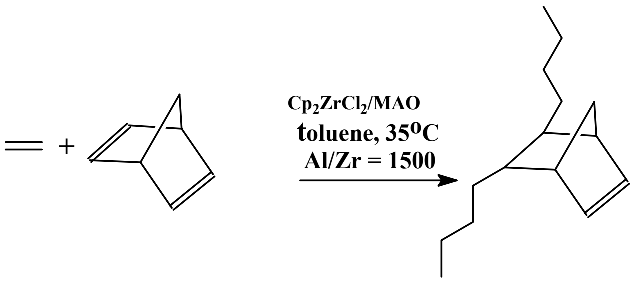


Scheme-1.40 Alternating copolymerization of ethylene and 1,9-decadiene

The resulting pendant double bond was quantitatively hydrosilylated using polysiloxanes to yield graft copolymers. The graft copolymers were found to be soluble in common organic solvents like hexane, chloroform etc. The quantitative grafting was evidenced by increase in molecular weight (Mw).

Copolymerization of ethylene with bicyclic dienes

Symmetrical bicyclic dienes have an added advantage over linear symmetrical dienes that the cyclopolymerization could be avoided due to their high rigid structure. In our laboratory, we have studied the copolymerization of ethylene with a symmetrical diene namely 2,5-norbornadiene (NBD) using various metallocene/MAO catalysts [180]. It was found that the copolymerization occurs exclusively through one of the equally reactive endocyclic double bonds for unbridged as well as ethylene bridged catalysts **(scheme-1.41)**. However, crosslinking occurs during copolymerization with dimethylsilylene bridged catalyst, probably due to the higher coordination angle along the Zr-Cl vector of the metallocene [181].



Scheme-1.41 Synthesis of olefin functionalized Poly(ethylene)

Recently Simanke et al reported the copolymerization of ethylene with 1,3-cyclopentadiene and dicyclopentadiene using *rac* Et(Ind)$_2$ZrCl$_2$/MAO catalyst [182]. Dicylopentadiene has shown higher activities than cyclopentadiene under similar conditions. 1,3-Cyclopentadiene dimerized during copolymerization, consequently resulted in a terpolymer of ethylene, cyclopentadiene and dicyclopentadiene.

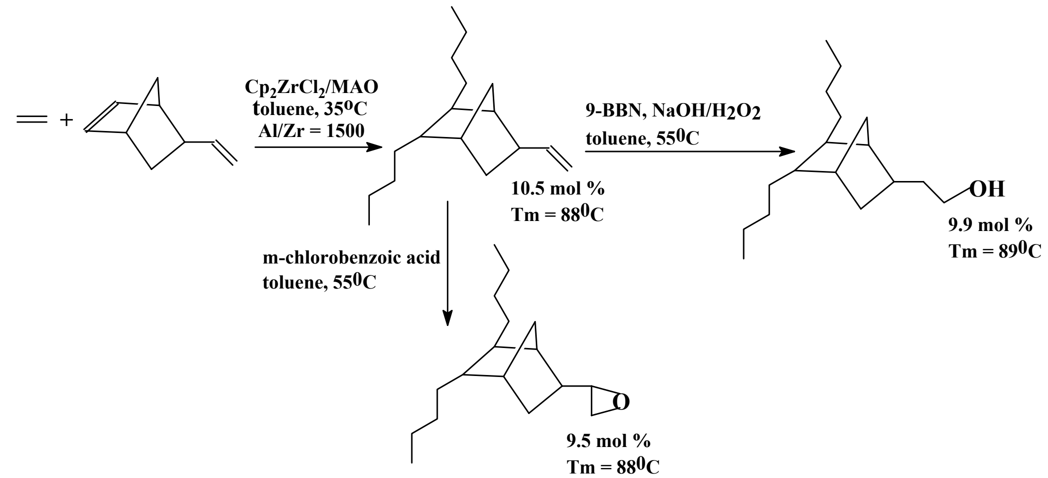
1.4.3.2 Copolymerization with unsymmetrical dienes

Copolymerization of olefins with unsymmetrical dienes, where one of the double bonds is more reactive than the other gives poly(olefin)s having pendant double bonds which can later be functionalized. Copolymerization of ethylene with 4-vinyl cyclohexene using Ph$_2$C(Cp)(Flu)ZrCl$_2$/MAO catalyst has been found to occur regiospecifically through the vinyl double bond [183]. The pendant cyclohexenyl double bonds were functionalized to hydroxyl groups. Introduction of hydroxyl groups increased the Tm while reduced the Tg, which was attributed due to hydrogen bond interaction.

Hackman et al [184] studied the polymerization behavior of three linear asymmetrically substituted dienes namely 6-phenyl-1,5-hexadiene (PHD), 7-methyl-1,6-octadiene (MOD), and *R*(+)-5,7-dimethyl-1,6-octadiene (isocitronellene) using *rac* Et(Ind)$_2$ZrCl$_2$/MAO catalyst. No polymerization was found to occur with PHD, where as MOD and isocitronellene polymerized with catalyst activities of 2.3 and 8.6 Kg poly/mol Zr/h respectively. The copolymerization of isocitronellene with propylene showed 15.6 mol% of diene incorporation, which is equal to the stoichiometric ratio of the monomers in the feed.

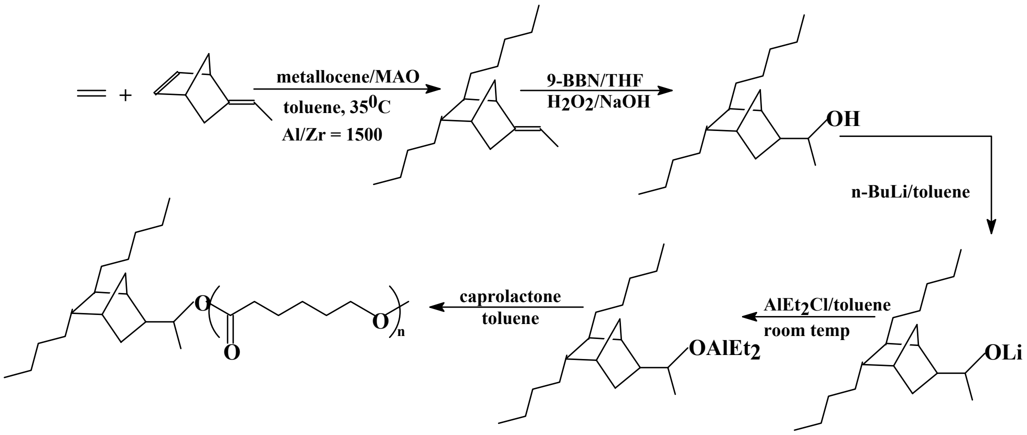
The isocitronellene homo and copolymers were epoxidized quantitatively and brominated to an extent of 90%. Perfluorohexyl iodide was grafted onto the isocitronellene/propene copolymer by free radical reaction (conversion 80%), yielding a polyolefin with fluorinated side chains. Recently Bochmann et al reported a variety of functionalization on pendant double bonds present in poly(propene-co-7-methyl-1,6-octadiene) namely epoxidation, ozonolysis etc. Quantitative functionalization was evidenced by NMR [185].

Copolymerization of ethylene with 5-vinyl-2-norbornene has been reported to occur regiospecifically through the endocyclic double bond [186] leaving the exocyclic vinyl double bond for post polymerization functionalization **(scheme-1.42).** These pendant groups have been quantitatively functionalized to epoxy and hydroxyl groups.



Scheme-1.42 Copoymerization of ethylene with 5-vinyl -2-norbornene and its post polymerization functionalization

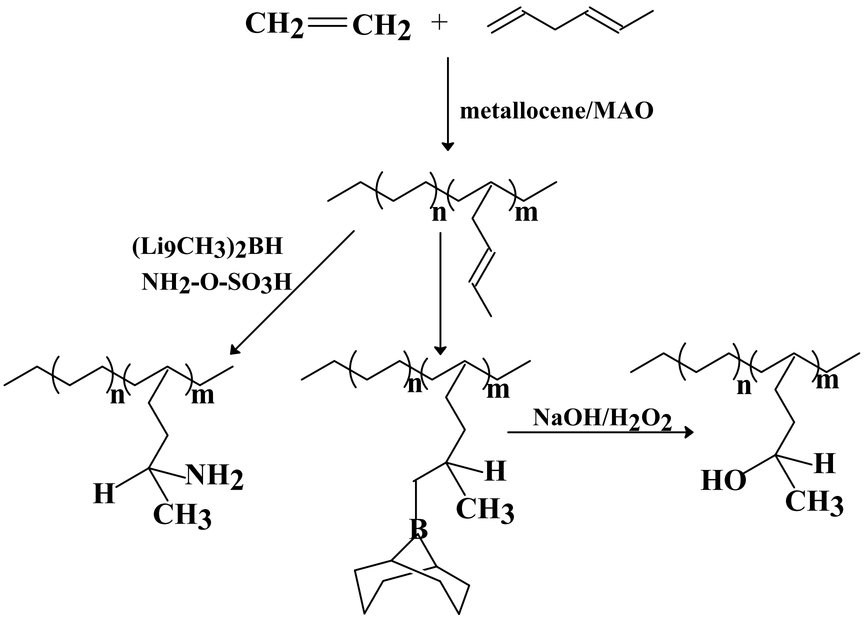
Wang et al [201] reported regiospecific copolymerization of ethylene with 5-ethylidene-2-norbornene using Cp_2ZrCl_2 and $Et(Ind)_2ZrCl_2$/MAO catalysts. The pendant ethylidene double bond (2.25 mol% diene incorporation) was readily converted to hydroxy group which in turn utilized for the graft copolymer preparation **(scheme-1.43).**



Scheme-1.43 synthesis of poly(ethylene)-graft-poly(caprolactone)

Shiono et al [187] studied the copolymerization of ethylene with *endo*-dicyclopentadiene using Cp_2ZrCl_2, $Et(Ind)_2ZrCl_2$ and $Ph_2C(Cp)(Flu)ZrCl_2$/MAO catalysts. The enchainment was found to occur through norbornene double bond. $Et(Ind)_2ZrCl_2$ has shown the best performance for copolymerization with 13.2 mol% comonomer incorporation. The pendant double bond in the copolymer was then epoxidized by reacting with *m*-chlorobenzoic acid. The quantitative conversion of double bond to epoxy group was found from NMR.

Copolymerization of ethylene with an unsymmetrical diene, namely 1,4 hexadiene has also been reported [188]. The pendant double bond was then hydroborated followed by chemical reaction on boron to give various functional groups **(scheme-1.44).**

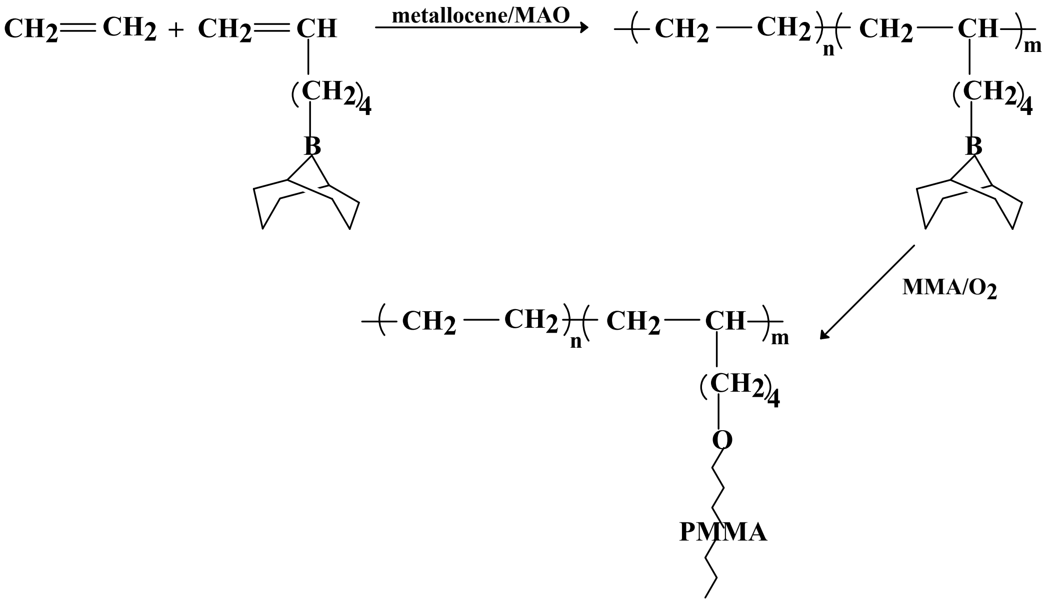


Scheme-1.44 Copolymerization of ethylene with 1,4 hexadiene and post polymerization functionalization of pendant double bonds

1.4.3.3 Synthesis of functional polyolefins by post polymerization functionalization of copolymers having borane pendant group

Poly(olefin)s having borane pendant groups [189-194] can also be prepared by copolymerizing olefins with ω-borane-α-olefins. Though poor comonomer incorporation was observed for ethylene/5-hexenyl-9-BBN copolymerization with Cp_2ZrCl_2, with the bridged metallocene, $Et(ind)_2ZrCl_2$ higher incorporation was reported.

Taking the advantage of borane chemistry functionalities other than hydroxy such as amines, aldehydes, halogens, and cyanides can also be accomplished (**scheme-1.45**).

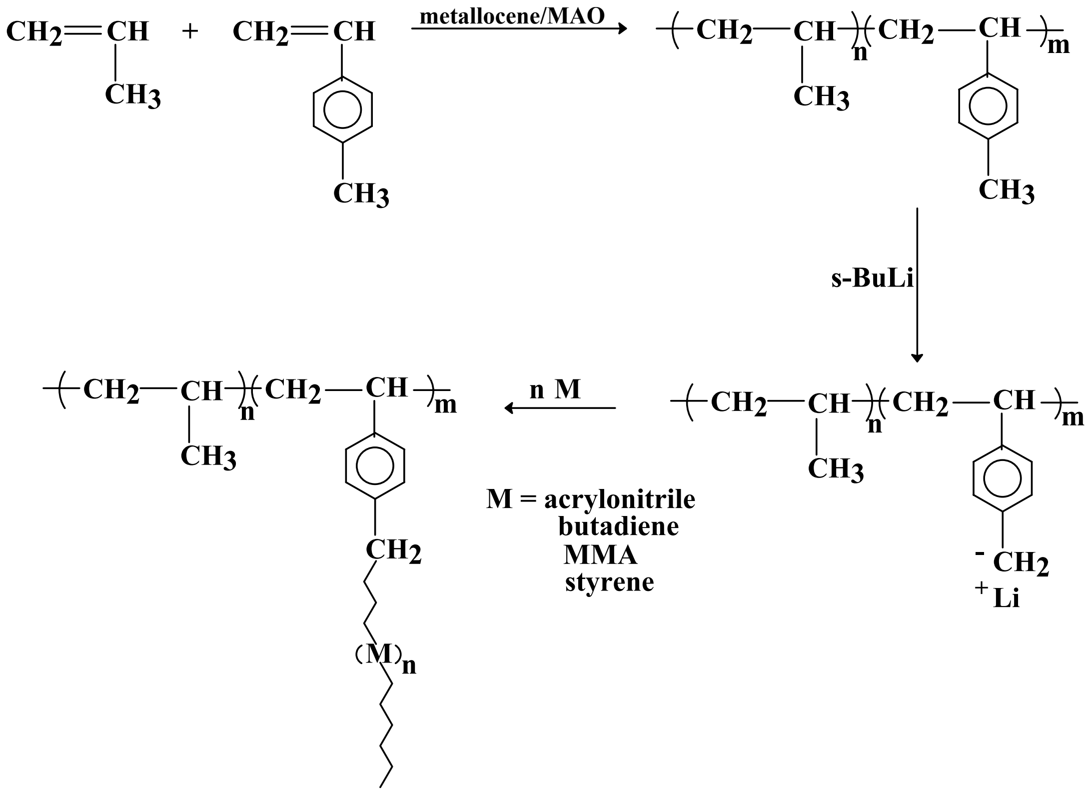


Scheme-1.45 Synthesis of functional polyolefins by post polymerization functionalization of copolymers having borane pendant group

1.4.3.4 Copolymerization of olefins with p-methyl styrene

This method enables introduction of a variety of functional groups in to poly(olefin) back bone. The chemistry involves the copolymerization of an olefin with reactive p-methyl styrene using metallocene catalysts and its post polymerization functionalization [195-199]. The benzylic protons in p-methyl group are known to be facile for many organic reactions such as halogenation, metallation, oxidation etc and can also be converted to stable anionic initiator for 'living' anionic graft from polymerization **(scheme-1.46).**

The copolymers obtained are random in nature with a broad composition range and narrow molecular weight distribution. Thus, the incorporated p-methylstyrene units in poly(olefin)s were converted to various functional groups, such as -OH, -NH_2, -COOH, anhydride, silane and halides, or transformed to stable anionic initiators for living anionic 'graft-from' polymerization reactions. Poly(olefin) graft copolymers were prepared containing poly(olefin) backbone poly(ethylene), poly(ethylene-co-propylne), poly(ethylene-co-1-octene), etc. with functional polymer side chains, such as PMMA, PAN, PS, etc.

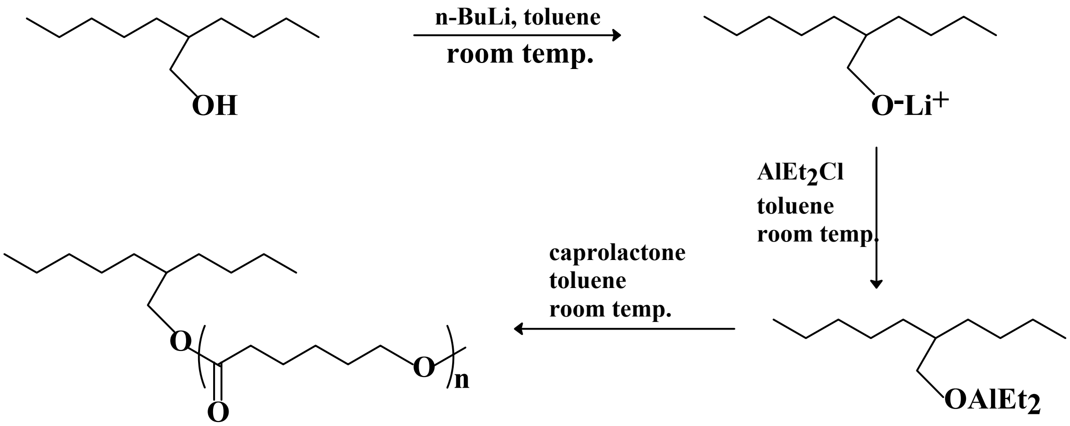


Scheme-1.46 Synthesis poly(olefin) graft copolymers by p-methylstyrene approach

Graft copolymer preparation

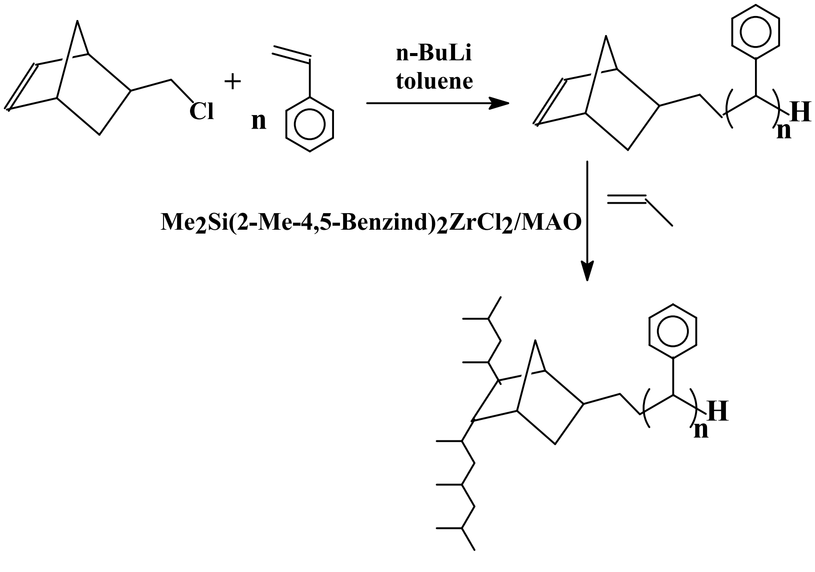
There are two different approaches for the synthesis of graft copolymers. In one method, the functional groups on the polymer backbone act as the initiator for the polymerization of another monomer. This method is generally referred to as 'graft from' method. The other method, 'graft onto' method, involves the termination of a growing polymer chain end by the functional group on the polymer backbone or by the coupling between the polymer having the end functional group with the pendant functional group on the polymer backbone.

Synthesis of graft copolymers of polyethylene and poly(caprolactone) have been reported using copolymers containing pendant hydroxyl groups **(Scheme-1.47).** The copolymers used for grafting were prepared either by direct copolymerization with functional monomer [200] or by post polymerization conversion of the pendant double bonds [201] (**see in scheme-1.43**).



Scheme-1.47 Synthesis of poly(ethylene)-g-polycaprolactone

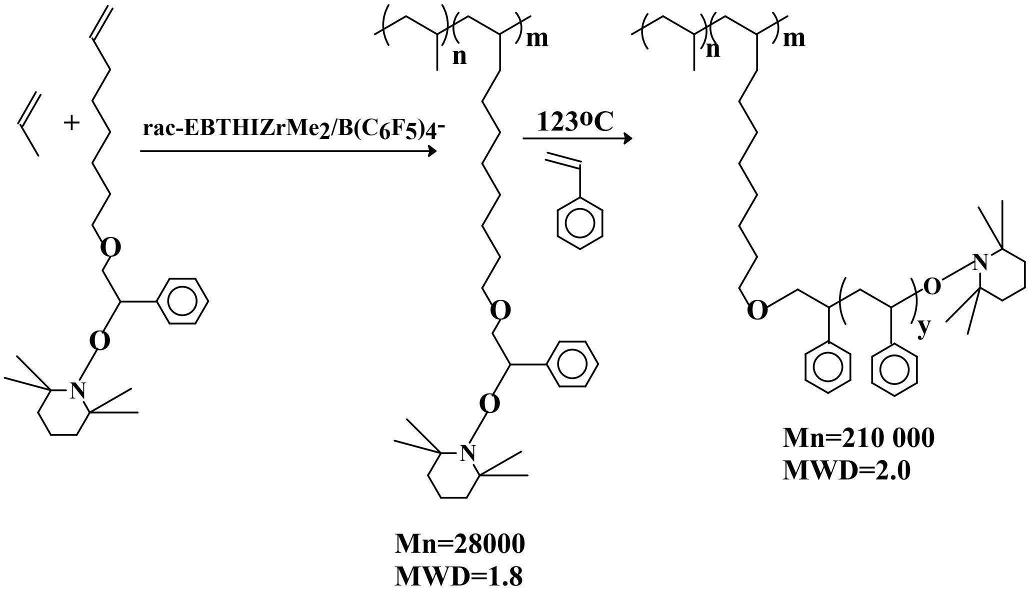
Poly(propylene) graft copolymers were also prepared by macromonomer method. Norbornenyl terminated poly(styrene) macromonomer prepared by anionic polymerization (Mw = 800-18500, MWD = 1.03-1.1) and vinyl terminated poly(isobutylene) macromonomer (Mw = 2500-10000, MWD = 1.09-1.2)) prepared by living carbocationic polymerization of isobutylene were copolymerized with propylene using $Me_2Si(2\text{-}Me\text{-}4,5\text{-}Benzind)_2ZrCl_2/MAO$ catalyst to give poly(propylene)-g-poly(styrene) and poly(propylene)-g-poly(isobutylene) respectively [202] **(scheme-1.48).**



Scheme-1.48 Synthesis of poly(propylene)-g-poly(styrene) copolymer by macromonomer method

The maximum incorporation of macromonomer was 69 wt% and 13.5 wt% for poly(styrene) and poly(isobutylene) respectively. The characterization of graft copolymers by GPC did not show presence of any macromonomer impurity in copolymers. Poly(propylene)-g-poly(styrene) copolymer showed good compatibilizing effect in isotactic poly(propylene) and atactic poly(styrene) blends.

Graft copolymers were also prepared by combination of metallocene and living free radical polymerization technique [203]. Propylene was copolymerized with vinyl monomer bearing alkoxyamine using rac Et(THI)$ZrMe_2/B(C_6F_5)_4^-$ catalyst. The alkoxyamine group present as pendant group was utilized as a living free radical initiator for styrene to give poly(propylene)-g-poly(styrene) with Mn 210 000 (**scheme-1.49**).

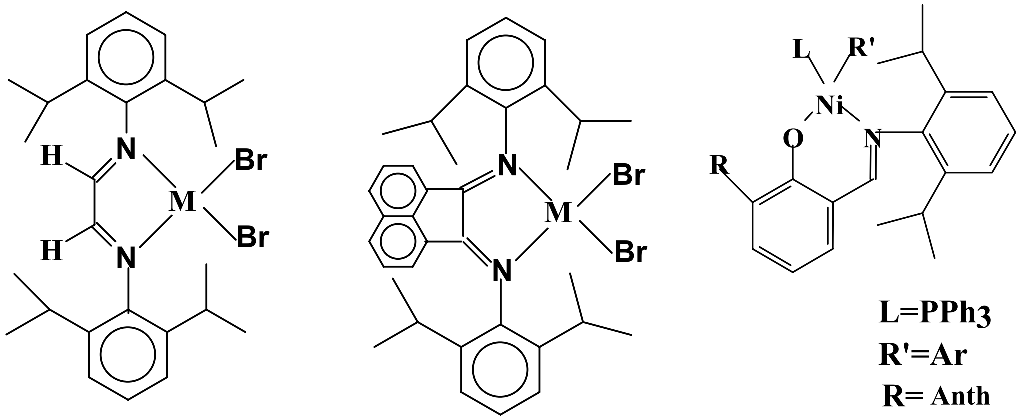


Scheme-1.49 Synthesis of poly(propylene)-g-poly(styrene) copolymer

The grafting efficiency was verified by cleaving the individual poly(styrene) graft from the poly(olefin) backbone by reacting the graft copolymer with trimethylsilyl iodide. The molecular weights of individual poly(styrene)grafts (MWD=1.1) were in good agreement with the theoretical values (molar ratio of styrene to initiator). Poly(butadiene) grafted poly(ethylene-co-butene) copolymers were also reported by the above living free radical polymerization technique [204].

1.4.4 Functional poly(olefin)s using 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 [205-210]. These metals generally prefer β-hydride elimination followed by reductive elimination. Brookhart and coworkers discovered a new family of catalysts based on Ni(II) and Pd(II) containing sterically hindered diimine ligands which were efficient for olefin polymerizations [211]. 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 (**scheme-1.50**).



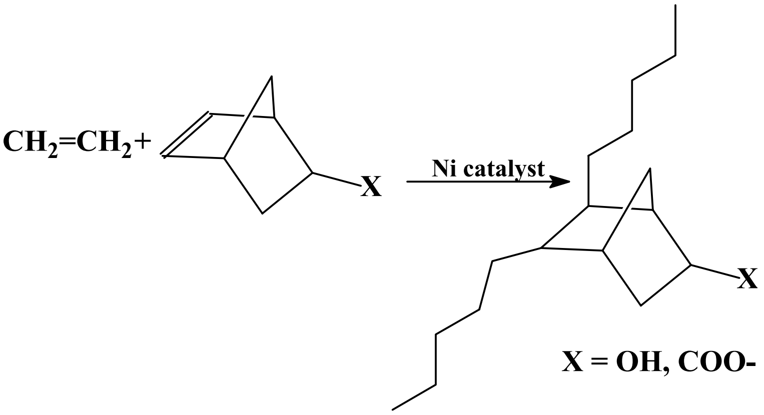
M = Ni, Pd

Complex-a **Complex-b** **Complex-c**

Scheme-1.50 Late transition metal catalysts for olefin polymerization

Klabunde and Ittel [208] first reported the copolymerization of ethylene with a variety of functional monomers using Ni complexes containing phosphorus-oxygen chelating ligands. Even though vinyl acetate and methyl methacrylate did not undergo copolymerization, but copolymers could be obtained if the functional group and vinyl double bonds were separated by at least two methylene spacers in the polar monomer.

Recently Grubbs et al [212, 213] reported the use of neutral salicylaldiimine Ni complexes **(complex-c)** for copolymerization of ethylene with functionalized norbornene monomers. The maximum comonomer incorporation was 22 and 12 wt% for NB-OH and NB-COOH respectively (**scheme-1.51**).



Scheme-1.51 Copolymerization of ethylene with functionalized norbornene using Ni catalyst

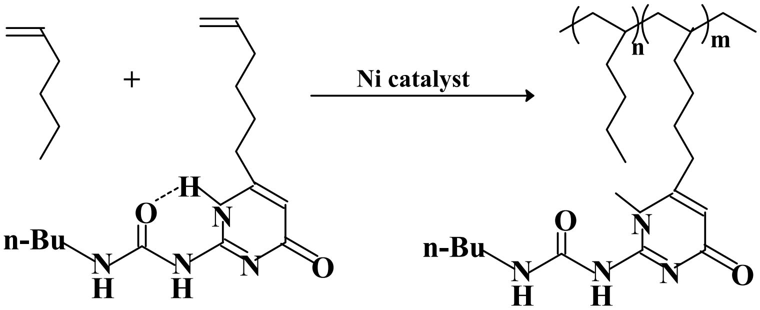
The copolymerization reactions were conducted in the presence of various polar additives at a level of 1500 equivalent per metal. Based on the decrease in molecular weight and catalyst turn over numbers has displayed that the catalyst is tolerant to various functional groups in the following order.

Ethers > ketones > esters > water > alcohols > tertiary amines.

Recently Carlini et al reported the synthesis of ethylene-methylmethacrylate copolymers using bis(salicylaldiimine) Ni(II) complexes [214].

In a series of publications Chein et al studied the copolymerization of ethylene and terpolymerization of ethylene and propylene with a variety of functional monomers using Ni(II) diimine catalyst (**complex-b**) activated by MAO. The functional monomers studied include 5-hexen-1-ol, 10-undecen-1-ol, 10-undecen-1-oic acid [215, 219], acrylamide [216], caprolactam, tetrahydrofuran [217], vinyl acetate, methyl methacrylate, acrylonitrile and methyl vinyl ketone [218]. The functional monomers were protected with various aluminum alkyls. Trimethyl aluminum was found to be a better protecting group for alkenols, alkenoic acid and tetrahydrofuran, where as tri-isobutylaluminum was preferred for acrylamide, caprolactam, MMA, etc.

Recently Coates et al [220] reported the copolymerization of 1-hexene with the functional monomer bearing 2-ureido-4[1*H*]-pyrimidinone derivative **(scheme-1.52)** using Ni(II) catalyst **(complex-b).** Diethyl aluminum chloride was an activator of catalyst as well as a protecting group for the functional group.



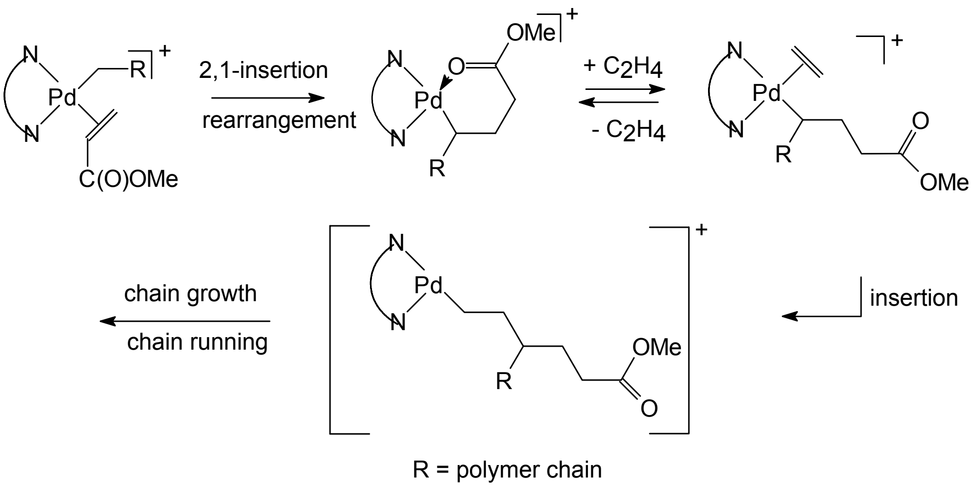
Scheme-1.52 Copolymerization of 1-hexene with the functional monomer bearing 2-ureido-4[1*H*]-pyrimidinone derivative

The maximum comonomer incorporation was 2 mol% under the employed reaction conditions. The pendant 2-ureido-4[1*H*]-pyrimidinone groups dimerize through intermolecular hydrogen bonding to form a reversible network as evidenced by viscosity studies. The viscosity of poly(1-hexene) solution in toluene is found to increase linearly with concentration, whereas for the above copolymer the viscosity an exponential increase with concentration. This was attributed to the increase in effective molecular weight through hydrogen bonding at higher concentration. Formation of gel was found at higher concentration of the copolymer solution.

The α,β-diimine Pd catalysts **(complex-b)** were reported to copolymerize ethylene with acrylic monomers and methyl vinyl ketone with modest comonomer incorporation [221-227]. The copolymers are highly branched, and the acrylate comonomer being incorporated predominantly at the ends of the branches as -CH_2CH_2COOMe groups. The NMR studies and the structure of the copolymers supported the mechanism described in **scheme-1.53.**

Brookhart et al reported the synthesis of poly(n-butyl acrylate)-g-branched poly(ethylene) by combining Pd mediated living polymerization of ethylene with atom transfer radical polymerization [228]. Methacrylate terminated branched poly(ethylene) macromonomer (Mn 10000 – 15000) was prepared by living polymerization of ethylene using Pd catalyst **(complex b)**. The macromonomer was then copolymerized with n-butylacrylate by ATRP using CuBr catalyst.

Copolymerization of ethylene and ω-unsaturated fatty acid methyl esters with chain length of C_6-C_{14} was also reported using Pd catalyst [225].



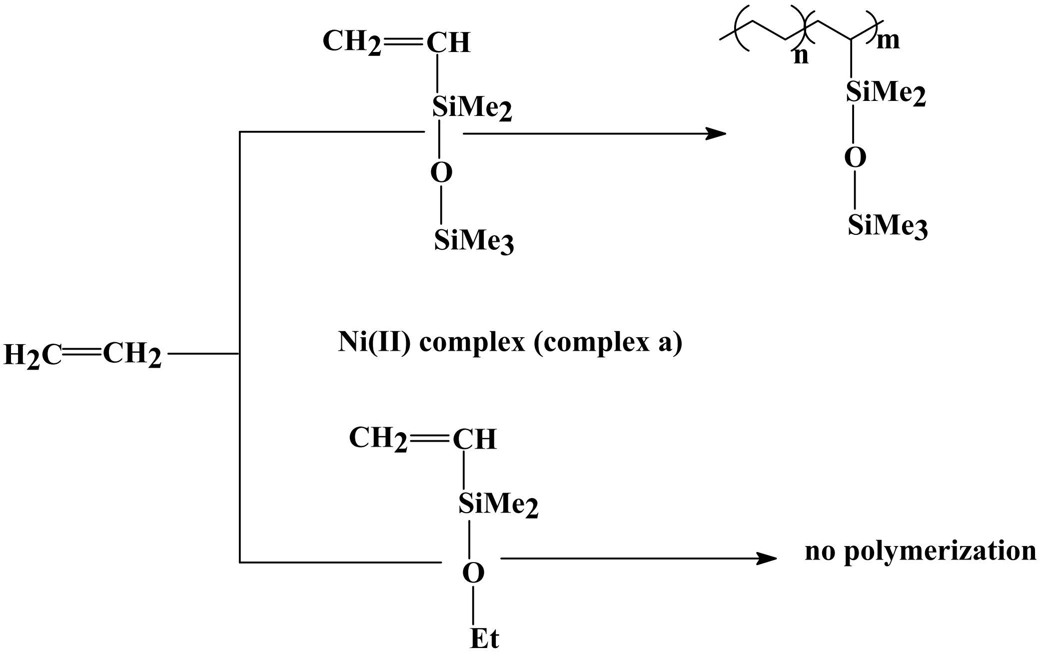
Scheme-1.53 copolymerization of ethylene with methyl methacrylate using Pd complex

Recently Goddard et al tried to copolymerize vinyl chloride and vinyl acetate with ethylene using Gibson's Fe(II) catalyst[229]. However, they found that the insertion with the either monomer leads to termination via β-elimination.

