# Organometallic Polymerization Catalysts

by

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To my Mother

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# Organometallic polymerization catalysts


## SUMMARY

A study has been made of the polymerization of styrene initiated by vanadium based Ziegler-Natta catalysts, the most active of which was formed from $VOCl_3/AlEt_{1.5}Cl_{1.5}$, the most active also for the copolymerization of ethylene and propylene.

A dilatometric study of the polymerization, using a device that could be filled rapidly, showed that there were three stages during the polymerization, two of which involved polymerization and the other depolymerization. It is likely that each stage was catalysed by a different vanadium complex. The decay in the rate of polymerization observed during the initial polymerization stage was correlated with a decrease in the rate of polymerization that occurred with increasing pre-mixing time, when the vanadium and aluminium compounds were pre-mixed. The depolymerization that occurred during the second stage of the reaction was correlated with the ability of catalysts formed by reacting $VOCl_3$ with $AlEt_{1.5}Cl_{1.5}$ to depolymerize polystyrene. No plausible thermodynamic reasons could be proposed for this depolymerization process.

The kinetic study of the polymerization showed that increasing the concentration of $AlEt_{1.5}Cl_{1.5}$ at constant $VOCl_3$ concentration caused an increase in the rate of polymerization. It is likely that increasing the concentration of $AlEt_{1.5}Cl_{1.5}$ did not lead to an increase in the number of active sites, but the increased rate of polymerization was caused by activation of the monomer towards polymerization by the formation of a $\pi$ complex between the monomer and the aluminium compound. At constant concentration of $AlEt_{1.5}Cl_{1.5}$ the rate of polymerization decreased with increasing concentration of $VOCl_3$.

UV/visible spectroscopy showed that a number of active species were present during the polymerization.



Keywords

Styrene, polymerization, vanadium-aluminium catalysts.

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CHAPTER 1

## 1.1 INTRODUCTION

In 1949, Ziegler and co-workers ( 1,2,3 ) discovered that the reaction of aluminium hydride and ethylene took place in a stepwise manner to yield aluminium triethyl ($AlEt_3$) which was able to react with additional ethylene to form higher alkyls of aluminium. The initial formation of $AlEt_3$ occurred between 60-80°C but the subsequent insertion of ethylene into the Al-C bond took place at a reasonable rate only above 100°C.

$$AlH_3 + 3CH_2{=}CH_2 \longrightarrow Al(C_2H_5)_3 \qquad (1)$$

Shortly afterwards Ziegler at al ( 1,2,3 ) reported that $AlR_3$ undergoes the following reaction with olefins, known as the Aufbau reaction:

$$Al(C_2H_5)_3 + mCH_2{=}CH_2 \rightleftharpoons Al\begin{cases}(C_2H_4)_n\,C_2H_5\\(C_2H_4)_p\,C_2H_5\\(C_2H_4)_q\,C_2H_5\end{cases} \qquad (2)$$

where $(n + p + q) = m$

The growth of this polyethylene alkyl chain was limited because of the spontaneous dissociation of the aluminium-carbon bond to give $AlH_3$ and a terminally unsaturated polyethylene:

$$C_2H_5(C_2H_4)_n - al \rightarrow (C_2H_5)(C_2H_4)_{n-1}CH{=}CH_2 + al\text{-}H \qquad (3)$$

where al = 1/3 Al

$AlH_3$, the product of the above reaction, immediately reacted with another mole of ethylene to initiate a new chain.

Ziegler observed (4,5 ) that when the reaction of aluminium triethyl and ethylene was carried out in an autoclave in which traces of colloidal nickel were present, butene-1 was

obtained in high yield, i.e.

$$CH_3CH_2-al + C_2H_4 \longrightarrow CH_3CH_2\ CH_2CH_2 - al \xrightarrow{C_2H_4}$$

$$CH_3CH_2 - al + CH_3CH_2CH=CH_2 \qquad (4)$$

Following the discovery of the activity of nickel as a catalyst in reactions of ethylene with aluminium alkyls, a systematic investigation was undertaken by Ziegler and his co-workers (5-7 ) who found that cobalt and platinum were active in this manner. However, in an experiment carried out with zirconium acetylacetonate ( 7 ) as cocatalyst a great mass of polyethylene was obtained.

After the disclosure of the details of Ziegler's work, G. Natta and co-workers disclosed (8,9) that the polymers obtained with these catalysts were not only of a high molecular weight, but were also sterically differentiated, a previously unknown phenomenon. Natta, using catalytic systems of the type disclosed by Ziegler, was able to show that the polymers of alkyl and aryl monosubstituted ethylenes, e.g. propylene, 1-butene and styrene, were stereoregular. A systematic determination of the conformation and configuration of these crystalline poly$\alpha$-olefins led Natta to define three steric arrangements of the polymer chain. These were atactic, isotactic ( 10 ), and syndiotactic ( 11 ).

It was thus claimed that the combination of transition metal compounds of groups IV to VIII of the periodic table with hydrides or alkyls of a metal in groups I to IV gave rise to catalysts which were capable of stereospecifically polymerizing $\alpha$ - olefins at low temperatures and pressures to crystallizable stereoisomeric polymers. These complex catalysts are now referred to as Ziegler-Natta catalysts.

Of the transition-metal catalysts, the most important are the halides, subhalides and oxyhalides of titanium, vanadium, zirconium and chromium, but compounds of iron, cobalt, scan-

dium, nickel, molybdenum, tungsten and chromium have been found to have catalytic activity. The halides have been the most commonly used compounds, but other groups, e.g. alkoxyl, phenyl, acetylacetonyl and cyclopentadienyl, may be associated to the transition metal. The main group of four transition elements that have proved most effective as the basis of polymerization catalysts are those originally classified by Natta (12,13) on the basis of the tendency of the metals to lose electrons as determined by the work function and the ionization potential. The most important organometallic compounds that have been employed include alkali-metal alkyls, alkyls, alkyl hydrides and alkyl halides of aluminium, lithium - aluminium alkyls, the alkyls of zinc, tin, lead, cadmium and beryllium and Grignard reagents. Natta (14 ) considered that the more highly electro positive elements of groups I to IV, i.e. those having small ion radii, e.g. lithium, beryllium, magnesium, zinc and aluminium are the more active co-catalysts.

Common examples of Ziegler-Natta catalysts are shown in Table 1 (1).

Table 1 (1) - Common examples of Ziegler-Natta Catalysts

| Metal Alkyl | Transition Metal Compound |
|---|---|
| Heterogeneous | |
| $AlEt_3$ | $TiCl_4$ |
| $AlEt_2Cl$ | $TiCl_3$ |
| $AlR_3$ | $VCl_3$ |
| $ZnEt_2$ | $VCl_4$ |
| Homogeneous | |
| $AlEt_2Cl$ | $VCl_4$ or $VOCl_3$ |
| $AlBr_3$+Sn $(C_6H_5)_4$ | $VCl_4$ or $VOCl_3$ |
| Al $(CH_3)_3$ | $(C_5H_5)_2$ $TiCl_2$ |

## 1.2 IMPORTANCE OF THE PHYSICAL STATE OF THE CATALYST

The present studies are concerned with a homogeneous Ziegler-Natta system, it is thus worthwhile considering a comparison of the applications of homogeneous and heterogeneous catalysts. The physical state of the catalyst may be important in a number of ways.

1. For many monomers, the particular stereoregulation that takes place during polymerization depends on the crystalline state of the catalysts. The preparation of isotactic poly-$\alpha$-olefins has been observed with heterogeneous Ziegler-Natta catalysts ( 10 ), whereas the formation of some highly syndiotactic polymers, eg. polypropylene (15 ) and polybutene-1 ( 16 ) seemed only to be possible with homogeneous catalysts.

2. Boor ( 17 ) stated that the copolymerization of ethylene and propylene yielded mainly random copolymers when soluble or colloidally dispersed catalysts such as $AlEt_2Cl$—$VO(OEt)Cl_2$ were used, whereas block copolymers were formed by heterogeneous catalysts, (e.g. $AlEt_3$ —$TiCl_3$).

3. Theoretically in soluble catalysts, if every atom acted as an active site, soluble catalysts would be theoretically more efficient than heterogeneous catalysts. In fact Carrick ( 18 ) reported that a three component catalyst system $[(C_6H_5)_4Sn - VCl_4 - AlBr_3]$ was a very efficient catalyst for the polymerization of ethylene at concentrations of the vanadium salt of $5 \times 10^{-5}$ moles litre$^{-1}$. Heterogeneous catalyst concentrations 500 times greater than this would be needed to obtain the same rates of polymerization. However, not every soluble catalyst is highly active ( 19 ) and this is possibly because complex formation occurs in solution and very few of the complexes formed are capable of acting as active polymerization sites ( 20 ).

The physical state of the polymer is also very important. When a solid polymer is formed by a heterogeneous catalyst system, the catalyst may become embedded in the polymer mass thus greatly reducing the number of active sites accessible for polymerization. For this reason it will be convenient to discuss the two types of catalyst separately.

a. Heterogeneous Catalysts

The heterogeneous catalyst consists of the soluble metal alkyl, e.g. $AlEt_2Cl$ and the insoluble transition metal salt, e.g. $TiCl_3$. When these two components are mixed, the active centres are formed on the ($TiCl_3$) crystal surface. Natta and co-workers proposed that the isotactic-type stereo regulation was closely dependent on the nature of the crystal surface of the solid component of the catalyst (10 ). The use of a compound in which the titanium or vanadium is initially in a lower valency state Ti(111), V(111) was found by Natta and co-workers (21 ) to give more isotactically specific catalysts than did those containing soluble transition metal salts in a higher valence state, e.g. $TiCl_4$, $VCl_4$. However one catalyst ($NbCl_5/AlEt_3$) was known in which the transition metal component was in its highest valency state and could form a stereoregulating catalyst for the polymerization of propylene.

(i) Composition and structure of titanium trichloride

$TiCl_3$ has been widely used as the transition metal salt component of a Ziegler-Natta catalyst. It is therefore appropriate to consider here the structural and compositional characteristics of the titanium subhalides. Structural analyses of $TiCl_3$ were undertaken by Natta and co-worker (22- 24 ) who showed that $TiCl_3$ exists in four major structural modifications $\alpha, \gamma$, and $\delta$ which are violet and $\beta$ which is brown-black. The $\alpha$ form, may be prepared by the reduction of $TiCl_4$ with hydrogen above $500^\circ$ and with aluminium above $250^\circ C$ ( 25-26 ).

The γ form, whose crystal structure was described by Natta ( 23 ), was obtained by heating the β variety above 150°C or by reducing $TiCl_4$ with an organo aluminium compound between 150° and 200°C (23 ). The α and γ layer modifications were shown to have similar structures, differing only in the mode of packing of the layers. In the α form the sequence of layers is such that a hexagonal packing of the chlorine ions is achieved whereas in the γ form, the succession of layers produces compact cubic packing of the anions. The δ variety was obtained either by prolonged grinding of the α or γ forms or by grinding aluminium chloride with α-$TiCl_3$ (24 ).

The β modification was formed by the reaction of $TiCl_4$ with an organoaluminium compounds at ambient temperature (26 ). By distilling $TiCl_4$ slowly into $Et_2AlCl$, large crystals of β-$TiCl_3$ could be formed (27 ). The methods of synthesis and structures of the resultant materials is shown in table 1 (2).

The preparation of $TiCl_3$ usually leads to a mixed salt $TiCl_3$ 1/3 $AlCl_3$ but the presence of $AlCl_3$ was not found to influence the stereo-regulating abilities of α, γ and δ $TiCl_3$ in α-olefin polymerizations (28 ). However in the case of the β modification $AlCl_3$ free β-$TiCl_3$ ( 29 ), when combined with $AlEt_2Cl$, was less active and less stereospecific for propylene polymerization than was the $AlCl_3$- containing preparation ( 30 ).

(ii) Location of sites on the crystal surfaces

It is generally agreed that the polymerization takes place on the edges or lateral faces, but not on the basal faces, of the crystalline $TiCl_3$ (21, 31-35). Hargitay, Rodriguez and Miotta concluded this on the basis of optical microscopy measurements on the ethylene polymerization using sublimed $TiCl_3$ crystals ( 33 ). Rodriguez, V. Looy and Gabant using electron microscopy to follow the initial polymerization of propylene on small α-$TiCl_3$ crystals, concluded that polymer growth took

place at the lateral faces where the Ti atoms were directly accessible for complexation by the olefin (35,36-40). Similar conclusions were obtained by Arlman and Cossee who developed a picture of the surface structure of crystalline $TiCl_3$ (32,34). Arlman (32) developed a picture of the surface structure of the crystalline transition metal chloride (i.e. $TiCl_2$, $TiCl_3$) from the principles of inorganic crystal chemistry. He proposed that every $Ti^{+3}$ ion in the surface layer was five coordinated with one chlorine vacancy at the edges of $TiCl_3$ to ensure the electroneutrality of the crystal. Such vacancies have been assumed to be active sites. Further the author distinguished the several types of $Cl^{\ominus}$ ion. Of the five chloride ions around each titanium ion arranged at five of the six corners of an octahedron, three are deeply buried in the interior of the crystal and associated also with a second $Ti^{+3}$ ion. Of the remaining two chloride ions one is also attached to a second positive ion, the other is attached to only the titanium ion considered. This situation is shown in fig. 1 (1).

(iii) Changes in the physical state of catalyst

When $AlEt_3$-$\alpha$-$TiCl_3$ was used as a catalyst Natta and coworkers noticed that during the initial polymerization period the activity of the catalyst increased to a constant value (21). It was suggested that under the mechanical action of the growing polymer chains the loosely held aggregates were broken up into smaller crystalline particles. The same forces continued to cleave the smaller, whole crystalline particles of the $\alpha$-$TiCl_3$ modification into smaller particles. The disintegration of the whole crystals was thought to take place by cleavage along the loosely held Cl - Cl layers.

Natta and co-workers offered the following experimental evidence:

1. The polymerization rate under steady-state

conditions was seen to be almost independent of the initial size of the $\alpha$-$TiCl_3$ particles.

2. The adjustment period was dependent upon the particle size of $\alpha$-$TiCl_3$. The initial period, characterized by an increasing rate of polymerization, was greatly reduced and modified by changing the particle size.
3. The steady-state rate seemed to be unaffected by a moderate amount of grinding.
4. The higher the steady-state rate the less the time needed to reach it.

Vecchi and co-workers ( 41 ) reported that mechanical grinding of $TiCl_3$ increased its surface area and that the catalytic activity was simultaneously increased.

(iv) The synthesis of $TiCl_3$ by the reaction of titanium (IV) chloride ($TiCl_4$) with aluminium alkyl ($AlR_3$)

$TiCl_4$ was found to react with aluminium alkyls ( 42,43 ) such as $AlEt_3$ to produce a brown black precipitate, a gas and sometimes low molecular weight polymer. During this reaction it was postulated that a series of alkyl-chlorine exchanges took place between the aluminium and titanium compounds to produce an alkyl $TiCl_3$. Various mechanisms have been proposed for the production of the brown precipitate:

$$TiCl_4 + AlEt_3 \longrightarrow EtTiCl_3 + AlEt_2Cl \qquad (5)$$

$$TiCl_4 + AlEt_2Cl \longrightarrow EtTiCl_3 + AlEtCl_2 \qquad (6)$$

$$TiCl_4 + AlEtCl_2 \longrightarrow EtTiCl_3 + AlCl_3 \qquad (7)$$

Early workers in the field ( 44- 50) suggested that the $RTiCl_3$ decomposed readily to a free radical that then underwent a number of possible reactions ( 8- 14 ) to produce gaseous products according to:

$$EtTiCl_3 \longrightarrow TiCl_3 + C_2H_5^{\bullet} \qquad (8)$$

$$2C_2H_5^{\bullet} \longrightarrow C_2H_4 + C_2H_6 \qquad (9)$$

$$2C_2H_5\cdot \longrightarrow n\text{-}C_4H_{10} \quad (10)$$

$$2C_2H_5\cdot \longrightarrow 2C_2H_4 + H_2 \quad (11)$$

$$2C_2H_5\cdot + C_2H_4 \longrightarrow n\text{-}C_6H_{14} \quad (12)$$

$$C_2H_5\cdot + RH\ (Solvent) \longrightarrow C_2H_6 + R\cdot \quad (13)$$

$$C_2H_5\cdot + TiCl_4 \longrightarrow TiCl_3 + C_2H_5Cl \quad (14)$$

The exchange reactions ( 5-7 ) were thought to be ionic in nature because Bestian and Clauss found ( 51 ) that the rate of exchange was greater in polar than in non polar solvents. An association complex between $TiCl_4$ and alkylaluminium compound was also proposed by Uelzmann ( 52 ) as the primarily formed product. Dissociation of this complex created a titanium cation and a complex aluminium anion such as:

$$TiCl_4 + AlEt_3 \longrightarrow Cl\text{-}\overset{\overset{Cl}{|}}{\underset{\underset{Cl}{|}}{Ti}}{}^{+\delta}\text{-}\overset{\overset{Et}{|}}{\underset{\underset{Et}{|}}{Al}}{}^{-\delta}\text{-}Et \longrightarrow (TiCl_3)^+ (AlR_3Cl)^- \quad (15)$$

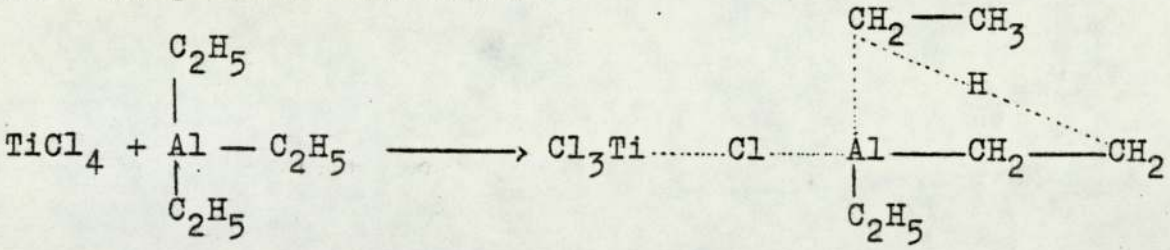
Arlmann and Jong ( 48 ) found that in the system $Al(CH_3)_3$-$TiCl_4$ the methyl radicals reacted quantitatively with the solvent, isooctane, at 80°C. The same system was investigated by Cooper and Rose ( 53 ) who obtained identical results. However Beerman and Bestian ( 54 ) and de Vries ( 55 ) investigated the decomposition of methyltitanium trichloride in hydrocarbon solvent using different techniques and reached the conclusion that no free alkyl radicals were formed.

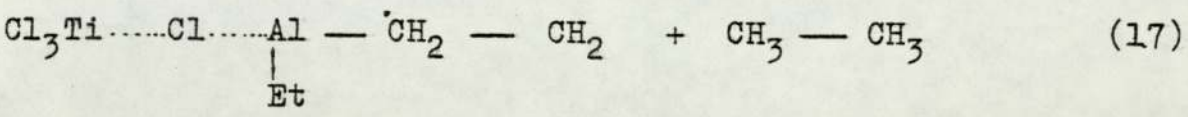
An association complex between $TiCl_4$ and $(CH_3)_2AlCl$ was proposed by Rodriguez and Gabant ( 56 ) which had the following structure:

$$TiCl_4 + (CH_3)_2AlCl \rightleftharpoons \underset{I}{Cl\text{-}\overset{\overset{Cl}{|}}{\underset{\underset{CH_3}{|}}{Ti}}{}^{+\delta+}\text{---}Cl\text{-}\overset{\overset{Cl}{|}}{\underset{\underset{CH_3}{|}}{Al}}{}^{\delta-}\text{-}Cl} \quad \text{or}$$

$$\underset{II}{Cl\text{-}\overset{\overset{Cl}{|}}{\underset{\underset{CH_3}{|}}{Ti}}{}^{\oplus}\ \left[Cl\text{-}\overset{\overset{Cl}{|}}{\underset{\underset{CH_3}{|}}{Al}}\text{-}Cl\right]^{\ominus}} \quad (16)$$

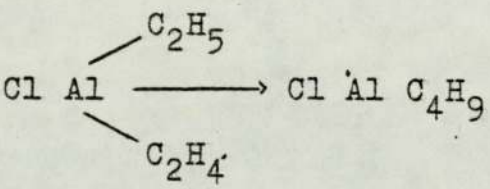
When $AlEt_3$ or $AlEt_2Cl$ was reacted with $TiCl_4$ by Eden and Feilchenfeld ( 57 ) no ethylchloride was formed. These authors postulated an intramolecular hydrogen abstraction via the following transition state:





(17)

The product ($Cl_3Ti$ Cl-Al $CH_2$ - $\dot{C}H_2$) rapidly rearranged as follows:



(18)

It was even suggested by the same authors that this species was the active site for the polymerization. This mechanism found support from the results of ESR measurements which were performed by Adema ( 58 ) who found that for the system $AlEt_2Cl$-$TiCl_4$ the curves for the polymerization of ethylene and for the concentration of unpaired electrons versus time were identical in shape. Ludlum and co-workers ( 43 ) mixed decalin solutions of $TiCl_4$ and $AlEt_3$ in cyclohexane as solvent at 80° and assumed that all ethyl radicals reacted with solvent, resulting in hydrogen abstraction.

Tepenitsuna and co-workers ( 59 ) studied the production of an alkyl titanium halide by the reaction of $AlEt_3$ with $TiCl_4$, which produced a complex of lower valency which was insoluble in hydrocarbons. It was capable of adsorbing the alkyls of aluminium, zinc, and beryllium to form unstable surface com-

plexes with them. It was further shown that upon interaction of the components, the solid phase obtained consisted essentially of titanium and chlorine whilst the liquid phase contained essentially aluminium and chlorine. Neither the precipitate nor the liquid phase in itself promoted polymerization of ethylene separately; however addition of $AlEt_3$ to the precipitate or of $TiCl_4$ to the liquid phase produced active catalysts for the polymerization.

Gray et al ( 60 ) used an IR investigation technique to study the reaction between $TiCl_4$ and $AlMe_3$ in the vapor phase at six different reactant ratios. It was suggested that the initial reaction at the equimolar reactant ratio was:

$$Me_3Al + TiCl_4 \longrightarrow Me_2AlCl + MeTiCl_3 \quad (19)$$

At lower molar ratios, $Me_2AlCl$ also alkylated $TiCl_4$ to some degree by achieving an equilibrium state as -

$$Me_2AlCl + TiCl_4 \rightleftharpoons MeAlCl_2 + MeTiCl_3 \quad (20)$$

It was suggested that even in the presense of excess $AlMe_3$ complete alkylation of titanium was not obtained. Finally the possibility of a disproportionation reaction for the $MeTiCl_3$ was proposed such as:

$$2\ MeTiCl_3 \longrightarrow Me_2TiCl_2 + TiCl_4 \quad (21)$$

Kollar and co-workers ( 61 ) investigated $TiCl_4$ - $AlR_3$ system to polymerize ethylene and concluded that the maximum polymerization rate occurred at a maximum concentration of trivalent titanium. It was proposed that the degree of reduction of titanium was proportional to the temperature and the reduction progressed with increasing Al/Ti molar ratio. They further showed that the activity of the catalyst was significantly affected by the aluminium alkyls in the liquid phase and showed that it was possible to displace one type of alkyl by another or to elute it from the adsorbed layer ( 62 ).

Schindler ( 63 ) investigated the catalyst system $TiCl_4$ or $TiCl_3$ in combination with $AlEt_3$ and $Et_2AlCl$ in the presence

of deuterium to polymerize ethylene. A H, D - exchange reaction involving the β - hydrogen of the growing chain was found to be characteristic for chain growth on Ti(IV) sites. The inactivity of BuLi or $Et_2Zn$ system in such exchange reaction led to the proposal that the complex was bimetallic. It was also proposed that the formation of $-CH_2D$ groups in the polymer by a transfer reaction was a proof for chain growth on Ti(III) sites. Finally it was suggested that the occurrence of an H-D exchange reaction, involving the monomer and formation of deuterated ethanes, was assigned to the presence of inactive titanium hydride sites, that formed at high catalyst ratios.

Rishina and co-workers ( 64 ) studied the product of the reaction between $TiCl_4$ and $AlR_2Cl$ and concluded that oligomerization of propylene by this system at ratios of Al:Ti<1:1 was not the result of formation of free radicals. It was shown that in toluene the solvent took part in the formation of the catalyst. In the oligomerization in toluene the solvent took part as a chain transfer agent and this involved alkylation of the toluene as follows:

$$TiCl_4 + AlEt_2Cl \longrightarrow TiCl_3Et + AlEtCl_2 \qquad (22)$$

$$TiCl_3C_2H_5 + \text{C}_6\text{H}_5\text{CH}_3 \longrightarrow TiCl_3.\text{C}_6\text{H}_5\text{CH}_2 + C_2H_6 \qquad (23)$$

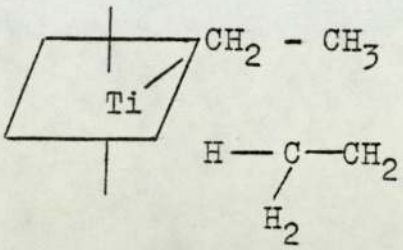
The oligomerization of olefins, reviewed by Olive,( 65 ) has been postulated to involve β -hydrogen abstraction from the alkyl chain in the termination reaction, thus forming a double bond between the first two carbons of the chain while breaking the Ti-α-C bond. It can be illustrated as:

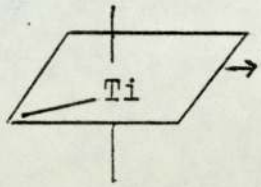
$$M - \overset{\alpha}{CH_2} - \overset{\beta}{CH}(H)\,R \longrightarrow MH + CH_2 = CH - R \qquad (24)$$

$$MH + CH_2{=}CH_2 \longrightarrow M - CH_2 - CH_3$$

Metal hydrides can subsequently produce an alkyl group able to continue the kinetic chain. The stability of the metal-

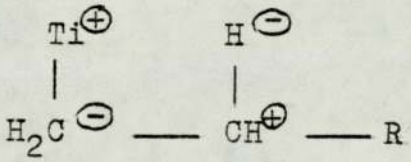
alkyl bond toward $\beta$-hydrogen abstraction depends on metal, its valency and on ligand environment. Having obtained an experimental second order rate for the reduction of Ti(1V) to Ti(111) the authors assumed the reaction was bimolecular, with $\beta$-hydrogen transfer from one Ti unit to the other. It was followed by donation of the hydrogen atom to the alkyl group of the second titanium unit which resulted in liberation of ethane and ethylene as follows:



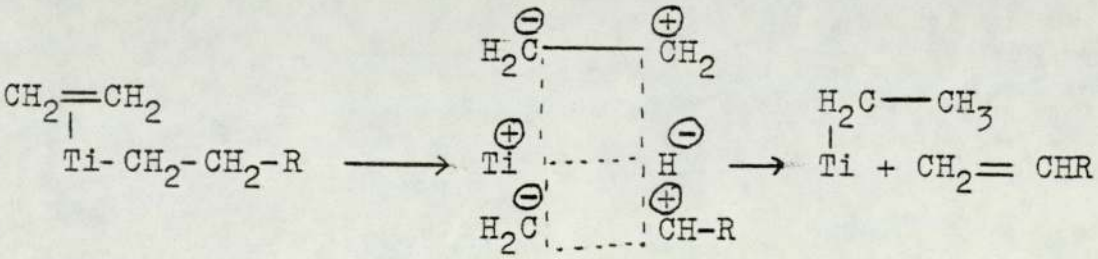

$\rightarrow 2Ti(111) + C_2H_6 + C_2H_4$ (25)

The low activation energy of the $\beta$-hydrogen abstraction process led the author to propose that the growing chain was highly polarized by the transition metal even in the ground state.



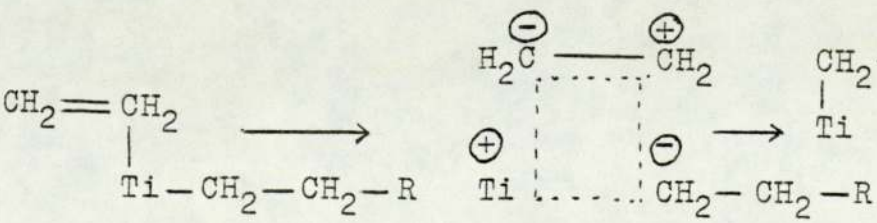

(26)

It was suggested that a six-centre, bicyclic highly polar transition state could account for the unusual activation parameters:




(27)

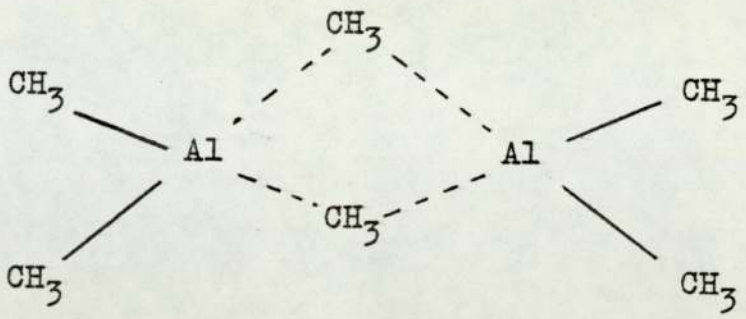
The propagation step was assumed to proceed via a normal four centre transition state:




(28)

(V) The cocatalyst component of a Ziegler-Natta catalyst

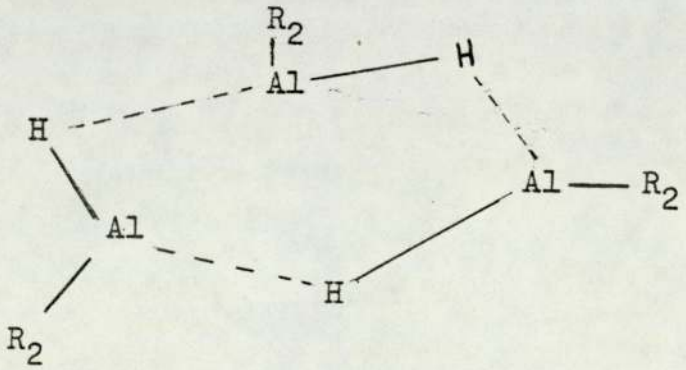
The cocatalyst in a Ziegler-Natta catalyst system is normally a trialkyl aluminium or alkyl aluminium chloride. These compounds exist as dimers at ambient temperature, such as:



(29)

Wherein the two alkyl groups act as bridges between the aluminium centres. In such compounds the Al-$CH_3$-Al bond is formed by the overlap or three atomic orbitals to produce a molecular orbital that encompasses all three centres. N.M.R. evidence for the rapid exchange of bridging and terminal methyls has been shown.

Aluminium alkyls of the general formula $AlR_3$, wherein R is a straight chain alkyl group, normally exist in hydrocarbon solvent as the dimer, whereas other trialkyl aluminium compounds of the structure Al $(CH_2CR_2R')_3$ where R' can be alkyl or aryl are monomeric, e.g. $Al-(CH_2-\underset{\displaystyle CH_3}{\overset{\displaystyle CH_3}{\underset{|}{\overset{|}{CH}}}})_3$ and dialkyl aluminium hydrides are timeric.



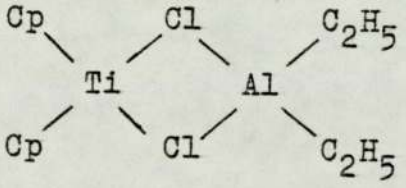
(30)

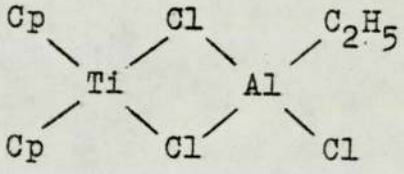
In general, electron-deficient molecules act as strong Lewis acids and react rapidly with electron donors. A substantial review of the properties of aluminium alkyls has recently been published ( 66 ).

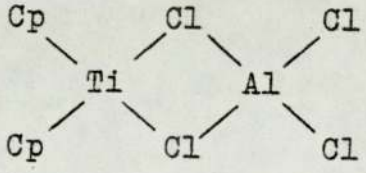
b. Homogeneous Catalysts

In 1955 a number of workers ( 19,20,67 - 70 ) reported that the reaction between aluminium alkyls and bis(cyclopentadienyl) titanium dichloride ($Cp_2TiCl_2$) gave rise to soluble products that polymerized ethylene. In aromatic solvent a fast reaction took place between these compounds to produce a dark red complex which gradually changed to green and finally to deep blue. The initial red complex was diamagnetic probably with bridging groups between the two metals. Reduction then occurred by elimination of ethane and ethylene to give eventually a blue titanium complex ( 19,20, 71 - 74 ).

The reaction end product could be isolated in the form of general composition $Cp_2TiCl_2AlX_2$ wherein X = chlorine or alkyl group, depending on the composition of the alkyl aluminium compounds. Such as -



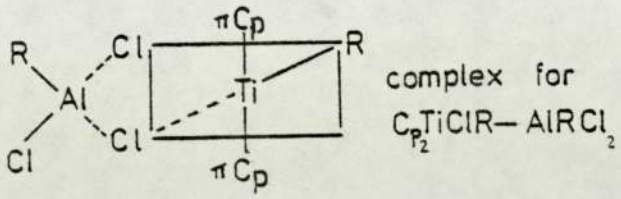



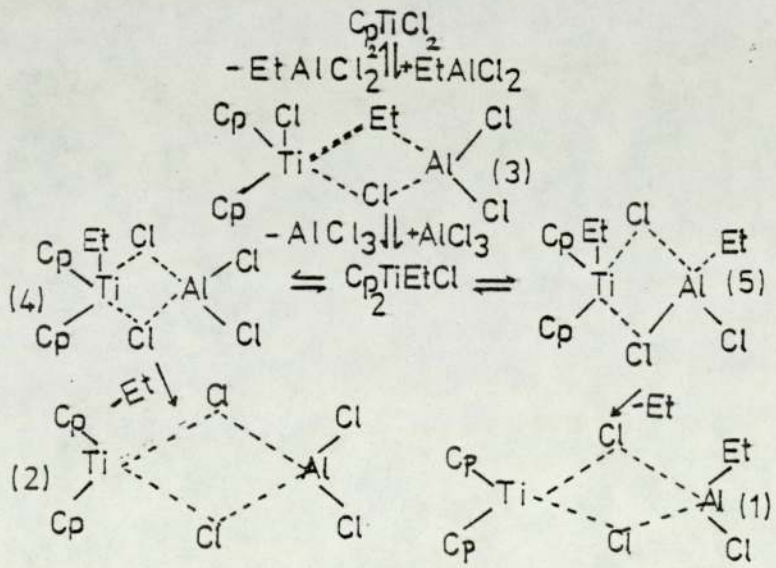

Henrici-Olive and Olive ( 75 ) used electron spin resonance evidence and suggested that the diethyl complex was also formed in this reaction and was then converted to the monoethyl derivative.

With $AlEt_3$ reduction was considerably faster giving the diethyl complex ( 20,67, 72- 74 ), while $EtAlCl_2$ reduced $Cp_2TiCl_2$ somewhat more slowly to the tetrachloro compound ( 72-73 ). Reduction of $Cp_2TiCl_2$ by $AlEt_3$ was almost complete in one hour, whereas with $EtAlCl_2$ reduction took one thousand hours. The rate for $Et_2AlCl$ fell between the two ( 65,75 ).

Henrici-Olivé and Olivé ( 76- 78 ) combined a kinetic study of the polymerization of ethylene with ESR and magnetic susceptibility measurements to relate catalyst activity, and configuration of complex and oxidation state of Ti atom in the $Cp_2TiCl_2$ - $AlEtCl_2$ and $Cp_2TiEtCl$ - $AlEtCl_2$ catalyst systems. They concluded that active centres were quadrivalent, because the rate of polymerization decreased at the same rate as Ti(1V) was reduced to Ti(111). The proposed complex model was:

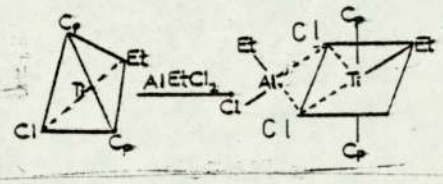



The activity of these systems resides in the presence of a complex molecule having an alkylated Ti(1V) and alkylated Al species linked with by chlorine bridge bonds.
The reactions that could occur when $Cp_2TiCl_2$ and $EtAlCl_2$ are brought together are shown below:




Using this scheme and also electron paramagnetic resonance and kinetic data the authors proposed ( 75,79 ) that the active site required a titanium-ethylated species in an octahedral environment that was depicted by the following

complex formation reaction:




i.e. Complex ( 5 ) was the active catalyst. The Ti atom was in an octa hedral state with one vacant site that was available for the coordination of ethylene. The bridged Al-alkyl caused a destabilisation of Ti-alkyl bond thus rendering it active for polymerization. The reduction Ti(1V)⟶Ti(111) in these systems, involved the irreversible change from octahedral to tetrahedral symmetry commensurate with loss of the catalytic activity.

Shilov supposed ( 80 ) that the $Cp_2TiRCl.AlRCl_2$ complex to be in equilibrium with positive ions containing titanium:

$$\underset{(A)}{Cp_2TiRCl.AlRCl_2} \rightleftharpoons [Cp_2TiR]^{\oplus} + [AlRCl_3]^{\ominus}$$

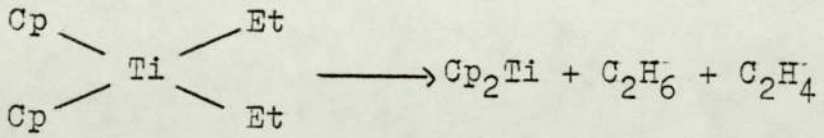
It was found that after the addition of $Cp_2TiCl_2$, the electrical conductivity of a benzene solution of dimethyl aluminium chloride increased by several fold because the $Cp_2TiCH_3Cl.AlCH_3Cl_2$ complex dissociated into ions. The electrodialysis of a $Cp_2TiCH_3Cl.AlCH_3Cl_2$ complex in dichloroethane showed that the number of titanium ions that migrated through a membrane to the cathode chamber was approximately 40% of the total ion current ( 81 ). Therefore more of positive ions contain the Ti atom in the $Cp_2TiCH_3Cl.AlCH_3Cl_2$ complex solution. Electrodialysis of the $Cp_2TiCH_3Cl.AlCH_3Cl_2$ complex ( 82 ) showed that the labelled $\overset{x}{CH_3}$ appeared together with titanium in the cathodic chamber. The $\overset{x}{CH_3}$/Ti ratio was close to unity which confirmed the dissociation of complex (A) according to the above equation.

EPR was used to study the systems: $VCl_4 + AlR_3$, $VOCl_3 + AlR_3$ ( 83 ) $Cp_2VCl_2 + AlR_3$, $AlR_2Cl$, $AlCl_2R$ ( 84 ). All the results

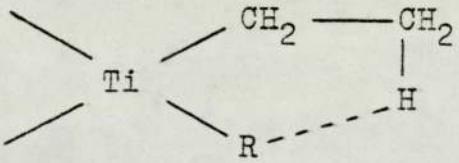
obtained could be summarized in the following way.

The formation of complexes of transition metal compounds took place by reduction by the aluminium compounds and subsequently interaction of the alkyls or alkyl halides of aluminium with the derivatives of vanadium (V) and vanadium (IV) by way of donor acceptor or electron deficient bonds.

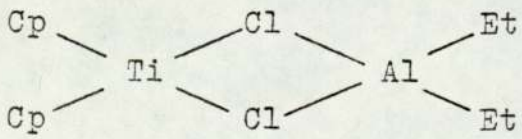
Zefirova ( 74 ) investigated the kinetics of the reaction of $Cp_2TiCl_2$ - $AlEt_2Cl$ system and suggested that the reduction rate determining step was the decomposition of a dialkyl titanium derivative.




The reaction proceeded as an intramolecular disproportionation through a five-membred cyclic complex.




Amass ( 85 ) reported the reaction between dichloro-biscyclopentadienyltitanium ($Cp_2TiCl_2$) and aluminiumtriethyl ($AlEt_3$). The reaction was carried out in the presence of excess $AlEt_3$. Because n-heptane is a good solvent for $AlEt_3$ but poor solvent for $Cp_2TiCl_2$. Keeping the ratio Al:Ti lower than 3:1 the reaction was accompanied by the production of an intense blue solution and also with the evolution of a ethane and ethylene gas mixture; a blue solid with melting point 126-38°C was obtained. Solution of complex in heptane gave a single line ESR spectrum. The complex designated which is identical with that isolated by Natta ( 67 ) as structure I.



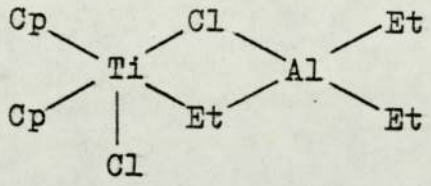

On addition of $AlR_3$ solution in to toluene to the $Cp_2TiCl_2$ solution up to molar ratio Al:Ti 1:1 the orange solution of

$Cp_2TiCl_2$ progressively turned red. This reaction was followed spectrophotometrically and a general shift in the absorption band to a lower wavelength was observed. After distilling off the solvent an orange solid was obtained.

The decanted red supernatant liquor was only weakly paramagnetic. Accordingly the author proposed that the complex had structure (11).

The catalytic activity for the polymerization of styrene and UV spectrum of complexes the author suggested the following reaction scheme and structure of complex:

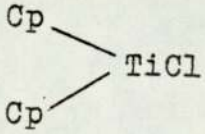
$$Al_2(Et_3)_2 + 2\ Cp_2TiCl_2 \rightleftharpoons 2\ Cp_2TiCl_2AlEt_3$$




(11)

Since tri (n-alkyl) aluminium compounds are normally dimeric in solution, the monomeric form of $AlEt_3$ is electron deficient and could form complexes with electron rich compounds.

Further reaction of $Cp_2TiCl_2$ with $AlR_3$ to a molar ratio of 3:1 was observed spectrophometrically and by ESR and concluded that the complex contained the unpaired electron of Ti(111) which came from the reduction of complex (11) by $AlR_3$. During the reaction a colour change from red to green was accompanied by the evolution of ethane and ethylene. The author suggested that the complex had a structure:




(111)

The author concluded from the polymerization of styrene initiated by the complexes (1, 11, 111). In their rate-conversion characteristic they were very similar, the order dependences of initial rates were different. He proposed that

the following mechanism was operative for the production of three complexes:

1) $2\ Cp_2TiCl_2 + Al_2(Et_3)_2 \rightleftharpoons 2\ Cp_2TiCl_2AlEt_3$

Complex II

2) Complex II + $AlEt_3 \rightleftharpoons Cp_2TiClEt + Al_2Et_5Cl$

$Cp_2TiClEt \longrightarrow Cp_2TiCl + C_2H_5^x$

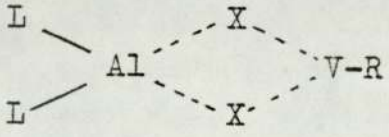
Complex III

$C_2H_5 \cdot \longrightarrow \frac{1}{2}C_2H_4 + \frac{1}{2}C_2H_6$

3) Complex III + $AlClEt_2 \underset{\text{in toluene}}{\overset{\text{in heptane}}{\rightleftharpoons}} Cp_2TiClAlEt_2$

Complex I

Carrick ( 18) reported the first soluble vanadium catalyst for the ethylene polymerization, using vanadium tetrachloride ($VCl_4$), aluminium bromide ($AlBr_3$) and triphenyl or triiso butyl aluminium in cyclohexane. He extracted the catalytic solution with sulphuric acid and polarographic analysis showed that the vanadium was exclusively divalent. The reduction of V(1V) was completed in less than one minute, but no further reduction to V(I) or V(0) was observed. Carrick concluded that the active species in the $VCl_4$ was also a V(11) - Al complex and in analogy to bridge-bonded Ti-Al complexes ( 86 ). The structure proposed by Carrick is as follows:




L = alkyl or halogen
X = halogen
R = alkyl or growing chain

The same author ( 87 ) later replaced the aluminium alkyl with tetraphenyltin ($SnPh_4$) and showed that the first process was the formation of an aluminium alkyl by reaction of $SnPh_4$ with $AlBr_3$. van der Kerk ( 88 ) demonstrated that the combination of $AlBr_3$ and $AlEt_3$ or $(Ph)_4Sn$ could be replaced by $AlEtCl_2$, leading to a catalyst which had quite comparable activity. They also ( 89 ) concluded from a spectroscopic investigation of $VCl_4$ or $VOCl_3$ with $EtAlCl_2$ in cyclohexane at room temperature that the catalytic species was a V(11)-Al alkyl complex.

