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The Ring-Opening
Polymerisations of
Cyclic Olefins

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To My Father

ACKNOWLEDGEMENT

I wish to thank Dr. A.J. Amass for all his help throughout the last three years. I would also like to thank my mother for typing this thesis and my wife for her support and encouragement during this work.

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SUMMARY

The Ring Opening Polymerisations of Cyclic Olefins

The ring opening polymerisations of cyclic olefins were investigated using a catalyst system of tungsten hexachloride and aluminium tri-isobutyl. The cyclic olefins investigated were cyclooctene and cyclopentene.

The monomers were purified and attempts were made to remove conjugated dienes that were found to be present in the monomers.

The rates of the polymerisation reactions were followed using dilatometric techniques. It was found that the rates of polymerisation were dependent upon:

(i) the order of the addition of the catalyst components. The tungsten compound was added to the monomer before the aluminium compound to give the greatest rate of polymerisation;

(ii) the time that elapsed between the addition of the tungsten compound to the monomer and the addition of the aluminium compound to the mixture;

(iii) the concentrations of the monomer and the catalysts and the molar ratio of the catalyst components.

The kinetics of the polymerisation reaction were considered and a series of reactions were proposed in which 2 tungsten complexes were formed which then combined with the aluminium compound to form 2 active species. A kinetic chain scheme was proposed which correlated the results obtained in this project with the results of previous workers. A mechanism was proposed to account for the deactivation of the polymerisation by the presence of conjugated dienes. The polymerisation mechanism was discussed in terms of the molecular orbital theory of bonding.

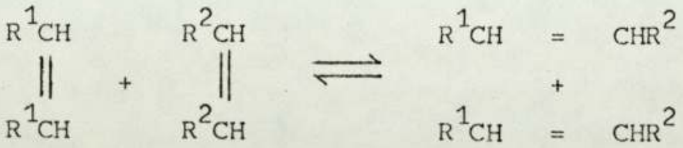
Key words: tungsten hexachloride, cyclo olefins, metathesis, polymerisation, catalysts.

CHAPTER I

Introduction and Literature Survey

I - (1) A General Description of the Olefin Metathesis Reaction

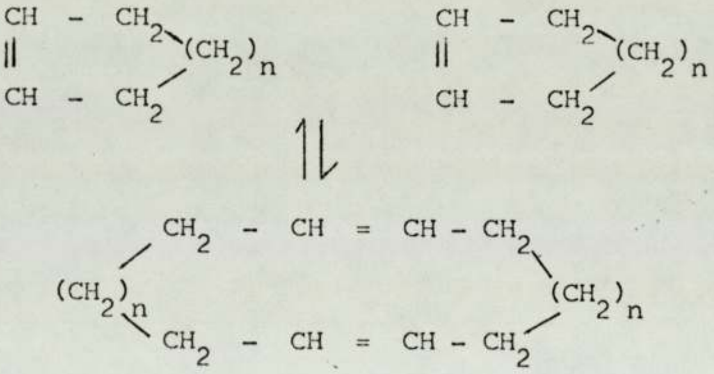
The polymerisation of cyclic olefins may be accomplished by an application of the olefin metathesis or disproportionation reaction. The olefin metathesis reaction is a recently discovered catalytic reaction, which may be described very generally as :-



$$R^1CH{=}CHR^1 + R^2CH{=}CHR^2 \rightleftharpoons R^1CH = CHR^2 + R^1CH = CHR^2$$

(I)

When the olefin used in the reaction (I) is cyclic, a polymerisation reaction may be seen to result, i.e:



(II)

although no reference is made here to the detailed mechanism of this reaction.

Schneider and Frohlich[1] discovered a non-catalytic equivalent of the olefin metathesis reaction in 1931, when the conversion of propylene to ethylene and butene was effected at 725°C. However, it was not until the discovery of homogeneous and heterogeneous catalysts that could promote the reaction at much lower temperatures, whilst minimizing side reactions, that the potential of the metathesis reaction could be realised. The homogeneous catalysts used in the olefin metathesis reaction are based on transition metal compounds, usually group IV or VI metal halides, for example, tungsten hexachloride ($W\,Cl_6$) and an organometallic compound, usually an aluminium alkyl or alkyl chloride, for example aluminium tri-isobutyl ($Al(iBu)_3$) or aluminium di-ethyl chloride ($AlEt_2Cl$). Heterogeneous catalyst systems used in the metathesis reaction involve a transition metal oxide, usually tungsten or molybdenum oxide, supported on an oxide or phosphate carrier, often alumina or silica.

The catalysed olefin metathesis reaction, (I), is an equilibrium reaction which is also athermal because the bonds broken in the reactants and made in the products are identical in nature. Equilibrium can be reached from either side of the reaction and a random distribution of alkylidene groups may thus be obtained in the products.

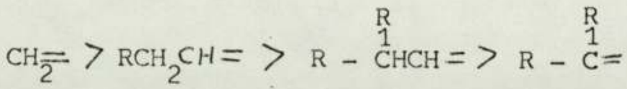
The uncatalysed metathesis reaction is symmetry-forbidden according to the Woodward-Hoffman rules governing organic reactions and this can be considered to be consistent with the high temperature necessary for the thermal reaction to proceed.

I - (2) Scope of the Metathesis Reaction

(i) Acyclic Olefins

Mono-Olefins

The metathesis of simple olefins, particularly those reactions where heterogeneous catalysts have been employed, have been studied extensively[4]. The rate of reaction of olefins in the metathesis reaction has been found to be controlled by steric factors[5] and decreased in the series:-



$$CH_2{=} > RCH_2CH{=} > R-\overset{R}{\overset{|}{C}}HCH{=} > R-\overset{R}{\overset{|}{C}}{=}$$

Substitution of vinylic hydrogens by chlorine has been shown to deactivate the double bond towards metatheses[5].

The potential of the metathesis reaction for redistribution of olefinic bonds in systems containing functional groups is considerable, although little exploited. Isolated examples recorded in the literature are :-

(i) the metathesis of methyl oleate yielded octadec-9-ene and the dimethyl ester of octa-9-enedioic acid, when $[WCl_6]$ - $[Me_4Sn]$ was employed as a catalyst[2].

(ii) the metathesis of acrylonitrile and propylene over a heterogeneous catalyst derived from ammonium tungstate, produced ethylene and 1-cyanopropylene[3].

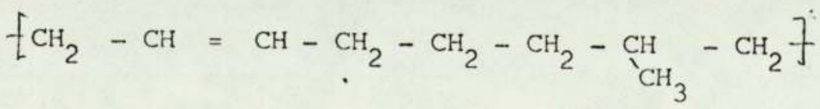
The metathesis reaction has also provided a valuable method for characterizing polymer structures. The monomer sequence distributions in a number of styrene - butadiene copolymers were determined by treating the polymers with a high proportion of but-2-ene in the presence of a suitable catalyst, which caused the polymer to degrade to low molecular weight species. The products of the degradation were analysed by gas chromatography[6]. The method has also been used to determine the extent of double bond migration during free-radical cross-linking of butadiene[7].

Di- and Tri-Olefins

Acyclic unsaturated hydrocarbons containing more than one double bond can undergo the metathesis reaction either inter or intra-molecularly. Deca-1,5,9 - triene was formed on metathesis of hexa-1,5 diene by $\left(Mo(NO_2)(PPh_3)_2Cl_2\right) - \left(Me_3Al\,Cl_3\right)$[8], but octa-1,7-diene reacted intramolecularly on treatment with the same catalyst to give cyclohexene as a major product[8]. Conjugated dienes do not take part in the metathesis reaction.

(ii) Cyclic Olefins

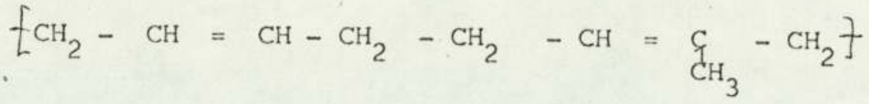
The metathesis reaction is not restricted to acyclic olefins. Polyalkenamers of the general formula $-\left[CH = CH(CHR)_n\right]-$ (n=2,3,5,6 or more, and R = H or alkyl, aryl, etc., without restriction) may be produced by the treatment of the appropriate cyclic mono-olefin with heterogeneous or homogeneous catalysts.(9-12) The polyalkenamers obtained by the metathetic ring opening polymerisation of cyclic olefins range from amorphous elastomers to crystalline materials, depending on the structure of the repeat units and the configuration about the olefinic bonds[13]; the crystallizability of these polymers in general is associated with their stereoregularity. Polymerisations of substituted cyclic olefins of medium size rings by metathesis has been shown to be a simple synthetic route to perfectly alternating copolymers, provided that side-reactions do not occur during the polymerisation process. The ring-opening of 5-methylcyclooctene by $\left[WCl_6\right] - \left[AlEt_2Cl\right]$ yielded a polymer with the repeat unit (III).



$$\left[CH_2 - CH = CH - CH_2 - CH_2 - CH_2 - \underset{CH_3}{CH} - CH_2\right]$$

(III)

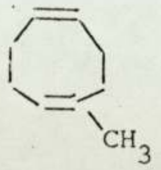
which is equivalent to the perfectly alternating copolymer of butadiene, ethylene and propylene[14]. A polyalkenamer containing the repeat unit (IV)



$$\left[CH_2 - CH = CH - CH_2 - CH_2 - CH = \underset{CH_3}{C} - CH_2 \right]$$

(IV)

equivalent to the alternating copolymer of butadiene and isoprene was obtained when 1 methyl-cycloocta-1,5-diene (V)



(V)

was treated with the olefin metathesis catalyst.

(iii) Metathesis of Cyclic Olefins with Acyclic Olefins

Cross-metathesis of cyclic and acyclic olefins is a convenient method for the synthesis of polyene species. The interaction of ethylene with cyclopentene or cyclooctene over $[Mo(CO)_6] - [Al_2O_3]$ or cobalt molybdate on alumina produced hepta-1,6-diene and deca-1,9-diene respectively[15]. The acyclic triene $C_{14}H_{24}$, the tetraene $C_{19}H_{32}$ and the pentaene $C_{24}H_{40}$, as well as the diene C_9H_{16}, have been isolated from the reaction of cyclopentene with pent-2-ene[16]. The products of the reaction of cyclic olefins with acyclic olefins depends on the molar ratio of cyclic to acyclic olefins.

(iv) Alkynes

The metathesis of alkynes have been observed but the reaction has received far less attention than reactions involving alkenes. Pent-2-yne has been converted to but-2-yne and hex-3-yne with a tungsten oxide-silica catalyst[17]. Terminal alkynes, for example propyne, also participated in metathesis reactions but the selectivity was low[18] because these alkynes preferentially cyclotrimerized to derivatives of benzene under the conditions required for metathesis.

The industrial potential of the olefin metathesis reaction is considerable and obvious. The first commercial plant to utilize the reaction was the Phillips Triolefin process to convert propylene into polymerisation-grade ethylene and high-purity butene and was in operation within three years of the first report of the catalyzed olefin metathesis reaction. Numerous other industrial processes have been patented in which olefin metathesis is an integral step, for instance, a new route to high-octane alkylate[19], and it has also been shown that the yield of ethylene from a naptha cracker can be economically increased through the addition of a propylene metathesis stage.[20]

I - (3) The Ring-Opening Polymerisation of Cyclic Olefins - A Special Case of Olefin Metathesis

The first example of the ring opening of cyclic olefins was reported in 1957 by Eleuterio[9] who polymerised cyclo-pentene using a solid catalyst obtained from molybdenum oxide supported on alumina and reduced by hydrogen. The reduced oxide was activated by lithium aluminium hydride but the yields of polypentenamer obtained were low, even after long reaction times.

Although similar catalyst systems were effective for the olefin metathesis reaction, the relationship between the ring opening polymerisation of cyclic olefins and olefin metathesis was not recognised at that time. The polymerisation reaction was thought to proceed via scission of the carbon-carbon single bond α to the double bond.[21] First to recognise that the ring opening polymerisation of cyclic olefins was a special case of olefin metathesis (at least for the tungsten-based homogeneous catalysts) was Calderon in 1968[22].

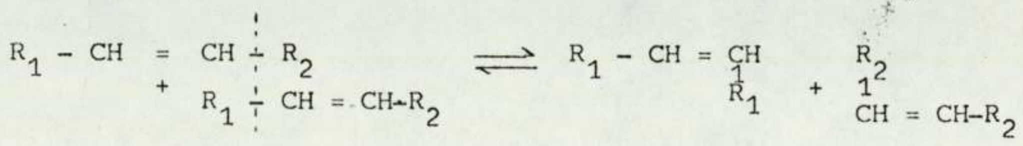
Olefin Metathesis - Main Features

Four general features of the metathesis reaction have been established:-[23]

(i) Transalkylation versus Transalkylidenation

Transalkylation

The transalkylation scheme involved the interchange of alkyl groups via scission of the carbon - carbon single bond α to the double bond. This can be described as :

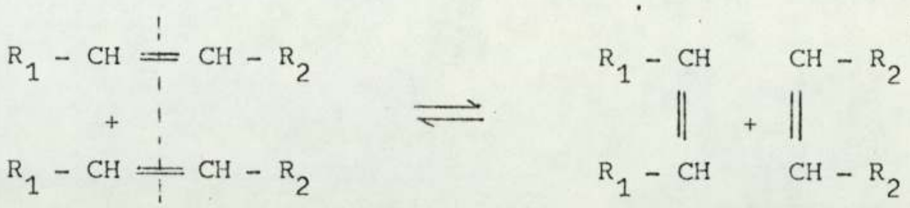


$$R_1-CH=CH \vdots R_2 + R_1 \vdots CH=CH-R_2 \rightleftharpoons R_1-CH=\underset{R_1}{CH} + \overset{R_2}{CH}=CH-R_2$$

(VI)

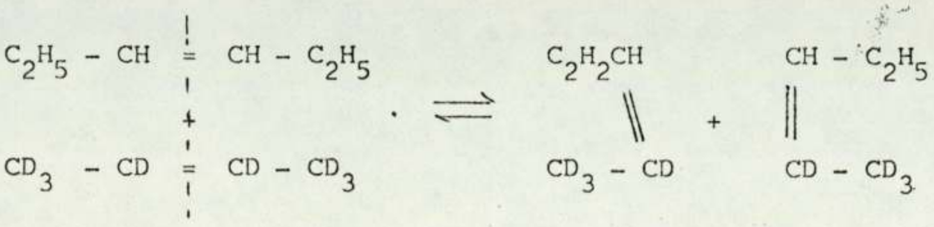
Transalkylidenation

The transalkylidenation involved cleavage of the double bond itself as a means of redistributing alkylidene species. This can be described as:



(VII)

Calderon[23] designed experiments with deuterated olefins to distinguish the relative contributions of transalkylation and transalkylidenation in olefin metathesis. But-2-ene and perdeuterated but-2-ene were reacted together in an initial molar ratio of 76:24 with a suitable metathesis catalyst. The transalkylation scheme would anticipate the formation of but-2-ene-d_2, ($C_4H_6D_2$), but-2-ene-d_3 ($C_4H_5D_3$), but-2-ene-d_5($C_4H_3D_5$) and but-2-ene-d_6($C_4H_2D_6$), as new olefins, while the transalkylidenation scheme would anticipate the formation of only one new olefin, but-2-ene-d_4 ($C_4H_4D_4$). In fact, only one new product was formed in the reaction and this had a molecular weight of 60, corresponding to $C_4H_4D_4$. This result suggested the elimination of the single transalkylation scheme contributing significantly to the olefin metathesis reaction; the observed product was entirely consistent with a transalkylidenation mechanism. These results were confirmed by the metathesis of but-2-ene-d_8 (C_4D_8) and hex-3-ene where the only new product had an observed molecular weight of 74, $C_5H_6D_4$:-



(VIII)

(ii) Random Distribution of Alkylidene Groups

The product mixture obtained from the metathesis of pent-2-ene contained but-2-ene, pent-2-ene and hex-3-ene and at equilibrium it was observed that these were present in the molar ratio of 1:2:1.[24] This product ratio corresponded to a random distribution of ethylidene ($CH_3 - CH =$) and propylidene ($CH_3 - CH_2 - CH =$) moieties. The composition of the but-2-ene mixture from the reaction of C_4H_8 with C_4D_8 also conformed to a random distribution of alkylidene species. To confirm these observations Calderon et al[23] carried out the metathesis of pent-2-ene with dodec-6-ene under conditions wherein the relative amounts of each alkylidene constituent could be varied. Good agreement between predicted and experimental results for the product equilibrium concentrations was obtained in accord with a random redistribution process.

(iii) Thermodynamically Controlled Redistribution Process

The composition of olefinic components at equilibrium was independent of the nature of the reactants, e.g. the metathesis reaction of pent-2-ene led to equimolar amounts of but-2-ene and hex-3-ene and vice versa.

It has also been demonstrated that the equilibrium constants observed in olefin metathesis reactions are independent of the catalyst concentrations.[23]

(iv) Cis-Trans Isomerisation by Transalkylidenation

Calderon et al[23] discovered that olefin metathesis catalysed by $[Et\ Al\ Cl_2/W\ Cl_6/C_2H_5OH]$ afforded mixtures of cis and trans isomers from pure cis or trans starting olefins and that the cis/trans composition of each olefin in the reaction mixture at equilibrium was the thermodynamically favoured composition. The equilibrium cis/trans isomer ratio was found to be independent of the starting material or its configuration. From studies of the steric course of the olefin metathesis reaction of pure trans cis pent-2-ene it was proposed that the formation of cis and trans isomers was provided for by the transalkylidenation step itself and was not the outgrowth of an independent isomerization reaction.

(v)Metathesis of Cyclicolefins

Important implications which bear directly on the nature of the ring-opening polymerisation of cyclicolefins by tungsten based catalysts do precipitate out of the understanding of the main features of the olefin metathesis reaction. These implcations are detailed below:

(1) During the ring-opening polymerisation of cyclicolefins every double bond is eligible to participate in an unlimited number of interchange steps. Hence a given alkylidene moiety which has undergone metathesis and has thus become an integral part of a higher molecular weight species remains eligible for further reaction and may participate in additional metathesis steps with other double bonds, whether they are constituents of another cyclicolefin monomer unit or the same macromolecule.

(2) The polymerisation possesses the basic features of an equilibrium polymerisation.

(3) Macrocyclic species resulting from intermolecular ring enlargement of two smaller rings or from intramolecular metathesis of two double bonds in the same macromolecule, are present in the polymerisation mixture at equilibrium:

(4) The composition of macrocyclic species depends on the frequency of occurrence of double bonds along the polymer chain.

(5) In the absence of all side reactions the metathesis of cyclicolefins yields only macrocyclic species.

(6) An interaction between a macrocyclic species and an acyclic compound leads to scission of the macrocyclic resulting in an open chain polymer.

Scott and Calderon et al[22] in their polymerisation studies of cyclo-octene and 1,5 cyclooctadiene initiated by the [Et Al Cl_2/W Cl_6/EtOH] catalyst system showed that items 1 - 6 were inherent properties of the polymerisation reaction and thus confirmed that the ring-opening polymerisation of cyclic olefins was a special case of the olefin metathesis reaction.

I - (4) The Nature of the Catalyst Components for Olefin Metathesis and Ring-Opening Polymerisation of Cyclic-Olefins

(i) Metals active for Olefin Metathesis and Ring Opening Reactions

Table I-(1) Transition Metals Proposed as Catalyst Components for Olefin Metathesis and Ring Opening Polymerisation

Metathesis Reactions	Transition Metals as Catalyst Components							
		IV	V	VI	VII	VIII		
Olefin Metathesis		Ti	V	Cr				Ni
		Zr	Nb	Mo		Ru	Rh	Pd
	La		Ta	W	Re	Os	Ir	
Ring Opening Polymerisation of low Ring Strain Cycloolefins		Ti	V					Ni
		Zr	Nb	Mo		Ru		
			Ta	W	Re		Ir	
Ring Opening Polymerisation of High Ring Strain Cycloolefins		Ti	V	Cr				Ni
		Zr		Mo		Ru	Rh	Pd
				W		Os	Ir	

Metathesis catalysts promote the ring-opening polymerisations of cyclic olefins and the metathesis of acyclic olefins and although it would appear that both types of reaction are governed by the same mechanism they differ in many chemical, kinetic and thermodynamic aspects which results in different catalyst efficiencies, operating conditions and applicabilities.

In general, group VI metals produce the most effective metathesis catalysts with tungsten the most effective.

Table I distinguishes between cyclic olefins having low or high ring strains. Highly strained cyclic olefins are those which contain at least one four-membered ring or an endocyclic five-membered unsaturated ring. In such olefins the release of ring strain is the driving force for the ring-opening and they are readily polymerised in the presence of nearly all metathetically active catalysts. Cyclic olefins with low ring strain (at least five-membered rings) are readily polymerised only by tungsten, molybdenum, tantalum and rhenium catalysts.

There are two main classes of metathesis catalysts, homogeneous and heterogeneous. Homogeneous catalyst systems consist of two main components: a transition metal compound and a Lewis acid cocatalyst. The transition metal compound is usually a halide, oxyhalide, organo salt or olefin complex of tungsten, molybdenum, tantalum or rhenium and the cocatalyst may be an organometallic compound of group I - IV metals or an electron deficient metal halide. More sophisticated homogeneous catalysts may also contain an activator and/or a molecular-weight regulator. All catalyst components are usually soluble in the monomer-solvent system or become soluble after reaction with the monomer or one of the other catalyst components. These homogeneous catalysts are primarily important in the ring-opening polymerisations of cycloolefins because of their high activity and versatility.

Heterogeneous catalyst systems generally consist of transition metal oxides or carbonyls, usually tungsten, molybdenum or rhenium, supported on oxide or phosphate carriers. Preferred supports are alumina, silica and silica-alumina. These catalysts exhibit appreciable metathesis activity only at relatively high temperatures, 100 - 400°C, and hence they are not very convenient for ring-opening polymerisations and are usually applied only to acyclic olefin metathesis.

(2) Development of Homogeneous Catalyst Systems

(a) Two-Component Tungsten and Molybdenum Catalysts

The homogeneous two-component tungsten or molybdenum plus organometallic compound catalyst systems were discovered by Natta, Dall'Asta and Mazzanti[10] in 1963 and this made possible the first practical polypentenamer synthesis. The catalyst systems contained a tungsten or molybdenum salt, usually the highly soluble hexa- or penta-chloride and an organometallic compound, preferably trialkyl aluminium or dialkyl aluminium chloride.

The most effective W:Al molar ratio lay between 1:0·5 and 1:8 depending on the particular components and on the microstructure of the desired polymer.

Cyclopentene was polymerised to polypentenamer with yields of 30 - 40% after reaction times of 1 hour at room temperature with the tungsten halide and aluminium alkyl catalyst systems.

The use of two-component catalyst systems of the same type was successively extended by Calderon and coworkers[14] to the ring opening polymerisation of some non-conjugated cyclopolyenes, e.g. 1,5 cyclooctadiene, 1,5,9 cyclododecatriene and also the polymerisation of substituted eight-membered rings, e.g. 3-methyl and 3-phenyl cyclo-octene[14]. For such rings the catalytic activity was shown to increase with increasing chlorine content of the cocatalyst in the series $EtAlCl_2 > Et_2AlCl > Et_3Al$.

(b) Three Component Tungsten and Molybdenum Catalysts

The two component catalyst systems developed by Natta et al were not completely satisfactory for a commercial production of polyalkenamers. The most significant disadvantage was the poor reproducibility of results, due probably to the partial insolubility of the reaction products and the instability of catalyst components. These factors combined to give considerable catalyst consumption and limited polymer conversion.

These difficulties were overcome in 1965 by Dall' Asta and Carella[25] upon the introduction of a three component catalyst system. These catalysts were prepared from tungsten or molybdenum halides or oxyhalides, an oxygen-containing activator and an organometallic or hydride cocatalyst. The oxygen-containing activators were: peroxides, hydroperoxides, molecular oxygen, alcohols, phenols and water. Two important features were disclosed with these activators:

(i) activation was generally a maximum if the amounts of activator were nearly equimolar with respect to the transition metal;

(ii) the activators had to be reacted with the transition metal prior to the addition of the organometallic compound.

The temperature range of the activity of these catalysts was approximately the same as for the two component catalysts.

Calderon and Scott[23] used a similar three-component catalyst system for the polymerisation of 1,5 cyclo octadiene and Ofstead[26] used a three-component catalyst system comprised of tungsten tetra carbonyl, O_2 and ethyl aluminium dichloride for ring opening polymerisations. Farbenfabri ken Bayer[27] used cyclopentene hydroperoxide to activate $WCl_6/Al(iBu)_3$ for the polymerisation of cyclopentene with high conversion to trans polypentenamer.

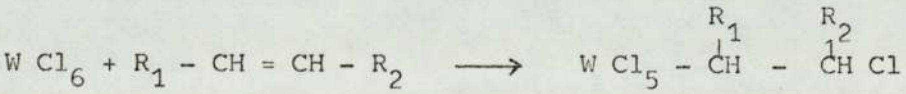
The three-component tungsten and molybdenum catalysts are the most efficient and economically viable systems described so far for the ring-opening polymerisations of cyclic olefins. They readily polymerise any cyclic olefin, except cyclohexene, to polyalkenamers. They show good reproducibility of results, increased solubility of the catalyst in the reaction medium, high polymerisation rate and conversion, low catalyst consumption and reduced side reactions of the Friedel-Crafts type. A high polymerisation rate was maintained at monomer-transition metal molar ratios of 20,000:1 and higher.

I - (5) Reactions of the Catalyst Components used for Olefin Metathesis Reactions and Metathetic Ring-Opening Polymerisation of Cyclic Olefins

(i) Transition Metal Compound

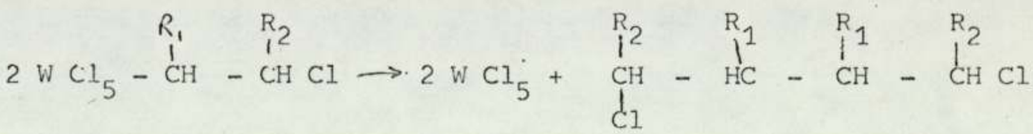
Tungsten has been shown to be the most active transition metal for the catalysis of the olefin metathesis reaction and there is a significant amount of evidence to suggest that the active oxidation state of the tungsten component in the metathesis catalyst is W^{IV}. Wang and Menapace[28] postulated that the active species contained a tetravalent tungsten atom because a $W\,Cl_6$/Bu Li catalyst system exhibited maximum activity for the metathesis of pent-2-ene at a Li/W ratio of 2:1. Pampus, Lehnert and Maerteus[29] showed that the $W\,Cl_6$/ $Sn\,Et_4$ catalyst showed a maximum activity towards the polymerisation of cyclopentene when the molar ratio of Sn:W was also 2:1.

The authors proposed that the organometallic components were acting as reducing agents in these two catalyst systems but the reaction between olefins and $W\,Cl_6$ is itself a standard method for the production of reduced tungsten halides[30] according to the following mechanism:



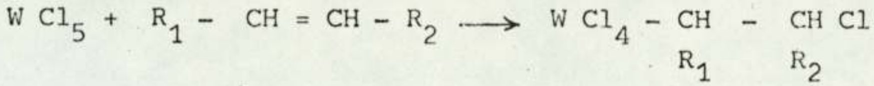
$$W\,Cl_6 + R_1 - CH = CH - R_2 \longrightarrow W\,Cl_5 - \overset{R_1}{\overset{|}{CH}} - \overset{R_2}{\overset{|}{CH}}\,Cl$$

(IX)



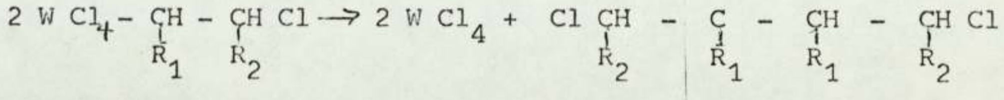
$$2\,W\,Cl_5 - \overset{R_1}{\overset{|}{CH}} - \overset{R_2}{\overset{|}{CH}}\,Cl \longrightarrow 2\,W\,Cl_5^{\cdot} + \underset{Cl}{\underset{|}{\overset{R_2}{\overset{|}{CH}}}} - \overset{R_1}{\overset{|}{HC}} - \overset{R_1}{\overset{|}{CH}} - \overset{R_2}{\overset{|}{CH}}\,Cl$$

(X)



$$W\,Cl_5 + R_1 - CH = CH - R_2 \longrightarrow W\,Cl_4 - \underset{R_1}{CH} - \underset{R_2}{CH}\,Cl$$

(XI)



$$2\,W\,Cl_4 - \underset{R_1}{CH} - \underset{R_2}{CH}\,Cl \longrightarrow 2\,W\,Cl_4 + Cl\,\underset{R_2}{CH} - \underset{R_1}{C} - \underset{R_1}{CH} - \underset{R_2}{CH}\,Cl$$

(XII)

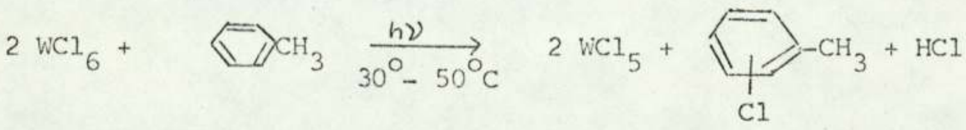
During the polymerisation of cyclopentene by $W\,Cl_6/Al\,(iBu)_2\,OiBu$ the changes in oxidation state of tungsten have been determined by ceric sulphate titration[31]. The results of this determination are shown in table I - (ii).

Table I - (ii) Changes in the Mean Oxidation States of Tungsten during the Reactions involved in the Polymerisation of Cyclopentene

Reaction Condition	Mean Oxidation State
1. WCl_6 Solution	6.0
2. WCl_6 + CP after 1 minute	5.1
3. WCl_6 + CP after 20 minutes	4.3
4. (3)+ $Al(iBu)_2Oi\,Bu$	4.3
5. (4) after 2 hours	4.4

The information suggested that tungsten was present in a mixture of oxidation states during the polymerisation of cyclopentene because non integral values of the oxidation state were obtained. This oxidation state data would also tend to suggest that the organometallic compound in the catalyst system was not functioning as a reducing agent but rather as a Lewis acid.

Pampus and coworkers[32] showed that halides of highly valent tungsten and molybdenum were also strong chlorinating agents for aromatic solvents under the influence of light according to -



Hence this could be another source of the reduced tunsten halide, $W\,Cl_5$, in a polymerisation or metathesis system.

It was thought that tungsten IV may be the active site for the metathesis reaction as there would be two vacant co-ordination sites at which the olefin molecules could co-ordinate to produce one of the possible transition states cited in the literature.

(ii) Oxygen containing compound

The catalyst system containing as a component an oxygenated activator showed quite different stability, decomposition temperatures and activities compared with the simple two catalyst component systems, which suggested significant differences in chemical structure of these three component systems

A possible interaction between the oxygen containing compound and the tungsten compound could have been the known oxygen abstraction capacity of tungsten. Tungsten hexachloride has been shown to react with alcohol[32] to form mono and dialkoxy tunsten halides as shown in XIII and XIV -

$$W\,Cl_6 + HOCH_2CH_2Cl \xrightarrow{-\,H\,Cl} Cl_5WOCH_2CH_2Cl$$

(XIII)

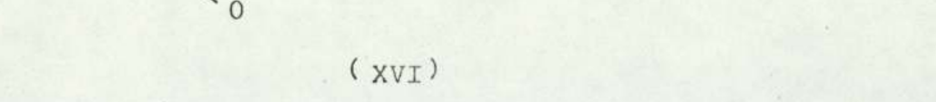
$$Cl_5WOCH_2CH_2Cl + HOCH_2CH_2Cl \xrightarrow{-\,H\,Cl} Cl_4W(OCH_2CH_2Cl)_2.$$

(XIV)

The characteristic red colours of the catalyst solutions, where alcohols were involved, were attributed to the presence of these alkoxy tungsten halides. The dialkoxy tungsten halides were shown to be more stable than the mono alkoxy halides and also yielded more active catalysts. Mono alkoxy tungsten halides were shown to decompose easily to tungsten oxytetrachloride:

$$Cl_5\,WOR \longrightarrow \underset{(XV)}{WO\,Cl_4} + R\,Cl$$

According to Pampus and coworkers[32] dialkoxy tungsten halides may also be formed in the reaction of tungsten hexachloride with epoxides, such as epichlorohydrin:



$$W\,Cl_6 + 2\,CH_2 - CH - CH_2Cl \longrightarrow W\,Cl_4 - (O - CH(CH_2Cl)_2)_2$$

(XVI)

This dialkoxy tungsten tetrachloride yielded a highly active catalyst for the polymerisation of cyclopentene upon the further addition of aluminium tri-isobutyl.

(iii)Organometallic Compound

The principal organometallic compounds used in the metathetic ring opening polymerisation of cyclic olefins have been aluminium alkyls. The metathesis reaction does not usually occur in the absence of these organometallic compounds, although the oxidation state studies described previously would suggest that the aluminium alkyl does not act as a simple reducing agent. The order of addition of the catalyst components to the monomer has been shown to be critical[31] because olefin metathesis was observed to take place rapidly if the aluminium alkyl was added to the tungsten compound only after the tungsten compound had been reacted with the olefin.

If the aluminium alkyl and tungsten compound were premixed prior to their addition to the cyclicolefin then no polymerisation was observed. The following series of reactions was thought to take place:

$$\mathrm{W\,Cl_6 + 2\ olefin} \underset{\mathrm{(XVI)}}{\rightleftharpoons} \mathrm{W^{*}(Olefin)_2}$$

$$\mathrm{W^{*}(Olefin)_2 + EtAl\,Cl_2} \underset{\mathrm{(XVII)}}{\rightleftharpoons} \mathrm{(Olefin)_2\,W^{*}/Al\,Et\,Cl_2}$$

$$\mathrm{W\,Cl_6 + Et\,Al\,Cl_2} \underset{\mathrm{(XVIII)}}{\rightleftharpoons} \left[\mathrm{W\,Cl_6\,Et\,Al\,Cl_2}\right]$$

The complex formed in reaction(XVIII)was thought to be the active species in the metathesis reaction. If the catalyst components were premixed then the complex formed in (XVIII) might be obtained and this complex was thought to have a high stability constant, or could react to produce an inactive species when the olefin was added , and thus result in no metathesis reaction.

I -(6) · The Stereochemistry of Ring Opening Polymerisations of Cycloolefins

A number of factors affect the stereoregularity of polyalkenamers produced by the ring-opening polymerisations of cyclic olefins.

The nature of the transition metal and the ligands which surround it have a profound effect upon the structure of the polyalkenamer.[31] Table I-(iii) shows the changes in the structure of polypentenamer, prepared under otherwise identical conditions, that occurred when the transition metal and/or the ligands surrounding it were changed.

Table I-(iii)

The effect of the nature of the transition metal compound on the microstructure of Polypentenamer

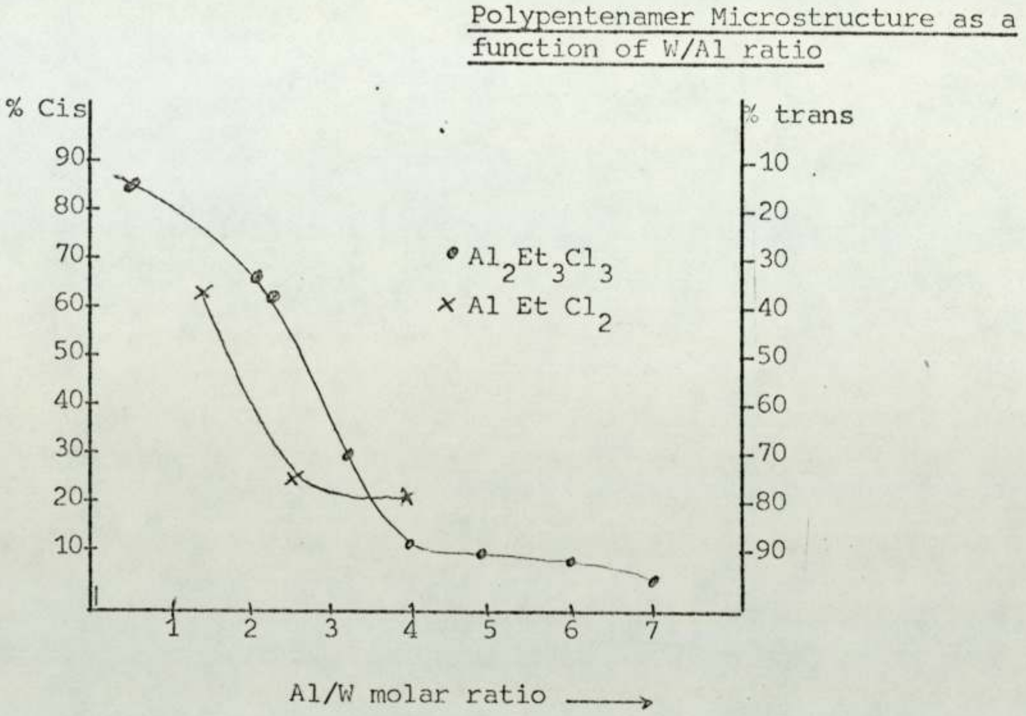
Transition Metal or Metal compound	Microstructure of the Polypentenamer
Titanium	Predominantly trans
Zirconium	Predominantly trans
Tungsten	Predominantly trans
$Mo\ Cl_5$	100% cis
$Mo\ (AcAc)_2$	100% cis
$Mo\ Cl_2\ (OPh)_3$	100% trans

The nature of the organometallic co-catalyst affects the structure of the polyalkenamer produced by ring-opening polymerisations. Gunther[32] has shown that by changing the nature of the organometallic cocatalyst, either essentially cis or trans polypentenamer could be formed. The WCl_6/Et_3Al initiated polymerisation of cyclopentene produced trans-polypentenamer, whilst the $WCl_6/Na_3\ W(C_6H_5)_5$ system produced essentially cis-polypentenamer.

The molar ratio of transition metal to organometallic compound has been shown to be effective in altering the microstructure of polyalkenamer produced by ring-opening polymerisations. Gunther[32] showed that by changing the W/Al molar ratio for the polymerisation of cyclopentene using the catalyst systems $WF_6/Et_3\ Al_2\ Cl_3$ and $WF_6/Et\ Al\ Cl_2$, the stereospecificity of the reaction could be completely changed as shown in Fig I-(i)

Fig.I -(i)

The Change in the Microstructure of Polypentenamer with the variation of W/Al molar ratio for the systems $WF_6/Et_3Al_2Cl_3$ and $WF_6/EtAlCl_2$



The cis/trans ratio varied continuously from about 85:15 to 10:90 when the W/Al ratio was varied between 0.5:1 and 7:1

The temperature of the reaction is of importance in determining the microstructure of the polymer. Dall'Asta and Motroni[33] gave some indication of this for the $MoCl_5/Et_3Al$ system and Minchak and Tucker[34] obtained a continuous variation of the cis/trans ratio of polypentenamer, using a tungsten catalyst, by varying the polymerisation temperature from - 50 to + 40°C.

A research team at Farbenfabricken Bayer[35] used a $W Cl_6/R_4Sn$ system to polymerise cyclopentene and higher-membered cycloolefins to trans polypentenamer at room temperature, whereas the same system produced cis polypentenamer at -30°C.

The monomer itself affects the stereostructure of the polymer, as Natta[36] et al showed that a $MoCl_5/Et_3Al$ catalyst system converted cyclopentene to cis polypentenamer, but converted higher-membered cycloolefins to trans polyalkenamers.

I - (7) Molecular Weights of Polyalkenamers produced by the Ring-Opening Polymerisations of Cyclic Olefins

(i) Behaviour of average molecular weights of Polyalkenamers during the Polymerisation Reaction

Pampus and coworkers[39] demonstrated that high molecular weight polypentenamer was formed in the initial stages of the polymerisation of cyclopentene with $W\,Cl_4\,[OCH\,(CH_2Cl)_2]_2$ and $Al\,Et_2\,Cl$ catalysts. The high molecular weight polymer formed was high in cis polypentenamer and as the polymerisation reaction proceeded both the molecular weight and the cis content of the polypentenamer fell as is shown in fig I - (2).

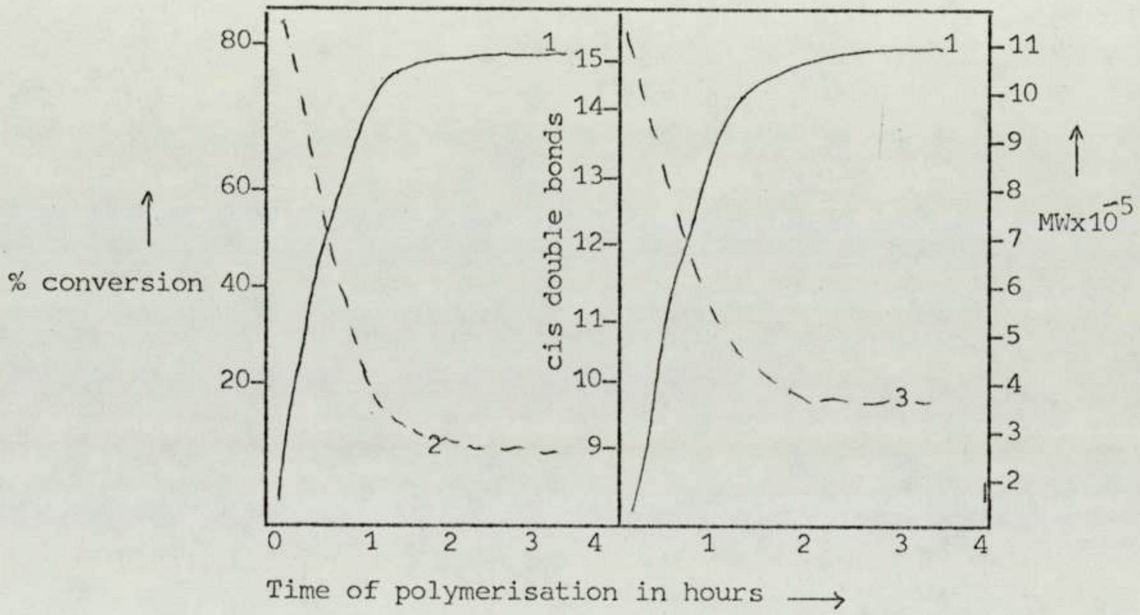


Figure I - (2)

Key:

1.) Conversion

2.) Cis double bonds

3.) Molecular Weight

Pampus showed that as the molecular weight fell there was a commensurate change in the microstructure as the cis double bond isomerised to the trans-form during the polymerisation. He showed also that the distribution of molecular weights was not significantly broadened as the molecular weight of the polymer fell, but rather that the high molecular weight-fraction present in the initial stages of the reaction disappeared as the reaction proceeded.

(ii)Factors influencing the molecular weights of Polyalkenamers

(a) Effect of the Catalyst

Pampus[39] demonstrated that the nature of the tungsten compound had a significant effect upon the M.W. of the polymer. Using $AlEt_2Cl$ as catalys in each case, a series of W compounds were reacted with polybutadiene that had an initial intrinsic viscosity of 2.2, measured in toluene at 25°C. Table 1-(iv) shows the dependence of the final intrinsic viscosity of the polymer on the nature of the W compound used.

Table I-(iv)

Influence of the Tungsten Catalyst on the Molecular Weight of cis 1,4-Polybutadiene.