The efficacy of organolanthanide(III) complexes for the polymerization of olefins as well as polar monomers like methyl methacrylate, though by entirely different mechanisms, have been effectively used for the synthesis of poly(ethylene)-b-poly(methyl methacrylate) copolymers [230]. The reverse addition of monomers, namely MMA followed by ethylene, resulted in homopolymerization of MMA only. The initial rate of ethylene polymerization was very rapid (completed in 2 min) compared to the subsequent methyl methacrylate polymerization (completed in 2 h). The relative molar ratio of poly(ethylene) to poly(methyl meyhacrylate) can be controlled in the range 100:1 to 100: 100 at a fixed Mn for poly(ethylene) (10,000). However the block length of methyl meyhacrylate is limited when Mn of poly(ethylene) exceeds 10,000. It was attributed to the diffusion limitation of methyl meyhacrylate through the partially crystallized poly(ethylene) matrix. Such limitations can be avoided by utilizing an amorphous poly(olefin) like poly(1-hexene) as poly(olefin) block.[231].

Recently Hou et al reported a novel one step block copolymerization of ethylene with styrene [232] using lanthanide initiators. The copolymers prepared under the employed conditions were found to be true block copolymers with Mw varying from 131,000 to 190,000.

The copolymerization of ethylene with various silicon containing monomers namely vinyltrimethylsilane (VTMS), allyltrimethylsilane (ATMS), trimethylsilyloxydimethylvinylsilane, and vinylethoxydimethylsilane using Ni(II) catalysts (**complexes a and b**) [149] have been studied in our laboratory **(scheme-54)**. Like metallocenes, Ni(diimine) catalysts are also active for the copolymerization of ethylene with VTMS and ATMS (**see scheme-34**). However, these catalysts are also found active when trimethylsilyloxydimethylvinylsilane was used as the comonomer. No polymerization occurred when vinylethoxydimethylsilane was used as the comonomer. This was attributed to the close proximity of the oxygen atom to the olefinic bond and the lack of steric protection.



Scheme-54 Copolymerization of ethylene with silicon containing monomers

Recently Philipp et al studied chain propagation steps in polar monomers with Pd-diimine catalyst using density functional theory (DFT) [233]. Insertion of four polar monomers namely methyl acrylate, vinyl acetate, vinyl chloride and acrylonitrile onto the Pd-C bond (complex formed from insertion of ethylene) were studied both in gas phase as well as considering the solvation effects. Results show that polar olefins form weaker π-complexes and have larger insertion barriers. Even if it is possible to make an initial insertion, the simulations predict that subsequent insertions are prohibited. Methyl acrylate and vinyl acetate insertions lead to products with strong interactions between carbonyl oxygen and metal and are in agreement with the experiments by Brookhart and coworkers. Insertion of vinyl chloride leads to a product in which the chloride prefers to dissociate onto the metal, thus poisoning the catalyst. Acrylonitrile forms such a strong σ-complex that no further insertions occur. Results show that during polymerization of polar monomers the polar end binds strongly to the metal resulting in large barriers for subsequent monomer insertions.

1.5 Conclusions

Functional poly(olefin)s have come to occupy an important place amongst the family of functional oligomers and polymers for a diverse variety of end use applications. Enabling chemistry is the key to the design and synthesis of functional poly(olefin)s. The emergence of new catalysts and activators have substantially enlarged the scope of new synthetic methods. Oligomers with relatively narrow polydispersities with high degrees of functionalizations have been prepared. Nevertheless, many challenges still remain. The range of molecular weights of functional poly(olefin)s is limited by the poor solubility of such polymers in most solvents at reasonable temperatures. Precise analytical methods for estimating chain end functional group concentration are yet unavailable. Monodisperse poly(olefin)s with precisely defined chain ends are still rare by direct catalytic polymerization of olefins. Transformation of chain ends of metal catalyzed polymerizations (carbon to metal bonds) to other types of chain ends (anionic), which can be more easily functionalized is still not very easy.

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Chapter 2. Scope and objectives

2.1 Introduction

Functional poly(olefin)s have assumed importance because they contribute to new properties to an otherwise inert poly(olefin)s [1-5]. Appropriately functionalized poly(olefin)s are useful as adhesion promoters and are capable of being coated, painted or dyed. Additionally, the functional groups either on the polyolefin backbone or at the chain end can be used for the synthesis of graft and block copolymers, which find application as compatibilizers and interfacial agents.

There are two broad approaches to the synthesis of functional poly(olefin)s, namely, "*chain end*" functionalization and "*in chain*" functionalization**.** Synthesis of functional poly(olefin)s by the first method involves either chemical reactions on preformed terminally unsaturated poly(olefin)s or through use of appropriate chain transfer agents, whereas, the second approach involves the copolymerization of olefins with precursors which do not interfere in polymerization followed by chemical transformations on the preformed polymers.

Functionalization of poly(olefin)s especially, poly(propylene), poly(ethylene) and poly(ethylene-co-propylene) has been extensively investigated using melt phase free radical grafting. This involves activation of the C-H bond on the backbone by shear in presence of free radical initiators or high energy radiation which creates carbon radical sites on the polymer backbone for reaction with acrylic monomers, maleic anhydride etc. Ionizing radiation such as X-rays, γ-rays and e-beams in the presence of air, ozone and UV radiation along with accelerators and free radical initiators (generally organic peroxides) are commonly employed for free radical grafting [6]. However melt phase free radical grafting is usually accompanied by several side reactions such as cross-linking and degradation of the polymer.

Synthesis of functional poly(olefin)s using conventional Ziegler-Natta catalysts have been extensively studied [7-10]. The direct copolymerization of olefins with functional monomers has not been successful due to the incompatibility of the Ziegler-Natta catalysts towards polar functionalities as well as heteroatoms present in the functional monomers.

Metallocene and post metallocene catalysts offer significant advantages for the synthesis of functional poly(olefin)s. When olefins are polymerized using homogeneous metallocene / MAO (methyl aluminoxane) catalysts, several chain transfer reactions (such as β-hydrogen transfer etc) are found to occur. Such chain transfer reactions results in terminally unsaturated poly(olefin)s. High degree of terminal unsaturation(> 95%) and narrow molecular weight distribution (MWD = 2) are some of the distinguishing features of poly(olefin)s obtained using metallocene catalysts. There are several reports in the literature, which define synthetic strategies for poly(olefin)s bearing various terminal functional groups such as OH, COOH and NH_2 etc by utilizing the terminally unsaturated poly(olefins) [11-19].

Copolymerization of olefins with dienes can be achieved with ease using metallocene catalysts [20-27]. Such copolymerizations are difficult to accomplish with conventional Ziegler-Natta catalysts in view the low reactivity of the dienes and unwanted side reactions such as cyclo polymerization and crosslinking. Dienes can be copolymerized with olefins with high regio specificity using metallocenes. Copolymerization of olefins with dienes results in poly(olefin)s with pendant double bonds, which can be further converted to functional groups by chemical reactions. Pendant unsaturation can also act as potential 'active sites' for the synthesis of graft copolymers.

2.2 Objectives of the present work

The objectives of the present work was to explore the capabilities of metallocene based catalysts for the synthesis of functional poly(olefin)s. Two methods, namely, synthesis of terminally unsaturated poly(α-olefin)s by exploiting the chain transfer reactions in metallocene catalyzed polymerization and copolymerization of α-olefins with dienes, were examined.

The first approach involved the introduction of functional groups on poly(olefin) chain end by post polymerization functionalization of terminally unsaturated poly(olefin)s. Terminally unsaturated poly(olefin)s were obtained by exploiting the chain transfer reactions in metallocene catalyzed polymerization of olefins.

The second approach involved the introduction of pendant double bonds in the copolymer by the copolymerization of olefin with a diene, where, only one of the double bonds participates in the polymerization leaving the other double bond intact as a pendant group. A study of the effect of various metallocenes on microstructure of copolymer was also undertaken.

2.3 Approaches

In the first method, a higher α-olefin namely hexene-1 was chosen as a model monomer. The objective was to combine the ease of handling a liquid monomer and the ability to measure the reaction rates. Bulk polymerization of hexene-1 using Cp_2ZrCl_2/MAO catalyst results in vinylidene terminated poly(hexene-1) via chain transfer reaction known as β-hydrogen transfer. Poly(hexene-1) with Mn varying from 500 - 15 000 was obtained with polymerization temperature (Tp) varying from -20 to 50^0C. The viscous liquid oligomers are readily soluble in common solvents like chloroform, n-hexane, toluene etc. at room temperature. Such end functionalized polymers can be utilized in a variety of transformation reactions for further functionalization.

Alkylation of phenols was carried out using vinylidene terminated poly(hexene-1) to give phenol terminated poly(hexene-1). Ritter reaction of vinylidene terminated poly(hexene-1) with various nitriles such as acrylonitrile, acetonitrile and benzonitrile using an acid catalyst gave N-poly(alkenyl)alkylamides. These chemistries were based on the ability of the terminal iso-olefin bond to participate in acid catalyzed reaction via the intermediacy of the stable tertiary carbocation.

In the second method, the objective was to synthesize a carboxylic acid functionalized copolymer. Accordingly hexene-1 was copolymerized with a symmetrical diene namely norborna-2,5-diene. The analysis of the microstructure of the copolymer and its functionalization was also studied.

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3.1 Introduction

One of the important features of the insertion mechanism for olefin polymerization is that the active metal center bearing the growing alkyl chain must have an available coordination site for the incoming monomer. It is well known that olefin insertion into metal-carbon bonds is predominantly primary. However, isolated secondary insertions (2,1 insertion or regio defects) are often detectable in metallocene-catalyzed polymerization of propylene. These regio defects play a major role in reducing crystallinity and melting point of isotactic poly(propylene).

The relative amounts of these regio defects are highly dependent on the nature of metal, ligand structure and polymerization conditions employed. However these regio defects are not well studied, possibly due to their low concentration. For example, a sequence of two secondary insertions has never been detected. In terms of regiochemistry, three propagation reactions can occur, namely, primary on primary chain end, secondary on primary chain end and primary on secondary chain end. The secondary growing chain end is relatively less reactive; however, it can be activated either by hydrogen or by copolymerizing with small amount of ethylene. The secondary growing chain end also undergoes a 3,1 isomerization to form active sites under specified reaction conditions like high temperature and low monomer concentration.

Effect of nature of metal on regio selectivity

There are only a few stereoselective and regioselective studies carried out by Ti and Hf complexes due to their lower activity. The published literature shows that *rac*-$Et(Ind)_2TiCl_2/MAO$ is both less stereoselective and regioselective compared to its Zr analogue [1-3]. However change in ligand structure also influences the regio selectivity, for eg. *rac* $Me_2Si(2\text{-}Me\text{-}4\text{-}Ph\text{-}1\text{-}Ind)_2TiCl_2/MAO$ has been reported to be more regioselective than its Zr and Hf analogues [4].

Effect of nature of cocatalyst on regio selectivity

The nature of co-catalyst does not have any role in regiospecificity. However there may be some variation in the catalyst activity [5].

Effect of nature of π-ligands on regio selectivity

The microstructure of low molecular weight atactic poly(propylene) using Cp_2ZrCl_2 catalyst has been studied in detail. No regioerrors have been detected by ^{13} C NMR [6]. This suggests that Cp_2ZrCl_2 is highly regioselective and chain propagation cannot proceed after an occasional secondary insertion. Similarly, the more active $(MeCp)_2ZrCl_2$ produces atactic poly(propylene) oligomers without detectable internal 2,1 units [7]. The propene oligomerization catalysts $(Me_5Cp)_2ZrCl_2$ and its Hf analogue are even more regioselective, since secondary units could not be detected even as chain ends. The $Me_2Si(9\text{-}Flu)_2ZrCl_2$ catalyst for high molecular weight atactic poly(propene) is of similar high regioselectivity. $(Ind)_2ZrCl_2$ and $(H_4Ind)_2ZrCl_2$/MAO catalysts, on the contrary, produce low molecular weight atactic poly(propylene) with about 1% of 3,1 units.

Both the C_s symmetric syndiospecific zirconocenes $Me_2C(Cp)(9\text{-}Flu)ZrCl_2$ and $Ph_2C(Cp)(9\text{-}Flu)_2ZrCl_2$ show no detectable 2,1 units. However, Busico was able to detect < 0.08% 2,1 units using ^{13}C enriched ethene in propene polymerization with a similar catalyst system [8].

C2-symmetric zirconocenes show the greatest variability in terms of both stereo- and regioselectivities, with total regio errors ranging from almost 0 - 20% in poly(propylene) [9-11]. Based on the experimental evidence it was concluded that, in the case of C2-symmetric zirconocenes (i) only the dimethyl-substituted bis-indenyl derivatives allow a significant degree of secondary insertions; (ii) hydrogenation of the indenyl moiety promotes a higher amount of 2,1 to 3,1 isomerization, (iii) substitution in C(2) increases regio selectivity as well as stereo selectivity; and (iv) substitution in C(3) produces highly regioselective catalysts, among the most regioselective of all metallocenes.

Effect of monomer concentration on regioselectivity

Even though the total amount of secondary insertions does not depend on monomer concentration, the chemical structure of the chain fragment generated by an isolated secondary unit does depend on both polymerization temperature and monomer concentration.

Busico [12] and Resconi [13] have shown that 2,1 to 3,1 isomerization is a unimolecular process, as the ratio of [2,1]/[3,1] follows a simple first order dependence on monomer concentration and the 2,1 units are more likely to isomerize into 3,1 propene units when the monomer concentration is lowered.

Effect of polymerization temperature on regio selectivity

The polymerization temperature is another important source of variability in the microstructure of poly(propylene) obtained from *ansa*-zirconocenes. In liquid propylene monomer, both the amount of secondary insertions and the rate of 2,1 to 3,1 isomerization increase with increasing temperature. For example, for *rac*-C_2H_4(1-Ind)$_2$$ZrCl_2$/MAO and *rac*-$C_2H_4$(4,7-$Me_2$ Ind)$_2$$ZrCl_2$/MAO, an increase in temperature from 20 and 70 °C increases the total 2,1 units (including end groups) from 0.4 to 0.7% and from 2.5 to 4.3%, respectively [14].

Polymerization of hexene-1

Polymerization of ethylene and propylene has been widely studied due to its commercial significance. The higher α-olefins, have, however, attracted less interest. Studies of polymerization and copolymerization of higher α-olefins greatly expand our understanding of the reaction mechanism and the relationship between polymer structure and properties.

Recently polymerization of higher α-olefins using metallocene and post metallocene catalysts has attracted academic interest. Amongst all the higher α-olefins, hexene-1 is well studied. Living polymerization of hexene-1 using including metallocene, non-metallocene and late transition metal catalysts is an area of significieant contemporary interest.

Polymerization of hexene-1 using metallocene/MAO: Catalysts and reaction conditions

A variety of metallocene catalysts including aspecific, stereospecific and syndio specific catalysts have been used for polymerization of hexene-1. **Table-3.1** summarizes the cited literature for polymerization of hexene-1 using various metallocene catalysts as well as microstructure analysis of poly(hexene-1).

Polymerization of hexene-1 using aspecific catalysts produces low molecular weight oligomers at higher temperatures [15-18]. However high molecular weight polymers can be produced at low temperature [19]. Microstructure analysis of the low molecular weight oligomers revealed that the major end groups are vinylidene, which arise due β-H transfer to metal.

Defflieux et al studied the kinetics of hexene-1 polymerization using *rac* $Et(Ind)_2ZrCl_2$/MAO catalyst system in several solvents [21]. Enhanced activity was observed in polar solvents compared to non-polar solvents. Chien et al reported the increase in catalyst activity with temperature using the same catalyst [22].

Chien et al studied microstructure analysis of isotactic poly(hexene-1) produced at 25, 0, -30^0C using *rac*$Et(Ind)_2Zr^+R/B(C_6F_5)_4^-$ catalyst system [23]. Internal vinylene unsaturation, which arises due to β-hydrogen transfer after 2,1 insertion, was found as the major end group at all temperatures. It was attributed to the migration of Zr^+ ion both along the polymer chain backbone and along n-butyl side groups. Hemi Isotactic poly(hexene-1) was produced by polymerization of hexene-1 using i-Pr(3-MeCp Flu)$ZrCl_2$/MAO catalyst system [27].

Recently polymerization of hexene-1 under pressure using metallocene/MAO catalyst has attracted research interest [36-40]. Maximum catalytic activity was observed at 250-500 MPa. However the activity became saturated or decreased at higher pressures. The molecular weight of the obtained poly(hexene-1) increased under elevated pressures, although increase was often smaller compared to the acceleration of catalytic activities. Poly(hexene-1) of extremely high molecular weight 1.02×10^7 (by GPC) was obtained using $(CH_3)_2Si(C_5Me_4)_2HfCl_2$ catalyst. The germylene-bridged hafnocenes exhibited four times higher activity than the silylene bridged complexes under high pressure.

The microstructure analysis of the poly(hexene-1) has shown that the ratio of vinylidene to internal vinylene end group decreased with increase in pressure. It was attributed to enhancement of bimolecular chain transfer reaction, namely, β-H transfer to monomer at higher pressure.

Living polymerization of hexene-1

Living polymerization techniques allow the synthesis of polymers with predictable molecular weight and narrow molecular weight distributions, end functionalized polymers and well defined block copolymers. Rapid chain transfer reactions in metallocene-catalyzed polymerizations restricted their use in living polymerization. However, recently there are a few reports in the literature, which describe the living polymerization of hexene-1, especially at low temperature using both metallocene and late transition metal catalysts [41-44].

Brookhart et al reported the living polymerization of hexene-1 using Ni (II) diimine catalyst activated by MAO [41]. Molecular weight Distribution as low as 1.09 was reported for poly(hexene-1) obtained at low temperature (-10^0C) and low monomer concentration (<1M). Poly(propylene -b- hexene-1) copolymer with MWD 1.12 were also synthesized by sequential addition of propylene and hexene-1 at -15^0C.

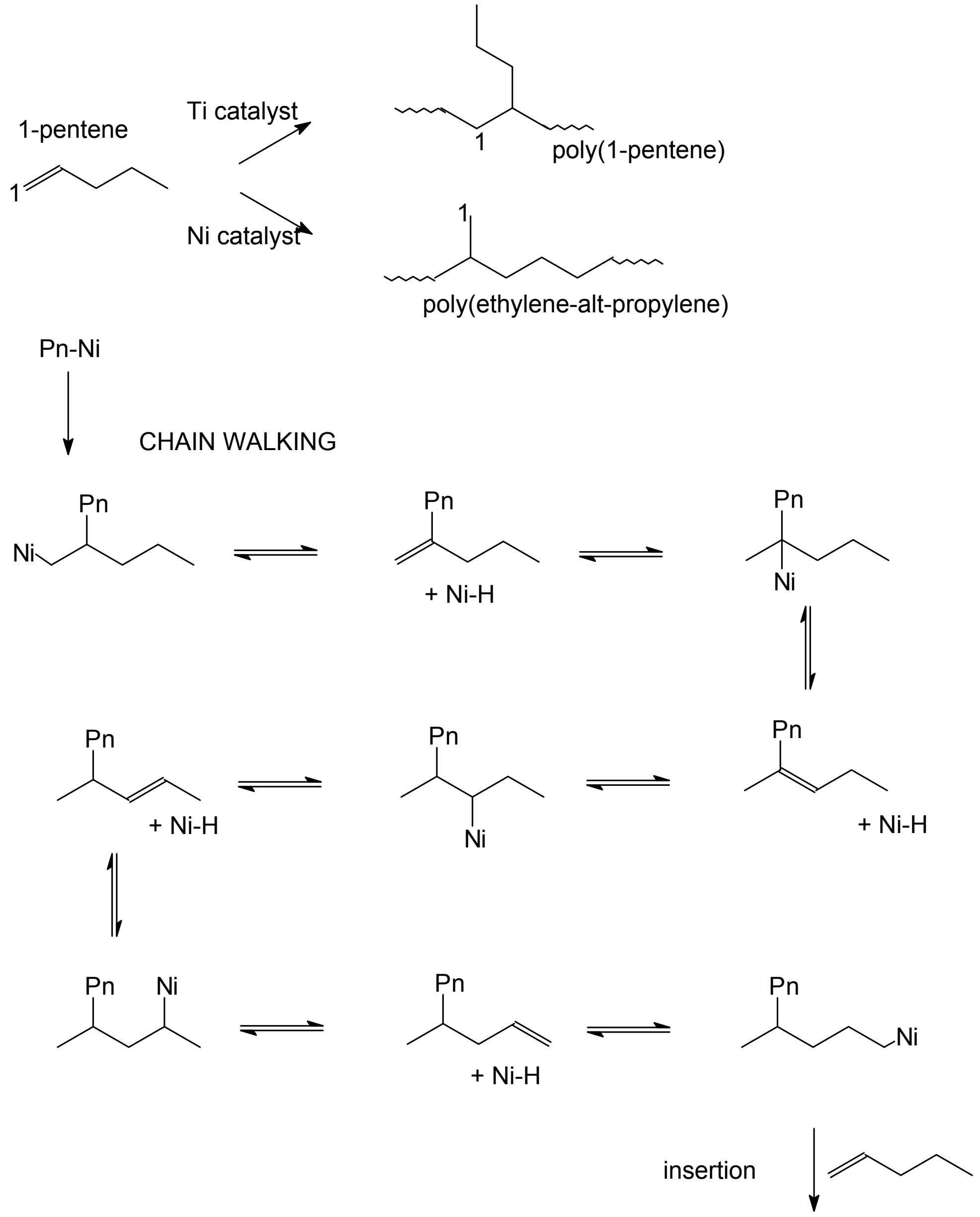
Shiono et al reported the living polymerization of hexene-1 using [t-BuNSiMe$_2$Flu]TiMe$_2$/B(C$_6$F$_5$)$_3$ catalyst system at -50^0C [42]. Poly(hexene-1) with molecular weight distribution as low as 1.07 with Mn 10,800 was obtained. The microstructure analysis revealed syndiotactic rich polymer.

Living polymerization was also carried out using *rac* Et(Ind)$_2$ZrMe$_2$/B(C$_6$F$_5$)$_3$ catalyst system at -78^0C [43]. However the lowest value of molecular weight distribution obtained was 1.22 with a Mn of 4300. The microstructure analysis by ^{13}C NMR revealed isotactic rich polymer.

Recently Sita et al reported the highly stereospecific polymerization of hexene-1 using Cp*ZrMe$_2$[NR^{1}C(Me)NR^2] / [B(C$_6$F$_5$)$_4$] catalyst system [44]. Poly(hexene-1) with molecular weight Distribution as low as 1.03 and a Mn of 49, 251 was obtained at-10^0C. The microstructure analysis revealed isotactic rich polymer (mmmm >95%).

Polymerization of hexene-1 using 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. Brookhart and coworkers developed Ni and Pd catalysts with sterically demanding (diimine) ligands which showed high activities [46]. The most important feature of these polymerizations is the structure of the poly α-olefins 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. This unexpected branching reaction is attributed to the migration of the transition metal alkyl along the olefin between two insertions as shown in the scheme. 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 (**scheme-3.1**). This process is known as the 'chain walking" or "chain running" mechanism [47].



Scheme-3.1 Chain walking mechanism

Table 3.1 Polymerization of hexene-1 using metallocene catalyst system.

S. No	Reference	Catalyst/cocatalyst	Reaction Conditions	Polymer Properties		Features
				Molecular Weight	End groups	
1.	Macromol. Rapid Comn. _16_, 643, **1995**	Cp_2ZrCl_2, $(^tBuCp)(Cp)ZrCl_2$, $(^tBuCp)_2ZrCl_2$, $(^tBu_2Cp)(Cp)ZrCl_2$, $(^tBu_3Cp)(Cp)ZrCl_2$, $(^tBu_2Cp)_2ZrCl_2$,	Tp = 50^0C Al/Zr = 4000 Bulk Polymerization	Mn = 200 - 1200	Vinylidene	The activity of the metallocene catalysts was found to decrease with increase in total number of t-Butyl groups in Cp ring.
2	Selectivity in Catalysis. ACS Symposium series _517_ 156, **1993**	Cp_2ZrCl_2 (**1**) $(Ind)_2ZrCl_2$ (**2**) *rac* $Et(Ind)_2ZrCl_2$ (**3**) $(M_3SiCp)_2ZrCl_2$ (**4**) $[1,3\text{-}(M_3Si)_2Cp]_2ZrCl_2$ (**5**) $(Cp)\ (M_3SiCp)ZrCl_2$ (**6**)	Tp = 0^0C Al/Zr = 1000	Mw 20 000 - 1 00 000	Vinylene end group with catalyst (**3**). All other catalysts shown vinylidene end group.	Introduction of one M_3Si group in Cp ring increases the catalyst activity. However introduction of two M_3Si groups reduce the catalyst activity due to steric effect.
3	Die Angewandte Makromolekulare Chemie _227_, 158, **1995**	Cp_2ZrCl_2/MAO	Tp= 60^0C, Al/Zr = 500 - 1000	Mn 200 - 600	Vinylidene	Kinetic study revealed that the degree of polymerization is independent of monomer conversion
4	Macromol Chem Macromol Rapid Comn. _19_, 391, **1998**	Cp_2ZrCl_2/MAO	Tp = -78 to 60^0C, Al/Zr = 5000	Mn = 400 – 75 000	Vinylidene	Stereo and regio selectivities were found to increase with decrease in polymerization temperature.

5	Macromol Chem. Phy. *203*, 129, **2002**	Cp_2ZrCl_2/MAO $Cp^*{}_2ZrCl_2$/MAO (Cp^* = Me, t-Bu substituted)	Tp = 60^{0}C, Al/Zr = 4000	Mn = 400 – 5600	Vinylidene	End group analysis of the oligomers by MALDI-TOF MS combined with NMR and SEC revealed that vinylidene is the only end group.
6	Poly Bull *25*, 567, **1991**	Et(THI)$_2$ZrCl$_2$/MAO 1-Me-1-ethylidene(Cp Flu) ZrCl$_2$/MAO	Tp= 30^{0}C, Al/Zr = 500	Mn = 6000 - 13000		Syndiotactic poly(hexene-1) by NMR.
7	Macromol Chem. Phy. *197*, 855, **1996**	*rac*Et(Ind)$_2$ZrCl$_2$/MAO	Tp = 20^{0}C, Al/Zr =0 - 5000			Enhanced activity was observed in polar solvents compared to non polar solvents.
8	JPS, pt A poly chem *31*, 1747, **1993**	*rac*Et(Ind)$_2$ZrCl$_2$/MAO (**1**) *rac*Et(Ind)$_2$ZrCl$_2$/Borate (**2**)	Tp=-30 to 50^{0}C, Al/Zr = 2800-6800	Mw = 18 000 – 97 000		The activity of catalyst (**1**) was found to decrease with decrease in Tp. However the catalyst (**2**) was found to have an opposite effect due to its coordination ability.
9	Macromolecules *27*, 3383, **1994**	*rac*Et(Ind)$_2$Zr$^+$R/ B(C$_6$F$_5$)$_4^-$	Tp=-30 to 25^{0}C Cat/cocat = 1	Mn = 15 000 – 23 000	Vinylene Vinylidene Trisubstituted	Internal unsaturation was found as a major end group.

10	Polymer *33*, 2408, **1992**	*rac*$Et(Ind)_2ZrCl_2$/MAO (**1**) Cp_2ZrCl_2/MAO (**2**)	Tp = 0^0C, Al/Zr = 1700	Mn = 18 000 (**cat 1**) Mn = 2200 (**cat 2**)		The molecular mass distribution measured by mass spectrometer and GPC revealed that polymerization with catalyst (**2**) proceeds steadily compared to catalyst (**1**).
11	J.M.S Pure Appl. Chem *A35*, 473, **1998**	$(CH_3)_2Si[Ind]_2ZrCl_2$ (**1**) $Et(Ind)_2HfCl_2$/MAO (**2**)	Tp =10^0C Al/Zr = 2000 (**1**) Tp =30^0C Al/Hf =830 (**2**)	Mw = 37 000 (**cat 1**) Mw = 95 000 (**cat 2**)		The Mw of polymer produced by catalyst (**2**) was found to be higher than catalyst (**1**)
12	Polymer Intl. 48, 257, **1999**	*rac* $Et(Ind)_2ZrCl_2$/MAO	Tp = 20^0C, Al/Zr = 0-2000			Kinetics and UV spectroscopic investigation of activation of catalyst.
13	Macromol Symp 66, 157, **1993**	i-Pr(3-MeCp Flu)$ZrCl_2$/MAO	Tp= 25^0C, Al/Zr = 645	Mw = 51 000		Microstructure analysis by ^{13}C NMR confirms that poly(hexene-1) has hemi isotactic structure.
14	Macromol Symp 89, 299, **1995**	$[(9\text{-}Flu)_2C_2H_4]Zr^+$ Me / MAO or $MeB(C_6F_5)_3^-$		Mn = 38 000 – 9 20 000		$MeB(C_6F_5)_3^-$ was found to be strong coordinating with metallocenium ion than MAO.
15	Macromol Chem. Phy. 200, 1208, **1999**	iPr (Cp Flu)$ZrCl_2$/MAO	Tp = 20^0C, Al/Zr = 0-3000			Enhanced activity was observed in polar solvents compared to non polar solvents

16	Macromol Chem Macromol Rapid Comn. 18, 581, **1997**	*rac* & meso $(CH_3)_2Si(2,3,5Me_3Cp)_2ZrCl_2$/MAO or $Ph_3C\ B(C_6F_5)_3^-$	Tp = 40^0C, Al/Zr = 1000	Mw = 60 000 - 1 34000		
17	Macromol Chem. Phy. 200, 1587, **1999**	*rac* & meso $(CH_3)_2Si[2\text{-}Me\ Ind]_2ZrCl_2$/MAO	Tp = 40^0C, Al/Zr = 1000	Mn = 9000 -36 000		Coordination of hexene-1 with sterically hindered meso isomer is difficult.
18	JPS, pt A poly chem 38, 1687, **2000**	*rac*-$Me_2\ Si(1\text{-}$ $C_5\ H_2\ \text{-}2\text{-}CH_3\ \text{-}4\text{-}\ t\ Bu)_2$ $Zr(NMe_2\ )_2\ /Al(\ iBu)_3$ $/[Ph_3\ C][B(C_6\ F_5\ )_4\ ]$	Tp = 30^0C, Borate/Zr = 1	Mw = 8000	Vinylidene = 79% Trisubstituted = 18% Vinyl = 3%	β-H transfer was found to be the major chain transfer reaction.
19	JPS, pt A poly chem 38, 3802, **2000**	*rac*-$Me_2\ Si(THI)_2$ /MAO	Tp = 0-100^0C, Al/Zr = 10 - 1200	Mn = 2000 – 20 000	Vinylidene= 10-80% Vinylene = 80-10% Trisubstituted = 10%	Vinylidene end group was found to decrease with increase in temperature. However internal end group has shown the opposite behavior.
20	JPS, pt A poly chem 38, 2333, **2000**	$(CH_3)_2Si(2\text{-}Me\ benz[e]Ind)_2ZrCl_2$/MAO	Tp = -15-180^0C, Al/Zr = 2000	Mn = 1200 – 80 000		Isotactic poly(olefin) content found to increase with decrease in temperature.
21	J. of Molecular Catalysis A: Chemical *128*, 1, **1998**	$Cp^*TiMe_2(\mu\text{-}Me)/B(C_6F_5)_3$	Tp = -78, 0, 22^0C.	Mw = 30000 (**-78^0C**) Mw=10000 (**22^0C**)	Vinylidene Vinylene	Vinylidene end group was found to decrease with increase in temperature. However internal end group has shown the opposite behavior.

In this chapter, chain transfer reactions in metallocene/MAO catalyzed polymerization of hexene-1 are explored. The advantages of hexane-1 as a monomer are its ease of handling and low propagation rates in bulk polymerization, thus rendering the preparation of low molecular weight oligomers easy. Results of polymerization of hexene-1 using four different catalysts namely dicyclopentadienylzirconium dichloride, di(n-butylcyclopentadienyl)zirconium dichloride, ethylenebis(indenyl) zirconium dichloride and dimethylsilyl dicyclopentadienylzirconium dichloride are described in this chapter. Effect of catalysts concentration, temperature, Al/Zr ratio and nature of metallocene on catalyst activity, number average molecular weight (Mn) and regio errors have been examined.

3.2 Experimental

All manipulations involving air sensitive compounds were carried out using standard bench top inert atmosphere techniques under high purity nitrogen.

3.2.1 Materials

Toluene (Loba Chemie, GR grade), was purified by refluxing over sodium wire and subsequent distillation under nitrogen. Hexene-1 (Aldrich, USA) was freshly distilled before use. Methylaluminoxane (MAO) (Me/Al ratio: 1.54, free TMA: 35 %, 14.1 % by wt. Al solution in toluene (Schering A.-G., Germany), Cp_2ZrCl_2 (Aldrich, USA), (n-buCp_2)$ZrCl_2$, Et(Ind)$_2ZrCl_2$ (Witco, Germany), were used as received . $Me_2SiCp_2ZrCl_2$ was prepared in the laboratory according to literature procedure [48].

3.2.2 Purification

Purification of hexene-1

Hexene-1 was stirred over CaH_2 for 24 h, fractionally distilled and finally distilled under reduced pressure. The distilled monomer was stored at 5 °C under positive pressure of nitrogen. The required amount of pre-distilled monomer was again subjected to further purification in inert atmosphere prior to the polymerization by freeze-thaw method using the apparatus shown in the following **figure-3.1.**

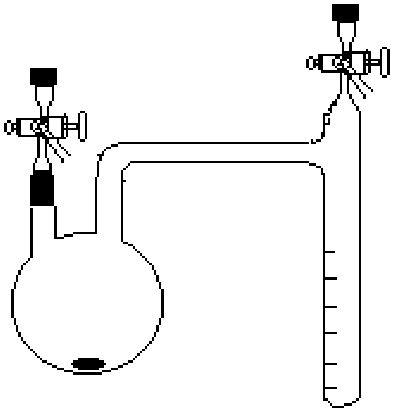


Fig-3.1 Apparatus for distillation of hexene-1 under reduced pressure

3.2.3 Polymerization

Kinetics of Hexene-1 Polymerization: Kinetics of hexene-1 polymerization was studied using Gas Chromatography by estimating unreacted monomer as a function of time. A single necked 250 mL round bottom flask along with magnetic needle was fitted with a septum adopter and flame dried and cooled under argon. The flask was charged with 50 mL (0.4028 mol) of freshly distilled hexane-1 through a hypodermic syringe. The required amount of internal standard cyclohexane (10.8 mL) was added.

2 mL of the solution was taken out for G.C analysis from the reaction mixture at time $\mathbf{t_0}$. The required amount of MAO (neat) was added to the reaction mixture. The reaction was initiated by adding metallocene catalyst at the specified temperature. Approximately 5 mL of the sample was taken out every two hours ($\mathbf{t_2}$, $\mathbf{t_4}$ etc), and diluted with 4 mL of toluene followed by termination of the polymer solution by the addition of 3-4 mL of methanol.

After termination the oligomer was found to separate from the unreacted monomer and methanol mixture. The supernatant liquid, which consists of unreacted monomer, internal standard and methanol, was taken out and analyzed by gas chromatography for monomer conversion.

Response Factor estimation

Response factor for hexene-1 and cyclohexane was calculated by injecting authentic mixtures with different mol ratios. The graph drawn between the area ratio (hexene-1/internal standard by GC) and mol ratio shows a straight line and the slope was calculated as 0.97.

The gas chromatography conditions used are as follows.

