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POLYMERIZATION STUDIES
WITH
ZIEGLER-NATTA TYPE CATALYST SYSTEMS

A Thesis
Submitted to
Panjab University
for
the degree of

DOCTOR OF PHILOSOPHY

in Chemistry

By

Lalit Chandra Anand

Division of Polymer Chemistry,
NATIONAL CHEMICAL LABORATORY
POONA - 8.
(1966)

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October 1966. Lalit Chandra Anand.

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CHAPTER I.

INTRODUCTION.

INTRODUCTION

Ziegler Natta catalysts are one of very few discoveries which have led to the development of a large variety of useful industrial products in a short period. In less than fifteen years since the discovery of Ziegler in 1953[1] it has been possible to obtain high density polyethylene, polypropylene, synthetic natural rubber and many other extremely useful products on commercial scale. This pioneering discovery has made possible the synthesis of macromolecules which possess stereo-regularity.

Following the discovery of Bakelite[2] in 1909, several laboratories became interested in synthesis and study of behaviour of macromolecules. By 1930 so much work had accumulated that Staudinger[3] was able to classify different types of polymers into distinctly different classes and a large variety of macromolecules were prepared.

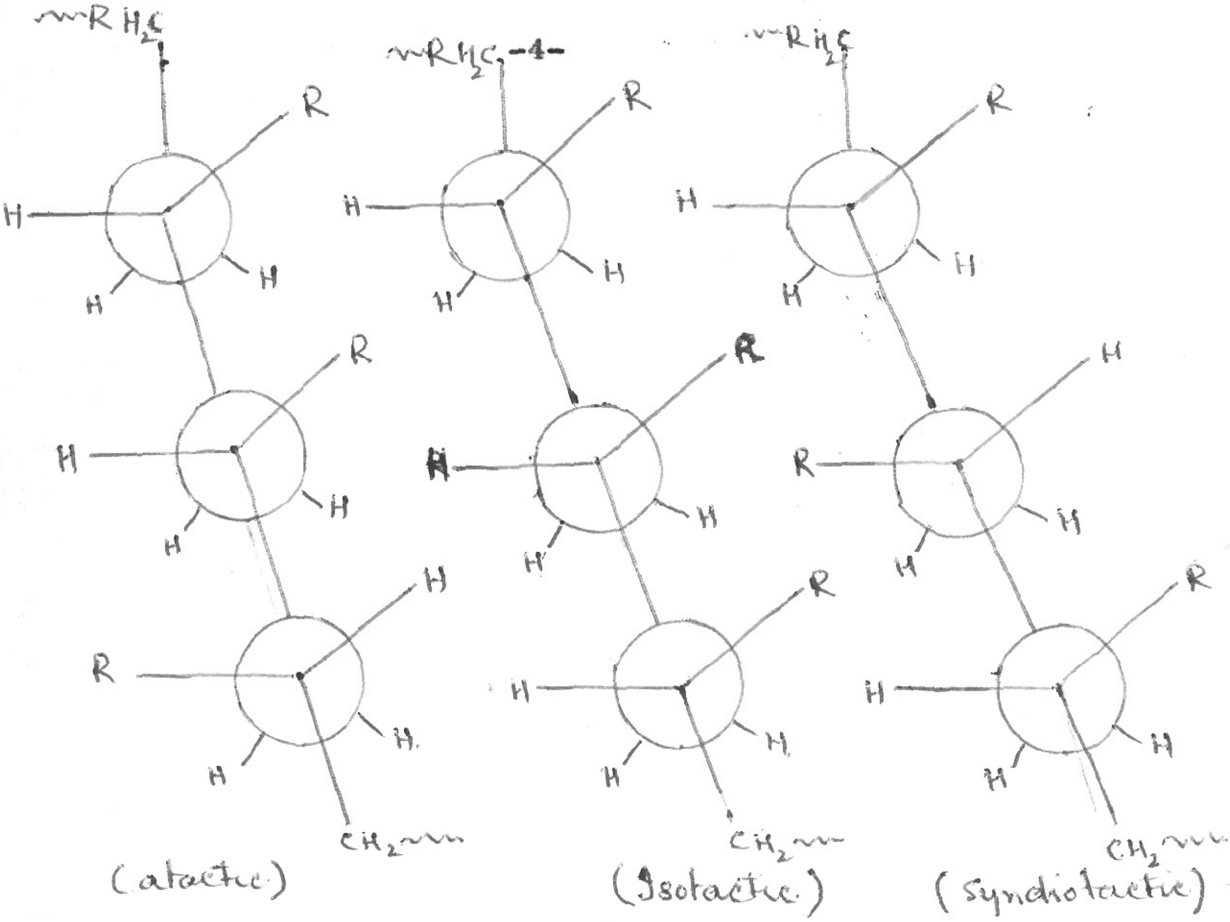
But discovery of Ziegler Natta catalysts gave a new dimension to the science of macromolecules. These catalysts are complexes of organo-metallic compounds with transition metal halides. A somewhat similar approach had been made earlier by some other groups of workers also. Among the earliest references to such polymerizations is the work of Kraus[5], who showed in 1940 that mixtures of inorganic halides were effective catalysts for the polymerization of olefins. As early as 1935 Hall and Nash[6] showed that mixtures of ethylene aluminium and aluminium chloride when heated together produced alkyl aluminium halides. In 1943, Fisher[7] applied for a patent wherein mixtures of aluminium, aluminium chloride and titanium tetrachloride were used as effective catalysts for the polymerization of ethylene. Since the conditions of Fisher's work were very similar to those of Hall and Nash, it seems likely that some alkylation of aluminium occurred and these metal-organic compounds with titanium tetrachloride constituted active catalyst for ethylene polymerization.

In the meantime Phillips Petroleum Company[8] showed that oxides of molybdnum, chromium and other transition metals when in partially reduced state and supported on substrates like silica-alumina, could be used to polymerize ethylene and propylene. The activity of such catalysts increased by promoters like metals, metal hydrides and metal alkyls, which led to the speculation of formation of organo-metallic intermediates.

But it was only after Ziegler and Natta's work that so widespread activity in the field of catalytic polymerization started. The work of Natta on polymerization of propylene and other α-olefins opened a new chapter in polymer science and the idea of tacticity came up which has proved to be of a great theoretical as well as practical interest to the chemists world over. It has made possible the synthesis of macromolecules with known steric configuration, which is a great step forward in the direction of duplicating complex phenomenon of nature.

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 the polymer molecules were in the same plane. These polymers were named as isotactic[10-13] by Natta. Another type of polymers with alternate groups in the same plane was named as syndiotactic[14-16] and those having random arrangement of groups were named as atactic. These polymeric structures can be illustrated by Newman[17] projection. The chains of isotactic and syndiotactic polymers will have a tendency to form crystalline lattices. In the crystalline form the



(atactic) (Isotactic) (syndiotactic)

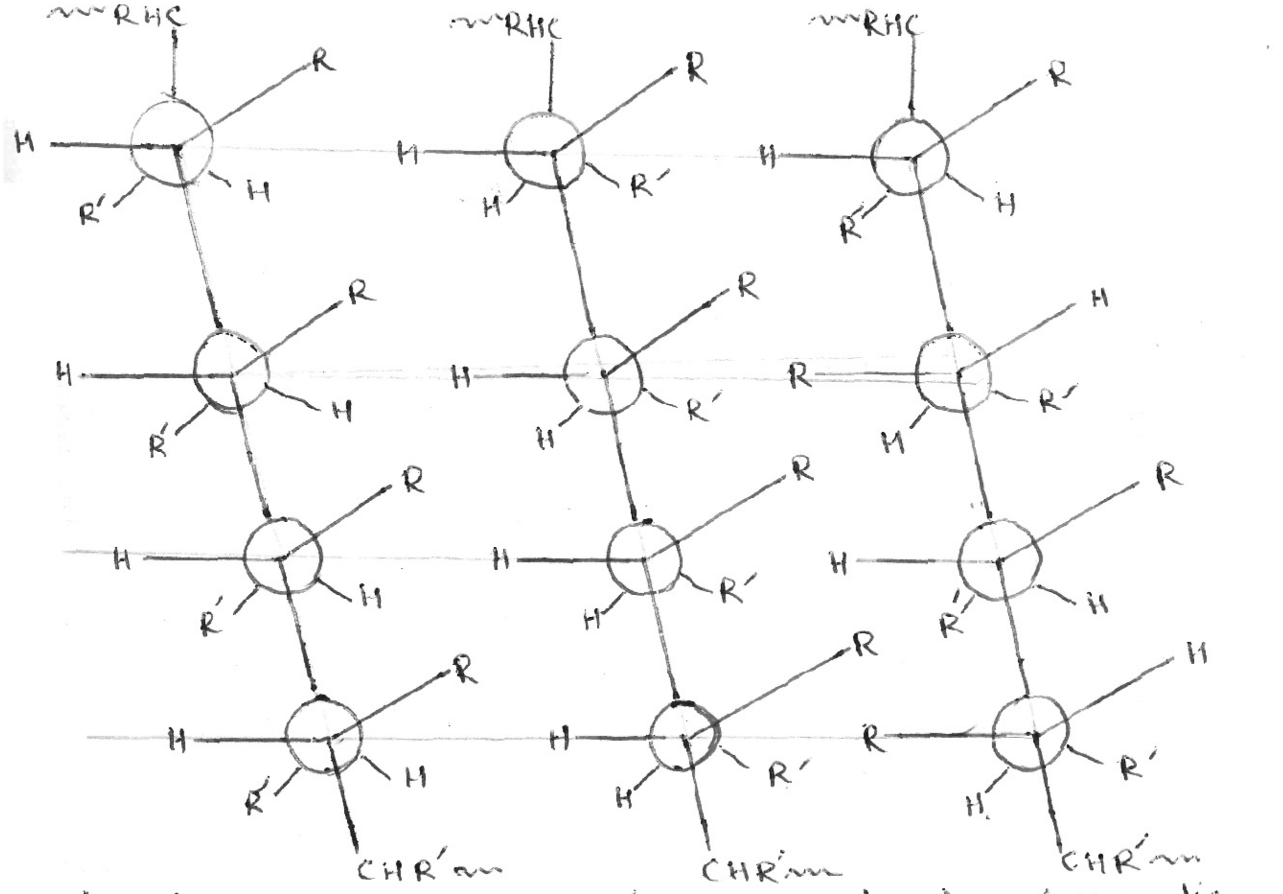
isotactic polymers tend to form halices with pendent groups protuding in the same plane.

Following table illustrates difference in properties due to stereo-regularity of the polymer.

		Density	Melt index	Softening pt.	Tensile strength psi.
Polyethylene[17]	Conventional	0.92	2.0	110°	2190
	Ziegler	0.95	0.5	135°	2960
Polypropylene[18]	Conventional	0.803	..	<25°	508
	Ziegler	0.909	..	146°	5400

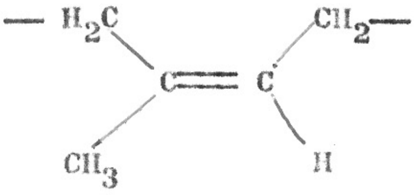
Ziegler catalysts have also been used with other olefins and it has been possible to obtain polymers of higher steric order and consequently better physical properties. Isotactic polystyrene[19] has a melting point of 240° whereas ordinary polystyrene melts at a temperature around 80°. The number of stereoregular forms will increase in the case of 1,2 disubstituted polyethylenes as shown below

If two different assymmetric c-atoms in the chain occur with the same configuration the polymer is called erythrio-di-isotactic. If the two assymmetric carbon atoms have alternating configuration, the polymer is called theo-diisotactic. When adjuscent pairs of carbon atoms have alternating configuration, the polymer

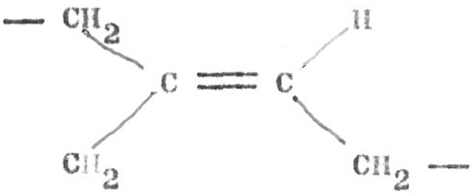


(erythrio-di-isotactic) (threo-di-isotactic) (di-syndiotactic) is known to be disyndiotactic. It will be observed that only one di-syndiotactic structure is possible.

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 Gutta percha and Balata.

PROCESS OF POLYMERIZATION

It is a common knowledge that in the formation of a macromolecule of vinyl type, essentially three steps[20] are involved. These are initiation, propagation and termination. For the production of useful polymeric materials, control[21] of all these steps is important.

Initiation

Free radical, anionic or cationic species produced from the catalyst are responsible for initiating a chain reaction.

Propagation

It is the addition of each individual monomer occurring hundreds and even thousands times in the course of the growth of a macromolecule.

Termination

A growing chain can be terminated by their mutual interaction or by reaction with certain chemical reagents.

Control of Initiation and Termination processes

Overall rate of polymerization can be controlled by regulating initiating and terminating processes. The effective control of initiating process is possible by producing initiating centres of certain type in any system (either aquous or non-aquous) at particular temperatures and in the presence of different monomers. Likewise, the control of average length of chains and with it of the molecular weights and end groups could be obtained by the addition of certain chain transfer or cessation agents to the polymerizing system.

Control of Propagation Process

A successful control of propagation process would help not only to speed up the polymer formation but also to produce macromolecules of greater geometrical regularity and as a consequence of better mechanical and thermal behaviour.

Temperature and environments can have great influence on the propagation step. In certain cases it has been possible to control the polymerization of chloroprene[22] isoprene[23], methyl methacrylate[24] to a great extent. Energetic and steric control can also explain the polymerization of vinyl alkyl ethers[25,26] to stereoregular polymers, which was carried out in 1948.

Pre-arrangement of monomer molecules in a favourable pattern before the polymerization can regulate the propagation step. Certain monomers especially dienes have been polymerized to give highly stereospecific polymers by pre-arranging the monomer molecules, as urea or thiourea canal complexes and then polymerizing them by high energy irradiations[27-30]. In the case of xylelene[31] and some other monomers pre-arrangement of monomer was carried out by condensing monomer on a solid surface.

Similar approach by Letort[32] for polymerization of acetaldehyde gave polymers with methyl groups in the same plane. Pre-dissolved polymer[33,34] in monomer can also have regulating effect. This polymerization is known as 'replica' polymerization.

Certain solid surfaces such as clays or mixtures of alumina and molybdina can orient the molecules by immobilizing and complexing them as in the case of Phillips catalysts[35].

Soluble complexes of monomers with counter ions in ionic polymerization, can put the monomer molecules in suitable position for a stereo-regular polymerization e.g. lithium alkyls, sodium alkyls etc. These complexes can also be used for stereospecific polymerization of acrylic esters[36,37], acryl-amide[38] and vinyl halides[39] in case of anionic initiators. Cationic initiators of the similar type have been employed for the polymerization of styrene derivatives[40] stereospecifically.

Optically active monomers may be used to know[41] whether the propagation steps have maintained or destroyed stereospecificity by finding optical activity of the polymers.

Complex catalysts prepared from alkali alcoholate with an olefin halide have been found by Morton and coworkers[42] to control propagation of butadiene and isoprene polymerization. These catalysts are also known as 'Alfin' catalysts.

Last and most effective catalyst for controlling the propagation step is organo-metallic mixed catalyst. This catalyst discovered by Ziegler[1] has proved to have a great controlling influence on the propagation step in the polymerization of ethylene and other monomers. Stereo-regular polymerization with Ziegler type catalysts has been reviewed widely in literature by many workers[9,21,43-48].

ZIEGLER-NATTA CATALYSTS

Ziegler type catalysts consist of transition metal halides from group IV to VI of periodic table and organo-metallics from group I to III. It was first prepared by Ziegler[1] by adding a solution of triethyl aluminium to a solution of titanium tetrachloride in hydrocarbon solvents such as heptane. The product of this reaction is a brown black insoluble compound which is essentially a reduced halide of titanium e.g. titanium trichloride or titanium dichloride, and this precipitate together with its supernatent phase is essential for catalytic activity. Natta has proposed that the active Ziegler type polymerization, catalyst is a complex containing more than one metal atom. It has been shown that most active stereospecific catalysts for polymerization of α-olefins are formed by the reaction between a metal alkyl of a highly electro-positive metal having a small diameter e.g. berylium, aluminium or lithium and a crystalline halide of transition metal from group IV to VI of periodic table in which the metal is in a valence less than maximum e.g. titanium trichloride, titanium dichloride vanadium dichloride etc. When the catalyst is prepared from the unreduced halides, the reduction might proceed through a series of states[49,50] e.g. reaction between triethyl aluminium and titanium tetrachloride can be considered as follows:

$\mathrm{AlEt_3 + TiCl_4 \longrightarrow AlEt_2Cl + Et\ TiCl_3}$

$\mathrm{Et\ TiCl_3 \longrightarrow TiCl_3 + Et^{\circ}}$

$\mathrm{Et\ TiCl_3 + AlEt_3 \longrightarrow Et_2TiCl_2 + Et_2AlCl}$

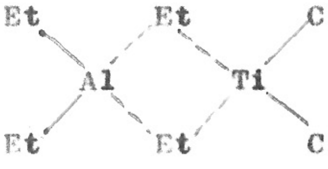
$\mathrm{Et_2\ TiCl_2 \longrightarrow Et\ TiCl_2 + Et^{\circ}}$

$\mathrm{TiCl_3 + AlEt_3 \longrightarrow} \cancel{\mathrm{Et\ TiCl_2}} \mathrm{+ Et\ TiCl_2 + Et_2\ AlCl}$

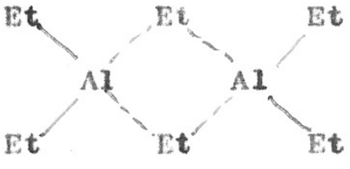
$\mathrm{Et\ TiCl_2 \longrightarrow TiCl_2 + Et^{\circ}}$ etc.

Recently unstable compounds like trichloro-ethyl titanium[49] (Et $TiCl_3$) have been isolated from these reactions.

Bridge complexes such as:



(i)



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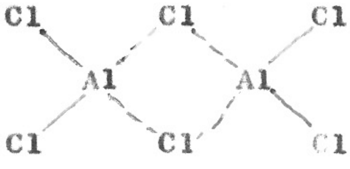


(iii)

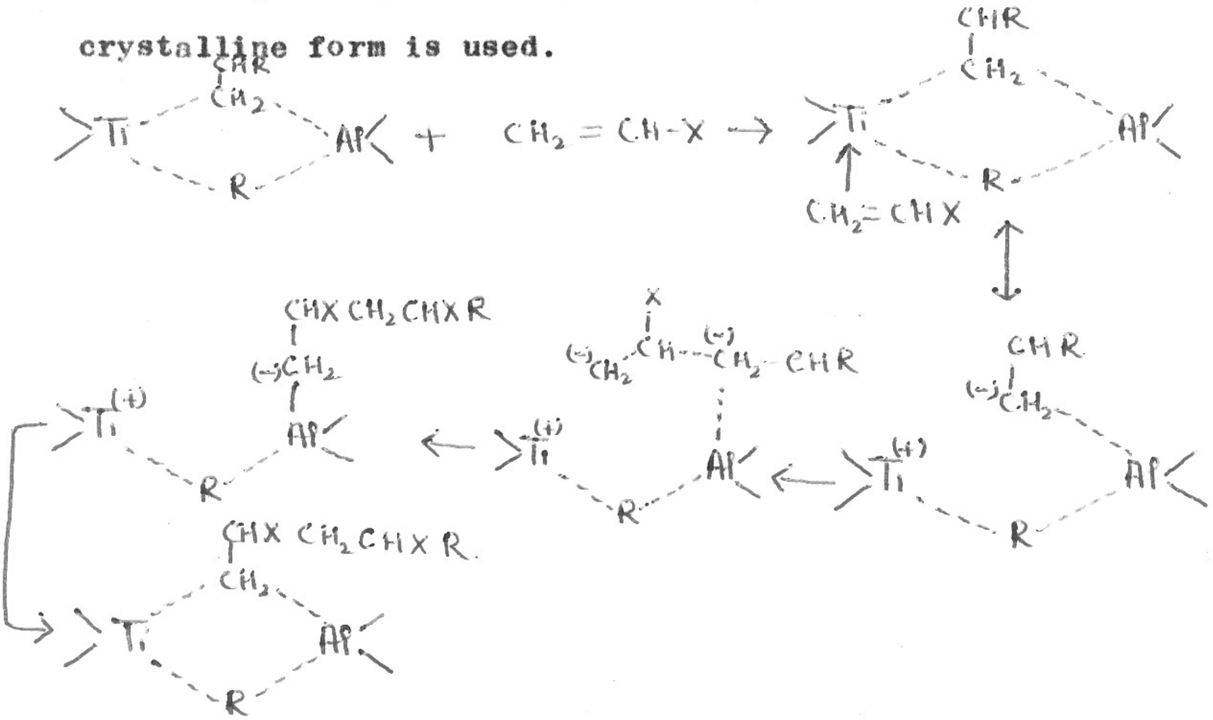
which are formally anologous to the well established bridge dimers of triethyl aluminium[51] and aluminium halides[52] have been proposed as active catalysts formed by reaction of unused aluminium alkyl with titanium trichloride or titanium dichloride.

MECHANISMS OF POLYMERIZATION WITH ZIEGLER TYPE CATALYSTS

Whatever mechanisms have been proposed for Ziegler type catalysts refer mainly to the chemical nature of propagation and they do not explain the highly stereo-specific qualities. But it is well accepted that monomer molecules get oriented in some way or the other before adding up to the chain. The nature of the orienting forces is not very well known. The actual number of mechanisms proposed or considered[21,43,45,53] for Ziegler type polymerizations is more than even number of catalyst variations employed. But there are two main theories, which attempt to explain the polymerization by Ziegler-Natta catalysts.

NATTA's MECHANISM

One of them assumes that the catalyst is a titanium aluminium compound. A typical theory of this type is by Natta[54] wherein the reaction of crystalline titanium trichloride and a solution of a trialkyl aluminium is postulated to result in a surface complex in which the titanium and aluminium are joined through alkyl bridges. Incoming monomer is first π bonded to the titanium. The bridge titanium carbon bond then opens whereupon the π bonded monomer unit is inserted into the chain with pendent group pointing away from the titanium trichloride surface. The steric effect of the surface therefore, imposes stereospecificity on polymerization. Titanium trichloride occurs in several crystalline forms. The rate of polymerization and the stereo-regularity of the polymer depends upon which crystalline form is used.



Presumably steric structure of the catalytic complex leading to isotactic polymer is same in all cases, but the effective concentration on some titanium trichloride crystal forms is higher than on others.

In the above mechanism Natta assumes the propagation of chain on aluminium carbon bond because:

(1) Soluble crystalline complexes of general formula $(C_5H_5)_2\ TiCl_2\ AlRR$ have been isolated and they are known to contain titanium-carbon-aluminium bridges. They obviously lend support to Natta's theory of bimetallic electron deficient complex[55,56].

(2) Phenyl end groups have been observed in the polymerization of ethylene by the catalysts prepared by the interaction of di-cyclopentadienyl titanium dichloride $\left[Ti(C_5H_5)_2Cl_2\right]$ and aluminium triphenyls but these phenyl end groups were not detected when catalysts derived from bicyclo-pentadienyl diphenyl titanium $\left[(C_5H_5)_2Ti(C_6H_5)_2\right]$ and triethyl aluminium are used under comparable conditions[55].

(3) When triethyl aluminium containing C^{14}-labelled ethyl groups is adsorbed into the surface of α-$TiCl_3$ and when this whole system is used as polymerization catalyst in the presence of non-labelled triethyl aluminium, the resulting polymer contains, as terminal groups, all the labelled alkyl groups[57]. Obvieusly all these ethyl groups could not have been involved

in alkylation of titanium.

(4) The chemical analysis of the resulting polymer showed the presence of aluminium[58]. Natta and Mazzanti[56] have explained this as being due to dissociation of each catalytic complex into two parts, one containing the titanium atom, the other containing alkyl group, including polymeric chains bound to aluminium. This dissociation is presumably followed by re-association of the titanium fragment with the other aluminium alkyl present in the solution.

(5) Kinetic data of Natta, Pasquon and Giachetti[69,60] agrees with the given mechanism and satisfactorily explain the observation that the rate of certain transfer processes and rate of chain propagation are both of the same order with respect to monomer and behave as if they were two parallel reactions proceeding through the same transition state. Coordination of olefinic π-electrons with vacant hybrid orbitals in the metal is primarily responsible for propagation reaction.

But there is certain evidence that goes against the mechanism of Natta:

i. Use of bis-cyclo pentadienyl diphenyl titanium as catalyst for the polymerization of ethylene has been reinvestigated by Carrick and Karapinka[46] and although they confirm the findings of Natta and coworkers that no phenyl groups are incorporated into the polymer, it was concluded that it does not constitute any real evidence for the growth on aluminium rather than titanium. The reaction of bis-cyclo pentadienyl diphenyl titanium with aluminium alkyl derivatives appears to proceed with an immediate exchange of alkyl and aryl groups between aluminium and titanium. Chain growth then occurs more readily at alkyl substituted metal atoms than at phenyl substituted sites. Furthermore it was also shown that π-bonding of cyclo-pentadienyl compounds is disrupted wholly or in part, during polymerization and at least part of catalyst reactivity is due to the decomposition products.

ii. Patat and Sinn[62,63] also proposed a mechanism similar to that of Natta. But Ziegler[64-66] critisized it on the ground that by anology with dimeric aluminium alkyls, electron deficient complexes involving aluminium and titanium are not likely to be involved in the actual growth reaction, even though such complexes may occur in polymerizing systems. Such criticism applies to Natta's mechanism also.

iii. A catalyst described in a Belgian patent of American Goodrich Gulf Co.[67] and closely related to Ziegler type catalysts prepared by the interaction of diethyl aluminium chloride with a trace of titanium tetrachloride in xylene solution has been referred to by Ziegler[64-66] where the titanium present is not enough to give an appreciable quantity of organo-titanium compound. Ziegler points out that function of highly reactive organo-titanium compounds will be considerably assisted (although sometimes obscured) by alkyl exchange with aluminium alkyl molecule present in the solution. Thus equilibria such as:

$$\text{Al-alkyl} + \text{Ti-alkyl} \rightleftharpoons \text{Al-Ti-alkyl complex}$$

can be envisaged. Alkyl exchange readily occurs in the complex but actual growth reaction can take place only at monomeric titanium alkyl. Although Zielger has not proposed his mechanism, most of the mechanisms can be reconciled to Ziegler's ideas.

iv. Carrick et al[68] and Badin[69] have confirmed that lower valency of transition metal forms active catalysts and change of reducing agent (metal alkyl) does not change the nature of catalytic species but change[70] in transition metal compound had a pronounced effect. Such evidence indicates chain growth at transition metal centre but still there is no definite indication that transition metal-reducing agent complex is catalytically active or not.

v. Alkyl titanium trichloride can initiate ethylene polymerization but only after considerable thermal decomposition[52,71,72]. Formation of solid titanium trichloride and perhaps lower valent titanium compounds can be envisaged by these reactions as shown below:

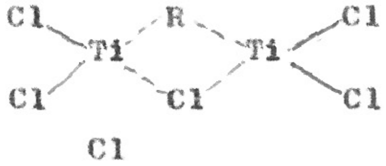
$$R\,TiCl_3 \longrightarrow \dot{R} + TiCl_3$$

$$TiCl_3 + R\,TiCl_3 \longrightarrow R\,TiCl_2 + TiCl_4$$

$$R\,TiCl_2 \longrightarrow \dot{R} + TiCl_2$$

$$R\,TiCl_3 + TiCl_2 \longrightarrow R\,TiCl + TiCl_4$$

Also complexes such as:



between alkyl titanium trichloride and titanium halides can be envisaged which also might be catalytically active.

The higher valent organo-transition metal compounds are highly unstable and hence they cannot act as active catalysts by themselves. But lowering the valence state of metal greatly increases the stability of metal carbon bond. Carrick et al[73] have shown that decrease in metal valency causes an increase in polarity of metal carbon bond. This follows since the decreasing transition metal valency decreases the electronegetivity of the metal e.g. electro negetivity

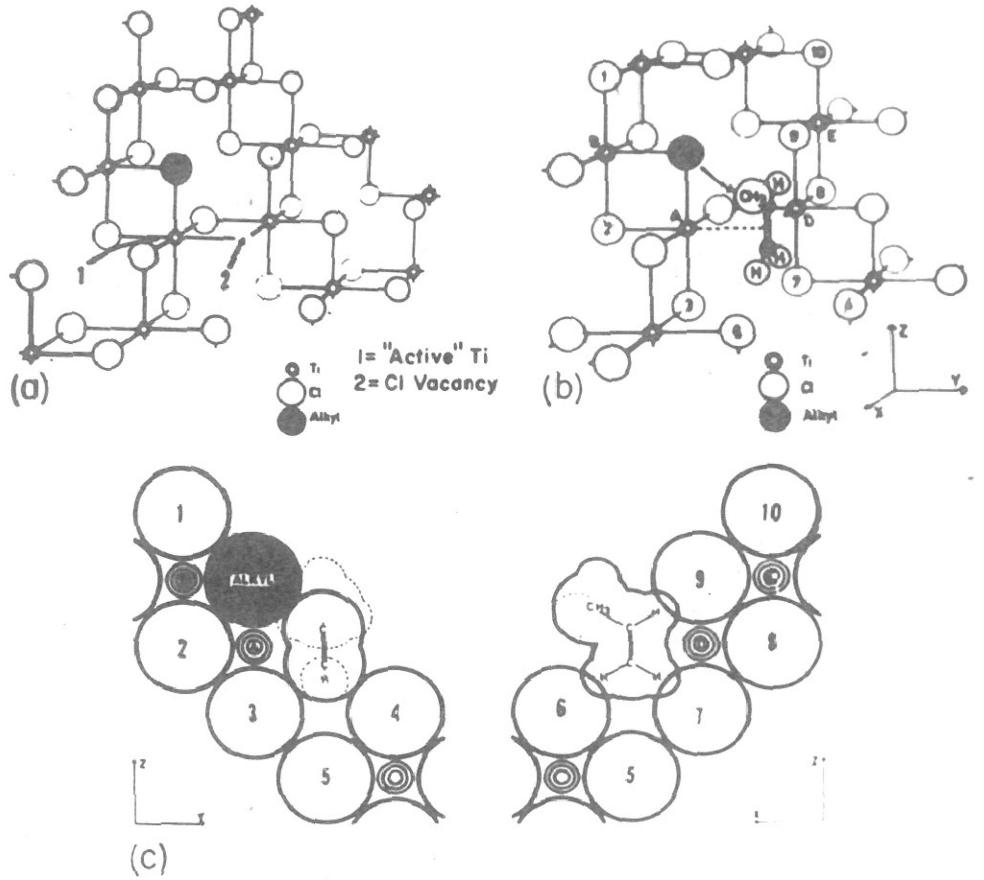


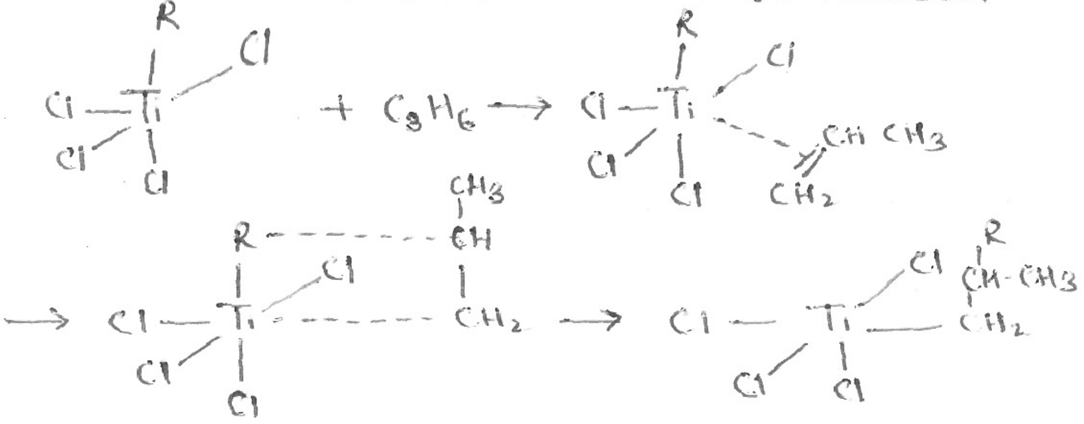
Plate.1. Mechanism of Ziegler-Natta polymerization according to Cossee

a. Activated $TiCl_3$ surface

b. Monomer π-bonded to surface

c. Stereochemistry of monomer-catalyst complex.

titanium atom (fig.(b) and then alkyl transfer.

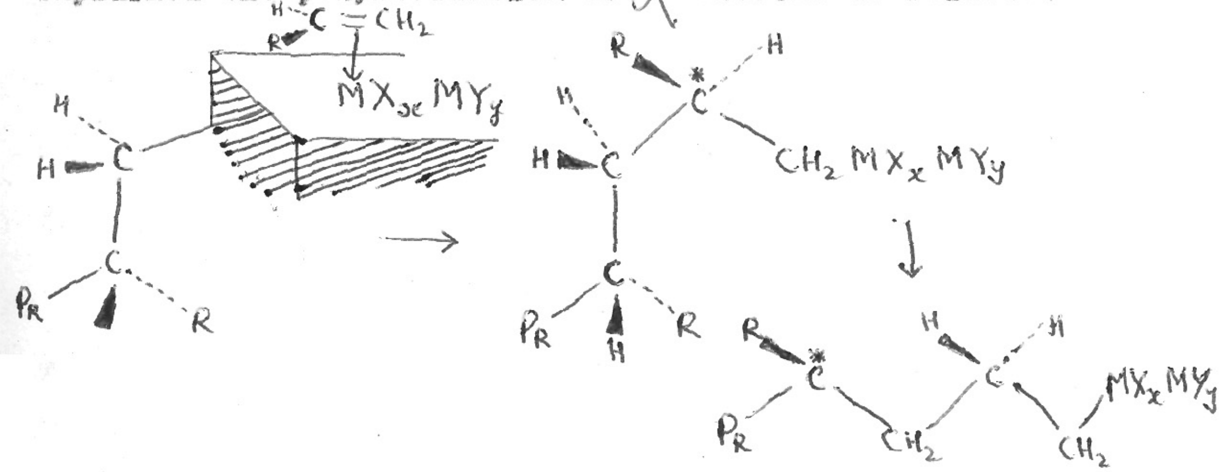


The R group in the lattice and the hole have changed places. It can be shown that there is only one way in which a propylene or other 1-alkene molecule can fit into the lattice of α or γ titanium trichloride and π bond to titanium and that is with the alkyl group protruding out (Fig.c). The π-bonded molecule can only add to the chain in the above propagation scheme in one way. Every alkyl group in the polymer chain therefore has the same conformation and the polymer is consequently isotactic. Recently Earlman[80] has extended the same approach to expalin the polymerization of dienes to cis 1,4 structures using β-titanium trichloride. Similar mechanism has been proposed by Ludlum Anderson and Ashby[81]. Further evidence favouring this mechanism is as follows:

(1) It permits a plausible picture of driving force of reaction. This is represented by Cossee as a π-type olefin complex similar to the platinous olefin[82] complexes, formed by overlapping of π-electrons of olefins with vacant $d_{x^2-y^2}$ orbitals of Titanium.

(2) Optical microscopal examination[83] of active crystalline titanium trichloride shows that chain growth occurs only at the edges of the crystal structure and such a result is in accord with the mechanism proposed by Cossee.

Cram and Kopecky[84] on the basis of steric repulsion between the monomer substituent and the substituent in the penultimate monomer unit have explained the polymerization of α-olefins as follows:

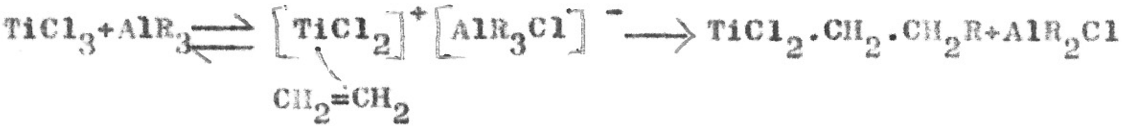


The growing polymer chain protrudes from the edge of crystal surface. Whilst it is insufficient by itself this mechanism can easily be superimposed on any other mechanism so far proposed, and it should be considered as complementary to any other mechanism. In addition, the idea of chain growth at the edge of a catalyst surface is in complete agreement with recent electron microscopical examination of an activated titanium trichloride crystal made during the polymerization of ethylene[83]. Furukawa and Tsuruta[85] have independently postulated that stereospecificity might be induced entirely due to steric repulsion.

An ion pair mechanism proposed by Uelzman[86,87] and Bier[88] is so far best amongst the other mechanisms proposed. Aluminium alkyls and titanium tetrachloride are known to form a deep red complex at -78° which decomposes on warming[89].

$$AlR_3 + TiCl_4 \xrightarrow{-78°} [TiCl_3]^+\,{}^-[AlR_3Cl] \xrightarrow{-30°} RTiCl_3 + AlR_2Cl$$

Titanium trichloride or titanium dichloride might be expected to form ion pairs such $[TiCl_2]^+[AlR_3Cl]^-$ which may polymerize as follows[87]:



$$TiCl_3 + AlR_3 \rightleftharpoons \underset{CH_2=CH_2}{[TiCl_2]^+}[AlR_3Cl]^- \longrightarrow TiCl_2.CH_2.CH_2R + AlR_2Cl$$

$$TiCl_2.CH_2\text{-}CH_2R + AlR_2Cl \longrightarrow [TiCl_2]^+[AlR_2Cl.CH_2.CH_2R]^- \quad \text{etc.}$$

According to Bawn and Ledwith[9] this mechanism might serve as a basis for rationalization of most of other mechanisms for the following reasons:

(a) Actual chain growth takes place by coordination of monomer with transition metal and this explains the findings of Carrick[70].

(b) The aluminium alkyl is essentially a chain carrier and this could account for conclusions of Natta et al and Ludlum Anderson and Ashby[81] regarding the end groups.

(c) The objection that titanium alkyl bonds are not sufficiently stable to exist for the life time of a growing polymer chain is disposed off.

(d) Cossee's mechanism which is entirely based on titanium alkyls in a crystal lattice can incorporate the idea of ion pairs since monomer will react similarly with reduced titanium halide cation as with a neutral alkylated titanium halide fundamentally.

(e) This type of mechanism adequately explains the enormous catalytic influence of small amounts of titanium halides on 'Aufban' reaction of aluminium alkyls. This point has been suggested by Ziegler[64].

KINETICS OF POLYMERIZATION

Kinetics studies play a very important role in the elucidation of mechanism of a reaction. For the good understanding of the mechanism of Ziegler type catalysts, exhaustive kinetic studies under various conditions are necessary. Study of following variables will constitute the kinetic studies.

1. Monomer concentration
2. Transition metal halide and organo-metallic concentrations
3. Ratio of the two
4. Temperature
5. Effect of temperature on molecular weight
6. Effect of catalyst on molecular weight

Collectively these points will give a general scheme to explain in qualitative and quantitative manner various features of Zielger type catalysts.

Earliest attempt~~s~~ to relate rate of polymerization with strength of monomer adsorption, nature of catalytic complex etc. was by Gaylord and Mark[21]. Later on Saltman and coworkers[90] gave a theoretical relationship based on polymerization of isoprene by Ziegler catalysts but this scheme was not elaborated. Saltman[91] proposed a more detailed scheme for the system $TiCl_4$-$AlEt_3$-propylene, which could explain the experimental results obtained by Natta[92,93]. Friedlander and coworkers[94] have also presented a kinetic scheme in order to explain the polymerization of ethylene by molybdena-alumina catalyst in the presence of ethylene. This scheme does not deal with Ziegler catalysts directly and is limited.

Stivala and Reich[95] have given a general kinetic scheme in which they have derived an expression for the rate law, taking into consideration various equilibria of monomer and catalyst components, initiation propagation and termination by various methods. They have been able to apply this scheme for a number of catalyst systems including some homogeneous ones.

Recently Schindler[96] has proposed another kinetic scheme to explain the polymerization of ethylene by Ziegler-Natta catalysts

SCOPE OF PRESENT WORK

Previous studies of the polymerization with Ziegler type catalysts mainly pertain to the use of titanium tetrachloride and aluminium alkyls for polymerization of ethylene and propylene. Some work is also reported for polymerization of styrene by the use of same catalyst system[97].

Besides this catalyst system, it is interesting to know the behaviour and nature of different combinations of various transition metal halides and organo-metallic compounds in polymerization reactions. Catalyst systems like lithium alkyl and titanium tetrachloride[98] show a different behaviour from that of aluminium alkyls and titanium tetrachloride. This catalyst system has been used for the polymerization of ethylene and propylene and a bound radical mechanism different from ionic type is postulated[98]. It will be interesting to understand the correct mechanism involved in the polymerization by the use of these catalyst systems, especially when titanium tetrachloride polymerizes styrene[99] cationically and lithium alkyl anionically.

Vanadium based catalysts, though suggested as being able to give better stereospecificity[100] in the case of styrene polymerization, have not been investigated. Vanadium halide-aluminium alkyl catalysts have recently been used for polymerization of ethylene and propylene, but detailed studies regarding mechanism have not yet appeared.

In the present studies (1) lithium isoamyl and vanadium oxichloride, (2) tin tetrapropyl and vanadium oxitrichloride, (3) diethyl aluminium bromide and vanadium oxitrichloride, (4) triethyl aluminium and vanadium oxitrichloride, and (5) triisobutyl aluminium and vanadium oxitrichloride systems have been used for the polymerization of styrene. Recently[101] polymerization of styrene with LiBu-$TiCl_4$ system is reported but these studies are restricted to know the effect of catalyst constituents at different ratios of lithium butyl to titanium tetrachloride on the molecular weight and stereospecificity.

Present studies concern the overall behaviour of these catalyst systems in polymerization of styrene and are based on following aspects:

(1) Ageing time of the catalyst after mixing the catalyst constituents, and its effect on the rate of polymerization.

(2) Activity of catalyst complex with reaction time from the percent conversion of polymer with time.

