STUDIES IN POLYMERIZATION WITH ZIEGLER-NATTA TYPE CATALYST SYSTEMS

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by

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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[1], who proposed long chain formulae for polystyrene, rubber and polyoxymethylene. Staudinger[2] 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[3] in Germany for the polymerization of ethylene at room temperature and atmospheric pressure. Subsequently G.Natta and his collaborators[4] in Italy further developed the use and scope of Ziegler catalysts for polymerization of propylene. The use of Ziegler-Natta catalysts has been extended[5,6] for the polymerization of α-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[7] 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(α-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 α-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.

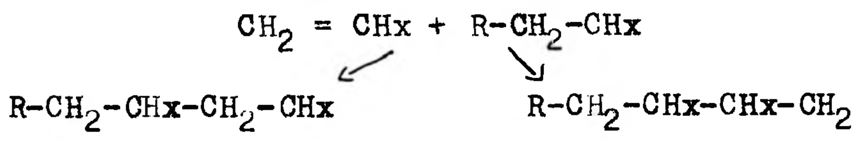
The co-ordinating catalysts such as Ziegler-Natta catalysts could generally act, at least in principle[15], according to one of the two mechanisms described below (1.2.1 and 1.2.2). These processes are mainly considered as co-ordinated because the catalyst consists of an electron-deficient complex having one co-ordinating atom capable of associating with the monomer.

1.2.1 Co-ordinated Radical Mechanism

In co-ordinate radical polymerization[16], the active metal carbon bond becomes more covalent, homolytic cleavage of the bond takes place giving rise to radical type polymerization, as shown below:

$$TiCl_4 + AlEt_3 \rightarrow AlEt_2Cl + EtTiCl_3$$

$$EtTiCl_3 \rightarrow TiCl_3 + Et \text{ (or R)}$$



$$CH_2 = CHx + R\text{-}CH_2\text{-}CHx$$

$$R\text{-}CH_2\text{-}CHx\text{-}CH_2\text{-}CHx \qquad R\text{-}CH_2\text{-}CHx\text{-}CHx\text{-}CH_2$$

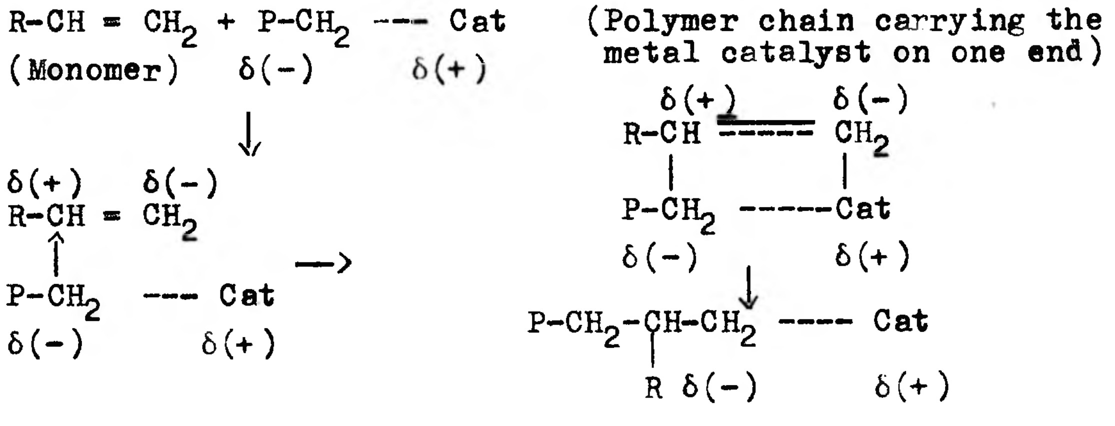
The end group of the growing polymeric chain is thus a free radical. The formation of the radicals becomes favourable, if the transition metal is in its highest valency state or the non-transition metal reacting with alkyl belongs to IV or V group of periodic table.

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:



$R\text{-}CH = CH_2 + \underset{\delta(-)}{P\text{-}CH_2} \text{ --- } \underset{\delta(+)}{Cat}$ (Monomer) (Polymer chain carrying the metal catalyst on one end)

$\downarrow$

$\overset{\delta(+)}{R\text{-}CH} = \overset{\delta(-)}{CH_2}$, $\uparrow$, $\underset{\delta(-)}{P\text{-}CH_2} \text{ --- } \underset{\delta(+)}{Cat}$ $\longrightarrow$ $\overset{\delta(+)}{R\text{-}CH} \text{ ----- } \overset{\delta(-)}{CH_2}$, $|$ $|$, $\underset{\delta(-)}{P\text{-}CH_2} \text{ ----- } \underset{\delta(+)}{Cat}$

$\downarrow$

$P\text{-}CH_2\text{-}\underset{R}{CH}\text{-}\underset{\delta(-)}{CH_2} \text{ ---- } \underset{\delta(+)}{Cat}$

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:

$$R_3Al + BF_3 \rightarrow (R_2Al)^+ + (BF_3R)^-$$

The counteranion $(BF_3R)^-$, can co-ordinate further to form a counteranion whose central metal possesses a positive charge:

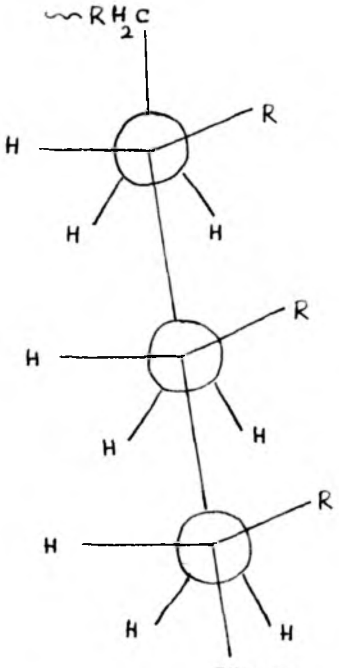
$$BF_3R^- + AlR_3 \rightarrow |R_3Al \rightarrow BF_3R|^-$$

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.

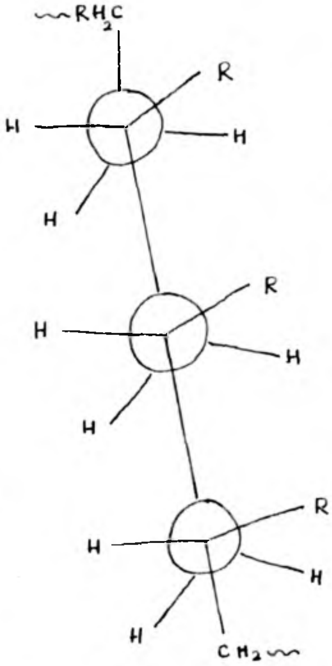
It is generally found that most of the Ziegler-Natta type catalyst systems act through co-ordinate ionic mechanism.

1.3. Concept of Tacticity

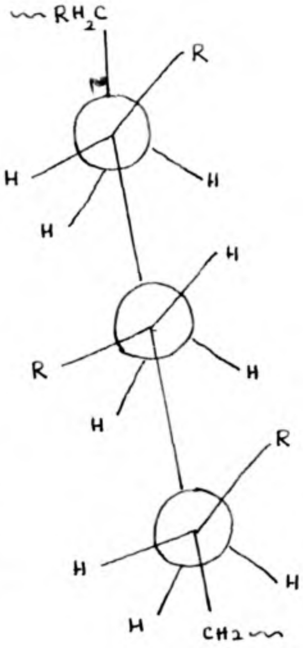
Natta and coworkers found that polypropylene prepared by these catalysts was crystalline in nature and also other polyolefins prepared by these catalysts showed better physical and technological properties. It was found that all the methyl groups (in the case of polypropylene) in polymer molecules were 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[21] 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.



Atactic.

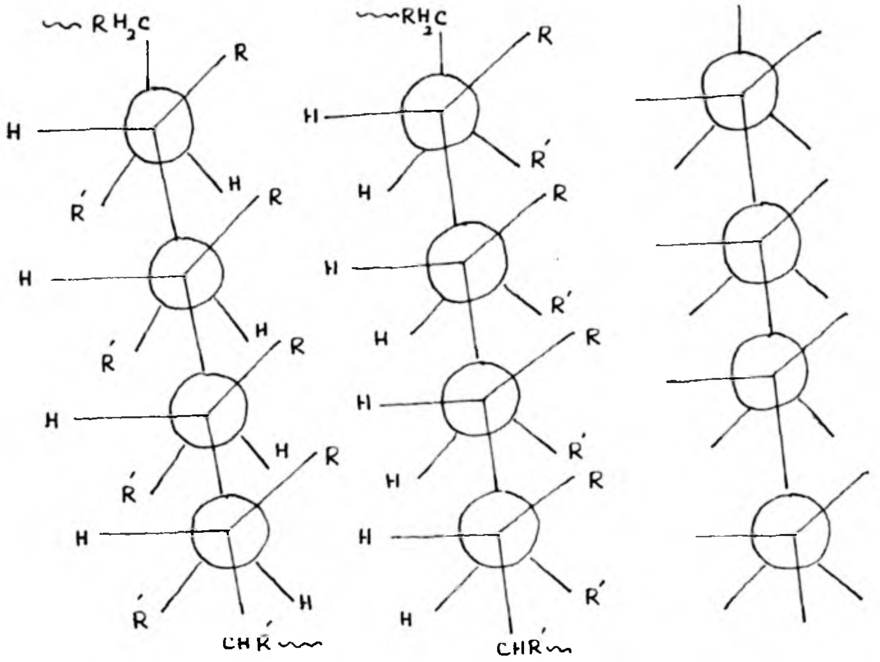


Isotactic.



Syndiotactic.

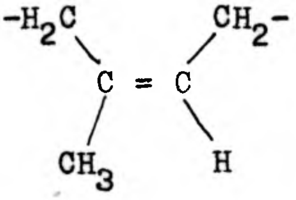
The number of stereoregular forms will increase in the case of 1,2 disubstituted polyethylene, as shown below:



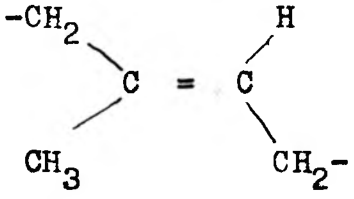
(Erythreo-di-isotactic) (Threo-di-isotactic) (di-Syndiotactic)

If two different assymetric 'C' atoms in chain occur with the same configuration, the polymer is called as erythrio-di-isotactic. If the two assymetric '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.



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 Guttapercha and Balata.

1.4 Stereospecificity of the Catalysts

Polymers obtained by free radicals are seldom stereospecific polymers[15] 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]. Probebly, 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[30,31], acryl amide[32] and vinyl halides[33]. Cationic initiator of similar type have been used for stereospecific polymerization of styrene derivatives[34].

Optically active polymers from the corresponding optically active monomers are studied to understand[35] whether the propagation steps have been maintained or destroyed into ionic polymerization.

Alfin catalysts used by Morton and coworkers[36] containing alkali alcoholate 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[37-45].

1.5 Ziegler-Natta Catalysts

The Ziegler-Natta catalysts are the result of reactions of two different species: (a) compounds of group IV-VIII transition elements called as catalyst and (b) organometallic compounds of group (I-IV) 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[46] 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 (β-$TiCl_3$) and evolution of gaseous hydrocarbons[47-49].

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.

$$TiCl_4 + Al(C_2H_5)_3 \rightarrow C_2H_5TiCl_3 + Al(C_2H_5)_2Cl$$

$$TiCl_4 + Al(C_2H_5)_2Cl \rightarrow C_2H_5TiCl_3 + Al(C_2H_5)Cl_2$$

$$TiCl_4 + Al(C_2H_5)Cl_2 \rightarrow C_2H_5TiCl_3 + AlCl_3$$

$$C_2H_5TiCl_3 \rightarrow TiCl_3 + C_2H_5\cdot$$

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

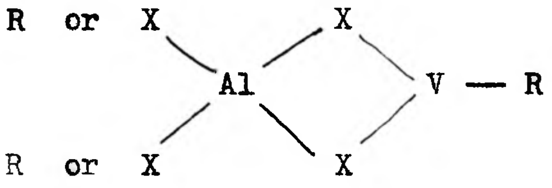
$$2\ C_2H_5\cdot \rightarrow C_2H_4 + C_2H_6$$

$$2\ C_2H_5\cdot \rightarrow n\text{-}C_4H_{10}$$

$$2\ C_2H_5\cdot \rightarrow 2\ C_2H_4 + H_2 \qquad \text{etc.}$$

1.6 Mechanism of Polymerization with Ziegler-Natta Catalysts

Several mechanisms[38] 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 someway or the other before adding upto 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[50], 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[51] or a simple organo-transition metal compound as proposed by Cossee[52]. 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:



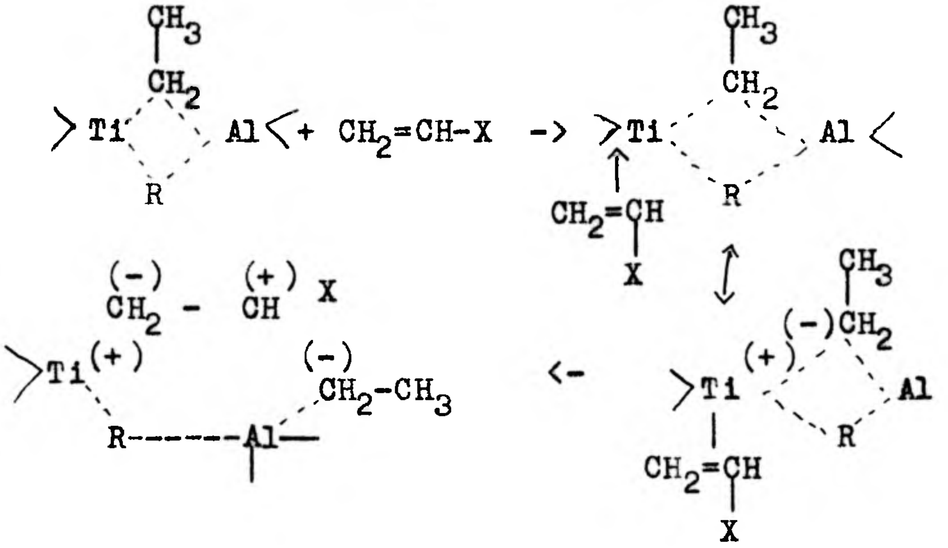
R=Aryl or Alkyl

X=Halogen

1.6.1 Natta's Mechanism

The reaction of crystalline $TiCl_3$ 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[53,54] of soluble crystalline complexes $(C_5H_5)_2TiCl_2$-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[51] is shown below:

Natta's Bimetallic Mechanism



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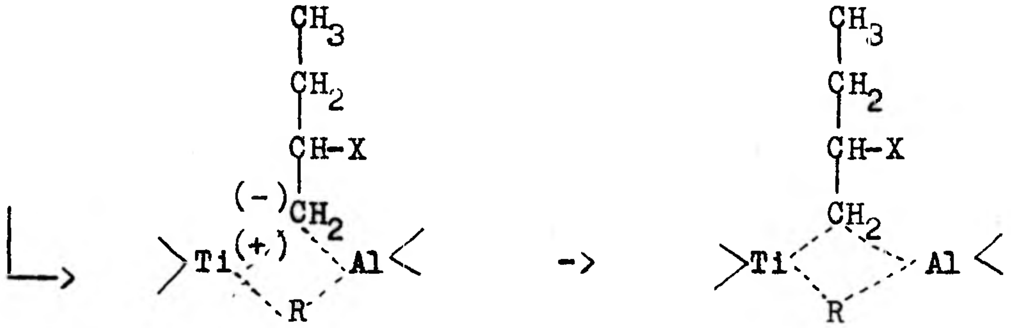


Chain termination is considered to occur mainly by chain transfer, dissociation and subsequent formation of a metal hydride bond.

Several experimental evidences have been given by Natta and others[53,55] for the above proposed mechanism. Natta and coworkers[54] 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[51]. 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[56] further reported that when α, γ or δ crystalline modifications of $TiCl_3$ were used in combination with different metal alkyls for propylene polymerization, the polymer isotacticities were dependent only on the metal alkyl.

Pozamantir[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 $AlEt_3$.

Natta gave further support[58] to this mechanism by using ^{14}C-labelled ethyl groups in triethyl aluminium as one constituent of the catalyst for the polymerization of ethylene. ^{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[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[59]. When deuterium[60] or tritium[61] is present, polymers having a lower molecular weight and containing bound deuterium (or tritium) are formed, as shown below:

$$\text{M-Et}^{14} + n\text{CH}_2\text{=CH}_2$$

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

$$\xrightarrow{D_2} \text{M-D} + \text{Et}^{14}(\text{CH}_2\text{-CH}_2)_n\text{-D}$$

where D is deuterium, and

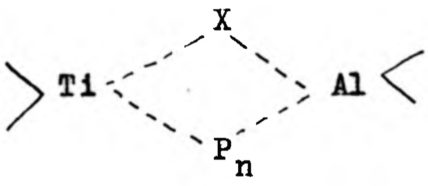
T is tritium.

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[62].

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



The monomer is co-ordinated to the titanium while simultaneously the Ti-polymer partial bond is broken. Patat and Sinn[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 σ 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[64] also proposed a similar mechanism which employed adsorbed layers of alkylaluminium chloride on the titanium chloride crystals.

Bier[65], Gumboldt and Schmidt[66] also proposed a bimetallic mechanism employing adjacent titaniums and adjacent aluminium alkyls wherein, on the $TiCl_3$ surface aluminium alkyl molecules are adsorbed.

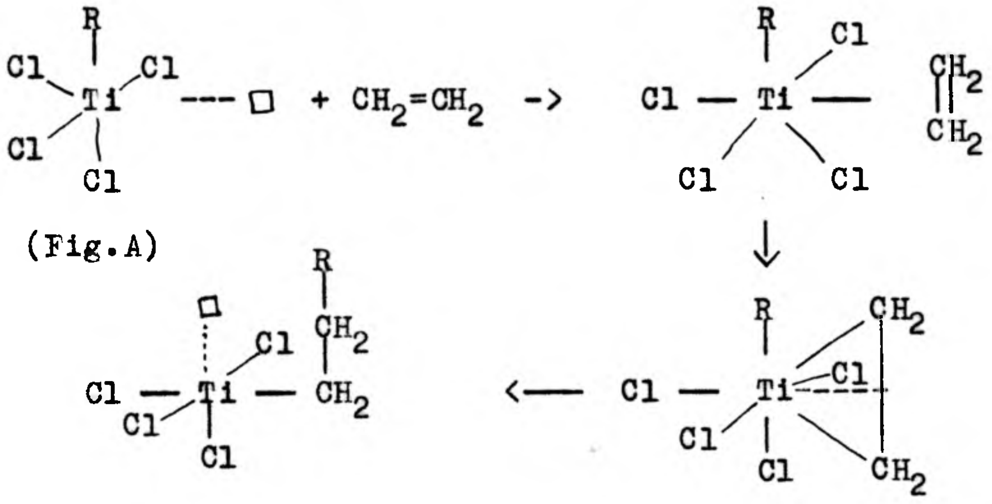
Uelzmann[67], in an attempt to consolidate the essential features of the different proposed mechanisms, suggested an ion-pair type of mechanism. Schindler[60] reported that the relative amounts of CHD and CH_2D units in the polyethylene polymer formed, when deuterium was present in the polymerization, 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[68], Huggins[69], Friedlander and Resnick[70] supported a bimetallic mechanism. This mechanism was further elaborated by Boor[71] 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 stereoregular polymer.

1.6.3 Cossee's Mechanism

Cossee[52] 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 $TiCl_3$ 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



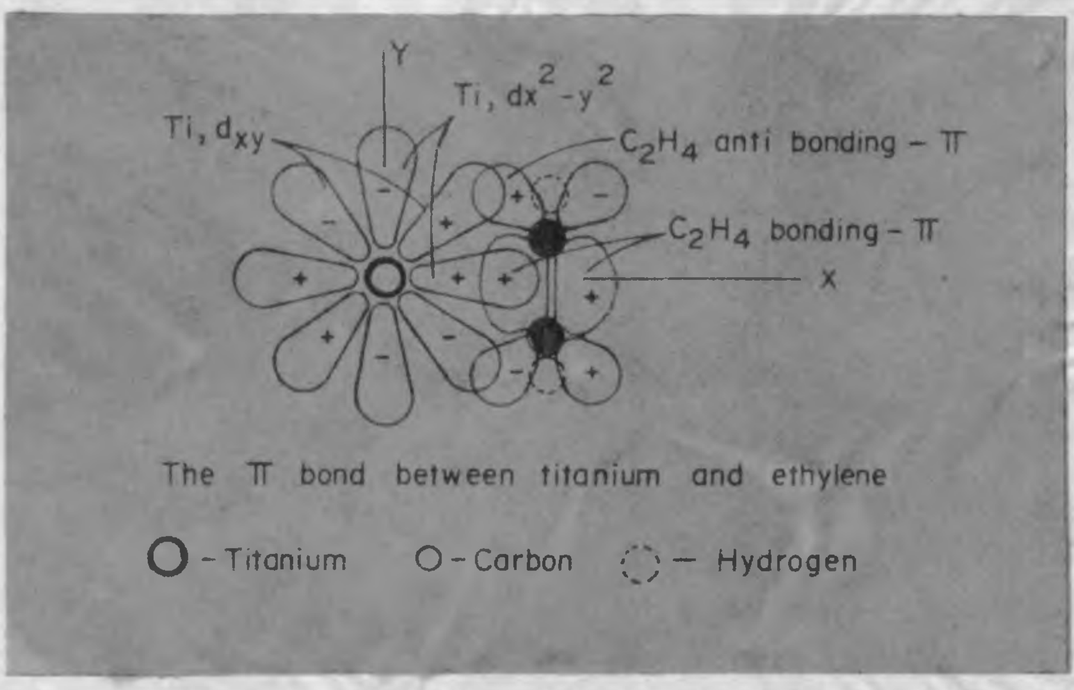
(Fig.A)

(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 scavanger 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:



The π bond between titanium and ethylene

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[52] 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-$TiCl_3$.

In the three dimensional schematic picture of titanium trichloride lattice, if one cross sects 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 $=CH_2$ 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 $\begin{array}{c} C \\ \| \\ C \end{array}$. The configuration with the minimum steric hindrance will be preferred in the lattice and this configuration is $\begin{array}{c} C \\ \| \\ C \end{array}$ as

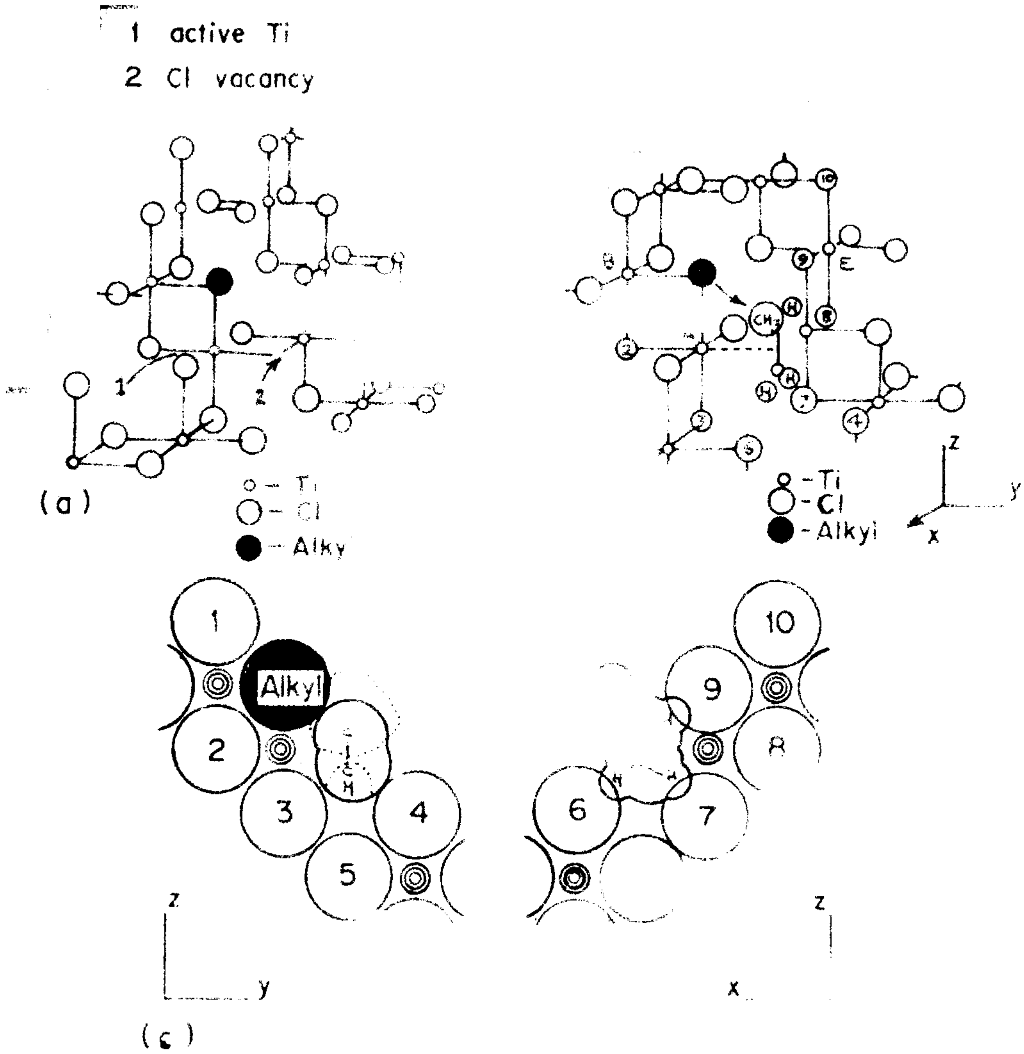


PLATE-I

MECHANISM OF ZIEGLER-NATTA POLYMERIZATION ACCORDING TO COSSEE. a, ACTIVATED $TiCl_3$. b, MONOMER π-BONDED TO SURFACE: AND c, STEREO CHEMISTRY 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.

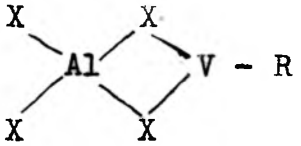
Nenitzescu and coworkers[74] had also thought of this type of mechanism, although they considered it less probable than strongly supported free radical mechanism. According to Nenitzescu, the metal alkyl component alkylated the titanium trichloride and the olefin insertion took place at a tetravalent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

$$R\text{-}Tix_3 \rightarrow R:\,]^-\ Tix_3\,]^+$$

$$R:\,]^-\ Tix_3\,]^+ + CH_2{=}CH_2 \rightarrow RCH_2\text{-}CH_2:\,]^-\ Tix_3\,]^-$$

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.

$VCl_4 + AlX_2R \rightarrow$



where X=Halogen, Alkyl or Aryl, R=Alkyl or Aryl

(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[75], 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[76] 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[14] 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[77] also recognized the existance of a Ti-C bond in $C_{p2}TiCl_2-AlEt_2Cl$ type catalyst on the basis of nuclear magnetic resonance spectra of the catalyst complex.

Dicarlo and Swift[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 $AlEt_2Cl$.

Coover[79] 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[14,80]. However, the activity of these catalysts were found unsatisfactory. It shows that[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 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[74] first suggested the possibility that the Ziegler- polymerization takes place by a free radical mechanism as given below:

$$nR\text{-}Al + TiCl_4 \rightarrow R_nTiCl(4-n) + nAlCl(n<4)$$

$$RTiCl_3 \rightarrow R^{\bullet} + TiCl_3$$

$$R^{\bullet} + CH_2=CH_2 \rightarrow R\text{-}CH_2\text{-}CH_2 \xrightarrow{etc.} \text{Polymer}$$

Topichev and coworkers[40,81] have also suggested that the chemisorbed aluminium alkyl alkylates the $TiCl_3$ surface. Consequently, existing Ti-R bond decomposes to yield an $R^{\bullet}$ 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[82] also proposed a free radical mechanism wherein initiation is by the transfer of an electron from the transition metal to the olefin.

Inspite 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[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[84].

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[84,85-89].

Ziegler[90] recognized that variation of the co-catalyst to catalyst ratio was a convenient method for controlling molecular weight.

The influence of ratio on 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[91].

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

The classical Ziegler-Natta catalyst system consisting of $TiCl_4-AlEt_3$ was assumed[92] to be inactivated by polar monomers containing nitrogen, oxygen, nitrile, amine groups and non-aromatic chlorine atoms etc. As a result, stereoregular 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, vinyl chloride, vinyl ethers, vinyl acrylates, alkyl acrylates and methacrylates to stereoregular polymers[93]. The stereoregular polymerization of acrylates, methacrylates, acrylic nitriles by organometallic compounds has been investigated by many workers and various mechanisms have been proposed[94].

However, Vandenberg[95] 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[96]. This method has been successfully used[96] to make crystalline poly(tert-butyl acrylate) with $TiCl_4$-LiBu catalyst system at below 0°C, crystalline[97,98] 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[14]. Thus, vinyl chloride-vinyl acetate copolymers prepared with $VOCl_3$-$Al(iBu)_3$ catalyst system are characteristically free radical[24] polymerized products. Recently, Berghmans and Smets[99] have reported that methyl methacrylate polymerized by $CoCl_2$+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[100,101] have reported that $Ti(n\text{-}C_3H_7O)_4$-$AlEt_3$, $TiCl_4$-$AlEt_3$ catalyst systems do not polymerize methyl methacrylate above 0°, but at -78°C, they have obtained a very highly syndiotactic polymer. Furukawa and coworkers[102] have reported that, in the polymerization of many polar monomers by Ziegler-Natta catalyst systems like $TiCl_4$-$AlEt_3$, $VOCl_3$-$AlEt_3$, the mechanism of polymerization is likely to be of free radical nature. n-Propyl vanadate -$Al(iBu)_3$ catalyst system[103] 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 $VOCl_3$-$AlEt_2Cl$ and $VOCl_3$-$AlEt_2Br$ in n-hexane give stereospecific polymethyl methacrylate by co-ordinate anionic mechanism.