Oven temperature = 60° C (Isothermal), Injector = 125° C, Detector = 150° C, Total run time = 8 min. Flow = 0.4 mL /min, Split = 1:60.

The conversion (mol%) of hexene-1 at any given time **"t"** can be calculated as follows.

Conversion at time "t" = 1-(area ratio at time t/area ratio at time t_0) X 100.

3.2.4 Analysis

The IR spectra were recorded on a Perkin-Elmer 16 PC FT-IR spectrometer. Quantitative ^1H and ^{13}C NMR were recorded at 30° C in $CDCl_3$ on a Bruker MSL 500 model spectrometer operating at 75.5 MHz. The number average molecular weight (Mn) was determined by Knauer-7000 VPO at 30° C in chloroform. The number average molecular weight (Mn) was also calculated based on the intensity of the protons attached to terminal double bond from ^1H NMR by following procedure.

Intensity at 4.7 ppm due to 2 terminal vinylidene protons = 2x, For 1 proton = x

As hexene-1 repeat unit contains 12 protons

Therefore the intensity due to 12 protons = 12x

The total intensity in aliphatic region due to CH_3(0.8-0.9ppm), CH_2(1.2-1.6 ppm) and CH(2.0 ppm) = y

Number of repeat units = y/12x

Mn = (y/12x) molecular weight of hexene-1

3.3 Results & discussion

Kinetics of hexene-1 polymerization was carried out at different temperatures with various concentrations of catalyst at different Al/Zr ratios using $Cp_2/ZrCl_2/MAO$ catalyst. Kinetics study was also carried out using different metallocenes. The rate of polymerization (Rp) was obtained from the slope of the curve plotted against monomer consumption (ln $[M_0/M]$, where M_0 and M are mol of monomer at time t_0 and t respectively) vs time.

3.3.1 Kinetics of hexene-1 polymerization

3.3.1.1 Effect of Al/Zr

The effect of Al/Zr ratio was studied at 50^0C over the range of 2000 to 10 000. A typical kinetic profile is shown in **fig-3.2**. The rate of polymerization Rp (h^{-1}) (calculated from the slope of the initial individual curve) was found to increase from 0.26 to 0.94 h^{-1} with increase in Al/Zr ratio from 2000 to 10 000 as shown in **fig-3.3.** This can be attributed to the increase in concentration of active sites with increase in concentration of Al. However increasing the Al/Zr ratio beyond above 8000 does not have any significant effect on Rp.

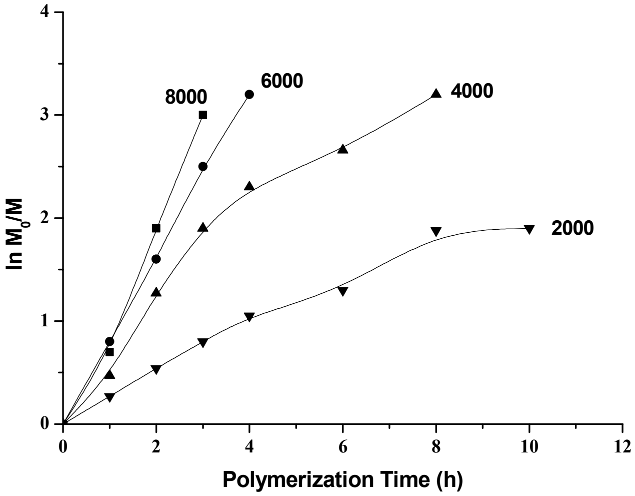


Fig-3.2 Plot of hexene-1 conversion with time as a function of Al/Zr

Reaction conditions: Hexene-1 = 20 mL = 13.56 g = 0.1611 mol, Cyclohexane = 5.0 mL = 3.87 g = 0.0460 mol, hexene-1/cyclohexane = 3.50, Temperature = 50^0C. [Zr] = $9.6x10^{-5}$ mol/L (concentration calculated considering both monomer 20 mL + 5 mL internal standard).

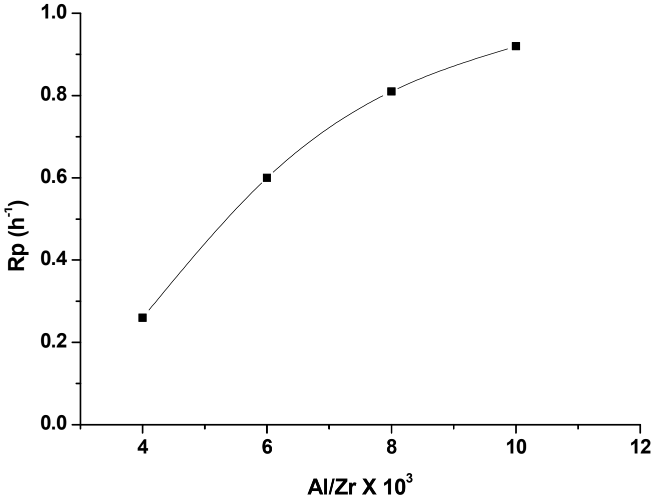


Fig-3.3 Plot of rate of polymerization as a function of Al/Zr mol ratio

3.3.1.2 Effect of metallocene concentration

A typical kinetic profile is shown in **fig-3.4**. The rate of polymerization (Rp) was found to increase from 0.1 to 0.76 h^{-1} with increase in metallocene concentration from 2.4 to $9.6x10^{-5}$ mol/L as shown in **fig-3.5**. The lower Rp at lower catalyst concentration is due to lower concentration of active sites.

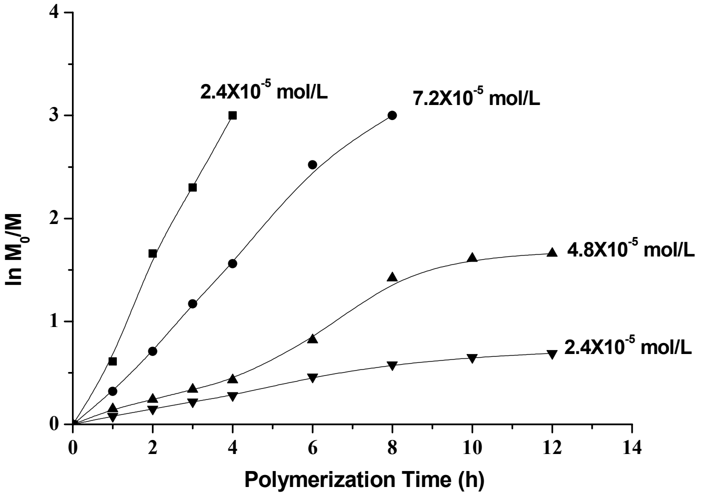


Fig-3.4 Plot of hexene-1 conversion with time as a function of metallocene concentration

Reaction conditions: Hexene-1 = 20 mL = 13.56 g = 0.1611 mol, Cyclohexane = 5.0 mL = 3.87 g = 0.0460 mol, hexene-1/cyclohexane = 3.50, Al/Zr = 8000.

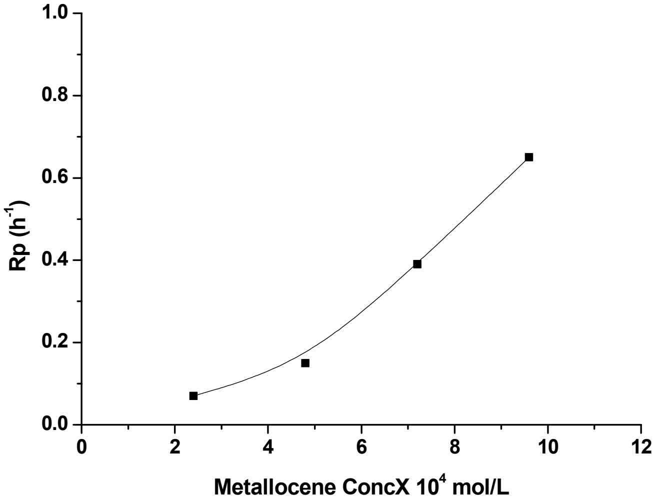


Fig-3.5 Plot of rate of polymerization as a function of metallocene concentration

3.3.1.3 Effect of temperature

Typical kinetic curves are shown in **fig-3.6**. The rate of polymerization (Rp) was found to increase from 0.2 to 0.81 h^{-1} with increase in temperature from 30 to 50^0C as shown in **fig-3.7**.

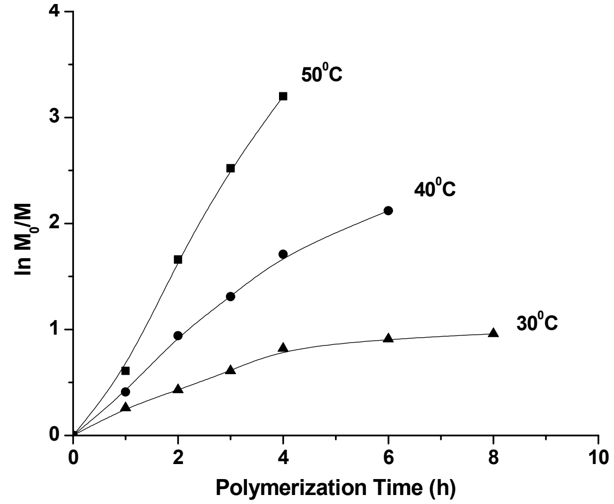


Fig-3.6 Plot of hexene-1 conversion with time as a function of temperature

Reaction conditions: Hexene-1 = 20 mL = 13.56 g = 0.1611 mol, Cyclohexane = 5.0 mL = 3.87 g = 0.0460 mol, hexene-1/cyclohexane = 3.50, Zr = $9.6x10^{-5}$ mol/L, Al/Zr = 8000.

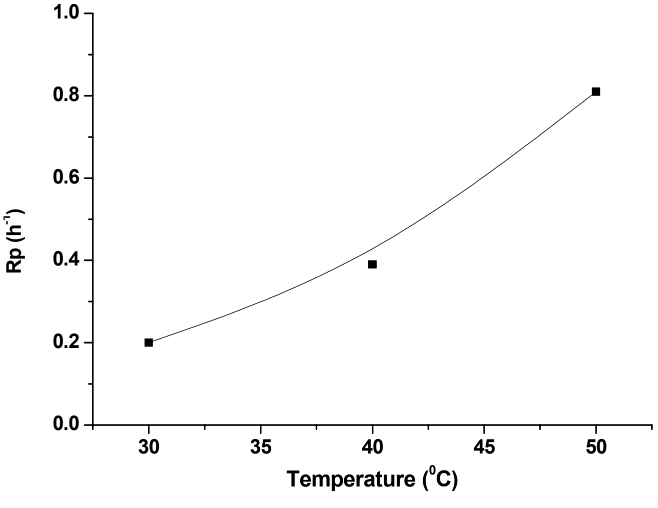


Fig-3.7 Plot of rate of polymerization as a function of temperature

3.3.1.4 Nature of metallocene

A typical kinetic profile is shown in **fig-3.8**. Rp was similar with both Cp_2ZrCl_2 and $(CH_3)_2SiCp_2ZrCl_2$ catalysts. $(n\text{-}buCp)_2ZrCl_2$ catalyst showed a marginally higher Rp.

rac Et(Ind)$_2$ZrCl$_2$ catalyst exhibited higher initial rate of polymerization, which declined after two hours. The change in Rp can be attributed to the electron donating capability of the π ligands attached to the zirconium center.

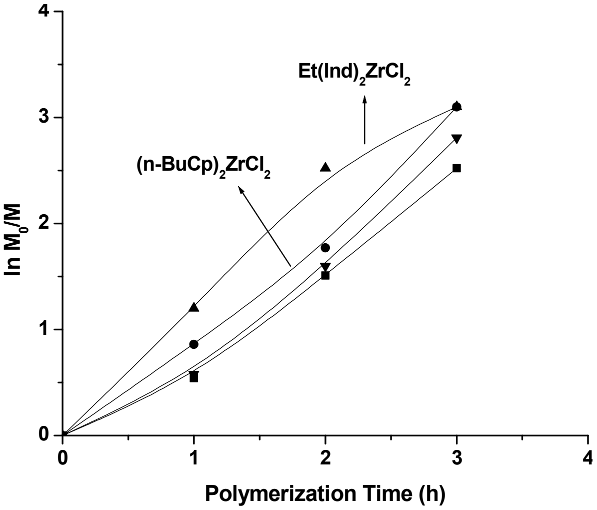


Fig 3.8-Plot of hexene-1 conversion as a function of time for different metallocenes

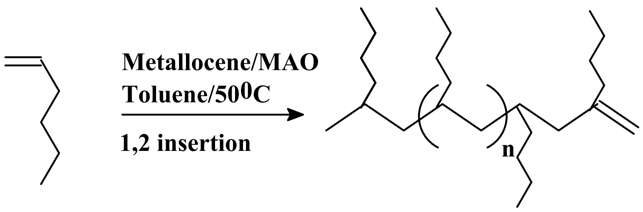
Reaction conditions: Hexene-1 = 20 mL = 13.56 g = 0.1611 mol, Cyclohexane = 5.0 mL = 3.87 g = 0.0460 mol, hexene-1/cyclohexane = 3.50, Temperature = 50^{0}C, Zr = 9.6x10^{-5} mol/L, Al/Zr = 8000.

3.3.2 Regiospecificity in hexene-1 polymerization

3.3.2.1 Nature of metallocene

The structure of end groups in hexane-1 polymerization were studied with low molecular weight poly(hexene-1) obtained with different catalysts. This, in turn, led to the investigation of the regio errors in hexane-1 polymerization.

Poly(hexene-1) obtained using Cp$_2$ZrCl$_2$, (n-BuCp)$_2$ZrCl$_2$ and (CH$_3$)$_2$SiCp$_2$ZrCl$_2$ catalysts at 50^o C show vinylidene end group which arise due to β-H transfer after 1,2 insertion as shown in **scheme-3.2**. The ^{1}H and ^{13}C NMR obtained with Cp$_2$ZrCl$_2$ are shown in **fig-3.9** and **3.10** respectively. The ^{1}H NMR showed broad singlets at 4.67 and 4.75 ppm for terminal vinylidene protons.



Scheme-3.2 Synthesis of vinylidene terminated poly(hexene-1) by metallocene/MAO catalyst system.

^{1}H NMR detected no other unsaturated end groups and hence the possibility of any other chain transfer reaction can be ruled out. The close proximity between the number average molecular weight obtained by VPO and ^{1}H NMR (discussed in the next section) reveals that the chain transfer to aluminum, which leads to the saturated end groups, is not operative under these conditions.

The ^{13}C NMR obtained by Cp_2ZrCl_2 catalyst showed two types of vinylidene end groups, which are indistinguishable by ^{1}H NMR. The peaks at 108.43 and 148.8 ppm were attributed to the vinylidene carbons obtained after 1,2 insertion. However the peaks at 110.2 and 150.2 were attributed to vinylidene carbons obtained after 1,2 insertion with regio error in the penultimate unit as reported by Odian et al for poly(butene-1) [45].

^{1}H NMR of poly(hexene-1) obtained by *rac* $Et(Ind)_2ZrCl_2$ catalyst **(fig-3.11)** showed both vinylidene as well as internal vinylene end group which arises due to β-H transfer after 2,1 insertion **(scheme-3.3).** The presences of internal vinylene double bonds are evidenced by a multiplet at 5.3-5.4 ppm in ^{1}H NMR. However, ^{13}C NMR of poly(hexene-1) **(fig-3.12)** revealed the presence of two kinds of vinylene double bonds as reported by Babu et al [23].

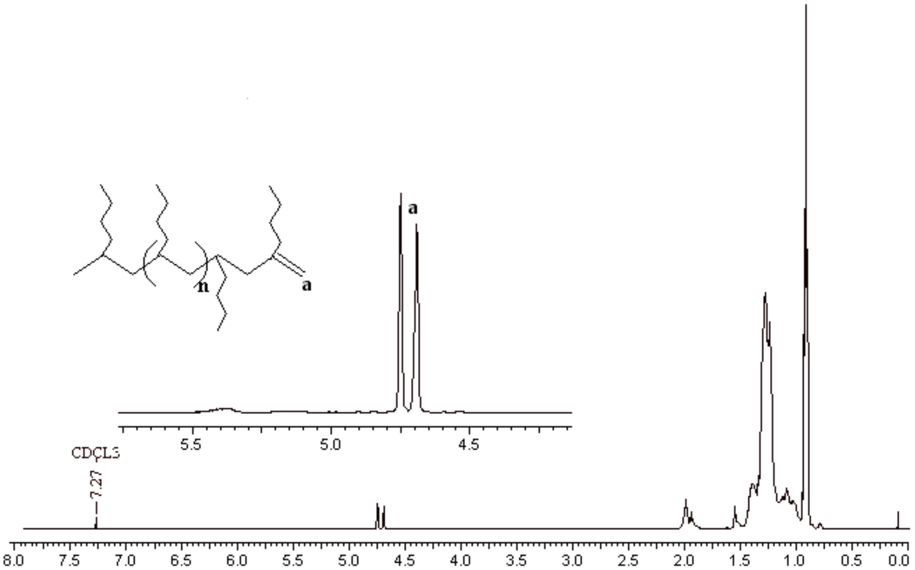


Fig-3.9 ^{1}H NMR of poly(hexene-1) produced by Cp$_2$ZrCl$_2$/MAO catalyst (run no 3 from table 3.2)

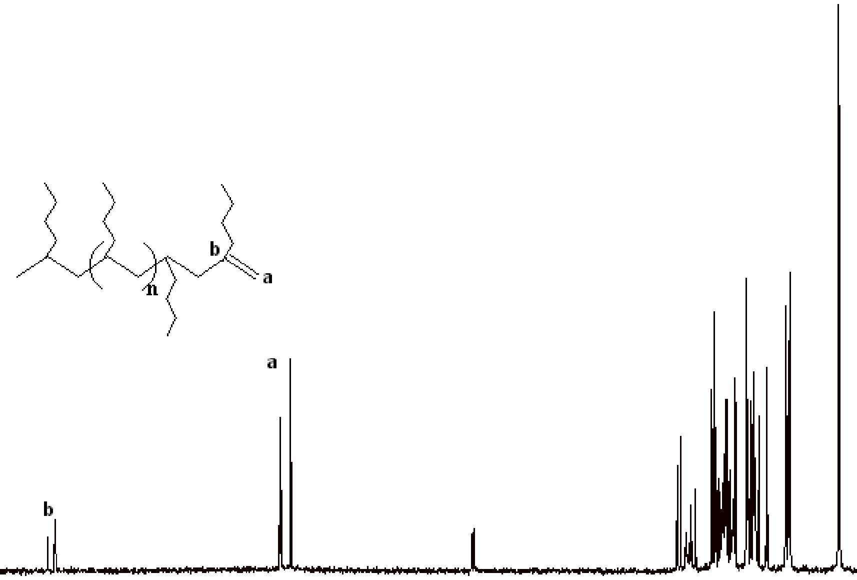


Fig-3.10 ^{13} C NMR of poly(hexene-1) produced by Cp$_2$ZrCl$_2$/MAO catalyst (run no 3 from table 3.2)

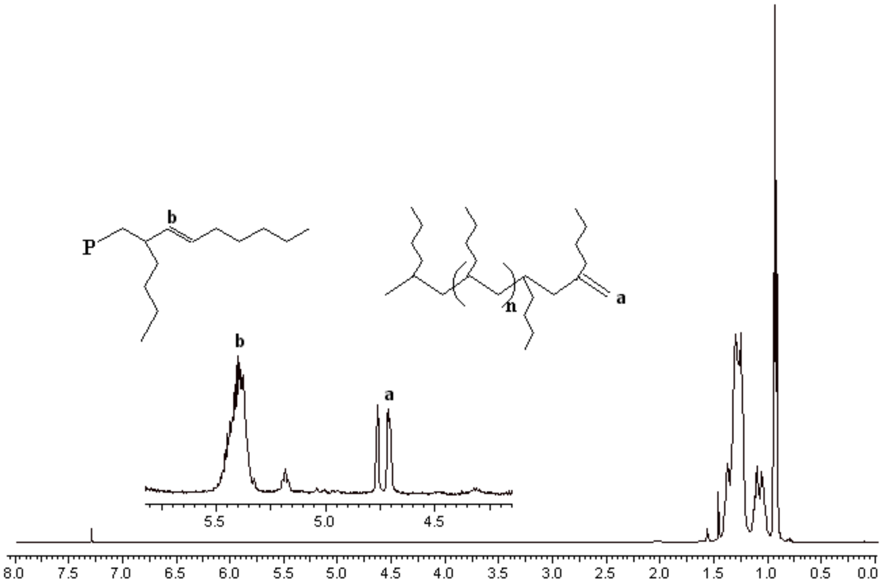
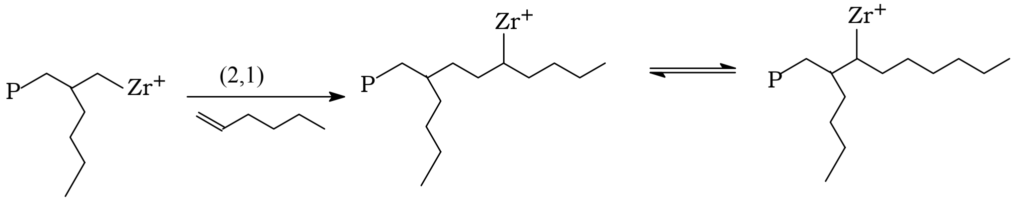


Fig-3.11 ^{1}H NMR of poly(hexene-1) produced by *rac* Et (Ind)$_2$ZrCl$_2$ catalyst (run no 1, table 3.4)



Scheme-3.3 β-hydrogen transfer after 2,1 insertion

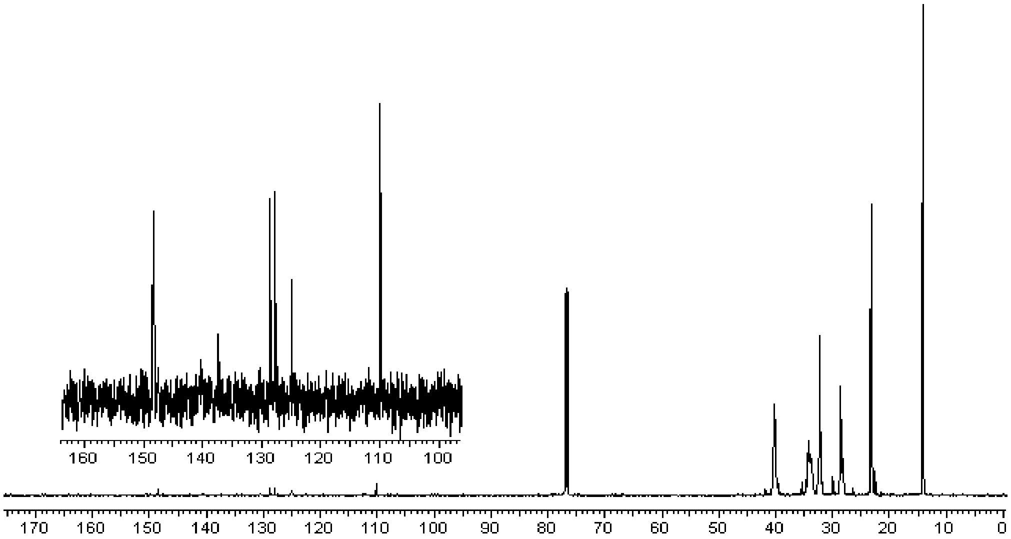


Fig-3.12 ^{13}C NMR of poly(hexene-1) produced by *rac* Et (Ind)$_2$ZrCl$_2$ catalyst (run no 1 (table 3.4)

3.3.2.2 Effect of temperature

The internal vinylene unsaturation was found to increase with decrease in temperature in poly(hexene-1) produced by Cp$_2$ZrCl$_2$, (n-buCp)$_2$ZrCl$_2$, and *rac* Et(Ind)$_2$ZrCl$_2$ catalysts as shown **table 3.2, 3.3 and 3.4** respectively.

Table-3.2 Polymerization of hexene-1 using Cp$_2$ZrCl$_2$/MAO catalyst system

Effect of temperature on end groups

Run No	Polymerization Temperature (^{0}C)	Mn		End groups (mol %)	
		VPO	^{1}H NMR	Vinylidene	Internal
1	50	320	330	>98	<2.0
2	40	550	560	97.5	2.5
3	30	1080	1150	94.0	6.0
4	15	1760	1880	92.0	8.0
5	0	2760	2980	90.0	10.0
6	-20	6840	7220	85.0	15.0

Reaction conditions: Hexene-1 = 20 mL = 13.56 g = 0.1611 mol, Zr = $9.6\text{x}10^{-5}$ mol/L, Al/Zr = 8000.

Table-3.3 Polymerization of hexene-1 using (n-buCp)$_2$ZrCl$_2$/MAO catalyst system

Effect of temperature on end groups

Run No	Polymerization Temperature (^{0}C)	Mn		End groups (mol %)	
		VPO	^{1}H NMR	Vinylidene	Internal
1	50	380	400	97.0	3.0
2	30	1400	1500	95.0	5.0
3	15	4300	4600	88.0	12.0
4	0	10 000	11 100	83.0	17.0
5	-20	21 800	24 700	77.0	23.0

Reaction conditions: hexene-1 = 20 mL = 13.56 g = 0.1611 mol, Zr = 9.6x10^{-5} mol/L, Al/Zr = 8000.

Table-3.4 Polymerization of hexene-1 using *rac* Et (Ind)$_2$ZrCl$_2$/MAO catalyst system

Effect of temperature on end groups

Run No	Polymerization Temperature (^{0}C)	Mn		End groups (mol %)	
		VPO	^{1}H NMR	Vinylidene	Internal
1	50	6 300	7 100	15.0	85.0
2	15	15 900	17 200	4.0	96.0
3	-20	27 800	30 300	<1.0	>99.0

Reaction conditions: hexene-1 = 20 mL = 13.56 g = 0.1611 mol, Zr = 9.6x10^{-5} mol/L, Al/Zr = 8000.

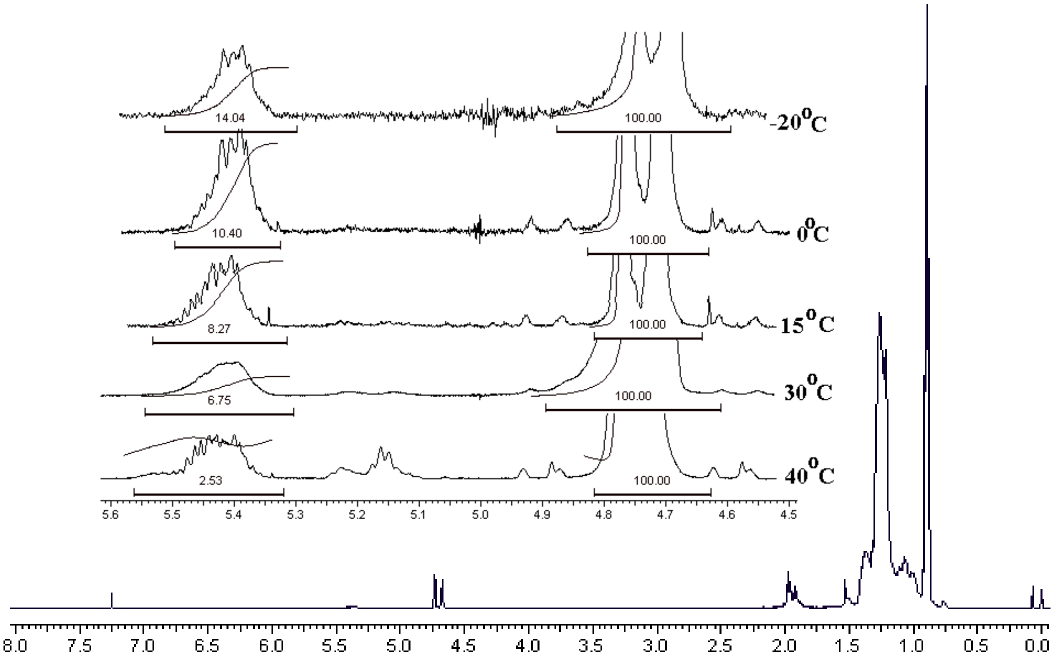


Fig-3.13 ^{1}H NMR of poly(hexene-1) obtained from Cp_2ZrCl_2 catalyst at different temperatures

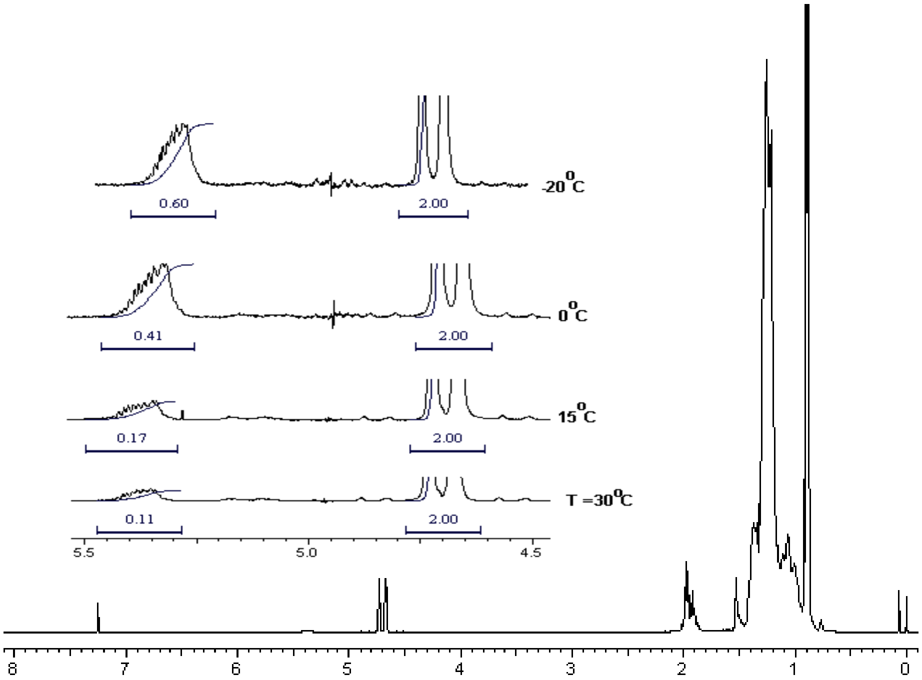


Fig-3.14 ^{1}H NMR of poly(hexene-1) obtained from $(n\text{-}buCp)_2ZrCl_2$ catalyst at different temperatures

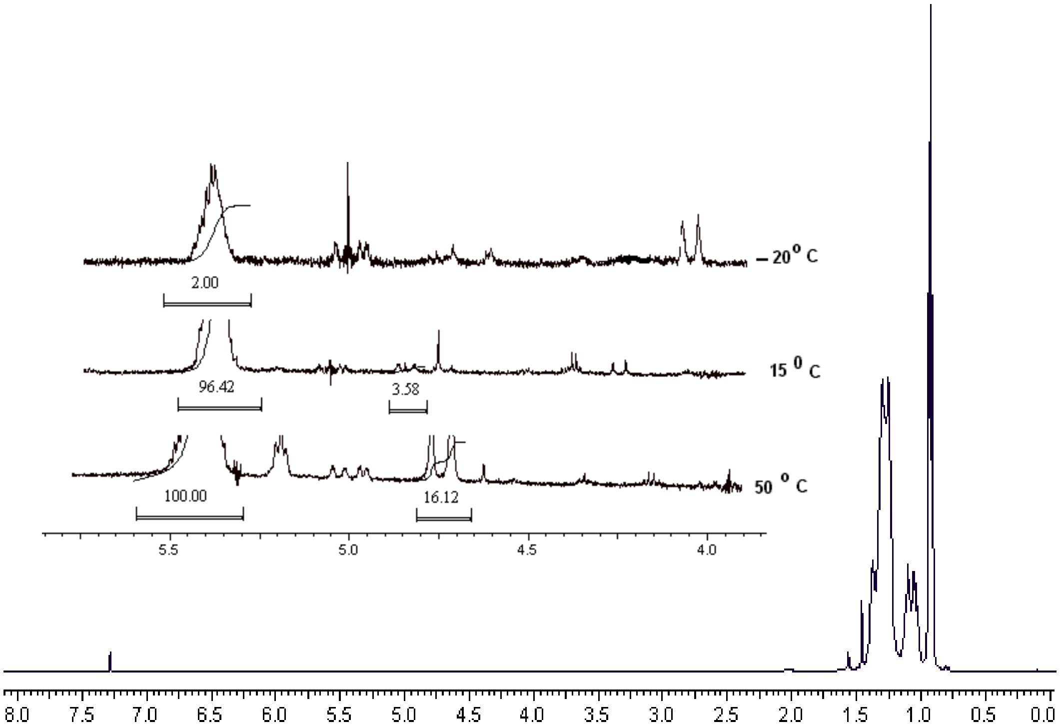


Fig-3.15 ^{1}H NMR of poly(hexene-1) obtained from *rac* Et(Ind)$_2$ZrCl$_2$ catalyst at different temperatures

From the above study it is clearly observed that the internal vinylene internal unsaturation increases with decrease in temperature with all the three catalysts. As shown **Scheme-3.2**, poly(hexene-1) with a penultimate inserted 2,1 unit is sterically hindered and further insertion is not energetically favorable. However at high temperature further 1,2 insertion may be possible on 2,1 penultimate unit. This was further confirmed by ^{13}C NMR analysis of poly(hexene-1) obtained with Cp$_2$ZrCl$_2$ catalyst at different temperatures as shown in **fig-3.16**. The vinylidene double bond, which arises due to regio error in the penultimate unit was found to decrease with a decrease in temperature.

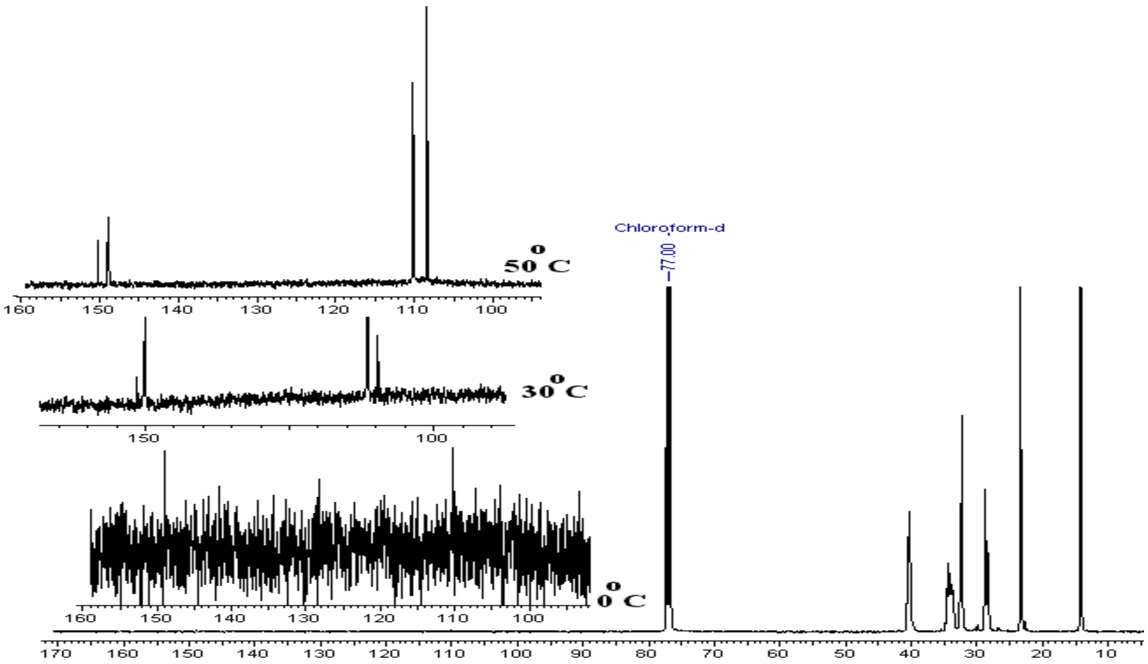


Figure-3.16 ^{13}C NMR of poly(hexene-1) obtained at different temperatures using Cp_2ZrCl_2 catalyst.

