SYNTHESIS OF ETHYLENE - BICYCLIC OLEFIN COPOLYMERS USING METALLOCENE/MAO CATALYST SYSTEM AND ITS FUNCTIONALIZATION

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by

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DEDICATED TO MY BELOVED MOTHER

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DECLARATION

Certified that the work incorporated in the thesis "***Synthesis of ethylene-bicyclic olefin copolymers using metallocene/MAO catalyst system and its functionalization***" submitted by Mr. K. Radhakrishnan 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

(S.Sivaram)

Research Guide

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* Synopsis

Abstract

This thesis presents the application of metallocene catalysts for the synthesis of functional polyolefins. Two methods, namely, copolymerization with dienes, where one of the double bonds undergoes enchainment, leaving the other double bond as a pendant group, capable of being functionalized and direct copolymerization with functional monomers were explored.

A study of copolymerization of ethylene with a symmetrical diene, namely, 2,5-norbornadiene, was undertaken. It was reasoned that the rigid bicyclic structure would prevent cyclopolymerization, commonly observed within symmetrical dienes, and enable introduction of a pendant endocyclic unsaturation. Enchainment occurred only through one of the highly reactive strained endocyclic double bonds with Cp_2ZrCl_2, $(n\text{-}buCp)_2ZrCl_2$ and $Et(ind)_2ZrCl_2$ catalysts while both the double bonds underwent enchainment with $Me_2SiCp_2ZrCl_2$. Effect of temperature, Al/Zr ratio and feed composition on copolymerization was studied. The reactivity ratios for ethylene and 2,5-norbornadiene were found to be 15.1 and 0.021and 10.9 and 0.001for Cp_2ZrCl_2 and $Et(ind)_2ZrCl_2$ catalysts respectively. This work demonstrated the capability of metallocene catalyst to distinguish between two reactive double bonds one in the monomer and the other in the polymer chain.

The pendant double bonds in ethylene/2,5-norbornadiene copolymer were functionalized to dicarboxylic acids under phase transfer conditions using $KMnO_4$. This is the first example of a post polymerization functionalization of a pendant double bond in a polyolefin to carboxylic acid group. 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.

A relatively facile route to the synthesis of hydroxyl functional polyolefin by copolymerization with trimethylaluminum prereacted 5-norbornene-2-methanol was identified. The removal of the active hydrogen and reduction of the electron donating nature of the oxygen by prereaction with TMA and the high reactivity of the strained endocyclic double bond facilitated the copolymerization. Effect of Al/Zr ratio,

temperature and the structure of the metallocene on copolymerization were studied. Copolymer containing as high as 6 mol % alcohol could be successfully synthesized.

Polyolefin having pendant vinyl double bonds in the polymer chain was synthesized by the copolymerization of ethylene with 5-vinyl-2-norbornene using $Me_2SiCp_2ZrCl_2$ catalyst. The reactivity ratio values (3.7 and 0.0135 for ethylene and 5-vinyl-2-norbornene) indicated that the copolymers are more random in nature compared to the one synthesized with Cp_2ZrCl_2.

The pendant vinyl double bonds in the ethylene/5-vinyl-2-norbornene copolymers were epoxidized using m-chloroperbenzoic acid and were used for the synthesis of novel, well-defined graft copolymers. Polyethylene-g-polystyrene copolymers were synthesized by terminating living polystyryl lithium anion with the epoxy functionalized polyethylene. The grafting efficiency achieved was 54 %. Attempts to increase the grafting efficiency were unsuccessful. Synthesis of amphiphilic copolymers by coupling epoxy pendant groups with amino end functionalized polyethylene glycol was attempted, but without success. Reasons for only partial success in the synthesis of graft copolymers have been discussed and suggestions made for overcoming the problem.

Glossary

9- BBN	9-borabicyclo[3.3.1]nonane
$AlEt_2Cl$	Diethylaluminum chloride
CGC	constrained geometry catalyst
Cp	cyclopentadienyl
Cp*	pentamethylcyclopentadienyl
DSC	Differential scanning calorimeter
ENB	5-ethylidene-2-norbornene
fluo	fluorenyl
g	gram
ind	indenyl
$indH_4$	tetrahydroindenyl
MAO	Methylaluminoxane
Me_2C	isopropyl
Me_2Si	dimethylsilylene
NBD	bicyclo[2.2.1]hepta-2,5-diene(2,5-norbornadiene)
NBOH	5-norbornene-2-methanol
Ph_2C	diphenylmethylene
$PhSiH_3$	Phenylsilane
SAN	styrene/acrylonitrile copolymer
Tg	Glass transition temperature
TGA	Thermogravimetric analysis
TIBAL	Triisobutylaluminum
TMA	Trimethylaluminum
TMEDA	N,N,N',N'-tetramethylethylenediamine
VNB	5-vinyl-2-norbornene
wt %	weight %
$ZrCl_4$	zirconium tetrachloride

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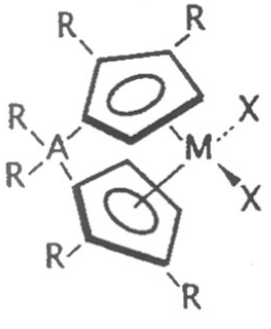
Chapter 1. Copolymerization of olefins with bicyclic olefins, dienes and functional monomers using metallocene catalysts and post polymerization functionalization of polyolefins

1.1 Introduction

Discovery of metallocene/methylaluminoxane catalyst system for olefin polymerization was a turning point in the field of Ziegler-Natta polymerization chemistry. Over nine hundred patents and a large number of papers published on metallocene catalysts based polymerizations show its importance in both industrial and academic fields. Though metallocene/alkylaluminum combination was 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 that methylaluminoxane (MAO) is a highly active cocatalyst by Kaminsky and Sinn for metallocene in 1980.[2]

Metallocene catalysts consist of a group IVB transition metal sandwiched between two cyclopentadienyl type ligands (**1**). The two ligands can optionally be tied up by a silicon or carbon containing bridging group. The R and X in (**1**) represent alkyl or aromatic and chloride groups respectively. MAO, which is a partial hydrolysis product of trimethylaluminum (TMA), is oligomeric in nature having a molecular



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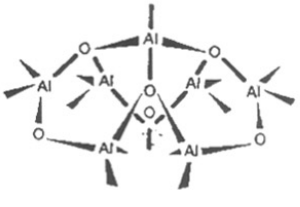

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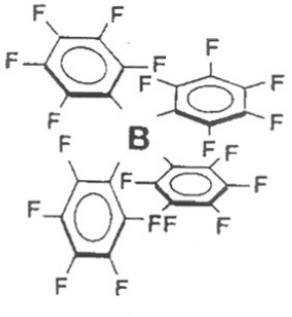

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weight in the range of 800 to 1,500. Though the exact structure of MAO is not known, it can be inferred from the available literature data that it possesses -Al(Me)-O- repeat units, with tetra-coordinated Al. MAO is always associated with some amount of unhydrolyzed TMA (**2**).

The significance of metallocene catalysts lies in their high polymerization activity and also in the breadth of the type and level of comonomer that can be incorporated. Proper tuning of the ligand around the metal enables the synthesis of isotactic, hemiisotactic, elastomeric, high molecular weight atactic and syndiotactic polypropylenes and ethylene/styrene interpolymers. The near random distribution of comonomer along the polymer chain along with narrow molecular weight distribution (MWD) (**Figure 1.1**) is an added advantage of the metallocence based copolymers.

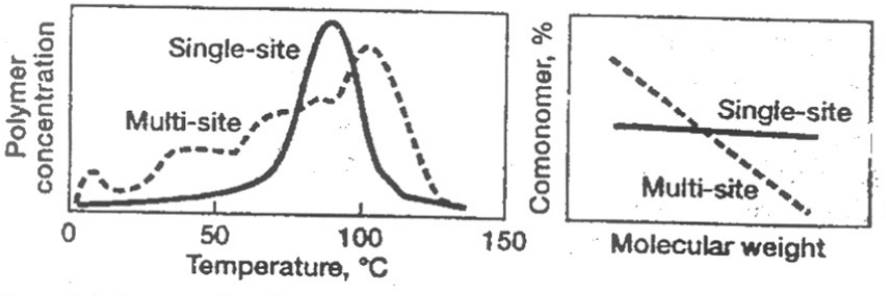

Figure 1.1 A comparison between the characteristics of polyolefins synthesized with multi-site Ziegler-Natta and single-site metallocene catalysts

Unlike in conventional Ziegler-Natta catalysts, where comonomers are distributed non uniformly among the chains, with lower molecular weight ones having higher amounts of comonomer, the intermolecular composition distribution is uniform in metallocene based copolymers.[3] The presence of only one kind of active site in contrast to multiple ones in conventional Ziegler-Natta catalysts has earned metallocene catalysts the name single site catalysts.

The homogeneous nature of the catalyst system opened up new opportunities for a better understanding of the polymerization mechanism. This in turn led to the conclusion that 14 electron cationic species is the active species responsible for polymerization. Methylaluminoxane, which facilitates methide abstraction to generate the cationic species, can also be replaced by non-coordinating lewis acids such as boron cocatalyst (**3**).

A number of reviews, namely, on stereospecific polymerization by Brintzinger et al.,[4] on the effect of cyclopentadienyl ring substituents on polymerization by Mohring and Coville,[5] on ethylene homopolymerization by Reddy and Sivaram,[6] on the mechanistic models for polymerization and stereoregularity by Huang and Rempel,[7] on olefin polymerization, in general, by Gupta et al.,[8] are available in the literature on metallocene catalysts. Recently an overview of metallocene catalyzed polymerization has been published by Kaminsky and Arndt.[9]

The efficiency of metallocene catalysts in the copolymerization of olefins with bulky cycloolefins like norbornene has drawn industrial as well as academic interest because of the high glass transition temperature (Tg) of the resulting copolymers. Synthesis of functional polyolefins using metallocene catalysts resulting in polyolefins having well defined functional groups either randomly distributed along the polymer chain or on chain ends is an emerging area of active interest. Such functional groups, introduce some hydrophilicity in an otherwise hydrophobic polyolefins as well as enable the synthesis of novel graft and block copolymers having a wide range of applications. In this introductory chapter, the published as well as patented literature on olefin/cyclic olefin copolymers and on the various approaches for the synthesis of functional polyolefins as well as graft and block copolymers will be briefly discussed.

1.2 Ethylene/cyclic olefin copolymers

One of the noteworthy copolymerizations using metallocene catalysts is the copolymerization of ethylene with norbornene type bicyclic olefins. The enchainment occurs exclusively through the endocyclic double bond, without ring opening or any other side reactions. Use of conventional Ziegler-Natta catalysts result in copolymers having unsaturation caused by ring opening. The driving force, in the case of metallocene catalysts, is largely due to the release of ring strain upon enchainment. The resulting copolymers have high Tg, whose value depends on the comonomer content and the nature of the comonomer. The well-studied bicyclic olefins are norbornene (NB) (**4**), 1,4,5,8-dimethano-1,2,3,4,4a,5,8,8a-octahydronaphthalene (DMON) (**5**), and 1,4,5,8,9,10-trimethano-1,2,3,4,4a5,8,8a,9,9a,10,10a-dodecahydro-anthracene (TMDA) (**6**).

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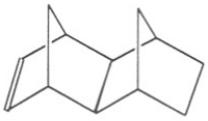

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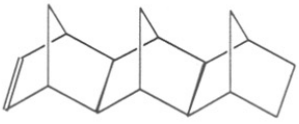

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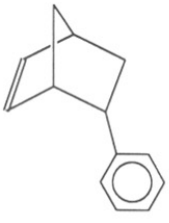
Copolymerization studies have also been reported with the bicyclic olefins phenyl norbornene (ph-NB) (**7**) and various alkyl substituted norbornenes (**8**).



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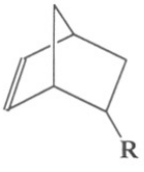

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1.2.1 Ethylene/norbornene copolymers

The copolymerization activity and the extent of comonomer incorporation depend on the metallocene used for copolymerization. In general, bridged metallocenes are more active and favor higher incorporation of norbornene compared to unbridged ones. The bridged ones, where the two ligands are tied together by a bridging group, have higher `co-ordination gap aperture'[10] enabling easy access of the bulky monomer to the active metal center.

The catalyst $Et(ind)_2ZrCl_2$ is 100 times more active than Cp_2ZrCl_2, and shows a maximum activity at a 1:1 feed composition.[11] Kaminsky and Noll[12] carried out a comparative study of ethylene/norbornene copolymerization over four different bridged metallocenes, two C_2 symmetric and other two C_s symmetric. The copolymerization activity for C_2 symmetric catalysts are lower than that for ethylene homopolymerization, while, for C_s symmetric ones, it was 4-5 times higher. From the copolymerization activity behavior, it was inferred that the C_s symmetric catalysts have better steric conditions for insertion of bulky olefins than C_2 symmetric ones. C_s symmetric ones produced copolymers of higher molecular weight and unimodal MWD.

A comparative study of ethylene/norbornene copolymerizations under identical conditions have shown that the catalyst Et $(ind)_2ZrCl_2$ gives the highest activity while Ph_2C (ind)(Cp)$ZrCl_2$ gives the highest incorporation.[13]

US patent 5,371,158[14] has described a process for the synthesis of ethylene/norbornene copolymers which are soluble in toluene at room temperature without the formation of gel, thus, making them suitable for coating and for the production of cast films. This was attributed to the disyndiotactic cycloolefin sequences. The process involves the bulk copolymerization using the syndiospecific Ph_2C(fluo)(Cp)$ZrCl_2$/MAO catalyst system. For the same mol % incorporation of norbornene, the bulk copolymerization was found to produce high molecular weight copolymers compared to solution polymerization. The copolymers have refractive index values very close to that of crown glass and can hence be used as a glass substitute. These copolymers having a MWD in the range of 2.9 to 6.0 are suitable for spray casting.

Cycloolefin copolymers having high heat distortion temperature have high melt viscosity and low toughness, which can be avoided by mixing it with a copolymer having a low Tg. Incompatibility between these two copolymers can be solved by adding an ethylene/cycloolefin block copolymer as phase promoter.[15] Such block copolymers are synthesized by abruptly changing the feed composition during polymerization. For example, under constant norbornene feed ethylene pressure was maintained at 2 bar for 30 min and then at 7 bar for 15 min to get a block copolymer having a Tg of 98°C. MWDs of the copolymers were low, in the range of 1.5 to 1.7, compared to random copolymers.

The nature of copolymerization also depends on the solvent used.[16] A mixture of toluene and hexane is preferred over toluene (**Table1.1**). This has been attributed to the high solubility of ethylene/norbornene copolymer in a mixture of toluene and hexane over toluene alone. Of the solvent mixtures which can effectively be used for such copolymerization, one of the solvents should have a solubility parameter, in terms of $(cal/cm^3)^{1/2}$, equal to or greater than 7.7 and the other solvent equal to or less than 7.5.

Copolymers synthesized with mirror symmetric metallocenes have low tensile strength. Though copolymers synthesized with C_2 symmetric catalysts have high

tensile strength they are less transparent due to the presence of partially crystalline ethylene polymers. Additional workup like multistage filtration is needed for the

Table 1.1 Effect of solvent on ethylene/norbornene copolymerization

Solvent	composition	Catalyst activity (g/mM Zr)	mol % norbornene in copolymer	Tg(°C)
Toluene/hexane	80/20	37,000	47.4	110
Toluene	100	35,000	38.4	95

removal of these ethylene polymers.[17] Use of $Me_2C(ind)(Cp)ZrCl_2$ as copolymerization catalyst overcomes this problem **(Table 1.2)**.[18]

Table 1.2 Effect of metallocene on ethylene/norbornene copolymerization

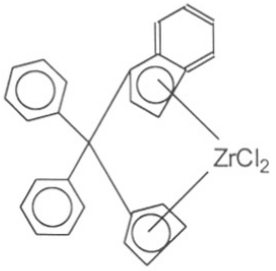
Metallocene	Tm(°C)	Tg(°C)
$Me_2C(ind)(Cp)ZrCl_2$	-	197
$Me_2Si(ind)_2ZrCl_2$	127	175

^{13}C NMR studies have revealed that the insertion occurs in such a way that the configuration of norbornene moiety is exo in copolymer and that the norbornene blocks synthesized with isospecific catalysts have diisotactic structure.[11]

1.2.2 Ethylene/DMON copolymers

Copolymerization studies with DMON using various metallocene catalysts have revealed that mol % incorporation increases in the order Cp_2ZrCl_2 < $(ind)_2ZrCl_2$ < $Et(ind)_2ZrCl_2$ < $Me_2Si(ind)_2ZrCl_2$ < $Me_2SiCp_2ZrCl_2$. This has been attributed to the difference in metallocene co-ordination angle along the Zr-Cl vector of the catalyst.[19] Under identical conditions, $Et(ind)_2ZrCl_2$ incorporates 6 times more DMON than Cp_2ZrCl_2 catalyst.[20] For the same mol % incorporation, ethylene/DMON copolymers have high Tg over ethylene/norbornene copolymer.[19] The highest incorporation of DMON (85 mol %) has been reported with the catalyst $Ph_2C(ind)(Cp)ZrCl_2$ (**9**).[21]

Unlike other metallocenes, the molecular weight of copolymers was found to increase with temperature and decreases only at very high DMON/ethylene ratio.



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1.2.3 Ethylene/TMDA copolymers

TMDA is bulkier than DMON and norbornene and, therefore, is less active in copolymerization. The highest incorporation (27 mol %) has been reported with $Ph_2C(fluo)(Cp)ZrCl_2$.[21]

1.2.4 Ethylene/phenyl substituted bicyclic olefin copolymers

Kaminsky and Noll[22] have reported the copolymerization of ethylene with phenyl norbornene and phenyl-DMON using $Me_2Si(ind)_2ZrCl_2$ and $Me_2C(fluo)(Cp)ZrCl_2$ catalyst. Phenyl substitution on norbornene increases the Tg of copolymer by 40°C. The highest Tg of 230°C achieved so far for an ethylene/bicyclic olefin copolymer has been reported with phenyl-DMON.

1.2.5 Terpolymers

Introduction of pendant double bonds in ethylene/bicyclic olefin copolymers increases the Tg.[22] Tg of ethylene/norbornene/VNB terpolymers were found to be almost 10°C higher than that of ethylene/norbornene copolymers of similar norbornene content.

Studies conducted at Idemitsu Kosan Co., Ltd, Japan have found that ethylene/cyclic olefin copolymers having small amounts of cyclic olefins, called as elastic polyolefins, possess high strain recovery at high strain modulus, which may be due to the restricted mobility of the amorphous region due to the presence of cyclic structure.[23]

1.2.6 Ethylene/other cyclic olefin copolymers

Copolymerization of ethylene with cyclopentene, cycloheptene and cyclooctene using $Et(ind)_2ZrCl_2$ have been reported by Kaminsky and Spiehl.[24] No polymerization activity was observed for cyclohexene. The activity decreases in the order cyclopentene > cycloheptene > cyclooctene. At a cyclopentene/ethylene feed ratio of 15.3, the activity for copolymerization was almost the same as for ethylene homopolymerization. Incorporation of cyclopentene needed to bring down the Tm of polyethylene is less as compared to 1-butene needed, namely, 0.6 mol % and 1.5 mol % respectively, for a Tm of 123°C.

1.2.7 Reactivity ratios

The reactivity ratio values for ethylene and various bicyclic olefin monomers for different metallocene catalysts are given in **Table 1.3**. It is surprising to note that the copolymerization parameter r_1 (reactivity ratio value for ethylene in ethylene/norbornene copolymerization) for $Et(indH_4)_2ZrCl_2$ is lower than that for ethylene/propylene copolymerization (1.5 to 3.2 and 6.6 respectively) indicating the ease with which the bulky norbornene undergoes enchainment.[11] The product of the reactivity ratios is a measure of the statistical random or alternating structures in the copolymer. From the available data, the copolymers are in between that of statistically random and alternate, depending on the catalyst used for copolymerization.

1.2.8 Glass Transition Temperatures

Ethylene/cyclic olefin copolymers have found a well entrenched place among engineering plastics due to their high Tg. The Tg of copolymer depends not only on the mol % of norbornene but also on the experimental conditions and the metallocene used for copolymerization.[26] For example, a copolymer having 29 mol % norbornene, synthesized at 30°C has a Tg of 77°C where as the one synthesized at 70°C having same mol % did not show any Tg above 0°C. Copolymers, having same mol % of norbornene, synthesized at higher catalyst concentration or Al/Zr ratio have high Tg. ^{13}C NMR microstructure of ethylene/norbornene copolymer showed peaks corresponding to block, alternate and isolated norbornene groups.[25] The Tg of the copolymers depends on the percentage of these groups in copolymer (**Table 1.4**), which depends on the copolymerization conditions used. Higher the amount of blocky and alternate structures higher is the Tg.

Table 1.3 Reactivity ratios of ethylene and various bicyclic olefins in ethylene/bicyclic olefin copolymerizations

Metallocene	temp(°C)	$r_{ethylene}$	$r_{cyclic\ olefin}$	ref.
Ethylene/NB copolymerization				
$Me_2Si(ind)_2ZrCl_2$	0	3.7	0.2	20
"	25	4.3	0.7	20
"	30	2.66	-	12
$Ph_2Si(ind)_2ZrCl_2$	30	3.44	-	12
$Me_2C(fluo)(Cp)ZrCl_2$	30	2.93	-	12
"	30	3.4	0.06	13
$Ph_2C(fluo)(Cp)ZrCl_2$	0	2.0	0.05	13
"	30	3.0	0.05	13
"	30	2.61	-	12
$Et(indH_4)_2ZrCl_2$	-25	1.5	-	11
"	0	1.9	-	11
"	25	2.2	-	11
$Et(ind)_2ZrCl_2$	25	6.6	-	11
Cp_2ZrCl_2	25	20	-	11
$Me_2C(fluo)(t\text{-}buCp)ZrCl_2$	30	3.1	0	13
Ethylene/DMON copolymerization				
$Ph_2C(fluo)(Cp)ZrCl_2$	50	7.0	0.02	21
$Ph_2C(ind)(Cp)ZrCl_2$	50	6.4	0.1	21
$Me_2C(fluo)(Cp)ZrCl_2$	50	7.1	0.04	21
$Et(indH_4)_2ZrCl_2$	25	50	-	30
$Et(ind)_2ZrCl_2$	25	15	-	30
Ethylene/TMDA copolymerization				
$Ph_2C(ind)(Cp)ZrCl_2$	50	15.6	0.94	21
Ethylene/Ph-NB copolymerization				
$Me_2Si(ind)_2ZrCl_2$	30	7.8	0.1	22
$Me_2C(fluo)(Cp)ZrCl_2$	30	7.0	0.05	22
Ethylene/Ph-DMON copolymerization				
$Me_2Si(ind)_2ZrCl_2$	30	11.5	0.05	22
$Me_2C(fluo)(Cp)ZrCl_2$	30	7.1	0.03	22

Table 1.4 Effect of microstructure on Tg

mol % norbornene in copolymer	Tg(°C)	BL/ALT/IS*
34	123	19/65/16
33	117	23/56/21
35	150	27/60/13

* BL, ALT and IS denotes the ratio of block, alternating and isolated norbornene moieties in the copolymer

Tg values reported in the published literature are given in **Table 1.5**. Those available from the patent literature are included in **Table 1.6**.

1.2.9 Applications

Mitsui Petrochemicals and Hoechst have announced the commercial production of ethylene/norbornene copolymers under the trade name TOPAS (Thermoplastic Olefin Polymers of Amorphous Structure) since 1996. They are made in slurry phase process. The copolymers are having densities 20 % less than conventional polycarbonate products and have a better signal to noise ratio because of their extremely low birefringence. Moreover, such copolymers are reported to have very low water absorption and high heat resistance. These copolymers are likely to find application as high performance optical lens and discs, pharmaceutical packages such as vial, ampoule, syringe, film etc. The applications in medical field are due to its high transparency, heat resistance against steam sterilization, low moisture permeability etc.[27] Another application of cycloolefin copolymers is as substituent for PVC films laminated with PVdC barrier resin in multi layer films for food and medical packaging.[28]

Table 1.5 Tgs of ethylene/bicyclic olefin copolymers

Monomer	Catalyst	mol % of comonomer in copolymer	Tg(°C)	Ref.
Norbornene	$Me_2C(fluo)(Cp)ZrCl_2$	> 56	175	12
	$Ph_2C(fluo)(Cp)ZrCl_2$	> 56	184	12
	$Me_2Si(ind)_2ZrCl_2$	35	82	12
	$Ph_2Si(ind)_2ZrCl_2$	34	86	12
	$Et(ind)_2ZrCl_2$	38	155	13
DMON	$Me_2C(fluo)(Cp)ZrCl_2$	28	125	21
	$Ph_2C(fluo)(Cp)ZrCl_2$	68	187	21
	$Ph_2Si(ind)_2ZrCl_2$	85	216	21
	$Me_2C(fluo)(Cp)HfCl_2$	73	203	21
	$Et(indH_4)_2ZrCl_2$	50	150	30
Phenyl-NB	$Me_2C(fluo)(Cp)ZrCl_2$	>25	102	22
	$Me_2Si(ind)_2ZrCl_2$	24	89	22
Phenyl-DMON	$Me_2C(fluo)(Cp)ZrCl_2$	26	127	22
	$Ph_2C(fluo)(Cp)ZrCl_2$	>30	229	22

Table 1.6 Representative patents on olefin/bicyclic olefin copolymers

CA No. and year	Patent No. and Company	Monomer/ comonomer	Catalyst/cocatalyst	Reaction parameters	features
127:95730r (1997)	DE 19,546,500 Hoechst A.-G.	ethylene/ norbornene	bis(dimethylamido) [(1-Cp-1-methylethyl) indenyl]zirconium	70°C, 6 bar	Tg 193°C vis. no. 69mL/g
127:66330c (1997)	5,635,573 Exxon Chemical Patents, Inc.	"	$Me_2Si(indH_4)_2HfMe_2$/ $[PhNHMe_2]^+[B(C_6F_5)_4]^-$	hexane	MWD 1.76 Mw 50, 810 18.6 mol % norbornene
126:131892k (1996)	EP 749,988 Hoechst A.-G.	"	[4-(η^5Cp)(η^5-tetrahydropentalene)] $ZrCl_2$	18 bar, 70°C	Tg 176°C
126:118323f (1996)	WO 96/40,806 Exxon Chemical Patents, USA	"	CGC	C_2:norbornene - 1:6	Tm 250°C (highly crystalline copolymer)

Table 1.6 Representative patents on olefin/bicyclic olefin copolymers (continued...)

CA No. and year	Patent No. and Company	Monomer/ comonomer	Catalyst/cocatalyst	Reaction parameters	Features
125:143571x (1996)	US 5,650,471 Mitsui Petrochemical Ind. Ltd., Hoechst A.-G.,Japan	ethylene/ norbornene	Me_2C(fluo)(Cp)$ZrCl_2$/ TIBAL/ MAO	toluene+hexane	Tg 110°C, 47.4 mol % norbornene [η] - 1.3dL/g (decalin, 135°C)
122:241364q (1994)	EP 610,852 Hoechst A.-G.	"	Me_2C(fluo)(Cp)$ZrCl_2$/ microwaved silica-supported MAO	---	High yield and viscosity compared to when using with out microwave treatment
122:215545e (1996)	US 5,498,677 EP 610,813 Hoechst A.-G.	"	(fluo)(Cp)$ZrCl_2$/MAO	---	Tm 210 - 320°C 50 % norbornene good solvent resistance
122:215544d (1994)	EP 610,843 Hoechst A.-G.	"	Me_2Si(2,7-t butyl fluo)(Cp)$ZrCl_2$/MAO	toluene	vis. no. 122mL/g

Table 1.6 Representative patents on olefin/bicyclic olefin copolymers (continued...)

CA No. and year	Patent No. and Company	Monomer/ comonomer	Catalyst/cocatalyst	Reaction parameters	Features
122:215543c (1994)	EP 610,851 Hoechst A.-G.	ethylene/ norbornene	$Me_2C(ind)(Cp)ZrCl_2$	---	good tensile strength as compared to one synthesized with $Ph_2C(fluo)(Cp)ZrCl_2$
122:214825j (1994)	EP 610,850 Hoechst A.-G.	"	Ph_2C(2,7-t butyl fluo)$(Cp)ZrCl_2$/MAO	toluene, 70°C, 6 bar, 1 h	Tg 155°C vis. no. 119 mL/g
122:83264a (1994)	EP 610,814 Hoechst A.-G.	"	zirconocene/ MAO	toluene, 2.5 bar, 70°C	Tg 126°C
122:83262y (1994)	EP 610,815 US 5,583,192 Hoechst A.-G.		metallocene	---	Tg 147°C special microstrcture vis. no. 90mL/g
122:82367z (1997)	US 5,637,400 Hoechst A.-G.	"	$Ph_2C(fluo)(Cp)ZrCl_2$	3.4 bar, 70°C, 1.5 h	Tg 181°C vis. no. 62 mL/g

Table 1.6 Representative patents on olefin/bicyclic olefin copolymers (continued...)

CA No. and year	Patent No. and Company	Monomer/ comonomer	Catalyst/cocatalyst	Reaction parameters	Features
122:82366y (1994)	DE 4,304,285 Hoechst A.-G.	"	$Me_2Si(ind)_2ZrCl_2$/ MAO	toluene, 3.7 bar, 70°C, 2.5 h	Tg 179°C
120:135477c (1997)	US 5,646,220 Hoechst A.-G.	"	metallocene	blockcopolymn.	MWD 1.7
118:192481g (1992)	EP 503,422 US 5,324,801 Hoechst A.-G.	"	Me_2C(fluo) (3-MeCp)$ZrCl_2$/MAO	70°C, 1 h	Tg 145°C 50 mol % norbornene vis. no. 32mL/g
117:251998k (1992)	EP 501,370 US 5,422,409 Hoechst A.-G.	"	$Me_2Si(ind)_2ZrCl_2$/ MAO	---	---
117:112263d (1992)	EP 485,893 Hoechst A.-G.	"	Ph_2C(fluo)(Cp)$ZrCl_2$	norbornene medium, 70°C	Tg 183°C
114:247975w (1991)	EP 407,870 Hoechst A.-G.	"	$Me_2Si(ind)_2ZrCl_2$/ MAO	1 bar, 20°C, 1 h	Tg 32°C vis. no. 244 mL/g

Table 1.6 Representative patents on olefin/bicyclic olefin copolymers (continued...)

CA No. and year	Patent No. and Company	Monomer/ comonomer	Catalyst/cocatalyst	Reaction parameters	Features
106:157019t (1986)	JP 61,221,206 Mitsui Petrochemical Industries, Ltd.	ethylene/ norbornene	Cp_2ZrCl_2/MAO	toluene	MWD 2.33 10 mol % norbornene [η] - 2.33dL/g (decalin,135°C) comparison with $MgCl_2/TiCl_4$catalyst
125:168994a (1996)	EP 719,806 Mitsui Petrochemical Ind., Ltd, Hoechst A.-G.	ethylene/ ethylene-norbornene	Me_2C (ind)(Cp)$ZrCl_2$/ MAO	hydrogenated butadiene-styrene block copolymer, 70°C, 1 h	Tg 141°C rubber content 17.8 %
125:13087h (1996)	JP 08 59,726 Idemitsu Kosan Co., Japan	ethylene/ 5-hexyl norbornene	Cp_2ZrCl_2/TIBAL/ $PhNH(CH_3)_2^+$ $B(C_6F_5)_4^-$	7 bar, 90°C, 1 h	[η] - 1.81dL/g

Table 1.6 Representative patents on olefin/bicyclic olefin copolymers (continued…)

CA No. and year	Patent No. and Company	Monomer/ comonomer	Catalyst/cocatalyst	Reaction parameters	Features
124:57037a (1995)	EP 678,530 Mitsui Petrochemical Ind., Ltd., Hoechst A.-G.	ethylene/ norbornene/ propene or 1-decene	metallocene	---	good control of molecular weight
120:56472u (1993)	JP 05,230,147 Idemitsu Kosan Co.	ethylene/ propylene/ norbornene	Cp_2ZrCl_2/TIBAL/ $[PhNH(CH_3)_2]^+$ $[B(C_6F_5)_4]^-$	C_3 2 bar, C_2 7 bar, 60°C, 1.5 h	8.6mol % norbornene 4.5mol % C_3 $[\eta]$ - 2.6dL/g
113:116078n (1990)	DE 3,835,044 Hoechst A.-G.	ethylene/ DMON	$Et(ind)_2ZrCl_2$/MAO	toluene, C_2:DMON 1:1.71, 3 bar, 25°C	---
110:173965m (1988)	US 5,003,019 Mitsui Petrochemical Industries, Ltd.	propylene/ DMON	$Et(ind)_2ZrCl_2$/MAO	20°C, 2 h	MWD 1.48 25 mol % comonomer 0.06 dL/g (decalin, 135°C)

1.3 Copolymerization of olefins with dienes

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 polyolefin 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 polyolefins, where the pendant double bonds in the copolymer are converted into functional groups by standard organic chemical reactions. Such functional groups on polyolefins increase their adhesive and wettability properties over the unfunctionalized one. More over, 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.

