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# Studies in Co-ordination Polymerization

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A Thesis  
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for  
the degree of

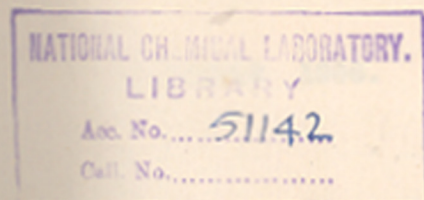
DOCTOR OF PHILOSOPHY

in Chemistry

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MAL

By  
SHADI LAL MALHOTRA  
M. Sc. (Hons.)



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

A C K N O W L E D G E M E N T

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NOVEMBER 1966.

*S.L. Malhotra*  
S.L. Malhotra.

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CHAPTER-I.

I N T R O D U C T I O N

## I N T R O D U C T I O N

The development of new and better polymeric materials is a progressive step in the field of polymer science. Amongst the several developments, the discovery of stereospecific polymers has not only bridged a gap between the man-made and natural products but signifies a sensational break-through and a big leap forward in the progress of science. This has been possible by the brilliant discovery of Ziegler-Natta catalysts. The novelty of these catalysts is to polymerise at room temperature and atmospheric pressure even those monomers which are difficult to polymerise ordinarily. New polymers like polypropylene, synthetic natural rubber and other vinyl polymers e.g. high density polyethylene, have been prepared with these catalysts.

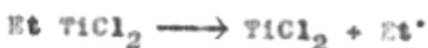
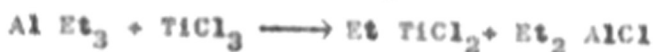
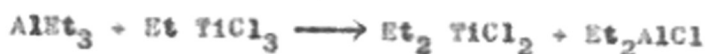
In 1953, K. Ziegler<sup>1</sup> discovered that ethylene could be polymerised at atmospheric pressure by the combination of titanium tetrachloride and aluminium alkyls. Researches carried out by G. Natta<sup>2-5</sup> and his collaborators showed that high

molecular weight, stereoregular<sup>6</sup> polymers with better physical and mechanical properties, as compared to those obtained with free radical and ionic catalysts could be obtained with this new class of catalysts. These catalysts are obtained by the reaction of metal alkyls or aryls from I to III group of periodic table with halides or esters of transition metals of groups IV to VI. Ziegler catalyst was first prepared by adding a solution of aluminium triethyl to a solution of titanium tetrachloride in a hydrocarbon solvent such as heptane or hexane. The product of reaction is a brown black insoluble compound which is essentially a reduced halide of titanium e.g. titanium trichloride, titanium dichloride and this precipitate together with its supernatant liquid is essential for catalytic activity. It has been shown that most active and stereospecific catalysts<sup>7-18</sup> for polymerisation of  $\alpha$ -olefins, vinyl monomers and dienes are formed by the reaction between an alkyl of a highly electro-positive metal having a small diameter e.g. beryllium, aluminium or lithium and a crystalline halide of a transition metal from group IV to VI of 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.



	Metal	Electro-negativity	Atomic radius Å°	Ionic radius Å°
(1)	Beryllium	1.5	0.90	0.35
(2)	Aluminium	1.5	1.26	0.51
(3)	Lithium	1.0	1.33	0.68
(4)	Zinc	1.5	1.31	0.74

When the catalyst is prepared from the un-reduced transition metal halides, its reduction is believed to proceed step-wise as shown below<sup>19</sup>.



Recently, unstable compounds like trichloro-ethyl titanium have been isolated from reactions similar to the one described above.

Bridge complexes of (1) aluminium triethyl and titanium dichloride ethyl<sup>20</sup> analogous to the well established bridge dimers of (2) aluminium triethyl and those of (3) aluminium halides<sup>21</sup> have also been proposed as effective Ziegler catalysts formed by

reaction of unused trialkyl aluminium and titanium tri or dichlorides.



It is well known that in the formation of macromolecules of vinyl type, essentially three steps are involved. These are initiation, propagation and termination. For the production of useful polymeric materials, control<sup>22</sup> of all these steps is important.

#### INITIATION

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

#### PROPAGATION

It is the addition of each individual monomer occurring hundreds or even thousands<sup>of</sup> times in the course of the growth of the macromolecule.

#### TERMINATION

Certain chemical reagents reacting with free

radicals or ions of growing chains are capable of stopping the further growth of the macromolecule.

It is known that overall rate of polymerization can be controlled by regulating initiation and termination steps. The propagation process on the other hand has remained essentially uncontrolled. Any successful control of propagation step would help not only to speed up the formation but also to produce macromolecules of great geometrical regularity and as a consequence of better mechanical and thermal behaviour.

The control of the propagating<sup>23</sup> reaction is possible by immobilising, complexing and orienting each individual monomer before it is introduced into the chain and chemically attached to its predecessor. Different stereoregulating forces e.g. temperature<sup>23,24,25</sup>, nature of the solvent<sup>26</sup>, monomer<sup>26</sup>, heterogeneity<sup>27</sup> of the catalytic system, layer lattice structure of the transition metal halide used, particle size of the catalyst<sup>28</sup> and the conditions under which the catalyst has been prepared i.e. mode of addition of the reactants, are considered for control of propagation step.

The vinyl butyl and vinyl isobutyl ethers yield polymers in bulk and solution in an amorphous and a crystalline form depending upon the solvent and

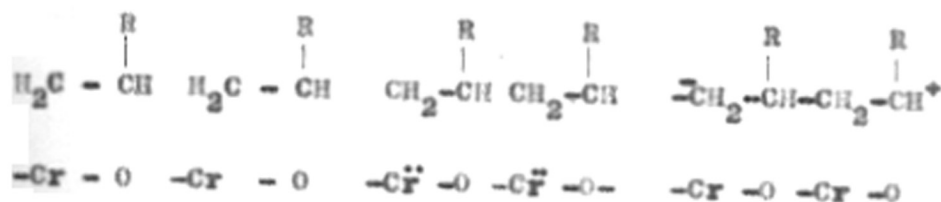
temperature of the reaction. In the case of radical polymerization, low temperature is effective for producing syndiotactic polymer. Polymethyl methacrylate prepared at  $-80^{\circ}$  by free radical polymerization contains syndiotactic structure.

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<sup>29</sup> has established that p-xylene and other related monomers do not polymerise in the gas phase but react rapidly and smoothly as soon as their vapours are condensed on a surface. Melville and Watson<sup>30</sup> 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. Morton and coworkers<sup>31</sup> studied the polymerization of isoprene and butadiene by the combination of alkali alcoholates and olefin halides and observed not only a high rate of polymerization but also the formation of 1,4 trans species without any formation of gelatinous by-products. But it was difficult to understand the specific action of the catalyst. These catalysts are termed as Alfin

catalysts.



Solid surfaces can also be used to adsorb and consequently orient the monomer. Molybdenum oxide deposited on alumina and chromium oxide on silica or alumina which are known as Phillips catalysts<sup>32</sup> can direct the polymerization of ethylene to linear high density polyethylene.



Nature of the surface of the catalyst plays an important role in stereo-regulating a propagation step. No homogeneous catalyst system of Ziegler-Natta

type has been reported so far to produce a stereoregular polymer. On the other hand heterogeneous catalyst systems are undoubtedly the most effective means of stereoregulating a propagation step. It is readily explained that if the polymer remains soluble in the reaction medium, stereoregularity remains undisturbed but the catalyst species must be in an undissolved state in the polymeric system, otherwise the stereospecificity would be affected. Dicyclopentadienyl titanium dichloride/aluminium diethyl chloride the soluble catalyst system can produce linear and high molecular weight polyethylene but cannot polymerise propylene monomer.

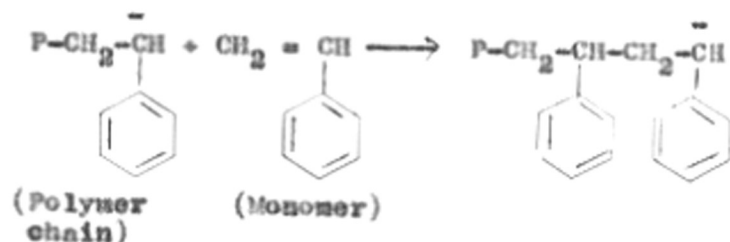
Crystal size and type of the reduced transition metal halide and reducing agents play important role in controlling the rate, molecular weight and stereo-chemistry of polymerization<sup>26</sup>. It has been shown that heterogeneous catalyst can actually change its particle size during the polymerization.

MECHANISM OF POLYMERIZATION  
WITH ZIEGLER-NATTA TYPE CATALYSTS

The mechanisms for addition polymerization are conventionally known as anionic, cationic and free radical. After the discovery of Ziegler-Natta catalysts, these conventions have been extended to coordinate anionic, coordinate cationic and coordinate free radical polymerizations. In polymerizations carried out by this new class of catalysts, the monomer gets coordinated with one part of the catalyst, prior to its addition to a partially stabilised chain end.

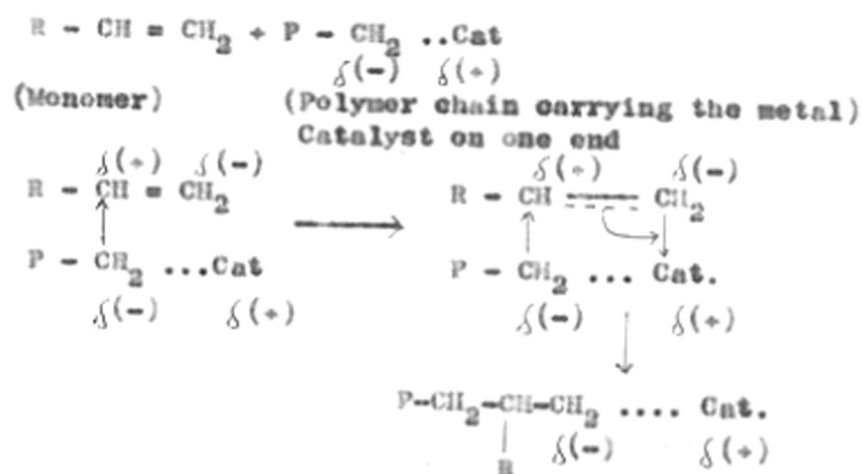
ANIONIC POLYMERIZATION

Anionic polymerizations are those in which the growing anion is essentially a free propagating ion and the cation only maintains electro neutrality. It can only be expected when the cation is derived from one of the most electro-positive metals, the cation is strongly solvated and the polymer anion is highly stabilised by resonance. These conditions are frequently met with sodium or potassium catalysts in basic solvents with polar monomers or dienes.



### COORDINATE ANIONIC POLYMERIZATION

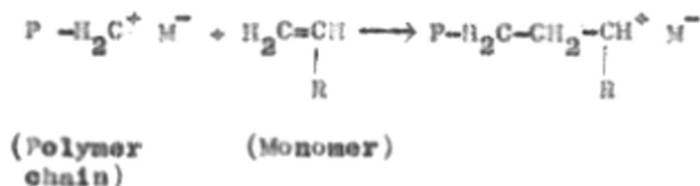
In coordinate anionic polymerizations each monomer unit is complexed and polarised by a positive centre, prior to its addition to the growing anion. The polymer migrates as an anion to the positive end of the double bond while the negative end of the double bond at the same time attaches itself to the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



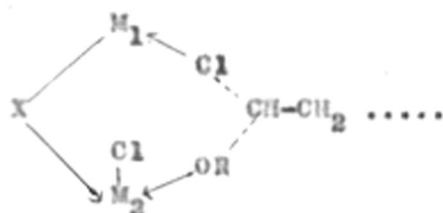


CATIONIC POLYMERIZATION

Cationic polymerizations are those in which the propagating end carries a positive charge. Transition metal halides, aluminium chloride and boron trifluoride etherates are a few examples of the catalysts in which such a type of polymerization takes place

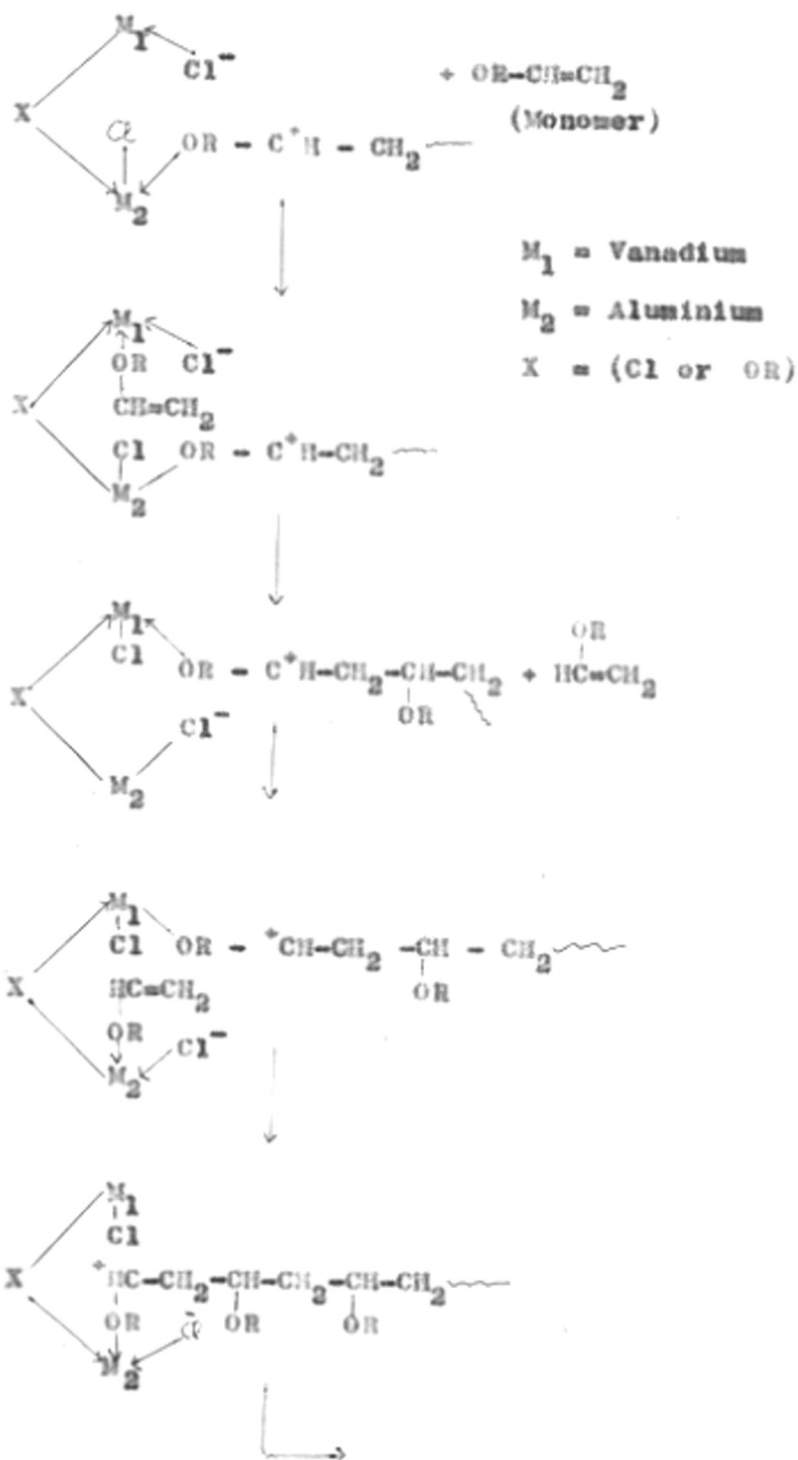
COORDINATE CATIONIC POLYMERIZATION

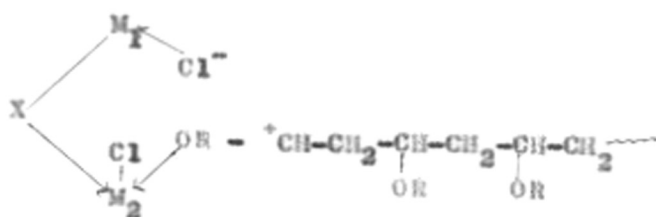
During the course of kinetic studies on the polymerization of vinyl ethyl ether by the use of vanadium tetrachloride and aluminium triethyl, Vandenburg<sup>33</sup> concluded that a bimetallic bridge complex of the type given below is formed.



In the propagation steps by coordinate cationic mechanism, coordination of the monomer occurs on one metal site followed by insertion between an adjacent

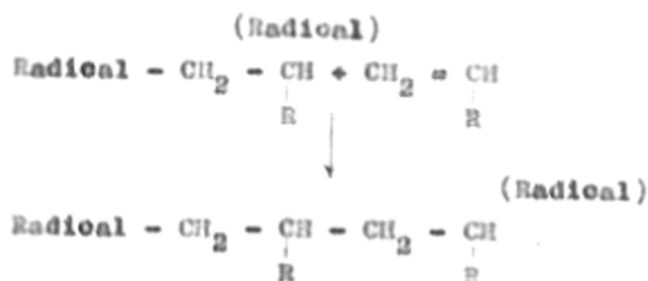
metal polymer bond.





### RADICAL POLYMERIZATION

In these polymerizations free radical formed by the decomposition of the initiators induce free radical in the monomer unit and starts chain growth. Benzoyl peroxide and azo bis isobutyro nitrile are examples of catalysts which give rise to such a type of polymerization.



Stereospecificity generally suffers in these systems because radical addition to a double bond is less selective for producing a head to tail structure.

### COORDINATE RADICAL POLYMERIZATION

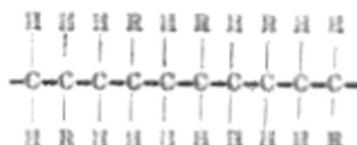
In coordinate radical polymerization, the active metal carbon bond becomes more covalent, homolytic



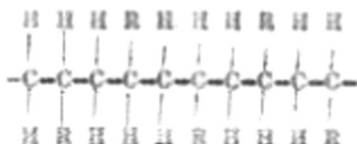
(b) Atactic

When the distribution of R groups is

random

(c) Syndiotactic

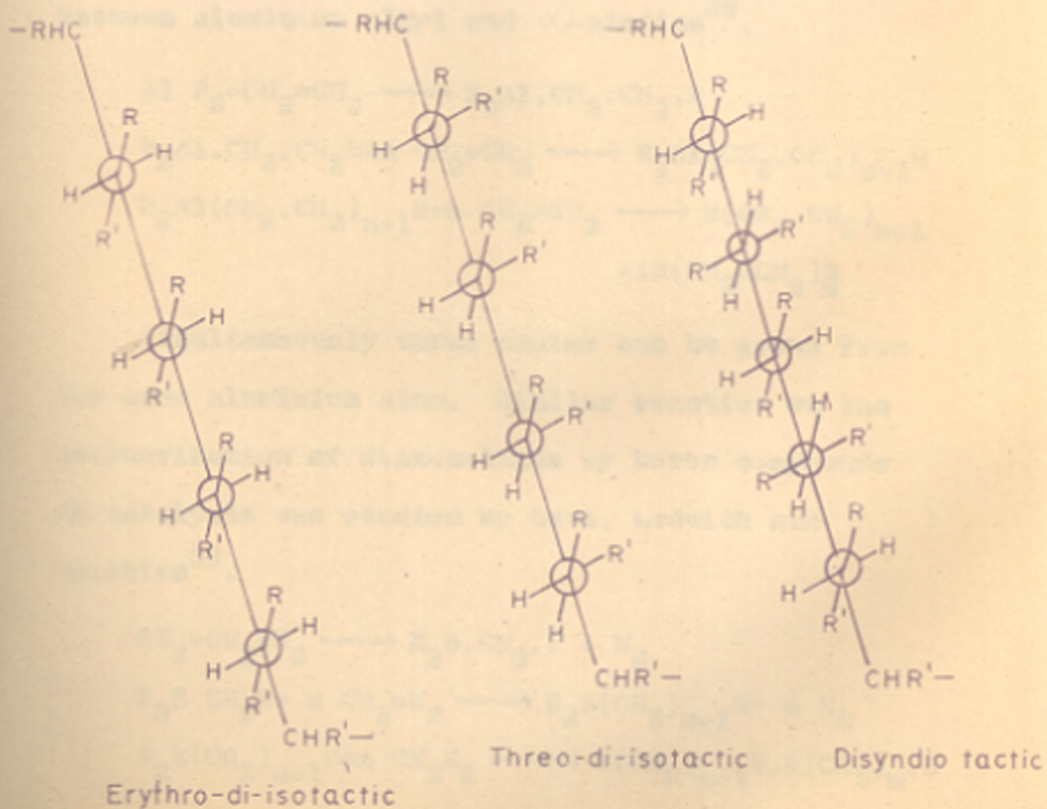
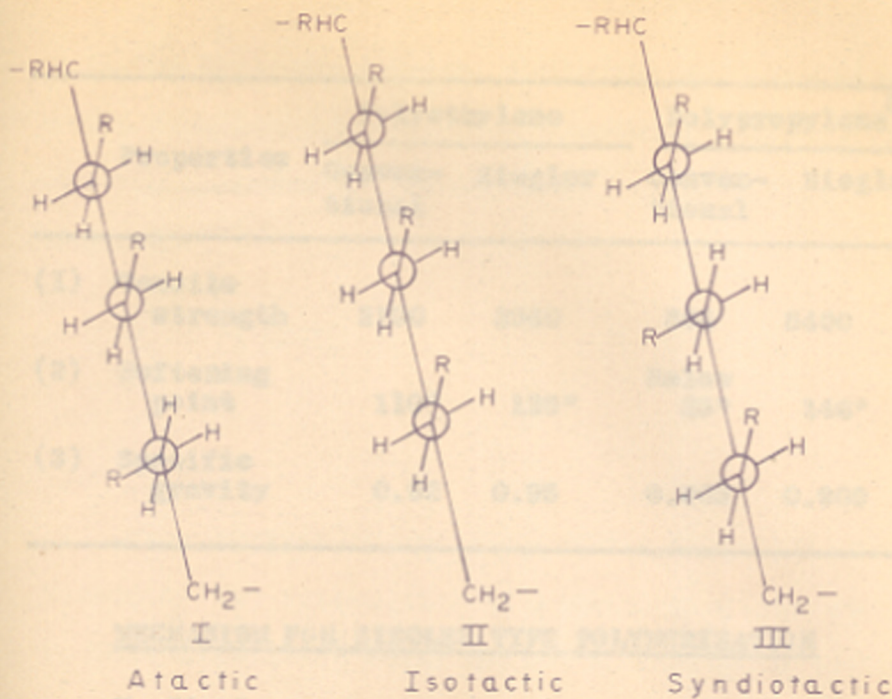
When R groups alternate regularly above and below the carbon backbone chain:



The above three forms can be better visualised by Newman's<sup>34</sup> projection as illustrated. G. Natta<sup>35</sup> and D. Breslow<sup>36</sup> have succeeded in polymerizing 1,2-disubstituted ethylenes of the type  $\text{RHC}=\text{CHR}'$ . Such monomers can give rise to polymer molecules with two different asymmetric carbon atoms in the backbone chain. The tactic forms obtained with such monomers are termed as erythro-di-isotactic, threo-di-isotactic and di-syndiotactic.

The stereochemical effects on the properties of conventional polymers are quite considerable as given overleaf where the properties of the conventional polymers are compared with Ziegler polymers.

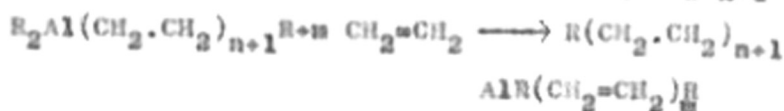
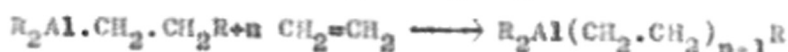
# NEWMAN'S PROJECTION



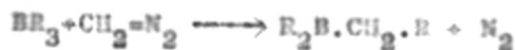
Properties	Polyethylene		Polypropylene <sup>37</sup>	
	Conven- tional	Ziegler	Conven- tional	Ziegler
(1) Tensile strength	2190	2960	506	5400
(2) Softening point	110°	135°	Below 25°	146°
(3) Specific gravity	0.92	0.95	0.863	0.909

#### MECHANISM FOR ZIEGLER TYPE POLYMERIZATION

K. Ziegler and coworkers studied the reaction between aluminium alkyl and  $\alpha$ -olefins<sup>38</sup>.



Simultaneously three chains can be grown from the same aluminium atom. Similar reaction on the polymerization of diazomethane by boron compounds as catalysts was studied by Bawn, Ledwith and Matthies<sup>39</sup>.



The reaction between  $\alpha$ -olefins and aluminium alkyl does not take place if aluminium alkyl is in dimeric form due to insufficient electrophilic character.



Many workers are of the opinion that the complex formed by the interaction of aluminium alkyls and reduced transition metal halide is analogous to the dimeric aluminium alkyl and therefore is incapable of any growth in or from ~~at~~ the aluminium atom due to its complete electronic shell. Titanium atom, with its vacant d-orbitals could be the centre of chain growth.

MECHANISM PROPOSED BY G. NATTA

According to G. Natta<sup>40</sup>, in the complexes containing titanium and aluminium the polymeric chain grows on the aluminium carbon bond and not from titanium carbon bond. The detailed mechanism proposed is that the initially incomplete coordination of titanium in reduced state of di and tri chloride facilitates chemisorption of organometallic

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compounds of strongly electro-positive metals having small ionic radius. This chemisorption leads to the formation of electron deficient complexes between titanium and the other metal, which contain alkyl bridges similar to those present in the dimeric aluminium and beryllium alkyls. The isolation of soluble crystalline complexes  $(C_5H_5)_2 TiCl_2 Al R.R'$ , which are known to contain Ti-C-Al bridges lends weight to the bimetallic electron deficient theory proposed by Natta.



G. Natta's mechanism

The catalysts derived from bis cyclopentadienyl<sup>41</sup> titanium  $(C_5H_5)_2 TiCl_2$  and triphenyl aluminium polymerise ethylene and the polymeric chain carries phenyl end groups. Such terminal phenyl groups cannot be detected when catalyst derived from  $(C_5H_5)_2 Ti (C_6H_5)_2$  and triethyl aluminium<sup>41</sup> are used under the same conditions. This indicates that the polymeric growth occurs on aluminium carbon bond and not on titanium carbon bond.

Natta and coworkers further proved their stand by adsorbing  $C^{14}$ -labelled ethyl groups on the surface of  $\Delta$ -titanium trichloride and using the whole system as a catalyst in the presence of non-labelled triethyl aluminium. The resulting polymer contained all of the labelled alkyl groups. The chemical analysis showed the presence of aluminium<sup>42</sup>. This result according to G. Natta and Mazzanti, is due to the dissociation of each catalytic complex in two parts one containing the titanium atom, the other containing alkyl groups, including polymeric chains bound to aluminium. The dissociation is followed by association of titanium counterpart with other aluminium alkyls present in the solution. This mechanism is in full accord with the kinetic data obtained by Natta, Pasquon and Giachetti<sup>41,43</sup>. Only Patat<sup>44</sup> and Sinn have proposed a mechanism

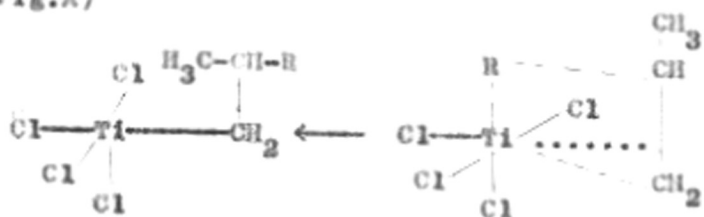
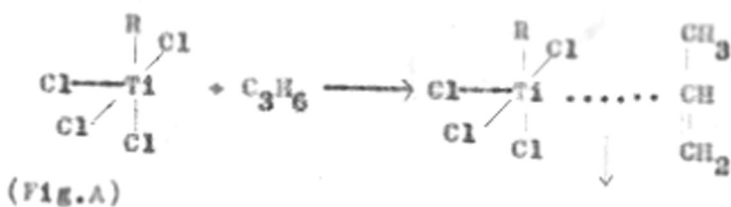
supporting Natta's view.

Carrick and Karapinka<sup>45</sup> used bis cyclopentadienyl diphenyl titanium as a catalyst for the polymerization of ethylene. They found that phenyl groups are present in the polymer but they concluded that this does not constitute any real evidence for growth on aluminium rather than on titanium. Carrick<sup>46</sup> showed that by changing the nature of the reducing agent the propagating species are not altered, but there is a change in species if the transition metal is varied. The relative reactivity ratio of two monomers, ethylene and propylene in copolymerization changed when different transition metal compounds were used but was not affected by use of reducing agents with a common transition metal compound. Such evidence clearly indicates that chain growth occurs at the transition metal.

#### MECHANISM PROPOSED BY COSSEE<sup>47</sup>

The surface of the catalyst system plays a large part in controlling the stereochemistry of propagation since no homogeneous catalysts (Ziegler type), which will produce stereoregular polymers of  $\alpha$ -olefins have so far been reported. A mechanism explaining stereoregular polymerization at

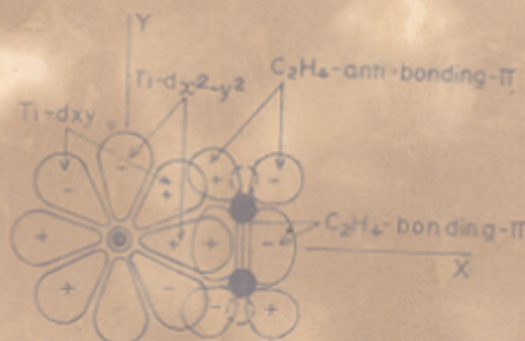
crystalline surface has been given by Cossee<sup>47</sup>. Cossee assumed that polymerization occurs at one titanium ion in the surface layer of trichloride or dichloride lattice (Fig.A) of which one chlorine atom is replaced by alkyl group R, while an adjacent chlorine site is vacant in order to accommodate the incoming molecule. Polymerization proceeds in a manner similar to that suggested by Ludlum, Anderson and Ashby. [ *J. Am. Chem. Soc.* 80, 1380 (1958) ]



The active centre retains a titanium alkyl bond and a vacant site, which have inter-changed their places. During polymerization, aluminium alkyl is thought to act as a chain transfer agent, in re-establishing the lost centres and as a scavenger of impurities but is not essential for propagation.

The complexes formed by titanium trichloride and

$\pi$ -olefins are similar to Platinous olefinic complexes.



The  $\pi$  bond between Titanium and Ethylene

○ = Titanium; ● = Carbon; ○ = Hydrogen

#### Platinous Olefinic Complex.

Titanium has vacant  $d_{x^2-y^2}$  orbital. During complexing of olefins and titanium metal, the bonding electrons overlap with this vacant  $d_{x^2-y^2}$  orbital resulting in a  $\pi$ -bond. Simultaneously the  $d_{xy}$  orbital of the metal overlaps with the antibonding  $\pi^*$ -electrons of the olefin. By this overlapping, the distances between bonding orbitals and the empty d-orbitals decrease. Such a situation weakens the carbon metal bond in transition metal alkyls. The alkyl group migrates to one end of the incoming molecule of the olefin. The reason why transition metals of small ionic radius and more electropositive

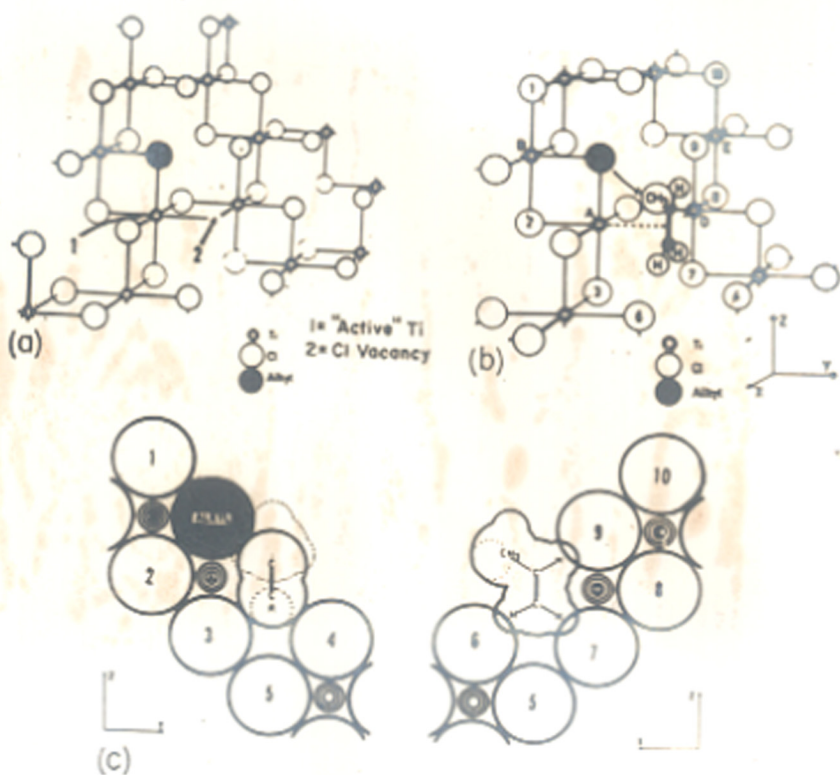


Plate.1. Mechanism of Ziegler-Natta polymerization according to Cossee

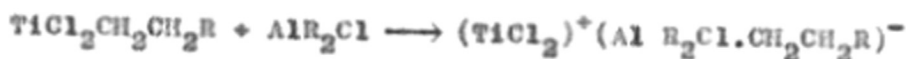
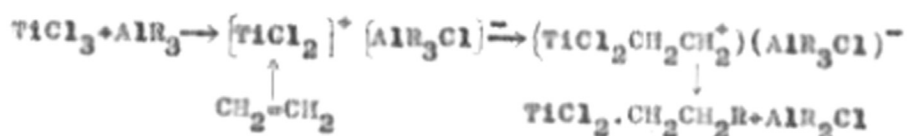
- a. Activated  $\text{TiCl}_3$  surface
- b. Monomer  $\pi$ -bonded to surface
- c. Stereochemistry of monomer-catalyst complex.

charge are preferred and are better catalysts, is obvious from the above discussion because in such transition metals the size of the empty d-orbitals enables them to overlap sufficiently with antibonding orbital of the olefins.

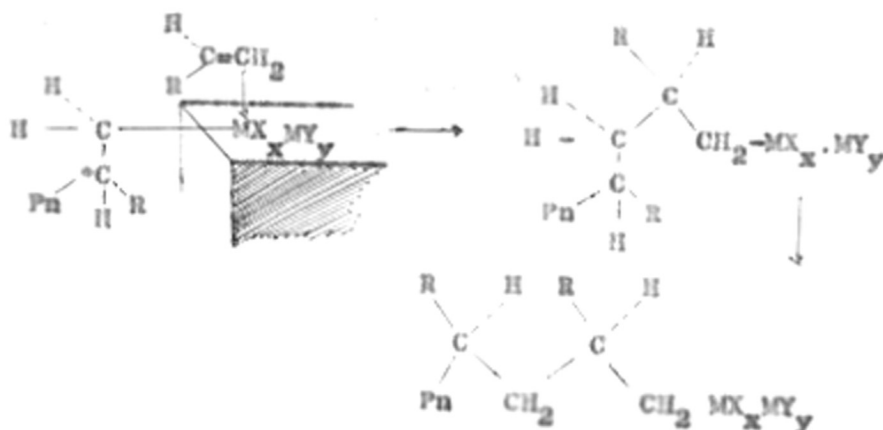
In the three dimensional schematic picture of titanium trichloride lattice, if we cross sect through the monomer in the chlorine vacancy parallel to the YZ and ZX plane, it can be seen that there is only one possibility for insertion of the propene molecule and that is with  $=CH_2$  group pointing into the lattice. This explains the reason for stereoregularity with such catalysts. There is an allowance for only two different orientations i.e.  $C=C$  or  $\begin{matrix} C \\ | \\ C \end{matrix}$ . The configuration with the minimum steric hindrance will be preferred in the lattice and this configuration is  $\begin{matrix} C \\ | \\ C \end{matrix}$  as shown in the Fig.C.

#### MECHANISMS PROPOSED BY OTHER WORKERS

Uelzmann<sup>48</sup> and Bier<sup>49</sup> have insisted 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 overleaf.



This mechanism has been supported by Bawn<sup>50</sup> and Ledwith. Cram and Kopecky<sup>51</sup> have explained stereospecific polymerization on the basis of steric repulsion between the monomer substituent and the substituent in the last but one monomer unit. The basic requirement of this mechanism is that the growing polymeric chain projects from the edge of the catalyst surface, which agrees with recent examination of activated titanium trichloride crystal made during polymerization of ethylene<sup>52</sup>, with electron microscope. The stereospecificity may be induced entirely by steric repulsions as indicated by Furukawa and Tsuruta<sup>53</sup>.





The incoming monomer is best able to react if R is on the same side as H of the asymmetric carbon atom.

These discussions clearly show that mechanism of polymerization with Ziegler type catalysts is somewhat complicated. The study on kinetics of polymerization with these catalyst systems would help to reveal something more on the mechanism of polymerization.

#### KINETICS OF POLYMERIZATION

Kinetic studies of polymerization with Ziegler type catalysts are carried out keeping into consideration the following factors:

- (1) The dependence of rate of polymerization on monomer concentration
- (2) The dependence of rate of polymerization on organo metallic compound and transition metal halide concentration
- (3) The dependence of rate of polymerization on catalyst ratio: organo-metallic compound/transition metal halide
- (4) Ageing time of the catalyst
- (5) Reaction time
- (6) The effect of temperature on molecular weight and rate of polymerization.

Mark and Gaylord<sup>52</sup> have presented an equation which relates polymerization rate as a function of strength of monomer adsorption, nature of the catalyst complex etc. but there is no explanation for the maxima obtained for various systems when polymerization rate is plotted against catalyst ratio.

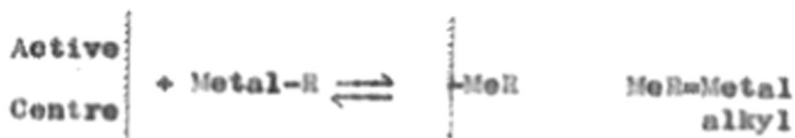
Saltman and coworkers<sup>54</sup> have developed theoretical relationship between the variables based on the polymerization of isoprene with Ziegler catalyst but the scheme was not elaborated.

Recently Saltman<sup>55</sup> has proposed a more detailed scheme for the system, propylene - $\text{TiCl}_4$ - $\text{AlEt}_3$ , which could explain results obtained by Natta<sup>56,57</sup>.