3.3.2.3 Al/Zr ratio

Variation in Al/Zr ratio did not show any significant change in regiospecificity.

3.3.2.4 Metallocene Concentration

Variation in metallocene concentration also did not show any significant change in regiospecificity

3.3.3 Effect of reaction conditions on molecular weight

The molecular weight of the poly(olefin)s is determined by the ratio of overall rate of propagation (Rp) to sum of the rates of chain transfer reactions (Rtr). The chain transfer reactions in metallocene catalyzed polymerization of olefins lead to terminally unsaturated poly(olefin)s. Hence it is an useful method to calculate the number average molecular weight by ^{1}H NMR. The number average molecular weight (Mn) of poly(hexene-1) determined by ^{1}H NMR and VPO were found to be in agreement. The number average degree of functionality (Fn) was observed in the range of 90 - 96 mol%. The effect of Al/Zr, metallocene concentration and temperature on Mn was studied by polymerization of hexene-1 using Cp_2ZrCl_2/MAO catalyst.

3.3.3.1 Al/Zr ratio

The number average molecular weight (Mn) obtained did not show any significant change with increase in Al/Zr ratio from 2000 to 10 000 at 50^0 C (Mn = 310-360 g/mol). This can be attributed to the increase in rate of propagation as well as rate of chain transfer at higher Al/Zr ratios.

3.3.3.2 Metallocene concentration

The number average molecular weight (Mn) was found to decrease marginally with increase in metallocene concentration as shown in table 3.5.

3.3.3.3 Temperature

The number average molecular weight (Mn) of poly(hexene-1) was found to decrease with increase in temperature as shown in table 3.6. The decrease in Mn with increase in polymerization temperature was expected due to the fact that the rate of chain transfer increases more sharply than rate of propagation with increase in temperature.

Table-3.5 Effect of metallocene concentration on Mn

Metallocene Concentration x10^5 (mol/L)	Mn		Fn (mol%) **b / a**
	^{1}H NMR **a**	VPO **b**	
2.4	440	420	95.0
4.8	390	370	96.0
7.2	350	330	95.0
9.6	310	300	97.0

Table 3.6 Effect of temperature on Mn

Temperature (^{0}C)	Mn		Fn (mol%)
	VPO	^{1}H NMR	
30	710	740	96.0
40	560	550	96.0
50	300	310	97.0

3.3.3.4 Nature of metallocene

Among the four catalysts studied, (n-buCp)$_2$ZrCl$_2$, *rac* Et(Ind)$_2$ZrCl$_2$ catalysts gave higher molecular weight poly(hexene-1) as shown in table 3.7. This was attributed to the decrease in rate of chain transfer reaction, as ligands around Zr become more electron releasing, the thermodynamic driving force for β-hydrogen elimination diminishes.

Table-3.7 Effect of metallocene structure on Mn

Catalyst	Mn	
	VPO	^{1}H NMR
Cp$_2$ZrCl$_2$	320	330
(n-buCp)$_2$ZrCl$_2$	380	400
rac Et(Ind)$_2$ZrCl$_2$	6 300	7 140
(CH$_3$)$_2$SiCp$_2$ZrCl$_2$	330	340

3.4 Conclusions

Hexene-1 was polymerized using four different metallocenes/MAO catalysts under various reaction conditions. Highly regiospecific catalysts like Cp$_2$ZrCl$_2$, (n-BuCp)$_2$ZrCl$_2$ and (CH$_3$)$_2$SiCp$_2$ZrCl$_2$ result in vinylidene unsaturation as the major end group which arise due to β-hydrogen transfer after 1,2 insertion. Both vinylidene as well as internal vinylene (arising due to β-hydrogen transfer after 2,1 insertion) end groups were observed with a poorly regiospecific catalyst like *rac* Et(Ind)$_2$ZrCl$_2$. Interestingly internal vinylene end group was found to increase with decrease in temperature with all the catalysts examined.

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Chapter-4 Copolymerization of hexene-1 with 2,5-norbornadiene using metallocene/MAO catalyst system

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4.1 Introduction

Synthesis of poly(olefin)s bearing pendant double bonds has attracted increasing interest in the field of functional poly(olefin) research. This is because the pendant double bonds of poly(olefin)s can be converted into functional groups by chemical transformations or can be used for crosslinking. Functional poly(olefin)s are potentially useful for application as adhesive interfaces and as compatibilizing agents.

The most direct approach to poly(olefin)s bearing pendant double bonds is by the copolymerization of olefin with α,ω-dienes. Use of classical Ziegler-Natta catalysts for the copolymerization of ethylene with α,ω-dienes is limited by poor catalyst activity, low incorporation of diene, broad molecular weight and composition distributions and undesirable side reactions [1,2]. The discovery of metallocene catalysts made it possible to overcome many of these drawbacks. Most of the co- and terpolymerizations using metallocene catalysts have been carried out using unsymmetrical dienes such as 1,4-hexadiene [3] vinyl cyclohexene [4,5], 6-phenyl-1,5-hexadiene, 7-methyl-1,6-octadiene, 5,7-dimethyl-1,6-octadiene [6], 3,7-dimethyl-1,6-octadiene [7,8].

The extreme high reactivity of endocyclic double bond in bicylic olefin, norbornene, due to ring strain has been utilized to introduce pendant double bonds in poly(olefin)s by copolymerizing ethylene with unsymmetrical dienes like 5-vinyl-2-norbornene [9], 5-ethylidene-2-norbornene [10] and dicyclopentadiene [11]. Use of symmetrical dienes in copolymerization is limited by undesirable cyclopolymerization and crosslinking. Kaminsky and Drogemuller [12] reported extensive crosslinking during the terpolymerization of 1,5-hexadiene with ethylene and propylene using *rac* $Et(Ind)_2ZrCl_2$ / MAO catalyst system. Copolymerization of ethylene with 1,3-butadiene is reported to result in copolymer containing cyclopentane ring as well as 1,4-trans addition product [13,14]. However, more recently copolymerization of olefins with symmetrical dienes without undesirable side reactions has been reported [15-17].

In this chapter, the use of 2,5-norbornadiene (NBD), a symmetrical diene having two equally reactive endocyclic double bonds, as a comonomer for hexene-1 polymerization in the presence of metallocene/MAO catalyst system has been explored.

The chain transfer reactions as well as regioerrors in presence of various metallocene catalysts and at different reaction parameters were also explored. Previously it has been reported that under specified conditions cyclopolymerization of the bicylic diene can be prevented and only one of the double bonds undergoes enchainment [16]. The studies on copolymerization of hexene-1 with NBD using dicyclopentadienylzirconium dichloride (Cp_2ZrCl_2), di-n-butylcyclopentadienyl zirconium dichloride ((n-buCp)$_2$ZrCl$_2$), Et(Ind)$_2$ZrCl$_2$, and dimethylsilyl dicyclopentadienylzirconium dichloride ($Me_2SiCp_2ZrCl_2$) are discussed in this chapter.

4.2 Experimental

All manipulations involving air sensitive compounds were carried out using standard bench top inert atmosphere techniques under high purity nitrogen.

4.2.1 Materials

Toluene (Loba Chemie, GR grade), was purified by refluxing over sodium wire and subsequent distillation under nitrogen. Hexene-1 (Aldrich, USA) was freshly distilled before use. Methylaluminoxane (MAO) (Me/Al ratio: 1.54, free TMA: 35 %, 14.1 % by wt. Al solution in toluene (Schering A.-G., Germany), Cp_2ZrCl_2 (Aldrich, USA), (n-buCp$_2$)ZrCl$_2$, Et(Ind)$_2$ZrCl$_2$ (Witco Gmbh, Germany), were used as such. 2,5-norbornadiene (E.Merck, Germany) was stirred over CaH_2 for 24 h and distilled under nitrogen atmosphere prior to use.

4.2.2 Purification

Purification of NBD

2,5-norbornadiene was purified using a procedure similar that used for hexene-1 as described in **section 3.2.2**.

4.2.3 Kinetics of NBD polymerization and hexene-1-NBD copolymerization

The kinetic experiments were conducted similar to that used for hexene-1 as described in **section 3.2.3**.

4.2.4 Analysis

The IR spectra were recorded on a Perkin-Elmer 16 PC FT-IR spectrometer. Quantitative ^1H and ^{13}C NMR were recorded at 30°C in $CDCl_3$ on a Bruker MSL 500 model spectrometer operating at 75.5 MHz. The number average molecular weight (Mn) was determined by Knaur-7000 VPO at 30^0C in chloroform. The number average molecular weight (Mn) was also calculated based on the intensity of the protons attached to terminal double bond from ^{1}H NMR by following procedure.

Calculation of Mn of Poly(hexene-1-*co*-2,5-norbornadiene) bearing vinylidene (4.7ppm) and vinylene (5.3ppm) end groups

(a) Molecular weight due to vinylidene end group

Mol fraction of vinylidene end groups=Intensity at 4.7ppm/Intensity at 4.7+5.3 ppm = m

Mol fraction of vinylene end groups = Intensity at 5.3 ppm / Intensity at 5.3+4.7 ppm = n

Number of NBD molecules per chain containing vinylidene end group = Intensity at 6.2 ppm(due to NBD) x m / Intensity at 4.7 ppm

Total number of hexene-1 repeat units containing vinylidene end groups = (Intensity at 0.8 – 0.9 ppm x 2 / 3) x m / Intensity at 4.7 ppm

Mn_1 = Number of NBD molecules x Molecular weight of NBD + number of hexene-1 repeat units x Molecular weight of hexene-1.

In a similar way Mn_2 can be calculated from vinylene end groups.

Therefore the actual Mn of the copolymer = Mn_1 from vinylidene x mole fraction of vinylidene (^{1}H NMR)(m) + Mn from vinylene x mole fraction of vinylene (^{1}H)(n).

Calculation of NBD incorporation in poly(hexene-1-*co*-2,5-norbornadiene)

Method-1

Area of peak at 6.2 ppm due to 2 H of endocyclic double bond = X

Area due to 1 H = X/2 = A

Area of peak at 0.9 ppm due to 3H (Methyl) of hexene-1 = Y

Area due to 1 H = Y/3 = B

Mol % NBD incorporation = A/A+B x 100

Method-2

Area of peak at 6.2 ppm due to 2H of endocyclic double bond = X

Area due to 1H of NBD = X/2 = A

As total 6 protons will appear in the aliphatic region (0 to 2ppm), therefore the total NBD area in the aliphatic region = 3X

The total aliphatic area (0 - 2ppm) = Y

The total area due to hexene-1 = y - 3X = Z

Area due to 1H of hexene-1 = Z/12 = B

Mol % NBD incorporation = A/A+B x 100

Good agreement was found between the two methods.

4.3 Results & discussion

Kinetics of 2,5-norbornadiene homopolymerization as well as hexene-1 and 2,5 norbornadiene copolymerization was carried out at different temperatures with various concentrations of catalyst at different Al/Zr ratios using $Cp_2/ZrCl_2/MAO$ catalyst. Kinetics study was also performed using different metallocene catalysts. The rate of polymerization (Rp) was obtained from the slope of the curve plotted against monomer consumption ($\ln M_0/M$) against polymerization time (h).

4.3.1 Kinetics of 2,5-norbornadiene homopolymerization

Kinetics of 2,5 norbornadiene homopolymerization was carried out under different conditions for purpose of comparing the polymerization kinetics with hexene-1 as well as hexene-1 and 2,5- norbornadiene copolymerization.

4.3.1.1 Effect of Al/Zr

Unlike hexane-1 polymerization, low rate of polymerization (Rp) was observed in the case of 2,5-norbornadiene polymerization using Cp_2ZrCl_2/MAO catalyst system under similar reaction conditions. The Rp was found to increase from 0.0092 to 0.021 h^{-1} with an increase in Al/Zr ratio from 4000 to 16 000. The results obtained are shown in **fig-4.1**.

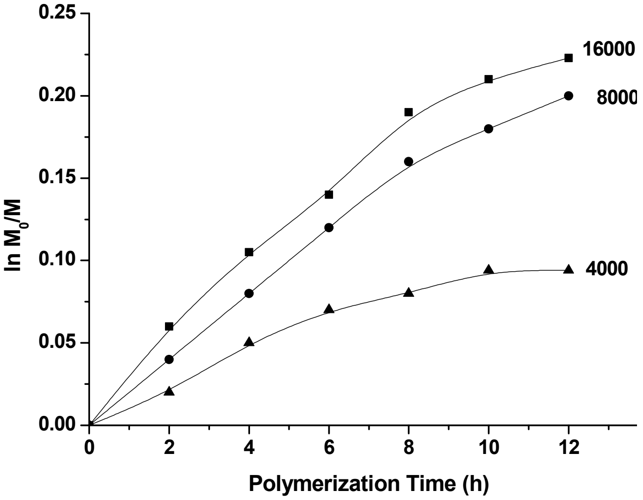


Fig-4.1 Plot of NBD conversion with time as a function of Al/Zr mol ratio

Reaction conditions: NBD = 16.4 mL = 14.84 g = 0.1611 mol, Cyclohexane = 5.0 mL = 3.87 g = 0.0460 mol, hexene-1/cyclohexane = 3.50, Temp = 50^{0}C. [Zr] = 8.2x10^{-5} mol/L.

4.3.1.2 Effect of metallocene concentration

The rate of polymerization (Rp) was found to increase from 0.018 to 0.023 h^{-1} with increase in metallocene concentration from 8.2 to 32.8 x 10^{-5} mol/L as shown in **fig-4.2**.

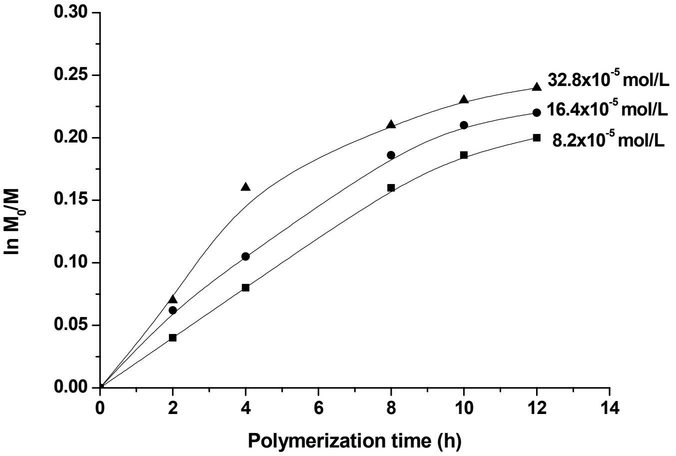


Fig-4.2 Plot of NBD conversion with time as a function of metallocene concentration

Reaction conditions: NBD = 16.4 mL = 14.84 g = 0.1611 mol, Cyclohexane = 5.0 mL = 3.87 g = 0.0460 mol, hexene-1/cyclohexane = 3.50, Temp = 50^{0}C, Al/Zr = 8000.

4.3.1.3 Effect of temperature

The Rp was found to decrease from 0.018 to 0.008 h^{-1} with decrease in temperature from 50 to 30^{0}C as shown in **fig-4.3**.

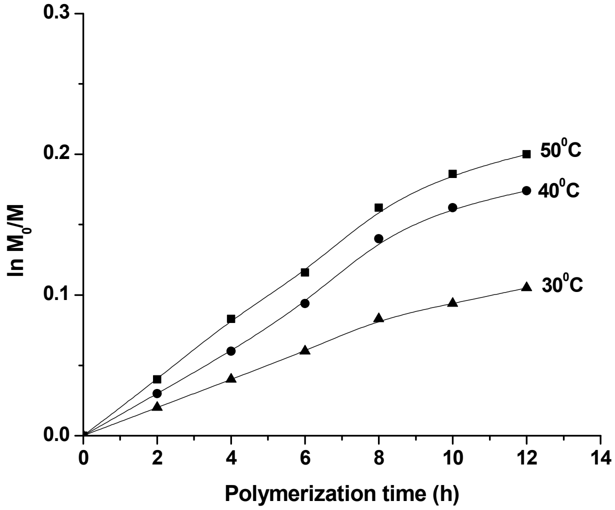


Fig-4.3 Plot of NBD conversion with time as function of temperature

Reaction conditions: NBD = 16.4 mL = 14.84 g = 0.1611 mol, Cyclohexane = 5.0 mL = 3.87 g = 0.0460 mol, hexene-1/cyclohexane = 3.50, [Zr] = 8.2x10^{-5} mol/L, Al/Zr = 8000.

4.3.1.4 Nature of metallocene

Typical kinetic profile obtained with different metallocenes for NBD polymerization is shown in **fig 4.4**. Amongst the four catalysts studied, *rac* Et(Ind)$_2$ZrCl$_2$ catalyst showed the highest value of Rp.

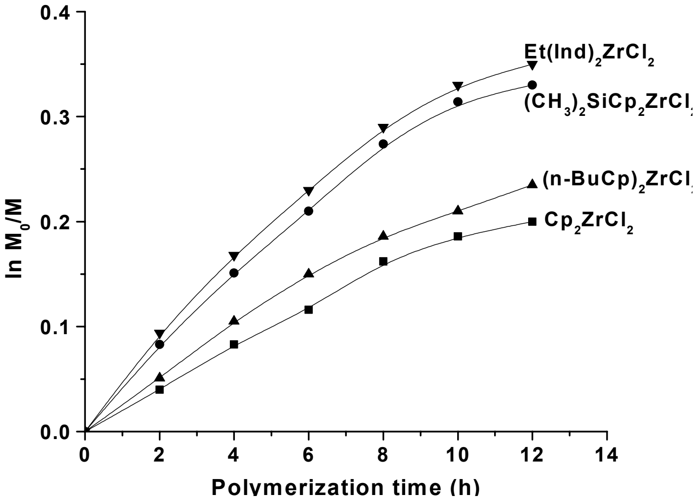


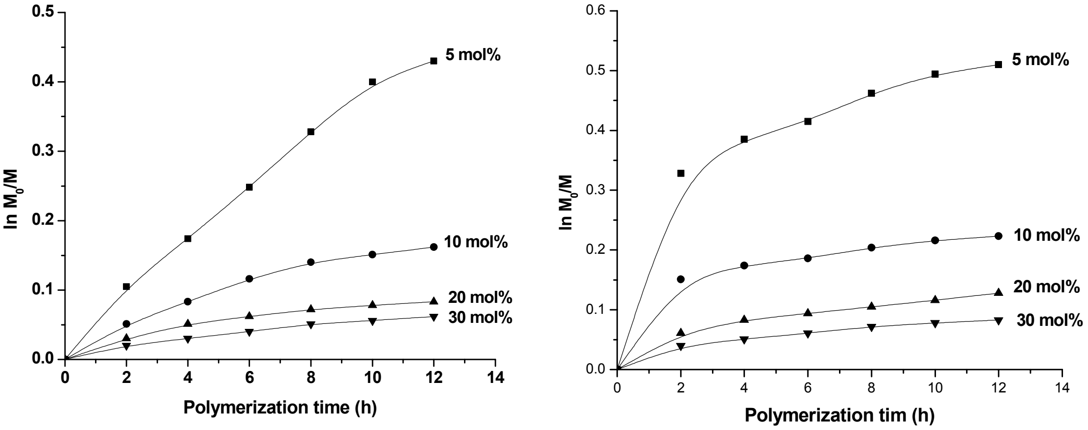
Fig-4.4 Plot of NBD conversion as a function of time for different metallocenes

Reaction conditions: NBD = 16.4 mL = 14.84 g = 0.1611 mol, Cyclohexane = 5.0 mL = 3.87 g = 0.0460 mol, hexene-1/cyclohexane = 3.50, Temp = 50^0C. [Zr] = $8.2x10^{-5}$ mol/L, Al/Zr = 8000.

4.3.2 Kinetics of hexene-1 - 2,5-norbornadiene copolymerization

4.3.2.1 Effect of NBD in feed

Copolymerization reactions were performed under conditions similar to that for hexene-1 polymerization at varying concentrations of NBD in feed. Typical kinetic profiles are shown in **fig-4.5**.



(a) Plot of hexene-1 conversion as a function of time for different NBD in feed

(b) Plot of NBD conversion as a function of time for different NBD in feed

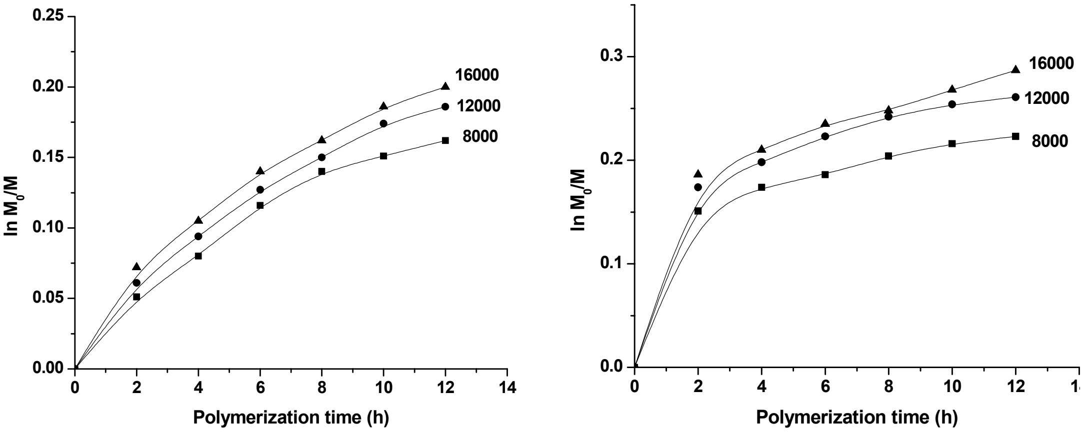
Fig 4.5-Plots of monomer conversions with time as a function of NBD in feed in copolymerization

Reaction conditions: Hexene-1 = 18.0 mL = 12.2 g = 0.145 mol, Cyclohexane = 5.0 mL = 3.87 g = 0.0460 mol, [Zr] = $9.6x10^{-5}$ mol/L, Al/Zr = 8000, Temp = 50^0C.

The rate of polymerization (Rp) of hexene-1 was found to decrease from 0.0389 to 0.0056 h^{-1} with increase in NBD in feed from 5 mol% to 30 mol%. However the Rp of NBD in copolymerization increased to 0.0534 h^{-1} at lower NBD in feed (5 mol% in feed), with further increase in NBD in feed, The Rp decreased to less than 0.0082 h^{-1}.

4.3.2.2 Effect of Al/Zr

Copolymerization reactions were conducted at 10 mol% NBD in feed with Al/Zr ratio varying from 8000 to 16 000. Typical kinetic profiles are shown in **fig-4.6**. The rate of polymerization of hexene-1 (0.0156 to 0.0389 h^{-1}) as well as NBD (0.0235 to 0.0294 h^{-1}) was found to increase marginally with increase in Al/Zr ratio.



(a) Plot of hexene-1 conversion with time as a function of Al/Zr mol ratio

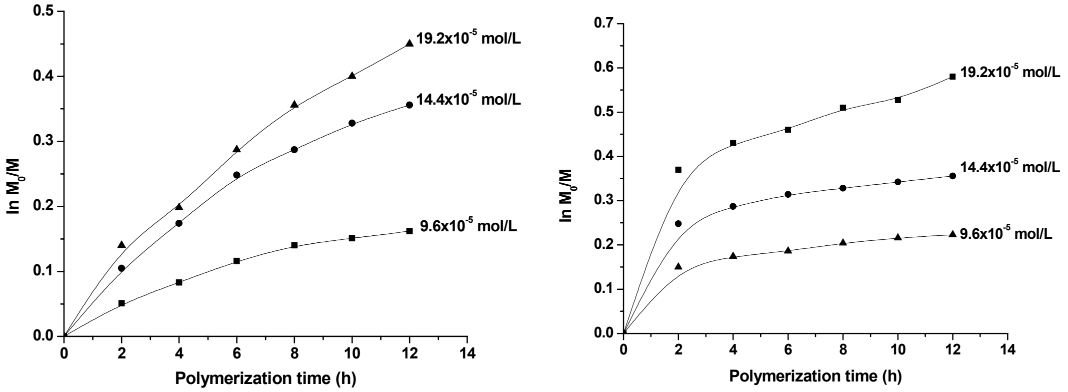
(b) Plot of NBD conversion with time as a function of Al/Zr mol ratio

Fig-4.6 Plots of monomer conversions with time as a function of Al/Zr mol ratio in copolymerization

Reaction conditions: Hexene-1 = 18.0 mL = 12.2 g = 0.145 mol, NBD = 1.64 mL =1.48 g = 0.0161 mol (10 mol % in the feed), Cyclohexane = 5.0 mL = 3.87 g = 0.0460 mol, [Zr] = 9.6x10^{-5} mol/L, Temp = 50^{0}C.

4.3.2.3 Effect of metallocene Concentration

Copolymerization reactions were conducted at 10 mol% NBD in feed and Al/Zr ratio of 8000 with variation in metallocene concentration from 9.6x10^{-5} mol/L to 19.2x10^{-5} mol/L. The results obtained are shown in **fig-4.7**.



(a) Plot of hexene-1 conversion with time as a function of metallocene concentration

(b) Plot of NBD conversion with time as a function of metallocene concentration

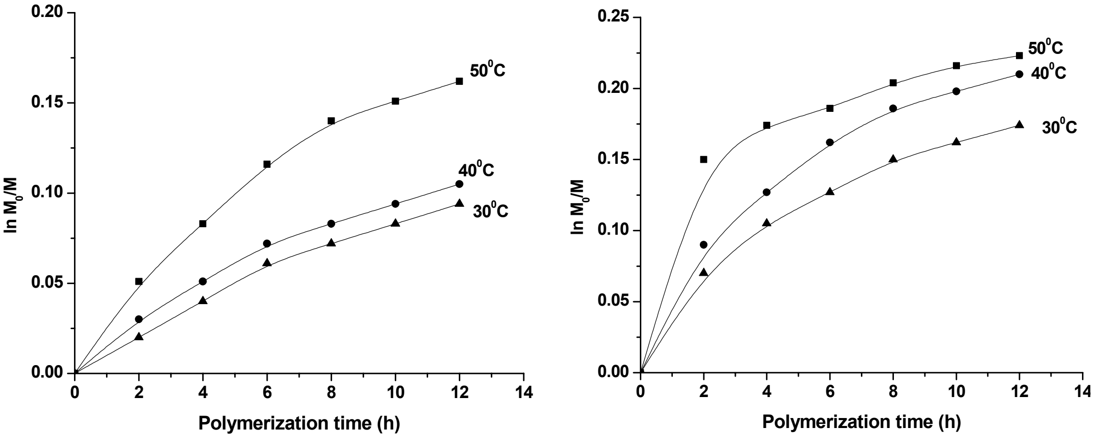
Fig-4.7Plots of monomer conversions with time as a function of metallocene concentration in copolymerization

Reaction conditions: Hexene-1 = 18.0 mL = 12.2 g = 0.145 mol, NBD = 1.64 mL =1.48 g = 0.0161 mol (10 mol % in the feed), Cyclohexane = 5.0 mL = 3.87 g = 0.0460 mol, Al/Zr = 8000, Temperature = 50^{0}C.

The Rp of hexene-1 was found to increase from 0.0156 to 0.0431 h^{-1} with increase in metallocene concentration from $9.6x10^{-5}$ mol/L to 19.2 $x10^{-5}$ mol/L. Further increase in metallocene concentration did not show any significant change in Rp. However, the Rp of NBD was found to increase from 0.0235 to 0.0591 h^{-1} with increase in metallocene concentration from $9.6x10^{-5}$ mol/L to 19.2 $x10^{-5}$ mol/L.

4.3.2.4 Effect of temperature

Copolymerization reactions were studied at 10 mol% NBD in feed and Al/Zr ratio 8000 at different temperatures. The results obtained are shown in **fig-4.8**. The rate of polymerization of hexene-1 (0.0156 to 0.0085 h^{-1}) as well as NBD (0.0235 to 0.0171 h^{-1}) was found to decrease with decrease in temperature from 50 to 30^0C.



(a) Plot of hexene-1 conversion with time as a function of temperature

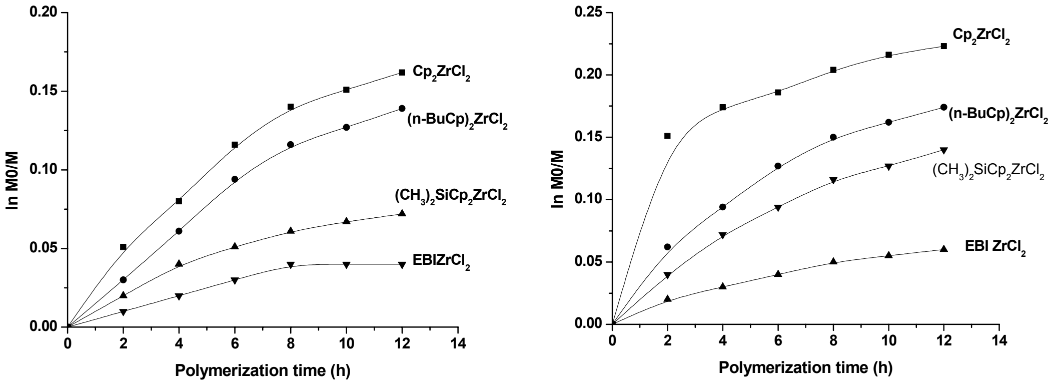
(b) Plot of NBD conversion with time as a function of temperature

Fig-4.8 Plots of monomer conversions with time as a function of temperature in copolymerization

Reaction conditions: Hexene-1 = 18.0 mL = 12.2 g = 0.145 mol, NBD = 1.64 mL =1.48 g = 0.0161 mol (10 mol % in the feed), Cyclohexane = 5.0 mL = 3.87 g = 0.0460 mol, [Zr] = $9.6x10^{-5}$ mol/L, Al/Zr = 8000.

4.3.2.5 Nature of metallocene

Kinetics of copolymerization reaction was studied under similar conditions using various metallocene catalysts. The results obtained are shown in **fig-4.9**. Amongst all the four catalysts studied, Cp_2ZrCl_2 catalyst showed maximum Rp for both hexene-1 and NBD. Unlike hexene-1 polymerization, the lower Rp observed with *rac* Et $(Ind)_2ZrCl_2$ catalyst in copolymerization could be due to more regioerrors.



(a) Plot of hexene-1 conversion as a function of time for different metallocenes

(b) Plot of NBD conversion as a function of time for different metallocenes

Fig-4.9 Plots of monomer conversions with time for different metallocenes in copolymerization

Reaction conditions: Hexene-1 = 18.0 mL = 12.2 g = 0.145 mol, NBD = 1.64 mL =1.48 g = 0.0161 mol (10 mol % in the feed), Cyclohexane = 5.0 mL = 3.87 g = 0.0460 mol, [Zr] = 9.6×10^{-5} mol/L, Al/Zr = 8000, Temp = 50^0C.

4.3.2.6 Reactivity Ratios

Reactivity ratios for hexene-1 and NBD for hexene-1/NBD copolymerization using Cp_2ZrCl_2 catalyst was evaluated using Kelen-Tudos method [18]. Copolymerizations were performed with different initial concentrations of NBD followed by compositional analysis of the copolymer by NMR.

Table 3.1 Calculation of reactivity ratios of hexene-1 and 2,5-norbornadiene in hexene-1/2,5-norbornadiene copolymerization with Cp_2ZrCl_2/MAO catalyst system using Kelen-Tudo's method

M_1	M_2	m_1	m_2	X	Y	G	F	η	ξ
95	5	94	6	19.0	15.6	17.8	23.1	0.56	0.73
90	10	86	14	10.0	6.1	8.4	16.4	0.34	0.66
80	20	74	26	4.0	2.8	2.6	5.7	0.18	0.40
70	30	63	37	2.3	1.7	0.9	3.1	0.08	0.27

Where M_1 and $m_1$are mol % hexene-1 in feed and copolymer respectively, M_2 and m_2 are mol % NBD in feed and copolymer respectively, X is M_1/M_2, Y is m_1/m_2,

G is X(Y-1)/Y, F is X^2/Y, η is G/(α+F) and ξ is F/(α+F)

where α is $(23.1 \times 3.1)^{1/2} = 8.46$

Kelen - Tudo's equation is $\eta = [r_{hexene-1} + (r_{NBD}/\alpha)] \times \xi - (r_{NBD}/\alpha)$

From the graph of η against ξ (**fig 4.10**), $y = 0.921\xi - 0.184$

ie, $r_{NBD}/\alpha = 0.184$, $r_{NBD} = 0.184 \times 8.46$

There fore $r_{NBD} = \pm$**1.55** and $r_{hexene\text{-}1} = 0.921 - 0.184 = \pm$ **0.737**.

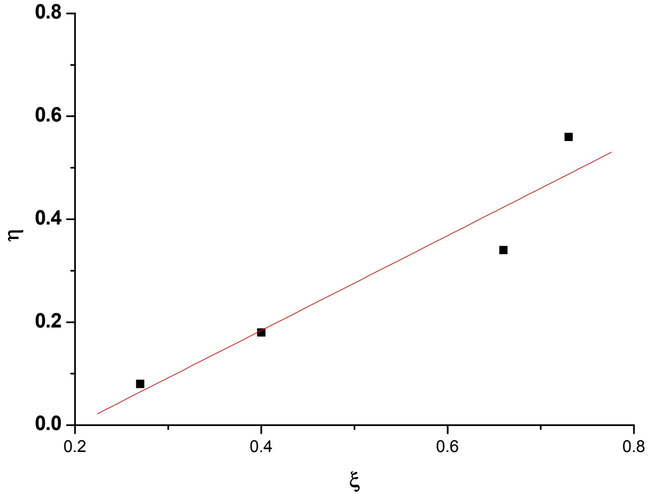


Fig-4.10 Kelen-Tudos plot for calculating reactivity ratios for hexene-1 and 2,5-norbornadiene in copolymerization using Cp_2ZrCl_2 catalyst

4.3.3 Comparison of Rp of homopolymerization vs copolymerization

The rate of polymerization of hexene-1 in homopolymerization was found to be higher than the rate of polymerization of NBD in homopolymerization under similar reaction conditions. However the Rp of hexene-1 decreased significantly in copolymerization. Interestingly the rate of polymerization of NBD in copolymerization was found to increase at lower NBD in feed (up to 10 mol% in feed). With further increase of NBD in the feed, the rate of polymerization decreased.

4.3.4 Effect of reaction conditions on regio errors

Effect of time

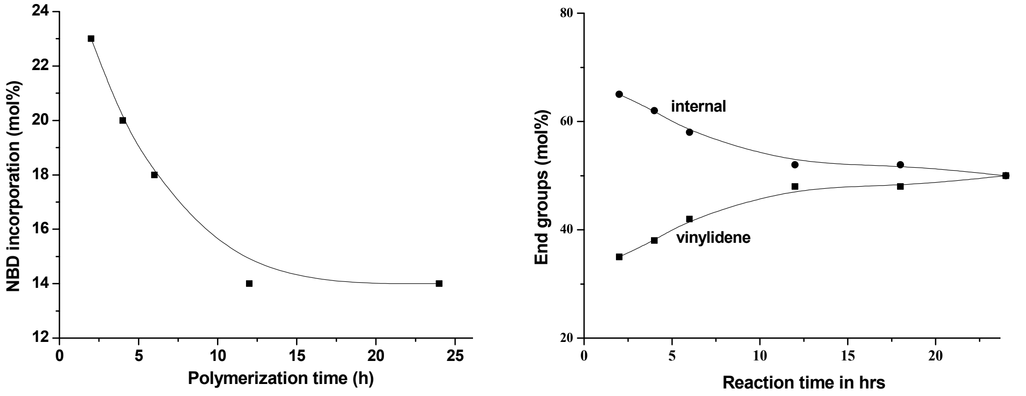
Preparative copolymerization reactions were carried out at different intervals of time at 10 mol % NBD in feed using Cp_2ZrCl_2/MAO catalyst to see the variation in the end groups with time. The results obtained are shown in **table-4.2**. The incorporation of norbornadiene was found to decrease with increase in time as shown in **fig-4.11**. It could be due to decrease in catalyst activity with time. Interestingly the internal unsaturation, which arise due to β-hydrogen transfer after 2,1 insertion was also found to decrease with time (**fig-4.11**). This implies a dependence of regio errors with increasing NBD incorporation.