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

(4) Rate law from the variation of the rate of polymerization with monomer concentration and catalyst

concentration.

(5) Dependence of molecular weight on the ratio of combination of catalyst constituents, monomer concentration, metal alkyl concentration, transition metal halide concentration to know the termination reaction.

(6) Copolymerization of styrene and acrylonitrile by $VOCl_3$-$AlEt_3$ system and determination of reactivity ratios of two monomers.

(7) Determination of valence distribution of vanadium in different catalyst systems to know the nature of catalytic species.

(8) I.R. examination of stereospecificity of polymers.

(9) Mechanism of polymerization is ascertained by observing the effect of zinc diethyl on molecular weights and rates of polymerization and by calculating activation energy of polymerization with each system.

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CHAPTER II

EXPERIMENTAL

EXPERIMENTAL

Dry Box

All the experiments were essentially carried out under an atmosphere of dry nitrogen, including the preparation of solutions of catalytic components and their mixing inside a dry glove box. The box consisted of a rectangular wooden frame with a glass top and two openings fitted with rubber gloves for manipulations inside. The box was painted with gray oil paint. One side of the box opened to an ante-chamber through a sliding door and all materials to be taken in or removed from inside were first placed in this chamber before pushing or pulling across the door so that the dry box was never exposed to the atmosphere directly. The box was flushed constantly with dry nitrogen through an inlet and the outlet was guarded by a silica gel tower. The nitrogen was made oxygen-free by successively passing through four columns of 8" length of Fieser solution and was then made free of sulphurous gases in a bubbler containing aqueous saturated basic lead acetate solution. After washing with distilled water, it was dried over calcium chloride, sulphuric acid, phosphorous pentaoxide, potassium hydroxide pellets, silica gel and dri-arite in all-glass purification train before admission to the dry box through polyethylene tubing. The box itself contained additional desiccants - dry arite and silica gel, spread in petri dishes, which were replaced every day by freshly reactivated silica gel. A small amount of potassium hydroxide pellets to facilitate quick removal of acid fumes inside and indicator type silica gel, were also kept.

The openings for the gloves (provided for entering of hands) were kept closed with tight-fitting wooden lids when not in use.

Reagents

Fieser Solution[102].

For removal of traces of oxygen from nitrogen, it was prepared by dissolving 15 gs. of sodium hydrosulphide ($Na_2S_2O_4$) per 100 ml. of an aquous solution of 12 gs. of sodium hydroxide (NaOH) followed by the addition of 2 gs. of anthraquinone β-sulphonic acid (sodium salt). The solution was blood-red initially and became dull-brown with formation of scum when exhausted and was then discarded.

Solvents

All solvents and reagents used in the experiments were purified and dried as completely as possible and preserved under nitrogen.

Commercial benzene, n-hexane and other hydrocarbons were washed by shaking repeatedly with concentrated sulphuric acid (CP) (100 ml. for each litre of solvent) till the acid layer became colourless, washed free of acid with distilled water, dried over anhydrous calcium chloride, distilled and kept over sodium wire. The pure solvents were refluxed over night on sodium under pure dry nitrogen and distilled before use in the polymerization experiments. Commercial methanol was refluxed over sodium hydroxide and distilled before use.

Isoamyl Chloride

$(CH_3)_2CH\ CH_2CH_2Cl$[103] was prepared by the reaction of 1 g. mole distilled anhydrous isoamyl alcohol (125°/710 mm) with 1 g. mole concentrated hydrochloric acid (33% by weight) and 2 gs. mole anhydrous zincchloride. The mixture was refluxed for 3 hours before distilling off the crude isoamyl chloride through an air condenser. The product was then refluxed for one hour with an equal volume of concentrated sulphuric acid, distilled, washed free of acid, dried over anhydrous sodium sulphate and fractionated to yield the pure isoamyl chloride (95°/710 mm) (yield 30%). I.R. confirmed isoamyl group.

Lithium Isoamyl[104]

3 gs. of lithium metal (E.Merk) were flattened out into thin pieces, taken into the dry box and the oxide layer scrapped out to expose the shining metal

surface under hexane in a flat petri dish. The metal was then cut into small pieces at the mouth of three necked flask and quickly allowed to drop against a current of nitrogen into 50 ml. of hexane contained in the flask.

The reaction flask was then stoppered, removed outside, fitted with pure nitrogen inlet, mercury-seal stirrer and a dropping funnel containing 20 ml. isoamyl chloride in 25 ml. hexane which was added drop-wise to the lithium metal with vigorous stirring. After initial addition of a few drops of the isoamyl chloride, the metal got tarnished. The flask was then quickly cooled with a mixture of ice and salt to -10° and the addition of the bulk of isoamyl chloride completed in 20 minutes. Stirring was continued for 3 hours while the reaction mixture was allowed to reach room temperature. The purple black solution was allowed to settle over night before supernatent liquid was filtered through glass-wool under nitrogen. The small amount of fine particles still suspended in the alkyl solution was further allowed to settle down and the supernatent solution was removed with a syringe to 100 ml. flask with a ground glass stopper. This flask with stock solution of isoamyl lithium was enclosed in a polyethylene bag and kept inside a desiccator with silica gel and the desiccator was stored at 5° in a refrigerator. Lithium isoamyl, thus stored, was preserved without decomposition for 15-20 days.

Aluminium Triethyl

It was obtained from M/s. Ethyl Corporation, 117-Parks Avenue, New York- 17 N.Y. It was distilled at 72° (1 mm) under nitrogen and its stock solution was made (2 M) in hexane.

Aluminium Triisobutyl

It was also obtained from M/s.Ethyl Corporation. It was distilled at 68° (1 mm) under nitrogen and its stock solution (1 M) was made in n-hexane.

Tin Tetra(n) Propyl

It was obtained from M/s. Pure Chemicals Ltd., Kirkby Industrial Estate, Liverpool, as a sample. It was distilled at reduced pressure (1 mm, b.p 76°) and used as such.

Diethyl Aluminium Bromide

It was prepared by the reaction of ethyl bromide with an aluminium magnesium alloy containing aluminium 69% and magnesium 33% corresponding to Al_2Mg[105].

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

Al_2Mg was prepared by the National Metallurgical Laboratory, Jamshedpur, and analysed as given above.

Alloy was chipped to small pieces and in a typical reaction 55 gs. of it were taken in a three-necked 250 ml. flask fitted with nitrogen inlet, dropping funnel, reflux condenser and mercury seal-stirrer. A slight excess over required quantity of ethyl bromide (viz. 204 gs.) 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 a 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 10° water in condenser. The reaction was allowed to proceed thus under continous stirring for about 2-3 hours till the refluxing of ethyl bromide had stopped, and taken to completion by raising the temperature to 160°.

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[106]. It was then redistilled under vacuum (b.p 70°/1mm) and stock solution was prepared in n-hexane (0.5 M).

Vanadium Oxitrichloride[107]

According to the following equation:

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

35 gs. of vanadium pentoxide dried at 110° was

cooled in dry box and mixed thoroughly with 50 gs. of anhydrous aluminium powder in a 250 ml. round bottom flask. Now this flask was attached to an all-glass distillation unit with ground-glass joints, which were greased with syrupy phosphoric acid. It was heated in a sand-bath upto 400° and vanadium oxitrichloride was distilled over. The brown liquid thus obtained was redistilled under inert conditions in a miniature distillation unit. Pure product was a pale yellow liquid. Stock solution was prepared in hexane (0.5 M) and preserved inside the dry box.

Zinc Diethyl[108]

It was prepared by the method of C.R.Noller.

$$4\ Zn + 2\ C_2H_5I + 2\ C_2H_5Br \longrightarrow 2\ Zn(C_2H_5)_2 + ZnI_2 + ZnBr_2$$

Zinc copper alloy containing about 8% copper was prepared by stirring zinc dust 60 gs. (May & Baker) with cuperous oxide (B.D.H) 5.5 gs. in hydrogen at 410° but below the fusion point of alloy (419°). The grey alloy was further treated with stoichiometric amount of ethyl-bromide, ethyl iodide mixture in equimolar proportion adding a trace of iodine as catalyst. Vigorous reaction ensued with refluxing of alkyl halides. After completion of the reaction (about 2 hr.) the product was distilled off (40°/2 mm). The zinc alkyl was redistilled with fractionating column at atmospheric pressure, collecting pure product at 110°/720 mm. (yield 30 ml.). Zinc diethyl was easily decomposed even by slight atmospheric contamination forming black deposit and hence was handled and stored carefully under pure dry nitrogen.

Estimation of Lithium Isoamyl

2 ml. of Lithium isoamyl was taken in an Erlenmeyer 250 ml. flask and hydrolysed by adding 20 ml. of distilled water. It was titrated against 0.1 N hydrochloric acid with phenol-phthalein as indicator.

Estimation of Triethyl Aluminium, Triisobutyl Aluminium and Diethyl Aluminium Bromide[109]

Nearly 1 ml. of alkyl was weighed into a 50 ml. well stoppered conical flask. This weighed amount was diluted with 30 ml. of dry n-hexane and hydrolyzed by slow addition of 50 ml. sulphuric acid (1 N). The solution was transferred to a beaker and heated on a water bath to evaporate the hydrocarbon, then made upto 250 ml. in a standard flask.

Reagents

Following reagents were prepared and used for the estimation of aluminium.

(1) Buffer Solution

38.5 gs. amonium acetate and 28.5 ml. glacial acetic acid were dissolved in water and diluted to 500 ml.

(2) Dithizone indicator

0.025 gs. of diphenyl thiocarbazone (B.D.H) was dissolved in 100 ml. of acetone.

(3) E.D.T.A. Solution

Disodium ethylene diamine tetraacetate (E.D.T.A) 0.2 N, was prepared by dissolving 15 gs. of E.D.T.A. in 400 ml. distilled water and filtered through Whatman filter paper No.41. This was then diluted to two litres. The pH of the solution was adjusted to 4.8 by addition of hydrochloric acid or sodium hydroxide.

(4) Zinc Sulphate Solution

5.4 gs. zinc sulphate ($ZnSO_4 6H_2O$) was dissolved in distilled water and diluted to 500ml. The solution was approximately 0.2 N and was accurately standardised.

(5) Standard Aluminium Solution

1.3555 gs. aluminium sheet (E.Merck) was weighed to the nearest 0.001 g. in 100 ml. round bottom flask and 5 ml. of 0.5 N sodium hydroxide solution added to it and allowed the evolution of bubbles from the aluminium to subside. It was diluted with 25 ml. of distilled water. The solution of 20 ml. 37% HCl. was introduced slowly through the reflux condenser and the mixture heated gently to ensure complete dissolution of aluminium and refluxed for 5 to 10 minutes. After cooling, it was transferred to 500 ml. standard flask and made upto mark to yield a standard solution.

This was subsequently used to standardise zinc-sulphate and E.D.T.A.

5 ml. standard aluminium solution and 40 ml. of E.D.T.A. by burrette were taken accurately into a 250 ml. titration flask and 100 ml. buffer solution with 75 ml. rectified spirit added to it. 1 ml. of dithizone was used as indicator giving blue colour to the solution. The solution was titrated against zinc sulphate solution, the end point was yellow colour of solution.

Estimation of Vanadium Oxitrichloride

2 ml. of $VOCl_3$ solution was taken and 25 ml. of sulphuric acid (4 N) were added to it. This solution was reduced to tetravalent state by addition of 0.1 N ferrous ammonium sulphate after evaporation of solvent, and then 5 ml. of excess ferrous ammonium sulphate solution were added to ensure completion of reduction to tetravalent state. Excess of 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 saturated calomel and Pt-indicator electrodes.

Determination of Valence of Vanadium in the Catalytic Complex

Valence determination was carried out potentiometrically in acidic solution (25 ml. of 4 N H_2SO_4). The potential of the solution of catalytic complex was measured using platinum indicator electrode and a saturated calomel electrode with Sergent 'Ampot' titration apparatus (S-29710) adjusted for potentiometric titrations. Potassium permanganate and ceric sulphate were used as oxidants.

Partial reactions when potassium permanganate is used as oxidant are[110]:

$$MnO_4^- + 8H + 5\bar{e} \longrightarrow Mn^{2+} + 4\ H_2O \qquad E° = 1.52$$

$$V^{2+} \longrightarrow V^{3+} + e \qquad E° = 0.255$$

$$H_2O + V^{3+} \longrightarrow VO^{2+} + 2H^+ + \bar{e} \qquad E° = 0.361$$

$$3H_2O + VO^{2+} \longrightarrow V(OH)_4^+ + 2H + \bar{e} \qquad E° = -1.00$$

In view of the normal potential values of the partial reactions, it is possible to oxidize quantitatively the lowest valence state first before the higher valence states are oxidized. Consequently, more than one break is found in the titration curve, when a valence state lower than +4 is present.

Oxidation with ceric sulphate is also an effective method[111] for determination of valence distribution of vanadium in the catalytic complex. Since the last end point (i.e. V^{4+} to V^{5+}) was not very sharp when using $KMnO_4$ as oxidant in the case of $VOCl_3$-$AlEt_2Br$ catalyst system, ceric sulphate was used which gave satisfactory results. In cases of other systems, both oxidants were found to give comparable results.

In the titration of vanadium with potassium permanganate as well as ceric sulphate, the equilibrium is reached slowly especially near the end point. It was found that potentials assumed constant values more rapidly if the titration is carried out at high temperatures. All the titrations were carried out at 80° by thermostating the reaction vessel.

Purified nitrogen was bubbled through the titration vessel to avoid oxidation of lower valence states by atmospheric oxygen. Purified nitrogen was bubbled also through the acid solution used, to remove dissolved air. Solutions of oxidants were also prepared with oxygen-free distilled water.

Colour of solution changes from violet to green then to blue and again green and pale yellow in the end. These colour changes are not characteristic of any valence change. Similar method has also been used by Carrick et al[112].

Purification of Monomers

Styrene

Dow Chemical styrene was washed with 5% alkali solution for 2-3 times till the alkali did not become coloured. Then it was washed with distilled water till it became free of alkali. It was dried over anhydrous sodium carbonate and stored over it in refrigerator. Just before the experiment, a small amount of purified monomer was redried over potassium hydroxide pellets for some time and distilled under vacuum (28 mm Hg) at 56° under dry nitrogen and kept over silica gel.

EXPERIMENTAL PROCEDURE

These catalyst systems consisting of metal alkyls and transition metal halides are very reactive with moisture and oxygen. Under these conditions, it was essential to use thoroughly dried glass equipments to avoid contamination and to keep reproducibility of results. All additions and mixing of the reagents were carried out in the dry box under an inert blanket.

The reaction flasks and magnetic elements (enclosed in glass) used in experiments were thoroughly cleaned with chromic acid and washed with distilled water and dried overnight at 160°. Before the experiment, they were transferred inside the dry box when still hot and cooled while purging the nitrogen inside. Similarly, all-glass hypodermic syringes with stainless steel needles were cleaned with chromic acid and washed with distilled water and dried at 110° and transferred inside the dry box while hot.

Stock solutions of catalysts, dry solvents and monomers were preserved inside the dry box and required amounts of reagents added with syringes (1-20 ml.) in the predetermined order. The reaction flask was immediately stoppered with well greased (Dow Corning silicone, high vacuum grease) standard joints before being thermostated outside the box in a bath (20 litres). Temperature of thermostat was controlled to ± .05° by a toluene regulator connected to electronic relay. The stirring element inside the reaction flask was moved by a magnetic stirrer held inside the thermostat under the reaction flask. A horse-shoe magnet was enclosed in a water-proof brass case[113] and carried on ball bearings to make the stirrer. The magnet was connected by a flexible speedometer shaft cable to a B.T.C. stirring motor and the speed of rotation adjusted. 50 ml. conical flasks with B_{19} (M) joint and with B_{19} (F) stoppers were used for all the systems.

After polymerization has been allowed to proceed to the required time, it was quenched by addition of acidified methanol and the polymer precipitated by further addition of large excess of methanol with 10% hydrochloric acid. Since the polymers were generally of low molecular weight, considerably large excess (5-10 times) of methanol was used and the precipitation completed while the mixture was cooled (with ice and salt mixture).

Molecular Weights

Molecular weights were determined by intrinsic viscosities of 0.05 to 0.1% solutions of polymers in benzene in an Ostwald U-tube viscometer suspended in a Towers viscometric bath at 25°.

Polystyrene prepared from $VOCl_3$-$AlEt_3$ and $VOCl_3$-$Al(iBu)_3$ was dissolved in toluene, under refluxing and soluble portion was filtered and reprecipitated. The standard solution was prepared in benzene. The polymers prepared from other systems were dissolved in benzene reprecipitated, filtered, dried and dissolved in benzene to make standard solutions in 25 ml. flasks.

The relationship of intrinsic viscosity with chain length[114], given below, was applied.

$$Pn = 1.770 \times [\eta]^{1.4} \qquad \text{(in benzene)}$$

Infrared Analysis

5% polymer solution was prepared in redistilled Analar carbon disulphide[115] and infrared spectra were recorded on infracord and Perkin Elmer spectrophotometer 221. The cell of 0.1 mm. thickness was used. Spectra of samples were also obtained by use of potassium bromide pellet technique. Approximately 3 mg. sample was mixed with 350 mg. of anhydrous KBr (B.D.H) and pressed into a pellet in the hydraulic press. Certain spectra of resinous polymers were examined by forming a film of the sample on the rock salt plate.

CHAPTER III

EXPERIMENTAL RESULTS

EXPERIMENTAL RESULTS

Polymerization of Styrene with Vanadium Oxitrichloride and Triethyl Aluminium at 40°

$VOCl_3$ reacts with $AlEt_3$ immediately to form a brown black mass, which is already known to polymerize ethylene and give copolymers of ethylene and propylene[116] It is also known to give copolymers of propylene and acrylonitrile[117] but it has not been used earlier for polymerization of styrene. Present studies use this catalyst system for styrene polymerization.

Aging Time Studies

Experiments were carried out for polymerization of styrene with this catalyst system, at different aging times between 10 to 60 minutes and 24 hours. It was found that there was no effect of aging time on the rate of polymerization. Hence it was concluded that there is no change in activity of catalyst system during first twenty four hours. Molecular weights also did not vary with aging time.

Results are tabulated in Table No.I.

Table No.I

Effect of Aging Time

$[VOCl_3]$ = 0.02 m/1 Styrene = 10 ml
$[AlEt_3]$ = 0.04 m/1 Reaction time = 3 hours
$Al/_V$ molar Ratio = 2 Temperature = 40°

	Aging time mm.	Yield in gs.	$R_p \times 10^8$ × 9.076 m/1/s	$[\eta]$	Molecular weight
1.	10	0.1930	75.67	0.5109	71980
2.	20	0.1974	77.39	0.5628	81345
3.	30	0.1983	77.75	0.6655	104105
4.	60	0.2335	91.54	0.5335	75385
5.	1440	0.2051	80.41	0.6825	105455

Ratio Studies

Polymerization studies were carried out at different ratios of $Al/_V$ and it was found that rate of polymerization decreased abruptly between ratio 1.2 and 2 and at higher ratios it decreased at a very slow rate. At ratios upto 1.2 the catalyst turns brown during polymerization but at higher ratios it remained black. Molecular weights increased steeply between ratio 1.2 and 2 $(Al/_V)$ giving a maxima at ratio 2 and it decreased with further increase in ratio. It was concluded that Ziegler type catalyst is formed at ratio $Al/_V = 2$ and hence all the further studies were carried out at ratio $Al/_V = 2$.

Results are given in Table No.2. (fig 1)

Table No.2

Ratio Studies

$VOCl_3$ = 0.02 m/l   Reaction time = 3 hours
Styrene = 10 ml   Aging time = 20 minuts
Temperature = 40°

	Molar Ratio Al/V	Yield in gs.	% age conversion		Molecular weight
1.	0.5	Total	100.0	0.08061	5425
2.	1.0	8.2421	90.80	0.06005	3390
3.	1.2	8.6800	95.63	-	-
4.	1.6	0.4226	4.66	0.5293	75535
5.	2.0	0.1974	2.17	0.5628	81345
6.	2.5	0.1656	1.83	0.5323	76160
7.	3.0	0.1486	1.64	0.4286	56220
8.	4.0	0.1560	1.72	0.2035	19815
9.	5.0	0.1406	1.55	0.2308	23630
10.	6.0	0.1341	1.48	0.2181	21840
11.	9.0	0.1541	1.70	-	-

Effect of Time

Polymerizations were carried out at different times keeping concentrations of catalyst, monomer and ratio of catalytic components as constant. It was found that rate of polymerization remained constant only during first hour and it started decreasing with increasing reaction times. Molecular weights showed a slight increase with increasing reaction times

Results are tabulated in Table No.III - Fig.2

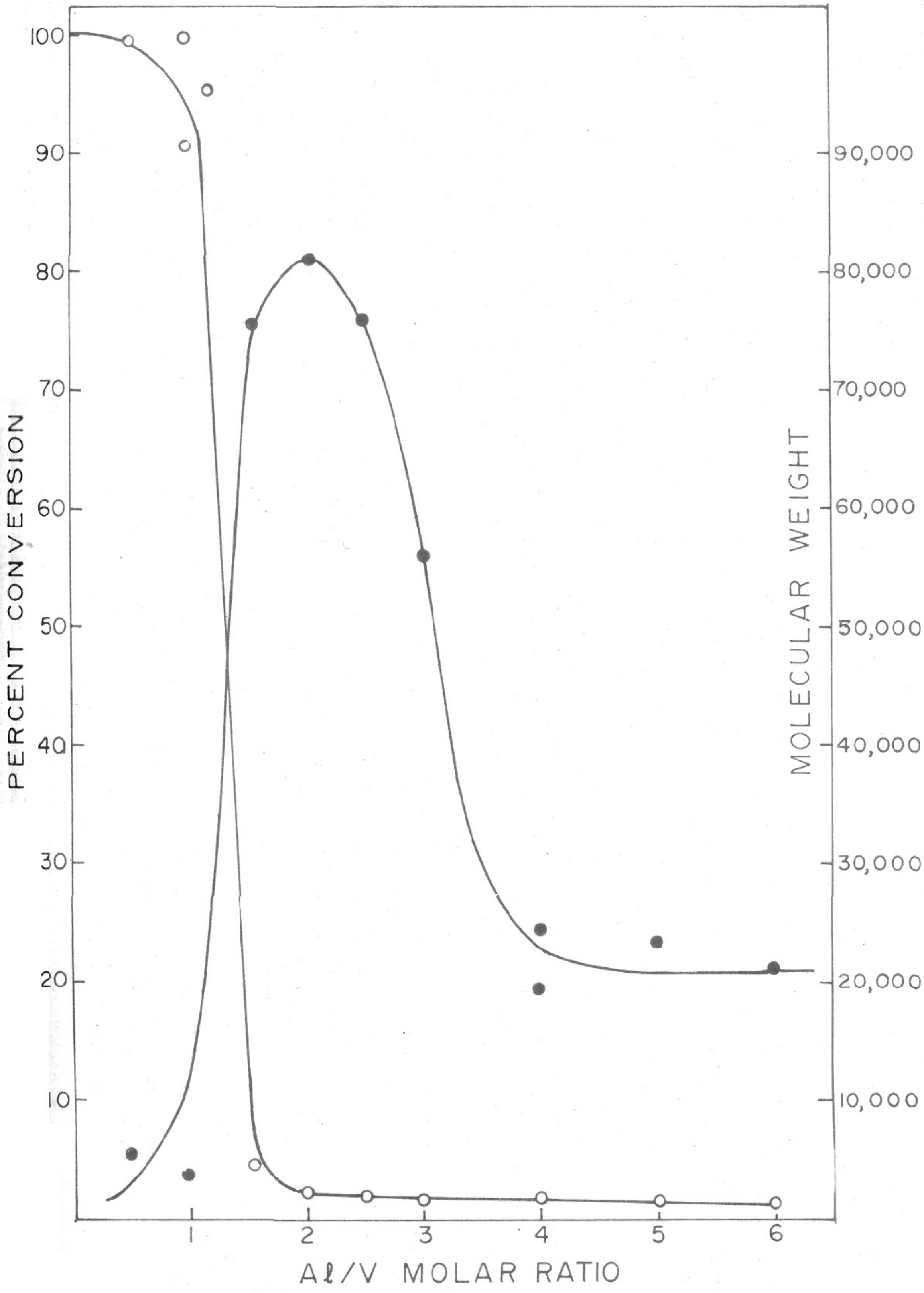


Fig 1: EFFECT OF Aℓ/V MOLAR RATIO ON $VOCl_3 - AlEt_3$ SYSTEM

$[VOCl_3] = 0{\cdot}02$ M/ℓ Styrene = 10 ml

Reaction time = 3 hrs. Aging time = 20 Min.

Temperature = 40°

—○— Percent conversion vs. Ratio —●— M.W. vs. Al/V Ratio

Table No.III

Effect of Reaction Time

$[VOCl_3]$	= 0.02 m/l		Styrene	=	10 ml
$[AlEt_3]$	= 0.04 m/l		Aging time	=	20 minuts
Al/V molar ratio	= 2		Temperature	=	40°

	Reaction time min.	Yield in gs.	% conversion	$[\eta]$	Molecular weight
1.	30	0.0786	0.87	0.5146	72645
2.	60	0.1333	1.47	0.5632	82410
3.	90	0.1151	1.27	0.6071	91540
4.	120	0.1467	1.62	0.6342	96300
5.	180	0.1974	2.17	0.5628	81345
6.	240	0.2076	2.28	0.6371	97925
7.	300	0.2300	2.53	0.7759	129065
8.	360	0.2555	2.81	0.6926	110135

Effect of Monomer Concentration and Catalyst Concentration

Studies were carried out on effect of monomer concentration on rate of polymerization keeping all other variables constant. It was found the rate of polymerization increased linearly with monomer concentration. Order of reaction was found to be one. Molecular weights increased first with increase in monomer concentration and beyond the monomer concentration of 4.36 m/l, they again started decreasing. Results are tabulated in Table No.IV Fig.3.

Effect of catalyst concentration was also studied at monomer concentration 3.488 m/l, and Al/V

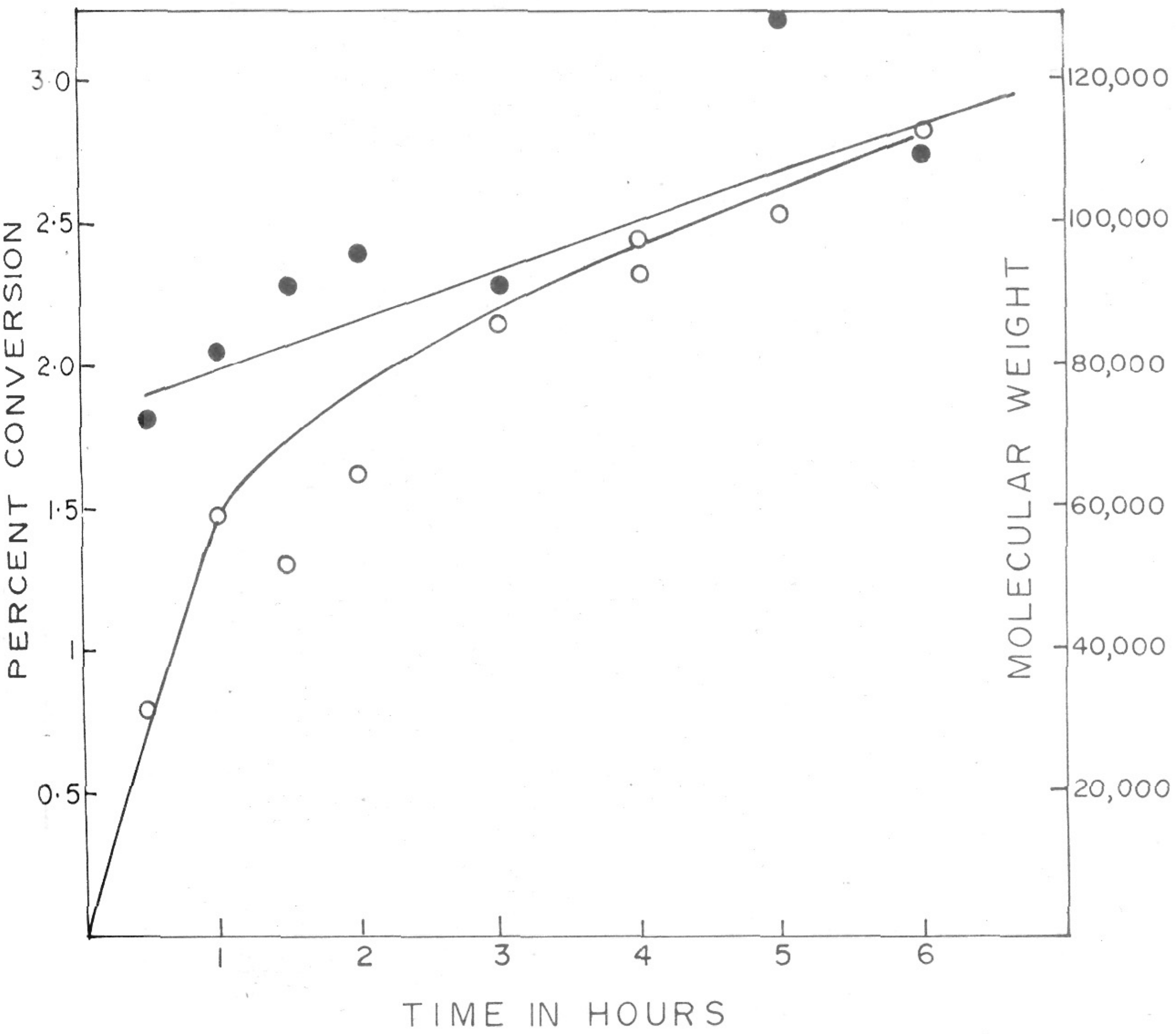


Fig 2: EFFECT OF TIME ON $VOCl_3$–$AlEt_3$ SYSTEM

$[VOCl_3] = 0{\cdot}02$ m/l $[AlEt_3] = 0{\cdot}04$ m/ℓ.

Aℓ/V molar ratio = 2; Styrene = 10 ml.;

Ageing time = 20 Min. Temperature = 40°;

—○— Percent conversion vs. Time; —●— M.W. vs. Time.

ratio 2. Rate of polymerization increased linearly with catalyst concentration and order of reaction was one with respect to catalyst concentration. Molecular weights decreased with increase in monomer concentration.

Results are presented in Table No.V Fig.4.

Table No.IV

Effect of Monomer Concentration

$[VOCl_3]$ = 0.02 m/l
$[AlEt_3]$ = 0.04 m/l
$Al/_V$ Ratio= 2

Aging time = 20 min.
Reaction time = 1 hr.
Temperature = 40°

	Monomer conc. m/l	Yield in gs.	R_p x 10^7 xx ~~x 4.076~~ m/l/s	$[\eta]$	Molecular weight
1.	1.744	0.0440	10.36	0.4542	60985
2.	2.616	0.0768	12.36	0.4397	58280
3.	3.488	0.1239	14.58	0.4934	68485
4.	4.360	0.2097	19.74	0.5682	84020
5.	5.232	0.3120	24.45	0.4420	58695
6.	6.279	0.3890	25.43	0.3996	50960
7.	6.975	0.4228	24.88	0.5114	72000

Effect of Temperature

Polymerization was carried out at different temperatures i.e. 30°, 40° and 50° at one hour reaction time. It was found that rate of polymerization kept on increasing with temperature. Molecular weights were

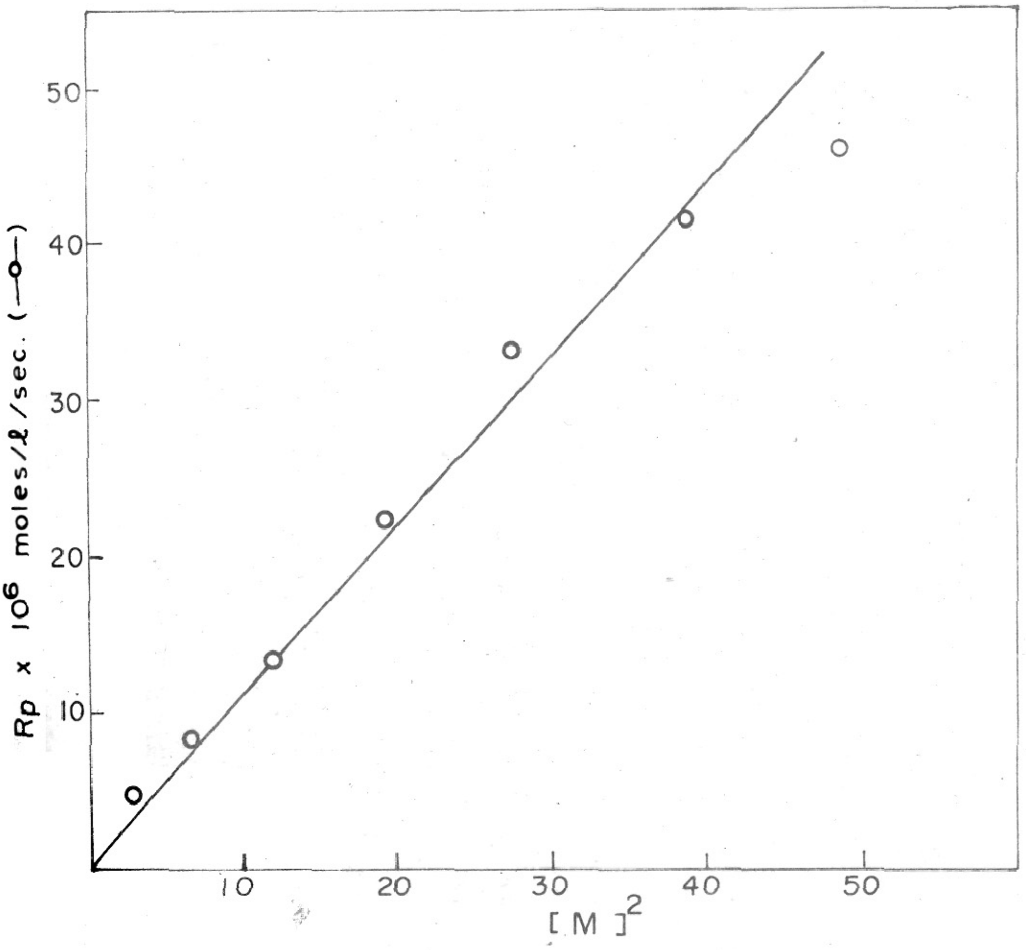


Fig. 3 $VOCl_3$-$AlEt_3$ System Rp vs. $[M]^2$

$[VOCl_3]$ = 0·02 m/l Al/V molar ratio = 2

Aging time = 20 Min. Reaction time = 1 hr.

Temperature = 40°

found to decrease with increase in temperature. Activation energy was calculated from the plot of log R_p vs. $\frac{1}{T}$.

Results are tabulated in Table No.VI. Fig. 5.

Table No.V

Effect of Catalyst Concentration

Styrene = 10 ml
Aging time = 20 min.
Al/V Molar ratio = 2
Reaction time= 1 hr.
Temperature = 40°

	Catalyst conc. m/l	Yield in gs.	$R_p \times 10^7$ ×9.076 m/l/s	[η]	Molecular weight
(1)	0.01	0.1436	16.90	0.2691	29285
(2)	0.02	0.1239	14.58	0.4934	68485
(3)	0.03	0.1373	16.16	0.7259	117625
(4)	0.04	0.1890	22.25	0.3588	45425
(5)	0.05	0.2690	32.06	0.2164	21600
(6)	0.06	0.2917	34.34	0.3228	37930
(7)	0.07	0.5741	67.57	0.2326	23890
(8)	0.08	0.7270	67.95	-	-

Table No.VI

Effect of Temperature

$[VOCl_3]$ = 0.02 m/l
Styrene = 10 ml
$[AlEt_3]$ = 0.04 m/l
Reaction time = 1 hr.
Al/V molar ratio = 2
Aging time = 20 min.

	Temp.°	Yield in gs.	$R_p \times 10^7$ ×9.076 m/l/s	[η]	Molecular weights	$\frac{1}{T} \times 10^3$	log R_p
(1)	30°	0.0952	11.19	0.8545	86810	3.3	6.0490
(2)	40°	0.1239	14.58	0.4934	68485	3.19	6.1638
(3)	50°	0.1882	22.15	0.4122	52875	3.09	6.3451

Activation Energy = 7.37 Kcal/mole.

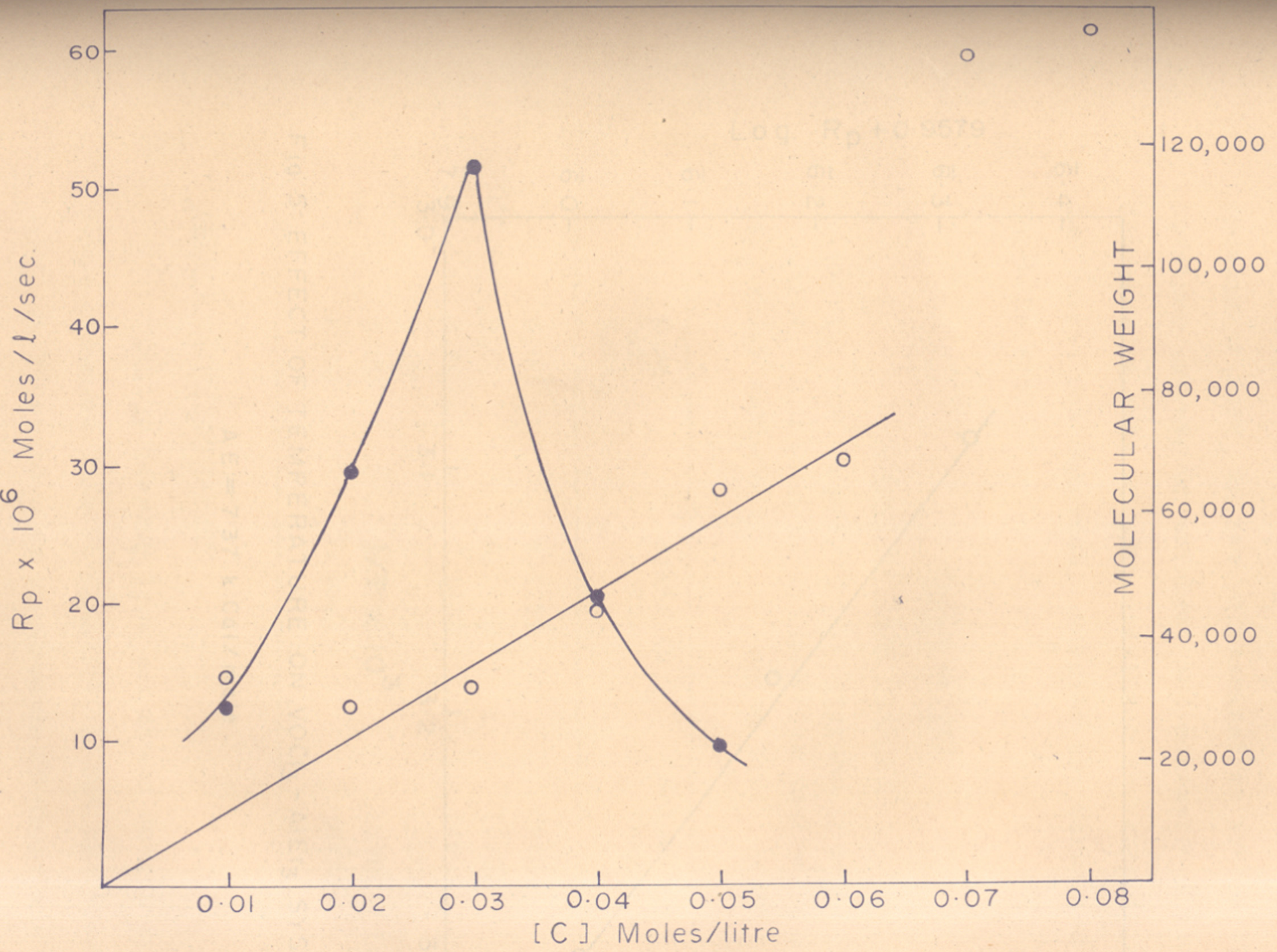


Fig 4: EFFECT OF CATALYST CONC ON $VOCl_3$ - $AlEt_3$ SYSTEM

Styrene = 10 ml. ; Al/V molar ratio = 2; Aging time = 20 Min.
Reaction time = 1hr. Temperature = 40°
—○— R_p vs. [C], —●— M. W. vs. [C]

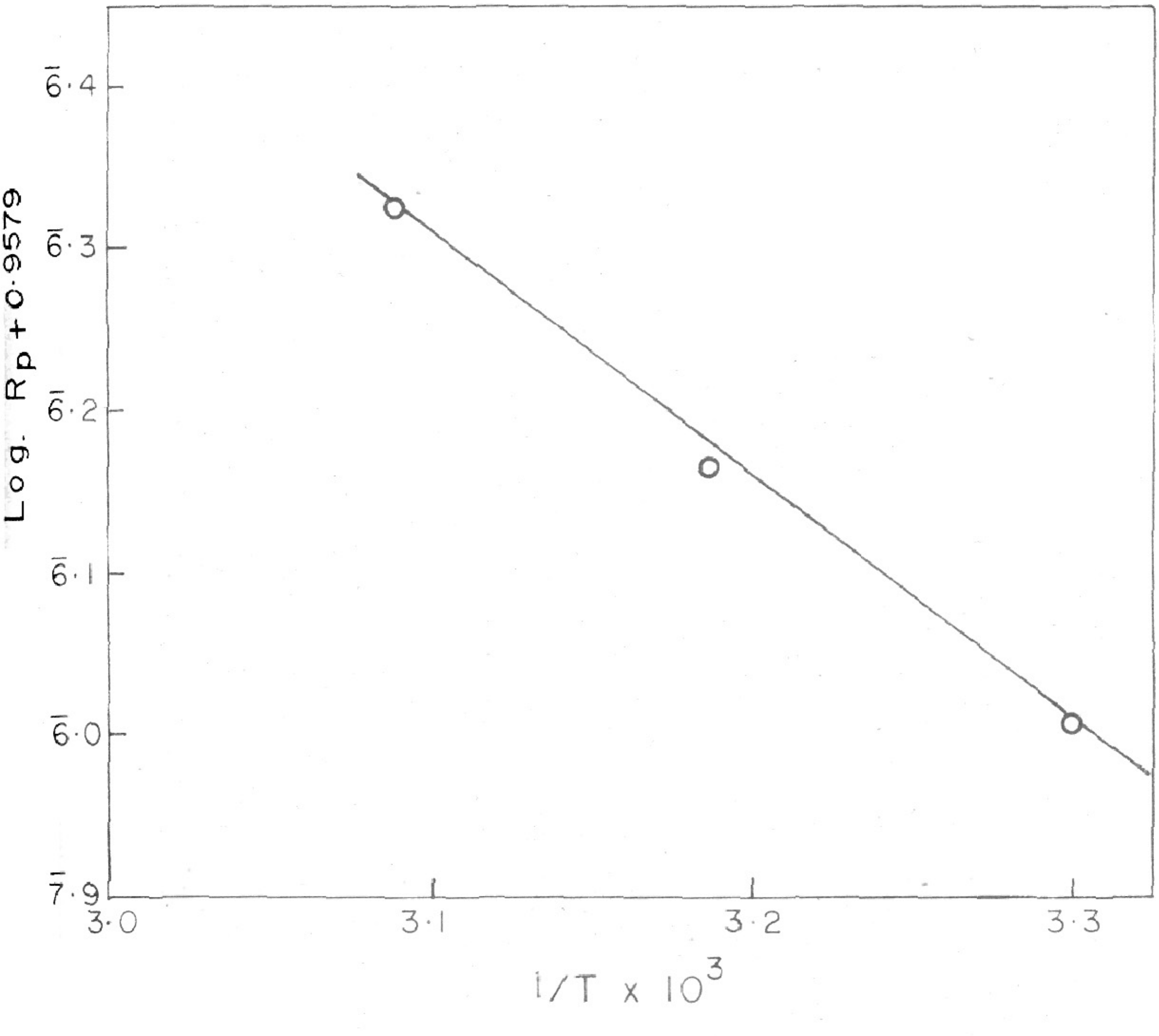


Fig. 5: EFFECT OF TEMPERATURE ON $VOCl_3$ - $AlEt_3$ SYSTEM

A E = 7·37 k Cal/mole

Effect of Zinc Diethyl

Polymerization were carried out with varying amounts of $ZnEt_2$ in the polymerization system with constant amounts of catalyst and monomer. A marked decrease in rate of polymerization and also in molecular weight was observed. Results are tabulated in Table No.VII.