Bier ( 90 ) used the $VOCl_3$ - $Et_3Al_2Cl_3$ system as a catalyst to copolymerize ethylene with propylene and proposed that the active species was a V(111) - Al complex. It was deactivated on reduction from V(111) to V(11).

Natta ( 91 ) also investigated the systems which consisted of $VCl_4$ or $V(acac)_3$ [acac = 2,4 - pentanedionate] with aluminium alkyls at $-78^{\circ}$ to polymerize propene and proposed that a necessary condition for an active catalyst was the presence of one halogen ligand at either of two components.

The catalytic solutions were stable only at low temperature, on heating to room temperature $VCl_2$ precipitated which was inactive towards polymerization. The following mechanism was proposed for its formation and destruction:

$$VCl_4 \xrightarrow{R_2AlCl} VCl_2R_2$$

$$VCl_2R_2 \longrightarrow VCl_2R + R^x$$

$$VCl_2R + \text{monomer} \longrightarrow VCl_2P$$

$$VCl_2P \longrightarrow VCl_2 + P^x$$

p = polymer $\qquad$ $p^x$ = polymer radical

A dialkylated V(1V) species was proposed as the catalyst precursor. ESR studies by Natta ( 91 ) showed that $VCl_4$ - $Et_2AlCl$ system did not exhibit any ESR signal at $-78^{\circ}C$. Heating to room temperature was accompanied by the appearance of a broad line signal which was due to solid $VCl_2$. It was not active catalytically.

The active oxidation state of vanadium in olefin polymerization catalysts prepared from $VCl_4$ - $R_2AlCl$ was studied by Lehr ( 92 ) who used ESR, spectrophotometric and NMR, spectroscopy to conclude that the more active catalyst evidently came from an inactive V(111) precursor. The data suggested that two active complexes containing V(111), one much more active, but less stable than the other were formed. Using potentiometric techniques he showed that the reduction of $VCl_4$ with $R_2AlCl$ was

about 90% complete after five minutes.

The author suggested that the following reaction scheme was operative:

$$R_2AlCl + VCl_4 \xrightarrow[\text{fast}]{k_1} VRCl_3 + RAlCl_2$$

$$4\ R_2AlCl + 2RVCl_3 \xrightarrow[\text{fast}]{k_2} 2\ VCl_3\cdot(R_2AlCl)_2 + 2R$$

$$VCl_3\cdot(R_2AlCl)_2\cdot \xrightarrow[\text{slow}]{k_3} RVCl_2\cdot(R_{3/2}AlCl_{3/2})_2$$

$$RVCl_2\cdot(R_{3/2}AlCl_{3/2})_2 + nM \xrightarrow[\text{slow}]{kp} RM_nVCl_2\cdot(R_{3/2}AlCl_{3/2})_2$$

However Lehr ( 93 ) discovered with the same catalyst system ($VCl_4$ - $R_2AlCl$) and by ESR measurement that after a few minutes at -78°C practically all V(1V) was reduced to V(111). He suggested that the active species was an alkylated vanadium (111) complex and that the precursor contained no alkyl vanadium bonds. This view was opposed by Svab ( 94 ) who used an oxidimetric technique to elucidate the reaction between $VCl_4$ or $VOCl_2$ with several aluminium alkyls and concluded that the active species was $RVCl_3$ at -78°C.

Thus there is agreement among different workers concerning certain points:

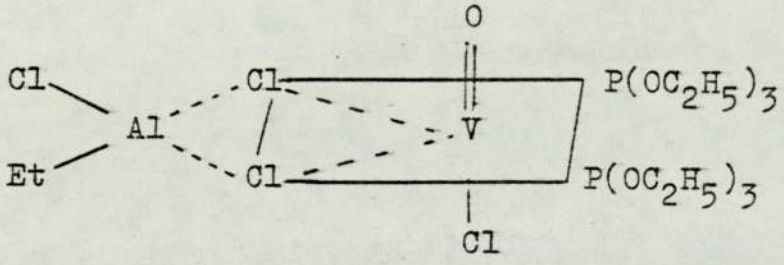
1. The active species is a complex containing Al as well as V.
11. One of the catalyst components must contain at least one halogen ligand.

111. No valence state lower than V(111) is active.

On the other hand disagreement has been found concerning the mechanism of formation of the active species, whether it is via a dialkylated V(1V) or a non-alkylated V(111) species. Furthermore disagreement occurs over the valence state of the transition metal whether it be V(1V), V(111) or V(11).

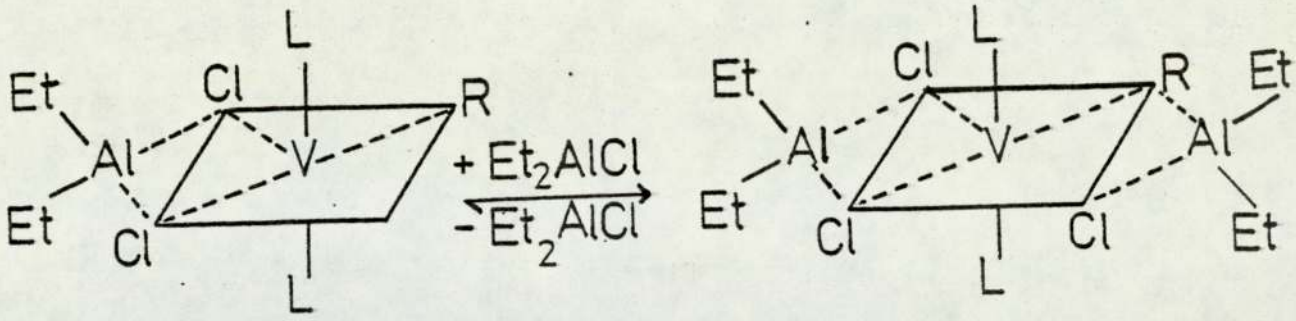
However Olivé chose a system which consisted of $VO(acac)_3$

and $Cr(acac)_3$ as transition metal components since these formed homogeneous catalysts with $Et_2AlCl$. The same author ( 95 ) had already investigated $VO(acac)_2$ - $R_2AlCl$ system and an ESR investigation revealed that the (acac) ligands were replaced rapidly by chlorine. The evidence was as follows: $VO(acac)_2$ dissolved in toluene to give the typical eight line signal of free $VO^{+2}$ ion. When $EtAlCl_2$ was added to solution containing the phosphite a new signal obtained which indicated that there was interaction of the unpaired electron of V with the phosphorus nucleus. The author concluded that a bridge-bond was formed which completed an octahedral configuration as shown:




The effective magnetic moment of V in the system was also determined $VO(acac)_2$ - $Et_2AlCl$ in benzene solution at different ratios of Al/V. ( 96 ).

From the result of magnetic measurement it was found that a steady increase from one to three unpaired electrons per vanadium centre obtained. At Al/V = 100 practically pure V(11) was reached. Since it has been proved by ESR that no V(1V) is detectable at Al/V$\rangle$5 after the mixing of components the magnetic effect ought to be distributed between V(111) and V(11). The author concluded that the presence of chlorine ligands at the vanadium centre permitted the formation of a bridge complex with one or two aluminium alkyls which then stabilized the vanadium in the valence state of II. Thus the final stable V(11) complex was:




L = solvent, phosphane, phosphite or $AlR_nCl_{n-1}$

Haszeldine and his co-workers ( 97 ) investigated the $VOCl_3$ - $Al(i\text{-}Bu)_3$ - THF system for the polymerization of vinyl fluoride and vinyl chloride in benzene. He suggested that tetra hydrofuran (THF) underwent complex-formation with the other catalyst components and restricted the reduction of vanadium to V(1V). The reaction between $VOCl_3$ and $Al(i\text{-}Bu)_3$ in the presence of THF formed a homogeneous catalyst and the author formulated the reaction as

$VOCl_3 .\ THF + AlR_3 .\ THF + THF \longrightarrow$

R = (i-Bu)

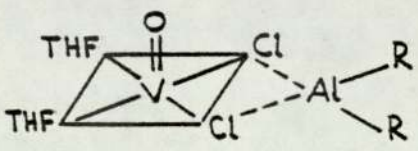
$VOCl_2 .\ 2THF + AlR_2Cl .\ THF + \frac{1}{2}C_4H_8 + \frac{1}{2}C_4H_{10}$

$VOCl_2 .\ 2THF + AlR_3 .\ THF \rightleftharpoons$

$AlR_2\ Cl.VOClR .\ 2THF + 2THF$

Complex I

Complex I was depicted as:




In order to establish the nature of the active site vanadium oxydichloride tetrahydrofuranate was used but alone did not produce an active site for polymerization. When sufficient THF was added to vanadium oxydichloride to form $VOCl_2.2THF$ on the addition of $Al(i\text{-}Bu)_3$/THF, a site that was active for the polymerization of vinyl chloride was formed.

The course of polymerization was similar to that observed for the system of $VOCl_3/Al(i\text{-}Bu)_3/THF$.

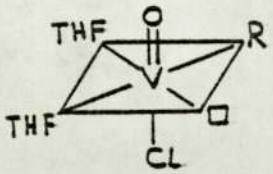
In addition the authors suggested that the following scheme might be established in the catalyst system:

$$AlR_2Cl.VOClR.2THF \rightleftharpoons VOClR.2THF + AlR_2Cl$$

Complex I — Complex II

$$AlR_3 + AlR_2Cl.VOClR.2THF \rightleftharpoons VOClR.2THF + Al_2R_5Cl$$

And complex II was proposed to have an octahedral symmetry with a vacant coordination position as follows:




This vacant site would then allow the usual formation of a $\pi$ complex with an olefin.

Similar work was described by Haszeldine and co-workers ( 98 ) who derived a soluble catalyst from $VOCl_3$-$Al(i\text{-}Bu)_3$-THF system to polymerize vinyl chloride. The solution of $VOCl_3$ and THF in benzene was opaque and black but addition of $Al(i\text{-}Bu)_3$ to this solution caused the formation of a transparent brown solution. Kinetic and copolymerization studies indicated that the polymerization was similar in nature to a conventional Ziegler-Natta system.

The polymerization of ethylene on the $Cp_2VCl_2$-$AlCH_3Cl_2$ and $CpVOCl_2$-$AlCH_3Cl_2$ systems were studied by Shilova ( 99 ). It was shown that polymerization took place using the system $Cp_2VCl_2$-$AlCH_3Cl_2$ only in the presence of oxygen. With the aid of labelled $Al^{14}CH_3Cl_2$ it was found that one methyl group from the aluminium alkyl entered each polymer chain. It was also shown that in those systems complexes of alkylated vanadium in the higher valence state were active catalytically.

Andreeva and his co-workers (100 ) investigated triethyl vanadate $VO(OC_2H_5)_3$-$AlEt_2Cl$ system for the polymerization of ethylene. They used radio spectrometric infra red and electroconductivity

measurements to propose that there was sequential reduction of the vanadium as follows:

$$V^{+5} \xrightarrow{k_1} V^{+4} \xrightarrow{k_2} V^{+3} \xrightarrow{k_3} V^{+2}$$

In order to detect the active site for the polymerization the ratio of Al:V was changed from 0.5/1 to 4:1 and from the recorded character of the spectrum, concluded that $V^{+3}$ was the active site for the polymerization of ethylene and this site was said to comprise a halogen forming bridge linked between vanadium and aluminium atoms.

Evans and his co-workers (101) worked on the system obtained on mixing dichloro bis ($\eta$)-cyclopentadienyl) vanadium in dichloromethane as solvent, with ethyl-aluminium dichloride in heptane. From the ESR spectrum observations they found three species of vanadium present, one of which was $\left[Cl(Cp)_2\ V\ (\mu\text{-}Cl)_2AlCl_2\right]$, i.e. vanadium in $V^{+3}$ oxidation state.

In addition it was found that pyridine attached this complex at the aluminium atom to complex with the alkyl aluminium compound.

$VOCl_3$-$Et_3Al_2Cl_3$ and a chlorinated activator was used as catalyst by Duck (102) to polymerize ethylene, in hexane in the presence of hydrogen. They reported the catalyst became inactive after twenty minutes, on addition of further ethyl-aluminium sesqui chloride (EASC) the original catalytic activity was regained. They proposed that the active site was V(111) state and inactive V(11) species was oxidized by an activator to V(111) active state. The modifying effect was shown by the occurrence of a reaction of the type:

$$-(CH_2)_n-V \longrightarrow -(CH_2)_n-Cl + Cl-V$$

The polymerization of styrene was undertaken Kapur and his coworkers (103) by using $VOCl_3$-$AlEt_3$ and $VOCl_3$-$Al(i\text{-}Bu)_3$ systems. They studied the nature of the catalytic species of vanadium's valence states, using potentiometric technique at various

ratios of Al to V. They concluded that the active site at $VOCl_3$-$AlEt_3$ system was tervalent but it was divalent in the $VOCl_3$-$Al(i\text{-}Bu)_3$ system. The same group (104) tried to polymerize methyl methacrylate using vanadium based catalysts, and found that $VOCl_3$-$AlEt_3$ and $VCl_4$-$AlEt_3$ systems were effective for the polymerization. They found that in the $VOCl_3$ system, the valency of V was 3 whereas in the case of $VCl_4$ system it was 2.

Later work extended the polymerization of methylmethacrylate using $VOCl_3$-$AlR_3$ to the addition of basic additives such as (diethylether and pyridine). It was concluded that the presence of three different sites occurred at one ratio of Al/V in $VOCl_3$-$AlEt_3$ system (105). One of these sites, responsible for syndiotactic structure, resulted from the adduct formation of the additive with organometallics. The same authors (106) also used $VOCl_3$-$AlEt_2Br$ system and polymerized methylmethacrylate to show that the catalyst system containing vanadium in $V^{+2}$ state was less active than $V^{+3}$ state for the polymerization.

1.3. ETHYLENE-PROPYLENE COPOLYMERS

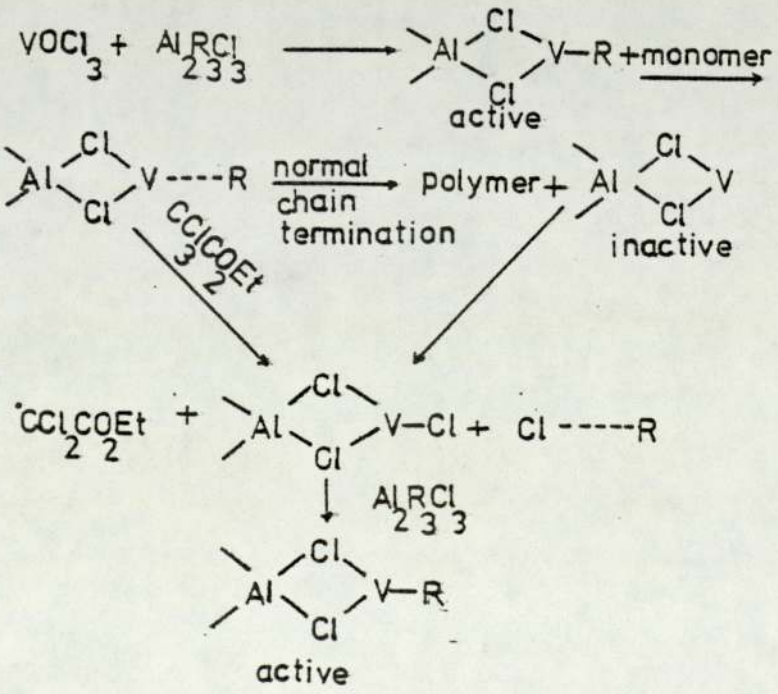
The most efficient 'Ziegler-Natta' catalyst for the copolymerization of ethylene and propylene is derived from the reaction of alkylaluminium compounds, e.g. $Al(i\text{-}Bu)_3$, $AlEt_2Cl$, $Al_2Et_3Cl_3$, $AlEtCl_2$ with hydrocarbon soluble vanadium compounds, e.g. $VOCl_3$, $VCl_4$, $V(Ac)_3$, alkylesters of vanadic or chlorovanadic acid. Other transition metals such as niobium, titanium, chromium have also been used.

The copolymers obtained in the presence of vanadium-based homogeneous catalysts have the advantages of being amorphous and thus possess elastomeric properties. There have been exhaustive reviews of the synthesis and properties of ethylene-propylene elastomers by Natta (107) and Baldwin and co-worker (108). The most significant features of these rubbers are their low specific gravity, good resistance to oxidation, heat

and chemicals, good electrical properties and low permeability to water vapour.

Junghanns and co-workers ( 90 ) studied catalyst systems prepared from $VOCl_3$-$AlEtCl_2$ and $VOCl_3$-$Al_2Et_3Cl_3$, and concluded that a loss in catalyst activity with time occurred during the polymerization. As the catalyst activity decreased a corresponding decrease in the vanadium oxidation state also took place. Using the same systems Kelly and co-workers (109) found that an increase in the Al/V ratio caused an increase in the catalyst efficiency. An increase in propylene content in the feed at constant total monomer concentration caused a decrease in the polymerization rate and in the intrinsic viscosity of the copolymer.

Duck ( 110) used $VOCl_3$-$Al_2Et_3Cl_3$ and $VOCl_3$-$Al_2Et_3Cl_3$ - activator systems and obtained soluble ethylene-propylene copolymers, which were completely random. Polymerization activity was restored by further addition of the alkyl aluminium compound or alkyl aluminium plus modifier. He proposed a reaction scheme for regenerating the active site as:



Mild oxidising agents such as $Cl_3CCOOEt$ were used as catalyst activators together with hydrogen as a molecular weight regulator.

An ethylene-propylene copolymer containing 38% wt propylene was prepared by Keim and co-workers (111), using a soluble catalyst made in situ from $Al_2Et_3Cl_3$-$VOCl_3$ system where the ethyl group was labelled with $C^{14}$. The initiation step in the polymerization was proposed as:

$$\overset{*}{Et}_3Al_2Cl_3 + VOCl_3 \longrightarrow Cl_2AlO\overset{Cl}{\overset{|}{Al}}Et + VCl_3 + CH_2{=}\overset{*}{C}H_2 + \overset{*}{C}H_3CH_3$$

$$VCl_3 + \overset{*}{Et}_3Al_2Cl_3 \longrightarrow Cl_2V\overset{*}{Et} + \overset{*}{Et}_2Al_2Cl_4$$

where * represents $C^{14}$ labelling.

The actual reactions were more complex since the various species were undoubtedly complex, if not the vanadium compounds would have precipitated whereas the polymerization was completely homogeneous. The propagation step proceeded by insertion of a monomer unit between the alkyl group and the vanadium atom,

$$Cl_2V\overset{*}{Et} + nRCH{=}CH_2 \longrightarrow Cl_2V(CH_2CHR)_n\overset{*}{Et}$$

Termination by disproportionation completed the chain,

$$2Cl_2V(CH_2{-}CHR)_n\overset{*}{Et} \longrightarrow (CH_3CH_2)\ (CH_2{-}CHR)_{n-1}\overset{*}{Et} + CH_2{=}CH(CH_2CHR)_{n-1}\overset{*}{Et} + 2VCl_2$$

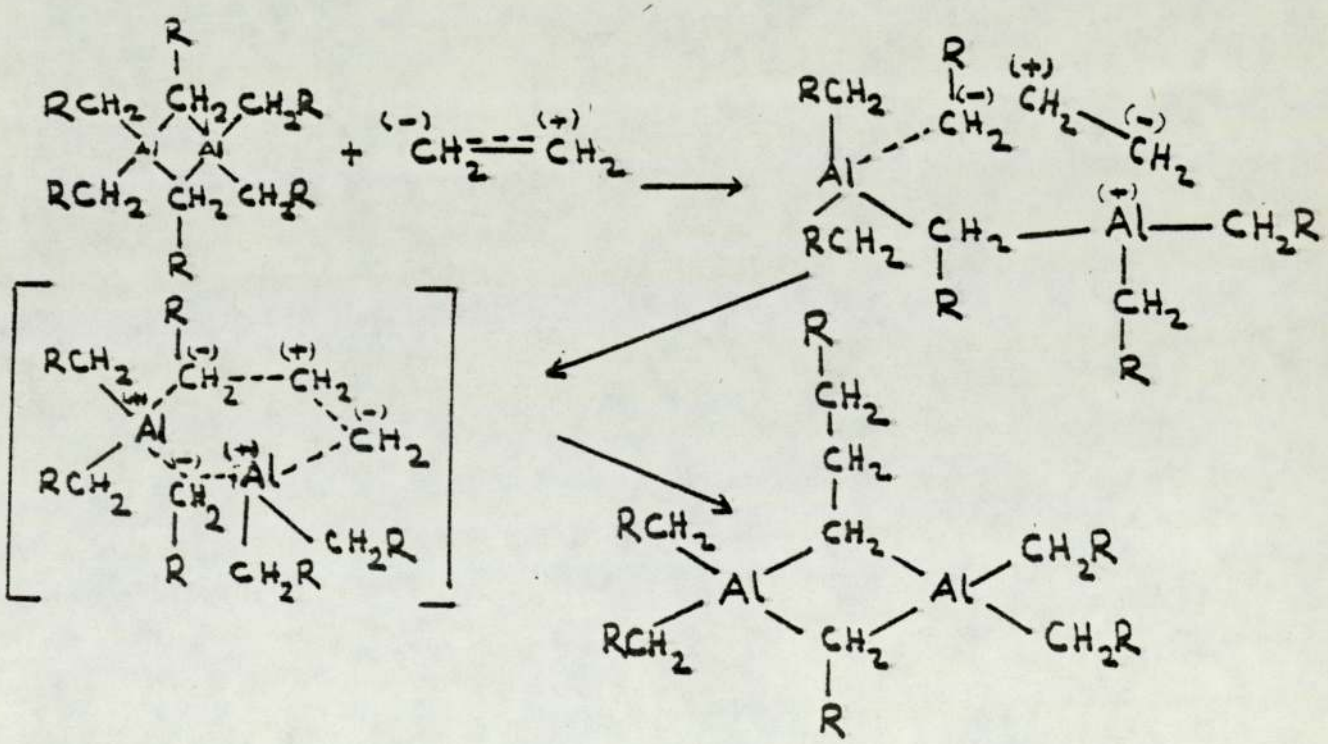
Because of the absence of detectable unsaturation in the ethylene-propylene copolymer chains, the most convenient way to unsaturate ethylene-propylene based elastomers and hence promote sulphur curing is to incorporate a termonomer which is a non conjugated diene possessing double bonds of different activities. Dienes are capable of entering the polymer back bone via one of these double bonds and can be cross linked under usual vulcanisation processes with sulphur and accelerators (112) through the other. Alkenyl, alkyl dienes and norbornenes are the common class of dienes used as termonomers.

## 1.4. INITIATION AND PROPAGATION REACTIONS

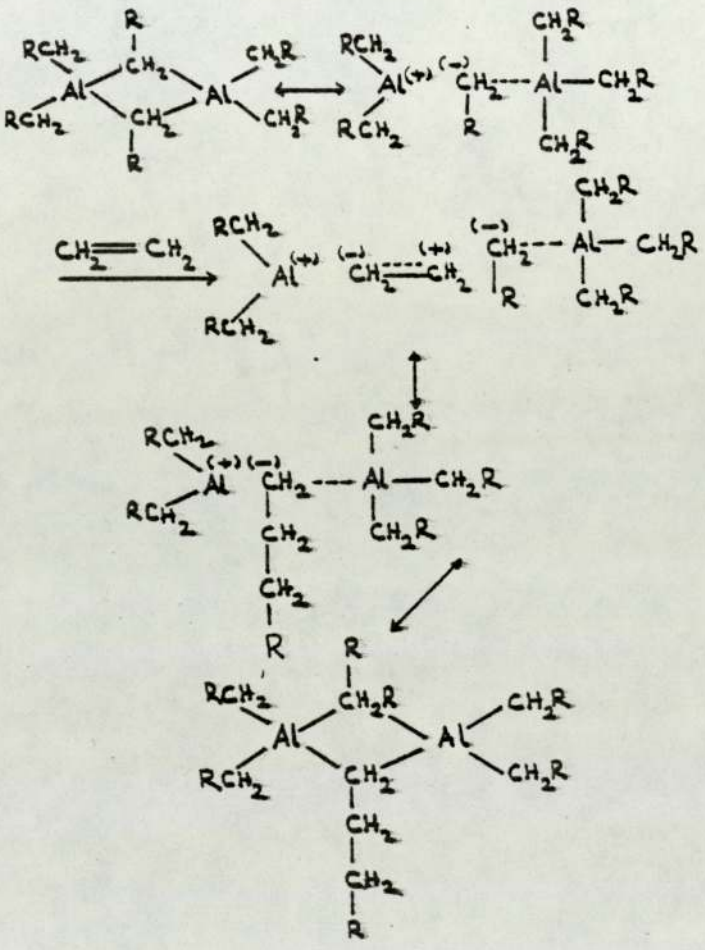
The mechanistic schemes are presented in four classifications

(a) The bimetallic mechanism

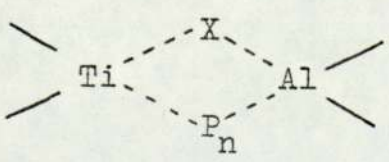
The polymerization of ethylene may be initiated by aluminium alkyls and Natta ( 14 ) suggested that propagation took place by insertion of an olefin molecule, polarized by $AlR_3$, into the electron deficient aluminium alkyl dimer. This occurred by a simultaneous dissociation of the metal alkyl bridge bond and the substitution of the negatively polarized carbon atom of the alkyl by the carbanion of the polarized olefin which can be depicted as:



Alternatively a mechanism can be proposed in which the aluminium alkyl dissociated ionically and the polarized ethylene molecule was placed between the two oppositely charged ions as follows:



The propagation reaction in both cases involved the repeated addition of monomer to the bond between the aluminium atom and the growing chain. Accordingly in the most cogent mechanisms employed by Natta ( 72 ) and Patat and Sinn(113,114)using bi-metallic catalysts, the basic structure of the bimetallic complex was proposed as:



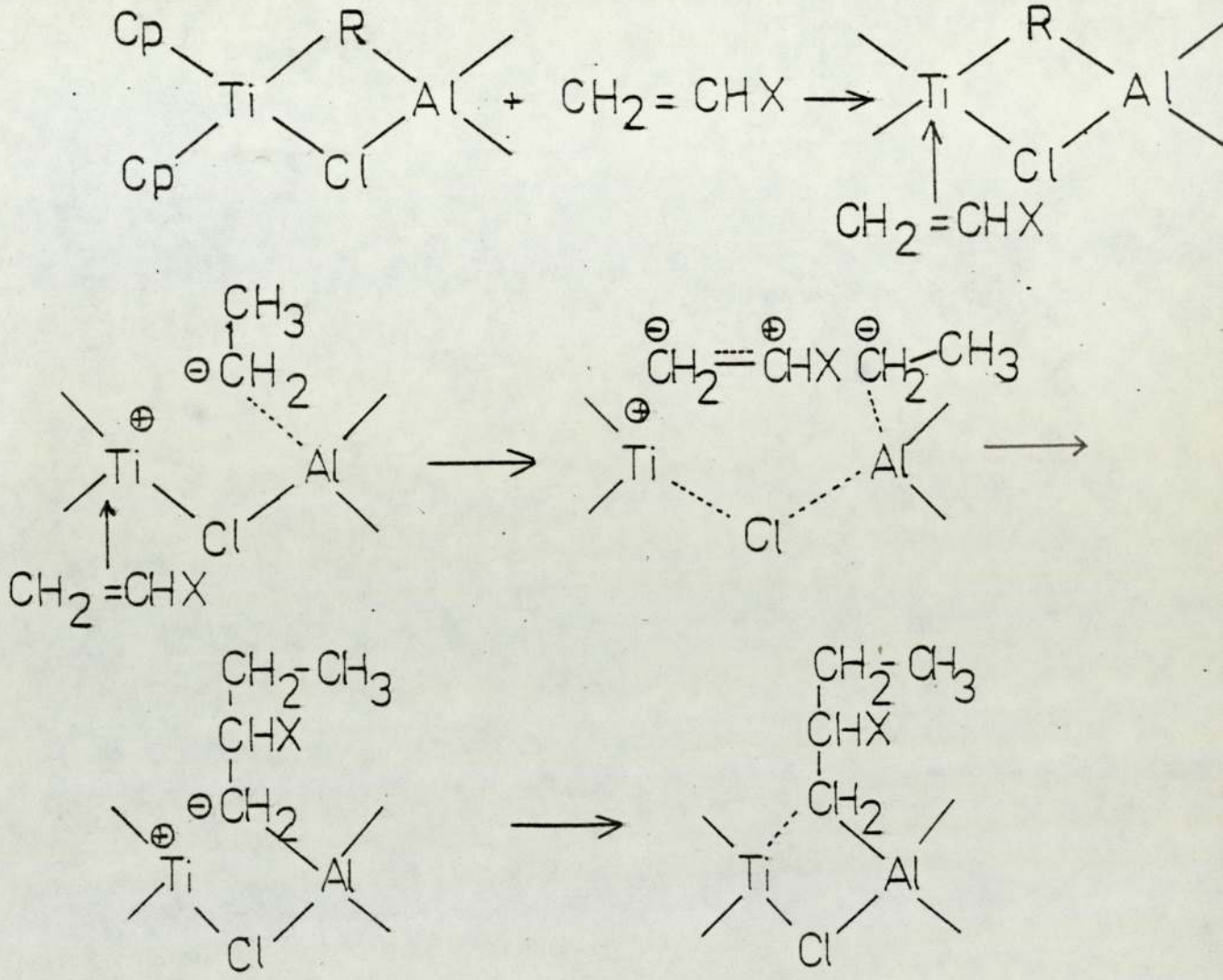

wherein X = halogen

$P_n$ = growing polymer chain

Natta believed ( 14 ) that the incomplete co-ordination of titanium in the reduced di - and tri - chlorides initially facilitated chemisorption of the organometallic compounds of strongly electropositive metals. This chemisorption led to the formation of electron-deficient complexes between the titanium and aluminium compounds, and the isolation of soluble crystalline complexes of the general formula $(C_5H_5)_2TiCl_2AlRR'$, which are known to contain titanium-carbon-aluminium bridges, lent weight to Natta's view.

During the polymerization of ethylene with catalysts derived from dichlorobiscyclopentadienyltitanium, $(C_5H_5)_2TiCl_2$ and triphenyl aluminium, $(Ph)_3Al$, the polymeric chains contained phenyl end groups (72,115 ) and hence it was proposed that the olefin was polarized and inserted into the Al-C bond of the complex.

However when the catalysts were derived from $Cp_2TiPh_2$ and $AlEt_3$, the polymeric chains contained no labelled phenyl end groups ( 115). It has also been shown that when $AlEt_3$ containing $^{14}C$-labelled ethyl groups was adsorb on to the surface of $\alpha$-$TiCl_3$ and used as a polymerization catalyst in the presence of non-labelled $AlEt_3$, the resulting polymer contained practically all the labelled alkyl groups as terminal groups (116 ). Natta was of the opinion that this could not be attributed to alkylation of the titanium centres, although this appears to be a moot point. Accordingly it was concluded that a dissociation of each catalytic complex into two parts took place, one containing the titanium atom, the other the alkyl groups, including polymeric chains bound to the aluminium atom. This dissociation was followed by reassociation of titanium atoms with other aluminium alkyls present in the solution as shown on the following page.

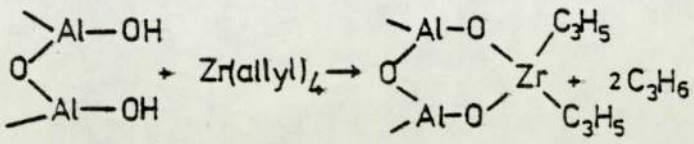


However recent work by Ballard (117) supports Natta's hypothesis. The author (118) investigated the behaviour of transition metal benzyl and trimethyl silyl derivatives as homogeneous catalysts for the polymerization of ethylene and styrene. It was concluded that during the polymerization, the olefin formed a complex with the metal centre, followed by a four-centre insertion reaction. As soon as one monomer molecule was inserted, the active centre became labile to $\beta$-hydrogen abstraction. The low activity of catalysts were attributed to two causes:

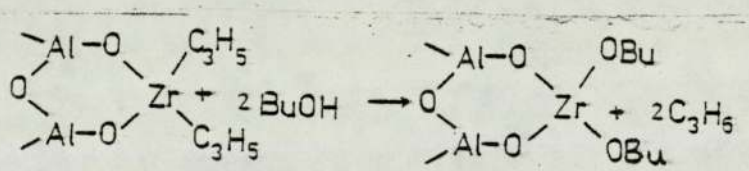
a. The difficulty of displacing a benzyl or silanyl methyl ligand by olefin insertion and b. $\beta$-hydrogen abstraction re-

actions which formed hydride-bridge dimers which were inactive as polymerization catalysts. It was shown that some increase in activity could be obtained by replacing one of the ligands by an anionic ligand such as $Cl^-$, $Br^-$.

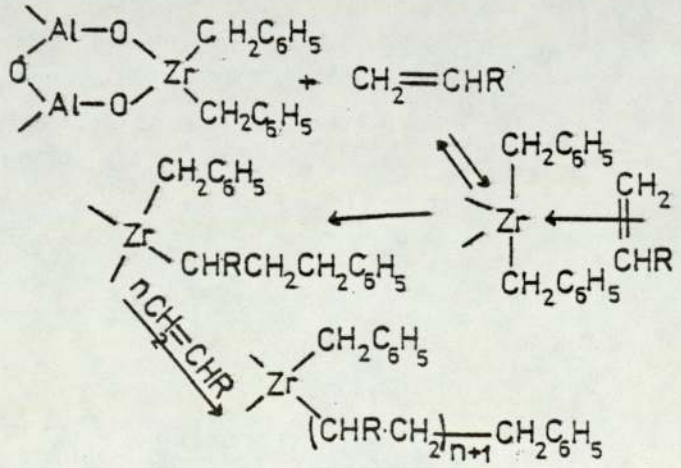
A highly active catalyst was obtained by the reaction of $Zr(CH_2CHCH_2)_4$ with the acidic hydroxyl groups on the surface of either silica or alumina (119). The reaction path was proposed as:




The structure for the transition metal centre was confirmed by measuring the amount of olefin produced, with n-butanol:

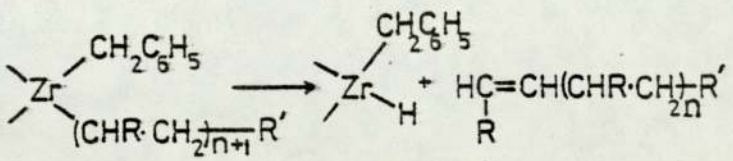


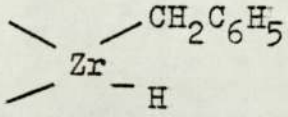

and by IR studies. Similar observations have been made with $Zr(CH_2C_6H_5)_4$, $Zr\left[CH_2Si(CH_3)_3\right]_4$, $Zr(CH_2OCH_3)_4$.

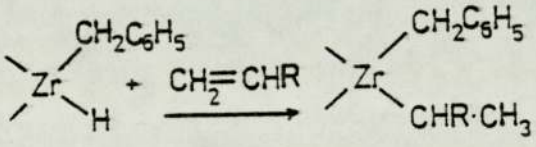


According to this mechanism the catalyst centre coordinated monomer then insertion of monomer between the benzyl group and metal atom occurred. Repetition of this process gave high molecular weight polymers.

The molecular weight control factor was $\beta$-hydrogen abstraction process:



Realkylation of the species  reactivated the propagation centre:



Chain termination by $\beta$-hydrogen abstraction occurred but the zirconium hydrides produced were unable to dimerize, so that realkylation occurs and polymerization proceeds.

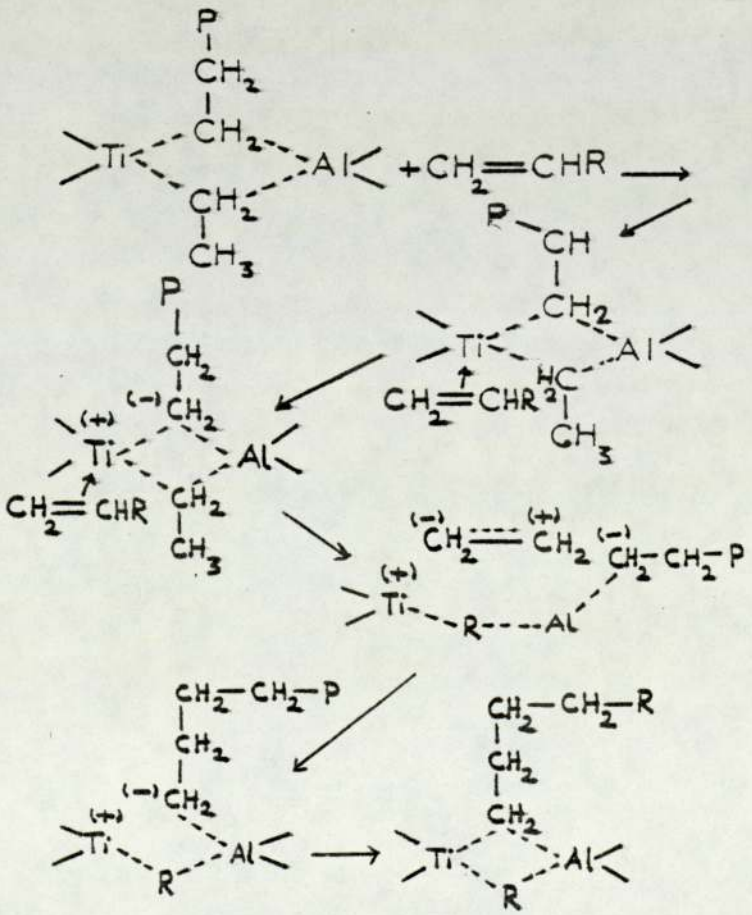
Direct evidence of the insertion between the zirconium-metal bond was obtained from the catalyst Zr $(^{14}CH_2C_6H_5)_4/Al_2O_3$ system to polymerize styrene. The amount of polymer derived from the initial insertion reaction remained stationary, but the proportion of the total declines as the amount of polymer originated from the re-alkylated Zr-H centres became more important.

However the replacement of the Zr compound by an aluminium alkyl also produced highly active catalysts for the polymerization of ethylene and it seems plausible that insertion into the Al-C bond of truly Ziegler-Natta catalysts could take place. Patat and Sinn(113,114)also considered the active complex to be bimetallic, the titanium and aluminium atoms being joined by

bridging alkyl groups. In this case, the olefin was partially bonded between the titanium and the methylene of the last added monomer which in turn was also partially bonded to the aluminium atom. The $\pi$ electrons of the olefin interacted with the 3d orbital of the titanium. Because of the planarity of the resulting orbital, free rotation around the olefin-titanium bond as well as around the carbon-carbon bond in the complex olefin was inhibited. The complexed monomer approached the alkyl group still attached to the aluminium atom, and overlap of the two 2p states developed and the resulting hybrid bond was of the $\sigma$ type.

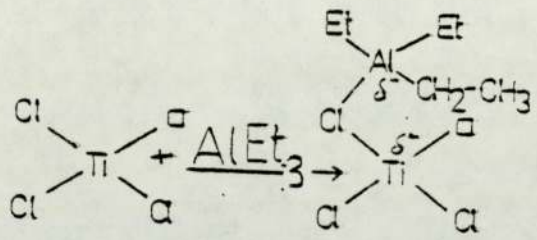
The alkyl group primarily attached to the aluminium atom was released but still remained partially bonded to the titanium atom of the bimetallic complex. Repetition of this sequence of steps constituted the polymerization.

Accordingly Patat and Sinn's mechanism can be written as follows:

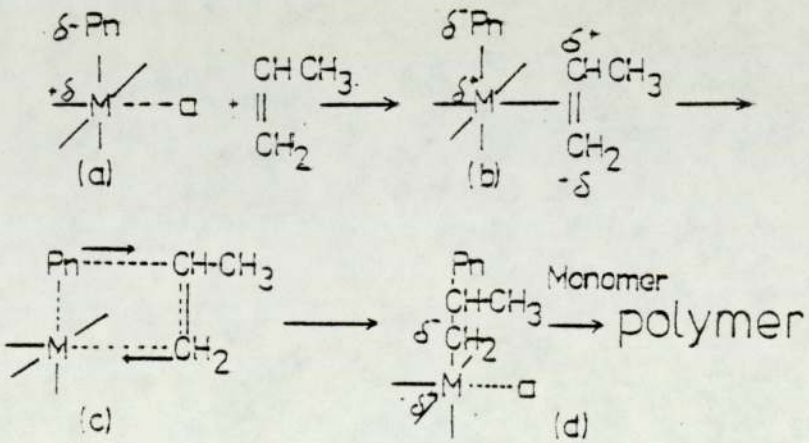


The radioactivity of the polymer was accounted for by the presence of radioactive bridging groups. These bridging groups could have originated from either the titanium or aluminium compounds because facile exchange could take place and hence radioactivity experiments cannot be used to distinguish between propagation at aluminium or titanium.

Boor (31 ) suggested that the bimetallic mechanism involved the formation of a complex between the aluminium alkyl with a chlorine atom on the surface of the $TiCl_3$ and those aluminium alkyls that were active were located next to chlorine vacancies



The titanium atom was then rendered electron deficient and readily coordinated the olefin; insertion of the olefin into the Ti–R bond then occurred by a concerted reaction

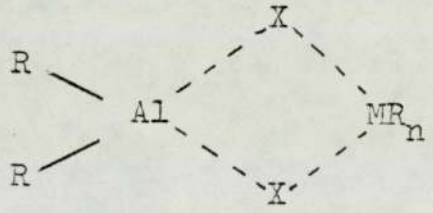



Propagation mechanism involved no prior coordination of monomer (120).

The Boor model required that the metal-carbon bond be highly polarizable and hence metal centres which have small radii and

bear a high positive charge were preferred. The driving force consisted of the transfer of the electrons, leading to the thermodynamically favoured conversion of the C=C double bond into two single C—C bonds, with retention of the metal-carbon σ-bond. As the olefin approached the metal centre, the polarized M—C bond became longer and the olefin was inserted directly into it. The advantage of the mechanism is that the polymer chain maintained its position in the octa hedral complex, i.e. structure (a) and (d) are equivalent hence eliminating the need for the polymer migration as shown on the previous page. The continuation of this process back and forth led to the production of large quantities of polymer on a limited surface area.

Carrick ( 121) proposed a bimetallic mechanism in which the catalysts were based on transition metal compounds and aluminium alkyls that formed bimetallic complexes, e.g.




X = halogen

R = halogen, alkyl or aryl

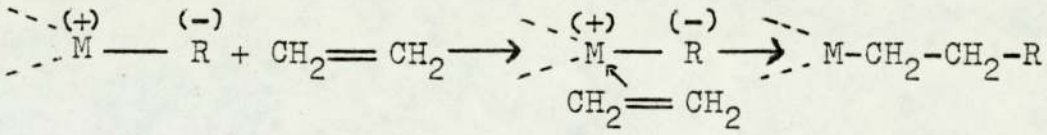
M = transition metal

It seemed unlikely that the aluminium end of the complex was catalytically active since this portion was structurally identical to one end of the aluminium alkyl or alkylaluminium halide dimer, which were shown to be specifically non-catalytic for the growth reaction ( 122 ).

Experimental evidence in support of propagation being governed by the transition metal centre, was that the relative reactivity ratios of monomers in copolymerization changed when different transition metal compounds were used, but were not affected by the use of different reducing agents with a particular transition metal compound ( 123 ).

Assuming that propagation occurred from a transition metal centre, a reasonable mechanism involved preliminary coordina-

tion of the olefin to a vacant d-orbital of the transition metal and then a re-arrangement to incorporate the polarized olefin into the growing polymer chain.



It was suggested that the -R group had to be hydride or alkyl rather than halogen or some oxy derivative in order to provide a low energy initiation reaction (M-R bonds are weaker than metal-halogen bonds). In this mechanism the transition metal valence also played an essential role, since in all transition metals there is a decrease in electronegativity of the metal centre with a decrease in valence. The progressive filling of the transition metal orbitals with increasing reduction should decrease the electron-attracting power of the metal for olefins. The stability of such complexes must be expected to increase with decreasing valence. At the same time the decreasing electronegativity makes the C-M bond more polar so that any co-ordinated (polarized) monomer was more readily incorporated into the growing chain by the re-arrangement reaction. Experimentally, the best catalytic activity was observed with the low transition metal valences, which suggests that a very polar C-M bond was essential. High valence transition metal compounds have electronegativities of 1.6-1.8 which is in the same range as aluminium; therefore if these compounds are catalytic, the rate of propagation might be expected to be low as it is with aluminium alkyls alone.