The polymerization of vinyl chloride[104] with $Ti(OR)_yCl_{4-y}$-AlR_xCl_{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_4Cl_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-$AlEt_2Br$ and $VOCl_3$-$AlEt_2Br$ 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 organometallio 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[45] related the rate of polymerization with extent of monomer adsorption, nature of catalytic complex etc. Saltman and coworkers[107] derived a theoretical relationship based on polymerization of isoprene with Ziegler catalyst, but this scheme was not further elaborated. Recently, Saltman[108] proposed a more detailed scheme for the polymerization of propylene with $TiCl_4-AlEt_3$ catalyst system which could explain the experimental results obtained by Natta[58,109]. Friendlander[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[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[112], Allen and coworkers[113] have also given a general kinetic scheme for some stereospecific catalysts. Coover[114] has also explained the mechanism of heterogeneous stereospecific α-olefin polymerization on the basis of kinetic studies for three component catalyst systems.

1.10 Scope of the Present Work

Ziegler-Natta catalyst systems[91] had been used for polymerization of polar and non-polar monomers. On the whole, these studies emphasized the polymerizability of certain hydrocarbon monomers like α-olefins and diolefins with various combinations of catalysts in order to elucidate the mechanism of polymerization. However, the mechanism of formation of crystalline polymers[95,115] by Ziegler-Natta catalyst system was not discussed in the literature. Preliminary findings by a few workers[95,102,116-118] 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[119-123] 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[119-121] anionic mechanism in non-polar solvent and free[123] radical mechanism in polar solvent.

Recently Svab, Jarslav et al[124] studied the catalytic efficiency of VCl_4 and $VOCl_3$ with alkyls such as $AlEt_3$, $AlEt_2Cl$, $Al(iBu)_3$ and $Al(iBu)_2Cl$ for polymerization of propylene. These catalyst systems were divided into three groups according to average valency of vanadium. Valence state[125] 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 VCl_4-$AlEt_2Br$ 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.

	Catalyst System	Medium	Monomer
(1)	$VOCl_3$-$AlEt_2Cl$	n-Hexane	Methyl Methacrylate
(2)	$VOCl_3$-$AlEt_2Br$	n-Hexane	Methyl Methacrylate
(3)	$VOCl_3$-$AlEt_2Br$	Carbon tetrachloride	Methyl Methacrylate
(4)	VCl_4-$AlEt_2Br$	Carbon tetrachloride	Methyl Methacrylate
(5)	VCl_4-$AlEt_2Br$	n-Hexane	Isoprene

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.

CHAPTER - II

EXPERIMENTAL

EXPERIMENTAL

2.1 Dry and Oxygen-free Environments

Atmospheric oxygen and traces of moisture have very adverse effect on transition metal halides, organometallic compounds and their reaction products. Therefore all the experiments were carried out under extremely dry and inert atmosphere. The preparation of catalyst solutions and their mixing were also carried out inside a dry glove box made of wood. A glass frame on the top and two rubber gloves by the side were fitted for manipulations inside the box. The box had an opening on one side to an antechamber through a sliding door. All materials to be taken in or out of the box were first kept in this chamber before transporting across the sliding door, so that the dry box was never open directly to the outside atmosphere. The box was constantly flushed with dry and oxygen free nitrogen introduced through an inlet and the outlet for outgoing gas was guarded by silica gel tower.

2.2 Purification of Nitrogen Gas

The nitrogen gas was made oxygen-free by successively passing through four columns of 8" of Fieser's solution (see 2.3.1). It was then passed through a bubbler containing aqueous saturated lead acetate solution to remove sulphurous gases. After bubbling through distilled water, it was successively dried over calcium chloride, sulphuric acid, phosphorous pentoxide, potassium hydroxide pellets, silica gel and drierite in the given order before passing into the dry box. In addition to this, few more dessicants such as silica gel and activated drierite, potassium hydroxide pellets and phosphorous pentoxide were kept in the dry box. Every day silica gel was freshly reactivated and replaced. Indicator type blue silica gel was used to determine the dryness inside the box.

2.3 Reagents and Solvents

All reagents and solvents used in experiments were pure, dry and were preserved over nitrogen atmosphere.

2.3.1 Reagents

Fieser's Solution[126]

Sodium hydrosulphite ($Na_2S_2O_4$) (15 gms) was dissolved in 100 ml. of water containing 12 gms. of sodium hydroxide (NaOH) and 2 gms. of anthraquinone-β-sulphonic acid-sodium salt (B.D.H.). The solution is blood red initially and becomes dull brown with the formation of white scum on the absorption of oxygen . At this stage, the solution was discarded.

Triethyl amine[127] was freed from traces of primary and secondary amines by distilling from acetic anhydride. It was further dried with activated alumina and fractionally distilled three times under reduced pressure. The 1 M solution of triethyl amine was prepared in n-hexane prior to use.

C.P. grade (B.D.H.) hydroquinone was recrystallised twice from benzene before use.

2.3.2 Solvents

Commercial grade n-hexane[128] was washed by shaking repeatedly with concentrated sulphuric acid (C.P) (100 ml. for each litre solvent) till the acid layer became colourless. Then it was washed free of acid with distilled water, dried over anhydrous calcium chloride, distilled and kept over sodium wire. The pure solvent was refluxed overnight over sodium under pure dry nitrogen atmosphere and fractionally distilled before use in polymerization experiments. Commercial methanol was fractionally distilled before use.

Carbon tetrachloride[128] was washed successively in three portions of alcoholic sodium hydroxide. The carbon disulphide free solvent was then washed several times with water, dried over anhydrous calcium chloride and then refluxed over 5% NaOH for about 1-2 hrs. and then distilled in nitrogen atmosphere at 74°C. The distilled solvent was stored in nitrogen atmosphere.

Commercial grade chloroform[128] was washed several times by shaking with concentrated sulphuric acid for removing alcohol, then washed with dilute sodium hydroxide and with water. The solvent was dried over potassium carbonate and stored in completely filled brown flask and distilled shortly before use.

2.4 Catalysts

2.4.1 Aluminium Diethyl Chloride

It was obtained from M/s. Polyolefins, Bombay, and was distilled under nitrogen and reduced pressure. A middle cut was used to prepare 2 M solution in n-hexane.

2.4.2 Diethyl Aluminium Bromide

It was prepared by reaction of ethyl bromide with an aluminium-magnesium alloy containing aluminium 69% and magnesium 33% corresponding to Al_2Mg[129], supplied by the courtesy of National Metallurgical Laboratory, Jamshedpur, and analysed as given below:

$$Al_2Mg + 4\ C_2H_5Br \rightarrow 2\ Al(C_2H_5)_2Br + MgBr_2$$

The alloy was chipped to small pieces and in a typical reaction 55 gms. of it were taken in a three necked 250 ml. flask fitted with nitrogen inlet, dropping funnel, reflux condenser and mercury sealed stirrer. A slight excess over the stoichiometric quantity of ethyl bromide (viz. 204 gms.) which was dried over phosphorous pentoxide, distilled (35° /710 mm.) and preserved over anhydrous calcium sulphate, was added drop-wise and the reaction initiated with a crystal of iodine. The exothermic reaction resulted in vigorous refluxing of ethyl bromide. Heat of reaction was removed by surrounding the reaction flask with oil bath and the evaporation loss minimised by circulating chilled water in the condenser. The reaction was allowed to proceed under continuous stirring for about 2-3 hours till the refluxing of ethyl bromide had stopped, and taken to completion by raising the temperature to 160°C.

The alkyl was soaked up in the even mass of magnesium bromide and removed by distillation under vacuum. The bromide content of the alkyl was estimated by hydrolysis and application of Vorld's method[130]. It was then redistilled under vacuum (b.p. 70° /1 mm.) and stock solution was prepared in n-hexane (0.5 M).

2.4.3 Vanadium Tetrachloride

It was obtained by the courtesy of M/s. Stauffer Chemical Co. U.S.A. It was distilled under inert conditions at 148.5°/760 mm. and its stock solution (0.5 M) was made in n-hexane. A fresh solution was made after every 4-5 days from freshly distilled VCl_4.

2.4.4 Vanadium Oxychloride

It was prepared by reacting[131] vanadium pentoxide with aluminium chloride:

$$V_2O_5 + 2\ AlCl_3 \rightarrow 2\ VOCl_3 + Al_2O_3$$

Vanadium pentoxide (Riedel) (35 g) was dried at 110°C, cooled in dry box and mixed thoroughly with 50 gms. of anhydrous aluminium chloride (E.Merck) powder in 250 ml. round bottom flask. This flask was attached to an all-glass distillation unit with ground glass joints, greased with syrupy phosphoric acid. It was heated on a sand bath upto 400°, when vanadium oxychloride distilled over. The brown liquid thus obtained was redistilled under inert conditions. The pure product obtained was a pale yellow liquid. Stock solution was prepared in n-hexane (0.5 M) and preserved inside the dry box.

2.4.5 Estimation of Vanadium Oxychloride

2 ml. of vanadium oxychloride solution was taken and 25 ml. of sulphuric acid (4 N) was added to it. The vanadium was reduced to tetravalent state by addition of 0.1 N ferrous ammonium sulphate and evaporating to dryness. A further quantity (5 ml.) of ferrous ammonium sulphate solution was added to ensure completion of reduction to tetravalent state.

The ferrous ammonium sulphate was destroyed with 10 ml. of 10% ammonium persulphate. This was titrated against standard potassium permanganate solution (0.1 N) potentiometrically using standard calomel and platinum indicator electrode.

2.5 Purification of Monomers[132]

2.5.1 Methyl Methacrylate

Methyl methacrylate (Rohm and Hass) monomer was washed with 5% alkali till it was free from the inhibitor tert-butyl catachol. It was then washed with distilled water, dried over anhydrous sodium carbonate overnight at low temperature and distilled under vacuum (28 mm Hg) at 25°C under dry nitrogen.

2.5.2 Isoprene

Isoprene (Phillips) was freed from tert butyl catachol by washing with 10% alkali solution followed by washing with a large quantity of distilled water. It was distilled and later stored over anhydrous magnesium sulphate. The required amount of monomer was redistilled over sodium under nitrogen prior to use.

2.6 Polymerization and Isolation of Polymers

The catalyst system under investigation consists of the metal alkyls and transition metal halides. Both are very sensitive to moisture and air. The reaction vessels and dispensers were thoroughly dried and kept under nitrogen. All the reaction flasks and magnetic stirrers (enclosed in glass) were thoroughly cleaned with chromic acid, washed with distilled water and dried overnight at 160° in an oven. They were first transferred inside the dry box when hot and cooled under the atmosphere of nitrogen. Similarly, all glass hypodermic syringes with stainless steel needles were cleaned with chromic acid, washed with distilled water, dried at 110° and transferred into dry box while hot.

Stock solutions of catalysts, dry solvents and monomers were preserved inside dry box and required amount of reagents were added with syringes (1-20 ml.) in the predetermined order. Conical flasks (50 ml.) with B_{19} (male) cone joint and with B_{19} (female) stoppers were used for all the systems. Temperature of the thermostat was controlled to ±0.05°C by a toluene-mercury regulator connected to an electronic relay. The stirring element inside the reaction flask was moved by a rotating horse-shoe magnet kept under it, enclosed in a water-proof brass case[133] and carried on ball bearings. The magnet was connected by a flexible speedometer shaft cable to a stirring motor and the speed of its rotation adjusted.

After allowing the polymerization to proceed to the required time, it was quenched by addition of acidified methanol and polymer precipitated by further addition of large excess of methanol. The mother liquor was treated with excess of methanol to make sure that the entire polymer precipitated. The polymers were settled in the container after keeping overnight in refrigerator. The polymers filtered through weighed sintered crusible, dried to constant weight and weighed

2.7 Molecular Weights

Polymers of methyl methacrylate prepared with $VOCl_3$-$AlEt_2Cl$ and $VOCl_3$-$AlEt_2Br$ catalyst systems were purified by reprecipitation from chloroform solutions using methanol as precipitant. Stock solutions were prepared in chloroform.

Molecular weights were determined viscometrically in an Ostwald viscometer. The following relationship[134] of intrinsic viscosity with molecular weight was used to calculate molecular weight of polymethyl methacrylate.

$$\eta = 4.3 \times 10^{-5} M^{0.8} \quad \text{(in chloroform at } 30^{\circ}\text{)}$$

2.8 Analysis of Polymers by NMR & IR Spectra

NMR spectra were recorded on a Varian T-60 mc/s spectrophotometer. The samples of polymethyl methacrylate were dissolved in purified chloroform (3-10% solution) and NMR spectra were recorded at 25° in chloroform.

The NMR spectra of polymethyl methacrylate were examined[135] for the tacticity of the polymers. This was done by calculating areas under the respective α-methyl triad units with a planimeter. The stereoregular sequence distribution in the polymers was then computed.

The IR spectra of complexes of methyl methacrylate were recorded with Perkin Elmer Infracord 137B spectrophotometer.

The IR absorption spectra of polyisoprene on KBr pellet (3.5 mgm/0.5 gm, 13 mm disc) were recorded on Perkin Elmer Infracord 137B Spectrophotometer.

CHAPTER - III

EXPERIMENTAL RESULTS

EXPERIMENTAL RESULTS

3.1 Polymerization of Methyl Methacrylate with Vanadium Oxychloride and Aluminium Diethyl Chloride at 40^o in n-hexane

It has been earlier shown that vanadium containing catalyst systems[119-122] are more effective for the polymerization of polar monomers than titanium containing catalyst systems, at room temperature. The mechanism of polymerization for both such systems is however co-ordinate anionic. Svab, Jaroslav[124] et al studied the catalytic efficiency of VCl_4 and $VOCl_3$ with alkyls such as $AlEt_3$, $AlEt_2Cl$, $AliBu_3$ and $AliBu_2Cl$ for polymerization of propylene in temperature range -80 to 25^oC. These catalyst systems were divided into three groups according to average valency of vanadium which also changes with temperature. Valence state[125] of transition metal depends very closely on the structure of metal alkyls and transition metal salts. It was reported[136] that on replacement of one ethyl group of aluminium triethyl by halogen, there is marked increase in stereospecificity of polypropylene.

Polymerization of methyl methacrylate with $VOCl_3$-$AlEt_3$ catalyst system[119] was reported in earlier studies in our Laboratory. The results of the kinetic studies with $VOCl_3$-$AlEt_2Cl$ catalyst system for the polymerization of methyl methacrylate are presented herewith.

3.1.1 Aging of the Catalyst System

The variable time allowed to form a complex on reacting the catalyst constituents either in the presence or absence of monomer has an effect on the nature and amount of catalyst sites. Catalyst complex was aged in the absence of monomer and the monomer was added after varying the aging time from 10 to 180 minutes, and the monomer was polymerized with the aged catalyst system at constant ratio of Al/V, constant time of reaction and constant temperature of reaction. It was observed that the catalyst aged for 20 minutes was very active and the polymer produced had high molecular weight.

It shows that a particular type of catalyst sites of highest activity are formed on aging of catalyst system for 20 minutes. Therefore, all the experiments were carried out by aging the catalyst system for 20 minutes.

Results are tabulated in Table - I (Fig.1).

3.1.2 Variation in the Ratio of Catalyst Constituents as Al/V

Vanadium oxychloride on reacting with aluminium alkyl in n-hexane forms a dark brown black colour precipitate, which does not change upon the addition of monomer, showing presence of undisturbed catalyst sites. The ratio of Al/V was changed by keeping the concentration of $VOCl_3$ constant in order to find out the ratio of optimum activity.

It was observed that the catalytic activity was maximum at ratio of Al/V=2 and 7. This indicates presence of two active sites. The rate of polymerization showed

Table - I

Effect of Aging Time

$VOCl_3$ = 0.05 mole/l
$AlEt_2Cl$ = 0.1 mole/l
Al/V ratio = 2

Methyl Methacrylate = 5.0 ml
Reaction time = 180 min.
Temperature = 40°C

	Aging time min.	Yield in gms.	$R_p \times 10^6$ M/L/S	$\|\eta\|$ dl/g	Mol.wt. $\bar{M}_v$
(1)	10	0.390	14.43	0.2481	50,290
(2)	20	0.900	19.24	0.2995	63,100
(3)	30	0.640	23.71	0.2966	62,850
(4)	60	0.639	23.12	0.2956	62,520
(5)	120	0.248	9.17	0.2340	46,720
(6)	180	0.262	9.66	0.2705	55,960
(7)	1440	0.040	0.38	0.2695	55,750

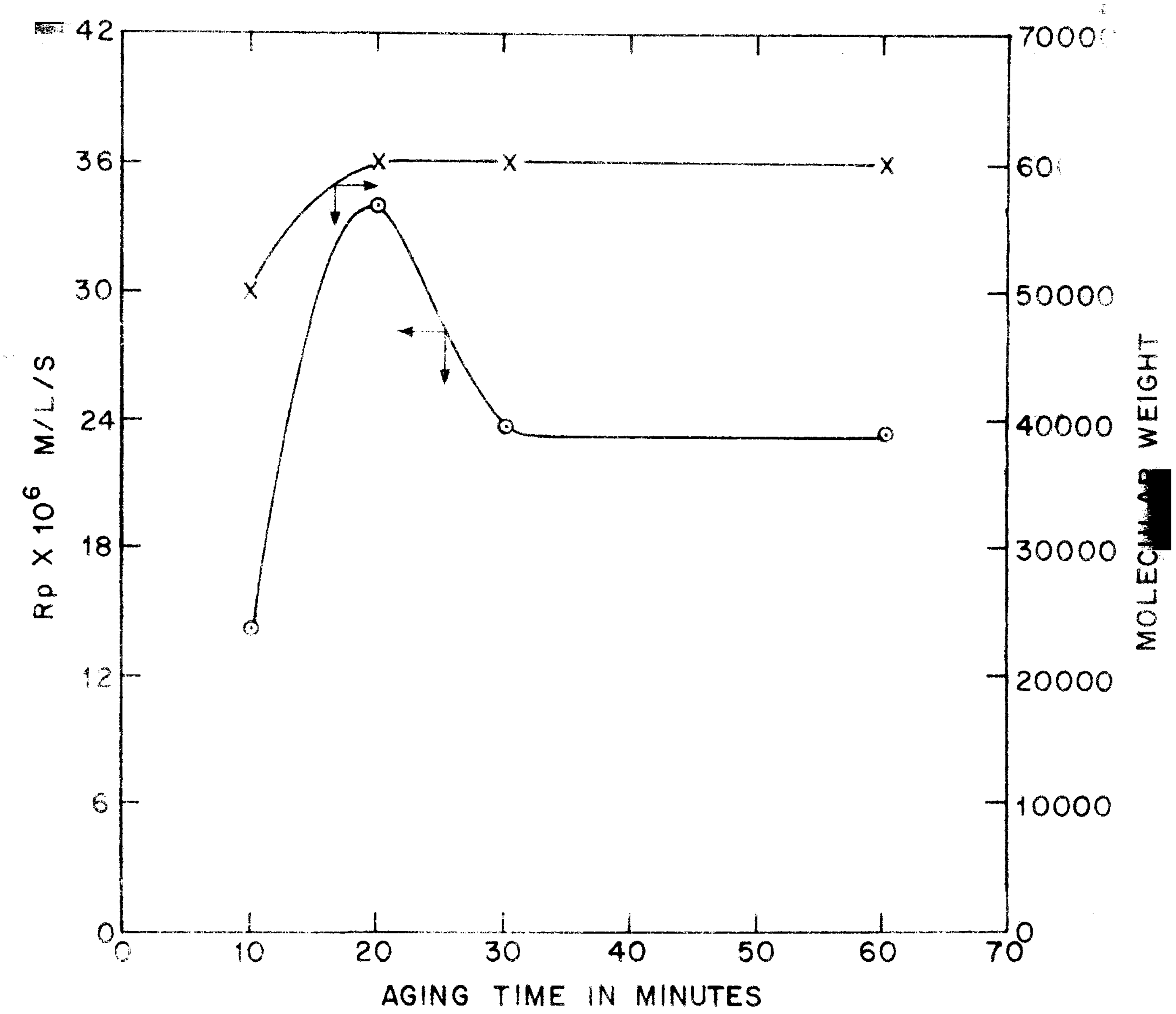


FIG. 1 EFFECT OF AGING TIME ON $VOCl_3-AlEt_2Cl$ SYSTEM

$VOCl_3$ 0.05 mole/l

$AlEt_2Cl$ 1 mole/l

Al/V RATIO = 2

METHYLMETHACRYLATE = 5·0 ml

REACTION TIME = 3 hrs

TEMPERATURE = 40 °C

Table - II

Effect of Al/V Molar Ratio

$VOCl_3$ =0.05 mole/l Aging time = 20 min.
Methyl Methacrylate = 5.0 ml Reaction time = 180 min.
Temperature = 40°C Total volume = 25 ml

	Molar Ratio	Yield in gms	Percent conversion	$\|\eta\|$ dl/g	Mol.wt. $\bar{M}_V$
(1)	1	0.138	2.96	0.1495	26,670
(2)	2	0.900	9.24	0.2995	63,100
(3)	3	0.365	7.80	0.1607	29,220
(4)	4	0.472	10.09	0.2223	43,750
(5)	5	0.428	9.14	0.1572	28,430
(6)	6	0.843	18.03	0.2340	50,092
(7)	7	1.810	38.66	0.2481	46,720
(8)	8	0.614	13.10	0.1317	22,270

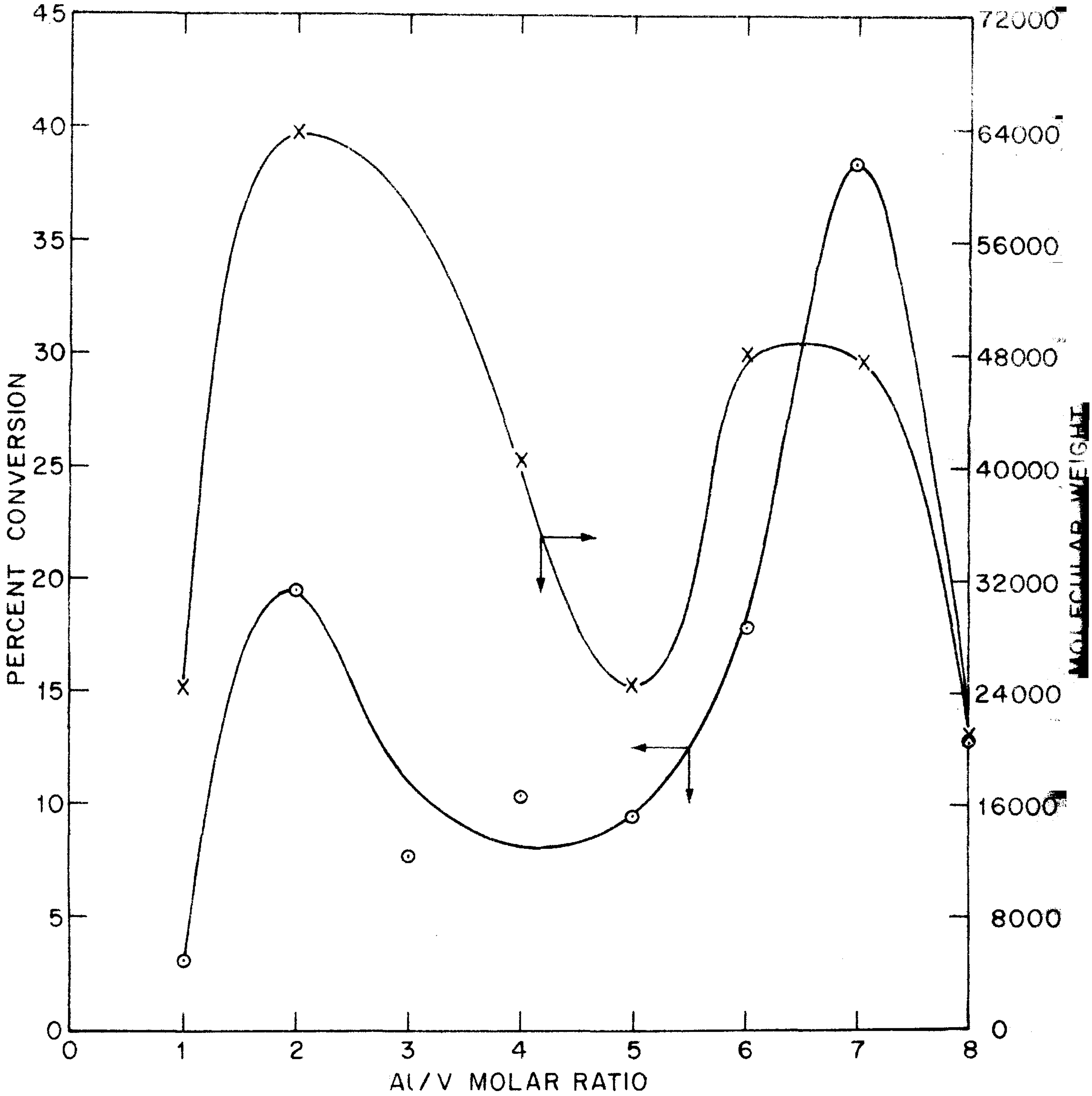


FIG. 2 EFFECT OF Al/V RATIO ON $VOCl_3-AlEt_2Cl$ SYSTEM

$VOCl_3$	= 0·05 mole/l	AGING TIME	= 20 min
METHYLMETHACRYLATE	= 5·0 ml	REACTION TIME	= 3 hrs
TOTAL VOLUME	= 25·0 ml	TEMPERATURE	= 40 °C

maximum activity at ratio of Al/V=2, but for comparison of catalytic efficiency and stereoregularity with $VOCl_3$-$AlEt_3$ catalyst system, the ratio of Al/V=2 was chosen for further studies, since the molecular weight of polymer was also maximum at ratio of Al/V=2.

Results are given in Table - II (Fig.2).

3.1.3 Effect of Reaction Time on the Polymerization

Polymerizations were carried out for different intervals of times by keeping constant concentration of catalyst, monomer and at fixed ratio of catalytic components. It was found that rate of polymerization increased linearly with time ~~upto~~ after 180 minutes, indicating unchanged concentration of catalyst sites after 180 minutes.

Results are tabulated in Table - III (Fig.3).

3.1.4 Dependence of the Rate of Polymerization on Catalyst and Monomer Concentrations

Kinetics of polymerization was studied at selected conditions such as ratio of Al/V=2, aging time = 20 min., reaction time = 180 min., in order to know the effect of catalyst and monomer concentration. It was found that the rate of polymerization increased with increase in catalyst concentration but molecular weight decreased with increase in catalyst concentration, indicating chain transfer with catalyst complex.

Results are tabulated in Table - IV (Fig.4).