Table No.VII

Effect of Zinc Diethyl

$[VOCl_3]$ = 0.02 m/l   Styrene = 10 ml
$[AlEt_3]$ = 0.04 m/l   Reaction time = 1 hr.
$Al/_V$ molar ratio = 2   Aging time = 20 min.

Conc. of $ZnEt_2$	Yield in gs.	Molecular weight
0.00	0.1239	68485
0.01	0.1730	12865
0.02	0.1462	14165
0.04	0.0942	15390
0.06	0.0945	31795
0.10	0.0944	15725

Effect of Hydroquinone

Usually Ziegler type catalysts do not polymerize ionic monomers like acrylonitrile, but the system $VOCl_3$-$AlEt_3$ is known to give copolymers of propylene with acrylonitrile[117]. And also, it is found in our studies to give copolymers of styrene and acrylonitrile and also styrene and methyl methacrylate. So it was suspected that mechanism of polymerization by this particular catalyst system may be free radical or partially free radical. To clarify this point polymerizations were carried out with varying amounts of hydroquinone and it was found that the rate of polymerization is not affected by the presence of hydroquinone, thus ruling out the possibility of a free-radical polymerization.

Results are presented in Table No.VIII.

Table No.VIII

Effect of Hydroquinone

$[VOCl_3]$ = 0.02 m/l
$[AlEt_3]$ = 0.04 m/l
Al/V molar ratio = 2
Styrene = 10 ml
Reaction time= 1 hr
Aging time = 20 min.

	Amount of hydroquinone	Yield in gs.	Molecular weight
(1)	0.0 mgs.	0.1239	68485
(2)	100.0 mgs.	0.1058	73675
(3)	200.0 mgs.	0.1069	75785
(4)	400.0 mgs.	0.1515	65890

Determination of Valence of Vanadium in the Catalyst Complex

Valence studies carried out using $KMnO_4$ as oxidant indicate that the average valence of vanadium in catalytic complex is 3 at ratio 2 and whole of vanadium is in travalent state (See Fig.6). Plot of average valence against ratio shows that even at ratio 1 most of vanadium is in travalent state (Av val 3.3). At higher ratios (above 3), the valence is reduced to less than 3 i.e. divalent form starts appearing (Fig.7 Table No.IX).

Table No.IX

Distribution of Valence of Vanadium in the Catalyst System $VOCl_3$-$AlEt_3$

$VOCl_3$ = 2 ml H_2SO_4 = 25 ml (4 N)

	Ratio $^{Al}/_V$	Distribution of Valence			Average valence
		V^{II} fraction	V^{III} fraction	V^{IV} fraction	
(1)	1.0	-	0.714	0.286	3.3
(2)	1.5	-	1.0	-	3.0
(3)	2.0	-	1.0	-	3.0
(4)	2.5	-	1.0	-	3.0
(5)	4.0	0.43	0.57	-	2.57
(6)	6.0	0.43	0.57	-	2.57

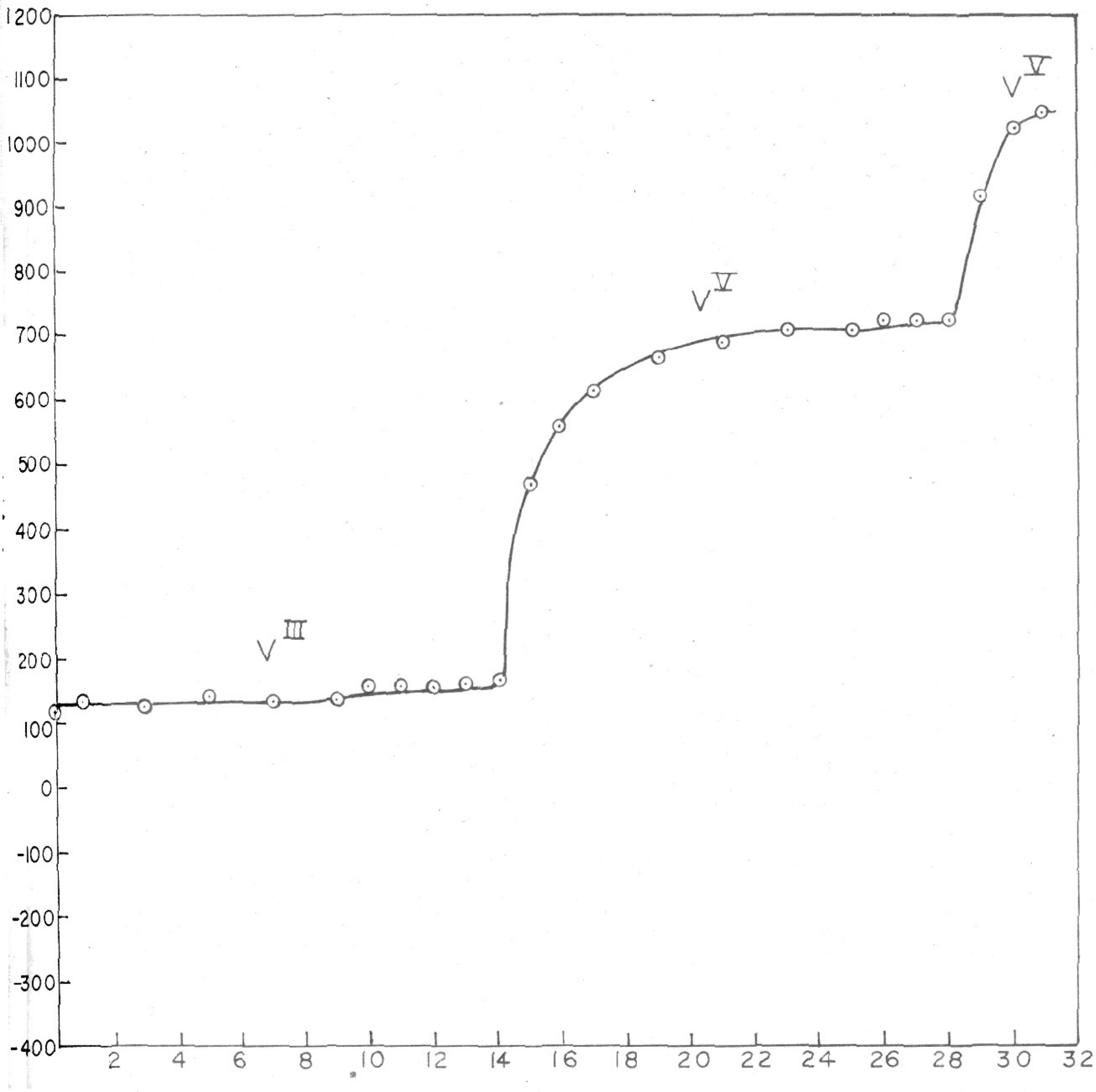


Fig. 6 VALENCE DISTRIBUTION OF VANADIUM IN $VOCl_3 - AlEt_3$ SYSTEM

Al/V ratio = 2.

$KMnO_4$ Soln. = 0·1 N; Temperature = 80°

H_2SO_4 Soln. = 4 N; Total Volume = 25 ml.

Av. Valence = 3·0

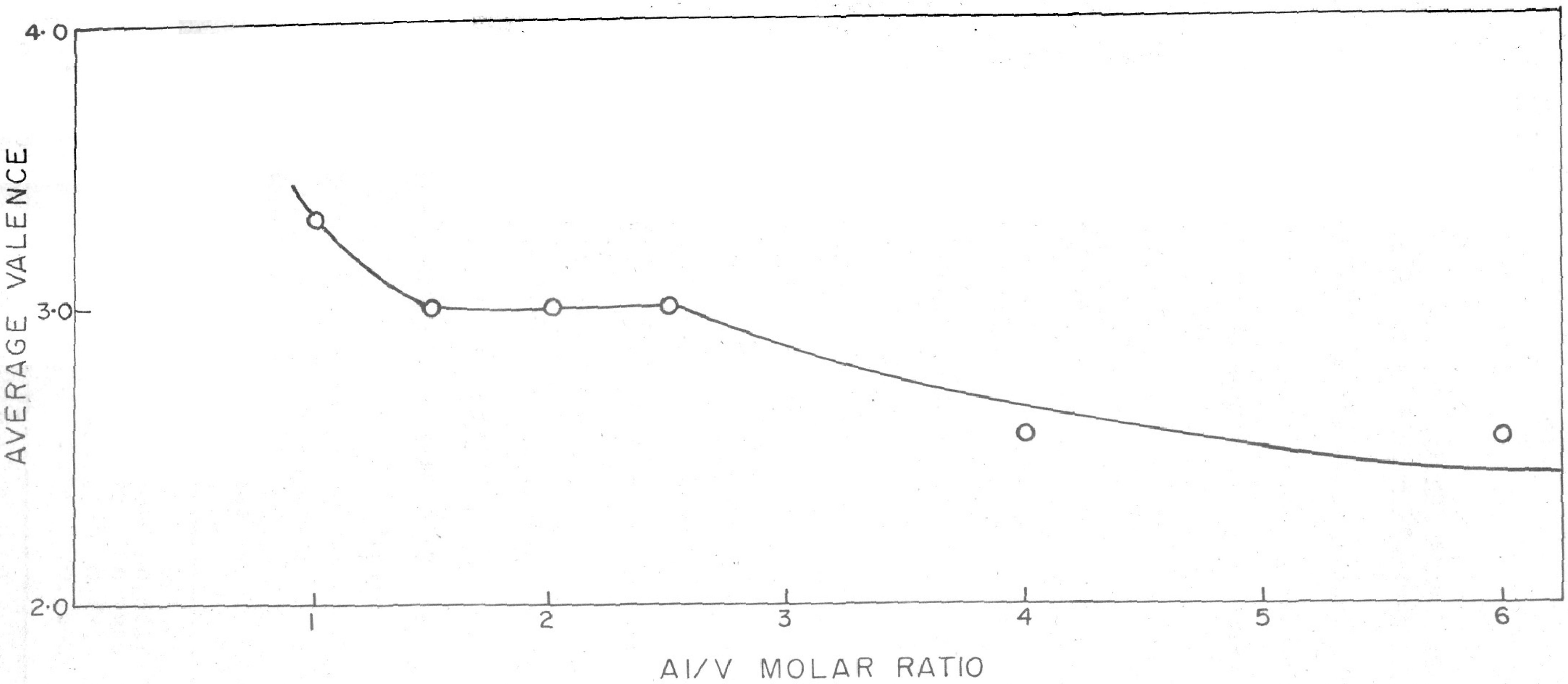


Fig 7: EFFECT OF Al/V MOLAR RATIO ON AV. VALENCE OF $VOCl_3$-$AlEt_3$ SYSTEM

Polymerization of Styrene with Vanadium Oxitrichloride and Aluminium Triisobutyl at 40°.

As soon as $VOCl_3$ solution is mixed with $Al(iBu)_3$ solution, a dark brown solid complex is formed, which is capable of polymerizing styrene. Order of addition was kept the same as in other cases viz. hexane, then $VOCl_3$ solution, then $\overset{Al(iBu)_3}{AlEt_2Br}$ solution and lastly styrene (after aging).

Aging Time Studies

Aging time of the catalyst was varied from 10 to 60 minutes and it was found that there was no change in rate of polymerization with aging time. Molecular weights also did not vary with variation of aging time. Another experiment was carried out with 24 hours aging and that also gave similar results. Thus it can be concluded that activity of catalyst does not change for at least first 24 hours.

Results are tabulated in Table No.X.

Table No.X.

Effect of Aging time

$[VOCl_3]$ = 0.01 m/l Styrene = 5 ml

$[Al(iBu)_3]$ = 0.03 m/l Reaction time = 15 min.

Al/V Molar ratio = 3 Temperature = 40°

	Aging time min.	Yield gs.	Percent conversion	$[\eta]$	Molecular weight
(1)	10	0.5010	11.04	0.1631	14540
(2)	20	0.4813	10.60	0.1226	9745
(3)	30	0.4173	9.19	0.1236	9860
(4)	60	0.5947	13.11	0.1343	11065
(5)	1440	0.4288	9.34	0.1595	14100

Ratio Studies

Effect of ratio of catalytic components on the rate of polymerization was studied. It was found that rate of polymerization fell sharply between ratios ($Al/_V$) 2 and 3 and beyond ratio 3 there was a very slow decrease in rate of polymerization. It was decided to carry out further experiments at ratio 3 because at lower ratios of $Al/_V$ the yields were very high for small reaction times and a cationic polymerization was suspected. But at ratio 3 and at higher ratios the rates were comparatively much lower and reaction of catalytic components was assumed to be complete. Molecular weights were also very low up to ratio 2 and they increased sharply between ratio 2 and 3. At higher ratios there was a slow increase in molecular weights with ratios.

Results are tabulated below (Table XI Fig.8)

Table No.XI

$[VOCl_3]$ = 0.01 m/l　　Aging time = 20 min.
Styrene = 5 ml　　Reaction time = 15 min.
Temperature = 40°

	Molar ratio $Al/_V$	Yield in gs.	% conversion.	$[\eta]$	Molecular weight.
(1)	1.0	3.4282	75.53	0.0431	2045
(2)	2.0	2.4802	54.64	0.0502	2795
(3)	2.5	0.8152	17.95	0.1006	7920
(4)	3.0	0.4813	10.60	0.1226	9745
(5)	4.0	0.2815	6.203	0.1431	12095
(6)	6.0	0.1023	2.254	0.1635	13925

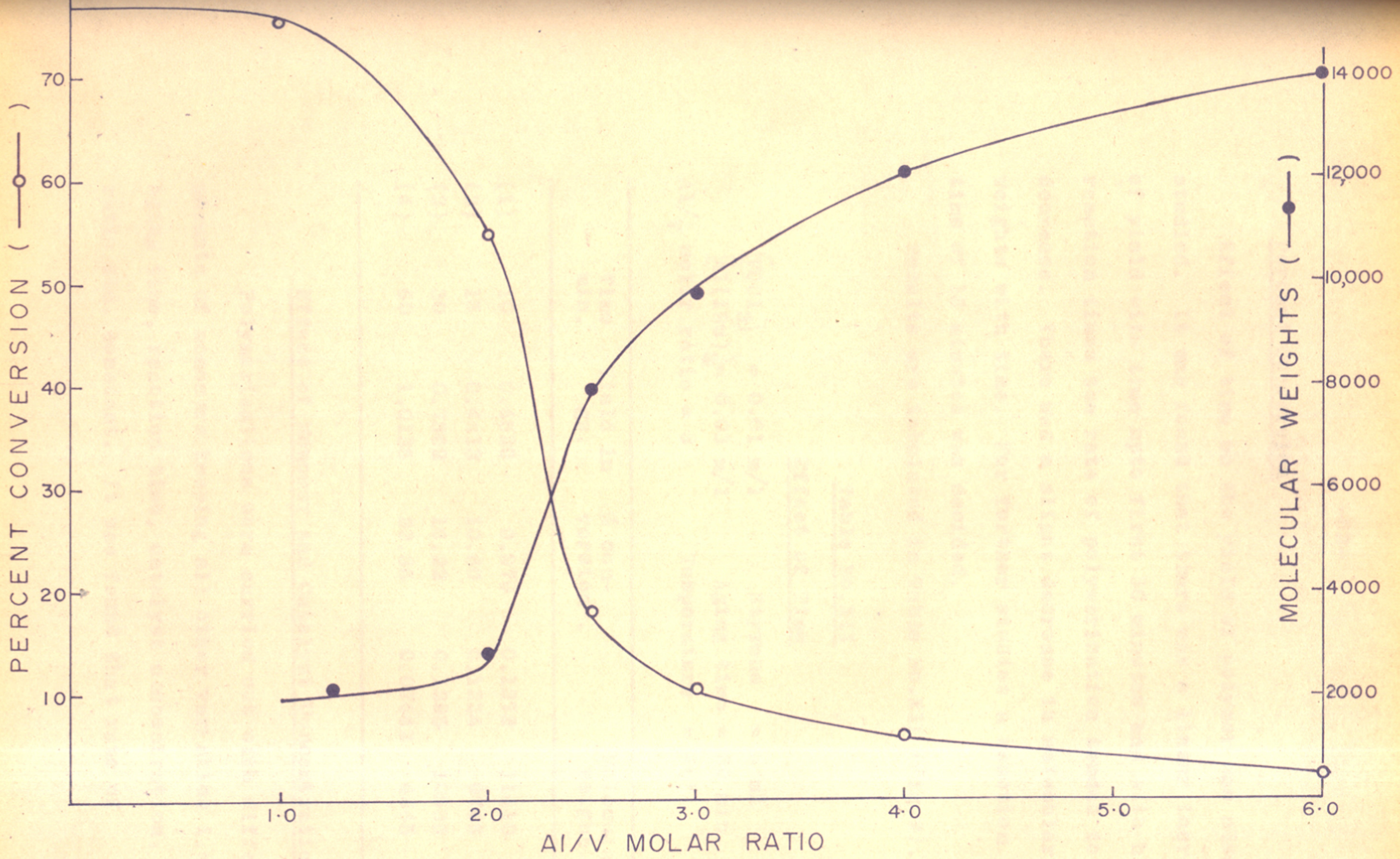


Fig. 8 EFFECT OF Al/V MOLAR RATIO ON $VOCl_3 - Al(iBu)_3$ SYSTEM

$[VOCl_3]$ = 0·01 m/l; Styrene = 5 ml.; Aging time = 20 Min.
Reaction time = 15 Min.; Temperature = 40°

Percent Conversion

Effect of time on the yield of polymer was also studied. It was found that there was a linear increase of yield with time upto first 30 minutes and with higher reaction times the rate of polymerization tended to decrease. There was a slight decrease in molecular weights with time. For further studies a reaction time of 15 minutes was decided.

Results are tabulated in Table No.XII (Fig.9).

Table No.XII

Effect of Time

$[VOCl_3]$ = 0.01 m/l Styrene = 5 ml
$[Al(iBu)_3]$ = 0.03 m/l Aging time = 20 min.
$Al/_V$ molar ratio = 3 Temperature = 40°

	Time min.	Yield in gs.	% conversion .		Molecular weight.
(1)	10	0.4529	9.979	0.1372	11410
(2)	15	0.4813	10.60	0.1224	9745
(3)	30	0.7362	16.22	0.1295	10535
(4)	60	1.0135	22.35	0.07442	4845

Effect of Monomer and Catalyst Concentrations

Polymerizations were carried out with different amounts of monomers keeping all other variables i.e. aging time, reaction time, catalyst concentration, $Al/_V$ ratio etc. constant. It was found that rate of

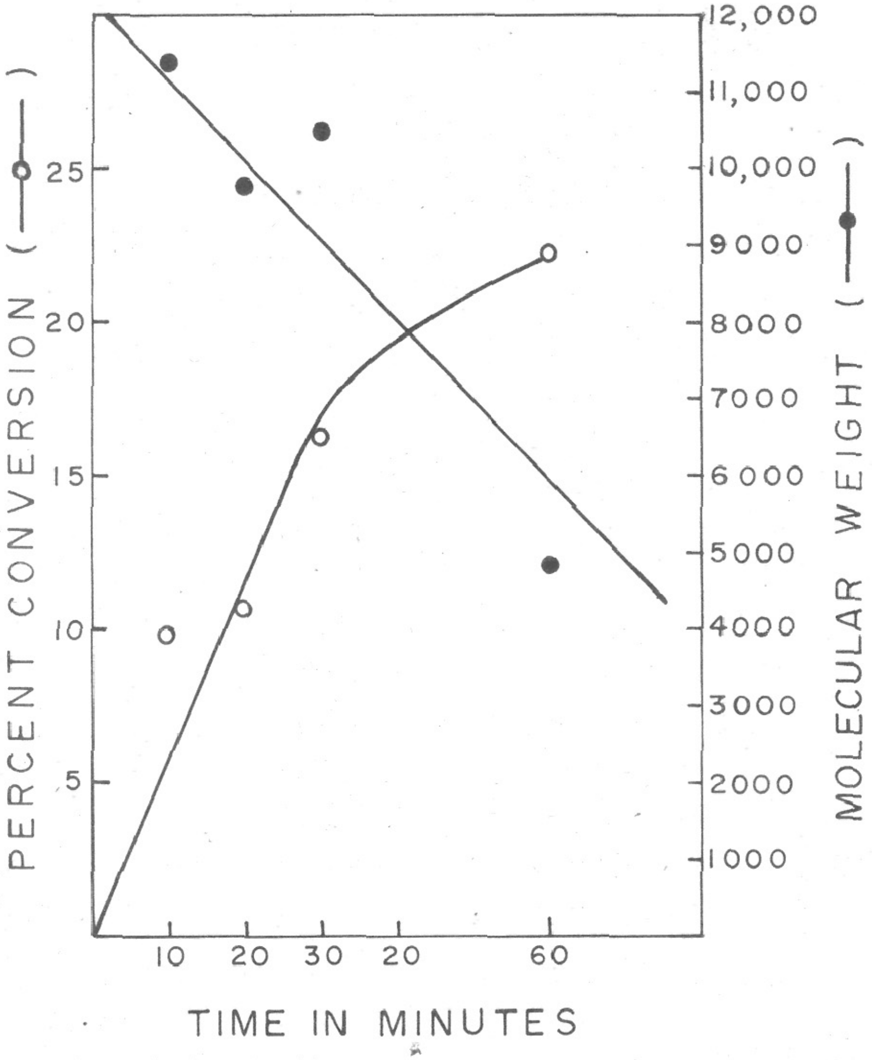


Fig. 9 EFFECT OF TIME ON $VOCl_3-Al(iBu)_3$ SYSTEM

$[VOCl_3] = 0{\cdot}01\,m/l$; Styrene = 5 ml.;

Al/V molar ratio = 3 ; Aging time = 20 Min.

Temperature = 40°

polymerization varied linearly with monomer concentration and order of reaction is one. There was no variation of molecular weights with monomer concentration. Results are tabulated in Table No.XIII (Fig.10).

Table No.XIII

Effect of Monomer Concentration

$[VOCl_3]$ = 0.01 m/l
$[Al(iBu)_3]$ = 0.03 m/l
$Al/_V$ molar ratio = 3
Reaction time = 15 min
Aging time = 20 min.
Temperature = 40°

	$[M]$ m/l	Yield in gs.	R_p x10^6 m/l/s.	$[\eta]$	Molecular weight
(1)	0.8720	0.1962	36.93	0.1318	10790
(2)	1.345	0.4271	50.23	-	-
(3)	1.743	0.4813	45.28	0.1226	9745
(4)	2.093	0.5648	44.28	0.1322	10845
(5)	2.616	0.9692	60.78	0.09028	6350
(6)	3.488	1.5758	74.15	0.1664	14945
(7)	4.360	1.7629	66.58	-	-

Effect of catalyst concentration at constant ratio and monomer concentration was studied and it was found that reaction is of second order with respect to catalyst concentration. Molecular weights had a tendency to decrease with increasing catalytic concentration. Results are presented in Table No.XIV (Figs. 11, 12).

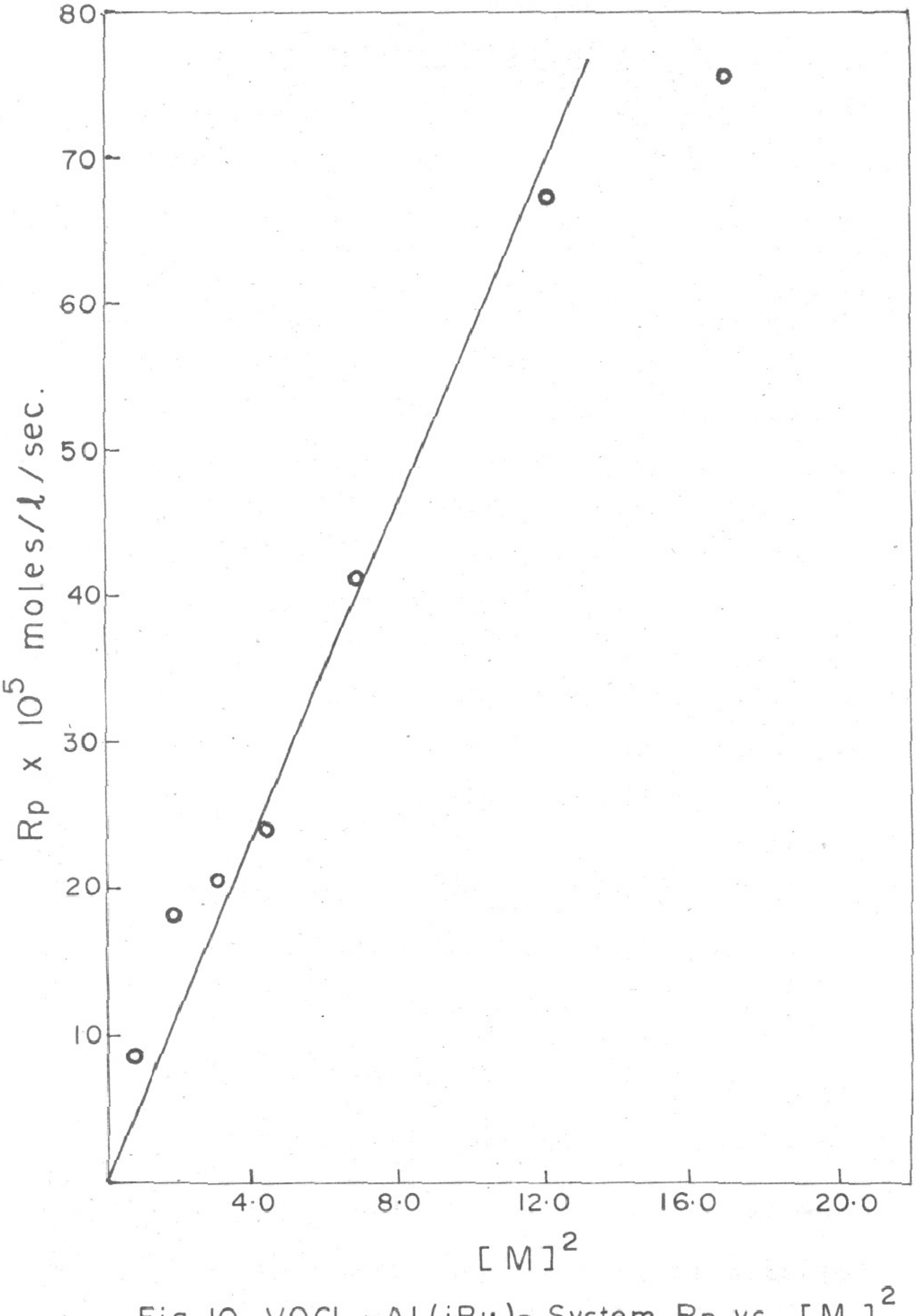


Fig. 10 $VOCl_3-Al(iBu)_3$ System Rp vs. $[M]^2$

$[VOCl_3] = 0.01$ m/l Al/V molar ratio = 3

Reaction time = 15 Min. Aging time = 20 Min.

Temperature = 40°

Table No.XIV

Effect of Catalyst Concentration

$Al/_V$ Molar ratio = 3 Reaction time = 15 min.
Styrene = 5 ml Aging time = 20 min.
Temperature = 40°

	Catalyst conc. m/l	Yield in gs.	$R_p \times 10^6$ m/l/s	$[\eta]$	Molecular weight	$[C]^2 \times 10^4$
(1)	0.003	0.0323	3.039	-	-	0.09
(2)	0.004	0.0717	6.745	0.1380	11525	0.16
(3)	0.005	0.1866	17.56	-	-	0.25
(4)	0.006	0.2094	19.70	0.1051	7850	0.36
(5)	0.007	0.3582	33.70	0.1425	12030	0.49
(6)	0.008	0.4458	41.95	0.1297	10545	0.64
(7)	0.009	0.5440	51.18	0.1621	14435	0.81
(8)	0.010	0.4813	45.28	0.1226	9745	1.00
(9)	0.011	0.5971	56.18	0.06774	4245	1.21
(10)	0.012	0.8245	77.59	0.08395	5735	1.44

Effect of Temperature

Polymerization studies were carried out at different temperatures between 30 and 60°. It was found that rate of polymerization increased with increase in temperature upto 50° and with further increase of temperature it decreased. Molecular weights did not vary with variation of temperature in this range. Activation energy of catalyst system was calculated from the plot of log R_p vs. $\frac{I}{T}$ between 40 and 50°. Results are presented in Table No.XV (Fig.13).

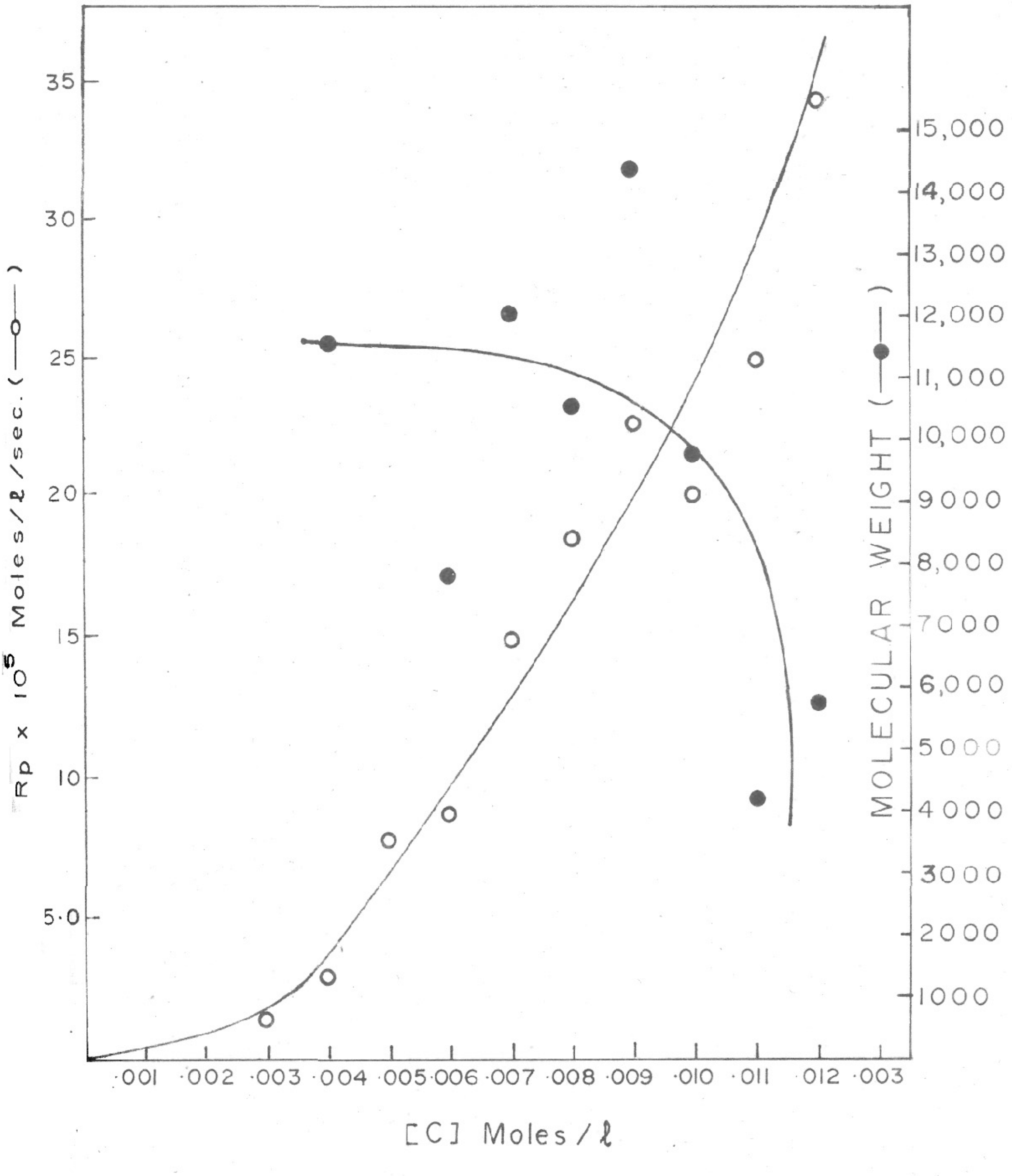


Fig. 11 EFFECT OF CATALYST CONCENTRATION ON $VOCl_3 - Al(iBu)_3$ SYSTEM

Styrene = 5 ml.; Al/V Molar ratio = 3;
Reaction time = 15 Min.; Aging time = 20 Min.
Temperature = 40°.

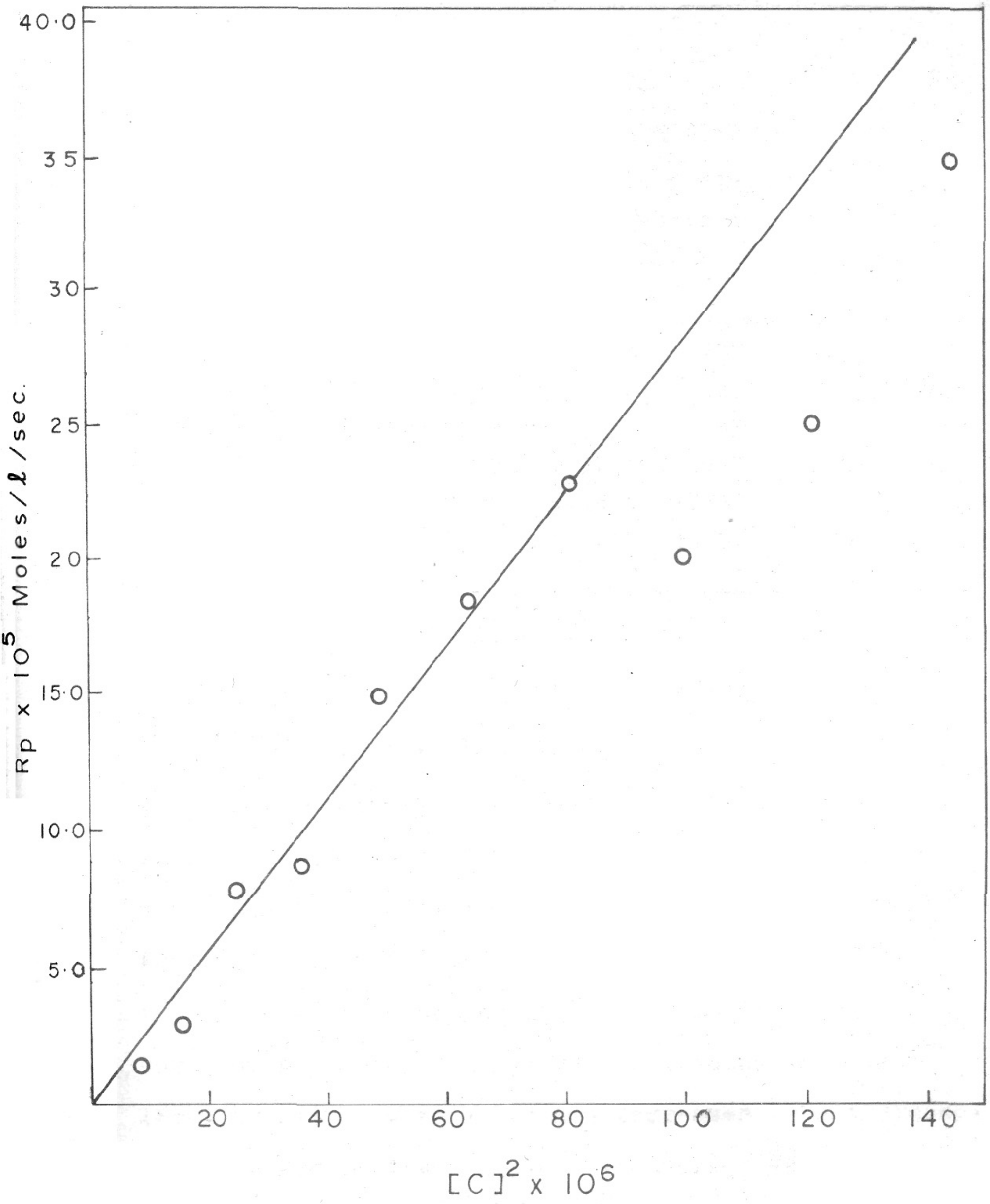


Fig. 12 $VOCl_3-Al(iBu)_3$ SYSTEM

R_p VS. $(C)^2$

Table No.XV

Effect of Temperature

$VOCl_3$ = 0.01 m/l
$Al(iBu)_3$=0.03 m/l
$Al/_V$ molar ratio = 3

Aging time = 20 min.
Reaction time= 15 min.
Styrene = 5 ml.

	Temp.°	Yield mgs.	$R_p \times 10^6$ m/l/s.	~~Styrene~~ [η]	Molecular weight	$\frac{I}{T}\times10^3$	log R_p
(1)	40	0.48130	45.28	0.1226	9745.8	3.19	$\bar{5}.6559$
(2)	45	0.6356	59.80	0.1577	13862.2	3.145	$\bar{5}.7767$
(3)	50	0.7765	73.07	0.1475	12625.6	3.09	$\bar{5}.8902$

A.E. = 11.26 Kcal/mole

Valence of Catalyst System

Valence of catalyst system was determined by potentiometric titration of the catalyst decomposed with H_2SO_4(4 N) against standard $KMnO_4$. It was found that catalyst had vanadium in the form of a mixture of V^{2+}, V^{3+}, V^{4+}. Average valence of the vanadium in catalyst at ratio 3 ($Al/_V$) was calculated as 2.43 (See Fig.14). Average valence decreased with increase in ratio and at lower ratios the average valence was more (See Fig.15, Table XVI).

