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'STUDIES ON THE RING OPENING POLYMERISATION OF CYCLOPENTENE'

SUBMITTED FOR THE DEGREE OF Ph.D.

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'Studies on the ring opening polymerisation of cyclopentene'

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Summary

This work describes investigations on the initiation and the propagation of the polymerisation of cyclic alkenes catalysed by tungsten based systems. Cyclopentene was polymerised using the bimetallic $WCl_6/Al(iBu)_3$ catalyst and infra-red spectroscopy showed that trans-polypentenamer was formed. A kinetic chain mechanism was invoked to describe the propagation step in the polymerisation and to account for the bimodal molecular weight distribution of the polymer it was proposed that two active propagating species were present in the polymerisation process. Oxidation state studies showed that during the polymerisation tungsten existed in at least two oxidation states.

Subsequently a monometallic catalyst system - WCl_6/O_2 - ,capable of polymerising cyclopentene, was developed. Infra-red studies showed that the product was again a trans-polypentenamer and oxidation state studies on an analogous system suggested similarities between the mechanism of the polymerisation initiated by the monometallic catalyst and that initiated by the bimetallic system. Ultra-violet spectroscopic investigations on the $WCl_6/Cp/O_2$ reaction further clarified the nature and mode of formation of the species active in the polymerisation.

It was finally concluded that a kinetic chain mechanism could be invoked to describe the propagation steps in both polymerisation systems wherein the initiation step was the formation of a tungsten carbene and the polymerisation proceeded by co-ordination of monomer to the tungsten and insertion into the growing kinetic chain. The role of the aluminium and that of the oxygen in their respective systems were thought similar and to be the production of the metal carbene from a tungsten metallocyclic which arose from a tungsten/cyclopentene reaction.

A molecular orbital treatment of the mode of formation of the various species in the polymerisation concludes the report.

Keywords Cyclic Alkene.
Metathesis.
Polypentenamer.

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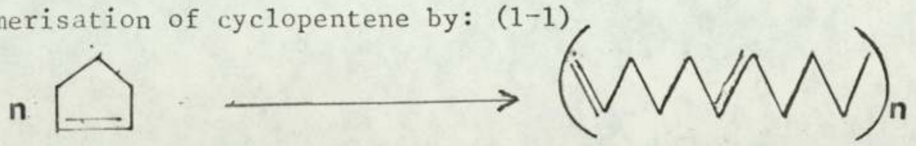
CHAPTER I

General introduction to the ring opening polymerisation of cyclopentene.

I - 1 Introduction

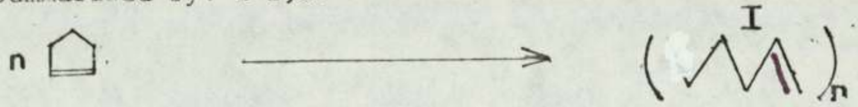
The search for new, commercially viable, synthetic rubbers has resulted in much research leading to the discovery of many new materials. The latest addition to this range of polymeric materials is the elastomer trans 1-5 polypentenamer which can be prepared by the polymerisation of cyclopentene by: (1-1)



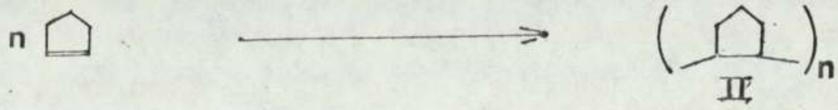
1-1

The production of trans polypentenamer* was first disclosed by Eleuterio in 1959 when cyclopentene was polymerised over a solid catalyst obtained by supporting, lithium aluminium hydride, activated molybdenum oxide on alumina[1]. Since this report many catalyst systems, based mainly upon tungsten and molybdenum compounds, have been widely discussed and researched so that it is now possible to produce linear polypentenamers of almost any required stereo structure[2].

There are two possible methods of polymerising cyclopentene which can be summarised by: I-2,3.



1-2



1-3

Polymerisation of cyclopentene to polycyclopentene (II) cannot be carried out with standard Ziegler-Natta type catalysts, The polymer obtained with cyclopentene over tungsten or molybdenum based catalysts is the linear polypentenamer (I) which maintains the unsaturation of the monomer and in this respect is different from conventional polymers.

Trans polypentenamer as a rubber The elastic nature of high polymers depends on the positions of their first and second order transition

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*Iupac nomenclature

temperatures[3] i.e. the melting point and the glass transition temperature which in turn depend on the steric and isomer distribution of the polymer. The melting point should be close to room temperature and the glass transition temperature should be below -50°C to ensure that the elastic properties of the rubber are not impaired within the normal working temperature range.

An elastomer should be amorphous at room temperature and any tendency towards crystallisation, which causes hardening of the vulcanised material, should only occur at low temperatures in the unstretched state. Conversely crystallisation in a rubber can be a desirable property because the ability to crystallise on stretching provides self reinforcement of raw compounds or vulcanisates thus improving the tensile strength and building tack of the material. Natural rubber is stereoregular and combines these crystallinity properties to advantage producing a high strength vulcanisate.

The problem of controlled crystallisation is not easily overcome in synthetic rubbers but a solution is possible with trans polypentenamer. This polymer which has a predominantly trans configuration (93%) has a first order transition point (m.pt.) of +20°C which is close to that of natural rubber and hence there is little tendency to crystallise in the unstretched vulcanisate. Indeed X-ray crystallography shows[3] that the unstretched polypentenamer is amorphous but the stretched material produces the X-ray spectrum of a highly oriented fibre with a repeat unit of 11.85Å. The polymer produces a rubber vulcanisate which has a stress/strain curve close to that of natural rubber when cured with low concentrations of conventional curing compounds. The commercial usefulness of the rubber is increased by the fact that it can be heavily loaded with extenders such as oils or carbon blacks without any appreciable impairment of physical properties. These properties of the trans polypentenamer vulcanisate together with its good building tack and viscosity characteristics make it a suitable material for use in the car tyre industry or other similar applications.

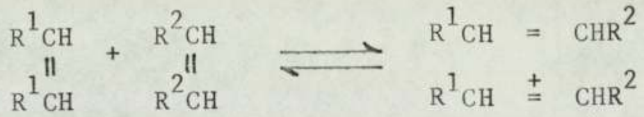
I - 2 Ring opening polymerisation of cyclic alkenes - a special case of olefin metathesis

The ring opening polymerisation of cyclic alkenes, in particular cyclopentene, involves the use of catalyst systems which contain:

(i) a transition metal compound usually of a transition metal in the second or third transition series of the periodic table of the elements; and

(ii) an organometallic compound of a group 1 - IV metal.

The olefin metathesis reaction can be represented by: 1-4



$$\begin{array}{c} R^1CH \\ \| \\ R^1CH \end{array} + \begin{array}{c} R^2CH \\ \| \\ R^2CH \end{array} \rightleftharpoons \begin{array}{c} R^1CH = CHR^2 \\ + \\ R^1CH = CHR^2 \end{array} \qquad 1\text{-}4$$

In 1931 Schneider and Frohlich described[4] a non catalysed reaction for the conversion of propylene to ethylene and but-2-ene - 1-5.

$$2CH_3 - CH = CH_2 \rightleftharpoons CH_3 - CH = CH - CH_3 + CH_2 = CH_2 \quad - 1\text{-}5$$

For this reaction to reach equilibrium temperatures of the order of 700°C were found to be necessary, this can be accounted for by the application of the Woodward-Hoffmann rules of orbital symmetry[5] whereby such thermally activated (2+2) cycloaddition reactions are symmetry forbidden. The metathesis reaction (1-4) is athermal and involves the making and breaking of carbon-carbon double bonds. Equilibrium can be reached from either side of the reaction giving a random product distribution. The potential of the metathesis reaction was not realised until the discovery of heterogeneous and homogeneous catalysts that could promote the reaction at much lower temperatures and with minimal side reactions.

Banks and Bailey[6] first reported the catalysis of the metathesis reaction as a result of their investigations on the catalytic activity of molybdenum hexacarbonyl supported on alumina. It was found, using this catalyst, that linear olefins of 3-8 carbons were converted into mixtures of lower and higher molecular weight olefins and in particular that propylene was converted into ethylene and but-2-ene. Relatively high pressures (~30 atms.) and temperatures (~150°C) were still found to be necessary for the formation of the reaction products.

Prior to this discovery by Banks and Bailey the polymerisation of cyclic alkenes by both heterogeneous catalysts[6] and homogeneous catalysts[13] had been reported; although similar catalyst systems were effective for both olefin disproportionation (1-4) and ring opening polymerisation (1-2) reactions the relationship between the two systems was not recognised at this early stage. The polymerisation of cyclic alkenes was considered to involve scission of the single bond α to the carbon-carbon double bond[39] before Calderon et al[8] suggested that the ring opening polymerisation of cyclic alkenes was a special case of the general olefin metathesis reaction.

