CHAPTER I

INTRODUCTION
INTRODUCTION

1.1 Organic chemists attempting to prepare pure compounds in high yields encountered many polymeric substances and quickly discarded them as oils, tars or undistillable residues. Styrene was polymerized as early as 1839, isoprene in 1879, and methacrylic acid in 1880. Again cyclic structures held together by 'partial valences' were assigned. Acceptance of the macromolecular hypothesis came about in the 1920's, largely because of the efforts of Staudinger, who proposed long chain formulae for polystyrene, rubber and polyoxymethylene. Staudinger was able to classify different types of polymers into distinctly different classes and a large variety of macromolecules were prepared.

But the discovery of Ziegler-Natta catalyst system gave a new dimension to the science of macromolecules. This catalyst system was first reported by Karl Ziegler in Germany for the polymerization of ethylene at room temperature and atmospheric pressure. Subsequently G. Natta and his collaborators in Italy further developed the use and scope of Ziegler catalysts for polymerization of propylene. The use of Ziegler-Natta catalysts has been extended for the polymerization of \( \alpha \)-olefins, diolefins and other monomers wherein the steric
arrangements of carbon backbone chain are different.

The Ziegler-Natta catalysts are more effective for the polymerization of ethylene to linear, high density, high molecular weight polyethylene. In fact the crystallinity, density, melting point and mechanical properties of polyethylene produced by Ziegler-catalysts are higher than those obtained using conventional high pressure and free radical catalysts.

The practical importance of stereospecific polymerization processes lies in the synthesis of high molecular weight and crystalline polymers with better mechanical and thermal properties.

The regular structure of resulting polymers particularly poly(\(\alpha\)-olefins) such as polypropylene, was visualised by Natta and coworkers\(^8-10\), who named the resulting polymers as isotactic, syndiotactic and atactic.

Thus, the work of Natta on polymerization of propylene and other \(\alpha\)-olefins opened a new era in polymer science and stereoregularity of polymer structure has since then popularised\(^11-13\).

Extensive work has been done on the polymerization of nonpolar and polar monomers with the Ziegler-Natta catalysts. Much effort has also been spent in many academic and industrial laboratories to elucidate the polymerization mechanism by these catalysts and to develop them for commercial applications. Today\(^14\) with the team work of chemists and engineers the plastics, polyethylene, isotactic
polypropylene and poly-4-methyl-1-pentene and also the elastomers cis-1,4 polyisoprene, cis-1,4 polybutadiene and ethylene-propylene copolymer are produced commercially with Ziegler-Natta catalyst systems.

1.2 Classification of the Catalyst Systems

Polymerization processes may be classified according to their initiation mechanisms. In general, these mechanisms will involve free radicals, positive or negative ions, co-ordination complexes, or an electron transfer step to monomer.

The co-ordinating catalysts such as Ziegler-Natta catalysts could generally act, at least in principle, according to one of the two mechanisms described below (1.2.1 and 1.2.2). These processes are mainly considered as co-ordinated because the catalyst consists of an electron-deficient complex having one co-ordinating atom capable of associating with the monomer.

1.2.1 Co-ordinated Radical Mechanism

In co-ordinate radical polymerization, the active metal carbon bond becomes more covalent, homolytic cleavage of the bond takes place giving rise to radical type polymerization, as shown below:

\[
\begin{align*}
\text{TiCl}_4 + \text{AlEt}_3 &\rightarrow \text{AlEt}_2\text{Cl} + \text{EtTiCl}_3 \\
\text{EtTiCl}_3 &\rightarrow \text{TiCl}_3 + \text{Et} \text{ (or } R) \\
\text{CH}_2 = \text{CH}_x + R-\text{CH}_2-\text{CH}_x &\rightarrow R-\text{CH}_2-\text{CH}_x-\text{CH}x-\text{CH}_2
\end{align*}
\]
The end group of the growing polymeric chain is thus a free radical. The formation of the radicals becomes favourable, if the transition metal is in its highest valency state or the non-transition metal reacting with alkyl belongs to IV or V group of periodic table.

1.2.2 **Co-ordinated Ionic Mechanism**

When the bond between the terminal atom of the growing chain and the catalyst is of ionic type due to strong polarization, ionic mechanism\(^{16,17}\) - either cationic when the end of growing chain has positive charge or anionic when the charge is negative, is proposed.

1.2.2.1 **Co-ordinate Anionic Mechanism**

In co-ordinate anionic polymerizations each monomer unit is complexed and polarized by a positive centre, prior to its addition to the growing anion, as shown below. The polymer migrates as an anion to the positive end of the double bond while the negative end of the double bond, at the same time, attaches itself to the positive metal site. Such a mechanism is frequently observed with Ziegler-Natta type catalyst systems. The propagation step in a co-ordinate anionic mechanism can be illustrated, as below:

\[
\begin{align*}
R-\text{CH}_2 + P-\text{CH}_2 & \quad \text{Cat} \\
& \quad \text{Monomer} \quad \delta(-) \quad \delta(+) \\
\downarrow & \\
\delta(+) \quad \delta(-) & \\
R-\text{CH} & \quad \text{CH}_2 \\
\uparrow & \\
\delta(-) & \\
P-\text{CH}_2 & \quad \text{Cat} \\
\delta(-) & \\
P-\text{CH}_2-\text{CH}_2-\text{CH}_2 & \quad \text{Cat} \\
R \delta(-) & \quad \delta(+) \\
\end{align*}
\]
1.2.2.2 **Co-ordinate Cationic Mechanism**