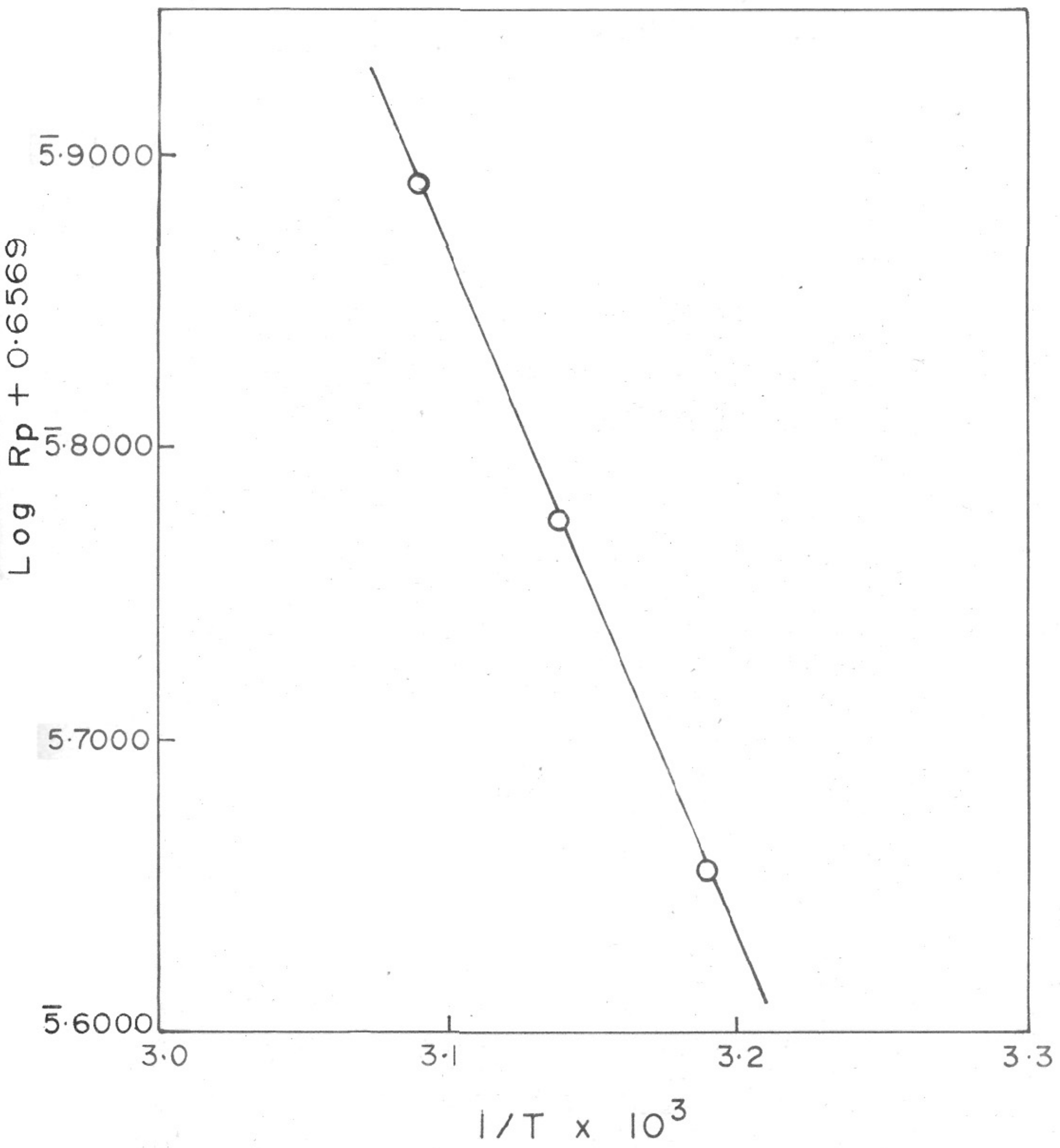


Fig. 13 EFFECT OF TEMPERATURE ON $VOCl_3$-$Al(iBu)_3$ SYSTEM

Al/V Molar ratio = 3 ;
[$VOCl_3$] = ·01 m/l ; Aging time = 20 Min. ;
Reaction time = 15 Min. ; Styrene = 5 ml.
A.E. = 11·26 K Cal/mole.

Table No.XVI

Distribution of Valence of Vanadium at Various Ratios in the Catalyst System $VOCl_3$-$Al(iBu)_3$

$VOCl_3$ = 2 ml (0.5 M)
H_2SO_4 = 25 ml(4 M) $KMnO_4$ = 0·1 N

	Ratio $Al/_V$	Distribution of Vanadium			Average valence
		V^{II} fraction.	V^{III} fraction.	V^{IV} fraction	
(1)	0.25	-	0.27	0.73	3.73
(2)	0.50	-	0.69	0.31	3.31
(3)	1.00	-	0.92	0.08	3.08
(4)	2.00	0.42	0.58	-	2.58
(5)	2.50	0.59	0.29	0.12	2.44
(6)	3.00	0.72	0.14	0.14	2.43
(7)	4.00	0.69	0.23	0.08	2.38
(8)	6.00	0.91	0.09	-	2.09

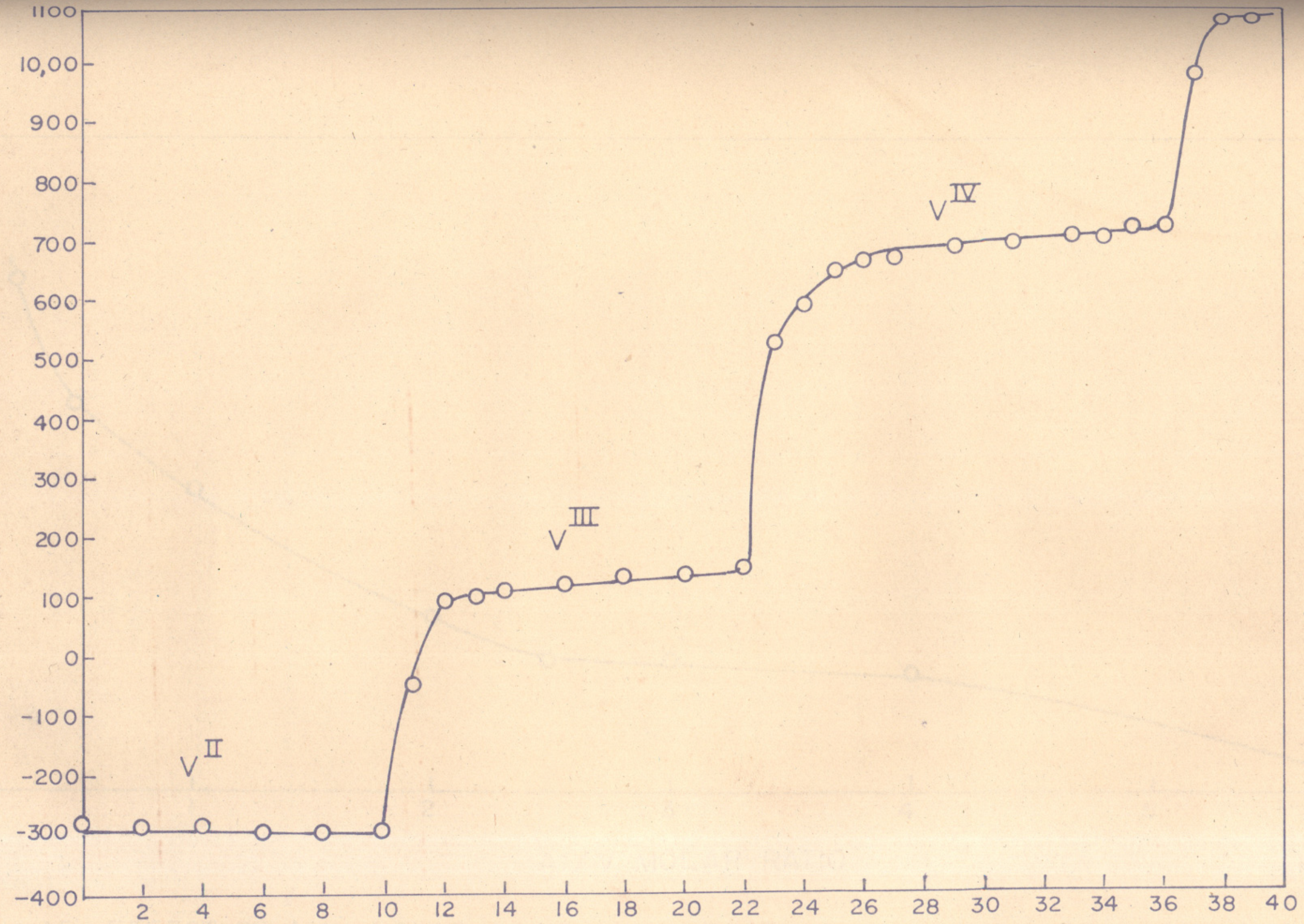


Fig. 14: VALENCE DISTRIBUTION OF VANADIUM IN $VOCl_3$-$Al(iBu)_3$ SYSTEM AT Al/V RATIO = 3

Average Valence = 2·43 ; [$VOCl_3$] = 0·04 m/l ; $KMnO_4$ Solution = 0·1N ; H_2SO_4(4N) = 25 ml. ;
Temperature = 80°.

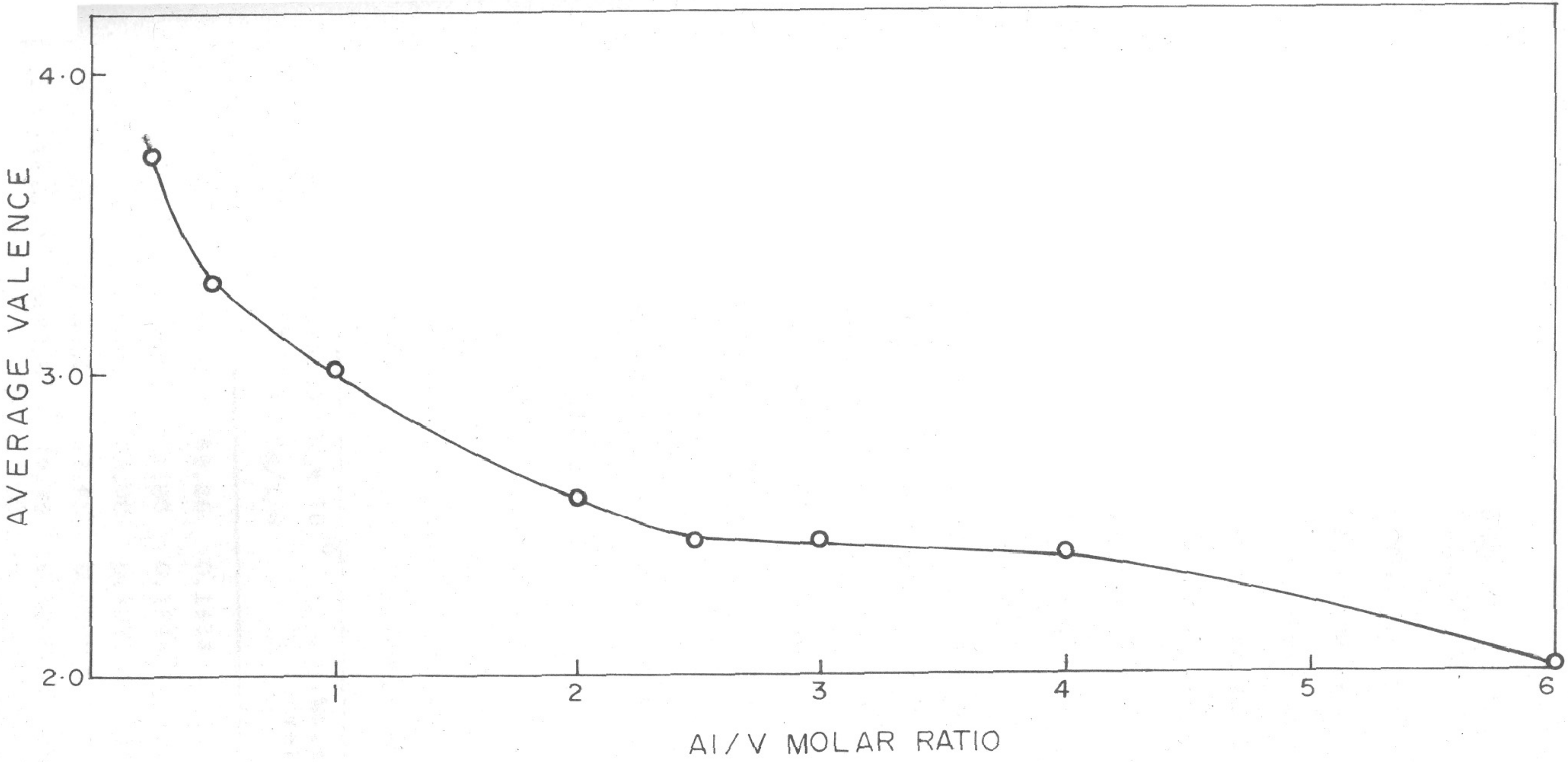


Fig. 15 EFFECT OF Al/V MOLAR RATIO ON VALENCE OF VANADIUM IN $VOCl_3$-$Al(iBu)_3$ SYSTEM

Polymerization of Styrene with Vanadium Oxitrichloride and Aluminium Diethyl Bromide at 30°.

$VOCl_3$ reacted immediately with $AlEt_2Br$ to give a dark brown to black coloured heterogeneous complex, which is an active catalyst for polymerization of styrene. $VOCl_3$ solution was first added to hexane in the reaction flask and $AlEt_2Br$ solution was added afterwards.

Aging Time Studies of Catalyst System

Experiments were carried out with different aging times for the polymerization of styrene. It was found that first ten minutes are enough for the completion of reaction between the components of catalyst and there is no change in activity of catalyst during first thirty minutes of aging as evidenced by a steady rate . Molecular weights were also found to be constant during this period. Further aging reduced catalytic activity.

Results are tabulated in Table No.XVII.

Table No.XVII

Effect of Aging Time

$[VOCl_3]$ = 0.002 m/l Styrene = 5 ml
$[AlEt_2Br]$ = 0.003 m/l Reaction time= 15 min.
$Al/_V$ molar ratio = 1.5 Temperature = 30°

	Aging time min.	Yield in gs.	$R_p \times 10^{-6}$ m/l/s	$[\eta]$	Molecular weight
(1)	10	0.6626	62.36	0.1414	11910
(2)	20	0.7639	71.86	0.1243	9925
(3)	30	0.6693	62.96	0.1378	11480
(4)	60	0.4536	42.68	0.0907	6395
(5)	1440	0.2210	20.79	0.0768	5065

Effect of Ratio of Aluminium Diethyl Bromide to Vanadium Oxitrichloride

Effect of the ratio of the catalytic components was studied on the polymerization ability of the catalyst system. It was found that yield of polymer increased with $Al/_V$ molar ratio upto a ratio $Al/_V=1.5$ and on further increase in ratio again it decreased. Hence maximum activity of the catalyst system was found at $Al/_V$ ratio 1.5 ie. Ziegler type catalyst was formed at this ratio. Molecular weights also varied in the same way and maximum molecular weight was obtained at ratio $Al/_V=1.5$.

Results are presented in Table No.XVIII (Fig.16).

Table No.XVIII

Ratio Studies

$[VOCl_3]$ = 0.002 m/l   Aging time = 20 min.
Styrene= 5 ml   Reaction time = 15 min.
Temperature = 30°

	Molar ratio al/V	Yield in gs.	% conversion	$[\eta]$	Molecular weight
(1)	0.5	0.5974	13.16	0.08177	5530
(2)	1.0	0.4886	12.08	0.08414	5755
(3)	1.5	0.7639	16.83	0.1243	9925
(4)	2.0	0.5885	12.92	0.1019	7540
(5)	2.5	0.7039	15.52	0.1178	9300
(6)	3.0	0.6152	13.55	0.0988	9335
(7)	4.0	0.2370	5.22	0.1530	13290
(8)	6.0	0.1195	2.635	0.07929	5125

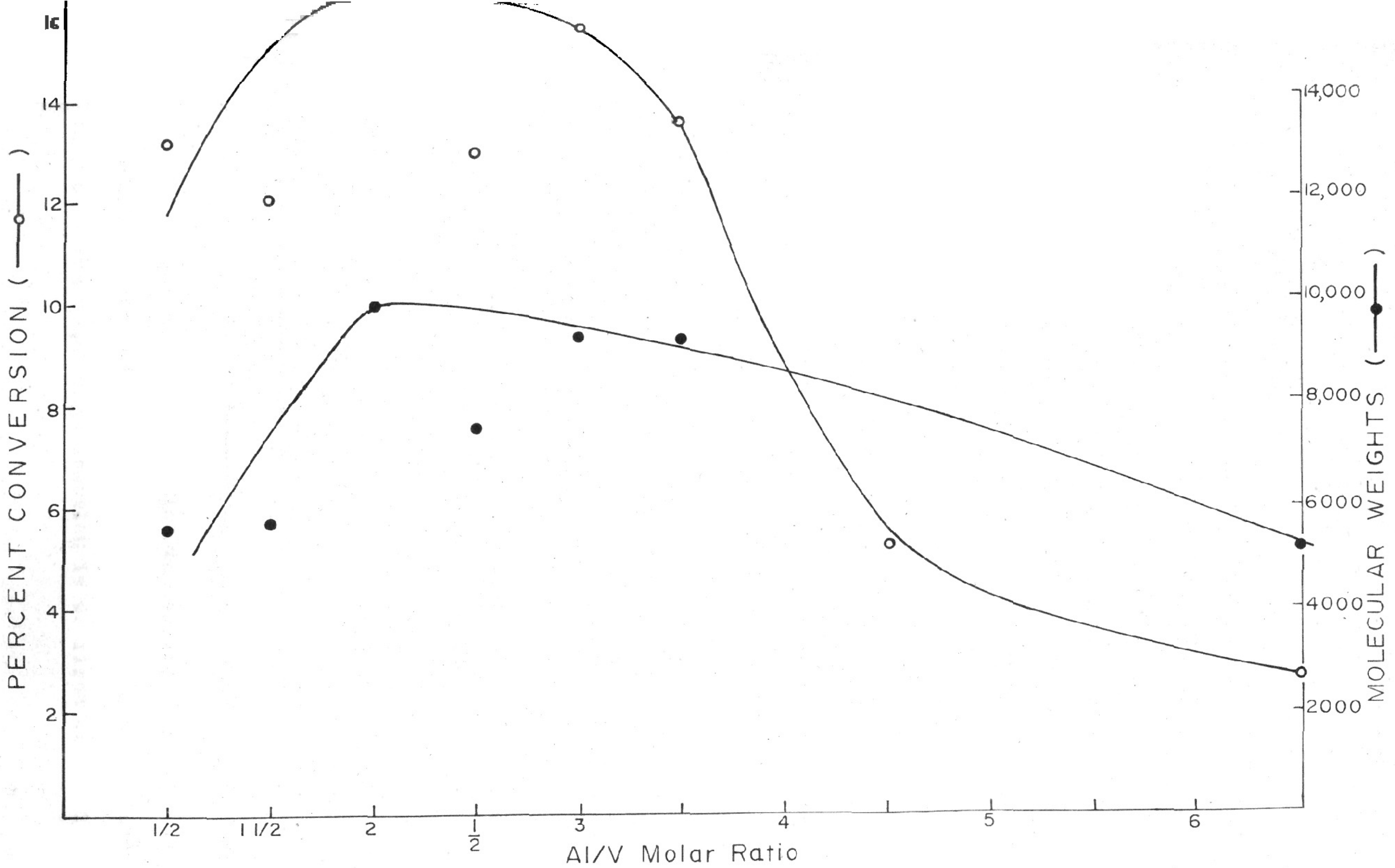


Fig. 16 EFFECT OF Al/V MOLAR RATIO ON $VOCl_3$-$AlEt_2Br$ SYSTEM

$[VOCl_3] = 0{\cdot}002$ ml.; Styrene = 5 ml.; Reaction time = 15 Min.; Aging time = 20 Min.; Temperature = 30°.

Percent Conversion

Effect of time was studied on the polymerization It was found that for first fifteen minutes, the yields increased linearly with time and after that it was not linear. This probably is due to covering of some of the catalyst sites with precipitated polymer, which is not soluble in n-hexane. Molecular weights had a tendency to decrease with higher reaction times. So 15 minutes was chosen as reaction time for further studies. Results are tabulated in Table No.XIX(Fig.17).

Table No.XIX

Effect of Time

$[VOCl_3]$ = 0.002 m/l Styrene = 5 ml.
$[AlEt_2Br]$ = 0.003 m/l Aging time= 20 min.
$Al/_V$ molar ratio = 1.5 Temperature = 30°

	Reaction time min.	Yield in gs.	% conversion	$[\eta]$	Molecular weight
(1)	5	0.3419	7.534	0.1269	10220
(2)	10	0.5117	11.28	0.1203	9495
(3)	15	0.7639	16.83	0.1243	9925
(4)	30	0.9164	20.19	0.06971	4430
(5)	60	1.1316	24.95	0.08814	6140

Effects of Monomer and Catalyst Concentrations

Monomer concentration was varied keeping the catalyst concentration constant during polymerization and it was found that reaction is of first order with

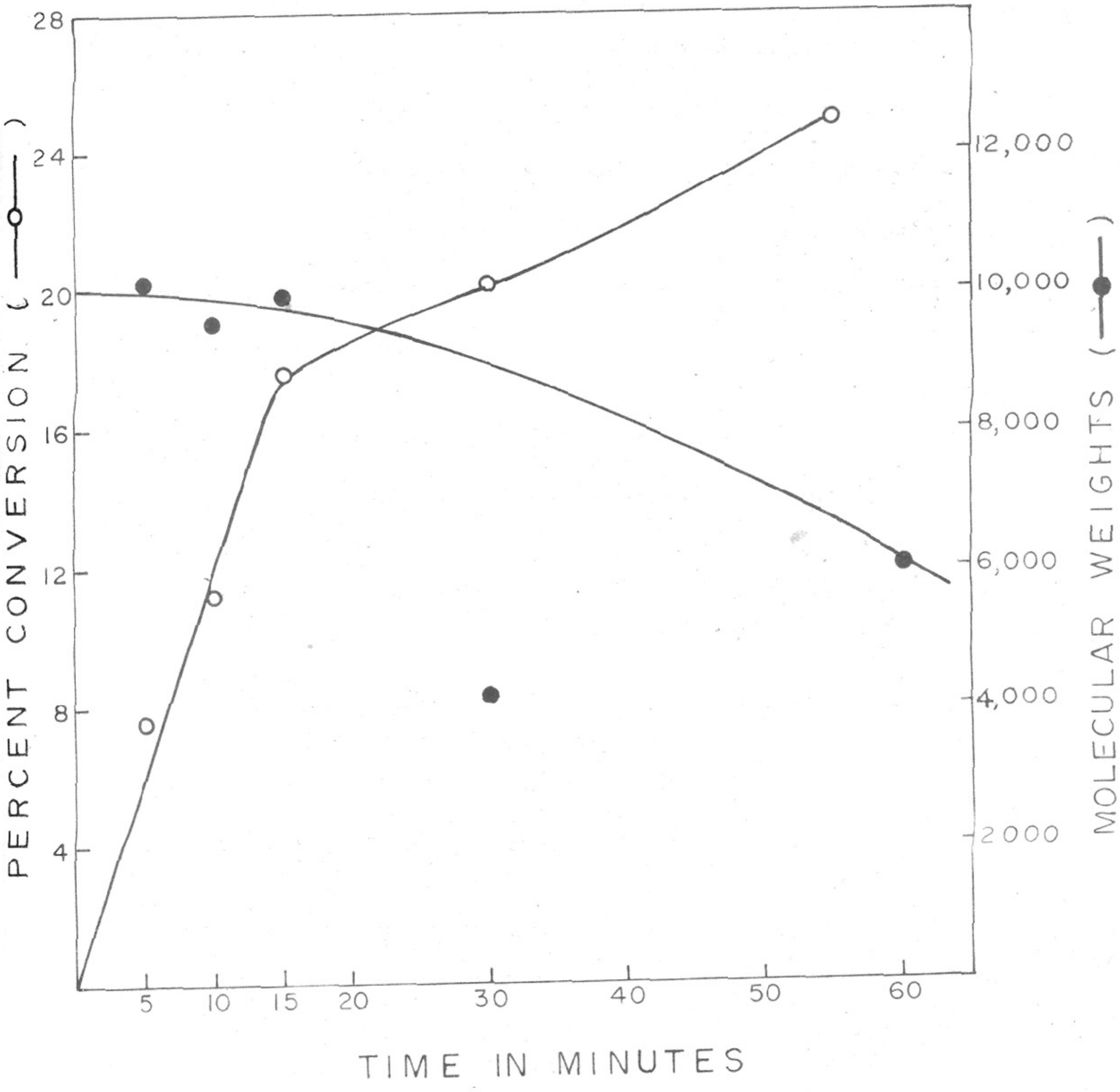


Fig. 17 EFFECT OF REACTION TIME ON $VOCl_3$ - $AlEt_2$ Br SYSTEM

$[VOCl_3] = 0.002$ m/l.; Al/V molar ratio = 1.5 ; Aging time = 20 Min ;

Temperature = 30°

respect to monomer. Molecular weights were found to be increasing with the increasing monomer concentration. Whole range of monomer concentrations could not be studied as at higher monomer concentrations the yields went beyond 20% even at the concentrations as low as 0.002 M of the catalyst. Results are tabulated in Table No.XX (Fig.18).

Table No.XX

Effect of Monomer Concentration

$[VOCl_3]$ = 0.002 m/l
$[AlEt_2Br]$ = 0.003 m/l
$Al/_V$ molar ratio = 1.5
Aging time = 20 min.
Reaction time = 15 min.
Temperature = 30°

	Monomer conc. m/l.	Yield in gs.	$R_p \times 10^6$ m/l/s.	$[\eta]$	Molecular weight
(1)	0.3488	0.0350	16.46	0.1120	8595
(2)	0.5232	0.0588	18.19	0.1284	10400
(3)	0.6976	0.0647	15.22	0.1252	9365
(4)	0.8720	0.1577	29.68	0.1379	11500
(5)	1.047	0.1951	30.59	0.1201	9470
(6)	1.221	0.2128	28.60	0.1339	11025
(7)	1.395	0.3480	40.93	0.1487	12760
(8)	1.570	0.4317	45.13	0.1298	10565
(9)	1.744	0.7639	71.86	0.1243	9925
(10)	1.919	0.7279	62.24	0.1659	14890
(11)	2.442	1.6703	112.20	0.1391	11635

Effect of catalyst concentration on polymerization was studied and it was found that reaction is

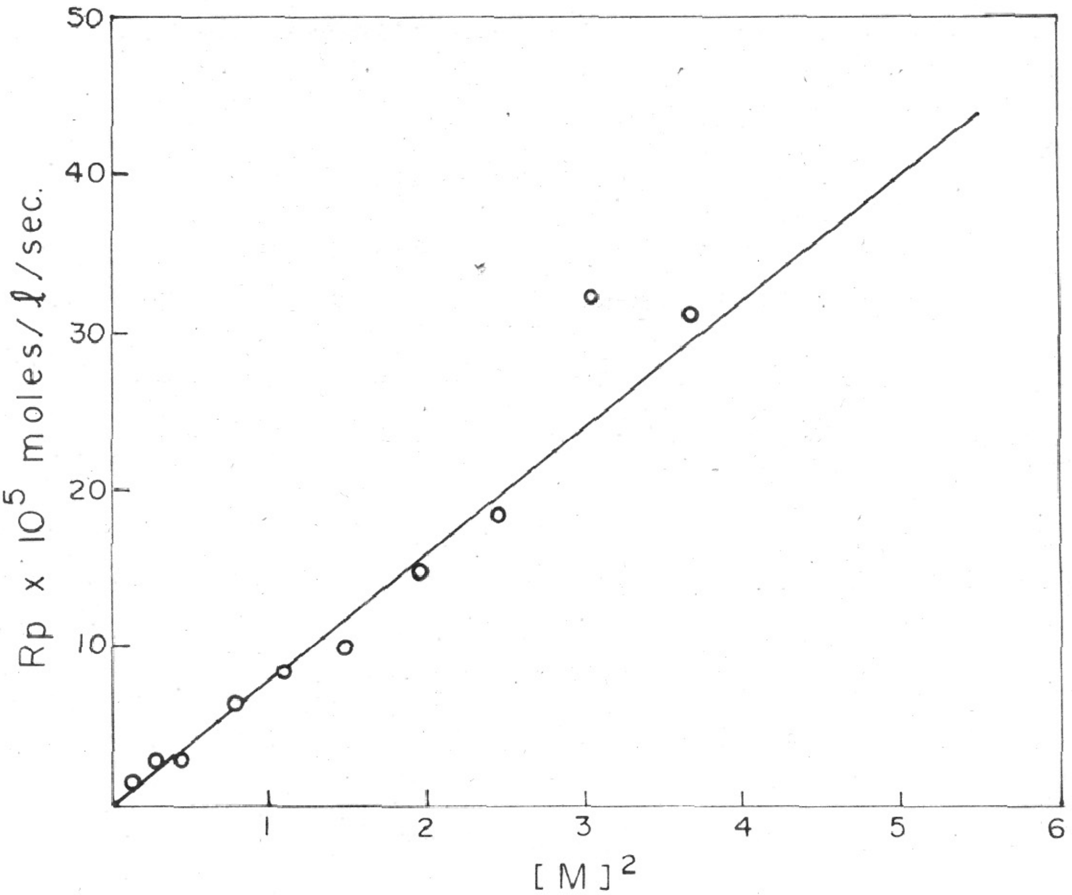


Fig. 18 $VOCl_3-AlEt_2Br$ System R_p vs. $[M]^2$

$[VOCl_3] = 0{\cdot}002$ m/l Al/V molar ratio = 1·5

Aging time = 20 Min. Reaction time = 15 Min.

Temperature = 30°

of first order with respect to catalyst. These studies were carried out at two monomer concentrations (5.0 ml and 2.5 ml). Molecular weights were not affected by catalyst concentration at both monomer concentrations studied. Results are tabulated in Table No.XXI (Fig.19).

Table No.XXI

Effect of Catalyst Concentration

Al/$_V$ molar ratio = 1.5 Reaction time = 15 min.
Aging time = 20 min. Temperature =30°

	Monomer (conc.)	Catalyst conc. m/l.	Yield in gs.	$R_p \times 10^{+6}$ m/l/s	$[\eta]$	Molecular weight
(1)	5 ml (1.744 m/l)	0.0010	0.2075	19.56	0.1385	11690
(2)		0.0015	0.4394	41.34	0.1224	9720
(3)		0.0020	0.7639	71.86	0.1243	9925
(4)		0.0025	0.5674	53.38	0.1344	11075
(5)		0.0030	0.7502	70.58	-	-
(6)		0.0040	1.25270	-	0.1116	9995
(1)	2.5 ml (.8720 m/l)	0.002	0.1577	29.68	0.1379	11500
(2)		0.003	0.1338	25.19	0.1120	8595
(3)		0.004	0.1858	34.97	0.0886	6210
(4)		0.005	0.3058	57.54	0.1086	8225
(5)		0.006	0.4012	75.54	0.09069	6540
(6)		0.007	0.3749	70.55	0.1009	7455
(7)		0.008	0.4596	86.50	0.06923	4380
(8)		0.009	0.4963	93.42	0.1059	7935

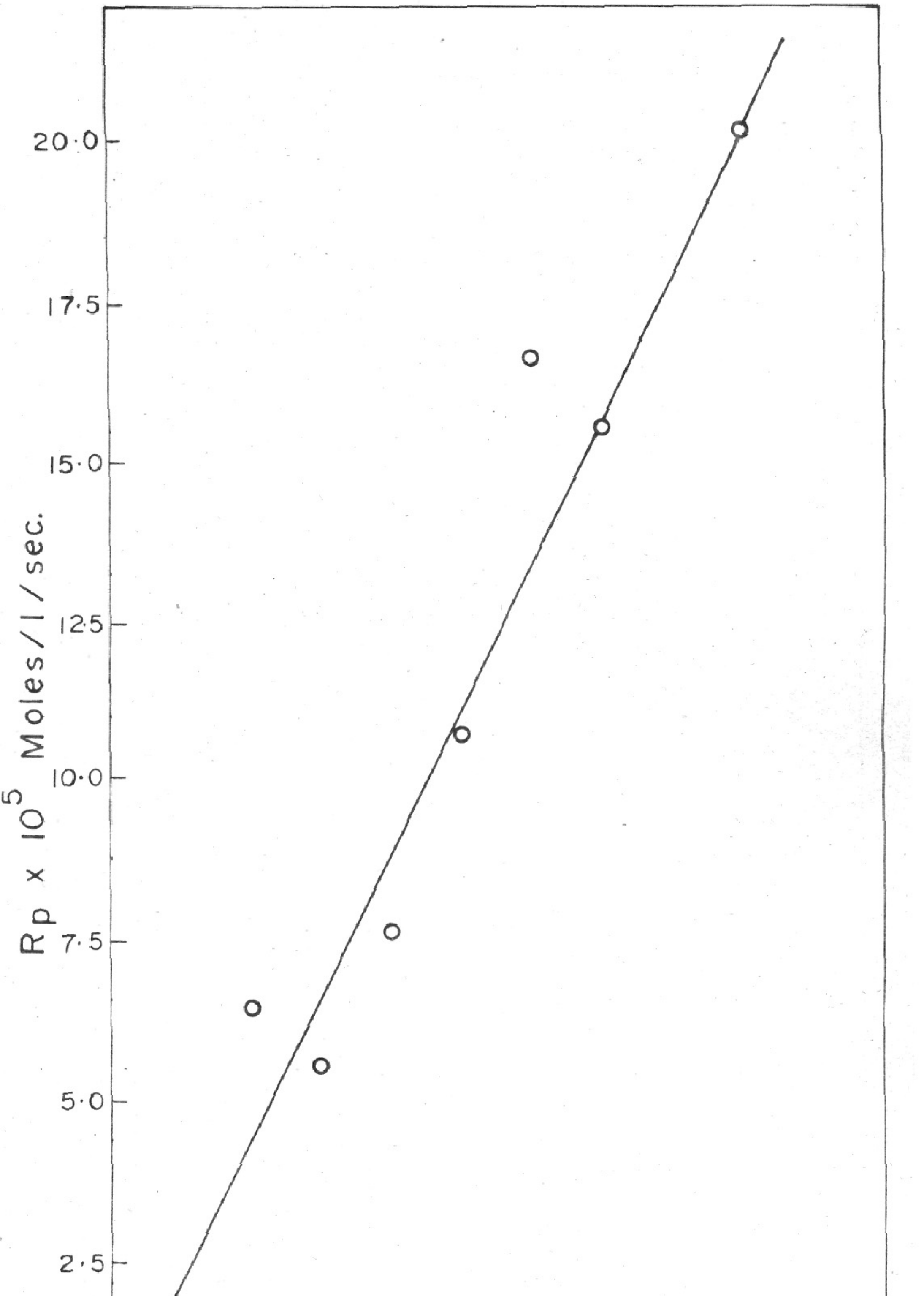


Fig. 19 $VOCl_3$- $AlEt_2$ Br SYSTEM

Styrene = 2·5 ml.; Al/V molar ratio = 1·5; Reaction time = 15 Min.; Aging time = 20 Min., Temperature = 30°.

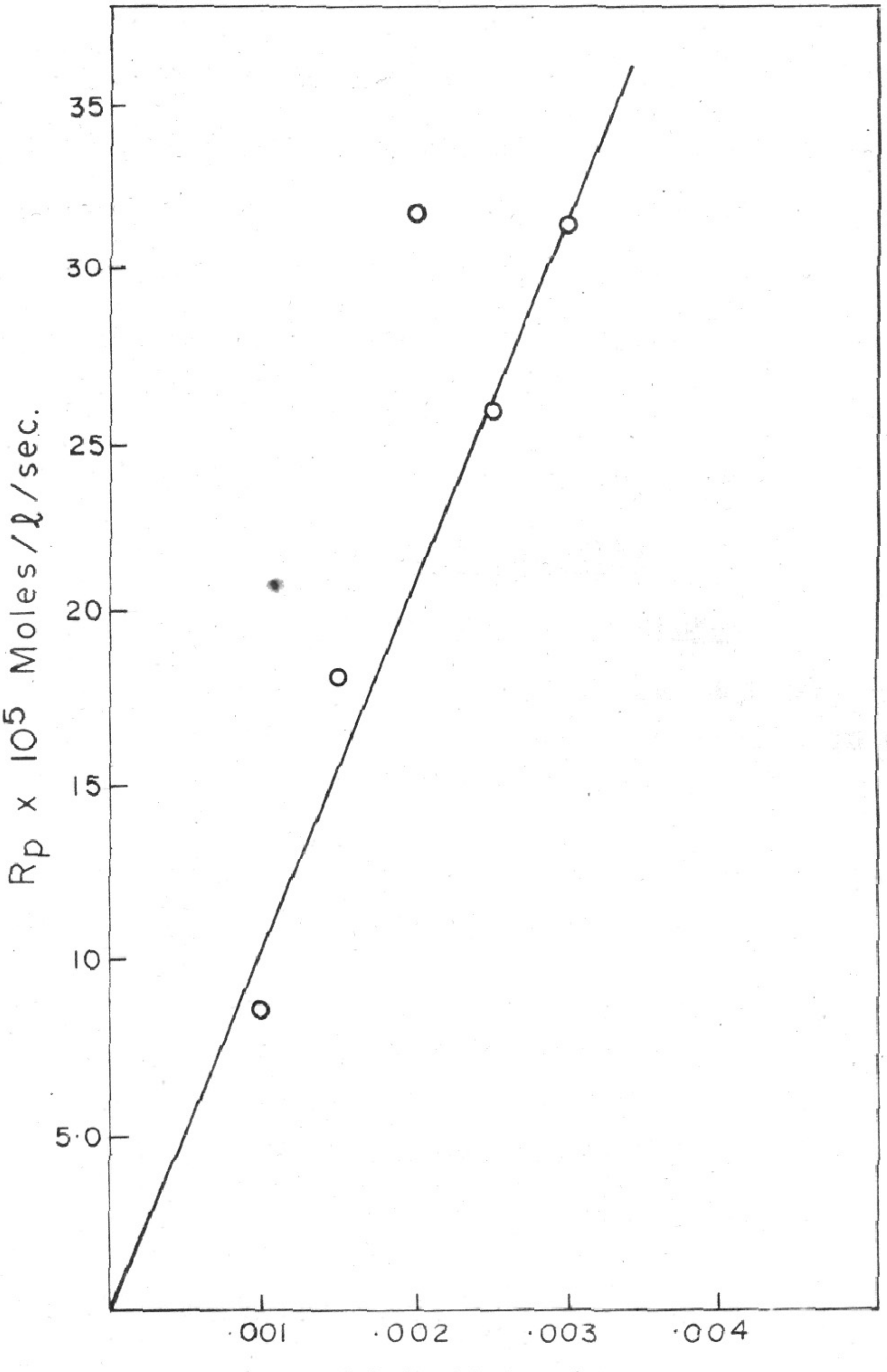


Fig. 19a $VOCl_3 - AlEt_2Br$ SYSTEM

Styrene = 5 ml.; Al/V molar ratio = 1·5;

Aging time = 20 Min.; Reaction time = Min .

Temperature = 30°.

Effect of Temperature

Effect of temperature was studied at 30°, 40° and 50° at constant concentrations of catalyst and monomer at $Al/_V$ molar ratio of 1.5. Rates were found to increase with increasing temperatures but molecular weights decreased. Activation energy of the system was calculated from a plot of log R_p vs. $\frac{I}{T}$. Results are tabulated in Table No.XXII (Fig.20).

Table No.XXII

Effect of Temperature

$[VOCl_3]$ = 0.002 m/l   Styrene = 5 ml
$Al/_V$ molar ratio = 1.5   Reaction time = 15 min.
Aging time = 20 min.

Temp.°	Yield in gs.	$R_p x10^6$ m/1/s	$[\eta]$	Molecular weight	$\frac{I}{T}$	log R_p	AE
30	0.7639	71.86	0.1243	9925	$3.3x10^{-3}$	$\bar{5}.8665$	6.048
40	0.9248	87.02	0.0862	5960	$3.19x10^{-3}$	$\bar{5}.9366$	Rcal/mole
50	1.3888	133.80	0.0499	2780	$3.09x10^{-3}$	$\bar{4}.1265$	-

Effect of Zinc Diethyl

Effect of $ZnEt_2$ was studied on the rate of polymerization and molecular weight. Concentration of $ZnEt_2$ was varied and catalyst concentration was maintained fixed at $Al/_V$ molar ratio of 1.5. Monomer concentration was also kept constant. Rate of polymerization and molecular weights decreased with increase in concentration of $ZnEt_2$. Results are recorded in Table No.XXIII.

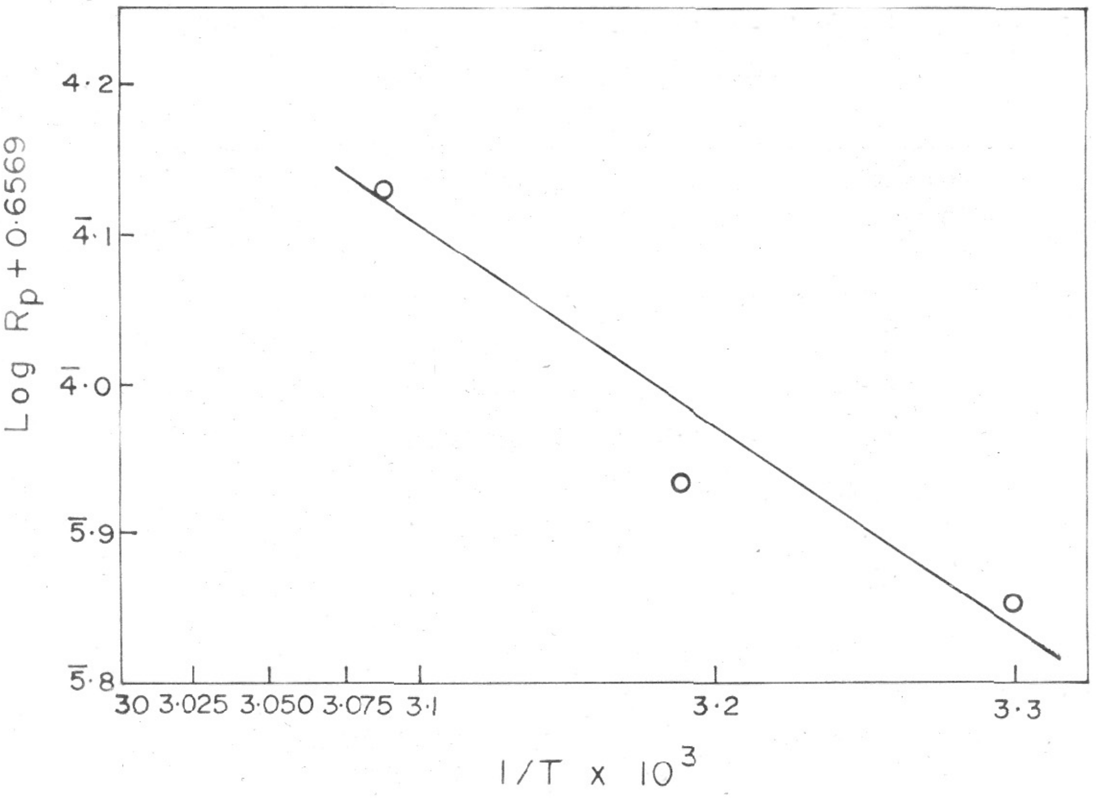


Fig. 20 EFFECT OF TEMPERATURE ON $VOCl_3$-$AlEt_2$ Br SYSTEM

[$VOCl_3$] = 0·02 m/l; Al/V molar ratio = 1·5; Styrene = 5 ml.;

Aging time = 20 Min.; Reaction time = 15 Min.;

Table No.XXIII

Effect of Zinc Diethyl

$VOCl_3$ = 0.002 m/l   Styrene = 5 ml
Al/$_V$ molar ratio = 1.5   Reaction time = 15 min.
Aging time = 20 min.