The author has recently reviewed (124) the mechanism of olefin polymerization and proposed that the reaction between $AlR_3$ and transition metal, e.g. $VCl_4$ could be written as:

$$AlR_3 + VCl_4 \rightleftharpoons R_2AlCl + RVCl_3$$

$$R_2AlCl + VCl_4 \rightleftharpoons RAlCl_2 + RVCl_3$$

$$RAlCl_2 + VCl_4 \rightleftharpoons AlCl_3 + RVCl_3$$

$$RVCl_3 \longrightarrow (R) + VCl_3$$

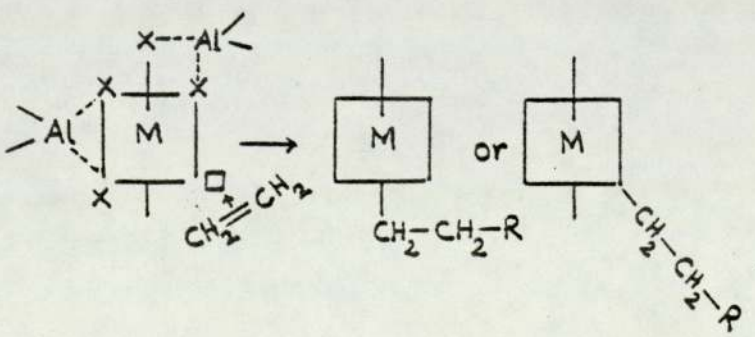
$$AlR_3 + VCl_3 \rightleftharpoons R_2AlCl + RVCl_2$$

$$RVCl_2 \longrightarrow (R) + VCl_2$$

$$AlR_3 + VCl_2 \rightleftharpoons R_2AlCl + RVCl$$

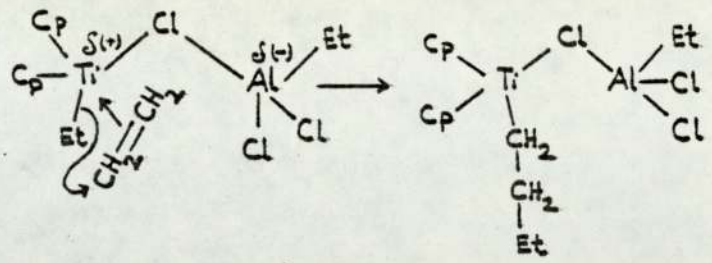
Again the active site was considered to be a bimetallic complex in which the transition metal was in its lowest valence (usually $M^{+2}$). The olefin was coordinated ($\pi$ -complex) to the transition metal centre prior to its incorporation into the growing chain, and this coordination step utilized the d-orbital of the transition metal. The bonding required the $\pi$-electron cloud of the olefin to be oriented towards the metal centre. This necessitated the metal possessing both an empty and a filled d-orbital so that the metal atom had to have a valency two units below the maximum for catalytical activity. In this case $\pi$-electron was donated from the olefin to the empty d-orbital (or hybrid orbital) and the filled d-orbital of the metal overlapped with the anti-bonding $\pi$-orbitals of the olefin.

No difference of any kind in the mechanism was implied between the previous one and this. The only difference was in the coordination number and hence geometry of the transition metal centre, shown below:




Breslow and Newburg(19,20) polymerized ethylene using a soluble catalyst $(C_5H_5)_2\ TiCl_2$ - $AlEt_2Cl$ system, and determined the effect of oxygen on the polymerization. From the spectroscopic, kinetic, magnetic susceptibility, and oxidimetric studies, they proposed that the active species was a $[Cp_2TiEtCl.EtAlCl_2]$ complex in which titanium was in its (1V) valence state and the

polymer grew by insertion of a monomer molecule between the alkyl group and the titanium, i.e.



The first step in the polymerization involved the formation of a $\pi$-type complex between titanium and the olefin. The aluminium was already tetra coordinated and a complex of it with olefin was unlikely. The function of aluminium alkyl was to alkylate the titanium and put a positive charge on the latter and increase its complexing ability.

Many other authors have proposed a variety of plausible mechanisms that may be considered to be of a bimetallic nature and these appear in reviews in the literature. Considerable experimental evidence is available to show that such bimetallic complexes can be formed in Ziegler-Natta systems. Recent work by Ballard has certainly regenerated interest in the possibility that propagation may occur via addition to an aluminium alkyl bond but it would appear that the polymerization could equally take place by addition to a titanium alkyl bond. It may well prove difficult to distinguish between these experimentally.

(b) The monometallic mechanism

The basic feature of the monometallic mechanism is that the growth process is deemed to occur entirely at one metal atom. Nenitzescu and co-workers (125 ) first suggested a monometallic mechanism in 1956 although it was suggested that it was less probable than the free radical mechanism which they also proposed. The metal alkyl component alkylated the $TiCl_3$ and the

olefin insertion took place at a tetravalent titanium as follows:

$$R - TiX_3 \rightarrow R:^{(-)} \quad {}^{(+)}TiX_3$$

$$R: \bar{]}\ TiX_3]^+ + CH_2 = CH_2 \longrightarrow R:] \quad \begin{matrix} - CH_2 = CH_2 \\ \downarrow \\ Ti\ X_3 \end{matrix}]^+ \longrightarrow$$

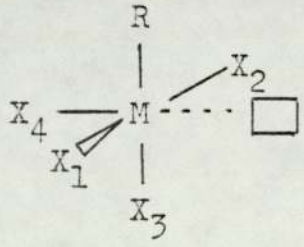
$$RCH_2CH_2:\bar{]}\ TiX_3^+ \ ....$$

A monometallic mechanism using a titanium in a lower valence state, e.g. RTiCl was suggested by Ludlum and co-workers (43) to be active site. It was postulated that an alkyl titanium chloride with a valence of two complexed with the ethylene molecule which then was inserted into titanium carbon bond, e.g.

$$ClTi-(C_2H_4)_nR + CH_2 = CH_2 \xrightarrow[\text{slow}]{k_p} Cl\ Ti\ \begin{matrix} CH_2 = CH_2 \\ / \\ -(C_2H_4)_n - R \end{matrix} \xrightarrow{\text{fast}}$$

$$Cl - Ti - (C_2H_4)_{\overline{n+1}} R$$

Cossee( 126) proposed that polymerization occurred at a titanium ion centre in the surface layer of a titanium trichloride lattice at which a surface chlorine atom was replaced by an alkyl group (R) from the $AlR_3$. Such centres were active when an adjacent chlorine site was vacant, so the incoming monomer molecule could be coordinated to the titanium atom. A diagrammatic representation of the active centre is shown below:



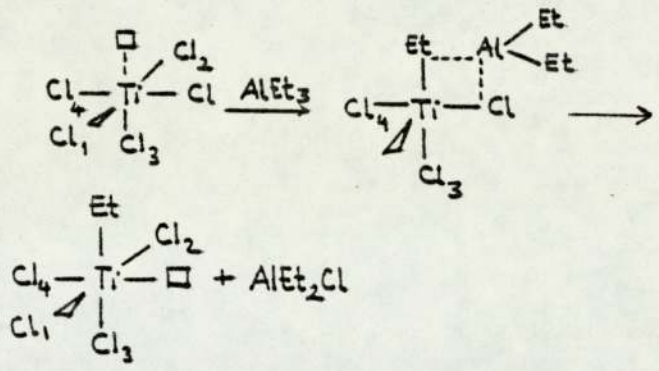

M = Transition metal

R = Alkyl group or growing polymer chain

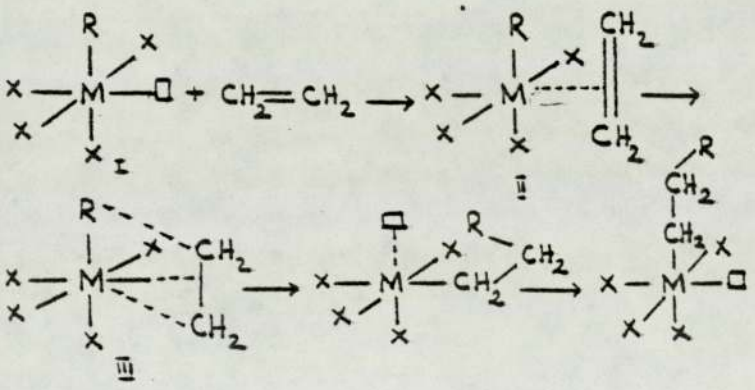
$X_1$ - $X_4$ are anions, ($Cl^-$)

□ = Vacancy

For the catalyst system $TiCl_3/AlEt_3$ to be active, the catalytic centre might have been formed by the following sequence of reactions:



This model provided a transition metal-alkyl bond and the facility for coordination of a monomer molecule with the transition element. Propagation of polymerization was assumed to be the interposition of a coordinated olefin molecule between the transition metal and the bonded alkyl group via a four-membered ring transition state, i.e.



R = The growing polymer and □ is the vacant octahedral position. Cossee's mechanism also suggested a driving force for the polymerization. The overall thermodynamic drive for any vinyl polymerization is the change from individual olefinic $sp^2$ hybridized carbon atoms to $sp^3$ hybridized carbon chain atoms, with the resultant relief of strain together with an overall decrease in free energy in the process.

The coordination of the olefin with the transition metal atom at the vacant octahedral position occurred through $\pi$-bonding figure 1( 2 ), producing a structure similar to Zeiss's (127) compounds $\left[C_2H_4PtCl_2\right]_2$ and $K^+\left[C_2H_4PtCl_3\right]^-$. This can be described molecular orbital terms as in figure 1( 3 ).

Figure 1(2) - Schematic diagram showing the formation of a $\pi$-bonded complex between a transition metal and ethylene

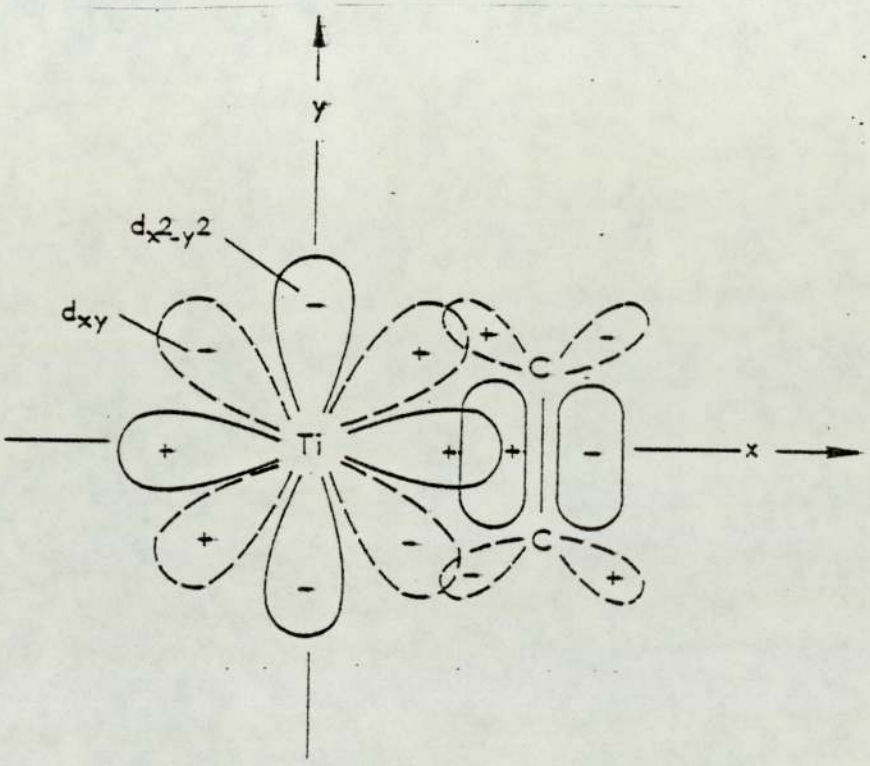
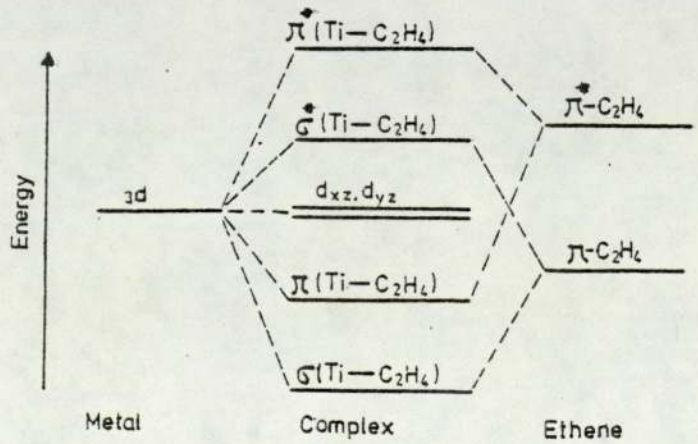



Figure 1(3) : Molecular orbital diagram for the octahedral complex



The migration IV to I proposed might not be necessary because I and IV in fact have coordination number 5 so might well be identical structures. Postulation that migration occurred may have been unnecessary.

The active species was represented by Cossee as a $\pi$-type olefin complex. The $\pi$-electrons of the olefin overlapped with the vacant $d_{x^2-y^2}$ orbital of titanium, forming a transitory bond. Simultaneously the $d_{xy}$-orbital of the metal can overlap with the vacant anti-bonding orbitals in the olefin and consequently decrease the energy between the highest filled bonding orbital and the empty or nearly empty d-orbitals of the $t_{2g}$-type. Chatt and Shaw (128) have shown that such a situation in transition-metal alkyls leads to a weakening of the carbon-metal bond and consequently facilitates migration of the alkyl group to one end of the in-going olefin molecule.

It can also be described in terms of a molecular orbital diagram figure 1(3) when an olefin is not complexed with $RTiCl_4$, $\Delta E$ represents the energy that an electron in the Ti-C bond must possess in order to weaken that bond. Since the catalyst can be stored for long periods without decomposition, $\Delta E$ is large enough to maintain the Ti-C bond intact in the absence of an olefin. When an olefin is coordinated to the $RTiCl_4$ octahedral complex a new energy level $\Psi_2(d\ yz)$, is formed by mixing metal d-orbitals and ethylene $\pi^x$-anti-bonding orbitals (back donation). This new orbital is sufficiently below the energy level of the original metal 3d-orbitals, that an electron from the metal-carbon bond ($\Psi RM$) can be excited into it much more readily. If $\Delta E$ is smaller than the critical energy gap in the Chatt and Shaw model, the alkyl group will be expelled as a radical which then attaches itself in a concerted process to the nearest carbon atom of the olefin. While at the same time the other side of the olefin becomes bonded in this way, the activation energy for such a rearrangement

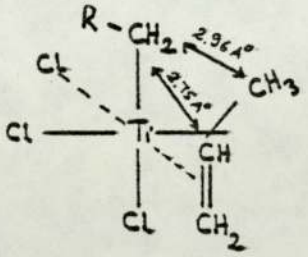
in which the alkyl group moved from a transiton metal towards the nearest carbon atom of the olefin is lowered. Cossee also said that the isolated, transition metal-carbon bonds had to be sufficiently stable in the absence of coordinated olefin, this coordination requiring the electronegativity of the metal ion to be sufficiently low. At the same time, the bonds became destabilized when an olefin molecule was coordinated in the vacant position.

Cossee's model predicted only certain transition elements would provide the correct conditions for activity. According to his molecular orbital diagrams, the catalytic activity of the transition metal compound did not require the presence of an electron in each of the $d_{yz}$- and $d_{xz}$-; $d_{zy}$- orbitals. However no two electrons are allowed to be present simultaneously in the $\Psi(d_{yz})^-$ orbital, so that only transition metal ions having from zero up to three unpaired d-electrons would produce suitable catalysts. It also followed from the diagram that the specific action of the transition metal ion was possible only when the energy of the metal 3d-level was between the bonding and anti-bonding energy levels of the olefin. Cossee ( 126 ) has made some rough computations on the relative position of some d-electron energy levels and has shown that those in $TiCl_3$ are very close to the $\pi$-electron energy levels of ethylene; whereas for example, $CrCl_3$ does not have this correlation and was known to be a very poor catalyst. The d-orbital energy level in chromium can be raised to correspond more closely to that of the $\pi$-orbitals of ethylene by coordination with oxygen instead of chlorine, as in Phillips-type ( 129 ) catalyst for the polymerization of ethylene.

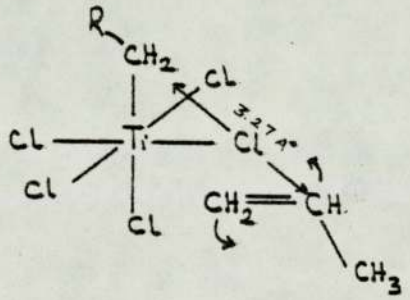
More recently, Kissin and Chirkov ( 130 ) criticised the Cossee theory. The use of molecular models enabled them to propose that polymer formation would block the single Cossee vacancy. Hence they suggested that two vacancies exist at the active

site one of which is not available for complexation of monomer. This mechanism itself is considered to be analogous to Cossee and Arlman.

Allegra (131 ) put forward a mechanism for the $TiCl_3/AlR_3$/propylene system which avoided the flip-back of the Ti-R bond which was proposed by the Cossee-Arlman theory. The active site was again an alkylated titanium atom on the surface of the $TiCl_3$ layer. The mode of monomer complexation proposed by Cossee was:

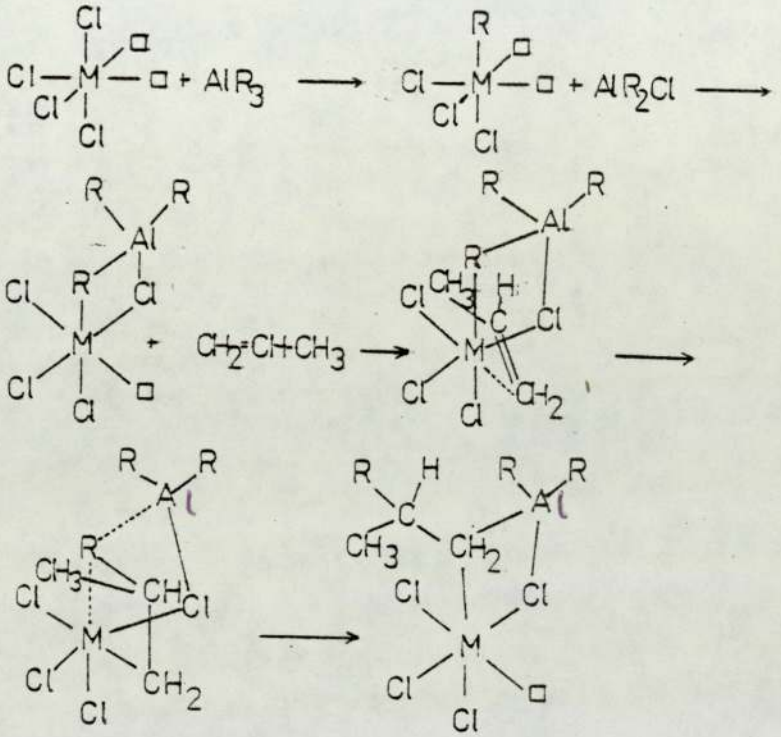



whereas Allegra proposed a complexation of the type:




In this case the atoms or groups in close contact during the complexation step are further apart than the sum of the van der Waals radii of the groups involved, thus no steric hindrance or electronic repulsion effects are involved. The olefin complexation is seen to be an outward trans-like type. After having complexed the monomer, bond rotation in the direction shown in the figure brings the olefin $\beta$-carbon atom into a suitable orientation for a mechanism similar to Cossee's. After the addition, the Ti-R bond changed place but another olefin unit can still coordinate on the free Ti valency with the same steric configuration as before.

This mechanism needs a lower activation energy for propagation than that necessary for the Cossee-Arlman theory. Rodriguez and van Looy ( 40 ) advocated a similar mechanism with a transition metal-carbon bond as the actual growth centre, but in addition they required a complexed base metal alkyl to be an integral part of the site. They proposed the mechanism as:



M = transition metal = a chlorine vacancy

Their scheme followed closely the Cossee-Arlman ( 126 ) mechanism and contained elements of the bimetallic mechanism as proposed by Natta ( 72 ), and Patat and Sinn (114 ). Stereospecific orientation of the methyl group of the propylene molecule being polymerized was dictated by the requirement of minimal steric interaction with the external groups carried by the Al atom. A driving force for the above migration was said to arise from the favourable coordination of carbon - 1 of the polymer growing chain and the Al atom.

(c) Free radical mechanisms

In this class of mechanisms, initiation has been suggested to occur by transfer of an electron from either a hydrocarbon radical R', a transition metal atom, or the Al metal atom to the

monomer.

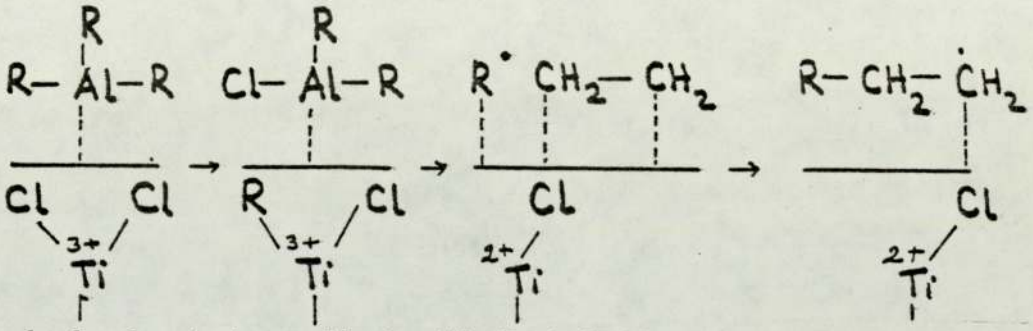
Nenitzescu and his workers first suggested that the Ziegler polymerization took place by a radical mechanism (125 ), for example:

$$nR\text{-}Al + TiCl_4 \longrightarrow RnTiCl_{4-n} + nAlCl \quad (n \leqslant 4)$$

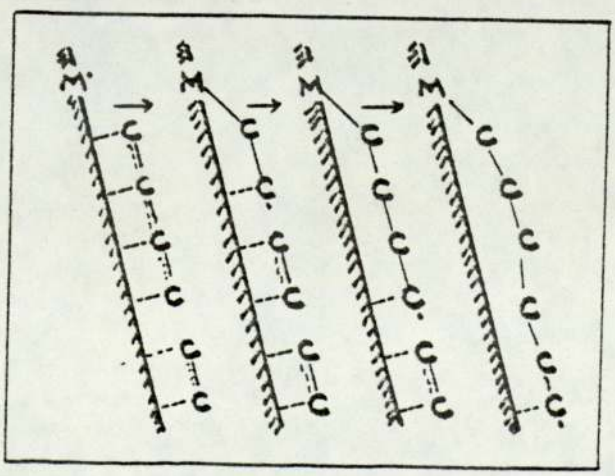
$$RTiCl_3 \longrightarrow R^{\cdot} + TiCl_3$$

$$R^{\cdot} + CH_2{=}CH_2 \longrightarrow R - CH_2 - \dot{C}H_2 \xrightarrow{\text{etc.}} \text{polymer}$$

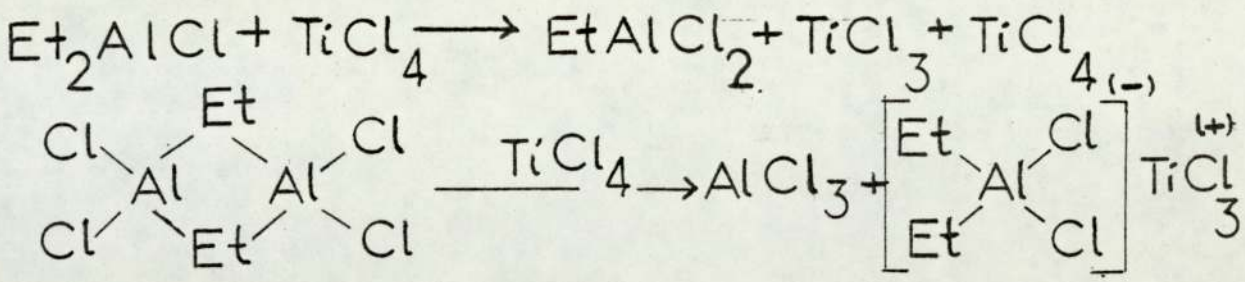
Topchiev and his workers (132,133) proposed the following path by which the radical R' could initiate and propagate the polymerization of an olefin as:



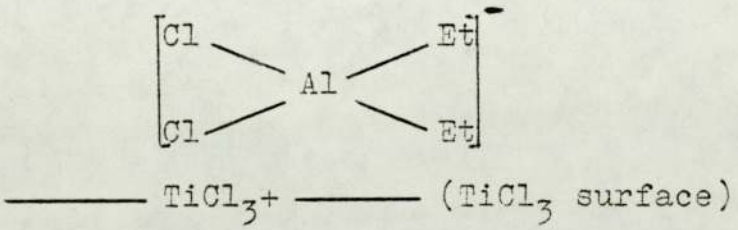
The chemisorbed aluminium alkyl alkylated the $TiCl_3$ surface; the formed Ti-R decomposed to give a radical R' which added to ethylene to form a new radical. This new radical also remained bound to the surface and propagation occurred by further additions of ethylene molecules, both the radical and the reacting ethylene molecules being bound to the $TiCl_3$ surface. Friedlander also proposed a similar mechanism but invoked a different initiation step (42 ). Initiation by transfer of an electron from the transition metal to the olefin was suggested to take place.



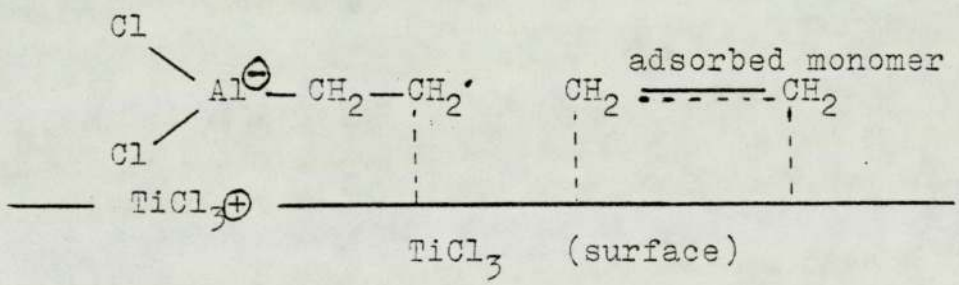
Duck has proposed (134) that the dimeric alkylaluminium compounds formed a Lewis complex with $TiCl_4$ and the complex was adsorbed on the $TiCl_3$ surface wherein $TiCl_3$+ ions represented the binding factor, e.g:



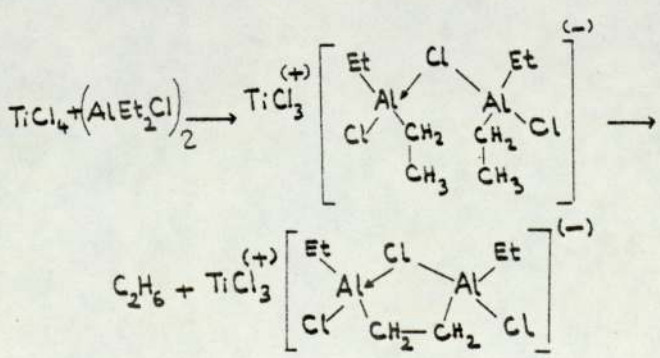
The latter ion pairs adsorbed on the surface of the $TiCl_3$



The complex lost ethane to give the active centre which reacts with the monomer adsorbed on the $TiCl_3$ surface.

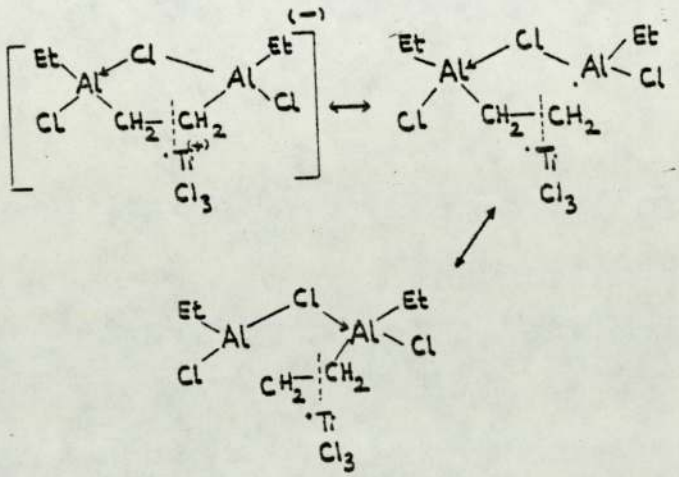


The mechanism suggested by van Helden (135) chain growth by a four-centred addition as follows was proposed:

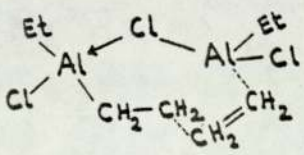


During the reaction of catalyst components very little butane formation was observed, the participation of free alkyl

radicals was ruled out and the formation of ethane was postulated to occur by means of an intramolecular process involving hydrogen abstraction from an alkyl group in the Al complex. Such a hydrogen abstraction could be facilitated by resonance stabilization of the resulting complex according to this reaction.



Chain growth occurred by a four-centre addition whereby resonance stabilized structures are formed similar to the initial complex:



The purpose of this project was to understand and to establish a general kinetic picture for the polymerization of styrene using $VOCl_3/AlR_3$ catalyst system.

Styrene has been used as monomer because it is a liquid which has advantages in the measurement of the rate of polymerization compared with ethylene and propylene polymerizations. In the latter cases when the gaseous monomer is fed into the reaction medium it would not be known whether the monomers rate of polymerization measured was a true rate of polymerization or the rate of some other process in the system.

Styrene a liquid monomer forms a soluble polymer with $VOCl_3/AlR_3$ systems and the measured rate of polymerization should be the true rate. It was hoped the behaviour of the polymerization of styrene could be related, particularly in the presence of activators such as ethyl trichloracetate, to the copolymerization of ethylene and propylene.

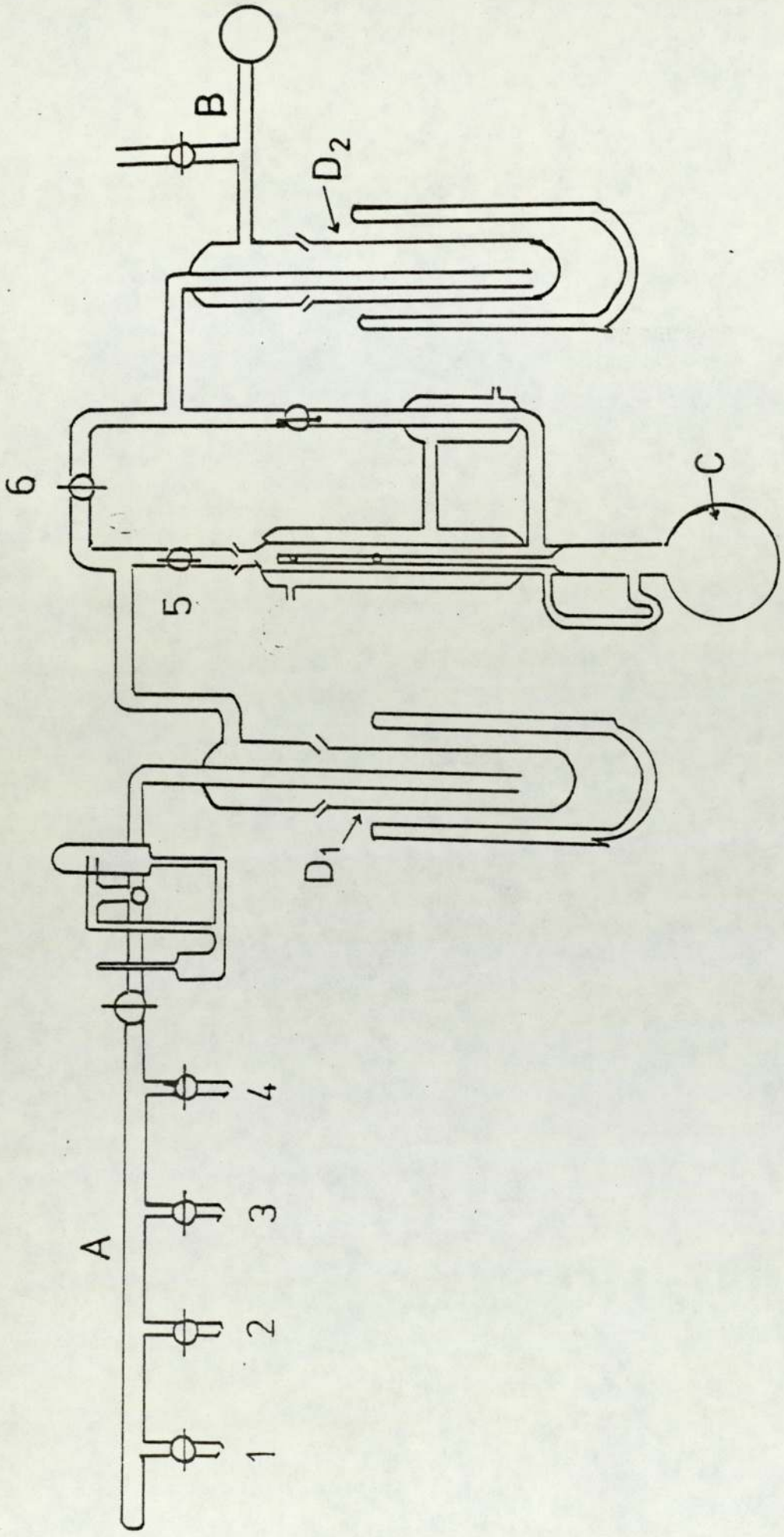



Figure 2(1) : The high vacuum line

CHAPTER 2

EXPERIMENTAL PROCEDURES

(1) HIGH VACUUM LINE

The purifications and preparations of solvents, monomers and catalyst solutions were carried out using high vacuum techniques wherever possible. The high vacuum line used is shown diagramatically in figure 2(1).

The high vacuum line consisted of a manifold (A) which had several male ground-glass joints of various sizes, e.g. B14, B19, B24 attached to the manifold by way of high vacuum taps. The manifold was evacuated by a rotary vacuum pump, assisted by a mercury diffision pump (B, C) respectively. Two liquid nitrogen cold traps ($D_1$, $D_2$) were incorporated into the system before and after the mercury diffusion pump. Any vapour from the manifold condensed in trap $D_1$ whilst mercury vapour from the diffusion pump was prevented from entering the rotary pump because condensation occurred in trap $D_2$.

The pressure in the manifold was measured by a 'Vacustat' and when both the mercury diffusion pump and rotary pump were in operation a high-vacuum ($10^{-5}$ - $10^{-6}$ Torr) was obtained. Under these conditions the mercury would stick in the stem of the 'Vacustat'. The taps 5 and 6 allowed the pumping system to by-pass the mercury pump when a low vacuum could be obtained ($10^{-2}$ - $10^{-3}$ Torr).

(2) VACUUM DISTILLATION

Distillations of monomer and solvents were carried out under high vacuum, following the procedure set out below.

A sticking vacuum was first obtained in the manifold. A clean and dry round-bottom flask containing the solvent or monomer was attached to the high vacuum line at one of the ground-glass joints(1-4). The flask was immersed in liquid nitrogen and the liquid was frozen. Whilst the liquid was frozen the tap was opened to the manifold to withdraw the gas above the solvent. A 'sticking-vacuum' was again obtained and the manifold was then closed to the vacuum pumps. The flask with frozen liquid was immersed in a methanol bath allowing the liquid to melt and gas dissolved in it to be released into the manifold. The flask was then re-frozen in liquid nitrogen before the gas above the surface was pumped from the system. This freeze - thaw technique of de-gassing the liquid was repeated until the gas dissolved in the liquid was removed.

The liquid was then vacuum distilled into a flask, fitted to the manifold and which had been evacuated to a high vacuum, by immersing this flask in liquid nitrogen. During this process the manifold was closed to vacuum pumps.

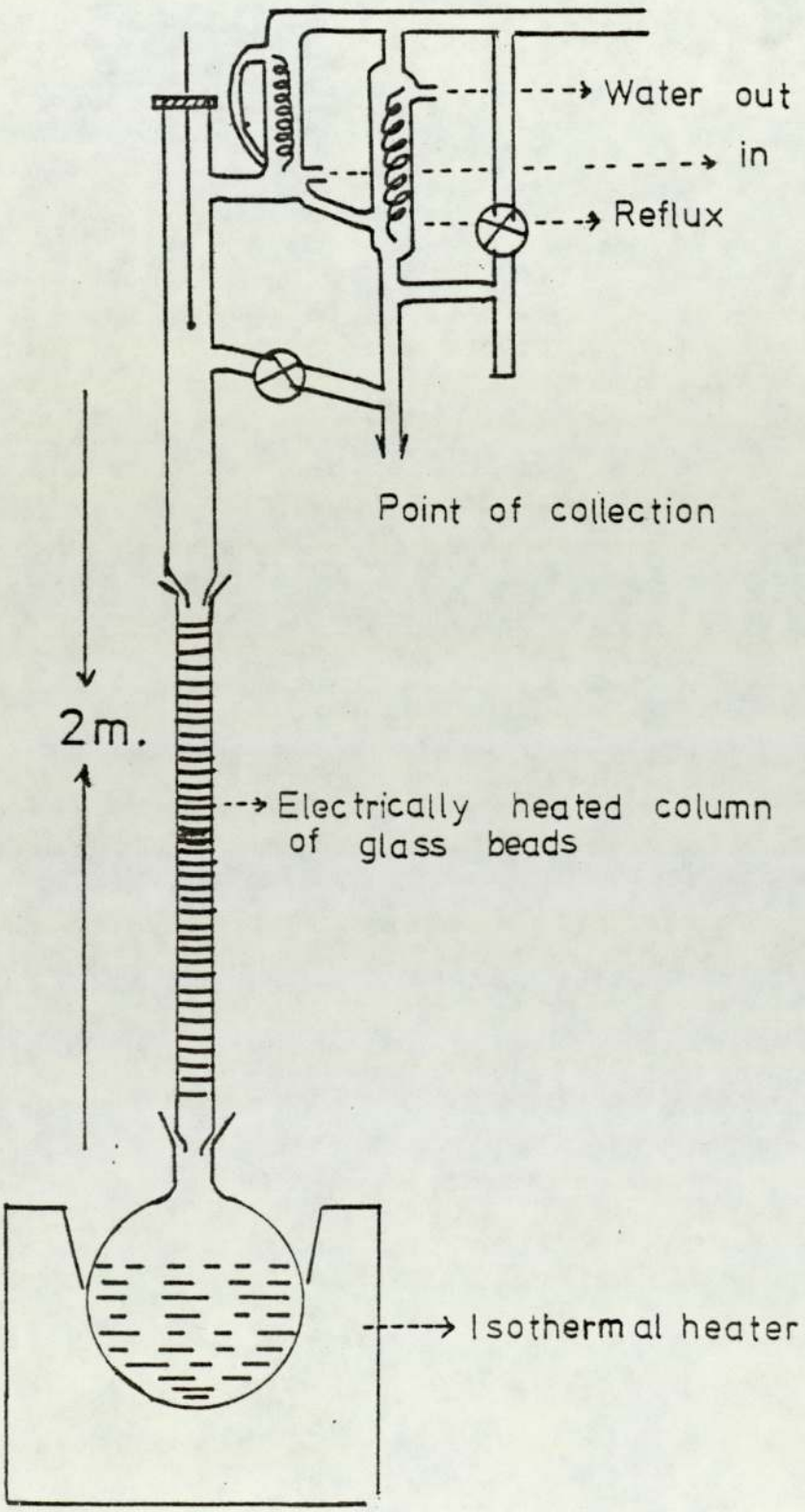
(3) MATERIALS

a) Solvent

(i) Toluene

Toluene (2 litre) was refluxed on sodium slices which first melted then disintegrated to small shiny particles. After refluxing for at least ten hours, the solvent was fractionated very slowly using a 2m. fractionation column. Each fraction (100 ml) was analysed by GLC (see appendix for comparison) and the fractions which had maximum purity were collected. The collected fraction was then dried over sliced sodium under vacuum and degassed. However the vacuum distilled solvent still contained some impurities that reacted with $VOCl_3$ to

Figure 2(2) : Reflux system for purification of solvents



give a dark brown precipitate. Even using $CaH_2$ or $Al(i\text{-}Bu)_3$ as a drying agent did not remove these impurities.

After collecting the purest portion of toluene it was placed into a flask fitted with 'Rota-flo' greaseless tap and fresh sodium was sliced into it. The flask was then attached to the vacuum line and the solvent was degassed. The solvent was then vacuum distilled into another flask fitted with 'Rota-flo' greaseless tap. 0.2 ml $Al(i\text{-}Bu)_3$ (3.98 moles litre$^{-1}$) was injected into the solvent through 'Suba-seal'. The solvent was again vacuum distilled and 1 ml $VOCl_3$ solution ($10^{-2}$ moles litre$^{-1}$) was injected into the toluene and was allowed to stand to react with impurities in toluene. Some dark brown precipitate was always obtained. The toluene was then vacuum-distilled into another flask and a very small amount of $VOCl_3$ distilled over as well so that the colour of $VOCl_3$ in toluene was obtained without any precipitate (a good indicator of purity).

It is known that (136) $VOCl_3$ forms a charge-transfer complex with aromatic hydrocarbons and $\alpha$-olefins, which for the $VOCl_3$ in toluene is dark red. An excess of $Al(i\text{-}Bu)_3$ was then injected to destroy the $VOCl_3$, to produce a dark brown precipitate. The solvent was kept under vacuum and used whenever needed. The purity was checked by GLC.

(ii) Hexane

n- Hexane was supplied by BDH Laboratory Reagents. Pressed sodium wire was added to 3 litre n-hexane contained in a dry single necked 5 litre flask. The flask was attached to an electrically heated 2 metre packed column, fitted with a fraction collection head as shown in figure 2( 2 ).

The solvent was refluxed first for ten hours. The first 500 mls fraction was collected very slowly (reflux/fraction ratio = 7:1) and discarded. The last 500 mls fraction was similarly discarded. The middle 2 litre fraction which was transparent

in the U.V region was collected. Pressed sodium wire was added to the middle fraction of n-hexane in a dry single necked flask (500 ml) which was attached to the high vacuum line and the solvent was degassed. When degassing was complete the solvent was vacuum distilled into a flask fitted with 'Rota-flo' greaseless tap from which the solvent was vacuum distilled whenever required. Although the optimum condition was obtained for dryness some impurities gave rise to a dark brown precipitate upon the addition of $VOCl_3$ solution which was thought to be due to the presence of some unsaturated hydrocarbons. When $CaH_2$, alumina, and $Al(i\text{-}Bu)_3$ were used as a drying agent these impurities were not removed but reacted with $VOCl_3$.

b) Styrene (Phenyl-ethene)

Many different techniques have been investigated for the manufacture of styrene monomer (137). The following methods have been used or considered for commercial production:

1. Dehydrogenation of phenyl ethane.
2. Oxidative conversion of phenyl ethane to 1-phenylethanol and the subsequent dehydration of the alcohol.
3. Side-chain mono chlorination of phenyl ethane followed by dehydrochlorination.
4. Side-chain chlorination of phenyl ethane and hydrolysis to the corresponding alcohol, followed subsequent dehydration of the alcohol.
5. Pyrolysis of petroleum and recovery from various petroleum products.
6. Oxidation of phenyl ethane to the hydroperoxide, which then reacted with propylene, produces 1-phenylethanol and propylene oxide. The alcohol is then dehyrated to styrene. The principal method of synthesis is now method (1).

(i) Purification of Styrene

Styrene as supplied by BDH laboratories had a nominal purity of 99.5%. The impurities contained in the styrene monomer included: aldehydes, peroxides, sulfur, chlorides, styrene polymer, phenyl ethane and 2-phenyl propane. In addition to these impurities p-tert-butyl catechol was added as an inhibitor. Some of the impurities, in particular aldehydes ketones and peroxides, resulted from the aerobic oxidation of styrene. Styrene is miscible with a large variety of organic liquids such as diethylether, methanol, ethanol, carbon disulfide, acetone, benzene and toluene, but its solubility in water is low, at 25°C approximately 0.01g/100g water.