I - 3 Metathesis Catalysts

(1) Transition metals active in general metathesis catalysts: Olefin metathetic disproportionation and ring opening polymerisation reactions are promoted by catalyst systems which contain a transition metal atom of the second or third transition series of the periodic table of the elements. Examples of transition metals which are active[9] in these reactions are shown in Table 1-1

Table 1-1

Activity of transition metals in metathesis catalyst systems

Metathesis reaction	Active transition metal
olefin disproportionation	Ti V Cr Zr Nb Mo Ru Rh Ta W Os Ir
Ring opening polymerisation of cyclic alkenes	Ti Nb Mo Ru Rh Zr Ta W Os Ir

To date the most widely researched transition metal compounds have been those of tungsten and molybdenum since these have been found to be the most efficient components of catalyst systems in promoting metathesis reactions.[9] Tungsten compounds are efficient for promoting metathesis reactions whether olefin disproportionation or ring opening polymerisation whereas use of a metal compound from the group (Mo, Rh, Ta) will produce a catalyst which is more efficient when used for acyclic olefin disproportionation.

(II) Development of catalyst systems for ring opening polymerisations:

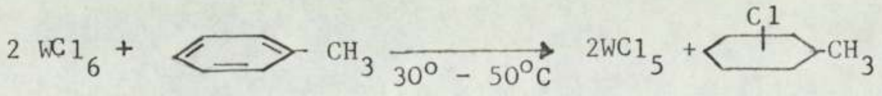
The first catalyst disclosed for the ring opening polymerisation of cyclic alkenes was discovered by Eleuterio in 1957.[1] Cyclopentene was polymerised over a solid catalyst obtained from molybdenum oxide (MoO_3) supported on alumina and reduced by hydrogen. The reduced oxide was activated by lithium aluminium hydride to give a catalyst of low activity which polymerised cyclopentene to polypentenamer in low yields even after long reaction times at 100°C. Heterogeneous catalysts of this type consisting of a reduced tungsten, molybdenum or rhenium oxide or carbonyl supported on alumina were found to be effective catalysts for olefin disproportionation reactions but were not efficient when used for the ring opening polymerisation of cyclic alkenes. Accordingly investigations on ring opening polymerisations using heterogeneous catalysts were limited; however, it was shown by Dall Asta[15] that the chain growth in molybdenum oxide catalysed cyclic alkene polymerisations proceeded via the formation of macrocycles.

The ring opening polymerisation of cyclic alkenes did not become a significant branch of polymer chemistry until 1963 when Natta and Dall'Asta etal found[15,17] that the two component catalyst-tungsten hexachloride/aluminium tri-ethyl-polymerised cyclopentene to trans polypentenamer to yields of 30-40% after reaction times of one hour at ambient temperature. Calderon and coworkers reported[18] that two component systems of this type were also effective in catalysing the ring opening polymerisation of higher membered cyclic alkenes. The activity of a tungsten hexachloride/ethyl aluminium chloride catalyst in the polymerisation of cyclic alkenes with ring sizes ranging from cycloheptene to cyclododecene was studied and a detailed investigation of the efficiency of this catalyst in the polymerisation of cyclo-octene and cyclo octa-1-5-diene was made. It was established that the polymerisation of cyclic alkenes, initiated by the tungsten/aluminium based catalyst produced a polymerisate which contained low as well as high molecular weight species.

Two component catalysts for ring opening polymerisation are prepared from a tungsten or molybdenum salt and an organo-metallic compound - usually an aluminium alkyl or alkyl halide - such that the W:Al molar ratio lies between 1:0.5 and 1:8 depending upon the particular components used and upon the desired stereo structure of the polymer. The transition metal salts are usually halides such as hexachlorides, pentachlorides or fluorochlorides or organic salts such as acetyl acetonates. High valent metal halides are preferred because they are normally soluble in the reaction medium although it is not suggested that the catalytically active species necessarily retains the high valent state throughout the course of the polymerisation.[19] It has been found that tungsten hexachloride and molybdenum pentachloride are the most efficient catalyst components for both acyclic olefin metathesis and ring opening polymerisations.[39]

The most useful and widely used organo-metallic components are organo aluminium compounds such as aluminium tri-isobutyl, aluminium tri-ethyl or aluminium diethyl chloride.

Although the two component catalyst systems described above are active in promoting ring opening polymerisations over a temperature range of -50°C —30°C they were found to be unsatisfactory for industrial applications since the maximum yield of polymer obtained from polymerisations carried out in toluene or hexane was not constant and varied from 30 - 50%. Solutions of tungsten hexachloride are unstable when exposed to sunlight and it has been suggested[20] by Pampus et al that the poor reproducibility in the polymerisations was due to the chlorinating action of tungsten hexachloride which could take part in reactions such as: 1-6, 1-7.



- 1 - 6

$$2\ WCl_5 \longrightarrow WCl_6 + WCl_4 \qquad - 1 - 7$$

An advance towards more stable catalysts and more reproducible results was made in 1965 by Dall'Asta and Carella when they polymerised cyclic alkenes using three component catalyst systems. It was found that oxygen containing compounds activated the two component catalyst systems for ring opening polymerisations and that these activators were particularly effective when used with catalysts made from tungsten halides and organo-metallic compounds. In the initial investigations alcohols, phenols, water, molecular oxygen, hydrogen peroxide, hydro-peroxides and peroxides were found to be efficient activators for the catalyst system;[21] later workers used epoxides [22] and aromatic nitro compounds while Calderon etal[24] have used a catalyst prepared from tungsten hexachloride, ethanol and ethyl aluminium dichloride in their work on ring opening polymerisation and olefin disproportionation.[7] It was found that this combination produced an efficient metathesis catalyst but its acidic nature promoted side reactions of the Friedel Craft type. Chlorinated alcohols, epoxides and cyclopentene hydroperoxide were found to be the most efficient activators for the polymerisation of cyclopentene.[20]

A typical process for the efficient solution polymerisation of cyclopentene is described in a patent specification.[25] The three component catalyst system - tungsten hexachloride/aluminium tri-isobutyl cyclopentene-2-hydroperoxide - is used with the following procedure:

(1) tungsten hexachloride is added to a 20% solution of cyclopentene in toluene at a temperature between 0 and 30°C resulting in a colour. change from blue to greenish blue to red brown.

(2) the oxygen containing compound - cyclopentene-2-hydroperoxide is added before or after the tungsten hexachloride but always before the addition of the aluminium tri-isobutyl.

(3) the aluminium tri-isobutyl is added at a temperature between 0 and 30°C.

A molar ratio of W:Al: Cyclopententene hydroperoxide: Cyclopentene of 1:2:1:1000 resp. results in the polymerisation of the cyclopentene to trans polypentenamer in yields of 80% after a polymerisation time of one hour. Four features of this type of catalyst system were notable:

(1) activation was at a maximum if the amounts of activator used were nearly stoichiometric relative to the transition metal.

(2) the activators had to be reacted with the transition metal prior to the addition of the organo-metallic compound.

(3) pre-mixing of the catalyst components did not produce an active catalyst.

(4) the temperature range of activity of these catalysts was the same as that for the two component catalysts - i.e. -30— +30°C.

These three component tungsten or molybdenum based catalyst systems, the most efficient known for the ring opening polymerisation of cyclic alkenes, readily polymerise any type of cyclic alkene, except cyclohexene, to polyalkenamers. The main advantage of these three component catalysts over the previously described two component systems are:

(1) good reproducibility of results.

(2) increased stability and solubility of the catalyst in the reaction mixture.

(3) high polymerisation rates and good conversion to polymer. even in dilute monomer solutions.

(4) low catalyst consumption.

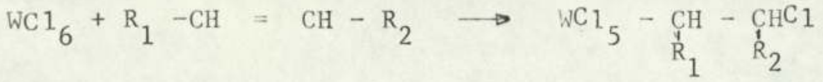
(5) reduced side reactions of the Friedel Craft type.

(6) high rates of polymerisation are obtained even at monomer: transition metal molar ratios of 20,000:1 or higher.

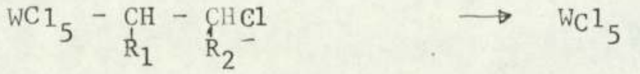
(III) The mechanism of catalysis in the metathesis reaction

The exact nature of the interaction between tungsten hexachloride and an aluminium alkyl is unknown and hence the structure of the complex formed between the catalyst and the olefin has not been resolved. However work has been carried out on the roles of the different components of the catalyst systems effective in the reaction.

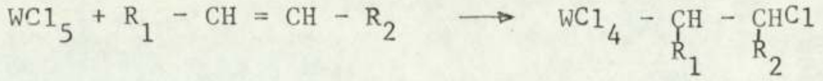
(a) The tungsten compound - tungsten hexachloride (WCl_6) is known to react with olefins to produce reduced tungsten halides[53] by the following mechanism.



