STUDIES IN POLYMERIZATION

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by

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CHAPTER-I

INTRODUCTION

INTRODUCTION

The technology of synthetic polymers has, in the last thirty years, undergone vast developments and mainly in the last ten years, progress in the field of new macromolecules such as high melting plastics, strong resistant fibres and synthetic rubbers with superior performance in recovery and tread wear, have been proved to be revolutionary and commendable. The credit goes to the recent discovery of truly stereospecific polymerization processes capable of leading, by polyaddition of monosubstituted ethylenic units to high yields of sterically regulated polymers. These new polymers with exceptional properties are available from certain low cost hydrocarbon monomers like ethylene propylene and butene. As a result, it has not only stimulated considerable scientific interest but has also opened up a new branch of macromolecular research which is bound to lead far reaching developments of great industrial importance. The most striking feature is that for the first time, perhaps, in the history of macromolecular chemistry, this scientific discovery has been followed rapidly by a vast amount of research in scientific and industrial laboratories all over the world.

This outstanding discovery is that of Ziegler-Natta catalyst which is an insoluble complex formed by the reaction of titanium tetrachloride with aluminium triethyl ($TiCl_4$+$AlEt_3$) in the medium of hydrocarbon solvent. The stereospecificity of polymer is defined as the placement of the substituents on the monomer molecule in a definite order in a polymeric chain. It has been observed that Ziegler-Natta catalyst has occupied a unique position among different catalyst systems which were used to polymerize polar and nonpolar monomers in order to obtain stereospecific polymers. Moreover, it has been emphatically pointed out from all these processes that the control of propagation step is very much necessary and can be obtained, generally, under the conditions such as 1) the effect of environment and temperature, 2) of soluble complexes of monomer with the counter ion, 3) of immobilising, complexing and orienting individual monomer.

In this context, it is worthwhile to study an application of Ziegler type catalysts for the polymerization of styrene and isoprene, which is the present subject of investigation. Since the subject is entirely new one, it is desirable to have some background of the topic. In this respect, an understanding of control of propagation step followed by a short account of different phenomena of polymerization will be considered primarily and then Ziegler-Natta catalyst will be described in detail with reference to its discovery, nature of stereoregulating forces, mechanisms and kinetic of polymerization, followed by an outline of the scope of present investigation.

It is a common knowledge that in the formation of macromolecules of vinyl type, essentially three[1] steps are involved. These are initiation, propagation and termination. For the production of useful polymeric materials, control[2] 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 many hundred and even thousand times in the course of the growth of a macromolecule.

Termination: Certain chemical reagents reacting with free radicals or ions of growing chains are capable of stopping the further growth of a macromolecule.

It is known that 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 aqueous or nonaqueous) at particular temperatures and in the presence of different monomers. Likewise, the control of average length of chains and with it of the molecular weight and of end groups could be obtained by the addition of certain chain transfer or cessation agents to the polymerizing system. The propagation process, on the other hand, has remained essentially uncontrolled. Any successful control of propagation reaction would help not only to speed up the polymer formation but also to produce macromolecules of great geometrical regularity and, as a consequence, of different mechanical and thermal behaviour.

Polymerization reactions which have been known for control of propagation step, have been considered further.

Polymerization reactionsconcerning with control of propagation step.

1) Temperature greatly influences the properties of polychloroprene and butadiene styrene copolymer[3] in emulsion polymerization. The high molecular weight cold rubbers[4] contain diene units in a larger proportion of 1,4-trans bonding. The systematic investigation of the differences in chain structure details, such as 1,4-trans, 1,4-cis and 1,2-addition of polybutadienes, polychloroprenes[4] and polyisoprenes[5] prepared with different types of catalysts free radical and ionic types reveals the existence of a certain influence of initiator and the environment on the propagation reaction itself.

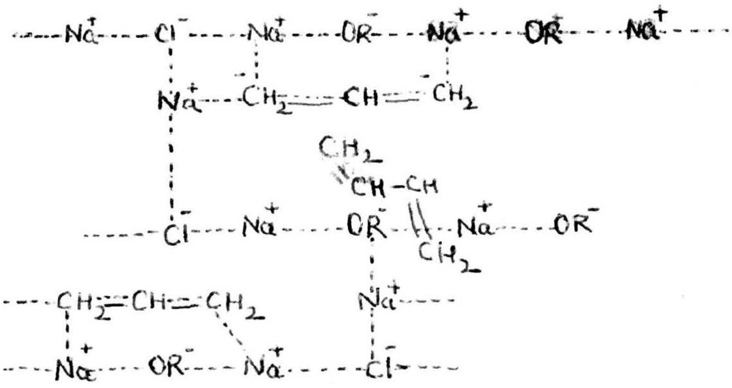
2) In fact, stereoregular polymers were obtained in 1948 by cationic polymerization of vinyl alkyl ether[6] but it was observed only after the discovery of Ziegler catalyst. Specifically, the vinyl butyl and vinyl isobutyl ethers yield polymers in bulk and solution, in an

amorphous and a crystalline form depending upon the initiator, the solvent and the temperature of polymerization. In case of this polymerization, concepts of configurational and conformational isomerism in linear macromolecules could be exposed to a certain energetic or steric control.

3) Free radical polymerization of vinyl and acrylic monomers at very low temperature in homogenous medium can even lead to stereoregular polymers. Polymethylmethacrylate prepared at -80°C by free radical polymerization contains syndiotactic structure.[20] Here, free chain ends can exert a regulating influence on the entry of the next monomer if the substituents are large and polar and if other conditions such as solvent and temperature favour sufficiently the prevalence of one stereotransition state over the other. Certain control of propagation could be counted in the so called get effect which, however, seems to be essentially the influence of the environment and particularly that of high viscosity on the ratio of the rate constants of propagation and termination.[7]

4) Morton and coworkers[8] found the control of propagation reaction during the studies of the action of certain complex catalysts on butadiene and isoprene. These catalysts which are known as Alfin catalysts, are prepared by the interaction of an alkali alcoholate such as sodium isopropoxide with an olefin halide such as

allyl chloride. The product of this combination - a slurry of NaCl on which $(CH_3)_2CHONa$ and $CH_2=CHCH_2Na$ are adsorbed - proved to polymerize butadiene not only at a surprisingly high rate, but also to a predominantly 1,4-trans species as shown in the diagram below, without any formation of gelatinous by-products. But it was difficult to understand the specific action of the catalytic system except by assuming an influence of the catalyst or the environment on each individual propagation step.

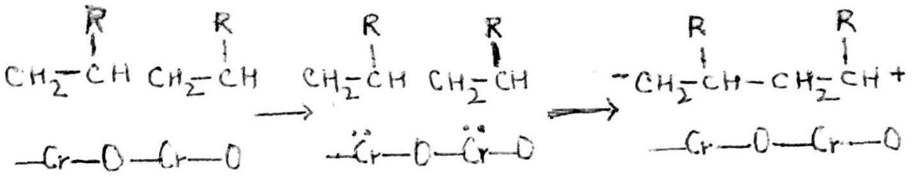


5) Addition polymerization can be greatly accelerated if the monomer molecules are arranged in a certain favourable pattern and hence held in a certain fixed position before they are chemically linked together to form a macromolecule. Szwarc[9] has established that p-xylelene and other related monomers do not polymerize in the gas phase but react rapidly and smoothly as soon as their vapour is condensed on a surface. At the same time

Letort[10] observed that polyacetaldehyde made under such conditions shows a regular steric arrangement of the methyl groups.

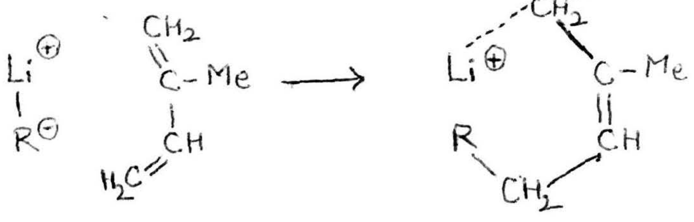
6) Prearrangement of the monomer molecules also works in 'Replica' polymerization. Melville and Watson[11] showed that predissolved polymethyl methacrylate in methyl methacrylate monomer induces a certain order in the individual monomer molecules by "adsorption" into a pattern which favourably affects the propagation reaction. Bamford and Ballard[12] have observed a strong influence of an already present polymer, namely 'polysarcosine dimethylamide' on the formation of synthetic polypeptide.

7) Solid surfaces can also be used to adsorb and consequently orient the monomer. Molybdenum oxide deposited on alumina and chromium oxide ~~and~~ on silica alumina which are known as Phillips catalysts,[13] can direct the polymerization of ethylene to linear high density polyethylene.



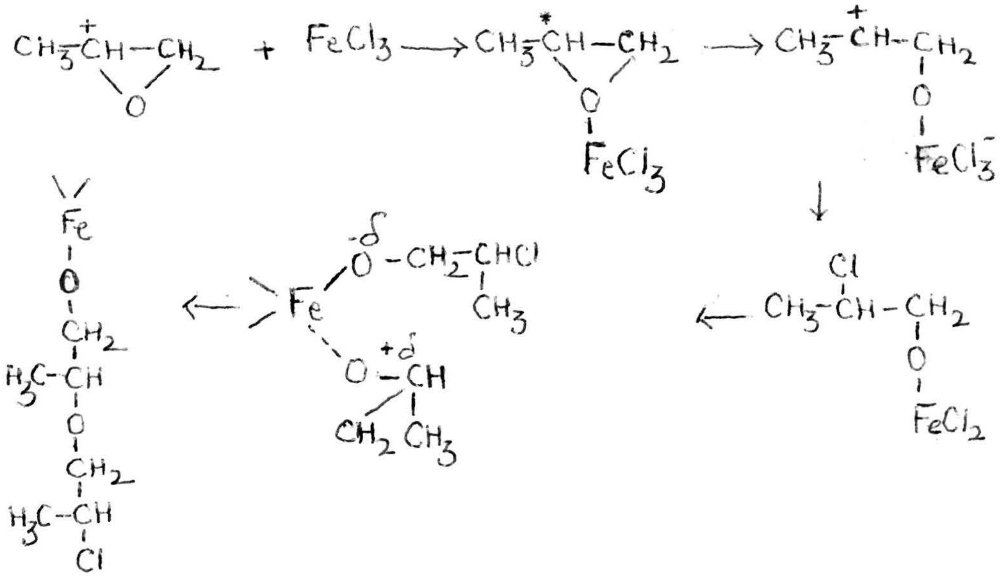
It can now be very well visualized that the control of propagation reactions discussed above is possible by immobilizing, complexing and orienting each individual monomer before it is introduced into the chain and chemically attached to its predecessor.

8) The control of propagation process is even possible by the effect of soluble complexes of monomers with the counter ions in ionic polymerization. The monomer molecule in the growing polymeric chain can be put in such a position that it will be chemically incorporated into the growing macromolecule under clearly restricted conditions. Lithium alkyls[14] and sodium alkyls[15] in hydrocarbon medium can polymerize dienes and styrene by exerting considerable degree of control on the propagation step. In these anionic polymerization systems, with the aid of complexing capacity of positive counter-ions, not only 1,4- addition polymerization of diene can be obtained but steric regularity of the substituents in vinyl polymerization can also be controlled. According to this, stereoregulated acrylate ester[16] and acrylamide[17] polymers as well as polyvinyl halides[18] have been obtained with anionic initiator in homogenous system.



At the same time, it was reported that under appropriate conditions of solvents and temperature cationic initiators employed by Schlidknecht for polymerization of vinyl ethers can stereopolymerize styrene derivatives[19] in the homogenous system. In all these cases, it appears that complexing of the monomer with the counterion before its introduction into the growing polymeric chain is the requirement for effective steric control, and that the average life time of these complexes has to be commensurate with the time interval between two subsequent propagation steps of the growing macromolecule.

9) C.C.Price[21] indicated the use of optically active monomer like propylene oxide in ionic polymerization to visualize the possibility of control of propagation reaction. Optical behaviour of the polymer can be used to establish directly whether the propagation steps have maintained or destroyed stereospecificity.



10) The most important and the last one is the action of the metal organic mixed catalysts which is far

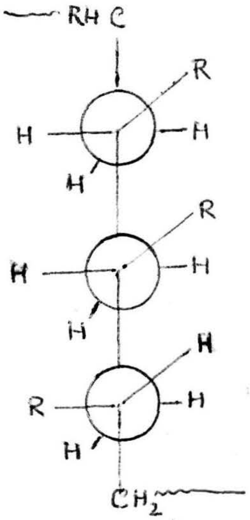
impressive and spectacular in controlling propagation reaction. These catalysts, discovered by Ziegler[22] immediately proved to have a highly regulative influence on the polymerization of ethylene. Nonpolar, and highly volatile monomers as ethylene, propylene or butylene require a very strong complexing capacity which can be contributed by an active centre which is adsorbed on a solid surface. This requirement is fulfilled by the application of Ziegler catalyst. Their capacity to exert an amazing steric control on the propagation step was soon afterwards established by G. Natta[23] in a series of brilliant investigations on the structure of olefin polymers prepared with Ziegler catalysts and certain modifications thereof. Stereoregular polymerization with Ziegler type catalyst has been reviewed widely in the literature by many workers.[2, 24-27]. It would be appropriate and essential to introduce it here in brief.

Ziegler-Natta Catalyst

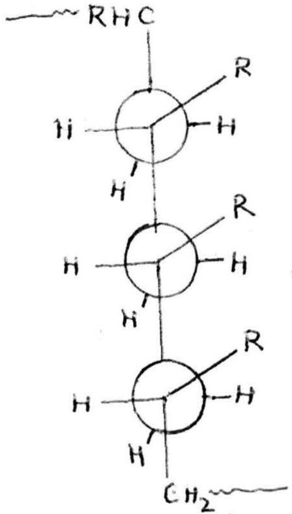
Discoveries by Professor Ziegler[22] showed for the first time that ethylene can be polymerized to high molecular weight, linear polymers at temperature and pressures very much lower than those used in the conventional high pressure process. This catalyst of low pressure polymerization is the combination of titanium tetrachloride or trichloride with aluminium triethyl which is now widely known as Ziegler-Natta catalyst. Ziegler type catalysts consist of transition metal halides from groups IV to VI and organometallics from groups I to III from the periodic table. Professor Natta[23] then observed that by applying this type of catalyst, particularly the titanium trichloride and aluminium triethyl combination to olefins such as propylene, two fractions of the polymer could be obtained. Out of them one fraction would be soft, soluble and rubbery and the other one dense, hard and of high softening point. Crystallographic examination showed that the latter fraction contains monomer units arranged in a particular well ordered pattern. According to the way in which monomer molecules are arranged in relation to their neighbours, various basic states of tacticity are possible, which Prof. G. Natta[28] called isotactic, syndiotactic and atactic.

Stereoisomerism and its effects on properties of polymers

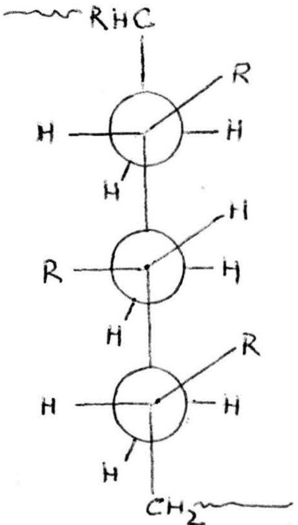
The simplified image of an isotactic polymer is one where there are long sequences in the polymer chain in which the asymmetric carbon atoms have identical configurations. In the syndiotactic arrangement, the asymmetric carbon atoms have regularly alternating configurations, whereas in the atactic structure the substituted groups are arranged around the polymer axis unsystematically and at random. The same definitions can be extended to disubstituted olefins[29] and they are distinguished as erythreodiisotactic like isotactic and threodiisotactic like syndiotactic. These polymeric structure can be illustrated in the Newman[30] projection.



Atactic



Isotactic



Syndiotactic

These chains of isotactic and syndiotactic polymers will have a tendency to form a crystalline lattice, that is stereochemistry of polymers. The stereochemical effects on the properties of polymers are quite considerable as given below where the properties of conventional polymers are compared with the Ziegler polymers.

Polyethylene[30]

	Conventional	Ziegler.
Density	0.92	0.95
Melt. Index	2.0	0.5
Softening point	110° C	135° C
Tensile strength	2190	2960

Polypropylene[31]

	Conventional	Ziegler
Specific gravity	0.803	0.909
Softening point (°C)	Below 25	146
Tensile strength	508	5400

The polymers obtained thus, generally, should have such a degree of crystallinity and isotacticity which may give efficient strength and rigidity without undue brittleness.

The Ziegler Natta catalysis, with its possibility of structure control, has also been applied to olefins higher than propylene, and it has been noticed that with increasing atom density in close proximity to the chain, there is an appreciable increase in second order transition point (Tg) as well as in the crystalline melting point (Tm). In this connection, Isotactic polystyrene[32] obtained by stereodirective catalysts can have melting point of the order of 240°C which provides a much higher service temperature than what one could get from ordinary polystyrene.

Crystallinity is some what important for rubbers also because otherwise the tensile properties of an unvulcanized rubber in the stretched state would be uselessly low. Ziegler type catalysts with certain modifications have a considerable structure controlling effect during polymerization. A diene of the type $\underset{1}{C} = \underset{2}{C} - \underset{3}{C} = \underset{4}{C}$ can polymerize by 1,2-addition, 3,4-addition or 1,4-addition, and as such monomers exist in an isomeric equilibrium between cis and trans polymers. Organometallic catalysts[33] produce 1,4-addition polymers by supressing 1,2-addition and this 1,4-addition leads to entirely the cis-polymer with little or no trans polymer or viceversa cis 1,4-addition polyisoprene is structurally identical to natural rubber.

Nature of Stereoregulating Forces in Ziegler Catalyst Polymerization

Different stereoregulating forces are considered for control of propagation reaction. In case of free radical polymerization, low temperature is shown effective for producing syndiatactic polymer.[34]

The stereospecific polypropylene can be prepared by Ziegler-Natta catalyst (titanium trichloride and aluminium triethyl) at any temperature. Considerable stereospecificity was observed even when the experiments were conducted above 120°C.[35] The steric consequences of polymer solvent interaction have been postulated by Szwarc[36] and Ham.[37] Both emphasized the tendency by macromolecules to form a regular helix in the crystalline state or in the solvents of very low solvating power. Alkanes invariably give a greater yield of crystalline polymers in almost any kind of polymerization. Very often, use of a poor solvent for the growing polymer necessarily ensures that the system containing the catalyst or growing end of the chain becomes heterogenous. Heterogenous catalyst systems are undoubtedly the most effective means of stereoregulating a propagation step. It is recently explained that if the polymer remains soluble in the reaction medium, stereoregularity remains undisturbed,[35] but the catalyst species must be in an undissolved state in the polymeric system, otherwise the stereospecificity would be affected. Dicyclopentadienyl titanium dichloride/aluminium diethylchloride, the soluble catalyst system,[38] can produce linear and high molecular weight polyethylene but can not polymerize propylene monomer. Crystal size and type of the reduced transition metal halide, and reducing agents[23] play important role in controlling the rate, molecular weight and stereochemistry of the polymerization.[39] It has been actually shown that heterogenous catalyst can actually change its particle size during the polymerization.

Preparation of Ziegler-Natta Catalyst

Ziegler catalyst[22] was first prepared by adding a solution of aluminium triethyl to a solution of titanium tetrachloride in hydrocarbon solvents such as heptane or hexane. The product of this reaction is a brown black insoluble compound which is essentially a reduced halide of titanium e.g. $TiCl_3$, $TiCl_2$ and this precipitate together with its supernatant liquid is essential for catalytic activity. Natta has proposed that the active Ziegler type polymerization catalyst is a complex containing organometallic bonds and more than one metal atom. It has been shown that the most active and stereospecific catalysts[40] for polymerization of α-olefins are formed by the reaction between an alkyl of a highly electropositive metal having a small diameter e.g. beryllium, aluminium, or lithium and a crystalline

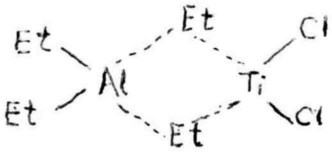
Metal	Electro-negativity	Atom radius	Ionic radius
Beryllium	1.5	0.90	0.35
Aluminium	1.5	1.26	0.51
Lithium	1.0	1.33	0.68
Zinc	1.5	1.31	0.74

halide of a transition metal from groups IV-VI from the periodic table in which the metal is in a valency state less than the maximum, e.g. titanium trichloride or dichloride or Vanadium dichloride. When the catalyst is prepared from the unreduced transition metal halides the reduction might proceed through a series of states[41] for example reaction between triethyl aluminium and titanium tetrachloride can be considered as follows:

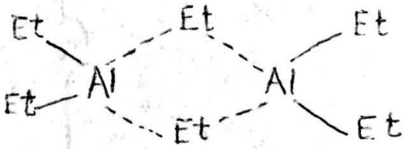
$$\begin{aligned}
\mathrm{AlEt_3 + TiCl_4} &\longrightarrow \mathrm{AlEt_2Cl + EtTiCl_3}\\
\mathrm{EtTiCl_3} &\longrightarrow \mathrm{TiCl_3 + Et^{\cdot}}\\
\mathrm{EtTiCl_3 + AlEt_3} &\longrightarrow \mathrm{Et_2TiCl_2 + Et_2AlCl}\\
\mathrm{Et_2TiCl_2} &\longrightarrow \mathrm{EtTiCl_2 + Et^{\cdot}}\\
\mathrm{TiCl_3 + AlEt_3} &\longrightarrow \mathrm{EtTiCl_2 + Et_2AlCl}\\
\mathrm{EtTiCl_2} &\longrightarrow \mathrm{TiCl_2 + Et^{\cdot}}
\end{aligned}$$

Recently unstable compounds like trichloroethyl titanium, $\mathrm{EtTiCl_3}$,[41] have been isolated from reactions similar to that described above.

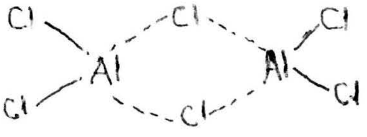
Bridge complexes such as (1) which is formally analogous to the well established bridge dimers of aluminium triethyl[44] (2) and aluminium halides[42] (3) have been proposed as effective Ziegler catalysts formed by reaction of unused trialkyl aluminium and either titanium trichloride or dichloride.



(1)



(2)



(3)

Thus, Ziegler type catalysts could mainly be used to prepare linear and in many cases, stereoregular[45] polymers of high molecular weight from almost all olefinic hydrocarbons with a basic structure $CH_2 = CHR$ and dines as well.[45]

Mechanism of Polymerization with Ziegler type catalyst

Until about 1953, the mechanism for addition polymerization could be classified in three main groups conventionally referred to as cationic, anionic and free radical polymerization.[1] Since then Ziegler type polymerization is known, this may be termed as co-ordinate polymerization. This type of polymerization allows maximum control of the propagation reaction and cannot readily be defined as anionic or cationic in the conventional sense.

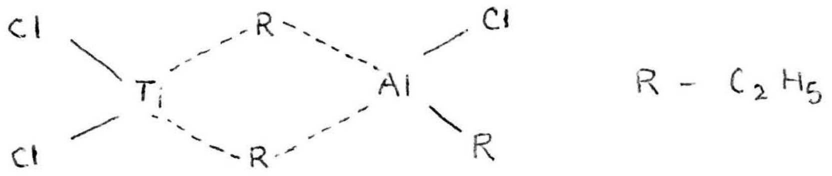
Polymerization reaction studied by Ziegler type catalysts are shown entirely consistent with a surface controlled, heterogenous reaction. Several kinetic studies have been made with this type of catalyst systems but the studies of polymerization of propylene carried out in the presence of triethyl aluminium and the crystalline form of titanium trichloride[39] have been used as the basis of all the studies of kinetics and mechanism of polymerization with Ziegler type catalyst systems. G. Natta has carried out much of the work on this catalyst system, reviewed in the following pages.

Mechanism of Polymerization proposed by Natta

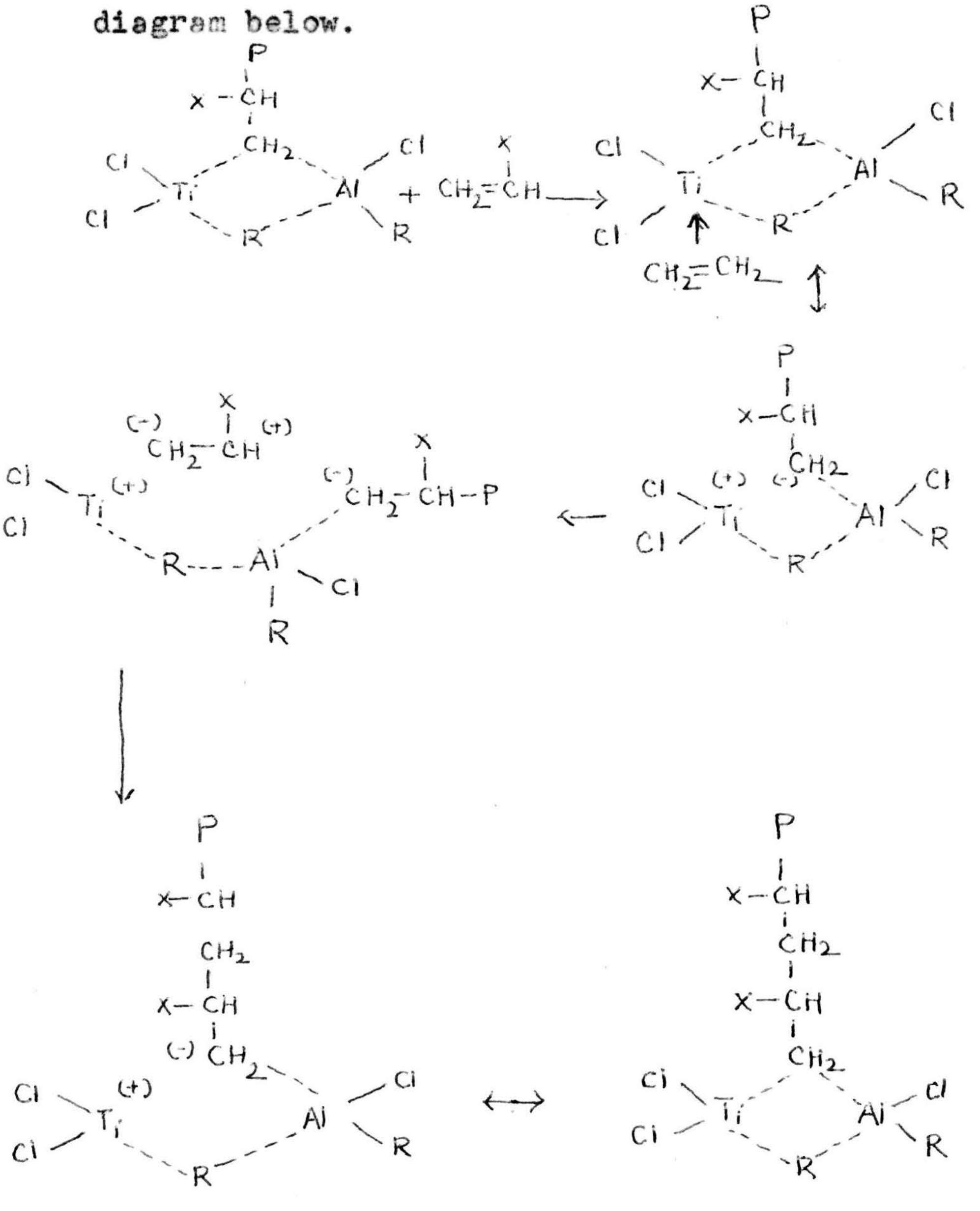
The titanium trichloride crystals were reduced by grinding until the average particle size was less than 2μ Heptane was used as solvent and the polymerization temperature was varied from 31° to 70°C. The rate of polymerization was proportional to the amount of solid catalyst ($TiCl_3$) , independent of the concentration of triethylaluminium, independent of the atomic ratio Al : Ti and proportional to the partial pressure of the olefin. The activation energy measured by means of the reaction rate was 11500 ± 500 cal/mole, and the most important chain termination process at temperatures below 80°C and pressures slightly above atmospheric pressure was a process that of first order with respect to monomer and was most likely to be a chain transfer with the monomer. It has been concluded that the kinetics of polymerization of propylene leading to atactic and isotactic polymers were essentially the same.

In full accord with the kinetic data obtained, Natta[18,38,46] suggested the mechanisms of reaction and he firmly believes that in the complexes containing titanium and aluminium, the polymeric chain grows from the aluminium-carbon bond and not from the titanium carbon bond. The detailed mechanism proposed is that the initially incomplete coordination of titanium in the reduced state of di and trichloride facilitates chemisorption of organometallic compounds of strongly electropositive metals having small ionic radius. This chemisorption leads to the formation of electron deficient complexes between titanium and the other metal which contains alkyl bridges similar to those present in the dimeric aluminium and beryllium alkyls.[44] This theory of bimetallic electron deficient complexes is supported[38] by the isolation of soluble crystalline complex of the general formula $(C_5H_5)_2TiCl_2AlRR$ containing Ti-carbon-Al bridges from the reaction of dicyclopentadienyl titanium dichloride and aluminium alkyls. Natta supported his mechanism with the help of certain evidences as described below. In the polymerization of ethylene Natta has used dicyclopentadienyl titanium dichloride and triphenyl aluminium[38] as a catalyst system and detected the presence of phenyl groups in the polymer. Phenyl groups cannot be detected in the polymer if biscyclopentadienyl diphenyl titanium is used in place of biscyclopentadiene titanium dichloride and $AlEt_3$ in place of $Al(phenyl)_3$. This detection of phenyl groups in the polymer was taken by Natta as a conclusive proof of the growth of polymeric chain at aluminium carbon bond. Additional evidence for convincing about the same mechanism was given by the use of Triethyl aluminium containing ^{14}C-labelled ethyl groups as one constituent of catalyst for the polymerization of ethylene. ^{14}C labelled ethyl groups are adsorbed into the surface of titanium trichloride and when this whole system was used as a polymerization catalyst in the presence of non-labelled triethyl aluminium, then the resulting polymer contains as terminal end groups practically all of the labelled alkyl groups[47] and chemical analysis of the resulting polymers showed the presence of aluminium.[48]

Now the Natta's mechanism can be formulated as given below. It may be assumed that the partial ionic dissociation of active complex containing organometallic bonds and more than one metal atom takes place as shown below.



A first step, then, will be an association of the monomer with the transition metal, caused by the high electronic density of the double bond and by the electron deficiency of the transition metal and thus the monomer is incorporated in the growing chain as visualized in the diagram below.



wherein, the complex bond of the Al ion shifts from the carbanion which is a part of the polymer chain to carbanion of the newly complexed monomer, along with the establishment of a normal σ bond between the negatively charged carbon on the chain and the positively charged carbon of the monomer.

Natta's mechanism provides a very satisfactory explanation for the experimental observation that the rate of certain transfer processes and the 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. This step should be followed by a polarisation of double bond of monomeric unit. The driving force of propagation is, of course, the primary coordination of olefinic π -electron with vacant orbitals in the metal. Only Patat and Sinn[49] have proposed a mechanism supporting Natta's view.

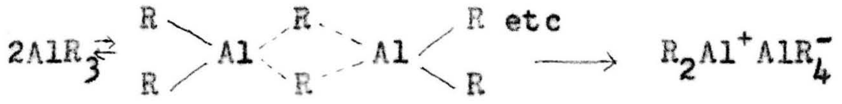
Mechanism proposed by others

Many workers, however differ from Natta's view, believing that chain growth may occur at the titanium-carbon bond.

Recently, Carrick and Karpinka[50] have reinvestigated the use of biscyclo-pentadienyl titanium diphenyl and triethyl aluminium as catalyst for polymerization of ethylene and although they confirmed Natta's findings that no phenyl groups are incorporated into the polymer, they concluded that this does not constitute any real evidence for growth on aluminium rather than on titanium. It is shown that in the reaction of biscyclopentadienyl-diphenyl titanium with alkyl aluminium derivatives, there is an immediate exchange of alkyl and aryl groups between aluminium and titanium and chain growth occurs more readily at alkyl substituted metal atoms than at phenyl substituted sites.

Ziegler has strongly objected Natta's mechanism on the grounds that by analogy with dimeric aluminium alkyls, electron deficient complexes containing titanium and aluminium are not likely to be involved in the actual "growth" reaction even though such complexes may occur in the polymerizing systems. Since dimeric aluminium alkyls are no longer electrophillic, they are unreactive in the Aufbau reaction (that is chain extension) of alkyl aluminium compounds.[51] Aufbau reaction is as given below:

Dimeric aluminium alkyls



Aufbau reaction

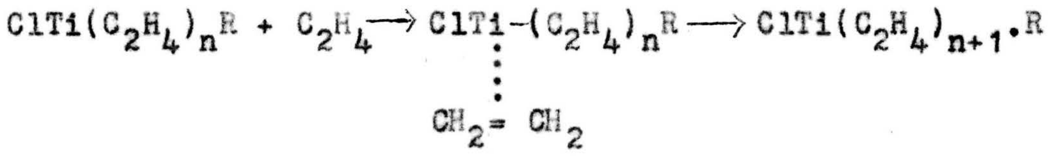
$$R_3Al + CH_2{=}CH_2 \longrightarrow R_2AlCH_2CH_2R$$

$$R_2AlCH_2CH_2R + CH_2{=}CH_2 \longrightarrow R_2Al(CH_2CH_2)_{n+1}R$$

$$R_2Al\ (CH_2CH_2)_{n+1}.R + mCH_2{=}CH_2 \longrightarrow R.(CH_2CH_2)_{n+1}AlR(CH_2CH_2)_m.R$$

Ziegler[51] has further stated that alkyl exchange can occur readily in the complex of titanium halide and aluminium alkyl, but the actual reaction could take place only at the monomeric titanium alkyl.

This mechanism of growth of polymeric chain at titanium carbon bond is further supported by some more workers. They suggest the initiation of polymerization of ethylene monomer by coordination of ethylene molecule with a bivalent titanium and bivalent vanadium alkyl compounds[52,53] as shown in the following equation.

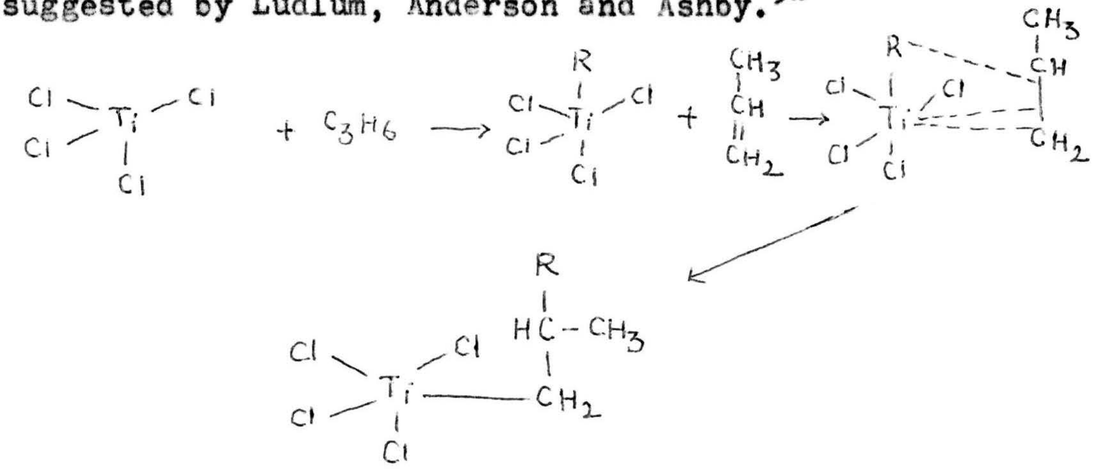


$$ClTi(C_2H_4)_nR + C_2H_4 \rightarrow \underset{\begin{array}{c}\vdots\\ CH_2=CH_2\end{array}}{ClTi}-(C_2H_4)_nR \rightarrow ClTi(C_2H_4)_{n+1}.R$$

It is well illustrated by the work of Carrick[53] who showed that the relative reactivity ratio of two monomers namely ethylene and propylene in copolymerization changed when different transition metal compounds were used but was not affected by the use of different reducing agents with a common transition metal compound which could be the principal active species in Ziegler type catalyst systems. The idea that an alkylated reduced halide of titanium (or any other transition metal) is the active catalyst has received much support of late and is further borne out by recent findings that alkyl titanium halides like $RTiCl_3$ can themselves act as catalyst for polymerization of ethylene.[42]

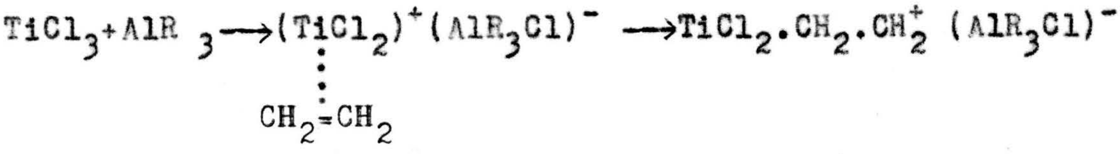
Also active catalyst can be formed by ultraviolet irradiation[54] or electron bombardment of reduced titanium halides[55] in the presence of ethylene.

All these ideas about growth of chain at titanium carbon bond are incorporated in the comprehensive mechanism proposed by Cossee.[56] Cossee assumed that polymerization occurs at one titanium ion in the surface layer of a titanium trichloride (or presumably dichloride) lattice of which one surface chlorine atom is replaced by an alkyl group R, while an adjacent chlorine site is vacant in order to accommodate the incoming monomer molecule. Polymerization then proceeds in a manner similar to that suggested by Ludlum, Anderson and Ashby.[52]



After this step the active centre retains a titanium alkyl bond and a vacant site which, however, has changed places. During the polymerization the aluminium alkyl is thought to act as a chain transfer agent in re-establishing lost centres and as a scavenger for adventitious impurities, but it is not essential for the propagation. This mechanism has considerable merit and provides an adequate explanation for several experimental observations.

Uelzmann[57] and Bier[58] have insisted independently on the mechanism involving the formation of an ion pair structure in the catalyst complex where the initiation of polymerization may be at the titanium ion and the propagation reaction at the aluminium ion as shown in the diagram.



$$TiCl_3 + AlR_3 \longrightarrow \underset{\overset{\vdots}{CH_2=CH_2}}{(TiCl_2)^+}(AlR_3Cl)^- \longrightarrow TiCl_2.CH_2.CH_2^+\ (AlR_3Cl)^-$$

$$TiCl_2.CH_2.CH_2R + AlR_2Cl \longrightarrow (TiCl_2)^+(AlR_2Cl.CH_2.CH_2.R)^- \text{ etc.}$$

Bawn[27] has suggested that this mechanism may serve as a basis for the rationalisation of most of other mechanisms.