Effect of monomer concentration showed that rate of polymerization as well as molecular weights increased

Table - III

Effect of Reaction Time

$VOCl_3$ = 0.05 mole/l
$AlEt_2Cl$ = 0.1 mole/l
Al/V ratio = 2
Methyl Methacrylate = 5.0 ml
Aging time = 20 min.
Temperature = $40^{o}C$

	Reaction time min.	Yield in gms.	Percent conversion	$\lvert\eta\rvert$ dl/g	Mol.wt. $\bar{M}_v$
(1)	30	0.443	9.46	0.2312	46,050
(2)	60	0.478	10.21	0.2330	46,540
(3)	120	0.789	16.87	0.2322	46,240
(4)	180	0.900	19.24	0.2995	63,100
(5)	240	1.030	22.02	0.2608	53,480
(6)	300	1.141	24.39	0.3031	64,570
(7)	360	1.242	26.53	0.2368	46,760

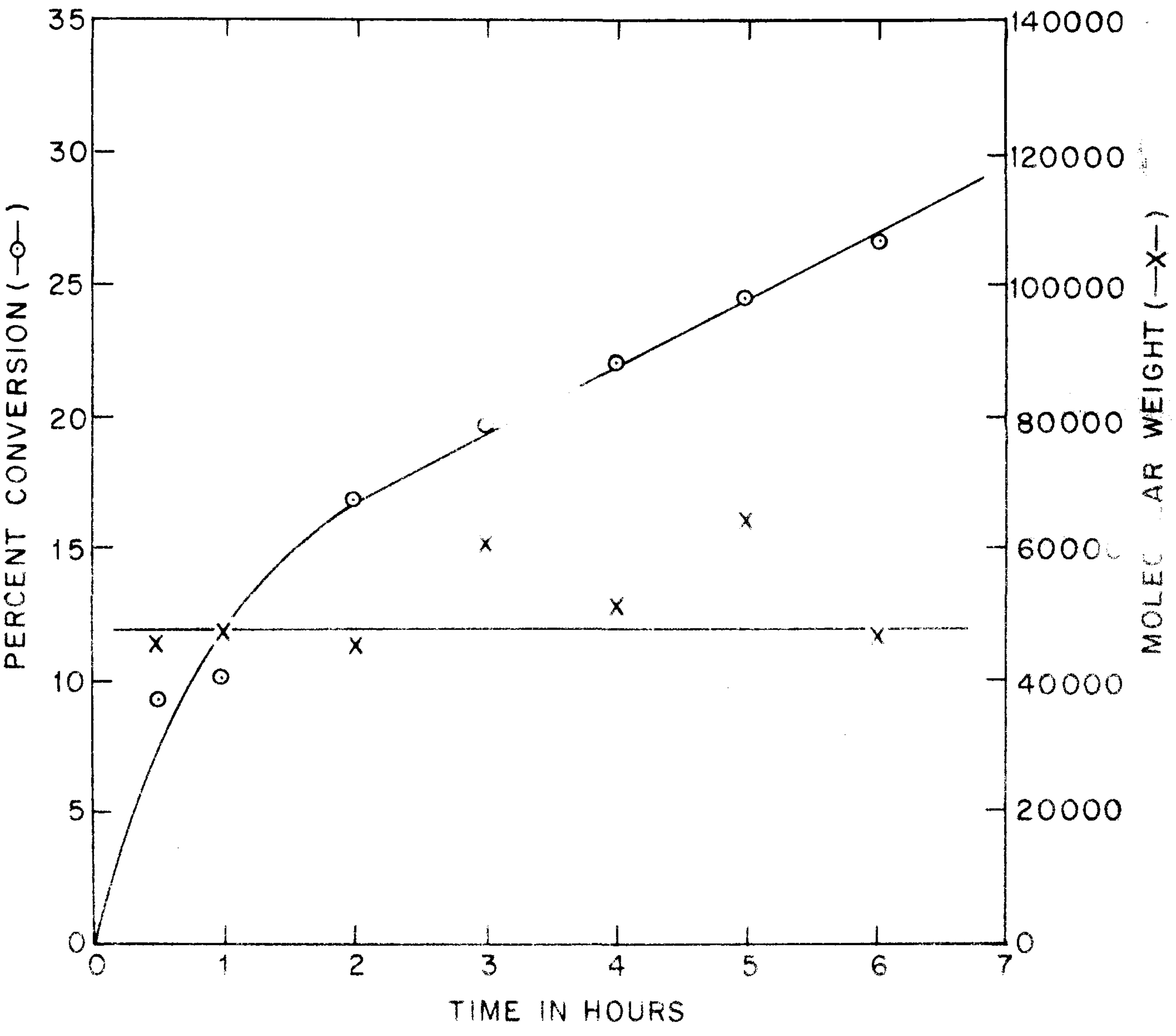


FIG. 3 EFFECT OF REACTION TIME ON $VOCl_3-AlEt_2Cl$ SYSTEM

$VOCl_3$ = 0·05 mole/l
$AlEt_2Cl$ = 0·1 mole/l
Al/V RATIO = 2

METHYLMETHACRYLATE = 5·0 ml
AGING TIME = 20 min
TEMPERATURE = 40 °C

Table - IV

Effect of Catalyst Concentration

Ratio Al/V = 2 Methyl Methacrylate = 5.0 ml
Aging time = 20 min. Temperature = 40°C
Reaction time = 180 min. Total volume = 25 ml

	Catalyst concentration M/L	Yield in gms	$R_p \times 10^6$ M/L/S	$\|\eta\|$ dl/g	Mol.wt. $\bar{M}_v$
(1)	0.01	0.021	0.75	0.5182	125,000
(2)	0.02	0.175	6.48	0.4135	94,200
(3)	0.025	0.298	11.05	0.3797	85,500
(4)	0.03	0.504	18.66	0.3425	74,800
(5)	0.04	0.608	22.53	0.3188	68,100
(6)	0.05	0.900	19.24	0.2995	63,100

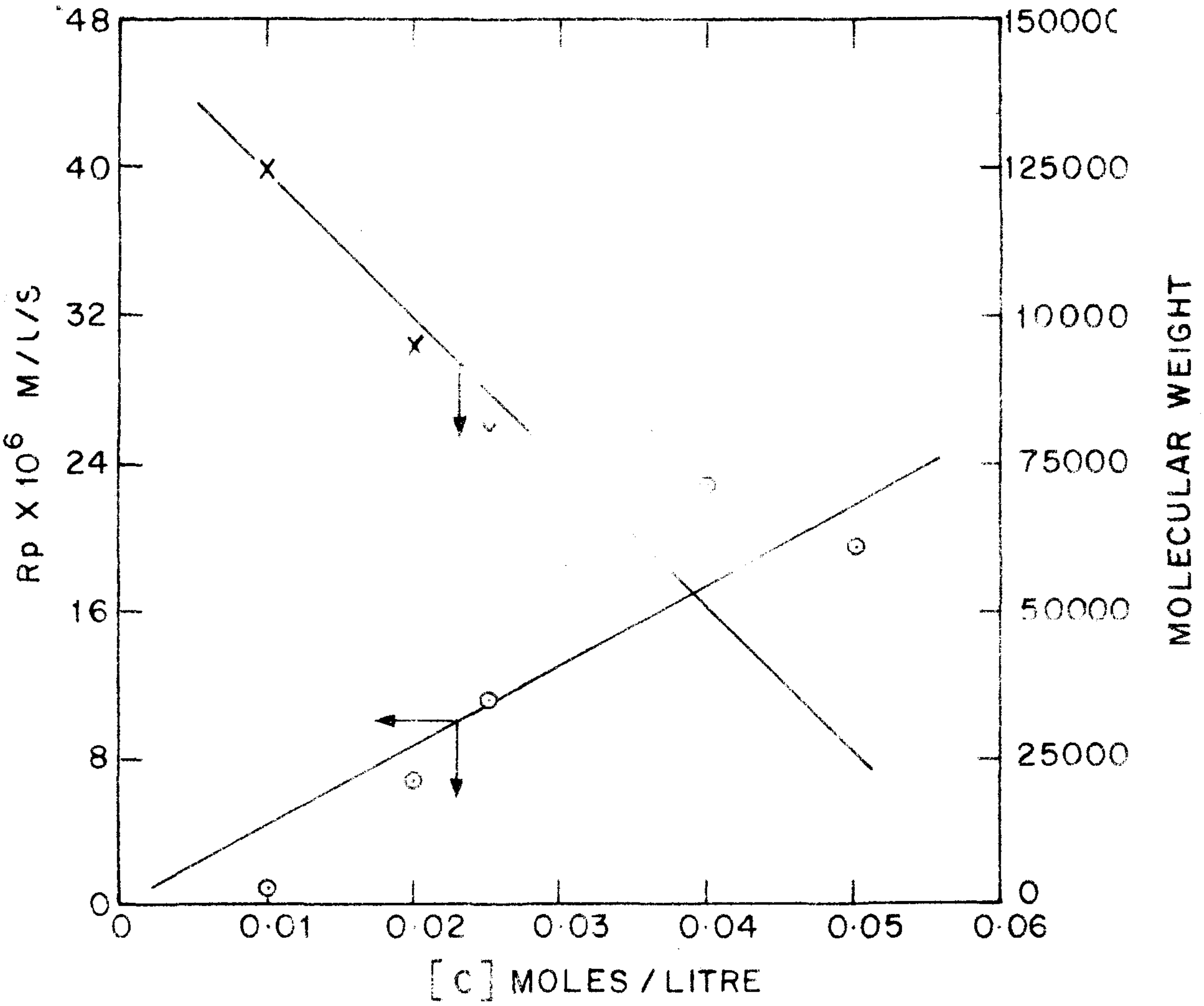


FIG. 4 EFFECT OF CATALYST CONC. ON $VOCl_3-AlEt_2Cl$ SYSTEM

Al/V RATIO

METHYLMETHACRYLATE = 5·0 ml

TOTAL VOLUME = 25·0 ml

AGING TIME = 20 min

REACTION TIME = 3 hrs

TEMPERATURE = 40 °C

linearly with increase in monomer concentration. Order of reaction was found to be unimolecular and the monomer was not responsible for the termination reaction.

Results are tabulated in Table - V (Fig.5).

3.1.5 Effect of Temperature on Polymerization

Polymerizations were carried out at different temperatures i.e. 20°, 30°, 40° and 50° with 180 min. reaction time. It was found that the rate of polymerization increased with temperature. The overall activation energy calculated from the plot of log R_p vs. 1/T between 20° and 50° was 9.25 Kcal/mole.

Results are tabulated in Table - VI (Fig.6).

3.1.6 Effect of an Electron Donor

It is well known that, when electron donors are added to the Ziegler-Natta catalyst systems, there is increase in the rate of polymerization as well as change in the structure of polymers.

It was observed that the rate of polymerization as well as molecular weights increased with the addition of triethyl amine.

Results are tabulated in Table - VII.

3.1.7 Effect of Hydroquinone

Usually Ziegler type catalysts do not polymerize polar monomers like acrylonitrile, methyl methacrylate but $VOCl_3$-$AlEt_3$ catalyst system is known to give co-polymers of propylene with acrylonitrile by a free radical mechanism[102].

Table - V

Effect of Monomer Concentration

$VOCl_3$ = 0.025 mole/l Aging time = 20 min.
$AlEt_2Cl$ = 0.05 mole/l Reaction time = 180 min.
Al/V ratio = 2 Temperature = 40°C

	Monomer concentration M/L	Yield in gms.	$R_p \times 10^6$ M/L/S	$\|\eta\|$ dl/g	Mol.wt. $\bar{M}_v$
(1)	0.94	0.098	3.62	0.3437	75,510
(2)	1.88	0.298	11.05	0.3797	85,500
(3)	2.82	0.248	9.18	0.3123	66,730
(4)	3.76	0.312	11.55	0.4057	92,170
(5)	4.7	0.356	13.18	0.4455	104,500

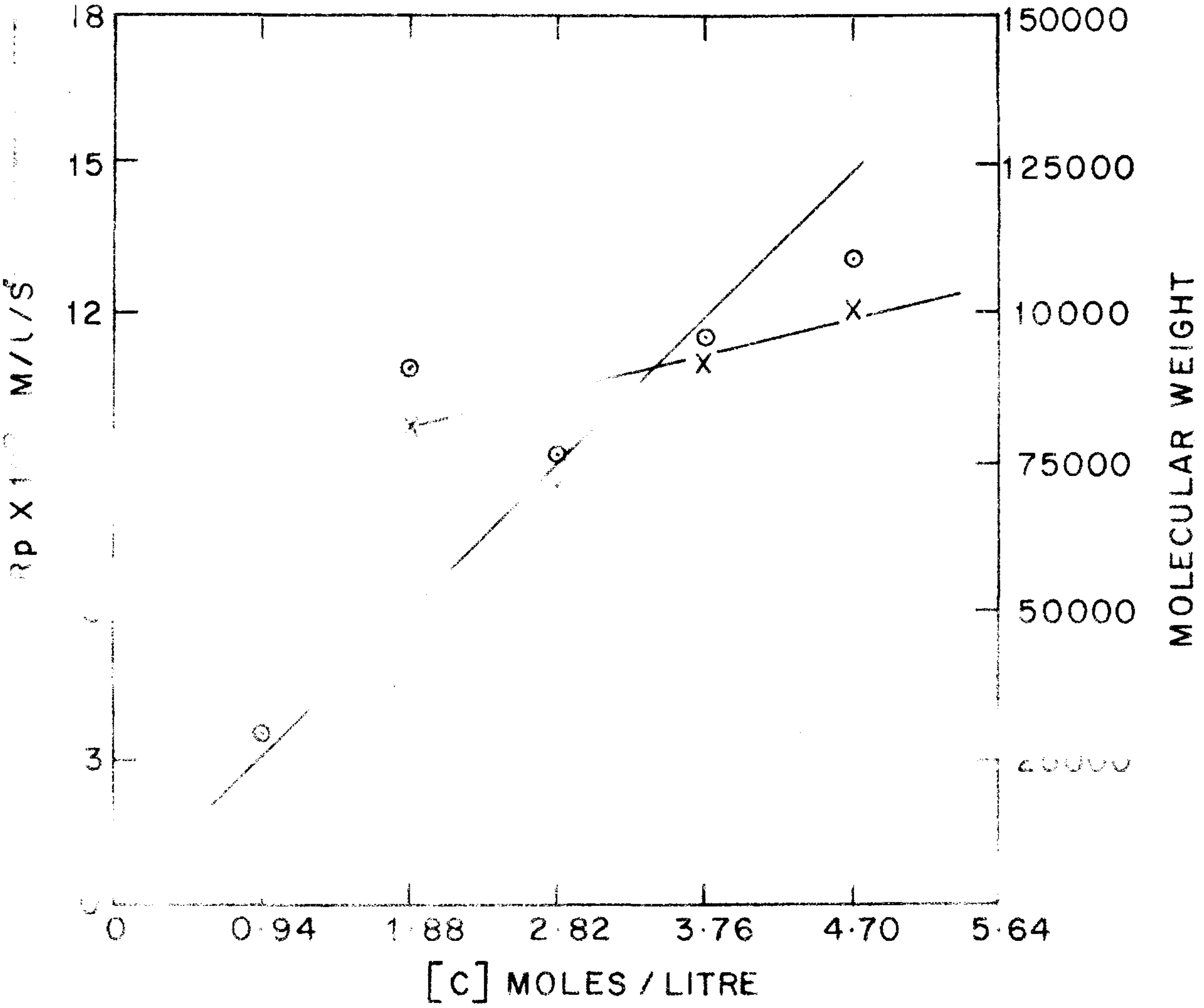


FIG. 5 EFFECT OF MONOMER CONC. ON $VOCl_3-AlEt_2Cl$ SYSTEM

$VOCl_3$ = 0·025 mole/l

$AlEt_2Cl$ = 0·05 mole/l

Al/V RATIO = 2

AGING TIME = 20 min

REACTION TIME = 3 hrs

TEMPERATURE = 40 °C

Table - VI

Effect of Temperature

$VOCl_3$ = 0.025 mole/l
$AlEt_2Cl$ = 0.05 mole/l
Al/V ratio = 2
Methyl Methacrylate = 5.0 ml
Aging time = 20 min.
Reaction time = 180 min.

	Temperature °C	Yield in gms.	$R_p \times 10^6$ M/L/S	Log R_p	$(10^3 \times \frac{1}{T})\ ^\circ K^{-1}$
(1)	20	0.237	8.77	$\bar{6}.9430$	3.41
(2)	30	0.269	9.96	$\bar{6}.9983$	3.30
(3)	40	0.298	11.00	$\bar{5}.0414$	3.19
(4)	50	0.346	12.80	$\bar{5}.1072$	3.09

Activation Energy = 3.25 K.cal/mole

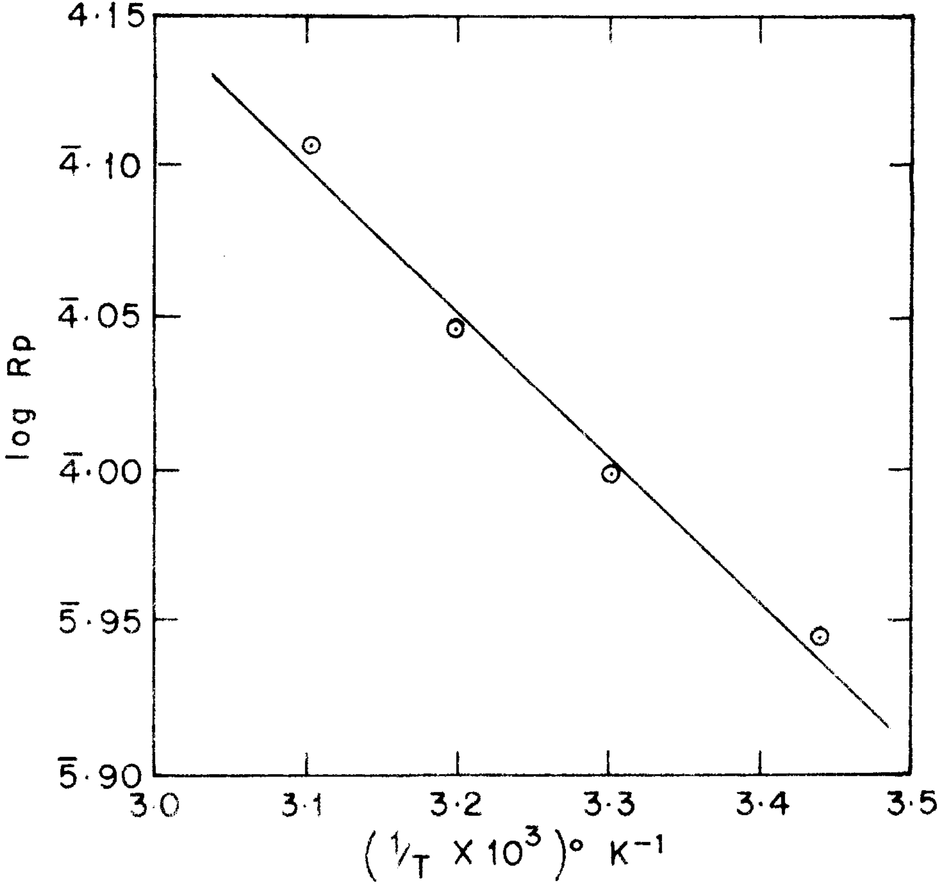


FIG. 6 EFFECT OF TEMPERATURE ON $VOCl_3-AlEt_2Cl$ SYSTEM

$VOCl_3$ = 0·025 mole/l	AGING TIME = 20 min
$AlEt_2Cl$ = 0·05 mole/l	REACTION TIME = 3 hrs
Al/V RATIO = 2	METHYLMETHACRYLATE = 5·0 ml

Table - VII

Effect of Triethylamine

$VOCl_3$ = 0.025 mole/l Methyl Methacrylate = 5.0 ml
$AlEt_2Cl$ = 0.05 mole/l Aging time = 20 min.
Al/V ratio = 2 Reaction time = 180 min.
Temperature = 40°C

	$\frac{Et_3N}{V}$ ratio	Yield in gms	$R_p \times 10^6$ M/L/S	Mol.wt. $\overline{M}_v$
(1)	-	0.298	11.04	85,500
(2)	2	0.506	18.74	98,120
(3)	4	0.365	13.52	88,300

Table - VIII

Effect of Hydroquinone

$VOCl_3$ = 0.025 mole/1 Methyl Methacrylate = 5.0 ml
$AlEt_2Cl$ = 0.05 mole/1 Aging time = 20 min.
Al/V ratio = 2 Reaction time = 180 min.
Temperature = 40°C

	Amount of hydroquinone	Yield gms.	$R_p \times 10^6$ M/L/S	Mol.wt. $\bar{M}_v$
(1)	-	0.298	11.04	85,000
(2)	50 mgm	0.242	8.96	114,000
(3)	100 mgm	0.290	10.74	122,000

Earlier studies[119-120] showed vanadium containing catalyst systems polymerizes methyl methacrylate by anionic mechanism. In order to confirm this, polymerizations were carried out with varying amount of hydroquinone and it was observed that the addition of hydroquinone had no effect on the rate of polymerization but the molecular weights increased.

Results are tabulated in Table - VIII.

3.2 Polymerization of Methyl Methacrylate with Vanadium Oxychloride and Aluminium Diethyl Bromide at 40° in n-hexane

In the Ziegler-Natta catalyst systems[83], the ratio of organometallic compound to transition metal compound and the valency state of transition metal has great influence on the rate of polymerization, structure and molecular weight of polymer. It is known that as there is increase in the ratio of Al/V, the average valency of vanadium decreases. It was also observed[137] that there is increase in amount of average valency V^{+2}, after long time of aging of catalyst at higher ratio of Al/V. In our previous studies[119-123] with vanadium based Ziegler-Natta catalyst systems for polymerization of methyl methacrylate, the ratio of Al/V chosen was in the range of 1-2, which is comparatively low.

The results of kinetic studies of polymerization of methyl methacrylate with $VOCl_3$-$AlEt_2Br$ catalyst system at ratio of Al/V=4, are presented herewith.

3.2.1 Aging of the Catalyst System

Because of long time of aging, there is increase in amount of average valency of V^{+2} at higher ratio of Al/V as observed by Lehr[137] and in order to compare the same catalyst system in carbon tetrachloride for polymerization of methyl methacrylate, the aging time of 24 hrs. was used in these studies.

3.2.2 Variation in the Ratio of Catalyst Constituents as Al/V

The dark brown solution containing fine precipitate after mixing the catalyst consituents remains unchanged after 24 hrs. of aging and after addition of monomer showing the presence of undisturbed catalyst sites. The ratio of Al/V was changed by keeping the concentration of vanadium oxychloride constant in order to find out the ratio of optimum activity. It was observed that the polymer yield was maximum at ratio of Al/V=4 and 8, but the molecular weight of polymer was maximum at ratio of Al/V=4. Therefore ratio of Al/V=4 was chosen for further studies.

The results are tabulated in Table - IX (Fig.7).

3.2.3 Effect of Reaction Time on the Polymerization

By keeping constant parameters such as aging time of catalyst, catalyst concentration, monomer concentration, polymerizations were carried out at different intervals of time at fixed ratio of Al/V=4. The rate of polymerization increased linearly even upto 180 min. Therefore reaction time of 180 min. was chosen for further kinetic studies.

Results are tabulated in Table - X (Fig.8).

Table - IX

Effect of Al/V Mole Ratio

$VOCl_3$ = 0.05 mole/l
Methyl Methacrylate = 5 ml
Temperature = 40^{o}C

Aging time = 24 hrs.
Reaction time = 3 hrs
Total volume = 25 ml

	Molar ratio	Yield in gms.	Percent conversion	$\lvert\eta\rvert$ dl/g	Mol.wt. $\overline{M}_v$
(1)	1	0.022	0.48	-	-
(2)	2	0.033	0.64	-	-
(3)	3	0.109	2.20	0.3886	87,900
(4)	4	0.215	4.57	0.3262	69,980
(5)	5	0.117	2.52	0.1955	37,340
(6)	6	0.094	2.01	0.1349	23,470
(7)	7	0.117	2.52	0.1643	30,000
(8)	8	0.190	4.07	0.1072	17,560
(9)	9	0.178	3.56	0.0753	11,330
(10)	10	0.166	2.50	0.0788	11,470

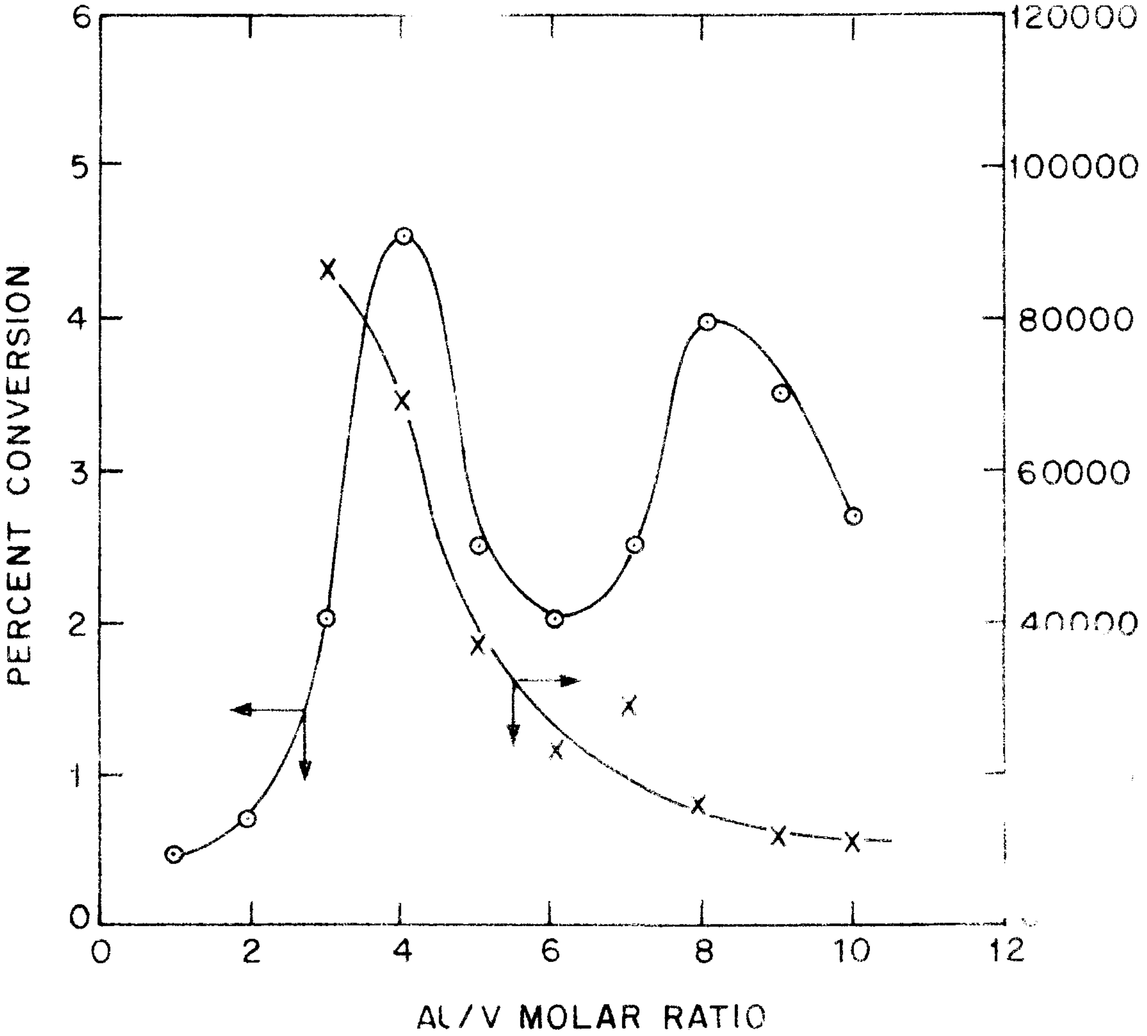


FIG. 7 EFFECT OF RATIO ON VOCl$_3$ – AlEt$_2$Br SYSTEM

VOCl$_3$ = 0·05 mole/l

METHYLMETHACRYLATE = 5·0 ml

TOTAL VOLUME = 25·0 ml

AGING TIME = 24 hrs

REACTION TIME = 3 hrs

TEMPERATURE = 40 °C

Table - X

Effect of Reaction Time

$VOCl_3$ = 0.05 mole/l Methyl Methacrylate = 5 ml
$AlEt_2Br$ = 0.2 mole/l Aging time = 24 hrs
Al/V ratio = 4 Temperature = 40°C

	Reaction time in min.	Yield in gms.	Percent conversion	$\lvert\eta\rvert$ dl/g	Mol.wt. $\overline{M}_v$
(1)	60	0.040	0.86	-	-
(2)	120	0.121	2.58	0.3686	81,150
(3)	180	0.215	4.57	0.3262	69,980
(4)	240	0.262	5.60	0.3934	88,720
(5)	300	0.278	5.94	0.3720	82,690
(6)	360	0.270	5.77	0.3568	78,520

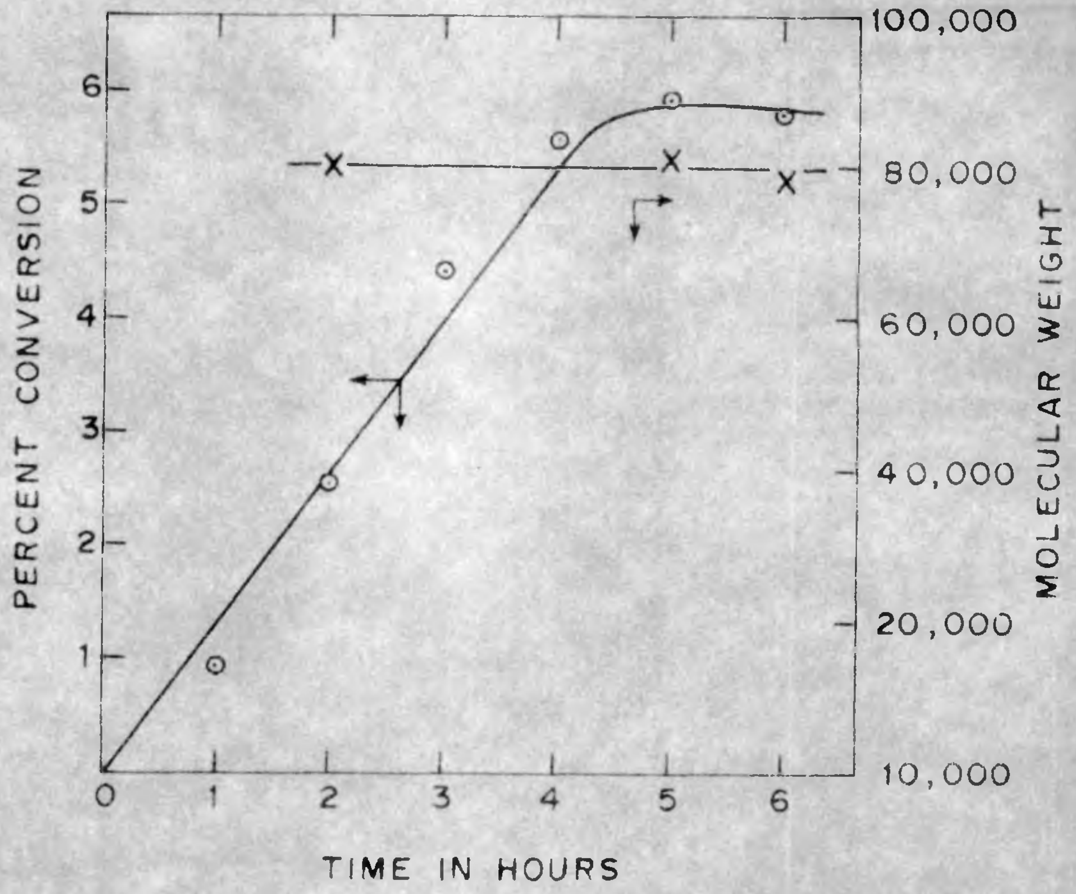


FIG.8 EFFECT OF REACTION TIME ON $VOCl_3 - AlEt_2Br$ SYSTEM

$VOCl_3$ = 0·05 mole/l	METHYLMETHACRYLATE = 5·0 ml
$AlEt_2Br$ = 0·2 mole/l	AGING TIME = 24 hrs
Al/V RATIO = 4	TEMPERATURE = 40 °C

3.2.4 Dependence of Rate of Polymerization on Catalyst and Monomer Concentrations

In the light of above observations, the conditions for studying the kinetics were established as: (1) Al/V=4, (2) polymerization time = 180 min. and (3) aging time = 24 hrs. Under these conditions, a fixed amount of methyl methacrylate was polymerized with varying concentration of catalyst components. It was observed that the rate of polymerization varied linearly with catalyst concentration. However, molecular weight decreased with increasing concentration of catalyst, indicating chain transfer with complex formed.

