HOMO- AND COPOLYMERIZATION OF BICYCLIC OLEFINS USING ZIEGLER-NATTA CATALYSTS

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

DOCTOR OF PHILOSOPHY
(IN CHEMISTRY)

BY

SUJATA MARATHE

DIVISION OF POLYMER CHEMISTRY
NATIONAL CHEMICAL LABORATORY
PUNE 411 008

OCTOBER 1994

DECLARATION

Certified that the work incorporated in thesis "**Homo- and copolymerization of bicyclic olefins using Ziegler-Natta catalysts**" submitted by Ms. Sujata Marathe was carried out by the candidate under my supervision, such material as has been obtained from other sources has been duly acknowledged.

S. Sivaram
(S. Sivaram)
Research guide

DEDICATED TO MY PARENTS

ACKNOWLEDGEMENTS

I wish to place on record my deep sense of gratitude, to Dr. S. Sivaram, Head, Polymer Chemistry Division, for his guidance, encouragement, constructive criticism and for providing ample facilities during all stages of my work. Being an outstanding scientist with a kind and understanding nature, he made this training period a comfortable, inspiring and enlightening experience.

I am grateful to Dr.T.P. Mohandas and Dr. S. Chakrapani for their valuable suggestions, useful discussions and help during various stages of the work.

I wish to thank all my friends especially, Varsha, Yamini, Mala, Deepa, Sunita, Iyer, Satya, Baskaran, Binod, Tushar, Mani, Nikhil, Arnab, Reddy, Soumen, Radhakrishnan, Sunita, Anjali, Soumya and Shruti who contributed in their own ways towards the successful completion of this thesis.

The efficient services rendered by Ms. S. Thombre, Dr.(Ms.) S.B. Idage, Ms. D. Dhoble and Mr. S.K. Menon of the analytical group are gratefully acknowledged.

I take this opportunity to extend my thanks to all the members of the Polymer Chemistry Division for their cooperation throughout my tenure.

I am indebted to my in-laws, my husband Vinayak and my daughter Monica for the love, patience, support and freedom they gave me, which contributed immensely towards the successful completion of this thesis.

Thanks are due to Mr. Anil Daithankar and Mr. P.D. Siddeshwar for the typing and Mr. Bhujang for the drawings.

Finally, I would like to thank the Director, N.C.L. for permission to submit this work in the form of a thesis and the Council of Scientific and Industrial Research for financial assistance.

Pune

7 *Oct., 1994*

Sujata Marathe

(Sujata Marathe)

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SYNOPSIS

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ABSTRACT

The main objective of the thesis is to study the homo- and copolymerization of selected bicyclic olefins using Ziegler-Natta catalysts. The bicyclic olefins used in the study are, (1) 2-allylnorbornane which is an α-olefin bearing a bicyclic ring on the carbon α to the double bond, and (2) 5-vinyl-2-norbornene which is an α,ω-diene consisting of one endocyclic and one exocyclic double bond.

The first part of the work deals with the homopolymerization of 2-allylnorbornane using conventional Ziegler-Natta, and homogeneous metallocene catalysts. The use of the conventional Ziegler-Natta catalysts gave rise to a solid polymer, namely poly(2-allylnorbornane). This was fractionated into a fraction soluble in xylene at 130^0C and another insoluble in xylene at 130^0C. The xylene insoluble fraction had a Tm of 355^0C. The insoluble nature and high melting temperature of the polymer are attributed to the presence of the bicyclic group. The homogeneous metallocene/MAO catalyst system gave only oligomers presumably due to increased β-hydrogen elimination reactions.

Copolymerization of ethylene with 2-allylnorbornane was studied using $TiCl_4$/(iso-Bu)$_3$Al, a conventional Ziegler-Natta catalyst, and Cp_2ZrCl_2/MAO, a homogeneous metallocene catalyst. The copolymers were characterized by IR, NMR, TGA, DSC, GPC and solution viscosity. Based on these analyses and the value of reactivity ratios, it was concluded that the copolymers obtained using $TiCl_4$/(iso-Bu)$_3$ catalyst are heterogeneous with a blocky distribution of comonomers, whereas, those obtained using Cp_2ZrCl_2/MAO catalyst are homogeneous with a random distribution of comonomer units. The thermal properties of both these sets of copolymers were compared with ethylene 4-methyl-1-pentene copolymers (their acyclic analogue), synthesized under identical conditions, in order to study the specific effect of the bicyclic pendant . It was found that at similar mol% incorporation of comonomers (2-allylnorbornane or 4-methyl-1-pentene), the decrease in melting point and crystallinity of the copolymer were the same. This is attributed to the fact that, contrary to expectations, the space filling characteristics of the two pendant groups (norbornyl or isopropyl) is not significantly different.

Copolymerization of ethylene with 5-vinyl-2-norbornene was studied using Cp_2ZrCl_2/MAO catalyst. A regioselective insertion of the endocyclic double bond of the comonomer into the growing polymer chain was observed leaving the vinyl bond as a pendant.

The poly(ethylene-co-5-vinyl-2-norbornene) containing pendant vinyl group was functionalized to epoxy and hydroxy group containing polymer using standard organic transformations. Further the epoxy group containing polymer was used in a "grafting onto" coupling reaction with living poly(styryllithium) resulting in poly(ethylene-co-5-vinyl-2-norbornene)-graft-polystyrene.

GLOSSARY

2-ANB	2-Allylnorbornane
Cp	Cyclopentadienyl
Cp*	Pentamethyl cyclopentadienyl
DEAC	Diethylaluminumchloride
DSC	Differential Scanning Calorimetry
En	Ethylene
E2ANB	Ethylene-2-allylnorbornane copolymer
E4MP	Ethylene-4-methyl-1-pentene copolymer
ENB	Ethylene-Norbornene Copolymer
E5V2N	Ethylene-5-vinyl-2-norbornene copolymer
Flu	Fluorenyl
Ind	Indenyl
IndH$_4$	Tetrahydroindenyl
K_p	Rate constant for propogation
K_t	Rate constant for termination
MAO	Methylaluminoxane
4MIP	4-Methyl-1-pentene
P2ANB	Poly(2-allylnorbornane)
P4MIP	Poly(4-methyl-1-pentene)
PE	Polyethylene
R_p	Rate of polymerization (M sec^{-1})
TIBAL	Triisobutylaluminum
TGA	Thermogravimetric analysis
5V2N	5-Vinyl-2-norbornene

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CHAPTER I

HOMO- AND COPOLYMERIZATION OF HIGHER OLEFINS USING ZIEGLER-NATTA CATALYSTS

1.1 INTRODUCTION

1.1.1 History

The origin of the sophisticated catalysts used in todays polyolefin plants can be found in the early 1950's when Karl Ziegler was investigating his new triethylaluminum catalyzed synthesis of higher olefins[1]. While studying this oligomerization reaction, known as the 'Aufbau reactions', he serendipitiously discovered that due to a colloidal nickel contaminant, instead of the usual oligomeric wax, the product he obtained was almost exclusively 1-butene, Ni having catalyzed the β-hydrogen elimination. In search of other displacement catalysts, Ziegler and coworkers, then tested triethylaluminum in combination with a wide variety of transition metal compounds. The actual breakthrough was made when zirconium acetylacetonate was found to catalyze the formation of high molecular weight polyethylene at low pressure, the transition metal in this case having catalyzed the propagating step. Out of the other transition metals studied those based on titanium halides and aluminum alkyls were subsequently developed for the manufacture of high density polyethylene (HDPE).

The full scope of Ziegler's discovery was realized by Giulio Natta's group in Italy. Natta's group elected to study the Ziegler catalysts performance with other olefins. In March 1954 they first succeeded in isolating crystalline polypropylene after solvent extraction of the product obtained using a $TiCl_4 + AlEt_3$ catalyst. X-ray diffraction studies carried out by the group revealed the white powder to be highly crystalline explaining its unexpected high rigidity and melting point. Natta determined that crystalline polypropylene (which he designated 'isotactic') comprises of extended sequences of monomer units with the same configuration. The amorphous analogs were termed 'atactic'. Natta also first recognized the importance of the catalyst structure and particularly the crystalline surface in determining the polymer isotacticity and found that when certain solid titanium chlorides, like $TiCl_3$ were used instead of $TiCl_4$, highly isotactic polypropylene was produced.

Ziegler's discovery, together with the ensuing work by Natta, gave rise to the development of new classes of both catalysts and polymers. The polyethylene produced was highly linear and in the case of polypropylene highly linear and stereoregular polymer could be obtained. In recognition of their contribution to chemistry Ziegler and Natta were awarded the Nobel Prize in 1963.

The commercial importance of the Ziegler-Natta catalyst system stimulated enormous amount of research in scientific and industrial laboratories. Since the efficiency and selectivity of the early catalysts was not very good, there was a clear incentive for the development of improved catalysts. Research directed along these lines resulted in the development of improved polymerization catalysts. These can be conveniently categorized as heterogeneous and homogeneous catalysts.

1.1.2 Catalysts

1.1.2.1 Heterogeneous Ziegler-Natta catalysts

Non supported catalysts

Here use was made of electron donors to improve stereoselectivity, and ball milling of the $TiCl_3$ x $AlCl_3$ catalyst was done in order to achieve higher productivity. The ball-milling step resulted in a higher surface area and in the reduction of the size of primary crystallities. Low to moderate activity was achieved with these catalysts.

Supported Ziegler-Natta Catalysts

In 1959 Natta and coworkers[2] demonstrated that only a small percentage of the titanium atoms (<1%) in the non supported catalysts were active. Hence, efforts came to be directed toward the development of transition metal catalysts supported on appropriate supports.

The most promising catalysts resulted from the use of anhydrous magnesium chloride as a support. The reason for this unique behavior is believed to be associated with similarities between the ionic radii of Ti^{+4} and Mg^{+2}, which are 0.68 and 0.65°A respectively. During catalyst preparation anhydrous $MgCl_2$ is ball milled with an internal donor like ethyl benzoate (EB). Ethyl benzoate prevents the reaggregation of freshly cleaved surfaces. The introduction of structural faults, increase in surface area and porosity are believed to result in the high activity of ball milled $MgCl_2$. This ball milled $MgCl_2$ is further treated with $TiCl_4$. During treatment $TiCl_4$ replaces EB not only from weakly bonded sites on the lateral faces but also from the more strongly coordinating corner sites. Activation of this procatalyst is achieved by alkylaluminum compounds. External donor like benzoates, toluates, anisates are further added to improve stereospecificity. The role the external donor is attributed to (1) complex formation with aluminum alkyl leading to a reduction in its capacity to reduce the titanium entity (2) deactivation of aspecific centers by selective complex formation or even conversion of aspecific centers to isospecific centers.

A typical catalyst consisting of $MgCl_2/EB/TiCl_4$ - $AlEt_3$ gives activities in the range of 500-1000 kg PP/g Ti . A new class of super high activity catalysts (SHAC) were also developed by Shell which have activities upto 2000 kg PP/g Ti together with high stereospecificities (95% isotactic). In addition the usual inverse relationship between isotactic index and polymer yield is virtually absent.

1.1.2.2 Homogeneous Ziegler-Natta catalysts

Homogeneous catalysts based on vanadium like VCl_4-$AlEt_3$, $V(acac)_2$ - $AlEt_2Cl$ have been used, since under the appropriate conditions they can be used to prepare syndiotactic polypropylene. Here polymerization temperatures of -78°C and Al/V ratios between 3-10:1 are required.

Homogeneous catalysts based on metallocenes were first identified by Breslow and Newburg.[3] They showed that biscyclopentadienyltitanium dichloride Cp_2TiCl_2, activated by aluminum alkyls could polymerize ethylene but with a relatively low activity viz. 50-200 g PE/mmol Ti. h. atm. However addition of small amounts of water was found to lead to increased activities. One of the most fascinating developments in the field of transition metal catalyzed polymerization, during recent years, has been the discovery by Kaminsky and Sinn[4] that homogeneous catalysts such as Cp_2ZrMe_2 or Cp_2ZrCl_2 in toluene solution when activated with the methylaluminum treated with one equivalent of water can polymerize ethylene with activities in excess of 25×10^6 g PE/g Zr. In the course of their studies they found that an oligomeric aluminoxane was formed by the reaction of TMA and water, which was responsible for the high polymerization activities.

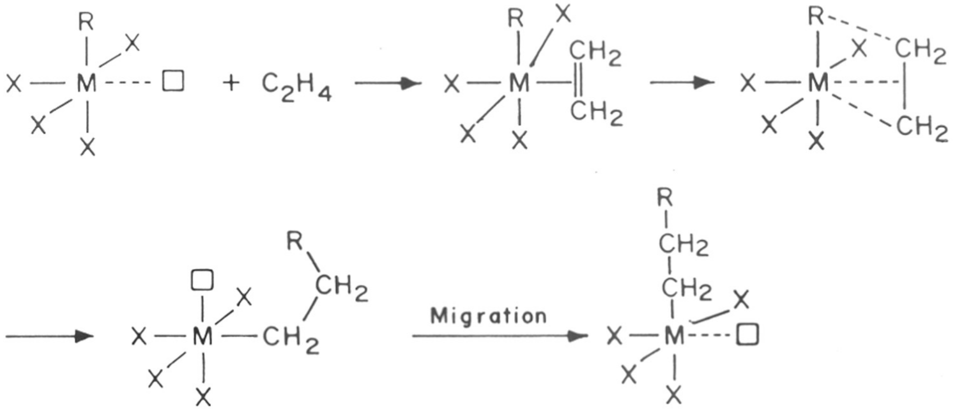
Recently, the racemic ethylene bis (indenyl) zirconium dichloride [En $(Ind)_2ZrCl_2$] or ethylene bis (tetrahydroindenyl) zirconium dichloride [$En(IndH_4)_2ZrCl_2$] have been shown to polymerize propylene to highly isotactic polypropylene[5]. Further exchanging the ethylene bridge between the indenyl rings by a disubstituted silyl group gave even higher activities, molecular weights and long isotactic sequences. Ewen[7] developed the fluorenylcyclopentadienyl based catalyst system [$Me_2C(fluo)(Cp)$]$ZrCl_2$ catalyst which produces syndiotactic polypropylene with relatively lower activities. This proved that even in a homogeneous system, if stable chiral transition metal compounds are used, polyolefins with desired tacticity may be produced.

1.1.3 Mechanisms of polymerization

Due to the complexities of the Ziegler-Natta catalyst system, no definitive, unequivocal polymerization mechanism has yet been devised to fully describe their behavior. For instance, the catalyst may react as a solid or be soluble in the reaction medium; activation by an organometallic compound is usually required but not always so; the monomers may be homo or copolymerized, may be gases or liquids, electron donors may be added and the whole process may be performed under slurry, solution or gas phase conditions. In the case of heterogeneous catalysts since the actual number of propagating species on the solid catalyst are small, direct spectroscopic evidence has been of limited value.

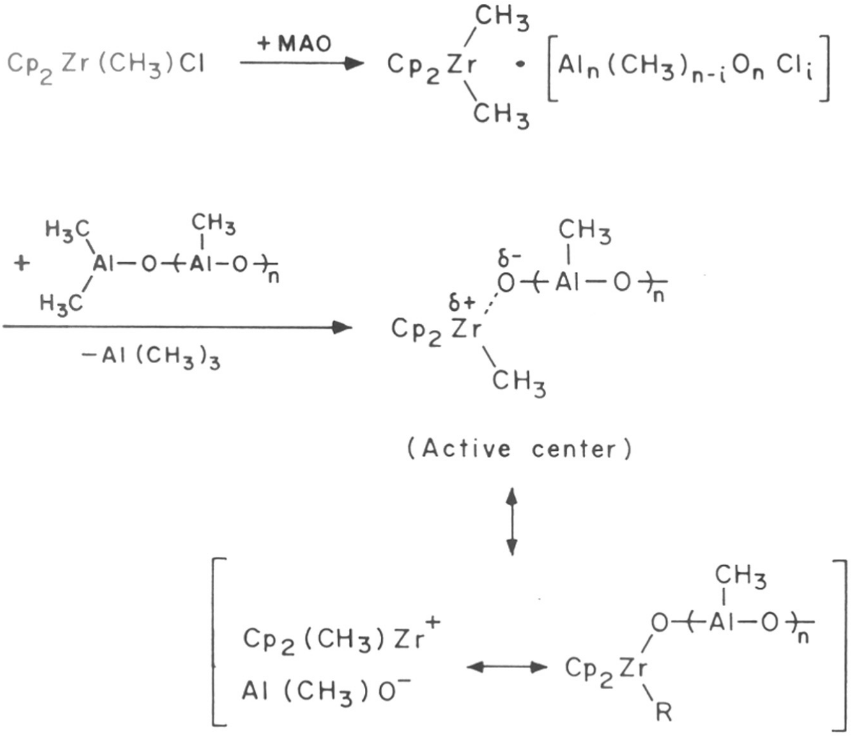
For heterogeneous catalysts, the most widely accepted mechanism is that devised by Cossee and Arlman,[8] with different representations of active centers depending on the support (Scheme1.1)

SCHEME 1·1



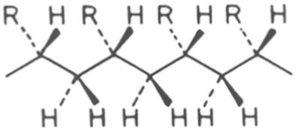
For the homogeneous catalysts also a monometallic active center is proposed. However the active center is thought to be 'cation like' eg. Cp_2M^+R. The mechanism proposed by Kaminsky[9] is shown in Scheme 1.2

SCHEME 1·2

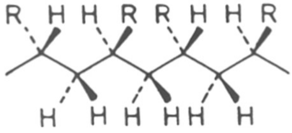


1.1.4 Stereospecificity of polymerization

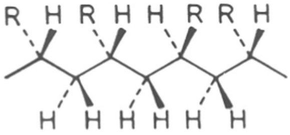
Stereoregularity arises because of order in the spatial structures of polymer chains. This order is determined by the catalyst used and polymerization conditions. Depending on the relative arrangement of the substituent R groups, the polymer may be classified as - isotactic, syndiotactic and atactic.



ISOTACTIC



SYNDIOTACTIC



ATACTIC

Stereospecificity arises due to the ability of the catalyst to discriminate between the two faces of the prochiral monomer. This requires at least one chiral species to participate in the polymerization mechanism. The steric control may be dictated by the configuration of the asymmetric tertiary carbon of the last inserted monomer unit (chain end control), or by the chirality of the organometallic complex of which the active site is a part (enantiomorphic site control). Bernoullian statistics are consistent with chain end stereo-control (here an occasional change in the configuration of the last inserted unit tends to be perpetuated) and non Bernoullian distribution is obtained with an enantiomorphic site control mechanism (here defects tend to be isolated).

In heterogeneous catalysts due to the asymmetric ligand environment, stereocontrol is attributed to enantiomorphic site control leading to isotactic polymers.

In homogeneous catalysts , based on the distribution of steric defects (analyzed by ^{13}C NMR), stereocontrol has been attributed in some cases to the chirality of the catalytic complex, eg. in rac-En(Ind)$_2$TiCl$_2$ to give an isotactic polymer) and in some cases to the chirality of the last inserted monomer unit in the growing chain, eg. in (Cp$_2$TiPh$_2$) at low temperatures.[10]

Syndiospecific polymerization has been achieved using (isopropylidene cyclopentadienyl-1-fluorenyl) zirconium dichloride.[7] Here site stereocontrol with chain migratory insertions resulting in site isomerizations are thought to operate.

1.2 HOMOPOLYMERIZATION OF HIGHER OLEFINS

1.2.1 Acyclic monoolefins

Polymerization of ethylene and propylene, due to its tremendous commercial significance has been widely studied as is evidenced by the enormous amount of publications and patents in the area. The higher olefins, have, however, not attracted much interest due to the low commercial significance of their polymers. Hence, literature in the area of higher olefin polymers is very meagre. However, a review of literature in this area is of interest, since one can attempt to correlate the characteristics of polymers with some basic structural properties. Representative patent literature on higher poly(olefin)s is shown in Table 1.1.

1.2.1.1 1-Butene

Out of the higher olefin polymers, poly (1-butene) is the most significant commercially, with a 30,000 tpa production capacity (1990). A couple of reviews[11,12] exist on poly(1-butene); hence in this section only the main aspects of polymerization and characterization will be discussed in brief. While many references exist in literature on the polymerization of 1-butene using the first and second generation TiCl$_3$ catalysts, only a few references using the high activity Mg-Ti catalysts exist although a large number of patents deal with these catalysts.

Table 1.1 Representative Patents on Homopolymers Of Higher Olefins

Monomer	CA No.& Company Name	Catalyst system	Polymerization conditions	Remarks
ACYCLIC MONOOLEFINS				
4-Methyl-1-pentene	Enichem Anic. EP 358,264 113 : 79201z	$MgCl_2$/2-ethylhexanol/ $Hf(OBu)_4$-Et_3Al_2-Cl_3	-	Activity : 0.12Kg/gHf $\overline{M}n$ = 7,40,000
4-Methyl-1-pentene	Mitsui Petrochem Inds. EP 328,348 112 : 78181k	Cp_2ZrCl_2/MAO	Press. = 1 atm Temp = 50°C M/Ti = 1,97,540	Liquid polymer $\overline{M}n$ = 1,300 $\overline{M}w/\overline{M}n$ = 2.2
4-Methyl-1-pentene	Mitsui Petrochem Inds. JP 01,20,209 111 : 58530z	Mg/Ti/Di-isobutylphthalate-Et_3Al, Me_3SiOMe	(Gas phase)	Activity : 242Kg/g Ti Isotactic index: 98.3%
1-Butene	Himont EP 387,609 114 : 62980a	(isoPr)(Cp)(flu)ZrCl-MAO	Temp = 0 °C Time = 18 h.	Syndiotactic poly(1-butene)
1-Hexene	Jpn. Synthetic Rubber JP 63,308,007 110 : 232298w	$MgCl_2$/$Ti(OBu)_4$ -Et_2AlCl	Temp = 40°C	Activity :0.63Kg/g Ti
1-Decene	Conoco Inc. US 4,945,142 113 : 153275v	$TiCl_3$/Bu_2O-isoBu_2AlCl	Temp = 0°C M/Ti = 400 Time = 24 h	[η] = 16.2 Friction loss reducer

Contd..

Monomer	CA No.& Company Name	Catalyst system	Polymerization conditions	Remarks
1-Octene	Conoco.Inc. US,4,433,123 101:24116x	$TiCl_3AA/n\text{-}Bu_3P/Et_2AlCl$	Temp. = 20°C Time = 30 min M/Ti = 375	[η] = 10.5dL/g drag reducing agent
1-Hexene	Mobil Oil US, 4,613,712 105:194332q	$TiCl_4/EtMgCl/silica$	Temp = 25-150°C	$\overline{M}n$ = 160,000 V I improver
CYCLIC/BICYCLIC MONOOLEFINS				
Vinylcyclohexane	US 4,226,965 94:16386g	$Et_2AlCl/(iso\text{-}PrO)_4Ti$ $(EtO)_3VO$	Time=4h Temp.=70°C	Act= 0.18Kg/g V [η]=2.41 dL/g
Cyclopentene	Mitsui Toatsu Chem. JP 03,139,506 115:208858m	$isoPr(Cp)(Flu)ZrCl_2/MAO$	Temp.=30°C Time = 6h	Act = 0.73Kg/g Zr $\overline{M}n$=4800 [η]=0.18dL/g PDI=6800/4800
CYCLIC/BICYCLIC DIOLEFINS				
Cyclopentene	Hoechst A.-G. DE 3,726,325 111:97941d	$En(Ind)_2ZrCl_2/MAO$	Temp.=30°C Time=90h	Act= 0.3Kg/g Zr Density=1.104
5-vinyl-2-norbornene	Diacel Chem.Inds. JP 02,180,910 113:192141t	Cp_2ZrCl_2/MAO	Temp.=80°C M/Zr=400 Time=24h	Act=0.2Kg/g Zr
Norbornadiene	Idemitsu Kosan JP 03,47,828 115:30157s	$CpTi(OMe)_3/MAO$	M/Ti=100 Al/Ti=200 Temp.=25°C	$\overline{M}w$=170,000

Conventional catalysts

Isotactic poly (1-butene) was first synthesized by Natta and co-workers in 1954.[13] In addition to the transition metal halide and organoaluminum compound, third component modifiers were used to achieve an improved isotacticity.[14] Isotacticity was found to increase in the series

$$AlEt_3 < AlEt_2Cl < AlEt_2Br < AlEt_2I$$

with activity showing the opposite trend[15].

The highly isospecific catalyst of Soga and Yanagihara, namely Solvay $TiCl_3$ with Cp_2TiMe_2 when used with 1-butene yielded a highly isotactic polymer (98.8% isotactic pentads from ^{13}C NMR).[16]

Kinetic studies have been made with $TiCl_3$-$Al(isoBu)_3$ and $TiCl_3$ - $AlEt_2Cl$ system.[17] Mason and Schaffhauser[18] studied the effect of hydrogen on the rate and molecular weight of polymer. They observed a doubling in rate due to presence of hydrogen. They attributed this to modification of the crystalline structure of $TiCl_3$ by hydrogen.

Supported Mg/Ti catalysts

Using the high activity catalysts activity could be increased from 1.5 kg polymer/g catalyst to 4 kg polymer/g catalyst.

Canova[19] compared the chain propagation constants and the number of active centers of high yield and conventional Ziegler-Natta catalysts. He found that there were as many as 30-40 times the number of active centers in the high yield system as compared to the conventional one.

Kashiwa et al[20] found that in the $TiCl_4/MgCl_2$ system as you increase the donor/Ti ratio isotacticity of the polymer could be increased. Using ethyl benzoate as the donor the poly(1-butene) analyzed by ^{13}C NMR for mmmm pentad fraction showed 70% isotacticity.

Homogeneous metallocene catalysts

There are very few reports on the polymerization of 1-butene using homogeneous metallocene catalysts. The chiral zirconocene [$En(IndH_4)_2ZrCl_2$] and methylaluminoxane were used by Kaminsky to give poly (1-butene) with high activity (2640 kg poly/mol Zr) and narrow molecular weight distribution.[21]

The other reference uses the bis(cyclopentadienyl)titanium diphenyl/methylaluminoxane-trimethylaluminum enriched with ^{13}C. They determined the stereochemical structure of the enriched end groups resulting from insertion of monomer into $M\text{-}^{13}CH_3$ bonds[22]. At -60°C a stereoregular poly (1-butene) was produced. The sequence distribution derived from NMR agrees with Bernoullian statistics (chain end control) with a probability of isotactic placement being 0.6. They argue that compared to polypropylene (0.88 isotactic), poly (1-butene) is less isotactic because the difference between the substituents on the chiral carbon (ethyl and polymer) is less than in the case of propylene (methyl and polymer).

Asanuma *et al*[23] used 1-methyl-1-ethylidene-(cyclopentadienyl-1'-fluorenyl) zirconium dichloride and MAO to synthesize poly(1-butene). It had an $\overline{M}_n$ of 20,000 and was found to be syndiotactic and crystalline based on XRD, DSC, and ^{13}C NMR.

Characterization

There have been no systematic studies reported on the relationship between catalyst composition and properties of the polymer achieved.

^1H NMR is not a useful tool for determining stereospecificity due to difficulty in interpretation of close and overlapping signals. ^{13}C NMR measurements on the homopolymer were carried out by a few workers[24,25,26,27].

Total pentad distribution was evaluated by Asakura et al[26]. They observed that atactic poly (1-butene) obtained by extraction in ethyl ether is not truly a random copolymer, and the residual polymer is not totally isotactic.

Icenogle and Klingensmith[27] studied three different poly(1-butene)s (a) a highly isotactic homopolymer prepared by using conventional titanium chloride/alkyl aluminum catalyst (b) moderately isotactic polymer prepared by a variation of the conventional catalyst and (c) a moderately isotactic homopolymer prepared by a high activity supported titanium chloride catalyst. Analysis of the three samples by ^{13}C NMR, GPC, DSC, XRD and stress strain measurements showed that the two materials prepared using the conventional catalyst are predominantly mixtures of atactic molecules with highly isotactic molecules, while the material prepared with the high activity catalyst contains a large proportion of molecules of intermediate tacticity. The polymer prepared with the conventional catalyst behaves like a plasticized thermoplastic, while the polymer of intermediate tacticity prepared with the supported catalyst shows more elastomeric properties. This is because the defects in stereoregularity are concentrated in specific molecules for polymers prepared with the conventional catalyst and are distributed more evenly between molecules for the polymer prepared by the supported catalysts.

Analysis of the crystalline structure of poly(1-butene) showed that five different crystalline structures are present of which two are important[11]. Poly(1-butene) crystallizes from the melt into the tetragonal crystalline form II which slowly transforms to the trigonal form I. During this transformation the lattice parameters change. This tendency to undergo crystalline transformation causes problems in melt processed articles. Linear alpha olefins and branched comonomers like 3-methyl-1-butene, 4-methyl-1-pentene in sufficient amounts (for example 7 wt % of 1-octene comonomer) can cause complete stabilization of form II. Similarly, sufficient amount of 1-pentene causes immediate crystallization of the melt into the stable crystal form-I.

1.2.1.2 4-Methyl-1-pentene

A review on the synthesis, structures and properties of poly(4-methyl-1-pentene) has appeared recently.[28] Due to the high optical transparency, high thermal stability and chemical resistance this polymer is fast gaining importance commercially. In this section information is mainly provided regarding the polymerization behavior of 4-methyl-1-pentene over the different types of catalyst systems.

Conventional catalysts

A variety of transition metal catalysts in conjunction with an aluminum alkyl polymerize 4-methyl-1-pentene to form head-to-tail isotactic polymers, with the Ti based catalysts being the most active and stereospecific.

Natta[29] first described the polymerization of 4-methyl-1-pentene using a process similar to that used for the low pressure polymerization of ethylene. Watt,[30] Campbell,[31] and Hewett and Weir[32] studied the polymerization and properties of 4-methyl-1-pentene using conventional $TiCl_4/AlR_3$ and δ $TiCl_3/AlEt_2Cl$ catalysts. Burfield, Tait and Mckenzie[33] in a series of papers investigated the kinetics of polymerization of 4-methyl-1-pentene over the catalyst system VCl_3/AlR_3, using a dilatometric technique. They proposed a kinetic scheme based on the fundamental concepts of monomer adsorption followed by its reaction with the active center. Expressions for rate, molecular weight, active center concentration were derived. A validity for the proposed kinetic scheme and the various expressions based on it was established from the agreement between predicted and experimental values. The initiation process for 4-methyl-1-pentene was found to be independent of the concentration of monomer, catalyst and cocatalyst but dependent upon the type of aluminum alkyl. The propagation rate was found to be first order in catalyst and also in monomer. Chain transfer appeared to be fastest with the triethyl and tri-isobutyl derivatives whereas with the n-hexyl compounds it was much slower.

Studies on the active site concentration showed that only 0.02 to 0.06% of the transition metals were active. With $AlEt_3$ the fraction of active sites was three times as large as with $(hexyl)_3Al$. The activation energy was found to be 13.7 kcal/mol which is typical of many catalytic reactions involving opening of a carbon carbon double bond.

A large promoting effect of hydrogen was observed by Pijpers and Roest[34]. Activity was found to increase upto an optimum value for hydrogen/monomer ratio and above this the activity decreases. The increase in initial activity was explained to be arising due to the less hindered monomer diffusion to the active site when hydrogen is present. Also the decay in catalytic activity slows down from a 1st order decay to a 2nd order decay. A bimolecular reduction of two neighboring Ti-H species was proposed to explain this effect.

Shteinbak *et al*[35] also studied the kinetics of 4-methyl-1-pentene polymerization using the catalyst systems δ $TiCl_3/AlEt_2Cl$. Values for rate constant of initiation K_i, active center concentration and activation energy were found. They found the active center concentration to be independent of temperature, hence increase in polymerization was attributed to the Arrhenius effect.

Toader *et al*[36] studied the effect of various Ziegler-Natta catalytic systems and reaction conditions on the stereoregularity of poly(4-methyl-1-pentene).

Supported Mg-Ti catalysts

Kashiwa and Yoshitake[37] studied short time polymerization of 4-methyl-1-pentene using the catalyst systems $MgCl_2/TiCl_4EB$ - Et_3Al. The concentration of active centers C^* and rate of polymerization k_p were determined for propylene, 1-butene, styrene as well as 4-methyl-1-pentene. It was found that C^* was almost constant for all monomers but k_p changes in the order propylene > 1-butene > 4-methyl-1-pentene > styrene.

Tait *et al*[38] studied the polymerization of 4-methyl-1-pentene using $MgCl_2$/electron donor/$TiCl_4$ systems, where, electron donor is ethylbenzoate (EB) or disobutylphthalate (DIP) along with the aluminum alkyls triethylaluminum, trisobutyl aluminum, tri-n-hexylaluminum and tri-n-dodecylaluminum. They observed that (a) when DIP is used as the electron donor, the number of active sites are low, 1.2 - 9.6 % of the titanium content, whereas, with EB almost 83% sites were found to be active. (b) The number of active sites, decreases as the alkylating power of the aluminum alkyl decreases (Et > isobutyl > n-hexyl > n-decyl). (c) They found that the number of active centers using $MgCl_2$/EB/$TiCl_4$ for 4-methyl-1-pentene polymerization was far higher than for propylene polymerization. They have explained this observation of higher activity of higher α-olefin as arising due to (1) complexation of an α-olefin with a deactivated or inactive center leading to the formation of an active polymerization center and (2) displacement of strongly adsorbed or complexed substances which have deactivated certain types of active centers leading to increased number of propagating centers.

Homogeneous metallocene catalysts

Asanuma *et al*[23] prepared poly (4-methyl-1-pentene) using 1-methyl-1-ethylidene (cyclopentadienyl-1'-fluorenyl) zirconium dichloride and methylaluminoxane as a catalyst. Based on ^{13}C NMR, DSC and XRD results they identified it as syndiotactic poly(4-methyl-1-pentene).

Luigi *et al*[39] studied the homopolymerization of propylene, 1-butene and 4-methyl-1-pentene using the catalyst system $Cp_2^* ZrCl_2$/MAO (Cp^* = pentamethylcyclopentadienyl). Based on end group analysis, they concluded that in the case of 4-methyl-1-pentene and propylene β-Me elimination is the preferred chain transfer reaction, whereas in the case of 1-butene only β-H elimination is observed.

Characterization

Poly (4-methyl-1-pentene) has been well characterized as regards to measurements on ΔH_f, density, crystallinity, thermal and mechanical behavior.[27]

1.2.1.3 1-Hexene

Conventional catalysts

Number of papers deal with the polymerization of 1-hexene using conventional catalysts.

Polymerization kinetics of 1-hexene with α-$TiCl_3AlEt_2Cl$ catalyst was studied in detail by Tu *et al.*[40] They found that the molecular weight stays constant with increasing conversion implying a stationary state with respect to initiation and propagation. Activation energy for polymerization was found to be 10.6 ± 3 kcal/mol.

Czaja[41] studied the polymerization of 1-hexene with $TiCl_4$, $TiCl_3$, $(iso\text{-}Pr)_2$ $TiCl_2$ and $VOCl_3$ with Et_3Al, Et_2AlCl or $EtAlCl_2$ catalysts. $VOCl_3$ did not give any polymer, $(iso\text{-}pro)_2$ $TiCl_2$ gave liquid oligomers and only catalysts comprising of $TiCl_4$ or $TiCl_3$ gave solid polymer. They studied the effect of the type and relative concentration of the catalyst components on yield, viscosity and degree of isotacticity of poly(1-hexene).

Gas chromatography has been used as a valuable tool in the study of the kinetics of 1-hexene using $TiCl_4$ - Et_3Al catalysts[42]. This was done by withdrawing 0.2 mL aliquots from the polymerization mixture at definite time intervals and recording the chromatogram of unreacted monomer. Then, concentration of monomer vs time was plotted to give an idea about the reaction rate. Soga[43] used the highly isospecific catalyst system Solvay $TiCl_3/Cp_2TiMe_2$ for the polymerization of 1-hexene.

Supported Mg - Ti catalysts

There is no detailed study of the polymerization of 1-hexene over $MgCl_2$ supported catalysts. However, there are a couple of reports, wherein a study of 1-hexene polymerization over $Mg(OEt)_2$[44] and MgO[45] supported catalysts has been conducted.

Baulin[45] made a comparative study of the polymerization of ethylene, propylene, 1-butene and 1-hexene over $TiCl_4/MgO\text{-}Et_3Al$ catalyst system. He noted that yield, k_{eff} and k_p reduce drastically when one goes from ethylene to the α-olefins. However, amongst the α-olefins, yield and k_p are of the same order.

Franz *et al*[44] studied the polymerization of 1-hexene and 1-octene using $TiCl_4/Mg(OEt)_2 - R_3Al$ catalysts. 1-Hexene, and 1-octene were chosen for the kinetic study since they form soluble polymers in the reaction medium and hence the influence of mass transfer is overcome when determining the concentration of active centers. However, they obtained very low conversions, which they tentatively attributed to the fact that no disintegration of catalyst particles was observed as in the case of ethylene polymerization.

Sukhova and Dyachkoviskii[47] prepared super high molecular weight poly(1-hexene) using $TiCl_4$-alkylaluminum fixed on graphite. They obtained high conversion and molecular weights upto 10^7 and high isotacticity upto 98.5% .

Homogeneous catalysts

Kaminsky reported that using the zirconocene and aluminoxane catalysts atactic polyhexene could be obtained. Luigi *et al*[46] reported, however, that Cp_2ZrMe_2/MAO catalysts gave oligomers of 1-hexene with DP = 6. Poly (1-hexene) with molecular weight in the range $\overline{M}_n = 13,000, \overline{M}_w = 23,000$ was reported by Asanuma[23] *et al* using a stereorigid metallocene. They obtained a non-crystalline poly (1-hexene) which was proved to have a syndiotactic structure based on ^{13}C NMR, XRD and DSC measurements.

A novel xylene soluble Mg-Ti catalyst prepared by supporting titanium-n-butoxide on $MgCl_2.2THF$ has been used in conjunction with Et_2AlCl for the polymerization of 1-hexene by Satyanarayana and Sivaram[48]. Very high molecular weight poly(1-hexene) with narrow MWD were obtained indicating that the active sites in the soluble Mg-Ti catalysts are homogeneous.

Characterization

Poly (1-hexene) has no appreciable crystallinity. It has a glass transition temperature between - 36 to - 55°C.

Tacticity assignments of the ^{13}C NMR of poly(1-hexene) has been done by Asakura *et al*[49]. A ^{13}C NMR study of poly(1-hexene) obtained using ethylene bis (indenyl) zirconium alkyl catalyst was done by Babu *et al*[50] indicating a highly isotactic microstructure with end groups arising from 1,2-disubstituted and 1,1,2-trisubstituted vinylene and vinylidene end groups.

1.2.1.4 1-Octene and higher mono olefins

Not much literature is available on the homopolymerization of olefins higher than 1-octene due to the prohibitively high monomer costs involved. Some of the higher α-olefins are available as by-products from commercial processes like refining of petroleum products and thermal cracking of hydrocarbons. Olefins with branched alkyl groups are produced by catalytic dehydration of the corresponding alcohols. Even - numbered - carbon α-olefin monomers e.g.1-octene, 1-decene and higher are produced by ethylene oligomerization with $(C_2H_5)_3Al$.

Conventional catalysts

Soga *et al*[43] found that the poly (1-octene) obtained using the Solvay $TiCl_3/Cp_2TiMe_2$ catalyst system had 99% of isotactic triads from ^{13}C NMR.

Haven and Campbell[51] synthesized a series of polyhydrocarbons by polymerization of monomers of the type R-CH=CH_2 where R varies from linear to branched. (Table 1.2).These polymers were characterized for solubility and crystallinity.

An elegant synthetic method for obtaining functional polyolefins has been demonstrated by Chung *et al.*[52] The monomers contain the borabicyclo [3.3.1] group next to the α-olefin and are obtained by monohydroborating non conjugated dienes such as 1,7-octadiene,1,5-hexadiene and 1,4-pentadiene . The polymerization reactivity of the monomer is dependent on the spacing between the double bond and the borane group. When there are only 3 methylenes as spacer, the reactivity is very low, but at 4 to 5 methylenes the activity becomes nearly constant . Typically a monohydroborated monomer like B-7-octenyl-9BBN was polymerized with $TiCl_3$.AA-$AlEt_2Cl$ and the polymer was terminated in pure 2-propanol. Then it was oxidized with NaOH/H_2O_2 to produce poly octen-8-ol. Similarly copolymers of B-5-hexenyl-9BBN and 1-octene were synthesized and later oxidized to give rise to novel copolymers poly(octene-co-hexenol) with a wide range of compositions.

Supported Mg - Ti catalysts

Franz *et al*[44] studied the kinetics of 1-octene polymerization. Polymerization of 1-decene over supported $MgCl_2$ catalysts was studied by Pena *et al.*[53] They found that the consumption of monomer does not obey a first order law and a second-order decay of the active ends is seen. They found that the addition of a Lewis base donor results in lowering of activity and an increase in the isotactic content and increase in molecular weight of poly(1-decene). DSC curves of the poly (1-decene) showed two endothermic peaks. They attributed this to either presence of two types of chains - isotactic and atactic, or due to the main chain and side chain aggregates.

Table 1.2 Crystallinity melting and solubility characteristics of some higher poly (α-olefin)s

Monomer	Crystallinity	T_m °C	Solubility in decalin at 135°C
$CH_2=CH-CH_3$	High	165	+
$CH_2=CH-CH_2CH_3$	High	125	+
$CH_2=CH-CH_2CH_2CH_3$	High	75	+
$CH_2=CH-CH_2CH_2CH_2CH_3$	None	None	+
$(CH_3)_2CH-CH=CH_2$	High	310	-
$(CH_3)_2CH-CH_2-CH=CH_2$	High	235	+
$(CH_3)_2CH-(CH_2)-CH=CH_2$	None	None	+
$\Phi-CH_2-CH=CH_2$	Medium	230	-
$\Phi-CH=CH_2$	High	250	+
$\Phi-(CH_2)_3-CH=CH_2$	None	None	+
$CH_2=CH-CH(\Phi)-CH_3$	Medium	> 360	-

Chien and Ang[54] studied 1-decene polymerization over the CW catalyst ($MgCl_2$/ethylbenzoate/p-cresol/$AlEt_3$/$TiCl_4$ - $AlEt_3$/Methyl-p-toluate) at 50°C. They found that in comparison to the data on propylene polymerization

-the same fraction of active sites were present, ranging from 1.4% at 0°C, over 12% at 50°C to 9.4% at 70°C,

-the decay rates were similar (second-order),

-the MWD's were similar (about 4)

However, with 1-decene, the rate of polymerization depends on fractional order of monomer concentration and decreases with increase in aluminum alkyl concentration. They attributed this to the larger coordination of 1-decene with the active sites.

Homogeneous Metallocene Catalysts

Polymerization kinetics of 1-octene catalyzed by metallocene/MAO was investigated by ATR-FT-IR spectroscopy[55]. Polymerization was conducted at 120°C by zirconocene/MAO in an ATR reaction cell. The progress of the reaction was followed by the observance of the disappearance of 1-octene using the 910 cm^{-1} band by FT-IR. The dependence of the reaction rate R_p on catalyst concentration and cocatalyst/catalyst ratio was examined. Second order catalyst deactivation was observed, possibly due to a biomolecular reduction. They found at an Al/Zr ratio of 4000, $k_p = 19.9\ Ms^{-1}$ and at Al/Zr = 300, $k_p = 9.6\ Ms^{-1}$ indicating that less than 50% of the initial Zr is active at a low Al/Zr ratio.

Characterization

The study of tacticity by ^{13}C NMR becomes progressively difficult with α-olefins with carbon number greater than six as the sensitivity to tacticity decreases.

Polymers of olefins with branched alkyl groups exhibit very high melting points (poly(3-methyl-1-butene) and poly(vinylcyclohexene) have the highest value 350°C).

Polymers with linear alkyl side chains have low crystallinities and behave as elastomers. Polymers with branched alkyl groups are highly crystalline and tough. But these are susceptible to oxidative degradation due to the presence of two tertiary carbons per monomer unit.

Polymers derived from higher α-olefins are found to have a helical conformation in the crystalline lattice, expanding from 3 monomer units per turn to 4 for longer α-olefins. The polymers of straight chain longer α-olefins give both main chain and side chain crystallinity as evidenced by the two endothermic peaks in DSC.

Wang *et al*[56] undertook a detailed investigation of the physical properties of a series of poly (1-olefins) containing linear pendant groups. (Table 1.3). They found that the melting temperatures first decrease with increasing side chain length, go through a minimum, and then gradually increase with increasing side chain length. The minimum is near poly (1-hexene) and poly (1-heptene). The minima in melting point and maxima in specific volume were discussed in terms of chain to chain packing density. They suggested that chain to chain packing density is minimum in this region. Two melting points were found for the higher poly(α-olefins) from poly(1-tridecene) to poly(1-octadecene).

Turner Jones[57] gave an explanation for the above phenomenon of melting point behavior based on crystallinity studies using x-rays. He found that as one goes down the series, from poly(1-butene) to poly(1-hexene) a changeover in crystallinity from entirely helical to type I/II type of crystallinity occurs which is reflected in the minimum of melting point vs side chain length curve. The type-I form is characterized by side chains extended at right angles to the main chain and in the type II form the side chains are at an angle of 130°C to the axes and pack

Table 1.3 Melting points of poly (α-olefin)s

Poly (α-olefin)s	**T_m °C**	**Specific volume (Vsp) ml/g**
Poly (1-butene)	126	1.153
Poly (1-pentene)	70	1.176
Poly (1-hexene)	-55	1.182
Poly (1-heptene)	38	1.197
Poly (1-octene)	-	-
Poly (1-nonene)	32	1.18
Poly (1-decene)	35	-
Poly (1-dodecene)	44	-
Poly (1-tridecene)	39, 55	1.17
Poly (1-hexadecene)	41, 70	-
Poly (1-octadecene)	42, 74	1.18

side by side as in orthorhombic polyethylene. The increase in melting point from poly(1-nonene) to poly(1-octadecene) is similar to that of the corresponding n-parrafins (crystallinity being derived from the side chains). Trafara[58] has also shown that isotactic poly(1-alkylethylenes) exhibit polymorphisim due to different crystal structure arrangements.

Stereoselectivity and stereoelectivity

Some of the higher poly α-olefins have been used to study the stereoselectivity and stereoelectivity of Ziegler-Natta catalysts. Due to the intrinsic asymmetric nature of the active sites in the Ziegler-Natta catalyst they are able to chirally discriminate between the enantiomers of α-olefins bearing an asymmetric C-atom in the α or β position to the double bond. If racemic mixtures of such α-olefins are polymerized with heterogeneous Ziegler-Natta catalysts the polymers can be separated into two fractions containing either the R or S isomer preferentially. This phenomenon is known as stereoselection. Polymerization of 3,7-dimethyl-1-octene with $TiCl_3/(isoBu)_3Al$ proceeds with a separation efficiency of 90%for R and S[59]. Stereoelectivity is a process in which the Ziegler-Natta catalyst containing one asymmetric component predominantly polymerizes one of the olefin stereoisomers (R or S) resulting in optically active polymers.

4-Methyl-1-hexene (R, S) was polymerized stereoelectively using a $MgCl_2$ supported Ti catalyst containing (S)-2-methylbutanol in the catalyst preparation step. This gave an optically active polymer with positive value for [α] showing that the S antipode is preferentially polymerized leaving the R isomer unreacted.[60]

In conclusion, based on the study of literature on polymerization of higher alpha olefins the following observations can be made

1. The order of reactivity amongst the olefins is 1-butene > 1-pentene > 1-hexene > 1-decene > 1-dodecene ....for linear olefins, and 5-methyl-1-hexene > 4-methyl-1-pentene > 4-methyl-1-hexene > 3-methyl-1-pentene > 3-methyl-1-butene .....for branched olefins.
2. Studies on active site concentration show that they all have almost the same number of active sites but the kp values of the higher olefins are lower.
3. The number of active sites reduce as the reducing power of the alkyl aluminum decreases.
4. Hydrogen has a positive effect on activity
5. Isomerization of the olefin occurs when conventional catalysts are used leading to reduced activity
6. The homogeneous aspecific catalysts lead to oligomers due to predominance of chain transfer reactions by β-H elimination

1.2.2 Cyclic / Bicyclic Olefins

1.2.2.1 Endocyclic Double Bond

Conventional catalysts

Boor *et al*[61] studied the homopolymerization of some cyclic olefins using $TiCl_3AA / Me_3Al$ catalysts. They found that the polymers contained both, enchained cyclic rings and cis and trans polyalkenamer as a result of 1,2-enchainment and ring opening. The polymerizability order was cyclobutene ≥ cyclopentene ≥ cyclohexene (inert). Relief of ring strain on polymerization is one of the factors responsible for the activity of cyclic olefins. Ring strain values of cyclopentane, cyclopentene, cyclohexane and cyclohexene are 6.1, 4.9, 0.1 and 1.0 kcal/mole respectively. Cyclopentene is less strained than cyclopentane and cyclohexene is more strained than cyclohexane. Based on this one would expect cyclohexene to show higher polymerization activity compared to cyclopentene. However, the other factor to be considered is the differences in steric hindrance for the insertion of monomer into the growing metal polymer bond. In cyclopentene and cycloheptene one side of a plane passing through the double bond and the carbon atoms on either side of it is free from other ring atoms. However, in cyclohexene and cyclooctene, other ring carbons project above and below such a plane and hinder the approach to the active center, thus explaining the observed polymerizability order. The ring opened structures are obtained due to the possibility of ring opening metathesis type of reactions with conventional catalysts[14].

Homogeneous metallocene catalysts

In contrast, to the conventional catalysts the polymers produced with the metallocene catalysts are a result of only insertion type of mechanism with no structures resulting from ring opening.

Kamnisky *et al*[62] studied the polymerization of cyclopentene, norbornene, dimethano-octahydronapthalene (dmon) using the chiral $En(Ind)_2ZrCl_2/MAO$ catalyst system. All three homopolymers were insoluble in 1,2,4 trichlorobenzene (TCB) at high temperatures and heat resistant upto temperatures over 400°C and highly crystalline. The insolubility caused problems in further characterization. The oligomer of cyclopentene obtained by polymerizing at high zirconocene concentration and temperature was found to be soluble in (TCB). Based on ^{13}C NMR analysis of this and model compounds the authors assigned an erythodiisotactic structure resulting out of 1,2 insertion. However, Collins and Kelly[63] have proposed that the structure is a result of a 1,3-enchainment, instead of 1,2-enchainment, based on structural analysis of hydro-oligomerization products of cyclopentene using chiral metallocene catalysts. They have also given a mechanism to explain this 1,3-enchainment.

Polymerization of cyclobutene and cyclopentene showed higher activity as compared to norbornene.[64] Again the activity for the polymerization of cyclobutene was found to be five times that of cyclopentene.

Characterization

The melting points (under vacuum) were found to be 485°C for polycyclobutene, 345°C for polycyclopentene and over 600°C for polynorbornene obtained with metallocene catalysts. Polymers obtained with conventional catalysts are elastomeric due to double bonds in the main chain.

1.2.2.2 Exocyclic Double Bond

Conventional catalysts

Vinylcyclohexane is the most studied monomer from this category. Interest in this polymer, arises due to its remarkable properties such as high melting point and crystallinity. A variety of transition metal halide-organometallic combinations have been used for the polymerization.

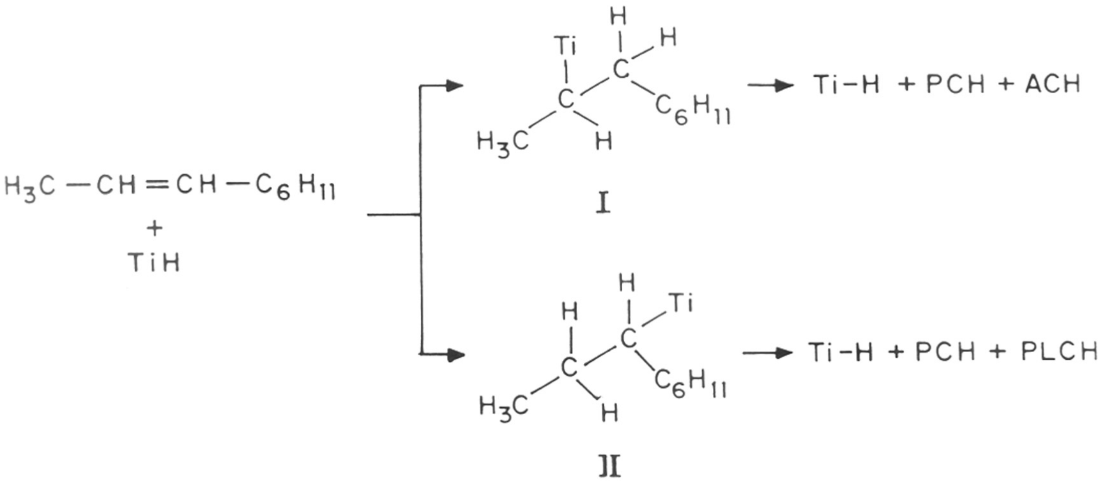
The rate of vinylcyclohexane polymerization in the presence of the $TiCl_3$-$AlEt_3$ catalyst has been studied.[65] The rate was found to be first order in monomer and catalyst concentration. The Arrhenius activation energy was calculated to be 5.2 kcal/mol.

Kleiner *et al*[66] conducted a more detailed study of the kinetics of polymerization and analyzed the nature and quantity of the by-products by gas-liquid chromatography. They observed that the polymerization of vinylcyclohexane is accompanied by side reactions, viz. isomerization of the double bond to other endo- and exo-cyclic isomers. They attributed the complexities encountered in the latter part of the polymerization to the adsorption of alkycyclohexenes with internal bonds on the active catalyst sites, deactivating the catalyst. Although the polymer yield decreases with time, the yield of the by-products increase linearly indicating different sites for isomerization and polymerization.

An interesting case of monomer isomerization polymerization has been reported by Endo and Otsu[67]. Isomerization of propenylcyclohexane (PCH) to allylcyclohexane (ACH) followed by polymerization occurred over $TiCl_3$ AlR_3 catalysts. The order of catalyst activity was $Et_3Al > isoBu_3Al >> Et_2AlCl=0$. This order is in agreement with the reducing ability of the aluminum alkyl as a reduced Ti is necessary to form the active site for isomerization.

The unreacted monomer analyzed by gas chromatography showed presence of alkylcyclohexane and propenylcyclohexane(PCH) and negligible amounts of propylidene cyclohexane (PLCH). They reasoned this based on a mechanism for isomerization as shown in Scheme 1.3

SCHEME 1·3



Due to steric reasons, structure (I) is more favorable than structure (II), hence allylcyclohexane (ACH) is the only isomer obtained.

The monomer isomerization polymerization was found to be accelerated by the addition of transition metal salts such as Nickel acetylacetonate.

1.2.3 Acyclic diolefins

Conventional catalysts

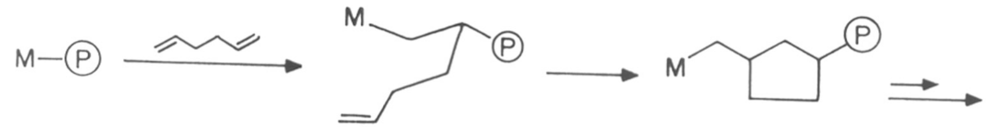
Marvel and Stille[68] obtained soluble polymers containing carbocyclic rings in the main chain on polymerization of 1,6-heptadiene, 1,5-hexadiene and 2,5-dimethyl-1,5-hexadiene using $TiCl_4$-Al (iso $Bu)_3$ catalyst. This shows that dienes favorable to cyclization undergo this type of cyclopolymerization.

Polymerization of 1,4-hexadiene was studied by Lal *et al.*[69] They found that using α-$TiCl_3/Et_3Al$ catalyst upto a maximum of 30% conversion to 1,2-poly (1,4-hexadiene) could be achieved. Conversion could not be increased beyond that due to isomerization of double bond to cis-2-trans-4-hexadiene, trans-2-trans-4-hexadiene and 1,3-hexadiene. In contrast when the catalyst used was $VOCl_3$ or β-$TiCl_3$ the microstructure of the polymers was quite complicated due to significant loss of unsaturation.

Homogeneous catalysts

Waymouth and Resconi[46] found that of the two monomers, namely 1,5-hexadiene and 1,6-heptadiene, 1,5-hexadiene gave rise to high molecular weight polymers due to cyclopolymerization, whereas the 1,6-heptadiene gave only oligomers with the homogeneous Cp_2ZrMe_2/MAO catalyst. They attributed this to the lower termination rate in the polymerization of 1,5-hexadiene due to a higher strain energy of the liberated olefin (methylenecyclopentane end groups, strain energy 6.4 kcal/mole). In case of 1,6-heptadiene, the lower molecular weight is consistent with the lower strain energy of methylenecyclohexane (1.9 kcal/mole). They also found that polymerization in bulk gave rise to 60% insoluble polymer indicating crosslinking. They proposed a mechanism for cyclopolymerization (Scheme 1.4)

SCHEME 1·4



Cis-diisotactic

Trans-diisotactic

Cis-disyndiotactic

Trans-disyndiotactic

It was found that use of Cp_2ZrCl_2 results in mainly trans or R type of enchainment with 91% trans at -78°C whereas using $Cp_2^*ZrCl_2(C_p^*=$ pentamethylcyclopentadienyl) at -25°C, 85% cis-ring content is obtained.

The trans selectivity in the presence of Cp_2ZrCl_2 catalyst was rationalized by a preference of the growing polymer chain to adopt an equatorial position in a pseudo-chair transition state during cyclization. With the more sterically hindered C_p^* ligands a twist boat conformation is accommodated, leading to a cis ring.

Subsequently Coates and Waymouth[71] reported the synthesis of an optically active poly(methylene-1,3-cyclopentane) (PMCP) using an optically active catalyst precursor [(R,R)-1] [ethylene-1,2-bis ($\eta^{5,}$ 4,5,6,7-tetrahydro-1-indenyl) zirconium (1,1'-bi-2-napthalate)]. Cyclopolymerization with (R,R)-1 yielded enantiomeric polymer with molar optical rotation of $(\varphi)^{28}_{405}$ + 51.0° and with (S,S)-1, $(\varphi)^{28}_{405}$ - 51.2. These polymers are 70% trans and optical activity is due to main chain chirality.

They also established that in these cyclopolymerizations chain transfer to aluminum is predominant with negligible amount of β-H transfer.[70,72]

1.2.4 Cyclic / Bicyclic diolefins

Conventional catalysts

Homopolymerization of 4-vinyl-1-cyclohexene was studied using $TiCl_3$-AlR_3 by Endo *et al.*[73] They concluded from IR that polymerization occurred through the vinyl group and the vinylene group did not participate in the reaction. Activity of 4-vinyl-1-cyclohexene was observed to be lower when compared to vinylcyclohexane. When the alkylaluminum used was Et_3Al or (iso $Bu)_3Al$ isomerization to 4-ethylidene-1-cyclohexane, 3-ethylidene-1-cyclohexane and 3-vinyl-1-cyclohexane was observed. No isomerization occurred when Et_2AlCl was used. The overall activation energy estimated from the initial polymerization rate (R_p) = 10 kcal/mol.

1.2.5. Applications

Poly(monoloefins)

Poly (1-butene) finds major application in industrial pipes, films and sheets, cables, fibers and composites. It has a use temperature upto 90°C with good flexibility and abrasion resistance and mechanical properties comparable to LLDPE.

Poly (4-methyl-1-pentene) due to its high transparency and melting point is used in medical and microwave equipment and for preparing optical memory disks.[74]

The lower molecular weight oligomers of higher α-olefins have found applications as synthetic oil base in formulations of lubricants and transformer oils.[75] Ultrahigh molecular weight polymers of higher α-olefins are expected to be used as drag reducing polymers.[76] Poly (1-hexene) and poly (1-octene) have been used to improve the impact resistance of polypropylene. Poly (3-methyl-1-butene) has been used as a component in the preparation of heat resistant compositions useful as dielectric materials.