The polymerization of styrene initiated by Ziegler-Natta type catalysts was known to take place only in absolutely dry and air free conditions, and accordingly a great deal of time was spent in order to establish optimum conditions for polymerization by the following procedures.

300 ml styrene were washed with 150 ml sodium hydroxide solution (10-15% in water) in a separating funnel until the colour of the sodium salt of the inhibitor had been removed from the monomer. The styrene was then washed with distilled water (callitre) to remove excess sodium hydroxide from the monomer. During this washing procedure the styrene was exposed to air and some oxidation took place so that the monomer became slightly yellow, due to the formation of the quinoid structures of the oxidation products of styrene (138). Alumina (ca. 100 gr), was activated in a furnace at 450°C for three hours added to the styrene and left to stand until the monomer was colourless. The alumina also acted as a powerful drying agent. The styrene was then decanted into a flask fitted with a 'Rota-flo' greaseless tap figure 2(3) that had been dried in an oven at 200°C for four hours and cooled down under high vacuum. The monomer was degassed by the procedure

described in 2:2 until absolutely air-free. When degassing was complete 0.5 ml $Al(i\text{-}Bu)_3$ (3.98 moles litre$^{-1}$) was injected into the styrene through a 'Suba-seal' to destroy any air and moisture left in the monomer. The monomer was vacuum distilled whenever required. The use of this technique to purify styrene was not successful because some unknown impurity destroyed the catalyst. Accordingly after styrene was washed with sodium hydroxide solution and distilled water and then dried over alumina, it was purified by a number of techniques.

(ii) It was purified further by a number of techniques: The alumina-dried styrene was decanted into a flask that was fitted with a greaseless tap and contained finely grounded calcium hydride2( 3 ), the flask was attached to the vacuum line and the monomer was thoroughly degassed. The contents were agitated by a magnetic stirrer for several days. However, again the necessary condition for the polymerization could not be obtained.

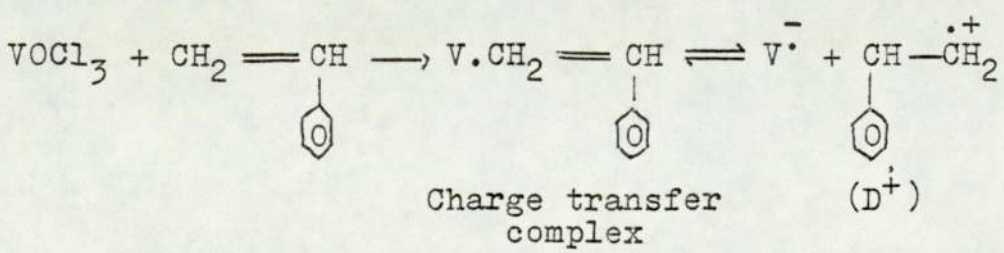
(iii) After having dried the monomer over alumina it was decanted in a one neck flask and metallic sodium was sliced into the monomer. Then the flask with styrene was attached to the vacuum line in order to degas the monomer. Hydrogen was evolved from the reaction between moisture and sodium. The monomer was degassed further until no gas left. Initially sodium reacted with the air and moisture present and became coated with a hydroxide layer. During the vacuum-distillation of styrene from this system the hydroxide layer became detached from the metal, thus producing a fresh sodium surface available for the drying process.

During the purification of styrene by this technique it was exposed to air so that oxidation products were formed which were efficient promoters of the sodium metal initiated polymerization of styrene (138 ). This polymerization was reduced by distillation from the sodium below room temperature. As

the sodium pellets became shiny the styrene solution became blue then intense red and the solution became viscous. The purity of the distilled monomer was checked by the addition of $VOCl_3$ solution in toluene, the styrene went light blue which meant that some impurities were still present.

(iv) After removing the stabilizer and drying over alumina the styrene was decanted into a dry clean flask into which fresh sodium was sliced in order to destroy any moisture left in the monomer. During this procedure maximum attention was paid to prevent undue exposure of the styrene to air. The monomer was again decanted into another flask which was fitted with a 'Rota-flo' greaseless tap and degassed until air free. 0.1 ml of $Al(i\text{-}Bu)_3$ (3.98 moles $litre^{-1}$) was injected into the monomer and any moisture left was destroyed. The monomer was then vacuum distilled into another flask and 0.5 ml ($10^{-2}$ moles $litre^{-1}$) $VOCl_3$ solution in toluene were injected into the monomer. A red solution of monomer was obtained and any impurities left were then destroyed. It was known that $VOCl_3$ formed a red charge transfer complex with styrene which was a good indicator of the purity of the monomer (136). The monomer was vacuum distilled and a slight excess of $Al(i\text{-}Bu)_3$ was added to the distillate in order to destroy any $VOCl_3$ present in the distilled monomer. ($VOCl_3$ has a very high vapour pressure and easily distilled.) The monomer was vacuum distilled whenever required.

Although $VOCl_3$ can initiate the polymerization of styrene (139) according to the scheme:




$$D^{\cdot+} + M \longrightarrow D + M^{\cdot+}$$

$$2M^{\cdot+} \longrightarrow +M \longrightarrow M+ \xrightarrow{nM} \text{Polymer}$$

The rate of polymerization was very slow and after distillation very little polymer was left in the flask.

c) ∝-Methyl Styrene (1-methyl 1-phenyl ethene)

∝-methyl styrene is an aromatic monomer with polymerization characteristic different from styrene polymerization. Radical polymerization of the pure monomer proceeds very slowly and is not a practical technique, but is readily polymerized by ionic catalysts. The 'Ziegler-Natta' catalyzed type polymers are still of academic interest.

It is produced commercially by the dehydrogenation of isopropyl benzene (cumene) and also as a by-product in the manufacture of phenol and acetone by the cumene oxidation process (140). The physical properties are given in table 2( 1 ). The main impurities in the monomer are aldehydes, peroxide, β-methyl styrene and cumene. In addition to these p-tert-butyl catechol is added as a stabilizer.

The purification technique used was as described for the purification of styrene.

Table 2(1)

Physical Properties of ∝-Methyl Styrene

| | |
|---|---|
| boiling point at 760 mmHg, °C | 165 |
| freezing point °C | -23.2 |
| refractive index, $n_d^{20}$ | 1.5386 |
| viscosity, at 20°C, cP | 0.94 |
| density, at 20°C g'/ml | 0.9106 |
| solvent compatibility | ∞ |
| acetone | " |
| carbon tetrachloride | " |
| benzene | " |
| n-heptane | " |
| ethanol | " |

d) Vanadium oxytrichloride

Vanadium oxytrichloride ($VOCl_3$) was supplied by 'Koch Light Laboratories' with nominal purity 99.9% in sealed ampoules and

was used without further purification. $VOCl_3$ is sensitive to traces of moisture and oxygen and hence was stored in a 100 ml flask such as that shown in figure2( 4 ). The flask was dried and purged with nitrogen and the $VOCl_3$ was transferred by syringe to the flask from the ampoule, which had been opened under nitrogen. A dilute solution of $VOCl_3$ was then prepared because pure $VOCl_3$ was too concentrated for the purpose of this work.

A 100 ml flask fitted with 'Rota-flo' greaseless tap was dried in the oven at 200°C for 4 hours and cooled in a stream of dry nitrogen. The flask was weighed with the appropriate suba-seal and then attached to the high vacuum line and evacuated. It was again flamed out under high vacuum and, when cold and a sticking vacuum had been obtained, the flask was cooled with liquid nitrogen and purified toluene distilled into it. The contents were melted and the greaseless tap was shut. The flask was removed from the manifold and the suba seal was attached to the female joint of the flask. The system was re-weighed to determine the amount of toluene within. The neck of the flask was purged with nitrogen and the required volume of pure $VOCl_3$ was added by syringe through the 'Suba Seal'. The $VOCl_3$ was mixed thoroughly with toluene to produce a dark red solution and this solution was stored with the 'Rota-flo' tap closed. Samples of $VOCl_3$ solution were withdrawn by syringe from the flask which was maintained under a nitrogen atmosphere.

The concentration of $VOCl_3$ was estimated as:

$$\left[ \frac{V_{VOCl_3} \rho_{VOCl_3}}{M} \cdot \frac{\rho_{tol}}{W_{tol}} \right] \times 1000 \text{ moles litre}^{-1}$$

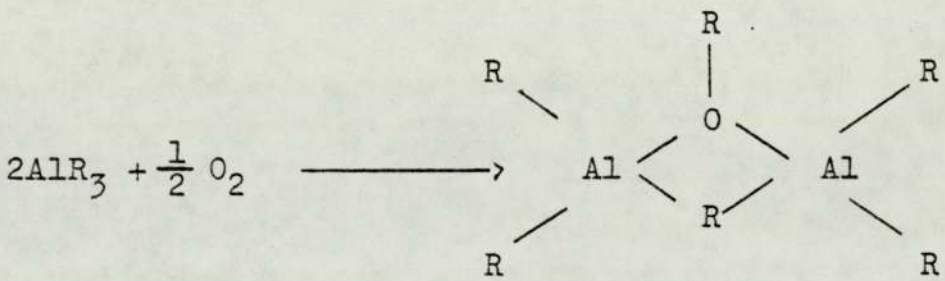
where $V_{VOCl_3}$ = volume of $VOCl_3$

$M$ = molecular weight of $VOCl_3$

e) Organoaluminium Compounds

The co-catalyst compound used in this work was 'Ethylaluminium sesquichloride' ($Et_3Al_2Cl_3$), but other alkylaluminium and alkylaluminiumchloride compounds were used as a co-catalyst for comparison.

Apart from a few exceptions the aluminium alkyls are clear, colourless liquids which are soluble in hydrocarbons. They are very sensitive to air and moisture although there are graded differences between them. The reaction with oxygen may be represented as:



or if sufficient oxygen is present -

$$AlR_3 + \frac{3}{2} O_2 \longrightarrow Al(OR)_3$$

and the reaction product can be used for synthesis of primary alcohol ( 6 ). As:

$$Al(OR)_3 \xrightarrow{H_2O} ROH + Al(OH)_3$$

The reaction with water, if it is in small amounts may be as follows (141 ):

$$AlEt_3 + H_2O \longrightarrow Et_2AlOH + C_2H_6$$

$$Et_2AlOH + AlEt_3 \longrightarrow Et_2AlOAlEt_2 + C_2H_6$$

$$Et_2AlOAlEt_2 + H_2O \longrightarrow Et_2AlOAlEtOH + C_2H_6$$

$$Et_2AlOAlEtOH + AlEt_3 \longrightarrow Et_2AlO\underset{\underset{Et}{|}}{Al}OAlEt_2 + C_2H_6$$

The alkyls are Lewis acids combining with donors such as amines, phospines, ethers to give tetrahedral four coordinated species.

(i) Preparation of solutions of aluminium alkyls

The aluminium alkyls were supplied by Cambrian Chem. Co. Ltd. Table 2(2) shows the physical properties of the aluminium

alkyls used in this work.

Table 2(2)

Physical properties of aluminium alkyls

| Aluminium Alkyls | Mol.Wt. | Boiling Point | Freezing Point | Density |
|---|---|---|---|---|
| Triethyl aluminium - $Al(C_2H_5)_3$ | 114.7 | 62°C at 1 Torr | -47C° | 0.84 |
| Triisobutyl aluminium - $Al(i\text{-}Bu)_3$ | 198.33 | 42°C at 1 Torr | 6C° | 0.79 |
| Ethylaluminium sesquichloride - $(C_2H_5)_3\ Al_2Cl_3$ | 247.51 | 90°C at 14 Torr | -20°C | 1.09 |
| Ethylaluminium dichloride $C_2H_5\ AlCl_2$ | 126.95 | 80°C at 12 Torr | 22°C | 1.23 |

A solution of aluminium triethyl ($AlEt_3$) was prepared as follows. Toluene was vacuum distilled into a weighed dry flask figure 2( 4 ) and the weight of toluene determined. The required volume of $AlEt_3$ was injected by syringe through the 'Suba Seal' directly into the toluene.

The concentration of $AlEt_3$ was estimated as follows:

$$(AlEt_3) = \frac{V_1 \rho_1}{M_1} \cdot \frac{\rho_{tol}}{m_{tol}} \quad \times 1000 \text{ moles litre}^{-1}$$

where $V_1$ = volume of $AlEt_3$

$\rho_1$ = density of $AlEt_3$

$M_1$ = mol.wt. of $AlEt_3$

$m_{tol}$ = mass of toluene in the solution

$\rho_{tol}$ = density of toluene

Solutions of aluminium diethyl chloride, ethyl dichloride and sesquichloride were prepared in a similar manner.

(ii) Synthesis of aluminium ethyl sesquichloride

Using aluminium trichloride and triethylaluminium, aluminium ethyl sesquichloride was prepared as a solution in a hydrocarbon solvent according to the reaction -

$$AlCl_3 + AlEt_3 \rightleftharpoons Et_3Al_2Cl_3$$

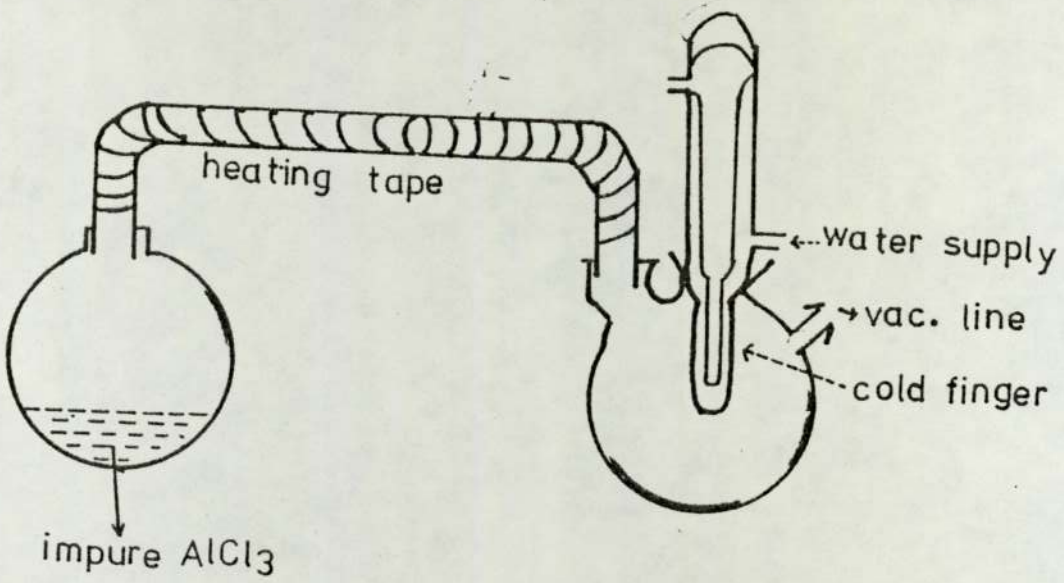



Figure 2(5) : The apparatus for the sublimation of $AlCl_3$

where the equilibrium is far to the right. Approximately 1 g of $AlCl_3$, that had been sublimed in the apparatus shown in figure 2( 5 ), was transferred under nitrogen to a weighed 'Suba Seal' stoppered 100 ml flask. The weight of $AlCl_3$ was then determined accurately. The flask was attached to the high vacuum line, evacuated until a sticking vacuum was obtained and purified toluene was vacuum distilled into this flask. The solvent was then melted to dissolve the $AlCl_3$ and the flask with $AlCl_3$ solution was detached from the vacuum line under a nitrogen atmosphere closed with 'Suba Seal' and was weighed. The concentration of $AlCl_3$ solution was determined as follows:

The molecular weight of $AlCl_3$ = 133.5

$$\left[AlCl_3\right] = \frac{m_1}{M_1} \times \frac{\rho_t}{m_t} \quad \text{X 1000 moles litre}^{-1}$$

where $m_1$ = the weight of $AlCl_3$

$M_1$ = 133.5 = mol. wt. of $AlCl_3$

$\rho_t$ = density of toluene

$m_t$ = the weight of toluene

The preparation of the $AlCl_3$ solution in a single neck flask had a great disadvantage in that the flask was closed with a 'Suba Seal' and the solvent dissolved some impurity contained within the 'Suba Seal' which caused the solution to become yellow. This method of preparing the solution was abandoned and a flask fitted with 'Rota-flo' greaseless tap, see figure 2 ( 4 ), was used instead. There was then no direct contamination from the suba seal.

The solution of $AlEt_{3/2}\ Cl_{3/2}$ was then prepared by transferring solutions of equimolar quantities of $AlEt_3$, that had been prepared as described in 2(3)(e)(i), and $AlCl_3$ to a known volume of toluene contained in a flask fitted with a 'Rota-flo' tap figure 2( 4 ).

The concentration of $AlEt_{3/2}\ Cl_{3/2}$ was determined in the usual fashion.

$$\left[AlEt_{3/2}\ Cl_{3/2}\right] = \frac{V_1M_1 + V_2M_2}{V_1 + V_2 + V_3} \quad \text{moles litre}^{-1}$$

where $V_1$ = volume of $AlCl_3$ solution/litre

$V_2$ = volume of $AlEt_3$ solution/litre

$V_3$ = volume of toluene solution/litre

$M_1$ = molarity of $AlCl_3$ solution

$M_2$ = molarity of $AlEt_3$ solution

f) Ethyltrichloro acetate (ETA) ($Cl_3C\ COOC_2H_5$)

ETA was supplied by 'Koch Light Lab. Ltd.' The physical properties of which are shown below:

molecular weight = 191

boiling point = 167.5°C

density = 1.38 g/ml

Two methods of purification were used -

(i) 20 mls of ETA was washed in a separating funnel with 20 mls 10% NaOH solution. The contents were separated and ETA washed thoroughly with distilled water. After separating the ETA it was dried and stored over activated alumina. A solution of ETA was prepared in toluene by injecting a known volume of ETA into vacuum distilled toluene that was contained in a suitable flask figure2(4). The solution was then degassed on the vacuum line. The concentration of the ETA was determined by -

$$[ETA] = \frac{V_1\rho}{M_{wt}} \times \frac{1000}{V_2} \quad \text{moles litre}^{-1}$$

where $V_1$ = volume of ETA/ml

$V_2$ = volume of toluene/ml

$\rho$ = density of ETA

$M_{wt}$ = mol.wt. of ETA

(ii) The ETA was purified by distillation, dried over activated alumina. After degassing it was vacuum distilled and the solution in toluene was prepared in the same manner as described above.

## (4) EXPERIMENTAL TECHNIQUES

### a) Gravimetry

A gravimetric technique was used to follow the rate of polymerization of styrene. A 100 ml flask fitted with 'Rota-flo' greaseless tap figure 2( 3 ) weighed and evacuated under the high vacuum. A known amount of monomer was distilled into the flask under high vacuum. The flask was immersed in a constant temperature bath and the catalyst solutions were injected through the 'Suba Seal'. At various time intervals after polymerization started a known amount polymer solution syringed from the flask, polymerization was terminated by the addition of methanol. The precipitated polymer was filtered and dried in the vacuum oven, and then was weighed. A graph of % conversion, or log (% conversion) against time was plotted from which the rate of polymerization was determined.

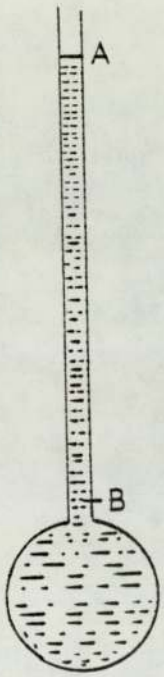
### b) Dilatometry

Dilatometry was originally used for measuring the thermal expansion or contraction of liquids or solids. A contraction in volume normally occurs during the polymerization of unsaturated compounds, when a double bond and a Van der Waals bond are replaced by two single bonds with a concomitant shrinkage of 5 - 25% in volume as the monomer enters the polymer chain. Dilatometry has been established as a sensitive technique for the measurement of the extent of conversion of monomer to polymer during the course of a polymerization and for greatest accuracy the polymer should be soluble in its own monomer or other solvents during the course of polymerization. The accuracy of the technique depends upon a number of factors, e.g.

(i) the dilatometer must be immersed in a constant temperature bath because of the necessity to control the temperature as closely as possible to prevent fluctuations in the meniscus height

(ii) the capillary must have a sufficiently small

Figure 2(6) : A simple dilatometer



diameter to furnish the sensitivity of the instrument

(iii) the extent of conversion should be low because the production of a highly viscous medium would prevent the movement of the meniscus during contraction of the system

(iv) maximum contact of the polymerizing monomer with a high heat transfer medium must be obtained in order to ensure isothermal polymerization

Factors (i), (ii) and (iii) can be readily controlled. There will inevitably be a temperature rise in the dilatometer and this rise will depend upon the rate of polymerization, the difference in temperature (lag) between the polymerizing medium and its surroundings, and the thermal conductivity of the medium. The temperature rise can therefore be minimised conveniently by reducing the rate of polymerization.

The decrease in volume that occurs during polymerization is associated with the difference in density of the monomer and the polymer. The density of the polymer should refer to its density in solution which is not necessarily that of the solid polymer. A crystalline or partly crystalline polymer is more dense than it would be in the liquid state or in solution, neither would the density of dissolved polymer be the same as in its glassy form. But the error that arises from these density differences is small compared with other sources of error in the measurement of rates of polymerization. The dilatometric method can be very useful for the study of polymerization kinetics, because the volume change originates solely from the conversion of monomer molecules to monomer units in the polymer chains.

A simple dilatometer is shown in figure 2( 6 ). If the meniscus decreased from A to B, the decrease in volume ($\Delta V$)

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would be -

$\Delta V = \pi r^2 \Delta h$ where $\Delta h$ is the height from A to B.

If m gram monomer polymerized completely to m gram polymer the contraction in volume would be -

$$\Delta V \simeq V_p - V_m$$

where $\Delta V = \frac{m}{\rho_p} - \frac{m}{\rho_m} = m\left(\frac{\rho_m - \rho_p}{\rho_p \rho_m}\right)$

$$\therefore \quad m = \Delta V \cdot \left(\frac{\rho_p \rho_m}{\rho_m - \rho_p}\right)$$

If $\Delta M$ is the number of moles of monomer polymerized then -

$$\Delta M = \frac{m}{M_m} = \frac{\Delta V}{M_m}\left(\frac{\rho_p \rho_m}{\rho_m - \rho_p}\right)$$

$M_m$ is molecular weight of monomer

If $\Delta V << V$ then the volume of system remains almost constant and the change in concentration of monomer $\Delta[M]$ can be written as:

$$\Delta[M] = \frac{\Delta M}{V} = \frac{\Delta V}{V} \cdot \frac{1}{M_m} \cdot \left(\frac{\rho_p \rho_m}{\rho_m - \rho_p}\right)$$

$$\Delta[M] = \underbrace{\frac{\pi r^2}{V M_m}\left(\frac{\rho_p \rho_m}{\rho_m - \rho_p}\right)}_{A} \Delta h$$

So that $\Delta[M] = A\Delta h$

The rate of polymerization (Rp) can then be obtained from a plot of change of meniscus height as a function of time. Since

$$Rp = \frac{-d[M]}{dt}$$

so that Rp is proportional to $\frac{\Delta h}{\Delta t}$

(i) Conventional dilatometry

The polymerization catalyst system studied was sensitive to traces of moisture and oxygen and hence it was necessary to design a dilatometer that incorporated a simple anaerobic

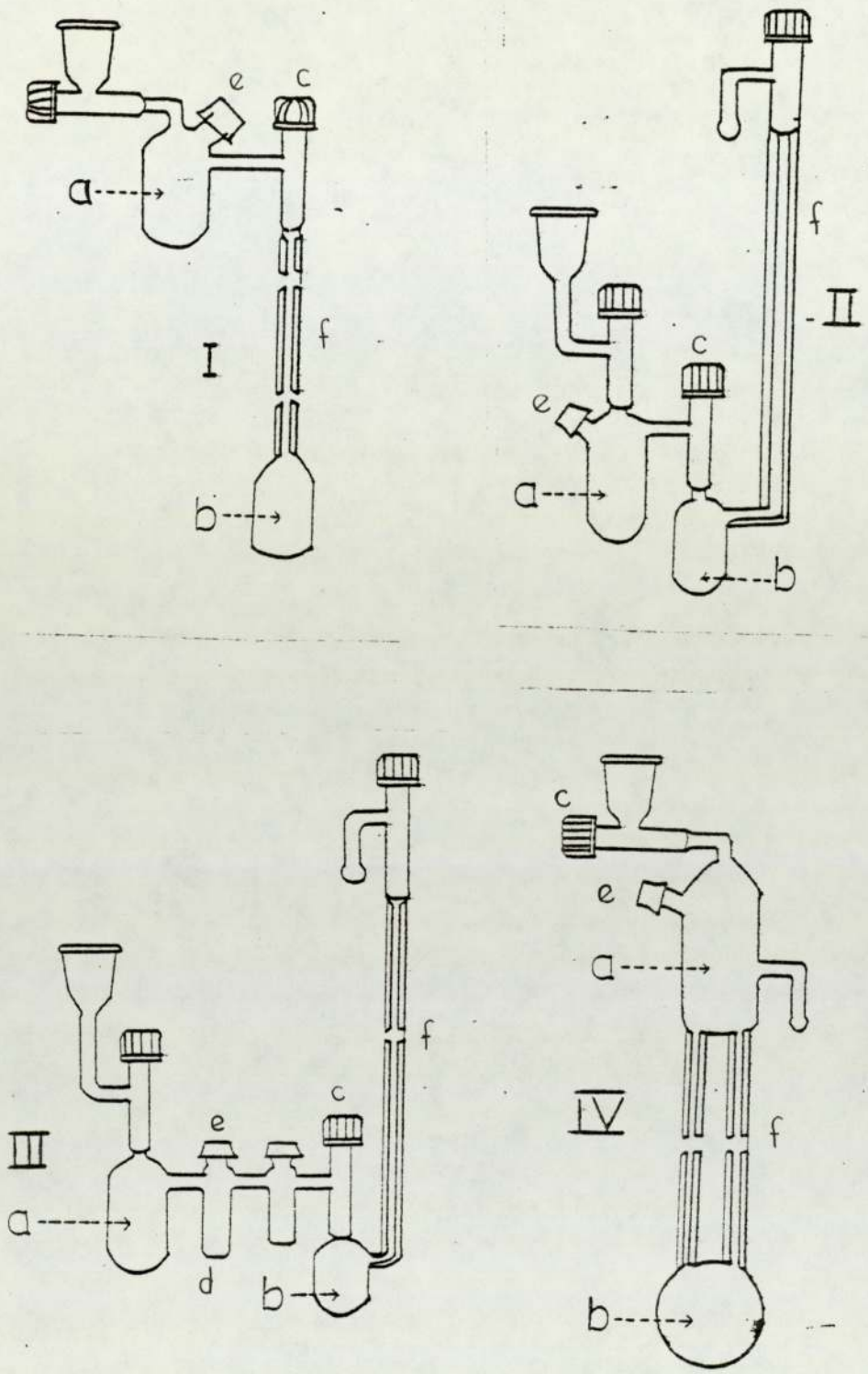



Figure 2(7) - Selection of dilatometers

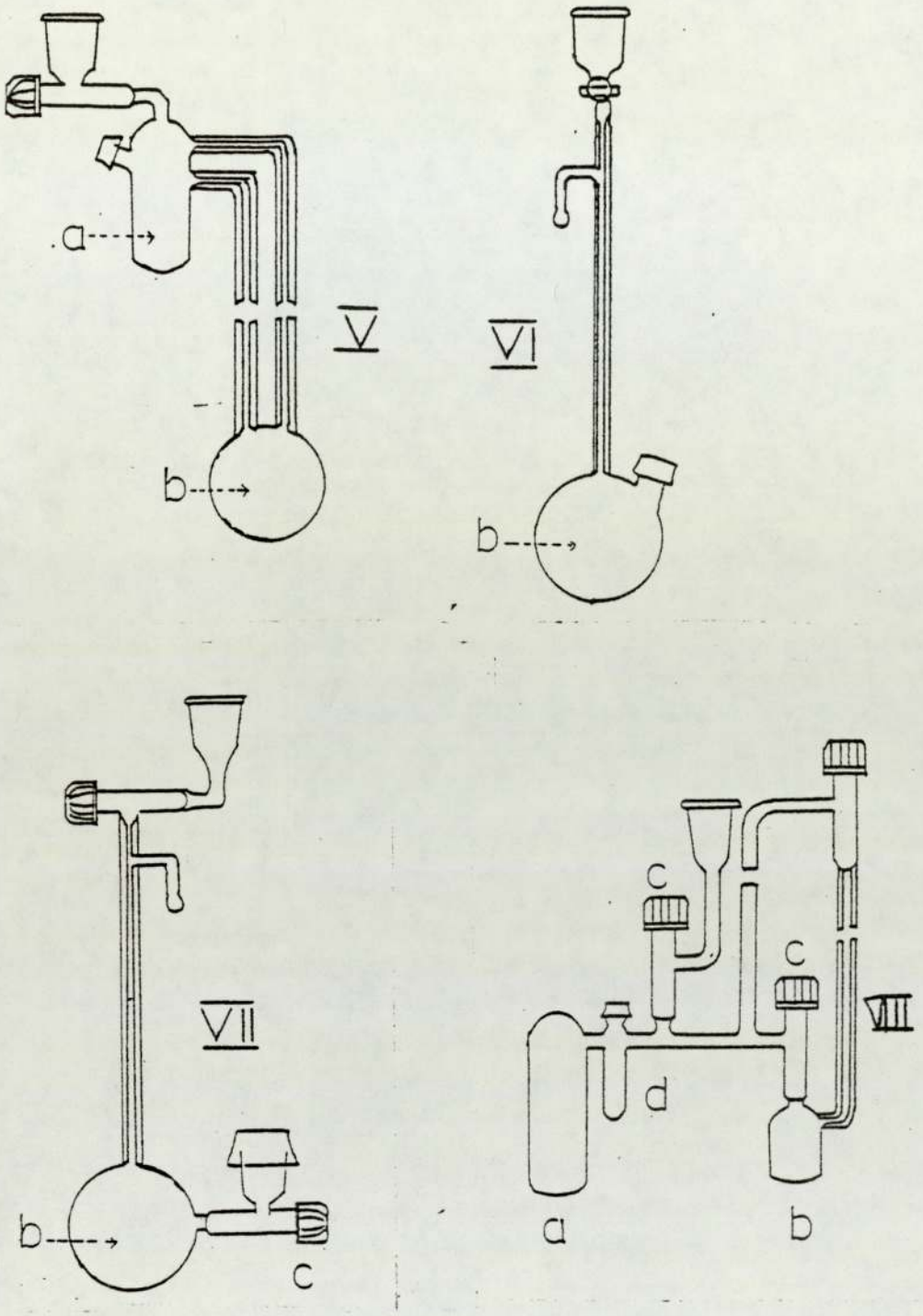
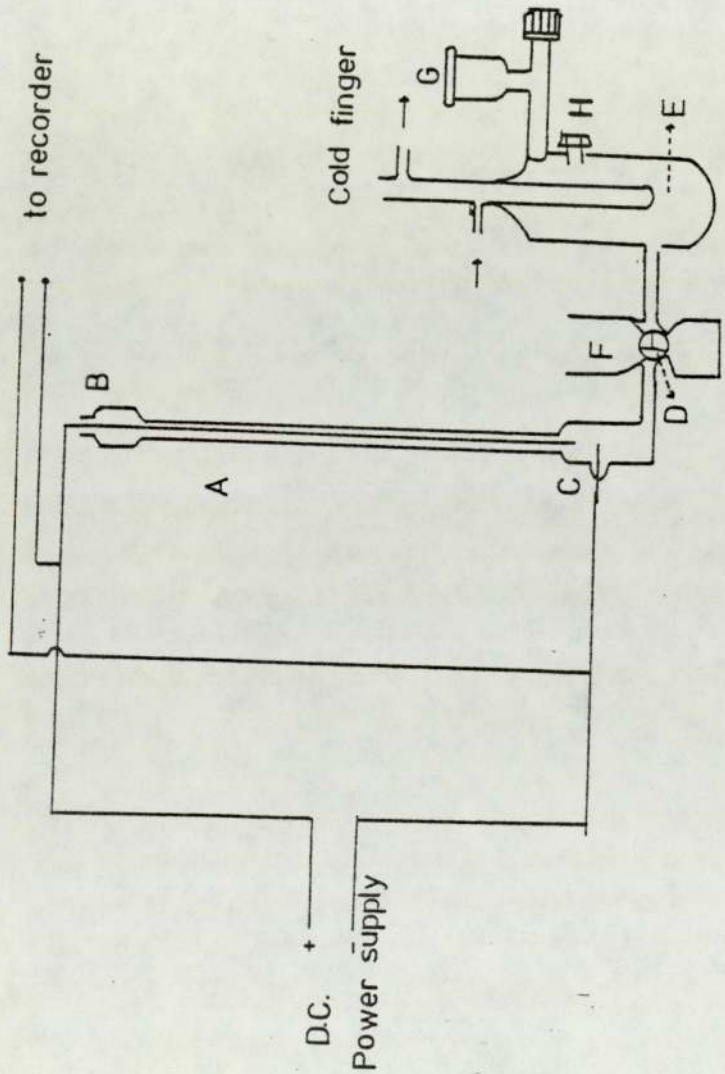



Figure 2(7) - Selection of dilatometers

Figure 2(8) : Recording dilatometer



filling system. A number of designs are shown in figure 2(7). Each dilatometer was constructed so that it could be removed under vacuum from the high vacuum line and hence had a ground glass joint attached to a greaseless tap (c). The weighed dilatometer was evacuated, flamed dry and styrene was distilled from a graduated tube into the reaction vessel (a) or the dilatometer bulb (b). The weight of styrene was determined and solvent was then distilled into the apparatus (the volume of solvent was determined from the weight distilled). The catalyst component solutions were then injected through the 'Suba Seal' (e) and the bulb of the dilatometer and a reasonable height of the capillary (f) were then filled with the solution. The apparatus was fixed in a Townsen and Mercer constant temperature bath and the decrease in height of the meniscus was determined by the use of a cathetometer.

(ii) Recording dilatometry

An electrical dilatometer shown in figure 2(8) was used to measure the rate of polymerization. Through the capillary tube (A) was a tungsten resistance wire (B) which acted as one terminal of the electrical circuit, shown in figure 2(8), the other terminal (C) was sealed into the apparatus at the mercury reservoir. During the course of polymerization the height of mercury in the capillary decreased and exposed a greater length of resistance wire. A Weir Minoreg 325 power supply was used to supply the circuit with a constant direct current so that as the polymerization proceeded and a greater length of resistance wire was exposed the potential difference (V) across the terminals of the dilatometer increased. It was assumed that the resistance between the points C and D was approximately the resistance of the exposed tungsten wire. A RE 541.20 recorder was used to determine the potential difference between C and D. A direct measure of the rate of polymerization could be obtained from the recorder trace since -

$$Rp = \frac{-d[M]}{dt} \propto \frac{dV}{dt}$$

The dilatometer was cleaned, dried and connected to the high vacuum line. Known amounts of the monomer and solvent were distilled into the reaction vessel (E). The apparatus was removed from the vacuum line and mercury which had been refluxed under vacuum and dried over alumina was placed in the reservoir (F), by tilting the apparatus mercury was allowed to fill the capillary tube. By suitably positioning the three way tap mercury was allowed to connect slowly with the monomer, solvent mixture. The height of mercury in the capillary was adjusted and the 3-way was positioned so that there was only contact between D and E.

The apparatus was immersed in a constant temperature bath to allow the system to equilibrate thermally with its surroundings. The chart recorder was set to operate at a known speed and the apparatus was then removed sufficiently from the bath to expose the 'Suba Seal' (H) through which were injected the catalyst solutions. The injection of the catalyst solutions caused the mercury to rise in the capillary tube and served as a marker for the zero time for polymerization. From the subsequent trace of potential difference between C and D against time the rate of polymerization could be determined.

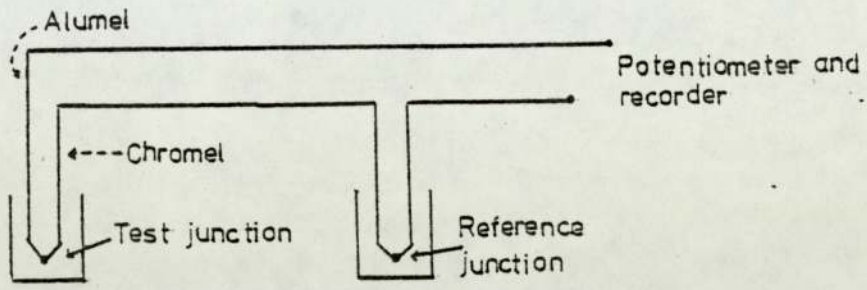
To obtain an absolute value for the rate of polymerization the apparatus was calibrated so that the decrease in height of mercury could be related to the potential difference across C and D.

c) Thermocouple

The polymerization of styrene is exothermic in character ($\Delta H_{25^oC} = 16.68$ kcal mole$^{-1}$) so that the rise in temperature associated with the polymerization may be used to measure the extent of polymerization in an adiabatic system. The chromel-alumel thermocouple is a simple device which responds very

rapidly to changes in temperature and consists of two dissimilar metal wires welded together at the two ends as shown in figure 2(9). If a temperature difference exists between the two junctions, a net electromotive force is developed, which may be detected by inserting a meter or a chart recorder into the loop.

Figure 2(9) : The simple thermocouple




The thermocouple was calibrated by maintaining the reference junction at $0^{o}C$ and by allowing the test junction to come to equilibrium at several known temperatures. The voltage (mV) was read at each temperature using the RE 541.20 recorder as a potentiometer. The calibration curve of voltage against temperature was then drawn by including a correction factor. A 100 ml flask fitted with 'Rota-flo' greaseless tap (E) was used figure 2(10) to follow the reaction by thermocouple. Alumel-chromel type of thermocouple was used.

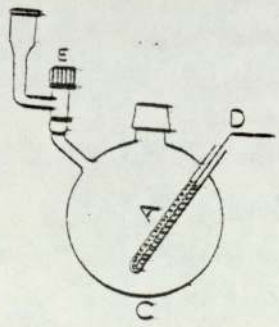



Figure 2(10) : The thermocouple reaction flask

A tube (A) which was extended into the flask (C) was filled with mercury in order to establish reasonable thermal contact with solution and conductivity, the thermocouple (D) was immersed in the mercury. Known amounts of styrene and solvent were distilled into the flask under high vacuum line. The flask was detached from the line and the solution was allowed

to reach thermal equilibrium with the constant temperature bath.

d) Co-polymerization of styrene with $\alpha$-Me styrene

A 100 ml flask fitted with 'Rota-flo' greaseless tap[2](3) was used for the copolymerization experiments. Known weights of the monomers and solvent were distilled under high vacuum into the flask which was equilibrated in a constant temperature ice-bath and the catalyst solutions were injected through 'Suba Seal'. The polymerization solution was precipitated with methanol, filtered and dried in a vacuum oven.

The experiments were repeated for different St/$\alpha$-MeSt ratio and the polymers were analysed using NMR and IR spectroscopy.

e) Ultra violet and visible spectra

A large number of coloured transition metal complexes absorb certain wavelengths of light in the visible or ultra violet region of the spectrum. The visible absorption arises when an electron is excited between two energy levels, e.g. the transition metal ion $t_{2g}$ and $e_g$ orbitals that are energetically split by the co-ordination of six ligand molecules. The resultant appearance of the material is the complementary colour of the absorbed light.

There exist a number of different possible origins for the electronic absorption of complexes, there are:

a) Spectra associated with the ligand

b) Spectra involving electronic transitions between the metal and the ligands (charge-transfer spectra)

c) Spectra associated with the metal, influenced by the presence of the ligands (d-d spectra)

d) Spectra associated with the counter ion

From the law of light absorption (the Beer-Lambert law)

$$A = \log \left( \frac{I_o}{I} \right) = \epsilon c l$$

where A = absorbance

Io = intensity of incident light

I = intensity of transmitted light

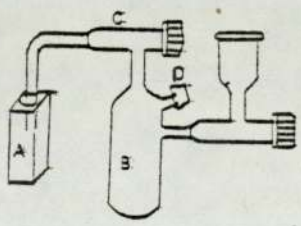
$\epsilon$ = molar extinction coefficient in 1000 $cm^2$/mole

c = concentration of solution in moles $litre^{-1}$

l = path length of the absorbing solution in cm

Commercial recording spectrophotometers automatically plot the spectrum as absorbance (A) against wavenumber or wavelength. A Perkin Elmer 137 UV type spectrophotometer was used to study the spectral changes that occurred during the polymerization of styrene initiated by $VOCl_3/AlR_3$ catalyst system. Because of the susceptible nature of the catalyst components to moisture and oxygen it was necessary to devise a closed system to study the spectral changes. The apparatus used is shown in figure 2( 11) and consisted of a silica-quartz cell (A) separated from a reservoir (B) by a greaseless tap (C). Solutions of $VOCl_3$ and $AlR_3$ could be injected by syringe through the 'Suba Seal' (D).

Figure 2(11) : The apparatus used for the study of UV and visible absorption spectra




The system was evacuated under high vacuum and then a known amount of solvent (toluene) was vacuum distilled into the reservoir (B). A required volume of $VOCl_3$ in toluene was injected through the 'Suba Seal' (D) into the reservoir (B). Because of the reactivity of $VOCl_3$ towards the Suba Seal the contents of the reservoir were transferred into the cell (A) as quickly as possible. The absorption spectrum of $VOCl_3$ solution in toluene was determined using toluene as a reference. Several different concentration of $VOCl_3$ solution in toluene were used in order to establish the absorption coefficient, the UV and visible absorbances. The contents of the cell were

then returned to the reservoir (B) and a known volume of $AlR_3$ solution in toluene was then added by syringe through the 'Suba Seal'. The cell was filled with the reaction mixture and the tap closed to prevent any reaction with the 'Suba Seal'. The absorption spectrum of the reaction solution contained in the cell was then determined as a function of time using toluene as a reference in the spectrophotometer.

A similar procedure was adopted when the spectral changes were studied in the presence of styrene in toluene which was also added by syringe to the reaction products of $VOCl_3/AlR_3$.

(5) ANALYTICAL TECHNIQUES

a) Analysis of aluminium alkyls and solution

(i) Gravimetric

The aluminium content of aluminium ethyl dichloride was determined by a gravimetric method ( 142).

A solution of $AlEtCl_2$ in toluene which contained 1 ml $AlEtCl_2$ and 53 ml toluene was prepared. X ml of this solution were added to the distilled water which contained 1 ml of 0.1N hydrochloric acid. The resulting solution was stirred and heated to approximately 60°C, when 25 ml of 2% solution of 8-hydroxyquinoline in 2N acetic acid was added. 25ml 2N ammonium acetate was then added slowly until a precipitate formed. The liquid was allowed to stand with frequent stirring for 1 hour, then filtered through a weighed sintered glass crucible. The precipitate was washed with cold distilled water, dried at 120°C and was weighed. The amount of aluminium was determined.

Al was precipitated as $(C_9H_6NO)_3Al$

Gram molecular weight of $(C_9H_6NO)_3Al$ 459 g.

1g atom of Al contained in 459 g. of precipitate

If the weight of precipitate y g.

y g contained y/459 g atoms of Al

x ml solution contained y/459 g atoms of Al

1 ml ≡ 54 ml solution contained $\frac{54}{459}\frac{y}{x}$ g atom of Al

$$[AlEtCl_2] = \frac{54 \times y}{459} \times \frac{1000}{x} \text{ moles litre}^{-1}$$

Three analysis of $AlEtCl_2$ were carried out and the results are shown in table 2( 3 ).

Table 2( 3 )

Analysis of $AlEtCl_2$

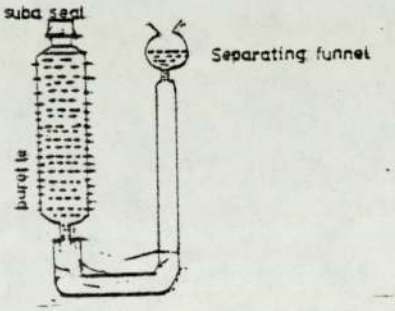
| Volume of $AlEtCl_2$ solution/ml | Weight of precipitate/g | $AlEtCl_2$ / moles litre$^{-1}$ |
|---|---|---|
| 2.6 | 0.078 | 3.53 |
| 2.6 | 0.065 | 2.94 |
| 2.6 | 0.086 | 3.80 |

Average $[AlEtCl_2]$ ≡ 3.45 moles litre$^{-1}$

(ii) Gas evolution

The strength of $AlEt_3$ determined by using a gas evolution technique.