Results are tabulated in Table - XI (Fig.9).

When the monomer concentration was changed at constant concentration of catalyst components, both the rate of polymerization and molecular weights increased linearly with increased ~~with~~ concentration of monomer, indicating that monomer has not taken part in chain transfer reaction.

Results are tabulated in Table - XII (Fig.10).

This shows that, as with other Ziegler-Natta catalyst systems, the rate of polymerization is first order with respect to the monomer and catalyst concentrations.

3.2.5 Effect of Temperature on Polymerization

Polymerizations were carried out at at different temperatures i.e. 20°, 30°, 40° and 50° with 180 minutes reaction time. It was found that the rate of polymerization increased with temperature. The overall activation energy calculated from plots of log R_p vs. 1/T is of the order of 6.67 Kcal/mole.

Table - XI

Effect of Catalyst Concentration

Al/V ratio = 4 Methyl Methacrylate = 5 ml
Reaction time = 3 hrs Temperature = $40^{\circ}C$
Aging time = 24 hrs Total volume = 25 ml

	Catalyst concentration M/L	Yield in gms.	$R_p \times 10^6$ M/L/S	$\|\eta\|$ dl/g	Mol.wt. $\overline{M}_v$
(1)	0.025	0.098	3.62	0.4058	92,040
(2)	0.050	0.215	7.96	0.3262	69,980
(3)	0.075	0.3685	13.66	0.2278	45,040
(4)	0.100	0.4380	16.22	0.1628	29,510
(5)	0.125	0.6082	22.52	0.0976	13,730

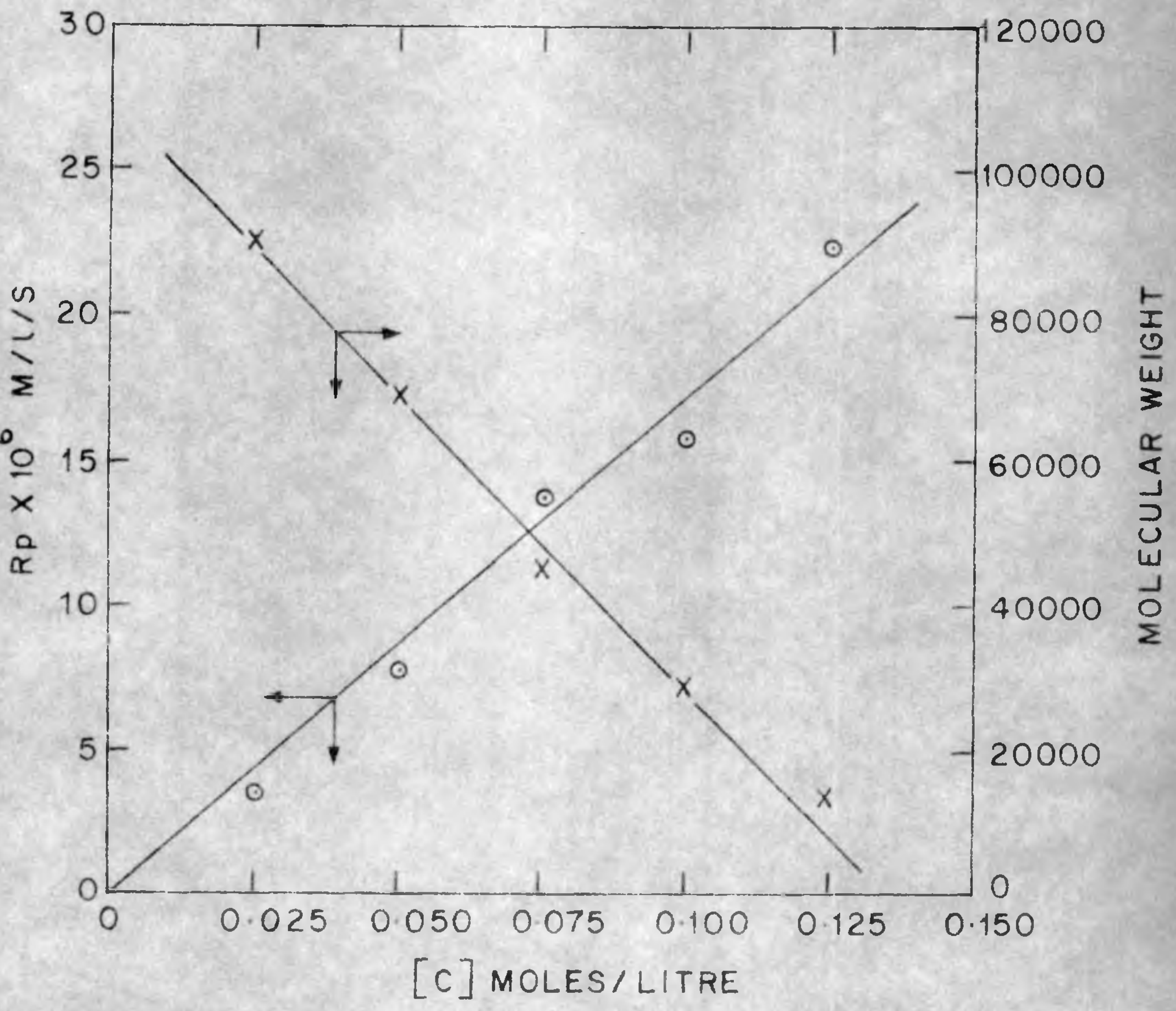


FIG.9 EFFECT OF CATALYST CONC. ON $VOCl_3-AlEt_2Br$ SYSTEM

Al/V RATIO = 4

METHYLMETHACRYLATE = 5·0 ml

TOTAL VOLUME = 25·0 ml

AGING TIME = 24 hrs

REACTION TIME = 3 hrs

TEMPERATURE = 40 °C

Table - XII

Effect of Monomer Concentration

$VOCl_3$ = 0.05 mole/l
$AlEt_2Br$ = 0.20 mole/l
Al/V ratio = 4
Aging time = 24 hrs.
Reaction time = 3 hrs.
Temperature = 40°C

	Monomer concentration M/L	Yield in gms	$R_p \times 10^6$ M/L/S	$\lvert\eta\rvert$ dl/g	Mol.wt. $\overline{M}_v$
(1)	0.376	0.075	2.78	0.2231	44,200
(2)	0.94	0.134	4.90	0.2836	59,300
(3)	1.88	0.215	7.96	0.3262	69,980
(4)	2.82	0.410	15.18	0.3796	85,400
(5)	3.76	0.500	18.52	0.3536	78,500

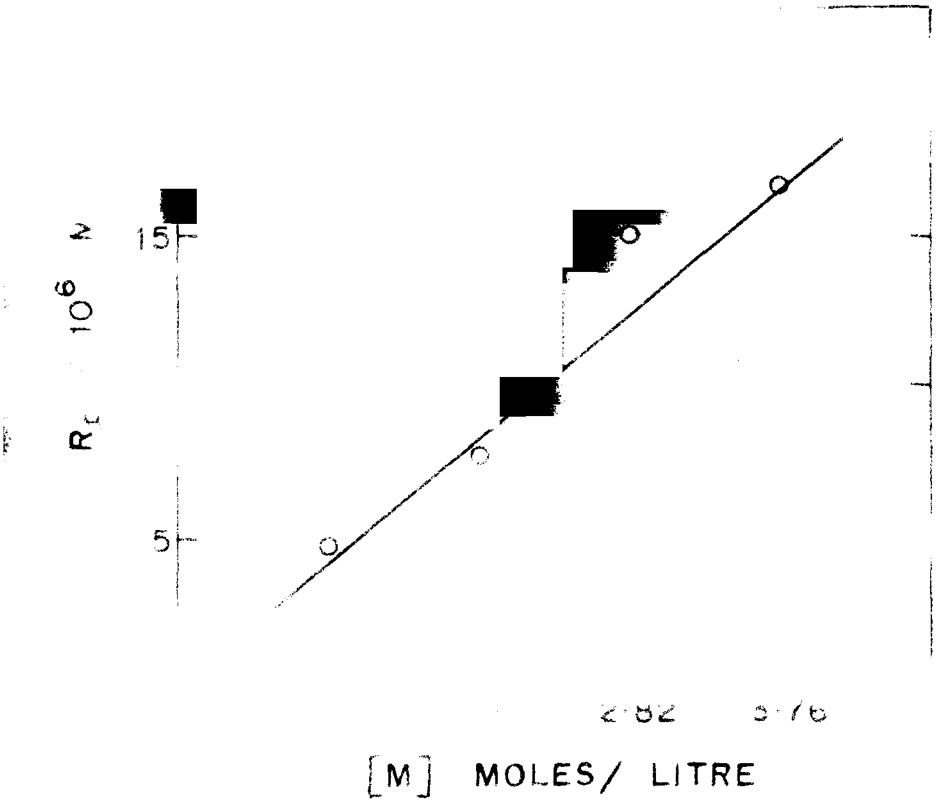


FIG. 10 EFFECT OF MONOMER CONC·ON $VOCl_3$–$AlEt_2Br$ SYSTEM

$VOCl_3$ = 0·05 mole/l

$AlEt_2Br$ = 0·2 mole/l

Al/V RATIO = 4

AGING TIME = 24 hrs

REACTION TIME = 3 hrs

TEMPERATURE = 40 °C

Results are tabulated in Table - XIII (Fig.11).

3.2.6 Effect of an (Electron Donor) Triethyl Amine

It was observed that the rate of polymerization as well as molecular weights of polymer were increased with the addition of triethyl amine.

Results are tabulated in Table - XIV.

3.2.7 Effect of Hydroquinone

Hydroquinone inhibits free radical polymerization in which rate of polymerization decreases as increase in addition of hydroquinone. Onthe contrary, in this study it was observed that both the rate of polymerization and molecular weight increased with addition of hydroquinone.

Results are tabulated in Table - XV.

3.3 Polymerization of Methyl Methacrylate with: (a) $VOCl_3$-$AlEt_2Br$ (b) VCl_4-$AlEt_2Br$ Catalyst Systems in Carbon Tetrachloride Medium at 40°C

Stereospecific polymerization of methyl methacrylate with Ziegler-Natta catalyst systems such as $VOCl_3$-$AlEt_3$ and VCl_4-$AlEt_3$ in hydrocarbon media were earlier studied in our Laboratory$^{119-123}$. Some work on polymerization of methyl methacrylate in polar solvent such as acetonitrile^{124} was also reported. C.Eden and H.Feilchenfeld^{138} observed that transition metals and their salts in lower valency state can be oxidized to higher valency state in presence of carbon tetrachloride. They found that carbon tetrachloride had inhibiting effect on reduction of transition metal

Table - XIII

Effect of Temperature

$VOCl_3$ = 0.05 mole/1 Methyl Methacrylate = 5.0 ml
$AlEt_2Br$ = 0.2 mole/1 Aging time = 24 hrs.
Al/V ratio = 4 Reaction time = 3 hrs.

	Temperature °C.	Yield in gms.	$R_p \times 10^6$ M/L/S	Log R_p	$(10^3 x \frac{1}{T})$ $^oK^{-1}$
(1)	20	0.068	2.52	$\bar{6}.4014$	3.41
(2)	30	0.148	5.48	$\bar{6}.7388$	3.30
(3)	40	0.215	7.96	$\bar{6}.9009$	3.19
(4)	50	0.203	7.518	$\bar{6}.8761$	3.09

Activation Energy = 6.67 K.cal/mole

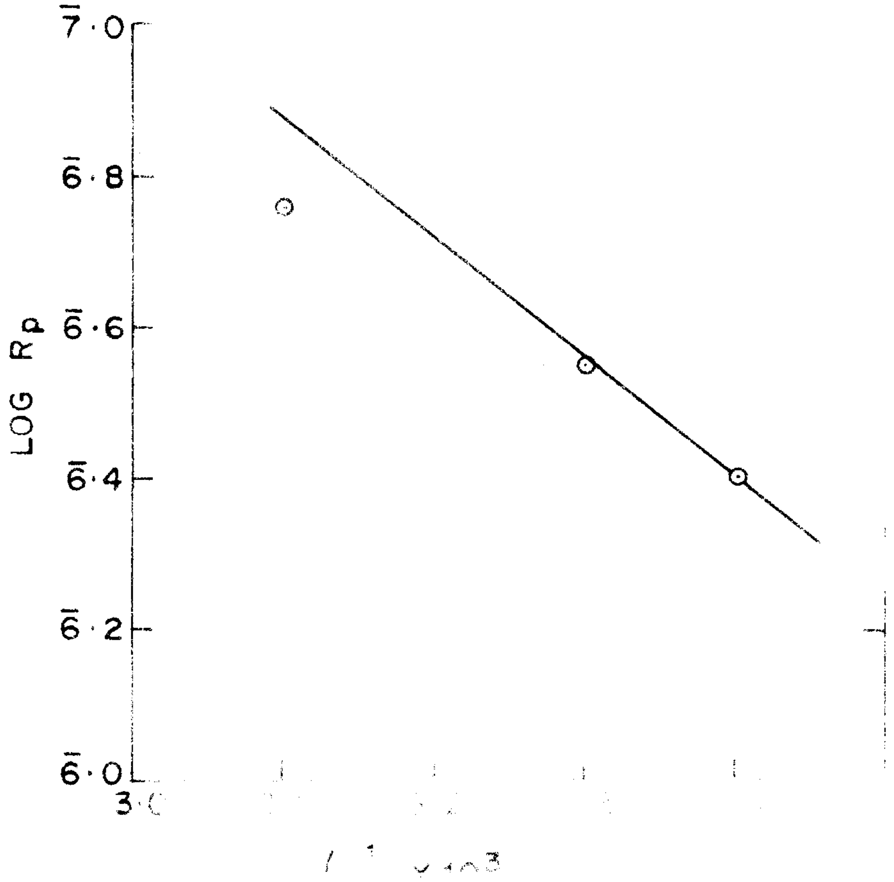


FIG.11 EFFECT OF TEMPERATURE ON $VOCl_3$-$AlEt_2Br$ SYSTEM

$VOCl_3$ = 0·05 mole/l
$AlEt_2Br$ = 0·2 mole/l
Al/V RATIO = 4

METHYLMETHACRYLATE = 5·0 ml
AGING TIME = 24 hrs
REACTION TIME = 3 hrs

Table - XIV

Effect of Trimethylamine

$VOCl_3$ = 0.05 mole/l Methyl Methacrylate = 5.0 ml
$AlEt_2Br$ = 0.20 mole/l Aging time = 24 hrs.
Al/V ratio = 4 Reaction time = 3 hrs.
Temperature = 40°C

	$\frac{Et_3N}{V}$ Mole ratio	Yield in gms.	$R_p \times 10^6$ M/L/S	Mol.wt. $\overline{M}_v$
(1)	-	0.215	7.96	69,980
(2)	1	0.298	11.14	80,200
(3)	2	0.429	15.87	93,400
(4)	4	0.615	22.74	76,600

Table - XV

Effect of Hydroquinone

$VOCl_3$ = 0.05 mole/l Methyl Methacrylate = 5.0 ml
$AlEt_2Br$ = 0.20 mole/l Aging time = 24 hrs.
Al/V ratio = 4 Reaction time = 3 hrs.
Temperature = 40°C

	Amount of hydroquinone	Yield in gms.	$R_{p_{M/L/S}} \times 10^6$	Mol.wt. $\overline{M}_v$
(1)	-	0.215	7.96	69,980
(2)	50 mgm	0.199	7.37	79,500
(3)	100 mgm	0.186	6.96	79,400

halides by aluminium alkyls. Ziegler-Natta catalyst systems have been mostly employed in non-polar medium for polymerization reactions and Ziegler in his patent gave a long list of solvents for polymerization of α-olefins (K.Ziegler, Israel Pat.8390) but carbon tetrachloride was not among them. Therefore it is interesting to study polymerization of methyl methacrylate with Ziegler-Natta catalyst systems in carbon tetrachloride medium.

3.3.1 Polymerization of Methyl Methacrylate with Vanadium Oxychloride and Diethyl Aluminium Bromide Catalyst System in Carbon Tetrachloride at 40°C

3.3.1.1 Effect of Aging Time on Catalyst System

It was observed that carbon tetrachloride had inhibiting effect on reduction of transition metal by aluminium alkyls. On the contrary, C.Eden and Feilchenfeld[138] showed that carbon tetrachloride helps the oxidation of transition metal halide and the amount of oxidised transition metal increases after long time of aging. Therefore aging time of 24 hrs. was chosen for further studies.

3.3.1.2 Variation in the Ratio of Catalyst Constituents as Al/V

When solution of $VOCl_3$ in hexane was added to the solvent carbon tetrachloride, pale yellow solution was formed. To this solution, solutions of different concentration of aluminium diethyl bromide in hexane were added in order to study the effect of ratio of Al/V. Instantaneous black precipitate was formed in all the cases. After an induction period, decomposition took place with evolution of gases and large amount of heat was produced. The heterogeneous solution of catalyst components were well stirred and aged for 24 hrs. and specific amount of methyl methacrylate was added to see the effect of ratio on polymerization.

It was observed that the yield increases as the ratio increases. But the product upto ratio of Al/V=3 was not soluble in chloroform. Therefore to compare the behaviour of this catalyst system with $VOCl_3$-$AlEt_2Br$ catalyst system in n-hexane, the ratio of Al/V=4 was chosen, for further study,at which the dark brown product soluble in chloroform, was obtained.

Results are tabulated in Table - XVI (Fig.12).

3.3.2 Polymerization of Methyl Methacrylate with Vanadium Chloride and Diethyl Aluminium Bromide Catalyst System in Carbon Tetrachloride at 40°C

3.3.2.1 Effect of Aging Time on Catalyst System

As in case of $VOCl_3$-$AlEt_2Br$ catalyst system for polymerization of methyl methacrylate, the aging period of 24 hrs. was chosen for further study.

3.3.2.2 Variation in the Ratio of Catalyst Constituents as Al/V

When solution of VCl_4 in hexane was added to the solvent carbon tetrachloride, red blood solution is formed. To this solution, solutions of different concentrations of aluminium diethyl bromide in n-hexane, were added, in order to study the effect of ratio of Al/V. Instantaneous black precipitate was formed in all the cases. After the induction period (which depends on ratio of Al/V, amount of CCl_4),

Table - XVI

Effect of Al/V Mole Ratio

$VOCl_3$ = 0.05 mole/l   Aging time = 24 hrs.
Methyl Methacrylate = 5.0 ml   Reaction time = 3 hrs.
Temperature = 40°C   Total volume = 25 ml

	Molar ratio	Yield in gms.	Percent conversion
(1)	1	0.022	0.47
(2)	2	0.143	3.06
(3)	3	0.258	5.52
(4)	4	0.339	7.25
(5)	5	0.372	7.96
(6)	6	0.367	7.82
(7)	7	0.334	7.14

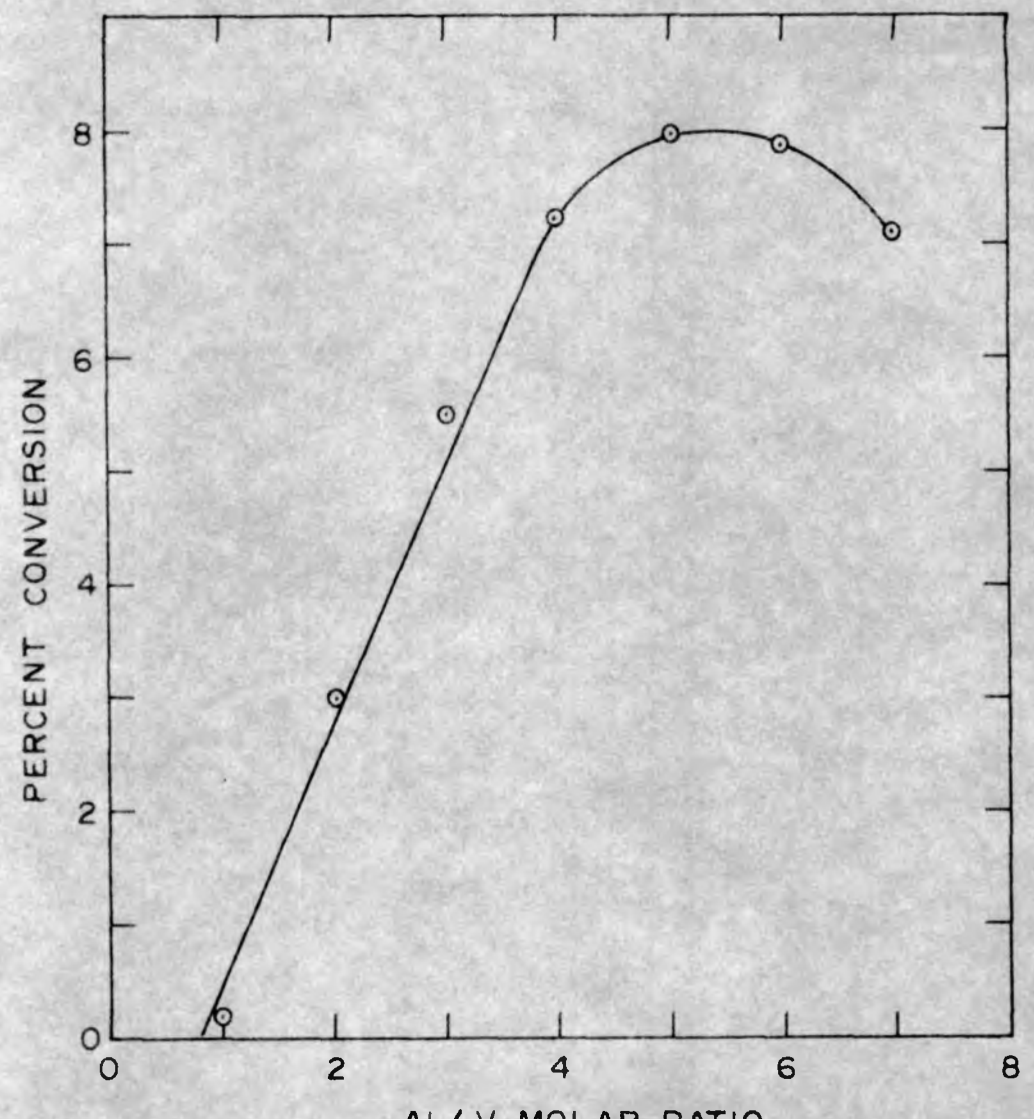


FIG. 12 EFFECT OF Al/V RATIO ON $VOCl_3-AlEt_2Br$ SYSTEM

$VOCl_3$ = 0·05 mole/l

METHYLMETHACRYLATE = 5·0 ml

TOTAL VOLUME = 25·0 ml

AGING TIME = 24 hrs

REACTION TIME = 3 hrs

TEMPERATURE = 40 °C

decomposition took place with evolution of gases and large amount of heat was produced. The heterogeneous solutions of catalyst components were well stirred and aged for 24 hrs. and specific amount of methyl methacrylate was added to see the effect of ratio on polymerization.

It was observed that the yield increases as the ratio of Al/V increases. The products at ratio of Al/V=1 and 2 were not soluble in chloroform, but the dark brown complex obtained at ratio of Al/V=3 was soluble in chloroform and can thus be purified. Therefore ratio of Al/V=3 was chosen for further study.

Results are tabulated in Table - XVII (Fig.13).

3.4 Polymerization of Isoprene with VCl_4-$AlEt_2Br$ Catalyst System in n-hexane at 30°C

The polymerization[139] of isoprene and butadiene with heterogeneous Ziegler-Natta catalyst system can lead to polymers with microstructure with all cis 1,4-, trans 1,4-, isotactic 1,2- or (3,4-), syndiotactic 1,2- or (3,4-) or combination of two or more of these structural units. The polymer microstructure may be dependent upon the ratio of catalyst components, the temperature of polymerization and reaction medium. Gaylord[140] et al and B.Matyska[141] et al have studied diene polymerization with Ziegler-Natta catalyst systems. They reported that the lower ratio of Al/Mg or Al/Ti favours formation of cyclopolyisoprene and the catalytic activity of systems for the formation of cyclic polymers increased with increase in acid character of

Table - XVII

Effect of Al/V Mole Ratio

VCl_4 = 0.05 mole/l Aging time = 24 hrs.
Methyl Methacrylate = 5.0 ml Reaction time = 3 hrs.
Temperature = 40°C Total volume = 25 ml

	Molar ratio	Yield in gms.	Percent conversion
(1)	1	0.068	1.45
(2)	2	0.233	4.92
(3)	3	0.350	7.49
(4)	4	0.392	8.39
(5)	5	0.469	10.04
(6)	6	0.542	11.57
(7)	7	0.442	9.42

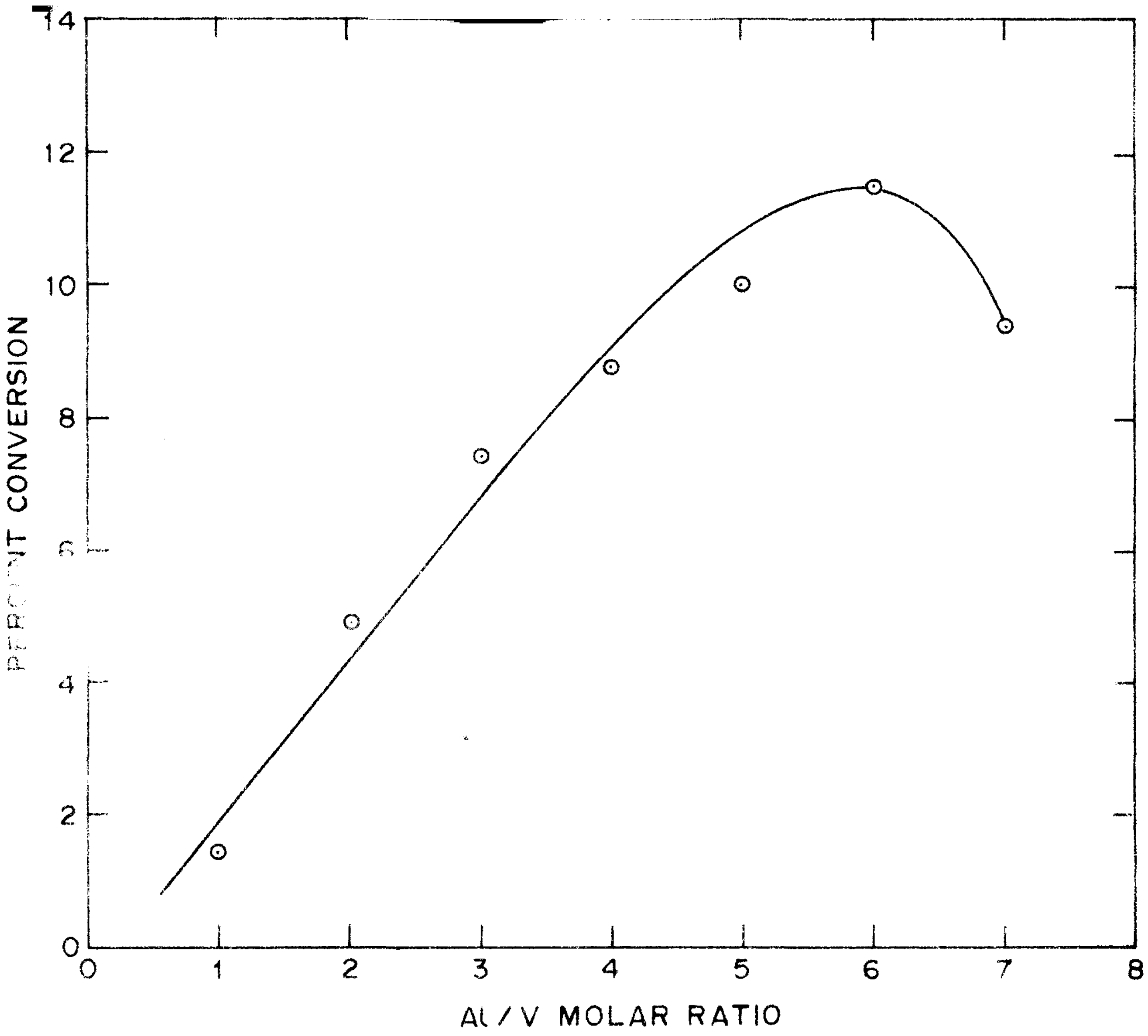


FIG. 13 EFFECT OF Al/V RATIO ON VCl_4-AlEt_2Br SYSTEM

VCl_4 = 0·05 mole/l	AGING TIME = 24 hrs
METHYLMETHACRYLATE = 5·0 ml	REACTION TIME = 3 hrs
TOTAL VOLUME = 25·0 ml	TEMPERATURE = 40 °C

reaction product. Recently Gaylord[142-145] et al suggested a cation-radical mechanism for cyclopolymerization of isoprene and Matyska[145,146] et al have made a detailed kinetic analysis of soluble and insoluble cyclopolyisoprene.