Table-4.2 Copolymerization of hexene-1 with NBD using Cp_2ZrCl_2/MAO catalyst[a]

Effect of time

Polymerization time h	Yield (g)	NBD in copoly mol %	Conversion[c]		Activity Kg/mol Zr/h	Mn		End groups[d] mol %	
			Hexene-1	NBD		^{1}H NMR	VPO	Vinylidene	Internal
2	0.6	23.0	5.3	14.7	400	840	890	35.0	65.0
4	0.7	20.0	6.5	15.0	233	1060	990	38.0	63.0
6	0.8	18.0	7.5	15.7	177	1170	1110	42.0	58.0
12	1.4	14.0	14.0	20.0	155	1350	1290	48.0	52.0
18	1.4	14.0	14.0	20.0	102	1380	1320	48.0	52.0
24	1.4	14.0	14.0	20.0	90	1370	1360	50.0	50.0

[a] *Reaction conditions:* Hexene-1 = 12.5 mL = 8.475 g = 0.10 mol, NBD = 1.12 mL =1.0192 g = 0.011 mol (10 mol % in the feed) Zr = 7.5×10^{-7} mol, Al/Zr = 8000, Temperature = 50^0C, **[b]** = polymerization time in h. [c] = based on yield



(a) Dependence of NBD incorporation as a function polymerization time

(b) Dependence of end groups as a function of polymerization time

Fig-4.11 Plots of variation in end groups and NBD incorporation with time

Effect of Al/Zr

Copolymerization reactions were carried out at 10 mol % NBD in the feed with different Al/Zr ratios as shown in **table-4.3**. Increase in Al/Zr ratio did not show any significant change either in NBD incorporation or end groups. However the marginal increase in catalyst activity was observed.

Table-4.3 Copolymerization of hexene-1 with NBD using Cp_2ZrCl_2/MAO catalyst[a]

Effect of Al/Zr

Al/Zr	Yield (g)	NBD in copolymer mol %	Conversion		Catalyst activity Kg/mol Zr/h	Mn		End groups	
			Hexene-1	NBD		^{1}H NMR	VPO	Vinylidene	Internal
8000	1.4	14.0	14.0	20.0	155	1350	1290	48.0	52.0
12000	1.6	13.0	16.2	22.0	177	1460	1400	50.0	50.0
16000	1.7	13.0	17.2	23.4	188	1480	1430	50.0	50.0

[a] *Reaction conditions:* Hexene-1 = 12.5 mL = 8.475 g = 0.1 mol, NBD = 1.12 mL = 1.0192 g = 0.0110614 mol (10 mol % in the feed) Zr = $7.5x10^{-7}$ mol, Temperature = 50^0C, Polymerization time = 12h.

Effect of NBD in feed

The NBD incorporation was found to increase with increase in NBD in feed. The regio errors were found to increase with increase in NBD in feed as shown in **table-4.4**.

Table-4.4 Copolymerization of hexene-1 with NBD using Cp_2ZrCl_2/MAO catalyst [a]

Effect of NBD in the feed

NBD in feed mol %	Yield (g)	NBD in copolymer mol %	Conversion		Catalyst activity Kg/mol Zr/h	Mn		End groups	
			Hex	NBD		^{1}H NMR	VPO	Vinylidene	Internal
5	3.1	5.8	34.4	38.0	344	1040	1070	57.0	43.0
10	1.4	14.0	14.0	20.0	155	1350	1294	48.0	52.0
20	0.9	26.0	7.6	10.8	100	1620	1590	21.0	79.0
30	0.8	37.0	5.7	8.0	89	1890	1800	24.0	76.0

[a] *Reaction conditions:* Hexene-1 = 12.5 mL = 8.475g = 0.10007, Zr = $7.5x10^{-7}$ mol, Al/Zr = 8000, Temp = 50^0C, Time 12 h.

Effect of metallocene concentration

The copolymerization reactions were carried out at different metallocene concentrations to examine the variation in regio errors. The results obtained are shown in **table-4.5**. The regio errors were found to increase with increase in metallocene concentration.

Table-4.5 Copolymerization of hexene-1 with NBD using Cp_2ZrCl_2/MAO catalyst [a]

Effect of metallocene concentration

$[Zr]X10^5$ mol/L	Yield (g)	NBD in copoly mol %	Conversion		Catalyst activity Kg/mol Zr/h	Mn		End groups	
			Hex	NBD		^1H NMR	VPO	Vinylidene	Internal
9.6	1.4	14.0	14.0	20.0	155	1350	1290	48.0	52.0
14.4	2.6	11.0	30.4	27.0	144	1680	1600	43.0	57.0
19.2	4.0	8.0	34.0	43.0	110	1720	1660	40.0	60.0

[a] *Reaction conditions:* Hexene-1 = 12.5 mL = 8.475 g = 0.1 mol, NBD = 1.12 mL = 1.0192 g = 0.01 mol (10 mol % in the feed), Al/Zr = 8000, Temperature = 50^0C, Polymerization time = 12h.

Effect of temperature

The NBD incorporation was found increase with decrease in temperature. The regio errors were also found to increase with decrease in temperature as shown in **table-4.6**.

Table-4.6 Copolymerization of hexene-1 with NBD using Cp_2ZrCl_2/MAO catalyst[a]

Effect of temperature

Temp	Yield (g)	NBD in copolymer mol %	Conversion		Catalyst activity Kg/mol Zr/h	Mn		End groups	
			Hex	NBD		^1H NMR	VPO	Vinylidene	Internal
30	0.9	17.8	8.6	16.0	100	2020	1880	30.0	70.0
40	1.2	15.5	9.8	19.0	130	1680	1700	41.0	59.0
50	1.4	14.0	14.0	20.0	155	1350	1290	48.0	52.0

[a] *Reaction conditions:* Hexene-1 = 12.5 mL = 8.475 g = 0.1 mol, NBD = 1.12 mL = 1.0192 g = 0.01 mol (10 mol % in the feed) Zr = $7.5x10^{-7}$ mol, Al/Zr = 8000, Polymerization time = 12h.

Nature of metallocene

To examine the regio errors in poly(hexene-1-*co*-2,5-norbornadiene), the copolymerization reactions were also carried out in presence of different metallocenes. The results obtained are shown in **table-4.7**. Among all the four catalysts studied Cp_2ZrCl_2 catalyst showed the highest catalyst activity with least regio errors. $(CH_3)_2SiCp_2ZrCl_2$ and *rac* $Et(Ind)_2ZrCl_2$ catalysts showed higher regio errors with lower activity.

Table-4.7 The effect of metallocene structure on the copolymerization of hexene-1 with 2,5, NBD using metallocene/MAO catalyst[a]

Metallocene	Yield (g)	NBD in copolymer mol %	Convn[c]		Catalyst activity kg/mol Zr/h	Mn		End groups	
			Hexene-1	NBD		^{1}H NMR	VPO	Vinylidene	Internal
Cp_2ZrCl_2	1.4	14.0	14.0	20.0	155	1350	1290	48.0	52.0
$(n\text{-}buCp)_2ZrCl_2$	1.2	12.0	12.3	15.2	133	1620	1550	40.0	60.0
$(CH_3)_2SiCp_2ZrCl_2$	0.7	18.0	6.6	13.0	78	1540	1480	15.0	85.0
$Et(Ind)_2ZrCl_2$	0.4	13.0	4.0	5.5	45	1960	1860	10.0	90.0

[a]*Reaction conditions:* Hexene-1 = 12.5 mL = 8.475 g = 0.1 mol, NBD = 1.12 mL = 1.0192 g = 0.01 mol (10 mol % in the feed) Zr = 7.5×10^{-7} mol, Al/Zr = 8000, Polymerization time = 12h.

4.3.5 Regio errors in presence of other bicyclic olefins

The occurrence regio errors in presence of 2,5-norbornadiene in the polymerization of hexene-1 using a highly regiospecific catalyst like Cp_2ZrCl_2 catalyst was further confirmed by copolymerizing hexene-1 with norbornene. The microstructure analysis of poly(hexene-1-co-norbornene) showed the presence of both vinylidene and internal unsaturation as shown in **fig-4.12**. The presence of internal unsaturation in poly(hexene-1-co-norbornene) confirms the occurrence of regio errors in presence of bicyclic olefins in the polymerization of hexene-1.

4.3.6 Effect of reaction conditions on Mn

Effect of time

Unlike in poly(hexene-1), the number average molecular weight (Mn) of copolymer was found to increase with time as shown in **table-4.2**. This could be due to decrease in regio errors (which are known to reduce the catalyst activity as well as molecular weight) with time.

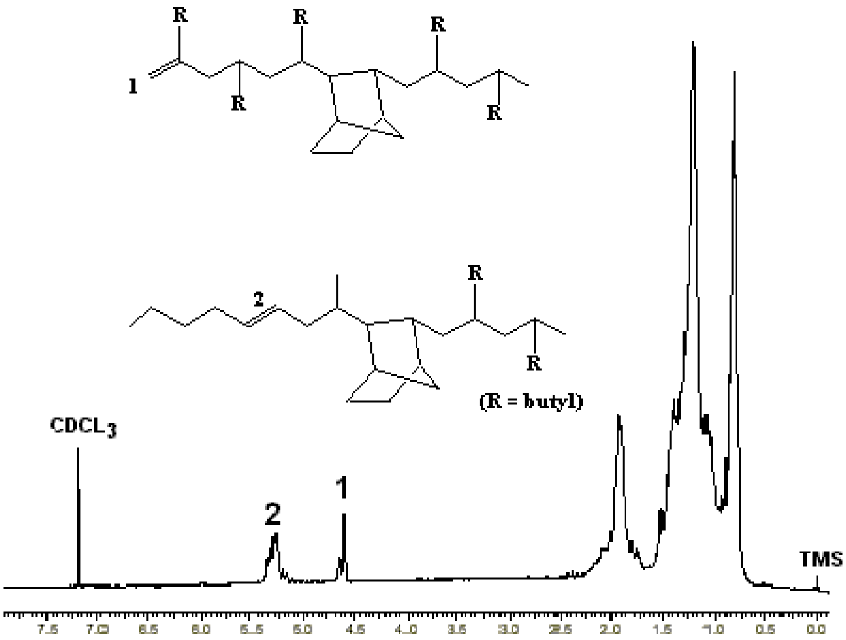


Fig 4.12 ^{1}H NMR of poly(hexene-1-*co*-norbornene)

Effect of Al/Zr

The number average molecular weight (Mn) was found to increase marginally with increase in Al/Zr ratio as shown in **table-4.3**. This could be as a result of an increase in rate of propagation compared to rate of chain transfer.

Effect of NBD in feed

Although the regio errors increased with increase in NBD incorporation, the number average molecular weight (Mn) increased with increase in NBD incorporation as shown in **table-4.4**.

Effect of metallocene concentration

Mn was found to increase with increase with metallocene concentration from $7.5\text{x}10^{-7}$ to $15\text{x}10^{-7}$ mol/L as shown in **table-4.5**. However, further increase in metallocene concentration did not have any significant effect on Mn.

Effect of temperature

Mn was found to increase with decrease in temperature as shown in **table-4.6.** The decrease in Mn with increase in polymerization temperature is expected since the rate of chain transfer increases more sharply than rate of propagation with increase in temperature.

Nature of metallocene

The Mn decreased in the order *rac* Et(Ind)$_2$ZrCl$_2$ > n-buCp$_2$ZrCl$_2$>(CH$_3$)$_2$SiCp$_2$ZrCl$_2$ > Cp$_2$ZrCl$_2$ (**table-4.7**). This can be attributed to the decrease in rate of chain transfer reaction, as ligands around Zr become more electron releasing, the thermodynamic driving force for β-hydrogen elimination diminishes.

4.3.7 Effect of various metallocenes on microstructure of the copolymer

Among the various metallocenes studied, poly(hexene-1-*co*-2,5 norbornadiene) obtained using highly regiospecific catalysts like Cp$_2$ZrCl$_2$, n-buCp$_2$ZrCl$_2$, (CH$_3$)$_2$SiCp$_2$ZrCl$_2$ catalysts showed the presence of both vinylidene and vinylene end groups (**fig-4.13**). However the copolymer obtained using a poorly regiospecific catalyst *rac* Et(Ind)$_2$Zr Cl$_2$ showed only vinylene as the major end group as shown in **fig-4.15**.

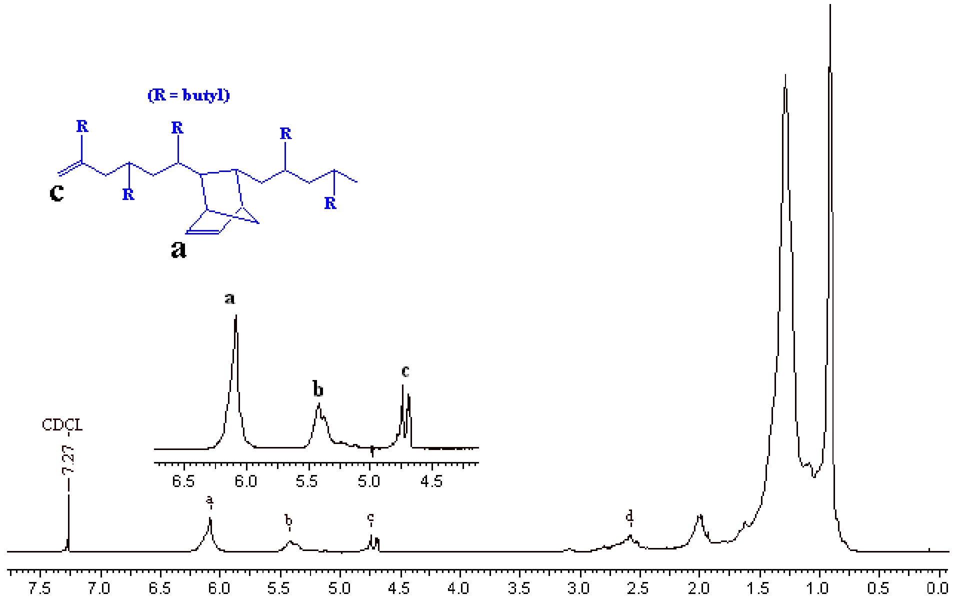


Fig 4.13 ^{1}H NMR of poly(hexene-1-*co*-2,5 norbornadiene) obtained by Cp$_2$ZrCl$_2$ catalyst (table 4.4, run no 3)

The ^{13}C NMR of the copolymer obtained by both Cp$_2$ZrCl$_2$ (**fig-4.14**) and rac Et(Ind)$_2$ ZrCl$_2$ (**fig-4.16**) catalysts showed the presence of various internal unsaturation, which arise due to migration of Zr$^+$ along the main chain or on side chain.

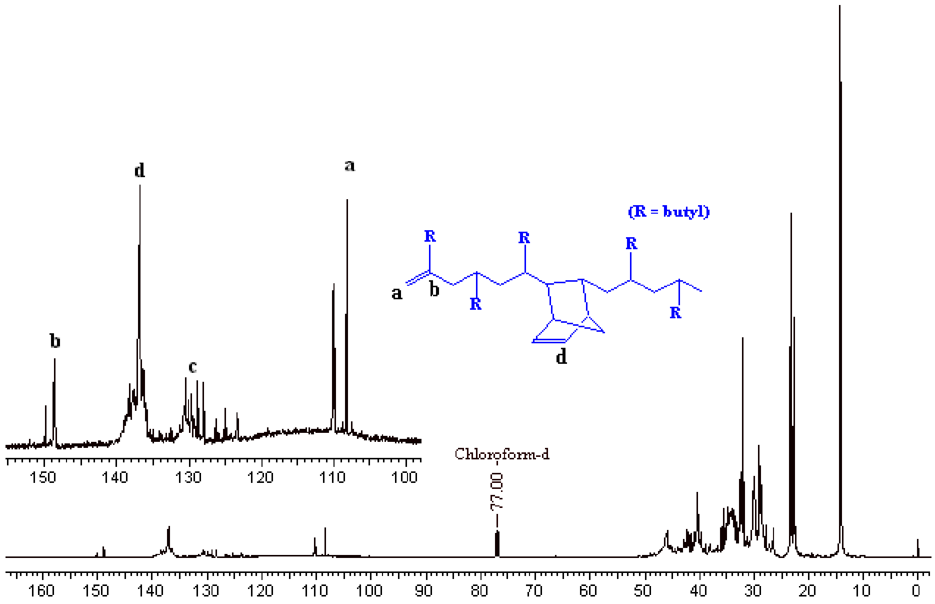


Fig-4.14 ^{13}C NMR of poly(hexene-1-*co*-2,5 norbornadiene) obtained by Cp_2ZrCl_2 catalyst (table 4.4, run no 3)

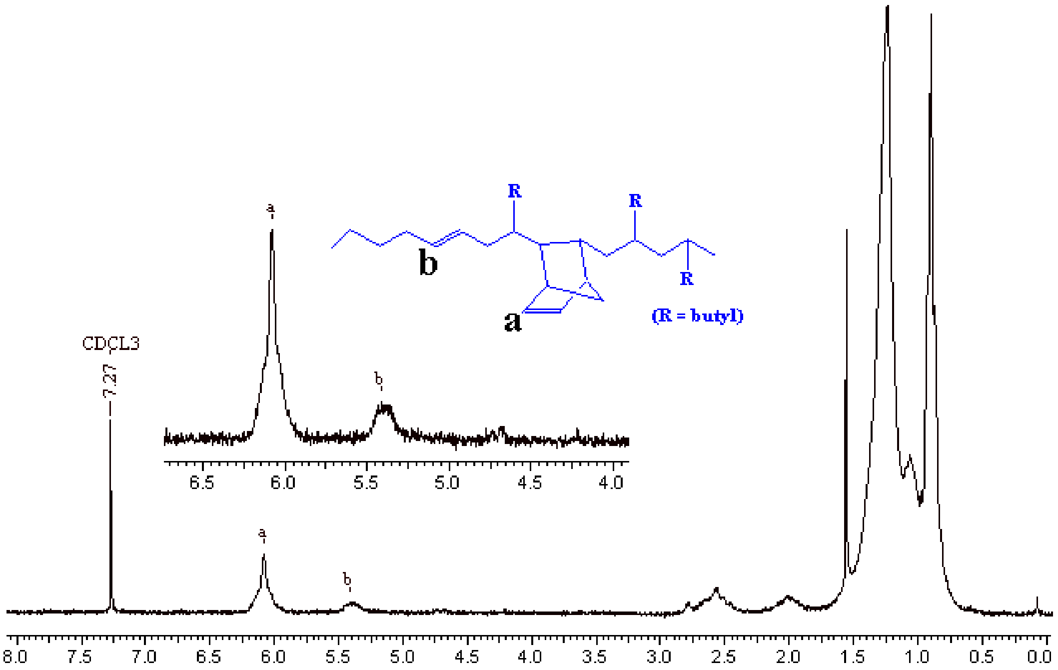


Fig-4.15 ^{1}H NMR of poly(hexene-1-*co*-2,5 norbornadiene) obtained by *rac* $Et(Ind)_2ZrCl_2$ catalyst

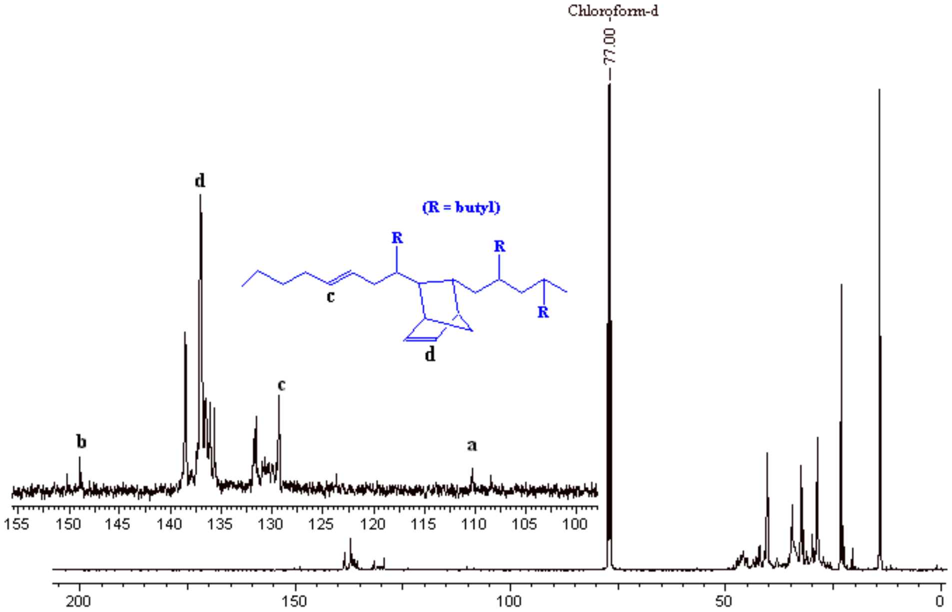


Fig-4.16 ^{13}C NMR of poly(hexene-1-co-2,5 norbornadiene) obtained by *rac* Et(Ind)$_2$ZrCl$_2$ catalyst

No crosslinking was observed during copolymerization with (CH$_3$)$_2$SiCp$_2$ZrCl$_2$ catalyst as was reported earlier for ethylene-2,5 norbornadiene copolymerization [16].

4.4 Conclusions

Copolymerization of hexene-1 with 2,5-norbornadiene using metallocene/MAO catalyst system occurs exclusively through one of the two equally reactive endocyclic double bonds for unbridged as well as ethylene bridged catalysts. No crosslinking occurs during copolymerization with any of the catalysts examined. The amount of incorporation of diene, catalytic activity, number average molecular weight (Mn), regio errors and end groups depend on the metallocene used and also on the experimental conditions.

The results of this study highlight the occurrence of regio errors in presence of diene using highly regio specific metallocene catalysts. The occurrence of regio errors was further confirmed by copolymerization with a bicyclic olefin like norbornene. The regio errors were also found to have strong influence on the number average molecular weight of the copolymer.

4.5 References

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Chapter 5. Alkylation of phenol with terminally vinylidene unsaturated poly(hexene-1)

5.1 Introduction

Functional poly(olefin)s have assumed importance because they contribute to new properties to otherwise inert poly(olefin)s [1-5]. Appropriately functionalized poly(olefin)s are useful as adhesion promoters, are capable of being coated, painted or dyed. Additionally, the functional groups either on the polyolefin backbone or at the chain end can be used for the synthesis of graft and block copolymers, which find application as compatibilizers and interfacial agents.

There are two broad approaches to the synthesis of functional poly(olefin)s, namely, "*chain end*" functionalization and "*in chain*" functionalization**.** Synthesis of functional poly(olefin)s by the first method involves either chemical reactions on preformed, terminally unsaturated poly(olefin)s or through use of appropriate chain transfer agents, whereas, the second approach involves the copolymerization of olefins with precursors which do not interfere in polymerization, followed by organic chemical transformations on the preformed polymers.

Synthesis of terminally functionalized poly(olefin)s by chain transfer method involves the use of appropriate chain transfer agent in metallocene catalyzed polymerization of olefins. The most commonly used chain transfer agents in heterogeneous Ziegler-Natta catalysts are molecular hydrogen [6-8] and $ZnEt_2$ [9]. Marks and coworkers studied silanes as efficient chain transfer agents in olefin polymerization using homogeneous catalysts[10, 11]. Xu and Chung [12, 13] demonstrated that organoboranes containing a B-H group are efficient chain transfer agents. Hessen and coworkers studied thiophene as a chain transfer agent in ethylene polymerization using neutral lanthanum catalyst system [14, 15]. More recently Chung and Dong reported the consecutive chain transfer to p-methylstyrene in presence of hydrogen during metallocene catalyzed copolymerization of propylene and p-methylstyrene [16]. There are several reports in the literature which define synthetic strategies for poly(olefin)s bearing various terminal functional groups such as OH, COOH, NH_2 etc by post polymerization functionalization of terminally unsaturated poly(olefins)s [17-25].

Metallocene and post metallocene catalysts offer significant advantages for the synthesis of functional poly(olefin)s. When α-olefins are polymerized using homogeneous metallocene / MAO (methyl aluminoxane) catalysts, several chain transfer reactions (such as β-hydrogen transfer etc) are found to occur. Such chain transfer reactions result in terminally unsaturated poly(olefin)s. High degree of terminal unsaturation(> 95%) and narrow molecular weight distribution (MWD = 2) are some of the distinguishing features of poly(olefin)s obtained using metallocene catalysts.

In this chapter synthesis of phenol/2,6-dimethyl phenol terminated poly(hexene-1) by alkylation of phenol/2,6 dimethyl phenol with vinylidene terminated poly(hexene-1) will be discussed. Characterization of phenol terminated poly(hexene-1) by NMR, (especially ^{31}P NMR), UV, IR etc. are presented.

5.2. Experimental

5.2.1 Materials

Vinylidene terminated poly(hexene-1) with Mn varying from 400-10 000 reported in chapter-3 was used for the alkylation of phenol / 2,6 dimethyl phenol. Phenol and n-hexane were obtained from s.d. fine chemicals, Boisar, India. Nonyl phenol was obtained from Herdillia Chemicals, Mumbai. 2,4,4-trimethyl 1-pentene, 2,6-dimethyl phenol, n-butylphenol, bisphenol-A, 2-chloro-1,3,2-dioxophospholane (DOP), and chromium tris (acetylacetonate) were obtained from Aldrich, USA. $BF_3:OEt_2$ was obtained from Fluka (Germany).

5.2.2 Purification

Vinylidene terminated poly(hexene-1)s obtained from chapter-3 were dissolved in n-hexane and dried over anhydrous sodium sulphate. Phenol and 2,6-dimethyl phenol were purified by distillation. n-Hexane was treated with H_2SO_4 to remove sulfur distilled and dried over sodium metal wire. 2,4,4-trimethyl 1-pentene was distilled under nitrogen atmosphere followed by distillation by freeze and thaw technique. $BF_3:OEt_2$ was distilled under reduced pressure and stored at 0^0C. 2-Chloro-1,3,2-dioxophospholane (DOP), bisphenol-A and chromium tris (acetylacetonate) were used as received.

5.2.3 Functionalization

Alkylation of phenol/2,6-dimethyl phenol

The alkylation of phenol/2,6-dimethyl phenol with either 2,4,4-trimethyl 1-pentene or vinylidene terminated poly (hexene-1) was carried out as described below.

A four necked 250 mL round bottom flask equipped with a magnetic needle, reflux condenser, addition funnel, septum adapter and thermowell was flame dried and cooled under argon. 50 mL of dried n-hexane was transferred into the flask by syringe followed by 50 mmol of phenol/2,6-dimethylphenol. The terminally unsaturated oligomer (10 mmol of > C=C) (dried) was dissolved in 50 mL of n-hexane in a separate round bottom flask. The oligomer solution was transferred into the separating funnel of four-necked flask by cannula. The boron trifluoride etherate catalyst (7.6 mmol) was added into the phenol solution followed by dropwise addition of oligomer solution from a separating funnel at 40-45^{0}C.

After the olefin addition (8-10 h), the temperature was raised to 50-55^{0}C and stirring was continued for 30 h. The flask was cooled to room temperature and approximately 150 mL of water was slowly added and the content of the flask was transferred to a separating funnel. The aqueous layer was removed and the organic layer was washed 8-10 times with hot water (40 -50^{0}C) followed by washing repeatedly with alkali and 50% aqueous solution of methanol. The alkali and methanol were removed by washing with cold water. Washing was continued until the aqueous and organic layers were free of phenol.

The organic layer was washed with 0.1 N HCl. The acid was removed by further washings, and the organic layer was dried over anhydrous Na_2SO_4. Finally the solvent was removed by rotary evaporation and the product was dried at 60^0 C under vacuum.

Alkylation of bisphenol-A

Alkylation of bisphenol-A was carried in 1,2-dichloroethane at 70^{0}C (since bisphenol-A is insoluble in n-hexane at 50^{0}C) using procedures identical to that for phenol. The reaction was worked up by extracting the organic layer several times with water followed by washing the organic layer with acetone to remove all unreacted bisphenol-A. The acetone was removed by further washing with water.

5.2.4 Analysis

The number average degree of functionality (Fn) was calculated as

Fn (mol %) = (Mn by VPO / Mn by NMR or UV) X 100.

Quantitative analysis of phenol end group using UV/Visible spectrophotometer

Concentration of phenol group in functionalized poly(hexene-1) was determined using UV/Visible spectrophotometer using n-butyl phenol as the standard. A standard experiment was carried out with n-butyl phenol.

First various solutions of n-butyl phenol in n-hexane was made in different concentration range. Absorbance for each solution was measured at λ_{max} =276.5 nm. Taking absorbance in the X- axis and concentration in the Y-axis, a standard plot was made. A straight line was obtained passing through the origin, and slope was calculated. Then a known weight of phenol terminated poly (hexene-1) dissolved in 10 mL of n-hexane and absorbance for the corresponding solution was noted. Knowing the absorbance of phenol terminated poly (hexene-1) solution and the slope of the line for n-butyl phenol, the concentration of phenol group in the poly (hexene-1) was determined.

Quantitative analysis of isomer composition (ortho / para) by ^{31}P NMR

A stock solution 0.4 mL of $CDCl_3$/pyridine (3:1, v/v) was prepared, in to which 200 mg (10%) of chromium tris (acetylacetonate) as a spin lattice relaxation reagent was added followed by 0.15 mL of 2-Chloro-1,3,2-dioxophospholane (DOP). The entire solution was transferred in to a 5 mm NMR tube containing approximately 100 mg of nonylphenol or phenol terminated poly (hexene-1). The solution was allowed to react for 10 min before analysis.

FT-IR: FT-IR spectra were obtained on a Perkin-Elmer 16 PC Spectrophotometer. A spectrum was recorded in chloroform solution. Spectra were corrected for $CHCl_3$ absorption.

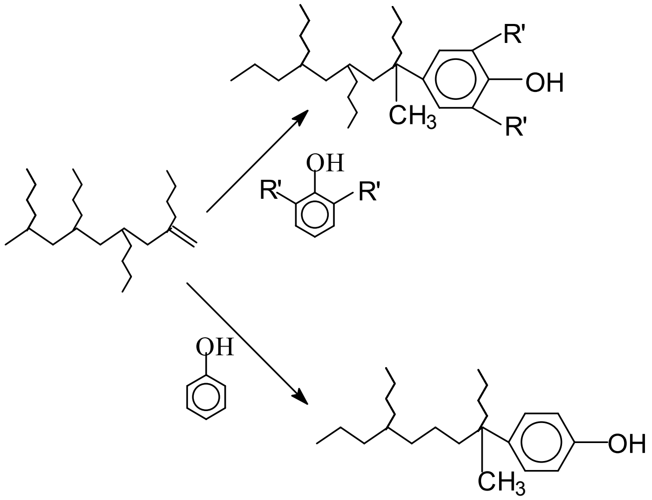
5.3 Results and discussion

The alkylation of phenol with *iso*-olefins in presence of acid catalyst to produce alkylphenols is a well known reaction. Para alkylphenols impart improved performance properties to the class of metallic detergents used in lubricating oils, known as "*phenates*". Additionally alkylphenols are the starting material for the preparation of a wide range of non-ionic surfactants called "*ethoxylates*". Activating iso-olefins in presence of an acid catalyst results in the formation of a carbocation which undergoes electrophilic substitution to activated aromatic rings.

Patil reported the alkylation of hydroquinone with vinylidene terminated EP copolymer (Mn = 870) having terminal vinylidene group >95% using amberlyst-15 catalyst [24]. Alkylation of phenol with telechelic vinylidene poly (isobutylene) using $BF_3{:}OEt_2$ catalyst was reported by Kennedy *et al* [26]. In both cases, para isomer as high as 90% was obtained. Alkylation of phenol with either poly (α-olefin)s (known as PAO, oligomers of decene-1) using amberlyst-15 catalyst or oligo (isobutylene) using $AlCl_3$

catalyst was also reported [27, 28]. However, the alkylated product was found to be a mixture of ortho and para (40-60%) isomers.

We explored the alkylation reaction of phenols with vinylidene terminated poly(hexene-1) with Mn 400 - 10 000 using BF_3:OEt_2 catalyst **(scheme-5.1)**.



Scheme-5.1 Alkylation of phenol/2,6 DMPh with vinylidene terminated poly(hexene-1)

5.3.1 Model alkylation of phenol with 2,4,4 trimethyl 1-pentene

To establish the experimental conditions, the alkylation of phenol with a model *iso*-olefin, namely, 2,4,4-trimethyl 1-pentene was carried out. Alkylation using BF_3:OEt_2 catalyst resulted in 4-(1,1,3,3-tetramethylbutyl) phenol in >95% yield and was characterized by melting point (84^0C) and ^{1}H NMR **(fig-5.1)**. The results are in agreement with literature data.

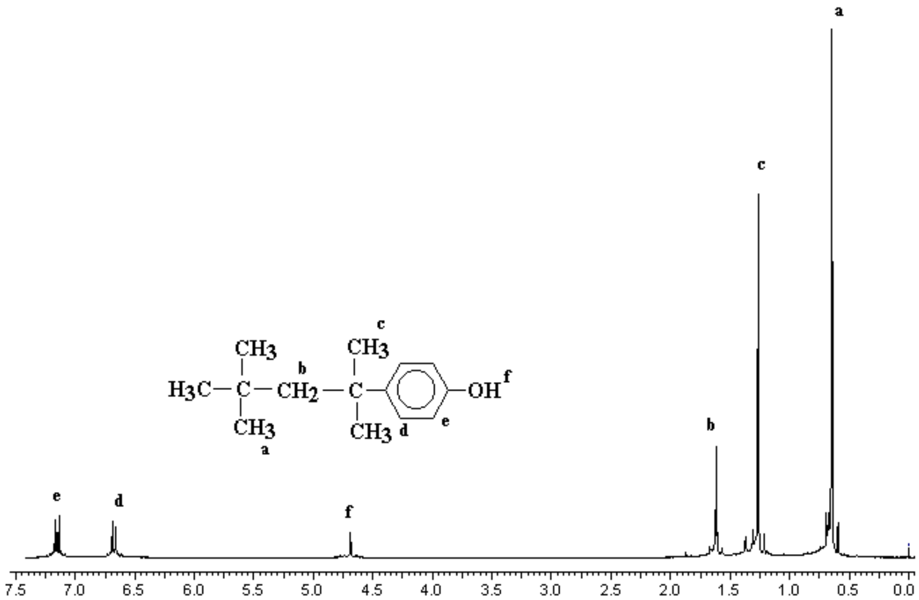


Fig-5.1 ^{1}H NMR of 4-(1,1,3,3-tetramethylbutyl) phenol

5.3.2 Alkylation of phenol/2,6-dimethylphenol/bisphenol-A with terminally vinylidene unsaturated poly(hexene-1)

After establishing the alkylation reaction conditions with a model olefin, namely, 2,4,4-trimethyl 1-pentene, alkylation of phenol/2,6-dimethyl phenol/bisphenol-A was carried out with vinylidene terminated poly(hexene-1) using BF_3:OEt_2 catalyst under similar reaction conditions. The samples of poly(hexene-1) as well as stoichiometry used for alkylation of phenol, 2,6-dimethyl phenol and bisphenol-A is shown in **table-5.1**. In all cases satisfactory material balance was obtained.

Alkylation was carried out with poly(hexene-1) having Mn in the range of 400 – 10 000. Good yields were obtained in all the runs except in few runs, where the low yield may be due to the loss of oligomers during work up. The higher amount of catalyst was used for high molecular weight polymers as unreacted terminal vinylidene unsaturation was observed at lower catalyst concentration.