1.3.1 Copolymerization with symmetrical dienes

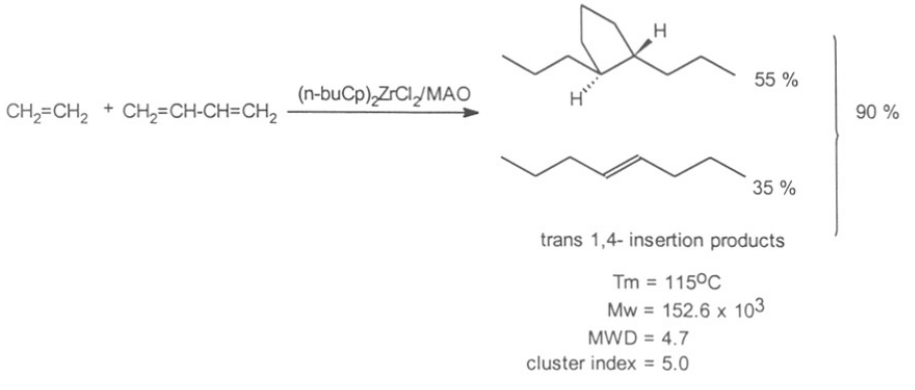
Copolymerization of olefins with symmetrical dienes usually results in copolymers having novel structures. The pendant double bond on the polymer chain formed after the insertion of one of the equally reactive double bonds of the diene gets enchained in the same polymer, generating cyclic structure on 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 (**Scheme 1.1**).[31] With $Et(indH_4)_2ZrCl_2$, enchainment was found to occur exclusively in 1,4-trans configuration with around 50 % as trans cyclopentane rings.[32,33] 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.[31] 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.



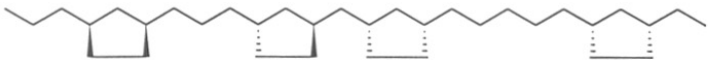
Scheme 1.1 Copolymerization of ethylene with 1,3-butadiene

Copolymerization of ethylene with 1,5-hexadiene was reported to occur through cyclopolymerization resulting in cyclopentane units along the polymer backbone (**Scheme 1.2**).[34]

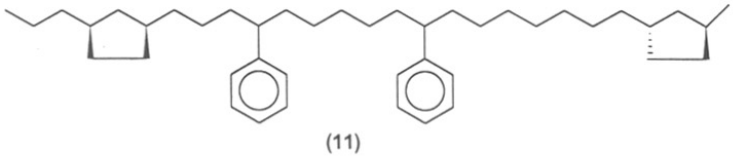
10 mol % comonomer
Mw = 120 x 10^3
MWD = 2.6
Tm = 103.6°C
cluster index < 5

Scheme 1.2 Copolymerizaton of ethylene with 1,5-hexadiene

Recently, copolymerization of ethylene with 1,5-hexadiene using constrained geometry catalyst has been reported. With a 1:1 feed composition for ethylene and 1,5-hexadiene, a copolymer having 31.2 mol % of comonomer (**10**), as cyclopentane units, having a Tg of 57°C has been obtained. At higher concentrations of 1,5-hexadiene, copolymers are found to have vinyl pendant groups due to uncyclized 1,5-hexadiene units. Though 1,5-hexadiene/styrene copolymerization did not work, terpolymerization with 1:1:1 feed composition a copolymer (**11**) having 2.1 mol % styrene and 19.3 mol % 1,5-hexadiene was obtained. [35]

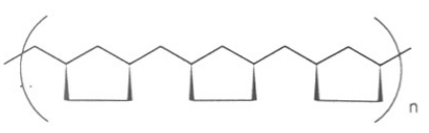


(10)

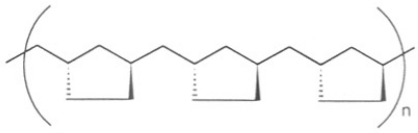


(11)

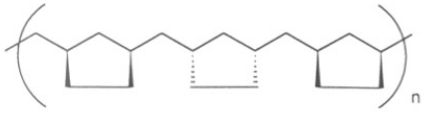
Though the discussion in this section of the chapter is centered on the copolymerization of olefins with symmetrical dienes, it is worth having a special discussion on the homopolymerization of symmetrical dienes using metallocene catalysts. Waymouth's group, in a series of publications, [36-38] has showed how a metallocene catalyst could be effectively used for the synthesis of chiral polymers by the cyclopolymerization of 1,5-hexadiene. Theoretically, cyclopolymerization of 1,5-hexadiene should give poly(methylene-1,3-cyclpentane)(PMCP) having four different structures (**12-15**).



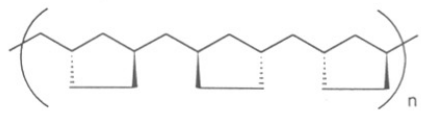
cis-isotactic
(12)



trans-isotactic
(13)

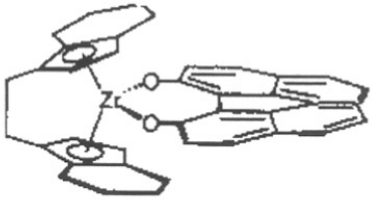


cis-syndiotactic
(14)



trans-syndiotactic
(15)

Of these, the trans-isotactic one (**13**) is chiral due to the absence of mirror planes of symmetry. For obtaining that structure, the polymer must be predominantly isotactic and must have predominantly trans rings. The enantioface selectivity of olefin insertion determines the tacticity while the diasteroselectivity determines the cis or trans ring selectivity. Utilizing the existing knowledge of metallocene catalysts that enantioface selectivity is determined by the structure of the metallocene, and that the racemic metallocene could be resolved into the isomers using 1,1'-binaphthol,[39] they could successfully synthesize the optically active trans-isotactic PMCP alone by homopolymerization. The (R,S)-Et(indH_4)$_2$ZrCl_2 was resolved into (+) and (-) isomers by (S)-(-)-binaphthol. Cyclopolymerization of 1,5-hexadiene using (R,R)-(-)-Et(indH_4)$_2$ZrCl_2BINOL (**16**) lead to PMCP having a molar optical rotation (per monomer unit) of +50.1°, Mw 35,000 and MWD 1.9.



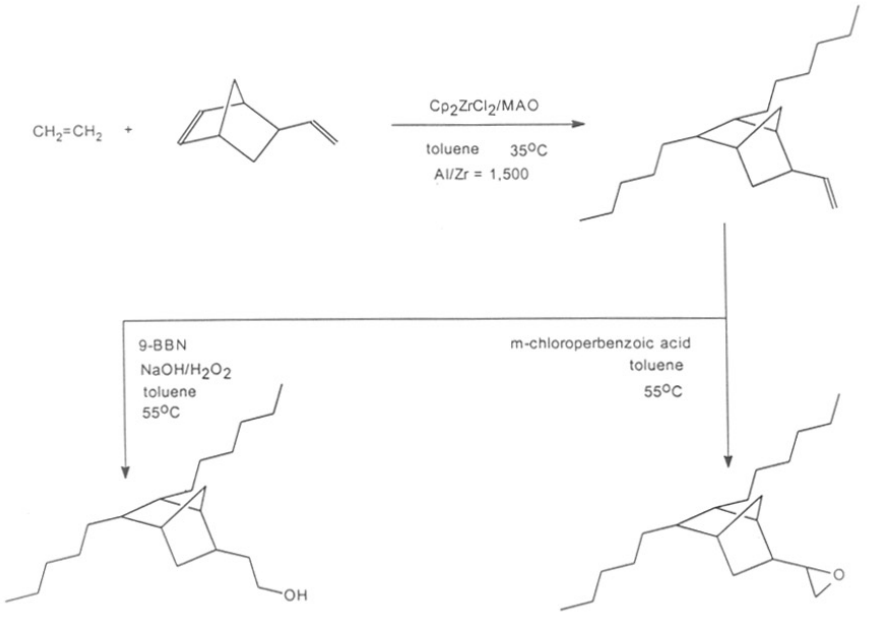
(16)

1.3.2 Copolymerization with unsymmetrical dienes

Copolymerization of olefins with unsymmetrical dienes, where one of the double bonds is more reactive than the other, gives polyolefins having pendant double bonds, which can later be functionalized. Such functionalization reactions are also included in this section.

Copolymerization of ethylene with 4-vinyl cyclohexene using $Ph_2C(fluo)(Cp)ZrCl_2$/ MAO catalyst system have been found to occur regiospecifically through the vinyl double bond. The pendant cyclohexenyl double bonds were functionalized to hydroxyl groups. Introduction of hydroxyl groups increased the Tm while reduced the Tg, which may be due to hydrogen bond interaction.[40]

Copolymerization of ethylene with 5-vinyl-2-norbornene has been reported to occur regiospecifically through the endocyclic double bond leaving the exocyclic vinyl double bond for post polymerization functionalization. These pendant groups have been quantitatively functionalized to epoxy and hydroxy groups (**Scheme 1.3**).[41]



Scheme 1.3 Copolymerization of ethylene with 5-vinyl-2-norbornene and its post polymerization functionalizations

Copolymerization of ethylene with the unsymmetrical diene 1,4-hexadiene have also been reported.[42] The reactivity ratio values for ethylene and 1,4-hexadiene for Cp_2ZrCl_2/MAO catalyst system are 120 and 0.01 respectively.[43] A number of patents are available on the copolymerization of olefins with dienes, both symmetrical as well as unsymmetrical (**Table 1.7**).

A novel route to the synthesis of polyolefin having pendant double bonds have been reported by Yang and Marks.[44] The procedure involves the copolymerization of

Table 1.7 Representative patents on copolymerization of olefins with dienes

CA. No. and year	Patent no. and Company Name	Olefin/ comonomer	Catalyst/cocatalyst	Reaction parameters	features
125:329806h (1996)	JP 08,239,415 Mitsui Petrochemical Ind., Japan	ethylene/ 5-ethylidene-2-norbornene	Cp_2ZrCl_2	Al/Zr 200, 20°C, 1h	[η] - 2.03dL/g MWD 1.97 crystallinity 0.8 %
125:11751w (1993)	JP 08 59,723 Showa Denko K k, Japan	ethylene/ 1,4-pentadiene	$(n\text{-}buCp)_2ZrCl_2$/TIBAL/ $(EtO)_3PO$ modified MAO	---	no gelation
123:144941p (1995)	JP 07,33,826 Idemitsu Kosan Co.	ethylene/VNB	Cp_2ZrCl_2/TIBAL/ $[PhNH(CH_3)_2]^+$ $[B(C_6F_5)_4]^-$	80°C, 7bar, 0.5h	[η] - 1.82dL/g
122:266340s (1994)	JP 06,271,617 Idemitsu Kosan Co., Ltd	ethylene/ 5-ethylidene-2-norbornene	Cp_2ZrCl_2/TIBAL $[PhNH(CH_3)_2]^+$ $[B(C_6F_5)_4]^-$	---	hydrogenation

Table 1.7 Representative patents on copolymerization of olefins with dienes (continued...)

CA. No. and year	Patent no. and Company Name	Olefin/comonomer	Catalyst/cocatalyst	Reaction parameters	features
109:150259z (1988)	WO 88/ 04,672 Exxon Chemical Patents, Inc.	ethylene/ 1,3-butadiene	$(n\text{-buCp})_2ZrCl_2$/MAO	isopentane	MWD 2.5 cluster index 5.0
127:81900j (1997)	WO 97/19,965 US 5,65,329 Dow Chemical Company, USA	ethylene/ 1-octene/ 1,7-octadiene	metallocene/MAO	---	vinylidene in 1000 carbon - 0.44 d - 0.867 g/cm^3
126:330960f (1997)	WO 97/12,970 DSM, N.V., Netherlands	olefin/ 1,2-polybutadiene	metallocene	---	---
122:292988d (1995)	JP 07,33,828 Idemitsu Kosan, Co.	ethylene/1-octene/ 2,5-norbornadiene	Cp_2ZrCl_2/TIBAL/MAO	---	1 mol % octene 0.06 mol % NBD

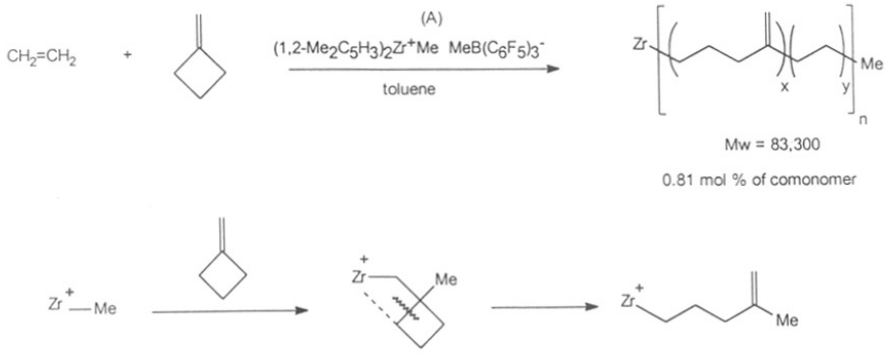
Table 1.7 Representative patents on copolymerization of olefins with dienes (continued...)

CA. No. and year	Patent no. and Company Name	Olefin/comonomer	Catalyst/cocatalyst	Reaction parameters	Features
115:256891p (1991)	WO 91/01,337 US 5,017,665 Exxon Chemical Patents, Inc.	ethylene/ 1-butene/ 1,4-hexadiene	$(ind)_2ZrCl_2$/MAO/silica	C_2:C_4:C_6 - 50:7:1, 63°C, fluidized bed	d - 0.9211 g/cm^3
121:281460d (1994)	JP 06,172,449 Idemitsu KosanCo.	propylene/VNB	$Me_2Si(ind)_2ZrCl_2$/ TIBAL/MAO	toluene, 50°C, 2h	MWD 2.9 6.3mol % VNB
119:73318v (1993)	JP 05,17, 530 Mitsui Petrochemical Co.	propylene/VNB	$Et(ind)_2ZrCl_2$/MAO	toluene, 50°C	MWD 2 Mw 28,000 0.5 mol % VNB
116:42220r (1991)	WO 91/15,523 Mitsui Toatsu Chemicals, Inc	propylene/ 5-methylene-2-norbornene	$Me_2C(fluo)(Cp)ZrCl_2$/ MAO	---	2.3 mol % diene

Table 1.7 Representative patents on copolymerization of olefins with dienes (continued...)

CA. No. and year	Patent no. and Company Name	Olefin/comonomer	Catalyst/cocatalyst	Reaction parameters	Features
123:287229y (1995)	JP 07,138,327 Mitsui Toatsu Chemicals	ethylene/propylene/ 1,5-hexadiene	$Me_2Si(2,4Me_2Cp)_2ZrCl_2$/ MAO	---	η - 1.21dL/g MWD 3.1 contains pendant unsaturation
124:318173c (1997)	US 5,652,308 WO 96/03445 Exxon Chemical Patents, Inc.	propylene/ 5-ethylidene-2-norbornene(ENB)	Cp_2ZrMe_2/TIBAL/ $[PhNH(CH_3)_2]^+$ $[B(C_6F_5)_4]^-$	80°C	Tg 52°C Mw 1165, MWD 2.34 60 mol % of ENB

ethylene with methylene cyclobutane with the cationic catalyst (**A**). The reaction involves the incorporation of zirconium- carbon bond on to the double bond followed by α-alkyl shift as shown in **Scheme 1.4**.



Scheme 1.4 Synthesis of exo-methylene functionalized polyethylene

1.4 Synthesis of functional polyolefins

There are three different routes for the synthesis of functional polyolefins. One is the direct copolymerization of olefin with functional monomer. Second method is the post polymerization grafting of functional groups on to the polyolefin backbone using either thermal or ionization energy. Non uniform distribution of the functional groups on the polymer, with functional group predominantly located in the amorphous region, degradation of the polyolefin backbone and crosslinking are some of the drawbacks of this method. The third, and the most preferred method, is the copolymerization with a precursor monomer which do not interfere in the polymerization but can be later converted into desired functional groups by standard organic chemical reactions. The homogeneous metallocene based catalysts have some unique characteristics, which enable the synthesis of functional polyolefins.

1.4.1 Synthesis of functional polyolefins by direct copolymerization with functional monomers

The direct route for the synthesis of functionalized polyolefins is by the copolymerization of olefin with comonomers having the desired functional group. But this method is restricted by the ability of the functional group to co-ordinate with the catalyst/co-catalyst components, thus, deactivating it. Different methods have been adopted to obviate this problem, like separating the functional group from the polymerizable double bond by spacer groups, by protecting the functional group

either by using externally added reagent or by increasing the bulkiness around the functional group and by decreasing the nucleophilicity of the functional group.

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.[45] 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 % with the metallocene Me_2Si[2-Me-4,5-Benzo Ind]$_2ZrCl_2$.[46] Copolymerization of ethylene with 5-hexen-1-ol and 10-undecen-1-ol using $(n\text{-buCp})_2ZrCl_2$/MAO catalyst system under identical conditions showed that increasing spacer group between the polymerizable double bond and the functional group does not have any effect on copolymerization activity. However, longer the spacer group higher was the incorporation.[47] Though hydroxyl group does 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.[47]

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.

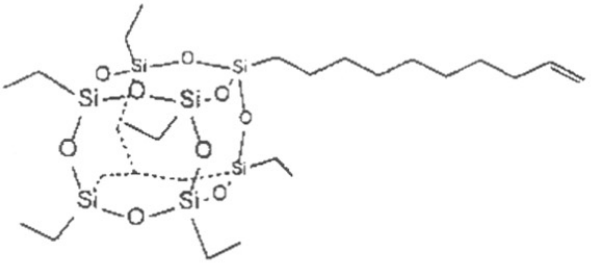
Pretreatment of 10-undecen-1-ol with MAO or increase in Al/Zr ratio increased the copolymerization activity, but marginally decreased the comonomer content[46] as well as molecular weight.[45] It can be presumed that the alcohol reacts with MAO 'in situ' to form alcoholate which underwent copolymerization. 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.[48] 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. 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.[49]

JP patent 6,172,447[50] 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; 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°C and 1.87 mol % of the functional monomer have been synthesized.

JP patent 4,45,108[51] has described 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°C. A few more patents on olefin/functional monomer copolymerizations are given in **Table 1.8**.

Synthesis of polyethylene having pendant cubic silsequioxane groups have been reported by Tsuchida et al.[52] by the copolymerization of ethylene with a novel monovinyl functional silsesquioxane 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 (**17**) using metallocene/MAO catalyst system. A maximum incorporation of 1.2 mol % has been reported. These copolymers possess superior thermal stability in air over polyethylene.



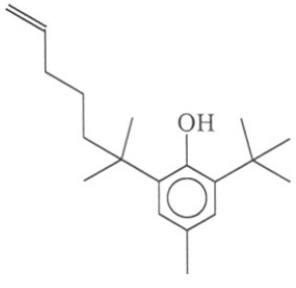
(17)

Antioxidants have been incorporated into polyolefin backbone by copolymerizing ethylene with the functional monomer 6-tert-butyl-2-(1,1-dimethyl hept-6-enyl)-4

Table 1.8 Representative patents on olefin/functional monomer copolymerization

CA. No. and year	Patent no. and Company Name	Olefin/ functional comonomer	Catalyst/cocatalyst	Reaction parameters	Features
126:8822k (1996)	WO 96/34,023 Borealis A/S, Denmark	ethylene/2-methyl-3-butene-2-ol	$(n\text{-}buCp)_2ZrCl_2$/MAO	elevated temp.	---
118:148240d (1992)	JP 04,309,507 Mitsui Toatsu Chemials, Inc.	styrene/phenyl maleimide	$Me_2C(fluo)(Cp)ZrCl_2$/ MAO	20°C, 4h	Mw 80,000
116:256248e (1991)	EP 430,112 Mitsui Toatsu Chemicals, Inc.	propylene/trimethyl allylsilane,	$Et(indH_4)_2ZrCl_2$/MAO	32°C, 1h.	[η] - 0.15 dL/g 1.9 % trimethyl allylsilane
125:329872b (1996)	US 5,578,690 Northwestern Univ., USA	ethylene/$PhSiH_3$	$(Cp^*)_2SmH$	---	Silyl end capped polyolefins
118:81627q (1992)	JP 04,309,508 Idemitsu Kosan Co., Ltd.	ethylene/ethyl Acrylate,	$CpZrMe_3/Et_3N\ B(C_6F_5)_4$	10 bar, 2h	Mw 18, 000 MWD 2.46

methyl phenol (**18**).[53,54] The activity was higher for copolymerization than that for the homopolymerization of ethylene for $Me_2Si(indH_4)_2ZrCl_2$, while no considerable difference was found with Cp_2ZrCl_2. 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 temp, the catalytic sites are more sensitive to donor interactions. But the incorporation of phenol rises with the increase in temperature.

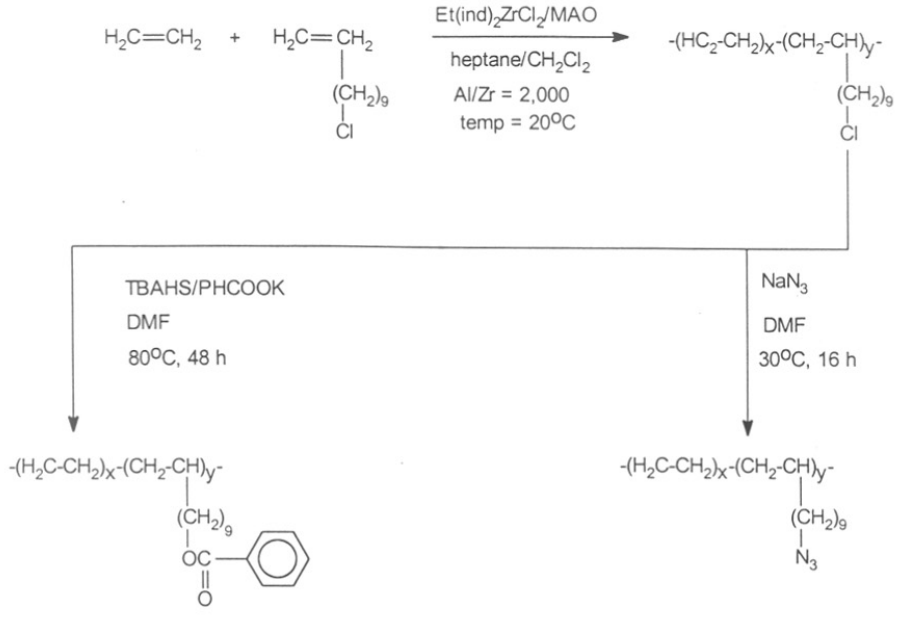


(18)

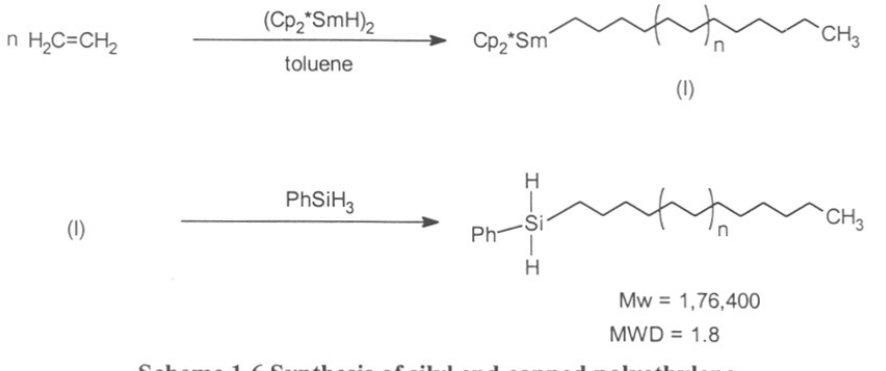
Copolymerization of ethylene and propylene with ω-chloro-α-olefins using $Et(ind)_2ZrCl_2$/MAO in heptane medium (**Scheme 1.5**) followed by functionalization of pendant chloro end groups to aromatic ester, hydroxyl and azide groups have been reported by Bruzaud et al. recently.[55,56] Copolymerization 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.

Fu and Marks[57] have demonstrated a route to silyl end capped polyolefins by polymerization of ethylene in presence of $PhSiCH_3$ as chain transfer agent (**Scheme 1.6**). Such silyl end capped polyethylenes are useful as adhesion promoters and as dispersing agents to enhance the filler dispersions in polyolefin matrix.

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.[58] They were successful in synthesizing

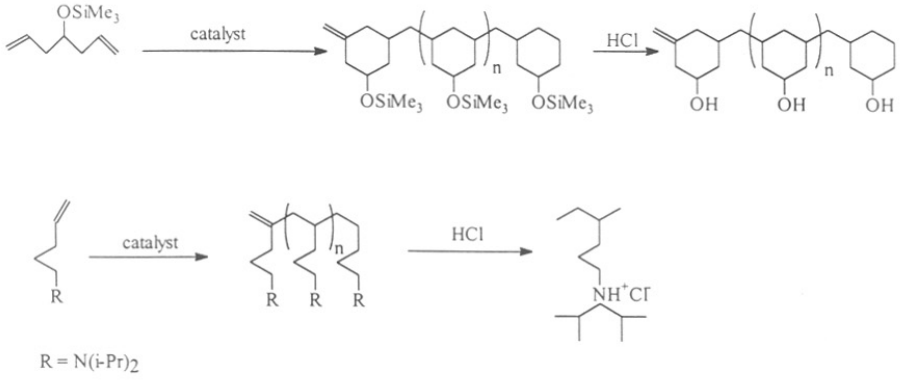


Scheme 1.5 Copolymerization of ethylene with ω-chloro-α-olefin and its post polymerization functionalizations



Scheme 1.6 Synthesis of silyl end capped polyethylene

poly(methylene-3,5-(1-trimethylsiloxy) cyclohexanediyl) of Mw 1,42,600 and MWD 3.1 using $[(C_5Me_5)_2HfMe]^+ [B(C_6F_5)_4]^-$ catalyst in neat monomer at -25°C with 30 % conversion which on treatment with aq.HCl gives the polyalcohol (**Scheme 1.7**).



Scheme 1.7 Cyclopolymerization of functional monomers

The chiral $[Et(IndH_4)_2ZrMe]^+ [B(C_6F_5)_4]^-$ catalyst was found to be easily poisoned by silyl ethers as compared to $[(C_5Me_5)_2ZrMe]^+ [B(C_6F_5)_4]^-$. Allyloxy-tert-butyl dimethyl silane, allyloxy trimethyl silane and 5-trimethyl siloxy-1-pentene were found to be inactive towards polymerization under the same conditions.

1.4.2 Post polymerization functionalizations

As mentioned earlier, 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 polyolefins having pendant functional groups. More over, metallocene catalysts have some special features, which result in polyolefins having terminal double bonds. Functionalization reactions on them result in polyolefins having end functional groups.

1.4.2.1 Synthesis of polyolefins having pendant functional groups

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

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

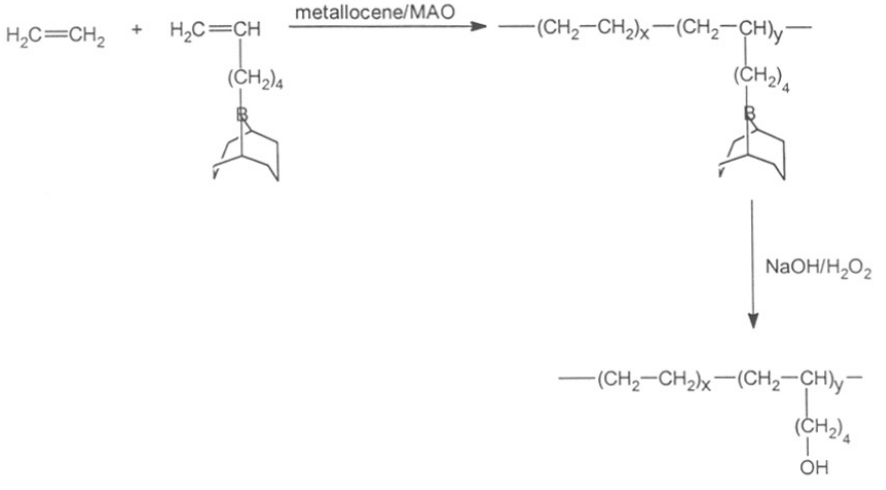
This section have been discussed in **Section 1.3.2**

1.4.2.1.2 Synthesis of functional polyolefins by post polymerization functionalization of copolymers having borane pendant groups

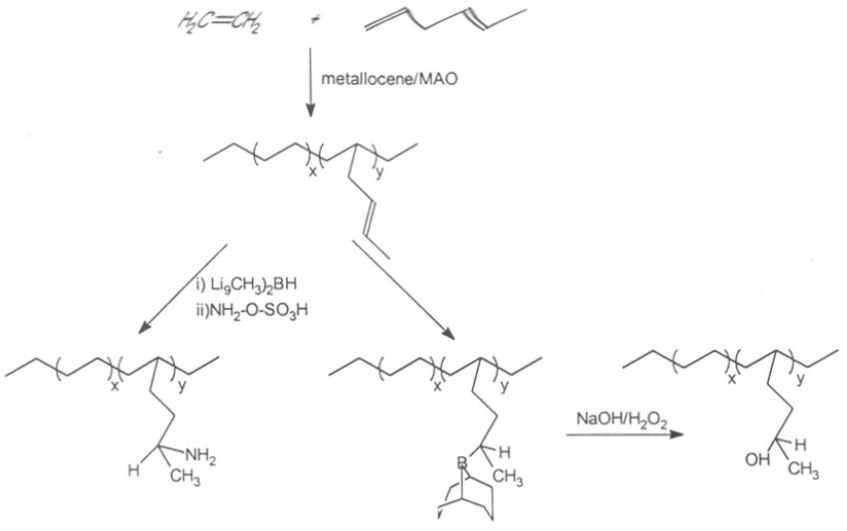
Synthesis of functionalized polyethylene by *borane approach*,[59] where ethylene is copolymerized with ω-borane-α-olefins (**Scheme 1.8**), or with unsymmetrical dienes followed by hydroboration (**Scheme 1.9**) using conventional Ziegler Natta catalysts, followed by chemical reaction on boron, have been extended to metallocene based catalyst system also. 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 incoporation was reported. Catalyst activity was found to increase with increase of comonomer in feed for the latter catalyst.[42]

1.4.2.2 Synthesis of end functionalized polyolefins

One of the most prominent chain transfer reactions in metallocene catalyzed polymerizations is β-H elimination reaction which results in polymer chains having terminal double bonds. The extent of chain transfer reaction by β-H elimination to other chain transfer reactions like chain transfer to Al alkyl etc resulting in polymers having saturated end groups highly depends on the experimental conditions. By properly choosing the experimental parameters, it is possible to synthesize polyolefins with 90 % polymer chains having at least one double bond per chain.