Tungsten Compound	Intrinsic Viscosity
WF_6	0.5
WCl_6	0.4
$WCl_5[OCH_2CH_2Cl]$	0.3
$WCl_4[OCH_2(CH_2Cl)_2]_2$	0.3

(b) Al/W Molar Ratio

Gunther et al[32] showed that the intrinsic viscosity of polypentenamer was also affected by the Al/W catalyst molar ratio, as shown in fig. I-(3)

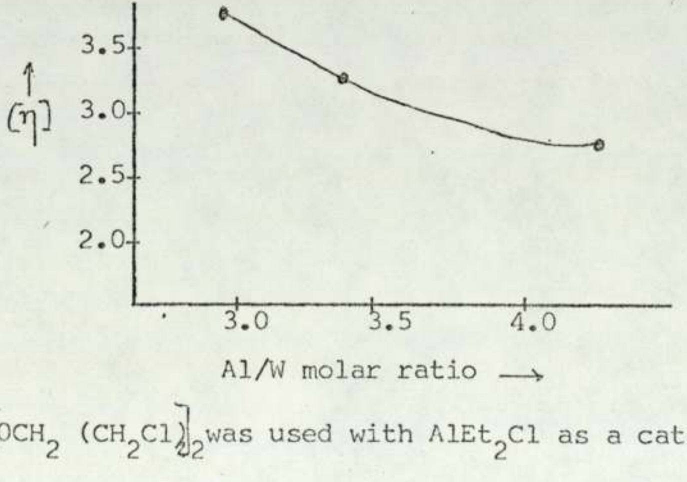


Fig I - (3)

$WCl_4\ [OCH_2\ (CH_2Cl)]_2$ was used with $AlEt_2Cl$ as a catalyst and the intrinsic viscosities of the polypentenamer samples were measured in toluene at 25°C.

(c) The Catalyst Concentration

Using the same system as above it has been shown that the catalyst concentration affected the molecular weight of polypentenamer formed, as shown in fig.I-(4)

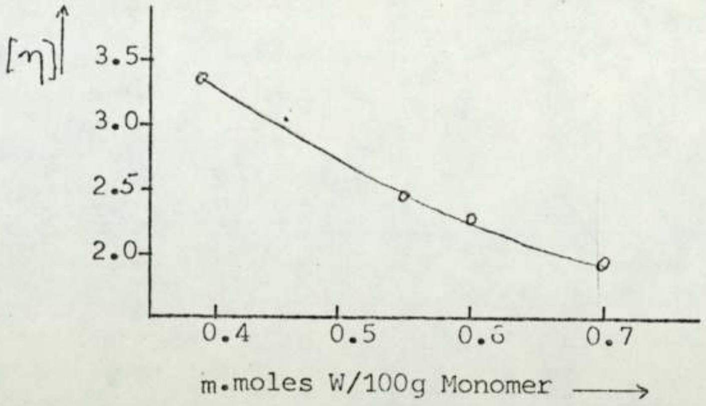


Fig. I-(4)

The reaction temperature was 5°C and the polymerisations were carried out in a 20% cyclopentene in toluene solution.

(d) Addition of Acyclic Olefins

The molecular weights of polyalkenamers could be controlled by the addition of small quantities of acyclic olefins. The regulating effect of the acyclic olefins depended upon their structure and Pampus[39] investigated the effect of several olefins on the molecular weight of polypentenamer by adding small amounts of the acyclic olefins to the polymerisation reaction.

Fig.I-(5) shows the effect of a number of acyclic olefins on the reciprocal of the molecular weight of the polymer:

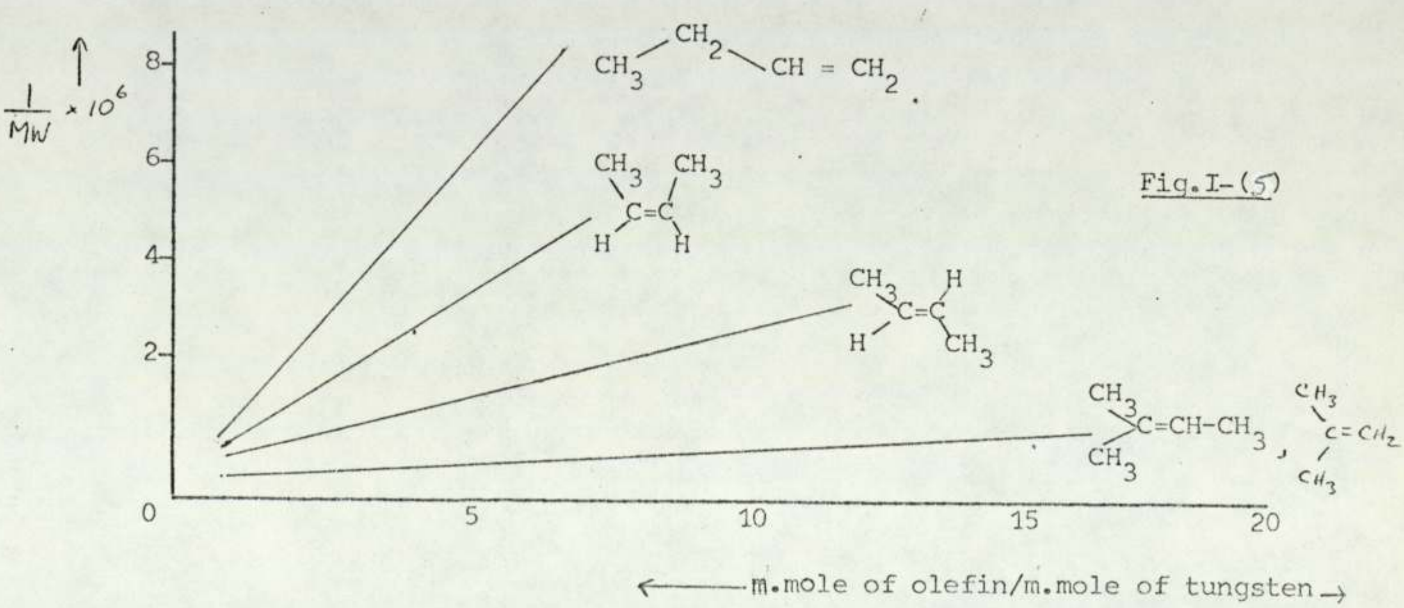


Fig.I-(5)

The effect of the unsubstituted olefin, but-1-ene was the greatest and as substitution of H on carbon atoms at the double bond was increased the effect of the olefin on the molecular weights of the polypentenamers was reduced. These results could be clearly linked to the ability of the substituted olefins to take part in the olefin metathesis reaction.

(e) Addition of Conjugated Dienes

Pampus showed that the addition of conjugated dienes to a polymerisation reaction greatly lowered the molecular weight of any polymer produced and also reduced the rate of reaction. He found that very small amounts of conjugated dienes completely prevented the polymerisation of cyclic olefins.

(iii) The Molecular Weight Distribution of Polyalkenamers

Hocker[66] showed that polyoctenamers and polydodecenamers prepared by metathetic ring-opening polymerisations possesed a bimodal molecular weight distribution. The low molecular weight fraction was found to contain cyclic oligomers up to the dodecamer and the high molecular weight fraction was assumed to be linear polymer. The distribution of the cyclic oligomers, together with the polymeric material, indicated a ring-chain equilibrium.

I - (8) Thermodynamic and Kinetic Features of the Ring-Opening Polymerisation of Cyclic Olefins

(i) Polymerisability of Rings

Ring-opening polymerisations exhibit somewhat different thermodynamic features to conventional addition polymerisations. Addition polymerisations are normally strongly favoured by enthalpy changes but weakly opposed by entropy changes during the course of the polymerisation. Ring-opening polymerisations are favoured by enthalpy changes and, in many cases, also by entropy changes. The enthalpy of reaction for a ring-opening polymerisation is mainly derived from the accompanying release during the reaction of ring-strain energy, which is high for four and five membered rings, but small in higher numbered rings. Cyclohexene is a strain-free ring and it is for this reason that cyclohexene is the only unsubstituted cyclic olefin that does not polymerise by a ring-opening mechanism. The entropy changes involved during cyclic olefin polymerisations are apparently negative for small rings, i.e. cyclobutene and cyclopentene, close to zero for cycloheptene and positive for higher membered alicyclic olefins. This behavour can be explained by assuming that the negative translational entropy change that occurs during the ring-opening polymerisation is very large for small rings but becomes less negative for larger ones. Conversely, the torsional and vibrational entropy changes, which are always positive in ring-opening polymerisations, decrease to a much smaller extent in the series from small to large rings. Thus, the negative translational entropy change prevails over the other two types in small rings up to cyclohexene, but the positive torsional and vibrational entropy changes prevail over the translational in larger cycles. Hence, the polymerisation of cyclopentene involves a negative entropy change and a positive enthalpy change, whereas that of cyclooctene involves positive enthalpy and entropy changes.

Natta and Dall'Asta[36] interpreted the polymerisability of cyclic olefins in terms of ring strain energy and their results are shown in table I-(5).

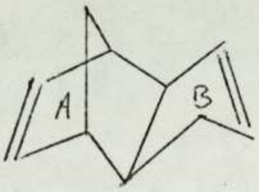
Table I -(V)

Dependence of Monomer Polymerisibility on Ring Size

Monomer	Equilibrium conversion of monomer to polymer (%)
Cyclopentene	70
Cyclohexene	0
Cycloheptene	18
Cyclooctene	60
Cis/trans cyclododecene	34

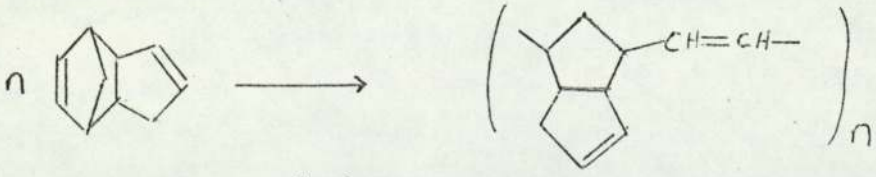
The polymerisation conditions were constant for all the cycloolefins and it can be seen that, with the exception of cyclohexene, which has a completely staggered conformation of carbon atoms and is as stable as the corresponding acyclic hexene, the conversions of monomers to polymers were generally decreased for increasing ring size and corresponding decrease in ring strain.

Another factor which governs the ring strain energy and hence the polymerisability of rings is the nature of the ring. Bi-cyclopentadiene contains two types of unsaturated five membered rings A and B as shown in (XIX).



(XIX)

Monomers which have a highly strained bridged ring (A) polymerise readily, whereas monomers which have a fused ring (B) are more difficult to polymerise. Oshiku and Tabuchi[37] polymerised bicyclopentadiene with $MoCl_5$ to give a trans-vinylene polymer by opening the bridged ring:



(XX)

The degree, position and nature of substitution of the ring affects the polymerisability of the cyclic olefin. In general, only cyclic olefins with unsubstituted double bonds are polymerisable. Small alkyl substituents on other positions of the ring do not normally render the monomer inactive towards polymerisation, unless the free energy of polymerisation is already small, which is the case for monomers such as 2-methyl tetrahydrofuran, whereas 3-methyl cyclopentene was found to be easily polymerisable[14].

Gunther et al[33] demonstrated that the position of the substituent on the ring was important. He showed that 1- and 4-methyl cyclopentene were unpolymerisable, but that 3-methyl cyclopentene was readily polymerisable. He also demonstrated that the nature of the substituant was important, by showing that 3-isopropyl cyclopentene was unpolymerisable.

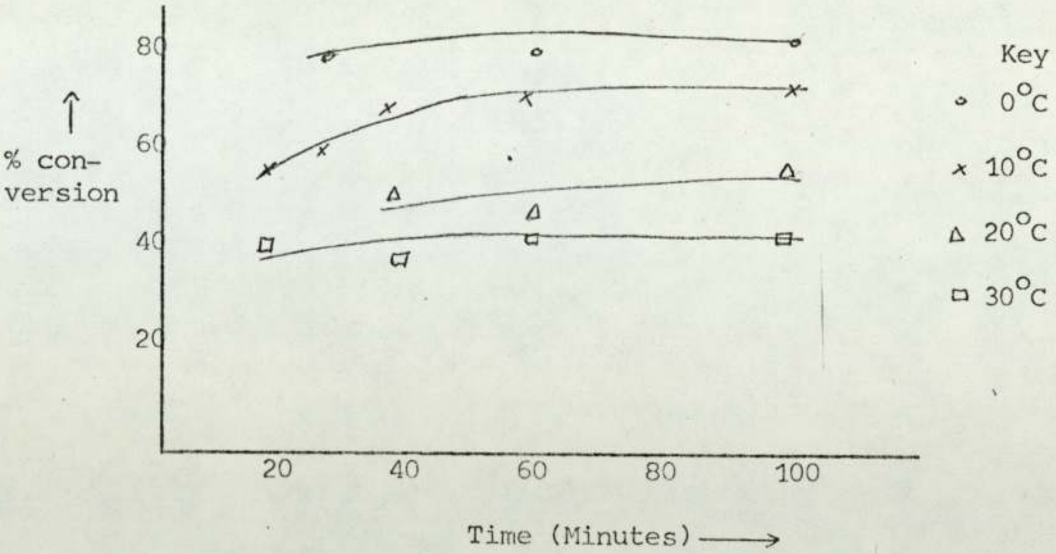
(ii) Equilibrium Polymerisation

The attainment of a statistical equilibrium is essentially entropy controlled during the metathesis of an acyclic olefin[23] since the reaction is thermoneutral, (if the cis/trans isomerisation of the double bond is neglected.) The ease with which equilibrium is reached is one of the characteristics of the metathesis reaction.

The ring-opening polymerisations of weakly strained cyclic olefins also presents the features of an equilibrium reaction, involving monomer-oligomer, oligomer-polymer and ring-chain equilibria. The energy resulting from the release of ring strain shifts these equilibria away from the statistical composition, and the equilibrium composition is then dependent upon temperature.

Ofstead and Calderon[38] investigated the temperature dependence of the monomer-polymer equilibrium for trans-polypentenamers in the temperature range from 0° to 30°C which is shown in fig.I-(6). Limiting conversions were obtained that varied between 50-80% polypentenamer.

Fig.I - (6) Dependance of Conversion of Cyclopentene to Polypentenamer on Temperature of Polymerisation.



The polymerisations were carried out using a $WCl_6/EtOH/EtAlCl_2$ catalyst system with the initial monomer concentration of 2.2 moles litre^{-1} and a tungsten hexachloride concentration of 9.9 x 10^{-3} moles litre^{-1}. Gas chromatographic examination of the low molecular weight fraction of the polymerisate revealed the expected presence of substantial amounts of all $(C_5H_8)_n$ terms from monomer to involatile polymer. The enthalpy (ΔH_p) and entropy (ΔS_p) of polymerisation were determined from the dependence of the equilibtium monomer concentration on temperature and found to be -4.4 K cal. mole^{-1}, and -14.9 cal. mole^{-1}. K^{-1} respectively. The ceiling temperature was predicted to be approximately 150°C. The reversibility of the monomer - polymer equilibria was shown in two ways :-

(a) A temperature change (up or down) during polymerisation resulted in a rapid shift of the conversion curve to that corresponding to the new temperature.

(b) Depolymerisation of purified low molecular weight polypentenamer in the presence of the same metathesis catalyst led to a monomer-polymer equilibrium close to that found during polymerisation.

(iii) Cis/trans control in Polyalkenamers

Thermodynamic control of the cis/trans equilibrium in olefin metathesis reactions was proposed by Calderon et al[23], (section I-(3,4), who concluded that the formations of trans and cis isomers were provided for by the transalkylidenation step itself and were not due to an independent isomerisation reaction. These results were in contrast with those numerous ring-opening polymerisations of cyclic olefins which were found to be stereospecific. It has been shown that it is possible to obtain 100% cis-polypentenamer or predominantly trans-polypentenamer by using the appropriate stereospecific catalyst. Cis-polypentenamer can be converted to trans-polypentenamer by contacting it with a normally trans-specific catalyst[39], whereas trans-polypentenamer can not be modified under similar conditions. The cis/trans ratio of transposed polybutadienes depended strongly on the catalyst composition, catalyst concentration and the temperature of reaction[40] and hence it would appear that the cis/trans ratio in ring-opening polymerisations was kinetically rather than thermodynamically controlled.

Cis and trans isomerisations were not the only features of the olefin metathesis and ring-opening polymerisation reactions that appeared to be kinetically rather than thermodynamically controlled. Calderon[41] concluded, after an observation of the early stages of the cis-2-pentene metathesis, that the disproportionated olefins did not leave the co-ordination complex in pairs. He suggested that one of the pentene units remained co-ordinated and then reacted further with an incoming olefin and that the leaving pairs, in fact, would have restricted product variability.

Dall'Asta[42] reacted purified polypentenamer with cyclooctene, which had been labelled with C^{14}, in the presence of a three component metathesis catalyst. He examined the poly-(pentenamer-octenamer) copolymer for the degree of randomness by a partial ozonolysis technique. The results of this examination led him to suggest that the copolymer was made up of blocks of pentenamer and octenamer units and was not a random copolymer.

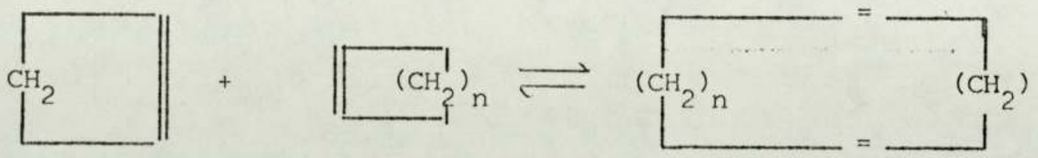
If the reaction had been thermodynamically controlled a random copolymer would have formed. Dall'Asta suggested that the site of insertions of cyclooctene into the polypentenamer remained with the polymer chain for a sufficient length of time for a block of octenamer units to be formed. He did not consider that the block nature of the copolymer produced could have arisen from the metathesis of polypentenamer chains with polyoctenomer chains, which would have been formed by the ring-opening polymerisation of cyclooctene by the metathesis catalyst. However, whether the block copolymer was formed by the metathesis of polypentenamer and polyoctenamer, or by the insertion of cyclooctene into polypentenamer, (or both), the suggestion of kinetic control of the metathetic ring opening polymerisation reaction was increased.

Further evidence for kinetic control of the ring opening polymerisation reaction came from Pampus and coworkers[29] who stated that during the polymerisation of cyclopentene, using a tungsten based catalyst system, one of the two double bonds associated with the active species always remained co-ordinated to the tungsten atom.

I - (9) The Mechanism of the Ring-Opening Polymerisations of Cyclic Olefins

(i) The Reaction Pathway

Calderon[23] proposed that the ring-opening polymerisations of cyclic olefins was a special case of the olefin metathesis reaction and it was suggested that a reaction scheme could be formulated whereby polymerisation took place by scission of the carbon-carbon double bond:



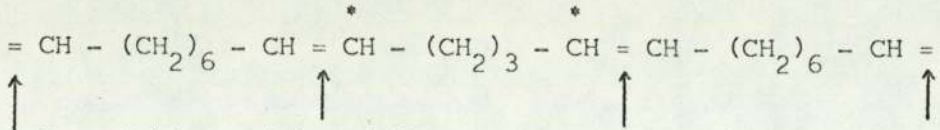
XXI

Calderon suggested that chain growth proceeded via the formation of macrocyclic rings that increased in size. Further evidence for this type of double bond scission was provided by Dall'Asta and Motroni[33] who studied the copolymerisation reaction between cyclopentene and cyclooctene. Excess cyclooctene was copolymerised with cyclopentene which had the carbon atoms at the double bond labelled with C^{14}. The random copolymers formed were subjected to destructive ozonolysis and subsequently reduced to the diols.

The following labelled diols should have resulted, depending on the site at which cleavage of the ring occurred:

(a) Cleavage at the double bond

The copolymer produced by cleavage at the double bond is shown in XXII



$$\underset{\uparrow}{=} CH - (CH_2)_6 - CH \underset{\uparrow}{=} \overset{*}{CH} - (CH_2)_3 - \overset{*}{CH} \underset{\uparrow}{=} CH - (CH_2)_6 - CH \underset{\uparrow}{=}$$

Degradation points of the copolymer after ozonolysis

* signifies C^{14}

XXII

The diols that would be produced from XXII after ozonolysis are shown below:

$$HO\text{-}CH_2 \quad - \quad (CH_2)_6. \quad - \quad CH_2OH$$

$$HO\overset{*}{C}H_2 \quad - \quad (CH_2)_3 \quad - \quad \overset{*}{C}H_2OH$$

$$HOCH_2 \quad - \quad (CH_2)_6 \quad - \quad CH_2OH$$

(b) Cleavage at the single bond α to the double bond

The copolymer produced by cleavage of the single bond α to the double bond is shown in XXIII

$$-CH \underset{\uparrow}{=} CH - (CH_2)_6 - \overset{*}{C}H \underset{\uparrow}{=} \overset{*}{C}H - (CH_2)_3 - CH \underset{\uparrow}{=} CH - (CH_2)_6-$$

Degradation points of the copolymer after ozonolysis

XXIII

The diols that would be produced from XXIII after ozonolysis are shown below:

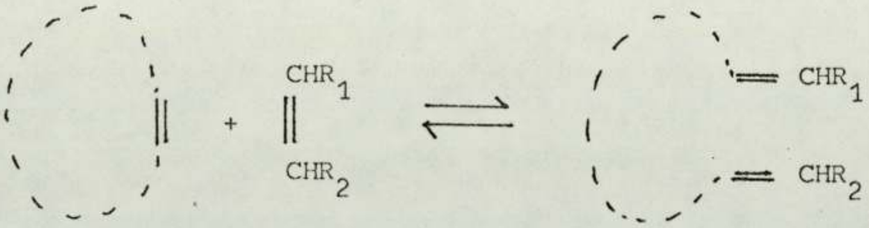
$$HOCH_2 \quad - \quad (CH_2)_6 \quad - \quad \overset{*}{C}H_2OH$$

$$HO\text{-}\overset{*}{C}H_2 \quad - \quad (CH_2)_3 \quad - \quad CH_2OH$$

$$HO\text{-}CH_2 \quad - \quad (CH_2)_6 \quad - \quad CH_2OH.$$

If ring opening had occurred by scission of the double bond, all the radioactivity would have been expected to be isolated in 1,5 pentane diol, which was found by radio - G.L.C. analysis, confirming that ring opening occurred by scission of the double bond.

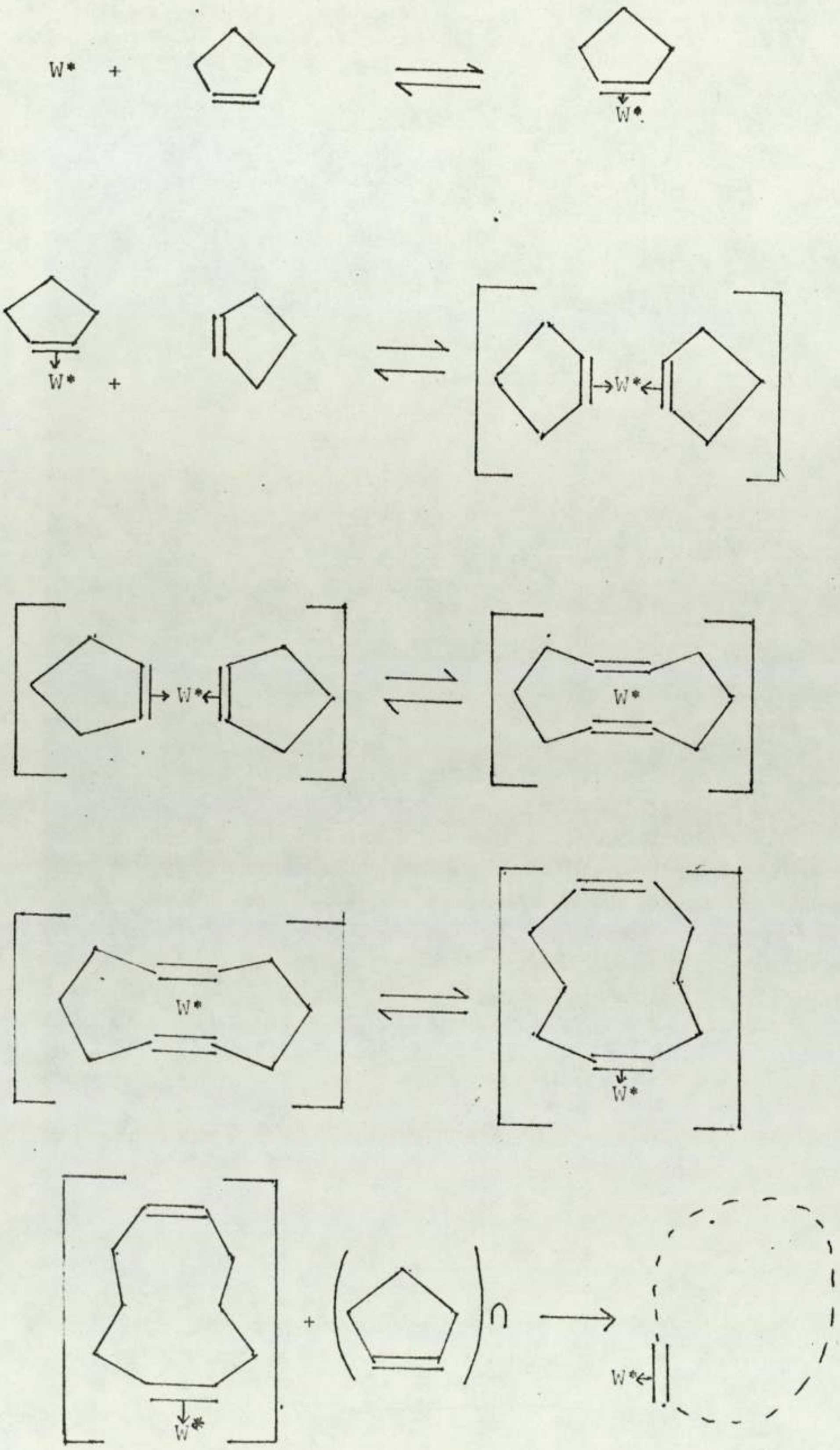
The formation of macrocycles during the growth of the polymer chain was confirmed by Calderon[22] when he showed that macrocyclic rings formed from every possible combination of cyclic olefin monomer units were present in the polymerisates. The existence of the large macrocyclic species that should be present in the polymerisates was very difficult to prove experimentally, and in any case side reactions which could transform macrocyclic rings into open chain macromolecules could easily have occurred. It was postulated that traces of acyclic olefins likely to be present in any monomer could have reacted with the macrocyclic rings to produce the open chain polymer as shown:



XXIV

For the larger macrocyclic rings the probability of them reacting with any acyclic olefin that was present in the polymerisate would be greater, and hence the high molecular weight polyalkenamer would be present as open chain polymer.

A reaction pathway for the ring opening polymerisation of cyclopentene by a tungsten based catalyst system was postulated and is shown in fig.I - (7):



XXV

XXVI

XXVII

XXVIII

XXIX

Fig I(7)

Reaction XXV involved the co-ordination of the active catalytic species (W*) with the double bond in the cyclopentene. Reaction XXVI involved the reaction of the co-ordinated cyclopentene with a further monomer unit, to give two cyclopentene molecules co-ordinated to the active catalyst. Reaction XXVII involved the simultaneous breaking and making of double bonds and reaction XXVIII shows that the tungsten complex remained co-ordinated to one of the double bonds. Reaction XXIX shows that the sequence of reactions from XXVI to XXVIII repeated for n units of cyclopentene would lead to the production of macrocyclic rings.

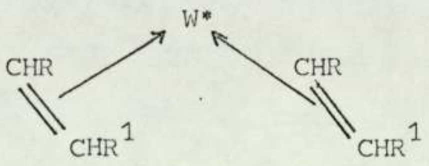
(ii) The Transition State

Four transition states, or intermediates, have been proposed in plausible mechanisms to describe the ring-opening polymerisations of cyclic olefins and the olefin metathesis reaction.

(a) The "Quasi-Cyclobutane" Intermediate

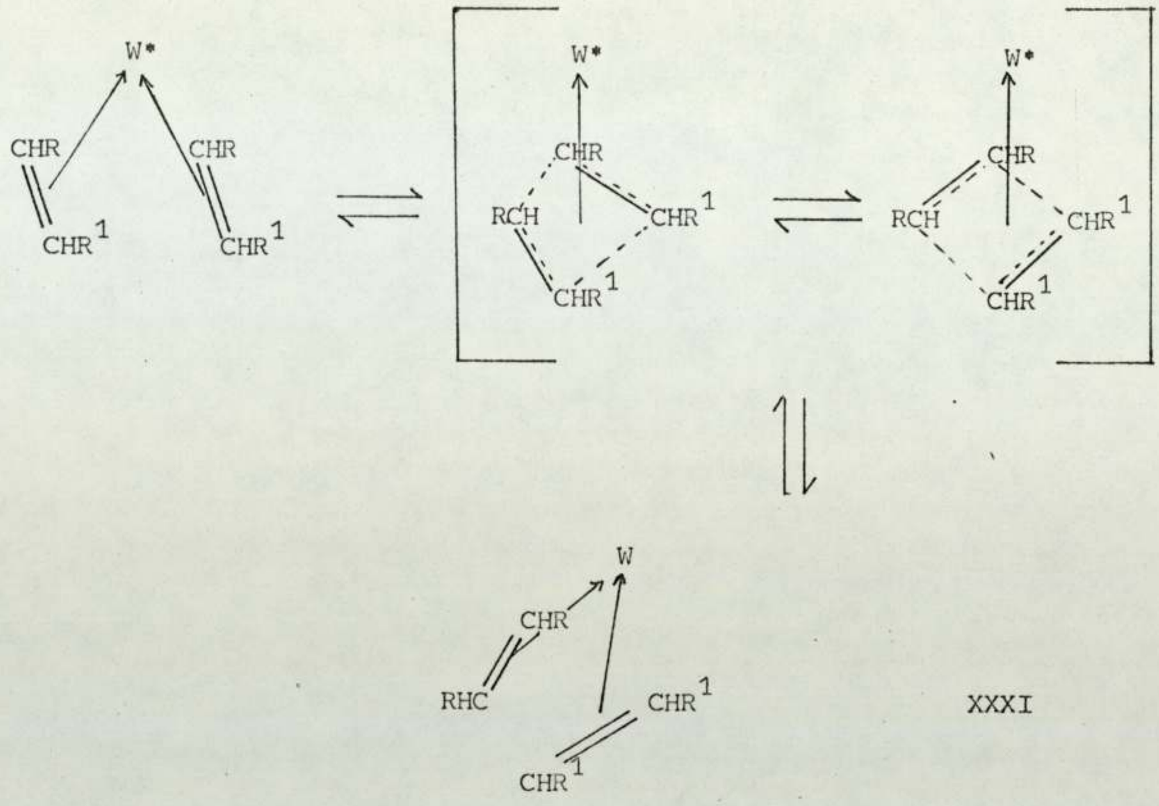
Bradshaw and coworkers[43] proposed that a "Quasi-Cyclobutane" intermediate was formed during the olefin metathesis reaction, although they admitted a lack of detailed knowledge to support such an intermediate. Calderon and coworkers[23] adopted this type of intermediate for the ring-opening polymerisation of cyclic olefins. It was proposed that the olefin metathesis and the ring-opening polymerisation reactions involved the following processes:

$$WCl_6 + C_2H_5OH + AlEtCl_2 + 2RCH = CHR^1 \longrightarrow$$



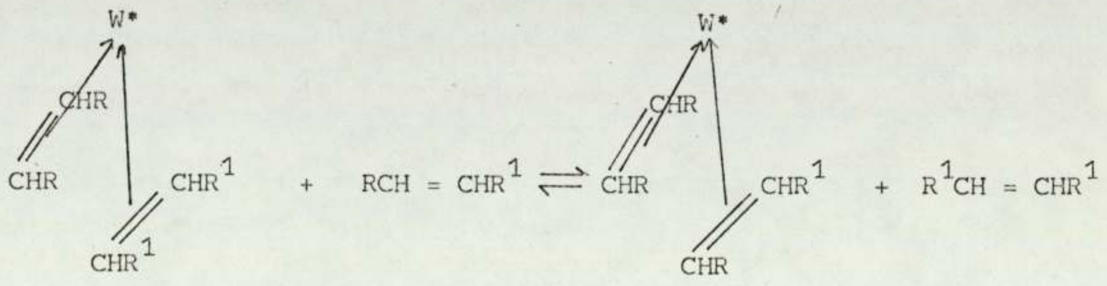
XXX

Reaction XXX involved the initial formation of a complex wherein the tungsten atom acquired two olefin ligands in a cis configuration. The tungsten atom W* was in a reduced oxidation state as a result of prior reaction, in the presence of the olefins, with the $AlEtCl_2$ compound.



XXXI

Reaction XXXI was proposed as the transalkylidenation process in which the bis olefin complex was electronically excited to a four-membered ring which did not convert to a ground state cyclobutane but transformed back to a bis-olefin metal complex.

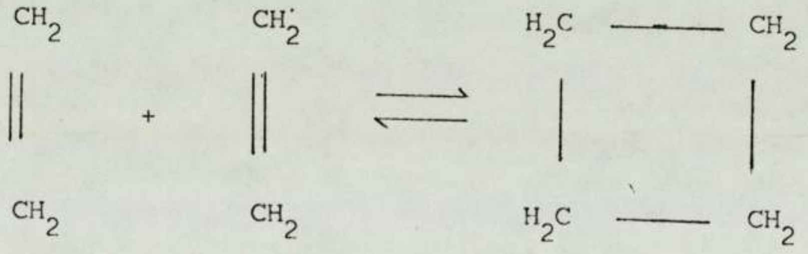


XXXII

This reaction was then followed by an olefin exchange reaction (Reaction XXXII) and Calderon suggested that the olefin exchange step was very rapid and alternated with the transalkylidenation step. This provision was necessary to account for the high rates of reactions that were obtained with very low catalyst concentrations.

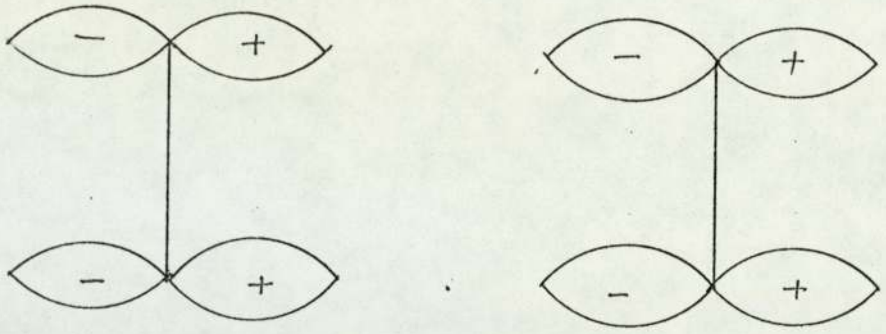
Mango and Schachtschneider[44] discussed the formation of a "quasi cyclobutane" intermediate within the scope of the Woodward-Hoffman rules, governing 1,2 cycloaddition reactions.

Cycloaddition reactions are transformations involving the fusion of open-chain substrates to cyclic products. Woodward and Hoffman[65] divided all concerted cycloaddition reactions into allowed and forbidden categories defined by a complete set of selection rules. Mango and Schachtschneider applied the Woodward Hoffman rules to the reaction depicted in XXXIII, which is an uncatalyzed 1,2 cycloaddition reaction of 2 ethylene molecules to form a cyclobutane molecule.



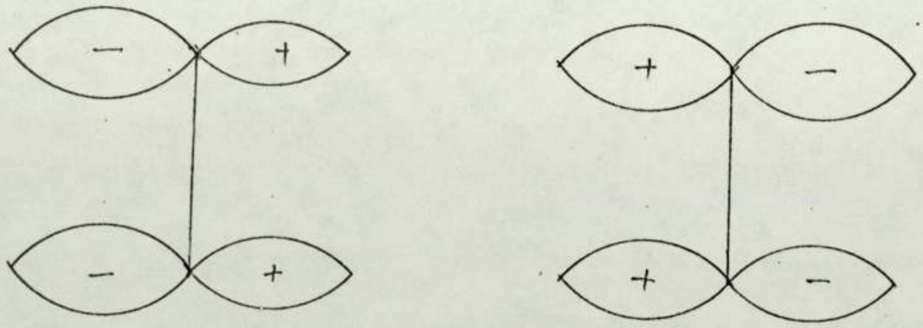
XXXIII

The fusion of two olefin π bonds to form cyclobutane σ bonds was described by applying the simple molecular orbital theory to the molecular orbitals representing the bonds undergoing character change during reaction XXXIII. Fig.I -(8) shows that the two π bonds of the olefins could be combined to give bonding and antibonding combinations:



$\pi - \pi$

Antibonding Combination

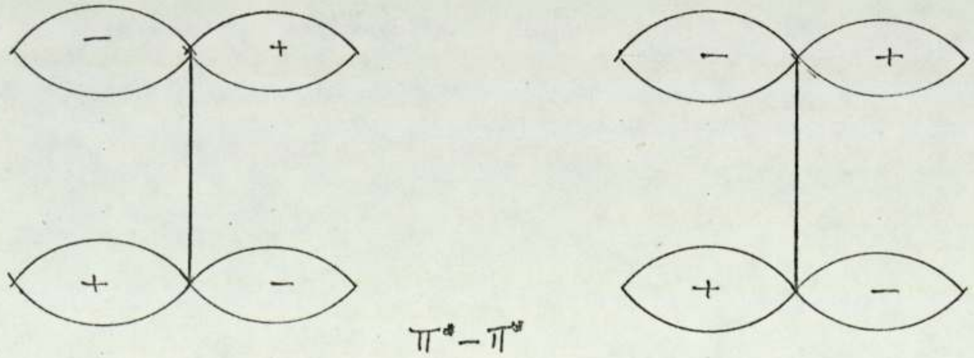


$\pi + \pi$

Bonding Combination

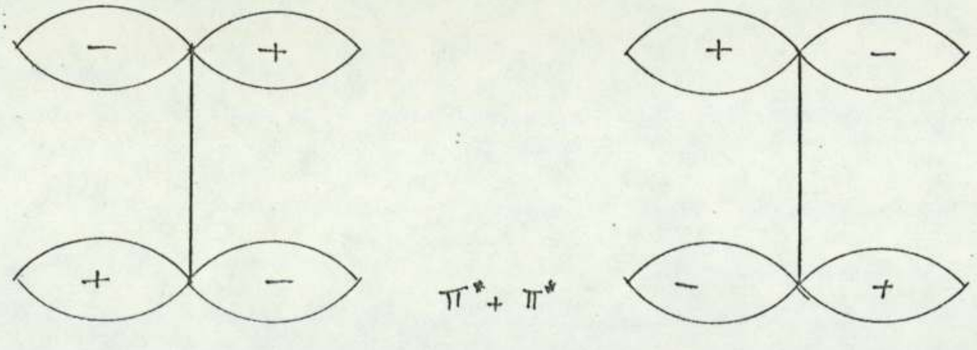
Fig I - (8)

Fig.I - (ix) shows that the two olefin antibonding orbitals (π^*) could also be combined to give bonding and antibonding combinations:



Anti-Bonding Combination

$\pi^* - \pi^*$

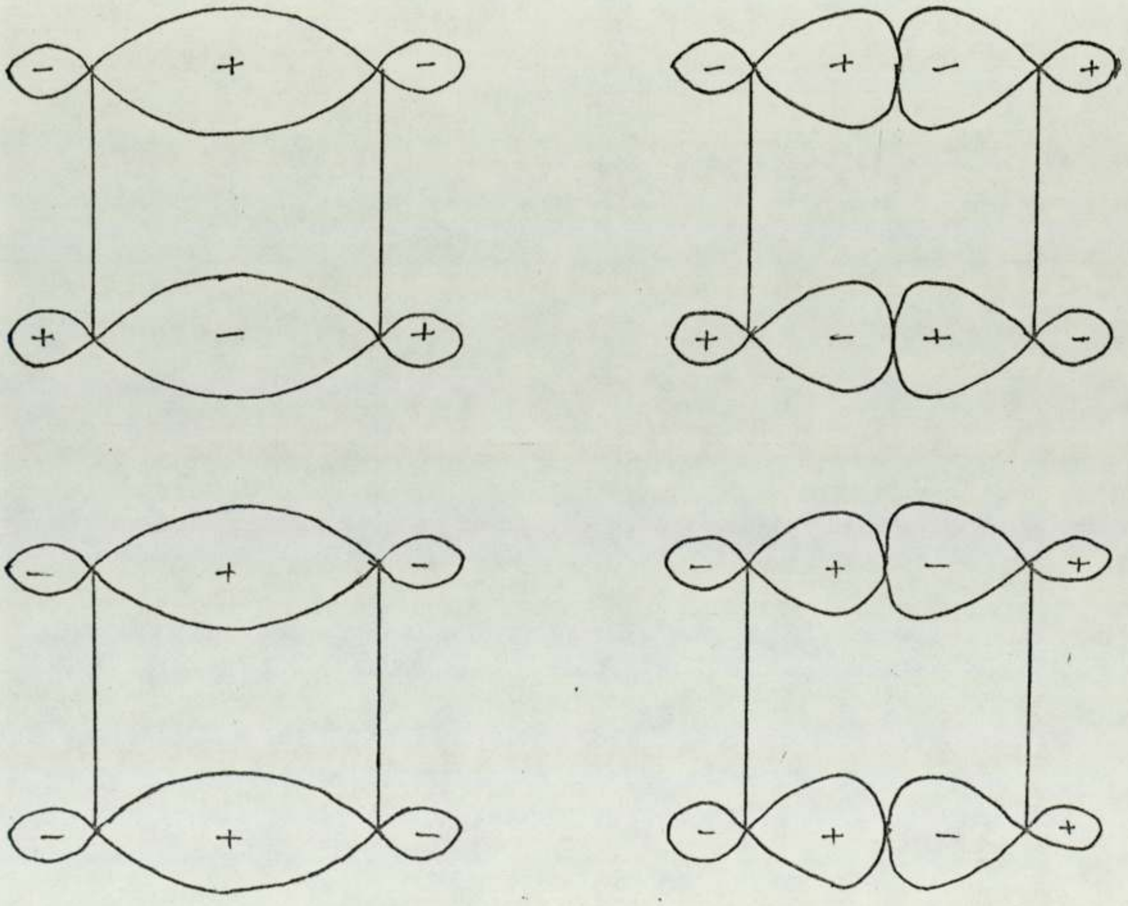


Bonding Combination

$\pi^* + \pi^*$

Fig.I - (9)

The σ bonds in cyclobutane corresponding to the transforming olefin bonds could then be described as shown in Fig.I - (10). There were two bonding molecular orbitals representing the two σ bonds and two antibonding combinations representing the corresponding σ^* bonds.