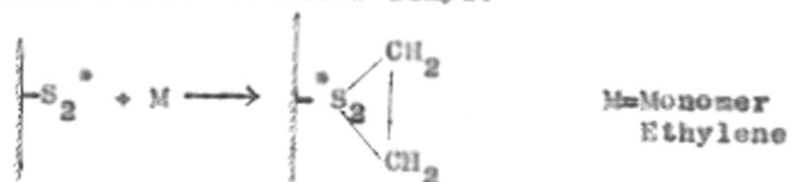
Friedlander and coworkers<sup>58</sup> have presented a kinetic scheme in order to explain the polymerization of ethylene by means of molybdena alumina catalyst in the presence of hydrogen. In a very recent paper L. Reich and S.S. Stivala<sup>59</sup> have proposed a general scheme for Ziegler type polymerization reactions. This scheme is based on the assumption that all Ziegler type polymerizations involve a similar mechanism. However, depending upon the system, some steps will predominate over the others.

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

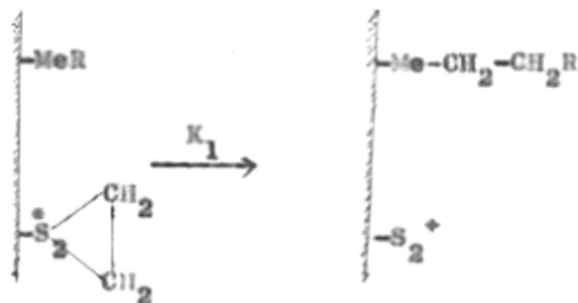
Active centres are formed by the reduced titanium halide and the metal alkyl.



The monomer has been postulated as being adsorbed on an active dual site,  $\text{S}_2^*$ <sup>58</sup>, which can orient the monomer in a unique position.

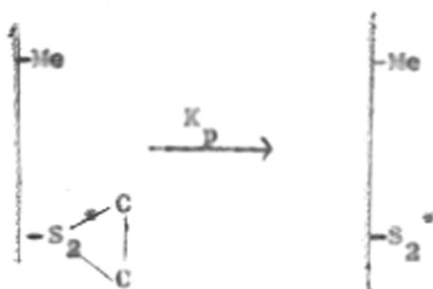
Initiation

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



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

#### Propagation

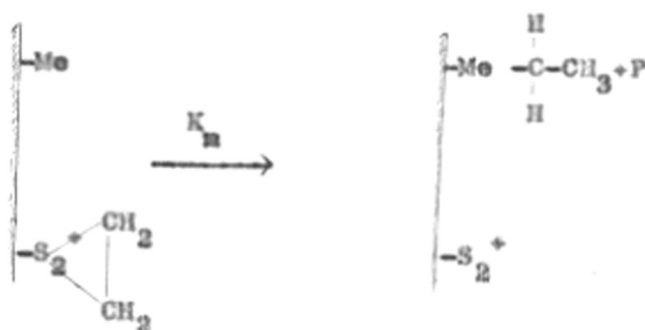


Natta<sup>56</sup> has postulated that adsorbed monomer is inserted between the metal and alkyl portion of the aluminium alkyl and in this insertion hypothesis two bonds are broken and two are formed but Huggins<sup>60</sup> postulated that during the propagation process, every step is accompanied by 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.

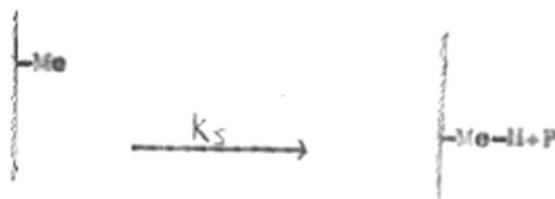
Monomer Transfer



P = Polymeric molecule

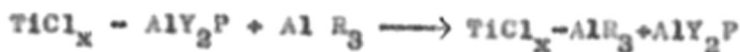
Termination may occur by monomer transfer.

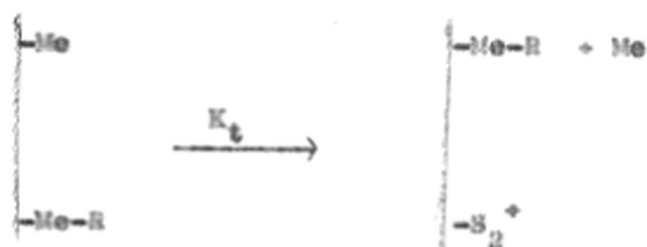
Spontaneous Transfer



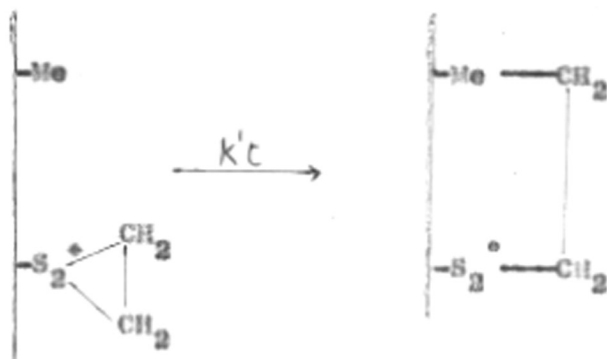
In this case termination may occur by spontaneous disproportionation. In both the cases a hydride ion is considered to be involved.

Transfer by means of catalyst has also been postulated viz.



Catalyst TransferTermination by Monomer

Reich and Stivala have proposed another type of termination by the monomers



$S_2^o$  is no longer active

The deactivation of dual site  $S_2^o$  would result in this termination. According to Saltman<sup>54</sup> termination could also result by interaction of a terminating site with aluminium alkyl or growing polymer chain containing aluminium alkyl.

SCOPE OF THE PRESENT WORK

The kinetics of polymerization with heterogenous catalysts formed by the combination of a transition metal halide and an organo-metallic compound have been actively studied in recent years. Zirconium tetrachloride was the first transition metal halide to be used in combination with aluminium triethyl for the polymerization of ethylene but very little data on its use except in the form of patents<sup>61</sup> is reported in literature. The relatively unstable nature of zirconium tetrachloride may be one of the reasons for its restricted use. Ziegler-Natta catalysts based on titanium tetrachloride have however received maximum importance.

It is well known that reaction between a liquid-liquid system e.g. titanium tetrachloride and aluminium triethyl will be smoother and faster than between a solid-liquid system e.g. zirconium tetrachloride and aluminium triethyl. It will, however, be interesting to study the kinetics of polymerization with the use of catalyst systems based on zirconium tetrachloride and zirconium trichloride and correlate them with the nature of polymers obtained therefrom.

These studies concerning the overall behaviour of these catalytic systems in the polymerization of

styrene are based on the following aspects.

- (1) Aging time of the 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 constituents and nature of the catalyst complex formed at different ratios
  - (4) Rate law from the variation of the rate of polymerization with monomer concentration.
  - (5) Dependence of the molecular weight on the ratio of combination of catalyst concentration, monomer concentration, metal alkyl concentration, and aluminium halide concentration and to know the mode of termination reaction. Mechanism of polymerization is ascertained by calculating activation energy of polymerization with each catalyst system.
-



CHAPTER-II

EXPERIMENTAL

EXPERIMENTAL

The catalysts obtained by the reaction of the metal alkyls and the transition metal compounds used in polymerization are sensitive to traces of moisture, air, other impurities in solvents and monomer. Therefore the kinetic studies were carried out under extremely dry inert atmosphere of nitrogen. All experiments were conducted inside a glove box made of seasoned wood, fitted with a glass top and two rubber gloves in the front for manipulation inside this box. On one side the box opened to another chamber through a sliding door. All materials to be taken in or out of the box were transported through this chamber so that the dry box was never exposed to the atmosphere. The dry box was constantly flushed with dry nitrogen and the outlet was well guarded by a silica gel tower. The nitrogen gas was purified, oxygen freed by successively passing through four columns of eight inches 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, phosphorous penta oxide, potassium hydroxide 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, potassium hydroxide pellets and calcium sulphate kept in petri dishes, which were replaced every day by activated batches. The openings of the gloves (provided for entering of the hands) were kept closed with tight fitting wooden discs.

#### REAGENTS

##### Fieser's Solution<sup>62</sup>

It was prepared by dissolving fifteen grams of sodium hydrosulphite per hundred millilitre of an aqueous solution of twenty grams potassium hydroxide, followed by two grams of anthraquinone sulphonic acid (sodium salt). The solution was blood red initially but became dull brown with formation of white scum when exhausted.

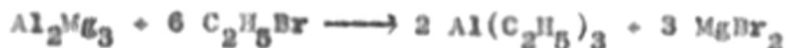
#### SOLVENTS

All solvents and reagents used in the experiments were purified, well dried and preserved under

nitrogen. Commercial toluene, n-hexane and cyclohexane were washed by stirring repeatedly with sulphuric acid, till the acid layer became colorless. The excess of acid was removed with distilled water. The solvents thus obtained were dried over anhydrous calcium chloride, distilled and kept over sodium wire. Prior to use these solvents were refluxed overnight on sodium under pure dry nitrogen and distilled.

#### Aluminium Triethyl

It was prepared by the method of Ziegler<sup>63</sup>, the reaction of ethyl bromide with an aluminium magnesium alloy containing Al 40% and Mg 60% corresponding to  $Al_2Mg_3$ .



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.  $Al_2Mg_3$  was prepared by the National Metallurgical Laboratory, Jamshedpur, India, and analysed as Al 36.5% and Mg.63.5%. Fifty five grams of this alloy were taken in a three necked 250 ml. flask fitted with a nitrogen inlet, dropping

funnel, reflux condenser and a mercury seal stirrer. A slight excess over required quantity of ethyl bromide, dried over phosphorous pentoxide, distilled ( $35^{\circ}/710$  mm.) and preserved over anhydrous calcium sulphate was added drop-wise and the reaction initiated by the addition of a little quantity of iodine to the reaction mixture. The exothermic reaction resulted in a vigorous refluxing of ethyl bromide, which was controlled by surrounding the reaction flask with oil bath. The evaporation loss was minimised by circulating ice cold water through the condenser. The reaction was allowed to proceed under continuous stirring for about two to three hours till refluxing of ethyl bromide stopped. The reaction was taken to completion by raising the temperature to  $160^{\circ}$ .

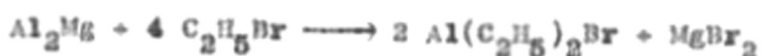
Aluminium alkyl was soaked in the evenly mass of magnesium bromide and removed by distillation under vacuum. The distilled product contained aluminium triethyl and diethyl bromide. The bromine content of the alkyl was estimated by hydrolysis and application of Volhard's<sup>64</sup> method. Depending upon the bromine content required amount of sodium was added to the alkyl. This reaction mixture of aluminium triethyl, aluminium diethyl bromide and sodium was heated to  $160^{\circ}$  for twenty four hours to obtain pure triethyl aluminium, vacuum distilled at about

CHAPTER-VI.

B I B L I O G R A P H Y

1.2 mm. (61°/1 mm.).

Similarly, reaction of  $\text{Al}_2\text{Mg}^{63}$  (Al=69%, Mg=31%) (also obtained from the National Metallurgical Laboratory) with ethyl bromide was used to prepare the aluminium diethyl bromide.



Tin tetra propyl was obtained from Kirby Industrial Estate, Liverpool, and isobutyl aluminium was obtained from Anderson Chemical Company, Weston, Michigan.

#### Zirconium Tetrachloride

Zirconium tetrachloride (commercial) was obtained from Chemische Fabrik Fluka, a Swiss company. It contained iron as impurity and was brown in color, brown color turned yellow in contact with moisture. There is very little direct information available on the purification of zirconium tetrachloride and it is essentially buried in a few patents. It became therefore necessary to work out actual details for its purifications. After carrying out few exploratory experiments on the lines of the available patent literature<sup>65-67</sup>, following procedure was found to give the best results.

Zirconium tetrachloride (10 g.) and zinc dust (500 to 1000 mg.) were intimately mixed on a glazed sheet of paper inside the dry glove box. It is very necessary to carry out the mixings inside the glove box because zirconium tetrachloride is very sensitive to moisture and if the mixings are carried out outside the dry box, part of zirconium tetrachloride gets converted to zirconium oxychloride. Ferric impurities, which are present in zirconium tetrachloride mainly in the form of ferric chloride also get oxidised. This oxidation of brown colored zirconium tetrachloride turns it yellow and the whole thing becomes a paste before transference can be done to the sublimation tube (a pyrex tube 25 cm. length  $3\frac{1}{2}$  cm. dia. with inlet for nitrogen on one end and B-29 cone joint on the other end).

The sublimation tube containing zirconium tetrachloride and zinc dust was heated to  $350^{\circ}$  in a tube furnace (dia. 4 cm. length 33 cm.). Temperature of the system was maintained with a dimmerstat. Nitrogen gas was allowed to pass through the apparatus to facilitate the movement of the sublimed particles towards receiver and avoid contamination with moisture and oxygen. Zirconium tetrachloride thus obtained was sublimed two to three times in the



absence of zinc dust. The pure product was stored in a stoppered flask, preserved over phosphorous pentoxide in a desiccator kept inside the dry box.

The function of zinc dust during purification of zirconium tetrachloride is to convert ferric chloride present in tetrachloride to ferrous chloride. Ferric chloride has a sublimation temperature of 315° which is quite close to that of zirconium tetrachloride, 331°. This nearness in the two sublimation points makes it impossible to separate the two components. The reduced state of ferric chloride i.e. ferrous chloride has a high sublimation point, much higher than that of zirconium tetrachloride and this makes it easy to sublime out the pure zirconium tetrachloride from ferrous chloride at 331°.

#### Conversion of Zirconium Tetrachloride to Zirconium Trichloride

Conversion of zirconium tetrachloride to trichloride was first tried out in 1923 by Ruff and Wallstein<sup>68</sup>. But they could not obtain the pure product. Since then from time to time many workers<sup>69-73</sup> have tried this conversion but without much success. Pure zirconium trichloride could not be obtained by any of these workers. First success for the conversion of tetrachloride to trichloride

was obtained by J.E. Newham and J.A. Watts<sup>74</sup> in 1959, who utilised atomic hydrogen for this conversion.

*in our laboratory*

Zirconium trichloride was prepared by the method similar to that reported in literature<sup>75</sup> for the conversion of titanium tetrachloride to titanium trichloride. 3 moles of zirconium tetrachloride were reacted with one mole of aluminium triethyl in decalin at 150° under an atmosphere of dry nitrogen with constant stirring with a mercury seal stirrer.



The reaction mixture was washed with pure, dry cyclohexane till the washings no longer showed any precipitate when treated with ethanol, which ensured complete removal of  $\text{AlCl}_3$ . The brown colored solid product thus obtained was dried and heated at 331° to remove residual unreacted zirconium tetrachloride. Pure zirconium trichloride thus obtained was stored over phosphorous pentoxide in a desiccator kept inside the dry box. Analysis of the  $\text{ZrCl}_3$  for chlorine was carried out by gravimetric method using  $\text{AgNO}_3$ . Chemical analysis established the composition of the zirconium trichloride (calculated for  $\text{ZrCl}_3$  Zr = 46.2 Cl 53.8 ) (Found Zr: 47 Cl:53).

### Purification of Styrene

Styrene (Dow Chemical Company, U.S.A) was treated with alkali, washed with water and dried over anhydrous sodium carbonate. It was distilled under reduced pressure in an atmosphere of dry nitrogen and stored over silica gel.

### EXPERIMENTAL PROCEDURE

The catalyst systems used consisting of the reactive metal alkyls and transition metal compounds were highly sensitive to moisture and air. So it was essential for the reproducibility of the result that the reaction vessels and dispensers be thoroughly dried. The reaction flasks, all glass hypodermic syringes and magnetic needles used in the experiments were thoroughly cleaned with chromic acid, washed with distilled water and dried. These were transferred inside the dry box when still hot and cooled by purging with nitrogen inside.

Stock solutions of catalysts, dry solvents and <sup>alkyls</sup> monomer were preserved inside the dry box and required amounts added with syringes (2-20 ml.) in the predetermined order.

Solid zirconium tetrachloride or zirconium trichloride was weighed in an erlenmeyer flask (50 ml.)

fitted with a B-19 cone joint. After the addition of required volume of toluene and the stirring element a calculated volume of aluminium triethyl solution was added to the reaction flask, which resulted in the formation of black colored complex. The reaction flask was immediately stoppered with well greased (Dow Corning silicone, high vacuum grease) standard joints and the black colored complex was aged for a specific time to study the effect of keeping the catalyst on its activity. Monomer styrene was added at this stage. The reaction flask was thermostated in a bath whose temperature was controlled to  $40^{\circ} \pm 0.05^{\circ}$  by a toluene regulator connected to an electronic relay. The stirring element inside the reaction flask was moved by a rotating horse-shoe magnet kept under it, enclosed in a water-proof brass case and carried on ball bearings. The magnet was connected by a flexible speedometer shaft cable to a B.T.C. stirring motor and the speed of the rotation adjusted. This stirring device was fabricated in our Laboratory<sup>76</sup>. After polymerization had been allowed to proceed to the required time, it was quenched by addition of large excess of acidified methanol and left overnight to settle down well. It was washed thoroughly with methanol over sintered glass disc of weighed crucible

and dried to a constant weight.

### Molecular Weights

Molecular weights were determined by intrinsic viscosities of 0.5 to 0.1% solutions of polymers in toluene in an Ostwald u-tube viscometer suspended in a Towers viscometric bath at 30°.

For polystyrene, the relationship of intrinsic viscosity with molecular weight as stated<sup>77</sup> below was used.

$$[\eta] = 1.1 \times 10^{-4} \times M_n^{0.725} \quad \text{in toluene.}$$

The original figures of the molecular weights have been rounded up and presented in this thesis e.g. 15780 to 15800 or 16330 to 16300 and so on.

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CHAPTER-III

EXPERIMENTAL RESULTS

EXPERIMENTAL RESULTSPOLYMERIZATION OF STYRENE WITH ZIRCONIUM TETRACHLORIDE AND ALUMINIUM TRIETHYL IN TOLUENE AT 40°

Zirconium tetrachloride alone i.e. in the absence of organometallics polymerises styrene to yield low molecular weight products and polymerization proceeds through a cationic mechanism. Results on the polymerization of styrene by zirconium tetrachloride alone at 40° in toluene have been tabulated below.

Table I.

[Styrene] = 1.743 M/l Time of aging = 3 hrs.

$[\text{ZrCl}_4] \times 10^3$ M/l	Time in minutes	Yield in gs.	$R_p \times 10^6$ M/L/S
3.74	15	3.40	14.520
7.58	15	3.80	16.229
15.16	15	4.40	18.792
9.86	30	4.40	9.412
9.86	60	4.40	4.696

The addition of styrene to zirconium tetrachloride in toluene resulted in the evolution of heat and the solution turned orange. Experiments were conducted by varying the time of reaction as

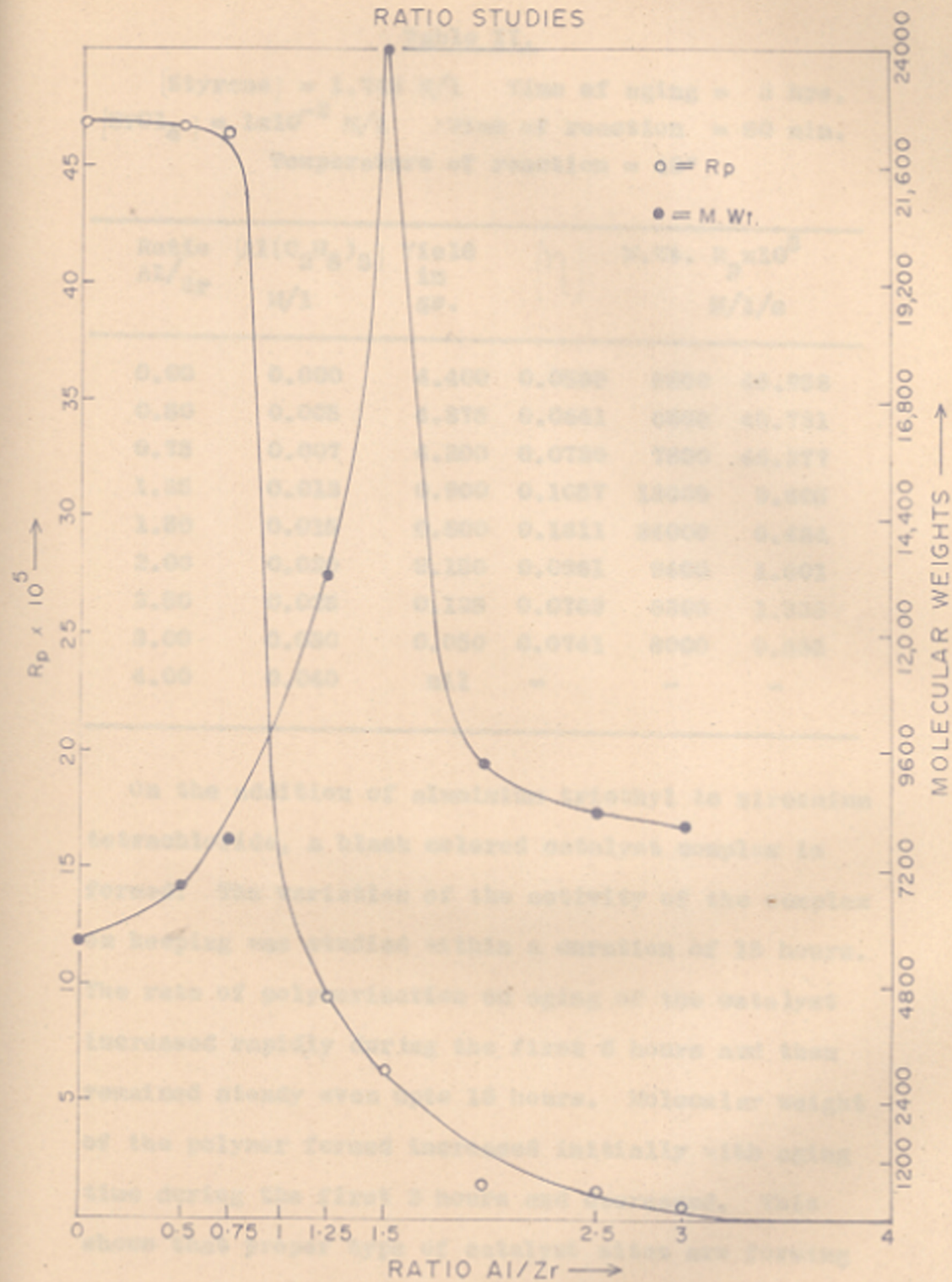
well as the concentration of zirconium tetrachloride. It was observed that the reaction depended much on the concentration of zirconium tetrachloride <sup>rather</sup> than the time of reaction for such polymerizations.

RATIO OF ALUMINIUM TRIETHYL/ZIRCONIUM  
TETRACHLORIDE

It is well known that nature of the catalyst sites changes with the ratio of the catalyst components. The activity of the catalyst complex at different molar ratios of mixing of zirconium tetrachloride and aluminium triethyl from Al/Zr ratio of 0.5 to 4.0 was studied. The concentration of zirconium tetrachloride was kept constant but that of aluminium triethyl was varied and increased. The yield of the polymer obtained from experiments conducted for 1 hour at different ratios was taken as the index of catalyst activity. Rate of polymerization decreased with increasing ratio of Al/Zr and became negligible at the Al/Zr ratio of 4.0. Molecular weights increased upto Al/Zr ratio of 1.5 and decreased beyond it. This indicated the formation of Ziegler-type catalyst sites around ratio 1.5 of Al/Zr, where the molecular weight is also maximum. Ratio 1.5 of Al/Zr was chosen for further studies. Results have been tabulated in Table No.II (Fig.1).



Fig. 1  
 $ZrCl_4$ - $Al(C_2H_5)_3$ -STYRENE  
 RATIO STUDIES



$[ZrCl_4] = 0.01 \text{ M/L}$   
 $[Styrene] = 1.743 \text{ M/L}$

Time of Reaction = 60 Min.  
 Time of Ageing = 3 hr.  
 Temp. of Reaction =  $40^\circ$

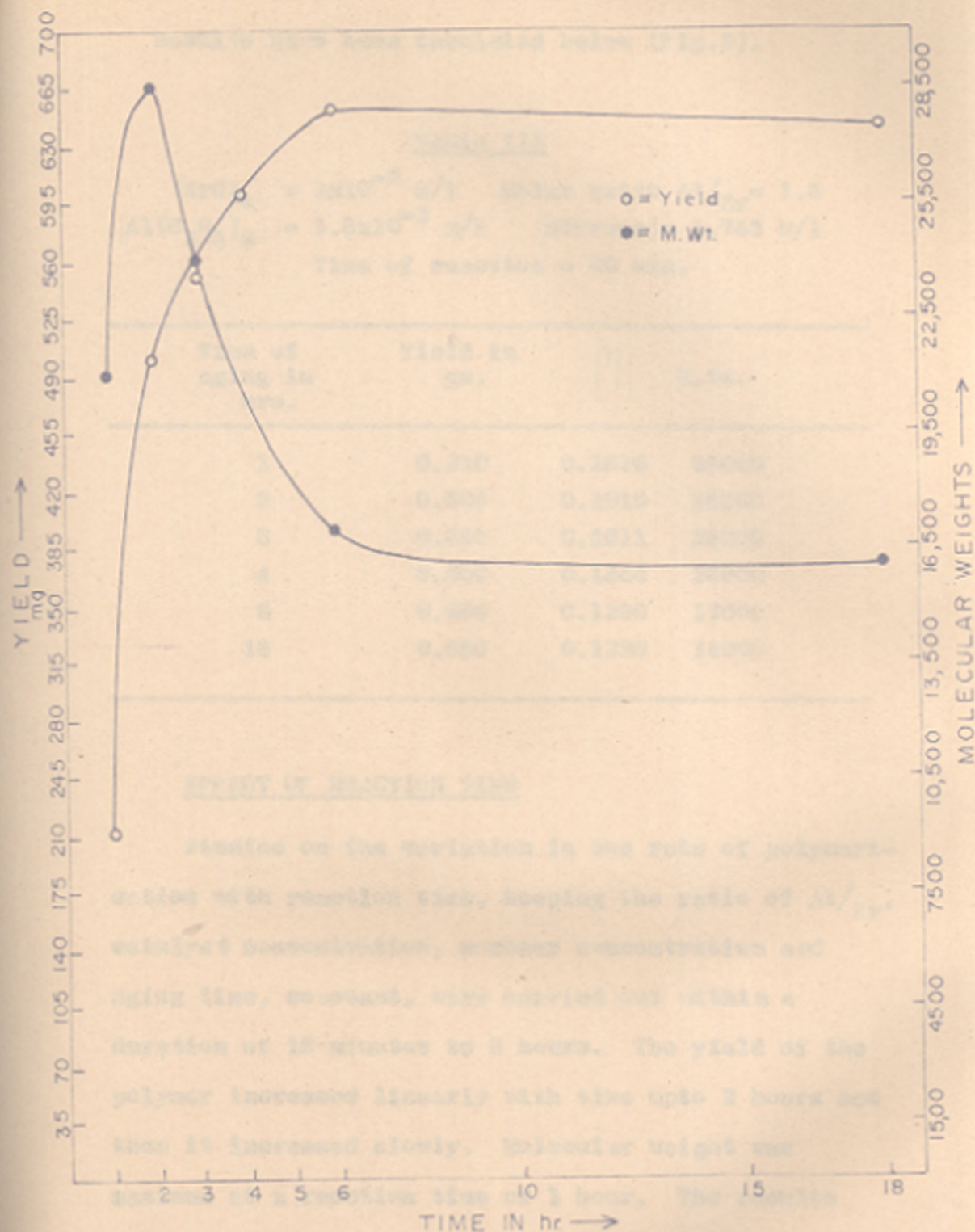
Table II.

[Styrene] = 1.743 M/l    Time of aging = 3 hrs.  
 [ZrCl<sub>4</sub>] = 1x10<sup>-2</sup> M/l    Time of reaction = 60 min.  
 Temperature of reaction = 40°

Ratio Al/Zr	[Al(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> ] M/l	Yield in gs.	[ $\eta$ ]	M.Wt. $R_p \times 10^5$ M/l/s
0.00	0.000	4.400	0.0589	5800 46.958
0.50	0.005	4.375	0.0661	6800 46.731
0.75	0.007	4.300	0.0730	7800 46.277
1.25	0.012	0.900	0.1057	13000 9.605
1.50	0.015	0.600	0.1611	24000 6.424
2.00	0.020	0.150	0.0861	9400 1.601
2.50	0.025	0.125	0.0763	8300 1.333
3.00	0.030	0.050	0.0741	8000 0.535
4.00	0.040	nil	-	- -

On the addition of aluminium triethyl to zirconium tetrachloride, a black colored catalyst complex is formed. The variation of the activity of the complex on keeping was studied within a duration of 18 hours. The rate of polymerization on aging of the catalyst increased rapidly during the first 6 hours and then remained steady even upto 18 hours. Molecular weight of the polymer formed increased initially with aging time during the first 3 hours and decreased. This shows that proper type of catalyst sites are forming between 2 to 3 hours of aging.

Fig. 2  
 $ZrCl_4 - Al(C_2H_5)_3 - STYRENE$   
 EFFECT OF AGEING TIME



$[ZrCl_4] = 0.01 \text{ M/L}$

$[Styrene] = 1.743 \text{ M/L}$

$[Al(C_2H_5)_3] = 0.015 \text{ M/L}$

Time of Reaction = 60 Min.

Molar Ratio Al/Zr = 1.5

Temp. of Reaction =  $40^\circ$

Results have been tabulated below (Fig.2).

Table III

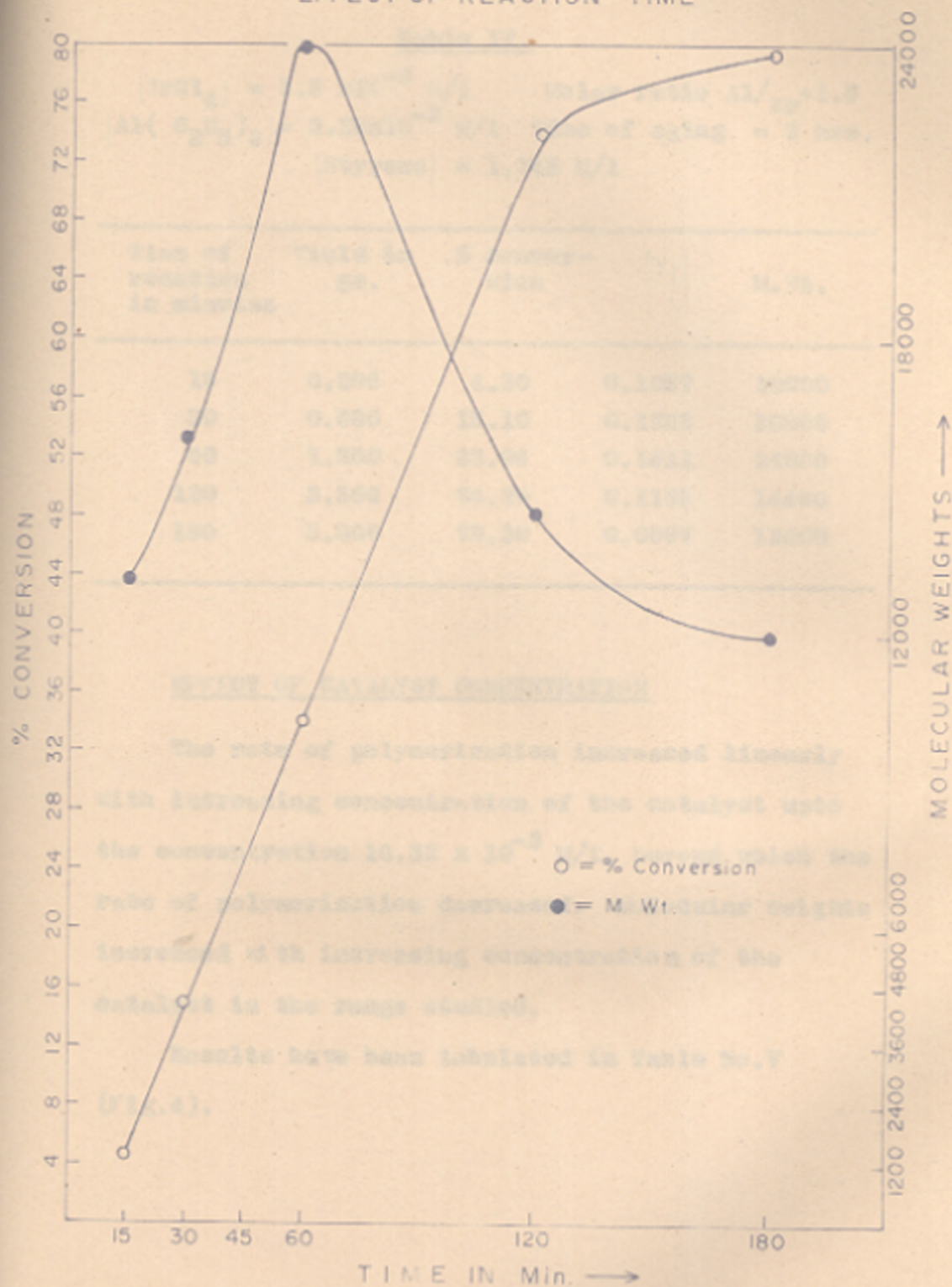
$[\text{ZrCl}_4] = 1 \times 10^{-2} \text{ M/l}$  Molar ratio  $\text{Al/Zr} = 1.5$   
 $[\text{Al}(\text{C}_2\text{H}_5)_3] = 1.5 \times 10^{-2} \text{ M/l}$   $[\text{Styrene}] = 1.743 \text{ M/l}$   
 Time of reaction = 60 min.

Time of aging in hrs.	Yield in gs.	$[\eta]$	M.Wt.
1	0.210	0.1519	21000
2	0.500	0.1919	28500
3	0.560	0.1611	24000
4	0.600	0.1444	20000
6	0.680	0.1285	17000
18	0.650	0.1228	16000

EFFECT OF REACTION TIME

Studies on the variation in the rate of polymerization with reaction time, keeping the ratio of  $\text{Al/Zr}$ , catalyst concentration, monomer concentration and aging time, constant, were carried out within a duration of 15 minutes to 3 hours. The yield of the polymer increased linearly with time upto 2 hours and then it increased slowly. Molecular weight was maximum at a reaction time of 1 hour. The results have been tabulated in Table No.IV (Fig.3).

Fig. 3  
 $ZrCl_4 - Al(C_2H_5)_3 - STYRENE$   
 EFFECT OF REACTION TIME



$[ZrCl_4] = 0.015 \text{ M/L}$

Time of Ageing = 3 hr.

$[Al(C_2H_5)_3] = 0.0225 \text{ M/L}$

Temp. of Reaction =  $40^\circ$

Molar Ratio  $Al/Zr = 1.5$

$[Styrene] = 1.743 \text{ M/L}$

Table IV.

$[\text{ZrCl}_4] = 1.5 \times 10^{-2} \text{ M/l}$       Molar ratio  $\text{Al/Zr} = 1.5$   
 $[\text{Al}(\text{C}_2\text{H}_5)_3] = 2.25 \times 10^{-2} \text{ M/l}$     Time of aging = 3 hrs.  
 $[\text{Styrene}] = 1.743 \text{ M/l}$

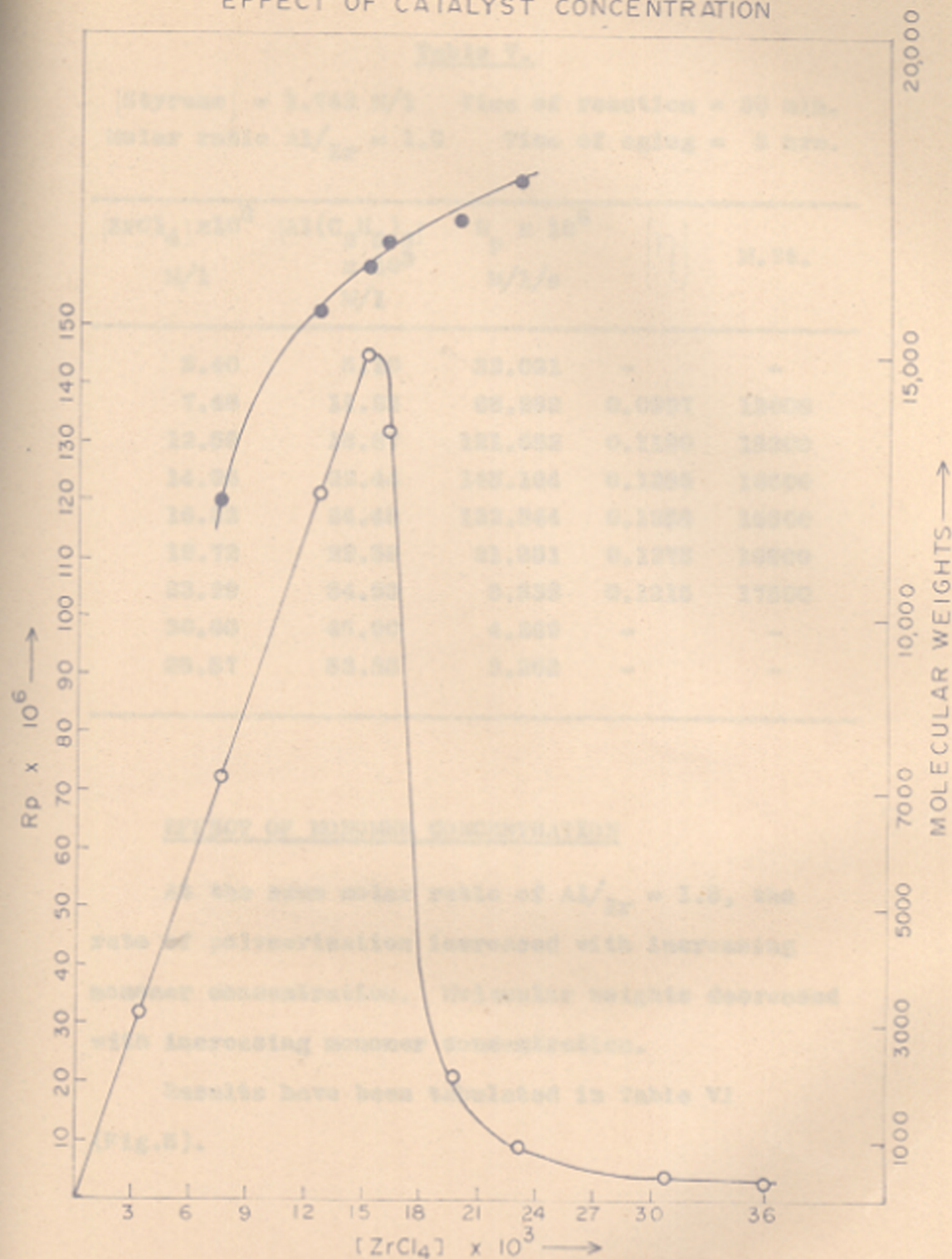
Time of reaction in minutes	Yield in gs.	% conversion	$[\eta]$	M. Wt.
15	0.206	4.30	0.1057	13000
30	0.686	15.10	0.1228	16000
60	1.500	33.06	0.1611	24000
120	3.366	74.20	0.1139	14400
180	3.600	79.30	0.0997	12000

#### EFFECT OF CATALYST CONCENTRATION

The rate of polymerization increased linearly with increasing concentration of the catalyst upto the concentration  $16.32 \times 10^{-3} \text{ M/l}$ , beyond which the rate of polymerization decreased. Molecular weights increased with increasing concentration of the catalyst in the range studied.

