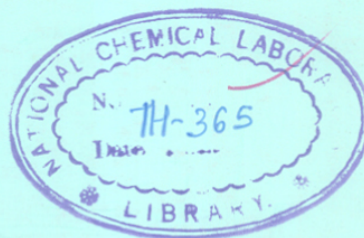


**KINETICS OF COORDINATION POLYMERIZATION
OF STYRENE WITH BUTOXY TITANIUM TRICHLORIDE
AND ALUMINIUM ALKYL**

COMPUTERISED

A THESIS SUBMITTED TO THE
UNIVERSITY OF POONA
FOR THE DEGREE OF
DOCTOR OF PHILOSOPHY IN CHEMISTRY



BY
JAGDISH CHANDRA SEHRA
M. Sc.

678.746.22 (043)
SEH

DEC.1982

DIVISION OF POLYMER CHEMISTRY
NATIONAL CHEMICAL LABORATORY
POONA-411 008.

COMPUTERISED

C E R T I F I C A T E

Certified that the work incorporated in the Thesis 'KINETICS OF COORDINATION POLYMERIZATION OF STYRENE WITH BUTOXY TITANIUM TRICHLORIDE AND ALUMINIUM ALKYLs' by Shri J. C. Sehra was carried out by the candidate under my supervision. Such material, as has been obtained from other sources, has been duly acknowledged in the Thesis.



(Dr.S. Gundiah)
SUPERVISOR.

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

The author records his deep sense of gratitude to Dr. S.Gundiah, Scientist, National Chemical Laboratory, Pune, for his inspiring guidance and keen interest at every phase of this investigation.

It is a pleasure to thank Dr. S.L. Kapur, Ex-Head: Division of Polymer Chemistry, NCL, for the encouragement. The ever-willing help of Dr. R.A. Kulkarni and Mr. A.A. Gunari is gratefully acknowledged.

Thanks are also due to Dr. V.Damodaran and Dr.C. Gopinathan of NCL for the analytical assistance. The valuable help from Glass Blowing Section of NCL, is appreciated.

The author is grateful to the Director, National Chemical Laboratory, Pune-411 008, for providing necessary facilities to carry out this investigation and permitting to submit this work in the form of a Dissertation.

—oo000oo—

C O N T E N T S

CHAPTER I :	<u>INTRODUCTION</u>	...	...	
***	a. <u>GENERAL INTRODUCTION</u>	...	...	1
***	b. <u>MECHANISM OF POLYMERIZATION</u>		...	6
**	b. 1. Cossee's Mechanism	...	...	9
**	b. 2. Homogeneous Polymerization		...	12
**	b. 3. Supported Catalysts	...	...	14
***	c. <u>KINETICS OF COORDINATION POLYMERIZATION</u>			14
**	c.1. Relevant Reactions	...	...	15
**	c.1(i) Catalyst Forming Reaction		...	15
**	c.1(ii) Initiation and Propagation		...	16
**	c.1(iii) Termination	...	...	17
**	c.2. Active Centre Concentration		...	19
**	c.3. Rate Laws	...	...	20
**	c.4. Electron Donors	...	...	24
**	c.5. Deactivation	...	...	26
***	d. <u>PRESENT INVESTIGATION</u>	...	...	28
CHAPTER II	<u>EXPERIMENTAL</u>			
***	a. <u>CHEMICALS</u>	...	...	31
**	a.1. Styrene Monomer	...	...	31
**	a.2. n-Butoxy Titanium Trichloride		...	32
**	a.3. Aluminium Alkyls	...	...	33
**	a.4. n-Heptane	...	...	35
**	a.5. Other Chemicals	...	...	35
***	b. <u>APPARATUS</u>	...	...	37
**	b.1. Vacuum Dilatometer	...	...	37
**	b.2. High Vacuum Line	...	...	38
**	b.3. Dry Box	...	...	38
**	b.4. Constant Temperature Baths.		...	39
**	b.5. Viscometer	...	...	39

***	c.	<u>EXPERIMENTAL METHODS</u>	...	...	39
**	c.1.	Nitrogen Purification	...	...	39
**	c.2.	Polymerization Procedure...	...	...	41
**	c.2 (i)	Purification of n-Heptane	...	...	41
**	c.2 (ii)	Purification of Styrene.	...	...	42
**	c.2 (iii)	Triethylamine	...	...	42
**	c.2 (iv)	Dilution of the Catalyst	...	...	43
**	c.2 (v)	Dilution of the Cocatalyst	...	...	43
**	c.2 (vi)	Catalyst Aging	...	...	44
**	c.2 (vii)	Order of Mixing	...	...	44
**	c.2 (viii)	Polymerization	...	...	45
**	c.2 (ix)	Polymer Isolation	...	...	46
**	c.2 (x)	Molecular Weights	...	...	47
**	c.3.	Analysis	...	...	47
**	c.3 (i)	Aluminium Triethyl	...	...	47
**	c.3 (ii)	Butoxy Titanium Trichloride	...	...	49
**	c.3 (iii)	Oxidation State of Titanium	...	...	51
<u>CHAPTER III</u>		<u>RESULTS AND DISCUSSION</u>	...	...	
***	a.	<u>KINETICS OF POLYMERIZATION OF STYRENE BY BuOTiCl₃-AlR₃</u>	...	...	54
**	a.1.	Treatment of Data	...	...	55
**	a.1 (i)	Dilatometer Equation...	...	...	55
**	a.1 (ii)	Rates of Polymerization	...	...	59
**	a.1 (iii)	Course of Polymerization	...	...	59
**	a.2.	Effect of Aging	...	...	60
**	a.3.	Effect of Aluminium Alkyl Concentration	...	...	63
**	a.4.	Effect of Catalyst Concentration	...	...	71
**	a.5.	Variation of Rate with Monomer Concentration	...	...	72
**	a.6.	Rate Laws	...	...	75
**	a.7.	Effect of Electron Donor...	...	...	79
**	a.8.	Chemical Nature of Active Centre	...	...	84

***	b.	<u>KINETICS OF STYRENE POLYMERIZATION USING BuOTiCl₃-AlEt₂Cl</u>	...	...	88
**	b.1.	Effect of Kinetic Parameters	...		94
**	b.1 (i)	Aging	...	...	94
**	b.1 (ii)	Aluminium Alky1 Concentration	...		96
**	b.1 (iii)	Catalyst Concentration..	...		98
**	b.1 (iv)	Monomer Concentration...	...		100
**	b.1 (v)	Temperature	...	...	102
**	b.2.	Kinetics of Deactivation...	...	...	103
**	b.3.	Deactivation due to Catalyst Poisoning	...	...	107
<u>CHAPTER IV :</u>		BIBLIOGRAPHY	...	...	110

... ... S y n o p s i s

CHAPTER I

INTRODUCTION

I.a. General Introduction

Vinyl polymerizations are repetitive addition reactions brought about by free radical, ionic or coordinated ionic mechanisms¹. Free radical may be generated by thermal or photochemical initiated reactions² and ionic polymerizations may be anionic or cationic^{3,4}. Free radical polymerizations, the earliest discovered and still the widely practised industrial method, have been investigated in great detail. The basic features and mechanism of free radical polymerizations are very well understood. However, in recent years, the coordinated type of polymerization, more commonly also known as the Ziegler-Natta polymerizations, have had the largest scientific and technological impact.

Ziegler, in the early 50's, discovered^{5,6} that higher aluminium alkyls can be prepared by the reaction of ethylene with aluminium triethyl at temperatures above 100°C, and pressures of 100 atmospheres. In the presence of colloidal nickel, instead of expected 'Aufbau' reaction, quantitative yields of 1-butene was obtained^{7,8} by the displacement reaction. Systematic investigations led^{9,10} to the discovery that ethylene could be polymerized to high molecular weight polymer at ambient conditions using transition metal compounds, particularly titanium and vanadium halides, in combination with aluminium alkyls.

Natta investigated¹¹, in greater detail, the polymerization

of α -olefins using catalyst systems consisting of titanium halides and aluminium alkyls. Propylene was polymerized¹² to high melting crystalline polypropylene using α - TiCl_3 - AlEt_3 catalyst system. The polymer had a regular head-to-tail structure with pendant methyl groups on the same side of the polymer chain and was designated as isotactic polypropylene¹². Syndiotactic polypropylene, which has alternate pendant methyl groups on the opposite sides of the polymer chain, was obtained^{13,14} by using VCl_4 - AlEt_2Cl catalyst at -78°C . Isotactic polymers of styrene¹⁵, 4 methyl pentene-1¹⁶ etc. were also prepared by the proper choice of catalysts.

Ziegler-Natta catalysts generally consist¹⁷ of transition metal halides of Group IV-VIII of the periodic table (catalysts) in combination with base metal alkyls from Group I-III (cocatalysts). Though a variety of catalyst-cocatalyst combinations are theoretically possible, the choice of the catalyst and cocatalyst has an inherent specificity for every monomer¹⁷. Heterogeneous catalyst systems generally result in isotactic polymers¹⁷.

Apart from isotactic and syndiotactic polymers of α -olefins, butadiene and isoprene have been polymerized with high selectivity to cis, trans and vinyl polydienes¹⁸, and polybutadienes have been obtained with a steric purity of about 98%. In the polymerization of racemic α -olefins, Pino and coworkers reported¹⁹ that optically active polymers were obtained by the use of optically active aluminium alkyls as the cocatalyst. However,

use of optically inactive aluminium alkyls resulted in a racemic mixture and the constituent optically active polymers could be separated by chromatography.

Ziegler-Natta catalysts are formed by the interactions of two components - a transition metal halide and a base metal alkyl. The cocatalysts alkylate and reduce the transition metal halide. The nature and the extent of the reaction is dependant on the ratio of catalyst to cocatalyst and the time of the reaction²⁰. Moreover, a minute fraction (<1%) of the catalyst concentration employed²² is active for polymerization, making it extremely difficult for the chemical identification of the active species. Aluminium alkyls, the more generally employed cocatalysts, also react vigorously²¹ with oxygen, moisture etc. which may be inadvertently introduced as impurities in the system. It is therefore not surprising that over the years, a large number of mechanisms have been proposed^{23,24} for the propagation reaction in Ziegler-Natta polymerizations.

The mechanism enjoying a wide acceptance envisages an alkylated transition metal halide as the active species²⁵. The alkylated transition metal halide has a hexa-coordinated configuration with a vacancy for the coordination of the incoming monomer. The monomer is coordinated at the vacant site and subsequently inserted into the metal-carbon bond (transition metal-alkyl bond). The crystal lattice in heterogeneous catalysts provides the driving force for the stereospecific addition and the necessary stabilization for the alkylated

4

transition metal species. In the homogeneous catalyst, the stabilization for the alkylated transition metal species, is envisaged²⁶ due to its complexation with the base metal alkyl.

The active centre concentration in conventional Ziegler-Natta catalysts is very low. From the point of view of technological implications, methods of increasing the activity of the catalyst is the subject of intensive study in recent years. The most significant advance in this direction is the development of supported catalysts^{27,28}. The transition metal component along with aluminium alkyls are deposited on inert carriers like MgO, MgOH etc. In contrast to less than 1% of the transition metal element being active in typical Ziegler-Natta catalysts, 30-50% of theoretically possible activity has been claimed²⁹ with the supported catalysts.

Most significant and comprehensive kinetic studies of co-ordination polymerizations have been carried out²² by Natta and his colleagues using propylene as the monomer. With α -TiCl₃ and AlEt₃, it was observed that the rate of polymerization attained a steady state rate after an initial settling period. With propylene pressure higher than 1 atmosphere, the steady state rate followed a first-order rate law with respect to monomer and TiCl₃. The rate was zero order with respect to AlEt₃, when Al/Ti > 1. At lower aluminium alkyl concentrations, the rate increased with increasing aluminium alkyl concentrations.

The kinetics of polymerization of styrene is quite ambiguous³⁰ probably due to the electron releasing and electron

attracting characteristics of the aromatic ring. Both coordinated anionic³¹ and cationic³² type of initiations have been proposed. Burnett and Tait reported³³ that the polymerization of styrene in n-heptane with $\alpha\text{-TiCl}_3\text{-AlEt}_2\text{Cl}$ resulted in rapidly decreasing rates followed by a slow decrease upto 400 min. However, use of $\alpha\text{-TiCl}_3\text{-AlEt}_3$ resulted in steady state polymerization after 200 min. Using $\text{TiCl}_4\text{-AlEt}_3$, Kern reported³⁴ that the rate of polymerization of styrene in benzene, decreased exponentially with time. Burnett and Tait reported³³ first-order dependence of the steady state rate with respect to styrene above a monomer concentration of 3.60 moles litre⁻¹. At lower concentrations, the rate was second-order. Otto and Parravano reported³⁵ three-half order of reaction rate with respect to monomer for the steady state polymerization of styrene in benzene using $\alpha\text{-TiCl}_3\text{-AlEt}_3$ catalyst system.

Generally variable rates of polymerization with time are observed³⁶ with tetravalent titanium halides in combination with aluminium alkyls. Minsker et al reported^{37,38} steady state polymerization of ethylene, after an initial decline in rate lasting for about 30 min. when one of the halide ligands in TiCl_4 is replaced by an alkoxy group. The alkoxy group was presumed to function as a microcarrier. Kinetic studies on polymerizations using alkoxy titanium trichlorides have not been reported with other monomers.

Polymerization of styrene in n-heptane using butoxy titanium trichloride and aluminium alkyls have been investigated

in this study, using a vacuum dilatometer. Two trialkyls, viz. aluminium triethyl and aluminium triisobutyl were used as cocatalysts. Steady state polymerization, after a short period of declining rates, was observed. Kinetic parameters including the effect of electron donors, have been investigated. The declining rates during the short settling period could not be probed in detail. When diethyl aluminium chloride was used as the cocatalyst, the rates of polymerization continuously decreased with time and the kinetics of deactivation has been studied in some detail for this system.

I.b. Mechanism of Polymerization

The mechanism of free radical initiated polymerization is well understood³⁹. The basic reactions involved are: (1) the decomposition of initiator, generally a peroxide, hydroperoxide or an azo compound, either thermally or photochemically yielding free radical species (2) the monomer adds on to the free radical repeatedly during the propagation step, and (3) the deactivation of the propagating species occurs either by recombination or disproportionation of macroradicals or by chain transfer processes.

The homogeneous ionic polymerizations proceed either by cationic or anionic mechanisms². The propagating species in anionic polymerizations is a carbanion³ and cationic polymerizations, which generally need a cocatalyst as well, are brought about by carbonium ions⁴. The propagating species can be a

free ion or ion-pair depending upon the polarity of the medium. Anionic polymerizations are termination free³ (living polymer) in the total absence of impurities such as water, carbon dioxide etc. In cationic polymerizations terminations occur through transfer and/or isomerization reactions⁴.

Mechanism of coordination polymerization, in contrast, is very complex and is still not very well defined. Active Ziegler-Natta catalysts are formed by the interaction of transition metal halides (catalyst) with base metal alkyls, generally alkyls and hydrides of aluminium (cocatalyst). The reaction of catalyst and cocatalyst results in the alkylation and reduction of transition metal compound⁴⁰. The extent of reaction depends on the ratio of reactants and time of the reaction²⁰. The simultaneous presence of several reaction products makes it extremely difficult to chemically identify the active species effecting polymerizations. Moreover, the earliest discovered catalytic systems (and technologically still the most important) are heterogeneous in nature. The concentration of active species responsible for polymerization depends on the surface area and differs significantly as compared to its bulk concentration. Several mechanisms for Ziegler-Natta polymerizations have been proposed in literature. They are adequately covered in several reviews^{23,26,41-43}.

Most of the mechanisms proposed for heterogeneous catalysts are with reference to $\alpha\text{-TiCl}_3$ as the catalyst and AlR_3 as the cocatalyst. However, the proposed mechanisms may be generalised

in terms of the transition metal compounds and base metal alkyls. In recent times, most of the workers favour the Cossee's mechanism^{25,44} in which the active centre is an alkylated transition metal sub-halide. For the sake of completeness, a few of the significant earlier proposed mechanisms are briefly presented here.

Early attempts to explain the mechanism assumed aluminium as the centre at which the growth reaction took place. The 'Aufbau' reaction involving aluminium alkyls led Natta to propose⁴⁵ a bimetallic complex formed by the transition metal halide and aluminium alkyl as the active centre. Adsorption of monomer at the transition metal and growth at the aluminium centre was proposed. In view of the accumulating evidence that the growth reaction took place at the transition metal centre, Natta's bimetallic mechanism was modified⁴⁶. The transition metal of the bimetallic complex was proposed as the centre for the growth reaction.

The experimental findings that the free radicals are detected in the reaction between titanium halides and aluminium alkyls led to the mechanistic proposal based on free radical propagation. Friedlander envisaged⁴⁷ monomer adsorption on the surface of TiCl_3 and propagation by surface-bound free radical, generated by the fission of chemisorbed aluminium alkyl on TiCl_3 . Topichiev envisaged⁴⁸ the generation of free radicals by the decomposition of the alkylated transition metal compound which remained bound to the surface and propagated the

polymerization by reacting with the adsorbed monomer. Uelzmann proposed⁴⁹ an ion-pair complex as the active species, the monomer being activated on the titanium cation and migrating to the aluminium anion for the propagation reaction.

I.b.1

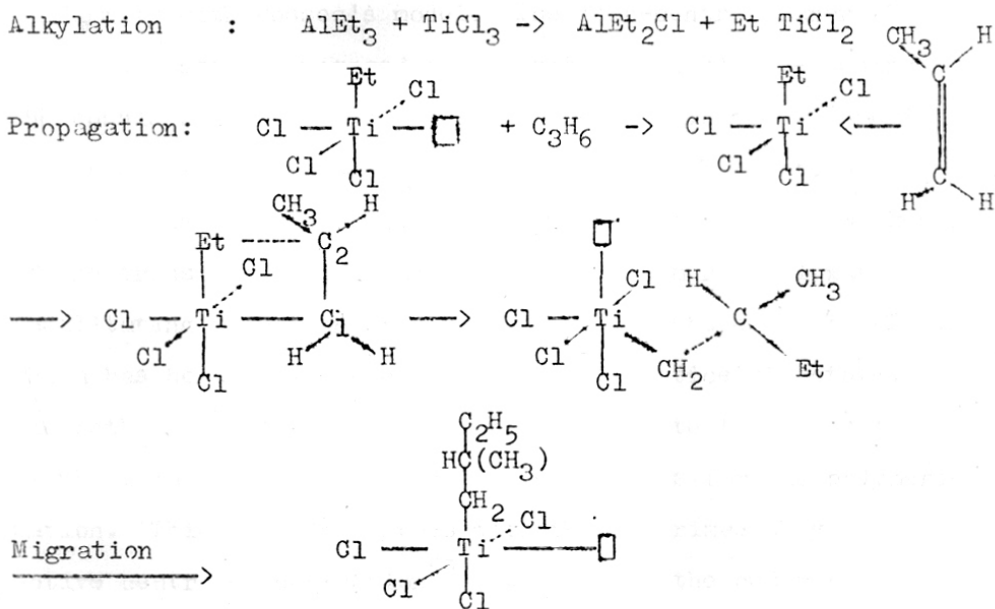
Cossee's Mechanism

With overwhelming evidence in favour of titanium as the active centre for the propagation reaction in Ziegler-Natta catalysts derived from titanium compounds and that the activation of the titanium-chloride is invariably effected by aluminium alkyls, the alkylated titanium chloride as the chemical entity effecting polymerization gained momentum⁵⁰. The earliest mechanistic proposal in this connection is that of Ludlum, who proposed⁵¹ a divalent alkylated transition metal compound as the active centre. Carrick foresaw⁵² the coordination of the ethylene at the transition metal centre, similar to the π -complexation of olefins on platinous compounds. These have been elegantly systematized in the mechanism proposed by Cossee⁵³. In addition, Cossee's mechanism offers a logical explanation for the occurrence of stereospecific propagation in Ziegler-Natta polymerizations.

Cossee proposed^{25,53} an alkylated transition metal sub-halide formed by the interaction of the transition metal halide and the base metal alkyl as the active centre. Cossee's mechanism assigns only alkylating function to aluminium alkyls instead of becoming an integral part of the active centre.

The transition metal is pentacoordinated with alkyl and chloride ligands. A vacancy exists in the octahedral symmetry of the active centre. The vacant sites are located at the edges, corners, lateral faces, defects etc. on the crystalline lattice of titanium halide. Cossee visualised π -complexation of the monomer perpendicular to the free valency of the transition metal ion. The monomer coordination permits the π -electrons to be used in σ bond formation. There is possibility of the overlap of d_{xy} orbitals with the antibonding π orbitals of the olefin. Olefin complexation also brings about weakening of the transition metal-carbon bond, thereby facilitating migration of the alkyl group through a planar four-centre transition state.

The reaction sequence envisaged for propylene polymerization is given below:



Scheme- 1.

The four chloride, ethyl and the vacancy surrounding the titanium are not equivalent. The Cossee's active centre thus has an asymmetric ligand environment. The asymmetry of the active centre favours only one mode of addition of the monomer. With the monomer insertion, the alkyl and the free vacancy would have changed places. Migration of the alkyl ligands and the free vacancy to their original positions would enable same asymmetric environment and thus isotactic addition⁵⁴. In the absence of migration, syndiotactic addition would result.

The presence of vinylidene end group in the polymers of α -olefins and the order of reactivity of different α -olefins are in favour of carbenionic nature of the propagating species²². Electron microscopic studies by Rodrigues revealed⁵⁵ chain growth on edges, lateral faces etc. of the α -TiCl₃ crystal, in conformity with Cossee's model. The four-centre planar transition state envisaged is characteristic of cis-opening of the double bond, which has been confirmed⁵⁶ in the polymerization of cis and trans-1 deuteriopropylene. Theoretical calculations by Armstrong and coworkers confirm⁵⁷ the weakening of the transition metal-carbon bond on monomer complexation facilitating migration of alkyl group. In the case of α -TiCl₃, which has hexagonal close packing layer lattice structure, theoretical calculations⁵⁸ by Arlman indicate that less than 1% of the titanium present forms active centres for the polymerization. This estimate agrees with the experimentally found active centre concentration⁵⁹ (at least in the order of

magnitude).

Several investigators have attempted refinement of Cossee's mechanism. Invariable presence of atactic polymer during isotactic polymerization and the decrease of the atactic fraction in the presence of an electron donor have led to the suggestion that more than one type of active centres⁶⁰ exist. Rodrigues postulated⁶¹ two vacancies (instead of one proposed in the Cossee's mechanism) for the active centre. One of the vacant site is used for the complexation of the aluminium alkyl and the steric interaction of the substituent of the olefin with the aluminium alkyl, provides the necessary impetus for the isotactic addition. Chirkov proposed⁶² two vacancies in the basal plane, the one being blocked by the polymer chain, the other being utilized for the coordination of the olefin. Transition metal carbenes, which are responsible for olefin metathesis⁶³, were also envisaged as active centres by Green and coworkers⁶⁴.

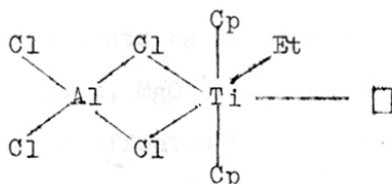
I.b. 2

Homogeneous Polymerization

Heterogeneous catalyst systems are complicated owing to the involvement of surface controlled reactions. Homogeneous catalyst systems, more easily amenable to physico-chemical methods of analysis, were therefore actively pursued with a view to better understand the mechanism. At low temperatures $\text{VCl}_4\text{-AlEt}_2\text{Cl}$ forms a homogeneous catalyst⁶⁵. Natta discovered⁶⁶ that cyclopentadienyl titanium halides in conjunction with aluminium alkyls form soluble catalysts at ambient temperatures.

Soluble catalysts based on cyclopentadienyl titanium compounds have been investigated in detail by Olive-Olive⁶⁷, Fink⁶⁸ and others^{69,70}.

According to Olive and Olive⁶⁷, the bimetallic bridged complex shown below is the active centre in the catalyst system $\text{Cp}_2\text{TiCl}_2\text{-AlEtCl}_2$



The bimetallic active complex has titanium in quadrivalent state. It has octahedral symmetry and a vacancy for the coordination of the monomer. Reduction of titanium to Ti^{+3} was shown, by magnetic susceptibility and E.S.R measurements, to bring about deactivation of the active centres. Monomer coordination at the vacant site and its incorporation into the Ti-C bond was visualised as in the Cossee's mechanism.

Armstrong et al⁵⁷, on the basis of theoretical calculations, assigned a bipyramidal structure for the bimetallic complex which on monomer coordination changes over to octahedral symmetry.

Alkylated transition metal halides are unstable and only CH_3TiCl_3 has been isolated in the pure form^{40,60}. It has been suggested that the presence of β -hydrogen in alkylated titanium halides brings about their instability and the existence of crystalline lattice results in the required stability for the alkylated transition metal halide in heterogeneous catalysts.

Similar stability is envisaged by complexation with the aluminium alkyls in case of homogeneous catalysts²⁶.

I.b.3 Supported Catalysts

Typical Ziegler-Natta catalysts are of low activity. Less than 1% of the titanium forms active centres for polymerization. High activity has been obtained²⁷⁻²⁹ by supporting the typical Ziegler-Natta catalysts on inert carriers of high surface area like alumina, silica, MgO etc. Isotactic polymerization of propylene has been affected by the use of $\text{TiCl}_4\text{-AlEt}_3$ -electron donor deposited on magnesium dichloride. It is suggested²⁷ that isotactic polymerization in this case is possible because of similarity of the crystalline structure of MgCl_2 with TiCl_3 . The following structure has been proposed for the active centre in the case of supported catalysts^{26,27}.



Monomer coordination at the vacant site and insertion at the M-C bond as discussed earlier, are envisaged.

I.c. Kinetics of Coordination Polymerization

Ziegler-Natta polymerization is a catalytic reaction⁷¹ initiated by an alkylated transition metal species. The monomer is coordinated at the transition metal centre and inserted into the metal-carbon bond. Kinetic studies do not discriminate whether the propagating centre is a transition metal or a base

metal entity. The simultaneous presence of atactic and isotactic fractions in α -olefin polymers prepared using several of these catalysts indicates that more than one type of active centres are present in the system²⁶. The kinetic rate constants determined therefore refer to the overall rates of reaction.

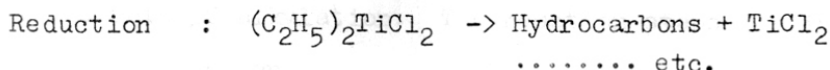
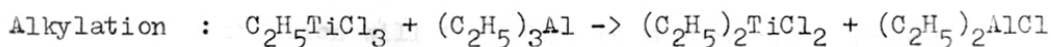
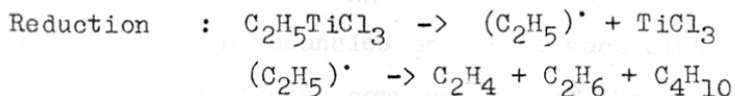
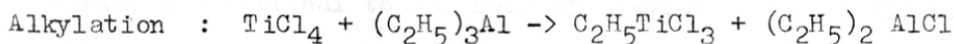
I.c 1 Relevant Reactions

The chemical nature of the active species in coordination polymerization is still not very well understood and explained to the total satisfaction. Dyachkovskii et al⁷² have shown that in the soluble catalyst, consisting of Cp_2TiCl_2 and AlEt_2Cl , the active species is very likely a charged species. However, the overwhelming evidence is in favour of an alkylated transition metal halide as the chemical species mainly responsible for coordination polymerization. The alkylation reaction of the transition metal halide with the base metal alkyls like aluminium alkyls and the reduction of the alkylated transition metal halide are well documented. A simplified picture of the chemical reactions involved in the polymerization of α -olefins by the use of coordination catalysts, mainly based on Cossee's mechanism, is given below.

I.c. 1 (i) Catalyst Forming Reaction

The initiating species are formed in situ by the interaction of transition metal halides and base metal alkyls⁴¹. Initially, an unstable alkylated transition metal halide is formed which decomposes to low valent transition metal halide and hydrocarbons.

The extent of alkylation and reduction depends on the ratio of the two components. One or more of the alkylated transition metal species formed initiate the polymerization. Typical reactions involved may be illustrated⁴⁰ taking TiCl_4 and aluminium triethyl, as an example.



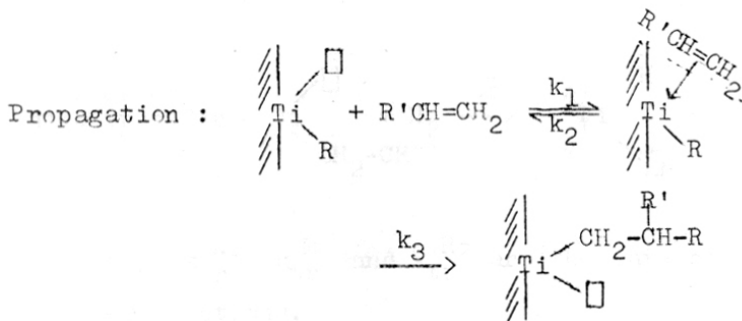
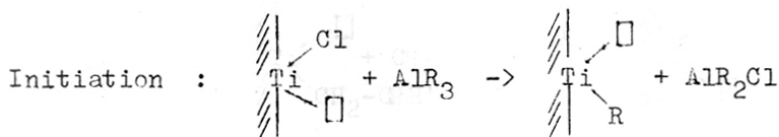
The alkylated species R TiCl_3 and/or R TiCl_2 initiate polymerizations.

Similar reaction sequences may be envisaged for other combinations of transition metal halides and base metal alkyls. In the case of crystalline TiCl_3 , the alkylated transition metal halide is believed to remain bonded to the surface and initiate the polymerization.

I.c. 1 (ii) Initiation and Propagation

Both the initiation and propagation reactions involve the coordination of the monomer at the vacant site followed by its insertion into the transition metal-carbon bond. The formation of alkylated species and the insertion of first monomeric unit may be treated as the initiation step⁷³ and subsequent monomer

insertions as propagation. In polymerization kinetics, propagation rate constants are deemed independent of the degree of polymerization. Hence there is no basic difference between the initiation and propagation reaction as far as the first insertion of the monomer is concerned and the rate of initiation is primarily proportional to the rate of alkylation⁷⁴. However, the formation of propagating species are dependant on the existence of coordination vacancies and these vacancies are located at the edges, lateral faces, corners etc. of the crystalline lattice. The rate of initiation will therefore be a very minor fraction of the rate of alkylation. The reaction steps for initiation and propagation are:

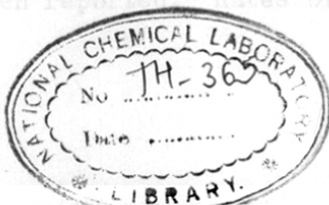


where k_1 , k_2 and k_3 are rate constants for adsorption, desorption and insertion of the monomer respectively.