Bonding σ Molecular Orbitals

Antibonding σ^* Molecular Orbitals

Fig.I - (10)

The two sets of molecular orbitals were then assigned symmetries relative to the common elements of symmetry maintained across the reaction co-ordinates. For cyclobutanation, the elements of symmetry were two planes, P_1 and P_2 as shown in fig. I-(11)

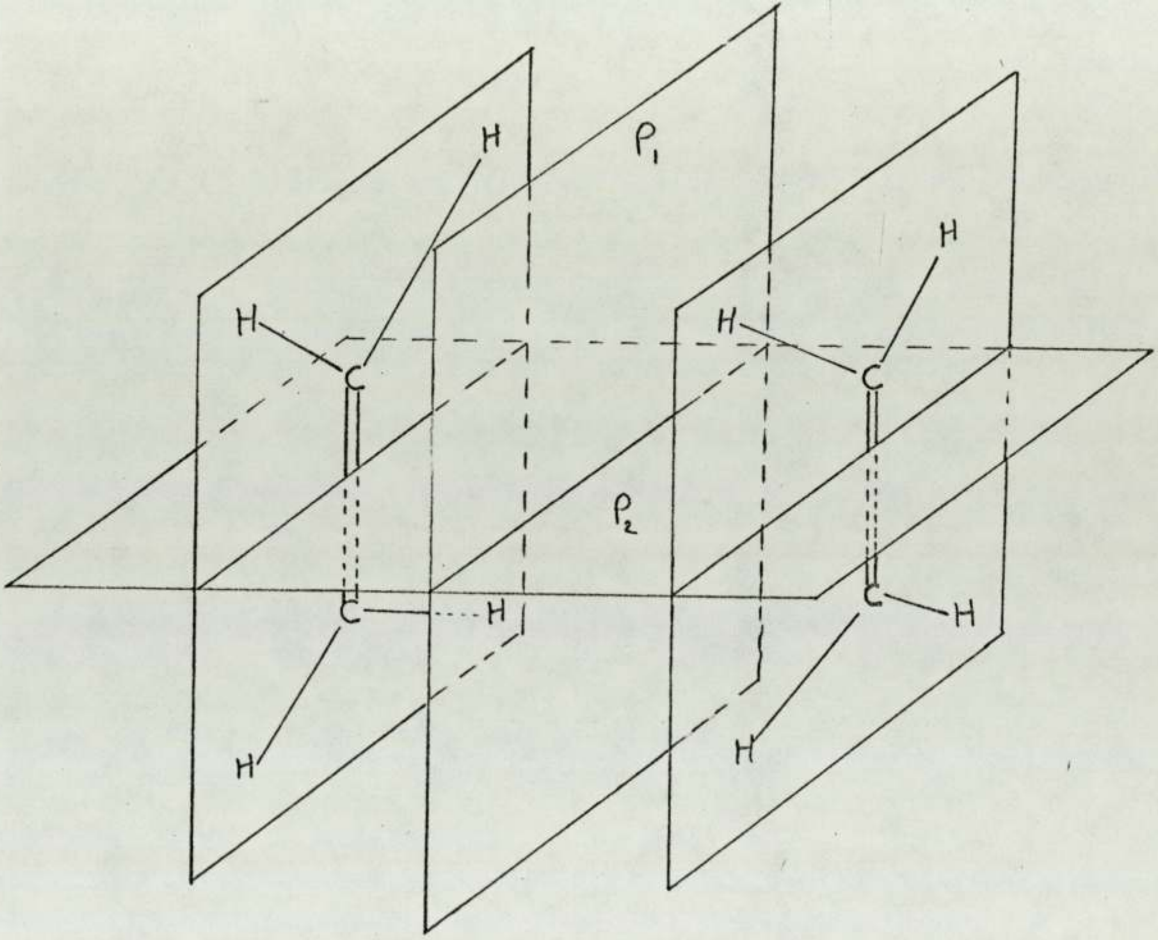
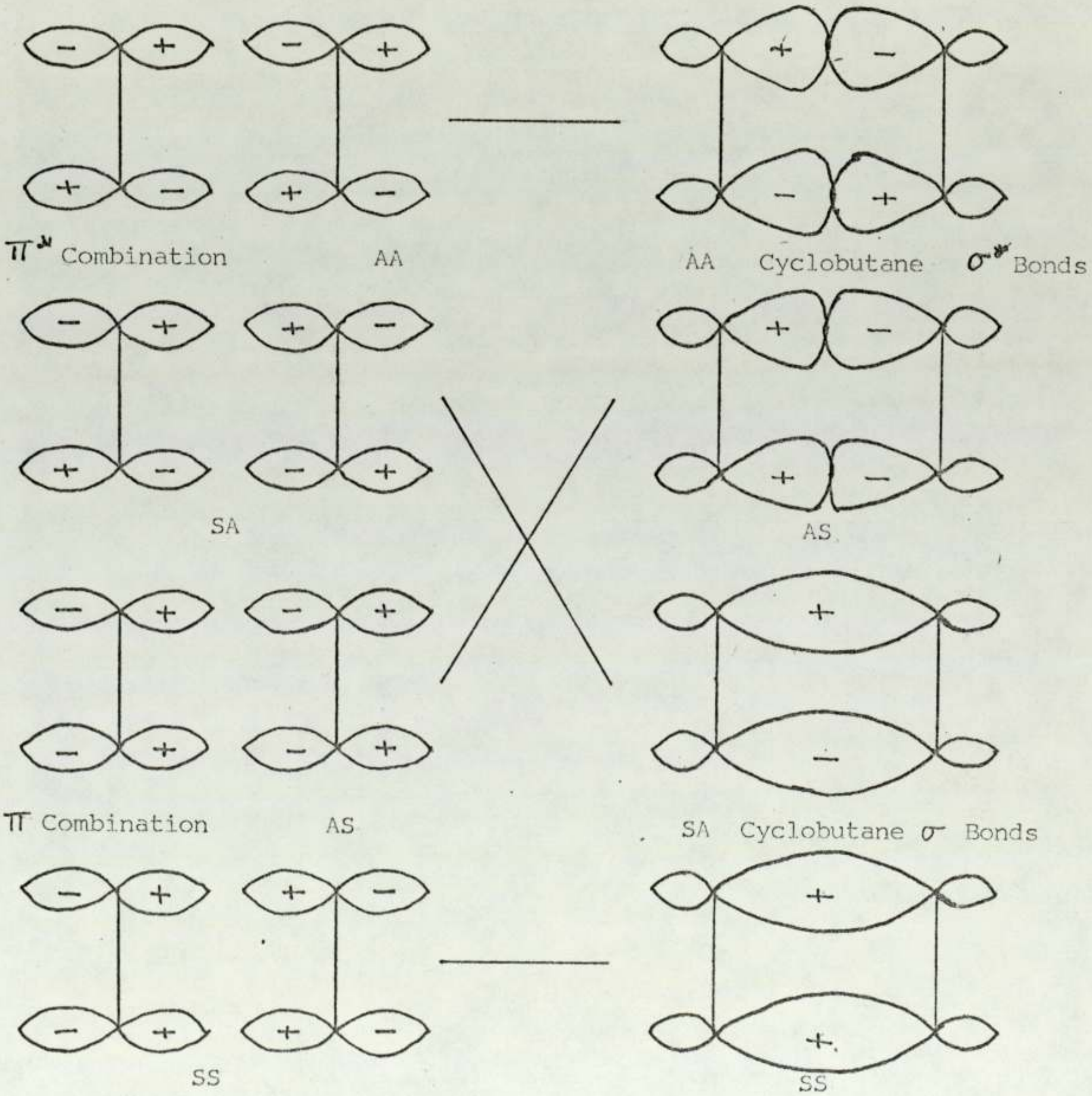


Fig.I - (11)

A correlation diagram was then constructed with the molecular orbitals ordered by relative energies and assigned symmetries relative to P_1 and P_2 (S, symmetric, A, antisymmetric). This is shown in fig.I - (12) where the assignment SA means symmetric about P_1 and antisymmetric about P_2. Molecular orbital symmetry conservation required that the molecular orbitals maintained their symmetry about the common elements across the reaction co-ordinates, which gave rise to the orbital correlations outlined in fig.I - (11).



Symmetries of Olefin Orbitals relative to P_1 and P_2

Fig.I - (12)

Symmetries of Cyclobutane Orbitals relative to P_1 and P_2

From fig.I - (12) it can be seen that the olefin AS π combination would transform into the cyclobutane AS σ^* orbital and that the olefin SA π^* combination would become a cyclobutane SA σ bond. The necessity for orbitals to cross was characteristic of a forbidden reaction. The forbidden nature of the reaction became more apparent when the bonding electron pairs were placed in the appropriate molecular orbitals. In two fusing olefins the electron pairs would reside in π orbitals SS and AS in fig.I - (9). During cyclobutanation, the electron pair in the SS π combination would flow into the cyclobutane SS σ bond and the electron pair in the AS π combination would move into the AS σ^* cyclobutane bond. The net bonding between the approaching olefins would therefore be essentially zero across the reaction co-ordinate. It was therefore shown that the uncatalysed 1,2 cycloaddition reaction between two olefins was symmetry forbidden by the Woodward-Hoffman rules.

Mango and Schachtschneider had therefore shown that the construction of a cyclobutane ring from two olefins required the electronic population of the SA and SS orbitals and the electronic vacancy of the AS and AA orbitals. Two of the prerequisites, population of the SS orbital and vacancy of the AA orbital, were assured since these orbitals were correlated with the appropriate orbitals in the olefin combinations. The fulfilment of the remaining two requirements could be effected by a catalyst whose function would be the removal of an electron pair from the olefin AS π combination and the insertion of an electron pair into the olefin SA π^* combination. A catalyst that could carry out this operation would have a pair of orbitals of SA and AS symmetry and an electron pair. A transition metal complex could carry out the operation required to switch olefin cyclobutanation from a symmetry-forbidden to a symmetry-allowed transformation by the use of the transition metal dyz and dzx orbitals. Fig. I - (13) shows the spatial arrangement of the olefins and catalyst.

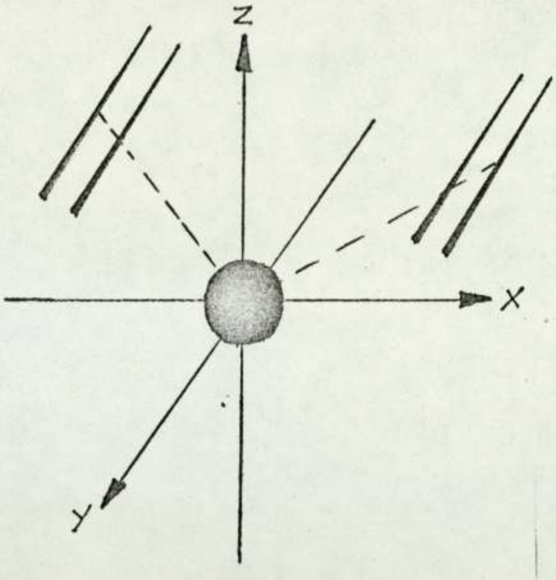
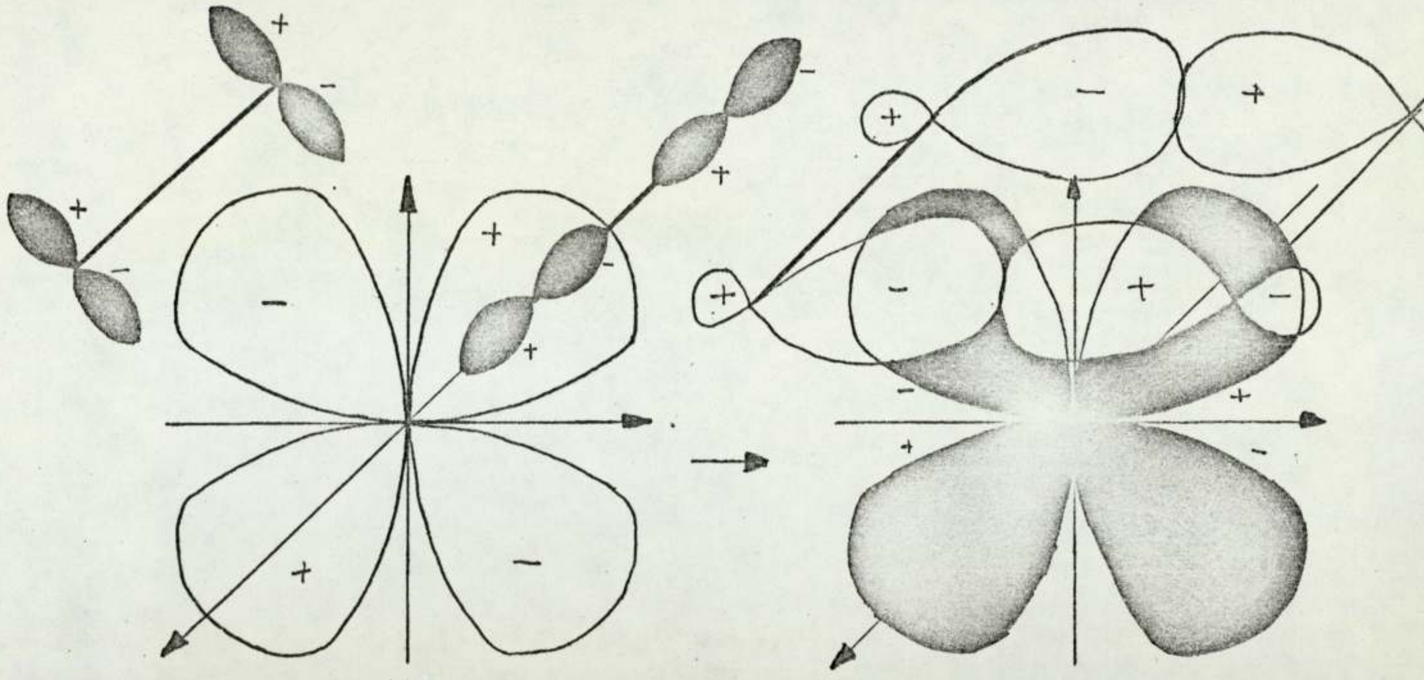


Fig.I - (13)

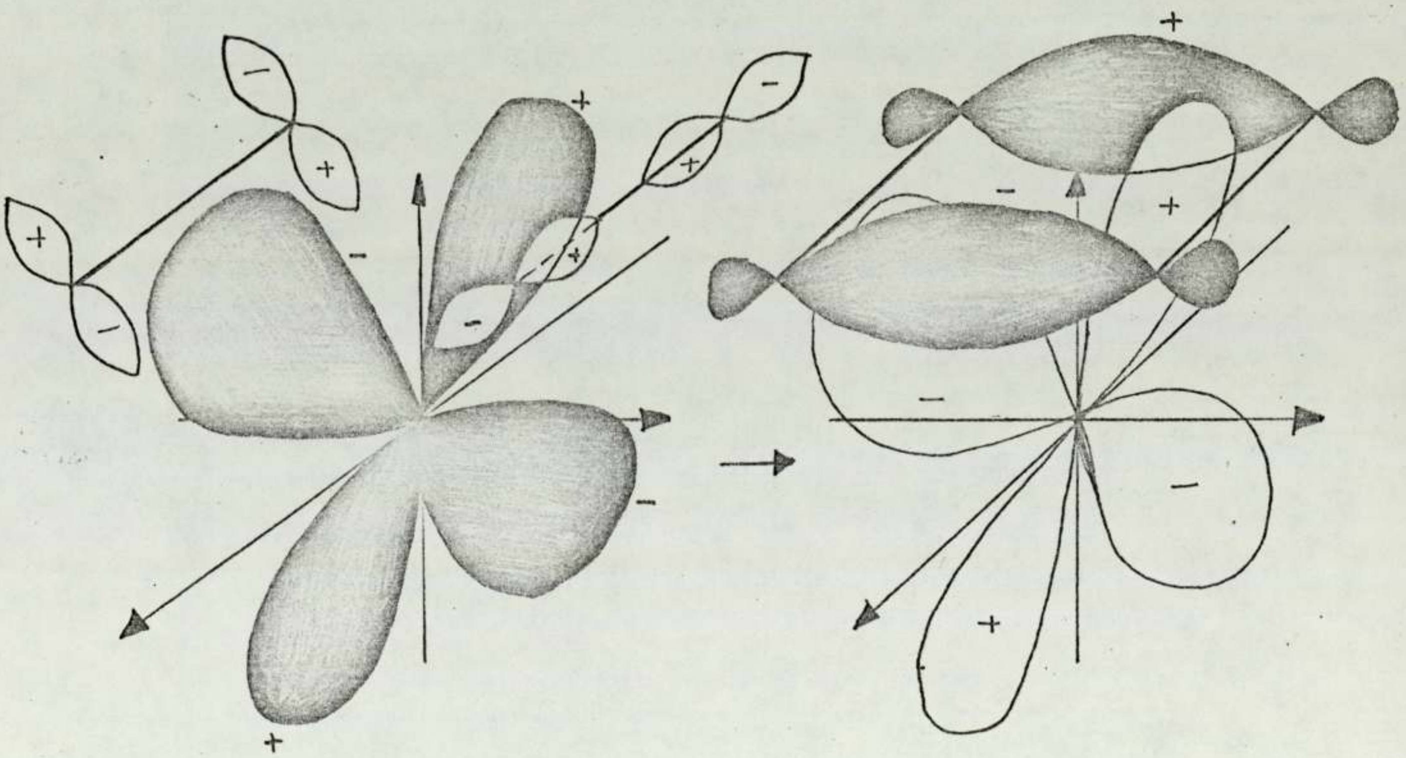
P_1 would be the zy plane and P_2 the zx plane. The positioning of the olefin ligands shown in fig.I - (xiii) would provide a ligand field which would split the energies of the dyz and dzx orbitals. A metal electron pair would occupy the lower energy dyz orbital forming the metal-olefin "back bond" through interaction with the olefin SA π* combination. The empty metal dzx orbital would accept an electron pair from the olefin AS π combination. This would be the electronic ordering essential to a concerted, ground state fusion of the olefin ligands, and if a relatively free flow of electron density was allowed, then a concerted reaction path would exist. The critical transfer of electron pairs is illustrated in fig.I - (14), the shaded orbitals showing the position of the electrons before and after the exchange.

Hence Mango and Schachtschneider showed that a cyclobutane intermediate for the metathesis reaction could be possible according to molecular orbital theory.



Olefin π Orbitals and
Metal dzx Orbital

Cyclobutane σ^* Orbital
and metal dzx Orbital



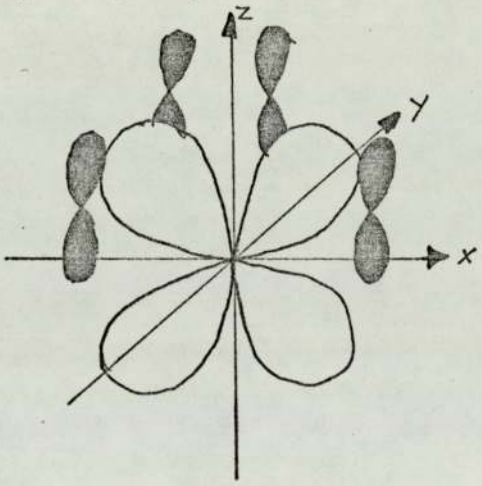
Olefin π^* Orbitals and
Metal dzy Orbital

Cyclobutane σ Orbital
and Metal dzy Orbital

Fig.I - (14)

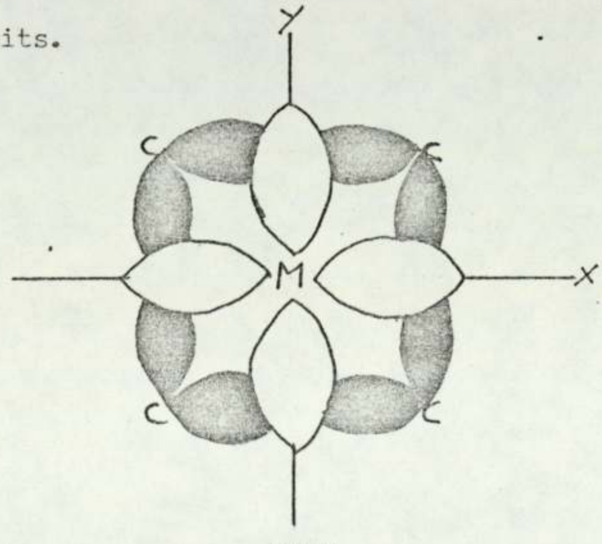
(b) The Tetramethylene Intermediate

This type of intermediate was proposed by Lewandos and Pettit[45] as an alternative to the "quasi-cyclobutane" intermediate. They felt that an alternative orbital symmetry pathway was required that was able to take into account the part played by the σ bonds of the ethylene molecules participating in the metathesis reaction. Their scheme involved the rupturing of the carbon-carbon σ bonds concurrently with the carbon-carbon π bonds so that a cyclobutane molecule was never formed. It was proposed that two ethylene molecules reacted with the transition metal to form a bis ethylene π complex XXXIV.



XXXIV

The complex XXXIV then rearranged into a multi-centred organometallic system XXXV in which the bonding was described as resulting from the interaction of a basic set of metal atomic orbitals and four methylenic units.



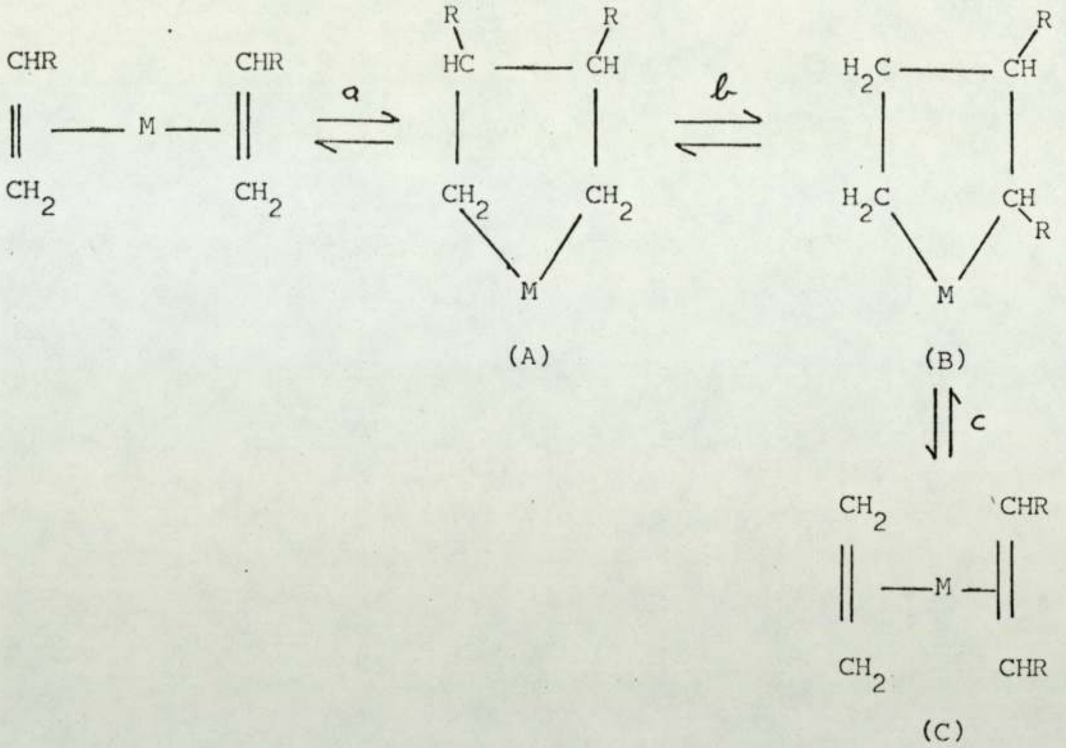
XXXV

The retraction of the complex XXXV along the x axis would then lead to the starting materials and the separation of XXXV along the y axis would lead to the reaction products.

The scheme was proposed after a study of a metathesis reaction of 4-nonene with a tetracarbonyl tungsten (W^0) catalyst. A feature of this mechanism was that in proceeding from the bis olefin π complex XXXIV to the tetramethylene complex XXXV the number of donor electrons provided by the olefinic ligands increased from four to eight. It was widely recognized that the most thermodynamically stable complexes of metals in zero or low oxidation states were those in which the inert gas rule was obeyed. In the 4-nonene metathesis reaction it was shown that alkylidene exchange resulted only under conditions which favoured the replacement of one CO ligand on the tungsten atom. If a carbonyl had not been removed from the transition metal complex during the transition state then there would have been excess electron donation by the olefin ligands and the inert gas rule would not have been obeyed.

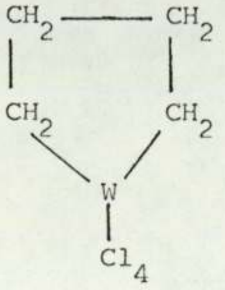
(c) The Metallocycle Intermediate

Grubbs and Brunck[46] proposed a metallocyclic intermediate for the metathesis reaction involving a metal to carbon σ bonded species. They cited the case of a metal carbon σ bonded intermediate discovered by Katz[47] for the rhodium catalysed rearrangement of strained carbocyclic ring systems as evidence that metal-carbon σ bonded species were known to be formed under similar conditions to those of the metathesis reactions. The proposed olefin metathesis mechanism is shown:



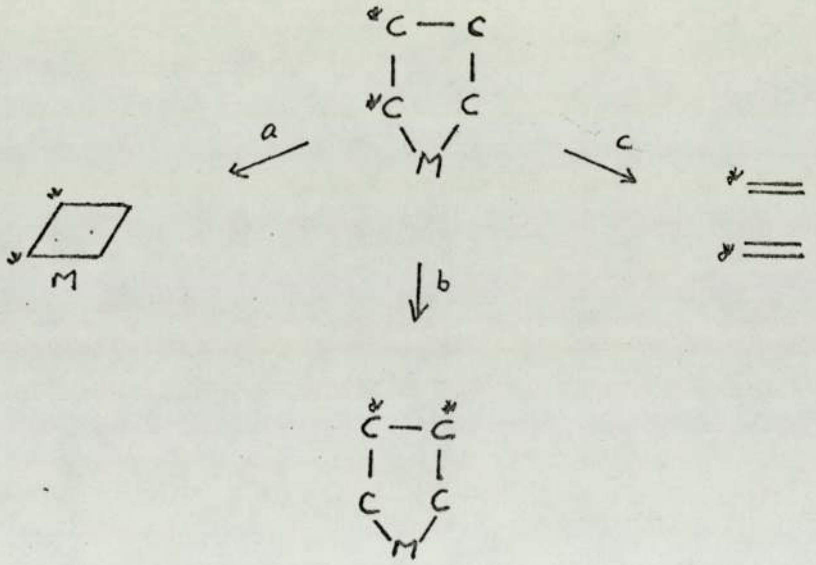
XXXVI

Grubbs stated that step (a) involved the rearrangement of the bis olefin complex into the metallocycle and that the metallocycle then underwent a rearrangement to yield the metallocycle (B). Step (C) was a direct reversal of step (a). He suggested that the rearrangement of A into B may have involved an unspecified symmetrical intermediate. To establish the feasibility of this mechanism Grubbs and Brunck investigated the reaction of WCl_6 with 1,4 dilithiobutane in benzene. They showed that ethylene was evolved quantitatively, and they suggested that it was formed by the breakdown of the complex shown below:



XXXVII

Experiments were carried out with deuterated dilithiobutane which showed definitely that rearrangements or metathesis occurred. The most difficult step of the proposed mechanism to interpret, was the rearrangement of (A) into (B). Three possible paths were considered[44] and they are shown below:



* denotes the identity of the carbon atom

XXXVII

(a) This pathway involved the reversible insertion of the metal into a cyclobutane ring. The cyclobutane-metal bond would have had to be maintained at all times, since there was no cyclobutane evolved during the reaction. Cyclobutane would not be capable of forming a strong bond with a metal atom and hence pathway (a) was not considered very likely.

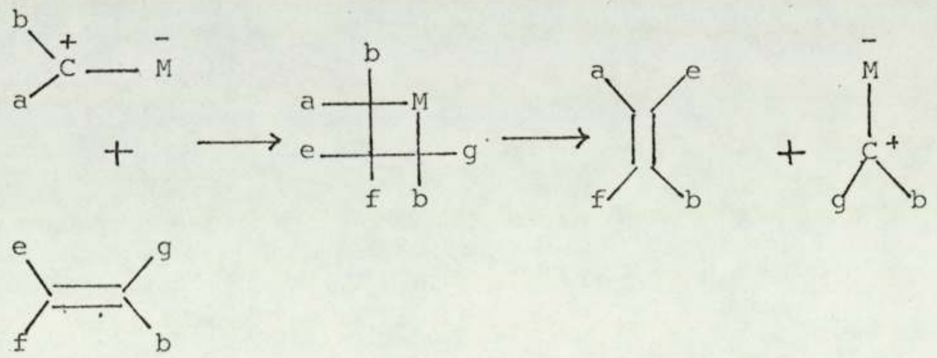
(b) This pathway suggested metal-carbon interactions across the ring, which would not be strong if the ring was planar.

(c) Pathway C suffered from symmetry restrictions which a d^2 metal would not be able to overcome, because it would have to become d^0 in the metallocycle.

Therefore, it was very difficult to show how the rearrangement from (A) to (B) could have occurred and hence the metallocycle intermediate lost a lot of credibility.

(d) The Chain Mechanism

The most recently proposed mechanism for the olefin metathesis reaction and the ring-opening polymerisations of cyclic olefins was proposed by Katz and McGinnis[47] who suggested a chain mechanism, which involved a four-membered metal-containing ring and a metal carbene as intermediates. Their reaction scheme is shown below:



XXXIX

They stated that since metal-carbenes[48] and four-membered rings containing metals[49] were known, and that additions of metal carbenes to olefins were common, their proposals required no unusual theoretical explanation and accounted for many of the known facts concerning the olefin metathesis reaction.

Each of the four proposed mechanisms have their merits and their drawbacks. They all provide low energy pathways for metathesis reactions, and they all account for a range of features of such reactions. Mechanism (a), the "quasi-cyclobutane" transition state, has some obvious drawbacks. Cyclobutane rings are unreactive with metathesis catalysts and are also virtually absent from the reaction products, although their formation would be conceivable according to the molecular orbital considerations by Mango and Schachtschneider[44]. Cyclobutane rings would imply severe steric restrictions and non-bonding interactions, especially in the case of the ring opening of small rings. The evidence for the tetramethyl intermediate in mechanism (b) is convincing but the system studied by Lewandos and Pettit may not have been typical. Reaction temperatures were high (approx. 100°C), whereas homogeneous metathesis catalysis usually occurs around 25°C, and the reaction was inhibited by excess olefin. (Generally, very high olefin: transition metal ratios are usual, 500:1, but in the tetramethylene system the proportions of olefin to transition metal were approx 1:1).

The metallocycle mechanism of (c) has several omissions and discrepancies. There appears to be no reason why the rearrangement <u>A</u> → <u>B</u> should occur, or why it should be rapid. Metallocycles of type <u>A</u> are not normally formed by ethylene, although there is some evidence that ethylene can form a metallocycle in a titanium complex[50]. It is not yet proven that metal-hydrogen bond formation is not involved in the transformation

$\underline{A} \rightarrow \underline{B}$, whereas experiments in other systems have excluded this route. The deuterated ethylenes formed from the reaction of WCl_6 with 1,4 dilithiobutane were not formed in the equilibrium proportions typical of the metathesis reaction. The chain mechanism of (d) seems to be a more satisfactory approach, but metal carbenes are usually only derived from electron-rich olefins. This mechanism also explains more easily how the ratios of products in metathesis of cycloolefins with unsymmetrically substituted acyclic olefins are obtained[47].

Hence, it can be seen that none of the mechanisms so far proposed for the metathetic ring opening polymerisation of cyclic olefins are entirely convincing, and it may be that the actual mechanism is a combination of several proposals. Also, no mechanism so far proposed offered any role to the metal alkyl (or comparable reagent) other than that of a reducing agent, or of a modifier of the base behaviour of the transition metal.

A polynuclear metal catalysed system has not been considered, although the formation of compounds with halogen or hydrogen bridges between tungsten and aluminium would be quite possible.

The aim of this project was to try and explore the kinetics of the ring-opening polymerisation of cyclooctene and cyclopentene and to use any kinetic results obtained, to try and elucidate the mechanism of the polymerisation. Very few, if any, kinetic studies had been previously carried out on the metathetic polymerisation reaction, mainly due to the difficulties in establishing a stable system for study, and the very rapid rates of polymerisation of cyclic olefins that were obtained, where the systems being studied were free from impurities. Hence, the first priority for a kinetic study of the ring-opening polymerisations of cyclic olefins was to establish a stable and impurity free system to study.

CHAPTER II

EXPERIMENTAL

II - (1) High Vacuum Line

The high vacuum line is shown diagramatically in fig.II-(1).

The high vacuum line was evacuated using an Edwards rotary vacuum pump assisted by a mercury diffüsion pump. Two cold traps were used to prevent solvent etc. from condensing in the oil in the rotary vacuum pump and to prevent mercury vapour from escaping into the laboratory. Liquid nitrogen was used as coolant for the cold traps. The pressure achieved in the high vacuum line was measured by the vacustat and was approximately equal to 10^{-5}mm Hg.

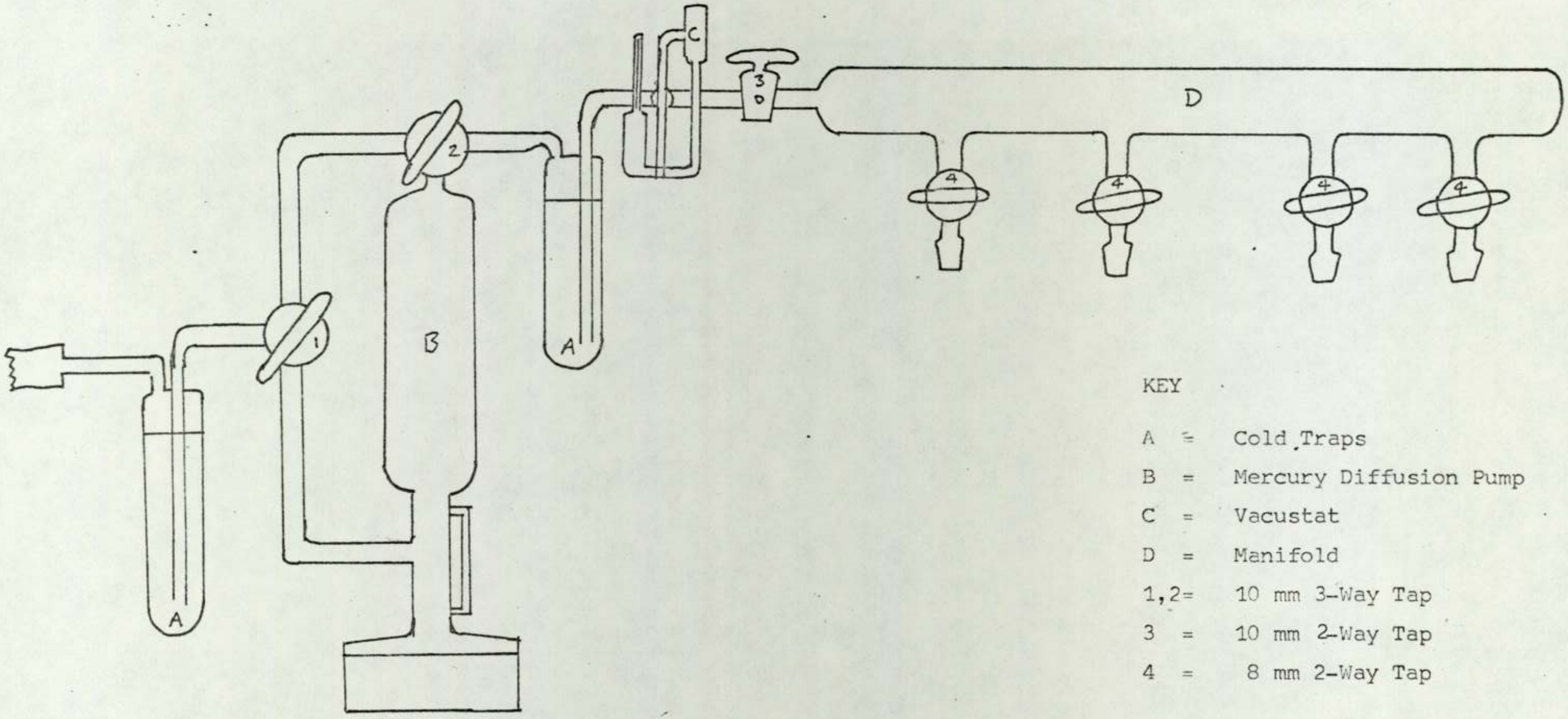
(i) Operations on the vacuum line

(a) Degassing of monomers, solvents, etc.

The flask containing the monomer or solvent to be degassed was attached to the vacuum line at the ground glass joints, at any of the (4) positions; tap 3 was closed and the appropriate tap 4 opened. A Dewar vacuum flask of liquid nitrogen was placed around the monomer/solvent flask and the liquid in the flask began to freeze. When the liquid was frozen tap 3 was opened and the manifold was evacuated until the pressure was approximately 10^{-3}mm of Hg. Tap 3 was then closed and the Dewar of liquid nitrogen was removed. The flask of liquid was gently warmed to room temperature and then refrozen. When frozen, tap 3 was re-opened and the evacuation procedure repeated. These freezing, warming and evacuating procedures were repeated until no gas bubbles escaped from the monomer/solvent on warming to room temperature.

(b) Trap to trap Distillations

A flask containing monomer or solvent was attached to the vacuum line at one of the positions (4) and the liquid was degassed as in (a). The contents of the flask could be transferred to a second flask attached to any of the other manifold taps by cooling the second flask in liquid nitrogen.



KEY

A = Cold Traps
B = Mercury Diffusion Pump
C = Vacustat
D = Manifold
1,2= 10 mm 3-Way Tap
3 = 10 mm 2-Way Tap
4 = 8 mm 2-Way Tap

Fig.II-(1)

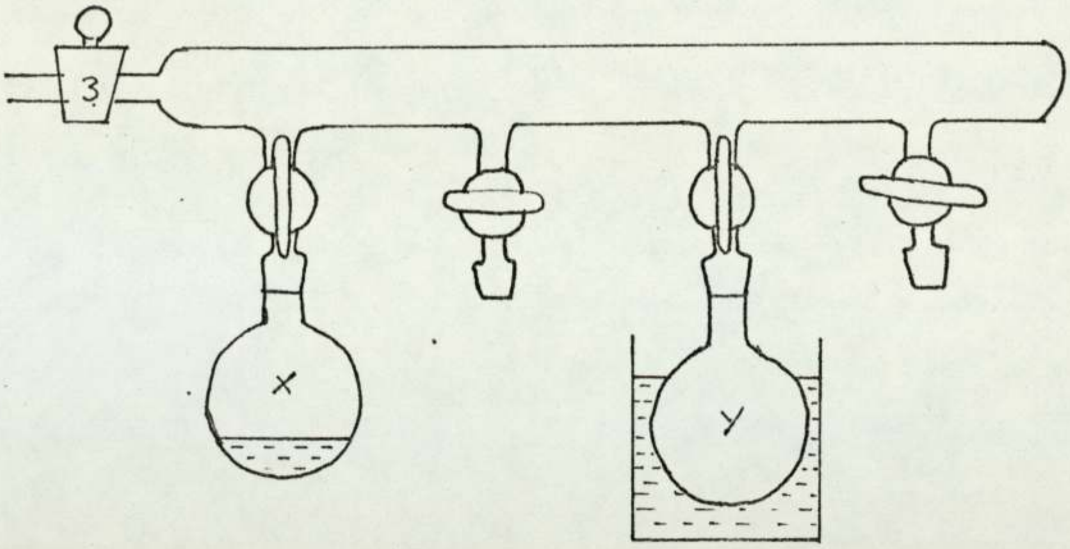


Fig.II-(2)

Flask Y was attached to the vacuum line and evacuated, flame dried and then allowed to cool. Tap 3 was then closed and a Dewar vessel containing liquid nitrogen was placed around flask Y. The relevant taps (4) were opened and the monomer or solvent contained in flask X distilled from flask X into flask Y. The rate of distillation could be increased by warming flask X with a warm air blower, or a bath of warm water.

(c) Storage of monomers and solvent

It was necessary to design storage vessels for monomers and solvents whereby the monomers and solvents could be stored over sodium metal and under vacuum.

500 ml flasks were used which had B_{19} necks, flat bottoms and a side arm with a "Rota-flo" greaseless tap and B_{19} socket. See fig.II-(3)

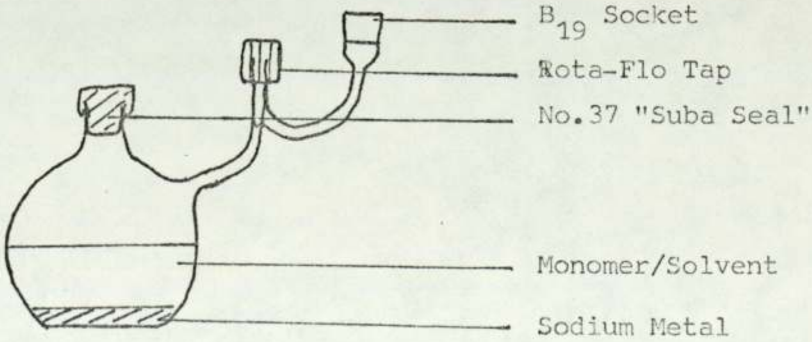


Fig.II-(3)

This vessel design was effective in several ways. It allowed the storage vessel to be easily removed from the vacuum line under vacuum when the "Rota-flo" tap was closed. The vacuum was maintained far more efficiently than with a greased tap and the absence of grease also minimized impurities.

Monomer or solvent was distilled into these flasks, which had already been flamed and the flasks were removed from the vacuum line under nitrogen. The "Suba Seal" was removed and a nitrogen bleed placed into the monomer/solvent. Sodium metal was sliced very thinly directly into the liquid under a stream of nitrogen. The "Suba-Seal" was replaced and the flask was returned to the vacuum line.

II-(2) Purification and Drying of Monomers and Solvent

(i) Cyclopentene

Cyclopentene was obtained from Koch Light laboratories. The purity of the cyclopentene was determined by gas chromatographic analysis which revealed that the cyclopentene contained traces of cyclopentadiene. The presence of cyclopentadiene was confirmed by adding small amounts of cyclopentadiene to cyclopentene and then examining the mixture by gas chromatography. One of the small peaks that had been observed in the gas chromatograph of the cyclopentene prior to the addition of cyclopentadiene was observed to have increased after the addition of cyclopentadiene.

Two methods were employed for drying cyclopentene:

(a) 100g of cyclopentene were shaken in a 250 ml round bottomed, single-necked flask with alumina, that had been activated by placing it in an oven at 350°C for four hours. The flask was then connected to the vacuum line and the cyclopentene/alumina mixture was degassed. The degassed cyclopentene was then distilled into a second flask which had previously been evacuated and flame dried. The second flask was a two-necked flask fitted with a "Suba Seal". 1 ml of aluminium tri-isobutyl was then added by injection from a syringe through the "Suba Seal" into the cyclopentene. Aluminium tri-isobutyl is a powerful drying agent and it reacts with water to yield aluminium hydroxide and isobutane. The cyclopentene was stored as an aluminium tri-isobutyl solution and was used as required.

This method was efficient for drying cyclopentene but unfortunately the cyclopentene, when distilled from this solution and analysed by gas chromatography, showed several new, although very minor, peaks. These new peaks were thought to be breakdown products of the aluminium tri-isobutyl.

(b) 100g of cyclopentene were placed in a 250 ml round bottomed, single necked flask and thin slivers of sodium metal were added. The flask was then attached to the vacuum line and the cyclopentene was degassed. The sodium metal was used to perform two functions:

(i) to remove water;

(ii) to react with cyclopentadiene present in cyclopentene.

Cyclopentadiene reacted with sodium to produce green cyclopentadienyl sodium. The cyclopentene was then distilled from the sodium metal into a second round bottomed flask, which contained more sodium and this distillation process was repeated until the cyclopentene sodium mixture remained colourless, when left for twelve hours. Gas chromatographic analysis of the cyclopentene at this point revealed the total disappearance of one of the small peaks, due presumably to cyclopentadiene.

Accordingly, method (b) was used for drying cyclopentene because of the ability of the sodium to remove any cyclopentadiene and cyclopentene was stored, under vacuum, over sodium metal.

(ii) Cyclooctene

Cyclooctene was obtained from Koch-Light laboratories in 1 litre bottles and was found on G.L.C. analysis to be 99.3 % pure. The cyclooctene was supplied with about 2% tertiary butyl catachol (not detected by G.L.C.) present as a stabilizer against oxidation. The tertiary butyl catachol was removed by shaking the cyclooctene with a 10% weight/volume solution of sodium hydroxide in a separating funnel and then washing the cyclooctene with distilled water. The cyclooctene was dried first with activated alumina and then under vacuum with sodium slivers. The cyclooctene was degassed in the same manner as cyclopentene. G.L.C. analysis of cyclooctene at this point showed that the amount of 1,3 cyclooctadiene present in the cyclooctene varied from batch to batch.