Poly(diolefins)

1,2 poly(1-4 hexadiene) and its copolymer with 1-hexene (hexyl rubber) is used as an elastomer since it contains a high amount of unsaturation and is ozone resistent by virtue of the unsaturation being present as a pendant.

1.3 COPOLYMERIZATION OF ETHYLENE WITH HIGHER OLEFINS

1.3.1 Introduction

Ziegler-Natta catalysts, ever since their original discovery, have been used for the copolymerization of alkenes and dienes. Representative patent literature on ethylene olefin copolymerization is shown in Table 1.4. These copolymerization reactions offer an intriguing insight into the nature of the catalyst and the polymerization reaction, in addition to yielding polymers with useful properties. The properties of these copolymers depend largely on the relative groups and placements of the comonomer, the comonomer molecular weight and the mode of addition. When two or more comonomers are present in a copolymerization mixture, each must compete with the other for the available centers. The structure, comonomer composition and distribution and molecular weight of the formed copolymer is a consequence of this competition.

Table 1.4 Representative Patent Literature on Ethylene-Olefin Copolymers

Comonomer	**Company, CA and Patent No.**	**Catalyst System**	**Polymerization Cond.**	**Features of Copolymer**
ACYCLIC OLEFIN COMONOMERS				
1-Butene	Tosoh Corpn. 115:9612b JP03,66,708	Mg/2Ethylhexanol/ Ti $(OBu)_4$/isoBuAlCl_2/ Si$(OMe)_4$/TiCl_4 - AlEt_3, AlEt_2Cl	Temp. = 180°C Press. = 22.6 kg/cm^2	Act. = 333 kg/gTi M.I. = 3.2 d = 0.92
1-Butene	Nippon Oil Co. Ltd. 114:229629g EP413,469	SiO_2/TiCl_4/Et_2AlCl/ MgCl_2/Al$(OEt)_3$/ Si$(OEt)_4Et_3$Al	Temp. = 80°C H_2 as regulator, 0.27:1 Butene:Ethylene	Act. = 200 kg/gTi M.I. = 1 d = 0.92 bulk d. = 0.47
1-Butene	Ube Inds. Ltd. 116:60217z JP 03,197,515	MgCl_2/Ethylbenzoate/ TiCl_4 - MAO (2.3 Ti)	Temp. = 140°C Press = 2000 kg/cm^2 62:38 Ethylene:Butene tubular reactor	Act. = 200 kg/gTi M.I. = 5 d = 0.924
1-Butene	Nippon Oil Co. 115:136988d EP 426,637	MgCl_2/Al$(OEt)_3$/ 2-methyl-1-pentanol/ Ti$(OEt)_4$/SiO_2/AlEt_2Cl -AlEt_3	Temp. = 80°C Press = 8 kg/cm^2	Act. = 240 kg/gTi M.I. = 1.02 d. = 0.92 bulk d. = 0.45

Contd..

Comonomer	Company, CA and Patent No.	Catalyst System	Polymerization Cond.	Features of Copolymer
1-Butene	Exxon Chem. Patents Inc. 112:99482g WO 89,09,237	SiO_2/Me_3Al/ bis/butylcyclopentadienyl) $ZrCl_2$	-	M.I. = 1.7 d. = 0.936
4M1P	Mitsui Petrochem. Inds. 114:7426z EP 363,029	bis(methylcyclopentadienyl)$ZrCl_2$/MAO	Temp. = 80°C Press = 8 kg/cm^2	Act. = 905 kg/gZr. M.I. = 1.1 d. = 0.887 PDI =2.3
4M1P	Mitsui Petrochem. Inds. 115:160017g EP 436,399	$MgCl_2$/EtOH/Et_2AlH/ $TiCl_4$(4.8 Ti)/ Cp_2ZrCl_2 - MAO	Temp. = 80°C Press = 8 kg/cm^2	d. = 0.913 PDI = 11.9
4M1P	Mitsui Petrochem. Inds. 115:233175u EP 447,035	Cp_2ZrCl_2-MAO	Temp. = 60°C Press = 8 kg/cm^2	Act. = 586 kg/gZr. M.I. = 0.82 d. = 0.901 $[\eta]$ = 1.82 dL/g
1-Hexene	Mitsubishi Yuka K.K. 117:8698p JP 04,46,907	$TiCl_3$/$MgCl_2$/Stearyl methacrylate/$SiCl_4$ - Et_2AlCl	Temp. = 240°C Press = 1000 kg/cm^2	Act. = 700 kg/gTi M.I. = 1.16 d. = 0.9197

Contd..

Comonomer	**Company, CA and Patent No.**	**Catalyst System**	**Polymerization Cond.**	**Features of Copolymer**
1-Hexene	Mobil. Oil. Corpn. 112:56979z US 4,863,886	MgO/2-ethoxybenzoic acid/ $TiCl_4/Al(C_6H_{13})_3$ - $isoBu_2Al\ H$	Temp. = 90°C	M.I. = 12.9 d. = 0.963
1-Hexene	Union Carbide Chem. 115:160022e US 5,030,605	VCl_3/THF/SiO_2/ $Et_2AlOEt/CFCl_3$ -$isoBu_3Al$	Temp. = 85°C Press = 1050 kPa	Act. = 44.5 kg/gV d. = 0.946
1-Hexene	Mobil Oil Corpn. 115:160025h US 5,032,562	$Cp_2ZrCl_2/TiCl_4/SiO_2$ - Bu_2Mg, MAO	Temp. = 85°C H_2 as regulator	Bimodal dist.
1-Hexene	Philips Petroleum Co. 118:148227e WO 92,15,619	Cp_2ZrMe_2/Cp_2TiMe_2 - $AlMe_3$, MAO	-	M.I. = 2.7 PDI = 5.8 Bimodal dist.
1-Octene	Idemitsu Petrochem. Co. Ltd. 112:78191p JP 01,229,010	$Ti(OBu)_4/Zr(OBu)_4$ -$Et_3Al_2Cl_3,(Hex)_2Mg$	Temp. = 185°C Press = 40 kg/cm^2	Act. = 37 kg/gTi d. = 0.941 PDI = 4.7

Contd..

Comonomer	**Company, CA and Patent No.**	**Catalyst System**	**Polymerization Cond.**	**Features of Copolymer**
1-Octene	Mitsui Petrochem. Inds. 113:232282y WO 90,07,526	$En(Ind)_2HfCl_2$-MAO	Temp. = 60°C	d. = 0.80 PDI = 2.6 $[\eta]$ = 1.71 dL/g
1-Octene	Idemitsu Petrochem. Co.Ltd. 112:8045 JP 01,172,408	$Ti(OBu)_4$-BuMgEt, $Et_3Al_2Cl_3$	Temp. = 185°C Press. = 70 kg/cm^2	Act. = 802 kg/gTi
CYCLIC AND BICYCLIC MONOOLEFIN COMONOMERS				
Norbornene	Hoechst A. - G. 117:251998K	dimethylsilylbis(1-indenyl) zirconium dichloride/MAO		$\overline{M}w/\overline{M}n$ =2
Tetracycl -ododecene	Mitsui Petrochem. Inds. Ltd. 116:60206V JP, 03,234,716	dimethylsilylbis-(cyclopentadienyl) zirconiumdichloride - MAO	Temp. = 80°C	Act. = 2.8x10^{-3}kg/gZr PDI = 2.33 $[\eta]$ = 0.15
Pentacyclo -pentadecene	Mitsui Petrochem. Inds. Ltd. 115:256980S JP 03,172,312	$VO(OEt)Cl_2$/ $Et_3Al_2Cl_3$	-	Tg = 149°C $[\eta]$ = 0.61 dL/g

Contd..

Comonomer	Company, CA and Patent No.	Catalyst System	Polymerization Cond.	Features of Copolymer
ACYCLIC DIOLEFIN COMONOMERS				
1,5-hexa-diene	Mitsui Petrochem. Inds. 116:256257g JP 04,11,615	$MgCl_2/TiCl_3$-pyridine complex - $Et_3Al_2Cl_3$		Act. = 2.5 kg Diene = 76.5%
1,7-Octa-diene	Mitsubishi Chem. Inds. 101:92065 e JP 59,56,412	$Mg(OEt)_2/Ti(OBu)_3Cl$ - $Et_3Al_2Cl_3$, Et_2AlCl	I. Stage (A) ethylene homopolymerization II. Stage (B) copolymerization	A:B ratio 3:7 -to- 7:3 diene 0.01 - 10%
1,4-hexa-diene	Exxon Chem. Patents 115:256891P WO 91,01,337	$(Ind)_2ZrCl_2$- MAO on silica	Temp. = 65°C Press = 25 Kg/cm^2 fluidized bed	M.I. = 17 - 21 d. = 0.921 - 0.923
CYCLIC AND BICYCLIC DIOLEFIN COMONOMERS				
Norborna-diene	Idemitsu Petrochem. Co. Ltd. 106:19183r JP 61,148,211	$Mg(OEt)_2/MgSO_4/TiCl_4$ $/Et_3Al$, Et_2AlCl	I. Stage (A) ethylene polymerization II. Stage (B) copolymerization	Norbornadiene = 0.78% A:B 60:40
5-vinyl-2-nor-bornene	Nippon Oil Co. Ltd. 108:151141 W JP 02,243,611	$MgCl_2/(EtO)_4Si/$ $POCl_3/TiCl_4$-$AlEt_3$	Temp. = 70°C Press = 10 kg/cm^2	d. = 0.93 bulk d. = 0.26
p-(3-butenyl)-styrene	Idemitsu Kosan Co. 120:9180 w JP 65,194,665	Cp_2TiCl_2/MAO	-	diene = 17 mol %

1.3.1.1 Copolymerization equation

The mechanistic features of the copolymerization reaction are assumed to be essentially similar to those of the homopolymerization reaction with certain modifications added to account for the propagation step which can proceed in at least four different ways.

$$T_m - M_1 - P + M_1 \overset{k_{11}}{\dashrightarrow} T_m - M_1 - M_1 - P \tag{1.1}$$

$$T_m - M_1 - P + M_2 \overset{k_{12}}{\dashrightarrow} T_m - M_2 - M_1 - P$$

$$T_m - M_2 - P + M_1 \overset{k_{21}}{\dashrightarrow} T_m - M_1 - M_2 - P$$

$$T_m - M_2 - P + M_2 \overset{k_{22}}{\dashrightarrow} T_m - M_2 - M_2 - P$$

From this scheme an expression for copolymer composition in terms of the comonomer feed concentration and comonomer concentration in the copolymer can be obtained.[77]

$$\frac{d[M_1]}{d[M_2]} = \frac{[M_1]\,(r_1[M_1] + [M_2])}{[M_2]\,(r_2[M_2] + [M_1]} \tag{1.2}$$

Where $r_1 = k_{11}/k_{12}$ is the reactivity ratio of comonomer 1

$r_2 = k_{22}/k_{21}$ is the reactivity ratio of comonomer 2

$d[M_1]/d[M_2]$ is the molar ratio of the two monomer units in the copolymer and $[M_1]$ and $[M_2]$ are the concentrations of the comonomer in the feed.

The reactivity ratio is a measure of the tendency of a comonomer to show a preference for insertion into a growing chain in which the last inserted unit was the same, rather than the other comonomer. Values are obtained by

(i) fitting the copolymer composition data at several comonomer feed ratios to a suitable form of the copolymer composition equation, using the method of Fineman-Ross[78], Kelen-Tudos[79] etc. In these studies the copolymer has to be terminated at a short time i.e. less than 10% conversion such that, the drift in comonomer feed is negligible, hence satisfying the condition for evaluation of copolymer composition based on equation - (1.1).

(ii) by microstructural analysis of the copolymer, usually by ^{13}C NMR determination of monomer sequence distribution.

The product of reactivity ratios $r_1.r_2$ gives an idea of the structure of the copolymer. When $r_1.r_2$ is approximately 1, the last added unit in the chain does not influence the next addition and Bernoullian statistics govern the formation of a random copolymer. When $r_1.r_2$ tends to zero, there is some influence from the last inserted unit (first order Markovian statistics), or from the penultimate inserted unit (second order Markovian statistics). An alternating copolymer is favoured in this case. Finally, when $r_1.r_2$ is greater than one there is a tendency for the comonomer to form long segments.

$r_1.r_2 = 1$ random EECECCECE

$r_1.r_2 < 1$ alternating ECECEC

$r_1.r_2 > 1$ block EEEECECCCEE

Analysis of the copolymer structure and the evaluation of reactivity ratios can therefore act as a valuable mechanistic probe since the structure provides a permanent record of the copolymerization reaction. However, the structural interpretation using reactivity ratio products should be applied with caution since (a) the $r_1.r_2$ product value obtained varies with the method of evaluation and (b) certain assumptions are made in deriving the copolymer composition equation which do not hold true in most Ziegler-Natta systems. This is mainly due to the time dependent changes in catalytic activity and the multiplicity of active centers in Ziegler-Natta systems.

1.3.1.2 Controlling Copolymer Composition

The properties of a copolymer are dependent on the following structural features of the copolymer chains :

(i) total comonomer content, i.e. the distribution of comonomer units along an individual chain (intramolecular composition), and the variation in comonomer content and distribution between different chains (intermolecular composition).

(ii) molecular weight and molecular weight distribution, and

(iii) relative content of head to tail and head to head and tail to tail addition.

A degree of control can be exercised over these factors and therefore over the copolymer properties by varying the following factors some of which are interdependent: (i) Operating conditions (ii) Chemical composition of the catalyst (iii) Physical nature of the catalyst (iv) structure of the comonomers.

Operating Conditions

A drift in comonomer feed composition results in a copolymer of non-uniform composition. In a batchwise process, conducted at low yield, a constant comonomer feed can be approximated, but this is difficult in a continuous process. In a slurry process the comonomers dissolved in the diluent must be kept in equilibrium with the gaseous phase, hence a high stirring rate, low solution viscosity and a reactant flow rate well above the copolymerization rate are necessary to achieve this. Similarly, temperature can exert an influence via its effect on monomer solubility and also on the overall reaction rate and rate of chain transfer reactions. Finally, the order of addition of reaction components is also important.

Catalyst Composition

The structure of the transition metal component and also the nature of the metal alkyl component can influence copolymer composition. It has been shown that the relative reactivity of comonomers can be influenced by the electronegativity and the oxidation state of the transition metal center. Ethylene reactivity for example is generally greater in titanium based catalysts rather than vanadium based catalysts.

Nature of the Catalyst

In heterogeneous catalysts, the presence of multiple active centers results in a broad molecular weight distribution. This also results in a distribution of the extent of comonomer incorporation or copolymer composition, as the variation in ligand environment at different centers influences the case of comonomer coordination at the center. In comparison, homogeneous catalysts generally possess a single type of active site and produce random or alternating type of copolymers with narrow MWD = 2 with little compositional variation.

Effect of Comonomer Structure

Copolymers can be formed from a combination of comonomers of different structure, However, in the Ziegler-Natta process there exist specific interactions between active site and comonomer as opposed to free radical polymerization. Hence the order of reactivity between ethylene and 1-butene, for example, varies by a magnitude of 10^3, whereas in free radical process the reactivity parameters differ in the range of 2. In general, the more active the monomer is for homopolymerization with the catalyst, the more active is its reactivity in a copolymerization i.e. reactivity of ethylene > propylene > 1-butene > 3-methyl-1-butene. The higher olefins become less and less readily polymerized as their size increases. The comonomer can also influence the copolymer structure by acting as a chain transfer agent during copolymerization.

1.3.2 Ethylene - acyclic mono olefins

Ethylene copolymerized with acyclic higher α-olefins results in a copolymer with side chains at points where the α-olefin is inserted. Copolymers of ethylene with higher α-olefins such as 1-butene, 1-hexene, 4-methyl-1-pentene, 1-octene etc. are collectively termed as LLDPE (linear low density polyethylene). LLDPE's have superior thermal and mechanical properties as compared to the high pressure LDPE and have replaced LDPE in many applications. Initially, the economics and production capacity established for LDPE did not encourage companies to replace the free radical route by the transition metal catalyzed one for LLDPE, except for the production of some speciality grades by solution process (DuPont) and slurry loop reactor (Philips). But, after 1977, Union Carbide introduced its low pressure gas phase fluidized bed process - Unipol process which saw a substantial rise in the market for LLDPE, especially in the high performance markets.

In the slurry process for producing LLDPE, swelling of the copolymer occurs especially when the polymer density drops below 0.93. The swelling results in resin solubility due to which reactor fouling can occur. This causes a severe limit on resin density and production rates. In the solution process, molecular weights are curtailed, because in products requiring high molecular weights the solution viscosity becomes too high. The gas phase fluidized bed process overcomes these problems as it does not require diluents and hence is not constrained by solubility and viscosity, thereby making it a viable route to all grades of LLDPE.

LLDPE is characterized by linear molecules of polyethylene with short chain branches (SCB's) at places where the α-olefin has been inserted. The number and length of these SCB's are directly related to the concentration and molecular weight of the α-olefin used. Hence, depending on whether the α-olefin used is 1-butene, 1-hexene, 1-octene or 4-methyl-1-pentene, it is possible to introduce ethyl, butyl, hexyl or iso-propyl branches on the linear polyethylene chain. The physical and mechanical properties of the LLDPE are also in turn dependent on the nature of the branch[80]. For products of low melt index, toughness depends on the comonomer type upto C_8, after which the increase is less significant. For higher melt index products, the increase is much less significant. The increased length of an SCB results in the inhibition of molecular chain folding into a growing crystal lamella as it solidifies. This results, on one hand in a decrease in overall crystallinity and density and on the other hand to an increase in toughness due to increase in the number of interlamellar tie-molecules. When the melt index is higher, the overall copolymer chains are shorter, thus reducing the opportunity for effective tie molecules.

The selection of a comonomer for LLDPE, thus, happens to be mainly based on process compatibility, cost and product properties. Inspite of the commercial significance of LLDPE, published literature on the polymerization of ethylene with various α-olefins is not very extensive. A few authors have studied the copolymerization parameters r_1, r_2 for various ethylene-α-olefin pairs over different catalyst systems. In comparison, the characterization and property evaluation of ethylene-α-olefin copolymers has received a lot more attention.

1.3.2.1 Ethylene-1-butene

Amongst all the LLDPE's, products based on 1-butene occupy the largest market and both Union Carbide (licensees of the Unipol process) and DuPont have placed a great emphasis on their development. This is because it is the least expensive comonomer which yields a product with toughness clearly superior to LDPE. This section and other similar sections dealing with ethylene higher olefin copolymers, contain details of polymerization with various catalyst systems followed by some discussion on the IR, NMR, DSC, TGA and viscometric characterization of the copolymers since, that forms the main theme of the thesis.

Conventional catalysts

Natta and coworkers[81] synthesized amorphous copolymers of ethylene and 1-butene using vanadium based catalysts. Using the catalyst system VCl_4-$(C_6H_{13})_3Al$ they found $r_1 = 29.6$, $r_2 = 0.019$ and $r_1.r_2 = 0.56$. Ethylene-1-butene copolymers containing more than 30% 1-butene were observed to be amorphous in studies using VCl_4-(iso $Bu)_2AlCl$ as the catalyst system.[82]

Holdsworth and Keller[83] found that the decline in crystallinity was accompanied by an increase in polyethylene lattice spacing which increases with branch content. This showed that more branches were accommodated within the lattice of the higher branched samples.

Bodily and Wunderlich[84] studied ethylene-1-butene copolymerization over a narrow range of copolymer composition i.e. 0 to 3.5 mol %. They found that as the comonomer content increased the melting point was lowered from 134.5 to 128.6°C and the width of the DTA peak was observed to increase significantly indicative of real copolymer formation.

IR studies on ethylene 1-butene copolymers obtained using $TiCl_3$ catalyst[85] and Cp_2TiCl_2[86] catalyst showed the presence of bands at 722 and 733 cm^{-1} assigned to $(CH_2)_n \geq 5$ and $(CH_2)_3$ rocking modes respectively indicating a predominance of head-to-tail addition. The band at 770 cm^{-1} corresponding to ethyl group vibration implied that 1-butene units are incorporated without isomerization.

In a study of the evaluation of olefin reactivity ratios over the highly isospecific catalyst Solvay type $TiCl_3$ and $(RCp)_2TiMe_2$[87], the reactivity ratio ethylene-1-butene was found to be $r_1 = 72$, $r_2 = 0.11$. The general reactivity order was found to be ethylene > propylene > linear olefin > branched olefins (1-hexene > 4-methyl-1-pentene). Although the catalyst is heterogeneous, the catalyst centers are considered to be uniform in nature.

A homogeneous catalyst system composed of $VOCl_3/Et_3Al_2Cl_3$ with Al/V ratio 40 was used in the copolymerization of a variety of α-olefins starting from propylene, 1-butene, 1-pentene, 1-hexene, 1-heptene, 1-octene and higher linear α-olefins.[88] The MWD for the samples was typically 2.0 . Fractionation studies and presence of a single melting point in DSC indicated a high level of homogeneity in the samples. The copolymers were found to have a random distribution from ^{13}C NMR.

Supported Mg-Ti catalysts

Kashiwa and Tsutsui[89,90] studied the solution copolymerization of ethylene with 1-butene at a temperature of 170°C at which the polymerization system is homogeneous. The study was performed using both $TiCl_4$ supported on $MgCl_2$ and a Vc catalyst obtained by pretreatment of $VOCl_3$ with $(n - C_8H_{17})$ Al. Hydrogen was used to control the intrinsic viscosity in the range 1.63 to 1.97. The $MgCl_2$ supported catalyst showed a high activity of copolymerization - 10,000 g poly/mmol Ti but the activity of the Vc catalyst was much lower 2000 g/mmol Ti. The other comonomers used in the study were propylene and 4-methyl-1-pentene, and it was found that the effect of monomer in lowering the density was, in the order of 4-methyl-1-pentene > 1-butene > propylene, which is explained to be due to decrease in bulkiness of the comonomer.

1-Butene has been demonstrated as an efficient chain transfer agent in presence of hydrogen by Pasquet and Spitz.[91] In the copolymerization of ethylene and 1-butene using the $MgCl_2$-supported Ziegler catalyst deposited over silica (bisupported catalyst), the reduction in molecular weight occurred due to chain transfer by β-elimination and leads to a vinylidene end group detected by IR. In the polymerization of ethylene, hydrogen is used as a chain transfer agent, the main mechanism being hydrogenolysis of the living metal-carbon bonds. They found that when ethylene and 1-butene are copolymerized in the presence of hydrogen a large decrease in molecular weight occurred. This means that hydrogenolysis of the

1-butene bond is more facile, this is supported by the low amount of vinylidene end groups. Thus, they showed that transfer efficiency of hydrogen was increased after 1-butene insertion. This observation was supported by the fact that during compositional fractionation the molecular weight of the fraction decreased as the comonomer content increased.

Copolymerization of ethylene with 1-butene over the highly active $MgCl_2$ supported Ziegler-Natta catalyst has been studied as a function of temperature by Bohm.[92]. The r parameters and the rate constants of the copolymerization process of ethylene and 1-butene at different temperatures are shown in Table1.5. From the temperature dependence of the rate constants, entropy and enthalpy values were calculated, which showed that the enthalpy values are small in comparison to entropy, meaning the processes are predominantly entropy controlled. He concluded that the complexation of the active site by the monomer goes along with a significant decrease in entropy depending on the molecular structure i.e. the entropy change during complexation of the active site by the monomer is the rate-determining factor. The entropy parameters for ethylene and 1-butene differ in the range of 50 J/K mol which corresponds to a factor of the order of 100 for the rate constants.

Ojala and Fink[93] have calculated the reactivity ratios of various ethylene-α-olefin pairs over $MgH_2/TiCl_4/AlEt_3$ catalysts(Table1.6). In the case of ethylene-1-butene copolymerization, $r_1 = 55 \pm 5$ $r_2 = 0.02 \pm 0.01$, $r_1.r_2 = 1.1$ though this implies a random copolymerization to be occurring, examination of the ^{13}C spectra showed that even at low 1-butene content (2 mol %) a shoulder next to the main peak, attributed to EBB sequences is well visible. This means that 1-butene once reacted supports the insertion of the next 1-butene unit.

This type of a synergistic effect was also observed by Seppala[94] in terpolymerization studies of ethylene-1-butene-higher-α-olefin like 1-dodecene, 1-hexadecene etc. In the absence of 1-butene, very low levels of 1-hexadecene

Table 1.5 r Parameters and rate constants of the copolymerization of ethylene (1) and 1-butene (2) at different temperatures

T °C	r_1	r_2	k_{11} (l/mol.s)	k_{12} (l/mol.s)	k_{21} (l/mol.s)	k_{22} (l/mol.s)
120	51	0.04	200	3.9	22	0.82
85	67	0.08	100	1.5	14	1.1
65	110	0.1	70	0.64	11	1.1
50	130	0.1	60	0.46	10	1

Table 1.6 **Copolymerization parameters r_1 and r_2 for ethylene and α-olefin copolymerizations in the presence of $MgH_2/TiCl_4/Et_3Al$ catalyst system**

α-olefin	r_1	r_2	r_1r_2
1-Butene	55±5	0.02±0.01	1.1
1-Pentene	50±5	0.02±0.01	1.0
1-Hexene	47±5	0.02±0.01	0.94
1-Heptene	75±10	0.013±0.007	0.98
1-Octene	90±10	0.01±0.005	0.9
1-Decene	550±50	0.004	
1-Dodecene	1500±150	0.0004	
1-Tetradecene	1400±140	0.0004	
1-Hexadecene	1050±100	0.0008	

[Ti] = 2.9 x 10^{-3}M, [A] = 14.5 x 10^{-3}M, T = 20°C incorporation (less than 3 wt. %) was observed. However, in the presence of 1-butene about 10 wt. % incorporation of hexadecene occurred i.e. after insertion of 1-butene insertion of 1-hexadecene is favoured.

Homogeneous metallocene catalysts

Heiland and Kaminsky[95] studied the copolymerization of ethylene and 1-butene using the catalyst system $En(Ind)_2ZrCl_2$/MAO and $En(Ind)_2HfCl_2$/MAO. They found that the Hf-catalyst had a much higher capacity of incorporating the comonomer than the Zr-catalyst Also the Hf-catalyst gave polymers with a higher molar mass.

Characterization

Characterization of ethylene-1-butene copolymers by ^{13}C NMR for composition analysis has been elucidated by Pooter *et al.*[96] A number of studies on the sequence distributions in ethylene-α-olefin copolymers prepared with heterogeneous Ziegler-Natta type catalysts have been carried out by means of ^{13}C NMR studies. In general, a heterogeneous catalyst has multiple active sites and it is not suitable to deduce the nature of the active site based on sequence distributions of unfractionated copolymers. Kuroda *et al*[97] conducted successive solvent fractionation on ethylene-1-butene copolymer and analyzed the fractions by ^{13}C NMR. The reactivity ratios determined from the sequence distribution were found to vary gradually on going from fractions of lower to higher solubility. They concluded that the active sites of the catalyst are distributed continuously from sites more reactive towards 1-butene to sites less reactive to 1-butene. They have recently suggested[98] that a simultaneous use of ^{13}C NMR and temperature rising elution fraction (TREF) be made to obtain insights into the nature of the active site. ^{13}C NMR studies of an ethylene-1-butene copolymer obtained using $VOCl_3/Al_2Et_3Cl_3$ catalyst showed that it has an alternating type sequence distribution and 80% of 1-butene units follow primary insertion. The branching distribution of copolymer determined by TREF was found to tally with a theoretical calculation based on the assumption of single active site. However, TREF results of a copolymer of using supported $TiCl_4/AlEt_3$ catalyst give a much broader branching distribution due to multiple active sites.

A large amount of patent literature on ethylene-1-butene copolymers exist on account of the commercial significance of these copolymers. Representative patents appearing in the last three years are presented in Table1.4.

1.3.2.2 Ethylene-4-methyl-1-pentene

Conventional catalysts

Kissin[99] studied the copolymers of ethylene and 4-methyl-1-pentene using the catalytic system $TiCl_3$-$(C_2H_5)_2AlCl$. They found predominantly 1,2 head to tail addition of the olefin units, inferred by the absence of $(CH_2)_{n=2}$ bands in IR spectra. However, ethylene 4-methyl-1-pentene copolymers obtained with the catalytic system vanadium acetylactonate-(iso-$C_4H_9)_2AlCl$ contain units from normal 1,2-addition and isomerized units of the type $-CH_2-CH_2-CH_2-C(CH_3)_2-$ characterized by the 1230 cm^{-1} band in IR.[100] Further, they found[99] that the reactivity ratio product for copolymer obtained using $TiCl_3$-$(C_2H_5)_2AlCl$ is $r_1.r_2 = 5$ i.e. the copolymer has a strong tendency toward block formation. This conclusion was qualitatively supported by the examination of the 730-720 cm^{-1} region in the IR spectra. All copolymers with ethylene content over 10% were found to have the 731-720cm^{-1} doublet, indicating the presence of long crystalline blocks, and the band of isolated ethylene units at 733 cm^{-1} appeared only in the spectra of copolymers with 7-5 mol % of ethylene. The $r_1.r_2$ value obtained in the case of copolymers from vanadium acetylacetonate - (iso $C_4H_9)_2AlCl$ system was much smaller (0.7) and about 20% 4-methyl-1-pentene in the copolymer was sufficient to make the product amorphous.

Copolymerization using $VOCl_3/Et_3Al_2Cl_3$ catalyst system gave rise to homogeneous copolymers.[88] The homogeneity of the samples was demonstrated by SEC, ^{13}C NMR and DSC measurements.

Kashiwa and Tsutsui[89] studied the solution copolymerization of ethylene and 4-methyl-1-pentene. The various formation and chain transfer reactions that are possible are

by deactivation

$$\text{Cat}^* - CH_2 - C(R)H - P \rightarrow \text{Cat} - CH_2 - C(R)H - P \qquad (1)$$

by transfer with alkyl aluminum

$$\text{Cat}^* - CH_2 - C(R)H - P + R_3'Al \rightarrow \text{Cat}^* - R' + R'_2 - Al - CH_2 - C(R)H - P \quad (2)$$

by transfer with hydrogen

$$\text{Cat}^* - CH_2 - C(R)H - P + H_2 \rightarrow \text{Cat}^* - H + CH_3 - C(R)H - P \qquad (3)$$

by transfer with β-hydride elimination

$$\text{Cat}^* - CH_2 - C(R)H - P \rightarrow \text{Cat}^* - H + CH_2 = C(R) - P \qquad (4)$$

$$\text{Cat}^* - C(R)H - CH_2 - P \rightarrow \text{Cat}^* - H + H(R)C = C(P)H \qquad (4')$$

by transfer with monomer

$$\text{Cat}^* - CH_2 - C(R)H - P + CH_2 = CH(R) \rightarrow \text{Cat}^* - CH_2 - CH_2(R) + CH_2 \; (5) \; C(R)P$$

$$\text{Cat}^* - C(R)H - CH_2 - P + CH_2 = C(R)H \rightarrow \text{Cat}^* - C(R)H - CH_3$$

$$\text{or Cat}^* - CH_2 - C(R)H_2 + H(R)C = C(P)H \qquad (5^1)$$

They monitored the terminal unsaturated bonds by IR. The vinyl and vinylidene end group is obtained when ethylene and α-olefin are placed in the end unit respectively. In the case of ethylene-4-methyl-1-pentene using $VOCl_3/(n\text{-}C_8H_{17})_3Al\text{-}Et_3Al/CHCl_3$ catalyst system they found an increase in the total number of vinylidene and trans-vinylene bonds with an increase in the content of comonomer. This meant that termination by chain transfer through 4, 4', 5, 5' occurred more easily when 4-methyl-1-pentene unit is present at the growing chain end as compared to other monomers like propylene, 1-butene etc.

Supported Mg/Ti catalysts

Mulhaupt *et al*[101] found that when a sterically hindered phenol (2,6-di-tert-butyl-4-methylphenol) was incorporated during the preparation of $MgCl_2$-supported titanium catalyst and used with aluminum alkyl modified with the same phenol, a non-classical behavior - i.e. simultaneous increase in activity and selectivity was observed. Also, the reactivity of the comonomer could be increased in copolymerizations. Ethylene 4-methyl-1-pentene copolymers with very low densities 0.919 could be obtained. In most LLDPE processes a density of 0.925 is limiting in slurry polymerizations, because at higher α-olefin concentration the reaction can run away. However, the stereospecific catalyst used by the authors resulted in an insoluble polymer with no net increase in viscosity.

Characterization

^{13}C NMR has been used to determine the composition[96] and triad monomer sequence distribution[107] of ethylene 4-methyl-1-pentene copolymers. An IR method for determining the composition is based on the intensities of the bands at 920 cm^{-1} (iso-propyl group mode) and 4310 cm^{-1} (internal thickness standard). The analytical expression is $A_{920}/A_{4310} = 0.038\ C_{4\text{-}MP} + 0.035$.[103]

1.3.2.3 Ethylene-1-hexene

Conventional catalysts

Copolymers of ethylene-1-hexene using $VOCl_3/Et_3Al_2Cl_3$ catalysts were found to be homogeneous on characterization by GPC, ^{13}C NMR and fractionation.[88] Seidov *et al*[82] also synthesized copolymers of ethylene and 1-hexene using the catalyst system vanadium tris (acetylacetonate)/iso-Bu_2AlCl. The reactivity ratio values obtained were $r_1 = 46$, $r_2 = 0.0125$ and $r_1.r_2 = 0.58$ i.e. random copolymers were formed. The polyethylene crystallinity sharply decreased on increasing

1-hexene content being 25% at 10 mol.% 1-hexene, 15% at 15 mol% 1-hexene and 5% at 20 mol% 1-hexene. Copolymers containing more than 25 mol. % hexene were found to be totally amorphous.

Using the highly isospecific catalyst system Solvay type $TiCl_3$ and $(Cp)_2$ $TiMe_2$ Soga *et al*[87] evaluated the reactivity ratio of ethylene 1-hexene to be $r_1 = 68$, $r_2 = 0.033$ with $r_1r_2 = 2.24$. When they used an aspecific catalyst system $TiCl_3/MgCl_2$-$AlEt_3$ they found $r_1 = 22$ and $r_2 = 0.078$ with $r_1r_2 = 1.716$.[104] The incorporation of 1-hexene seems to be easier with the aspecific catalyst showing a tendency to give more random copolymers. Also the copolymers with the aspecific catalyst display lower melting points and crystallinity. This means copolymer structure is markedly dependent upon the catalyst stereospecificity. Considerable differences in the ^{13}C NMR of the two copolymers were noted.

Munoz-Escalona et al.[105] studied the homo- and copolymerization of ethylene with highly active catalysts based on $TiCl_4$ and Grignard compounds. The catalysts exhibited the highest activities when used in the copolymerization with 1-hexene. By thermal analysis and SEM techniques, they found that an incorporation of the comonomer into the polymer chain brought about a decrease in the polymer crystallinities and an increase in the porosities of the growing particles. Due to this the diffusion of the monomer to the catalytic active centers was thought to take place more easily, thus explaining the increase in the polymerization rate.

Supported Mg/Ti catalysts

Kim et al.[106] also observed a similar rate enhancing effect using the highly active $TiCl_4/THF/MgCl_2$ catalyst. They studied six catalysts with varying Mg/Ti ratios. The rate enhancing effect was observed for catalysts where the Mg/Ti ratio was less than 2.5. They attributed this to the activation of the occluded Ti anion sites in the catalyst, thus increasing the number of active polymerization centers. However at higher Mg/Ti ratios the Ti anion sites are activated without the help of 1-hexene due to the smaller size of the catalyst subparticles.

Homogeneous metallocene catalysts

Uzomi and Soga[107] studied the copolymerization using the homogeneous Kaminsky-Sinn catalysts. They used the aspecific (Cp_2ZrCl_2), isospecific [$En(IndH_4)_2ZrCl_2$] and syndiospecific [iso-Pr(Cp)(Flu)$ZrCl_2$] catalysts and found that the incorporation of 1-hexene decreases in the order syndiospecific catalyst>isospecific catalyst>aspecific catalyst. In all the copolymers, melting point and crystallinity decreased markedly and eventually disappeared with increase in 1-hexene content.

Seppala[108] has observed the effect of 1-hexene in the copolymerization with ethylene using the homogeneous Kaminsky-Sinn catalysts. He found that when the reaction temperature was high (90°C) and the copolymer formed dissolved in the reaction medium no effect of comonomer was observed. However, when copolymerization was performed at 50°C rate enhancing effect was observed at low 1-hexene incorporation followed by a rate decrease at higher 1-hexene incorporation.

Characterization

The chemical composition distribution (CCD) ethylene-1-hexene copolymer prepared using $TiCl_3$-$AlEt_2Cl$ catalyst was studied by Kakugo et al.[109] using TREF technique. On fractionation of a 52 mol% ethylene copolymer, a predominant peak located at 28 mol% ethylene, a middle peak at 100 mol% ethylene and lowest at 80 mol% ethylene was obtained. This wide composition distribution was attributed to the multiple active centers. The isospecific, stereoblock and non-stereospecific catalysts produce copolymers with increasing ethylene content in that order.

Ethylene-1-hexene copolymers were characterized by IR.[104] using the 1380 cm^{-1} methyl deformation band as a measure of the 1-hexene content and the 4310 cm^{-1} band as internal thickness standard. The analytical expression is

C_{hex} (wt%) = $15.225\ A_{1378}/A_{4210} - 1.26$

and $C_4H_9/100C = 2\ A_{1378}/A_{4310} + 0.5$

A number of studies [96,110,111] using ^{13}C NMR for the quantitative determination of comonomer content, comonomer distribution, triad distribution and average sequence length in ethylene-1-hexene copolymers are found in literature.

1.3.2.4 Ethylene 1-octene

LLDPE products based on 1-octene developed by Dow Chemicals have better performance characteristics as compared to ethylene-1-butene. Although the 1-octene based products are more expensive, owing to the higher comonomer cost, they are required in higher performance applications.

Conventional catalysts

The copolymerization parameters as determined by Ojala *et al*[93] over $MgH_2/TiCl_4/AlEt_3$ catalysts are as follows : $r_1 = 90 \pm 10$, $r_2 = 0.01 \pm 0.005$, $r_1.r_2 = 0.9$.

Homogeneous copolymers of ethylene-1-octene were prepared using an ethylaluminum sesquichloride vanadium oxychloride catalyst system.[88] A random distribution of branches was inferred from ^{13}C NMR and melting behavior of the copolymers.

Homogeneous metallocene catalysts

Recently the Dow Chem. Co.[112] using their single site constrained geometry catalysts have prepared ethylene 1-octene copolymers which contain both short chain and long chain branches. These copolymers due to the presence of the long chain branches have better melt processibility characteristics as compared to other

LLDPE's. Ethylene 1-octene copolymers with less than 20 wt.% 1-octene are being developed as polyolefin plastomers(POP's) and those with more than 20 wt.% 1-octene as polyolefin elastomers(POE's).

Characterization

^{13}C NMR for determination of copolymer composition is elucidated in reference by Pooter *et al*[96] and Kimura *et al*[102]. Complete assignments followed by determination of polymer composition, sequence distribution, and determination of apparent reactivity ratio has been elucidated by Cheng.[113]

A preparative scale temperature rising elution fractionation (PTREF) was performed on commercial 1-octene containing LLDPE.[114] Each fraction collected over a 3°C range contained 2.9 to 28.2 branches/1000C atoms compared to an average value of 9.7. This demonstrates the intermolecular heterogeniety existing in the copolymer.

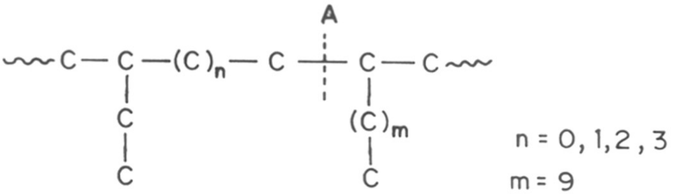
1.3.2.5 Ethylene higher-α-olefin

Due to the prohibitively high costs of higher olefins, literature on their copolymerization is scarce. Hence olefins higher than 1-decene are all discussed under this section.

Several of the characteristic properties of LDPE are due to long chain branches and it can be reasonably assumed that some of these properties can be produced in polyethylene grades using Zeigler Natta catalyst using comonomers producing long branches. For example due to the long branches, melt processing parameters are more favorable in LDPE as compared to LLDPE, and it is expected that these properties can be attained by introducing long branches in LLDPE. However longer α--olefins react only slowly 60-90° in a slurry process.

Conventional catalysts

Seppala[94] observed that by conducting a terpolymerization of ethylene-1-butene-higher α-olefin, he was able to introduce reasonably high amounts of higher α-olefin in the polymer. Using aluminum activated $TiCl_3/Et_3Al$ he found that in the absence of 1-butene in the reactor 1-decene concentration in the polymer remained at 2 wt. %. But, when 1-butene was added, due to a synergistic effect 1-decene incorporation increased to 13.5 wt. %. Similar results were observed when 1-dodecene was used as the long chain α-olefin. Pyrolysis hydrogenation gc was used to study the structure of the samples. He found an abnormally high concentration of fractions caused by the long α-olefin when ^{13}C NMR and IR were used as references. This indicates that in the structure:



where A represents the most probable site of sission, the pyrolysis results indicate that n is small, hence, 1-butene branches and 1-dodecene branches are probably located near each other. He concluded from this study that 1-butene temporarily removes the steric hindrances resulting in a better reactivity of the long α-olefin.

Ethylene higher α-olefin copolymers were also obtained using $VOCl_3/Et_3Al_2Cl_3$ catalysts and their properties studied.[88]

Kissin and Beach[115] studied the copolymerization of ethylene and mixtures of linear α-olefins using $\delta TiCl_3 0.33AlCl_3$-$AlEt_3$ and supported $TiCl_4/MgCl_2$-$AlEt_3$ catalyst systems in heptane at 90°C. The olefin mixture was obtained by ethylene oligomerization using a Ni ylide catalyst or using $(Et)_3Al$ at high temperature and pressure. Bar diagram of the olefin distribution prior to copolymerization and after copolymerization is shown in Fig.1.1. It can be seen that the relative amounts of higher α-olefins C_{10}-C_{16} decrease with the reaction conversion, whereas relative amounts of heavier olefins C_{18}-C_{32} increase. This can be rationalized if one assumes that lighter olefins are more reactive in copolymerization than heavier ones. Using GC the amount of olefin consumed in the reaction was used to obtain the value of r_2 for the various olefins. They found that the absolute values of r_2 for the supported system are six to ten times less than those for δ $TiCl_3/AlEt_3$ system.

Supported Mg/Ti catalysts

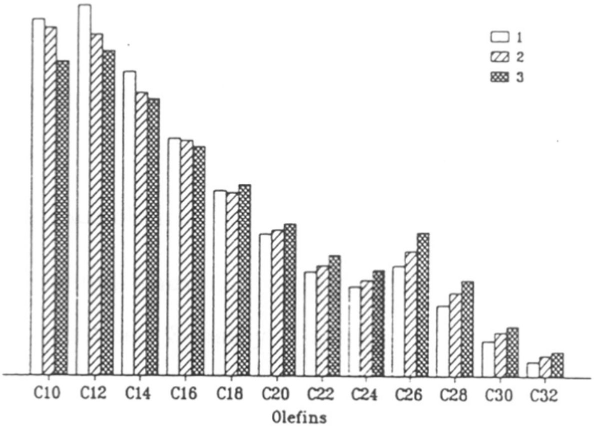
Ojala and Fink[93] have calculated the reactivity ratios of some higher α-olefins over $MgH_2/TiCl_4/AlEt_3$ catalyst system (Table 1.6).

Homogeneous metallocene catalysts

Koivumaki and Seppala[116] observed that using a homogeneous zirconocene/methyl-aluminioxane catalyst system reasonably high incorporation of 1-hexadecene was obtained as compared to a marginal incorporation when a heterogeneous titanium catalyst was used. Also the TREF fractogram of this copolymer closely resembles that of LDPE, whereas TREF of copolymer from a heterogeneous titanium catalyst has a very broad distribution.

1.3.2.6 Relationship between structure and reactivity

The best way to compare monomer reactivities in a particular polymerization reaction is by the comparison of their reactivity ratios in copolymerization reactions. Kissin[117] has discussed olefin reactivity on the basis of reactivity ratio values for olefin copolymerization over stereospecific $TiCl_3$ based catalyst systems. He compared the reactivity of different olefins in copolymerization reactions with a standard olefin (propylene), to avoid the interference of the effect of the last unit in a growing chain on reactivity ratios. The value of $K_{1i}/K_{11} = 1/r_1$



1.1 Bar diagram of the olefin distribution before (1), in the course (2), and after (3) their copolymerization reaction with ethylene in the presence of the δ-$TiCl_3/Et_3Al$ system at 90°C.

is a measure of the reactivity of olefin "i" in relation to propylene reactivity. In cases where propylene copolymerization data for some olefins was not available, a semiquantitative procedure was adopted. Table 1.7 lists the data on relative olefin reactivity, inductive Taft parameter σ^* and steric parameter E_s from reference 118 of some linear and branched olefins. The data on olefin reactivity correlated well with the previously published qualitative data on the order of reactivity for a variety of olefins.

For linear olefins

Propylene > 1-butene > 1-pentene > 1-hexene $\simeq$ 1-heptene > 1-decene > 1-octadecene

and for branched olefins

5-methyl-1-hexene > 4-methyl-1-pentene > 4-methyl-1-hexene > 3-methyl-1-pentene > 3-methyl-1-butene

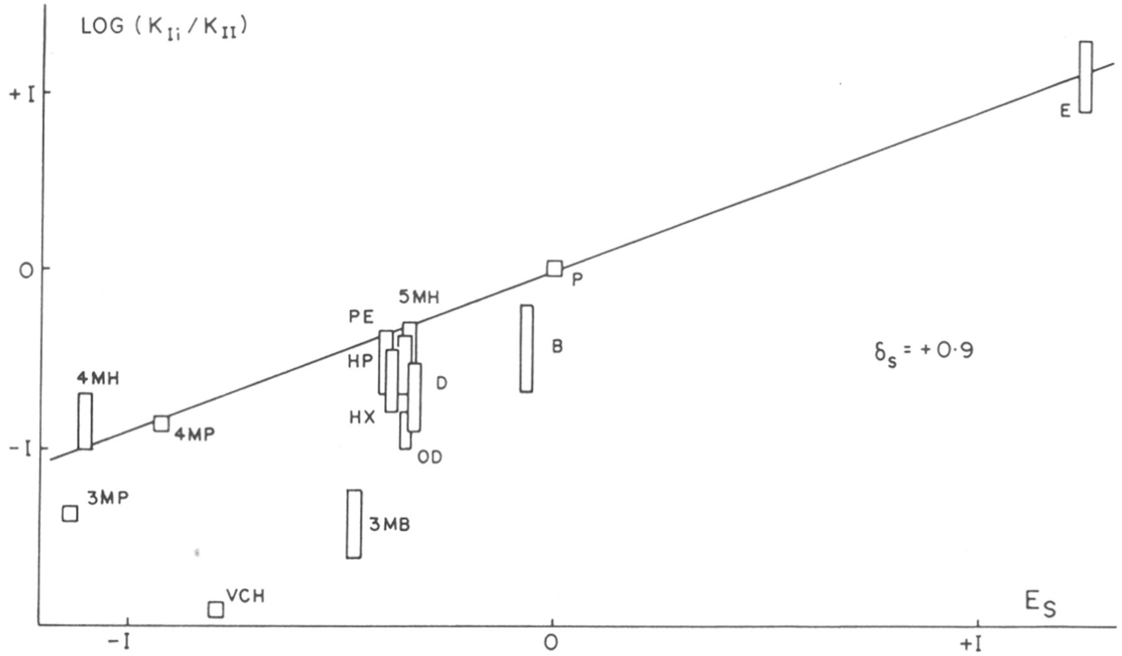
On comparing the inductive Taft parameter σ^*, they found that most of the groups have similar values indicating that electronic properties do not have much effect on olefin reactivity. On the other hand the value of E_s experiences a large variation through the series. They plotted log olefin reactivity parameter K_{1i}/K_{11} Vs E_s(Fig.1.2).A straight line was obtained and the δ_s parameter in the equation ; log (reactivity) = δ_s E_s was found to be $\delta_s = +0.9$, indicating substantial reaction sensitivity to olefin steric characteristics. The fact that olefins with α-branched alkyl groups 3-methyl-1-butene, 3-methyl-1-pentene, vinylcyclohexane fall below the correlation was explained by the severe space limitation in the transition state of the propagation step.

1.3.2.7 Structure property relationship

The effect of the nature of the branch, introduced by copolymerizing ethylene with various α-olefins, on the thermal and mechanical properties of the copolymer provides an interesting study.

Table 1.7 **Olefin reactivity in polymerization reactions with heterogeneous Ziegler-Natta Catalysts**

Monomer	Reactivity K_{1i}/K_{11}	σ^*	E_s
Ethylene (E)	20-8	0.49	1.24
Propylene (P)	1 (Std.)	0	0
1-Butene (B)	0.62-0.22	-0.1	-0.07
1-Pentene (P)	0.45-0.2	-0.11	-0.36
1-Hexene (HX)	0.36-0.16	-0.13	-0.4
1-Heptene (HP)	0.45-0.2	-0.16	-0.4
1-Decene (D)	0.28-0.12	-	-0.3
1-Octadecene (OD)	0.15-0.1	-	-0.35
3-Methyl-1-Butene (3MB)	0.06-0.02	-0.19	-0.47
3-Methyl-1-Pentene (3MP)	0.048	-0.21	-1.13
4-Methyl-1-Pentene (4MP)	0.15	-0.12	-0.93
4-Methyl-1-Hexene (4MH)	0.17-0.1	-	-1.1
Vinylcyclohexane (VCH)	0.012	-0.15	-0.7



1.2 Reactivity-structure correlations for olefins. Abbreviations correspond to olefins in Table 1.7 log(K_{1i}/$K_{11)}$ vs Es.

The effect of the nature of the branch on melting point of the copolymer has been studied by a number of workers.[119,120,121,122]

Clas *et al*[121] studied ethylene - olefin copolymers obtained with the homogeneous $VOCl_3/Et_3Al_2Cl_3$ catalyst system. The copolymers obtained were essentially of a random and homogeneous nature, as indicated by ^{13}C NMR and TREF studies. They compared the T_m lowering with increasing comonomer incorporation for various comonomers, namely 1-butene, 1-octene and 1-octadecene. They found that at low mol % incorporation T_m is independent of branch length. However, at higher mole % incorporation they observed a smooth decrease in T_m with increasing branch length which they attributed to a reduction in average crystallite thickness. For example at 8 mol % incorporation T_m of an ethylene - 1-butene copolymer was found to be 92°C whereas for ethylene-1-octadecene the T_m was found to be 65°C. This difference arises because an 8 mol % ethylene-1-butene copolymer contains, 85 wt % ethylene thus, in addition to the normal effect on T_m of randomly spaced defects along the polymer chain, the $C_{16}H_{33}$ branches of 1-octadecene dilute the ethylene sequences and prevent them from building thicker crystallites.

The above case is an extreme one, and it was found by Shirayama[120] *et al* and Burfield[122] that when the difference in branch length is not too high, the crystallinity of the samples is determined principally by the number of chain irregularities rather than by the size of the substituent. Burfield demonstrated this in a plot of ΔH_m vs comonomer content. He attributed the independence of crystallinity on comonomer type to the close similarity in molecular weight, MWD and comonomer dispersity of copolymers due to polymerization with the same catalyst under standard reaction conditions.

Although the nature of comonomer used is known to affect properties such as tensile impact strength and transparency of the LLDPE films, very few papers can be seen which clearly refer to the relationship between structural factors and the mechanical properties of ethylene-α-olefin copolymers. This might be because it is hard to discuss the effect of some selected structural factors strictly on the mechanical properties so long as the whole polymer which includes various structural factors is used as a sample.

Hosoda and Uemura[123] studied the effect of structural distribution on the large-strain mechanical properties of similar fractions of various LLDPE's. Fractionation by molecular weight was done by solvent gradient elution fractionation (SGEF) techinique and cross-fractions based on crystallinity were obtained by temperature rising elution fractionation (TREF). They found that an ethylene-1-butene copolymer has a tendency to make thicker lamellae than those of the higher α-olefin copolymers of the same level of molecular weight and comonomer content. They attributed this to the inclusion of short chain branches - like C_2H_5 into the lamella resulting in a wider distribution of lamellar thickness in ethylene-1-butene copolymers compared to higher α-olefin copolymers.

The authors also carried out tensile and tensile impact tests on ethylene-α-olefin copolymer fractions of same molecular weight of various α-olefins. They found that elongation of break (E_b) increased discretely at $\overline{M}_w/\overline{M}_n=3\text{x}10^4$ for 1-butene copolymers and at $2\text{x}10^4$ for higher α-olefin copolymers and above this molecular weight, E_b did not show any dependence on molecular weight or kind of comonomer. Higher α-olefin copolymers showed higher values of ultimate strength (σ_u) and necking stress (σ_s) compared to those of 1-butene. Similarly, the molecular weight above which tensile impact strength (σ_{Ti}) could be measured was $2\text{x}10^4$ for higher α-olefin copolymers, $4\text{x}10^4$ for 1-butene copolymers and $8\text{x}10^4$ for ethylene homopolymer fractions. They found that higher α-olefin copolymers showed higher σ_{Ti} than that of 1-butene copolymers at the same degree of chemical composition distribution (CCD).

In general, tie molecules are considered to play an important role in the mechanical properties of crystalline polymers under stress. The tie molecules are in turn governed by the structural distribution on the crystalline level with a larger number of tie molecules being present in a narrower distribution of crystallinity and lamella thickness. Hence, higher impact strength, ultimate strength and necking stress is observed in the case of higher-α-olefin copolymers as compared to ethylene-1-butene copolymers which have a wide lamella thickness distribution.

Based on the literature on ethylene-higher monoolefin copolymerization the following conclusions may be drawn-

Effect of catalyst type and copolymerization conditions

(a) The use of heterogeneous Ti based catalyst is seen to result in block formation during copolymerization, whereas, homogeneous V based or metallocene catalysts lead to random copolymer formation during copolymerization.

(b) Except for some V based catalysts, where some amount of head to head insertion is seen , most catalysts result in head to tail insertions.

(c) alpha olefins act as efficient chain transfer agents by β-H transfer. As comonomer content increases molecular weight decreases.

(d) In presence of hydrogen the hydrogenolysis of the M-α-olefin bond is more facile.

(e) A synergistic effect can be observed during co- and terpolymerizations, i.e. insertion of one olefin favours the insertion of a higher α-olefin.

(f) Among the heterogeneous catalysts the aspecific catalysts give higher incorporation of comonomer than the specific catalysts; and among the homogeneous metallocene catalysts the specific catalysts give more incorporation than the aspecific catalysts

Effect of comonomer structure on copolymer properties-

(a) The reactivity order established is as follows

For linear olefins

Propylene > 1-butene > 1-pentene > 1-hexene = 1-heptene > 1-decene > 1-octadecene

and for branched olefins

5-methyl-1-hexene > 4-methyl-1-pentene > 4-methyl-1-hexene > 3-methyl-1-pentene > 3-methyl-1-butene

(b) The effect in reducing Tm and density is as follows

-when the difference in branch length is large Tm decreases with increases in branch length due to decrease in crystallite thickness.

-when the difference in branch is not large amongst linear and branched comonomers it is the number and mol.% incorporation of comonomer that has an effect on Tm rather than the type of branch.

1.3.3 Ethylene - cyclic / bicyclic mono-olefins

1.3.3.1 Endocyclic double bond

Conventional catalysts

The early studies on ethylene-cyclic olefin copolymerization using heterogeneous Ziegler-Natta catalysts yielded products wherein the cyclic olefin participated via both double bond and ring opening mechanism.[77]

Homogeneous metallocene catalysts

Recently, with the advent of the Kaminsky-Sinn catalysts, it has been possible to homo- and copolymerize cyclic olefins without double bond opening. Kaminsky and Spiehl[124] demonstrated the facile copolymerization of cyclopentene, cycloheptene and cyclooctene with ethylene, using the chiral catalyst $En(Ind)_2ZrCl_2/MAO$. They found cyclopentene to be an extraordinarily suitable comonomer, with copolymerization activity nearly comparable to that observed for ethylene homopolymerization (20,700 g polymer per mol of Zr and s). Upto 28 mol % incorporation of cyclopentene was achieved. The melting points of copolymers decreased from 120 to 80°C for small increase in comonomer incorporation. The copolymerization parameters are $r_1 = 300$, $r_2 = 0.007$ at 20°C. Cyclohexene could not be copolymerized with this system, probably due to its high stability and low ring tension. Cycloheptene and cyclooctene on the other hand were found to be favorable for copolymerizations. The contents of the cycloolefins were found to be enhanced on decreasing the polymerization temperature, by raising the monomer mole ratio (cycloolefin/ ethylene) and by using a higher catalyst concentration.

Norbornene was found to be yet another favorable comonomer by Kaminsky *et al.*[125] The ethylene-norbornene copolymers show interesting properties. They are amorphous, have a high resistance to chemicals and heat and are useful as materials for optical discs and fibres. The catalyst $En(Ind)_2ZrCl_2/MAO$ shows a maximum of the activity, whereas the activity of the simple Cp_2ZrCl_2/MAO is 100 times lower. The copolymerization parameter $r_1 = 2.2$ for $En(Ind\ H_4)_2\ ZrCl_2$ and $r_1 = 20$ for Cp_2ZrCl_2 catalysts. At 12 to 14 mole % of norbornene the copolymers were found to be amorphous. A high glass transition temperature of 120° could be reached at norbornene concentration greater than 60 mole %. Higher Tg could be obtained using the more rigid 1, 4, 5, 8 - dimethano 1, 2, 3, 4, 4a, 5, 8, 8a - octahydronapthalene (DMON) comonomer.[126] At about 50 mole % DMON in the polymer chain, the Tg was found to be 150°C. The copolymerization parameter r_1 was 50 for the rac-En (ind H_4) $ZrCl_2$ catalyst and 15 for rac-En $(ind)_2$ $ZrCl_2$ catalyst in comparison to 2.2 for ethylene-norbornene.

1.3.3.2 Exocyclic double bond

Homogeneous catalysts

Nekhaeva et al[127] studied the copolymerization of ethylene-vinyl cyclohexane using the homogeneous zirconocene-methyl aluminoxane catalyst system. They found that vinylcyclohexane in the reaction mixture led to the formation of active centers with higher reactivity. On further increasing the vinylcyclohexane concentration led to decrease in polymerization rate due to lower reactivity of vinylcyclohexane as compared to ethylene. The presence of only 1 mol.% vinylcyclohexane in the copolymer led to decrease in density of polymer from 0.98 to 0.96 and melting point from 127 to 122°C.

A study of the copolymerization of ethylene and vinylcyclohexane using soluble Cp_2ZrCl_2 or Cp_2ZrMe_2/MAO catalysts at 70°C was conducted by Mani et al,[127] upto 1.7 mol% vinylcyclohexane could be introduced into the polymer chain. The molecular structure and comonomer content was determined by ^{13}C NMR. The activity and molecular weights of the copolymers were found to decrease on increasing comonomer concentration. The cyclohexyl branches were found to decrease the melting point and crystallinity of the copolymers.