I.c.1(iii)

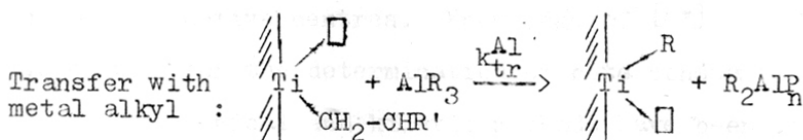
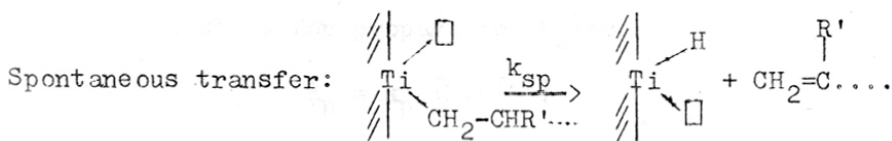
Termination

The deactivation of the growing chain occurs mostly by

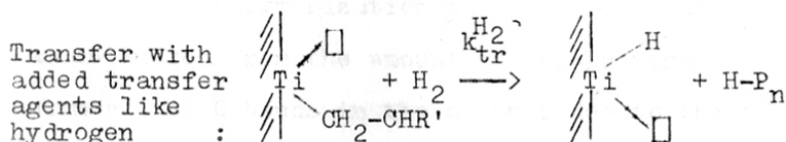
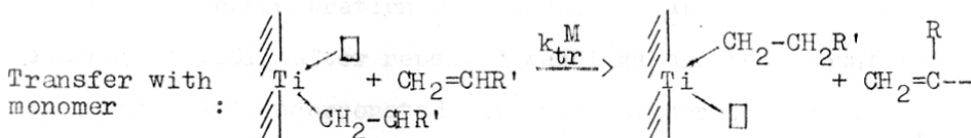


678-746.22(04)
SEH

transfer reactions. Transfer to base metal alkyl predominates and transfer to transition metal complex is rare. Termination otherwise is infrequent^{71,75}.



P_n is the polymeric chain



where k_{sp} , k_{tr}^{Al} , k_{tr}^{M} and $k_{tr}^{\text{H}_2}$ are the rate constants for the transfer reactions.

Several kinetic studies on the coordination polymerization of α -olefins using various catalyst systems under divergent experimental conditions have been reported in the literature^{40,42,71,75}. Generally, overall rates of polymerization and transfer rate constants have been reported. Rates of initiation and

termination have been reported in isolated cases⁷⁴.

I.c. 2

Active Centre Concentration

The overall rate of polymerization, R_p , is related⁷⁶ to the rate constant for propagation(k_p) by:

$$R_p = k_p [M] [C^*]$$

[M] is the monomer concentration and [C*] represents the concentration of active centres. Knowledge of [C*] is of primary importance for the determination of rate constants.

Radiochemical and kinetic methods have been employed for the determination of the concentration of active centres. Natta utilized the concentration of radioactive aluminium alkyl retained on $TiCl_3$ after repeated washings and the amount of aluminium alkyl incorporated into the polymer to deduce the concentration of the active centres. Feldmen and Parry⁷⁷ quenched the polymerization with tritiated alcohol and the [C*] was estimated from the amount of tritium incorporated into the polymer. Al-C bonds in the polymer due to the transfer reaction with aluminium alkyl are also liable to be included in the metal-carbon bond concentration estimated by this method. The initial concentration of the metal-polymer bond extrapolated to zero conversion or time was used for the estimation of [C*].

Yermakov and coworkers used $C^{14}O$ and $C^{14}O_2$ as propagation inhibitors and from the radioactivity of the resulting polymer, [C*] was evaluated. However, $C^{14}O$ is liable to be incorporated as a comonomer into the polymer. Later, Yermakov and coworkers⁷⁸

used PH_3 along with C^{14}O to prevent the copolymerization. Non-radioactive inhibitors have also been used for the determination of $[\text{C}^*]$. The prominent among these inhibitors is allene⁷⁹ which adsorbs on the active centre. From the consumption of allene, active centre concentration can be estimated.

In the kinetic method, the molecular weight of the resultant polymer and the values of the individual transfer constants are utilized for the determination of active centre concentration^{71,80}. The number of molecules formed at any given instant is the sum of the number of molecules formed from all the termination steps. The inverse of number-average molecular weight at different times is plotted against the time of polymerization. The intercept accounts for the number of molecules formed from the different transfer reactions and the slope gives $1/k_p [\text{M}]$. Thus the rate constant for propagation can be deduced and hence $[\text{C}^*]$ from the overall rate of polymerization.

The active centre concentrations determined by different methods lie in the range of 0.1 to 1.0 mole percent of the bulk concentration of the transition metal element in the catalyst⁷⁶. This estimate is in good agreement with that predicted by Cossee-Arlman theory⁴⁴. The average life-time of the growing chain estimated from $[\text{C}^*]$ range from few minutes to several hours⁸¹, as compared to short life-time of free radical initiated chains.

I.c. 8

Rate Laws

Generalised rate laws governing the polymerization employing

coordination catalysts have not been accomplished due to inherent complexities. In the very early stages of polymerization, a settling period is generally observed during which the rate either increases or decreases depending upon the physical status of the catalyst⁸². Subsequently, a declining rate throughout the remaining period of polymerization have been observed in very many cases⁴⁰. Higher valent transition metal halide⁸³ like TiCl_4 , VCl_4 , VOCl_3 etc. along with aluminium alkyls and several of the homogeneous catalysts⁶⁷ are typical examples of this case. The declining rate with time has been dealt in a subsequent section of this introductory chapter.

Catalysts derived from crystalline TiCl_3 or VCl_3 , however, yield a region of steady state polymerization lasting over a sizeable period after an initial settling period⁷¹. The rate declines again after the steady state. The kinetic rate laws reported are generally valid for the steady state polymerization.

The dependence of the rate of polymerization, R_p , on different reaction variables which affect the rate, have been studied for different monomers^{40,60} with many catalyst systems. The concentration of the monomer and the transition metal compound greatly affect R_p as expected. In agreement with the earliest findings of Natta²² (in propylene polymerization with $\alpha\text{-TiCl}_3\text{-AlEt}_3$), the concentration of the base metal alkyl does not greatly influence R_p . However, at very low concentrations, R_p increases with increasing alkyl concentration and beyond a certain low concentration (usually base metal alkyl : transition

metal compound = 1:1), the rate of polymerization is zero order with reference to base metal alkyl. It has been reported⁸⁴ by some investigators that R_p depends on the concentration of base metal alkyl at very high alkyl concentrations.

The dependence of R_p on the concentration of the transition metal compound for steady state polymerization, usually follows a first order rate law^{60,71}.

The dependence of R_p on monomer concentration is not that straightforward. In several cases, a first-order rate law with reference to monomer during the steady state polymerization have been observed^{60,71}. However, at low monomer concentrations (for example below one atmosphere of propylene²² pressure and 3.6 mole litre⁻¹ of styrene³³), a second-order rate law has been reported. Dyachkowski has reported⁸⁵ a zero-order rate law in ethylene polymerization at very low temperatures.

In view of the above, for the steady state polymerizations and at base metal alkyl and monomer concentrations not too low, the following rate law appears to be valid.

$$R_p = A [M] [M_T] [\text{base metal alkyl}]^0 e^{-\Delta E/RT}$$

where $[M_T]$ is the concentration of transition metal compound.

Kineticists have used adsorption equilibrium in order to account for the observed rate laws. As first pointed out by Mark and coworkers^{86,87}, the heterogeneous nature of a wide variety of Ziegler-Natta catalysts implies that adsorption plays a major role. Rideal and Langmuir-Hinshelwood isotherms have

been employed to explain the observed rate laws^{40,88,89}. In the Rideal mechanism, an adsorption equilibrium exists between the aluminium alkyl and the heterogeneous surface and the monomer is incorporated into the metal-carbon bond directly from the solution⁴⁰. In the Langmuir-Hinshelwood mechanism⁴⁰, adsorption equilibria exist for both monomer and aluminium alkyl and the adsorbed monomer is incorporated into the metal-carbon bond. The rate of polymerization, R_p , in the case of Langmuir-Hinshelwood mechanism, taking into consideration the competitive adsorption of the two for the same sites, is given by:

$$R_p = \frac{k_p K_M K_A [M] [A] [C^*]}{(1 + K_A [A] + K_M [M])^2}$$

where K_A and K_M are the equilibrium constants for the adsorption of the alkyl and the monomer respectively and $[C^*]$ is the concentration of catalyst sites.

In the case of direct insertion of monomer into the metal-carbon bond viz. in Rideal isotherm^{case}, the rate of polymerization is given by

$$R_p = k_p [M] [C^*] \frac{K_A [A]}{1 + K_A [A]}$$

Langmuir-Hinshelwood mechanism accounts for the experimentally observed first order dependence⁹⁰ with respect to monomer. A maximum in rate, as the concentration of base metal alkyl is increased, is also predicted⁸⁹. Rideal mechanism predicts⁹¹ an initial increase of R_p with increase in the concentration of

base metal alkyl, R_p becomes independent at higher concentrations. Assuming that the propagation takes place with the catalyst species incorporating the first monomeric unit, a second-order dependence with respect to monomer can be deduced on the basis of Rideal mechanism⁹⁰. Zero-order dependence with respect to monomer can be visualized with very high equilibrium constant for the adsorption of monomer.

Several generalised reaction schemes have been published in the literature to account for the kinetics of coordination polymerization. All the schemes treat the alkylated transition metal entity as the active species. The monomer and alkyl are reversibly adsorbed onto the active centre and the monomer insertion, transfer etc. occur only with the adsorbed reactants. In Tait's⁹² scheme insertion is the rate controlling step, whereas in Yermakov's scheme⁹³, adsorption is the rate determining step. Tait's scheme has been used for explaining the kinetics of polymerization of 4 methylpentene-1 with $VOCl_3-AlR_3$ and Yermakov's scheme has been employed to account for the kinetics of ethylene and propylene polymerization using $TiCl_3-AlEt_3$. Bohm has recently proposed⁹⁴ a reaction scheme which is claimed to include both homogeneous and heterogeneous coordination polymerizations.

I.c.4

Electron Donors

Electron donors greatly influence the coordination polymerization of α -olefins⁶⁰. Stereospecific polymerization is also

possible by the use of transition metal halides along with electron donors in place of aluminium alkyls⁶⁰. These alkyl-free catalyst systems have provided convincing evidence⁶⁰ in favour of the growth at transition metal entity. The use of electron donors along with transition metal compounds and base metal alkyls bring about an increase in the isotactic fraction apart from a decrease or an increase in the rate of polymerization⁶⁰. The increase in the isotactic fraction has been attributed to preferential complexation of electron donor on the more exposed sites of the heterogeneous catalyst surface.

The variation in the rates of polymerization with the incorporation of electron donor in the typical Ziegler-Natta catalysts, however, is more complex. At very small ratios of electron donor-base metal alkyl, there is generally a decrease in the rates of polymerization. At higher ratios (but still less than 1) the rates increase^{60,95} and in several cases even higher than the rates in the absence of electron donor.

Electron donors are capable of complexation with both the catalyst and the cocatalyst components. The initial decrease in rate may be ascribed to the complexation of the electron donor at the active centre⁹⁵ resulting in their reduced effective concentration. The increased rates may be explained⁹¹ in terms of competitive complexation of the aluminium alkyl with the electron donor and the transition metal halide. Depletion of the complexed aluminium alkyl from the transition metal halide surface provides additional sites for polymerization. Recently

Simon suggested⁹⁶ variation in the polarity of the active centre with varying number of electron donor molecules complexed as the reason for the variation in the rates of polymerization.

I.c. 5

Deactivation

It has been pointed out earlier that Ziegler-Natta catalyst systems derived from higher valent transition metal compounds such as TiCl_4 , VCl_4 , VOCl_3 etc. yield continuously varying rates of polymerization. Even in the case of low valent transition metal halides which may yield steady state, a declining rate is observed at later stages of polymerization. An initial settling period of varying rates is common to all the Ziegler-Natta polymerizations.

The deactivation, especially at later stages of polymerization, can be due to physical restrictions such as diffusion controlled reactions and/or chemical deactivation of sites. Diffusion controlled polymerizations can be visualised in heterogeneous polymerizations, especially at higher conversions. In homogeneous polymerizations, and in polymerizations carried out to low conversions, diffusion may not play a major role.

In the context of the bimetallic complex proposed for the active centre in the coordination polymerization, Köhn proposed⁹⁷ that the presence of an alkyl ligand in the bridged complex is necessary for the polymerization activity. He proposed that the formation of two chlorine bridged complex results in deactivation. Keii investigated⁹⁸, in detail, the

settling period (during the initial stages) in the polymerization of propylene with ground α - TiCl_3 and AlEt_3 . He proposed the migration of chloride ligands from the adjacent layer to the surface defect as the cause of deactivation. Caunt ascribed⁸⁰ the rate decay, in the propylene polymerization using TiCl_3 - AlEt_2Cl , to the site poisoning by AlEtCl_2 formed. He demonstrated the declining rates with addition of AlEtCl_2 to the system and restoration of the rate by complexation of AlEtCl_2 formed with KET , NaCl etc.

There is no agreement amongst the different investigators about the rate law of deactivation. First-order decay of catalyst sites have been reported in propylene polymerization using TiCl_3 - AlEt_3 , TiCl_3 - AlEt_2Cl by Keii⁹⁸, Kohn⁹⁷ and Bier⁹⁹ respectively. Begley, however, concluded¹⁰⁰ a second-order decay of sites for polymerization of propylene with TiCl_3 - AlEt_2Cl . Karasev also observed¹⁰¹ second-order deactivation in the copolymerization of ethylene-propylene with colloiddally dispersed catalyst derived from VOCl_3 . Friedlander, on the basis of analysis of several heterogeneous catalyst systems, concluded that kinetics is more in agreement with mixed-order mode of deactivation¹⁰². For homogeneous catalyst systems, a second-order deactivation is observed due to the reduction of the catalytically active higher valent transition metal to its lower valent state⁶⁷.

The first-order decay of catalytic sites is easily understood. The second-order decay would involve site

migration which is permissible in homogeneous systems only. Therefore, second order deactivation in heterogeneous catalyst systems is difficult to visualise.

I.d.

Present Investigation

Kinetics of coordination polymerization of several α -olefins have been reported in the literature. Polymerization studies have been carried out under diverse experimental conditions using several catalyst-cocatalyst combinations. As described in earlier sections, tetravalent transition metal compounds like $TiCl_4$, VCl_4 etc. when employed in combination with aluminium alkyls yield⁸³ continuously varying rates of polymerization with time. Even in the case of soluble catalysts like Cp_2TiCl_2 -Aluminium alkyls, where the transition metal component is in the tetravalent state, continuous variation of rates of polymerization with time have been observed⁶⁷. Alkoxy titanium halides, with the transition metal in the tetravalent state, however, have been reported³⁸ to yield steady state polymerization of ethylene (after an initial short duration of settling period) when used in conjunction with aluminium trialkyls. In contrast, Nowakowska et al¹⁰³ reported continuously declining rates of polymerization of ethylene when alkoxy titanium halides were used with ethyl aluminium sesquichloride. Polymerization kinetics with alkoxy titanium halides and aluminium alkyls have not been reported for other monomers.

Kinetics of polymerization of styrene using butoxy titanium

trichloride and aluminium alkyls are studied in this investigation. The butoxy titanium trichloride was prepared from titanium tetrachloride and n-butyl alcohol. Two trialkyls, aluminium triisobutyl and aluminium triethyl were used as representative trialkyl cocatalysts and aluminium triethyl used was synthesized. In view that varying rates have been reported in the polymerization of ethylene by the use of ethyl aluminium sesquichloride (along with alkoxy titanium halide as catalyst), diethyl aluminium chloride was also used as the cocatalyst.

The kinetics of polymerization have been studied using a vacuum dilatometer so as to facilitate easy monitoring of the rates of polymerization with time. The rates were deduced from the volume contraction as monitored by the changes in the heights of the meniscus by the use of dilatometer equation. In several cases, the end conversions were cross checked by gravimetry and the values determined by both the methods are in satisfactory agreement with each other.

Steady state polymerization of styrene was observed when aluminium trialkyls were employed along with butoxy titanium trichloride. The rate laws and activation energies have been determined for the steady state polymerization. In agreement with the findings of Nowakowska et al¹⁰³ in the polymerization of ethylene, diethyl aluminium chloride as cocatalyst yielded continuously decreasing rates of polymerization. The results have been analyzed in terms of first and second-order deactivation of catalyst sites.

The oxidation states of titanium at various Al:Ti ratios have been determined. In analogy with the widely accepted nature of the active species in heterogeneous coordination polymerizations, a possible mechanism of polymerization with these colloiddally dispersed catalysts has been proposed.

CHAPTER II

EXPERIMENTAL

II.a. Chemicals

Purification, preparation (if any) etc. of the chemicals used in this study are detailed in this section. Monomer, solvents, catalyst etc. for the polymerization were further purified on a high vacuum manifold which will be described under a subsequent section.

II.a.1. Styrene Monomer

Styrene was freed of the inhibitor by washing with aqueous alkali, dried over fused calcium chloride and calcium hydride. It was fractionally distilled under reduced pressure and the middle fraction was collected.

Polymerization grade styrene (98% pure) obtained from M/s. Polychem Ltd., Bombay, was used. About 250 ml was taken in a 500 ml separating funnel. One-fifth its volume of sodium hydroxide solution (5%) was added. The contents were thoroughly mixed by shaking. The lower alkaline layer was withdrawn and the styrene was washed with a fresh aliquot of alkali. The alkali wash was repeated 3-4 times till the alkaline layer remained colourless. The monomer was subsequently washed with distilled water repeatedly and dried over fused calcium chloride for 12-15 hrs. It was further dried over calcium hydride for 8-10 hrs. and fractionally distilled under reduced pressure. Middle cut fraction boiling at 40-42°C (at 20 mm Hg pressure) was collected and stored in a stoppered round bottom flask at 5°C in a refrigerator. supply was discontinued.

II.a.2. n-Butoxy Titanium Trichloride

Butoxy titanium trichloride (BuOTiCl_3) was prepared according to the method reported in the literature^{104,105}. Equi-molar quantities of titanium tetrachloride and n-butyl alcohol were reacted at 0°C under a blanket of carbon dioxide gas. BuOTiCl_3 formed was recovered by fractional distillation at reduced pressure in nitrogen atmosphere.

TiCl_4 ($\sim 99\%$) obtained from the Process & Development Division, NCL, was refluxed over copper turnings (about 0.5 weight percent) for 3 hrs. and fractionally distilled at ambient pressures. Middle fraction boiling at $132-133^\circ\text{C}$ was collected and stored in a flask. The flask was stoppered with self sealing screw rubber cap.

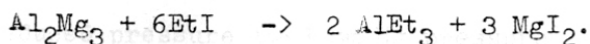
Purified n-butyl alcohol (26 g) was taken in a 500 ml three necked round bottom flask. The flask was fitted with a dropping funnel (having a side arm for pressure equalisation), a gas inlet and outlet tubes. It was placed in an enamel basin and surrounded with crushed ice. Carbon dioxide gas was inlet to the flask. The outlet tube was connected to a long rubber tube (with one end outside the laboratory window) for venting the acid vapours formed. Freshly distilled TiCl_4 (75 g) was taken in the dropping funnel. TiCl_4 was added after the contents of the flask have reached 0°C . Successive aliquots (2-3 ml) were added after the cessation of fumes. After the complete addition of TiCl_4 , carbon dioxide supply was discontinued. The flask was degassed (30 mm Hg pressure) for 20 min. to completely remove

the HCl formed. Carbon dioxide was again admitted and the dropping funnel removed from the flask. Cyclohexane (10 ml) was added through a syringe to dissolve the unreacted TiCl_4 . The bottom cyclohexane layer was withdrawn with the syringe. The flask was removed from the ice bath and placed on a heating mantle. A condenser with a short fractionating column was attached to the flask. Carbon dioxide was cut off and the contents of the flask were blanketed by nitrogen. BuOTiCl_3 formed was fractionally distilled at $127-129^\circ\text{C}$ at reduced pressure (40-42 mm Hg pressure). Middle cut fraction was collected in a flask. Flask was removed under a positive pressure of nitrogen, transferred to the high vacuum line and diluted by distilling n-heptane. The diluted catalyst solution was removed under a positive pressure of nitrogen and stoppered with self sealing screw rubber cap. It was stored till use at 5°C in a refrigerator.

II.a.3.

Aluminium Alkyls

Aluminium Triethyl: AlEt_3 was prepared¹⁰⁶ by the reaction of ethyl iodide with aluminium magnesium alloy.



AlEt_3 formed was dispersed in liquid paraffin and recovered by fractional distillation under reduced pressure.

Aluminium-magnesium alloy (Al_2Mg_3) was obtained from the National Metallurgical Laboratory, Jamshedpur. The alloy was powdered using a brass pestle and mortar. Powdered alloy (32.5 g) was transferred to a four necked round bottom flask.

The flask was fitted with a motor driven glass stirrer, a reflux condenser, a pressure equalising graduated dropping funnel and a gas inlet tube. Oxygen-free dry nitrogen was inlet to the flask and the flask was heated. Purified ethyliodide: (155 ml) was taken in the dropping funnel. When the contents of the flask reached $70-80^{\circ}\text{C}$, about 5 ml ethyliodide was added to catalyze the reaction. Remaining portion of ethyliodide was added in 10 ml aliquots taking care that the drippings from the condenser ceased before each subsequent addition. The heating of the flask was continued for one more hr. after complete addition of ethyliodide and the flask was cooled to 30°C under a blanket of nitrogen. The reflux condenser was disconnected from the flask and simultaneously 20 ml of dry liquid paraffin was added and the flask was stoppered. The cake formed was dispersed in liquid paraffin. The stirrer was disconnected under a fast stream of nitrogen. A condenser with a short fractionating column was attached to the flask. The disconnected stirrer rod dipped and the condenser was washed with liquid paraffin as soon as they were removed from the flask. Aluminium triethyl formed was fractionally distilled at 80°C at reduced pressure (~ 3 mm Hg pressure). Middle fraction was collected. The receiver was removed under a positive pressure of nitrogen, stoppered with a self sealing rubber cap and stored in a dry box.

Triisobutyl aluminium (min purity 93%) was obtained from M/s. Scherring A.G., West Germany. The requisite quantity of the alkyl was transferred into a 100 ml round bottom flask under total nitrogen blanketing. It was distilled under

reduced pressure (2 mm Hg pressure) and the middle fraction boiling at 50°C was collected in a flask, stoppered with a self-sealing rubber cap and stored in a dry box.

Diethyl aluminium chloride (also from M/s. Scherring A.G., West Germany, min. purity 90%), was transferred under a positive pressure of nitrogen and distilled under reduced pressure. The fraction boiling at 89°C (3 mm Hg pressure) was collected, stoppered with self sealing rubber cap and stored in a dry box.

II.a.4. n-Heptane

n-Heptane was freed of the olefinic impurities by treating it with conc. sulphuric acid, washed, dried and distilled.

To about 500 ml of CP grade n-heptane taken in a one litre separating funnel, 50 ml conc. H_2SO_4 was added and thoroughly mixed by shaking. The acid layer was withdrawn, a fresh aliquot of H_2SO_4 added and mixed. The washings were repeated 3-4 times till the acid layer was pale yellow. n-Heptane was subsequently washed with aqueous sodium carbonate solution (10%) and repeatedly washed with distilled water. It was dried over fused calcium chloride for 18-20 hrs. The dried heptane was refluxed over freshly cut sodium for 10 hrs. and fractionally distilled. The middle fraction boiling at 95°C (ambient pressures) was collected and stored.

II.a.5. Other Chemicals

Triethylamine (CP grade) was refluxed first over sodium hydroxide pellets for 3 hrs. and later over calcium hydride for

6 hrs. It was distilled over calcium hydride and the fraction boiling at $85-86^{\circ}\text{C}$ (ambient pressures) was collected and stored over Linde Molecular Sieves ($4 \text{ \AA}$).

Butyl alcohol (CP grade) was distilled over calcium hydride. The fraction boiling at 115°C (ambient pressures) was collected and stored over Linde Molecular Sieves ($4 \text{ \AA}$).

Ethyl iodide (CP grade) was dried for 6 hrs over P_2O_5 and distilled over calcium hydride. The middle fraction boiling at $66-68^{\circ}\text{C}$ (ambient pressures) was collected and used in the preparation of triethyl aluminium.

Ethyl alcohol (commercial absolute alcohol, 99%) was refluxed over magnesium turnings and iodine. The middle cut fraction boiling at 76°C was collected.

Sulphuric acid, nitric acid, hydrochloric acid, sodium hydroxide, ammonium acetate, zinc sulphate, ethylene diamine tetraacetate (disodium salt), dithiozone, ferric chloride (sublimed), ceric ammonium sulfate, barium diphenylamine sulphonate, silver nitrate, potassium thiocyanide etc. used for analysis were AR grade chemicals.

Phosphorous pentoxide, silica gel, drierite, calcium hydride, sodium metal, sodium hydroxide pellets and potassium hydroxide pellets used as drying agents were CP grade chemicals.

Anthraquinone sulphonic acid (sodium salt), lead acetate, copper chloride, kieselguhr, liquid paraffin etc. used in nitrogen purification were CP or laboratory reagent grade chemicals.

II.b.

Apparatus

II.b.1.

Vacuum Dilatometer

The principal use of dilatometry in polymerization kinetics is that volume changes, more generally contraction, occurs during the course of polymerization. The change in volume is proportional to the conversion. In its simplest form, the dilatometer has a cylindrical bulb of about 30-50 ml capacity connected to a measuring capillary for monitoring the volume changes. Initially the monomer/monomer solution is taken with the bulb full and the meniscus in some part of the capillary. The small changes in volume during polymerization are reflected in larger fall in the height of the meniscus in the capillary. With a knowledge of the specific volumes of the monomer and polymer, the course of the polymerization can therefore be monitored by measuring the changes in heights of the meniscus in the capillary.

The vacuum dilatometer employed in this investigation is shown in Fig.1. It is similar to that used by Amass and Tuck¹⁰⁷. It consists of a graduated cylindrical (dilatometer) bulb A (approx. 35 ml capacity) connected to the measuring capillary C (precision bore: 0.2 cm dia, 31 cm length) through a side arm. The dilatometer bulb A is connected to a graduated cylindrical bulb B of about 100 ml capacity through a side tube T_1 . Two T-tubes, T_2 and T_3 are fused to the connecting tube T_1 such that the dilatometer can be attached to the high vacuum line for vacuum manipulations. T_3 functions as a pressure equilibration tube for rapid and easy dilatometer filling. The dilatometer

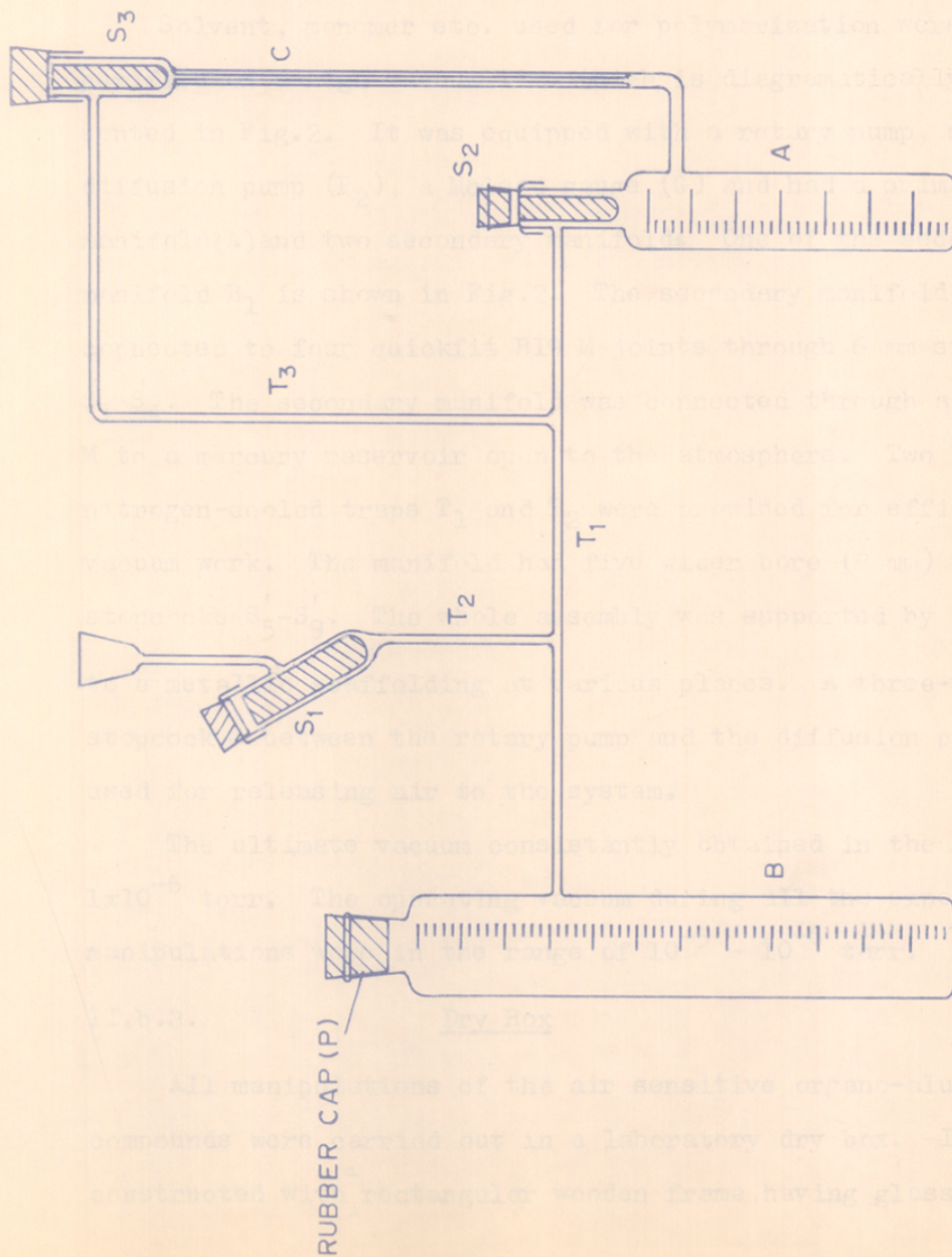


FIG. 1. VACUUM DILATOMETER

is equipped with teflon rotaflo type stopcocks S_1 , S_2 and S_3 for suitable manipulations.

II.b.2. High Vacuum Line

Solvent, monomer etc. used for polymerization were rigorously purified on a high vacuum line which is diagrammatically represented in Fig.2. It was equipped with a rotary pump, mercury diffusion pump (P_2), a Mcleod gauge (G) and had a primary manifold(A) and two secondary manifolds. One of the secondary manifold B_1 is shown in Fig.2. The secondary manifold was connected to four quickfit B19 M joints through 6 mm stopcocks $S'_1-S'_4$. The secondary manifold was connected through a side arm M to a mercury reservoir open to the atmosphere. Two liquid nitrogen-cooled traps T_1 and T_2 were provided for efficient high vacuum work. The manifold had five wider bore (8 mm) two-way stopcocks $S'_5-S'_9$. The whole assembly was supported by clamping to a metallic scaffolding at various places. A three-way stopcock S between the rotary pump and the diffusion pump was used for releasing air to the system.

The ultimate vacuum consistently obtained in the setup was 1×10^{-6} torr. The operating vacuum during all the experimental manipulations were in the range of $10^{-5} - 10^{-6}$ torr.