Table-5.1 Alkylation of phenol / 2,6-dimethylphenol/bisphenol-A with vinylidene terminated poly (hexene-1) using BF_3:OEt_2 catalyst[a]

Run no	Poly(hexene-1)		PhOH mol	BF_3:OEt_2 mmol
	Mn	mol		
1	380	0.01	0.05	7.8
2	550	0.01	0.05	7.8
3	1080	0.01	0.05	15.6
4	1760	0.005	0.025	15.6
5	2760	0.0025	0.0125	15.6
6	4260	0.001	0.005	15.6
7	6840	0.001	0.005	15.6
8	10 020	0.001	0.005	15.6
Alkylation of 2,6-dimethyl phenol				
9	380	0.01	0.05	7.8
10	550	0.01	0.05	7.8
11	1080	0.01	0.05	15.6
12	1760	0.005	0.025	15.6
Alkylation of bisphenol-A				
13*	380	0.01	0.03	7.8
14*	550	0.01	0.03	7.8

[a] ***Reaction conditions:*** [phenol] = 1 M in n-hexane, [olefin] = 0.2 M in n-hexane, Temp = 50^0C, Time 36 h after addition of oligomer solution.

* Bisphenol-A was dissolved in 1,2-dichloroethane at 70^0C.

5.3.3 Characterization of phenol/2,6-dimethylphenol/bisphenol-A terminated poly(hexene-1)

The phenol/2,6-dimethylphenol terminated poly(hexene-1) was characterized by elemental analysis, NMR, FT-IR, UV etc. The results obtained are discussed below.

5.3.3.1 Elemental analysis

The elemental analysis results are shown in **table-5.2**. Good agreement was observed between the values calculated and found with in the experimental errors.

Table-5.2 Elemental analysis of phenol terminated poly(hexene-1)

Run no	Before alkylation				After alkylation			
	Calculated		found		Calculated		found	
	C	H	C	H	C	H	C	H
1	85.71	14.29	85.45	14.40	83.91	12.35	84.47	13.40
2	85.71	14.29	84.14	15.35	84.47	13.55	84.55	12.36
3	85.71	14.29	85.41	14.83	85.08	13.73	85.53	13.68
4	85.71	14.29	84.14	13.58	85.43	14.04	85.40	12.80
5	85.71	14.29	86.21	13.39	85.57	14.16	85.83	12.37

5.3.3.2 NMR (^{1}H, ^{13}C and ^{31}P)

Structural analysis of phenol terminated poly(hexene-1) was carried out by ^{1}H, ^{13}C and ^{31}P NMR. The ^{1}H NMR obtained is shown in **fig-5.2**.

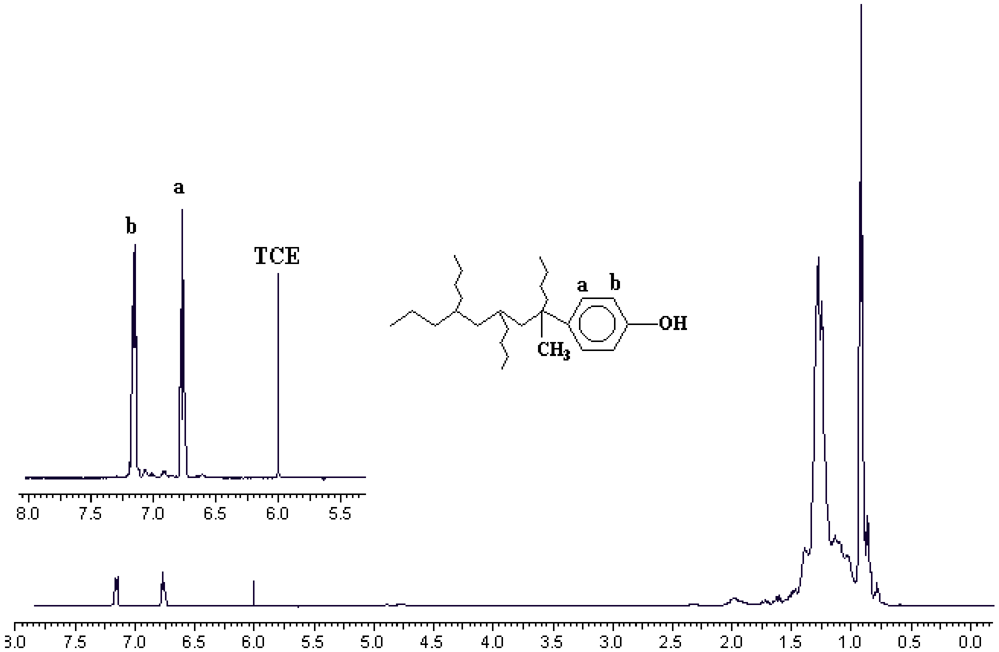


Fig-5.2 ^{1}H NMR of phenol terminated poly(hexene-1) (from run no 2)

The ^{1}H NMR spectra (tetrachloroethane-d_2 solvent was used to avoid peaks in aromatic region) shows exclusively para alkylated phenol. It was further confirmed by ^{13}C NMR (**fig-5.3**).

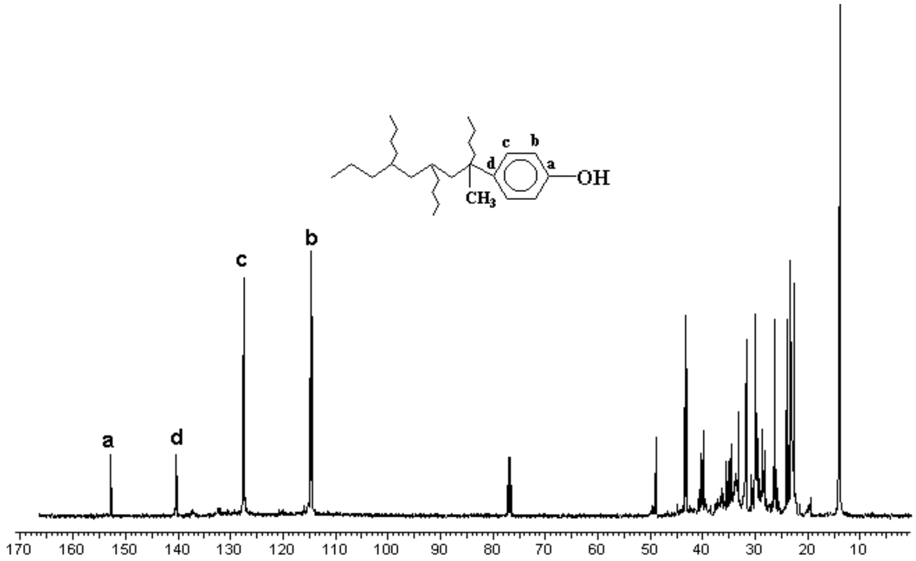
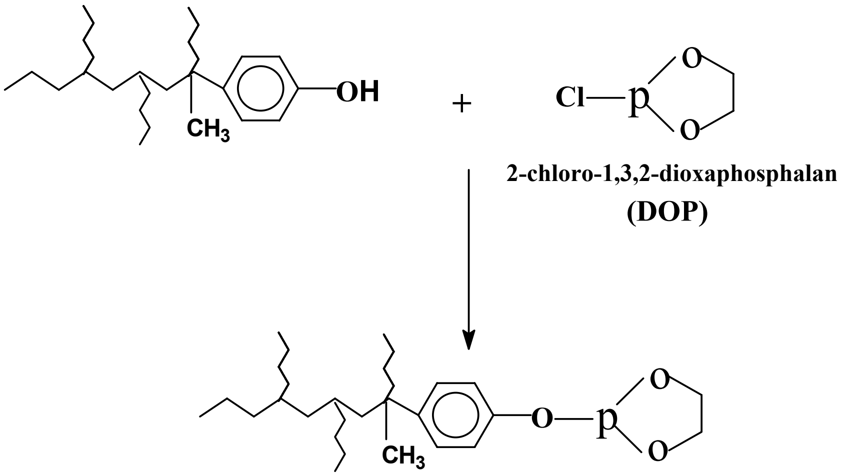


Fig-5.3 ^{13}C NMR of phenol terminated poly(hexene-1) (from run no 2)

Although, the ^{13}C NMR spectrum differentiates the ortho and para isomers, however presence of small amount of ortho/para disubtituted phenol overlaps with para isomer. Hence, in order to confirm the isomer distribution in the phenol terminated poly(hexene-1), a derivatization method reported by Chan et al [29] was employed.

According to this method, derivatization of alkyl phenols with phosphitylating reagent followed by ^{31}P NMR analysis results in quantification of para and ortho/para disubstituted phenols **(scheme-5.2)**. However this method does not separate ortho and ortho/para disubstituted isomers. The best reagent for derivatization was found to be 2-chloro-1,3,2-dioxaphospholane (DOP).



Scheme-5.2 Derivatization of phenol terminated poly(hexene-1) with DOP

Derivatization was first carried out with nonyl phenol as a reference. ^{31}P NMR spectrum is shown **in fig-5.4** and **5.5**. The peaks at 127-129 ppm are due to the product. The peak at 167.5 ppm was also observed due to excess DOP. The protic impurities present in the system reacts with DOP resulting in a peak at 121 ppm.

Expanding the product region (127-129 ppm) revealed more information about different isomers. The major peak (>95%) between 126.8-127.8 was attributed para isomer. The minor peak between 128-129 was attributed to either ortho or ortho/para disubstituted phenol.

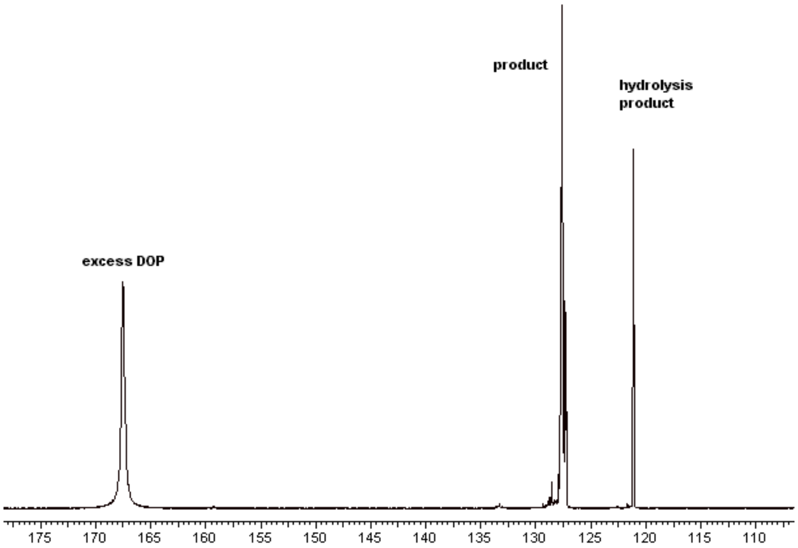


Fig 5.4 ^{31}P NMR of derivatized nonyl phenol

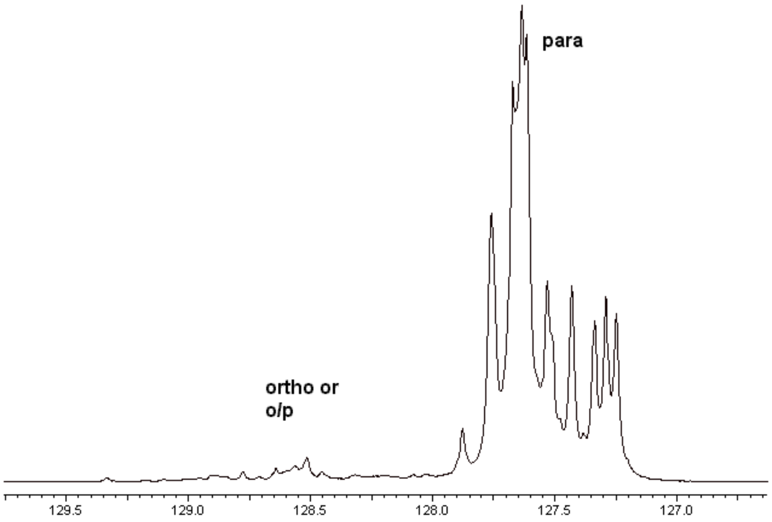


Fig 5.5 Expanded region of 127-129 ppm

Derivatization was also carried out for phenol terminated poly(hexene-1) under conditions similar to that employed for nonyl phenol. ^{31}P NMR spectrum is shown in **fig-5.6** for the compound obtained from run number 2 (**table-5.1**).

The expanded region form 126 – 129 ppm shows presence of small amount of ortho or o/p disubstituted phenol. It was observed that use of higher molecular weight oligomers of poly(hexene-1) decreases the selectivity for para substitution as shown in **fig-5.7**.

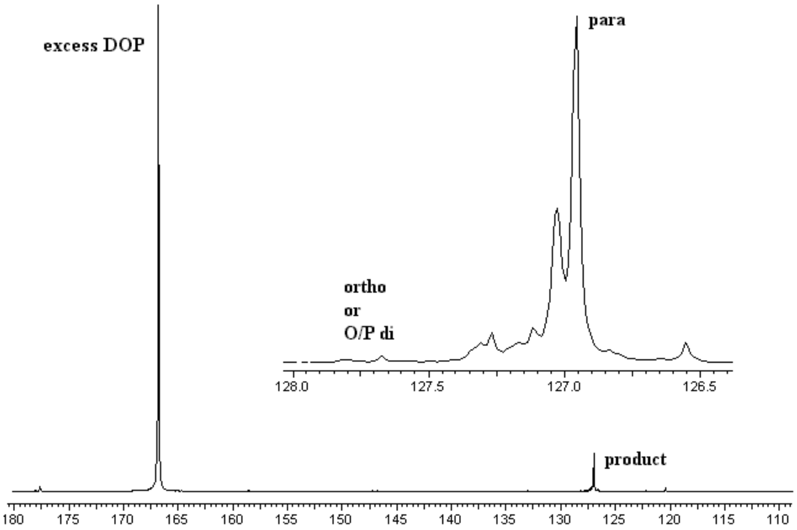


Fig-5.6 ^{31}P NMR of derivatized phenol terminated poly(hexene-1) (from run no 2)

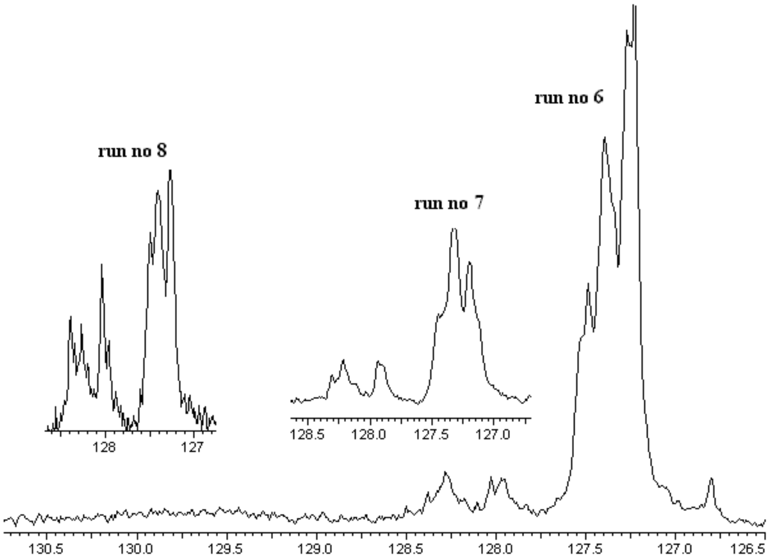


Fig-5.7 ^{31}P NMR of high molecular weight phenol terminated poly(hexene-1)

As shown in **fig-5.7** the intensity of the peaks for corresponding ortho or ortho/para disubstituted isomers increases from run no 6-8. The ^{1}H NMR for run no 6-8 also showed similar results as shown in **fig-5.8.**

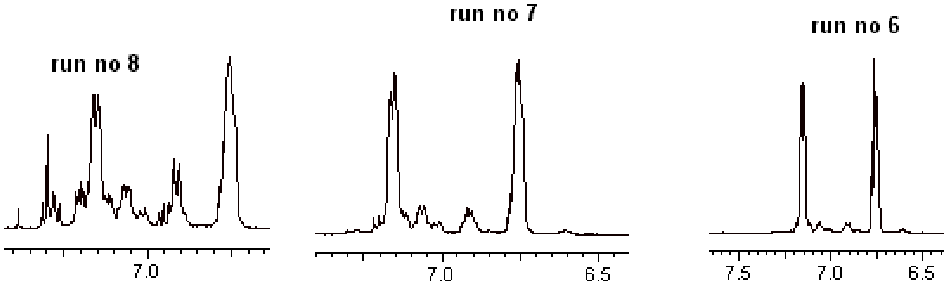


Fig-5.8 ^{1}H NMR (aromatic region) of runs 6-8

The ^{31}P NMR results obtained are shown in **table 5.3** including other characterization data like UV and VPO.

5.3.3.3 Quantitative estimation of phenol by UV/titration

Concentration of phenol group in phenol terminated poly(1-hexene) was determined using UV/Visible spectrophotometer by taking n-butylphenol as a standard. Known concentrations phenol terminated poly(hexene-1) in n-hexane were made and their corresponding absorbance were measured at λ_{max} =276.5 nm. The concentration of phenol in phenol terminated poly(hexene-1) was measured from the slope of n-butyl phenol (y = mx). The number average molecular weight (Mn) was measured by comparing the concentration of phenol and Mn obtained by VPO. The results obtained are shown in **table-5.3**.

5.3.3.4 FT-IR

The FT-IR spectra for phenol terminated poly(hexene-1) showed a strong peak at 1512 cm^{-1} due to aromatic C=C streching and virtual absence of a shoulder at 3065 cm^{-1} and peaks at 1640 and 888 cm-1 due to terminal vinylidene double bond **(fig-5.9** and **5.10).**

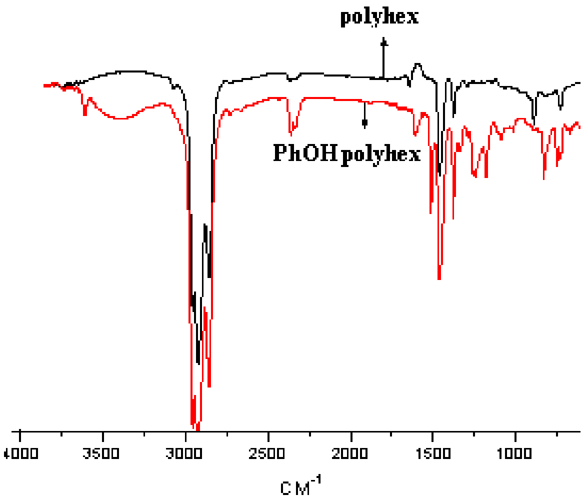


Fig-5.9 FT-IR spectra of poly(hexene-1) and phenol terminated poly(hexene-1) (from run no 2)

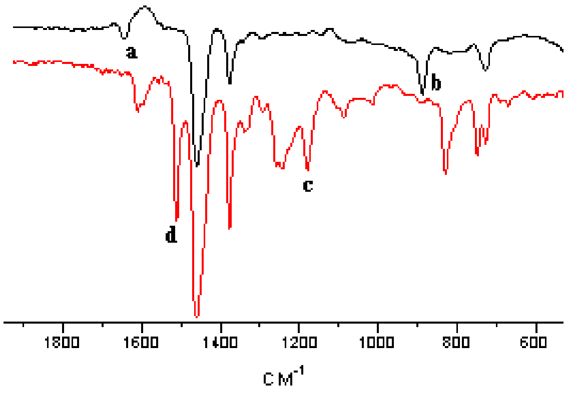


Fig-5.10 Expanded region of FT-IR

Peaks: (a) 1640cm^{-1} C=C streching, (b) 888 cm^{-1} C-H alkene bending, (c) 1180 cm^{-1} C-O streching, (d) 1512 cm^{-1} aromatic C=C sreching.

Table-5.3 Characterization of the phenol terminated poly(hexene-1)s

Run no	Mn							Isomer distribution by ^{31}P NMR (%)		Fn mol% **c / e**
	before alkylation				after alkylation					
	VPO	NMR	End groups (mol%)		VPO	NMR	UV	ortho	para	
			a	**b**	**c**	**d**	**e**			
1	380	390	98	2	510	540	550	<5.0	>95.0	93.0
2	550	560	97	3	680	740	750	<5.0	>95.0	91.0
3	1080	1150	94	6	1280	1480	1430	<5.0	>95.0	90.0
4	1760	1880	92	8	1920	2300	2200	8.0	92.0	87.0
5	2760	2980	90	10	3000	3620	3530	14.0	86.0	85.0
6	4260	4400	88	12	4380	n.d	5410	19.0	81.0	81.0
7	6840	7220	85	15	7200	n.d	9200	21.0	79.0	78.0
8	10 020	11 090	83	17	10 300	n.d	14 000	23.0	77.0	74.0

a = vinylidene, b = internal

The number average degree of functionality was found to decrease with increase in number average molecular weight. This is presumably a consequence of the decreased mol% of the vinylidene unsaturation in the oligomers.

The structure of 2,6 dimethyl phenol terminated poly(hexene-1) was also examined by ^{1}H and ^{13}C NMR (**fig-5.11** and **5.12**). The NMR analysis revealed that the alkylation of 2,6-dimethyl phenol with vinylidene terminated poly(hexene-1) occurs selectively at para position.

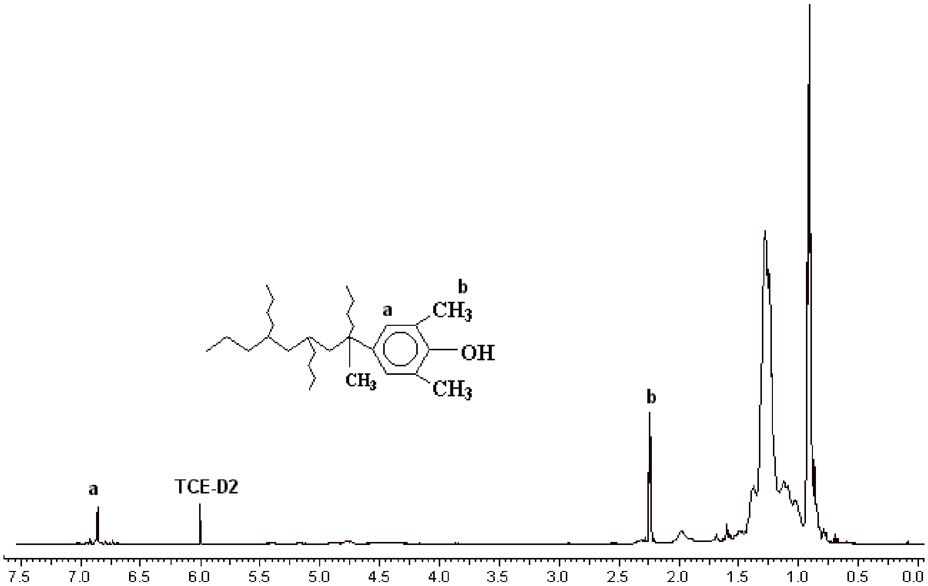


Fig-5.11 ^{1}H NMR of 2,6-dimethylphenol terminated poly(hexene-1) (run no11)

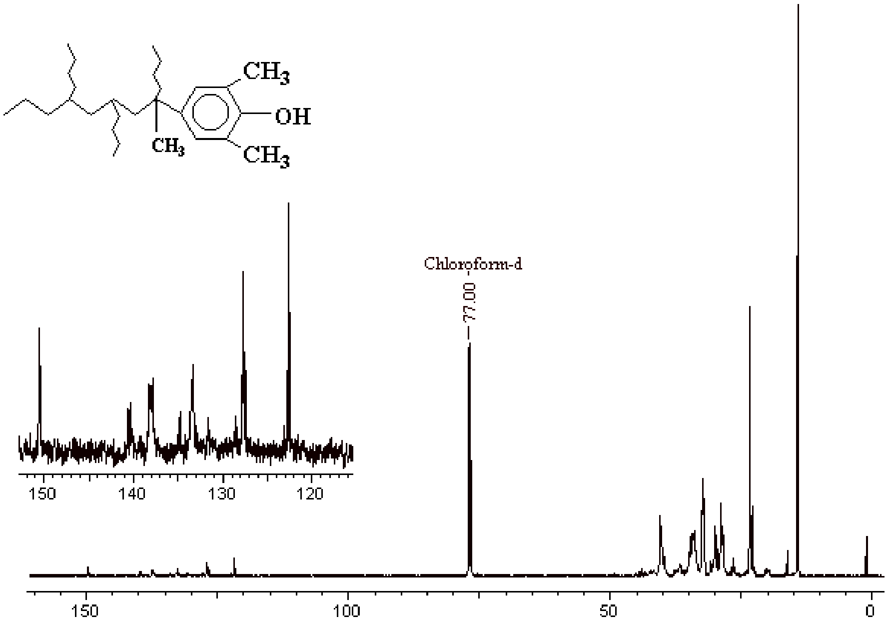


Fig-5.12 ^{13}C NMR of 2,6-dimethylphenol terminated poly(hexene-1) (run no 11)

The alkylation of bisphenol-A (BPA) with vinylidene terminated poly(hexene-1) using BF_3OEt_2 catalyst in 1,2 dichloroethane at 70^{0}C was attempted (**run numbers 13 & 14 table-5.1**). In this particular reaction, the unreacted bisphenol-A from the functionalized oligomer was removed by further washings with acetone. The products obtained were characterized by VPO and NMR (^{1}H & ^{13}C) as shown below (**fig-5.13 to 5.15**).

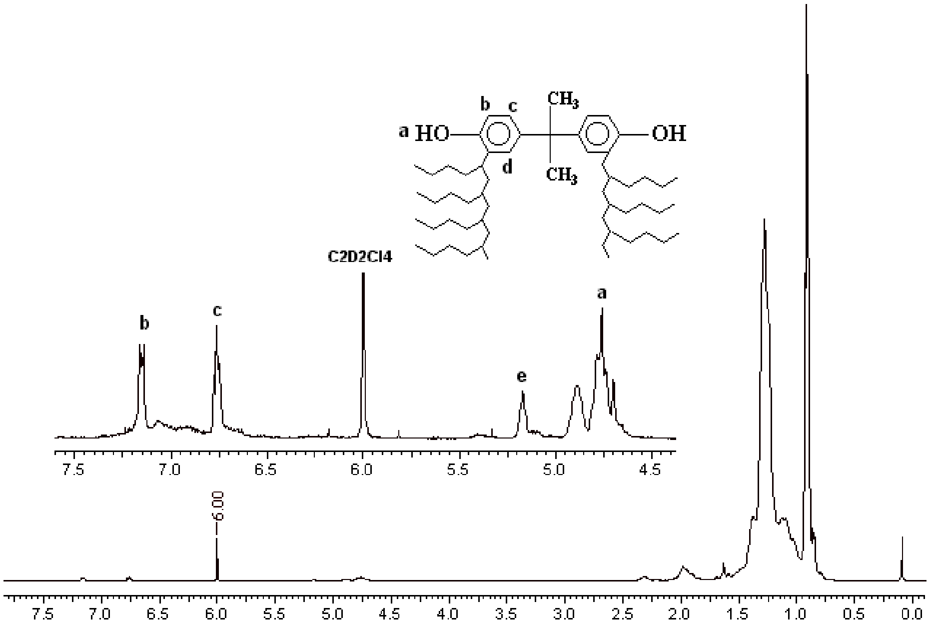


Fig-5.13 ^{1}H NMR of BPA terminated poly(hexene-1) (run no 14)

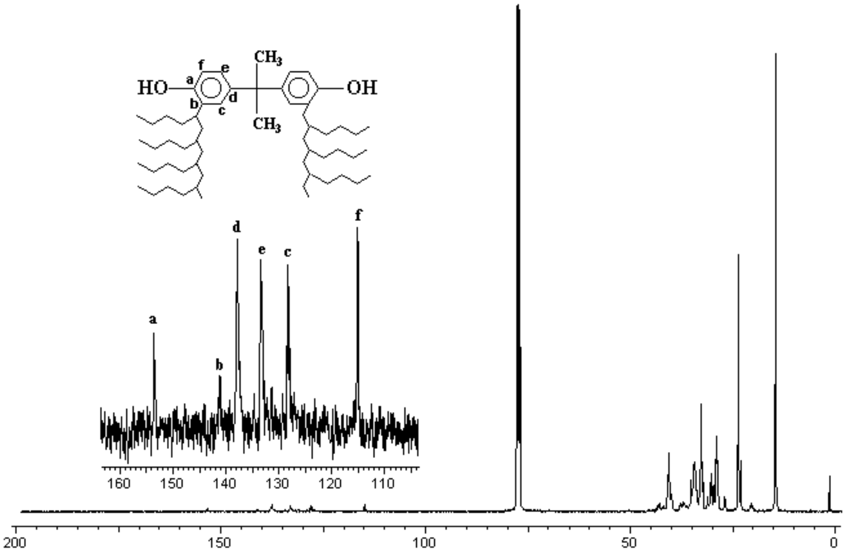


Fig-5.14 ^{13}C NMR of BPA terminated poly(hexene-1) (run no 14)

Although the ^{1}H NMR showed two aromatic protons (peaks **b** and **c**), the presence another meta proton (peak **d**) (assuming mono akylation at ortho position) was not detected. However, the ^{13}C NMR (**fig-5.14**) showed all the six expected carbons. The assignment was further confirmed by the absence of three tetra substituted carbons (peaks **a**, **b** and **d**) in DEPT as shown below.

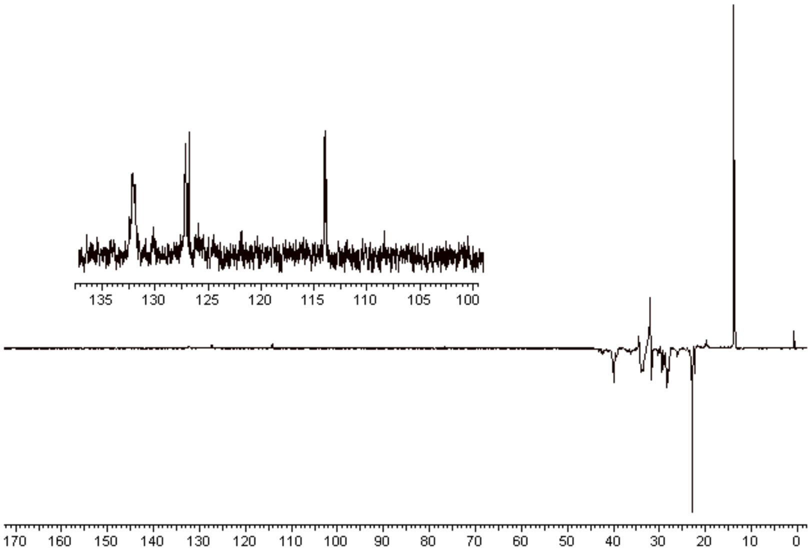


Fig-5.15 DEPT spectra of BPA terminated poly(hexene-1) (run no 14)

In both runs (**13 and 14**) the number average molecular weight of the alkylated products was found to be lower (560 and 750) than expected. Based on these results, it is not possible to conclusively establish the structure of the product. Further studies are necessary.

5.4 Conclusions

Poly(hexene-1) bearing terminal phenol/2,6-dimethylphenol functional group could be synthesized by alkylation of phenol/2,6-dimethylphenol with terminal vinylidene unsaturation of poly(hexene-1) using BF_3:OEt_2 catalyst. The number average degree of functionality (Fn) as high as 95 mol % was obtained for low molecular weight oligomers with >95 mol% para selectivity. The selectivity of para isomer was found to decrease with increase in number average molecular weight (Mn). Alkylation of bisphenol-A with poly(hexene-1) in 1,2-dichloroethane at 70^0C gave preliminary indication of the formation of O,O^1- alkylated bisphenol-A. However, further work is necessary to conclusively establish the structure of the product.

5.5 References

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Chapter 6. Synthesis of N-poly(alkenyl) alkylamides by Ritter reaction of vinylidene terminated poly(hexene-1) with nitriles

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6.1 Introduction

N-alkylacrylamides, such as N-isopropyl, N-*tert*-butylacrylamide, N-n-octylacrylamide etc are an important class monomers for the synthesis of polymers which are useful as sizing agents, thickeners and water soluble fibers etc [1]. Amongst these N-isopropylacrylamide is an important monomer due to the commercial importance of its polymer. Poly(N-isopropylacrylamide) (PNIPAAM) has been widely studied for its novel thermal behaviour in aqueous media [2]. It possesses inverse solubility upon heating, a property contrary to the behaviour of most polymers in organic solvents under atmospheric pressure near ambient temperature. Its macromolecular transition from a hydrophilic to hydrophobic structure occurs at what is known as lower critical solution temperature (LCST). Experimentally, this temperature lies between 30-35^{0}C, the exact temperature being a characteristic of the microstructure of the polymer. At molecular level, poly(N-isopropylacrylamide) has been used in many forms including single chains, macroscopic gels, microgels, latexes, thin films, membranes, coatings, and fibres.

Another area where N-alkylacrylamides (alkyl = C_6 to C_{18}) are widely used is hydrophobically modified polyelectrolytes [3-6]. These polymers consist of a water soluble backbone containing a small proportion of hydrophobic groups (<3 mol%) usually in the form of pendant side chains or terminal groups. In aqueous solution the hydrophobic groups aggregate to minimize their exposure to water and thereby form hydrophobic microdomains in a fashion analogous to that of surfactants above their critical micelle concentration. Above a certain concentration (C_{ag}), intermolecular hydrophobic interactions lead to the formation of a three dimensional network of polymer chains resulting in an increase in the apparent molecular weight and consequently, a substantial viscosity enhancement. This concentration occurs well below the entanglement overlap observed in the unmodified parent polymer of equivalent molecular weight. Upon elevated shear solicitation, these network structures are disrupted. However, if this solicitation is removed, the associations between the polymer chains reform and the viscosity recover its initial value.

The reversible association/dissociation process gives rise to particular rheological behaviour as a function of shear rate or shear time. These thickening properties depend on different parameters such as length of the hydrophobic groups, degree of modification and repartition along the hydrophilic backbone [7-10]. According to the method of synthesis, the polymer can present a blocky or a random distribution of the hydrophobic groups. Such materials can be prepared either by chemical modification of a precursor polymer or by free radical copolymerization. The former route is mainly applied to the derivatives of cellulose [11, 12], poly(oxyethylene) [13-15] and poly(acrylic acid) [16, 17]. The free radical copolymerization concerns essentially copolymers based on acrylamide. However, the insolubility of the hydrophobic monomer in water can generate some difficulties. Different experimental strategies are available to overcome this problem [18]. The hydrophobic monomer can be dispersed into the water medium or made soluble by the use of a water miscible co-solvent. In this way, the copolymers have a random structure. An alternative approach, first developed by Evani [19] and Turner et al. [20], involves the use of an aqueous surfactant solution, which ensures the solubilization of the hydrophobe within the micelles dispersed in the water continuous medium. This one-step micellar copolymerization route was found to be well suitable for preparation of products with both a high molecular weight and an adequate hydrophobe incorporation for use as aqueous thickeners [19,21]. The formation of a blocky structure, promoting interactions between the hydrophobic groups, was first suggested by Peer [22] and confirmed experimentally by Dowling et al. [23] and Ezzel et al. [24] from photophysical studies on polyacrylamide derivatives. The length of the hydrophobic blocks could be monitored by adjusting the hydrophobe to surfactant ratio [25,26], i.e, the number of hydrophobe per micelle ($\mathbf{N_H}$). Nevertheless, no clear information has been established about the exact microstructure of these copolymers such as the size and the number of the hydrophobic blocks.

Hydrogels are another class of water swollen networks of hydrophilic homopolymers or copolymers. These networks may be formed by various techniques. However, the most common synthetic route is the free radical polymerization of vinyl monomers in the presence of a difunctional crosslinking agent and a swelling agent. The resulting polymer is interesting in that it exhibits both liquid-like and solid like properties. The liquid-like properties result from the fact that the major constituent (>80%) is water. However, the polymer also exhibits solid like properties due to the network formed by the crosslinking reaction. These solid-like properties take the form of a shear modulus, which is evident upon deformation. If an ionic or hydrophobic monomer is incorporated into the hydrogel network, a responsive polymer is often created. This responsiveness takes the form of a volume phase transition, which is characterized by a sudden change in the degree of swelling upon a small change in environmental conditions. This behavior follows the trends seen in linear polymer systems showing response to environmental pH, salt concentrations, and temperature. For example it is well known that poly(N-isopropylacrylamide) contains a LCST at ~34^0C. Likewise N-isopropylacrylamide hydrogels undergo a discrete collapse of the polymer network ~32^oC. Discrete changes in swelling behavior may also be seen in hydrogels incorporating a monomer containing a carboxylic acid moiety. Therefore, with changes in pH, the hydrogel's charge density will change and thus, the swelling behavior of the gel. By changing the amount of water associated with the network, one is effectively changing the hydrophilic/hydrophobic balance and therefore, one may utilize these systems to reversibly interact with hydrophobic materials.