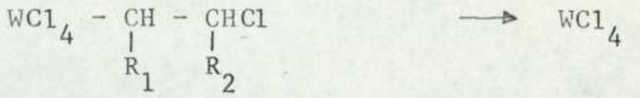
$$\mathrm{WCl_6 + R_1-CH = CH-R_2 \longrightarrow WCl_5-\underset{R_1}{CH}-\underset{R_2}{CHCl}} \qquad \text{--- 1-8}$$



$$\mathrm{WCl_5-\underset{R_1}{CH}-\underset{R_2}{CHCl} \longrightarrow WCl_5} \qquad \text{--- 1-9}$$

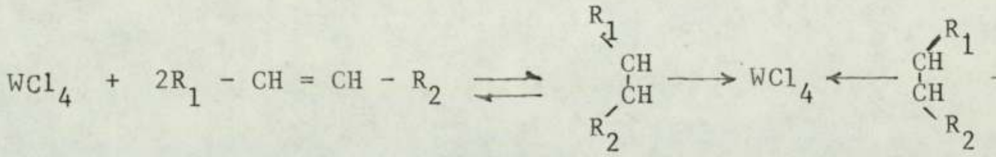


$$\mathrm{WCl_5 + R_1-CH = CH-R_2 \longrightarrow WCl_4-\underset{R_1}{CH}-\underset{R_2}{CHCl}} \qquad \text{--- 1-10}$$



$$\mathrm{WCl_4-\underset{R_1}{CH}-\underset{R_2}{CHCl} \longrightarrow WCl_4} \qquad \text{--- 1-11}$$

When its oxidation state is (IV) the tungsten atom has two vacant coordination sites which can be used to coordinate two olefin molecules (I-II) during metathesis if the atom has a coordination number 6. Accordingly:



1-12

It has been shown by means of ceric sulphate titration that the mean oxidation state of tungsten changes during the course of the polymerisation.[19] A summary of the oxidation state changes obtained is shown in table 1-2.

TABLE 1-2

Changes in the mean oxidation states of tungsten during the reactions involved in the polymerisation of cyclopentene

	Reacn. condition	Mean ox. state
1	WCl_6 solution	6.0
2	WCl_6 + cp after 1 min	5.1
3	WCl_6 + cp after 2o min	4.3
4	3 + Al $(iBu)_2OiBu$	4.3
5	4 after 2 hours	4.4

The information suggested that tungsten was present as a mixture of oxidation states during the polymerisation of cyclopentene because non integral values of the oxidation state were obtained. It was thought that the two vacant co-ordination sites of tungsten (IV) were used to co-ordinate a cyclopentene molecule and a carbon/carbon double bond in a molecule of polypentenamer. This would allow the formation of the transition state complex as described in the literature, i.e. a quasi cyclobutane ring,[40] a four centred tetra-carbene complex[49] or a metal carbene complex as described for a chain reaction mechanism.[50]

Although the presence of these complexes has been proposed no evidence has been produced for their presence in either cyclic alkene polymerisations or olefin disproportionation reactions. A great deal of evidence remains to be gathered concerning the nature of the reactions between olefins, whether cyclic or acyclic, and tungsten halides.

(b) Aluminium compound

Various mechanisms have been proposed for the metathesis type reactions, all of which suggest that the transition metal atom and its associated 'd' orbitals plays a significant role in providing a pathway for the reaction to proceed. However, none of these mechanisms have taken into account the role played by the aluminium compound in such reactions, without which it was suggested the polymerisation would not occur.

The oxidation state data listed in table 1-4 would tend to suggest that the aluminium compound did not function as a reducing agent and since aluminium tribromide was also known to act as a co-catalyst for the ring opening polymerisation of cyclic alkenes[54] it was suggested that the aluminium compound did not act in any manner to form a transition metal alkyl bond as has been proposed in some mechanisms to account for the Ziegler-Natta polymerisation. It is possible that the aluminium compound acted in some way as a complexing agent with either the olefin or the transition metal compound, for example it could remove halide ligands from the metal thereby creating vacant coordination sites.

The order of mixing of the catalyst components and olefin has been shown to be critical.[55] Olefin metathesis takes place rapidly in benzene if the tungsten compound (WCl_6) is added to the olefin followed by the aluminium compound ($EtAl\ Cl_2$). If the catalyst components were premixed and then added to the olefin, only alkylation of the benzene occurred and not olefin metathesis.[55] It is possible that the following series of reactions occurred.

$$WCl_6 + 2\ \text{olefin} \rightleftharpoons W^*\ (\text{olefin})_2 \quad \text{——} \quad 1\text{-}13$$

$$W^*\ (\text{olefin})_2 + EtAlCl \rightleftharpoons (\text{olefin})_2\ W^*/AlEtCl_2 \quad \text{——} \quad 1\text{-}14$$

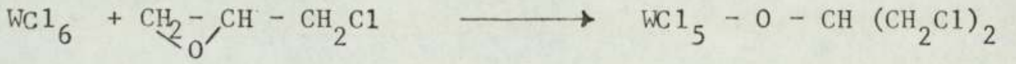
$$WCl_6 + EtAlCl_2 \rightleftharpoons \left[WCl_6\ Et\ AlCl_2\right] \quad \text{——} \quad 1\text{-}15$$

The complex formed in 1-14 is thought to be the active species in the catalysis of the metathesis reaction and is considered capable of promoting the symmetry forbidden formation of a transition complex leading to the formation of two new olefins in the olefin disproportionation reactions or to the formation of polymer in the case of ring opening polymerisations. If the catalyst components were premixed the complex formed in 1-15 was obtained. This complex, probably had a high equilibrium constant or reacted in such a way as to produce an inactive species so that when the olefin was added no reaction giving an active species took place.

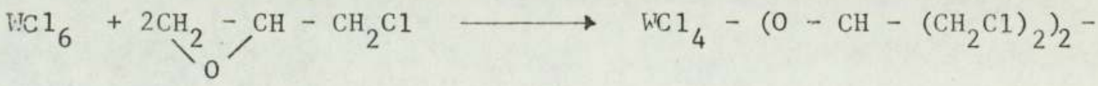
(c) Oxygen containing compound

Certain oxygen containing compounds act as activators for the ring opening polymerisation of cyclic alkenes. The WCl_6/AlR_3 catalyst for the polymerisation of cyclopentene has been shown to be activated by epoxides, hydroperoxides, epichlorohydrins,[20] giving particularly high rates of polymerisation and conversion. Cyclopentene 3-hydroperoxide has been quoted as a particular example of a hydroperoxide type activator. When cyclopentene 3-hydroperoxide was added to a solution of tungsten hexachloride in cyclopentene and toluene, the dark red solution turned blue and on standing changed further to dark red-brown. The addition of aluminimium tri-alkyl at this point caused the rapid polymerisation of the cyclopentene[23] Organic peroxides other than hydroperoxides did not have such a strong effect on the polymerisation rate and hence it is unlikely that cyclopentene 3-hydroperoxide initiated the polymerisation by a simple free radical mechanism. The epoxidation of olefins is peculiar to organic hydroperoxides when the reaction is carried out in the presence of tungsten and molybdenum compounds.[56] It is possible that the change from blue to red-brown on the addition of cyclopentene 3-hydroperoxide to cyclopentene accompanied the formation of cyclopentene epoxide. This cyclopentene epoxide could then have acted in some manner as an activator since it is well known that epoxides themselves act as activators for the polymerisation of cyclopentene catalysed by the $WCl_6/Al(iBu)_3$ catalyst.

The addition of epoxides or epichlorohydrin to tungsten hexachloride in cyclopentene causes the formation of alkoxy tungsten chlorides which act as catalysts on the further addition of aluminium tri-isobutyl[23]: 1-16,17.



$$WCl_6 + CH_2{-}CH{-}CH_2Cl \ (\text{O bridge}) \longrightarrow WCl_5{-}O{-}CH(CH_2Cl)_2 \quad \text{- 1-16}$$



$$WCl_6 + 2CH_2{-}CH{-}CH_2Cl \ (\text{O bridge}) \longrightarrow WCl_4{-}(O{-}CH{-}(CH_2Cl)_2)_2 \quad \text{- 1-17}$$

Recent results by Tuck and co-workers[60] would tend to suggest that an oxygen containing compound is not needed for high rates of reaction or to obtain high yields of polymer. In this work rigorously purified cyclopentene produced high conversion to polymer with fast reaction rates when a two component W/Al catalyst was used. It is possible that the purification procedures removed all trace impurities, such as cyclopentadiene, from the monomer. It is thought that cyclopentadiene can react with tungsten halides to reduce the tungsten to an oxidation state below that which is active in the polymerisation. The oxygen containing compound could prevent this by preferentially reacting with such impurities thus allowing the tungsten to remain active for polymerisation or by subsequently reacting with the reduced tungsten compounds to reform the active oxidation state.