Results have been tabulated in Table No. V (Fig. 4).

Fig. 4.  
 $ZrCl_4 - Al(C_2H_5)_3 - STYRENE$   
 EFFECT OF CATALYST CONCENTRATION



[Styrene] = 1.743 M/L

Molar Ratio Al/Zr = 1.5

Time of Reaction = 30 Min.

Time of Ageing = 3 hr.

Temp. of Reaction = 40°.

Table V.

[Styrene] = 1.743 M/l    Time of reaction = 30 min.  
 Molar ratio Al/Zr = 1.5    Time of aging = 3 hrs.

$[\text{ZrCl}_4] \times 10^3$ M/l	$[\text{Al}(\text{C}_2\text{H}_5)_3] \times 10^3$ M/l	$R_p \times 10^6$ M/l/s	$[\eta]$	M.Wt.
3.40	5.10	32.031	-	-
7.48	11.22	68.282	0.0997	12000
12.58	18.87	121.682	0.1190	15300
14.96	22.44	145.184	0.1256	16500
16.32	24.48	132.344	0.1256	16500
19.72	29.58	21.351	0.1273	16800
23.29	34.93	8.539	0.1315	17500
30.60	45.90	4.269	-	-
35.87	53.35	3.203	-	-

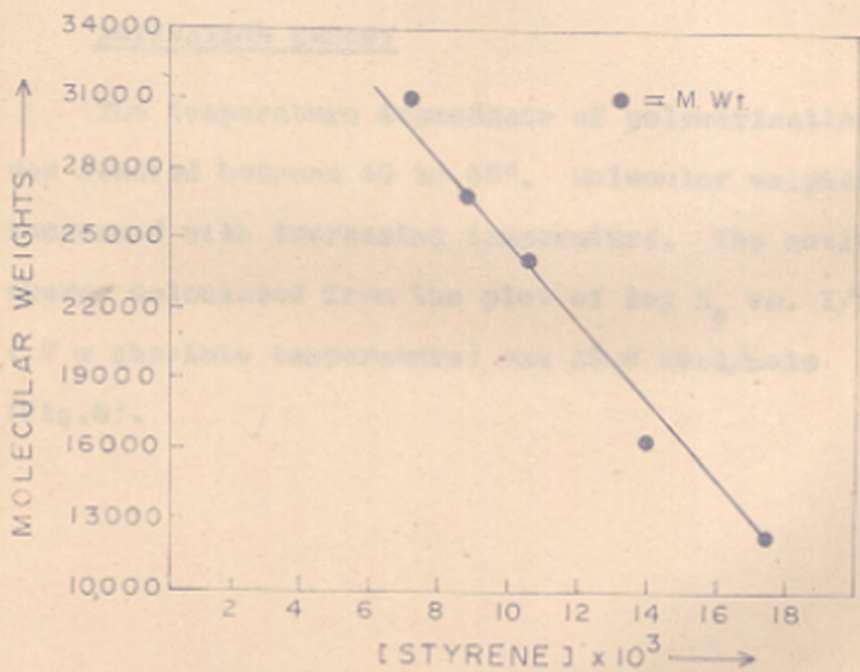
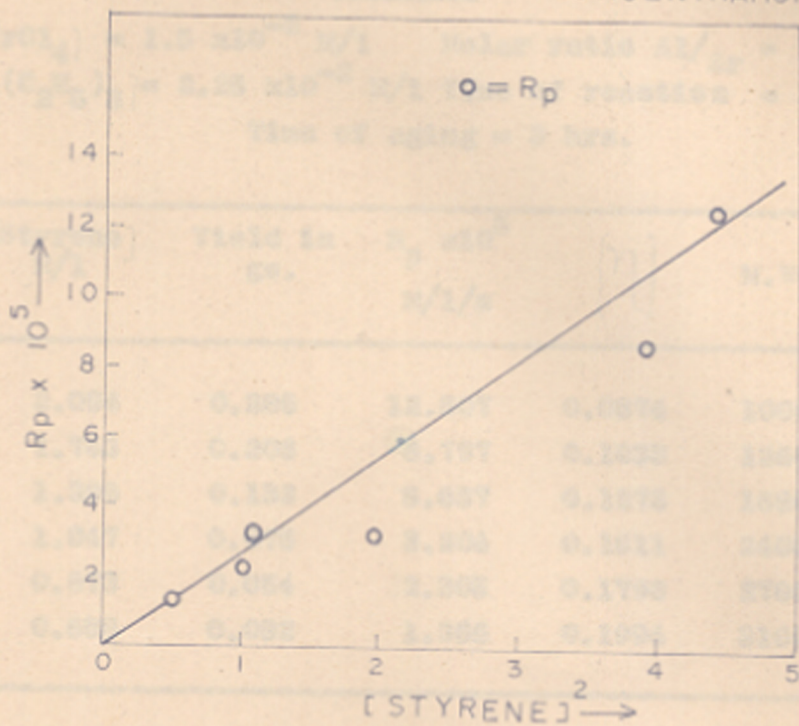
#### EFFECT OF MONOMER CONCENTRATION

At the same molar ratio of Al/Zr = 1.5, the rate of polymerization increased with increasing monomer concentration. Molecular weights decreased with increasing monomer concentration.

Results have been tabulated in Table VI (Fig.5).



Fig. 5  
 $ZrCl_4 - Al(C_2H_5)_3 - STYRENE$   
 EFFECT OF MONOMER CONCENTRATION



$[ZrCl_4] = 1.5 \times 10^{-2} M/L$

Time of Reaction = 15 Min.

$[Al(C_2H_5)_3] = 2.25 \times 10^{-2} M/L$

Time of Ageing = 3 hr.

Molar Ratio Al/Zr = 1.5

Temp. of Reaction =  $40^\circ$

Table VI.

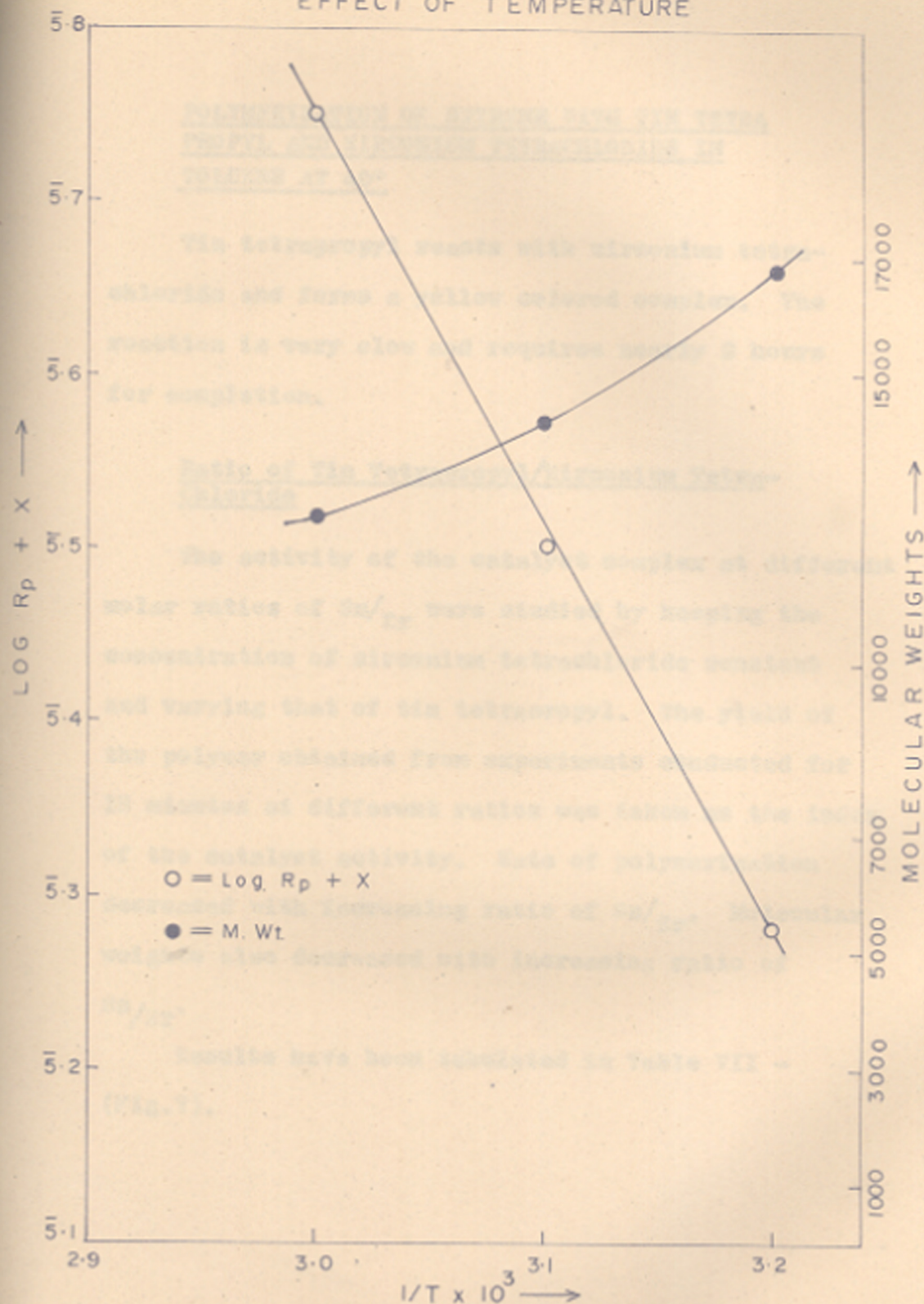
$[\text{ZrCl}_4] = 1.5 \times 10^{-2} \text{ M/l}$     Molar ratio  $\text{Al/Zr} = 1.5$   
 $[\text{Al}(\text{C}_2\text{H}_5)_3] = 2.25 \times 10^{-2} \text{ M/l}$     Time of reaction = 15 min.  
 Time of aging = 3 hrs.

[Styrene] M/l	Yield in gs.	$R_p \times 10^5$ M/l/s	$[\eta]$	M. wt.
2.094	0.286	12.507	0.0874	10000
1.743	0.206	8.797	0.1033	12600
1.396	0.132	5.637	0.1273	16800
1.047	0.075	3.204	0.1611	24000
0.873	0.054	2.305	0.1796	27000
0.698	0.032	1.366	0.1994	31000

#### ACTIVATION ENERGY

The temperature dependence of polymerization was studied between 40 to 60°. Molecular weights increased with increasing temperature. The activation energy calculated from the plot of  $\log R_p$  vs.  $1/T$  ( $T$  = absolute temperature) was 10.9 Kcal/mole (Fig. 6).

Fig. 6  
 $ZrCl_4 - Al(C_2H_5)_3 - STYRENE$   
 EFFECT OF TEMPERATURE



$[ZrCl_4] = 0.015 \text{ M/L}$

Time of Reaction = 15 Min.

$[Al(C_2H_5)_3] = 0.0225 \text{ M/L}$

Time of Ageing = 3 hr.

Molar Ratio Al/Zr = 1.5

$[Styrene] = 1.743 \text{ M/L}$

$X = 4.537$

POLYMERIZATION OF STYRENE WITH TIN TETRA  
PROPYL AND ZIRCONIUM TETRACHLORIDE IN  
TOLUENE AT 40°

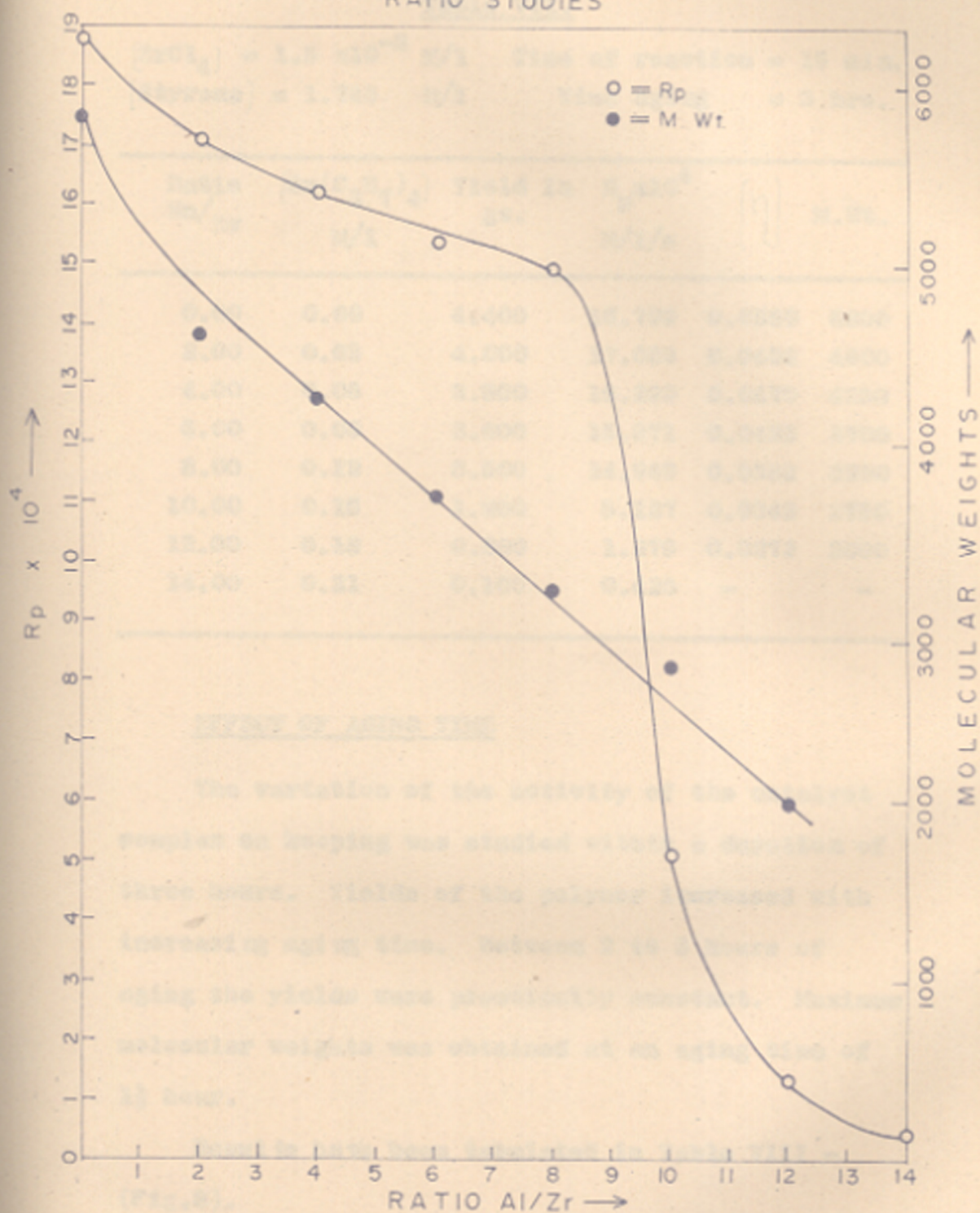
Tin tetrapropyl reacts with zirconium tetrachloride and forms a yellow colored complex. The reaction is very slow and requires nearly 2 hours for completion.

Ratio of Tin Tetrapropyl/Zirconium Tetra-  
Chloride

The activity of the catalyst complex at different molar ratios of  $\text{Sn/Zr}$  were studied by keeping the concentration of zirconium tetrachloride constant and varying that of tin tetrapropyl. The yield of the polymer obtained from experiments conducted for 15 minutes at different ratios was taken as the index of the catalyst activity. Rate of polymerization decreased with increasing ratio of  $\text{Sn/Zr}$ . Molecular weights also decreased with increasing ratio of  $\text{Sn/Zr}$ .

Results have been tabulated in Table VII -  
(Fig.7).

Fig. 7  
 $ZrCl_4 - Sn(C_3H_7)_4 - STYRENE$   
 RATIO STUDIES



$[ZrCl_4] = 0.015 \text{ M/L}$

$[Styrene] = 1.743 \text{ M/L}$

Time of Reaction = 15 Min.

Time of Ageing = 3 hr.

Temp. of Reaction =  $40^\circ$

Table VII.

[ZrCl<sub>4</sub>] = 1.5 x 10<sup>-2</sup> M/l      Time of reaction = 15 min.  
 [Styrene] = 1.743 M/l      Time aging = 3 hrs.

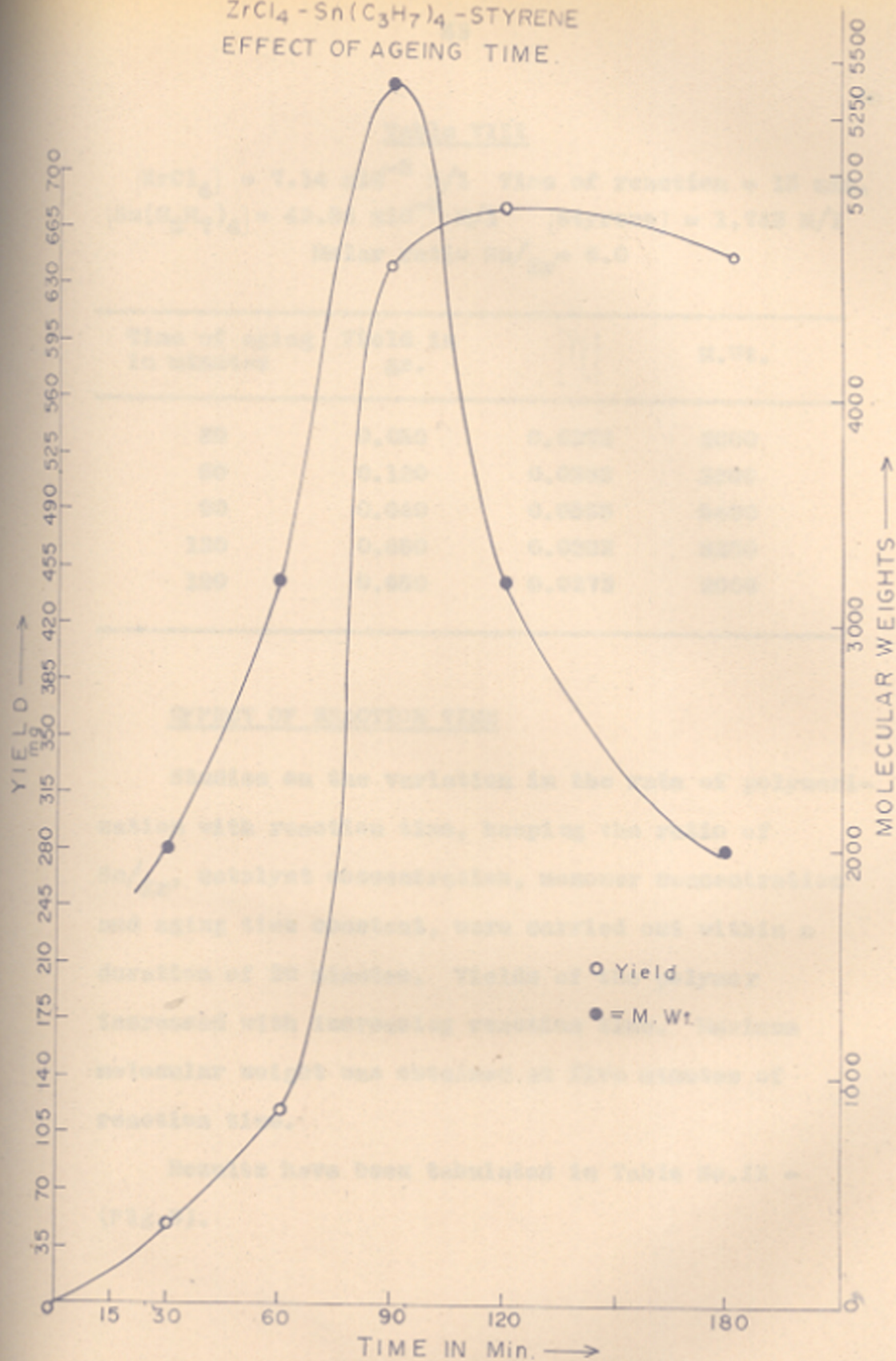
Ratio Sn/Zr	[Sn(C <sub>3</sub> H <sub>7</sub> ) <sub>4</sub> ] M/l	Yield in g <sup>s</sup> .	R <sub>p</sub> x 10 <sup>4</sup> M/l/s	[η]	M.Wt.
0.00	0.00	4.400	18.792	0.0589	5800
2.00	0.03	4.000	17.082	0.0498	4600
4.00	0.06	3.800	16.229	0.0470	4250
6.00	0.09	3.600	15.371	0.0425	3700
8.00	0.12	3.500	14.949	0.0382	3200
10.00	0.15	1.200	5.127	0.0342	2750
12.00	0.18	0.300	1.279	0.0272	2000
14.00	0.21	0.100	0.426	-	-

#### EFFECT OF AGING TIME

The variation of the activity of the catalyst complex on keeping was studied within a duration of three hours. Yields of the polymer increased with increasing aging time. Between 2 to 3 hours of aging the yields were practically constant. Maximum molecular weights was obtained at an aging time of 1½ hour.

Results have been tabulated in Table VIII - (Fig.8).

Fig. 8  
 $ZrCl_4 - Sn(C_3H_7)_4 - STYRENE$   
 EFFECT OF AGEING TIME.



$[ZrCl_4] = 0.00714 \text{ M/L}$

$[Styrene] = 1.743 \text{ M/L}$

$[Sn(C_3H_7)_4] = 0.04284 \text{ M/L}$

Time of Reaction = 15 Min.

Molar Ratio Sn/Zr = 6.0

Temp. of Reaction =  $40^\circ$

Table VIII

$[\text{ZrCl}_4] = 7.14 \times 10^{-3} \text{ M/l}$  Time of reaction = 15 min.  
 $[\text{Sn}(\text{C}_3\text{H}_7)_4] = 42.84 \times 10^{-3} \text{ M/l}$  [Styrene] = 1.743 M/l  
 Molar ratio Sn/Zr = 6.0

Time of aging in minutes	Yield in gs.	$[\eta]$	M.Wt.
30	0.050	0.0272	2000
60	0.130	0.0382	3200
90	0.640	0.0558	5400
120	0.680	0.0382	3200
180	0.650	0.0272	2000

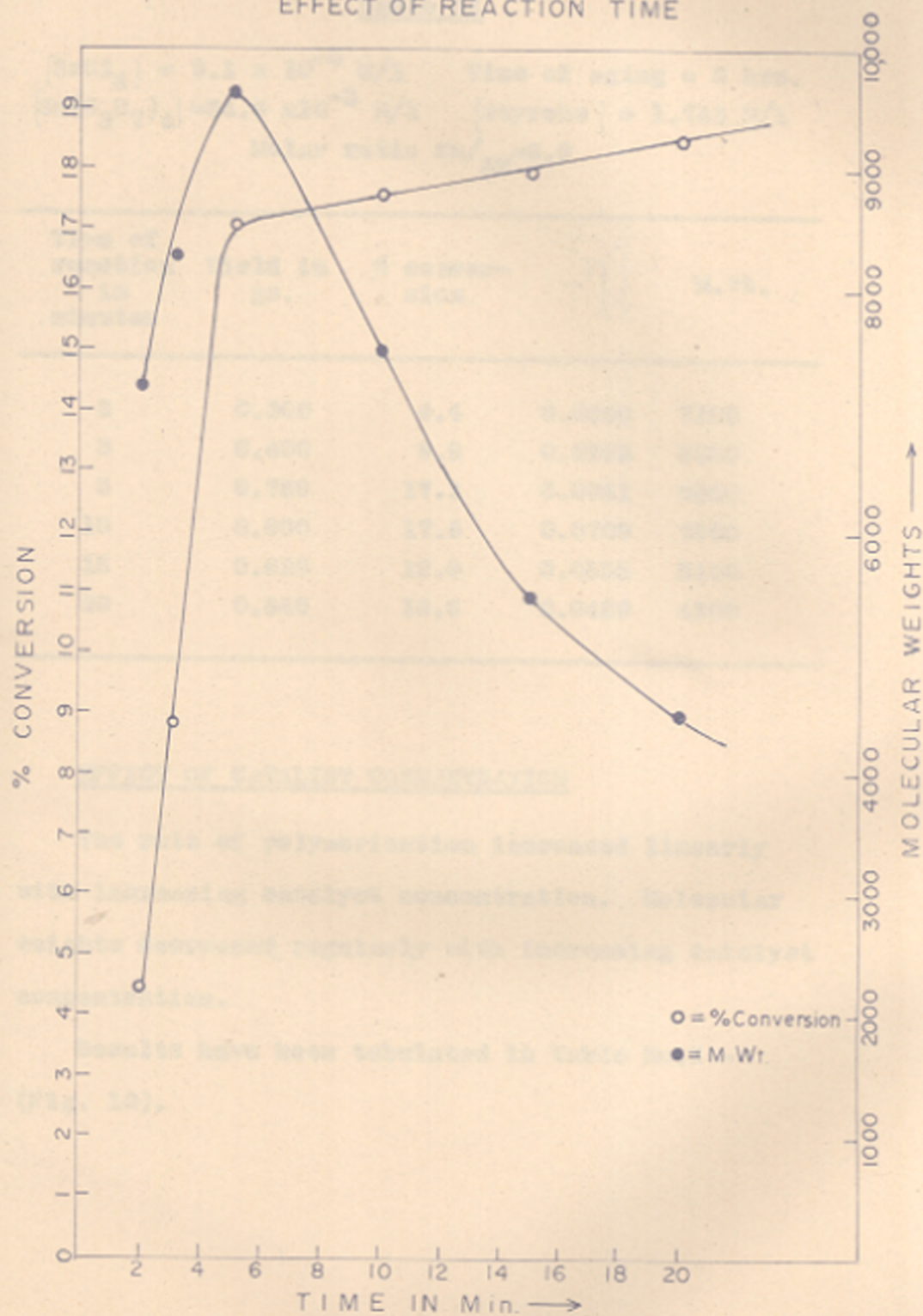
#### EFFECT OF REACTION TIME

Studies on the variation in the rate of polymerization with reaction time, keeping the ratio of Sn/Zr, catalyst concentration, monomer concentration and aging time constant, were carried out within a duration of 20 minutes. Yields of the polymer increased with increasing reaction time. Maximum molecular weight was obtained at five minutes of reaction time.

Results have been tabulated in Table No. IX - (Fig.9).



Fig. 9  
 $ZrCl_4 - Sn(C_3H_7)_4 - STYRENE$   
 EFFECT OF REACTION TIME



$[ZrCl_4] = 0.0091 \text{ M/L}$

$[Sn(C_3H_7)_4] = 0.0546 \text{ M/L}$

Molar Ratio Sn/Zr = 6.0

$[Styrene] = 1.743 \text{ M/L}$

Time of Ageing = 3 hr.

Temp. of Reaction =  $40^\circ$

Table IX

$[\text{ZrCl}_4] = 9.1 \times 10^{-3} \text{ M/l}$       Time of aging = 3 hrs.  
 $[\text{Sn}(\text{C}_3\text{H}_7)_4] = 54.6 \times 10^{-3} \text{ M/l}$        $[\text{Styrene}] = 1.743 \text{ M/l}$   
 Molar ratio  $\text{Sn/Zr} = 6.0$

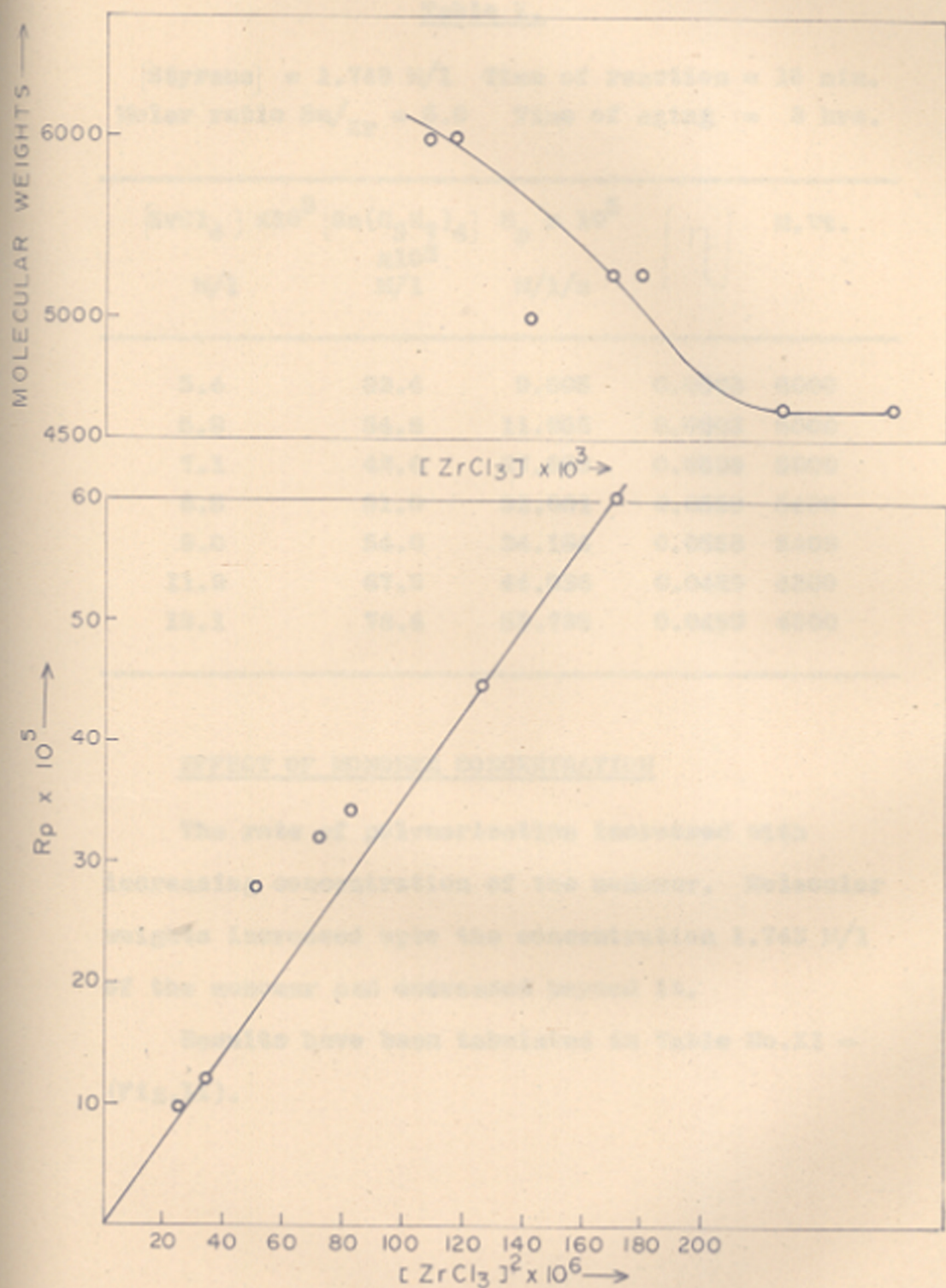
Time of reaction in minutes	Yield in gs.	% conversion.	$[\eta]$	M. wt.
2	0.200	4.4	0.0688	7200
3	0.400	8.8	0.0768	8250
5	0.780	17.1	0.0851	9650
10	0.800	17.6	0.0709	7500
15	0.820	18.0	0.0558	5400
20	0.840	18.5	0.0489	4500

EFFECT OF CATALYST CONCENTRATION

The rate of polymerization increased linearly with increasing catalyst concentration. Molecular weights decreased regularly with increasing catalyst concentration.

Results have been tabulated in Table No. X - (Fig. 10).

Fig. 10  
 $ZrCl_4 - Sn(C_2H_5)_4$  - STYRENE  
 EFFECT OF CATALYST CONCENTRATION



$[Styrene] = 1.743 \text{ M/L}$

Molar Ratio Sn/Zr = 6.0

Time of Reaction = 15 Min.

Time of Ageing = 3 hr.

Temp. of Reaction =  $40^\circ$

Table X.

[Styrene] = 1.743 M/l Time of reaction = 15 min.  
 Molar ratio Sn/Zr = 6.0 Time of aging = 3 hrs.

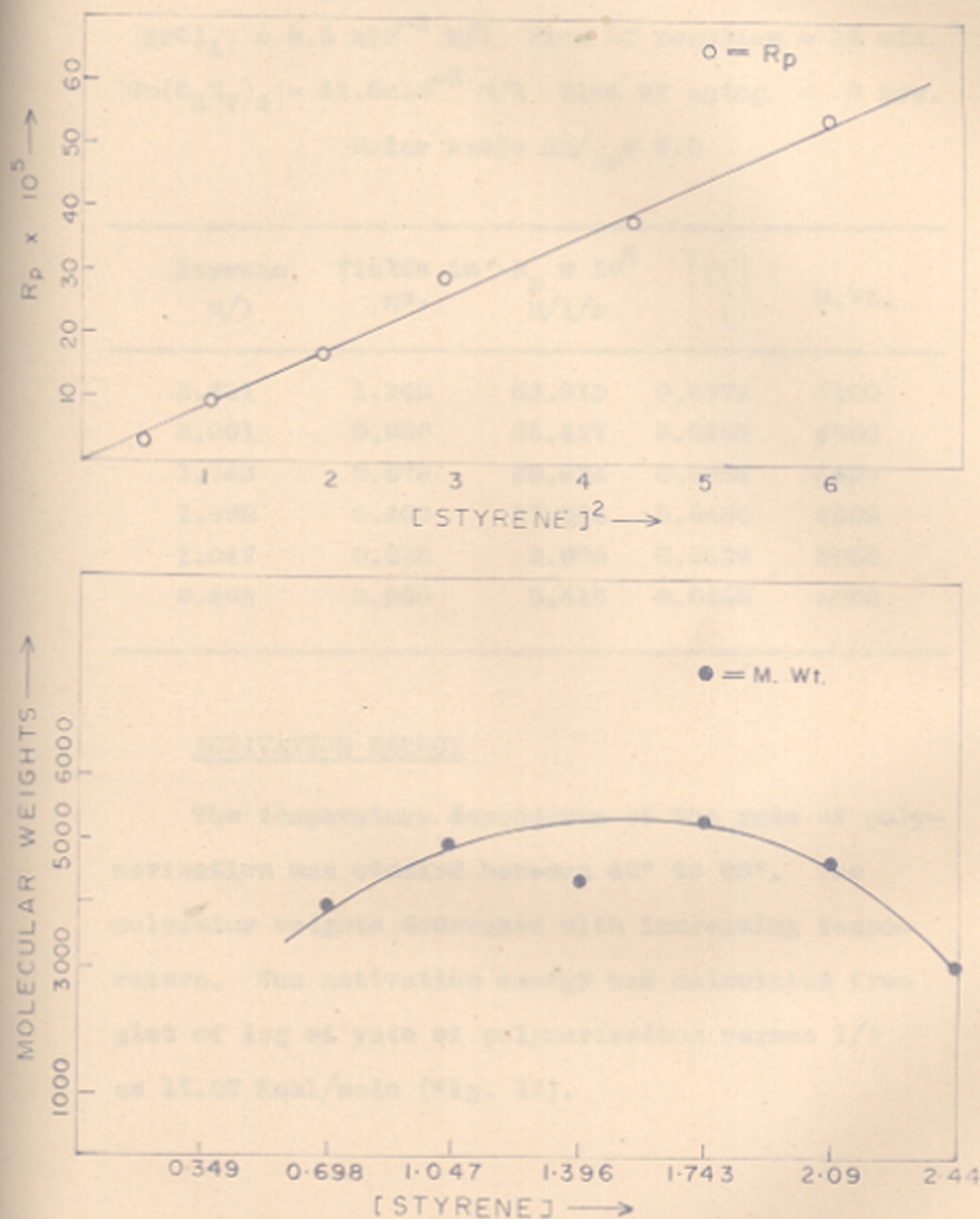
$[\text{ZrCl}_4] \times 10^3$ M/l	$[\text{Sn}(\text{C}_3\text{H}_7)_4] \times 10^3$ M/l	$R_p \times 10^5$ M/l/s	$[\eta]$	M. wt.
5.4	32.4	9.605	0.0603	6000
5.8	34.8	11.955	0.0603	6000
7.1	42.6	27.689	0.0528	5000
8.5	51.0	32.031	0.0558	5400
9.0	54.0	34.164	0.0558	5400
11.2	67.2	44.826	0.0489	4500
13.1	78.6	59.798	0.0489	4500

EFFECT OF MONOMER CONCENTRATION

The rate of polymerization increased with increasing concentration of the monomer. Molecular weights increased upto the concentration 1.743 M/l of the monomer and decreased beyond it.

Results have been tabulated in Table No. XI - (Fig. 11).

Fig. 11  
 $ZrCl_4-Sn(C_3H_7)_4$ -STYRENE  
 EFFECT OF MONOMER CONCENTRATION



$[ZrCl_4] = 0.0086$  M/L

$[Sn(C_3H_7)_4] = 0.0516$  M/L

Molar Ratio Sn/Zr = 6.0

Time of Reaction = 15 Min.

Time of Ageing = 3 hr

Temp. of Reaction =  $40^\circ$

Table XI.