1.3.4 Ethylene-acyclic diolefins

Conventional catalysts

One of the most studied systems is ethylene-1,5-hexadiene. Makowski et al.[129] observed the cyclization of 1,5-hexadiene units during copolymerization with ethylene using $TiCl_3/AlR_3$ catalysts. The copolymers were highly rigid and crystalline due to the presence of cyclopentane units in the main chain as a result of 1,5-hexadiene cyclization. A homogeneous catalyst $V(acac)_3/Et_2AlCl$, on the other hand, was found to result in a copolymer where the predominant form of enchainment was through the double bond[130]. The 1,2-enchainment was found to be more prevalent at lower temperatures.

Another acyclic diene to be used in copolymerization with ethylene is methyl-1,4-hexadiene.[131] The catalyst system used was $TiCl_3/AlEt_2Cl$ in presence of hydrogen. The copolymer was found to have pendant double bonds arising from the trisubstituted double bond.

The factors which seem to favor 1,2 addition are use of soluble, colliodal or non-isotactic catalysts and low polymerization temperatures. The factors favoring cycloaddition are use of heterogeneous isotactic specific catalysts and intermediate polymerization temperatures.

Supported Mg/Ti catalysts

Kurusu et al.[132] have reported the copolymerization of ethylene and 1,9-decadiene using $MgCl_2$ supported Ti catalysts to give rise to a copolymer with pendant double bonds. However, due to the Mg-Ti catalysts being less active toward comonomer, the level of incorporation achieved is about 1 mol % only.

1.3.5 Ethylene - cyclic / bicyclic di-olefins

In such copolymerizations the more reactive double bond is expected to participate in the reaction.

Conventional catalysts

Alieva et al.[133] studied the copolymerization of ethylene with 4-vinyl-1-cyclohexene using $V(acac)_3$/iso Bu_2AlCl catalyst system. They found that increasing the concentration of ethylene in the liquid phase decreased the incorporation of diene and increased the molecular weight, rate of polymerization and rate of crosslinking of the copolymer. The rates of polymerization and crosslinking were also found to increase with increase in catalyst concentration, Al/V ratio and temperature. The reactivity ratios were found to be $r_1 = 30$, $r_2 = 0.011$. The copolymers were found to be rigid with high Tg.

The other cyclic diene to be studied is 5-vinyl-2-norbornene. Here it is the cyclic double bond which is expected to react in polymerization, since it would result in a release of ring strain. This type of incorporation was reported by Lohse et al.[134] during preparation of an EPDM using $VOCl_3/Et_3Al_2Cl_3$.

Supported Mg/Ti catalysts

In copolymerization of 4-vinyl-1-cyclohexene with ethylene the vinyl double bond is expected to participate in the reaction. Mulhaupt et al.[101] studied the copolymerization of ethylene with 4-vinyl-1-cyclohexene using the catalyst system composed of $MgCl_2$ incorporated with 2,6-ditert-butyl-4-methylphenol (BHT), $TiCl_4$ and $AlEt_2BHT$. They obtained a low incorporation < 5 wt % of the diene.

1.3.6 Applications of ethylene-higher (mono- and diolefin) copolymers

Ethylene-higher alpha olefin copolymers like ethylene-1-butene, ethylene-1-hexene, ethylene-1-octene (LLDPE's) have found widespread application and have replaced LDPE in many applications. Compared to LDPE, LLDPE has a higher use temperature, tensile strength, and tensile impact strength. These properties give a significant advantage in the downguaging of films. LLDPE is also used in kitchenware, toys, industrial articles, drip irrigation tubing etc.

Ethylene-cyclic olefin copolymers due to their excellent transparency, chemical and solvent resistance and mechanical strength are expected to be used as materials for optical disks and fibers.[135]

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CHAPTER II

OBJECTIVES OF THE PRESENT INVESTIGATION

2.1 OBJECTIVE IN UNDERTAKING THE WORK

The copolymerization of ethylene with linear α-olefins to produce polyethylene with short chain branches at places where the α-olefin has been incorporated (LLDPE) has gained considerable importance in recent years.[1] LLDPE has steadily replaced LDPE in many applications due to its better performance which arises as a result of its lower density, higher strength and modulus. The presence of the short chain branches is believed to inhibit the molecular chain folding of polyethylene molecule into a growing crystal lamella as it solidifies. This leads to an increase in the number of interlamellar tie molecules , resulting in a stronger material[2].

Linear α-olefins such as 1-butene, 1-hexene, 1-octene form the commercial grades of LLDPE and a large amount of literature exists on the synthesis and characterization of these copolymers. However α-olefins containing a cyclic/bicyclic group have not been studied in literature, possibly due to their poor reactivity. Furthermore, when using conventional Ziegler-Natta catalysts unwanted side reactions of the monomers could complicate the polymerization.

Recently some reports have appeared in literature on the copolymerization of ethylene with vinylcyclohexane. The authors were interested in these copolymers because they expected the bulky cyclohexyl substituent might lower the melting point and density of polyethylene more effectively than linear α-olefins. Mani and Burns[3] synthesized copolymers of ethylene and vinylcyclohexane using the soluble catalyst system Cp_2ZrCl_2/MAO and Cp_2ZrMe_2/MAO. They found that the cyclohexyl branches affect the physical properties of the copolymer by decreasing the melting point and crystallinity of the polymer. At 1.7 mol% incorporation they obtained a Tm of 119°C. Nekhaeva et al[4] also obtained similar results using the Cp_2ZrCl_2/MAO catalyst. At 1 mol% vinylcyclohexane incorporation they found that the melting point decreased from 127 to 122°C and density from 0.98 to 0.96.

An ethylene copolymer where the α-olefin contains a bicyclic substituent has not been reported in literature. One such α-olefin that we chose to study is 2-propenyl-bicyclo [2.2.1] heptane or 2-allylnorbornane. We expected the norbornyl pendant to lower the melting point and density of the polyethylene. Since all α-olefins when copolymerized with ethylene lead to a decrease in density and melting point, we decided to compare the properties of the ethylene-2-allylnorbornane copolymers with those of ethylene-4-methyl-1-pentene copolymers at similar mol% incorporation, in order to study the specific effect of the bicyclic pendant. 4-Methyl-1-pentene was chosen because it is the acyclic analogue of 2-allylnorbornane.

As in the case of copolymers there are very few reports on the homopolymerization of cyclic/bicyclic α-olefins. The study of the coordination polymerization of cyclic/bicyclic α-olefins is of theoretical and practical interest since their polymers are expected to have high thermal stability and good mechanical properties. Poly(vinylcyclohexane) which contains a cyclohexyl pendant is known to be a tough polymer with a melting point above 300°C.[5] We were therefore interested in synthesizing poly(2-allylnorbornane) and study its properties.

Ethylene-α,ω- diene copolymers having moderate levels of diene incorporation, not only possesss properties such as improved tensile strength and impact strength due to the presence of short chain branches arising from the comonomer as in LLDPE's, but also possess improved properties such as better paintability, printability and adhesion. The presence of residual unsaturation also makes them amenable for further functionalization. Generally a diene containing an alpha olefin and a hindered di or tri substituted double bond is used in which case the enchainment occurs through the alpha olefin.

One of the interesting features of the homogeneous catalysts based on metallocene/MAO is their ability to polymerize and copolymerize cyclic olefins,such as, cyclopentene and norbornene with high levels of comonomer incorporation and without any accompanying ring opening reactions.[6,7]

We reasoned that if a diene like 5-vinyl-2-norbornene (5V2NB) containing an endocyclic strained double bond and exocyclic less strained vinyl bond, is chosen and the metallocene/MAO catalyst system is employed, then, one can expect the endocyclic olefin to selectively take part in polymerization, leaving the less strained exocyclic vinyl double bond free as a pendant unsaturation.

A few patents exist on the copolymerization of ethylene with 5-vinyl-2-norbornene, using Mg-Ti catalysts. However, the amount and selectivity of diene insertion is not specified. Lohse *et al*[8] have studied the terpolymerization of ethylene and propylene with 5-vinyl-2-norbornene using $VOCl_3$/ethylaluminum sesquichloride catalyst. They confirmed by IR that the enchainment of the diene in the terpolymer occurred through the endocyclic vinylene bond. The level of incorporation of the termonomer was restricted to less that 1 mol. %.

Polyolefins, have very desirable properties such as good mechanical strength, rigidity, chemical and solvent resistance and relatively good environmental stability, however, due to their chemical inertness, they form incompatible blends with other families of polymers and also lack the ability to form block and graft copolymers with functional group containing monomers.

The introduction of a small amount of functionality in polyolefins can help in overcoming their inertness and improving their paintability, permeability, printability, adhesion and compatibility with other functionalized polymers. Furthermore, the functional group offers sites for initiating graft copolymerization, which leads to useful applications such as compatibilizers in blends containing polyolefins. Chung *et al*[9,10] in a series of papers have demonstrated the utility of borane containing olefin monomers in Ziegler-Natta polymerizations and copolymerizations. The borane group does not interfere in the polymerizations and can be subsequently converted to polar functionalites, resulting in functional polyolefins. In view of the current interest in functional polyolefins we were interested in examining the possibilities of functionalization of residual double bond of the ethylene 5-vinyl-2-norbornene copolymers.

Approaches

a) study the homo- and copolymerization of an α-olefin containing a bicyclic pendant namely, 2-propenylbicyclo[2.2.1]heptane or 2-allylnorbornane using Ziegler-Natta catalysts and characterize the resultant polymers. Furthermore the properties of the above polymers were to be compared with the corresponding homo- and copolymers of their acyclic analogue namely 4-methyl-1-pentene. It was hoped that this would lead to an understanding of the effect of the bicyclic pendant on polymer properties.

b) conduct polymerization of ethylene with a bicyclic diolefin namely, 5-vinyl-2-norbornene, and hence to examine the regioselectivity of insertion between a hindered endocyclic vinylene double bond and a less hindered exocyclic vinyl double bond.

c) examine approaches to functionalization of the pendant double bond in the ethylene-5-vinyl-2-norbornene copolymers.

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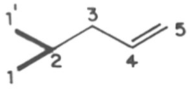
CHAPTER III

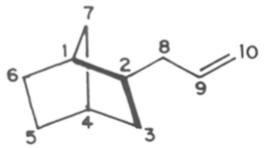
HOMOPOLYMERIZATION OF 2-ALLYLNORBORNANE USING ZIEGLER-NATTA CATALYSTS

3.1 INTRODUCTION

The study of the coordination polymerization of higher α-olefins is of theoretical and practical interest since their polymers are expected to have high thermal stability and good mechanical properties. 4-Methyl-1-pentene(**1**) which has an isopropyl branch at the β position has a melting point of 235°C and excellent optical transparency[1]. Poly(vinylcyclohexane) which contains a cyclohexyl pendant is known to be a tough polymer with a melting point above 300°C.[2] Surprisingly, olefins with more complex branching at the β position have received practically no attention. One such olefin which is a bicyclic analogue of 4-methyl-1-pentene is 2-propenyl-bicyclo [2.2.1] heptane (2-allylnorbornane) (2ANB,**2**).



1



2

Monomers **1** and **2** differ mainly in the type of branching at the position β to the unsaturation. It was therefore of interest to examine the properties of poly (2-allylnorbornane) (PANB) and compare them with the properties of poly (4-methyl-1-pentene) (PMP) in order to understand the effect of the bicyclic group. Except for a solitary patent[3] there are no reports on the homopolymerization of 2-allylnorbornane.

This chapter describes the results of the synthesis and characterization of poly (2-allylnorbornane).

3.2 EXPERIMENTAL SECTION

All manipulations involving polymerization were performed using standard inert atmosphere bench top techniques.

3.2.1 Materials

Heptane (S.D. Chem.) was washed with concentrated sulfuric acid followed by water and dried over anhydrous $CaCl_2$. It was distilled over sodium-benzophenone prior to polymerization.

Norbornene (Aldrich), allylbromide (Aldrich), magnesium turnings (Loba Chemie), triisobutyl aluminum (TIBAL), diethylaluminum chloride (DEAC) and methylaluminoxane (MAO, 5% wt. of Al, Me/Al=1.53) (all from Schering A.G-., Germany)), $TiCl_4$ (99%, Aldrich) and $TiCl_3$ 0.33 $AlCl_3$ (Toho Titanium Co., Japan) were used as received.

3.2.2 Preparation of 2-allylnorbornane

The method adopted for the preparation of 2-allylnorbornane is shown [illegible]

(a) Preparation of 2-chloronorbornane

2-Chloronorbornane was prepared according to reference 4. A slow stream of HCl gas was passed through a solution of norbornene in n-hexane at -70°C till complete addition of HCl to the double bond occurred. The temperature was then increased to 30°C. The reaction mixture was concentrated on a rotavapor and then distilled to yield 2-chloronorbornane, yield = 90%, b.p = 161°C (lit[4] b.p= 52°C/11 torr). ^1H NMR ($CDCl_3$, ppm) : 3.8 (doublet of triplet, 1H), 2.4 - 0.9 (aliphatic H's, 10H).

(b) Grignard coupling of norbornylmagnesium chloride with allylbromide

2-Allylnorbornane was prepared by a Grignard coupling reaction of norbornylmagnesium chloride with allylbromide as follows : A 500 mL four necked flask fitted with a nitrogen inlet, condenser, addition funnel and an overhead stirrer was cooled under a flow of nitrogen. To this 11.6 g (0.4 mol + 20% excess) of magnesium turnings and a crystal of iodine was added and the flask flamed under nitrogen. Then 80 mL THF was added and allowed to reflux with stirring to activate the magnesium turnings. To this 53 g (0.4 mol) of chloronorbornane in 100 mL THF was added dropwise through the addition funnel. The exothermic addition lasted 3 h. The norbornylmagnesium chloride was refluxed for a further 3 h and cooled. A 1 L three necked flask fitted with a condenser, addition funnel, magnetic stirrer bar, nitrogen inlet and outlet was cooled under nitrogen. Then 55 g (0.45 mol) allylbromide in 200 mL THF was added. The norbornylmagnesium bromide prepared earlier was transferred into the addition funnel of the 1 L flask and added at a rate to maintain reflux. The addition took place over a period of 3 h and was stirred for a further 2 h. The reaction mixture was then worked up by hydrolyzing with aq. ammonium chloride and extracting the organics in pet-ether. The organic layer was concentrated on a rotavapor and then distilled to yield 2-allylnorbornane (2-ANB) 50 g (90% yield). b.p = 164°C (lit[6] b.p = 50°C/3 torr).

^{1}H NMR ($CDCl_3$, ppm) 5.5-6 (m, 1H, - CH=C), 4.8-5.1 (m, 2H, -C=CH_2) 1-2 (13H, aliphatic H). ^{13}C NMR ($CDCl_3$, ppm) 138.9 (=CH, endo), 138.2 (=CH, exo), 114.9 (=CH_2, exo), 114.5 (=CH_2, endo) 40-20 (aliphatic C's). IR (smear, cm^{-1}) 3080-C-H stretch, 1630 C=C stretch, 1460 δC-H in plane, 900, 1000 δ C-H out of plane. Density at 30°C = 0.8659. Purity by G.C. 97% 2-allylnorbornane, 3% chloronorbornane.

(c) Purification of 2-allylnorbornane by treatment with triethylaluminum

Due to the close boiling points of 2-allylnorbornane and 2-chloronorbornane the unreacted 2-chloronorbornane in the Grignard coupling reaction distills out along with 2-allylnorbornane as is evident from the G.C. results. It was decided to convert the 3% 2-chloronorbornane into ethylnorbornane (inert to Ziegler-Natta catalysts) using triethylaluminum. The procedure followed is similar to reference 5.

A 500 mL three-necked flask was fitted with a nitrogen inlet, condenser with ice water circulation, nitrogen outlet and septum. To this 120 mL dry CH_2Cl_2 was added followed by a solution of 6 g (0.05 mol) triethylaluminum in 5 mL CH_2Cl_2. This was followed by dropwise addition of 2-allylnorbornane 130g containing 3% 2-chloronorbornane impurity. A slight exotherm was observed. The reaction was refluxed for a further 1h and then the excess triethylaluminum was treated with 10 mL cold methanol. It was then treated with 15-20 mL sat. aq. sodium potassium tartarate and the organics were extracted in n-hexane. 2-Allylnorbornane was recovered by concentrating on a rotavapor and distillation G.C. : 95% 2-allylnorbornane, 4.5% ethylnorbornane. Since 2-ethylnorbornane is inert to Ziegler-Natta catalysts this purity was considered sufficient for polymerizations.

(d) Preparation of exo-2-allylnorbornane

This was prepared following the procedure reported in reference 6.

To 10 g (0.2 mol + 20% excess) of magnesium turnings activated with a crystal of iodine was added 50 mL of dry THF. The pot temperature was brought to -5 to 0°C and 24 g of allylbromide dissolved in 170 mL THF was added in a dropwise manner over a period of 16 h such that the reaction temperature does not exceed 0°C. It was then slowly brought to room temperature. In an ampoule was added 18.4 g (0.2 mol) norbornene dissolved in 12 mL THF. The Grignard reagent (allylmagnesium bromide) was added through a cannula into the ampoule, shaken and sealed. The ampoule was kept in an oil bath at 80-90°C for 5 days. The seal of the ampoule was broken and poured into aq. NH_4Cl on ice and organics were extracted into pet-ether concentrated on a rotavapor and distilled. b.p = 164°C (lit[6] b.p = 50°C/3 torr). Yield = 6.5 g (conversion = 25%). ^1H NMR ($CDCl_3$, ppm) similar to that under section 3.2.1(b), ^{13}C NMR ($CDCl_3$, ppm) 138.2 (=CH, exo), 114.9 (=CH_2, exo) 40-20 (aliphatic C's).

3.2.3 Homopolymerization of 2-allylnorbornane using $TiCl_4/(isoBu)_3Al$

To an ampoule, which was oven dried for 12 h and cooled under nitrogen was added 42 mL of heptane, 9.9 mL of 30% triisobutylaluminum in heptane (0.015 mol), 9.5 mL of 10% $TiCl_4$ solution in heptane (0.005 mol) and 11.8 mL (10.2g, 0.075 mol) 2-allylnorbornane. The ampoule was frozen under liquid nitrogen, evacuated and sealed. It was then maintained at 80°C for 4 h and polymerization terminated by pouring in excess of acidified methanol. Yield of poly (2-allylnorbornane) (PANB1) = 6.8 g (65 % conversion). ^{13}C NMR : (1,2, 4 trichlorobenzene, ppm) no peaks in the region 115, 130, 45-20 (aliphatic C's) IR (film, cm^{-1}) absence of peak at 1630, presence of peaks at 3050-2800 C-H stretch, 1460 C-H bending.

Unreacted monomer was recovered from the filtrate by extracting into pet-ether, concentrated on a rotavapor and distilled using a microdistillation unit. The recovered monomer was analyzed by G.C. and N.M.R.. G.C. conditions : oven temp. 90°C, injection temp. and detector temp.= 150°C, nitrogen flow rate = 30 mL/min., retention time:5.54 min(2 ANB 60%), 6.22 min(40%).^{1}H N.M.R. ($CDCl_3$, ppm) 6 - 4.7 (multiplet), 2 - 0.5 (aliphatic H's).

3.2.4 Homopolymerization of 2-allylnorbornane using $TiCl_3$ 0.33 $AlCl_3/Et_2AlCl$

A 75 mL three necked jacketed reactor fitted with a nitrogen inlet, rubber septum, condenser and nitrogen outlet was cooled under a flow of nitrogen. In a dry box, a preweighed quantity of $TiCl_3$ 0.33 $AlCl_3$ (0.903 g, 4.5×10^{-3} mol) was transferred into the flask. This was followed by syringing in 60 mL of n-heptane, 10 mL of 2-ANB (0.0682 mol) followed by 5.5 mL of a 30% solution of Et_2AlCl in n-heptane (0.0136 mol). The reactor was maintained at 80°C for 4 h after which the polymerization was terminated by pouring in excess of acidified methanol. Yield of poly(2-allylnorbornane) (PANB2) = 7.3 g (61% conversion). ^{1}H NMR and IR as reported for PANB1. The unreacted monomer was recovered in a similar manner as section 3.2.3. G.C. retention time 5.56 min (2-ANB 70%), 22.5 min (30%).

3.2.5 Homopolymerization of 2-allylnorbornane using Cp_2ZrCl_2/MAO

2-Allylnorbornane (1.57 g, 0.0115 mol) was distilled over triisobutylaluminum into a Schlenk type round bottomed flask containing a magnetic needle and septum fixed over it. To this MAO solution (0.25 mL, 5×10^{-4} mol of Al) was added followed by a solution of Cp_2ZrCl_2 in toluene (5×10^{-7} mol)· The reaction was left stirring for 24 h and terminated by pouring into acidified methanol. An oligomer was obtained as a sticky whitish mass. Yield = 1.25 g (conversion = 80%). IR (smear, cm^{-1}) 3050-2800 C-H stretch, 1660 C=C stretch, 1470 C-H bend, 900 C-H bend. ^{1}H NMR ($CDCl_3$, ppm) 4.66 (singlet, 2H) 2.2-0.5 (multiplet, 46 H aliphatic H).

3.2.6 Analytical techniques

IR spectra were recorded on a Perkin-Elmer PC 16 FTIR on films (150-200 μ thickness) compression moulded on a Carver Press at 155°C and 500 psi. ^{13}C NMR of the homopolymers were recorded using a 300 MHz Bruker MSL spectrometer at 120°C on 10 wt. % samples in 1,2, 4 trichlorobenzene containing about 10% by volume of deuterated benzene for lock purpose. The spectra were recorded under quantitative conditions (pulse delay > 5 T_1). ^{1}H NMR and ^{13}C NMR of 2 ANB were recorded on a 80 MHz spectrometer. Thermogravimetric analysis was carried out using a Netzsch thermal analysis apparatus model STA 409. Differential scanning calorimetric analysis was done on a Perkin Elmer DSC 7. X-ray diffraction analysis was done using a Philips x-ray diffractometer. G.C. analysis was done on Hewlett Packard 5730, gas chromatograph using a 10% SE-30 column and nitrogen as a carrier gas..

3.3 RESULTS AND DISCUSSION

3.3.1 Homopolymerization of 2-ANB using heterogeneous Ziegler-Natta catalysts

The results of the homopolymerization of 2ANB using $TiCl_4/(iso\text{-}Bu)_3Al$ and $TiCl_3$ 0.33 $AlCl_3/Et_2AlCl$ catalysts is shown in Table 3.1. The main features of this polymerization are the relatively low catalyst activity and isomerization of the monomer. As can be seen from Table 3.1 the activities are low (6-8 g polymer/gTi/h) and high Ti concentrations are required. Krentzel *et al*[7] in a study on homopolymerization of 3-methyl-1-butene, 4-methyl-1-pentene and vinyl cyclohexane using $TiCl_4/Et_3Al$, $TiCl_3/(isoBu)_3Al$ have also observed such high catalyst consumption rates especially in the case of 3-methyl-1-butene. This can be attributed to :

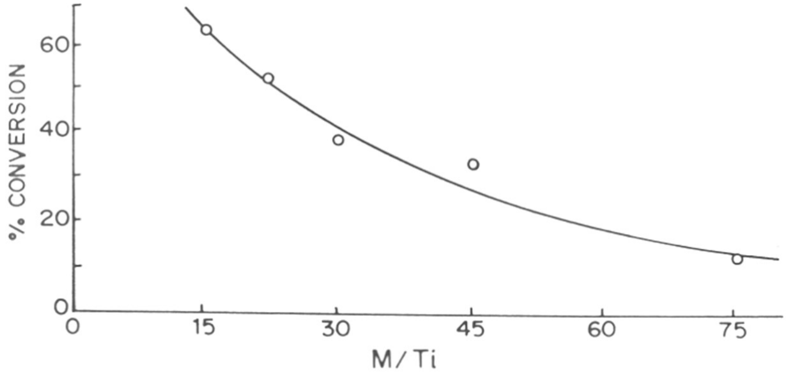
(1) the adsorption of isomers on the catalytically active sites of polymerization.

(2) the adsorption of poly (2-allylnorbornane) on the catalyst sites which lead to diffusion retardation of 2 ANB polymerization, especially so because PANB is practically insoluble in common solvents for polyolefins.

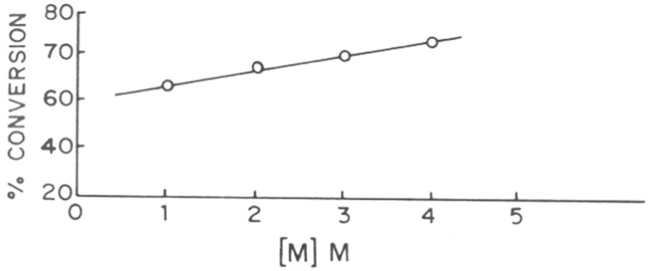
Use of only $TiCl_4$ or $(isoBu)_3Al$ did not result in any polymerization, implying the absence of cationic processes.

A preliminary study of the kinetics of 2ANB polymerization over $TiCl_4/(isoBu)_3Al$ catalyst was conducted.

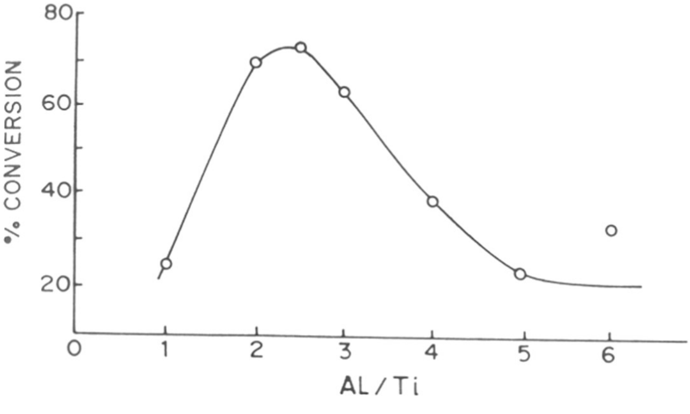
A first order dependance of conversion on monomer concentration was observed (Fig 3.1) and a second order dependance on catalyst concentration (Fig 3.2). Fig 3.3 shows the effect of Al/Ti ratio on polymerization. Conversion increases upto Al/Ti = 2.5 and then decreases with further increase in the Al/Ti ratio. This is attributed to the competition between the aluminum alkyl and monomer for



3.1 Effect of M/Ti ratio on % conversion.



3.2 Effect of monomer concentration on % conversion.



3.3 Effect of Al/Ti ratio on % conversion.

Table 3.1 **Homopolymerization of 2-allylnorbornane using conventional heterogeneous Ziegler-Natta catalysts[a]**

Sr. No.	Catalyst system	[Al] M	[Ti] x 10^2 M	Yield 'g'	Conversion %	Activity g poly./gTi/h
1.	$TiCl_4$ /Al(iso Bu)$_3$	0.2	6.8	6.8	65	7.1
2.	$TiCl_3$.O.33 $AlCl_3$/Et_2AlCl	0.18	6.06	7.3	61	8.0

(a) Polymerization conditions : solvent = heptane(70mL), Al/Ti = 3, temperature = 80°C, time = 4 h, [M] = 1M.

Table 3.2 Fractionation of poly(2-allylnorbornane)

Sr. No.	Fraction	Weight %	1DT	T_m	ΔH_f J/g
1.	Whole polymer	-	382	-	-
	Xylene soluble[a]	60	383	-	-
	Xylene insoluble	40	414	351	9.7
2.	Whole polymer	-	373	-	-
	Xylene soluble	11	376	-	-
	Xylene insoluble	88	414	355	17.5

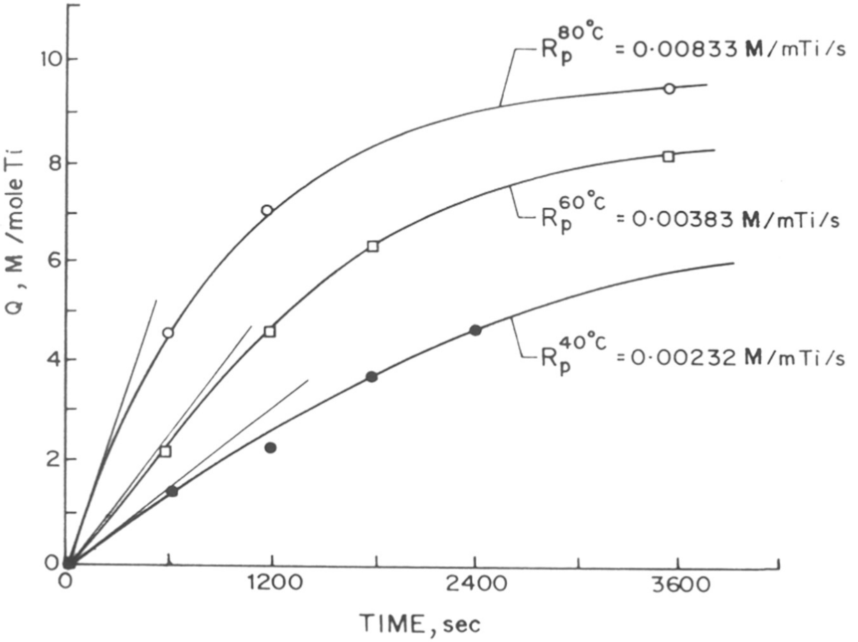
(a) Intrinsic viscosity in 1,2,4, trichlorobenzene at 135°C = 0.096 dL/g.

catalyst absorption sites or to the reduction of $TiCl_4$ to its lower active forms.

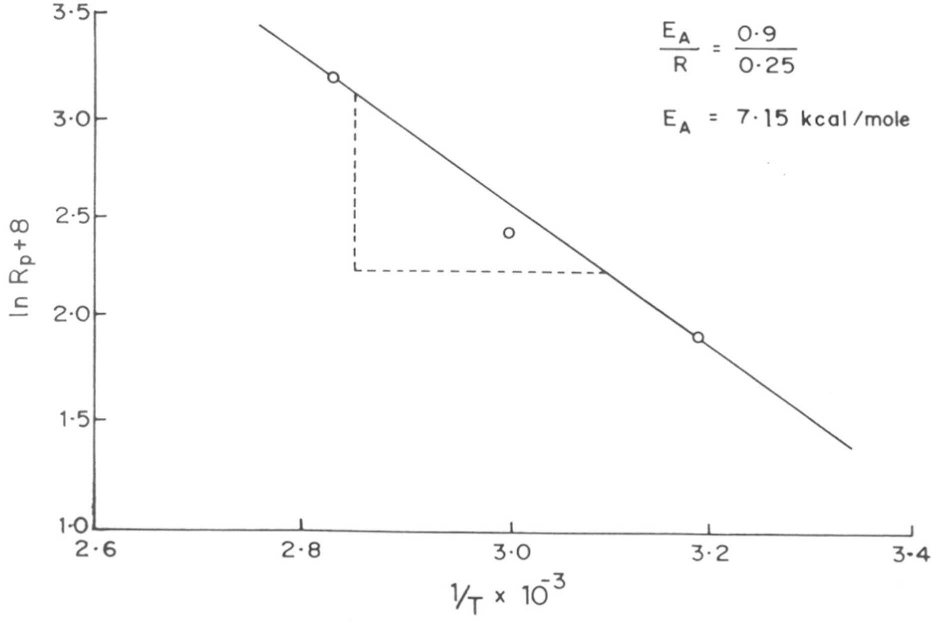
When the polymerization was conducted at three different temperatures 40°, 60° and 80°C the conversion was found to decrease with decrease in temperature. Further the conversion Vs time plots at any particular temperature (Fig 3.4) show an initial high rate of polymerization upto 60 min after which the conversion remains unchanged. This behavior was already explained as arising due to the adsorption of internal isomers and the polymer which is unswelling and insoluble in the reaction medium. The slope of the initial part of the conversion versus time plots was used to calculate the initial rate of polymerization. On plotting in Rp Vs 1/T (Fig 3.5) on Ea value of 7.4 kcal/mol was obtained which falls within the range of values observed in the case of coordination polymerization of a double bond.

The low yields and plateau in the conversion versus time plots were attributed partly due to the competitive isomerization transformations of 2-allylnorbornane. This is supported by the analysis of the recovered monomer. The gas chromatographic analysis of the monomer recovered from polymerization (Fig.3.6) using a $TiCl_4/(isoBu)_3Al$ catalyst shows a peak at retention time 5.36 min (60% corresponding to 2-ANB) and at 6.04 min (40% corresponding to isomerized monomer). Its ^1H NMR shows a multiplet pattern between 6 and 4.7 ppm which can be interpreted as arising from unisomerized monomer 6 - 5.48 ppm (= CH) and 5.1-4.77 ppm (= CH_2) and isomerized monomer 5.44-5.2 ppm (HC=CH)(Fig.3.7). The ^{13}C NMR also shows a large number of peaks in the region 110-140 ppm mainly at 137, 124 and 114 ppm attributable to the monomer and the 2-isomer (Fig.3.8). Though the probability of the double bond migrating to an endocyclic position exists the exocyclic 2-isomer appears to be the most favoured isomer.

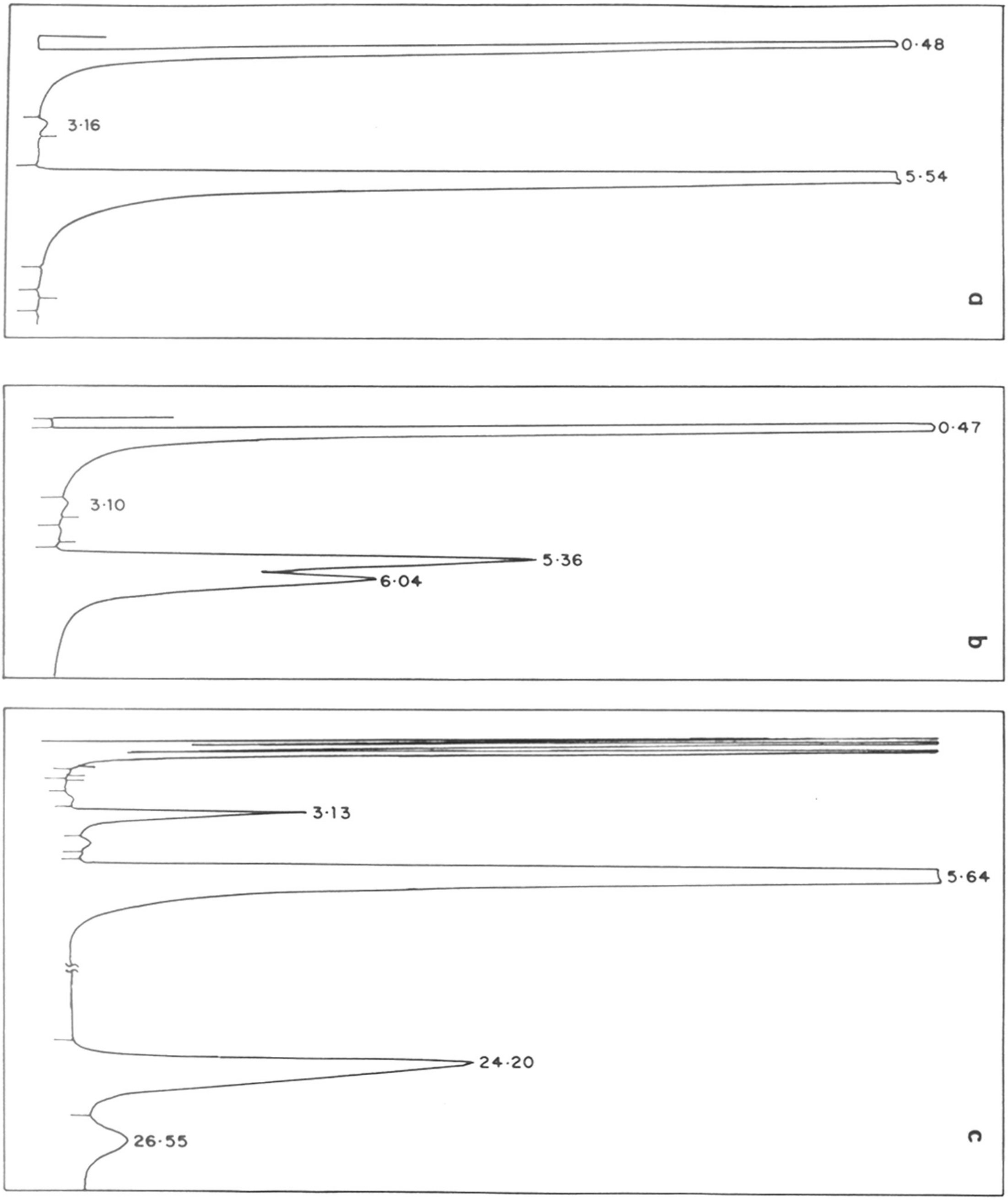
The monomer recovered from polymerization using $TiCl_3$ 0.33 $AlCl_3/Et_2AlCl$ catalyst was also analyzed by G.C. and N.M.R. G.C. shows peak at retention time 5.64 (70% corresponding to 2-ANB) and peak at 24.2 (30%



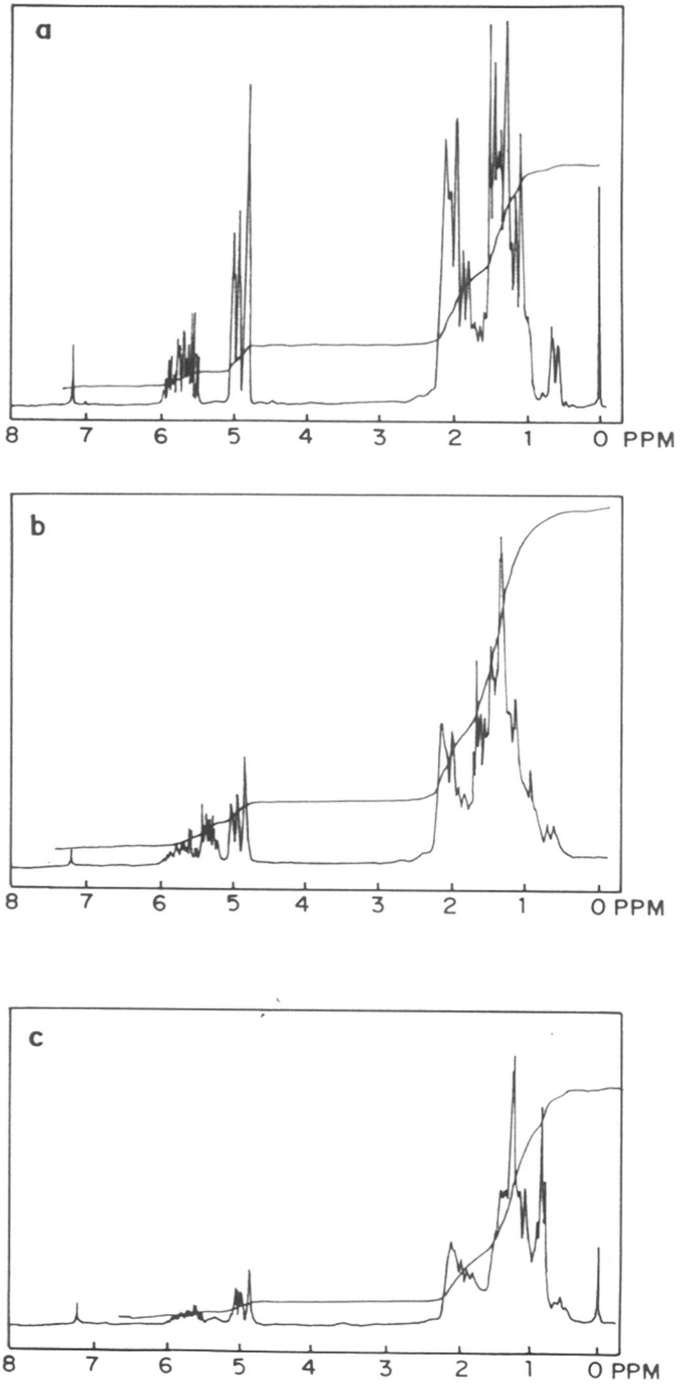
3.4 Plot of yield of poly(2-allylnorbornane) (Q) vs time at 40°C, 60°C and 80°C.



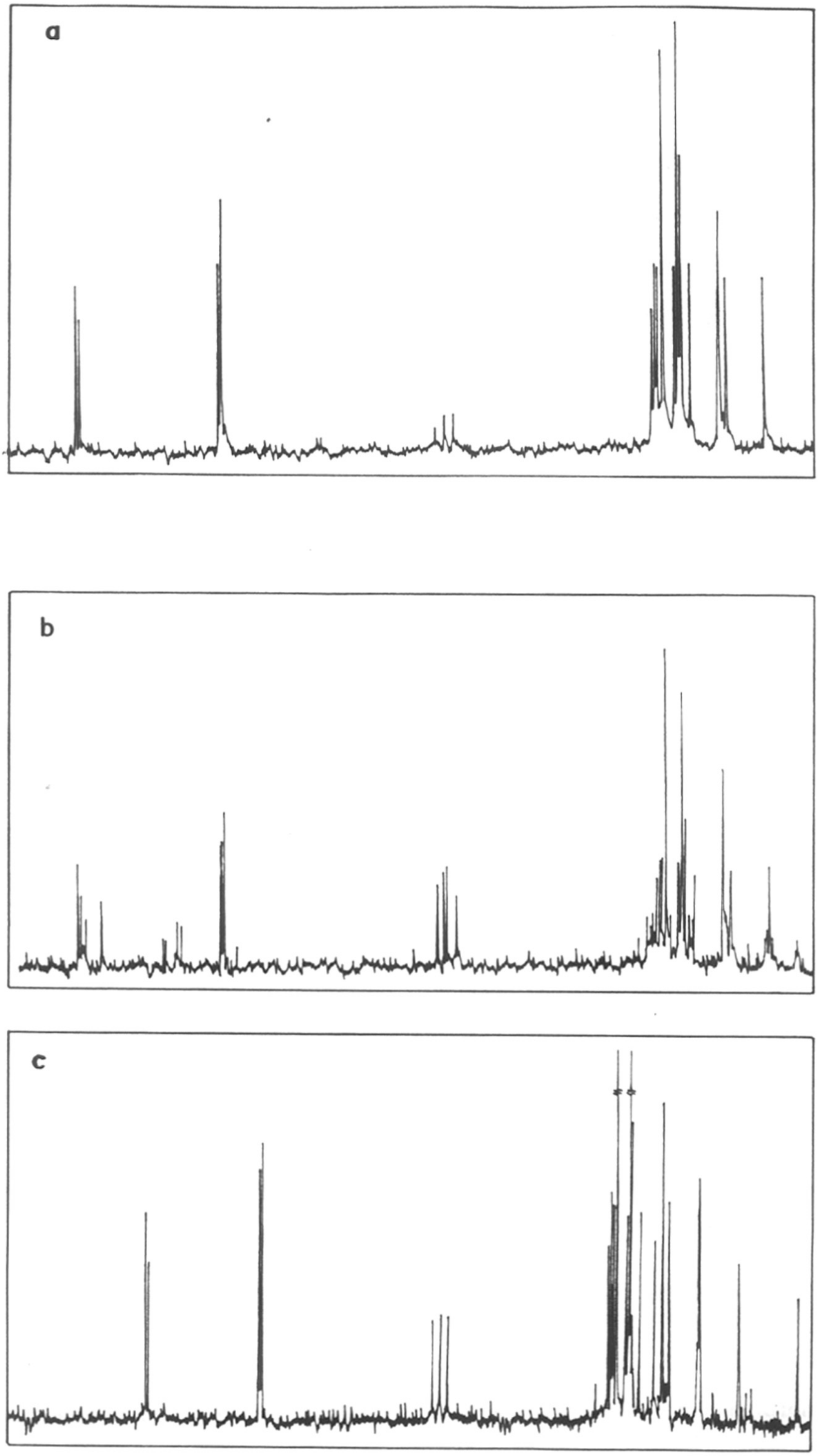
3.5 Activation energy determination from plot of ln Rp vs 1/T.



3.6 Gas chromatogram of (a) monomer (2-ANB), (b) recovered monomer (catalyst : $TiCl_4$/(iso $Bu)_3Al$) and (c) recovered monomer (catalyst : $TiCl_3$ 0.33 $AlCl_3/Et_2AlCl$).



3.7 ^{1}H NMR spectrum of (a) monomer (2-ANB), (b) recovered monomer (catalyst : $TiCl_4$/(iso $Bu)_3Al$) and (c) recovered monomer (catalyst : $TiCl_3$ 0.33 $AlCl_3/Et_2AlCl$).



3.8 ^{13}C NMR spectrum of (a) monomer (2-ANB), (b) recovered monomer (catalyst : TiCl$_4$/(iso Bu)$_3$Al) and (c) recovered monomer (catalyst : TiCl$_3$ 0.33 AlCl$_3$/Et$_2$AlCl).

corresponding to some high boiling oligomer) (Fig.3.6). This was fractionated into the low and high boiling fractions. The ^1H NMR of the low boiling fraction shows presence of a multiplet at 6-5.5 ppm corresponding to =CH and 5.1-4.8 corresponding to $=CH_2$ in addition to signals in the aliphatic region (Fig.3.7); whereas the high boiling fraction shows peaks in the aliphatic region only (2.2 - 0.6) ppm indicative of oligomer. The ^{13}C NMR of the low boiling fraction showed peaks at 138.9 (=CH, endo), 138.2 (=CH, exo), 114.9 ($=CH_2$ exo) and 114.5 ($=CH_2$, endo) in addition to peaks in the aliphatic region (Fig.3.8).

Furthermore, the ratio of endo : exo in the recovered monomer is the same as in the monomer that is 55:45. This implies that both the endo and exo isomers participate equally in the polymerization, with no selective insertion of either the endo or exo isomer.

Krentzel's studies[7] on 3-methyl-1-butene and 4-methyl-1-pentene showed that isomerization and polymerization occur on two different active sites with the isomerization proceeding on the Ti^{+2} sites. This holds true in our case also since no isomerization was observed with $TiCl_3$ catalyst due to the low content of Ti^{+2} as a result of the weak reducing capacity of Et_2AlCl. In the case of the $TiCl_4/(iso\text{-}Bu)_3Al$ isomerization of monomer occurs due to presence of Ti^{+2} sites in addition to $Ti.^{+3}$

Krentzel also found that though isomerization is observed during the polymerization 3-methyl-1-butene and 4-methyl-1-pentene, higher yields are obtained in the case of 4-methyl-1-pentene because of the higher rate of polymerization when compared to isomerization. When the rate of polymerization is low as in the case of 3-methyl-1-butene or 2-allylnorbornane, isomerization becomes competitive and results in low yields of polymer.

3.3.2 Characterization of poly (2-allylnorbornane) P2ANB

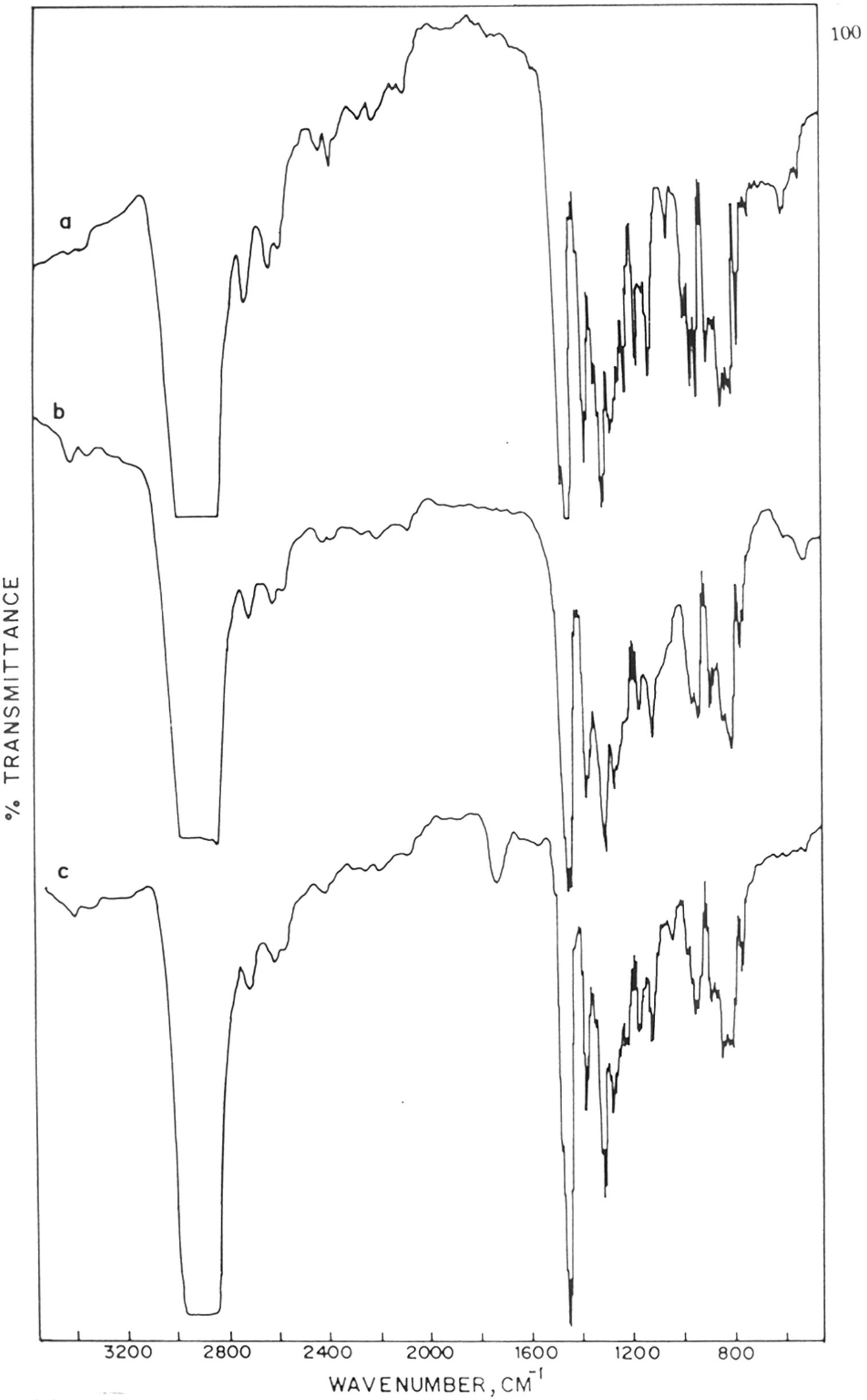
3.3.2.1 Solubility : The whole polymers, samples 1 and 2 (Table 3.1) are found to be partially soluble in 1,2,4 trichlorobenzene, xylene, decalin etc. Fractionation of these two samples was done in xylene using standard procedures (Table 3.2). A major fraction of PANB obtained using $TiCl_3$ catalyst and about 50% of PANB obtained using $TiCl_4$ catalyst is insoluble in hot xylene. Branched polymers such as poly (3-methyl-1-butene), poly (2-phenyl-1-propene)[8] are examples of polymers which are also only partially soluble in hot xylene. If one assumes the xylene soluble fraction to be nonstereospecific and the xylene insoluble fraction to be stereospecific, then the $TiCl_4$ catalyst gives 40% isotacticity and the $TiCl_3$ catalyst gives 88% isotacticity.

The bulk, soluble and insoluble fractions of poly(2-allylnorbornane) were characterized using NMR, IR, XRD and thermal techniques.

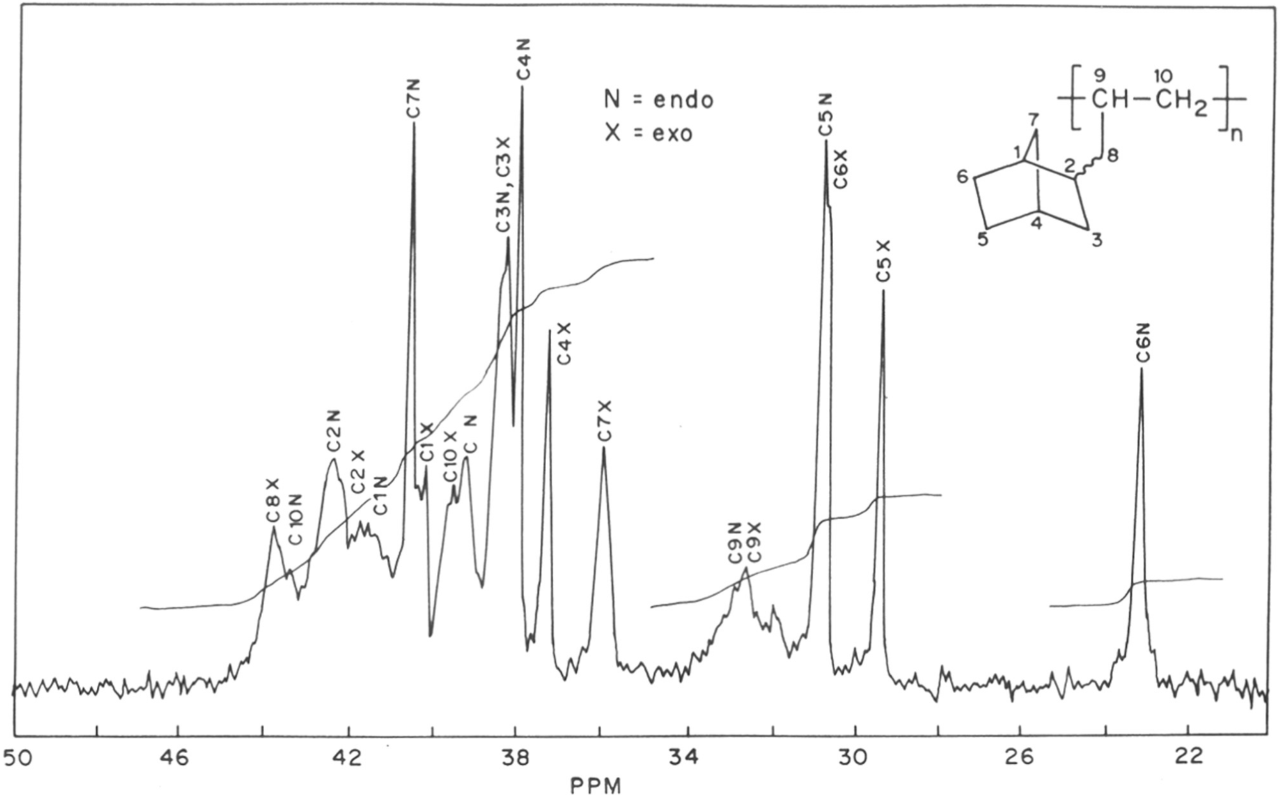
3.3.2.2 Infrared spectroscopy : Peaks characteristic of the norbornane ring[9] and polyethylene signals are seen in the IR spectra (Fig.3.9). No peaks characteristic of tacticity could be distinguished.

3.3.2.3 Nuclear magnetic resonance spectroscopy : The ^{13}C NMR spectra were recorded of the PANB whole polymer, the xylene soluble and xylene insoluble fractions. The spectra were recorded at 120°C at which temperature the xylene insoluble fraction is not soluble but exists as swollen gel particles. It was found that there is not much difference between the spectra of the xylene soluble and xylene insoluble fractions. The ^{13}C NMR of PANB shows presence of a large number of peaks in the 20-45 ppm region (Fig 3.10). The peak assignments of the polymer, were based on the peak assignments of exo/endo 2-ANB, DEPT spectra(Fig.3.11), and peak assignments of 2-vinylnorbornane[10].

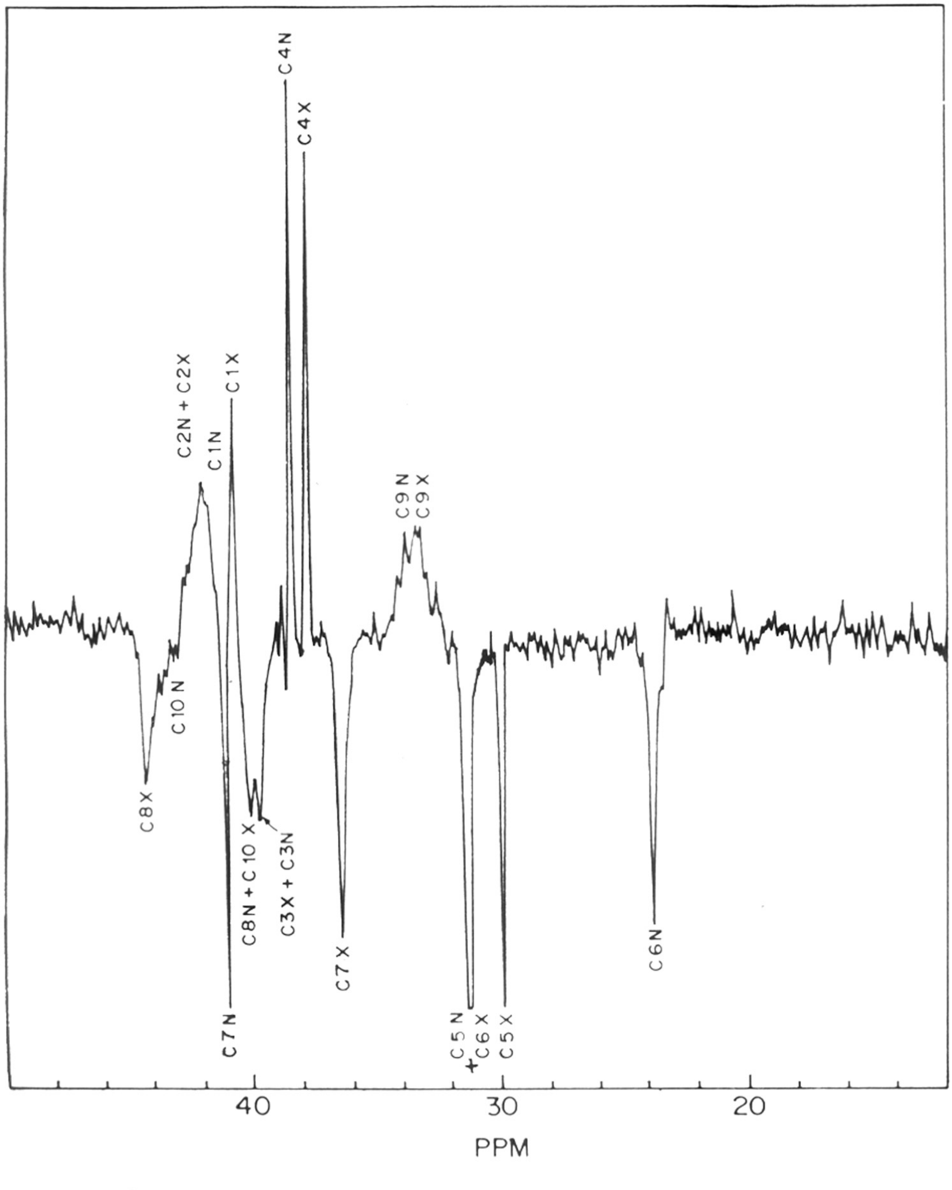
The chemical shifts of the monomer (Table 3.3) were used to assign the bicyclic carbons shifts in the polymer spectra. As observed in the case of 4-methyl-1-pentene and poly (4-methyl-1-pentene) (Table 3.4) we expect only the carbons participating in the polymerization to appear at new positions, with the pendant carbons appearing at the same positions as in the monomer.