I - 4 Factors controlling the stereochemistry in ring opening polymerisations

The stereoregularity of polyalkenamers produced with two component catalyst systems depends upon:

(1) the nature of the transition metal and the ligands surrounding it.

(2) the nature of the organo-metallic co-catalyst.

(3) the molar ratio of the transition metal to the organometallic compound.

(4) the temperature of polymerisation

and (5) the monomer.

Table I-3 shows the changes in the microstructure of the polypentenamer produced by varying the transition metal or the transition metal compound in the catalyst system with otherwise constant reaction conditions.

TABLE I-3

The effect of the nature of the transition metal compound of the soluble catalyst on the microstructure of the polymer

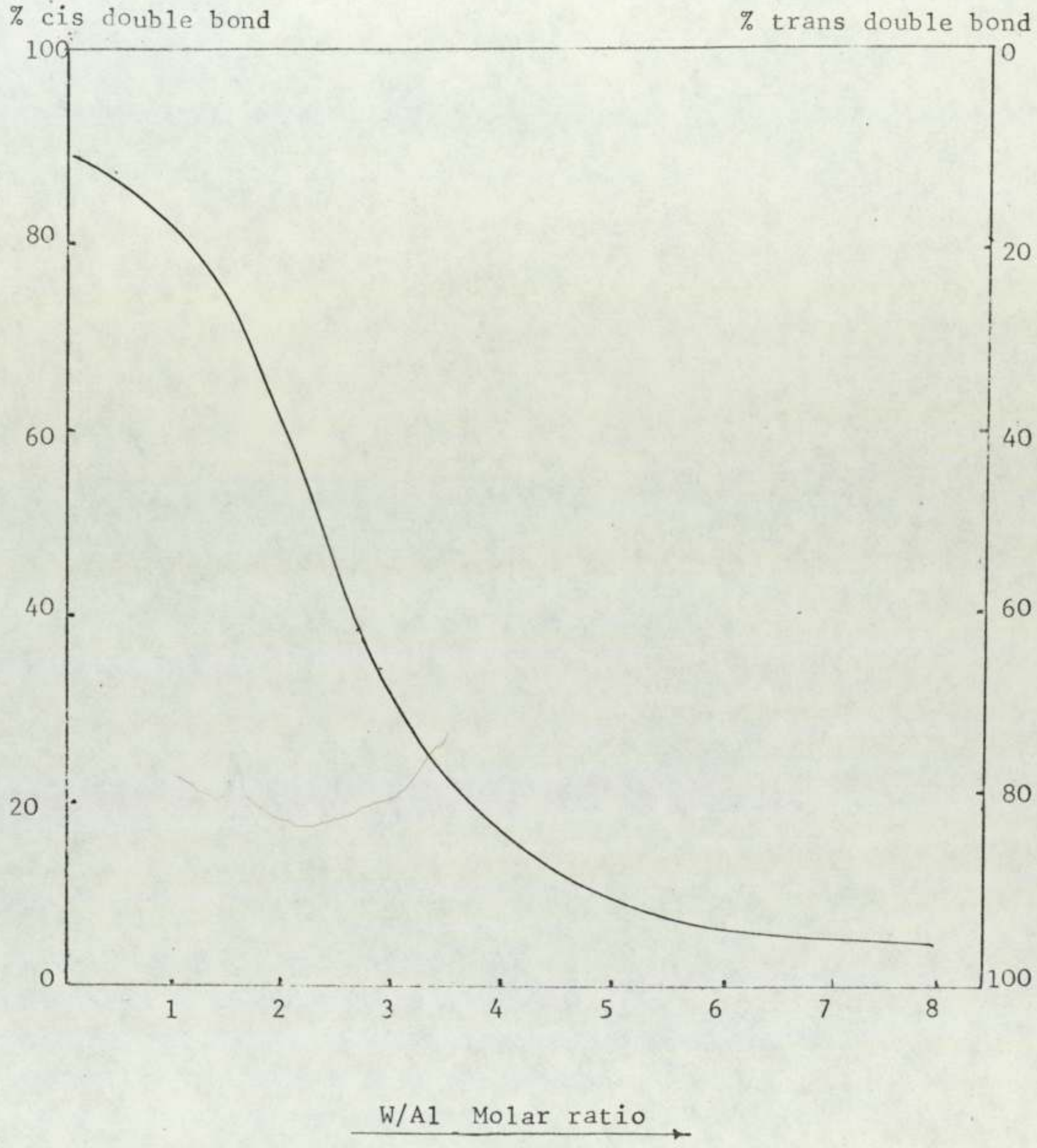
Transition metal/or metal compound	Microstructure of the polypentenamer
Titanium	predominantly trans.
Zirconium	" "
Tungsten	" "
Mo Cl_5	100% cis
Mo $(AcAc)_2$	100% cis
Mo Cl_2 $(OPh)_3$	100% trans.

It is seen that the stereospecificities of these catalyst systems vary with the transition metal and in the case of molybdenum depends also on the ligands surrounding the metal atom.

When the organometallic co-catalyst is varied a change in the stereostructure of the polymer occurs. Gunther et al found[20] that a tungsten hexachloride/ $AlEt_3$ catalyst produced a trans polypentenamer whereas tungsten hexachloride/Na_3W $(C_6H_5)_5$ produced the cis polymer. In the same work it was found [20] that a continuous variation in the cis:trans ratio of a polypentenamer sample could be achieved by varying the aluminium:tungsten molar ratios in the catalyst.

Polypentenamer microstructure as a function of W/Al ratio.

Fig. I-1



It is seen that a variation of the Al/W molar ratios.in the Al(Et)$_3$Cl$_3$/WF$_6$ catalyst, between 0.5:1 and 7:1 produced a polypentenamer with a cis/trans ratio that varied continuously between 85:15 and 10:90.

Dall'Asta and Motroni et al[26,27] have found that the cis/trans ratio of a polypentenamer can be changed by varying the polymerisation temperature.

A continuous variation of the cis/trans ratio in the polymer was obtained from the polymerisation of cyclopentene with a tungsten based catalyst when the polymerisation temperature was varied from $-50^{o}C$ to $+40^{o}C$.

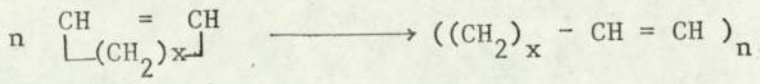
Lastly Natta et al[17] have shown that varying the monomer can affect the polymer stereostructure when it was found that a molybdenum based catalyst polymerised cyclopentene to cis polypentenamer but it converted higher membered cyclic alkenes to trans polyalkenamers.

It is possible to say that these ring opening polymerisations of cyclic alkenes are in general stereo-specific since the use of the appropriate catalyst system and reaction conditions will produce a polyalkenamer of any desired stereoregularity. It has been observed by Pampus et al[32] that cis polypentenamer is converted to the trans isomer by contacting it with a trans specific catalyst whereas the trans polypentenamer remains unchanged when contacted with a cis specific catalyst and it is suggested that the cis/trans ratio in ring opening polymerisation products is kinetically controlled. This applies to the stereocontrol of the polymerisation and may be extended to cover monomer/polymer equilibria and molecular weight control. It is reported[32] that in the initial period of the polymerisation of cyclopentene, by a W/Al based catalyst, high molecular weight polymer is produced which contains predominantly cis double bonds, with increasing conversion the molecular weight and the cis content decreases.

I - 5 Polymerisability of monomers

(1) Thermodynamic factors - when compared with the addition polymerisation of a vinyl monomer (I-18) a significant feature of the ring opening polymerisation of cyclic alkenes (I-19) is that the number and types of bonds in the cyclic alkene monomer are the same as those in the polymer.

$$n\ CH_2 = CHX \longrightarrow (CH_2 - CHX)_n \qquad 1 - 18$$



$$n\ \underbrace{CH = CH}_{(CH_2)_x} \longrightarrow ((CH_2)_x - CH = CH\ )_n \qquad 1 - 19$$

The ring opening polymerisation of cyclic alkenes can be expected to show many of the thermodynamic features of other ring opening polymerisations such as the polymerisation of lactams.[29] In such polymerisations the enthalpy of polymerisation of the cyclic monomer to an open chain polymer (ΔH) is a measure of the ring strain energy of the monomer and the entropy of polymerisation is dependent upon the configurational changes occurring during the polymerisation. The polymerisability of the monomer can be determined by application of the equation - 1-20 where:

$$\Delta G = \Delta H - T\Delta S \qquad 1-20$$

If ΔG is negative polymerisation will occur.