	Conc.of $ZnEt_2$ mole/l	Yield in gs.	R_p x10^{+6} m/l/s.	Molecular weight
(1)	0.0000	0.7639	71.86	9925
(2)	0.0002	0.5456	51.34	2105
(3)	0.0004	0.2213	20.82	2135
(4)	0.0010	0.1271	11.96	2270
(5)	0.0020	0.1079	10.15	2765
(6)	0.0100	0.1037	9.75	3650

Ethyl Bromide Effect (On $VOCl_3$-$AlEt_3$ and $TiCl_4$-$AlEt_3$ Systems)

Possibility of EtBr, which may be formed in small quantities during the catalyst forming reaction acting as chain transfer agent was investigated. Known quantities of EtBr were added to the standard catalyst systems ($VOCl_3$-$AlEt_3$ at ratio Al/$_V$=2 and $TiCl_4$-$AlEt_3$ at ratio Al/$_{Ti}$=3) and its effect was studied on rate as well as molecular weight formed. Results are tabulated in Table No.XXIV.

Table No.XXIV

Effect of Ethyl Bromide

Styrene = 10 ml Aging time = 20 min.
Reaction time = 1 hr. Temperature = 40°

	Conc. of EtBr.	Yield in gs.	Molecular weight	Catalyst system
(1)	0.000	0.1327	82409.6	$VOCl_3$-$AlEt_3$ R= 2 $[VOCl_3]$=.02M
(2)	0.002	0.1091	-	
(3)	0.010	0.1005	79372.8	
(4)	0.020	0.1112	77043.2	
(1)	0.000	0.0526	72768.8	$TiCl_4$-$AlEt_3$ R = 3 $[TiCl_4]$ =.02M
(2)	0.001	0.0728	53008.8	
(3)	0.002	0.0649	50856.8	
(4)	0.020	0.1324	31876.0	
(5)	0.060	0.1449	27612.0	

It was found that the effect of EtBr is negligible in the case of $VOCl_3$-$AlEt_3$ but in case of $TiCl_4$-$AlEt_3$, there was a regular increase in yield and a regular decrease in molecular weight with increasing concentration of EtBr.

Valence of Vanadium in Catalytic Complex

Potentiometric titration of the decomposed catalyst in H_2SO_4 (4 N) with $CeSO_4$ showed that vanadium exists in the form of a mixture of trivalent and tetravalent forms in the catalytic system at

$Al/_V$ molar ratio 1.5. The amount of trivalent form goes on increasing with increasing ratio but there was no reduction to divalent form even at ratios as high as 6. At lower ratios of $Al/_V$ than 1.5, the reduction to trivalent state was negligible (See Figs. 21, 22).

Table No.XXV

Distribution of Valance of Vanadium at Various Ratios in the Catalyst System $VOCl_3$-$AlEt_2Br$.

$VOCl_3$ = 2 ml (0.5 M) H_2SO_4 = 25 ml (4 m)
$CeSO_4$ as oxidant

	Ratio $Al/_V$	Distribution of Vanad.		Average valence
		V^{III} fraction	V^{IV} fraction	
(1)	0.75	0.077	0.923	3.923
(2)	1.50	0.35	0.65	3.65
(3)	2.25	0.42	0.58	3.58
(4)	3.75	0.55	0.45	3.45
(5)	4.5	0.46	0.54	3.54

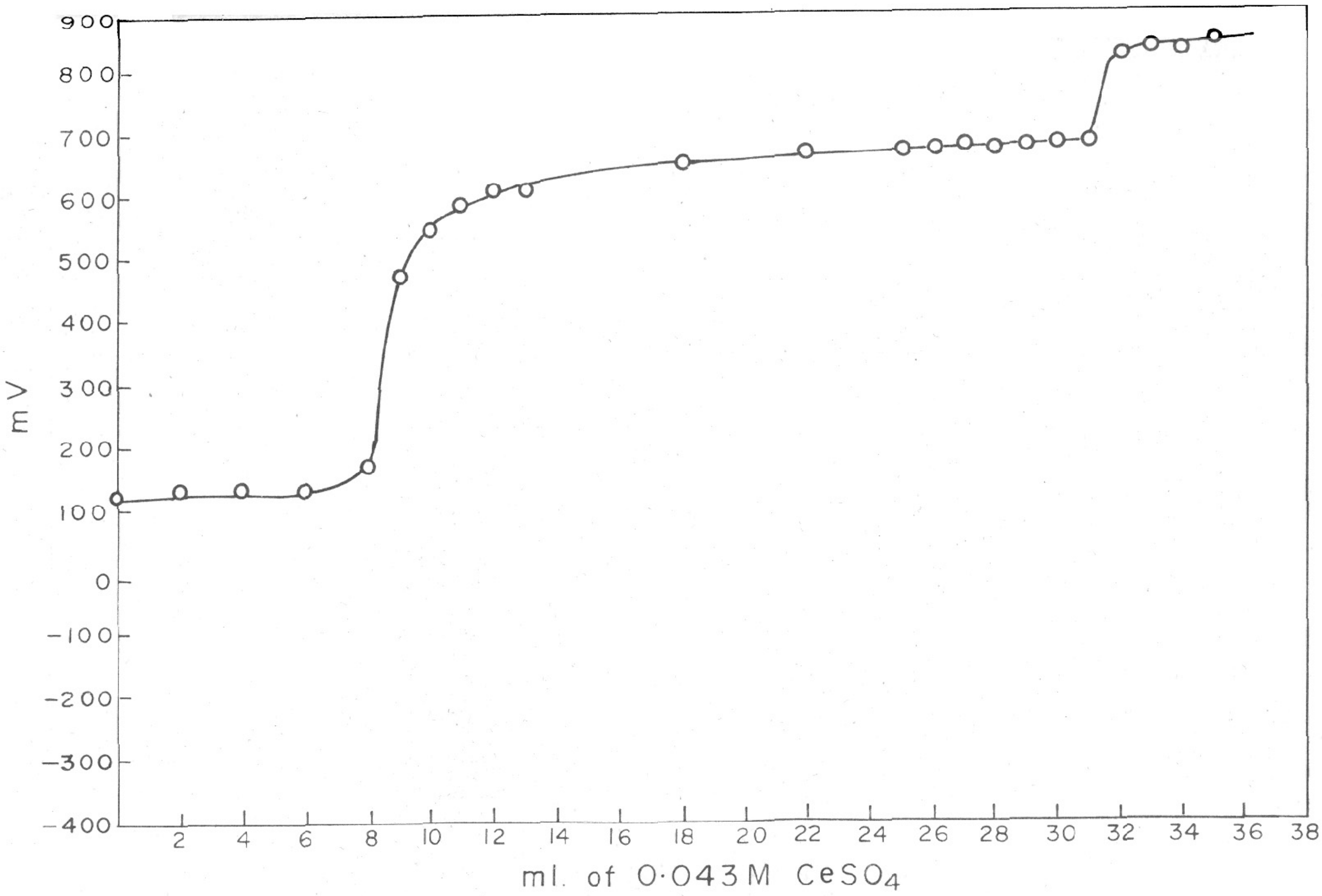


Fig. 21 DISTRIBUTION OF VALENCE OF VANADIUM IN $VOCl_3$-$AlEt_2$ Br SYSTEM AT Al/V MOLAR RATIO = 1·5

Av Valence = 3·65; [$VOCl_3$] = 0·04 m/l; H_2SO_4 (4 N) = 25° ml.; $CeSO_4$ Solution = 0·043 N; Temperature = 80°.

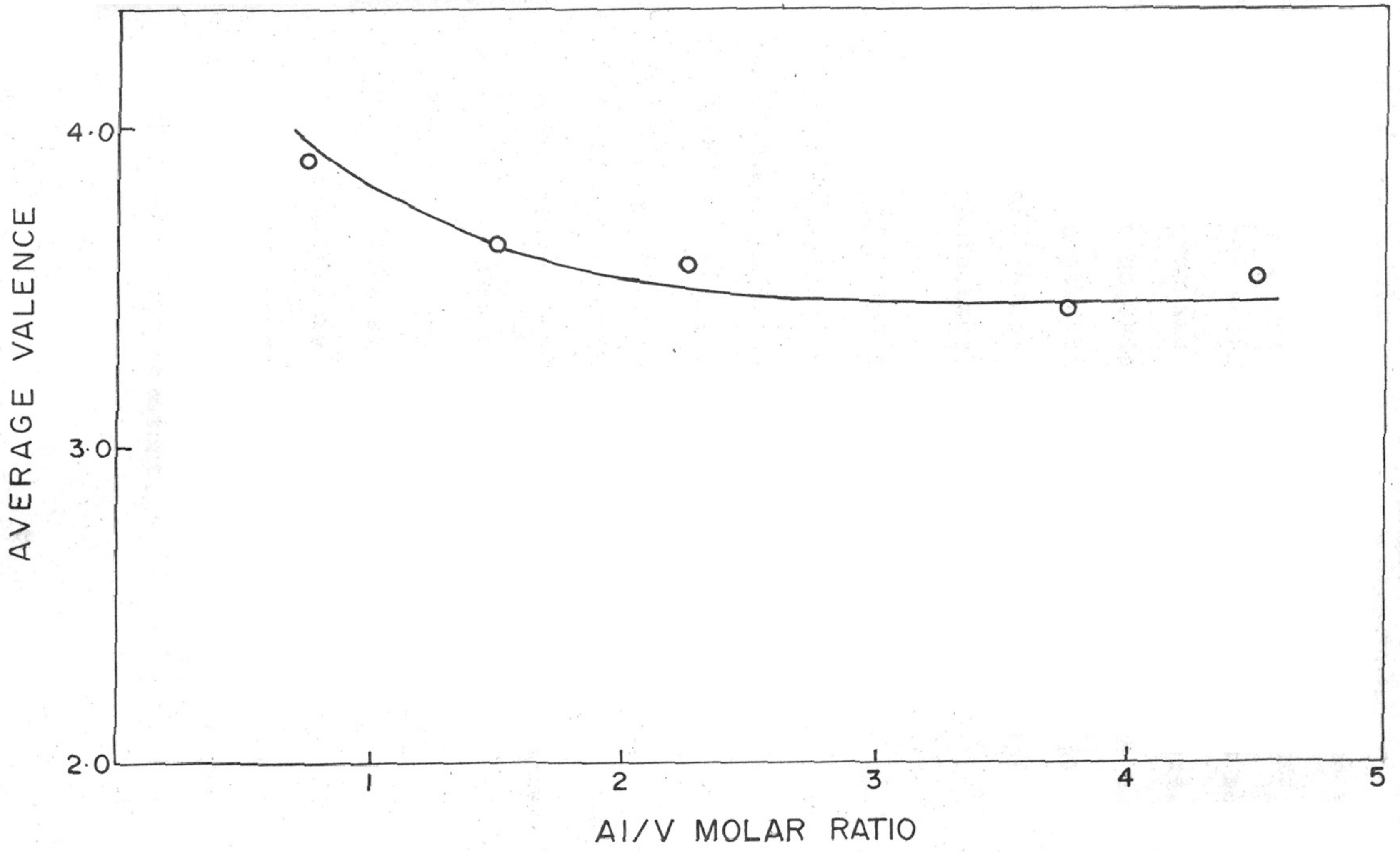


Fig. 22 EFFECT OF MOLAR RATIO ON THE AVERAGE VALENCE OF VANADIUM IN $VOCl_3$-$AlEt_2Br$ SYSTEM

Polymerization of Styrene with $VOCl_3$-$Sn(nC_3H_7)_4$ at 40°

Mixing of $VOCl_3$ with $Sn(nC_3H_7)_4$ gives a red coloured liquid, which on stirring under closed conditions gives a dark grey solid which is an active catalyst for the polymerization of styrene. $VOCl_3$ itself is capable of polymerizing styrene but the following studies clearly show that the polymerization in the following cases is due to the complex and not due to unreacted free $VOCl_3$.

Aging Time Studies

Variation of R_p as well as molecular weight was studied against aging time. Aging time was varied from 30 minutes to 4 hours. An abrupt decrease in the yield of polymer was found between the aging times of 60 and 90 minutes and with more than 90 minutes aging times yields remained practically constant with additional aging upto 3 hours and further aging reduced the activity of catalyst probably due to decomposition of catalytic species.

Results are tabulated in Table No.XXVI (Fig.23).

As can be seen from the table, the molecular weights also increases with aging upto first 90 minutes and then become constant.

Table No.XXVI

Effect of Aging Time

$[VOCl_3]$ = 0.02 m/1   Styrene = 10 ml.
Al/$_V$ molar ratio = 1.5   Reaction time = 1 hr.
Temperature= 40°

	Aging time min.	Yields in gs.	$R_p \times 10^{+7}$ m/1/s.	$[\eta]$	Molecular weight
(1)	30	2.5672	301.60	0.7031	4475
(2)	60	0.4624	54.38	0.1606	14235
(3)	90	0.2647	31.13	0.1294	10515
(4)	120	0.2724	32.03	0.1854	17451
(5)	180	0.1915	22.52	0.2428	25365
(6)	240	0.1330	15.65	0.0566	3310
(7)	1440	0.1410	16.58	0.2135	21295

Ratio Studies

Variation of catalytic activity was studied with varying of molar ratios. It was found that at aging time of 120 minutes the yields decreased with increasing ratio of Sn/$_V$ upto ratio 1.5 and at higher ratios they remained practically constant. Thus it was concluded that reaction of catalytic components resulting in active catalytic species was complete at Sn/$_V$ molar ratio of 1.5. Higher yields at lower ratios being due to the presence of unreacted $VOCl_3$ in the catalytic mixture, which polymerizes the monomer at a higher rate. Molecular weights also increase with

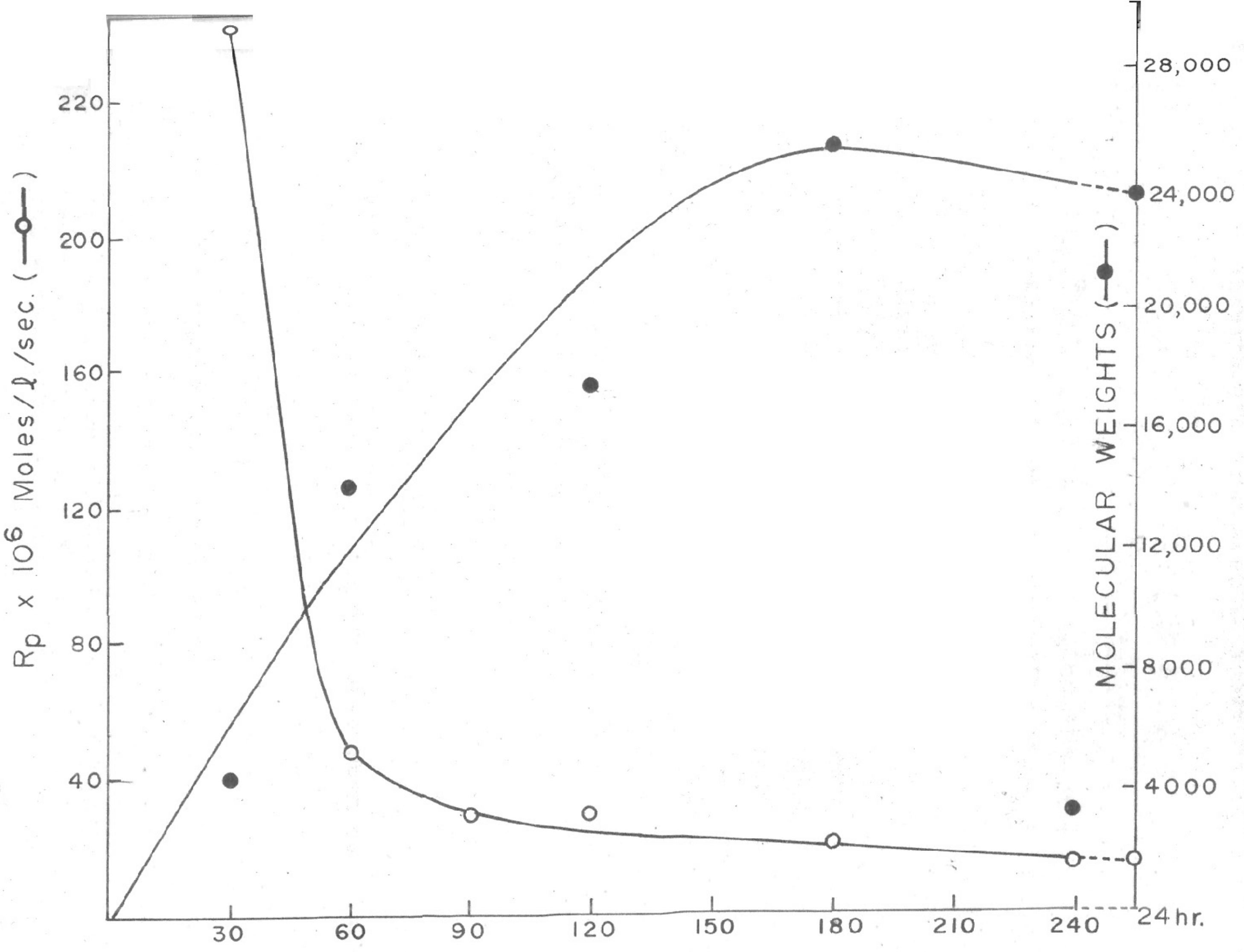


Fig. 23 EFFECT OF AGING TIME ON $VOCl_3$-$Sn(nC_3H_7)_4$ SYSTEM

$[VOCl_3] = 0{\cdot}02$ m/l; Sn/V molar ratio = 1·5; Styrene = 10 ml.; Reaction time = 1 hr.; Temperature = 40°.

$Sn/_V$ molar ratio upto ratio $Sn/_V = 2.0$ and then decreased.

Results are tabulated in Table No.XXVII (Fig.24).

Table No.XXVII

Ratio Studies

$[VOCl_3] = 0.02$ m/1   Aging time = 2 hr.
Styrene= 10 ml.   Reaction time= 1 hr.

	Molar ratio $Sn/_V$	Yield in gs.	% conversion	$[\eta]$	Molecular weight
(1)	0.5	0.5096	5.614	0.09806	7125
(2)	1.0	0.3967	4.369	0.1636	14501
(3)	1.5	0.2724	3.001	0.1858	17450
(4)	2.0	0.2922	3.210	0.2709	29530
(5)	3.0	0.1667	1.837	0.3049	35005
(6)	4.0	0.3127	3.445	0.0936	6685
(7)	6.0	0.2674	2.946	0.0432	2260

Percent Conversion

All the following studies have been carried out at molar ratio $Sn/_V = 1.5$ and aging time = 90 minutes. Under these conditions percent conversion was found to increase linearly with time upto a period of 4 hours. This shows that the rate of polymerization is not affected by time. Molecular weights, though not varying very regularly, have a trend to increase with increasing time.

Results are presented in Table No.XXVIII (Fig.25).

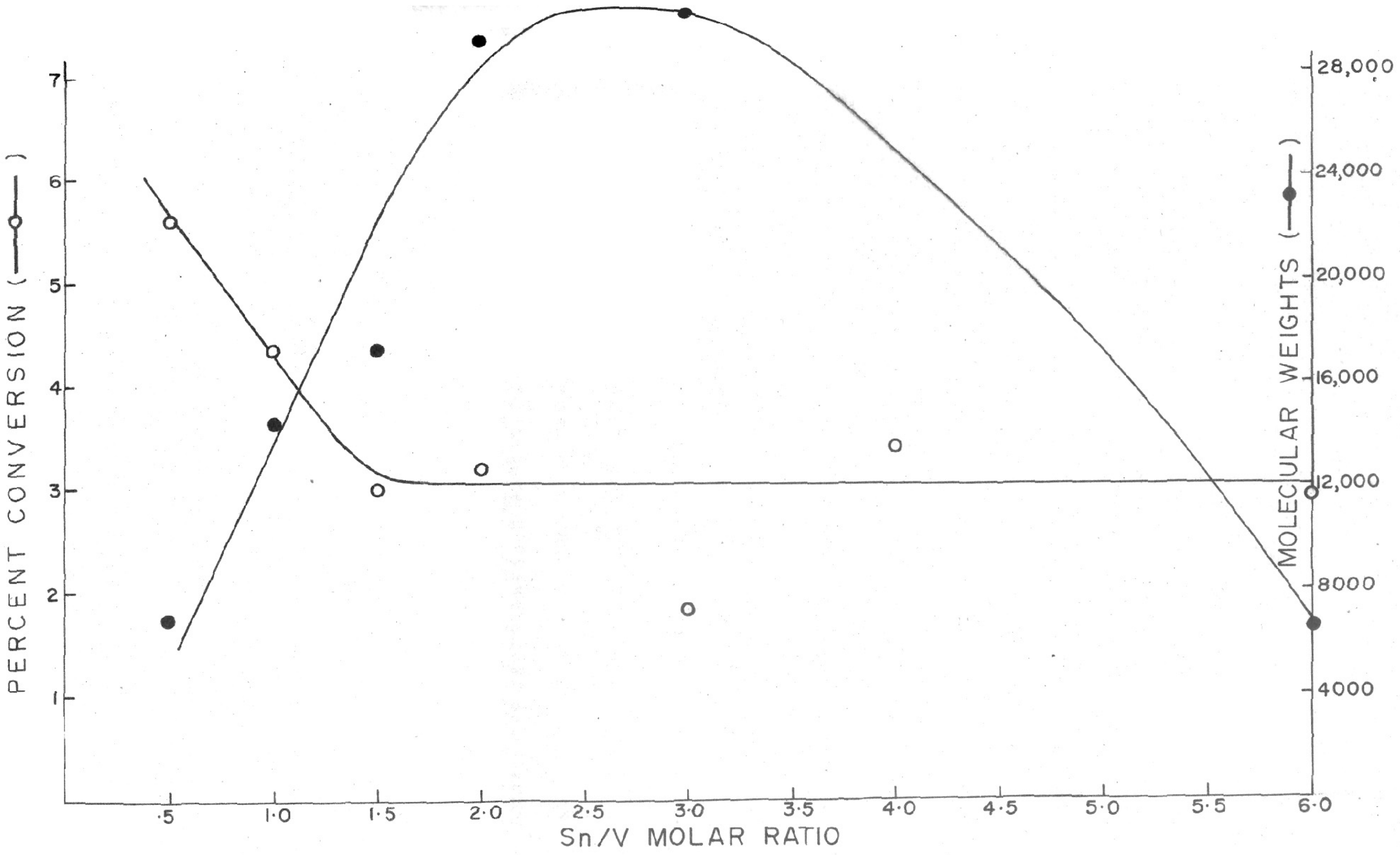


Fig. 24 EFFECT OF Sn/V MOLAR RATIO ON $VOCl_3$ – $Sn(nC_3H_7)_4$ SYSTEM

[$VOCl_3$] = 0·02 ml.; Styrene = 10 ml.; Aging time = 2 hr.; Reaction time = 1 hr.; Temperature = 40°

Table No.XXVIII

Effect of Time.

$[VOCl_3]$ = 0.02 m/l   Sn/V molar ratio = 1.5
~~$SnPr_3$~~ = 0.03 m/l   Styrene = 10 ml
$[Sn(nC_3H_7)_4]$ Aging time = 90 min.

	Reaction time min.	Yield in gs.	% conversion	[η]	Molecular weight
(1)	30	0.15650	1.72	0.09977	7305
(2)	60	0.26475	2.92	0.1294	10515
(3)	90	0.49420	5.45	0.09109	6430
(4)	120	0.41440	4.56	0.2616	28165
(5)	150	0.33160	3.65	0.1290	10475
(6)	210	0.77980	8.59	0.05489	2885
(7)	240	0.8812	9.71	0.1529	13280

Effect of Catalyst and Monomer Concentration.

Variation of monomer concentration at constant catalyst concentration gave a first order reaction with respect to monomer. Molecular weights did not show any marked variation with monomer concentration. Results are tabulated in Table No.XXIX (Fig.26).

When catalyst concentration was varied keeping the amount of styrene constant the yields increased with the catalyst concentration and order of reaction, as calculated from the log log plot of R_p vs. $[C]$, was two. The variation of molecular weights with the catalyst concentration was not marked. Table No. XXX (Fig. 27,28) presents the results.

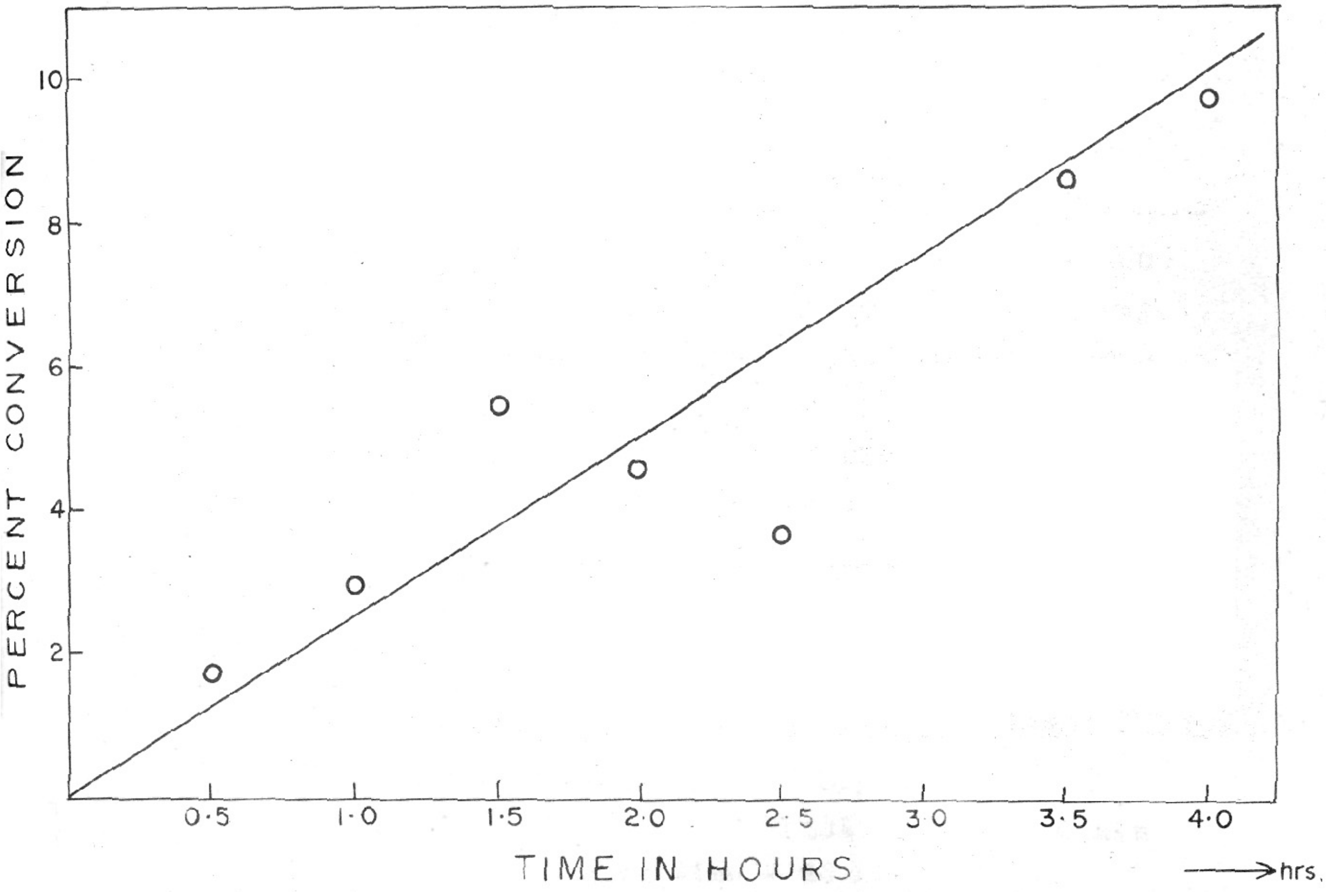


Fig. 25 EFFECT OF OF TIME ON $VOCl_3 - Sn(nC_3H_7)_4$ SYSTEM

$[VOCl_3] = 0{\cdot}02$ m/l ; Sn/V molar ratio = 1·5

Styrene = 10 ml.; Aging time = 90 Min.;

Temperature = 40°

Table No.XXIX

Effect of Monomer Concentration

$[VOCl_3]$ = 0.02 m/l $Sn/_V$ molar ratio = 1.5
$[Sn(nC_3H_7)_4]$ = 0.03 m/l   Reaction time = 60 min.
Aging time=90 min.

	Vol.of styrene mls.	Monomer conc. m/l	Yield in gs.	$R_p x10^7$ m/l/s	$[\eta]$	Molecular weight
(1)	4.0	1.395	0.1379	40.54	0.0729	5080
(2)	5.0	1.744	0.2006	47.18	0.0964	6965
(3)	7.5	2.616	0.2167	33.89	0.1658	14970
(4)	10.0	3.488	0.2640	31.13	0.1294	10515
(5)	12.5	4.360	0.4989	46.93	-	-
(6)	15.0	5.232	0.6524	51.14	0.0768	8705

Table No.XXX

Effect of Catalyst Concentration

~~$[VOCl_3$ = 0.02 m/l~~   Styrene = 10 ml
$Sn/_V$ molar ratio = 1.5   Reaction time= 60 min.
Aging time = 90 min.

	$[VOCl_3]$ m/l	Yield in gs.	$R_p x 10^7$ m/l/s.	$[\eta]$	Molecular weight	C^2x10^4
(1)	0.010	0.0882	10.37	0.0745	4865	1.00
(2)	0.015	0.1042	12.26	-	-	2.25
(3)	0.020	0.2640	31.05	0.1294	10515	4.00
(4)	0.025	0.4704	55.33	0.1209	9560	6.25
(5)	0.030	0.3799	44.67	0.1385	11575	9.00
(6)	0.035	1.3345	157.00	-	-	12.25
(7)	0.040	0.9613	113.10	0.0581	3425	16.00

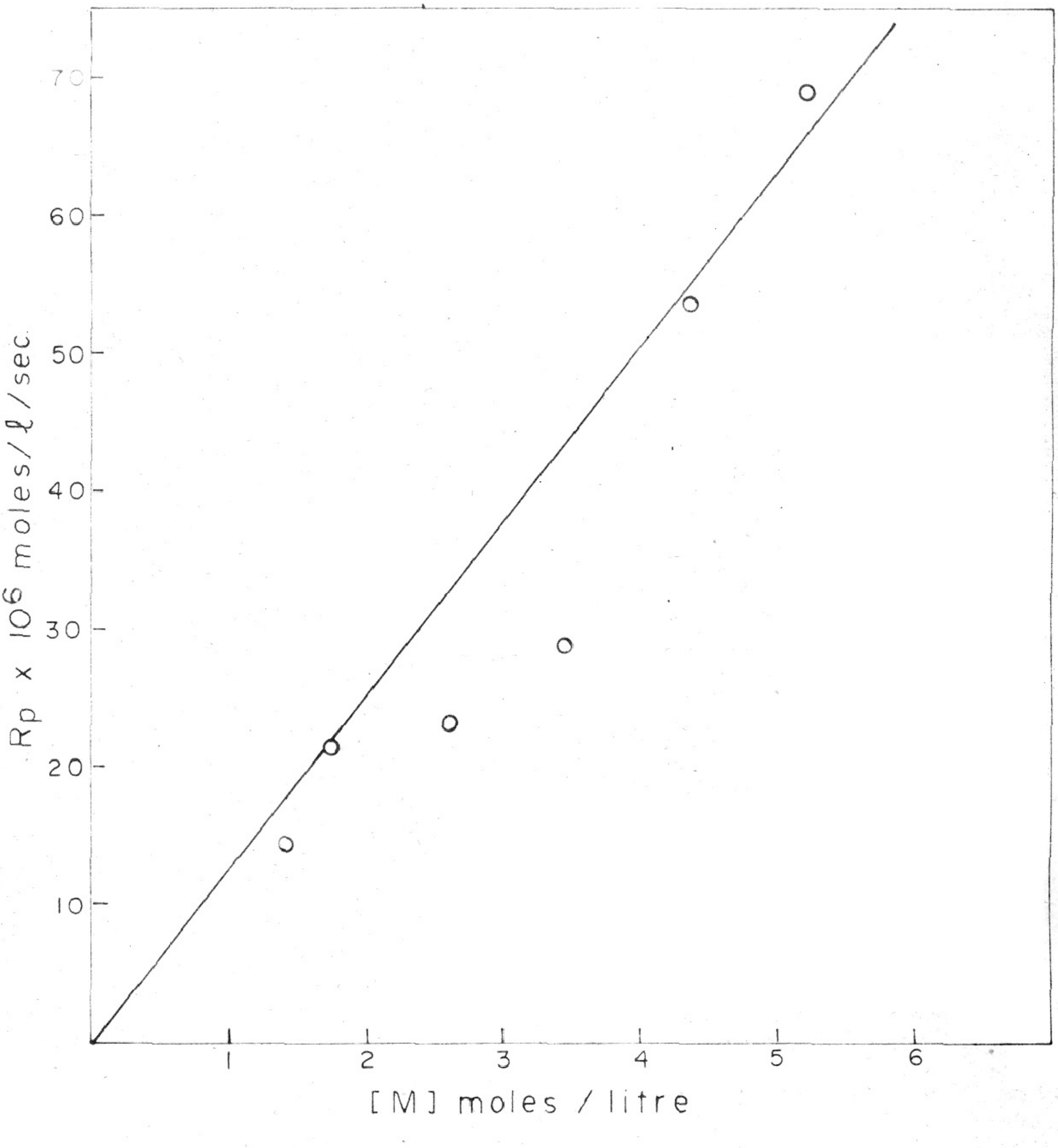


Fig. 26 Effect of monomer concentration on $VOCl_3$-$Sn(nC_3H_7)_4$ system

$[VOCl_3] = 0{\cdot}02$ m/l Sn/V molar ratio = 1·5

Aging time = 90 Min. Reaction time = 1 hr.

Temperature = 40°

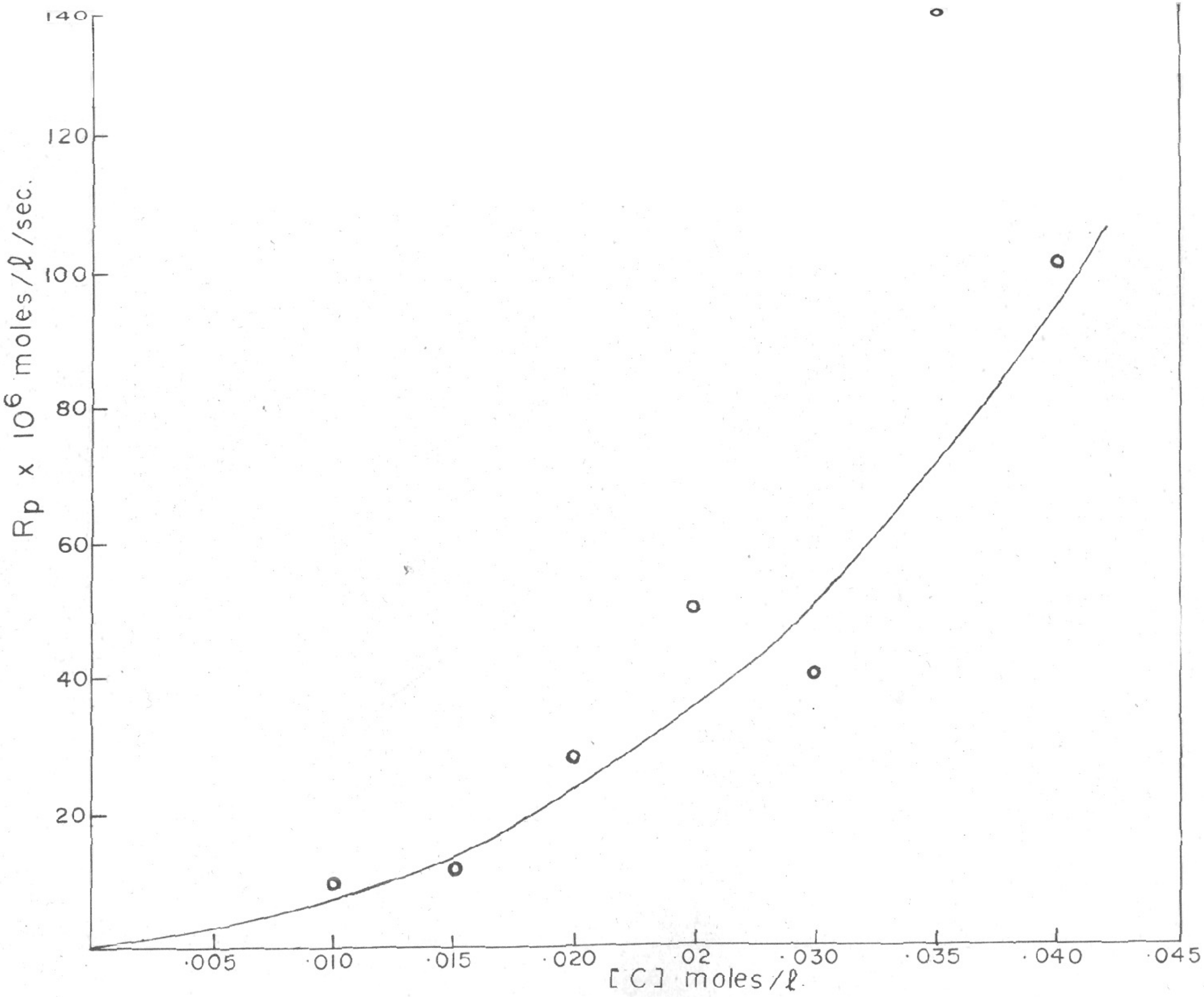


Fig. 27 EFFECT OF CATALYST CONCENTRATION ON $VOCl_3$ - $Sn(n\,C_3H_7)_4$ SYSTEM

Styrene = 10 ml.; Sn/V molar ratio = 1·5; Aging time = 90 Min.; Reaction time = 1hr. Temperature = 40°.

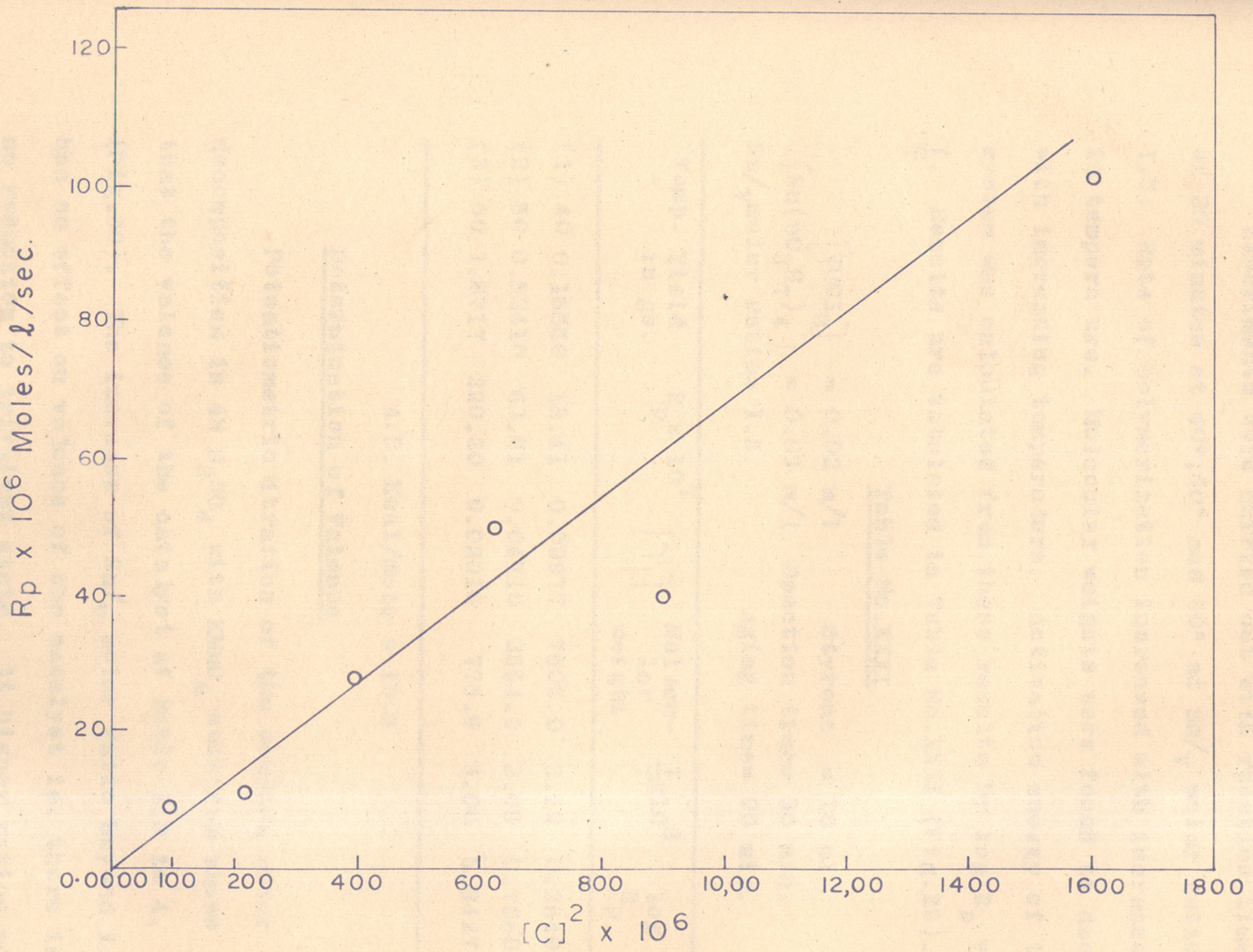


Fig. 28 $VOCl_3 - Sn(nC_3H_7)_4$ SYSTEM

R_p vs $[C]^2$

Effect of Temperature

Experiments were carried out with reaction time of 30 minutes at 40°,50° and 60° at $Sn/_V$ molar ratio 1.5. Rate of polymerization increased with increase in temperature. Molecular weights were found to decrease with increasing temperature. Activation energy of the system was calculated from these results by log R_p vs. $\frac{I}{T}$. Results are tabulated in Table No.XXXI (Fig.29).