When triethyl aluminium is added to the solution of BF$_3$ in diethyl ether, following reaction takes place:

$$ R_3\text{Al} + BF_3 \rightarrow (R_2\text{Al})^+ + (BF_3\text{R})^- $$

The counteranion (BF$_3$R)$^-$, can co-ordinate further to form a counteranion whose central metal possesses a positive charge:

$$ BF_3\text{R}^- + AlR_3 \rightarrow |R_3\text{Al} - BF_3\text{R}|^- $$

The resulting counter ion can induce stereoregular polymerization by its complex formation with the polymer chain wherein two neighbouring ether oxygens which are linked to the polymer chain in the vicinity of the positively charged chain end, can co-ordinate onto the partially positively charged metal centre of complex anion.

It is generally found that most of the Ziegler-Natta type catalyst systems act through co-ordinate ionic mechanism.

1.3. **Concept of Tacticity**

Natta and coworkers found that polypropylene prepared by these catalysts was crystalline in nature and also other polyolefins prepared by these catalysts showed better physical and technological properties. It was found that all the methyl groups (in the case of polypropylene) in polymer molecules were in the same plane. These polymers were named isotactic$^6,11$ by Natta. Another type of polymers with alternate groups in the same plane was named as syndiotactic$^{18-20}$ and those having random arrangement of groups were named as
atactic. These polymeric structures can be illustrated by Newman projection. The chains of isotactic and syndiotactic polymers will have a tendency to form crystalline lattices. In the crystalline form the isotactic polymers tend to form helices with pendent groups projecting in the same plane.

The number of stereoregular forms will increase in the case of 1,2 disubstituted polyethylene, as shown below:
If two different asymmetric 'C' atoms in chain occur with the same configuration, the polymer is called as erythrodii-isotactic. If the two asymmetric 'C' atoms have alternating configuration, the polymer is called threo-di-isotactic. When adjacent pairs of 'C' atoms have alternating configuration, the polymer is known to be di-syndiotactic. It will be observed that only one di-syndiotactic structure is possible.

Conjugated di-olefins can have a variety of above structures but more important in these cases is geometric isomerism. In case of isoprene, for example, we can get -1,4 cis and -1,4 trans polymers.

\[
\begin{align*}
\text{cis} & \quad \text{trans} \\
\begin{array}{c}
\text{CH}_3 \quad \text{H} \\
\text{C} = \text{C} \quad \text{C} = \text{C} \\
\text{CH}_2^- \quad \text{CH}_2^- \\
\end{array}
\end{align*}
\]

1,4 cis 1,4 trans

In addition to these we can get addition at 1,2 as well as 3,4 positions.

1,4 cis polyisoprene exists in nature and is known as Hevea rubber and also trans 1,4 polyisoprene exists in the form of Guttepercha and Balata.

1.4 Stereospecificity of the Catalysts

Polymers obtained by free radicals are seldom stereospecific polymers and this is attributed to the fact that, in general, free radical propagation reaction is less influenced by steric limitations such as those occurring in the complexing of the monomer with the transition metal.
of Ziegler-Natta catalyst. In some cases, however, syndiotactic stereoregular polymers are formed. This, in particular, arises when very low temperatures are employed for the polymerization of monomers containing hetero atoms (acrylates, methacrylates, vinyl chloride, acrylic nitrile)$^{22-24}$. Probably, this is a result of the thermodynamic factor$^{25}$. There is higher free energy variation in the formation of syndiotactic polymer in comparison to the formation of isotactic and atactic polymers.

A very particular case of stereoregular radical polymerization is the polymerization of monomers entrapped in some crystals having channels of particular size. For example, trans 1,3-pentadiene held in perhydrotriphenylene can be polymerized by the action of high energy radiations to trans 1,4-isotactic polypentadiene$^{26}$. In this case, the entrapped monomer molecules are arranged one after the other in the trans conformation and have less mobility to form other conformations. This indicates that stereospecificity in polymerization is possible when the monomeric units are placed in an ordered fashion irrespective of the mechanism of reaction.

Pre-dissolved polymer in monomer can also have regulating effect$^{27,28}$. This polymerization is known as 'replica' polymerization.

Phillips catalysts$^{29}$ containing certain solid surfaces such as clays or mixture of alumina and molybdena can orient the monomer molecules by immobilizing and complexing them
to give stereoregular polymerization e.g. lithium alkyls, sodium alkyls etc. These complexes are particularly used for stereospecific polymerization of acrylic esters, acrylic amide and vinyl halides. Cationic initiator of similar type have been used for stereospecific polymerization of styrene derivatives.

Optically active polymers from the corresponding optically active monomers are studied to understand whether the propagation steps have been maintained or destroyed into ionic polymerization.

Alfin catalysts used by Morton and coworkers containing alkali alcohols with an olefin halide, control the propagation in the polymerization of diene polymers.

Effective control of propagation step is achieved by organometallic mixed catalysts. The Ziegler-Natta catalysts have a great controlling influence on the propagation step in the polymerization of ethylene and other monomers. Stereoregular polymerization with Ziegler-Natta catalysts have been reviewed widely in literature.