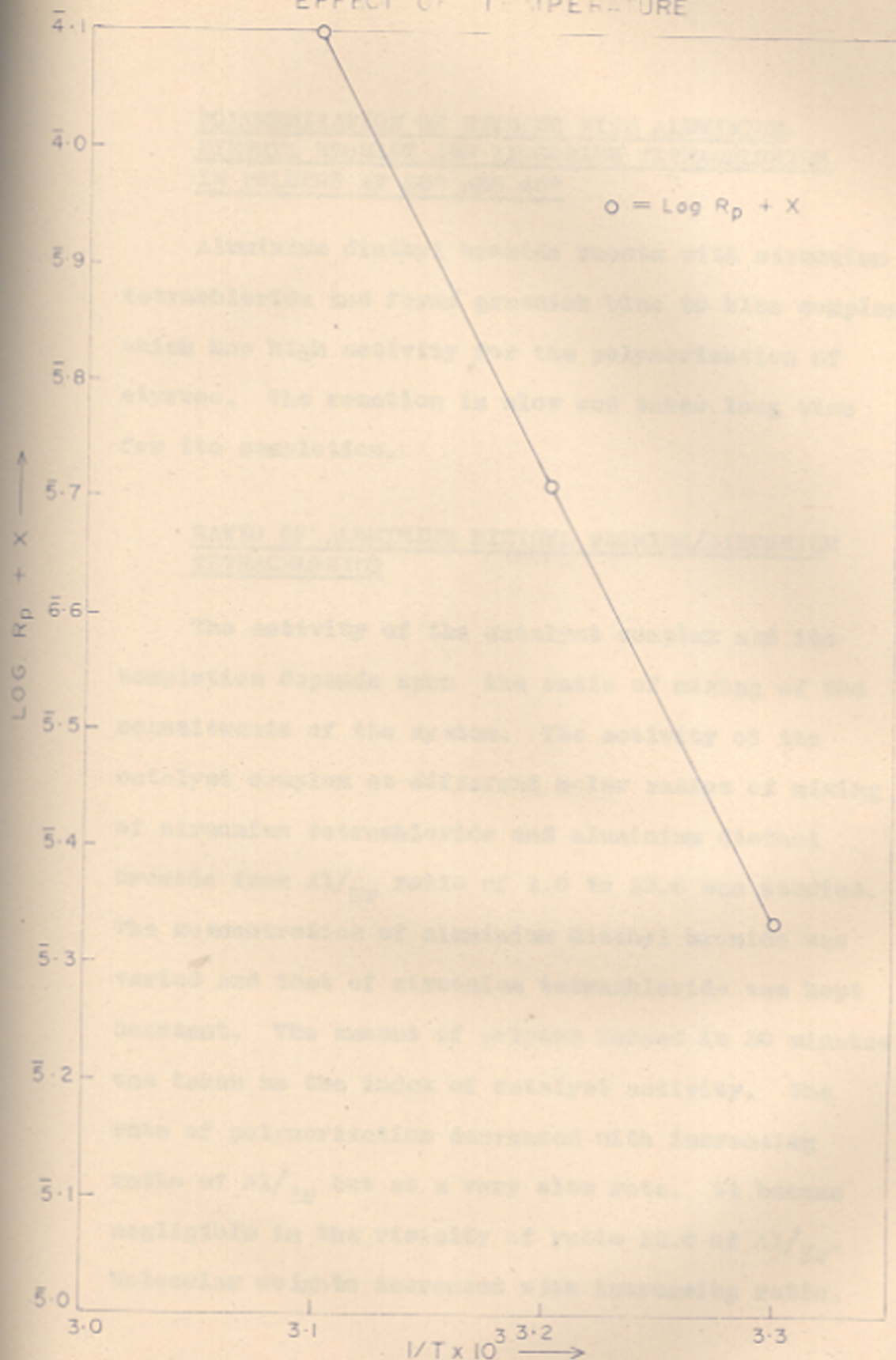
$[\text{ZrCl}_4] = 8.6 \times 10^{-3} \text{ M/l}$  Time of reaction = 15 min.  
 $[\text{Sn}(\text{C}_3\text{H}_7)_4] = 51.6 \times 10^{-3} \text{ M/l}$  Time of aging = 3 hrs.  
 Molar ratio  $\text{Sn/Zr} = 6.0$

[Styrene] M/l	Yields in g <sub>s</sub> .	$R_p \times 10^5$ M/l/s	$[\eta]$	M. <sup>w</sup> t.
2.441	1.360	53.812	0.0374	3100
2.091	0.900	38.427	0.0505	4700
1.743	0.675	28.824	0.0558	5400
1.396	0.400	17.084	0.0486	4400
1.047	0.225	9.609	0.0528	5000
0.698	0.080	3.415	0.0449	4000

ACTIVATION ENERGY

The temperature dependence of the rate of polymerization was studied between 40° to 60°. The molecular weights decreased with increasing temperature. The activation energy was calculated from plot of log of rate of polymerization versus  $1/T$  as 17.27 Kcal/mole (Fig. 12).

FIG. 2  
 $ZrCl_4-Sn(C_2H_5)_2$ -STYRENE  
 EFFECT OF TEMPERATURE



$[ZrCl_4] = 0.008 \text{ M/L}$

$[STYRENE] = 1.743 \text{ M/L}$

Molar Ratio Sn/Zr = 6.0

Time of Reaction = 15 Min.

Time of Ageing = 3 hr.

Temp of Reaction =  $40^\circ$

$X = 4.537$

POLYMERIZATION OF STYRENE WITH ALUMINIUM  
DIETHYL BROMIDE AND ZIRCONIUM TETRACHLORIDE  
IN TOLUENE AT 30° AND 40°

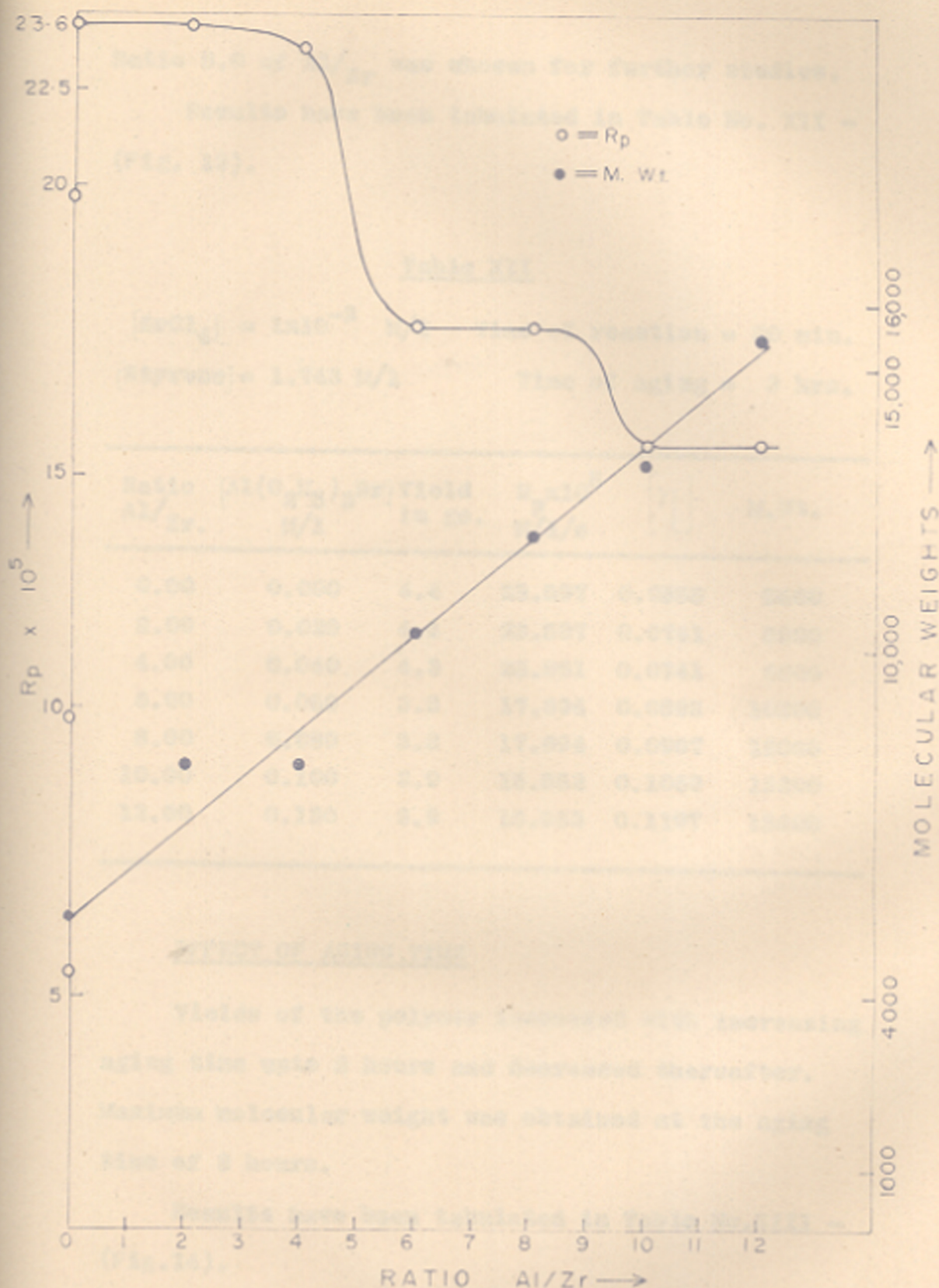
Aluminium diethyl bromide reacts with zirconium tetrachloride and forms greenish blue to blue complex which has high activity for the polymerization of styrene. The reaction is slow and takes long time for its completion.

RATIO OF ALUMINIUM DIETHYL BROMIDE/ZIRCONIUM  
TETRACHLORIDE

The activity of the catalyst complex and its completion depends upon the ratio of mixing of the constituents of the system. The activity of the catalyst complex at different molar ratios of mixing of zirconium tetrachloride and aluminium diethyl bromide from Al/Zr ratio of 1.0 to 12.0 was studied. The concentration of aluminium diethyl bromide was varied and that of zirconium tetrachloride was kept constant. The amount of polymer formed in 30 minutes was taken as the index of catalyst activity. The rate of polymerization decreased with increasing ratio of Al/Zr but at a very slow rate. It became negligible in the vicinity of ratio 12.0 of Al/Zr. Molecular weights increased with increasing ratio.



Fig. 13  
 $ZrCl_4-Al(C_2H_5)_2Br$ -STYRENE  
 RATIO STUDIES



$[ZrCl_4] = 0.01$  M/L

$[STYRENE] = 1.743$  M/L

Time of Reaction = 30 Min.

Time of Ageing = 3 hr.

Temp. of Reaction =  $40^\circ$

Ratio 8.0 of Al/Zr was chosen for further studies.

Results have been tabulated in Table No. XII -  
(Fig. 13).

Table XII

$[\text{ZrCl}_4] = 1 \times 10^{-2}$  M/l Time of reaction = 30 min.  
 $[\text{Styrene}] = 1.743$  M/l Time of aging = 3 hrs.

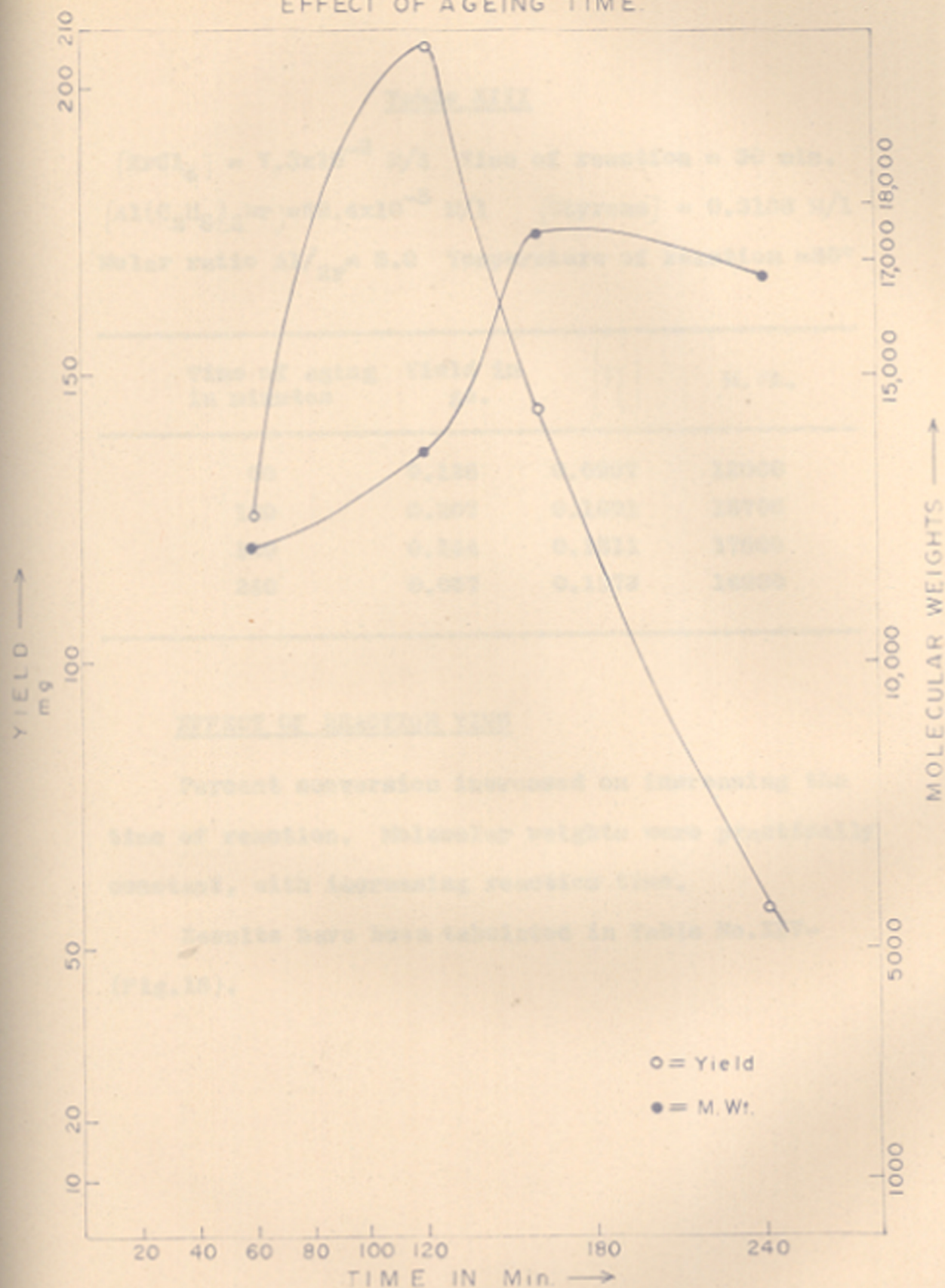
Ratio Al/Zr.	$(\text{Al}(\text{C}_2\text{H}_5)_2\text{Br})$ M/l	Yield in gs.	$R_p \times 10^5$ M/l/s	$[\eta]$	M.Wt.
0.00	0.000	4.4	23.597	0.0558	5400
2.00	0.020	4.4	23.597	0.0741	8000
4.00	0.040	4.3	23.061	0.0741	8000
6.00	0.060	3.3	17.694	0.0893	10300
8.00	0.080	3.3	17.694	0.0997	12000
10.00	0.100	2.9	15.552	0.1069	13200
12.00	0.120	2.9	15.553	0.1197	15400

EFFECT OF AGING TIME

Yields of the polymer increased with increasing aging time upto 2 hours and decreased thereafter. Maximum molecular weight was obtained at the aging time of 3 hours.

Results have been tabulated in Table No. XIII -  
(Fig. 14).

Fig.14  
 $ZrCl_4 - Al(C_2H_5)_2Br$ -STYRENE  
 EFFECT OF AGEING TIME.



$[ZrCl_4] = 0.0073 \text{ M/L}$   
 $[Al(C_2H_5)_2Br] = 0.0585 \text{ M/L}$   
 Molar Ratio Al/Zr = 8.0

Time of Reaction = 30 Min.  
 $[Styrene] = 3.135 \times 10^{-1} \text{ M/L}$   
 Temp. of Reaction =  $40^\circ$

Table XIII

$[\text{ZrCl}_4] = 7.3 \times 10^{-3}$  M/l Time of reaction = 30 min.  
 $[\text{Al}(\text{C}_2\text{H}_5)_2\text{Br}] = 58.4 \times 10^{-3}$  M/l  $[\text{Styrene}] = 0.3138$  M/l  
 Molar ratio  $\text{Al/Zr} = 8.0$  Temperature of reaction =  $30^\circ$

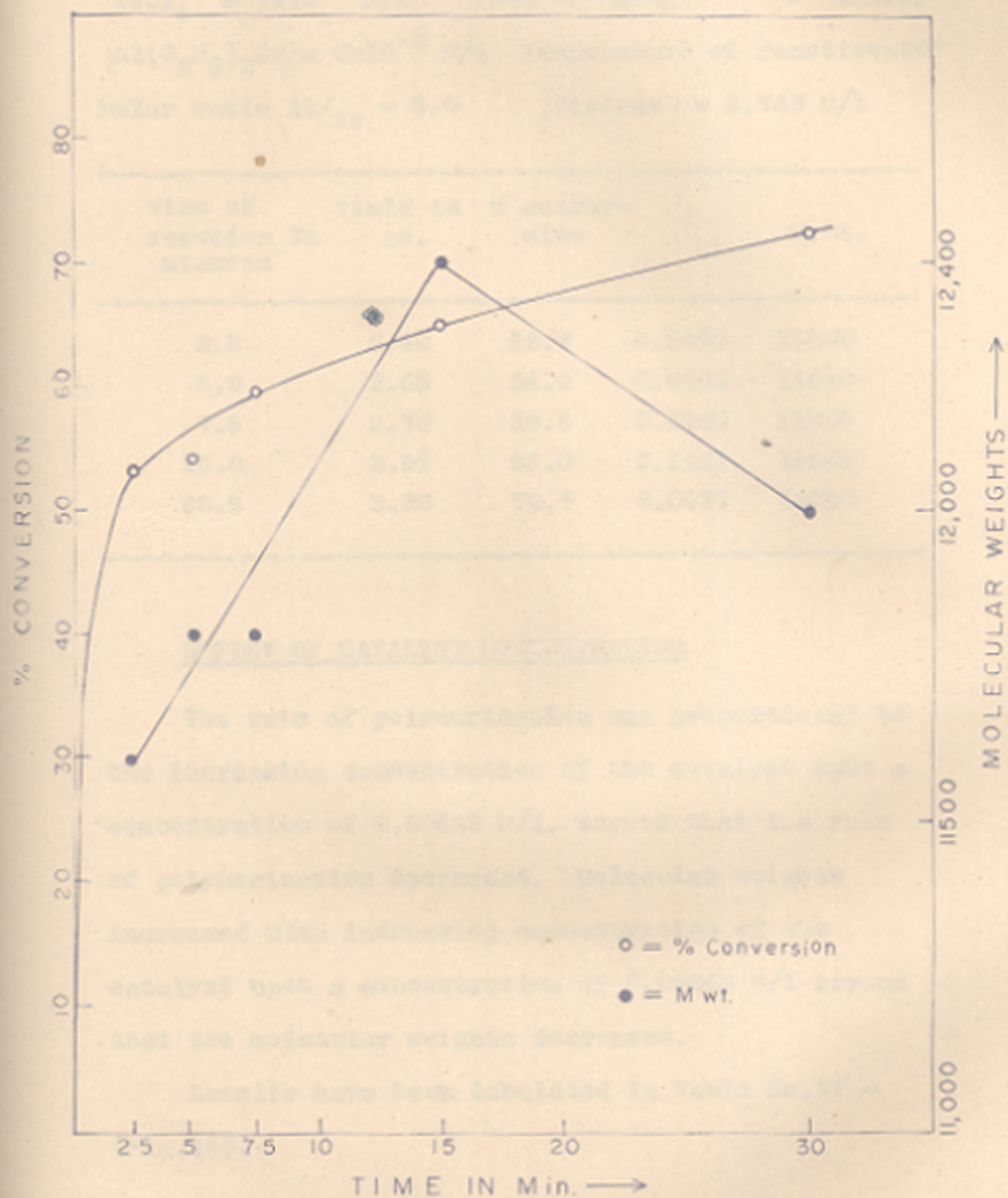
Time of aging in minutes	Yield in gs.	$[\eta]$	M. wt.
60	0.126	0.0997	12000
120	0.207	0.1091	13700
180	0.144	0.1311	17500
240	0.057	0.1273	16800

EFFECT OF REACTION TIME

Percent conversion increased on increasing the time of reaction. Molecular weights were practically constant, with increasing reaction time.

Results have been tabulated in Table No. XIV-  
(Fig. 15).

Fig.15  
 $ZrCl_4 - Al(C_2H_5)_2Br$ -STYRENE  
 EFFECT OF REACTION TIME



$[ZrCl_4] = 0.01 \text{ M/L}$   
 $[Al(C_2H_5)_2Br] = 0.08 \text{ M/L}$   
 Molar Ratio  $Al/Zr = 8.0$

$[Styrene] = 1.743 \text{ M/L}$   
 Time of Ageing = 3 hr.  
 Temp of Reaction =  $40^\circ$

Table XIV.

$[\text{ZrCl}_4] = 1 \times 10^{-2} \text{ M/l}$     Time of aging    = 3 hrs.  
 $[\text{Al}(\text{C}_2\text{H}_5)_2\text{Br}] = 8 \times 10^{-2} \text{ M/l}$     Temperature of reaction =  $40^\circ$   
 Molar ratio  $\text{Al/Zr} = 8.0$      $[\text{Styrene}] = 1.743 \text{ M/l}$

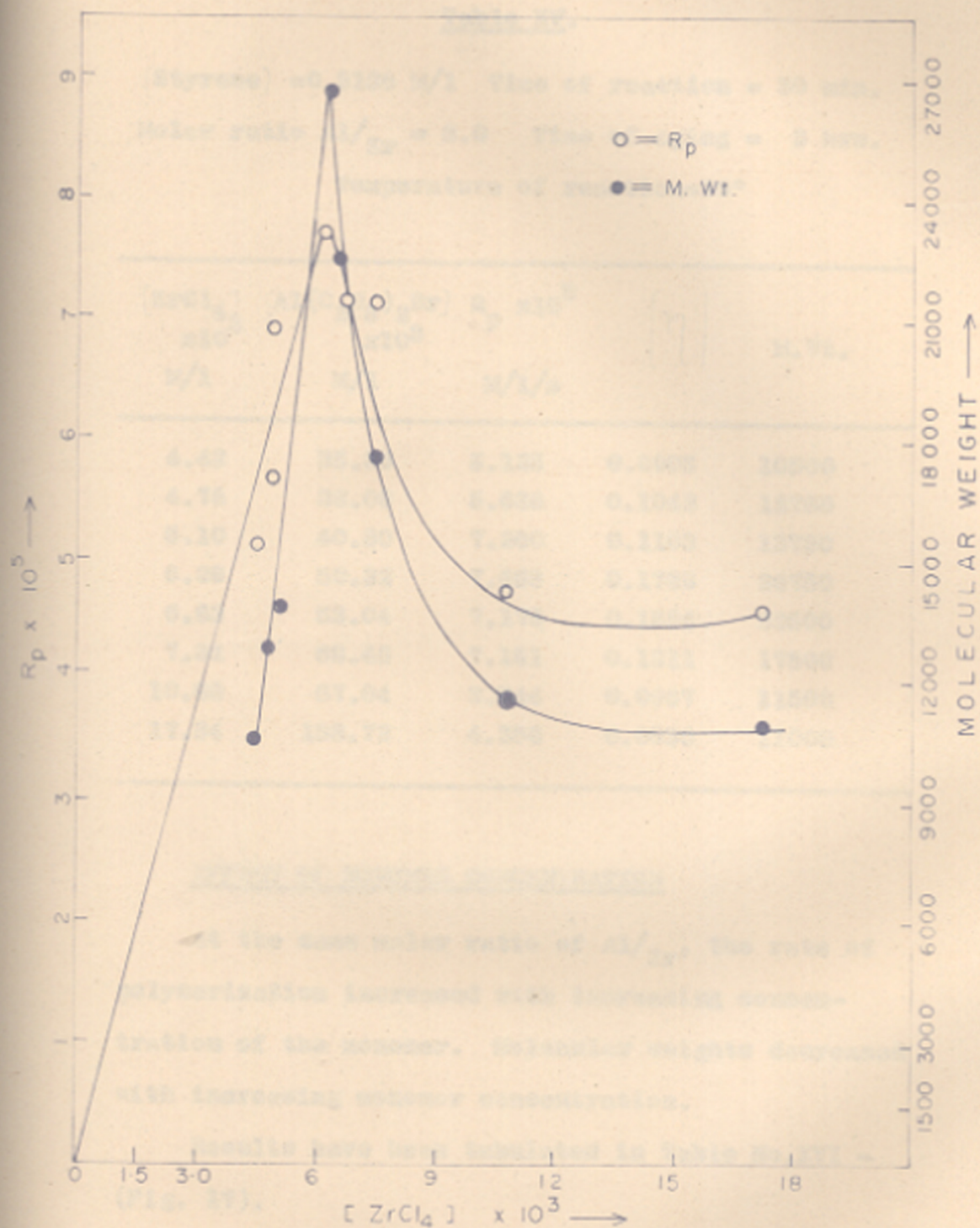
Time of reaction in minutes	Yield in g.	% conversion	$[\eta]$	M. wt.
2.5	2.40	52.9	0.0973	11600
5.0	2.45	54.0	0.0985	11800
7.5	2.70	59.5	0.0985	11800
15.0	2.95	65.0	0.1021	12400
30.0	3.30	72.7	0.0997	12000

#### EFFECT OF CATALYST CONCENTRATION

The rate of polymerization was proportional to the increasing concentration of the catalyst upto a concentration of 0.00629 M/l, beyond that the rate of polymerization decreased. Molecular weights increased with increasing concentration of the catalyst upto a concentration of 0.00663 M/l beyond that the molecular weights decreased.

Results have been tabulated in Table No. XV - (Fig. 16).

Fig 16  
 $ZrCl_4 - Al(C_2H_5)_2 Br$ -STYRENE  
 EFFECT OF CATALYST CONCENTRATION



$[Styrene] = 3.138 \times 10^{-1} M/L$

Molar Ratio  $Al/Zr = 8.0$

Time of Reaction = 30 Min

Time of Ageing = 3 hr.

Temp. of Reaction =  $30^\circ$

Table XV.

[Styrene] = 0.3138 M/l Time of reaction = 30 min.  
 Molar ratio Al/Zr = 8.0 Time of aging = 3 hrs.  
 Temperature of reaction = 30°

$[\text{ZrCl}_4]$ $\times 10^3$ M/l	$[\text{Al}(\text{C}_2\text{H}_5)_2\text{Br}]$ $\times 10^3$ M/l	$R_p \times 10^5$ M/l/s	$[\eta]$	M.Wt.
4.42	35.36	5.125	0.0905	10500
4.76	38.08	5.638	0.1042	12750
5.10	40.80	7.260	0.1103	13750
6.29	50.32	7.688	0.1783	26750
6.63	53.04	7.175	0.1584	22500
7.31	58.48	7.151	0.1311	17500
10.88	87.04	3.844	0.0967	11500
17.34	138.72	4.356	0.0936	11000

EFFECT OF MONOMER CONCENTRATION

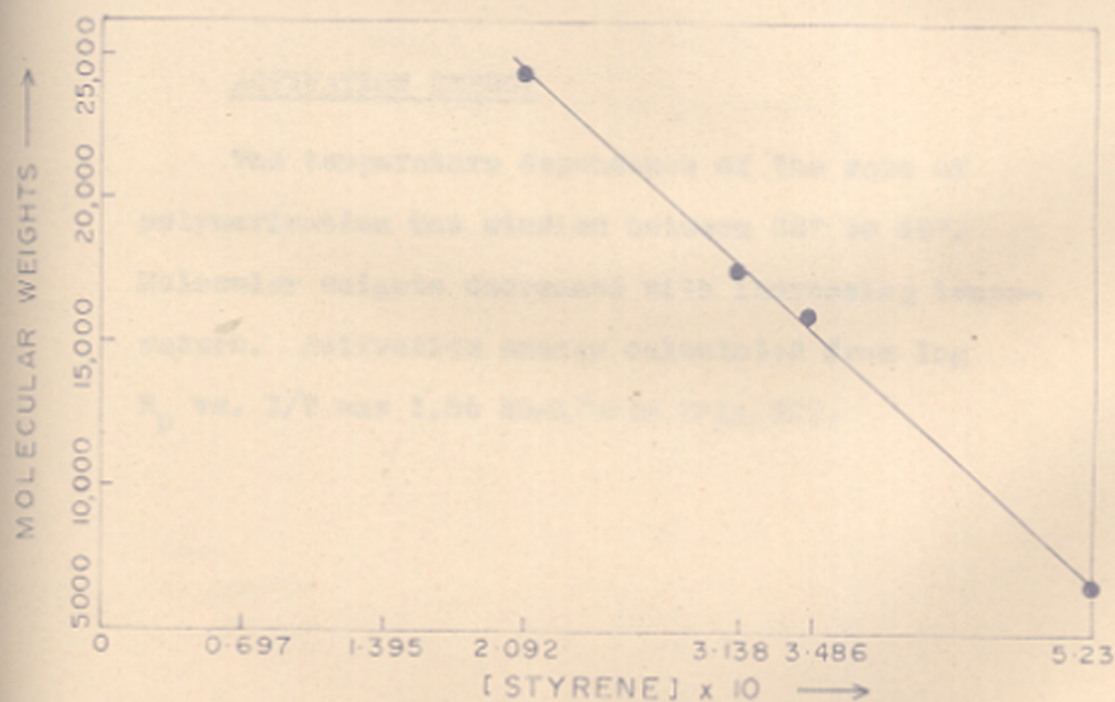
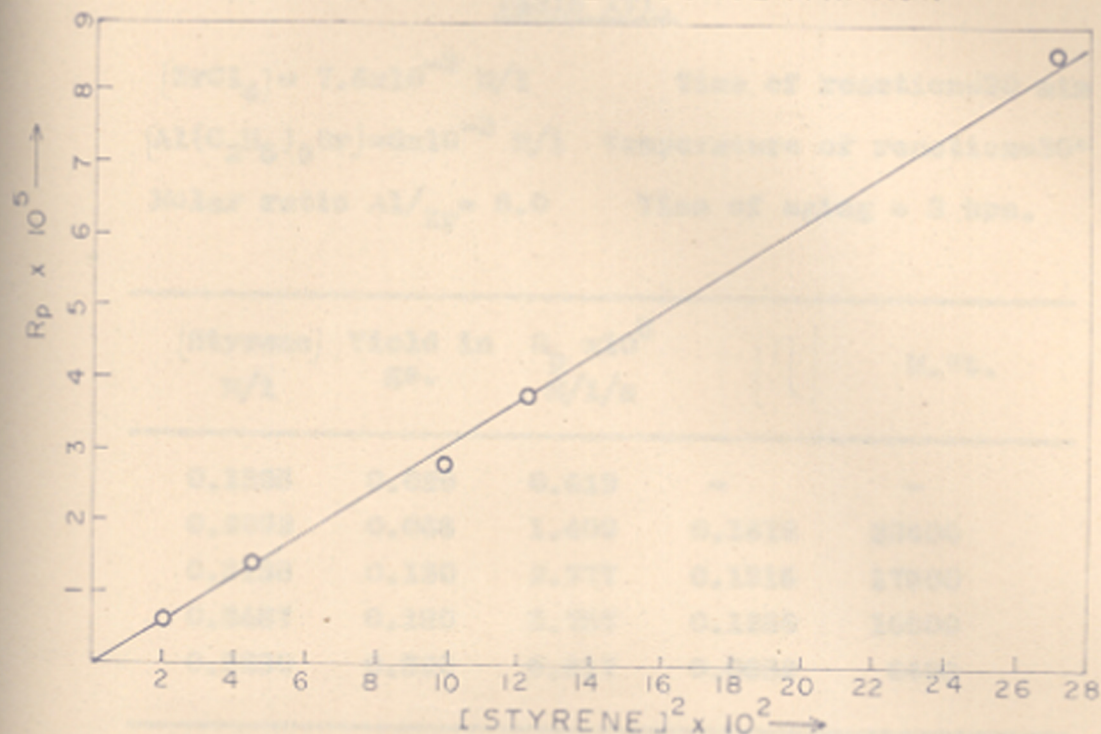
At the same molar ratio of Al/Zr, the rate of polymerization increased with increasing concentration of the monomer. Molecular weights decreased with increasing monomer concentration.

Results have been tabulated in Table No. XVI - (Fig. 17).



Fig. 17

ZrCl<sub>4</sub>-Al(C<sub>2</sub>H<sub>5</sub>)<sub>2</sub> Br-STYRENE  
EFFECT OF MONOMER CONCENTRATION



$[\text{ZrCl}_4] = 0.0075 \text{ M/L}$

Time of Reaction = 30 Min.

$[\text{Al}(\text{C}_2\text{H}_5)_2 \text{Br}] = 0.06 \text{ M/L}$

Time of Ageing = 3 hr.

Molar Ratio Al/Zr = 8.0

Temp. of Reaction = 30°

Table XVI.

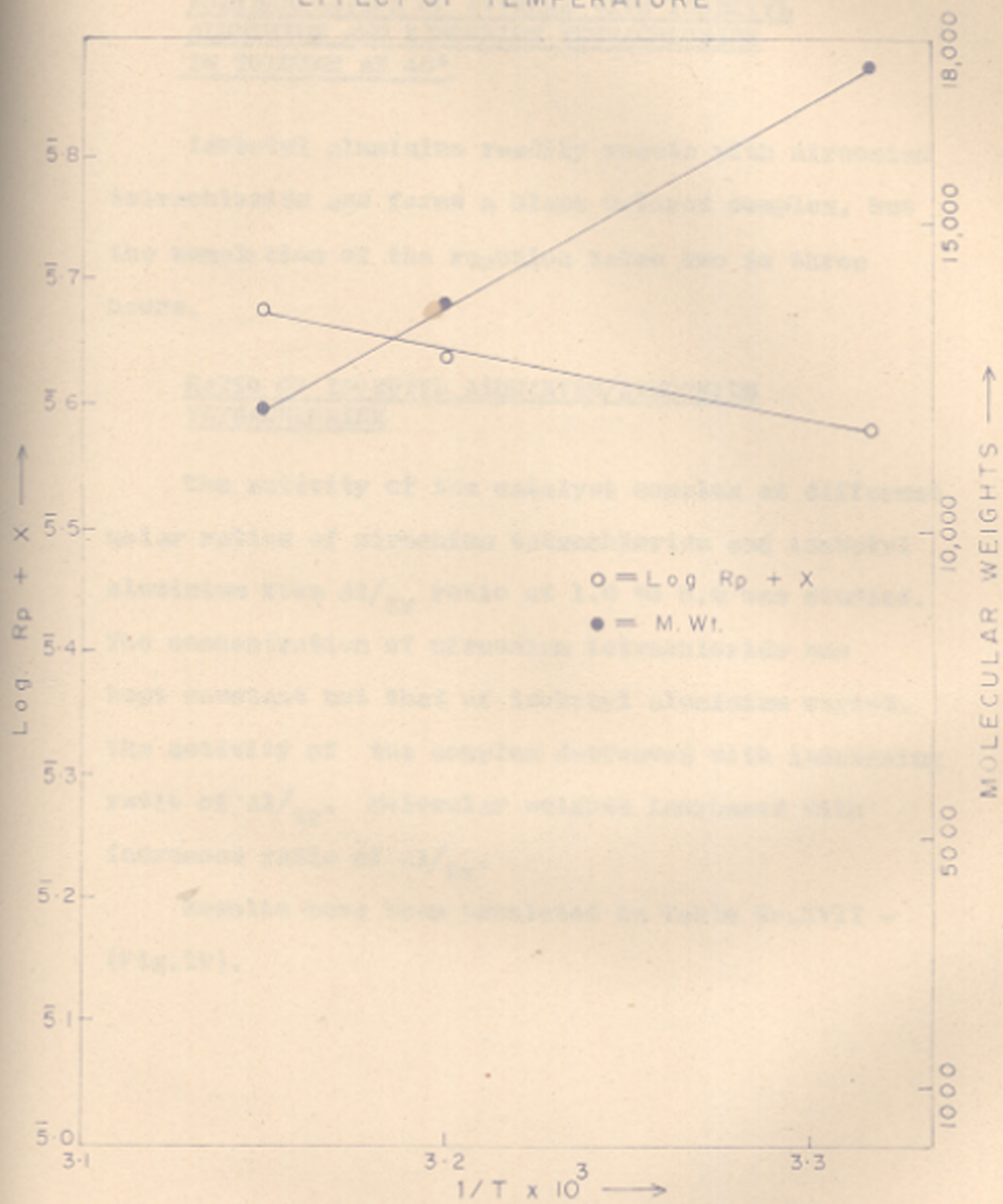
$[\text{ZrCl}_4] = 7.5 \times 10^{-3} \text{ M/l}$       Time of reaction = 30 min  
 $[\text{Al}(\text{C}_2\text{H}_5)_2\text{Br}] = 6 \times 10^{-2} \text{ M/l}$       Temperature of reaction = 30°  
 Molar ratio  $\text{Al/Zr} = 8.0$       Time of aging = 3 hrs.

[Styrene] M/l	Yield in g <sup>s</sup> .	$R_p \times 10^5$ M/l/s	$[\eta]$	M. wt.
0.1395	0.029	0.619	-	-
0.2092	0.066	1.409	0.1618	23400
0.3138	0.130	2.777	0.1315	17500
0.3487	0.180	3.757	0.1228	16000
0.5230	0.320	6.817	0.0632	6400

ACTIVATION ENERGY

The temperature dependence of the rate of polymerization was studied between 30° to 45°. Molecular weights decreased with increasing temperature. Activation energy calculated from  $\log R_p$  vs.  $1/T$  was 1.54 Kcal/mole (Fig. 18).

Fig. 18  
 $ZrCl_4 - Al(C_2H_5)_2 Br - STYRENE$   
 EFFECT OF TEMPERATURE



$[ZrCl_4] = 0.0074 \text{ M/L}$

Time of Reaction = 30 Min.

$[Al(C_2H_5)_2 Br] = 0.0592 \text{ M/L}$

Time of Ageing = 3 hr.

Molar Ratio  $Al/Zr = 8.0$

$[STYRENE] = 3.138 \times 10^{-1} \text{ M/L}$

$X = 0.8166$

POLYMERIZATION OF STYRENE WITH ISOBUTYL  
ALUMINIUM AND ZIRCONIUM TETRACHLORIDE  
IN TOLUENE AT 40°

Isobutyl aluminium readily reacts with zirconium tetrachloride and forms a black colored complex, but the completion of the reaction takes two to three hours.

RATIO OF ISOBUTYL ALUMINIUM/ZIRCONIUM  
TETRACHLORIDE

The activity of the catalyst complex at different molar ratios of zirconium tetrachloride and isobutyl aluminium from Al/<sub>Zr</sub> ratio of 1.0 to 5.0 was studied. The concentration of zirconium tetrachloride was kept constant but that of isobutyl aluminium varied. The activity of the complex decreased with increasing ratio of Al/<sub>Zr</sub>. Molecular weights increased with increased ratio of Al/<sub>Zr</sub>.

Results have been tabulated in Table No.XVII - (Fig.19).