Scheme 1.8 Synthesis of polyethylene having borane containing pendant groups and its post polymerization functionalizations



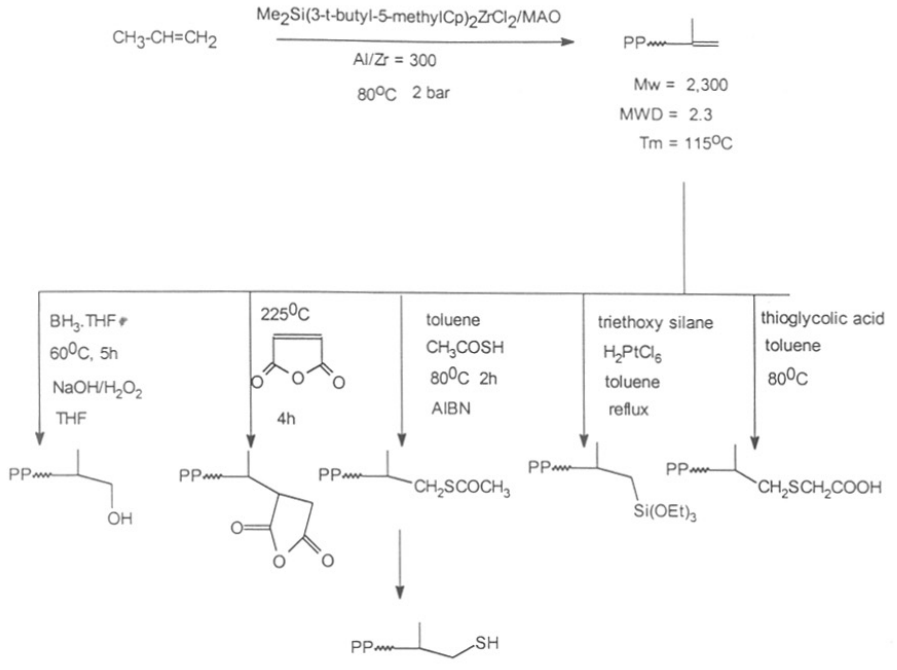
Scheme 1.9 Copolymerization of ethylene with 1,4-hexadiene and the post polymerization functionalization of pendant double bonds

Mulhaupt et al.[60] have reported the synthesis of low molecular weight isotactic polypropylene having at least one vinylidene end group per chain using bis(3-t-butyl-5-methyl cyclopentadienyl)$ZrCl_2$/MAO catalyst system. Double bonds were later converted into various functional groups by standard organic chemical reactions **(Scheme 1.10).**

Epoxy and hydroxy end functionalized liquid ethylene/propylene random copolymers having a propylene content of 58 mol %, Mw of 1,958, MWD of 1.78 and an iodine value of 23 are useful as lubricant oil additive and paint additive respectively.[61] The liquid copolymers synthesized with metallocene/MAO catalyst system has a B value in between 1.03 to 2, where B is given

$B = P_{OE}/(2P_O.P_E)$

Where P_E, P_O and P_{OE} are molar fractions of ethylene, propylene and propylene/ethylene sequence in the total dyad, respectively, in the copolymer. Larger B values show that the copolymer contains less block like sequence for the copolymer and has a more uniform distribution of ethylene and propylene and a narrow composition distribution. Generally, the copolymer is considered to be random in



Scheme 1.10 Synthesis of polypropylene having vinylidene end groups and its post polymerization functionalizations

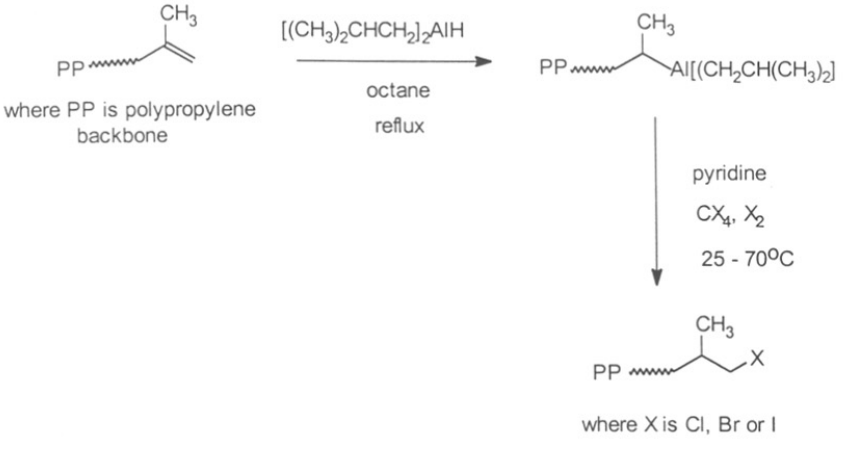
nature when the B value satisfies the following condition.

When the ethylene content in copolymer is not more than 50 mol %, $1.0 + 0.5 \times P_E < B < 1/(1-P_E)$ and when ethylene content is more than 50 mol % $1.5 - 0.5 \times P_E < B < (1/P_E)$.

WO 93/24539[62] describes the synthesis of functionalized 1-propene, 1-butene, 1-pentene and 1-hexene oligomers. In a comparative study using various metallocene catalysts it was found that the degree of oligomerization increases in the order $Cp_2ZrCl_2 \cong (n\text{-}buCp)_2ZrCl_2 < (MeCp)_2ZrCl_2 << (Me_5Cp)_2ZrCl_2 < Ind_2ZrCl_2$ under identical conditions (Al/Zr = 220, 40°C, 20 h). Oligomers having vinylidene end groups were successfully silylated, chlorinated, hydroxylated and formylated.

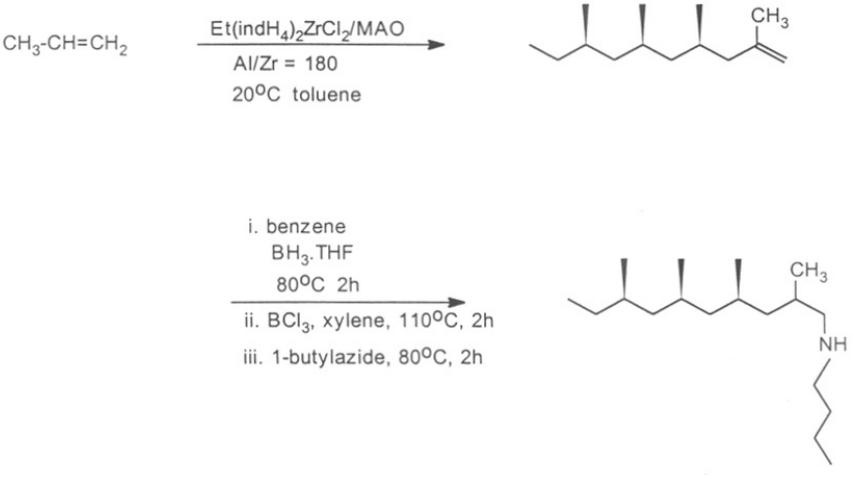
The synthesis of terminally halogenated isotactic polypropylene[63] and ethylene/propylene copolymers[64] has been reported by Shiono et al. The procedure involves the hydroalumination of vinylidene double bonds of polymer synthesized

using $Et(indH_4)_2ZrCl_2$/MAO catalyst system. The conversion of vinylidene group to halogen atoms were 85 % for Cl, 97 % for Br and 74 % for I(**Scheme 1.11**).



Scheme 1.11 Post polymerization halogenation of vinylidene end groups in polypropylene

Shiono et al.[65] have also synthesized amino end functionalized polypropylenes (**Scheme 1.12**). Atactic and isotactic polypropylenes having terminal vinylidene groups synthesized by Cp_2ZrCl_2 and $Et(indH_4)_2ZrCl_2$ catalyst systems were functionalized by the following method.



Scheme 1.12 Synthesis of polypropylene having vinylidene end groups and its post polymerization functionalizations

Synthesis of amino and epoxy end functionalized syndiotactic polypropylene (s-PP) by the functionalization of vinylidene end groups of s-PP synthesized by $Me_2C(fluo)(Cp)ZrCl_2$ are described in the patents US 5,444,125[66] and EP 487, 278[67] respectively.

1.5 Synthesis of graft and block copolymers from functional polyolefins

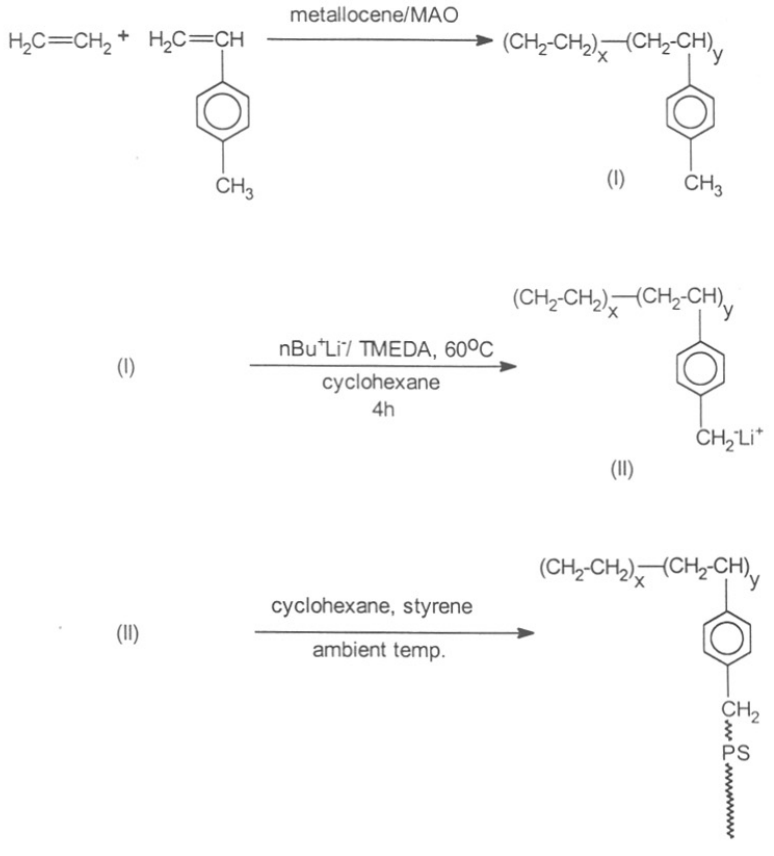
In the above section, the synthesis of polyolefins having functional groups present either as pendant ones or on chain ends was discussed. Such functional groups can be effectively used for the synthesis of graft and block copolymers.

1.5.1 Synthesis of graft copolymers

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.

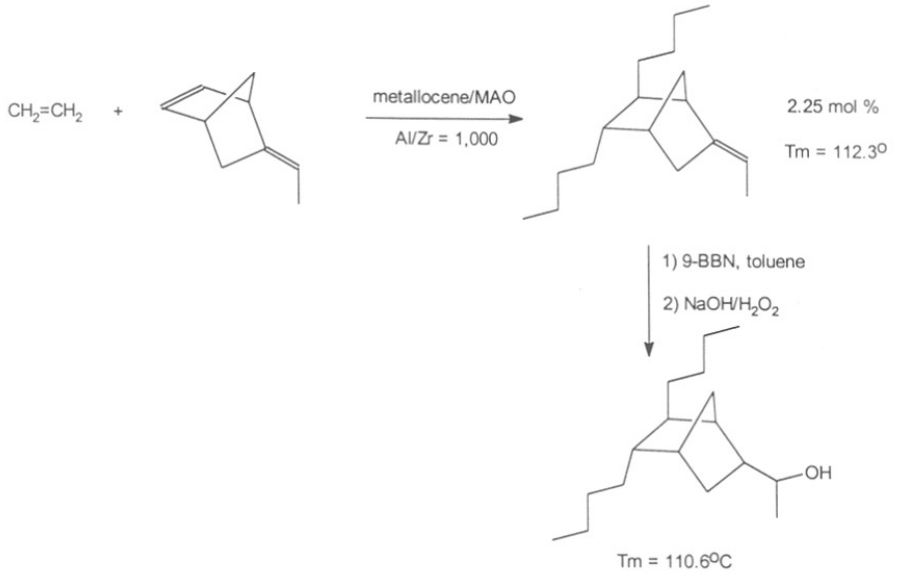
The boron containing polyolefins can act as potential free radical polymerization initiating center. Though no work has yet been published on grafting of this kind from boron containing copolymers synthesized using metallocene catalysts, synthesis of polyethylene-g-polymethyl methacrylate and polyethylene-g-polycaprolactone have been reported using boron containing copolymers synthesized using conventional Ziegler-Natta catalysts.[59] The same can be extended to metallocene based copolymers also with out any premonition.

Synthesis of polyethylene-g-polystyrene have been reported recently starting with ethylene/p-methyl styrene copolymer synthesized with $Et(ind)_2ZrCl_2$ and CGC.[68] Inspite of the heterogeneous reaction conditions used for lithiation of the parent copolymer, 67 mol % lithiation could be achieved. The polystyrene graft length varied from 4,100 to 52,200 mol.wt. (**Scheme 1.13**). The graft copolymer so synthesized acts as an excellent compatibilizer for polyethylene/polystyrene blends.

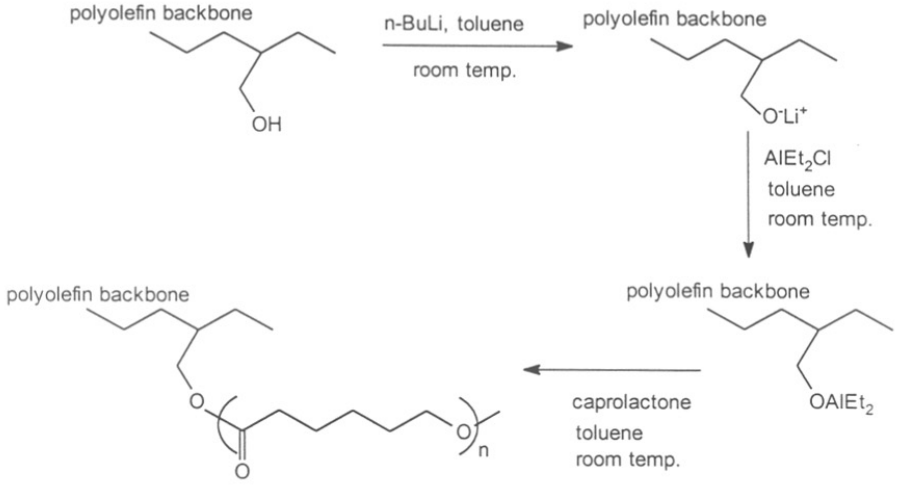


Scheme 1.13 Synthesis of polyethylene-graft-polystyrene copolymers

Synthesis of graft copolymers of polyethylene and polycaprolactone has been reported recently. The procedure involves the synthesis of copolymers containing pendant hydroxyl groups either by direct copolymerization with functional monomer[69] or by post polymerization conversion of the pendant double bonds to hydroxyl groups[70] (**Scheme 1.14**) followed by conversion of hydroxyl group to $OAlEt_2$ group, which acts as the initiator for the cationic ring opening polymerization of caprolactone (**Scheme 1.15**).



Scheme 1.14 Synthesis of polyethylene having pendant hydroxyl groups



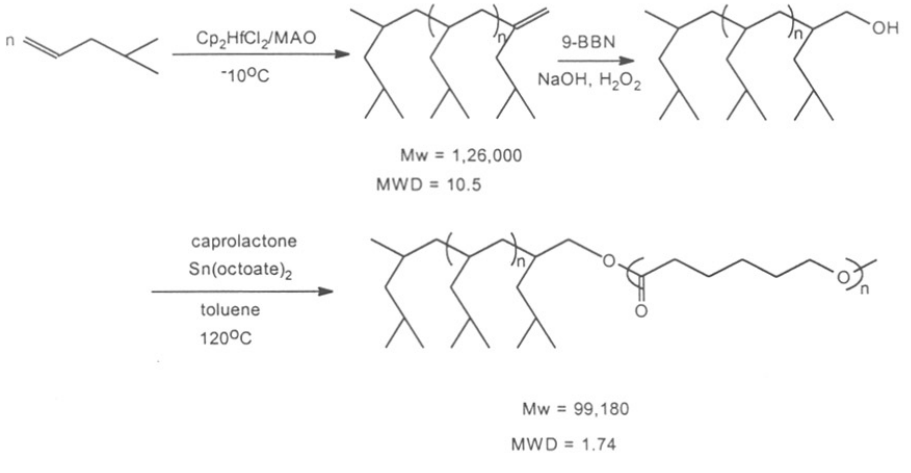
Scheme 1.15 Synthesis of polyethylene-graft-polycaprolactone

1.5.2 Synthesis of block copolymers

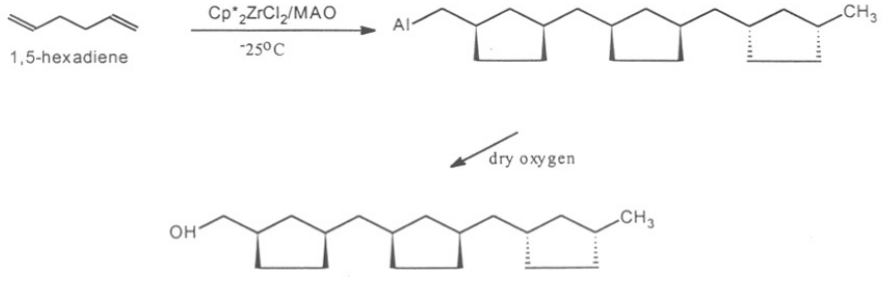
There are three different routes for the synthesis of block copolymers. They are, (1) coupling of the end functionalized polymer onto to the end of another polymer, where the coupling can be either by a simple organic reaction between two functional groups

or by termination of the growing polymer chain end by the functionalized polymer chain end, (2) using the end functionalized polymer as the initiator for the polymerization of second monomer and (3) using a catalyst system for the polymerization of the first monomer which can polymerize the second one also.

Polyolefin-b-polycaprolactone could be synthesized by using polyolefin having hydroxyl end group as the initiator for the polymerization of caprolactone. Polyolefins having hydroxyl end groups could be generated either by the functionalization of the vinylidene end groups in poly(α-olefins) (**Scheme 1.16**), as reported by Wang[71] et al., or by the oxidation of the aluminum end groups of PMCP, generated during the cyclopolymerization of 1,5-hexadiene with $Cp^*_2ZrCl_2$/MAO catalyst system (**Scheme 1.17**).[72,73]

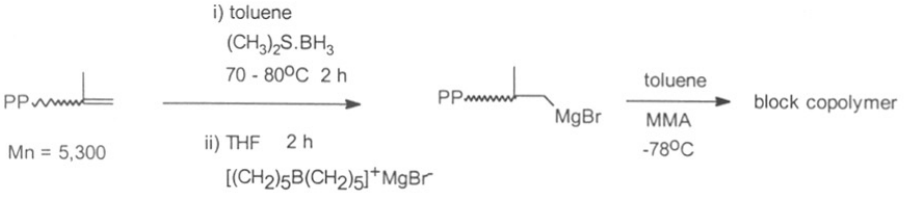


Scheme 1.16 Synthesis of polyolefin-block-polycaprolactone



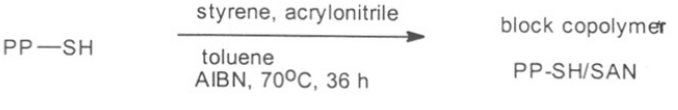
Scheme 1.17 Synthesis of hydroxyl functionalized poly(methylene-1,3,-cyclopentane)

Shiono et al.[74] have also reported the synthesis of polypropylene-b-polymethyl methacrylate copolymer by using MgBr terminated i-PP as the anionic initiator for the polymerization of methyl methacrylate (MMA). MgBr terminated i-PP was synthesized from vinylidene terminated polymer obtained with $Et(indH_4)_2ZrCl_2$/MAO catalyst. At -78°C, a block copolymer having polymethyl methacrylate of Mn 3,000 has been obtained (**Scheme 1.18**).



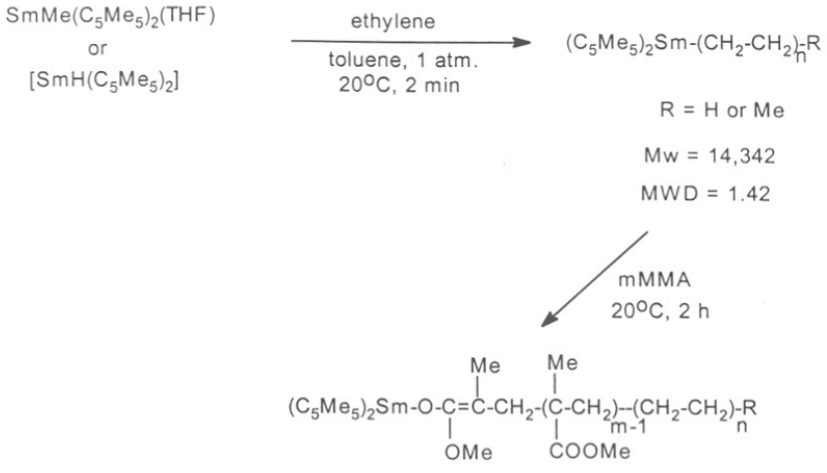
Scheme 1.18 Synthesis of polyethylene-block-polymethyl methacrylate copolymer

The thiol end functionalized polypropylene, obtained as shown in **Scheme 1.10**, have been used as free radical chain terminator for styrene/acrylonitrile copolymerization to obtain PP-b-SAN copolymer, which is useful as a compatiblizer (**Scheme 1.19**).[60]



Scheme 1.19 Synthesis of block copolymer by using functional group on chain end as free radical chain terminator

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 polyethylene-b-polymethyl methacrylate copolymers (**Scheme 1.20**).[75] The reverse addition of monomers, namely MMA followed by ethylene, resulted in homopolymerization of MMA only.



Scheme 1.20 Synthesis of polyethylene-block-polymethyl methacrylate copolymer

1.6 Conclusions

The discussion in this chapter illustrates the enormous opportunity offered by the metallocene catalysts to tailor polymer structures. Metallocene catalysts enable the synthesis of polyolefins having high Tg, polyolefins possessing unique structures, main chain optically active polyolefins, functional polyolefins as well as novel graft and block copolymers from such functional polyolefins. The synthesis of polyolefins having functional groups, especially by the functionalization of double bonds present either as pendant groups or as chain ends opens up the way to the discovery of new materials because of the relative ease of conversion of the double bonds to a wide range of functional groups. Synthesis of functional polyolefins by direct copolymerization has also attracted much attraction as it avoids the post polymerization functionalization step.

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Chapter 2. Scope and objectives

2.1 Introduction

Functional polyolefins have assumed importance because they contribute to new properties in an otherwise inert polyolefins. Appropriately functionalized polyolefins are useful as adhesion promoters, are capable of being coated, painted or dyed. Additionally, the functional groups on the polyolefin backbone can be used for the synthesis of graft copolymers which find application as compatibilizers and interfacial agents.[1]

There are three different routes for the synthesis of functional polyolefins.[2] One, is the direct copolymerization of olefin with a functional monomer. However, functional groups, especially, if polar, adversely affect the catalytic activity. The second method is the post polymerization grafting of functional groups onto the polyolefin backbone using either thermal or ionization energy. Non uniform distribution of the functional groups on the polymer, with functional groups predominantly located in the amorphous region, degradation of the polyolefin backbone and crosslinking are some of the drawbacks of this method. The third, and the most preferred method, is the copolymerization of olefins with a precursor monomer which does not interfere in the polymerization, but, can later be converted into the desired functional group by standard organic chemical reactions.

The homogeneous metallocene based catalysts possess some unique characteristics, which enable the synthesis of functional polyolefins. The high catalytic activity, uniform and random distribution of comonomers, narrow molecular weight distribution, ability to polymerize a wide range of monomers and synthesize a wide variety of stereospecific polymers ranging from isotactic to syndiotactic are some of the salient features of metallocene catalysts.[3] The metallocene catalysts are unique in the sense that they promote the polymerization of bicyclic olefins such as, norbornene, resulting in copolymers with high glass transition temperatures.[4] This feature has been taken advantage for introducing pendant double bonds in polymer by copolymerizing an olefin with a diene, such as, 5-vinyl-2-norbonene[5] and 5-ethylidene-2-norbornene.[6] Such

copolymers having pendant double bonds can later be functionalized by simple organic chemical reactions.

Recently, direct copolymerization of olefins with functional monomers like 10-undecen-1-ol,[7] 11-chloroundec-1-ene,[8] and 6-tert-butyl-2-(1,1-dimethylhept-6-enyl)-4-methylphenol[9] has also been reported using metallocene/MAO catalyst system.

2.2 Objective of the present work

The objective of the present work was to explore the capabilities of metallocene based catalysts for the synthesis of functional polyolefins. Two methods, namely, one, copolymerization with precursor monomers that can later be converted into functional groups and second, direct copolymerization with functional monomers were explored to achieve this goal.

(a)The first approach involved 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 copolymerization with dienes was undertaken.

(b)The second approach involved the direct copolymerization of a hydroxyl functional group containing monomer with ethylene. In order to prevent the deleterious effect of the functional group on the catalyst and cocatalyst the functional monomer was prereacted with an alkylaluminum.

2.3. Approaches

In order tosynthesizepolyolefins having pendant double bonds, a symmetrical diene, 2,5-norbornadiene, was chosen as the comonomer. The extreme rigidity of this bicyclic diene may prevent cyclopolymerization and crosslinking, which are usually observed during the copolymerization with symmetrical dienes.[10,11] The endocyclic pendant double bonds thus obtained can be converted into diacid, acid salt and anhydride by simple organic chemical reactions.

For the synthesis of functional polyolefin by direct copolymerization, trimethylaluminum

prereacted 5-norbornene-2-methanol was used as the functional monomer. It was reasoned that the extreme reactivity of the endocyclic double bond in the functional monomer would facilitate its incorporation.

Copolymerization of ethylene with 5-vinyl-2-norbornene using dicyclopentadienyl zirconium dichloride catalyst occurs regioselectively through the endocyclic double bond leaving the exocyclic one as a pendant group that can later be functionalized.[5] The ethylene/5-vinyl-2-norbornene copolymer so synthesized is blocky in nature as evidenced by the $r_1.r_2$ value of 5.5.[5] The silicon bridged metallocene, dimethylsilyl dicyclopentadienylzirconium dichloride ($Me_2SiCp_2ZrCl_2$) facilitates higher incorporation of norbornene type bicyclic olefins.[12] It was reasoned that the use of this catalyst for ethylene/5-vinyl-2-norbornene copolymerization will result in copolymers having more random distribution of the comonomer and hence the pendant double bonds as compared to the copolymer synthesized with Cp_2ZrCl_2 catalyst.

Having synthesized functionalized polyolefins by two different approaches a few grafting reactions were also examined for the synthesis of graft copolymers. Synthesis of polyethylene-g-polystyrene by grafting living polystyryl lithium anion onto an epoxy functionalized ethylene/5-vinyl-2-norbornene copolymer synthesized using $Me_2SiCp_2ZrCl_2$/MAO catalyst system was explored. With an objective of making amphiphilic graft copolymers, grafting of amine terminated polyethylene glycol onto epoxidized ethylene/5-vinyl-2-norbornene copolymer was also attempted.

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Chapter 3. Copolymerization of ethylene with 2,5-norbornadiene using metallocene/MAO catalyst system

3.1 Introduction

Synthesis of polyolefins bearing pendant double bonds is attracting increasing interest in the field of polyolefin research. This is because the pendant double bonds of polyolefins can be converted into functional groups by chemical transformations or can be used for crosslinking. Functional polyolefins are potentially useful for application as adhesive interfaces, barrier materials and as compatibilizing agents.

The most direct approach to polyolefins 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] and vinyl cyclohexene.[4,5] The extreme high reactivity of endocyclic double bond in the bicylic olefin, norbornene, due to ring strain has been utilized to introduce pendant double bonds in polyolefins by copolymerizing ethylene with unsymmetrical dienes like 5-vinyl-2-norbornene[6] and 5-ethylidene-2-norbornene.[7] Use of symmetrical dienes in copolymerization is limited by undesirable cyclopolymerization and crosslinking. Kaminsky and Drogemuller[8] have reported extensive crosslinking during the terpolymerization of 1,5-hexadiene with ethylene and propylene using ethylenebis(indenyl)zirconium dichloride ($Et(Ind)_2ZrCl_2$)/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.[9-11] Patent issued to Exxon[12] showed the presence of cyclopentane rings in copolymerization of ethylene with 1,5-hexadiene, presumably, due to cyclopolymerization.

In this chapter the use of 2,5-norbornadiene (NBD), a symmetrical diene having two equally reactive endocyclic double bonds, as a comonomer for ethylene

polymerization in the presence of metallocene/MAO catalyst system has been explored. It was reasoned that the extreme rigidity of the bicyclic diene may inhibit cyclopolymerization. The studies on copolymerization of ethylene with NBD using dicyclopentadienylzirconium dichloride (Cp_2ZrCl_2) (**19**), di-n-butylcyclopentadienyl zirconium dichloride ((n-buCp)$_2$ZrCl$_2$) (**20**), Et(Ind)$_2$ZrCl$_2$ (**21**), and dimethylsilyl dicyclopentadienylzirconium dichloride ($Me_2SiCp_2ZrCl_2$) (**22**) are discussed in this chapter.

3.2 Experimental

All manipulations involving air sensitive compounds were carried out using standard benchtop inert atmosphere techniques under a stream of ultra high purity nitrogen.

3.2.1 Materials

Toluene (Loba Chemie, GR grade) was purified by refluxing over sodium wire and subsequent distillation under nitrogen. Polymerization grade ethylene was procured from the C_2-C_3 Gas Cracker unit of Indian Petrochemical Corp. Ltd., Nagothane, Maharashtra. 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 (**19**) (Aldrich, USA), (n-buCp$_2$)ZrCl$_2$ (**20**), Et(Ind)$_2$ZrCl$_2$ (**21**) (Witco Gmbh, Germany), and Irganox 1010 (Ciba-Giegy) were used as such. NBD (E.Merck, Germany) was stirred over CaH_2 for 24 h and distilled under nitrogen atmosphere prior to use. $Me_2SiCp_2ZrCl_2$ (**22**) was prepared as per given below.

3.2.2 Synthesis of $Me_2SiCp_2ZrCl_2$[13]

3.2.2.1 Synthesis of sodium sand[22]

Sodium sand was prepared by melting 2.3 g (0.1 mol) of sodium in 45 mL toluene by refluxing followed by vigorous stirring for 15 min. Toluene, after the formation of the sodium sand was siphoned off using a cannula under N_2 pressure and the sodium sand was dried under vacuum for 30 min.

3.2.2.2 Synthesis of sodium cyclopentadienylide

130 mL of freshly distilled tetrahydrofuran was then added into the sodium sand and 35 mL (0.28 mol) of cyclopentadiene was directly distilled into it over a time of 45 min. The system was stirred till all the sodium was dissolved. THF was removed under vacuum to obtain a slightly yellow colored sodium cyclopentadienylide.

Sodium cylocpentadienylide is very moisture and light sensitive and the next step was carried out immediately after this.

3.2.2.3 Synthesis of dimethylsilylcyclopentadiene

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

3.2.2.4 Synthesis of $ZrCl_4$.THF adduct

Meanwhile, 12.03 g (0.05 mol) of $ZrCl_4$ was taken in a 100 mL round bottom flask and 100 mL THF was added drop by drop at -78°C. The temperature was then allowed to rise to 0°C and was stirred for 1 h.

3.2.2.5 Synthesis of the metallocene

To the $ZrCl_4$.THF adduct thus formed the dianion was transferred through cannula over a period of one hour. The reddish brown solution so obtained was stirred overnight and then heated at 50°C for 2 h. The solvent was then removed by vacuum. To the reddish brown mass so obtained 50 mL of dry pentane was added and then stirred for 1 h. The pentane was syringed out and the residual mass was vacuum dried. It was then soxhlet extracted with dichoromethane. The yellow colored solution was concentrated and then cooled in refrigerator to form the crystals of the metallocene and it was then recrystallized to give pale green crystals. The yield was 10 % based on $ZrCl_4$. ^1H NMR ($CDCl_3$, 25°C, ppm) 6.97 (-C_5H_4, singlet, 4H), 5.97 (-C_5H_4, singlet, 4H) and 0.75(-$(CH_3)_2Si$, singlet, 6H) (**Figure 3.1**).