Table No.XXXI

$[VOCl_3]$ = 0.02 m/l Styrene = 10 ml
$[Sn(nC_3H_7)_4]$ = 0.03 m/l Reaction time= 30 min.
$Sn/_V$ molar ratio= 1.5 Aging time= 90 min.

Temp. °	Yield in gs.	$R_p x 10^7$	$[\eta]$	Molecular weight	$\frac{I}{T}x10^3$	log R_p
(1) 40	0.15650	18.41	0.09977	7606.0	3.19	$\bar{6}.2649$
(2) 50	0.53410	62.81	0.04710	2554.2	3.09	$\bar{6}.7980$
(3) 60	1.8717	220.20	0.02010	775.9	3.00	$\bar{5}.3427$

A.E. Kcal/mole = 19.5

Determination of Valence

Potentiometric titration of the complex after decomposition in 4N H_2SO_4 with $KMnO_4$ solution shows that the valence of the catalyst at ratio 1.5 is 4. (Fig.30). The increase of $Sn/_V$ molar ratio beyond 1.5 has no effect on valence of the catalyst ie. there is no reduction to trivalent state. At higher ratios no trivalent V was observed but the end point V^{IV} to V^V became less sharp hence ratio vs.valence are not tabulated.

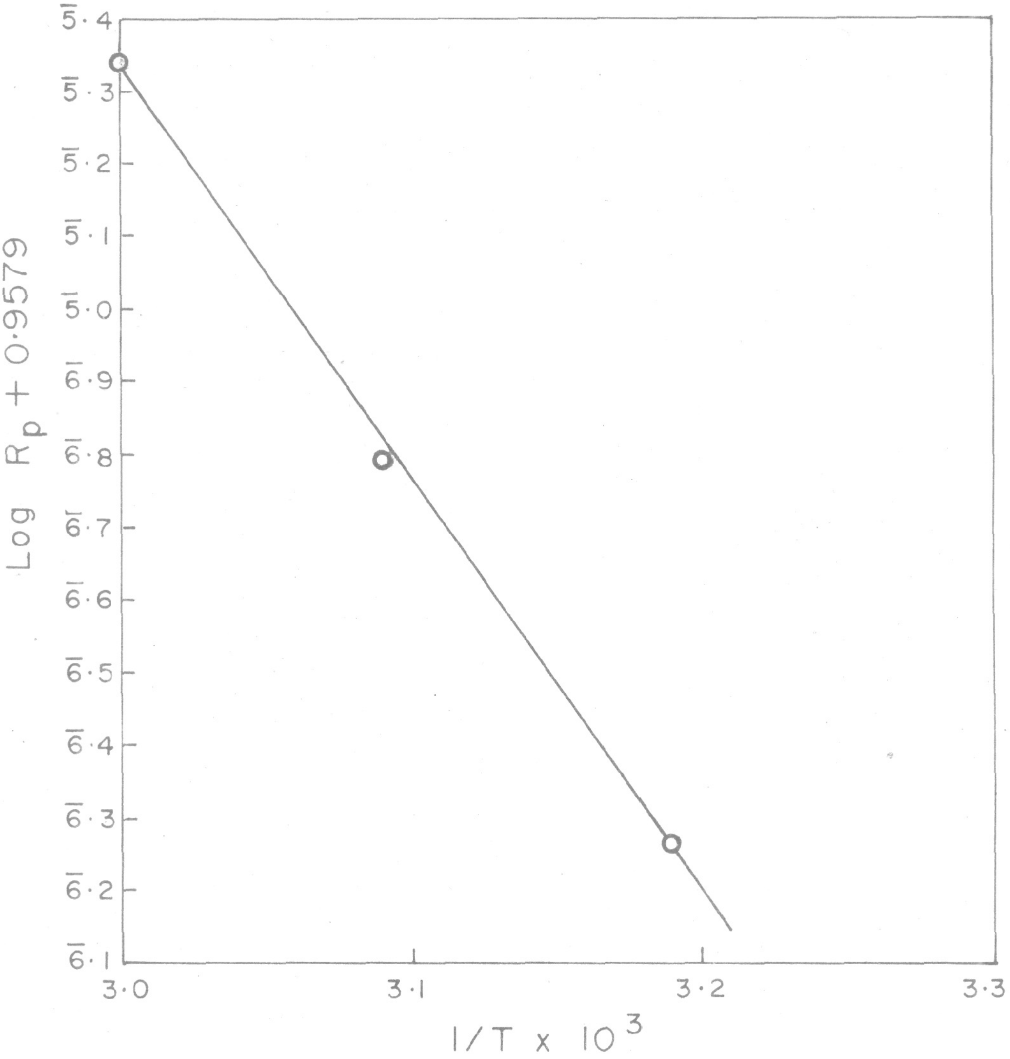


Fig. 29 EFFECT OF TEMPERATURE ON $VOCl_3$ - $Sn(nC_3H_7)_4$ SYSTEM

$[VOCl_3]$ = 0·02 m/l ; Sn/V molar ratio = 1·5;

Styrene = 10 ml. ; Aging time = 90 Min .

Reaction time = 30 Min.

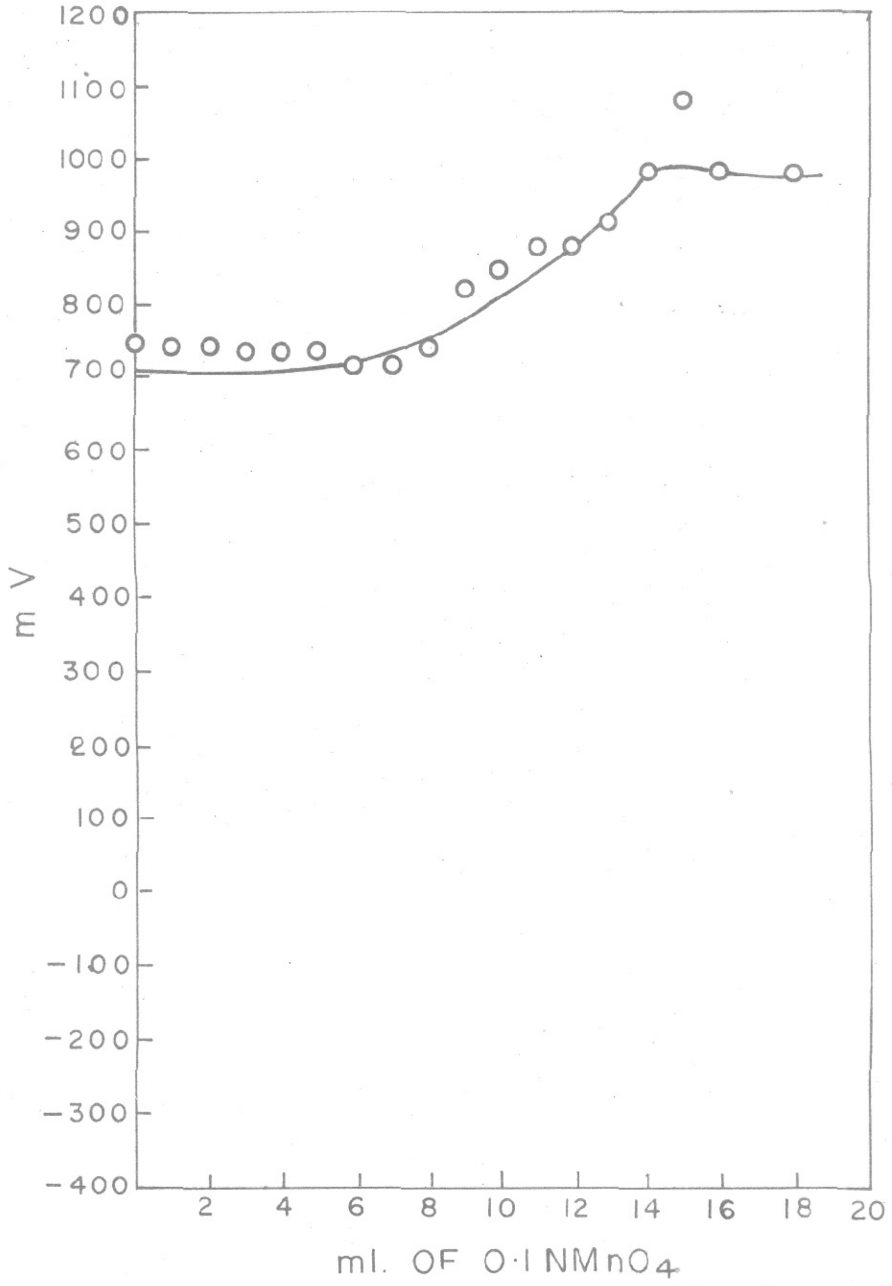


Fig. 30 DISTRIBUTION OF VANADIUM VALENCE IN $VOCl_3$-$Sn(nC_3H_7)_4$ SYSTEM

Sn/V molar ratio = 1·5; [$VOCl_3$] = 0·04 m/l;

H_2SO_4 (4N) = 25 ml.; Temperature = 80°;

Average valence = 4·07.

Polymerization of Styrene with $VOCl_3$-$Li(iC_5H_{11})$ in Hexane at 40°

$VOCl_3$ polymerizes styrene at room temperature in hexane and toluene cationically and $Li(iC_5H_{11})$ polymerizes styrene anionically[118]. Polymerization by $Li(iC_5H_{11})$was conducted at 30° in n-hexane and the rates of polymerization for different concentrations of $Li(iC_5H_{11})$ have been given in Table No.XXXII.

Table No.XXXII

Styrene = 5 ml. n-hexane = 45 ml.

	[Li-Isomyl] x 10^2	Time in min.	Weight of polymer in gs.	R_p x 10^5 m/l/s.
(1)	4.00	30	0.92095	9.799
(2)	2.16	60	1.02830	5.473

$Li(iC_5H_{11})$ was added to hexane to have required concentration. 5 ml. of styrene was then added to that solution. Total solution was made 50 ml. Immediately on addition of styrene, the solution turned orange. Polymer precipitated out during progress of the reaction due to its insolubility in n-hexane. It was filtered, washed, dried and weighed.

$VOCl_3$-$Li(iC_5H_{11})$ Complex Catalyst System

$VOCl_3$ readily reacts with $Li(iC_5H_{11})$ and forms a dark brown catalyst complex, which precipitates out immediately. This complex has high catalytic activity for the polymerization of styrene.

Aging Time of the Catalyst System

The variation of activity of catalytic complex was first studied during 10 to 60 minutes of aging time. It was found the activity of the catalyst did not change or deteriorate during this interval. The results are tabulated in Table No.~~XI~~XXXIII. Experiment carried out with 24 hours aging time showed a decrease in rate of polymerization, indicating deactivation (or decomposition) of the complex with higher aging times.

Table No.XXXIII

Effect of Aging Time

$[VOCl_3]$ = 0.005 m/l Styrene = 5 ml
$[Li(iC_5H_{11})]$ = 0.005 m/l Total volume = 25 ml
Molar ratio = 1 Time of reaction = 15 min.

	Aging time min.	Yield in gs.	$R_p \times 10^6$ m/l/s.	$[\eta]$	Molecular weight
(1)	10	0.7841	73.79	0.1621	14362.4
(2)	20	0.6777	63.78	0.0899	6315.9
(3)	30	0.6589	62.00	0.1086	8225.4
(4)	60	0.8249	77.45	0.1081	8177.5
(5)	60	0.6741	63.45	0.0583	3446.6
(6)	1440	0.2222	20.91	0.1193	9417.2

Ratio Studies

The activity of the catalyst and the complete formation of Ziegler type catalyst complex depend upon the molar ratio of mixing of the constituents of the system. The activity of the catalyst complex at different molar ratios of mixing of $VOCl_3$ and $Li(iC_5H_{11})$ from 0.5 - 4.0 was studied. The concentration of $VOCl_3$ was maintained constant and $Li(iC_5H_{11})$ concentration was varied and increased. The amount of polymer isolated from the experiments conducted for 15 minutes at different ratios was found to decrease sharply becoming negligible at ratio 4. But there was a sharp increase in molecular weight at $Li/_V$ molar ratio 1 and the latter decreased again with increase in $Li/_V$ molar ratio. The colour of the complex was increasing with the increase in molar ratio ($Li/_V$).

The results are given in Table No.XXXIV (Fig.31).

Table No.XXXIV

Ratio Studies

$[VOCl_3]$ = 0.02 m/l n-hexane = 20 ml.
Styrene = 5 ml. Time of reaction= 15 min.
Aging time = 20 min.

	Molar ratio $Li/_V$	Yield in gs.	% conversion.	$[\eta]$	Molecular weight
(1)	0.5	3.3134	73.05	0.1028	8616.9
(2)	1.0	2.8523	62.85	0.1601	14840.8
(3)	1.5	2.1900	48.26	0.0692	4379.4
(4)	2.0	1.0495	23.12	0.0414	2132.0
(5)	2.5	0.1074	2.37	0.1395	11689.6
(6)	3.0	0.0036	0.08	-	-
(7)	4.0	-	0.00	-	-

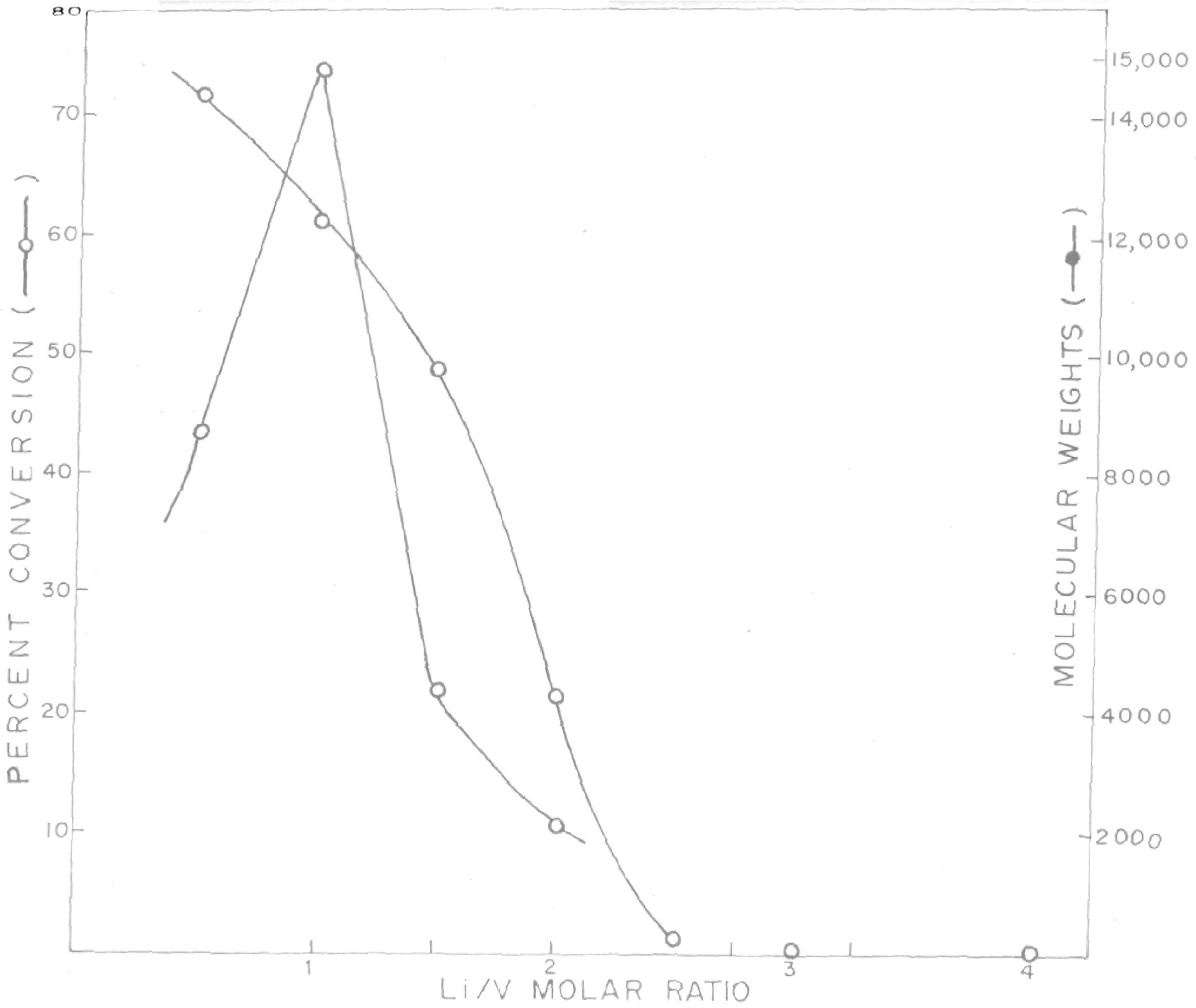


Fig. 31 EFFECT OF Li/V MOLAR RATIO ON $VOCl_3$-$Li(iC_5H_{11})$ SYSTEM

$[VOCl_3] = 0{\cdot}02$ m/l; Styrene = 5 ml.; Reaction time = 15 Min.; Aging time = 20 Min.; Temperature = 40°

Percent Conversion

As n-hexane is a non-solvent for polystyrene, the polymer starts precipitating as soon as the catalyst comes in contact with the monomer. Studies of percent conversion against time showed that the rate of polymerization remains steady upto first fifteen minutes and there is no change in conversion at higher reaction time. This clearly points out the possibility of decomposition of catalytic species in the presence of monomer. There was no variation of molecular weight with time. Results are given below in Table No.XXXV (Fig.32).

Table No.XXXV

Effect of Reaction Time

$[VOCl_3] = 0.005$ m/l Styrene = 5 ml
$[Li(iC_5H_{11})] = 0.005$ m/l n-hexane = 20 ml
Molar ratio $Li/_V = 1$ Aging time = 20 min.

	Reaction time min.	Yield in gs.	% conversion	$[\eta]$	molecular weight
(1)	5	0.3397	7.485	0.1040	9748.9
(2)	10	0.6200	13.67	0.0710	4533.4
(3)	15	0.6770	14.94	0.0899	6315.9
(4)	30	0.6720	14.81	0.1115	8523.8
(5)	45	0.9209	20.29	0.0883	7748.0
(6)	60	0.6730	14.83	0.0299	1356.2

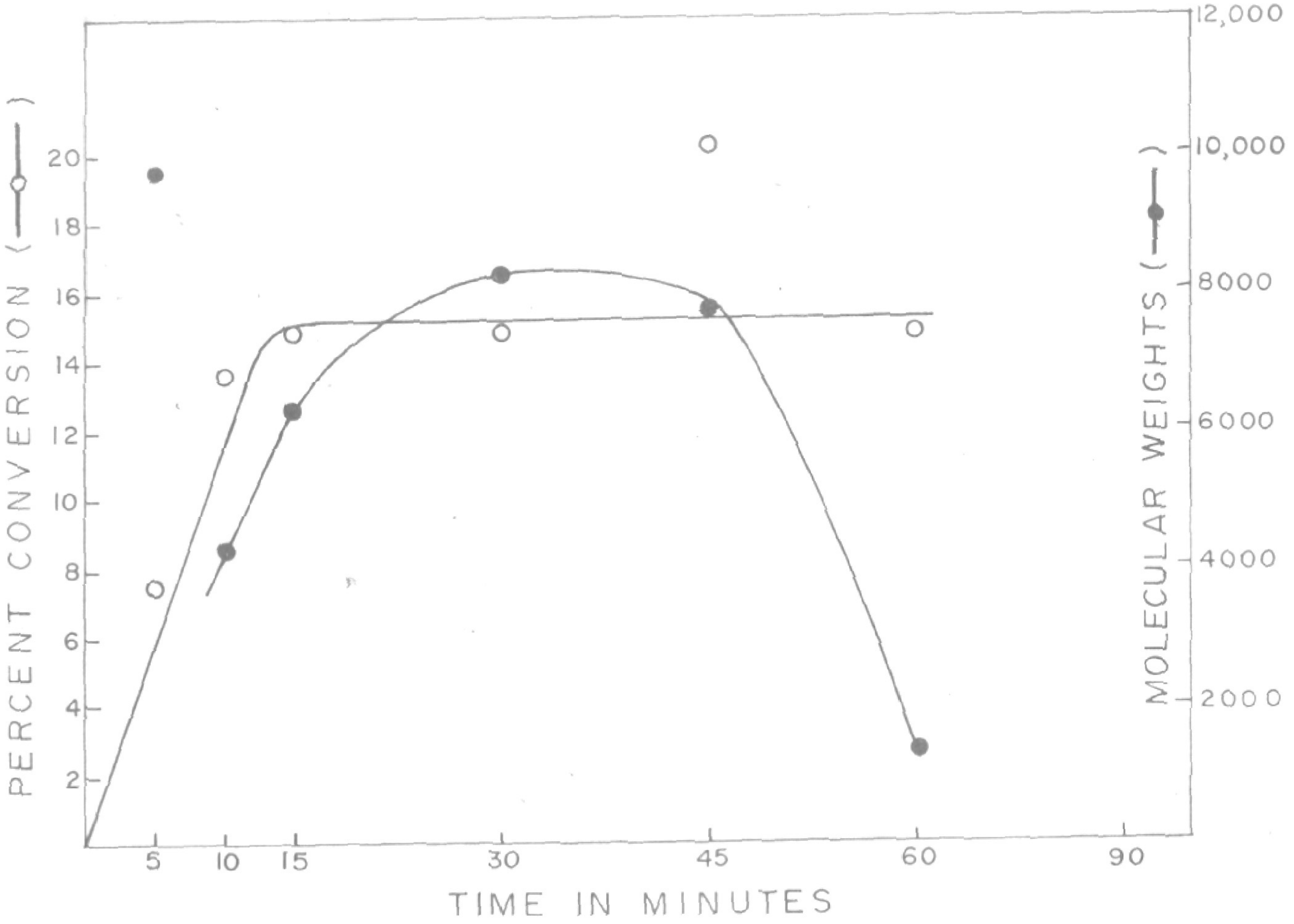


Fig. 32 EFFECT OF REACTION TIME ON $VOCl_3 - Li(iC_5H_{11})$ SYSTEM

$[VOCl_3] = 0{\cdot}005$ m/l; Li/V molar ratio = 1·5;

Styrene = 5 ml.; Aging time = 20 Min.;

Temperature = 40°

Effect of Catalyst Concentration

The rate of polymerization was found to be proportional to the concentration of $VOCl_3$ at the fixed molar ratio $Li/_V = 1$. There was no effect of catalyst concentration on the molecular weights in the range of catalyst concentration studied. Results are given in Table No.XXXVI (Fig.33).

Table No.XXXVI

Rate of Polymerization vs. [Catalyst]

$Li/_V$ molar ratio = 1 n-hexane = 20 ml
Monomer = 5 ml Aging time= 20 min.
Reaction time = 15 min.

	$[VOCl_3]$ m/l	[LiAm] m/l	Yield	R_px10^{-6} m/l/s	$[\eta]$	Molecular weight
(1)	0.002	0.002	0.2776	26.12	0.0848	5821.9
(2)	0.003	0.003	0.4235	39.85	0.0980	7129.2
(3)	0.004	0.004	0.5444	51.23	0.0575	3374.8
(4)	0.005	0.005	0.6777	63.78	0.0899	6315.9
(5)	0.006	0.006	0.8135	78.34	0.0798	5325.8
(6)	0.007	0.007	0.9395	90.46	0.0705	4496.9

Effect of Monomer Concentration

There was a linear change of yield with increasing monomer concentration but there was no variation of rate of polymerization. Hence it can be clearly seen that rate of polymerization is independent of monomer concentration. Molecular weights were found to be

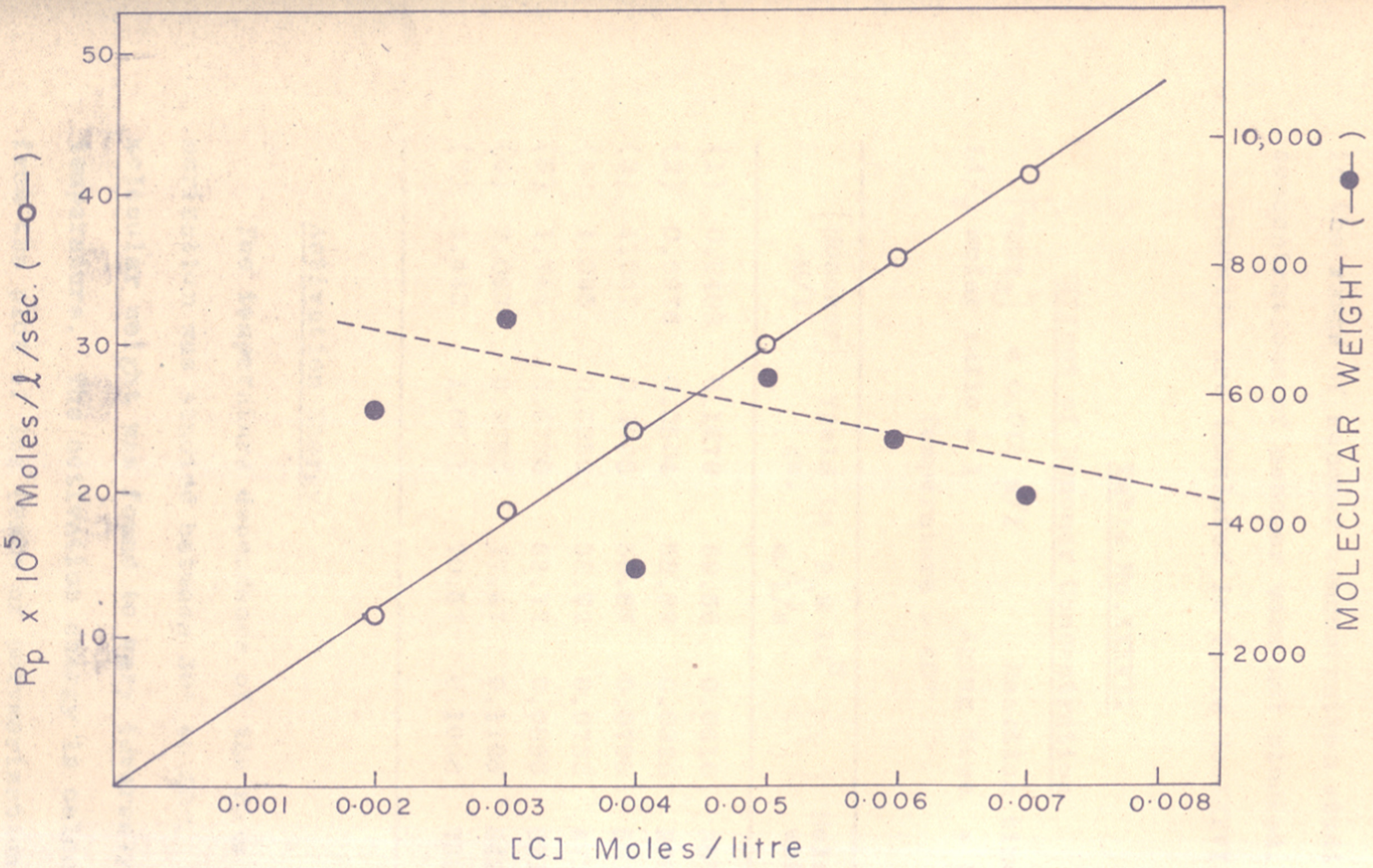


Fig. 33 EFFECT OF CATALYST CONCENTRATION ON $VOCl_3 - Li(iC_5H_{11})$ SYSTEM

$[VOCl_3] = 0·005$ ml.; Li/V molar ratio = 1·0;

Styrene = 5 ml.; Aging time = 20 Min.;

Reaction time = 15 Min.; Temperature = 40°.

increasing as the monomer concentration was increased, in the range of monomer concentration studied. Higher concentrations of monomer were not studied.

Results are tabulated in Table No.XXXVII (Fig.34).

Table No.XXXVII

Effect of Monomer Concentration

$[VOCl_3]$ = 0.005 m/l   Reaction time = 15 min.
$Li/_V$ molar ratio = 1   Aging time = 20 min.
Temperature = 40°

	[Monomer] M/1	Yield in gs.	$R_p \times 10^6$ m/1/s	$[\eta]$	Molecular weight
(1)	0.3488	0.1479	69.56	0.0610	3675
(2)	0.6976	0.2504	58.89	0.0320	2560
(3)	1.047	0.3626	56.85	0.0795	5315.
(4)	1.395	0.5259	58.92	0.0732	4735
(5)	1.744	0.6770	63.77	0.0899	6315
(6)	2.093	0.9755	77.47	0.1105	8425
(7)	2.442	1.0501	70.57	0.1006	7385

Activation Energy

The temperature dependence of the rate of polymerization was studied between 30° to 50°. The molecular weight was found to vary inversely with temperature. The activation energy is calculated from the plot of log (rate of polymerization) vs. $\frac{I}{T}$. Results are tabulated in Table No.XXXVIII (Fig.35).

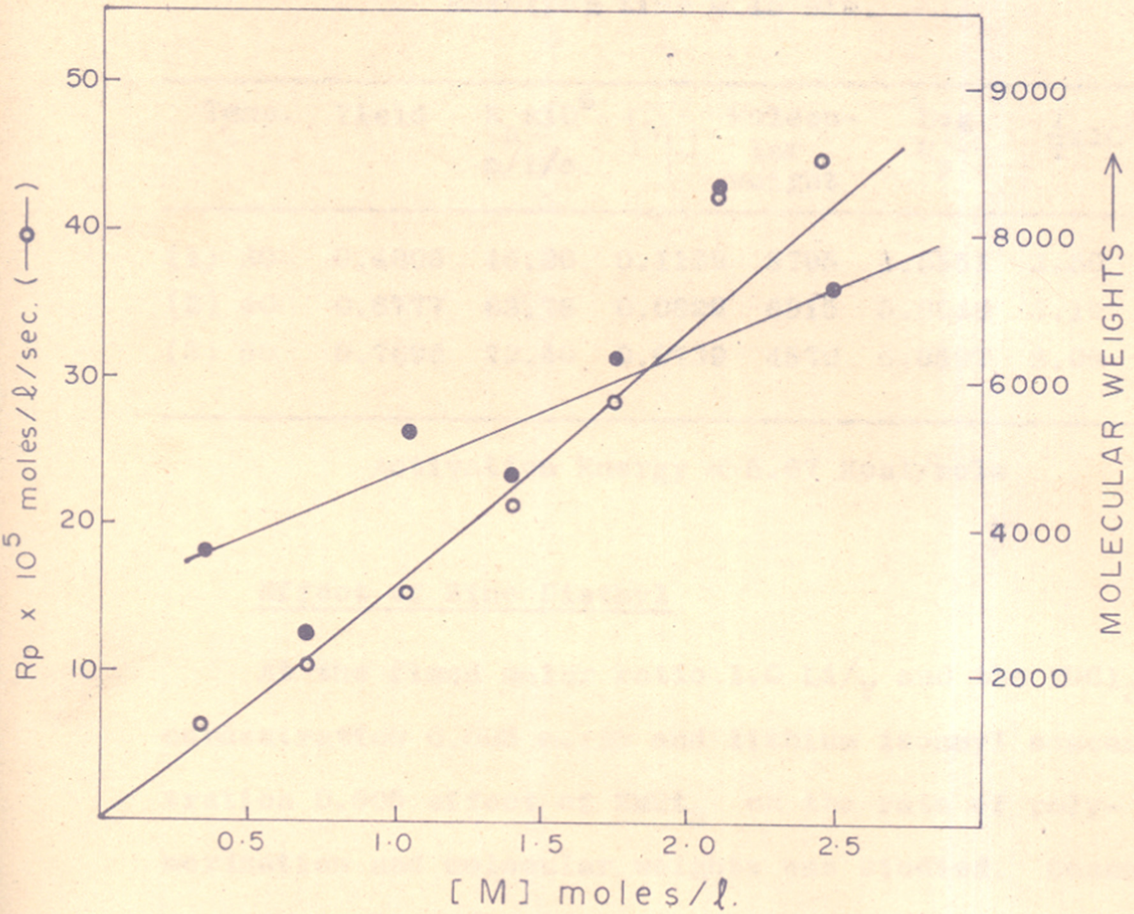


Fig. 34 Effect of monomer concentration on $VOCl_3$-$Li(iC_5H_{11})$ system

Styrene = 5 ml.   Li/V molar ratio = 1·0

Aging time = 20 Min.   [$VOCl_3$] = 0·005 m/l

Temperature = 40°   Reaction time = 15 Min.

Table No.XXXVIII

Effect of Temperature

$[VOCl_3]$ = 0.005 m/l   Styrene = 5 ml
$Li/_V$ molar ratio = 1   Aging time= 20 min.
Reaction time = 15 min.

Temp. °	Yield	$R_p x10^6$ m/1/s.	$[\eta]$	Molecular weight	Log R_p	$\frac{I}{T}x10^3$
(1) 30	0.4805	45.20	0.1139	8795	5.6551	3.30
(2) 40	0.6777	63.78	0.0899	6315	5.8046	3.19
(3) 50	0.7696	72.40	0.0739	4570	5.8597	3.09

Activation Energy = 5.67 Kcal/mole

Effect of Zinc Diethyl

At the fixed molar ratio 1.0 $Li/_V$ and the $VOCl_3$ concentration 0.005 molar and lithium isoamyl concentration 0.005 effect of $ZnEt_2$ on the rate of polymerization and molecular weights was studied. Concentration of $ZnEt_2$ was varied from 0.0004 to 0.01 moles/litres. A considerable decrease in molecular weights was observed. Also there was a decrease in the rate of polymerization. Results are presented in Table No.XXXIX.

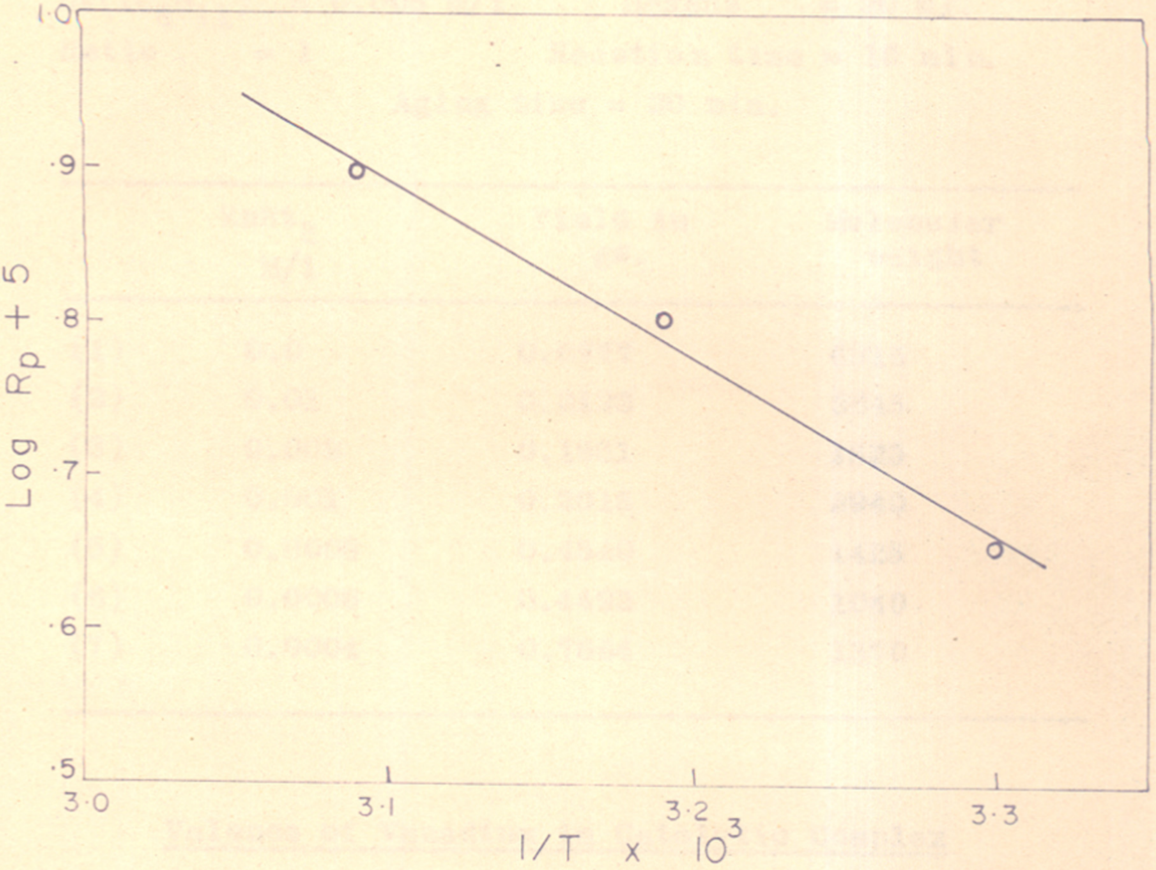


Fig. 35 Effect of temperature on $VOCl_3 - Li(iC_5H_{11})$ System.

$[VOCl_3] = 0{\cdot}005$ m/l Li/V molar ratio = 1·0

Styrene = 5 ml Aging time = 20 Min.

Reaction time = 15 Min.

Table No.XXXIX

Effect of Zinc Diethyl

$VOCl_3$ = 0.005 m/1 Monomer = 5 ml
$Li(iC_5H_{11})$ = 0.005 m/1 Hexane = 20 ml.
Ratio = 1 Reaction time = 15 min.
Aging time = 20 min.

	$ZnEt_2$ M/1	Yield in gs.	Molecular weight
(1)	0.0	0.6777	6315
(2)	0.01	0.2122	2845
(3)	0.002	0.1961	1825
(4)	0.001	0.2016	2940
(5)	0.0008	0.4540	1425
(6)	0.0006	0.4492	1040
(7)	0.0004	0.7664	1370

Valence of Vanadium in Catalytic Complex

It can be clearly seen that (See Figs.36,37) average valence of vanadium in the catalytic complex as determined by potentiometric titration is 4, at ratio 1, at which all the studies have been carried out. Plot of average valence against ratio shows that at higher $Li/_V$ ratios further reduction takes place to trivalent state. But there is no reduction to divalent form even at ratio $Li/_V = 6$. Comparing this with the plot of ratio vs. activity of catalyst, it can be safely concluded that tetravalent vanadium is the active catalyst.