Fig 19  
 $ZrCl_4 - Al(iC_4H_9)_3 - STYRENE$   
 RATIO STUDIES

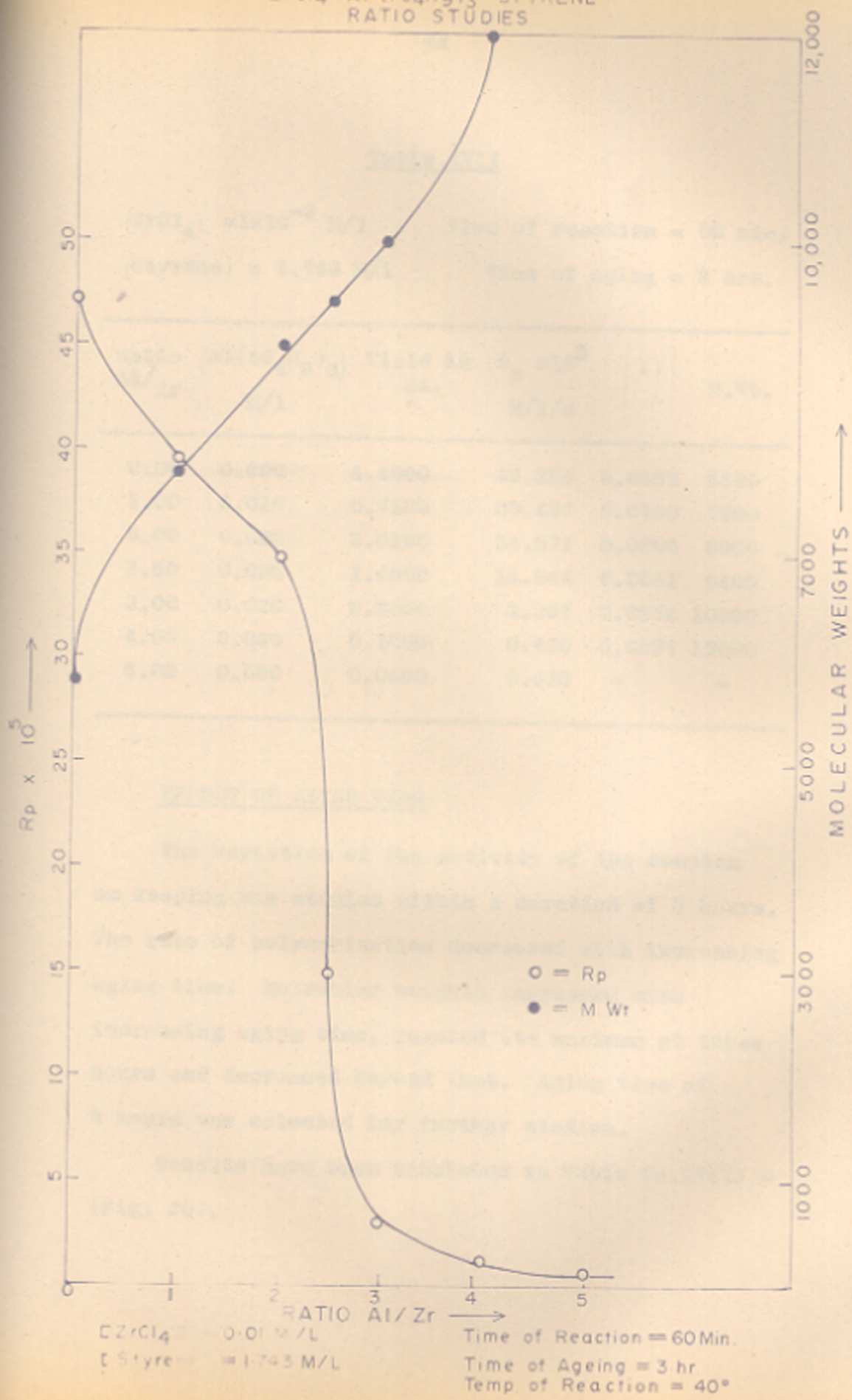


Table XVII

[ZrCl<sub>4</sub>] =  $1 \times 10^{-2}$  M/l      Time of reaction = 60 min.  
 [Styrene] = 1.743 M/l      Time of aging = 3 hrs.

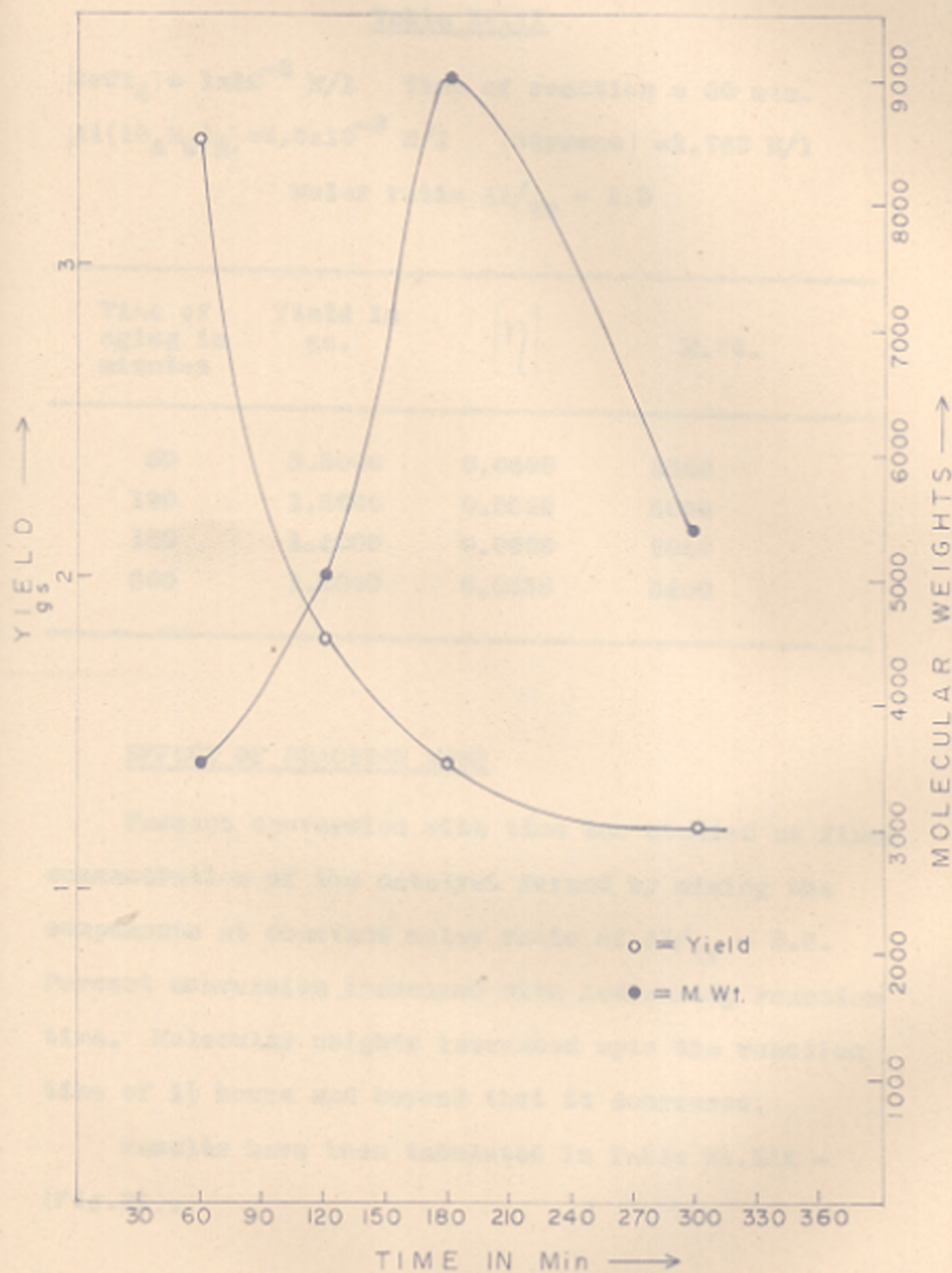
Ratio Al/Zr	[Al(iC <sub>4</sub> H <sub>9</sub> ) <sub>3</sub> ] M/l	Yield in gms.	R <sub>p</sub> x 10 <sup>5</sup> M/l/s	[ $\eta$ ]	M.Wt.
0.00	0.000	4.4000	46.858	0.0589	5800
1.00	0.010	3.7100	39.499	0.0730	7800
2.00	0.020	3.0100	34.871	0.0809	9000
2.50	0.025	1.4000	14.945	0.0861	9400
3.00	0.030	0.3000	3.207	0.0874	10000
4.00	0.040	0.1000	0.426	0.0997	12000
5.00	0.050	0.0400	0.426	-	-

EFFECT OF AGING TIME

The variation of the activity of the complex on keeping was studied within a duration of 5 hours. The rate of polymerization decreased with increasing aging time. Molecular weights increased with increasing aging time, reached its maximum at three hours and decreased beyond that. Aging time of 3 hours was selected for further studies.

Results have been tabulated in Table No. XVIII - (Fig. 20).

Fig. 20  
 $ZrCl_4 - Al(iC_4H_9)_3 - STYRENE$   
 EFFECT OF AGEING TIME



$[ZrCl_4] = 0.01 \text{ M/L}$

Time of Reaction = 60 Min.

$[Al(iC_4H_9)_3] = 0.025 \text{ M/L}$

$[Styrene] = 1.743 \text{ M/L}$

Molar Ratio Al/Zr = 2.5

Temp of Reaction =  $40^\circ$

Table XVIII

$[\text{ZrCl}_4] = 1 \times 10^{-2} \text{ M/l}$  Time of reaction = 60 min.

$[\text{Al}(\text{iC}_4\text{H}_9)_3] = 2.5 \times 10^{-2} \text{ M/l}$  [Styrene] = 1.743 M/l

Molar ratio  $\text{Al/Zr} = 2.5$

Time of aging in minutes	Yield in gs.	$[\eta]$	M. wt.
60	3.5000	0.0408	3500
120	1.8000	0.0528	5000
180	1.4000	0.0809	9000
300	1.2000	0.0558	5400

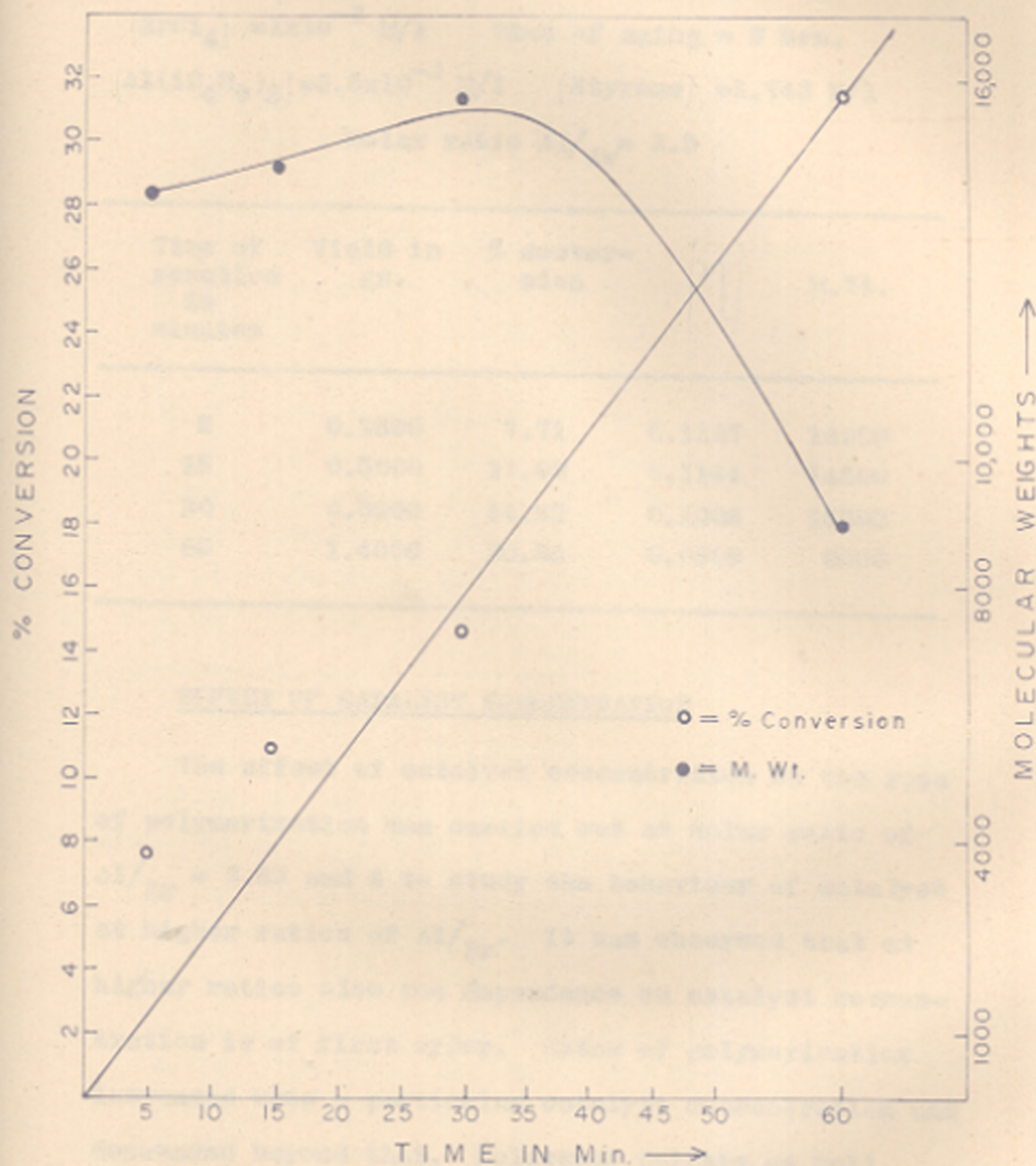
#### EFFECT OF REACTION TIME

Percent conversion with time was studied at fixed concentration of the catalyst formed by mixing the components at constant molar ratio of  $\text{Al/Zr} = 2.5$ . Percent conversion increased with increasing reaction time. Molecular weights increased upto the reaction time of  $1\frac{1}{2}$  hours and beyond that it decreased.

Results have been tabulated in Table No. XIX - (Fig. 21).



Fig. 21  
 $ZrCl_4 - Al(iC_4H_9)_3 - STYRENE$   
 EFFECT OF REACTION TIME



$[ZrCl_4] = 0.01 \text{ M/L}$

Time of ageing = 3 hr

$[Styrene] = 1.743 \text{ M/L}$

Temp. of Reaction =  $40^\circ$

$[Al(iC_4H_9)_3] = 0.025 \text{ M/L}$

Molar ratio  $Al/Zr = 2.5$

Table XIX.

$[\text{ZrCl}_4] = 1 \times 10^{-2}$  M/l      Time of aging = 3 hrs.  
 $[\text{Al}(\text{iC}_4\text{H}_9)_3] = 2.5 \times 10^{-2}$  M/l       $[\text{Styrene}] = 1.743$  M/l  
 Molar ratio  $\text{Al}/\text{Zr} = 2.5$

Time of reaction in minutes	Yield in gs.	% conversion	$[\eta]$	M.Wt.
5	0.3500	7.71	0.1127	14200
15	0.5000	11.02	0.1144	14500
30	0.6500	14.32	0.1206	15600
60	1.4000	30.86	0.0809	9000

#### EFFECT OF CATALYST CONCENTRATION

The effect of catalyst concentration on the rate of polymerization was carried out at molar ratio of  $\text{Al}/\text{Zr} = 2.53$  and 4 to study the behaviour of catalyst at higher ratios of  $\text{Al}/\text{Zr}$ . It was observed that at higher ratios also the dependence on catalyst concentration is of first order. Rates of polymerization increased upto a particular catalyst concentration and decreased beyond that. Molecular weights as well were high at low concentrations and low at higher concentrations of the catalyst. Results have been tabulated in Tables XX, XXI, XXII - (Fig.22).

Table XX.

[Styrene] = 1.743 M/l Time of reaction = 30 min.  
 Molar ratio Al/Zr = 2.5 Time of aging = 3 hrs.

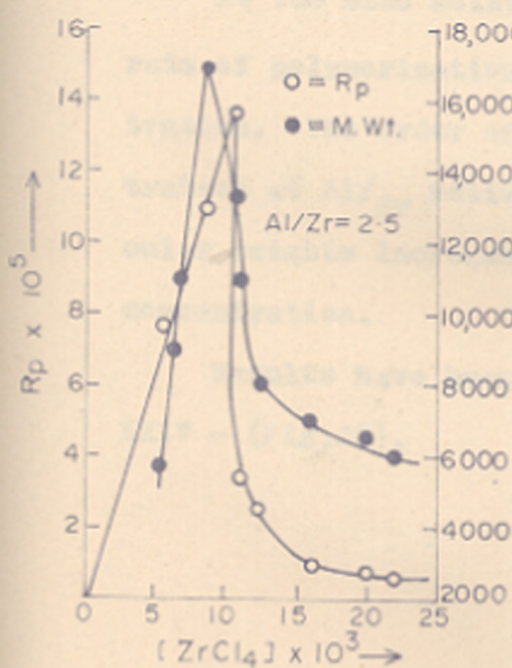
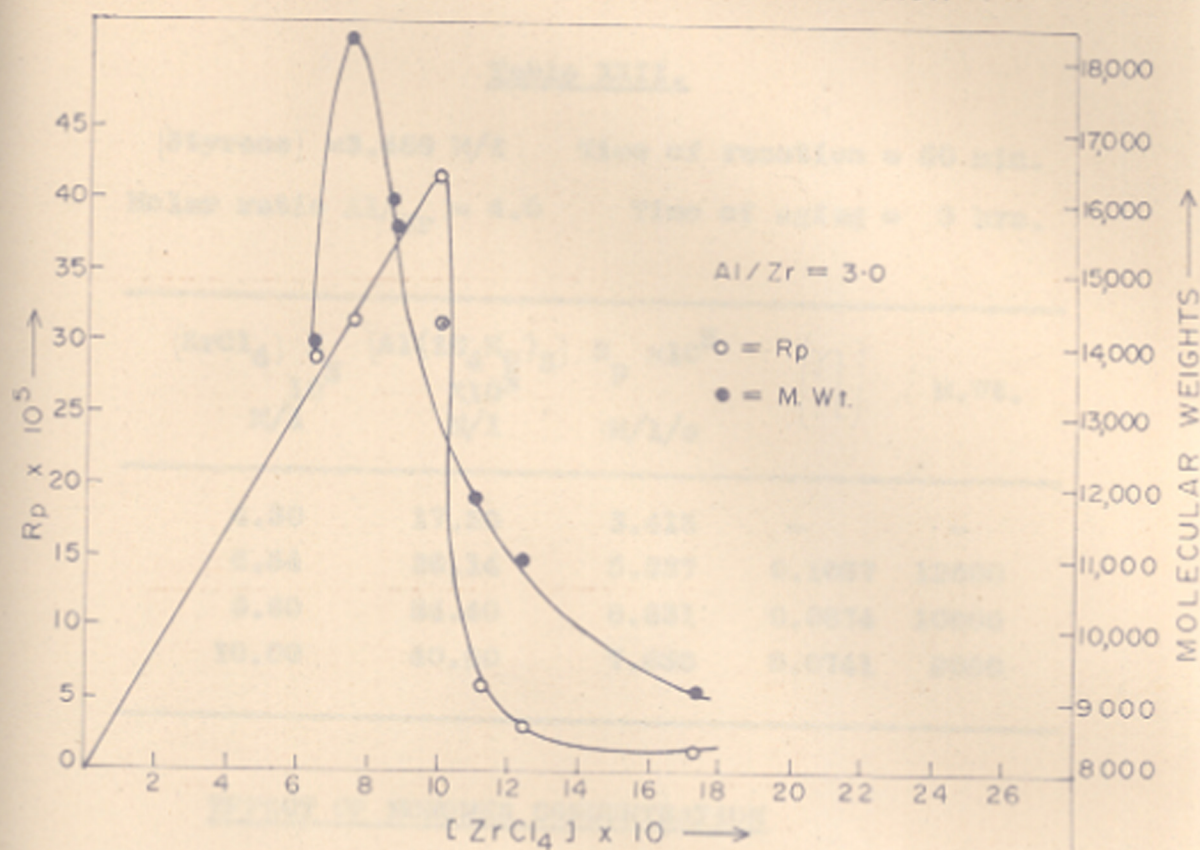
$[\text{ZrCl}_4]$ $\times 10^3$ M/l	$[\text{Al}(\text{iC}_4\text{H}_9)_3]$ $\times 10^3$ M/l	$R_p \times 10^5$ M/l/s	$[\eta]$	M. wt.
5.78	14.45	7.599	0.0889	5800
6.46	16.15	8.893	0.0809	9000
8.50	21.25	11.002	0.1273	16800
10.00	25.00	13.655	0.1057	13000
10.88	27.20	3.415	0.0936	11000
11.90	29.75	2.562	0.0741	8000
16.32	40.80	1.068	0.0673	7000
19.72	49.30	0.854	0.0654	6700
22.21	55.52	0.642	0.6030	6000

Table XXI.

[Styrene] = 3.486 M/l Time of reaction = 60 min.  
 Molar ratio Al/Zr = 3.0 Time of aging = 3 hrs.

$\text{ZrCl}_4$ $\times 10^3$ M/l	$\text{Al}(\text{iC}_4\text{H}_9)_3$ $\times 10^3$ M/l	$R_p \times 10^5$ M/l/s	$[\eta]$	M. wt.
6.536	19.608	29.037	0.1115	14000
7.568	22.704	31.596	0.1359	18400
8.944	25.832	38.437	0.1228	16000
10.000	30.000	41.523	0.1127	14200
11.180	33.540	5.980	0.0991	11900
12.384	37.052	3.412	0.0936	11000
17.200	51.600	1.706	0.0823	9200

Fig 22.  
 $ZrCl_4 - Al(iC_4H_9)_3 - STYRENE$ .  
 EFFECT OF CATALYST CONCENTRATION

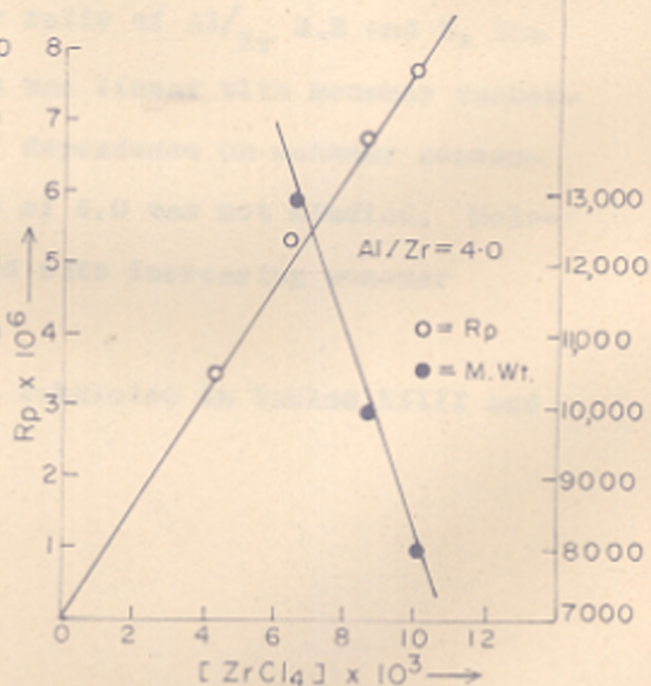


$[Styrene] = 1.743 \text{ M/L}$

Molar Ratio Al/Zr = 2.5

Time of Reaction = Min.

Time of Aging = 3 hr.



$[Styrene] = 3.486 \text{ M/L}$

Molar Ratio Al/Zr = 3.0, 4.0

Time of Reaction = 60 Min.

Time of Aging = 3 hr.

Table XXII.

[Styrene] = 3.486 M/l      Time of reaction = 60 min.  
 Molar ratio Al/Zr = 4.0      Time of aging = 3 hrs.

$[\text{ZrCl}_4] \times 10^3$ M/l	$[\text{Al}(\text{C}_2\text{H}_5)_3] \times 10^3$ M/l	$R_p \times 10^5$ M/l/s	$[\eta]$	M. wt.
4.30	17.20	3.415	-	-
6.54	26.14	5.337	0.1057	13000
8.60	34.40	6.831	0.0874	10000
10.00	40.00	7.686	0.0741	8000

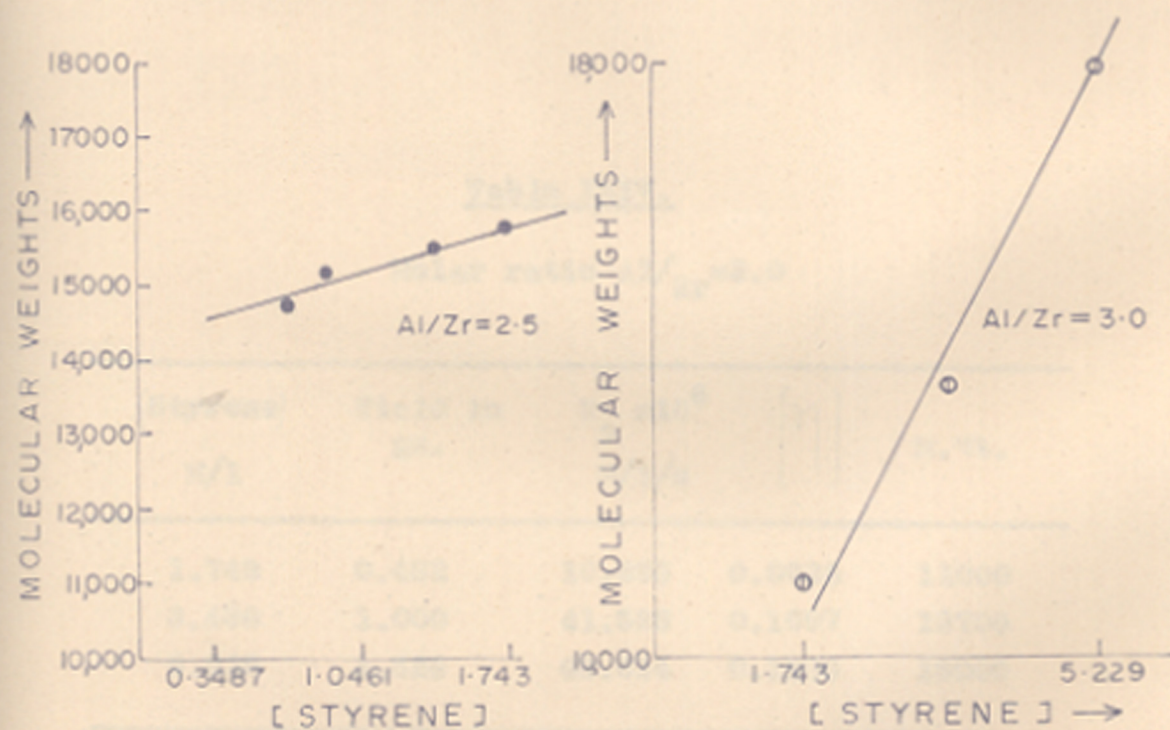
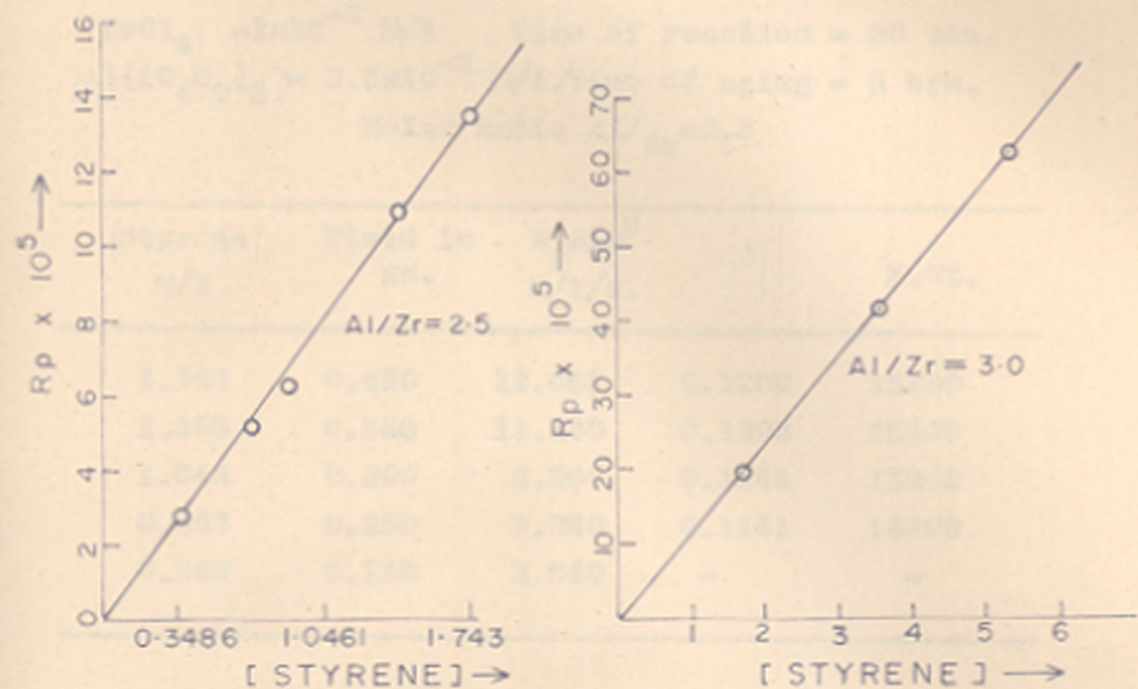
EFFECT OF MONOMER CONCENTRATION

At the same molar ratio of Al/Zr 2.5 and 3, the rate of polymerization was linear with monomer concentration. The order of dependence on monomer concentration at Al/Zr ratio of 4.0 was not studied. Molecular weights increased with increasing monomer concentration.

Results have been tabulated in Tables XXIII and XXIV - (Fig. 23).

Fig 23

ZrCl<sub>4</sub>-Al(iC<sub>4</sub>H<sub>9</sub>)<sub>3</sub> - STYRENE  
EFFECT OF MONOMER CONCENTRATION



[ZrCl<sub>4</sub>] = 0.01 M/L

Temp. of Reaction = 40°

Time of Reaction = 30 Min.

Time of Ageing = 3 hr.

Table XXIII

$[\text{ZrCl}_4] = 1 \times 10^{-2}$  M/l Time of reaction = 30 min.  
 $[\text{Al}(\text{iC}_4\text{H}_9)_3] = 2.5 \times 10^{-2}$  M/l. Time of aging = 3 hrs.  
 Molar ratio Al/Zr = 2.5

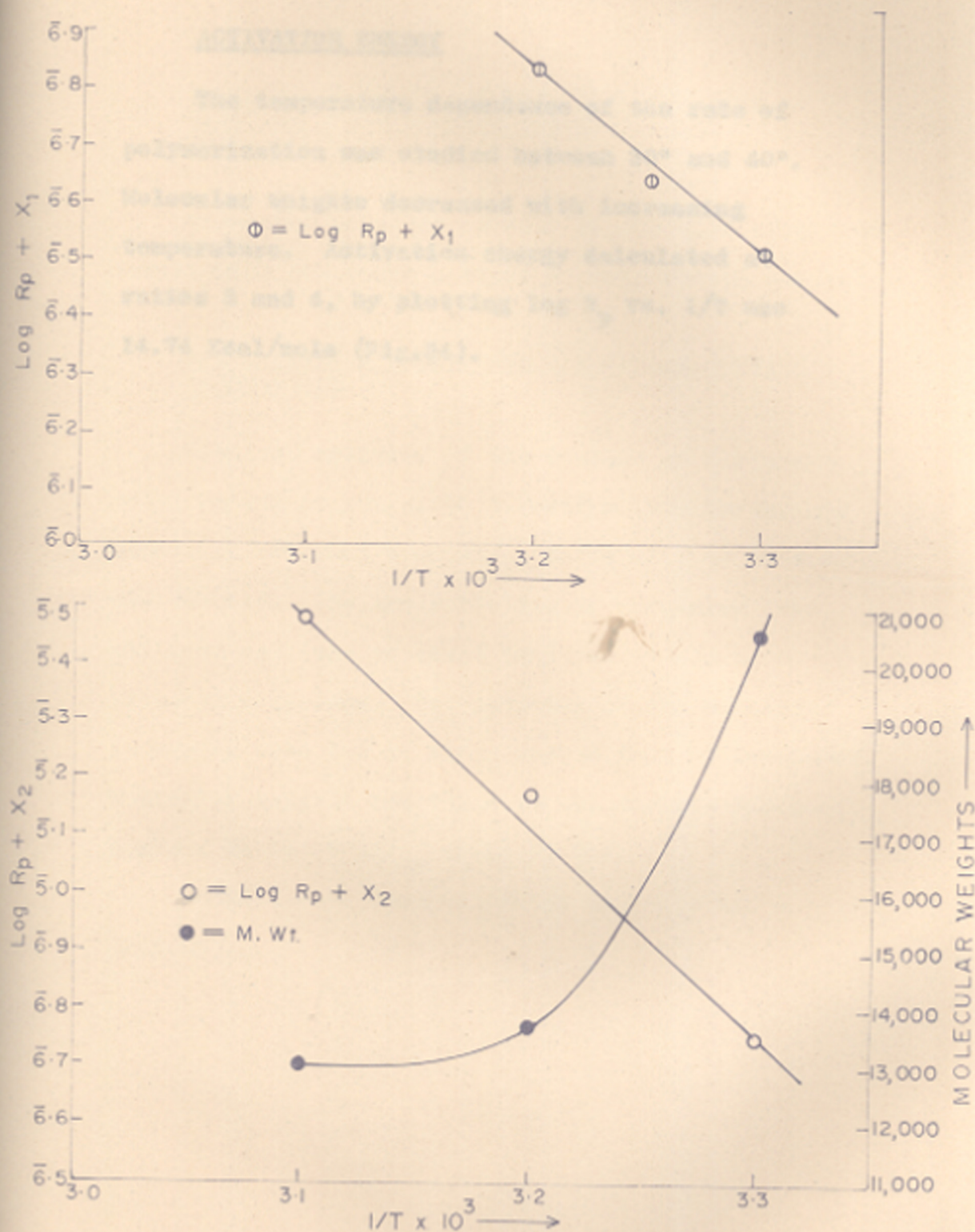
(Styrene) M/l	Yield in gms.	$R_p \times 10^6$ M/l/s.	$[\eta]$	M.wt.
1.743	0.650	13.655	0.1209	15700
1.395	0.530	11.130	0.1200	15500
1.046	0.300	6.300	0.1184	15200
0.697	0.250	5.250	0.1161	14800
0.349	0.140	2.940	-	-

Table XXIV.

Molar ratio Al/Zr = 3.0

(Styrene) M/l	Yield in gms.	$R_p \times 10^6$ M/l/s	$[\eta]$	M.wt.
1.743	0.482	19.895	0.0936	11000
3.486	1.000	41.523	0.1097	13700
5.229	1.526	63.014	0.1336	18000

Fig. 24  
 $ZrCl_4 - Al(iC_4H_9)_3 - STYRENE$   
 EFFECT OF TEMPERATURE



$[ZrCl_4] = 0.01 \text{ M/L}$   
 $[Al(iC_4H_9)_3] = 0.03 \text{ M/L}$   
 Molar Ratio  $Al/Zr = 3.0$   
 $X_1 = 4.537$

○ =  $[Styrene] = 1.743 \text{ M/L}$   
 ○ =  $[Styrene] = 3.486 \text{ M/L}$   
 Time of Reaction = 60 Min.  
 Time of Aging = 3 hr.  
 $X_2 = 9.074$



ACTIVATION ENERGY

The temperature dependence of the rate of polymerization was studied between 30° and 40°. Molecular weights decreased with increasing temperature. Activation energy calculated at ratios 3 and 4, by plotting  $\log R_p$  vs.  $1/T$  was 14.74 Kcal/mole (Fig. 24).

POLYMERIZATION OF STYRENE WITH ALUMINIUM  
TRIETHYL AND ZIRCONIUM TRICHLORIDE IN  
TOLUENE AT 40°

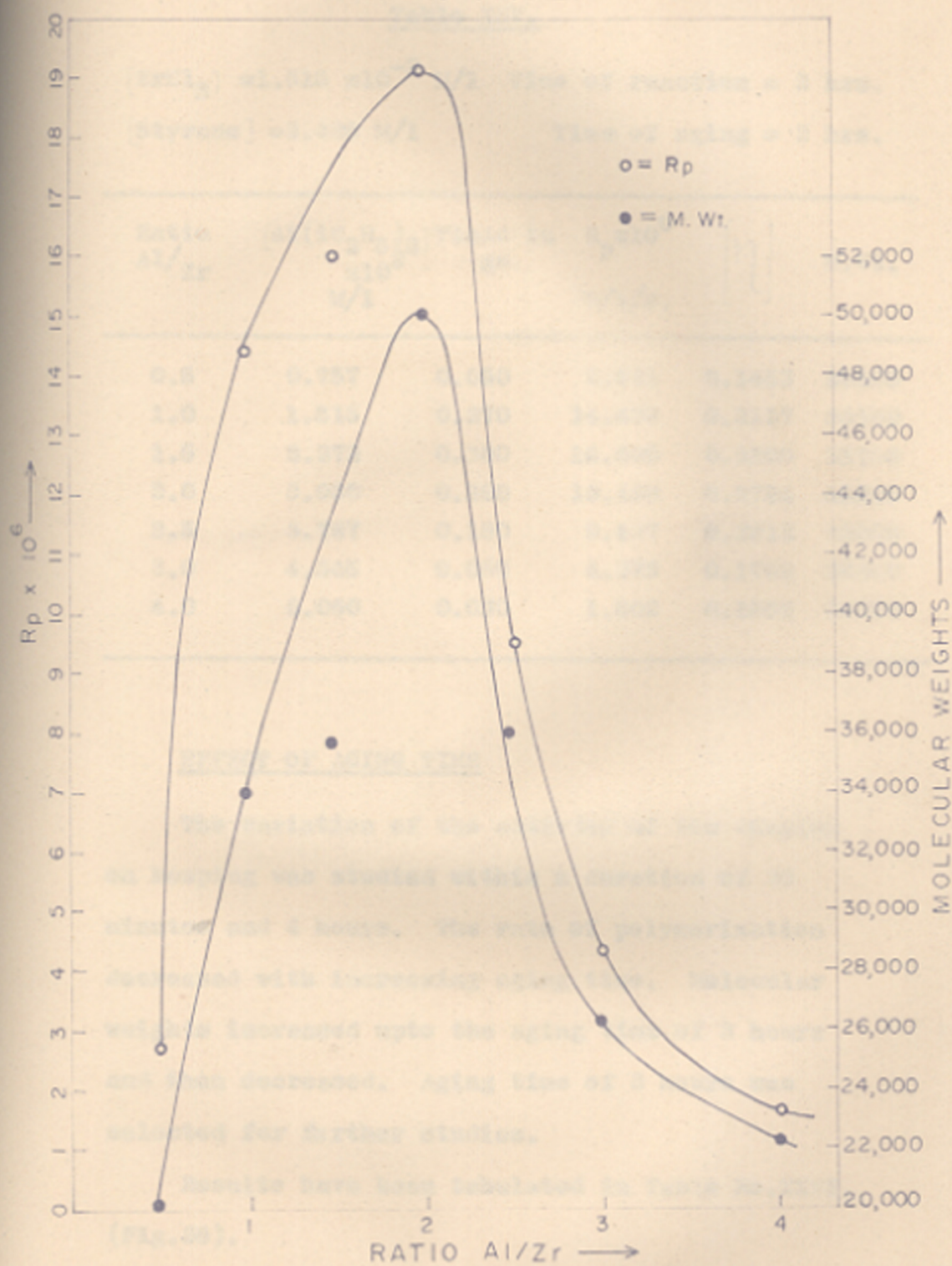
Aluminium triethyl readily reacts with zirconium trichloride and forms a black to deep violet complex.