1.5 Ziegler-Natta Catalysts

The Ziegler-Natta catalysts are the result of reactions of two different species: (a) compounds of group IV-VI transition elements called as catalyst and (b) organometallic compounds of group (I-V) called as co-catalysts. However, not all compounds and not all combinations are equally effective in stereoregulation. The particular choice of catalyst and co-catalyst, the ratio of components, the
physical state of the catalyst and the reaction conditions have a great effect on nature of polymer obtained.

A substantial number of detailed studies has now been carried out, and skillfully reviewed to elucidate the chemical transformations occurring in the reactions of organometallic compounds, primarily organo aluminium reagents, with titanium halides.

The reaction of an alkyl aluminium compound with titanium tetrachloride produces, at room temperature, an almost instantaneous brown to black precipitation of lower valence titanium chloride (\(\beta\)-TiCl\(_3\)) and evolution of gaseous hydrocarbons.

The net reaction may be represented, as follows, by a ligand exchange reaction of an alkyl and a chloride group, followed by reductive dealkylation of the unstable organotitanium compound.

\[
\begin{align*}
\text{TiCl}_4 + \text{Al(C}_2\text{H}_5)_3 & \rightarrow \text{C}_2\text{H}_5\text{TiCl}_3 + \text{Al(C}_2\text{H}_5)_2\text{Cl} \\
\text{TiCl}_4 + \text{Al(C}_2\text{H}_5)_2\text{Cl} & \rightarrow \text{C}_2\text{H}_5\text{TiCl}_3 + \text{Al(C}_2\text{H}_5)\text{Cl}_2 \\
\text{TiCl}_4 + \text{Al(C}_2\text{H}_5)\text{Cl}_2 & \rightarrow \text{C}_2\text{H}_5\text{TiCl}_3 + \text{AlCl}_3 \\
\text{C}_2\text{H}_5\text{TiCl}_3 & \rightarrow \text{TiCl}_3 + \text{C}_2\text{H}_5.
\end{align*}
\]

The alkyl radicals resulting from the decomposition of the unstable organotitanium compound yield different gaseous products according to the following equations:

\[
\begin{align*}
2 \text{C}_2\text{H}_5^* & \rightarrow \text{C}_2\text{H}_4 + \text{C}_2\text{H}_6 \\
2 \text{C}_2\text{H}_5^* & \rightarrow \text{n-C}_4\text{H}_{10} \\
2 \text{C}_2\text{H}_5^* & \rightarrow 2 \text{C}_2\text{H}_4 + \text{H}_2 \text{ etc.}
\end{align*}
\]
1.6 Mechanism of Polymerization with Ziegler–Natta Catalysts

Several mechanisms have been proposed to account for the action of the co-ordination complex in the propagation step of polymerization, but very few have been so far substantiated with full experimental data. It is well accepted that the monomer molecules get oriented in some way or the other before adding up to the chain between metal alkyl and transition metal bridge bond. Since nature of the orienting forces is not very well known, various mechanisms of reactions have been proposed depending on the experimental results. Specifically, for olefin polymerization with these catalyst systems, there are two views as to whether the active site is a bimetallic complex involving both the transition metal and alkylating agent as proposed by Natta or a simple organo-transition metal compound as proposed by Cossee. In a monometallic mechanism, growth takes place at one metal centre. According to this view, mechanism of polymerization is monometallic even though two metal centres are present in the form of a bimetallic complex, provided growth takes place only at one of these metal centres as depicted below:

\[
\begin{align*}
R \text{ or } X & \quad X \\
-AI & \quad V \quad -R \\
R \text{ or } X & \quad X
\end{align*}
\]

1.6.1 Natta's Mechanism

The reaction of crystalline TiCl₃ and a solution of aluminium triethyl is postulated to lead to a surface complex
(already discussed in 1.5) in which the titanium and aluminium atoms are joined through alkyl bridges. According to Natta, in the complexes containing titanium and aluminium, the polymeric chain grows on the aluminium carbon bond and not on the titanium carbon bond. The detailed mechanism proposed is that the initially incomplete co-ordination of titanium in the reduced state of di and tri chloride, facilitates chemisorption of organometallic compounds of the strongly electropositive metals with a small ionic radius. This chemisorption leads to the formation of electron deficient complexes between titanium and the other metal, which contain alkyl bridges similar to those present in the dimeric aluminium and beryllium alkyls. The isolation of soluble crystalline complexes \((\text{C}_5\text{H}_5)_2\text{TiCl}_2\cdot\text{AlRR}^*\) which are known to contain Ti-C-Al bridges lends weight to the bimetallic electron deficient theory. The growth of a polymeric chain on the Al-C bond as proposed by Natta is shown below:

**Natta's Bimetallic Mechanism**

\[
\begin{align*}
\text{Ti}^+ & \quad \text{Al} <^< \quad \text{CH}_2\text{=CH-}X \quad \rightarrow \quad \text{Ti}^+ & \quad \text{Al} <^< \\
\text{CH}_2 & \quad \text{CH}_3 \\
\text{R} & \quad \text{CH}_2 \quad \text{CH}_2 \\
\end{align*}
\]
Chain termination is considered to occur mainly by chain transfer, dissociation and subsequent formation of a metal hydride bond.