II.b.3. Dry Box

All manipulations of the air sensitive organo-aluminium compounds were carried out in a laboratory dry box. It was constructed with ^a rectangular wooden frame having glass front

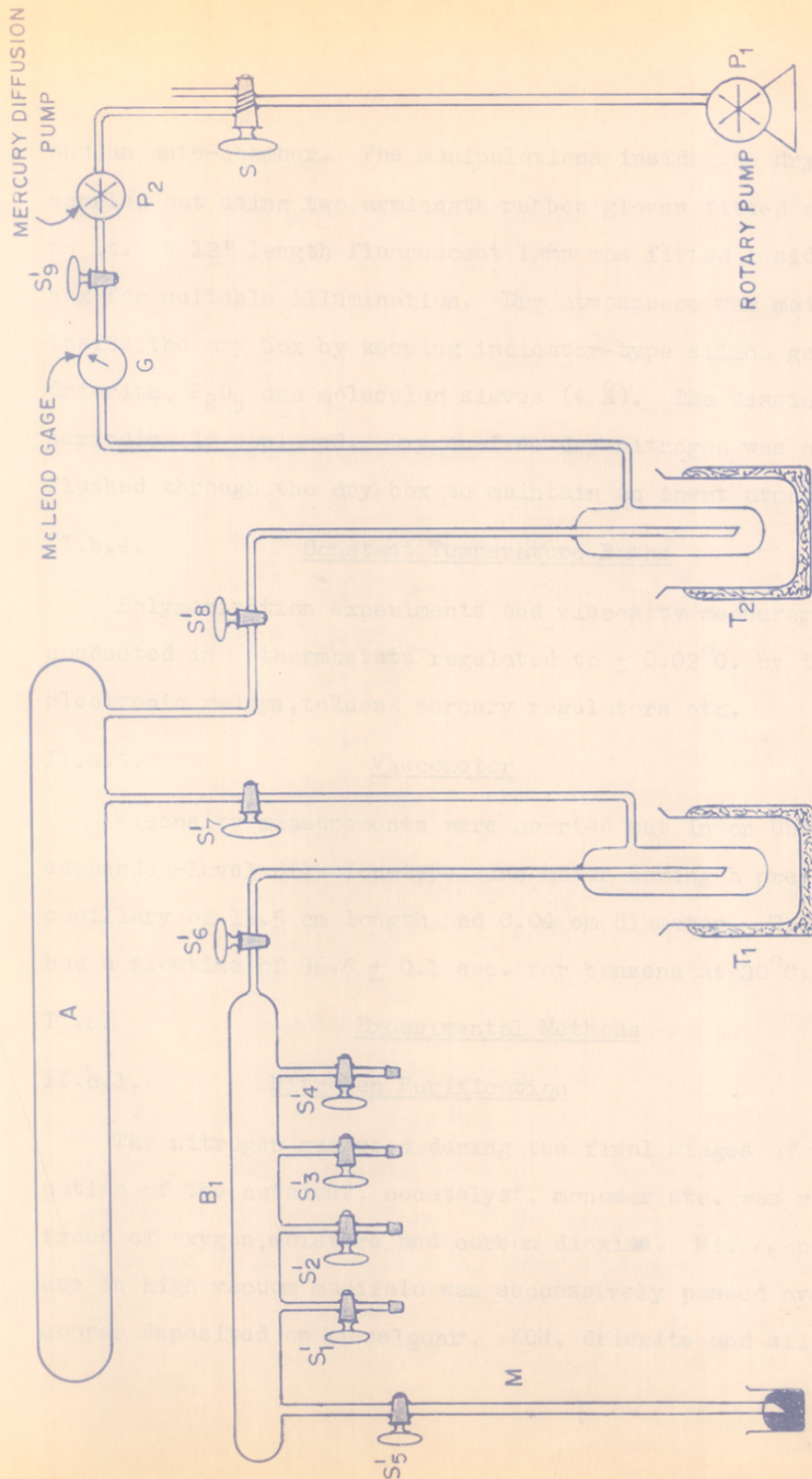


FIG. 2. HIGH VACUUM LINE

and an ante-chamber. The manipulations inside the dry box were carried out using two armlength rubber gloves fitted air-tight to it. A 12" length fluorescent lamp was fitted inside the dry box for suitable illumination. Dry atmosphere was maintained inside the dry box by keeping indicator-type silica gel and drierite, P_2O_5 and molecular sieves (4 Å). The dessicants were periodically replaced. Oxygen-free dry nitrogen was continuously flushed through the dry box to maintain an inert atmosphere.

II.b.4. Constant Temperature Baths

Polymerization experiments and viscosity measurements were conducted in thermostats regulated to $\pm 0.02^\circ\text{C}$. by the use of electronic relays, toluene mercury regulators etc.

II.b.5. Viscometer

Viscosity measurements were carried out in an Ubbelohde suspended-level dilution-type viscometer having a precision bore capillary of 11.5 cm length and 0.04 cm diameter. The viscometer had a flowtime of 96.6 ± 0.1 sec. for benzene at 30°C .

II.c. Experimental Methods

II.c.1. Nitrogen Purification

The nitrogen gas used during the final stages of purification of the catalyst, cocatalyst, monomer etc. was rigorously freed of oxygen, moisture and carbon dioxide. Nitrogen gas for use in high vacuum manifold was successively passed over heated copper deposited on kieselguhr, KOH, drierite and silica gel.

A paraffin monometer was located prior to the entry of nitrogen gas into the manifold to ensure positive pressure of nitrogen. For use in the dry box, nitrogen gas was successively passed over Fieser solution, saturated lead acetate solution, KOH pellets, P_2O_5 and silica gel prior to inletting into the dry box.

Activated Copper: To a 2 litre aqueous solution containing 250 g of $CuCl_2 \cdot 7H_2O$, 250 g kieselguhr was added. The $CuCl_2$ solution was precipitated by adding slowly 500 ml of 2% sodium hydroxide solution at $60^\circ C$ with stirring. The precipitated copper oxide along with kieselguhr was filtered. The cake was removed from the filter paper and packed into a 2 mm I.D. cylindrical tube. The cylindrical cake was pushed out of the tube by a rod and cut into pieces of approximately 5 mm length. The pieces were loosely packed into a glass tube (75 cm long and 4 cm wide) having a B19 M and B29 M joints at either end of the glass tube. A water trap with an outlet for hydrogen was attached through the B19 F joint. A heating wire was wound along the entire length of the tube and surrounded by a glass jacket supported by asbestos rings. Hydrogen gas was passed from the top of the tube and simultaneously its temperature was raised to $170^\circ C$. The water formed collected at the bottom of the tube. The heating of the column and passing of the hydrogen was continued till the trickling of the water ceased. The column was cooled to room temperature under continuous stream of hydrogen.

The nitrogen gas prior to inletting it into the vacuum

line was passed over hot activated copper for freeing from oxygen. The temperature of the column was maintained at 170-180°C.

Fieser Solution: To 100 ml of 20% potassium hydroxide solution containing 2 g of anthraquinone sulphonic acid (sodium salt), 15.0 g of sodium hydrosulphite was added. The solution was heated to 60°C for 10 minutes to affect complete dissolution of sodium hydrosulphite. A blood-red coloured solution was obtained. The Fieser solution thus prepared was used for freeing the nitrogen from traces of oxygen before inletting into the dry box. Fieser solution in the bubbler was replaced with a freshly prepared solution when the formation of precipitate and change in colour was noticed.

II.c.2. Polymerization Procedure

II.c.2 (i) Purification of n-heptane

A 250 ml round bottom flask with B19 F joint and a side arm connected to another B19 F joint through a rotaflo. teflon stopcock was used as the n-heptane reservoir. About 150 ml purified heptane was taken in the flask and about 2 g freshly cut sodium pieces were added. The flask was stoppered with self sealing rubber cap and attached to the high vacuum line through the side arm opening. Heptane was frozen by cooling with liquid nitrogen and evacuated to 10^{-5} torr. for about half-an-hour. Stopcock S_6 on secondary manifold was closed and heptane thawed. Freezing, evacuation and thawing were repeated 5-6 times, the

rotaflo stop cock was closed and the flask was left in the vacuum line for 3 days. Subsequently, heptane was distilled and stored over calcium hydride into a graduated cylindrical reservoir. The reservoir was equipped with a rotaflo stop cock for isolating it from the high vacuum line. The solvent was left on the high vacuum line till required after closing the stopcock.

II.c.2 (ii) Purification of Styrene

Purified styrene (100 ml) was taken in a 250 ml round bottom flask with a B19 F joint and a side arm connected to a B19 F joint through a rotaflo stopcock. Freshly cut sodium pieces (ca 2 g) were added and the flask was attached to the high vacuum line. After about 24 hrs. styrene turned slightly viscous due to partial polymerization. The prepolymerized styrene was evacuated to 10^{-5} torr. for about an hr., after freezing with liquid nitrogen. The secondary manifold stopcock, S'_6 was closed and styrene was allowed to thaw. Freezing, evacuation and thawing were repeated for 3-4 times. Subsequently, the styrene was distilled on the high vacuum line into a graduated cylindrical reservoir containing activated calcium hydride. The rotaflo stopcock on the receiver was closed. Styrene from the reservoir was distilled into the dilatometer in about 4-12 hrs.

II.c.2 (iii) Triethylamine

Triethylamine was similarly further purified on the high vacuum line. Freezing, evacuating and thawing were carried over activated calcium hydride and the distillate also collected

over activated calcium hydride on the high vacuum line. Triethylamine was diluted with n-heptane by successively distilling on the high vacuum line the required quantities of the two to another container from the reservoir. The flask was removed under the positive nitrogen pressure and stoppered with self sealing rubber cap. The flask was weighed before and after transferring the triethylamine and the molarity of the solution was calculated from the known weights.

II.c.2 (iv) Dilution of the Catalyst

The flask containing BuOTiCl_3 was attached to the high vacuum line, evacuated for 10 min. at 10^{-5} torr. It was taken off the high vacuum line under a positive pressure of nitrogen, closed with self sealing rubber cap and weighed. Evacuation and weighings were repeated till two consecutive weights agreed within ± 0.005 g. The flask was again evacuated and heptane from the graduated reservoir on the high vacuum line was distilled to the predetermined extent by cooling the catalyst container with liquid nitrogen. The flask containing the diluted catalyst solution was removed under a positive pressure of nitrogen and weighed. The molarity of the catalyst solution was calculated from the known weights of the catalyst and the diluted solution.

II.c.2 (v) Dilution of the Cocatalyst

A weighed 50 ml round bottom flask was attached to the secondary manifold and purified n-heptane collected and stored over calcium hydride was distilled into the flask by cooling it

with liquid nitrogen. When requisite quantity of the solvent had distilled over, the container was removed from the high vacuum line under a positive pressure of nitrogen, closed with self sealing rubber cap and weighed. The flask was transferred to the dry box and required quantity of aluminium alkyl was added through a syringe. The flask was stoppered, removed from the dry box and weighed. The molarity of the aluminium alkyl solution was calculated from the weighings.

II.c.2 (vi) Catalyst Ageing

To the evacuated dilatometer assembly containing the requisite quantity of n-heptane in bulb B, aliquots of diluted solutions of cocatalyst followed by catalyst were added with the help of a syringe. The self sealing rubber cap (P in Fig.1) was pierced by the syringe needle for transferring the solutions. The completion of the addition of the catalyst solution was taken as the beginning of the aging period. The solutions were mixed by shaking the dilatometer assembly and aged for predetermined times at room temperature ($\sim 29^{\circ}\text{C}$) before mixing it with the monomer. The colour of the solution changed from brown to black immediately on mixing and a brownish/^{black} precipitate was observed to settle down. No further changes were observed during the course of aging.

II.c.2 (vii) Order of Mixing

Same order of mixing of the catalyst, cocatalyst, monomer, solvent etc. was maintained throughout the course of this

investigation. The order of mixing was solvent/cocatalyst/catalyst/monomer.

II.c.2 (viii)

Polymerization

The dilatometer assembly was attached to the high vacuum line at the quickfit Bl9 F joint, the rotaflo stopcock S_1 was opened and evacuated to 10^{-5} - 10^{-6} torr. for about an hour. Simultaneously bulbs A and B, and the connecting tubes were flamed to achieve efficient evacuation. Bulb A was cooled with liquid nitrogen. Requisite quantity of monomer stored over activated calcium hydride on the vacuum line was distilled into the bulb A. Liquid nitrogen container was removed. The monomer was thawed with ethyl alcohol and allowed to reach room temperature by immersing bulb A in ethyl alcohol. Stopcocks S_2 and S_3 were closed. The bulb B was cooled with liquid nitrogen and purified n-heptane from the reservoir on the high vacuum line was distilled to the required graduation mark. Stopcock S_1 was closed and the assembly detached from the high vacuum line.

Requisite quantities of cocatalyst and catalyst were added to the bulb B with the help of a syringe. After mixing and aging the catalyst solution, the monomer was added by opening stopcocks S_2 and S_3 and suitably tilting and shaking the assembly. The contents were transferred to the dilatometer bulb A. Stopcock S_2 followed by S_3 were closed simultaneously manipulating the level of the meniscus in capillary C to a convenient height. The whole assembly was mounted in a thermostat set to the

polymerization temperature. The contents of the dilatometer bulb were continuously stirred magnetically¹⁰⁸.

The level of the meniscus in the dilatometer began to rise almost immediately and reached maximum height in about 7-8 min. from the mixing time. The readings were commenced from the time meniscus reached the maximum height. The fall in height was continuously monitored using a cathetometer reading to ± 0.002 cm. The readings were continued till reaching limiting conversions in the case of $AlEt_2Cl$ system (150-400 minutes). In the case of trialkyl systems, the readings were monitored till the end of the steady state period (ca 200 and 400 minutes in the case of aluminium triethyl and aluminium triisobutyl respectively).

The rates of polymerization at different times were deduced from the known volume of dilatometer bulb A and the quantity of the monomer taken, using the known specific volumes of the monomer and polymer.

II.c.2 (ix) Polymer Isolation

At the end of the polymerization experiment, the contents of the dilatometer were poured to 3 times its volume of acidified methanol. The dilatometer was rinsed with about 5 ml benzene and the rinsings also poured to the same acidified methanol. The separated polymer was allowed to settle overnight. The supernatant layer was decanted and the polymer slurry filtered through G3 sintered disc. The sintered disc along with the polymer was transferred to an oven and dried at $60^\circ C$ for

3 hrs in vacuum.

II.c.2 (x)

Molecular Weights

Viscosity measurements were carried out at 30°C in benzene solutions in an Ubbelohde suspended-level dilution viscometer. The flow times were determined to an accuracy of ± 0.1 sec. Dilutions were carried out in the viscometer by pipetting aliquots of solvent. Reduced viscosities were determined at five varying concentrations and intrinsic viscosities ($[\eta]$) were deduced by linear extrapolations of η_{sp}/C vs C to zero concentration. Molecular weights were calculated, using the relationship: $[\eta] = K M^a$. The value of K and a used were 9.52×10^{-5} and 0.744 respectively¹⁰⁹.

II.c.3.

Analysis

110

II.c.3 (i)

Aluminium Triethyl

Aluminium alkyls were complexed with ethylene diamine tetraacetate. Unreacted EDTA was determined by titration with 0.2 N $ZnSO_4$ using dithiozone as the indicator. The following standard solutions were prepared:

0.5 N NaOH was prepared by dissolving 20 ± 0.005 g of NaOH pellets in distilled water in a 500 ml volumetric flask and standardised by titrating against potassium hydrogen phthalate.

1 N H_2SO_4 was prepared by dissolving 13 ml of conc. H_2SO_4 in distilled water in a 500 ml volumetric flask and standardised against 0.5 N NaOH.

0.2 N $ZnSO_4$ was prepared by dissolving 5.4 ± 0.005 g zinc

sulphate ($\text{ZnSO}_4 \cdot 6\text{H}_2\text{O}$) in distilled water and diluted to 500 ml in a volumetric flask. The solution was standardised by titrating against EDTA using dithiozone as an indicator.

0.2 N EDTA was prepared by dissolving 15 ± 0.01 g EDTA (disodium salt) in 2 l. of distilled water and its pH adjusted to 4.8 with dilute HCl.

0.1 N aluminium solution: Aluminium sheet (1.355 ± 0.005 g) was taken in a 250 ml round bottom flask and a reflux condenser was attached to it. 5 ml of 0.5 N NaOH was added. After the dissolution of the aluminium, 25 ml distilled water was added. 20 ml of conc. HCl was slowly introduced through the reflux condenser and the flask gently heated for half-an-hour. Subsequently, the solution was refluxed for 10 min. to ensure complete dissolution. The flask was cooled and the contents were transferred to a 500 ml volumetric flask. The volume was made upto the graduation mark with distilled water.

To 40 ml of 0.2 N EDTA solution taken in a 250 ml conical flask, 10 ml buffer solution (containing 38.5 g of ammonium acetate and 28 g of glacial acetic acid in 500 ml) and 1 ml of dithiozone indicator were added. The solution turned dark green and was titrated to red colour against 0.2 N zinc sulphate.

$$\text{Conversion factor} = \frac{\text{EDTA taken for analysis}}{\text{Titre value of } \text{ZnSO}_4}$$

To 5 ml of 0.1 N aluminium solution in a 250 ml beaker, 40 ml of 0.2 N EDTA solution was added followed by 10 ml buffer solution and 1 ml indicator.

The unreacted EDTA was titrated against ZnSO_4 (to red colour)

$$\text{Normality of EDTA} = \frac{\text{ml of Al solution} \times \text{its normality}}{\text{ml EDTA} - (\text{ml ZnSO}_4 \times \text{conversion factor})}$$

Estimation of AlEt_3

30 ml of purified n-heptane was transferred to a 500 ml round bottom flask and stoppered with a self sealing rubber cap. The flask was weighed. 1 ml AlEt_3 was transferred to the flask through a syringe. The flask was weighed. AlEt_3 hydrolyzed by adding 50 ml of 1 N H_2SO_4 . The solution was transferred to a beaker and heated on a water bath to evaporate the solvent. The hydrocarbon-free solution was made upto 250 ml in volumetric flask. 10 ml of the solution was pipetted in a 250 ml beaker and to it were added 40 ml of 0.2 N EDTA and 10 ml buffer solution. The solution was titrated against 0.2 N ZnSO_4 using dithiozone the indicator. The percentage of aluminium is given

$$\% \text{ Al} = \frac{(\text{ml EDTA added} \times N_1) - (\text{titer value of ZnSO}_4 \times N_2)}{\text{Weight of aluminium alkyl taken for analysis}} \times 2.698$$

N_1 and N_2 are the normalities of the EDTA and ZnSO_4 solutions respectively.

Percentage of aluminium in AlEt_3 : Found: 23.2; Theoretical 23.7.

II.c.3(ii) Butoxytitanium Trichloride¹¹¹

The titanium in BuOTiCl_3 was estimated as TiO_2 by igniting a known weight of the sample. The chloride content was estimated as AgCl by decomposing BuOTiCl_3 with 1 N NaOH and treating with excess 0.1 N AgNO_3 . Excess silver nitrate is determined by

titration against 0.1 N KCNS with ferric alum as an indicator.

Estimation of Ti

To a known weight of BuOTiCl_3 (~ 0.6 g) in a silica crucible, a few drops of conc. sulphuric acid were added. The crucible was heated to about 500°C initially for 1 hr. Later the temperature was raised to 1000°C , and maintained for 2 hrs to ignite the titanium compound. The crucible was cooled and weighed. The heating, cooling and weighings were repeated till constant weight was obtained. The percentage of Ti is calculated as follows:

$$1.68 \text{ Ti} = \text{TiO}_2 = \frac{\text{Wt. of sample taken for analysis} \times 79.9}{227.4}$$

$$\text{Ti Found} = 20.6\% ; \text{Ti theoretical } 21.1\%$$

Estimation of Chloride

The following standard solutions were prepared:

0.1 N AgNO_3 was prepared by dissolving 1.69 ± 0.005 g AgNO_3 in distilled water in a 100 ml volumetric flask and standardised against 0.1 N NaCl.

0.1 N KCNS was prepared by dissolving 0.98 g KCNS in distilled water in a 100 ml volumetric flask and standardised against 0.1 N AgNO_3 using ferric alum as the indicator.

15 ml of 3% BuOTiCl_3 solution was transferred to a 100 ml flask by syringe and weighed. The solution was decomposed by slowly adding 10 ml of 0.5 N NaOH and boiled on the water bath for half-an hour to evaporate the solvent and cooled. The solution was acidified with dilute HNO_3 . 20 ml of 0.1 N AgNO_3

was added and the contents stirred. The unreacted AgNO_3 was back titrated against 0.1 N KCNS containing (one drop of nitrobenzene) using ferric alum as the indicator.

$$\% \text{ Cl} = \frac{0.0354 \times N_1 \times (20 - V_1) \times 100}{W_1}$$

where V_1 , N_1 are the ml of the unreacted AgNO_3 and normality of AgNO_3 respectively. W_1 is the weight of BuOTiCl_3 taken for analysis.

Chlorine Found 46.2% ; Theoretical 46.8%

II.c.3(iii) Oxidation State of Titanium

The oxidation state of titanium in the catalyst employed was determined by the method of Martin and Stedfeder¹¹² as modified by Moyer¹¹³. Known weights of BuOTiCl_3 and aluminium alkyl were mixed and aged for the required times in an inert atmosphere of purified nitrogen. At the end of the aging period, the reaction was quenched by cooling to 0°C for the determination of total oxidation and to -70°C for the determination of trivalent state. The Ti-alkyl bonds were cleaved with ethanol and titanium reacted with excess 0.1 N FeCl_3 . Ferrous ion liberated were determined by titration against 0.02 N ceric ammonium sulphate using barium diphenylamine sulphonate as the indicator. The following standard solutions were prepared.

0.1 N FeCl_3 was prepared by dissolving 1.62 ± 0.005 g of FeCl_3 in purified absolute alcohol in a 100 ml volumetric flask.

0.02 N ceric ammonium sulphate was prepared by dissolving 1.008 ± 0.002 g ceric ammonium sulphate in distilled water in

a 100 ml standard flask.

Total Oxidation of Ti

The oxidation state ^{/of} Ti was determined at the concentrations at which they were employed in the polymerization experimentations. The stock solutions were 40 m.moles and 20 m.moles in the case of trialkyls and 3 m.moles in the case of alkylaluminium chloride.

5 ml BuOTiCl_3 solution in n-heptane was transferred to the flask under a blanket of purified nitrogen, stoppered with self sealing rubber cap and weighed. To it 5-15 ml aluminium alkyl solution in n-heptane was added through a syringe. The catalyst-cocatalyst solutions were mixed gently by shaking, weighed and aged for the required period at ambient temperatures. At the end of the aging period, the flask was immersed in a bath cooled to 0°C . 10 ml of ethanol (cooled to 0°C) was added through a syringe to decompose the metal alkyl bonds and 10 ml 0.1 N FeCl_3 solution in alcohol was added to the mixture. The ferrous ion formed was titrated against 0.02 N ceric ammonium sulphate using barium diphenyl-amine sulphonate indicator to bluish end point.

$$\% \text{ Total oxidised Ti} = \frac{V_1 \times N_1 \times 0.0479}{W_1} \times 100$$

where V_1 and N_1 are the titre and normality of ceric ammonium sulphate. W_1 is the weight of the TiCl_3OBu taken for analysis.

Ti(iii)

Exactly the same procedure as above was followed except that the reaction flask was cooled to -70°C to prevent oxidation

of Ti^{+2} to Ti^{+3} .

Ti(ii)

Ti(ii) content was estimated as the difference between the total Ti oxidation and the Ti^{+3} content.

CHAPTER III

RESULTS AND DISCUSSION

III.a. Kinetics of Polymerization of Styrene by $\text{BuOTiCl}_3\text{-AlR}_3$

The kinetics of polymerization of styrene with BuOTiCl_3 and aluminium alkyls are studied in this investigation. Generally reduced transition metal halides like TiCl_3 , in combination with AlR_3 , yield a period of steady state polymerizations. Maximum valent transition metal halides, like TiCl_4 , yield continuously declining rates of polymerizations (after an initial settling period). Though the active species in homogeneous polymerizations (like $\text{Cp}_2\text{TiCl}_2\text{-AlEt}_2\text{Cl}$ system) are in the maximum valent state, a continuous decline in rates of polymerization is characteristics of these systems as well. Minsker et al reported³⁷ the steady state polymerization of ethylene by the use of alkoxy derivatives of TiCl_4 with aluminium alkyls. However, total substitution of chloride ligands by alkoxy groups result in homogeneous polymerizations. Catalyst formed by partly substituted alkoxy titanium halides and aluminium alkyls are colloiddally dispersed. Except for ethylene³⁸ and propylene¹¹⁴, the polymerization of other monomers with these alkoxy derivatives of titanium halides has not been reported in literature.

The kinetics of polymerization has been studied by using a vacuum dilatometer shown in Fig.1 as already discussed in experimental section. Rigorously purified monomer and solvent were distilled into the dilatometer bulb A and B respectively. The cocatalyst and catalyst solutions were added to n-heptane in bulb B. After aging the catalyst to the requisite extent

at room temperature, the aged catalyst solution and the monomer were mixed and transferred to the dilatometer bulb A such that the meniscus in the capillary C was at a convenient height. The dilatometer was mounted in a thermostat set to the polymerization temperature and the course of the polymerization was determined by periodically monitoring the level of the meniscus in

Polystyrenes obtained in this investigation by use of butoxy titanium trichloride with aluminium alkyls were completely soluble in methyl ethyl ketone at ambient temperatures showing the absence of stereoregular addition. I.R. spectrum scanned in carbon tetrachloride showed the absence of splitting of adsorption peak at 1070 cm^{-1} confirming the atactic nature of polystyrene obtained.

III.a.1. Treatment of Data

The height of the meniscus in the measuring capillary C was measured at various times of polymerization with the help of a cathetometer reading to $\pm 0.002\text{ cm}$. From the measured heights, the conversions and hence the rates of polymerizations were deduced.

III.a.1(i) Dilatometer Equation^{115,116}

Assuming additivity of volumes, the density of the polymer solution (ρ_s) is given by:

$$\rho_s = \frac{W}{V - \pi r^2 \Delta h} = \frac{1}{x \bar{V}_p - (1-x) \bar{V}_m}$$

where W is the weight of the monomer, r is the radius of the capillary, Δh the change in height at conversion x (in g). V is the volume of the monomer and $\bar{V}_m$ and $\bar{V}_p$ are the specific volumes of monomer and polymer respectively. From the above equation:

$$\text{Conversion } x = \frac{\pi r^2 \Delta h}{W(\bar{V}_m - \bar{V}_p)}$$

$$\text{Rate of polymerization, } R_p (\text{mole.l}^{-1} \text{ s}^{-1}) = \frac{x}{t} \times \frac{W}{M} \times \frac{1}{V_0} \times 1000$$

where M is the molecular weight of the monomer and V_0 is the volume of the dilatometer bulb A and t is the time of polymerization in sec.

Substituting densities for specific volumes,

$$R_p = \frac{\pi r^2 \cdot \Delta h \cdot \rho_p \cdot 1000}{V_0 \cdot (\rho_p - \rho_m) \cdot M \cdot t} \quad (1)$$

In the present case, r , the radius of the capillary was 0.1 cm. V_0 the volume of the dilatometer bulb was 36 ml. M , the molecular weight for styrene is 104.

The rates of polymerization can also be calculated by evaluating the maximum height difference, Δh_∞ for the total monomer conversion.

$$\Delta h_\infty = \frac{\rho_p - \rho_m}{\rho_m \rho_p} \times \frac{W}{\pi r^2}$$

where W is the weight of the monomer used in polymerizations.

Rates of polymerization, R_p , at time t corresponding to a change in height Δh is given by:

Table 1
Data used for the calculation of R_p from the
Dilatometer readings

<u>Dilatometer</u>			
Volume of bulb = 35.8 ml			
Capillary radius = 0.1 cm			
<u>Densities¹¹⁷</u>			
Temp. (°C)	Styrene (g.ml ⁻¹)	Polystyrene (g.ml ⁻¹)	
20	0.9056	1.0510	
25	0.9020	1.0495	
30	0.8970	1.0480	
40	0.8870	1.0450	
50	0.8750	1.0430	
60	0.8680	1.0400	

Table 2
Calculation of rates of polymerization
from dilatometric readings

[Styrene] = 3.60 Temp. = 50°C
 [Ti] = 0.04 [AlEt₃] = 0.06
 Aging time = 10 min.

Time of polymerization (min.)	Meniscus reading	Δh (cm)	$10^6 R_p^*$ (overall rate in mole.l. ⁻¹ s ⁻¹)
0	15.192	0	-
15	15.026	0.166	8.40
25	14.920	0.272	8.26
45	14.756	0.436	7.36
55	14.690	0.502	6.93
75	14.510	0.682	6.90
95	14.328	0.864	7.39
115	14.072	1.120	7.29
135	13.896	1.296	7.34
155	13.694	1.498	7.34
185	13.414	1.778	7.30
205	13.360	1.832	6.78
225	13.212	1.980	6.69

* R_p from Eq. 1

$$R_p = \frac{\Delta h}{\Delta h_{\infty}} \times \frac{1}{t} \times [M] \quad (2)$$

where, $[M]$ is the molar concentration of monomer taken for polymerization.

III.a.1(ii) Rates of Polymerization

The rates of polymerization were calculated from the equations (1) and (2) using the values of the densities¹¹⁷ of polymer and monomer listed in Table 1.

At the end of polymerization, the polymer was precipitated with acidified methanol. In several of these experiments, the final conversions were checked gravimetrically. Generally, the results tallied within about 2-5%. However, in polymerizations carried out to very low conversions, especially with $AlIBu_3$ as cocatalyst, the differences between the gravimetrically determined conversions and these determined by the use of equations (1) and/or (2) were about 8-10%. The greater divergence at very low conversions is not surprising in view of the difficulties in quantitatively isolating low conversion (0.5 to 4%) polymers.

III.a.1(iii) Course of Polymerization

A typical polymerization experiment is illustrated by data in Table 2 as an example. The first column lists the times of polymerization and the corresponding cathetometer readings are listed in the column 2. The overall rates of polymerizations at different reaction times were calculated by the use of equation (1) and are listed in the last column of Table 2.