Table No.XL

Distribution of Valence of Vanadium In the Catalyst System $VOCl_3-Li(iC_5H_{11})$

$VOCl_3$ = 2 ml(0.5 M); H_2SO_4 = 25 ml(4 N)

	Ratio $Li/_V$	Distribution of Valence			Average Valence
		V^{iii} Fraction	V^{iv} Fraction	V^{v} Fraction	
(1)	0.5	-	0.40	0.60	4.60
(2)	1.0	-	0.88	0.12	4.12
(3)	1.5	0.12	0.88	-	3.88
(4)	2.5	0.40	0.60	-	3.60
(5)	4.0	0.62	0.38	-	3.38
(6)	6.0	0.54	0.48	-	3.46

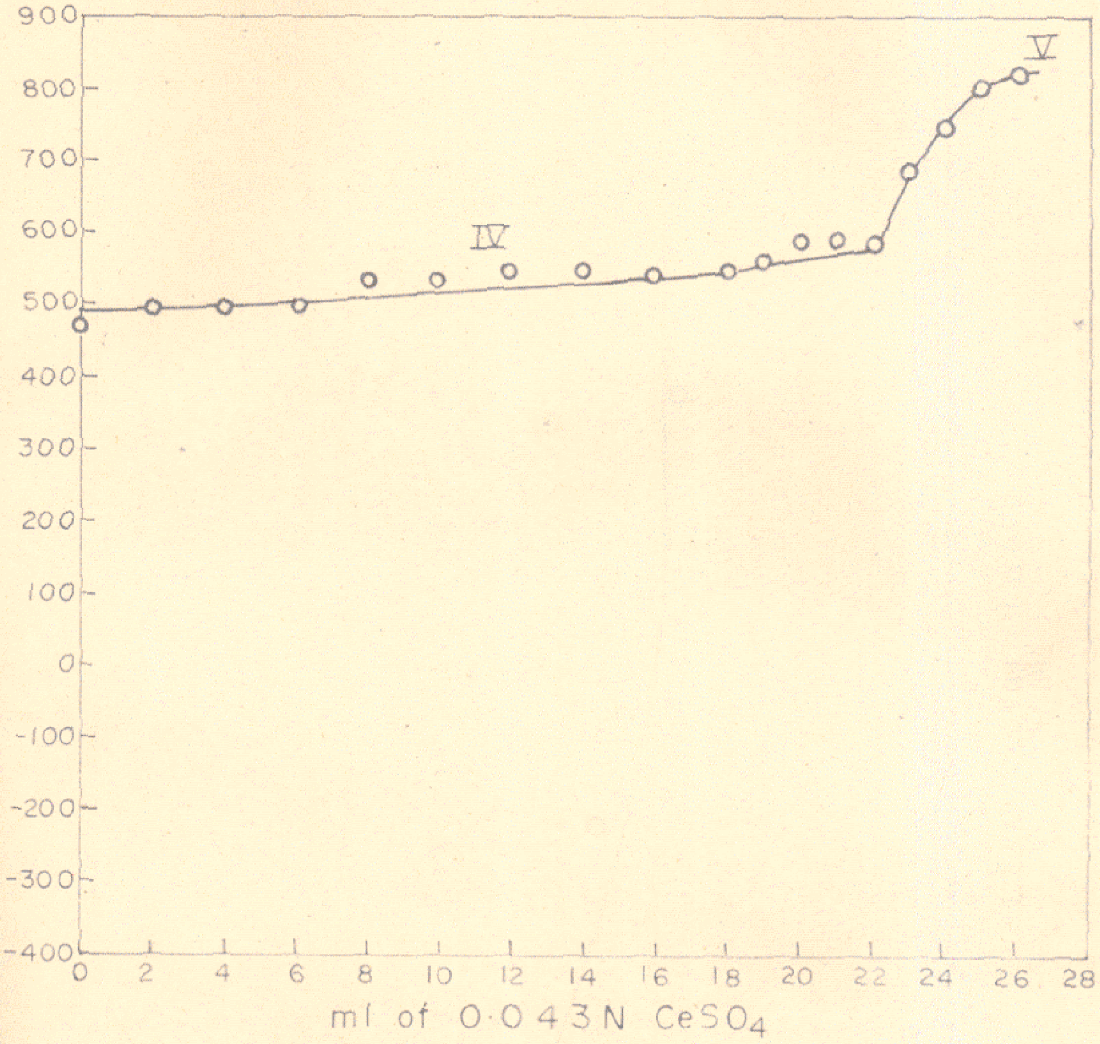


Fig. 36 Distribution of valence of vanadium in $VOCl_3$-$Li(iC_5H_{11})$ system

Li/V molar ratio=1·0 [$VOCl_3$] = 0·04 m/l

H_2SO_4(4N) = 25 Min. $CeSO_4$ Solution = 0·043N

Temperature = 80°

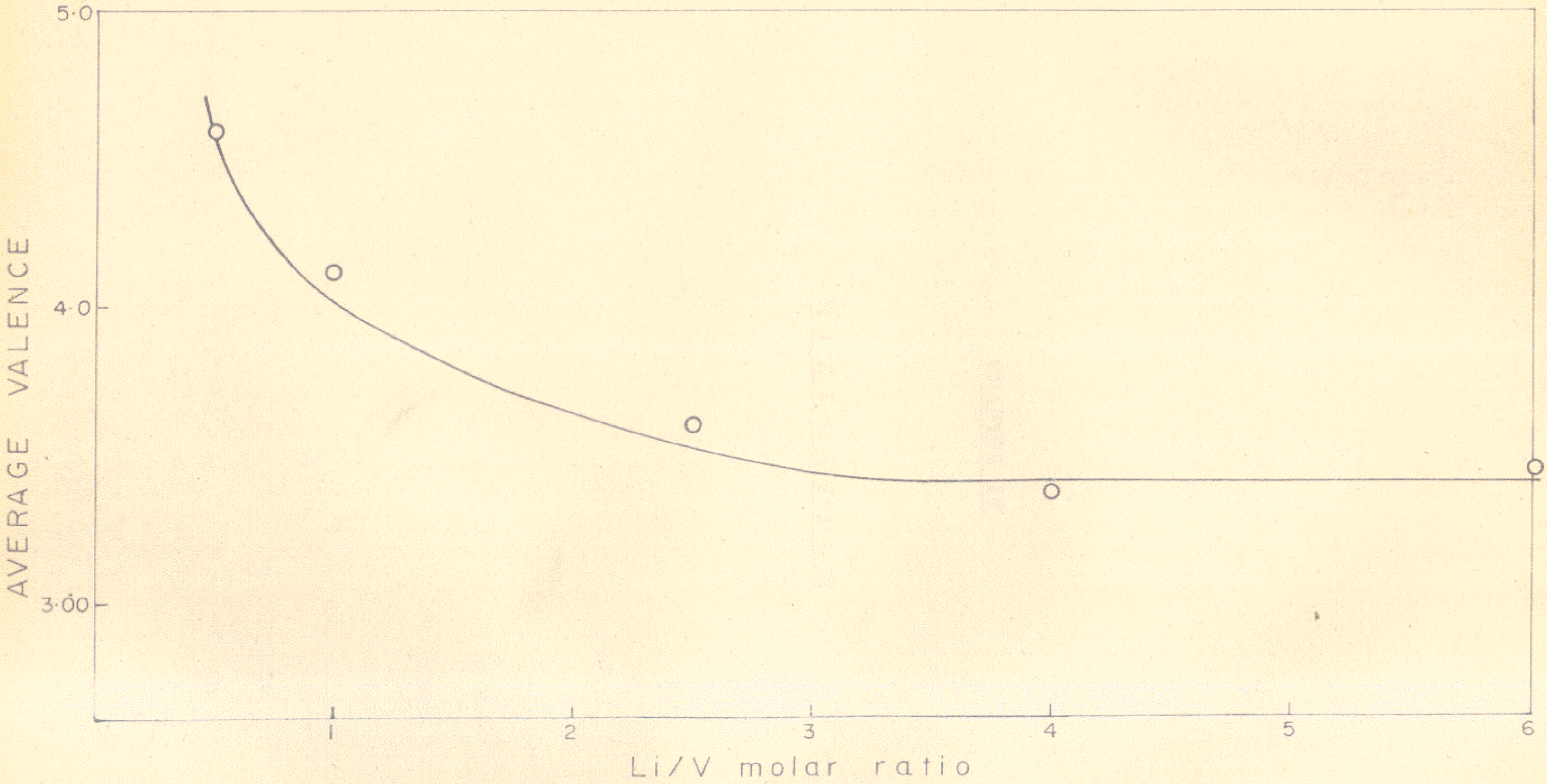


Fig. 37 Effect of Li/V molar ratio on the average valence of vanadium in $VOCl_3 - Li(iC_5H_{11})$ system

CHAPTER IV

DISCUSSION

DISCUSSION

Reproducibility of Results

Since in this type of polymerization reactions, traces of moisture, air and other impurities in solvent, monomer and reactants have pronounced effect on the catalyst obtained by the reaction of metal alkyls and the transition metal compounds, kinetic studies are beset with many difficulties. As explained in the experimental part, every effort was made and all possible precautions undertaken to purify and dry the reagents thoroughly and also to exclude contamination during mixing in the dry box and subsequent removal of the reaction vessel to the thermostat. The standardization of the conditions achieved thus could not be considered as thoroughly fool-proof, since the particle size of the catalyst precipitate was still an uncontrolled variable and the effect of variable surface area on the heterogeneous catalyst could not be negligible. The agitation of the reaction mixture controlled by r.p.m. of magnetic stirrer is another important factor not only for heat dissipation to the thermostat but also for dispersion of the catalysts and possibly also for separation of polymer from the catalyst surface. Actually significant changes in reaction rate observed in polymerization of propylene with Ziegler type catalysts due to variation in the speed of agitation have been reported[119]. It was hence necessary to control the stirring by adjustment of variable speed of the stirring motor at constant level (1000 r.p.m.).

Reproducibility obtained in our experiments varied from system to system and was found to be within 5 to 10% except in the case of $VOCl_3$-$Al(iBu)_3$ which gave 20% reproducibility.

It can be seen that reproducibilities are fairly good considering the difficulties inherent with such systems. The system $TiCl_4$-$Al(iBu)_3$ is reported to give more than 20% variable results[120], which is attributed to decomposition of $Al(iBu)_3$ during reactions. All other systems are giving less than 10% variability which is in the same range as reported by many other workers[121,122].

Order of Addition

Vanadium oxitrichloride alone polymerizes styrene by a cationic mechanism, especially in the ranges of concentration under which the present studies have been made. In case of organo-metallic compounds $AlEt_3$, $AlEt_2Br$, $Al(iBu)_3$ and $Sn(nC_3H_7)_4$ donot polymerize styrene while $Li(iC_5H_{11})$ is known to give polystyrene by anionic mechanism[118]. We confirmed that $Li(iC_5H_{11})$ at 10^{-2} M concentration yield 1 g. of polystyrene in half an hour reaction time when used alone with 5 ml. of styrene in 50 ml. hexane. To avoid the possibility of polymerization either by $VOCl_3$ alone or organo-metallic compound it was desirable to carry out all the experiments with the catalyst preformed in the absence of monomer. All the results reported here thus refer to catalyst prepared in the absence of monomer.

The presence or absence of monomer during formation of the catalyst from the reaction of the components can have a profound effect on the behaviour of the catalyst. In the case of polymerization of butene[128], the combinations of $Li(C_4H_9)$-$TiCl_4$ is effective only if addition is done in presence of monomer. For the polymerization of ethylene, however, the same components functioned effectively when mixed either in the presence or in the absence of monomer[98] though the rate was lower with catalyst prepared in the absence of ethylene. These difficulties would imply that the olefin can take part in the complex formation and could possibly lead, thus to catalysts of different structures and reactivities. But these possibilities could not obviously be experimentally confirmed with styrene monomer which is readily polymerized by $VOCl_3$ itself.

In the case of catalyst systems containing $AlEt_3$ and $AlEt_2Br$, there is possibility of evolution of ethyl radicals which subsequently disproportionate to C_2H_4 and C_2H_6. Also in the cases of other alkyls there is possibility of formation of alkyl radicals which may start polymerization of styrene by radical mechanism. Hence it is necessary to add monomer only after the formation of the catalyst is complete.

It is equally possible that the addition of metal alkyl to $VOCl_3$ and addition of $VOCl_3$ to metal alkyls may vary the physical nature of the complex formed. Under this circumstance particular order of addition of reagents has to be observed in order to get same type of catalyst complex. The following order has been retained throughout the studies:

(1) Solvent
(2) $VOCl_3$ solution
(3) Alkyl solution
(4) Monomer (after aging).

Formation of Catalyst Species

A chemical reaction is immediately seen on addition of metal alkyl to $VOCl_3$ solution. This reaction is very fast in the cases of $VOCl_3$-$AlEt_3$, $VOCl_3$-$AlEt_2Br$, $VOCl_3$-$Al(iBu)_3$ and $VOCl_3$-$Li(iC_5H_{11})$ but is comparatively slower in the case of $VOCl_3$-$Sn(nC_3H_7)_4$. In the first four cases, the colour changes quickly from pale yellow, which is the colour of $VOCl_3$

solution, to dark brown to black. There is some effervescence also in the cases of $VOCl_3$-AlEt3 and $VOCl_3$-$AlEt_2Br$. But in the case of $VOCl_3$-$Sn(nC_3H_7)_4$, the reaction was slower and changes taking place during the reaction could at least be partly visualised. The yellow solution turned light brown in no time and this colour slowly turned to dirty green and then to dirty blue and finally the colour of the precipitated solid was chocolate brown.

These precipitates obtained after the completion of the reaction of metal alkyl with $VOCl_3$ obviously contained various complexes that can be formed with different atomic ratios of vanadium and other metal and very likely also differ in the valence state of vanadium in them (See Tables IX, XVI, XXV & XL - Figs. 7,15,22 & 37). A series of step-wise reactions, fast as well as slow, can be visualised forming different catalytic species of different stabilities leading to final catalyst.

In order to have reproducible results of polymerization with these catalysts, it is necessary to find conditions under which the catalyst complexes, once formed, do not apparently change. It has been shown that reaction between $TiCl_4$ and $Li(iC_5H_{11})$ is essentially complete in 10 minutes[7]. Reaction of $TiCl_4$ with $AlEt_3$, $Al(iBu)_3$ or $AlEt_2Br$ is known to be over in first ten minutes[123].

Ashikari and Honda[124] have studied the reaction of tin alkyls with $TiCl_4$ at different temperatures and they found that time taken for completion of reaction depended on temperature. In the case of $Sn(nC_3H_7)_4$ reaction was complete in 60 minutes at 40°, 30 minutes at 60° and 15 minutes at 80°, when it was carried out in the absence of solvent.

It was assumed that reaction between $VOCl_3$ and different alkyls will probably take place in comparable times to those taken by $TiCl_4$ to react with same alkyls. Results of polymerization described in Tables I, X, XVII, XXVI and XXXIII on the effect of aging time show that activity of stable catalyst does not vary upto 30 minutes in the case of $VOCl_3$-$AlEt_3$ (A), $VOCl_3$-$AlEt_2Br$ (B), $VOCl_3$-$Al(iBu)_3$(C) and $VOCl_3$-$Li(iC_5H_{11})$ (D) while $VOCl_3$-$Sn(nC_3H_7)_4$(E) system (Fig.XXVI) attained the stable state only after 90 minutes of aging. Hence the preformed catalyst was aged for 20 minutes in the first four cases (A, B, C, D) and for 90 minutes in the fifth case (E), before the commencement of polymerization.

The catalyst activity was observed to be falling on keeping it beyond 60 minutes in the cases of systems $VOCl_3$-$Li(iC_5H_{11})$ and $VOCl_3$-$AlEt_2Br$. In the case of $VOCl_3$-$Sn(nC_3H_7)_4$ system, there was no change in activity upto 4 hours and then it slowly went down. There was no effect of aging upto 24 hours in the cases of $VOCl_3$-$AlEt_3$ and $VOCl_3$-$Al(iBu)_3$ systems.

Heterogeneous Catalyst Sites

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

Except in the case of $VOCl_3$-$AlEt_3$ system (Table III - Fig.2) where the activity is maintained for 60 minutes during polymerization, the initial catalytic activity decreased in less than 20 minutes in all the cases to low steady values (Tables XII, XIX, XXVIII & XXXV Fig. 9,17,25 & 32). The initial decrease 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 - hexane. The propagation reaction, thus slows down due to the lesser availability of monomer at the catalyst sites on the surface and when the slow steady rate is reached, it is probably entirely controlled by the diffusion of the monomer. A spontaneous termination reaction would not be affected by rate of diffusion of monomer and the retardation of propagation due to diffusion control will, hence manifest itself by a decrease in the rate of polymerization. But in the case of $VOCl_3$-$AlEt_3$ this stage of diffusion control is reached only after one hour at ratio 2 $Al/_V$ which is shown by linear variation of percent (Table III- Fig.2) yield with time for one hour.

Loss of catalytic activity due to deposition of polymer on the catalyst particles has been reported also for styrene polymerization with $TiCl_4$-$AlEt_3$ catalyst system by Burnett[122]. Photomicrographs taken at various stages of reaction, in fact, revealed considerable agglomeration of particles bound together by polymer. 3 methyl butene-1 and b$\overset{e}{u}$tne-1[125] have also been found to yield an insoluble crystalline copolymer with $Al(iBu)_3$-$TiCl_4$ catalyst system and the rate of polymerization fell gradually to zero after about an hour. The same effect of agglomeration of particles has been determined from the temperature effect on the rate of polymerization of ethylene with Zielger-Morton catalysts[126]. The rates were found to decrease considerably more rapidly at 20° than at 60°. This effect is not expected due to poisoning of the catalyst sites. The reasonable explanation given is the build up of a polymer coating around the catalyst particles and the diffusion of ethylene through high density 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 larger than 10 μ . The importance of the role of the solvent in desorption and dissolution of the 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 Grievson[127] also clearly show the phenomenen of agglomeration in the polymerization of ethylene with a stable catalyst ($\gamma TiCl_3$-$AlEt_2Cl$). Rise in particle size as the polymerization proceeds can be clearly observed in the microphotographs.

<u>$VOCl_3$-Al-alkyls</u> ($AlEt_3$ and $Al(iBu)_3$)

Reactions of aluminium alkyls with vanadium compounds have not been studied, indetail, but all the available evidence indicates a general parallelism between the behaviour of Ti-compounds and vanadium compounds. Following steps have been postulated for the reaction of $TiCl_4$ with aluminium alkyls[128].

$$TiCl_4 + AlR_3 \longrightarrow TiCl_3^{+} + AlR_3Cl^{-} \qquad (1)$$

$$TiCl_3 + AlR_3Cl \longrightarrow \begin{cases} TiCl_3 + AlR_2Cl + R^{\cdot} & (2a) \\ TiCl_2 + AlR_2Cl + RCl & (2b) \end{cases}$$

$$TiCl_4 + 2AlR_3 \longrightarrow (TiCl_2R)^{+}AlR_3Cl^{-} + AlR_2Cl \quad \text{or} \qquad (3a)$$

$$\longrightarrow (TiCl_2)^{2+}\,(AlR_3Cl)_2^{2-} \qquad (3b)$$

$$(TiCl_2)^{2+}(AlR_3Cl)_2 \longrightarrow \begin{cases} TiCl + AlR_2Cl + RCl + R^{\cdot} & (4a) \\ TiCl_2 + AlR_2Cl + 2\,R^{\cdot} & (4b) \end{cases}$$

This scheme essentially consists of alkylation of halides and their reduction and then the complexing of the reduction products.

A similar series of reactions can be anticipated to take place when the reaction is between $VOCl_3$ and aluminium alkyls. Following are the reactions which may be taking place:

(1) Formation of alkyl vanadium halides like $RVOCl_2$

(2) Decomposition of alkyl vanadium halides thereby reducing the transition metal compounds.

(3) Reaction of reduced vanadium halides with aluminium alkyls and alkyl aluminium halides formed to give vanadium alkyl halides of reduced vanadium.

(4) Further decomposition of vanadium alkyls reducing vanadium to a lower valence state.

(5) Complexing of reduced or unreacted compounds with metal alkyls and metal alkyl halides formed during the reaction.

The extent to which the reduction of vanadium will take place will depend on the type of aluminium compound used.

Formation of organo-vanadium compounds during the reaction of vanadium halides with metal alkyls has been studied and reported by Carrick et al[112] in the case of 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 equation:

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

This reaction is very rapid and the precipitation of

Ph.HgCl is essentially complete in 10 minutes at room temperature. All vanadium in pentavalent state as well as half of phenyl groups originally charged remained in solution. The organo-vanadium compound so formed is unstable and decomposes over a period of about one hour at 30° giving quantitative conversion to biphenyl and $VOCl_2$ as:

$$C_6H_5\ VOCl_2 \longrightarrow \tfrac{1}{2}\ C_6H_5C_6H_5 + VOCl_2 \qquad (2)$$

These experiments clearly indicate the formation of a compound with $VOCl_3$ and $HgPh_2$ but its structure was not rigorously proved. Transition metals can form compounds containing a simple metal carbon single bond or they can also form bonded complex (sandwich) compounds as with aromatic hydrocarbons[129,130] or cyclopentadienyl anion[131,132]. In order to distinguish between these possibilities I.R. studies have been carried out in cyclohexane solutions, which concluded that a new phenyl containing compound is formed. Also quenching of solution with gaseous HBr produced two aromatic compounds in solution, namely biphenyl and benzene. Biphenyl concentration was same as at any instance without HBr addition but additional phenyl groups that appeared as benzene by addition of HBr were undoubtedly due to reaction.

$$C_6H_5VOCl_2 + HBr \longrightarrow C_6H_6 + VOCl_2Br \qquad (3)$$

Existance of biphenyl in unquenched solutions rules out the sandwich type compounds known to exist in chromium compounds[129,133]. As hydrolysis gave benzene, which is good evidence that the phenyl group in this organo-vanadium compound is still intact and is bound to vanadium primarily by C-V single bond. The strength of this bond is probably increased by some π bond contribution but this factor is believed to be secondary and not dominant.

Unimolecular kinetics of decomposition after the initial induction period, also gave support to decomposition of $C_6H_5\,VOCl_2$ by radical route as indicated by equation (2) but other evidence such as formation of 93-100% biphenyl, attempts to capture phenyl radicals by carrying out decomposition in presence of azobis-isobutyronitrile and reaction with carbon monoxide gave no evidence favouring the existance of free radicals. Also the experiments at high temperature discard the hypothesis of phenyl radicals remaining complexed with $VOCl_3$ or $VOCl_2$.

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

$$2\ C_6H_5\ VOCl_2 \rightleftharpoons (C_6H_5)VOCl + VOCl_3 \tag{4}$$

$$(C_6H_5)\ VOCl \longrightarrow (C_6H_5)(C_6H_5) + VOCl \tag{5}$$

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

$$(C_6H_5)_2Hg + VCl_4 \rightleftharpoons (C_6H_5)VCl_3 + C_6H_5HgCl \tag{6}$$

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

$$C_6H_5\ VCl_3 \longrightarrow \tfrac{1}{2}\ C_6H_5C_6H_5 + VCl_3 \tag{7}$$

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. In the case of reaction of aluminium alkyls (ethyl and isobutyl) with $VOCl_3$, vanadium gets converted to lower valence states. In the case of reaction of $VOCl_3$ with $AlEt_3$, it has been fouhd[134] that as the ratio of $Al/_V$ is increased, there is a sharp decrease in valence of vanadium in the catalyst which becomes two at $Al/_V$ 2 and it remains constant which corresponds to VCl_2 bound in the complex $VCl_2(C_6H_5)AlCl$. 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 was explained by an exchange reaction given below:

$$VCl_2.AlCl(C_2H_5) + Al(C_2H_5)_3 \rightleftharpoons VCl_3Al(C_2H_5)_3 + AlEt_2Cl$$

$$VCl_2.Al(OC_2H_5)(C_2H_5) + Al(C_2H_5)_3 \rightarrow VCl_2.AlEt_3 + Al(OC_2H_5)(C_2H_5)_2$$

The above type of reactions give one of the explanations for drop in catalytic activity with the increase in $Al/_V$ ratio. The authors have suggested that complex of VCl_2-$AlEt_3$ would not be effective in polymerization.

But the determinations of valence carried out by us show that average valence of vanadium in the complex is three at ratio $Al/_V = 2$ (See Fig.6) and not two as suggested by these authers. There is always a possibility of slight oxidation of decomposed complex to higher valence state during the experiments, but our results clearly show that there is no divalent vanadium at ratio 2 (See Fig.7 Table IX). Most of vanadium is found in trivalent state between $Al/_V$ ratios of 1.5 and 2.5; the area where the catalyst has maximum activity (See Fig.1 Table II). At higher ratios the reduction to divalent state occurs. These results 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. Natta[135] has also studied the valence at low temperature (-78°) for the catalysts made from VCl_4 and $AlEt_3$, $V(AcAc)_3$+$AlEt_2Cl$ for the polymerization of propylene, by electron paramagnetic resonance. It was found that the catalyst was active at lower temperatures when the valence was three, but on further reduction by increasing the temperature, the activity of the catalyst vanished. A similar observation has been made by Bier et al[136] during the copolymerization of ethylene and propylene with $VOCl_3$-Al-alkyl halides, when the activity of the catalyst vanished as the reduction V(III) to

V(II) took place, as is the case with the present system, which gives much higher molecular weights for the polymerization of styrene than the others studied. Further reduction of catalyst at higher ratio can partly account for the lower molecular weights as the $Al/_V$ molar ratio is increased. The other reason being chain transfer due to excess of metal alkyl.

Natta's[137] studies with the system VCl_3-$AlEt_3$-propylene show that the activity of the catalyst system decreases as the temperature of reaction is increased. At lower temperature only surface alkylation of VCl_3 has taken place and an active catalyst is formed but at higher temperatures when the reduction to VCl_2 has taken place the activity of catalyst falls. When the same studies were carried out by using $AlEt_2Cl$, the catalytic activity increased with increase of temperature. In this case no divalent vanadium was detected. These studies also show that trivalent vanadium is active catalyst.

On the other hand, average valence of vanadium in the case of $VOCl_3$-$Al(iBu)_3$ at ratio of $Al/_V$ of 3 was 2.3. By looking at the plot of mV vs. titrant (Fig.14) it can be seen that a very large percentage of vamdium is in divalent form. Carrick et al have also studied[68] the reaction of $VOCl_3$ with $Al(iBu)_3$

and found that at ratio $Al/_V \simeq 2$ very large proportion of vanadium (98%) was in the bivalent form.

Second order of reaction with respect to catalyst in the case of system $VOCl_3$-Al(iBu)$_3$ also points out that two types of catalyst sites are present out of which only one functions in the polymerization of styrene.

<u>$VOCl_3$-$AlEt_2Br$ System</u>

Reaction between $TiCl_4$ and $AlEt_2Br$ has been studied by Dubose et al[138]. It was found that when organo-aluminium compound was added to $TiCl_4$, the average composition of gas evolved was ethane 70%, ethylene 15%, butane 10% and 5% isobutane. The reaction ceased at a ratio of $Al/_V = 1$ indicating that only one ethyl group reacts, Ti(IV) was reduced to Ti(III). X-ray studies have shown that the catalyst $2BrAlEt_2$+$TiCl_4$ does not change its crystalline structure during polymerization. There is no structural relation between catalyst and crystallinity of polypropylene and the same catalyst is responsible for the amorphous polymer of styrene. Probably the crystalline nature of the catalyst will not be relating with the stereospecificity but with the number of metal carbon bonds available for the polymerization since $TiCl_3$-$AlEt_2Br$ gave better conversions than $TiCl_4$-$AlEt_2Br$ in the pllymerization of propylene.

However this does not excluse the orientation phenomenon of monomer on the surface of the catalyst. Visible spectroscopy also has shown that the structure of crystals is same for the 3 ratios (ie. $\frac{1}{2}$,1 and 2) of $-TiCl_4-AlEt_2Br$ studied.

Reaction involving alkylation, reduction and realkylation are quite likely in the case of $VOCl_3$-$AlEt_2Br$. As the ratio of $Al/_V$ is increased from zero, there is an increase in the rate of polymerization, which proceeds till a ratio $Al/_V=1.5$. At higher ratios of $Al/_V$ above 1.5, the rate of polymerization falls off (Table XVIII- Fig.16) thus showing a maximum in catalytic activity at ratio 1.5. The plot of $Al/_V$ vs. molecular weight also shows a peak at the same ratio, thus indicating the formation of catalyst of maximum activity. Average valence of vanadium at this ratio is 3.69 (Fig.21). This indicates that only one ethyl group from each metal alkyl molecule takes part in the reduction phenomenon unlike $TiCl_4$-$AlEt_2Br$ system, where at ratio $Al/_{Ti}=\frac{1}{2}$ reduction to trivalent state is complete and compound of type $Al_2Br_2Cl_4$ is detected.

The maximum activity at particular ratio of $Al/_V$ is similar to those found in the cases of polymerization of styrene[122], butadiene[120], ethylene[81,139] and isoprene[90].

The characteristic difference of this system from the other systems studied is that the maximum in activity at particular ratio of $Al/_V$ was not observed in other systems and in this regard this catalyst system compares very well with $TiCl_4$-$AlEt_3$ system. It seems that depending on the alkylating capacity of $AlEt_2Br$ and polarity of the system, the number of catalyst sites are increasing with increasing ratio of aluminium to vanadium and beyond particular ratio the active sites might not have a closer contact to the monomer due to the coagulation of the catalyst complex.

The absence of a similar peak, however, in the cases of other systems studied, does not mean that Ziegler type catalytic species are not formed. There is always a possibility of formation of low molecular weight polymer by $VOCl_3$ at very high rate, which can superimpose the ascend of the curve of ratio vs. percent conversion at lower ratios, which is taking place in the other systems (Tables II,XI, XXVII & XXXIV - Figs. 1,8,24 & 31) studied. But this peak is obtained here as the concentration of catalyst at which the studies are made,is much lower than in other cases and also the temperature at which the studies are carried out is lower (30°).

$VOCl_3$-$Sn(nC_3H_7)_4$ System

Reaction of the components can product a variety of compounds. This is quite apparent fromthe colour changes taking place during the reaction of catalyst components.

Though $VOCl_3$-tin tetraalkyl have scarcely been used for the polymerization of any monomer, a few studies are available on $TiCl_4$-Tin tetraalkyls used for the polymerization of ethylene, propylene and isoprene[124,140,141].

The reaction between $TiCl_4$ and Sn-tetraalkyls has been reported by Yasuo Takami[~~145~~] in a series of publications[142-144] and Osipov et al[145]. From the analysis of gases evolved and the analysis of liquid as well as solid, it has been concluded that the following reactions occur:

$$R_4Sn + TiCl_4 \longrightarrow R_3SnCl + RTiCl_3 \qquad (1)$$

$$R\,TiCl_3 \longrightarrow TiCl_3 + R \qquad (2)$$

From this catalyst complex in hydrocarbon neither the precipitated $TiCl_3$ nor the soluble portion present in the supernatent layer was able to polymerize ethylene independently indicating the necessity of both for the polymerization. Authors suggested that true catalyst may be either the pair of $TiCl_3$ or R-Sn compound which fits the experimental facts or $TiCl_3$ alone in the transition state for the lattice formation. Formation of RCl was observed which gave support to the idea of alkyl-titanium compound formation.

On comparing the results of polymerization similar reactions can be proposed to be taking place between $VOCl_3$-$Sn(nC_3H_7)_4$ involving the alkylation of vanadium compounds. Average valence of vanadium in the catalyst system is 4 (Fig.30) for ratios of $Al/_V$ between 1 and 2. This indeed helps to understand that alkylation of vanadium has taken place and alkylated product is decomposed and active complex formed, with unreacted $Sn(nC_3H_7)_4$. This follows from the same yield of polymer with further excess of alkyl after ratio $Sn/_V = 1.5$ (See Fig. 24 Table XXVII) and also molecular weight reached the highest value at $Sn/_V = 1.5$. Thus we can say that the active Ziegler type catalyst is formed at ratio $Sn/_V = 1.5$.

As pointed out by Ashikari and Honda[124] that end point of reaction between $TiCl_4$ and Sn tetraalkyls is obscure if the reaction is carried out in the presence of solvent. A similar reaction appears to be taking place here also because while studying the effect of monomer concentration it was observed that R_p increases inversely as monomer concentration, if the aging is carried out in presence of more solvent.

$VOCl_3$-$Li(IC_5H_{11})$ System

From the available evidence in the literature regarding $Li(nC_4H_9)$-$TiCl_4$ and $Li(nC_4H_9)$-$TiCl_3$[128] it may be assumed that the reaction of $Li(iC_5H_{11})$ with $VOCl_3$ employed in these investigations may result in forming complex containing non-uniform active sites. It is now very well established that the reaction of metal halides, having metal atom in higher valence, with metal-alkyls, leads to Ziegler-Natta type catalyst systems, which have lesser stereospecificity than the catalyst prepared by adding metal-alkyls to the transition metal halides in lower valent state and at the same time rates of polymerizations obtained are higher. Jones[128] found that reaction products of $TiCl_4$-$AlEt_3$ and $TiCl_4$-LiR form different types of complexes. $TiCl_4$-$AlEt_3$ complex is crystalline and $TiCl_4$-$Li(nC_4H_9)$ was gelly like. X-ray studies also distinguished crystalline nature of one from the other. He proposed the following reaction scheme for reaction between $TiCl_4$ and LiBu:

$$\mathrm{LiR + TiCl_4 \longrightarrow Li^+(TiCl_4R)^- \longrightarrow LiCl.TiCl_3+R} \qquad (1)$$

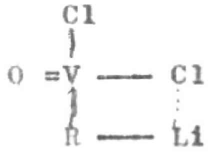
$$\hookrightarrow \mathrm{LiCl.TiCl_2+R.Cl}$$

$$\mathrm{2LiR+TiCl_4 \longrightarrow (Li^+)_2(TiCl_4R) \longrightarrow 2LiCl.TiCl_2+2R} \qquad (2)$$

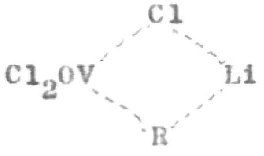
$$\hookrightarrow \mathrm{2Li\ Cl.TiCl_4+R+R}$$

This type of reaction scheme is also chalked out theoretically by Uelzmann[86,87]. Similar reactions have been envisaged by Junes et al for $TiCl_3$+LiR. In both the systems formation of a solid substrate of mixed crystals of Ti and Li along with another unidentified component as an alkylated compound has been observed. Other soluble as well as insoluble complexes of Ti and Li might have been adsorbed on the surface of precipitated halide. Polymerization is considered to take place at metal carbon bond - either Ti-C or Li-C of an organo-metallic complex present in the surface of precipitated catalyst.

As we have used $VOCl_3$ in place of $TiCl_4$ with lithium alkyls, it will not be out of way to assume similar type of catalyst complex. This argument can be well supported by the polymerization studies with $VOCl_3$ and various alkyls. In the polymerization, it has been found that there is a great similarity in the polymerization behaviour by these catalysts and of $TiCl_4$ with various organo-metallic compounds. Even in the studies of valence of vanadium in the complex, vanadium was found to be in tetravalent state at ratio $Li/_V = 1$ showing alkylation and complexing like titanium[86,87,128]. Further addition of alkyl at higher ratios may decompose the alkylated vanadium compound (as complexed with lithium) thereby causing a reduction of vanadium to a lower valence and rendering it unfit for polymerization of styrene (See Table XXXIV Fig.31). The structure of the complex can be presumably postulated as:



or



The maximum rate of polymerization at particular ratio of $Li/_V$ lends evidence to supposition that polymerization occurs by the reaction of strongly adsorbed metal alkyl to weakly adsorbed monomer. This system, then, can be treated on the basis of a Langmuir-Hinshelwood[90] type mechanism.

If θ and θ' are the fractions of surface covered by metal-alkyl and monomer respectively:

$$\theta = \frac{K'[A]}{1+K'[A] + K[M]} \qquad (10)$$

M= Monomer
A= Alkyl
K'= Absorption const.of alkyl
K= Absorption const.of monomer

$$\theta' = \frac{K[M]}{1+K[M] + K'[A]} \qquad (11)$$

If S is the number of active sites, rate of polymerization is given by:

$$R_p = k\ S\ \theta'\ \theta = \frac{k\ KK'\ [A][M][S]}{(1+K'\ [A] + K\ [M])^2} \qquad (12)$$

For weakly adsorbed monomers we get:

$$R_p = \frac{k\ KK'\ [A][M][S]}{(1+K'\ [A]\ )^2}$$

R= Rate constant

As the concentration of alkyl is increased (in this case lithium isoamyl) the rate would drop down after initial formation of solid substrate by the reaction of the components. This is due to the displacement of weakly adsorbed monomer molecules by strongly adsorbed alkyl molecules.

The absence of a maxima peak in the plot of R_p vs. ratio in contrast with observations of others for the polymerization of styrene by $TiCl_4$-$Li(iC_5H_{11})$ [146] and isoprene with $TiCl_4$-$Al(iBu)_3$[90] may be due to the fact that polymerization due to cationic sites is more than that by the formed catalyst in the cases of lower ratios of $Li/_V$. This can be verified from the molecular weight vs. ratio plot (Table No.XXXIV- Fig. 31) which shows a maximum at ratio 1, showing that very low molecular weight polystyrene which forms due to cationic polymerization gives higher conversions and at ratio 1 Ziegler type catalyst forms and molecular weight increases. Further increase of metal alkyl has given lower molecular weights due to the chain transfer reaction with alkyl which is familiar in the cases when aluminium alkyl is used. Here also this has been observed in all the systems except $VOCl_3$-$AlEt_2Br$.

KINETICS OF POLYMERIZATION

(1) Rate of polymerization when $VOCl_3$-$AlEt_3$ system is used for the polymerization of styrene at 40° is of first order with respect to catalyst and second order ~~as well as~~ with respect to monomer concentrations (See Tables IV,V- Fig. 3,4).

$$R_p \propto [\text{Monomer}]^2 [\text{Catalyst}] \qquad (1)$$

(2) Rate of polymerization when $VOCl_3$-$Al(iBu)_3$ system is used for the polymerization of styrene at 40° is ~~first~~ second order with respect to monomer concentration and also second order with respect to catalyst concentration (See Tables XIII, XIV Figs.10-12)

$$R_p \propto [\text{Monomer}]^2 [\text{Catalyst}]^2 \qquad (2)$$

(3) When the polymerization of styrene is carried out using $VOCl_3$-$AlEt_2Br$ as catalyst system at 30°, the rate of polymerization was found to be first order with respect to catalyst and second order with respect t ~~as well as~~ monomer concentrations (See Tables XX,XXI- Figs. 18,19).

$$R_p \propto [\text{Catalyst}] [\text{Monomer}]^2 \qquad (3)$$

(4) Rate of polymerization when $VOCl_3$-$Sn(C_3H_7)_4$ system is used for the polymerization of styrene at 40° is of first order with respect to monomer concentration and second order with respect to catalyst concentration (See Tables XXIX, XXX Figs.26-28).

$$R_p \propto [\text{Monomer}] [\text{Catalyst}]^2 \qquad (4)$$

(5) The rate of polymerization of styrene with the catalyst system $VOCl_3$-$Li(iC_5H_{11})$ in n-hexane at 40° is first order with respect to catalyst concentration ~~but it is zero~~ and also first order with respect to monomer concentration (Tables XXXVI, XXXVII - Figs.33,34).

$$R_p \propto [\text{Monomer}] [\text{Catalyst}] \qquad (5)$$

The rate constants in each case were calculated from the slops of plots of rate vs. Monomer as well as $VOCl_3$ as shown in Figs.34,10,12,18,19,26,27,33,34. Values of K, the reaction constant, obtained thus from both plots agree with each other in each case.

Rate Constants with Respect to Catalyst and Monomer Variations in various Catalyst Systems

Catalyst systems		K from monomer variation.	K from catalyst variation.
$VOCl_3$-$AlEt_3$	(40°)	$K=4.831x10^{-5}$	$K=5.746x10^{-5}$
$VOCl_3$-$Al(iBu)_3$	(40°)	$K=9.615x10^{-1}$	$K=6.006x10^{-1}$
$VOCl_3$-$AlEt_2Br$	(30°)	$K=3.699x10^{-2}$ $K=2.999x10^{-2}$	$K=3.999x10^{-2}$
$VOCl_3$-$Sn(C_3H_7)_4$	(40°)	$K=2.000x10^{-2}$	$K=3.125x10^{-2}$
$VOCl_3$-$Li(iC_5H_{11})$	(40°)	$K=3.521x10^{-2}$	$K=3.429x10^{-2}$

For comparison, the activities of catalyst systems containing $TiCl_3$ or $TiCl_4$ are given below[128].

Rate Constants for Styrene Polymerization By Ziegler Type Catalyst Systems

	Catalyst Systems		K (l/mole/min.)
(1)	$TiCl_3$-$AlEt_2Cl$	(60°)	$13.7 x10^{-4}$
(2)	$TiCl_3$-$AlEt_2Br$	(60°)	$12.6 x10^{-4}$
(3)	$TiCl_3$-$AlEt_3$	(60°)	$22.7 x10^{-4}$

It can be seen that values of rate constants obtained are considerably higher than those reported in the cases of styrene polymerization with $TiCl_3$-$AlEt_3$-diethyl aluminium halides.

A second order with respect to catalyst has not been reported with Ziegler-Natta type catalyst systems but its occurence in the cases of $VOCl_3$-$Al(iBu)_3$ and $VOCl_3$-$Sn(nC_3H_7)_4$ systems does not imply a departure from the Ziegler type behaviour. It however shows the complexity of catalyst forming reactions. It is postulated that reactions between the catalyst components result into two types of species (in equal proportions in this case) only one of which is active in the polymerization of styrene and it can be written as:

$$2\,C \rightleftharpoons C^{*1} + C^{*2} \qquad (6)$$

(where C^{*2} is not active in polymerization)

Mechanism based on kinetics is discussed in detail for various cases below.

$VOCl_3$-$AlEt_3$ System

A second order dependence on monomer concentration and a first order dependence on catalyst concentration in the case of $VOCl_3$-$AlEt_3$ system can be explained by either a Rideal or a Langmuir-Hinshelwood mechanism, as has been done by Geylord, Kwei and Mark[120].

When two molecules react on the surface of a catalyst either one or both of reacting molecules are bound by chemisorption forces. In case of Rideal mechanism both molecules hit the surface of catalyst but only one of them is chemisorbed. The other molecule hits the chemisorbed molecule and a reaction occurs. The second molecule may also, however, be adsorbed by Van der Wall's forces and react with chemisorbed reaction partner from a Vander Wall's layer. In the Langmuir Hinshelwood mechanism the two reactant molecules have to be chemisorbed side by side. Such pairs can be formed by localized adsorption at neighbouring active spots or they may result from collisions of molecules moving along the surface of catalyst ie. mobile adsorption.

According to Rideal mechanism one can postulate a simple scheme

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

$$(CM) + M \xrightarrow{k_1} (CM) + \text{Polymer} \qquad \text{(Slow)}$$

Assuming that the adsorption of monomer by active catalyst centres is a rapid equilibrium process and that the reaction between the adsorbed monomer and another monomer molecule is the rate determining step, we can write:

$$\frac{-dM}{dt} = k_1 \left[(CM)\right] \left[M\right]$$

and

$$K_1 = \frac{\left[(CM)\right]}{\left\{\left[C\right] - \left[(CM)\right]\right\} \left[M\right]}$$

Solving the above equation, one obtains

$$(CM) = \frac{K_1 \left[C\right]\left[M\right]}{1 + K_1 \left[M\right]}$$

Substituting it in rate equation

$$\frac{-dM}{dt} = \frac{k_1 K_1 \left[M\right]^2 \left[C\right]}{1 + K_1 \left[M\right]} \qquad (7)$$

when K_1 M is small compared with unity e.g. at low monomer concentration, this equation simplifies to

$$\frac{-dM}{dt} = k_1 K_1 \left[M\right]^2 \left[C\right]$$

in agreement with experimental rate expression.

Localized adsorption in the Langmuir-Hinshelwood mechanism can be represented by the scheme:

$$C + M \xrightleftharpoons{K_2} (CM) \qquad \text{(Rapid equilibrium)}$$

$$(CM) + M \xrightleftharpoons{K_3} (CM_2) \qquad \text{(Rapid equilibrium)}$$

$$(CM_2) \xrightarrow{k_2} \left[C\right] + \text{Polymer} \qquad \text{(Slow)}$$

Assuming that two rapid equilibrium processes are involved in the formation of the active monomer-catalyst complex and that the formation of polymer from this complex is the rate determining step, we can write:

$$\frac{-dM}{dt} = k_2 \quad (CM_2)$$

$$K_2 = \frac{[(CM)]}{\{[C] - [CM]\}[M]}$$

$$K_3 = \frac{[(CM)]}{\{[(CM)] - [(CM_2)]\}[M]}$$

Solving these equations

$$(CM_2) = \frac{K_2K_3[M]^2 [C]}{1+K_2 [M])(1+K_3 [M])}$$

and

$$\frac{-dM}{dt} = \frac{k_2K_2K_3 [M]^2 [C]}{(1+K_2 [M])(1+K_3 [M])}$$

The last equation again reduces to the experimental rate expression when both $K_2 [M]$ and $K_3 [M]$ are small compared to unity.

$$\frac{-dM}{dt} = k_3K_2K_3 [M]^2 [C] \qquad (8)$$

The scheme leading to equation (8) assumes that the formation of polymer removes both monomer units from (CM_2) and regenerates the active catalyst C. If only one monomer unit becomes part of the polymer and the regenerated active catalyst is (CM)

$$(CM_2) \xrightarrow{k'_2} (CM)+\text{Polymer}$$

where k'_2 is different from k_2. Then

$$\frac{-dM}{dt} = k'_2 \left[(CM)_2\right]$$

and solution of the equations leads to a different version of equation (8) where k'_2 is substituted for k_2.