3.2.3 Copolymerization

Copolymerization was carried out at 1 atm pressure in a jacketed glass reactor connected to a 1 L gas buret. The schematic diagram of the setup used for the copolymerization is shown in **Figure 3.2**. Toluene (30 mL) was introduced into the reactor and saturated with ethylene. NBD (0.3 mL, 2.96 x 10^{-3} mol) was added to the reactor followed by toluene solution of MAO. The copolymerization was initiated by the addition of toluene solution of Cp_2ZrCl_2 (1.44 x 10^{-6} mol). Temperature was

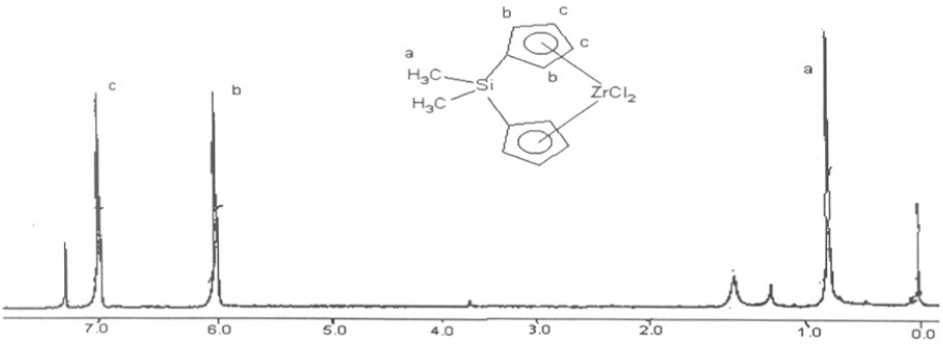
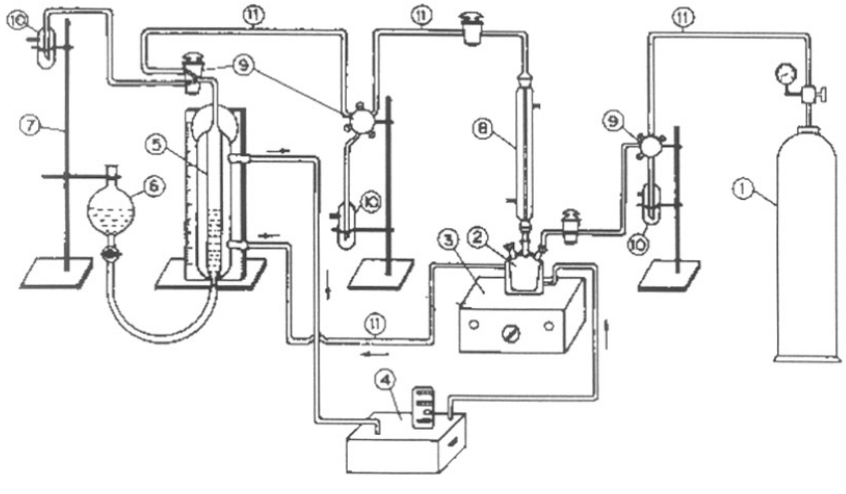


Figure 3.1 ^{1}H NMR spectrum of $Me_2SiCp_2ZrCl_2$



1. ethylene gas cylinder
2. glass reactor
3. magnetic stirrer
4. constant water bath
5. calibrated gas buret on wooden platform
6. silicon oil reservoir
7. iron stand
8. glass condenser
9. three way stopcocks
10. silicon oil bubbler
11. polyethylene pressure tubing

Figure 3.2 Schematic diagram of the experimental set up used for ethylene/ 2,5-norbornadiene copolymerizations at one atmosphere

maintained by circulating water at the desired temperature. Ethylene consumption was noted as a function of time. Copolymerization was terminated by the addition of 5 mL methanol containing 0.2 % Irganox 1010. The copolymer was precipitated using methanol containing 2 % HCl and 0.2 % Irganox 1010, filtered, and dried under vacuum at room temperature for 4 h. ^{1}H NMR (C_7D_8, 25°C, ppm) 6.2 (=CH endocyclic), 2.8 (-CH bridge head) and 2-1 (aliphatic CH and backbone). IR (KBr pellet, cm^{-1}) 3065 (=CH stretching) 3000-2900 (C-H stretching), 1640 (C=C stretching), 908.7 (=CH bending) and 725 (CH_2 rocking).

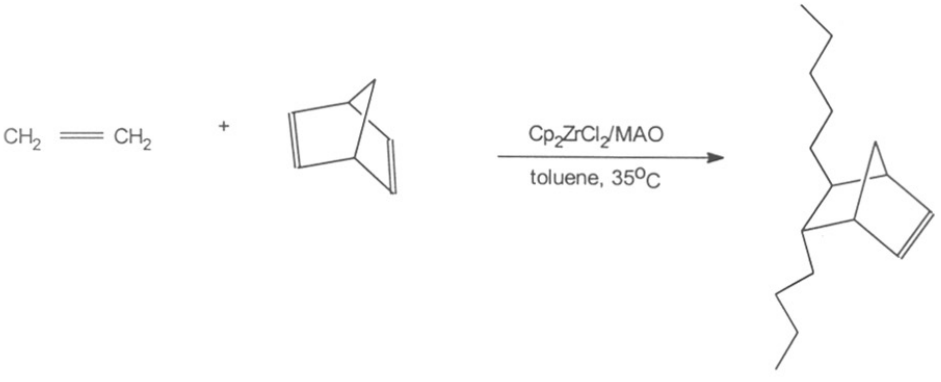
3.2.4 Analysis

The IR spectra were recorded on a Perkin-Elmer 16 PC FT-IR spectrometer. ^{1}H NMR spectra were recorded using a 200 MHz Bruker NMR spectrometer at room temperature. ^{13}C NMR was recorded at 30°C in $CDCl_3$ on a Bruker MSL 300 model spectrometer operating at 75.5 MHz. The ^{13}C NMR peaks were assigned on the basis of assignments of ethylene/norbornene copolymers by Kaminsky et al.[14] The molecular weight distributions were determined using a Waters Gel Permeation Chromatograph model GPC/ALC 150C instrument equipped with a refractive index detector with μ-styragel columns (10^6, 10^5, 10^4, 10^3 and 500°A) at 135°C and 1,2,4-trichlorobenzene as solvent with 1 mL/min flow rate. Intrinsic viscosities were determined in decalin at 135°C using an Ubbelhode viscometer. Thermogravimetric and differential scanning calorimetric analysis were carried out on Perkin Elmer TGA-7 and DSC-7 instruments respectively.

3.3 Results and discussion

3.3.1 Copolymerization

Ethylene undergoes copolymerization readily with 2,5-norbornadiene with Cp_2ZrCl_2/MAO catalyst system exclusively through one of the endocyclic double bonds (**Scheme 3.1**). Copolymers with as high as 19 mol % NBD could be synthesized without crosslinking as evidenced by the solubility of copolymers in toluene at room temperature (**Table 3.1**). The very fact that the extreme reactivity of the endocyclic double bond in cyclic olefins like norbornene, 5-vinyl-2-norbornene and 5-ethylidene-2norbornene are utilized for their efficient copolymerizations with olefins using metallocene catalyst systems signifies the importance of the above observation. Inspite of the extreme reactivity of the pendant double bond, the fact that



Scheme 3.1 Copolymerization of ethylene with 2,5-norbornadiene using metallocene/MAO catalyst system

it is not undergoing enchainment shows the ability of the metallocene catalysts to distinguish between a double bond in a polymer chain and the one in a monomer.

Table 3.1 Effect of [NBD] on copolymerization of ethylene with 2,5-norbornadiene using Cp_2ZrCl_2/MAO catalyst system[a]

[NBD] 10^2 (M)	time (min)	yield (g)	catalyst activity (in kg copoly./ g.Zr. atm.h.)	mol % NBD in copoly. (by ^{1}H NMR)	conv. of NBD (%)
9.8	60	0.40	3.0	4.0	30.0
19.6	60	0.25	1.9	9.7	12.8
29.4	120	0.18	0.7	15.4	8.4
39.2	120	0.18	0.7	18.8	7.8

[a] Polymerization conditions: [Zr] = 4.8 x 10^{-5} M, Al/Zr = 1,500, toluene = 30mL, temperature = 35°C, $P_{ethylene}$ = 1 atm.

3.3.1.1 Effect of temperature

Higher temperature caused reduced incorporation of NBD in copolymer with corresponding increase in catalytic activity and molecular weight (**Table 3.2**). Higher temperature favors the incorporation of ethylene over NBD. This is inspite of the fact that the concentration of ethylene in the feed is less as compared to that at low temperature due to the decrease in solubility of ethylene with rise in temperature.

Chain termination reactions in such copolymerizations usually occur when norbornyl moiety is at the growing chain end. So as the incorporation of NBD decreases chain termination decreases and molecular weight increases.

3.3.1.2 Effect of Al/Zr ratio

Increase in Al/Zr ratio has the same effect as temperature on the course of copolymerization. The results are given in **Table 3.3.**

Table 3.2 Effect of temperature on copolymerization of ethylene with 2,5-norbornadiene using Cp_2ZrCl_2/MAO catalyst system[a]

temp. (°C)	yield (g)	catalyst activity (in kg copoly/g.Zr. atm.h.)	mol % NBD in copoly. (by ^{1}H NMR)	conv. of NBD (%)	[η] dL/g (in decalin at 135°C)
35	0.40	3.0	4.4	17	0.19
50	0.51	3.9	3.0	15	0.26
70	0.65	5.0	1.6	13	0.35

[a] Polymerization conditions: [Zr] = 4.8 x 10^{-5} M, [NBD] = 9.8 x 10^{-2} M, Al/Zr = 1,500, toluene = 30 mL, $P_{ethylene}$ = 1 atm., time = 1 h.

Table 3.3 Effect of Al/Zr ratio on copolymerization of ethylene with 2,5-norbornadiene using Cp_2ZrCl_2 /MAO catalyst system[a]

Al/Zr	time (min)	yield (g)	catalyst activity (in kg copoly./g.Zr. atm.h.)	mol % NBD in copoly. (by ^{1}HNMR)	conv. of NBD (%)	[η] dL/g (in decalin at 135°C)
1,500	60	0.40	3.0	4.4	17	0.19
5,000	40	0.92	7.0	3.0	27	0.28
10,000	40	1.05	8.0	2.6	23	0.33

[a] Polymerization conditions: [Zr] = 4.8 x 10^{-5} M, [NBD] = 9.8 x 10^{-2} M, toluene = 30 mL, temperature = 35°C, $P_{ethylene}$ = 1 atm.

3.3.1.3 Effect of metallocene

Ethylene/NBD copolymerizations were carried out using four different metallocene catalysts under identical condition inorder to study the effect of catalyst on comonomer incorporation and molecular weight. The results are given in **Table 3.4.**

3.3.1.3.1 Cp_2ZrCl_2

This unbridged metallocene gave low molecular weight copolymers compared to other metallocenes used in this study.

3.3.1.3.2 $(n\text{-}buCp)_2ZrCl_2$

Introduction of n-butyl substitution in the cyclopentadienyl ring of the metallocene caused an increase of both catalyst activity as well as copolymer molecular weight at similar levels of incorporation of NBD. n-Butyl substitution in cyclopentadienyl ring is reported to increase the propagation rate due to the increased electron density at the metal centre.[16]

Table 3.4 Copolymerization of ethylene with 2,5-norbornadiene using various metallocenes[a]

no.	metallocene	time (min)	yield (g)	catalyst activity (in kg copoly./ g.Zr.atm.h)	mol % of NBD in copoly. (by ^1H NMR)	conv. of NBD (%)	[η] dL/g (in decalin at 135°C)
1	Cp_2ZrCl_2(**19**)	30	0.20	3.0	4.4	11	0.19
2	$(n\text{-}buCp)_2ZrCl_2$(**20**)	30	0.47	7.2	4.0	22	0.40
3	$Et(Ind)_2ZrCl_2$(**21**)	9	0.18	6.7	6.6	10	0.22
4	$Me_2SiCp_2ZrCl_2$(**22**)	---------- Crosslinking during copolymerization ---------					

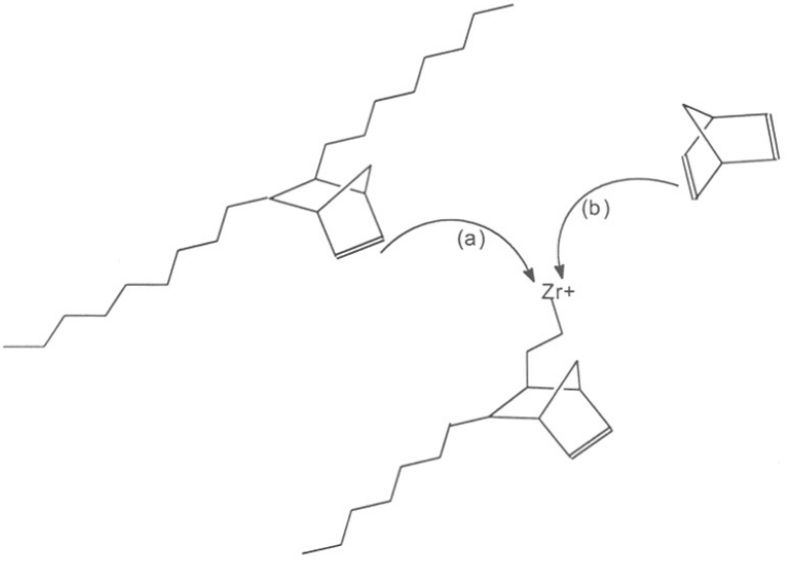
[a] Polymerization conditions: [Zr] = 4.8 x 10^{-5} M, [NBD] = 9.8 x 10^{-2} M, Al/Zr =1,500, toluene = 30 mL, temperature = 35°C, $P_{ethylene}$ = 1 atm.

3.3.1.3.3 $Et(ind)_2ZrCl_2$

The stereorigid catalyst (**21**) further increased the catalyst activity as well as incorporation of NBD with an insignificant increase in molecular weight.

3.3.1.3.4 $Me_2SiCp_2ZrCl_2$

Catalyst (**22**), with a dimethylsilylene bridge, gave only an insoluble copolymer of ethylene and NBD. The insoluble copolymer showed no unsaturation in FT-IR (**Figure 3.3**) indicating the participation of both the endocyclic double bonds in copolymerization. Unlike with other metallocene catalysts studied, where the double bond in the copolymer is inactive in copolymerization, the pendant endocyclic double bond in the copolymer is also undergoing enchainment here (**Scheme 3.2**). Higher incorporation of the bicyclic olefin, DMON, in ethylene/DMON copolymerization with catalyst (**22**) over (**21**) have been reported by Goodall et al.[17] This was attributed to the higher coordination angle along the Zr-Cl vector for the metallocene (**22**). On the contrary, nearly similar mol % incorporation of 1-hexene has been reported by Quijada et al.[18] in the copolymerization of ethylene with 1-hexene with both (**21**) and (**22**). This raises doubts as to the significance of coordination angle in determining the



Scheme 3.2 Crosslinking reaction occuring during the copolymerization of ethylene with 2,5-norbornadiene using $Me_2SiCp_2ZrCl_2$ catalyst (a) crosslinking (b) propagation

copolymerization activity and extent of incorporation of comonomers in metallocenes. Nonlocal density functional calculations have shown that ethylene insertion into $SiH_2Cp_2Zr\text{-}CH_3^+$ cation is more exothermic by about 12 kJ/mol compared to the *unbridged one owing to the low steric hindrance and increased electron deficiency* at the metal center.[19] For the insertion of the endocyclic double bond of NBD exothermicity may be even higher due to the release of ring strain on insertion. This higher reaction enthalpy may be the cause for the observed crosslinking in the ethylene/NBD copolymer synthesized using catalyst (**22**).

3.3.1.4 Effect of feed composition

Effect of feed composition on ethylene/NBD copolymerization was studied using Cp_2ZrCl_2 and $Et(ind)_2ZrCl_2$ catalysts, results of which are given in **Table 3.1** and **3.5** respectively. Higher amount of NBD in the feed increases the comonomer incorporation, but reduces the copolymerization activity as well as molecular weight.

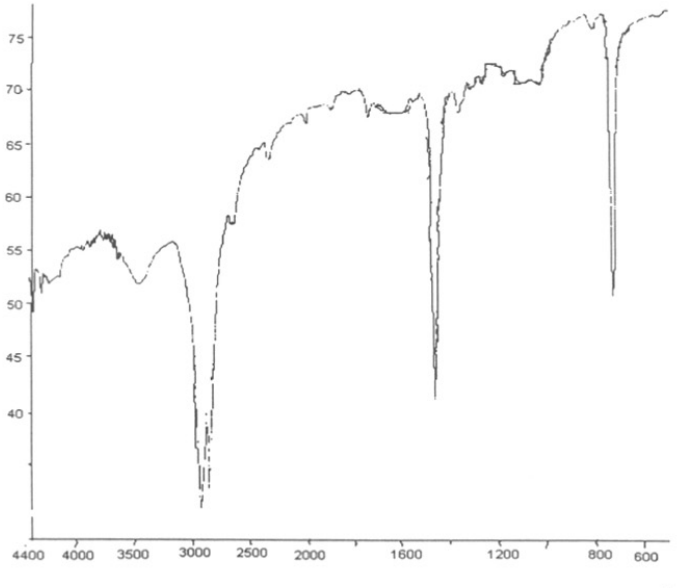


Figure 3.3 IR spectrum of ethylene/2,5-norbornadiene copolymer synthesized using $Me_2SiCp_2ZrCl_2$ catalyst (Table 3.4, entry no. 4)

Peaks: Absence of peaks at 3065, 1583 and 908.7 cm^{-1} due to C=C

Table 3.5 Effect of [NBD] on copolymerization of ethylene with 2,5-norbornadiene using $Et(Ind)_2ZrCl_2$ catalyst system[a]

no.	[NBD] 10^2 (M)	time (min)	yield (g)	catalyst activity (in kg copoly./ g.Zr.atm.h.)	mol % NBD in copoly. (by ^1H NMR)	conv. of NBD (%)
1	9.8	15	0.52	16.1	5.1	20.0[c]
2	19.6	30	0.32	4.8	18.0	20.0
3	29.4	60	0.49	3.7	16.3	24.3
4	39.2	60	0.28	2.2	21.0	12.6

[a] Polymerization conditions: [Zr] = 4.8 x 10^{-5} M, Al/Zr = 1,500, toluene = 30 mL, temperature = 35°C, $P_{ethylene}$= 1 atm., [c] 100% conversion on calculation based on weight difference.

3.3.1.5 Kinetics of polymerization

The rates of ethylene consumption in copolymerization for the four catalysts examined in the present study are shown in **Figure 3.4**. The unusually low rate of ethylene consumption for the catalyst (**22**) could be due to the competitive and fast incorporation of both the endocyclic double bonds in NBD during copolymerization.

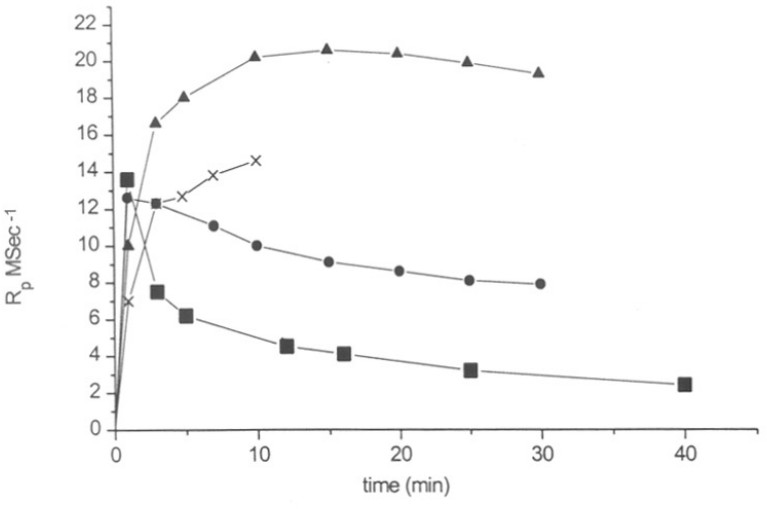


Figure 3.4 Kinetic profile of ethylene consumption for ethylene/ 2,5-norbornadiene copolymerization using (●)Cp_2ZrCl_2, (▲) (n-buCp)$_2ZrCl_2$, (×) Et(ind)$_2ZrCl_2$ and (■) $Me_2SiCp_2ZrCl_2$ catalysts

3.3.1.6 Reactivity ratios

Reactivity ratios for ethylene and NBD for ethylene/NBD copolymerization using catalysts (**19**) and (**21**) were evaluated using Kelen-Tudos method (**Table 3.6** and **3.7** respectively).[20] Copolymerizations were performed with different initial concentrations of NBD. In all cases conversion of the diene was restricted to less than 10 %. The reactivity ratio values are given in **Table 3.8**. The reactivity ratio values for ethylene in ethylene/norbornene copolymerization are reported to be 20 and 6.6 for Cp_2ZrCl_2 and Et(ind)$_2ZrCl_2$ catalysts respectively.[14] Comparing the reactivity ratio values for ethylene in ethylene/NBD as well in ethylene/norbornene copolymerizations show that there is a difference of around 30 % in the values.

Table 3.6 Calculation of reactivity ratios of ethylene and 2,5-norbornadiene in ethylene/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
51	49	94.4	5.6	1.04	11.116.86	0.98	0.064	11.14	0.73
34	66	89.2	10.8	0.52	8.26	0.46	0.033	8.10	0.56
25.6	74.4	83.0	17.0	0.34	4.5.6288	0.27	0.024	5.62	0.50
20.5	79.5	82.6	17.4	0.26	4.75	0.21	0.014	5.53	0.37
17.0	83.0	79.9	20.1	0.21	3.98	0.16	0.011	4.57	0.31
13.0	87.0	72.1	27.9	0.15	2.58	0.09	0.009	2.73	0.27

Where M_1 and m_1 are mol % ethylene 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 $G/(\alpha+F)$ and ξ is $F/(\alpha+F)$ where α is $(0.064 \times 0.009)^{1/2}$

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

From the graph of η against ξ (**Figure 3.5**), y = 16.3 - 1.17

ie, $r_{NBD}/\alpha = 1.17$,

There fore $r_{NBD} = 0.28$ and $r_{ethylene} = 16.3 - 1.17 = 15.1$

Table 3.7 Calculation of reactivity ratios for ethylene and 2,5-norbornadiene in ethylene/2,5-norbornadiene copolymerization with $Et(ind)_2ZrCl_2$/MAO catalyst system using Kelen-Tudos method

M_1	M_2	m_1	m_2	X	Y	G	F	η	ξ
51	49	92.3	7.7	1.04	11.99	0.95	0.09	7.57	0.72
34	66	87.6	12.4	0.52	7.064	0.45	0.038	6.12	0.52
25.6	74.4	82.7	17.3	0.34	4.78	0.27	0.024	4.54	0.403
20.5	79.5	78.7	21.3	0.26	3.695	0.19	0.018	3.55	0.34
17.0	83.0	76.0	24.0	0.21	3.17	0.144	0.014	2.91	0.283

Where M_1 and m_1 are mol % ethylene 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 $G/(\alpha+F)$ and ξ is $F/(\alpha+F)$ where α is $(0.014 \times 0.09)^{1/2}$

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

From the graph of η against ξ (**Figure 3.6**), $y = 10.9\,\xi - 0.0132$

ie, $r_{NBD}/\alpha = 0.0132$

There fore $r_{NBD} = 0.00046$ and $r_{ethylene} = 10.9 - 0.00046 = 10.89$

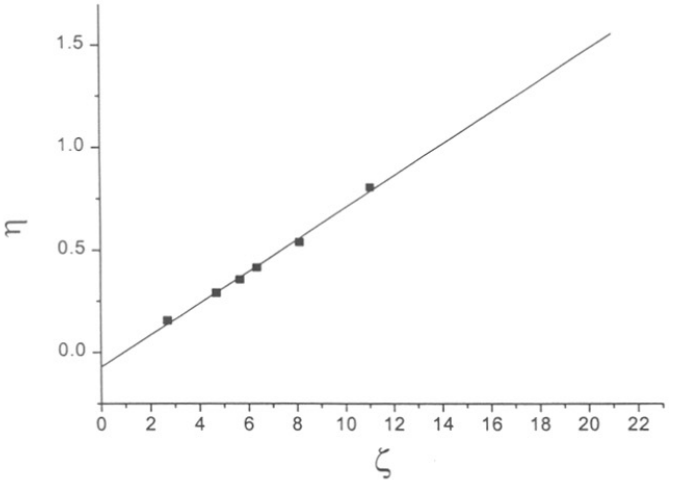


Figure 3.5 Kelen-Tudos plot for calculating reactivity ratios for ethylene and 2,5-norbornadiene in ethylene/2,5-norbornadiene copolymerization using Cp_2ZrCl_2 catalyst

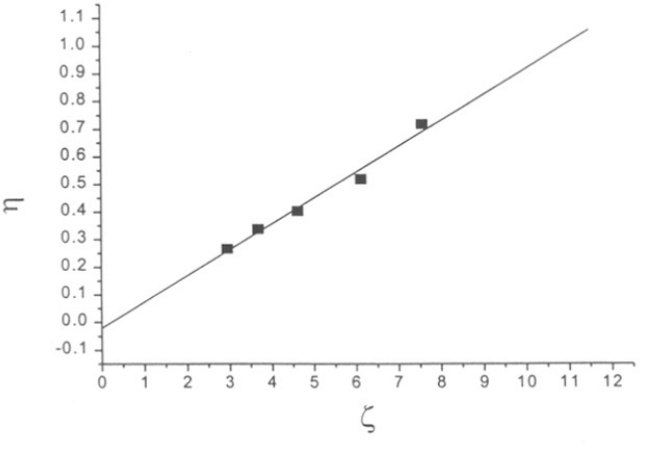


Figure 3.6 Kelen-Tudos plot for calculating reactivity ratios for ethylene and 2,5-norbornadiene in ethylene/2,5-norbornadiene copolymerization using $Et(ind)_2ZrCl_2$ catalyst

Table 3.8 Reactivity ratios for ethylene and 2,5-norbornadiene at 35°C according to Kelen-Tudos method

Metallocene	$r_{ethylene}$	r_{NBD}
Cp_2ZrCl_2(**19**)	15.1±0.1	0.021±0.009
$Et(Ind)_2ZrCl_2$(**21**)	10.9±0.2	0.001±0.005

The observed difference in conversion of NBD for catalyst (**21**), as calculated by two different methods (Table 3.5, entry no. 1), may be due to the near quantitative incorporation of the diene in the copolymer within less than 15 min. The polymer isolated after 15 minutes of polymerization may be a mixture of homo and copolymers of ethylene, resulting in a decrease in the conversion calculated from NMR. With a 7.7 mol % initial incorporation and assuming that incorporation of NBD in copolymer decreases with time (since feed is being depleted of the diene), a 100 % conversion of diene within 15 minutes is unexpected. With an initial incorporation of 5.6 mol % the conversion was only 11 % in 30 minutes for catalyst (**19**). Presuming that the incorporation of NBD in copolymer increases with time, a series of copolymerizations were carried out for varying time intervals. The incorporation of the diene was found to increase with time (**Figure 3.7**).

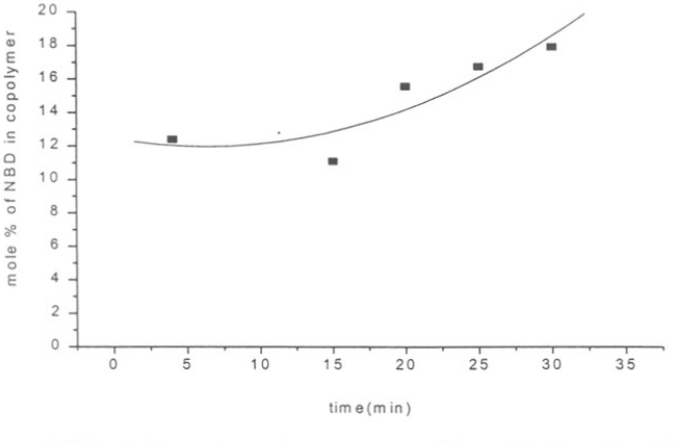


Figure3.7 Variation of copolymer composition with time for ethylene/ 2,5-norbornadiene copolymerization with $Et(ind)_2ZrCl_2$ catalyst

3.3.2 Characterization of copolymers

3.3.2.1 IR

The IR spectrum of the copolymer showed a shoulder at 3065 cm^{-1} and peaks at 1583.5 and 908.7 cm^{-1} indicative of the presence of unsaturation in the copolymer (**Figure 3.8**).

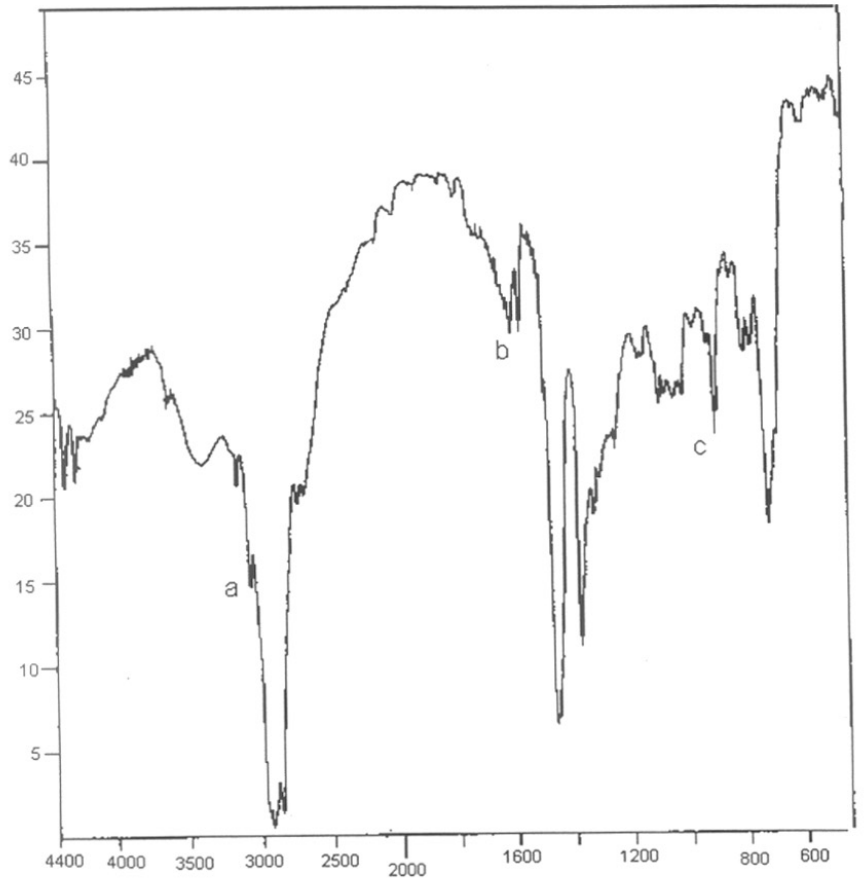


Figure 3.8 IR spectrum of ethylene/2,5-norbornadiene copolymer having 18 mol % of the diene (Table 3.5, entry no. 2)

Peaks: (a) 3065 cm^{-1} C-H alkene stretching, (b) 1583 cm^{-1} C=C stretching, (c) 908.7 cm^{-1}C-H alkene bending

3.3.2.2 NMR

The ^{1}H NMR spectrum of the copolymer is shown in **Figure 3.9**. The spectrum showed a peak at 6.2 ppm indicating the presence of endocyclic double bonds in the copolymer. The mol % of NBD in the copolymer was calculated as shown below.