Dicyclopentadienyltitanium dichloride and derivatives of aluminium alkyls[59] form a homogenous system of catalyst in the hydrocarbon medium. In this system tetravalent titanium compounds like $(C_5H_5)_2TiEtCl.EtAlCl_2$ were found active for polymerization and if the oxygen[60] is introduced in this system of polymerization, all the complex compounds in the trivalent state of titanium are converted to tetravalent state and the activity of the catalyst system for polymerization increased.

Isolation of crystalline compounds (C_5H_5) $TiEtCl.EtAlCl_2$ is also possible and this compound being tetravalent and active for polymerization, it is being suggested[69] that it can also form the ion pair structure of Uelzmann mechanism. These complexes proved effective for the polymerization of ethylene only.

These discussions clearly show that mechanism of polymerization with Ziegler type catalyst system is the most complicated one. So the study of kinetics of polymerization with these catalyst system is necessary. These studies would certainly help to reveal something more of the mechanism of polymerization.

Kinetics of Polymerization

Kinetic studies of polymerization with Ziegler type catalyst are required to be carried out by taking into consideration the following factors.

1) The dependence of polymerization rate on monomer concentration, 2) The dependence of rate on organo metallic compound and transition metal halide concentrations, 3) the dependence of rate on catalyst ratio, 4) the factors upon which the molecular weight is dependent, 5) the effect of temperature on molecular weight, 6) the effect of temperature on polymerization rate.

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

Earlier Mark and Gaylord[2] have presented equations which related polymerization rate as a function of strength of monomer adsorption, nature of the catalyst complex, etc. but there was no explanation for the maxima obtained for various systems when polymerization rate is plotted against catalyst ratio.

Saltman and Coworkers[61] also developed theoretical relationship based on the polymerization of isoprene with Ziegler catalyst, but the scheme was not elaborated. Recently Saltman[62] proposed a more detailed scheme for the system, propylene-TiCl-$AlEt_3$ which could explain experimental results obtained by Natta.[63,64] Friedlander and coworkers[65] have also presented a kinetic scheme in order to explain the polymerization of ethylene by means of molybdena - alumina catalyst in the presence of hydrogen. This scheme does not deal directly with Ziegler catalyst and is limited. Very recently, L. Reich and S.S.Stivala[66] have given quite general kinetic scheme for Ziegler type polymerization. This scheme appears to be most comprehensive and covers up the most polymerization reactions done with Ziegler type catalyst. Even, the soluble catalyst system of polymerization of ethylene like orthobutyltitanate and aluminium alkyl[67] which is not analogous to conventional Ziegler type catalyst system could be explained with the help of this kinetic scheme. With a view to follow the reaction kinetics of polymerization of Ziegler type catalysts, we will briefly review the general kinetic scheme reported by Leich and Stivala[66] only.

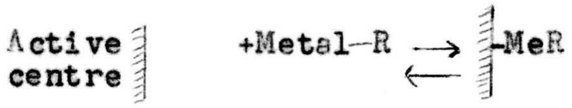
Kinetics of polymerization includes equilibrium processes and initiation, propagation, transfer and termination processes.

The basic assumption in the general scheme is that Ziegler type polymerization all involve a similar basic mechanism. However, depending upon the system, some steps will probably predominate over the others. It is also assumed that catalyst ratio can play an important role in changing the catalyst surface. However, reactions occurring on the surface are postulated as playing the predominant role in determining the shape of the curves obtained in kinetic studies, provided there are no large surface alternations as the catalyst ratio is markedly changed e.g. the system[61] isoprene $TiCl_4$-$Al(iBu)_3$.

A general kinetic scheme

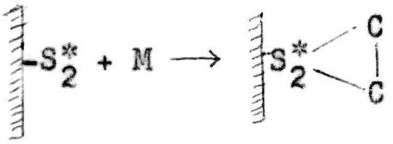
Equilibrium processes have been presented for the adsorption of monomer and metal alkyl in a Ziegler catalyst surface. Both alkyl and monomer are adsorbed on the surface and compete for available sites.

Equilibria:



MeR - Metalalkyl.

Active centres are formed by the reduced titanium halide and the metalalkyl.

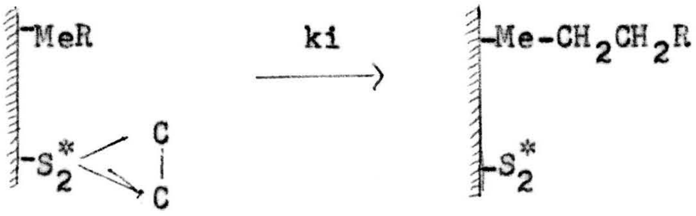


M - Monomer - ethylene

The monomer has been postulated as being adsorbed on an active dual site, S_2^*,[65] which can orient the monomer in a unique position.

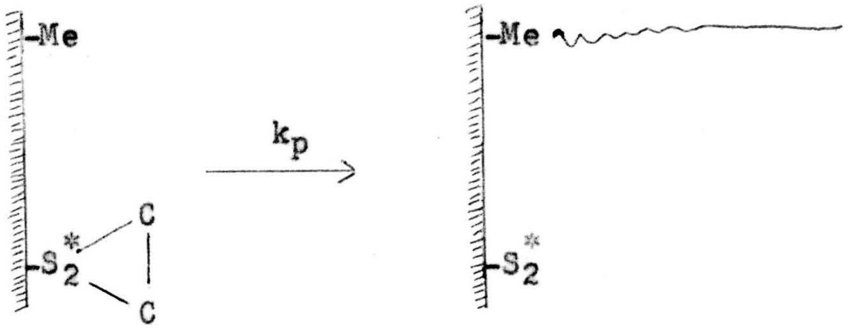
The monomer being hydrocarbon and hence non-polar in nature, is less strongly adsorbed than the polar metal alkyl.

Initiation:



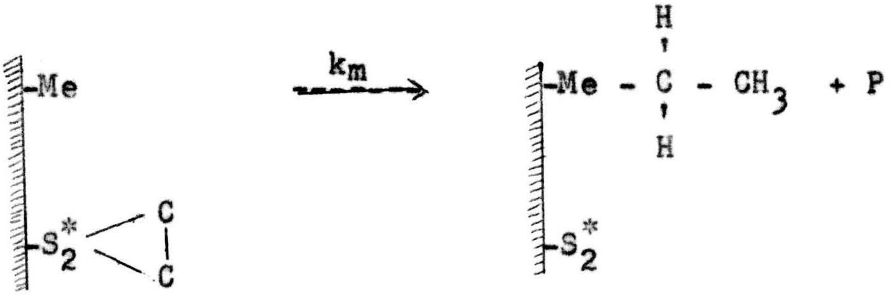
The initiation is postulated as occurring between adsorbed alkyl and a neighbouring adsorbed or unadsorbed monomer.

Propagation



Natta[63] has postulated that adsorbed monomer is inserted between the metal and alkyl portions of the aluminium-alkyl and in this insertion hypothesis, two bonds are broken and two are formed but Huggins[68] recently postulated that during the propagation process, every step is accompanied by the breaking of one bond and the formation of the other. The growing chain shifts its position along the edge of a $TiCl_x$ sheet molecule with each addition of monomer.

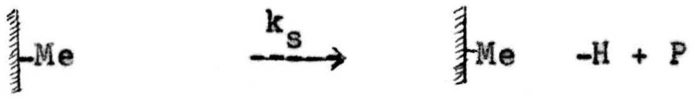
Monomer transfer



P - polymeric molecule

Termination may occur by monomer transfer.

Spontaneous transfer



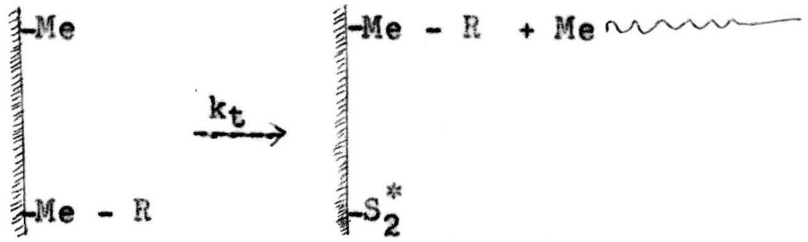
In this case termination may occur by spontaneous disproportionation.

In both the cases a hydride ion is considered to be involved.

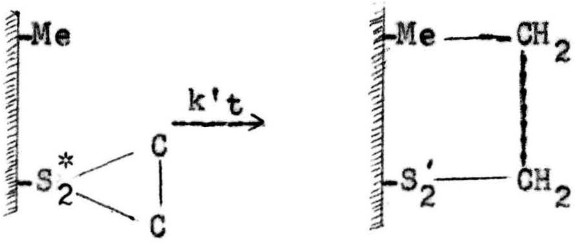
Transfer by means of catalyst has also been postulated viz.

$$TiCl_x-AlY_2P + AlR_3 \longrightarrow TiCl_x—AlR_3 + AlY_2P$$

Catalyst transfer



In the general scheme, Reich and Stivala proposed another type of termination by the monomer which involves termination by monomers:



S_2' - is no longer active.

The deactivation of dual active site S_2^* would result in this termination.

On the other hand, Saltman[61] proposed a termination step which involved a site having only termination activity. Termination could result from interaction between this site and aluminium alkyl or a growing polymer chain containing the aluminium alkyl or a growing polymer chain containing the aluminium alkyl moiety. A desorption step was also postulated which resulted in a dormant long chain organometallic (cf. Spontaneous transfer reaction).

Interaction between adsorbed molecules:

If we assume high stirring speeds are used (where polymerization rate is not diffusion controlled) the monomer is ethylene and solvent becomes rapidly saturated.

We may write for the concentration of ethylene in solution $[C_2H_4]_s$, assuming Henry's law applies,

$$[C_2H_4]_s = K_s [C_2H_4]_g \quad . \quad . \quad . \quad . \quad . \quad (1)$$

K_s - Equilibrium contant at saturation and $[C_2H_4]g$ is the partial pressure of ethylene in gas phase.

The concentration of adsorbed monomer will be

$$[C_2H_4]_a = K\,[C_2H_4]_g \cdot [C]_s \quad . \quad . \quad . \quad . \quad . \quad (1a)$$

C_s - concenttration of bare surface sites.

Similarly for the adsorption of alkyl in solution (AlR_3 - $AlR_2\,X$, etc.) we may write:

$$[AlK]_a = K'[AlK]_s C_s \quad . \quad . \quad . \quad . \quad . \quad (2)$$

$$[C_2H_4]_a + [AlK]_a + C_s = L \quad . \quad . \quad . \quad (3)$$

where L is the concentration of active surface sites when the surface is completely bare. From equations (1), (2) and (3) we obtain

$$[C_2H_4]_a = \frac{KL[C_2H_4]_s}{1 + K[C_2H_4]_s + K'[AlK]_s} \quad . \quad . \quad (4)$$

and

$$[AlK]_a = \frac{K'L[AlK]_s}{1 + K[C_2H_4]_s + K'[AlK]_s} \quad . \quad . \quad (5)$$

From equations (4) and (5), the expressions for the fraction of the surface covered by the monomer and the alkylane are respectively

$$[C_2H_4]'_a = [C_2H_4]_a/L = \frac{K[C_2H_4]_s}{1 + K[C_2H_4]_s + K'[AlK]_s} \quad \ldots (4a)$$

$$[AlK]'_a = [AlK]_a/L = \frac{K'[AlK]_s}{1 + K[C_2H_4]_s + K'[AlK]_s} \quad \ldots (5a)$$

The average of number of adsorbed alkyls adjacent to any given adsorbed monomer is equal to $S\theta'$, where S is the maximum number of possible near neighbours and $\theta' = (AlK)_a/L$. Then the total number of adsorbed alkyl monomer pairs becomes:

$$\frac{SLKK'[C_2H_4]_s[AlK]_s}{(1 + K[C_2H_4]_s + K'[AlK]_s)^2}$$

Thus it is seen from the above that if the surface remains uniform during the reaction (S — constant), a constant reactions temperature is maintained, and if it is assumed that partition functions and activation energies remain constnt, then the reaction rate may be expressed in terms of adsorbed monomer and alkyl.

From the proposed scheme, we may write (neglecting initiation step) for the rate of monomer consumption per unit of active surface sites.

$$-dM/dt = \left(k_p + k_m\right) \left[C_2H_4\right]'_s \sum_n \left[\text{Polymer}\right]_a \; ..... \; (6)$$

k_p - rate constant for propagation.

k_m - rate constant for termination.

and assuming steady state considerations:

$$\left[\text{Polymer}\right]_s = \frac{k_i \left[AlK\right]'_a \left[C_2H_4\right]'_a}{k_s + k_t \left[AlK\right]'_a + k'_t \left[C_2H_4\right]'_a} \; ..... \; (7)$$

k_i - rate constant for initiation.

From equations (4a), (5a), (6) and (7) we obtain

$$-dM/dt = \frac{\left(k_p+k_m\right)k_i \left[AlK\right]_s K' K^2 \left[C_2H_4\right]_s^2}{\left(1+K\left[C_2H_4\right]_s+K'\left[AlK\right]_s\right)^3 \left\{k_t+\dfrac{k_t K'\left[AlK\right]_s+Kk'_t\left[C_2H_4\right]_s}{1+K\left[C_2H_4\right]_s+K'\left[AlK\right]_s}\right\}} . (8)$$

Equation (8) can be reduced to any number of simple forms, depending upon which processes in the scheme predominate. Thus if termination occurs essentially by means of monomer, and adsorbed monomer reacts with adsorbed alkyl on the surface, e.g. (8) becomes:

$$-dM/dt = \frac{k_i(k_p+k_m)KK_1'\left[AlK\right]_s\left[C_2H_4\right]_s}{\left(1 + K\left[C_2H_4\right]_s + K'\left[AlK\right]_s\right)^2} \quad .....(9)$$

For the case where the concentration of active dual surface sites varies again (9) becomes:

$$\text{Rate} = \frac{B\left[AlK\right]_s\left[C_2H_4\right]_s}{\left(1 + K\left[C_2H_4\right]_s + K'\left[AlK\right]_s\right)^2} f(Ti) \quad ....(10)$$

where $B = k_i(k_p+k_m)$, KK_1' = constant and f(Ti) is a function of active dual sites formed and denotes the titanium halide concentration introduced into the system.[68]

By an approach similar to the one above, nearly ten different expressions may be obtained depending upon the mechanism, predominant termination step and the type of surface reaction. These can be appropriately used to calculate rate data of different Ziegler type systems.

Relation of the catalyst ratio with the active surface can be explained by the use of rate expression (8).

Some molecular weight expression can also be derived from this scheme. For example, in case of termination by monomer and monomer transfer:

$$\bar{P} = \frac{k_p\left[M\right]_a \sum_n\left[\text{Polymer}\right]_a}{\left(k_m + k_t'\right)\left[M\right]_a \sum_n\left[\text{Polymer}\right]_a} \quad ....(11)$$

$$= k_p/\left(k_m + k_t'\right)$$

k_m - constant for monomer transfer

k_t' - constant for termination by monomer

If it is assumed that termination occurs by catalyst and monomer

then

$$\frac{1}{\bar{P}} = \left(k_m/k_p\right) + \left(k_t\left[\mathrm{AlK}\right]/k_p\left[\mathrm{M}\right]\right) \ldots\ldots.(12)$$

Both these expressions of degree of polymerization are applicable to different reaction systems.

The temperature dependence of polymerization rate can be predicted by applying the proper rate expression. For example, supposing that the predominant termination is via monomer and alkyl, and both are adsorbed on the surface

$$\mathrm{Rate} = \mathrm{B}[\mathrm{M}]_s \cdot [\mathrm{Ti}] / \mathrm{K}\,[\mathrm{AlK}]_s \quad . \; . \; \ldots\ldots.(13)$$

assuming high alkyl concentration or $\mathrm{K}\left[\mathrm{AlK}\right]_s \gg 1 + \mathrm{K}'\left[\mathrm{M}\right]_s$.

In equation 13, K is a function of adsorption equilibrium constants and $\mathrm{B} = f\ (k_i,\ k_p,\ k_t)$. Then the expression will be

$$\begin{aligned}\mathrm{Rate} &= \mathrm{A}\exp\left\{\left[-(E_t+E_p-E_t') + \Delta F_a\right]\right\} / RT \\ &= \mathrm{A}\exp\left\{(\Delta F_a - \Delta E)/RT\right\} \quad . \; . \; \ldots\ldots.(14)\end{aligned}$$

ΔF_a - free energy of adsorption.

ΔE - Sum of activation energies of the initiation, termination and propagation steps.

Lastly, the beauty of this scheme and its general nature is that it can be used to explain homogenous catalyst system of $\mathrm{Ti(OR)_4\text{-}AlR_3}$[67] which is not analogous to any Ziegler type catalyst system.

Thus, if it is assumed that termination is by monomer and monomer adsorption, and if both alkyl and unreacted metal halide (alkoxide) participate in the adsorption competition then the following expression can be obtained

$$\text{Rate} = \frac{B\,[\text{AlK}]_s\,[M]_s\,[\text{Ti}]}{\left(1+K\,[\text{AlK}]_s + K'[M]_s + K'[\text{Ti}]_s\right)^2} \quad \ldots\ldots(15)$$

This confirms the rate data given by Bawn and others. The explanation for the increasing cut off pressure with increasing Ti(OR)_4 concentration would be the competition that Ti(OR)_4 offers the monomer for active surface sites.

Scope of present investigations

Previous studies of the polymerization with Ziegler type catalysts are mainly pertaining to the use of combination of titanium tetrachloride and aluminium alkyls for the polymerization of ethylene and propylene. Certain work is also reported with styrene polymerization by the use of the same catalyst system.[70] Besides this catalyst system, it is interesting to know the behaviour and nature of different combinations of various transition metal halides and organometallic compounds in the polymerization reactions. Catalyst system like lithiumalkyl and titanium tetrachloride[71] behaves quite differently from that of aluminium alkyl and titanium tetrachloride. This catalyst system has been used for the polymerization of ethylene and propylene and the bound radical mechanism different from ionic type,[71] is postulated. It is a matter of some studies to understand the correct mechanism involved in the polymerization by the use of this catalyst system, especially, when titanium tetrachloride[72] polymerizes styrene cationically and lithium alkyl[14] anionically. The use of combination of titanium tetrachloride and lithium alkyl in the polymerization of styrene will naturally give some interesting results.

Similarly, Chromium acetylacetonate and aluminium alkyl catalyst[73] has been used only for the polymerization of diolefins to obtain sterespecific polymers. An interesting aspect of this catalyst system is that it is apparently homogenous.

In the present studies, 1) Lithium isoamyl and titanium tetrachloride, 2) Chromium acetylacetonate and aluminium triethyl, and 3) Chromium acetylacetonate and diethyl aluminium bromide catalyst systems have been used for the polymerization of styrene and isoprene. Only recently, polymerization of styrene with lithium butyl and titanium tetrachloride catalyst system[74] is reported.[58] But these studies are restricted to know the effect of combination of catalyst constituents at different ratios of LiC_4H_9 to $TiCl_4$ on the molecular weight and stereospecificity. Also, at different ratios of combination of LiC_4H_9 to $TiCl_4$, the formation of trans-stilbene in situ is reported, which has some effects on the molecular weight, rate of polymerization and stereospecificity.

Our studies concerning the overall behaviour of these catalyst systems in the polymerization of styrene and isoprene are based on the following aspects:

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

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

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

4) Rate law from the variation of the rate of polymerization with monomer concentration and catalysts concentration.

5) Dependence of the molecular weight on the ratio of combination of catalyst consituents, monomer concentration, metal alkyl concentration and transition metal halides concentration to know the termination reaction.

6) Termination reaction in the homogenous and heterogeneous catalyst system.

7) Effect of trans stilbene on the stereospecificity, the rate of polymerization and the molecular weight in the presence of conventional catalyst systems like $TiCl_4$ - $AlEt_3$.

8) Ultraviolet and Infrared examination for stereospecificity, isomerism of polymeric units and incorporation of trans stilbene in the polymer.

Mechanism of polymerization is ascertained by observing the effect of additive like Zinc diethyl on the molecular weight and the rate of polymerization and by calculating the activation energy of polymerization with each catalyst system.

CHAPTER - II

EXPERIMENTAL

EXPERIMENTAL

Dry glove box:

Since all experiments had to be conducted under a dry nitrogen atmosphere, including dispensing and mixing of catalyst solutions, a glove box was got ready initially, made of wood and fitted with a glass window on top and two rubber gloves for manipulations inside. The box opened to an ante chamber through a sliding door and all materials to be taken in or removed from inside were first kept in this chamber before transportation across the sliding door or out so that the dry box was never exposed to the atmosphere of the room. The dry box was flushed constantly with dry nitrogen through an inlet and the outlet was guarded by silica gel tower. The nitrogen was purified, oxygen free, by successively passing through 4 columns of 8" of Fieser's solution and washed free of sulphurous gases in a blubber containing aqueous saturated basic lead acetate solution. After washing with distilled water it was dried over calcium chloride, sulphuric acid, P_2O_5 and KOH pellets and silica gel in all glass purification train before admission to the dry box through polyethylene tubing. The box itself contained additional desiccants, silica gel and calcium sulphate, kept in petri dishes which were replaced everyday by freshly reactivated lots. A small amount of KOH pellets to facilitate quick removal of acid fumes inside and indicator type silica gel were also kept inside.

The mouths of the gloves (provided for entering of the hands) were kept closed with tight fitting wooden stoppers when not in use. The whole box was painted with oil paint.

Reagents:

Fieser's solution[75]: For removal of trace of oxygen from nitrogen it was prepared by dissolving 15 gms sodium hydrosulphite ($Na_2S_2O_4$) per 100 ml of an aqueous solution of 20 gms KOH followed by addition of 2 gms anthraquinone sulphonic acid sodium salt (silver salt). The solution was blood red initially and became dull brown with formation of white scum when exhausted and was then discarded. If NaOH was used instead of KOH, it was limited to less than 12%

Solvents

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

Commercial Benzene, hexane and other hydrocarbons were wahhed by stirring repeatedly with H_2SO_4 (C.P.) (100 ml for each litre of solvent) till the acid layer remained colourless, washed free of acid with distilled water, dried over anhydrous $CaCl_2$, distilled and kept over sodium wire. The pure solvents were refluxed overnight on sodium under pure dry nitrogen and distilled first before use in the polymerization experiments.

Isoamyl chloride

$(CH_3)_2CHCH_2CH_2Cl$[76] was prepared by the reaction of 1 gm mole distilled anhydrous isoamyl alcohol (125°C/710 mm) with one gram mole conc. hydrochloric (33% by wt) and 2 gm. mole anhydrous zinc chloride. The mixture was refluxed for 3 hours before distilling off the crude isoamyl chloride through an air condenser. The pure product was then refluxed for an hour with equal volume of conc. H_2SO_4, distilled, washed free of acid, dried over anhydrous sodium sulphate and fractionated to yield the pure isoamyl chloride, (95°C/710 mm) (Yield 30 %). I.R. confirmed isoamyl group.

Lithium isoamyl[77]

3 gms 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 a 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 dropwise 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 in a bath of ice and salt at -20°C and the addition of the bulk of the 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 overnight before the supernatant 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 supernatant solution was removed with a syringe to 100 ml. flask with a ground glass stopper. This flask with stock solution of lithium isoamyl was enclosed in a polyethylene bag and kept inside a desiccator with silica gel and the desiccator was stored at 5°C in a refrigerator. Lithium isoamyl stored thus, was preserved without decomposition for 15-20 days.

Aluminium triethyl

It was prepared by the method of Ziegler,[78] the reaction of ethyl bromide with an aluminium magnesium alloy containing Al 40% and Mg 60% corresponding to Al_2Mg_3.

$$Al_2Mg_3 + 6C_2H_5Br \longrightarrow 2Al(C_2H_5)_3 + 3MgBr_2$$

This initial reaction product contained small amounts upto 30 % of the aluminium ethyl bromide which was converted to the aluminium triethyl subsequently with more of alloy or stoichiometric quantity of sodium.[79] Al_2Mg_3 was prepared by the National Metallurgical Laboratory, Jamshedpur and analysed as Al 36.5% Mg 66.5%. The brittle alloy could be provided easily and in a typical reaction 55 gms of it were taken in 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. 204.9 g) dried over P_2O_5 distilled (35°C/710 mm) and preserved over anhydrous calcium sulphate, was added dropwise and the reaction initiated with a little iodine. The exothermic reaction resulted a vigorous refluxing of ethyl bromide which was controlled by surrounding the reaction flask with oil bath and the evaporation loss minimised by circulating 10°C water in the condenser. The reaction was allowed to proceed thus under continuous stirring for about 2-3 hours till the refluxing of ethyl bromide had stopped and taken to completion by raising the temperature to 160°C.

The aluminium alkyl was soaked up in the evenly mass of magnesium bromide and removed by distillation under vacuum. The bromine content of the alkyl was estimated by hydrolysis and application of Vorld's method.[80] It was then added contiously to an equivalent amount of sodium and heated to 160°C for 24 hours to obtain the pure triethyl aluminium vacuum distilled at about 1.2 mm - (61°C/1mm). It would be stored in a ground glass stoppered flask inside the dry box without decomposition.

Similarly, reaction of Al_2Mg[79] (also obtained from the National Metallurgical Laboratory (Al = 69%)(Mg = 33%)) with ethyl bromide was used to prepare the aluminium diethyl bromide.

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

Both $Al(C_2H_5)_3$ and $Al(C_2H_5)_2Br$ were analysed for aluminium, after hydrolysis with sulphuric acid, as the EDTA complex.

Stock solutions were prepared in benzene.

Titanium tetrachloride

Prepared in the Inorganic chemistry division of the laboratory, was purified by distillation on copper fillings (132°C/110mm) and stock solution 25 ml (0.5N) prepared in hexane and stored in glass container.

Chromium acetylacetonate[81]

It was prepared according to the equation given below:

$$CrCl_3 + 3C_5H_8O_2 + 3NH_3 \longrightarrow Cr(C_5H_7O_2)_3 + 3NH_4Cl$$

16 gms chromium chloride ($CrCl_3\ H_2O$, May and Baker analysed) was taken in 600 ml. water along with 120 gms urea and heated overnight on a steam bath. The product formed in crimson red shining crystals, was separated by filtration of the cooled reaction mixture, dried and crystallised from benzene-hexane.

450 ml. hot hexane was added to a hot solution of 20 gms $Cr(AcAc)_3$ in 120 ml. benzene and crystallisation completed by cooling gradually to -20°C in ice-salt bath. After second crystallisation, the pure product was dried in vacuum (at 4 mm, 60°C for 4 hours) and stored in the dry box. Stock solutions were prepared in benzene.

Zinc diethyl[82]

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

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

Zn-Cu alloy containing about 8 % Cu was paepared by stirring Zinc dust 60 gms (May and Baker) with red cuprous oxide (Cu_2O) 5.5 gms (B.D.H.) in hydrogen at 410°C but below the fusion point (419°C) of the alloy. 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 the alkyl halides. After completion of the reaction for about 2 hours, the product was distilled off (40°C/2mm). The Zinc alkyl was redistilled with a fractionating column at atmospheric pressure, collecting pure product at 110°C/720 mm. yield 30 ml. The Zinc diethyl was easily decomposed even by slight atmospheric contamination forming a black deposit and hence was handled and stored carefully under pure dry nitrogen.

Benzoin

Benzoin[83] was prepared by refluxing the mixture of 20 gms benzaldehyde (Ridel Haën), 4 gms potassium cyanide in 15 ml. water and 40 ml. rectified spirit for about a hour. On cooling, yellow benzoin crystals separated out which were recrystallized to yield a colourless product, m.p. 133°C.[83]

Trans - stilbene

Trans stilbene[84] was prepared by the reduction of benzoin with zinc amalgam as described in Organic Synthesis Vol.23, p.86-87 by Spriner and Berges, except that the amalgam was prepared under acid condition, since othersie the yield was very poor.

In a 600 ml. flask, 7.5 gms. of mercuric chloride was taken in 75 ml. water and 1 ml. conc. HCl added. 30 gms Zinc wool (May and Baker) was rapidly sifted into the suspension, under vigorous stirring of the mixture for 20 minutes, till $HgCl_2$ was dissolved completely. The bright shining amalgam was allowed to settle and separated by filtration and repeatedly washed with distilled water.

The zinc amalgam was taken in the 500 ml. Erlenmeyer flask, cooled with ice. 75 ml. rectified spirit and 15 gms benzoin were added to it. Under vigorous stirring 75 ml. concentrated hydrochloric acid (33 % by wt.) solution was introduced dropwise in 5 hours through dropping funnel. The reaction was maintained below 15°C throughout this period. The stirring of reaction was still continued for 2 more hours after complete addition of hydrochloric acid. Large excess of cold distilled water was then added to precipitate the reaction product which was filtered through a Buchner funnel and recrystallized from hot alcohol thrice. The pureproduct had m.p. 123°C.

Estimation of Lithium isoamyl

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

Estimation of $Al(C_2H_5)_3$ and $Al(C_2H_5)_2Br$[85]

Nearly 1 ml. of akyl was weighed into a 50 ml. well stoppered conical flask. This weighed amount was diluted with 30 ml. dry hexane and hydrolysed 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 have been prepared and used for the estimation of aluminium:

1) Buffer solution - 38.5 g ammonium acetate and 28.5 ml. glacial acetic acid were dissolved in water and diluted to 500 ml.

2) Dithizone indicator - 0.025 of diphenylthiocarbazone (B.D.H.) dissolved in 100 ml acetone.

3) EDTA solution - Disodium ethylene diamine tetraacetate (EDTA) 0.2 N was prepared by dissolving 15 g. EDTA 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 solution.

4) Zinc sulphate solution - 5.4 gms zinc sulphate ($ZnSO_4$, $6H_2O$) was dissolved in distilled water and diluted to 500 ml. The solution was approximately 0.2 N and was accurately standardized.

5) Standard aluminium solution - 1.3555 gm. aluminium sheet (E.Merck) to the nearest 0.001 gm was weighed 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 the mark to yield a standard solution.

This was subsequently used to standardize zinc sulphate and EDTA.

5 ml. standard Al solution by pipette and 40 ml. of EDTA by Burette were taken accurately into a 250 ml. titrating flask and 10 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.

Purification of Monomers

Styrene monomer (Dow Chemical) was purified by washing with 5 % alkali solution for two to three 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 K_2CO_3 and stored over it after distillation in N_2 under reduced pressure. Just before the experiment, a small amount of purified monomer was allowed to stand over KOH pellets for some time and distilled fresh under water pump vacuum at 60°C under dry nitrogen gas and stood over activated silica gel till use in the polymerization experiment.

Isoprene monomer (Phillips Pure Grade) was washed with 10 % alkali solution two or three times, till alkali did not show any colour. After removing alkali by repeated washing with distilled water, the monomer was dried over anhydrous calcium chloride overnight and preserved on anhydrous $MgSO_4$ after distillation. For every experiment, this purified isoprene was removed in small quantity on anhydrous $MgSO_4$ and refluxed on sodium metal for some time in the flask and distilled at 31°C at atmospheric pressure und under bubbling of pure dry nitrogen.

Experimental

The catalyst systems used consisting of the reactive metal alkyls and transition metal compounds were highly sensitive to contamination by moisture and air and it was essential to the reproducibility of the experiments that the reaction vessels and dispensers be thoroughly dried. All additions and mixing of the reagents were carried out in the dry box under an inert nitrogen blanket.

Generally, the reaction flasks and magnetic elements (enclosed in glass) used in the experiments were thoroughly cleaned with chromic acid and washed with distilled water and dried overnight at 160°C. Before the experiment, they were transferred inside the dry box when still hot and cooled while purging with 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°C 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 added with syringes (2-20 ml) in the predetermined order. The reaction flask was immediately stoppered with well greased (Dow Corning Silicone, High vacuum grease) standard joints before being thermostatted outside in a bath (20 litre) whose temperature was controlled to ± 0.05°C by a toluene regulator connected to electronic relay. The stirring element inside the reaction flask was moved by a rotating horse shoe magnet kept under it, enclosed in a water proof brass case and carried on ball bearings. The magnet was connected by a flexible speedometer shaft cable to a BTC stirring motor and the speed of rotation adjusted. F.B.250 ml. three necked flask with standard joints was used for LiC_5H_{11}-$TiCl_4$ system and 50 ml. conical flask with B19 cone joint with B19 stopper used for $Cr(AcAc)_3$-Al alkyls systems.

After polymerization had 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 both systems, methanol with 1 % HCl for styrene and methanol with 2 % acetic acid for isprene were used to destroy the catalyst. Since the polymers were generally of low molecular weight, considerably large excess of (5-10 times) of methanol was used and precipitation completed while the mixture was cooled as low as possible, usually -20°C (ice and salt mixture).

Molecular Weight

Molecular weights were determined by intrinsic viscosities of 0.5 to 0.1 % solutions of polymers in benzene in an Ostwald U-tube viscometer suspended in a Tower's viscometric bath at 25°C.

For polystyrene the relationship of intrinsic viscosity with chain length,[86] given below, was applied.

$$P_n = 1770 \times [\eta]^{1.4} \quad \text{(in benzene)}$$

For polystyrene prepared by aluminium triethyl and titanium tetrachloride, the relationship of intrinsic viscosity with molecular weight as stated below, was used.

$$[\eta] = 1.10 \times 10^{-4} \times M_n^{0.725} \quad \text{(in toluene)}$$

For polyisoprene intrinsic viscosity only was calculated.

Infrared and Ultraviolet analysis

5 % polymer sample was prepared in redistilled

Analar carbon disulphide[89] (E.Merck) and the infrared spectra were measured on infrachord and Perkin Elmer Spektrophotometer 221. The cell used was 0.1 mm thickness. Spectra of certain samples were obtained by the use of potassium bromide pellets' technique. Nearly 3 mg sample was mixed with 350 mg of anhydrous potassium bromide (B.D.H.) and pressed in the hydraulic press. Certain spectra of resinous polymers were taken by forming a film of the sample on the rock salt plate.

Ultraviolet analyses were done of the samples dissolved in purified chloroform.[90] The sample were prepared 0.05 % in chloroform. Perkin Elmer 350 recording Spektrophotometer was used for the measurements.

CHAPTER - III

EXPERIMENTAL RESULTS

EXPERIMENTAL RESULTS

Polymerization of Styrene with Lithium isomayl and Titanium tetrachloride in Hexane and Benzene at 30°C

Titanium tetrachloride polymerizes styrene at room temperature in n hexane and toluene cationically[72] and lithium isoamyl polymerizes styrene anionically.[14] Date on initiation of styrene polymerization by titanium tetrachloride have been reported by Plesch. Polymerization by lithium isoamyl was conducted by us at 30°C in n hexane and the rates of polymerization for different concentration of lithium isoamyl have been given in the table No.1.

Table No.1.

Styrene 5 ml. n-Hexane = 45 ml.

[Liisoamyl] X10^2 M/1	Time in min.	Wt.of Polymer in gms.	RpX10^5 M/1/S
4.0	30	0.92095	9.799
2.16	60	1.0283	5.473

Lithium isoamyl was added to n hexane to have required concentration. 5 ml. 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.

Titanium tetrachloride lithium isoamyl complex catalyst system.

Lithium isoamyl readily reacts with titenium tetrachloride and forms a brown catalyst complex which precipitates out immediately. This complex has high catalytic activity for the polymerization of styrene.

Ageing time of catalyst system.

The variation of the activity of this complex on keeping was first studied during 10 to 30 minutes of ageing time. It was found that the activity of the catalyst did not change or deteriorate during this interval upto 30 minutes. First ten minutes sufficed for complete reaction of the reactants. The results are tabulated in the table No.2.

Table No.2.

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

Time of Reaction = 15 minutes.

$[TiCl_4]$ = .02 M/l $[LiC_5H_{11}]$ = .01663 M/l

Molar Ratio Li/Ti = 0.75

Ageing time in min.	Yield in gms.	$Rp \times 10^4$ M/1/S
10	1.13285	2.303
20	1.23767	2.634
30	1.08827	2.316

Ratio of Liisoamyl/$TiCl_4$

The activity of the catalyst and the complete formation of Ziegler type catalyst complex depend upon the ratio of mixing of the constituents of the system. The activity of the catalyst complex at different molar ratios of mixing of $TiCl_4$ and Liisoamyl from 0.5 to 3.0 Li/Ti was studied. The concentration of $TiCl_4$ was maintained constant and Lithium isomayl concentration was varied and increased. The amount of polymer isolated from the experiments conducted for 15 minutes at different ratios was taken as the index of the catalyst activity. The activity was found increasing and becoming nearly negligible at ratio 3.0 Li/Ti. The colour of precipitate was yellow and intense yellow below ratio 1 Li/Ti and brown and dark brown upto ratio 2.25 Li/Ti; at the ratios 2.5 and 3.0 the colour of precipitate was completely black. The molecular weight was found increasing with increasing quantity of lithium isoamyl.

The results are given in the Table No.3, Fig.2.

Table No.3.

Ratio studies

Styrene = 5 ml. n-Hexane = 70 ml.

$[TiCl_4]$ = 0.01 M/1 Time of reaction = 15 Minutes.

Ratio $^{Li}/_{Ti}$	$[LiC_5H_{11}]$ M/1	Yield in gms.	$R_p \times 10^4$ M/1/S	$[\eta]$	M.W.
0.25	0.0025	0.3973	0.8457	0.0531	3046
0.5	0.005	0.5619	1.195	0.0504	2758
1.0	0.01	0.7336	1.561	0.0532	3046
1.5	0.015	0.8455	1.800	0.0574	3348
2.0	0.02	1.2451	2.649	0.0652	4052
2.25	0.0225	0.4531	0.064	0.0870	6063
2.5	0.025	0.3426	0.728	0.0827	5645
3.0	0.03	0.023	0.489	-	-

Percent conversion

As soon as the reaction started, the polymer precipitated out and the colour of the complex appeared faded out, probably due to getting mixed with polymer. Studies of percent conversion with time showed that the rate of polymerization after 15 minutes decreased sharply and became steady upto 3 hours. Conversion with time was studied at different concentration of catalyst formed by mixing the components at constant molar ratio of $LiR:TiCl_4$ = 1.5. It is seen that the molecular weight of the polymer remained fairly constant with varying reaction times.