In this work, the results of kinetic studies on polymerization of isoprene with VCl_4-AlEt_2Br catalyst system are presented.

3.4.1 Variation in the Ratio of Catalyst Constituents as Al/V

It is known that when soluble vanadium halide or oxyhalide are reacted with aluminium alkyls, the reaction takes place through the same steps as with titanium tetrachloride. It is also important that in order to have catalytic activity the vanadium must be reduced, at least partially to divalent state. Therefore by keeping concentration of VCl_4 constant, concentration of $AlEt_2Br$ was varied in order to study the effect of ratio of Al/V on percent conversion. There were two maxima in the plot of conversion against ratio of Al/V. The ratio of Al/V=3 giving maximum conversion was chosen for further study.

Results are tabulated in Table - XVIII (Fig.14).

3.4.2 Aging of the Catalyst System

In order to see the effect of aging of catalyst components on rate of polymerization, the catalyst complex was aged in the absence of monomer and after varying the aging time from 10 to 360 minutes, the monomer was polymerized with the aged catalyst system at constant ratio of Al/V, at

Table - XVIII

Effect of Al/V Mole Ratio

VCl_4 = 0.025 mole/l Aging time = 20 min.
Isoprene = 5.0 ml Reaction time = 120 min.
Temperature = 30°C Total volume = 25 ml

	Molar ratio	Yield in gms.	Percent conversion	Percentage of insoluble and cyclic polymer
(1)	1	0.433	13.32	67.5
(2)	2	0.615	18.03	75.6
(3)	2.5	0.629	18.19	62.6
(4)	3.0	0.655	19.22	62.5
(5)	3.5	0.602	17.68	61.1
(6)	4.0	0.496	14.56	95.8
(7)	5.0	0.326	9.56	86.7
(8)	6.0	0.414	12.16	79.1
(9)	7.0	0.365	10.72	88.5

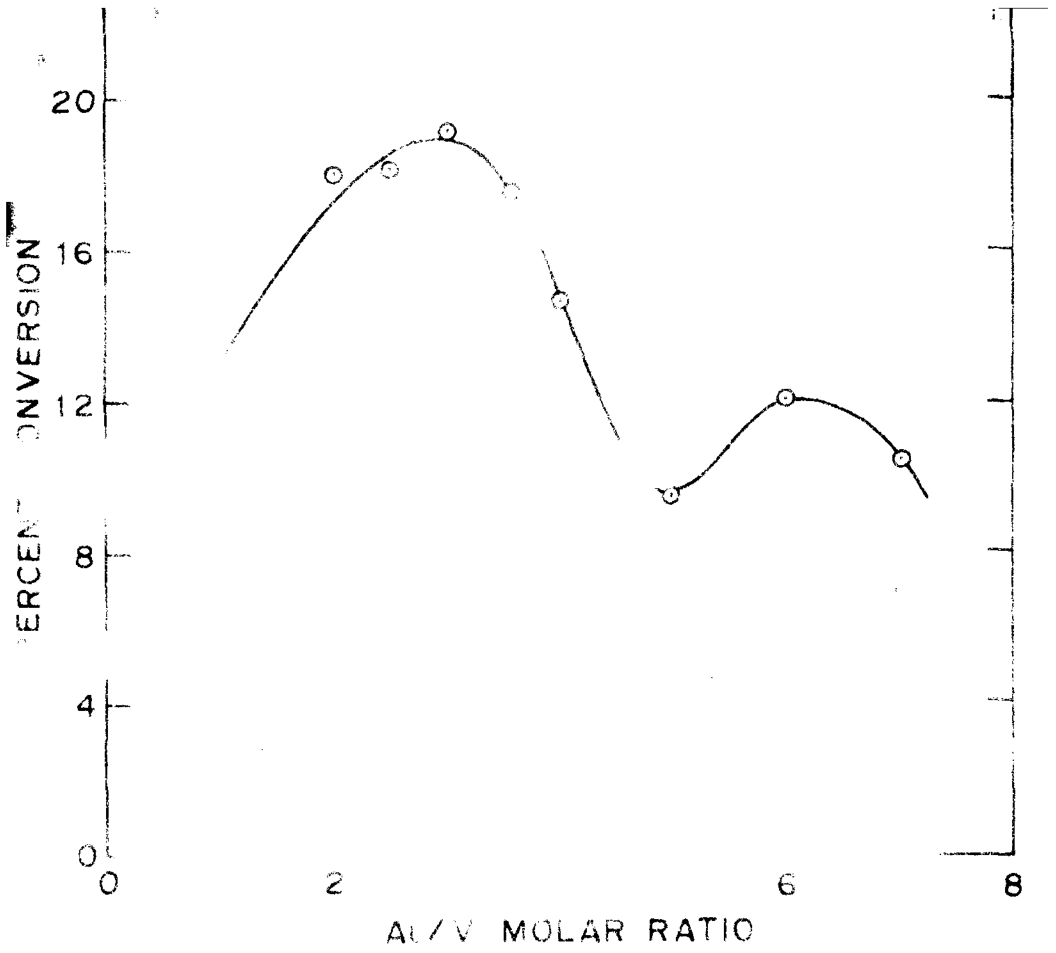


FIG. 14 EFFECT OF Al/V RATIO ON VCl_4-AlEt_2Br SYSTEM

VCl_4 = 0·025 mole/l		AGING TIME	= 20 min
ISOPRENE		REACTION TIME	= 120 min
TOTAL VOLUME = 25.0 ml		TEMPERATURE	= 40 °C

constant time of reaction and at constant temperature. It was observed that the catalyst aged for 1 hour yields maximum conversion and after that period of aging, activity of catalyst decreases. Therefore aging time of 1 hour was taken for further experiments.

Results are tabulated in Table - XIX (Fig.15).

3.4.3 Effect of Reaction Time on the Polymerization

By keeping constant aging time of catalyst, catalyst concentration, monomer concentration, polymerizations were carried out at different intervals of time at fixed ratio of Al/V=3. The rate of polymerization was found to be increasing linearly upto 2 hours and thereafter remained constant and increased steeply. At the reaction time of 1 hour, percentage conversion was less than 10%. Therefore the reaction time of 1 hour was chosen for further studies.

Results are tabulated in Table - XX (Fig.16).

3.4.4 Dependence of Rate of Polymerization of Catalyst and Monomer Concentrations

The kinetic behaviour with respect to catalyst and monomer concentrations was studied at selected conditions such as ratio of Al/V=3, aging time = 1 hr., and reaction time = 1 hr.

The rate of polymerization was found to be first order with respect to catalyst and monomer concentrations and such linear dependence is well known for typical Ziegler-Natta type catalyst system of heterogeneous nature.

Results are tabulated in Table - XXI (Fig.17) and

Table - XIX

Effect of Aging Time

VCl_4 = 0.025 mole/l

$AlEt_2Br$ = 0.075 mole/l

Al/V ratio = 3

Isoprene = 5.0 ml

Reaction time = 120 min.

Temperature = 30°C

	Aging time min.	Yield in gm.	Percent conversion	Percentage of insoluble and cyclic polymer
(1)	20	0.654	19.22	62.4
(2)	40	0.706	20.77	66.7
(3)	60	0.718	21.11	59.6
(4)	180	0.505	14.80	69.3
(5)	360	0.276	8.13	71.4
(6)	1440	0.173	5.08	71.8

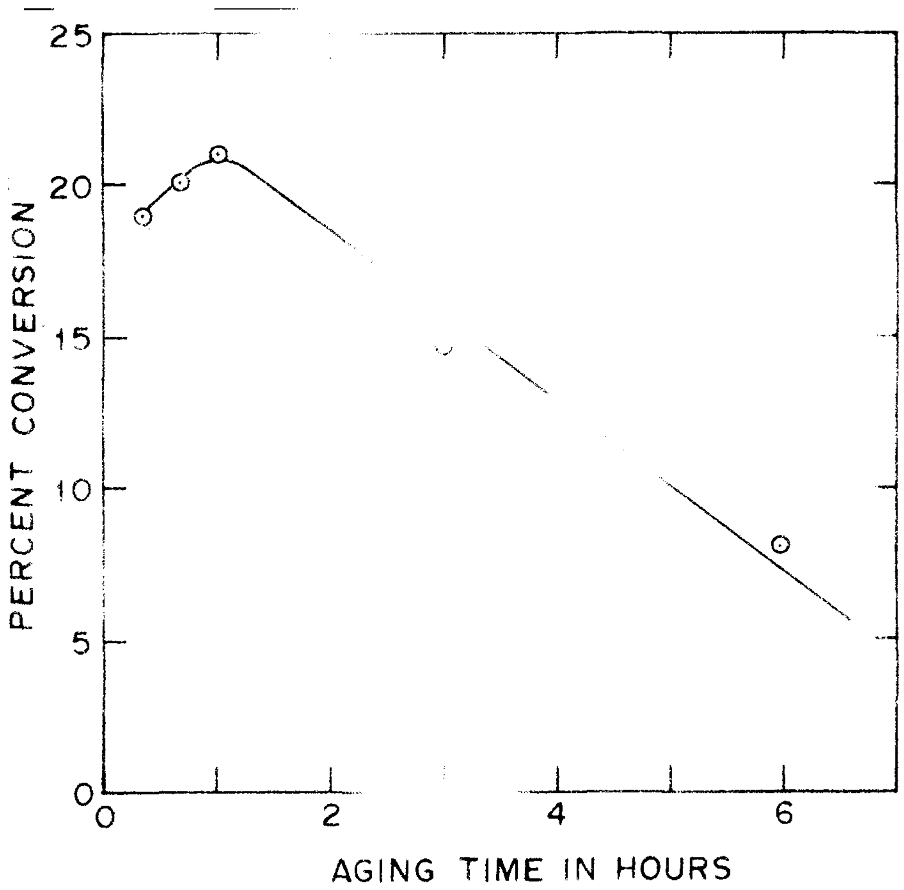


FIG. 15 EFFECT OF AGING ON VCl_4-AlEt_2Br SYSTEM

VCl_4	= 0·025 mole/l	REACTION TIME	= 120 min
$AlEt_2Br$	= 0·075 mole/l	ISOPRENE	= 5·0 ml
Al/V RATIO = 3		TEMPERATURE	= 30 °C

Table - XX

Effect of Reaction Time

VCl_4 = 0.025 mole/1 Isoprene = 5.0 ml
$AlEt_2Br$ = 0.075 mole/1 Aging time = 1 hr.
Al/V ratio = 3 Temperature= 30°C

	Reaction time min.	Yield in gms.	Percent conversion	Percentage of insoluble and cyclic polymer
(1)	30	0.224	6.60	44.0
(2)	60	0.385	11.32	51.4
(3)	120	0.718	21.11	68.6
(4)	180	0.648	19.05	61.9
(5)	240	0.658	19.34	57.2
(6)	300	0.828	24.33	51.4
(7)	360	1.488	43.73	47.2

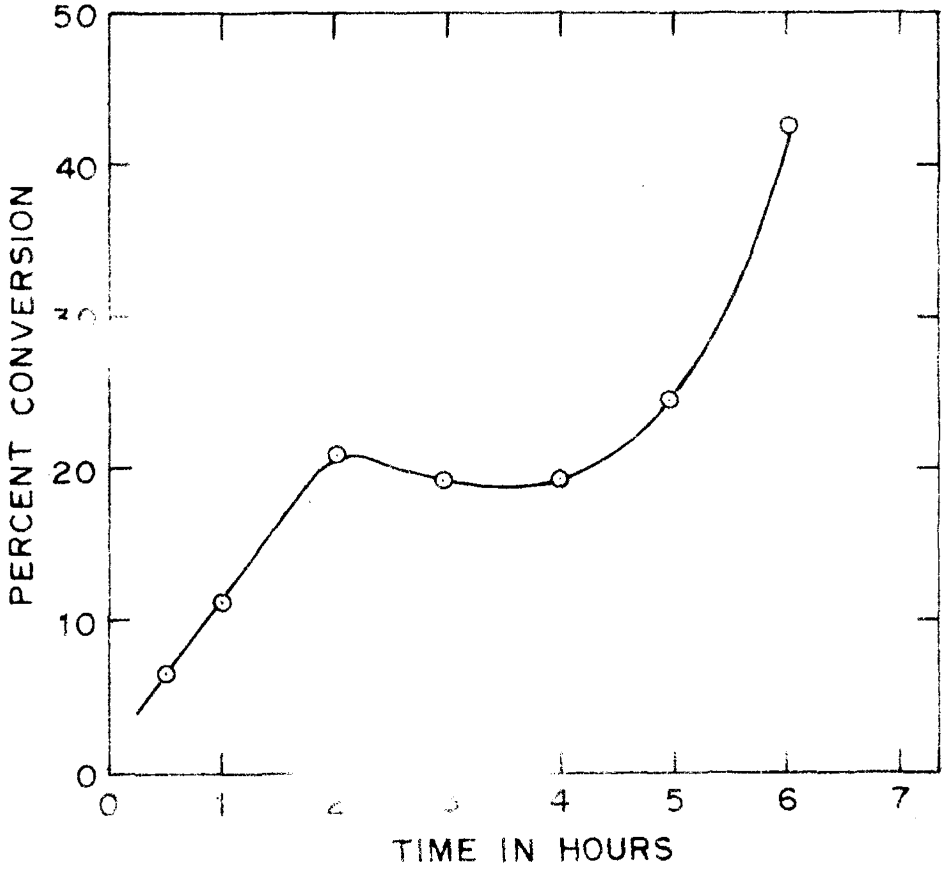


FIG. 16 EFFECT OF REACTION TIME ON VCl_4-AlEt_2Br SYSTEM

VCl_4 = 0·025 mole/l

$AlEt_2Br$ = 0·075 mole/l

Al/V RATIO = 3

AGING TIME = 1 hr

ISOPRENE = 5·0 ml

TEMPERATURE = 30 °C

Table - XXI

Effect of Catalyst Concentration

Al/V ratio = 3 Isoprene = 5.0 ml
Reaction time = 1 hr. Temperature = 30°C
Aging time = 1 hr. Total volume = 25 ml

	Catalyst concentration M/L	Yield in gms.	$R_p \times 10^5$ M/L/S
(1)	0.01	0.159	2.62
(2)	0.02	0.351	5.30
(3)	0.025	0.385	6.04
(4)	0.03	0.579	9.44
(5)	0.04	0.751	11.88

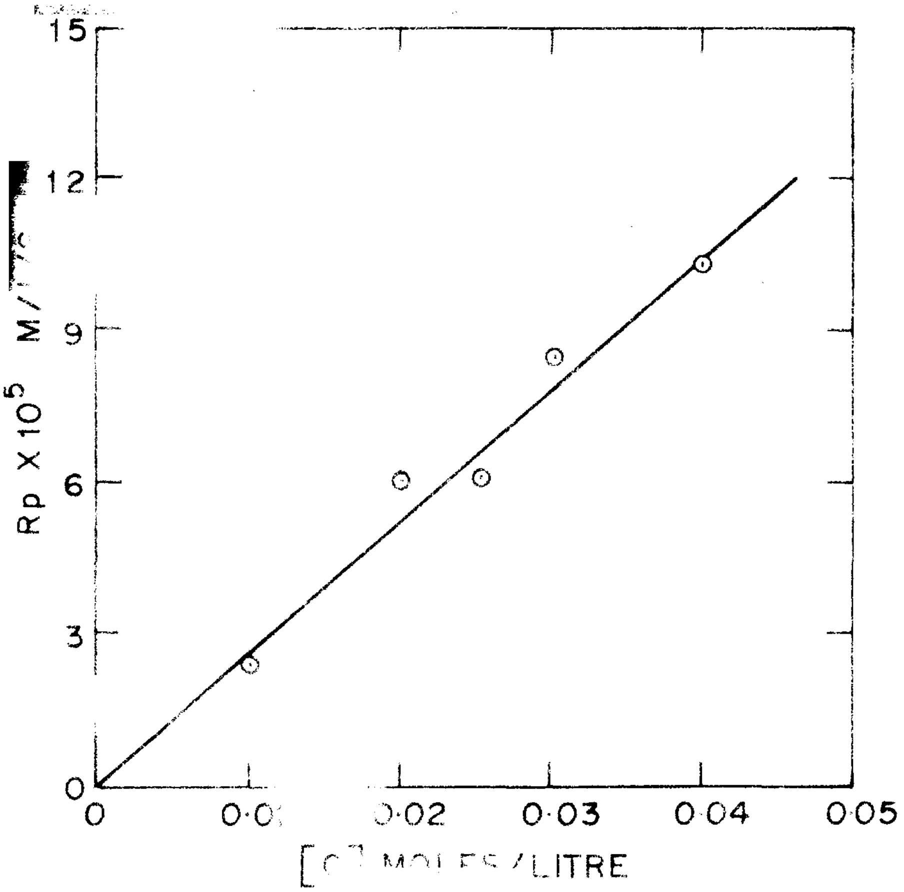


FIG. 17 EFFECT OF CATALYST CONC. ON VCl_4–$AlEt_2Br$ SYSTEM

ISOPRENE = 5·0 ml
TOTAL VOL. = 25 ml
Al/V RATIO = 3

AGING TIME = 1 hr
REACTION TIME = 1 hr
TEMPERATURE = 30 °C

Table - XXII (Fig.18).

3.4.5 Effect of Temperature on Polymerization

Polymerizations were carried out at different temperatures i.e. 20°, 30°, 40° and 50°C with 60 minutes reaction time. It was found that the rate of polymerization increased with temperature, the overall activation energy calculated from the plot of log R_p vs. 1/T between 20° and 50° was 8.96 Kcal/mole.

Results are tabulated in Table - XXIII (Fig.19).

Table - XXII

Effect of Monomer Concentration

VCl_4 = 0.025 mole/l   Aging time = 1 hr.
$AlEt_2Br$ = 0.075 mole/l   Reaction time = 1 hr.
Al/V ratio = 3   Temperature = 30°C

	Monomer concentration M/L	Yield in gms.	$R_p \times 10^5$ M/L/S
(1)	0.8	0.188	3.10
(2)	1.6	0.436	7.12
(3)	2.0	0.386	6.04
(4)	2.4	0.745	12.26
(5)	3.2	0.912	15.01

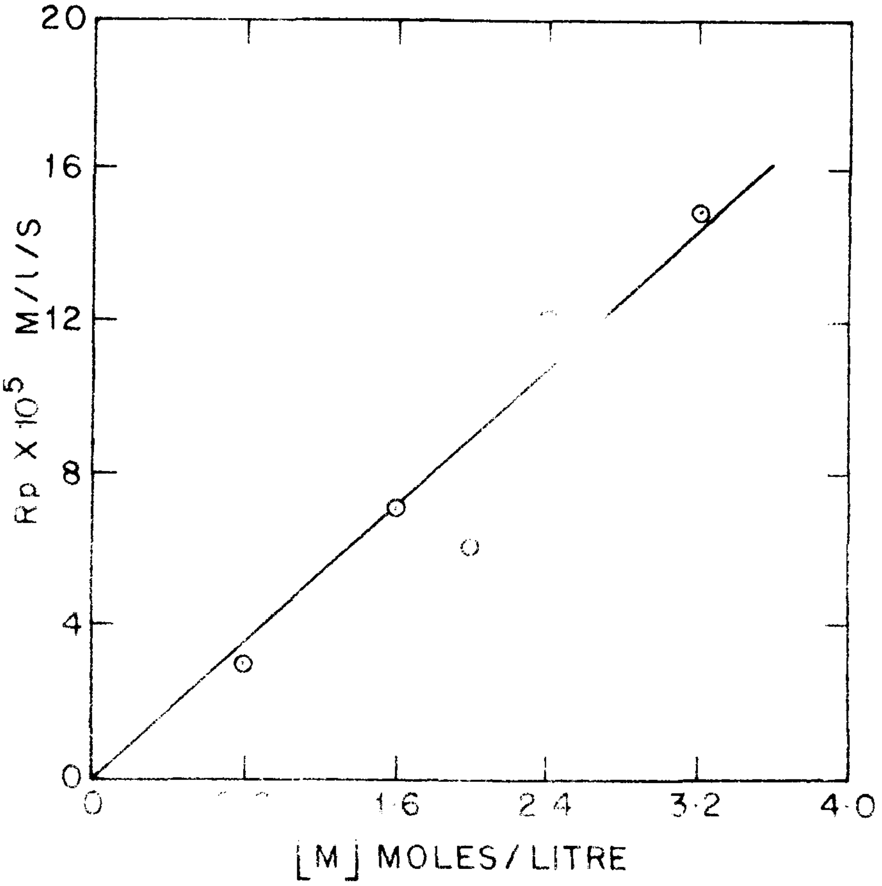


FIG. 18 EFFECT OF MONOMER CONC. ON VCl_4-AlEt_2Br SYSTEM

VCl_4 = 0·025 mole/l
$AlEt_2Br$ = 0·075 mole/l
Al/V RATIO = 3

AGING TIME
REACTION TIME = 1 hr
TEMPERATURE 30 °C

Table - XXIII

Effect of Temperature

VCl_4 = 0.025 mole/l   Isoprene = 5.0 ml
$AlEt_2Br$ = 0.075 mole/l   Aging time = 1 hr.
Al/V ratio = 3   Reaction time = 1 hr.

	Temperature °C	Yield in gms.	$R_p \times 10^5$ M/L/S	Log R_p	$(10^3 \times \frac{1}{T})$ $°K^{-1}$
(1)	20	0.250	4.12	$\bar{5}.6141$	3.41
(2)	30	0.385	6.04	$\bar{5}.8025$	3.30
(3)	40	0.686	11.13	$\bar{4}.0525$	3.19

Activation Energy = 8.96 K.oal/mole.

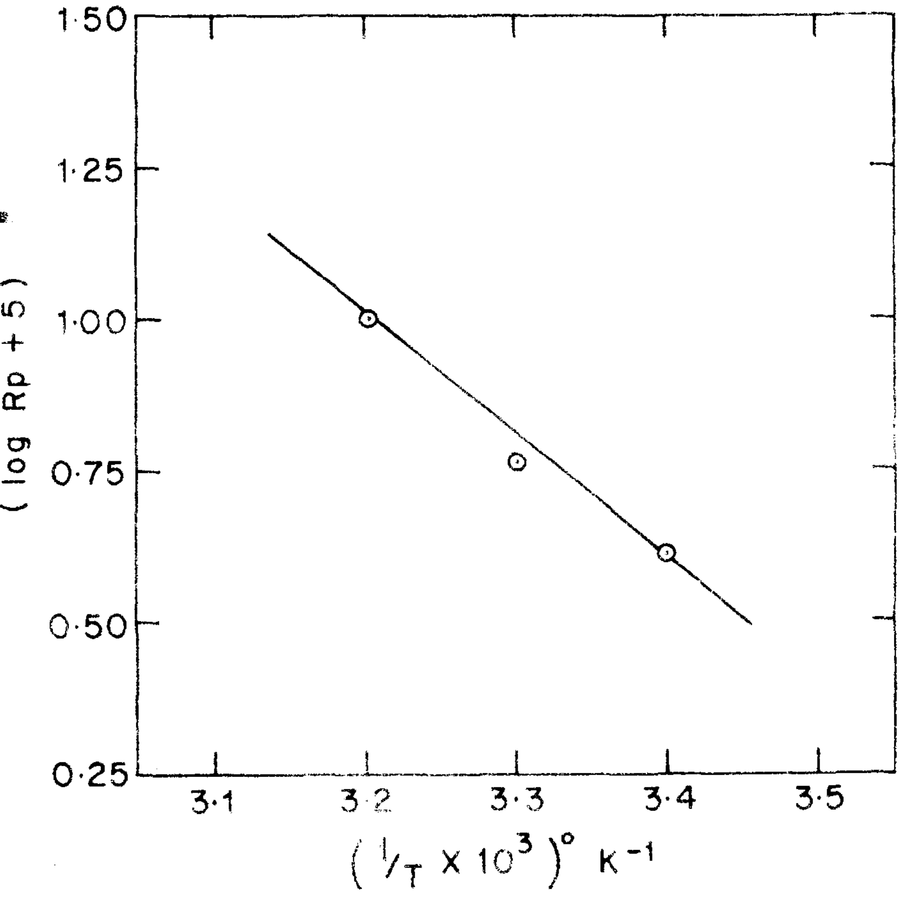


FIG. 19 EFFECT OF TEMPERATURE ON VCl_4–$AlEt_2Br$ SYSTEM

VCl_4 = 0·025 mole/l

$AlEt_2Br$ = 0·075 mole/l

Al/V RATIO = 3

AGING TIME = 1 hr

REACTION TIME = 1 hr

ISOPRENE = 5·0 ml

CHAPTER - IV

DISCUSSION

DISCUSSION

4.1 Preparation of the Catalyst System

4.1.1 Purity of Catalyst Components and Stirring of Reaction Mixture

As explained in the Experimental Section, every effort was made and all precautions were taken to purify and dry the reagents thoroughly, to exclude contamination during mixing in the 'dry box' and subsequent handling of the reaction vessel in the thermostat. However, the particle size of the catalyst precipitate and its surface area are still uncontrolled variables. The agitation of reaction mixture by magnetic stirrer is another important factor not only for heat dissipation but also for the separation of the polymer formed from the catalyst surface. It was hence necessary to control the stirring at a constant level (1000 rpm.).

Reproducibility obtained in our experiments varied from system to system and was found to be (5 to 10%) within the same range as reported by other workers[147-149]. It can be seen that reproducibilities are fairly good, considering the various difficulties inherent with such systems containing highly reactive metal alkyls and transition metal halides.

4.1.2 Order of Addition of the Catalyst Components

In order to obtain reproducible results of polymerization with these catalysts, it is necessary to find the conditions under which the catalyst complexes once formed, do not apparently change in activity in a given time. Therefore to get catalyst sites of constant activity, the catalyst solutions were mixed and aged for definite periods prior to the addition of monomer. The presence or absence of monomers during the preparation of catalyst from the reaction of catalyst[150,151] components can have a profound effect on the behaviour of the catalysts. The following order of addition of reagents as given below, was therefore observed in order to get same type of catalyst complex.

(1) Solvent
(2) Transition metal halide
(3) Metal alkyl solution
(4) Monomer (after aging of the catalyst complex)

4.1.3 Colour of Reaction Complex

A chemical reaction was immediately seen on addition of metal alkyl solution to $VOCl_3$ or VCl_4 in hydrocarbon and carbon tetrachloride medium. This reaction is very fast in case of carbon tetrachloride medium but is comparatively slower in case of hydrocarbon medium. In the case of $VOCl_3$-$AlEt_2Cl$ and $VOCl_3$-$AlEt_2Br$ catalyst system, the colour changes quickly from pale yellow (the colour of $VOCl_3$ solution) to dark brown and later to black. There was also some effervescence. A dark brown coloured precipitate was instantaneously formed on ~~the~~ mixing the solution of alkyls with VCl_4 solution, irrespective of their concentration.

In the case of $VOCl_3$-$AlEt_2Br$ and VCl_4-$AlEt_2Br$ catalyst systems in carbon tetrachloride medium, instantaneous~~ly~~ black precipitate was formed, and after induction period which depends on concentration of alkyl as well as amount of carbon tetrachloride, decomposition took place with evolution of gases and large amount of heat was produced.

The precipitate obtained after the completion of reaction of metal alkyl with $VOCl_3$ or VCl_4 obviously contained various complexes that can be formed with different atomic ratios of aluminium metal to vanadium and very likely differ in the valence state of vanadium, as observed in previous study. A series of step-wise reactions, fast as well as slow, can be visualised forming various catalytic species of differing stabilities leading to the final catalyst complex.

4.1.4 Location of Catalyst Sites on the Heterogeneous Surface

The location of active catalyst sites on the precipitated complex could be surmised from the percent conversion vs. time plots.

It was observed that in the case of $VOCl_3$-$AlEt_2Cl$ and $VOCl_3$-$AlEt_2Br$ for polymerization of methyl methacrylate, the activity was maintained for 180 minutes. However, in case of $VOCl_3$-$AlEt_2Cl$ catalyst system, activity increases rapidly upto 3 hours reaction time and thereafter increases slowly (Table - III, Fig.3). In case of $VOCl_3$-$AlEt_2Br$ for polymerization of methyl methacrylate and VCl_4-$AlEt_2Br$ for polymerization of isoprene, the initial catalytic activity decreased to low steady values in 240 min. and 120 min. reaction time respectively (Tables - X, XX, Fig.8, 16).

The initial decrease of catalytic activity in these cases is probably not due to deactivation of catalysts but more likely due to clogging of the catalyst surface by polymer precipitated in the insoluble medium e.g. n-hexane. The propagation reaction thus slows down due to lesser availability of monomer at the catalyst sites on the surface. The steady rate is probably controlled entirely by the diffusion of monomer through the polymer covering the catalyst sites. A spontaneous termination reaction would not be effected by the rate of diffusion of monomer. The retardation of diffusion controlled propagation will hence manifest itself as a decrease in the rate of polymerization. This is clearly visible in case of $VOCl_3$-$AlEt_2Br$ catalyst system for polymerization of methyl methacrylate and isoprene. In the heterogeneous catalyst systems in n-hexane percentage conversion reaches a low steady value after fixed reaction time due to poor availability of catalyst sites and the molecular weight remains constant, thereby showing that the decrease in the activity of catalyst is entirely controlled by diffusion of monomer (Table - III, X, Fig. 3, 8).