A feature of most ring opening polymerisations is that the entropy of polymerisation is low because the decrease in entropy associated with the conversion of a large number of momomer molecules to one polymer molecule is offset by the increase in configurational entropy associated with the opening of the ring. Therefore the enthalpy of polymerisation is usually the factor that controls the polymerisability of a monomer and since the ring strain energy of cyclohexene is expected to be low it can be predicted that the 6 membered ring monomer is likely to be stable.

Much research has been carried out on the various factors that affect the polymerisability of cyclic alkenes. This has included an examination of the effects of ring strain and the steric effects of any substituents present in the cyclic alkene ring. The equilibrium monomer concentration $[M]_e$ can be used as a measure of the ability of a monomer to polymerise.[32] The propagation step in the ring opening polymerisation can be written very generally as - 1-21.

$$Pn^* + M \underset{k_b}{\overset{k_f}{\rightleftharpoons}} P^*_{n+1} \qquad 1 - 21$$

When the polymerisation has reached an equilibrium conversion i.e. when:

rate of polymerisation = rate of depolymerisation

and: $k_f\,[Pn^*]\,[M]_e = k_b\,[P^*_{n+1}]$ - 1 - 22

then the equilibrium constant K is given by:

$$K = \frac{k_f}{k_b} = \frac{1}{[M]_e} \qquad - 1 - 23$$

where $[M]_e$ is the equilibrium concentration of the monomer and where k_f and k_b are the rate constants for the polymerisation and depolymerisation reactions respectively.

Since: $\Delta G = - RT \ln K$ - 1 - 24

then from 1-23: $\Delta G = RT \ln [M]_e$ - 1 - 25

According to 1-25 the free energy of the polymerisation may be determined from a measure of the concentration of the monomer at equilibrium in an active polymerisation system. Accordingly the more readily a monomer polymerises the larger will be the negative value of ΔG and hence the lower will be the concentration of monomer at equilibrium.

(II) The effect of ring size and structure on monomer polymerisability

Natta and Dall'Asta[17] have interpreted the polymerisability of cyclic alkenes in terms of ring strain energy and their results are summarised in Table 1-4.

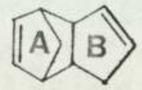
TABLE 1-4

Monomer polymerisability vs. ring size[17]

Monomer	Equilibrium conversion of monomer to polymer (%)
cyclopentene	70
cyclohexene	0
cycloheptene	18
cis cyclo-octene	60
cis/trans cyclo-dodecene	34

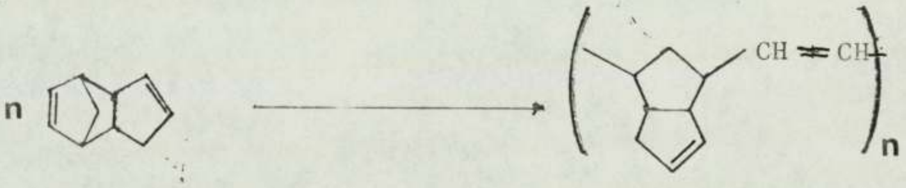
The only monomer which did not yield high polymers using tungsten/aluminium based catalysts was cyclohexene. Under constant polymerisation conditions it was found[17] that the conversion of monomer to polymer was generally decreased as the ring size increased illustrating the importance of the contribution to ΔG which is made by the ring strain energy. In the polymerisation of vinyl monomers the disappearance of one double bond in the monomer unit followed by the formation of a single bond in the polymer strongly favours the polymerisation from an energetic point of view. In the formation of linear polyalkenamers from cyclic alkenes the overall numbers and type of bond remain unchanged with the cleavage of a double bond in the ring being followed by the formation of a new double bond in the polymer. Therefore the main energy contribution which favours the ring cleavage polymerisation of cyclic alkenes is the gain of the ring strain energy. This ring strain energy is large in cyclopentene and decreases as one proceeds from cycloheptene through cyclo-octene to cyclo-dodecene. It is zero in cyclohexene where the conformation of the carbon atoms is completely staggered and is as stable as that existing in the corresponding linear unsaturated chain with the result that cyclohexene is not polymerised by tungsten/ aluminium based catalysts. However it may well be that the temperatures at which these polymerisations were carried out were above the ceiling temperatures for the cyclo-hexene monomer.

Dicyclopentadiene (III) contains two types of unsaturated five membered rings A and B.



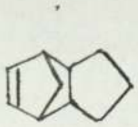
III

Monomers which have a highly strained bridged ring (A) polymerise readily whereas monomers with a fused ring (B) are difficult to polymerise.[33] Oshika and Tabuchi polymerised bicyclopentadiene using various catalyst systems and concluded,[35] from NMR studies of the polymer structure, that all polymerisations occurred by opening of the bridged ring according to 1-26.

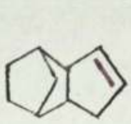


1-26

Similarly Eleuterio has shown[36] that tricyclo 5,2, $10^{2,6}$ dec-8-ene IV is polymerisable whereas its isomer tricyclo (5,2, $10^{2,6}$ dec-3-ene (V) did not polymerise when treated with tungsten based catalysts.

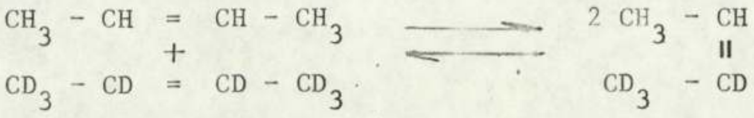


IV



V

These results were in agreement with those of Oshika and Tabuchi since it was the highly strained, bridged, five membered, unsaturated ring that polymerised whereas the fused ring did not polymerise. Hence in general monomers which polymerise readily possess strained unsaturated rings. This fact is not inconsistent with the activity of molecules such as but-2-ene and D_8 but-2-ene in the athermal metathesis reaction (1-27).



$$\begin{matrix} CH_3 - CH = CH - CH_3 \\ + \\ CD_3 - CD = CD - CD_3 \end{matrix} \rightleftharpoons \begin{matrix} 2\ CH_3 - CH \\ \| \\ CD_3 - CD \end{matrix} \qquad 1\text{-}27$$

Here there is a large increase in entropy associated with the reaction and consequently a large negative free energy of reaction.

The polymerisability of large strain free ring monomers has been verified[33] by Calderon and co-workers when it was found that 1 - 9-1.7 cyclo tetra eicosatriene (a 24 membered cyclic trimer of cyclo-octene) was converted to high polymer in good yields using tungsten/aluminium based catalysts. This polymerisation shows that entropy factors can make a large contribution to the free energy change. Dainton and Ivin[28] have confirmed this fact from their work with monomers which have low ring strain and showed that entropy considerations predict an increase in polymerisability (i.e. a decrease in $[M]_e$) for cyclic alkenes as the ring size increases, where;

$$\Delta G = \Delta H - T\,\Delta S \qquad 1 - 20$$

$$\Delta G = RT\ \ln[M]_e \qquad 1 - 25$$

and $$\ln[M]_e = \frac{\Delta H_p}{RT} - \frac{\Delta S^{o}_{p}}{R} \qquad 1 - 28$$

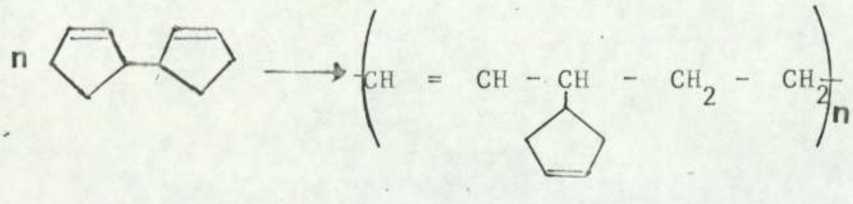
Dainton etal[53] estimated the entropy changes for the hypothetical ring opening polymerisation of a homologous series of saturated hydrocarbons and from their results it is apparent that ring strain is required for monomer polymerisability only where the monomer ring has less than eight ring carbons i.e. where negative entropies of polymerisation are found.

(III) Structural and substituent factors:

In general the ring opening polymerisation of cyclic alkenes is restricted to those which contain an unsubstituted double bond structure; this is consistent with the fact that only double bonds of the general structure $R_1 - CH = CH - R_2$ take part in the olefin metathetic disproportionation reaction. <u>Small</u> alkyl substituents at other positions on the ring do not usually render the monomer inactive towards polymerisation except where ΔG_p is very small. For a given homologous series and with otherwise constant reaction conditions Dainton and co-workers[28] deduced that the polymerisability of a member is affected by the ring size and by the degree position and type of substituent.