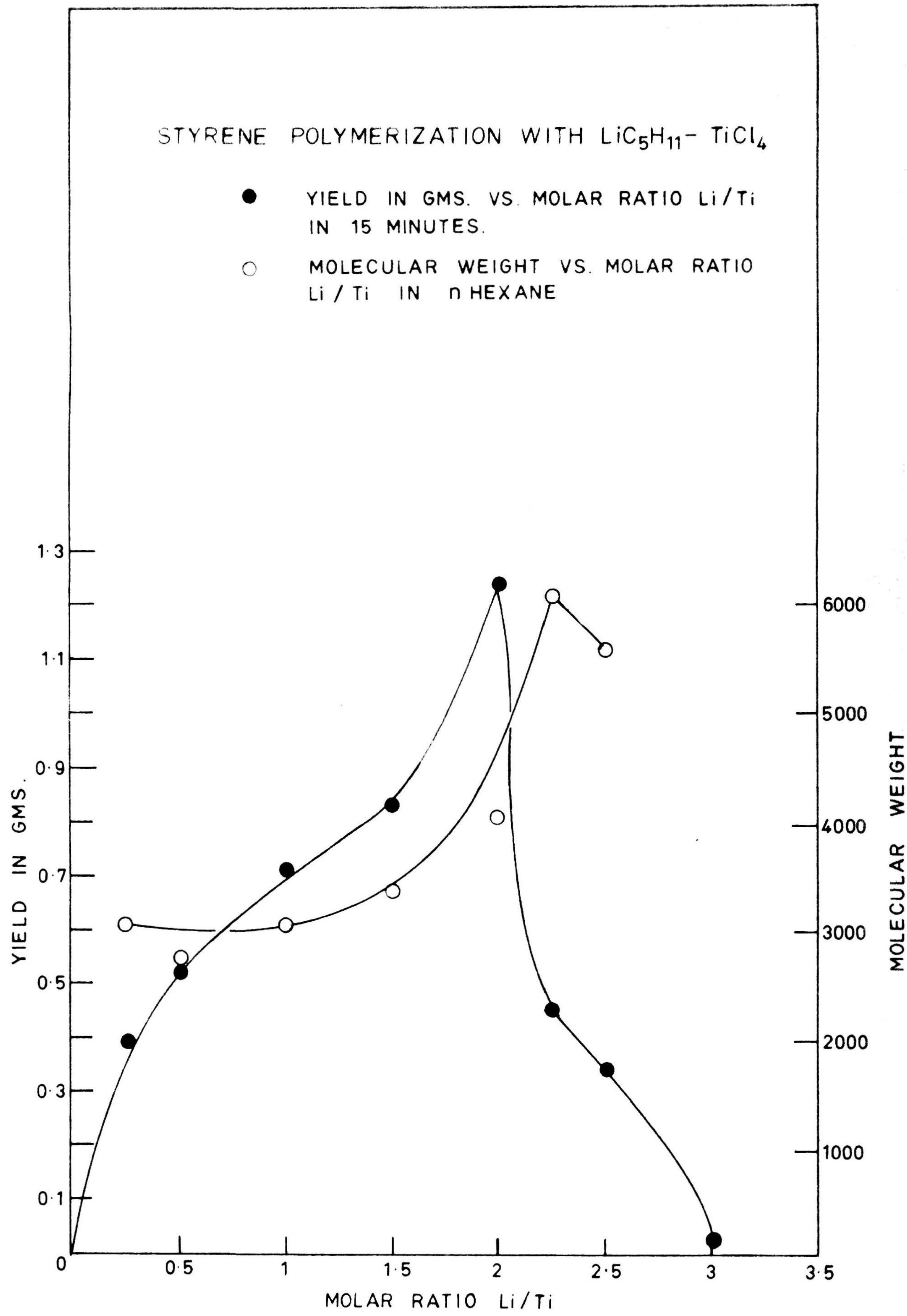

STYRENE POLYMERIZATION WITH LiC_5H_{11} - $TiCl_4$
● YIELD IN GMS. VS. MOLAR RATIO Li/Ti IN 15 MINUTES.
○ MOLECULAR WEIGHT VS. MOLAR RATIO Li/Ti IN n HEXANE
YIELD IN GMS.
1·3
1·1
0·9
0·7
0·5
0·3
0·1
0
MOLECULAR WEIGHT
6000
5000
4000
3000
2000
1000
0·5
1
1·5
2
2·5
3
3·5
MOLAR RATIO Li/Ti

FIG.-2.

Table No.4 gives the results below. Fig. No.1 shows the nature of the curve.

Table No.4

Percent conversion with time

Styrene = 5 ml. n-Hexane = 70 ml. Molar ratio Li/Ti = 1.5

$[TiCl_4] \times 10^3$ M/l	$[LiC_5H_{11}] \times 10^3$ M/l	Time in min.	Yield in gms	%	$[\eta]$	M.W.
8.976	11.54	15	0.7339	16.25	0.05518	3204
"	"	30	0.7970	17.65	0.05340	3068
"	"	60	0.9334	20.67	0.05304	3039
6.645	10.7	15	0.5594	12.39	0.05740	3348
"	"	30	0.6855	15.16	0.05526	3211
"	"	60	0.776	17.19	0.04677	2539
"	"	90	0.882	19.53	0.04837	2665
4.984	7.233	15	0.5163	11.44	0.05993	3595
"	"	30	0.5447	12.06	0.05353	3074
"	"	60	0.6005	13.30	0.05024	2809
"	"	120	0.7154	15.84	0.05380	3095
"	"	180	0.7480	16.53	0.05400	3102
0.323	5.032	15	0.2826	6.258	0.06205	3773
"	"	30	0.2816	6.236	0.05934	3554
"	"	60	0.3213	7.115	0.06037	3620
"	"	120	0.3205	7.094	0.05874	3505

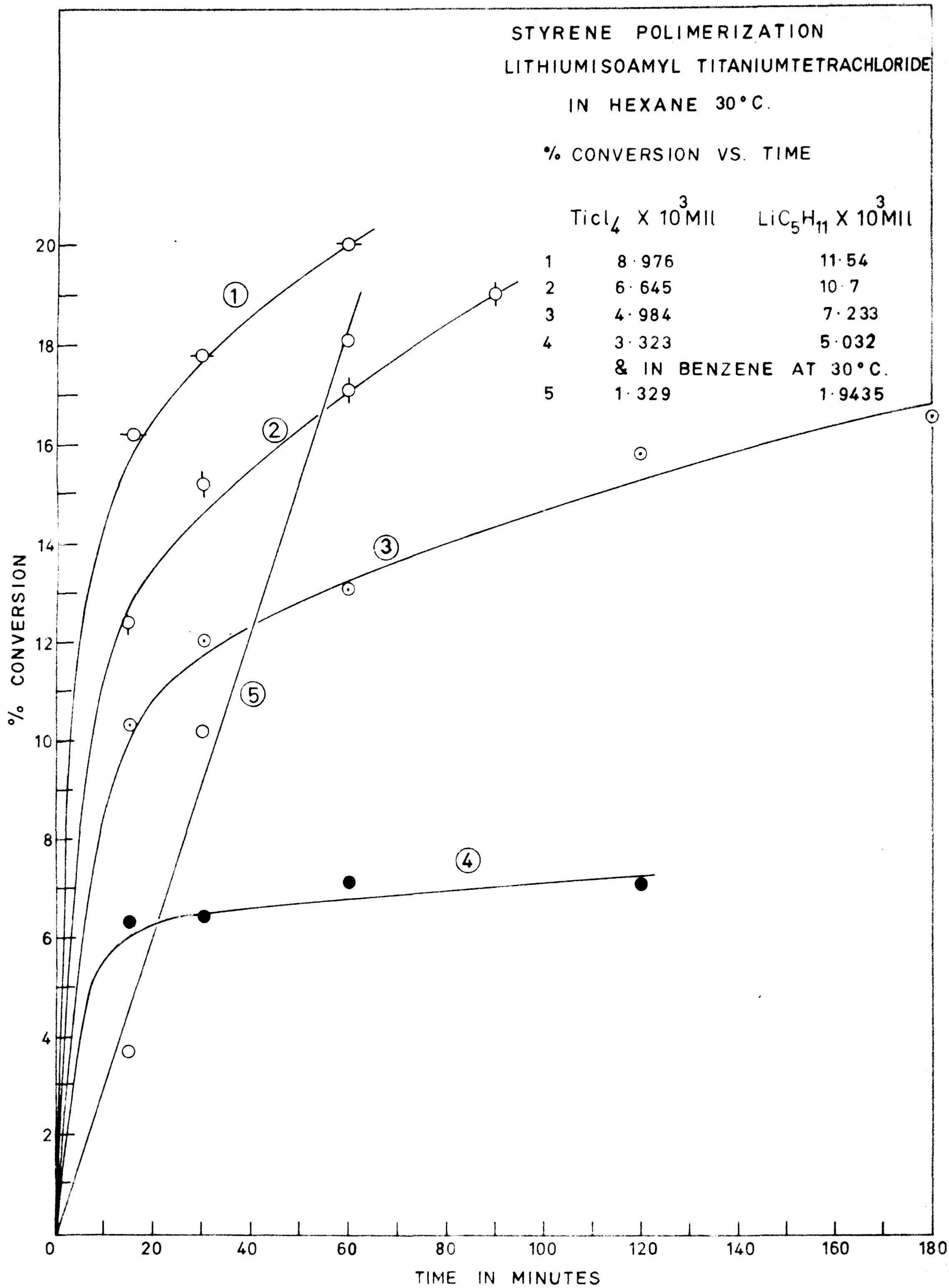

STYRENE POLIMERIZATION
LITHIUMISOAMYL TITANIUMTETRACHLORIDE
IN HEXANE 30°C.
% CONVERSION VS. TIME
$TiCl_4 \times 10^3$ M/L
$LiC_5H_{11} \times 10^3$ M/L
1 8·976 11·54
2 6·645 10·7
3 4·984 7·233
4 3·323 5·032
& IN BENZENE AT 30°C.
5 1·329 1·9435
① ② ③ ④ ⑤
% CONVERSION
TIME IN MINUTES
0 2 4 6 8 10 12 14 16 18 20
0 20 40 60 80 100 120 140 160 180

FIG.-1.

The rate of polymerization was found proportional to the concentration of titanium tetrachloride, but the molecular weight decreased with increasing catalyst concentration at the fixed molar ratio of $LiR/TiCl_4 = 1.5$. Varying rates of polymerization with Ti^+ are taken from table No.3. Results are given in the table No.5 and Fig.3.

Table No.5.

Rate of polymerization with $[TiCl_4]$

Monomer = 5 ml.(0.5766 M/l) n-Hexane = 70 ml.
Molar ratio Li/Ti = 1.5

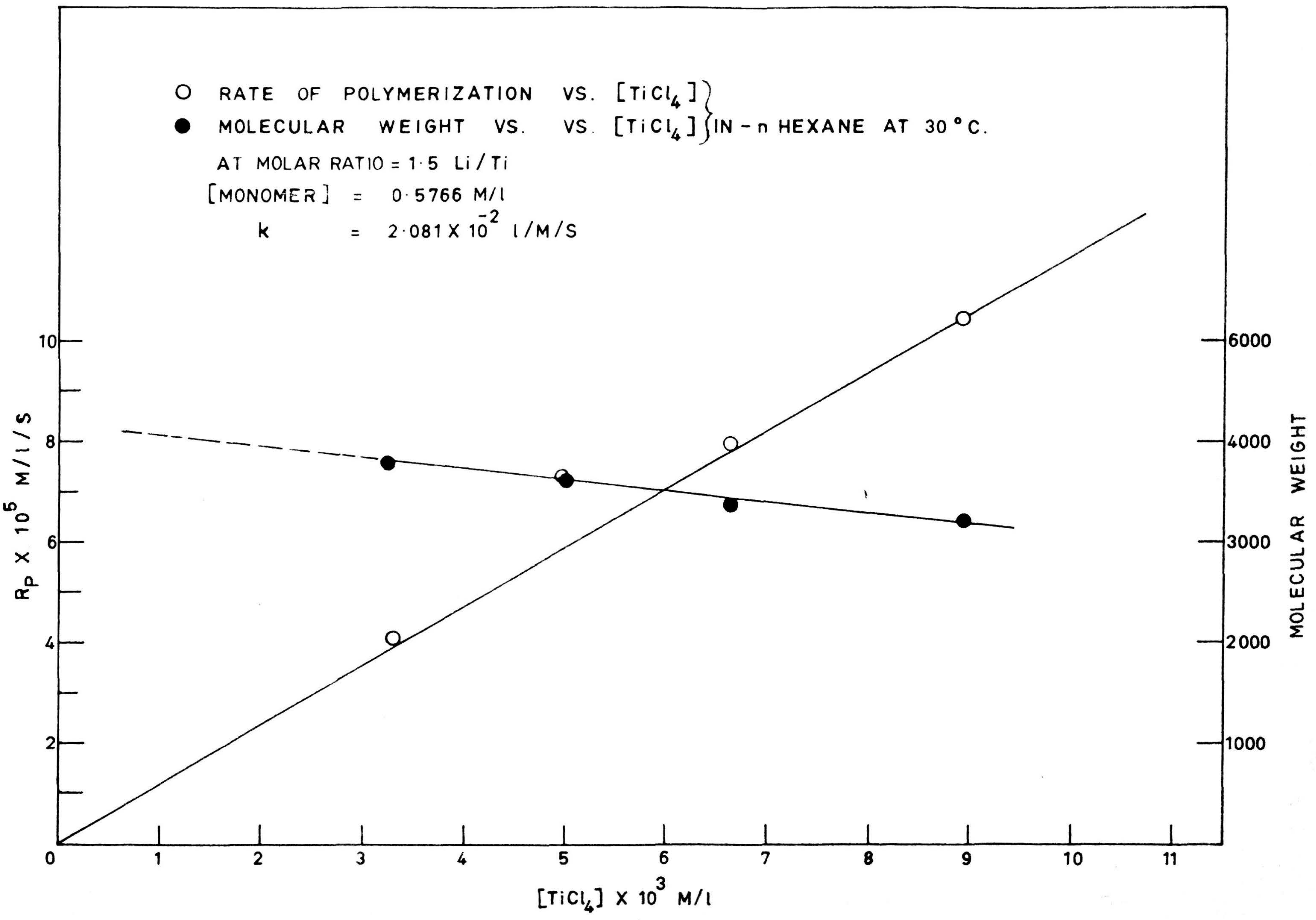
$[TiCl_4] \times 10^3$ M/l	$[LiC_5H_{11}] \times 10^3$ M/l	$Rp \times 10^5$ M/l/S	$[\eta]$	M.W.
8.976	11.54	10.45	0.05518	3204
6.645	10.7	7.966	0.05740	3348
4.984	7.233	7.350	0.05993	3595
3.323	5.032	4.023	0.06205	3773

1/Pn is also proportional to the square root of the concentration of titanium tetrachloride given in table No.6 and Fig.No.8.

Table No.6.

Values are taken from the Table No.5.

1/Pn	$[TiCl_4]^{1/2} \times 10^2$ $(M/1)^{1/2}$
0.03278	9.473
0.03119	8.151
0.02882	7.061
0.02767	5.76


○ RATE OF POLYMERIZATION VS. [TiCl4]
● MOLECULAR WEIGHT VS. VS. [TiCl4]
IN - n HEXANE AT 30 °C.
AT MOLAR RATIO = 1·5 Li / Ti
[MONOMER] = 0·5766 M/l
k = 2·081 X 10-2 l/M/S
Rp X 105 M/l/S
0
2
4
6
8
10
1
3
5
7
9
11
[TiCl4] X 103 M/l
MOLECULAR WEIGHT
1000
2000
3000
4000
6000

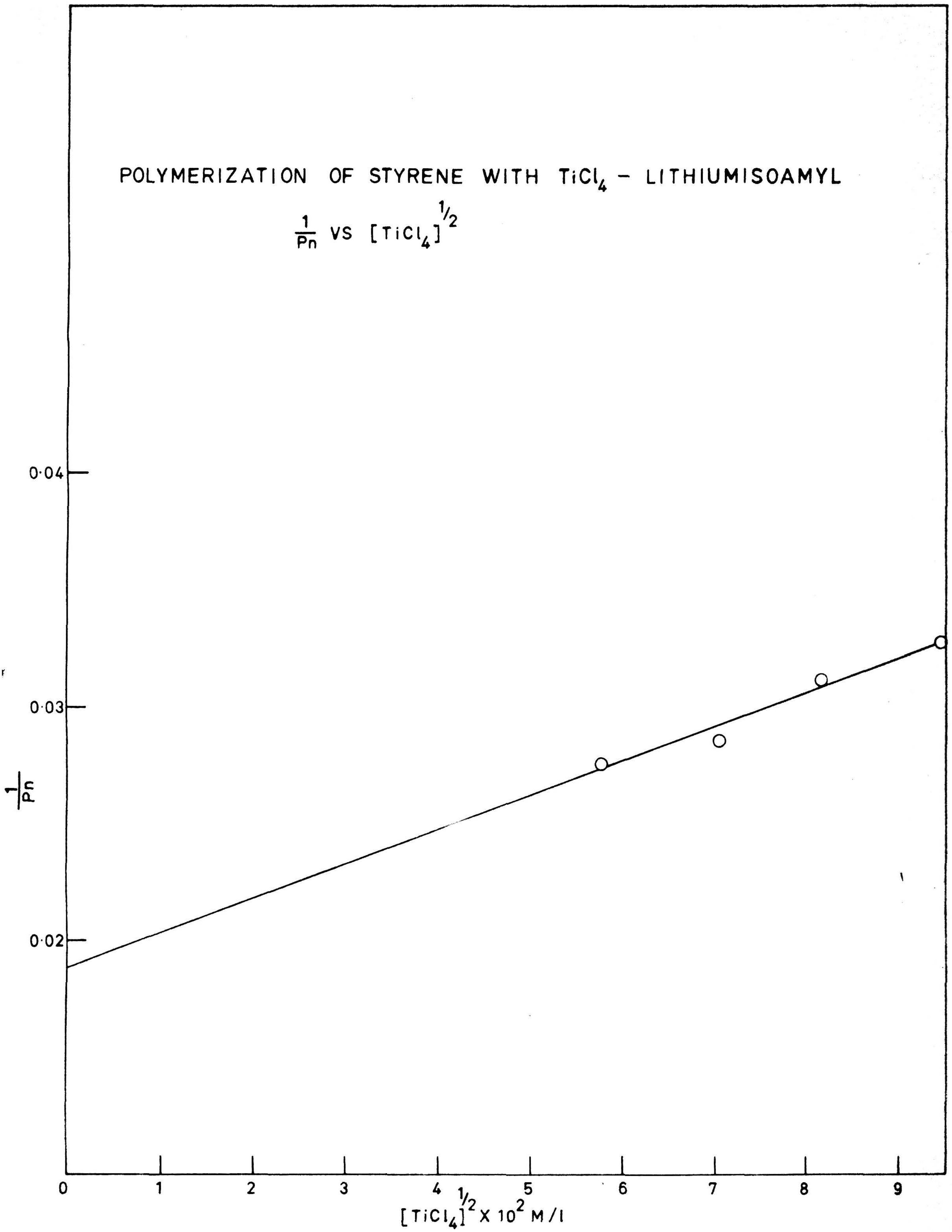

POLYMERIZATION OF STYRENE WITH $TiCl_4$ - LITHIUMISOAMYL
$\frac{1}{Pn}$ VS $[TiCl_4]^{1/2}$
0·04
0·03
0·02
$\frac{1}{Pn}$
0
1
2
3
4
5
6
7
8
9
$[TiCl_4]^{1/2} \times 10^2$ M/l

FIG.- 8.

At the same molar ratio Liisoamyl/$TiCl_4$ = 1.5, the rate of polymerization was linear with the monomer concentration upto 2.3 M/l concentration of monomer and above this molar ratio the rate of polymerization was found increasing rapidly and giving yield more than 30 % in 15 minutes. The molecular weight was found increasing with monomer concentration upto 4.5 M/l and it was decreased at the monomer concentration 6.0 M/l

Results are given in the table No.7 and Fig.No.4,6.

Table No.7.

Rate of polymerization with [Monomer]

n-Hexane = 75.0 ml. $[TiCl_4] = 6.645 \times 10^{-3}$ M/l

$[LiC_5H_{11}] = 10.7 \times 10^{-3}$ M/1

Molar ratio Li/Ti = 1.5. Time of reaction = 15 minutes.

[Monomer] M/1	Yield in gms.	Rpx10^4 M/l/S	[η]	M.W.
0.346	0.4079	0.7330	0.04624	2500
0.5766	0.5594	0.7966	0.05740	3348
1.6	3.4839	5.009	0.08044	5429
2.30	3.1157	4.417	0.09099	6450
3.4	14.7590	22.23	0.1007	7256
4.6	28.573	40.58	0.08067	5417

Effect of Zinc diethyl

At the fixed molar ratio 1.5 Li/Ti and titanium tetrachloride concentration 0.01 molar and Lithium isoamyl

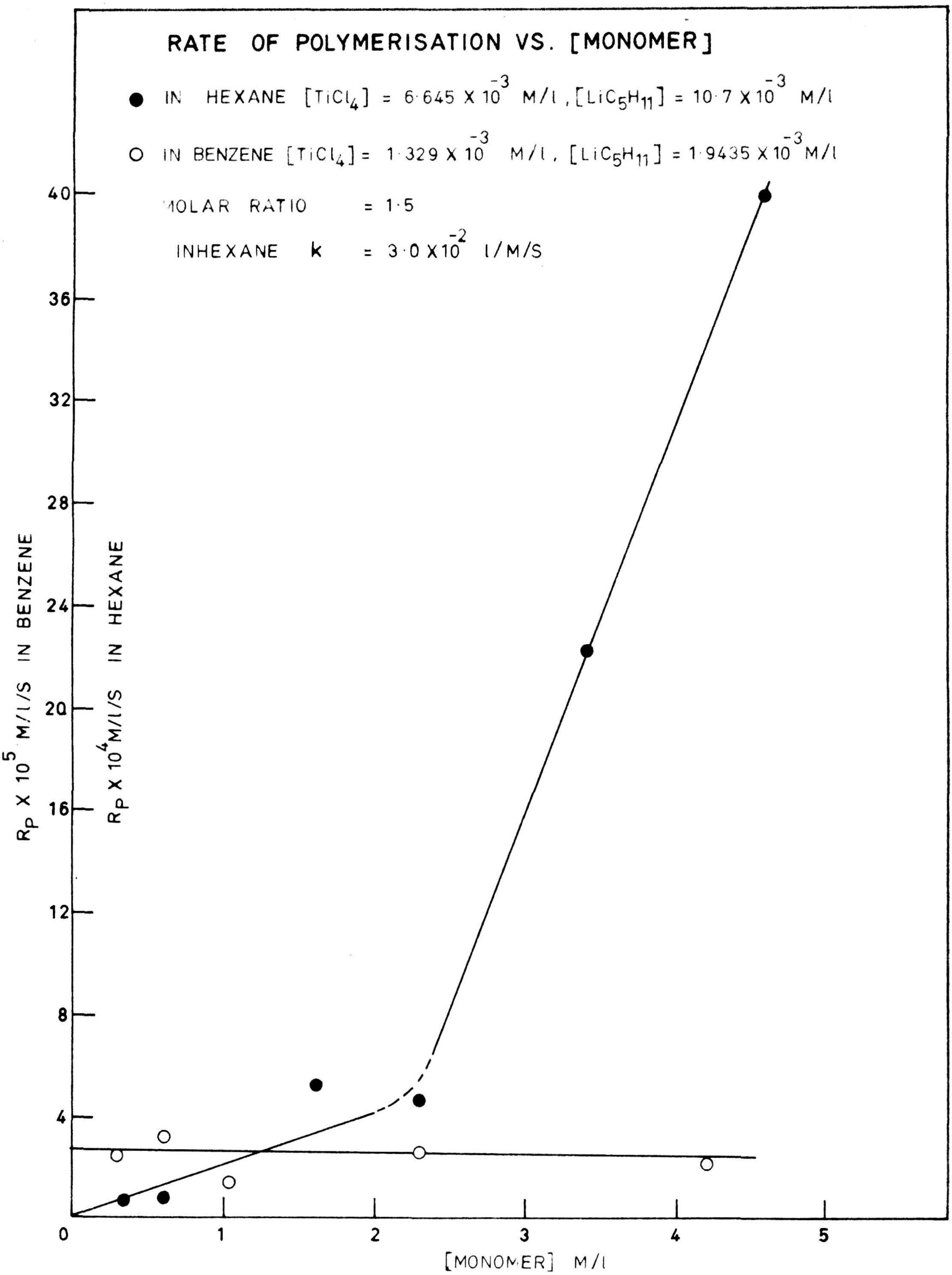

RATE OF POLYMERISATION VS. [MONOMER]
● IN HEXANE [$TiCl_4$] = $6{\cdot}645 \times 10^{-3}$ M/l, [LiC_5H_{11}] = $10{\cdot}7 \times 10^{-3}$ M/l
○ IN BENZENE [$TiCl_4$] = $1{\cdot}329 \times 10^{-3}$ M/l, [LiC_5H_{11}] = $1{\cdot}9435 \times 10^{-3}$ M/l
MOLAR RATIO = 1·5
IN HEXANE k = $3{\cdot}0 \times 10^{-2}$ l/M/S
$R_P \times 10^5$ M/l/S IN BENZENE
$R_P \times 10^4$ M/l/S IN HEXANE
40
36
32
28
24
20
16
12
8
4
0
1
2
3
4
5
[MONOMER] M/l

FIG.-4

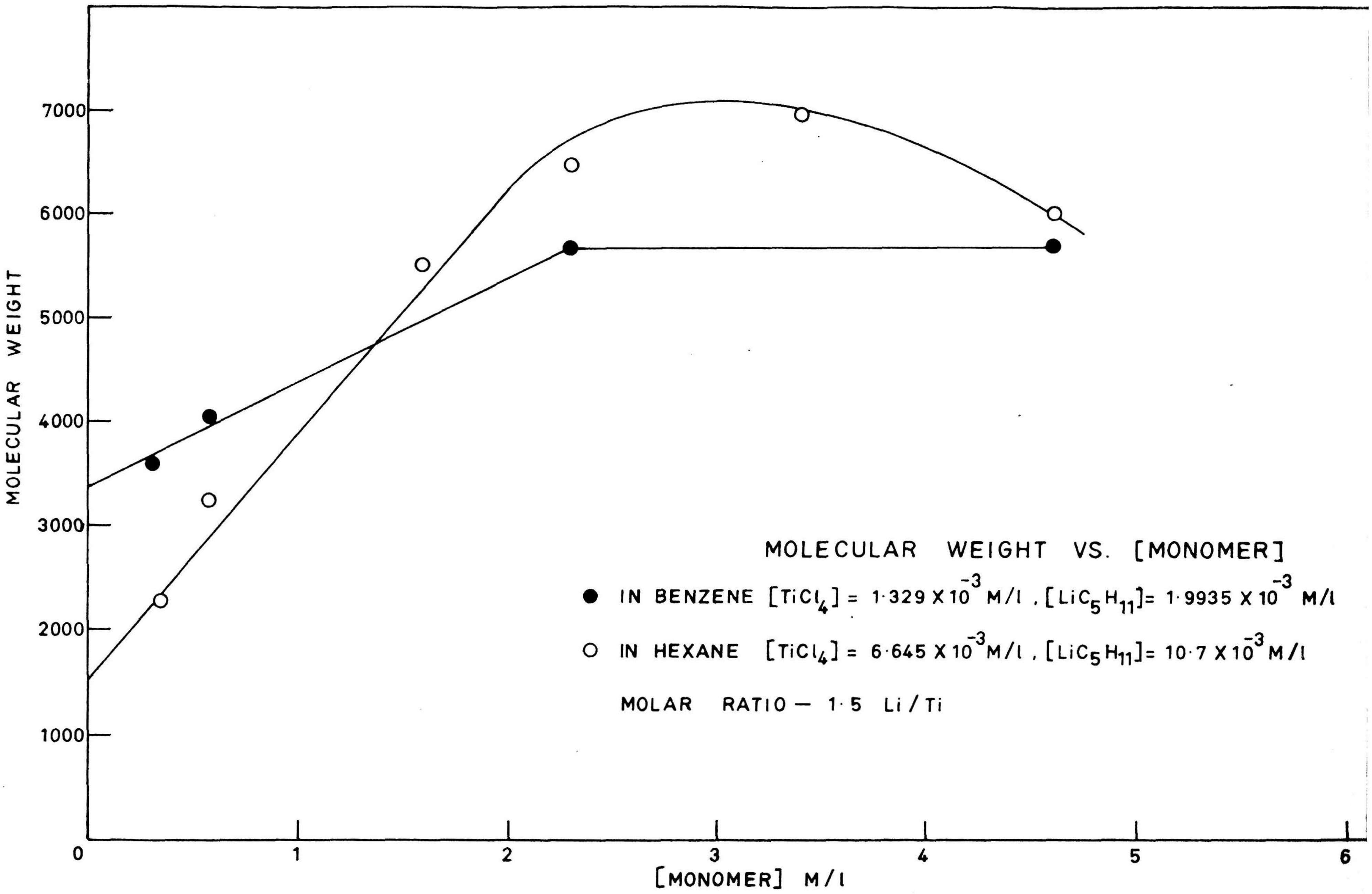

MOLECULAR WEIGHT VS. [MONOMER]
● IN BENZENE $[TiCl_4] = 1{\cdot}329 \times 10^{-3}$ M/l , $[LiC_5H_{11}] = 1{\cdot}9935 \times 10^{-3}$ M/l
○ IN HEXANE $[TiCl_4] = 6{\cdot}645 \times 10^{-3}$ M/l , $[LiC_5H_{11}] = 10{\cdot}7 \times 10^{-3}$ M/l
MOLAR RATIO — 1·5 Li / Ti
MOLECULAR WEIGHT
7000
6000
5000
4000
3000
2000
1000
0
1
2
3
4
5
6
[MONOMER] M/l

FIG.- 6.

concentration 0.015 M/l, effect of zinc diethyl on rate of polymerization and molecular weight was studied. Concentration of zinc diethyl was varied from 0.0125 M to 0.1 M. The rate of polymerization was found decreasing at lower concentration of zinc diethyl but at higher concentration (0.05 to 0.1 M) the rate of polymerization increased but still this rate of polymerization is less than the rate of polymerization of styrene in absence of zic diethyl. The molecular weight of polymers decreased with increasing concentration of zinc diethyl.

Results are given in the table No.8 and Fig.No.9.

Table No.8.

Monomer = 5 ml. Hexane = 45 ml.

$[TiCl_4]$ = .01 M/l $[LiC_5H_{11}]$ = .015 M/l

Molar ratio Li/Ti = 1.5. Time of reaction = 15 minutes.

$[ZnEt_2]$ M/l	Yield in gms.	$Rp \times 10^4$ M/l/S	$[\eta]$	M.W.
0.0	0.48175	2.050	0.08744	6105
0.0125	0.23125	0.9842	0.08392	5750
0.025	0.21055	0.8960	0.07939	5330
0.05	0.2695	1.115	0.08330	5698
0.1	0.3505	1.492	0.07939	5330

Activation energy

The temperature dependence of the rate of polymerization was studied between 22°C to 50°C. The

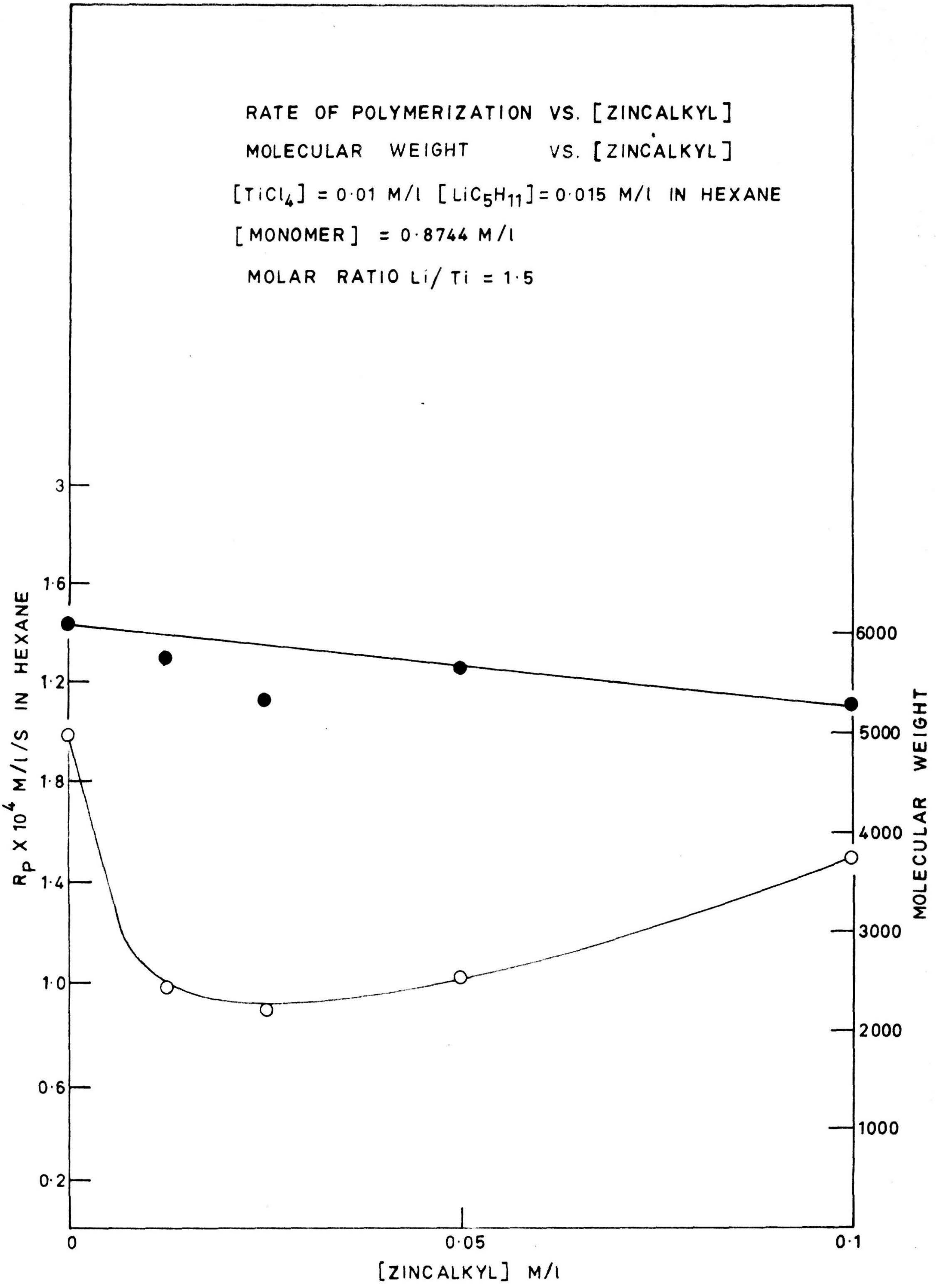

RATE OF POLYMERIZATION VS. [ZINCALKYL]
MOLECULAR WEIGHT VS. [ZINCALKYL]
[TiCl$_4$] = 0·01 M/l [LiC$_5$H$_{11}$] = 0·015 M/l IN HEXANE
[MONOMER] = 0·8744 M/l
MOLAR RATIO Li/Ti = 1·5
R$_p$ X 10^4 M/l/S IN HEXANE
3
1·6
1·2
1·8
1·4
1·0
0·6
0·2
MOLECULAR WEIGHT
6000
5000
4000
3000
2000
1000
0
0·05
0·1
[ZINCALKYL] M/l

FIG.- 9.

molecular weight was found fairly constant with temperature The activation energy is calculated from plot of ln rate of polymerization versus 1/T (T is absolute temperature) as 2.047 K cal/mole. Fig.7.

Polymerization of styrene with lithium isoamyl and titanium tetrachloride in benzene.

The rates are found much higher in benzene than in hexane under comparable conditions. Polymer was observed soluble in the benzene medium.

Percent conversion

Experiments of polymerization of styrene were conducted in benzene medium at fixed molar ratio 1.5 Li/Ti with 0.0013 M/1 titanium tetrachloride concentration during time intervals varying from 10 minutes to 1 hour.

Results of conversion versus time are shown in table No.9, Fig.No.1.

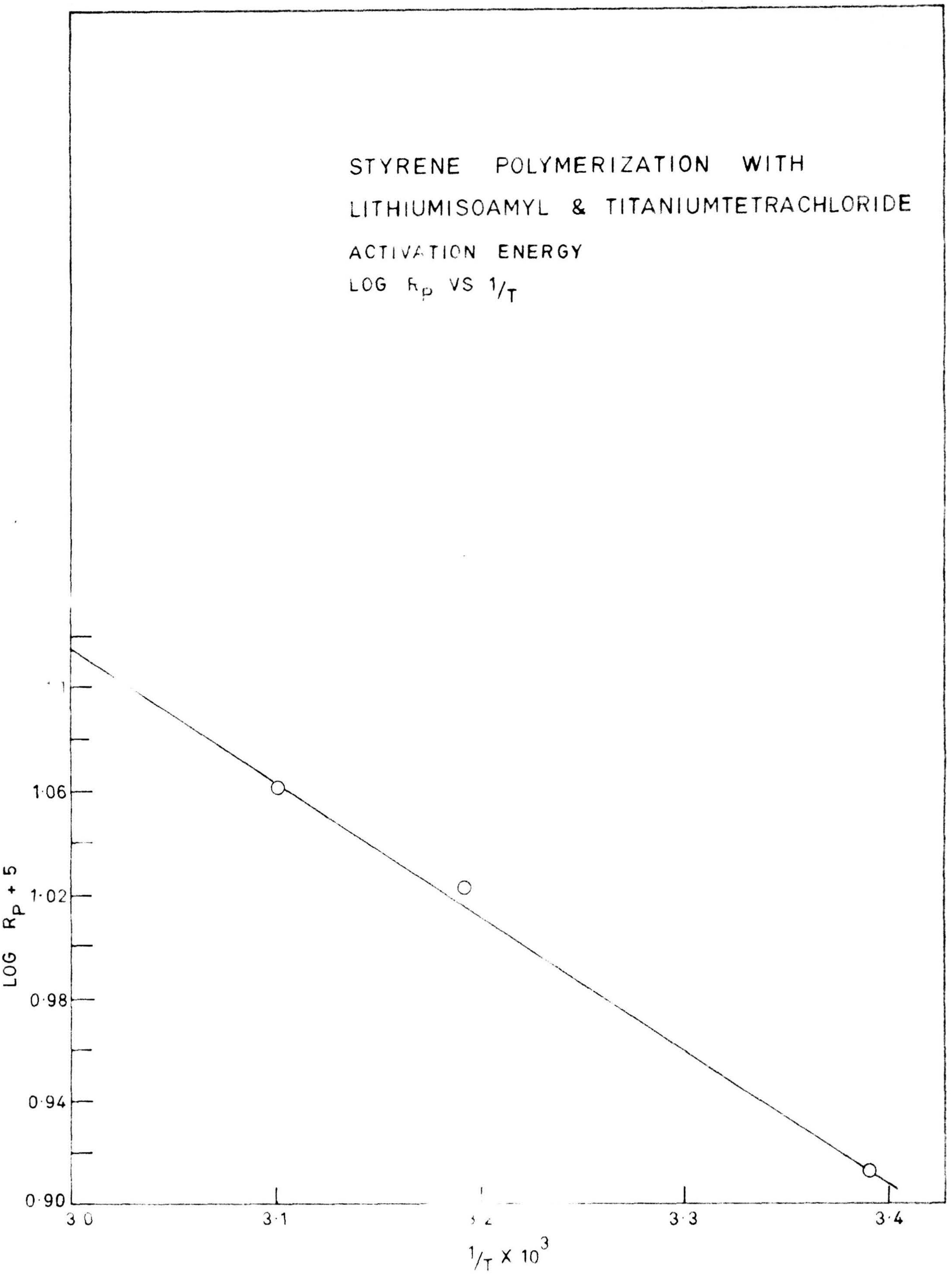
Table No.9.