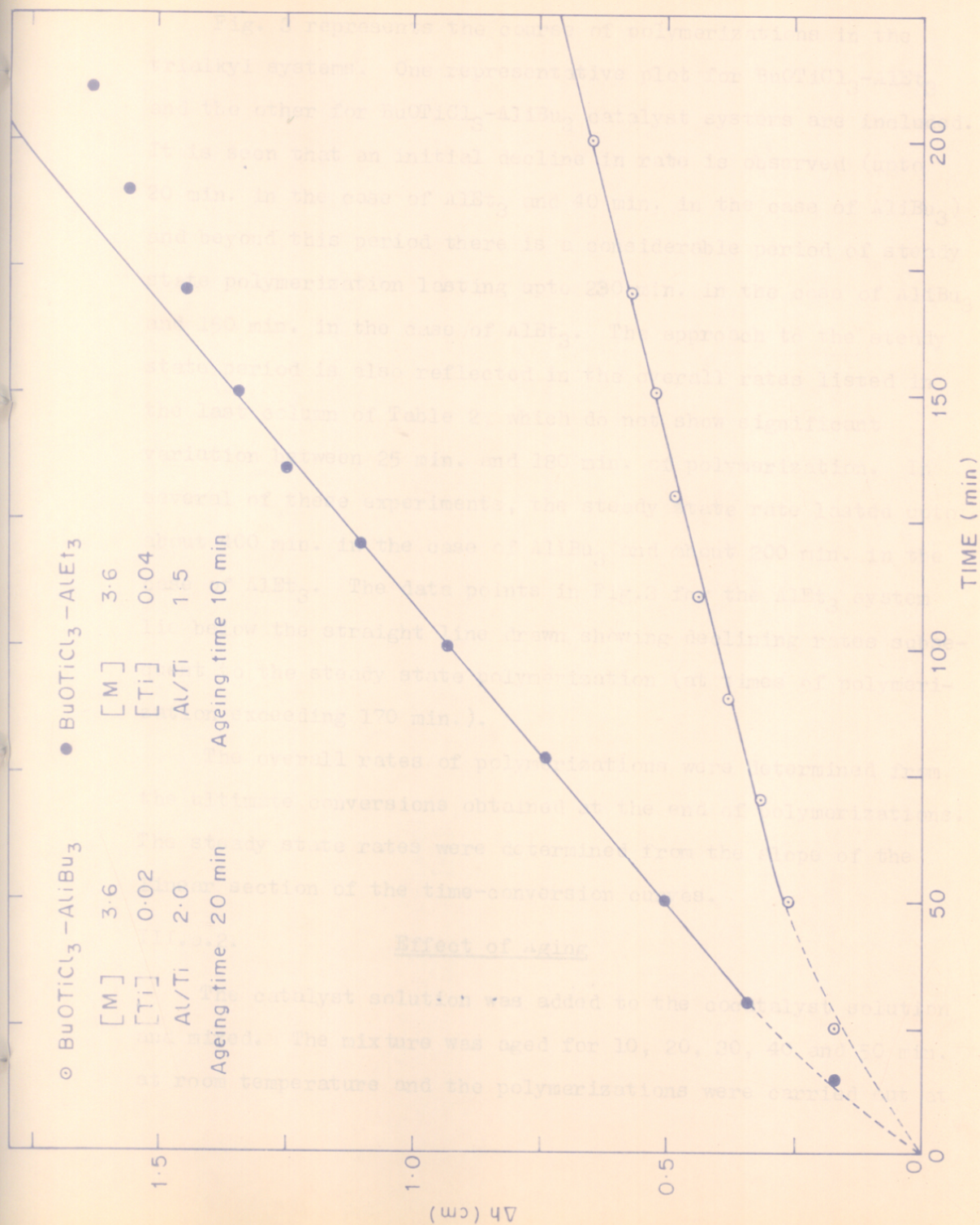


FIG. 3. CONVERSION vs. TIME OF POLYMERIZATION PLOTS FOR BuOTiCl₃ - AIR₃ AT 50 °C

Fig. 3 represents the course of polymerizations in the trialkyl systems. One representative plot for $\text{BuOTiCl}_3\text{-AlEt}_3$ and the other for $\text{BuOTiCl}_3\text{-Al}i\text{Bu}_3$ catalyst systems are included. It is seen that an initial decline in rate is observed (upto 20 min. in the case of AlEt_3 and 40 min. in the case of $\text{Al}i\text{Bu}_3$) and beyond this period there is a considerable period of steady state polymerization lasting upto 230 min. in the case of $\text{Al}i\text{Bu}_3$ and 150 min. in the case of AlEt_3 . The approach to the steady state period is also reflected in the overall rates listed in the last column of Table 2, which do not show significant variation between 25 min. and 180 min. of polymerization. In several of these experiments, the steady state rate lasted upto about 400 min. in the case of $\text{Al}i\text{Bu}_3$ and about 200 min. in the case of AlEt_3 . The data points in Fig.3 for the AlEt_3 system lie below the straight line drawn showing declining rates subsequent to the steady state polymerization (at times of polymerization exceeding 170 min.).

The overall rates of polymerizations were determined from the ultimate conversions obtained at the end of polymerizations. The steady state rates were determined from the slope of the linear section of the time-conversion curves.

III.a.2.

Effect of Aging

The catalyst solution was added to the cocatalyst solution and mixed. The mixture was aged for 10, 20, 30, 40 and 50 min. at room temperature and the polymerizations were carried out at

Table 3
Effect of aging on catalyst activity

Alkyl : AliBu₃

Temp. = 50°C [M] = 3.6
 [Ti] = 0.02 [Al] = 0.04

Aging time (min.)	Rate of polymerization, $R_p \times 10^6$ (mole.l. ⁻¹ .s ⁻¹)	
	Steady state rate	Overall rate
10	1.53	2.23
20	1.96	2.26
30	1.80	2.20
40	1.67	2.00
50	1.40	1.68

Table 4
Effect of aging on catalyst activity

Alkyl : AlEt ₃		
Temp.	= 50°C	[M] = 3.6
[Ti]	= 0.04	[Al] = 0.06
Aging time (min.)	Rates of polymerization, $R_p \times 10^6$ (mole.l ⁻¹ .s ⁻¹)	
		Overall rate
10	7.05	6.67
20	6.59	5.91
30	6.41	5.91
40	5.87	5.41
50	5.15	4.86

50°C using 3.60 mole.l⁻¹ styrene. A catalyst concentration of 0.02 mole.l⁻¹ and Al/Ti ratio of 2 was used for BuOTiCl₃-Al_iBu₃ system and 0.04 mole.l⁻¹ catalyst and Al/Ti=1.5 was used for BuOTiCl₃-AlEt₃ system.

After an initial decline in rates of polymerization lasting upto 20-30 min. in the case of AlEt₃ and 40-60 min. in the case of Al_iBu₃, steady state rates were obtained. The overall rates and steady state rates obtained for catalyst solutions aged for different times are listed in Tables 3 & 4. In the case of BuOTiCl₃-Al_iBu₃ system, the overall rates remained constant upto aging times of 30 min. and declined subsequently. The steady state rates increased upto 20 min. aging and subsequently declined. For BuOTiCl₃-AlEt₃ system, a continuous decline of both the overall rates and steady state rates with increase in aging time were observed.

For further experimentation, the catalysts were aged for 20 min. and 10 min. in the case of BuOTiCl₃ containing Al_iBu₃ and AlEt₃ as cocatalyst respectively.

III.a.3. Effect of Aluminium Alkyl Concentration

The effect of varying aluminium alkyl concentration on the rates of polymerization was probed at varying Al/Ti ratios from 0.5 to 3.0. Extremely rapid polymerizations, beyond the range of dilatometer used, were observed at Al/Ti = 0.5, probably due to cationic initiation. The steady state rates of polymerization and molecular weight of final polymers

Table 5
Effect of Al/Ti on polymerization

Alkyl : AliBu₃

Temp. = 50°C [M] = 3.6
[Ti] = 0.02 Aging time = 20 min.

Al/Ti	Steady state rate $R_p \times 10^6$ (mole.l ⁻¹ .s ⁻¹)	Oxidation state		Molecular weight $\times 10^{-4}$
		Ti ⁺³ (%)	Ti ⁺² (%)	
0.75	2.14	85	-	2.38
1.00	2.48	95	5	3.63
1.50	2.97	86	14	4.37
2.00	1.96	80	20	3.18
2.50	1.52	78	22	2.74
3.00	1.06	75	25	2.16

Table 6

Effect of Al/Ti on polymerizationAlkyl : AlEt₃

Temp. = 50°C [M] = 3.60
 [Ti] = 0.04 aging time = 10 min.

Al/Ti	Steady state rate $R_p \times 10^6$ (mole.l ⁻¹ .s ⁻¹)	Oxidation state		Molecular weight $\times 10^{-4}$
		Ti ⁺³ (%)	Ti ⁺² (%)	
0.75	3.68	90	-	1.64
1.00	4.55	97	-	2.04
1.50	7.05	90	10	3.06
2.00	3.15	85	15	2.71
2.50	2.30	82	18	2.40
3.00	1.23	78	22	2.05

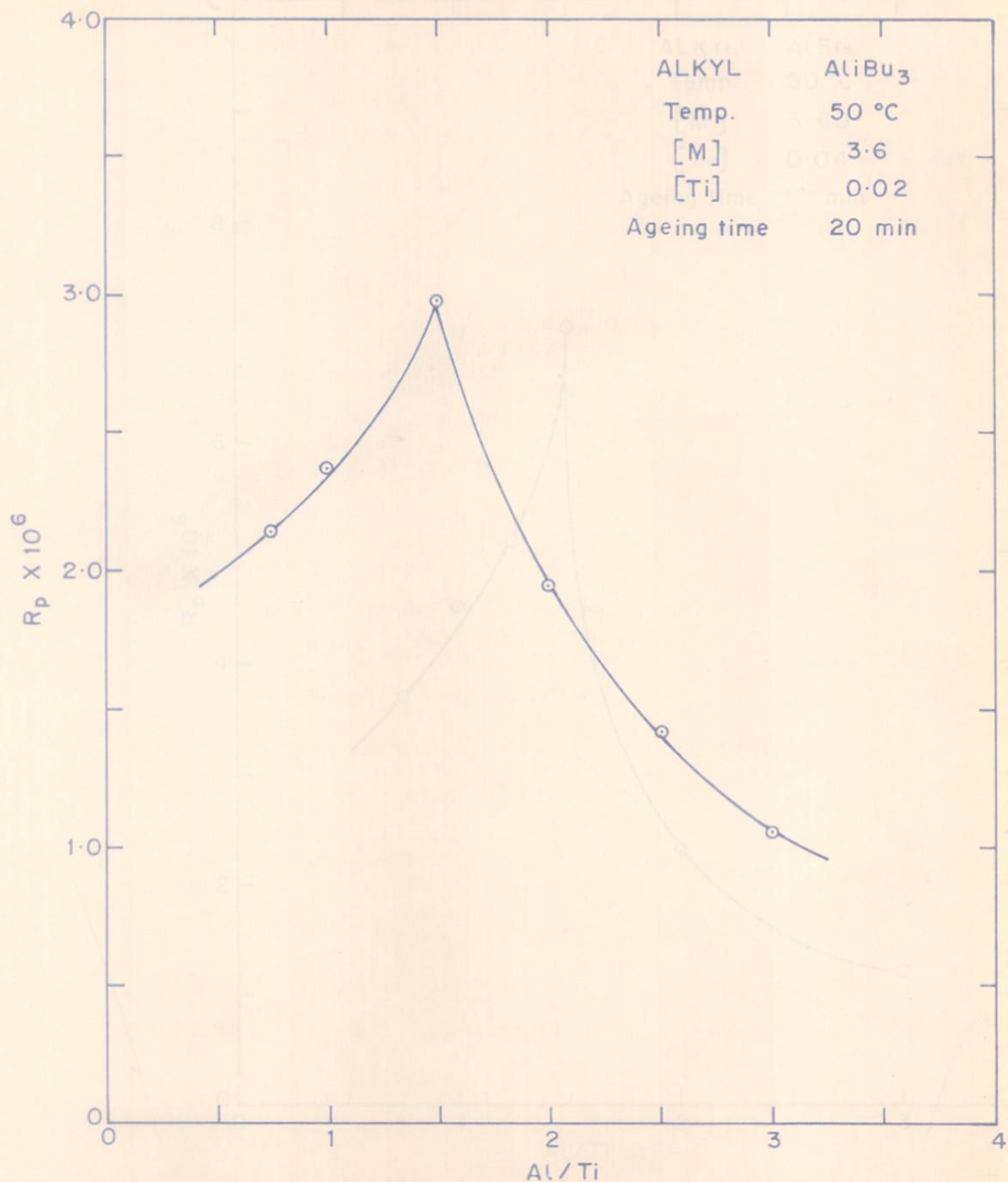


FIG. 4. VARIATION OF STEADY STATE RATE OF
POLYMERIZATION WITH Al/Ti RATIO

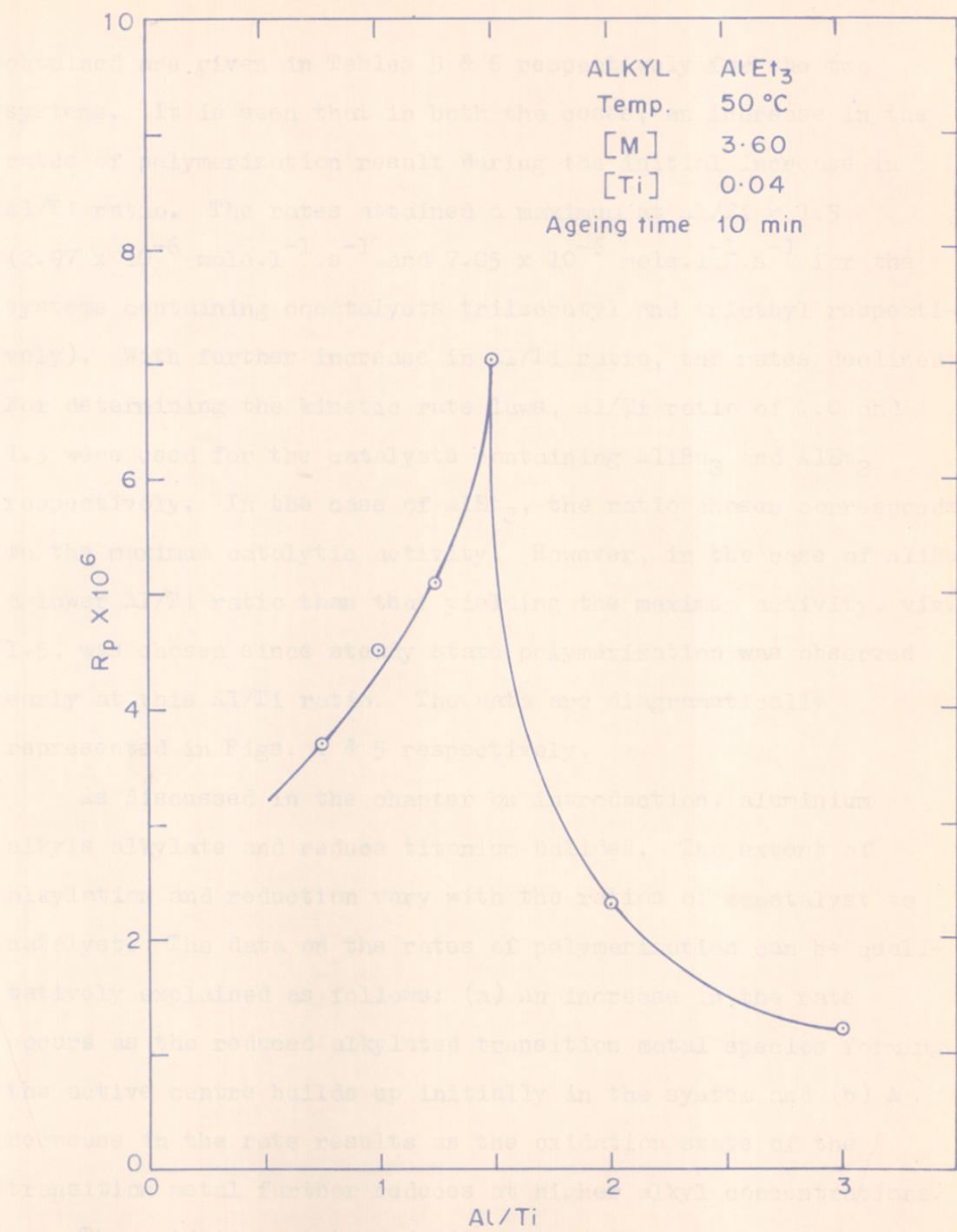


FIG. 5. VARIATION OF STEADY STATE RATE OF POLYMERIZATION WITH AL/TI RATIO

obtained are given in Tables 5 & 6 respectively for the two systems. It is seen that in both the cases, an increase in the rates of polymerization result during the initial increase in Al/Ti ratio. The rates attained a maximum at Al/Ti = 1.5 (2.97×10^{-6} mole.l⁻¹.s⁻¹ and 7.05×10^{-6} mole.l⁻¹.s⁻¹ for the systems containing cocatalysts triisobutyl and triethyl respectively). With further increase in Al/Ti ratio, the rates declined. For determining the kinetic rate laws, Al/Ti ratio of 1.0 and 1.5 were used for the catalysts containing Al_iBu₃ and AlEt₃ respectively. In the case of AlEt₃, the ratio chosen corresponds to the maximum catalytic activity. However, in the case of Al_iBu₃, a lower Al/Ti ratio than that yielding the maximum activity, viz. 1.5, was chosen since steady state polymerization was observed early at this Al/Ti ratio. The data are diagrammatically represented in Figs. 4 & 5 respectively.

As discussed in the chapter on introduction, aluminium alkyls alkylate and reduce titanium halides. The extent of alkylation and reduction vary with the ratios of cocatalyst to catalyst. The data on the rates of polymerization can be qualitatively explained as follows: (a) an increase in the rate occurs as the reduced alkylated transition metal species forming the active centre builds up initially in the system and (b) A decrease in the rate results as the oxidation state of the transition metal further reduces at higher alkyl concentrations.

The oxidation states of titanium in the catalyst for catalyst solutions aged similarly and containing identical

ratios of Al/Ti were evaluated by redox titrimetry¹¹². The Ti^{+3} and Ti^{+2} contents obtained at varying ratios of Al/Ti ratio are listed in Tables 5 & 6 respectively for $AlIBu_3$ and $AlEt_3$ containing catalyst systems. It is seen that upto a ratio of 1.0, the Ti^{+3} increases, reaches a maximum at that ratio and subsequently Ti^{+2} content increases with a resultant decrease in the Ti^{+3} content. The initial increase in the Ti^{+3} content and its decrease beyond an Al/Ti ratio of 2 parallel the catalyst activity as shown by the increasing and declining polymerization rates. However, the maximum content of Ti^{+3} results at an Al/Ti ratio of 1.0, whereas maximum catalyst activity is observed at Al/Ti = 1.5. The results qualitatively show that the active species in the polymerization of styrene using $BuOTiCl_3-AlR_3$ catalyst is in the trivalent state of titanium.

The maximum observed in the variation of rates as a function of Al/Ti ratio is characteristic of polymerization by the use of higher valent transition metal halides. It has already been pointed out (in introduction) that maximum in the rate obtained by variation of Al/Ti ratio is better understood in terms of Langmuir-Hinshelwood adsorption equilibrium, rather than Rideal equilibrium prevailing in the polymerization system.

In the Langmuir-Hinshelwood mechanism⁸⁹, both the monomer and the aluminium alkyl are reversibly adsorbed at the catalyst surface and the adsorbed monomer is incorporated into the transition metal-carbon bond. The rate of polymerization, taking into consideration the competitive adsorption of the two,

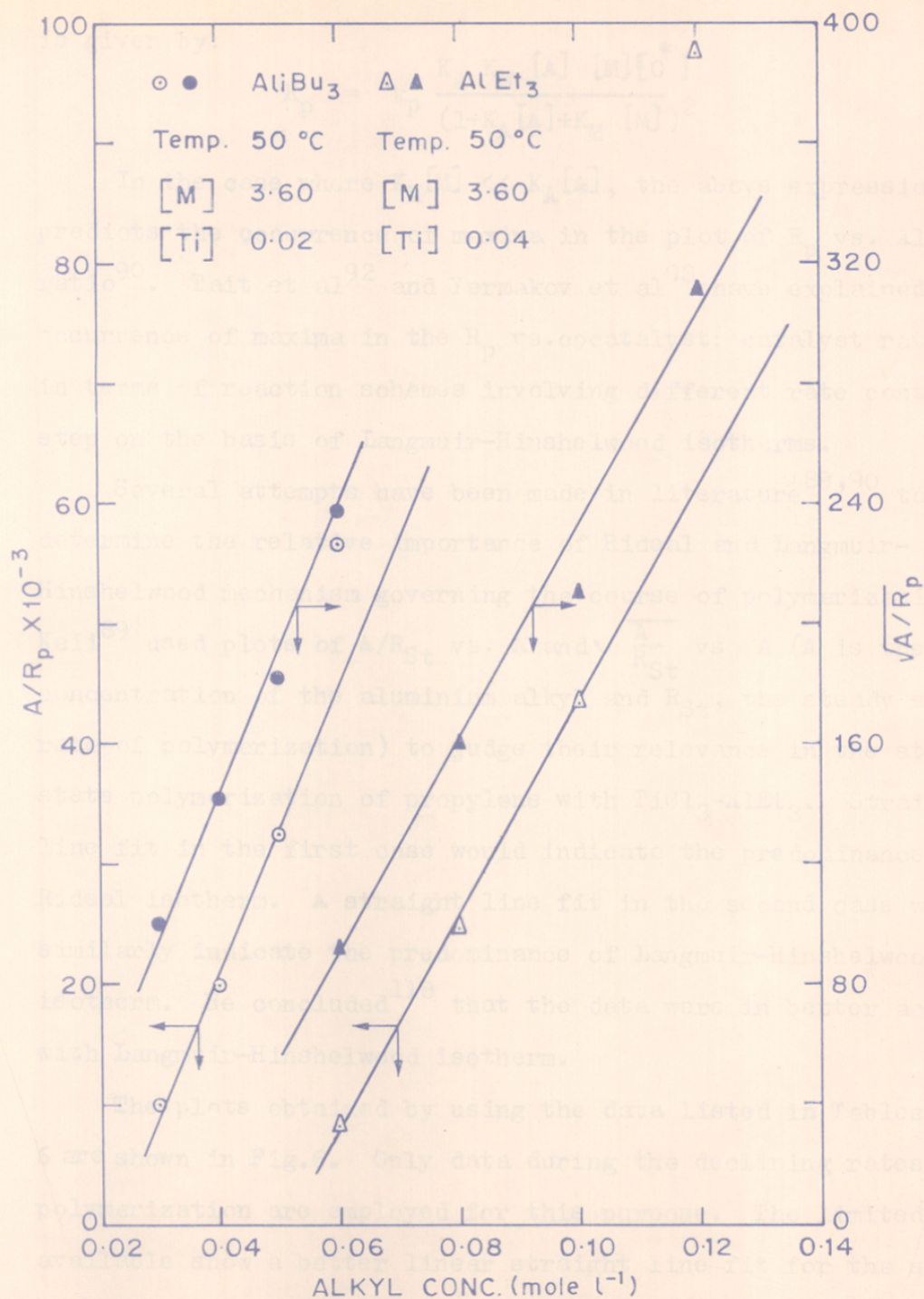


FIG. 6. PLOT OF A/R_p AND $\sqrt{A/R_p}$ vs. ALKYL CONCENTRATIONS

is given by:

$$R_p = k_p \frac{K_A K_M [A] [M] [C^*]}{(1 + K_A [A] + K_M [M])^2}$$

In the case where $K_M [M] \ll K_A [A]$, the above expression predicts the occurrence of maxima in the plot of R_p vs. Al/Ti ratio⁹⁰. Tait et al⁹² and Yermakov et al⁹³ have explained the occurrence of maxima in the R_p vs. cocatalyst: catalyst ratio in terms of reaction schemes involving different rate controlling step on the basis of Langmuir-Hinshelwood isotherms.

Several attempts have been made in literature^{89,90} to determine the relative importance of Rideal and Langmuir-Hinshelwood mechanism governing the course of polymerization. Keii⁸⁹ used plots of A/R_{St} vs. A and $\sqrt{\frac{A}{R_{St}}}$ vs. A (A is the concentration of the aluminium alkyl and R_{St} , the steady state rate of polymerization) to judge their relevance in the steady state polymerization of propylene with $TiCl_3-AlEt_3$. Straight line fit in the first case would indicate the predominance of Rideal isotherm. A straight line fit in the second case would similarly indicate the predominance of Langmuir-Hinshelwood isotherm. He concluded¹¹⁸ that the data were in better accord with Langmuir-Hinshelwood isotherm.

The plots obtained by using the data listed in Tables 5 & 6 are shown in Fig.6. Only data during the declining rates of polymerization are employed for this purpose. The limited data available show a better linear straight line fit for the square-root plot indicating that Langmuir-Hinshelwood case better

Table 7

Variation of the steady state rates with
catalyst concentration

Alkyl : AliBu3

Temp. = 50°C [M] = 3.60
Aging time = 20 min. Al/Ti = 1.0

[Ti] (m. mole.l ⁻¹)	Steady state rate R _p x 10 ⁶ (mole.l ⁻¹ .s ⁻¹)	Molecular weight x 10 ⁻⁴
5	0.72	1.64
10	1.15	2.65
20	2.48	3.63
30	3.28	3.48
40	4.52	3.07
50	5.06	2.84
60	5.21	3.12

Table 8

Variation of the steady state rates with
catalyst concentration

Alkyl : AlEt₃

Temp. = 50°C [M] = 3.60
Aging time = 10 min. Al/Ti = 1.5

[Ti] (m.mole l ⁻¹)	Steady state rate R _p x 10 ⁶ (mole.l ⁻¹ .s ⁻¹)	Molecular weight x 10 ⁻⁴
10	1.82	2.46
20	3.21	2.54
30	5.30	3.12
40	7.05	3.06
50	9.04	3.18
60	9.72	2.96

represents the data.

III.a.4. Effect of Catalyst Concentration

$\text{BuOTiCl}_3\text{-Al iBu}_3$ and $\text{BuOTiCl}_3\text{-AlEt}_3$ were mixed in the ratio of 1:1 and 1:1.5 respectively. Catalysts containing Al iBu_3 and AlEt_3 were aged for 20 and 10 min. respectively. The polymerizations were carried out at 50°C using 3.6 mole.l^{-1} of styrene by varying the catalyst concentration in the range of $0.005 \text{ mole.l}^{-1}$ to 0.06 mole.l^{-1} .

The course of polymerization for four varying concentrations of catalyst are depicted in Figs. 7 & 8 for $\text{BuOTiCl}_3\text{-Al iBu}_3$ and $\text{BuOTiCl}_3\text{-AlEt}_3$ respectively.

As discussed with reference to Fig. 3, the time-conversion curves in Fig. 7 & 8 show an initial declining rate lasting about 40-80 min. in the case of $\text{BuOTiCl}_3\text{-Al iBu}_3$ and 20-40 min. in the case of $\text{BuOTiCl}_3\text{-AlEt}_3$. Subsequently, steady state polymerizations lasting upto about 400 min. with $\text{BuOTiCl}_3\text{-Al iBu}_3$ and 150 min. for $\text{BuOTiCl}_3\text{-AlEt}_3$ are observed. In the case of AlEt_3 cocatalyst, the duration of the steady state rate appears to decrease with increasing catalyst concentration. But in the case of Al iBu_3 cocatalyst, no declining rate of polymerization is observed beyond the steady state period. The increasing slope with increase in catalyst concentration shows the higher rates of polymerizations at higher catalyst concentrations.

Steady state rates of polymerizations were obtained from the linear portion of the rate conversion curves and are listed

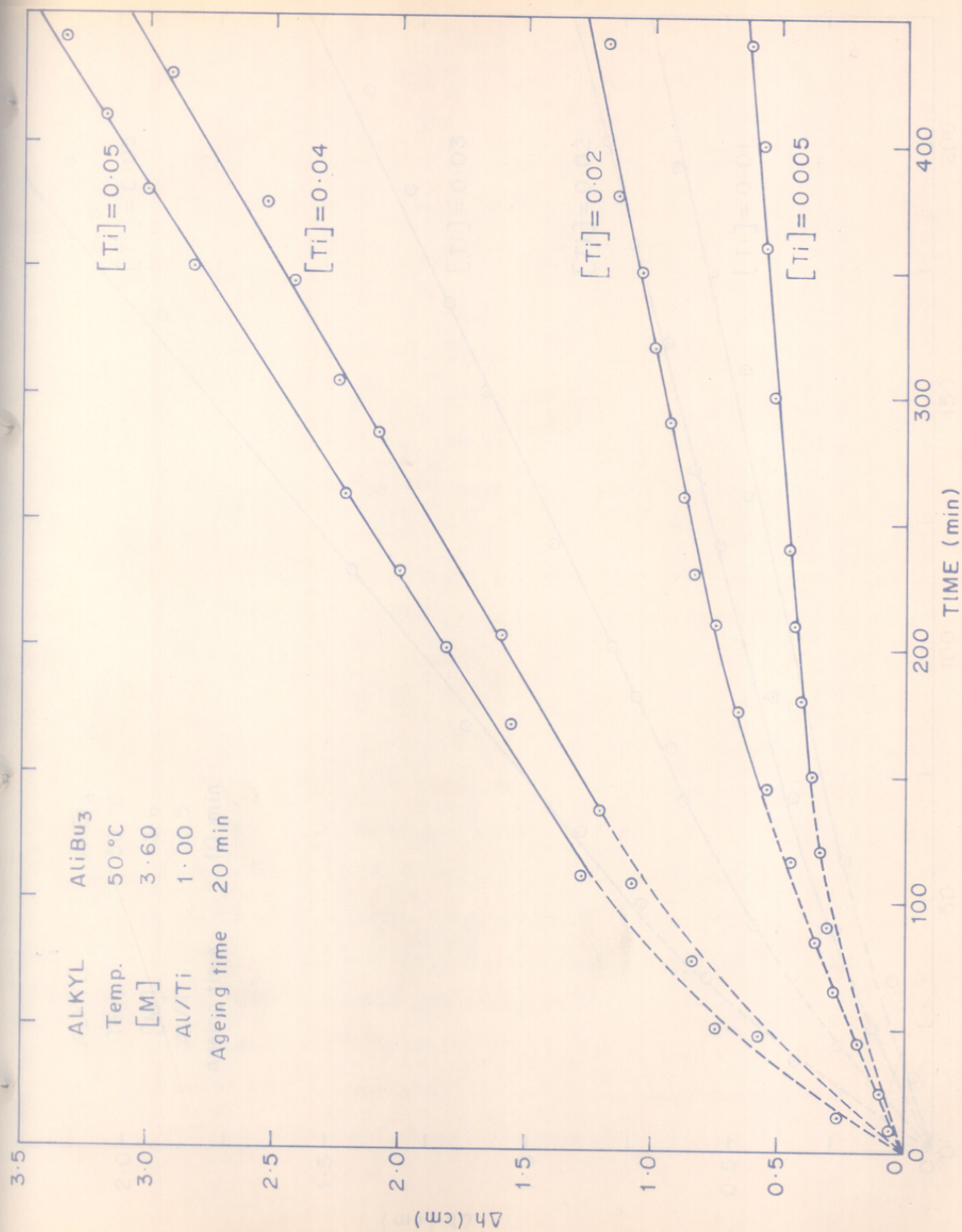


FIG. 7. CONVERSION vs. TIME OF POLYMERIZATION PLOTS AT VARYING CATALYST CONCENTRATIONS

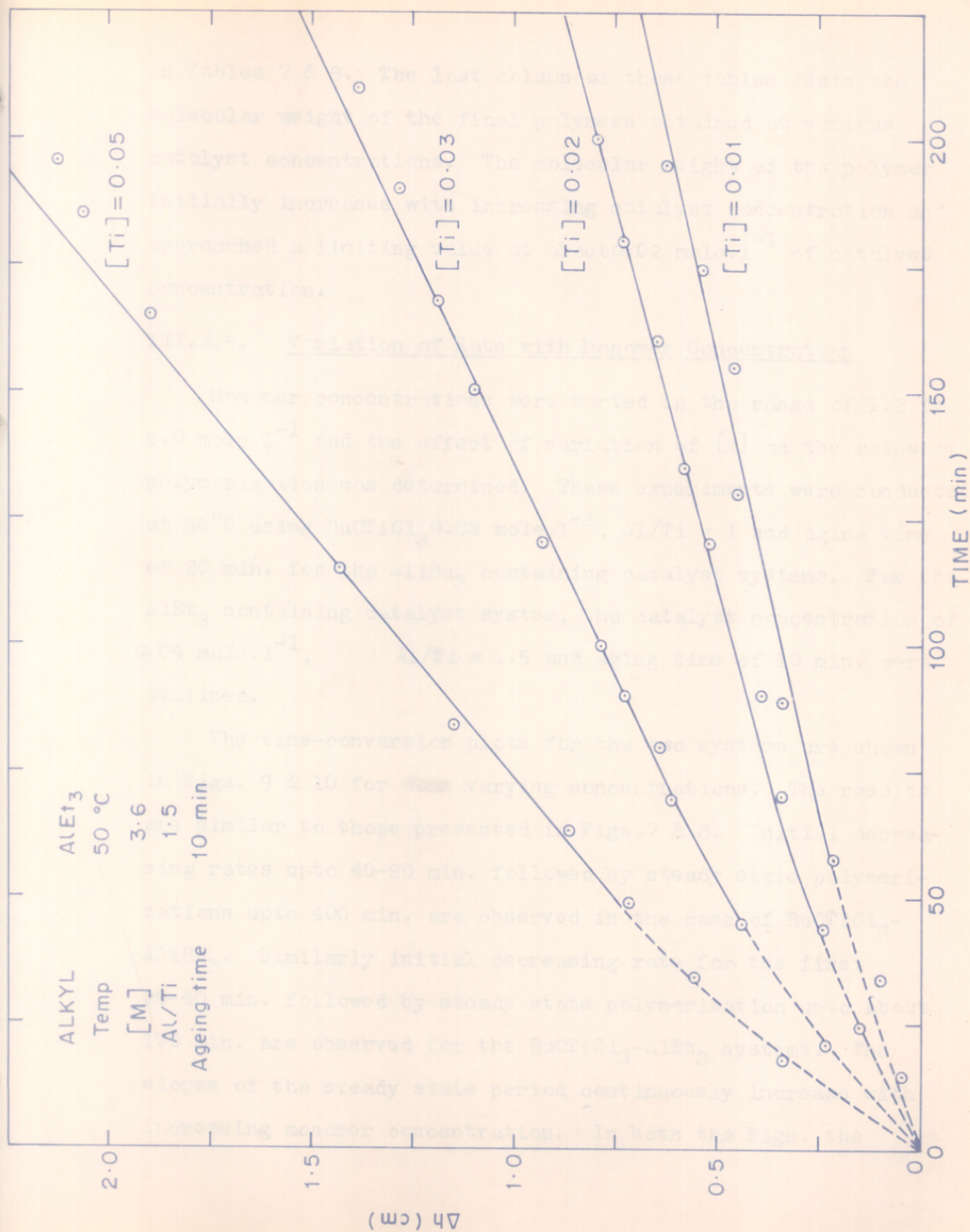


FIG. 8. CONVERSION vs. TIME OF POLYMERIZATION PLOTS AT VARYING CATALYST CONCENTRATIONS

in Tables 7 & 8. The last column of these tables lists the molecular weight of the final polymers obtained at various catalyst concentrations. The molecular weight of the polymer initially increases with increasing catalyst concentration and approached a limiting value at about 0.02 mole.l^{-1} of catalyst concentration.