MOLAR RATIO OF ALUMINIUM TRIETHYL/ZIRCONIUM  
TRICHLORIDE

Catalyst activity of the complex at different molar ratios of mixing of zirconium trichloride and aluminium triethyl from Al/Zr ratio of 0.05 to 4.0 was studied. The concentration of zirconium trichloride was kept constant but that of aluminium triethyl increased. The activity of the catalyst increased upto 2.0 of Al/Zr beyond that it decreased. Molecular weights increased in the similar fashion; maximum being at Al/Zr ratio of 2.0.

Results have been tabulated in Table XXV -  
(Fig. 25).

Fig 25  
 $ZrCl_3 - Al(C_2H_5)_3 - STYRENE$   
 RATIO STUDIES



$[ZrCl_3] = 1.515 \times 10^{-2}$

$[Styrene] = 3.486 \text{ M/L}$

Time of Reaction = 2 hr.

Time of Aging = 2 hr.

Temp. of Reaction =  $40^\circ$

Table XXV.

[ZrCl<sub>3</sub>] = 1.515 x 10<sup>-2</sup> M/l Time of reaction = 2 hrs.  
 [Styrene] = 3.486 M/l Time of aging = 2 hrs.

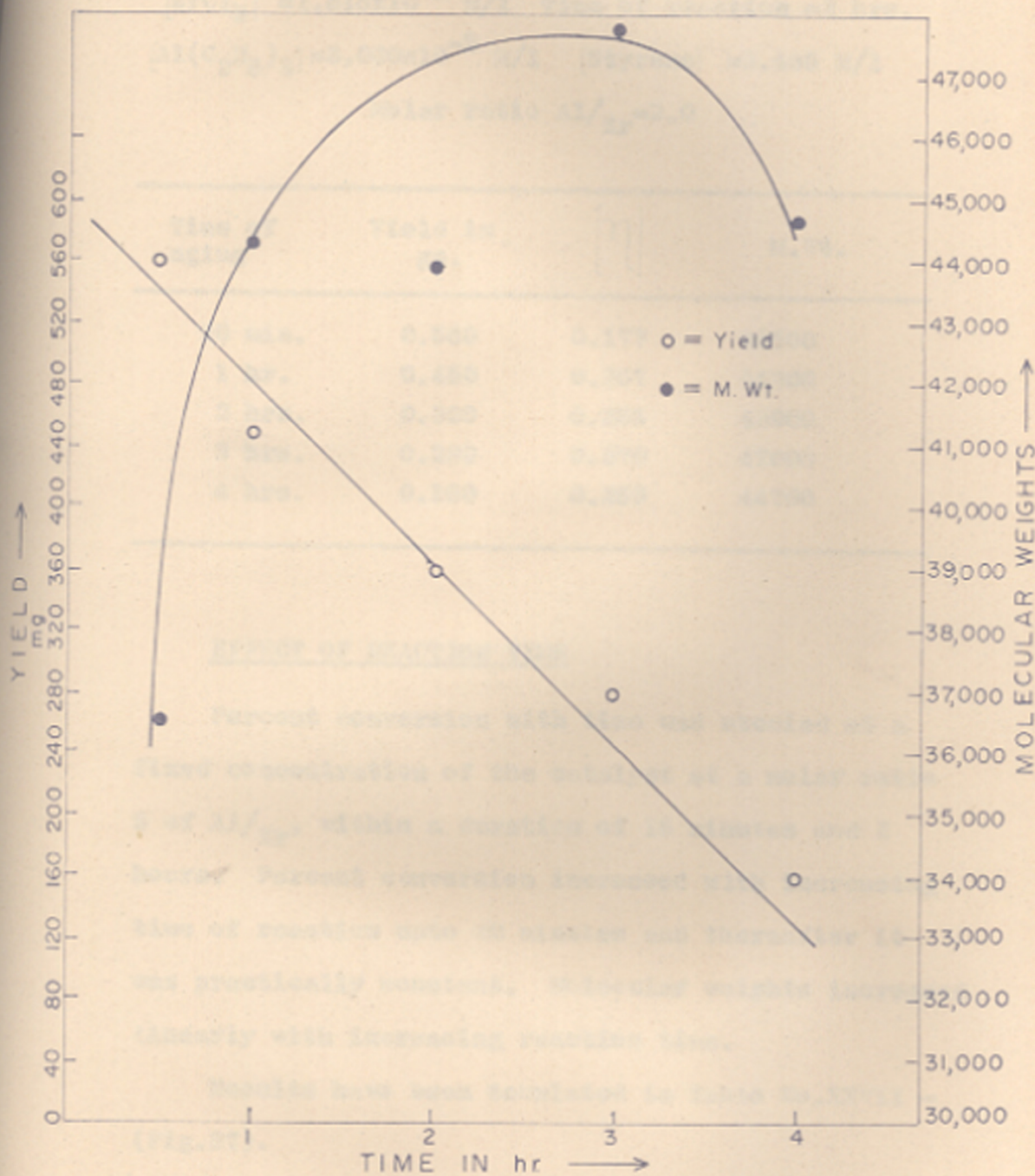
Ratio Al/Zr	[Al(iC <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> ] x 10 <sup>2</sup> M/l	Yield in g <sup>s</sup> .	R <sub>p</sub> x 10 <sup>6</sup> M/l/s.	[η]	M.Wt.
0.5	0.757	0.050	2.671	0.1453	20200
1.0	1.515	0.270	14.438	0.2127	34100
1.5	2.272	0.300	16.025	0.2200	35700
2.0	3.030	0.360	19.128	0.2724	48000
2.5	3.787	0.180	9.437	0.2312	36000
3.0	4.545	0.080	4.275	0.1762	26300
4.0	6.060	0.030	1.602	0.1562	22300

EFFECT OF AGING TIME

The variation of the activity of the complex on keeping was studied within a duration of 30 minutes and 4 hours. The rate of polymerization decreased with increasing aging time. Molecular weights increased upto the aging time of 3 hours and then decreased. Aging time of 3 hours was selected for further studies.

Results have been tabulated in Table No. XXVI. (Fig. 26).

Fig. 26  
 $ZrCl_3 - Al(C_2H_5)_3 - STYRENE$   
 EFFECT OF AGING TIME



$[ZrCl_3] = 1.515 \times 10^{-2} \text{ M/L}$

$[Styrene] = 3.486 \text{ M/L}$

$[Al(C_2H_5)_3] = 3.030 \times 10^{-2} \text{ M/L}$

Time of Reaction = 2 hr.

Molar Ratio Al/Zr = 2.0

Temp of Reaction =  $40^\circ$

Table XXVI

$[\text{ZrCl}_3] = 1.515 \times 10^{-2}$  M/l Time of reaction = 2 hrs.  
 $[\text{Al}(\text{C}_2\text{H}_5)_3] = 3.030 \times 10^{-2}$  M/l (Styrene) = 3.486 M/l  
 Molar ratio  $\text{Al}/\text{Zr} = 2.0$

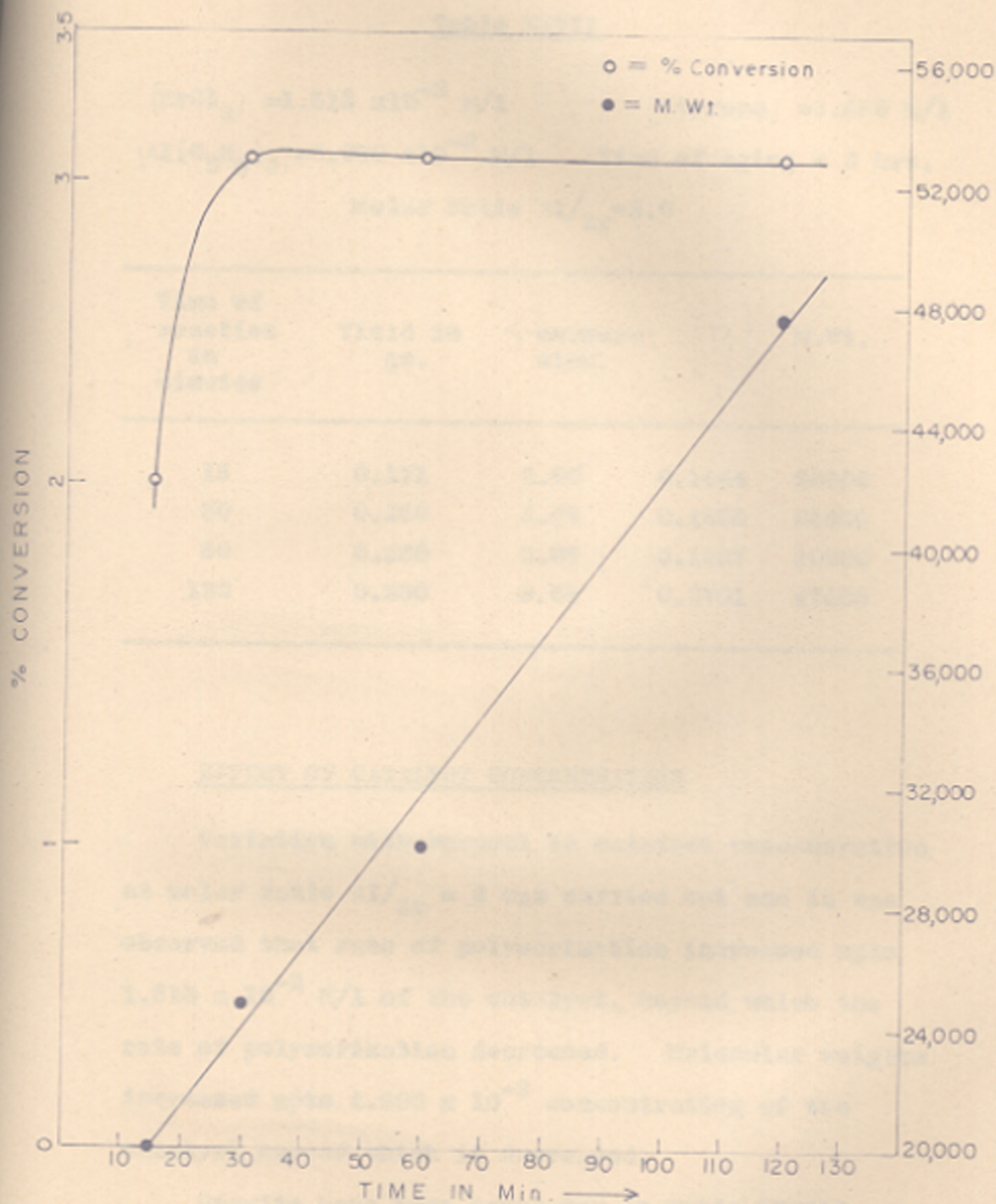
Time of aging	Yield in gs.	$[\eta]$	M.Wt.
30 min.	0.560	0.177	36500
1 hr.	0.450	0.257	44300
2 hrs.	0.360	0.255	43900
3 hrs.	0.280	0.270	47600
4 hrs.	0.160	0.259	44700

EFFECT OF REACTION TIME

Percent conversion with time was studied at a fixed concentration of the catalyst at a molar ratio 2 of  $\text{Al}/\text{Zr}$ , within a duration of 15 minutes and 2 hours. Percent conversion increased with increasing time of reaction upto 30 minutes and thereafter it was practically constant. Molecular weights increased linearly with increasing reaction time.

Results have been tabulated in Table No. XXVII - (Fig. 37).

Fig. 27  
 $ZrCl_3-Al(C_2H_5)_3$ -STYRENE  
 EFFECT OF REACTION TIME



$[ZrCl_3] = 1.515 \times 10^{-2} M/L$

$[Styrene] = 3.486 M/L$

$[Al(C_2H_5)_3] = 3.030 \times 10^{-2} M/L$

Time of Aging = 3 hr.

Molar Ratio Al/Zr = 2.0

Temp. of Reaction =  $40^\circ$

Table XXVII

$[\text{ZrCl}_3] = 1.515 \times 10^{-2} \text{ M/l}$        $[\text{Styrene}] = 3.486 \text{ M/l}$   
 $[\text{Al}(\text{C}_2\text{H}_5)_3] = 3.030 \times 10^{-2} \text{ M/l}$       Time of aging = 3 hrs.  
 Molar ratio  $\text{Al/Zr} = 2.0$

Time of reaction in minutes	Yield in gs.	% conversion	$[\eta]$	M. wt.
15	0.171	2.00	0.1444	20000
30	0.280	3.08	0.1685	24800
60	0.280	3.08	0.1937	30000
120	0.280	3.08	0.2701	47600

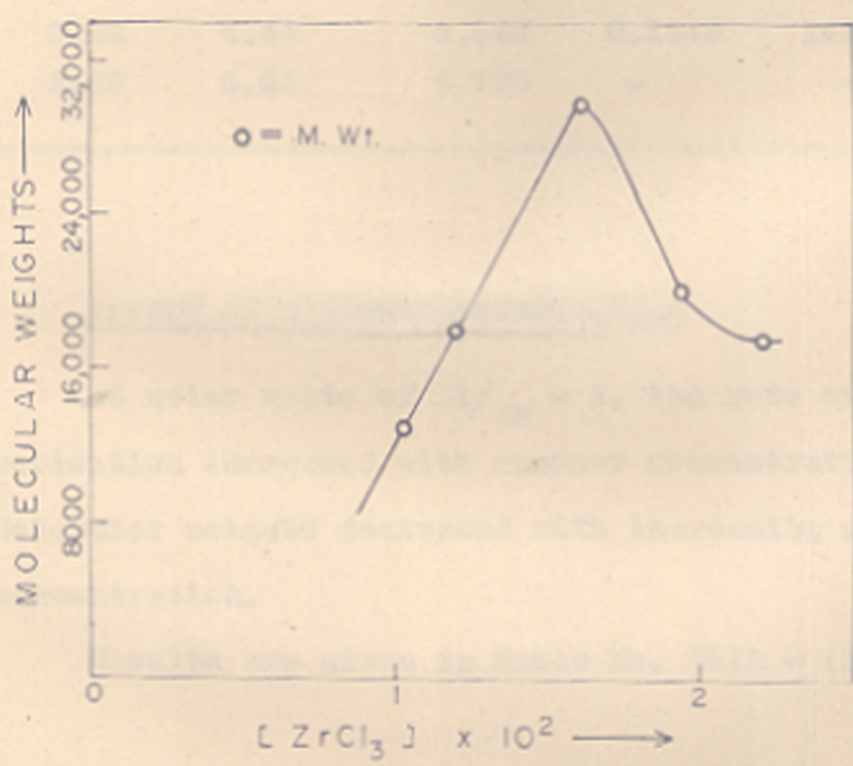
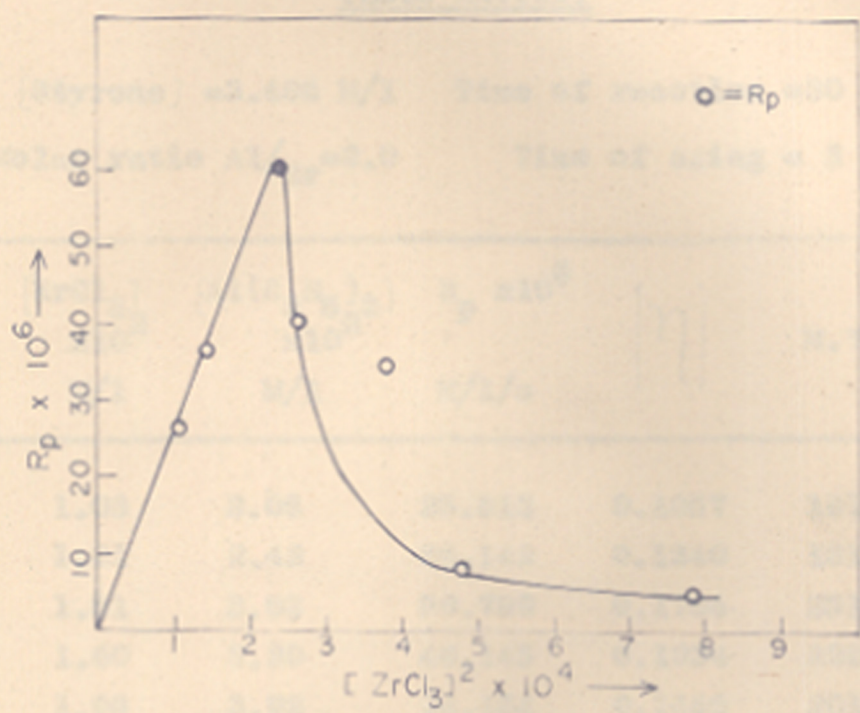
EFFECT OF CATALYST CONCENTRATION

Variation with respect to catalyst concentration at molar ratio  $\text{Al/Zr} = 2$  was carried out and it was observed that rate of polymerization increased upto  $1.515 \times 10^{-2} \text{ M/l}$  of the catalyst, beyond which the rate of polymerization decreased. Molecular weights increased upto  $1.600 \times 10^{-2}$  concentration of the catalyst beyond which it decreased.

Results have been tabulated in Table XXVIII -  
 (Fig. 28)



Fig. 28  
 $ZrCl_3 - Al(C_2H_5)_3 - STYRENE$   
 EFFECT OF CATALYST CONCENTRATION



$[Styrene] = 3.486 \text{ M/L}$   
 Molar Ratio  $Al/Zr = 2.0$

Time of Reaction = 30 Min.  
 Time of Aging = 3 hr.  
 Temp. of Reaction =  $40^\circ$

Table XXVIII.

[Styrene] = 3.486 M/l      Time of reaction = 30 min.  
 Molar ratio Al/Zr = 2.0      Time of aging = 3 hrs.

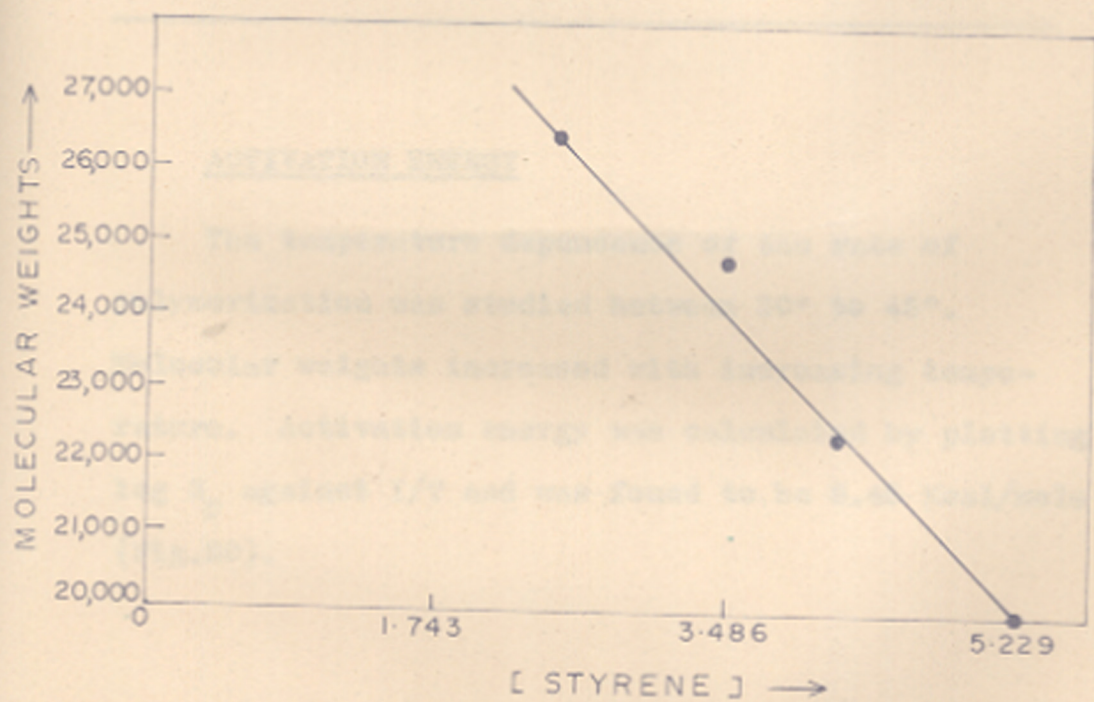
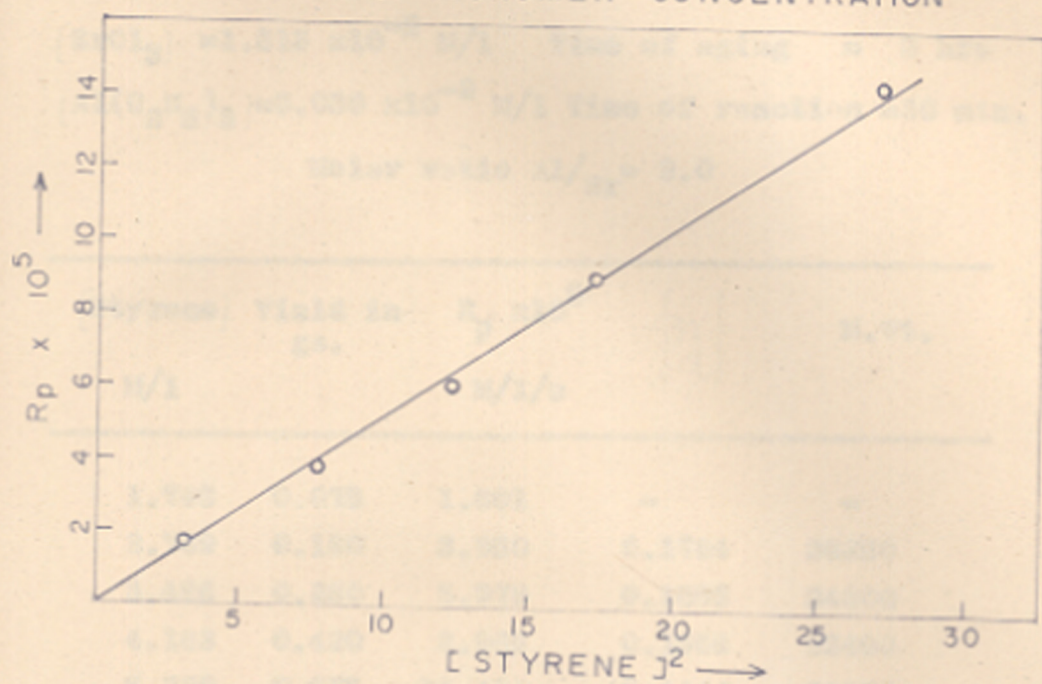
$[\text{ZrCl}_3]$ $\times 10^2$ M/l	$[\text{Al}(\text{C}_2\text{H}_5)_3]$ $\times 10^2$ M/l	$R_p \times 10^6$ M/l/s	$[\eta]$	M. wt.
1.03	2.06	25.612	0.1057	13100
1.21	2.42	36.142	0.1340	18100
1.51	3.03	59.789	0.1704	25100
1.60	3.20	40.143	0.1934	29900
1.96	3.92	34.154	0.1446	20100
2.22	4.44	8.540	0.1340	18100
2.82	5.64	4.770	-	-

EFFECT OF MONOMER CONCENTRATION

At molar ratio of Al/Zr = 2, the rate of polymerization increased with monomer concentration. Molecular weights decreased with increasing monomer concentration.

Results are given in Table No. XXIX - (Fig. 29)

Fig.29  
 $ZrCl_3-Al(C_2H_5)_3$ -STYRENE  
 EFFECT OF MONOMER CONCENTRATION



$[ZrCl_3] = 1.515 \times 10^{-2} M/L$

Time of Reaction = 30 Min.

$[Al(C_2H_5)_3] = 3.03 \times 10^{-2} M/L$

Time of Aging = 3 hr.

Molar Ratio Al/Zr = 2.0

Temp. of Reaction =  $40^\circ$

Table XXIX.

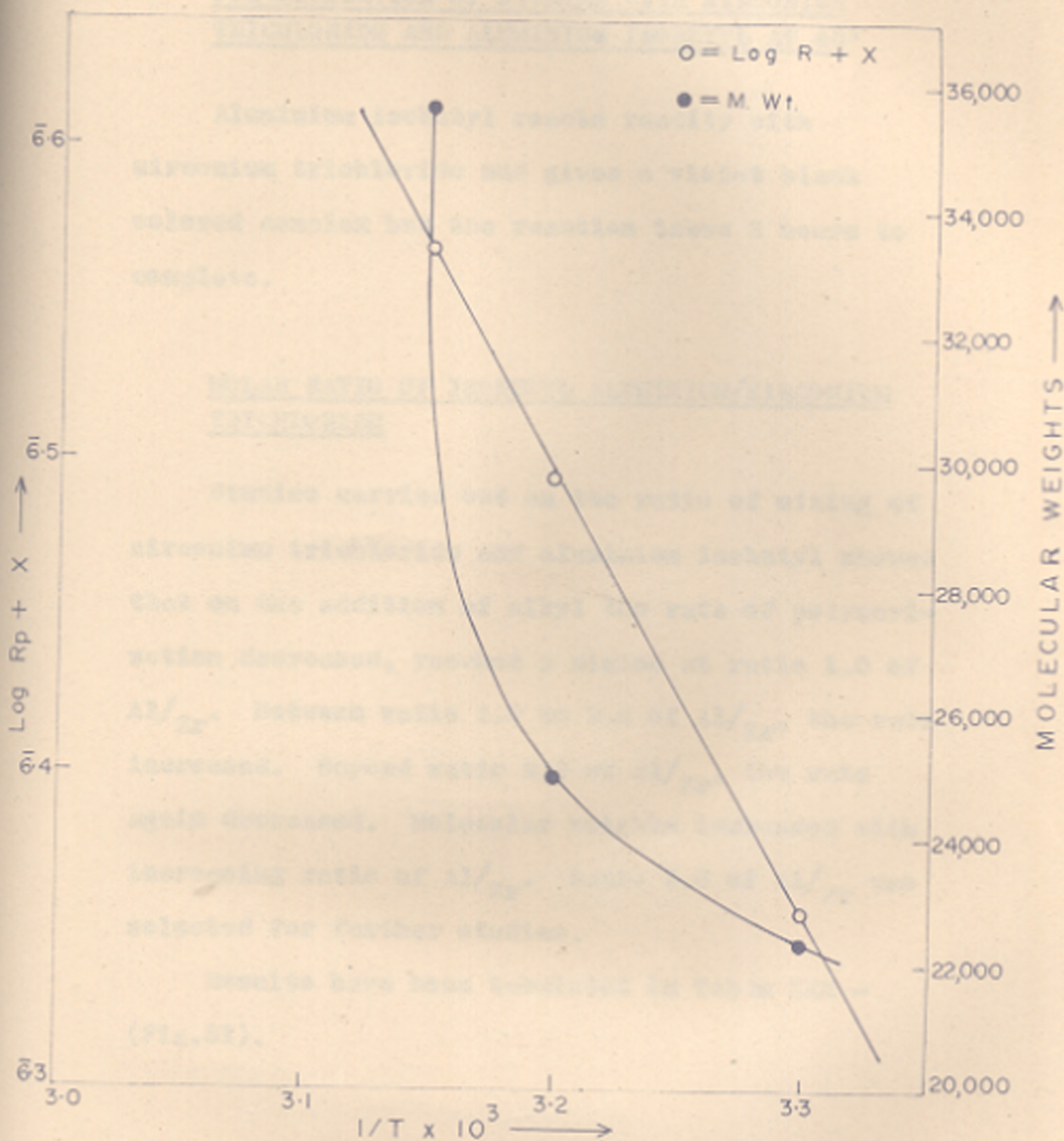
$[\text{ZrCl}_3] = 1.515 \times 10^{-2}$  M/l Time of aging = 3 hrs  
 $[\text{Al}(\text{C}_2\text{H}_5)_3] = 3.030 \times 10^{-2}$  M/l Time of reaction = 30 min.  
 Molar ratio  $\text{Al/Zr} = 2.0$

[Styrene] M/l	Yield in Gs.	$R_p \times 10^5$ M/l/s	$[\eta]$	M.Wt.
1.743	0.075	1.601	-	-
2.789	0.160	3.950	0.1764	26350
3.486	0.260	5.979	0.1685	24800
4.183	0.420	8.965	0.1565	22400
5.229	0.675	14.414	0.1444	20000

ACTIVATION ENERGY

The temperature dependence of the rate of polymerization was studied between 30° to 45°. Molecular weights increased with increasing temperature. Activation energy was calculated by plotting  $\log R_p$  against  $1/T$  and was found to be 6.45 Kcal/mole (Fig.30).

Fig. 30  
 $ZrCl_3 - Al(C_2H_5)_3 - STYRENE$   
 EFFECT OF TEMPERATURE



$$[ZrCl_3] = 1.515 \times 10^{-2} \text{ M/L}$$

$$[Styrene] = 3.486 \text{ M/L}$$

$$[Al(C_2H_5)_3] = 3.030 \times 10^{-2} \text{ M/L}$$

$$\text{Time of Reaction} = 30 \text{ Min.}$$

$$\text{Molar Ratio Al/Zr} = 1.5$$

$$\text{Time of Aging} = 3 \text{ hr.}$$

$$X = 9.074$$

POLYMERIZATION OF STYRENE WITH ZIRCONIUM  
TRICHLORIDE AND ALUMINIUM ISOBUTYL AT 40°

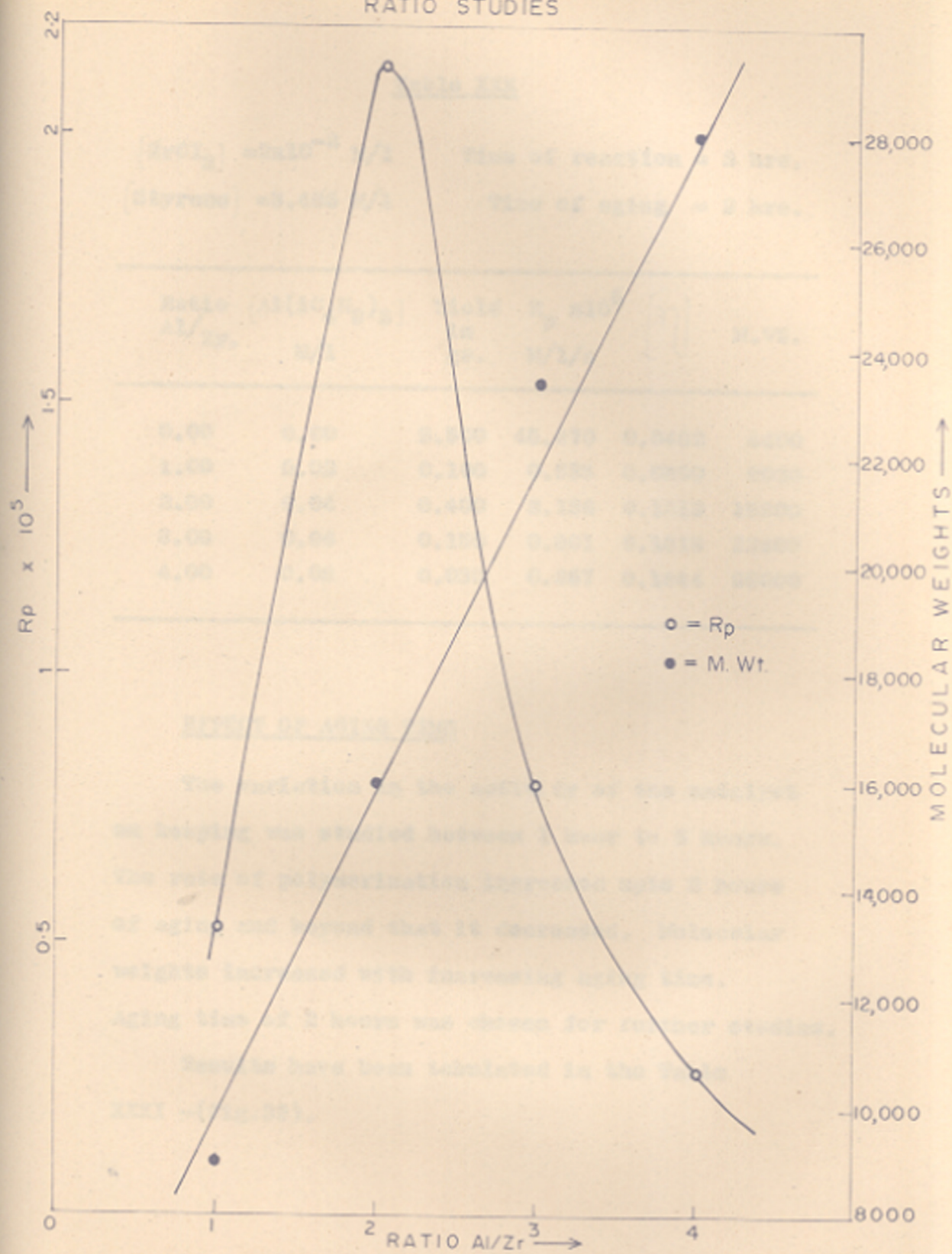
Aluminium isobutyl reacts readily with zirconium trichloride and gives a violet black colored complex but the reaction takes 2 hours to complete.

MOLAR RATIO OF ISOBUTYL ALUMINIUM/ZIRCONIUM  
TRICHLORIDE

Studies carried out on the ratio of mixing of zirconium trichloride and aluminium isobutyl showed that on the addition of alkyl the rate of polymerization decreased, reached a minima at ratio 1.0 of  $Al/Zr$ . Between ratio 1.0 to 2.0 of  $Al/Zr$ , the rate increased. Beyond ratio 2.0 of  $Al/Zr$ , the rate again decreased. Molecular weights increased with increasing ratio of  $Al/Zr$ . Ratio 2.0 of  $Al/Zr$  was selected for further studies.

Results have been tabulated in Table XXX - (Fig.31).

Fig 31  
 $ZrCl_3 - Al(iC_4H_9)_3 - STYRENE$   
 RATIO STUDIES



$[ZrCl_3] = 0.02 \text{ M/L}$

$[Styrene] = 3.486 \text{ M/L}$

Time of Reaction = 2 hr.

Time of Aging = 2 hr.

Temp. of Reaction =  $40^\circ$

Table XXX

$[ZrCl_3] = 2 \times 10^{-2}$ M/l	Time of reaction = 2 hrs.
$[Styrene] = 3.486$ M/l	Time of aging = 2 hrs.

Ratio Al/Zr.	$[Al(C_4H_9)_3]$ M/l	Yield in gms.	$R_p \times 10^6$ M/l/s	$[\eta]$	M.Wt.
0.00	0.00	8.500	45.470	0.0482	4400
1.00	0.02	0.100	0.535	0.0809	9000
2.00	0.04	0.400	2.136	0.1212	15800
3.00	0.06	0.150	0.801	0.1618	23400
4.00	0.08	0.050	0.267	0.1844	28000

EFFECT OF AGING TIME

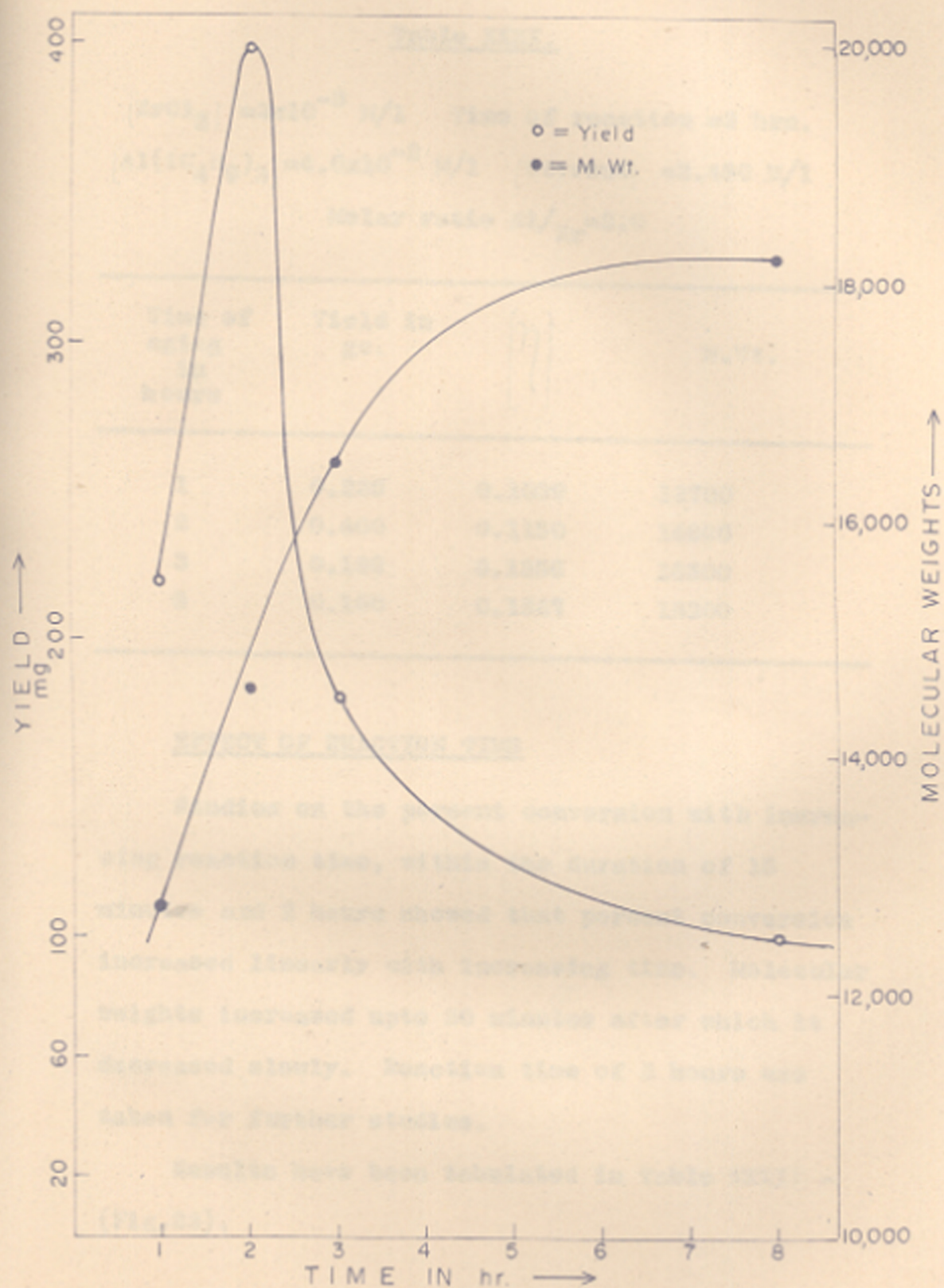
The variation in the activity of the catalyst on keeping was studied between 1 hour to 8 hours. The rate of polymerization increased upto 2 hours of aging and beyond that it decreased. Molecular weights increased with increasing aging time. Aging time of 2 hours was chosen for further studies.

Results have been tabulated in the Table XXXI -(Fig.32).



Fig. 32

ZrCl<sub>3</sub> - Al(iC<sub>4</sub>H<sub>9</sub>)<sub>3</sub> - STYRENE  
EFFECT OF AGING TIME



[ZrCl<sub>3</sub>] = 0.02 M/L

[Al(iC<sub>4</sub>H<sub>9</sub>)<sub>3</sub>] = 0.04 M/L

Molar Ratio Al/Zr = 2.0

Time of Reaction = 2 hr.