Styrene = 5 ml. (0.5766 M/1) Benzene = 70 ml.

$[TiCl_4]$ = 1.329×10^{-3} M/1 $[LiC_5H_{11}]$ = 1.9435×10^{-3} M/1

Molar ratio = 1.5 Li/Ti Reaction time = 15 minutes.

Time in minutes	yield in gms	%	$[\eta]$	M.W.
15	0.1641	3.634	0.07111	4567
30	0.4589	10.16	0.06708	4205
60	0.8417	18.64	0.06536	4061



STYRENE POLYMERIZATION WITH LITHIUMISOAMYL & TITANIUMTETRACHLORIDE

ACTIVATION ENERGY

LOG R_p VS $1/T$

FIG – 7.

The rate of polymerization was constant without any decrease during reaction times upto 1 hour, and plot of percent conversion against time was linear. The molecular weight of products obtained at various reaction times was found constant.

The rate of polymerization with catalyst concentration and monomer concentration.

The rate of polymerization was studied at different concentration of titanium tetrachloride varying from 0.6×10^{-3}M to 3.3×10^{-3}M.

Results are given in the table No.10, Fig.5.

Table No.10.

Styrene = 5 ml.(0.5766 M/1) Benzene = 70.0 ml.

Molar ratio Li/Ti = 1.5

$[TiCl_4] \times 10^3$ M/l	$[\text{Liisoamyl}] \times 10^3$ M/l	$Rp \times 10^4$ M/l/S
3.323	5.032	2.188
2.659	3.988	1.771
1.994	2.993	1.224
1.662	2.493	0.5321
1.329	1.993	0.3258
0.6645	0.9967	0.06384

The rate of polymerization showed linear relationship with titanium tetrachloride concentration.

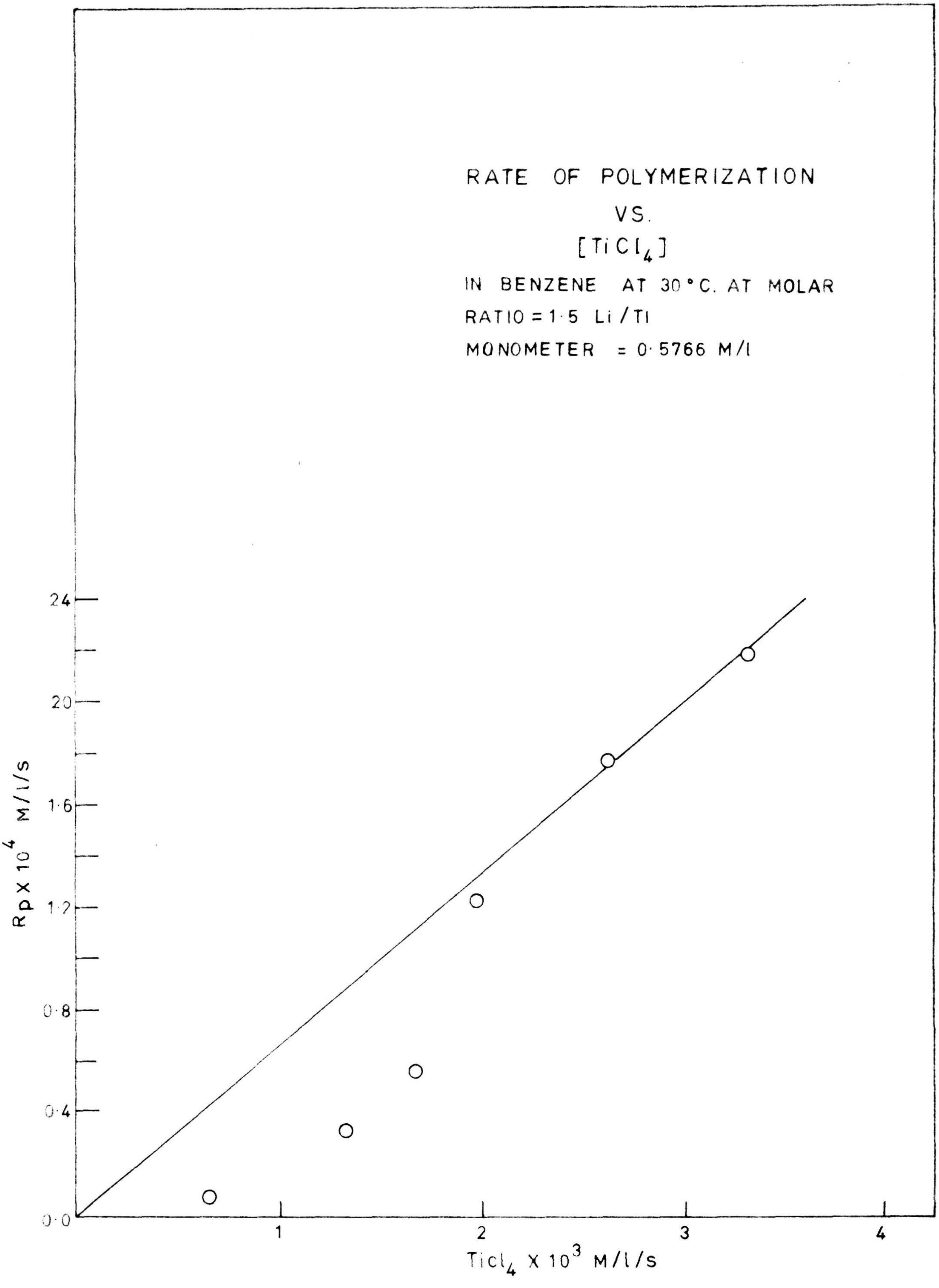

RATE OF POLYMERIZATION
VS.
[TiCl$_4$]
IN BENZENE AT 30 °C. AT MOLAR
RATIO = 1·5 Li / Ti
MONOMETER = 0·5766 M/l
24
20
1·6
1·2
0·8
0·4
0·0
1
2
3
4
Rp X 10^4 M/l/s
Ticl$_4$ X 10^3 M/l/s

FIG.- 5

The rate of polymerization was studied with varying concentration of monomer.

The results are given in the Table No.11, Fig.4,6

Table No.11

$[TiCl_4]$ = 1.329×10^{-3} M/1. $[LiC_5H_{11}]$ = 1.9935×10^{-3} M/1.

Benzene = 75 ml. Molar ratio Li/Ti = 1.5

[Monomer] M/l	$Rp \times 10^5$ M/1/S	$[\eta]$	M.W.
4.2128	2.000	0.08561	5895
2.7064	2.686	0.08565	5926
1.0532	1.362	-	-
0.5766	3.258	0.06708	4205
0.2883	2.437	0.06005	3612

The rate of polymerization was found unchanged at various monomer concentrations but the molecular weight increased upto 2.7 molar concentration of monomer and afterwards remained constant.

Effect of trans stilbene

It was reported by Tsou et al that the molecular weight of polystyrene prepared by titanium tetrachloride lithium butyl catalyst system was considerably low. The reasons for the decrease in the molecular weight was given that trans stilbene formed in this system by the reaction of styrene with $TiCl_4$ and LiBu was incorporated into the polymer. This trans stilbene formed in situ could act as a chain transfer agent, decreasing the molecular weight and increasing the rate of polymerization.

In our system of polymerization of styrene with isoamyl lithium and titanium tetrachloride there was obtained low molecular weight polymer with remarkably high rate of polymerization and polymer had blue fluorescence in the ultraviolet light. Even though the polymerization reaction was conducted at 80° C. at molar ratio of $LiR:TiCl_4 = 2.0$, the incorporated trans stilbene in the polymer could be detected. The filtrate of methanol after separating the polymer on sintered disc of crucible was treated with concentrated hydrochloric acid. The acidified methanol was removed by vacuum distillation under nitrogen. The residual product remaining at the bottom of the flask was extracted with ether and ether from the product was again removed under vacuum and again the product was dissolved in methanol. This solution, intense yellow in colour, was concentrated and left for crystallization. The product separated at the bottom of the flask was found resinous and no pure crystals of trans stilbene could be separated. The resinous product might be oligomers of styrene which might have escaped precipitation. Infrared examination of the product showed a clear absorption band at 964 cm^{-1}, characteristic of trans HC=CH[72] and served to confirm formation of trans stilbene in the reaction system.

Polymerization of styrene with titanium tetrachloride and aluminium triethyl in presence of trans stilbene at 30°C in benzene.

Polystyrene prepared by this system has no blue fluorescence in the ultraviolet light and it is established that the polymer is highly isotactic with high molecular weight. Since trans stilbene could not be isolated from the reaction system of polymerization of styrene with lithium isoamyl and titanium tetrachloride, experiments were carried out with trans stilbene added to $TiCl_4$-$AlCt_3$ catalyst system to reveal any possible effect on the tacticity, rate of polymerization and the molecular weight.

Results are given in the table No.12.

Table No.12.

Styrene = 2.5 ml.   Benzene = 2.5 ml.

$[TiCl_4]$ = .02 M/1 $[AlEt_3]$ = .06 M/1

Molar ratio Al:Ti = 3.0   Reaction time = 2 hours.

[Trans-stilbene] M/1	Yield in gms.	Rpx10^6 M/1/S	% amorphous product	% crystalline product		M.W. x10^{-5}
0	0.09995	3.597	67.83	32.13	0.9868	2.838
0.1	0.15975	5.746	86.42	13.58	0.7543	1.954
0.2	0.15930	5.728	88.33	11.77	0.4095	0.8147

The rate of polymerization was found increased on addition of trans stilbene to polymerization system. The atacticity was increased while the molecular weight was decreased with increasing concentration of trans stilbene.

Another interesting observation is the ultraviolet absorbence of 0.78 in agreement with the literature value.[89] Polystyrene prepared in presence of trans stilbene by $TiCl_4$-$AlEt_3$ catalyst gave absorbence 0.82 at 269 mμ even after two repeated precipitations. The polystyrene prepared by lithium isoamyl titanium tetrachloride catalyst system was found having absorbence of 1.16 at the same wavelength. This increase in absorbence shown in fig.6A, might be considered as the effect of trans stilbene incorporated in the polymer. Actually a mixture of trans stilbene and polystyrene was found to show a large increase in absorbence at the same wave length 269 mμ

Polymerization of styrene with chromium acetylacetonate and aluminium triethyl at 30°C in benzene

Chromium acetyl acetonate reacts immediately with aluminium triethyl in benzene medium and forms a dark brown reaction product. The solution is apparently homogenous.

Ratio studies:

(a) Variation of concentrations of both constituents (CrAcAc and $AlEt_3$):

Chromium acetyl acetonate was taken in the reaction

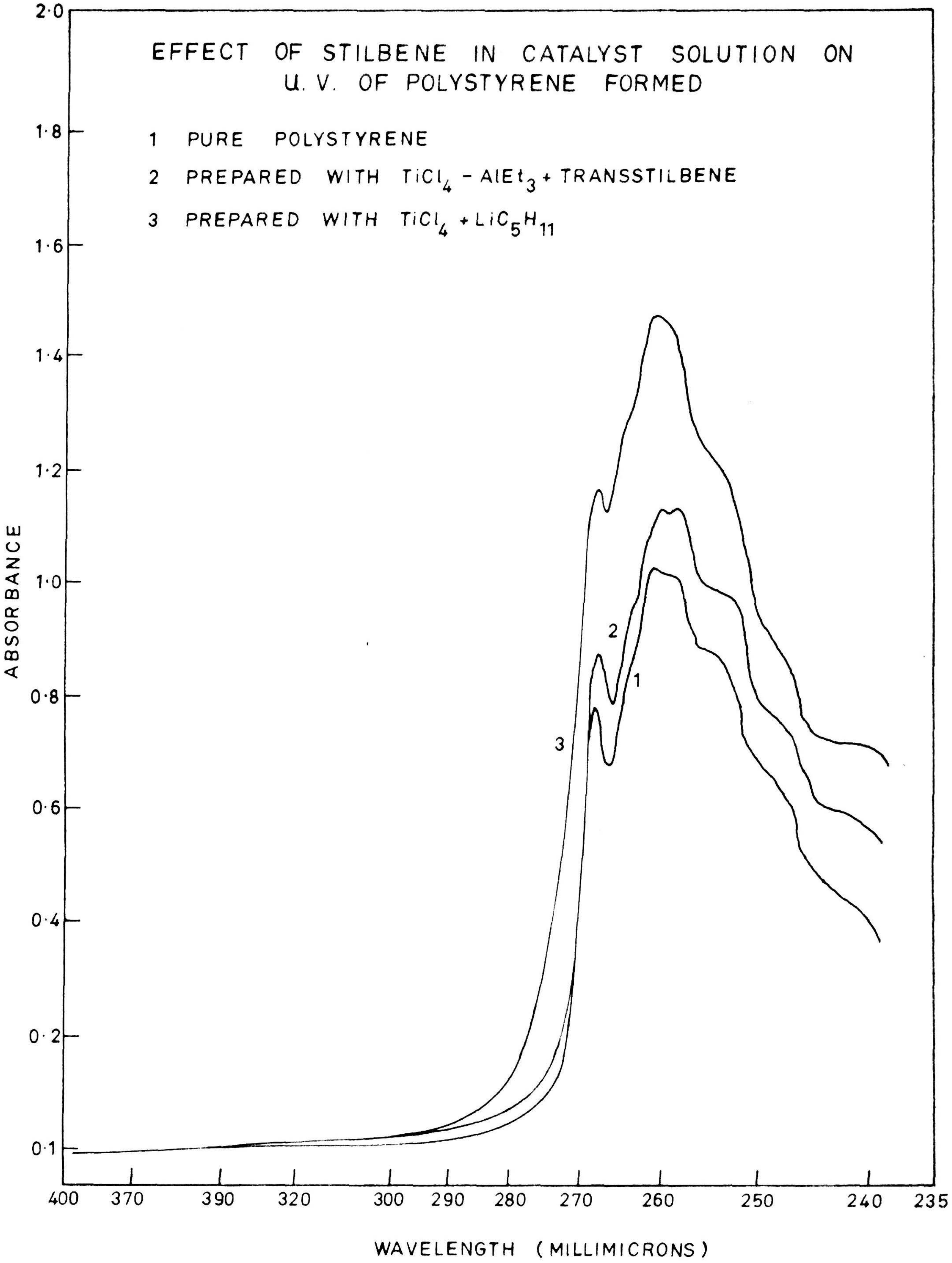

EFFECT OF STILBENE IN CATALYST SOLUTION ON U. V. OF POLYSTYRENE FORMED
1 PURE POLYSTYRENE
2 PREPARED WITH $TiCl_4 - AlEt_3$ + TRANSSTILBENE
3 PREPARED WITH $TiCl_4 + LiC_5H_{11}$
ABSORBANCE
2·0
1·8
1·6
1·4
1·2
1·0
0·8
0·6
0·4
0·2
0·1
1
2
3
400
370
390
320
300
290
280
270
260
250
240
235
WAVELENGTH (MILLIMICRONS)

FIG.-8A

flask and aluminium triethyl added to it. The solution became dark brown. Ageing time of 10 minutes was chosen to obtain catalytic species of constant activity. After ten minutes ageing time, the required amount of styrene was added and polymerizations conducted by varying concentrations of both the components of the catalyst and keeping the sum total of both concentrations constant.

The variation of the catalytic activity for polymerization was studied at various molar ratios of mixing of catalytic components. The molar ratios of aluminium alkyl to chromium acetyl acetonate was varied from 1 to 13. The maximum activity was observed at molar ratio of 3:1 Alalkyl/CrAcAc.

The molecular weight of polymer at this ratio was found minimum compared to the molecular weight of polymers obtained at other ratios.

The results are tabulated in the table No.13, and plotted in Fig. 11.

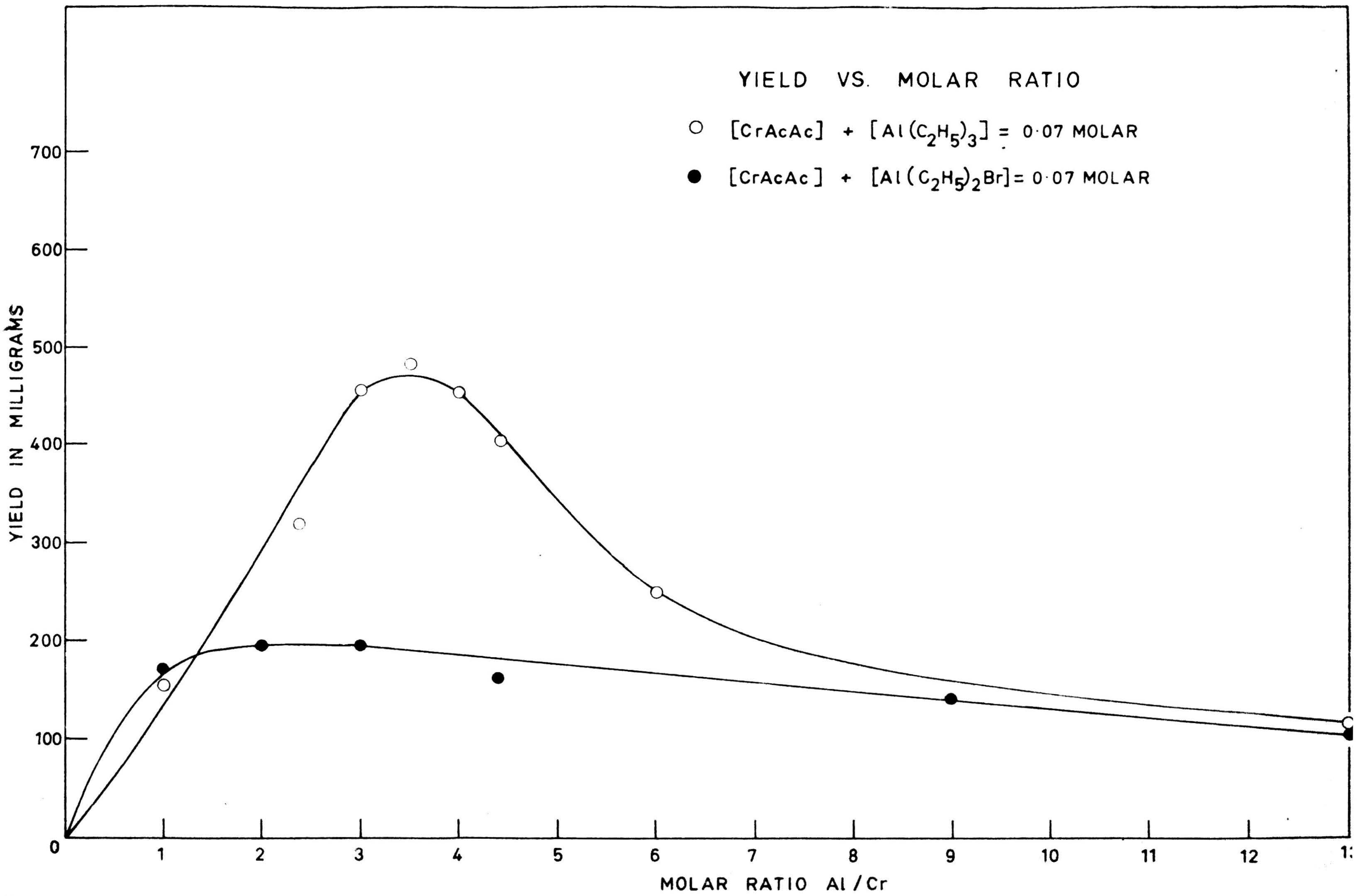

YIELD VS. MOLAR RATIO
○ [CrAcAc] + [Al(C_2H_5)$_3$] = 0·07 MOLAR
● [CrAcAc] + [Al(C_2H_5)$_2$Br] = 0·07 MOLAR
YIELD IN MILLIGRAMS
700
600
500
400
300
200
100
0
1
2
3
4
5
6
7
8
9
10
11
12
1
MOLAR RATIO Al / Cr

FIG. – 11.

Table No.13

Styrene = 10 ml. Benzene = 10 ml. Reaction time = 3 hrs.

Total concentration of catalyst = 7.0×10^{-2}M/1

Ratio Al/Cr	[CrAcAc] $\times10^{2}$ M/1	[Alalkyl] $\times10^{2}$ M/1	Yield in mgm	M.W.	Concentration of complex calculated at the ratio Al/Cr = 3 $\times10^{2}$ M/1
1	3.5	3.5	174.67	56080	1.167
2	2.35	4.65	198.45	33360	1.55
3	1.75	5.25	198.45	33350	1.75
3.5	1.5	5.5	168.95	45160	1.5
4.4	1.3	5.7	186.05	41840	1.3
6	1.0	6.0	160.9	39650	1.0
9	0.7	6.3	121.7	48060	0.7
13	0.5	6.5	106.2	30470	0.5

(b) CrAcAc concentration constant:

The chromium acetyl acetonate concentration was maintained constant and the aluminium triethyl concentration varied so as to have molar ratios of Alalkyl/CrAcAc varying from 1 to 9.

The yield of polymer increased abruptly to a near maximum value at ratio of 3 which was maintained fairly constant even at higher ratio 9 Al/Cr with only slight increase further. The variation of molecular weight at different ratios was studied and it was found decreasing with increasing molar ratio.

The results are given in the table 14, Fig.13.

Table No.14

Benzene = 10 ml. Styrene = 10 ml.

Reaction time = 3 hrs.

Ratio Al/Cr	[CrAcAc]x10^2 M/l	[Alkyl]x10^2 M/l	yield in mgm.	M.W.	$[\text{Altriethyl}]^{1/2}$ x10 $(M/l)^{1/2}$	1/Pn
1	1.0	1.0	78.12	54610	1	0.001914
3	"	3.0	168.9	37970	1.732	0.002749
6	"	6.0	185.3	36180	2.507	0.002887
9	"	9.0	190.0	23510	3.000	0.004442

Percent conversion

The experiments of polymerization were conducted at a fixed molar ratio 3:1 AlR/CrAcAc and the reaction time was varied from 1 to 8 hours. The rate of polymerization was fairly constant upto 3 hours then it decreased slightly.

The molecular weight of polymers at different reaction times did not show any regular variation and was also fairly constant. However all further experiments were carried out for 2 hours reaction time only.

The results are given below in the Table No.15, Fig.10.

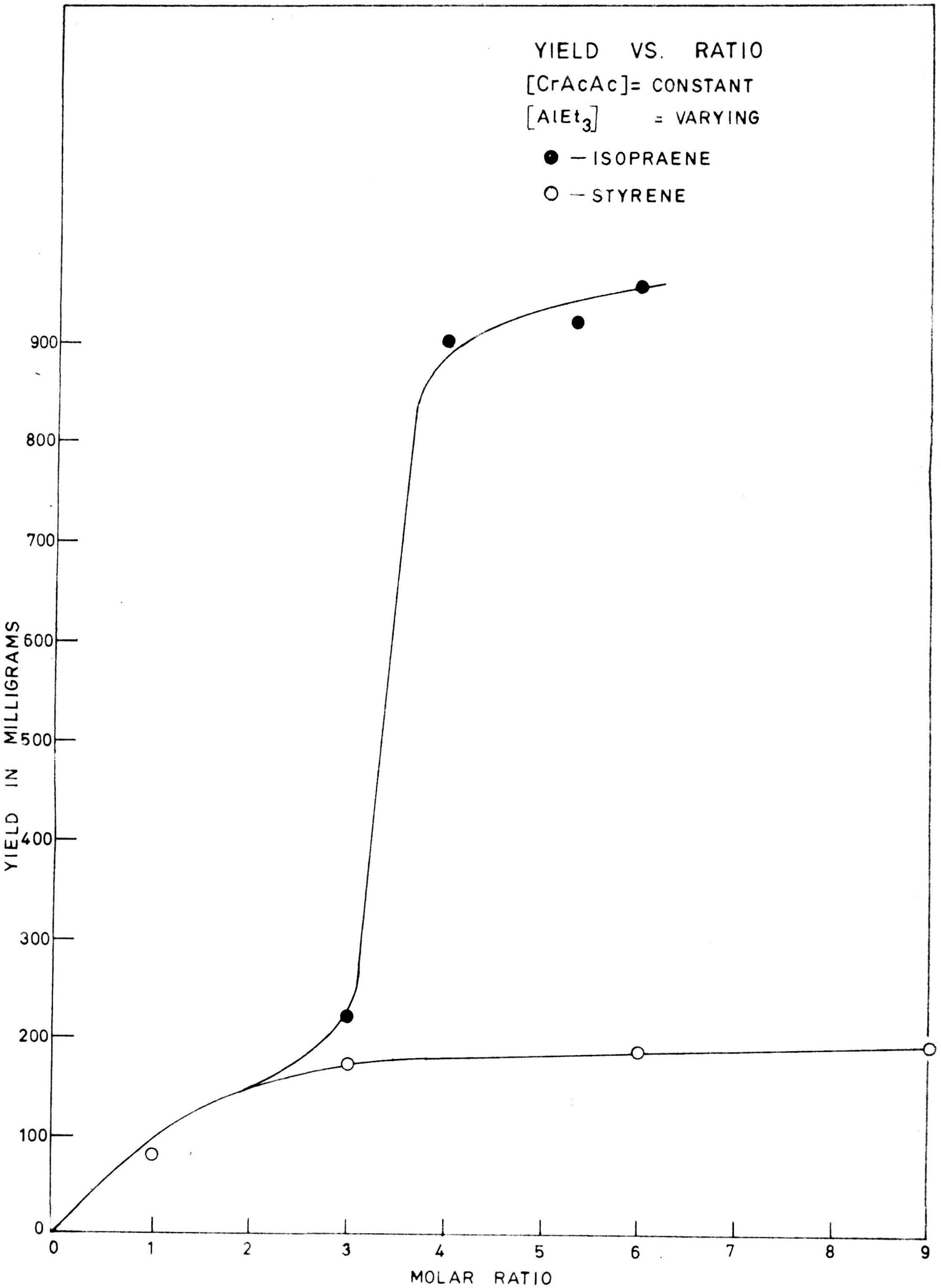

YIELD VS. RATIO
[CrAcAc]= CONSTANT
[AlEt$_3$] = VARYING
● — ISOPRAENE
○ — STYRENE
YIELD IN MILLIGRAMS
0
100
200
300
400
500
600
700
800
900
0
1
2
3
4
5
6
7
8
9
MOLAR RATIO

FIG.-13.

Table No.15

Amount of styrene = 10 ml. Total volume = 20 ml.

$[\mathrm{CrAcAc}] = 1.75 \times 10^{-2}$ M/l $[\mathrm{Alalkyl}] = 5.25 \times 10^{-2}$ M/l

Time in hrs.	Yield in mgm	%	M.W.
2	148	1.639	23150
3	198.4	2.198	33350
4	256.9	2.84	18510
5	263.75	2.92	24820
6	325.6	3.606	21470
8	367.78	4.07	23210

Dependence of rate of polymerization on catalyst concentration and monomer concentration.

The rate of polymerization was studied at a constant molar ratio 3 Al/Cr for different concentrations of the catalyst and the monomer. The rate of polymerization showed half order dependence on Chromium acetylacetonate concentration and first order on monomer concentration. In the studies of molecular weight with catalyst concentration, molecular weight decreased with increasing catalyst concentration and with monomer concentration, molecular weight increased with increasing monomer concentration.

The results are tabulated in the table 16 and 17

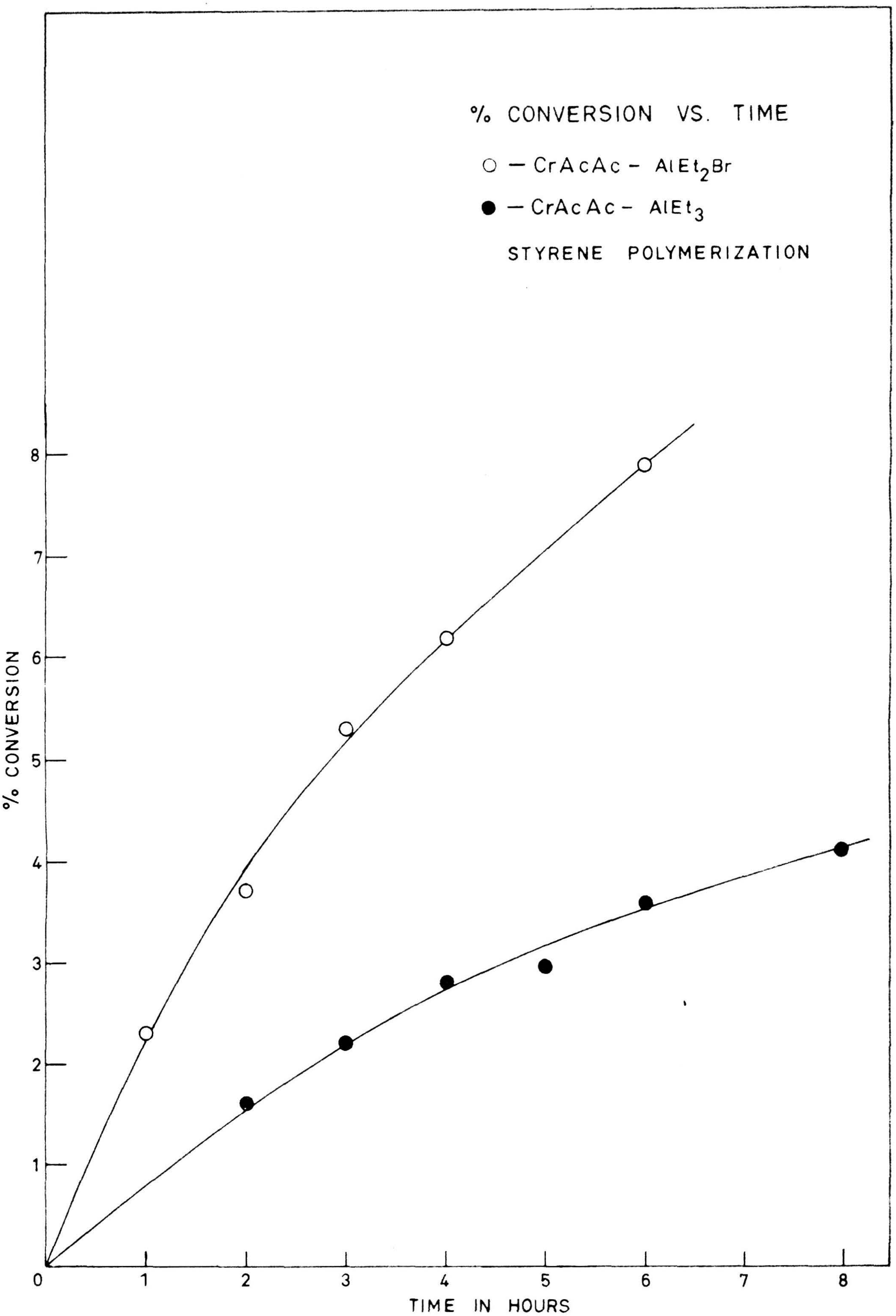

% CONVERSION VS. TIME
○ — CrAcAc – AlEt₂Br
● — CrAcAc – AlEt₃
STYRENE POLYMERIZATION
% CONVERSION
1
2
3
4
5
6
7
8
0
1
2
3
4
5
6
7
8
TIME IN HOURS

FIG. – 10.

and plotted in Fig.14, 15.

Table No.16

Amount of styrene = 10 ml. Benzene = 10 ml.

Reaction time = 2 hours.

[CrAcAc]x10^2 M/l	[Alalkyl]x10^2 M/l	Rpx10^6 M/1/S	M.W.
2.625	7.875	11.86	16440
2.187	6.5625	11.61	16400
1.75	5.25	9.858	23150
0.825	2.625	6.548	22510
0.437	1.312	5.856	41170

Table No.17

Total volume = 20 ml. Reaction time = 2 hours.

[CrAcAc] = 1.75x10^{-2} M/l [Altriethyl] = 5.25x10^{-2} M/l

[Monomer] M/l	Rpx10^6 M/l/S	M.W.
6.054	15.56	20290
4.325	9.858	17000
3.713	8.065	14000
2.16	4.3777	9760
1.08	0.7782	-
0.54	0.3715	-

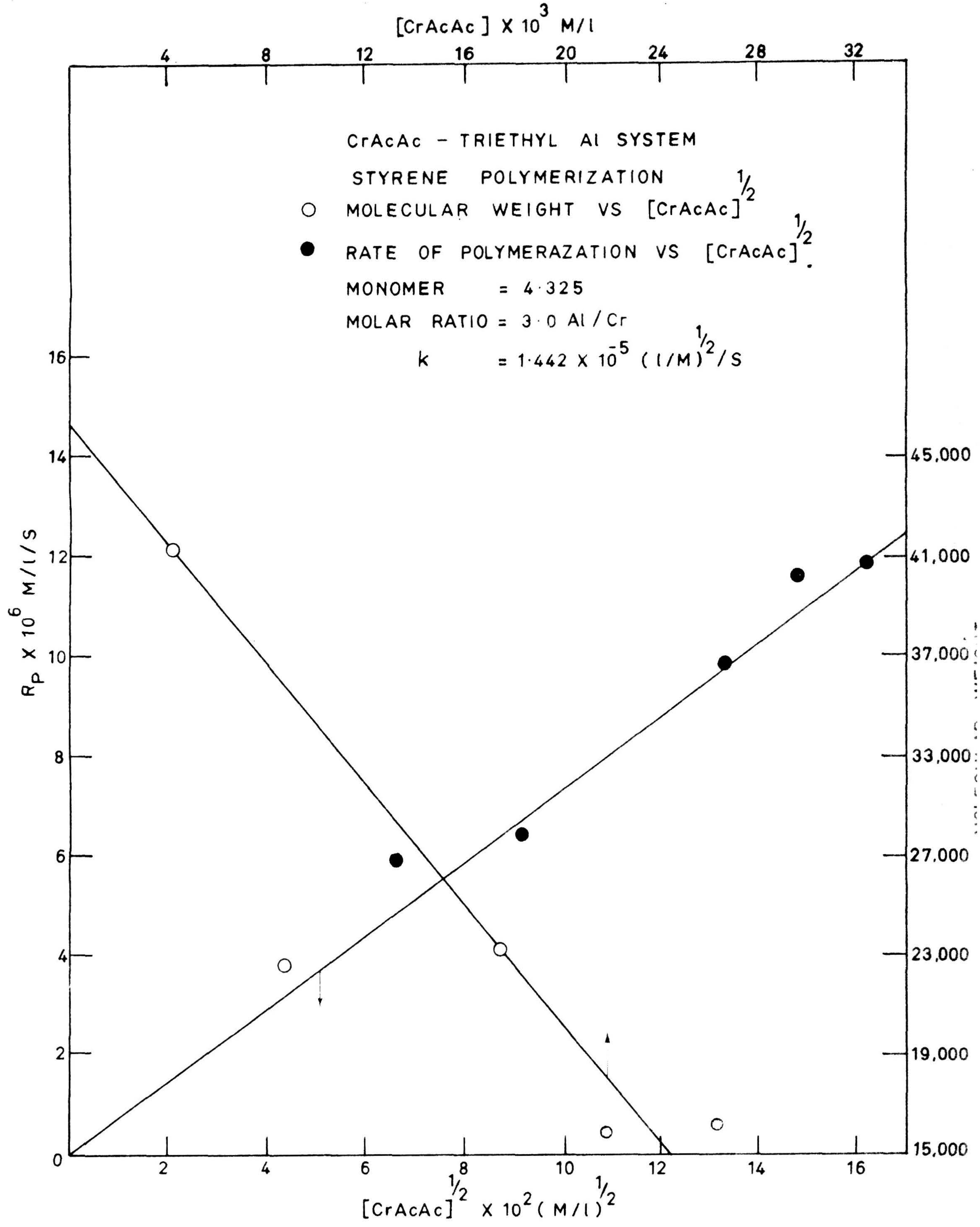
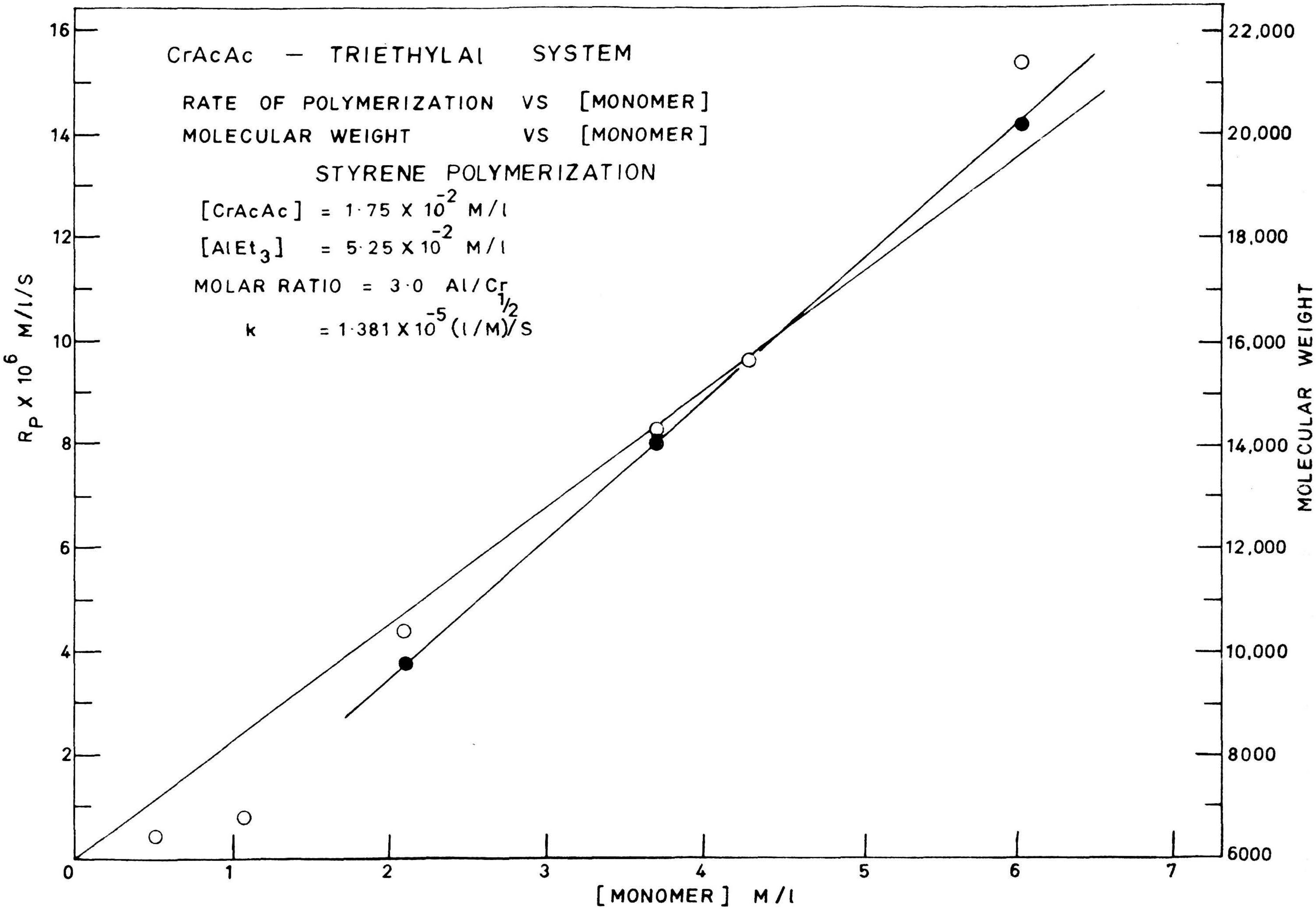

[CrAcAc] X 10^3 M/l
4
8
12
16
20
24
28
32
CrAcAc - TRIETHYL Al SYSTEM
STYRENE POLYMERIZATION
○ MOLECULAR WEIGHT VS $[CrAcAc]^{1/2}$
● RATE OF POLYMERAZATION VS $[CrAcAc]^{1/2}$.
MONOMER = 4·325
MOLAR RATIO = 3·0 Al / Cr
k = $1{\cdot}442 \times 10^{-5}\ (l/M)^{1/2}/S$
$R_P \times 10^6$ M/l/S
0
2
4
6
8
10
12
14
16
15,000
19,000
23,000
27,000
33,000
37,000
41,000
45,000
2
4
6
8
10
12
14
16
$[CrAcAc]^{1/2} \times 10^2\ (M/l)^{1/2}$

FIG.- 14.