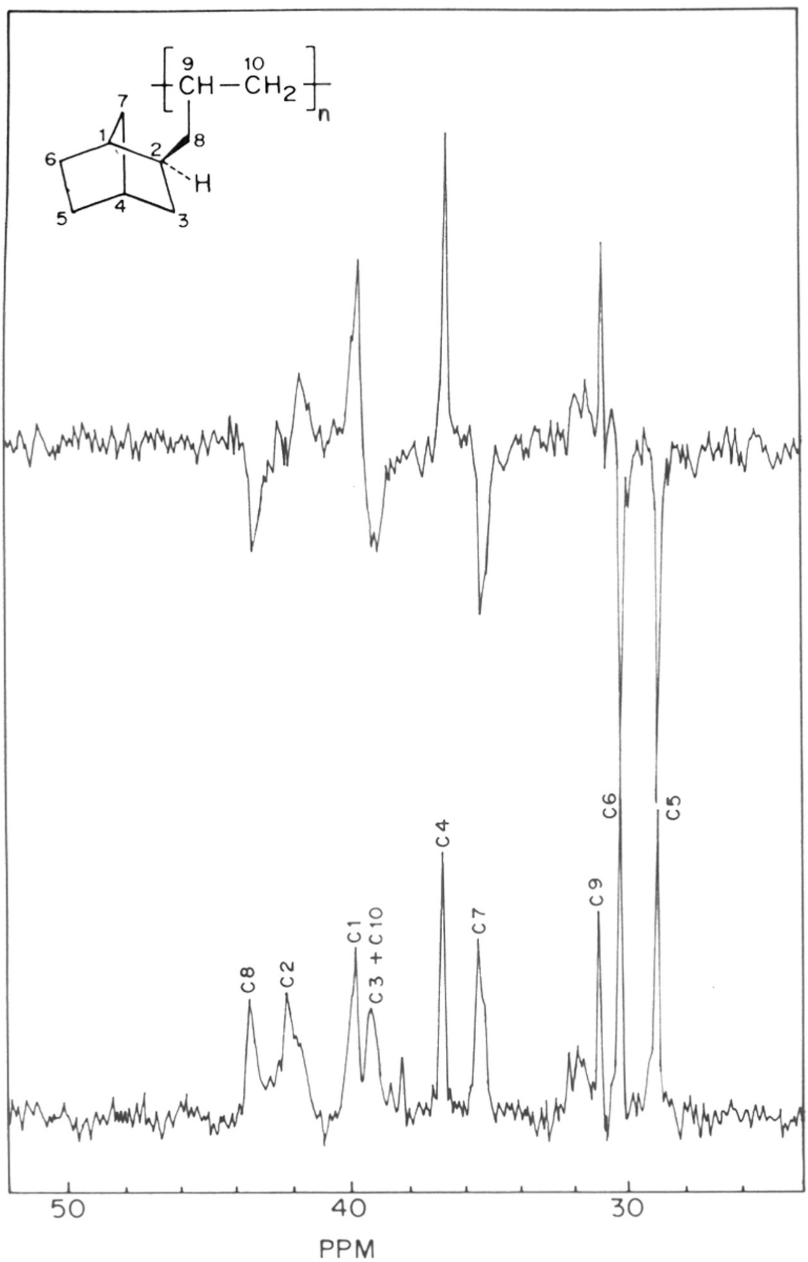
3.9 IR spectra of (a) poly(2-allylnorbornane) (P2ANB) obtained using $TiCl_4$/(iso-Bu)$_3$Al, (b) its xylene soluble and (c) xylene insoluble fraction.



3.10 ^{13}C NMR spectrum of poly(2-allylnorbornane) (P2ANB).



3.11 DEPT spectrum of poly(2-allylnorbornane) (P2ANB).



3.12 ^{13}C NMR and DEPT spectrum of poly (exo-2-allylnorbornane).

Table 3.3 Peak assignments of the monomer (2-ANB) and polymer (PANB) spectra

Compound	C1	C2	C3	C4	C5	C6	C7	C8	C9	C10
exo-2ANB	40.6	41.6	37.7	36.6	28.8	30.0	35.1	41.0	137.9	114.7
P(exo-2ANB)	40.2	42.6	38.25	37.2	29.4	30.7	35.9	43.9	32.3- 31.5	39.78
endo-2-ANB	39.8	39.9	36.80	37.20	30.1	22.4	39.9	37.3	138.6	114.2
P(endo-2-ANB)	41.39	41.9	38.2	37.95	30.8	23.3	40.6	39.2	32.3 - 32.6	43.2 - 43.0

Table 3.4 Peak assignments of the monomer (4M1P) and polymer (P4M1P)

Compound	C1	C1^1	C2	C3	C4	C5
4M1P	22.32	22.32	28.32	43.58	137.83	115.41
P4M1P	22.40	22.40	24.80	45.00	30.30	41.40

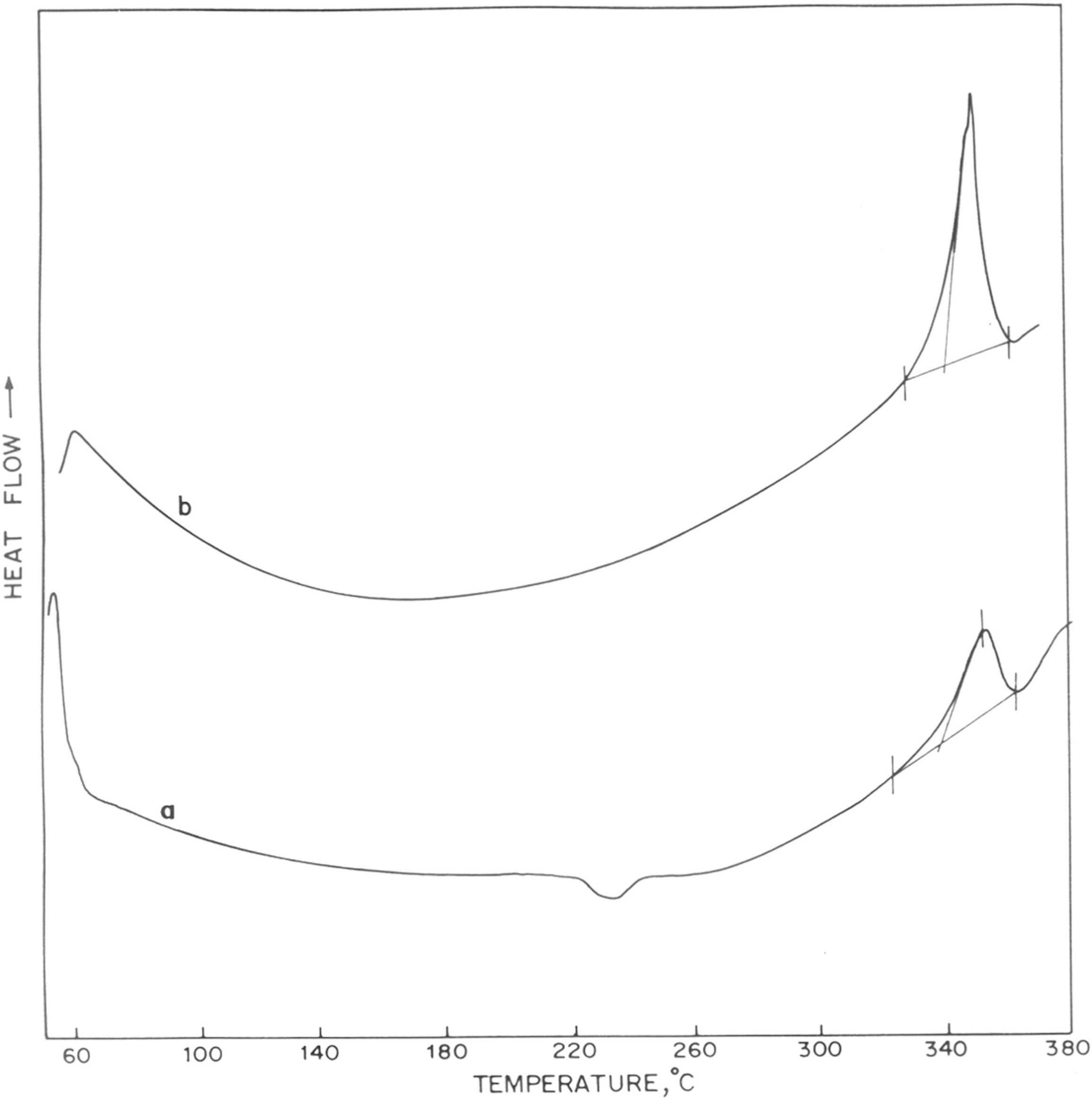
Before the assignments of poly (endo/exo-2-allylnorbornane) the peaks of poly (exo-2-allylnorbornane) (Fig 3.12) were assigned (Table 3.3). Here the chemical shifts of the bicyclic carbons are almost the same as in the case of the monomer and the change in shift of the backbone carbons as well as the β methylene is similar to that in the case of poly (4-methyl-1-pentene).

The peaks corresponding to the endo isomer in poly(exo/endo-2-allylnorbornane) are also assigned with the β methylene appearing upfield due to γ interaction with C6 carbon.

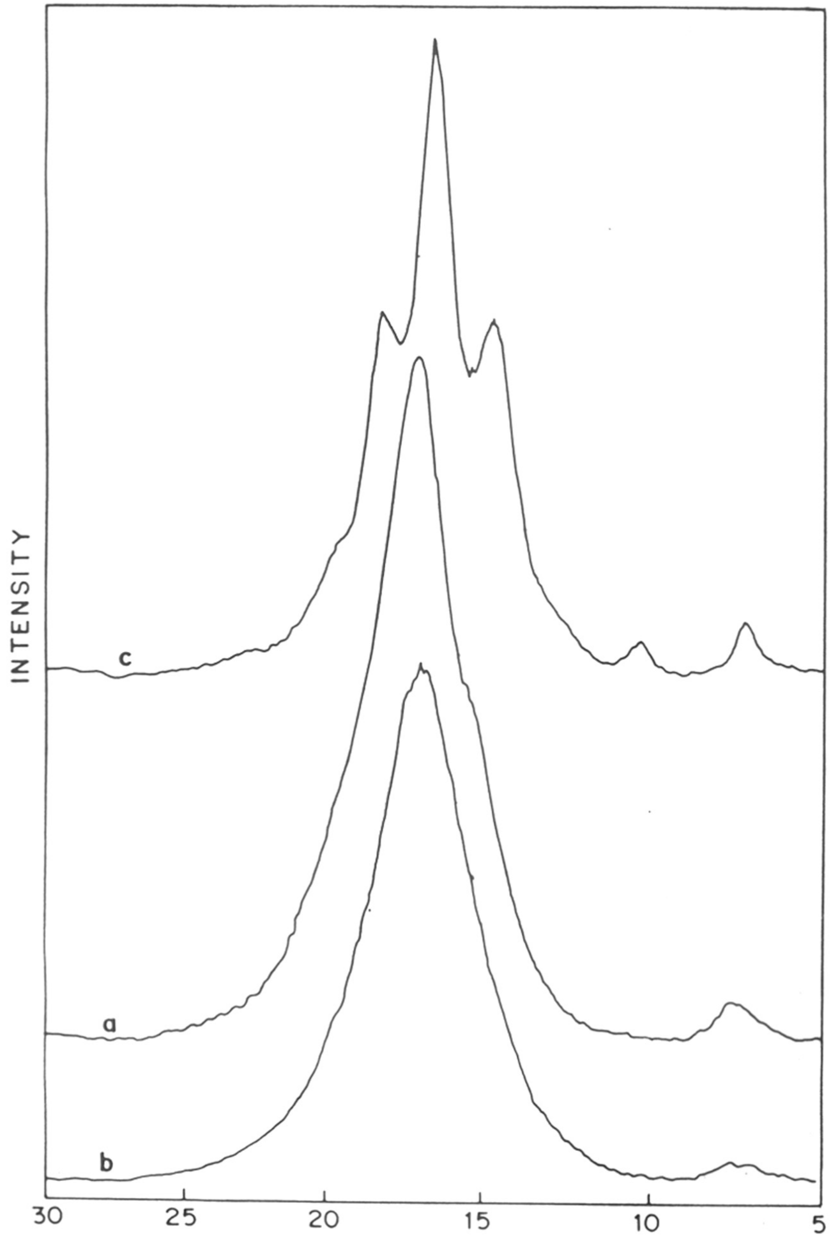
The endo C6 and the exo C5 carbon can be seen to appear well separated from the rest of the peaks. Based on the integral values of these two carbons it is found that the ratio of endo : exo isomer in the polymer is 55:45 which is the same as the endo:exo ratio present in the monomer used for the polymerization. This indicates that there is no selectivity towards either the endo or exo isomer during the insertion step in the polymerization. The same conclusion was also reached earlier based on quantification of the endo:exo ratio in the monomer and unisomerized recovered monomer. Absence of any selectivity during the enchainment could be attributed to the fact that the norbornyl pendant is one carbon away from the polymerization center.

3.3.2.4 Thermal analysis : The IDT, % decomposition and DSC data of samples 1 and 2 and their fractions are shown in Table 3.2. Poly (2-allylnorbornane) has a good thermal stability with IDT > 380°C under nitrogen. Out of all the fractions only the xylene insoluble fractions show a Tm between 351-355°C (Fig. 3.13).

3.3.2.5 X-ray diffraction : The x-ray diffraction patterns of PANB and its fractions are shown in Fig. 3.14. The whole polymer shows a major peak at 17.3° with a half width of 3.8 cm. The xylene insoluble fraction has two shoulders at 15.4° and 18.6° appearing on either side of the main peak at 17.2°. As can be seen from the x-ray diffraction patterns the degree of ordering is not high. This could be because neither the main chain nor the side chain can crystallize out due to the bicyclic pendant.



3.13 DSC plots of the xylene insoluble fraction of poly(2-allylnorbornane) (a) catalyst : $TiCl_4/(iso\text{-}Bu)_3Al$ and (b) catalyst : $TiCl_3$ 0.33 $AlCl_3/Et_2AlCl$.



3.14 X-ray diffraction pattern of (a) poly(2-allylnorbornane) (P2ANB) obtained using $TiCl_4$/(iso Bu)$_3$Al, (b) its xylene soluble and (c) xylene insoluble fraction.

3.3.3 Homopolymerization of 2-allylnorbornane using Cp_2ZrCl_2/MAO catalyst

It was found that under a variety of conditions (Table 3.5) only oligomers could be obtained. Earlier literature on the polymerizability of α-olefins using the catalyst system Cp_2ZrCl_2/MAO shows that except for propylene, other α-olefins give rise to oligomers or liquid polymers. 4-Methyl-1-pentene at M/Zr = 196,000, Al/Zr = 10 and monomer concentration 3.9 M is reported[11] to give rise to a liquid oligomer. 1-Hexene oligomers were obtained using Cp_2ZrMe_2/MAO at Al/Zr = 2500 by Resconi and Waymouth[12]. A patent[13] on the dimerization of olefins using metallocene/MAO catalysts reports that in the case of propylene a dimer is obtained at M/Zr = 500, Al/Zr = 32 and [M] = 5 M and small amounts of polymer start forming along with dimer at M/Zr = 10,000, Al/Zr = 600 and [M] = 5 M. However, we obtained a liquid oligomer even when the M/Zr ratio was 25,000 and monomer concentration was increased from 1 M to 4.8 M.

3.3.4 Characterization of the oligomer of 2-allylnorbornane

3.3.4.1 Vapor phase osmometry : The value of Mn as determined using VPO was 380. Mn expected in case of trimer = 408.

3.3.4.2 Infrared spectroscopy : Peaks characteristic of vinylidene double bonds at 1660 cm^{-1} and 900 cm^{-1} are observed.

3.3.4.3 ^{1}HNMR : A singlet at 4.66 ppm corresponding to the two vinylidene protons and a number of peaks in the region 0.5 to 2.2 ppm are seen. The ratio of integration of the vinylidene to aliphatic protons is 2:46 (Fig.3.15). This matches with the integration expected in the case of a 2-allylnorbornane trimer.

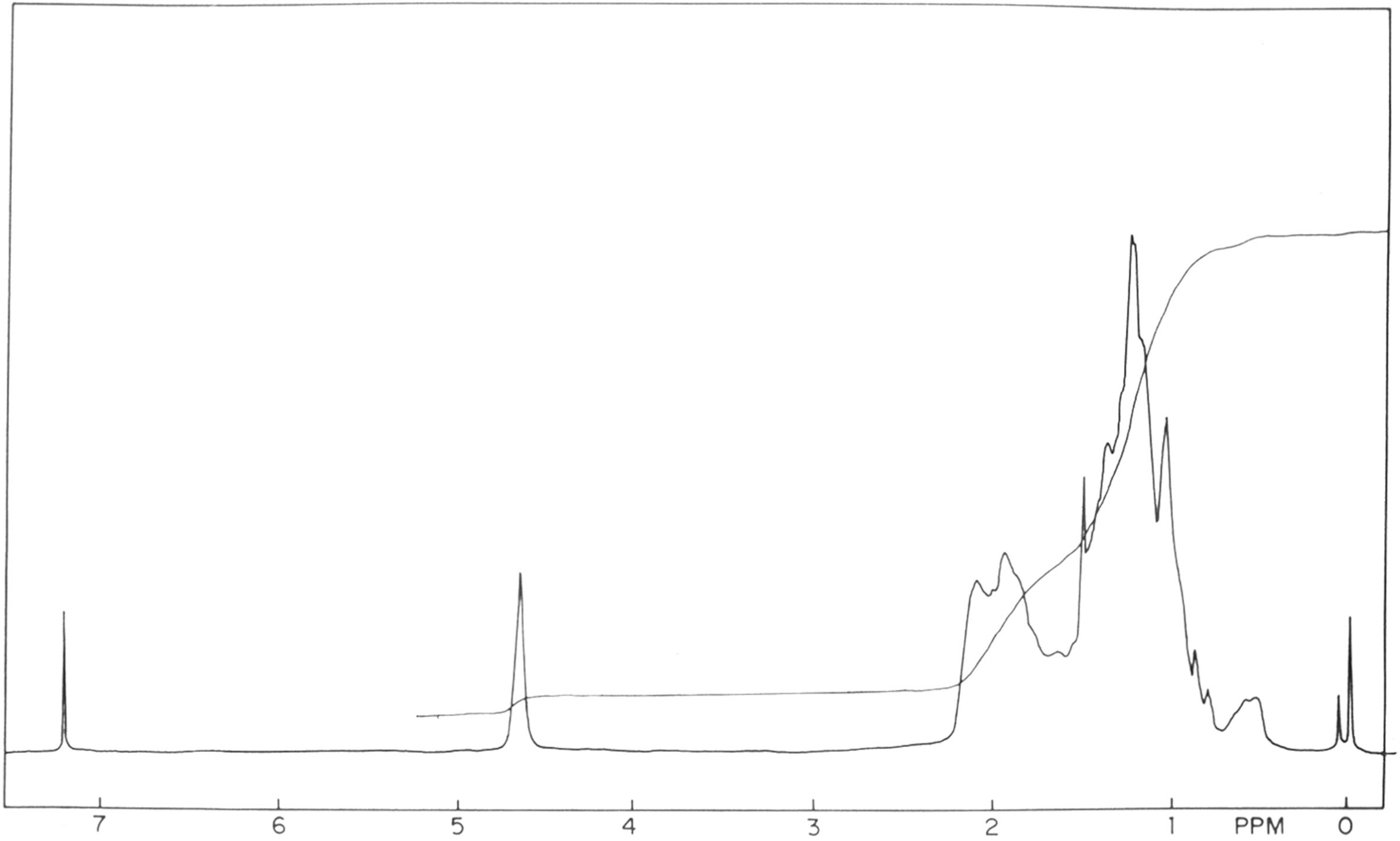
3.4 SUMMARY AND CONCLUSIONS

Polymerization of 2-allylnorbornane using $TiCl_4$ catalyst results in a polymer which is 40% insoluble in xylene at 130°C, whereas with $TiCl_3$ catalyst, a

Table 3.5 **Homopolymerization of 2-allylnorbornane using Cp_2ZrCl_2/MAO catalyst system**[a]

Sr. No.	[M] M	[Zr] M	[Al] M	[M]/[Zr]	[Al]/[Zr]	Yield 'g'	Activity Kg/mol Zr/h	$\overline{M}_n$
1.	1	5×10^{-5}	5×10^{-2}	25,000	1000	-	-	-
2.	3	1×10^{-4}	1×10^{-1}	30,000	1000	traces of oligomer	-	-
3.	4.8	2×10^{-4}	2×10^{-1}	23,190	1000	1.05	87.5	380

(a) Polymerization conditions : solvent = toluene, temperature = 50°C, time = 24 h.



3.15 ^{1}H NMR spectrum of oligomer of 2-allylnorbornane.

Table 3.6 Comparative data on 2-ANB and 4M1P polymerization

Polymerization System	**Conv. %**	**T_m °C**	**Fractionation**
2-ANB-$TiCl_4$/$(iso\text{-}Bu)_3Al$	65	351 (xylene insol. frac.)	60% hot xylene soluble 40% hot xylene insoluble
2-ANB-$TiCl_3 0.33AlCl_3$/Et_2AlCl	61	355 (xylene insol. frac.)	11% hot xylene soluble 88% hot xylene insoluble
4M1P-$TiCl_4$/$(iso\text{-}Bu)_3Al$	80	233(bulk)	53% xylene soluble 47% xylene insoluble
4M1P-$TiCl_3 0.33\ AlCl_3$/Et_2AlCl	89	235(bulk)	7% xylene soluble 93% xylene insoluble

polymer with 88% insolublity in xylene at 130°C is obtained. The whole polymers and fractions were characterized by spectroscopic and thermal methods. The xylene insoluble fractions gave a very high Tm = 355°C. The predominant features of these polymerizations are high catalyst consumption and low activity and in the case of $TiCl_4$ catalyst isomerization transformation of the monomer are observed. On comparison with the properties of poly(4-methyl-1-pentene) (Appendix I, Table 3.6) the partly insoluble nature of poly (2-allylnorbornane) and its high melting point are attributed to the presence of the bicyclic pendant.

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CHAPTER IV

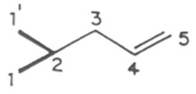
COPOLYMERIZATION OF ETHYLENE WITH 2-ALLYLNORBORNANE USING ZIEGLER-NATTA CATALYSTS

4.1 INTRODUCTION

The copolymerization of ethylene with linear α-olefins to produce polyethylene with substituted alkyl side groups (linear low density polyethylene) has gained considerable commercial importance as is evident from the literature presented in Chapter I. Linear α-olefins such as 1-butene, 1-hexene and 1-octene the most widely used comonomers due to their commercial significance are the most studied in literature, whereas α-olefins containing cyclic and bicyclic groups are not well studied. This could be because of the commercial non-significance of such copolymers due to the prohibitively high costs of such comonomers, and due to the fact that such α-olefins exhibit poor reactivity and unwanted side reactions with conventional Ziegler-Natta catalysts.

Recently, few reports have appeared in literature on the copolymerization of ethylene with vinylcyclohexane. The interest in these copolymers arises because of the anticipation that the bulky cyclohexyl substituent might lower the melting point and density of polyethylene more effectively than linear α-olefins. With this aim in mind Mani and Burns[1] synthesized copolymers of ethylene and vinylcyclohexane using the soluble catalyst system Cp_2ZrCl_2/MAO and Cp_2ZrMe_2/MAO. They found that upto 1.7 mol% of vinylcyclohexane could be incorporated into the polyethylene chains. The comonomer was found to be statistically distributed with the formation of short blocks at high comonomer concentration. They found that the cyclohexyl branches affect the physical properties of the copolymer by decreasing the melting point and crystallinity of the polymer. At 1.7 mol% incorporation they obtained a Tm of 119°C. Nekhaeva et al[2] also obtained similar results using the Cp_2ZrCl_2/MAO catalyst. At 1 mol% vinylcyclohexane incorporation they found that the melting point decreased from 127 to 122°C and density from 0.98 to 0.96. They also noted that the addition of vinylcyclohexane led to centers of higher activity. A similar rate enhancing effect of comonomer has been reported by many authors for both homogeneous and heterogeneous catalysts.[3-9]

An ethylene copolymer wherein the α-olefin contains a bicyclic substituent has not been reported in literature. One such α-olefin that we chose to study was 2-propenyl-bicyclo [2.2.1] heptane or 2-allylnorbornane. We expected the norbornyl pendant to lower the melting point and density of the polyethylene. Since α-olefins when copolymerized with ethylene lead to a decrease in density and melting point, it was of interest to compare the properties of the ethylene-2-allylnorbornane copolymers with those of ethylene-4-methyl-1-pentene copolymers at similar mol% incorporation. This could elucidate the specific effect of the bicyclic pendant. 4-Methyl-1-pentene was chosen because it is the acyclic analogue of 2-allylnorbornane.



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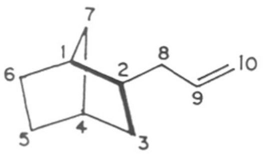

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Ethylene-4-methyl-1-pentene copolymers prepared with conventional Ziegler-Natta catalysts were studied by Kissin.[10] Copolymers were synthesized using the homogeneous $V(acac)_3/(isoBu)_2AlCl$ catalyst as well as the heterogeneous $TiCl_3/Et_2AlCl$ catalyst. The characteristic features of the copolymer prepared with the homogeneous catalyst were (i) IR indicated the copolymer contained both units from normal 1,2-addition and isomerized units of the type $-CH_2-CH_2-CH_2-C(CH_3)_2-$ (ii) The value of the reactivity ratio product $r_1.r_2$ was found to be equal to 0.7 implying a random type of copolymerization, with the copolymer becoming amorphous at about 20 mol% incorporation of 4-methyl-1-pentene. The characteristic features of the copolymer obtained with the $TiCl_3$ catalyst were, (i) the copolymer contained predominantly units arising from a normal 1,2-addtion, (ii) the product of reactivity ratios r_1r_2 was found to be $r_1.r_2$equal to 5, showing that the copolymer had a strong tendency towards block formation.

Copolymerization of ethylene and 4-methyl-1-pentene using supported catalysts was studied by Mulhaupt et al.[11] They found that using $MgCl_2$ incorporated with 2,6-d-tert-butyl-4-methylphenol a highly stereospecific catalyst is obtained. This catalyst when used in copolymerization resulted in low densities 0.919 of the copolymer.

Since the mol% incorporation and decrease in melting point and crystallinity are known to be dependent on the catalyst and conditions used, it was decided to synthesize ethylene-4-methyl-1-pentene copolymers in our laboratory (Appendix I) under conditions identical to those used for the synthesis of ethylene-2-allylnorbornane copolymers and then compare the melting and crystallinity data at same mol% incorporation.

It is well known that the homogeneous metallocene catalysts result in copolymers, which are more random and homogeneous in nature as compared to the heterogeneous Ziegler-Natta catalysts. The other objective of the study was to make a comparative study of the properties of the ethylene-2-allylnorbornane copolymers obtained with the heterogeneous $TiCl_4$-Al $(isoBu)_3$ catalyst and the homogeneous Cp_2ZrCl_2/MAO catalyst.

4.2 EXPERIMENTAL SECTION

All manipulations were performed using standard inert atmosphere bench top techniques.

4.2.1 Materials

Heptane (S.D. Chemicals, India) was washed with concentrated sulfuric acid and then neutralized with Na_2CO_3 and water and dried over anhydrous $CaCl_2$. It was distilled over sodium-benzophenone prior to use. Toluene (S.D. Chemicals, India) was also distilled over sodium-benzophenone prior to use. Preparation and purification of 2-allylnorbornane was done as described in Section 3.2.2. Polymerization grade ethylene was obtained from Indian Petrochemical Corporation Limited, Nagothane ($O_2 < 3$ ppm, $H_2O < 4$ ppm). Triisobutylaluminum (TIBAL), diethylaluminum chloride (DEAC), methylaluminoxane (MAO) (Me/Al =1.54, 15% Al solution in toluene) all from Schering A.-G. (Germany), $TiCl_4$(99%, Aldrich) $TiCl_3$ 0.33 $AlCl_3$ (Toho Titanium Company, Japan) and Cp_2ZrCl_2 (98%, Aldrich) were used as received.

4.2.2 Copolymerization of ethylene with 2-allylnorbornane using $TiCl_4/(isoBu)_3$.

[The catalyst system $TiCl_4/(iso\text{-}Bu)_3Al$ suffers the drawback that an over reduction of Ti^{+4} by $Al(iso\ Bu)_3$ might occur.[12] The preferred catalyst for copolymerization is $TiCl_3$ 0.33 $AlCl_3$. Some authors have used it as a suspension in heptane.[9] However, handling suspensions poses problems in transferring and causes ambiguity in determining precisely the concentration of catalyst charged. Since the amount of catalyst required for the copolymerization runs was too small (less than 10 mg) to be accurately weighed and transferred to the polymerization vessel, it was decided to conduct the studies using the $TiCl_4/(isoBu)_3Al$ catalyst system].

A 75 mL three necked jacketed reactor connected to a 1L gas burette was used for the copolymerizations. (The experimental set-up is shown in Fig. 4.1). n-Heptane (25 mL) was syringed into the reactor and saturated with ethylene. To this 0.86 g (6.6×10^{-3} mol) of 2-allylnorbornane was syringed in followed by 0.6 mL of a 5% triisobutylaluminum solution in heptane (1.5×10^{-4} mol). The copolymerization was initiated by the addition of 0.1 mL of a 10% $TiCl_4$ solution in heptane (5.2 x 10^{-5} mol). Consumption of ethylene was noted at various intervals of time. The copolymerization was terminated after 10 min by pouring the contents of the reactor into acidified methanol. Yield of the copolymer = 0.86 g.

4.2.3 Copolymerization of ethylene with 2-allylnorbornane using Cp_2ZrCl_2/MAO

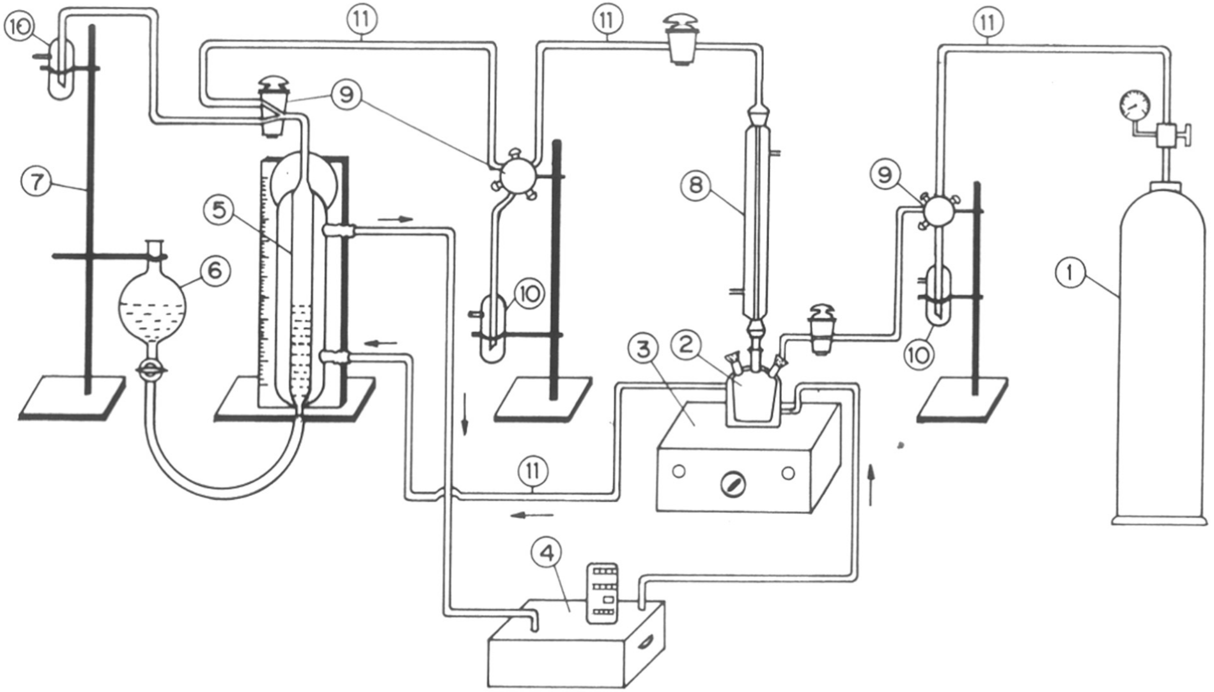
The experimental set-up used was the same as shown in Fig. 4.1. 25 mL of toluene was syringed into the reactor and allowed to saturate with ethylene. To this 0.86 g (6.6 x 10^{-3} mol) of 2-allylnorbornane was syringed in followed by 0.82 mL (1.87 x 10^{-3} mol) of a 6.2% Al solution of methylaluminoxane. The copolymerization was initiated by the addition of 0.4 mL of a Cp_2ZrCl_2 solution in toluene (1.25 x 10^{-6} mol). Consumption of ethylene was noted at various intervals of time. The copolymerization was terminated after 10 min. by pouring the contents of the reactor into acidified methanol. Yield of copolymer = 0.81 g

4.2.4 Analytical techniques

IR spectra were recorded on a Perkin-Elmer PC 16 FTIR on films (150-200 μ in thickness) compression moulded on a Carver hydraulic Press at 155°C and 150 Kg/cm^2.

^{13}C NMR of the copolymers were recorded using a 300 MHz Bruker MSL spectrometer at 120°C on 10 wt% samples in 1,2,4 trichlorobenzene containing about 10% by volume of deuterated benzene for lock purpose. Spectra were recorded under quantitative conditions (pulse delay > $5T_1$).

Thermogravimetric analysis was carried out using a Netzsch thermal analysis apparatus model STA 409. Differential scanning calorimetric analysis was done on a Perkin-Elmer DSC-7. X-ray diffraction patterns were recorded on a Philips X-ray diffractometer.



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

4.1 Schematic diagram of the experimental set up used for ethylene higher olefin copolymerizations at one atmosphere.

Gel permeation chromatograms of copolymer samples were run on a Water Associates, model ALC GPC 150C at 135°C using 1,2,4 trichlorobenzene as the mobile phase and μstyragel columns($10^5 A^0$, $10^4 A^0$, $10^3 A^0$ and$500 A^0$). Flow rate = 1mL/min, detector = RI. A universal calibration was used.

4.2.4.1 Quantitative estimation of 2-allylnorbornane in the copolymers.

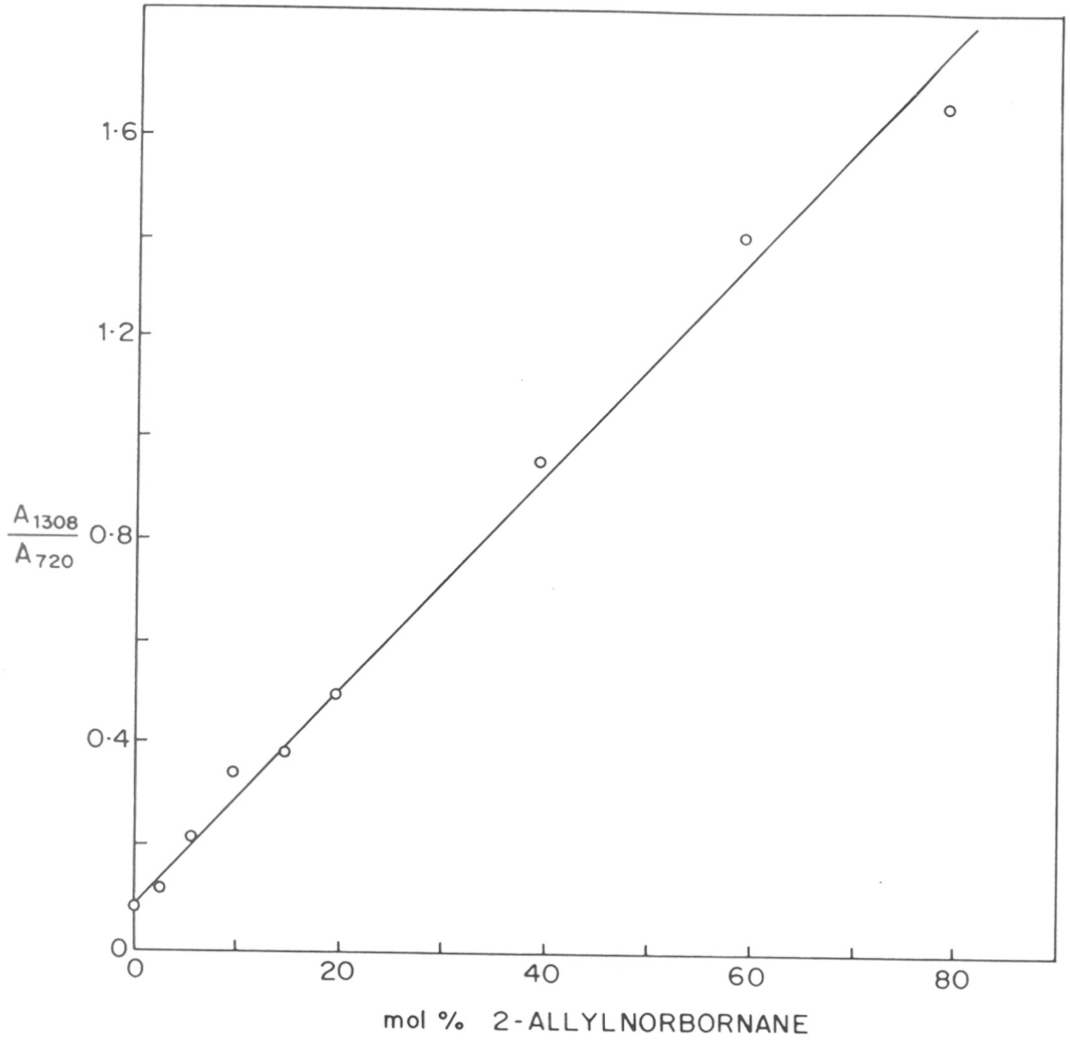
(a) ^{13}C NMR spectra of the copolymers recorded under quantitative conditions were used (Fig.4.6). Though the spectrum is very crowded with overlapping of a number of peaks some characteristic signals such as endo and exo C_3, endo and exo C_4 and endo C_6 are easily distinguished and used in quantitative estimation.

$$mol\%of2 - allylnorbornane = \frac{B}{1/2(A - 10B) + B} \times 100$$

where, A= sum of the integral over all C's

B= integral of the C_3 endo + C_3 exo, or C_4 endo + C_4 exo

(b) An FTIR method for quantitative estimation of 2-allylnorbornane was also established. The absorption at 1308 cm^{-1} in the spectrum of poly(2-allylnorbornane) is characteristic of bridgehead -C-H bending[13]. The absorption at 720 cm^{-1} is characteristic of $(CH_2)n$ i.e. long chain methylene sequences in the spectrum of polyethylene. Homopolymer mixtures of 0 to 80 mole % of poly(2-allylnorbornane) and polyethylene were prepared by heating the appropriate amounts of homopolymers in xylene and coprecipitating in methanol. These were then dried and IR spectrum recorded. A straight line fit was obtained for a graph of A_{1308}/A_{720} versus mol% 2-allylnorbornane in the mixture of copolymers (Fig. 4.2). By the method of interpolation, the composition of copolymers was found out using the value of A_{1308}/A_{720}.



4.2 Calibration curve (A_{1308}/A_{720} vs mol% 2-ANB) used for determination of mol% 2-ANB in copolymer samples.

4.3 RESULTS AND DISCUSSION

4.3.1 Copolymerization of ethylene with 2-allylnorbornane using $TiCl_4/(iso\text{-}Bu)_3Al$ catalyst system.

4.3.1.1 Effect of comonomer concentration

Copolymerization of ethylene with 2-allylnorbornane was performed at 35°C and atmospheric pressure. Table 4.1 shows the effect of comonomer concentration on copolymer properties. It can be seen that conversion and Rp decreases with increase in the comonomer feed (Fig. 4.3). The value of intrinsic viscosity $[\eta]$ is also seen to decrease. This could be attributed to the increased chain transfer reactions in presence of 2-allylnorbornane. The value of ΔHf decreases with increase in 2-allylnorbornane incorporation leading to a decrease in the value of % crystallinity. However the decrease in Tm is not considerable.

4.3.1.2 Determination of reactivity ratios

Reactivity ratios were determined by terminating the copolymerization at less that 20% conversion (Table 4.2). Copolymer composition was determined by FTIR using the calibration curve shown in Fig.4.2. Analysis of data using the Fineman-Ross method (Fig. 4.4) gave a value of $r_{ethylene} = 39.6$ and $r_{2\text{-}ANB} = 0.0706$ with $r_{ethylene} \cdot r_{2\text{-}ANB} = 2.8$, whereas, using the Kelen-Tudos method (Fig. 4.4) gave $r_{ethylene} = 40$, $r_{2\text{-}ANB} = 0.077$ with $r_{ethylene} \cdot r_{2\text{-}ANB} = 3.1$. An r_1r_2 value greater than one is indicative of complex catalysis and this tendency toward block formation is known to be more pronounced when the two comonomers have alkyl groups of different size, for example ethylene-4-methyl-1-pentene, propylene-styrene, propylene-4-methyl-1-pentene, propylene-vinylcyclohexane. Based on this reasoning it is concluded that the ethylene-2-allylnorbornane copolymers also have a blocky microstructure.

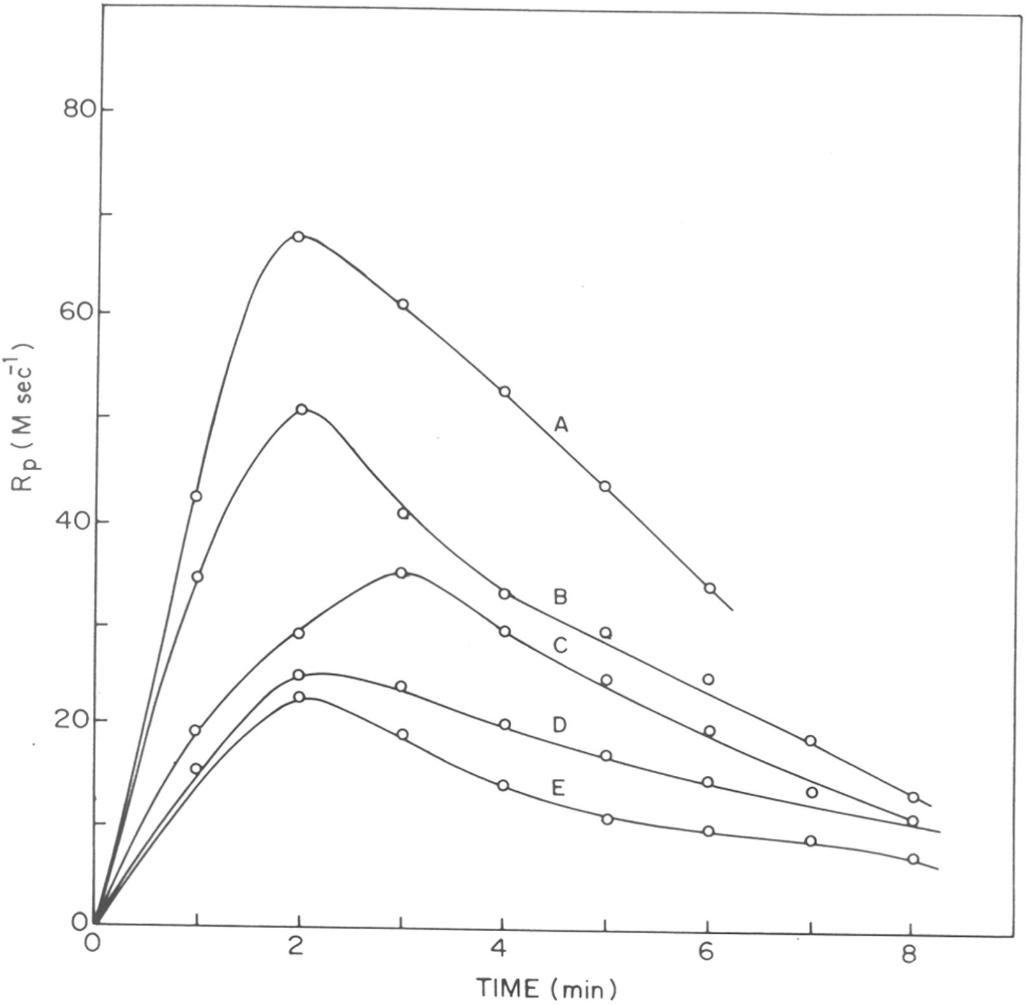
Table 4.1: Copolymerization of ethylene with 2-allylnorbornane using TiCl4/(iso-Bu)3Al catalyst system[a]

Sr. No.	Concentration of 2-Allylnorbornane in feed		Yield (g)	Activity Kg/gTi/h	Conversion (%)	mol% 2-ANB in copolymer		$[\eta]^b$ (dL/g)	T_m °C	% Cryst.[c]
	M	mol %				IR	NMR			
1.	-	-	0.52	2.0	100	-	-	7.6	131.6	45
2.	0.127	56.9	0.70	1.7	69	6	7	5.3	127.3	31
3.	0.254	72.5	0.85	2.0	60	11	12	4.3	127.2	21
4.	0.509	84.0	0.67	1.6	34	18	19	3.3	128.0	16
5.	0.636	86.8	0.81	1.9	32	20	-	2.8	126.5	13
6.	0.764	89.0	0.71	1.7	25	26	-	2.1	126.0	10

(a) Copolymerization conditions : temp. = 35°C, press. = 1 atm., solvent = heptane (25 mL), time = 10 min., [E] = 0.096M, [Ti] = 2×10^{-3} M, [Al] = 6×10^{-3} M

(b) In 1,2,4 trichlorobenzene at 135°C

(c) % Crystallinity calculated from $\frac{\Delta H_f \text{sample}}{\Delta H_f \text{std}}$ x 100



4.3 A plot of R_p vs time for ethylene 2-allylnorbornane copolymerization (catalyst : $TiCl_4$/(iso Bu)$_3$ Al) at different 2-ANB feeds (A) 0.0 M, (B) 0.127 M, (C) 0.25 M, (D) 0.509 M, and (E) 0.76 M.

Table 4.2 Ethylene 2-allylnorbornane copolymerization (at low conversion) together with the evaluation of some parameters (catalyst: $TiCl_4/(iso\text{-}Bu)_3Al$)[a]

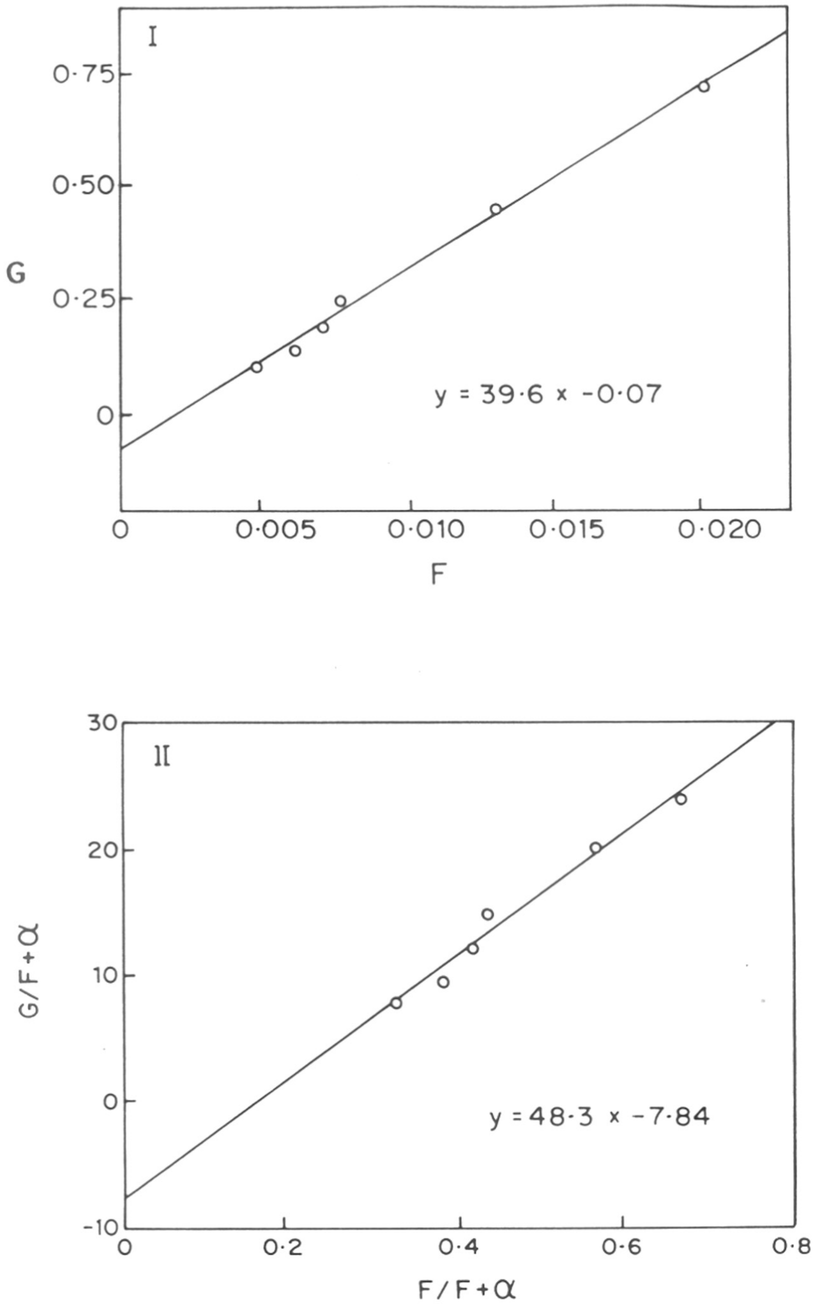
Sr. No.	Conc. of 2-ANB in heptane M	2-ANB in copolymer in mol %[b]	$F_1=(m_1/m_2)$	$f_1=(M_1/M_2)$	F^c	G^c	$\frac{F}{F+\alpha}$	$\frac{G}{F+\alpha}$
1.	0.127	3.5	0.745	27.57	0.0202	0.718	0.67	23.8
2.	0.191	5.0	0.496	19.00	0.0129	0.458	0.565	20.1
3.	0.254	5.5	0.373	17.18	0.0082	0.351	0.452	19.4
4.	0.331	8.5	0.286	10.76	0.0076	0.259	0.434	14.8
5.	0.407	11.5	0.233	7.69	0.0070	0.203	0.415	11.98
6.	0.509	15.5	0.186	5.66	0.0062	0.153	0.38	9.56
7.	0.636	18.0	0.15	4.55	0.0048	0.116	0.33	7.83

(a) Copolymerization conditions : temp. = 35°C, press. = 1 atm., solvent = heptane (25 ml), time = 2 min., [E] = 0.096 M, [Ti] = 2×10^{-3} M, [Al] = 6×10^{-3} M

(b) Calculated from IR

(c) $F = \frac{F_1^2}{f_1}$, $G = \frac{f_1 - 1}{f_1} x F_1$ Fineman - Ross eqn. : $G = - r_{comonomer} + r_{ethyelene} F$

Kelen-Tudos eqn. : $G/(F + \alpha) = (-r_{comonomer}/\alpha) + (r_{ethylene} + r_{comonomer}\,\alpha^{-1})\,(F / F + \alpha)$



4.4 Fineman-Ross (I) and Kelen-Tudos (II) plots for ethylene 2-allylnorbornane copolymerization over $TiCl_4/(iso\text{-}Bu)_3Al$ catalyst system.

4.3.2 Characterization of the ethylene-2-allylnorbornane copolymers obtained using the $TiCl_4/(iso\text{-}Bu)_3Al$ catalyst system

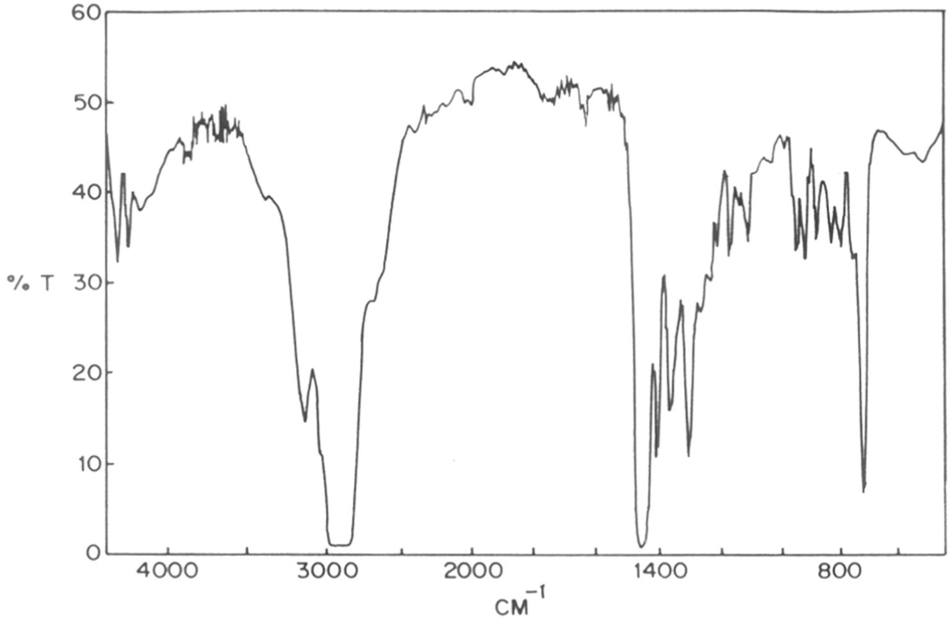
4.3.2.1 Solubility : All copolymers are completely soluble in 1,2,4 - trichlorobenzene at 120°C.

4.3.2.2 Fractionation : Fractionation gives an idea of the heterogenity of the copolymers. Two samples 2 and 5 (from Table 4.1) were fractionated in a Soxhlet extraction unit using heptane for 12 hours.

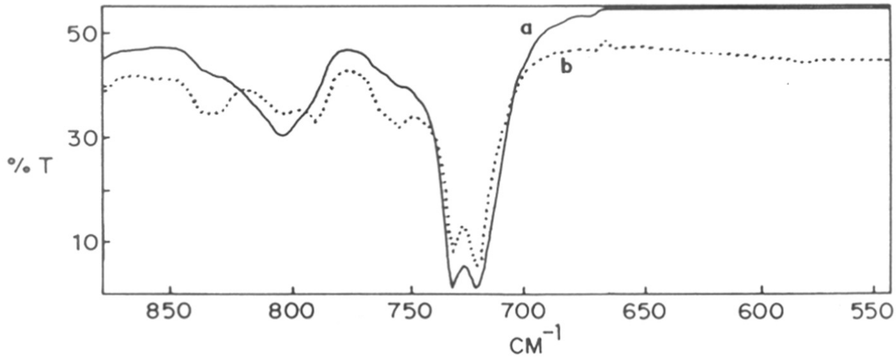
Sample No.	mol. % of 2-ANB	Weight g	Heptane soluble g	Heptane insoluble g
5	6	0.24	0.06	0.017
2	20	0.27	0.16	0.1

The sample containing higher amount of 2-allylnorbornane has higher amount of heptane soluble fraction. This could be because the 2-allylnorbornane disrupts the crystallinity of polyethylene thus rendering it more soluble. Also, the comonomer acts as a chain transfer agent decreasing molecular weight and hence increasing solubility of the fractions.

4.3.2.3 Infrared spectroscopy : All the spectra show the absence of peaks at 1695-1540 cm^{-1} corresponding to C=C double bond stretch implying that copolymerization has occurred through the C=C (Fig.4.5a). Peaks attributed to $-CH_2-CH_2-$ and allylnorbornane repeat units can be easily identified. To determine the composition of the copolymers the absorbance of peak at 720 cm^{-1} characteristic of $(CH_2)_{4+}$ and absorbance of peak at 1308 cm^{-1} characteristic of bridgehead -CH bending[13] was used as described in section 4.2.3.1b. The spectrum of polyethylene has very few characteristic infrared absorption peaks and those of poly(2-allylnorbornane) also a saturated hydrocarbon occur mostly in the same



4.5 a IR spectrum of an ethylene-2-allylnorbornane copolymer.



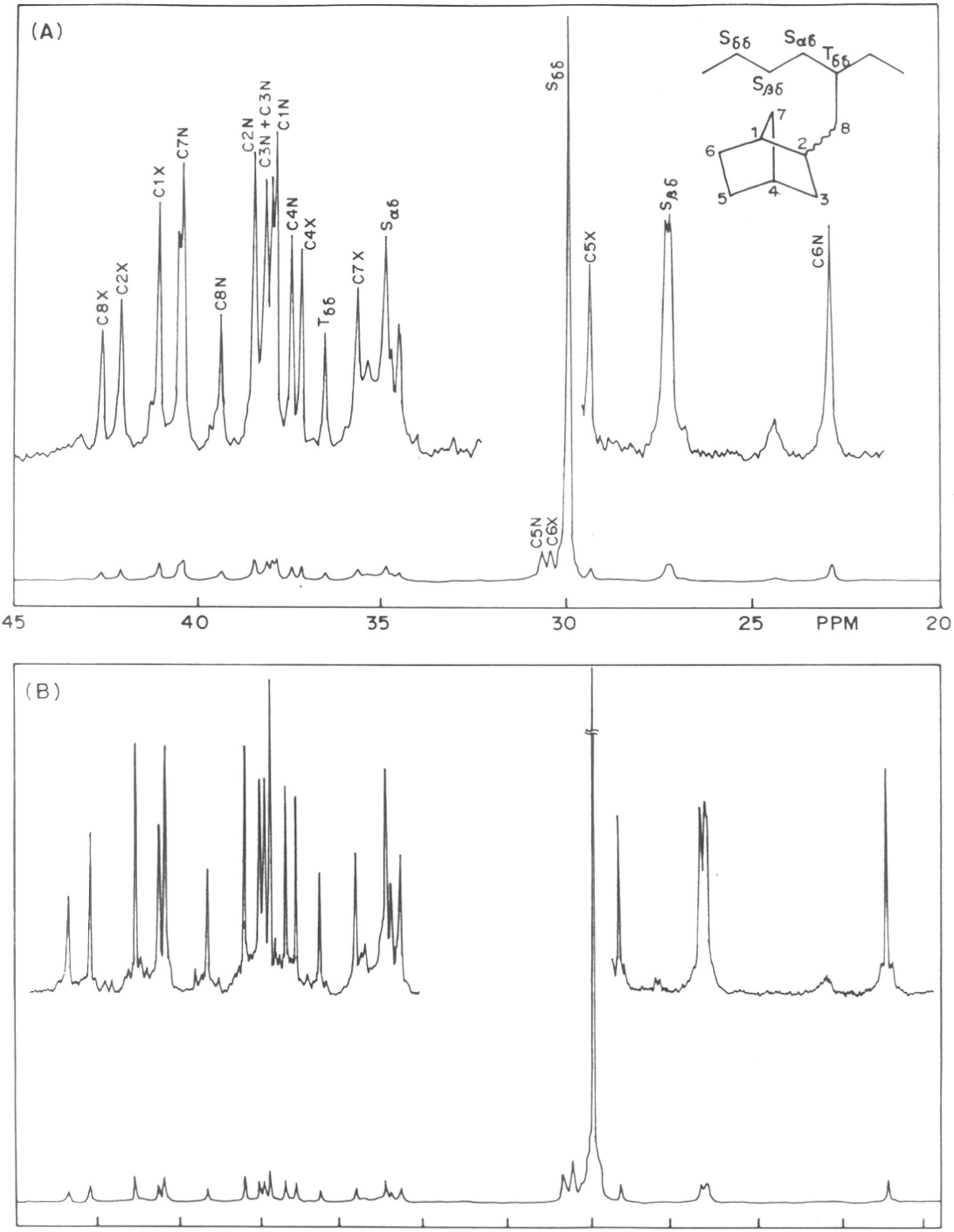
4.5 b Zoom of the 730,720 cm^{-1} region of E2ANB (a) 20 mol% incorporation of 2-ANB and (b) 6 mol% incorporation of 2-ANB.

region. In view of the limited choice of peaks available, the peaks at 720 cm^{-1} (no absorption by poly (2-allylnorbornane in this region) and 1308 cm^{-1} (marginal absorption by polyethylene in this region) were chosen. Wei and Gossl have also used the absorption at 720 cm^{-1} as characteristic of ethylene content in ethylene propylene copolymers.[14]

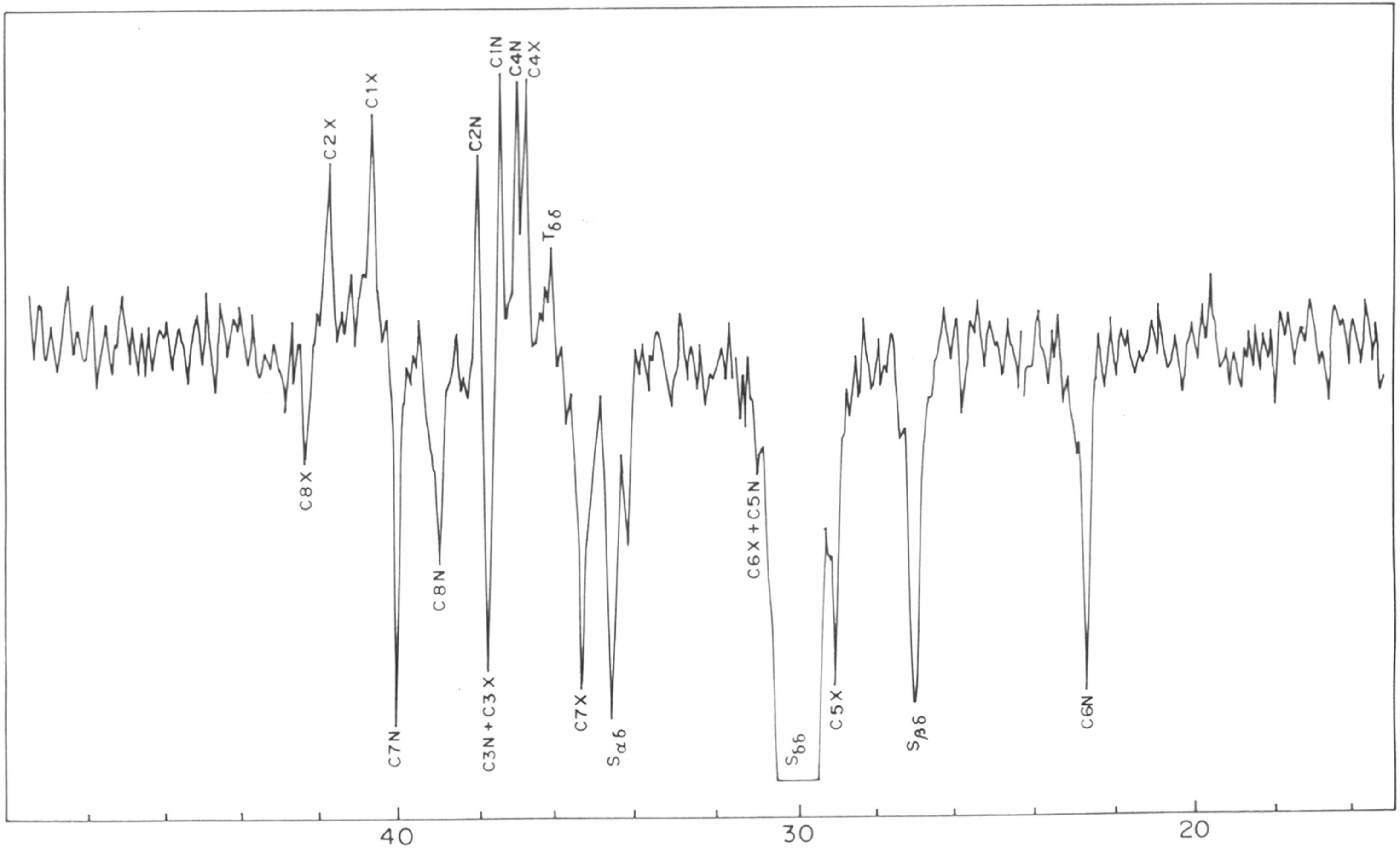
A close look at the 720 - 730 cm^{-1} region (Fig. 4.5b) showed that the doublet at 720 and 730 cm^{-1} is still present at 20 mole % allylnorbornane incorporation implying persistence of crystallinity. This implies that blocky type of copolymers are formed.