It was found[33] that cyclopentene is thermodynamically less stable with respect to polypentenamer than tetrahydrofuran is with respect to its polymer and indeed substituted tetra-hydrofurans do not undergo ring opening polymerisations whereas substituted cyclopentenes (e.g. 3-methyl cyclopentene) do polymerise with ring opening at the double bond.[20] It was found, however, that 3 isopropyl cyclopentene was inactive and it was thought that this was due to steric hindrance which prevented formation of the transition state complex. It has been shown that mono and disubstituted eight membered rings undergo polymerisation; thus 3 methyl and 3 phenyl cyclo-octene have been polymerised by tungsten/aluminium based catalysts.[18] Similarly a series of mono and disubstituted cyclo-octadienes have been polymerised in good yields.[33] Hence any decrease in the polymerisability of the eight membered ring arising from the substituents is not sufficient to render it unpolymerisable. It is possible that the mobility of the eight membered ring is greater than that of a five membered ring and this reduces the possibility of steric hindrance by the substituents during transition state formation.

Ofstead and Calderon have reported the polymerisation of 3.3^1 bicyclopentene, in low yield, using tungsten/aluminium based catalysts. N.M.R. data would suggest a polymerisation such that: 1-29.



- 1-29

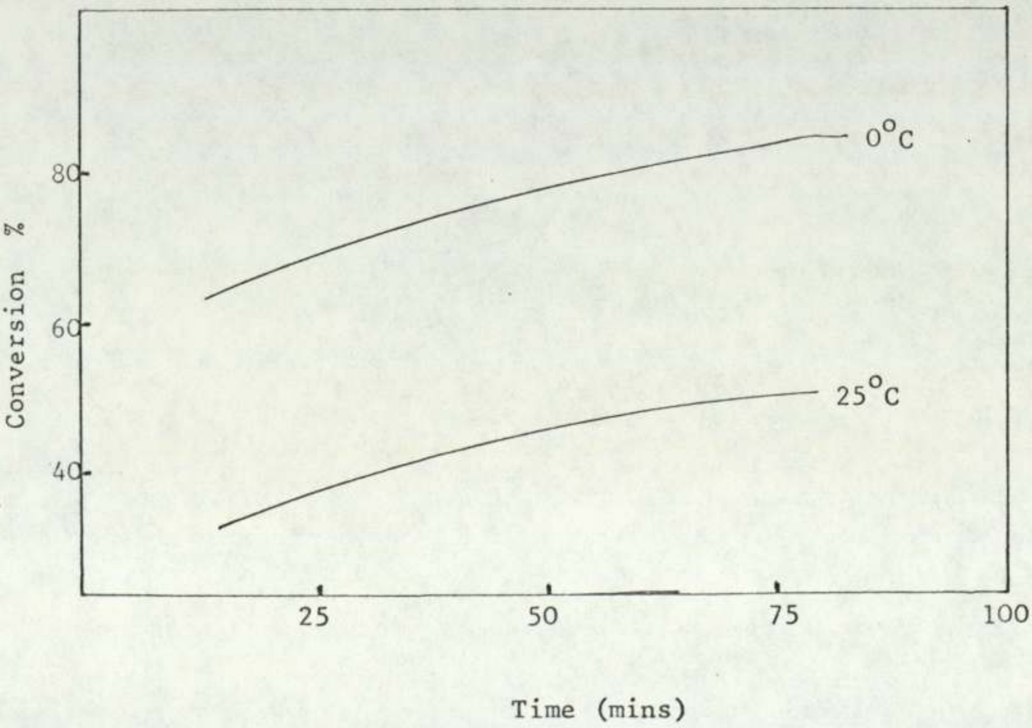
The effect of substituents on the polymerisation of a monomer of this type has not yet been elucidated.

(IV) Cyclopentene polymerisability: It has been found that quantitative yields of polymer have not been generally obtained in the course of solution polymerisations of cyclopentene. Results reported by Gunther and co-workers[20] suggest that ultimate conversions to polymer were not totally dependent on catalyst activity. Polymerisations of cyclopentene at 0°C were conducted using various catalyst systems all of which converted the monomer to polymer in yields of ~70% when an initial monomer concentration of 15% in benzene was used.

When parallel polymerisations of cyclopentene were carried out at 0°C and 25oC the type of conversion/time plots obtained[51] are shown in fig. 1-2

Fig. I-2

Dependence of conversion of cyclopentene to polypentenamer on temperature of polymerisation



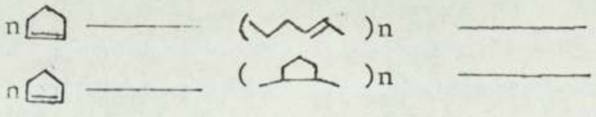
Calderon and Ofstead[33] also showed that when cyclopentene was polymerised at 0°C giving conversions of 70 - 80% and then the polymerisation temperature was increased, the maximum yield obtained after a further 45 minutes was ~60%. This type of behaviour is characteristic of systems where a monomer/polymer equilibrium is present and it is possible that in cyclopentene polymerisations reversible monomer/polymer interconversion occurs.

I - 6 The mechanism of the ring opening polymerisation of cyclic alkenes:

A number of possible mechanisms have been suggested to explain olefin metathesis reactions. It is possible that the reaction pathway depends upon the state of the catalyst - i.e. whether homogeneous or heterogeneous, and upon the composition of the catalyst system itself. In view of the inherent similarities between olefin metathesis reactions and the ring opening polymerisation of cyclic alkenes a general reaction scheme could be postulated to explain both these reactions.

(1) Development of the reaction pathway for ring opening polymerisations:

There are at least two possible methods of polymerising cyclopentene which can be summarised by 1-2,3.

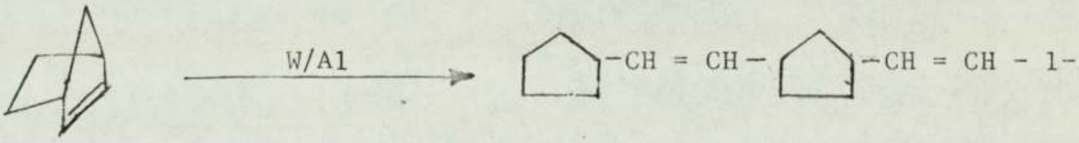


1-2

1-3

The polymerisation of cyclopentene to polycyclopentene (1-3) cannot be carried out using conventional two component transition metal alkyl catalysts although it is possible to form copolymers of cyclopentene with ethylene such that polymerisation of cyclopentene occurs by addition across the double bond.[38] The polymers obtained from the polymerisation of cyclopentene with tungsten and molybdenum based catalysts showed infra-red absorbances at 10.35 μ and 13.8-13.9μ which could be attributed to the presence of trans and cis carbon to carbon double bonds respectively. The spectra also showed an absence of bonds at 8.0 and 8.5μ characteristic of cyclo-alkyl structures. Accordingly the absence of cyclic structures in the polymer, obtained from the polymerisation of cyclopentene initiated by tungsten/aluminium based catalysts, would suggest that the polymerisation did not occur by the mechanism described in 1-3 whereas the presence of double bonds in the polymer could be accounted for by some form of ring opening process - i.e. reaction 1-2.

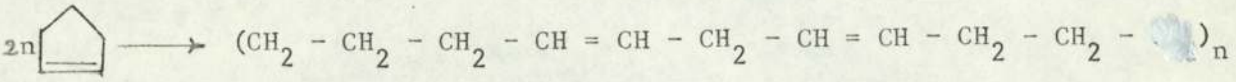
It was initially suggested[39] that ring opening polymerisations, initiated by tungsten based catalysts, occurred by scission of the carbon-carbon single bond alpha to the double bond because norbornene polymerised in the following manner: 1-30.



1-30

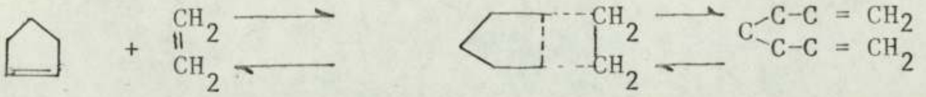
The possibility that polymerisation could occur in any manner other than by cleavage of a carbon-carbon single bond in the ring was not considered because the dissociation energy of the carbon-carbon single bond is appreciably less than that of the carbon-carbon double bond. Furthermore the polymerisation of norbornene ruled out the possibility of the ring opening polymerisation of cyclic alkenes by scission of a carbon-carbon single bond further removed from the double bond than the alpha position. Trans polypentenamer obtained by the ring opening polymerisation of cyclopentene has been shown by X-ray analysis to contain a regular structure with a repeat unit equivalent to two pentenamer units.[39] Ozonolysis studies on trans polypentenamer have shown that in this structure only units with three methylene groups separate the double bonds. Units that could be derived from an irregular head to head or tail to tail addition were absent; such units could be present if ring opening occurred at a carbon-carbon single bond as shown

- 1-31.



- 1-31.