Attempts were made to remove this impurity because it was important to control the presence in the monomer of the amount of 1,3 cyclooctadiene, as conjugated dienes were known to react preferentially with the catalyst components[41], and thus affect the rate of polymerisation.

The amount of 1,3 cyclooctadiene in the cyclooctene batches was approximately 0.2% and several attempts, described below, were made to remove the impurity.

(a) Tungsten Hexachloride (WCl_6)

It was thought that the reason that 1,3 cyclo-octadiene had such a marked effect on the rate of polymerisation of cyclooctene may have been due to the preferential reaction of 1,3 cyclooctadiene with WCl_6. It was thought that the 1,3 cyclooctadiene may have been able to form a complex with the WCl_6 and thus a method of removing the 1,3 cyclooctadiene from cyclooctene might have been available. Therefore, solid WCl_6 was placed in a single necked flask and attached to the vacuum line. Cyclooctene was distilled from sodium metal on to it. The cyclooctene/WCl_6 solution was stirred for four hours with a magnetic stirrer and after this time the cyclooctene was distilled from the flask and a sample analysed by G.L.C. The chromatograph revealed, however, that there was no reduction in the concentration of 1,3 cyclooctadiene.

(b) Prepolymerisation

(i) Solid tungsten hexachloride was placed in a two necked flask and the flask attached to the vacuum line. 40 ml of cyclooctene were then distilled from sodium metal on to the WCl_6. The amount of WCl_6 used was calculated so that the molar ratio of 1,3 cyclooctadiene: WCl_6 was 1:1 (i.e. approximately 1.54×10^{-2} moles $litre^{-1}$ 1,3 cyclooctadiene for 7.7 moles $litre^{-1}$ cyclooctene).

The cyclooctene/WCl_6 solution was then stirred for five minutes and 0.25 ml of a 0.07M solution of aluminium tri-isobutyl were injected by syringe through a"Suba Seal". The cyclooctene polymerised very rapidly and it was not possible to distil from the polymerisate any unconverted monomer.

(ii) The same procedure was followed as in (i) except that much less WCl_6 (1.8×10^{-3} moles $litre^{-1}$) corresponding to a molar ratio of 1,3 cyclooctadiene : WCl_6 of 8.5:1 was used. The conversion of monomer to polymer was generally low and the unreacted cyclooctene was distilled into another flask and analysed by G.L.C. The chromatograph revealed a reduction in the amount of 1,3 cyclooctadiene present, but it was not removed totally. The above procedure was repeated three times but on each occasion, although more 1,3 cyclooctadiene was removed, the rate and amount of polymerisation increased and very little pure monomer was left after these successive polymerisations.

(c) Reduction of 1,3 Cyclooctadiene to Cyclooctene

Ziegler and Wilms[51] stated that 1,3 cyclooctadiene could be reduced to cyclooctene, by reaction with lithium and N-methyl aniline.

40 ml of cyclooctene were reacted with 0.244g of N-methyl aniline and 0.015g lithium, under vacuum, with di-ethyl ether as solvent and the reaction mixture was stirred for twelve hours. Analysis of the cyclooctene after this time showed that there had been no reduction in the amount of 1,3 - cyclooctadiene present.

(d) Copper I Complex with 1,3 - Cyclooctadiene.

Cuprammonium acetate was known to react with 1,3 cyclooctadiene to form a stable complex[52]. Cuprammonium acetate was prepared from Cu^{I} acetate and 8M ammonium hydroxide solution. The Cu^{I} acetate was prepared by the reaction of Cu^{II} acetate with anhydrous acetonitrile and copper powder[53]. Equal volumes of cuprammonium acetate and cyclooctene were shaken together in a separating funnel and the cyclooctene was then washed with distilled water. Analysis of the cyclooctene showed that there was no reduction in the concentration of 1,3 cyclooctadiene present.

Hence it can be seen that it proved impossible to remove all the 1,3 cyclooctadiene from cyclooctene and so the cyclooctene was used as obtained, dried and stored over sodium metal.

(iii) Toluene

Toluene was used as solvent during the polymerisation reactions and was supplied by B.D.H. G.L.C. analysis showed it to be rather impure. The toluene was refluxed with sodium metal for six hours and then fractionated on a five foot column packed with glass rings. 50ml fractions were taken and these fractions were analysed by G.L.C. The final purity of the toluene was about 99.6%. The pure toluene was dried with sodium metal under vacuum, degassed and stored on the vacuum line over sodium metal.

II - (3) Preparation of Catalyst Solutions

(i) Tungsten Hexachloride

Tungsten hexachloride was supplied by Pfaltz and Bauer Inc.U.S.A. as a 99% pure solid contained in sealed glass ampoules. The glass ampoule was opened under a stream of dry nitrogen, and the WCl_6 was divided into ten other ampoules and each was sealed under nitrogen. One of the smaller ampoules was then opened, in a stream of nitrogen, and approximately 0.5g of WCl_6 was weighed out into a single-necked 100 ml flask that had been dried in an oven and purged with dry nitrogen. The ampoule was immediately resealed. The flask containing WCl_6 was attached to the vacuum line and dry toluene was distilled into the flask. When a known volume of toluene had been distilled the flask containing the blue solution of WCl_6 in toluene was removed from the vacuum line, under nitrogen, and a "Suba Seal" was fitted to the neck of the flask. The WCl_6 solution was stored in a refrigerator, in the dark, because it was reported by Gunther[32] et al that WCl_6 could react with toluene at room temperature, in the presence of sunlight, to form reduced tungsten halides. The strength of the WCl_6 solution could be calculated from the weight of WCl_6 used and the volume of toluene added.

A more accurate check on the concentration was carried out by atomic absorption spectroscopy. There was found to be a close agreement between the two methods for the strength of the solution. The amount of chloride present in the WCl_6 solution was determined by the standard method of addition of excess silver nitrate solution. The excess of $Ag NO_3$ was determined by back titration with standard potassium thiocyanate solution.

(ii) Aluminium Tri-isobutyl

Aluminium tri-isobutyl was supplied as a pure liquid contained in a special steel vessel by Schuchardt of Munich. To make a solution of $Al(iBu)_3$ in toluene, toluene was distilled under vacuum into a previously weighed and dried flask and this flask was removed from the vacuum line under nitrogen and fitted with a weighed "Suba Seal". The flask was reweighed and hence the amount of toluene in the flask was known. A calculated amount of Al $(iBu)_3$ was withdrawn from the special container in an oven dried 1 ml syringe and injected through the "Suba Seal" into the toluene, thus preparing a 0.07 molar solution of $Al(iBu)_3$ in toluene.

Aluminium tri-isobutyl and tungsten hexachloride are both extremely sensitive to air and moisture and it was necessary to prepare fresh solutions of each at regular intervals.

II-(4) The Determination of the Rate of Polymerisation of Cyclopentene and Cyclooctene by Dilatometry

Three dilatometer designs were employed for following the rates of polymerisation of cyclopentene and cyclooctene.

(a) Electrical Dilatometer

See figure II-(4)

The electrical dilatometer is shown diagramatically in fig.II-(4). The resistance wire that is shown inside the capillary tube had a uniform resistance of 0.0283 $\Omega\ \text{cm}^{-1}$. This compared to the resistance of the mercury of $0.227 \times 10^{-4}\ \Omega\ \text{cm}^{-3}$. The total length of the resistance wire was 20 cm. The full scale deflection of the chart recorder was 5 mv and a power source of 1.5 volts was used.

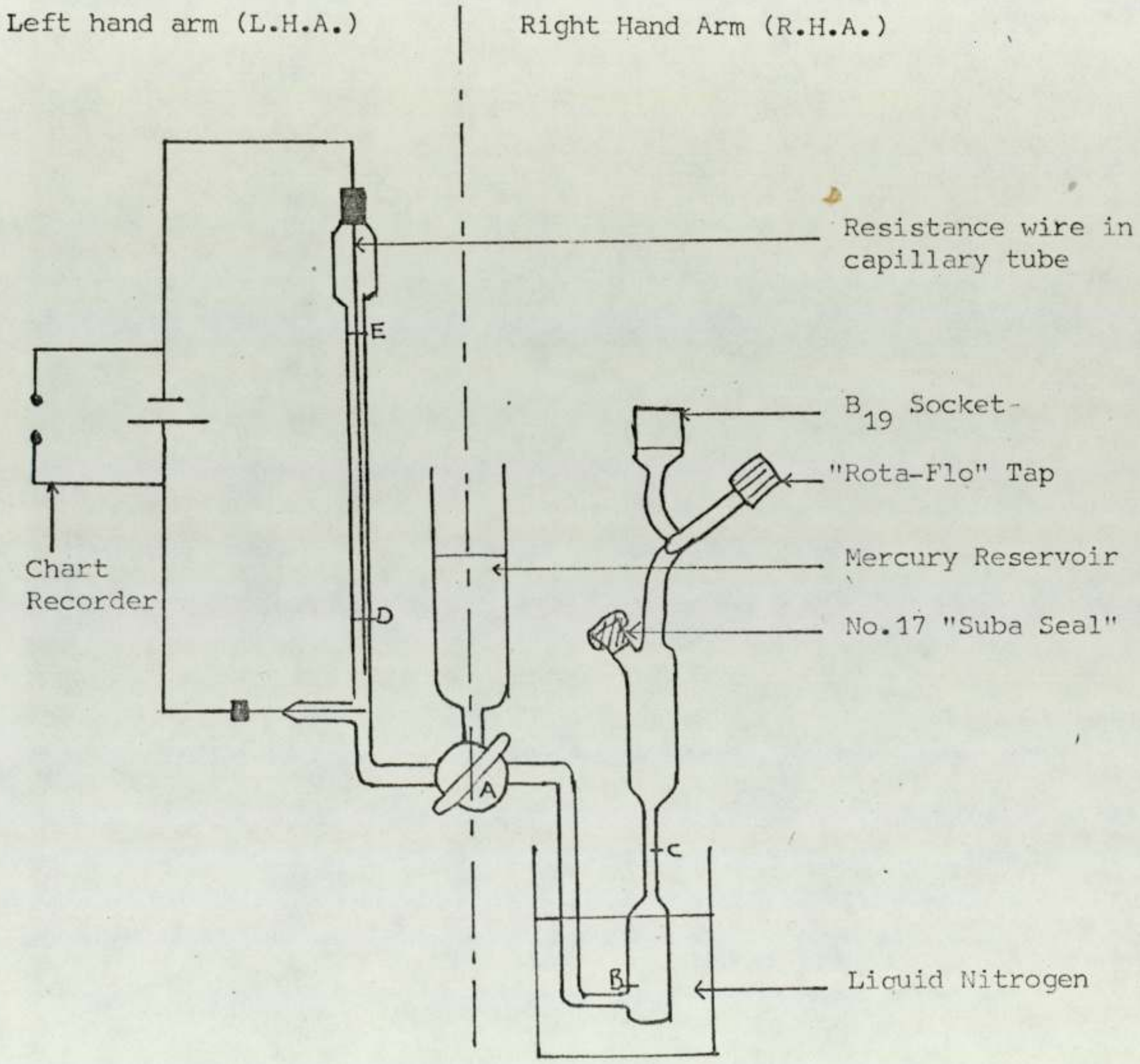


Fig.II - (4)

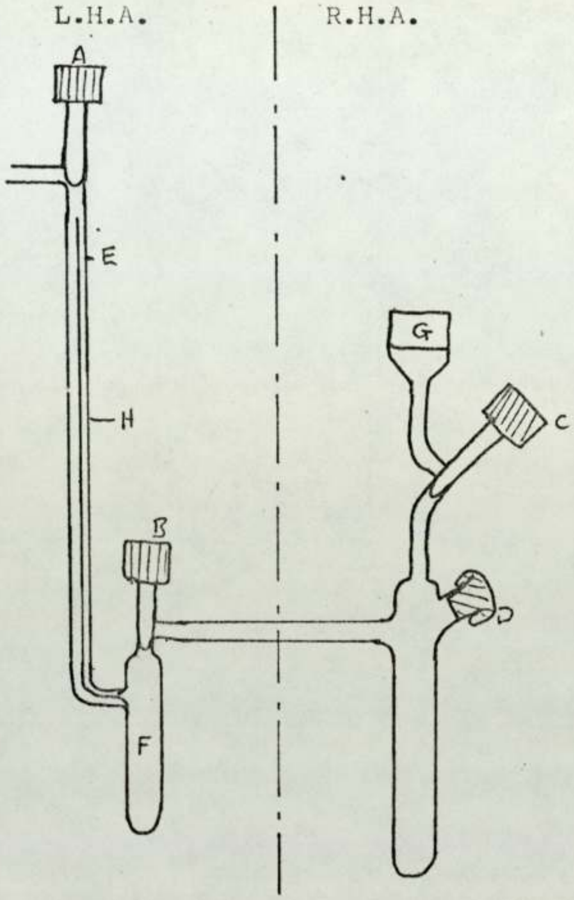
Function of Dilatometer (a)

The dilatometer was dried in an oven and whilst it was still warm the "Rota-flo" tap and the "Suba-Seal" were inserted and the mercury reservoir was filled. The tap A was used to connect the mercury reservoir with the capillary tube but the R.H.A. was isolated at this stage. The dilatometer was then attached to the vacuum line by the B_{19} joint and evacuated. The "Rota-flo" tap was then closed and mercury admitted to the R.H.A. by manipulating tap A. Mercury was allowed in as far as point B. A vessel containing liquid nitrogen was then placed around the lower part of the R.H.A., freezing the mercury and preventing its flow.

The "Rota-flo" tap was then opened and monomer and solvent were distilled into the R.H.A. up to point C. The "Rota-flo" tap was then closed and the liquid nitrogen bath removed, allowing the dilatometer to regain room temperature. Mercury from the reservoir was then allowed into the R.H.A. via tap A until the R.H.A. was completely full of mercury and monomer. The level of mercury in the L.H.A. of the dilatometer was then adjusted to point D and the two arms of the dilatometer were connected via tap A, thus isolating the reservoir. The calculated amount of catalyst, WCl_6 followed by $Al(iBu)_3$, solutions were then injected through the "Suba Seal". This injection of extra volume effected a change in mercury level in the L.H.A., from point D to point E.

The course of the polymerisation could then be followed on the chart recorder. As the monomer polymerised there was an accompanying decrease in volume which produced a drop in height of the mercury in the L.H.A. A greater length of resistance wire was exposed and an increase in the voltage drop across the power source which was reflected on the chart recorder.

(b) Dilatometer II



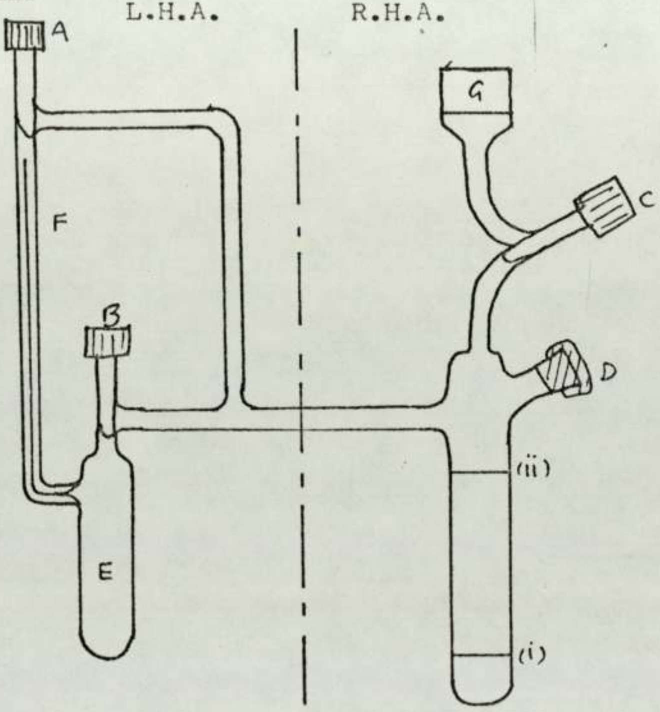
A,B,C = Rota-Flo Taps
D = B_{10} Socket and "Suba-Seal"
F = Bulb Volume 3.5ml
G = B_{19} Socket
H = Capillary Tube, Diameter = 1.5 mm

Fig.II-(5)

Operation of Dilatometer II

The dilatometer was set up as shown in fig.II-(5) with the three "Rota-flo" taps and the "Suba Seal" in place. The dilatometer was connected to the vacuum line by the B_{19} socket, taps A closed, B and C open. The evacuated dilatometer was then flamed out to ensure complete dryness. A Dewar flask containing liquid nitrogen was then placed around the lower portion of the R.H.A. and monomer was distilled into the dilatometer from a graduated tube. Solvent was then distilled in from another graduated tube. Tap C was closed and the dilatometer was removed from the vacuum line and placed in a water bath at 25°C for approximately twenty minutes. The dilatometer was removed from the water bath and the catalyst solutions were injected through the "Suba Seal" and mixed with the monomer/solvent solution by vigorously shaking the dilatometer. The dilatometer was tilted to allow the left hand arm to be filled completely. The dilatometer was then held vertically to allow the liquid level to reach point E and then tap B was closed. The dilatometer was returned to the water bath and the course of the reaction was followed by observing the decrease in height of the liquid meniscus in the capillary by means of a cathetometer.

(c) Dilatometer III



A,B,C = Rota-Flo Taps
D = No.17 "Suba Seal"
E = Bulb Volume 7.5 ml
F = Capillary Tube, Diameter 1.5 mm
G = B_{19} Socket

Fig.II - (6)

Operation of Dilatometer III

The operation of dilatometer III was very similar to that of dilatometer II. It was evacuated and flamed in the same way, except that tap A was open as well as taps B and C. Tap C was then closed and the dilatometer removed from the vacuum line and weighed. The dilatometer was returned to the vacuum line and monomer was distilled into the R.H.A. up to graduation mark (i). The dilatometer was removed from the line and re-weighed.

On returning the dilatometer to the line, the monomer was distilled from the R.H.A. into the L.H.A. and taps A and B were closed. Solvent was then distilled into the R.H.A. up to graduation mark (ii). The dilatometer was then weighed again and solvent was either distilled out of, or into, the dilatometer until the exact amount of solvent required for the individual experiment was present. Taps A and B were then opened and monomer and solvent were efficiently mixed. The rest of the procedure followed for dilatometer III was identical with that followed for dilatometer II.

II - (5) Analytical Techniques

(i) Gas Chromatography

Gas chromatography was used to determine the purity of monomers and solvent. The gas chromatogram used was the Perkin Elmer F.30.

(a) Preparation and packing of the gas chromatogram column

The column material was tritolyl phosphate supported on chromosorb P. Tritolyl phosphate was dissolved in methanol and the solution was mixed with the chromosorb support. The methanol was then removed using a rotary evaporator so that the column material was easily coated on to the support. The column was 12 feet of stainless steel with an outside diameter of $\frac{1}{8}$". The column material was packed into the column under vacuum. The column was then conditioned by placing it in the column oven and the temperature programmer was used to raise the oven temperature from 20°C to 110°C over a period of four hours. The column was then left at 110°C for twelve hours. The maximum operating temperature of the column was 115°C.

(b) Operating Conditions of the Gas Chromatogram

The gas chromatogram operating conditions for the monomers and solvent were essentially similar, except that the column oven temperature was lower for the analysis of cyclopentene than toluene and cyclooctene. The carrier gas was nitrogen at a flow rate of 30 $cm^3 min^{-1}$ and the detector was a flame ionisation detector using a hydrogen pressure of 20 p.s.i. and air pressure of 15 p.s.i. The detector was used at a sensitivity of 100. 1 ml samples of monomers and solvent were injected on to the column, the temperature of which was set at 60°C for cyclopentene and 110°C for cyclooctene and toluene.

(ii) Atomic Absorption Spectrophotometry

The concentration of tungsten atoms in WCl_6 solutions was determined by atomic absorption spectrophotometry.

(a) Principles of Atomic Absorption Spectrophotometry

A solution containing the element to be determined is aspirated into a flame of sufficiently high temperature to promote the dissociation of the molecules containing the metal atom to be determined. The atoms of the element will normally be in the ground state and will not emit radiation but they will be capable of absorbing radiation and so being promoted to higher electronic level. The frequency of radiation required to promote the sample atoms can be produced by a hollow-cathode discharge lamp, the cathode of which consists of the element to be determined. Radiation from the hollow cathode lamp is focussed on to the flame and from there on to the entrance slit of a monochromater. When pure solvent or blank solution is aspirated the deflection of the recording galvanometer is adjusted to read 100% transmittance. A solution containing the element to be determined is then aspirated and the metal atoms in the flame absorb radiation, the transmitted intensity of which decreases.

(b) Conditions for the determination of tungsten in WCl_6 Solution

The tungsten analysis was carried out by comparison of the unknown WCl_6 solution with a standard calibration graph, produced from a sodium tungstate standard solution. A standard solution containing 10,000 μg of tungsten per millilitre was made by dissolving 17.95g of sodium tungstate in 200 ml of deionised water, to which was added 100 ml of 10% (w/v) sodium hydroxide. This solution was diluted to 1 litre with deionised water.

The maximum concentration of a tungsten solution that could be determined by atomic absorption was 1500 μg/ml, hence the strength of the "unknown" WCl_6 had to be known approximately. This approximate strength was known gravimetrically. To produce a solution of tungsten for atomic absorption analysis which had a concentration below 1500 µg/ml, a known volume of WCl_6 in toluene, blue solution, was withdrawn from the storage flask and syringed into an excess of hydroxide solution. The blue mixture was shaken until clear. The aqueous solution was separated from the toluene and made up to 25 ml with deionised water. The calculated strength of this solution was then approximately 1000 µg/ml. For the determination of tungsten an acetylene - nitrous oxide flame was used.

The percentage absorption of this unknown tungsten solution was converted to absorbance using tables and this absorbance read off on the calibration graph to give the quantity of tungsten present in parts per million. The accuracy of an atomic absorption determination is about 2% (standard deviation expressed as a percentage of the element determined)[54].

(iii)The determination of Chlorine in a WCl_6 Solution

The estimation of chlorine in a WCl_6 solution was carried out by a titrimetric method. 5 ml of a WCl_6 solution in toluene were added to 10 ml of NaOH. The reaction:

$$8\ NaOH + WCl_6 \longrightarrow 6\ NaCl + Na_2WO_4 + 4\ H_2O$$

XXXX

occurred. The tungstate was then removed by addition of dilute HNO_3 so that tungstic acid was precipitated according to:

$$2\ HNO_3 + Na_2WO_4 \longrightarrow \downarrow H_2WO_4 \cdot 2H_2O + NaNO_3$$

XXXXI

The solution was then filtered and 5 ml of 6M HNO_3 and 14 ml of standard $AgNO_3$ solution were added to the filtrate.

$$NaCl + AgNO_3 \longrightarrow \downarrow AgCl + NaNO_3$$

XXXXII

The solution was then filtered again to remove the precipitated silver chloride and washed with 1% HNO_3. 2 ml of ferric alum indicator were added and the excess silver nitrate was determined by titration with standard potassium thiocyanate.

It was essential to remove the tungstate because of the reaction of silver nitrate with sodium tungstate:

$$2\ AgNO_3 + Na_2WO_4 \longrightarrow Ag_2WO_4 + 2\ NaNO_3$$

XXXXIII

(iv) Electron Spin Resonance Spectroscopy

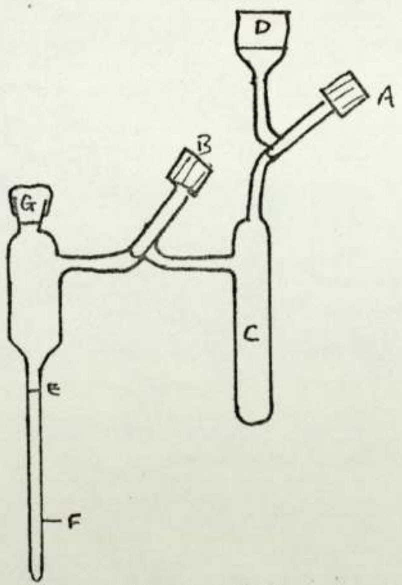
Electrons have a spin quantum number of $\frac{1}{2}$, and an unpaired electron subjected to a strong magnetic field will have two possible magnetic orientations in this field corresponding to two different energies. Transitions between these energy levels are allowed and the frequency of resonance is given by:

$$\nu = \frac{g\mu e H}{h}$$ where H is the applied field strength

Electrons in most atoms and molecules are paired and hence their total resultant spins are zero, but in the cases of certain transition element compounds and free radicals, unpaired electrons are involved and the environment of these electrons can be studied by electron spin resonance spectrometry

E.S.R. analyses of WCl_6 solution and WCl_6 + cycloolefin were carried out so that any e.s.r. absorbances could be examined. From work on the oxidation states of tungsten during the reaction of WCl_6 with cyclopentene[31] a reduction of WCl_6 to W(V) and W(IV) was thought to take place. These oxidation states are normally associated with unpaired electrons that occupy the metal *d*-orbitals.

Apparatus designed for the e.s.r. analysis is shown in fig.II-(7)



A,B = Rota-Flo Taps

D = B_{19} Socket

E = Graded Seal

F = "Spectrasil" Quartz Tube

G = No.17 "Suba Seal"

Fig.II-(7)

The apparatus was attached to the vacuum line by the B_{19} socket and evacuated with taps A and B open. Tap B was then closed and monomer was distilled into the bulb (C). Tap A was then closed and the apparatus removed from the vacuum line. The "spectrasil" quartz tube was inserted into the cavity of the e.s.r. spectrometer and the cavity was tuned. A quantity of WCl_6 solution was then injected through the suba seal into the quartz tube. The solution of WCl_6 alone was then examined for any possible e.s.r. absorptions.

Tap (B) was then opened and the monomer and WCl_6 solutions were mixed and this mixture was returned to quartz tube so the WCl_6/monomer solution was examined for unpaired electrons as soon as the monomer and WCl_6 had been mixed and also five minutes, thirty minutes, one hour and twelve hours after mixing.

(v) Infra-Red Analysis of Polymers obtained from Cyclopentene and Cyclooctene

Infra-red spectra of the polymers were used to indicate that they were polyalkenamers by observing absorbances at 10.35 μm (trans double bond) and 13.8 to 13.9 μm (cis double bonds). Absorbances at 8.0 and 8.5 μm indicated the presence of cyclic structures. The polymer samples were dissolved in chloroform and cast into thin films by allowing the chloroform to evaporate.

(vi) The determination of the densities of Polypentenamer and Polyoctenamer

The density of polypentenamer was determined by using a density gradient column and the density of polyoctenamer was calculated from the weight of the polymer in air and the weight of the polymer in pure methanol. Samples of both polymers were prepared in the same way by dissolving the polymer in chloroform and then precipitating in methanol, three times. The polymers were dried in a vacuum oven at 25°C.

The density gradient column was constructed by adding 10 solutions of carbon tetrachloride and xylene of varying concentrations, (100% CCl_4 $\longrightarrow$ 100% xylene), to a 250 ml measuring cylinder. The density gradient up the column was measured by using floats of known density and the density of these floats plotted against their position in the column. A sample of polypentenamer, about 1 mm diameter, was then dropped into the column and its position noted. The density corresponding to this position was read from the calibration graph.

(vii) Determination of molecular weights of Polypentenamer samples by viscosity

The viscosity average molecular weight of a polymer is given by the equation,

$$[\eta] = K\bar{M}_v^{\,a}$$

Where K and a are constants for a given polymer/solvent system, at any particular temperature, $\bar{M}v$ is the viscosity average molecular weight and $[\eta]$ is the intrinsic viscosity. $\bar{M}v$ approaches the weight average molecular weight, $\bar{M}w$, as (a) increases towards its maximum value of 0.8. $[\eta]$, the intrinsic viscosity of the polymer solution is related to the specific viscosity by the expression -

$$\left[\frac{\eta_{sp}}{C}\right]_{\lim C \to 0} = [\eta]$$

Where C is the concentration of the polymer solution,

and $\eta_{sp} = \dfrac{\eta - \eta_o}{\eta_o}$ where η = viscosity of the solution

η_o = viscosity of the solvent.

Apparatus for measuring the viscosity of the polymer solutions is shown in fig. II-(8)

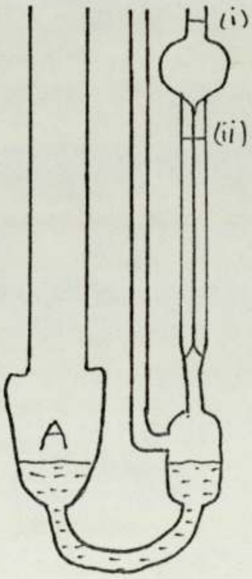


Fig.II-(8)

Procedure

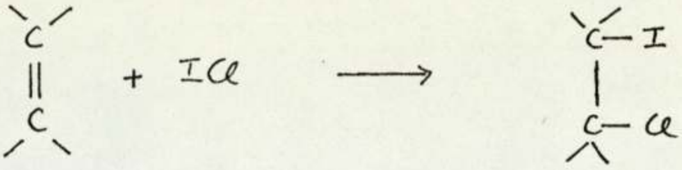
A solution of polypentenamer of known concentration was prepared in toluene. The solvent and the solution were filtered separately through sintered glass filters into clean dry flasks. Solvent was placed in bulb A and the viscometer was immersed in a water bath at 30°C. The solvent was drawn up through the capillary to beyond graduation mark (i). The time (t_o) for the solvent meniscus to flow between marks (i) and (ii) through the capillary tube was noted. The procedure was repeated to check that the flow times were reproducible. This solvent flow time was proportional to the viscosity of the solvent. The viscometer was then emptied of solvent and washed and dried. The filtered polymer solution was placed in bulb A and the flow time (t) of the polymer solution was determined in the same way as for the solvent. The polymer solution in bulb A was then diluted by the addition by pipette of more solvent and the solution was mixed by blowing air, saturated with solvent vapour, down the central viscometer tube. The average flow time of this concentration of polymer solution was observed. Successively dilute solutions were obtained by the addition of filtered solvent and the flow times of each were determined.

A graph of $\left[\eta_{sp}/C\right]$ against C was obtained by plotting $1/C\left(\frac{t-t_0}{t_0}\right)$ against C and $[\eta]$ was obtained by extrapolating this plot to infinite dilution.

(viii) Determination of the degree of unsaturation of a copolymer of cyclopentene and cyclooctene

Copolymers of cyclopentene and cyclooctene were prepared with different concentrations of cyclopentene and cyclooctene present at the start of the reaction. The composition of the copolymer was obtained by analysing the polymers for unsaturation by using iodine monochloride. The results obtained were checked (in one case only) by N.M.R. spectroscopy.

The routine procedure for the determination of unsaturation by iodine monochloride is to add an accurately known excess of I Cl to a solution of the polymer in a chlorinated solvent and to determine the excess I Cl after a suitable period by thiosulphate titration. The reaction of iodine monochloride with olefins is addition to the double bond:



Interfering side reactions can be of three types:

(a) Substitution reactions

(b) Splitting-out reactions yielding hydriodic acid

(c) Further addition of iodine monochloride to the product obtained from splitting out.

Lee, Kolthoff and Johnson[56] have shown that the following sequence of reactions occurs:

(1) $C_nH_{2n} + I\,Cl \xrightarrow{\text{very fast}} C_nH_{2n}\,I\,Cl$ (normal addition)

(2) $C_nH_{2n}\,I\,Cl \xrightarrow{\text{fast}} C_nH_{2n-1}Cl + HI$ (splitting out)

(3) $HI + I\,Cl \xrightarrow{\text{very fast}} I_2 + H\,Cl$

(4) $C_nH_{2n-1}\,Cl + ICl \longrightarrow C_nH_{2n-1}\,I\,Cl_2$ (second addition)

In developing the procedure for the analysis the problem is to define conditions so that substitution is negligible (short time of reaction) while reaction (1) proceeds rapidly to completion and reaction (4) is suppressed. Reactions (2) and (3) occurring together will not alter the total iodometric titration, which will be the same as if only reaction (1) occurred.

The procedure adopted was that which Lee, Kolthoff and Mairs[57] used for polybutadiene. A 0.11M iodine monochloride solution was prepared by adding 17.8g of I Cl to 1 litre of dry chloroform and the solution stored in the dark. A 0.1M solution of sodium thiosulphate was prepared and standardised against potassium iodate. 80 mg of polypentenamer/octenamer copolymer was weighed into a conical flask and dissolved in 80 ml of chloroform. 20 ml of the iodine monochloride solution were added and the reaction mixture allowed to stand at room temperature for one hour.

50 ml of distilled water containing 0.5g of potassium iodide were added to the flask and the reaction mixture was stirred with a magnetic stirrer and titrated with thiosulphate solution. Starch was added near the end point. A blank, containing no polymer, was prepared and titrated in the same way.

CHAPTER III DILATOMETRY

III-(1) Dilatometric Principals and Design

Dilatometers are instruments that were used originally for measuing the thermal expansion or contraction of liquids or solids. A contraction in volume is normally associated with the polymerisation of unsaturated compounds and these instruments were adapted to study these reactions. Dilatometry was first employed by Starkweather and Taylor[58] to measure the rate of polymerisation of vinyl acetate. The dilatometric method produces more meaningful results for systems in which the polymer is soluble in its own monomer or the solvents used during polymerisation. Both polypentenamer and polyoctenamer are soluble in their own monomers as well as the solvent toluene.

A dilatometer for studying rates of polymerisation consisted of:

(a) A reaction vessel;

(b) a volume-sensing device;

(c) filling, stirring and temperature control apparatus.

The design of the dilatometer depends upon the nature of the reactions studied and the type of data required. The size and design of the reaction vessel is governed by the accuracy desired, the expected volume change, the rate of heat evolution and the stirring requirements. The change in liquid level in a capillary attached to the reactor furnishes a sensitive method of measuring the volume change associated with the polymerisation. Capillaries with internal diameters as small as 0.04 cm have been used,[59] but normally the capillary tube has a diameter of 0.1 to 0.2 cm.

When the dilatometer is immersed in a constant temperature bath the contents will change volume until thermal equilibrium with the bath is reached. It is necessary that the temperature of the bath be controlled as closely as possible to prevent fluctuations in the meniscus height caused by thermal expansion or contraction. Control of the bath temperature with an accuracy of ± 0.01°C is necessary for accurate determinations of rates of polymerisation at low conversions, whereas less accurate temperature control, (± 0.1°C), suffices under conditions of greater total volume change.

The measurement of the volume change occurring during the polymerisation reaction can be made either by direct observation of the liquid meniscus in a graduated capillary, or by the use of a cathetometer.

III-(2) Treatment of Dilatometric Data

The major problem in interpretation of dilatometric data is the establishment of the precise relationship between the density of the monomer-polymer solution and the polymer concentration.

Additivity of monomer and polymer volumes, as experienced in an ideal thermodynamic solution process, would permit the use of the equation:

$$V_{ps} = \left[(\text{wt } \%p)V_p + (\text{wt } \% m)V_m\right] / 100,$$

to calculate the specific volume of a polymer solution as a function of its concentration. In terms of the densities of the monomer, polymer and solution:

$$\rho_{ps} = 100 \Big/ \left[(\text{wt}\% \, p/\rho_p) + (\text{wt}\% \, m/\rho_m)\right]$$

where ρ = density,

V = specific volume,

ps = polymer solution,

p = polymer,

m = monomer.

This relationship was confirmed, within experimental error, by Starkweather and Taylor[58].

In the above treatment an estimation of the density of the polymer must be made and this in fact may vary with its number average degree of polymerisation. However, East, Margerison and Pulat[64] showed that an expression for the change of volume (ΔV), associated with the production of a linear polymer, could be expressed in terms of the density of high molecular weight polymer alone:

$$\Delta V = \left({}^{1}/\rho_p - {}^{1}/\rho_m \right) \Delta W_m$$

where ΔW_m represents the mass of monomer converted to polymer in the reaction mixture. This expression involved only the use of the density of high molecular weight polymer, even though low molecular weight material could be the only product of the reaction, because the volume change originated solely from conversion of monomer molecules to monomer units in the polymer chains. The weight fraction of end groups remained unchanged during the polymerisation.

III-(3) Dilatometer designs employed for observing the rates of polymerisation of cyclopentene and cyclooctene

I An automatically recording dilatometer

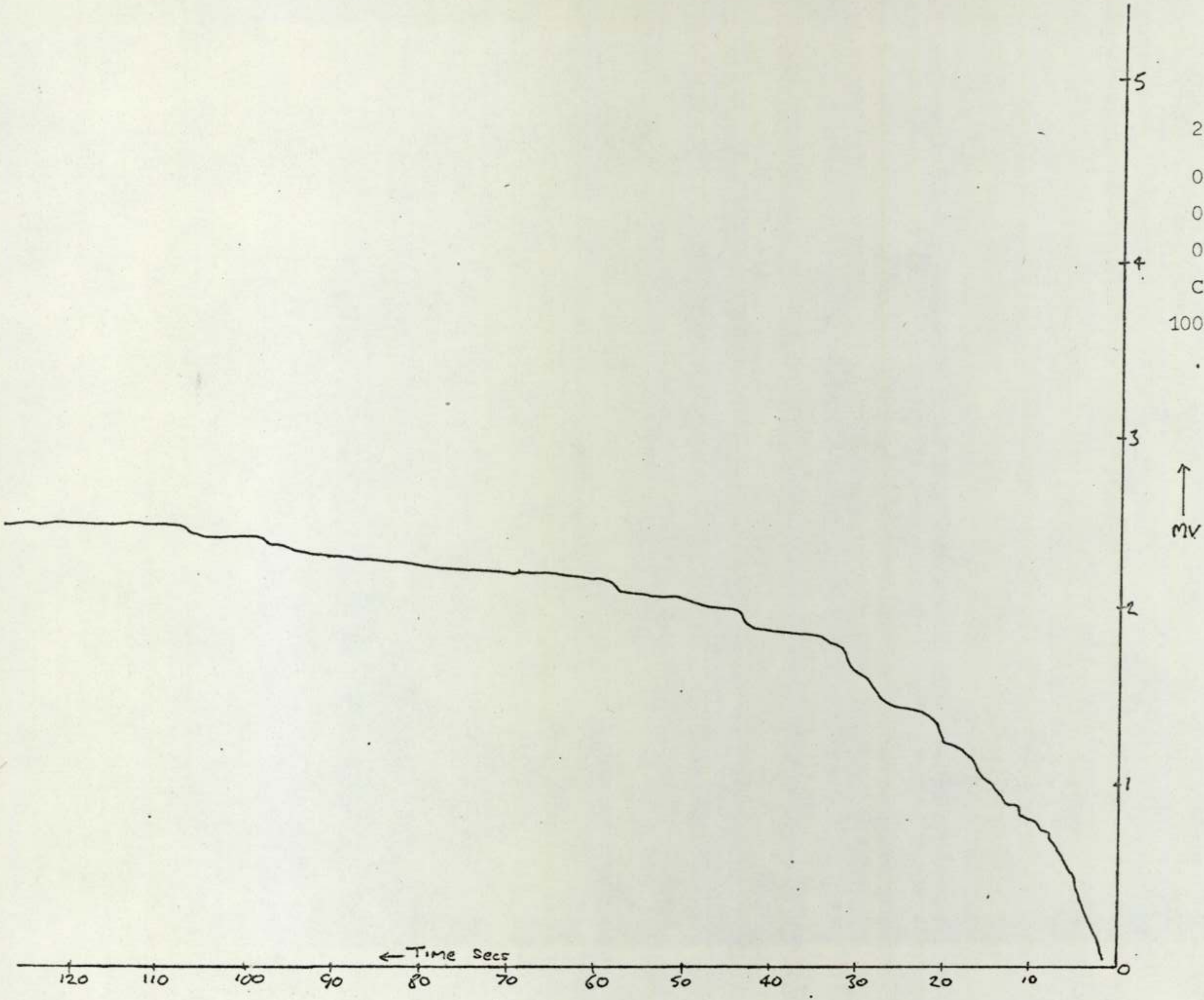
Dilatometer I is shown in figure II-(5) and its method of operation has been described in section II-(3)-(iv). This dilatometer was designed so that very fast initial rates of polymerisation could be followed. The first few minutes of the polymerisation could also be recorded because, as soon as the catalyst components were injected through the "Suba-seal", they were effectively mixed with the monomer/solvent by the force of the injections, and the drop in height of the mercury thread was immediate and sensitive. Hence initial rates of polymerisation could be recorded from time zero.

In a typical polymerisation 1ml of cyclopentene and 4ml of toluene were distilled into the apparatus as described in section II-(3)-(iv). When the mercury thread had been correctly adjusted 0.15 ml of a 0.075 molar solution of WCl_6 followed by 0.30 ml of a 0.075 molar solution of $Al(iBu)_3$ were added. These concentrations of catalyst -

($WCl_6 = 2.0 \times 10^{-3}$ moles litre^{-1}, $Al(_iBu)_3 = 4.0 \times 10^{-3}$ moles litre^{-1}) produced a high rate of polymerisation which would have been impossible to follow without some automatic recording device. The recorder trace obtained from this polymerisation is shown in fig.III-(1).

The advantage of using a high catalyst concentration was that a higher level of impurity of monomer or solvent could be tolerated.

The disadvantages of dilatometer design I centred around the state of dryness and purity of the mercury used in the dilatometer. Trebly distilled mercury was used which was dried by refluxing under vacuum in a flask attached to the vacuum line. The mercury was then transferred to the dilatometer reservoir and during this time could have absorbed water. The mercury was not redistilled and hence could well have contained impurities. Freshly dried mercury was used for each reaction. The mercury also adhered to the resistance wire and caused the recorded trace to be



20% CP/TOL

0.0113 moles CP

0.0000113 moles WCl_6

0.0000227 moles $Al(iBu)_3$

CP : W : Al

1000 : 1 : 2

Fig.III-(1)

stepped. This situation was improved when the resistance wire was cleaned with a fine emery paper.

The results obtained from this dilatometer were totally unreproducible mainly due to the concentration of water in the mercury. In many reactions the WCl_6 was hydrolysed before the $Al(iBu)_3$ had been added and as there was no apparent way of keeping the mercury separate from the reactants, or of maintaining a consistent level of dryness or purity in the mercury, this method was not considered suitable for accurate, reproducible measurement of the rate of polymerisation.

The results obtained by the use of dilatometer I came only from a study of the initial rates of polymerisations of cyclopentene as a function of the concentration of $Al(iBu)_3$. The concentrations of cyclopentene and WCl_6 were kept constant and three reactions were carried out, the various concentrations of $Al(iBu)_3$ of which are shown in table III-(1).

Table III-(i) The dependance of the initial rates of polymerisation of cyclopentene on the $[Al(iBu)_3]$ using dilatometer I

$\left[\dfrac{\text{concentration of Al(iBu)}_3}{\text{moles litre}^{-1}}\right] \times 10^3$	$\left[\dfrac{\text{Initial rate of polymerisation}}{\text{millivolts minute}^{-1}}\right] \times 10$
1.7	1.6
2.1	1.1
4.2	6.8

$[\text{Cyclopentene}]$ = 2.14 moles litre^{-1}

$[W\ Cl_6]$ = 2.1×10^{-3} moles litre^{-1}

Although no reliance can be placed upon these results, the great increase in the initial rate of polymerisation observed at a Al:W molar ratio of 2 was in agreement with the literature[32].