4.3.2.4 Nuclear magnetic resonance spectroscopy : The assignments of the peaks in ethylene-2-allylnorbornane copolymers were done similar to those of ethylene-4-methyl-1-pentene copolymers.[15] The ^{13}C NMR spectrum of an ethylene-2-allylnorbornane copolymer is shown in Fig 4.6a. The nomenclature for assigning peaks has been adopted from the literature as is reported by Randall and Hsich[16]. A good agreement of the assigned experimental values with those calculated using Grant and Paul rules[17] is obtained. Assignments for the norbornyl pendant were done in accordance with the chemical shifts of model compounds, and monomer. A DEPT spectrum of the copolymer (Fig. 4.7) was also obtained to distinguish between the methine and methylene signals. The assignments of the peak positions are shown in Table 4.3. The shifts of the main chain carbon atoms do not appear to be sensitive to the endo/exo isomerism in the pendant moiety. Here endo C_1 and C_2 are assigned values different from the homopolymer based on DEPT spectrum.

^{13}C NMR spectra were used to determine the copolymer composition as elucidated in section 4.2.4.1a. Based on integration, an endo:exo ratio of 55:45 for 2-allylnorbornane is obtained. This means absence of selectivity towards insertion of either endo or exo isomer during copolymerization.



4.6 ^{13}C NMR spectrum of poly(ethylene-co-2-allylnorbornane) (A) catalyst : TiCl$_4$/(iso Bu)$_3$ Al and (B) catalyst : Cp$_2$ZrCl$_2$/MAO.



4.7 DEPT spectrum of poly(ethylene-co-2-allylnorbornane).

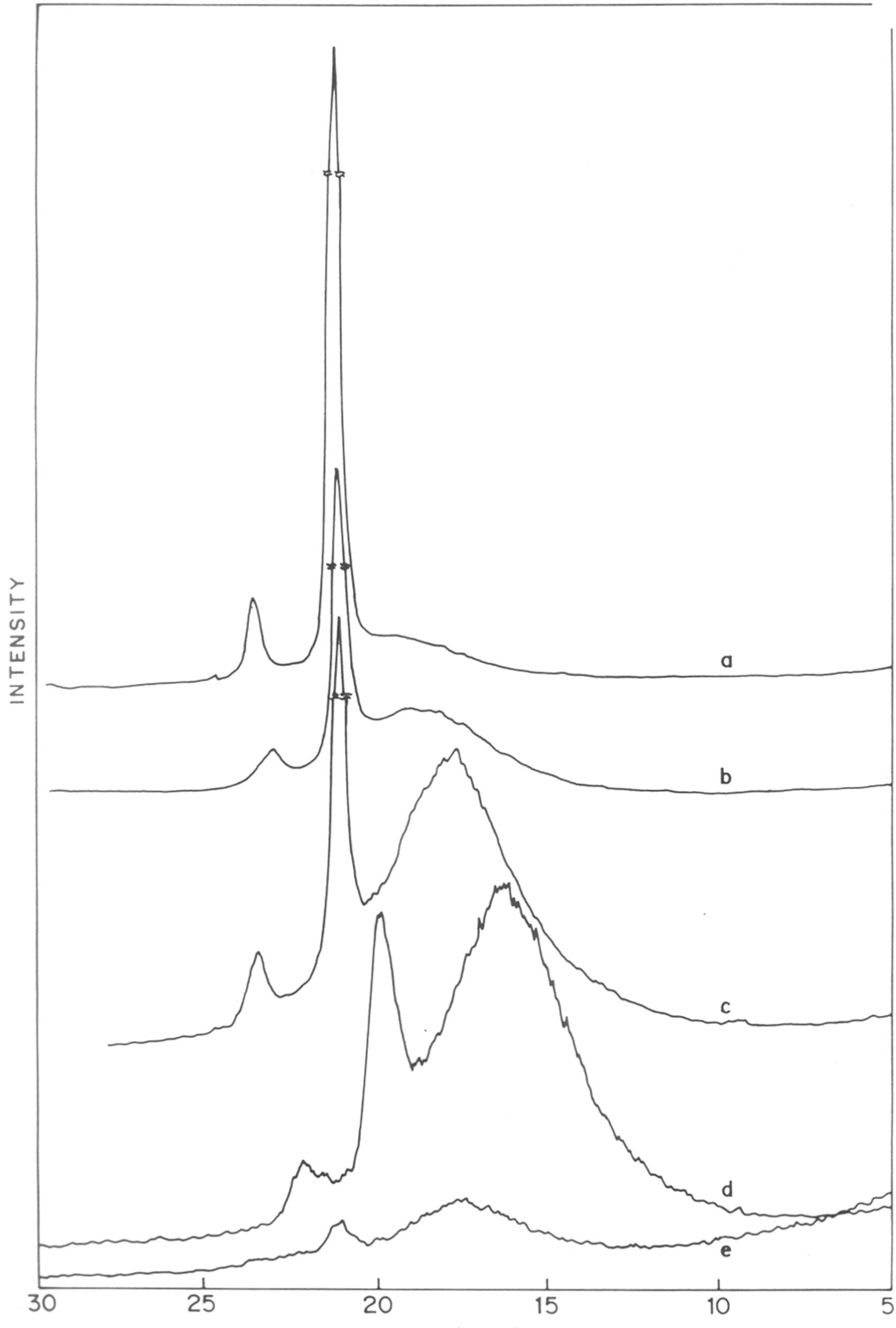
Table 4.3 Peak positions of the comonomer (2-ANB) and copolymer (E2-ANB)

Sample		C1	C2	C3	C4	C5	C6	C7	C8	C9	C10	$T_{\delta\delta}$	$S_{\alpha\delta}$	$S_{\beta\delta}$	$S_{\delta\delta}$
2-ANB	Exo	40.6	41.6	37.7	36.6	28.8	30.0	35.1	41.0	137.9	114.7	-	-	-	-
	Endo	39.8	39.9	36.8	37.2	30.1	22.4	39.9	37.3	138.6	114.2	-	-	-	-
E2-ANB	Exo	41.05	42.11	38.05	37.1	29.3	30.6	35.6	42.6	-	-	36.4	35.34-34.84	27.12-27.22	29.91
	Endo	37.78	38.4	37.89	37.3	30.6	22.9	40.4	39.3	-	-	36.4	35.34-34.84	27.12-27.22	29.91

4.3.2.5 X-ray diffraction : The x-ray diffraction patterns of the ethylene-2-allylnorbornane copolymers (compression moulded into thin films (100-150μm) 150°C and 150 Kg/cm^2 in a hydraulic press) are shown in Fig. 4.8. In samples having low levels of comonomer the x-ray diffraction patterns show the presence of two crystalline peaks (110 at $2\theta = 21.4$ and 200 at $2\theta = 23.8$) along with an amorphous halo. As the comonomer concentration increases, the peak positions of the 200 and 110 reflections shift to lower values indicating an increase in the dimensions of the unit cell which could be a consequence of the reduced crystallite dimensions which decrease as branching increases. At even higher 2-allylnorbornane concentration a new reflection at $2\theta = 18.5°$ appears, and the intensity of this peak increases with increase in the comonomer content, and at 26 mol% 2-allylnorbornane incorporation a substantial loss in crystallinity is observed. Clas *et al*[18] have observed a similar peak at 19.4° in ethylene-1-octadecene samples of high comonomer content. This has been attributed to a triclinic form that competes in stability with orthorhombic polyethylene. The appearance of this peak in the present samples makes the estimation of crystallinity difficult because an estimate based on the 110 and 200 orthorhombic reflections would result in ignoring the ordered material contributing to $2\theta = 18$ resulting in a value probably lower than the true value. Hence percent crystallinity based on x-ray diffraction was not estimated.

4.3.2.6 Thermal analysis : Thermogravimetric analysis under nitrogen atmosphere shows that the initial decomposition temperature of all copolymers is above 380°C with a marginal decrease in the value of IDT with increasing comonomer concentration.

Results of the differential scanning calorimetric analysis are shown in Table 4.1 (Fig.4.14.I). It can be seen that the value of ΔH_f decreases with increase in comonomer content. The percent crystallinity was estimated assuming that ΔH_f = 290 J/g for 100% crystalline polyethylene.[19] In the case of copolymers the DSC



4.8 X-ray diffraction patterns of poly(ethylene-co-2-allylnorbornane) with (a) 0 mol%, (b) 6 mol%, (c) 18 mol%, (d) 20 mol% and (e) 26 mol% of 2-ANB incorporation.

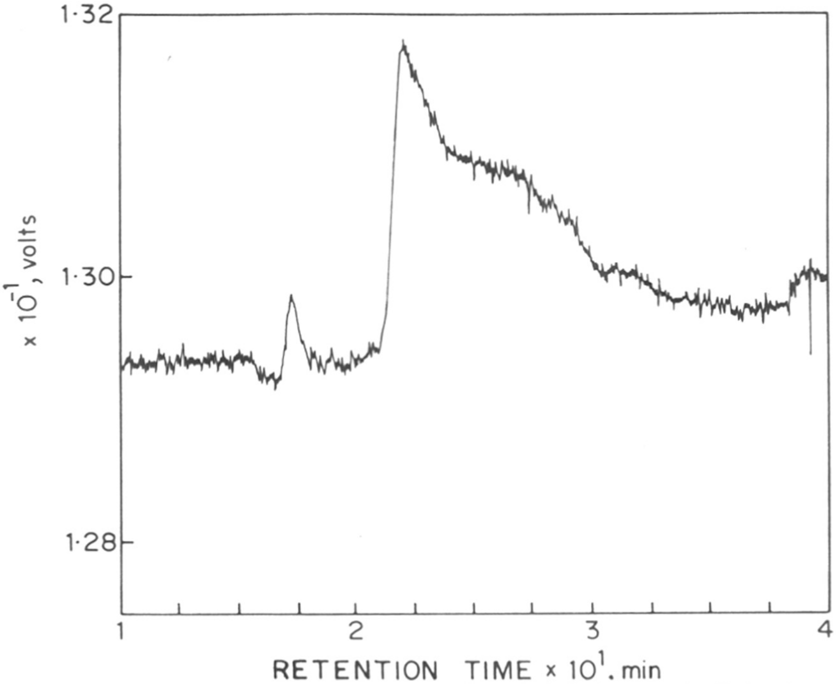
estimate of crystallinity has partially compensating errors due to (a) an assumption of ΔH_f reference that is too high and (b) incorporation in the endotherm of the melting of interfacial materials. The percentage of crystallinity calculated from the ΔH_f values decreases with increase in comonomer content. However, even in samples with a high comonomer content the depression in T_m is not considerable. From this observation it can be deduced that regardless of the total composition of the copolymer, they contain the same kind of larger crystallites. This can happen if the copolymers have a blocky microstructure. A similar observation of only a slight decrease in melting point with increase in comonomer content was noted in the case of ethylene-hexene copolymers[20]. Analysis of these copolymers by XRD, GPC, DSC and extraction showed them to be heterogeneous in nature. The ethylene-2-allylnorbornane copolymers also, appear to be heterogeneous in nature. The decrease in the value of ΔH_f can be explained by a dilution effect since at a high mol % incorporation of comonomer the mass fraction of ethylene derived main chains is reduced.

The DSC of the fractions of samples 2 and 5 were also obtained. It was observed that the heptane soluble fraction did not show a noticeable T_m whereas the heptane insoluble fraction showed a T_m at a slightly higher value than the unfractionated sample.

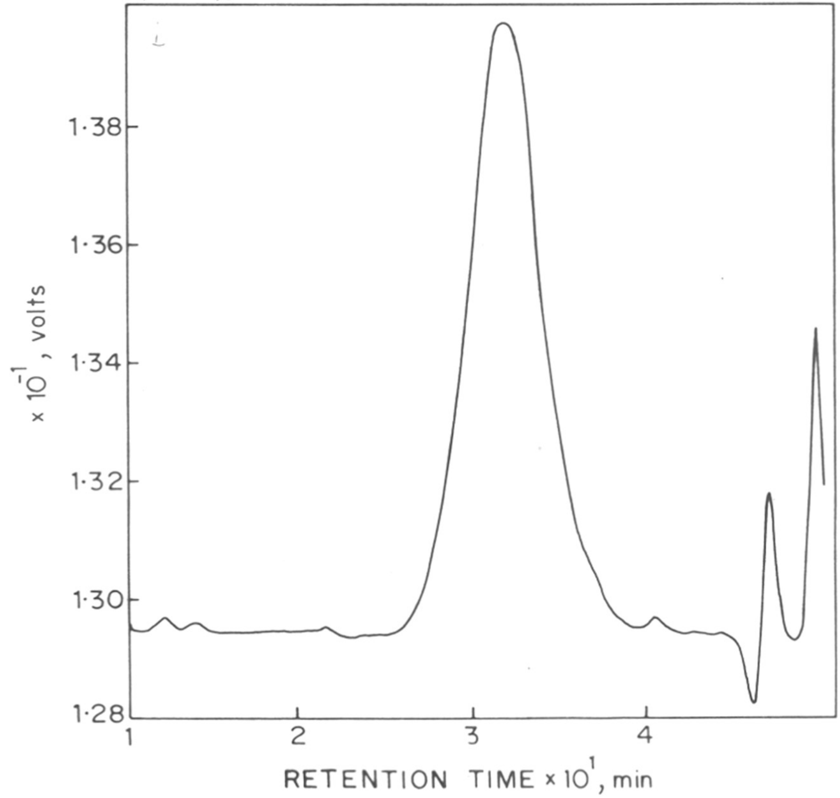
4.3.2.7 Gel permeation chromatography : Sample 2 (Table 4.1, Fig. 4.9a) was analyzed by GPC. It was found to have a broad molecular weight distribution with $\overline{M}n = 48,413$, $\overline{M}w = 3,229,31$ and PDI = 6.7.

4.3.3 Copolymerization of ethylene with 2-allylnorbornane using the Cp_2ZrCl_2/MAO catalyst system

As seen in section 4.3.2 characterization of ethylene-2-allylnorbornane copolymers obtained with the $TiCl_4$/(iso-Bu)$_3$Al catalyst showed the copolymers to be heterogeneous in nature. This is attributed to the multiple active sites obtained



4.9 a Gel permeation chromatogram of poly(ethylene-co-2-allylnorbornane) using TiCl$_4$/(iso-Bu)$_3$ Al catalyst (6 mol% 2-ANB).



4.9 b Gel permeation chromatogram of poly(ethylene-co-2-allylnorbornane) using Cp ZrCl /MAO catalyst (4 mol% 2-ANB).

on the reduction of $TiCl_4$ with (iso-Bu)$_3$Al. Many publications have reported on the heterogeneity of copolymers obtained with both conventional[10] and $MgCl_2$ supported[22] catalysts. In this respect, the homogeneous metallocene catalysts have considerable advantages over the traditional catalysts. When used in the copolymerization of ethylene and higher α-olefins they give a highly random distribution of comonomers.[6,23,24] Hence we decided to synthesize copolymers of ethylene and 2-allylnorbornane using the catalyst system Cp_2ZrCl_2/MAO.

4.3.3.1 Effect of comonomer concentration

Table 4.4 shows the effect of comonomer concentration on activity and copolymer properties. The salient features of the copolymerization are as follows - (1) the activity and R_p (Fig. 4.10) of copolymerization is seen to increase with increasing 2-allylnorbornane in the feed. A similar rate-enhancing effect of comonomer has been found by several authors(3-9). Tsutsui and Kashiwa[7] attribute this to an increasing rate constant by heterogeneous catalysts. Tait[8] assumed a rise in the number of active centers. Munoz-Escalona *et al*[3] attributed this to the increase in porosity of the growing particles. In the case of homogeneous catalysts Koivumaki and Seppala[5] have also observed a similar rate enhancing effect in ethylene-1-hexene copolymerization at 50°C which was found to disappear at a reaction temperature of 90°C when the copolymer formed was soluble in the reaction medium. They attributed the rate enhancing effect to an increased monomer diffusion which disappears when the copolymer is soluble in the reaction medium. Copolymer intrinsic viscosities are lower than those obtained with the conventional heterogeneous catalysts. The intrinsic viscosity of the copolymers decreases with an increase in the comonomer content due to increased chain transfer to monomer. The DSC scans of the copolymers show that T_m (two close melting points are observed) and ΔH_f both gradually decrease indicating that homogeneous copolymers are formed (Fig.4.15).

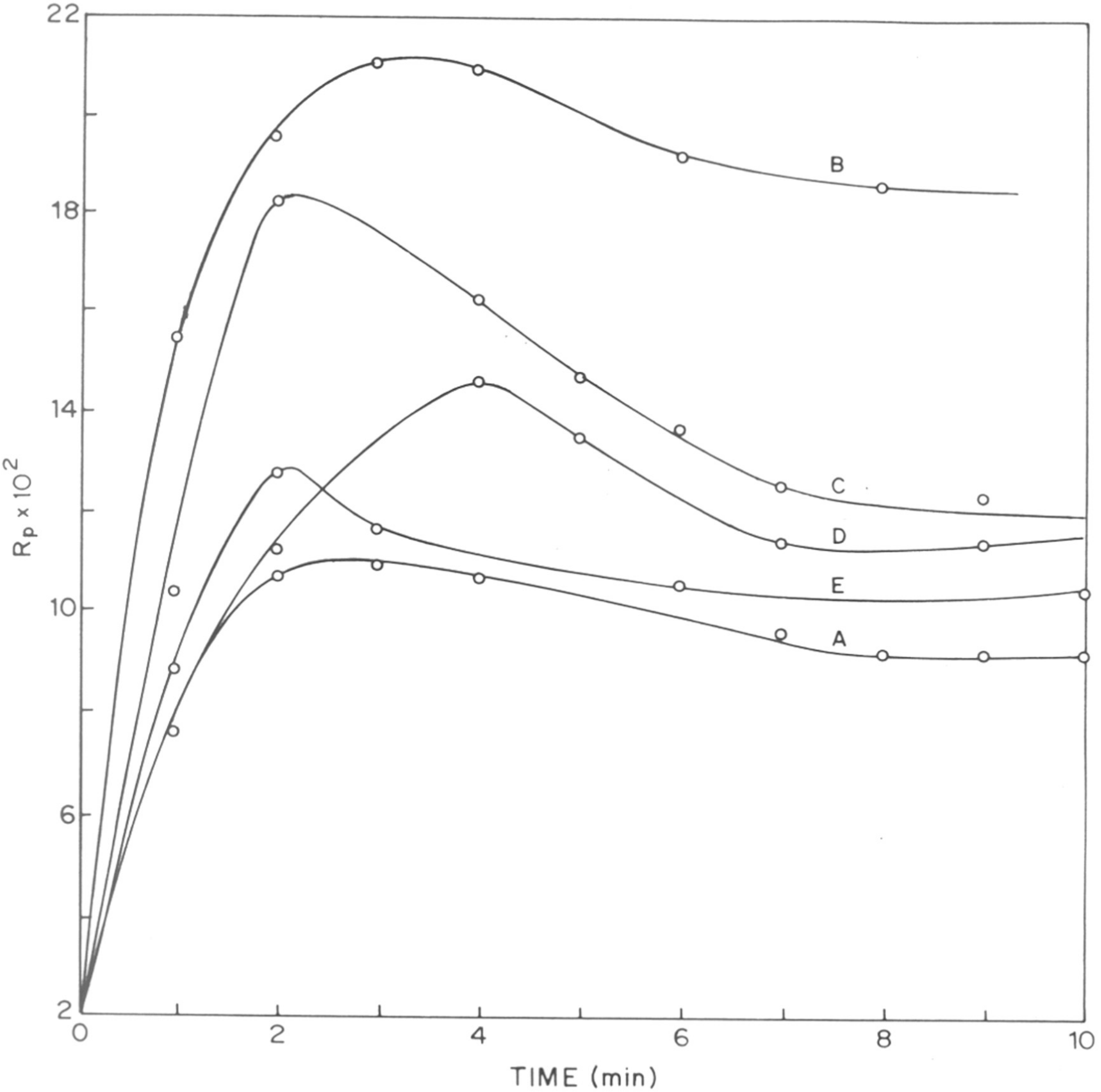
Table 4.4 Copolymerization of ethylene with 2-allylnorbornane using Cp_2ZrCl_2/ MAO catalyst system [a]

Sr. No.	2-Allylnorbornane in feed		Yield (g)	Activity Kg/gZr/h	Conv. %	Mol % 2-ANB in copoly		$[\eta]^b$ dL/g	T_m °C		% Cryst.[c]
	M	mol %				IR	NMR				
1.	-	-	0.48	25.2	100	-	-	1.60	132.5		67.0
2.	0.101	47.8	0.75	39.2	80	3	-	0.92	110	116	28.6
3.	0.178	61.8	0.79	52.1	62	4	4	0.71	103	108.4	24.1
4.	0.254	69.7	0.81	53.4	57	5	-	0.32	97.1	104.3	15.8
5.	0.382	77.6	0.86	45.5	47	11	-	0.28	91.0	99.5	8.6
6.	0.509	82.2	0.72	37.7	33	18	16	0.19	86.9	94.8	3.4

(a) Copolymerization conditions : temp. = 35°C, press. = 1 atm., solvent = toluene (25 mL), time = 8-10 min., [E] = 0.11 M, [Zr] = 5 x 10^{-5} M, [Al] = 0.075 M

(b) In 1,2,4 trichlorobenzene at 135°C

(c) % Crystallinity calculated from $\frac{\Delta H_f \text{sample}}{\Delta H_f \text{std}}$ x 100



4.10 A plot of R_p vs time for ethylene 2-allylnorbornane copolymerization (catalyst : Cp_2ZrCl_2/MAO) at different 2-ANB feeds (A) OM, (B) 0.101 M, (c) 0.18 M, (D) 0.38 M and (E) 0.509 M.

4.3.2.2 Determination of reactivity ratios

The data from copolymerizations terminated at less than 20% conversion was used for the determination of reactivity ratios (Table 4.5). Copolymer composition was determined from the IR spectra of the copolymers as described earlier. Treatment of data according to the Fineman-Ross method (Fig 4.11) gave a value of $r_{ethylene}$ = 43.7 $r_{2\text{-}ANB}$ = 0.038 with the $r_{ethylene}.r_{2\text{-}ANB}$ = 1.62. Treatment of data according to the method of Kelen and Tudos (Fig. 4.11) gave $r_{ethylene}$ = 42.6, $r_{2\text{-}ANB}$ = 0.027 with $r_{ethylene}$ $r_{2\text{-}ANB}$ = 1.15. The value of r_1r_2 being close to 1.0 indicates that the copolymers formed are random in nature as supported by the observation of a steady decrease in the melting point with increase in comonomer incorporation.

4.3.4 Characterization of ethylene-2-allylnorbornane copolymers obtained using the Cp_2ZrCl_2/MAO catalyst system.

4.3.4.1 Solubility : All the copolymers were found to be completely soluble in 1,2,4-trichlorobenzene at 120°C.

4.3.4.2 Fractionation : Fractionation was attempted in order to obtain some idea about the homogeneity or heterogeneity of the copolymers. Two samples 2 and 6 (Table 4.4) were selected. However, Soxhlet extraction using heptane showed absence of any heptane insoluble fraction, with both the copolymers being completely soluble in heptane. Extraction using acetone or ether gave negligible amount of soluble fraction. These results indicate that the copolymers are homogeneous in nature consisting mainly of fractions having very close similarity as regards to their molecular weight and comonomer composition and distribution.

4.3.4.3 Infrared spectroscopy : The general information derived from the IR spectra of these copolymers is similar to that derived from the copolymers obtained using $TiCl_4$/(iso-Bu)$_3$Al catalyst with characteristic peaks due to ethylene and allylnorbornane repeat units being present (Fig.4.12a). However in the case of the catalysts derived from $TiCl_4$/(iso-Bu)$_3$Al the 722 cm^{-1} polymethylene chain vibration

Table 4.5 **Ethylene 2-allylnorbornane copolymerization (at low conversion) together with the evaluation of some parameters (catalyst system: Cp_2ZrCl_2/MAO)[a]**

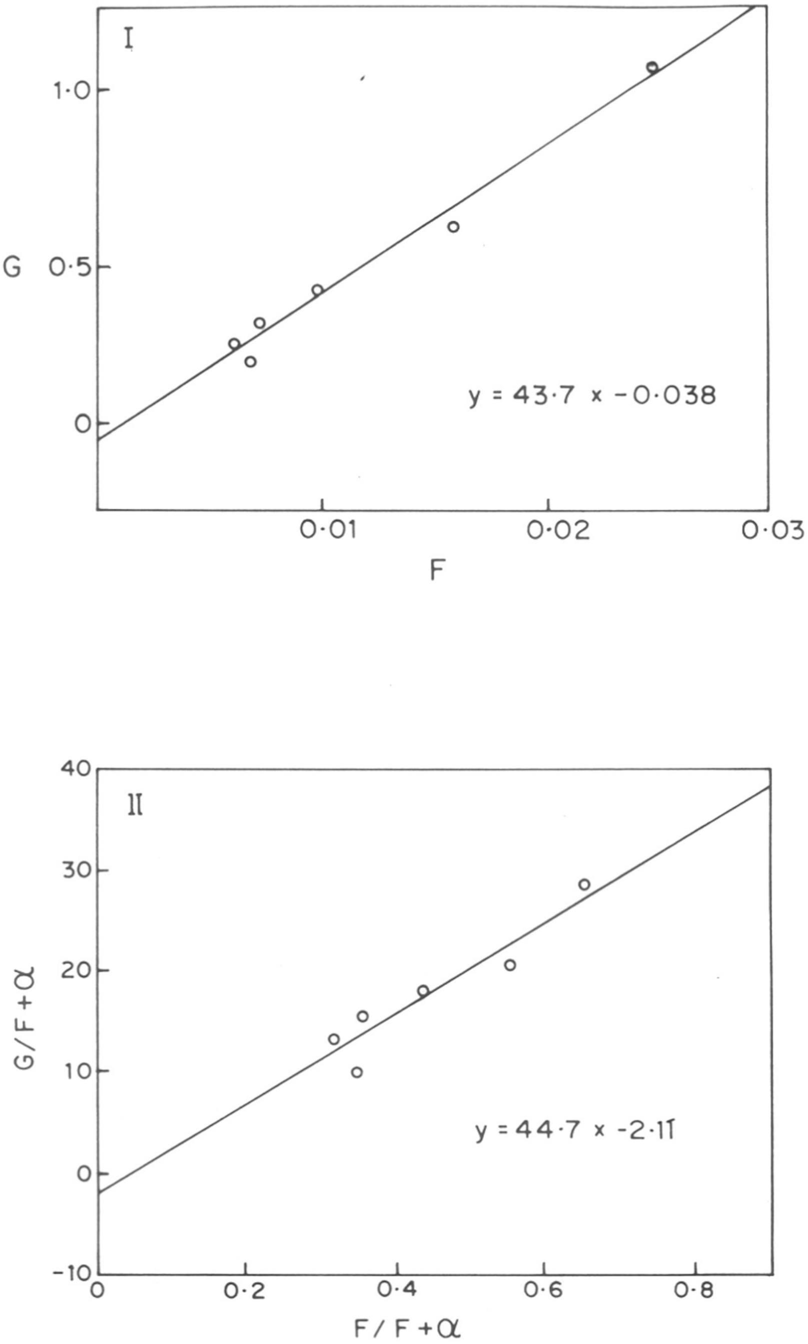
Sr. No.	Conc. of 2-ANB in toluene M	2-ANB in copoly.in mol % (b)	$F_1=(m_1/m_2)$	$f_1=(M_1/M_2)$	F^c	G^c	$\dfrac{F}{F+\alpha}$	$\dfrac{G}{G+\alpha}$
1.	0.101	2.0	1.10	49.0	0.024	1.070	0.657	28.48
2.	0.178	4.0	0.618	24.0	0.016	0.592	0.553	20.58
3.	0.254	5.0	0.432	19.0	0.0098	0.409	0.432	18.05
4.	0.331	6.0	0.332	15.6	0.007	0.310	0.353	15.58
5.	0.407	7.5	0.27	12.3	0.0059	0.248	0.314	13.21
6.	0.484	12	0.23	7.6	0.0067	0.197	0.342	10.10

(a) Copolymerization conditions : temp. = 35°C, press. = 1 atm., solvent = toluene (25 mL), time = 1-2 min., [E] = 0.11 M, [Zr] = 5×10^{-5} M, [Al] = 0.078 M

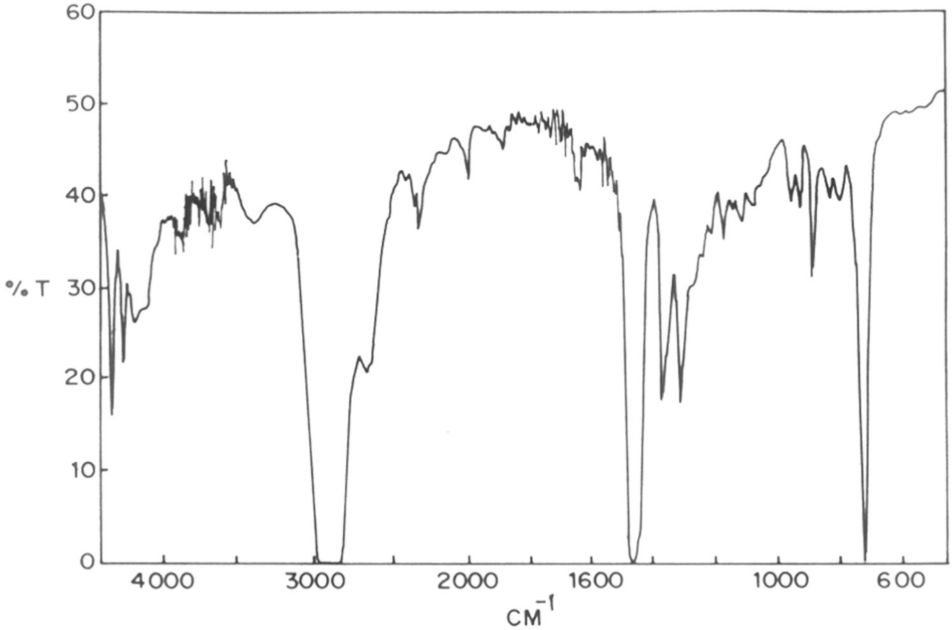
(b) Calculated from IR

(c) $F = \frac{F_1^2}{f_1}$, $G = \frac{f_1 - 1}{f_1} x F_1$ Fineman - Ross eqn. : $G = - r_{comonomer} + r_{ethyelene} F$

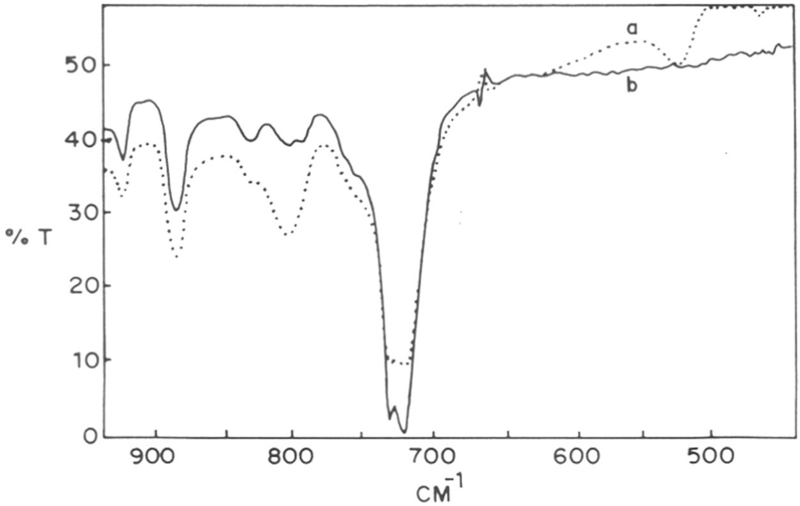
Kelen-Tudos eqn. : $G/(F + \alpha) = (-r_{comonomer}/\alpha) + (r_{ethylene} + r_{comonomer} \alpha^{-1}) (F / F + \alpha)$



4.11 Fineman Ross (I) and Kelen-Tudos (II) plots for ethylene 2-allylnorbornane copolymerization over Cp_2ZrCl_2/MAO catalyst system.



4.12 a IR spectrum of an ethylene-2-allylnorbornane copolymer (catalyst : Cp_2ZrCl_2)MAO)



4.12 b Zoom of the 730,720 cm^{-1} region of P2ANB (a) 18 mol% incorporation of 2-ANB and (b) 4 mol% incorporation of 2-ANB.

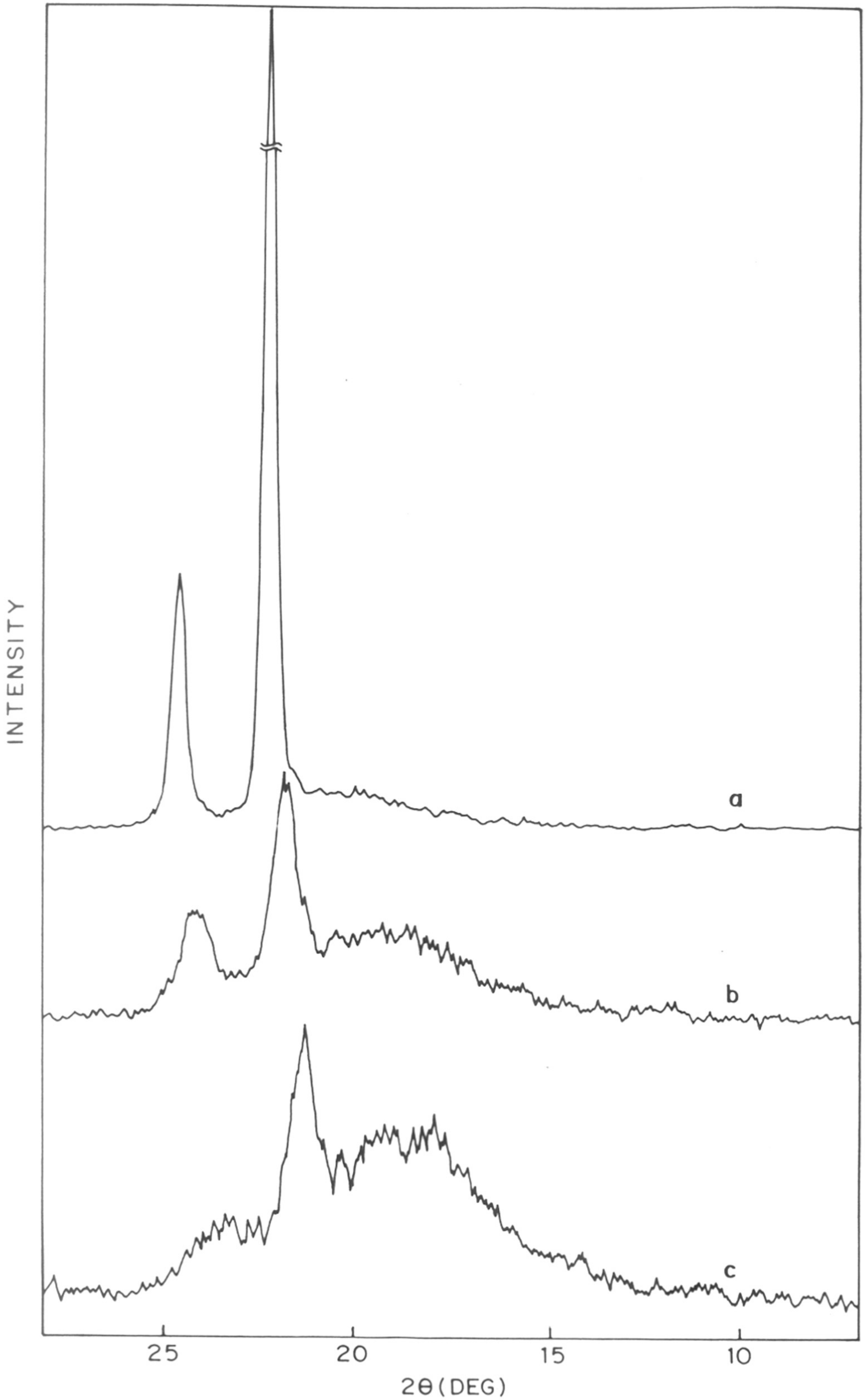
band splits into a doublet at 730 and 720 cm^{-1} corresponding to the rocking models of the two chains in the crystal cell[25] even at high 2-ANB incorporation. But, in the case of the copolymers obtained using Cp_2ZrCl_2/MAO at high 2-ANB incorporation only a broad peak centered at 725 cm^{-1} is obtained (Fig. 4.12b) the absence of its splitting into a doublet indicating disruption of polyethylene crystallinity to a large extent. This indicates that the copolymers obtained with the Cp_2ZrCl_2/MAO catalyst are more random in nature.

4.3.4.4 Nuclear magnetic resonance spectroscopy : The NMR spectra of the copolymers obtained using Cp_2ZrCl_2/MAO catalyst resemble those obtained using the $TiCl_4$/(iso $Bu)_3Al$ catalyst (Fig. 4.6b).

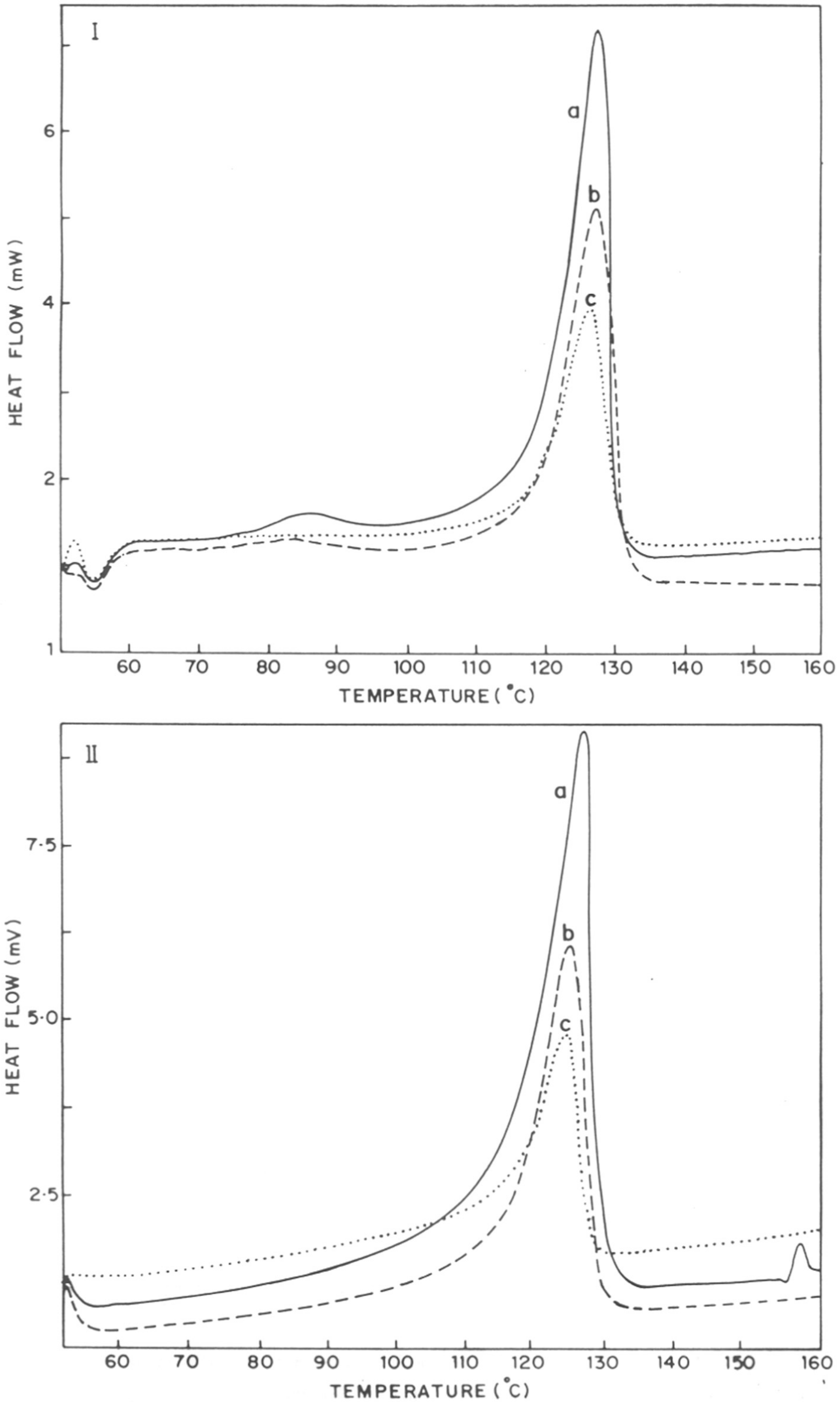
4.3.4.5 X-ray diffraction : The x-ray diffraction patterns of the copolymers are shown in Fig.4.13. At 9.5 mol% incorporation of 2-allylnorbornane almost total loss of crystallinity is observed. This could be due to a random nature of the copolymers as compared to the higher value of 2-allylnorbornane incorporation required for a similar loss of crystallinity in copolymers obtained using $TiCl_4$/(iso-$Bu)_3$ catalyst

4.3.4.6 Thermal analysis : Thermogravimetric analysis of the copolymers under nitrogen show the copolymers to be stable above 380°C in all cases with a slight decrease in IDT with increase in comonomer content.

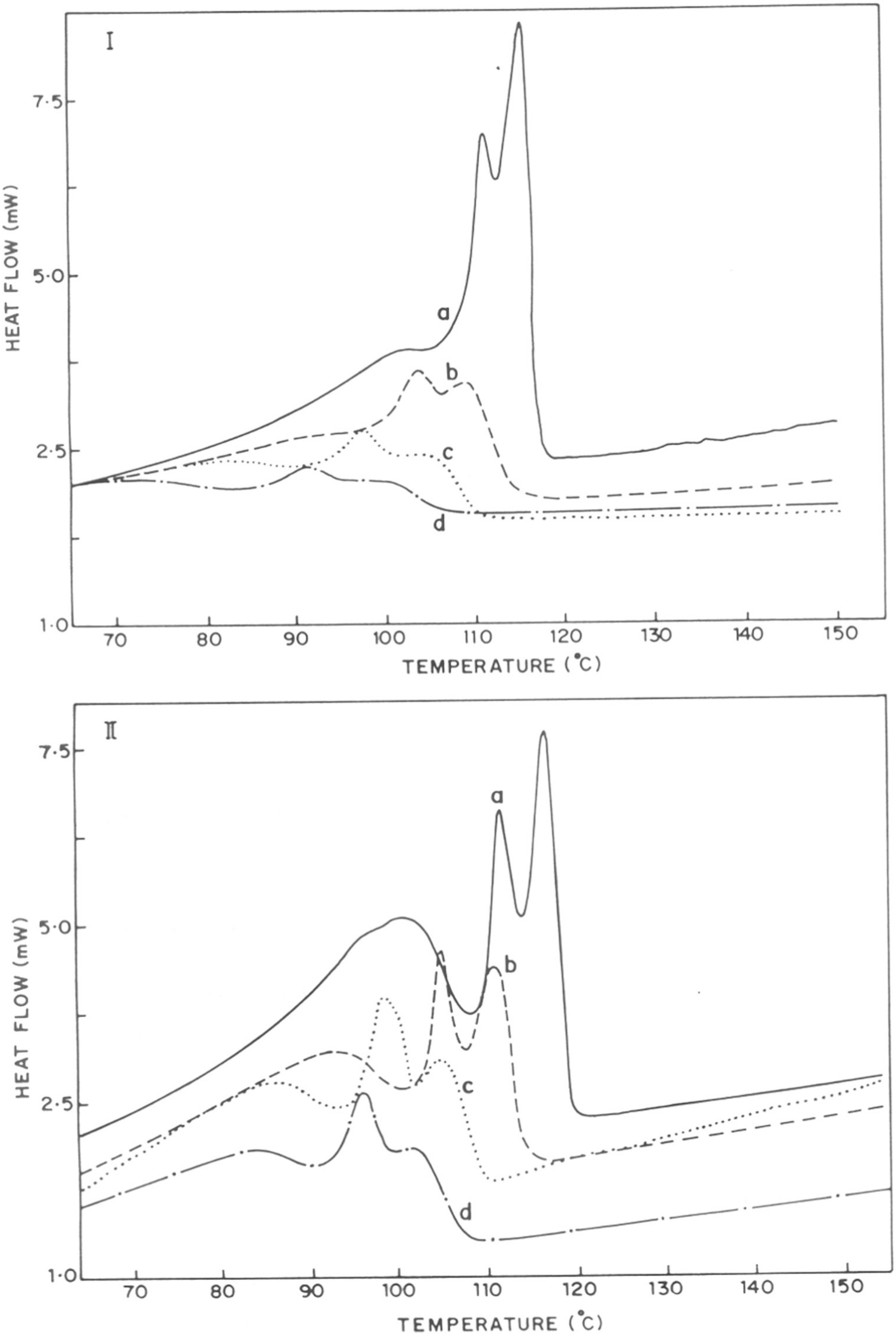
Results of the differential scanning calorimetric studies are tabulated in Table 4.3, Fig.4.15.I. A steady decrease in ΔH_f and percent crystallinity is obtained with increasing comonomer content. On comparing with the data in Table 4.1 it is noted that at similar mol % incorporation of comonomer the copolymer obtained using the Cp_2ZrCl_2/MAO catalyst results in a larger decrease in the value of ΔH_f and percentage crystallinity than the copolymer obtained using $TiCl_4$/(iso $Bu)_3Al$. This implies that these copolymers are more random in nature resulting in the disruption of polyethylene crystallinity to a larger extent. This conclusion is also supported by the $r_1.r_2$ values. A prominent feature of all these copolymers is that the melting is observed as two endotherms separated by about 5°C. A similar



4.13 X-ray diffraction patterns of poly(ethylene-co-2-allylnorbornane) with (a) 0 mol%, (b) 4 mol% and (c) 9.5mol% of 2-ANB incorporation.



4.14 DSC scans of(I) ethylene-2-allylnorbornane copolymers (catalyst : $TiCl_4/(iso\ Bu)_3Al$) having (a) 7 mol%, (b) 11 mol% and (c) 20 mol% of 2-ANB incorporation and (II)ethylene-4-methyl-1-pentene copolymers (catalyst : $TiCl_4/(iso\ Bu)_3Al$) having (a) 6 mol%, (b) 11 mol% and (c) 19 mol% of 4M1P incorporation.



4.15 DSC scans of(I) ethylene-2-allylnorbornane copolymers (catalyst : Cp_2ZrCl_2/MAO) having (a) 3 mol%, (b) 4 mol%, (c) 5 mol% and (d) 9.5 mol% of 2-ANB incorporation and (II)ethylene-4-methyl-1-pentene copolymers (catalyst : Cp_2ZrCl_2/MAO) having (a) 2.5 mol%, (b) 3.8 mol%, (c) 5.7 mol% and (d) 7.5 mol% of 4M1P incorporation.

observation was also made in the case of ethylene-4-methyl-1-pentene copolymers obtained with Cp_2ZrCl_2/MAO catalyst (Appendix I, Fig.4.15.II). There is no prior report in the literature of such a behavior though in some of the ethylene-hexadecene copolymers synthesized by Koivumaki and Seppala[26] a multiple melting endotherm can be seen. A multiple melting endotherm normally implies compositional heterogeneity, but results from fractionation, reactivity ratios and melting and ΔH_f values indicates the copolymers are random and homogeneous in nature. We can only speculate that the multiple melting endotherm could be due to a consequence of two types of active sites proposed by Chien and Wang[27] and Vela Estrada and Hamietec[28] in the case of Cp_2ZrCl_2/MAO catalyst.

4.3.4.7 Gel permeation chromatography : Sample 3 (Table 4.4, Fig. 4.9b) was analyzed by GPC. A narrow molecular weight distribution is obtained as expected with homogeneous metallocene catalysts. It has an $\overline{Mn}$ = 15,499, $\overline{Mw}$ = 40,216 and a PDI = 2.6. The molecular weights are lower probably due to an increased amount of β-hydrogen transfer with this catalyst.

4.3.5 Comparison of the thermal and crystalline properties between ethylene-2-allylnorbornane and ethylene-4-methyl-1-pentene copolymers

A comparative evaluation of properties of ethylene 2-allylnorbornane and ethylene 4-methyl-1-pentene copolymers is shown in Table 4.6 and Figs.4.14 and 4.15. It can be seen that, contrary to expectation, at essentially similar mol % incorporation of comonomers, the depression in the value of T_m and ΔH_f (within the limits of experimental error) depends largely on the catalyst system used but not on the type of comonomer used. A similar independence of crystallinity and ΔH_f on comonomer type was observed by Burfield[29] in his studies on a series of linear low density polyethylenes containing propylene, 1-butene or 4-methyl-1-pentene. He found that the disruption of polymer crystallinity is determined principally by the

Table 4.6 **Comparison of the thermal properties of ethylene - 2-allylnorbornane copolymers with those of ethylene - 4-methyl - 1-pentene copolymers**

Ethylene - 2-allylnorbornane copolymers					**Ethylene - 4-methyl - 1-pentene copolymers**				
Sr. No.	**mol % comonomer**	**T_m °C**	**ΔH_f J/g**	**% Cryst.**	**Sr. No.**	**mol % comonomer**	**T_m °C**	**ΔH_f J/g**	**% Cryst.**
$TiCl_4/(iso-Bu)_3Al$ catalyst system									
1.	-	131.6	128.6	45	1.	-	131.6	128.5	45
2.	7	127.3	86.2	30	2.	6	126.6	89.4	31
3.	11	126.7	61.0	21	3.	11	125.2	60.0	21
4.	20	126.0	37.6	13	4.	19	124.0	38.4	13
Cp_2ZrCl_2/MAO catalyst system									
1.	-	132.5	194.7	67	1.	-	132.5	194.7	67
2.	3	110, 115	83	28	2.	2.5	112,117	96	33
3.	4	103,108	71	24	3.	3.6	105,110	67	23
4.	5.7	97,104	52	18	4.	5.0	98,104	51	17.5
5.	9.5	91,99.9	26	9	5.	7.5	96,101	41	14

number and distribution of chain irregularities rather than branch length. He attributed this to the use of similar catalyst and reaction conditions resulting in copolymers of similar molecular weight and molecular weight distribution.

On the other hand Clas *et al*[30] observed that in a series of copolymers of ethylene and 1-alkene ranging from 1-butene to 1-octadecene prepared using $VOCl_3/Et_3Al_2Cl_3$ catalyst, at low comonomer contents the melting points are independent of branch length but at higher comonomer content the melting points decrease in the order 1-butene > 1-octene > 1-octadecne. For example, at 8 mol % comonomer the melting point of ethylene-1-butene copolymer was 92°C whereas for ethylene-1-octadecene copolymer it was 65°C. This case is an extreme one with a large difference in branch lengths between the two comonomers. In our case however, it can be concluded that probably due to the bridging, the norbornyl ring acquires a compact structure on account of which its influence on the folding of polyethylene chains is not very different from that of an isopropyl group as in the case of 4-methyl-1-pentene comonomer.

4.4 SUMMARY AND CONCLUSIONS :

The results of the study of ethylene-2-allylnorbornane copolymers are summarized as follows

The copolymers obtained using Cp_2ZrCl_2/MAO give rise to homogeneous and random copolymers and the $TiCl_4/(iso\ Bu)_3Al$ catalyst gives rise to heterogeneous and blocky type of copolymers. These conclusions are drawn based on results of reactivity ratio analysis, fractionation, gel permeation chromatograms, infrared and differential scanning calorimetric studies of the two copolymers.

At the same mol % of incorporation, the copolymers obtained using the Cp_2ZrCl_2/MAO catalyst have much lower values of crystallinity and T_m. However the values of intrinsic viscosity are also lower.

The copolymers were studied using NMR and peak positions were assigned. An IR calibration method was devised for routine analysis of the composition of the copolymers.

Contrary to expectation the bicyclo (2.2.1) pendant does not result in an additional lowering of crystallinity and density when compared to the isopropyl pendant. This conclusion is drawn based on the comparison of the thermal properties of ethylene-2-allylnorbornane and ethylene-4-methyl-1-pentene copolymers at similar mol % incorporation if comonomer. This could be due to the unique space filling structure of the norbornyl pendant which arises as a result of bridging.

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CHAPTER V

COPOLYMERIZATION OF ETHYLENE WITH 5-VINYL-2-NORBORNENE USING HOMOGENEOUS Cp_2ZrCl_2/MAO CATALYST SYSTEM

5.1 INTRODUCTION

Copolymerization of ethylene with an α,ω-diene has not been studied very extensively in literature. This could be because of the high costs of the diene comonomer and the fact that if a good selectivity on the double bond insertion is not achieved, it could lead to the formation of crosslinked gelled products, due to the participation of both the double bonds in copolymerization. However, interest in this area is growing since ethylene-α,ω-diene copolymers having moderate levels of diene incorporation, not only possess properties such as improved tensile strength and impact strength due to the presence of short chain branches arising from the comonomer as in LLDPE's, but also have improved properties such as better paintability, printability and adhesion . The presence of residual unsaturation also makes them amenable for further functionalization.

A survey of both published and patented literature in this area, shows that some of the diene comonomers studied for copolymerization are 1,5-hexadiene, 1,9-decadiene, 1,4-hexadiene, 4-vinyl-1-cyclohexene, 5-vinyl-2-norbornene, 1,7-octadiene, etc.

Conventional catalysts

Valvassori et al[1] studied the copolymerization of ethylene with 1,5-hexadiene at atmospheric pressure using both heterogeneous and homogeneous catalyst systems. They found that using a heterogeneous catalyst like $VCl_4/(C_6H_{13})_3Al$ resulted predominantly in a copolymer containing structures arising from a cyclization of the diene comonomer. On the other hand, using a homogeneous catalyst like $V(acac)_3/Et_2AlCl$ resulted in a copolymer, where the predominant form of diene insertion was a 1,2 –enchainment. Further, 1,2-enchainment of the diene was favoured by lowering the temperature. Thus, at 25°C 1,2-enchainment of the diene was 30-35% and at -20°C it was 75-80%.

Cyclization of 1,5-hexadiene was also observed by Makowski et al.[2] during its copolymerization with ethylene using $TiCl_3/R_3Al$ catalyst system. The resulting copolymers containing 15-93 mole % of ethylene were found to be highly crystalline and stiff due to the presence of cyclopentane units in the main chain as a result of hexadiene cyclization. Thus, in an α,ω -diene, cyclization leading to a five or six membered ring is more favorable than a 1,2-enchainment.Copolymerization of ethylene with methyl-1,4-hexadiene was studied using $TiCl_3/Et_2AlCl$ and hydrogen as a molecular weight regulator by Fujii et al.[3] Here the tri-substituted double bond did not take part in the copolymerization and hence remained as a pendant. The properties of the copolymer were similar to polyethylene but had additional features such as good paintability and adhesion strength.

Supported Mg-Ti catalysts

Mulhaupt et al[4] during a study of ethylene-α-olefin copolymerization using a catalyst composed of $MgCl_2$ incorporated with 2,6-di-tert-butyl-4 methylphenol (BHT), $TiCl_4$ and $AlEt_2BHT$, also studied the copolymerization of ethylene with a few dienes. However, the levels of diene incorporation were low, i.e. less than 5 wt.% in case of 4-vinyl-1-cyclohexene and less than 4 wt. % in case of styrene.

Copolymerization of ethylene with 1,9-decadiene[5] using $MgCl_2$ supported Ti catalysts has been reported by Kurusu *et al*. The copolymer was found to contain pendant vinyl bonds. However, the level of diene incorporation was very low i.e. around 1 mol.%.