N-alkylacrylamides are thus a useful class of monomers. N-isopropyl and N-octylacrylamide are generally prepared by the Ritter reaction of acrylonitrile with isopropanol or 2,4,4-trimethyl-1-pentene [27]. Higher N-alkylacrylamides such as N-n-dodecyl and N-n-octadecyl acrylamide are prepared by the reaction of corresponding amines with acryloyl chloride [28-30].

Poly(olefin) oligomers with high vinylidene unsaturation at the terminal end is a potential precursor to N-alkylacrylamides via Ritter reaction. Such a reaction may provide access to a diverse range of hydrophobically modified acrylamides with varying chain lengths of the alkyl chain as well as branching characteristics.

In this chapter we explore the feasibility and generality of Ritter reaction with vinylidene terminated poly(hexene-1) oligomers.

6.2. Experimental

6.2.1 Materials

Vinylidene terminated poly(hexene-1) with Mn varying from 400-10 000 reported in chapter-3 was used for Ritter reaction. Acrylonitrile, acetonitrile, benzonitrile, H_2SO_4, chlorobenzene, n-pentane and n-hexane were obtained from s.d. fine chemicals, Boisar, India.

6.2.2 Purification

Vinylidene terminated poly(hexene-1) obtained from chapter-3 was dissolved in n-hexane and dried over anhydrous sodium sulphate. Acrylonitrile, acetonitrile and benzonitrile were purified by distillation and stored at 0^0C. n-Pentane and n-hexane were treated with H_2SO_4 to remove sulfur and distilled before use. H_2SO_4 was used as received.

6.2.3 Ritter reaction of vinylidene terminated poly(hexene-1) with nitriles

Ritter reaction was carried out by a solvent free method for low molecular weight oligomers (Mn < 1000). However, for high molecular weight polymers, the reaction was carried out in chlorobenzene. Reaction was carried out with the vinylidene terminated poly(hexene-1) in presence of acrylonitrile using 70% H_2SO_4 as catalyst. A two necked round bottom flask, fitted with a dropping funnel and reflux condenser was charged with 5.2g (0.1 mol) of acrylonitrile and 70% H_2SO_4 (2 mL) was transferred into the round bottom flask at room temperature. After the addition, temperature was increased to 75^0C, followed by addition of 3.8 g (0.01 mol) of liquid oligomer (Mn = 380) from dropping funnel. The addition was continued for a period of 1 hour. After the addition, the reaction was continued for a period of 12 hours. The reaction was worked up by addition of 10-15 mL of distilled water was slowly added, and both organic and aqueous layers were transferred into a separating funnel. The product was extracted with diethyl ether to obtain a yield of 4.2 g of a viscous liquid. In case of high molecular weight polymers, the polymer solution either in chlorobenzene or n-hexane was transferred from dropping funnel to the round bottomed flask containing the mixture of acrylonitrile and 70% H_2SO_4. Similar procedure was followed in the case of acetonitrile and benzonitrile.

6.2.4 Analysis

The number average molecular weight (Mn) of functionalized poly(hexene-1) was determined by VPO as well as ^{1}H NMR. Structural analysis was carried out by both ^{1}H and ^{13}C NMR. The peaks due acrylamide group were observed at 6.2, 5.5 and 5.2 ppm for the corresponding protons of CH_2, CH and NH respectively in ^{1}H NMR. The peaks due to acetamide group were observed at 2.0 and 5.2 ppm for corresponding CH_3 and NH protons. The peaks due to benzamide group were observed at 7.7, 7.5, 7.45 and 5.7 ppm for corresponding aromatic and NH protons.

The number average degree of functionality (Fn) of N-poly(alkenyl) alkylamides was calculated as Fn (mol %) = (Mn by VPO / Mn by ^{1}H NMR) X 100.

Mn of N-poly(alkenyl) acrylamide, acetamide and benzamide was calculated based on protons of vinyl, amide and aryl groups respectively.

The aggregation behaviour of N-poly(alkenyl) acrylamide was characterized by following techniques.

FT-IR: FT-IR spectra were obtained on a Perkin-Elmer 16 PC Spectrophotometer. A spectrum was recorded in KBr pellet as well as in chloroform solution. Spectra were corrected for both KBr and $CHCl_3$ absorption.

DSC: DSC analysis was carried out using Perkin Elmer DSC-7 by scanning in the temperature range of -60^0 C to 85^0C at the rate of 5^0C/min under N_2 atmosphere.

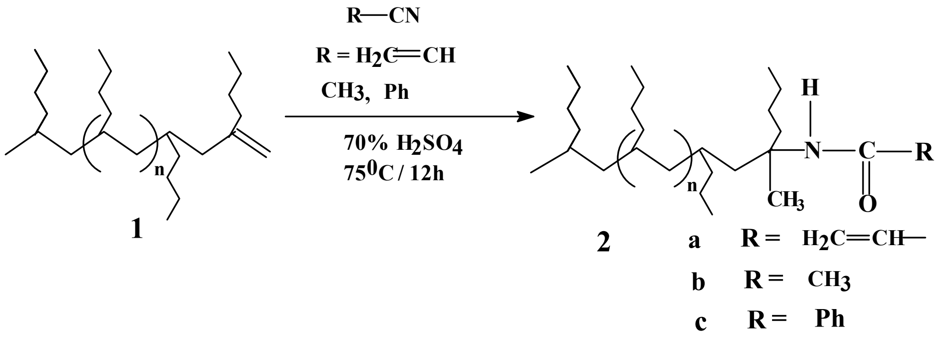
WAXS: The oligomer samples were crystallized on a copper plate and the WAXS pattern was obtained in reflection mode using a Rigaku Dmax 2500 diffractometer fitted with a diffracted beam graphite monochromator. The radiation was Cu- $K\alpha$ and scanned between 2θ =2 to 30 deg. The generator was operated at 40 KV and 150 mA.

Optical Microscopy: Optical micrographs were taken from Olympus PM-C35B microscope equipped with camera. The sample was prepared on a glass plate by solvent evaporation from oligomer solution in n-pentane.

Scanning Electron Microscopy: SEM microphotographs were taken using a Leica Cambridge (Stereoscan 440) scanning electron microscope. The crystals of N-poly(alkenyl) acrylamide were grown on gold in an automatic sputter coater by slow evaporation of solvent from n-pentane solution (Polaron equipment Ltd., scanning electron microscope coating unit E 5000, UK). Photographs of representative areas of the sample were taken at different magnifications.

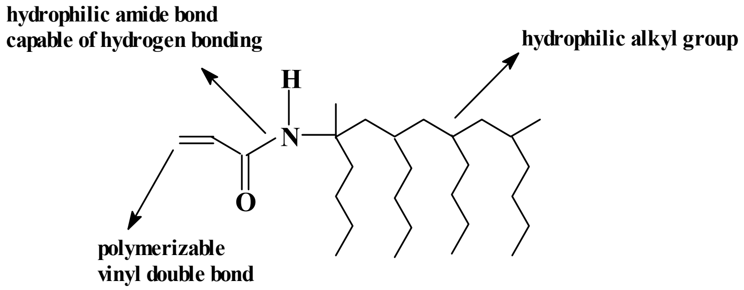
6.3 Results and discussion

Reaction of nitriles with “in situ” generated carbocations to give N-*tert*-alkylamides is called the *Ritter reaction* and is one of the well known methods for the introduction of nitrogen functionality at a tertiary carbon atom. A variety of N-substituted amides have been prepared using either *iso*-olefins or *tert*-alcohols and an acid catalyst. Therefore, it was decided to extend the Ritter reaction to terminal vinylidene unsaturated poly(hexene-1) in presence of nitriles to give N-poly(alkenyl) alkyl amides (**scheme-6.1**). We reasoned that the terminal vinylidene unsaturation bearing an *iso*-olefin can form a tertiary carbocation in presence of an acid catalyst.



Scheme-6.1 Ritter reaction of vinylidene terminated poly(hexene-1) with nitriles

Ritter reaction was carried out using vinylidene terminated poly(hexene-1) with three different nitriles, namely, acrylonitrile, acetonitrile and benzonitrile using 70% H_2SO_4 catalyst. The Ritter reaction of poly(hexene-1) oligomers with acrylonitrile can lead to N-poly(alkenyl)acrylamide **2a**, which has several interesting structural features (**scheme 6.2**).



Scheme-6.2 Structural features of N-poly(Alkenyl) acrylamide

Ritter reaction of acrylonitrile with poly(hexene-1) with Mn < 1000

Ritter reaction was carried out by direct addition of oligomers of poly(hexene-1)s whose number average molecular weight (Mn) is less than 1000 **(runs 1-3 in table-6.1)**. The number average degree of functionality (Fn) as high as 90 mol % was obtained for lower molecular weight oligomer (Mn = 400). However, with further increase in Mn up to 1080, the Fn decreased to 80 mol%. The reactions carried out (not shown in the table) at lower nitrile/olefin ratio also resulted in lower Fn. Satisfactory material balance was obtained in all the runs.

Table-6.1 Ritter reaction of vinylidene terminated poly(hexene-1) with acrylonitrile

Run no.	Poly(hexene-1)				Acrylonitrile mol	Yield (g)	Mn after functionalization		Fn (mol%) a / b
	Mn	mol	End groups (mol%)				VPO	^{1}H NMR	
			vinylidene	**internal**			**a**	**b**	
1	380	0.01	98.0	2.0	0.1	4.2	440	490	89
2	550	0.01	97.0	3.0	0.1	5.8	610	720	85
3	1080	0.005	94.0	6.0	0.05	5.6	1140	1440	80
4	1760	0.005	92.0	8.0	0.05	9.0	1800	3000	62
5	2760	0.0025	90.0	10.0	0.025	7.0	2820	5660	50
6	4260	0.001	88.0	12.0	0.01	4.0	4260	11 800	36
7	6840	0.001	85.0	15.0	0.01	6.6	6890	20 900	33
8	10 020	0.001	83.0	17.0	0.01	9.8	10 080	34 760	29

Reaction conditions: Temp = 75^{0}C

Table-6.2 Ritter reaction of vinylidene terminated poly(hexene-1) with acetonitrile

Run no.	Poly(hexene-1)				Acetonitrile mol	Yield (g)	Mn after functionalization		Fn (mol%) a / b
	Mn	mol	End groups (mol%)				VPO	^{1}H NMR	
			vinylidene	**internal**			**a**	**b**	
9	380	0.01	98.0	2.0	0.1	4.0	430	620	70
10	550	0.01	97.0	3.0	0.1	5.6	600	970	63
11	1080	0.005	94.0	6.0	0.05	5.3	1140	1900	60
12	1760	0.005	92.0	8.0	0.05	9.0	1800	3600	50

Reaction conditions: Temp = 80^{0}C

Table-6.3 Ritter reaction of vinylidene terminated poly(hexene-1) with benzonitrile

Run no.	Poly(hexene-1)				Benzonitrile mol	Yield (g)	Mn after functionalization		Fn (mol%) a / b
	Mn	mol	End groups (mol%)				VPO	^{1}H NMR	
			vinylidene	**internal**			**a**	**b**	
13	380	0.01	98.0	2.0	0.1	4.3	490	580	85
14	550	0.01	97.0	3.0	0.1	5.7	640	800	79
15	1080	0.005	94.0	6.0	0.05	5.5	1170	1680	70

Reaction conditions: Temp = 80^{0}C

6.3.1 Structural analysis by NMR (^{1}H & ^{13}C)

The analysis of N-poly(alkenyl)acrylamide by ^{1}H NMR showed the presence of acrylamide as well as internal unsaturation, which arise due to unwanted side reactions such as isomerization of terminal vinylidene end groups as shown in **fig-6.1**. The peak obtained at 4.8 ppm was assigned to a product from a side reaction. However, no unreacted terminal vinylidene unsaturation was observed in ^{13}C NMR as shown in **fig-6.2**.

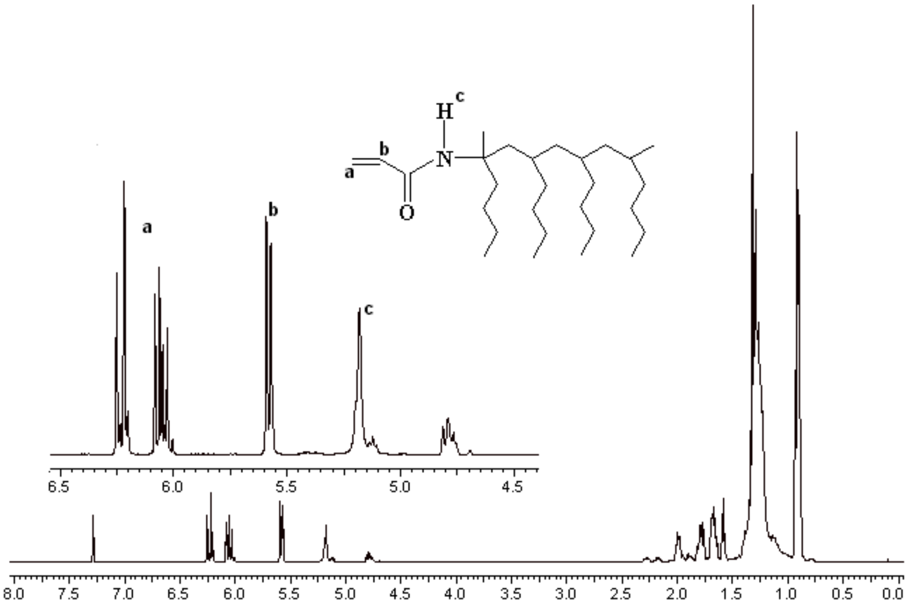


Fig 6.1 ^{1}H NMR of N-poly(alkenyl)acrylamide (from run no1)

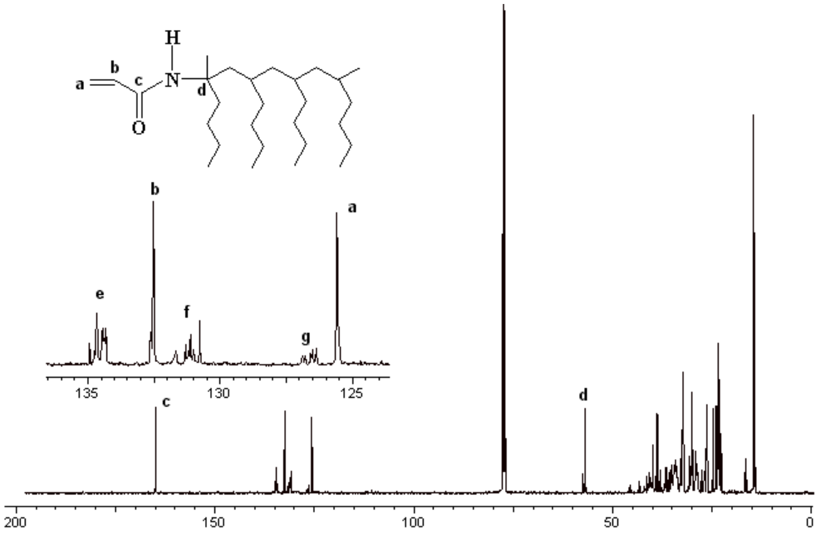


Fig 6.2 ^{13}C NMR of N-poly(alkenyl)acrylamide (from run no1)

The peaks **e, f, and g** in ^{13}C NMR were attributed due to products arising from side reaction. The DEPT spectra shown in **fig-6.3** also confirm the above structure.

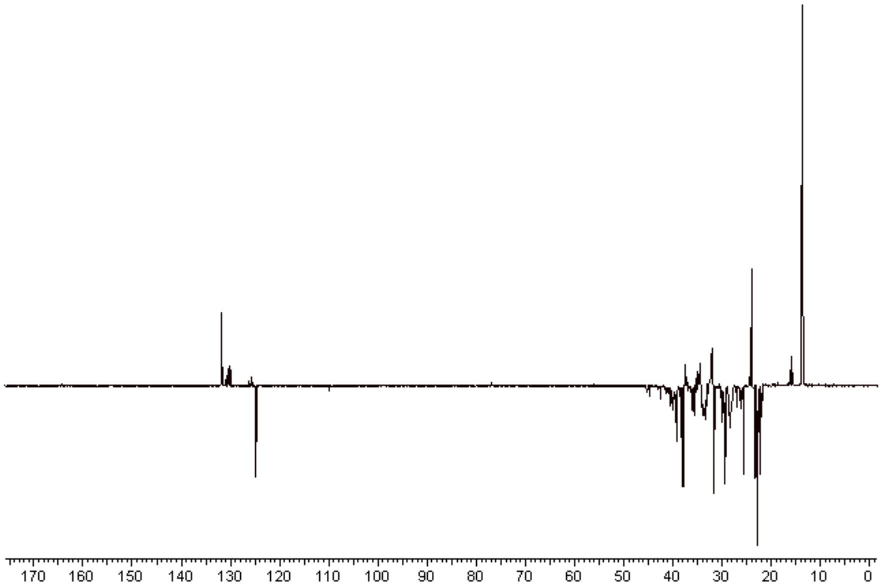


Fig 6.3 DEPT of N-poly(alkenyl) acrylamide (from run no 1)

Ritter reaction of acrylonitrile with poly(hexene-1) with Mn >1000

Runs 4-8 in **table-6.1** were carried out using a solution of oligomer in chlorobenzene. Among the various modes of additions studied, the addition of vinylidene terminated poly(hexene-1) (both in solution and bulk) to nitrile and catalyst mixture proved to be a better method. In all these runs, significantly lower number average degree of functionality (Fn) was observed than the solvent-less method. The Fn further reduced to with increase in Mn of the oligomer. It could be due to increase in internal unsaturation with increase in Mn of poly(hexene-1). However the reduction in Fn of functionalized polymer is relatively higher compared to decrease in Fn due to internal unsaturation before functionalization.

The analysis of high molecular weight N-poly(alkenyl) acrylamides by ^{1}H NMR showed an increase in intensity of the peak at 4.8 (which arise due to side reaction) as well as internal unsaturation at 5.3 ppm with increase in number average molecular weight (**fig-6.4**). In other words, it is more abundant when the reactions are carried out in solvent.

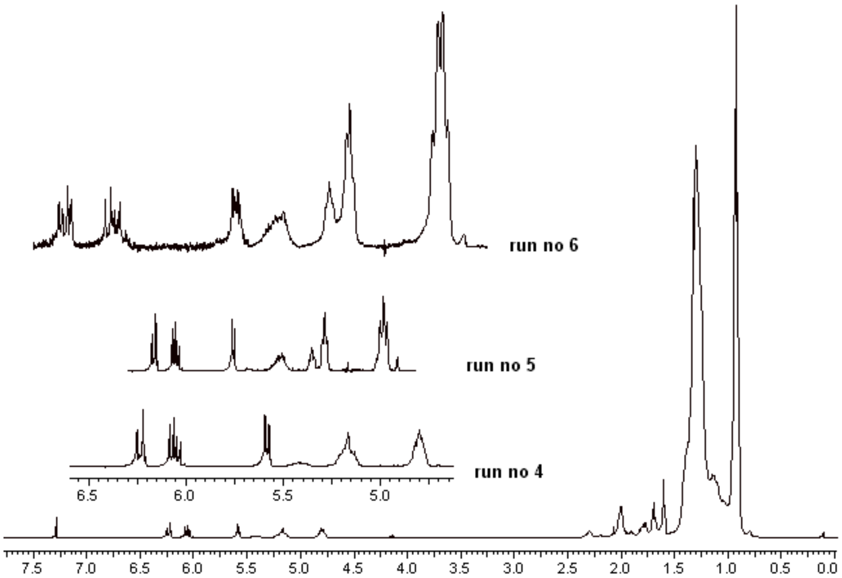


Fig-6.4 ^{1}H NMR of high molecular weight N-poly(alkenyl) acrylamides

Ritter reaction with aceto and benzonitrile

After establishing the Ritter reaction with acrylonitrile, reactions were also carried out with acetonitrile and benzonitrile. The results are shown in **table-6.2** and **6.3** for aceto and benzonitrile respectively. The results establish the generality of the reaction. The Fn of N-poly(alkenyl) acetamide calculated from ^{1}H NMR may not be quantitative, as it was calculated based on the absorption due to proton attached to amide group.

^{1}H, ^{13}C and DEPT spectra of N-poly(alkenyl) acetamide and arylamide are shown in **figures-6.5 to 6.10**. The peak at 4.8 ppm due to a side reaction was also observed in both the reactions.

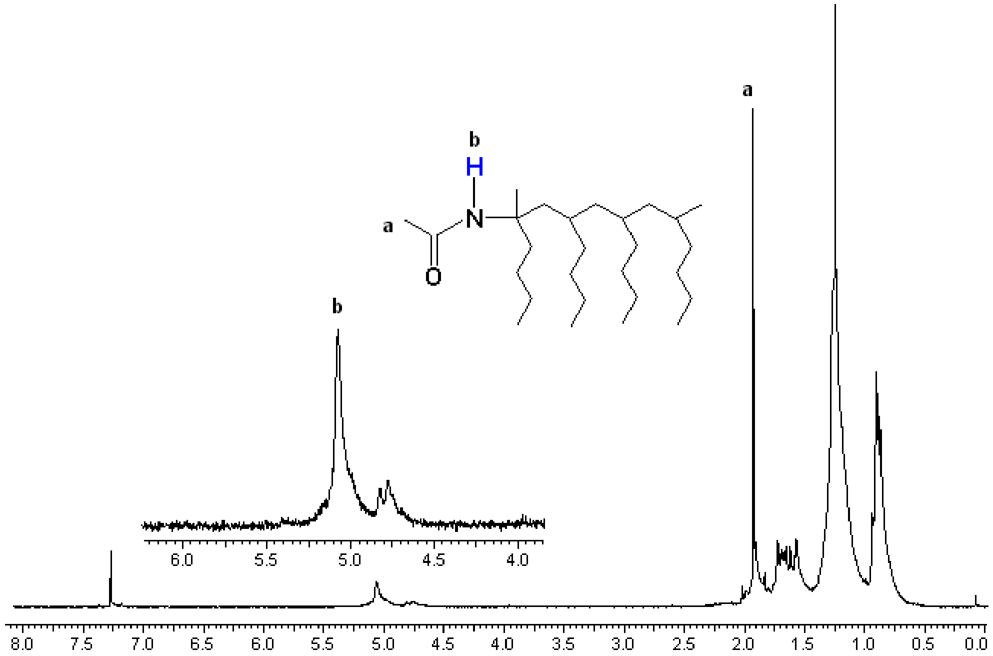


Fig-6.5 ^{1}H NMR of N-poly(alkenyl) acetamide (from run no 9)

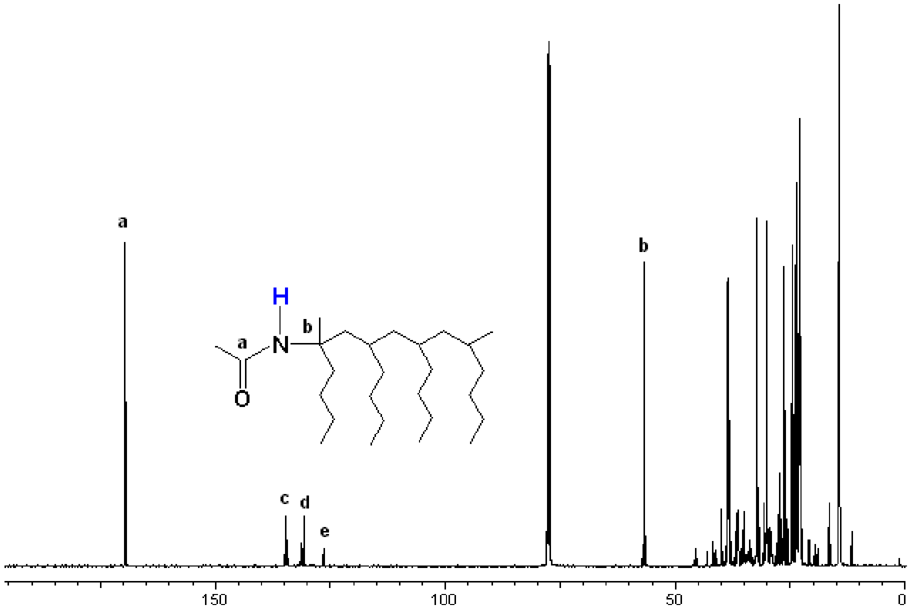


Fig-6.6 ^{13}C NMR of N-poly(alkenyl) acetamide (from run no 9)

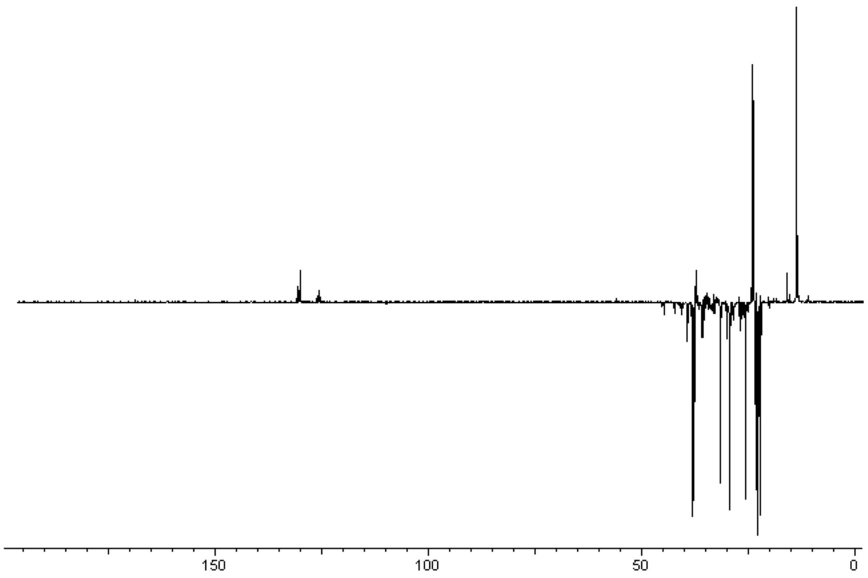


Fig-6.7 DEPT of N-poly(alkenyl) acetamide (from run no 9)

The above NMR spectra confirm the structure of N-poly(alkenyl) acetamide. In a similar way the structure of N-poly(alkenyl) arylamide was confirmed by both ^{1}H and ^{13}C NMR.

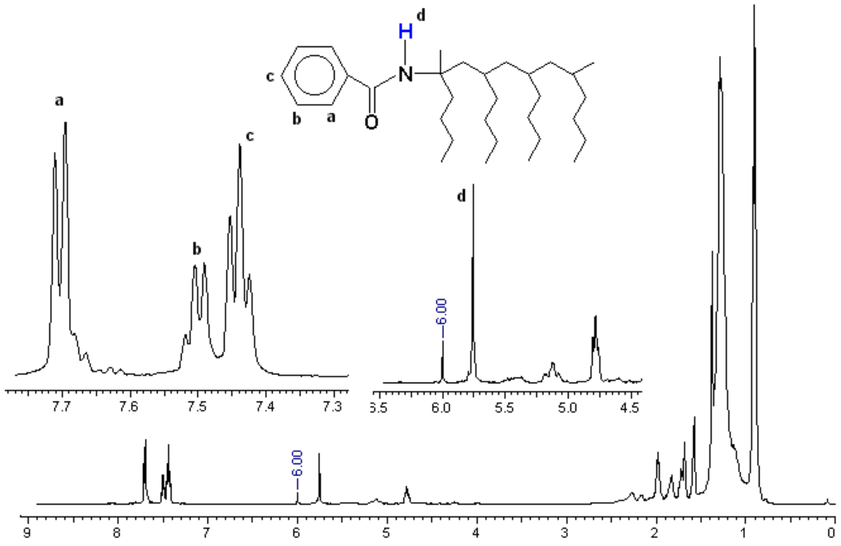


Fig-6.8 ^{1}H NMR of N-poly(alkenyl) arylamide (from run no 13)

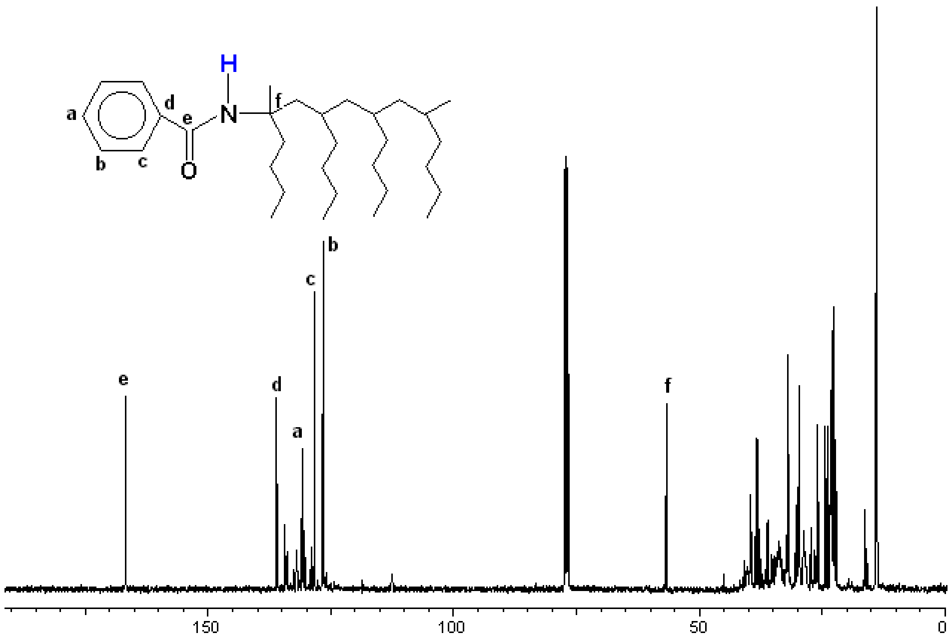


Fig-6.9 ^{13}C NMR of N-poly(alkenyl) arylamide (from run no 13)

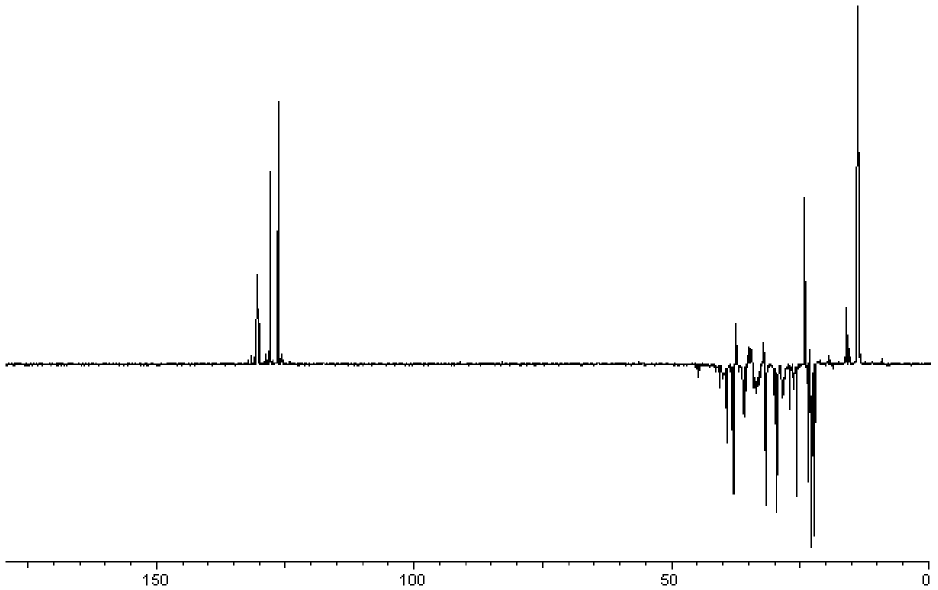


Fig-6.10 DEPT of N-poly(alkenyl) arylamide (from run no 13)

6.3.2 Physical state of the material

N-poly(alkenyl) acrylamide obtained from **run numbers 1** and **2** were found to be solid materials after slow evaporation of solvent from n-pentane solution. However the oligo(hexene-1) was a free flowing liquid. This behaviour was attributed to the intermolecular hydrogen bonding between amide groups. Hence it (sample obtained from run number 1) was further subjected to characterization by FT-IR, DSC, WAXS, Optical microscopy and SEM along with NMR (^{1}H & ^{13}C) to confirm its aggregation behavior. Such a aggregation behaviour was not observed either with N-poly(alkenyl) acetamide or benzamide with similar Mn. This could be due to the strong proton acceptor and donor characteristics of acrylamide compared to either acetamide or benzamide.

6.3.3 Solubility characteristics

N-poly(alkenyl) acrylamides obtained from run numbers 1 and 2 were found to be soluble in both polar and non-polar solvents, such as methanol, acetonitrile, $CHCl_3$, and n-pentane. However, the corresponding oligo(hexene-1)s were not soluble in polar solvents like methanol, acetonitrile etc. This solubility behaviour is attributed to its amphiphilic nature.

6.3.4 Elemental Analysis

The results of elemental analysis of N-poly(alkenyl) acrylamide obtained form runs 1 &2 are shown in **table-6.4**. Good agreement was observed between the calculated and theoretical values.

6.3.5 Intermolecular hydrogen bonding by FT-IR

In order to understand the precise role of amide groups in the process of solidification, detailed FT-IR studies were carried out. FT-IR spectra in KBr pellet and in chloroform solution were compared **(fig-6.11)**. The N-H strech bands in KBr and chloroform solution were found to be 3278 and 3434 cm^{-1} respectively. Secondary amide groups engaged in amide – amide hydrogen bonds display N-H strech bands in the range 3250-3370 cm^{-1} [39]. Also the C=O strech in KBr and in $CHCl_3$ were found to be 1671 and 1658 cm^{-1} respectively **(fig-6.12)**.