CrAcAc — TRIETHYLAl SYSTEM
RATE OF POLYMERIZATION VS [MONOMER]
MOLECULAR WEIGHT VS [MONOMER]
STYRENE POLYMERIZATION
[CrAcAc] = 1·75 X 10^{-2} M/l
[AlEt$_3$] = 5·25 X 10^{-2} M/l
MOLAR RATIO = 3·0 Al/Cr
k = 1·381 X 10^{-5} (l/M)$^{1/2}$/S
R_p X 10^6 M/l/S
0
2
4
6
8
10
12
14
16
1
2
3
4
5
6
7
[MONOMER] M/l
MOLECULAR WEIGHT
6000
8000
10,000
12,000
14,000
16,000
18,000
20,000
22,000

Effect of Trans stilbene

Effect of trans stilbene on the rate of polymerization and the molecular weight was studied. The catalyst and monomer concentrations were kept constant and polymerization conducted at molar ratio 6:1 alkyl/CrAcAc. The rate of polymerization slightly increased and the molecular weight was generally lower in presence of stilbene but definite relation between trans stilbene concentration and molecular weight or rate of polymerization was not noticed.

Results are given in the Table No.18.

Table No.18

Styrene = 10 ml. Total volume = 20 ml.

[CrAcAc] = 1.0×10^{-2} M/1 [Alalkyl] = 6.00×10^{-2} M/1

Reaction time = 3 hours.

(Trans stilbene) M/1	$Rp\times10^{6}$ M/1/S	M.W.
0.02	9.723	30720
0.01	9.506	30370
0.005	9.076	27340
0.0025	9.754	27490
0.0	8.213	36180

Effect of Zinc diethyl

Effect of zinc diethyl was studied on the rate of polymerization and molecular weight. Concentration of zinc diethyl was varied and catalyst concentration was maintained fixed at molar ratio 6:1 AlR/CrAcAc. Monomer concentration was also kept constant. Rate of polymerization and molecular weight decreased linearly with increasing concentration of Zinc diethyl.

Results are recorded in Table No.19 and plotted in fig. 22.

Table No.19

Styrene = 10 ml. Benzene = 10 ml.

[CrAcAc] = 1.0×10^{-2} M/l [Alalkyl] = 6.0×10^{-2} M/l

Molar ratio Alalkyl:CrAcAc = 6. Reaction time = 2 hours.

[Zinc diethyl] M/l	$R_p \times 10^6$ M/l/S	M.W.	1/Pn
0.1	3.921	13570	0.74
0.05	6.474	15190	0.66
0.025	8.149	18310	0.5
0.0125	8.925	18500	0.5
0.0	9.826	36180	0.29

Progress of reaction in presence of zinc alkyl

The concentration of zinc alkyl, catalysts and monomer were maintained constant and the percent conversion upto 4 hours was studied.

Molecular weight remained fairly constant during 4 hours. Results are given in the table No.20.

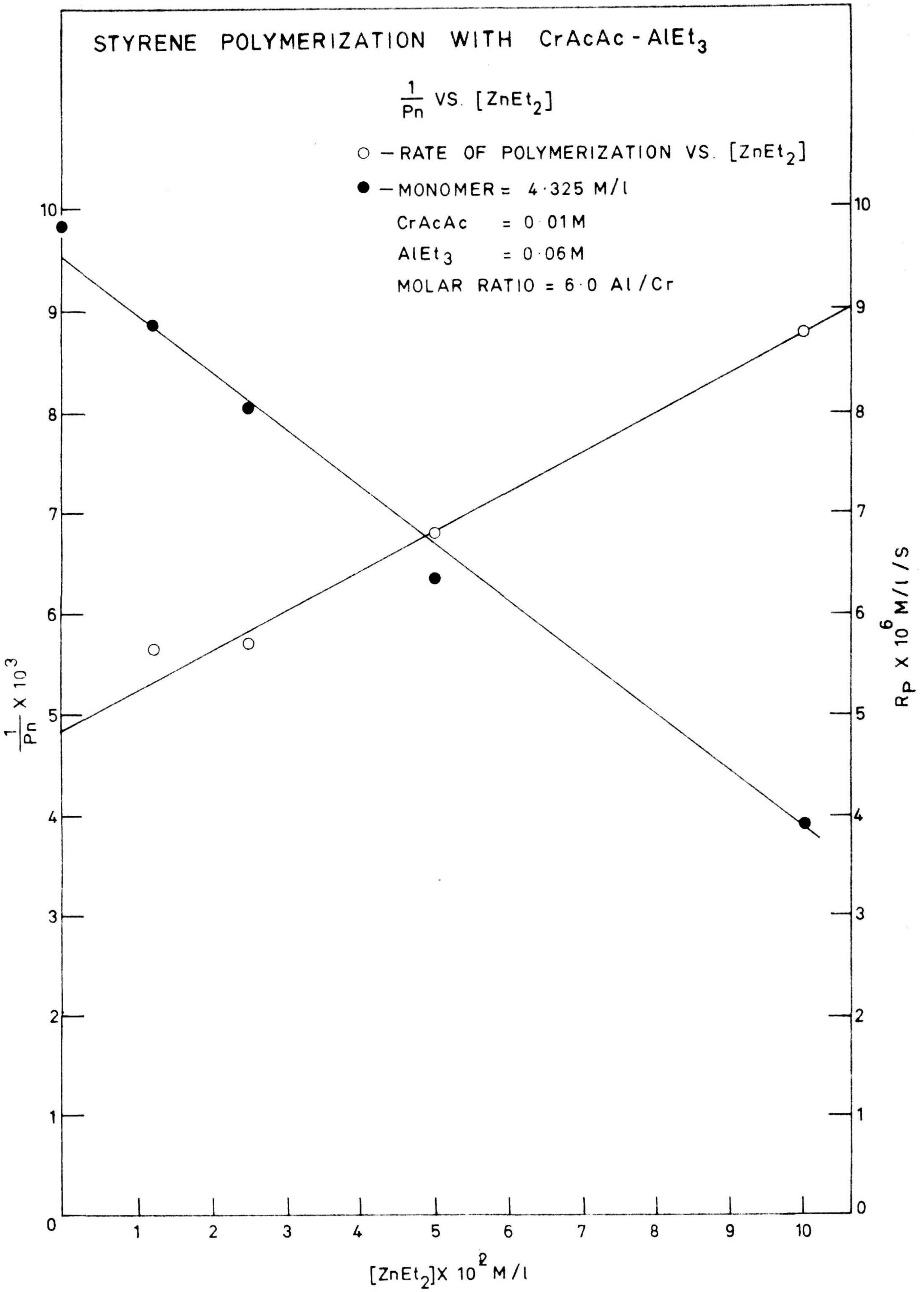

STYRENE POLYMERIZATION WITH CrAcAc - AlEt3
1/Pn VS. [ZnEt2]
○ – RATE OF POLYMERIZATION VS. [ZnEt2]
● – MONOMER = 4·325 M/l
CrAcAc = 0·01 M
AlEt3 = 0·06 M
MOLAR RATIO = 6·0 Al/Cr
1/Pn X 10^3
Rp X 10^6 M/l/S
[ZnEt2] X 10^2 M/l
0
1
2
3
4
5
6
7
8
9
10

FIG.-22

Rate of polymerization was considerably reduced with time.

Table No.20

Styrene = 10 ml. Total amount of solution = 20.0 ml

Reaction time = 2 hrs. [CrAcAc] = 1.0×10^{-2} M/l

[Znalkyl] = .05 M/l [Alalkyl] = 6.0×10^{-2} M/l

Time in hrs.	% conversion	M.W.
2	1.058	15190
3	1.25	14710
4	1.546	15260

Effect of monomer concentration on rate of polymerization and molecular weight in presence of zinc alkyl.

Monomer concentration was varied and other factors like catalyst zinc alkyl were kept constant and effect of monomer concentration on the rate of polymerization and molecular weight in the presence of zinc alkyl was studied. The rate of polymerization and molecular weight increased with increasing monomer concentration.

Table No.21.

Total volume = 20 ml. [CrAcAc] = 1.0×10^{-2} M/l

Reaction time = 2 hrs. [Alalkyl] = 6.0×10^{-2} M/l

[Zinc alkyl] = .05 M/l

[Monomer] M/l	$Rp\times10^{6}$ M/l/S	M.W.
6.054	12.34	21390
4.325	6.474	15190
3.713	3.202	13110

Activation Energy

The rate of polymerization was studied at 30°, 40° and 50°C and the activation energy was calculated from slope of the plot of ln Rp against 1/T as 10.235 Kcal/Mole which is given in the table 22 and fig.23.

Table No.22

Monomer = 10 ml.

[CrAcAc] = 1.75×10^{-2} M/1

[Alalkyl] = 5.25×10^{-2} M/1

Benzene = 10 ml.

Ratio of $\frac{\text{CrAcAc}}{\text{Alalkyl}} = 3.0$

Temperature °C	$Rp \times 10^{6}$ M/1/S	M.W.
30	9.858	23150
40	18.05	14610
50	28.84	20600

Copolymerization studies

At the fixed molar ratio of 5.3 Alalkyl/CrAcAc at 30°C copolymerization of styrene and isoprene was studied.

The polymer isolated even in presence of antioxidants was found to be easily susceptible to gelling, thus vitiating all attempts to estimate proportion of styrene in copolymer solutions by U.V. absorption.

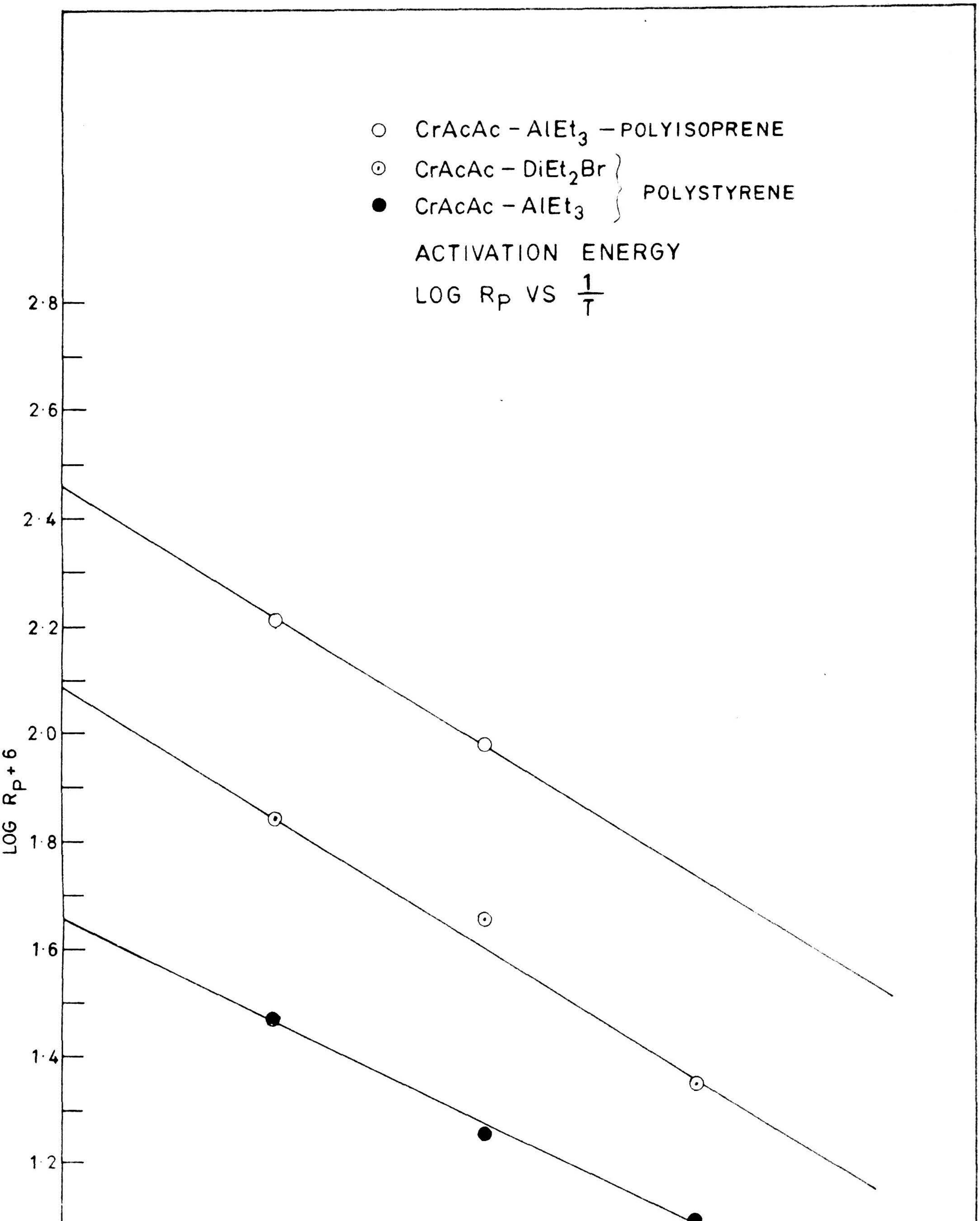

○ CrAcAc – AlEt3 – POLYISOPRENE
⊙ CrAcAc – DiEt2Br
● CrAcAc – AlEt3
POLYSTYRENE
ACTIVATION ENERGY
LOG Rp VS 1/T
LOG Rp + 6
2·8
2·6
2·4
2·2
2·0
1·8
1·6
1·4
1·2
0·90
3·0
3·1
3·2
3·3
3·4
1/T x 10^3

FIG. – 23.

Chromium acetyl acetonate and diethyl-aluminium bromide at 30°C in benzene.

Chromium acetyl acetonate reacted with aluminium diethyl bromide immediately and formed a heterogeneous system.

Similar to chromium acetyl acetonate - aluminium triethyl catalyst system, chromium acetyl acetonate was taken in the reaction flask and aluminium diethyl bromide added to it. Reaction product immediately turned greenish and after 2 or 3 minutes the product precipitated and settled at the borrom while the solution turned dark brown. Due to quick reaction of catalysts components with each other and constant catalytic activity for long time, the ageing time of 10 minutes was conveniently chosen to obtain catalyst complex of constant activity through out the experimental work.

The catalyst was allowed ageing for 10 minutes and the freshly distilled styrene added to it to conduct the polymerization reactions.

Percent Conversion

Percent conversion studies were done during time intervals varying from 1 to 6 hours. The rate of polymerization showed slight tendency of decreasing after 3 hours.

With the progress of the reaction, studies of molecular weights were done.

Molecular weights were found having fairly constant value.

Results are given in the Table No.23 and Fig.10.

Table No.23

Benzene = 10 ml. $[CrAcAc]$ = 1.5×10^{-2} M/l

Styrene = 10 ml. $[AlR_2Br]$ = 5.5×10^{-2} M/l

Molar ratio $AlR_2Br/CrAcAc$ = 3.5.

Time in hours	%	M.W.
1	2.224	17610
2	3.754	19150
3	5.350	15310
4	6.284	15280
6	7.891	20380

Ratio studies

Chromium acetyl acetonate was reacted with diethyl aluminium bromide at different molar ratios of diethyl aluminium bromide to chromium acetyl acetonate varying from 1 to 13. The concentrations of both constituents were varied in such a way as to have the sum total of concentrations of both constant.

The maximum yield of polymerization was observed at the molar ratios of 3.5 AldiethylBr/CrAcAc. The molecular weight of polymer calculated at this ratio was found higher compared to neighbouring ratios but at ratios 6 and 13 it was found considerably high and increasing.

Results are in the Table No.24 and fig. 13.

Table No.24.

Styrene = 10 ml. Benzene = 10 ml.

Total concentration of both constituents = 0.7×10^{-2} M/l

Reaction time = 3 hours.

Ratio Al/Cr	$[CrAcAc] \times 10^2$ M/l	$[AldiethylBr] \times 10^2$ M/l	Yield in mgm	M.W.
1	3.5	3.5	157.25	19800
2.5	2.0	5.0	448.6	16900
3	1.75	5.25	454.0	11250
3.5	1.5	5.5	483.0	15310
4.0	1.4	5.6	453.0	13060
4.4	1.3	5.7	401.0	16670
6.0	1.0	6.0	205.8	32550
13.0	0.5	6.5	110.25	59710

Dependence of rate of polymerization on chromium acetyl acetonate concentration and aluminium diethyl bromide.

Rate of polymerization at fixed molar ratio 3.5 AlalkylBr/CrAcAc was studied with varying concentration of catalyst by keeping monomer concentration constant. Secondly, the catalysts concentration was kept constant and the monomer concentration varied.

The rate of polymerization was observed linear with chromium acetyl acetonate and monomer concentration. Molecular weight of polymers decreased with increasing concentration of chromium acetyl acetonate, unlike this, molecular weight increased with increasing concentration of monomer.

The results are tabulated in the tables 25 and 26 and shown in fig. No.16 and 17.

Table No.25

Styrene = 10 ml. Benzene = 10 ml.

Reaction time = 2 hrs. Molar ratio = $\frac{\text{AlalkylBr}}{\text{CrAcAc}}$ = 3.5

[CrAcAc]x10^2 M/1	[AlalkylBr] x10^2 M/1	Rpx10^6 M/1/S	M.W.
2.25	8.25	27.88	11290
1.8	6.875	26.44	16400
1.5	5.5	22.5	19150
0.75	2.75	12.15	20960
0.375	1.375	2.551	21900

Table No.26

Benzene = 10 ml. Total volume = 20 ml.

[CrAcAc] = 1.5x10^{-2}M/1

[AlalkylBr] = 5.5x10^{-2} M/1 Ratio = 3.5 Al/Cr.

[Monomer] M/1	Rpx10^6 M/1/S	M.W.
6.054	33.43	12810
4.325	22.5	19150
2.163	10.21	4610
1.0815	3.286	2116
0.9294	1.134	888.6

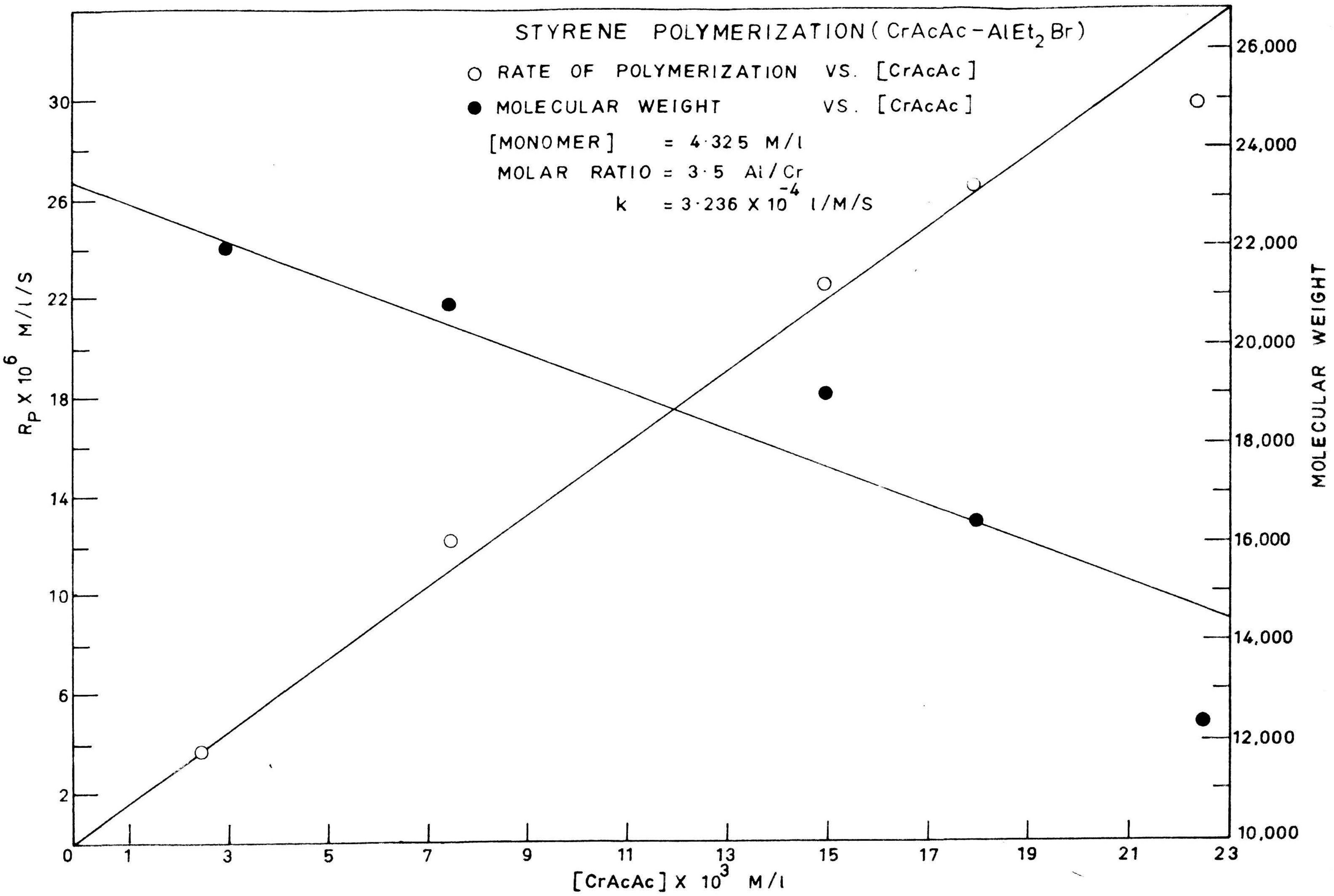

STYRENE POLYMERIZATION (CrAcAc-AlEt$_2$Br)
○ RATE OF POLYMERIZATION VS. [CrAcAc]
● MOLECULAR WEIGHT VS. [CrAcAc]
[MONOMER] = 4·325 M/l
MOLAR RATIO = 3·5 Al/Cr
k = 3·236 X 10^{-4} l/M/S
R_P X 10^6 M/l/S
30
26
22
18
14
10
6
2
0
1
3
5
7
9
11
13
15
17
19
21
23
[CrAcAc] X 10^3 M/l
MOLECULAR WEIGHT
26,000
24,000
22,000
20,000
18,000
16,000
14,000
12,000
10,000

FIG.- 16.

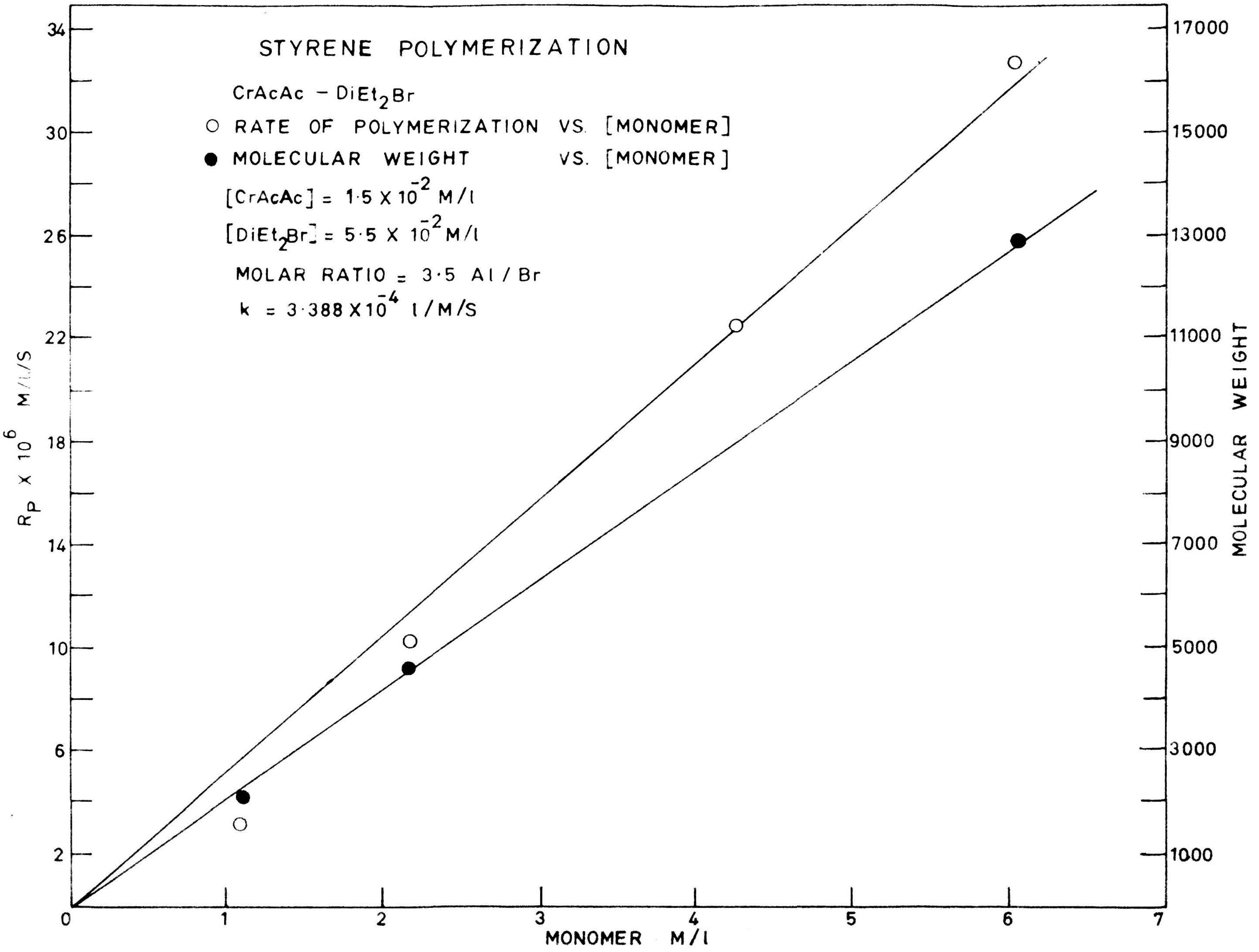

STYRENE POLYMERIZATION
CrAcAc − DiEt$_2$Br
○ RATE OF POLYMERIZATION VS. [MONOMER]
● MOLECULAR WEIGHT VS. [MONOMER]
[CrAcAc] = 1·5 X 10^{-2} M/l
[DiEt$_2$Br] = 5·5 X 10^{-2} M/l
MOLAR RATIO = 3·5 Al / Br
k = 3·388 X 10^{-4} l/M/S
R$_P$ X 10^6 M/l/S
2
6
10
14
18
22
26
30
34
MOLECULAR WEIGHT
1000
3000
5000
7000
9000
11000
13000
15000
17000
0
1
2
3
4
5
6
7
MONOMER M/l

FIG.- 17.

Activation energy

Activation energy of reaction was studied from the rates of polymerization at 30°, 40° and 50°C. Activation energy from the slope of plot of ln Rp against 1/T was obtained as 11.52 kcal/Mole.

The molecular weight of product at different temperatures was found giving no definite relation.

Table No.27 Fig.23

Styrene = 10 ml.

[CrAcAc] = 1.5×10^{-2} M/l

[AlalkylBr] = 5.5×10^{-2} M/l

Benzene = 10 ml.

Molar ratio=3.5 Al/Cr.

Reaction time = 2 hours.

Temperature °C	$Rp\times10^{6}$ M/l/S	M.W.	A.E. Kcal/mole
30	22.5	19150	
40	42.87	8804	10.52
50	59.69	13420	

Polymerization of Isoprene with chromium acetyl acetonate and aluminium triethyl at 40°C.

Since polymerization of isoprene with the same catalyst used in case of styrene was found absent at 30°C, reactions were conducted at higher temperature 40°C and with higher concentrations of catalysts at the molar ratio of 5.3 Alalkyl/CrAcAc.

The order of addition of catalyst components was maintained the same as it was used with styrene polymerization. The ageing time used was also of 10 minutes.

Percent conversion

The reaction of polymerization was conducted with constant catalyst and monomer concentrations at fixed molar ratio 5.3 Alalkyl/CrAcAc for various reaction times changing from 1 to 4 hours. The rate of polymerization was fairly constant and the intrinsic viscosity calculated of the crude products was also fairly constant with time.

The results are tabulated in the table No.28, Fig.18.

Table No.28.

Isoprene = 10 ml.
Benzene = 10 ml.
Ratio = 5.3 Al/Cr
[CrAcAc] = 0.045 M/1
[Alalkyl] = 0.24 M/1

Time in hours	%	$[\eta]$
1	7.021	0.1302
2	13.52	0.1584
3	22.38	0.1482
4	28.72	0.1457

In case of polyisoprene, only intrinsic viscosity was calculated as the polymer may contain mixtures of all structures and every structure would have separate equation for molecular weight relation with intrinsic viscosity.

Ratio studies

The chromium acetyl acetonate concentration was

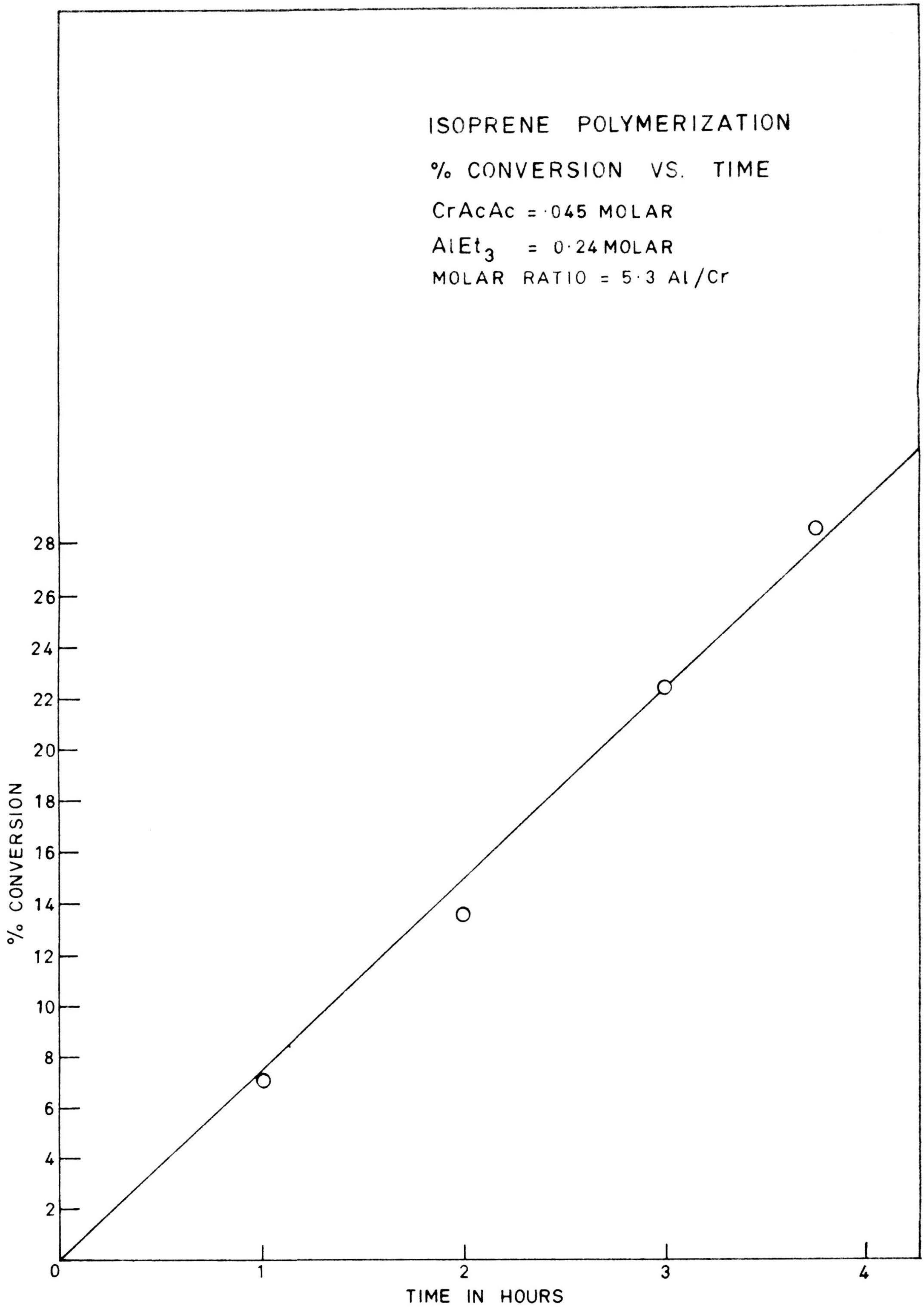

ISOPRENE POLYMERIZATION
% CONVERSION VS. TIME
CrAcAc = ·045 MOLAR
$AlEt_3$ = 0·24 MOLAR
MOLAR RATIO = 5·3 Al/Cr
% CONVERSION
28
26
24
22
20
18
16
14
12
10
8
6
4
2
0
1
2
3
4
TIME IN HOURS

FIG. – 18.

maintained constant and the aluminium alkyl concentration was varied so as to obtain different molar ratios of mixing of catalyst components. The molar ratios were varied from 3 to 6 Alalkyl/CrAcAc.

The sharp increase in yield was found upto ratio 4 Al/Cr and afterwards the yield remained fairly constant upto ratio 6.

The intrinsic viscosity calculated at various ratios was fairly constant.

The results are in table No.29, Fig.13.

Table No.29.

Isoprene = 10 ml. Benzene = 10 ml.

Reaction time = 2 hours.

Ratio Al/Cr	[CrAlkyl] M/l	[Alalkyl] M/l	Yield in mgm	$[\eta]$
3	0.045	0.135	227.2	0.1570
4	"	0.18	906.35	0.1258
5.3	"	0.24	918.35	0.1584
6	"	0.27	953.30	0.1719

Dependence of rate of polymerization on catalyst concentration and monomer concentration.

The rate of polymerization was studied with varying concentrations of catalyst and monomer. The rate of polymerization showed linear relation with catalyst concentration as well as monomer concentration.

Intrinsic viscosity was found increasing with increasing concentrations of catalyst and monomer.

The results are given in the table No.30 and 31.

Table No.30 Fig.19

Isoprene = 10 ml. Benzene = 10 ml.

Molar ratio = 5.3 Alalkyl/CrAcAc.

[CrAcAc] M/l	[Alalkyl] M/l	$Rp \times 10^5$ M/l/S	$[\eta]$
0.045	0.24	9.363	0.1584
0.0375	0.20	12.34	0.08930
0.030	0.16	7.577	0.06841
0.0225	0.12	5.75	0.08226

Table No.31 Fig.20.

Ratio = 5.3 Benzene = 10 ml. Isoprene = 10 ml.