[Styrene] = 3.486 M/L

Temp. of Reaction = 40°

Table XXXI.

$[\text{ZrCl}_3] = 2 \times 10^{-2} \text{ M/l}$  Time of reaction = 2 hrs.  
 $[\text{Al}(\text{C}_4\text{H}_9)_3] = 4.0 \times 10^{-2} \text{ M/l}$  (Styrene) = 3.486 M/l  
 Molar ratio  $\text{Al/Zr} = 2.0$

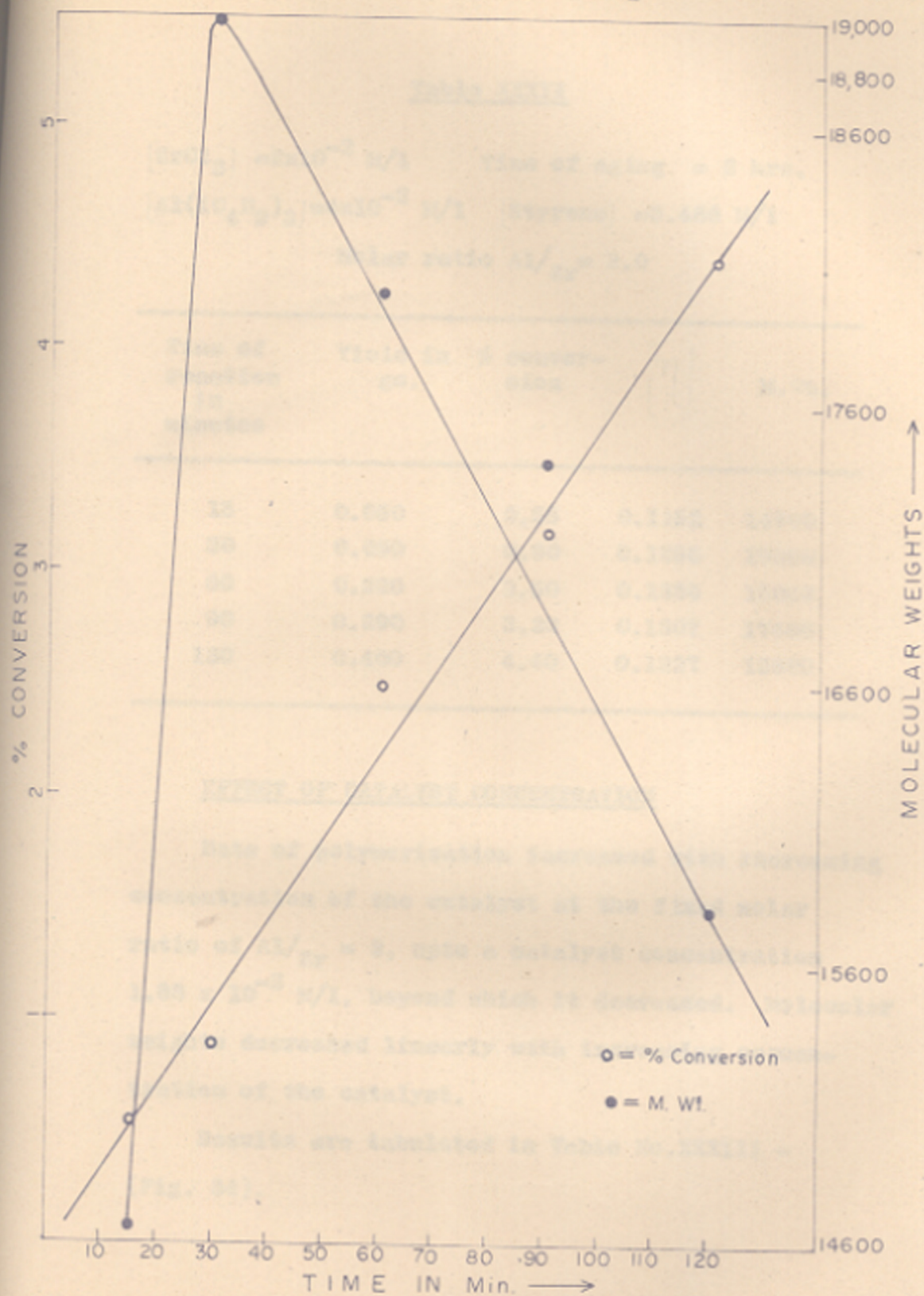
Time of aging in hours	Yield in gs.	$[\eta]$	M. Wt.
1	0.230	0.1039	12700
2	0.400	0.1150	14600
3	0.180	0.1256	16500
8	0.100	0.1347	18200

EFFECT OF REACTION TIME

Studies on the percent conversion with increasing reaction time, within the duration of 15 minutes and 2 hours showed that percent conversion increased linearly with increasing time. Molecular weights increased upto 30 minutes after which it decreased slowly. Reaction time of 2 hours was taken for further studies.

Results have been tabulated in Table XXXII - (Fig.33).

Fig 33  
 $ZrCl_3 - Al(iC_4H_9)_3 - STYRENE$   
 EFFECT OF REACTION TIME



$[ZrCl_3] = 0.02 \text{ M/L}$

Time of Aging = 2 hr.

$[Al(iC_4H_9)_3] = 0.04 \text{ M/L}$

$[Styrene] = 3.486 \text{ M/L}$

Molar Ratio Al/Zr = 2.0

Temp of Reaction =  $40^\circ$

Table XXXII

$[\text{ZrCl}_3] = 2 \times 10^{-2} \text{ M/l}$       Time of aging = 2 hrs.  
 $[\text{Al}(\text{C}_4\text{H}_9)_3] = 4 \times 10^{-2} \text{ M/l}$      $[\text{Styrene}] = 3.486 \text{ M/l}$   
 Molar ratio  $\text{Al/Zr} = 2.0$

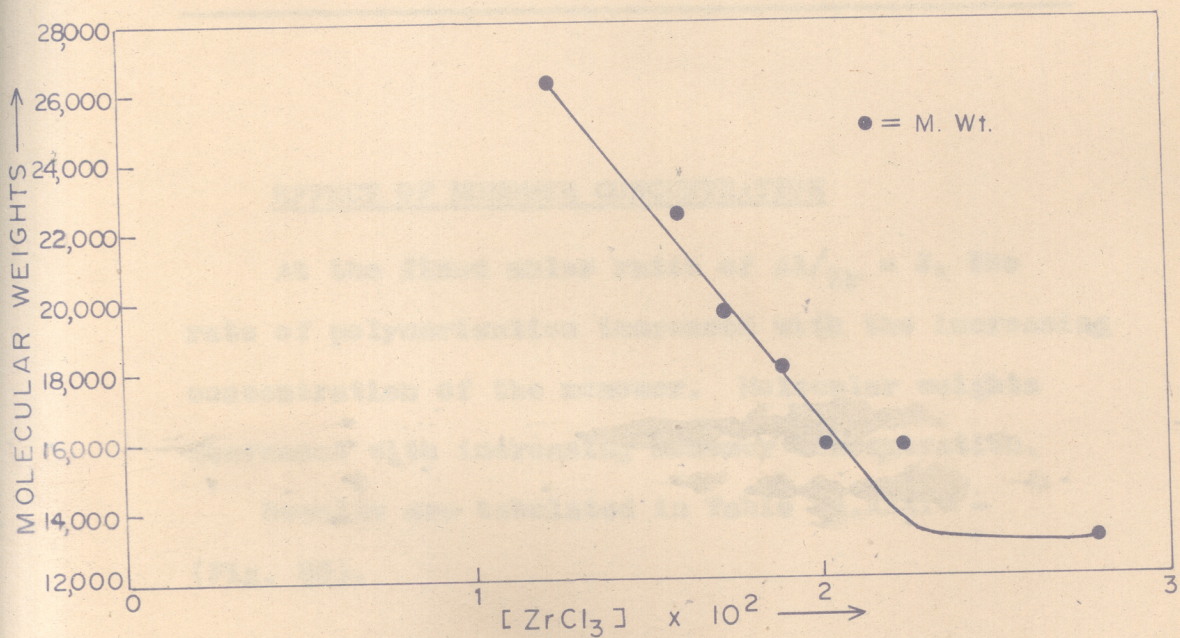
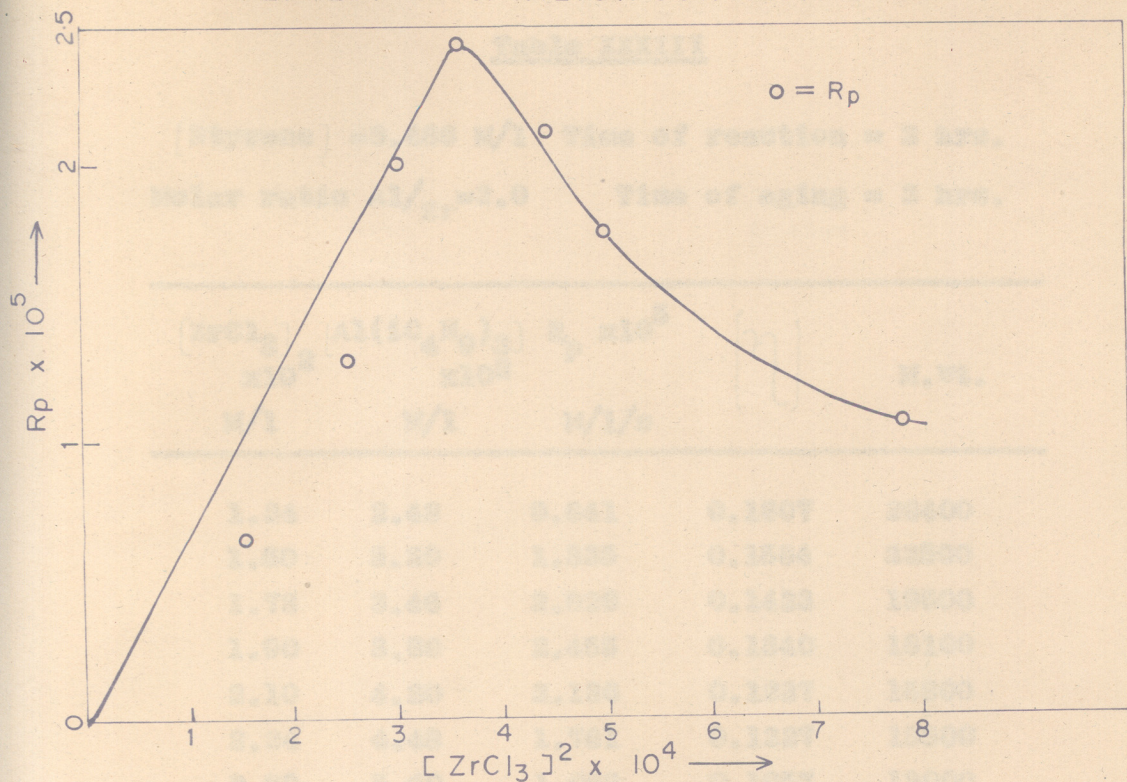
Time of reaction in minutes	Yield in gm.	% conversion	$[\eta]$	M. wt.
15	0.050	0.55	0.1152	14700
30	0.060	0.90	0.1356	19000
60	0.220	2.50	0.1336	18000
90	0.290	3.20	0.1307	17400
120	0.400	4.40	0.1227	15800

EFFECT OF CATALYST CONCENTRATION

Rate of polymerization increased with increasing concentration of the catalyst at the fixed molar ratio of  $\text{Al/Zr} = 2$ , upto a catalyst concentration  $1.88 \times 10^{-2} \text{ M/l}$ , beyond which it decreased. Molecular weights decreased linearly with increasing concentration of the catalyst.

Results are tabulated in Table No. XXXIII - (Fig. 34).

Fig. 34  
 $ZrCl_3 - Al(iC_4H_9)_3 - STYRENE$   
 EFFECT OF CATALYST CONCENTRATION



$[Styrene] = 3.486 \text{ M/L}$

Molar Ratio Al/Zr = 2.0

Time of Reaction = 2 hr.

Time of Aging = 2 hr.

Temp. of Reaction =  $40^\circ$

Table XXXIII

[Styrene] = 3.486 M/l Time of reaction = 2 hrs.  
 Molar ratio Al/Zr = 2.0 Time of aging = 2 hrs.

$[\text{ZrCl}_3]$ $\times 10^2$ M/l	$[\text{Al}(\text{iC}_4\text{H}_9)_3]$ $\times 10^2$ M/l	$R_p \times 10^5$ M/l/s	$[\eta]$	M. wt.
1.24	2.48	0.641	0.1807	26400
1.60	3.20	1.335	0.1584	22500
1.73	3.46	2.629	0.1423	19600
1.90	3.80	2.455	0.1340	18100
2.10	4.20	2.136	0.1227	15800
2.24	4.48	1.761	0.1227	15800
2.80	5.60	1.068	0.1057	13000

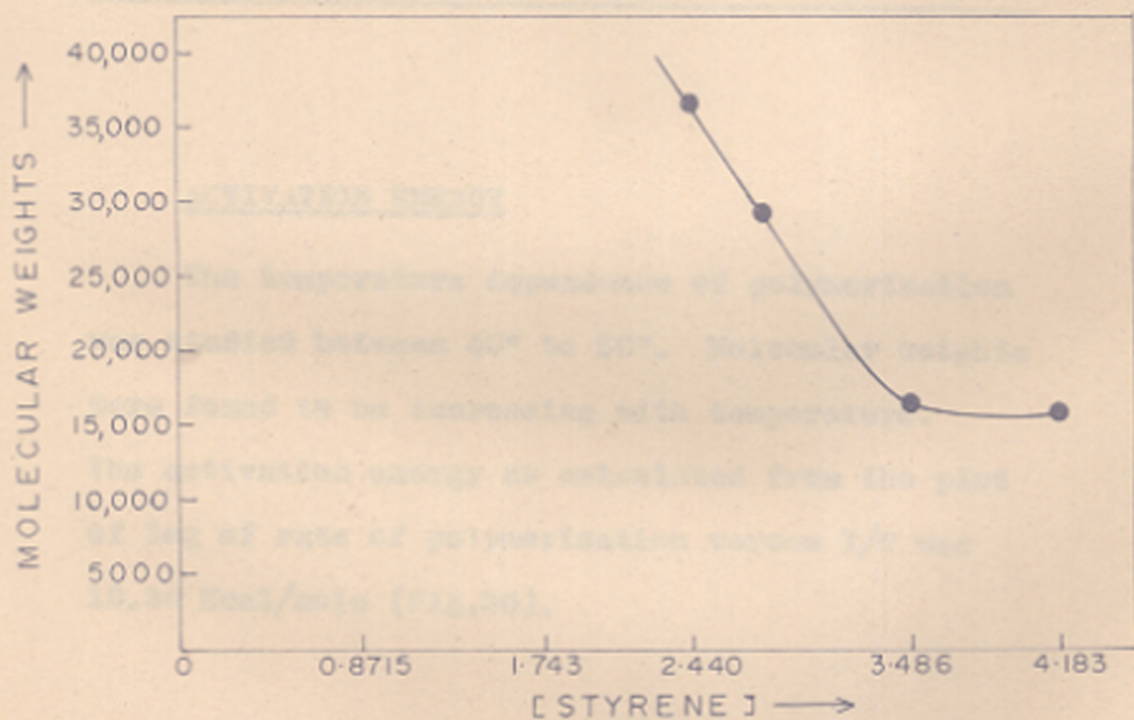
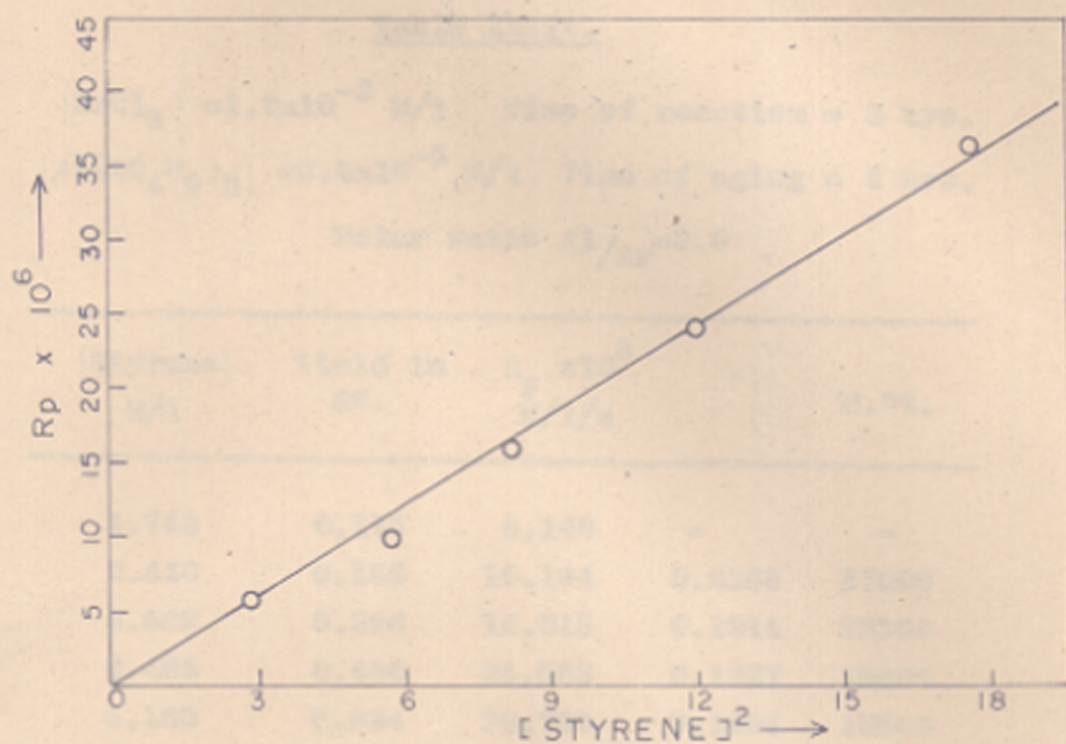
EFFECT OF MONOMER CONCENTRATION

At the fixed molar ratio of Al/Zr = 2, the rate of polymerization increased with the increasing concentration of the monomer. Molecular weights decreased with increasing monomer concentration.

Results are tabulated in Table No. XXXIV -  
 (Fig. 35).

Fig. 35

ZrCl<sub>3</sub> - Al (iC<sub>4</sub>H<sub>9</sub>)<sub>3</sub> - STYRENE  
EFFECT OF MONOMER CONCENTRATION



[ZrCl<sub>3</sub>] = 1.9 x 10<sup>-2</sup> M/L

Time of Reaction = 2 hr.

[Al (iC<sub>4</sub>H<sub>9</sub>)<sub>3</sub>] = 3.8 x 10<sup>-2</sup> M/L

Time of Aging = 2 hr.

Molar Ratio Al/Zr = 2.0

Temp. of Reaction = 40°

Table XXXIV.

$[\text{ZrCl}_3] = 1.9 \times 10^{-2} \text{ M/l}$  Time of reaction = 2 hrs.  
 $[\text{Al}(\text{IC}_4\text{H}_9)_3] = 3.6 \times 10^{-2} \text{ M/l}$  Time of aging = 2 hrs.  
 Molar ratio Al/Zr = 2.0

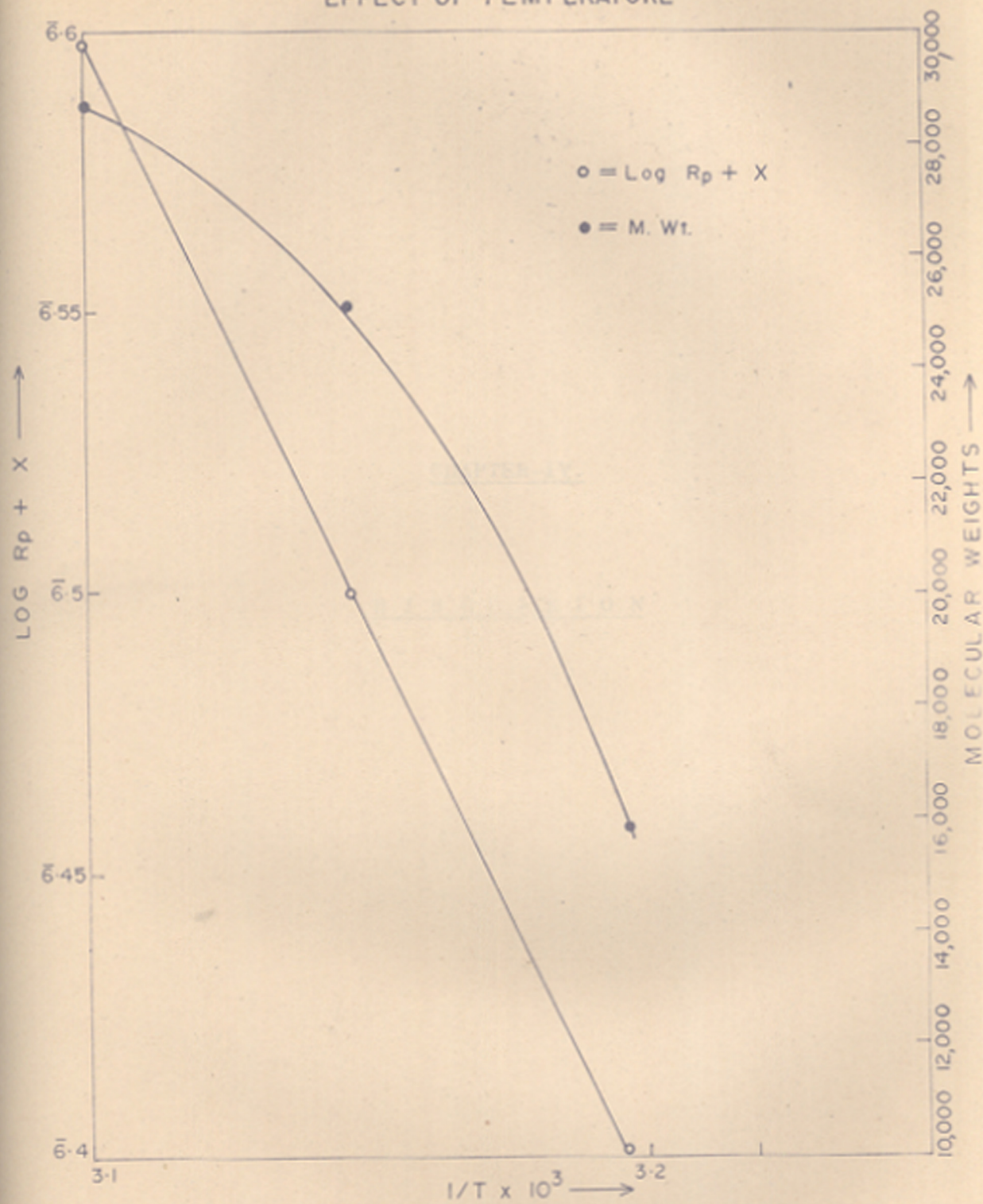
[Styrene] M/l	Yield in gms.	$R_p \times 10^6$ M/l/s	$[\eta]$	M.Wt.
1.743	0.115	6.140	-	-
2.440	0.189	10.144	0.2355	37000
2.689	0.296	16.015	0.1914	29500
3.486	0.460	24.563	0.1327	15800
4.183	0.684	36.750	0.1204	15800

ACTIVATION ENERGY

The temperature dependence of polymerization was studied between 40° to 50°. Molecular weights were found to be increasing with temperature. The activation energy as calculated from the plot of log of rate of polymerization versus  $1/T$  was 10.30 Kcal/mole (Fig.36).



Fig. 36  
 $ZrCl_3 - Al(iC_4H_9)_3 - STYRENE$   
 EFFECT OF TEMPERATURE



$[ZrCl_3] = 1.70 \times 10^{-2} M/L$

Time of Reaction = 2 hr.

$[Al(iC_4H_9)_3] = 3.4 \times 10^{-2} M/L$

Time of Aging = 2 hr.

Molar Ratio Al/Zr = 2.0

$X = 9.074$

CHAPTER-IV.

D I S C U S S I O N

DISCUSSIONREPRODUCIBILITY OF THE RESULTS

The same batches of zirconium tetrachloride and zirconium trichloride were used for all zirconium tetrachloride-aluminium triethyl and zirconium trichloride-aluminium triethyl runs because it has been reported<sup>78</sup> in the case of titanium trichloride-aluminium triethyl system that the activity of the catalyst decreases on keeping and it affects the reproducibility of the results. It has also been stated that the decrease in activity does not change the relationship between the variables influencing the rate of polymerization, if the same batch of the catalyst is used. The use of zirconium tetrachloride and zirconium trichloride from the same batch further ensured the same particle size of the catalyst throughout the reaction. The stirring 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 catalyst and possibly also for the separation of

the polymer from the catalyst surface. Significant changes in reaction rate observed in polymerization of propylene with Ziegler type catalyst due to the variation in speed of agitation are known<sup>79</sup>. It was hence necessary to control the stirring of the reaction medium by adjustment of the variable speed of the stirring motor. The results obtained were generally reproducible to about 5%. The accuracy of results obtained by other workers<sup>80</sup> with such catalysts are also in this range. Zirconium tetrachloride<sup>81</sup> or zirconium trichloride alone i.e. in the absence of alkyl, polymerise styrene through a cationic mechanism. Aluminium triethyl, aluminium diethyl bromide, aluminium isobutyl and tin tetrapropyl do not polymerise styrene. To avoid polymerization by transition metal halides alone, it was desirable to carry out polymerization reactions in the absence of the monomer.

The complex metal catalyst were prepared in toluene by adding aluminium triethyl to zirconium halide. All the results reported thus refer to catalyst prepared in the absence of monomer. The presence or absence of monomer during formation of the catalyst can have a profound effect on the behaviour of the catalyst. In the case of polymerization of butene<sup>82</sup> the combination of lithium butyl

is effective only if the addition is done in the presence of monomer. The combination of lithium butyl and titanium tetrachloride, for the polymerization of ethylene<sup>83</sup> is effective in the presence as well as in the absence of monomer. The rate of polymerization was lower with catalyst prepared in the absence of monomer.

In the catalyst systems containing aluminium triethyl, aluminium diethyl bromide and isobutyl aluminium, there is a possibility of formation of ethyl radicals which may start polymerization by a free radical mechanism. Therefore it becomes necessary to add monomer only after the formation of the catalyst is complete.

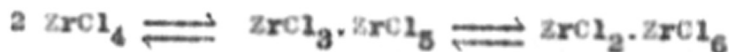
The order of addition of catalyst components is another factor, in the formation of catalyst complex, which has to be kept fixed, because the complexes formed by the addition of organometallic compound to transition metal halide or the complexes formed by adding transition metal halide to organometallic compound may vary in their physical nature. In all the experiments conducted, formation of the catalyst complex was done by the addition of organometallic compound to a dispersion of zirconium tetra or tri-chloride in toluene.

CATALYST SITES

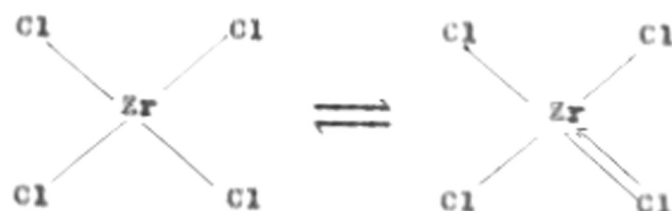
Zirconium tetrachloride is a crystalline solid at room temperature<sup>84</sup>. Its crystal structure has not been completely determined but Zr-Cl distances varying from 2.27 to 2.396 Å have been noted. The corresponding distances in titanium tetrachloride are  $2.18 \pm 0.04$  Å to  $2.21 \pm 0.05$  Å. Like titanium tetrachloride, zirconium tetrachloride is a mono-molecular compound. It does not form complexes with covalent compounds but does so with ionic compounds. Zirconium belongs to the group of elements which show no evidence of forming mono atomic ions in the sense of parting with their valency electrons and establishing ionic bonds. It appears most likely that the crystal of zirconium tetrachloride consists of complex cations and anions formed by the exchange of chloride ions between neighbouring atoms. This can be represented as:



In view of evidence from other sources of the existence of pentachloro zirconate and hexa chloro zirconate anions, it can be said that:

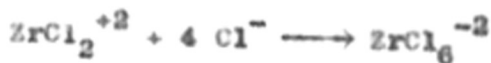


The association of molecules through formation of complex ions occurs appreciably only in the crystalline state. But it is to be presumed that even in the vapour phase, zirconium in the monomolecular tetrachloride increases its coordination number by forming double bonds with some of its chloride atoms. It is already recognised that a certain amount of double bond character is present in the Si-Cl, P-Cl and S-Cl bonds, and that in the chlorine molecule there is the equivalent of about 30% double bond character due to the  $\pi$  bonding. Double bond formation by the zirconium tetrachloride in monomeric state may be written as:



The tendency of the Zr-Cl bond to take on double bond character would tend to favour the disproportionation of the chloride ions in the crystal, the unstable  $(\text{Cl-Zr-Cl})^{+2}$  tending to approach the arrangement  $(\text{Cl} \rightleftharpoons \text{Zr} \rightleftharpoons \text{Cl})^{+2}$ . Some justification for this presumption might well be found in values for Zr-Cl distance in zirconium tetrachloride being slightly less than the calculated values for

the single bond distances. Crystalline zirconium tetrachloride thus has a very complex nature, comprising in effect several different cation and anion species containing doubly as well as singly bonded chlorine atoms. In the presence of chlorine ions from alkali chlorides, the chloride poor species of zirconium tetrachloride should combine with chloride ions.



The overall effect is to form chloro-zirconates. The same unsaturation of the covalency of zirconium in the tetrachloride that gives the compound such a structurally complex nature, leads to the formation of a large number and variety of coordination compounds when the tetrachloride is brought into contact with suitable substances. The coordination number of zirconium tetrachloride in all its coordination compounds is six. This is another point of similarity between zirconium tetrachloride and titanium tetrachloride which also has a coordination number six i.e.  $d^2 sp^3$  configuration.

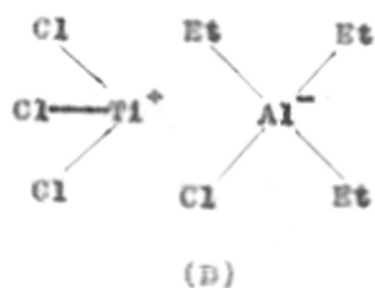
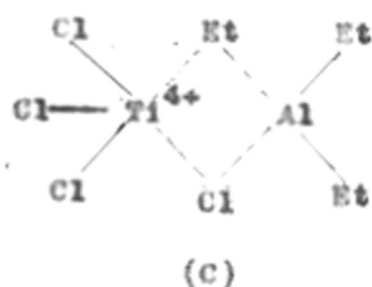
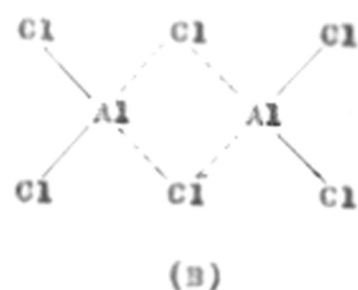
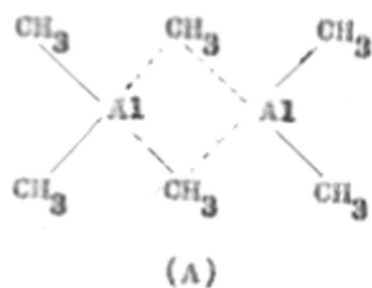
Since the chemistry of titanium tetrachloride and zirconium tetrachloride is essentially similar,



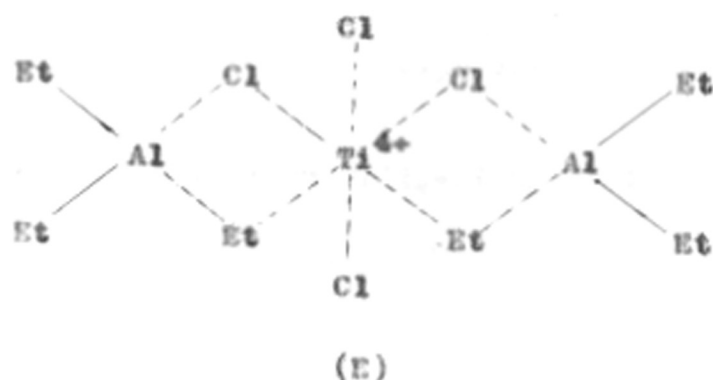
it is probable that the complex formation of zirconium tetrachloride with organometallics may be on similar lines as that of titanium tetrachloride.

On the addition of aluminium triethyl to zirconium tetrachloride, formation of brown black to black complex occurred, the color depending on the amount of aluminium triethyl added. These complexes formed at different atomic ratio of  $Al/Zr$  may differ in the valency state of zirconium in them as suggested by Gilman, H and Jones, R. Most of the work in the last decade has been conducted with the combination of organometallics, and titanium or vanadium halides.

Titanium tetrachloride reacts with aluminium triethyl at a low temperature and a deep red<sup>85</sup> ionic complex soluble in hydrocarbon solvents and containing most of the titanium in the trivalent state is formed. This complex with titanium tetrachloride or complexes from other transition metal halides contain the same type of bonds as are present in the associated molecules of aluminium alkyls<sup>86</sup> (A) or aluminium halides (B). The initial complex can be formulated as (C) or (D) depending on its ionic character.



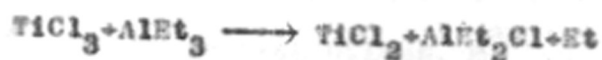
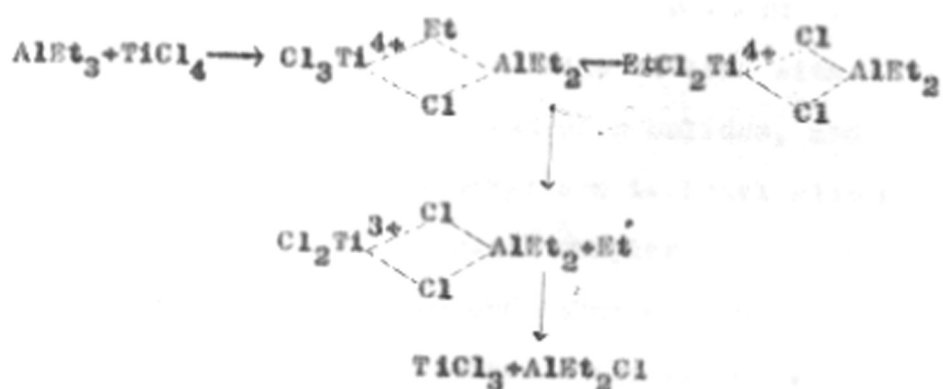
The high entropy of activation for the reaction has led to the suggestion that the initial complex is formed from two molecules of metal alkyl with one of titanium halide<sup>87</sup> (E).



Organo-titanium compounds are intermediates in the reaction since under certain conditions they can be isolated. Titanium-carbon bonds were long thought to be incapable of existence but in recent years a

number of compounds having methyl, phenyl, naphthyl, neopentyl and cyclopentadienyl linked to titanium, have been prepared. The stability of the titanium carbon bond is increased by electron attracting substituents but is also dependent on the nature of the other groups attached to titanium.

The initial product of titanium tetrachloride and aluminium triethyl is presumably an organo-titanium complex which decomposes and gives lower valent compounds as written below:



It shows that titanium can exist in different valency states in the same complex formed by the reaction of  $\text{AlEt}_3$  with  $\text{TiCl}_4$ .

The reduction of vanadium compounds by organo-metallic compound is similar to that observed for titanium. Organo-vanadium intermediates are probably formed although only one vanadium compound which contains a covalently linked organic group (bis cyclopentadienyl vanadium) has been prepared and yet no alkyl vanadium has been isolated. The precipitates of vanadium sub-halides contain substantial amounts of adsorbed aluminium alkyls, and the extent of reduction, particularly as to whether divalent or trivalent vanadium is formed, is not certain<sup>88</sup>.

Zirconium tetrachloride falls in line with titanium tetrachloride and vanadium halides, and reacts with aluminium triethyl and isobutyl aluminium to form a brown black to black complex, which polymerizes ethylene, styrene and other olefinic compounds at room temperature. Like titanium vanadium halides it is reduced to lower valency state.

Twenty years back Gilman, H<sup>89</sup> and coworkers first studied the reaction of transition metal La, Ti and Zr with organometallic compounds like phenyl lithium, n-butyl magnesium bromide and phenyl magnesium bromide.



In the reaction of the halides or alkoxides of

titanium and zirconium with organo lithium compounds or the Grignards reagents, the first stage is the formation of the complex. The stability of this complex is markedly influenced by the temperature and to some extent by the medium which can significantly affect stability and reactivity by the formation of coordination compounds. In the relatively low coordination of petroleum ether, a moderately stable complex of the type  $ZrCl_4 \cdot x C_4H_9Li$  is probably formed from zirconium tetrachloride and n-butyl lithium.

In the second stage of the reaction, which generally takes place with rapidity at room temperature the initial complex is converted to other complexes having the metal in a lower valency state. Typical examples are  $TiX_3 \cdot x RLi$  or  $TiX_2 \cdot x RLi$ . In some cases the reduction appears to descend to the free metal.

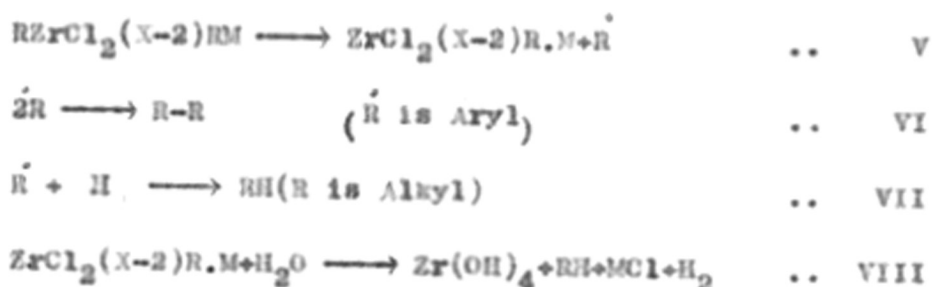
This second stage is accompanied by liberation of alkyl (R) groups. Further reactions of alkyl (R) groups are determined largely by the nature of the group and somewhat by the medium. When the R group is aryl, coupling is the chief reaction and this leads to biaryls. When the RM compound is phenyl lithium or phenyl magnesium bromide the yields of diphenyl range upto 56%. However, when the R group

is alkyl almost pure RH compound is formed in yields upto 70%. These simple alkanes may, probably be formed by the action of the corresponding free radical on the solvent with the second stage of the reaction. It appears that there may be the formation of the double organometallic compounds or a complex of the (R-Ti) or (R-Zr) with the R-Li or R-Mg-X compounds. Such complexes could decompose with the reduction of the metal and the expulsion of the free radical. Related evidence in support of such a mechanism is the work of Hein on the spontaneous decomposition of  $(C_6H_5)_5CrOH$  in the presence of an alkali metal halide or a hydro-halogen acid whereby a phenyl group is liberated as a free phenyl radical.