Several experimental evidences have been given by Natta and others for the above proposed mechanism. Natta and coworkers isolated bimetallic complexes from the reaction of aluminium alkyls and bis-(cyclopentadienyl)-titanium dichloride which polymerized ethylene at low pressure. They also found that bis-(cyclopentadienyl)-titanium dichloride and aluminium triphenyl produced polyethylene containing phenyl end groups, whereas bis-(cyclopentadienyl)-titanium diphenyl and aluminium triethyl produced polymer which did not have phenyl end groups. Since the phenyl group attached to aluminium appeared as an end group in the polymer (presumably during the initiation reaction) it was suggested that the polymer must be growing at the aluminium centre in a bimetallic complex.

Natta and coworkers further reported that when α, γ or δ crystalline modifications of TiCl₃ were used in combination with different metal alkyls for propylene polymerization, the polymer isotacticities were dependent
only on the metal alkyl.

Pozamentir\textsuperscript{57} concluded that the formation of polyethylene took place on the Al-atom, on the basis of his finding that the efficiency of alkyl chlorides, as polymer chain terminator during polymerization, varied in the same order as their reactivities towards AlEt\textsubscript{3}.

Natta gave further support\textsuperscript{58} to this mechanism by using \textsuperscript{14}C-labelled ethyl groups in triethyl aluminium as one constituent of the catalyst for the polymerization of ethylene. \textsuperscript{14}C-labelled ethyl groups are absorbed onto the surface of titanium trichloride and this whole system was used as the polymerization catalyst, in the presence of non-labelled triethyl aluminium. In the resulting polymer, terminal end groups contained practically all of the labelled alkyl groups and the chemical analysis showed that, at the end of a polymerization, most of the polymer chains were bound to aluminium. Natta and Mazzanti\textsuperscript{54} have explained their results by proposing a dissociation of the catalyst complex into two parts one containing the aluminium atom with the attached polymer chain and the other containing the titanium centre, which might associate again with surplus alkyl aluminium and yield a new active complex. Obviously all these terminal ethyl groups could not have been involved in alkylation of titanium.

When the polymerization is terminated by addition of tritiated alcohol, the isolated polymer contains bound tritium\textsuperscript{59}. When deuterium\textsuperscript{60} or tritium\textsuperscript{61} is present,
polymers having a lower molecular weight and containing bound deuterium (or tritium) are formed, as shown below:

\[ M-\text{Et}^{14} + n\text{CH}_2=\text{CH}_2 \rightarrow M(\text{CH}_2-\text{CH}_2)_n-\text{Et}^{14} \xrightarrow{\text{ROT}} \text{MOR} + \text{Et}^{14}(\text{CH}_2-\text{CH}_2)_n-T \]

\[ \frac{1}{2} \rightarrow \text{M-D} + \text{Et}^{14}(\text{CH}_2-\text{CH}_2)_n-\text{D} \]

where D is deuterium, and T is tritium.

All these findings support the view that the growth centre is a alkyl metal-carbon bond.

1.6.2 Additional Evidences for the Bimetallic Mechanism

A bimetallic mechanism employing only the transition metal atoms was proposed by de Bruijn\textsuperscript{62}.

The most cogent bimetallic mechanism which employed two different metals was also proposed by Patat and Sinn\textsuperscript{63} using the basic model structure of the bimetallic complex site having X=halogen and \( P_n \)=growing polymeric chain.

\[ \begin{array}{c}
\text{X} \\
\text{Ti} \\
\text{Al} \\
\text{P}_n
\end{array} \]

The monomer is co-ordinated to the titanium while simultaneously the Ti-polymer partial bond is broken. Patat and Sinn\textsuperscript{63} have shown that the olefin becomes partially bonded between the titanium and the methylene of the last added monomer, which is also partially bonded to the aluminium.
At that moment a \( \sigma \) bond forms between the olefin and this methylene, the methylene group becomes detached from the aluminium but still remains partially bonded to the titanium atoms of the bimetallic complex. Eirich and Mark also proposed a similar mechanism which employed adsorbed layers of alkylaluminium chloride on the titanium chloride crystals.

Bier, Gumboldt and Schmidt also proposed a bimetallic mechanism employing adjacent titaniums and adjacent aluminium alkyls wherein, on the TiCl\(_3\) surface aluminium alkyl molecules are adsorbed.

Uelzmann, in an attempt to consolidate the essential features of the different proposed mechanisms, suggested an ion-pair type of mechanism. Schindler reported that the relative amounts of CHD and CH\(_2\)D units in the polyethylene polymer formed, when deuterium was present in the polymerization, depended on the metal alkyl structure. He has interpreted that either the metal atom of the reducing agent represents the centre of chain propagation or the catalyst site is bimetallic complex, which is strongly influenced in its reactivity by the participation of the reducing agent.

On the basis of simultaneous formation of only one bond and breaking of another bond at each step, Furukawa and Tsuruta, Huggins, Friedlander and Resnick supported a bimetallic mechanism. This mechanism was further elaborated by Boor and it was also suggested that chlorine vacancies at the surface of the transition metal halide play
an important role in the formation of an isotactic stereo-
regular polymer.