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

Area of peak at 1.6 ppm due to 4H of ethylene and 4H of NBD = Y

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

Area due to 1H of ethylene = $\left[\frac{Y - (X/2) \times 4}{4} \right] =$

Mol % of NBD in the copolymer = $\frac{A}{(A + B)} \times 100$

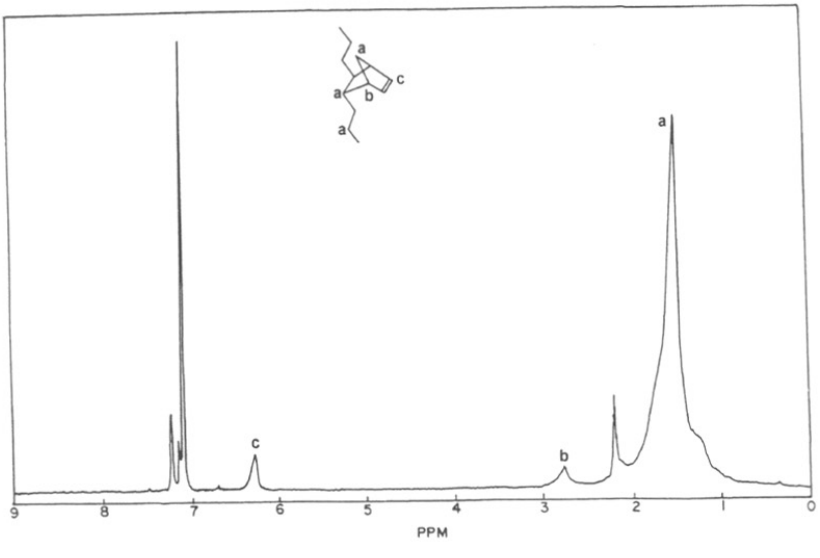
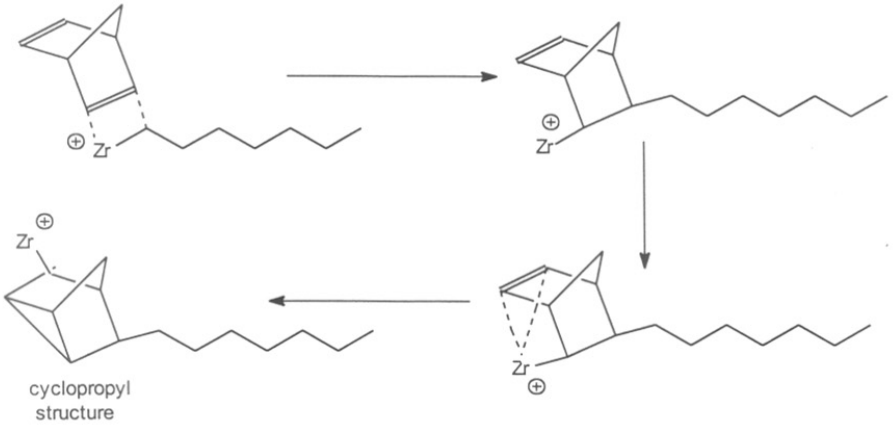


Figure 3.9 ^{1}H NMR spectrum of ethylene/2,5-norbornadiene copolymer having 4.4 mol % of 2,5-norbornadiene (Table 3.4, entry no. 1)

The ^{13}C NMR spectrum showed peak at 136.6 ppm (**Figure 3.10**) indicating the presence of pendant endocyclic double bonds in the copolymer. The absence of any peak at 14.7 ppm in ^{13}C NMR, due to cyclopropyl structure (**Scheme 3.3**),[15] and the near equal peak area for the bridge head protons at 2.8 ppm and that of the double

bond protons at 6.2 ppm in ^{1}H NMR are indicative of the fact that copolymerization occurs exclusively in a 1,2 fashion and through only one of the endocyclic double bonds.



Scheme 3.3 Formation of cyclopropyl structure during the copolymerization of ethylene with 2,5-norbornadiene

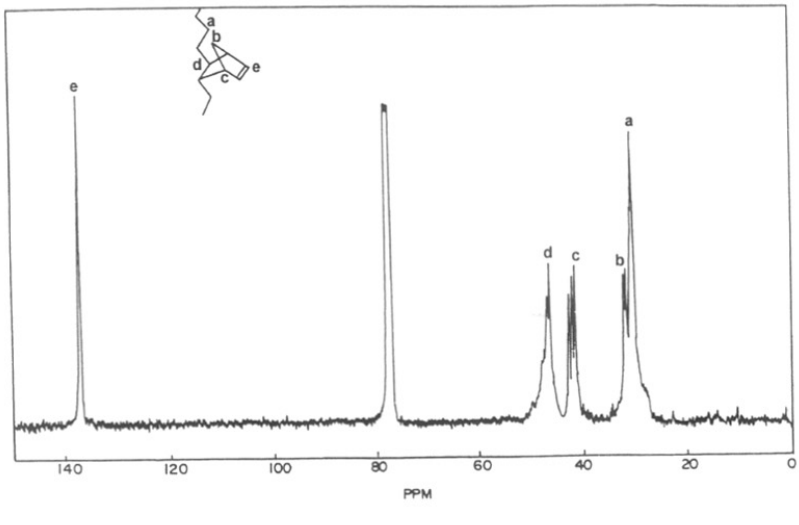


Figure 3.10 ^{13}C NMR spectrum of ethylene/2,5-norbornadiene copolymer having 18 mol % of 2,5-norbornadiene (Table 3.5, entry no. 2)

3.3.2.3 GPC

The MWDs of the ethylene/NBD copolymers are in the range of 2.0 to 2.8, consistent with the single site nature of the catalyst.

3.3.3 Copolymer Properties

3.3.3.1 Solubility

All the copolymers other than the one synthesized with $Me_2SiCp_2ZrCl_2$ were found to be soluble in toluene and o-dichlorobenzene at 30°C and in benzene at 50°C.

3.3.3.2 Thermal Properties

Thermogravimetric analysis of the copolymer having 4.4 mol % of NBD showed an initial decomposition temperature of 390°C (**Figure 3.11**). The small but significant ~12 % weight loss observed at 300°C is attributed to the retro Diels-Alder reaction occurring in the copolymer resulting in an ethylene/butadiene type copolymer (**Scheme 3.4**).[21] The theoretically expected weight loss was 10 wt %. In order to prove that retro-Diels-Alder actually occurs, a TGA run of the copolymer was carried out only upto 350°C so that the sample could be later analyzed. But the sample became reddish brown in color on heating upto 350°C, which may be due to degradation, and was found to be insoluble in toluene. In another experiment, the sample was taken in a small 10 mL round bottom flask and heated to 300°C under 10^{-4} mm vacuum for 2 h. Though the color of the polymer did not change, it was also not soluble in toluene even at high temperatures indicating some crosslinking.

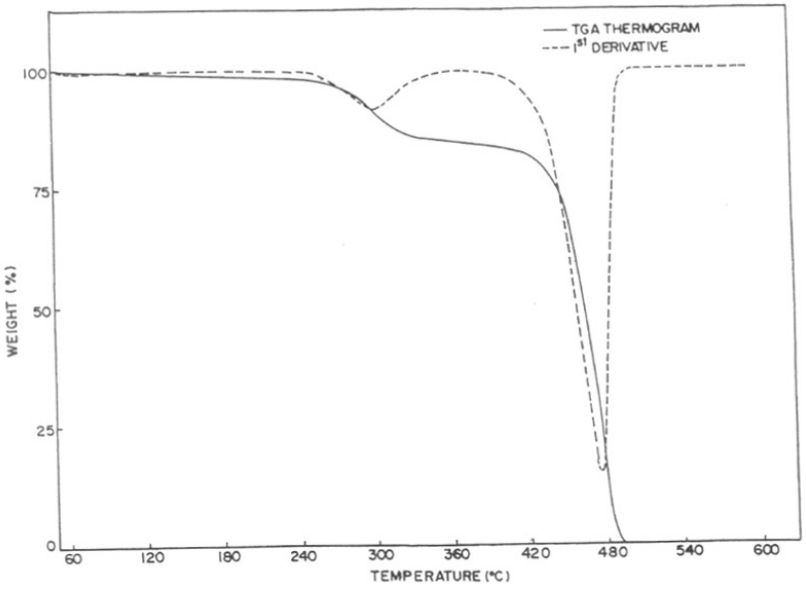
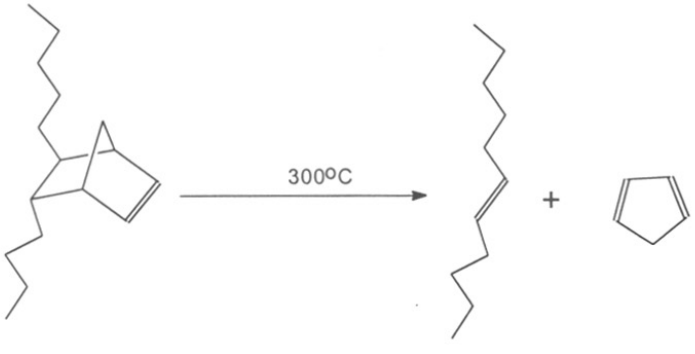


Figure 3.11 TGA thermogram of ethylene/2,5-norbornadiene copolymer having 4.4 mol % of 2,5-norbornadiene (Table 3.4, entry no. 1)



Scheme 3. 4 Retro Deils Alder reaction taking place on ethylene/ 2,5-norbornadiene copolymer

No melting points (Tm) were observed for any of the copolymers synthesized other than the one using catalyst (**20**). The copolymer synthesized with the catalyst (**20**) showed a broad peak with a maxima at 90°C (**Figure 3.12**).

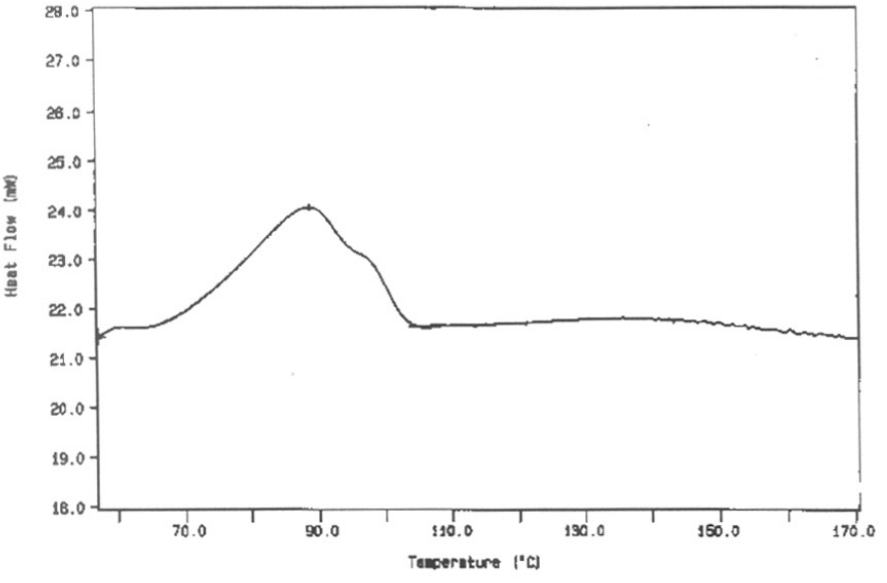


Figure 3.12 DSC thermogram of ethylene/2,5-norbornadiene copolymer having 4.0 mol % of NBD synthesized with (n-buCp)$_2$ZrCl$_2$ catalyst (Table 3.4, entry no. 2)

Typically for an ethylene/norbornene copolymer with 4-6 mol % norbonene, Kaminsky et al.[14] have reported Tm. The absence of a Tm in the present case could be due to the relatively low molecular weight of the copolymer. In order to establish this fact, copolymerizations were carried out at three different feed compositions. The results are given in **Table 3.9**. A copolymer having an intrinsic viscosity of 0.33 dL/g did not show any crystalline melting point (**Figure 3.13**), but the one having an intrinsic viscosity of 0.40 dL/g and having 4.0 mol % of NBD showed a Tm (**Table 3.4**). This indicates that the limiting value of intrinsic viscosity for observing the Tm in ethylene/NBD copolymers is about 0.40 dL/g.

Table 3.9 Effect of molecular weight on Tm of ethylene/2,5-norbornadiene copolymers synthesized with Cp_2ZrCl_2/MAO catalyst system[a]

no.	[NBD] 10^2 (M)	time (min)	yield (g)	catalyst activity (in kg copoly./ g.Zr. atm.h.)	mol % of NBD in copoly. (by ^1H NMR)	[η] dL/g (in decalin at 135°C)	Tm(°C) (from DSC)
1	9.8	30	0.20	3.0	4.4	0.19	nil
2	6.5	30	0.45	6.8	3.1	0.33	nil
3	3.3	15	0.40	12.1	nd	0.66	109

[a] Polymerization conditions: [Zr] = 4.8 x 10^{-5} M, Al/Zr = 1,500, toluene = 30 mL, $P_{ethylene}$ = 1 atm., temperature = 35°C, nd = not determined.

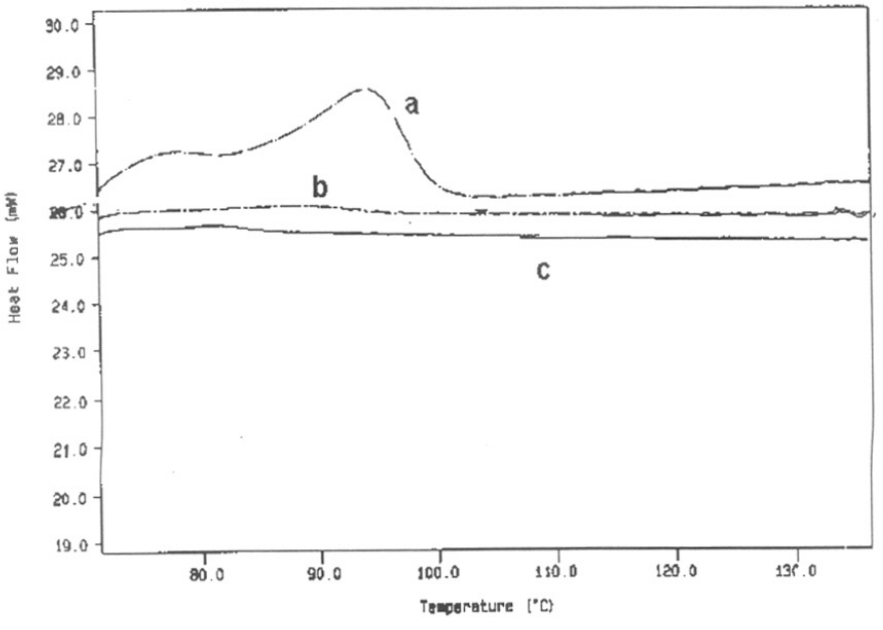


Figure 3.13 DSC thermograms of ethylene/2,5-norbornadiene copolymers having intrinsic viscosities (a) 0.66 (b) 0.33 (c) 0.19 dL/g synthesized with Cp_2ZrCl_2 catalyst (Table 3. 9, entry no. 1, 2 and 3 respectively)

3.4 Conclusions

Copolymerization of ethylene with 2,5-norbornadiene using metallocene/MAO catalyst system occurs exclusively through one of the equally reactive endocyclic double bonds for unbridged as well as ethylene bridged catalysts. However, crosslinking occurs during copolymerization with dimethylsilylene bridged catalyst. The amount of incorporation of diene, catalytic activity and molecular weight depend on the metallocene used and also on the experimental conditions.

The results of this study highlight the unusual selectivity of metallocene catalysts in olefin polymerizations. The ability of metallocene catalysts to distinguish between two prochiral faces in propylene is well documented in the literature. This study reveals the efficacy of metallocene catalyst to distinguish between a reactive double bond in a polymer and in a monomer.

3.5 References

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Chapter 4. Synthesis of carboxylic acid functionalized polyolefin from ethylene/2,5-norbornadiene copolymer

4.1 Introduction

There are three different routes for the synthesis of functional polyolefins.[1] One is the direct copolymerization of olefin with functional monomer. However, functional groups, especially, if polar, adversely affect the catalytic activity. The second method involves the post polymerization attachment of functional groups onto the polyolefin backbone using either thermal or ionization energy. Non uniform distribution of the functional groups on the polymer, with functional groups predominantly located in the amorphous region, degradation of the polyolefin backbone and crosslinking are some of the drawbacks of this method. The third, and the most preferred method, is the copolymerization with a precursor monomer which does not interfere in the polymerization, but, can later be converted into the desired functional group by chemical transformations.

There are two different approaches reported in the literature for the third method. These involve the synthesis of polyolefins having either boron moiety[2] or unsaturation as pendant group which are synthesized either by copolymerization with boron containing monomer or with a diene where only one of the double bonds is involved in copolymerization respectively.

Several reports are available in the literature regarding post polymerization conversion of pendant double bonds to various functional groups by simple organic chemical transformations. Marathe and Sivaram[3] reported the conversion of pendant double bonds of ethylene/VNB copolymer to epoxy and hydroxyl groups. Kaminsky[4] et al. reported the conversion of the cyclohexenyl pendant groups on ethylene/4-vinylcyclohexene copolymer to hydroxyl groups. Shiono[5,6] et al. have reported the conversion of terminal double bonds present in ethylene/propylene and propylene polymers to a variety of functional groups. Patent issued to Amoco[7] has shown the functionalization of terminal double bonds in poly α-olefins.

Synthesis of carboxylic acid functionalized polyolefin by direct copolymerization is difficult compared to the synthesis of hydroxyl functional polyolefin 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]

Polyethylene-b-polymethyl methacrylate copolymers have been successfully synthesized using organolanthanide (III) complexes like $SmMe(C_5Me_5)_2(THF)$ or $[SmH(C_5Me_5)_2]$ which are active for the homopolymerization of ethylene as well as for the living polymerization of methyl methacrylate.[9] However, no random copolymerization could be achieved by this catalyst. Recently, copolymerization of ethylene with alkyl acrylates like methyl acrylate using Pd(II) and Ni(II) complexes have been reported. Copolymers having as high as 12 mol % methyl acrylate could be synthesized.[10] These copolymers, similar to ethylene homopolymers synthesized using the same catalysts, are highly branched with approximately 100 branches per 1000 carbon atoms. They are hence amorphous in nature.

The synthesis of a copolymer having pendant endocyclic double bonds was described in **Chapter 3**. In this chapter, the functionalization of this pendant double bond to dicarboxylic acid, under mild conditions, is reported. Post polymerization modifications enable retention of the desirable properties of polyolefins.

4.2 Experimental

4.2.1 Materials

An ethylene/NBD copolymer (**23**) having 4.0 mol % NBD synthesized with $(n\text{-}buCp)_2ZrCl_2$/MAO catalyst system as given in **Chapter 3, Table 3.4, entry no. 2** was selected for the functionalization. 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.

4.2.2 Functionalization

4.2.2.1 Oxidation of norbornene to cyclopentane-1,3-dicarboxylic acid

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 seperated 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).

4.2.2.2 Oxidation of pendant double bonds in ethylene/NBD copolymer

In a 100 mL round bottom flask, 1 g of copolymer (**23**) (1.43 mmol of double bonds) was taken and 50 mL toluene and 0.045 g (0.14 mmol) of tetrabutylammonium bromide were added. It was stirred for 1 h to enable complete solubilization of the copolymer. To this 0.7 g (4.3 mmol) of $KMnO_4$ dissolved in 50 mL of distilled water was added. The stirring was continued for 24 h. To the reaction mixture 0.6 g (5 mmol) of Na_2SO_3 was added to oxidize the excess $KMnO_4$ and then 2 mL of conc. HCl in 2 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. The polymer was found to be in the interphase of the two layers. The lower water layer was removed using a separating funnel and to the remaining part methanol was added and stirred for 12 h. The polymer thus precipitated was filtered, dried and weighed. 0.98 g of the product was isolated.

4.2.3 Analysis

The IR spectrum was recorded on a Perkin-Elmer 16 PC FT-IR spectrometer. ^1H NMR spectra of cyclopentane-1,3-dicarboxylic acid was recorded on a 200 MHz Bruker NMR spectrometer at room temperature in DMSO-d_6. ^1H NMR spectra of the carboxylic acid functionalized copolymer was recorded on a 300 MHz Bruker MSL

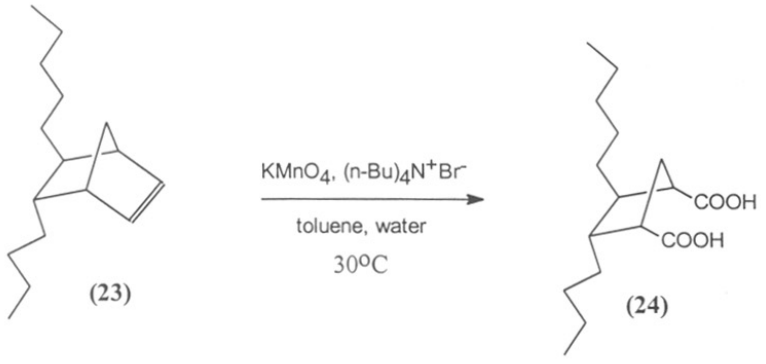
300 model NMR spectrometer at 80°C in a solvent mixture of toluene-d_8 and DMSO-d_6 (85/15 v/v). ^{13}C NMR was recorded at 120°C in a mixture of o-dichlorobenzene and DMSO-d_6 (85/15 v/v) on a Bruker MSL 300 model spectrometer operating at 75.5 MHz. Thermogravimetric and differential scanning calorimetric analysis were carried out on Perkin Elmer TGA-7 and DSC-7 instruments respectively.

4.3 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 tetraoxide 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.

The limited solubility of the copolymer precluded the utilization of these methods for the oxidative cleavage of norbornene moiety in the copolymer. There is 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.

It was, therefore, decided to extend this method for the oxidation of the endocyclic double bonds in the copolymer. Since the copolymer 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. Before performing the oxidation on the copolymer a model reaction was carried out on norbornene. Cyclopentane-1,3-dicarboxylic acid could be obtained in ~ 95 % isolated yield. Having successfully established the conditions for the oxidation of the double bond in norbornene, the reaction was then carried out on the copolymer. A much-prolonged reaction time of 24 h, rather than the 3 h was used for the oxidation of the pendant double bonds on the polymer. Under these conditions, the endocyclic double bonds could be converted to the corresponding dicarboxylic acid (**Scheme 4.1**).



(23) (24)

Scheme 4.1 Conversion of pendant endocyclic double bond in ethylene/NBD copolymer to dicarboxylic acid

4.3.1 Characterization of the oxidized copolymer

4.3.1.1 IR

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 (**Figure 4.1**).

4.3.1.2 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 (**Figure 4.2**). 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 (**Figure 4.3**) 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.

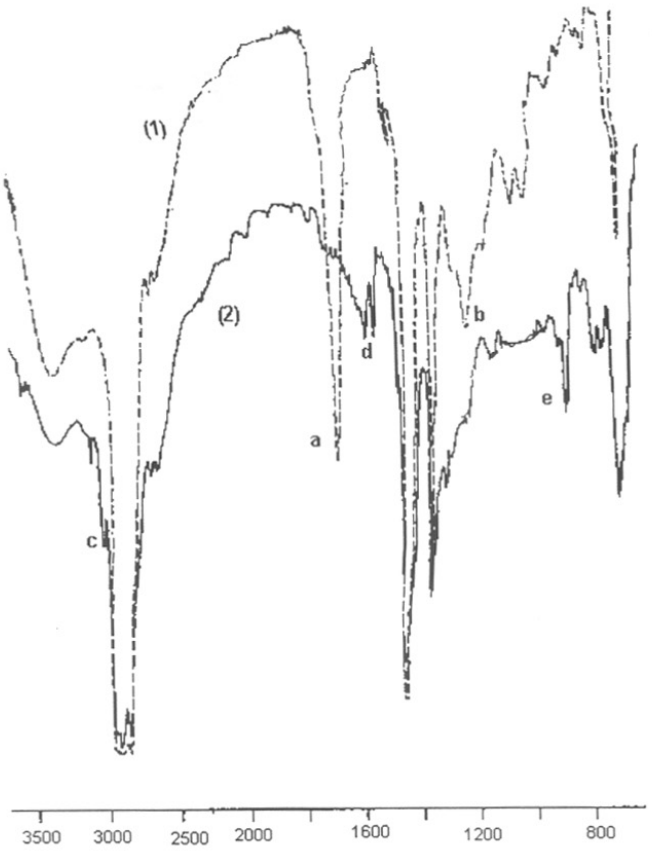


Figure 4.1 IR spectrum of (1) ethylene/2,5-norbornadiene copolymer (23) and (2) carboxylic acid functionalized ethylene/2,5-norbornadiene copolymer (24)

Peaks: (a) 1725 cm^{-1} C=O stretching, (b) 1240 cm^{-1} C-O stretching, (c) 3065 cm^{-1} C-H alkene stretching, (d) 1583 cm^{-1} C=C stretching, (e) 908.7 cm^{-1} C-H alkene bending

4.3.2 Copolymer properties

4.3.2.1 Solubility

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 because of the presence of highly polar carboxylic acid groups. It was also not soluble in any of the common solvents of polyolefins like xylene, o-dichlorobenzene etc. The copolymer was found to be soluble in a mixture of any of the above solvents and DMSO (85:15 (v/v) ratio) at temperatures above 80°C.

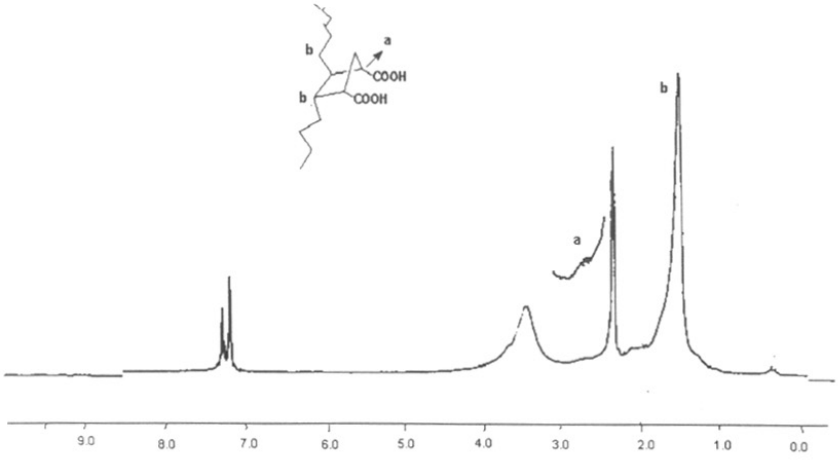


Figure 4.2 ^{1}H NMR spectrum of carboxylic acid functionalized ethylene/ 2,5-norbornadiene copolymer (24)

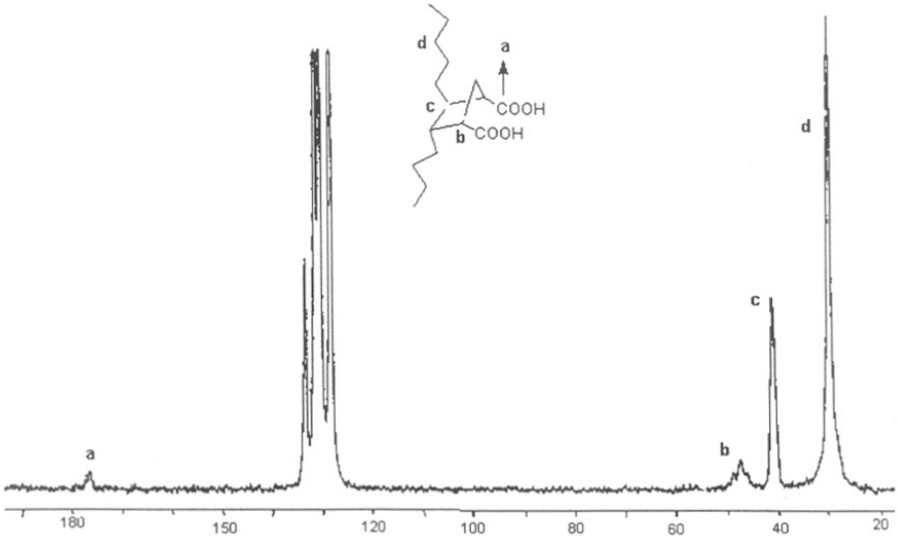


Figure 4.3 ^{13}C NMR spectrum of the carboxylic acid functionalized ethylene/2,5-norbornadiene copolymer (24)

4.3.2.2 Thermal properties

The TGA thermogram (**Figure 4.4**) of the functionalized copolymer showed the absence of any weight loss at 300°C. This observation is unlike the precursor copolymer, wherein, the weight loss occuring at 300°C was attributed to retro Diels Alder reaction. The fact that the double bond is absent in the oxidized copolymer may

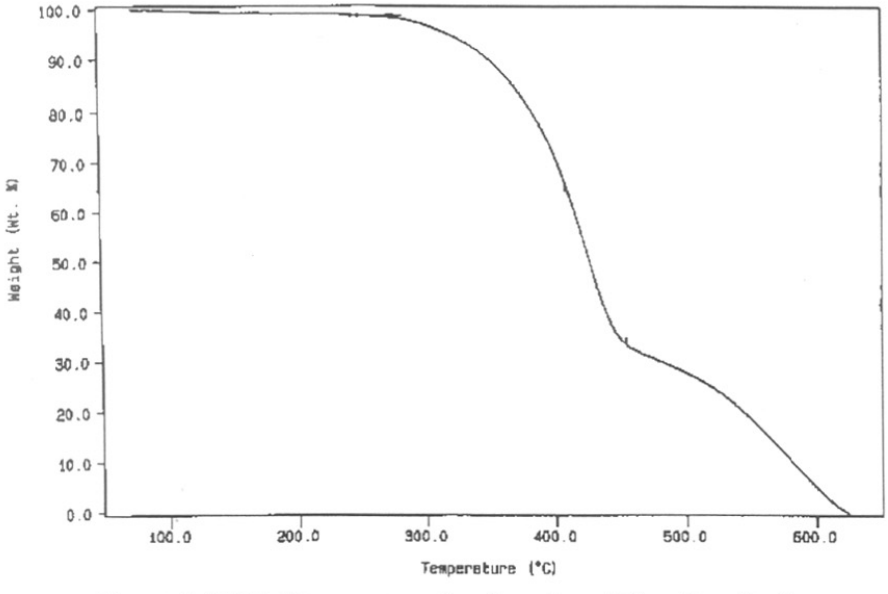


Figure 4.4 TGA thermogram of carboxylic acid functionalized ethylene/2,5-norbornadiene copolymer (24)

may explain the difference in TG behavior. The initial decomposition temperature of the dicarboxylic acid functionalized copolymer was found to be around 390°C which is same as that of the precursor copolymer. However, functionalized copolymer underwent complete decomposition only at 620°C, whereas, the precursor copolymer decomposed fully at 490°C.

Functionalization does not appear to have any effect on the crystallinity of the copolymer. The DSC thermograms (**Figure 4.5**) of the parent as well as the functionalized copolymers were having similar broad melting endotherms in the region of 85 to 100°C.

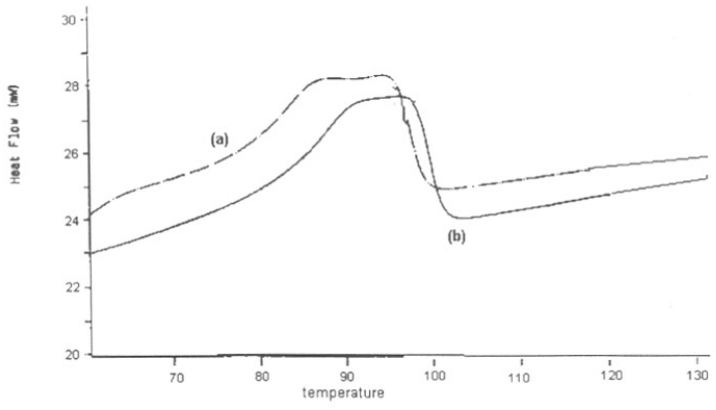


Figure 4.5 DSC thermograms of (a) ethylene/2,5-norbornadiene copolymer (23) and (b) carboxylic acid functionalized copolymer (24)

4.4 Conclusions

A polyolefin having carboxylic acid functional group could be synthesized by the oxidation of the pendant double bonds in ethylene/NBD copolymer under mild conditions. This is the first example of a post polymerization functionalization of a pendant double bond in a polyolefin to carboxylic acid group. 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. A novel method for the two phase oxidation of polyolefin bearing unsaturation has been identified. Such oxidized polyolefins are likely to possess interesting applications as adhesion promoters, tie layers in multilayer barrier packaging and emulsifyable polyethylene waxes for coating applications.

4.5 References

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Chapter 5. Copolymerization of ethylene with 5-norbornene-2-methanol prereacted with alkylaluminum: An approach to hydroxy functional polyolefins

5.1 Introduction

The simplest route to the synthesis of functional polyolefins is by the direct copolymerization of olefin with the comonomer having the desired functional group. But the functional group, having lone electron pairs, usually co-ordinate with either the catalyst or the cocatalyst rendering them inactive for polymerization. Different approaches have been adopted to overcome this problem, like separating the functional group from the polymerizable double bond by spacer group, by protecting the functional group either by using externally added reagent or by increasing the bulkiness around the functional group and by decreasing the nucleophilicity of the functional group.