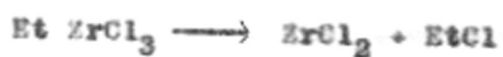
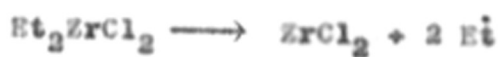
The following series of reactions probably best account for the reactions of zirconium tetrachloride with RLi or RMgX compounds.





This gives an evidence for the formation of complexes with low valency state with organometallic compounds. It shows that the reaction of zirconium tetrachloride and organometallics follows the same path as that of titanium tetrachloride. In the last decade reactions of titanium tetrachloride have been studied exhaustively. The studies on zirconium tetrachloride are limited to the patent literature. But from the above discussion we can assume that the reaction of zirconium tetrachloride with aluminium triethyl produce complexes which contain both the metals in the lower valent state. Reaction kinetics reveal that the formation of complexes with zirconium tetrachloride is in line with those formed by titanium tetrachloride.

The probable reaction scheme will be as follows:





ZIRCONIUM TETRACHLORIDE-ORGANOMETALLICS-STYRENEFORMATION OF CATALYST SPECIES

Zirconium tetrachloride was reacted with aluminium triethyl in two different solvents i.e. toluene and n-hexane, in two different experiments. It was observed that the activity of the catalyst complex was considerably low in n-hexane, as compared to the complex in toluene. The reaction between zirconium tetrachloride and alkyls i.e. aluminium triethyl, aluminium isobutyl, tin tetrapropyl and aluminium diethyl bromide gave violet black, violet black, yellow and blue colored complexes respectively. The color of the complex was taken as a measure to ensure the maintenance of the activity of the complex. The reactions between different alkyls and zirconium tetrachloride are very sluggish. In order to accelerate the reaction, high speed of stirring is used to make an intimate mixing of the reactants. The catalyst systems were aged for comparatively longer time. For obtaining reproducible results of polymerization, conditions were established under which the catalyst complexes are formed invariably

under the same conditions of reaction.

EFFECT OF AGING TIME ON CATALYST SPECIES

Rate of polymerization with zirconium tetrachloride-aluminium triethyl (Fig.2 -Table III) on aging the catalyst from 1 to 18 hours showed that the concentration of the active sites of the catalyst increased linearly upto 2 hours, reached a maximum in 6 hours and remained practically constant even after 18 hours of aging. Molecular weights increased upto 2 hours of aging and decreased beyond it.

Rate of polymerization with zirconium tetrachloride-tin tetrapropyl (Fig.8 - Table VIII) on aging the catalyst from 30 minutes to 3 hours showed a linear increase with increasing aging time upto 1 hour. Between 1 and  $1\frac{1}{2}$  hour of aging, the rates increased fast and beyond  $1\frac{1}{2}$  hour the rates increased smoothly upto 2 hours and then became constant, between 2 to 3 hours aging. This indicated the high activity of the catalyst complex during 1 and  $1\frac{1}{2}$  hour of aging. Molecular weights increased with increasing aging time upto  $1\frac{1}{2}$  hour beyond which the molecular weights decreased.

Rate of polymerization with zirconium tetrachloride-aluminium diethyl bromide (Fig.14 -Table XIII)

on aging the catalyst showed that the activity of the catalyst sites is maintained upto 2 hours only, beyond that the activity falls, may be due to the decomposition of the catalyst sites. Molecular weights increased regularly with increasing time, upto an aging time of 3 hours beyond which it decreased.

Rate of polymerization with zirconium tetrachloride-aluminium isobutyl (Fig.20 - Table XVIII) on aging showed that the activity of the catalyst decreased with increasing aging time, indicating that the activity of the catalyst is maintained for a very short time. Maximum molecular weight was obtained on three hours aging of the catalyst, which is the proper aging time to form proper catalyst sites.

#### EFFECT OF RATIO OF Al/Zr AND Sn/Zr ON CATALYST SPECIES

The intensity of the color of the complex formed on the addition of alkyls to zirconium tetrachloride depends on the amount of alkyl added. It also indicates the presence of different sites<sup>90</sup>. The complexes that are formed at different atomic ratios of Al/Zr or Sn/Zr can have zirconium in different states.

Rate of polymerization with zirconium tetra-

chloride-aluminium triethyl (Table II - Fig.1) on increasing the ratios of  $Al/Zr$  showed a sharp decrease between ratio 0.0 to 2.0 of  $Al/Zr$ . Beyond ratio 2.0 of  $Al/Zr$  the rates of polymerization remained practically constant. It indicated that the completion of the formation of the catalyst complex may be taking place around ratio 2.0 of  $Al/Zr$ . The maximum molecular weight at ratio 1.5 of  $Al/Zr$  also showed that the active catalyst species are formed at ratio 1.5 of  $Al/Zr$  (i.e. around ratio 2.0). Species formed above ratio 2.0 of  $Al/Zr$  are practically of the same type. Molecular weights are affected by the excess of aluminium triethyl, which may act as a chain transfer agent.

Rate of polymerization with zirconium tetrachloride-tin tetrapropyl (Table VII - Fig.7) on increasing ratio from 0.0 to 8.0 of  $Sn/Zr$  showed a slow decrease. Beyond ratio 8.0 of  $Sn/Zr$  it had a sudden fall and reached a low value at ratio 12.0 of  $Sn/Zr$ . Molecular weights were proportional to the reciprocal of the ratio of  $Sn/Zr$  indicating that tin tetrapropyl takes part in the chain transfer reactions from the beginning. Rate of polymerization with zirconium tetrachloride-aluminium diethyl bromide (Fig.13 - Table XII) on increasing the ratio of  $Al/Zr$  decreased slowly. Molecular weight increased

with increasing ratio of  $Al/Zr$  indicating that aluminium diethyl bromide does not act as chain transfer agent.

Rate of polymerization with zirconium tetrachloride-isobutyl aluminium (Table XVII - Fig.19) on increasing the ratio of  $Al/Zr$  showed a linear decrease upto ratio 2.0 of  $Al/Zr$ . Between ratio 2.0 to 3.0 of  $Al/Zr$  the rates had a sharp fall. Beyond ratio 3.0 of  $Al/Zr$  the rates decreased slowly and regularly. It showed that the catalyst had maximum activity between ratio 2.0 to 3.0 of  $Al/Zr$ . Molecular weights increased linearly with increasing ratio of  $Al/Zr$  indicating that aluminium isobutyl does not take part in the chain transfer reaction.

#### EFFECT OF REACTION TIME ON CATALYST SITES

Yield of the polymer with zirconium tetrachloride-aluminium triethyl (Fig.3 - Table IV) on increasing the reaction time increased linearly upto 2 hours. Beyond 2 hours the yields of the polymer formed were practically the same. Molecular weights increased with increasing reaction time upto 1 hour beyond which the molecular weights decreased. It indicated that same type of catalyst species are formed but their concentration falls at higher reaction time. Yield of the polymer with zirconium tetrachloride-

tin tetrapropyl (Fig. 9 -Table IX) on increasing the reaction time, increased, fast, in the initial stages of the reaction. The increase in yield was regular and slow between 5 to 15 minutes reaction time. Molecular weights increased upto 5 minutes and decreased beyond that. Yield of the polymer with zirconium tetrachloride-aluminium diethyl bromide (Table XIV -Fig.15) on increasing the reaction time increased with time. Molecular weights increased with increasing reaction time. It indicated longer life of the catalyst species formed in the reaction. Yield of the polymer with zirconium tetrachloride-aluminium isobutyl (Table XIX -Fig.21) on increasing the reaction time, increased linearly with time. Molecular weights increased linearly upto 30 minutes reaction time. It indicated the formation of active catalyst sites with same concentration.

#### KINETICS OF POLYMERIZATION

The rates of polymerization were studied at various concentrations of zirconium tetrachloride at the same ratio of combination of  $Al/Zr$  at constant monomer concentration. Then the catalyst concentration was maintained constant, at the same ratio,

the rates of polymerization were studied with increasing concentration of the monomer.

The rate of polymerization with (1) zirconium tetrachloride-aluminium triethyl (Fig.4 - Table V), (2) zirconium tetrachloride-aluminium isobutyl (Fig.22 - Tables XX, XXI, XXII) and (3) zirconium tetrachloride-diethyl aluminium bromide (Fig. 16 - Table XV) increased linearly with increasing catalyst concentration upto a certain concentration of the catalyst. Beyond which the rates decreased. But with zirconium tetrachloride-tin tetrapropyl- (Fig.10 - Table X) the rate of polymerization was proportional to the square of the catalyst concentration. There was no fall in the rate of polymerization at higher concentrations of the catalyst.

The decrease in the rate of polymerization at higher concentration of the catalyst may be due to the aggregation<sup>91</sup> of the catalyst whereby enough catalyst sites are not available to the monomer for polymerization. Studies carried out by I.V. Nicolescu and E.M. Angelescu, on the correlation between catalyst activity and electrical conductivity of  $Al(C_2H_5)_3-Ti(OC_4H_9)_4$  catalysts in the synthesis of stereo-regular polyacetylene show that in the catalyst system the complex ions are present in an associated state or aggregates which reduced the rate of

polymerization.

Zirconium tetrachloride is more ionic in nature than titanium tetrachloride. The catalyst complexes formed with zirconium tetrachloride may therefore be more ionic in character than those formed with titanium tetrachloride and it would explain the aggregation observed in the case of system with zirconium tetrachloride which is however absent in catalysts formed with titanium tetrachloride.

#### EFFECT OF MONOMER CONCENTRATION

(a) At constant ratio of  $Al/Zr = 1.5$  in the system zirconium tetrachloride-aluminium triethyl (Fig. 5 - Table VI) the rate of polymerization is proportional to the square of monomer concentration and the order of reaction is two.

$$R_p = K [M]^2 [C]$$

(b) At constant ratio of  $Sn/Zr = 6$ , in the system zirconium tetrachloride-tin tetrapropyl (Fig. 10 - Table XI) the rate of polymerization is proportional to the square of monomer<sup>88</sup> concentration and the order of reaction is two. The second order dependence on catalyst concentration will be explained along with zirconium trichloride-organometallic compound systems



$$R_p = K [C]^2 [M]^2$$

(c) At constant ratio of  $Al/Zr = 8.0$  in the system zirconium tetrachloride-aluminium diethyl bromide (Table XVI - Fig.15) the rate of polymerization is proportional to the square of the monomer concentration

$$R_p = K [C] [M]^2$$

The experimentally observed second order dependence on monomer concentration and first order dependence on the catalyst concentration at  $Al/Zr$  ratio of 2.0, can be explained on similar grounds as for butadiene by N.G. Gaylord, T.K. Kevai and H.F. Mark<sup>92</sup>. The polymerization reaction can be visualised as proceeding by two steps, the first involving the adsorption of the monomer on a catalytic site or the formation of an active monomer-catalyst complex and the second involving the addition of a monomer to the growing polymer chain. When two molecules react on the surface of a catalyst, either one or both of the reacting molecules are bound by chemisorption forces<sup>93</sup>. In the first case which is called as the Rideal mechanism, both molecules hit the surface of the catalyst but only one of them is chemisorbed. The other molecule hits the chemisorbed

molecule and a reaction occurs. The second molecule may also however be adsorbed by Van der Waals forces and react with the chemisorbed reaction partner from a Van der Waals layer. In the second case, known as Langmuir Hinshelwood mechanism, the two reactant molecules get chemisorbed side by side. Such pairs can be formed by localized adsorption at neighbouring active spots or they may result from collisions of the molecules moving along the surface of the catalyst.

According to the Rideal mechanism, it can be postulated that:



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

$$\frac{-dM}{dt} = k_1 [C.M] [M]$$

and

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

Solving these equations

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

Substituting in the rate equation:

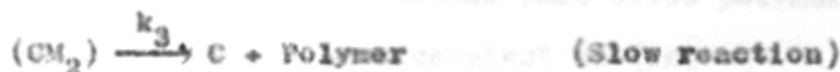
$$\frac{-dM}{dt} = \frac{k_1 K_1 [M]^2 [C]}{1 + K_1 [M]}$$

when  $K_1 [M]$  is small compared with unity, at low monomer concentration, the equation simplifies to:

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

in agreement with experimental rate expression.

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



Assuming that two rapid, equilibrium processes are involving in the formation of the active monomer-catalyst complex and that the formation of the polymer from this complex is the rate determining step, it can be written:

$$\frac{-dM}{dt} = k_3 [CM_2]$$

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

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

Solving these equations, it can be written:

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

and

$$\frac{-dM}{dt} = \frac{k_2 K_2 K_3 [M]^2 [C]}{(1 + K_2 [M])(1 + K_3 [M])}$$

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

$$\frac{-dM}{dt} = k_2 K_2 K_3 [M]^2 [C]$$

In this above scheme assumption has been made that the formation of the polymer removes both monomer units from  $(CM_2)$  and regenerates active catalyst C. If only one monomer unit becomes part of the polymer and the regenerated active catalyst is  $(CM)$



$k_2'$  may differ from  $k_2$

$$\frac{-dM}{dt} = k_2' [CM_2]$$

Whether one or both monomer molecules are involved in the polymer formation cannot be determined but when only one monomer molecule is incorporated into the polymer, thus, above scheme also becomes analogous to the Rideal mechanism.

(d) At constant ratio of  $Al/Zr = 3.5$  and  $3$  in the system zirconium tetrachloride-aluminium isobutyl (Tables XXIII, XXIV - Fig.20) the rate of polymerization is proportional to the monomer concentration and the order of reaction is one

$$R_p = K [M] [C]$$

First order dependence of rate on monomer concentration and concentration of the catalyst can be written as:



where  $C$  is an active catalyst centre,  $M$  is a monomer molecule and  $(CM)$  is the adsorbed monomer catalyst complex. Assuming that the adsorption of monomer by the catalyst centres is a rapid, equilibrium process resulting in the formation of an active monomer-catalyst complex and that the formation of polymer from this complex is the rate determining step, it can be written:

$$\frac{-dM}{dt} = k_4 (CM)$$

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

where  $[C] - [CM]$  is the number of active centres

unoccupied by monomer molecules. Solving these equations:

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

$$\frac{-dM}{dt} = k_4 \frac{K_4 [M] [C]}{1 + K_4 [M]}$$

when  $K_4 [M]$  is small as compared to unity:

$$\frac{-dM}{dt} = k_4 K_4 [M] [C]$$

At high concentration  $K_4 [M]$  is much larger than unity, the rate becomes independent of  $[M]$ .

$$\frac{-dM}{dt} = k_4 [C]$$

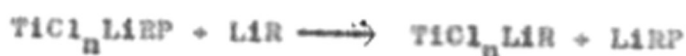
#### MOLECULAR WEIGHTS

With increasing rate of polymerization on increasing the monomer concentration of the catalyst system, zirconium tetrachloride-aluminium triethyl and zirconium tetrachloride-aluminium diethyl bromide, the molecular weights decreased showing chain transfer effect due to monomer. In the case of the catalyst system zirconium tetrachloride-tin tetrapropyl, the rate of polymerization was proportional to the monomer concentration but the molecular weights increased upto concentration 1.743 M/l of the monomer and decreased

beyond it, showing the chain transfer effect due to the monomer beyond the concentration 1.743 M/l. Molecular weights of the system zirconium tetrachloride-aluminium isobutyl increased with increasing concentration of the monomer showing that monomer does not act as a chain transfer agent.

Molecular weight variation with catalyst concentration in the system zirconium tetrachloride-aluminium triethyl showed an increase with increasing concentration of the catalyst. It indicated that catalyst sites are not short lived and soluble complexes, if any, present in the catalyst system do not take part in the chain transfer reaction. With the catalyst systems zirconium tetrachloride-aluminium diethyl bromide, molecular weights increased upto a particular concentration of the catalyst and decreased beyond that concentration. These can be explained on the basis that, in the catalyst system, during the course of reaction, certain soluble species were formed which took part as chain transfer agents. With the catalyst system zirconium tetrachloride-tin tetrapropyl, there was a progressive decrease in molecular weights, with increasing concentration of the catalyst. These can also be explained on similar basis as for zirconium tetrachloride-aluminium isobutyl system. The formation of soluble catalyst

species of the type  $ZrCl_nAlRP$  ( $R = \text{alkyl}$ ,  $P = \text{growing chain}$ ) can be assumed similar to that postulated in the case of propylene polymerization with titanium trichloride and lithium<sup>94</sup> alkyls.



#### ACTIVATION ENERGY

The catalyst systems:

- (1) Zirconium tetrachloride-aluminium triethyl
- (2) Zirconium tetrachloride-tin tetrapropyl
- (3) Zirconium tetrachloride-aluminium diethyl bromide, and
- (4) Zirconium tetrachloride-aluminium isobutyl

gave activation energies 10.90 Kcal/mole, 17.27 Kcal/mole, 1.54 Kcal/mole and 14.74 Kcal/mole respectively.

These activation energies are in the range of activation energies of other Ziegler-Natta type catalysts<sup>95,96</sup> and are much below than those for a free radical polymerization.

#### RATE CONSTANTS

In the case of catalyst systems zirconium tetrachloride-aluminium triethyl and zirconium tetrachloride-tin tetrapropyl, the rate laws

$$R_p = K [C] [M]^2 \quad \text{and} \quad R_p = K [C]^2 [M]^2$$



were observed. Values for the rate constants are given below.

Organometallic compound	(1) $R_p$ vs. $[C]$	$R_p$ vs. $[M]^2$
	(2) $R_p$ vs. $[C]^2$	
	1/M/S	1/M/S
(1) Aluminium-triethyl	$3.172 \times 10^{-3}$	$2.08 \times 10^{-3}$
(2) Tin tetra-propyl	1.40	1.20

With the catalyst systems zirconium tetrachloride-aluminium diethyl bromide and zirconium tetrachloride-aluminium isobutyl, the rate laws

$$R_p \text{ vs. } [C] [M]^2 \quad \text{and} \quad R_p \text{ vs. } [C] [M]$$

were observed. Values for rate constants have been tabulated below:

Organometallic compound	$R_p$ vs. $[C]$	$R_p$ vs. $[M]$
(1) Aluminium-diethyl bromide	$1.44 \times 10^{-1}$	-
(2) Aluminium-isobutyl	$1.75 \times 10^{-3}$	$1.9 \times 10^{-3}$

These rate laws were calculated from the linear plots of rate of polymerization against increasing monomer as well as catalyst concentration because the rates of polymerization with increasing catalyst concentration increased linearly upto certain concentration of the catalyst and beyond that the rates decreased. These rate constants indicated that the activity in the case of catalyst systems obtained with zirconium tetrachloride were considerably high than those obtained with catalysts from titanium tetrachloride or vanadium tetrachloride.

ZIRCONIUM TRICHLORIDE-ORGANOMETALLIC COMPOUNDSFORMATION OF CATALYST SITES

Zirconium trichloride, initially a brown colored crystalline compound, in combination with aluminium triethyl or aluminium isobutyl, produced violet black complexes. This reaction was very sluggish in spite of vigorous stirring and took two hours to complete. The color of the complex formed was unchanged during the course of the polymerization reaction, indicating the invariable activity of the catalyst complex. In order to obtain reproducible results of polymerization, experimental conditions were established under which the catalyst complex once formed may not change apparently.

EFFECT OF AGING TIME

Yield of the polymer with the catalyst system zirconium trichloride-aluminium triethyl (Fig. 26 - Table XXVI) decreased with increasing aging time, showing the formation of short lived catalyst sites. Molecular weights were independent of increasing

aging time. It showed that the same type of catalyst sites were present but their concentration decreased due to decomposition of catalyst on keeping. Yield of the polymer with the system zirconium trichloride-aluminium isobutyl (Fig. 32 - Table XXXI) on aging the catalyst increased upto 2 hours and decreased beyond that. Molecular weights increased constantly with increasing time of aging. It indicated that due to the decomposition of the catalyst beyond 2 hours aging, the yield of the polymer decreased but the catalyst species throughout the course of reaction were essentially the same.

#### EFFECT OF RATIO STUDIES

The intensity of the color of the complex on the addition of the organometallic compound to zirconium trichloride depends on the amount of organometallic compound added. With increasing concentration of aluminium triethyl in the system zirconium trichloride-aluminium triethyl (Fig. 25 - Table XXV), the rates of polymerization decreased upto ratio 0.5 of Al/Zr. Between ratio 0.5 to 2.0 of Al/Zr the rate again increased and attained a maxima at ratio 2.0 of Al/Zr. Beyond ratio 2.0 of Al/Zr the rates decreased and attained a low value. Molecular weights showed the same pattern. Maximum molecular weight

was obtained at ratio 2.0 of Al/Zr. It showed that at this ratio proper complex of Ziegler-Natta type is formed. With increasing ratio of Al/Zr in the catalyst system zirconium trichloride-isobutyl aluminium (Fig. 31 - Table XXX), the rates of polymerization decreased, attained a minima at ratio 1.0 of Al/Zr. Between ratio 1.0 to 2.0 of Al/Zr the rates increased and attained a maxima at ratio 2.0 of Al/Zr and beyond ratio 2.0 of Al/Zr the rates decreased. Molecular weights increased with increasing ratio. It indicated that no constituent of the catalyst system took part as chain transfer agent.

#### EFFECT OF REACTION TIME

The effect of reaction time on the catalyst system zirconium trichloride-aluminium isobutyl (Fig. 33 -Table XXXII) showed that high yields of the polymer were obtained between 1.0 hour and 1½ hour of reaction time. Beyond 1½ hour of reaction time the yields increased slowly. Molecular weights increased with increasing reaction time. It indicated the long life of the catalyst. In the catalyst system zirconium trichloride-aluminium triethyl (Fig.27 -table XXVII) with increasing reaction time from 15 minutes to 30 minutes, the yields of the polymer increased. Between the reaction

time of 30 minutes and 2 hours, the yields were constant. Molecular weight was maximum at 30 minutes reaction time. It showed that proper type of catalyst species were formed at 30 minutes reaction time.

#### CATALYST SITES

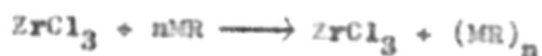
Zirconium trichloride on reaction with aluminium triethyl or aluminium isobutyl forms violet black colored complexes. It shows that part of zirconium trichloride gets converted to zirconium dichloride along with the formation of other complexes. The reactions of zirconium trichloride with organometallics can be written in the following way:



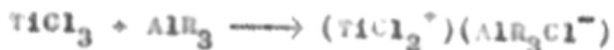
Alkylated zirconium halides may be present in the complex initiating the actual polymerization.

In the case of titanium halides, Ludlum, Anderson and Ashby<sup>97</sup> have indicated that the active catalyst species is an alkylated titanium compound in a lower valency state. It is possible to comprehend that zirconium complexes may be formed in lines with the following proposition suggested for titanium complexes. The alkyl titanium compound resulting from the interaction of a titanium halide and a metal alkyl decomposes by a free radical mechanism to give a lower valent titanium compound such as  $R_2TiCl_2$ , which may be the actual catalytic species. This may also be the case with zirconium trichloride and the resulting catalytic species may be in the form of  $R_2ZrCl_2$ .

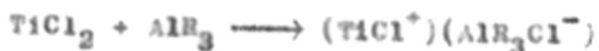
Natta<sup>98</sup> has pointed out that aluminium alkyls cannot be separated from the di and trivalent transition metal halides (Ti) and has suggested that the aluminium trialkyl or dialkyl aluminium chloride is coordinated with transition metal sub-halide. It is reasonable to assume that  $ZrCl_3$  may also behave in a similar manner:



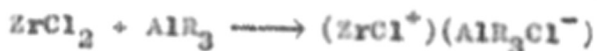
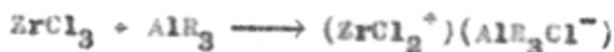
According to Uelzmann<sup>48</sup> the active catalyst is derived from an interaction in which the aluminium trialkyl forms an electron octet by using one chlorine atom of titanium trichloride as an electron donor.



Titanium dichloride would give a  $(\text{TiCl}^+)$  ion



A similar expression can be written for  $\text{ZrCl}_3$



The polymers obtained by using zirconium trichloride are stereospecific, crystalline and possess high molecular weight. The crystallinity is estimated from the insolubility of the polymer in organic solvents. The stereospecificity depends not only on the electro-positive nature and the ionic radius of the metal from metallo-organic compound, used for the preparation of the catalyst but also on the lattice structure of the crystalline substrate made of the transition metal compound. It is quite likely that the configuration as well as the lattice structure of the reduced halides of titanium and zirconium may be identical, which may produce a layer lattice structure for  $\text{ZrCl}_3$  like  $\text{TiCl}_3$ . Because  $\text{TiCl}_3$  has a layer lattice in crystalline form the assumption that zirconium trichloride may have same type of structure can be manifested from the comparison



of polymerization behaviour of the catalyst system with that of titanium trichloride catalyst system.

#### KINETICS OF POLYMERIZATION

Rate studies were carried out with the variation of the catalyst concentration at constant ratio of  $Al/Zr$ . The rate of polymerization is found proportional to the square of the catalyst concentration, upto the catalyst concentration ( $1.515 \times 10^{-2}$  M/l) for aluminium triethyl (Fig. 28 - Table XXVIII) and ( $1.9 \times 10^{-2}$  M/l) for isobutyl aluminium (Fig. 34 - Table XXXIII), beyond which the rate of polymerization decreased and attained a low value.

This behaviour of zirconium trichloride is very much similar to that of zirconium tetrachloride, discussed earlier. The dual behaviour of accelerating and retarding the reaction may be explained on similar grounds as for zirconium tetrachloride, where it has been stated that aggregation of the catalyst sites may be taking place, at higher concentrations of the catalyst, whereby enough catalyst sites are not available to the monomer for polymerization. At the same ratio of  $Al/Zr$  in the catalyst system, zirconium trichloride-aluminium triethyl (Fig. 29 - Table XXIX) and zirconium trichloride-aluminium isobutyl (Fig. 35 - Table XXXIV), the rates of

polymerization are proportional to the square of the <sup>monomer</sup> catalyst concentration. The reaction shows second order dependence on monomer concentration also.

The second order dependence on catalyst concentration<sup>88</sup> does not imply a behaviour different from Ziegler-Natta catalysts but it clearly shows the complexity of the catalyst forming reaction resulting in two types of species with equal concentration, only one of which is active in polymerization.



The second order dependence on monomer concentration can again be explained on similar basis as for zirconium tetrachloride-organometallic systems (pages 104-110) by the application of Rideal or Langmuir-Hinshelwood mechanism. According to Rideal mechanism



$$\frac{-dM}{dt} = k_5 (C_1^*M) [M]$$

$$K_5 = \frac{[C_1^*M] [M]}{\{[C_1^*] - [C_1^*M]\} [M]}$$

Solving these two equations:

$$C_1^* M = \frac{K_5 [C_1]^* [M]}{1 + K_5 [M]}$$

Substituting in the rate equation:

$$\frac{-dM}{dt} = \frac{k_5 K_5 [M]^2 [C_1]^*}{1 + K_5 [M]}$$

when  $K_5 [M]$  is small as compared to unity.

$$\frac{-dM}{dt} = K_5 k_5 [M]^2 [C_1]^*$$

$$\frac{-dM}{dt} = K_5 k_5 [M]^2 [C]^2$$

This equation is in agreement with experimental rate expression.

According to Langmuir-Hinshelwood mechanism:



From these equation:

$$\frac{-dM}{dt} = \frac{k_6 K_6 K_7 [M]^2 [C_1]^*}{1 + K_6 [M]}$$

where  $K_6 [M]$  is small as compared to unity, we get:

$$\frac{-dM}{dt} = k_6 K_6 K_7 [M]^2 [C_1]^*$$

or... 
$$\frac{-dM}{dt} = k_6 K_6 K_7 [M]^2 [C]^2$$

#### RATE CONSTANTS

The rate laws  $R_p$  vs.  $[C]^2 [M]^2$  were observed upto a particular concentration of the catalyst beyond which the rate of polymerization decreased due to aggregation of the catalyst species. Values for the rate constants have been tabulated below.

Organometallic compound	$R_p$ vs. $[C]^2$ 1/M/S	$R_p$ vs. $[M]^2$ 1/M/S
(1) Aluminium-triethyl	$1.99 \times 10^{-2}$	$2.288 \times 10^{-2}$
(2) Aluminium-isobutyl	$4.29 \times 10^{-3}$	$5.200 \times 10^{-3}$

These values for rate constants can be compared with those obtained by G. Burnett<sup>99</sup> at 60°.

Catalyst	$K \times 10^4$ l/M/Min.
$TiCl_4-AlEt_2Cl$	13.7
$TiCl_3-AlEt_2Br$	13.6
$TiCl_3-AlEt_3$	22.7

#### MOLECULAR WEIGHTS

Variation of molecular weights with increasing catalyst concentration with the catalyst system zirconium trichloride-aluminium triethyl showed an increase upto the catalyst concentration  $1.6 \times 10^{-2}$  M/L. Beyond this catalyst concentration the molecular weights decreased, showing that certain soluble complexes are formed in the catalyst system, which act as chain transfer agent, beyond the concentration  $1.6 \times 10^{-2}$  M/L of the catalyst. In the catalyst system zirconium trichloride-aluminium isobutyl, molecular weights decreased with increasing concentration of the catalyst. This also may be due to the chain transfer effect of the soluble catalyst species formed in the reaction system. Molecular weights decreased with increasing concentration of the monomer in both the systems showing the chain transfer effect of the monomer.

ACTIVATION ENERGY

Activation energies calculated from the plots of  $\log R_p$  vs.  $1/T$  in the catalyst systems zirconium trichloride-aluminium triethyl (Fig. 30) and zirconium trichloride-aluminium isobutyl (Fig. 36) were 6.4 Kcal/mole and 10.3 Kcal/mole. These activation energies are in the range of those of other Ziegler-Natta catalysts and are much below to that of a free radical polymerization.

CONCLUSIONS

These systems of catalysts prepared from zirconium tetrachloride and zirconium trichloride differed in their rates of polymerization. The variations in the rates of polymerization when varying the organometallic compound can be substantially due to the variation in the number of stereospecific active centres, which are stated to be the alkylated products of the metal halide<sup>100</sup>. But at the same time alkylation of the transition metal halide on the surface, alone does not explain the variation in the number of active centres, with the change of the organometallic compounds in the catalyst systems.

On the basis of their experimental findings G. Natta<sup>101</sup> and coworkers have stated that all the catalytic systems containing the same transition metal halide have stereospecific centres which are kinetically equivalent. On the contrary the kinetic constants of the stereospecific centres are quite different in the catalytic systems containing different transition metal halides. According to G. Natta, the kinetic determining stage in the chain propagation is the complexing of the  $\chi$ -olefin on the transition metal and not an addition of  $\chi$ -olefin on the transition metal-carbon bond as postulated by Cossee.

Nothing conclusive can be said regarding the validity of the mechanism of polymerization, but it has been agreed by most of the workers that the mechanism of polymerization need not strictly be the same in different catalytic systems. Results of some of the catalytic systems are better explained on bimetallic complex formation and in some other cases monometallic complex formation holds good.

During the course of studies carried out on the activity of different catalytic systems containing titanium trichloride<sup>100</sup>, it was observed that little depends on the concentration of the organometallic compound. But our findings show that the concentration of the organometallic compound plays an important role in deciding the activity of the catalytic complex. It cannot be said whether bimetallic or monometallic complex formation is taking place in these catalyst systems studied but it cannot be disagreed that organometallic compound is not merely to alkylate the transition metal halide but is an important constituent even after the alkylation has taken place. May be the active centres contain the organometallic compound in addition to the alkyl radical.

The complexes formed by zirconium tetra or trichloride have higher activity as indicated by the rate constants, than those formed with titanium



tetrachloride or vanadium tetrachloride. This may be one of the reasons why the molecular weights of the products obtained with zirconium tetrachloride or zirconium trichloride are low. Higher molecular weights in the case of zirconium trichloride as compared to tetrachloride can be explained on the basis that lower valent transition metal halides crystallize with a layer<sup>102,103</sup> lattice ( $\alpha\text{TiCl}_3$ ,  $\text{TiCl}_2$ ,  $\text{VCl}_3$ ), which brings out stereospecificity.

The activation energy of the catalyst system studied lies in the range of those of coordinate ionic catalysts. Rate studies are also in good agreement with Ziegler-Natta catalyst systems. The second order dependence on monomer concentration has been explained on the basis that the reaction proceeds through two steps. The first involving the adsorption of the monomer on a catalytic site or the formation of an active monomer-catalyst complex and the second involving the addition of a monomer to the growing polymer chain. The second order dependence on catalyst concentration may be due to the formation of two catalytic species of equal concentrations, out of which only one is taking part in the polymerization reaction. In short zirconium tetrachloride and zirconium trichloride in combination with different alkyls polymerise styrene and polymerization proceeds through coordinate anionic mechanism.

CHAPTER-V.

S U M M A R Y

S U M M A R Y

The discovery of stereospecific polymerization by K. Ziegler in 1953 and intensive researches later on by G. Natta and coworkers have minimized the gap between manmade and natural polymeric products. The novelty of these catalysts lies in their ability to polymerise at room temperature and atmospheric pressure even those monomers which are difficult to polymerise ordinarily. New polymers like polypropylene, synthetic natural rubber and other vinyl polymers have been prepared by this new class of Ziegler-Natta catalysts. These catalysts are comprised of the complexes formed by the interaction of transition metal halides from group IV to VI and organometallic compounds from group I to III of the periodic table.

Zirconium tetrachloride was the first transition metal halide to be used by Ziegler in combination with aluminium triethyl for the polymerization of ethylene, but later studies were mainly concentrated on titanium halides. The relatively unstable nature of zirconium tetrachloride and trichloride may be one of the reasons for their restricted use.

Following catalyst systems with zirconium tetrachloride and zirconium trichloride in combination with

different alkyls have been studied in toluene, for the polymerization of styrene at 40°.

- (1) Zirconium tetrachloride-aluminium triethyl
- (2) Zirconium tetrachloride-aluminium diethyl bromide
- (3) Zirconium tetrachloride-tin tetra propyl
- (4) Zirconium tetrachloride-aluminium isobutyl
- (5) Zirconium trichloride-aluminium triethyl
- (6) Zirconium trichloride-aluminium isobutyl

Studies concerning the overall behaviour of these catalytic systems in the polymerization of styrene at 40° are based on the following aspects.

- (1) Aging time of the catalyst after mixing of the catalyst constituents and its effect on the rate of polymerization
- (2) Activity of the catalytic complex with reaction time
- (3) Ratio of combination of catalyst constituents and nature of the catalyst complex formed at different ratios
- (4) Rate law for the variation of the rate of

polymerization with monomer concentration and catalyst concentration

- (5) Dependence of the molecular weight on the ratio of combination of the catalyst and the organo-metallic compound, catalyst and monomer concentrations, to study the mode of termination reaction
- (6) Activation energy of the catalytic systems to ascertain the mechanism of polymerization.

Same batches of zirconium tetrachloride and zirconium trichloride were used for all polymerization runs because the activity of these transition metal halide decreases on keeping. But the decrease in activity does not change the overall relationship between the variables if same batches of transition metal halide are used. Uniform particle size, stirring of the reaction medium and order of addition of the catalyst constituents were other factors which were controlled to ensure identical conditions while studying the reaction kinetics.

On the addition of aluminium triethyl, aluminium diethyl bromide, tin tetrapropyl and aluminium isobutyl to a dispersion of zirconium tetrachloride in toluene gave violet black, blue, yellow and violet black complexes respectively. The color of the complex

formed on addition of alkyls to transition metal halide was taken as a measure to ensure the maintenance of the activity of the complex. The intensity of color of the complex formed depended on the ratio of Al/Zr or Sn/Zr. With increasing ratio of organometallic compound to transition metal halide, the rates of polymerization decreased. In the systems zirconium tetrachloride-aluminium triethyl and zirconium tetrachloride-aluminium diethyl bromide, the alkyls also act as chain transfer agents. But in the other two systems viz zirconium tetrachloride-aluminium isobutyl and zirconium tetrachloride-tin tetrapropyl, chain transfer effect due to the organometallic compounds was absent. Rest of the kinetic studies were carried out at ratios where maximum molecular weights and workable yields were obtained.

Studies on the effect of reaction time on rate of polymerization showed a linear behaviour upto a certain time of reaction beyond which the increase was regular but slow.

The effect of aging time of the catalyst on the rate of polymerization showed that the proper type of catalyst sites are formed only after an aging time of two to three hours. On keeping the catalyst for a longer time the catalyst activity decreased.

With the catalyst systems zirconium tetrachloride-aluminium triethyl, zirconium tetrachloride-tin tetrapropyl and zirconium tetrachloride-aluminium diethyl bromide, there was a second order dependence on the concentration of the monomer. The polymerization reaction was supposed to proceed in two steps, the first involving the adsorption of the monomer on the catalyst site or the formation of an active monomer-catalyst complex and the second involving the addition of a monomer to the growing polymer chain.

Variation with catalyst concentration for these systems showed a first order dependence in the case of zirconium tetrachloride-aluminium triethyl, zirconium tetrachloride-aluminium diethyl bromide and a second order dependence in case of zirconium tetrachloride-tin tetrapropyl:

$$R_p = K [C] [M]^2$$

$$R_p = K [C]^2 [M]^2$$

The catalyst system zirconium tetrachloride-aluminium isobutyl showed a first order dependence with respect to monomer as well as catalyst.

$$R_p = K' [C] [M]$$

It was observed that at very high catalyst concentrations, the rate of polymerization decreased and reached low values. The fall in the rate of polymerization has been explained on the basis that beyond a certain catalyst concentration, aggregation of the catalyst sites takes place and active sites are not available to the monomer for polymerization.

Activation energies of all the four systems calculated by plotting  $\log (R_p)$  vs.  $1/T$  lies in the range of activation energies of Ziegler-Natta catalysts.

The results of studies on the effect of ratio of  $Al/Zr$ , time of reaction, aging time and monomer concentration for the system zirconium trichloride and organometallics are similar to that of zirconium tetrachloride. But the effect of increasing catalyst concentration on the rate of polymerization for both the systems i.e. zirconium trichloride-aluminium triethyl and zirconium trichloride-isobutyl aluminium, exhibit a typical behaviour. These two catalyst systems exhibited a second order dependence on monomer concentration as well as on catalyst concentration. The second order dependence can be explained on the similar basis as for the systems zirconium tetrachloride-aluminium triethyl



and zirconium tetrachloride-tin tetrapropyl. The second order dependence on catalyst concentration has been explained on the basis that two types of catalyst sites of equal concentrations are formed out of which only one is reactive in polymerization. The activation energies of these two systems as well lies in the range of Ziegler-Natta catalysts.

These systems of catalysts studied exhibit a behaviour similar to that of other Ziegler-Natta catalysts and these catalysts polymerize styrene with a coordinate anionic mechanism.

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