II Design of a conventional dilatometer

A dilatometer of a more traditional design, shown in fig.II-(6), was used to study the rate of polymerisation of cyclopentene. The operation of dilatometer II has already been described in section II-(3). In a typical polymerisation 3.5 ml of cyclopentene were distilled into the right hand arm (RHA) and the dilatometer was placed in the constant temperature bath for approximately 20 minutes. The temperature control of the bath was $\pm$ 0.01°C at 25°C. The dilatometer was then removed from the bath and 0.02 ml of a 0.036 molar solution of WCl_6 were added, followed by 0.02 ml of a 0.07 molar solution of $Al(iBu)_3$. The monomer and catalyst components were effectively mixed by shaking the dilatometer. The contents of the dilatometer were then poured into the reaction bulb in the left hand arm (LHA) and the appropriate "Rotaflo" tap closed and the dilatometer was returned to the water bath. The rate of polymerisation of cyclopentene was determined, by following the decrease in the meniscus height using a cathetometer, as a function of time. The result is shown in figure III-(2).

The main disadvantages of this dilatometer were the small size of the reaction bulb and the difficulties encountered while filling the LHA of the dilatometer with an unbroken thread of liquid. The small size of the reaction bulb meant that very small quantities of catalysts were required to produce rates of polymerisation that were not too fast to follow and also the maximum decrease in meniscus height that could occur was small. It was very difficult to fill the capillary of the dilatometer with an unbroken thread of liquid and, as can be see from fig.III-(2), the initial observation of the meniscus height took place after nine minutes of the reaction was over. Previous gravimetric studies of the polymerisation of cyclopentene, cited in the literature, suggested that a substantial amount of polymerisation takes place in the first ten minutes of the reaction and hence it was important to observe as much of the initial stages of the reaction as possible.

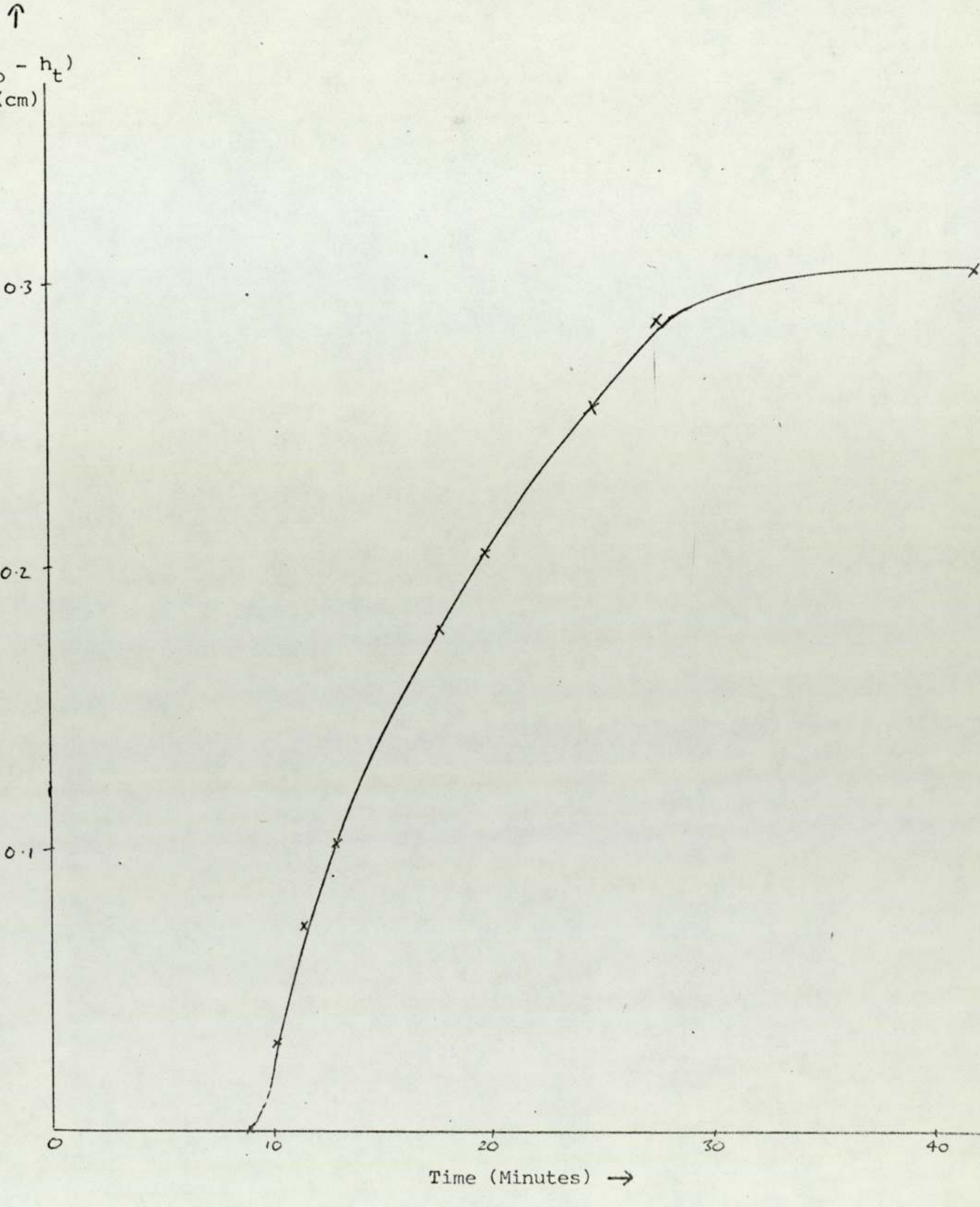


Fig.III-(2)
Polymerisation of Cyclooctene using Dilatometer II

III Modifications to design of dilatometer II

The principal disadvantages of the previously described dilatometer were the difficulty experienced in filling the device and the small size of the reaction bulb. A modification of the design of dilatometer II is shown in figure II-(7) as dilatometer III, and incorporated a pressure levelling tube and an increased bulb capacity of 7.5 ml as compared to the 3.5 ml of dilatometer II. The pressure levelling tube allowed the bulb to be filled much more easily with an unbroken liquid thread in the capillary tube. This meant that the height of the meniscus in the capillary could be read sooner than in dilatometer II and much less of the initial stage of the reaction was unrecorded. The increase in size of the reaction bulb meant that a greater variation in monomer concentration could be used and the instrument was sufficiently sensitive at low concentrations of monomer. A typical polymerisation of cyclopentene involved the distillation of 1 ml of cyclopentene into the RHA followed by 6.5 ml of toluene. The dilatometer was then placed in the constant temperature bath for approximately 20 minutes. The bath temperature was $25^{\circ}C \pm 0.01^{\circ}C$.

The dilatometer was then removed from the constant temperature bath and 0.38 ml of a 0.026 molar solution of WCl_6 were injected through the "Suba Seal" followed by 0.44 ml of a 0.07 molar solution of $Al(iBu)_3$. The dilatometer was shaken to mix the contents and then tilted so that the reaction bulb and capillary tube were filled with the reaction mixture. The appropriate taps (see Section II-(3)) were then closed and the dilatometer was returned to the constant temperature bath. The rate of polymerisation was again determined by following the decrease in meniscus

Polymerisation of Cyclopentene using Dilatometer III

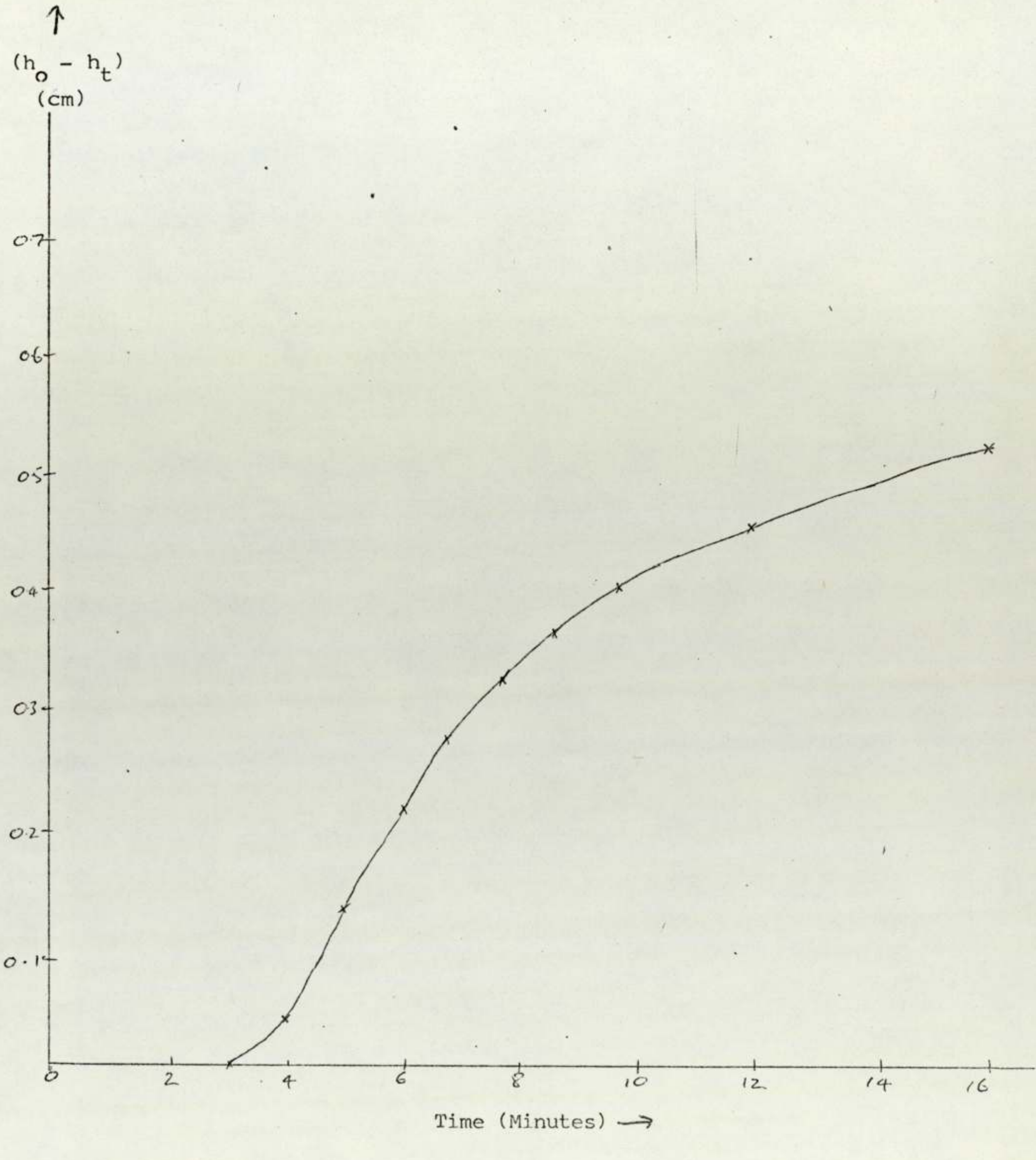


Fig.III-(3)

height as a function of time, by use of a cathetometer. The results for this reaction are shown in figure III-(3).

The improvements in design of dilatometer III over dilatometer II were the ease of filling the reaction bulb and capillary tube, which enabled the initial stages of the reaction to be followed from approximately three minutes after the addition of the $Al(iBu)_3$, as can be seen in fig.III-(3), and the increased size of the reaction bulb which allowed a greater variation in monomer and catalyst concentractions without detriment to the sensitivity of the dilatometer. The mixing characteristics that were good in dilatometer II were maintained in dilatometer III.

The design of dilatometer III was such that it was felt that the reproducibility of conditions of temperature, concentrations of monomer, catalysts and solvent, dryness of apparatus and manipulation of the dilatometer itself, were adequate for a study of the kinetics of the polymerisations of cyclooctene and cyclopentene to be undertaken.

III-(4) Calculation of the initial rates of polymerisation of cyclooctene and cyclopentene from dilatometric data

East, Margerison and Pulat[64] showed that the volume change involved in the production of linear polymers could be related to the density of the monomer and the density of high molecular weight polymer alone. Hence the change in volume, (ΔV) produced when monomer is completely converted into polymer would be :

$$\Delta V = M \frac{(\rho_m - \rho_p)}{\rho_m \rho_p}$$

where M is the weight of monomer at the start of the reaction and ρ_m and ρ_p are the densities of monomer and polymer respectively.

This change in volume can be related to a theoretical change in the height of the meniscus in the capillary tube of the dilatometer at 100% conversion of monomer to polymer by the expression:

$$\Delta h_\infty = \frac{\Delta V}{\pi r^2}$$

where r is the radius of the capillary. The initial rate of polymerisation, (Δh_1), expressed as a rate of change of meniscus height may be obtained from the tangent drawn to the curve of Δh as a function of time, (cm s^{-1}) at time zero.

The initial rate of polymerisation, (percentage conversion per second), is written as

$$Rp = \frac{\Delta h_1}{\Delta h_\infty} \times 100$$

or

$$Rp_{.} = \frac{\Delta h_1}{\Delta h_\infty} \times 100 \times X \text{ moles litre}^{-1}.s^{-1}$$

where X is the initial concentration of monomer expressed in moles litre^{-1}.

III-(4) Calculation of the initial rates of polymerisation of cyclooctene and cyclopentene from dilatometric data

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or

$$Rp. = \frac{\Delta h_1}{\Delta h_\infty} \times 100 \times X \quad \text{moles litre}^{-1}.s^{-1}$$

where X is the initial concentration of monomer expressed in moles litre^{-1}.

CHAPTER IV

THE POLYMERISATIONS OF CYCLOOCTENE

IV-(1) Reproducibility of Experimental Conditions

The initial studies of the polymerisation of cyclooctene (CO) were designed to test the reproducibility of experiments and to ascertain over what range of catalyst concentrations the rates of polymerisations could be determined. The polymerisations were carried out in bulk monomer using a cyclooctene : WCl_6 : $Al(iBu)_3$ molar ratio of 1000:1:2.

Experiment 1A

6.0 ml of cyclooctene were distilled into the RHA of the dilatometer shown in fig.II-(7) and the dilatometer placed in the constant temperature bath at 25°C for twenty minutes. The dilatometer was withdrawn from the water bath and 1.1 ml of WCl_6 (5.5×10^{-3} moles litre^{-1}) were injected through the "Suba Seal", followed by 1.3 ml (1.1×10^{-2} moles litre^{-1}) of $Al(iBu)_3$. The dilatometer was tilted as described in section II-(3) to fill the LHA and the dilatometer was clamped in the constant temperature bath. The height of the liquid meniscus in the capillary was observed using a cathetometer. A graph of $(h_o - h_t)$ against time was plotted and is shown in figure IV-(1).

(h_o) was the height of the meniscus at time, t = 0 and (h_t) was the meniscus height at time = t. The slope of the curve shown in figure IV-(1) was typical for all polymerisations of cyclooctene.

Polymerisation of Cyclooctene

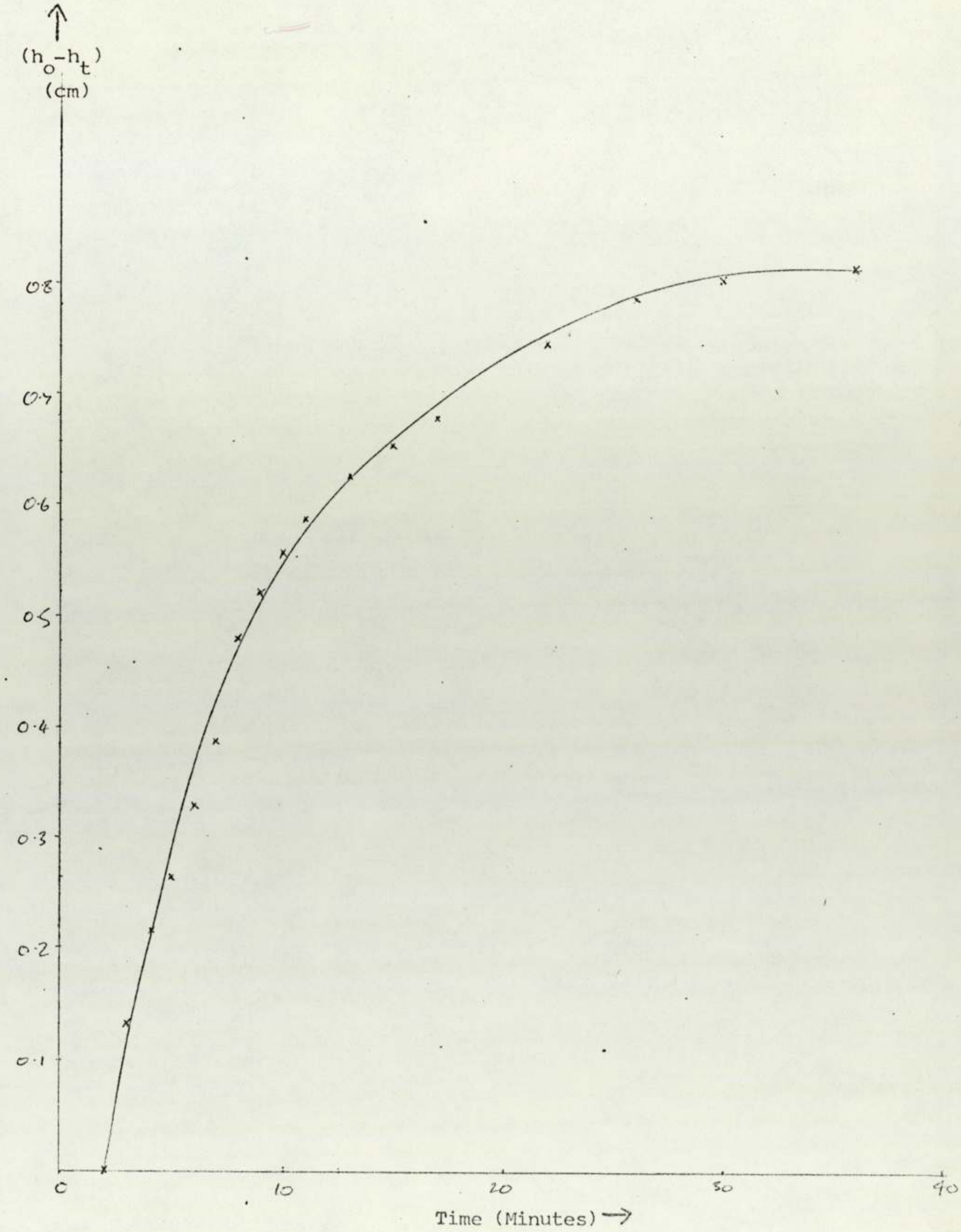


Fig.IV-(1)

The maximum possible drop in meniscus height, Δh_∞, i.e. the decrease in height at 100% conversion of monomer to polymer and the initial rate of polymerisation were calculated as described in section III-(4). Δh_∞ was calculated to be 8.22 cm and the initial rate of polymerisation was found to be 1.15×10^{-1} moles litre^{-1} s^{-1}.

The experiment 1A was repeated in further experiments (1B, 2A, 2B, 2C and 2D), using exactly the same concentrations of cyclooctene, tungsten hexachloride and aluminium triisobutyl and identical reaction conditions in order to ascertain the reproducibility of the procedure. The initial rates of polymerisations for these experiments were calculated as for experiment 1A and are shown in table IV-(i).

Table IV(i) Initial Rates of Polymerisation in Experiments 1A - 2D

Experiment Number	$\frac{\Delta h}{cm.s^{-1}}$	$\left[\frac{\text{Initial rates of polymerisation}}{\text{moles litre}^{-1}\ s^{-1}}\right] \times 10^{2}$
1A	0.00171	11.4
1B	0.000733	4.9
2A	0.00080	5.3
2B	-	Reaction too fast to follow
2C	0.000733	4.9
2D	0.00042	2.8

The results shown in table IV-(i) show that there was a great variation in the initial rates of polymerisations under seemingly identical reaction conditions. In one case (experiment 2B), the rate of polymerisation was so fast that it was impossible to fill the LHA of the dilatometer because in a matter of seconds the reaction mixture became extremely viscous. The results obtained were inconsistent and it was obvious that there was another variable that was not being controlled. This variable was thought to be the length of time that elapsed between the addition of the tungsten hexachloride solution to the cyclooctene and the subsequent addition of the aluminium tri-isobutyl solution. Hence experiments 3A - 3C were set up wherein the concentrations of cyclooctene, WCl_6 and $Al(iBu)_3$ were kept constant at 5.5 moles litre^{-1}, 1.1×10^{-3} moles litre^{-1} and 2.2×10^{-3} moles litre^{-1} respectively and the time between additions of WCl_6 and $Al\ (iBu)_3$ was maintained at two minutes. This time was called the premixing time of monomer and tungsten hexachloride.

The initial rates of polymerisations for experiments 3A - 3C are shown in table IV-(ii).

Table IV-(ii) Initial rates of polymerisation of cyclooctene

Experiment Number	$(\Delta h_1/cm\ s^{-1})$ $\times 10^3$	$\left[\frac{\text{Initial rates of polymerisation}}{(\text{moles litre}^{-1}\ s^{-1}}\right] \times 10^2$
3A	1.22	8.16
3B	1.09	7.31
3C	1.16	7.75

Accordingly, it is obvious that the consistency of these results would suggest that the premixing time of the cyclooctene and WCl_6 was an important variable in the reaction system. The standard deviation of the rates of polymerisation shown in table IV-(ii) was 4.5%.

This variation was considered to be within acceptable experimental limits.

IV -(2) A Study of the Effect of the Premixing Time of Cyclooctene and WCl_6 on the Initial Rates of Polymerisation of Cyclooctene

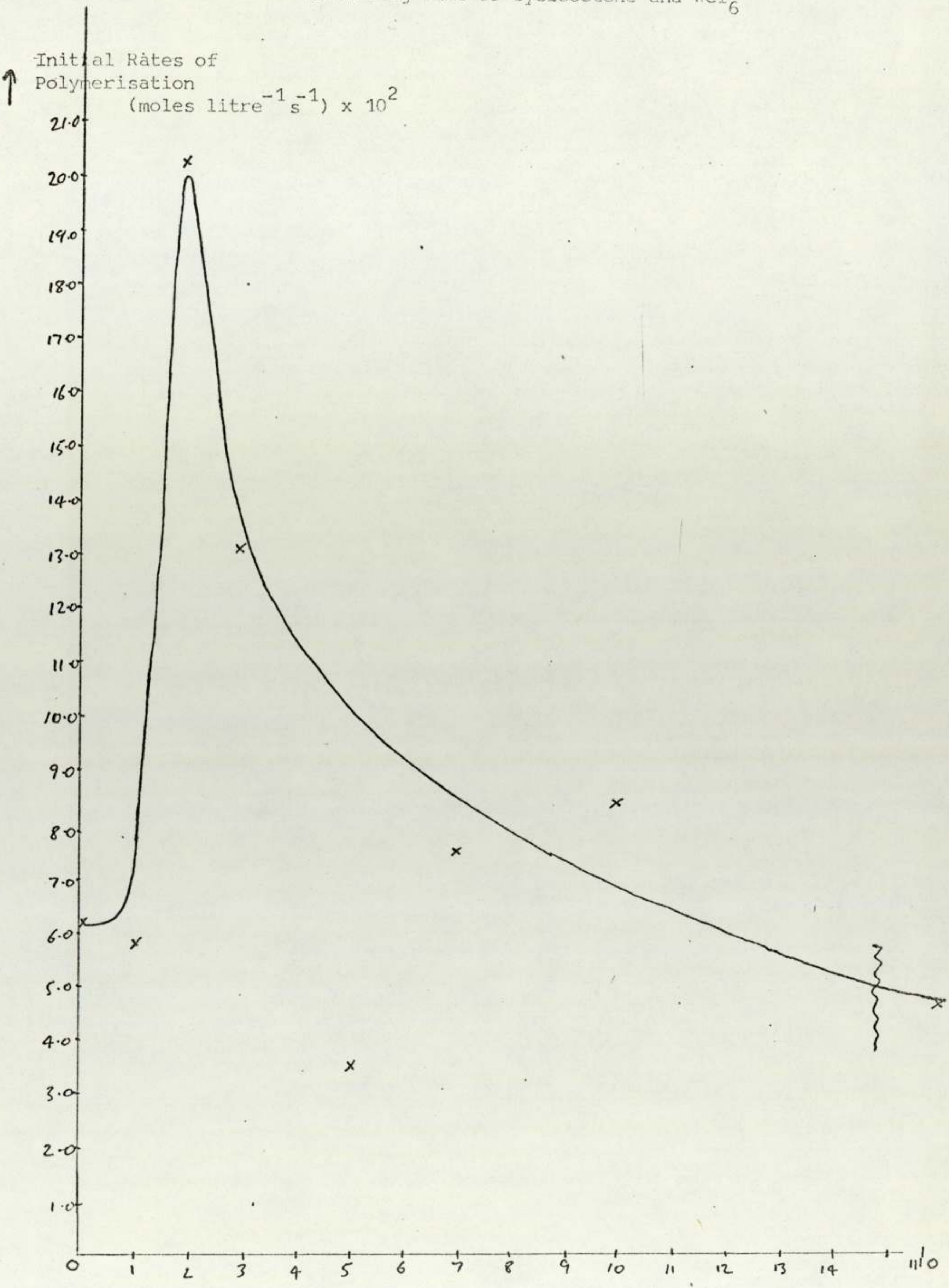
The premixing time of cyclooctene and WCl_6 was seen to be an important variable for the rate of polymerisation of cyclooctene from Section IV-(1), and so experiments were designed to observe the effect of this variable on the initial rate of polymerisation.

Experiments 3D to 3L were set up wherein the concentrations of cyclooctene, WCl_6 and $Al(iBu)_3$ were constant at 7.05 moles litre^{-1} 1.41 moles litre^{-1} and 2.82 moles litre^{-1} respectively. The premix time of cyclooctene and WCl_6 was varied between 0 minutes and 18½ hours. The initial rates of polymerisations were calculated as in experiment 1A. Δh_∞ was calculated to be 18.27 cm. The dependence of the rate of polymerisation on the premix time is shown in table IV-(iii) and figure IV-(2).

Table IV-(iii) Effect of Premixing Time on the Rate of Polymerisation of Cyclooctene

Experiment Number	$\frac{\Delta h_1}{cm.s^{-1}} \times 10^3$	$\left(\frac{\text{Premixing time}}{\text{minutes}}\right)$	$\left[\frac{\text{Initial rate of polymerisation}}{(\text{moles litre}^{-1}\text{s}^{-1})}\right] \times 10^2$
3E	1.58	0	6.1
3D	1.50	1	5.7
3H	5.23	2	20.1
3G	3.40	3	13.1
3L	0.92	5	3.5
3K	1.95	7	7.5
3F	2.18	10	8.4
3J	1.23	1110	4.7

The results show that for a premixing time of two minutes there was a maximum rate of polymerisation of 20.1 x 10^{-2} moles litre^{-1} s^{-1}



Initial Rates of Polymerisations against Premixing Time of Cyclooctene and WCl_6

Fig.IV-(2)

IV-(3) Effect of impurities on the rate of polymerisation of cyclooctene

The results described in sections IV-(1) and IV-(2) were obtained using a single batch of cyclooctene. The purity of each batch of cyclooctene was estimated before use by gas chromatography and the chromatogram of the first batch of cyclooctene is shown in fig.IV-(3)-(a). The chromatogram shows a major peak (cyclooctene) and three other minor peaks. Despite the reproducible results obtained in sections IV-(1) and IV-(2), these experiments were not reproducible when a new supply of cyclooctene was obtained and purified by conventional techniques. Examples of this irreproducibility were manifest in experiments 4A and 4B. The conditions of experiments 4A and 4B were identical with those of experiments 3H, i.e. the concentrations of cyclooctene, WCl_6 and $Al(iBu)_3$ were 7.05 moles litre^{-1}, 1.41 moles litre^{-1} and 2.82 moles litre^{-1} respectively and the premixing time of cyclooctene and WCl_6 was two minutes. The results of experiments 4A, 4B and 3H can be seen in table IV-(iv).

Table IV-(iv) The irreproducibility of experiments with different batches of cyclooctene

Experiment Number	Batch No. of cyclooctene	$\left[\dfrac{\text{Initial rate of polymerisation}}{\text{moles litre}^{-1}\ \text{s}^{-1}}\right] \times 10^2$
3H	1	20.17
4A	2	2.88
4B	2	2.94

(i) Assignment of Chromatogram Peaks

The chromatogram of batch (2) of cyclooctene can be seen as a scaled reproduction in fig.IV-(3)-(b) and can be compared with the chromatogram of batch (1) of cyclooctene that is shown in fig.IV-(3)-(a).

Perkin Ellmer F.30 Gas Chromatogram

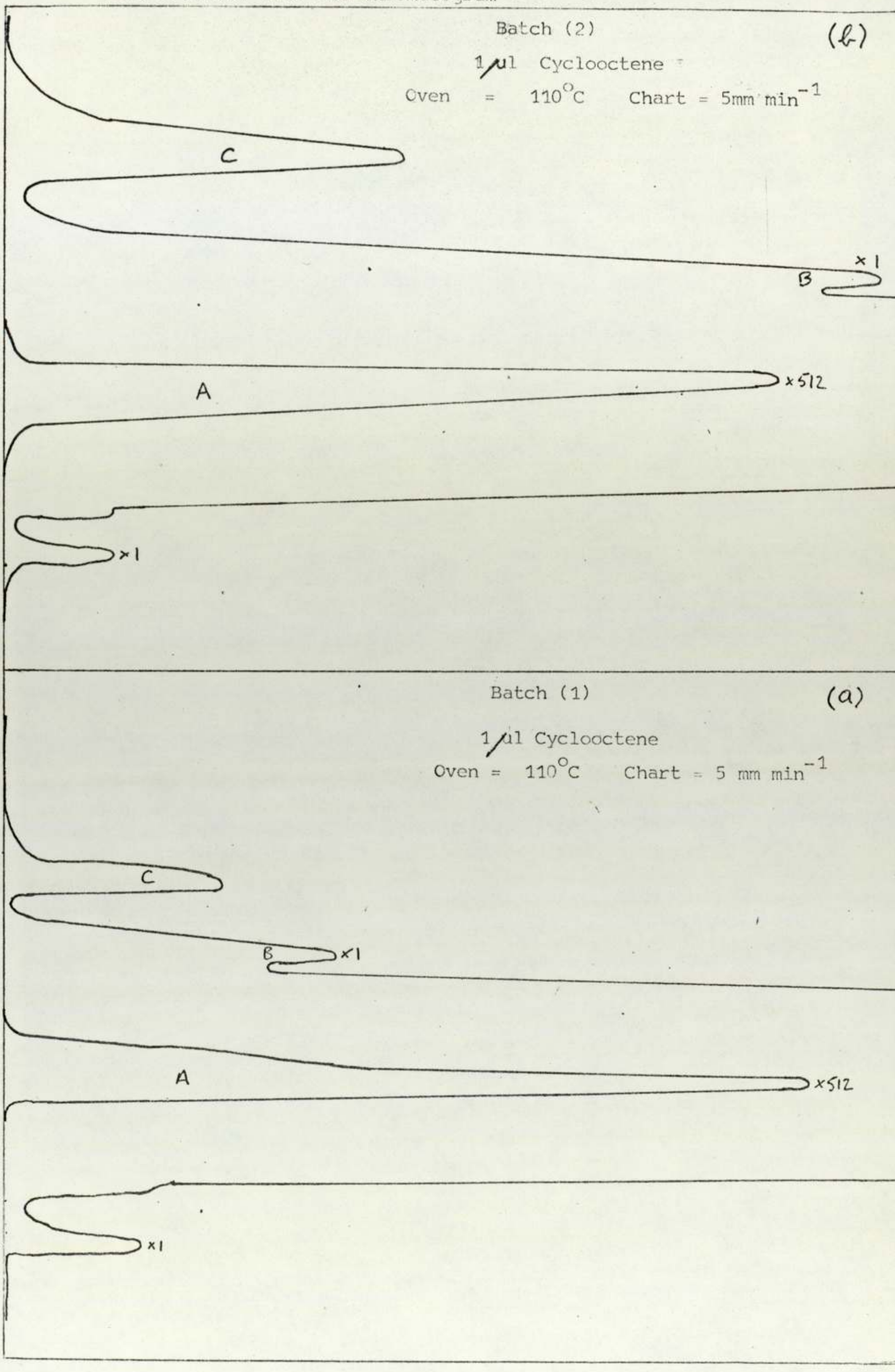


Fig.IV-(3)

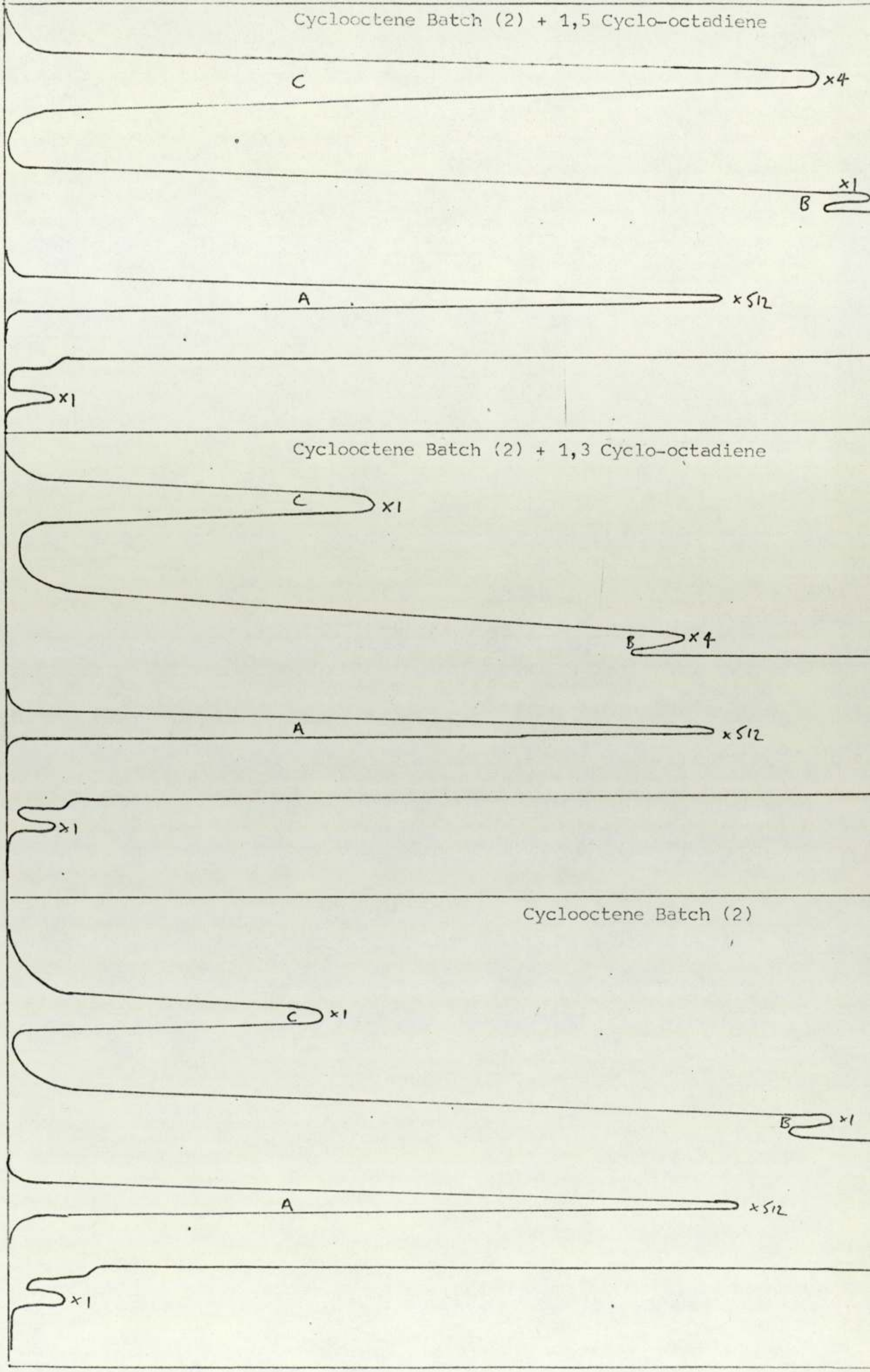
The two impurity peaks, B and C, were larger for batch (2) than for batch (1). It was thought that these impurity peaks were due to 1,3 cyclooctadiene and 1,5 cyclooctadiene. To determine which, if either, of the peaks was 1,3 cyclooctadiene, a small quantity of 1,3 cyclooctadiene was added to batch (2) of cyclooctene and the mixture was analysed by gas chromatography. The same procedure was adopted for 1,5 cyclooctadiene and the results of these determinations can be seen in fig.IV-(4).

It can be seen from the chromatograms in fig.IV-(4) that the addition of 1,3 cyclooctadiene to cyclooctene caused an increase in the size of the peak labelled (B) and hence peak (B) in the cyclooctene batch (2) was due to 1,3 cyclooctadiene. Similarly, peak (C) in batch (2) was assigned to 1,5 cyclooctadiene.

(ii) To determine the effects of 1,3 and 1,5 cyclooctadiene on the rate of polymerisation of cyclooctene.

(a) 1,3 Cyclooctadiene

The effect of 1,3 cyclooctadiene on the rate of polymerisation of cyclooctene was studied by injecting small amounts of 1,3 cyclooctadiene to cyclooctene/toluene solutions contained in the dilatometer, through the "Suba Seal". The concentration of 1,3 cyclooctadiene in the polymerisate was varied between 2.44 x 10^{-5} moles litre^{-1} and 26.88 x 10^{-5} moles litre^{-1}. WCl_6 was then injected into the dilatometer followed two minutes later by the $Al(iBu)_3$ solution. The concentrations of cyclooctene, WCl_6 and $Al(iBu)_3$ were 1.1 moles litre^{-1}, 1.8 x 10^{-3} moles litre^{-1} and 2.1 x 10^{-3} moles litre^{-1} respectively. The concentration of 1,3 cyclooctadiene indigenously present in the cyclooctene batch was calculated by calibrating the G.L.C. column with cyclooctene samples containing known amounts of 1,3 cyclooctadiene and plotting a graph of area under the 1,3 cyclooctadiene peak, compared with the area under the cyclooctene peak, against the



Cyclooctene Batch (2) + 1,5 Cyclo-octadiene

Cyclooctene Batch (2) + 1,3 Cyclo-octadiene

Cyclooctene Batch (2)

Fig.IV-(4)

concentration of 1,3 cyclooctadiene. The indigenous concentration of 1,3 cyclooctadiene was obtained by extrapolation of the graph. The initial rates of polymerisations of cyclooctene were found for different concentrations of 1,3 cyclooctadiene and the results are shown in table IV-(V), and graphically in Fig.IV-(5)

<u>Table IV-(V) Initial rates of polymerisation of cyclooctene for different concentrations of 1,3- cyclooctadiene</u>

Experiment Number	[Concentration of 1,3 COD / moles litre^{-1}] $\times 10^5$	Molar % of 1,3 C.O.D. of cyclooctene	[Initial rate of polymerisation / moles l^{-1} s^{-1}] $\times 10^2$
4C	2.44(indigenous)	0.28	11.4
4D	6.68	0.77	6.8
4E	10.59	1.22	8.3
4F	18.74	2.17	5.7
4G	26.88	3.11	0.8

(b) <u>1,5 Cyclooctadiene</u>

The effect of the presence of 1,5 cyclooctadiene was observed by adding a small amount of 1,5 cyclooctadiene to cyclooctene contained in the dilatometer. The concentration of 1,5 cyclooctadiene in the polymerisation was 20.22×10^{-5} moles litre^{-1}. This was a substantial concentration of 1,5 cyclooctadiene but it was not expected to interfere with the rate of polymerisation, other than to polymerise, as Calderon stated that 1,5 cyclooctadiene was easily polymerisable[41]. The concentrations of cyclooctene, WCl_6 and $Al(iBu)_3$ were again 1.1 moles litre^{-1}, 1.8×10^{-3} moles litre^{-1} and 2.1×10^{-3} moles litre^{-1} respectively

Concentration of 1,3 Cyclooctadiene against Initial Rate of Polymerisation of Cyclooctene

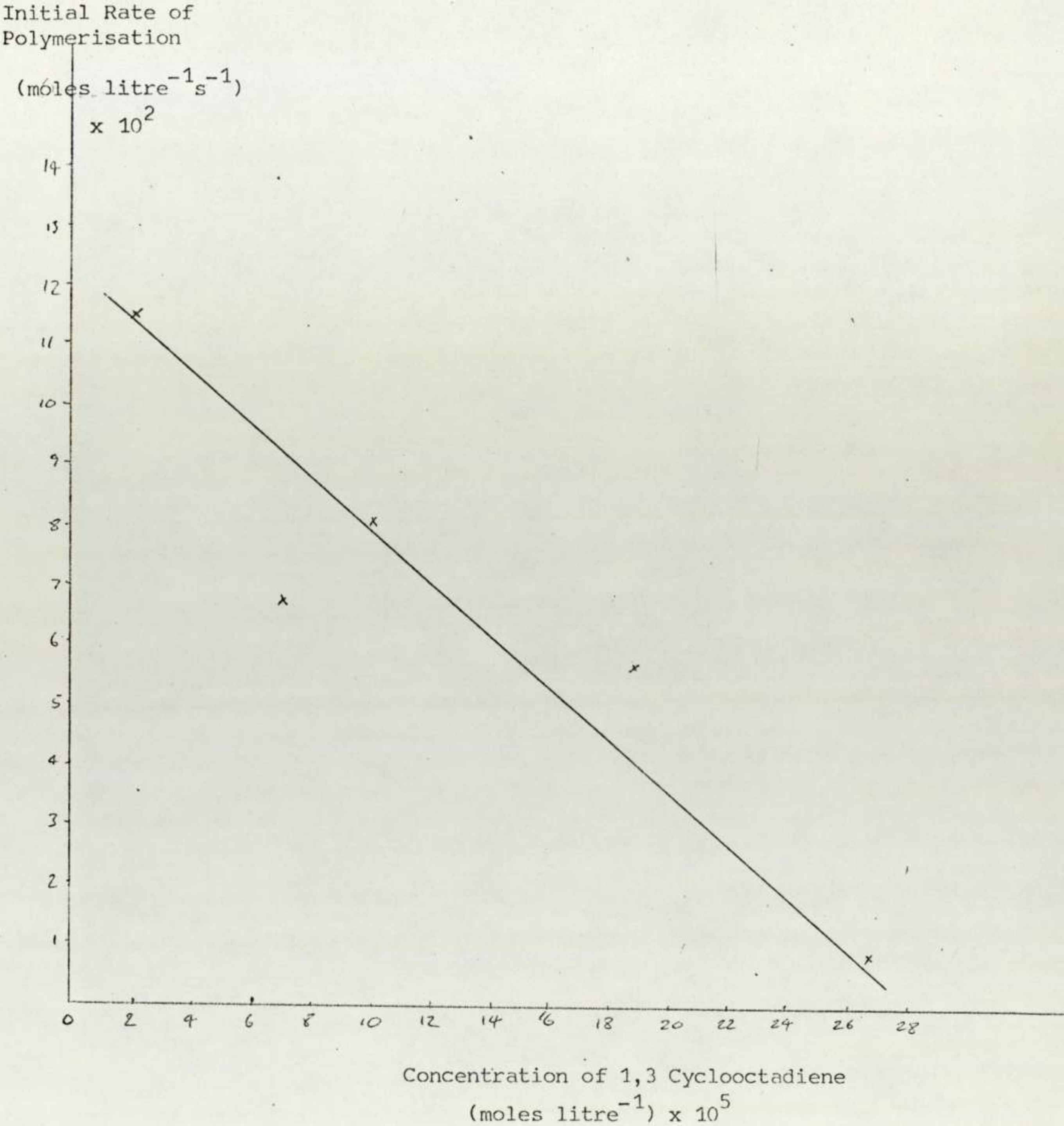


Fig.IV-(5)

The WCl_6 and cyclooctene/ 1,5 cyclooctadiene premix time was two minutes. The experiment was then repeated in the absence of 1,5 cyclooctadiene. The initial rate of polymerisation for the cyclooctene, devoid of 1,5-cyclooctadiene, was 10.6×10^{-2} moles $litre^{-1}$ s^{-1} and the initial rate of polymerisation for the cyclooctene and 2.02×10^{-4} moles $litre^{-1}$ of 1,5-cyclooctadiene was 10.2×10^{-2} moles $litre^{-1}$ s^{-1}. These two experiments were labelled 4H and 4I respectively.