The first evidence for the application of the type of reaction, found in olefin metathetic disproportionation (1-4), to the polymerisation of cyclic alkenes was produced by Ray and Crain in 1966.[41] It was discovered that cyclopentene and ethylene produced hepta 1-6 diene in the presence of the disproportionation catalyst - MoO_3/CoO - by reaction 1-32.



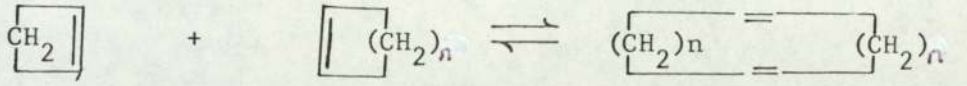
--- 1-32

Calderon et al[7,8] advanced the understanding of the olefin metathesis reaction (1-4) and confirmed that a relationship existed between the behaviour of acyclic olefins and cyclic olefins in the presence of metathesis catalysts. It was shown that olefin disproportionation (1-4) took place in the presence of a three component tungsten based catalyst which until then had been used only for the ring opening polymerisation of cyclic alkenes. It was found that the ring opening polymerisation catalyst - tungsten hexachloride/ethanol/ethyl aluminium dichloride - promoted the disproportionation of but-2-ene and deuterated but-2-ene according to 1-33.

$$\underset{VI}{CH_3-CH=CH-CH_3} + \underset{VII}{CD_3-CD=CD-CD_3} \rightleftharpoons \underset{VIII}{2CH_3-CH=CD-CD_3} \quad - 1\text{-}33$$

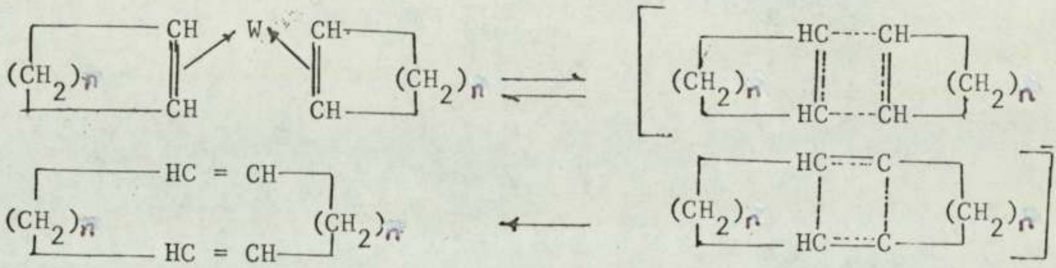
Only one new olefin $C_4H_4D_4$ was produced which showed that the reaction was the result of an exchange of alkylidene (R-CH=) rather than alkyl (R-) groups. The metathesis reaction of linear alkenes was athermal and the final distribution of the products was random. At equilibrium the molar ratio of VI:VII:VIII in the product mixture was 1:1:2 - i.e. the condition of maximum entropy of the system.

In 1968 Scott et al[24] proposed that the ring opening polymerisation of cyclic alkenes was a special case of the olefin metathesis reaction and suggested a reaction scheme wherein polymerisation took place by scission of the carbon-carbon double bonds - 1-34.



- 1-34

It was believed that in cyclic alkene polymerisations, in the presence of tungsten based metathesis catalysts, two double bonds co-ordinated to the tungsten atom underwent alkylidene exchange via a quasi cyclobutane intermediate such that 1-35.



1-35

This reaction pathway suggested that ring opening occurred by ring scission at the carbon-carbon double bond and that during chain growth macrocycles of increasing size were formed. Evidence that this type of polymerisation reaction occurred by scission of the carbon-carbon double bond was supplied by Dall'Asta and Motroni.[42] Cyclooctene was copolymerised with cyclopentene, which was (C^{14}) labelled at the double bond, to produce a random copolymer. This copolymer was then broken down into monomeric units by ozonolysis and these ozonolysis products were reduced to the corresponding α,ω diols.

Polymerisation by ring cleavage at the double bond would produce a polymer with units (IX) derived in the following manner - 1-36.

$$C_8H_{14} + \overset{*}{C}_5H_8 \rightleftharpoons = \underbrace{CH - (CH_2)_6 - CH}_{C_8\ \text{unit}} = \underbrace{\overset{*}{C}H - (CH_2)_3 - CH}_{C_5\ \text{unit}} = \underbrace{CH - (CH_2)_6 - CH}_{C_8\ \text{unit}} = \quad - 1\text{-}36$$

IX

After ozonolysis and reduction of this type of unit (IX) the following products would be obtained:

$HO - CH_2 - (CH_2)_8 - CH_2OH$ --- 1-8 octanediol

$HO - \overset{*}{C}H_2 - (CH_2)_3 - CH_2OH$ --- (^{14}C) 1-5 pentanediol.

Polymerisation by ring cleavage of a single bond would result in the formation of polymer containing units of the following structures (X,XI)

$$\underbrace{- CH = CH - (CH_2)_6}_{C_8\ \text{unit}} \underbrace{- \overset{*}{C}H = CH - (CH_2)_3}_{C_5\ \text{unit}} \underbrace{- CH = CH - (CH_2)_6}_{C_8\ \text{unit}} \quad \text{--- X}$$

and

$$\underbrace{- CH = CH - (CH_2)_6}_{C_8\ \text{unit}} \underbrace{- CH = \overset{*}{C}H - (CH_2)_3}_{C_5\ \text{unit}} \underbrace{- CH = CH - (CH_2)_6}_{C_8\ \text{unit}} \quad \text{--- XI}$$

After ozonolysis and reduction of the polymers with these structures (X,XI) the following products would be obtained.

$HO\ CH_2 - (CH_2)_6 - CH_2OH$ ... 1-8 octanediol

$HO\ \overset{*}{C}H_2 - (CH_2)_8 - CH_2OH$ .... ^{14}C 1-8 octanediol

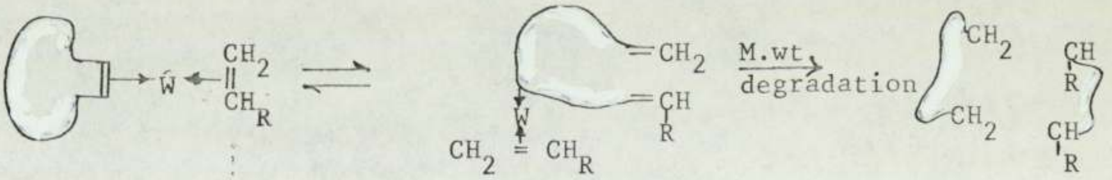
$HO\ CH_2\ C-(CH_2)_2 - CH_2OH$ ... 1-5 pentanediol

$HO\ \overset{*}{C}H_2 - (CH_2)_3 - CH_2OH$ ... ^{14}C 1-5 pentanediol

Ozonolysis of structures (X,XI) followed by reduction would divide the radio-activity equally between 1-8 octanediol and 1-5 pentanediol whereas ozonolysis and reduction of structure IX would give only one radioactive product - 1-5 pentanediol.

Dall'Asta and Motroni found that ozonolysis of the copolymer obtained from reaction 1-36, followed by radio chemical analysis showed that all the radioactivity was contained in the 1-5 pentanediol which confirmed that the polymerisation took place by scission of the carbon-carbon double bond in the monomers as preditted by the olefin metathesis reaction theory.[24]

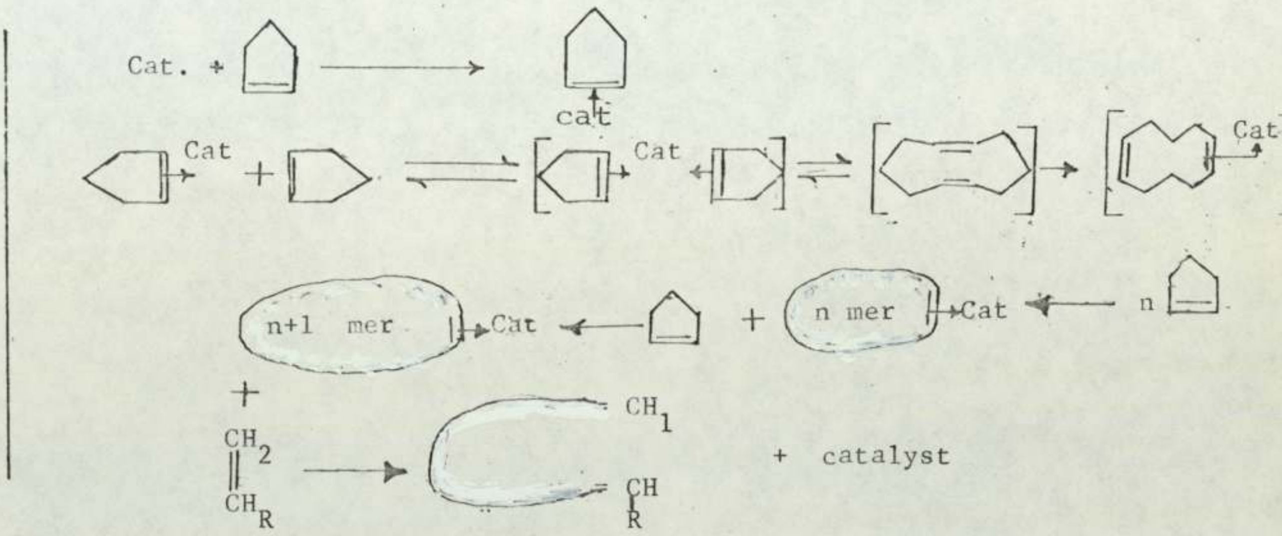
The formation of macrocyclic rings was thought to occur in at least the initial stages of the polymerisation since large ring compounds have been isolated from cyclo-octene polymerisates. In fact all possible ring equilibria with the monomer were found to be present which suggested that formation of macrocyclic rings could occur throughout the polymerisation. The existence of high molecular weight macrocyclic polyalkenamers is difficult to prove experimentally and moreover a number of side reactions which transform macrocycles into open chain macromolecules can occur. For example traces of an acyclic olefin, present as impurity or derived from the decomposition of the organo-metallic catalyst, can act as agents for the cleavage of the macrocyclic rings by a reaction such as 1-37.