III.a.5. Variation of Rate with Monomer Concentration

Monomer concentrations were varied in the range of 1.2 to 5.0 mole.l^{-1} and the effect of variation of $[M]$ on the rates of polymerization was determined. These experiments were conducted at 50°C using BuOTiCl_3 0.03 mole.l^{-1} , $\text{Al/Ti} = 1$ and aging time of 20 min. for the AlIBu_3 containing catalyst systems. For the AlEt_3 containing catalyst system, the catalyst concentration of 0.04 mole.l^{-1} , $\text{Al/Ti} = 1.5$ and aging time of 10 min. were utilized.

The time-conversion plots for the two systems are shown in Figs. 9 & 10 for four varying concentrations. The results are similar to those presented in Figs. 7 & 8. Initial decreasing rates upto 40-80 min. followed by steady state polymerizations upto 400 min. are observed in the case of BuOTiCl_3 - AlIBu_3 . Similarly initial decreasing rate for the first 20-40 min. followed by steady state polymerization upto about 170 min. are observed for the BuOTiCl_3 - AlEt_3 systems. The slopes of the steady state period continuously increase with increasing monomer concentration. In both the Figs. the

Table 9

Variation of the steady state rates with
monomer concentration:

Alkyl : $\text{Al}(\text{iBu})_3$

Temp. = 50°C [Ti] = 0.03
Aging time = 20 min. Al/Ti = 1.0

Monomer concentration (mole.l ⁻¹)	Steady state rate $R_p \times 10^6$ (mole.l ⁻¹ .s ⁻¹)	Molecular weight $\times 10^{-4}$
1.20	0.81	0.66
1.68	1.25	1.76
2.16	1.93	2.38
2.64	2.22	2.73
3.12	2.58	3.24
3.60	3.03	3.34
4.08	3.48	4.44
4.56	3.79	4.66
5.04	4.20	4.50

Table 10

Variation of the steady state rates with

monomer concentration

Alkyl : AlEt_3

Temp. = 50°C $[\text{Ti}] = 0.04$
 Aging time = 10 min. $\text{Al/Ti} = 1.5$

Monomer concentration (mole.l ⁻¹)	Steady state rate $R_p \times 10^6$ (mole.l ⁻¹ .s ⁻¹)	Molecular weight $\times 10^{-4}$
1.20	1.96	0.68
1.68	2.85	1.04
2.16	3.93	1.79
2.64	4.96	2.27
3.12	5.85	2.84
3.60	7.05	3.06
4.08	8.30	3.61
4.56	8.71	3.39

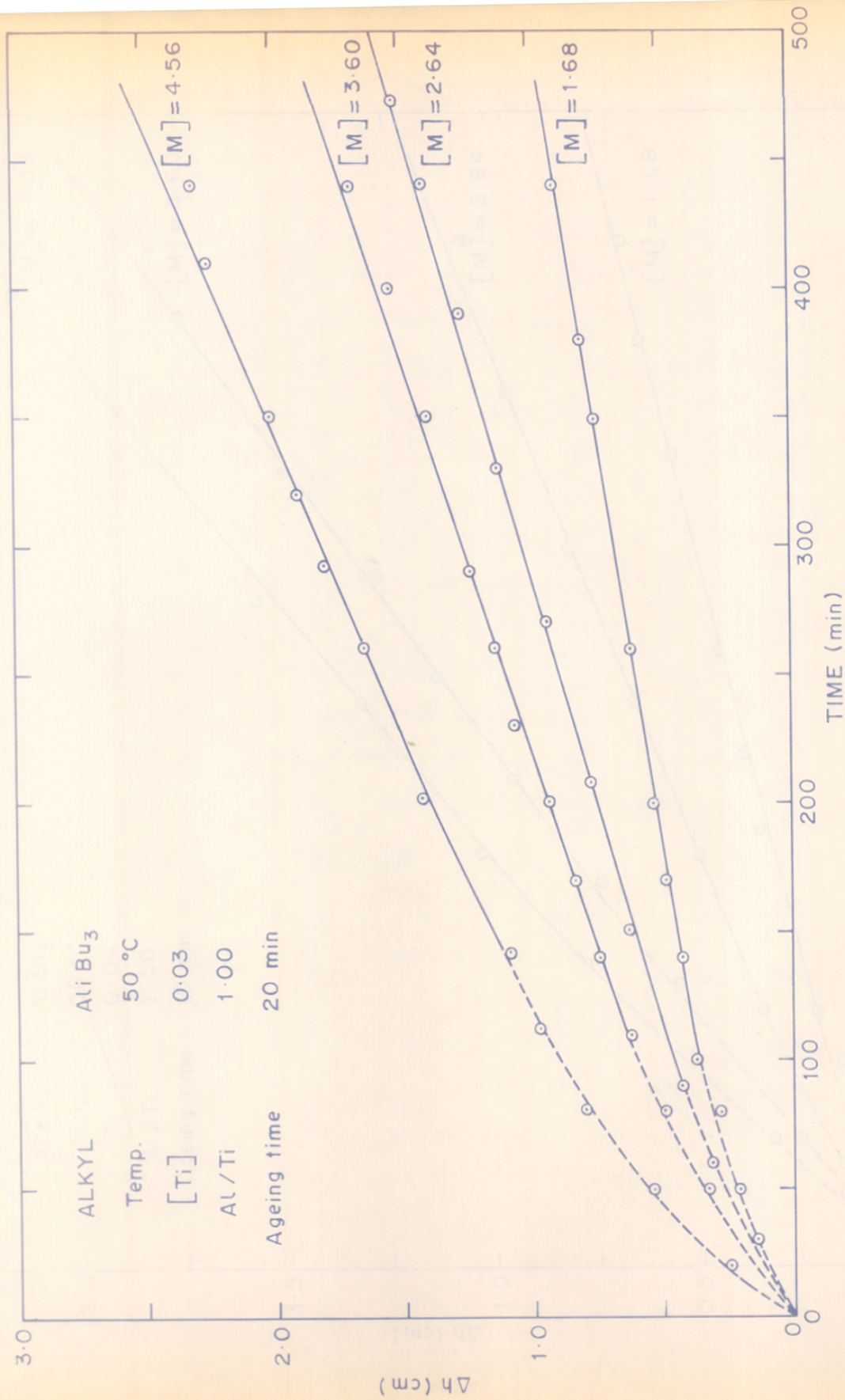


FIG. 9. CONVERSION vs. TIME OF POLYMERIZATION PLOTS
AT VARYING MONOMER CONCENTRATIONS

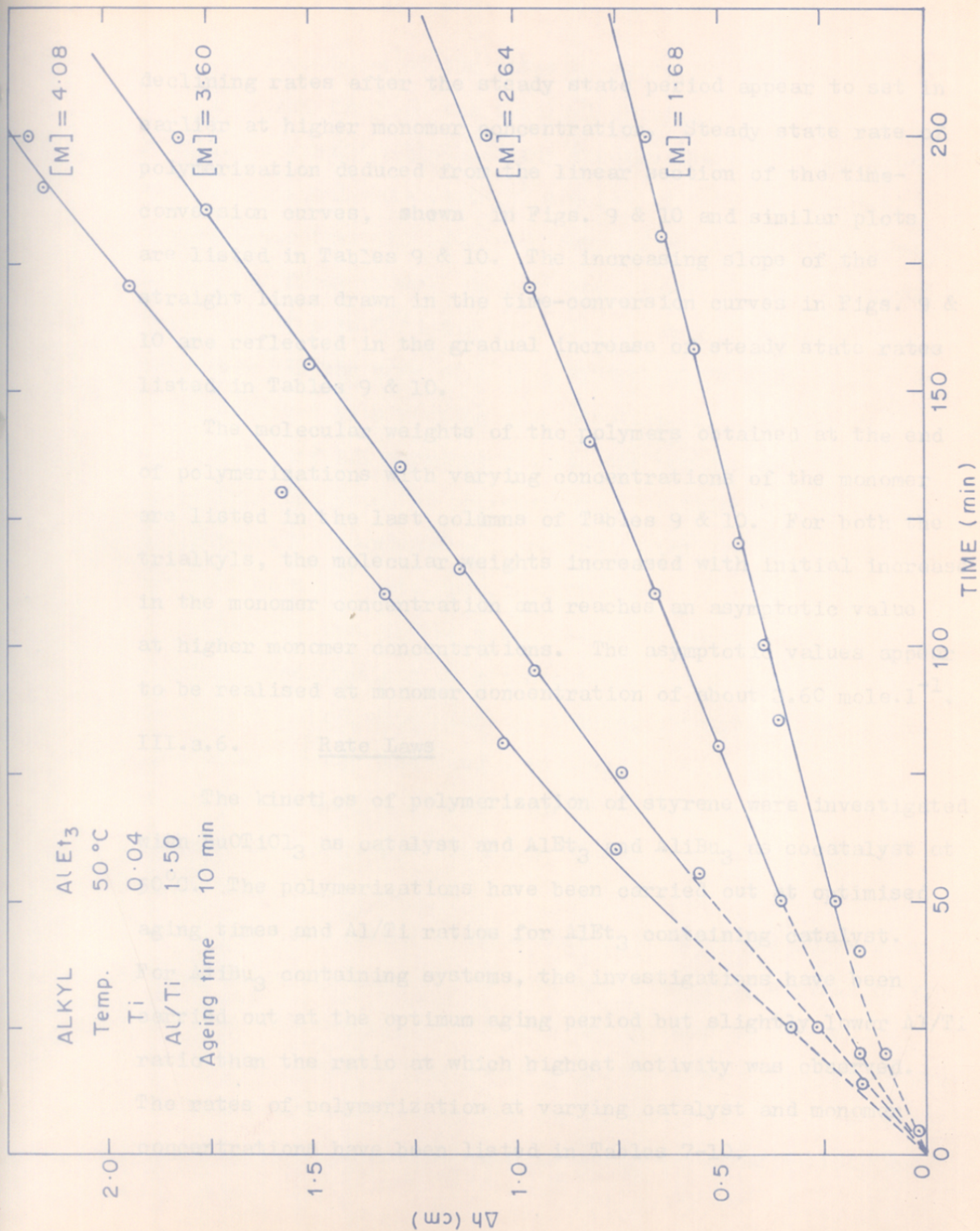


FIG. 10. CONVERSION vs. TIME OF POLYMERIZATION PLOTS AT VARYING MONOMER CONCENTRATIONS

declining rates after the steady state period appear to set in earlier at higher monomer concentration. Steady state rate of polymerization deduced from the linear section of the time-conversion curves, **shown** in Figs. 9 & 10 and similar plots are listed in Tables 9 & 10. The increasing slope of the straight lines drawn in the time-conversion curves in Figs. 9 & 10 are reflected in the gradual increase of steady state rates listed in Tables 9 & 10.

The molecular weights of the polymers obtained at the end of polymerizations with varying concentrations of the monomer are listed in the last columns of Tables 9 & 10. For both the trialkyls, the molecular weights increased with initial increase in the monomer concentration and reaches an asymptotic value at higher monomer concentrations. The asymptotic values appear to be realised at monomer concentration of about 3.60 mole.l^{-1} .

III.a.6. Rate Laws

The kinetics of polymerization of styrene were investigated with BuOTiCl_3 as catalyst and AlEt_3 and $\text{Al}i\text{Bu}_3$ as cocatalyst at 50°C . The polymerizations have been carried out at optimised aging times and Al/Ti ratios for AlEt_3 containing catalyst. For $\text{Al}i\text{Bu}_3$ containing systems, the investigations have been carried out at the optimum aging period but slightly lower Al/Ti ratio than the ratio at which highest activity was observed. The rates of polymerization at varying catalyst and monomer concentrations have been listed in Tables 7-10.

The dependence of the rates of polymerization on catalyst concentration for both the trialkyl aluminiums are shown in Fig.11. A straight line passing through the origin and most of the experimental data (upto 50 m.mole) in both the catalyst systems show that the rate with respect to the catalyst concentration is first order. Only at the highest catalyst concentration (9.06 mole.l^{-1}) the data depart from the first-order rate law. In the case of $\text{Al}(\text{iBu})_3$ system, polymerizations were also conducted with varying concentration of the catalyst at Al/Ti ratio of 1.5 corresponding to the maximum catalytic activity. The rates of polymerization in this case also showed a first order dependence with regard to catalyst concentration upto 0.05 mole.l^{-1} catalyst concentration.

The variation in the steady state polymerization with varying concentrations of monomer is depicted in Fig.12, for both the trialkyl aluminium containing catalyst. A straight line drawn through the data points and passing through the origin is a good fit of the data. Thus with reference to monomer also, steady state rates of polymerization follow a first-order rate law.

It is interesting to note that in most of the cases where steady state polymerizations have been reported, a first order rate law with respect to catalyst and monomer is generally observed⁴⁰. This is especially so in the case of propylene and ethylene polymerization by the use of TiCl_3 and AlR_3 . In the case of styrene polymerization in n-heptane using $\alpha\text{-TiCl}_3$ and

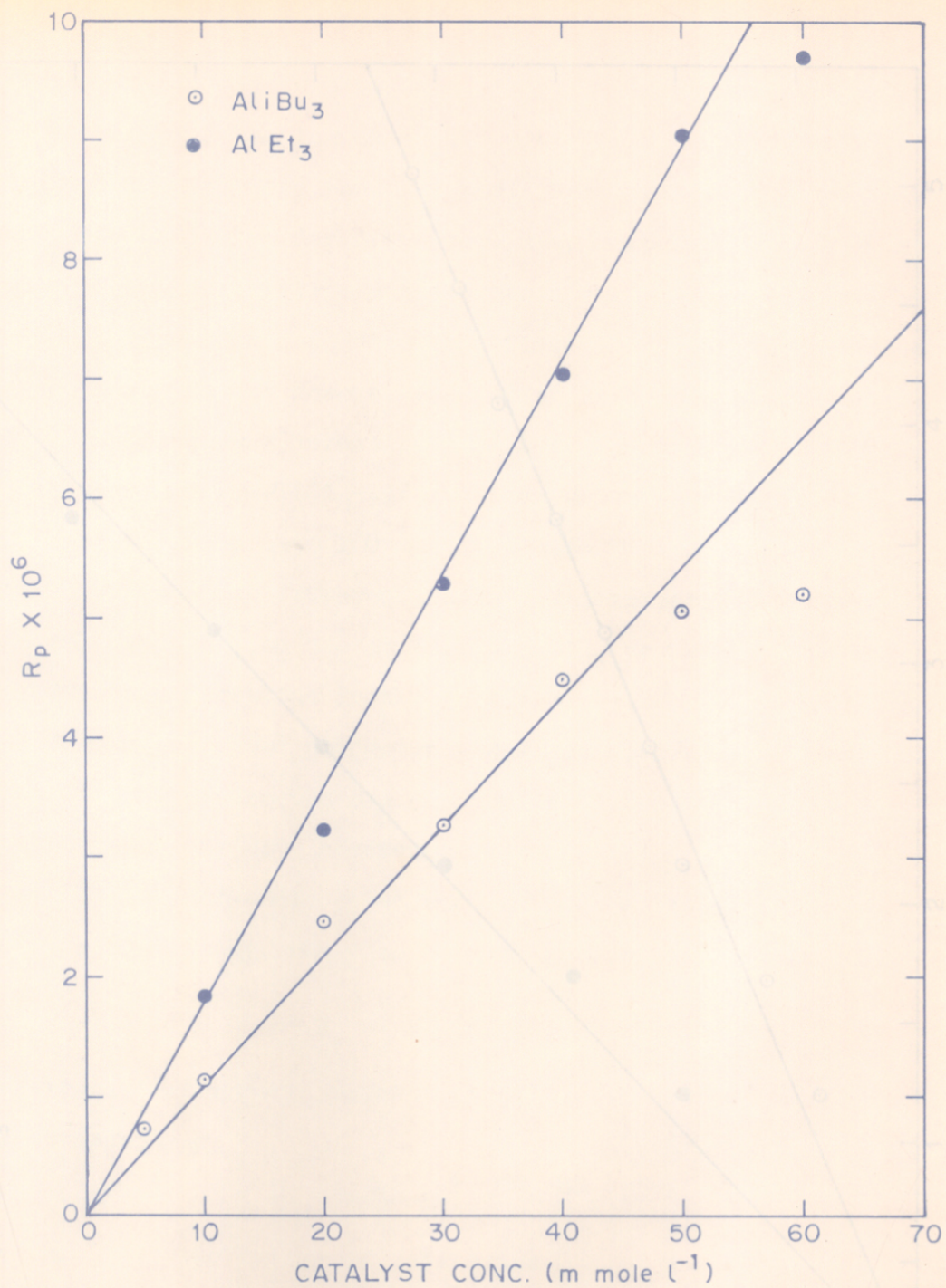


FIG. 11. VARIATION OF STEADY STATE RATE WITH CATALYST CONCENTRATION

aluminium alkyls, Burnett and Tait reported a varying rate of polymerization lasting about 200 min. Subsequently, steady state polymerization was observed. More interestingly, they reported a first-order dependence with respect to monomer only above a certain minimum concentration viz. 3.6 mole.l^{-1} . In the present case, the data show that first-order dependence holds good to the lowest monomer concentration examined (1.2 mole.l^{-1}). Otto and Parravano investigated³⁵ the polymerization of styrene in benzene with $\alpha\text{-TiCl}_3\text{-AlEt}_3$. They observed an initial increase in rate upto 100 min. followed by a steady state period. With reference to time-conversion characteristics, our results in n-heptane by the use of $\text{BuOTiCl}_3\text{-AlR}_3$ are similar to those of Otto and Parravano in that after a short initial settling period steady state polymerizations are observed. However, Otto and Parravano reported a 1.5 power dependence of rates of polymerizations with reference to monomer.

With first-order dependence of rate with $[\text{M}]$ and $[\text{Cat}]$ in the present study, the rate law may be represented as:

$$R_p = k_p [\text{M}] [\text{C}]$$

where k_p is the rate constant of polymerization.

More generally,

$$R_p = A [\text{M}] [\text{C}] e^{-E_a/RT}$$

where E_a is the energy of activation.

Polymerizations were conducted at 40, 50 and 60°C in order to determine the effect of temperature on the rates of

Table 11
Steady state polymerizations at different temperatures

Temp. (°C)	AlIBu ₃ ^a		AlEt ₃ ^b		Mol.wt. $\times 10^{-4}$
	Steady state rate $R_p \times 10^6$ (mole.l ⁻¹ .s ⁻¹)	Mol.wt. $\times 10^{-4}$	Steady state rate $R_p \times 10^6$ (mole.l ⁻¹ .s ⁻¹)	Mol.wt. $\times 10^{-4}$	
40	2.187	5.30	4.10	4.24	
50	3.48	4.43	7.05	3.06	
60	6.11	2.94	11.50	1.81	

(a) [M] = 4.08, [Ti] = 0.03, [Al] = 0.03, Aging time = 20 min.

(b) [M] = 3.60, [Ti] = 0.04, [Al] = 0.06, Aging time = 10 min.

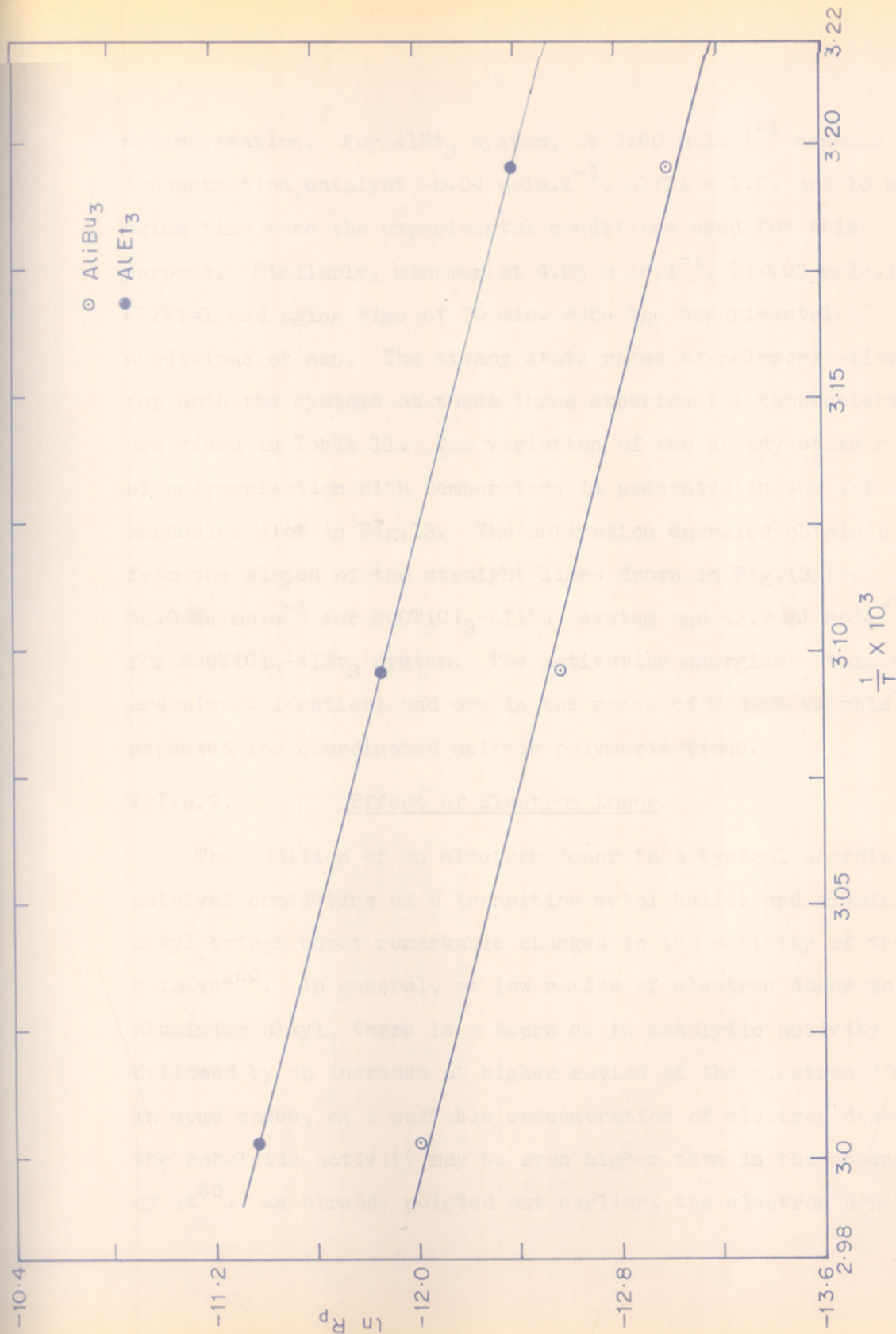


FIG. 13. ARRHENIUS PLOT FOR STYRENE POLYMERIZATION WITH BuOTiCl₃-AlR₃

polymerization. For AlEt_3 system, a 3.60 mole.l⁻¹ monomer concentration, catalyst = 0.04 mole.l⁻¹, Al/Ti = 1.5, and 10 min. aging time were the experimental conditions used for this purpose. Similarly, monomer at 4.05 mole.l⁻¹, Ti 0.03 mole.l⁻¹, Al/Ti=1 and aging time of 20 min. were the experimental conditions chosen. The steady state rates of polymerizations for both the systems at these three experimental temperatures are given in Table 11. The variation of the steady state rates of polymerization with temperature is presented in the form of Arrhenius plot in Fig.13. The activation energies obtained from the slopes of the straight lines drawn in Fig.13 are 46.0 kJ mole⁻¹ for $\text{BuOTiCl}_3\text{-Al}i\text{Bu}_3$ system and 43.7 kJ mole⁻¹ for $\text{BuOTiCl}_3\text{-AlEt}_3$ system. The activation energies obtained are almost identical and are in the range of 29-64 kJ mole⁻¹ expected for coordinated anionic polymerizations.

III.a.7. Effect of Electron Donor

The addition of an electron donor to a typical coordination catalyst consisting of a transition metal halide and aluminium alkyl brings about remarkable changes in the activity of the catalyst⁶⁰. In general, at low ratios of electron donor to aluminium alkyl, there is a decrease in catalytic activity followed by an increase at higher ratios of the electron donor. In some cases, at a suitable concentration of electron donor, the catalytic activity may be even higher than in the absence of it⁶⁰. As already pointed out earlier, the electron donors

in combination with transition metal compounds can also form 'alkyl-free' catalysts, which bring about polymerization of α -olefins (especially ethylene and propylene).

Analysis of the coordination polymerization reactions in the presence of electron donors is complicated by the fact that electron donor can complex both with transition metal component as well as the base metal alkyls like aluminium alkyl. Several of the reactions involving aluminium alkyls (other than polymerizations) are profoundly effected by electron donors⁴¹. Hence the effect of electron donors in the coordination polymerizations were mainly explained on the basis of its complexing ability with the aluminium alkyls.

Boor tried⁶⁰ to circumvent the complexities due to the ability of the electron donor to complex simultaneously with the aluminium alkyls and the titanium halides by employing ZnEt_2 so that the resultant effect of the electron donor can only be explained on the basis of its complexation with the transition metal component. Complexes formed between electron donors and aluminium alkyls are well known. Tait and Burfield opine⁹⁵ that the complexing ability of ZnEt_2 with electron donor cannot be completely ignored.

The effect of triethylamine, an electron donor, in the course of polymerization was probed in the two trialkylaluminium containing catalyst systems investigated here. These polymerizations were conducted at 50°C with styrene concentration of 3.6 mole.l^{-1} . A catalyst concentration of 0.03 and 0.04 mole.l^{-1} ,

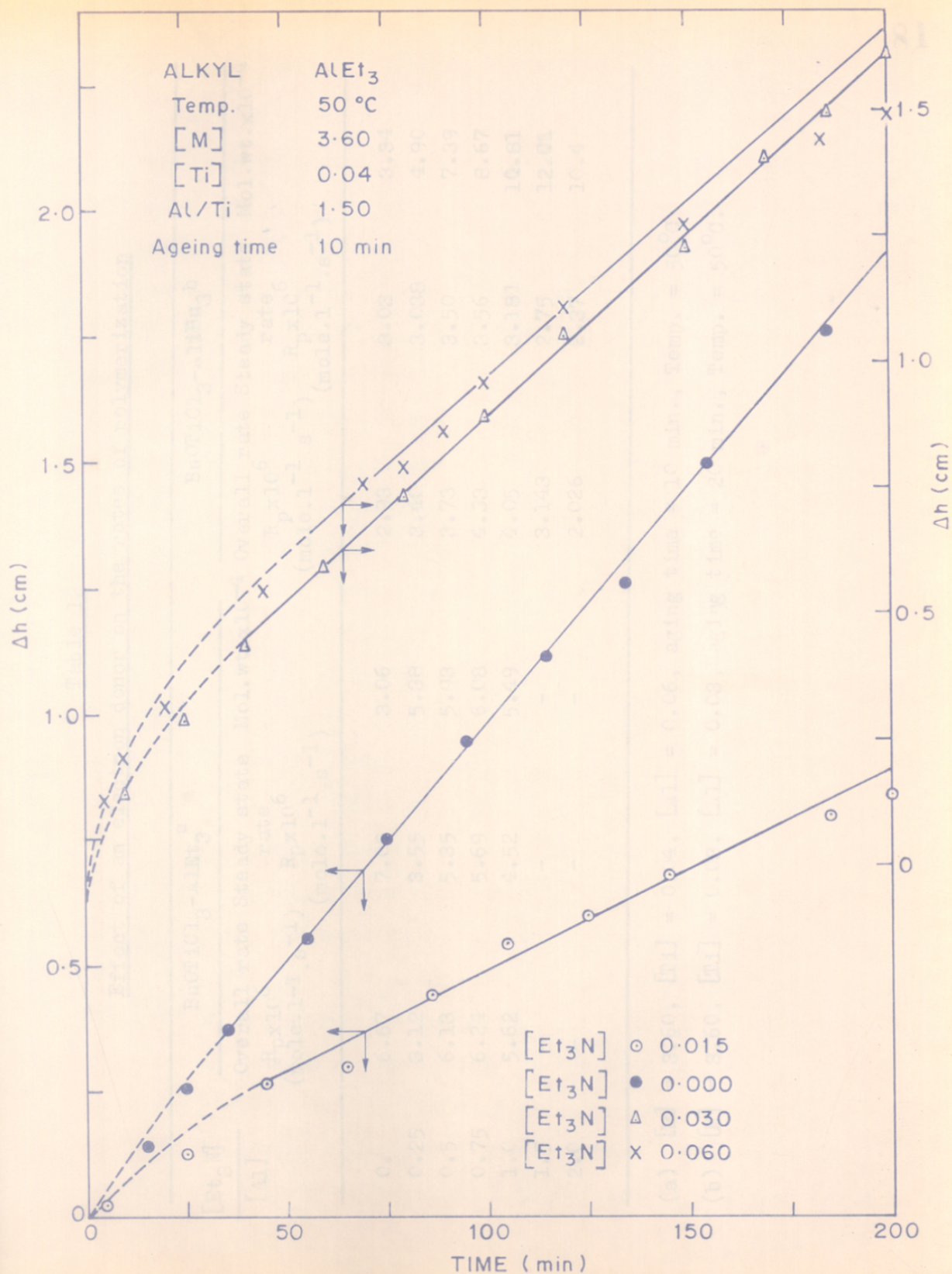


FIG. 14. CONVERSION-TIME CURVES AT VARYING CONCENTRATIONS OF TRIETHYLAMINE

Table 12

Effect of an electron donor on the rates of polymerization

$\frac{[Et_3N]}{[Al]}$	BuOTiCl ₃ -AlEt ₃ ^a		BuOTiCl ₃ -Al <i>i</i> Bu ₃ ^b		
	Overall rate $R_p \times 10^6$ (mole.l ⁻¹ .s ⁻¹)	Steady state rate $R_p \times 10^6$ (mole.l ⁻¹ .s ⁻¹)	Mol.wt. $\times 10^{-4}$	Overall rate $R_p \times 10^6$ (mole.l ⁻¹ .s ⁻¹)	Steady state rate $R_p \times 10^6$ (mole.l ⁻¹ .s ⁻¹)
0	6.67	7.05	3.06	2.93	3.03
0.25	3.12	3.55	5.38	3.40	3.038
0.5	6.13	5.35	5.93	3.73	3.50
0.75	6.24	5.69	6.08	4.33	3.56
1.0	5.62	4.52	5.49	4.05	3.181
1.5	-	-	-	3.143	2.75
2.0	-	-	-	2.026	2.37
					10.4

(a) $[M] = 3.60$, $[Ti] = 0.04$, $[Al] = 0.06$, aging time = 10 min., Temp. = 50°C(b) $[M] = 3.60$, $[Ti] = 0.03$, $[Al] = 0.03$, aging time = 20 min., Temp. = 50°C.