Loss of catalytic activity due to deposition of polymer on the catalyst particles has been also reported for styrene polymerization with $TiCl_4$-$AlEt_3$, $VOCl_3$-Al alkyls[152] catalyst systems by Burnett and coworkers[147] and earlier from this Laboratory[153]. In fact, photomicrographs taken at various stages of reaction revealed considerable agglomeration of catalyst particles bound together by polymer[14,154]. 3-Methyl butene-1 and butene-1 have been also found to yield an insoluble crystalline co-polymer with $TiCl_4$-$Al-(iBu)_3$ catalyst system[149] and the rate of polymerization fell gradually to zero after about an hour. The same effect of covering of the catalyst particles has been also observed from the studies of the effect of temperature on rate of polymerization of ethylene with Ziegler-Morton catalysts[155]. This effect is not expected to be due to poisoning of the catalyst sites. The probable explanation given is the build up of a polymer around the catalyst particle. The diffusion of ethylene through a layer of polyethylene could be a possible rate limiting process if the catalyst is present as particles larger than 1 to 10 μ in diameter. From the sedimentation and filtration behaviour, the agglomerates were reported to be larger than 10 μ. Thus the observation of rate limiting process is confirmed if the catalyst particle size is larger than 10 μ.

The importance of the role of solvent in desorption and dissolution of polymer from the catalyst surface, to keep the sites active, is evident if the experiments are carried out with reaction times higher than 15 minutes. Recent studies of Berger and Grieveson[156] also clearly show the phenomena of agglomeration in the polymerization of ethylene with a stable catalyst δ $TiCl_3$-$AlEt_2Cl$. Increase in particle size as the polymerization proceeds can be clearly observed in the microphotographs. Similarly, Hargitay et al[157] and more recently Rodriguez and Van Looy and Gabant et al[158] using electron microscopy to follow the initial polymerization of propylene on α-$TiCl_3$ crystals, concluded that polymer growth took place at the lateral faces where the titanium atoms are directly accessible for complexing of the olefin. Similar conclusions were reached by Arlman and Cossee[159].

From the above considerations as well as our experimental results, it can be concluded that the catalyst sites are located on the surface of precipitated complexes in the system and one type of catalyst sites exist for certain period of time. The polymer precipitated may cover the catalyst sites, ultimately bringing a change in the course of reaction. Finally, it may be concluded that the catalyst sites having particular behaviour can be obtained on strictly maintaining the above observed conditions.

4.2 Active Catalyst Sites

Anhydrous nitrogen atmosphere is indispensible for the preparation of the active catalyst complex of Ziegler-Natta catalyst system. Immediately on exposure to the atmosphere, moisture and atmospheric oxygen react with them, resulting in the destruction of various active compounds. Furthermore, the catalyst complex being in the precipitated form, they could not be analysed by conventional physical methods, which have been extensively used with homogeneous solutions.

The determination of the yield of polymer and molecular weight by changing the ratio of catalyst components and variations of temperature of reaction, has led to the probable composition of the catalyst complex containing maximum number of active sites. However, the composition of catalyst complex is mandatory to understand exactly the oriented state of the monomer and the placement during its polymerization.

Inspite of the difficulties of handling of the catalyst components due to their sensitivity to moisture and oxygen, the field of investigation with the physical methods progressed rapidly only after the discovery of homogeneous catalyst systems such as dicyclopentadienyl titanium chloride and aluminium alkyl[37] as well as titanium tetrabutoxide and aluminium alkyls[41]. Physical methods have been focussed mainly on the size of the particles of catalyst complex, the crystalline nature of the transition metal salt, the position and nature of various molecular groups in the complex and the formation of bridge bond between the metal and carbon atom. The maximum activity of catalyst complex is usually related to the molar ratio of catalyst components which are responsible to produce active sites[136].

The heterogeneous nature of the catalyst has been observed to be responsible for the stereoregularity of polymers. The homogeneous catalyst systems could not produce the stereoregular polymer of α-olefins. Natta et al[54] pointed out that $TiCl_3$ exists in three different crystalline forms of α, β, γ . In the polymerization of propylene, α and γ

forms are hexagonal crystals and they produce more stereoregularity whereas β form which produces a less stereoregular polymer is a linear crystal. The particle size of catalyst complex was also not very much important, since it changes during polymerization reaction. Under these circumstances, the chemical nature of the propagation mechanism remained ambiguous. In this respect, the determination of the structure of catalyst complex is very essential to understand the mechanism of reaction.

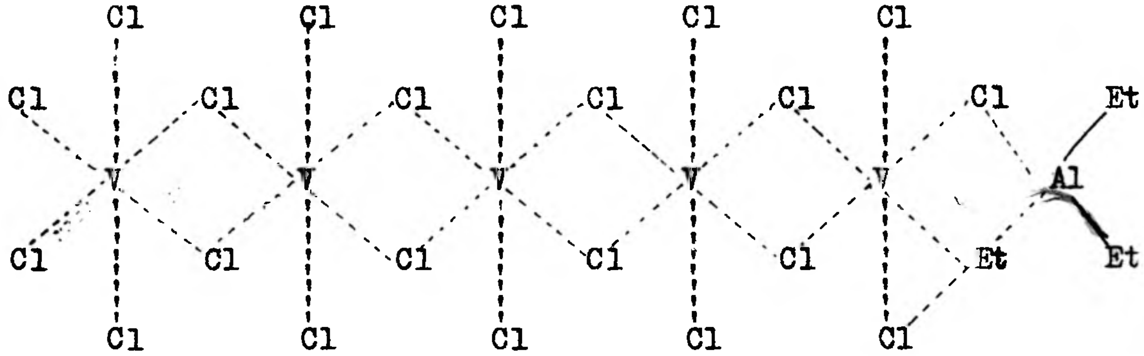
4.3 Valence of Vanadium in the Catalyst Complex

The variation of valency of transition metal on mixing with different co-catalysts has been the subject of considerable study[91,136]. Many investigations have assigned a formal oxidation state of vanadium in Ziegler-Natta polymerization. For example, Carrick and his coworkers[162-164] concluded that some divalent vanadium may be prerequisite for catalyst activity. They found that the vanadium based catalyst had no activity until part of vanadium was reduced to bivalent state.

Catalysts active for ethylene and propylene polymerizations are formed by combining VCl_2 and $AlEt_3$ showing that divalent salts are active. Cossee's theory[165] of catalytic polymerization activity includes V(II) because it allows for activity in transition metal ions with three unpaired electrons.

De Liefde Meijer et al[166,167] looked at similar catalysts and concluded that either V(II) or V(III) could be active sites. Netta's[12] study showed that when temperature increased V(II) in catalyst complex increased and activity decreased for the polymerization of propylene with VCl_3-$AlEt_3$ catalyst system. When same study was carried out by using $AlEt_2Cl$, the catalytic activity increased with increase in temperature. In this case, no divalent vanadium was detected. These studies showed that trivalent vanadium was an active catalyst.

Cooper[41] and A.Zambelli et al[168] suggested that the active catalyst contains, the alkylated grouping $RVCl_2$. The conditions which yielded increased activity in the presence of monomer also lead to increased V(II) formation than in its absence, and this is consistant with the active centre containing $RVCl_2$. Since VCl_3 has a layer structure like $TiCl_3$, it is not reasonable to assume that the active catalytic centre has the structure, with epitactic absorption of the aluminium alkyl on the crystal surface as shown below:



Recently[169] even V(IV) and V(V) oxidation states have been suggested for catalyst complex. A good agreement between the conductivity and activity has been established by Bushik and others[170], in case of esters of orthovanadic compounds and aluminium tri(iso)butyl catalyst systems. The conductance decreased in order of $VOCl(OC_2H_5)_2$ > $VOCl_2(OC_2H_5)$ > $VO(OC_2H_5)_3$ > $VO(O\text{-}n\text{-}C_4H_9)_3$ and maximum conductivity was obtained in the range of ratios for Al/V of 4 to 8. There is good co-relation between the activity and ionic character of catalyst systems, showing that these catalyst systems are ionic in nature in the active sites.

Other investigators[171-176] studying different vanadium catalysts concluded that V(II) is active state. Marvin Lehr[137] has successfully suggested two active complexes containing V(III), by determination of the active oxidation state of vanadium in olefin polymerization with catalysts prepared from VCl_4-$AlEt_2Cl$ catalyst system. One of oxidation state was much more active but less stable than the other. The more active catalyst sites evidently are produced from an inactive V(III) precursor and the origin of the less active V(III) catalyst could not be traced out. A potentially active V(II) complex was examined under the same conditions as for V(III) complex. On the whole there is no conclusive evidence for catalytic activity in the V(II) complex from the experimental study, even though theoretically it was suggested that V(II) oxidation state should be more active in olefin polymerization, as given in the scheme overleaf.

$$VCl_4 + R_2AlCl \xrightarrow[\text{fast}]{K_1} RVCl_3 + RAlCl_2$$

$$4R_2AlCl + 2\ RVCl_3 \xrightarrow[\text{fast}]{K_2} 2\ VCl_3\cdot(R_2AlCl_2)_2 + 2R\cdot$$

$$VCl_3(R_2AlCl)_2 \xrightarrow[\text{slow}]{K_3} RVCl_2\cdot(R_{1.5}AlCl_{1.5})_2$$

$$RVCl_2\cdot(R_{1.5}AlCl_{1.5})_2 + nM \xrightarrow[\text{slow}]{K_p} RMn\ VCl_2\cdot(R_{1.5}AlCl_{1.5})_2$$

$$2RMnVCl_2\cdot(R_{1.5}AlCl_{1.5})_2 \xrightarrow[\text{slow}]{K_t} 2(RMn)+2VCl_2\cdot(R_{1.5}AlCl_{1.5})_2$$

In our present study with $VOCl_3$-$AlEt_2Cl$ catalyst system for polymerization of methyl methacrylate, it was observed that the catalyst activity increased very much in comparison with $VOCl_3$-$AlEt_3$ catalyst system. The increase in activity may be related to the increase in V(III) catalyst complex as observed by Svab, Jaroslav et al[124]. The catalytic activity observed in case of $VOCl_3$-$AlEt_2Br$ was low as at higher ratio of Al/V and after 24 hours aging time there is decrease in activity due to aging and due to increase in V(II) catalyst complex, as observed by Lehr[137]. We found that at higher valence states of vanadium, $VOCl_3$-$AlEt_2Br$ and VCl_4-$AlEt_2Br$ catalyst systems in carbon tetrachloride did not polymerize methyl methacrylate, instead complexes were formed.

Recently Svab, Jaroslov et al[124] studied the catalytic efficiency of VCl_4 and $VOCl_3$ with alkyls such as $AlEt_3$, $AlEt_2Cl$, $AliBu_3$ and $AliBu_2Cl$ for polymerization of propylene in temperature range -80° to 25°C. These catalyst systems were divided into three groups according to average valency of vanadium which also changes with temperature.

4.4 Reaction Schemes for Complex Formation and the Structure of Catalyst Complex

4.4.1 Reactions of Al-alkyls and Vanadium Compounds

Reactions of aluminium alkyls with vanadium compounds have not been studied in detail, but all the available evidence indicates a general parallelism between the behaviour of Ti-compounds and vanadium compounds.

Very recently on the basis of infrared spectroscopy and gasometry studies, Misono and coworkers[177] have given further insight into the active site of the $VO(OEt)_3$-$AlEt_3$ catalyst systems. Results obtained have suggested that the catalyst system is not a mere mixture of the two components but that some ligand exchange reaction had taken place, leading to the formation of Al-O-Et and V-Et structure in the catalyst complex

$$VO(OEt)_3 + AlEt_3 \rightarrow EtVO(OEt)_2 + AlEt_2(OEt)$$

This is followed by the reductive dealkylation of the unstable organovanadium compound.

$$EtVO(OEt)_2 \rightarrow VO(OEt)_2 + Et.$$

At higher Al/V molar ratios, ligand exchange and reductive dealkylation may be considered to proceed successively.

All the results obtained can be summarised in the statement that the interaction of aluminium alkyls with

V(V) and V(IV) derivatives, yields reduction products of these compounds. The active sites contain an unstable vanadium-carbon bond resulting from the ligand exchange reaction taking place between the two components

Formation of organo vanadium compounds during the reaction of vanadium halides with metal alkyls has been studied and reported by Carrick et al[162-164] for a reaction of diphenyl mercury with $VOCl_3$. Reaction carried out in cyclohexane at room temperature produced a deep red solution with the formation of phenyl mercuric chloride in the precipitate according to the equation given below:

$$(C_6H_5)_2Hg + VOCl_3 \rightleftarrows C_6H_5VOCl_2 + C_6H_5HgCl \downarrow$$

This reaction is very rapid and the precipitation of C_6H_5HgCl is essentially complete in 10 min. at room temperature. All vanadium is in the pentavalent state and half of phenyl groups of original amount remained in solution. The organo-vanadium compound so formed is unstable and decomposes over a period of about one hour at 30^o giving quantitative conversion to biphenyl and $VOCl_2$, as:

$$C_6H_5VOCl_2 \quad \rightarrow \tfrac{1}{2}\, C_6H_5C_6H_5 + VOCl_2$$

These experiments clearly indicate the formation of a compound with $VOCl_3$ and $HgPh_2$ but its structure was not rigorously proved. On the basis of a chemical reaction with HBR and IR studies, hydrolysis experiments showed that the phenyl group in this organo-vanadium compound is still intact and is bound to vanadium primarily by V-C single bond.

A kinetic study of VCl_4 or $VOCl_3$ with $(C_6H_5)_2Hg$ also led to the conclusion that the reaction involves intermediate formation of a diaryl derivative of vanadium. In this case, the mechanism includes intramolecular recombination with the formation of biphenyl. This mechanism of recombination is probably general for aryl derivatives, since biphenyl is very frequently the only or the main reaction product.

An alternate mechanism which satisfied unimolecular kinetics without production of radicals is illustrated by the sequence:

$$2C_6H_5VOCl_2 \rightleftharpoons (C_6H_5)_2\ VOCl + VOCl_3$$

$$(C_6H_5)_2\ VOCl \rightarrow (C_6H_5)(C_6H_5) + VOCl$$

Similarly, the reaction between VCl_4 and $Hg(Ph)_2$ has been found to occur as:

$$(C_6H_5)_2Hg + VCl_4 \rightleftharpoons (C_6H_5)VCl_3 + C_6H_5HgCl$$

and a decomposition through the non-radical type of mechanism as:

$$C_6H_5VCl_3 \rightarrow \tfrac{1}{2}\ C_6H_5C_6H_5 + VCl_3$$

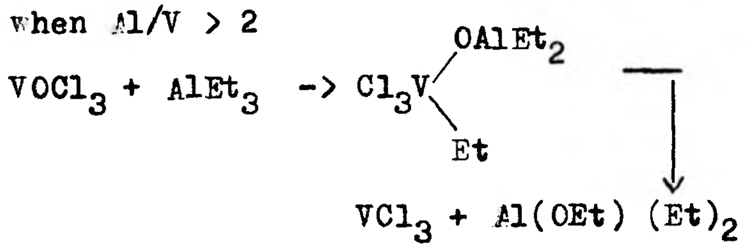
As biphenyl mercury is a mild alkylating agent compared to aluminium alkyls, the reaction between $VOCl_3$ and strong metal alkyls can be easily assumed to go to further stages of alkylation and reduction as the reaction proceeds. This is known from the reaction of $VOCl_3$ with aluminium alkyl, wherein vanadium gets converted to lower valence state. In reaction of $VOCl_3$ with $AlEt_3$ reported by Petrov and Korotkov[178], when the ratio of Al/V is increased, there is a sharp decrease in valence of vanadium in the catalyst which becomes +2 at Al/V=2 and it remains constant corresponding to VCl_3 bound in the complex as $VCl_2.AlClEt_2$. The amount of chlorine in the solution over the precipitate goes on increasing as the ratio is increased though the valence of vanadium remains constant. This reaction has been explained by an exchange reaction given as follows:

Case (I) when $Al/V < 2$

$$VOCl_3 + AlEt_3 \rightarrow EtVOCl_2 + AlClEt_2$$

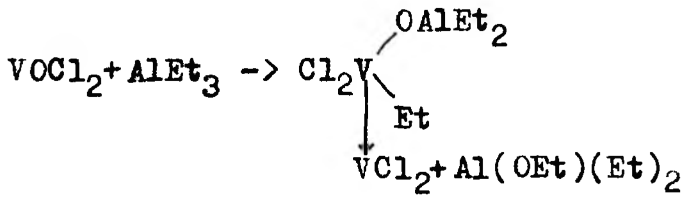
$$EtVOCl_2 \rightarrow VOCl_2 + Et$$

Case (II) when $Al/V > 2$



$$VOCl_3 + AlEt_3 \rightarrow Cl_3V\begin{matrix} OAlEt_2 \\ Et \end{matrix} \rightarrow VCl_3 + Al(OEt)(Et)_2$$

$$VCl_3 + AlEt_3 \rightarrow EtVCl_2 + AlCl(Et)_2 \rightarrow VCl_2 + AlCl + (Et)_2 + Et$$



$$VOCl_2 + AlEt_3 \rightarrow Cl_2V\begin{matrix} OAlEt_2 \\ Et \end{matrix} \rightarrow VCl_2 + Al(OEt)(Et)_2$$

$$VCl_2.AlCl.(Et)_2 + AlEt_3 \rightleftharpoons VCl_2.AlEt_3 + AlCl(Et)_2$$

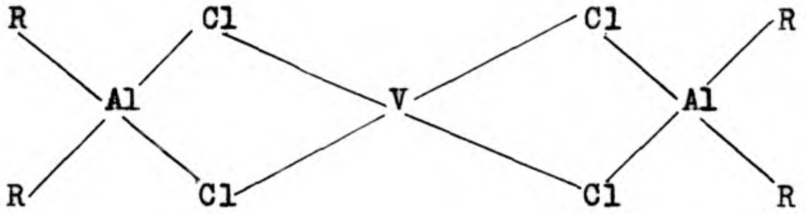
$$VCl_2Al(OEt)(Et)_2 + AlEt_3 \rightleftharpoons VCl_2.AlEt_3 + Al(OEt)(Et.)_2$$

These reaction schemes can provide an explanation for the drop in catalytic activity with the increase in Al/V ratio. However, it is suggestive from this scheme that complex of VCl_2-$AlEt_3$ would not be effective in polymerization. The average valence of vanadium earlier reported from this Laboratory[179] for this catalyst system was +3 at various Al/V ratios and differed from that of +2, suggested by Carrick et al[162-164] and Korotkor et al[178]. The above findings indicate that only one ethyl group reacts from one $AlEt_3$ molecule for reduction, and there will be two ethyl groups per aluminium atom in the complex.

4.4.2 Determination of the Structure of Catalyst Complex by Physical Methods

In case of vanadium based catalyst systems, modern techniques of analysis of catalyst complex by ESR, NMR are found to be very useful to determine the structure of the catalyst complex.

Natta et al[180] and Schulyndin et al[181] tried to establish the structure of vanadium containing catalyst system with ESR and NMR and from hyperfine structure, they proposed a structure for vanadium catalyst system. Natta[180] found the valence of vanadium as +2 observing the close resemblance of signals between VCl_2 and that of VCl_4-$AlEt_2Cl$, VCl_4-$AlEt_2Cl$-anisole and $V(AcAc)_3$-$AlEt_2Cl$ catalyst systems. Angelescu et al[182] independently reported that the catalyst system $VO(AcAc)_2$-$AlEt_2Cl$ produced a typical 8 lines spectrum. In case of VCl_4-$AlEt_3$, the 'g' value in benzene obtained by Schulyndin et al[181] was 1.992 which is typically close to a free radical value. The overall width of 510 oersted is split into 8 equivalent lines. It is attributed to the interaction of an unpaired electron with the vanadium nucleus (I=7/2) as each component of catalyst system has a fine structure of 11 to 13 lines and the replacement of C_2H_5 by C_2D_5 did not alter the spectrum. The fine structure is hence assumed to be formed by the interactions with 4 Cl atoms of a bridge complex



Natta[180] also reported that at lower temperatures when the valence of vanadium was +3, it gave highly isotactic polypropylene whereas at higher temperatures, when the valence of vanadium was +2, it gave poor isotactic polymer. Thus, at higher temperatures, vanadium is reduced to lower valence state due to more alkylation and reduction.

On the basis of ESR spectra at various temperatures, Zambelli et al[183] discussed the reaction between VCl_4 and AlR_2X. Formation of some products as VCl_2R and $AlCl_2R$ were determined and it was proposed that this catalyst system did not contain divalent vanadium. The active species were a halogen-bridged bimetallic complex between $EtVCl_2$ and $AlEtCl_2$ formed in the reaction sequence, as given overleaf.

$$VCl_4 + 2AlEt_2Cl \rightarrow Et_2VCl_2 + 2AlEtCl_2$$

$$Et_2VCl_2 \rightarrow EtVCl_2 + Et.$$

No divalent vanadium was detected in the catalyst formed by combining VCl_3 and $AlEt_2I$[184]. Nicolescu and Angelescu[185] have also carried out a detailed investigation on the activity and electrical conductivity of $VO(C_5H_7O_2)_2$-$AlEt_3$ catalyst system, and have suggested a structure for the complex formed. The highest catalytic activity of this system was found at Al/V ratio of 2. The visible and ultraviolet absorption spectra showed that the catalytic complexes formed in the case of $VO(AcAc)_2$-$AlEt_3$, $Cr(C_5H_7O_2)_3$-$AlEt_3$ and $Co(C_5H_7O_2)_3$-$AlEt_3$ had identical structures. Variation of extinction coefficient as a function of the $AlEt_3/M(C_5H_7O_2)_n$ established that the optimal complexing ratio was identical with the ratio of the maximum catalytic activity. The maximum conductivity values were also found at Al/V ratio of 2 in $VO(C_5H_7O_2)_2$-$AlEt_3$ catalyst system. The activation energies obtained by the electrical conductivity method showed small values of about 3000 cal/mole for the above catalyst system. The valence of vanadium as determined by ESR was +3, the following structure was proposed for the above catalyst complex:

$$[\ AcAc\ V^{+3}\ OAlEt\ AcAc\ ]^+$$

Obloj and coworkers[186] reported that the $VOCl_3$-$AlEt_2Cl$ catalyst system, active for copolymerization of ethylene and propylene, contained vanadium with an average valence of 2-3.

For elucidation of mechanism of vinyl polymerization with Ziegler-Natta catalysts, the ESR absorption of the polymerization system was attempted by Furukawa and coworkers[45,102]. $VOCl_3$ had shown absorption signals when dissolved in methyl methacrylate or THF. VO^{++} and V^{4+} have also been shown to have absorption signals. However, in the case of $VOCl_3$-$AlEt_3$ no signals were observed even at the temperature of dry ice thus disproving the presence of free radicals in the polymerization reaction.

4.4.3 Effect of an Electron Donor on Catalyst Sites

Basic additives[15] have been reported to improve the selectivity of Ziegler-Natta catalyst systems considerably. The introduction of additives in the complex is known to change[170] the bond energy and the environment of Ziegler-Natta catalyst components. Various explanations have been suggested[15,79] for enhancement of rate of polymerization by the addition of the electron donor.

In earlier studies[187], it was shown that the basic additives increase the rate of polymerization of methyl methacrylate and change the structure and molecular weight of polymer. It was also concluded that the basic additives particularly favour the sites for syndiotactic structure. In our studies for polymerization of methyl methacrylate with $VOCl_3$-$AlEt_2Cl$ and $VOCl_3$-$AlEt_2Br$ catalyst systems, we observed that there is increase in percentage of syndiotacticity with the addition of triethyl amine (see Table - XXIV).

4.5 Behaviour and Mechanism of Ziegler-Natta Catalyst Complexes in the Polymerization Reactions and Structure of Polymer

4.5.1 $VOCl_3$-$AlEt_2Cl$ Catalyst System in n-hexane for the Polymerization of Methyl Methacrylate

As already known[119-121] the colour of reaction became dark brown upon addition of catalyst components in n-hexane. The same colour persisted on addition of monomer, indicating presence of undisturbed catalyst sites. The ratio of Al/V was changed by keeping the concentration of $VOCl_3$ constant in order to find out the ratio of maximum activity. It was observed that the catalytic activity was maximum at ratio of Al/V=2 and 7 (Table - II, Fig.2). This showed the formation of two active sites. It is certain that active sites are varying with ratio of Al/V but the behaviour of catalyst complex at Al/V ratio of 2 and 7 does not seem to be different. The rate of polymerization showed maximum activity at ratio of Al/V=7, but for comparison of catalytic efficiency and stereospecificity with $VOCl_3$-$AlEt_3$ catalyst system, the ratio of Al/V=2 was chosen for further studies, since the molecular weight of polymer was maximum at ratio of Al/V=2. It was observed that the catalyst after aging for 20 minutes was very active and the polymer produced after 3 hours reaction time had high molecular weight (see Table - I, III (Fig.1,3).

In order to study kinetics of polymerizations, the

Table - XXIV

Effect of Additives on Polymerization

Additive	$R_p \times 10^6$ M/L/S	Molecular weight	Percentage of syndiotactic, heterotactic and isotactic units from NMR spectra		
			S 9.14 τ ppm	H 8.98 τ ppm	I 8.78 τ ppm
(1) No additive	11.00	85,500	47	38	15
(2) Hydroquinone (50 mgm)	8.96	114,000	46	40	14
(3) Triethylamine (0.05 mole/1)	18.74	98,120	60.5	35	14.5

$VOCl_3$-$AlEt_2Cl$ Catalyst System

Al/V ratio = 2 Aging time = 20 min.

[Catalyst] = 0.025 mole/1 Reaction time = 180 min.

[MMA] = 1.88 mole/1 Temperature = 40°C

polymerizations were carried out by changing catalyst and monomer concentration at selected conditions such as ratio of Al/V=2, aging time =20 min., reaction time = 180 min. It was observed that the rate of polymerization increased linearly with increase in catalyst (Table -IV, Fig.4) and monomer (Table - V, Fig.5) concentrations. However, the molecular weight was inversely proportional to catalyst concentrations and linearly increased with monomer concentration, as in case of other Ziegler-Natta catalyst[119-121].

In view of this, polymerization of methyl methacrylate at ratio of Al/V=2 seems to follow co-ordinate anionic mechanism. The overall activation energy equal to 9.25 Kcal/mole obtained from plot of log R_p vs. 1/T (Table - VI, Fig.6) for this system further lends support to co-ordinate anionic mechanism of polymerization.

It is a well known fact that the mechanism of polymerization has great influence on the structure of polymer. Likewise, the structure of polymer obtained throws light on the mechanism of polymerization.

The structure of polymethyl methacrylate was studied by examining the NMR spectra recorded at ratio of Al/V=2 (Fig.20a). The NMR spectra of polymethyl methacrylate showed presence of isotactic 8.78 ↑, heterotactic 8.98 ↑ and syndiotactic 9.14 ↑ units, indicating that the polymer has stereoblock structure.

Wiles[188] had given very good account of crystalline and stereoregular polymethyl methacrylate with different catalysts. Coleman and Fox[189] have proposed that the stereoblock polymers are produced by two stage anionic polymerization. Very recently, stereoblock formation of methyl methacrylate with anionic initiators is also supported by the work of Lim et al[190].

The study of effects of addition of hydroquinone - an inhibitor of free radical polymerization- and triethyl amine to catalyst complex revealed that there is no effect on rate of polymerization with the addition of hydroquinone but molecular weight increased and the rate of polymerization as well as molecular weight increased with the addition of triethyl amine (Table - VII, VIII). These facts clearly rule out free radical mechanism and seem to lend support to co-ordinate anionic mechanism of polymerization.

Further, the NMR spectra recorded for these polymer samples showed that with addition of hydroquinone (Table - XXIV, Fig.20b), stereoblock structure remained same but there is increase in the percentage of syndiotacticity with the addition of triethyl amine (Table -XXIV, Fig.20c) as observed earlier[187].

The slight increase in percentage of syndiotacticity observed with $VOCl_3$-$AlEt_2Cl$ catalyst system, as compared with $VOCl_3$-$AlEt_3$ catalyst system (Table - XXXII), may be attributed to increase in amount of average V(III)[191] because of less reduction to V(II) by $AlEt_2Cl$.