Figure 2(12) : Gas burette for $AlR_3$ analysis




The apparatus used for this method is shown in figure 2( 12). The apparatus contained de-aerted 0.5.M. $H_2SO_4$. The space above the liquid was filled with nitrogen and volume of nitrogen contained above the acid was determined at atmospheric pressure. A solution of $AlEt_3$ was prepared in toluene (1 ml $AlEt_3$ + 18 ml toluene) and x ml of this solution was injected into the $H_2SO_4$ solution through 'Suba Seal'. A gas (ethane) was evolved on the hydrolysis of the alkyl and the acid level dropped. When the level of the liquid was station-

ary, the volume of gas contained in the burette was determined at atmospheric pressure.

If the volume of gas evolved is v ml. The volume of gas (vo) at STP evolved is given by -

$$v_o = v. \quad \frac{273.18}{T} \quad \frac{P}{760} \quad ml$$

$Al(C_2H_5)_3 + H^+_{aq} \longrightarrow 3C_2H_6$

1 mole of $AlEt_3$ $\longrightarrow$ 67.2 litre ethane

1 litre of ethane $\equiv \frac{1}{67.2}$ mole $AlEt_3$

x ml of $AlEt_3$ solution $= \frac{v_o}{0.0672}$ mole $AlEt_3$

1 ml $AlEt_3$ = 19 ml of $AlEt_3$ solution

$[AlEt_3] = \frac{v_o}{x}$ moles litre$^{-1}$

The analysis of $AlEt_3$ is shown below in table 2( 4 ).

Table 2( 4 )

| Volume of $AlEt_3$ solution/ml | Volume (at STP) of gas evolved/ml | $[AlEt_3]$ moles-litre$^{-1}$ |
|---|---|---|
| 0.2 | 5.4 | |
| 0.2 | 5.35 | 7.648 |
| 0.2 | 5.5 | |

b) Gas-liquid chromatography (GLC)

Chromatography is a method of separation of the components of a mixture by their distribution (partition) between a stationary and mobile phase. When the stationary phase consists of involatile liquid absorbed on an inert support, the technique is called GLC.

The gases used as the mobile phase are chosen according to the nature of the mixture to be separated and the type of detector used. The carrier gas should be inert to both the stationary phase and the mixture to be separated, so that many of the inert gases can be used as a carrier gas. Nitrogen is the most commonly used because it is the least expensive.

The stationary phase is the medium on which separation occurs in chromatography. It must possess the following properties:-

(a) In-volatility at the desired column operating temperature.

(b) Stability - thermal and chemical.

(c) Resistance to oxidation.

(d) Ability to form thin films on the support.

(e) Good solvent properties for the solute to be analysed.

The stationary phases may be classified in three ways:-

(a) Non polar

(b) Polar

(c) Selective

The best stationary phase is one which has a similar chemical group to the solute

The forces affecting separations can be considered in terms of three main factors:-

(1) Cohesion forces

  (a) dipole-dipole interactions

  (b) induction forces

  (c) dispersion forces

(2) Hydrogen bonding

(3) Polarity

Solutes would elute in order of increasing boiling point if the solutes and stationary phase form ideal solutions, but it is not always the case.

Any solid granular material can be used as the support of the stationary phase. It should have mechanical strength and a large specific surface, but its surface must be inactive as an adsorbant. If the material is porous the chromatography will proceed by adsorption as well as by partition. The support is usually impregnated with a solution of the stationary phase in

a volatile organic solvent which is then evaporated and the columns are packed in a tube made of glass, copper, stainless steel or polyethylene.

Various types of detectors are used in gas chromatography. The changes in composition of the gas emerging from the column are converted by the detector into an electrical signal which can then be recorded as a function of time. The most common detectors are:-

(i) flame ionisation detector

(ii) catharometer

(iii) electron-capture detector

A Perkin-Elmer F30 gas chromatograph was used in order to analyse the monomer and solvent. Nitrogen was used as carrier gas and hydrogen for combustion in a flame ionisation detector. The column packing was 10% tritolyl phosphate or Chromosorb P (60 - 80 mesh).

1$\mu$ of solvent was injected into the column and the analysis was carried out under the following conditions:-

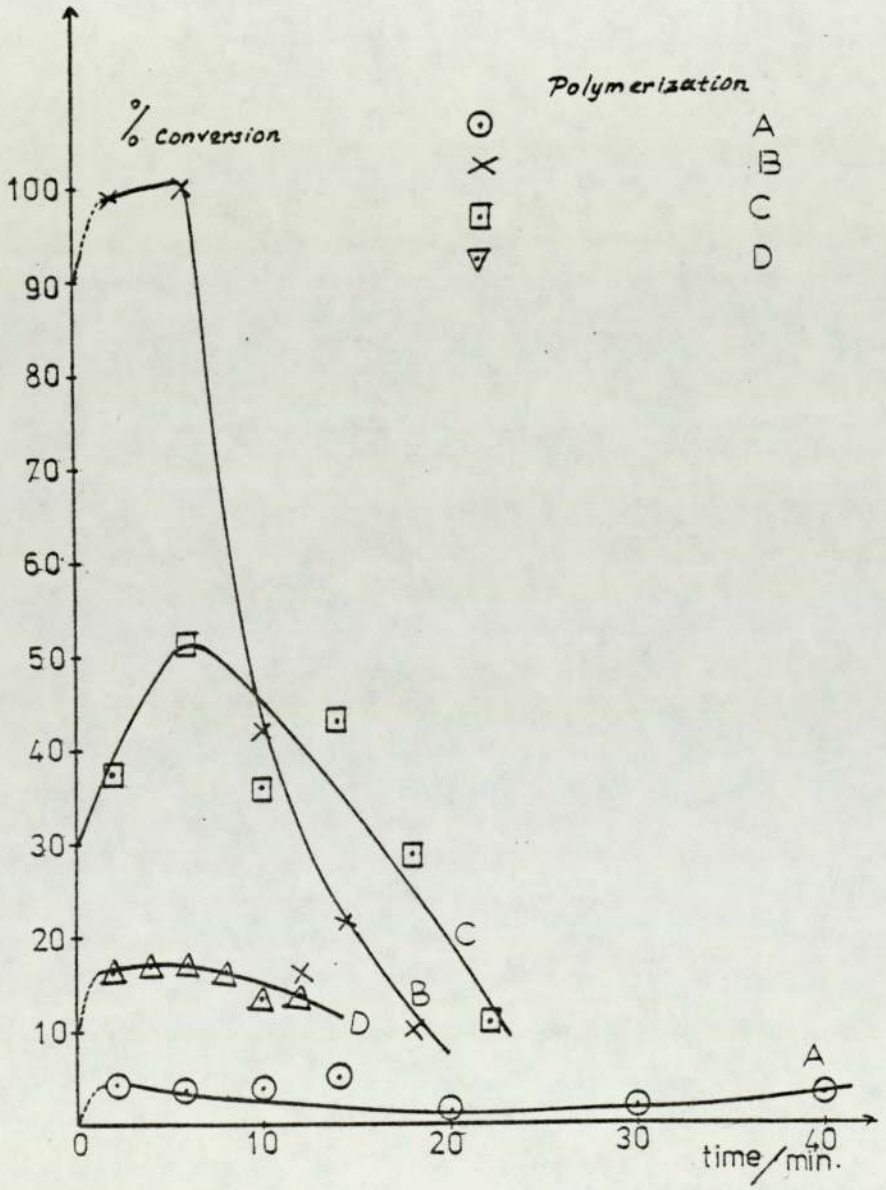
$N_2$ flow rate = 30 ml $min^{-1}$

Injection temperature = 150°C

Column temperature = 110°C

Typical chromatographs of impure and pure materials are shown in the Appendix.

Figure 3(1) : Gravimetrically determined % conversion-time curves



CHAPTER 3

## The Polymerization of Styrene: Techniques for the measurement of the rate of polymerization

### a) Gravimetric

A gravimetric technique was used to determine the rate of polymerization of styrene using the catalyst system $VOCl_3$-$AlEt_{1.5}Cl_{1.5}$.

23.88 g of purified dry styrene were distilled into a 100 ml flask and 0.15 ml of a $10^{-3}$ moles $litre^{-1}$ solution of $VOCl_3$ and $AlEt_{1.5}Cl_{1.5}$ were added to it by syringe through the 'Suba Seal'. The flask was filled with dry nitrogen and maintained at 25°C in a constant temperature bath. Known volume (1 or 2 ml) samples of the polymerizate were removed at regular intervals. Polymer was obtained by precipitating each sample in turn in methanol. The samples were dried in a vacuum oven at 60°C. The catalyst component concentrations were $0.63 \times 10^{-5}$ moles $litre^{-1}$ and a negligible precipitate was obtained after a long reaction time (3 hours).

When the concentration of catalyst was increased the rate of polymerization was sufficiently large for reasonable samples of polymer to be obtained. Table 3(1) shows the conversion in typical polymerizations carried out under the conditions cited. This information is also shown in figure 3(1).

TABLE 3(1)
Gravimetric determination of rate of polymerization

| Polymerization | Time/ Min. | Volume of Polymerizate/ ml. | Weight of Sample/g | % Conversion |
|---|---|---|---|---|
| A | 2 | 2 | 0.076 | 4.2 |
| | 6 | 2 | 0.068 | 3.7 |
| | 10 | 1 | 0.034 | 3.8 |
| | 14 | 1 | 0.049 | 5.4 |
| | 20 | 1 | 0.012 | 1.3 |
| | 30 | 1 | 0.020 | 2.2 |
| | 40 | 1 | 0.029 | 3.2 |
| | 50 | 1 | 0.026 | 2.9 |
| B | 2 | 4 | 3.56 | 98.9 |
| | 6 | 4 | 3.588 | 99.6 |
| | 10 | 2 | 0.750 | 41.7 |
| | 12 | 2.2 | 0.314 | 15.9 |
| | 14 | 2 | 0.396 | 22 |
| | 16 | 1 | 0.086 | 9.6 |
| C | 2 | 5 | 1.684 | 37.4 |
| | 6 | 5.2 | 2.396 | 51.1 |
| | 10 | 5 | 1.624 | 36.1 |
| | 14 | 5 | 1.940 | 43.1 |
| | 18 | 5.2 | 1.390 | 29.3 |
| | 22 | 1 | 0.103 | 11.4 |
| D | 2 | 5 | 0.746 | 16.6 |
| | 4 | 5 | 0.771 | 17.1 |
| | 6 | 5 | 0.778 | 17.3 |
| | 8 | 5 | 0.728 | 16.2 |
| | 10 | 5 | 0.614 | 13.6 |
| | 12 | 3.6 | 0.455 | 14.0 |

Conditions of Polymerization:

A

$[Styrene] = 8.66$ moles litre$^{-1}$

$[VOCl_3] = 0.27 \times 10^{-3}$ moles litre$^{-1}$

$[AlEt_{1.5}Cl_{1.5}] = 0.27 \times 10^{-3}$ moles litre$^{-1}$

Temperature = 25°C

B

$[Styrene] = 8.66$ moles litre$^{-1}$

$[VOCl_3] = 0.52 \times 10^{-3}$ moles litre$^{-1}$

$[AlEt_{1.5}Cl_{1.5}] = 0.52 \times 10^{-3}$ moles litre$^{-1}$

Temperature = 25°C

C

$[Styrene] = 8.66$ moles litre$^{-1}$

$[VOCl_3] = 0.14 \times 10^{-3}$ moles litre$^{-1}$

$[AlEt_{1.5}Cl_{1.5}] = 0.14 \times 10^{-3}$ moles litre$^{-1}$

Temperature = 25°C

D

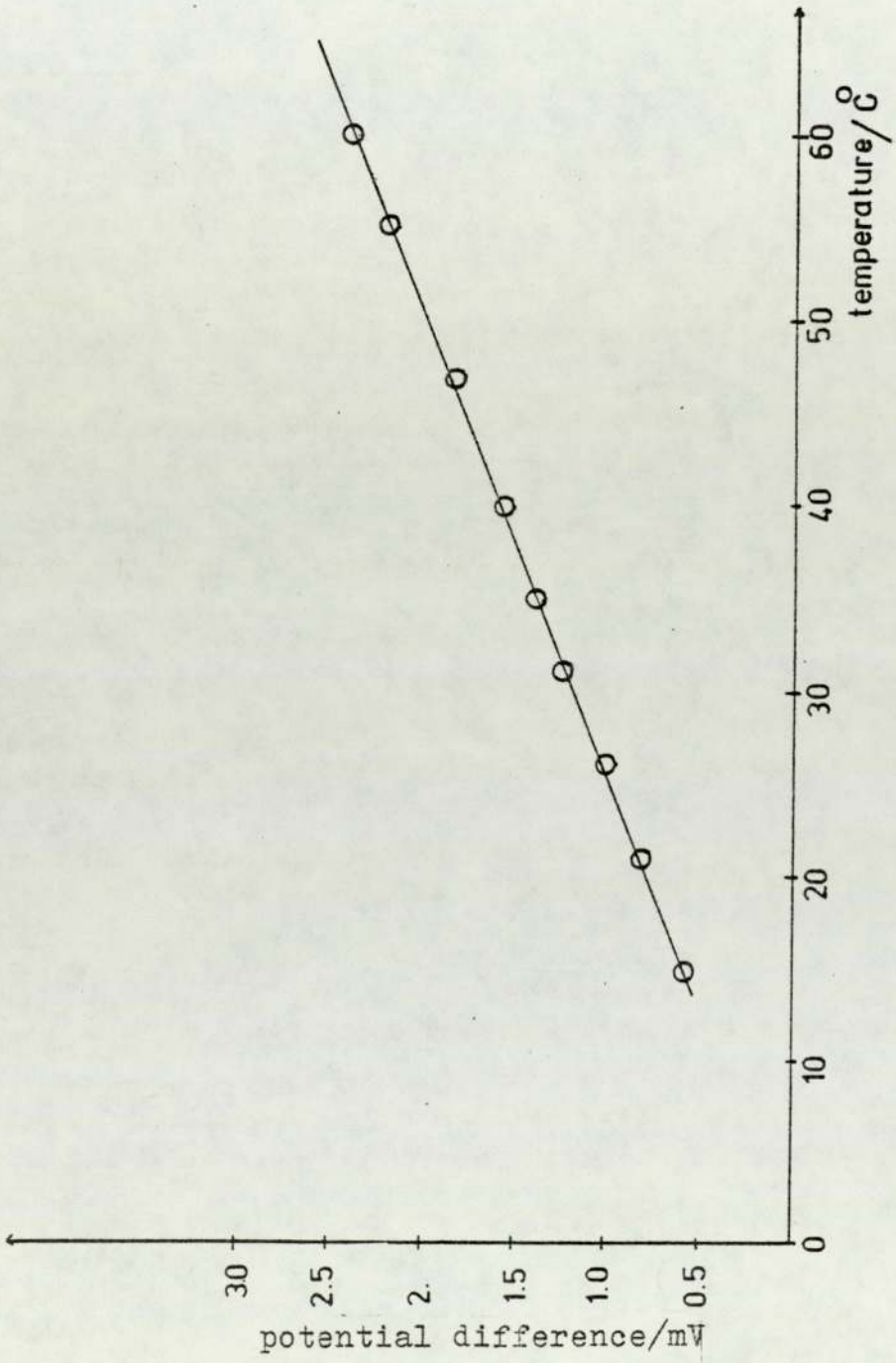
$[Styrene] = 8.66$ moles litre$^{-1}$

$[VOCl_3] = 0.24 \times 10^{-3}$ moles litre$^{-1}$

$[AlEt_{1.5}Cl_{1.5}] = 0.24 \times 10^{-3}$ moles litre$^{-1}$

Temperature = 25°C

Figure 3(2) : The calibration curve for the thermocouple



From the figure 3(1), a comparison of curves A and D shows a large error in the reproducibility of the polymerization rate under similar conditions and within an experiment, best shown in C, large errors were involved in the determination of % conversion.

The latter could have been due to -

(i) loss of polymer during the precipitation procedure and

(ii) inaccuracies in the measurement of the volume of polymerizate taken.

It was impossible to measure the initial rate of polymerization from the curves, but it would appear that the polymerization was followed by a depolymerization reaction.

b) Thermocouple

An alumel-chromel thermocouple was used to study the rate of polymerization of styrene, using $VOCl_3/AlEt_{1.5}Cl_{1.5}$ as a catalyst. The apparatus used is shown in figure 2( 10 ). Figure 3( 2 ) shows the calibration of the instrument carried out to establish the relationship between the potential difference (mV) recorded and the change in temperature ($C^o$).

(i) 20 ml styrene were distilled into the reaction vessel and system was allowed to reach thermal equilibrium with the surrounding bath. 0.95 ml of 0.05M solution of $AlEt_{1.5}Cl_{1.5}$ followed by 0.95 ml of 0.05M solution of $VOCl_3$ were added through the 'Suba Seal'. The rate of reaction was very fast, the contents of the flask became viscous and the recorder pen jumped to the end of the tracing paper.

(ii) 10 ml styrene and 10 ml toluene were distilled into the reaction vessel and when the system had reached thermal equilibrium with the surrounding bath, 0.1 ml of 0.05M solution of $AlEt_{1.5}Cl_{1.5}$ and 0.1 ml of 0.05M solution of $VOCl_3$ were injected through the 'Suba Seal'. The extent of reaction was followed, but the response was very poor and no change could be observed, probably because of the lack of good adiabatic conditions.

Figure 3(3) : The thermocouple recorder trace obtained during polymerization of styrene

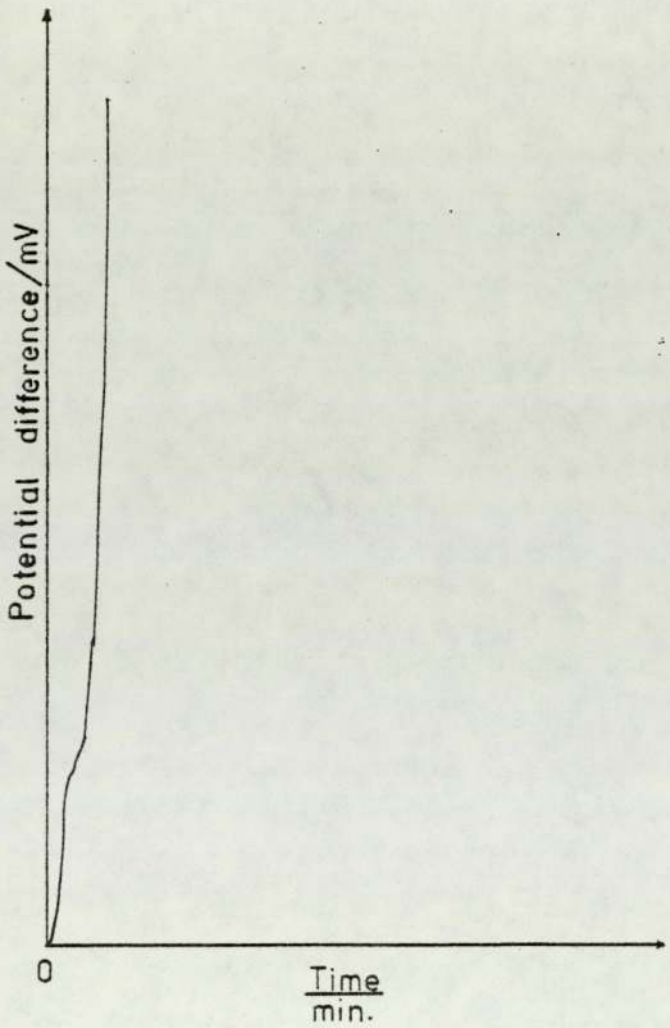
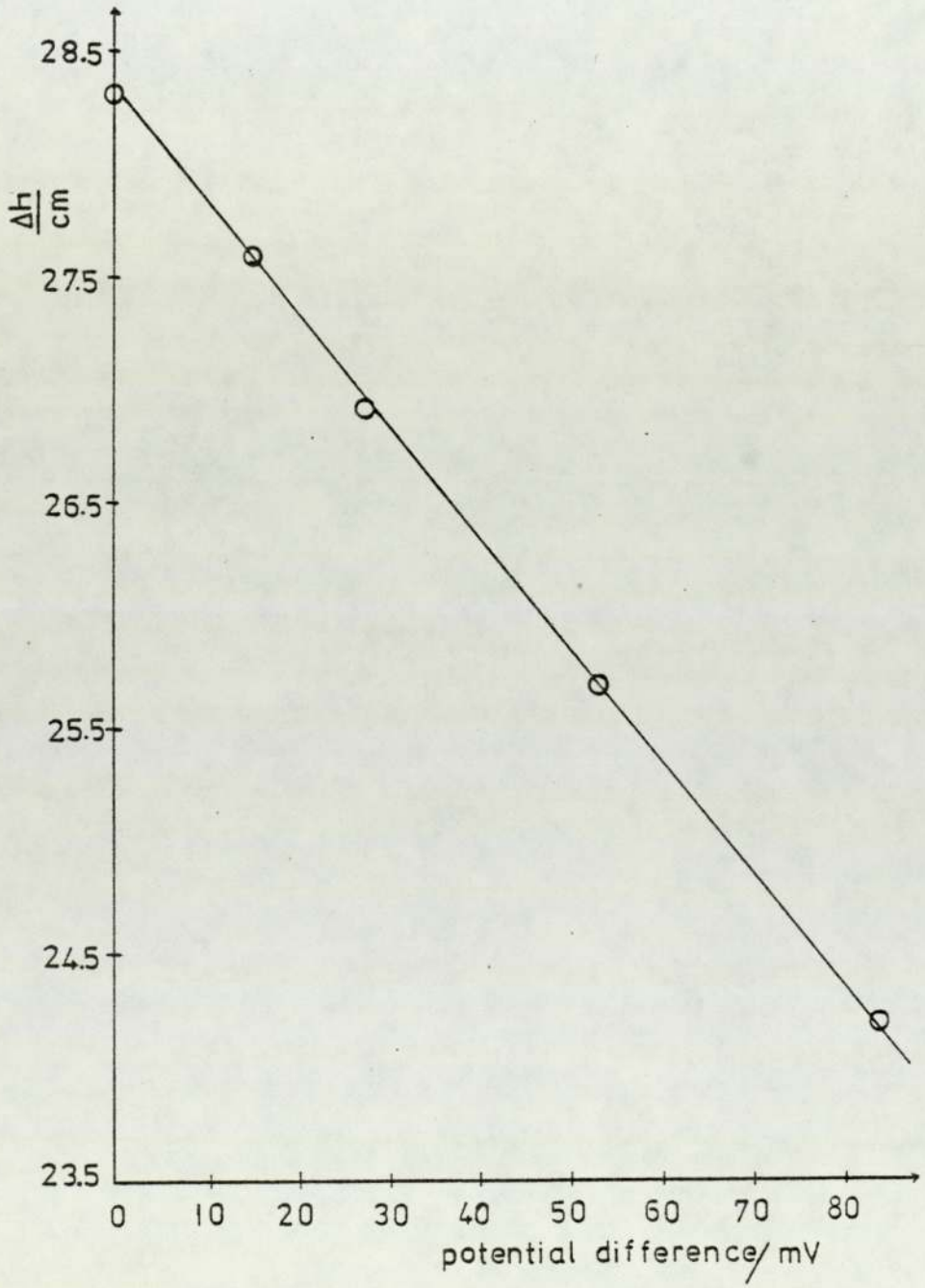


Figure 3(4) : The calibration of recording dilatometer



(iii) 10 ml styrene and 10 ml toluene were distilled into the reaction vessel, the flask was assembled in a Dewar flask, in an attempt to obtain adiabatic conditions. 0.20 ml of 0.05M solution of $AlEt_{1.5}Cl_{1.5}$ and $VOCl_3$ were added to the reaction vessel. The recorded trace obtained is shown in figure 3( 3 ). In all cases the response obtained from the thermocouple was very poor. This was probably because the thermocouple was not in direct contact with the reaction medium, from which separated by a glass wall. Furthermore truly adiabatic conditions could not be obtained.

c) Recording Dilatometer

The automatic recording dilatometer was used to study the rate of polymerization of styrene using $VOCl_3/AlEt_{1.5}Cl_{1.5}$ as catalyst. Figure 3( 4 ) shows the calibration of the instrument carried out to find the relationship between the potential difference recorded, and the change in height ($\Delta h$) in the capillary of the mercury thread.

5.7 ml of styrene was distilled into the apparatus shown in figure 2( 8 ). When the mercury thread had been correctly positioned and the system had reached thermal equilibrium with the surrounding bath, 0.075 ml of 0.082M solution of $AlEt_{1.5}Cl_{1.5}$ followed by 0.15 ml of 0.041M solution of $VOCl_3$ were added through the 'Suba Seal' (H). The resulting chart recorder trace of potential difference against time obtained during the polymerization is shown as section OA of figure 3( 5 ). When the initial polymerization of styrene had ceased at the point represented by A a further 0.075 ml of 0.082M solution of $AlEt_{1.5}Cl_{1.5}$ was added. It can be seen from figure 3( 5 ) that the polymerization of styrene recommenced until the point B was reached, when the rate had dropped to zero. At this point a further 0.8 ml of styrene was added to the dilatometer, but no further polymerization took place.

In a similar polymerization 4.6 ml styrene was distilled into

Figure 3(5) : The recorder trace of polymerization of styrene

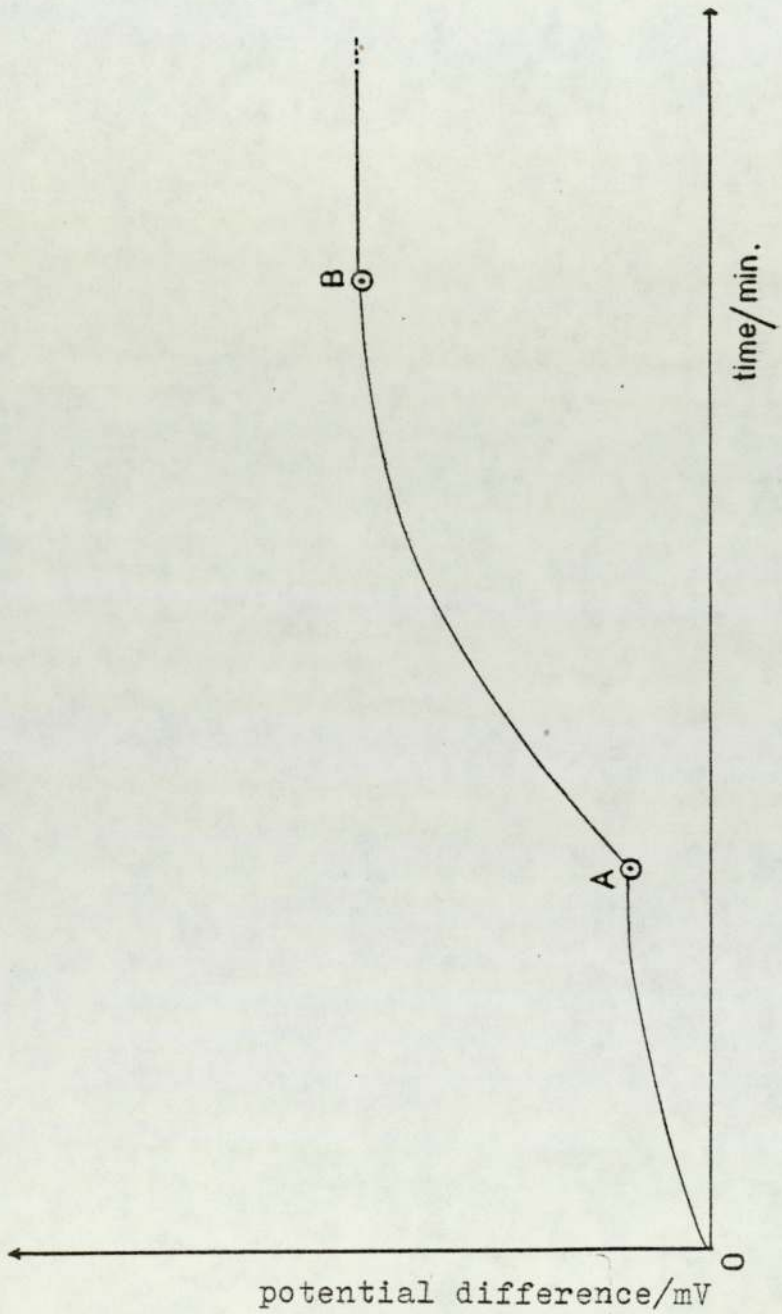
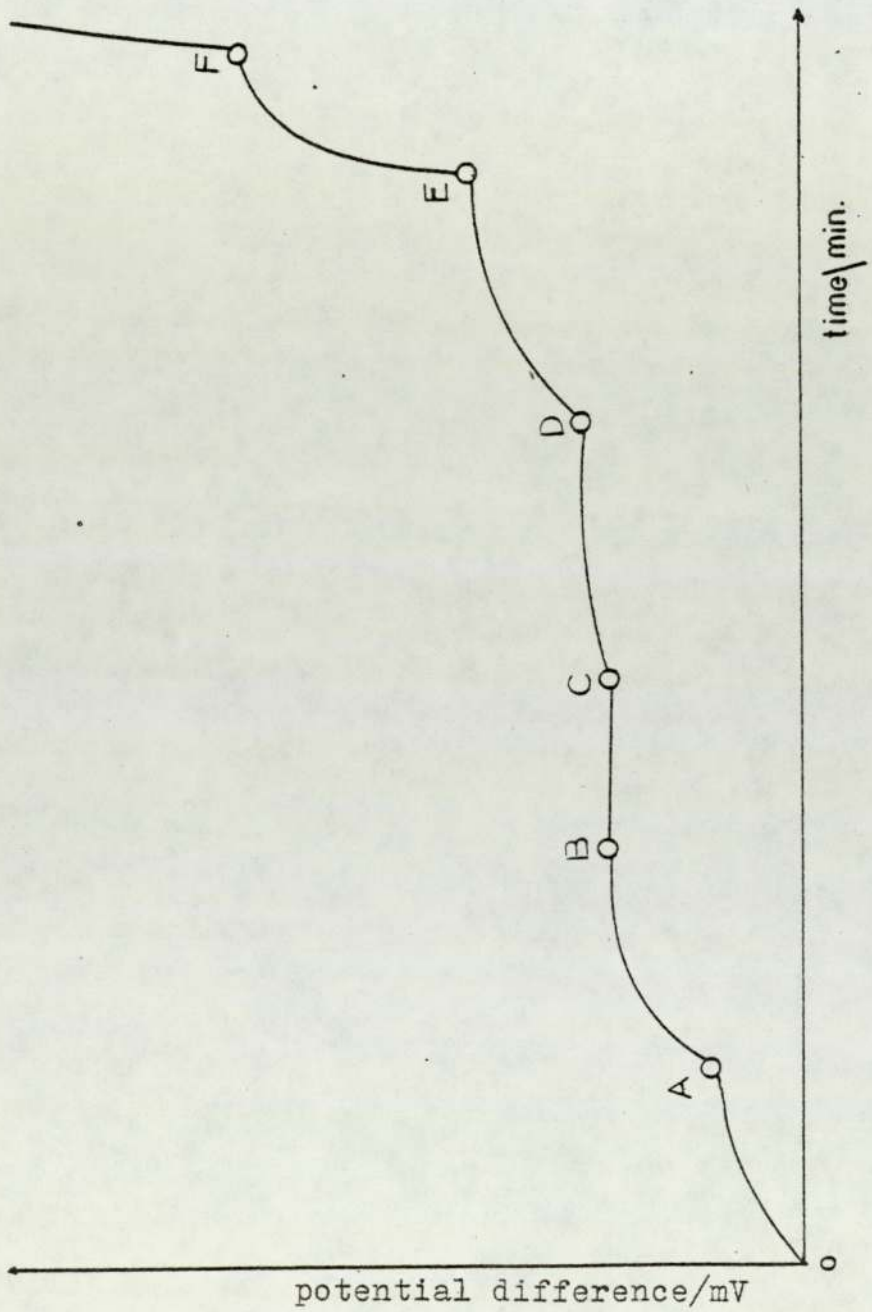


Figure 3(6) : The recorder trace of polymerization of styrene obtained by recording dilatometer



the apparatus and 0.075 ml of 0.082M solution of $AlEt_{1.5}Cl_{1.5}$ followed by 0.15 ml of 0.041M solution of $VOCl_3$ were added to the styrene. After allowing the reaction to run for 50 minutes and polymerization had ceased at the point represented by A in figure 3( 6 ). The points A→F represents the following changes in conditions:

A. a further addition of 0.075 ml of 0.082M solution of $AlEt_{1.5}Cl_{1.5}$,

B. a further 0.2 ml styrene were added to the reaction mixture,

C, D, E, F. further addition of 0.075 ml of 0.082M solution of $AlEt_{1.5}Cl_{1.5}$.

It can be seen from the figure 3( 6 ) that the polymerization of styrene recommenced by addition of the $AlEt_{1.5}Cl_{1.5}$ solution at the points represented by (A, C, D, E, F), but there is no change in polymerization of styrene by adding styrene into the system as represented by addition point B. It can therefore be presumed that whereas the addition of $AlEt_{1.5}Cl_{1.5}$ created more active species the system did not show the properties of a living system because the addition of more styrene did not cause further polymerization. The initial rate of polymerization was calculated from the recorder trace to be $2.0 \times 10^{-7}$ moles.litre$^{-1}$.sec$^{-1}$. In comparison with the gravimetric technique the rate of polymerization was very small, although the catalyst concentrations were similar for each technique. The recording dilatometer displayed many interesting properties of the polymerization studied but suffered from an overwhelming disadvantage in that it was impossible to ensure the dryness of the system. It can be seen from figure 3( 6 ) that the final additions of $AlEt_{1.5}Cl_{1.5}$ caused a much faster rate of polymerization than the initial addition, so it can be assumed at this stage that the previous additions of $AlEt_{1.5}Cl_{1.5}$ had completely dried the system. The use of $AlEt_{1.5}Cl_{1.5}$

as an 'insitu' drying agent can cause many complications in the study of the kinetics of the polymerization, because the exact natures of the components present may be unknown and irreproducible. Indeed on many occasions polymerizations carried out under seemingly identical conditions produced vastly different rates of polymerizations.

d) Dilatometry

Dilatometric techniques were used to determine the rate of polymerization of styrene, using $VOCl_3/AlR_3$ system as a catalyst. Several types of dilatometer were used, as shown in figure 2 ( 7 ).

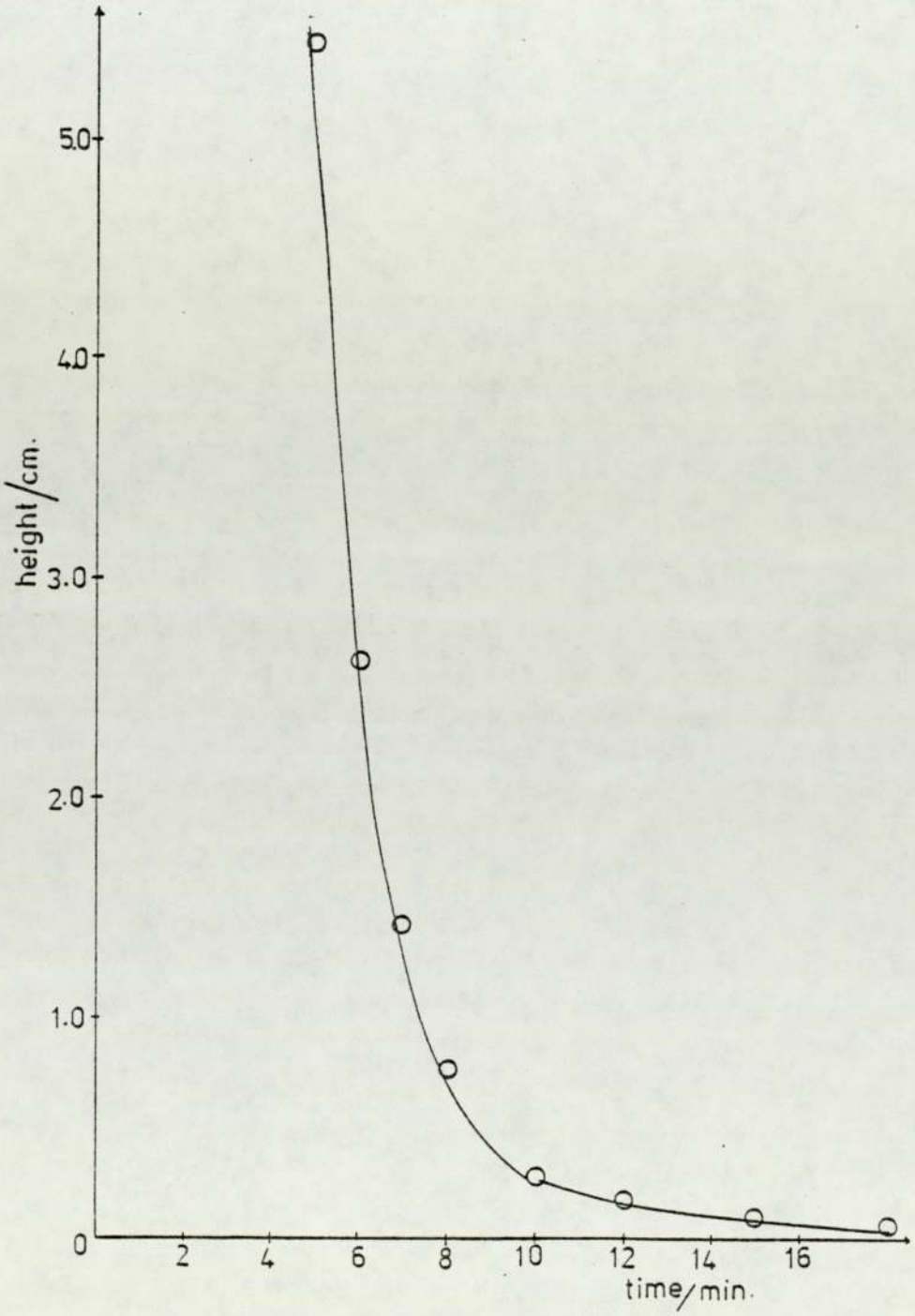
These dilatometers can be classified as follows:-

(1) those that consisted of a reaction vessel (a) into which was distilled under high vacuum the monomer and solvent. The catalyst component solution were then injected by syringe through the 'Suba Seal' into the solution of monomer, and the dilatometer bulb (b) could be filled with the reaction mixture. Dilatometers (i) - (v) inclusive are examples of this type of dilatometer; (iv) and (v) also possessed two capillary tubes in an effort to aid filling the bulb.

(2) those that consisted of a bulb (b) into which the solvent and monomer were distilled. The catalyst component solutions were then added by syringe through the 'Suba Seal' directly to the contents of the bulb. Dilatometers (vi) and (vii) are examples of this type of device one of which (vi) had the 'Suba Seal' in direct contact with the polymerising medium and the other (vii) possessed a greaseless tap (c) to separate the seal from the medium.

(3) those that possessed a reaction vessel (a), into which could be distilled the monomer and solvent, and also a compartment (d), to which the catalyst component solutions could be added. When the contents of (a) and (d) were thoroughly mixed, the bulb (b) could be filled and then separated from the re-

Figure 3(7) : A typical polymerization conversion-time curve obtained by the conventional dilatometer



mainder of the reaction mixture by closing the two greaseless taps (c). Dilatometer (viii) is an example of this type of device.

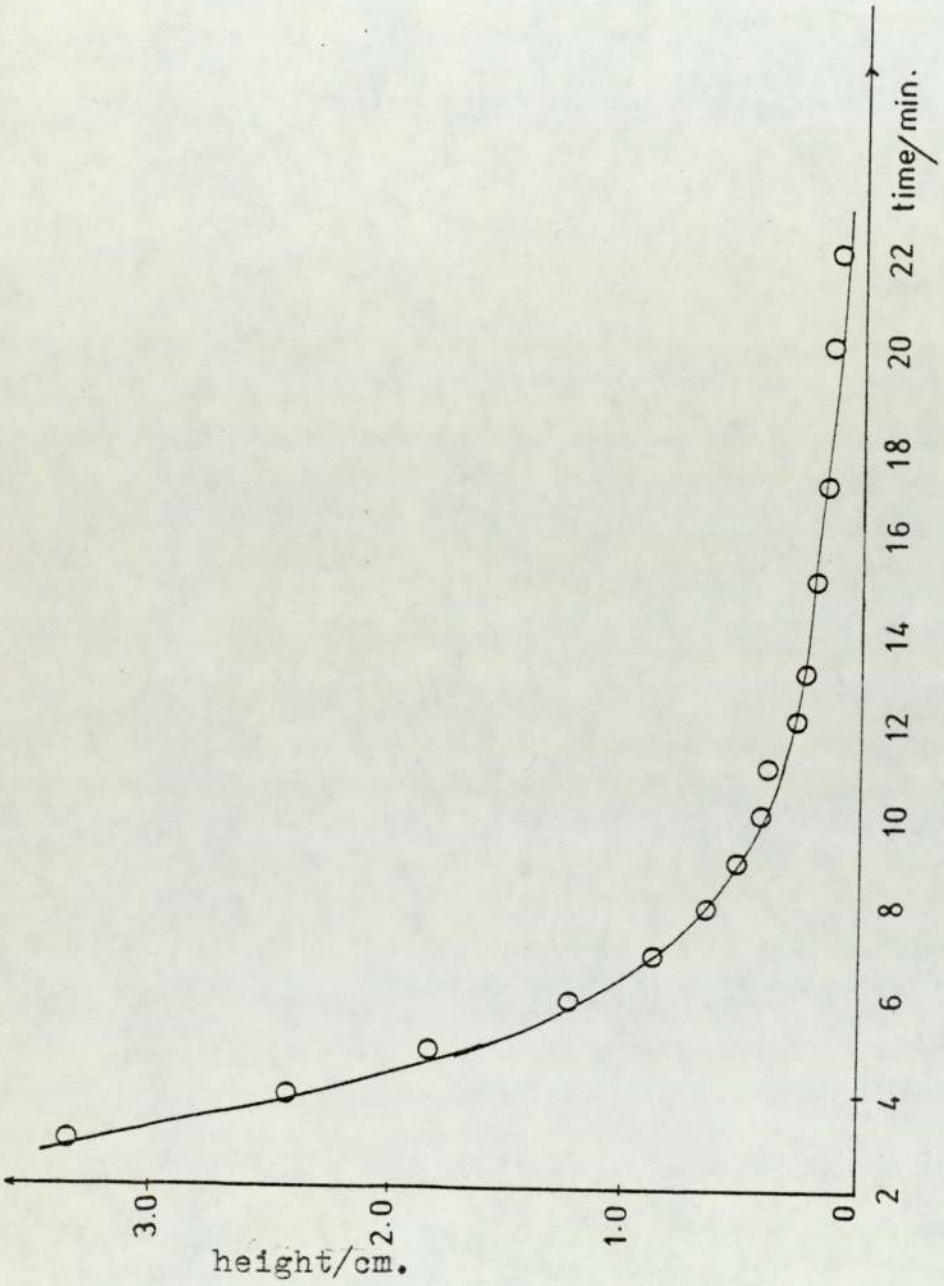
The addition of the catalyst components to the solution of monomer or to solvent alone was accompanied by the evolution of a gas or mixture of gases. This evolution created problems in filling many of the devices shown in figure 2( 7 ). In many instances the bulbs of type 1 devices could not be filled in the short time necessary to permit measurement of the initial rate of polymerization. The evolution of the gas continued during the filling process and caused bubbles to form in the capillary; in many cases the pressure of gas in the bulb would eject much of the reaction mixture from the bulb and capillary.

Only after prolonged warming and freezing operations could the bulb be filled. Moreover the filling time was not constant for a given set of conditions and could vary from 5 to 20 minutes. Devices of type 2, in which direct additions of the catalyst components to the bulb were made, were found to be useless because the volume of gas evolved even at low concentrations of catalyst was sufficient to eject a great deal of the monomer solution from the bulb.

It was found that the evolution of the gas presented no problems in the filling of devices of type 3, where rapid filling of the bulb could be made without the formation of bubbles in the capillary thread of liquid.