With the discovery of metallocene/MAO catalyst system for olefin polymerizations there is a renewed interest in such methods for introducing functional groups on polyolefins. Copolymerization of ethylene with 10-undecen-1-ol using (n-buCp)$_2$ZrCl$_2$/MAO catalyst system, with a maximum incorporation of 1.7 mol %, have been reported by Aaltonen et al.[1] 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 % with the metallocene Me$_2$Si[2-Me-4,5-Benzo Ind]$_2$ZrCl$_2$.[2] Copolymerization of ethylene with the antioxidant, 6-tert-butyl-2-(1,1-dimethyl hept-6-enyl)-4-methyl phenol, have also been reported recently.[3]

It can be presumed that the active hydrogen of the alcohol reacts with MAO 'in situ' to form alcoholate which then undergoes copolymerization. The reaction of MAO with active hydrogen, with the release of methane gas, will lower the Me/Al ratio which itself is a decisive factor in polymerization.[4] So it was reasoned that 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. Further more,

it was proposed to increase the reactivity of comonomer by attaching the -OH functionality to a norbornyl type skeleton, possessing a strained endocyclic double bond.

Hence the monomer, 5-norbornene-2-methanol (NBOH), prereated with an alkyl aluminum and having a reactive double bond, was chosen as the comonomer. In this chapter, the copolymerization of ethylene with NBOH "prereated" with alkylaluminum using metallocene/MAO catalyst system is discussed.

5.2 Experimental

All the manipulations involving air sensitive materials were carried out using standard benchtop inert atmosphere techniques under a positive pressure of high purity nitrogen.

5.2.1 Materials

5-norbornene-2-methanol (Aldrich Chemical Company, USA) was freshly distilled (110°C/30 mm) before copolymerizations. A 2 M solution of trimethylaluminum (TMA) was prepared by dissolving 7.20 g of neat TMA (Witco GmbH, Germany) in 50 mL of dry toluene.

5.2.2 Synthesis of dimethylaluminum-5-norbornene-2-methoxide (27)

A dry 100 mL round bottom flask fitted with a rubber septum was cooled under N_2 atmosphere. The flask was connected to an external bubbler through a syringe needle. 0.3 mL (2.5×10^{-3} moles) of NBOH was added first, followed by 3 mL of dry toluene. The flask was then cooled to 0°C using ice-salt mixture. To this, 1.24 mL of 2 M TMA solution (2.5×10^{-3} moles) was added, drop by drop, under vigorous stirring. The evolved methane gas was allowed to escape through the bubbler. The reaction mixture was kept at 0°C for 30 min and then raised to 30°C and stirred for 15 min.

5.2.3 Copolymerization

Copolymerization was carried out at 1 atm ethylene pressure in a jacketed glass reactor connected to a 1 L gas burette. The experimental set up used for the copolymerization is shown in **Figure 3.2.** Toluene (30 mL) was introduced into the reactor and saturated with ethylene. The toluene solution of MAO (2.23×10^{-3} moles as Al) was added first followed by dimethylaluminum-5-norbornene-2-methoxide (**27**) in toluene. The copolymerization was initiated by the addition of toluene solution

of Cp_2ZrCl_2 (1.44 x 10^{-6} mol). Temperature was maintained by circulating water at the required temperature. Ethylene consumption was noted as a function of time. The copolymerization was terminated by the addition of 5 mL methanol. The copolymer was precipitated using methanol containing 2 % HCl, filtered, and dried under vacuum. ^{1}H NMR (toluene-d_8, ppm), 3.6 (2H, -CH_2-O-), 3.3 (1H, -CH-CH_2-O-), 2.1 (2H, bridge head), and 1.4 (aliphatic).

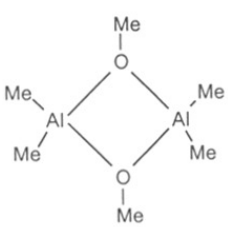
5.2.4 Analysis

The IR spectrum was recorded on a Perkin-Elmer 16 PC FT-IR spectrometer. ^{1}H NMR spectra were recorded on a 300MHz Bruker MSL 300 model spectrometer operating at 75.5 MHz in toluene-d_8 at 60 to 80°C. Intrinsic viscosities were determined in decalin at 135°C using an Ubbelhode viscometer. Differential scanning calorimetric analysis were carried out on a Perkin Elmer DSC-7 instrument.

5.3 Results and discussion

5.3.1 Reaction between 5-norbornene-2-methanol and trimethylaluminum

Addition of any primary alcohol to TMA in a 1:1 ratio is reported to result in the formation of aluminum alkoxides.[6] For example, addition of R-OH to TMA (where R = Me, Et, n-Pr, ^{i}Pr, n-Bu, sec-Bu, n-C_5H_{11}, $CH_2CH_2{}^i$Pr, $CH_2{}^t$Bu) result in the formation of alkoxides by the reaction of active hydrogen with the methyl group of TMA. From ^{1}H, ^{13}C, ^{17}O, ^{27}Al NMRs, IR and mass spectroscopy studies it was found that, with the exception of alkoxide of ^{i}PrCH$_2$CH$_2$OH, all the compounds with branched chain alkoxides were dimeric (**25**) in nature, where as, the alkoxide of ^{i}PrCH$_2$CH$_2$OH and all the n-alkyl alkoxides exist as a mixture of dimer (**25**) and trimer (**26**).



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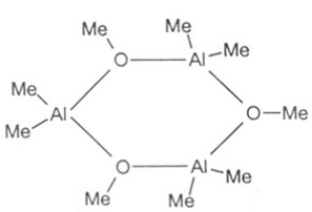

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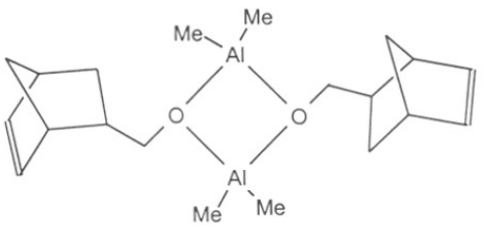
No attempts were made in this study to establish the structure of the product obtained by the reaction of NBOH with TMA. However, it is reasonable to assume that the product has a μ-bridged dimeric structure (**27**).



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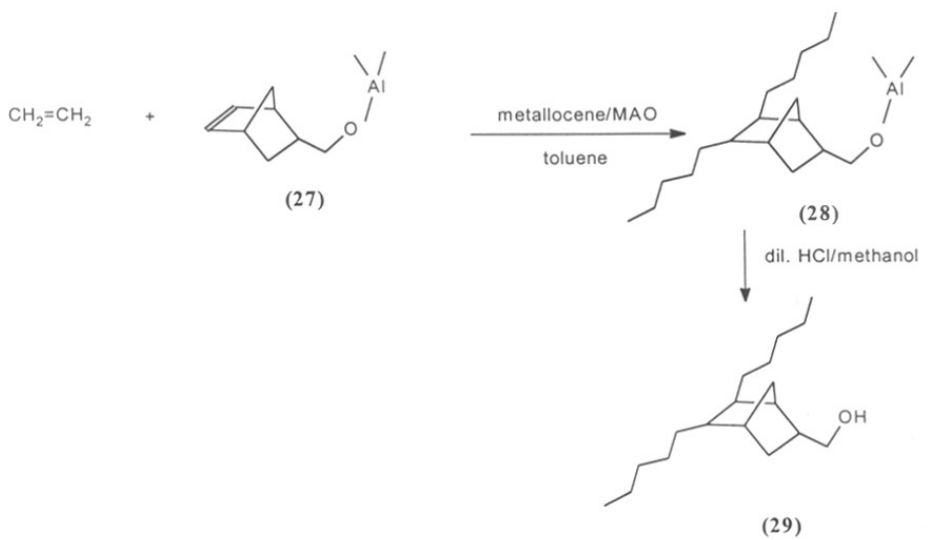
5.3.2 Copolymerization

The dimethylaluminum-5-norbornene-2-methoxide (**27**) undergoes copolymerization with ethylene efficiently (**Scheme 5.1**). Copolymerization activity, comonomer incorporation and molecular weights 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 (**28**) 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 5.1 Copolymerization of ethylene with dimethylaluminum-5-norbornene-2-methoxide using metallocene/MAO catalyst system

5.3.2.1 Effect of metallocene

In order to study the effect of metallocene on copolymerization, three metallocenes were selected and copolymerizations were carried out under identical conditions. The results are given in **Table 5.1**. It was found that the use of silicon bridged metallocene, $Me_2SiCp_2ZrCl_2$, resulted in maximum incorporation of the comonomer. The higher co-ordination aperture angle of the metallocene might be the reason for the higher incorporation. The efficacy of this metallocene in incorporating strained bicyclic olefins is discussed in detail in **Chapter 3**. **Figure 5.1** shows the kinetic profile of ethylene consumption for all the three catalysts studied under identical conditions.

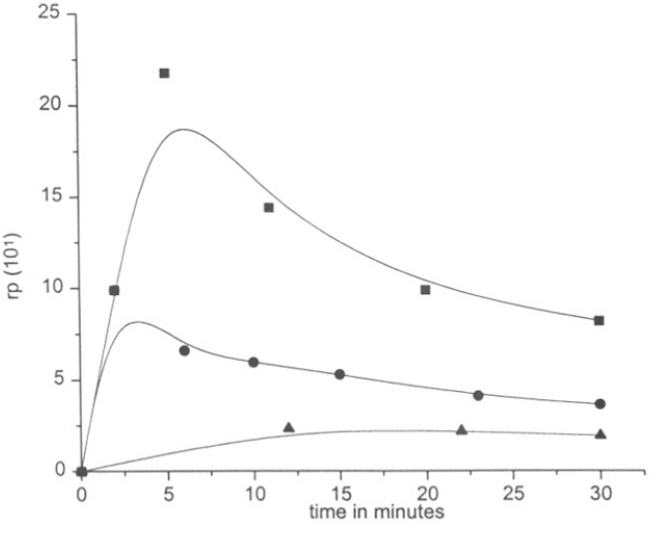


Figure 5.1 Kinetic profile for ethylene consumption in ethylene/ dimethylaluminum-5-norbornene-2-methoxide copolymerization using (■) Cp_2ZrCl_2, (●) $Et(ind)_2ZrCl_2$, and (▲) $Me_2SiCp_2ZrCl_2$ catalysts

The unbridged metallocene, Cp_2ZrCl_2, showed the highest consumption of ethylene, while the Si bridged metallocene (**22**) showed the least consumption. It seems that there is a direct relationship between the extent of comonomer incorporation and ethylene consumption. Higher the incorporation of the comonomer, the lower was the copolymerization activity. In a typical copolymerization involving a bicyclic olefin,

Table 5.1 Copolymerization of ethylene with dimethylaluminum-5-norbornene-2-methoxide using various metallocenes[a]

no.	metallocene	yield (g)	catalyst activity (in kg copoly./ g.Zr. atm.h.)	mol % of alcohol in copoly. (by ^{1}H NMR)	conv. of alcohol (%)	[η] dL/g (in decalin at 135°C)	Tm (°C) (from DSC)
1	Cp_2ZrCl_2(**19**)	0.125	1.9	nd	-	2.25	126,134
2	$Et(ind)_2ZrCl_2$(**21**)	0.079	1.2	3.1	3	0.97	112
3	$Me_2SiCp_2ZrCl_2$(**22**)	0.046	0.7	5.4	3	0.42	92 (broad)

[a] Polymerization conditions: [Zr] = 4.8 x 10^{-5} M, [NBOH] = 8.3 x 10^{-3} M, Al/Zr = 1,500, toluene = 30 mL, temperature = 35°C, $P_{ethylene}$= 1 atm., nd = not determined.

catalyst activity for copolymerization is lower than that for homopolymerization. For the metallocene Cp_2ZrCl_2, though the comonomer incorporation was negligible as evidenced by the Tm, activity was found to be very low compared to homopolymerization (20 kg/g.Zr. atm. h.). It seems that the lone pair of electrons on the oxygen of the comonomer is adversely affecting the course of copolymerization reaction. This is inspite of the fact that the electron donating power of oxygen is considerably reduced due to oxygen to aluminum $p\pi - d\pi$ dative bond.[7]

5.3.2.2 Effect of protecting group

No polymerization activity was observed when alcohol was used as such without the "prereaction" with TMA. This indicates the efficacy of TMA as protecting agent for alcohols.

5.3.2.3 Effect of TMA in MAO

It is well documented in the literature that MAO contains considerable amount of TMA co-ordinated with the aluminoxane.[5] It was reasoned that if TMA is replaced by dimethylaluminum-5-norbornene-2-methoxide (**27**), it will occupy the positions occupied by TMA and thus the oxygen atoms in (**27**) will be co-ordinated with the other aluminum atoms in MAO making it less deleterious. So in one reaction, the TMA in MAO was removed by applying vacuum for 1 h^4 and (**27**) was added into it. The polymerization carried out with this MAO using Cp_2ZrCl_2 catalyst resulted in a polymer having a Tm of 134^{O}C indicating practically no incorporation of the alcohol. Also the copolymerization activity was found to be less (1.4 kg polymer/g.Zr.atm.h.).

5.3.2.4 Effect of feed ratio

Copolymerizations were carried out at around a feed ratio of 1:1. The fact that such a high feed ratio of alcohol could be used in copolymerizations is due to the removal of active hydrogen of the alcohol by trimethylaluminum. When NBOH was added into MAO a large evolution of gas was observed. Under these conditions no polymerization was observed. Presumably the active hydrogens might have reacted with Al-CH_3 bonds in MAO resulting in its complete destruction. It is pertinent to note that ratio of MAO (as Al) to alcohol used in copolymerizations were near to 1. Aaltonen and Lofgren have observed no polymerization activity at ratios lower than 3 when alcohol was used directly.[1] Thus removal of active hydrogen by TMA facilitated the use of higher amounts of alcohol in the feed and thus also higher incorporation of

alcohol in the copolymer. However, no copolymerization activity was observed at ratios lower than 1.

5.3.2.5 Effect Al/Zr ratio

Inorder to study the effect of Al/Zr ratio on copolymerization, copolymerizations were carried out at three different ratios, results of which are given in **Table 5.2**. Higher Al/Zr ratios increased the copolymerization activity as well as comonomer incorporation. This observation was quite different from the one in ethylene/NBD copolymerization where comonomer incorporation was found to decrease with increase in Al/Zr ratio. The catalytic center seems to be less sensitive to oxygen of

Table 5.2 Effect of Al/Zr ratio on copolymerization of ethylene with dimethylaluminum-5-norbornene-2-methoxide using $Me_2SiCp_2ZrCl_2$catalyst[a]

Al/Zr ratio	yield (g)	Catalyst activity (in kg copoly./g.Zr. atm.h.)	mol % of alcohol in copoly. (by ^{1}H NMR)	conv. of alcohol (%)	[η] dL/g (in decalin at 135°C)
1,500	0.046	0.7	5.4	3.0	0.42
3,000	0.046	0.7	5.9	4.3	0.37
5,000	0.078	1.2	6.2	7.2	0.28

[a] Polymerization conditions: [Zr] = 4.8 x 10^{-5} M, [NBOH] = 8.3 x 10^{-3} M, toluene = 30 mL, temperature = 35°C, $P_{ethylene}$= 1 atm.

the alcohol at higher Al/Zr ratios. Or, the oxygen of the comonomer may be co-ordinating with the lewis acidic aluminum present in MAO.

5.3.2.6 Effect of temperature

Increase in temperature increased the catalyst activity. However, there was a drastic decrease in intrinsic viscosity (**Table 5.3**). But unlike in ethylene/NBD copolymerizations, the mol % of comonomer incorporated did not decrease considerably.

Table 5.3 Effect of temperature on copolymerization of ethylene with dimethyl aluminum-5-norbornene-2-methoxide using $Me_2SiCp_2ZrCl_2$ catalyst[a]

temp. (°C)	yield (g)	Catalyst activity (in kg copoly./g.Zr. atm.h.)	mol % of alcohol in copoly. (by ^{1}H NMR)	conv. of alcohol (%)	[η] dL/g (in decalin at 135°C)
35	0.046	0.7	5.4	3	0.42
50	0.072	1.1	5.1	7	0.30
70	0.131	2.0	4.8	10	0.15

[a] Polymerization conditions: [Zr] = 4.8 x 10^{-5} M, [NBOH] = 8.3 x 10^{-3} M, Al/Zr = 1,500, toluene = 30 mL, $P_{ethylene}$= 1 atm.

5.3.3 Characterization of copolymers

5.3.3.1 IR

The IR spectrum of the copolymer is shown in **Figure 5.2**. A peak at 1130 cm^{-1} due to C-O stretching vibration indicates the presence of alcohol in the copolymer. Only a very small broad band at around 3300cm^{-1} due to -OH vibration could be detected which may be due to the relatively low amount of alcohol present in the copolymer.

5.3.3.2 NMR

The ^{1}H NMR spectrum of the copolymer is shown in **Figure 5.3**. The spectrum showed a peak at 3.5 ppm indicative of $-CH_2-O-$ group. The mol % of alcohol in the copolymer was calculated as shown below.

Area of peak at 3.5 ppm due to 2H of the alcohol = X

Area of peak at 1.6 ppm due to 4H of ethylene = Y

$$\text{Mol \% of alcohol in the copolymer} = \frac{X/2}{\left(X/2 + Y/4\right)} \times 100$$

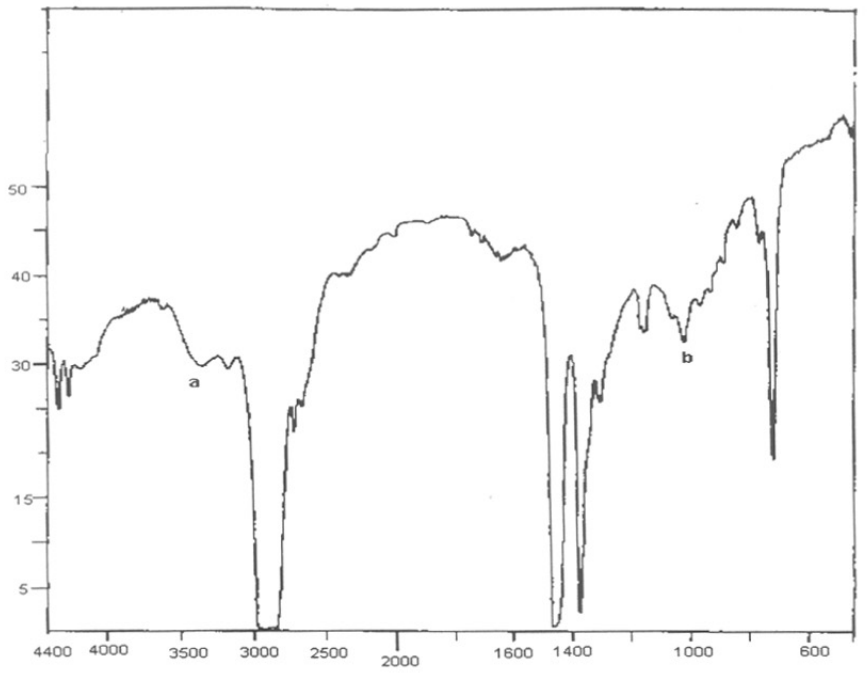


Figure 5.2 IR spectrum of ethylene/5-norbornene-2-methanol copolymer having 6.2 mol % of alcohol (Table 5.1, entry no. 3)

Peaks: (a) 3300 cm^{-1} -OH group, (b) 1130 cm^{-1}, C-O group

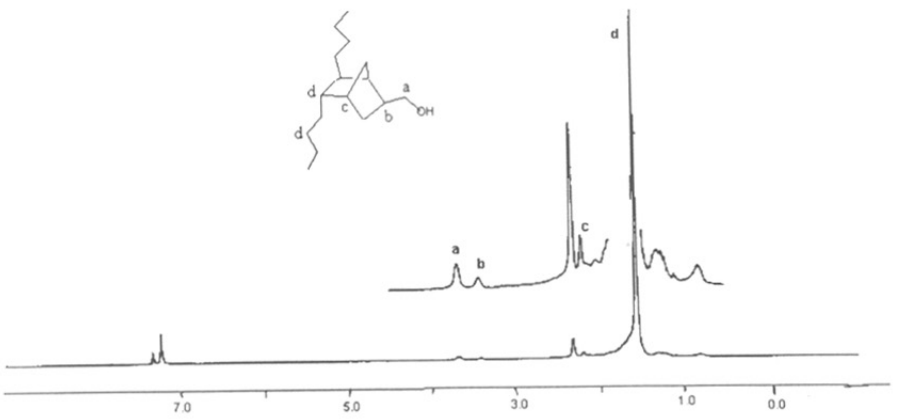


Figure 5.3 ^{1}H NMR spectra of ethylene/5-norbornene-2-methanol copolymer having 6.2 mol % of alcohol (Table 5.1, entry no. 3)

5.3.4 Copolymer properties

5.3.4.1 Solubility

All the copolymers were found to be soluble in o-dichlorobenzene at temperatures greater than100°C. All the copolymers synthesized with $Me_2SiCp_2ZrCl_2$ were soluble in toluene at around 60°C while the one synthesized with $Et(ind)_2ZrCl_2$ was soluble only at temperatures greater than 70°C in toluene.

5.3.4.2 Thermal properties

The DSC thermograms of the copolymers synthesized with the three different metallocene catalysts are shown in **Figure 5.4**. The copolymer synthesized with Cp_2ZrCl_2 showed two peaks, one at 126°C and the other at 134°C. The peak at low temperature may be due to copolymer whereas, the one at higher temperature may be due to homopolymer of ethylene. The polymer seems to be a mixture of homopolymer and copolymer. The copolymer synthesized with $Et(ind)_2ZrCl_2$ showed a sharp peak at 112°C. The copolymer synthesized with $Me_2SiCp_2ZrCl_2$ showed a very broad peak with a maxima at 92°C indicating the compositional heterogeneity of the copolymer.

5.4 Conclusions

A relatively facile route for the synthesis of polyolefins having pendant hydroxyl functional groups has been identified. A copolymer containing as high as 6 mol % hydroxyl groups could be successfully synthesized. Such a high incorporation of alcohol by direct copolymerization is unprecedented in the literature. Results in this chapter show that the deleterious nature of hydroxyl group containing functional monomers in polymerizations can be considerably reduced by prereacting it with alkylaluminum. Such a prereaction removes the active hydrogen as well as reduces the electron donating nature of the oxygen. It may be possible to reduce the electron donating nature further by incorporating the alcohol in an aluminoxane like caged structure.

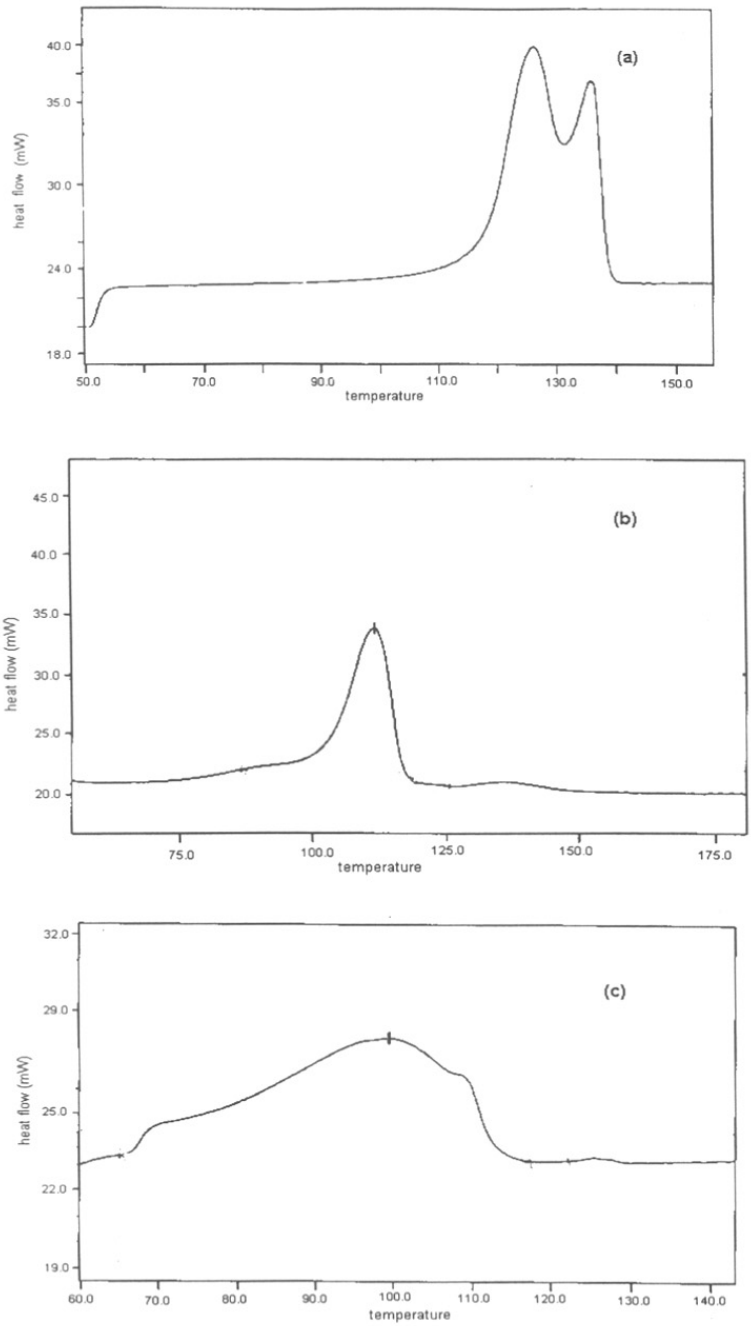


Figure 5.4 DSC thermograms of ethylene/5-norbornene-2-methanol copolymers synthesized using (a) Cp_2ZrCl_2, (b) $Et(ind)_2ZrCl_2$ and (c) $Me_2SiCp_2ZrCl_2$ catalysts (Table 5.1, entry no. 1, 2 and 3 respectively)

5.5 References

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Chapter 6. Copolymerization of ethylene with 5-vinyl-2-norbornene using dimethylsilyldicyclopentadienylzirconium dichloride /MAO catalyst system

6.1 Introduction

Introduction of pendant double bonds on to polyolefin backbone is an area of increasing interest in the field of metallocene because of the ease of functionalization of the pendant double bonds. Marathe and Sivaram[1] reported that the copolymerization of ethylene with 5-vinyl-2-norbornene (VNB) using Cp_2ZrCl_2/MAO catalyst system occur with the regioselective insertion of the endocyclic double bond, leaving the exocyclic vinyl double bond as pendant group. But the reactivity ratio value for ethylene and VNB indicates that the copolymer is rather blocky in nature. Goodall[2] et al. have reported that among a series of metallocenes the silicon bridged one, $Me_2SiCp_2ZrCl_2$, gives the highest incorporation of bicyclic olefins. The higher coordination aperture angle of the metallocene was attributed as the reason for this. In **Chapter 3**, it was found that copolymerization of the symmetric diene, NBD, both the double bonds were involved in copolymerization indicating the openness of the metal center to the double bond on the polymer chain.

It was reasoned that the use of this metallocene for ethylene/VNB copolymerization would result in copolymers having higher VNB contents with a more random distribution of comonomer in the copolymer. This chapter deals with the detailed study of ethylene/VNB copolymerization using $Me_2SiCp_2ZrCl_2$/MAO as the catalyst system.

6.2 Experimental

All manipulations involving air sensitive compounds were carried out using standard benchtop inert atmosphere techniques under a stream of ultra high purity nitrogen.

6.2.1 Materials

Toluene (Loba Chemie, GR grade) was purified by refluxing over sodium wire and subsequent distillation under nitrogen. Polymerization grade ethylene was procured

from the C_2-C_3 Gas Cracker unit of Indian Petrochemical Corp. Ltd., Nagothane, Maharashtra. Methylaluminoxane (MAO) (Me/Al ratio: 1.54, free TMA: 35 %, 14.1 % by wt. Al solution in toluene(Schering A.-G., Germany)and Irganox 1010 (Ciba-Giegy) were used as such. VNB (Aldrich Chemical Co., USA) was stirred over CaH_2 for 24h and distilled under nitrogen atmosphere prior to use. $Me_2SiCp_2ZrCl_2$ was prepared as per literature report,[3] details of which are given in **Chapter 3, section 3.2.2.**

6.2.2 Copolymerization

Copolymerizations were carried out as per procedure given in **Chapter 3, section 3.2.3**.

6.2.3 Analysis

The IR spectrum was recorded on a Perkin-Elmer 16 PC FT-IR spectrometer. ^1H NMR spectra were recorded using a 200 MHz Bruker NMR spectrometer at room temperature. The molecular weight distributions were determined using a Waters Gel Permeation Chromatograph model GPC/ALC 150C instrument equipped with a refractive index detector with μ-styragel columns (10^6, 10^5, 10^4, 10^3 and 500^OA) at 135^OC and 1,2,4-trichlorobenzene as solvent with 1 mL/min flow rate. Intrinsic viscosities were determined in decalin at 135°C using an Ubbelhode viscometer. Differential scanning calorimetric analyses were carried out on a Perkin Elmer DSC-7 instrument.

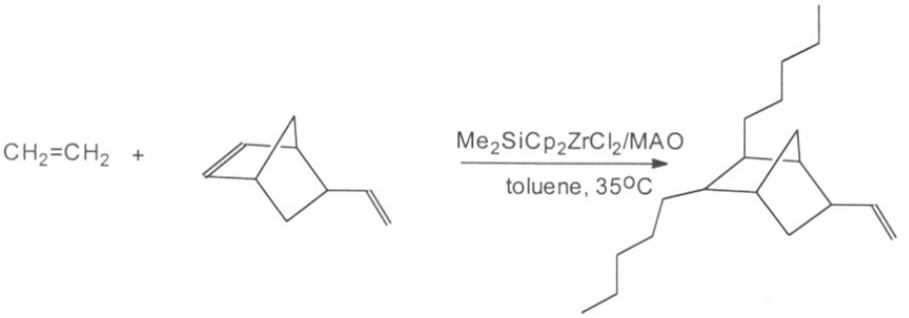
6.3 Results and discussion

6.3.1 Copolymerization

Ethylene undergoes facile copolymerization with VNB using $Me_2SiCp_2ZrCl_2$/MAO catalyst system (**Scheme 6.1**). By varying the feed composition copolymer containing as high as 27 mol % VNB could be successfully synthesized.

6.3.1.1 Effect of feed composition

In order to study the effect of feed composition on copolymerization and copolymer properties, a series of reactions under varying feed ratios were carried out, and the resulting copolymers were analyzed for their composition and intrinsic viscosity. The results are given in **Table 6.1.** The efficacy of the metallocene in incorporating the bulky bicyclic olefin, VNB, is evidenced by the fact at a 1:1 feed ratio a neat 100 %



Scheme 6.1 Copolymerization of ethylene with 5-vinyl-2-norbornene using $Me_2SiCp_2ZrCl_2$/MAO catalyst system

incorporation of the comonomer was observed within first 20 minutes of copolymerization. Higher amounts of VNB in the feed increased the comonomer content in the copolymer at the same time decreased the activity as well as intrinsic viscosity.

Table 6.1 Copolymerization of ethylene with 5-vinyl-2-norbornene using $Me_2Si(C_5H_4)_2ZrCl_2$/MAO catalyst system[a]

no.	[VNB] 10^2 (M)	time (min)	yield (g)	catalyst activity (in kg copoly./ g.Zr.atm.h.)	mol % of VNB in copoly. (by ^{1}H NMR)	conv. of VNB (%)	[η] dL/g (in decalin at 135°C)
1	9.86	20	0.82	18.7	11.9	100	0.55
2	12.0	30	0.64	9.8	15.0	89	0.42
3	14.0	60	0.96	7.3	17.5	91	0.25
4	17.5	60	0.79	6.0	24.3	83	0.19
5	30.8	60	0.26	2.0	25.9	68	0.12
6	35.0	120	0.26	2.0	27.0	74	0.12

[a] Polymerization conditions: [Zr] = 4.8 x 10^{-5} M, [Al] = 7.2 x 10^{-2} M, Al/Zr = 1,500, temperature = 35°C, toluene = 30mL.