Al/Ti ratio of 1.0 and 1.5 and aging times of 20 min. and 10 min. respectively were employed for the $\text{Al}(\text{iBu})_3$ and AlEt_3 containing systems. The electron donor to alkylaluminium ratios were varied from 0.25 to 2.0 and 0.25 to 1.0 respectively. Fig.14 shows the time-conversion plots at three varying ratios of electron donor in the case of $\text{BuOTiCl}_3\text{-AlEt}_3$. For comparative purposes, the data for the electron donor-free system are also given. Table 12 lists the overall and stationary state rate for both trialkyl aluminium containing catalysts along with the molecular weight of the final polymer obtained from the polymerization. The variation of the steady state rate of polymerization with varying ratios of electron donor to aluminium alkyl is shown in Fig.15. It is seen (Fig.15) that at very low ratios of electron donor: AlEt_3 , there is a sharp decrease in the rates of polymerization. With further increase in electron donor concentration, the value of R_p increases reaching a maximum at an electron donor to aluminium triethyl ratio of 0.75. Further increase in electron donor concentration brings about a decreased rate. However, in the case of $\text{Al}(\text{iBu})_3$, though investigated over wider range of electron donor concentration, the variation in the rates of polymerization is not significant. A shallow maximum is observed at an electron donor: $\text{Al}(\text{iBu})_3$ ratio of 0.75. Significant decrease in rate is observed only at the $\text{Et}_3\text{N}:\text{Al}(\text{iBu})_3$ ratio of 2.0, the highest concentration of electron donor investigated.

The following experimental results have to be taken into consideration in order to explain the effect of electron donor

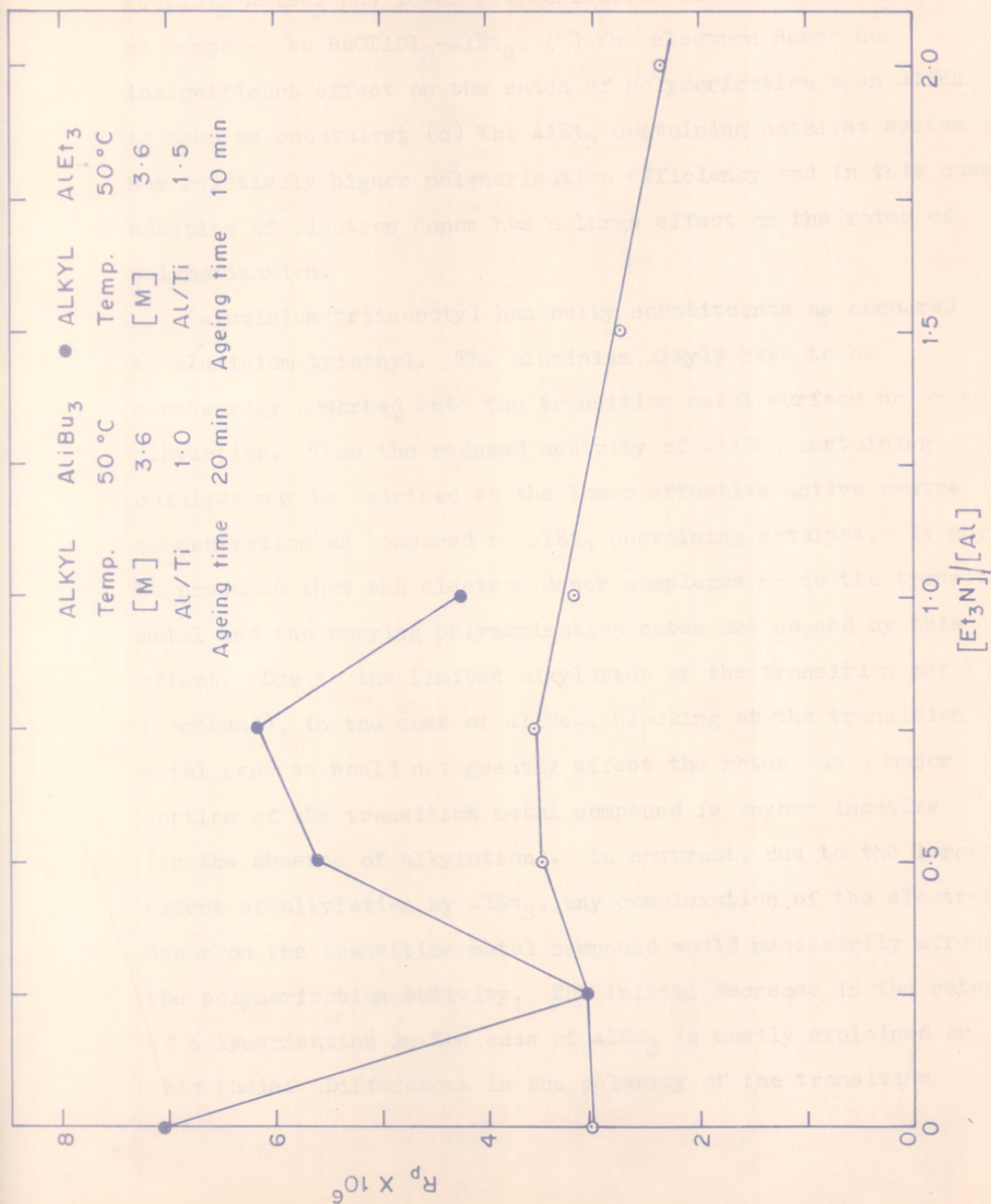


FIG. 15. VARIATION OF STEADY STATE RATE WITH TRIETHYLAMINE

on the rates of polymerization observed in this study. (a) $\text{BuOTiCl}_3\text{-Al}(\text{iBu})_3$ has lower polymerization activity for styrene as compared to $\text{BuOTiCl}_3\text{-AlEt}_3$, (1) The electron donor has insignificant effect on the rates of polymerization when $\text{Al}(\text{iBu})_3$ is used as cocatalyst (c) The AlEt_3 containing catalyst system has relatively higher polymerization efficiency and in this case addition of electron donor has a large effect on the rates of polymerization.

Aluminium triisobutyl has bulky substituents as compared to aluminium triethyl. The aluminium alkyls have to be necessarily adsorbed onto the transition metal surface prior to alkylation. Thus the reduced activity of $\text{Al}(\text{iBu})_3$ containing catalyst may be ascribed to the lower effective active centre concentration as compared to AlEt_3 containing catalyst. It may be presumed that the electron donor complexes on to the transition metal and the varying polymerization rates are caused by this effect. Due to the limited alkylation of the transition metal (compound), in the case of $\text{Al}(\text{iBu})_3$, blocking at the transition metal centres would not greatly effect the rates, as a major portion of the transition metal compound is anyhow inactive (in the absence of alkylation). In contrast, due to the larger extent of alkylation by AlEt_3 , any complexation of the electron donor on the transition metal compound would necessarily effect the polymerization activity. The initial decrease in the rates of polymerization in the case of AlEt_3 is easily explained on this basis. Differences in the polarity of the transition

metal-carbon bond with the extent of complexation of electron donor as proposed by Simon et al⁹⁶ can explain the increased activity at electron donor to aluminium triethyl ratio of 0.5 to 0.75 and decreased at still higher concentrations of Et_3N .

The molecular weights obtained from final polymerization are also listed in Table 12. In the case of AlEt_3 , there is a large and continuous increase in molecular weight upto $\text{Et}_3\text{N}/\text{Al}$ ratio of 1.5. Only slight decrease in molecular weight with further increase in electron donor concentration is observed. In the case of AlEt_3 , the initial addition of electron donor brings about a large increase in molecular weight. With further increase in electron donor concentration, the molecular weights do not increase appreciably. The variation in molecular weights can be attributed to the complexation of electron donor with the aluminium alkyl resulting in depletion of aluminium alkyl and hence lesser extent of alkyl transfer in the presence of electron donor.

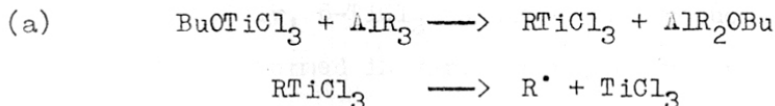
III.a.8. Chemical Nature of the Active Centre

The chemical nature of the active species effecting coordination polymerization is still not established to the total satisfaction. However, consensus appears to be emerging^{60,28} that the active species in the heterogeneous catalysts is the alkylated σ -bonded transition metal compound at a valence state lower than the permissible maximum. In the case of homogeneous catalysts, complexes of the maximum valent titanium

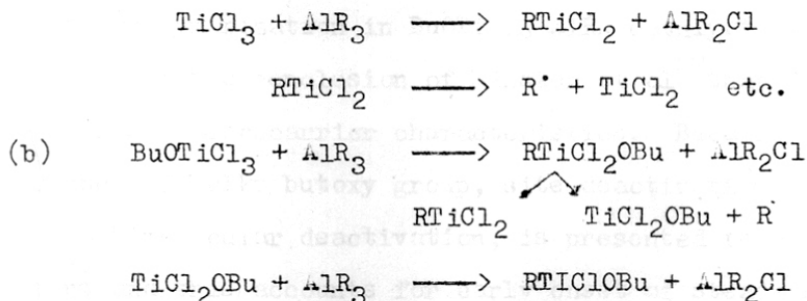
halide with the aluminium alkyl are believed to bring about polymerization⁶⁷. Yermakov et al²⁷ suggested a lower valent alkylated transition metal compound bonded to the crystalline lattice of the support as the active species in supported catalysts.

The activity of the $\text{BuOTiCl}_3\text{-AlR}_3$ catalyst investigated here parallel the Ti^{+3} content implying a trivalent titanium halide as the active species in these polymerizations. In analogy with the reaction schemes proposed for TiCl_4 and AlR_3 , the possible reaction scheme in the case of BuOTiCl_3 and AlR_3 can be formulated.

The alkylation of the transition metal compound may follow reaction sequences (a) involving exchange of butoxy ligand for alkyl in the first reaction sequence (b) involving chloride ligand exchange for the alkyl ligands.



and with further alkylation and reduction, ~~the following reaction scheme is proposed~~

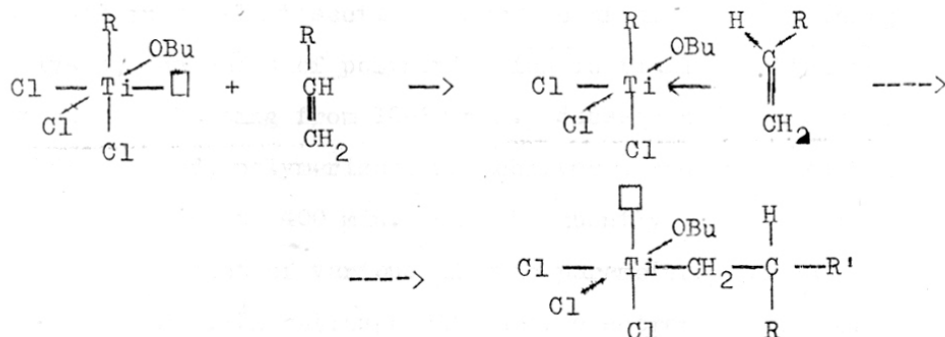


The trivalent titanium species ~~are~~ possible are RTiCl_2

and RTiClOBu . TiCl_2OBu which may be formed in the reaction can be ruled out as the active species for it does not possess a transition metal-alkyl bond. RTiCl_2 and RTiClOBu are the other possible alkylated transition metal halides. The low polymerization activity of the present system does not favour RTiCl_2 as the active species, since $\text{TiCl}_3\text{-AlR}_3$ catalyst system is generally more vigorous in polymerization than observed in this case. For example, the overall rate constant of polymerization of ethylene with $\text{TiCl}_3\text{-AlR}_3$ are of the order of magnitude $2.5 \text{ l.mole}^{-1}.\text{s}^{-1}$. Whereas both the overall and steady state rate constants of polymerization observed here for both the trialkyl aluminium systems are in the range of $10^{-5} - 10^{-6} \text{ l.mole}^{-1}.\text{s}^{-1}$. The low reactivity would indicate that RTiClOBu as the possible active species. The formation of $\beta\text{-TiCl}_3$ in the reaction of BuOTiCl_3 with aluminium alkyls has been inferred³⁷ on the basis of ESR studies. Possibly, $\beta\text{-TiCl}_3$ is the major product formed and RTiClOBu may be formed in very minor proportion. This may be the reason for the low reactivity in these catalyst systems. The proposal that RTiClOBu may be the active species responsible for the polymerization in $\text{BuOTiCl}_3\text{-AlR}_3$ catalyst system is in accord with the conclusion of Minsker et al³⁷ that the alkoxy group has a microcarrier characteristics. Because of the presence of bulky butoxy group, site deactivation especially due to bimolecular deactivation, is presented to a very large extent and this accounts for early onset of steady state polymerization.

RTiClOBu may be assumed to possess an octahedral symmetry and a vacancy in analogy with Cossee's mechanism.

The reaction mechanism, coordinated-anionic type, on the basis of activation energy observed may be formulated as follows:



The mechanism proposed is in analogy with Cossee's mechanism in heterogeneous polymerizations.

Molecular weights at intermittent conversions corresponding to 20, 40 and 60 min. of polymerization were determined in one of the experiments for both the trialkyl systems. It was observed that maximum molecular weights obtained at the final conversion were attained at 40 min. of polymerization showing that the life-time of growth is short as compared to large life-time reported by Bier et al.¹¹⁹ for propylene polymerization using $\text{AlEt}_2\text{Cl}-\text{TiCl}_3$.

III.b. Kinetics of Styrene Polymerization using
BuOTiCl₃-AlEt₂Cl

The kinetics of styrene polymerization in heptane using butoxy titanium trichloride and aluminium trialkyls has been discussed in the last section. For the trialkyls containing catalysts, the rates of polymerization initially decline for a short period lasting from 10-60 min. Subsequent to the short settling period, polymerizations achieved a steady state behaviour lasting from 150 to 400 min. and subsequently showed declining rates. The effect of various kinetic parameters such as aging times, varying Al/Ti ratios, addition of electron donor etc. as well as varying concentration of catalyst and monomer were investigated. The steady state rate of polymerization showed a first-power rate-law with reference to the catalyst and the monomer. The rates exhibited a maximum with varying Al/Ti ratio.

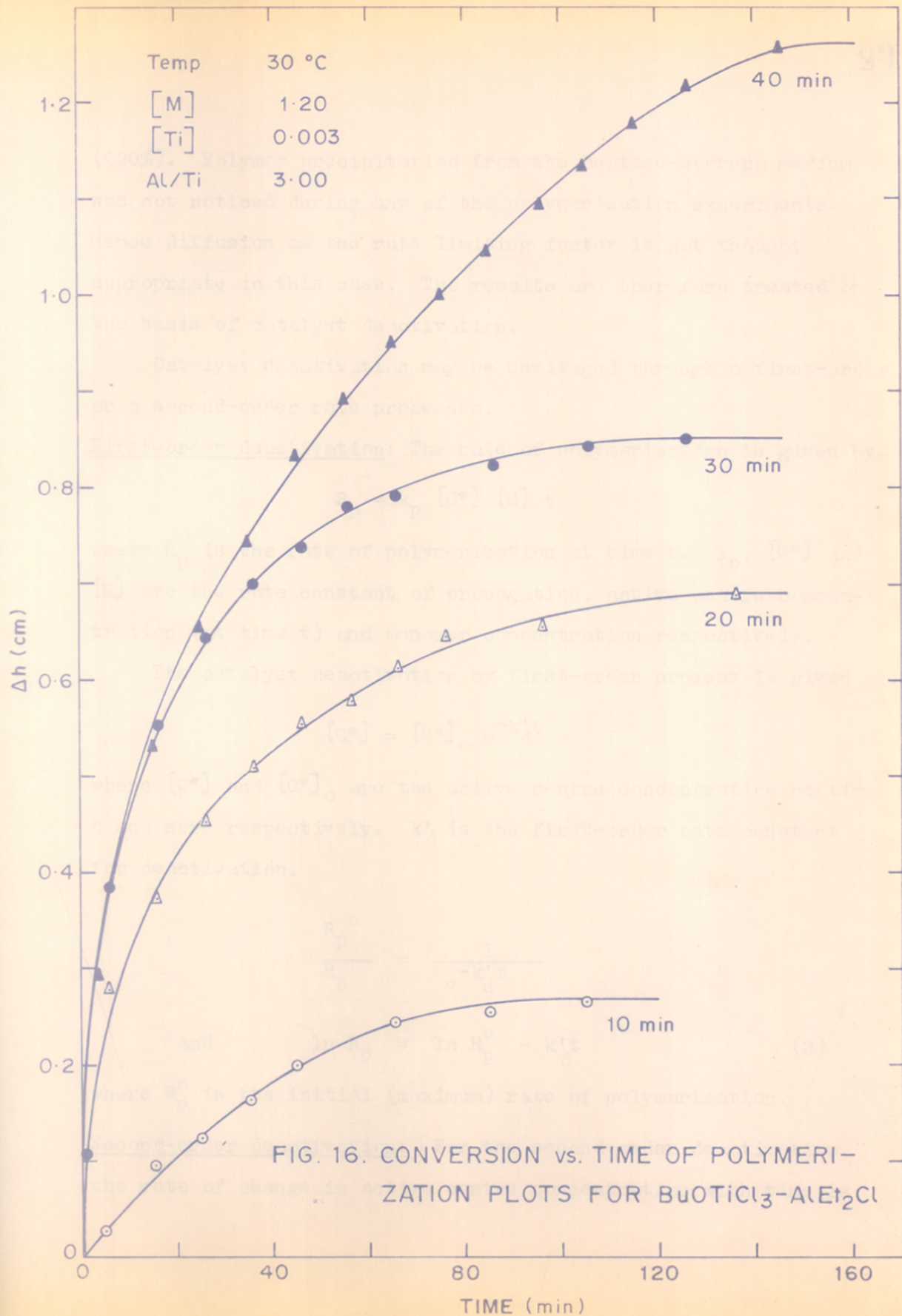
On the basis of steady state behaviour and oxidation state of transition metal element, a trivalent alkylated transition metal species was proposed as the active centre for polymerization. However, the initial settling period during which the rates declined before achieving a steady state, could not be probed in detail due to the short duration of the settling period.

The polymerization of styrene in n-heptane was also studied using BuOTiCl₃-AlEt₂Cl as catalyst. The rates of polymerization were observed to decline continuously. Hence the catalyst system BuOTiCl₃-AlEt₂Cl was utilized for the study of deactivation in some detail.

The method of experimentation was identical to those employed for trialkyl containing systems. The cocatalyst and the catalyst solutions were mixed in the dilatometer and the catalyst aged at ambient temperature. Monomer was mixed with the aged catalyst and the mixture transferred to the dilatometer bulb. The dilatometer was mounted in a thermostat and the course of polymerization monitored by following the height of the meniscus at various reaction times. The rates of polymerizations were calculated by using equations (1) or (2)

Fig.16 shows the time conversion curves obtained for catalyst aged to 10, 20, 30 and 40 min. It is observed that the rates continuously declined and in some cases achieve limiting conversions e.g. catalyst solutions aged to 10, 20 and 30 min. in Fig.16. In some of the experimentations, polymerizations were monitored upto 350 min. and in no case a period of steady state polymerization could be observed.

The continuously declining rates of polymerization can either be due to (i) physical limitations such as diffusion controlled reactions, or (ii) decreasing activity of catalyst with time. In heterogeneous polymerizations, especially for ethylene and propylene polymerizations, diffusion control has been proposed¹²⁰ as the cause of the lower activity at higher conversions. However, Begley on the basis of theoretical calculations concluded¹⁰⁰ that even in such cases, diffusion need not be the rate controlling factor. In the present case, polymerizations were carried out to low ultimate conversions



(<20%). Polymer precipitation from the heptane-styrene medium was not noticed during any of the polymerization experiments. Hence diffusion as the rate limiting factor is not thought appropriate in this case. The results are therefore treated on the basis of catalyst deactivation.

Catalyst deactivation may be envisaged through a first-order or a second-order rate processes.

First-order deactivation: The rate of polymerization is given by:

$$R_p = k_p [C^*] [M] t$$

where R_p is the rate of polymerization at time t . k_p , $[C^*]$ and $[M]$ are the rate constant of propagation, active centre concentration (at time t) and monomer concentration respectively.

The catalyst deactivation by first-order process is given by:

$$[C^*] = [C^*]_0 e^{-k'_d t}$$

where $[C^*]$ and $[C^*]_0$ are the active centre concentration at time t and zero respectively. k'_d is the first-order rate constant for deactivation.

$$\frac{R_p^0}{R_p} = \frac{1}{e^{-k'_d t}}$$

$$\text{and} \quad \ln R_p = \ln R_p^0 - k'_d t \quad (3)$$

where R_p^0 is the initial (maximum) rate of polymerization.

Second-order deactivation: For the second-order deactivation, the rate of change in active centre concentration with time is

Table 13

First and Second-Order rates of deactivation in styrenePolymerization using BuOTiCl_3 - AlEt_2Cl at 30°C

$$[\text{M}] = 1.677$$

$$[\text{Ti}] = 0.002$$

$$[\text{Al}] = 0.006$$

Aging time = 40 min.

$$\Delta h_\infty = 32.1036 \text{ cm}$$

$$R_p = \frac{\Delta h}{\Delta h_\infty} \times \frac{1}{t} \times [\text{M}]$$

Time (min.)	Δh (cm)	$\frac{R_p}{[\text{M}]} \times 10^3$	$\ln \frac{R_p}{[\text{M}]}$	$\frac{[\text{M}]}{R_p}$
0	-	-	-	-
10	0.560	1.740	-6.35	574
20	0.916	1.428	-6.55	700
35	1.218	1.084	-6.82	922
55	1.436	0.813	-7.11	1229
70	1.520	0.676	-7.19	1479
90	1.670	0.578	-7.45	1730
130	1.730	0.414	-7.78	2411
170	1.840	0.337	-7.99	2967
190	1.884	0.308	-8.08	3246

First-order deactivationSecond-order deactivation

$$k_d' = 0.0182 \text{ min}^{-1}.$$

$$[\text{C}^*]_0 \cdot k_d'' = 0.039 \text{ min}^{-1}$$

$$R^0 = 5.81 \times 10^{-5} \text{ mole.l}^{-1}\text{s}^{-1}. R^0 = 6.98 \times 10^{-5} \text{ mole.l}^{-1}\text{s}^{-1}.$$

given by:

$$-\frac{dC^*}{dt} = k_d'' [C^*]^2$$

Rearranging and integrating,

$$\frac{1}{[C^*]} - \frac{1}{[C^*]_0} = k_d'' t \quad \text{or}$$

$$\frac{[C^*]_0}{[C^*]} = 1 + [C^*]_0 k_d'' t$$

Substituting $\frac{R_p^0}{R_p}$ for $\frac{[C^*]_0}{[C^*]}$, and $k_p [M] [C^*]_0$ for R_p^0

$$\frac{1}{R_p} = \frac{1}{R_p^0} + \frac{k_d''}{k_p} \cdot \frac{1}{M} \cdot t \quad (4)$$

According to equation (3), a plot of $\ln R_p$ vs time resulting in a straight line, indicates a first-order deactivation. The first-order constant k_d' for deactivation is obtained from the slope of such a plot. Similarly, a linear plot of $\frac{1}{R_p}$ vs. t confirms an effective second order deactivation, in accordance with Eq. (4). The slope of such a plot multiplied by the inverse of intercept yields the composite second-order decay constant $[C^*]_0 k_d''$.

The intercept in the first and second-order plots yield initial rates valid for first and second-order deactivation rate laws.

Table 13 lists the fall in height of the meniscus at various times of polymerization, the rates of polymerization calculated by the use of equation (2), $\ln R_p$ and $\frac{1}{R_p}$ as an example of the

Table 14

Effect of aging on catalyst activity

[Styrene] = 1.2 Temp. = 30°C
 [Ti] = 0.003 [Al] = 0.009

Aging time (min.)	First-order deactivation			Second-order deactivation	
	Limiting rate $R_p \times 10^6$ (mole.l ⁻¹ .s ⁻¹)	$R^0 \times 10^5$ (mole.l ⁻¹ .s ⁻¹)	k'_d (min. ⁻¹)	$R^0 \times 10^5$ (mole.l ⁻¹ .s ⁻¹)	$[Co^*]_0 \cdot k_d''$ (min. ⁻¹)
10	2.19	0.63	0.011	0.54	0.010
20	4.20	2.49	0.025	2.49	0.032
30	5.87	7.20	0.047	7.98	0.107
40	7.00	2.91	0.025	3.99	0.037
50	6.64	2.32	0.025	3.77	0.044

data obtained. The data refer to the polymerization of styrene in heptane at 30°C using $\text{BuOTiCl}_3\text{-AlEt}_2\text{Cl}$ with $[\text{Styrene}]=1.677$, $[\text{Ti}]=0.002$, $\text{Al/Ti}=3$, aging time=40 min. The first and second-order rates of deactivation obtained from the plots of $\ln R_p$ vs. t and $1/R_p$ vs t are also included in the Table 13.

III.b.1. Effect of Kinetic Parameters

III.b.1.(i) Aging

Catalysts containing $0.003 \text{ mole.l}^{-1}$ of BuOTiCl_3 and $0.009 \text{ mole.l}^{-1}$ of AlEt_2Cl were aged for 10 to 50 min. and polymerization activities were determined using 1.2 mole.l^{-1} of styrene in n-heptane at 30°C. From the time-conversion data obtained, the first and second-order initial rates and rate constants of deactivation were determined as discussed above. The data are listed in Table 14. The second column of the table lists the limiting rates of polymerization obtained. The overall rates were maximum for the catalyst aged for 40 min. In view of the low alkylating ability of AlEt_2Cl as compared to AlR_3 , it is not surprising that longer aging periods were needed for optimum activity as compared to low aging periods in AlR_3 containing catalysts. For further experimentations to probe the effect of other kinetic variables, the catalysts were aged for 40 min.

The first-order deactivation plots were linear only during the initial stages of polymerization and second-order deactivation plots were linear throughout the course of polymerization. The deactivation kinetics is dealt in more detail in the next

Table 15

Effect of Al/Ti ratio on catalyst activity

[Styrene] = 1.2 Temp. = 30°C
 [Ti] = 0.003 Aging time = 40 min.

Al/Ti	(%)Ti+3 by titrimetry	Limiting rate $R_p \times 10^5$ (mole. $l^{-1}.s^{-1}$)	First-order deacti- vation		Second-order deacti- vation		Molecu- lar weight $\times 10^{-4}$
			$R^0 \times 10^4$ (mole. $l^{-1}.s^{-1}$)	k_d (min. $^{-1}$)	$R^0 \times 10^4$ (mole. $l^{-1}.s^{-1}$)	$[C^*]_0 \cdot k_d$ (min. $^{-1}$)	
1	80.5	4.76	4.93	0.026	6.65	0.072	2.16
2	85.4	2.60	2.21	0.032	3.07	0.062	1.93
3	90.1	0.70	0.29	0.025	0.39	0.037	1.84
4	93.5	0.56	0.84	0.045	0.58	0.090	1.37
5	95.5	0.46	0.36	0.028	0.61	0.100	1.21
6	96.0	0.43	0.12	0.018	0.12	0.025	0.74

section (III.b.2).

III.b.1(ii) Aluminium Alkyl Concentration

Polymerizations were conducted at 30°C with 1.2 mole.l⁻¹ styrene, catalyst = 0.003 mole.l⁻¹, with Al/Ti ratio varying from 1 to 6 after aging the catalyst mixture for 40 min. at room temperature. The limiting rates obtained are given in the third column of the Table 15. The oxidation state of Ti, as determined by redox titrimetry, are listed in the second column. The first-order and composite second-order rate constants are also listed. The molecular weights of the final polymers are listed in the last column.

It is seen that the limiting rates of polymerizations and molecular weights continuously decrease with increasing ratios of Al/Ti and maximum in rates have been obtained at the lowest Al/Ti ratio of 1.0 examined. The oxidation state of titanium shows continuous increase in Ti⁺³ with increasing Al/Ti ratio. No Ti⁺² content was detected even at the highest Al/Ti ratio (6.0) employed. Because of the known ability of the tetravalent titanium halides to bring about cationic polymerizations¹²¹, it is possible that some of the polymerization is due to cationic addition. Cationic polymerizations are more vigorous than the rates of coordinated anionic polymerizations obtained by the use of titanium halide-AlR₃ as catalysts. In order to make the reaction more representative of the coordinated ~~cationic~~ anionic type addition, Al/Ti ratio of 3.0 was chosen for further experimen-

Table 16

Variation of catalyst activity with catalyst concentration

[Styrene] = 1.677 Temp. = 30°C
 Aging time = 40 min. Al/Ti = 3.00

Catalyst concentration (mole l ⁻¹ .)	Initial rate(upto 30 min.) $R_p \times 10^5$ (mole. l ⁻¹ .s ⁻¹)	Overall rate(upto 150 min.) $R_p \times 10^5$ (mole. l ⁻¹ .s ⁻¹)	First-order deactivation		Second-order deactivation		Molecular weight $\times 10^{-4}$
			$\frac{R^0 \times 10^5}{k' d}$	$k' d$ (min. ⁻¹)	$\frac{R^0 \times 10^5}{[C^*]_0 k_d}$	$\frac{R^0 \times 10^5}{[C^*]_0 k_d}$ (mole. l ⁻¹ .s ⁻¹)	
1	2.18	0.60	3.35	0.016	4.29	0.042	2.73
2	3.24	1.03	5.81	0.018	6.98	0.039	2.55
3	5.22	1.48	13.21	0.027	12.42	0.049	2.00
4	8.53	1.82	37.90	0.054	37.20	0.125	1.65
5	10.40	2.21	48.70	0.060	46.50	0.142	1.64

tation, though low overall rates are obtained at this ratio.

In the case of these experiments as well, first-order deactivation could account only at the very early stage of polymerization and second-order deactivation fitted the data over a wide range of conversions.