1.6.3 Cossee's Mechanism

Cossee has assumed the essential reaction to occur at one Ti-alkyl bond. Unfilled d-orbitals in the transition elements are responsible for this kind of reaction. An active centre is thus defined as a Ti-ion in the surface layer of trichloride or dichloride (Fig.A) lattice, of which one surface Cl-atom is replaced by an alkyl group R, while an adjacent Cl-site is vacant in order to accommodate the incoming monomer molecule. This is shown below and is supposed to be the result of the reaction of solid TiCl₃ with Al-alkyls. The role of the Al-alkyl is thus primarily to alkylate and to reduce the transition metal halide. The polymerization reaction proceeds as follows (Fig.B).

Cossee's Monometallic Mechanism

Cl
\[ \begin{array}{c}
\text{Cl} \\
\text{Ti} \\
\text{Cl}
\end{array} \] + \[CH_2=CH_2\] \[\rightarrow\] Cl
\[ \begin{array}{c}
\text{Ti} \\
\text{Cl}
\end{array} \] \\
R
(Fig.A)

Cl
\[ \begin{array}{c}
\text{Cl} \\
\text{Ti} \\
\text{CH}_2
\end{array} \] \[\rightarrow\] Cl
\[ \begin{array}{c}
\text{Ti} \\
\text{Cl}
\end{array} \] \\
R
(Fig.B)

R=Alkyl (growing polymeric chain)
=Ligand vacancy
The formation of Ti-alkyl bond depends on the electron vacancy in the catalyst complex. This vacancy later moves to other places on the surface of a lattice, develops another Ti-alkyl bond and a vacant site for polymerization. Likewise, the sites are produced with the movement of the electron vacancy in the catalyst complex for the polymerization. During polymerization, aluminium alkyl is thought to act as a chain transfer agent in re-establishing the lost centres and as a scavenger of impurities but is not essential for propagation.

The complexes formed by titanium trichloride and α-olefins are similar to platinous olefinic complexes, as shown below:

Titanium has vacant $d_{x^2-y^2}$ orbital. During complexing of olefins and titanium metal, the bonding electrons overlap with this vacant $d_{x^2-y^2}$ orbital resulting in a π-bond. Simultaneously, the $d_{xy}$ orbital of the metal overlaps with the anti-bonding π-electrons of the olefin.
By this overlapping, the distances between bonding orbitals and the empty d-orbitals decreases. Such a situation weakens the carbon-metal bond in transition metal alkyls. The alkyl group migrates to one end of the incoming molecule of the olefin.

From the above considerations it is clear that in order to show the desired catalytic effect, the empty d-orbitals of the metal must be large enough to overlap sufficiently with the antibonding orbitals of the olefin. Therefore only ions with a comparatively low effective nuclear charges are expected to be good catalysts. This is approximately equivalent to Natta's statement that metals with an ionization potential of the first electron smaller than 7 e.v. are particularly suitable. The unique position of Ti may thus be explained from the size of the orbitals in close packed Cl-lattices and may possibly be related to the antiferromagnetic properties of α-TiCl₃.

In the three dimensional schematic picture of titanium trichloride lattice, if one crosssects through the monomer in the chlorine vacancy parallel to the yz and zx plane, it can be seen that there is only one possibility for the insertion of the propene molecule and that is with =CH₂ group pointing into the lattice. This explains the reason for the stereoregularity with such catalysts. There is an allowance for only two different orientations i.e. C=C or ||. The configuration with the minimum steric hindrance will be preferred in the lattice and this configuration is || as
MECHANISM OF ZIEGLER-NATTA POLYMERIZATION ACCORDING TO COSSEE. a, ACTIVATED TiCl₃. b, MONOMER Ti-BOUND TO SURFACE; AND c, STEREOCHEMISTRY OF MONOMER CATALYST COMPLEX
shown in the Plate-1, Fig.C.

The above mechanism thus also explains the formation of an isotactic material when propylene is polymerized under the influence of α-TiCl$_3$ and Al-alkyls.

1.6.4 Additional Evidences for the Monometallic Mechanism

Stereospecific polymerization at one alkylated Ti-ion had been put forward by Ludlum$^{72}$, and Ziegler$^{73}$ also supported these views. Agreement with Cossee's mechanism regained the support to these assumptions made in early days of Ziegler-Natta catalysts.

Nenitzescu and coworkers$^{74}$ had also thought of this type of mechanism, although they considered it less probable than strongly supported free radical mechanism. According to Nenitzescu, the metal alkyl component alkylated the titanium trichloride and the olefin insertion took place at a tetravalent titanium according to the following scheme:

$$R - TiX_3 \rightarrow R: \overset{+}{\text{Tix}}_3^-$$

$$R: \overset{+}{\text{Tix}}_3^- + CH_2=CH_2 \rightarrow RCH_2-CH_2: \overset{-}{\text{Tix}}_3^-$$

Initially, Carrick$^{14,50}$ and others emphasized on the participation of the transition metal in the propagation step and not the aluminium atom. Nevertheless, evidence was obtained for a monometallic mechanism by employing a lower valence state alkylated vanadium, RVCl. It was stabilized by a metal alkyl or an AlCl$_3$ molecule to prevent further reduction.
\[ \text{VCl}_4 + \text{AlX}_2\text{R} \rightarrow \text{X} \]

where \( X = \text{Halogen, Alkyl or Aryl}, \text{R= Alkyl or Aryl} \)

\((\text{Valence of Vanadium} = 2)\)

In this mechanism, co-ordination takes place at the vanadium atom followed by insertion of a polarised monomer into the V-R bond. Repetition of this two step process constitutes the propagation step for polymerization.