It can therefore be seen that the impurity which retarded the rate of polymerisation of cyclooctene in the batches of cyclooctene used was 1,3 - cyclooctadiene, a result which was consistent with the results obtained by Calderon[41].

Each batch of cyclooctene used for the polymerisation reactions was examined by gas chromatography and the area under the 1,3 C.O.D. peak was noted. The impurity (1,3 C.O.D.) level in each batch was noted against the experiment in which it was used and the results are shown in table IV-(vi).

Table IV-(vi) Level of 1,3 cyclooctadiene present in each batch of cyclooctene used for polymerisations

Batch No. of cyclooctene	Experiments Conducted	$\left[\frac{\text{Area of 1,3 C.O.D. peak in chromatograph}}{cm^2}\right]$
1	1A - 3J	5.8
2	4A - 4I	15.3
3	5A - 5E	13.3
4	6A - 6S	0.0

IV -(4) Dependence of the Rate of Polymerisation on the Concentration of Aluminium Tri-isobutyl

Polymerisations of cyclooctene were carried out in which the concentrations of cyclooctene and WCl_6 were constant at 7.05 moles $litre^{-1}$ and 1.41×10^{-3} moles $litre^{-1}$ respectively. The premix time of WCl_6 and cyclooctene was constant at two minutes. The concentration of $Al(iBu)_3$ was varied between 0.7×10^{-3} and 5.6×10^{-3} moles $litre^{-1}$. Δh_∞ was calculated to be 18.27 cm. The effect of the concentration of $Al(iBu)_3$ on the initial rate of polymerisation is shown in table IV (vii) and in figure IV-(7).

Table IV-(vii) Effect of $Al(iBu)_3$ concentration on the rates of polymerisation of cyclooctene.

Experiment Number	$\left[\frac{\text{Concentration } Al(iBu)_3}{\text{moles litre}^{-1}}\right] \times 10^3$	Al:W ratio	$\left[\frac{\text{Initial rates of polymerisation}}{\text{moles litre}^{-1} s^{-1}}\right] \times 10^2$
5A	0.71	0.5	0.4
5B	1.41	1	2.8
5C	2.82	2	10.6
5D	4.23	3	0.6
5E	5.64	4	1.7

The graph shown in fig.IV-(7) gave a maximum rate of polymerisation for an aluminium/tungsten ratio of 2.

Molar Ratio of Al:W against the Initial Rate of Polymerisation of Cyclooctene

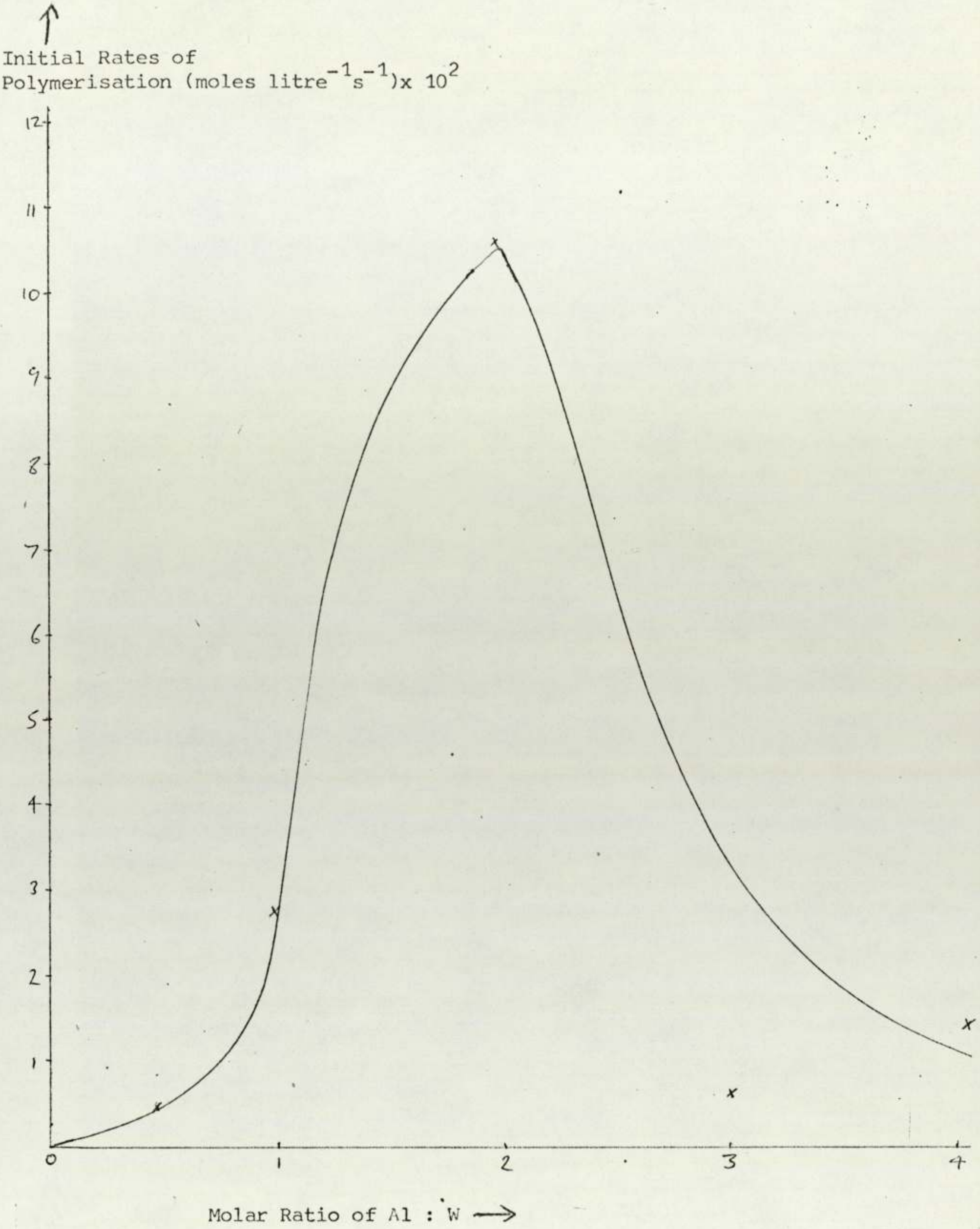


Fig.IV-(7)

IV-(5) Variation of the Premixing Time of Cyclooctene and WCl_6 for Different Concentrations of Cyclooctene

A batch of cyclooctene was obtained (4) which after pre-polymerisation proved to be free of 1,3 cyclooctadiene impurity and this cyclooctene was used to investigate the dependence of the rate of polymerisation on the premixing time of WCl_6 and cyclooctene, for different concentrations of cyclooctene at constant catalyst concentration. The premixing time was varied for each concentration of monomer and graphs of initial rate of polymerisation versus premix time were plotted for the given concentration of cyclooctene. The values of the peak initial rate and the premix time at which the peak initial rate occurred were noted. These polymerisations were solution polymerisations as cyclooctene, devoid of any 1,3 cyclooctadiene polymerised at too fast a rate to follow in bulk. The WCl_6 and $Al(iBu)_3$ concentrations were maintained at 7×10^{-4} moles litre^{-1} and 1.4×10^{-3} moles litre^{-1} respectively. The results of the initial rates of polymerisation at different premix times for the various monomer concentrations are shown in table IV-(viii) and figure IV-(8).

Table IV-(viii) Initial Rates of Polymerisation of Cyclooctene for different premix times of monomer and WCl$_6$ at various cyclooctene concentrations

Experiment Number	[Cyclooctene concentrations] moles litre^{-1}	(Premix time) minutes	[Initial rates of polymer moles litre^{-1} s^{-1}] x 10^2
6 A	0.73	1	1.6
B	0.73	2	9.4
C	0.73	3	6.2
D	0.73	4	1.8
E	1.10	2	2.8
F	1.10	4	5.5
G	1.10	6	11.5
H	1.10	8	4.7
I	1.40	Al before W	0.8
J	1.40	0	1.9
K	1.40	2	4.9
L	1.40	5	15.3
M	1.40	10	7.1
N	1.40	15	2.8
O	1.46	4	5.1
P	1.46	5	5.9
Q	1.46	6	11.5
R	1.46	6.5	10.4
S	1.46	7	11.0
T	1.46	8	2.2
U	1.83	2	2.5
V	1.83	4	13.0
W	1.83	6	18.2
X	1.83	7	12.8
Y	1.83	8	11.2
Z	1.83	10	8.3

Initial Rates of Polymerisation of Cyclooctene against premixing time of WCl_6 and CO for various concentrations of cyclooctene

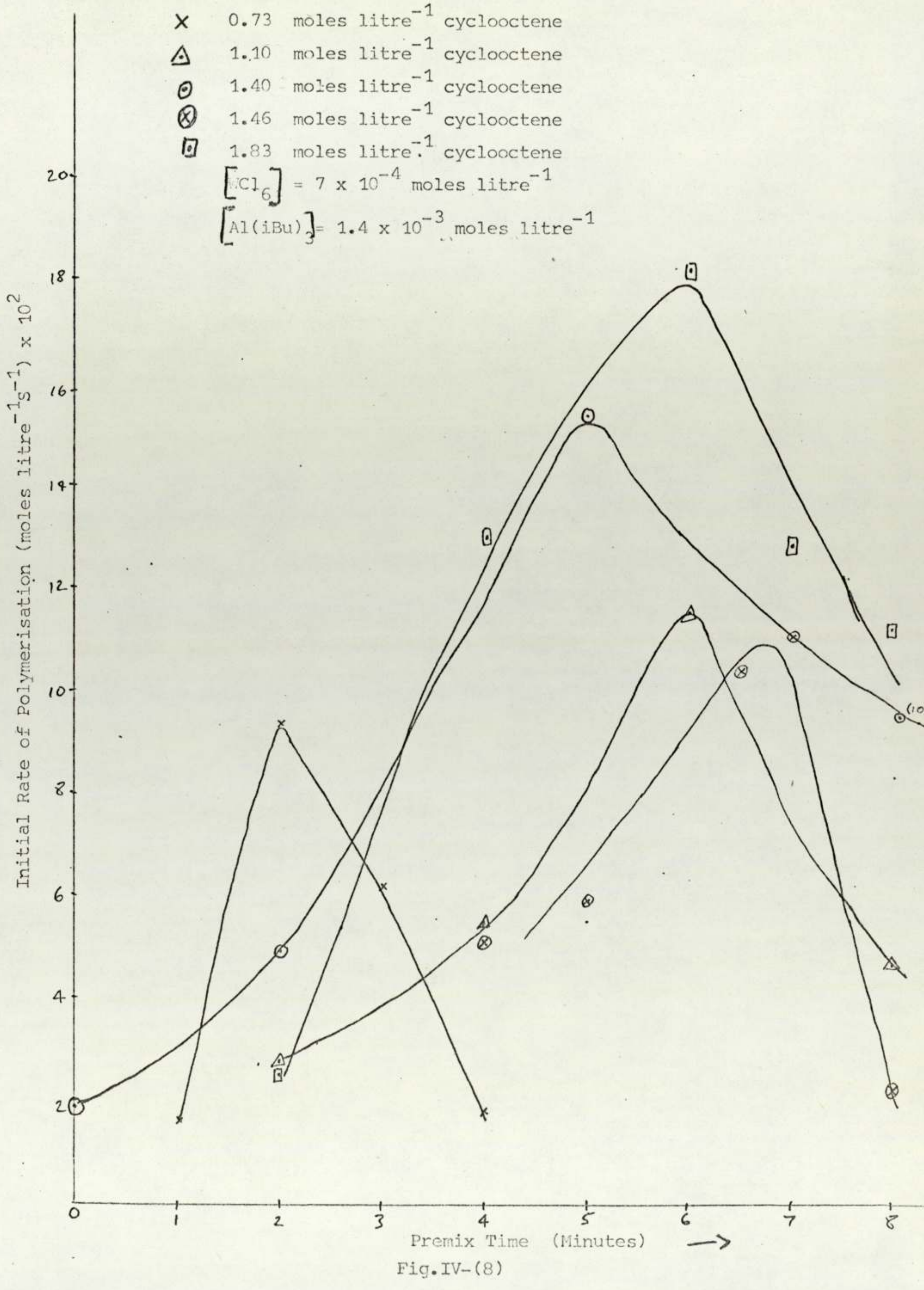


Fig.IV-(8)

Table IV-(viii) shows that for a cyclooctene concentration of 1.46 moles litre^{-1} the peak initial rate of polymerisation was 11.5×10^{-2} moles litre^{-1}s^{-1}, which was rather lower than anticipated when compared with the peak initial rates of 11.5×10^{-2} for a cyclooctene concentration of 1.098 moles litre^{-1} and 15.3×10^{-2} moles litre^{-1}s^{-1} for a cyclooctene concentration of 1.40 moles litre^{-1}. Unfortunately, the experiments using a cyclooctene concentration of 1.46 moles litre^{-1} could not be repeated as the batch of cyclooctene used for the series of experiments shown in table IV-(viii) had been consumed.

For the experiments shown in table IV-(viii) the colour changes that occurred during the various stages of the reactions were noted. The tungsten hexachloride solution in toluene was a deep blue colour and when it was added to cyclooctene in toluene the colour changed to a light pink colour instantaneously, and remained that colour no matter how long the premixing time, or what the concentration of cyclooctene. When the aluminium tri-isobutyl solution was added to the dilatometer the colour of the reaction mixture changed instantaneously from light pink to brown/red for the concentrations of cyclooctene of 0.73, 1.10, 1.40 and 1.46 moles litre^{-1}, and to green/blue for the cyclooctene concentration of 1.83 moles litre^{-1}. The colour produced after the aluminium alkyl addition remained throughout the reaction, even if the reaction was left for twelve hours or more.

IV-(6) The Effect on the Rate of Polymerisation of Cyclooctene of the Order of Catalyst Component Addition to Cyclooctene

The effect on the rate of polymerisation of cyclooctene of premixing the WCl_6 and $Al(iBu)_3$ catalyst components and of adding the $Al(iBu)_3$ component to the cyclooctene before the WCl_6 component, was studied using the dilatometer. A cyclooctene concentration of 7.05 moles $litre^{-1}$, a WCl_6 concentration of 1.41×10^{-3} moles $litre^{-1}$ and an $Al(iBu)_3$ concentration of 2.82×10^{-3} moles $litre^{-1}$ were used. The premix times of the cyclooctene and WCl_6, cyclooctene and $Al(iBu)_3$ and WCl_6 and $Al(iBu)_3$ were constant at 2 minutes. The results of the 3 polymerisations are shown in table IV-(ix).

Table IV-(ix) Order of Catalyst Component Additions

Premix Composition	Initial Rate of Polymerisation / moles $litre^{-1}$ s^{-1} $\times 10^2$
WCl_6 + Cyclooctene	10.7
$Al(iBu)_3$ + Cyclooctene	0.3
WCl_6 + $Al(iBu)_3$	0.0

As can be seen from Table IV-(ix) the order of addition of the catalyst components had a profound effect on the initial rate of polymerisation of cyclooctene. When the catalyst components were premixed prior to their addition to cyclooctene there was no polymerisation reaction. This effect was checked by repeating the reaction in which the WCl_6 and $Al(iBu)_3$ were premixed. The result was the same, no polymerisation reaction occurred.

CHAPTER V

The Polymerisations of Cyclopentene

V-(1) Reproducibility of Cyclopentene Polymerisations

(i) Purity of the Monomer

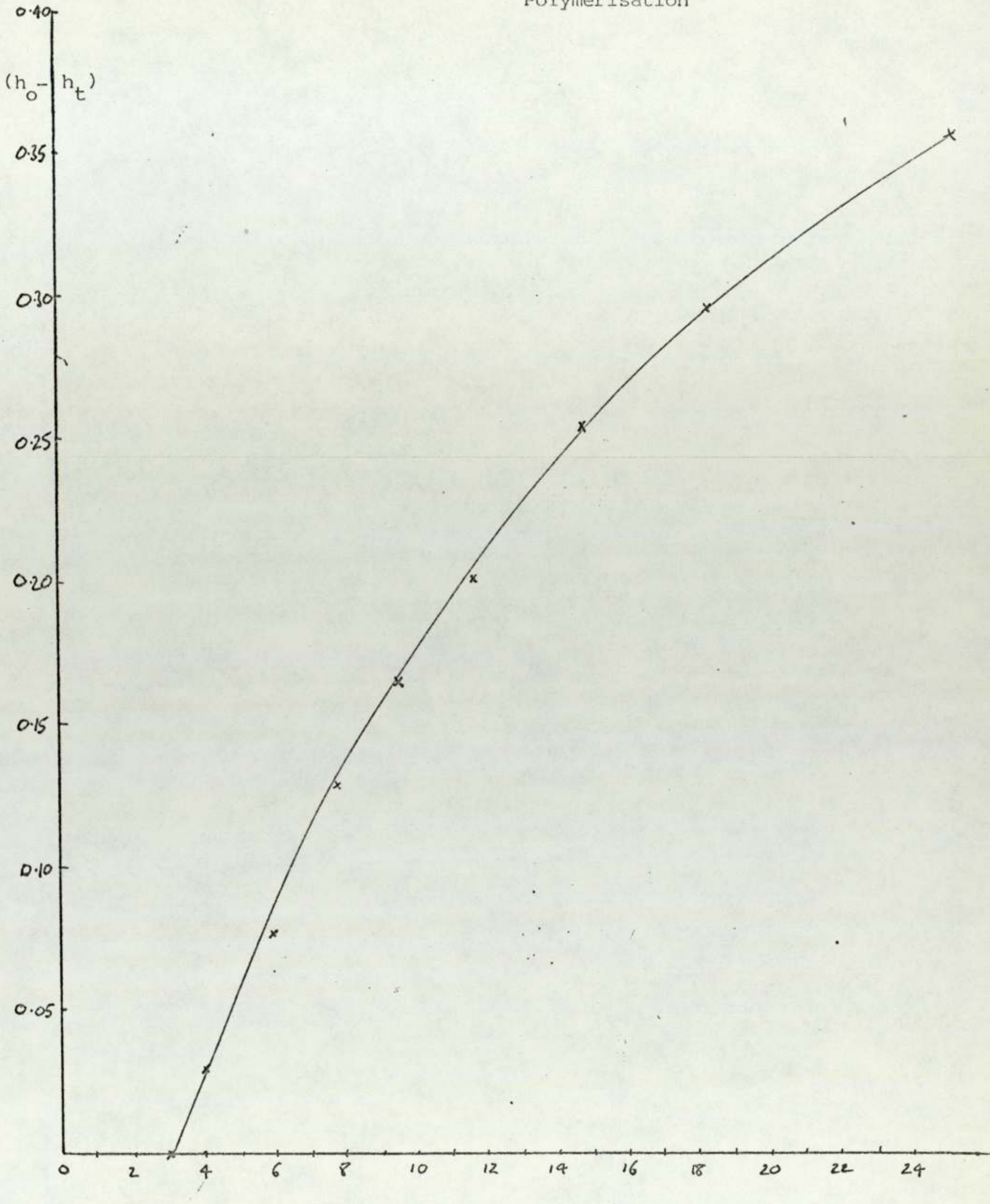
The difficulties encountered in establishing standard polymerisation conditions for the polymerisation reactions of cyclooctene centred around the purity of the cyclooctene itself and, in particular, the presence of the conjugated diene, 1,3-cyclooctadiene as an impurity present in the cyclooctene. However, as mentioned in Section II-(2), a convenient method of removing any conjugated diene from cyclopentene was the reaction of cyclopentadiene with sodium to yield cyclopentadienyl sodium. Hence the cyclopentene used for the polymerisation reactions was free from conjugated dienes and according to gas chromatographic analysis was approximately 100% pure.

(ii) The Shapes of the Curves of $(h_0 - h_t)$ against time for the Dilatometric Studies of the Rates of Polymerisation of Cyclopentene.

The rates of polymerisations of cyclopentene were determined dilatometrically using the apparatus shown in fig.II-(6).

In a typical polymerisation 1.13 ml of cyclopentene were vacuum distilled into the dilatometer, followed by 7.24 ml of toluene. The concentration of cyclopentene was therefore 1.49 moles litre^{-1}.0.056 ml of an 0.046 M solution of WCl_6 were added to the cyclopentene solution. 0.074 ml of an 0.07M solution of $Al(iBu)_3$ were added to the mixture of WCl_6 and cyclopentene after a time interval of two minutes. The bulb of the dilatometer was then filled and the rate of polymerisation was determined. The curve of $(h_0 - h_t)$ against time obtained for the above polymerisation conditions is shown in fig.V-(1).

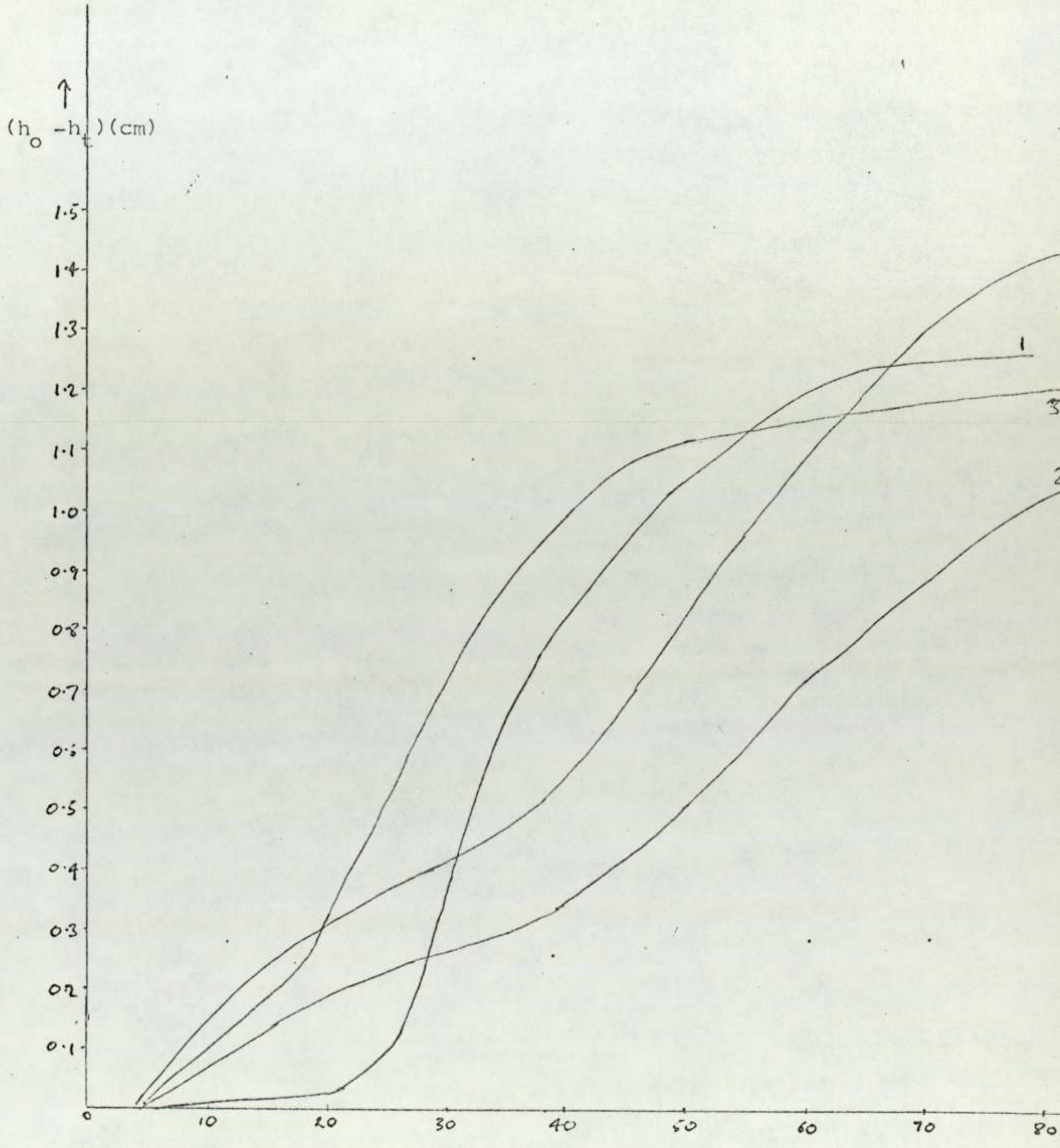
$(h_o - h_t)$ Against time for a cyclopentene Polymerisation



Time (Minutes) →

Fig.V-(1)

$(h_o - h_t)$ Against time for Polymerisations of Cyclopentene



Time (Minutes) ⟶

Fig. V-(2)

The shape of the curve shown in fig.V-(1) was similar to that obtained for the polymerisations of cyclooctene and for many polymerisations of cyclopentene. However, for certain polymerisations of cyclopentene the curves of $(\Delta h_o - \Delta h_t)$ against time showed marked differences from the "normal". These curves are shown in fig.V-(2) and the polymerisation conditions which produced these curves are listed in table V-(i).

Table V-(i) "Abnormal" Polymerisations of Cyclopentene

Curve Number	$\left[\frac{\text{Concentration of Cyclopentene}}{\text{moles litre}^{-1}}\right]$	$\left[\frac{\text{Initial rate of polymerisation}}{\text{moles litre}^{-1}\ \text{s}^{-1}}\right] \times 10^{-3}$
1	1.15	1.4
2	1.57	4.7
3	1.71	6.0
4	1.82	7.6

The curves shown in figure V-(2) showed an increase in the rate of polymerisation after periods of time ranging from 15 minutes to 35 minutes. The early stages of curves 1 - 4 were "normal" and these parts of the curves were used to determine the initial rates of polymerisation.

Explanation of the "Abnormal" Curve Shapes

(a) One possible explanation of the increase in the rates of polymerisations after different time intervals could be that there was a peculiarity in the kinetics of the system, but this seems unlikely as there appeared to be no consistency of trends during the four polymerisations.

(b) An alternative explanation of the "abnormal" curves could be the presence of a non-reproducible variable in the polymerisation system. Such a non-reproducible variable would have been the presence of oxygen and/or water in the dilatometer during the polymerisation. The oxygen or water could possibly have diffused into the dilatometer passed the "rota-flo" tap during the polymerisation. Oxygen has been cited in the literature as a co-catalyst for metathetic ring opening polymerisations and hence experiments were designed to examine whether oxygen and/or water were capable of increasing the yield of polypentenamer from cyclopentene and WCl_6 and $Al(iBu)_3$.

The yield of polypentenamer from a dilatometric experiment was measured by allowing methanol into the dilatometer on completion of a polymerisation reaction before any air was allowed into the dilatometer and the precipitated polypentenamer was then extracted by redissolving in toluene. This yield of anaerobic polypentenamer was then compared to the yield of polypentenamer obtained by allowing oxygen (air) into the dilatometer on completion of a polymerisation reaction (which showed a "normal" polymerisation curve), before the reaction was killed with methanol. The yields from the two experiments are shown in table V-(ii). The gravimetric yields from the two polymerisations were compared with the calculated yield from volume measurements.

Table V-(ii) Effect of Oxygen on the Yield of Polypentenamer from the polymerisation of cyclopentene with WCl_6 and $Al(iBu)_3$

Polymerisation	$\left[\frac{\text{Gravimetric Yield}}{\text{g}}\right] \times 10^2$	Percentage conversion	$\left[\frac{\text{Calculated Yield}}{\text{g}}\right] \times 10^2$
Aerobic	11.0	12.7	1.8
Anaerobic	1.4	1.6	1.6

As can be seen from table V-(ii), the yield of polypentenamer from a polymerisation reaction that was exposed to oxygen was considerably greater than the polypentenamer yield from a corresponding polymerisation where oxygen was excluded. Hence it can be seen that a possible cause for the increase in the rates of polymerisations in certain polymerisation reactions could have been the presence of oxygen in the reaction vessel. To prevent oxygen or water being able to diffuse into the dilatometer the "Rota-flow" taps were replaced with new taps on a regular basis, and in fact no further "abnormal" curves were obtained after this procedure had been adopted.

Polymerisations of cyclopentene in the dilatometer described in Figure II-(6) gave results reproducible to within 4% when all reaction conditions were identical and this figure was considered to be within acceptable experimental limits.

V-(2) Premixing time of Cyclopentene and Tungsten Hexachloride

Dilatometric studies were conducted on cyclopentene to ascertain whether the premixing time of cyclopentene and WCl_6 had a similar effect on the initial rate of polymerisation of cyclopentene, as the premixing time of cyclooctene and WCl_6 had on the initial rate of polymerisation of cyclooctene.

1.13 ml of cyclopentene were distilled into the dilatometer, followed by 7.24 ml of toluene. WCl_6 solution was injected through the "Suba Seal" to give a WCl_6 concentration of 2×10^{-4} moles litre^{-1}. $Al(iBu)_3$ solution was then added to the mixture in the dilatometer to give a concentration of $Al(iBu)_3$ of 4×10^{-4} moles litre^{-1}. The rate of polymerisation was then determined in the usual manner. A series of experiments were carried out in which the time interval between the addition of the WCl_6 solution and the $Al(iBu)_3$ solution was varied. The effect of premixing time on the initial rate of polymerisation is shown in table V-(iii).

Table V-(iii) Effect of Premixing Time of Cyclopentene and WCl_6 on the Initial Rate of Polymerisation

$\left[\frac{\text{Premixing Time}}{\text{Minutes}}\right]$	$\left[\frac{\text{Initial Rate of Polymerisation}}{\text{moles litre}^{-1}\ \text{s}^{-1}}\right] \times 10^3$
0.5	6.7
1.0	7.8
2.0	8.7
2.5	7.3
3.0	3.7

Temperature = 25°C

Concentration of cyclopentene = 1.49 moles litre^{-1}

The results shown in table V-(iii) are depicted graphically in fig.V-(3), from which it can be seen that the initial rate of polymerisation shows a maximum for a premixing time of 2 minutes. Thus it can be seen that the premixing time of the monomer and tungsten catalyst is an important variable for the rates of polymerisations of both cyclopentene and cyclooctene and hence the mechanisms of both polymerisations would be expected to be essentially the same.

Premixing Time of Cyclopentene and WCl_6 against Initial Rate of Polymerisation

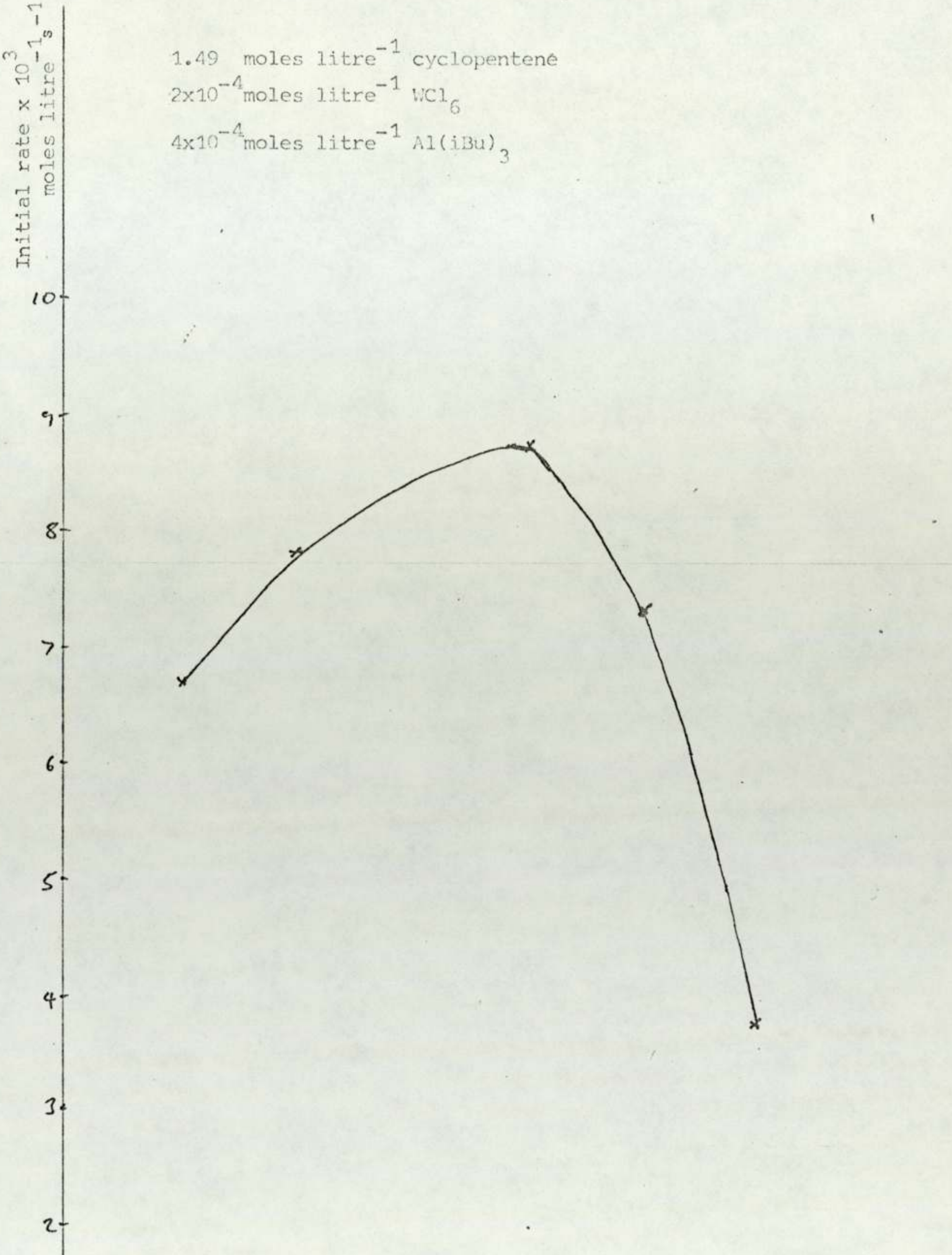


Fig.V-(3)

V-(3) Study of the effect of the concentration of catalysts on the Initial Rates of Polymerisations of Cyclopentene

In a series of polymerisations designed to establish the order of reaction with respect to the catalyst concentration, a ratio of tungsten to aluminium concentrations of 1 : 2 was chosen. This ratio was chosen because of the results of the experiments with cyclooctene which established a maximum polymerisation rate with a 1 : 2 W:Al ratio and also the reports in the literature which suggested that this ratio of catalyst components yielded the most active catalyst system.

Hence the rate of polymerisation of cyclopentene as a function of WCl_6 concentration, at a constant W:Al ratio, was determined dilatometrically by maintaining the concentration of cyclopentene and the premixing time of cyclopentene and WCl_6 constant, during a series of polymerisations. The concentration of WCl_6 was varied between 1×10^{-4} and 15×10^{-4} moles litre^{-1}. The results of these polymerisations are shown in table V-(iv).

Table V-(iv) Dependance of the Initial Rate of Polymerisation of Cyclopentene on the concentration of Catalysts

$\left(\frac{[WCl_6]}{\text{moles litre}^{-1}}\right)\times 10^4$	$\left(\frac{[Al(iBu)_3]}{\text{moles litre}^{-1}}\right)\times 10^4$	$\left(\frac{\text{Initial Rate of Polymerisation}}{\text{moles litre}^{-1}\ \text{s}^{-1}}\right)\times 10^3$
1	2	2.4
2	4	8.7
4	8	10.0
5	10	23.0
8	16	23.3
10	20	30.5
11	22	32.0
12	24	31.5
15	30	39.8

Cyclopentene concentration = 1.49 moles litre^{-1}
Temperature = 25°C
Premixing Time = 2 minutes
W : Al ratio = 1 : 2

The concentration of cyclopentene was maintained constant in the series of reactions and hence a general equation for the rate of polymerisation (Rp) may be written as -

$$Rp = k \left[Cat\right]^a$$

where the rate constant k includes a term in the concentration of cyclopentene. The order of the reaction with respect to the catalyst concentration may be determined as the slope of a conventional log rate against log concentration plot. The results shown in table V-(iv) have been used to construct the log(rate of polymerisation) against log$[WCl_6]$ plot shown in figure V-(4).

The order of reaction was calculated to be 0.97 from a standard least squares determination of the slope of the line shown in fig.V-(4). Therefore the rate of polymerisation of cyclopentene was shown to be first order in catalyst concentration and this was confirmed by a plot of Initial rate of Polymerisation against WCl_6 concentration shown in figure V-(5).

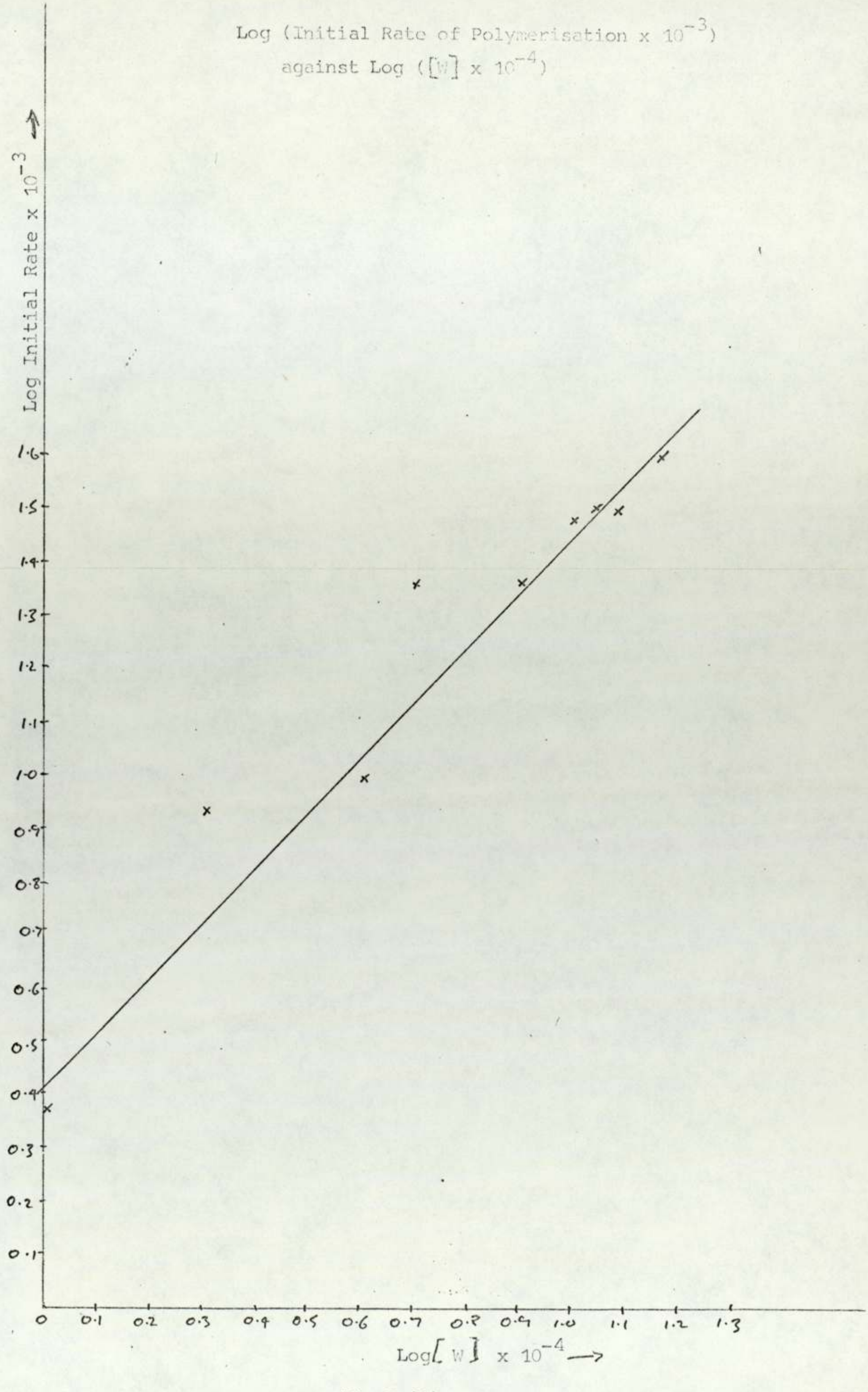
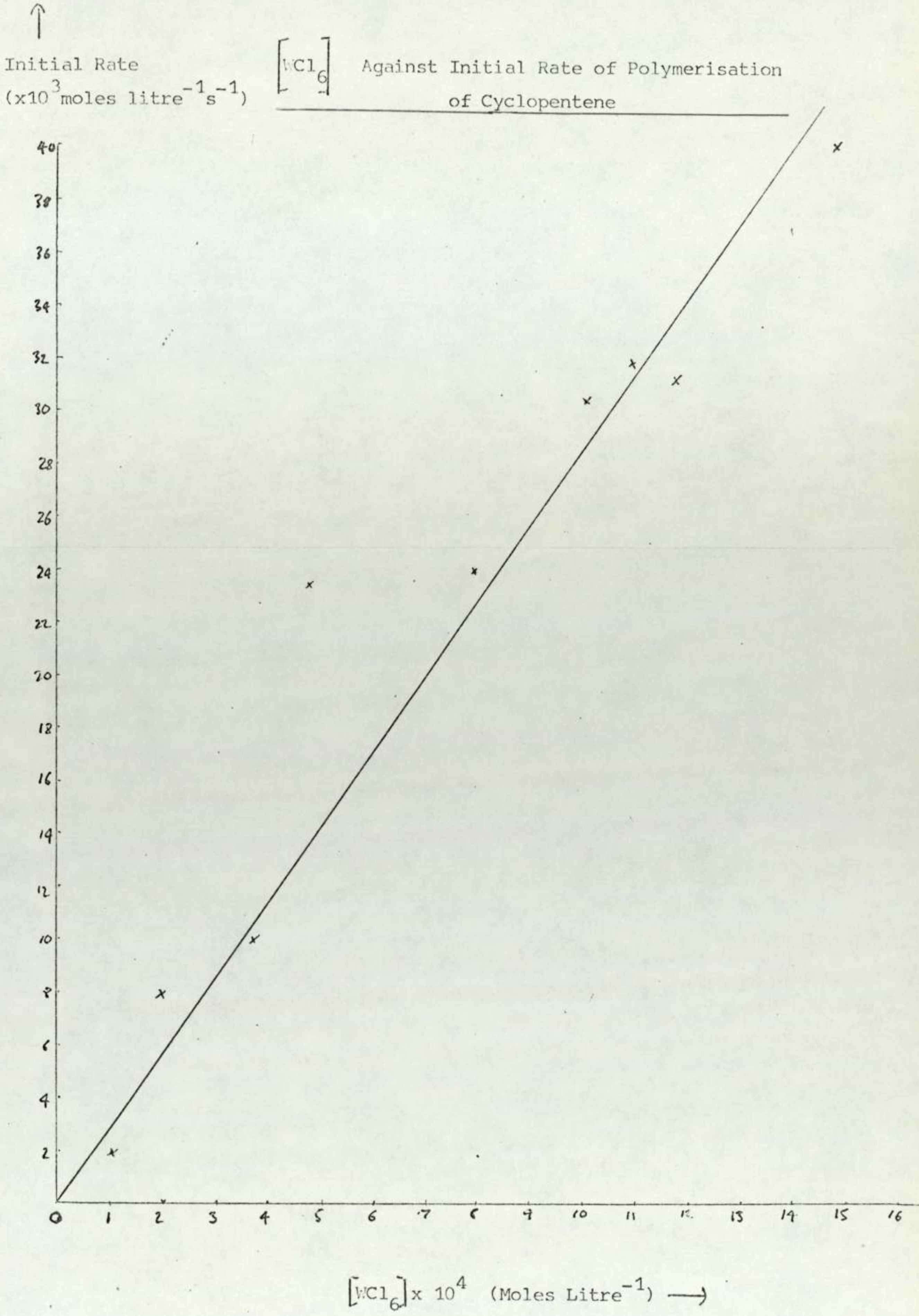

Log (Initial Rate of Polymerisation x 10^{-3})
against Log ([W] x 10^{-4})
Log Initial Rate x 10^{-3}
1·6
1·5
1·4
1·3
1·2
1·1
1·0
0·9
0·8
0·7
0·6
0·5
0·4
0·3
0·2
0·1
0
0·1
0·2
0·3
0·4
0·5
0·6
0·7
0·8
0·9
1·0
1·1
1·2
1·3
Log[W] x 10^{-4}

Fig.V-(4)



[WCl_6] Against Initial Rate of Polymerisation of Cyclopentene

Fig.V-(5)

V-(4) The Effect on the Initial Rate of Polymerisation of Cyclopentene of the concentration of Cyclopentene and the Premixing Time

To study the effect on the rate of polymerisation of premix time at different monomer concentrations, the rates of polymerisation of cyclopentene were determined dilatometrically at constant concentrations of catalyst components, for various premix times of WCl_6 and cyclopentene. These experiments were then repeated for three other concentrations of cyclopentene. The concentration of WCl_6 was constant at 3×10^{-4} moles litre^{-1} and the concentration of $Al(iBu)_3$ was 6×10^{-4} moles litre^{-1}. The concentrations of cyclopentene were not exactly the same within each concentration series, as the amount of solvent distilled into the dilatomater varied slightly with each reaction. The results of these experiments are shown in table V-(v), and graphically in figure V-(6).