$VOCl_3/AlEt_{1.5}Cl_{1.5}$ produced a very effective catalyst system for the polymerization of styrene. It can be seen from figure 3( 7 ) that the rate of polymerization of styrene using low concentrations of catalysts may be extremely rapid and associated with this rapid polymerization was a steep rise in temperature of the reaction medium. To study the rate of polymerization effectively by dilatometry, low concentrations of initiator ($\sim 10^{-5}$ M) and monomer ($\sim$ 1M) had to be used. When polymerizations were carried out under these conditions, the reactions

Figure 3(8) : A typical polymerization conversion-time curve obtained by the conventional dilatometer



were susceptible to traces of impurities (present in few parts per million). It was necessary therefore to isolate the dilatometer bulb and its contents from any source of impurity. It was found that the 'Suba Seal' which had been pierced by the syringes was the prime source of such impurities and hence those devices of types 1 and 2 wherein there was direct contact with the 'Suba Seal' often led to polymerization that were rapidly terminated. The 'Suba Seal' could be isolated from the bulb in dilatometer (viii) and meaningful polymerization curves, such as that shown in figure 3( 8 ), could be obtained and this type of dilatometer was used throughout.

CHAPTER 4

## Studies on the polymerization of styrene

The copolymerization of ethylene and propylene and their ter-polymerization with a non-conjugated diene is most effectively catalysed by the $VOCl_3/AlEt_{1.5}Cl_{1.5}$ system. The object of the current work was to use styrene as a monomer to study this catalyst system but it is well known that the activity of a Ziegler-Natta catalyst may vary from monomer to monomer depending on the catalyst combination. In order to establish the use of styrene as a substitute monomer for this catalyst system, the activities of various catalysts based on the combination of $VOCl_3$ with aluminium alkyls were measured.

### (a) Effect of the nature of the aluminium alkyl on the activity of $VOCl_3/AlR_3$ catalysts towards the polymerization of styrene

3 ml of purified styrene and 28 ml of pure toluene, the purities of which were determined by gas chromatography, were distilled into the reaction vessel of dilatometer VIII shown in figure 2( 7 ). The dilatometer was immersed in the constant temperature bath at 25°C for 20 minutes before 0.35 ml of $1.1 \times 10^{-3}$ M solution of $VOCl_3$ and 0.35 ml of $1.1 \times 10^{-3}$ M solution of $AlEt_{1.5}Cl_{1.5}$ were added to the small reaction vessel ( a ) and allowed to react together for 2 minutes. The contents of the dilatometer were thoroughly mixed and the bulb of the dilatometer was filled. The dilatometer was returned to a fixed position in the constant temperature bath and the decrease in height of the meniscus was determined using a cathetometer. Similar polymerizations were carried out using $AlEt_3$ and $AlEtCl_2$ as cocatalysts with $VOCl_3$. The effect of the nature of the aluminium alkyl on the rate of polymerization is shown in Table 4(1) for the conditions cited.

TABLE 4(1)

Effect of nature of $AlR_3$ on rate of polymerization (Rp) of Styrene

| Aluminium Alkyl | $[VOCl_3] \times 10^5$ / moles litre$^{-1}$ | $[AlR_3] \times 10^5$ / moles litre$^{-1}$ | [Styrene] / moles litre$^{-1}$ | $Rp \times 10^6$ / moles litre$^{-1}$ s$^{-1}$ | $\frac{Rp \times 10^{-3}}{[St][VOCl_3][AlR_3]} \cdot \frac{1}{\text{moles}^{-2}\ \text{litre}^2\ s^{-1}}$ |
|---|---|---|---|---|---|
| $AlEt_3$ | 21 | 21 | 1.5 | 110 | 2.7 |
| $AlEt_{1.5}Cl_{1.5}$ | 1.2 | 1.2 | 0.84 | 400 | 3,300 |
| $AlEtCl_2$ | 1.2 | 1.2 | 0.84 | 3.2 | 27 |

It can be seen from Table 4(1) that $AlEt_{1.5}Cl_{1.5}$ was the most effective cocatalyst with $VOCl_3$ for the polymerization of styrene. The alkyl aluminium compounds selected as cocatalysts cover a range of reducing powers and Lewis acidities and it would appear that, as is the case for the copolymerization of ethylene and propylene, $VOCl_3/AlEt_{1.5}Cl_{1.5}$ represented the most effective catalyst combination. It seemed reasonable to undertake a study of this catalyst system using styrene as monomer in the hope that the results obtained could be correlated with ethylene propylene polymerizations.

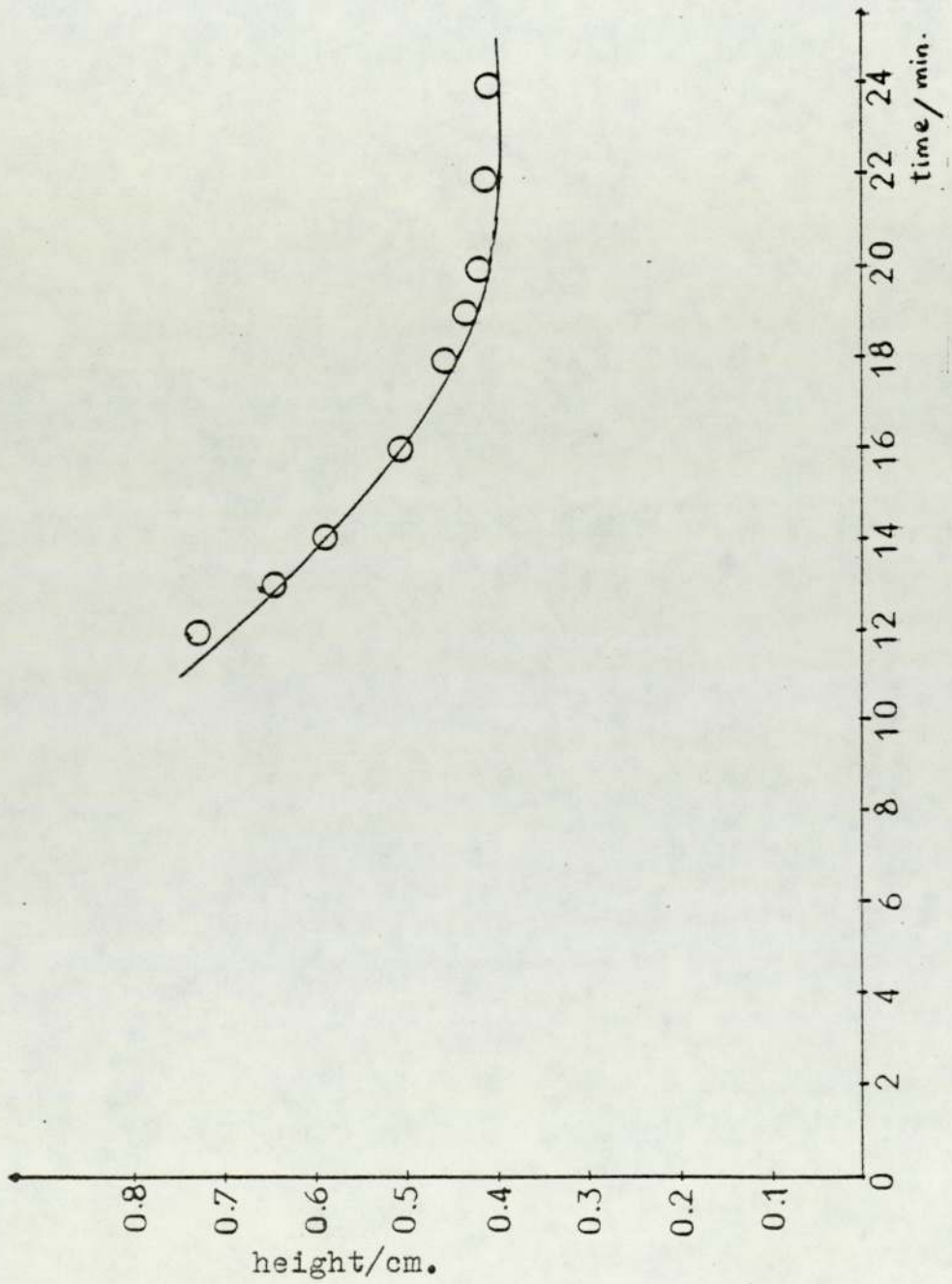
(b) Bulk polymerization of styrene initiated by $VOCl_3/AlEt_{1.5}Cl_{1.5}$

(i) Effect of Al:V molar ratio on rate of polymerization

To study the effect of Al:V molar ratio on the activity of the catalyst, attempts were made to determine the rate of polymerization of bulk styrene, at constant $[VOCl_3]$ and various $[AlEt_{1.5}Cl_{1.5}]$. The styrene was purified according to that procedure explained in 2(b)(i). 20 ml of this purified monomer was distilled into the reaction vessel (a) of dilatometer $\overline{IV}$ and $\overline{V}$ shown in figure 2( 7 ). The dilatometer was immersed in the constant temperature bath at 25°C for 20 minutes before 0.55 ml of 0.145 M solution of $VOCl_3$ and 3.2 ml of 0.05 M solution of $AlEt_{1.5}Cl_{1.5}$ were added to the reaction vessel (a) so that $[VOCl_3] = 3.4 \times 10^{-3}$ moles litre$^{-1}$, $[AlEt_{1.5}Cl_{1.5}] = 6.8 \times 10^{-3}$ moles litre$^{-1}$ and $[\text{styrene}] = 7.29$ moles litre$^{-1}$. Polymerization occurred instantaneously. The solution became extremely hot and so viscous that the bulb of the dilatometer could not be filled to determine the rate of polymerization.

Similar polymerizations were carried out in which the catalyst concentration was decreased by approximately 10 fold. After the monomer was distilled into the reaction vessel (a), the dilatometer was immersed in the constant temperature bath at 25°C for

Figure 4(1) : A typical bulk polymerization of styrene



20 minutes. The catalyst solutions were added through the 'Suba Seal' (e) and the reaction mixture was thoroughly mixed and the bulb of the dilatometer was filled. The dilatometer was positioned into the constant temperature bath and the decrease in height of the meniscus was determined using a cathetometer.

The effect of rate of polymerization on the conditions of polymerization are shown in Table 4(2).

Table 4(2)

The effects of polymerization conditions on the rate of bulk polymerization of styrene (Rp)

| $\frac{[\text{Styrene}]}{\text{moles litre}^{-1}}$ | $\frac{[VOCl_3] \times 10^6}{\text{moles litre}^{-1}}$ | $\frac{Rp \times 10^5}{\text{moles litre}^{-1}\,\text{s}^{-1}}$ |
|---|---|---|
| 8.1 | 98 | 3.9 |
| 8.4 | 22 | 2.2 |
| 8.3 | 22 | 8.4 |
| 7.8 | 8 | 2.1 |
| 8.4 | 1.6 | 0.0 |

Temperature = 25°C $\quad [VOCl_3] = [AlEt_{1.5}Cl_{1.5}]$

Figure 4(1) shows a typical polymerization conversion time curve obtained in these studies. It will be noted that the initial rate of polymerization could not be determined, because of the difficulties experienced in filling dilatometers under these conditions. Great irreproducibility of the rate of polymerization was observed and under certain conditions, i.e. low $[VOCl_3]$, polymerization did not take place. The values quoted in Table 4(2) are the rates of polymerization obtained after 10 minutes. Under these and other conditions it was highly likely that some irreproducible amount of the catalyst was scavenged by impurities.

(c) Solution polymerization

Great difficulty was experienced in the measurement of the rate of polymerization of bulk styrene but rough estimates of

expected rates of polymerization indicated that a measurable rate of polymerization would be expected if the concentration of catalyst and monomer of polymerization in Table 4(2) were each reduced by a factor of 10.

Toluene and styrene, purified by procedures 2(a)(ii) and 2(b)(i), were distilled into the reaction vessel of dilatometer VIII of figure 2( 7 ). So that [styrene] = 0.5 M. Solutions of $VOCl_3$ and $AlEt_{1.5}Cl_{1.5}$ were then added by syringe so that $[VOCl_3]$ = $[AlEt_{1.5}Cl_{1.5}]$ = $5.5 \times 10^{-5}$ M the dilatometer bulb was filled but the expected measurable rate of polymerization (approximately 0.1%/min.) was not obtained; the rate of polymerization was found to be zero.

The contents of the dilatometer were redistilled under vacuum into a dry evacuated flask, 0.5 ml of $5.5 \times 10^{-3}$ M of $VOCl_3$ solution and 0.1 ml of 3.98 M of $Al(i\text{-}Bu)_3$ were added to the flask. The dilatometer was washed, dried and returned to the vacuum line and the contents of the flask (toluene, styrene mixture) were redistilled into it. Samples of $VOCl_3$ and $AlEt_{1.5}Cl_{1.5}$ solutions were then added so that the catalyst components concentrations were again $5.5 \times 10^{-5}$ M.

The dilatometrically determined rate of polymerization was $31.3 \times 10^{-5}$ moles $litre^{-1}s^{-1}$. It can therefore be assumed that the polymerization under the initial conditions was inhibited by the presence of an impurity that was removed by $VOCl_3/Al(i\text{-}Bu)_3$. The latter system was chosen to purify styrene because:

(i) as Table 4(1) shows, catalysts based on $VOCl_3/AlEt_3$, and presumably other trialkyls, were low activity catalysts for the polymerization of styrene.

(ii) $Al(i\text{-}Bu)_3$ is less volatile than $AlEt_3$, see Table 2( 2 ).

(i) Effect of $[AlEt_{1.5}Cl_{1.5}]$ on the rate of polymerization of styrene

To study the effect of Al:V molar ratio on the activity of the catalyst, a series of polymerizations of styrene were carried out in solvent at constant $[VOCl_3]$ and various $[AlEt_{1.5}Cl_{1.5}]$. The styrene and toluene were purified by the technique described in 2, mentioned above. 7 ml of purified styrene and 25 ml of purified toluene were distilled into the reaction vessel (a) of dilatometer VIII shown in figure 2( 7 ). The dilatometer was immersed in the constant temperature bath at 25°C for 20 minutes. 0.6 ml of $5.5 \times 10^{-3}$ M of $VOCl_3$ and 0.6 ml of $5.5 \times 10^{-3}$ M of $AlEt_{1.5}Cl_{1.5}$ solutions were added through the 'Suba Seal' (e) into the compartment (d). The contents of (a) and (d) were thoroughly mixed immediately, the bulb (b) of dilatometer was filled and the contents then separated from the remainder of the reaction mixture by closing the two 'Rota-flo' greaseless taps (c). The dilatometer was positioned in the constant temperature bath, and the decrease in height of the meniscus was determined, using a cathetometer. The effect on the rate of polymerization of the concentration of $AlEt_{1.5}Cl_{1.5}$ is shown in Table 4(3). When the catalyst ratio of Al:V was 3 the reaction became hot and it was difficult to fill the bulb of dilatometer so the initial rate of polymerization could not be measured.

A similar series of experiments was then carried out in which the $VOCl_3/AlEt_{1.5}Cl_{1.5}$ solutions were reacted together for 2 minutes before addition to the monomer-solvent mixture took place. Table 4(4) shows the effect of Al:V molar ratios on the activity of catalysts for the polymerization of styrene.

TABLE 4(3)

The effect of Al:V molar ratio on the rate of polymerization of styrene

| Al:V | $\frac{[VOCl_3] \times 10^4}{\text{moles litre}^{-1}}$ | $\frac{[AlEt_{1.5}Cl_{1.5}] \times 10^4}{\text{moles litre}^{-1}}$ | $\frac{[\text{Styrene}]}{\text{moles litre}^{-1}}$ | $\frac{Rp \times 10^4}{\text{moles litre}^{-1}\,s^{-1}}$ | $\frac{Rp}{[VOCl_3]}\ s^{-1}$ |
|---|---|---|---|---|---|
| 1:1 | 1.0 | 1.0 | 1.83 | 8.5 | 8.5 |
| 2:1 | 1.0 | 1.96 | 1.79 | 15.0 | 15.0 |
| 3:1 | 1.0 | 2.9 | 1.76 | 3.3 | 3.3 |

TABLE 4(4)

The effect of Al:V molar ratio on the rate of polymerization of styrene

| Al:V | $\frac{[VOCl_3] \times 10^5}{\text{moles litre}^{-1}}$ | $\frac{[AlEt_{1.5}Cl_{1.5}] \times 10^5}{\text{moles litre}^{-1}}$ | $\frac{[\text{Styrene}]}{\text{moles litre}^{-1}}$ | $\frac{Rp \times 10^4}{\text{moles litre}^{-1}\,s^{-1}}$ | $\frac{Rp}{[VOCl_3]\ s^{-1}}$ |
|---|---|---|---|---|---|
| 1:1 | 11 | 11 | 1.38 | 1.2 | 0.0109 |
| 2:1 | 10 | 21 | 1.34 | 6.2 | 0.062 |
| 3:1 | 10 | 31 | 1.31 | 1.3 | 0.013 |
| 4:1 | 10 | 40 | 1.28 | 5.1 | 0.051 |
| 1:1 | 2.4 | 2.4 | 0.61 | 3.1 | 0.13 |
| 3:1 | 2.4 | 4.8 | 0.57 | 1.1 | 0.046 |
| 4:1 | 2.4 | 9.6 | 0.57 | 4.7 | 0.19 |
| 5:1 | 2.4 | 12.0 | 0.57 | 6.4 | 0.27 |
| 10:1 | 1.15 | 11.5 | 0.85 | 7.3 | 0.63 |

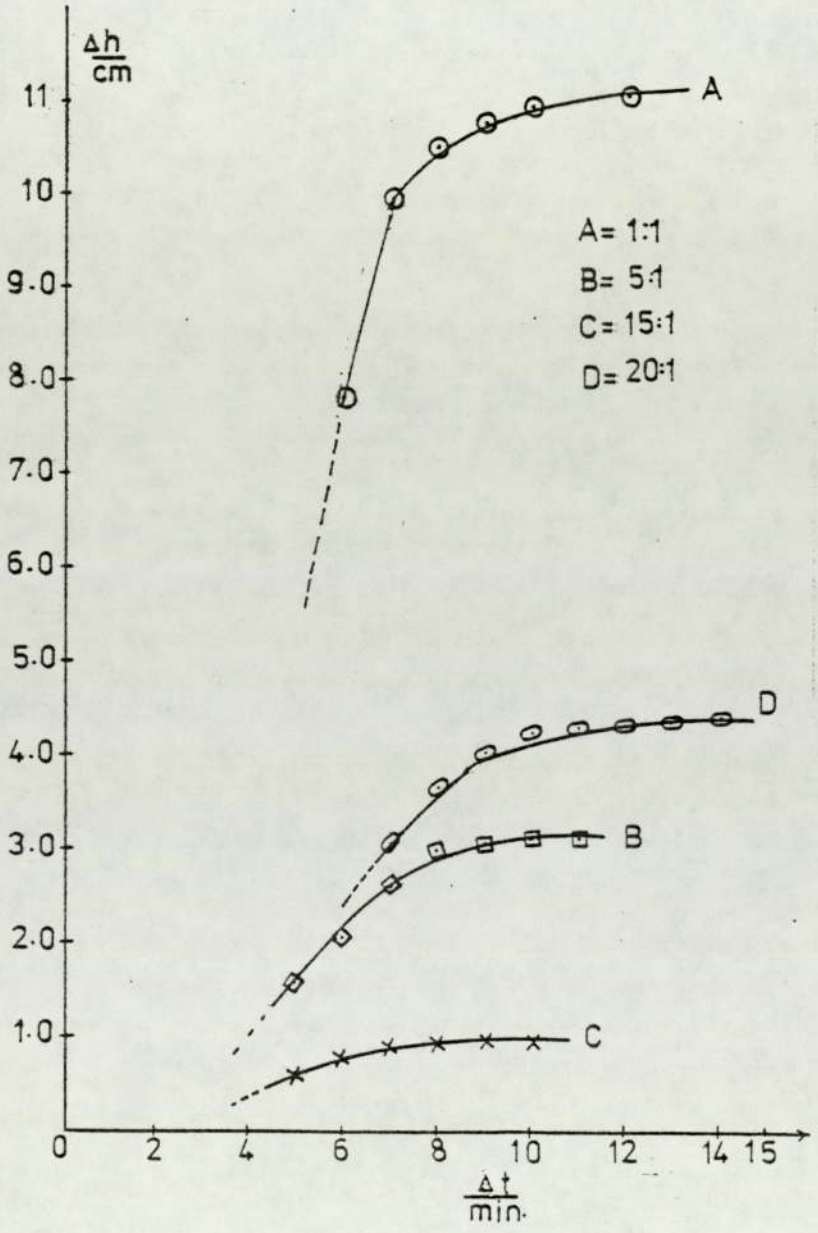
The results shown in Tables 4(3) and 4(4) would indicate that the rate of polymerization depended upon the Al:V molar ratio. However the rates of polymerization measured for molar ratios Al:V $\geq$ 2:1 were somewhat meaningless, in that the measured rates of polymerization were not the initial rates of polymerization. In these cases the polymerizates became viscous during the filling operations and the temperatures of the systems rose rapidly. This procedure proved to be of no use for the measurement of catalyst activity as a function of Al:V molar ratio. Premixing the catalyst components for a period of 2 minutes had no advantageous effect upon these studies, although a noticeable difference in corresponding rates of polymerization was observed. Even when the concentration of $VOCl_3$ was reduced to $2.4 \times 10^{-5}$ moles $litre^{-1}$ the maximum ratio that could be studied was Al:V = 5:1.

(ii) Effect of $[VOCl_3]$ on the activity of the catalyst for the polymerization of styrene

To study the effect of V:Al molar ratio on the catalyst, a series of polymerization of styrene were carried out in solvent at constant $[AlEt_{1.5}Cl_{1.5}]$ and various $[VOCl_3]$.

The styrene and toluene were purified by the technique described in 2(b)(iv), 2(a)(i) respectively. 3 ml of purified styrene and 28 ml purified toluene were distilled into the reaction vessel (a) of dilatometer VIII shown in figure 2( 7 ). The dilatometer was immersed in the constant temperature bath at 25°C for 20 minutes. The $VOCl_3/AlEt_{1.5}Cl_{1.5}$ solutions were added through the 'Suba Seal' (e) into the compartment (d) and allowed to react together for 2 minutes before addition to the monomer-solvent mixture. The contents of (a) and (d) were thoroughly mixed immediately, the bulb (b) of dilatometer was filled and the contents then separated from the remainder of the reaction mixture by closing the two 'Rota-flo' greaseless taps (c). The dilatometer was positioned in the constant temperature bath, and the

Figure 4(2) : The effect of V:Al ratio on the rate of the polymerization of styrene



decrease in height of the meniscus was determined, using a cathetometer. The effect on the rate of polymerization of the concentration of $VOCl_3$ is shown in Table 4(5). And the polymerization conversion-time curves shown in figure 4(2).

TABLE 4(5)

The effect of $[VOCl_3]$ on rate of polymerization (Rp) of styrene

| $[VOCl_3] \times 10^5$ / moles litre$^{-1}$ | [Styrene] / moles litre$^{-1}$ | Rp $\times 10^4$ / moles litre$^{-1}$ s$^{-1}$ | Rp $\times 10^4$ / [Styrene] s$^{-1}$ |
|---|---|---|---|
| 1.2 | 0.82 | 26 | 31 |
| 5.8 | 0.78 | 11 | 14 |
| 15.7 | 0.71 | 2.7 | 3.8 |
| 20.0 | 0.68 | 3.5 | 5.1 |

$[AlEt_{1.5}Cl_{1.5}]$ = $1.2 \times 10^{-5}$ moles litre$^{-1}$

Temperature = 25°C

The estimation of the initial rate of polymerization in this series of reactions was hampered by the fact that the initial polymerization period was often not recorded. However it can be seen from the polymerization conversion-time curves that increasing the $[VOCl_3]$ did not have a significant effect upon the shapes of the polymerization curves and in each case the rate of polymerization fell rapidly to zero. In this series of experiments the $[VOCl_3]$ was increased 20 fold, but this increase caused a decrease in the initial rate of polymerization. Comparison of these results with those obtained at constant $[VOCl_3]$ would suggest that increasing $[AlEt_{1.5}Cl_{1.5}]$ led to an increase in the number of active sites produced, whereas an increase $[VOCl_3]$ led to a destruction of active sites.

(d) Investigations of conversion-time curves for the polymerisation of styrene

Figure 4(3) : A typical polymerization conversion-time curve for extended periods of polymerization of styrene

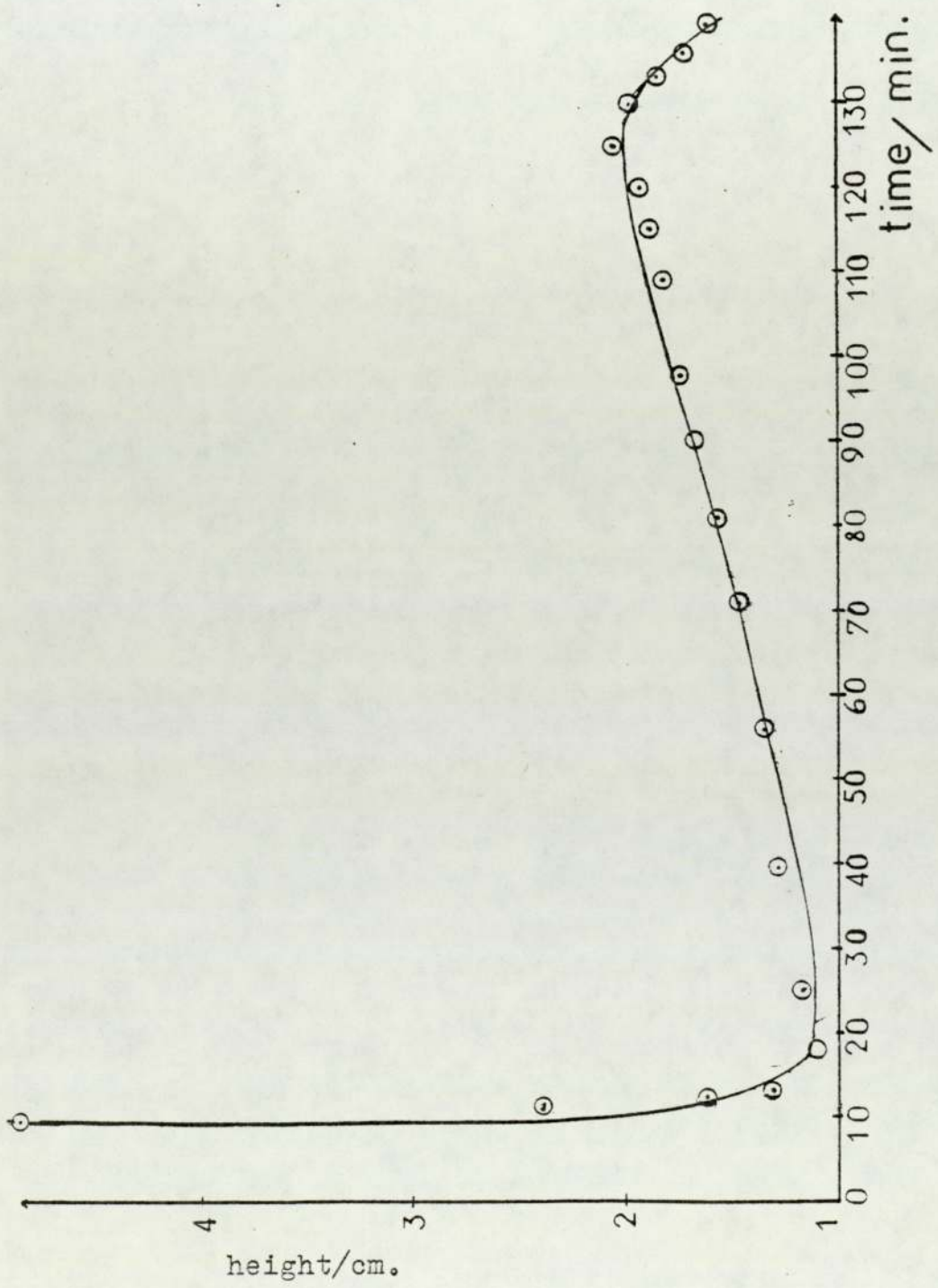


Figure 4(3) shows a typical polymerization conversion-time curve for extended periods of polymerization. An inspection of this curve shows that there were three distinct periods during the course of the polymerization two of which, the initial and final periods, were associated with a decrease of meniscus height, and the other an increase of meniscus height.

The decreases in meniscus height associated with the initial and final periods are readily explained by the polymerization of styrene but it is more difficult to explain the increase in height during the intervening period, especially since the concentration of monomer was greater than the equilibrium concentration monomer for the polymerization of styrene at 25°C, which according to Dainton and Ivin (147) is $1\bar{0}^{6}$ moles $litre^{-1}$, equivalent to 99.99% conversion in this system.

Two possible explanations for this increase in meniscus height are:

(i) a gas was evolved during this period and, trapped in the bulb of the dilatometer, forced the meniscus height to increase,

or

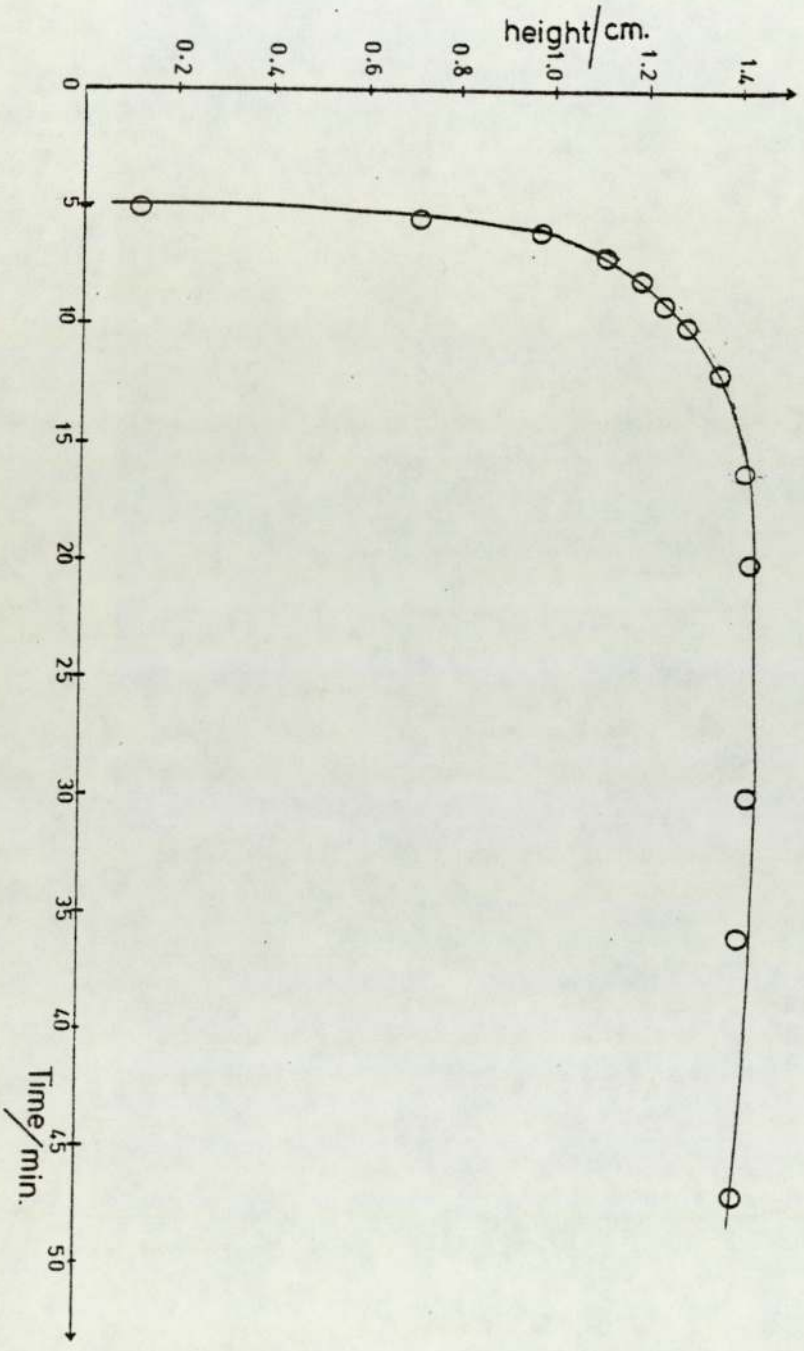
(ii) depolymerization occurred by some mechanism

(i) Changes of meniscus height in absence of monomer

Sufficient purified toluene was distilled into the dilatometer and the catalysts were added in the usual manner so that $\left[VOCl_3\right] = \left[AlEt_{1.5}Cl_{1.5}\right] = 1.2 \times 1\bar{0}^{5}$ moles $litre^{-1}$, equal to that in a typical polymerization. The dilatometer was filled, placed in a constant temperature bath and the meniscus height was recorded over a long period of time. No change in meniscus height was recorded in this experiment and a similar result was obtained when the concentrations of catalysts components was increased to $1 \times 1\bar{0}^{2}$ moles $litre^{-1}$.

It is therefore likely that the increase in height of the meniscus observed during a polymerization was not caused by the evolution

Figure 4(4) : The changes in heights of meniscus with time at the presence of catalyst components ($VOCl_3$/($AlEt_{1.5}Cl_{1.5}$)) and polystyrene solution



of a gas, unless that evolution was catalysed by the presence of styrene.

(ii) Effect of polymerization catalyst on a solution of polystyrene

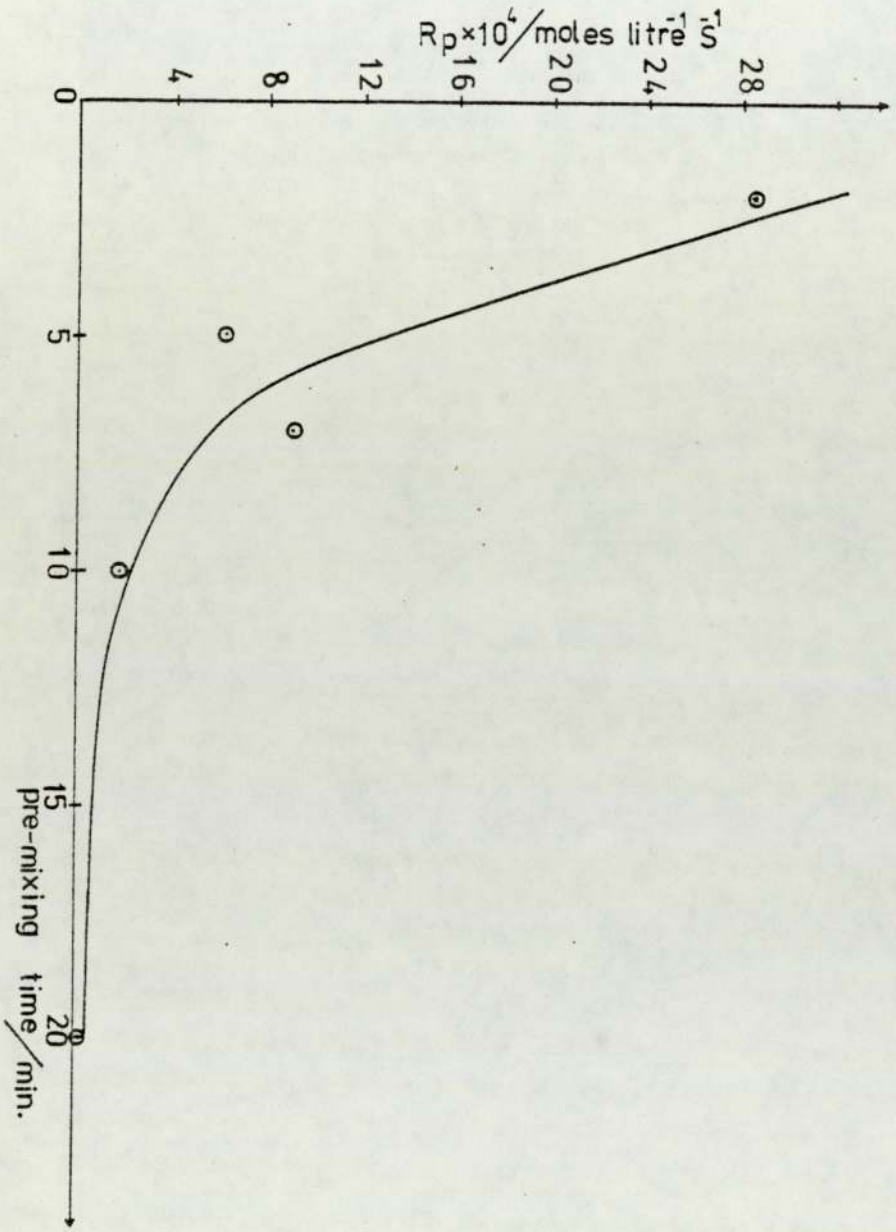
Polystyrene was prepared by the catalyst system $VOCl_3$/ $AlEt_{1.5}Cl_{1.5}$, purified and dried in a vacuum oven at 60°C. A known amount of polystyrene was placed in the dilatometer VIII shown in figure 2( 7 ) and the purified toluene was distilled into the vessel (a) of the dilatometer. The polystyrene was dissolved completely in the toluene and the toluene was redistilled from the dilatometer in order to remove any moisture and air left in the polystyrene. This procedure of solution and distilling was repeated three times. 30 ml of purified toluene was then distilled into the reaction vessel (a) of the dilatometer. The polystyrene (3g) was completely dissolved in toluene, and the dilatometer was immersed into the constant temperature bath for 30 minutes at 25°C. The catalyst solutions were injected into the compartment (d) of the dilatometer and the contents of (a) and (d) were mixed thoroughly. The bulb (b) of the dilatometer was filled as soon as possible and the dilatometer was positioned in the constant temperature bath, the change in height of the meniscus was determined using a cathetometer. The change in height of the meniscus with time is shown in figure 4(4) when the catalyst component concentrations were $1.1 \times 10^{-3}$ moles $litre^{-1}$.

The increase in height observed is similar to that observed in the polymerization of styrene and it is likely that this was associated with the depolymerization, by some mechanism, of polystyrene.

(e) Effect of pre-mixing time of catalyst components on the rate of polymerization

During the course of the polymerization of styrene with $VOCl_3$/ $AlEt_{1.5}Cl_{1.5}$ system it appeared the activity of the catalyst decreased with time. To determine whether the activity of

Figure 4(5) : The effect of pre-mixing time of catalyst components on the rate of polymerization of styrene



the catalyst decayed in the absence of monomer the effect of ageing the catalysts on the rate of polymerization of styrene was studied. The catalysts and monomer concentrations were kept constant and the time for which the catalyst components were allowed to react before addition of the mixture to the monomer was varied.

The monomer and toluene were purified by procedures 2(b)(iv) and 2(a)(i ) respectively, and distilled into the reaction vessel (a) of dilatometer VIII of figure 2( 7 ). So that [styrene] = 0.82 M. The contents of dilatometer was immersed into the constant temperature bath at 25°C for 20 minutes. Solutions of $VOCl_3$ and $AlEt_{1.5}Cl_{1.5}$, so that during polymerization $[VOCl_3] = [AlEt_{1.5}Cl_{1.5}] = 1.2 \times 10^{-5}$ M were then added by syringe into the compartment (d) through the 'Suba Seal' and allowed to react for a known time period. The contents of (a) and (d) were mixed thoroughly and the bulb (b) of dilatometer was filled as quickly as possible, the bulb was separated from the remainder of the reaction mixture by closing the two 'Rota-flo' greaseless taps (c). The dilatometer was positioned in the constant temperature bath, and the change in height was determined using a cathetometer.

Table 4(6) shows the changes in condition for these series of polymerization and the resulting effect upon the rate of polymerization of styrene. This information is also shown graphically in figure 4(5).

Figure 4(6) - The effect of pre-mixing time on the polymerization time curves

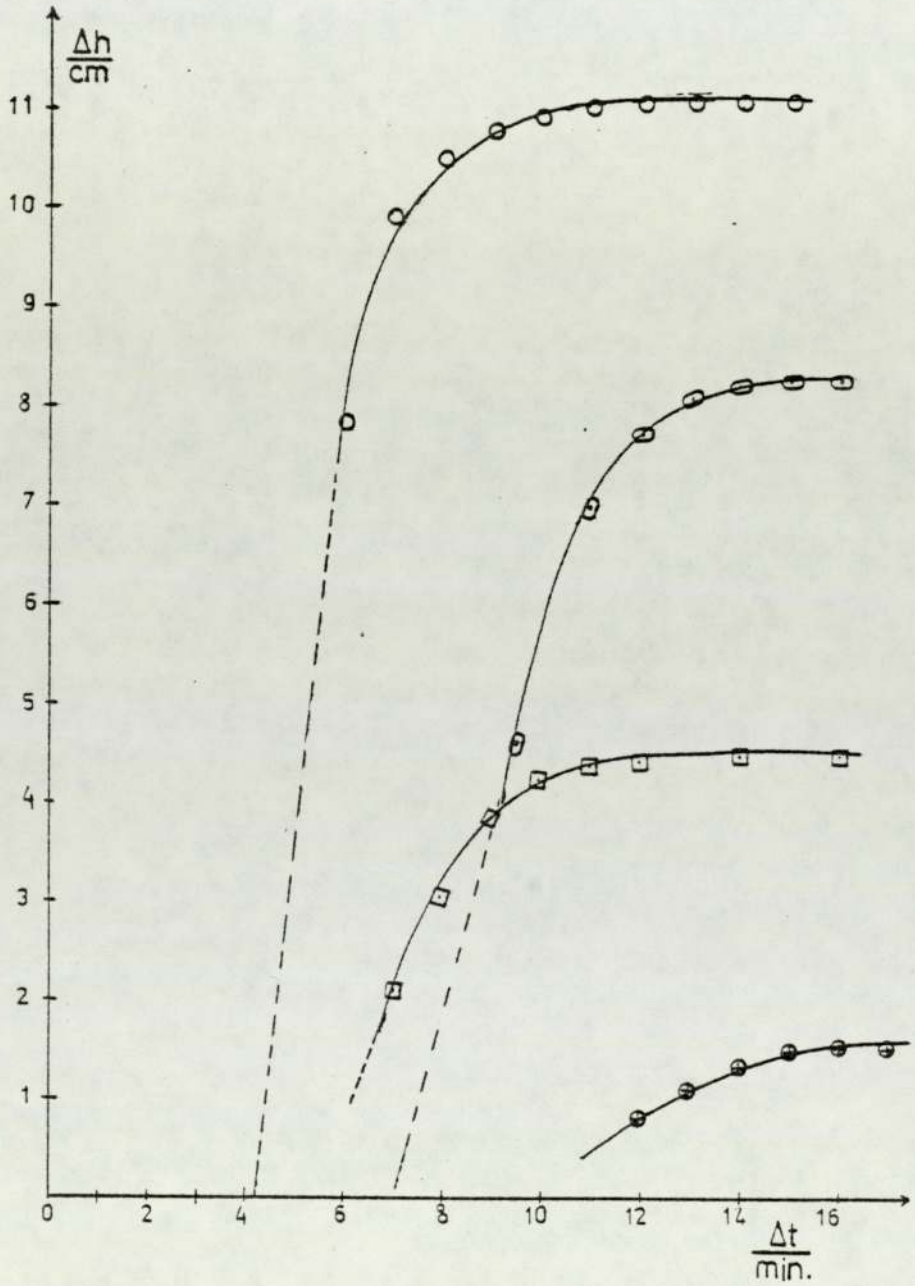


TABLE 4(6)

The effect of catalysts pre-mixing time on the rate of polymerization of styrene

| Pre-mixing time min. | Rates of polymerization x $10^4$ moles $litre^{-1}s^{-1}$ |
|---|---|
| 2 | 28.5 |
| 5 | 6.0 |
| 7 | 9.0 |
| 10 | 1.6 |
| 20 | 0.0 |

$[VOCl_3] = [AlEt_{1.5}Cl_{1.5}] = 1.2 \times 10^{-5}$ moles $litre^{-1}$

[Styrene] = 0.82 moles $litre^{-1}$

Temperature = 25°C

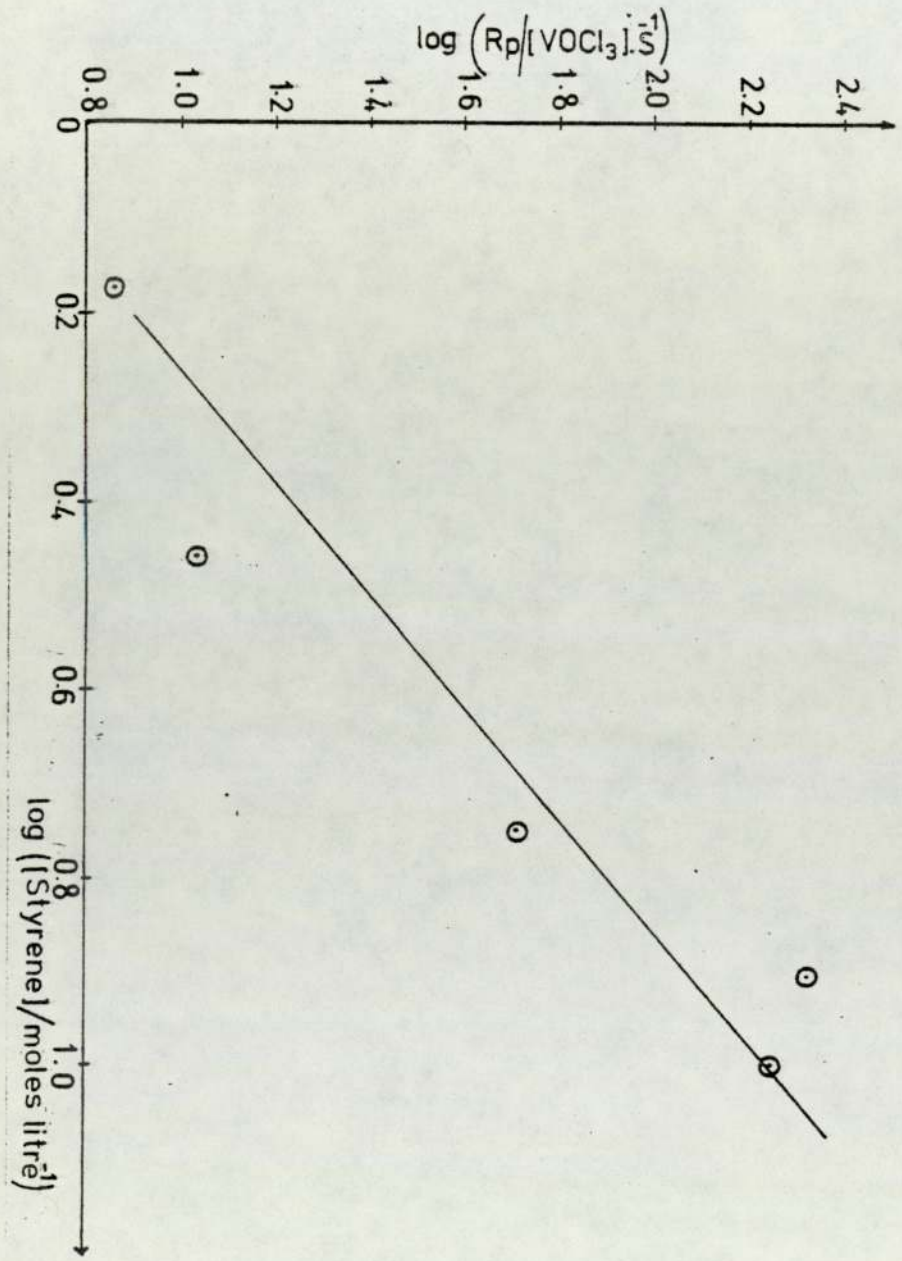
It can be seen from figure 4( 5 ) the activity of catalysts mixture appeared to decrease as the pre-mixing time of $VOCl_3$ with $AlEt_{1.5}Cl_{1.5}$ was increased.