III.b.1(iii) Catalyst Concentration

The effect of varying catalyst concentration on the course of polymerization at 30°C using $\text{BuOTiCl}_3\text{-AlEt}_2\text{Cl}$ as the catalyst was probed with varying concentrations of titanium from 0.001 - 0.005 mole.l⁻¹. A monomer concentration of 1.67 mole.l⁻¹, and Al/Ti ratio of 3 and catalyst aging time of 40 min. were used for this purpose. The initial rates upto 30 min., overall rates of polymerization upto 150 min., first and second-order rate constants of deactivation and initial rates according to first and second order deactivation are listed in Table 16. The last column lists the molecular weight of the final polymers obtained.

It is seen that the overall rates and initial rates increase with increasing catalyst concentration, whereas the molecular weight of the polymer continuously decreases. Fig.17 shows the variation in initial rates of polymerization with varying concentration of catalyst on a log-log plot. The slope of the straight line drawn is 1.0 showing that the initial rates follow a first order rate law with respect to catalyst concentration.

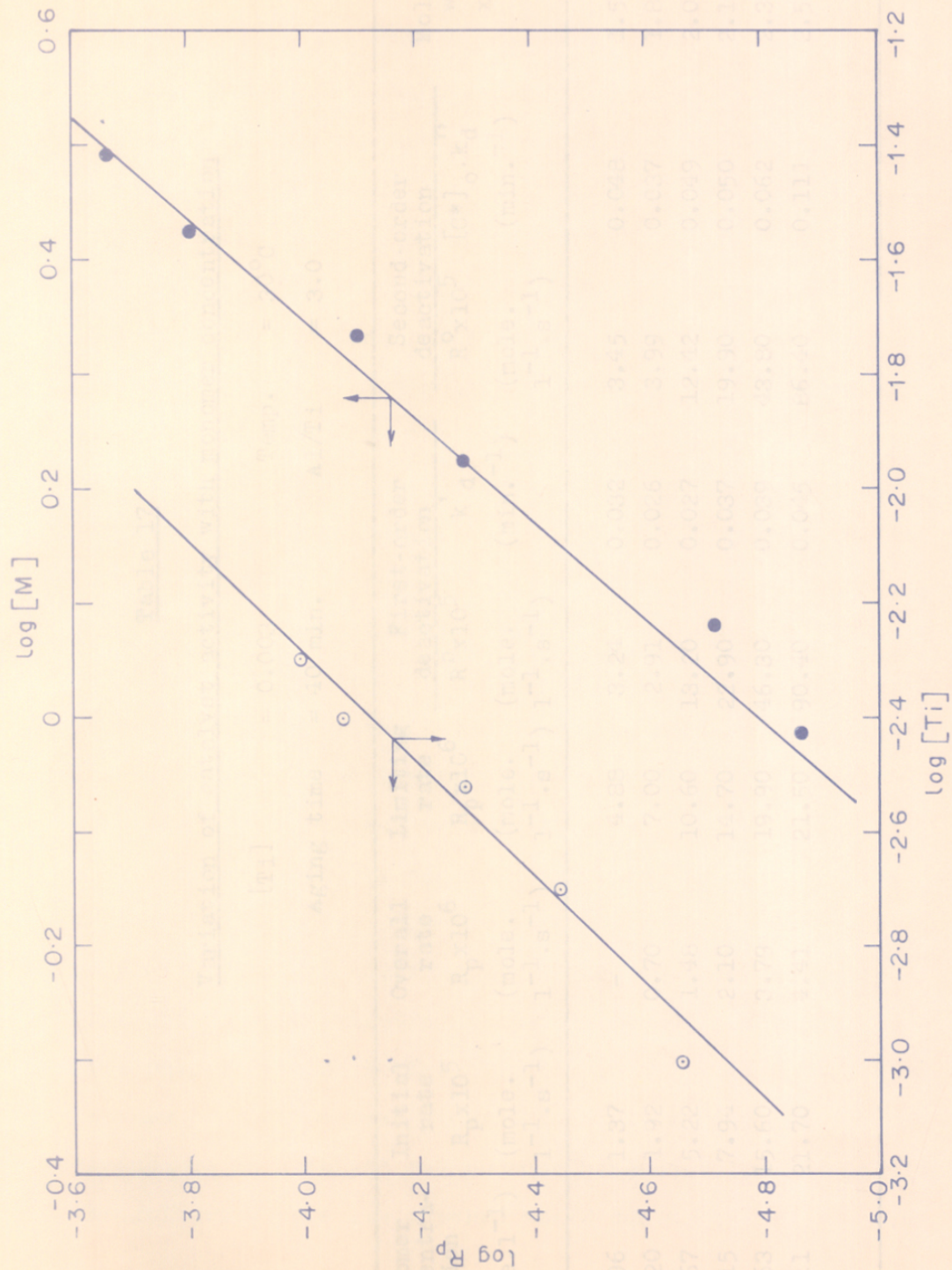


FIG. 17. VARIATION OF INITIAL RATE WITH CATALYST AND MONOMER
CATALYST SYSTEM: $\text{BuOTiCl}_3 - \text{AlEt}_2\text{Cl}$

Table 17

Variation of catalyst activity with monomer concentration

[Ti] = 0.003 Temp. = 30°C
 Aging time = 40 min. Al/Ti = 3.0

Monomer concentra- tion (mole.l ⁻¹)	Initial rate $R_p \times 10^5$ (mole. l ⁻¹ .s ⁻¹)	Overall rate $R_p \times 10^6$ (mole. l ⁻¹ .s ⁻¹)	Limiting rate $R_p \times 10^6$ (mole. l ⁻¹ .s ⁻¹)	First-order deactivation $R^0 \times 10^5$ k _d (min. ⁻¹)	Second-order deactivation $R^0 \times 10^5$ [C*] ₀ .k _d (min. ⁻¹)	Molecular weight x10 ⁻⁴
0.96	1.37	-	4.88	0.032	3.45	1.53
1.20	1.92	0.70	7.00	0.026	3.99	1.84
1.67	5.22	1.48	10.60	0.027	12.42	2.00
2.15	7.94	2.10	14.70	0.037	19.90	2.16
2.63	15.60	3.79	19.90	0.039	43.80	2.38
3.11	21.70	4.41	21.50	0.045	86.40	2.57

III.b.1 (iv)

Monomer Concentration

The effect of varying monomer concentration on the course of polymerization was investigated by varying the monomer concentration from 0.95 to 3.10 mole.l⁻¹. Catalyst concentration of 0.003 mole.l⁻¹ with Al/Ti=3 and catalyst aging time of 40 min. were utilized for this purpose. The initial, overall (upto 150 min.) and limiting rates of polymerization obtained are given in Table 17. The molecular weights of the polymers obtained are listed in the last column. As expected, the rates of polymerization (initial, overall and limiting) increase with increasing monomer concentration. The variation in the initial rate with monomer concentration is diagramatically shown in Fig.17. The straight line fit to the data shows a 2.2 power dependence of the initial rate of monomer. Similarly a 1.8 power dependence of the overall rate on monomer concentration was observed and the limiting rate showed a first power dependence with respect to monomer.

Kinetic rate laws are meaningful for the steady state of polymerization only. With continuously varying rates of polymerization and deactivation being dependant not only on time but on other kinetic parameters as well, the rate laws have only very qualitative significance in this case. However, in view of the observed first and almost second-order dependence on catalyst and monomer concentrations respectively, the following rate law appears valid during the very early

Table 18

Variation of catalyst activity with temperature

[Styrene] = 1.677 [Ti] = 0.003
 Aging time = 40 min. Al/Ti = 3.00

Temp. (°C)	Initial rate $R_p \times 10^5$ (mole. $l^{-1}.s^{-1}$)	Limiting rate $R_p \times 10^5$ (mole. $l^{-1}.s^{-1}$)	First-order deactivation		Second-order deactivation		Molecular weight $\times 10^{-4}$
			$R^0 \times 10^4$ (mole. $l^{-1}.s^{-1}$)	k'_d (min. $^{-1}$)	$R^0 \times 10^4 [C^*]$ (mole. $l^{-1}.s^{-1}$)	$\rho.k_d$ (min. $^{-1}$)	
20	9.61	1.61	5.11	0.066	5.58	0.153	3.60
25	7.06	1.32	2.69	0.047	3.98	0.152	2.74
30	5.22	1.06	1.39	0.026	1.24	0.049	2.00

stages of polymerization.

$$R_p = A [M]^{2.2} [Cat]^1 e^{-E_a/RT}$$

In the case of Ziegler-Natta polymerizations with changing rates, the rate laws reported in the literature widely differ. McCarty and Parravano¹²² observed declining rates lasting over considerable period prior to steady state in the polymerization of vinyl cyclohexane with $TiCl_3-AlEt_3$ catalyst. They reported a variable rate with respect to monomer depending on the monomer concentration.

In the present investigation, where no steady state polymerization was observed, the overall rate was almost proportional to the second power in monomer concentration. The initial rates show 2.2 power dependence on monomer, a first order dependence law could be fitted through the data for the limiting conversions.

III.b.1(v) Temperature

Effect of temperature on the course of polymerization was probed by conducting the experiments at 20, 25 and 30°C. For this purpose, a monomer concentration of $1.677 \text{ mole.l}^{-1}$, catalyst = $0.003 \text{ mole.l}^{-1}$, Al/Ti = 3 and aging time of 40 min. were used. However, for this purpose, the catalysts were aged at the temperatures of polymerization. The initial and limiting rates of polymerization as well as the first and second-order rate constants for deactivation are listed in Table 18. Fig.18 shows the Arrhenius plot for the initial rates. The activation

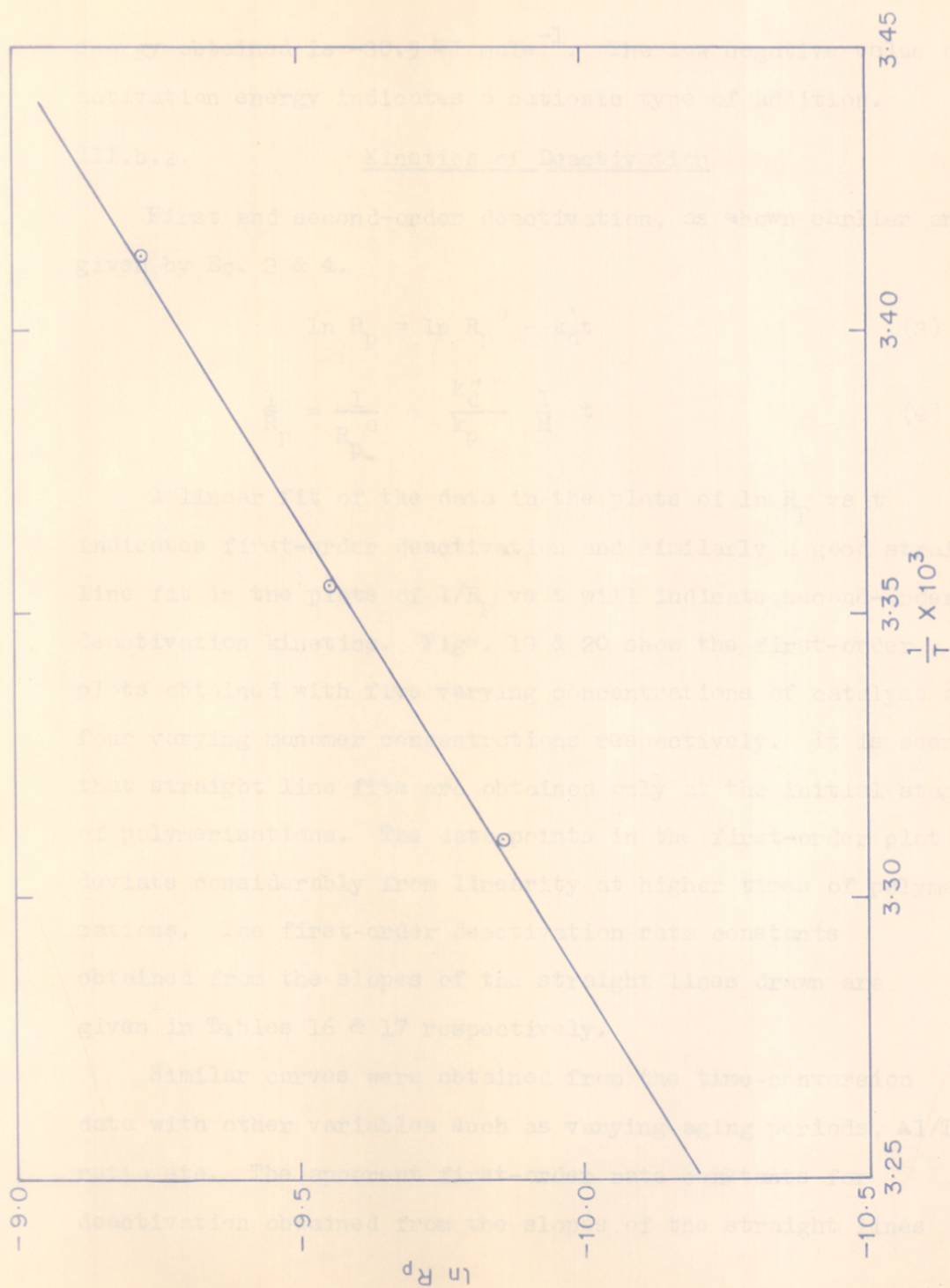


FIG. 18. ARRHENIUS PLOT FOR THE INITIAL RATES OF POLYMERIZATION
FOR SYSTEM: $\text{BuOTiCl}_3 - \text{AlEt}_2\text{Cl}$

energy obtained is $-30.5 \text{ kJ mole}^{-1}$. The low negative value of activation energy indicates a cationic type of addition.

III.b.2.

Kinetics of Deactivation

First and second-order deactivation, as shown earlier are given by Eq. 3 & 4.

$$\ln R_p = \ln R_p^0 - k_d' t \quad (3)$$

$$\frac{1}{R_p} = \frac{1}{R_p^0} + \frac{k_d''}{k_p} \frac{1}{M} t \quad (4)$$

A linear fit of the data in the plots of $\ln R_p$ vs t indicates first-order deactivation and similarly a good straight line fit in the plots of $1/R_p$ vs. t will indicate second-order deactivation kinetics. Figs. 19 & 20 show the first-order plots obtained with five varying concentrations of catalyst and four varying monomer concentrations respectively. It is seen that straight line fits are obtained only at the initial stages of polymerizations. The data points in the first-order plot deviate considerably from linearity at higher times of polymerizations. The first-order deactivation rate constants obtained from the slopes of the straight lines drawn are given in Tables 16 & 17 respectively.

Similar curves were obtained from the time-conversion data with other variables such as varying aging periods, Al/Ti ratio etc. The apparent first-order rate constants for deactivation obtained from the slopes of the straight lines

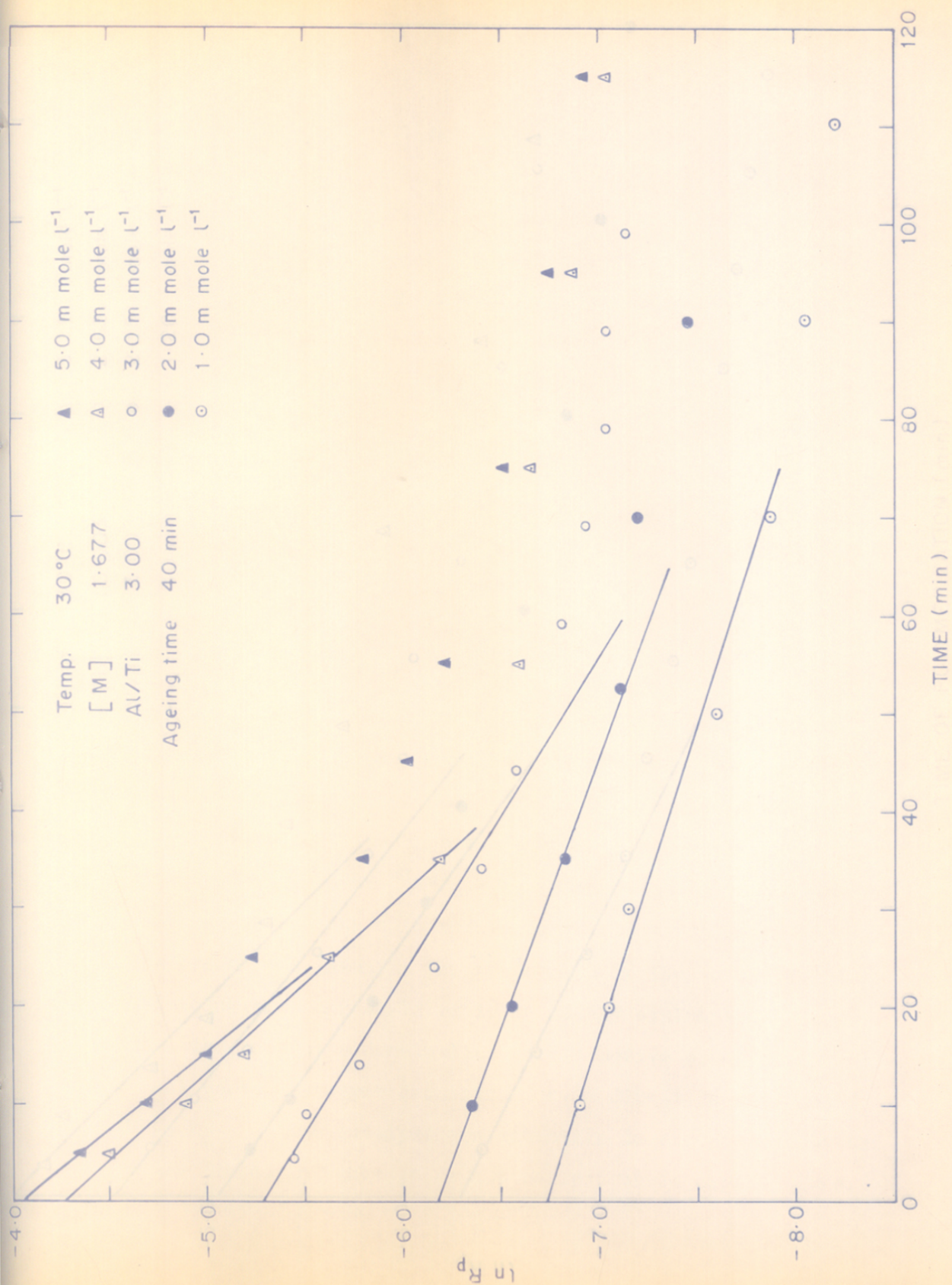


FIG. 19. $\ln R_p$ vs. TIME AT DIFFERENT CATALYST CONCENTRATIONS

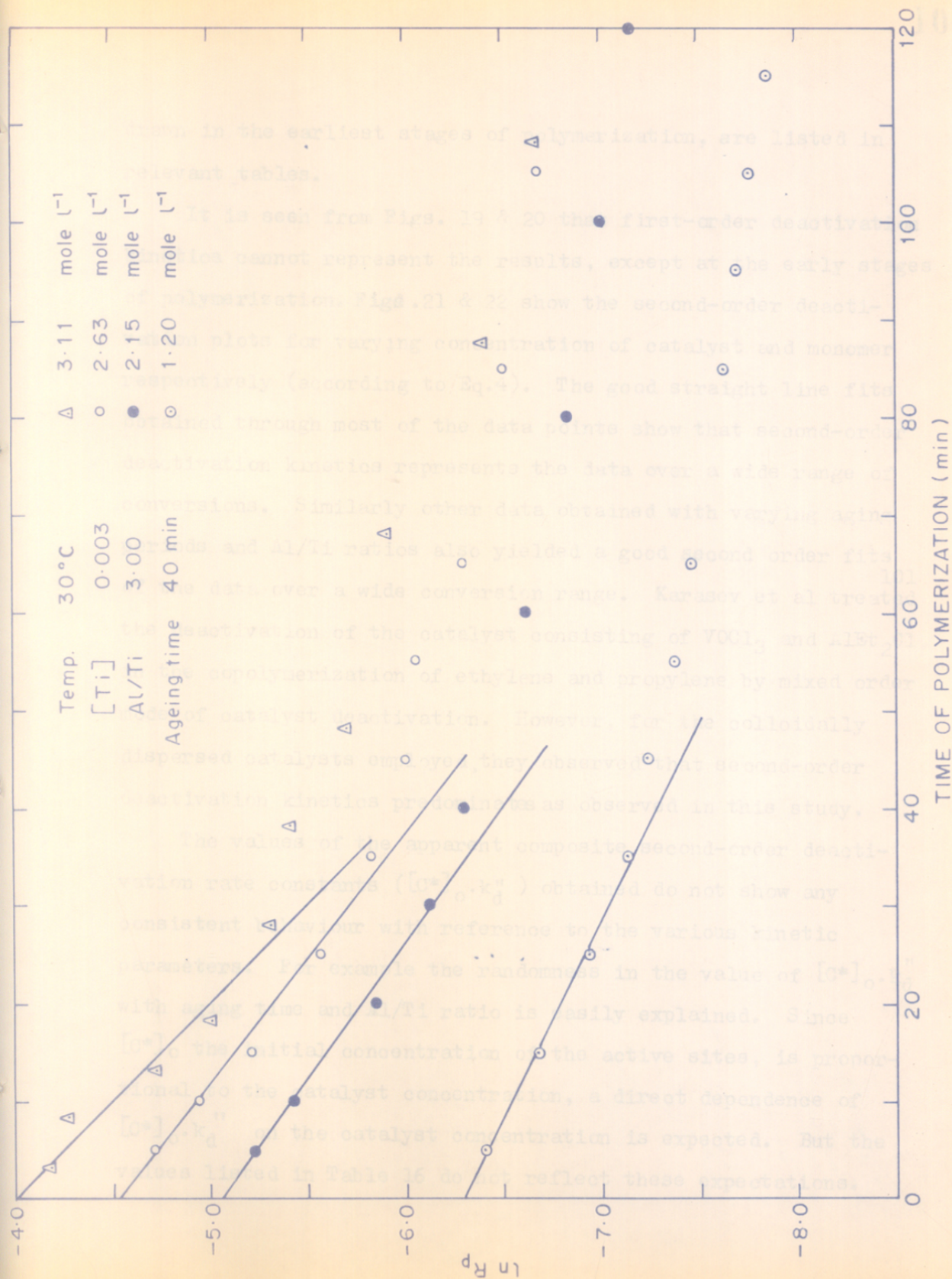


FIG. 20. $\ln R_p$ vs. TIME AT DIFFERENT MONOMER CONCENTRATIONS

drawn in the earliest stages of polymerization, are listed in relevant tables.

It is seen from Figs. 19 & 20 that first-order deactivation kinetics cannot represent the results, except at the early stages of polymerization. Figs. 21 & 22 show the second-order deactivation plots for varying concentration of catalyst and monomer respectively (according to Eq.4). The good straight line fits obtained through most of the data points show that second-order deactivation kinetics represents the data over a wide range of conversions. Similarly other data obtained with varying aging periods and Al/Ti ratios also yielded a good second order fits of the data over a wide conversion range. Karasev et al treated the deactivation of the catalyst consisting of VOCl_3 and AlEt_2Cl , in the copolymerization of ethylene and propylene by mixed order mode of catalyst deactivation. However, for the colloiddally dispersed catalysts employed, they observed that second-order deactivation kinetics predominates as observed in this study.

The values of the apparent composite second-order deactivation rate constants ($[\text{C}^*]_0 \cdot k_d''$) obtained do not show any consistent behaviour with reference to the various kinetic parameters. For example the randomness in the value of $[\text{C}^*]_0 \cdot k_d''$ with aging time and Al/Ti ratio is easily explained. Since $[\text{C}^*]_0$ the initial concentration of the active sites, is proportional to the catalyst concentration, a direct dependence of $[\text{C}^*]_0 \cdot k_d''$ on the catalyst concentration is expected. But the values listed in Table 16 do not reflect these expectations.

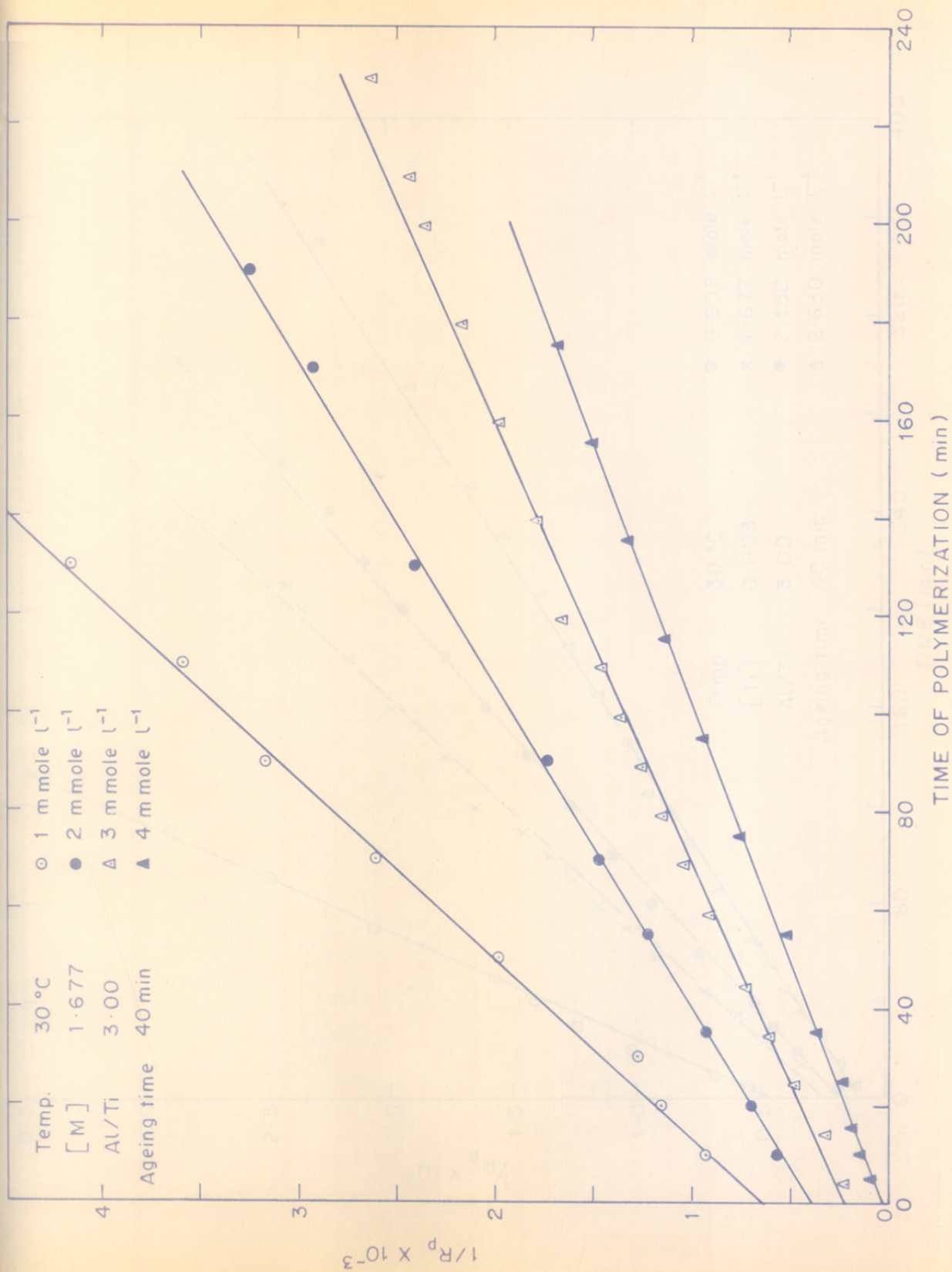


FIG. 21. $\frac{1}{R_p}$ vs. TIME AT DIFFERENT CATALYST CONCENTRATIONS.

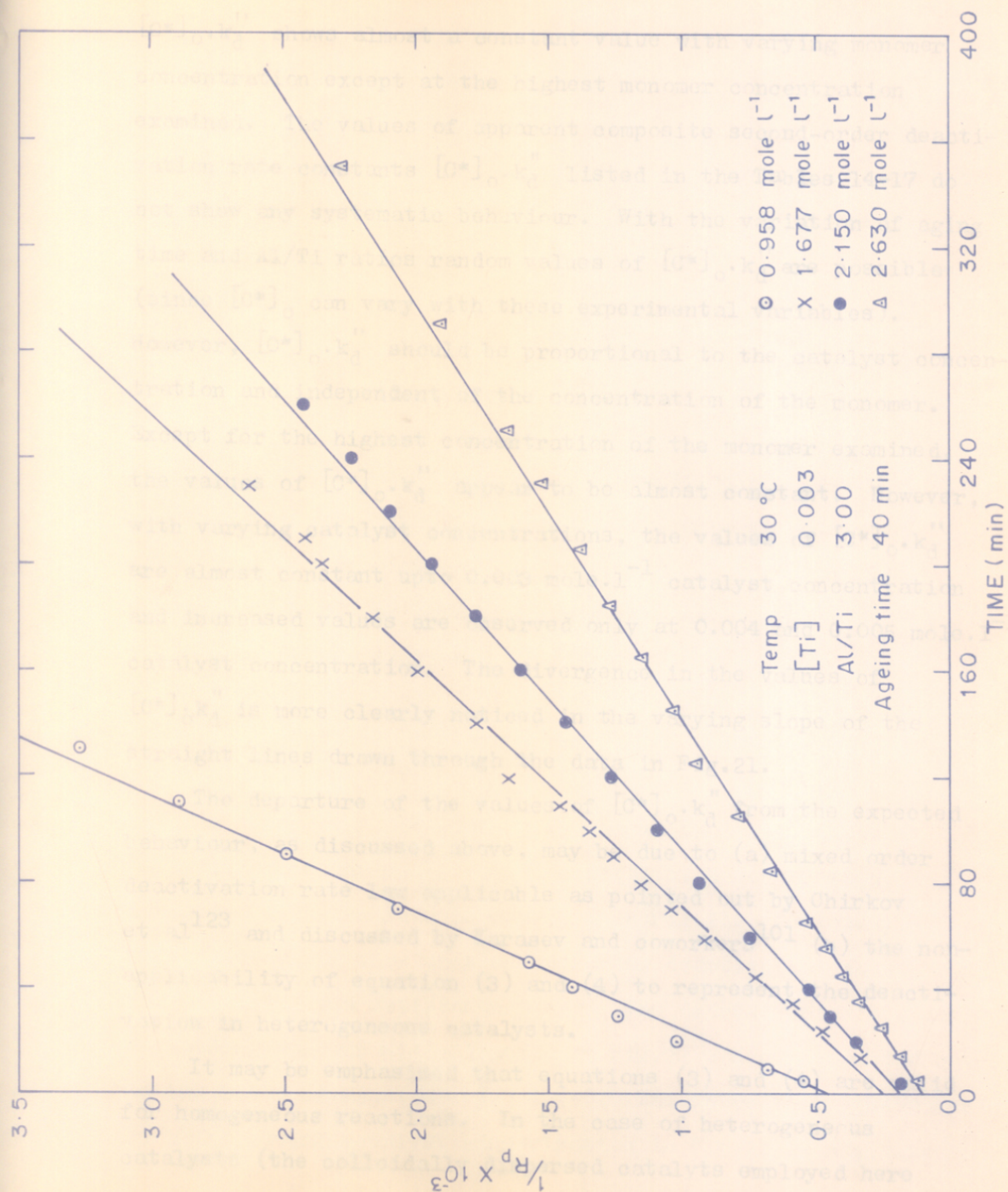


FIG. 22. $1/R_p$ vs. TIME AT DIFFERENT MONOMER CONCENTRATIONS

$[C^*]_o \cdot k_d''$ shows almost a constant value with varying monomer concentration except at the highest monomer concentration examined. The values of apparent composite second-order deactivation rate constants $[C^*]_o \cdot k_d''$ listed in the Tables 14-17 do not show any systematic behaviour. With the variation of aging time and Al/Ti ratios random values of $[C^*]_o \cdot k_d''$ are possible (since $[C^*]_o$ can vary with these experimental variables). However, $[C^*]_o \cdot k_d''$ should be proportional to the catalyst concentration and independent of the concentration of the monomer. Except for the highest concentration of the monomer examined, the values of $[C^*]_o \cdot k_d''$ appear to be almost constant. However, with varying catalyst concentrations, the values of $[C^*]_o \cdot k_d''$ are almost constant upto $0.003 \text{ mole.l}^{-1}$ catalyst concentration and increased values are observed only at 0.004 and $0.005 \text{ mole.l}^{-1}$ catalyst concentration. The divergence in the values of $[C^*]_o \cdot k_d''$ is more clearly noticed in the varying slope of the straight lines drawn through the data in Fig.21.