Table V-(v) Dependence of Initial Rate of Polymerisation of Cyclopentene on Premix Time and Cyclopentene Concentration

$\left(\frac{\text{Concentration of Cyclopentene}}{\text{moles litre}^{-1}}\right)$	$\left(\frac{\text{Premix Time}}{\text{minutes}}\right)$	$\left(\frac{\text{Initial Rates of Polymerisation}}{\text{moles litre}^{-1}\ s^{-1}}\right) \times 10^3$
1.46	4	2.0
1.48	5	4.0
1.47	6	2.4
1.75	1	2.0
1.74	2	4.1
1.75	3	4.1
1.75	4	4.9
1.74	5	4.1
1.74	8	2.4
1.79	2	2.9
1.80	3	5.5
1.80	4	3.2
1.96	1	3.9
1.96	2	5.7
1.97	3	5.0
1.96	4	3.7
1.97	5	3.6
1.96	6	1.9

WCl_6 concentration = 3×10^{-4} moles litre^{-1}

$Al(^{i}Bu)_3$ concentration = 6×10^{-4} moles litre^{-1}

Temperature = 25° C

Initial Rate of Polymerisation against Premix Time for Various Concentrations of Cyclopentene

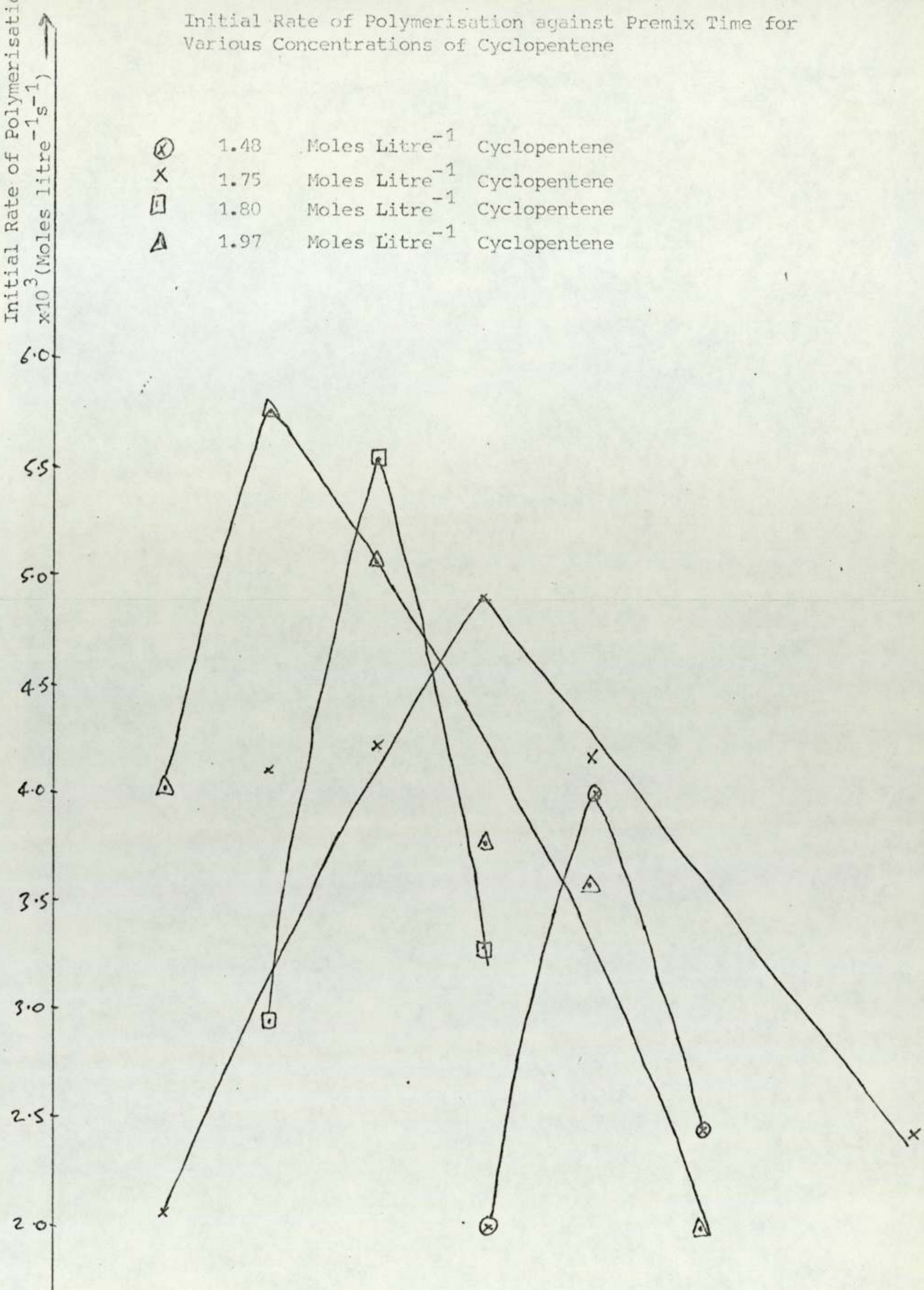


Fig.V-(6)

The peak initial rate of polymerisation and the premix times at which these peaks occurred were withdrawn from table V-(v) and are shown in table V-(vi).

<u>Table V(vi)</u> <u>Peak Initial Rates of Polymerisation and Premix Times at which they occur</u>

$\left(\frac{\text{Concentration of Cyclopentene}}{\text{moles litre}^{-1}}\right)$	$\left(\frac{\text{Peak Initial Rate of Polymerisation}}{\text{moles litre}^{-1}\text{s}^{-1}}\right) \times 10^{3}$	$\left(\frac{\text{Premix Time}}{\text{Minutes}}\right)$
1.48	4.00	5
1.74	4.92	4
1.80	5.50	3
1.96	5.75	2

The premix time at which the maximum initial rate of polymerisation occurred was called t max. A graph of t max against the reciprocal of the concentration of cyclopentene was plotted using the results shown in table V-(vi) and is shown in figure V-(7). The significance of this graph is discussed in Chapter VI.

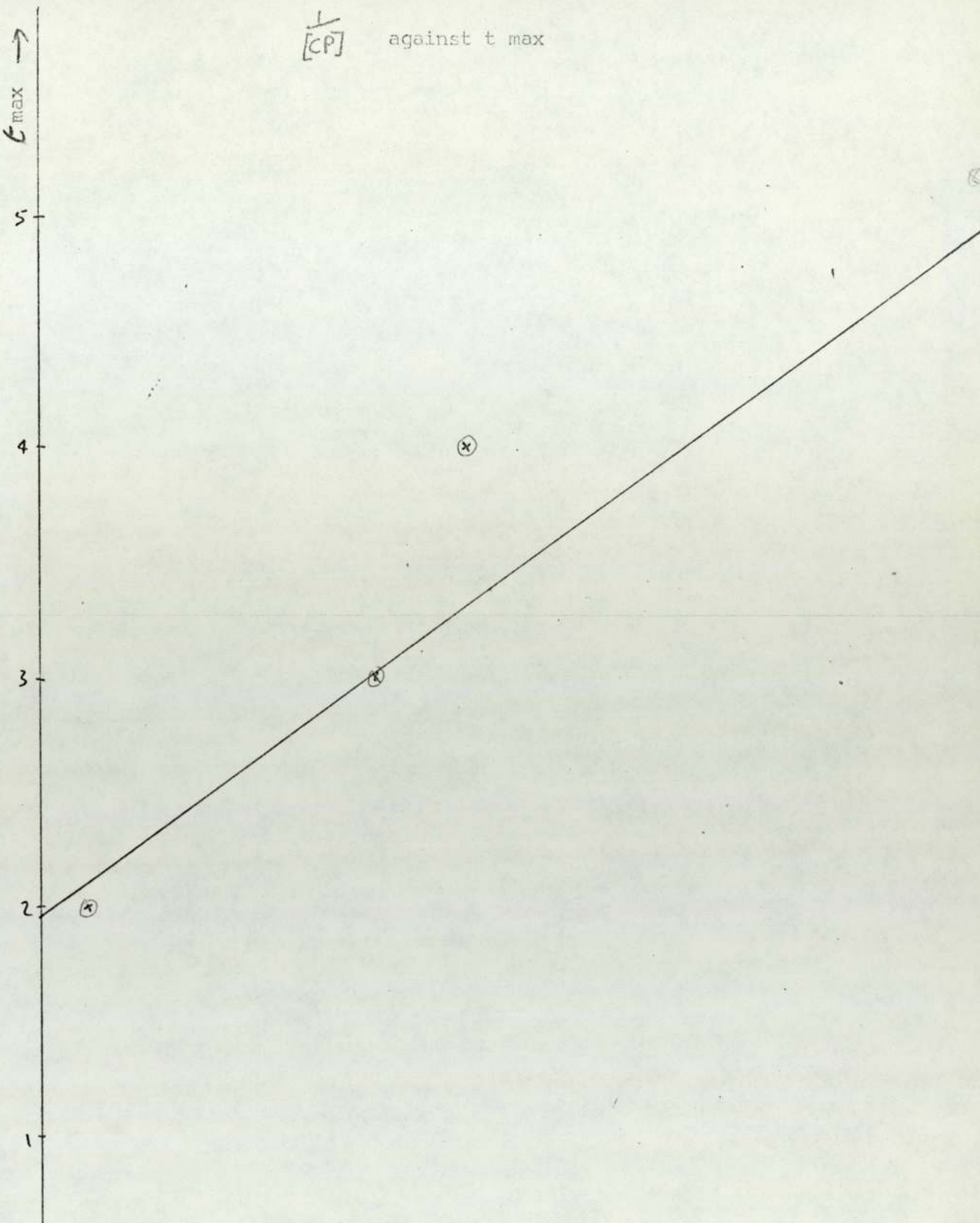

$\frac{1}{[CP]}$ against t max

Fig.V-(7)

V-(5) Molecular Weight of Polypentenamer Samples determined from solution viscosity measurements

The viscosity average molecular weights of polypentenamer samples were determined using the method described in Section II-(5)-(vii). The samples of polypentenamer used in these determinations were obtained from the series of polymerisations described in Section V-(3), where the concentration of cyclopentene was constant and the concentrations of WCl_6 and $Al(iBu)_3$ were varied. The polymerisations were terminated by the addition of methanol to the dilatometer at the end of the polymerisation reaction. The polymer precipitated immediately and the reaction of catalyst species with impurities was minimised. Solutions of polypentenamer samples were prepared and purified. The intrinsic viscosities of these samples were determined in toluene and the viscosity average molecular weights were calculated using the Mark-Houwinke parameters determined by Gianotti, Bonizelli and Borghi[55], and are shown in table V-(vii).

Table V-(vii)

$\left(\dfrac{\text{Concentration of } WCl_6}{\text{moles litre}^{-1}}\right) \times 10^4$	$\left(\dfrac{\text{Concentration } Al\ (iBu)_3}{\text{moles litre}^{-1}}\right) \times 10^4$	$\bar{M}v$
4	8	265,000
5	10	151,000
8	16	183,000
10	20	98,000
15	30	176,000

Solvent = Toluene
Temperature= $30^{\circ}C$

The results shown in table V-(vii) appear to be inconclusive. This may have been due to either oxygen or water reacting with the active catalysts before the polymer was precipitated and the catalyst destroyed. The failure to incorporate some small amount of anti-oxidant in the precipitated polymer during the purification process may have enabled the polypentenamer to cross-link in the presence of oxygen and the viscosity average molecular weight could have been significantly altered.

V - (6) Electron Spin Resonance Studies

(1) Examination of a solution of WCl_6 in toluene by electron spin resonance spectroscopy.

A solution of WCl_6 in toluene was prepared and placed in the apparatus described in section II-(5)-(iv) and shown in fig.II-(7). The quartz tube was filled and the filled tube placed in the cavity of the e.s.r. spectrometer. As expected no e.s.r. signal was observed as tungsten would be in the VI oxidation state in WCl_6 and would not have any unpaired *d* electrons.

(2) Changes in the E.S.R. spectrum associated with the reactions of WCl_6 with olefins.

Solutions of olefins and WCl_6 were prepared for e.s.r. examination as described in section V-(5)-(iv). The solution of WCl_6 and cyclopentene did not produce a signal in the e.s.r. spectrometer and this would tend to suggest that no free *d*-electrons were present in the system, contrary to expectations, since tungsten found to be in lower oxidation states is normally associated with an octahedral complex with the presence of one or more unpaired *d*-electrons.

The solution of WCl_6 and cyclooctene also failed to produce any signal in the e.s.r. spectrum.

V-(7) Copolymerisation of Cyclooctene and Cyclopentene

Three copolymerisation reactions were carried out with three different monomer molar ratios. The molar ratios of cyclooctene to cyclopentene were:

(i) 1: 1.8

(ii) 1: 1

(iii) 1: 0.6

The average molecular weights of the repeat units in the copolymers, from the molar ratio of the comonomers in the copolymers, could be calculated by the iodine monochloride method described in Section II-(5)-(viii). The copolymer compositions determined at various comonomer ratios are shown in table V-(viii).

Table V-(viii) Cyclooctene-Cyclopentene Copolymer Composition

Copolymerisation number	Average Molecular Weight of Copolymer Repeat Unit	Percentage of Cyclopentene units
(i)	73	90
(ii)	92	44
(iii)	98	29

$[WCl_6]$ = 7.7×10^{-5} moles litre^{-1}

$[Al(iBu)_3]$ = 1.54×10^{-4} moles litre^{-1}

Total [Monomer] = 9.06 moles litre^{-1}

Temperature = 25°C

The copolymer composition (i) was also determined by analysis of the N.M.R. spectrum of the copolymer in deuterated chloroform. This analysis showed that the molar percentage of cyclopentene in the copolymer from (i) was 96% as compared with the I Cl value of 90%. Unfortunately it was not possible to analyse the copolymers from (ii) and (iii) because these were found to be insufficiently soluble in deuterated chloroform.

The reactivity ratios of the two monomers could be calculated from the copolymer composition equation:

$$\frac{M_1}{M_2} = \frac{m_1}{m_2} \cdot \frac{r_1 \frac{m_1}{m_2} + 1}{r_2 + \frac{m_1}{m_2}}$$

M_1 = fraction of monomer (1) in the copolymer

M_2 = fraction of monomer (2) in the copolymer

m_1 = mole fraction of monomer (1) in the polymerisation reaction

m_2 = mole fraction of monomer (2) in the polymerisation reaction

r_1 = reactivity constant of monomer (1)

r_2 = reactivity constant of monomer (2)

Monomer (1) was cyclopentene and monomer (2) was cyclooctene.
From the three copolymer compositions, three values of the reactivity constants could be obtained and these are shown in table V-(ix).

Table V-(ix) Reactivity Constants from the Copolymer Composition Equation

r_1	r_2
2.05	2.36
3.09	4.30
3.70	2.99

The average values of r_1 and r_2 were calculated to be 2.94 and 3.22 respectively.

From these results it can be seen that r_1 and r_2 are both greater than 1 and this situation would lead to a copolymer composition of long blocks of polypentenamer and long blocks of polyoctenamer, when the monomer concentrations in the feed were identical.

CHAPTER VI

Discussion of Results

VI-(1) The Effect of Premixing Time of Monomer and WCl_6

(i) The initial inconsistency obtained in the measurement of the rate of polymerisation was shown to be due to a variation of the premixing time of the monomer and WCl_6 and a dependence of the initial rate of polymerisation of either cyclooctene or cyclopentene on this premixing time has been shown to occur at 25°C.

Because the premixing time was a rate controlling factor, some reaction or reactions involving WCl_6 and monomer must have occurred before the addition of $Al(iBu)_3$, which then reacted with one of the products of these reactions to form an active species, W_1^*. The concentration of this active catalyst depended upon the concentrations of WCl_6, $Al(iBu)_3$ and monomer, as well as the premixing time of the monomer and WCl_6. A simple reaction scheme can be postulated to occur and is shown below.

$$M + WCl_6 \longrightarrow W_1$$

$$W_1 + Al(iBu)_3 \longrightarrow W_1^*$$

XL

Cyclopentene and WCl_6 have been shown[31] to react to produce reduced oxidation states of tungsten, so that it is possible to postulate that W_1 contained tungsten atoms in some lower oxidation states.

Premixing the WCl_6 and $Al(iBu)_3$ prior to the addition of monomer did not produce a polymerisation reaction and hence any WCl_6 that had not reacted with the monomer during the premix time could have reacted with the $Al(iBu)_3$ upon its addition to form a complex that was not active towards the polymerisation reaction.

The plot of rate of polymerisation against premixing time (fig.V-(3)) showed that the rate of polymerisation was a maximum after a premixing time of two minutes, but fig.V-(6) showed that the time after which the maximum rate of polymerisation occurred depended upon the monomer concentration.

If W_1^* was the active species and this was formed from W_1 then the concentration of W_1^* and hence the concentration of W_1 must also have been a maximum at this premixing time. It therefore follows that not only was W_1 produced by some reaction involving WCl_6 and monomer but it was also itself consumed in some reaction, probably involving monomer or WCl_6. The reaction scheme,(XL), has to be extended to account for this phenomenon, as shown below -

$$W_1 \ + \ M \longrightarrow W_2 \qquad - \quad (a)$$

$$\text{or} \quad W_1 \ + \ WCl_6 \longrightarrow W_2 \qquad - \quad (b)$$

XL1

The reaction of W_1 with monomer could be a further reduction of the tungsten to a lower oxidation state.

(ii)The Kinetics of the Formation of W_1

Consider the reactions

$$WCl_6 \ + \ M \xrightarrow{k_1} W_1$$

$$W_1 \ + \ M \xrightarrow{k_2} W_2$$

then the rate of formation of W_1 can be written as

$$\frac{d\,[W_1]}{dt} = k_1 [WCl_6]\,[M] - k_2 [W_1]\,[M]$$

The concentration of WCl_6 varies during the reaction and can be written as:

$$[WCl_6] = [WCl_6]_o \; e^{-k_1 [M] t}$$

where $[WCl_6]_o$ is the concentration of WCl_6 at the time of its injection into the monomer solution.

$$\therefore \quad \frac{dW_1}{dt} + k_2 W_1 M = k_1 M W_o \; e^{-k_1 M t}$$

where W_1, M and W_o represent the concentrations of W_1, monomer and $(WCl_6)_o$

then, multiplying both sides of the equation by $e^{\int k_2 M dt}$,

$$e^{k_2 Mt} \cdot \frac{dW_1}{dt} + k_2 M e^{k_2 M t} W_1 = k_1 W_o M e^{(k_2 - k_1) Mt}$$

$$\therefore \quad \frac{d(W_1 e^{k_2 Mt})}{dt} = k_1 W_o M e^{(k_2 - k_1) Mt}$$

$$= \int k_1 W_o M e^{(k_2 - k_1) Mt} dt$$

and hence:

$$W_1 e^{k_2 M t} = \frac{k_1 W_o e^{(k_2 - k_1) Mt}}{(k_2 - k_1)} + \text{constant}$$

At time zero it can be assumed that $[W_1] = 0$

$$\therefore \quad 0 = \left(\frac{k_1}{k_2 - k_1}\right) W_o + \text{constant}$$

hence constant $= \dfrac{-k_1 W_o}{k_2-k_1}$

Accordingly the $[W_1]$ may be expressed as a function of time

whereby: $$[W_1] = \frac{k_1 W_o}{k_2-k_1}\left(e^{-k_1 M t} - e^{-k_2 M t}\right) \quad - (1)$$

A maximum concentration of W_1 occurred during the reactions at the time, (t_{max}), when $\dfrac{dW_1}{dt} = 0$

$$\therefore \quad \frac{dW_1}{dt} = \frac{k_1 W_o}{k_2-k_1}\left(- k_1 Me^{-k_1 Mt} + k_2 Me^{-k_2 Mt}\right) = 0$$

$$\therefore \quad k_1 . e^{-k_1 Mt_{max}} = k_2 . e^{-k_2 Mt_{max}}$$

$$e^{(k_1 - k_2)Mt_{max}} = \frac{k_1}{k_2}$$

From this t_{max} can be evaluated as

$$t_{max} = \frac{1}{[M]}\left(\frac{1}{(k_1 - k_2)} . \ln \left(\frac{k_1}{k_2}\right)\right) \quad - (2)$$

According to equation (2), t_{max} should be a function of monomer concentration such that a graph of t_{max} against the reciprocal of the monomer concentration should produce a straight line with a slope of $\left(\frac{1}{(k_1 - k_2} . \ln \left(\frac{k_1}{k_2}\right)\right)$

The results shown in table V-(vi) can be used to provide the premix times that produced the maximum initial rates of polymerisation, (t_{max}), at the corresponding cyclopentene concentrations and a plot of t_{max} against the reciprocal of the cyclopentene concentration was shown in fig.V-(7). As can be seen from this figure the plot yielded a straight line and hence this was in agreement with the reaction described earlier. It can be assumed therefore that W_1 was consumed in a reaction involving monomer and not WCl_6.

(iii) The Order of the Reaction with respect to the Monomer Concentration

If the rate of polymerisation, R_p, is represented as

$$R_p = k_p \left[W_1\right]^y \left[M\right]^x$$

then to determine x, the order of reaction in monomer, $[W_1]$ must be constant and a graph of log (rate of polymerisation) against log (monomer concentration) will yield a straight line with a slope equal to x. According to equation (2),

$$t_{max}\left[M\right] = \frac{1}{(k_1 - k_2)} \cdot \ln\left(\frac{k_1}{k_2}\right) = \text{constant}$$

and from equation (1),

$$\left[W_1\right] = \frac{W_o k_1}{k_2 - k_1} \left(e^{-k_1 [M] t_{max}} - e^{-k_2 [M] t_{max}}\right)$$

the exponential term involved $t_{max}\left[M\right]$ which is a constant, and hence:

$$\left[W_1\right] \propto \left[W\right]_o$$

Therefore the concentration of W_1 would be a constant at t_{max} for a given initial concentration of WCl_6 $[W_o]$. Hence plots of log (maximum initial rate of polymerisation at t_{max}) against log (monomer concentration) at constant catalyst concentrations, can be drawn for cyclopentene and cyclooctene using the results shown in sections V-(6) and IV-(5). These graphs are shown in figures VI-(1) and (2). The slopes of these graphs were calculated at 0.70 for cyclooctene and 1.22 for cyclopentene. These values showed that x, the order of polymerisation in monomer was approximately first order for both monomers.

Equation (1) shows that the concentration of the active species W_1 is dependent upon the initial concentration of WCl_6. This fact was shown experimentally in section V-(3) where the graph of log (initial rate of polymerisation) versus log (concentration of WCl_6), at constant monomer concentration and constant premix time, was a straight line with a slope approximately equal to unity.

(iv) Analysis of a typical polymerisation curve

A typical polymerisation curve is shown in fig.VI-(3) and the rate of polymerisation can be seen to be falling with time, tailing off to a constant rate of polymerisation. The constant rate of polymerisation obtained after approximately 35 minutes of reaction suggested that the proposed W_2 compound, formed from the reaction of W_1 with monomer, (reaction XL1-(a)), was capable of forming an active catalyst with $Al(iBu)_3$, W_2*. This second active catalyst would have a lesser activity than W_1* but its contribution to the rate of polymerisation would increase as the catalyst site formed from W_1 was used up. Hence the different stages of the polymerisation curve shown in fig. VI-(3) would be:

(1) The polymerisation initiated by W_1* and possibly some W_2*, depending upon the premix time.

(2) The polymerisation initiated by W_1* and W_2*.

(3) The polymerisation initiated by W_2* alone.

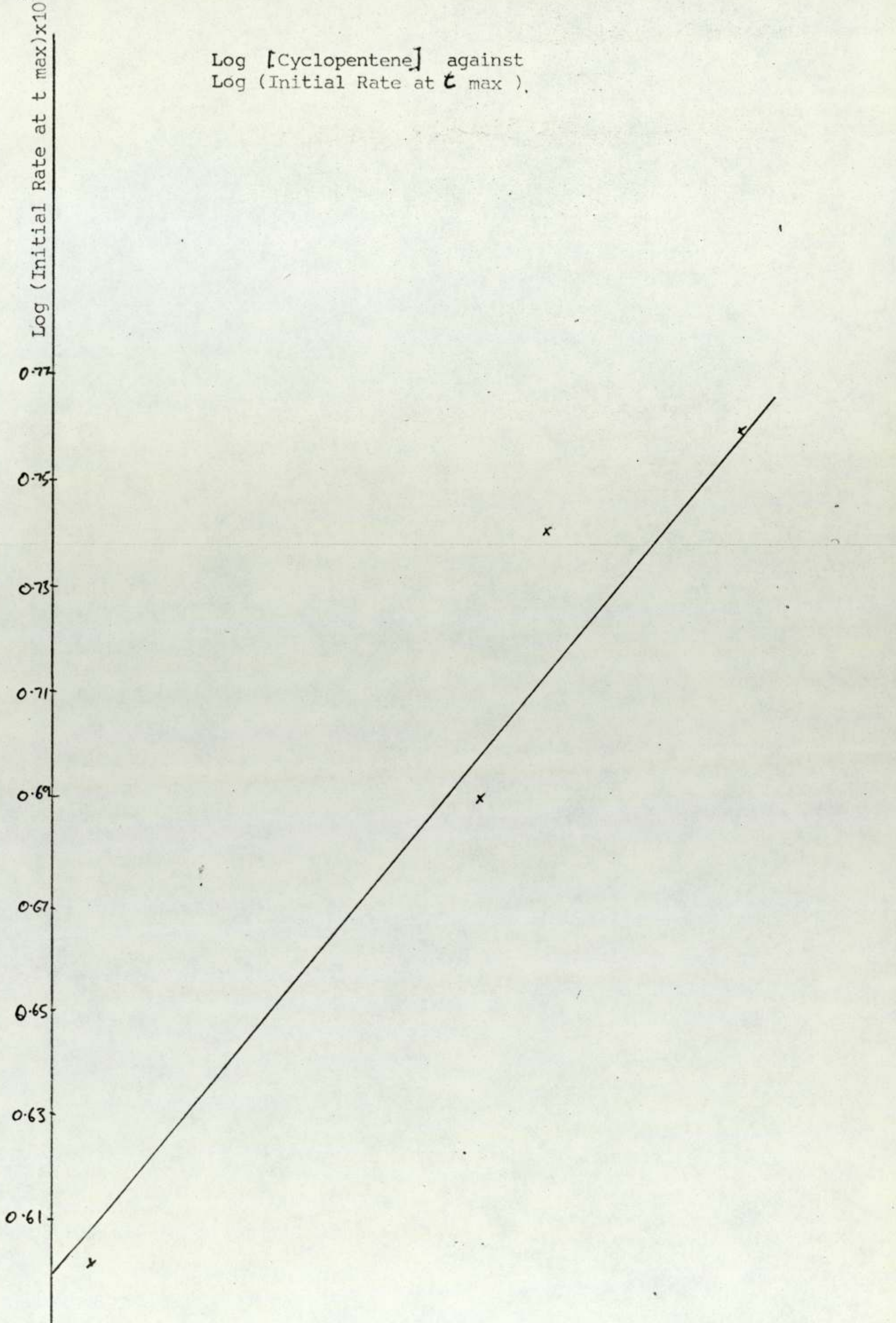

Log [Cyclopentene] against
Log (Initial Rate at t max).
Log (Initial Rate at t max)x10^2
0·77
0·75
0·73
0·71
0·69
0·67
0·65
0·63
0·61
0·16
0·18
0·20
0·22
0·24
0·26
0·28
0·30
Log [CP] →

Fig. VI-(1)

Log [Cyclooctene] against
Log (Initial Rate at t max)

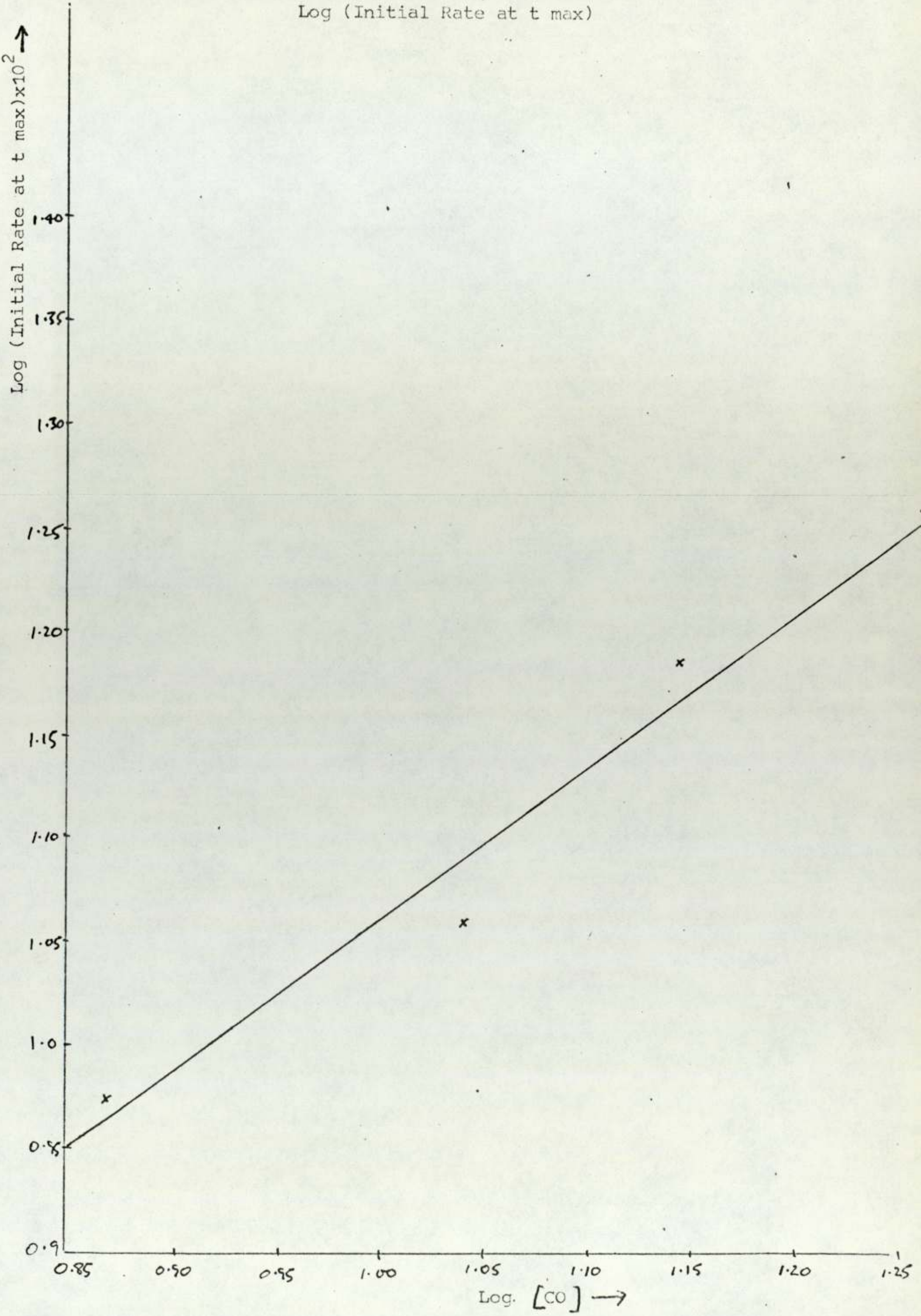


Fig.VI-(2)

Cyclopentene concentration = 1.91 moles litre^{-1}

WCl_6 = 6×10^{-4} " "

$Al(iBu)_3$ = 1.2×10^{-3} moles litre^{-1}

Premix Time = 2 minutes

Temperature = 25°C

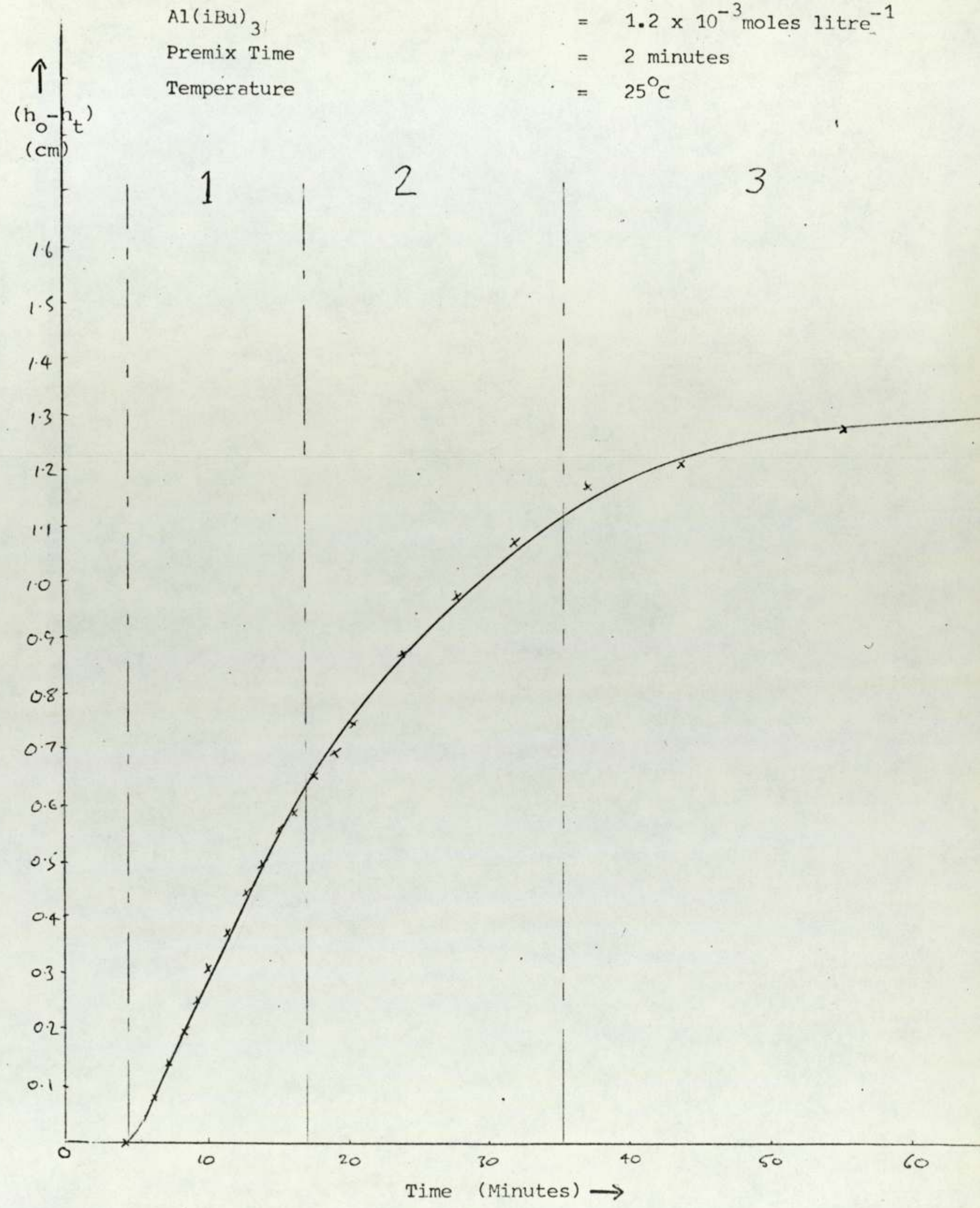


Fig. VI-(3)

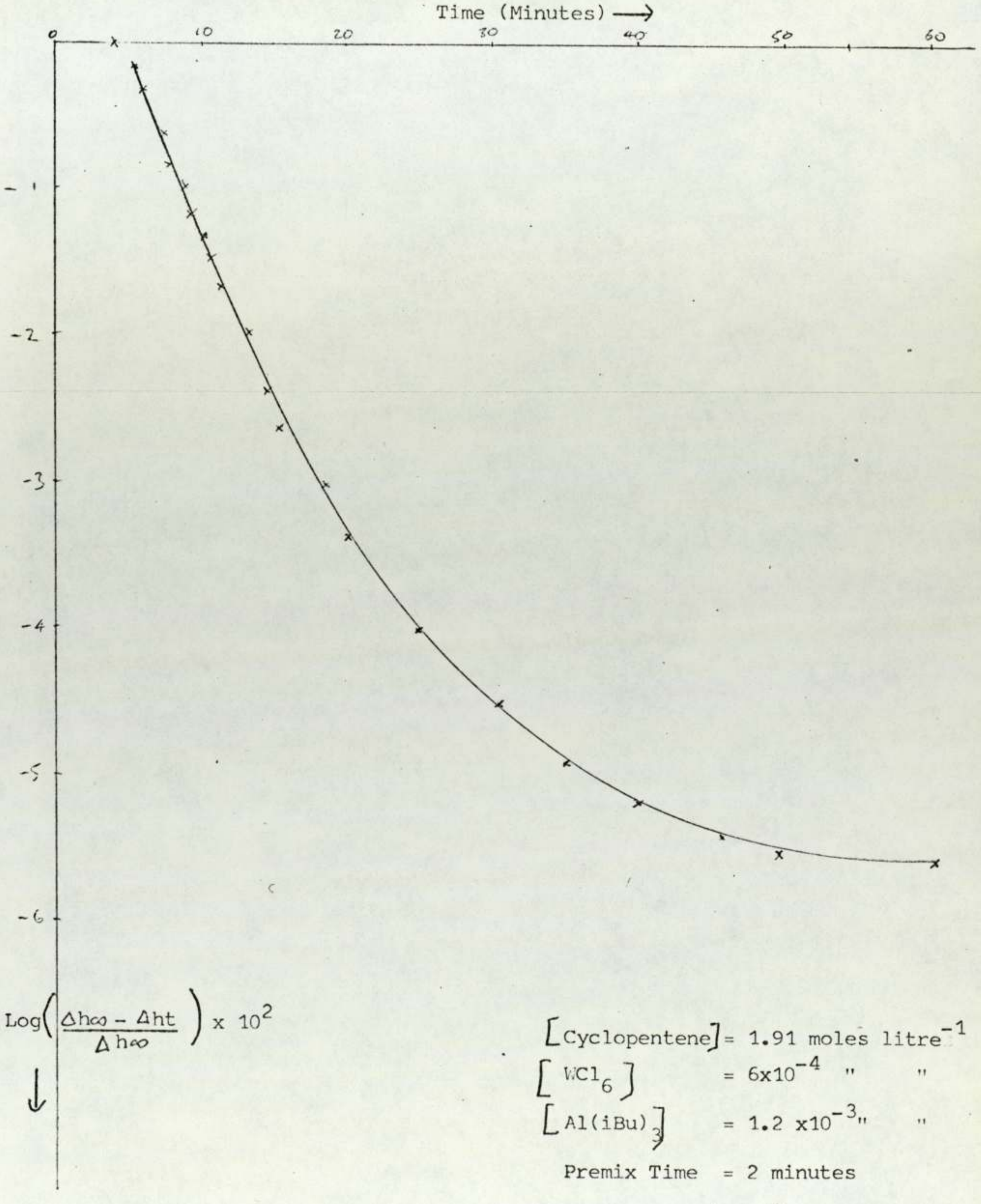
The decay in the rate of polymerisation was investigated by plotting a graph of log ($\frac{\Delta h_\infty - \Delta h_t}{\Delta h_\infty}$) against time of polymerisation, where Δh_∞ was the total possible change in meniscus height in the dilatometer for a theoretical conversion of monomer to polymer of 100% and Δh_t was the change in meniscus height in the dilatometer at time t. Hence the function $\left(\frac{\Delta h_\infty - \Delta h_t}{\Delta h_\infty}\right)$ is proportional to the monomer concentration via the equation:

$$\frac{[M]}{[M]_0} = \left(\frac{\Delta h_\infty - \Delta h_t}{\Delta h_\infty}\right)$$

where $[M]_0$ is the initial concentration of monomer.

The graph of log $\left(\frac{\Delta h_\infty - \Delta h_t}{\Delta h_\infty}\right)$ against time is shown in fig.VI-(4). If the decay in the rate of polymerisation was due to the consumption of monomer, then the plot of log $\left(\frac{\Delta h_\infty - \Delta h_t}{\Delta h_\infty}\right)$ against time would have been a straight line. Hence the decrease in the rate of polymerisation was due to the consumption of catalyst. To show that the consumption of catalyst was first order a graph of log $\left(\log\left(\frac{\Delta h_\infty - \Delta h_t}{\Delta h_\infty}\right)\right)$ against log (time) was plotted and this graph is shown in fig.VI-(5), and was the expected straight line.