Homogeneous metallocene catalysts

There are no published reports on the copolymerization of ethylene with α,ω-dienes using metallocene catalysts. However a considerable amount of patents have been issued in the last couple of years (Table 5.1). One can see that dienes such as 1,4-hexadiene, 1,5-hexadiene, 4-vinyl-1-cyclohexene and 2,5-norbornadiene

Table 5.1 Representative Patent Literature on Ethylene - α,ω - diene Copolymerization

Name of Company Patent No. and CA no.	Comonomer	Cat. System	Polym. Cond.	Features of the Copolymer
Mitsubishi Chem. Inds. Ltd. JP 59,56,412 101:92065e	1,7-Octadiene	$(EtO)_2Mg/(BuO)_3$ $TiCl/Et_3Al_2Cl_3/Et_2AlCl$	I Stage (A) ethylene polymerization II stage (B) copolymerization	A:B ratio 3:7 - 7:3 diene content 0.01-10% pdt. has few fish eyes, good mouldability and rigidity.
Idemitsu Petrochem. Co.Ltd. JP 61, 148, 211 106:19183r	Norbornadiene	$Mg(OEt)_2/MgSO_4/TiCl_4/$ Et_3Al, Et_2AlCl	I stage (A) ethylene polymerization II stage (B) copolymerization	Norbornadiene 0.78%, [η]=5.5, A:B ratio 60:40 gives good tensile impact, stress cracking resistance.
Nippon Oil Co.Ltd. JP 02, 243,611 108:151141w	5-vinyl-2-norbornene	$MgCl_2/(EtO)_4Si/POCl_3$ $/TiCl_4/Et_3Al$	Temp. = 70°C Press = 10 kg/cm^2	[η] = 14.9 dL/g density = 0.93 bulk den. = 0.26
Exxon Chem. Patents Inc. WO 88,04,673 109:130214c	1,5-hexadiene	bis (butylcyclopentadienyl) zirconiumdichloride/MAO	Temp. = 70°C	$\overline{M}_w = 120 \times 10^3$ $\overline{M}_w/\overline{M}_n = 2.6$ Cluster index $<$ 5
Exxon Chem. Patents Inc. WO 88,04,674 110:9126t	1,4-hexadiene, 4-vinyl-1-cyclohexene	bis (butylcyclopentadienyl) zirconiumdichloride/MAO	Temp. = 60°C	$\overline{M}_w/\overline{M}_n = 1.75$ Cluster index = 5 M.pt = 111.9°(narrow) improved toughness, printability.

Contd..

Name of Company Patent No. and CA no.	Comonomer	Cat. System	Polym. Cond.	Features of the Copolymer
Exxon Chem. Patents Inc. WO 91,01,337 115:256891p	1,4 hexadiene	bis indenyl zirconium dichloride/MAO on silica	Temp. = 63°C Press = 330 psia fluidized bed	MFI = 17.7-21.3 dg/min d = 0.9211 - 0.9237
Exxon Chem. Patents Inc. Ind. Pat. Appl. 172282 ICPA,9(1),1993	1,5-hexadiene	metallocene/MAO	-	diene ‹ 15 wt%
Idemitsu Kosan Co. JP 65,194,665 120:9180n	p-(3-butenyl) styrene	Cp_2 $TiCl_2$/MAO	-	diene = 17 mol%
Mitsui Petrochem. Inds. JP 04,11,615 116:256257g	1,5-hexadiene	$MgCl_2$, $TiCl_3$ - pyridine complex, $Et_3Al_2Cl_3$	-	Act. = 5Kg/gTi E=22.5mol%
Idemitsu Kosan Co.Ltd. JP 04,279,611 118:125301k	2,5-norbornadiene	$CpTiCl_3$/MAO	-	-
Imperial Chem. Inds. WO 9118,030 116:10729g	7-methyl-1,6 - octadiene	Mg-Ti/Et_3Al	slurry,3h.	diene 6.7 mol

have been used in copolymerization with ethylene using metallocene catalysts to give rise to copolymers with narrow molecular weight distribution, low cluster index and having improved paintbility, printability, mouldability etc.

Based on the published and patented literature it can be noted that

1) The catalyst type has a prominent effect on the copolymer microstructure as well as the level of comonomer insertion and the selectivity of the process. Thus, in processes which use Ti based catalysts, the level of diene incorporation is either low or not mentioned. Ti catalysts are also known to produce copolymers with a blocky microstructure. However, processes using metallocene catalysts result in higher levels of diene incorporation with features like low melting points having narrow distribution, low polydispersity index and low cluster index.

$$Cluster\,index = \frac{10[(X) - (E\;X\;E)]}{[2(X^2) - (X^3)]}$$

where x = mole % of comonomer, EXE = mole fraction of triad. A cluster index = 10 means random distribution and cluster index = 0 means no more than one continuous unit of comonomer.

2) For an efficient incorporation of the diene the structural features of the diene should favour insertion of one of the double bonds leaving the other double bond free. Most authors have used a diene containing an alpha olefin and a hindered di or tri substituted olefin such as, 1,4-hexadiene, 7-methyl-1,6-octadiene etc. in which case the enchainment occurs through the alpha olefin.

Recent work by Kaminsky *et al*[6] has shown the copolymerization of ethylene with a bicyclic olefin (norbornene) using metallocene/MAO catalysts occurs very efficiently with high levels of norbornene incorporation and without any ring opening reactions of bicyclic unit. The driving force of the reaction is the release in ring strain upon insertion. All other Ziegler Natta type catalysts, when used for polymerization of norbornene, result in products in which at least 30% of the structures are a result of ring opening reactions.[7]

Following the earlier line of thought of choosing a diene with a built-in preference for insertion of one type of double bond, we reasoned that if a diene like 5-vinyl-2-norbornene (5V2N) containing an endocyclic strained double bond and exocyclic less strained vinyl bond, is chosen and the metallocene/MAO catalyst system is employed, then, one can expect the endocyclic olefin will selectively take part in polymerization, leaving the less strained exocyclic vinyl double bond free as a pendant unsaturation.

A few patents exist on the copolymerization of ethylene with 5-vinyl-2-norbornene,using Mg-Ti catalysts (Table 5.1). However, the amount and selectivity of diene insertion remains unspecified. Lohse et al[8] studied the terpolymerization of ethylene and propylene with 5-vinyl-2-norbornene using $VOCl_3$/ethylaluminum sesquichloride catalyst. They confirmed by IR that the enchainment of the diene in the terpolymer occurred through the endocyclic vinylene bond. The level of incorporation of the termonomer was, however less that 1 mol. %.

Based on the work by Kaminsky et al. and our own results on ethylene-norbornene copolymerization (Appendix II), we expected a higher level of diene incorporation with regioselective insertion of the strained endocyclic double bond in the copolymerization of ethylene with 5-vinyl-2-norbornene using a metallocene/MAO catalyst system (Scheme 5.1).

5.2 EXPERIMENTAL SECTION

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

5.2.1 Materials

Toluene (Loba-Chemie AR grade) was washed over conc. H_2SO_4, followed by dil. Na_2CO_3 solution and then with distilled water. Preliminary drying was done with anhyd. $CaCl_2$ followed by refluxing over sodium wire and finally it was distilled under nitrogen prior to use. Polymerization grade ethylene was obtained from the C_2-C_3 gas cracker unit of Indian Petrochemical Corporation Ltd., Nagothane, Maharashtra (O_2 = 3 ppm, H_2O = 4 ppm). Methylaluminoxane (MAO) [(Me)/(Al) = 1.54, free TMA = 35%, 15.5% Al solution in toluene, Schering A.-G., Germany) was used as a 4.5% solution after dilution. 5-vinyl-2-norbornene (5V2N) (Aldrich, 70:30 endo:exo) was stirred over CaH_2 for 24 h and distilled under nitrogen prior to use. Cp_2ZrCl_2 (Aldrich) and Irganox 1010 (Ciba-Geigy) were used as received.

5.2.2 Copolymerization of ethylene with 5-vinyl-2-norbornene

Ethylene was copolymerized with 5V2N (**1**) at 1 atm. and 35°C in a jacketed reactor connected to a IL gas burette, using the experimental setup shown in Fig.4.1. Toluene (25 mL) was introduced into the reactor and was saturated with ethylene. 5V2N (1.17 g, 9.8×10^{-3} mol) was added to the reactor followed by a toluene solution of MAO (1.875×10^{-3} mol.). The copolymerization was initiated by the addition of a toluene solution of Cp_2ZrCl_2 (0.00125×10^{-3} mol). Consumption of ethylene was measured by a rise in the level of the gas burette, as a function of time. The polymerization was terminated after 45 min by the addition of a 2% solution of HCl in methanol. The ethylene-co-5-vinyl-2-norborene polymer (**2**) (yield 0. 39 g) was further washed with methanol containing 0.1% Irganox 1010, filtered and dried under vacuum at 40°C for 8 h. IR (film, cm^{-1}) : 2950 - 2850 (C-H stretch), 1638 (C=C stretch), 1470 (C-H def.), 990, 910 (CH_2 = CH def.), 725 (CH_2 rock). ^1H NMR ($CDCl_3$, ppm) 5.4 - 6 (=CH), 4.8 - 5.1 (=CH_2), 2.6 - 0.95 (backbone and aliphatic H). ^{13}C NMR ($CDCl_3$ at 50°C, ppm) : 144.37 (=CH, exo), 141.70 (=CH, endo), 113.78 (=CH_2, endo), 111.30 (=CH_2, exo), 47.32-34.28 (CH and CH_2 of bicyclic unit), 30.00 (backbone CH_2).

As described above, copolymerization batches were carried out by either varying the temperature, catalyst concentration or comonomer concentration keeping the other factors constant.

A large scale synthesis of copolymer (**2**) was carried out in a IL SOTELEM reactor at 35°C and at a constant ethylene pressure of 1.5 atm. Initially, the reactor furnace was heated to 170°C and the reactor to 120°C under an ethylene pressure of 2-3 atm. When the required temperature had reached the reactor was evacuated under 1 mm Hg vacuum for half an hour. It was then filled with 6 atm. ethylene and then leaving a slow stream of ethylene from the outlet of the reactor, it was allowed to cool to 35°C and the furnace to 40°C. Toluene (250 mL) was then introduced through the feed tube and allowed to saturate with ethylene with stirring. This was followed by addition of 2 mL (10%) trimethylaluminum solution, 15 mL (0.105 moles) of 5-vinyl-2-norbornene and 4.5 mL MAO solution(22.5×10^{-3} moles). After each addition the feed tube was washed down with 10 mL toluene. The polymerization was initiated by addition of 2.7 mL (1.5×10^{-5} moles) of Cp_2ZrCl_2 after which the feed tube inlet was closed and the reactor was connected directly to the ethylene gas ballast, the pressure in the reactor being maintained at 1 to 1.5. atm. After a pressure drop of 3 atm. in the ballast (23 min time) the pressure in the reactor was released and the reaction mixture poured into 1 L of methanol containing 2% HCL with stirring. The polymer was further washed with methanol containing 0.1 % Irganox 1010 and dried. Yield of the copolymer = 7.6 g.

5.2.3 Analytical techniques

^{1}H NMR spectra of samples as 2 wt% solutions were recorded using a Bruker AC-200 spectrometer at room temperature or 50°C in $CDCl_3$ or C_6D_6. The mole % incorporation of 5-vinyl-2-norbornene was calculated from ^{1}H NMR as follows.

Integral over 6 ppm - 5.6 ppm = A

Integral over 5.2 ppm - 4.8 ppm = B

Integral over 2.8 ppm - 0.8 ppm = C

$$Then, mol\%5V2NB incorporation = \frac{B/2}{B/2 + 1/4(C - 9B/2)}$$

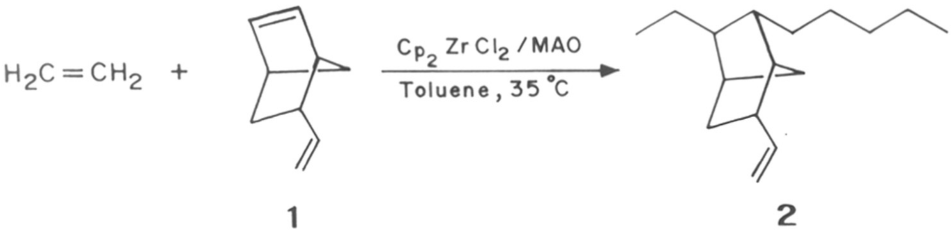
The ^{13}C NMR spectrum of a 10 wt% solution was recorded using a Bruker MSL 300 spectrometer at 50°C in $CDCl_3$. IR spectra of films cast from toluene solution were recorded using a Perkin-Elmer PE 16 FTIR spectrometer. Thermogravimetric analysis was carried out using a Netzch thermal analysis apparatus (Model STA 409), and differential scanning calorimetric analysis was carried out on a Perkin-Elmer DSC 7. Intrinsic viscosity measurements were done using an Ubbelohde viscometer in 1,2,4-trichlorobenzene at 135°C.

5.3 RESULTS AND DISCUSSION

5.3.1 Copolymerization of ethylene with 5-vinyl-2-norbornene:

Ethylene was found to undergo a facile copolymerization with 5-vinyl-2-norbornene (5V2N) in the presence of the Cp_2ZrCl_2/MAO catalyst system. (Scheme 5.1) A study of the effect of various copolymerization parameters on activity, Rp max, intrinsic viscosity and comonomer incorporation was conducted.

SCHEME 5·1



5.3.1.1 Effect of comonomer concentration

The results are shown in Table 5.2. By varying the comonomer feed from 0.23 M to 0.44 M the mole % of 5V2N incorporated could be increased from 6 to 14 mol %. This is accompanied by a decrease in intrinsic viscosity of the copolymer from 0.75 dL/g to 0.3 dL/g. This could be attributed to the increase in chain transfer to monomer. Further, the activity and Rp max. both decrease with increasing

Table 5.2 Copolymerization of ethylene with 5-vinyl-2-norbornene : Effect of comonomer concentration[a]

Sr. No.	[Ethylene] (M)	[VNB] (M)	Yield (g)	Conv. (%)	Activity kgcopoly./gZr	R_p $Msec^{-1}$	VNB in copolym.[b] (mol %)	$[\eta]^c$ (dL/g)
1.	0.11	0.22	0.79	70	9.3	223.7	nd	0.75
2.	0.11	0.28	0.61	49	7.1	190.1	6	0.50
3.	0.11	0.33	0.35	29	4.1	144.3	11	0.37
4.	0.11	0.39	0.39	28	4.6	108.0	10	0.32
5.	0.11	0.44	0.30	20	3.5	86.4	14	0.29

(a) Copolymerization conditions : temp. = 35°C; time = 45 min.; total solvent volume(toluene+5V2N) = 25 mL; [Al] = 7.5×10^{-2} M; [Zr] = 5×10^{-5} M; ethylene pressure = 1 atm

(b) Calculated from ^1H NMR

(c) In 1,2,4 trichlorobenzene at 135°C

comonomer concentration. This negative comonomer effect could be explained as arising from a competition between ethylene and 5V2N in a complexation with the metallocene. A similar effect was observed by Kaminsky[9] during ethylene-norbornene copolymerizations. This observation however is in contrast to the rate enhancement effect of comonomer observed in the case of an acyclic olefin like 1-hexene[10] and a monocyclic olefin like cyclopentene[11]. Here at low comonomer feed ratio a rate enhancing effect was observed followed by a decrease in activity at higher comonomer feeds. The rate enhancement or depressing effect is generally understood to be arising as a result of many factors, namely, increase in monomer diffusion due to decrease in crystallinity and molar mass of the polymer, modification of active centers by comonomer, increase or decrease in number of active centers etc. Without a thorough investigation of the influencing factors no simple explanation to the rate depressing effect of 5V2N can be given at present.

5.3.1.2 Effect of catalyst concentration

In the range of catalyst concentration studied here (Table 5.3), an increase in catalyst concentration led to an increase in activity and Rp max. A marginal increase in comonomer incorporated is seen along with slight decrease in intrinsic viscosity. A similar positive effect of catalyst concentration on comonomer incorporation was noted by Kaminsky et al[9].

5.3.1.3 Effect of temperature

Temperature has a positive effect on the Rp max and activity but the comonomer incorporated decreases (Table 5.4). The intrinsic viscosity decreases with increase in temperature. Similar observation of the effect of temperature have been made by a number of other workers[11,12,13] using metallocene/MAO catalysts for polymerization of ethylene and copolymerization of ethylene and α-olefins.

Table 5.3 Copolymerization of ethylene with 5-vinyl-2-norbornene : Effect of catalyst concentration[a]

Sr.No.	Catalyst concentration M	Yield (g)	Activity Kgpoly/gZr	R_p max M sec^{-1}	Mol % incorporation	[η] (dL)/g
1.	5×10^{-5}	0.2327	2.040	190.2	9.8	0.4403
2.	8×10^{-5}	0.4729	2.570	212.5	10.4	0.4012
3.	14×10^{-4}	0.8487	2.635	284.6	11.0	0.3824

(a) Copolymerization conditions : temp. = 35°C; time = 45 min.; total solvent volume(toluene+5V2N) = 25 mL; [Al] = 7.5×10^{-2} M; [Zr] = 5×10^{-5} M; ethylene pressure = 1 atm

Table 5.4 Copolymerization of ethylene with norbornene : Effect of temperature[a]

Sr.No.	Temp.	Yield (g)	Activity Kgpoly/gZr	R_p max M sec^{-1}	Mol % incorporation	[η] (dL)/g
1.	35	0.2327	2.040	190.2	9.8	0.4403
2.	45	0.5163	4.49	216.2	8.4	0.3924
3.	55	0.9524	8.28	252.2	7.0	0.3108

(a) Copolymerization conditions : temp. = 35°C; time = 45 min.; total solvent volume(toluene+5V2N) = 25 mL; [Al] = 7.5×10^{-2} M; [Zr] = 5×10^{-5} M; ethylene pressure = 1 atm

5.3.1.4 Calculation of reactivity ratios

For the calculation of reactivity ratios copolymerizations were terminated at very short time (60-120 s.) over a range of comonomer feed ratios (Table 5.5). Reactivity ratios r_1 (ethylene) and r_2 (5V2N) found out by the method of Fineman-Ross are $r_1 = 21.3$; $r_2= 0.18$, Kelen Tudos are $r_1 = 20.13$, $r_2 = 0.14$ with $r_1r_2 = 2.8$ (Fig.5.1). Kaminsky[9] reports a value of $r_1 = 20$ for ethylene-norbornene copolymerization using Cp_2ZrCl_2/MAO at 25°C.

5.3.2 Characterization of ethylene-co-5-vinyl-2-norbornene

5.3.2.1 Solubility : By a suitable adjustment of 5V2N feed ratios copolymers containing 5 - 20 mole % of VNB could be synthesized. Copolymers containing high amount of 5V2N (more than 5 mole %) were completely soluble in toluene, $CHCl_3$, xylene, 1,2,4 trichlorobenzene at 50°C indicating they were gel-free. Copolymers containing less than 5 mol % 5V2N were soluble only at 135°C in 1,2,4-trichlorobenzene.

5.3.2.2 Infrared Spectroscopy : The copolymers were examined in the form of films cast from toluene solution by IR. Examination of the spectrum (Fig. 5.2) shows the following features 3125 - 3030 cm^{-1} (weak, =C-H stretch) 2950 - 2850 cm^{-1} (strong, -C-H skeletal stretch) 1638 cm^{-1} (medium, C=C stretch), 1470 cm^{-1} (strong, -C-H bending), 990 and 910 cm^{-1} (medium, $CH_2 = CH$ deformation), 720, 730 cm^{-1} (medium CH_2 rock). In samples having low content of 5V2N a clear doublet is seen at 720, 730 cm^{-1}, but in sample having high content of 5V2N (15 mole %) only a shoulder is observed at 730 cm^{-1} on the 720 cm^{-1} absorption, indicating a substantial loss in crystallinity at high 5V2N content. The band at 1820 cm^{-1} is an overtone of the 910 cm^{-1} absorption.

The absorptions at 1638, 990 and 910 cm^{-1} which are typical of a vinyl unsaturation led us to infer that the copolymerization occurs via a selective

Table 5.5 **Ethylene 5-vinyl-2-norbornene copolymerization (at low conversion) together with evaluation of some parameters (catalyst : Cp_2ZrCl_2/MAO)**

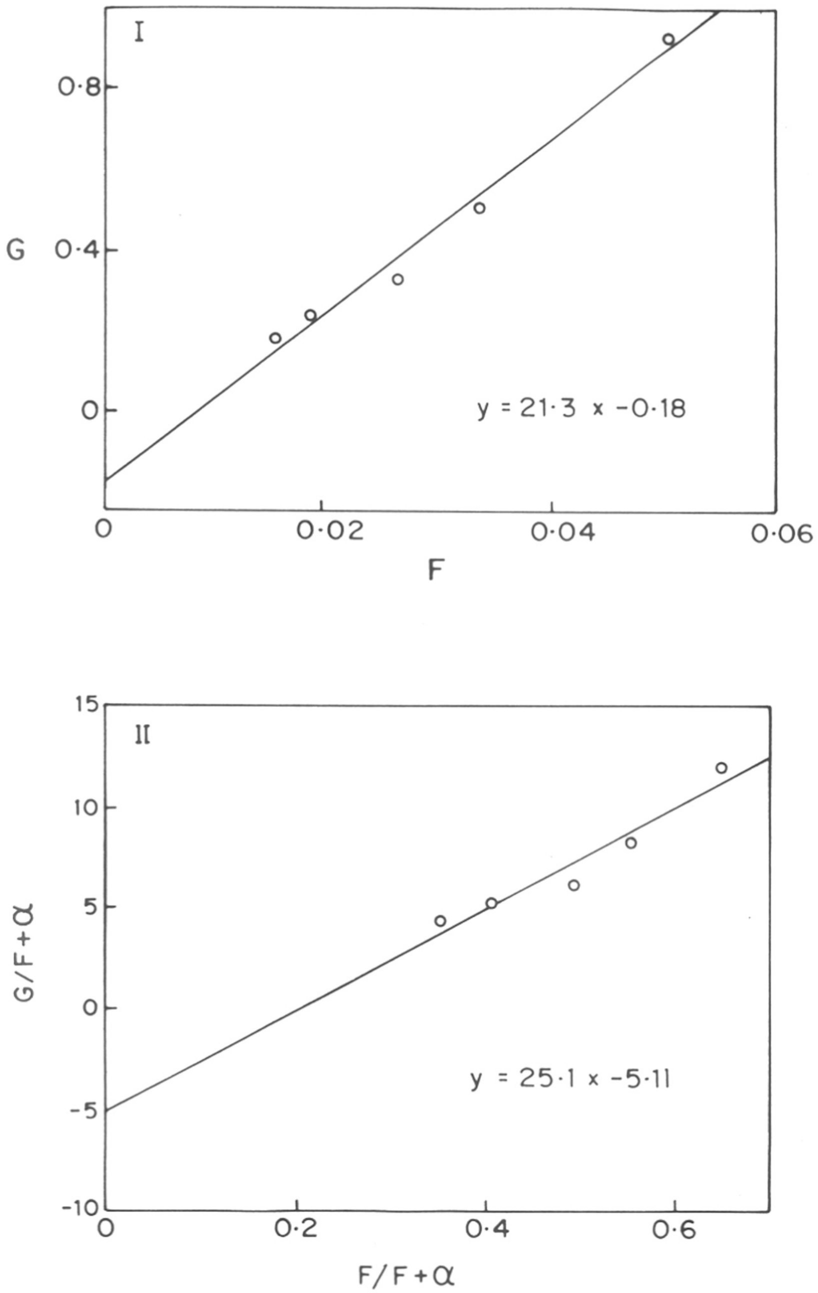
S.No.	Conc. of 5V2N in feed M	5V2NB in Poly[b]	$F_1=(m_1/m_2)$	$f_1=(M_1/M_2)$	F^c	G^c	$\frac{F}{F+\alpha}$	$\frac{G}{F+\alpha}$
1.	0.112	5.0	0.982	19.00	0.0507	0.930	0.6483	11.89
2.	0.196	9.6	0.561	9.41	0.0334	0.501	0.5484	8.23
3.	0.280	14.5	0.393	5.89	0.0262	0.326	0.4878	6.07
4.	0.364	17.0	0.302	4.88	0.0186	0.240	0.4034	5.20
5.	0.448	20.0	0.245	4.00	0.0150	0.183	0.3523	4.29

(a) Copolymerization conditions : temp. = 35°C; time = 1-2 min.; total solvent volume(toluene+5V2N) = 25 mL; [Al] = 7.5×10^{-2} M; [Zr] = 5×10^{-5} M; ethylene pressure = 1 atm

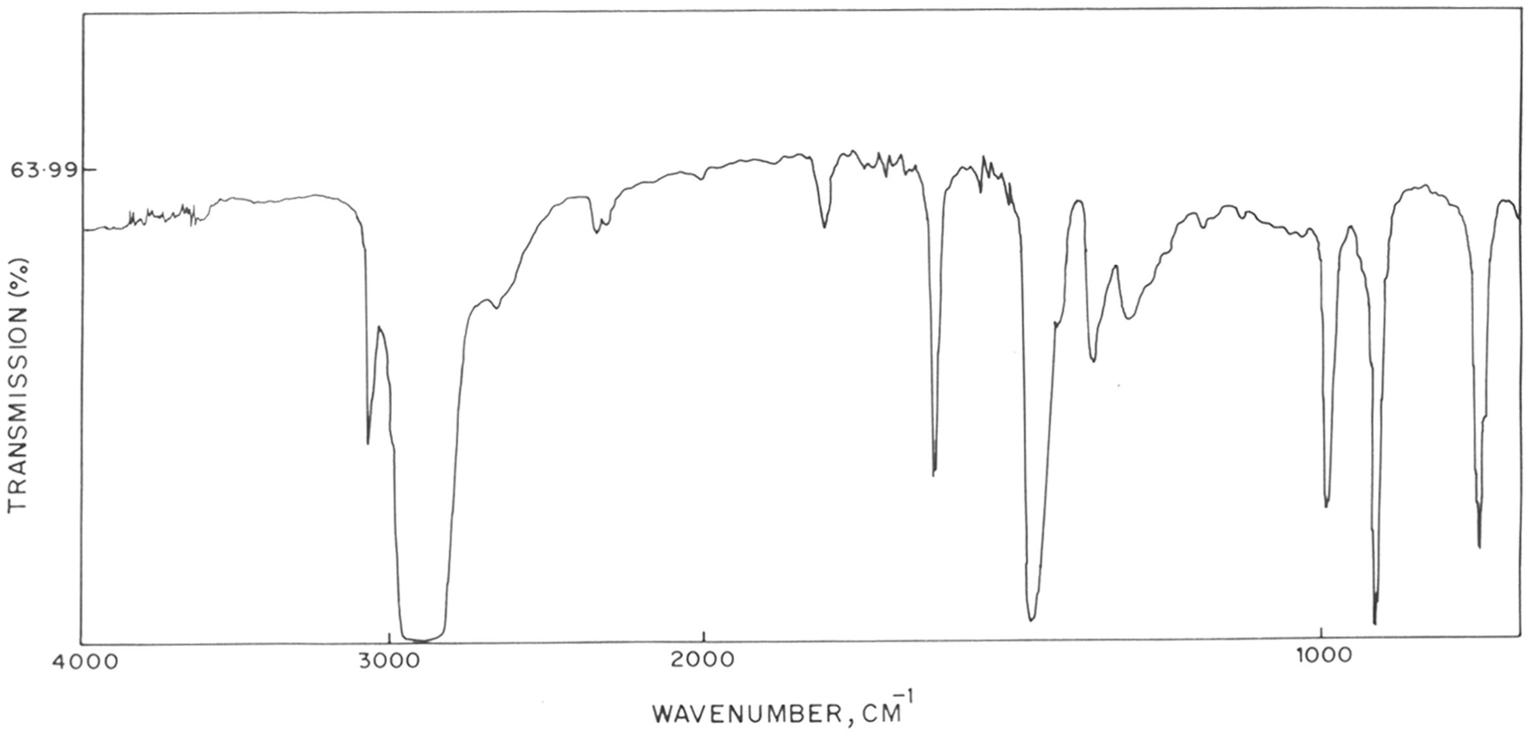
(b) Calculated from ^1H NMR

(c) $F = \frac{F_1^2}{f_1}$, $G = \frac{f_1 - 1}{f_1} x F_1$ Fineman - Ross eqn. : $G = - r_{comonomer} + r_{ethyelene} F$

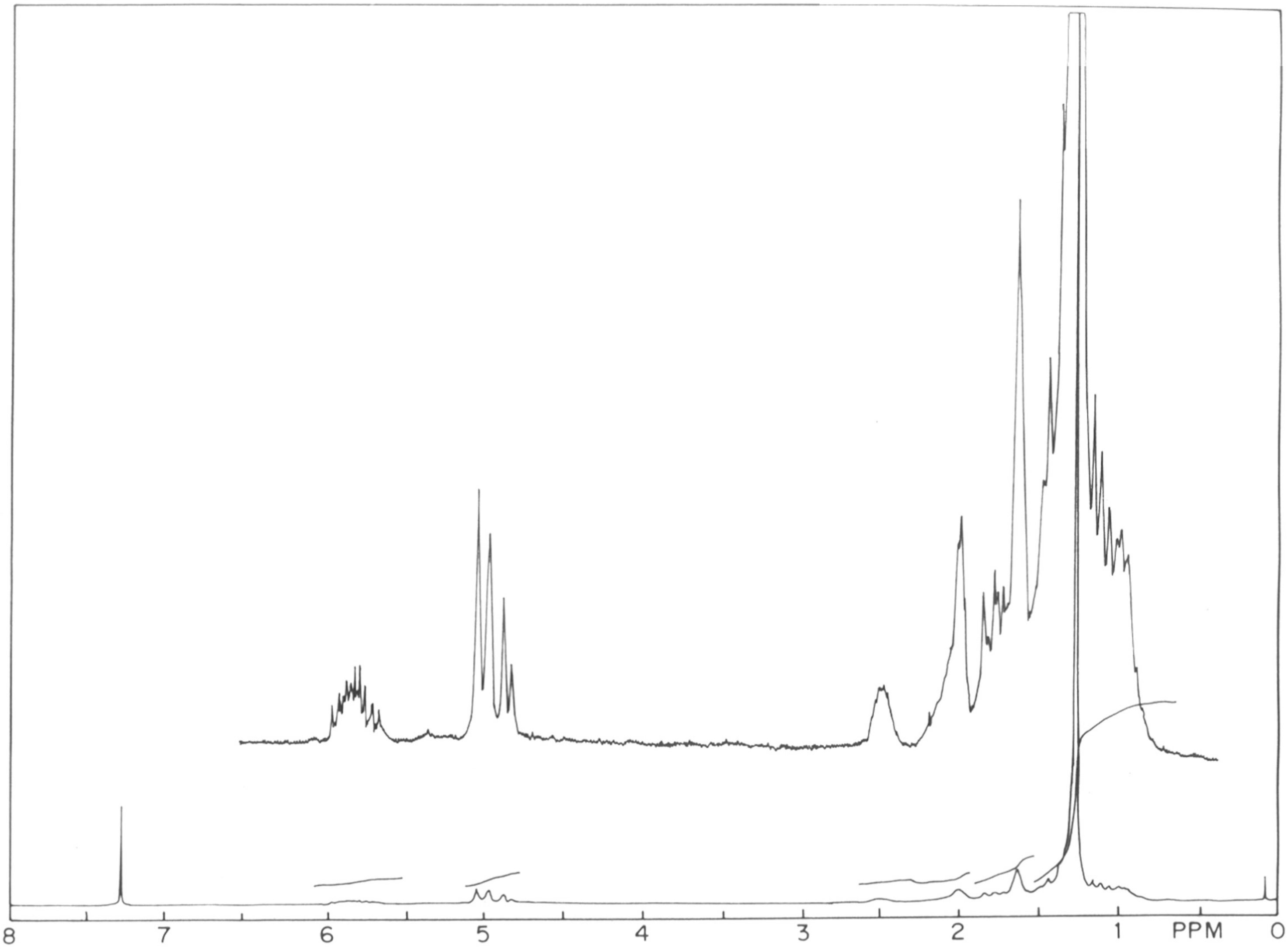
Kelen-Tudos eqn. : $G/(F + \alpha) = (-r_{comonomer}/\alpha) + (r_{ethylene} + r_{comonomer}\, \alpha^{-1}) (F / F + \alpha)$



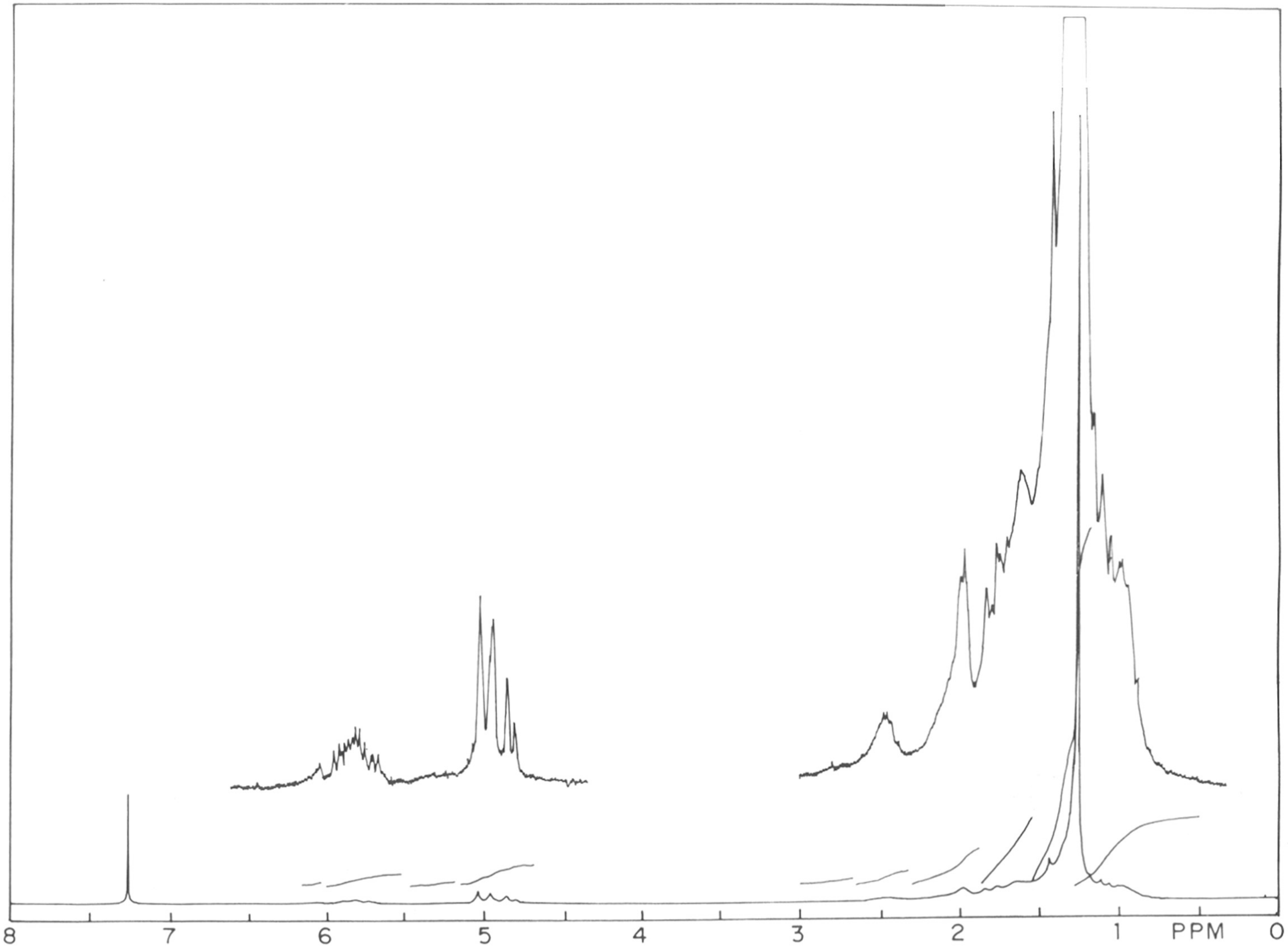
5.1 Fineman-Ross (I) and Kelen-Tudos plots for ethylene 5-vinyl-2-norbornene copolymerization over Cp_2ZrCl_2/MAO catalyst system.



5.2 IR spectrum of an ethylene-5-vinyl-2-norbornene copolymer (E5V2N).



5.3 ¹H NMR spectrum of an ethylene-5-vinyl-2-norbornene copolymer (E5V2N).



5.4 ^{1}H NMR spectrum of a 95:5 weight ratio of poly(ethylene-co-5-vinyl-2- norbornene) : poly(ethylene-co-norbornadiene).

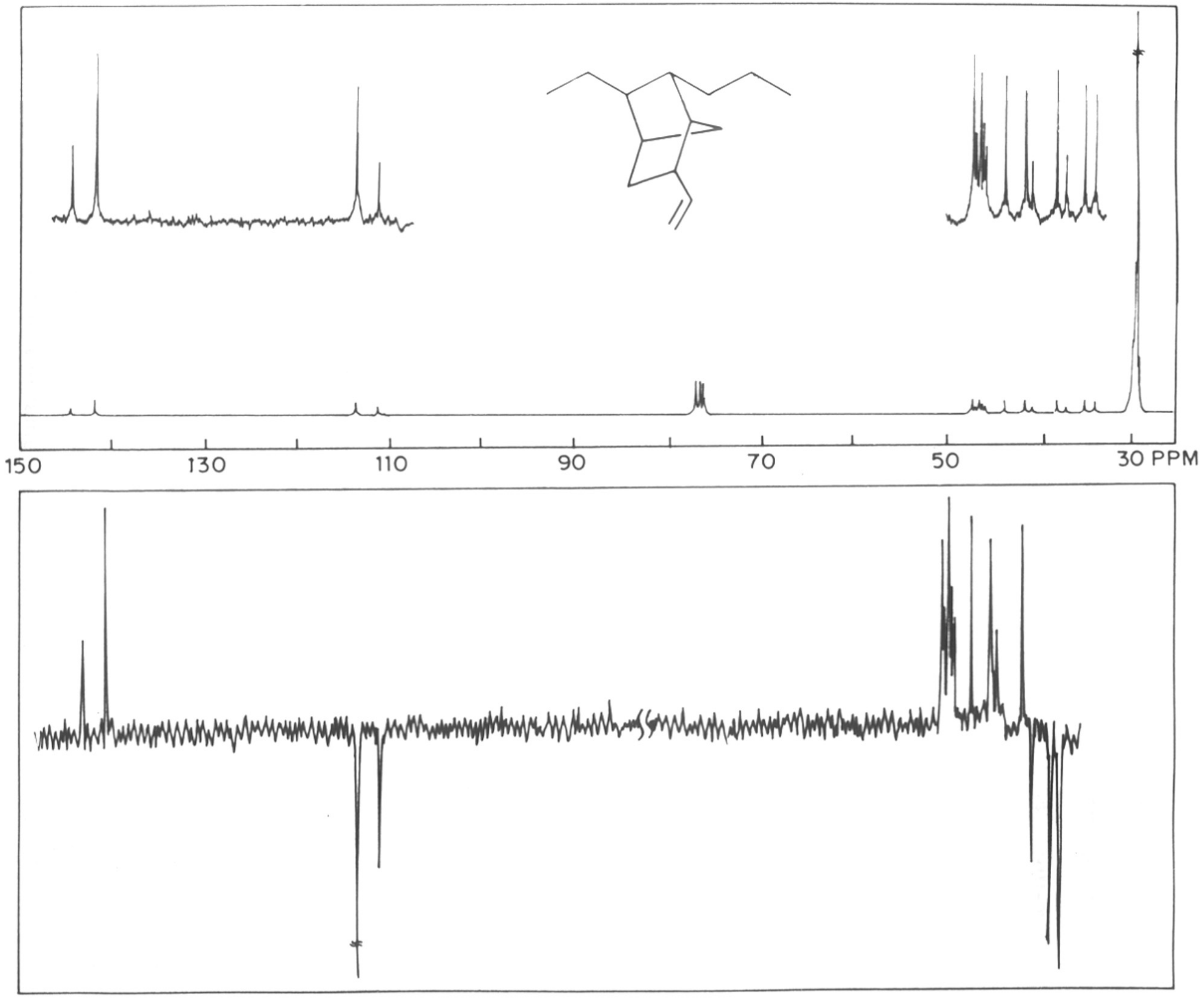
enchainment of the endocyclic double bond leaving the exocyclic double bond as a pendant. Further absorption at 710 cm^{-1}, which could have arisen if the copolymer contained an endocyclic double bond is absent.

5.3.2.3 Nuclear magnetic resonance spectroscopy

^1H NMR : The ^1H NMR spectrum of the E5V2N copolymer shows a typical vinyl pattern between 4.8 and 6.0 ppm and an intense peak at 1.3 ppm from the $-CH_2$ backbone (Fig. 5.3). No peak is seen at 6.1 ppm indicating absence of endocyclic olefin. In order to check the % selectivity of copolymerization through enchainment of the endocyclic olefin, ^1H NMR of a physical mixture 90:10 and 95:5 of poly(ethylene-co-5-vinyl-2-norbornene) : poly(ethylene-co-norbornadiene) (which has a pendant endocyclic bond) was recorded (Fig. 5.4). It was found that even at a 95 : 5 ratio, peak at 6.1 ppm is seen distinctly apart from the vinyl pattern. Since our E5V2N copolymer does not show this peak it was concluded that the selectivity of enchainment is greater than 95%.

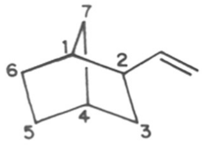
^{13}C NMR : Fig (5.5) shows the ^{13}C NMR of E5V2N copolymer in the region 0-150 ppm. Peaks at 144.37 (= CH, exo), 141.70 (=CH, endo), 113.78 ($=CH_2$, endo) 111.30 ($=CH_2$, exo) showing presence of a free vinyl double bond, confirm our earlier observation that enchainment of 5V2N occurs regioselectively through the endocyclic double bond. It can also be seen that the ratio endo:exo isomer in the polymer is 70:30 i.e. same as the starting mixture, implying no selectivity of insertion towards either monomer. This could be because the endo/exo substituent is far away from the reaction center.

The aliphatic region 0-50 ppm is very crowded due to signals from the exo/endo isomers of the bicyclic unit. Assignment of peaks was done with the help of DEPT spectrum, ^{13}C NMR data of model compounds and using the simple additivity rules as applied in the case of alicyclic systems [16]. DEPT spectrum (Fig.5.5) shows presence of 3-methylenes and 9-methine signals. C2 and C7 are the two methylenes and hence four signals are expected (two for endo and two for

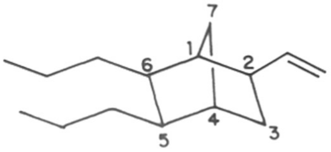


5.5 ^{13}C and DEPT spectrum of poly(ethylene-co-5-vinyl-2-norbornene).

exo). C1, C2, C4, C5, C6 are the 5-methines and hence 10 signals are expected. According to Whitesell and Minton[16] stereochemical analysis of alicyclic compounds is best done by considering the shifts of the parent hydrocarbon as base values to which the effects of all substituents other than the ring carbons are added (Δδ shift-of-shift addtitvity rules). Here 2-vinylnorbornane (III) is considered as the parent compound (peak positions are given in reference 17) and Δδ (shift-of-shift) values have been applied to predict the peak position, when it becomes part of a polymer backbone (IV) due to additional α and β and γ gauche carbons



3



4

The bias imposed by the bridging present in bicyclo (2.2.1) heptanes favours a boat or doghouse type of conformation. The shift in ppm due to additional α or β substituents, being electronic in nature is not much affected by stereochemistry, but the γ effect (which is maxmimum in an eclipsed butane relationship) has to be considered only when the γ substituent and the carbon under consideration are close together (reference 16).

Starting with C1 carbon, it appears at 42.7 (X) and 42.5 (N) in **3**. In **4** there is an additional β carbon and hence it gets shifted to 47.34 (N) and 47.12 (X). The C2 carbon appears at 46.4 (X) and 44.7 (N) in **3**. In **4** since there are no additional α or β carbons the values are almost unchanged 46.1 (X) and 44.13 (N). Similarly the C3 carbon has almost the same shift as in **3** i.e. 37.5 (N) and 35.4 (X). The C4 carbon in **4** has an additional β carbon and hence experiences downfield shift to 41.98 (N) and 41.29 (X). The C5 carbon in **4** has an additional α, two β and two γ compared to **3** resulting in a net downfield shift of 16 ppm. Similarly C6 which appears at 23.3 (N), 31.4 (X) in **3** now appears at 38.5 (N), 46.50 (X). The C7 carbon appears at 35.8 (X) and 40.3 (N) in **3**, the exo being shifted upfield due to a γ interaction with the exo substituent on C2. In **4** with the $-CH_2-CH_2$ main chain expected to be exo on C6 it would introduce yet another γ interaction and hence C7 can be expected to appear at 34.3 (N) and 30.0 (X), out of which 30.0 gets merged in the backbone signal. However, since these calculations are done based on empirical rules, slight variations in the calculated and actual values are observed, which are well within the limits.

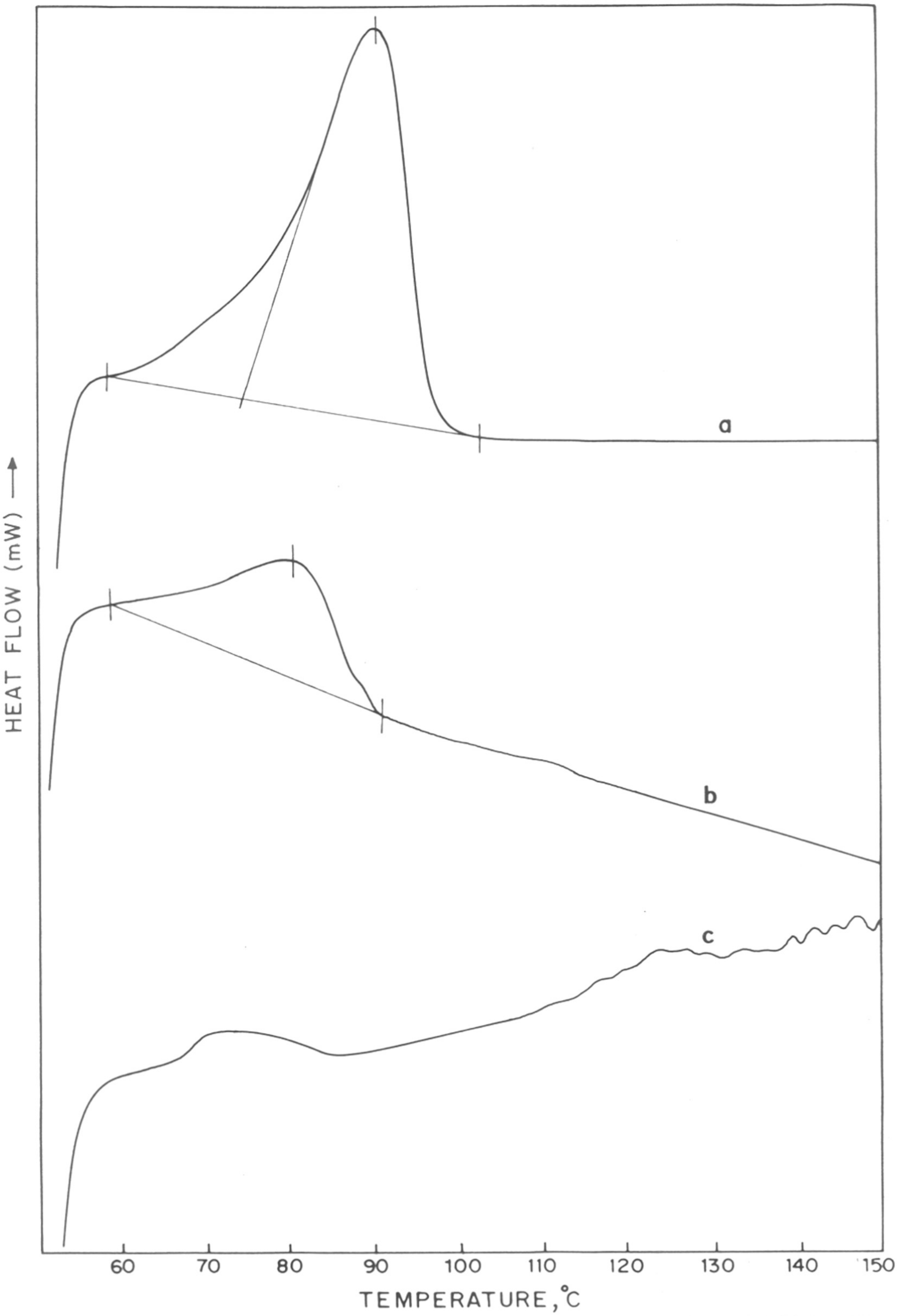
At about 10 mol% concentration of 5V2N in the copolymer the only other signals seen in the ^{13}C NMR are the $S_{\delta\delta}$, $S_{\alpha\delta}$ and $S_{\beta\delta}$ at 30.0ppm (calculations similar to those under Appendix II).

Hence, based on the additivity rules applied for bicyclic systems as elucidated in reference 16 reasonable assignments for the ^{13}C NMR spectrum could be reached.

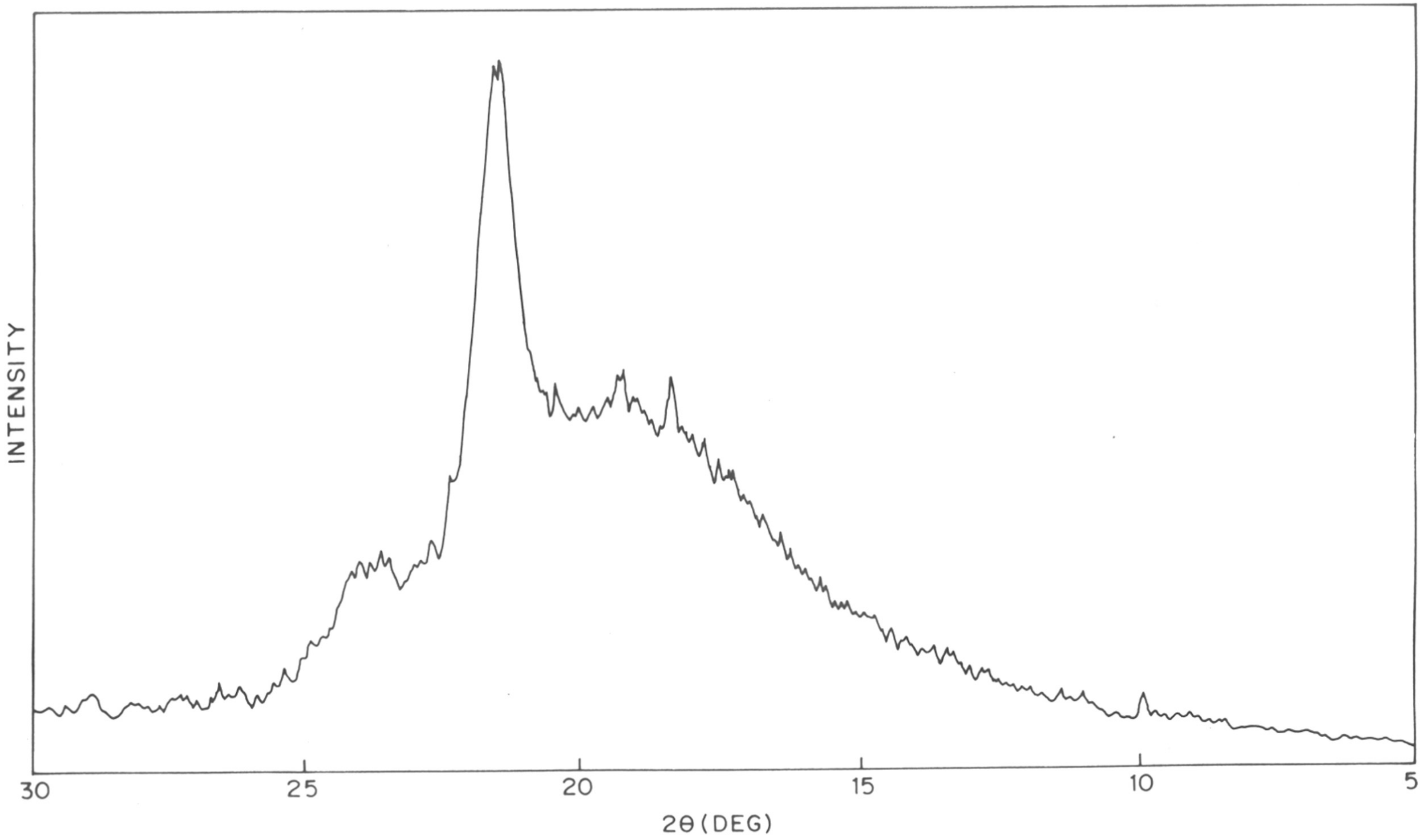
5.3.2.4 Thermal Analysis : All the E5V2N copolymers studied were found to be stable upto 400°C under nitrogen similar to the parent polyethylene.

DSC scans recorded under N_2 showed an initial decrease in Tm and ΔH_f with increase in comonomer content, until above some level no Tm could be detected. Thus, an E5V2N copolymer with 6 mol % comonomer shows Tm = 90.3°C and δH_f = 55 J/g, copolymer with 9 mol % incorporation shows Tm = 80.5°C, δH_f = 20 J/g and a copolymer with 14 mol % incorporation does not show any Tm (Fig. 5.6) implying loss of crystallinity.

5.3.2.5 X-ray diffraction : X-ray diffraction pattern of E5V2N copolymer containing 10.5 mole %. 5V2N shows a substantial loss of crystallinity as compared to polyethylene (Fig.5.7).



5.6 DSC scans of ethylene-5-vinyl-2-norbornene copolymers with (a) 6 mol% (b) 9 mol% and (c) 14 mol% 5V2N incorporation.



5.7 X-ray diffraction pattern of an ethylene-5-vinyl-2-norbornene copolymer.

5.4 SUMMARY AND CONCLUSIONS

This study has shown that the copolymerization of ethylene with 5-vinyl-2-norbornene using zirconcene - MAO affords a simple route to polyolefins with pendant vinyl groups. Without resorting to measurement of individual polymerization rate constants this proves the higher reactivity of the endocyclic bond over a vinyl exocyclic bond in copolymerization. Due to the high level of regioselectivity of insertion of the endocyclic double bond, high levels of comonomer incorporation could be achieved without any crosslinking reactions.

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CHAPTER VI

POST-POLYMERIZATION REACTIONS OF ETHYLENE-5-VINYL-2-NORBORNENE COPOLYMER

6.1 INTRODUCTION

Polyolefins, one of the largest commodity polymers, have very desirable properties such as good mechanical strength, rigidity, chemical and solvent resistance and relatively good environmental stability. However, due to their chemical inertness, they form incompatible blends with other families of polymers and also lack the ability to form block and graft copolymers with functional group containing monomers.

In recent years, there has been a tremendous interest in producing new block and graft copolymers and a whole range of polymer blends. This is due to the ability of combining the desirable properties of two polymers which are derived from radically different chemistries, by the above two techniques.

The introduction of a small amount of functionality in polyolefins can help in overcoming their inertness and improving their paintability, permeability, printability, adhesion and compatibility with other functionalized polymers. Furthermore, the functional group offers sites for initiating graft copolymerization, which leads to useful applications such as compatibilization in blends containing polyolefins.

In general there are three different routes to the synthesis of functional polyolefins : (1) direct copolymerization of functional comonomers (2) post-polymerization chemical modification of polyolefins, and (3) formation of precursors which can readily be transformed to functional polymers.

It is difficult to copolymerize a functional group bearing comonomer with olefins using a Ziegler-Natta catalyst. This is because the non-bonded electron pairs on N, O and X of functional monomers tend to complex with the Ziegler catalyst component resulting in deactivation of active sites and thus inhibiting polymerization.[1] Limited success has been achieved using an ester type unsaturated monomer, wherein the ester functionality was separated by a spacer group from the unsaturation.[2] The ester functionality is relatively inert during polymerization, however, the levels of comonomer incorporation are low and it is difficult to convert the ester functionality to other functional groups eg. -OH, $-NH_2$.

The other approach is the chemical modification of polyolefins in melt, within the barrel of an extruder, with polar compounds like maleic anhydride, maleimide and acrylic monomers in the presence of free radical initiators.[3] Such 'reactive processing' techniques form the basis of synthesis of many useful polyolefin based compatibilizing agents. However, these processes are difficult to control, yield complex reaction mixtures and are limited to low levels of incorporation of functional groups.

A preferred approach to the synthesis of functional polyolefins involves the use of precursor monomers possessing functionalities, which do not interfere with copolymerization, yet can be readily converted to functional polymers by post-polymerization chemical reactions.

Chung in a series of papers has elegantly shown how borane containing olefin monomers can be used in Ziegler-Natta polymerizations and copolymerizations. The borane group does not interfere in the polymerizations involving isotactic specific Ziegler-Natta catalysts, and can be subsequently converted to polar functionalities such as -OH, $-NH_2$, -X, -CHO and -CN.[4,5] The borane monomers and polymers are soluble in pure hydrocarbon media, which ensures the formation of high mol. wt. copolymers with desirable functional group concentration. He has exploited this novel idea to synthesize poly(octenol) by polymerization of B-7-octenyl-9BBN followed by oxidation[6], copolymers of 1-octene and 1-hexanol[7] by copolymerization of 1-octene and B-5-hexenyl-9BBN and copolymers of propylene and B-5-hexenyl-9BBN, which were converted to hydroxy containing or iodine containing copolymers[8]. He further extended this chemistry for the post-polymerization functionalization of 1,2-poly(butadiene)[9], poly (propylene-co-1,4-hexadiene)[10] and for the synthesis of diblock copolymers containing both polydiene and polyalcohol blocks by the hydroboration oxidation of the 1,2-polybutadiene blocks of poly (2-methyl-1,3-pentadiene)-b-poly(1,2-butadiene).[11]

He further utilized the borane functionality of the polyolefin copolymers to initiate a "graft from" reaction to obtain graft copolymers of polyolefins containing a polyolefin backbone and several functionalized polymers in the side chains. The borane containing poly(octene)[12] or polypropylene acts as a free radical source to initiate the graft from polymerization of free radically polymerizable monomers such as methylmethacrylate and is extendable to vinyl acetate, acrylonitrile and styrene. Another type of graft copolymer, polypropylene graft polycaprolactone (PP-g-PCL) was obtained by the aluminum alkoxide initiated ring opening of ε-caprolactone.[14] Microscopy studies revealed the effectiveness of these PP-g-PCL graft copolymers in blends of PP/PCL, PP/PVC and PP/PC by reducing the phase sizes and improving the dispersion of the minor component in the PP matrix.

Mulhaupt et al.[15] and Soga et al.[16] have utilized another approach to the formation of end-functionalized polypropylene. The authors utilized the β-hydride elimination reaction in the polymerization with stereospecific soluble metallocene/methylaluminoxane catalysts to prepare low molecular weight polypropylenes with chain end unsaturation e.g. vinylidene or vinylene. In the second step, either in solution or melt process, the olefin chain ends were converted into different polar functional groups, such as, anhydride, silane, epoxy, carboxylic acid, borane, alcohol and thiol. The use of soluble metallocene catalysts offers an additional advantage of control over molecular weight, molecular weight distribution, microstructure and olefinic end groups. Mulhaupt used the thiol-terminated isotactic polypropylenes as polymeric chain transfer agents in styrene/acrylonitrile polymerizations to prepare polypropylene-block-poly(styrene-co-acrylonitrile) and showed them to be effective compatibilizers in blends containing polypropylene/poly (styrene-co-acrylonitrile).

Another method of obtaining terminally hydroxylated polyolefins was followed by Soga et al[17]. Propylene and 1-hexene were polymerized with the conventional, $TiCl_3$ - $(C_2H_5)AlCl$ catalyst in the presence of $Zn(C_2H_5)_2$ as chain transfer agent. The produced Zn-polymer bonds were reacted with oxygen gas followed by hydrolysis to produce terminally hydroxylated polyolefin.