[CrAcAc] = 0.075 M/l [Alalkyl] = 0.24 M/l

Monomer M/l	$Rp \times 10^5$ M/l/S	$[\eta]$
4.997	9.363	0.1584
2.498	4.693	0.07163
1.499	2.504	-

Activation energy

At the fixed molar ratio of 5.3 Alalkyl/CrAcAc and for the same concentration of catalyst and monomer rate of

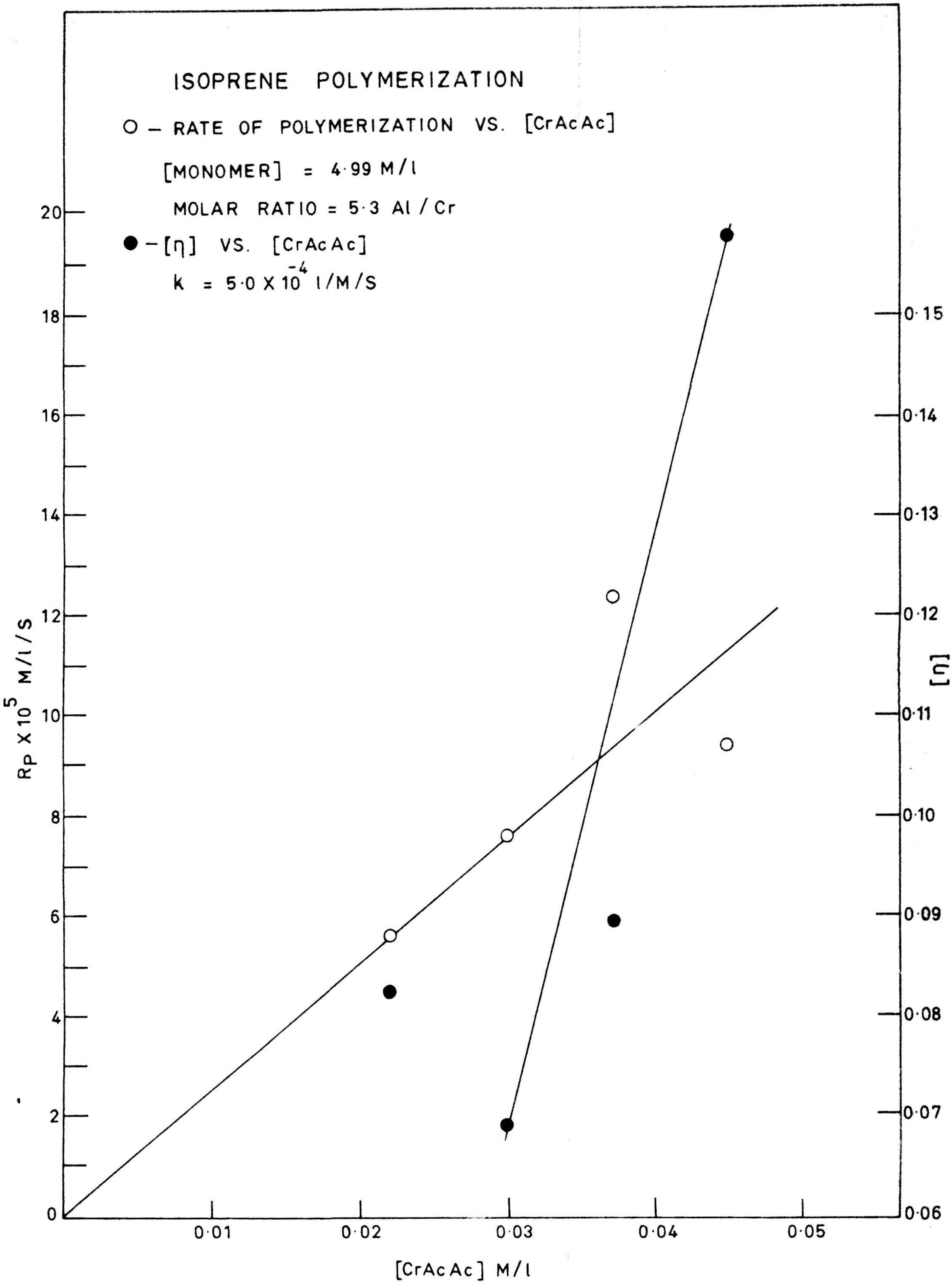

ISOPRENE POLYMERIZATION
○ – RATE OF POLYMERIZATION VS. [CrAcAc]
[MONOMER] = 4·99 M/l
MOLAR RATIO = 5·3 Al / Cr
● – [η] VS. [CrAcAc]
k = 5·0 X 10^{-4} l/M/S
R_P X 10^5 M/l/S
0
2
4
6
8
10
12
14
16
18
20
[η]
0·06
0·07
0·08
0·09
0·10
0·11
0·12
0·13
0·14
0·15
0·01
0·02
0·03
0·04
0·05
[CrAcAc] M/l

FIG.-19.

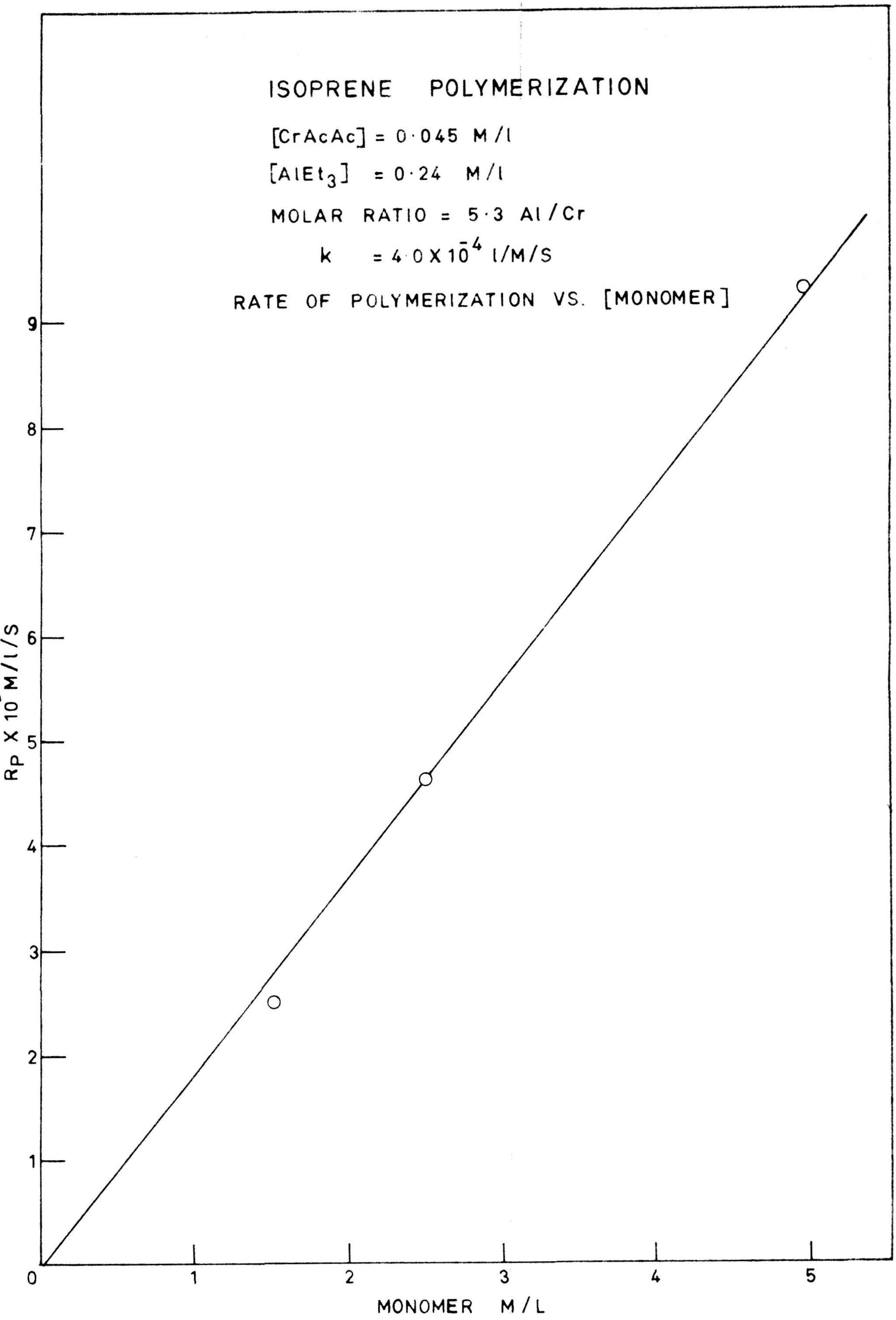

ISOPRENE POLYMERIZATION
[CrAcAc] = 0·045 M/l
[AlEt$_3$] = 0·24 M/l
MOLAR RATIO = 5·3 Al/Cr
k = 4·0 X 10^{-4} l/M/S
RATE OF POLYMERIZATION VS. [MONOMER]
R_P X 10^5 M/l/S
0
1
2
3
4
5
6
7
8
9
MONOMER M/L

FIG.-20.

polymerization was found at temperature 40°C and 50°C and the activation energy calculated from the plot of ln R_p against $1/T$ as 11.52 Kcal/Mole. (Fig.23)

CHAPTER - IV

DISCUSSION

Discussion of Lithium isoamyl Titanium tetrachloride catalyst system.

Reproducibility of Results:

Since the catalyst obtained by reaction of the metal alkyls and the transition metal compounds and used in polymerizations here are extremely sensitive to traces of moisture air and other impurities in solvent and monomer, 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 standardisation of conditions achieved thus could not be considered as thoroughly foolproof, since the particle size of the catalyst precipitate was still an uncontrolled variable and the effect of variable surface area of the heterogeneous catalyst would 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 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 speed of agitation have been reported recently.[90] It was hence necessary to control the stirring of the reaction medium by adjustment of the variable speed of the stirring motor at constant level (1000 rpm).

It was hence gratyfying to find that the results here were generally reproducible to about 5 %. The accuracy of results obtained by other workers,[91,92] with such catalysts are also in this range.

Order of addition:

It is well known that lithium alkyls[14] and Titanium tetrachloride[72] can act individually as initiator for polymerization of styrene which undergoes facile polymerization by all three mechanisms of polymerizations, cationic, anionic and free radical. We confirmed that lithium isoamyl at 10^{-2}M concentration yield 1 gm of polystyrene in half an hour when used alone with 5 ml. styrene in 50 ml. hexane (Table No.1 Page No. 54). So, the complex metal organic catalyst was preformed in hexane by mixing lithium isoamyl with titanium tetrachloride and monomer was added finally. All the results reported thus refer to catalyst prepared in absence of monomer.

The presence or absence of monomer during formation of the catalyst from reaction of the components can have a profound effect on the behaviour of the catalyst. In the case of polymerization of butene,[93] the combinations LiBu - $TiCl_4$ is effective only if the addition is done in presence of monomer. For the polymerization of ethylene, however, the same components functioned effectively when mixed either in presence or absence of the monomer ethylene,[71] though the rate was lower when the catalyst was formed in the absence of ethylene. These differences would imply that the olefin can take part in complex formation and could possibly lead, thus, to catalysts of different structure and reactivity. But these possibilities could not obviously experimentally confirmed with styrene monomer which is readily polymerized by either lithium isoamyl or titanium tetrachloride.

Formation of catalyst species:

There is an immediate formation of light brown to black coloured precipitates on addition of lithium isoamyl to titanium tetrachloride, the colour depending on the amount of the lithium isoamyl added. These precipitates obviously are composed of the various complexes that can be formed with different atomic ratios of lithium to titanium and very likely also differ in the valence state of titanium in them. A series of stepwise reactions, fast or slow, can be visualised leading to different catalytic species which might decompose after different life time.

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[71,93] that the ready reaction of lithium butyl and titanium tetrachloride is essentially complete in about 10 minutes. It can be expected therefore that the reaction of lithium isoamyl with titanium tetrachloride will proceed to completion at comparable rates. Results of polymerization described in (Table No.2, Page No.55) on the effect of ageing of the catalyst from 10 - 30 minutes confirm this and also show that the activity of the stable catalyst complex does not vary during intervals upto 30 minutes. Hence the preformed catalyst complex was aged for 10 minutes in all experiments. Since the polymerization reactions were usually limited to 15 minutes after ageing, it is reasonable to consider that the data pertains to the maximum activity of the catalyst species initially formed. The catalyst activity steadily deteriorated in keeping beyond 1 hour.

Heterogeneous catalyst sites.

The location of active catalyst sites on the precipitated complex could be surmised from the nature of the conversion versus time plots (Fig.1).

It is seen that the initial high activity of the catalyst quickly decreases in less than 20 minutes to a low steady rate which is maintained for times even upto 3 hours (Fig.1. Curve No.3). The initial decrease is probably, not due to deactivation of catalyst but more likely due to clogging of the catalyst surface by the polymer precipitated in the insoluble medium, hexane. The propagation reaction slows down due to lesser availability of monomer at the catalyst sites on the surfaces and when the slow steady rate of polymerization is reached, it is probably entirely controlled by 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 rate of polymerization.

To confirm the validity of this explanation, same catalyst from lithium isoamyl and titanium tetrachloride was prepared in benzene in which polystyrene is easily soluble. Now the conversion versus time curves were linear with the initial catalyst activity maintained without decrease (Fig.1. Curve 5). The same phenomenon can be observed to operate in the experiments on effect of variation of monomer concentration. Initially, a linear relation is observed between rate of polymerization in hexane and monomer concentration. But with increase in styrene content in the medium, the solubility of the polystyrene in the system results in rapid acceleration of the rate of polymerization (Fig.4). Loss of catalytic activity due to deposition of polymer on the catalyst particles has been reported also for styrene polymerization with $TiCl_3$ - $AlEt_3$ catalyst system by Burnett.[92] Photomicrographs taken at various stages of the reaction, in fact, revealed considerable agglomeration of particles bound together by polymer. Recently 3 methyl butene-1 and Butene-1[94] has also been found to yield an insoluble crystalline copolymer with triisobutyl aluminium and titanium trichloride catalyst system and hence 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 Ziegler Martin Catalyst.[95] The rates were found to decrease considerably more rapidly at 20°C than at 60°C. This effect is not expected due to poisoning of the catalytic sites. The reasonable explanation given is the build up of a polymer coating around the catalyst particles and the diffusion ofethylene through high density polyethylene could be a possible rate limiting process if the catalyst is present as a particle larger than 1 to 10μ in diameter. From the sedimentation and filtration behaviour, the agglomerates were reported to be larger than 10μ . The importance of the role of the solvent in desorption or dissolution of the polymer from the catalyst surface to keep the active sites on it accessible and free for renewed propagation reaction is thus evident.

All the available evidence indicates that the reaction of lithium isoamyl with titanium tetrachloride employed in our investigation would result in highly complex mixtures of active sites. Reduction of titanium tetrachloride with metal alkyls generally leads to Ziegler type catalysts which are much less stereospecific than the catalysts prepared by adding metal alkyl to the reduced halide of the transition metal, though higher rates of polymerization are obtained with the former catalysts. With AlR_3-$TiCl_4$ for example, the high degree of polydispersity in the polyethylene produced precludes any formation of a single well defined type of catalyst site. Polystyrene prepared by $TiCl_4$-$AlEt_3$ catalyst has low stereospecificity (about 10 %).[96] The highly stereospecific catalyst of Natta are made from crystalline $TiCl_3$ and $Al(C_2H_5)_3$.

The course of the reaction of lithium butyl with titanium tetrachloride and titanium trichloride has been investigated in detail by M.H.Jones et al.[93] and found to differ considerably in the type of products formed and final valence state of titanium from the reaction of aluminium triisobutyl with $TiCl_4$ and $TiCl_3$. The solid reaction product of the system $TiCl_3$-$Al(Isobutyl)_3$ is shown to be principally $TiCl_3$ fetaining its crystallinity and X-ray diffraction pattern with small quantities of aluminium alkyl adsorbed on it. The system $TiCl_4$-AlR_3 produced more complex products and formation of $TiCl_2$, TiCl etc. in addition to $TiCl_3$, indicated by the low chloride and alkyl content of the solid precipitate. Existence of alkylated titanium compounds with titanium in the valence state of four was also indicated and the catalyst system was thus much more complicated and the following series of reactions could be postulated to account for the products.

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

$$TiCl_3^+ . AlR_3Cl^- \dashrightarrow \left[\begin{array}{ll} \rightarrow TiCl_3 + AlR_2Cl + R^\cdot & (2a) \\ \rightarrow TiCl_2 + AlR_2Cl + RCl & (2b) \end{array}\right\rbrace (2)$$

$$\left.\begin{array}{lll} TiCl_4 + 2AlR_3 \longrightarrow & (TiCl_2R^+)\ AlR_3Cl^- + AlR_2Cl & (3a) \\ & \text{OR} & \\ & (TiCl_2)^{2+} . (AlR_3Cl)_2^= & (3b) \end{array}\right\rbrace (3)$$

$$(TiCl_2)R^+ . (AlR_3Cl)_2^= \dashrightarrow \left[\begin{array}{ll} \rightarrow TiCl + AlR_2Cl + RCl + R^\cdot & (4a) \\ \text{or} & \\ \rightarrow TiCl_2 + AlR_2Cl + 2R^\cdot & (4b) \end{array}\right\rbrace (4)$$

Decomposition reactions (2) and (4) can account for loss of alkyl or chlorine and the presence of ethyl chloride in $AlEt_3$-$TiCl_4$ system has been reported by Malatesta.[41a] However, the high Ti^{iv} content of the analysis could not be based on the scheme of reactions shown above.

The addition of lithium butyl to $TiCl_3$ in contrast to the behaviour observed with aluminium alkyl leads to the formation of greenish precipitates containing two component as evidenced by X-ray diffraction pattern. One had a NaCl type cubic lattice with a lattice constant of 5.2 A° which is higher than that of LiCl which is 5.14 A°. The line intensities of LiCl are different from those of the cubic component which is supposed to be a mixed crystal of lithium and titanium chlorides of probable composition $(LiCl_n).TiCl_2$ and $(LiCl_n)TiCl$. The pattern of the second component could not be identified with certainty but is thought to be an alkylated compound due to its higher symmetry.

Reaction of lithium butyl with $TiCl_4$ yielded jelly like precipitates of brown colour with no crystalline component below molar ratio of $LiBu/TiCl_4$ of 1. But at higher ratios of Li/Ti, two broad lines were observed in the position of the two main lines of the cubic component observed in the reaction of $TiCl_3$ with LiBu. The mixed crystals of Li and Ti chlorides are possibly formed in this case also. The chlorine to titanium ratio in the solid precipitates was 3 - 3.5 which is much higher than the atomic ratio observed in the aluminium-titanium systems and Li : Ti ratio in the solid also increased with the ratio of Lithium butyl to Titanium halide e.g. from 1.34 at LiR/Ti = 0.5 to 2.06 at LiR/Ti = 2 employed in the reaction which is again at a higher level than that observed in the Al-Ti system.

The alkyl content in the precipitate was, however, quite low. R : Ti was between 0.5 - 0.86 and R : Li was from 0.18 - 0.65. Loss of alkyl radicals from the precipitate is confirmed by the isolation of butane and butene in the gaseous products evolved. All these observations can stem from the presence of LiCl as an intimate component with reduced titanium halides in the precipitate. Since lithium is considerably more electropositive, it is probable that titanium is bound in complex anions. Based on the suggestions of Uelzmann[57] for AlR_3 - $TiCl_4$, the following reactions could be written for LiBu - $TiCl_4$.

$$\text{I.}\quad LiR+TiCl_4 \longrightarrow Li^+\,(TiCl_4R)^- \begin{array}{ll} \nearrow LiCl.TiCl_3+R^\cdot & \quad (5a) \\ \searrow LiCl.TiCl_2+RCl & \quad (5b) \end{array}$$

$$\text{II.}\quad 2LiR+TiCl_4 \longrightarrow (Li^+)_2(TiCl_4R_2)^= \begin{array}{ll} 2LiCl.TiCl_2+2R^\cdot & (6a) \\ 2LiCl.TiCl+RCl+R^\cdot & (6b) \end{array}$$

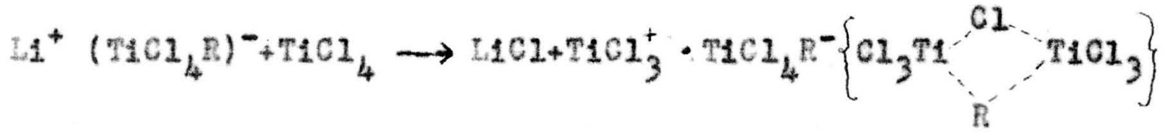
Analogous reactions with $TiCl_3$ can be written as

$$\text{III.}\quad LiR+TiCl_3 \longrightarrow Li^+\,(TiCl_3R)^- \longrightarrow LiCl.TiCl_2+R^\cdot \qquad (7)$$

$$2LiR+TiCl_3 \longrightarrow Li_2{}^+(TiCl_3R_2)^= \longrightarrow 2LiCl.TiCl+2R^\cdot \qquad (8)$$

The existence of tetravalent titanium according to the above scheme, is entirely as $Li^+\,(TiCl_4R)^-$ complex or $(Li^+)_2(TiCl_4R_2)^=$, but this conflicts with the poor alkyl content to titanium (ratio of 0.5 - 0.86 R:Ti) and high Ti^{iv} value, experimentally found by Jones. It has been offered as an explanation that Ti^{iv} is formed in the hydrolysis step preceeding analysis from complex anions and cations of Ti of valency less than three.

It is conceivable again as Uelzmann has postulated that $Li^+ (TiCl_4R)^-$ reacts with $TiCl_4$ as follows to form a dimeric tetravalent titanium complex

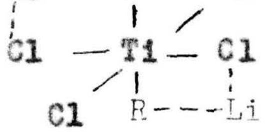


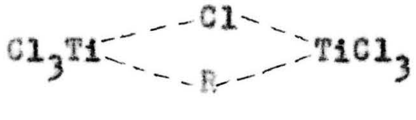
$$Li^+ (TiCl_4R)^- + TiCl_4 \longrightarrow LiCl + TiCl_3^+ \cdot TiCl_4R^- \left\{ Cl_3Ti \begin{smallmatrix} Cl \\ \\ R \end{smallmatrix} TiCl_3 \right\}$$

.... (9)

and this can in some measure also cause low R:Ti with high Ti^{iv} content.

It is thus seen that as solid substrate mixed crystals of Ti and Li are formed along with another unidentified component which is probably an alkylated compound and the possibility of formation as indicated in the above reaction schemes, of many other complexes of Ti and Li, soluble and insoluble, which may be adsorbed on the surface of the halide precipitate, leads to a situation where it is difficult to describe the initiating species except in the most general terms. Taking into consideration the evidence described later, it can only be said that initiation occurs most probably at a metal carbon bond, either Ti-C or Li-C of an organometallic complex present in the surface of the precipitated catalyst system e.g.





$$Cl_3Ti \begin{smallmatrix} Cl \\ \\ R \end{smallmatrix} TiCl_3$$

The variation of rate of polymerization with molar ratio of Li/Ti in the catalyst lends evidence to the supposition that polymerization occurs by reaction of strongly adsorbed metal alkyl with weakly adsorbed monomer. Treating this system on the basis of a Langmuir Hinshelwood type mechanism.

If θ & θ^1 are the fractions of the surface covered by metal alkyl and monomer respectively

$$\theta = \frac{K^1[A]}{1+K^1[A]+K[M]} \tag{10}$$

M - Monomer

A - Alkyl

K^1 - Adsorption constant of alkyl

$$\theta^1 = \frac{K[M]}{1+K[M]+K^1[A]} \tag{11}$$

K - Adsorption constant of monomer

If [S] is the concentration of active sites, rate of polymerization is given by

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

For a weakly adsorbed monomer we get

$$R_p = \frac{kKK^1[A][M][S]}{(1+K^1[A])^2} \tag{13}$$

k - Rate constant

Accordingly as the concentration of alkyl (in our case lithium isoamyl) is increased, a maximum should be observed in the rate, after which as the more strongly adsorbed alkyl displaces the monomer molecules, the rate would drop down.

The shape of the curve (Fig. 2) with maximum rates at molar ratio Li:Ti = 2 is as predicted by this equation.

Similar relationship has been observed in case of polymerization of Isoprene with Titanium tetrachloride and triisobutyl aluminium where maximum ratio of polymerization is at molar ratio Li/Ti = 1.25. This has been interpreted as shown above on the basis of operation of Langmuir Hinshelwood type mechanism.[61] Such a relationship has been observed with many Ziegler catalysts when $[M]$ is kept constant and $[A]$ is varied and the rate of polymerization passes through maximum and then decreases as the more stronger adsorbed reactant displaces the other.

It is relevant now to compare our results with the recent findings of Tsou et,al.[74] on the polymerization of styrene by using a similar catalyst system, Lithium butyl $TiCl_4$ which was published when our studies had mostly been completed.

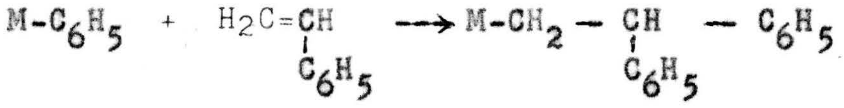
The investigation of Tsou et,al. were mainly concerned with the influence of molar ratio of $LiBu/TiCl_4$ on yield, molecular weight and tacticity of the polymer formed; but rates were not measured and the kinetics of the polymerization not studied. The conversions during

20 hours (at 40°C) were however measured and when the total yield of polymer was plotted against Li/Ti ratio where ($TiCl_4$) was constant, two maxima were observed in the curve; one at 1.5 Li/Ti and another at 2.2. When the experiments were conducted at 80°C, one more maxima appeared at 2.7 Li/Ti. This might arise from a change in the nature of the active catalyst at different temperatures.[74,51,97] In our experiments with lithium isoamyl and titanium tetrachloride, only a small plateau is observed at ratio $\sim$ 1.5 Li/Ti but not a well defined maximum which occurs only at $\sim$ 2 Li/Ti. It is useful to mention now that the experiments were done at 30°C and the times were very short, only 15 minutes. Compared to 20 hours allowed in Tsou's experiments at 40°C, If the change in the nature of the catalyst is brought about by a slow reaction dependent on the time and temperature, it is readily understandable that the maximum at 1.5 was not observed clearly in our curve for 30°C. It is obvious that both systems LiBu-$TiCl_4$ and Liisoamyl-$TiCl_4$ produce mostly only amorphous polystyrene and the molecular weight of the polystyrene is very low 3000 - 6000. But Tsou et. al.[74] have found a general increase in the molecular weight to 45000 at Li/Ti = 2 and a very sharp increase at 2.25 and 2.7 (170900 and 208000) and very small amounts of isotactic polystyrene e.g. 1 gm in total polymer yield in 20 hours varying upto 2.5 gms. Beyond molar ratio 3.6 at 40°C, the poor

capacity of the catalytic systems from Lialkyl-$TiCl_4$ to produce stereospecific polymers seems to be thus clearly established, since with lithium butyl-titanium tetrachloride also, even the small amount of isotactic polymer could not be observed to be formed even in experiments which were conducted upto 20 hours at 30°C. The molecular weight of the polymer was higher at 80°C and considering the fact that a new maximum appears at 3.6 Li/Ti at 80°C and molecular weights of polymer at Li/Ti, in the range of Li/Ti = 3 to 5, are much higher than at lesser Li/Ti ratios, it seems to be indicated that this effect is also due to change in the nature of catalyst with temperature.

Since, generally, high molecular weight and stereospecific polymers are formed with metal organic catalysts, the formation of only low molecular weight amorphous polystyrene is in the range of Li/Ti upto 1.75 lead Tsou et.al. to suggest a cationic mechanism of polymerization with LiBu-$TiCl_4$ in this range. They have further suggested that pure anionic mechanism operates at Li/Ti=2.7 and in between 1.75 - 2.7 Li/Ti an anionic coordinated mechanism operates. Similar reasoning led Natta et.al.[98] to suggest the formation of more amorphous polymer with very little isotactic polymer of styrene using $AlEt_3$ - $TiCl_4$ of cationic and anionic mechanism respectively.

However, it must be pointed out that the formation of amorphous polystyrene does not necessarily imply cationic mechanism. There is much to favour the view that the metal organic synthesis resulted high molecular weight polymer by the anionic coordinated mechanism using Ziegler type catalyst, can sometimes with certain combinations of metal alkyl and transition metal compound lead to low molecular weight amorphous polymer by the same mechanism of growth at a metal carbon bond. It has unambigously, been shown in the case of polymerization of styrene with phenyl MgBr-$TiCl_4$ system[91] that the low molecular weight polymers formed carried the phenyl group of phenyl MgBr as end group. This must surely arise from initiation of polymerization at

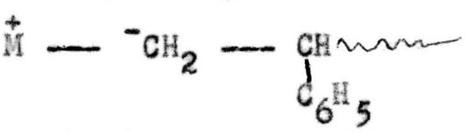


$$M-C_6H_5 + H_2C=\underset{C_6H_5}{\underset{|}{CH}} \longrightarrow M-CH_2-\underset{C_6H_5}{\underset{|}{CH}}-C_6H_5 \qquad (14)$$

Under our experimental conditions of Li/Ti = 1.5, the presence of free $TiCl_4$ is not a likely possibility since even at 1.55 Li/Ti it has been shown by Evans A.G.[99] that free $TiCl_4$ is completely absent. In the presence of excess LiR the formation of TiOH species by hydrolysis of Ti compounds by trace moisture in the monomer can also be discounted.

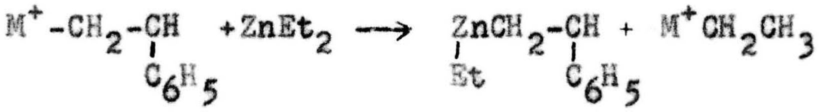
Further, the overall activation energy observed with this polymerization system 2.05 kcal/mole.(fig.7) does not support the occurrence of cationic mechanism. The value for cationic polymerization of styrene by $TiCl_4$ is about -2 to -8 kcal/mole[72] is much lower than that observed here, viz. (2.05 kcal/mole) and there is no reason to suppose that a heterogeneous cationic mechanism will result in higher activation energy. This value of 2.05 kcal/mole is admittedly much lower than than that usually observed with Ziegler type catalyst ($\sim$ 10-14 kcal/mole). However with certain systems like $AlEt_3$ - $TiCl_4$ and $AlEt_3$ - $TiCl_3$, in case of ethylene and propylene polymerization at low temperature, activation energy is in the same range of 2.5 kcal to 5 kcal[100] and values closed to the observed activation energy here have been obtained. It is true that the observed overall activation energy E is related to so many reactions occurring with the complex catalyst and comparisons of such a composite quantity cannot be strictly accurate. But it is very difficult also to neglect the strong evidence that the fair agreement provides for a mechanism similar to that of Ziegler catalyst.

Again, the lowering of molecular weight of polymers by added Zinc diethyl discussed in detail below is also typical of the behaviour observed with Ziegler type catalyst. (Table No.8. fig.9) shows clearly that molecular weight is inversely proportional to Zinc diethyl. The molecular weight of the polymers obtained in the presence of added Zinc diethyl (0.005 to 0.1 M) is reduced proportionately to the concentration of Zinc diethyl. This is the same relationship as obtained for polypropylene polymerized by $AlEt_3$ - $TiCl_3$ with Zinc diethyl,[101] the highly stereospecific catalyst for production of isotactic polypropylene. Representing the growing centre as polarized metal alkyl bond,



$\overset{+}{M} — {}^{-}CH_2 — \underset{C_6H_5}{CH}\sim\sim$

the reduction of molecular weight is accounted by (a molecular chain termination-kinetic chain transfer) an alkyl exchange reaction with Zinc diethyl, whereby the growing polymer chain is transferred to the Zinc alkyl in solution from which one C_2H_5 group has been exchanged to the catalytic site.



(15)

$$M^{+}\text{-}CH_2\text{-}\underset{C_6H_5}{CH} + ZnEt_2 \longrightarrow \underset{Et}{Zn}CH_2\text{-}\underset{C_6H_5}{CH} + M^{+}CH_2CH_3 \qquad (15)$$

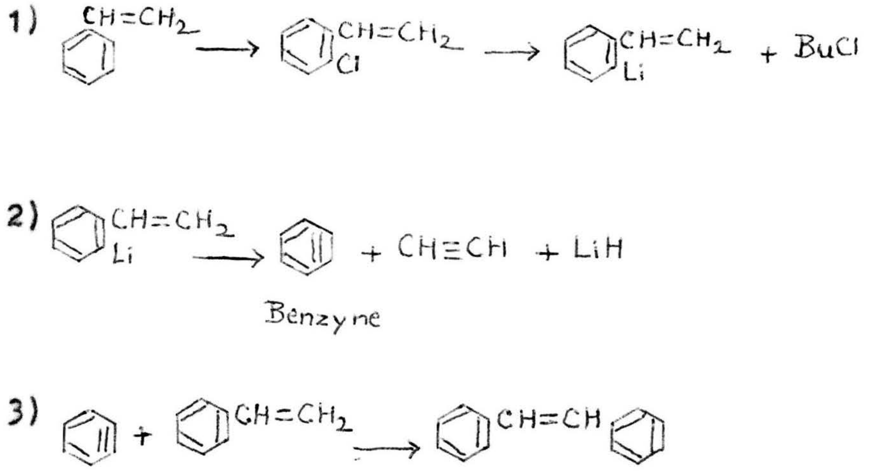
The molecular weight is thus reduced but the chemical structure of the catalyst site - viz. a metal alkyl system is preserved and hence the catalytic activity also.

It seems then that a cationic growing end is very improbable in our system.

It is relevant to point out that the presence of metal halides with $TiCl_4$ as mixed crystal has been found to result in lowering of stereospecificity, molecular weight and increase of rate. Addition of metal halides such as $AlCl_3$, $ZnCl_2$ or $FeCl_2$ as mixed crystals with $TiCl_3$ or $TiCl_2$ increases the rate of polymerization of propylene considerably.[102] Reduction in molecular weight and crystallinity of products may also occur, however, halides such as $FeCl_2$ reduces the crystallinity greatly, presumably the result of less effecient orientation of monomer molecules in the vicinity of catalyst site.[102]

Formation of Stilbene:

An important observation made by Tsou et.al.[74] is the formation in the polymerization reaction mixture of stilbene which was isolated from the filtrate after removal of polymer by precipitation with methanol. It was suggested that it might be formed via benzyne intermediate as follows:

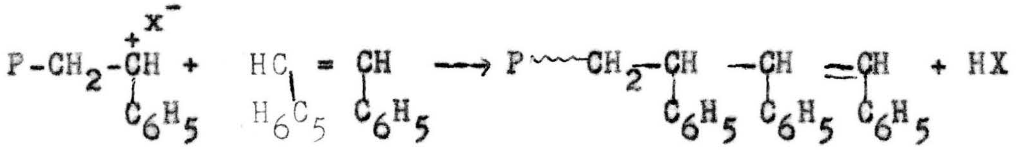


While this appears very plausible, it is difficult to visualise free $TiCl_4$ present when Lithium alkyl is 4-5 times in excess of $TiCl_4$ taken and even at Li/Ti = 5.4 stilbene is formed. We could confirm formation of trans stilbene in our experiments with Lithium isoamyl-titanium tetrachloride, though it could not be isolated as a crystalline product. However, the resinous residue obtained on evaporation of filtrate after removal of precipitated polymer showed absorption bands in IR spectra, characteristic of stilbene (monosubstituted benzene 698 and 760 cm^{-1} (13.2 and 14.3 μ) and trans unsaturations 964 cm^{-1}).[72]

The polystyrene from this system even after several reprecipitations had a strong blue fluorescence as reported by Tsou and the I.R. also showed band for trans unsaturation (974 cm^{-1}) and Para substitution.

It is hence very likely that the stilbene unit is incorporated in the polymer to provide a conjugated system which will result in fluorescence.

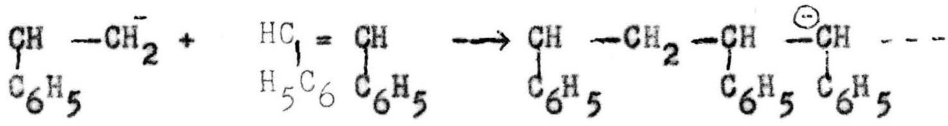
Again Tsou et.al. suggest two mechanisms, cationic (1) and anionic (2) for incorporation of stilbene unit as a polymer end group via chain transfer step similar to that suggested by Overberger[101] and Plesch.[62]



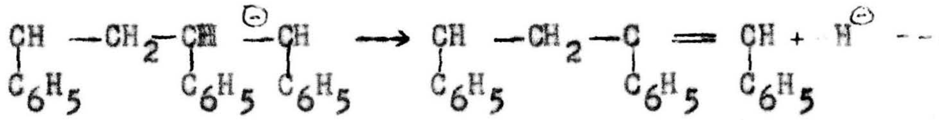
$$P-CH_2-\underset{C_6H_5}{\overset{+\,X^-}{CH}} + \underset{H_6C_5}{HC} = \underset{C_6H_5}{CH} \longrightarrow P\sim CH_2-\underset{C_6H_5}{CH}-\underset{C_6H_5}{CH}=\underset{C_6H_5}{CH} + HX \qquad (16)$$

Since it has been shown that $CH = \underset{C_6H_5}{CH}$ (1) is ortho para disubstitution in electrophilic substitution,[103] the above mechanism bending to disubstituted product stands confirmed.

On the other hand, trans-stilbene could first copolymerize with an anionic growing polymer chain and then termination could occur by hydride transfer as follows



$$\underset{C_6H_5}{CH}-\overset{-}{CH_2} + \underset{H_5C_6}{HC} = \underset{C_6H_5}{CH} \longrightarrow \underset{C_6H_5}{CH}-CH_2-\underset{C_6H_5}{CH}-\underset{C_6H_5}{\overset{\ominus}{CH}} \;---\; (17)$$



$$\underset{C_6H_5}{CH}-CH_2-\underset{C_6H_5}{CH}-\underset{C_6H_5}{\overset{\ominus}{CH}} \longrightarrow \underset{C_6H_5}{CH}-CH_2-\underset{C_6H_5}{C}=\underset{C_6H_5}{CH} + H^{\ominus} \;---\; (18)$$

This would be in accordance with the observations, that yield of polymer were not reducéd under conditions (variation of lithium alkyl concentration) when large amounts of stilbene were formed, but only molecular weights were very low. Obviously the kinetic chain is not terminated considerably. The metal hydride can initiate polymerization again.

The slight shift observed in the fluorescent maximum of the polystyrene compared to that of trans-stilbene would also warrant consideration of the above mechanism.

It was of interest hence to study the effect of trans stilbene on the course of polymerization with the classical Ziegler catalyst, AlR_3-$TiCl_4$. The results have been rewarding (Table No.12. Page No.). The reduction in molecular weight of polystyrene brought about by increasing concentrations of trans stilbene is clearly noticeable. We have also tried to find the effect of stilbene on the proportion of crystalline polymer formed. (Table No.12). Hence, the increasing amount of amorphous polystyrene formed in the presence of trans stilbene is evident. The results definitely show that stilbene can effect a reduction of molecular weight of the polymer growing by anionic coordinated mechanism favouring equationsNo.17 and 18 above.

The fluorescence of the polymer was not, however strong enough to be unambiguously proved certain by visual observation.

It is also observed that the rates of polymerizations are accelerated considerably by the presence of trans stilbene.