Table-6.4 Elemental Analysis of N-poly(alkenyl) acrylamide

Run No	Elemental Analysis					
	Before Ritter Reaction			After Ritter Reaction		
	C	H	N	C	H	N
1	85.7	14.0	-	77.1	10.8	3.8
2	84.9	14.3	-	80.0	14.2	2.8

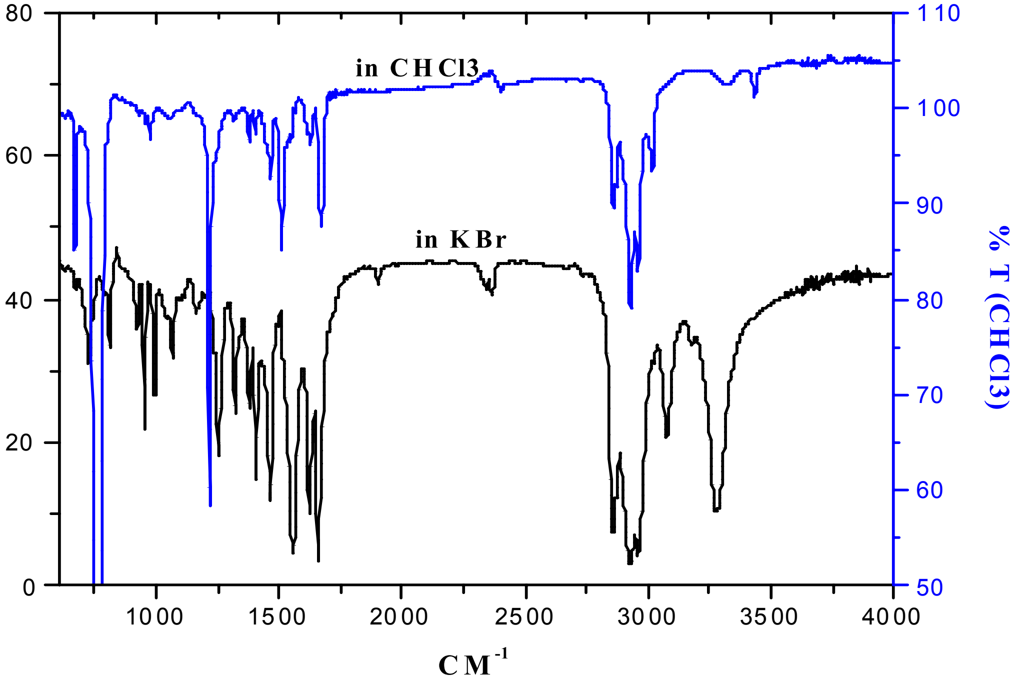


Fig-6.11 FT-IR spectra of N-poly(alkenyl) acrylamide in KBr and $CHCl_3$ (run no 1)

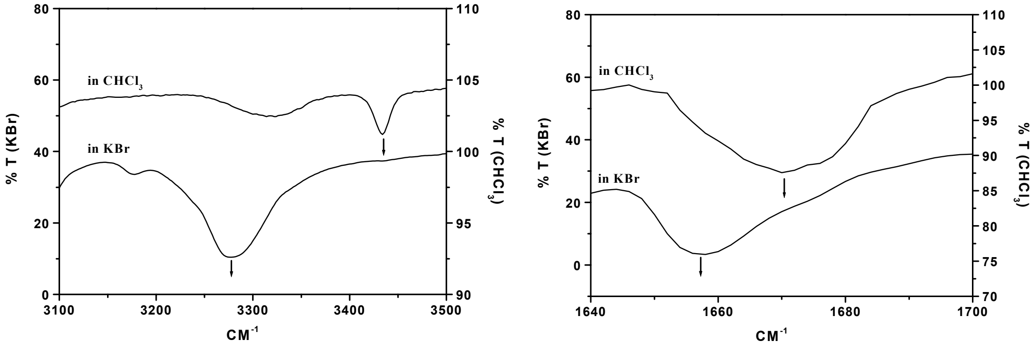


Fig-6.12 Expanded Region of FT-IR

6.3.6 DSC

DSC traces were taken by heating the sample from –60 to 85^{0}C as shown in **fig-6.13**. An endotherm observed at 54^{0}C was attributed to melting temperature, presumably caused by the disruption of hydrogen bonding.

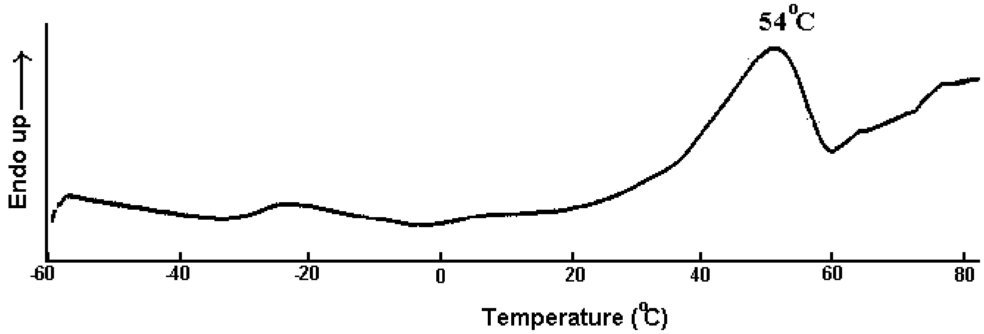


Fig-6.13 DSC traces of N-poly(alkenyl) acrylamide (run no 1)

6.3.7 WAXS

WAXS diffraction pattern (**fig-6.14**) exhibited sharp peaks, characteristics of a crystalline material.

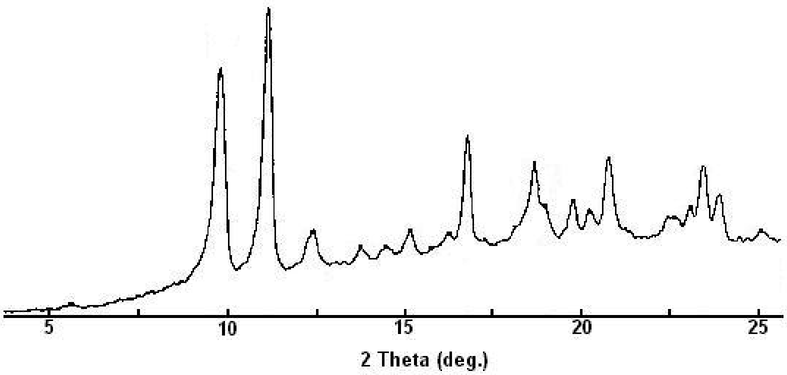


Fig-6.14 WAXS pattern of N-poly(alkenyl) acrylamide (run no 1)

6.3.8 Optical Microscopy

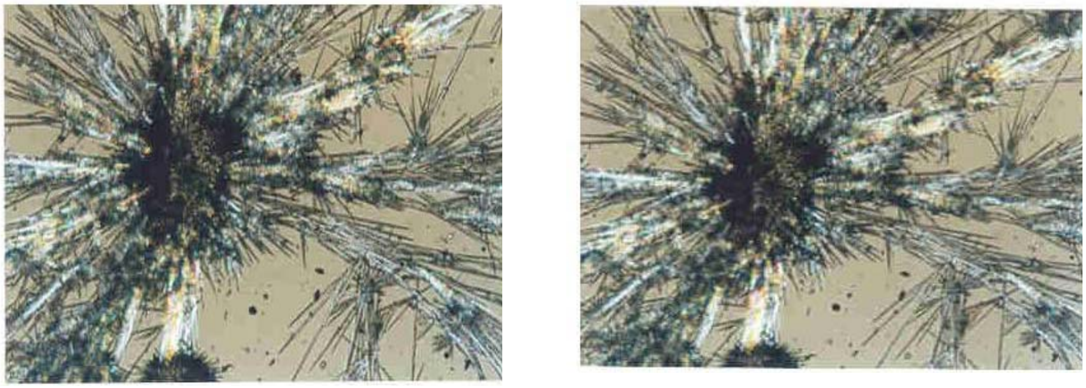


Fig-6.15 Optical Micrographs of N-poly(alkenyl) acrylamide (run no 1)

6.3.9 Scanning Electron Microscopy

Typical scanning electron micrographs are shown in **fig-6.16**.

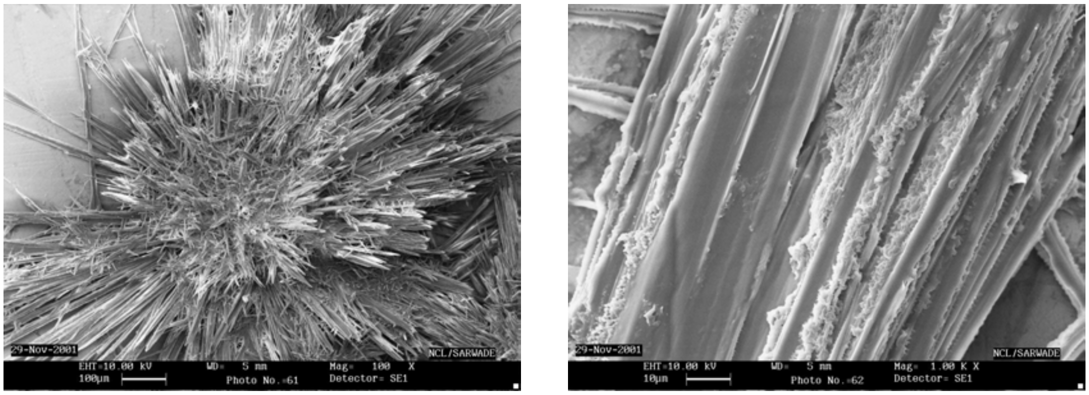


Fig-6.16 Scanning Electron Micrographs of N-poly(alkenyl) acrylamides (run no 1)

6.4 Conclusions

A polyolefin bearing terminal alkylamide functional group could be synthesized by Ritter reaction of terminal vinylidene double bonds in poly(hexene-1) with various nitriles using an acid catalyst. This is the first example of a post polymerization functionalization of terminal vinylidene double bond in a polyolefin to alkylamide group. The number average degree of functionality (Fn) as high as 90 mol% was obtained. Among the three N-poly(alkenyl) alkylamides, only N-poly(alkenyl) acrylamide was found to undergo aggregation via intermolecular hydrogen bonding as evidenced by FT-IR. The dissociation of hydrogen bonding was observed at 54^0C as evidenced by an endothermic peak in DSC. Further analysis by WAXS, optical microscopy and scanning electron microscopy reveals the process of crystallization to form rod like dendritic structure. N-poly(alkenyl) acrylamide is a useful macromonomer and can be used in the synthesis of hydrophobically modified polymers.

6.5 References

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Chapter 7. Synthesis of carboxylic acid functionalized poly(olefin) from hexene-1 / 2,5-norbornadiene copolymer

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7.1 Introduction

One approach to the synthesis of functional poly(olefin)s is via copolymerization of olefins with a precursor monomer, which can be later converted into functional groups. This approach leads to poly(olefin)s having pendant functional groups. Three types of precursor monomers are generally reported in the literature. These are α,ω-dienes, ω-borane-α-olefins and para-methyl styrene. Copolymerization of olefins with such co-monomers result in copolymers having pendant either double bonds, borane moiety or p-methylstyryl groups respectively. These pendant functionalities can be subsequently transformed.

Copolymerization of olefins with α,ω-dienes catalyzed by metallocenes has attracted considerable attention. Copolymerization of olefins with symmetrical dienes usually results in side reactions such as "*cyclopolymerization*" or "*crosslinking*". However, such side reactions can be avoided by selecting an appropriate metallocene catalyst. Copolymerization of olefins with unsymmetrical dienes, where one of the double bonds is more reactive than the other, gives poly(olefin)s having pendant double bonds.

Several reports are available in the literature regarding post polymerization conversion of pendant double bonds to various functional groups by simple organic chemical transformations. Recently Uozomi et al [1] reported the hydrosilylation of pendant double bond present in poly(ethylene-*alt*-1,9-decadieene). Marathe and Sivaram [2] reported the conversion of pendant double bonds of ethylene/VNB copolymer to epoxy and hydroxyl groups. Kaminsky [3] et al. reported the conversion of the cyclohexenyl pendant groups on ethylene/4-vinylcyclohexene copolymer to hydroxyl groups.

Hackman et al [4] reported the epoxidation and bromination of isocitronellene / propene copolymer. The pendant double bonds in poly(ethylene-*co*-1,4 hexadiene) were hydroborated followed by chemical reaction on boron to give various functional groups by Chung et al [5]. Suzuki et al [6] studied the copolymerization of ethylene with *endo*-dicyclopentadiene using Cp_2ZrCl_2, $Et(Ind)_2ZrCl_2$ and $Ph_2C(Cp)(Flu)ZrCl_2$/MAO catalysts. The enchainment was found to occur through norbornene double bond. The pendant double bond in the copolymer was then epoxidized by reacting with *m*-

chlorobenzoic acid. The quantitative conversion of double bond to epoxy group was found from NMR. Recently Song et al reported the ozonolysis of pendant double bonds present in poly(propene-co-methyloctadiene) to give aldehyde and carboxylic acid containing poly(olefins) [7].

Synthesis of carboxylic acid functionalized poly(olefin)s by direct copolymerization is difficult compared to the synthesis of hydroxyl functional poly(olefin)s due to the presence of two kinds of groups, namely, a carbonyl and a hydroxyl group which are known to interfere in the copolymerization reaction. It has been reported that the copolymerization activity as well as incorporation is only one half of that for the hydroxyl functional analogue when carboxylic acid or ester containing functional monomers are used for copolymerization [8].

Copolymerization of ethylene with a symmetrical diene namely, 2,5-norbornadiene (NBD) using various metallocene/MAO catalysts have been previously explored [9]. It was found that the copolymerization occurs exclusively through one of the equally reactive endocyclic double bonds for unbridged as well as ethylene bridged catalysts **(scheme-41 in chapter-1**). However, crosslinking occurs during copolymerization with dimethylsilylene bridged catalyst, probably due to the higher coordination angle along the Zr-Cl vector of the metallocene [10].

Oxidation of pendant double bonds present in poly(hexene-1-*co*-2,5 norbornadiene) was attempted with an objective of synthesizing a carboxyl functional poly(olefin). The synthesis of a copolymer having pendant endocyclic double bonds was described in **chapter-4**.

7.2 Experimental

7.2.1 Materials

Poly(hexene-1-*co*-2,5 norbornadiene) with different mol% NBD incorporation and Mn are reported in **chapter-4,** was selected for functionalization. Poly(ethylene-*co*-2,5 norbornadiene) was synthesized according to the literature [9]. Norbornene (Aldrich Chemical Company, USA), potassium permanganate ($KMnO_4$), sodium sulfite (Na_2SO_3), hydrochloric acid (HCl), dimethylsulfoxide (DMSO), toluene (all from s.d. fine chemicals, Boisar, India) and tetrabutylammonium bromide (Fluka A. G., Switzerland) were used as such.

7.2.2 Purification

Purification of the solvents was carried out as described in **chapter–3**.

7.2.3 Oxidation of norbornene to cyclopentane-1,3-dicarboxylic acid (model studies)

In a 100 mL round bottom flask, 1 g norbornene (10.6 mmol) was taken and 50 mL of toluene was added. Into this 0.34 g (1.06 mmol) of tetrabutylammonium bromide was added and was stirred well for 30 min. To this 5.17 g (31.8 mmol) of $KMnO_4$ dissolved in 50 mL of distilled water was added. After 3 h of continuous stirring, 4.56 g (38.0 mmol) of Na_2SO_3 was added into the reaction mixture to oxidize the excess $KMnO_4$ and then 14 mL of conc. HCl in 14 mL of water was added. The solution color changed from brown to white. It was then stirred for 24 h to remove all the MnO_2 formed. Two layers, water and benzene, were clearly visible. The lower water layer was separated by a separating funnel. The water layer was extracted with ether in a continuous extractor for 48 h. The product was obtained by evaporating ether and was purified by recrystallization from benzene-ether mixture to give 95 % yield. ^1H NMR (DMSO-d_6, ppm) 1.67-1.94 (5H), 2.11 (1H), 2.64-2.80 (2H) and 12.1 (2H).

Oxidation of poly(hexene-1-*co*-2,5-norbornadiene)

In a 100 mL round bottom flask, 3 g (10 mol% NBD incorporation) of the copolymer (Mn 1100, 3.5 mmol of cyclic unsturation and 2.7 mmol of terminal unsaturation) was taken and 50 mL toluene and 0.2 g (0.62 mmol) of tetrabutylammonium bromide were added. To this 2.9 g (18.6 mmol) of $KMnO_4$ dissolved in 50 mL of distilled water was added. The stirring was continued for 24 h at ambient temperature. To the reaction mixture 2 g (17 mmol) of Na_2SO_3 was added to oxidize the excess $KMnO_4$ and then 5 mL of conc. HCl in 5 mL of water was added. The color of the solution changed from brown to white. It was then stirred for 24 h to remove all the MnO_2 formed. The functionalized oligomer was found to be in the interphase of the two layers. The lower water layer was removed using a separating funnel and from the remaining organic layer the insoluble fraction (1.1g) was filtered and dried. The solvent was removed from the soluble fraction under vacuum to collect the unfunctionalized oligomer (1.7g).

7.2.3 Analysis

The IR spectra were recorded on a Perkin-Elmer 16 PC FT-IR spectrometer. ^1H NMR spectra of the copolymers before and after oxidation were recorded on a 200 MHz

Bruker NMR spectrometer at room temperature in $CDCl_3$ and $CDCl_3$/DMSO-d_6 (85/15, v/v) respectively. Quantitative ^{13}C NMR spectra of the copolymer before and after oxidation were recorded on a Bruker MSL 500 model spectrometer with a pulse delay 10 sec. Approximately 5000 scans were made.

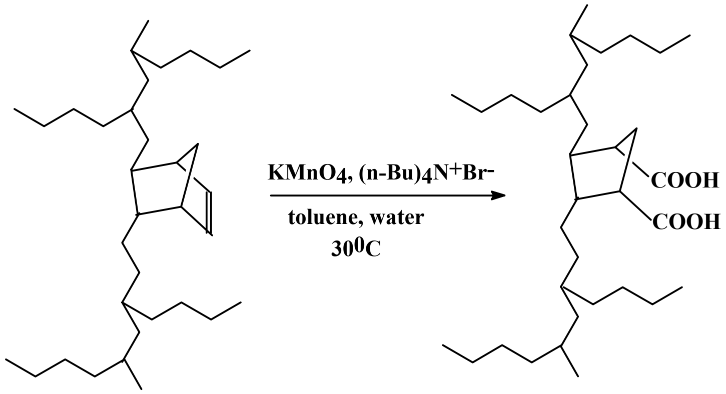
7.3 Results and discussion

A number of procedures are reported in the literature for the oxidative cleavage of the double bond in norbornene to dicarboxylic acid. Clark [11] used a catalyst combination of hydrated ruthenium trichloride and sodium periodate in chloroform for the oxidation. Henry and Weinreb [12] used Jone's reagent/osmium tetra oxide catalyst system in a mixture of acetone and water for the oxidation of norbornene. Hronowski and Szarek [13] employed $KMnO_4$ in a mixture of 2,2,4-trimethyl pentane and water in 1:5 ratio (v/v) with continuous bubbling of carbon dioxide and later sulfur dioxide for the oxidation of norbornene. In our earlier study, the limited solubility of poly(ethylene-co-2,5 norbornadiene) precluded the utilization of these methods for the oxidative cleavage of norbornene moiety in the copolymer. There was a report by Herriott and Picker [14] that stilbene could be oxidized under phase transfer conditions using tetrabutylammonium bromide/$KMnO_4$ in benzene/water biphasic medium.

We studied the oxidation of the endocyclic double bonds in poly(ethylene-co-2,5 norbornadiene) according the procedure by Herriott and Picker. Since poly(ethylene-co-2,5 norbornadiene) was only partially soluble in benzene at ambient temperatures it was decided to carry out the reaction in toluene where the copolymer is completely soluble.

Though the parent copolymer was soluble in toluene at room temperature, the carboxylic acid functionalized copolymer was found to be insoluble in toluene even at high temperatures, presumably, because of the presence of highly polar carboxylic acid groups. The product was also not soluble in any of the common solvents of polyolefins like xylene, o-dichlorobenzene etc. However, it was found to be soluble in a mixture of xylene or ODCB and DMSO (85:15 (v/v) ratio) at temperatures above 80^oC.

The same oxidation procedure was extended for the synthesis of carboxylic acid functionalized polyolefin from poly(hexene-1-co-2,5 norbornadiene) (**scheme-7.1**). It was felt that a higher α-olefin like hexene-1 in copolymer would improve its solubility after functionalization and thus enable better characterization of the copolymer.



Scheme 7.1 Synthesis of carboxylic acid functionalized hexene-1-2,5 norbornadiene copolymer

Table 7.1 Oxidation of hexene-1-NBD copolymer under phase transfer conditions[a]

Run No	Copolymer (g)	NBD in copoly[b] mol%	Mn	End groups (mol%)		Yield (g)	Solubility in toluene (%)	
				vinylidene	vinylene		Soluble	Insoluble
1	3.0	6.0	1070	57	43	2.6	>99.0	<1.0
2	4.0	8.0	1120	55	45	3.8	>95.0	<5.0
3	5.0	14.0	1300	48	52	4.7	49.0	51.0
4	4.0	26.0	1600	21	79	3.6	33.0	66.0
5	4.7	37.0	1800	24	76	4.4	23.0	77.0
6	3.6	15.0	1700	41	59	3.5	52.0	48.0
7	5.0	12.0	1620	40	60	4.9	47.0	53.0
8	4.0	13.0	1860	10	90	3.8	45.0	55.0
9[c]	5.0	14.0	1300	48	52	4.7	27.0	73.0
10[c]	4.0	26.0	1600	21	79	3.6	22.0	78.0

[a] ***Reaction conditions***: KMnO$_4$/olefin/TBAB = 30/10/1(mol/mol), Reaction time = 12h,
[b] Based on ^{1}H NMR . [c] Oxidation in DCM.

As shown in **table-7.1** oxidation of the copolymer resulted in toluene soluble and insoluble (found at interphase of two layers) fractions **(except run numbers-1and 2**). The analysis revealed that the toluene soluble fraction is the unfunctionalized oligomer. The insoluble fraction was found to be a carboxylated poly(olefin). A copolymer containing <10 mol% NBD (**run no-1 and 2**) resulted in a single toluene soluble fraction and was found to be a carboxylated poly(olefin).

The increase in NBD incorporation in copolymer gave more toluene insoluble fraction (**run numbers 3-5**). No significant change was observed on Mn of copolymer with solubility. The oxidation reactions carried out in dichloromethane (**runs 9 & 10 compared to 3 & 4**) gave higher carboxylated poly(olefin) than in toluene.

7.4 Characterization of the oxidized copolymer

7.4.1 NMR

Near complete conversion of the pendant endocyclic double bonds to dicarboxylic acids was evident by the absence of any residual pendant unsaturation in the copolymer as evidenced by ^{1}H NMR (**fig-7.1**). The peaks due to the cyclopentane rings in the copolymer could not be properly identified in the NMR spectra due to overlapping with DMSO peaks. The ^{13}C NMR (**fig-7.2**) spectrum showed a peak at 179 ppm due to carboxylic acid carbon and absence of peak at 139 ppm indicative of the absence of unsaturation.

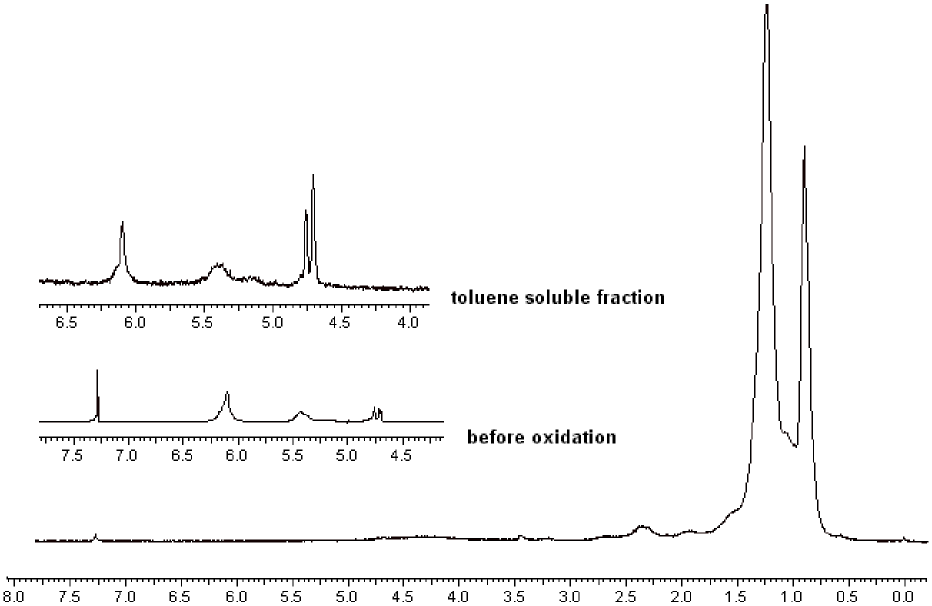


Fig-7.1 ^{1}H NMR of carboxylic acid functionalized copolymer (toluene insoluble from run no 3, solvent CDCL3/DMSO-D6, 85/15 V/V)

In both ^{1}H and ^{13}C spectrum, the absence of terminal unsaturation was also observed. The toluene soluble carboxylic acid functionalized copolymer showed traces of terminal vinylidene unsaturation (**fig-7.3**).

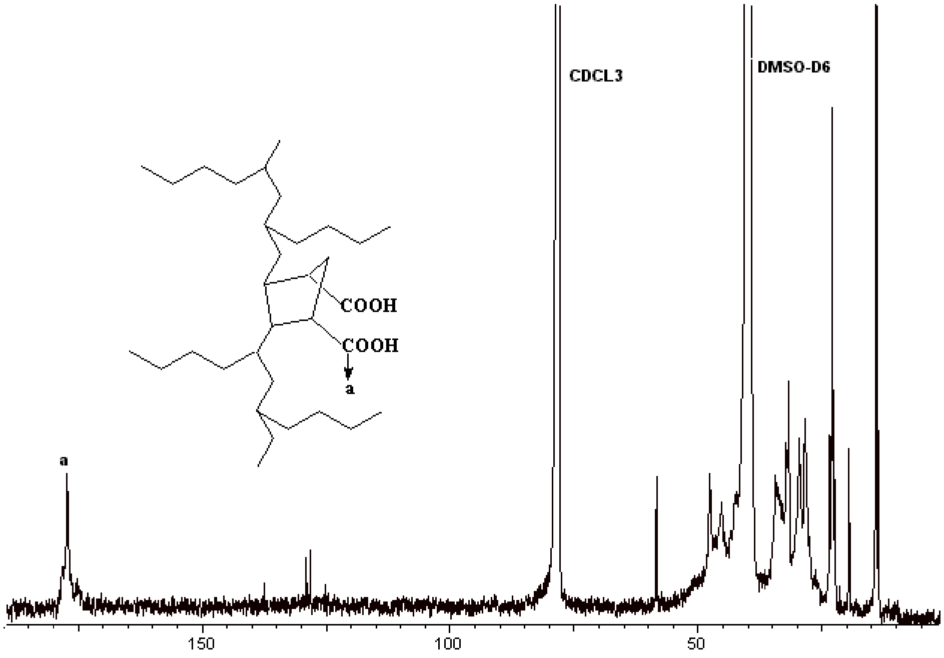


Fig-7.2 ^{13}C NMR of carboxylic acid functionalized copolymer (toluene insoluble fraction from run no 2, solvent CDCL3/DMSO-D6, 85/15 V/V)

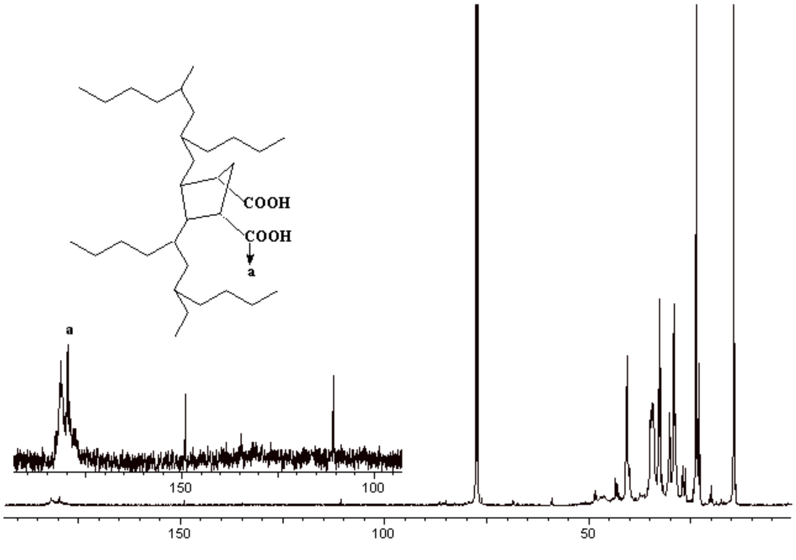


Fig-7.3 ^{13}C NMR of carboxylic acid functionalized copolymer (toluene soluble fraction from run no 1, solvent CDCL3)

7.4.2 FTIR

IR spectrum of the copolymer showed a very strong peak at 1725 cm^{-1} due to C=O stretching vibration of the diacid and virtual absence of a shoulder at 3065 cm^{-1} and peaks at 1583 and 908.7 cm^{-1} due to C=C double bonds.

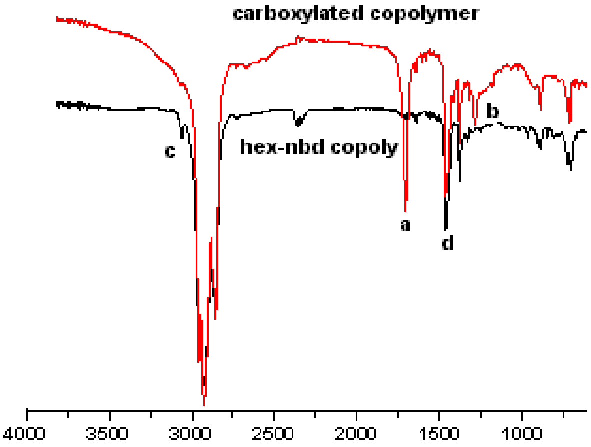


Fig-7.4 IR spectrum of copolymer before and after functionalization (run no 5)

Peaks: (a) = 1725 cm^{-1} C=O stretching, (b) 1240 cm^{-1} C-O stretching, (c) 3065 cm^{-1} C-H alkene stretching, (d) 1483 cm^{-1} C=C stretching.

7.4.3 Quantitative analysis of carboxylic acid of carboxylated poly(olefin)

Quantitative carboxylic acid analysis of toluene soluble carboxylated polyolefin obtained from **run numbers 1 and 2** was determined by dissolving samples in toluene/ethanol mixture and titrating the solution against alcoholic KOH. The carboxylic acid content obtained from titration (3.6 and 4.2 x 10^{-3} mol/g respectively) was higher than the theoretical values calculated from mol% NBD in copolymer. It could be due to the oxidation of terminal unsaturation as well.

7.5 Copolymer properties

Though all the parent copolymer was soluble in toluene at room temperature, the carboxylated oligomers were found to be only partially soluble in toluene. It was found that the soluble fraction had no acid functionality where as the insoluble fraction showed the presence of carboxylic acid functional group. However, when the mol % NBD was <6% all the product formed was soluble, and was found to be the carboxylated oligomer. The presence of intermolecular hydrogen bonding between the -COOH groups in the functionalized co-polymer may result in poor solubility. The toluene insoluble fraction was found to be soluble in a mixture of $CDCl_3$/DMSO (85:15 (v/v) ratio) at room temperature.

7.6 Conclusions

Copolymerization of hexene-1 with a symmetrical diene, namely, 2,5-norbornadiene, was found to occur through only one of the highly strained endocyclic double bonds leaving the other one as a pendant group. The pendant double bonds could be converted into carboxylic acid groups under mild conditions. The functionalized copolymer was found to be insoluble in toluene with NBD incorporation more than 6 mol%. The fact that the double bond was part of a strained endocyclic [2.2.1] skeleton enabled it to be oxidized under a very mild condition. Such oxidized poly(olefin)s are likely to possess interesting applications as adhesion promoters, tie layers in multilayer barrier packaging and emulsifiable polyolefin waxes for coating applications.

7.7 References

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Chapter 8. Summary and conclusions

8.1 Conclusions

This thesis presents the capabilities of metallocene based catalysts for the synthesis of functional poly(olefin)s. Two methods, namely synthesis of terminally unsaturated poly(α-olefin)s by exploiting the chain transfer reactions in metallocene catalyzed polymerization of α-olefins and copolymerization with dienes were examined.

A study of bulk polymerization of hexene-1 using different metallocene/MAO catalysts was undertaken to produce terminally unsaturated poly(hexene-1)s via chain transfer reactions. Poly(hexene-1) with Mn varying from 500 - 15 000 was obtained with polymerization temperature (Tp) varying from -20 to 50^0C. Highly regiospecific catalysts like Cp_2ZrCl_2, $(n\text{-}BuCp)_2ZrCl_2$ and $(CH_3)_2SiCp_2ZrCl_2$ result in vinylidene as the major end group which arise due to β-hydrogen transfer after 1,2 insertion. Both vinylidene as well as internal vinylene (arises due to β-hydrogen transfer after 2,1 insertion) end groups were observed with a poor regiospecific catalyst like *rac* $Et(Ind)_2ZrCl_2$. Interestingly internal vinylene end group was found to increase with decrease in temperature with all the catalysts.

A study of copolymerization of hexene-1 with a symmetrical diene namely 2,5-norbornadiene using different metallocene/MAO catalysts was found to occur exclusively through one of the two equally reactive endocyclic double bonds for unbridged as well as ethylene bridged catalysts. No crosslinking occurs during copolymerization with any of the catalysts examined. The amount of incorporation of diene, catalytic activity, number average molecular weight (Mn), regio errors and end groups depend on the metallocene used and also on the experimental conditions.

A simple facile route for the synthesis of phenol/2,6 dimethylphenol terminated Poly(hexene-1) was identified by alkylation of phenol/2,6 dimethylphenol with terminal vinylidene unsaturation of poly(hexene-1) using $BF_3{:}OEt_2$ catalyst. The number average degree of functionality (Fn) as high as 95 mol % was obtained for low molecular weight oligomers with >95 mol% para selectivity. The selectivity of para isomer was found to decrease with increase in number average molecular weight (Mn). Alkylation of bisphenol-A with vinylidene terminated poly(hexene-1) was also attempted. Although the results showed complex results, however, improved methods can be identified.

A polyolefin bearing terminal alkylamide functional group was synthesized by Ritter reaction of terminal vinylidene double bonds in poly(hexene-1) with various nitriles using an acid catalyst. This is the first example of a post polymerization functionalization of terminal vinylidene double bond in a polyolefin to alkylamide group. The number average degree of functionality (Fn) as high as 90 mol% was obtained. Amongst the three N-poly(alkenyl) alkylamides, N-poly(alkenyl) acrylamide was found to undergo aggregation via intermolecular hydrogen bonding as evidenced by FT-IR. *N*-poly(alkenyl) acrylamide is a useful macromonomer and can be used in the synthesis of hydrophobically modified polymers.

The pendant double bonds in hexene-1/2,5-norbornadiene copolymer were functionalized to carboxylic acid groups under mild conditions using $KMnO_4$. The functionalized copolymer was found to be insoluble in toluene with NBD incorporation more than 6 mol%. The fact that the double bond was part of a strained endocyclic [2.2.1] skeleton enabled it to be oxidized under a very mild condition.

In conclusion, the work presented in this thesis illustrates the versatility of metallocene catalysts for the synthesis of functional poly(olefin)s. The chain transfer reactions in metallocene catalyzed polymerization of hexene-1 are exploited to synthesized terminally functionalized poly(hexene-1). Presence of regio errors in copolymers of hexene-1 with either norbornene or norbornadiene using highly regiospecific catalysts is also an important observation.

8.2 Scope for future work

Vinylidene terminated poly(hexene-1) can be used as a macromonomer in copolymerization of isobutylene by carbocationic polymerization to give branched poly(isobutylene). Synthesis of such branched poly(isobutylene)s is not well established.

Phenol terminated poly(hexene-1) offers several future opportunities. The phenol group can be further converted to caprolactone, caprolactum, by post modification, which finds applications as reactive steric stabilizer for dispersion polymerization. Phenol group can also ethoxylated by ethylene oxide to find applications as surfactants etc. Accessibility of control over hydrophobic and hydrophilic balance can be achieved by appropriate reaction conditions. Ethoxylated phenols called "ethoxylates" are an important class of surfactants, which are widely used, in our daily life. These compounds in general are prepared by ethoxylation of commercially available alkyl phenols such as nonyl phenol, dodecyl phenol etc. The properties these compounds are in general sensitive to hydrophobic and hydrophilic balance. However, the major concern with this kind of compounds is control of hydrophobic moiety, which is restricted to less than C-18. In order to synthesize ethoxylates with a wide range of hydrophobic content (C-40-100), alkylation of phenol with terminally vinylidene polypropylene (Mn 500 – 1000) can also be attempted.

We first time reported the Ritter reaction of vinylidene terminated poly(hexene-1)s with nitriles. It can be further extended with various other nitriles to give novel structures, which are not accessible, by other conventional techniques. N-poly(alkenyl) acrylamide is an important macromonomer, which could be further copolymerized with acrylamide to give novel hydrophobically modified copolymers. It is an interesting phenomenon to analyze nature of copolymers (random or random block). The hydrophobic moiety in the synthesis of commercially available N-alkyl acrylamides is restricted to C-6 to 18 due to their method of preparation.