The departure of the values of $[C^*]_o \cdot k_d''$ from the expected behaviour, as discussed above, may be due to (a) mixed order deactivation rate law applicable as pointed out by Chirkov et al¹²³ and discussed by Karasev and coworkers¹⁰¹ (b) the non-applicability of equation (3) and (4) to represent the deactivation in heterogeneous catalysts.

It may be emphasized that equations (3) and (4) are valid for homogeneous reactions. In the case of heterogeneous catalysts (the colloiddally dispersed catalysts employed here

essentially fall in this category), surface reactions are to be taken into consideration for interpreting the results.

Schindler has given consideration⁴⁰ that the deactivation can occur only on the catalyst surface and the surface concentration and the bulk concentrations are necessarily different.

The surface concentration of the active sites, S at time t , for second-order deactivation is given by⁴⁰:

$$[S] = \frac{[S]_0}{k_d'' [S]_0 t + 1}$$

where $[S]_0$ is the initial surface concentration. Assuming that all catalyst particles have same surface concentration and that the rate of polymerization is proportional to the surface concentration of the active centres, the deactivation is related to rate of polymerization R_p by:

$$\frac{1}{R_p} = \frac{1}{R_p^0} + \frac{k_d''}{k_p [M] [Cat]} \times t \quad (5)$$

In contrast to Eq.(4), Eq.(5) shows that the slopes of $1/R_p$ vs. t decreases inversely with the catalyst concentration, in agreement with the results depicted in Fig.21. The results presented so far show that second-order deactivation accounts for the data in a satisfactory way. The decrease of slope with increasing monomer concentration in Fig.22 can be accounted both on the basis of equations (4) & (5). The decrease in the slope with increasing catalyst concentration in Fig.21 is explained

on the basis of equation (5) which essentially incorporates the effect of surface in these reactions. However, second-order deactivation involving bimolecular termination of active centres is difficult to visualise except in terms of site-migration. In the typical heterogeneous Ziegler-Natta catalysts, proposals involving site migration are of very limited reality. In contrast, bimolecular termination in these colloiddally dispersed catalysts are not improbable due to their reduced size.

Burfield has shown¹²⁴ that the initial complexation of the monomer with catalyst components results in higher rates of polymerization. The declining rates of polymerization with time by second-order deactivation processes can also be accounted by varying extents of complexation during the course of polymerization.

According to Greco et al¹²⁵, incorporation of MnCl_2 in TiCl_3 , the catalyst system results in partial solubilization of the $\text{TiCl}_3\text{-AlEt}_3$ heterogeneous catalysts in propylene polymerization. Similarly, it is possible that AlCl_3 formed from the reaction of BuOTiCl_3 and AlEt_2Cl in the catalyst results in partial solubilization and second-order deactivation, characteristics of soluble catalysts, predominates.

III.b.3. Deactivation due to Catalyst Poisoning

Gaunt demonstrated⁸⁰ that AlEtCl_2 formed by the reaction of titanium halide with AlEt_2Cl acts as a catalyst poison. He showed that the addition of AlEtCl_2 to the polymerization

system caused decreased rates of polymerization and the complexation of AlEtCl_2 formed with KEt , NaCl etc. restored the original rates of polymerization. Adsorption/complexation plays a vital part in coordination polymerizations and some of the products of the reaction between catalyst and cocatalyst components like AlEtCl_2 are also capable of complexation at the site. Therefore data obtained here, are analyzed in terms of site poisoning by the adsorbed reactant.

The method followed here is similar to that of Benson¹²⁶, who examined the clay catalyzed cationic polymerization of styrene. A Langmuir type adsorption governing the reaction kinetics was assumed. The expression obtained by Benson is given below:

$$-\frac{dM}{dt} = \frac{k_p^2 K_M [M]^2 [S]_0}{k_{tr}(1 + K_I [I] + k_p K_M [M])} \quad (6)$$

where k_p and k_{tr} are the propagation and transfer rate constants respectively. $[M]$, $[S]_0$ and $[I]$ are the concentrations of monomer, total concentration of sites and inhibitor respectively.

In the above expression K_M and K_I are the equilibrium constants for the adsorptions of monomer and inhibitor respectively.

Rearranging Eq.6 and integrating,

$$\frac{(1 + K_I [I])}{K_M \frac{k_p}{k_{tr}}} \left(\frac{1}{M} - \frac{1}{M_0} \right) - \ln \frac{M_0}{M} = k_p [S]_0 t \quad (7)$$

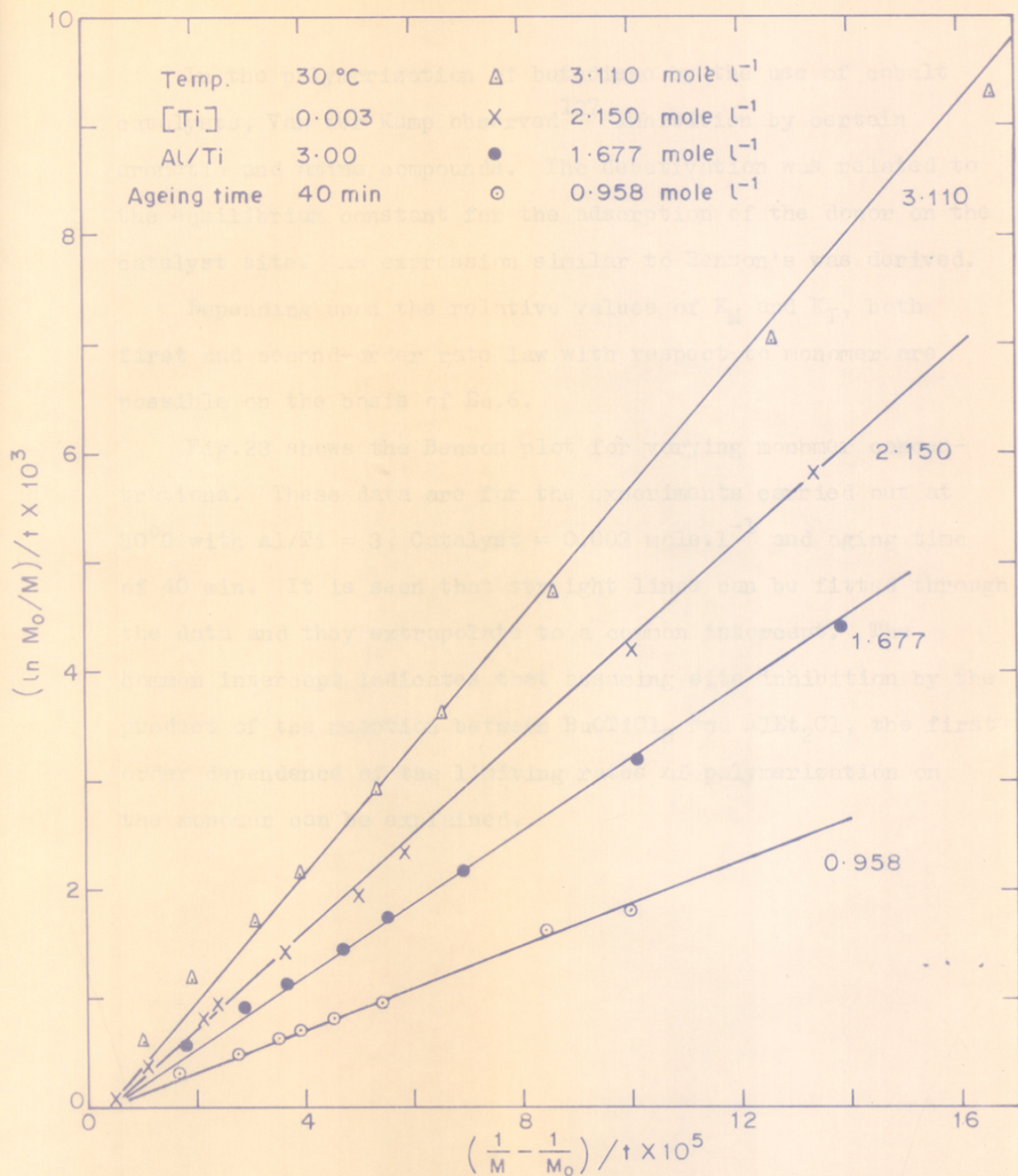


FIG. 23. BENSON PLOT FOR THE DEACTIVATION OF THE CATALYST BY SITE POISONING

In the polymerization of butadiene by the use of cobalt catalysts, Van der Kamp observed¹²⁷ inhibition by certain aromatic and amine compounds. The deactivation was related to the equilibrium constant for the adsorption of the donor on the catalyst site. An expression similar to Benson's was derived.

Depending upon the relative values of K_M and K_I , both first and second-order rate law with respect to monomer are possible on the basis of Eq.6.

Fig.23 shows the Benson plot for varying monomer concentrations. These data are for the experiments carried out at 30°C with $Al/Ti = 3$, Catalyst = 0.003 mole.l⁻¹ and aging time of 40 min. It is seen that straight lines can be fitted through the data and they extrapolate to a common intercept. The common intercept indicates that assuming site inhibition by the product of the reaction between $BuOTiCl_3$ and $AlEt_2Cl$, the first order dependence of the limiting rates of polymerization on the monomer can be explained.

CHAPTER IV

BIBLIOGRAPHY

1. D.A.Smith, 'Addition Polymers', Butterworth, London, 1968
Chap. 3.
2. P.J.Flory, 'Principles of Polymer Chemistry', Cornell
University Press, Ithaca, New York, 1953, Chap. IV.
3. M.Szwarc, 'Carbanion Living Polymers and Electron Transfer
Processes', Interscience Publishers, John Wiley and Sons,
New York, 1968.
4. P.H.Plesch, 'The Chemistry of Cationic Polymerisations',
Pergamon Press, 1963.
5. K.Ziegler, Angew.Chem. 64, 323 (1952)
6. K.Ziegler, Brennstoffe-Chem. 33, 193 (1952)
7. K.Ziegler, Belgian Pat. 533,362 (1954)
8. K.Ziegler, Petrol.Refiner 34, 111 (1955)
9. K.Ziegler, E.Holzkamp, H.Breil and H.Martin, Angew.Chem.
67, 426 (1955)
10. K.Ziegler, E.Holzkamp, H.Breil and H.Martin, Angew.Chem.
67, 541 (1955)
11. G.Natta, P.Pino, P.Corradini, F.Dannuso, E.Mantica,
G.Mazzanti and G.Moraglio, J.Am.Chem.Soc. 77, 1708 (1955)
12. G.Natta and P.Corradini, Att.Acad.Naz. Lincei. 4 (Ser.8),
73 (1955)
13. G.Natta, I.Pasquon and A.Zambelli, J.Am.Chem.Soc. 84,
1488 (1962)
14. G.Natta, P.Corradini and P.Ganis, J.Polymer Sci. 58,
1191 (1962)
15. F.Dannuso, G.Natta and I.Pasquon, Coll.Czech.Chem.Commun.
22, 191 (1957)

16. T.W.Campbell, J.Appl.Polymer Sci. 5, 184 (1961)
17. D.O.Jordon, in 'The Stereochemistry of Macromolecules', Vol.1, Ed. A.Ketley, Mercel Dekker, Inc. N.Y. 1967 Chap.I.
18. W.Cooper and G.Vaughan, in 'Progress in Polymer Science', Vol.1, Ed.A.D.Jenkins, Pergamon Press, 1967, Chap.4.
19. P.Pino and R.Mülhaupt, Angew.Chem.Int.Ed.Engl. 19, 857 (1980)
20. J.Ambroz, P.Oseky, J.Mejzlik and O.Harrik, J.Polymer Sci. C16, 427 (1967)
21. H.Feilchenfeld and M.Jesselson, J.Phys.Chem. 63, 720 (1959)
22. G.Natta, J.Polymer Sci. 34, 21 (1959)
23. C.E.H.Bawn and A.D.Ledwith, Quart.Rev.(London) 16, 361 (1962)
24. E.I.Klabunovskii, Russ.Chem.Rev. 37, 969 (1968)
25. P.Cossee, in 'Advances in the Chemistry of Coordination Compounds', MacMillan, New York, 1961, pp.241.
26. J.Boor, Jr. Ind.Eng.Chems.Prod.Res.Develop. 9, 437 (1970)
27. V.A.Zakharov, G.D.Bukatov, N.B.Chumaevskii and Yu.I. Yermakov, Kinet.Katal. 18, 704 (1977)
28. P.J.T.Tait, Specialist Periodical Report, Macromolecular Chemistry, 1, 3 (1980)
29. A.Munoz-Escalona, A.Martin and J.Hidalgo, Eur.Polym.J. 17, 367 (1981)
30. M.Roha, Adv.Polym.Sci. 5, 353 (1966)
31. B.D.Phillips, T.L.Hanlon and A.V.Tobalsky, J.Polymer Sci. A2, 2431 (1964)
32. C.G.Overberger and P.A.Jarovitzky, J.Polymer Sci. A3, 1483 (1965)

33. G.M.Burnett and P.J.T.Tait, Polymer 1, 151 (1960)
34. R.J.Kern, H.G.Hurst and W.R.Richards, J.Polymer Sci. 45, 195 (1960)
35. F.D.Otto and G.Parravano, J.Polymer Sci. 42, 4231 (1964)
36. I.N.Meshkova, S.A.Kuman'kova, V.I.Tsvetkova and N.M. Chirkov, Vysokomol. Soedin. 3, 1816 (1961)
37. A.I.Ilyasova, Yu.I.Sangalov and K.S.Minsker, Plastichess Massey. 7, 13 (1975)
38. Yu.A.Sangalov, A.I.Ilyasova and K.S.Minsker, Polymer Science U.S.S.R., A18, 876 (1976)
39. C.H.Bamford, W.G.Barb, A.D.Jenkins and P.F.Onyan, 'The Kinetics of Vinyl Polymerisation by Radical Mechanism', Butterworth, London, 1958
40. L.Reich and A.Schindler, 'Polymerisations by Organometallic Compounds', Interscience, 1966
41. D.F.Hoeg, in 'The Stereochemistry of Macromolecules', Vol.1, Ed. A.Ketley, Merrell Dekker, Inc. N.Y. 1967, Chap.II.
42. A.Schindler, in 'Crystalline Olefin Polymers', Pt.1, Eds. R.A.F. Raff and K.W.Doak, Interscience, 1965, Chap.3.
43. W.L.Garrick, Adv.Polym.Sci. 13, 64 (1972)
44. P.Cossee, in 'The Stereochemistry of Macromolecules', Vol.1 Ed.A.Ketley, Merrell Dekker, Inc. N.Y. 1967, Chap. III.
45. G.Natta, Tetrahedron 8, 86 (1960)
46. I.Pasquon, G.Natta, A.Zambelli, A.Meriangeli and A.Surico, J.Polymer Sci. C16, 2501 (1967)
47. H.N.Friedlander and K.Oita, Ind.Eng.Chem.49, 1885 (1957)

48. A.V.Topchiev, B.A.Krenstel and L.G.Sidorova, Dokl.Akad.Navk. S.S.S.R. 128, 732 (1959)
49. H.Uelzmann, J.Polymer Sci. 32, 457 (1958)
50. K.Oita and T.D.Nevitt, J.Polymer Sci. 43, 585 (1960)
51. D.B.Ludlum, A.W.Anderson and C.E.Ashby, J.Am.Chem.Soc. 80, 1380 (1958)
52. W.L.Carriek, A.G.Chaser and J.J.Smith, J.Am.Chem.Soc. 82, 5319 (1960)
53. P.Cossee, Tetrahedron Letters 17, 12 (1960)
54. P.Cossee, J.Catalysis 3, 80 (1964)
55. L.A.M.Rodrigues and J.A.Gabant, J.Polymer Sci. C4, 125 (1964)
56. T.Miyazawa and Y.Ideguchi, J.Polymer Sci. B1, 389 (1963)
57. D.R.Armstrong, P.G.Perkins and J.J.P.Stewart, J.Chem.Soc. Dalton Trans. 1972 (1972)
58. E.J.Arlman, J.Catalysis 3, 89 (1964)
59. Yu.I.Yermakov, Catal.Rev.-Sci.Eng. 13, 77 (1976)
60. J.Boor, Jr., Macromol.Rev. 2, 115 (1967)
61. L.A.M.Rodrigues and H.M.Vanloo, J.Polymer Sci. A4, 1971 (1966)
62. Yu.V.Kissin and N.M.Chirkov, Eur.Polym.J. 6, 525 (1970)
63. J.C.Sehra and S.Gundiah, J.sci.industr.Res. (in press)
64. M.L.H.Green, Pure Appl.Chem. 50, 27 (1978)
65. E.A.Youngman and J.Boor Jr. Macromol.Rev. 2, 33 (1967)
66. G.Natta, P.Pino, G.Nazzanti and U.Giannini, J.Am.Chem.Soc. 79, 2975 (1957)
67. G.Henrici-Olive and S.Olive, Angew.Chem. Int.Ed. Engl. 6,

- 790 (1967); Chem.Tech. 746 (1981)
68. G.Fink, R.Rottler, D.Schnell and W.Zoller, J.Appl.Polymer Sci. 20, 2779 (1976)
 69. K.H.Reichert and E.Schubert, Makromol.Chem. 123, 58 (1969)
 70. J.A.Waters and G.A.Mortimer, J.Polymer Sci. A10, 895 (1975)
 71. G.Natta and I.Pasquon, Advances in Catalysis 11, 1 (1959)
 72. F.S.D'yachkovskii and A.E.Shilov, Russian Journal of Physical Chemistry, 41, 364 (1967)
 73. G.Natta, I.Pasquon, J.Svab and A.Zambelli, Chim.Ind. 44, 621 (1962)
 74. J.C.W.Chien, J.Am.Chem.Soc. 81, 86 (1959)
 75. D.F.Hoeg and S.Liebman, Ind.Eng.Chem., Process Design Development 1, 120 (1962)
 76. Yu.I.Yermakov and V.A.Zakharov, Russian Chemical Reviews. 41, 203 (1972)
 77. G.F.Feldman and E.Perry, J.Polymer Sci. 46, 217 (1960)
 78. V.A.Zakharov, G.D.Pukatov, N.B.Chumaevskii and Yu.I.Yermakov, React.Kinetic.Catal.Lett.1, 247 (1974)
 79. A.D.Caunt, Brit.Polym.J. 13, 22 (1981)
 80. A.D.Caunt, J.Polymer Sci. C4, 49 (1964)
 81. I.Pasquon, A.Valvassori and G.Sartori, in 'The Stereochemistry of Macromolecules' Vol.1, Ed. A.D.Ketley, Merrell Dekker, Inc. N.Y. 1967, Chap. IV.
 82. T.Keii, Nature 196, 160 (1962)
 83. V.N.Karasev, A.A.Berlin and K.S.Minsker, Polymer Science U.S.S.R. 15, 1071 (1973)

84. K.Vesley, J. Ambroz, R.Volim and O.Hamrik, J.Polymer Sci. 55, 25 (1961)
85. N.V.Bok-reva, V.I.Tsvetkova and F.S.D'yachkovski, Polymer Science U.S.S.R. 20, 3037 (1978)
86. F.Eirich and H.F.Mark, J.Colloid Sci. 11, 748 (1956)
87. N.G.Gaylord and H.F.Mark, 'Linear and Stereoregular Polymers', Interscience, N.Y. 1959
88. N.G.Gaylord, T.K.Kwei and H.F.Mark, J.Polymer Sci. 42, 417 (1960)
89. T.Keii, J.Res.Inst.Catalysis, Hokkaido University, 28, 243 (1980)
90. K.Vesley, Pure & Appl.Chem. 4, 407 (1962)
91. W.M.Saltman, J.Polymer Sci. 46, 375 (1960)
92. D.R.Burfield, I.D.McKenzie and P.J.T.Tait, Polymer, 13, 302 (1972)
93. V.I.Zakharov, G.D.Bukatov, N.B.Chumaevskii and Yu.I.Yermakov, Makromol.Chem. 178, 967 (1977)
94. L.L.Böhm, Polymer, 19, 545 (1978)
95. D.R.Burfield and P.J.T.Tait, Polymer, 15, 87 (1974)
96. A.Simon, Gy.Fezler and A.Szonyi, J.Polymer Sci. P.C.E. 17, 1871 (1979)
97. E.Kohn, H.J.Schürmans, J.V.Cavender and R.A.Mendelson, J.Polymer Sci. 58, 681 (1962)
98. T.Keii, 'Kinetics of Ziegler-Natta Polymerisation', Kodansha Ltd., Tokyo (1972)
99. Von G.Bier, W.Hoffmann, G.Lehmann and G.Seydel, Makromol.

- Chem. 58, 1 (1962)
100. J.W.Begley, J.Polymer Sci. 14, 319 (1966)
 101. V.N.Karasev, A.I.Berlin and K.S.Minsker, Polymer Science U.S.S.R. 16, 1504, 2880 (1974)
 102. H.N.Friedlander, J.Polymer Sci. 12, 3885 (1964)
 103. M.Nowakowska, K.Czaja, M.Makowski, K.Marcinkiewicz and L.Maizner, Polymer Science U.S.S.R. 20, 2523 (1978)
 104. A.Archambault and R.Rivest, Can.J.Chem. 35, 879 (1957)
 105. S.Minami and T.Ishino, J.Chem.Soc. Japan 61, 66 (1958)
 106. A.N.Nesmeyanov and R.A.Sokovlik, 'Methods of Elementary Organic Chemistry' Vol.1 'The Organic Compounds of Boron, Aluminium, Gallium, Indium and Thallium', North Holland Company, Amsterdam, Holland, 1967 pp.381-2.
 107. A.J.Mass and C.N.Tuck, Eur.Polym.J. 14, 813 (1978)
 108. A.B.Deshpande, S.L.Kapur and R.V.Subramanian, Ind.J.Chem. 3, 426 (1965)
 109. W.R.Krigbaum, J.Polymer Sci. 11, 37 (1953)
 110. T.R.Crompton, 'Analysis of Organo Aluminium and Organo Zinc Compounds', Pergamon Press, London, 1968. pp.159-162.
 111. A.I.Vogel, 'A Text book of Inorganic Analysis', Longmans London, 1961, pp.266-7
 112. H.Martin and J.Stedefeder, Ann.Chem. 618, 17 (1958)
 113. P.H.Moyer, J.Polymer Sci. 13, 199 (1965)
 114. T.Suzuki, S-Ichi Izwia, S.Kondo and Y.Takegami, J.Makromol.Sci.-Chem, 111, 633 (1977)
 115. A.Adicoff and R.Yee, J.Appl.Polymer Sci. 20, 2473 (1976)

116. D.C.Pepper, Trans.Faraday Soc., 45, 397 (1949)
117. F.Patnode and W.J.Schreiber, J.Am.Chem.Soc. 61, 3449 (1939)
118. T.Keii, E.Suzuki, M.Tamura, M.Murata and Y.Doi, Makromol. Chem. 183, 2285 (1982)
119. G.Bier, A.Gumboldt and G.Lehmann, Plastics Inst.(London) Trans.J. 28, 98 (1960)
120. W.R.Schmeal and J.R.Street, ~~AIChE~~ J 17, 1188 (1971)
121. J.P.Kennedy in 'Cationic Polymerisation of Olefins' A Wiley Interscience Publication, John Wiley & Sons N.Y.1975 p.22
122. W.H.McCarty and G.Parravano, J.Polymer Sci. A3, 4029 (1965)
123. L.F.Borisova, E.A.Fushman, E.I.Vizen and N.M.Chirkov, Eur.Polym.J. 9, 953 (1973)
124. D.R.Burfield, Makromol.Chem. 180, 1565 (1979)
125. A.Greco, G.Bertolini, M.Bruzzone and S.Cesca, J.Appl.Polymer Sci. 23, 1333 (1979)
126. J.A.Bittles, A.K.Chowdhury and S.W.Benson, J.Polymer Sci. A2, 3203 (1964)
127. F.P.Van Der Kamp, Makromol.Chem. 93, 202 (1966)

SYNOPSIS

Vinyl polymers are formed by the repetitive addition processes initiated by free radical, ionic or coordinated ionic modes through a chain mechanism. A combination of alkyls of metals of Gr. I-III in the periodic table (cocatalysts) with salts of transition metals of Gr. IV-VIII (catalysts) forms the largest body of coordination (Ziegler-Natta) catalysts. In polymerizations involving these catalysts, the monomer is coordinated to the catalyst site, and according to Cossee, the coordination occurs at the vacant site of the alkylated penta-coordinated transition metal complex. The migration of the alkyl group to the complexed monomer results in the creation of new vacant site and the process occurs repeatedly. The metal-polymer bond is finally cleaved either by hydride transfer or chain transfer processes.

Typical Ziegler-Natta catalysts exhibit complexities not common with other modes of vinyl polymerizations. Several catalyst sites of varying nature and reactivity are simultaneously active at any given instant. The number of active sites also vary during the course of polymerization. Kinetically, therefore, non-steady state behaviour is generally encountered in polymerizations involving these catalyst systems. However, steady state kinetics are observed in a few cases such as propylene polymerization with preformed TiCl_3 or supported TiCl_4 and aluminium alkyls. More recently alkoxy titanium trichlorides in combination with trialkyl aluminium are reported to function as steady state catalysts in ethylene polymerization. Kinetics

(ii)

of polymerization of other vinyl monomers using alkoxy titanium halides and aluminium alkyls have not been reported in literature

In this study, kinetics of polymerization of styrene, a liquid monomer conveniently amenable to accurate kinetic experimentation, is probed in n-heptane using butoxy titanium trichloride and aluminium alkyls. Measurements were carried out in a vacuum dilatometer and the rates of polymerization were deduced from the changes in heights with time of polymerization using known specific volumes of the polymer and the monomer. Triethylaluminium, triisobutylaluminium and diethylaluminium chloride were used as cocatalysts. The effect of triethylamine, an electron donor, on the rate of polymerization was also investigated in the case of trialkylaluminium.

With trialkylaluminium as cocatalyst, the polymerizations attained steady state rate after an initial decline during the first 10-60 min. The initial settling period was lower for the AlEt_3 containing catalysts. The steady state persisted upto about 200-400 min. when triisobutylaluminium was used. However, in case of triethylaluminium as cocatalyst, the steady state behaviour lasted upto about 100-200 min. The rates declined subsequent to the steady state period. Optimum rates of polymerizations were achieved with an aging time of 10 min. and 20 min. for catalysts containing triethylaluminium and triisobutylaluminium respectively. The maximum rates of polymerization and molecular weights were obtained at Al/Ti ratio of 1.5 in both the cases. The highest steady state rates obtained

(iii)
were 2.97 and 7.05×10^6 mole.l⁻¹.s⁻¹, for aluminium triisobutyl and aluminium triethyl containing catalysts at a catalyst concentration at 20 and 40 m.mole.l⁻¹ respectively. The steady state rates exhibited a first order rate law with reference to the monomer and the catalyst. The molecular weights of the polymers were independent of the catalyst concentration and attained limiting values at higher monomer concentrations.

The steady state rates of polymerization exhibited a sharp maximum in the plot of R_p vs. Al/Ti ratio indicating Langmuir-Hinshelwood mechanism governing the competition of the aluminium alkyl and monomer at the active sites. However, the limited data available did not clearly discriminate between Rideal and Langmuir-Hinshelwood mechanism.

Triethylamine was observed to greatly influence the steady state rates when triethylaluminium was used as the cocatalyst. In contrast, triisobutylaluminium did not show any significant variation with electron donor concentration. However, for both the trialkylaluminium containing systems, a maximum in the rate of polymerization was observed at an electron donor to aluminium alkyl ratio of 0.75 . The observed results were explained by competitive adsorption of aluminium alkyl and triethylamine at the active centre.

In contrast to the catalyst systems containing trialkyl aluminium, BuOTiCl₃-AlEt₂Cl catalyst exhibited higher activity for polymerization and continued to decline in catalyst activity with time. Higher aging times (40 min.) were needed for maximum

(iv)

catalyst activity. The initial rates were $10^{-4} \sim 10^{-5} \text{ mole.l}^{-1}.\text{s}^{-1}$ as compared to $10^{-6} \text{ mole.l}^{-1}.\text{s}^{-1}$. The initial and overall rates were proportional to the square of the concentration of the monomer. However, the limiting rates were proportional to the first power of monomer concentration. The initial rates were also proportional to the first power of the concentration of the catalyst.

The varying rates of polymerization with time were analyzed in terms of deactivation by first and second-order processes. It was observed that the first-order deactivation was valid only for the very early stages of polymerization. Second-order deactivation was observed to predominate during most of the course of polymerization. Contrary to expectations, the composite second-order rate constant for deactivation remained almost constant upto $0.003 \text{ mole.l}^{-1}$ catalyst concentration. Similarly, though the values of $[C^*]_0 k_d''$ were independent of the monomer concentration for most of the data obtained, the value was higher at the highest monomer concentration examined. The results obtained have been examined in terms of surface controlled reactions. Deactivation by catalyst poisoning could explain the first-order dependence of limiting rates with monomer concentration on the basis of competitive adsorption governed by Langmuir mechanism.

The activation energies for steady state polymerization for the trialkyl containing systems were 44 kJ.mole^{-1} . However, the activation energy for the system $\text{BuOTiCl}_3\text{-AlEt}_2\text{Cl}$ was -30 kJ.mole^{-1} for initial rates of polymerization. These values

(v)

indicate a coordinated anionic type mechanism in the systems containing trialkylaluminium and a cationic type initiation when AlEt_2Cl was employed.

The polystyrenes obtained were readily soluble in methyl ethyl ketone. IR spectra showed atactic nature of polystyrene formed.

In conclusion, the results demonstrate that trialkylaluminium with BuOTiCl_3 yield steady state catalysts for the polymerization of styrene after a short settling period. A cationic type initiation is observed with $\text{BuOTiCl}_3\text{-AlEt}_2\text{Cl}$. The catalyst deactivation in $\text{BuOTiCl}_3\text{-AlEt}_2\text{Cl}$ follows second-order kinetics during the largest course of polymerization. Surface characteristics of these colloiddally dispersed catalysts, can explain the variation of composite second-order deactivation rate constant $[\text{C}^*]_0 k_d''$ with reference to catalyst concentration. A probable mechanism of polymerization (similar to Cossee's) involving a reduced alkylated titanium halide in an octahedral configuration for the active centre has been suggested. The active centre also has a bulky butoxy ligand accounting for the early onset of steady state polymerization.