It must be admitted that there was a large error in the measurement of the initial rates of polymerization in this series of experiments, but without doubt the activity of catalyst decayed significantly with increasing pre-mixing time so that after a pre-mixing time of 20 minutes the catalyst had lost all its activity. Inspection of the polymerization conversion-time curves shown in figure 4( 6 ) shows that the activity of the catalyst decayed during the course of the polymerization because the rate of polymerization decreased at a rate faster than the rate of consumption of monomer.

The effect of styrene concentration upon the rate of polymerization

To determine the order of reaction with respect to the concentration of styrene, a series of polymerizations was carried out in which the concentration of styrene was varied from 0.15 M to 1.06 M, and catalyst concentration was kept constant. The catalyst components were allowed to react for 2 minutes before

Figure 4(7) : The effect of styrene concentration upon the rate of polymerization



addition to the monomer solution. A known amount of purified styrene and sufficient toluene to ensure a constant volume of the system, were distilled into the dilatometer VIII. 0.35 ml of $1.1 \times 10^{-3}$ M $VOCl_3$ solution and 0.35 ml of $1.1 \times 10^{-3}$ M $AlEt_{1.5}Cl_{1.5}$ solution were pre-mixed and the polymerization was carried out in the usual manner.

Table 4( 7 ) shows the effect of change of concentration of styrene on the rate of polymerization under the catalyst conditions cited. Figure 4( 7 ) shows a plot of $\log \frac{(Rp)}{([VOCl_3])}$ against $\log [\text{styrene}]$, from which the order of reaction with respect to styrene was determined to be $1.8 \pm 0.9$.

TABLE 4( 7 )

The effect of styrene concentration on the rate of polymerization of styrene

| $[VOCl_3] \times 10^5$ / moles litre$^{-1}$ | [Styrene] / moles litre$^{-1}$ | $Rp \times 10^4$ / moles litre$^{-1}$ s$^{-1}$ | $Rp \times 10^{-1}$ / $VOCl_3$ s$^{-1}$ |
|---|---|---|---|
| 1.3 | 0.15 | 0.94 | 0.72 |
| 1.29 | 0.29 | 1.4 | 1.09 |
| 1.25 | 0.56 | 6.6 | 5.28 |
| 1.21 | 0.82 | 26 | 21.5 |
| 1.17 | 1.06 | 21 | 17.9 |

$[AlEt_{1.5}Cl_{1.5}] = [VOCl_3]$

Temperature = 25°C

The effect of ethyl trichlor acetate upon the rate of polymerization of styrene

A considerable volume of work has appeared in the literature on the use of activators such as ethyl trichlor acetate (ETA) for the copolymerization of ethylene and propylene, usually in conjunction with hydrogen. It has already been shown that such $VOCl_3/AlEt_{1.5}Cl_{1.5}$ catalyst systems also decayed in activity when styrene was used as a monomer, and it was decided that the effect of ETA on the activity of these catalysts for styrene

Figure 4(8) : The absorption spectra of $VOCl_3$ in hexane (A), in toluene (B) and in styrene (C)

polymerization should also be determined.

Purified toluene and styrene were distilled into the reaction vessel (a) of the dilatometer VIII, and the dilatometer was immersed in the constant temperature bath for 20 minutes at 25°C. The solutions of $VOCl_3$ and $AlEt_{1.5}Cl_{1.5}$ were injected into the compartment (d) of the dilatometer and allowed to react for 2 minutes. The solution of ETA was added to the catalyst solution after 2 minutes. The contents of (a) and (d) were mixed thoroughly and the bulb (b) of the dilatometer was filled. The dilatometer was positioned in constant temperature bath and the changes in height in meniscus was determined, using a cathetometer. A series of polymerizations was carried out in which the concentration of ETA was varied from 0.12 - 3.3 x $10^{-5}$ moles litre$^{-1}$ and in each case a complete inhibition of polymerization took place.

Ultraviolet and visible spectra

A spectrophotometric technique was used to follow the absorption changes of the species present during the polymerization of styrene using the catalyst system $VOCl_3/AlEt_{1.5}Cl_{1.5}$.

The apparatus used for this series of experiments is shown in figure 2( 11 ). 16 ml of purified hexane was distilled into the reservoir (B) and 0.2 ml 6.6 x $10^{-2}$ M $VOCl_3$ solution in hexane was injected through the 'Suba Seal' (D) so that $[VOCl_3]$ = 8.1 x $10^{-5}$ M, the contents of (B) were transferred to the cell (A) as quickly as possible, and the cell was closed to (B) by a 'Rota-flo' greaseless tap ( C ). The absorption spectrum was recorded using hexane as reference. The spectrum is shown in figure 4( 8 ) as spectrum (A). The spectrum recorded showed maxima at approximately 250 mμ and 345 mμ. The solution of $VOCl_3$ was lemon yellow in hexane, but because of the presence of some impurity a dark brown precipitate formed. Difficulty was found in removing this impurity.

The same experimental procedure was repeated using toluene as solvent. The spectrum of $VOCl_3$ in toluene is shown in figure

Figure 4(9) : The absorption spectra changes of the $VOCl_3/AlEt_{1.5}Cl_{1.5}$ solution

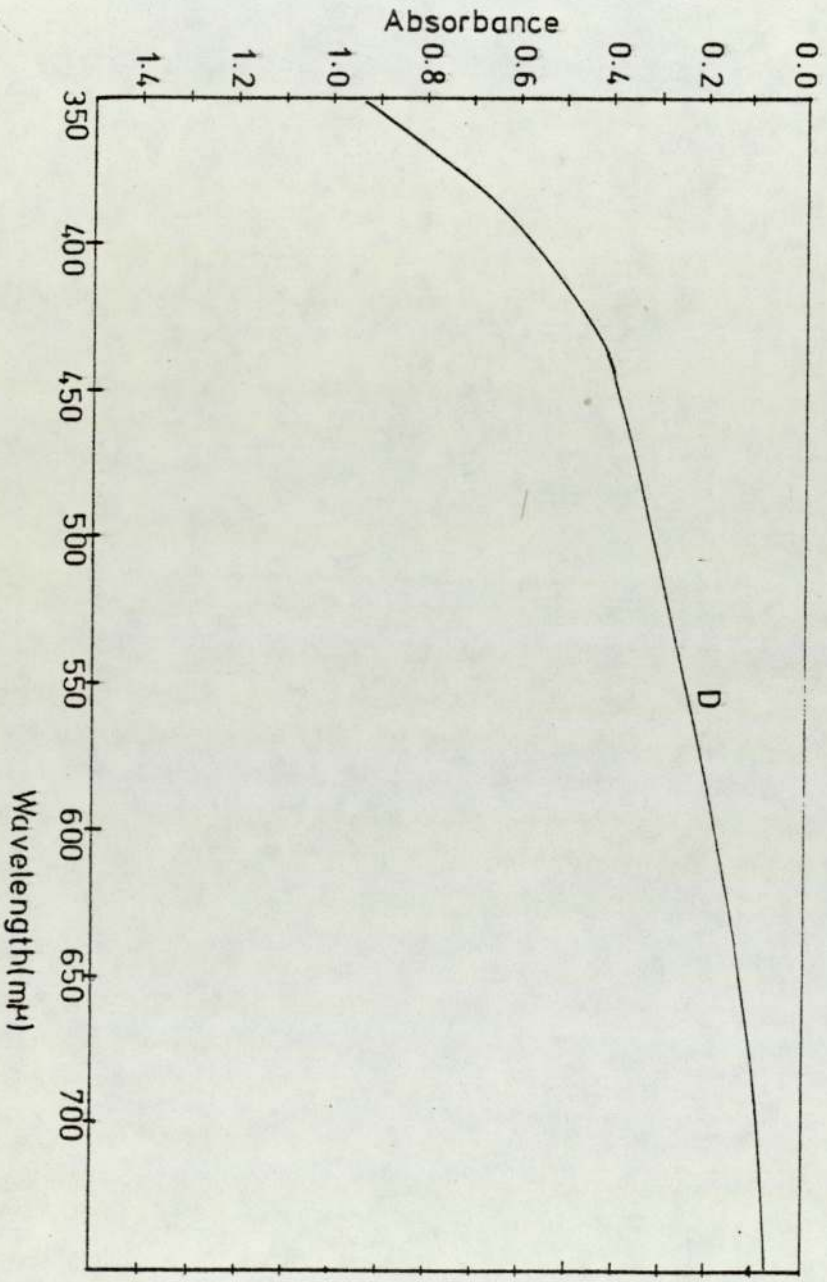


Figure 4(9) : The absorption spectra changes of the $VOCl_3/AlEt_{1.5}Cl_{1.5}$ solution

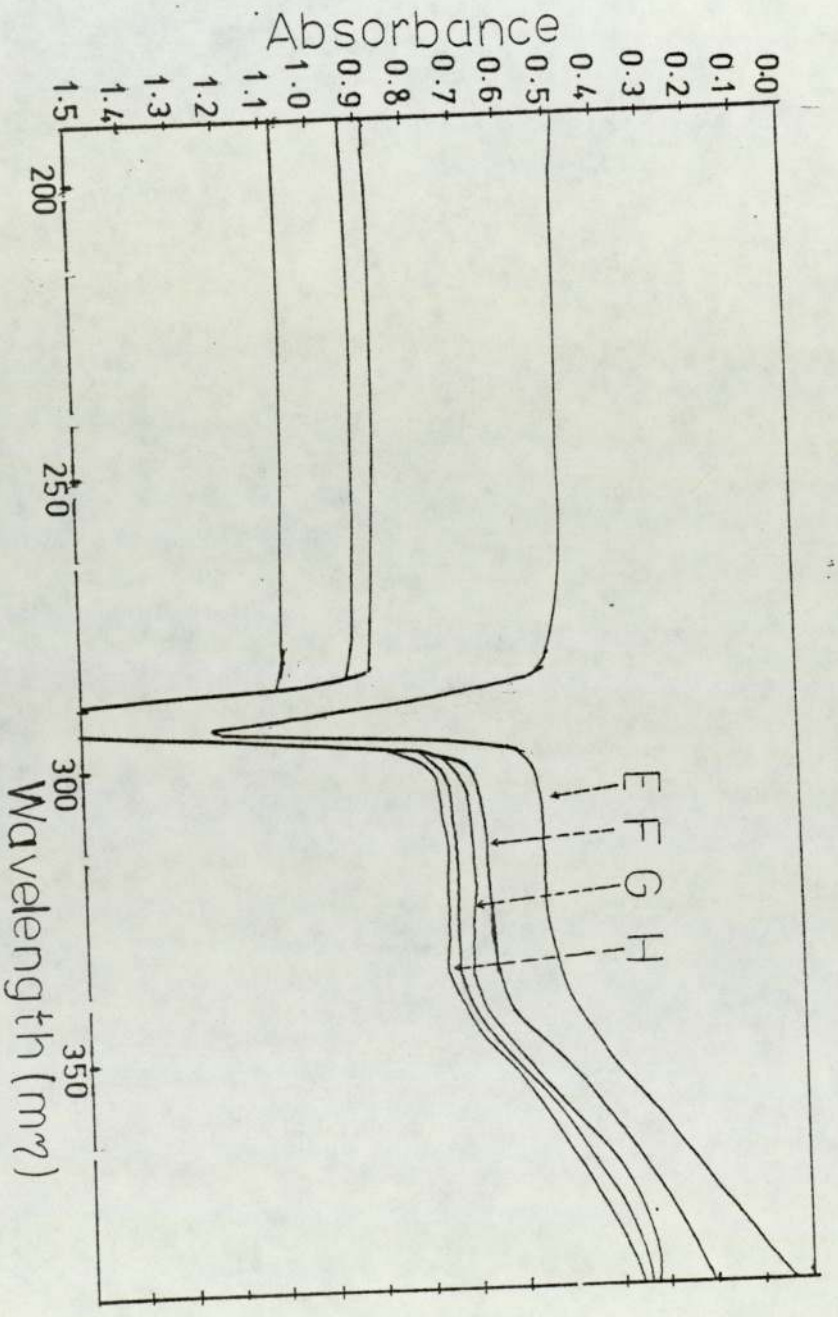
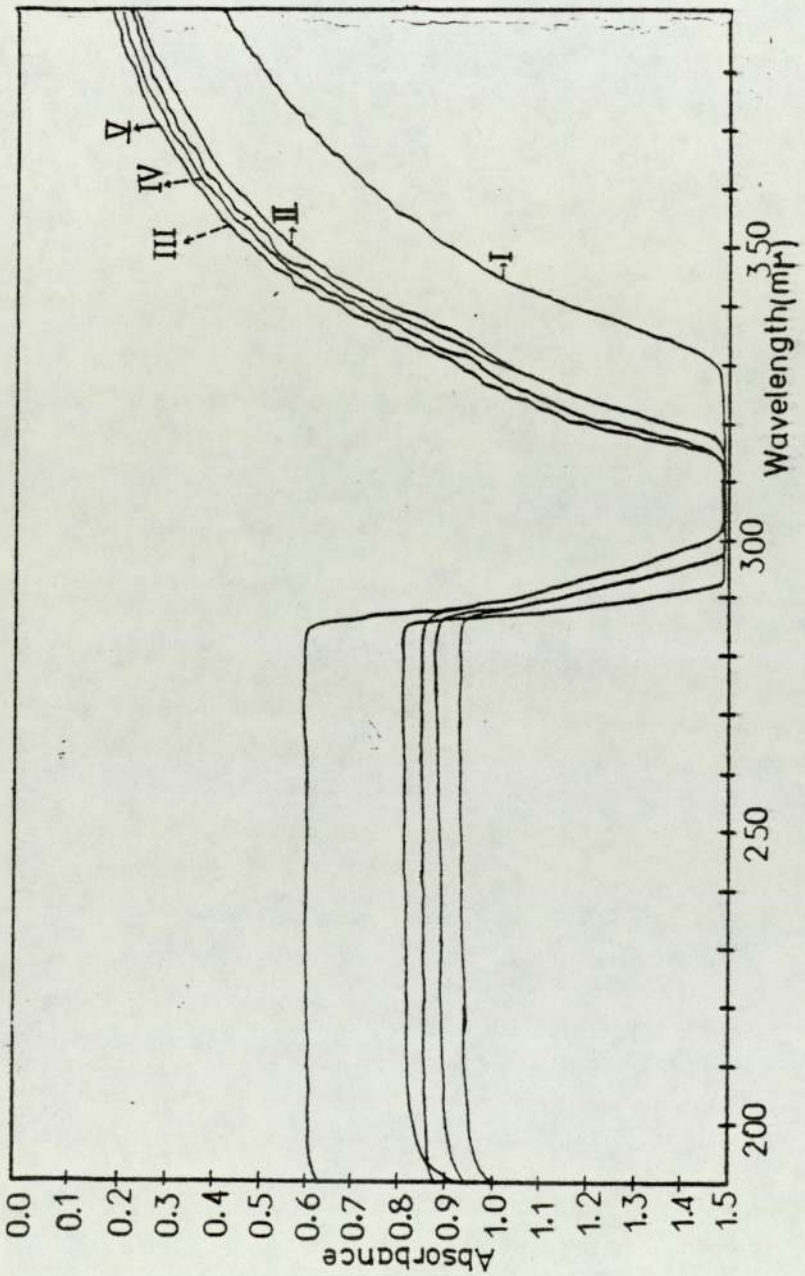


Figure 4(10) : The changes in absorbance associated with the addition of styrene to the solution of $VOCl_3$ and $AlEt_{1.5}Cl_{1.5}$



4( 8 ) as spectrum (B), toluene was used as reference and $[VOCl_3]$ = 3.8 x $10^{-4}$ M. The spectrum recorded showed maxima at approximately 325 mμ and 470 mμ as (B).

The addition of styrene to the solution so that the [styrene] = 0.16 M and $[VOCl_3]$ = 7.4 x $10^{-4}$ M had little effect upon the position of the absorption peak at 470 mμ, immediately after addition of styrene.

It is well known (136) that $VOCl_3$ produces charge-transfer complexes with aromatic solvents. The absorption shown at 470 mμ was due to the formation of a charge-transfer complex in toluene and styrene; the introduction of styrene into a solution of toluene caused little detectable change in the position of the absorbance.

Upon the addition of $AlEt_{1.5}Cl_{1.5}$ to a solution of $VOCl_3$ the absorbance at 470 mμ disappeared. The spectrum of a solution of the reaction product between $VOCl_3$ and $AlEt_{1.5}Cl_{1.5}$ obtained immediately after the reaction is shown as spectrum (D) in figure 4( 9 ), but the absorption spectrum of this solution was time-dependent. Spectra E - H, shown in figure 4( 9 ), were recorded at 5 minute intervals after mixing the reactants. Accordingly it is apparent that the species produced upon reaction of $VOCl_3$ with $AlEt_{1.5}Cl_{1.5}$ is rapidly converted to some other compound.

Figure 4( 10 ) shows the change in absorbance associated with the addition of styrene ( [styrene] = 1.98 M) to a solution of $VOCl_3$ and $AlEt_{1.5}Cl_{1.5}$ in toluene.

Spectrum (I) was recorded immediately after reaction of $VOCl_3$ and $AlEt_{1.5}Cl_{1.5}$ and comparison of this spectrum with those shown in figure 4( 10 ) would show no significant change in position but the absorption peak would appear to be somewhat sharper. Again the absorption spectrum was time-dependent, spectra II - V show the changes in absorption observed at 5 minute intervals.

CHAPTER 5

GENERAL DISCUSSION

It is now well established that catalysts suitable for ethylene-propylene co-polymerizations are obtained by the reaction of alkylaluminium compounds, e.g. $Al(i\text{-}C_4H_9)_3$, $AlEt_2Cl$, $AlEt_{1.5}Cl_{1.5}$, $AlEtCl_2$ with hydrocarbon soluble vanadium compounds such as: $VOCl_3$, $VCl_4$, $VOAc_3$, and the alkylesters of vanadic or chlorovanadic acids. Soluble vanadium-based catalysts have the advantage of producing amorphous copolymers that have good elastomeric properties and a low homopolymer blockiness.

The principal catalyst used industrially is based upon the combination of $VOCl_3/AlEt_{1.5}Cl_{1.5}$ and reports in the literature suggested that the activity of this catalyst decayed rapidly during copolymerization but was restored when ethyl trichloracetate was used as an activator provided that hydrogen was used as a transfer agent in such copolymerizations.

The object of the present work was to undertake a kinetic study of the $VOCl_3/AlEt_{1.5}Cl_{1.5}$ catalyst system in order to elucidate the mechanism of action of ETA. Styrene was selected as a potential monomer to study the catalyst system because as a liquid monomer it would be relatively easy to study the kinetics of the polymerization. The use of a liquid monomer was preferred to a gaseous monomer because:-

(i) the measured rate of polymerization of a gaseous monomer might in fact be a measure of the rate of dissolution of gas or the rate of transfer of dissolved gas to the active site rather than a true rate of polymerization

(ii) although ethylene may be polymerized by the catalyst the product is insoluble in common hydrocarbon solvents and the catalyst site would consequently become encapsulated in

the polymer particle. This process could lead to a decrease in the measured activity of the catalyst

(iii) propylene and other higher $\alpha$ olefins are not in general polymerized to high molecular weight polymer by soluble Ziegler-Natta catalysts

1. Measurement of rate of polymerization

Cunningham has established that $VOCl_3/AlEt_{1.5}Cl_{1.5}$ acted as a catalyst for the polymerization of styrene but because of the extremely exothermic nature of the polymerization under the conditions of his experiments a kinetic study of the system was not attempted. Published work on the copolymerization of ethylene and propylene (110) indicated that a measurable rate of copolymerization was obtained with a concentration of $VOCl_3$ of the order of $10^{-3}$ moles $litre^{-1}$. The initial studies on the bulk polymerization of styrene described in Chapter 3 showed that an extremely fast rate of polymerization was obtained when the concentration of $VOCl_3$ was $9.8 \times 10^{-5}$ moles $litre^{-1}$. The accurate measurement of such extremely fast rates of polymerization presented great difficulties and a considerable amount of work was carried out to establish a suitable experimental technique for the measurement of these rates. A gravimetric technique was used and as shown in Figure 3(1) it was impossible to measure the initial rate of polymerization. A large error was involved in the determination of the % conversion of monomer to polymer.

The technique proved to be most unsatisfactory for the reproducible measurement of the rate of polymerization but an interesting observation was made from these studies.

Although during the first few minutes a substantial amount of monomer was polymerized, after 10 - 20 minutes the overall % conversion began to decrease, suggesting that a depolymerization

process took place. Further experimental evidence gave support to this view which will be discussed later.

The use of a technique involving a thermocouple proved to be most unsatisfactory for the measurement of the rate of polymerization. However a technique that relies on the automatic recording by electrical means of some physical change in the system has many obvious advantages over a manual one. To this end a recording dilatometer was used to study the rate of polymerization of styrene by the method explained in 2(4)(b)(ii).. The results obtained by the use of the recording dilatometer are shown in Figures 3(5) and 3(6).

The significant advantage of this technique was the ability to record immediately the decrease in volume associated with the polymerization. However, although such a technique has many other potential uses, in this case it was felt that reproducible results could not be obtained, principally because it proved extremely difficult to ensure that the mercury used was pure and dry.

However it can be seen from Figure 3(6) that the polymerization of styrene recommenced by further additions of $AlEt_{1.5}Cl_{1.5}$ solution at the times represented by (A, C, E, F) but there was no change associated with the addition of more styrene into the system as represented by addition point (B).

It is possible that the further additions of $AlEt_{1.5}Cl_{1.5}$ to the polymerization resulted in the regeneration of active sites by the reaction of $AlEt_{1.5}Cl_{1.5}$ with the appropriate vanadium species present in the reaction mixture. It is reported in the literature that the efficiency of the vanadium compound in the polymerization of ethylene is between 0.5 - 1%, it is possible that sufficient vanadium species were present in the system studied in this work to produce further active sites on the further addition of $AlEt_{1.5}Cl_{1.5}$. The addition of more styrene did not make any difference to polymerization, so it can be

assumed that the polymerization of styrene was not a living type under these conditions and during the course of polymerization consumption of the catalytically active species took place.

Obviously the measurement of the rate of polymerization under conditions similar to those of the copolymerization of ethylene and propylene proved to be impossible, so that it was decided that a study of the system should be made under much more dilute conditions by dilatometry. Many dilatometer designs were investigated and the most useful was found to be that shown in Figure 2( 7 ) as dilatometer VIII. This enabled rapid filling of the device to be carried out so that the initial rate of polymerization could be estimated reasonably. It also became obvious during this stage of the project that rigorous purification of materials was essential because the catalyst was extremely sensitive to traces of impurities. Only when the monomer was purified by a technique that included a pre-polymerization stage initiated by a less active catalyst, was sufficiently pure monomer obtained. Similar treatment of the solvent was essential; the purification system selected was $VOCl_3/Al(i\text{-}Bu)_3$.

2. Comparison of catalysts for the polymerization of styrene

It appeared in the literature that the nature of the alkylaluminium or alkylaluminium halide used in combination with $VOCl_3$ to copolymerize ethylene and propylene had a marked effect on the activity of the resulting catalyst, because both their alkylating and reducing powers decrease in the order $AlR_3 > AlR_2Cl > AlEt_{1.5}Cl_{1.5} > AlRCl_2$. Problems are known to be involved in the over-reduction of the transition metal and the resulting catalyst stability. It has been claimed that a chlorine bridge is more stable than an alkyl one ( 148 ) so that using $AlEt_{1.5}Cl_{1.5}$ in combination with $VOCl_3$ produced the most

active catalyst for the copolymerization of ethylene and propylene. In order to obtain a relation between ethylene-propylene copolymerization and styrene homopolymerization using $VOCl_3$/$AlR_nCl_{n-1}$ catalyst system, a series of polymerizations of styrene were carried out with the different alkylaluminium compounds.

The experiments showed that the $VOCl_3/AlEt_{1.5}Cl_{1.5}$ system was by far the most active for the polymerization of styrene. For comparison, the polymerization conditions are given in Table 4( 1 ). It was therefore hoped that there was a correlation between the polymerization of styrene and ethylene-propylene copolymerization using soluble vanadium based catalysts.

3. $VOCl_3/AlEt_{1.5}Cl_{1.5}$ as a catalyst for the polymerization of styrene

A series of dilatometric experiments were carried out to establish the effect of the Al:V ratio upon the rate of polymerization of styrene, without pre-mixing the catalyst components, by keeping $[VOCl_3]$ constant and varying the $[AlEt_{1.5}Cl_{1.5}]$. The changes in conditions are given in Table 4( 3 ). The reaction was very rapid and the polymerization became hot above the ratio Al:V = 4:1. In a similar manner the polymerizations of styrene were carried out in toluene except the catalyst components were pre-mixed for 2 minutes prior to the addition of monomer. Above the ratio Al:V = 5:1 the reaction was rapid and hence a sufficiently large range of concentrations of $AlEt_{1.5}Cl_{1.5}$ was not available to determine the order of the effect of Al:V ratio upon the rate of polymerization of styrene. It is generally agreed that the oxidation state for active catalyst is +3 for the vanadium species ( 91 ) and it is also known that the role of alkylaluminium compounds is to reduce vanadium to the desired oxidation state and to alkylate the transition metal, but increasing $[AlEt_{1.5}Cl_{1.5}]$ did not seem to lead to over-reduction.

It would appear however from the results in Chapter 4 that the role of $AlEt_{1.5}Cl_{1.5}$ might well be more complex than simply reduction and alkylation to produce the active site for propagation. The shapes of the polymerization conversion-time curves would indicate that the duration of the initial polymerization period was approximately independent of the initial concentration of $AlEt_{1.5}Cl_{1.5}$, this period referring to that time up to which the rate of polymerization fell to zero. If this was the case it would suggest that the concentration of active sites was constant in each polymerization and that the rate at which these sites were destroyed was unaffected by an increased concentration of $AlEt_{1.5}Cl_{1.5}$.

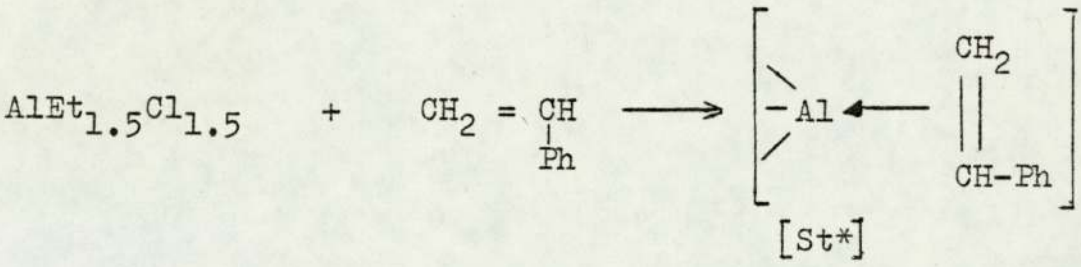
However, if the concentration of active sites was constant throughout, any excess $AlEt_{1.5}Cl_{1.5}$ may have increased the polymerization rate by some other mechanism.

It is generally accepted that polymerization by Ziegler-Natta type catalysts involves two steps:

(i) co-ordination of the olefin to the transition metal atom followed by:

(ii) insertion of the olefin into a transition metal-alkyl bond

It is likely that co-ordination of the monomer to the transition metal atom leads to an activation of the monomer towards attack by the nucleophilic alkyl group in stage (ii). Increasing the concentration of $AlEt_{1.5}Cl_{1.5}$ above that of $VOCl_3$ may have led in this case to activation of the monomer so that direct insertion into a conventional transition metal alkyl bond may have been possible without necessarily requiring the monomer to co-ordinate to the transition metal atom, i.e.



so that under these conditions the rate of polymerization would have been given by -

$$Rp = k_p [St][Pn^*] + k_p [Pn^*][St^*]$$

where Pn* is an active site and St* represents styrene activated by the formation of a complex with excess $AlEt_{1.5}Cl_{1.5}$. Complexes of aromatic compounds with alkylaluminium compounds are well known and such complexes would lead to a reduction of electron density in the double bond and hence an activation of the monomer towards nucleophilic attack by a metal alkyl.

4. Effect of concentration of $VOCl_3$ on rate of polymerization

The experiments described in 4( 5 ) showed that the rate of polymerization decreased as the concentration of $VOCl_3$ increased at constant concentration of $AlEt_{1.5}Cl_{1.5}$. A number of possible explanations can be envisaged to account for this effect. These include -

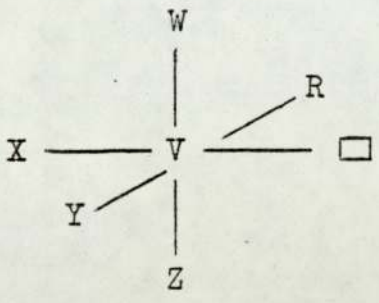
(i) complex formation between the active catalyst and excess $VOCl_3$

(ii) adjustment of the mean oxidation state of V by excess $VOCl_3$ to a less active or inactive state

(iii) removal from the polymerization by excess $VOCl_3$ of any aluminium alkyl that might be required to activate the monomer in the manner described above

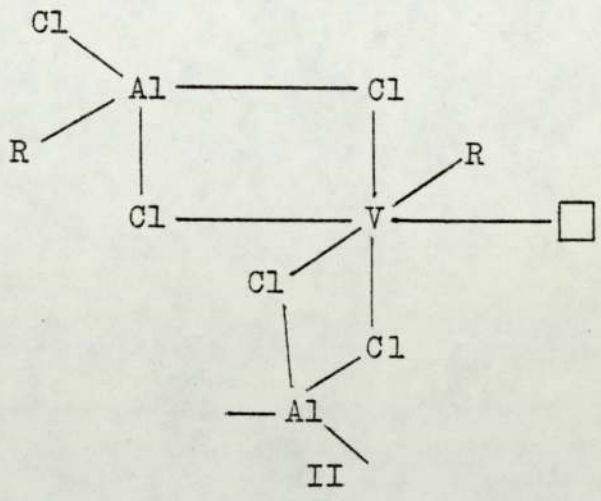
In principle the catalyst species whether mono or bimetallic must possess a transition-metal alkyl bond and a vacant co-

ordination site. The olefin is thought to complex with this vacant site by overlap of the $\pi$-orbitals of the olefin and d-orbitals of the transition metal. The accompanying weakening of the metal-alkyl bond ( 65 ) allows an insertion of the co-ordinated olefin. One could write a structure of a vanadium based catalyst species as -




I

or




II

where -

R = alkyl

W, X, Y, Z = halogen, alkoxide

□ = unoccupied co-ordination site

which is consistent with Olive's general thesis.

The structure (II) would satisfy the requirement of an alkylated trivalent vanadium compound which is prepared from hydro carbon soluble components, while having a bridge-complex with the alkylaluminium. It was proposed ( 148 ) that the bridge bonds involved halogens and these were more stable than alkyl bridge bonds which were known to interchange rapidly ( 149 ).

The decrease in rate of polymerization in the presence of excess $VOCl_3$ can be explained to a certain extent by the presence of the oxygen atom in $VOCl_3$. The unpaired electrons on the oxygen could have co-ordinated with the vacancy of (I) or (II) to form some complex with the active $VOCl_3/AlEt_{1.5}Cl_{1.5}$ complex and thus the number of active sites was reduced. As a result of this one would have expected the rate of polymerization to have decreased.

The existence of different oxidation states of the vanadium atom has been recognized in systems using V($\overline{V}$) or V($\overline{IV}$) derivatives with aluminium alkyls ( 90,91,150,151 ). It is thus very likely that several types of centre differing in both valency and type of catalytic activity were present in polymerizations initiated by $VOCl_3/AlEt_{1.5}Cl_{1.5}$. For example Evans and co-workers ( 101 ) using the $(\pi\text{-}C_5H_5)_2VCl_2$ - $AlEtCl_2$ system to polymerize ethylene detected three types of species and Andreeva and his workers ( 100 ), using $VO(OC_2H_5)_3/AlEt_2Cl$, $AlEtCl_2$, $AlEt_2Br$, $AlEtBr_2$ systems to polymerize ethylene, found that there was a sequential reduction of vanadium at room temperature as follows:

$$V^{+5} \xrightarrow{k_1} V^{+4} \xrightarrow{k_2} V^{+3} \xrightarrow{k_3} V^{+2}$$

If this was so then there was an oxidation/reduction equilibrium between $V^{+5}$ and other oxidation states of vanadium, which in the presence of excess $VOCl_3$ could have been displaced towards the $V^{+5}$ end of this equilibrium resulting in a decrease in the number of vanadium atoms in the active oxidation state. Finally if the proposal described earlier for the mode of action of excess alkyl aluminium is correct then the concentration of such excess alkyl would be expected to be reduced by the presence of excess $VOCl_3$. This reduction in free $AlEt_{1.5}Cl_{1.5}$ would subsequently lead to a reduction in the rate of polymerization.

It is generally considered that a combination of these three factors has to be taken into account to explain the effects of excess $VOCl_3$ on the rate of polymerization of styrene.

5. Effect of concentration of styrene on rate of polymerization

To determine the order of reaction with respect to the concentration of styrene, the concentration of styrene was varied from 0.15M to 1.06M, and catalyst concentration was kept constant. The catalyst components were allowed to react for 2

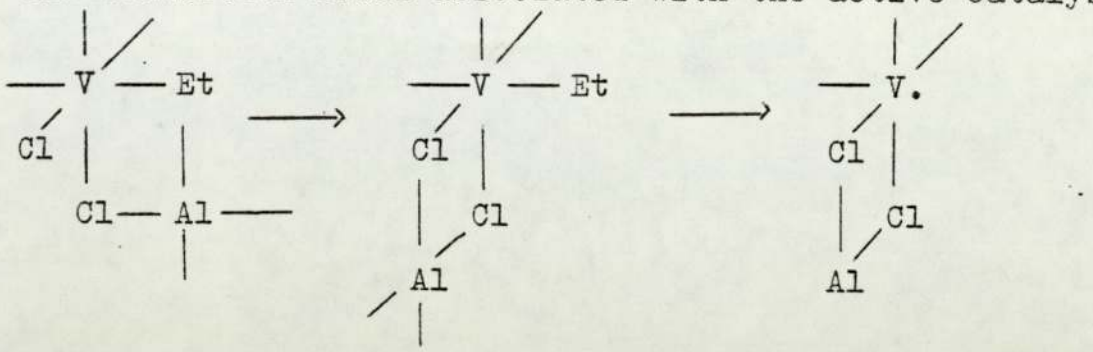
minutes before addition to the monomer solution. Table 4( 7 ) shows the effect of change of concentration of styrene on the rate of polymerization. The order of reaction with respect to styrene concentration was found to be 1.8$\pm$ 0.9. A first order of reaction with respect to styrene was possible allowing for a great degree of error in the measurement of the order, and this dependence would fit with work previously published in the field of Ziegler-Natta catalysis.

6. Decay of catalyst activity

Throughout all experiments a loss of catalyst ($VOCl_3$/AlEtCl) activity occurred after 20 minutes in the presence of monomer. Investigations were undertaken to ascertain whether the same effect occurred in the absence of monomer, by ageing the catalyst components in the reaction vessel prior to their addition to the monomer. The catalyst components were pre-mixed for periods between 2 - 20 minutes and it can be seen from the Figure 4( 5 ) that there was a decrease in the activity of $VOCl_3/AlEt_{1.5}Cl_{1.5}$ catalyst system with ageing time. The rate of polymerization was almost zero after 20 minutes pre-mixing time. It is known from the literature that vanadium based catalysts lose their activity with time. Duck (110) used the $VOCl_3/AlEt_{1.5}Cl_{1.5}$ system to polymerize ethylene and observed that the catalyst activity was lost after approximately 20 minutes, an observation similar to that of Cunningham ( 152 ) who studied the ethylene-propylene non-conjugated diene terpolymerisation. Natta showed that when the catalytic complexes were brought to $0^{o}C$ or room temperature there was a progressive reduction of V(111) to V(11) which was not active for $\alpha$-olefin polymerization.

The decay of activity with time could be explained in terms of the action of the organo-aluminium compound as a Lewis acid. $AlEt_{1.5}Cl_{1.5}$ was a component of the catalytic complex which should have had the octahedral co-ordination of V(111) ( 65 )

which was able to exchange its ligands with the components of the transition metal. When the exchange of the ligand or partial dissociation of the catalytic complex took place the number and the type of co-ordination vacancies also changed. This subsequently resulted in a change of the oxidation state of the transition metal associated with the active catalyst.




It is known from the literature ( 90,92,100,150 ) that the reaction of vanadium based compounds with alkylaluminium compounds was accompanied by the reduction of valence state of vanadium. If one oxidation state was more active then the number of active sites, and consequently the rate of polymerzation, would decrease with time. Such a reaction could be expected to take place in the presence or absence of monomer to account for the decay of rate of polymerization under observed conditions.

In all experiments the reaction stopped after 20 minutes, but after a further 5 - 10 minutes the level of the meniscus started to rise in the capillary. A typical example of this is shown in Figure 4( 3 ). It was thought that either a depolymerization process took place or that a gas was evolved during the course of the reaction to force the meniscus up the capillary. Calculations based upon the concentrations of catalyst components showed that the expected volume of gas evolved would in no way cause such a dramatic rise in the level of the meniscus and indeed in the absence of monomer no such rise was recorded. The rise in meniscus level would have been expected to be 0.4 cm but increases of the order of 1.2 cm were recorded.

The depolymerization experiments of polystyrene in toluene with $VOCl_3/AlEt_{1.5}Cl_{1.5}$ proved that some reaction took place between polystyrene and $VOCl_3/AlEt_{1.5}Cl_{1.5}$ to cause a depolymerization. The typical depolymerization of styrene with time is shown in Figure 4( 4 ).

The rate of depolymerization in these experiments was not as great as that during a typical polymerization reaction but this may have been due to the fact that the rate of generation of sites capable of causing depolymerization may have been greater when such sites were produced from sites that were catalytically active for polymerization. In any event it is difficult to account thermodynamically for this depolymerization process, although attempts to establish by G.L.C. the presence of styrene in solutions of depolymerized polystyrene were not successful.

This period of depolymerization ceased to be replaced by another polymerization period in which a slower rate was observed compared with the initial rate of polymerization. It seems that at least three types of active site were present during the reaction differing in both valency and type of catalytic activity, which is in agreement with the results obtained by Junhanns Obloj and Evans ( 90,101,150 ). In fact the latter author proposed that three different sites were present during the reaction and that their relative concentrations changed during the course of the polymerization of ethylene.

7. Effect of ethyl trichloracetate (ETA) on the rate of polymerization

Higher catalytic activities from vanadium based systems have been accomplished by the use of chlorinated molecules ( 110 ) in the case of ethylene, propylene copolymerizations, during which the catalytic activity was restored several times. The mechanism of activation has been interpreted in terms of chlorination of a V(11) inactive species to an active V(111) species.

However molecules not containing halogen atoms have also been found to be useful catalyst activators ( 110,153 ).

A series of experiments were carried out, in the absence of hydrogen, to study the effect of ETA on the catalyst system $VOCl_3/AlEt_{1.5}Cl_{1.5}$ to polymerize styrene. The catalytic activity was not restored and somehow ETA inhibited the polymerization of styrene under these conditions. It is likely that ETA could have reacted with the active vanadium site to cause deactivation. It is also possible thatcomplexation of ETA with the $AlEt_{1.5}Cl_{1.5}$ occurred. Further work will be required to establish whether hydrogen is a necessary co-activator in such systems.

8. U.V./visible spectroscopy

Ultra violet and visible spectroscopy wereused to follow the absorption changes of the species present during the polymerization of styrene by the catalyst system $VOCl_3/AlEt_{1.5}Cl_{1.5}$. The spectrum recorded for $VOCl_3$ solution in hexane showed $\lambda$ max at approximately 250 mμ and 345 mμ shown in Figure 4( 8 ). In a similar manner the spectrum of $VOCl_3$ was recorded in toluene, and the spectrum recorded showed maxima at approximately 325 mμ and 470 mμ, and the addition of styrene to the solution had little effect upon the position of the absorption peak at 470 mμ, immediately after addition of styrene. Upon addition of $AlEt_{1.5}Cl_{1.5}$ to a solution of $VOCl_3$ in the absence of monomer the absorbance at 470 mμ disappeared. The spectrum is shown as (D) in Figure 4( 9 ). The absorption spectrum of this solution was time-dependent as shown by spectra E - H in Figure 4( 10 ). If the species responsible for the spectra D - H was also responsible for the initiation of polymerization it is possible to account for the decay in the activity of the catalyst as a function of ageing time, in terms of the decay in concentration of initiating species. Similar results were obtained in the presence of styrene.

CHAPTER 6

CONCLUSIONS AND FUTURE WORK

The polymerization of styrene was initiated by vanadium based Ziegler-Natta catalysts, but the study of the kinetics of polymerization of the most active system was somewhat hampered by the extremely high rates of polymerization observed. Eventually a dilatometric technique was developed but the rates of polymerization had to be observed under extremely low concentrations of catalyst. Nevertheless it is felt that provided the rates of polymerization were sufficiently controlled, dilatometry provided an accurate and convenient measure of the rate of polymerization.