The reduction in the molecular weight and crystalline polymer with a concurrent acceleration of rate brought about by trans stilbene can be compared to the same effect resulting from the addition of ether to Alfin catalyst.[104] The 2 % addition of diethyl ether in hexane medium reduced the crystallinity of the polystyrene from a high to a low value.

This is a very strong indication of complexing at the catalyst surface of the added reagent.

A natural extension would be a study of the effect of stilbene on polymerization of other monomers, also with Ziegler type catalysts.

We could not try influence of trans stilbene on cationic polymerizations. It would be interesting to do so.

Kineticsof Polymerization.

(1) The rate of polymerization in hexane at constant ratio Li/Ti is found to be proportional to the amount of Titanium tetrachloride. Fig.3. Table 10. This is in accordance with the view[39] that the active catalyst sites are formed on the surface of the reduced transition metal halides.

(2) At constant Li/Ti = 1.5 and with $[LiC_5H_{11}] = 10.7 \times 10^{-3}$ M/l, $[TiCl_4] = 6.645 \times 10^{-3}$ M/l, the rate of

polymerization is proportional to monomer concentration in hexane, upto monomer concentration = 2.1 M/l (Fig.4. Table 7). The rapid rise in rate after monomer concentration = 2.1 M/l is to be attributed, as discussed earlier (Page 5) to the solubilization of polymers from the catalyst surface and exposure of fresh catalyst sites for polymerization. So, it is reasonable to take R_p versus $[M]$ for the order of reaction below 2.1 M concentration of Monomer. This is further substantiated by calculating rate law from results of R_p versus $[cat]$ and R_p versus $[M]$. Rate constants from both plots are in good agreement.

Values of rate constant given below:

R_p Vs $[Cat]$ K 1/M/S $\times 10^2$	R_p Vs $[M]$ K 1/M/S $\times 10^2$
2.081	3.0

This value of rate constant is considerably higher than that value obtained in case of styrene polymerization with titanium trichloride and aluminium triethyl or diethyl aluminium halides.

Rate constants at 60°C

Burnett[92]

Catalyst	K x 10^4 1/M/min.
-$TiCl_3$-$AlEt_2Cl$	13.7
-$TiCl_3$-$AlEt_2Br$	12.6
-$TiCl_3$-$AlEt_3$	22.7

But the rate of polymerization is proportional to catalyst concentration and monomer concentration as observed with different Ziegler type catalyst of polymerization of propylene, ethylene and styrene.

$$Rp = K [M][Cat] \qquad (19)$$

K - Overall constant
M - Monomer. Cat - Catalyst.

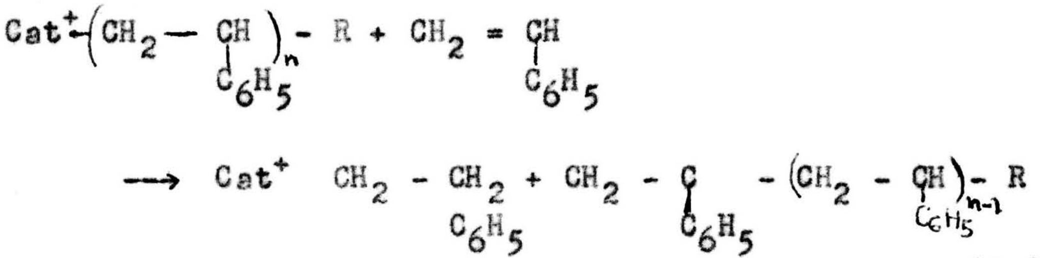
In benzene also, rate of polymerization is proportional to the catalyst concentration (Fig.5) but the general level of rate is much higher at the same catalyst concentration than in hexane. The removal of polymer from catalyst surface and prevention of clogging at catalyst site is a contributory factor to the higher rate. Again, it is also possible that the catalyst precipitate formed in benzene is more finely dispersed, exposing a larger surface area. Actually, it could be observed that the catalyst formed in benzene settled down much more slowly than was the case in hexane where quick agglomeration and sedimentation took place in the absence of adequate stirring.

Molecular weight:

$\frac{1}{Pn}$ varies linearly with square root of titanium tetrachloride concentration. (Table 6, fig.8). Hence soluble titanium compounds probably take part in chain termination. The formation of soluble catalyst components like $TiCl_n$ LiRP (R - alkyl group and P - growing chain) can be assumed similar to that postulated in case of polymerization of propylene with titanium trichloride and aluminium alkyls.

$$TiCl_nLiRP + LiR \longrightarrow TiCl_nLiR + LiRP \qquad (20)$$

Molecular weight increases initially with monomer concentration but after certain monomer concentration at 2.1 Molar, the molecular weight decreases (Table 7,fig.6). This expresses that monomer has taken part in the chain transfer reaction with the growing chain of polymerization and through the chain transfer reaction, the termination of polymer has taken place as shown in the following equation



$$Cat^{+}\!-\!(CH_2 - \underset{C_6H_5}{\underset{|}{CH}})_n - R + CH_2 = \underset{C_6H_5}{\underset{|}{CH}}$$

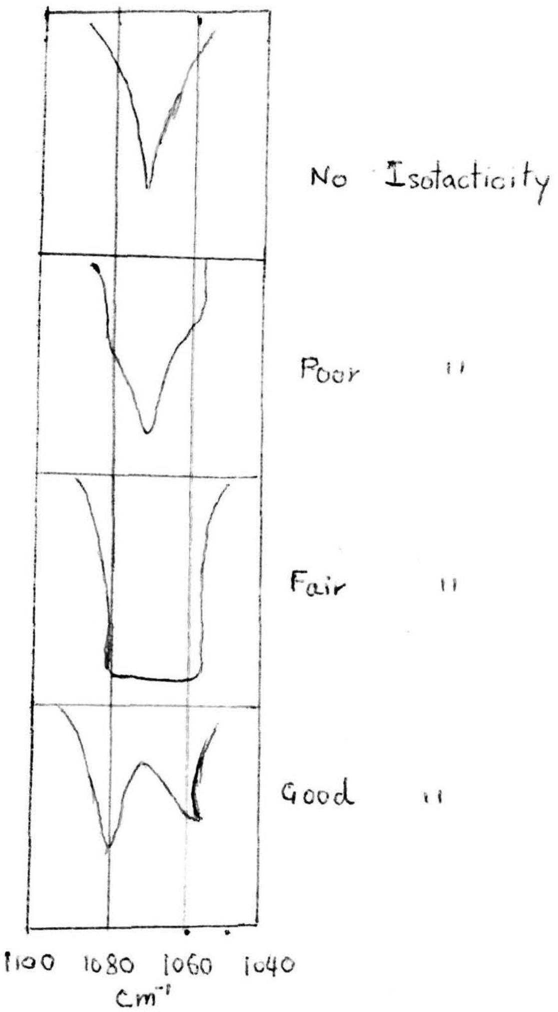
$$\longrightarrow Cat^{+} \; CH_2 - \underset{C_6H_5}{CH_2} + CH_2 - \underset{C_6H_5}{\underset{|}{C}} - (CH_2 - \underset{C_6H_5}{\underset{|}{CH}})_{n-1} - R$$

........(21)

In case of ratio study, the titanium tetrachloride concentration was constant and lithium isoamyl concentration was varied. It was found that the molecular weight of polymer instead of decreasing increased with the concentration of lithium isoamyl (Table 3. Fig.2). This indicates that lithium isoamyl does not take part in the chain transfer reaction like aluminium alkyl taking part in the chain transfer reaction in the polymerization of styrene with CrAcAc-Altriethyl catalyst system. So, there is no chain transfer and termination through metal alkyl in this reaction system.

The molecular weights are undoubtedly low and stereospecificity negligible. Methyl-ethyl-ketone extraction left little residue of high molecular weight istactic polymer. But I.R.spectra did show some peaks 1364 cm^{-1}, 1314 cm^{-1}, 1297 cm^{-1} and 1185 cm^{-1}, specifically described for the isotacticity of polystyrene.[105]

Morton[106] has discussed the absorption at 1070 cm^{-1} in infra spectra of different polystyrene samples containing high isotacticity to nil isotacticity. According to the isotacticity he found different gradation of absorption at 1070 cm^{-1}. He classified them as nil, poor, fair, good tacticity peaks. He has observed very sharp absorption peak at 1070 cm^{-1} for sample of no tacticity and the absorption peak at 1070 cm^{-1} was bifurcated into 1080 cm^{-1} and 1060 cm^{-1} for good isotactic polymer sample. For poor isotacticity, absorption peak is not sharp and the fair isotactic sample has absorption peak in between bifurcated absorption peak of good isotacticity and blunt peak of poor isotacticity sample as shown in the diagram.

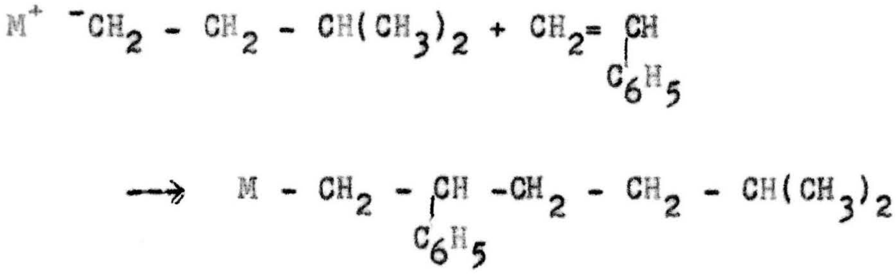


When our solutions of polymers were examined by infrared, it was observed that the absorption peaks at 1070 cm^{-1} were not definitely sharp but they did not have bifurcation into 1060 cm^{-1} and 1080 cm^{-1}. So we can conclude that the isotacticity of polystyrene prepared by lithium isoamyl and $TiCl_4$ can be varying from poor to fair.

It can now be justified to attempt to write a mechanism of polymerization of styrene with lithium isoamyl and titanium tetrachloride on lines similar to that proposed by many workers for polymerization of propyelene[38] and styrene[91,9] using AlR_3-$TiCl_3$, PhMgBr-$TiCl_4$.

All the evidence discussed above indicating the kinetics of the reaction and effect of zinc diethyl and trans stilbene strongly support the view that an anionic coordinated mechanism operates in the system. We can proceed to write for initiation.

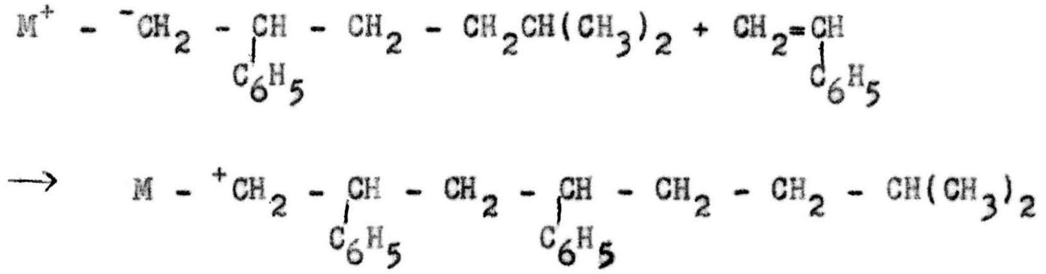
Initiation



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

(22)

Propagation



$$M^+-{}^-CH_2-\underset{\substack{|\\ C_6H_5}}{CH}-CH_2-CH_2CH(CH_3)_2+CH_2{=}\underset{\substack{|\\ C_6H_5}}{CH}\rightarrow M-{}^+CH_2-\underset{\substack{|\\ C_6H_5}}{CH}-CH_2-\underset{\substack{|\\ C_6H_5}}{CH}-CH_2-CH_2-CH(CH_3)_2$$

...........(23)

where M stands for metal cation. It is not specified whether M is Ti or Li., Since our experiments do not provide evidence conclusively for either supposition. As shown earlier with LiR-$TiCl_4$, the possibilities of many catalytic complexes being formed are numerous.

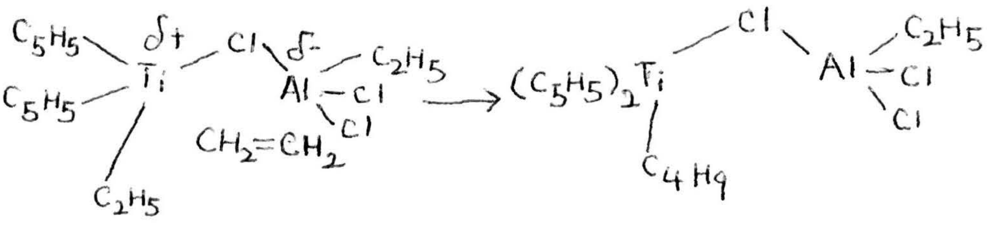
Natta[38,46] explicitly favoured the growth of polymeric chain from aluminium carbon bond and kinetic evidences are completely in agreement with the reaction mechanism which he has proposed. In addition to this, he made it clear by detecting the presence of phenyl from phenyl aluminium in the growing polymeric chain of polyethylene prepared by dicyclopentadienyl titanium dichloride and aluminium triphenyl catalyst system and further showed that if dicyclopentadienyl titanium phenyl is used with aluminium triethyl, there was no phenyl group present in the growing polymer. By inserting C^{14} labelled in aluminium triethyl and using this radioactive carbon containing aluminium triethyl with dicyclopentadienyl titanium dichloride for polymerization of ethylene, he pointed out again the presence of alkyl from organometallic 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 re-investigating the catalyst system used above that the alkyl or aryl groups can be transferred from aluminium to titanium and growth of polymeric chains can be from titanium carbon bond.

This proposition is further made strong by Carrick,[53] showng that the rate of polymerization of ethylene and the reactivity ratio of ethylene propylene copolymer were different with different transition metal halide with the same organometallic compound, but there was no change in the rate or reactivity with different organometallic compounds with the same transition metal halide. Of late, it was observed that organo titanium chloride[42] itself act as the initiator of polymerization of ethylene.

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

Mechanism of propagation using dicyclopentadienyl titanium dichloride and aluminium triethyl[60] for the polymerization of ethylene is described as the simple addition of ethylene to the titanium carbon bond in the organo-titanium complex. Role of aluminium alkyl is to supply alkyl groups to titanium and to make more positive in character. First step in the polymerization would probably involve a π-type complex between the titanium and the olefin..



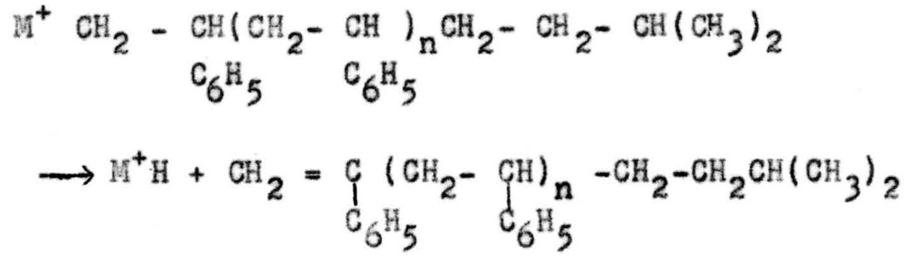
According to this structure, aluminium is tetracoordinated and complex of olefin is unlikely with[107] it. Thus only titanium carbon bond is involved in the propagation reaction.

So there is much to support, however, that growth at Ti occurs by degradation or $TiCl_4$ produced catalyst system by forming π -complex with monomer as postulated by different workers.

The chain termination as discussed earlier could occur by (1) spontaneous decomposition, (2) monomer transfer.

Spontaneous Decomposition

1)

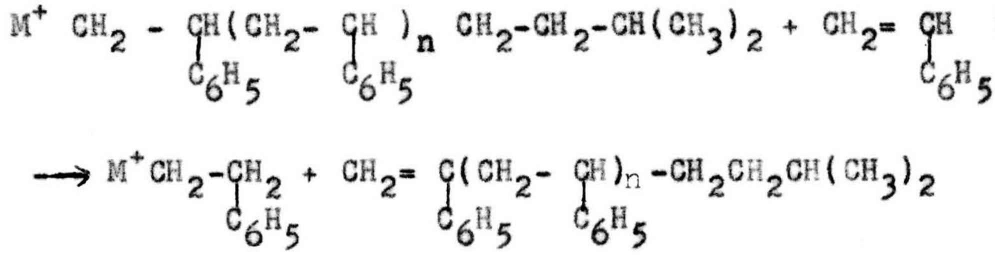


$$M^+ CH_2 - \underset{C_6H_5}{CH}(CH_2 - \underset{C_6H_5}{CH})_n CH_2 - CH_2 - CH(CH_3)_2 \qquad (24)$$

$$\longrightarrow M^+H + CH_2 = \underset{C_6H_5}{C}(CH_2 - \underset{C_6H_5}{CH})_n - CH_2 - CH_2CH(CH_3)_2$$

Chain transfer to Monomer

2)



$$M^+ CH_2 - \underset{C_6H_5}{CH}(CH_2 - \underset{C_6H_5}{CH})_n CH_2 - CH_2 - CH(CH_3)_2 + CH_2 = \underset{C_6H_5}{CH} \qquad (25)$$

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

Discussion of Chromium acetyl acetonate and Aluminium alkyl catalyst system.

Reproducibility of Results.

Chromium acetyl acetonate and aluminium alkyls were found to be quite stable in nitrogen atmosphere under our experimental condition of handling and the activity of the reaction complex formed by the reaction of aluminium alkyl and chromium acetyl acetonate at various concentrations were observed to be quite constant even upto 8 hours, as evident from the conversion versus time plots (Fig.10). The catalyst from aluminium triethyl and chromium acetyl acetonate was apparently homogeneous in the reaction system and the variation in agitation of reaction mixture had little effect on the reproducibility of results which did not vary more than 2 % in any case.

Order of addition

Though chromium acetyl acetonate or aluminium triethyl does not initiate polymerization of styrene independently, there is evolution of gases[108] ethylene and ethane, when the active catalyst complex formed by the reaction of chromium acetyl acetonate and aluminium triethyl.

$$3Al(C_2H_5)_3 + Cr(AcAc)_3 \longrightarrow 3(C_2H_6 + C_2H_4) + X \qquad (1)$$

(X = black reaction product)

Ethyl radicals are formed initially in this reaction and subsequently disproportionate to form ethane and ethylene. To avoid radical polymerization of styrene initiated by these radicals in the reaction system, styrene was added to the reaction flask after formation and ageing of the catalyst for 10 minutes, during which time the initial reaction of the catalyst components was complete. Hence, the contribution of initiation by ethyl radicals to the rates measured in our experiments can be considered negligible.

Formation of catalyst sites

Chromium acetyl acetonate and aluminium triethyl react instantaneously to form a brown black reaction product, the intensity of colour depending on the dilution of the system. The complex appears quite stable as the colour of the solution was unchanged during nearly 8 hours. Further it has been shown that poly-butadiene[73] produced with this catalyst system showed little difference in the yield and the structure of polymer after ageing the catalyst system, even for 240 minutes. Under our experimental conditions also, ageing time of 10 minutes was found sufficient to yield catalyst of constant activity which would indicate that the same catalyst was present throughout the polymerization reaction extending upto 4 hours. Only when exposed to air or kept in closed conditions for many days at a stretch in presence of monomer, it turns green, possibly, due to slow decomposition.

The reaction product of diethyl aluminium bromide with chromium acetyl acetonate was initially green and gradually the solution changed to black brown and a fine yellow precipitate settled at the bottoom. These changes were over within 10 minutes of ageing. This system is clearly heterogeneous with the fine precipitate separating out. The appearance of greenish colour instantaneously may be due to oxidation of the chromium acetyl acetonate to transient chromium halides[109] (Cr^{3+}) which may be reduced immediately.

The use of dialkyl aluminium bromide instead of the trialkyl aluminium thus results in a heterogeneous catalyst which also differs, in all probability, in chemical composition from the catalyst obtained with aluminium triethyl.

In case of isoprene polymerization, higher concentration of chromium acetyl acetonate (0. 45M) and aluminium triethyl (0.135M) was required to be used to obtain measurable rates of polymerization. At these higher concentrations, the amount of catalyst complex formed obviously exceeded the limit of solubility in the medium of benzene in the presence of the aliphatic hydrocarbon, isoprene and a black brown precipitate was formed and the catalyst system was heterogeneous, in contrast to the homogeneous solution obtained of the same catalyst at lower concentrations employed in polymerization of styrene in benzene.

Thus, we have the formation of both heterogeneous and homogeneous catalyst systems from the same reaction product of chromium acetyl acetonate and aluminium triethyl under different conditions. The insoluble product of diethyl aluminium bromide with chromium acetyl acetonate, possibly, differs in chemical composition as mentioned earlier but its structure was not investigated. But with all these catalyst systems ageing for 10 minutes was sufficient enough to produce active species for polymerization whose catalytic activity was also maintained constant during the reaction times employed in our experiments.

Catalytic Species

The nature of the catalytic complex formed by the reaction of chromium acetyl acetonate with aluminium trialkyl has been investigated in detail by G.Sarton and G.Costa.[108]

The product of the reaction of aluminium triethyl with chromium acetyl acetonate is dark brown and either soluble or highly dispersible in benzene. But it can be flocculated by n-heptane. Immediately after reaction ethylene and ethane were evolved. Chromium acetyl acetonate was reacted with increasing concentration of aluminium triethyl, varying the molar ratio of reacting of aluminium triethyl to chromium acetyl acetonate from 1 to 9 Al/Cr. The amount of gases evolved and the chromium acetyl acetonate reacted were estimated. One mole of gas is (ethane + ethylene) is obtained per $Cr(AcAc)_3/3$ reacted. Since the reaction mixture is unstable even under nitrogen, it is very difficult to isolate reaction product.

The black precipitate separates out slowly in the concentrated solution or it can be obtained by addition of dry n-heptane. Either solution and precipitate turn rapidly greyish green in air. Decomposition of reaction mixtures with methanol causes further evolution of ethane and ethylene which when added to gases evolved during the reaction, amounted to 3 moles of gas per mole of aluminium triethyl.

Analysis of black brown precipitate is obtained as Al/Cr = 3 even at high ratios of Al/Cr in reagents.

Al/Cr (reagents)	Al/Cr in ppt (by adding in heptane)
7.01	3.33
7.83	3.15
9.79	3.141

In the I.R.Spectra of reaction products (from reagents Al/Cr = 6) and the flocculation products, the characteristic of $Cr(AcAc)_3$ like perturbed double bond and carbonyl bonds and also characteristic bands of aluminium triethyl have been maintained in both the substances.

Magnetic measurements, by Gouy's method, on reaction solution in dry nitrogen are shown in the table below. The reaction product of $Cr(AcAc)_3$ and aluminium triethyl has zero susceptibility.

Substance	Sample + Solvent weight of	Susceptibility 10^6 per g.
$Cr^{3+}(AcAc)$	0.0305 + 1.0638 solvent	+ 15.5
Cr^{3+}-in $Cr(acac)_3$	0.0306 in 1.0638 solvent	+107.5
$Al(C_2H_5)_3$	0.0742 in 0.9222 solvent	+ 0.81
Reaction product between $Al(C_2H_5)_3$ & $Cr(AcAc)_3$	0.1015 in 0.9687	0.00

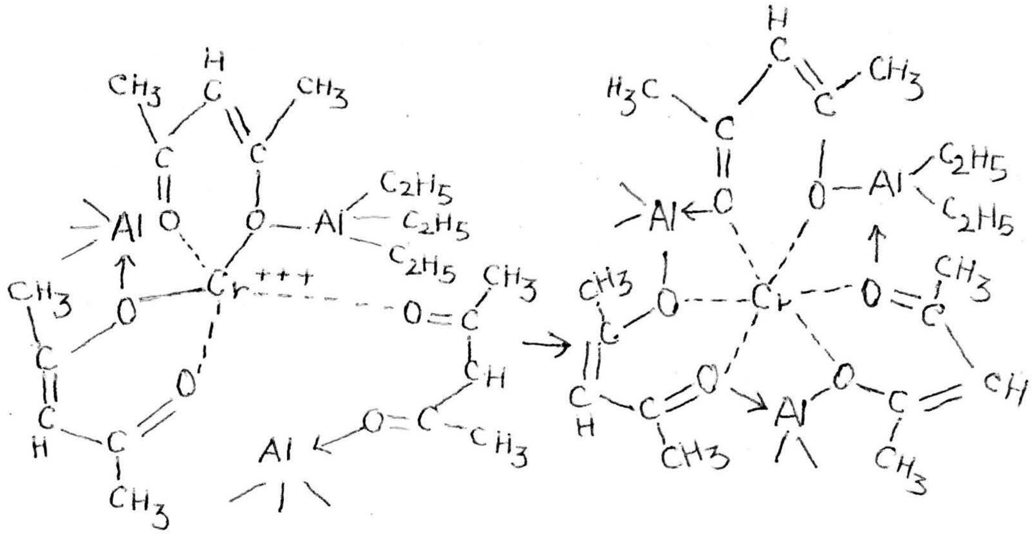
From composition of crude reaction product as isolated by flocculation and washed with dry n-heptane as well as from amount of gases evolved, the stoichiometry of reaction results as:

$$3Al(C_2H_5)_3 + Cr(AcAc)_3 \longrightarrow 3(C_2H_6 + C_2H_4) + X$$

Where X is reaction product in which Al/Cr = 3.

Chromium is reduced by the reaction to zero valency state, but characteristic structure of acetyl acetonate ring appears substantially unchanged. in reaction products, two C_2H_5 groups per mole of $Al(C_2H_5)_3$ reacted are present and can be removed by decomposition with water or methanol.

From the above results and accounting for the electron deficient character of aluminium triethyl and as well as from the results from researches on reaction between organo aluminium and carbonyl containing compounds the following mechanism involving of one C_2H_5 group and formation of C-O-Al bond is depicted.



Three new C-O-Al bonds are formed in place of three C-O-Cr bonds.

The chelate ring structure of acetyl acetonate as well as the six C-O equivalent bonds with intermediate character between single and double bond will be maintained.

All six O-Al bonds will also have the same bond character. It is, hence, strongly indicated that the complex is one shown above with a stoichiometry of 3 Al to 1 Cr.

When variation of rate of polymerization at different molar ratios of Al/Cr from 1 to 9 was investigated, the rate of polymerization was maximum at the molar ratio of 3 Al/Cr. This molar ratio of maximum activity was verified under two different conditions. In one case, the concentration of chromium acetyl acetonate was maintained constant and aluminium triethyl concentration was varied to yield different molar ratios of Al/Cr. In the second case, concentrations of chromium acetyl acetonate and aluminium triethyl were varied but the sum total of their individual concentrations was kept constant at all ratios of Al/Cr.

The maximum activity in both sets of experiments was obtained at the molar ratio of 3 Al/Cr. Also by assuming a stoichiometry of reaction of 3 moles of triethyl aluminium and one mole of chromium acetyl acetonate, the molar concentration of the catalyst complex formed was calculated in the second set of experiments (Table 13, page No.69). The rate of polymerization was found varying linearly with calculated value of concentration of complex (Fig.12). It is hence reasonable to conclude that the catalyst complex of maximum activity in the polymerization of styrene is formed from the reaction of 3 moles of aluminium triethyl with one mole of chromium acetyl acetonate and which has probably the structure suggested above. Excess aluminium triethyl even upto Al/Cr = 13 does not produce any different maximum in catalytic activity curve. This

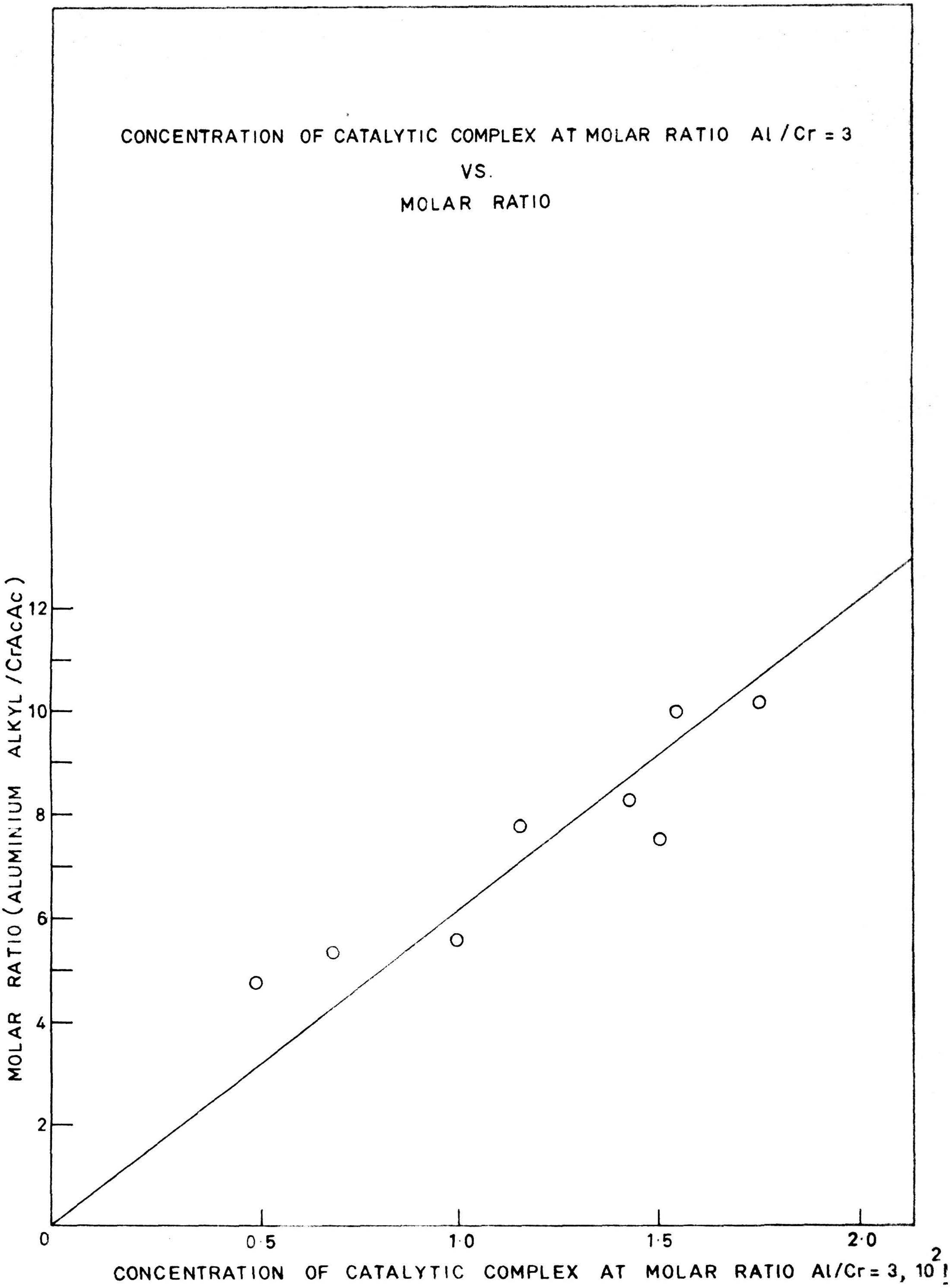

CONCENTRATION OF CATALYTIC COMPLEX AT MOLAR RATIO Al / Cr = 3
VS.
MOLAR RATIO
MOLAR RATIO (ALUMINIUM ALKYL / CrAcAc)
12
10
8
6
4
2
0
0·5
1·0
1·5
2·0
CONCENTRATION OF CATALYTIC COMPLEX AT MOLAR RATIO Al/Cr = 3, 10² !

FIG. - 12.

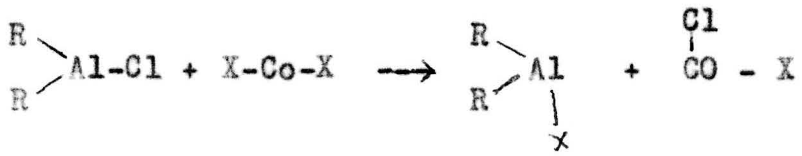
is in agreement with the fact that even at different molar ratios of Al/Cr employed initially, the molar ratio of combined Al/Cr in the flocculated reaction product is only 3.

There is a shift in maximum catalytic activity to molar ratio of Al/Cr = 4 in case of isoprene (Fig. 13). This shows that when different monomers are polymerized with the same catalyst components, maximum activity need not be observed at the same molar ratio of components.

Similar observations have been made in case of isoprene and butene-1 polymerizations with titanium tetrachloride and aluminium triisobutyl. With isoprene the maximum activity is at 1.25[61] but in the case of butene-1 the ratio of maximum activity is 1.75.[110] Similarly, the molar ratio of maximum activity is different for propylene and ethylene with lithium butyl and titanium tetrachloride catalyst system. For ethylene the ratio is 1.5 to 2.0[111] and for propylene it is 1.8 to 2.5.[112] Hence it is not easy to conclude that the catalyst species responsible for polymerization (of isoprene and styrene) in our experiments are radically different in each case. They could essentially be the same.

The product of the reaction of di-ethyl aluminium bromide with chromium acetyl acetonate may form by exchange reaction of halogen groups.

It has been shown in the case of di-ethyl aluminium chloride and cobalt acetyl acetonate[113] that the precipitated reaction product is cobalt chloride formed by the exchange reaction.



$$\begin{matrix}\mathrm{R}\\ \mathrm{R}\end{matrix}\!>\!\mathrm{Al{-}Cl} + \mathrm{X{-}Co{-}X} \longrightarrow \begin{matrix}\mathrm{R}\\ \mathrm{R}\end{matrix}\!>\!\underset{\substack{|\\ \mathrm{X}}}{\mathrm{Al}} + \overset{\substack{\mathrm{Cl}\\ |}}{\mathrm{CO}} - \mathrm{X} \qquad (2)$$

(R = alkyl)

Similarly the reaction product of Vanadium acetyl acetonate and diethyl chloride[114] in benzene is ethyl vanadium dichloride, which is precipitated and settled at the bottom.

Reaction product of ethyl aluminium bromide and chromium acetyl acetonate is much less stable than that from tri-ethyl aluminium and chromium acetyl acetonate and in about 3 hours a greenish tinge could be detected in the reaction system indicating formation of different products.

During polymerization with both catalysts, it is observed that the molecular weights of the polymers do not vary. This would not be the case if the growing chain has long lifetime of growth as found with[115] Hoechst modifications of Ziegler catalyst. With such catalyst producing chains of long life time of the order of hours or many minutes, it has been possible to synthesize block polymers of increasing molecular weight and changing composition by admitting different monomers after the chains have been grown to certain length of time. But the constancy of the molecular weight during the reaction time used have indicated that the growing macromolecules do not have long lifetime as observed with the above catalysts of similar nature but are terminated after short time of the order of one or two minutes or less. The number and the nature of catalyst sites obviously are not altered measurably by this termination since constant polymerization rates are observed throughout the reaction times. Then the catalysts are regenerated. (Table No.15, 23).

Kinetics of polymerization

1) The rate of polymerization of styrene in homogeneous medium by the catalyst from chromium acetyl acetonate and aluminium tri-ethyl system is half order with respect to chromium acetyl acetonate concentration and first order with respect to monomer concentration.

$$Rp \propto [\text{Monomer}][\text{Cr AcAc}]^{1/2} \quad \ldots\ldots\ (3)$$

Table No.16,17.
Figs. 14,15.

2) But the rate of polymerization is first order with respect to isoprene concentration as well as chromium acetyl acetonate concentration.

$$Rp \propto [\text{Monomer}][\text{Cr AcAc}] \quad \ldots\ldots\ (4)$$

Table No.25,26.
Figs. 19,20.

3) In case of heterogeneous system of polymerization of diethyl aluminium bromide, the rate of polymerization of styrene is first order with respect to chromium acetyl

acetonate concentration as well as monomer concentration.

$$Rp \propto [\text{Monomer}][\text{Cr AcAc}] \quad \ldots\ldots.(5)$$

Table No.30,31.
Fig. 16,17.

The rate constants in each case were calculated from the slope of the plots of rate versus Monomer as well as Cr AcAc as shown in figures 14, 15, 19, 20, 16, 17. Values of K obtained thus from both plots agree with each other in each case.

Styrene polymerization with CrAcAc and $AlEt_3$

[CrAcAc] Variation	[Monomer] Variation
$K \times 10^5\ (1/M)^{1/2}/S$	$K \times 10^5 (1/M)^{1/2}/S$
1.442	1.381

Isoprene polymerization with CrAcAc and $AlEt_3$

[CrAcAc] Variation	[Monomer] Variation
$K \times 10^4$ 1/M/S	$K \times 10^4$ 1/M/S
5.0	4.0

Styrene polymerization with CrAcAc and Et_2AlBr

[CrAcAc] Variation	[Monomer] Variation
$K \times 10^4$ 1/M/S	$K \times 10^4$ 1/M/S
3.276	3.388

The activity of these catalyst systems was much more than $TiCl_3$ and Aluminium alkyl and diethylaluminium halides.[92] given in the following table.

Rate constants at 60°C.

Catalyst	K X 10^4 ($min.^{-1}$ $mole^{-1}$ l)
$TiCl_3$-$AlEt_2cl$	13.7
$TiCl_3$-$AlEt_2Br$	12.6
$TiCl_3$-$AlEt_3$	22.7

Chromium acetyl acetonate and aluminium triethyl catalyst system is apparently homogeneous system in benzene and bimolecular termination could take place easily. But it will be difficult to visualise a bimolecular termination of growing species located in heterogeneous catalyst sites. Indeed, in the case of isoprene polymerization with the same chromium acetyl acetonate and aluminium triethyl catalyst system which becomes heterogeneous at higher concentration, first order is obtained.