Almost all supporters of monometallic mechanism have attempted to show the active part taken by Ti-C bond in the polymerization.

Rodriguez and Van Looy, on the basis of IR and electron microscopy, demonstrated that the actual growth took place on Ti-C bond and the complexed metal-alkyl is an integral part of the active site.

Long and Breslow, on the basis of u.v. studies of the soluble cyclopentadienyl titanium chloride catalysts, demonstrated the formation of alkylated titaniums as catalyst complex for the polymerization.

More recently Natta and coworkers have considered that the growth at the transition-metal carbon bond was plausible. They proposed that, at least part of the stereospecific catalyst complexes contain both metals, in order to explain the dependence of total stereospecificity of each catalyst on the nature of its components.

Dyachkovskii, Yarovitskii and Bystrov also recognized
the existence of a Ti-C bond in \( \text{C}_2\text{TiCl}_2\text{-AlEt}_2\text{Cl} \) type catalyst on the basis of nuclear magnetic resonance spectra of the catalyst complex.

Dicarlo and Swift\textsuperscript{78} carried out aluminium-27 NMR investigations and convinced that structures of the type involving Al and paramagnetic Ti joined by Cl atom bridges were not formed on reacting TiCl\(_3\) with AlEt\(_2\)Cl.

Coover\textsuperscript{73} has argued that metal alkyl structure should not influence the stereospecific process, if propagation took place at a transition-metal carbon site via a monometallic mechanism.

Transition metals in the alkylated form or transition metals alone have also been used for the polymerization of different monomers\textsuperscript{14,80}. However, the activity of these catalysts were found unsatisfactory. It shows that\textsuperscript{14} the transition metal alone can be responsible for the stereospecific polymerization but the presence of aluminium alkyl in the complex is essential to improve the stereospecific activity of the catalyst systems.

1.6.5 \textbf{Evidences for the Free Radical Mechanism with Ziegler-Natta Catalysts}

Besides bimetallic and monometallic mechanisms for the Ziegler-Natta type catalyst systems many other mechanisms by different workers have been also proposed. Particularly free radical polymerization was suggested on the basis of radicals formed during the formation of catalyst complex.

Nenitzescu and coworkers\textsuperscript{74} first suggested the possibility that the Ziegler-polymerization takes place by
a free radical mechanism as given below:

\[
\begin{align*}
\text{nR-Al + TiCl}_4 & \rightarrow \text{R}_n\text{TiCl}(4-n) + n\text{AlCl}(n<4) \\
\text{RTiCl}_3 & \rightarrow \text{R}^* + \text{TiCl}_3 \\
\text{R}^* + \text{CH}_2=\text{CH}_2 & \rightarrow \text{R-CH}_2-\text{CH}_2 \quad \text{etc.} \rightarrow \text{Polymer}
\end{align*}
\]

Topichev and coworkers \cite{40, 81} have also suggested that the chemisorbed aluminium alkyl alkylates the TiCl₃ surface. Consequently, existing Ti-R bond decomposes to yield an R' radical which adds to ethylene to form a new radical. The new radical also remains bound to the surface and adds another chemisorbed ethylene molecule and thus propagation takes place.

Friedlander and Oita \cite{82} also proposed a free radical mechanism wherein initiation is by the transfer of an electron from the transition metal to the olefin.

In spite of several mechanisms proposed by various workers for Ziegler-Natta catalyst systems, the mechanism of chain growth taking place at transition metal carbon bond, as in the monometallic mechanism, has been almost accepted for the stereospecific polymerization.

1.7 The Ratio of Organometallic Compound to Transition Metal and the Valence State of Transition Metal

The molar ratio of the organometallic co-catalyst to the transition metal catalyst is an important variable in all Ziegler-Natta polymerization, and it is now recognized that this ratio can affect the yield of polymer, the rate of polymerization reactions, the degree of stereoregularity and the molecular weight of resulting polymer \cite{83}.
Generally it was found that for a given Ziegler-Natta catalyst system, the ratio of the components giving maximum yield is frequently very critical with specific monomer. The degree of stereoregularity of polymer is often found to be maximum at maximum conversion, although this sometimes varies in a complex manner and may even be at minimum when the conversion is maximum.

The rate of polymerization generally shows a marked variation with the ratio of co-catalyst to catalyst that may or may not correspond with the ratio of maximum yield.

Ziegler recognized that variation of the co-catalyst to catalyst ratio was a convenient method for controlling molecular weight.

The influence of ratio of yield of polymer, stereoregularity and molecular weight is closely connected with catalyst structure and most significantly with valency state of the transition metal forming catalyst.

The question of transition metal valence state in the active site of soluble and heterogeneous Ziegler-Natta type catalyst has been raised by a number of workers. In general, valence state of 4+(Sc), 3+(Sc, Ti, V), 2+(Ti, V, Co) and +1(Co) have been suggested for the particular catalysts which were investigated.