A series of alkyl aluminium compounds was used in conjunction with $VOCl_3$ to polymerize styrene, from which it was established that the $VOCl_3/AlEt_{1.5}Cl_{1.5}$ system was the most active for the polymerization and a correlation was assumed between the ethylene-propylene Ziegler-Natta co-polymerization and styrene homopolymerization.

In the case of ethylene co-polymerization with propylene most workers used a catalyst concentration of the order of $10^{-3}$ moles $litre^{-1}$. To study the kinetics of the polymerization of styrene a much more lower catalyst concentration was necessary.

The Al:V molar ratio had a significant effect upon the rate of polymerization of styrene.

At constant $[VOCl_3]$, increasing the ratio of Al:V increased the rate of polymerization of styrene, but above a ratio 5:1 it was difficult to control the reaction.

From an analysis of the polymerization conversion time curves it was proposed that the alkyl aluminium compound had a multifunctional role during the polymerization. It is likely that the aluminium compound reduced the vanadium compound to the desired oxidation state and also provided a means of production of an alkyl vanadium bond in the active species. However, at constant

$[VOCl_3]$ the polymerization activity was lost completely after an approximately constant reaction time, which would suggest that the concentration of active sites was not increased by increasing $[AlEt_{1.5}Cl_{1.5}]$ above a 1:1 molar ratio. Accordingly it is possible that the third role of $AlEt_{1.5}Cl_{1.5}$ was to activate the monomer by way of $\pi$ complex formation.

At constant $[AlEt_{1.5}Cl_{1.5}]$, increasing the V:Al ratio decreased the rate of polymerization of styrene from that observed for the V:Al molar ratio 1:1.

A number of possible explanations have been proposed to account for this effect. Because the oxygen atom in $VOCl_3$ has a lone pair of electrons, in the presence of excess $VOCl_3$ this lone pair of electrons could have formed a complex with the active site, and as a result the number of active sites were reduced. It is also known that different oxidation states were present in the polymerization medium and excess $V^{+5}$ could have shifted the equilibrium towards the $V^{+5}$ state which was not active for the polymerization.

Finally excess $VOCl_3$ could have removed by complex formation any $AlEt_{1.5}Cl_{1.5}$ from the reaction mixture so that there was no free $AlEt_{1.5}Cl_{1.5}$ to activate the styrene monomer.

Analysis of the polymerization conversion time curves showed that there were probably at least 3 types of species present in the polymerization medium, two of which caused polymerization of styrene and one depolymerization of polystyrene. The presence of 3 species is in agreement with the work of Evans ( 101 ) who has studied the polymerization of ethylene using $(C_5H_5)_2 VCl_2$/ $AlEtCl_2$. These workers have also shown that 2 of these species cause polymerization but they report that the third has no activity at all. However it is possible that the structure of the polyethylene was such that depolymerization was not initiated by the third species, which it is thought was responsible for the slow depolymerization of pre-formed polystyrene.

The decay in the activity of the initial complex formed on the mixing of the catalyst components was also shown to take place in the absence of the monomer. The initial rate of polymerization was found to decay rapidly to zero after a pre-mixing time of 20 minutes. However it was not established whether the activity of the catalyst was restored if the pre-mixing time was lengthened considerably to allow the formation of the species of low polymerizing activity. The decrease in activity has been reported by other authors when vanadium based catalysts have been used.

The presence of a number of different species was also used to explain the successive changes that occurred in the UV/visible absorption spectra during the course of polymerization.

Although it has been reported that the $VOCl_3/AlEt_{1.5}Cl_{1.5}$ systems activity can be regenerated several times by the addition of appropriate compounds such as chlorinated activators (ETA) for ethylene, propylene co-polymerization, this was not found to be the case for styrene polymerization.

Future Work

The experiments carried out to determine the effect of ETA upon the catalyst activity showed negative results. The lost activity could not be regenerated, but it might be possible to regenerate the catalyst activity with the activator (ETA) in the presence of hydrogen. Further work should be carried out in this area.

One of the difficulties faced in this project was controlling the rate of polymerization because the $VOCl_3/AlEt_{1.5}Cl_{1.5}$ system was very active for the polymerization of styrene. In order to obtain reproducible results it might be possible to use $AlEtCl_2$ as a co-catalyst in combination with $VOCl_3$. The activity of the $VOCl_3/AlEtCl_2$ system was very much less than that of $VOCl_3/AlEt_{1.5}Cl_{1.5}$. The $AlEtCl_2$ would be expected to reduce $VOCl_3$ much more slowly to the active state than either $AlEt_{1.5}Cl_{1.5}$ or $AlEt_3$.

$AlEtCl_2$ is probably to be prefered to $AlEt_3$ in a study of the kinetics of the polymerization of styrene because the lower activity of $VOCl_3/AlEtCl_2$ may have been due to a reduced rate of production of sites active in the initial stages of the polymerization, whereas it is felt that the low activity of $VOCl_3/AlEt_3$ may have been due to an over-reduction of vanadium to an inactive state. A study of the $VOCl_3/AlEtCl_2$ or other combinations may also lead to an establishment of a general picture for the polymerization of styrene by vanadium based Ziegler catalysts. Further work on such Ziegler catalysts will need to establish the number and structures of the species produced during the polymerization. Spectroscopic, particularly electron spin resonance, and polarographic techniques may be of great assistance in separating and characterising the species present.

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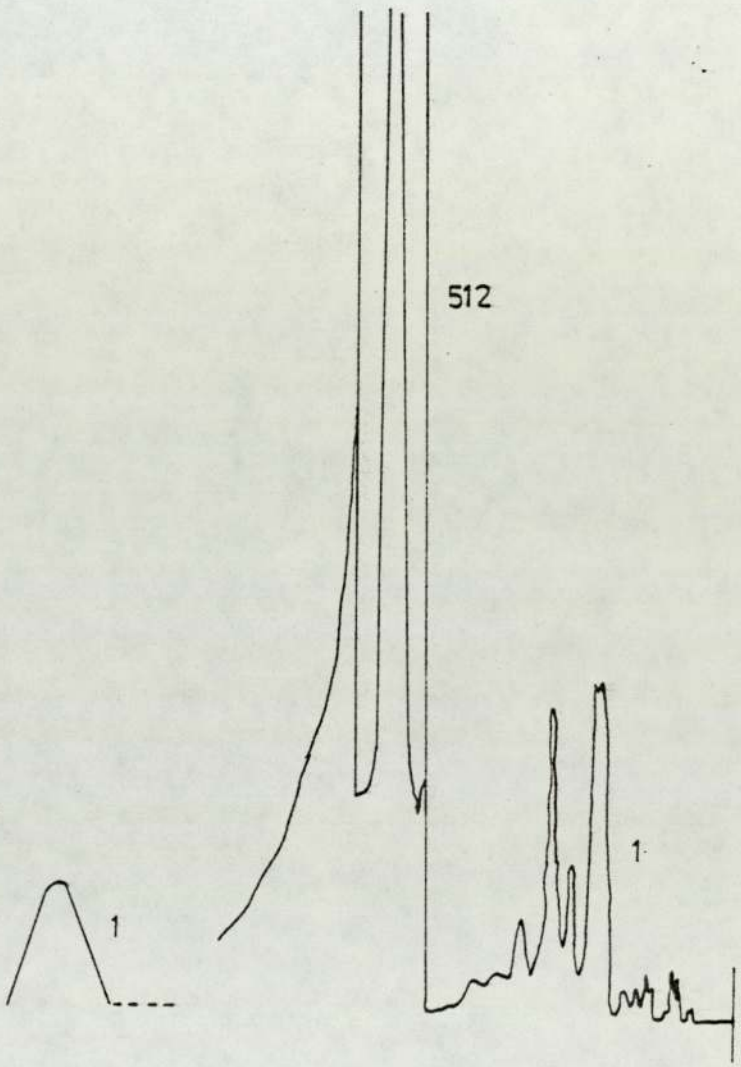
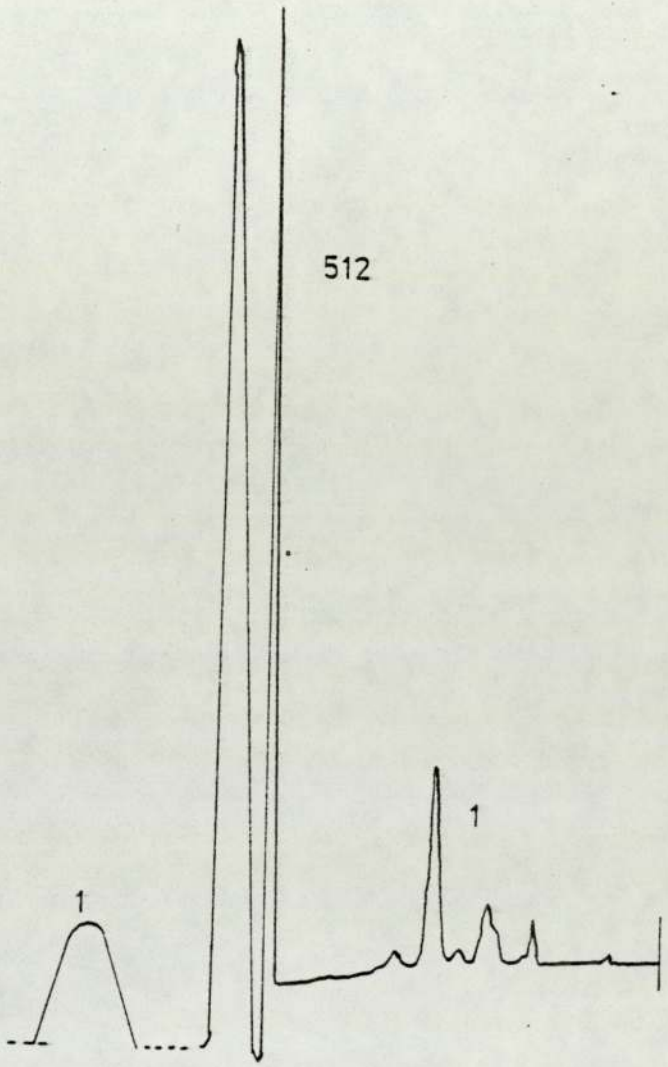
# APPENDIX I

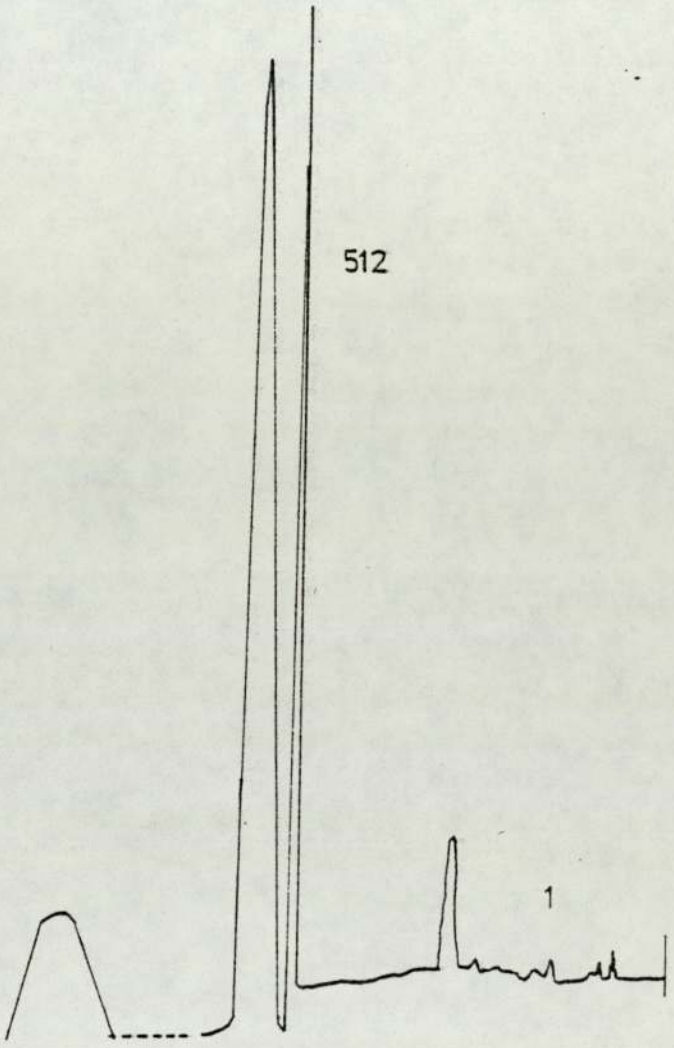
G.L.C. analysis of toluene - 1st fraction



G.L.C. analysis of toluene - 2nd fraction

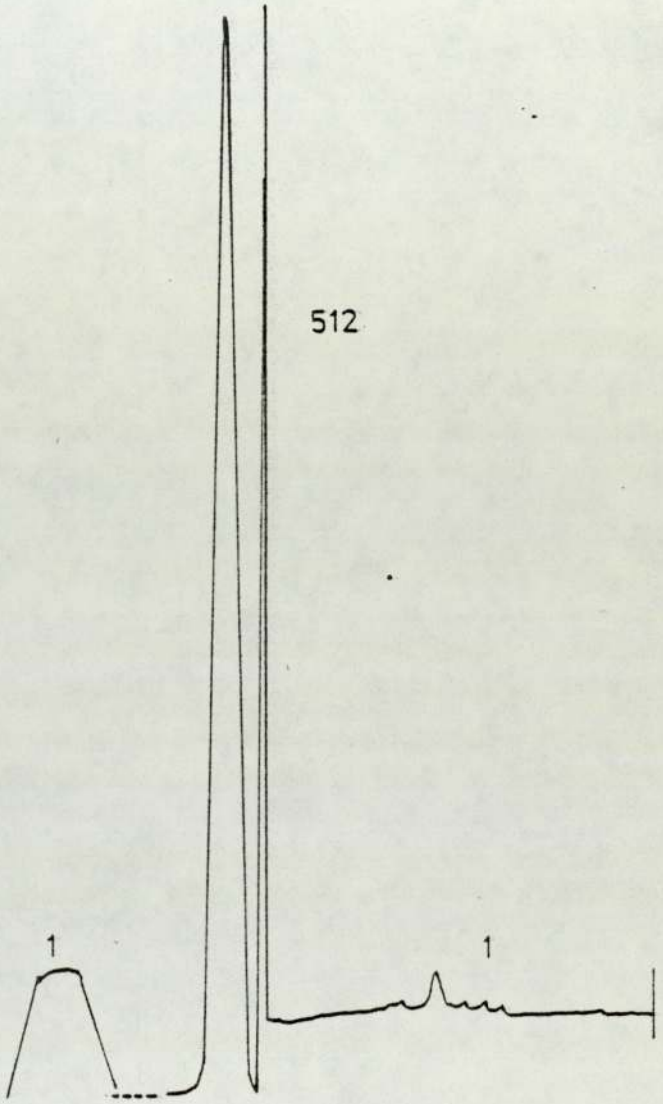


G.L.C. analysis of toluene - 3rd fraction

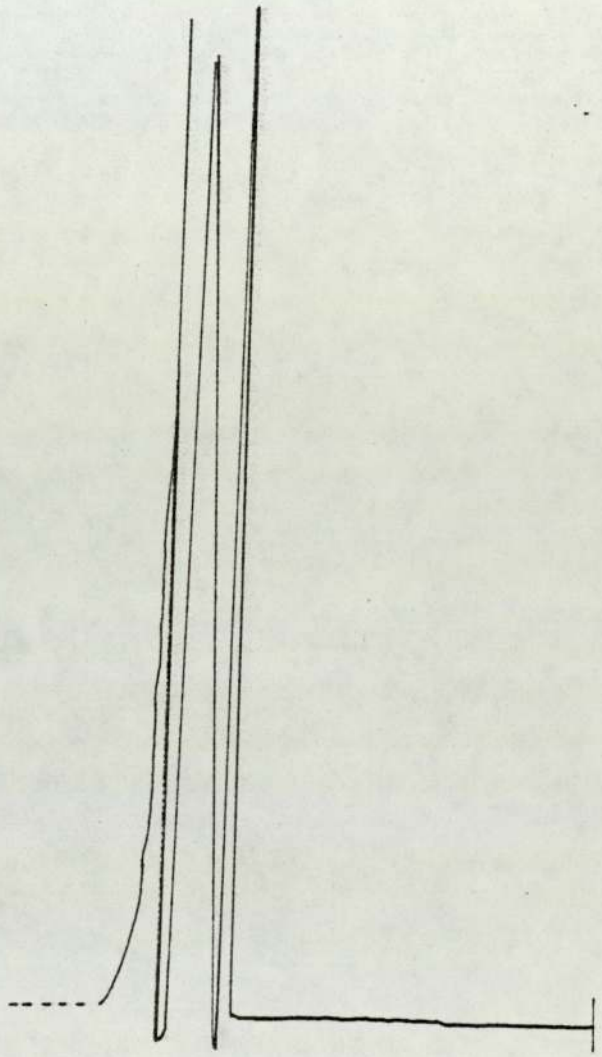



(3)

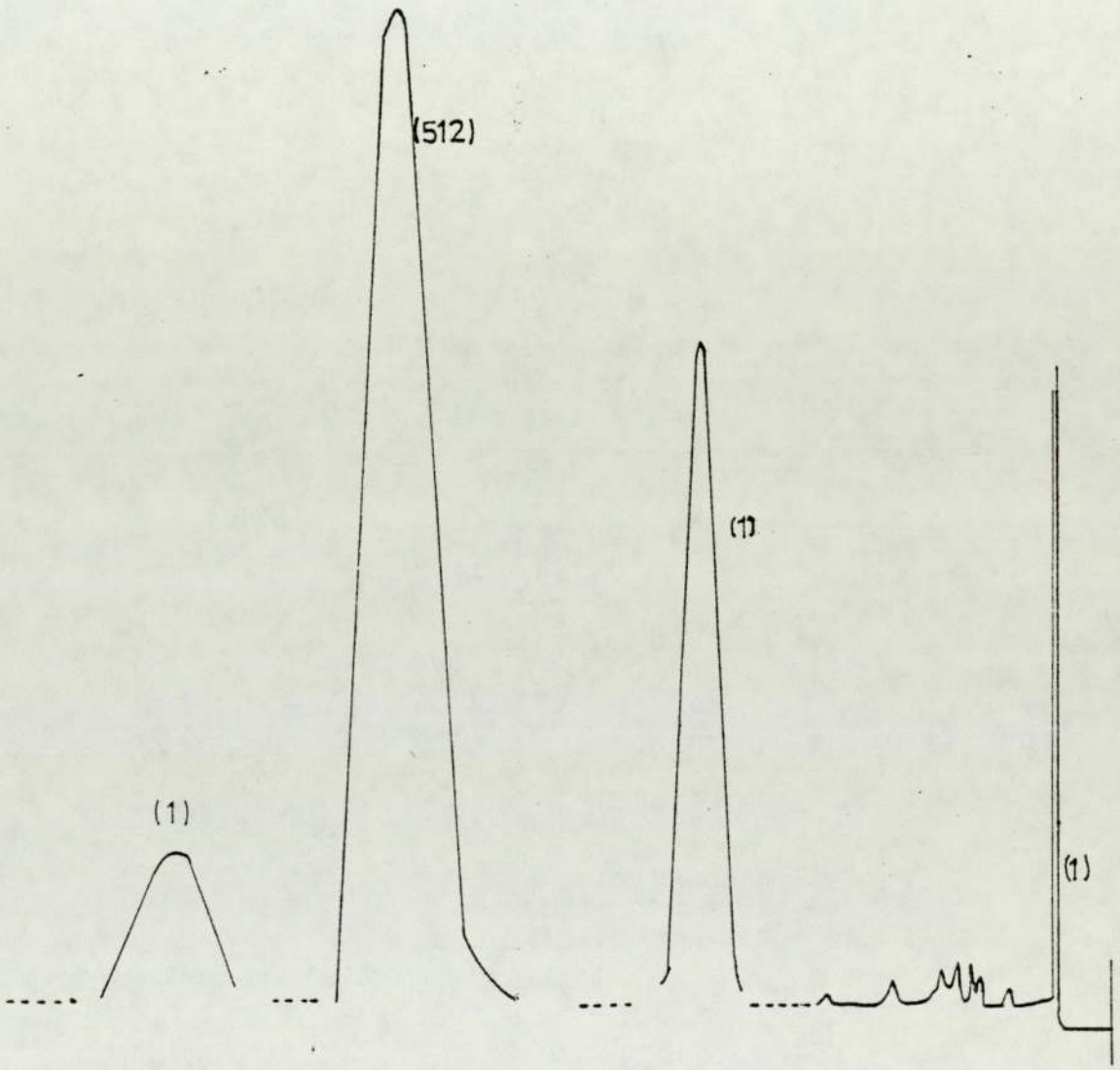
G.L.C. analysis of toluene - 4th fraction



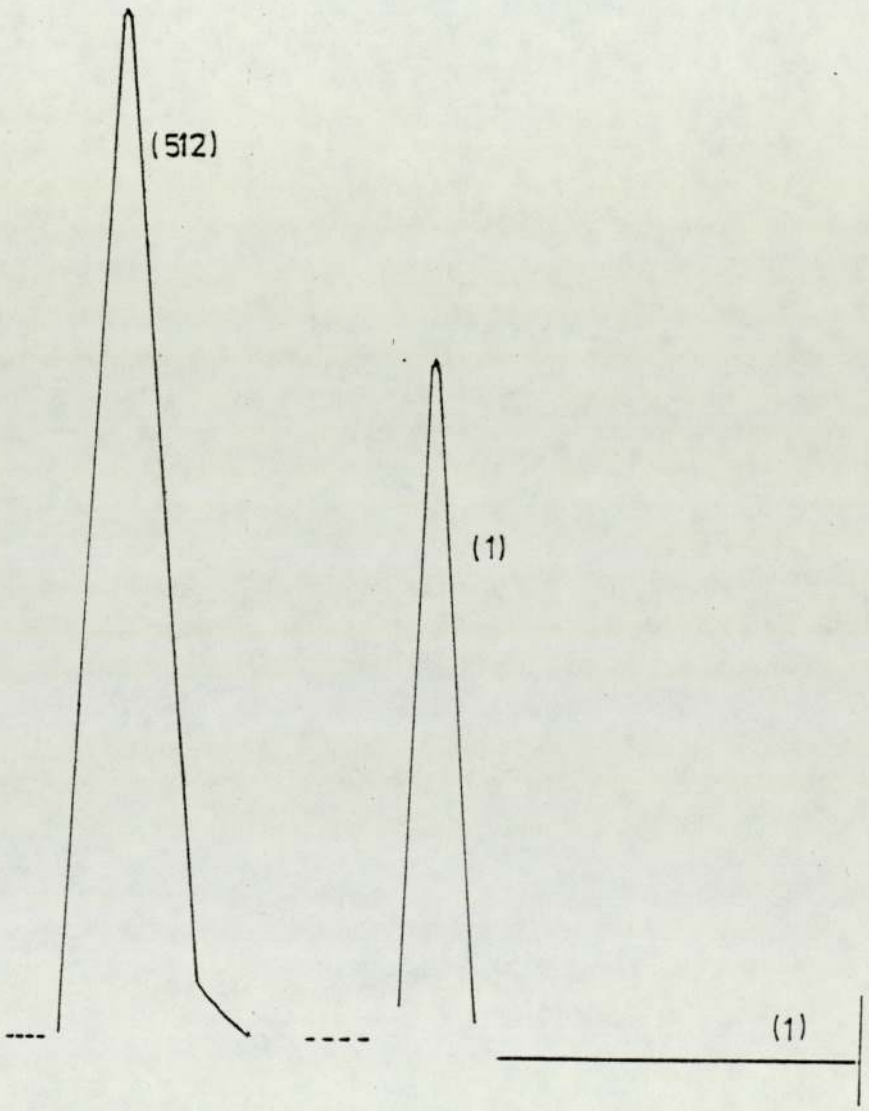
G.L.C. analysis of toluene after purification with $VOCl_3/AliBu_3$



G.L.C. analysis of commercial styrene



G.L.C. analysis of purified styrene

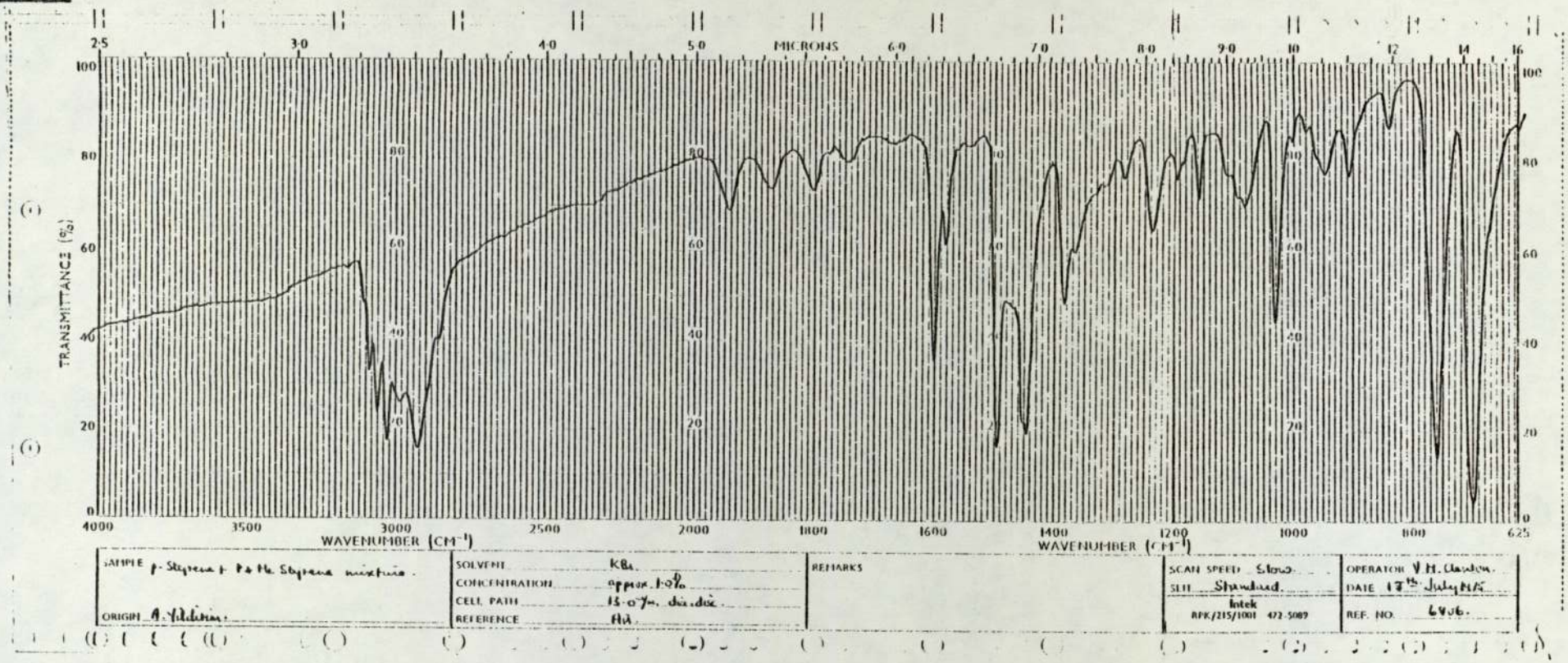


# APPENDIX II

# Infra red spectrum of polystyrene

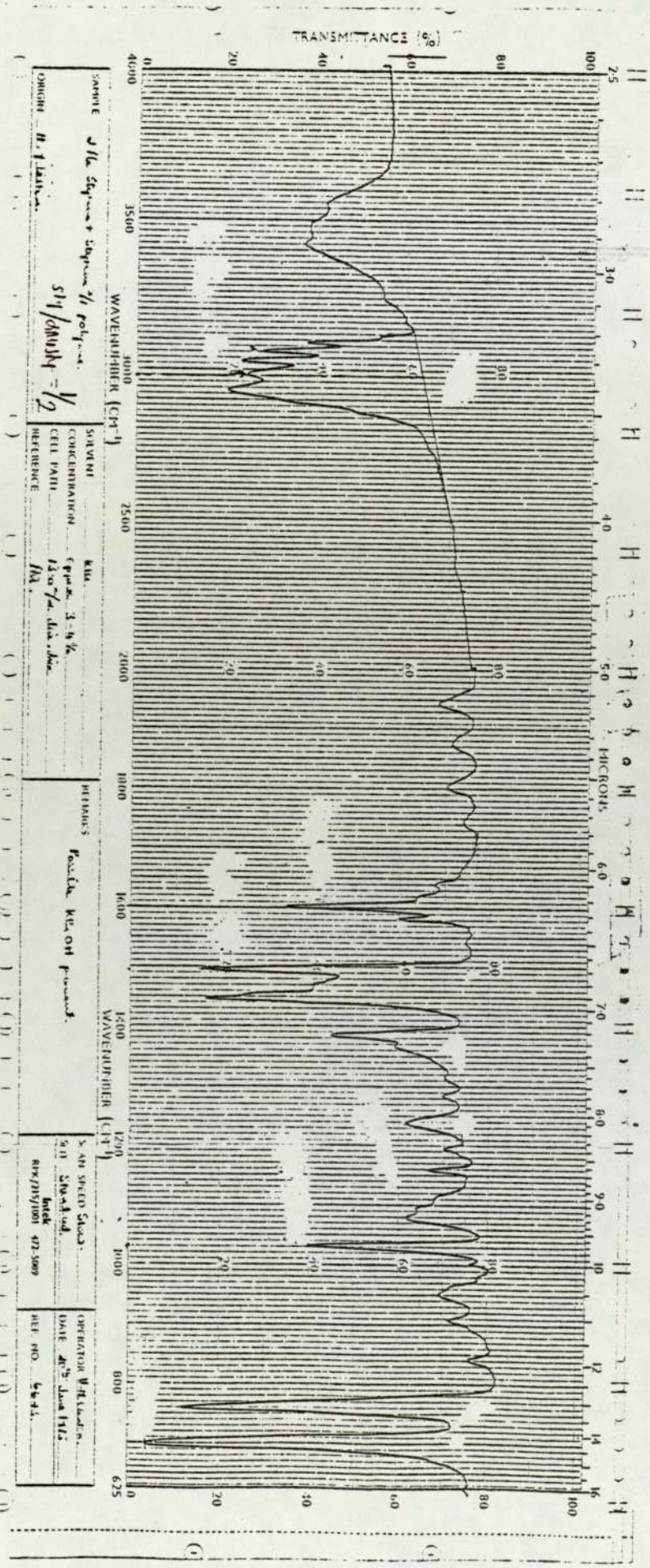
Infra red spectrum of poly-α-methyl styrene

Infra red spectrum of mixture of polystyrene and poly-α-methyl styrene

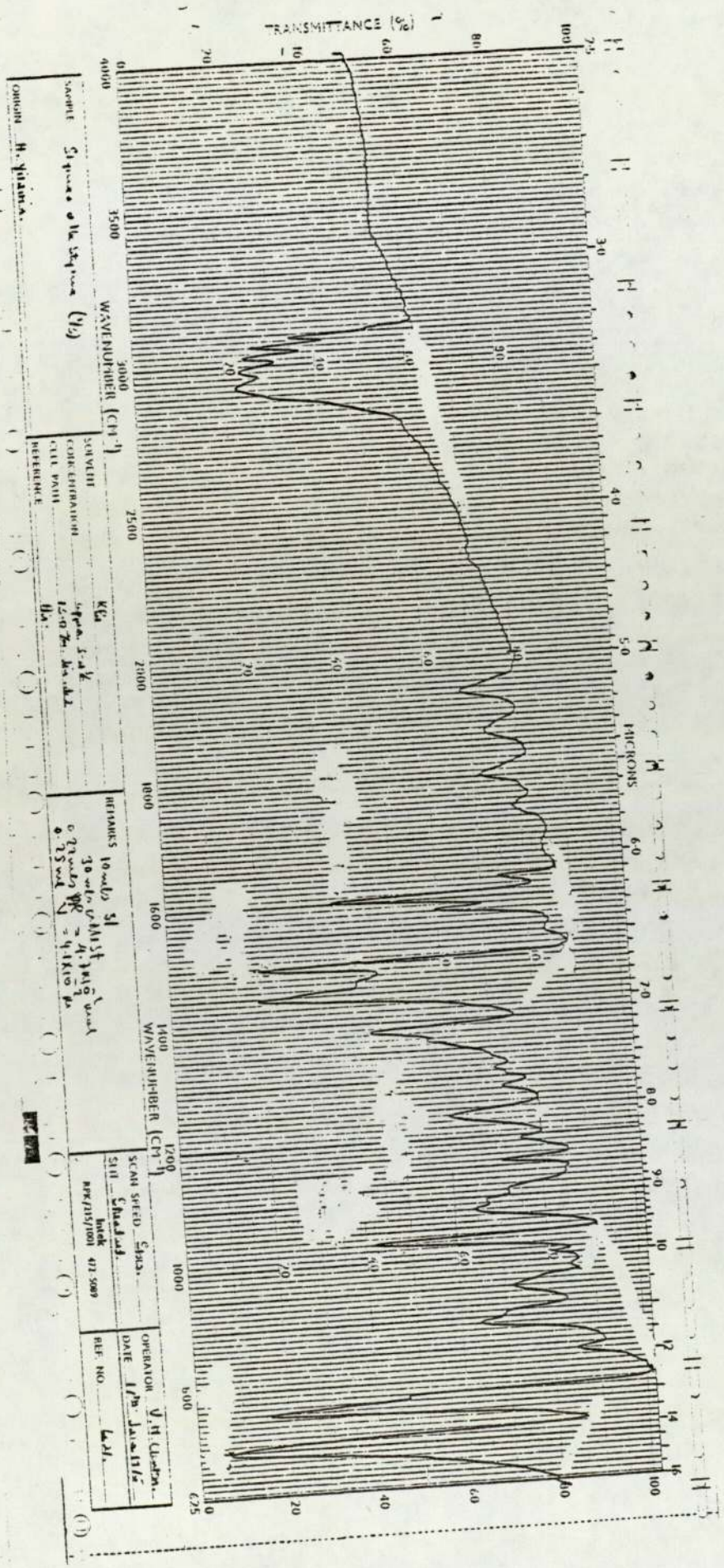


Infra spectrum of styrene, $\alpha$ methyl styrene copolymer (1:1)

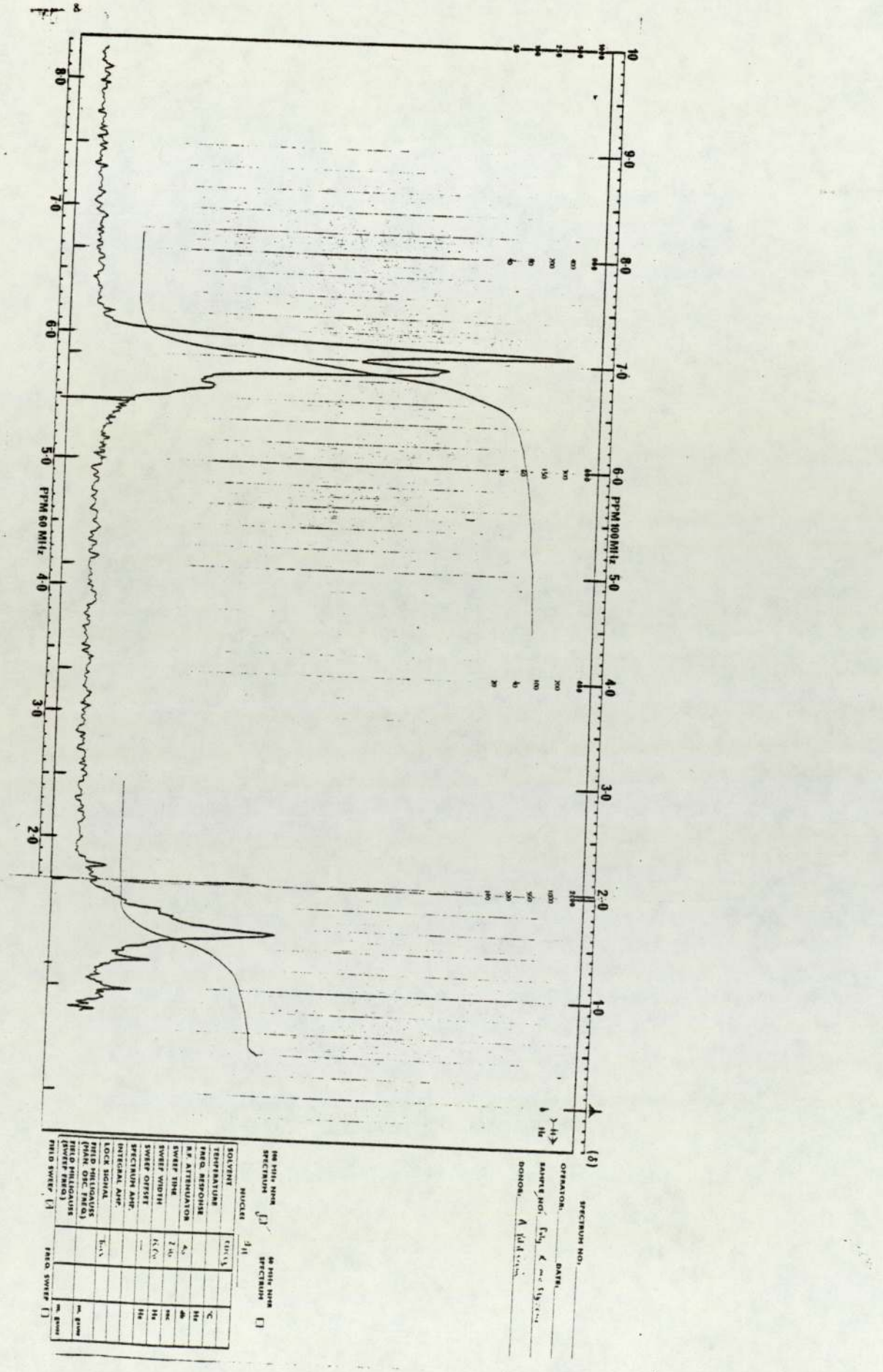
# Infra red spectrum of styrene, $\alpha$ methyl styrene copolymer (1:2)



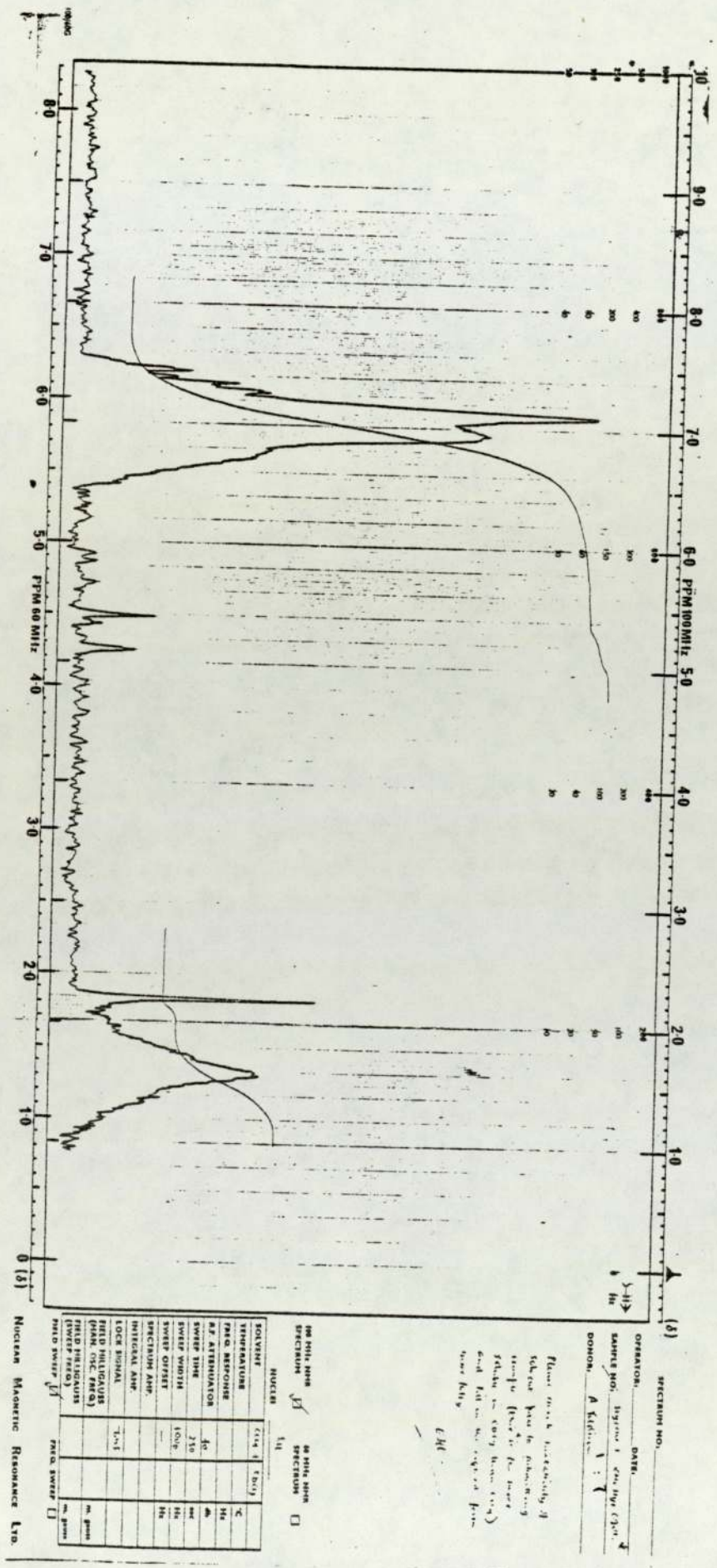
Infra red spectrum of styrene, ∝ methyl styrene copolymer (1:3)



# N.M.R. spectrum of poly∝ methyl styrene



N.M.R. spectrum of styrene, methyl α styrene copolymer (1:2)



# APPENDIX III

Properties of vanadium oxytrichloride ($VOCl_3$)

$VOCl_3$ is a lemon yellow liquid with a boiling point of 127° and a freezing point of -79.5°C. Its specific gravity is 1.83 and dielectric constant at 25°C = 3.7. It is a non-conductor of electricity, completely miscible with hydrocarbons and halides such as toluene, hexane, $CCl_4$, $TiCl_4$, $SnCl_4$. More polar solvents react with $VOCl_3$ to form addition compounds (145) and it also forms charge-transfer complexes with the aromatic hydrocarbons (136). According to the molecular orbital theory a charge-transfer complex is regarded as a resonance hybrid of a donor-acceptor complex (D ..... A), stabilized by van der Waals forces, and an ionized donor-acceptor complex ($D^+$ ..... $A^-$) stabilized by electrostatic forces. The stability of the latter is determined by the ionization potential (Ip) of the donor and the electron affinity (EA) of the acceptor. The stability of the charge-transfer complexes is expected to be large when the sum of Ip and EA is small.

$VOCl_3$ may be synthesised by the action of dry chlorine on the oxides $V_2O_3$ or $V_2O_5$ at 600-800°C, but temperatures of 500-600°C are adequate in the presence of charcoal or sulphur (143). It may also be made by passing hydrogen chloride gas over the pentoxide between 150-400°C. Other chlorinating agents such as thionyl chloride (144) and acetyl chloride can react with the pentoxide to produce $VOCl_3$. The liquid is normally purified by fractional distillation in the presence of sodium.

$VOCl_3$ reacts with air and moisture very rapidly and becomes foggy upon the addition of small quantities of water that result in the formation of the hydrated pentoxide:-

$$VOCl_3 + 3H_2O \rightleftharpoons V_2O_5 + 6HCl$$

If the addition of water is excessive the solution becomes clear yellow. Loss of chlorine results in a change of colour to blue by ageing or heating. Addition complexes of the type $VOCl_3.L$ and $VOCl_3.2L$ have been characterized (145) where L = a variety

of oxygen or nitrogen donor ligands. $VOCl_3$ is reduced by pyridine to produce green V(1V) complex $VOCl_2.3Py$ (145). It also reacts with ligands containing a replaceable hydrogen atom to produce $VO(OMe)_3$, $VOCl_2(OMe)$, $VOCl_2(OEt)$, $VOCl(OEt)_2$, $VOCl_2$ (acac) (145). Electron diffraction data on the vapour indicated that the four bonds to the vanadium are directed almost exactly tetrahedrally (146).