6.3.1.2 Comparison with Cp_2ZrCl_2 catalyst

For a comparative study of ethylene/VNB copolymerizations using $Me_2SiCp_2ZrCl_2$ and Cp_2ZrCl_2 catalysts, two copolymerizations were carried out under identical conditions. The results are shown in **Table 6.2**. A higher incorporation of VNB was observed with the silylene bridged catalyst. This shows the efficacy of silylene bridged metallocene in the incorporation of the bulky comonomer. How ever, the catalytic activity as well as molecular weight of the copolymer were low for the

Table 6.2 Copolymerization of ethylene with 5-vinyl-2-norbornene using Cp_2ZrCl_2 and $Me_2SiCp_2ZrCl_2$ catalysts[a]

no.	metallocene	yield (g)	catalyst activity (in kg copoly./ g.Zr.atm.h.)	mol % of VNB in copoly. (by ^1H NMR)	conv. of VNB (%)	[η] dL/g (in decalin at 135°C)
1	$Me_2SiCp_2ZrCl_2$	0.26	2.0	25.9	68	0.12
2	Cp_2ZrCl_2	0.35	4.1	11.0	29	0.37

[a] Polymerization conditions: [Zr] = 4.8 x 10^{-5} M, [VNB] = 30.8 x 10^{-2} M, Al/Zr = 1,500, temperature = 35°C, toluene = 30mL, time = 60 min.

silylene bridged metallocene. This may be due to the relatively slow insertion of VNB over ethylene and increased chain termination reactions when VNB is at the growing chain end respectively.

6.3.1.3 Reactivity ratio

A series of copolymerizations under varying feed compositions were carried out and terminated such that the conversion of the VNB in less than 10 % for determining the reactivity ratio values for ethylene and VNB. Reactivity ratios were calculated using Kelen-Tudo's method (**Table 6.3**).[4] The values were found to be $r_{ethylene}$ = 3.7 and r_{VNB} = 0.0135. The reactivity ratio values with Cp_2ZrCl_2 catalyst are $r_{ethylene}$ = 18.6 and r_{VNB} = 0.3. The $r_{ethylene}$ value of 3.7 with $Me_2SiCp_2ZrCl_2$ catalyst shows that ethylene is preferred only 3.7 times over VNB inspite of the bulkiness of VNB, while with Cp_2ZrCl_2 catalyst ethylene is preferred 18.6 times over VNB. This indicates that

Table 6.3 Calculation of reactivity ratio values for ethylene and 5-vinyl-2-norbornene in ethylene/5-vinyl-2-norbornene copolymerization using $Me_2SiCp_2ZrCl_2$/MAO catalyst system using Kelen-Tudo's method

M_1	M_2	m_1	m_2	x	y	G	F	η	ξ
67	33	90.3	9.7	2.03	9.31	1.812	0.443	3.32	0.81
50	50	82.9	17.1	1.00	4.86	0.794	0.206	2.57	0.67
34	66	76.2	23.8	0.515	3.20	0.354	0.083	1.90	0.45
26	74	71.0	29.0	0.351	2.45	0.208	0.050	1.36	0.33
21	79	68.8	31.2	0.266	2.20	0.145	0.032	1.07	0.24
18	82	66.7	33.3	0.219	2.00	0.110	0.024	0.87	0.19

Where M_1 and m_1 are mol % ethylene in feed and copolymer respectively, M_2 and m_2 are mol % VNB 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 $G/(\alpha+F)$ and ξ is $F/(\alpha+F)$ where α is $(0.443 \times 0.0240)^{1/2}$

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

From the graph of η against ξ (**Figure 6.1**), $y = 3.83 - 0.131$

ie, $r_{VNB}/\alpha = 0.131$

There fore $r_{VNB} = 0.0135$ and $r_{ethylene} = 3.83 - 0.131 = 3.7$

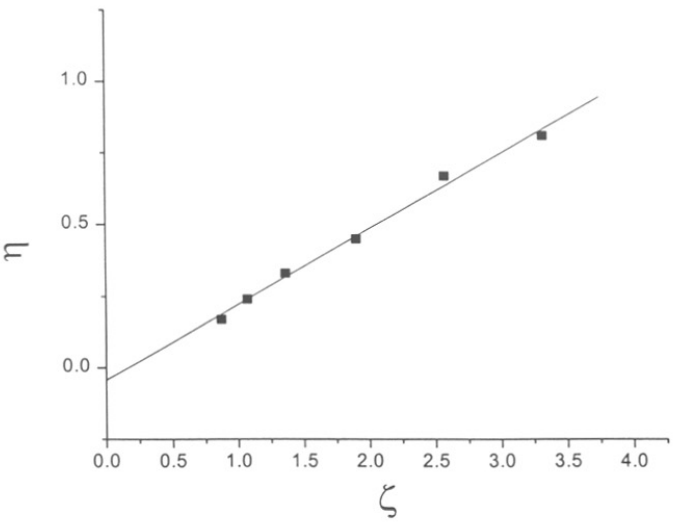


Figure 6.1 Kelen-Tudo's plot for calculating reactivity ratios of ethylene and 5-vinyl-2-norbornene in ethylene/5-vinyl-2-norbornene copolymerization using $Me_2SiCp_2ZrCl_2$ catalyst

the copolymer obtained with $Me_2SiCp_2ZrCl_2$ is more random in nature compared to the one synthesized with Cp_2ZrCl_2.

6.3.2 Characterization

6.3.2.1 IR

The FT-IR spectrum of the copolymer (**Figure 6.2**) showed peaks at 3065 cm^{-1} (=CH stretching), 1640 cm^{-1} (C=C stretching), and 990, 910 cm^{-1}(CH_2=CH def.) indicative of the presence of pendant double bonds in the copolymer.

6.3.2.2 NMR

^{1}H NMR spectrum of the copolymer (**Figure 6.3**) showed peaks in the range 5.4 to 6 (=CH hydrogen), 4.8 to 5.1 (=CH_2) due to vinyl pendant group. No peak could be detected in the range of 6.1 ppm (endoocyclic olefinic hydrogen), indicating that enchainment occurs exclusively through the endocyclic double bond. Mol % of VNB in the copolymer was calculated as shown below.

Area of the peak at 4.8 to 5.1 ppm due to 2H of double bond = A

Area of 1H of 5-vinyl-2-norbornene = A/2 = B

Area of the peaks in the range of 2 to 1 ppm = C

Area of 1H of ethylene = (C - 7B)/4 = D

Mol % VNB in the copolymer = [B/(B+D)] x 100

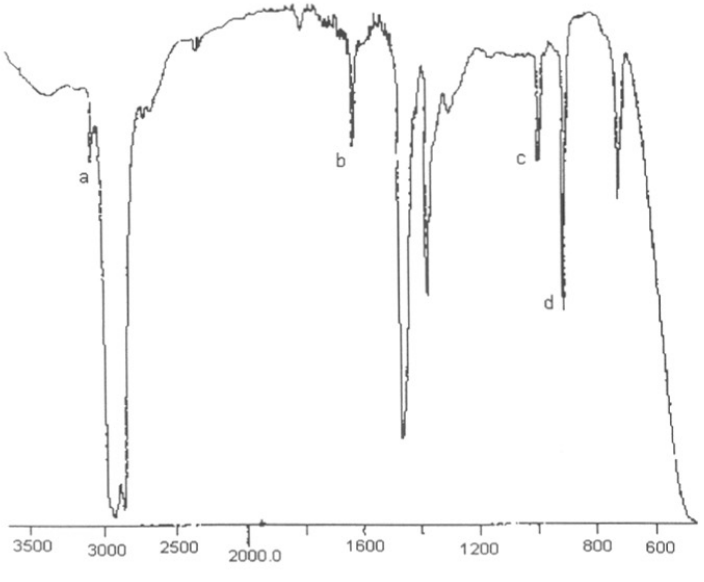


Figure 6.2 IR spectrum of ethylene/5-vinyl-2-norbornene copolymer having 15 mol % of 5-vinyl-2-norbornene (Table 6.1, entry no. 2)

Peaks: (a) 3065 C-H alkene stretching (b) 1640 C=C stretching, (c) 990 and (d)910 cm^{-1} C-H alkene bending

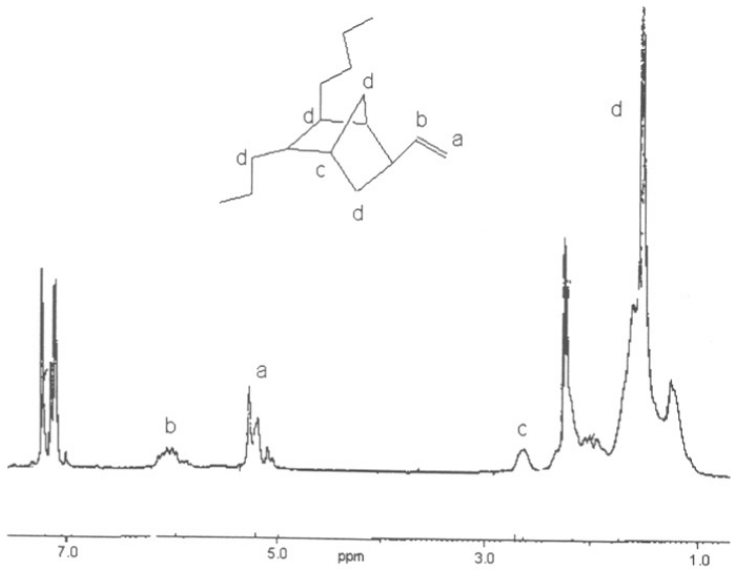


Figure 6.3 ^{1}H NMR of ethylene/5-vinyl-2-norbornene copolymer having 15 mol % 5-vinyl-2-norbornene (Table 6.1, entry no. 2)

6.3.2.3 GPC

The GPC chromatogram of the copolymer is given in **Figure 6.4**. The MWD was in the range of 2.0 to 2.5 indicative of the single site nature of the catalyst.

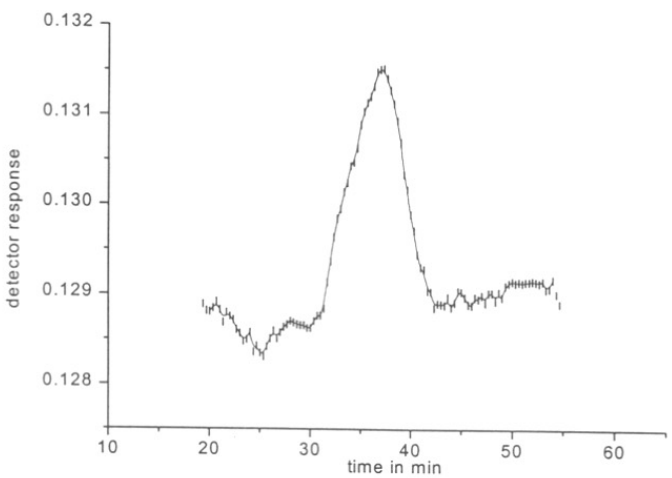


Figure 6.4 GPC chromatogram of ethylene/5-vinyl-2-norbornene copolymer (Table 6.1, entry no. 1)

6.3.3 Copolymer properties

6.3.3.1 Solubility

All the copolymers synthesized were found to be soluble in toluene, o-dichlorobenzene and xylene at 30°C and in benzene at 50°C.

6.3.3.2 Thermal properties

Neither Tg nor Tm could be observed for any of these copolymers in the temperature range of 50 to 150°C. Ethylene/norbornene copolymers having norbornene in the range of 10 -30 mol % showed Tg in the range of 0 - 40°C.[5] Ethylene/VNB copolymer synthesized with Cp_2ZrCl_2 catalyst having 9 mol % VNB showed a Tm at 80°C, where as the copolymer having 14 mol % showed no Tm.[6] No Tm was observed for the copolymer having the lowest incorporation of VNB 11.9 mol % (Table 6.1, entry no. 1). The absence of Tm in the copolymers synthesized with $Me_2SiCp_2ZrCl_2$ catalyst may be, thus, typical of an ethylene/VNB copolymer.

6.4 Conclusions

Ethylene/VNB copolymers, having random distribution of pendant double bonds along the polymer chain, as compared to the one synthesized using Cp_2ZrCl_2 catalyst, have been synthesized using the silylene bridged metallocene, $Me_2SiCp_2ZrCl_2$, as the catalyst for copolymerization. Such copolymers having pendant double bonds randomly distributed along the polymer chain can be used for the synthesis of functional polyolefins and various types of comb-like graft copolymers.

6.5 References

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Chapter 7. Synthesis of graft copolymers from epoxy functionalized ethylene/5-vinyl-2-norbornene copolymer

7.1 Introduction

Graft copolymers find a wide range of applications such as compatibilizer and interfacial agents. The efficiency of such graft copolymers depend on the molecular weight of the backbone as well as the pendant side chains, their molecular weight distributions, distribution of the grafted chain along the polymer chain and on the extent of grafting. In general, 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 an end functional group with the pendant functional group on the polymer backbone.

A number of reports are available in the literature on the synthesis of graft copolymers by 'graft from' method.[1,2] This method is usually employed over the other method due to the inability to introduce a proper functional group that can efficiently act as chain terminator or coupling agent. Though literature reports are available on the synthesis of polymers having epoxy and anhydride pendant functional groups, by free radical grafting, which can effectively act as a chain terminator or coupling agent, the extremely vigorous reaction conditions used for such grafting reactions ends up in side reactions. Moreover, as described in **Chapter 4**, such functional groups are not uniformly distributed along the polymer chain. Graft copolymers by 'graft from method' are usually synthesized by free radical polymerization, where the graft chain lengths are not controllable or are not well defined. Recently, graft copolymer synthesis by using anionic technique has been reported. The anion generated by the addition of sec-BuLi on to ethylene/4-methyl styrene copolymer was used for the synthesis of polyethylene-g-polystyrene copolymers.[3]

The synthesis of graft copolymers by 'graft onto' method provides an excellent opportunity to control the graft copolymer characteristics since the polymer to be

grafted is being synthesized separately and in a controllable manner. This provides adequate opportunity to vary the graft copolymer characteristics at will and enables one to study the effect of graft copolymer characteristics on the apparent end use or applications

In **Chapter 6**, the synthesis of a copolymer having pendant vinyl groups was described. The vinyl groups can be converted to epoxy groups by simple organic chemical transformation. By terminating living polystyryl lithium anion by the epoxy pendant group on the polyethylene backbone it was hoped that well defined polyethylene-g-polystyrene copolymer could be synthesized. Polyethylene-g-polystyrene copolymers finds application as compatibilizer for polyethylene/polystyrene blends.[4] It is well documented in the literature that living polystyryl lithium can be terminated by epoxy compounds. Quirk and Ma[5] have reported the synthesis of hydroxy end functionalized polystyrene by terminating polystyryl lithium by ethylene oxide in benzene at 25°C with almost 100 % efficiency. No block copolymer formation was observed, even when the concentration of ethylene oxide was four times that of polystyryl lithium. Epoxides are generally reported to be not polymerized by lithium bases presumably due to the unreactivity of associated lithium alkoxides.[6]

Amphiphilic copolymers are unique in the sense that they have both hydrophilic and hydrophobic segments. Such copolymers exhibit unique properties in selective solvents, at surfaces as well as in bulk. They may even organize themselves in selective solvents in the form of aggregates like micelles and microemulsions. Synthesis and applications of such amphiphilic copolymers have been recently reviewed by Velichkova and Christova.[7]

Attachment of polyethylene glycol to the backbone of polyolefins through the reactive pendant epoxy groups could result in a novel class of amphiphilic copolymers, having polyethylene and polyoxymethylene segments. Synthesis of block copolymer having polyethylene and polyoxymethylene segments has been recently reported.[8] Synthesis of amphiphilic block copolymers by epoxidation of pendant double bonds in polystyrene-b-polybutadiene copolymers followed by reaction with various nucleophiles like acid, amine and acid chloride has also been reported recently.[9]

This chapter describes the synthetic approaches to polyethylene-g-polystyrene and polyethylene-g-polyethylene glycol.

7.2 Synthesis of epoxy functionalized ethylene/5-vinyl-2-norbornene copolymer

7.2.1 Experimental

7.2.1.1 Materials

Ethylene/5-vinyl-2-norbornene copolymer synthesized with $Me_2SiCp_2ZrCl_2$ catalyst, as described in **Chapter 6,** containing 15 mol % of VNB (**Table 6.1, entry no. 2**) (**30**) was used for the grafting reaction. m-Chloroperbenzoic acid (Acros Organics, USA) containing 80 % active epoxy groups was used as such.

7.2.1.2 Epoxidation

Epoxidation was carried out as per literature report.[10] A simple procedure is given below. A 100 mL, two-necked, round-bottom flask equipped with a Teflon coated magnetic stirring bar, nitrogen inlet, and septum was cooled under a stream of nitrogen. About 100 mg of ethylene/5-vinyl-2-norbornene copolymer (**30**) having 15 mol % of VNB (0.358 mmol of unsaturation) was added to the flask followed by 40 mL of dry toluene, and the mixture was stirred at room temperature till the copolymer dissolved completely. About 100 mg of m-chloroperbenzoic acid (0.463 mmol) dissolved in 10mL dry toluene was added and the reaction mixture was stirred for 4 h. The reaction mixture was then poured into methanol, filtered, and dried under vacuum. Yield of the epoxy functionalized copolymer (**31**) isolated was 100 mg. IR (film) cm^{-1}, 2950-2850 (C-H stretch), 1470 (C-H def.), 1250 (C-O stretch), 876 (epoxy ring vibration), 725 (CH_2 rock). ^1H NMR (benzene-d_6, ppm) 3-2.85 (CH-C), 2.7-2.85 (CH_2-C), 2.5-0.95 (backbone and aliphatic H).

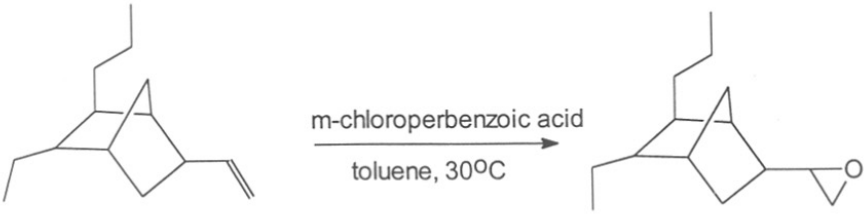
7.2.1.3 Analysis

The IR spectrum was recorded on a Perkin-Elmer 16 PC FT-IR spectrometer. ^1H NMR spectra was recorded on a 200 MHz Bruker NMR spectrometer at room temperature using toluene-d_8 as solvent.

7.2.2 Results and discussion

A complete conversion of double bonds in ethylene/5-vinyl-2-norbornene copolymer to epoxy groups (**Scheme 7.1**) was evident by the disappearance of peaks

corresponding to double bonds both in IR (**Figure 7.1**) and ^{1}H NMR (**Figure 7.2**) and appearance of peaks of epoxy groups.



(30) **(31)**

Scheme 7.1 Epoxidation of pendant vinyl double bonds in ethylene/ 5-vinyl-2-norbornene copolymer

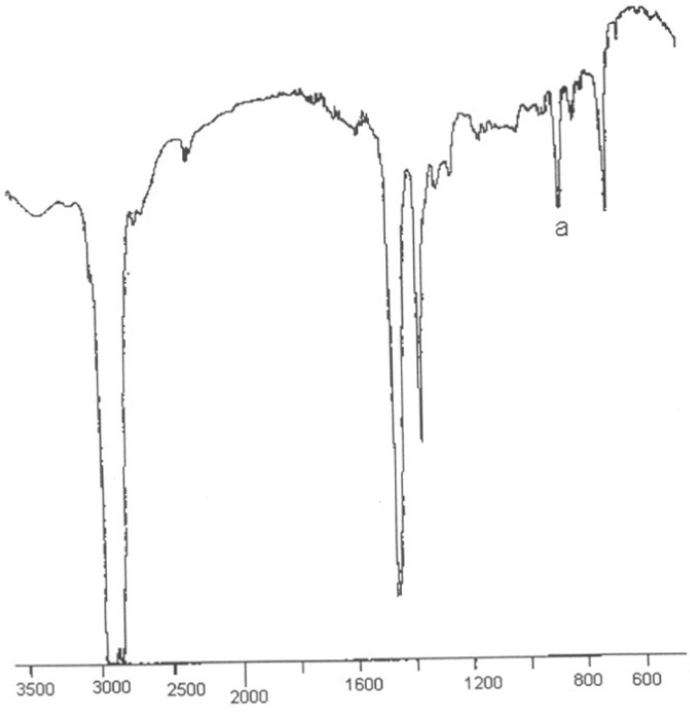


Figure 7.1 IR spectrum of epoxy functionalized ethylene/5-vinyl-2-norbornene copolymer (31)

Peak: 897 cm^{-1} epoxy group

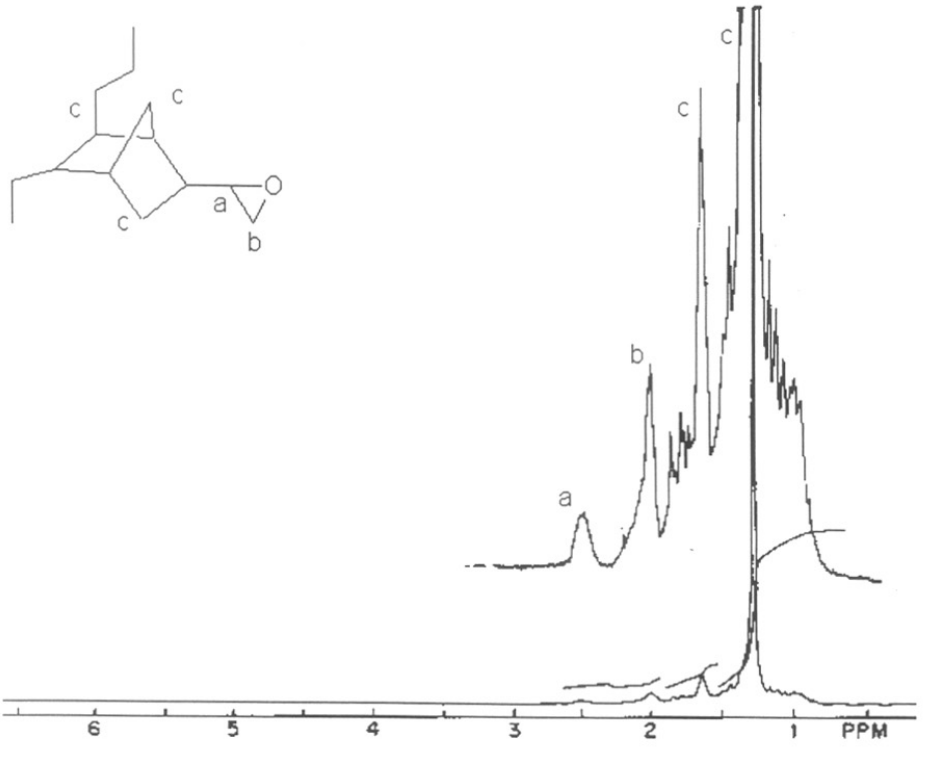


Figure 7.2 ^{1}H NMR of epoxy functionalized ethylene/5-vinyl-2-norbornene copolymer (31)

7.3 Polyethylene glycol (MPEG-2000-NH_2) grafting

7.3.1 Experimental

7.3.1.1 Materials

Dimethyl formamide (DMF), dichloromethane (CH_2Cl_2), diethylether, methanol (S.D. fine chemicals, AR grade) and triphenyl phosphine (PPh_3) (Aldrich Chemical Company, USA) were used as such. Sodium azide (NaN_3) (s.d. fine chemicals) was activated by hydrazine prior to use. Activation involved thorough mixing of the azide with a drop of hydrazine, dissolution of azide in water, precipitation by acetone and vacuum drying. Pyridine and thionyl chloride (s.d. fine chemicals) were freshly distilled prior to use. Polyethylene glycol of Mn 2000 having one methoxy and one hydroxy end group (MPEG-2000-OH) (**32**) was procured from Aldrich Chemical Company.

7.3.1.2 Synthetic methods

7.3.1.2.1 Conversion of MPEG-2000-OH to MPEG-2000-NH_2

The hydroxyl end group of MPEG-2000-OH was converted to amine by following literature procedure.[11]

7.3.1.2.1.1 Conversion of MPEG-2000-OH to MPEG-2000-Cl

MPEG-2000-OH (**32**) (20 g, 10 mmol) was dissolved in toluene (100 mL) and dried by azeotropic distillation. Dry pyridine (10 mmol) was added and freshly distilled thionyl chloride (30 mmol) was added drop wise using a syringe under reflux conditions. The mixture was heated for 4 h, cooled to room temperature and pyridine hydrochloride was filtered off and toluene was evaporated under vacuum. The residue was dissolved in CH_2Cl_2, dried over anhydrous potassium carbonate and filtered. The polymer (**33**) was recrystallized from ether. Yield obtained was 19 g. IR spectrum (in nujol) showed a peak at 663cm^{-1} due to C-Cl bond. No peak could be observed in the range of 3300 to 3500 cm^{-1} due to hydroxyl group.

7.3.1.2.1.2 Conversion of MPEG-2000-Cl to MPEG-2000-N_3

To a solution of MPEG-2000-Cl (**33**) (18 g, 9.0 mmol) DMF (100mL), activated NaN_3 was added and the mixture was stirred at 120°C for 2 h. The solution was cooled, filtered to remove sodium chloride (NaCl) and the DMF was removed under vacuum. The residue was dissolved in CH_2Cl_2, filtered to remove remaining NaCl and precipitated by ether. Yield obtained was 17.5 g. IR spectrum showed peaks at 2108 cm^{-1} due to N_3 group. No peak was observed at 663 cm^{-1}.

7.3.1.2.1.3 Conversion of MPEG-2000-N_3 to MPEG-2000-NH_2

In a 100 mL round bottom flask, 17 g (8.5 mmol) of MPEG-2000-N_3 (**34**) was taken and 60 mL of THF was added and stirred well to dissolve the azide. Then, 3.1g (12 mmol) of PPh_3 was added followed by 0.2 mL (10 mmol) of distilled water. The reaction mixture was stirred for 24 h at room temperature. THF was then removed under vacuum, followed by addition of 20 mL of petroleum ether. The slurry so formed was stirred for 30 min and then filtered. The residue was then washed with ethyl acetate and then dried under vacuum. The residue was then dissolved in methanol and precipitated by cold ether. The yield obtained was 16.0 g. IR spectrum

showed the absence of N_3 peak and presence of a broad peak around 3300 cm^{-1} due to NH_2 group.

7.3.1.2.2 Grafting

In a 100 mL round bottom flask around 30 mg of the epoxy copolymer (**31**) (0.107 mmol of epoxy groups) was taken. 25 mL of toluene was then added and stirred till the polymer was completely dissolved. In another 100 mL round bottom flask, 2.148 g (1.07 mmol) of MPEG-2000-NH_2 (**35**) was taken and dried by azeotropic distillation with toluene. 25 mL of toluene was added and the resulting solution was cannula transferred into the first round bottom flask. Into that 0.7 mL of 0.268 M $Ti(O^iPr)_4$ (0.193 mmol) in toluene was added using a syringe. The reaction mixture was kept for stirring for 24 h at 30°C. After 24 h, toluene was removed completely under vacuum and then excess methanol was added. The precipitated polymer was filtered, dried and weighed. The amount of polymer (**36**) that could be isolated was approximately 30 mg.

7.3.1.3 Analysis

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

7.3.2 Results and discussion

7.3.2.1 Synthesis of polyethylene glycol having amino functional group

The terminal hydroxyl group in MPEG-2000-OH was converted into amino group in three steps (**Scheme 7.2**). First it was converted into chloro group by reacting with thionyl chloride. Complete conversion of the hydroxyl group to chloro group is evident from the absence of the broad peak at around 3500 cm^{-1} in IR spectrum (**Figure 7.3**). The chloro group was then converted into azide group by reacting it with NaN_3. The transformation was quantitative as evident by the complete disappearance of the chloride peak at 663 cm^{-1} in IR spectrum (**Figure 7.4**). The conversion of the azide to amine was also found to be quantitative. Polyethylene glycol having terminal amino group, thus synthesized, was obtained as a weight powder.

Scheme 7.2 Conversion of hydroxyl end group in polyethylene glycol to amino group

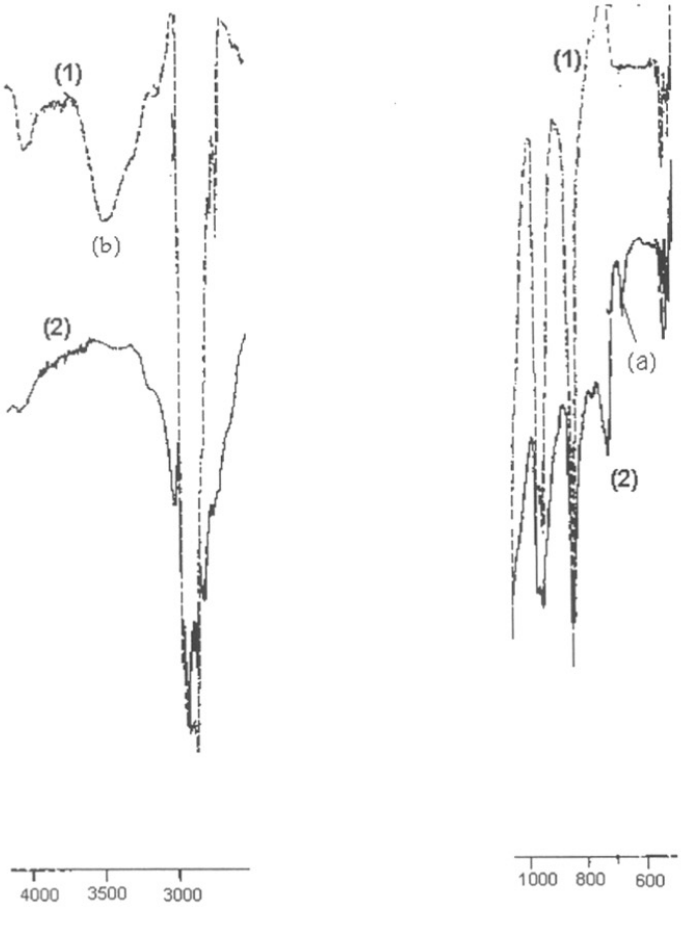


Figure 7.3 IR spectrum of (1) MPEG-2000-OH and (2)MPEG-2000-Cl (area from 2500 to 1050cm^{-1} have been omitted for better clarity)

Peaks: (b) 3500 cm^{-1} OH group, (a) 663 cm^{-1} C-Cl group

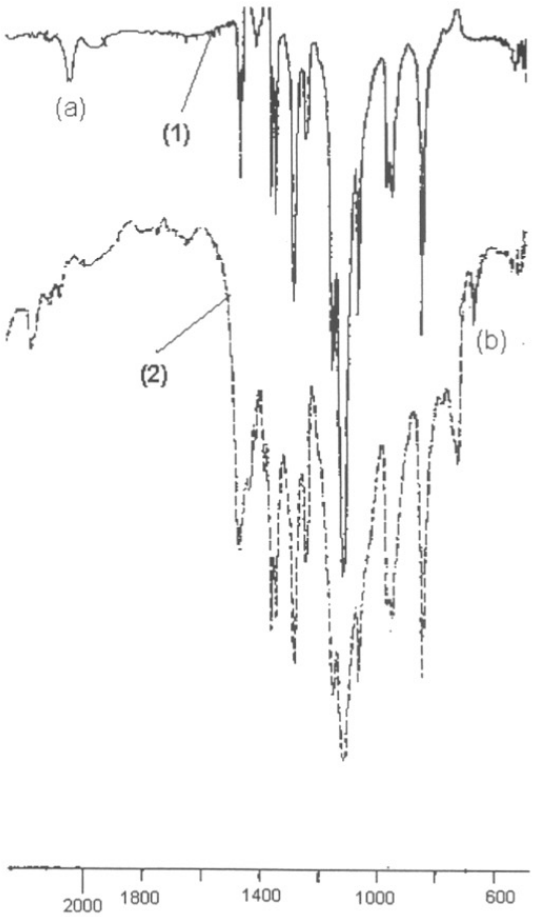
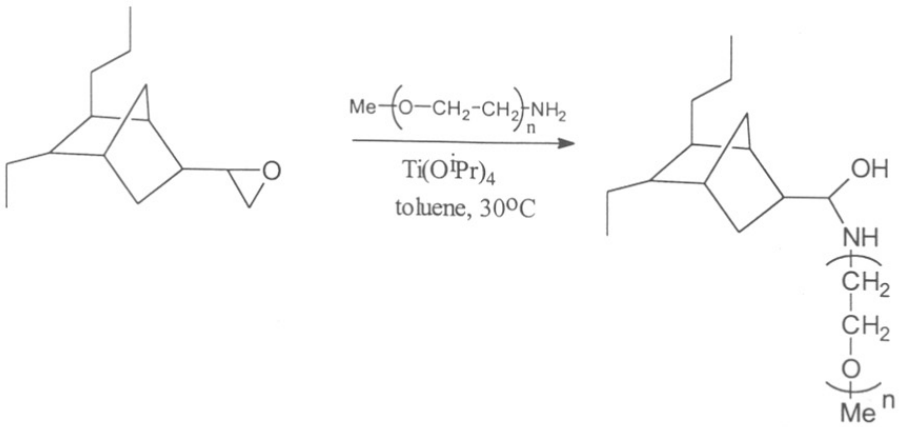


Figure 7.4 IR spectra of (1) MPEG-2000-N_3 and (2) MPEG-2000-Cl

Peaks: (a) 2108 cm^{-1} N_3 group (b) 663 cm^{-1} Cl group

7.3.2.2 Grafting

The most direct method for the synthesis of the graft copolymer is by reacting polyethylene glycol having hydroxy end group with the epoxy pendant groups. But the stringent inert atmosphere experimental conditions needed for such a grafting reaction and the possibility of side reactions like crosslinking prompted the search for a viable alternative procedure. The reaction of an epoxy group with an amino group terminated polyethylene glycol was, thus, identified for the synthesis of graft copolymer (**Scheme 7.3**).