Natta[103] has discussed in detail the formation and properties of the stereoblock, isotactic, atactic

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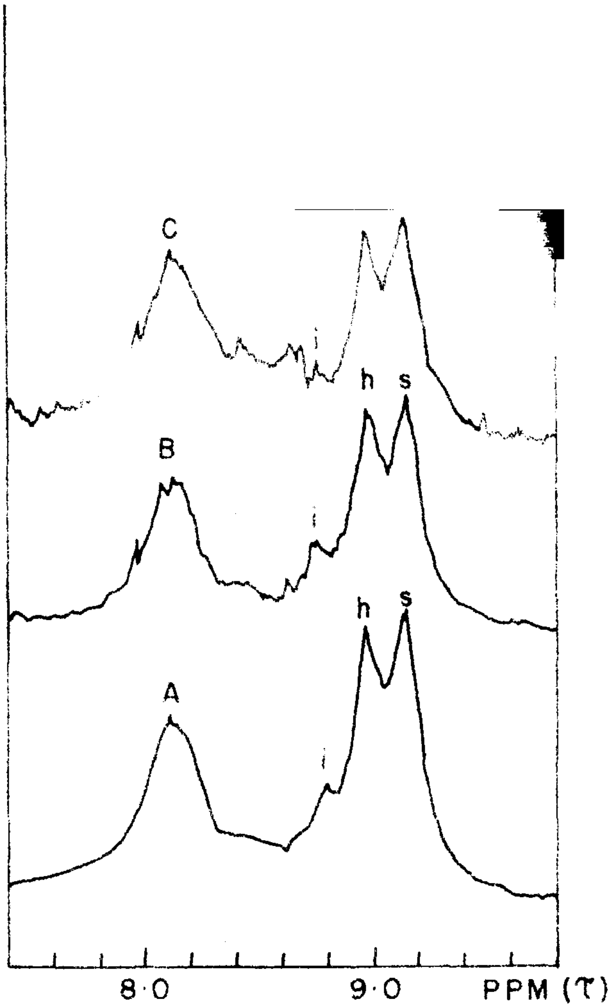


FIG. 20 NUCLEAR MAGNETIC RESONANCE SPECTRA OF PMMA WITH $VOCl_3 - AlEt_2Cl$ SYSTEM IN 3 % (W/V) CHLOROFORM SOLUTIONS

(A) Al/V RATIO = 2

(B) 50 mgm OF HYDROQUINONE ADDED TO CATALYST SYSTEM

(C) 0·05 MOLE OF TRIETHYL AMINE ADDED TO CATALYST SYSTEM homopolymers of olefins. According to Natta, the most important factors influencing the formation of a stereoblock polymer are the nature of transition metal compound, its crystallinity, its ability to yield complexes with metallo-organic compounds and the stability of the complexes produced. For instance, some vanadium compounds with valence higher than +3 are more suitable than the titanium compounds to prepare purely stereospecific polymers. They give high yields of stereoblock polymers having very high molecular weight.

Table - XXV shows comparison of two catalyst systems under identical conditions. It is apparent from the data that the catalyst system of $VOCl_3$-$AlEt_2Cl$ is more active than $VOCl_3$-$AlEt_3$ catalyst system for stereospecific polymerization of methyl methacrylate in n-hexane at 40°C. However, the molecular weight of polymer was found to be in the same range in both systems.

4.5.2 $VOCl_3$-$AlEt_2Br$ Catalyst System in n-hexane for the Polymerization of Methyl Methacrylate

The dark brown solution containing fine precipitate after mixing the catalyst components remained unchanged after addition of monomer showing presence of undisturbed catalyst sites. Even after 24 hours of aging the catalyst colour remains same. The ratio of Al/V was changed by keeping concentration of $VOCl_3$ constant, in order to find out ratio of optimum activity. It was observed that the polymer yield was maximum at ratio of Al/V=4 and 8, but

Table - XXV

Comparison of Catalyst Systems

Catalyst system	Percentage conversion	Rate constants L/M/S w.r.t catalyst	Rate constants L/M/S w.r.t monomer	Percentage of syndiotactic, heterotactic and isotactic units from NMR spectra S 9.14 ↑ppm	H 8.98 ↑ppm	I 8.78 ↑ppm
(1) $VOCl_3$-$AlEt_3$	4.58	5.61×10^{-5}	4.63×10^{-5}	41	29	30
(2) $VOCl_3$-$AlEt_2Cl$	19.29	23.21×10^{-5}	12.79×10^{-5}	47	38	15
(3) $VOCl_3$-$AlEt_2Br$*	4.57	9.30×10^{-5}	9.04×10^{-5}	32	31	37

Al/V ratio = 2   Aging time = 20 min.   [Catalyst] = 0.05 mole/l

Temperature = 40°C   Reaction time = 180 min.   [MMA] = 1.88 mole/l

*In case of $VOCl_3$-$AlEt_2Br$:

Al/V ratio = 4   Aging time = 24 hrs.

the molecular weight of polymer was maximum at ratio of Al/V=4. At the same time the rate of polymerization increases linearly with time upto 240 minutes.

The kinetic study of polymerization was carried out at ratio of Al/V=4, aging time = 24 hours and reaction time = 3 hours. It was observed that the rate of polymerization was found to be first order with respect to catalyst (Table - XI, Fig.9) and monomer concentrations (Table - XII, Fig.10) and such a linear dependence is well known for typical Ziegler-Natta type catalyst systems of heterogeneous nature[119-121]. Similarly, the value of 6.67 Kcal/mole (Table - XIII, Fig.11) for the activation energy of polymerization, obtained from the plot of log value of polymerization in the temperature range of 20-50°C versus reciprocal of absolute temperature, is also in agreement with the value reported for other Ziegler-Natta catalysts. This showed the co-ordinate anionic mechanism of polymerization, which can be confirmed by further studies such as effect of hydroquinone and triethyl~~ene~~ amine on rate of polymerization and structure of polymer (Table - XXVI).

It was observed that the rate of polymerization increased with addition of triethyl amine but addition of hydroquinone had no effect on rate of polymerization (Table - XIV, XV). Molecular weights of polymer were increased with addition of triethyl amine as well as with addition of hydroquinone.

The stereoblock structure (Table - XXVI) of polymethyl

Table - XXVI

Effect of Additives on Polymerization

Additive	$R_p \times 10^6$ M/L/S	Molecular weight	Percentage of syndiotactic, heterotactic and isotactic units from NMR spectra		
			S 9.14 ↑ppm	H 8.98 ↑ppm	I 8.78 ↑ppm
(1) No additive	7.96	69,980	32	31	37
(2) Hydroquinone (50 mgm)	7.37	74,500	35	40	25
(3) Triethylamine (0.05 mole/l)	15.87	93,400	34	40	26

$VOCl_3$-$AlEt_2Br$ Catalyst System

Al/V ratio = 4

[Catalyst] = 0.05 mole/l

[MMA] = 1.88 mole/l

Aging time = 24 hrs.

Reaction time = 180 min.

Temperature = 40°C

methacrylate as recorded by NMR (Fig.21a) further lends support to co-ordinate anionic mechanism of polymerization.

It has been earlier[119-120] reported from this Laboratory that the stereoblock structure of polymethyl methacrylate is produced by the co-ordinate anionic type of mechanism. Heteroblock structure of polymethyl methacrylate has been obtained by many workers[93,135,192,193] and they have proposed a free radical type of mechanism. There is remote possibility for a double propagation, first by anion and later by free radical, as proposed by Smets et al[99] on the basis of structure of polymethyl methacrylate obtained with $CoCl_2$ + PhMgBr catalyst system.

Besides these studies, it has been observed that vanadium even in the valence state of +2 is responsible for producing a stereoblock polymethyl methacrylate. Natta[109] has observed that the vanadium based catalyst systems with a valence state higher than +3 are more suitable than the titanium compounds to give mostly amorphous and stereoblock polymers. However, Lehr[137] has reported the presence of vanadium in the valence state of +3 at the temperature of -78°C. It has been already observed that vanadium even in the valence state of +2 is responsible for the stereoblock structure of polymethyl methacrylate, indicating that the structure of polymer is independent of valence state of vanadium, which is contrary to the suggestion of Natta[109] and others[137].

Our present study showed that the structure of polymer

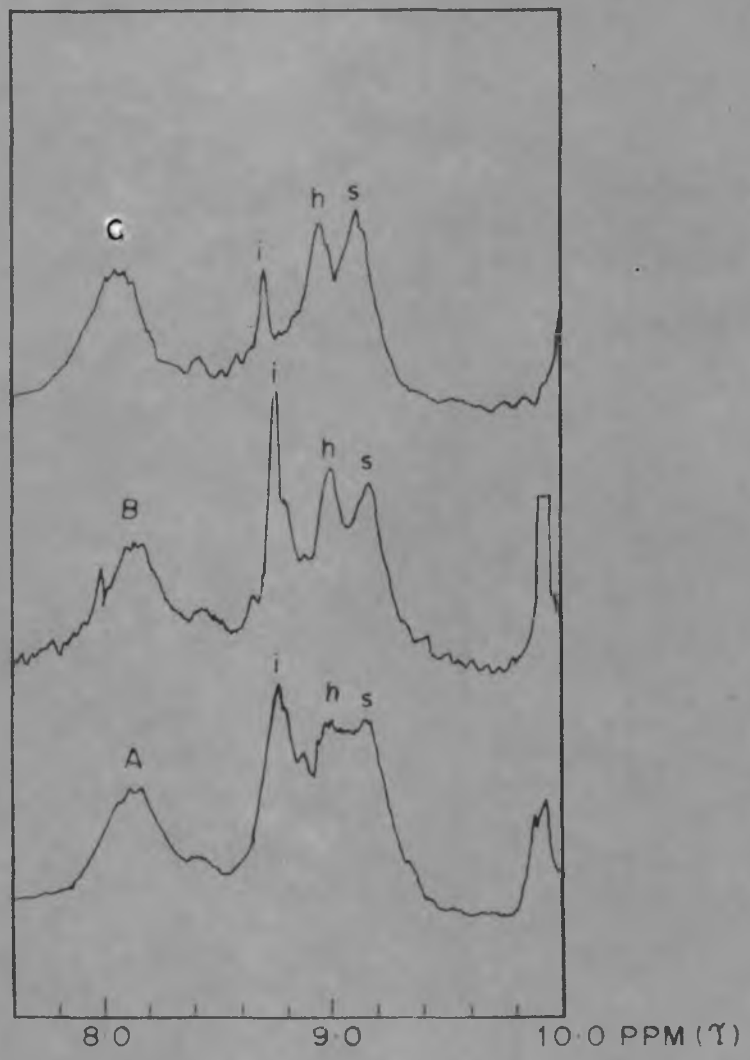


FIG. 21 NUCLEAR MAGNETIC RESONANCE SPECTRA OF PMMA WITH $VOCl_3 - AlEt_2Br$ SYSTEM IN 3 % (W/V) CHLOROFORM SOLUTIONS

(A) Al/V RATIO = 4

(B) IN PRESENCE OF 50 mgm OF HYDROQUINONE

(C) IN PRESENCE OF 0·05 MOLE TRIETHYL AMINE is independent of valence state of transition metal. However the comparative study (Table - XXV) of the structure of polymer obtained with $VOCl_3$-$AlEt_2Cl$ and $VOCl_3$-$AlEt_2Br$ after 24 hours aging showed that there is increase in percentage isotacticity of polymethyl methacrylate with the increase in V(II) or there was increase in percentage syndiotacticity of polymethyl methacrylate with the increase in V(III) as observed by Svab, Jaroslav et al[191].

Carrick and coworkers[15] first focussed attention on the valence problem by relating the activity and valence state of a site. These workers suggested that two opposing factors come into play when the valence state of metal is decreased. First, with all the transition metals, there is a decrease in electronegativity of the metal centre as its valence state decreases e.g. electronegativity values for V(+4) and V(+2) are 1.8 and 1.2 respectively. The lower electronegativity makes the metal-carbon bond more polar so that any co-ordinated (polarized) monomer is readily incorporated into growing metal-carbon bond site. Secondly with progressive filling of transition metal orbitals with decreasing valence state, the electron acceptor character of metal decreases. This has the effect of decreasing co-ordination of olefin at the metal centre and thus lowering catalyst activity.

4.5.3 $VOCl_3$-$AlEt_2Br$ and VCl_4-$AlEt_2Br$ Catalyst Systems in Carbon Tetrachloride for Polymerization of Methyl Methacrylate

A dark black precipitate was formed instantaneously on mixing the catalyst components in carbon tetrachloride, as in the case of Ziegler-Natta catalyst in hydrocarbon medium. But unlike the behaviour of Ziegler-Natta catalyst in hydrocarbon medium, after induction period[194], decomposition took place with evolution of gases and large amount of heat was produced. Further it was observed that the heterogeneous solution of catalyst components aged for 24 hours gave dark brown product after 3 hours reaction time with methyl methacrylate.

The changes in the ratio of Al/V in both catalyst systems i.e. $VOCl_3$-$AlEt_2Br$ and VCl_4-$AlEt_2Br$ showed that the yield increases as the ratio of Al/V increases (Table - XVI, XVII, Fig. 12, 13). It was also observed that the induction period decreased as the ratio of Al/V increased and amount of carbon tetrachloride decreased. Such type of behaviour was also studied by Eden and Feilchenfeld[194]. The purified products at ratio of Al/V=4 were dark brown, highly crystalline and stable upto 350°C.

In order to know the structure of product, IR and NMR spectra were recorded. IR of these samples at ratio of Al/V=4 in both cases (Fig.22) showed a predominant absorption peak at 1700 cm^{-1} due to C=O group of methyl methacrylate. Fig. 22 also shows the absence of absorption peaks at 1160 cm^{-1}, 1200 cm^{-1}, 1300 cm^{-1} due to $-OCH_3$ group of methyl methacrylate. The absence of $-OCH_3$ group in IR spectra was confirmed by NMR spectra (Fig.23) of these samples. From these observations, it can be concluded that methyl

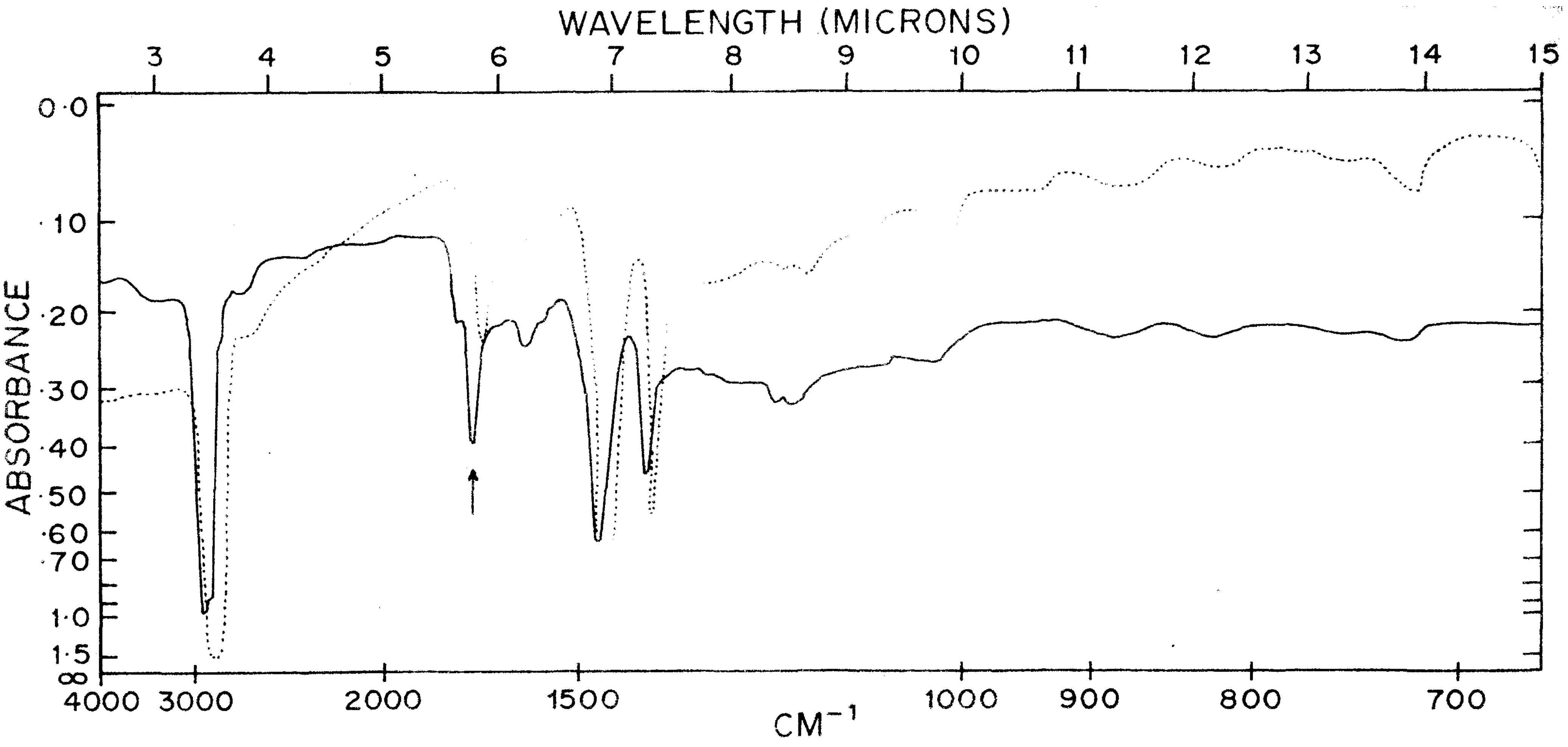


FIG. 22 IR SPECTRA OF COMPLEXES (MC) OF METHYL METHACRYLATE AFTER REACTION WITH ZIEGLER-NATTA CATALYST COMPLEX

[redacted] VO[redacted] $AlEt_2Br$ [redacted] VCl[redacted] $AlEt_2Br$

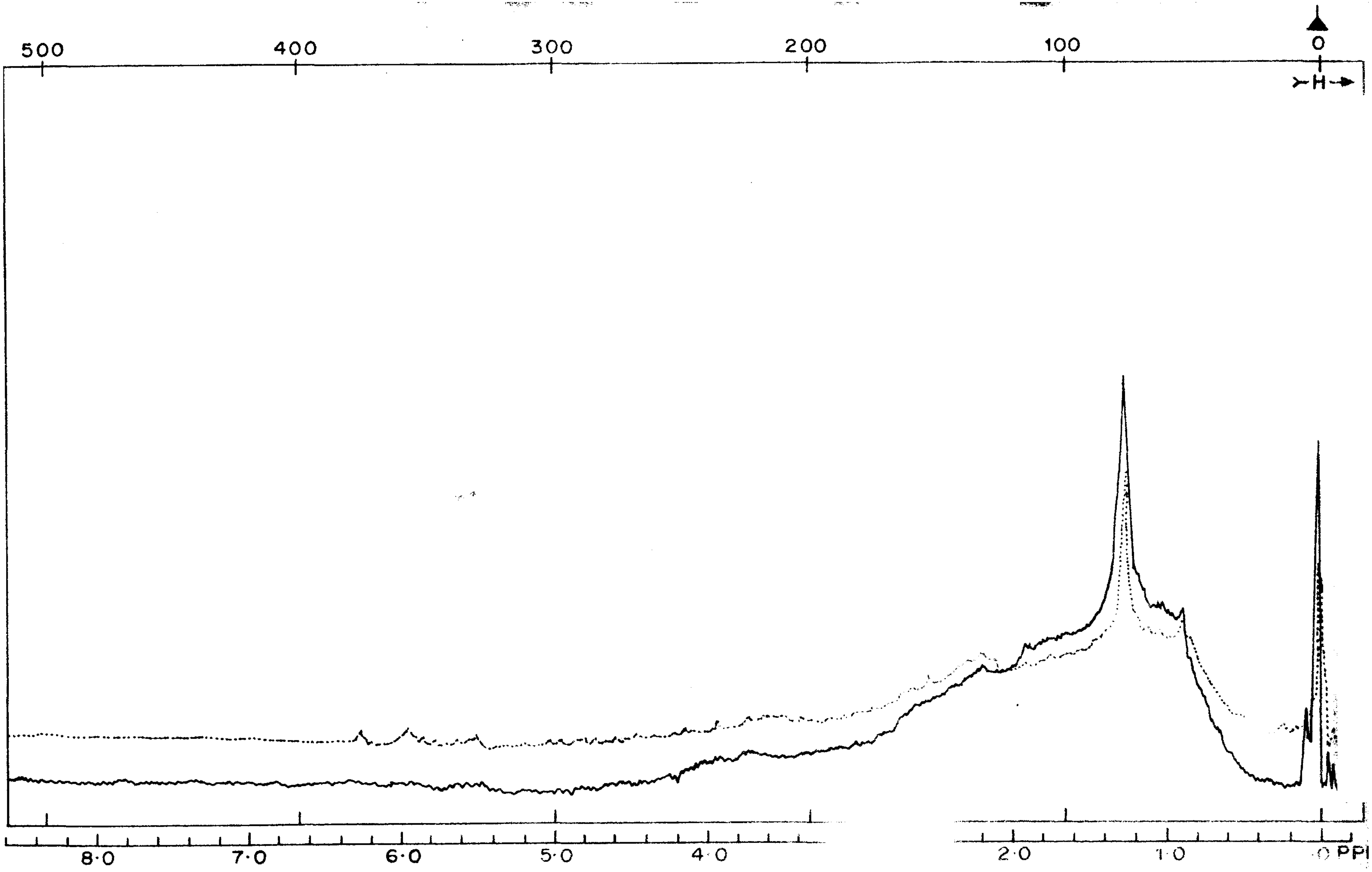


FIG. 23 NMR SPECTRA OF COMPLEXES (MC) OF METHYL METHACRYLATE AFTER REACTION WITH ZIEGLER-NATTA CATALYST COMPLEX

(1) ——— VOCl — AlEt Br (2) ········· VCl — AlEt Br

methacrylate had reacted with Ziegler-Natta catalyst complex (ZC) to form a new complex (MC) and while reacting with this complex (ZC), the $-OCH_3$ group must have been knocked off.

Further, it was observed that when only catalyst mixture was poured in acidified methanol after 24 hours aging and 3 hours reaction time at 40°C, a black precipitate (ZC) separates out from the solution in both cases. The IR (Fig.24) and NMR (Fig.25) spectra of these samples are identical showing the presence of C-Cl only. This observation leads to conclude the formation of Ziegler-Natta catalyst complex (ZC) in carbon tetrachloride medium.

Elemental analysis of these Ziegler-Natta catalyst complexes (ZC) alone and their products after reaction with methyl methacrylate (MC) is shown in Table -XXVII.

The mechanism of these reactions of Ziegler-Natta catalyst components in carbon tetrachloride and the reaction of methyl methacrylate with the complex formed, is difficult to understand.

Eden[194] has studied the reaction between carbon tetrachloride, aluminium triethyl and $TiCl_4$ and has concluded that triethyl aluminium had an inhibiting effect on its own decomposition in presence of carbon tetrachloride and $TiCl_4$. He further showed that when $TiCl_4$ was added to $AlEt_3$ in carbon tetrachloride, after induction period decomposition took place and suggested a carbonium ion[194] mechanism to this process.

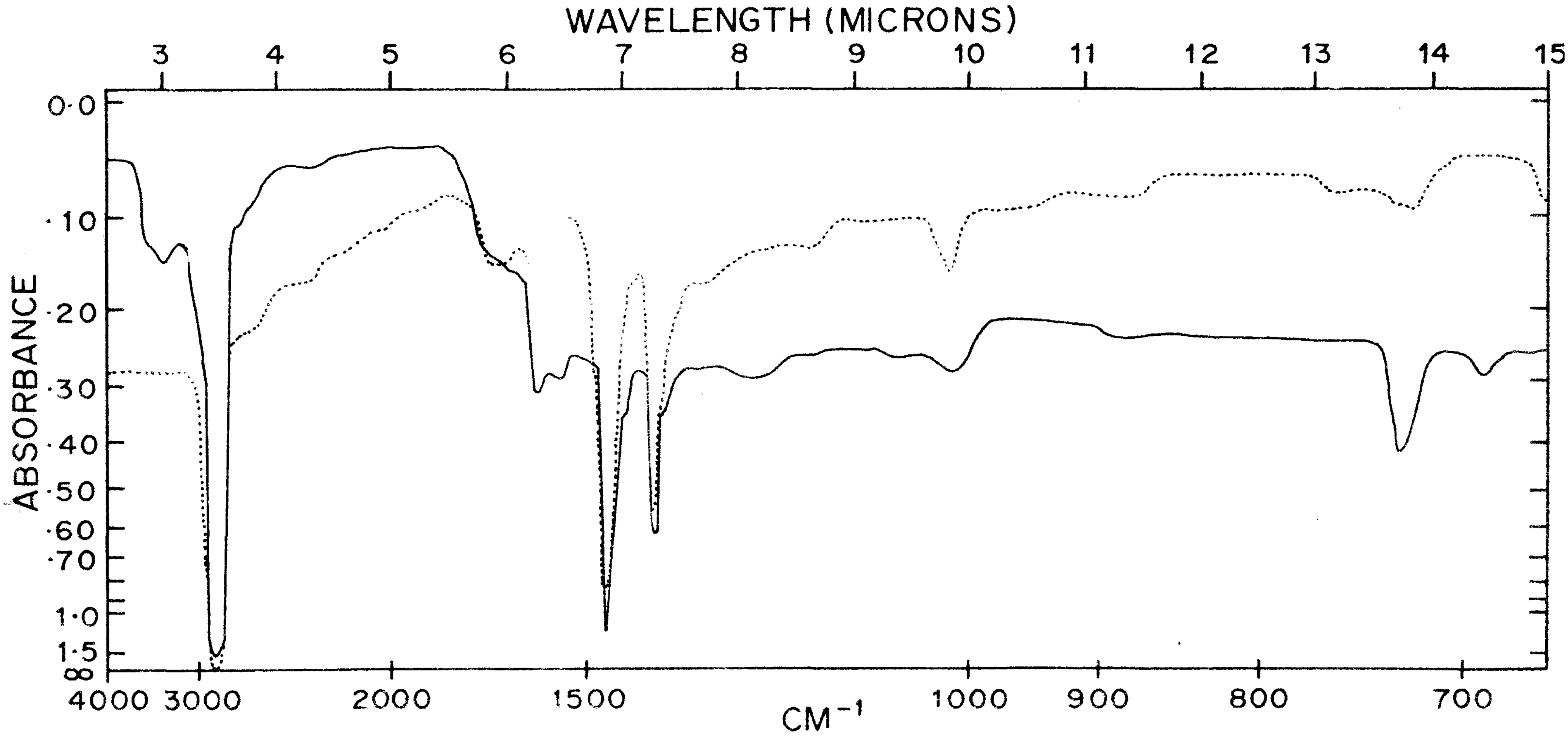


FIG. 24 IR SPECTRA OF ZIEGLER–NATTA CATALYST COMPLEXES (ZC)

(1) ——— $VOCl_3-AlEt_2Br$ (3) ········ VCl_4-AlEt_2Br VC

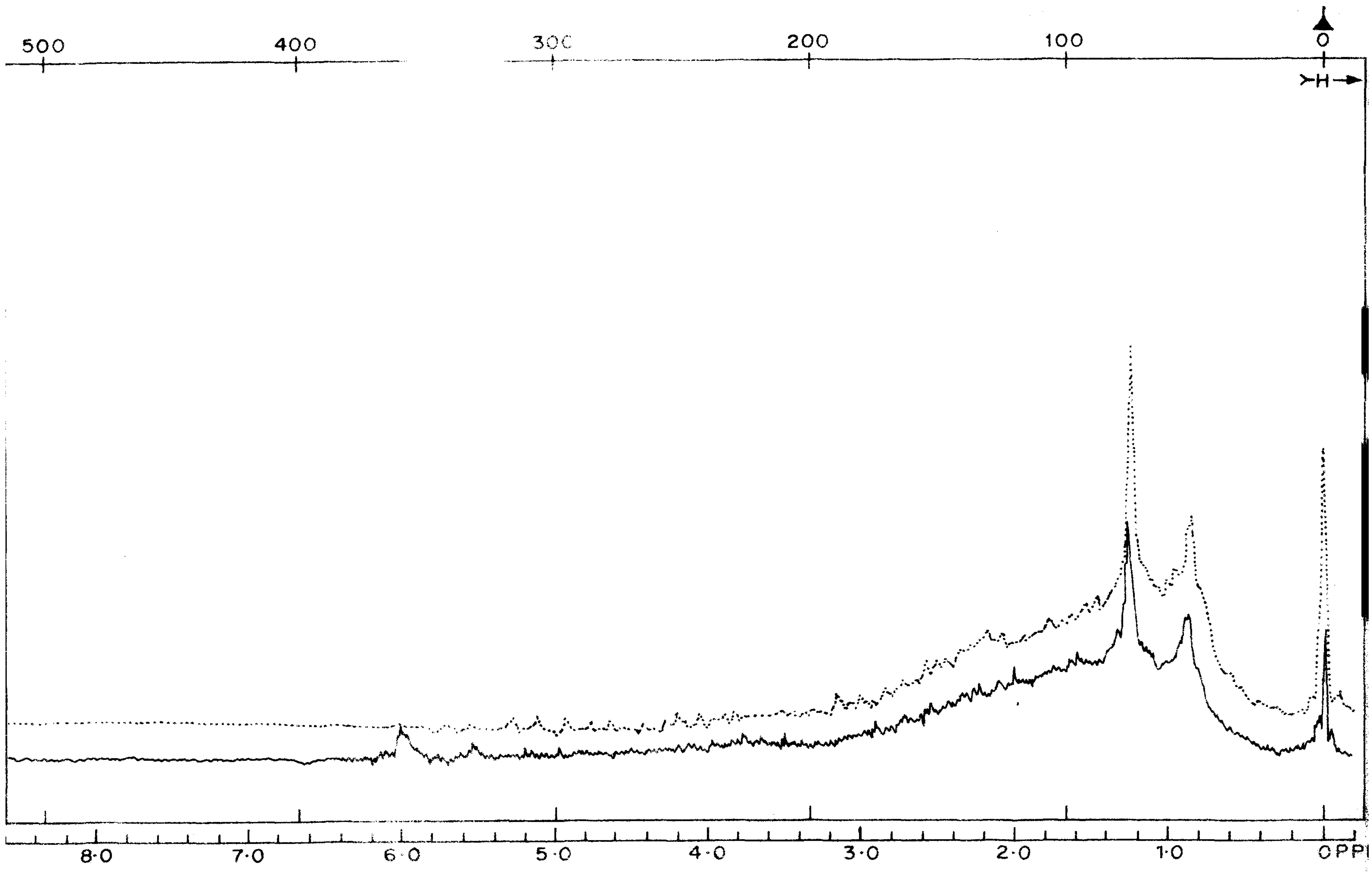


FIG. 25 NMR SPECTRA OF ZIEGLER – NATTA CATALYST COMPLEXES (ZC)

(1) ——— $VOCl_3 - AlEt_2Br$ (2) ·········· $VCl_4 - AlEt_2Br$

VC

Table - XXVII

Elemental Analysis of Complexes

		'C'	'H'	'Cl'
A.	Ziegler-Natta Catalyst complexes (ZC)			
	(1) $VOCl_3$-$AlEt_2Br$-CCl_4	80.41	7.60	5.03
	(2) VCl_4-$AlEt_2Br$-CCl_4	70.84	7.77	13.06
B.	Complexes (MC) after Reaction of (ZC) with Methyl Methacrylate			
	(1) $VOCl_3$-$AlEt_2Br$-CCl_4-MMA	84.55	8.91	6.83
	(2) VCl_4-$AlEt_2Br$-CCl_4-MMA	80.24	7.25	6.04

Al/V ratio = 4 Aging time = 24 hrs.
[Catalyst] = 0.05 mole/l Reaction time = 180 min.
[MMA] = 1.88 mole/l Temperature = 40°C

First an equilibrium passing through intermediate step is set up, as:

$$2\ CCl_4 + C_2H_5AlCl_2 \rightleftharpoons 2\ CCl_3\cdot + C_2H_5^{+}AlCl_4^{-}$$

The equilibrium is displaced towards right by recombination of $CCl_3\cdot$ radicals giving C_2Cl_6 hexachloroethane and the ethyl carbonium ion will react further with both CCl_4 and $C_2H_5AlCl_2$

(a) $C_2H_5^{+}AlCl_4^{-} + CCl_4 \rightarrow C_2H_5Al + CCl_3^{+}.AlCl_4^{-} \rightarrow CCl_4 + AlCl_3$

(b) $C_2H_5^{+}AlCl_4^{-} + C_2H_5AlCl_2 \rightarrow C_2H_6 + AlCl_4^{-}C_2^{+}H_5AlCl_2 \rightarrow$
$C_2H_4 + 2AlCl_3$

However, this carbonium ion mechanism is in contrast with carbanionic and free radical mechanisms established for these normal decompositions of metal carbon bond.