We can now deduce the rate law as given below:

Since the concentration of growing catalyst species $[c^*]$ will be proportional to the catalyst concentration, that is $[CrAcAc]$

We can write

$$\frac{dc^*}{dt} = K[CrAcAc] \quad \dots\dots\dots \quad (6)$$

K - Reaction constant

and for bimolecular termination

$$2c^* \xrightarrow{kt} \text{polymer product} \quad . \; . \; . \; . \; . \; (7)$$

$$\text{i.e.} \quad \frac{-dc^*}{dt} = kt\,(c^*)^2$$

kt - Termination constant

It is debatable whether a steady state can be assumed, but if steady state with respect to c^* is obtained, then

$$kt\,[c^*]^2 = K\ \text{CrAcAc} \quad . \; . \; . \; . \; (8)$$

i.e.

$$[c^*] = \frac{K^{1/2}}{kt^{1/2}}\ \text{CrAcAc}^{1/2} \quad . \; . \; . \; (9)$$

and since $Rp = kp\ c^*\ (M)$

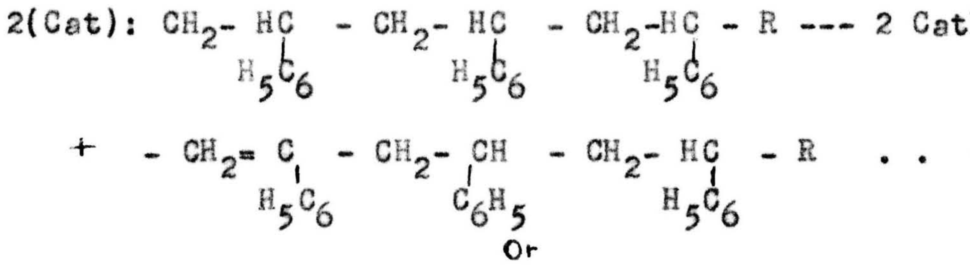
$$= kp\,\frac{K^{1/2}}{kt^{1/2}}\ \text{CrAcAc}^{1/2}\ (M) \; . \; . \quad . \; (10)$$

kp - Propagation constant

K - Initiation constant

As mentioned earlier this is further supported by the fact that with the same catalyst species which is heterogeneous in isoprene polymerization, where it is difficult to postulate bimolecular termination, only first order reaction is obtained.

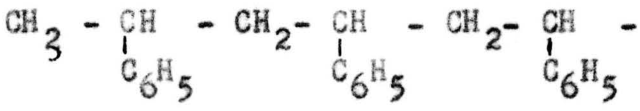
Bimolecular termination may be as given below:



$$2(\text{Cat}):\ \mathrm{CH_2-\underset{H_5C_6}{HC}-CH_2-\underset{H_5C_6}{HC}-CH_2-\underset{H_5C_6}{HC}-R}\ ---\ 2\,\text{CatH}$$

$$+\ -\mathrm{CH_2=\underset{H_5C_6}{C}-CH_2-\underset{C_6H_5}{CH}-CH_2-\underset{H_5C_6}{HC}-R}\quad . \; . \quad (11)$$

Or



$$CH_3 - \underset{C_6H_5}{CH} - CH_2 - \underset{C_6H_5}{CH} - CH_2 - \underset{C_6H_5}{CH} - R \; . \; . \; . \quad (12)$$

but No.12 will be a remote possibility.

Similarly, bimolecular termination has also been obtained in case of ethylene polymerization with dicyclopentadienyl titanium dichloride and aluminium trimethyl catalyst system.[116] Dicyclopentadiene titanium dichloride and trimethyl aluminium catalyst system is apparently homogenous in toluene. In this polymerization bimolecular termination is facilitated by solubility of catalyst species in medium. Reaction kinetics is studied by radioactive method at 30°C in toluene. Initiation is studied by using C^{14} labelled $(CH_3)_2AlCl$. Instantaneous concentration of propagating metal alkyl complex $[C]$ is obtained by quenching the aliquots of polymerizing mixtures with I_2.[131] The propagation step is first order in monomer and $[C]$. Termination is second order with respect to $[C]$. These kinetics relations obtained in case of metal alkyl complex are used to find the order of rate of polymerization with respect to actual catalyst used in the reaction. Square root of concentration of dicyclopentadienyl titanium dichloride is proportional to metal alkyl complex $[C]$.

$$Rp = Kp\ C\ \ M = Kp\left[(C\ H_5)_2TiCl_2\right]^{\frac{1}{2}} . [M] \; . \; . \; . \; . \quad (13)$$

Kp - rate constant of propagation.

The possibility of radical polymerization is ruled out since the overall activation energy of polymerization of ethylene with dicyclopentadienyl titanium dichloride and trimethyl aluminium system is 11.75 kcal/mole which is in agreement with the value of activation energy estimated as 11.5 kcal/mole in the propylene polymerization with titanium trichloride and aluminium triethyl.[39] This polymerization of propylene with titanium trichloride and aluminium triethyl is proved as anionic. On the other hand in radical polymerization of ethylene by di-azon methane[117] the activation energy estimated is 34.8 kcal/mole and in thermal polymerization of ethylene also, it is 43.7 kcal/mole.[118] Both the values of activation energy are very high as compared to that of an ionic polymerization. It is showed that even though the bimolecular termination reaction works in homogeneous catalyst system of polymerization, the mechanism of polymerization can be an anionic type.

Besides bimolecular termination in homogeneous catalyst system for polymerization, certain other termination reactions operate.

It appears that the aluminium alkyl has reacted with the growing chain of polystyrene by a chain transfer process since it was observed that the degree of polymerization was inversly proportional to the square root of aluminium triethyl concentration, at constant concentration of chromium acetyl acetonate. (Fig.21. Table 14). It was further noticed that the rate of polymerization did not increase or decrease with the increasing amount of aluminium triethyl, so it makes clear that the chain termination is obtained through chain transfer to aluminium triethyl. (Fig.13. Table 14).

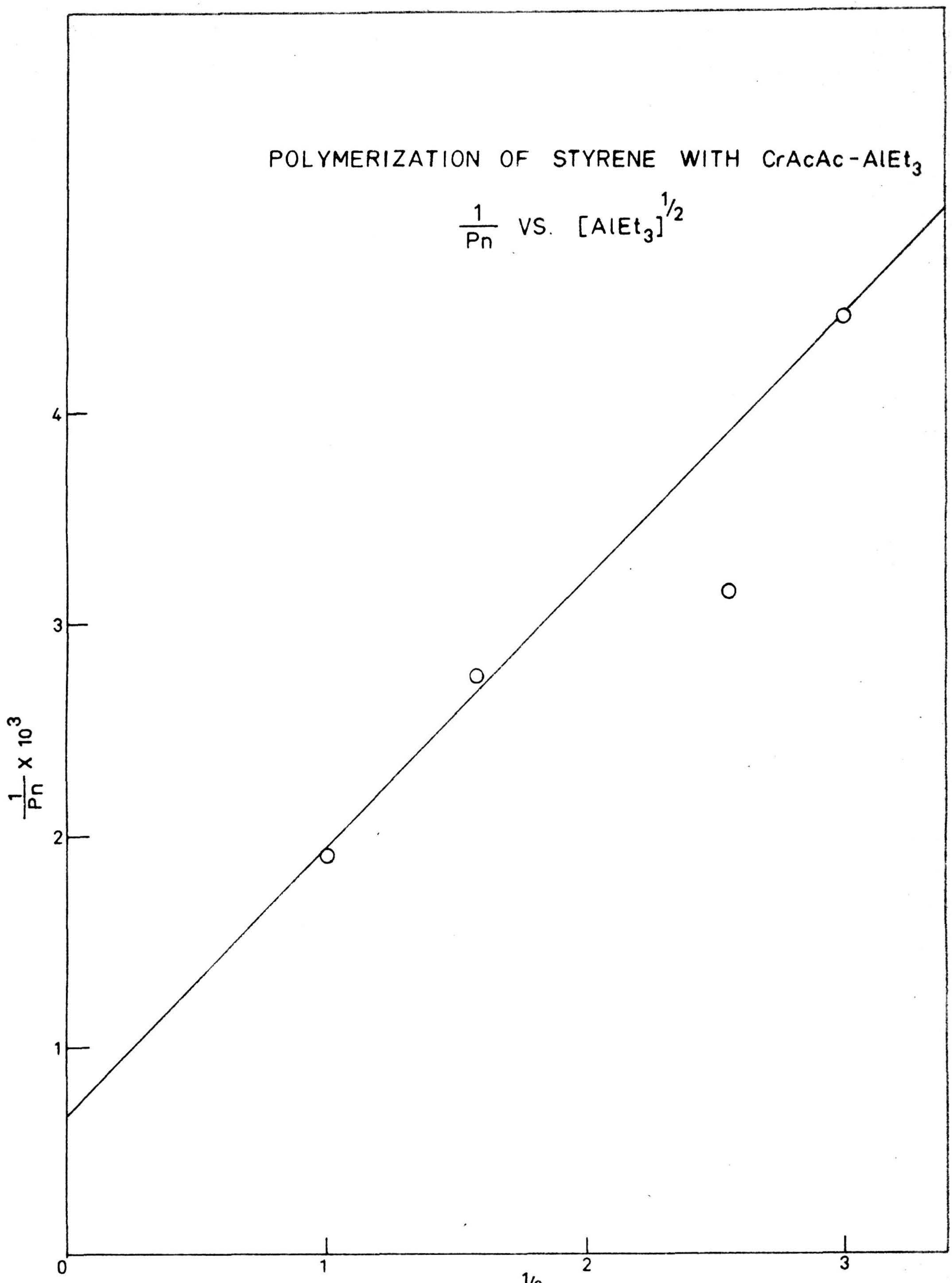

POLYMERIZATION OF STYRENE WITH CrAcAc-AlEt3
1/Pn VS. [AlEt3]^1/2
1/Pn X 10^3
[AlEt3]^1/2 X 10^1 M/l
0
1
2
3
4
1
2
3

FIG.- 21.

It can be assumed that the aluminium triethyl acts in the dissociated monomeric form in the chain transfer process since aluminium triethyl is normally dimeric, in equilibrium with monomeric structure.

We can write chain transfer

$$(AlEt_3)_2 \longrightarrow 2\,AlEt_3 \quad \ldots\ldots\ldots\ldots \quad (14)$$

$$AlEt_3 + CatP \longrightarrow AlEt_2P + CatEt \quad \ldots\ldots \quad (15)$$

$$AlEt_3 = [AlEt_3]_2^{1/2} \quad \ldots\ldots \quad (16)$$

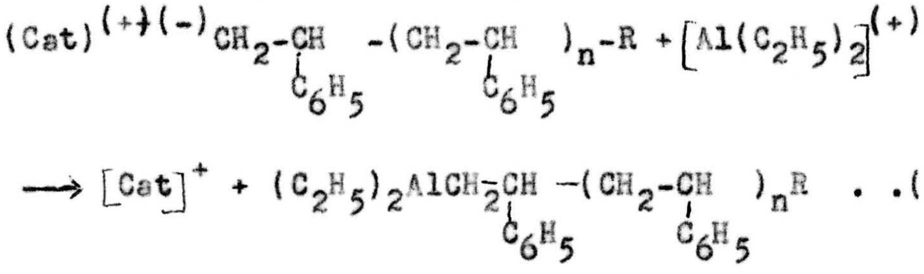
hence

$$\frac{1}{Pn} \propto [AlEt]_2^{1/2} \quad \ldots\ldots \quad (17)$$

There can be heteropolar dissociation as follows besides homopolar dissociation

$$Al_2(C_2H_5)_6 \longrightarrow [Al(C_2H_5)_2]^+ + [Al(C_2H_5)_4]^- \ . \ (18)$$

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



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

$$\longrightarrow [Cat]^+ + (C_2H_5)_2AlCH_2\underset{C_6H_5}{CH}-(CH_2-\underset{C_6H_5}{CH})_nR \quad ..(19)$$

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

$$\ldots\ldots\ldots\ldots\ldots \quad (20)$$

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 monomer alkyl aluminium takes part in the equilibrium of association with other alkyls in solution.

In case of soluble species of catalysts in the solvent, there can be a total substitution of the polymeric alkyl aluminium compound which is bound to a catalytically active complex containing the transition metal as follows:

$$\mathrm{CrAcAcAlY_2P + Al(C_2H_5)_3 \rightarrow CrAcAcAl(C_2H_5)_3 + AlY_2P} \quad ..(21)$$

P = Polymeric chain.

Y = Alkyl group (ethyl or polymeric chain)

This is just kinetically equivalent to the scheme in equations 19 and 20. This type of chain transfer mechanism involving aluminium triethyl has been observed in the polymerization of propylene with titanium chloride and aluminium triethyl.[64] According to equation 21, termination reaction in case of heterogeneous polymerization of styrene with $\mathrm{AlEt_2Br}$ - CrAcAc can be by chain transfer with certain soluble catalytic species in the reaction system, since the molecular weight decreases with increasing concentration of chromium acetyl acetonate. (Fig.16. Table 25). But this decrease in molecular weight with increasing concentration of catalyst supports the bimolecular termination of the polymerization reaction of styrene in the homogeneous system of chromium acetyl acetonate and aluminium triethyl (Fig. 14.Table 16).

It seems that in isoprene polymerization with the same catalyst system used for styrene polymerization, the termination reaction is altogether different. The molecular weight increases with increasing concentration of chromium acetyl acetonate, (fig.19. Table 30), and at constant concentration of chromium acetyl acetonate, the molecular weight is fairly constant with increasing concentration of aluminium alkyl (fig.13. Table 29). Since this catalyst system is heterogeneous for isoprene, these all data obtained above in case of isoprene polymerization suggest the spontaneous termination of polymerization of isoprene.

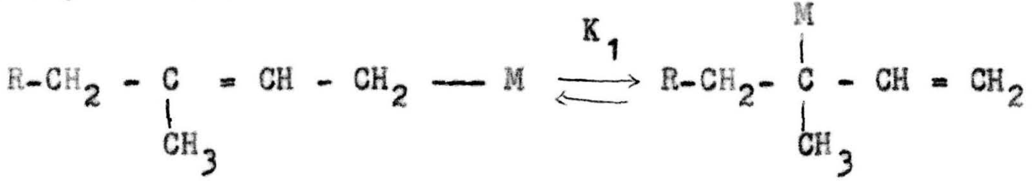
Strucrure of Polymers

The molecular weight of polystyrene obtained with these catalyst systems is comparatively low and varying between 6000 to 60,000 and methyl ethyl ketone left little residue of high molecular weight isotactic polymer. But the infrared spectra analysis showed the absorption bands at 1364, 1314, 1297 and 1185 cm^{-1} which are characteristic of isotactic polymers.[105] On comparing the absorption band at 1070 cm^{-1} of these sample with that reported by Morton,[106] it was found that these polymers have poor isotacticity. Morton and Taylor observed that the shape of absorption band at 1070 cm^{-1} changes according to the gradation of isotacticity in the polymer. For the good isotactic polymer, there is bifurcation of the absorption band at 1070 cm^{-1} into two bands at 1080 cm^{-1} and 1060 cm^{-1}

and for atactic sample, there is sharp absorption at 1070 cm^{-1}. This has been shown in the picture drawn on the page No. 112

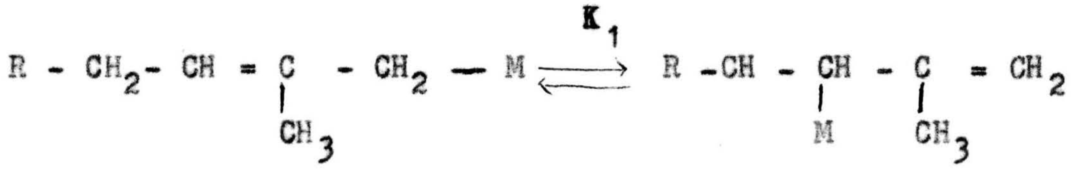
Microstructure of Polyisoprene

By anionic mechanism, polymer structures given below are possible.



$$R\text{-}CH_2 - \underset{\displaystyle CH_3}{C} = CH - CH_2 — M \overset{K_1}{\rightleftharpoons} R\text{-}CH_2 - \underset{\displaystyle CH_3}{\overset{\displaystyle M}{C}} - CH = CH_2$$

I II

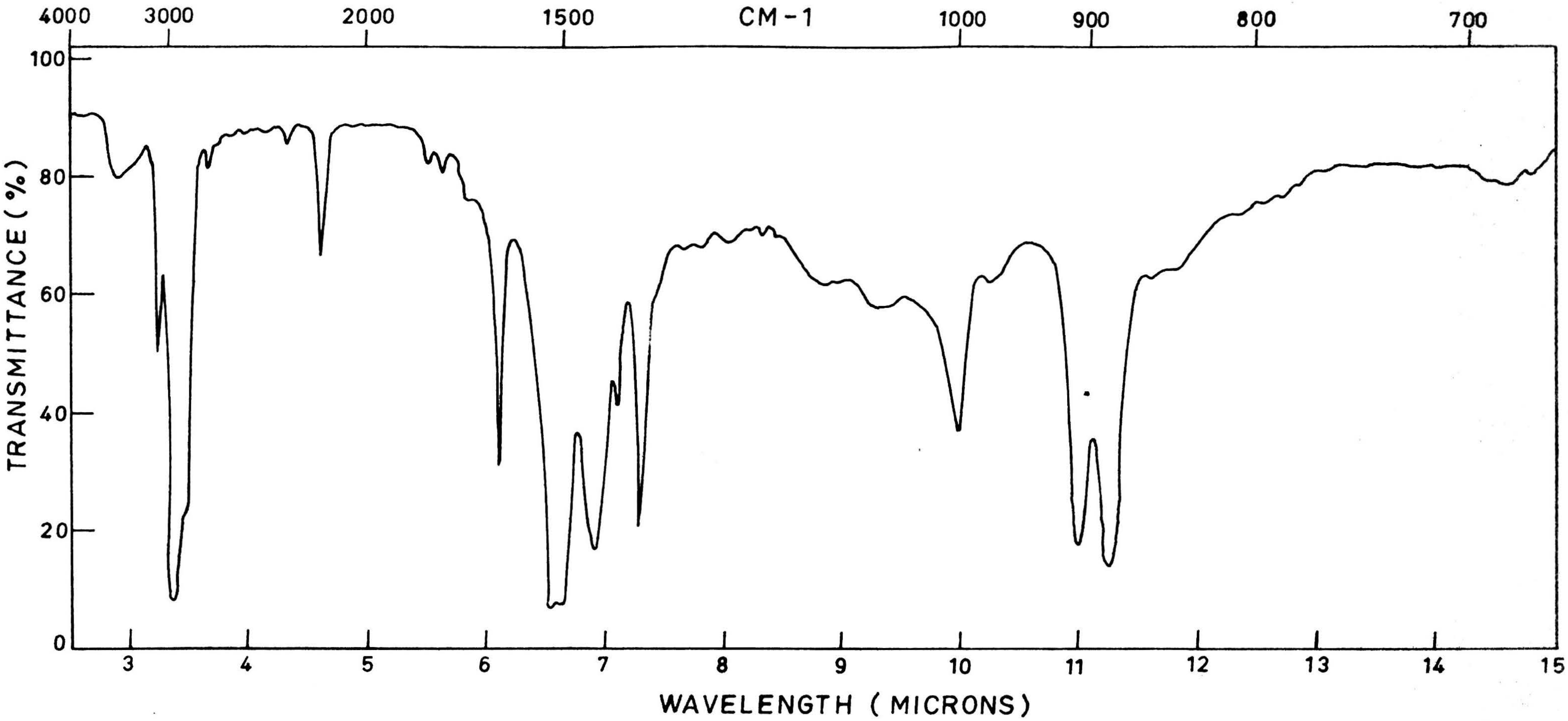


$$R - CH_2 - CH = \underset{\displaystyle CH_3}{C} - CH_2 — M \overset{K_1}{\rightleftharpoons} R - CH - \underset{\displaystyle M}{CH} - \underset{\displaystyle CH_3}{C} = CH_2$$

III IV

R - Radical. M - Metal.

Polyisoprene obtained by chromium acetyl acetonate and aluminium alkyl catalyst system was found having strong absorption bands at 3077 cm^{-1}, 1645 cm^{-1}, 890 cm^{-1} and 909 cm^{-1}. Absorption bands at 3077 cm^{-1}, 1645 cm^{-1} and 890 cm^{-1} are due to the isopropenyl groups in the polymer structure. This showed that the polymer contains 3,4-addition structure.[119] Similarly absorption band at 909 cm^{-1} indicates the presence of vinyl groups in the structure and these vinyl groups indicate 1,2 addition structure in the polymer. So it can be concluded that the polyisoprene is formed mainly by 3,4-addition and



POLYISOPRENE (1-2 & 3-4 ADDITION STRUCTURE)-CrAcAc-$AlEt_3$

FIG - 24

1,2-addition (Fig.24). Polybutadiene[73] obtained by the same catalyst system, was shown containing 90-95 % 1,2 addition and 4,6-% 1,4 addition structures.Polybutadiene obtained by $TiOBu_4$-Alalkyl[120] catalyst system also contains mainly 1,2-addition structure. These all examples of formation of 1,2-addition structure in the diolefin polymerizations lead to the theory of π-complex formation of monomer with transition metal compounds.

Mechanism of polymerization

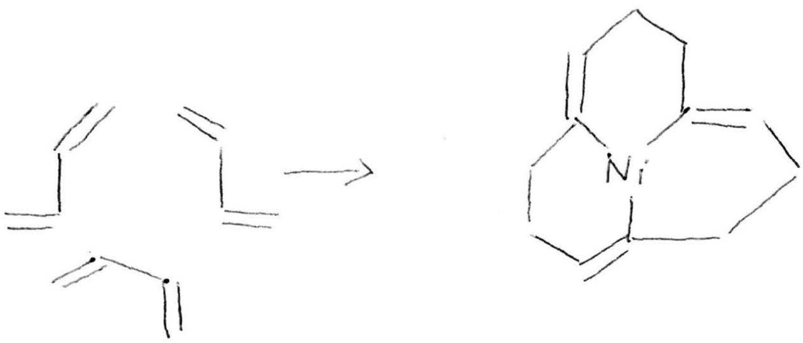
From available evidence, it can be postulated that styrene and isoprene react with chromium metal in the complex catalyst formed by the reaction of chromium acetyl acetonate with aluminium triethyl, resulting in a π-complex of chromium. Chromium, Cobalt and Nickel are known to react with butadiene, forming π-complexes.[121] Monomer forms a π-metal complex by overlapping of its π- electrons with metal orbitals, probably the 3d orbitals of metals.[122]

In the mechanism postulated for polymerization of ethylene with dicyclopentadienyl titanium dichloride and trimethyl aluminium,[116] the propagation step is through the π-metal complex formation. The catalyst may have ability to hold the monomers via π-bonding until the transition state complex is formed. It is also likely that the configuration of this complex enables easier transfer of energies among various vibrational modes of freedom than in the case of free radical polymerization.

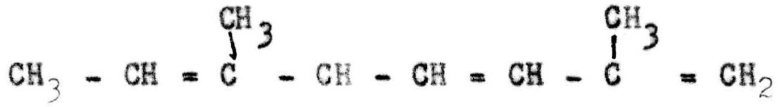
Zeiss[123] has also shown that metal complex of chromium as triphenyl chromium forms in the reaction of chromium chloride and phenyl magnesium bromide in tetrahydrofuran. This triphenyl chromium reacts with acetylene or substituted acetylene, resulting in cyclisation and polymerization reactions.

We can get a better idea of this complex formation from the reaction product of Nickel acetyl acetonate with organometallic compounds. Intermediate complex formed in the Nickel acetyl acetonate reaction with organometallic compounds can be isolated[121] and the nature of these complexes has been studied by conducting reactions with butadiene. It has not been possible for us to isolate intermediate products in case of chromium compounds.

Nickel acetyl acetonate even reacts with $P(C_6H_5)_3$ or $As(C_6H_5)_3$ and forms a complex as $Ni\text{-}(0)\text{-}\ P(C_6H_5)_{3\ 4}$ or $Ni\text{-}(0)\text{-}\ As(C_6H_5)_{3\ 4}$, as an active catalyst. Nickel in these complexes is reduced to zero valent state and these complexes react with butadiene to produce cyclooctadiene, vinyl cyclohexane and cyclo-dodecatriene.



The mechanism of this reaction from studies of nickel compounds is assumed as π -complex formation between butadiene molecules and the transition metals, which are present in the lower valent states in the catalyst, will tend to fill up their electron systems as much as possible in order to attain the next higher inert gas configuration. This will cause the transition metal atoms to share in the π -electron systems of the conjugated double bonds of butadiene molecules, leading to the formation of π -electron complexes. Substituted methyl groups in conjugated diolefins influence the course of reaction especially, isoprene is converted to open chain dimer.[124]



$$CH_3 - CH = \overset{CH_3}{\overset{|}{C}} - CH - CH = CH - \overset{CH_3}{\overset{|}{C}} = CH_2 \qquad (22)$$

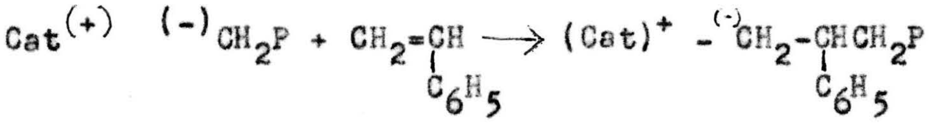
Thus there is a ready reaction of π -electrons of olefins with 3δ orbitals of transition metals, resulting in the π -complex formation of different stabilities, leading to different reactions like cyclisation, polymerization etc. But the first step is an activation of monomer by π -complex formation.

Chromium acetyl acetonate and aluminium alkyl is also reported polymerizing acetylene to linear high molecular weight product.[125]

Now it can be justifiably assumed that styrene reacts with the catalytic complex of the reaction of chromium acetyl acetonate and aluminium triethyl. Initially, the reaction would be between the styrene and the chromium metal which is in the reduced valence state in the catalytic complex, resulting the formation of metal complex of chromium with styrene in the activated state. Activated state of styrene will be the polarization of the monomer, facilitating a C - C bond formation as in the cyclisation reaction of butadiene. The C - C linking results in the loss of double bonds and therefore of π -electrons from the system.

Propagation of polymerization can be considered by the insertion of this activated monomeric molecule across the metal carbon bond just as postulated in the polymerization of olefins by different types of homogeneous and heterogeneous Ziegler type catalyst systems.

This metal carbon bond contains positively charged metal and negatively charged organic radical from the organometallic compounds in the complex. This metal carbon bond is a bridge bond which is dissociated ionically at time of activation of monomer and from this weaker type of bond the growth of polymer is possible according to the following equations:



$$Cat^{(+)}\ {}^{(-)}CH_2P + CH_2{=}\underset{C_6H_5}{\underset{|}{C}}H \longrightarrow (Cat)^{+} - {}^{(-)}CH_2-\underset{C_6H_5}{\underset{|}{C}}HCH_2P \qquad (23)$$

P - Polymeric chain.

It is not certain whether synthesis of polymer occurs at aluminium carbon bond or chromium carbon bond. There has been evidence of involving both types of bonds in the propagation reaction.

Especially, in the polymerization of styrene with chromium acetyl acetonate and diethyl aluminium bromide from the nature of the product as discussed in the formation of the catalyst species, chromium carbon bond can be considered as the propagating site. Vanadium carbon bond in the catalytic complex of Vanadium acetyl acetonate and diethyl aluminium chloride is also postulated as the propagating site in the copolymerization of 1,3 -butadiene and 1,3-pentadiene.[111]

We have already discussed in the first chapter about this metal carbon bond and whether titanium or aluminium is involved in the propagating bond.

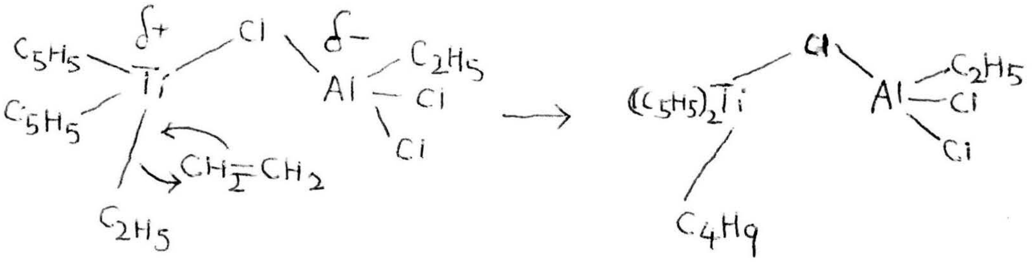
Here, some relevant discussion of metal carbon bond is given in short.

G. Natta[38,46] favours the mechanism of propagation across aluminium carbon bond in the detailed studies of polymerization of propylene with titanium trichloride and aluminium alkyls[39] and further he brought support to his mechanism from the studies of polymerization of ethylene with dicyclopentadienyl titanium dichloride and aluminium phenyl catalyst system where the phenyl groups were detected in the polymer, also triethyl groups from triethyl aluminium containing C^{14} labelled were found in the polymer by the estimation of radiocarbon.

This location of phenyl groups or ethyl group in the polymer is not conclusive proof for its presence in the aluminium carbon bond since these groups can be transferred from aluminium to titanium and growth of polymerization could be from titanium carbon bond.[50] However, the growth of polymeric chain across titanium carbon bond is supported by number of workers.[42,52,53,56]

It has been observed from the changes in the rates of polymerization and reactivity ratio of copolymer of ethylene propylene with various transition metal halides and one metal alkyl but with various metal alkyls and one transition metal, there is constant rate of polymerization and also reactivity ratio of copolymerization of ethylene propylene remains unchanged.[53] Propagation reaction is assumed from transition metal centre. The reasonable mechanism involves preliminary coordination of the olefin to a vacant d-orbital of the transition metal and rearrangement to incorporate the polarised olefin into a growing polymeric chain.

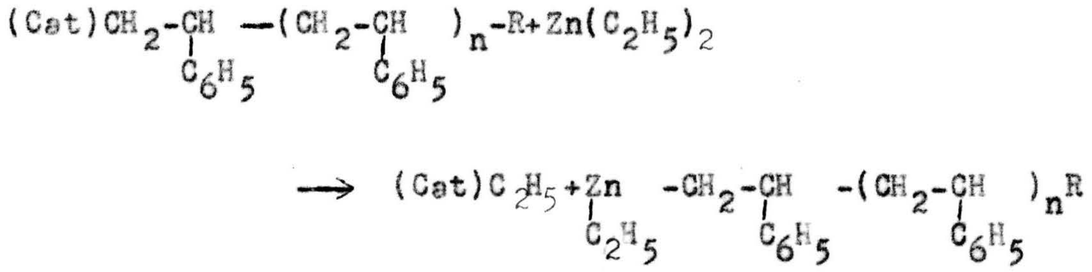
In the soluble catalyst system dicyclopentadienyl titanium dichloride and aluminium alkyl or alkyl aluminium halides of ethylene polymerization, the simple addition of ethylene to the titanium carbon bond in the organo-titanium complex is considered and the role of aluminium alkyl is nothing but to supply alkyl groups to titanium and to make titanium more positive in character to attract the olefin molecules more strongly.



Hence, though it is not established whether chromium or aluminium is involved in the propagating metal carbon bond, it can be believed that the propagation is at metal carbon bond.

Even though the exact location of the propagation reaction is not definite, overall polymerization reaction is believed as anionic . This is evident from the chain transfer reactions of aluminium alkyl and zinc diethyl with the polymeric chain. Chain transfer reaction with aluminium triethyl has been already discused on pages

The degree of polymerization was observed decreasing with increasing concentration of zinc diethyl. This shows that zinc diethyl is involved as a chain transfer agent. Zinc diethyl can react at the anionic propagating end of the growing chain by transferring ethyl zinc to that end and stopping the growth of the chain. The equation of the reaction given below explains it clearly.



$$\mathrm{(Cat)CH_2-\underset{C_6H_5}{CH} -(CH_2-\underset{C_6H_5}{CH})_n-R+Zn(C_2H_5)_2 \longrightarrow (Cat)C_2H_5+\underset{C_2H_5}{Zn} -CH_2-\underset{C_6H_5}{CH} -(CH_2-\underset{C_6H_5}{CH})_nR}$$

$(Cat)C_2H_5$[101] may not be that effective to initiate the polymerization, since the rate of polymerization was found decreasing with increasing concentration of zinc diethyl. This effect of zinc diethyl on the molecular weight of polymer is also observed in the polymerization of propylene with titanium trichloride and aluminium triethyl and is the conclusive test of anionic mechanism.[101]

Recently, polymerization of ethylene with different forms of titanium trichloride as well as different titanium aluminium complexes and zinc diethyl systems has been investigated to observe the effect of zinc diethyl.[125]

Here the molecular weight estimated has been found decreasing with zinc diethyl concentration indicating that zinc diethyl acts as a chain transfer agent whatever the nature of the transition metal may be.

Anionic mechanism is also evident from the overall activation energy. Fig.No.23.

Activation energy.	Catalyst system	Monomer
Kcal/mole		
10.235	$CrAcAcAlEt_3$	Styrene
11.52	$CrAcAcAlEt_3Br$	"
11.52	$CrAcAcAlEt_3$	Isoprene

Overall activation energy estimated with polymerization by chromium acetyl acetonate and aluminium alkyl is in agreement with values of activation energy of polymerization with different catalyst systems polymerizing anionically. The results are tabulated below

Activation energy.	Catalyst	Monomer
Kcal/Mole		
9.4	$TiCl_3AlEt_3$[90]	Styrene
20.0	$PhenylMgBr.TiCl_4$[91]	"
17.0	BuLi[14]	"
14.4	$TiCl_4$-$AliBu_3$[61]	Isoprene

So it can be viewed that chromium acetyl acetonate aluminium triethyl and diethyl aluminium bromide catalyst systems polymerize styrene and isoprene by coordinate anionic mechanism.

Now we can give the complete mechanism of polymerization as under:

1) Initiation of polymerization by π-complex formation of styrene and isoprene with chromium in the catalytic complex.

2) Propagation of polymerization at metal carbon bond.

3) And bimolecular termination as well as termination through chain transfer with aluminium alkyl is for styrene polymerization. But for isoprene is by spontaneous decomposition of the polymeric molecule having metal at one end into metal hydride and polymeric molecule.

SUMMARY

The discovery was made by Ziegler in 1953 that ethylene could be polymerized at atmospheric pressure and normal temperatures to yield linear high density polyethylene by using catalysts combination of transition metal halides and metal alkyls of group I-III. These Ziegler type catalysts were later extended and modified by Natta to the polymerization of Olefins to stereoregular, crystallisable polymers. Since then the detailed study of the kinetics and mechanism of polymerizations using these powerful catalyst systems has grown remarkably in interest and importance.

The present investigations relate to polymerizations of styrene with

1) Lithium isoamyl-$TiCl_4$ in n-hexane and benzene.

2) Aluminium triethyl chromium acetyl acetonate in in benzene.

3) Aluminium diethyl bromide chromium acetyl acetonate in benzene in the temperature range 30-50°C and polymerization of isoprene with aluminium triethyl and chromium acetyl acetonate at 40°C.

All polymerizations and dispensing of catalyst solutions were done under an inert atmosphere of nitrogen maintained in a 'dry box' fabficated for the purpose. Metal alkyls used were prepared by standard methods.

The dependence of polymerization rate, molecular weight, structure and stereospecificity of polymers formed

on the following variables have been studied. 1) order of addition of catalyst components and monomer, 2) ageing of catalysts, 3) mole ratio of catalysts components, 4) time, 5) monomer concentration, 6) catalyst concentration, 7) solvent medium, 8) added reagents like stilbene and zinc diethyl. The results obtained are summarized below.

Since the lithium isoamyl or titanium tetrachloride separately polymerize styrene, the mixing of the catalyst components was done prior to addition of monomer to preform the brown precipitate of bimetallic complex catalyst which behaved reproducibly after an ageing time of 10 minutes during which time evolution of gaseous products was observed. A maximum rate of polymerization was obtained at Li/Ti = 2. The rate decreased sharply with polymerization time indicating that the catalyst sites were being covered probably by precipitated polymer in hexane. This was confirmed by the disappearance of this effect in benzene which dissolved the polymer. The molecular weight of the polymer was constant which showed that the growing macromolecule was short lived. The rate of polymerization was first order with respect to monomer and the rate was directly proportional to (Ti^+) at constant Li/Ti ratio which would mean that active catalyst sites are on the heterogeneous surface of $TiCl_3$ formed in direct proportion to titanium tetrachloride employed. Trans-stilbene was found among polymeric reaction products and was part of it also shown to be chemically bound to the polymer by observation of fluorescence and infrared spectra of the purified polymer. The effect of added stilbene on other conventional Ziegler type catalysts was hence taken up and a measurable lowering of molecular weight and stereospecificity and increase of rate of polymerization were noticed. This is significant in view of the high rates of polymerization and low molecular weight and poor stereospecificity of the polymer obtained with LiR-$TiCl_4$ catalyst system.

In contrast to the heterogeneous catalyst from LiR-$TiCl_4$ the combination of $Cr(AcAc)_3$ with $Al(Et)_3$ resulted in apparently homogenous dark brown complex solution in benzene. The maximum rate of polymerization was observed at the ratio of Al/Cr=3. There was no increase in the rate of polymerization within 3 hours showing that there was no change in the nature of active catalyst. The molecular weight of the polymer was fairly constant during reaction time upto 8 hours which showed that growing macromolecule was short lived. The rate of polymerization was found to be proportional to $CrAcAc^{1/2}$ and first order with respect to Monomer at constant Al/Cr ratio.

To gauge better the effect of trans-stilbene formed in LiR-$TiCl_4$ system, known amounts of trans-stilbene were added to this catalyst system. Some increase in rate of polymerization with decrease in molecular weight was observed, but the bound stilbene in the polymer could not be detected as the product did not show fluorescence under ultraviolet light but infrared confirmed it.

Known amount of Zinc diethyl was added to the polymeric system and reduction in the molecular weight was found proportionate to increasing amount of zinc diethyl. This helped to establish participation of $Zn(Et)_2$ in chain termination by the transfer of ethyl group from Zinc diethyl to the growing polymeric chain.

Similar catalyst system of $AlEt_2Br$ and CrAcAc to triethyl Al and CrAcAc, unlike the CrAcAc and $Al(Et)_3$ formed heterogeneous dark brown product. The maximum rate of polymerization was noticed at the ratio of 3.5 Al/Cr. The rate of polymerization was first order with respect to Monomer and directly proportional to CrAcAc . In both the systems molecular weight was found varying inversely with CrAcAc and directly proportional to Monomer .

Activation energy of the overall polymerization reaction was determined to be 9-10 kcal/mole with both the catalysts and 2.05 kcal/mole with lithium isoamyl - titanium tetrachloride. This served to point out a mechanism as coordinate anionic type obtained in these systems. In case of polymerization of isoprene with $Al(Et)_3$ and CrAcAc, probably due to the presence of the aliphatic hydrocarbon isoprene the catalyst was found to be heterogeneous and the kinetics confirmed to that observed in the case of other heterogeneous catalysts used here and elsewhere and differed with the results obtained with styrene when the same catalyst was in homogeneous solution.

Copolymer of styrene and isoprene was prepared with both the catalyst systems. Further studies were held up due to the immediate gelling of product.

With the heterogeneous catalysts, results have been examined on the basis of surface reactions after the initial reduction of the transition metal compound to a lower valency 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) dissociation of the growing macromolecule from the catalyst site and/or 2) chain transfer with metal alkyl especially when $Zn(Et)_2$ was present. The applicability of equations derived on the basis of a Langmuir Hinshelwood type mechanism has been tested and discussed.