As discussed in Chapter V, as a result of the remarkably improved copolymerization activity obtained with the soluble metallocene catalysts such as Cp_2ZrCl_2/MAO we succeeded in obtaining ethylene-co-5-vinyl-2-norbornene copolymers with comonomer content varying from 0-20 mol. %, which are non-crosslinked and gel free. Due to a high level of regioselectivity the vinyl double bond remained as a pendant in all the copolymers. In view of the current interest in functionalized polyolefins, we examined the functionalization and grafting reactions using ethylene-co-5-vinyl-2-norbornene (Scheme 6.1). This chapter summarizes the results of these studies.

6.2 EXPERIMENTAL SECTION

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

6.2.1 Materials

Toluene (Loba Chemie AR grade) was purified by refluxing over sodium wire and subsequent distillation under nitrogen over oligomeric styryl lithium solution in toluene. Styrene (Sisco Chem.) was stirred over calcium hydride and distilled under reduced pressure. Ethylene-co-5-vinyl-2-norbornene (E5V2N) prepared in a large scale batch (Chapter V) containing 10.5 mol% 5V2N was used for post-polymerization reactions. Butyl lithium (Chemetall GMBH, Germany, a 15% solution in n-hexane was further diluted to 0.501M), 9-BBN (0.5 M solution in THF), m-chloroperbenzoic acid (all from Aldrich) were used as received.

6.2.2 Hydroboration oxidation

A 250 mL, three-necked round-bottom flask equipped with a reflux condenser, nitrogen inlet, Teflon-coated magnetic stirring bar, and septum was cooled under a flow of nitrogen. About 200 mg E5V2N copolymer (0.748 mmol unsaturation) was added followed by 100 mL of dry toluene, and the mixture stirred at 55°C to dissolve the copolymer. A 2.2 mL aliquot of a 0.5 M THF solution of 9-BBN (1.1 mmol) was added, and the reaction mixture was stirred at 55°C for 3 h. Oxidation was carried out by the addition of 0.2 mL of a 6N NaOH solution (1.12 mmol) followed by dropwise addition of 0.4 mL of 30% H_2O_2 (3.2 mmol) solution. The mixture was stirred at room temperature for 2 h to ensure complete reaction. The product was poured into methanol, washed a number of times with warm methanol to remove boric acid, filtered and dried. Yield of the hydroxy functionalized copolymer **2** = 160 mg.

IR (film, cm^{-1}) : 3350 (O-H stretch), 2950-2850 (C-H stretch), 1470 (C-H def.), 1058 (C-O stretch), 725 (CH_2 rock). ^1H NMR ($CDCl_3$, ppm) : 3.65 (CH_2-O) 2.0 - 0.95 (backbone and aliphatic H).

6.2.3 Epoxidation

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 E5V2N copolymer (0.374 mmol of unsaturation) was added to the flask followed by 40 ml of dry toluene, and the mixture heated at 55°C till the copolymer dissolves. About 100 mg of m-chloroperbenzoic acid (0.575 mmol) dissolved in 10 ml of dry toluene was added and the reaction mixture stirred for a further 3 h. Then the reaction mixture was poured into methanol, filtered and dried under vacuum. Yield of the epoxy functionalized copolymer **3** = 100 mg. IR (film,

cm^{-1}) : 2950-2850 (C-H stretch), 1470 (C-H def.), 1250 (C-O stretch), 876 (epoxy ring vib.), 725 (CH_2 rock) ^1H NMR ($CDCl_3$, ppm) 3 - 2.85 (CH--C), 2.7 - 2.85 (CH_2--C), 2.5 - 0.95 (backbone and aliphatic H).

6.2.4 'Grafting onto' reaction of polystyryl lithium on epoxy-functionalized E5V2N copolymer

To a single necked 100 mL round-bottomed flask (A) containing a Teflon coated magnetic stirring bar and fitted with a septum and nitrogen inlet containing adaptor, was added 100 mg (0.214 mmol of epoxy group (60% epoxidized)) of epoxy functionalized E5V2N 3. To this 20 mL of dry toluene was added stirred at 50°C and then azeotropically distilled off. The azeotropic distillation was repeated twice to remove all traces of moisture/methanol and then a further quantity of 20 mL dry toluene added and maintained at 50°C with stirring.

In another single necked 100 mL round bottomed flask (B) fitted with a septum and nitrogen inlet containing adaptor was added 35 mL of toluene (distilled over styryl lithuim). This was followed by the addition of styrene 2 mL (distilled over fluorenyl lithium). Then 8.54 mL nBuLi (0.428 mmol) was added to initiate polymerization. A deep red color indicative of the living species was obtained. After 18 h the living poly(styrlithium) solution was transferred using a cannula into the flask (A). Excess of this solution (more than half) was added in order to take care of adventitious impurities present in the flask (A) till the red color persisted. The remaining polystyryl lithium solution was terminated with deaereated methanol and precipitated into excess of methanol, filtered and dried for analysis. The flask containing the reactants was left stirring for a further 48 h time period to ensure completeness of the grafting reaction. The reaction mixture was then treated with methanol to terminate the excess polystyrllithium chains and then precipitated in methanol and dried under vacuum. Yield of grafted polymer + excess polystyrene = 1.39 g. Weight of polystyrene left back in flask B = 0.4 g. The grafted polymer containing excess polystyrene was subjected to Soxhlet extraction using acetone for 10 h. The hot acetone insoluble fraction obtained = 0.6154 g. IR (film, cm^{-1}) 3125-2855 C-H stretch, 2000-1665 overtone bands indicating aromatic ring substitution, 1665-1430 C = C stretch, C-H bending, 1250-1000 aromatic C-H rock, 725 CH_2 rock. ^1H NMR ($CDCl_3$, ppm) 7.3 - 6.4 (aromatic H), 2.2 - 1.7 (ϕ-C$\underline{H}$-), 1.65 - 1.2 (ϕ-CH-C$\underline{H_2}$), 1.3 (-CH_2-CH_2). GPC of polystyrene from flask B : M_n = 4189, M_w = 5271 MWD = 1.25)

6.2.5 Analytical techniques

^1H NMR spectra of the samples as 2 wt% solutions were recorded using a Bruker AC-200 spectrometer at room temperature. IR spectra of films cast from toluene solution were recorded using a Perkin-Elmer PE16 FTIR spectrometer. Thermogravimetric analysis and differential scanning calorimetric analysis was carried out on a Perkin Elmer TGA and DSC respectively. Intrinsic viscosity measurements were done using an Ubbelohde viscometer in 1,2,4-trichlorobenzene at 135°C. Gel permeation chromatograms of samples were run on a Water Associates, model ALC GPC 150C at 135°C using 1,2,4 trichlorobenzene as the mobile phase and μstyragel columns(10^5A^0, 10^4A^0, 10^3A^0 and500A^0). Flow rate = 1mL/min, detector = RI and polystyrene standards.

6.3 RESULTS AND DISCUSSION

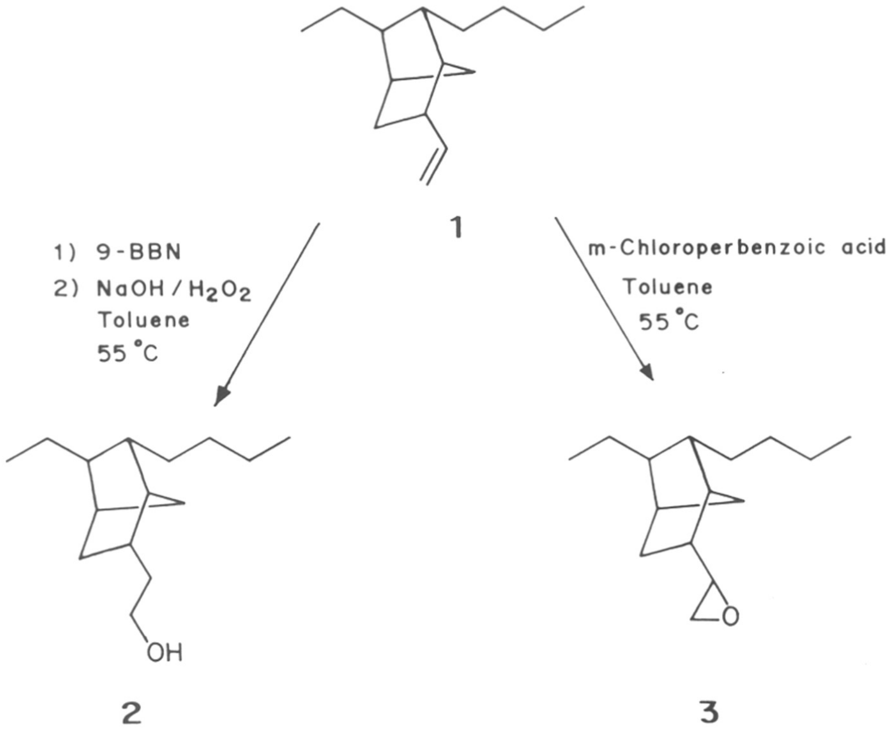
6.3.1 Hydroboration-oxidation

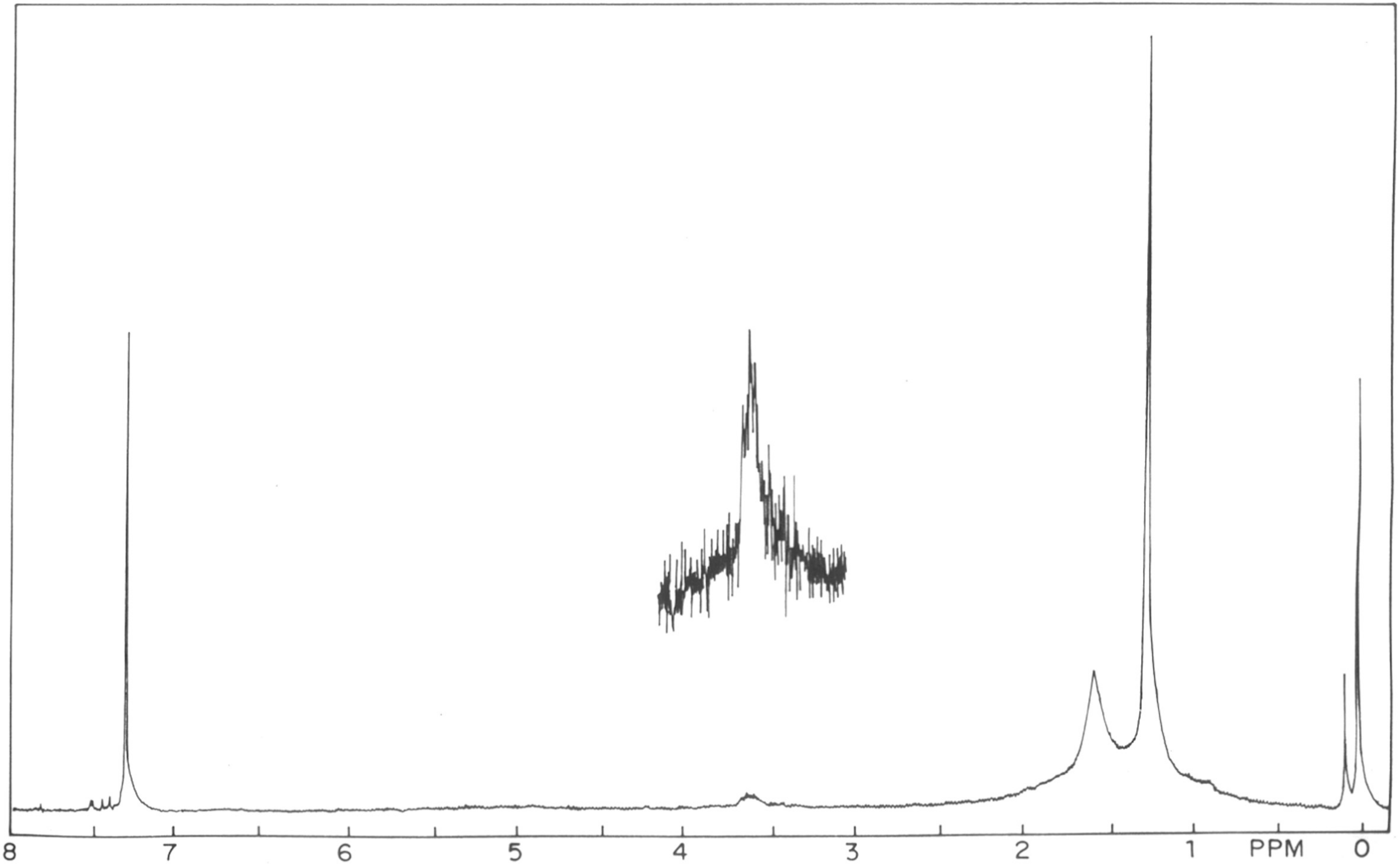
According to the strategy developed by Chung we decided to use hydroboration followed by oxidation of the pendant vinyl bond in order to introduce -OH groups in the copolymer (Scheme 6.1). 9BBN was preferred over $NaBH_4/BF_3$ etherate since the use of the latter gave rise to crosslinked product. When 9BBN was used as hydroborating agent it was observed that during the addition of NaOH and H_2O_2 some solid separated out (probably crosslinked material) which was held back during precipitation with methanol. This resulted in a decrease in the yield of the hydroxylated polymer to 80%.

The ^{1}H-NMR of the copolymer 2 (Fig. 6.1) shows a triplet at 3.55 ppm indicating presence of CH_2O protons, and absence of peaks due to unsaturation between 6.0 to 4.8 ppm. The hydroxyl content of the copolymer as estimated by integration of the ^{1}H NMR spectrum is ca. 10 mol% indicating nearly quantitative functionalization. The IR spectrum (Fig 6.2 b) shows bands at 3350 and 1050 cm^{-1} which are characteristic of CH_2OH groups and absence of peak at 990, 910 cm$_{-1}$. The intrinsic viscosity, IDT and Tm (Table 6.1) of **2** were similar to those of **1**.

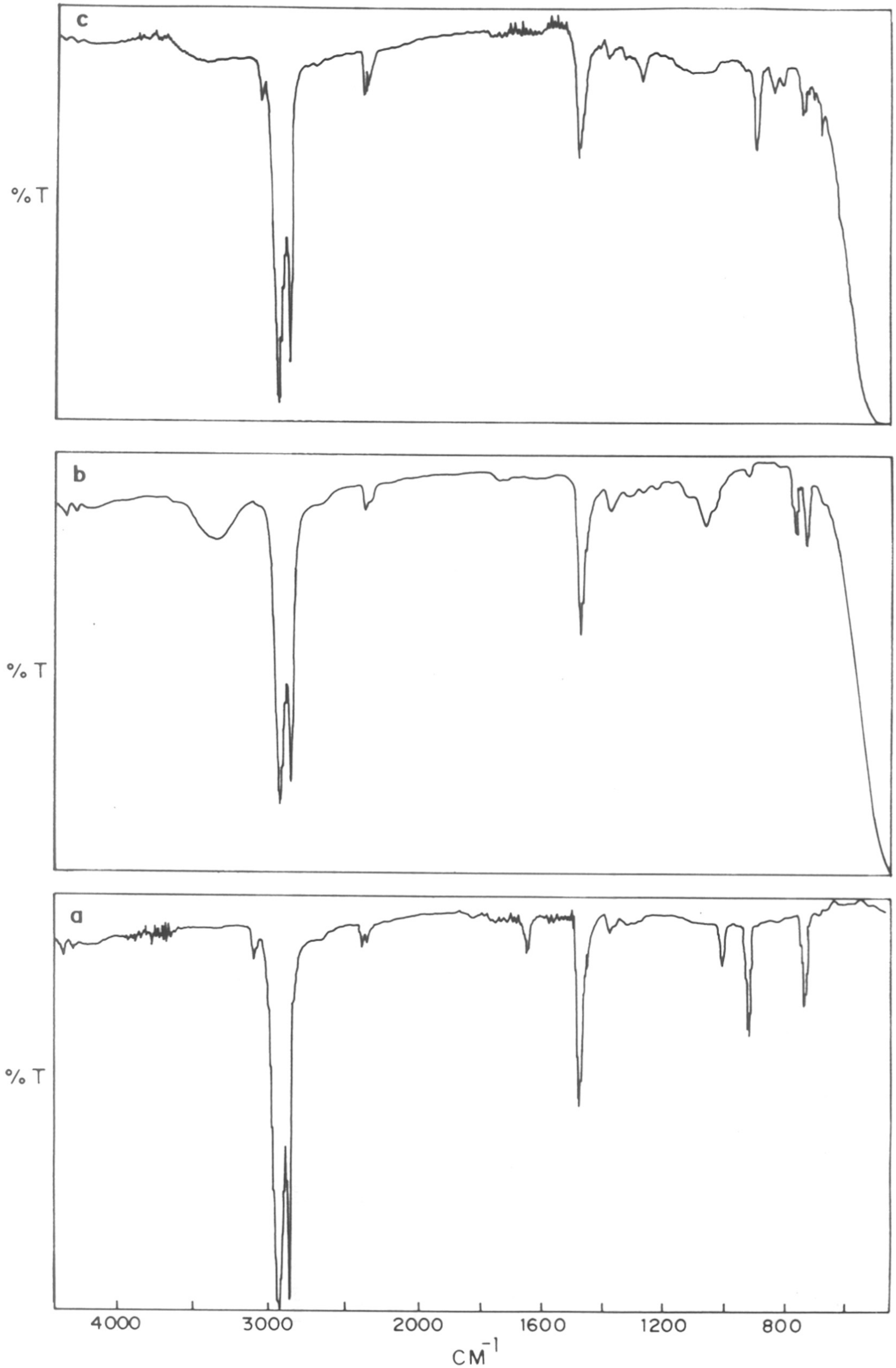
The copolymer **2** was soluble in toluene, 1,2,4-trichlroabenzene, xylene and $CHCl_3$ above 50°C.

SCHEME **6·1**





6.1 ^{1}H NMR spectrum of the hydroxy functionalized copolymer (**2**).



6.2 IR spectrum of (a) ethylene-5-vinyl-2-norbornene copolymer, (b) hydroxy functionalized and (c) epoxy functionalized copolymer.

Table 6.1 Properties of E5V2N and functionalized copolymers *2* and *3*

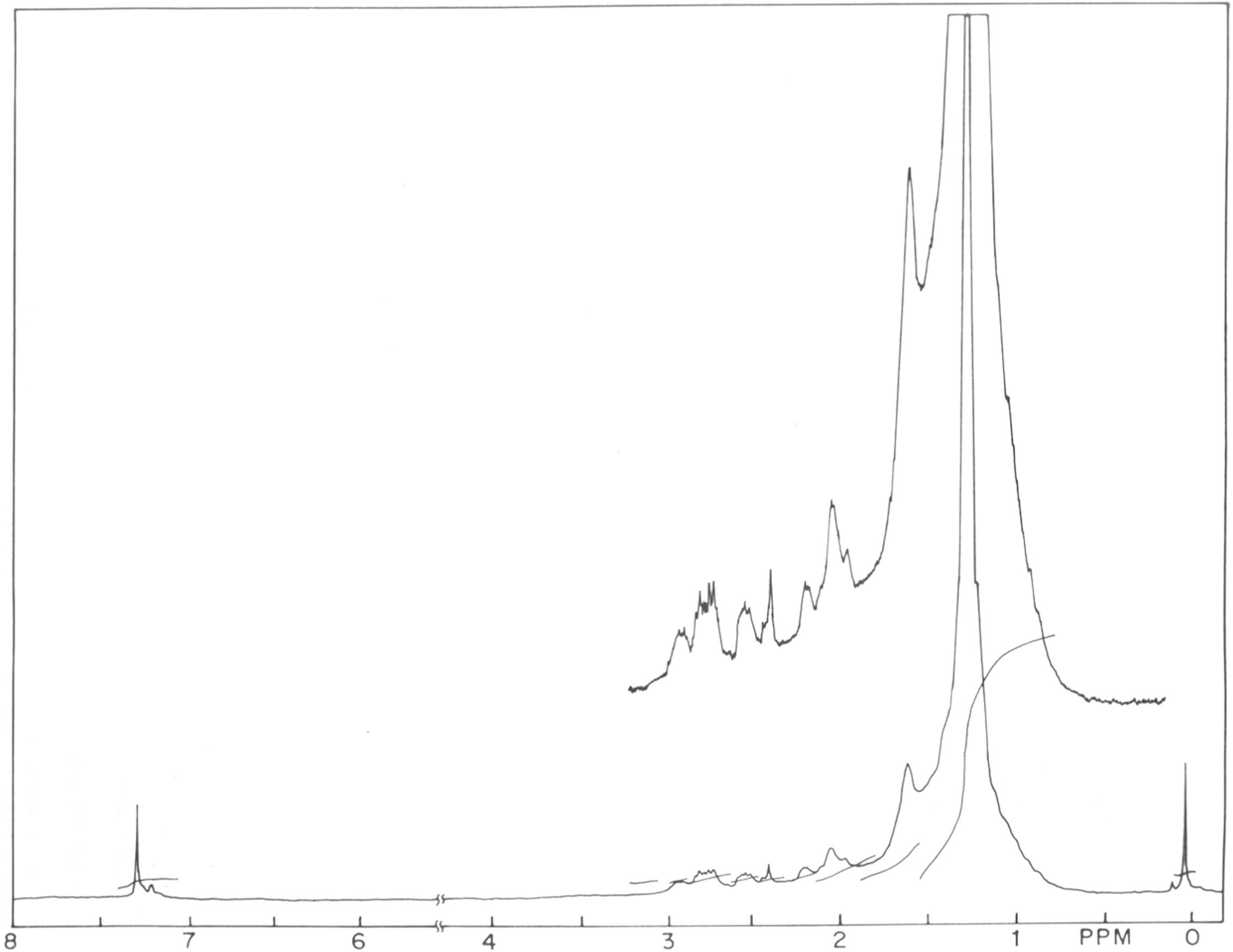
Sr. No.	Copolymer	mol % functionality	$[\eta]^b$ (dL/g)	1DT (°C)	T_m (°C)	ΔH_f (J/g)
1.	1	10.5	1.00	399	88	36
2.	2	9.9	1.00	391	89	35
3.	3	9.5	0.96	351	88	29

6.3.2 Epoxidation

Initially $HCOOH/H_2O_2$ were used for the epoxidation reaction according to the procedure of Kurusu *et al*[18]. However, it was found that with the passage of time the IR spectra of the copolymer showed presence of a band at 1730 in addition to those due to epoxy group. This could arise as a result of the epoxy ring opening to hydroxy and formate ester in presence of HCOOH. It was found more suitable to use m-chloroperbenzoic acid as the epoxidizing agent. Kurusu et al[19] also found that m-chloroperbenzoic acid was an effective reagent for the epoxidation of poly(ethylene-co-1,9-decadiene). Complete epoxidation is evident from the disappearance of peaks due to unsaturation and the appearance of peaks due to epoxy group at 2.5 - 3.0 ppm (Fig. 6.3). The IR spectrum shows new absorptions at 876 and 1250 cm^{-1} due to epoxy group (Fig. 6.2 c). The epoxy group content in copolymer **3** as estimated from the integration of the ^{1}H-NMR spectrum is found to be 9.5 mol% indicating a near quantitative epoxidation of the pendant vinyl bonds in the copolymers. The copolymer **3** was soluble in toluene 1,2,4-trichlorobenzene, xylene and $CHCl_3$ above 50°C. Its intrinsic viscosity was 0.96 dL/g indicating no main chain degradation. The copolymer showed a Tm similar to and an IDT lower than that of the precursor copolymer 1 (Table 6.1).

6.3.3 Grafting onto 'reaction of polystyryl lithium onto epoxy functionalized E5V2N copolymer'

The oldest method for forming graft polymers containing polyolefin backbone was free radical grafting. Here radicals were generated on the polyolefin backbone by allylic hydrogen abstraction, which initiated free radical polymerization of the monomer to be grafted. Unfortunately, these free radical grafting reactions were difficult to control and gave rise to gel fractions. The preferred methods for grafting by which some control on the length of graft and number of grafts can be exerted are the 'grafting onto' and 'grafting from' techniques.



6.3 ^{1}H NMR spectrum of epoxy functionalized copolymer (**3**)

Lohse et al[20] synthesized a novel graft copolymer, viz., isotactic-polypropylene grafted on to ethylene-propylene-diene backbone polymer. In the first step the EPDM was synthesized using a diene such as vinylnorbornene using $VOCl_3/Et_3Al_2Cl_3$ catalyst with diene incorporation of less that 1 mol %. In the second step, using $TiCl_3/AlEt_3$ catalyst i-PP chains were grown through the pendant double bonds of the EPDM to form the graft copolymer. This graft copolymer acted as an excellent compatibilizer in EP/iPP blends.

Chung et al successfully used the 'grafting from' techniques to prepare polyoctene-graft-polymethyl methacrylate,[12] polypropylene-graft-polymethyl methacrylate[13] and polypropylene-graft-polycaprolactone.[14]

Having obtained the epoxy functionalized E5V2N copolymer it was thought that the epoxy pendant group may be exploited as a chain terminator in ionic polymerizations resulting in graft polymers by the 'grafting onto' technique. Hence, the 'grafting onto' reaction of polystyryl lithium on the epoxy functionalized E5V2N copolymer was investigated. (Scheme 6.1)

Results of 'grafting onto' reactions are shown in Table 6.2. The backbone used was a 60% epoxidized ethylene-5-vinyl-2-norbornene copolymer obtained in a scale up batch. This corresponds to 2×10^{-4} mol of pendant epoxy groups in 0.1 g of **3**. The product obtained after performing the coupling reaction in flask A and precipitating in methanol was subject to a Soxhlet extraction using acetone for 10 h. All homopolystyrene was found to be effectively removed and weight of the acetone insoluble polymer was taken as the weight of graft copolymer. The molecular weight and MWD of the acetone soluble fraction and the corresponding polystyrene left back in flask B were found to be identical. The MWD of polystyrene is not very narrow 1.2 - 1.5 probably due to impurities in the polymerization vessel. From the difference in weights of graft copolymer and backbone, the weight of polystyrene is obtained, based on which, the number of mol of polystyrene grafted is obtained. In all cases the number of mol of polystyrene grafted are less than the

Table 6.2 Results of the "grafting onto" reaction of polystyryllithium on epoxy-functionalized ethylene-co-5-vinyl-2-norbornene

Sr. No.	**Amt. of epoxy E5V2N**[a]	**Amt. of acetone insoluble graft copolymer**	**M_n and MWD of PS**	**No. of moles of PS grafted**[b]	**% grafting**[c]	**mol. ratio PS : PE**	
						nmr	gravimetry
1.	0.1	0.409	3529, 1.5	8.7×10^{-5}	44	46 : 54	56:44
2.	0.1	0.615	4189, 1.25	1.2×10^{-5}	62	58 : 42	58:42
3.	0.1	0.728	4208, 1.3	1.5×10^{-4}	75	66 : 34	66:34

(a) 0.1 g epoxy = E5V2N contains 2×10^{-4} moles of epoxy.

(b)

$$\frac{\text{wt. of grafted PS}}{\text{Mn}} = \text{moles of grafted PS}$$

(c)

$$\frac{\text{moles of grafted PS}}{2 \times 10^{-4}} \times 100 = \%\ \text{grafting}$$

expected value of 2 x 10^{-4} mol. This is attributed to two reasons (1) at 55°C in toluene the epoxy-functionalized E5V2N is not completely dissolved (GPC in toluene at 50°C of backbone could not be run due to filtration problems), due to this the epoxy groups present in the insoluble part may not be accessible for grafting; (2) since the MWD are not 1.0 there exists some error in the calculation of the number of mol or PS grafted. Possibly, due to the above two reasons grafting efficiency observed is not 100%. By fine tuning of the reaction conditions it might well be possible to obtain near quantitative grafting.

Fig. 6.4 shows the ^{1}H NMR of the graft polymer. Peaks originating from the polystyrene moiety are clearly visible at 7.3 - 6.4 ppm (aromatic H), 2.2 - 1.2 - methine proton and 1.65 - 1.2 methylene protons. Singlet at 1.3 ppm originating from the -CH_2-CH_2-polyethylene backbone is also clearly seen.

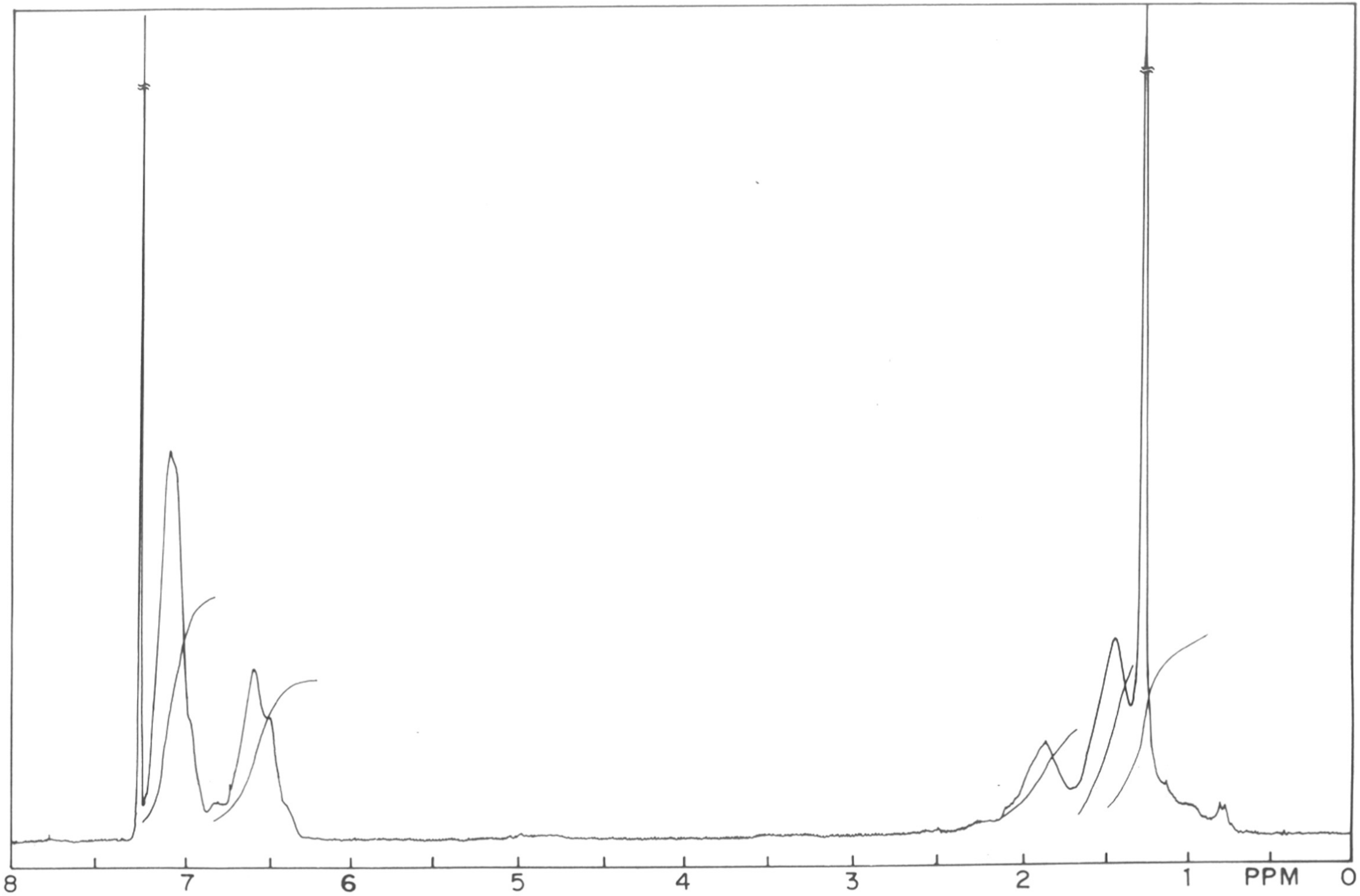
$$The\, mol\%of\, the\, PS\, is\, calculated\, as = \frac{A/5}{A/5 + 1/4(B - 3A/5)} \times 100$$

where A is integration under the region 7.3 - 6.4 ppm and B is integration under the region 2.2 to 1.2 ppm. The IR spectrum of the graft polymer is similar to that of polystyrene with the peaks due to polyethylene being overlapped by polystyrene peaks in the same region.

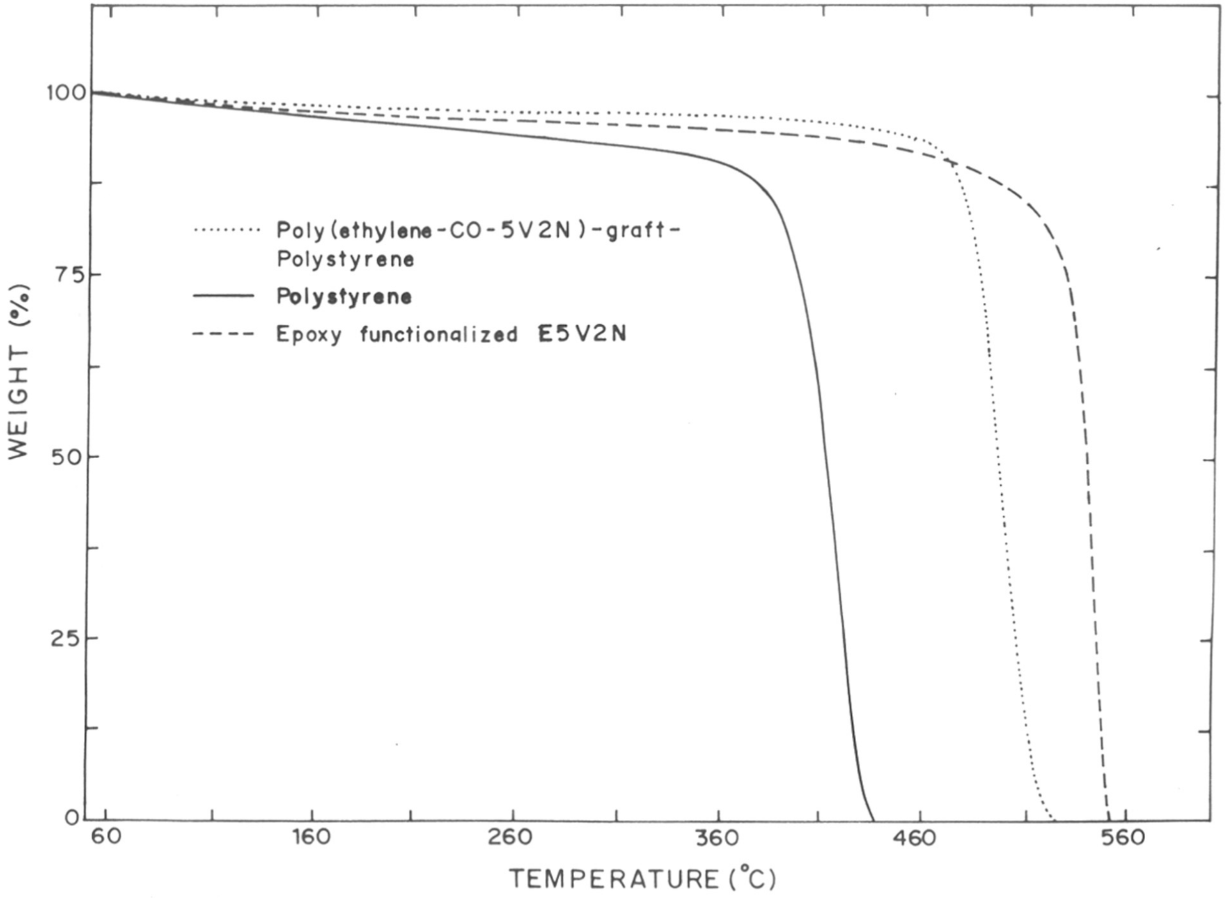
Results of thermogravimetric analysis are shown in Fig. 6.5. The value of IDT of the graft polymer lies between the values of PS and epoxy functionalized E5V2N copolymer indicating true graft polymer formation.

Fig. 6.6. shows DSC curves of polystyrene, polystyrene-graft-epoxy E5V2N and epoxy functionalized E5V2N. The epoxy functionalized copolymers 3 shows Tm at 87.8°C, polystyrene shows a Tg at 100°C. Whereas the graft polymer shows a Tm at 84°C and Tg at 109°C indicative of true graft polymer formation.

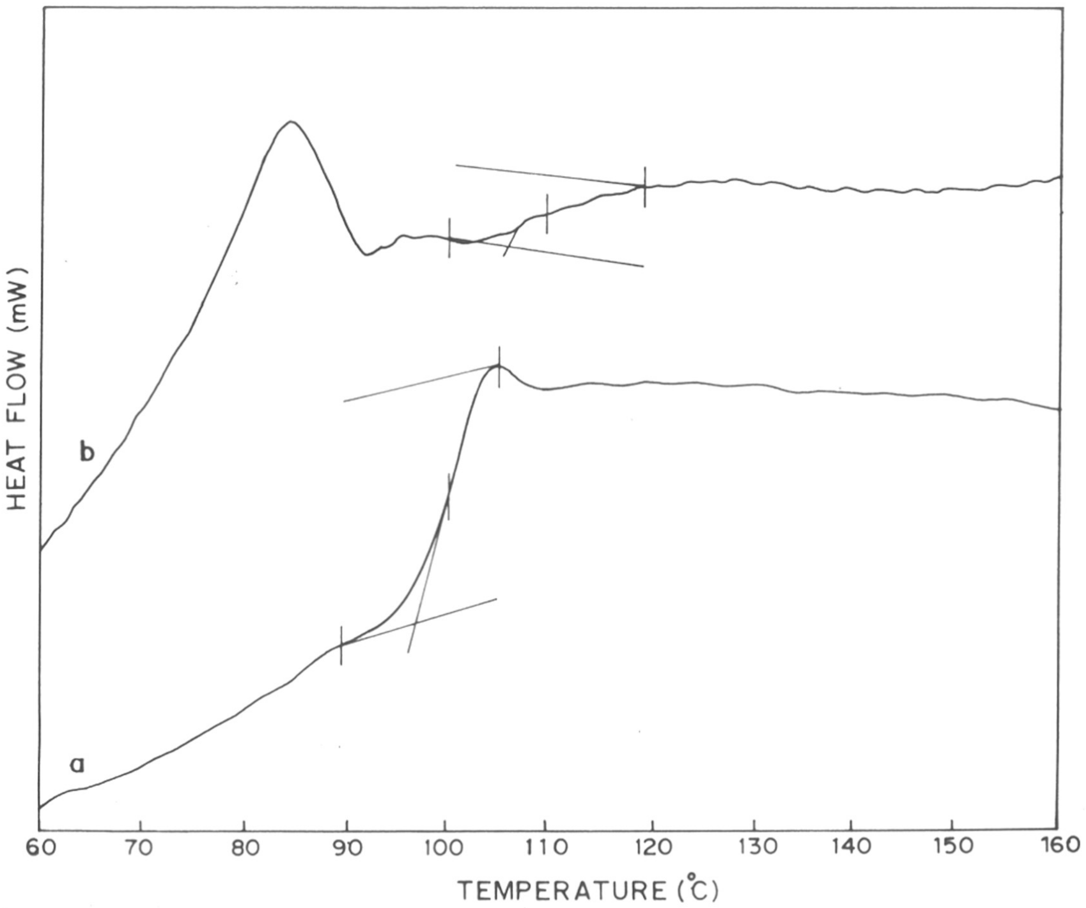
Fig.6.7 shows the GPC curves of the epoxy functionalized E5V2N (backbone polymer) and the graft copolymer. A shift in peak maxima from 28.35



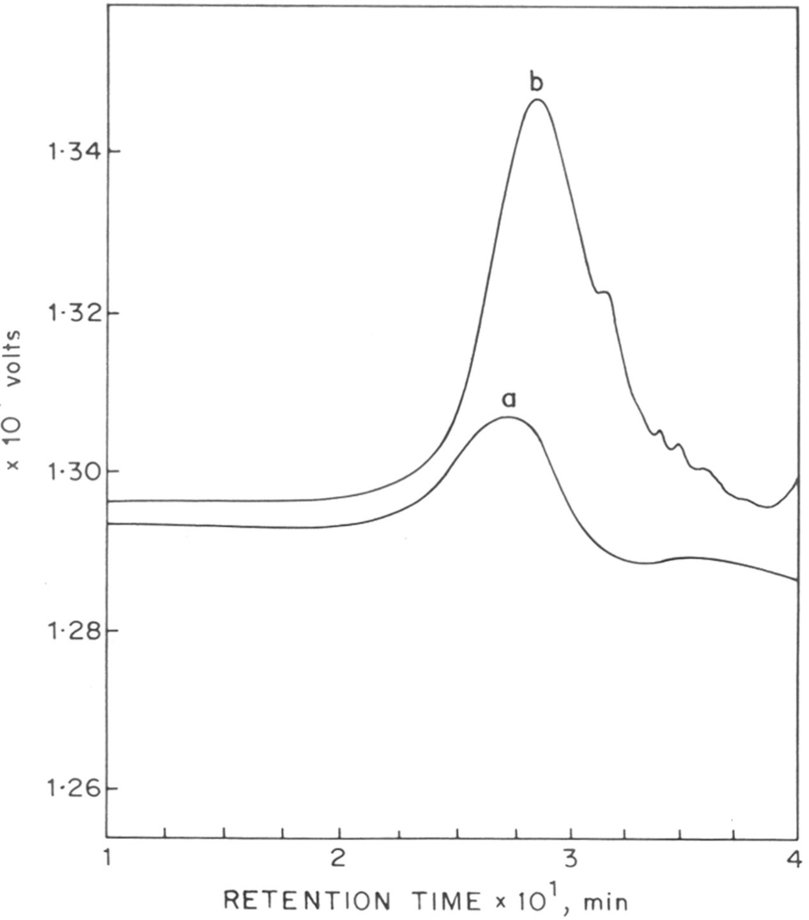
6.4 ^{1}H NMR spectrum of poly(ethylene-co-5-vinyl-2-norbornene)-graft-polystyrene.



6.5 TGA scans of polystyrene, graft copolymer and the epoxy functionalized E5V2N copolymer.



6.6 DSC scans of (a) polystyrene and (b) graft copolymer.



6.7 Gel permeation chromatogram of (a) graft copolymer and (b) epoxy functionalized E5V2N backbone polymer.

min to 27.3 min on grafting is observed. The backbone has $\overline{M}n$ = 55,180, $\overline{M}w$ = 1,60,311 and MWD = 2.95, the grafted polymer has $\overline{M}n$ = 1,58,833, $\overline{M}w$ = 3,51,413 and MWD = 2.21 indicating a shift to higher molecular weight on grafting.

6.4 SUMMARY AND CONCLUSIONS

The pendant vinyl group of the ethylene-5-vinyl-2-norbornene copolymers has been shown to be quantitatively functionalized using standard organic chemical transformations. Further, the epoxy functionalized E5V2N copolymer has been used in a 'grafting onto' coupling reaction with polystyryl lithium to generate polystyrene-graft-poly (ethylene-co-5-vinyl-2-norbornene). The advantages of using the 'grafting onto' method is that the length of the graft can be controlled and also separately characterized facilitating structure determination of the resultant graft copolymer. The number of grafts can be controlled by the percentage of epoxy groups introduced (the vinyl bonds were found to not react with polystyryl lithium). In principle, this methodology can be extended for the grafting of various other ionically polymerizable monomers since the epoxy group can be used for terminating both an anionic and cationic chain end.

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CHAPTER VII

CONCLUSIONS

The salient conclusions of the study are :

Poly(2-allylnorbornane) obtained using conventional Ziegler-Natta catalysts could be fractionated into a fraction insoluble in xylene at 130°C and the other soluble in xylene at 130°C. The whole polymers and fractions were characterized by spectroscopic and thermal methods. The xylene insoluble fractions gave a very high Tm = 355°C. The significant feature of these polymerizations are (a) high catalyst consumption (b) low catalyst activity and (c) in case of $TiCl_4$ catalyst concomitant isomerization of the monomer along with polymerization. When compared with the properties of poly(4-methyl-1-pentene), the partly insoluble nature of poly (2-allylnorbornane) and its high melting point are attributed to the presence of the bicyclic pendant.

Copolymerization of ethylene with 2-allylnorbornane was studied using the conventional $TiCl_4$/(iso-Bu)$_3$Al catalyst and the homogeneous Cp_2ZrCl_2/MAO catalyst. The copolymers obtained using Cp_2ZrCl_2/MAO give rise to homogeneous and random copolymers, whereas, the $TiCl_4$/(iso Bu)$_3$Al catalyst gives rise to heterogeneous and blocky type of copolymers. These conclusions were drawn based on the results of reactivity ratio analysis, fractionation, GPC, infrared and differential scanning calorimetric studies of the two copolymers.

The copolymers were studied using NMR and peak positions were assigned. An IR calibration method was devised for routine analysis of the composition of the copolymers.

Contrary to expectation, the bicyclo (2.2.1) pendant did not contribute to substantial lowering of crystallinity when compared to the isopropyl pendant derived from 4-methyl-1-pentene as comonomer. This conclusion is based on the comparison of the thermal properties of ethylene-2-allylnorbornane and ethylene-4-methyl-1-pentene copolymers at similar mol % incorporation of comonomer. This could be due to the unique space filled structure of the norbornyl pendant which arises as a result of bridging.

The copolymerization of ethylene with 5-vinyl-2-norbornene using zirconocene-MAO resulted a copolymer wherein, a regioselective insertion of the endocyclic double bond was observed leaving the exocyclic double bond as a pendant. Without resorting to measurement of individual polymerization rate constants, this proves that the endocyclic bond has a higher reactivity relative to the vinyl exocyclic bond in copolymerization. Due to the high level of regioselectivity of insertion of the endocyclic double bond, high levels of comonomer incorporation could be achieved without any crosslinking reactions.

The pendant vinyl group of the ethylene-5-vinyl-2-norbornene copolymers could be quantitatively functionalized using standard organic chemical transformations. Further, the epoxy functionalized E5V2N copolymer was used in a 'grafting onto' coupling reaction with poly(styryllithium) to generate poly (ethylene-co-5-vinyl-2-norbornene)-g-poly(styrene). The advantages of using the 'grafting onto' method is that the length of the graft can be controlled and also separately characterized facilitating precise structure determination of the resultant graft copolymer.

Future scope of the work

-The study of the synthesis and polymerization of 2-butenylnorbornane may give rise to polymers with improved solubility, since the bicyclic pendant is further removed from the main chain.

-The copolymerization of ethylene with other α, ω-dienes such as vinylcyclopentene, vinylcyclohexene and norbornadiene may be studied in order to understand the scope and limitations of such copolymerizations.

-The epoxy functionalized poly(ethylene-co-5-vinyl-2-norbornene) can be explored as a candidate for the synthesis of graft copolymers with other room temperature anionically polymerizable monomers such as t-butylmethyacrylate, ethylene oxide etc. Further, it may also be used as a chain terminator in cationic polymerizations.

APPENDIX I

POLYMERIZATION OF 4-METHYL-1-PENTENE AND ITS COPOLYMERIZATION WITH ETHYLENE USING HETEROGENEOUS AND HOMOGENEOUS ZIEGLER - NATTA CATALYSTS

A.1.1 Introduction

A number of reports on the polymerization of 4-methyl-1-pentene exist in literature.[1,2,3] Its copolymerization with ethylene using conventional Ziegler-Natta catalysts has been studied by Kissin.[4]

It was desired to compare the properties of poly-2-allylnorbornane with poly(4-methyl-1-pentene); and poly(ethylene-co-2-allylnorbornane) with poly(ethylene-co-4-methyl-1-pentene) with a view to study the effect of the bicyclic group on polymer properties. To make such a comparative study, it was necessary to prepare polymers under similar conditions of polymerization. Hence poly(4-methyl-1-pentene) and poly(ethylene-co-4-methyl-1-pentene) were prepared under conditions similar to those used for the preparation of poly(2-allylnorbornane) and poly(ethylene-co-2-allylnorbornane) resp.(see Chapter III and Chapter IV).

A.1.2 Experimental Section

All manipulations were carried out under standard inert atmosphere bench top techniques.

Materials: 4-methyl-1-pentene (98% purity, Fluka) was distilled over triisobutylaluminum prior to use. The purification methods and specification of the $TiCl_4$, $TiCl_3$ 0.33 $AlCl_3$, (iso Bu)$_3$Al, Et_2AlCl, ethylene and heptane are similar to that described in section 3.2.1., 4.2.1 and those of Cp_2ZrCl_2 and MAO are similar to that described in section 4.2.1

A.1.2.1 Homopolymerization of 4-methyl-1-pentene using $TiCl_4$/(iso-Bu)$_3$Al catalyst.

The procedure followed is similar to that described in section 3.2.3. Heptane(40mL) was syringed into the ampoule followed by 5.5 mL of 30% (iso-Bu)$_3$Al solution (8.3×10^{-3} mole), 5.3 mL of 10% $TiCl_4$ solution (2.7×10^{-3} mol).

4-methyl-1-pentene (10.5mL, 0.083 mol)was added to the catalyst mixture. After 4 h at 80°C the polymerization was terminated by pouring into acidified methanol. Yield = 7 g (80% conversion). [η] = 2.65 dL/g(in 1,2,4 trichlorobenzene at 135^{0}C).

A.1.2.2 Homopolymerization of 4-methyl-1-pentene using $TiCl_3$ 0.33 $AlCl_3/Et_2AlCl$ catalyst

The procedure followed is similar to that described in section 3.2.4. $TiCl_3$ 0.33 $AlCl_3$ (0.59 g, 2.9 x 10^{-3} mol) was transferred into the reaction cell in a dry box. This was followed by syringing in 45 mL heptane, 3.5 mL of a 30% diethylaluminum chloride solution in n-heptane and finally 11 mL (0.088 mol) of 4-methyl-1-pentene. The polymerization was conducted for 4 h at 45°C. The reaction was terminated by pouring into acidified methanol. Yield = 7.2 g (89% conversion) [η] = 5.9 dL/g(in 1,2,4 trichlorobenzene at 135^{0}C).

A.1.2.3 Copolymerization of ethylene with 4-methyl-1-pentene using $TiCl_4/(iso\text{-}Bu)_3Al$ catalyst

The procedure followed is similar to that under section 4.2.1. Heptane (25mL) was syringed into the reaction cell and allowed to saturate with ethylene. This was followed by addition of 0.5 mL 4-methyl-1-pentene, 0.6 mL of 5% triisobutylaluminum solution (1.51 x 10^{-4} mol) and copolymerization begun by addition of 0.25 mL of 4% $TiCl_4$ solution (5.27 x 10^{-5} mol). The copolymerization was terminated after 10 min by addition of acidified methanol. Yield = 0.542 g (66% conversion) [η] = 4.8 dL/g (in decalin at 135^{0}C).

A.1.2.4 Copolymerization of ethylene with 4-methyl-1-pentene using Cp_2ZrCl_2/MAO catalyst

The procedure followed is similar to that under section 4.2.2. Toluene (25mL) was syringed into the reaction flask and allowed to saturate with ethylene. This was followed by addition of 0.4 mL 4-methyl-1-pentene, 0.85 mL (1.87 x 20^{-3} mol) of methylaluminoxane solution in toluene . Copolymerization was initiated by addition of 0.75 mL (1.25×10^{-6} mol) of Cp_2ZrCl_2 solution in toluene. The copolymerization was terminated after 10 min. by addition of acidified methanol. Yield = 0.54 g (77% conversion) $[\eta]$ = dL/g (in decalin at 135^0C).

A.1.2.5 Analytical techniques : All analyses were performed according to procedures described in section 3.2.6 and 4.2.3.

A.1.3 Results and discussion

Poly (4-methyl-1-pentene) was polymerized using $TiCl_4/(iso\text{-}Bu)_3Al$ and $TiCl_3$ 0.33 $AlCl_3/Et_2AlCl$ catalyst (Table A.1.1). The polymers were fractionated and characterized using ^{13}C NMR, $[\eta]$, XRD and thermal analytical methods. The ^{13}C NMR is similar to that reported in literature.[5] The melting points of the polymers were found to be = 233-235°C (reported = 235°C). The isotactic index (based on xylene insoluble fraction) for the poly(4-methyl-1-pentene) obtained using $TiCl_4/Al(iso\ Bu)_3$ catalyst was 47% and for that obtained using the $TiCl_3$ catalyst was 93%.

Copolymerization of ethylene with 4-methyl-1-pentene was carried out under conditions similar to that used for copolymerization of ethylene with 2-allylnorbornane (Table A.1.2 and A.1.4). As in the case of 2-allylnorbornane 4-methyl-1-pentene had a rate depressing effect on the copolymerizations(Fig.A.1.1a). Reactivity ratios using the $TiCl_4/(iso\ Bu)_3Al$ catalyst (Table A.1.3, Fig.A.1.2) are calculated to be $r_{ethylene} = 58.0$, $r_{4M1P} = 0.105$, $r_1.r_2 = 6$ (Finemann-Ross);$r_{ethylene} = 53.4$, $r_{4M1P} = 0.073$, $r_1.r_2 = 3.89$ (Kelen-Tudos) (reported r_1r_2 = 4.8 using $TiCl_3$. 0.33 $AlCl_3$ catalyst).[4] This suggests that the copolymers obtained using the $TiCl_4$ catalyst are blocky in nature. The same conclusion is reached on a close examination of the 730-720 cm^{-1} doublet region implying long crystalline methylene sequences even at 4-methyl-1-pentene concentration as high as 18 mol%(Fig.A.1.3b).

Table A.1.1 **Homopolymerization of 4-methyl-1-pentene using conventional heterogeneous Ziegler-Natta catalysts[a]**

Sr. No.	Catalyst system	Temp. °C	[Al] x 10^1 M	[Ti] x 10^2 M	Yield (g)	Conv. %	Xylene soluble fraction, %	Xylene insoluble fraction, %
1.	$TiCl_4$ /(iso $Bu)_3Al$	80	1.2	3.8	7.0	80	53	47
2.	$TiCl_3$.O.33 $AlCl_3/Et_2AlCl$	45	1.2	4.2	7.2	89	7	93

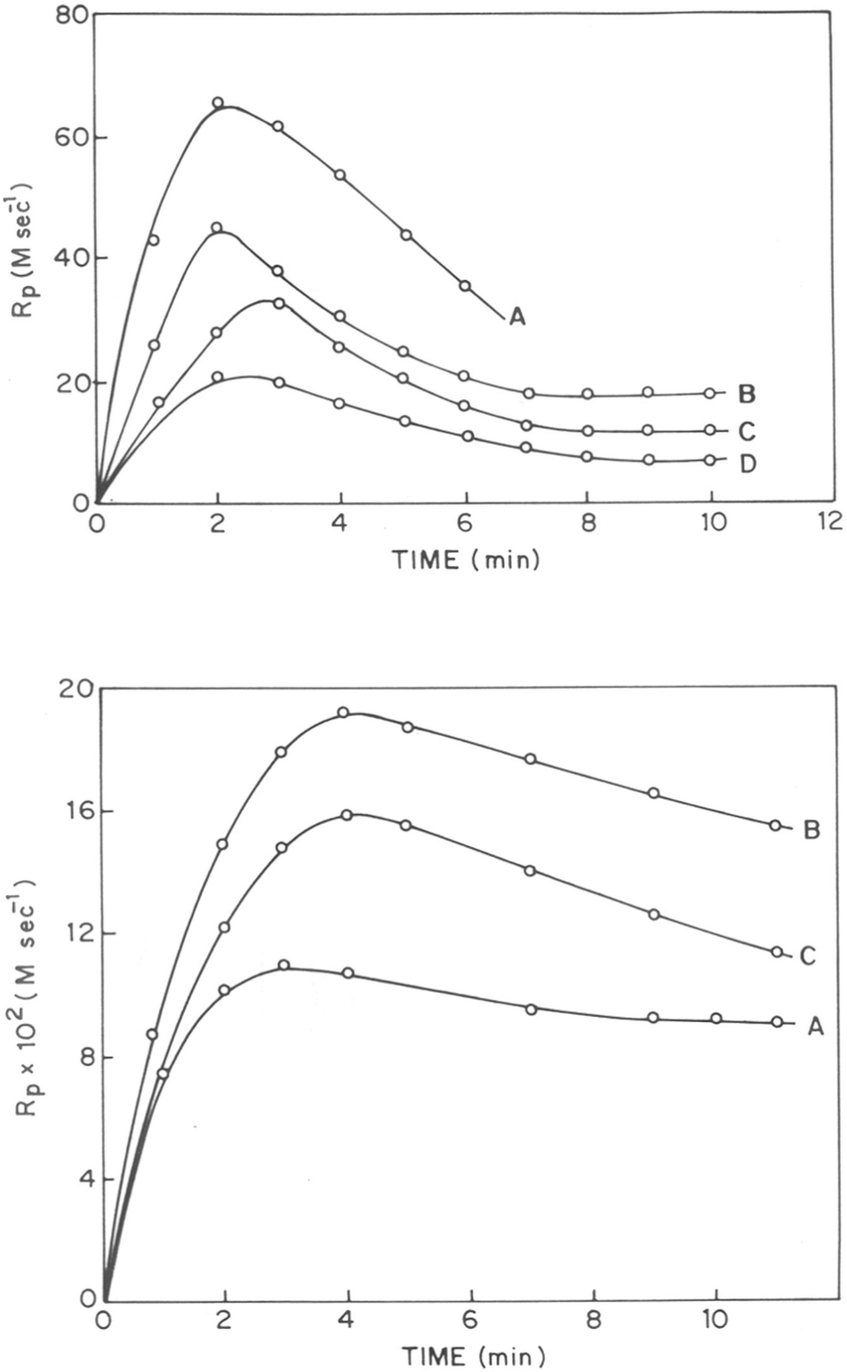
(a) Polymerization conditions : sovent = heptane(70mL), Al/Ti = 3, time = 4 h, [4M1P] = 1.4M.

Table A.1.2 **Copolymerization of ethylene with 4-methyl-1-pentene using conventional heterogeneous $TiCl_4$ /(iso $Bu)_3Al$ catalyst**[a]

Sr. No.	Conc. of 4M1P in feed		Yield (g)	Activity Kg/gTi/h	Conv. %	mol % 4M1P in copoly.[b]	T_m °C	ΔH_f J/g
	M	mol %						
1.	-	-	0.52	2.1	100	-	131.6	128.4
2.	0.16	62.5	0.54	1.3	66	4.6	126.7	86.8
3.	0.32	76.9	0.49	1.2	44	6.7	124.5	76.9
4.	0.48	83.3	0.64	1.6	43	10.7	124.7	55.3
5.	0.80	89.2	0.57	1.4	28	18	124.3	46.5

(a) Copolymerization conditions : solvent = heptane (25 mL), temp.= 35°C, press. = 1 atm., time = 10 min., [E] = 0.096 M, [Ti] = 2×10^{-3} M, [Al] = 6×10^{-3} M

(b) Calculated from IR.



A.1.1 Rp vs time plots for ethylene 4-methyl-1-pentene copolymerizations (I) catalyst: $TiCl_4/(iso\text{-}Bu)_3Al$ (A) 0 M; (B)0.32M ;(C)0.48 M and(D)0.8 M.(II) catalyst: Cp_2ZrCl_2/MAO (A) 0M; (B)0.128 M and (C)0.321M of 4M1P in the feed.