Time Against Log$\left(\frac{\Delta h_\infty - \Delta h_t}{\Delta h_\infty}\right)$



[Cyclopentene] = 1.91 moles litre^{-1}
[WCl_6] = 6×10^{-4} " "
[$Al(iBu)_3$] = 1.2×10^{-3} " "
Premix Time = 2 minutes
Temperature = 25°C

Fig.VI-(4)

Log (Log($\frac{\Delta h_{\infty} - \Delta h_t}{\Delta h_{\infty}}$)) against Log (Time)

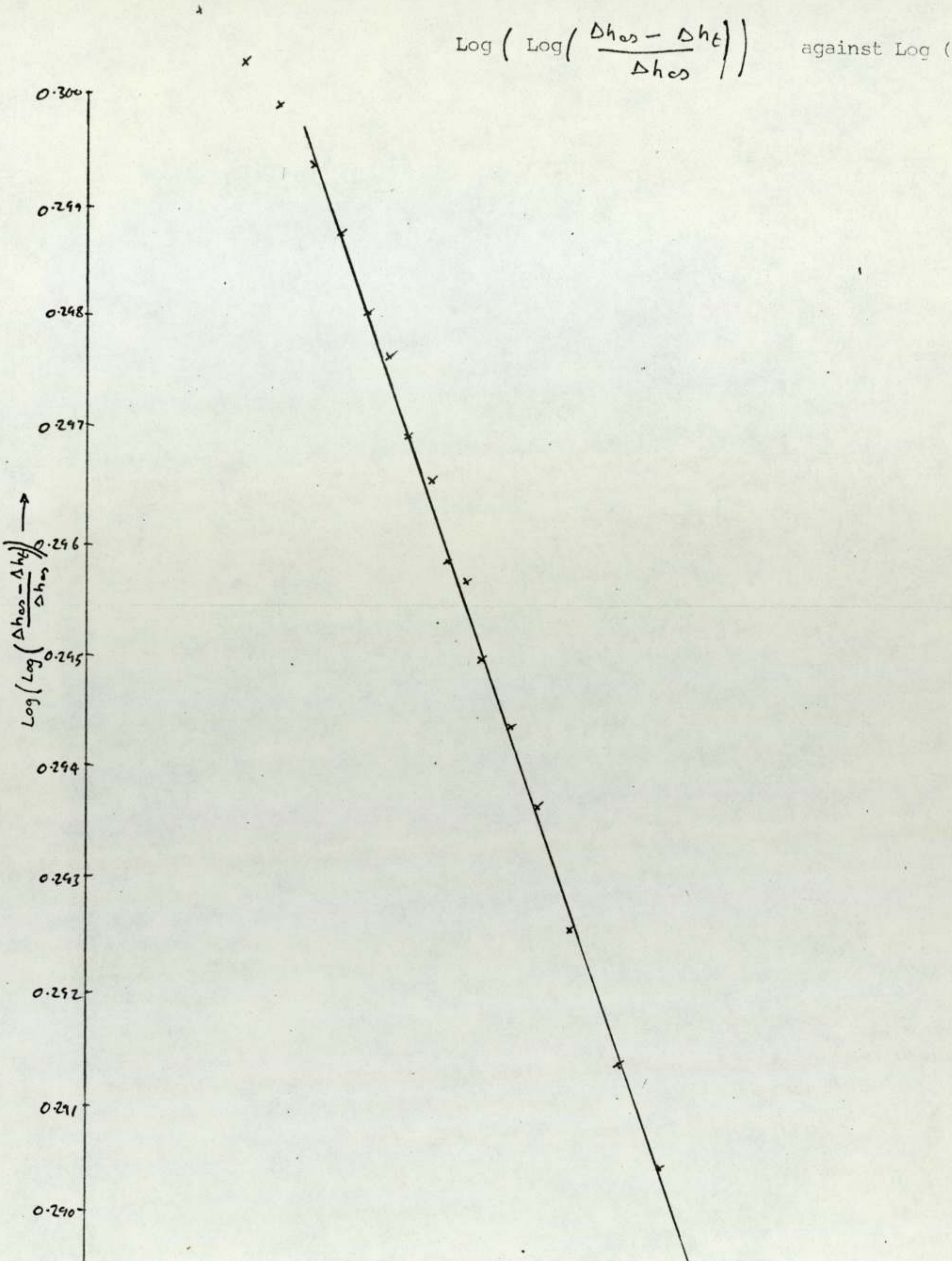


Fig.VI-(5)

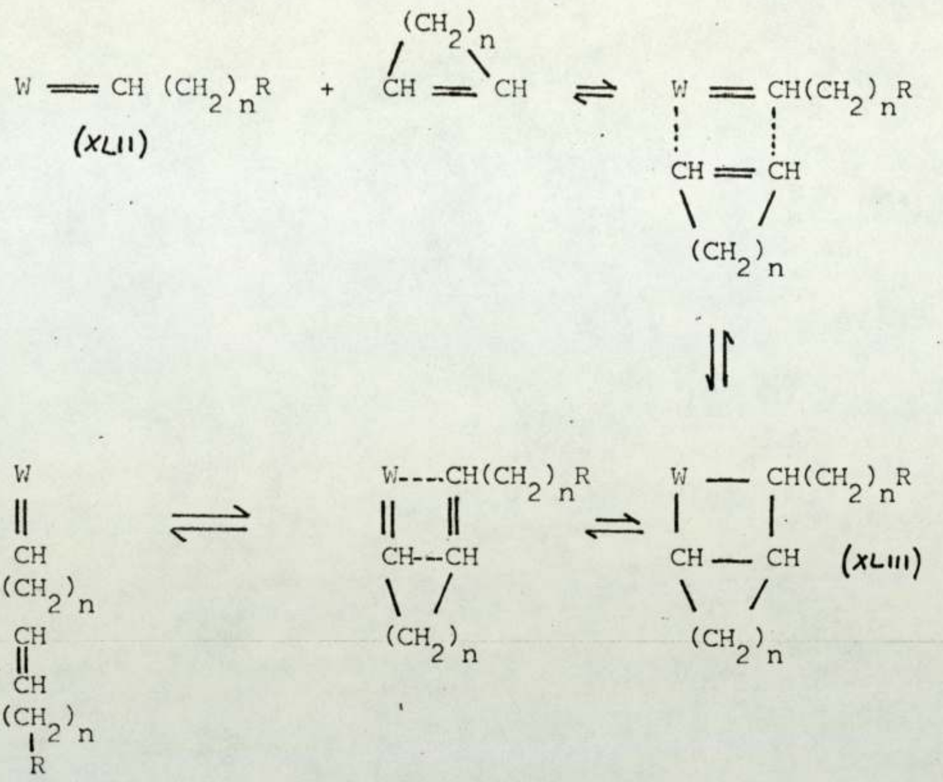
VI-(2) The Mechanism of the Polymerisations

In proposing a mechanism for the ring opening polymerisations of cyclic olefins and the olefin metathesis reaction there are several factors to be explained from the results seen in chapter IV, V and VI as well, as from the work that has already been published on the subject:

1. The natures of the W_1 and W_2 compounds and their subsequent reactions with Al $(iBu)_3$ to form the active catalyst sites, W_1^* and W_2^*.
2. Polymerisation of cyclic olefins did not take place in the absence of Al $(iBu)_3$.
3. The lack of any absorbance in the e.s.r. spectra of WCl_6 and its reaction products with cyclic olefins, despite the fact that tungsten had been shown to be in a reduced oxidation state[31] after the reaction of WCl_6 with cyclopentene.
4. There was a maximum initial rate of polymerisation when the ratio of Al $(iBu)_3$ to WCl_6 was 2:1.
5. There was no polymerisation when the catalyst components, WCl_6 and Al $(iBu)_3$, were premixed prior to their addition to the cyclic olefin.

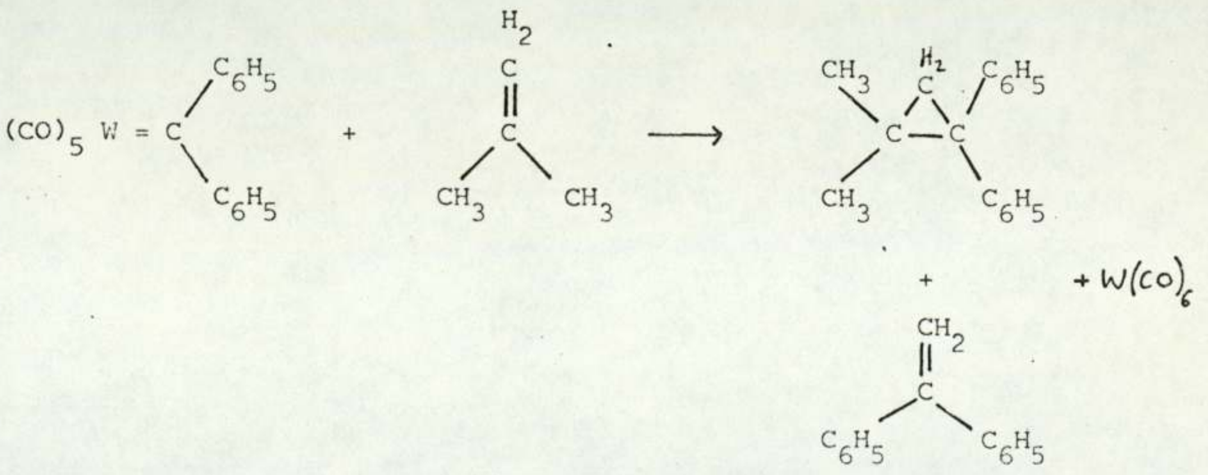
Kinetic chain mechanism

A kinetic chain mechanism involving metal carbenes would seem to fit these requirements similar to the mechanism first suggested by Chauvin[16]. His mechanism involved as a first step the formation of a metal carbene (XLII) between the tungsten atom and the cyclic olefin. It was not explained how this metal carbene could have been formed but the subsequent stages of the proposed mechanism are shown overleaf:



(XLII) (XLIII)

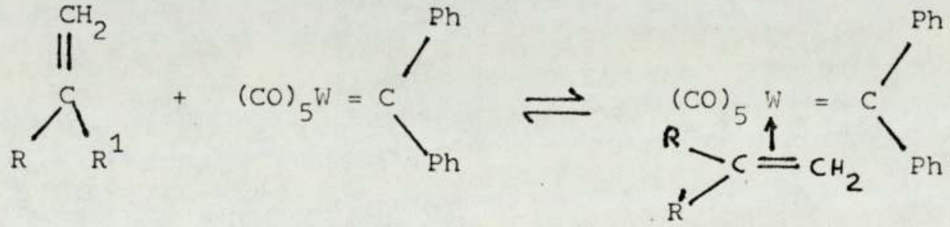
The transition complex XLlll was a metallocyclobutane. Further evidence for this mechanism was provided by Casey and Burkhardt[67]. They synthesized a reactive metal-carbene complex, (diphenyl carbene) penta carbonyl tungsten (0), and used this reactive carbene in reactions with alkenes. The carbene complex was reacted with isobutylene at 100°C for 2.5 hours and 1,1 diphenylethylene, tungsten hexacarbonyl and 1,1 - di-methyl - 2,2 diphenyl cyclopropane were obtained, as is shown in XLIV.

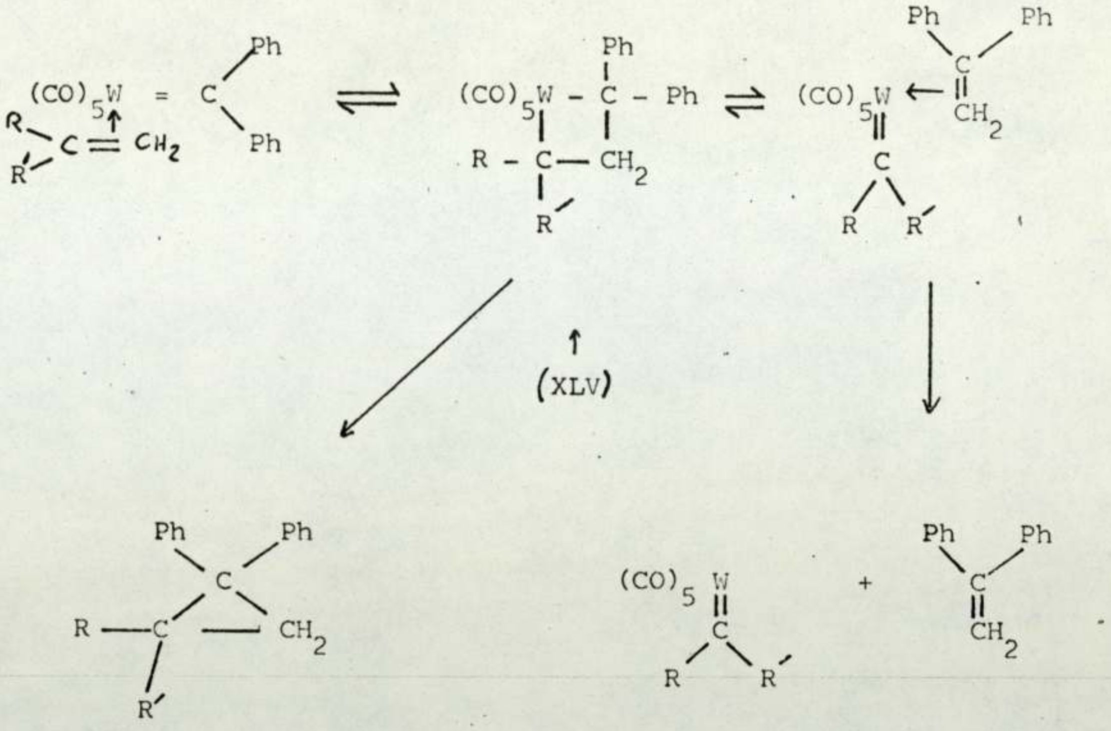


XLIV

To determine the source of the methylene fragments in the 1,1-diphenyl ethylene, Casey studied the reaction of trans-2-butene with the metal carbene. The reaction produced 1,2 dimethyl-3,3-diphenylcyclopropane in trace quantities and 1,1 diphenyl-1-propene. These experiments demonstrated that scission of the carbon-carbon double bond of the alkene and the combination of a methylene fragment with the diphenyl carbene group of the metal carbene occurred. The possibility that the second fragment from the alkene scission could have been incorporated as the carbene ligand in a new metal carbene complex was investigated by reacting the diphenyl carbene penta-carbonyl tungsten with 1-methoxy - 1 - phenylethylene, because the expected new carbene complex, $(CO)_5 WC (OCH_3) C_6H_5$, was known to be stable under the reaction conditions. A 26% yield of the expected new carbene complex was obtained.

Hence the cyclopropanation and alkene scission reactions could be explained in terms of Chauvin's original mechanism:

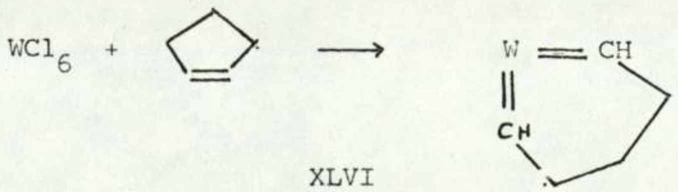




The metalocyclobutane transition state XLV formed by the rearrangement of a metal complex containing both a carbene and alkene ligand was the key intermediate in the reaction. XLV could then undergo a reductive elimination to produce a cyclopropane or cleavage to produce a metal complex containing both a co-ordinated 1,1 diphenylethylene and a new carbene ligand. The latter procedure would be a metathesis reaction and hence strong evidence was provided for Chauvin's original mechanism.

An adaption of Chauvin's mechanism can be used to explain the kinetic features of the ring-opening polymerisation of cyclooctene and cyclopentene discussed earlier in this chapter.

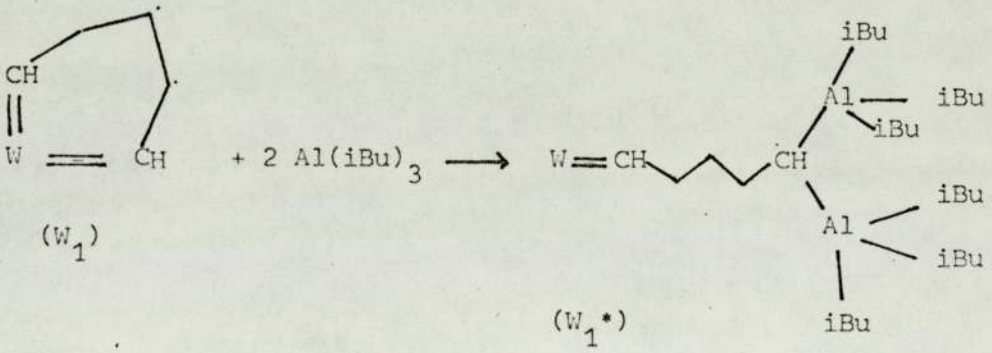
(1) The formation of W_1 from the action of WCl_6 with cyclic olefin can be described by Chauvin's mechanism as the formation of the metal carbene complex wherein perhaps:



XLVI

The complex XLVI would be formed from the insertion of the tungsten atom into the double bond of the olefin. This complex would be the W_1 complex.

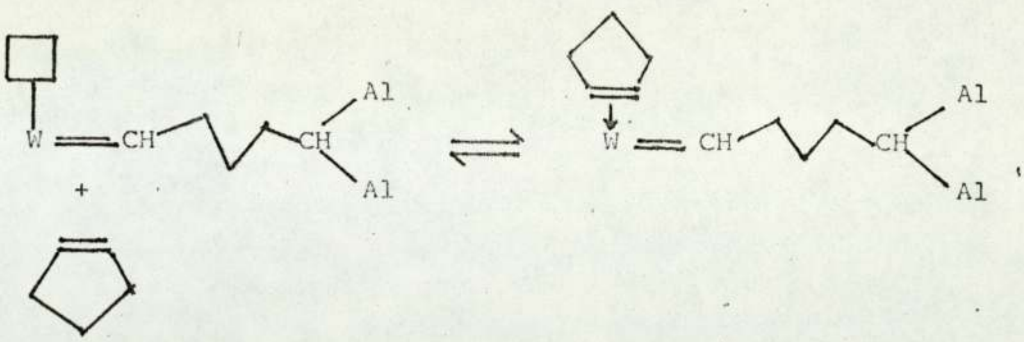
(2) The next step in the kinetic scheme involved the reaction of W_1 with $Al(iBu)_3$ to form the active catalyst complex W_1*. This step can be rationalised in Chauvin's mechanism by recalling that the maximum rate of polymerisation of cyclooctene occurred when the molar ratio of Al $(iBu)_3$ to WCl_6 was 2 : 1 and hence it could be visualised that two moles of Al $(iBu)_3$ were required for every mole of tungsten to initiate the polymerisation. It may be that the activation of W_1 may take place as follows :-



XLVII

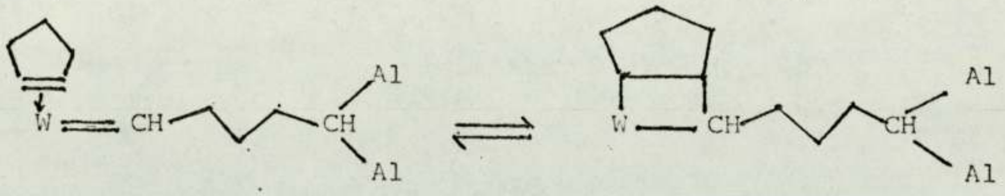
This reaction could possibly occur as the W_1 complex would be relatively unstable. The W_1* complex formed would then have a vacant co-ordination site for possible co-ordination of a reacting monomer molecule.

(3) This step involves the co-ordination of the second monomer molecule with the W_1* catalyst as shown in XLVIII.



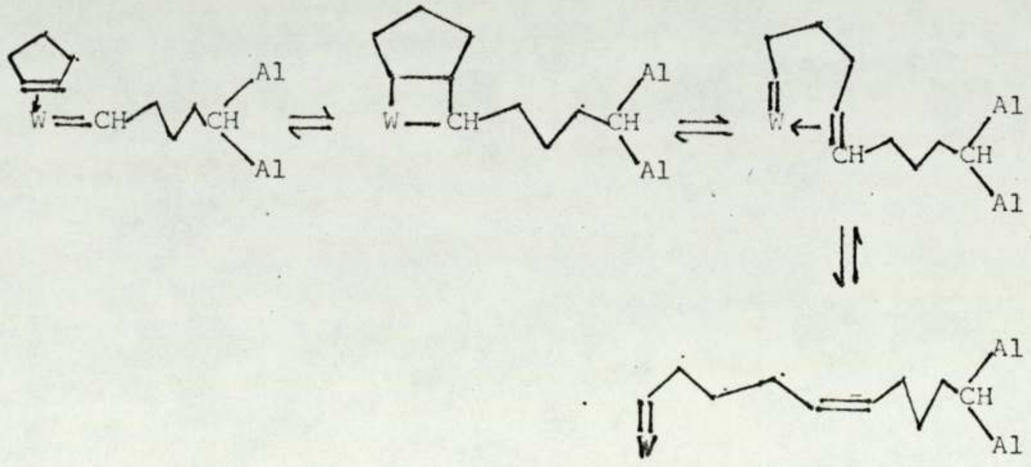
XLVIII

The intermediate (XLVIII) formed in the reaction would then rearrange into the metallocyclobutane transition state envisaged by Chauvin:



XLIX

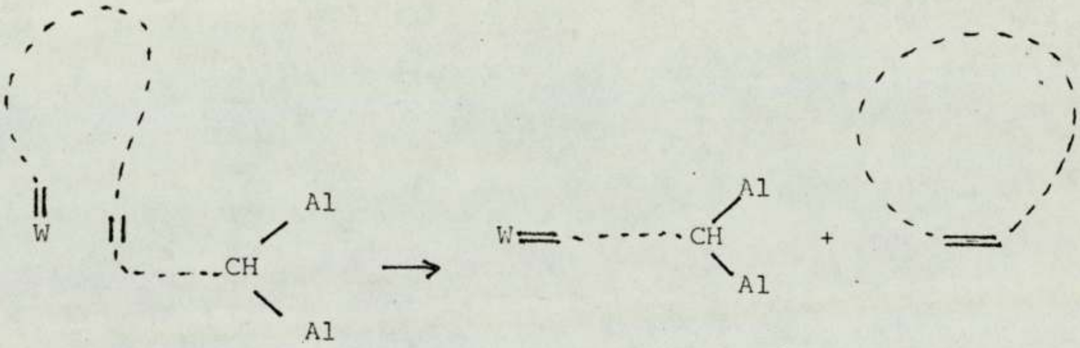
4. The metallocyclobutane transition state could now undergo cleavage to give either the original metal complex of (XLVIII) or to yield the new metal complex, (L)



(L)

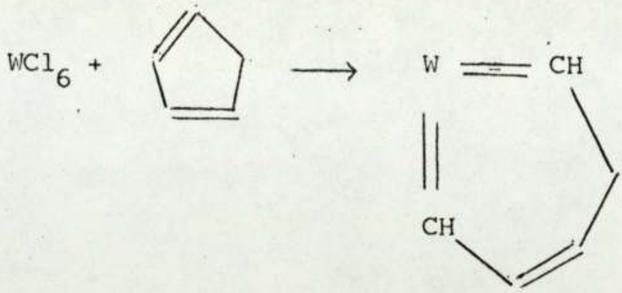
The reactions XLVIII to L would constitute a propagation mechanism and these reactions would be repeated for a polymerisation reaction.

The presence of macrocyclic species in the polymerisate of a cyclopentene polymerisation that were confirmed by Calderon[5], can be explained by this mechanism by considering their formation to be due to a "back-biting" process. This is shown in reaction LI.



LI

To explain how conjugated dienes could slow or even prevent the polymerisation reaction, consider the interaction of the cyclic diene with the WCl_6, similar to that of reaction XLVl.



L11

The carbene complex L11 formed between the diene and the WCl_6 could be a more stable complex than the carbene formed in reaction XLV1 because of possible electron delocalisation around the 6-sided ring. This "stable" complex would then react much more slowly with the $Al(iBu)_3$ than would the complex XLV1. Hence, if sufficient conjugated dienes were present in the monomer, the polymerisation reaction would be prevented.

VI - (3) Molecular Orbital Considerations

It is possible to describe the propagation mechanism proposed by Chauvin in terms of the molecular orbital theory of bonding.

(i) It is first worth considering the structure of the tungsten carbene complex itself, which is the propagating centre in the mechanism. According to the mechanism there exists a double bond between the tungsten atom and a carbon atom of the last alkylidene unit of the polymer chain. Both the carbon and tungsten atoms must have orbitals of similar symmetry that can overlap to form this double bond. The tungsten atom has the orbitals dz^2, dxz, dyz, $d(x^2-y^3)$ which would have the correct symmetry to form σ or π bonds with the olefin molecule. The carbon atom of the olefin passes a px orbital of the correct symmetry, in addition to the olefin π bonding and π * (antibonding) orbitals.

A σ bond between tungsten and carbon could be formed by overlap of the tungsten $d(x^2 - y^2)$ orbital and the px orbital of the carbon as shown in fig. VI-(6).

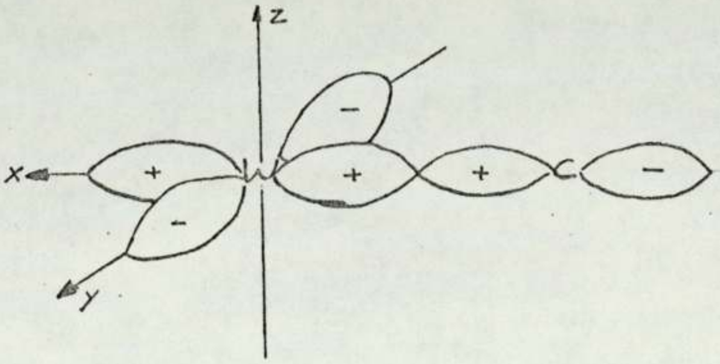


Fig.VI-(6)

It is possible to consider the formation of the π bond of the tungsten - carbon double bond to be the result of the interaction of the dxz orbital of the tungsten and the pz orbital of the carbon as shown in fig.VI-(7).

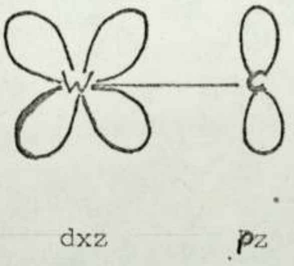


Fig.VI-(7)

The electrons for this orbital would be supplied one each by the tungsten and the carbon atoms. It can be readily seen that the tungsten atom must contribute the dxz electron for the formation of the double bond, in which case it would need to be present in a reduced oxidation state, i.e. W(III), (IV) or (V), and the carbon atom the pz electron. The molecular orbital diagram for the formation of this double bond is shown in fig.VI-(8).

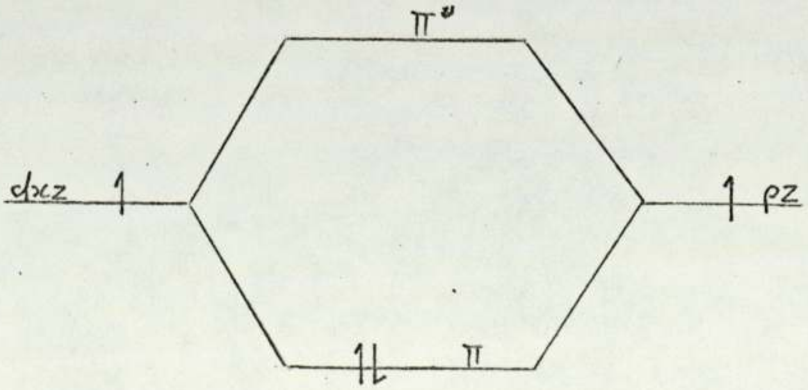


Fig.VI-(8)

This molecular orbital diagram would suggest that the unpaired dxz electron, that would normally be present in the reduced oxidation state, would have been paired with the electron from the carbon atom and consequently would not be expected to display an electron spin resonance absorption signal, in agreement with the experimental evidence.

(ii) Interaction of the W_1* complex with a cyclopentene molecule.

The interaction between the W_1* complex and the cyclopentene double bond would involve the dz^2 orbital of the tungsten and the carbon-carbon π bond of the olefin, as shown in fig.VI-(9). This bonding would be a σ - type bond.

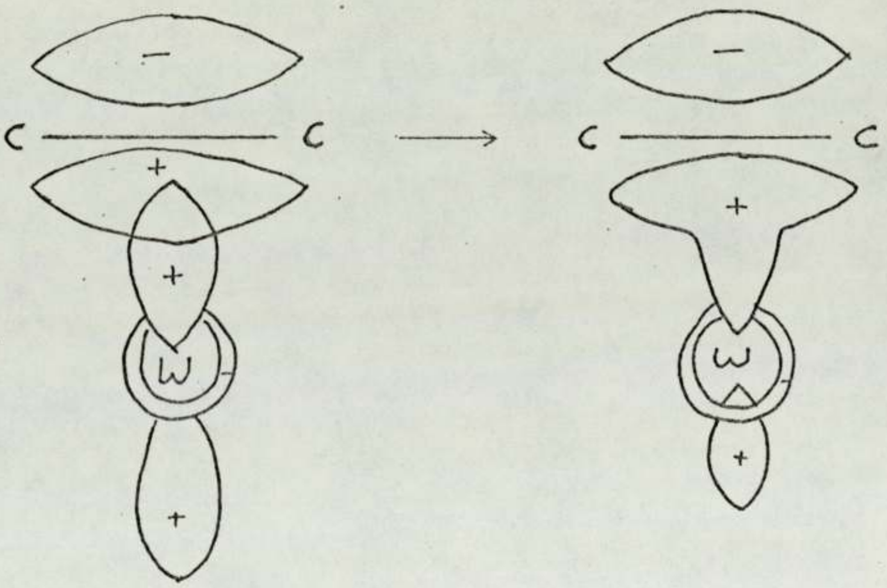


Fig.VI-(9)

Further interaction between the W_1* complex and the incoming cyclic olefin could occur by overlap of the π* orbital of the olefin and the dxz orbital of the tungsten atom, as shown in fig.VI-(10).

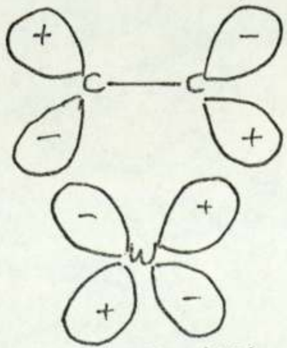


Fig.VI-(10)

(iv) Description of the bonding in the "metallocyclobutane".

The bonding in the transition state "metallocyclobutane" would involve essentially 3 σ - type bonds and a molecular orbital surrounding three atoms. The bonding in the transition state would involve the combination of the orbitals shown in figures VI-(6) to VI-(10) to form a molecular orbital encompassing all four atoms and the combination is shown in fig.VI-(11). The electrons for the bonding would be supplied by the olefins (6) and two electrons from the tungsten.

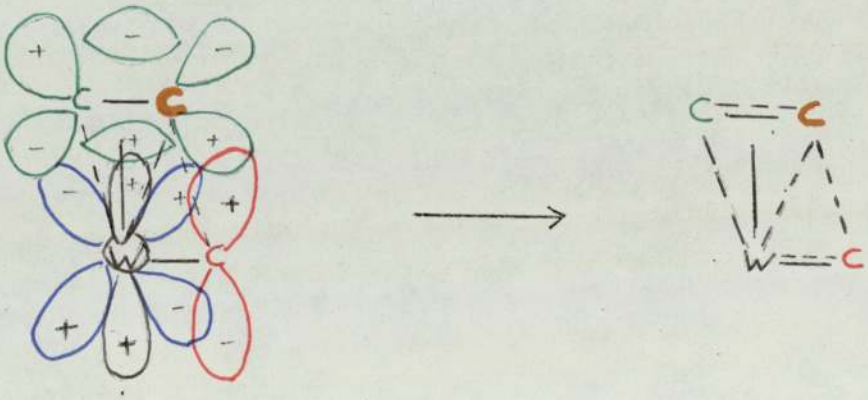


Fig VI-(11)

The three σ bonds are shown as single unbroken lines and the other bonds are shown by broken lines.

The bonding in the transition state would then undergo a subtle change. A σ bond would be formed between the "orange" and "red" carbon atoms due to overlap of 2pz orbitals. A π bond would also form between the "orange" and "red" carbon atoms due to the overlap of 2 px orbitals. An interaction between the new π orbital formed and the tungsten $dx^2 - y^2$ orbital would lead to a σ type bond between tungsten and the "orange" and "red" carbon atoms. A σ bond would be formed between the tungsten dz^2 orbital and the pz orbital of the "green" carbon atom, and a π bond formed from the px orbital and the dxz W orbital. A new three centre bond between the π^* bonding orbital of the "red" and "orange" carbons, the dxz tungsten orbital and the px orbital of the "green" carbon atom would also be formed. This new structure is shown in fig.VI-(12)

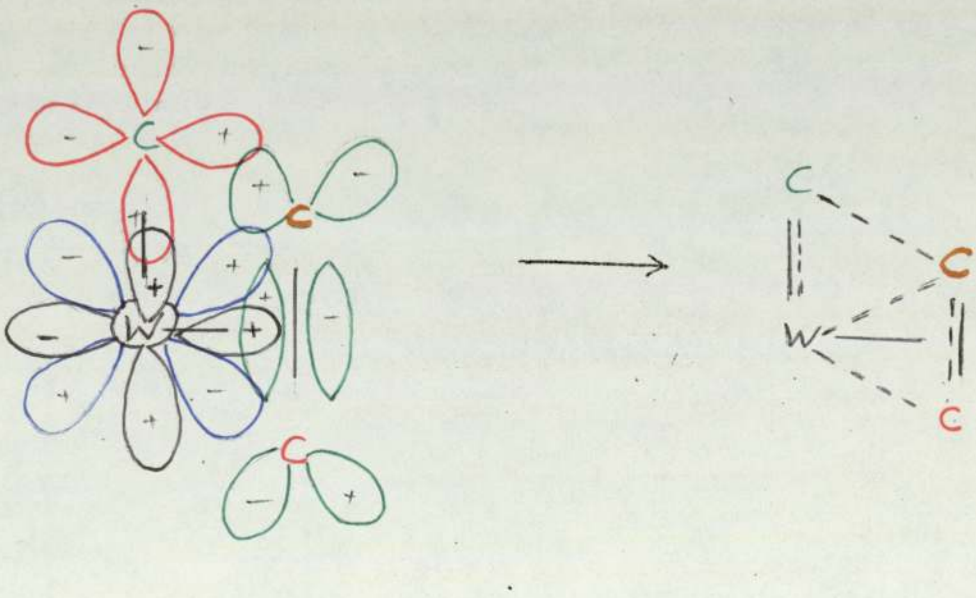
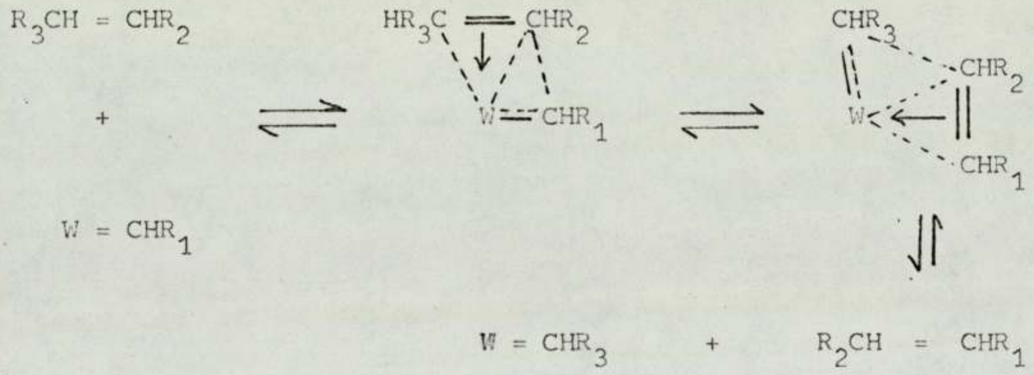


Fig VI-(12)

To complete the reaction pathway the newly formed carbon-carbon π bond may be displaced by another molecule because the de-co-ordinating process is accompanied by a release of ring strain energy of the cyclic olefin.

The overall mechanism of the olefin metathesis reaction may thus be described as:



CHAPTER VII

Conclusions and Suggestions for Further Work

The conclusions that can be drawn from the results obtained during this project can be divided into 3 sections.

1. The Order of Addition of the Catalyst Components.

It was shown in Chapter IV that the order in which the WCl_6 and $Al(iBu)_3$ were added to cyclooctene was an important factor in determining the rate and extent of the polymerisation reaction. The WCl_6 was added to the monomer before the $Al\ (iBu)_3$ for the greatest catalyst efficiency. If the $Al(iBu)_3$ was added to the monomer prior to the WCl_6, the efficiency of the catalyst system was reduced by a factor of 35, for a given set of polymerisation reaction conditions. If the catalyst components were premixed prior to their addition to the monomer, then there was no polymerisation. These results can be interpreted according to the proposed kinetic scheme by suggesting that the reduced rate of polymerisation produced when the $Al(iBu)_3$ was added to the monomer prior to the WCl_6 was due to the fact that cyclopentene had to compete with $Al(iBu)_3$ for reaction with WCl_6 to form W_1, i.e. :-

$$WCl_6 + CP \longrightarrow W_1$$

$$WCl_6 + Al(iBu)_3 \longrightarrow W/Al \quad - \quad \text{Inactive.}$$

When $Al(iBu)_3$ and WCl_6 were premixed before their addition to the monomer, no catalyst was formed, possibly due to the formation of a stable complex between WCl_6 and $Al(iBu)_3$, as described above. Hence, under normal polymerisation conditions, when the WCl_6 and monomer were premixed, it is possible that the amount of W_1 present in the system at the time when the $Al(iBu)_3$ was added represented the fraction of WCl_6 that led to active catalyst sites. Any WCl_6 left unreacted at this stage would immediately form a stable complex with the $Al(iBu)_3$ and take no further part in the reaction.

2. The importance of the presence of Conjugated Dienes in the Monomers.

It was shown in Chapter IV that the presence of a conjugated diene, 1,3 cyclooctadiene, had a marked effect on the rate of polymerisation of cyclooctene. The removal of conjugated dienes from the monomers used in the ring opening polymerisations was vitally important if any meaningful kinetic results were to be obtained. Fortunately, cyclopentadiene could be removed easily from cyclopentene using sodium metal as described in Chapter II, but 1,3 cyclooctadiene could not be removed from cyclooctene by any of the methods described in Chapter II. A further possible method for the removal of 1,3 cyclooctadiene from cyclooctene was suggested in a paper by McCleverty and Wilkinson[68] who stated that 1,3 cyclooctadiene may be converted to 1,4 cyclooctadiene by the reaction of 1,3 cyclooctadiene with dichloro-tetra carbonyl dirhodium, and hence it may be possible in any further work on the ring opening polymerisation of cyclooctene to prepare conjugated diene-free cyclooctene using this technique.

3. Kinetics of Cyclic Olefin Polymerisation.

The experimental determination of the rate of polymerisation of cyclopentene produced meaningful results when it was observed that the rate of polymerisation depended to a great extent upon the mode of preparation of the catalyst. The normal procedure of synthesis of the catalyst was to add a solution of WCl_6 in toluene to a solution of cyclopentene, followed by the addition of a solution of $Al(iBu)_3$ in toluene. The time delay between the additions of these components significantly affected the initial rate of polymerisation; so that a maximum initial rate of polymerisation was observed after a delay time that depended upon the concentration of the monomer. This suggested that some species, that could react with $Al(iBu)_3$ to produce an active catalyst, was formed and also destroyed during this period. A simple kinetic scheme was devised to test this hypothesis which was:

$$WCl_6 + CP \longrightarrow W_1 \xrightarrow{Al(iBu)_3} W_1^{\bullet}$$

$$W_1 + CP \longrightarrow W_2 \xrightarrow{Al(iBu)_3} W_2^{\bullet}$$

It was shown that, if it is assumed that the initial rate of polymerisation was a measure of the concentration of W_1 at the time of the addition of $Al(iBu)_3$, the rate of polymerisation at constant monomer and catalyst concentrations would be a maximum at a time (t max) given by:

$$t\ max = \frac{1}{[CP]_o} \cdot \left(\frac{1}{k_1 - k_2} \right) \cdot \ln \left(\frac{k_1}{k_2} \right)$$

The straight line obtained for the plot of t max against $[CP]^{-1}$ would indicate agreement with this type of mechanism.

According to the above scheme the concentration of W_1 was given by:

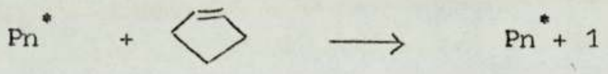
$$[W_1] = \frac{k_1}{k_2 - k_1} [WCl_6]_o \left(e^{-k_1 [CP]_o t} - e^{-k_2 [CP]_o t} \right)$$

where t is the time between the addition of WCl_6 and $Al(iBu)_3$. According to this equation the fraction of WCl_6 acting as an active species in the polymerisation, at constant concentration of monomer and pre-mixing time, is independent of the initial concentration of WCl_6.

The first order plot obtained from a dependence of initial rate of polymerisation against concentration of WCl$_6$ after 2 minutes premixing time would appear, therefore, to be a true first order dependence of the rate on the concentration of WCl$_6$.

It is also apparent from the 2 equations quoted above that at a given concentration of cyclopentene the maximum rate of polymerisation should occur at a constant premixing time for all initial concentrations of WCl$_6$. This aspect of the kinetics of the polymerisation has not been studied and it is suggested that this should be an important area of future work.

The first order dependence of the rate of polymerisation on the initial concentration of WCl$_6$ would suggest that a simple chain mechanism is operative during the course of the polymerisation and that a general propagation step such as:



can be postulated. The nature of this propagation step has been described earlier but it would appear from the shape of the conversion-time curves that the concentration of active catalyst (Pn^*) decayed during the course of the polymerisation. The decay in catalyst activity would appear to be a first order process which may well be similar in nature to the conversion of W_1 to W_2 during the reaction of WCl$_6$ with cyclopentene. In order to postulate the nature of this termination reaction the structures of the products of the reaction of WCl$_6$ with cyclopentene should be determined if possible.

The decay in the rate of polymerisation during the course of the polymerisation, not to zero, but to a constant rate, would suggest that, if W_1^* was consumed, it formed either a species of considerably lower activity (W_2) which was stable during the polymerisation, or that the catalytic activity during the initial stages should not be ascribed to one species but 2, (W_1 and W_2), and only one of these, (W_1), was unstable, leaving the second, (W_2), to continue the polymerisation,

$$
\begin{array}{llll}
\text{i.e.} & WCl_6 & \xrightarrow{CP} & W_1 + W_2 \\
 & W_1 & \xrightarrow{CP} & W_3 \quad \text{(Inactive)} \\
 & W_2 & \xrightarrow{CP} & \text{Stable}
\end{array}
$$

The presence of 2 species can be invoked to account for the bimodal molecular weight distribution of the polymer produced but more detailed studies will be needed to distinguish between possible reaction mechanisms. This in fact may well be obtained from an analysis of the molecular weight distribution curves as a function of premixing time and conversion.

It is also possible to write an equation for the rate of production of W_2 according to the mechanism described on page 136:

$$\frac{d\left[W_2\right]}{dt} = k_2 \left[W_1\right] \left[CP\right]$$

substituting for $\left[W_1\right]$ in this equation:

$$\frac{d\left[W_2\right]}{dt} = \frac{k_2\, k_1}{k_2 - k_1} \left[WCl_6\right]_o \left\{ e^{-k_1 \left[CP\right]_o t} - e^{-k_2 \left[CP\right]_o t} \right\}$$

$$\therefore \left[W_2\right] = \frac{\left[WCl_6\right]_o}{k_2 - k_1} \left\{ k_1 \left(\exp.-k_2 \left[CP\right]_o t - 1\right) - k_2 \left(\exp.-k_1 \left[CP\right]_o t + 1\right) \right\}$$

This is an expression for $\left[W_2\right]$ at the time of addition of $Al(iBu)_3$ which converts W_2 to W_2^*.

It can be seen that at the time of addition of $Al(iBu)_3$,

$$\frac{[W_1]}{[W_2]} = \frac{k_1 \left(\exp - k_1 [CP]_o\, t - \exp - k_2 [CP]_o\, t\right)}{k_1 (\exp - k_2 [CP]_o\, t+1) - k_2 (\exp - k_1 [CP]_o\, t + 1)},$$

Of importance in the consideration of this ratio is the fact that if the initial concentration of cyclopentene is constant and the pre-mixing time is also constant the ratio $\frac{[W_1]}{[W_2]}$ is constant, and independent of the initial concentration of WCl_6. Thus, if W_1^* and W_2^* give rise to the different peaks in the molecular weight distribution the ratio of areas under these peaks should be independent of the initial concentration of WCl_6, if the initial concentration of cyclopentene and the pre-mix time are kept constant. This again represents a useful area for further study.

The elucidation of the exact natures of the propagating species in the polymerisation has not been possible in this work. The effect of the structure of the aluminium compound on the rate of polymerisation and the dependence of the rate of polymerisation on pre-mixing time may lead to a better understanding of the polymerisation process. Attempts should also be made, if possible, to separate and characterise all the intermediates present in the polymerisation.

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