1.8 Polymerization of a Polar Monomer Containing Oxygen with Ziegler-Natta Catalyst System

The classical Ziegler-Natta catalyst system consisting of TiCl₄-AlEt₃ was assumed to be inactivated by polar monomers containing nitrogen, oxygen, nitrile, amine groups.
and non-aromatic chlorine atoms etc. As a result, stereo-
regular polymers of polar monomers were considered a
remote possibility. Several well defined catalyst systems
like n-butyl lithium, isobutyl magnesium bromide, diethyl
aluminium chloride and boron trifluoride etherate, modified
Friedel-Crafts type catalysts are already known to polymerize
several non-polar and polar monomers like α-olefins, dienes,
v vinyl chloride, vinyl ethers, vinyl acrylates, alkyl
acrylates and methacrylates to stereoregular polymers.33
The stereoregular polymerization of acrylates, methacrylates,
acrylic nitriles by organometallic compounds has been
investigated by many workers and various mechanisms have
been proposed.34

However, Vandenberg35 was the first to report that,
certain modified Ziegler-Natta type catalysts in the presence
of polar medium like tetrahydrofuran, N-N' dimethyl formamide,
diethyl ether as solvents, polymerize polar vinyl monomers
such as alkyl vinyl ethers, vinyl acetate and methyl
methacrylate to crystalline polymers. Stereoregular polymers
are also produced from monomers containing bulky substituents
that shield the polar group in monomer and impede its reaction
with catalysts.36 This method has been successfully used36
to make crystalline poly(tert-butyl acrylate) with TiCl4-
LiBu catalyst system at below 0°C, crystalline poly
N-N'-dialkyl acrylamide and poly N-N'-isopropyl acrylamide
polymers.

It was concluded in many cases that polymerization of
these monomers did not take place at transition metal-carbon bond. Thus, vinyl chloride-vinyl acetate copolymers prepared with $\text{VOCl}_3$-$\text{Al(iBu)}_3$ catalyst system are characteristically free radical polymerized products. Recently, Berghmans and Smets have reported that methyl methacrylate polymerized by $\text{CoCl}_2+\text{PhMgBr}$ catalyst system gives stereospecific polymer. The mechanism of polymerization was discussed on the basis of NMR results indicating initiation first by anion and later by free radicals.

Abe and coworkers have reported that $\text{Ti}(\text{n-C}_3\text{H}_7\text{O})_4$-$\text{AlEt}_3$, $\text{TiCl}_4$-$\text{AlEt}_3$ catalyst systems do not polymerize methyl methacrylate above 0°, but at -78°C, they have obtained a very highly syndiotactic polymer. Furukawa and coworkers have reported that, in the polymerization of many polar monomers by Ziegler-Natta catalyst systems like $\text{TiCl}_4$-$\text{AlEt}_3$, $\text{VOCl}_3$-$\text{AlEt}_3$, the mechanism of polymerization is likely to be of free radical nature. n-Propyl vanadate-$\text{Al(iBu)}_3$ catalyst system is actually reported to operate by free radical mechanism.

In the present investigation it has been observed that the Ziegler-Natta catalyst systems such as $\text{VOCl}_3$-$\text{AlEt}_2\text{Cl}$ and $\text{VOCl}_3$-$\text{AlEt}_2\text{Br}$ in n-hexane give stereospecific polymethyl methacrylate by co-ordinate anionic mechanism.

The polymerization of vinyl chloride with $\text{Ti(OR)}_y\text{Cl}_{4-y}$-$\text{AlR}_x\text{Cl}_{3-x}$ in carbon tetrachloride has been studied by A.Guyot and P.Rocaniere. Polymerization of vinyl chloride and co-polymerization with ethylene with
AlEt$_3$-C$_4$Cl$_2$-CCl$_4$ was studied by Wasaburo Kawai$^{105}$. Recently polymerization of propylene and ethylene with Ziegler-Natta catalyst system in carbon tetrachloride was studied by Sokolskii$^{106}$.

In our studies of polymerization of methyl methacrylate with VCl$_4$-AlEt$_2$Br and VOCl$_3$-AlEt$_2$Br catalyst systems in carbon tetrachloride medium, it has been observed that methyl methacrylate cannot be polymerized, but dark reddish brown, crystalline complexes were formed.

1.9 Kinetics of Polymerization

Kinetic studies throw light on the mechanism of polymerization. For a proper understanding of mechanism of Ziegler-Natta catalysts, exhaustive kinetic examination with various catalyst systems under different conditions has been carried out.

The following parameters are evaluated for a better understanding and revealing the correct mechanism of polymerization.

1. The dependence of rate of polymerization and molecular weights on concentrations of the organometallic compound and transition metal halide.

2. The dependence of rate of polymerization on monomer and catalyst concentrations.

3. Dependence of the activity of catalyst complex on temperature and calculation of activation energy.

4. Effect of various additives to the catalyst system and their effect on structure and molecular weight of polymer.
Gaylord and Mark\textsuperscript{45} related the rate of polymerization with extent of monomer adsorption, nature of catalytic complex etc. Saltman and coworkers\textsuperscript{107} derived a theoretical relationship based on polymerization of isoprene with Ziegler catalyst, but this scheme was not further elaborated. Recently, Saltman\textsuperscript{108} proposed a more detailed scheme for the polymerization of propylene with TiCl\textsubscript{4}–AlEt\textsubscript{3} catalyst system which could explain the experimental results obtained by Natta\textsuperscript{58,109}. Friendlender\textsuperscript{110} has also presented a kinetic scheme in order to explain the polymerization of ethylene by means of molybdena-alumina catalyst in presence of hydrogen. This scheme does not deal directly with the mechanism of polymerization by Ziegler-Natta catalysts and is limited to a fixed bed catalyst system. Stivala and Reich\textsuperscript{111} have derived a general kinetic scheme which can be applied even to the soluble Ziegler-Natta catalyst system for polymerization of ethylene.