Table A.1.3 Ethylene 4-methyl-1-pentene copolymerization (at low conversions) together with the evaluation of some parameters (catalyst : $TiCl_4$/(iso Bu)$_3$Al[a]

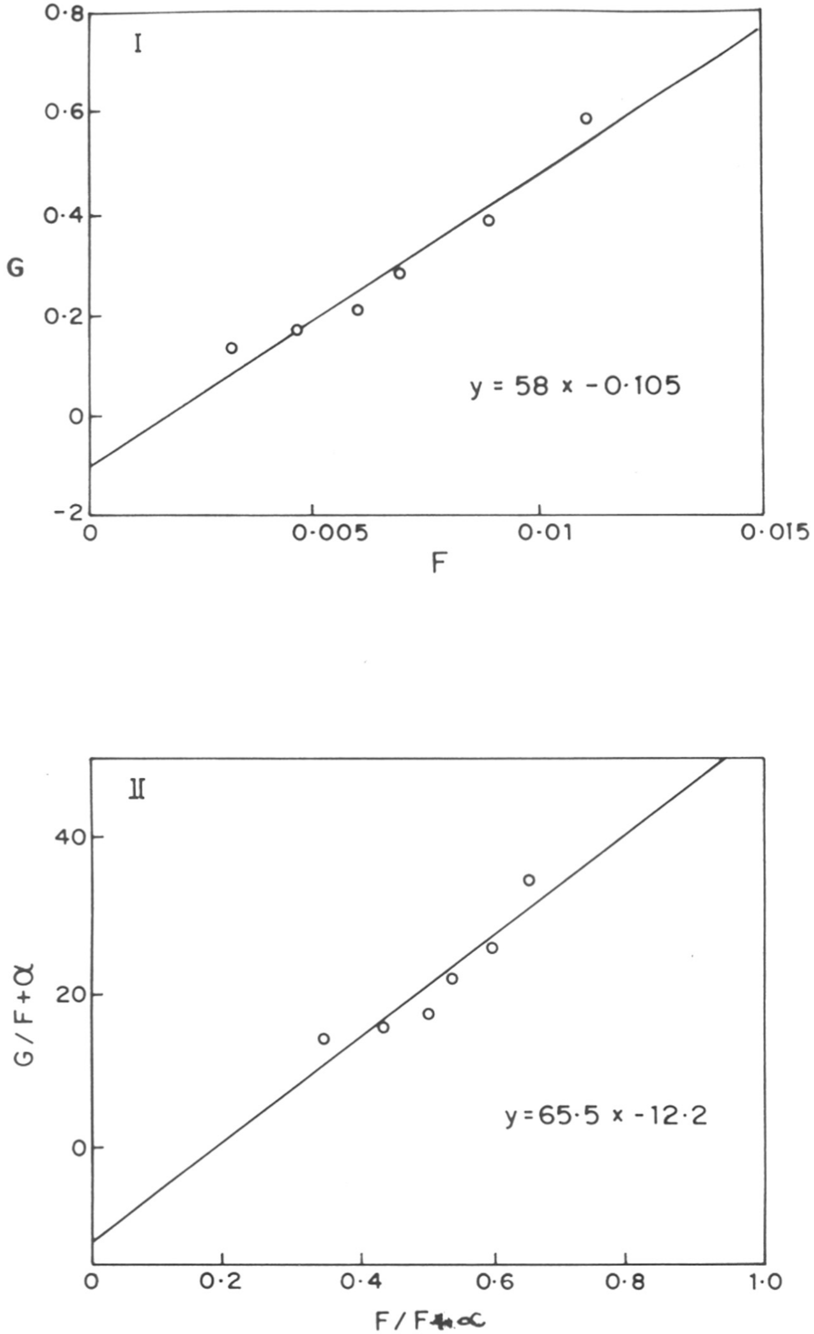
Sr. No.	Conc. of 4M1P in heptane M	4 MIP in copolymer mol %[b]	$F_1=(m_1/m_2)$	$f_1=(M_1/M_2)$	F[c] x 10^{-3}	G[c]	$\frac{F}{F+\alpha}$	$\frac{G}{F+\alpha}$
1.	0.160	2.9	0.6037	32.67	11.15	0.5852	0.649	34.06
2.	0.241	5.2	0.4025	18.2	8.9	0.3802	0.596	25.46
3.	0.321	7.1	0.3015	13.0	6.9	0.2784	0.534	21.53
4.	0.412	10.1	0.2319	8.9	6.0	0.2059	0.498	17.11
5.	0.514	11.6	0.1886	7.59	4.68	0.1637	0.437	15.28
6.	0.642	12.5	0.1509	6.98	3.26	0.1292	0.351	13.92

(a) Copolymerization conditions : solvent = heptane (25 mL), temp.= 35°C, press. = 1 atm., time = 2 min., [E] = 0.096 M, [Ti] = 2 x 10^{-3} M, [Al] = 6 x 10^{-3} M

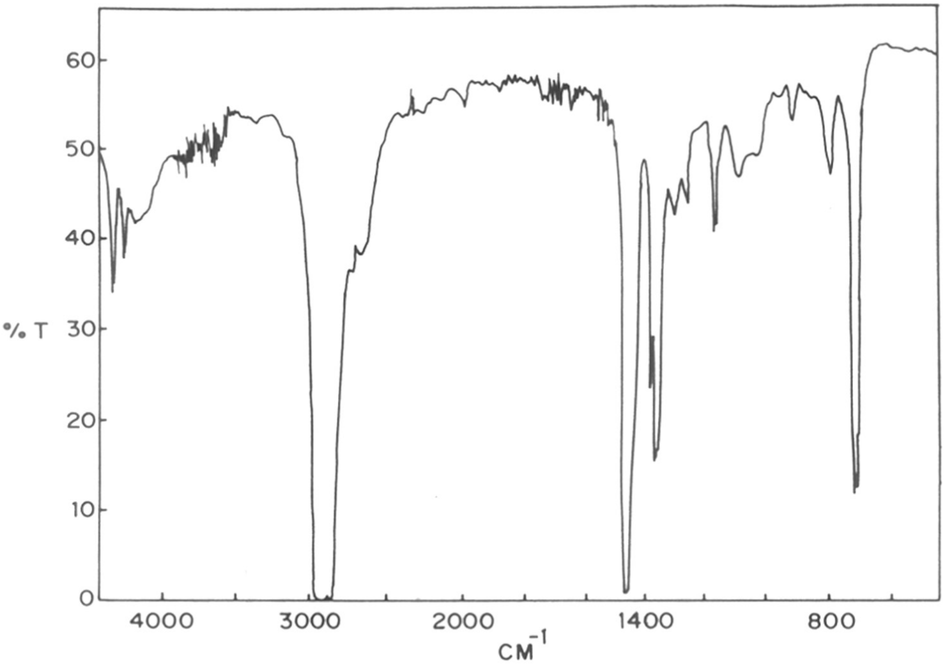
(b) Calculated from IR.

(c) $F = \frac{F_1^2}{f_1}$, $G = \frac{f_1 - 1}{f_1} x F_1$ Fineman - Ross eqn. : $G = - r_{comonomer} + r_{ethyelene} F$

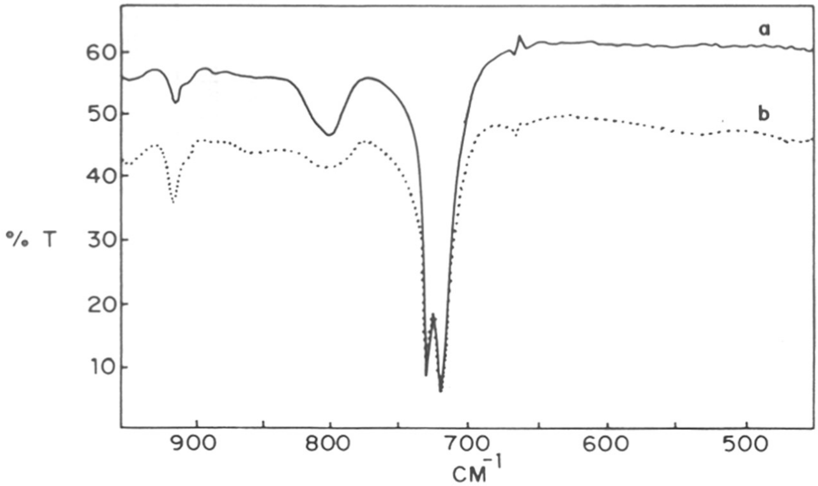
Kelen-Tudos eqn. : $G/(F + \alpha) = (-r_{comonomer}/\alpha) + (r_{ethylene} + r_{comonomer}\, \alpha^{-1}) (F / F + \alpha)$



A.1.2 Fineman-Ross (I) and Kelen-Tudos (II) plots for ethylene 4-methyl-1-pentene copolymerization over $TiCl_4/(iso\text{-}Bu)_3Al$ catalyst system.



A.1.3 a IR spectrum of an ethylene-4-methyl-1-pentene copolymer (catalyst : $TiCl_4$/(iso Bu)$_3$Al).



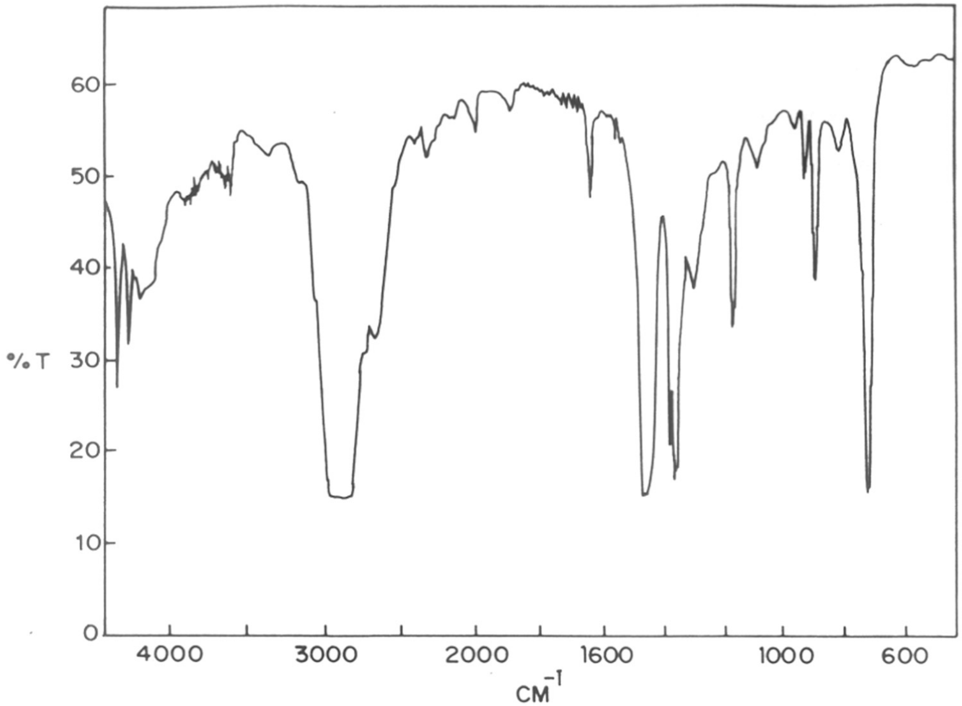
A.1.3 b Zoom of the 730,720 cm^{-1} region of E4M1P (a) 6 mol% incorporation of 4M1P and (b) 19 mol% incorporation of 4M1P.

Table A.1.4 Copolymerization of ethylene with 4-methyl-1-pentene using Cp_2ZrCl_2/MAO catalyst[(a)]

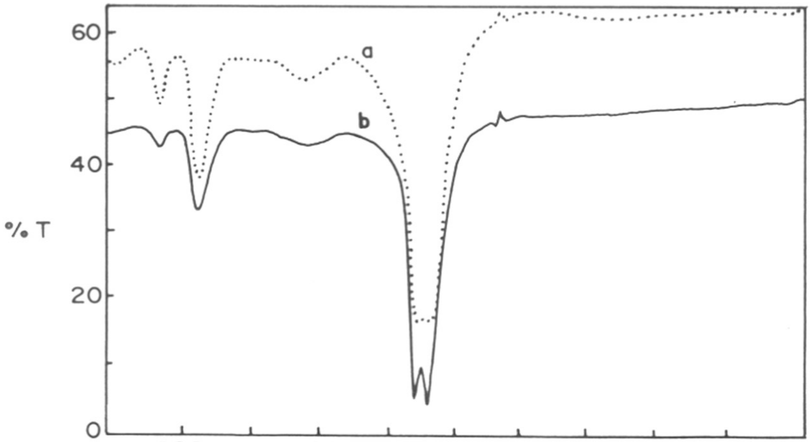
Sr. No.	Conc. of 4M1P in the feed		Yield (g)	Conv. %	Activity Kg/gZr/h	mol % 4M1P in copoly.[(b)]	T_m °C	ΔH_f J/g
	M	mol %						
1.	-	-	0.48	100	25.2	-	132.5	194.7
2.	0.128	53.7	0.54	77	28.1	2.5	112,117.1	82.7
3.	0.321	74.4	0.65	54	43.0	3.8	105.1,110	61.09
4.	0.417	79.1	0.72	50	37.7	5.7	98.3,104	35.8
5.	0.514	82.3	0.76	44	39.1	7.5	96.1,101.5	31.1

(a) Copolymerization conditions : solvent = toluene (25 mL), temp.= 35°C, press. = 1 atm., time = 8-10 min., [E] = 0.11 M, [Zr] = 5 x 10^{-5} M, [Al] = 0.075 M]

(b) Calculated from IR



A.1.4 a IR spectrum of an ethylene-4-methyl-1-pentene copolymer (catalyst : Cp_2ZrCl_2/MAO)



A.1.4 b Zoom of the 730,720 cm^{-1} region of E4M1P (a) 7.5 mol% incorporation of 4M1P and (b) 2.5 mol% incorporation of 4M1P.

The copolymers obtained with the Cp_2ZrCl_2/MAO catalyst however appear to be random in nature. A rate enhancing effect of 4-methyl-1-pentene on the copolymerizations was observed (Fig.A.1.1b). At a 4-methyl-1-pentene incorporation of 7.5 mol% the doublet appears to have disappeared with only a broad peak centered at 725 cm^{-1} in the IR spectrum (Fig.A.1.4b). The melting points of the copolymers also decrease gradually with increase in 4-methyl-1-pentene incorporation indicative of true copolymer formation (Table A.1.4).

The copolymer composition was found out using IR[6] and was found to agree well with the value calculated from NMR.[7]

A.1.4 References

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APPENDIX II

A STUDY OF THE COPOLYMERIZATION OF ETHYLENE WITH BICYCLO(2.2.1)HEPT-2-ENE (NORBORNENE) USING Cp_2ZrCl_2/MAO

A.2.1 Introduction

Copolymers of ethylene with bicyclo (2.2.1)hept-2-ene (norbornene) have aroused a lot of research interest in the last few years. They have achieved commercial success as high performance materials with exceptional properties such as high clarity, low moisture absorption and high uv stability.[1] The use of homogeneous metallocene/methylaluminoxane catalyst have enabled the synthesis of linear ethylene-norbornene copolymers without any accompanying ring opening reactions.[2] The conventional Ziegler-Natta catalysts always gave rise to products in which the norbornene moiety was inserted either through the double bond or by a ring opening reaction.[3] Kaminsky *et al*[4,5] conducted a study of the copolymerization of ethylene with norbornene and characterized the resultant copolymers. They found that the rate of the copolymerization decreases with increase in norbornene feed ratio. They also found that above a certain norbornene concentration in the copolymer (above 50 mol %) the copolymer was totally amorphous (Tg = 120°C) with a refractive index value of 1.535 which is very close to that of glass.

In the course of our study on the copolymerization of ethylene with 5-vinyl-2-norbornene (Chapter V), we needed a reference study of copolymerization of ethylene with norbornene for purposes of comparison of results. This section reports the results of the study using Cp_2ZrCl_2/MAO catalyst system.

A.2.2 Experimental Section

All manipulations were done using standard inert atmosphere bench top techniques.

Materials: Norbornene (Merck) was used after distillation under nitrogen atmosphere. The origins and specifications of the ethylene, Cp_2ZrCl_2 and MAO used are given in section 5.2.

Copolymerization of ethylene with norbornene

The general procedure followed is similar to that described in section 5.2.1. Toluene (20mL) was added to the reactor and allowed to saturate with ethylene. Norbornene (0.25 g, 2.6 x 10^{-3} mol) dissolved in 5 mL of toluene was added with the help of a syringe to the reactor followed by the addition of 1 mL of MAO (1.87 x 10^{-3} mol). The copolymerization was started by the addition of 0.45 mL of a solution of zirconocene dichloride in toluene (1.25 x 10^{-6} mol). The copolymerization was terminated after 65 min using acidified methanol. The copolymer was filtered and dried under vacuum. Yield = 0.645 g (83 % conversion). ^{1}H NMR ($CDCl_3$, ppm) 2.05 singlet 2H bridgehead protons, 0.5 - 2 ppm backbone methylene and remaining ring protons.

Analytical Techniques : ^{1}H NMR spectra of samples as 2 wt % solutions and ^{13}C NMR of 10 wt % solutions in D_6 - benzene or $CDCl_3$ were recorded using a Bruker AC-200 spectrometer. IR spectra of films cast from toluene were recorded using a Perkin-Elmer PE 16 FTIR spectrometer.

A.2.3 Results and discussion

Copolymerization of ethylene with norbornene:

The copolymerization of ethylene with norbornene was studied with respect to the following parameters :

Effect of feed composition

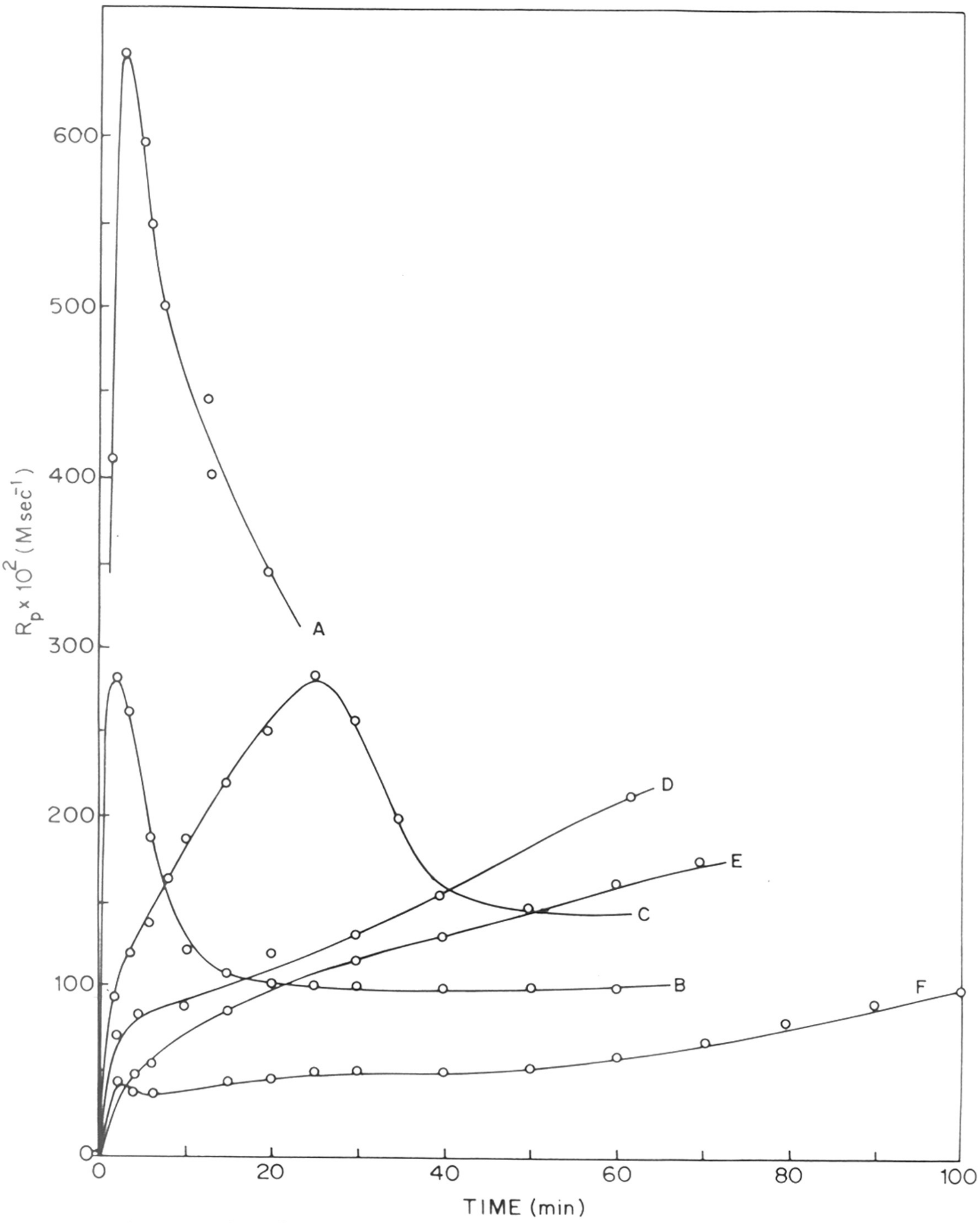
The results of this study are presented in Table A.2.1. An increase in the norbornene concentration in the feed resulted in an increased incorporation of norbornene in the copolymer, but the overall activity of the catalyst decreased. Figure A.2.1 shows the variation in R_p versus time for the different feed ratios. It can be seen that as the feed of norbornene is increased the curve changes from a decay type to a steady state type. At low feed ratios (curve b) the polymer is seen to precipitate out in two minutes and only a decay type of rate curve is seen. At a

Table A.2.1 **Copolymerization of ethylene with norbornene : Effect of feed composition**[a]

Sr. No.	Conc. of NB M	Conc. of NB mol %	Time min.	Yield 'g'	Activity Kg/gZr/h	Conc. of NB in copoly. mol %[b]
1.	0.074	40.2	45	0.55	6.5	10
2.	0.108	49.5	65	0.65	5.2	-
3.	0.159	59.1	72	0.64	4.6	14
4.	0.216	66.2	130	0.79	3.2	20
5.	0.318	74.3	180	0.7	2.0	25

(a) Copolymerization conditions : solvent = toluene (25mL), temp. = 35°C, press. = 1 atm., [E] = 0.11 M, [Al] = 0.075 M, [Zr] = 5×10^{-5} M, Al/Zr = 1500

(b) Determined from ^{1}H NMR.



A.2.1 A plot of Rp vs time for ethylene norbornene copolymerizations (catalyst : Cp_2ZrCl_2/MAO) at different NB feeds (A)0.0M, (B) 0.04M, (C) 0.074M, (D) 0.108M, (E) 0.159M and (F) 0.216M.

slightly higher feed ratio (curve c) an initial build-up curve is observed which changes to decay type after the polymer was seen to have become insoluble in the reaction medium. At higher feed ratios (d), (e) an initial increase followed by a steady state behavior in the R_p versus time graph is noted.

In general, norbornene has a deactivating effect on the copolymerization, since the max R_p value of all copolymerizations lie below that of ethylene homopolymerization. A similar effect was observed by Kaminsky *et al*[4]. However an activating effect has also been noted by a few workers in the case of cyclopentene[6] and 1-hexene[7].

The rate of any polymerization depends on catalyst activity, number of active centers and diffusion of monomer to the active center. At low feed ratios (curve b) the copolymer is insoluble in the reaction medium and hence due to a diffusion limitation a decay type of curve is observed.

At a higher feed ratio (curve c) the copolymer formed is soluble in the reaction medium and diffusion limitation does not exist. As the copolymerization proceeds the norbornene concentration drifts to a lower value thus explaining the initial part of the curve which is build-up type. At some point of time the copolymer becomes insoluble in the reaction medium, after this point the diffusion becomes a limiting factor and a decay type of curve is seen.

At even higher feed ratios (curve d and e) the copolymer formed is soluble in the reaction medium, under the time limit studied, hence diffusion limitation does not exist. A slight build-up curve can be noticed as a result of the steady drift in norbornene concentration to lower value as copolymerization proceeds.

Effect of catalyst concentration

The metallocene concentration was varied from 2.5×10^{-5} M to 1×10^{-4} M. The catalyst activity was found to be higher at higher catalyst concentration (Table A.2.2).

Table A.2.2 **Copolymerization of ethylene with norbornene : effect of catalyst concentration**[(a)]

Sr. No.	[Zr] M x 10^{-5}	Al/Zr	Time min.	Yield 'g'	Activity Kg/gZr/h
1.	2.5	3000	72	0.54	3.94
2.	5.0	1500	65	0.64	5.18
3.	10.0	750	35	0.55	8.31

(a) Copolymerization conditions : solvent = toluene (25mL), temp. = 35°C, press. = 1 atm.,[E] = 0.11 M, [NB] = 0.108 M, [Al] = 0.075 M.

Table A.2.3 **Copolymerization of ethylene with norbornene : effect of temperature**[(a)]

Sr. No.	[E] M	Temp. °C	Time min.	Yield 'g'	Activity Kg/gZr/h
1.	0.11	35	65	0.64	5.18
2.	0.13	45	37	0.57	8.09
3.	0.15	55	27	0.58	11.23

(a) Copolymerization conditions : solvent = toluene (25mL), [NB] = 0.108 M, [Al] = 0.075 M, Al/Zr = 1500, [Zr] = 5 x 10^{-5} M.

Effect of temperature

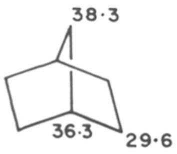
An increase in temperature from 35°C to 55°C led to an increase in the activity of the catalyst (Table A.2.3).

Characterization of ethylene-norbornene copolymers

^{1}H NMR : The ^{1}H NMR spectra were used to determine the composition of the ethylene-norbornene copolymers (Fig. A.2.2). The signal at 2.05 ppm corresponds to the norbornane bridgehead protons and appear apart from the backbone methylene and other ring protons. If I_1, is the intensity of the signal at 2.05 ppm and I_2 is the intensity of the signal between 0.5 to 2 ppm, then,

$$mol\%of norbornene = \frac{(I_1/2)}{(I_1/2) + \frac{(I_2 - 4I_1)}{4}} x\,100$$

^{13}C NMR : Figure A.2.3 shows the ^{13}C NMR spectra of three copolymers of ethylene - norbornene with 10, 20 and 30 mol % norbornene incorporation. Using the methodology of Whitesell and Minton[8] (also described in section 5.3.5.3) the stereochemical assignments for the ring carbons are calculated, considering the values of norbornane (I) as base values and adding the correction $\Delta\delta$ (shift - of - shift) for additional α, β and γ gauche carbons as a result of enchainment with the methylene backbone.



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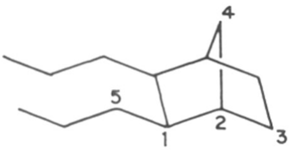

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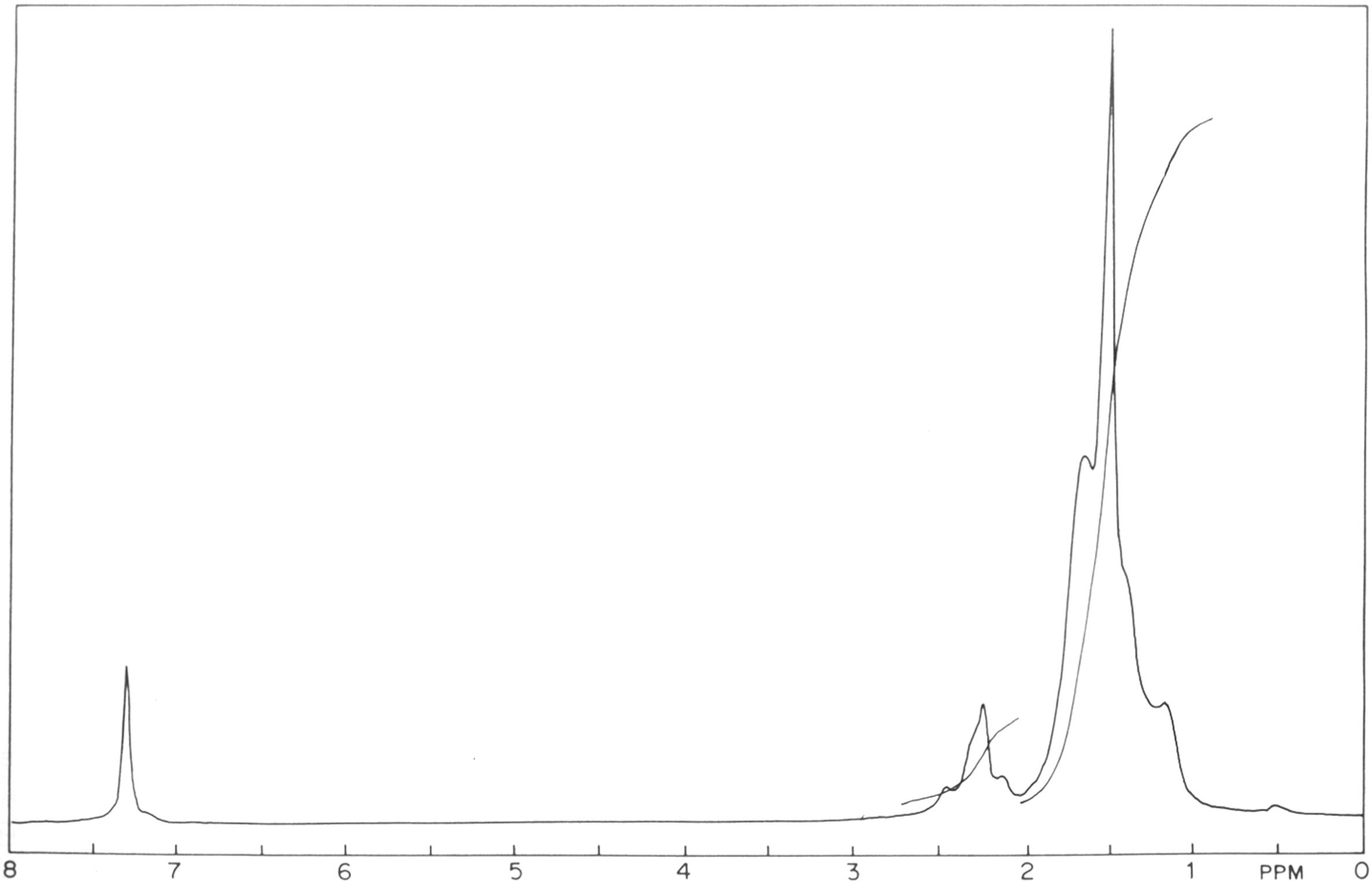
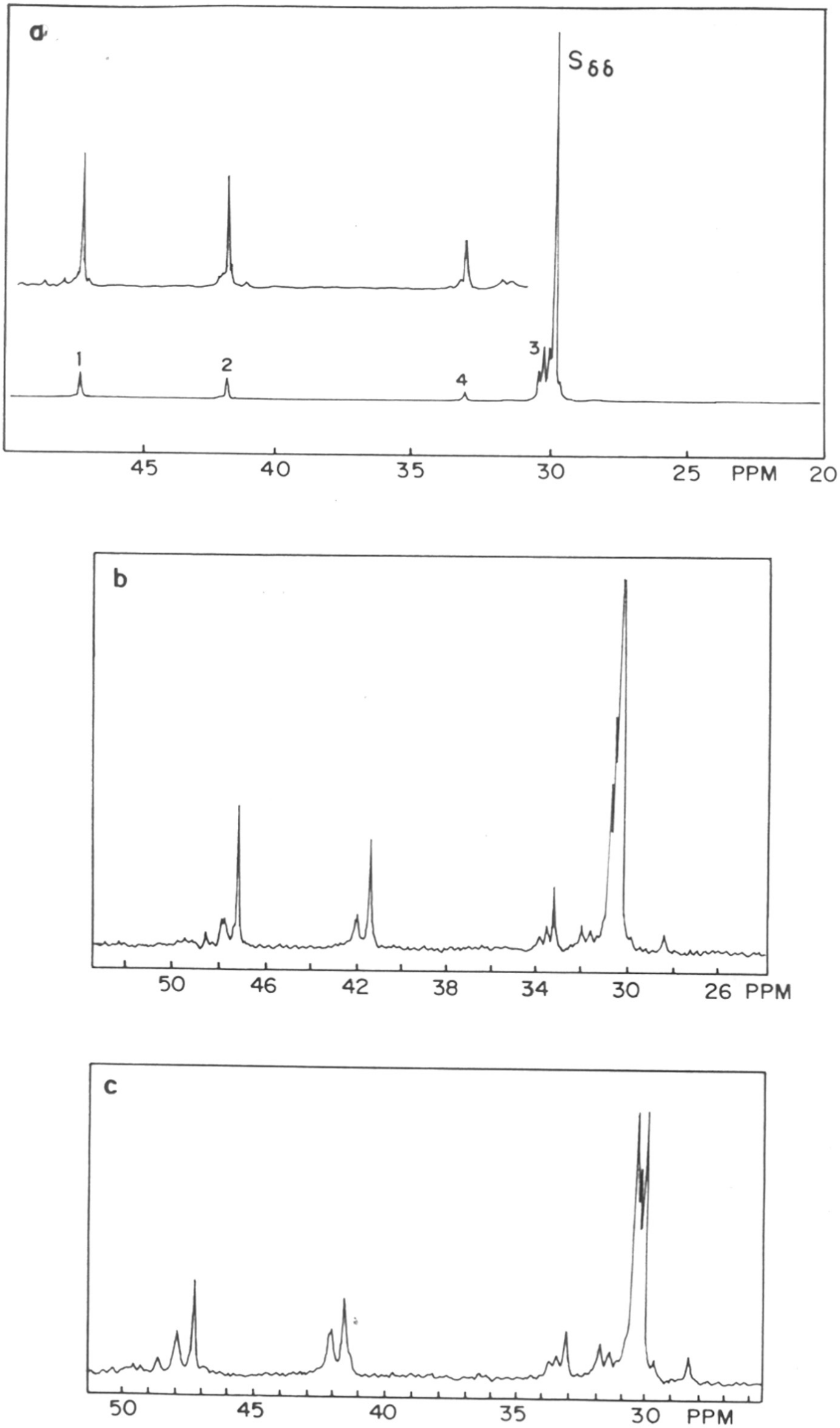


A.2.2 1H NMR spectrum of an ethylene-norbornene copolymer.



A.2.3 ^{13}C NMR spectrum of ethylene-norbornene copolymers (1) 10 mol%, (2) 20 mol% and (3) 30 mol% of norbornene incorporation.

Two unique cases of the γ effect are described by Whitesell and Minton in the case of bicyclic systems, and use of these values are made wherever necessary.

(1) When the norbornane ring has two exo substituents (eg 5, 5^1 in II) the two γ carbons are held rigidly eclipsed with a dihedral angle of 0°. In such cases the γ correction is as high as - 6ppm.

(2) When the substituent carbon,for example C5 in II is in exo configuration, it exerts a strong γ effect of - 3.5ppm on the C4 carbon and it also gets shifted upfield by - 3.5ppm.

With the above information, assignments for the C1, C2, C3 and C4 are calculated as follows :

In II C1 has one additional α, two β and two γ substituents compared to I. Hence its shift would be :

C1 = 29.6 + 8 + 2(7.5) - 2 (2.34) = 48 obs. 47.3 ppm

C2 has an additional β and γ

C2 = 36.3 + 8 - 2.3 = 42 obs. 41.5 ppm

C3 is unchanged = 29.6 obs. 30.5 ppm

C4 has two additional γ

C4 = 38.3 - 2 (3.5) = 31.3 obs. 33 ppm.

A close agreement between observed and calculated values is attained. In the calculation for C4 the two additional methylenes are considered to be exo or close to exo to explain the observed shift. This assignment of close to exo/exo configuration agrees well with that predicted by Kaminsky based on model compounds.[4] Using the isotactic specific catalyst $En(Ind)_4ZrCl_2$ Kaminsky had obtained an exclusively exo/exo enchainment of norbornene units in his copolymer.

From Fig. A.2.3 it can also be seen that as the norbornene content in the copolymer increases, the signal at 30 ppm splits and additional signals downfield to the ring carbons start appearing. Such an observation has not been reported by earlier workers in this area.

To explain this, the following tetrads according to the nomenclature of Carmen[9] are considered (The designation S stands for secondary and T for tertiary C atoms and the subscript α, β, γ refers to the position of the nearest branched carbon atom on either side.

EEEE	$S_{\delta\delta}$
EEE*N, EE*EN	$S_{\alpha\delta}$, $S_{\beta\delta}$, $S_{\gamma\delta}$
EE*NE, EEN*E	$S_{\alpha\delta}$, $S_{\beta\delta}$, $T_{\alpha}\delta$
EE*NN, EE*NN	$S_{\alpha\delta}$, $S_{\beta\delta}$, $T_{\alpha\delta}$, $T_{\alpha\alpha}$
EN*NE	$T_{\alpha\delta}$, $T_{\alpha\alpha}$
EN*EN, ENE*N	$T\alpha\gamma$, $S_{\alpha\beta}$
NE*EN	$S_{\alpha\delta}$, $S_{\beta\gamma}$
EN*NN, ENN*N	$T_{\alpha\alpha}$, $T_{\alpha\beta}$
NE*NN, NEN*N	$S_{\alpha\beta}$, $T_{\alpha\gamma}$
NN*NN	$T_{\alpha\alpha}$

As the copolymer becomes richer in norbornene we expect signals $S_{\beta\gamma}$, $S_{\alpha\beta}$ and $T_{\alpha\gamma}$, $T_{\alpha\beta}$ and $T_{\alpha\alpha}$ originating from tetrads richer in norbornene to start appearing.

Grant and Paul[10] rules are used in order to calculate these values and in cases where the substituent carbon under consideration is part of a bicyclic ring the methodology of Whitesell and Minton is followed.

Shift for $S_{\delta\delta}$ = 29.9 ppm

Shift for $S_{\alpha\delta}$ = $-2.35 + 2(\alpha) + 3(\beta) - \gamma - (C4\gamma)$ - (eclipsed γ) - branching correction

= $-2.35 + 2(8.85) + 3(9.51) - 2.34 - 3.5 - 6 - 2.11$

= 29.93 ppm

Shift for $S_{\beta\delta}$ = $-2.35 + (2\alpha) + 2(\beta) - 2(\gamma)$

= $-2.35 + 2(8.85) + 2(9.51) - 2(3.34)$

= 29.67 ppm

Shift for $S_{\beta\gamma}$ = $-2.35 + 2(\alpha) + 2(\beta) - 2(\gamma)$

= 29.67 ppm

Shift for $S_{\alpha\beta}$ = $-2.35 + 2(\alpha) + 3(\beta)$ - (eclipsed γ) $- 2(\gamma)$ - branching correction

= $-2.35 + 2(8.85) + 3(9.51) - 6 - 2(2.34) - 2.11$

= 31.09ppm

Shift for $T_{\alpha\delta}$ (calculated according to Whitesell and Minton)

= norbornane base + $(\alpha) + 2(\beta) - 2(\gamma)$

= $29.5 + (8) + 2(7.5) - 2(2.34)$

= 48ppm

Shift for $T_{\alpha\alpha}$ = norbornane base + $1(\alpha) + 3(\beta)$ - (eclipsed γ) - $(C_4\,\gamma)$ - γ - 2 branching correction (3°C 3°)

= $29.5 + 8.8 + 3(9.5) - 6 - 3.5 - 2.35 - 2(9.05)$

= 36.9ppm

Shift for $T_{\alpha\beta} = T_{\alpha\gamma}$

= norbornane base + $1(\alpha) + 2(\beta) - 2(\gamma)$ - [branching correction 3° (3°) + 3°(2°)]

$$= \quad 29.5 + 8.8 + 2(9.5) - 2(2.35) - 9.05 - 3.04)$$

$$= \quad 40.5 \text{ ppm}$$

From the ^{13}C NMR spectra it can be seen that at low norbornene content we see signals mainly at 29.2 ($S_{\delta\delta}$), 30.09 ($S_{\alpha\delta}$), 30.3 ($S_{\beta\delta}$) along with 47.3 ($T_{\alpha\delta}$) and other ring carbons.

At higher norbornene content the contribution from $S_{\alpha\beta}$ (30.5), $S_{\beta\gamma}$ (30.3) increases due to presence of sequences richer in norbornene and hence a number of peaks in the 30 ppm region are seen. However, blocks of NN appear to be absent as can be inferred from the absence of peaks in the 36 - 40 ppm region corresponding to $T_{\alpha\alpha}$ and $T_{\alpha\beta}$. Downfield splliting of the bicyclic ring carbons 1,2,3 and 4 is also observed due to contribution from additional δ and ε carbons in the calculations, arising from sequences rich in norbornene. Kamnisky and Noll[5] have observed peaks in the region 36-40 ppm which they attributed to norbornene blocks in ethylene norbornene copolymers of high norbornene content obtained with [$Ph_2C(Fluo)(Cp)ZrCl_2$] catalyst.

Thus, based on additivity rules as applied to bicyclic systems, reasonable assignments for the ^{13}C NMR spectra could be reached. However, since these are empirical rules, slight variations in calculated and actual values are observed, which are well within the limits.

A.2.4 Summary and Conclusions

A preliminary study of ethylene - norbornene copolymerization using the simple Cp_2ZrCl_2/MAO catalyst system was conducted. An attempt has been made to explain the change in the R_p versus time curves with change in norbornene feed ratios. Assignments for ethylene - norbornene copolymers containing 10, 20 and 30 mol % norbornene have been reached using additivity rules as applied to bicyclic systems.

A.2.5 References

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APPENDIX III

THERMAL AND X-RAY INVESTIGATIONS OF ETHYLENE-α-OLEFIN COPOLYMERS OBTAINED WITH HIGHLY ACTIVE SUPPORTED Ti-Mg AND V-Mg CATALYSTS

A.3.1 Introduction

A number of reports have appeared in the literature on the structure and properties of ethylene-α-olefin copolymers prepared with highly active supported transition metal catalyst.[1-9] The influence of the composition of supported titanium-magnesium (TMC) and vanadium-magnesium (VMC) catalysts on the reactivity ratios of ethylene and α-olefins, the microstructure and compositional heterogeneity of the copolymers has been reported.[10,11] It is generally understood that such differences in polymer microstructure should alter the physical and thermal properties of copolymers. Hence a detailed study of the thermal behaviour and crystallinity of ethylene-propylene, ethylene-1-butene and ethylene-1-hexene copolymers prepared using titanium-magnesium and vanadium-magnesium catalysts was undertaken.

A.3.2 Experimental Section

Titanium-magnesium (TMC) and vanadium-magnesium (VMC) catalysts were prepared by methods described previously.[12,13] Ethylene and α-olefins were copolymerized according to methods described in reference 11 and 12.

Analysis

Thermogravimetric analysis (TGA) of polyethylene samples was carried out using a Netzsch thermal analysis apparatus model STA 409. The sample was heated at a rate of 10°C/min in N_2. A Perkin Elmer DSC-2 differential scanning calorimeter equipped with a Thermal Analysis Data Station (TADS) was used for thermal characterization. The thermal parameters were determined from the heating and cooling scans. The heating (cooling) rate was 10°C/min. In order to obtain additional information regarding composition, ethylene-1-hexene copolymers were fractionated using hexane, heptane and toluene as solvents in a Soxhlet extractor for 6 h. These samples were then characterized using DSC.

X-Ray diffraction analysis was done using a Philips X-ray diffractometer consisting of an X-ray generator and a goniometer. The degree of crystallinity was determined by measuring the area under the sharp diffraction peaks and the amorphous halo. The CH_3/1000C and comonomer content were determined by IR spectroscopy using a compression moulded film.[14,15] The comonomer content in ethylene-propylene (EP) copolymers was determined using ^{13}C NMR spectroscopy and calculated according to the method of Randall.[16] The NMR spectra were scanned at 135°C at 75 MHz using a Bruker MSL-300 NMR spectrometer. Melt flow index (MFI) was determined according to the ASTM-D-1238 procedure.

A.3.3 Results and discussion

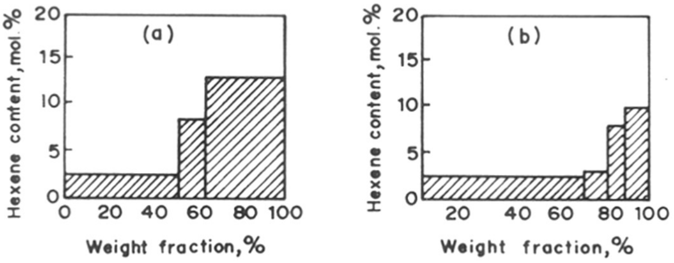
Details of the polymer samples used in the present investigation are given in Table A.3.1.

The thermal degradation behavior of polymers 1-8 was investigated by TGA in N_2. The results are given in Table A.3.2. Initial decomposition temperature (IDT) was more sensitive to the nature of the comonomer. The copolymers with longer short-chain branching led to lower IDT. Temperature of maximum rate of decomposition (T_{max}) was practically independent of the nature of the short-chain branching. No major differences in the thermal stability were found between TMC and VMC catalysts.

The melting point (T_m), heat of fusion (ΔH_f), temperature of crystallization (T_c) and heat of crystallization (ΔH_c) were evaluated for the various polymers by DSC. The results are summarized in Table 3. T_m ΔH_f, T_c and ΔH_c for copolymers prepared with TMC and VMC catalysts were uniformly lower than the values for corresponding homopolymers. The ΔH_f of copolymers derived with VMC catalyst showed only a marginal decrease depending of the nature of the comonomer. This means that ΔH_f is independent of comonomer type. A similar observation was reported for ethylene copolymers containing different α-olefin comonomers

Table A.3.1 Polymer samples used in the investigation

Polymer	Catalyst	Comonomer	Content of CH_3/1000C	Comonomer (mol%)	Melt index (g/10 min, 5 kg load, 230°C)
1	TMC	-	-	0	18.5
2	TMC	Propylene	26	5.4	0.16
3	TMC	1-Butene	30	6.4	22.0
4	TMC	1-Hexene	29	6.6	42.0
5	VMC	-	-	0	6.5
6	VMC	Propylene	27	5.5	4.0
7	VMC	1-Butene	23	4.8	13.2
8	VMC	1-Hexene	20	4.5	5.4



A.3.1 Compositional distribution for ethylene-1-hexene copolymers (a) TMC 6.6 mol% 1-hexene and (b) VMC, 4.5 mol% 1-hexene.

Table A.3.2 Thermal behavior of polyethylene and copolymers from TGA data

Polymer	IDT[a]	T_{max}[b]
1	395	457
2	400	454
3	384	457
4	389	452
5	400	462
6	395	462
7	395	457
8	389	457

(a) Initial decomposition temperature (°C)

(b) Temperature of maximum rate of decomposition (°C)

Table A.3.3 Melting and crystallization parameters for polymer samples

Polymer	T_m (°C)	ΔH_f (cal/g)	ΔT^a (°C)	T_c (°C)	ΔH_c (cal/g)
1	137.2	41.47	27.0	116.53	45.00
2	127.8	28.57	51.2	107.94	29.82
3	127.3	18.13	71.3	102.44	17.09
4	125.3	13.53	63.2	105.72	13.46
5	132.1	38.14	29.5	116.23	41.17
6	124.3	28.85	59.7	106.62	29.34
7	123.0	26.63	64.3	107.51	25.46
8	124.5	24.69	41.7	110.56	30.61

(a) Temperature difference at the beginning and end of fusion.

prepared using Ti-Mg catalysts by Burfield and Kashiwa.[17] They concluded that the disruption of polymer crystallinity is determined mainly by the number and distribution of chain irregularities rather than the type of chain disruptions. However, the ΔH_f of copolymers derived with TMC catalyst showed a decrease depending on the nature of the comonomer.

The ethylene-1-hexene copolymers from TMC and VMC catalysts (sample numbers 4 and 8, Table A.3.1) were fractionated successively in hexane, heptane and toluene. The fractions were analyzed for comonomer composition by IR spectroscopy.[14,15] The comonomer content in the various fractions is shown as a histogram in Fig.A.3.1 for two copolymers of similar composition, ca. 6.6 and 4.5 mol% of hexene-1, produced with the TMC and VMC catalysts respectively (samples 4 and 8). It can be seen that in spite of having similar average compositions, they have very different compositional distributions. The TMC-derived copolymer has a wide compositional distribution with significant amounts of high hexene content fraction (C_H = 12.7 mol%, fraction weight = 36%) and low hexene content fraction (C_H = 2.2 mol%, fraction weight = 51%). The VMC-derived copolymer has a more uniform composition with a small amount of high hexene content fraction (C_H = 9.5 mol%, fraction weight = 10.8%) and its major fraction (80%) consists of molecules with hexene content in the 2-3 mol% range.

The above observation that VMC-derived copolymer is compositionally more homogeneous than the TMC-derived copolymer is also supported by results obtained from a study of the thermal behavior and crystallinity of these copolymer fractions. Melting and crystallization parameters for the various fractions were evaluated by DSC and are shown in Table A.3.4. T_m, ΔH_f and T_c increased with successive fractionation. The hexane-soluble sample (4A) was completely amorphous, whereas a similar sample (8A) from VMC catalyst showed 17% crystallinity. The former fraction also had a greater proportion of the comonomer. The hexane-and heptane-insoluble polymer was lower in the case of VMC catalyst

Table A.3.4 Melting and crystallization parameters for fractionated ethylene-1-hexene copolymers

Polymer	Fraction	Fraction weight (%)	Content of comonomer (mol %)	T_m (°C)	ΔH_f (cal/g)	T_c (°C)	ΔH_c (cal/g)	Crystallinity (%)[a]
4A	Hexane	36.8	12.7[b]	88.3	0.75	66.5	1.2	1
4B	Heptane	12.2	8.2	102.0	11.2	91.3	10.9	16
4C	Residue	51.0	2.2	124.1	23.2	107.1	24.5	33
Total Polymer		100.0	6.6	125.3	13.5	105.7	13.5	20
8A	Hexane	10.8	9.5	94.8	11.9	88.5	12.7	17
8B	Heptane	7.1	-	112.4	24.6	101.8	23.1	35
8C	Toluene	11.4	3.0	120.3	29.9	108.1	28.1	43
8D	Residue	70.7	2.3	126.1	31.2	110.3	29.7	45
Total Polymer		100.0	4.5	124.5	24.7	110.6	30.6	36

a) Calculated from ΔH_f

b) Calculated from ^{13}C NMR.

compared with TMC catalyst. Samples (4A) and (4B) showed broad DSC peaks with multiple inflections, indicating that the copolymers were compositionally heterogeneous. Samples (8A) and (8B) were relatively more homogeneous. The copolymers derived from VMC catalyst were relatively more crystalline than those derived from TMC catalyst.

Thus, the thermal properties and crystallinity of copolymers of ethylene with α-olefin are found to be significantly influenced by the nature of the catalyst. The VMC catalyst produces copolymers of higher crystallinity compared with TMC catalyst. Both the heat of fusion and crystallization values of ethylene-α-olefin copolymers and fractionation studies of ethylene-1-hexene copolymers indicate that the VMC-derived copolymers are compositionally more homogeneous than the TMC-derived copolymers.

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SYNOPSIS

Introduction

One of the most important achievements in the field of synthetic polymer chemistry during the past 50 years has been the discovery in 1953 by Ziegler and his coworkers[1], that transition metal halides used along with aluminum alkyl compounds in an inert hydrocarbon medium could polymerize ethylene under conditions of normal temperature and pressure to yield a solid polymer of high molecular weight and of a linear structure. Ziegler's discovery together with the ensuing work by Natta and coworkers[2] on polymerization of propylene and other α -olefins, has given rise to the development of new classes of catalysts and polymers. The principal polymers, namely, high density polyethylene (HDPE) and polypropylene (PP) form a major volume of todays commodity polymers. Along with HDPE, linear low density polyethylene (LLDPE) is also steadily gaining importance due to its unique physical properties i.e., a combination of low density with high strength and modulus of the polymer. LLDPE is obtained by copolymerizing ethylene with a higher α -olefin and it consists of linear polyethylene chains with short chain branches at places where the α -olefin has been incorporated[3]. The number and length of these short chain branches are directly related to the concentration and structural features of the α -olefin comonomer. A large amount of published and patent literature is available on the production and characterization of copolymers of ethylene with butene-1, hexene-1 and octene-1[4,5,6]. However, except for a few scattered reports[7,8] relatively less is known about the properties and structure of a copolymer of ethylene and an α -olefin containing a cyclic/bycyclic pendant group. As in the case of copolymerization, very few reports exist on the homopolymerization of cyclic/bicyclic group containing α -olefins. The bicyclic pendant due to its unique space filling properties can be expected to give rise to properties not found in the homo-and copolymers of its acyclic analogues.

Also, till the advent of the metallocene based catalysts, polymerization and copolymerization of cyclic/bicyclic olefins like cyclopentene and norbornene with Ziegler catalysts resulted in polymers in which at least 30% of the structures were a result of ring opening metathesis type of reactions[9]. The discovery of the metallocene catalysts has made it possible to homo- and copolymerize cyclic/bicyclic olefins like cyclopentene/norbornene[10,11] to high molecular weight linear polymers where insertion of the endocyclic double bond occurs with release in ring strain and without any ring opening metathesis reactions. In such polymers the cyclic/bicyclic group being a part of the main chain could be considered to be responsible for the amorphous nature and good thermal and optical properties of the polymers. A bicyclic diolefin having an exocyclic vinyl double bond on one hand and an endocyclic vinylene double bond on the other, under conditions of polymerization can participate either as an α -olefin or as a bicyclic olefin. It would be therefore of interest to explore which of these two double bonds would participate in polymerization. This would lead to an understanding of the regioselectivity of insertion.

Objectives of the present investigation

The research embodied in the present thesis was undertaken with a view to

a) study the homo- and copolymerization of an α -olefin containing a bicyclic pendant namely, 2-propenylbicyclo[2.2.1]heptane or 2-allylnorbornane using Ziegler-Natta catalysts and characterize the resultant polymers. Furthermore the properties of the above polymers were to be compared with the corresponding homo- and copolymers of their acyclic analogue namely 4-methyl-1-pentene. It was hoped that this would lead to an understanding of the effect of the bicyclic pendant on polymer properties.

b) conduct polymerization of ethylene with a bicyclic diolefin namely, 5-vinyl-2-norbornene and hence to examine the regioselectivity of insertion between a hindered endocyclic vinylene double bond and a less hindered exocyclic vinyl double bond.

c) attempt to functionalize the unreacted double bond in the ethylene-5-vinyl-2-norbornene copolymers.

OUT LINE OF THE THESIS

The present thesis titled "**Homo- and Copolymerization of Bicyclic Olefins using Ziegler-Natta Catalysts**" is divided into seven chapters

Chapter I

This introductory chapter begins with a brief introduction to Ziegler-Natta polymerization. Then a survey of literature covering the area of synthesis, properties and applications of homo- and copolymers of higher alpha olefins which includes linear, branched, cyclic and bicyclic olefins, is presented. Extensive literature, based on patents and published reports, on homopolymers and copolymers with ethylene, of higher acyclic, cyclic and bicyclic diolefins is also described.

Chapter II

The scope and objective of the present investigations are described in this chapter.

Chapter III

This chapter deals with the homopolymerization of 2-propenylbicyclo(2.2.1) heptane or 2-allylnorbornane (ANB) using heterogeneous and homogeneous Ziegler-Natta catalysts. Homopolymerization of 2-allylnorbornane was studied using classical Ziegler-Natta catalysts. Using the catalyst system $TiCl_4/Al(iso\ Bu)_3$ the preliminary kinetics of homopolymerization of ANB was studied. This includes the effect of catalyst concentration, effect of monomer concentration, effect of Al/Ti ratio and effect of temperature and time on the polymer conversion. The polyallylnorbornane (PANB) was characterized by solubility, NMR, IR, DSC and X-ray diffraction techniques. Its properties were compared with poly(4-methyl-1-pentene) (PMP) which is its acyclic analogue. Homopolymerization of 2-allylnorbornane using the homogeneous catalyst Cp_2ZrCl_2/MAO was also attempted.

Chapter IV

This chapter deals with the copolymerization of 2-allylnorbornane with ethylene using heterogeneous and homogeneous Ziegler-Natta catalysts. Using the catalyst system $TiCl_4/Al(iso\ Bu)_3$ the kinetics of copolymerization, with respect to effect of comonomer concentration, effect of catalyst concentration, effect of cocatalyst concentration and temperature on copolymerization was studied. Reactivity ratios for the ethylene-ANB pair were found to be r_1(ethylene) = 43.75 and r_2 (ANB) = 0.07. The properties of poly(ethylene-co-2-allylnorbornane) were compared with the properties of poly(ethylene-co-4-methyl-1-pentene) to study the effect of the bicyclic pendant. It was found that at a similar mole % incorporation both 2-allylnorbornane and 4-methyl-1-pentene have a similar effect on the crystallinity and melting point of the copolymers. Copolymerizations using the homogeneous catalyst Cp_2ZrCl_2/MAO were studied at various comonomer concentrations and the resulting copolymers were characterized.

Chapter V

Copolymerization of ethylene with 5-vinyl-2-norbornene (VNB) using a Cp_2ZrCl_2/MAO catalyst system was conducted in order to investigate the regioselectivity of double bond insertion between a more strained endocyclic vinylene double bond and a less strained exocyclic vinyl double bond. The ethylene -5-vinyl-2-norbornene copolymers were characterized by IR, NMR, intrinsic viscosity and thermal methods. Based on IR and NMR data it was found that the copolymerization of ethylene with 5-vinyl-2-norbornene occurred by a regioselective insertion of the endocyclic double bond leaving the exocyclic vinyl double bond free as a pendant group. The effect of catalyst concentration, cocatalyst concentration and temperature on the copolymerization activity was studied. Reactivity ratios for the ethylene-5-vinyl-2-norbornene pair were found out by terminating the copolymerizations at less than 20% conversion, r_1(ethylene) = 18.6 and r_2 (VNB) = 0.3.

Chapter VI

This chapter deals with the functionalization of the pendant vinyl double bond of the ethylene-5-vinyl-2-norbornene copolymers using standard organic chemical transformations. A hydroxy group was introduced via the hydroboration-oxidation reaction on the pendant vinyl bond. Use of a mild epoxidizing agent such as m-chloroperbenzoic acid led to an epoxy group containing ethylene-5-vinyl-2-norbornene copolymer. Both the functionalization reactions were observed to proceed with near quantitative conversion. The epoxy group containing poly(ethylene-co-5-vinyl-2-norbornene) was further used in a "grafting onto" coupling reaction with living polystyryllithium giving rise to poly(ethylene-co-5-vinyl-2-norbornene)-graft-polystyrene. All the above functionalized polymers were characterized by IR, NMR, intrinsic viscosity and thermal techniques wherever applicable.

Chapter VII

This chapter summarizes the results and describes the salient conclusions of this study. Additional thoughts for further research are also indicated.

Homo- and copolymerization of a bicyclic α -olefin namely 2-allylnorbornane has been conducted and the resultant polymers characterized. By a process of comparison of the properties of poly(2-allylnorbornane) with poly(4-methyl-1-pentene) and poly(ethylene-co- 2-allylnorbornane) with poly(ethylene-co- 4-methyl-1-pentene) the effect of bicyclic pendant on polymer properties is envisaged. In the homopolymer the bicyclic group results in a lowered solubility and an increase in Tm, whereas in the copolymer the bicyclic pendant does not give any appreciable lowering in crystallinity and Tm, over that its acyclic analogue at similar mole% incorporation.

The research has also resulted in the synthesis of ethylene-5-vinyl-2-norbornene copolymers with 5-20 mole% comonomer incorporation. It was found that a regioselective insertion of the endocyclic double bond of the comonomer into the growing polymer chain occurs, leaving the vinyl double bond as pendant.

The poly(ethylene-co-5-vinyl-2-norbornene) has been functionalized to epoxy, hydroxy group containing polymer using standard organic chemical transformations. Further, the epoxy group containing polymer was used in a "grafting onto" coupling reaction with living polystyryllithium to give rise to poly(ethylene-co-5-vinyl-2-norbornene)-graft-polystyrene.

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