Scheme 7.3 Grafting of polyethylene glycol having amino end group onto epoxidized ethylene/5-vinyl-2-norbornene copolymer

A number of catalysts are reported to be efficient for the ring opening of epoxide with an amine. These are lithium perchlorate,[14] lanthanum triflate,[15] and titanium isopropoxide $Ti(O^iPr)_4$.[12] The utility of such catalysts are reported for simple organic molecules like 1-epoxy octane and diethylamine. However, their extension to polymer analogue reaction is not reported in the literature. The absence of a suitable common solvent, where, both the catalyst as well as the epoxy polymer is soluble, limited the use of some of the catalysts. For example lithium perchlorate is a very efficient ring opening catalyst in tetrahydrofuran. But the lack of solubility of the epoxy copolymer in THF prevented its use. $Ti(O^iPr)_4$ is reported to be an efficient ring opening catalyst of α-hydroxy epoxy compounds in toluene. So it was decided to use this catalyst for ring opening grafting reaction. However, use of this reagent led to some problems. Initially no polymer could be isolated from toluene, the medium in which the reaction was carried out, by adding even very large excess of methanol. It was presumed that grafting might have occurred, other wise, the epoxy polymer should have precipitated out of toluene when excess methanol was added. So in order to isolate the product after the reaction, toluene was completely removed under vacuum and then excess methanol was added. Some polymer got precipitated. The precipitated polymer, presuming that it is graft copolymer, was repeatedly washed to remove the ungrafted polyethylene glycol and was dried and weighed. No significant weight increase was observed. The IR spectrum of the product (**Figure 7.5**) showed the presence of ether linkages in the polymer. However, the product showed the presence of epoxy groups

also. The copolymer thus isolated was later found to be insoluble in toluene also in spite of being soluble during the reaction. Two more reactions, one at 50°C instead of 30°C for 24 h and one for 48 h instead of 24 h at 30°C, were carried out to see whether change in the experimental parameters would make any difference. However, the results were similar.

7.3.2.3 Characterization

7.3.2.3.1 IR

The IR spectrum of the isolated polymer showed the presence of -CH_2-O- group as evidenced by the peaks at 1088 and 1040 cm^{-1}. However, unreacted epoxy groups was also present (889 cm^{-1}).

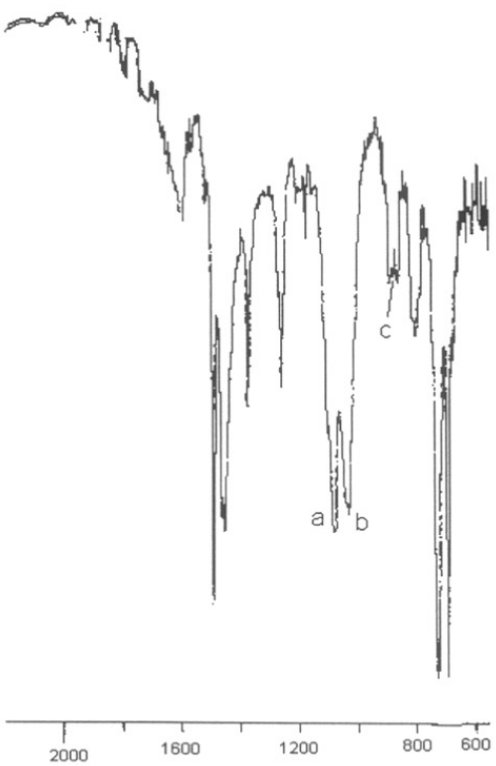


Figure 7.5 IR spectrum of the polymer (36) obtained after the reaction between epoxy functionalized ethylene/5-vinyl-2-norbornene copolymer (31) and MPEG-2000-NH_2 (35)

Peaks: (a) 1088 cm^{-1} and (b) 1040 cm^{-1} C-O group and (c) 889 cm^{-1} epoxy group

7.3.2.4 Copolymer properties

7.3.2.4.1 Solubility

Though the parent epoxy copolymer was soluble in toluene, the copolymer isolated after the grafting reaction was found to be insoluble in toluene. It was neither soluble in methanol nor in a mixture of the above two solvents of any composition.

7.4 Grafting of living polystyryl lithium anion onto epoxy functionalized ethylene/5-vinyl-2-norbornene copolymer

7.4.1 Experimental

7.4.1.1 Materials

Styrene (Thermax Limited, Pune) was stirred over calcium hydride for 12 h and distilled under reduced pressure. sec-BuLi synthesized in the laboratory was used as such. Toluene was freshly distilled from sodium/potassium alloy just prior to use.

7.4.1.2 Synthesis of polystyryl lithium anion

In a single neck 250 mL round bottom flask, 100 mL of freshly distilled toluene was taken. Then 3 mL of 0.466 M sec-BuLi (1.432 mmol) was added, which was followed by the addition of 3 mL (26.2 mmol) of freshly distilled styrene. A deep red color indicative of the living species was obtained. This was kept for stirring at room temperature for 4 h.

7.4.1.3 Grafting

In a single neck 250 mL round bottom flask, 0.1 g (**31**) (0.358 mmol of epoxy groups) of the copolymer was taken. To this 25 mL of freshly distilled toluene was added and then stirred for 30 min. The toluene was removed by azeotropic distillation to remove all traces of methanol/moisture in the copolymer. 20 mL of toluene was again added and then stirred for 30 min to ensure complete dissolution of the copolymer. Into this solution, living polystyryl lithium anion in toluene (90 mL, 1.288 mmol) was cannula transferred under vigorous stirring. The reaction was terminated after 2 h by the addition of 2 mL of degassed methanol. The polymers present in the reaction mixture were precipitated by the addition of excess methanol. The mixture of polymers, thus obtained, was soxhlet extracted with acetone to remove the ungrafted polystyrene homopolymer. The acetone insoluble fraction is the graft copolymer (**37**). ^{1}H NMR

($CDCl_3$, ppm) 7.3 - 6.4 (5H, aromatic), 2.2 - 1.7 (1H, C_6H_5-CH-), 1.65 -1.2 (2H, C_6H_5-CH-CH_2) and 1.3(4H, -CH_2-CH_2-).

7.4.1.4 Analysis

The IR spectrum was recorded on a Perkin-Elmer 16 PC FT-IR spectrometer. ^1H NMR spectrum was recorded on a 200 MHz Bruker NMR spectrometer at room temperature. The molecular weight distribution was determined using a Waters Gel Permeation Chromatograph model GPC/ALC 150C instrument equipped with a refractive index detector with μ-styragel columns (10^6, 10^5, 10^4, 10^3 and 500°A) at 30°C and THF as solvent with 1 mL/min flow rate. Differential scanning calorimetric analysis was carried out on a Perkin Elmer DSC-7 instrument.

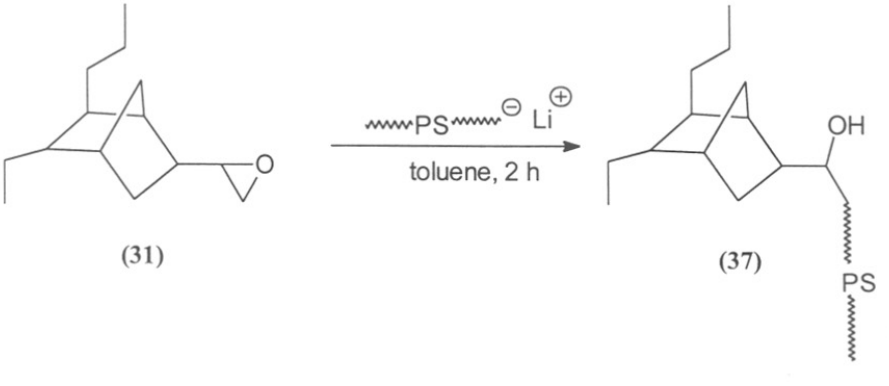
7.4.2 Results and discussion

7.4.2.1 Synthesis of polystyryl lithium

Polystyrene of Mn = 2000 was targeted, the Mn of polystyrene formed was found to be 2,400 with Mw/Mn = 1.4.

7.4.2.2 Grafting

The living anionic chain ends in polystyryl lithium were terminated by pendant epoxy functional groups available on polyethylene backbone (**Scheme 7.4**).



Scheme 7.4 Grafting of living polystyryl lithium anion onto epoxidized ethylene/5-vinyl-2-norbornene copolymer

Two hours after the addition of solution of polystyryl lithium into the solution of copolymer (**31**) in toluene, methanol was added to quench the reaction. The polymer precipitated by the addition of large excess of methanol was soxhlet extracted with

acetone to separate the polystyrene homopolymer present since polystyrene is soluble in acetone. The results are given below.

Wt. of copolymer (**31**) taken for grafting = 0.1 g (contains 2.03 mmol of ethylene and 0.358 mmol of VNB)

Amount of polymer obtained by precipitating in methanol = 2.80 g

Amount of acetone insoluble polymer = 0.56 g

Amount of styrene grafted = 0. 46 g (4.416 mmol)

Mol % of styrene in the graft copolymer (by wt. difference) = 63 %

Mn (polystyrene) = 2,400

Mol % of styrene in the graft copolymer (by ^{1}H NMR) = 58.7

The grafting efficiency was calculated as per the equation given below.[3]

Mole of epoxy groups reacted =

$$\frac{\text{(wt. of graft copolymer - wt. of polyethylene backbone)}}{\text{mol. wt. of polystyrene}}$$

$$\text{There fore, grafting efficiency} = \frac{\text{mol. of epoxy groups reacted}}{\text{total mol. of epoxy groups in the copolyme}}$$

The grafting efficiency as calculated by the above equation was found to be 54 %. In order to increase the grafting efficiency a reaction was carried out for 24 h. But 6 h after the addition of polystyryl lithium anion into the parent copolymer solution, the reaction mixture became hazy in appearance. The acetone insoluble part after the termination of the reaction, after 24 h of the reaction, was found to be only 0.2 g. This isolated product was found to be insoluble in chloroform and toluene even at high temperatures. The IR spectrum of the product showed the presence of styrene in it, in addition to the peaks of the parent copolymer (**31**). The insoluble material may be a crosslinked copolymer. The crosslinked material obtained in the experiment may be due to the attack of lithium alkoxide, formed by the reaction of polystyryl anion with epoxy group on another polymer, though literature reports do suggest that the initiation of epoxide polymerization by Li alkoxide is quite improbable. It may be

pertinent to note that the coupling reactions between epoxy group and styryl lithium reported in the literature are with ethylene oxide monomer and not with epoxy group attached to a polymer. The presence of another epoxy group in the near vicinity of the lithium alkoxide formed, due to higher mol % of epoxy group (15 mol %) in the polymer may the reason for this attack of lithium alkoxide. This problem can be avoided by using a polymer having relatively lower mol % of epoxy groups.

7.4.2.3 Characterization of the graft copolymer

7.4.2.3.1 IR

The IR spectrum of the graft copolymer showed peaks at 1600, 1492, 756 and 698 cm^{-1} due to the polystyrene (**Figure 7.6**) in addition to the peaks of the parent epoxy copolymer.

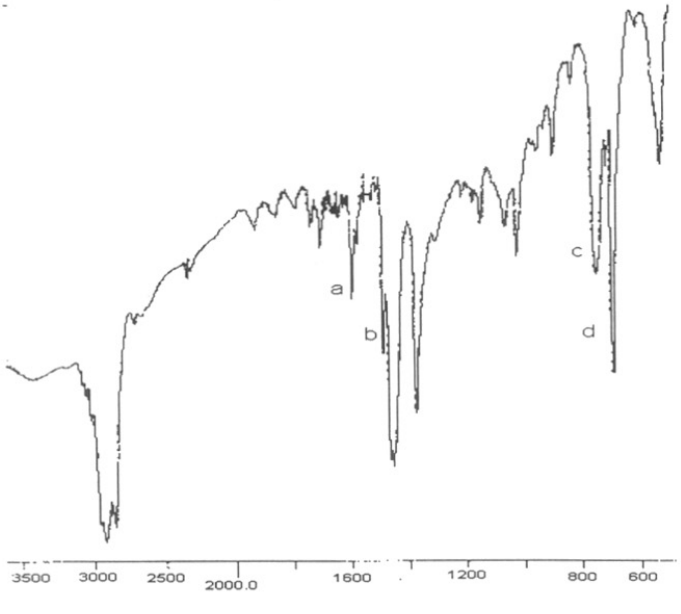


Figure 7.6 IR spectrum of polyethylene-graft-polystyrene (37)

Peaks: (a) 1600 cm^{-1}aromatic C=C groups (b) 1492 cm^{-1} aromatic C=C group (c) 756 cm^{-1} and (d) 698 cm^{-1} aromatic C-H group

7.4.2.3.2 NMR

The NMR spectrum of the graft copolymer is shown in **Figure 7.7**. The peaks in the range of 7.2 to 6.3 ppm are due to the aromatic ring protons of the polystyrene. The peaks at 1.55 ppm and 2 ppm are due to $-CH_2-$ and -CH- protons of polystyrene. Singlet at 1.3 ppm originating form the $-CH_2-CH_2-$ polyethylene part is also clearly visible.

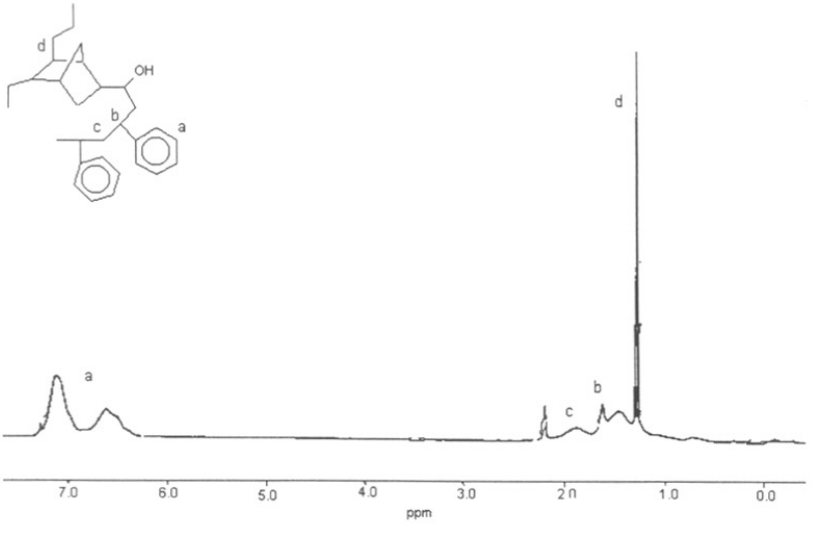


Figure 7.7 ^{1}H NMR of polyethylene-g-polystyrene copolymer (37)

The mol % styrene in the graft copolymer is calculated as shown below.

Area of the aromatic peaks in the range 7.2 to 6.3 ppm = X

Area corresponding to 1H of styrene = X/5 = Y

Area due to 4H of ethylene and 2H of styrene in the range 1.6 to 1.2 ppm = A

Area due to 1H of ethylene = (A - 2Y)/4 = B

$$\text{Mol \% styrene in the graft copolymer} = \frac{Y}{(Y+B)} \times 100$$

Mol % of styrene thus calculated = 58.7 %

7.4.2.4 Copolymer properties

7.4.2.4.1 Solubility

Though the parent epoxy copolymer was not soluble in chloroform, the graft copolymer was found to be soluble in chloroform. The graft copolymer was also soluble in toluene and benzene.

7.4.2.4.2 Thermal properties

DSC thermogram of the graft copolymer showed a Tg at 94°C (**Figure 7.8**). No Tm was observed for the graft copolymer. It may be noted that the parent copolymer (**30**) also showed no Tm (**Chapter 6**).

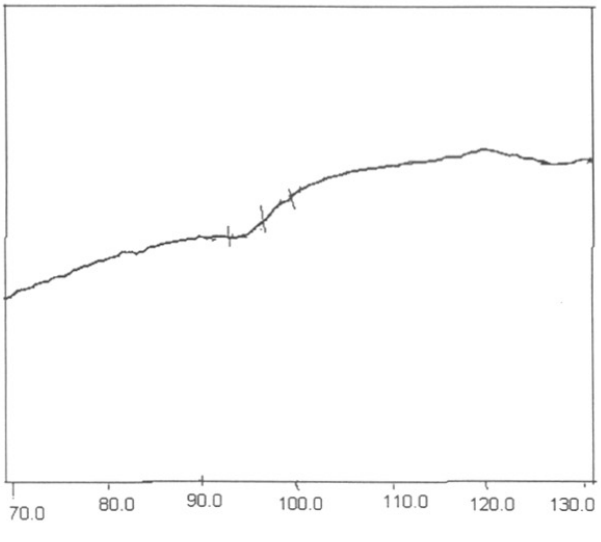


Figure 7.8 DSC thermogram of polyethylene-g-polystyrene copolymer (37)

7.5 Conclusions

Synthesis of well defined polyethylene-g-polystyrene as well as polyethylene-g-polyethylene glycol by using 'graft onto' approach were attempted. How ever the grafting reactions were met with only limited success.

Higher grafting efficiency in polyethylene-g-polystyrene copolymer synthesis could not be achieved due to crosslinking reactions. It is reported in the literature that epoxy polymerization occurs through enhanced polymerization wherein the alkoxide formed

is co-ordinated with another epoxy group and then undergoing polymerization. Such polymerizations can be reduced by complexing the alkoxide by chelating ligands like crown ether etc.[6] Use of such crown ethers or cryptands during grafting may be beneficial. Since there is a competitive reaction between polystyryl lithium anion and lithium alkoxide use of a much more reactive anion like polyisoprenyl lithium can also be tried. Use of an aldehyde group rather than an epoxy group, as the terminating agent, might also be a much better option. Epoxy group can be converted into aldehyde group by refluxing in benzene in presence of LiBr.HMPA adduct.[13]

No conclusive evidence of grafting of polyethylene glycol onto epoxy functionalized ethylene/5-vinyl-2-norbornene copolymer was obtained. The most important factor here was the selection of a suitable catalyst for the ring opening of epoxy group by an amine. The lack of solubility of the parent epoxy polymer in most of the solvents used for such ring opening reactions restricted the usage of the some of most efficient catalysts. This problem can, probably, be overcome by converting the double bond to hydroxyl group and reacting, it with isocyanate or carboxylic acid end functionalized polyethylene glycol.

7.6 References

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Chapter 8. Summary and Conclusions

Metallocene catalysts have some unique characteristics which enable the synthesis of functional polyolefins. In this thesis, the application of metallocene catalysts for the synthesis of functional polyolefins is presented. Two methods, namely, copolymerization with dienes, where one of the double bonds undergoes enchainment, leaving the other double bond as a pendant group, capable of being functionalized and direct copolymerization with functional monomers were explored.

Copolymerization of olefin with symmetrical dienes usually result in met with unwanted side reactions like crosslinking and cyclopolymerization, especially, when the objective is to retain a pendant double bond on the polyolefin backbone. However, the copolymerization of ethylene with a symmetrical diene, namely, 2,5-norbornadiene, possessing two extremely equi-reactive endocyclic double bonds, was found to occur through only one of the double bonds. The very fact that the extreme reactivity of the endocyclic double bond in cyclic olefins like norbornene, 5-vinyl-2-norbornene and ethylidene norbornene are utilized for their efficient copolymerizations with olefins using metallocene catalyst systems signifies the importance of the above observation. Inspite of the extreme reactivity of the pendant double bond, the fact that it does not participate in chain growth shows the efficacy of the metallocene catalysts to distinguish between a double bond on a monomer and on a propagating chain. A detailed study of the copolymerization using a number of metallocenes revealed that the selectivity depends on the structure of the metallocene. Enchainment occurred only through one of the endocyclic double bonds with Cp_2ZrCl_2, $(n\text{-}buCp)_2ZrCl_2$ and $Et(ind)_2ZrCl_2$ catalysts while both the double bonds underwent enchainment with $Me_2SiCp_2ZrCl_2$.

The endocyclic pendant double bonds on the polymer backbone could be converted into dicarboxylic acid under mild conditions. This is the first example of a post polymerization functionalization of a pendant double bond in a polyolefin to carboxylic acid group. 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. A novel method for the two phase oxidation of polyolefin bearing unsaturation has been identified. Such oxidized polyolefins are likely to possess interesting applications as

adhesion promoters, tie layers in multilayer barrier packaging and emulsifiable polyethylene waxes for coating applications

A relatively facile route to the synthesis of hydroxyl functional polyolefin by copolymerization with trimethylaluminum prereacted with 5-norbornene-2-methanol was identified. The removal of the active hydrogen and reduction of the electron donating nature of the oxygen by prereaction and the high reactivity of the strained endocyclic double bond facilitated the copolymerization. With a judicious selection of the metallocene as well as Al/Zr ratio, a copolymer having as high as 6.2 mole % of alcohol could be synthesized. Such a high amount of incorporation of alcohol in copolymerization is unprecedented in the literature.

Polyolefin having pendant vinyl double bonds in the polymer chain was synthesized by the copolymerization of ethylene with 5-vinyl-2-norbornene using $Me_2SiCp_2ZrCl_2$ catalyst. The reactivity ratio values indicated that the copolymers are more random in nature compared to the copolymer synthesized with Cp_2ZrCl_2.

The pendant vinyl double bonds in the ethylene/5-vinyl-2-norbornene copolymer were epoxidized using m-chloroperbenzoic acid and were used for the synthesis of novel, well defined graft copolymers. Synthesis of polyethylene-g-polystyrene copolymers by 'graft onto' method using epoxy functionalized ethylene/5-vinyl-2-norbornene copolymer as terminating agent for living polystyryl lithium anion was met with partial success. A grafting efficiency of only 54 % could be achieved. Attempts made to increase the grafting efficiency resulted in crosslinked copolymers. Attempts to graft polyethylene glycol having NH_2 end group onto epoxy functionalized copolymer was unsuccessful. It seems that a much more judicious selection of the coupling agents is needed.

In conclusion, the work presented in this thesis illustrates the versatility of metallocene catalysts in olefin polymerization. The ability to distinguish between a double bond in a polymer chain and in the monomer, ability to synthesize functionalized polyolefins and copolymers having pendant double bonds of varying reactivities are some of the important observations made during the course of the study. Copolymers having pendant double bonds provided wide scope for the synthesis of functional polyolefins like polyolefin having carboxylic acid functional group and novel graft copolymers.

Scope for future work

The dicarboxylic acid functionalized polyethylene offer further scope for work The dicarboxylic acid can further be converted into anhydride. Since such an anhydride functionalized polymer is akin to a maleic anhydride grafted polyethylene, all the graft copolymerizations which can be carried out on a maleic anhydride grafted polyethylene can be done with the former also. The well defined grafting sites are an added advantage compared to maleic anhydride grafted copolymer prepared in melt. Also, synthesis of ionomers can be attempted and the properties can be studied.

The facile incorporation of hydroxyl functional comonomer when prereacted with trialkylaluminum indicates that if the functional group is efficiently protected, thereby considerably reducing the electron donating nature of oxygen, even homopolymerization may be feasible. Incorporation of the functional monomer into methylaluminoxane, while synthesizing it by partial hydrolysis of trimethylaluminum, can be attempted.

The introduction of pendant double bonds on polyethylene provide opportunity for their further conversion into a range of functional groups enabling the synthesis of a wide variety of graft copolymers.

Synopsis

The thesis entitled 'Synthesis of ethylene-bicyclic olefin copolymers using metallocene/MAO catalyst system and its functionalization' consists of seven chapters and chapter 8 summarizes the work reported in the thesis.

Introduction

Functional polyolefins have assumed importance because of their enhanced properties such as adhesion and coatability. More over, the functional groups on the polyolefin backbone can be used for the synthesis of graft copolymers, which finds application as compatiblizers and interfacial agents.[1]

There are three different routes for the synthesis of functional polyolefins.[2] One is the direct copolymerization of olefin with functional monomer. However, functional groups, especially, if polar, adversely affect the catalytic activity. Second method is the post polymerization grafting of functional groups on to the polyolefin backbone using either thermal or ionization energy. Non uniform distribution of the functional groups on the polymer, with functional group predominantly located in the amorphous region, degradation of the polyolefin backbone and crosslinking are some of the drawbacks of this method. The third, and the most preferred method, is the copolymerization with a precursor monomer which do not interfere in the polymerization but can later be converted into desired functional groups by standard organic chemical reactions.

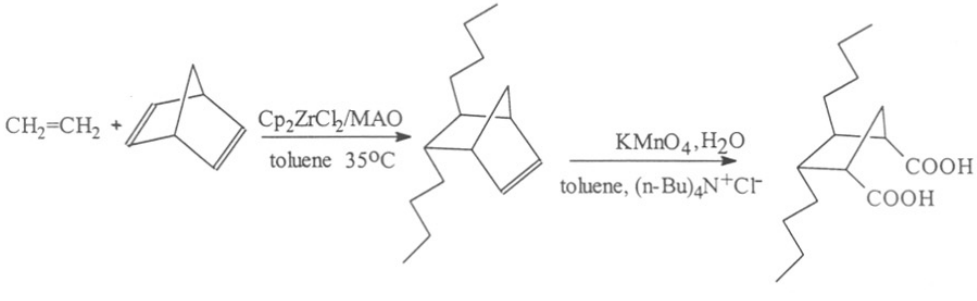
The homogeneous metallocene based catalysts, have some unique characteristics which enable the synthesis of functional polyolefins. The high catalytic activity, uniform and random distribution of comonomers, narrow molecular weight distribution, ability to polymerize a wide range of monomers and a wide variety of stereospecific polymers ranging from isotactic to syndiotactic are some of the salient features of metallocene catalyst.[3] The metallocene catalysts are unique in the sense that they promote the polymerization of bicyclic olefins such as, norbornene, resulting in copolymers with high glass transition temperatures.[4] This feature has been taken advantage for introducing pendant double bonds on polymer by copolymerizing an

olefin with a diene, such as, 5-vinyl-2-norbonene(VNB)[5] and ethylidene norbornene.[6] Recently, direct copolymerization of olefins with functional monomers like 10-undecen-1-ol,[7] 11-chloroundec-1-ene,[8] and 6-tert-butyl-2-(1,1-dimethylhept-6-enyl)-4-methylphenol[9] have also been reported using metallocene/MAO catalyst system.

Objective of the present work

The objective of the present work was to explore the capabilities of metallocene based catalysts for the synthesis of functional polyolefins. Two methods, namely, direct copolymerization with functional monomer and copolymerization with precursors which can later be converted into functional groups were explored to achieve this goal.

(1)One of the objectives of the work was to introduce pendant double bond in the copolymer. A symmetrical diene, 2,5-norbornadiene, was chosen as the comonomer. The extreme rigidity of this bicyclic diene may prevent cyclopolymerization and crosslinking, which are usually observed during the copolymerization with symmetrical dienes.[10,11] The endocyclic pendant double bonds thus obtained can be converted into diacid, acid salt and anhydride by simple organic chemical reactions. The anhydride-functionalized polyethylene is similar to an ethylene-g-maleic anhydride copolymer. All the grafting reactions that can be carried out on an ethylene-g-maleic anhydride copolymer can be carried out here also, with the added advantage of well-defined grafting site.



(2)Another objective of the work was to incorporate functional groups on to polyethylene backbone by direct copolymerization with functional monomer. A multi-pronged strategy was evolved for achieving this objective. The separation of the functional group from the double bond, the extreme reactivity of the endocyclic

double bond and protection of the functional group by aluminum alkyl forced the selection of aluminum alkyl protected 5-norbornene-2-methanol as the functional monomer.

(3)Copolymerization of ethylene with VNB using dicyclopentadienylzirconium dichloride catalyst occurs regioselectively through the endocyclic double bond leaving the exocyclic one as a pendant group that can later be functionalized.[5] The ethylene-co-VNB copolymer so synthesized is blocky in nature as evidenced by the $r_1.r_2$ value of 5.5.[5] The silicon bridged metallocene, dimethylsilyldicyclopentadienylzirconium dichloride ($Me_2SiCp_2ZrCl_2$) facilitates higher incorporation of norbornene type bicyclic olefins.[12] A study of copolymerization of ethylene with VNB using this silicon bridged metallocene was another objective of the work.

(4)Synthesis of polyethylene-g-polystyrene by grafting living polystyryl lithium anion onto epoxy functionalized ethylene-co-VNB copolymer synthesized using $Me_2SiCp_2ZrCl_2$/MAO catalyst system have been examined. With an objective of making amphiphilic copolymers, grafting of amine terminated polyethylene glycol onto epoxidized ethylene-co-VNB copolymer was also attempted. Such amphiphilic copolymers having hydrophobic backbone and hydrophilic side chains may exhibit interesting solution properties and have a wide range of applications.

Chapter 1. ***Copolymerization of ethylene with bicyclic olefins, dienes and functional monomers using metallocene catalyst***

A general literature survey, inclusive of patents, on copolymerization of ethylene with bicyclic olefins, dienes and functional monomers using metallocene catalyst have been described in this chapter.

Chapter 2. ***Objective in undertaking the present work***

This chapter covers the scope and objective in undertaking the present work.

Chapter 3. ***Copolymerization of ethylene with 2,5-norbornadiene using various metallocene catalysts***

Results of copolymerization of ethylene with 2,5-norbornadiene with four different metallocene catalysts, namely, dicyclopentadienylzirconium dichloride, di (n-butylcyclopentadienyl)zirconium dichloride, ethylenebis(indenyl)zirconium

dichloride, and dimethylsilyldicyclopentadienylzirconium dichloride are described in this chapter. Effect of temperature, Al/Zr ratio, and comonomer concentration in feed on copolymerization activity, molecular weight and mole % incorporation of NBD are reported in this chapter.

Chapter 4. ***Post polymerization functionalization of ethylene-co-2,5-norbornadiene copolymer***

This chapter covers the post polymerization functionalization of the pendant endocyclic double bonds in the ethylene-co-NBD copolymer to diacid, acid salt and anhydride.

Chapter 5. ***Copolymerization of ethylene with aluminum alkyl protected 5-norbornene-2-methanol***

Results of copolymerization of ethylene with aluminum alkyl protected 5-norbornene-2-methanol are included in this chapter. The effect of various protecting groups, metallocene catalyst type, Al/Zr ratio, temperature and feed ratio on copolymerization activity, molecular weight, and copolymer composition are described in this chapter.

Chapter 6. ***Copolymerization of ethylene with 5-vinyl-2-norbonene using dimethylsilyldicyclopentadienylzirconium dichloride/MAO catalyst system***

The results of copolymerization of ethylene with 5-vinyl-2-norbonene using dimethylsilyldicyclopentadienylzirconium dichloride are described in this chapter. The reactivity ratios calculated according to Kelen-Tudo's method are also included.

Chapter 7. ***Post polymerization functionalization of ethylene-co-5-vinyl-2-norbornene copolymer***

Results of the grafting of living polystyryl lithium anion and polyethylene glycol having amino end group are reported in this chapter. The characterization of the graft copolymers using various spectroscopic techniques is also reported.

Chapter 8. ***Summary and conclusions***

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

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