Guyot and Rocaniere[195] polymerized vinyl chloride with the catalyst system of $Ti(OR)_yCl_{4-y}$-AlR_xCl_{3-x} in carbon tetrachloride. They suggested that the free radical formed due to decomposition of catalyst complex by carbon tetrachloride polymerizes vinyl chloride.

In our studies we found that Ziegler-Natta catalyst complexes (ZC) were formed in carbon tetrachloride after the reaction between Ziegler-Natta catalyst components and these complexes in situ when reacted with polar monomers such as methyl methacrylate, formed new complex (MC).

From these observations it may be concluded that the course of reaction must be as follows:

(i) Either the aluminium alkyl must be reacting with transition metal halide to form addition product, which is active complex and the excess of alkyl must be reacting with carbon tetrachloride causing decomposition reaction, or

(ii) The aluminium alkyl must be reacting with transition metal halide forming Ziegler-Natta catalyst complex, which further must be reacting with carbon tetrachloride, causing decomposition reaction and giving active complex.

The active complex, thus formed, is ineffective for the polymerization of methyl methacrylate but gave a new complex (MC).

The TGA, DTA, BM, UV and mass spectra of these complexes will throw more light on the structure of these complexes and will help for understanding the mechanism of reaction.

Thus it was observed that at higher valence state of vanadium in catalyst complex, $VOCl_3$-$AlEt_2Br$ and VCl_4-$AlEt_2Br$ catalyst systems in carbon tetrachloride did not polymerize methyl methacrylate; instead complexes were formed.

4.5.4 VCl_4-$AlEt_2Br$ Catalyst System in n-hexane for Polymerization of Isoprene

It was observed that dark brown coloured solution containing fine precipitate was formed, on mixing catalyst components. The specific amount of isoprene was added to this catalyst mixture after aging of catalyst for 1 hour. It was observed that the ratio of Al/V=3 and 6 gave maximum polymer yield (Table - XVIII, Fig.14). Thus there were two maxima in the plot of conversion against ratio of Al/V, as observed in case of $C_6H_5MgBr-TiCl_4$ system[140]. The kinetic behaviour with respect to catalyst and monomer concentrations was studied at selected conditions such as ratio of Al/V=3, where maximum yield obtained, aging time = 1 hour, and reaction time = 1 hour.

The rate of polymerization was found to be first order with respect to catalyst (Table - XXI, Fig.17) and monomer (Table - XXII, Fig.18) concentrations and such a linear dependence is well known for typical Ziegler-type catalyst systems of heterogeneous nature. Similarly, the value 8.96 Kcal/mole (Table - XXII, Fig.19) for the activation energy of polymerization obtained from plot of log rate of polymerization in temperature range 20-50°C versus reciprocal of absolute temperature, is also in agreement with value reported for typical Ziegler-Natta catalyst[196] in the polymerization of isoprene under heterogeneous condition.

The changes in molar ratio of Al/V within range of 1 to 8 showed that linear structural units did not exceed 30% (Table - XVIII). The IR spectra (Fig.26) of polymer sample at ratio of Al/V=3, showed intense absorption bands at 840 cm^{-1}, 1020 cm^{-1}, 1090 cm^{-1} and 1265 cm^{-1}, which were also found for cyclic units in isoprene polymerization[197]. Intense absorption bands are observed at 840 cm^{-1}, 1020 cm^{-1}, 1090 cm^{-1} and 1265 cm^{-1} which are also noted in the IR spectra of cyclopolyisoprene obtained with cationic catalyst[198].

The physical properties such as high temperature of decomposition of polymer (360°C) supports the cyclic structure

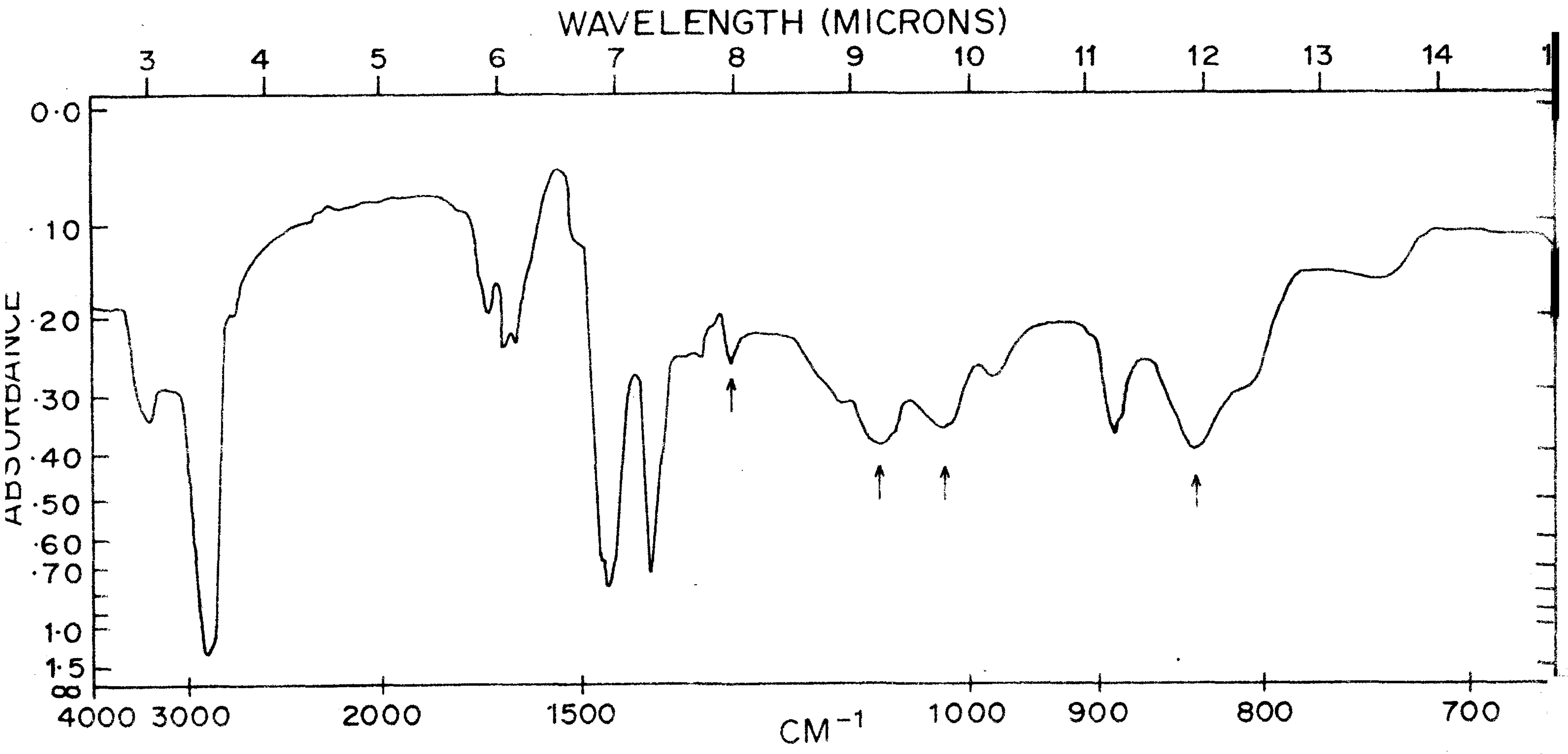


FIG. 26 IR SPECTRUM OF CYCLOPOLYISOPRENE AT RATIO OF Al/V=3

of polyisoprene. Thus from the above results, it can be concluded that the Ziegler-Natta catalyst system containing vanadium chloride, can also give cyclo polyisoprene as in the case of titanium chloride based Ziegler-Natta catalyst systems.

Gaylord et al[144] suggested a cation-radical mechanism for cyclopolymerization of butadiene and isoprene with $TiCl_4$ and aluminium alkyls containing Ziegler-Natta catalyst systems.

It has been proposed that the reaction of $TiCl_4$ and $C_2H_5AlCl_2$ yields a complex $C_2H_5TiCl_3.Al_2Cl_5C_2H_5$. The catalytically active species in cyclopolymerization of isoprene may be ions formed by dissolution of the complex, as shown in reaction (1) and (2) below:

(1) $$(C_2H_5AlCl_2)_2 + TiCl_4 \rightleftarrows [C_2H_5TiCl_3.Cl_5C_2H_5]$$

(2) $$[C_2H_5TiCl_3.Cl_5C_2H_5] \rightarrow C_2H_5TiCl_2^+ + AlCl_3C_2H_5AlCl_3^-$$

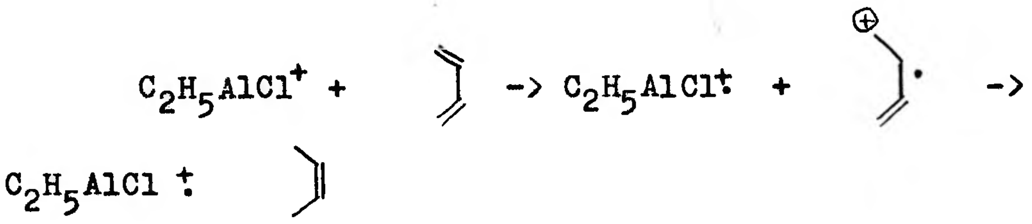
or

$$C_2H_5TiCl_3AlCl_2^+ + C_2H_5AlCl_3^-$$

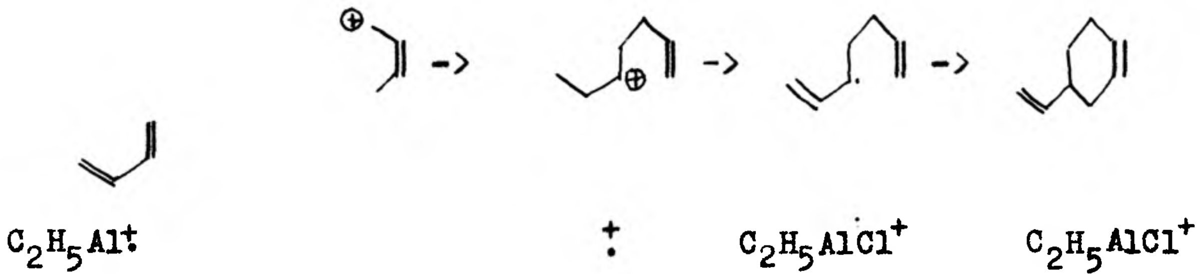
Similarly, $C_2H_5AlCl_2$ leads to ion pair:

(i) $Al(C_2H_5)_2^+ \; AlCl_4^-$, and

(ii) $C_2H_5AlCl^+.C_2H_5AlCl_3^-$, which react with monomer to form π complex, thus:



The one electron transfer reaction to the catalyst cation results in the neutralization of charge.



(1) (2)

Cationic end of monomercation radical react with a monomer molecule to produce a new cation radical, as in equation (1). The latter accepts an electron from 'neutral' ethyl aluminium chloride to produce diradical and regenerate ethyl aluminium chloride as in equation (2).

Similar type of reaction may be taking place with vanadium chloride based catalyst system.

It is interesting to study the same catalyst system in carbon tetrachloride as a medium. It was observed that as the medium changes from n-hexane to carbon tetrachloride, the rate of polymerization increased tremendously (Table - XXVIII).

Table - XXIX showed the effect of ratio of Al/V on the rate of polymerization(in carbon tetrachloride) of isoprene and the percentages of insoluble and cyclic polymer. It was also observed that the percentage of soluble polymer increased as the medium changed from n-hexane to carbon tetrachloride, as observed by Gaylord et al[198].

Table - XXVIII

Effect of Change of Medium on Percentage Conversion of Isoprene

	Moles of carbon-tetrachloride	Yield in gms.	Percentage conversion	Percentage of insoluble and cyclic polymer
(1)	0	0.655	19.2	62.5
(2)	1	2.958	86.0	64.4
(3)	5	3.078	90.4	53.5
(4)	7	3.176	93.0	52.1

Al/V ratio = 3 Aging time = 24 hrs.
Isoprene = 5.0 ml Reaction time = 24 hrs.
Temperature = 30°C

Table - XXIX

Effect of Ratio of Al/V on VCl_4-$AlEt_2Br$ System in Carbontetrachloride

	Ratic	Yield in gms.	Percentage conversion	Percentage of insoluble and cyclic polymer
(1)	0.5	0.258	7.58	72.0
(2)	1	0.612	17.96	51.3
(3)	2	0.897	26.36	66.2
(4)	3	1.021	30.03	48.8
(5)	4	1.186	36.53	63.3
(6)	5	1.686	49.55	57.2
(7)	6	2.250	66.07	52.8

VCl_4 = 0.01 mole/l Aging time = 24 hrs.
Isoprene = 5.0 ml Reaction time = 1 hr.
Total volume = 25.0 ml Temperature = 30°C.

4.6 Evaluation of Parameters such as Order of Reaction, Rate Constants and Activation Energy

4.6.1 The Order of Reaction

The first order dependence on both catalyst and monomer concentrations in all these systems studied (Table - XXX), can be explained on the basis of Riedel or Langmuir-Hinshelwood[199] mechanism, as given below:

First, monomer molecule is adsorbed at the active catalyst centre:

$$C + M \overset{K_1}{\rightleftharpoons} (CM) \qquad \text{Rapid equilibrium}$$

The above active monomer catalyst complex is in equilibrium with the polymer obtained from this complex:

$$(CM) \xrightarrow{K_i} C + \text{Polymer (slow)}$$

where C is an active catalyst centre, M is a monomer molecule, and (CM) is the adsorbed monomer-catalyst complex.

Assuming that the adsorption of monomer by the catalyst complex is a rapid equilibrium process, resulting in the formation of an active monomer catalyst complex and that the formation of polymer from this complex is the rate determining step, one can write:

$$\frac{-dM}{dt} = K_i \left[(CM)\right]$$

$$K_{ii} = \frac{[(CM)]}{\left[[C] - (CM)\right] [M]}$$

where $\left[[C] - (CM)\right]$ is the number of active centres unoccupied

Table - XXX

Kinetics of Polymerization

	Catalyst system	Medium	Monomer	The order of reaction with respect to catalyst	The order of reaction with respect to monomer	Ref.
(1)	$VOCl_3$-$AlEt_2Cl$	n-Hexane	Methyl Methacrylate	First	First	Tab.IV,V Fig.4,5
(2)	$VOCl_3$-$AlEt_2Br$	n-Hexane	Methyl Methacrylate	First	First	Tab.XI,XII Fig.9,10
(3)	VCl_4-$AlEt_2Br$	n-Hexane	Isoprene	First	First	Tab.XXI, XXII Fig.17,18

by monomer molecules. Solving the above equation, one obtains:

$$[(CM)] = \frac{K_{ii}[M]\ [C]}{[1+K_{ii}\ [M]\ ]} \qquad \text{and}$$

$$\frac{-dM}{dt} = K_i \frac{K_{ii}[M]\ [C]}{1+K_{ii}\ [M]}$$

when $K_{ii}[M]$ is small compared to unity, as in our experimental systems where low monomer concentrations were used, this equation simplifies to:

$$\frac{-dM}{dt} = K_iK_{ii}\ [M]\ [C]$$

4.6.2 Rate Constants

The rate constants in each case were calculated from the slopes in the plots of rate versus catalyst and monomer concentrations, as shown in Figs. 4,5,9,10,19 and 20.

The values of 'K', the overall reaction rate constants thus obtained from both catalyst and monomer concentration plots agreed very well with each other in each catalyst system (Table - XXXI).

The values of rate constants reported in the literature for catalyst systems[178,151] containing $VOCl_3$, $TiCl_3$, $TiCl_4$ are comparable to those found in the present investigation.

4.6.3 Activation Energy

Overall activation energy values calculated from the

Table - XXXI

The Rate Constants with respect to Catalyst and Monomer Variations in different Catalyst Systems

	Catalyst system	Medium	Monomer	K from catalyst variation L/M/S	K from monomer variation L/M/S
(1)	$VOCl_3$-$AlEt_2Cl$	n-Hexane	Methyl Methacrylate	23.21×10^{-5}	12.79×10^{-5}
(2)	$VOCl_3$-$AlEt_2Br$	n-Hexane	Methyl Methacrylate	9.30×10^{-5}	9.04×10^{-5}
(3)	VCl_4- $AlEt_2Br$	n-Hexane	Isoprene	1.33×10^{-3}	1.78×10^{-3}

plots of log R_p vs. 1/T are given below (Table - XXXII).

Overall activation energy values are in the same range of 5 - 12 Kcal/mole, usually reported for Ziegler-Natta catalyst systems.

4.7 General Conclusions from the Present Work

Earlier work in this laboratory showed[119-123] that vanadium based catalyst systems, which were also used for polymerization of styrene, are more effective for the polymerization of polar monomers than titanium based Ziegler catalyst systems at room temperature. The mechanism of polymerization in vanadium containing Ziegler catalyst is of co-ordinate anionic type, similar to that of the titanium based catalyst systems of $TiCl_4$-$AlEt_3$. It was found that the stereospecificity of the catalyst varies with the monomer. In case of polymerization of methyl methacrylate, the $VOCl_3$-$AlEt_3$[120] catalyst system is more stereospecific than the VCl_4-$AlEt_3$[119] catalyst systems, whereas in case of styrene VCl_4-Al-alkyls catalyst system[179] is more stereospecific than $VOCl_3$-Al-alkyls catalyst system[153].

4.7.1 Activity of Catalyst

On the basis of the results of present work on kinetic studies of polymerization of methyl methacrylate with vanadium containing Ziegler-Natta catalyst systems, it is possible to classify these catalyst systems into three groups in terms of average valence state of vanadium in the active catalyst complex and its activity for the polymerization of methyl methacrylate.

Table - XXXII

Activation Energy

Catalyst system	Monomer	Medium	Temperature range °C	Overall activation energy K.cal/mole
(1) $VOCl_3$-$AlEt_2Cl$	Methyl Methacrylate	n-Hexane	20-50	9.25
(2) $VOCl_3$-$AlEt_2Br$	Methyl Methacrylate	n-Hexane	20-50	6.67
(3) VCl_4-$AlEt_2Br$	Isoprene	n-Hexane	20-40	8.96

(1) Vanadium in lower valency state $<$ V(III): less active
(2) Vanadium in middle valency state V(III): more active
(3) Vanadium in higher valency state $>$ V(III): inactive

It is well known that the valence of vanadium decreases with increase in metal alkyl/vanadium halide ratio. It was also found that the various metal alkyls can reduce the valency of vanadium to different extents which in turn effects the type of catalyst sites.

It was found that at higher ratio of Al/V=4 and after 24 hours of aging in $VOCl_3$-$AlEt_2Br$ catalyst system, for polymerization of methyl methacrylate, the catalytic activity is less as compared to $VOCl_3$-$AlEt_2Cl$ catalyst system. It is found that the activity of catalyst complex in $VOCl_3$-$AlEt_2Cl$ catalyst system is four times larger than the $VOCl_3$-$AlEt_3$ and $VOCl_3$-$AlEt_2Br$ catalyst systems.

The higher activity of catalyst complex in $VOCl_3$-$AlEt_2Cl$ catalyst system can be accounted on the basis of less reduction of vanadium to lower valence state by $AlEt_2Cl$. It shows that the average valence state of vanadium V(III) in catalyst complex enhances the rate of polymerization of methyl methacrylate.

Thus, the ratio of Al/V and structure of aluminium alkyl, which ultimately determines the valence state of vanadium, has great influence on the activity of catalysts.

4.7.2 Structure of Polymers

From the NMR spectra of polymethyl methacrylate for all samples obtained with these catalyst systems, it seems that all polymer samples contain the three units i.e. isotactic, heterotactic and syndiotactic, only the percentage of these units is different. From this it can be concluded that the stereoblock structure of polymethyl methacrylate is independent of the average valence state of active catalyst complex, but the difference in percentage tacticities leads to conclude that active sites containing V(III) has preference for syndiotactic polymerization, while V(II) has preference for isotactic polymerization.

Further it was observed that at higher valence state of vanadium in catalyst complex in carbon tetrachloride, the active catalyst species (ZC) are inactive for polymerization of polar monomers such as methyl methacrylate, but they can complex with methyl methacrylate yielding new complex (MC). It was also observed that these active complexes (ZC) are highly active for polymerization of styrene and isoprene. The reactions of Ziegler-Natta catalyst components forming such a highly active catalyst for non-polar monomers and forming complex with polar monomers show that the active catalyst species are cationic in nature.

The molecular weights of polymer samples in all cases lie in the range of 40,000 to 80,000, which shows that molecular weights do not change with the change in average valency of active catalyst complex.

From the study of polymerization of isoprene with VCl_4-$AlEt_2Br$ catalyst system, it may be concluded that vanadium chloride containing Ziegler-Natta catalyst system can also give cyclic structural units in polyisoprene as titanium chloride containing catalyst system.

CHAPTER - V

SUMMARY

SUMMARY

Since the discovery of Ziegler-Natta catalyst system, several catalyst systems have been used for stereospecific polymerization of non-polar and polar vinyl monomers in polar and non-polar solvents.

Earlier work has shown that vanadium based Ziegler-Natta catalyst systems are more effective than titanium based Ziegler-Natta catalyst systems for polymerization of methyl methacrylate. It has been also reported that the catalytic activity and stereospecificity of Ziegler-Natta catalyst systems containing VCl_4 and $VOCl_3$ in combination with aluminium alkyls, for polymerization of propylene, are dependent on average valence state of vanadium in catalyst complex.

In order to throw more light on the effect of valence state of vanadium in catalyst complex on polymerization of polar monomers, the systematic kinetic studies of following Ziegler-Natta catalyst systems have been carried out for polymerization of methyl methacrylate and isoprene. The mechanism of polymerization and structure of polymers obtained have been discussed.

(1) $VOCl_3$-$AlEt_2Cl$ Catalyst System in n-hexane for Polymerization of Methyl Methacrylate

The percentage conversion plots showed a maximum at Al/V=2 and at 7, indicating presence of two active sites.

Molecular weight of polymer was found to be maximum at ratio of Al/V=2, after 20 minutes aging and 3 hours reaction time.

Rate of polymerization was observed to be first order with respect to catalyst and monomer concentrations. The molecular weight decreased with increased catalyst concentration but increased linearly with increase in monomer concentration. This is a typical behaviour of Ziegler-Natta catalyst system. The overall activation energy 9.25 Kcal/mole and kinetic behaviour suggested a co-ordinate anionic mechanism of polymerization.

The stereoblock structure of polymer obtained and heteroblock structure of polymer sample obtained after addition of triethyl amine and hydroquinone, supports co-ordinate anionic mechanism. The structures of polymer were determined by NMR spectra and molecular weights of all polymer samples were calculated from intrinsic viscosity measurement in chloroform at 30°C.

(2) $VOCl_3$-$AlEt_2Br$ Catalyst System in n-hexane for the polymerization of Methyl Methacrylate

It was observed that the ratio of Al/V=4 gave maximum conversion and the polymer obtained had maximum molecular weight, after 3 hours reaction time and 24 hours aging time of catalyst components.

Rate of polymerization was found to be first order with respect to catalyst and monomer concentrations but molecular weight was inversely proportional to catalyst concentration and directly proportional to monomer concentration. The overall activation energy was found to be in the range of 5 - 12 Kcal/mole, usually reported for Ziegler-Natta type catalyst systems.

The NMR spectra of polymer sample recorded showed presence of stereoblock structure.

Thus the kinetic behaviour and the formation of stereoblock structure indicated a co-ordinate anionic mechanism of polymerization by this catalyst system.

(3) (a) $VOCl_3$-$AlEt_2Br$ (b) VCl_4-$AlEt_2Br$ Catalyst Systems in Carbon Tetrachloride for the Polymerization of Methyl Methacrylate

It was observed that in both cases (a) and (b), the heterogeneous black catalyst mixture aged for 24 hours gave brown complexes on addition of methyl methacrylate, after 3 hours reaction time at 40°C and polymerization of methyl methacrylate did not take place. The complexes were precipitated in acidified methanol and purified by dissolving in chloroform and recrystallization. The dark red brown complexes were highly crystalline and thermally stable (upto 350°C).

The IR spectra of these complexes showed presence of absorption band at 1600 cm^{-1} due to C=C of methyl methacrylate, and absence of absorption bands at 1160 cm^{-1}, 1200 cm^{-1} and 1300 cm^{-1} due to -OMe group of methyl methacrylate, which is also confirmed by the absence of absorption peak at 6.5| in the NMR spectra of the sample. These observations showed that methyl methacrylate had reacted with Ziegler-Natta catalyst complex (ZC) to form a new complex (MC) and while reacting with these complexes (ZC) the -OMe group must have been knocked off.

(4) Polymerization of Isoprene with VCl_4-$AlEt_2Br$ Catalyst System in n-hexane at 30°C

It was observed that there was a maximum in conversion plots at Al/V=3 and at Al/V=7. The maximum yield obtained at ratio of Al/V=3, was chosen for further kinetic studies.

Kinetics of polymerization at ratio of Al/V=3, aging time 24 hours, reaction time 1 hour, had showed the rate of polymerization increased with increase in catalyst and monomer concentration.

The overall activation energy was found to be 8.92 Kcal/mole, which is also in agreement with the value reported for a typical Ziegler-Natta catalyst in the polymerization of isoprene under heterogeneous condition.

The changes in ratio of Al/V within the range 1 - 8 showed that linear structural units do not exceed 30%. IR spectra recorded showed predominant absorption bands at 820 cm^{-1}, 1040 cm^{-1}, 1090 cm^{-1} and 1265 cm^{-1}, which are also noted in the IR spectra of cyclopolyisoprene obtained with cationic catalysts.

Conclusion

Our present studies on vanadium based Ziegler-Natta catalysts have shown that the catalytic activity and stereospecificity are greatly dependent on the valence state of vanadium in the catalyst complex and ratio of Al/V. From the present work, it may be concluded that the increase in average valence of V^{+3} enhances the rate of polymerization of methyl methacrylate. Similarly, at lower valence state of vanadium the catalytic activity of the complex is low. Higher valence state of vanadium in $VOCl_3$-$AlEt_2Br$ and VCl_4-$AlEt_2Br$ catalyst systems in carbon tetrachloride, did not yield any polymer of methyl methacrylate but complexes were obtained.

From the polymerization studies of isoprene, it is concluded that the catalyst system containing vanadium chloride can also give cyclopolyisoprene as titanium chloride containing Ziegler-Natta catalyst system.

Following are the publications based on the experimental results reported in this Thesis:

(1) 'Complex formation of methyl methacrylate with Ziegler-Natta catalyst complex in carbon tetrachloride medium'. J.Polymer Sci. Part B- Polymer Letters.

(2) 'Kinetics and mechanism of stereospecific polymerization of methyl methacrylate with $VOCl_3$-$AlEt_2Cl$ catalyst system'. J.Polymer Sci. Part A-1. (in press)

(3) 'Cyclopolymerization of isoprene with VCl_4-$AlEt_2Br$ catalyst system'. J.Polymer Sci. Part A-1. (in press)

(4) 'Stereoblock polymerization of methyl methacrylate with $VOCl_3$-$AlEt_2Br$ catalyst system'. (to be communicated).

CHAPTER - VI

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