Recently, Schindler\textsuperscript{112}, Allen and coworkers\textsuperscript{113} have also given a general kinetic scheme for some stereospecific catalysts. Coover\textsuperscript{114} has also explained the mechanism of heterogeneous stereospecific \(\alpha\)-olefin polymerization on the basis of kinetic studies for three component catalyst systems.

\textbf{1.10 Scope of the Present Work}

Ziegler-Natta catalyst systems\textsuperscript{31} had been used for polymerization of polar and non-polar monomers. On the whole, these studies emphasized the polymerizability of certain hydrocarbon monomers like \(\alpha\)-olefins and diolefins with
various combinations of catalysts in order to elucidate the mechanism of polymerization. However, the mechanism of formation of crystalline polymers by Ziegler-Natta catalyst system was not discussed in the literature. Preliminary findings by a few workers on the ease of polymerization of polar monomers with Ziegler-Natta catalyst systems stimulated further work on polymerization of polar monomers with different catalysts under various conditions.

Earlier studies from this Laboratory have revealed that the vanadium based Ziegler-Natta catalysts can be effectively used for polymerization of methyl methacrylate in non-polar and polar solvents.

The kinetics of the polymerization with these catalyst systems and structure of polymethyl methacrylate obtained, showed co-ordinate enionic mechanism in non-polar solvent and free radical mechanism in polar solvent.

Recently Svab, Jarslav et al. studied the catalytic efficiency of $\text{VCl}_4$ and $\text{VOCl}_3$ with alkyls such as $\text{AlEt}_3$, $\text{AlEt}_2\text{Cl}$, $\text{Al(iBu)}_3$ and $\text{Al(iBu)}_2\text{Cl}$ for polymerization of propylene. These catalyst systems were divided into three groups according to average valency of vanadium. Valence state of transition metal depends very closely on the structure of metal alkyls and transition metal salts.

It was therefore considered worthwhile to carry out a systematic study of Ziegler-Natta catalyst systems based on vanadium halides for the polymerization of methyl methacrylate.
at various conditions in order to examine the effect of ratio and the valence state of vanadium on catalytic activity, stereospecificity and molecular weight of polymer obtained.

The polymerization of non-polar monomer such as isoprene with $\text{VCl}_4-\text{AlEt}_2\text{Br}$ catalyst system was also undertaken to compare the behaviour of Ziegler-Natta catalyst systems.

A detailed kinetic study with the following catalyst systems comprising of vanadium halides and organometallic compounds of aluminium, has been carried out with methyl methacrylate and isoprene.

<table>
<thead>
<tr>
<th>Catalyst System</th>
<th>Medium</th>
<th>Monomer</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1) $\text{VOCl}_3-\text{AlEt}_2\text{Cl}$</td>
<td>$\text{n-Hexane}$</td>
<td>$\text{Methyl Methacrylate}$</td>
</tr>
<tr>
<td>(2) $\text{VOCl}_3-\text{AlEt}_2\text{Br}$</td>
<td>$\text{n-Hexane}$</td>
<td>$\text{Methyl Methacrylate}$</td>
</tr>
<tr>
<td>(3) $\text{VOCl}_3-\text{AlEt}_2\text{Br}$</td>
<td>$\text{Carbon tetra-chloride}$</td>
<td>$\text{Methyl Methacrylate}$</td>
</tr>
<tr>
<td>(4) $\text{VCl}_4-\text{AlEt}_2\text{Br}$</td>
<td>$\text{Carbon tetra-chloride}$</td>
<td>$\text{Methyl Methacrylate}$</td>
</tr>
<tr>
<td>(5) $\text{VCl}_4-\text{AlEt}_2\text{Br}$</td>
<td>$\text{n-Hexane}$</td>
<td>$\text{Isoprene}$</td>
</tr>
</tbody>
</table>

For a better understanding of reaction mechanism, effect of added reagents such as triethyl amine, hydroquinone during polymerization, was also studied.

Present studies concern with the overall behaviour of these catalyst systems in the polymerization of above monomers and hence are based on following aspects:

1) Aging time of catalyst after mixing of the catalyst components and its effect on rate of polymerization.
2) Activity of catalyst complex with reaction time from percent conversion of polymer with time.

3) Ratio of combination of catalyst constituents and nature of catalyst complex formed at different ratios.

4) Reaction rate constants from variation of rate of polymerization with monomer and catalyst concentrations.

5) Dependence of molecular weight on the ratio of combination of catalyst constituents, monomer and catalyst concentrations.

6) Effect of amine, hydroquinone to ascertain the change in catalytic activity and the effect on the catalyst sites and to know the mechanism of polymerization.

7) NMR absorption spectra in determination of tacticity of polymers.

8) IR spectra to study the structure of polyisoprene and methyl methacrylate complexes.