The kinetic data obtained in the present study does not permit distinction between the two mechanisms.

It appears that $AlEt_3$ has reacted with the growing chain of polystyrene by a chain transfer process since it was observed that degree of polymerization was inversely proportional to the square-root of $AlEt_3$ concentrations at constant concentration of $VOCl_3$ (Fig.38). It was further noticed that the rate of polymerization did not increase with the increasing amount of aluminium triethyl (See Table 11, Fig.1[illegible] So it is clear that the chain termination is obtained through chain transfer to aluminium triethyl.

It can be assumed that aluminium triethyl acts in the dissociated monomeric form in the chain

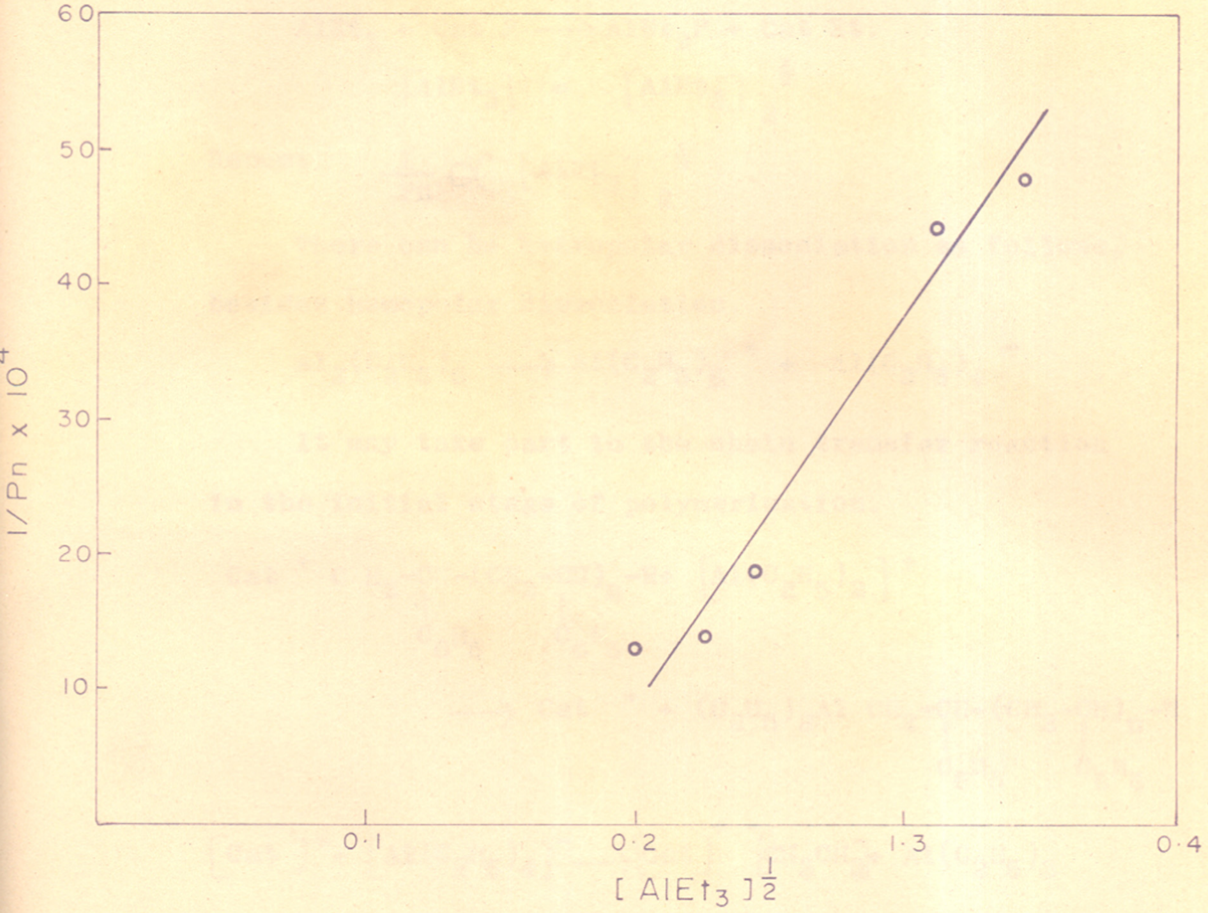


Fig. 38 $VOCl_3 - AlEt_3$ - System $1/Pn$ vs. $[AlEt_3]^{1/2}$

transfer process since aluminium triethyl is normally dimeric, in equilibrium with monomeric structure.

We can write chain transfer

$$(\mathrm{AlEt_3})_2 \rightleftarrows 2\,\mathrm{AlEt_3}$$

$$\mathrm{AlEt_3} + \mathrm{Cat\ P} \longrightarrow \mathrm{AlEt_2P} + \mathrm{Cat\ Et.}$$

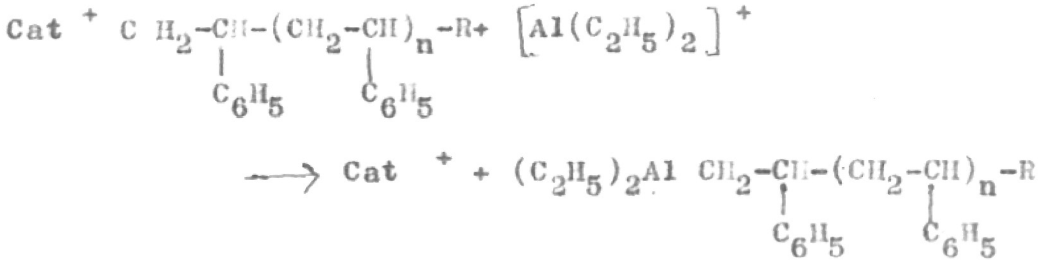
$$[\mathrm{AlEt_3}] = [\mathrm{AlEt_3}]_2^{\frac{1}{2}}$$

Hence: $$\frac{1}{\mathrm{Pn}} \propto [\mathrm{AlEt_3}]_2^{\frac{1}{2}}$$

There can be hetropolar dissociation as follows, besides homopolar dissociation.

$$\mathrm{Al_2(C_2H_5)_6} \longrightarrow \mathrm{Al(C_2H_5)_2}^{+} + \mathrm{Al(C_2H_5)_4}^{-}$$

It may take part in the chain transfer reaction in the initial stage of polymerization.



$$\mathrm{Cat}^{+}\ \mathrm{CH_2{-}\underset{C_6H_5}{CH}{-}(CH_2{-}\underset{C_6H_5}{CH})_n{-}R} + [\mathrm{Al(C_2H_5)_2}]^{+}$$

$$\longrightarrow \mathrm{Cat}^{+} + \mathrm{(C_2H_5)_2Al\ CH_2{-}\underset{C_6H_5}{CH}{-}(CH_2{-}\underset{C_6H_5}{CH})_n{-}R}$$

$$[\mathrm{Cat}]^{+} + [\mathrm{Al(C_2H_5)_4}]^{-} \longrightarrow [\mathrm{Cat}]^{+}\,{}^{-}[\mathrm{CH_2CH_3}] + \mathrm{Al(C_2H_5)_3}$$

In the later stages of polymerization it is possible that there may occur transfer process involving more than one ethyl group per aluminium atom. In this way the catalyst will be regenerated, while the monomeric aluminium alkyl takes part in the equilibrium of association with other alkyl in solution.

$VOCl_3$-$Al(iBu)_3$ System

A second order with respect to catalyst as well as monomer can be easily rationalized using equations (7) or (8) and substituting C^{*1} for C where C^{*1} is the active component of the catalyst in styrene polymerization and we can write equation (7) as:

$$\frac{-dM}{dt} = \frac{k_1K_1[M]^2[C^{*1}]}{1+ K_1 [M]} \qquad (9)$$

and when K_1 M is much lesser than unit, we get:

$$\frac{-dM}{dt} = k_1K_1 [M]^2 [C^{*1}]$$

and when only half of the catalyst is active for styrene polymerization, as given in equation (6), we get:

$$\frac{-dM}{dt} = k_1K_1 [M]^2 [C]^2$$

Also equation (8) can be written as:

$$\frac{-dM}{dt} = \frac{k_2K_2K_3 [M]^2 [C^{*1}]}{(1+K_2[M])(1+K_3[M])} \qquad (10)$$

and when $K_2[M]$ and $K_3[M]$ are much smaller than unit, we get:

$$\frac{-dM}{dt} = \underline{k_2K_2K_3[M]^2[C^{*1}]}$$

and replacing C^{*1} by C as from equation (6), we get:

$$\frac{-dM}{dt} = k_2K_2K_3[M]^2[C]^2$$

VOCL$_3$-AlEt$_2$Br System

A first order with respect to catalyst and a second order with respect to monomer in the case of VOCl$_3$-AlEt$_2$Br can be explained in the same way as in the case of VOCl$_3$-AlEt$_3$ system (See equations 7&8).

VOCl$_3$-Li(iC$_5$H$_{11}$) System

A first order with respect to catalyst as well as monomer concentrations can be obtained as follows:

$$C + M \overset{K_4}{\rightleftharpoons} (CM) \qquad \text{(Rapid equilibrium)}$$

$$(CM) \xrightarrow{k_3} C + \text{Polymer} \qquad \text{(Slow)}$$

Where C is the active centre and M is a monomer molecule. Assuming that the adsorption of monomer by the catalyst centres is a rapid equilibrium process resulting in an active monomer-catalyst complex and that the formation of polymer from this complex is the rate determining step one can write:

$$\frac{-dM}{dt} = k_3 \left[(CM)\right]$$

and

$$K_4 = \frac{\left[(CM)\right]}{\left\{\left[C\right] - \left[(CM)\right]\right\}\left[M\right]}$$

Where $\left\{\left[C\right] - \left[(CM)\right]\right\}$ is the number of active centres unoccupied by monomer molecules. Solving the above equations, one obtains

$$(CM) = \frac{K_4 \left[M\right]\left[C\right]}{1 + K_4\left[M\right]}$$

and
$$\frac{-dM}{dt} = k_3 \frac{K_4 [M][C]}{1 + K_4[M]} \qquad (11)$$

when K_4 M is small compared to unity, the equation simplifies to:

$$\frac{-dM}{dt} = k_3K_4 [M][C]$$

At sufficiently high concentrations when K_4M is much larger than unity, the rate will become independent of M

$$\frac{-dM}{dt} = k_3 [C]$$

Bawn and Symcox in their study of ethylene polymerization by a soluble tetra butyl titanate and $AlEt_3$ catalyst system, actually observed rate changes similar to these equations.

$\underline{VOCl_3\text{-}Sn(nC_3H_7)_4 \text{ System}}$

A second order with respect to catalyst and first order with respect to monomer can be rationalized by replacing C in equation (11) by C^{*1} which is the active part of catalyst complex formed and we get:

$$\frac{-dM}{dt} = \frac{k_3K_4 [M][C^{*1}]}{1 + K_4 [M]} \qquad (12)$$

and when $K_4 [M]$ is much lesser than unity, we get:

$$\frac{-dM}{dt} = k_3K_4 [M](C^{*1})$$

and when C^{*1} is only half of C (See equation 6), we get:

$$\frac{-dM}{dt} = k_3K_4 [M][C]^2$$

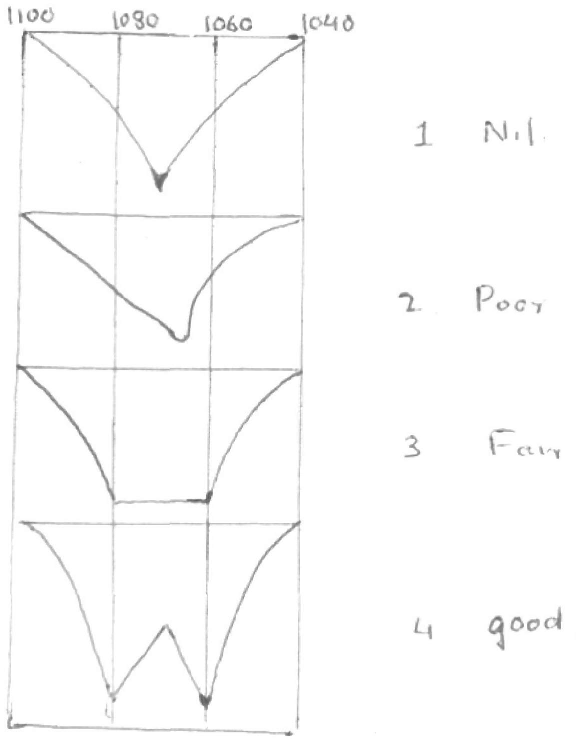
which is analogous to the results obtained.

minor role as scavange but it is responsible in shaping the catalyst sites.

STRUCTURE OF POLYMERS

The molecular weights of polystyrene obtained with these catalyst systems are comparatively low and are in the range of 6000 to 20000 in the cases of $VOCl_3$-$AlEt_2Br$, $VOCl_3$-$Li(C_5H_{11})$, $VOCl_3$-$Sn(C_3H_7)_4$ and $VOCl_3$-$Al(iBu)_3$ and only in the case of $VOCl_3$-$AlEt_3$ between 40,000 to 100,000. No residue of high molecular weight isotactic polymer was left after extraction of polymer with methyl-ethyl ketone. But the infrared spectra analysis showed the absorption bands at 1364, 1314,1297 and 1185 cm^{-1} which are characteristic of isotactic polymers[148-150].

Morton[151] has discussed the absorption at 1070 cm^{-1} in I.R. spectra of different polystyrene samples



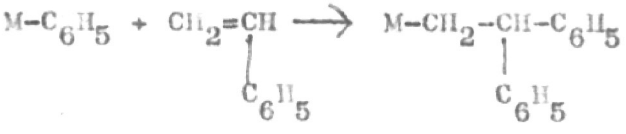
containing high isotacticity to nil isotacticity. According to the isotacticity, different gradation of absorption at 1070 cm^{-1} were classified as (1) nil, (2) poor, (3) fair, and (4) good. Depending on the shape of the peak, very sharp absorption peak at 1070 cm^{-1} is for samples of no isotacticity and the absorption peak at 1070 cm^{-1} was bifurcated into 1060 cm^{-1} and 1080 cm^{-1} for good isotactic polymer sample. For poor isotacticity, absorption peak is not sharp and the fair isotactic sample has adsorption peak inbetween bifurcated adsorption peak of good isotacticity and less sharp peak of poor isotacticity sample as shown in the diagram.

When solutions of polymers were examined by infrared it was observed that the absorption peaks at 1070 cm^{-1} were not definitely sharp but they did not have bifurcation into 1060 cm^{-1} and 1080 cm^{-1}. It may therefore be concluded that isotacticity of polystyrene prepared by these catalyst systems (ie. $VOCl_3$ and different alkyls) can be varying from poor to fair.

In the cases of $VOCl_3$-$AlEt_3$ and $VOCl_3$-$Al(iBu)_3$ a small fraction of polymer (0.04% - 0.4%) was separated as insoluble product in methyl ethyl ketone as well as in hot toluene in which even isotactic polystyrene is supposed to be soluble. This was considered to be due to formation of either very highly isotactic variety or gel. Topchiev[152] in his studies with $VOCl_3$-$AlEt_3$ system has also mentioned that this type of polymer is produced due to the shifting of active centres inside the ring bringing a phenyl ring in the growing chain.

High molecular weight and stereospecific polymers are generally obtained with metal organic catalysts with most of the monomers but in the case of styrene tacticity is comparatively less. This may be due to bulky structure of monomer. Natta[153] has also shown that in the case of $VOCl_3$-$AlEt_3$ isotacticity of polystyrene obtained is low.

However, it is quite reasonable to say that the formation of amorphous polystyrene does not necessarily imply cationic mechanism. There is much to favour the view that the metal-organic synthesis resulting high molecular weight by anionic coordinated mechanism, can sometimes with certain combinations of metal alkyl and transition metal halides, lead to low molecular weight polymers of styrene by the same mechanism of growth of polymer chain at a metal-carbon bond. It has been un-ambiguously shown in the polymerization of styrene with PhMgBr-$TiCl_4$[154] that polymers were low molecular weight and carried the phenyl of PhMgBr as end group. This must arise in the following way.



$$M-C_6H_5 + CH_2=\underset{\displaystyle C_6H_5}{\underset{|}{CH}} \longrightarrow M-CH_2-\underset{\displaystyle C_6H_5}{\underset{|}{CH}}-C_6H_5$$

Under our experimental conditions of polymerization the presence of free $VOCl_3$ is not very likely, since the valence determination of vanadium shows clearly that at the ratios of combination of $VOCl_3$ with different organo-metallic compounds, at which the studies have been carried out, vanadium is present in reduced valence state which is undoubtedly obtained by alkylation and reduction of vanadium in the catalyst complex.

It can be said that just as in the system $TiCl_4$-LiBu, the presence of metal halides with $TiCl_4$ as mixed crystals has resulted in lowering the stereospecificity molecular weight and increase of rate of polymerization. In case of $VOCl_3$-$Li(C_5H_{11})$ mixed crystal effect on molecular weight and rate of polymerization might be predominant. Addition of metal halides such $AlCl_3$, $ZnCl_2$ or $FeCl_2$ as mixed crystals with $TiCl_3$ or $TiCl_2$ increase the rate of polymerization of propylene considerably[45]. The halides such as $FeCl_2$ reduce crystallinity greatly, presumably the result of less efficient orientation of monomer molecules in the vicinity of catalyst sites.

In the following way, we can explain step-wise the possible reasons for lowering of molecular weight and increase in rate of polymerization. The low molecular weight with styrene may be obtained on the following groupds:

(1) Bulky nature of styrene molecules explains its inability to get arranged stereospecifi~~city~~cally. Even the catalyst systems which are very highly stereospecific for the polymerization of other olefins do not give very highly stereospecific polymers of styrene[153].

(2) VCl_4 and VCl_3 are known to give stereospecific catalysts in combination with metal-alkyls. But catalyst systems containing $VOCl_3$ as transition metal compound is poor for stereospecificity. This is probably due to the presence of oxygen ligand in the latter case. Resonance forms such as:

$$M \longrightarrow \ddot{\underset{..}{O}} \longrightarrow V \longrightarrow R \longleftrightarrow M \longleftarrow \overset{\delta(+)}{\underset{..}{O}} \longrightarrow \overset{\delta(-)}{V} \longrightarrow R$$

would effectively decrease the electron attracting power of vanadium centre and it has also lower relative reactivity with propylene compared to $VOCl_4$ and VCl_3 systems[73].

(3) In the case of $VOCl_3$-$AlEt_2Br$ the possibility of formation of EtBr in the reaction mixture and its action as chain transfer agent was investigated. In the standard catalyst system $TiCl_4$-$AlEt_3$, EtBr was added in various quantities and its effect on molecular weights and activity was studied. It was found (Table XXIV) that rates increased and molecular weights decreased showing that bromide is also in some manner responsible for lower molecular weights

with $VOCl_3$-$AlEt_2Br$.

(4) While comparing the systems $VOCl_3$-$AlEt_3$ and $VOCl_3$-$Al(iBu)_3$, it can be seen that presence of divalent form in the catalyst reduces the molecular weights with increase in molar ratio ($Al/_V$) above a ratio of 2 (See Table II Fig.1) where whole of vanadium is in trivalent form. At ratios higher than 2 of $Al/_V$, molecular weights decrease as the amount of vanadium in divalent form increases. This clearly shows that though an active catalyst is formed by the vanadium reduced to divalent state, it is not capable of giving high molecular weights. I. Pasquon et al[155,156] have used the same catalyst ($VOCl_3$-$Al(iBu)_3$ system for the polymerization of propylene to atactic stereoblock polymers instead of isotactic polymers.

(5) A recent study by Bushik and Stearn[157] has shown that ionic character of organo-metallic compound in the catalyst affects the rates of polymerization and also found that dissociation constant of $AlEt_3$ is about 30 times that of $Al(iBu)_3$. The highly ionic nature of $Al(iBu)_3$ may also be responsible for much higher rates and thus lower molecular weights in the case of $VOCl_3$-$Al(iBu)_3$ than in the case of $VOCl_3$-$AlEt_3$ system.

EFFECT OF TEMPERATURE AND ACTIVATION ENERGY

Activation energies calculated from the data of polymerization at different temperatures are tabulated below (See Tables VI, XV, XXII, XXXI, XXXVIII Figs. 5,13,20,29,35).

		Temp. range	Activation energy
(1)	$VOCl_3-AlEt_3$	35-50	7.37 Kcal/mole
(2)	$VOCl_3-Al(iBu)_3$	30-50	11.26 Kcal/mole
(3)	$VOCl_3-AlEt_2Br$	30-50	6.4 Kcal/mole
(4)	$VOCl_3-Sn(Pr)_4$	40-60	21.33 Kcal/mole
(5)	$VOCl_3-Li(C_5H_{11})$	30-50	5.67 Kcal/mole

Overall activation energy values are in the same range as the values reported in literature by other workers with this type of catalyst systems, which are definitely known to behave by coordinated anionic mechanism. Standard values are presented in table given below for comparison.

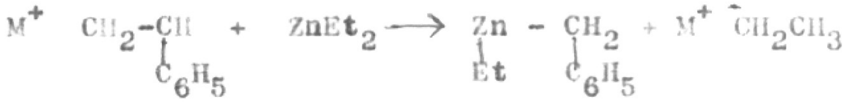
	Monomer	Catalyst	Activation Energy	
(1)	Styrene	$TiCl_3-AlEt_3$ [119]	9.4 Kcal/mole	
(2)	Styrene	$PhMgBr+TiCl_4$ [154]	20.0 Kcal/mole	
(3)	Styrene	BuLi [118]	17.0 Kcal/mole	
(4)	Isoprene	$TiCl_4-Al(iBu)_3$ [90]	14.4 Kcal/mole	
(5)	Styrene	$TiCl_4-AlEt_3$ [97]	11.0 Kcal/mole	
(6)	Propylene	$TiCl_3-AlEt_3$ [158]	8.7 Kcal/mole	
(7)	Propylene	$TiCl_3-ZnEt_2$ [159]	8.2 Kcal/mole	
(8)	Propylene	$TiCl_3-BeEt_2$ [160]	16.2 Kcal/mole	E_p
			26.4 Kcal/mole	E_{tr}

Cationic polymerization of styrene is known to give negative values for activation energy ($TiCl_4$- 26.8 Kcal/mole[99]) and the values obtained by free-radical initiators are of much higher magnitude. Hence activation energy results clearly point out a coordinated anionic mechanism.

In the catalyst systems $VOCl_3$-$AlEt_3$, $VOCl_3$-$AlEt_2Br$, $VOCl_3$-$Sn(C_3H_7)_4$ and $VOCl_3$-$Li(C_5H_{11})$, there is an increase in the rate of polymerization with increase in temperature, between 30-70° showing that catalysts remained stable during this range. But in the case of $VOCl_3$-$Al(iBu)_3$ system rate of polymerization was found to decrease with increasing temperature above 50° showing thereby that the catalyst species were decomposed above 50°. Similar phenomenon has been reported in certain Ziegler-Natta type catalyst systems[127].

EFFECT OF ZINC DIETHYL AS CHAIN TRANSFER AGENT

Molecular weights were found to decrease to a considerable extent when $ZnEt_2$ was added to the polymerizing systems (Table Nos.VII,XXIII,XXXIX). This is one of the typical behaviours of Ziegler type systems. Reduction in molecular weight was observed for polypropylene with $AlEt_3$-$TiCl_3$[161] by addition of $ZnEt_2$. Representing the growing centre as polarized metal-alkyl bond $M^+-CH_2-CH(C_6H_5)$ the reduction of molecular weight is accounted by (a molecular chain termination, kinetic chain transfer) an alkyl exchange reaction with metal centre of catalyst, whereby growing polymer chain is transferred to the zinc-diethyl in solution from which one C_2H_5 group has been exchanged to catalyst site as shown below:



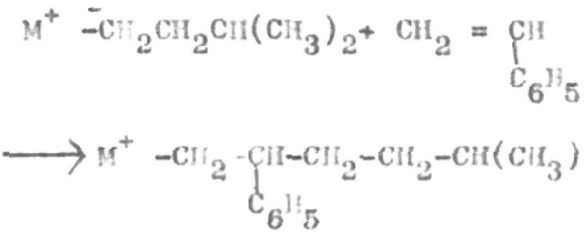
$$M^+ \; CH_2-\underset{C_6H_5}{\underset{|}{CH}} + ZnEt_2 \longrightarrow \underset{Et}{\underset{|}{Zn}} - \underset{C_6H_5}{\underset{|}{CH_2}} + M^+ \; {}^{-}CH_2CH_3$$

The molecular weight is thus reduced. The catalyst sites which are produced after the exchange reaction do not remain equally active to initiate the polymerization and hence the rate of polymerization is decreased. A similar phenomenon has been observed during the polymerization of styrene by $Li(iC_5H_{11})-TiCl_4$ and styrene by $Cr(AcAc)_3-AlEt_2Br$[146,162] This behaviour cannot be expected if the mechanism of reaction is assumed to be other than anionic. The decrease in rate on addition of $ZnEt_2$ has also been observed by Firsor et al[163] for propylene polymerization. This is explained by the fact that the reinitiation rate following the chain transfer with alkyl is much slower (1/300 in this case) whereas in the case of $BeEt_2$, $ZnEt_2$ or $AlEt_3$ reinitiation is just as rapid as propagation.

MECHANISM OF POLYMERIZATION

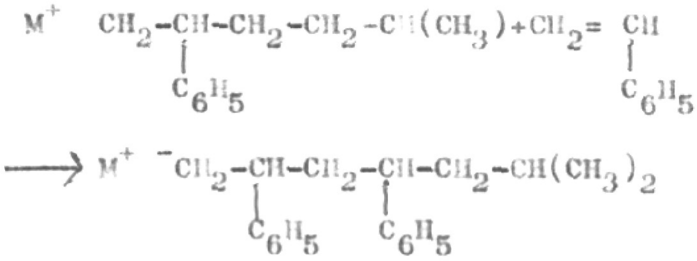
All the evidence discussed above indicating the kinetics of reaction and the effect of zinc-diethyl and activation energy support the view that an anionic coordinated mechanism operates in these systems. We can proceed to write for initiation and propagation as:

Initiation:



$$M^{+}\ {}^{-}CH_2CH_2CH(CH_3)_2 + CH_2 = \underset{\displaystyle C_6H_5}{\underset{|}{CH}} \longrightarrow M^{+}\ -CH_2-\underset{\displaystyle C_6H_5}{\underset{|}{CH}}-CH_2-CH_2-CH(CH_3)$$

Propagation:



$$M^{+}\ CH_2-\underset{\displaystyle C_6H_5}{\underset{|}{CH}}-CH_2-CH_2-CH(CH_3)+CH_2=\underset{\displaystyle C_6H_5}{\underset{|}{CH}}$$

$$\longrightarrow M^{+}\ {}^{-}CH_2-\underset{\displaystyle C_6H_5}{\underset{|}{CH}}-CH_2-\underset{\displaystyle C_6H_5}{\underset{|}{CH}}-CH_2-CH(CH_3)_2$$

where M stands for the metal cation. It is not specified whether M is vanadium or the metal ion from alkyl (Al, Li, Sn in specific cases), since our experiments do not provide conclusive evidence for either supposition. As noticed earlier, with $VOCl_3$ and metal alkyls, possibilities of many catalytic species being formed are numerous.

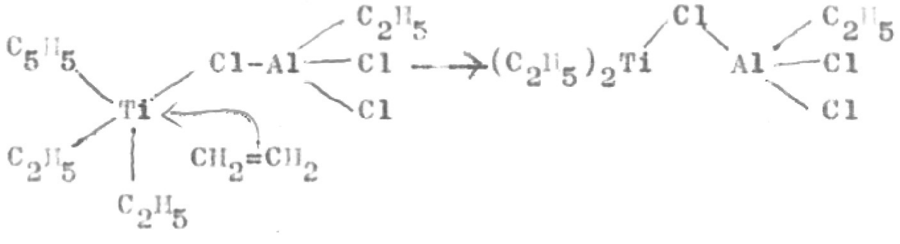
Natta[55,56] explicitly favours the growth of polymeric chain from Al-C bond and kinetic evidences are completely in agreement with the reaction mechanism which he has proposed. In addition to this, he made it clear by detecting the presence of phenyl from phenyl-aluminium in the growing chain of polyethylene prepared by dicyclo pentadienyl titanium dichloride and aluminium triphenyl catalyst system and further showed that if dicyclo pentadienyl titanium phenyl is used with aluminium triethyl, there was no phenyl group present in the growing polymer. By labelling C^{14} in aluminium triethyl and using this radioactive carbon containing aluminium triethyl with dicyclo pentadienyl titanium dichloride for polymerization of ethylene, he pointed out again the presence of alkyl from organo-metallic compound in the polymer obtained.

But this was not conclusive proof of involving aluminium carbon bond in the propagation of polymerization since it has been further proved by reinvestigating the catalyst system used above, that the alkyl or aryl group can be transferred from aluminium to titanium and the growth of polymeric chain can be from titanium carbon bond.

This preposition is further established by Carrick[68] showing that rate of polymerization of ethylene and the reactivity ratio of ethylene-propylene copolymer were different with different transition metal halides with the same organometallic compound, but there was no change in the rate or reactivity with different organo-metallic compounds with the same transition metal-halide. Of late, it has been found that organo-titanium halide when used for the polymerization of ethylene gave very low activity whereas the same compound was found to be very active in the ethylene polymerization, when it was used in combination with VCl_4 or $VOCl_3$.

It has been assumed that there is preliminary coordination of olefin to a vacant d-orbital of the transition metal and a re-arrangement to incorporate the polarised olefin into the growing polymer chain.

Mechanim of propagation using dicyclopenta dienyl-titanium dichloride and aluminium triethyl[164] for polymerization of ethylene is described as the simple π-complex formation of ethylene with titanium in the organo-titanium complex. Role of aluminium alkyl is to supply alkyl groups to titanium and to make it more positive in character. First step in polymerization would involve type complex between the titanium and the olefin.

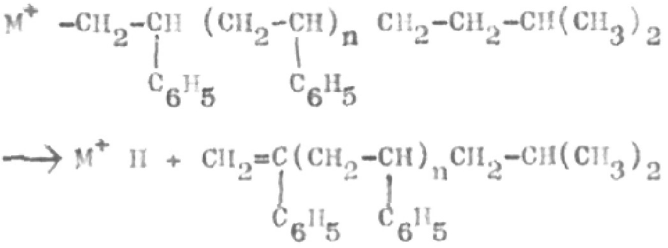


According to this structure, aluminium is tetra-coordinated and the formation of complex of olefin with it is unlikely[165]. Thus only titanium carbon is involved in propagation reaction.

The chain termination as discussed earlier could occur by:

(1) Spontaneous decomposition
(2) Monomer transfer
(3) Alkyl transfer.

(1)

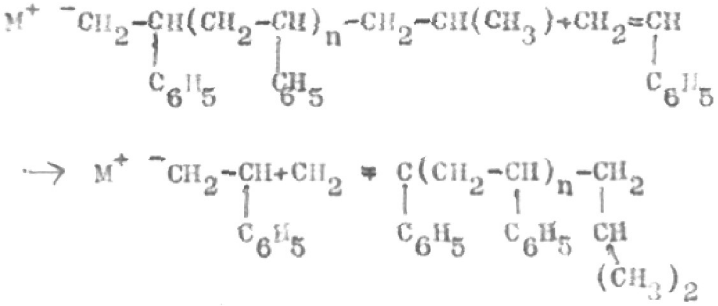


$$M^+ -CH_2-\underset{C_6H_5}{CH}\ (CH_2-\underset{C_6H_5}{CH})_n\ CH_2-CH_2-CH(CH_3)_2$$

$$\longrightarrow M^+\ H + CH_2=\underset{C_6H_5}{C}(CH_2-\underset{C_6H_5}{CH})_n CH_2-CH(CH_3)_2$$

Chain Transfer to Monomer

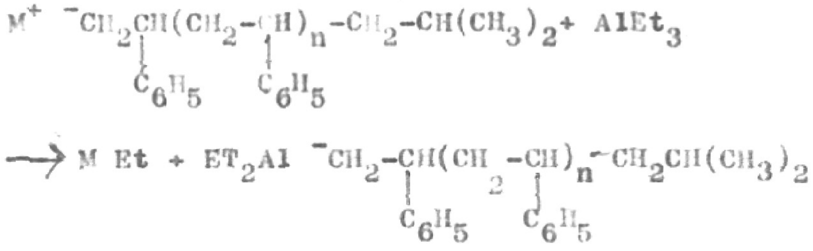
(2)



$$M^+\ {}^-CH_2-\underset{C_6H_5}{CH}(CH_2-\underset{C_6H_5}{CH})_n-CH_2-CH(CH_3)+CH_2=\underset{C_6H_5}{CH}$$

$$\rightarrow M^+\ {}^-CH_2-\underset{C_6H_5}{CH}+CH_2=\underset{C_6H_5}{C}(CH_2-\underset{C_6H_5}{CH})_n-\underset{\underset{(CH_3)_2}{CH}}{CH_2}$$

(3) Chain Transfer to Alkyl



$$M^+\ {}^-CH_2\underset{C_6H_5}{CH}(CH_2-\underset{C_6H_5}{CH})_n-CH_2-CH(CH_3)_2+ AlEt_3$$

$$\longrightarrow M\ Et + ET_2Al\ {}^-CH_2-\underset{C_6H_5}{CH}(CH_2-\underset{C_6H_5}{CH})_n-CH_2CH(CH_3)_2$$

CHAPTER V

SUMMARY

SUMMARY

Ziegler discovered in 1953 that ethylene could be polymerized at atmospheric pressure and normal temperature to yield linear high density polyethylene by using catalyst systems made up of transition metal halides in combination with metal alkyls of group I-III. These Zeigler type catalysts were later extended and modified by Natta to give stereo-regular and crystalline polymers of α-olefins. Since then the detailed studies of the kinetics and mechanism of polymerization using these catalyst systems have grown remarkably in interest and importance.

The present investigations relate to the polymerization of styrene with:

(1) $VOCl_3$-$AlEt_3$ system in n-hexane at 40°
(2) $VOCl_3$-$Al(iBu)_3$ system in n-hexane at 40°
(3) $VOCl_3$-$Al(Et_2Br$ system innhexane at 30°
(4) $VOCl_3$-$Sn(C_3H_7)_4$ system in n-hexane at 40°
(5) $VOCl_3$-$Li(iC_5H_{11})$system in n-hexane at 40°

All the polymerizations and dispensing of catalyst solutions were done under an inert atmosphere of nitrogen maintained in a dry box fabricated for the purpose.

The dependence of polymerization rate, molecular weight, structure and stereo-regularity of polymers formed, on the following variables has been studied.

(1) order of addition of catalyst components and monomer, (2) aging of catalysts, (3) molar ratio of catalyst components, (4) time, (5) monomer concentration, (6) catalyst concentration, (7) solvent medium, and (8) added reagents like zinc-diethyl and ethyl bromide. Valence of vanadium in the catalytic complexes was determined potentiometrically to understand the nature of catalyst species. The results obtained are summarised below.

$VOCl_3$ reacts with various alkyls to give complexes which act as catalysts for styrene polymerization. The reaction is fast or slow depending upon the nature of metal alkyls. Whereas aluminium and lithium alkyls react with $VOCl_3$ instantaneously, reaction between the catalyst components being essentially complete in first ten minutes, the reaction of $VOCl_3$-$Sn(iC_3H_7)_4$ takes 90 minutes to complete under vigorous stirring. Ratio of catalyst components plays a big role in deciding the type of catalyst sites. In the case of $VOCl_3$-$AlEt_3$ system, the active catalyst sites producing polymer with highest molecular weight are obtained at ratio of $Al/_V$ of 2. The rate of polymerization also shows a sharp fall after ratio of $Al/_V$ of 1.5; showing thereby that Ziegler type catalyst species are formed only after 1.5 and it is complete at ratio 2. A similar fall in rate of polymerization is obtained in the case of $VOCl_3$-$Al(iBu)_3$, $VOCl_3$-$Li(C_5H_{11})$ and $VOCl_3$-$Sn(C_3H_7)_4$ systems, but in the case of $VOCl_3$-$AlEt_2Br$ system where these studies have been carried out at lower catalyst concentrations and lower temperatures as the rates of polymerization were very high, a peak of maxima is obtained at $Al/_V$ molar ratio of 1.5. A similar peak at molar ratio 1.5 is obtained in molecular weight vs.molar ratio plot also showing the maximum activity of Ziegler-Natta type sites. In case of $VOCl_3$-$Al(iBu)_3$ the molecular weights increase gradually as the molar ratio of $Al/_V$ increase. But in the case of $VOCl_3$-$Sn(nC_3H_7)_4$ and $VOCl_3$-$Li(iC_5H_{11})$ maximum molecular weights are observed at molar ratios 1.5 and 1 respectively. Thus the kinetics studies were carried out at molar ratio $Al/_V$ =2 for $VOCl_3$-$AlEt_3$,systems at molar ratio $Al/_V$=3 for $VOCl_3$-$Al(iBu)_3$ system, at molar ratio $Al/_V$=1.5 for $VOCl_3$-$AlEt_2Br$ system, at molar ratio $Sn/_V$=1.5 for $VOCl_3$-$Sn(nC_3H_7)_4$ system and at molar ratio Li/V =1.0 for $VOCl_3$-$Li(iC_5H_{11})$ system.

The polymerization was found to be first order with respect to catalyst and second order with respect to monomer in the case of $VOCl_3$-$AlEt_3$ and $VOCl_3$-$AlEt_2Br$ systems, second order with respect to catalyst and monomer concentrations in the case of $VOCl_3$-$Al(iBu)_3$ system, second order with respect to catalyst and first order with respect to monomer in case of $VOCl_3$-$Sn(nC_3H_7)_4$ system and first order with respect to catalyst as well as monomer concentrations in the case of $VOCl_3$-$Li(iC_5H_{11})$ systems. These orders of reaction have been discussed in the light of Rideal and Langmuir-Hinshelwood mechanisms.

Known amount of zinc-diethyl was added to the polymeric systems $VOCl_3$-$AlEt_3$, $VOCl_3$-$AlEt_2Br$ and $VOCl_3$-$Li(iC_5H_{11})$ and a reduction in molecular weights was observed. This helped to establish the participation of zinc-diethyl in chain termination by the transfer of ethyl group from zinc-diethyl to the growing polymeric chain.

Activation energy of overall polymerization reaction was determined to be between 5-180 Kcal/mole in all the cases. This served to point out the mechanism as coordinate anionic type in these systems.

Valence of vanadium in the catalytic complexes formed was studied in different systems and at various ratios. It was found that the valence of vanadium goes on decreasing with the increase in metal alkyl/$VOCl_3$ molar ratio in all the systems. It was also found that various metal alkyls can reduce the valence of vanadium to different extents which in turn affects the types of catalyst species formed.

Results have been examined on the basis of surface reactions after the initial reduction of transition metal compound to a lower valence state by the metal alkyl. The important steps are considered to be the adsorption of monomer and metal alkyl on the active catalyst sites followed by the propagation reaction and termination by (1) termination of growing macromolecule from the catalyst site and/or (2) chain transfer with metal alkyl especially when $ZnEt_2$ was present. The applicability of equations derived on the basis of a Langmuir Hinshelwood type mechanism has been tested and discussed. Also the reasons for observed lower molecular weights and low tacticity are discussed.

CHAPTER VI.

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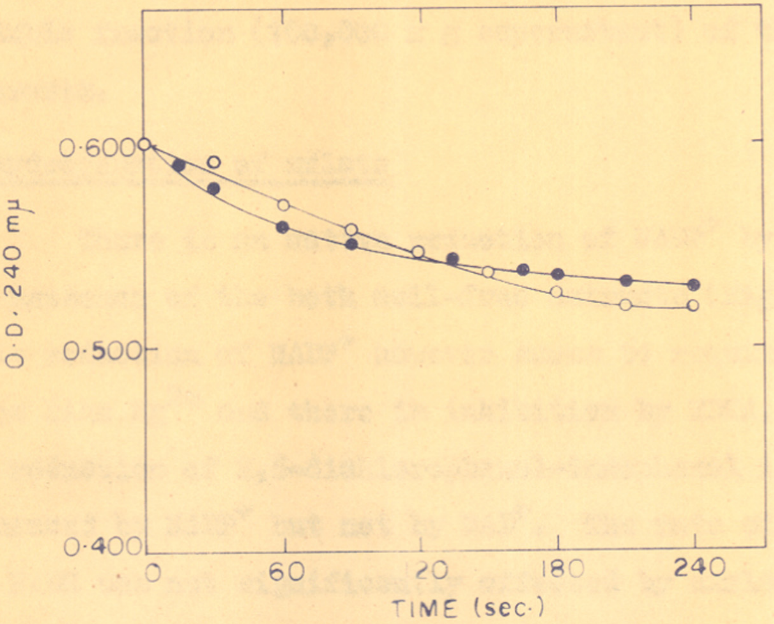

FIG. 30. FUMARASE

The test system contained 100 μ moles K-phosphate buffer (pH 7·4); 1·0 μ mole K-fumarate; 0·23 mg. protein of *P. trans A* extract and 0·18 mg. protein of *P. TCL* extract; water to a final volume of 3 ml

● = *P. trans A* extract
O = *P. TCL* extract

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