For statistical reasons this type of ring opening operates at the highest molecular weight fractions and hence the high molecular weight polyalkenamers are likely to be present as open chain macromolecules.[42] The reaction between a further molecule of an acyclic olefin and an open chain polyalkenamer molecule would result in degradation leading to a lowering of the molecular weight. Indeed this type of reaction has been employed for molecular weight regulation of polyalkenamers using conjugated dienes[44] or aliphatic olefins[23] as the regulating agents.

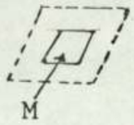
A tentative reaction scheme (1-38), based on the foregoing information, can be drawn for the polymerisation of cyclopentene by tungsten based catalysts. This incorporates ring opening at the double bond and chain growth via the formation of macrocyclics with open chain polymer being formed by a reaction such as 1-37.

1.38



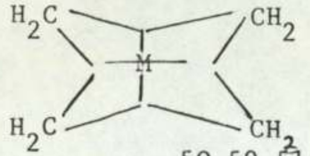
(11) <u>Formation of the transition state</u> It has been established that both the olefin disproportionation reaction and the ring opening polymerisation of cyclic alkenes involve the exchange of alkylidene groups and it must be assumed that the transition metal plays an important role in any pathway that allows such reactions to proceed. Three types of mechanism have been proposed for the reaction:

(a) the formation of an intermediate where a quasi cyclobutane ring (XII) is co-ordinated to the transition metal atom.[40]



(XII)

(b) the formation of a tetra carbene transition metal complex.[49] - (XIII)



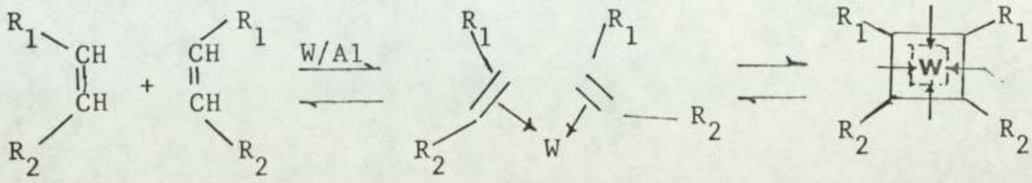
(XIII)

50,59,51.

(c) a chain mechanism.

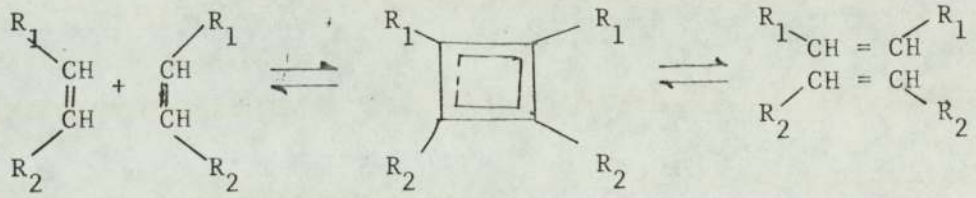
<u>(a) The quasi cyclobutane intermediate (XII)</u> The formation of a

quasi cyclobutane derivative was first proposed by Bradshaw et al.[40,8] In such a reaction it was suggested that two molecules of the olefin co-ordinate to the transition metal atom in such a way that they possess the correct symmetry elements for the overlap of the π bonding and antibonding orbitals to produce a cyclobutane ring 1-39.



--- 1-39

The substituted cyclobutane ring then decomposes either to the original olefins or to two new olefins which is a change equivalent to the exchange of alkylidene groups - 1-40.



--- 1-40

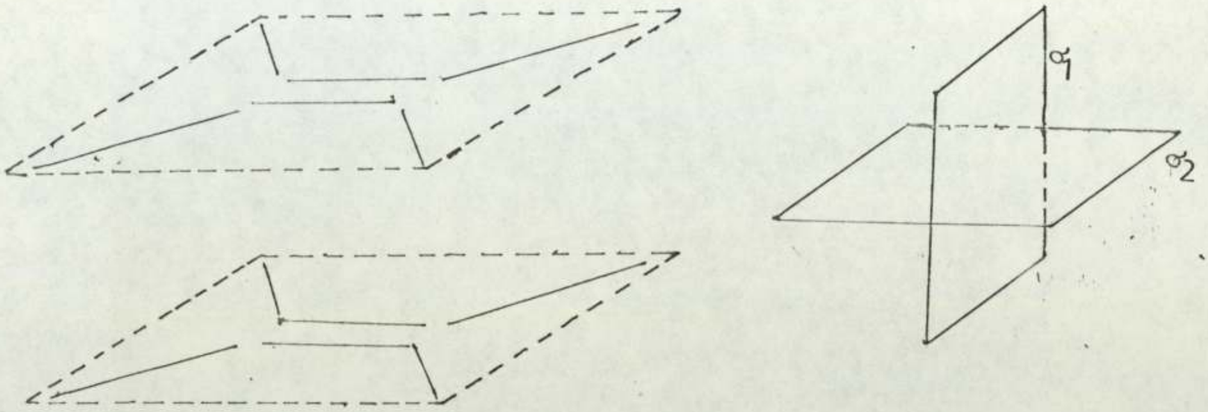
This (2+2) cyclo addition reaction is considered to be symmetry forbidden according to the Woodward-Hoffmann rules governing the symmetry of organic reactions.[46] This means that such reactions, when thermally activated, have a high activation energy. Accordingly it is likely that the tungsten atom provides an allowed reaction pathway by co-ordination with the olefins and the reaction proceeds by the transient formation of a cyclobutane type ring.

Application of the Woodward-Hoffmann rules of orbital symmetry to the ring opening polymerisation of cyclic alkenes and to the metathesis of acyclic olefins via a cyclobutane intermediate

If a cyclobutane ring is formed in an olefin metathesis reaction then the overall transformation can be represented by 1-40 i.e. two reversible reactions. The geometry of approach[19] of two ethylene molecules in the (2+2) cycloaddition reaction is shown - Fig. 1-3.

Fig. 1-3

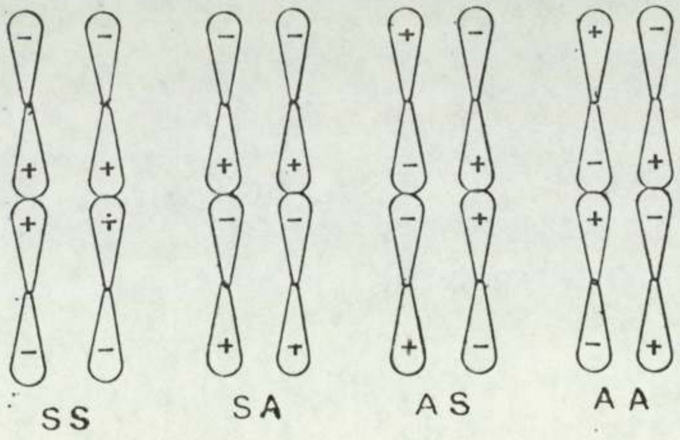
The geometry of approach of two ethylene molecules ina(2+2) cycloaddition reaction



The ethylene molecules are shown to be in parallel planes thereby allowing the formation of the cyclobutane ring. Fig. 1-4 shows the symmetry elements of the interacting olefin bonding and antibonding orbitals with reference to the planes σ_1 and σ_2

Fig. 1-4

Orbital combinations in a (2+2) cycloaddition reaction



Symmetry elements with respect to σ_1 and
planes.

S = Symmetrical

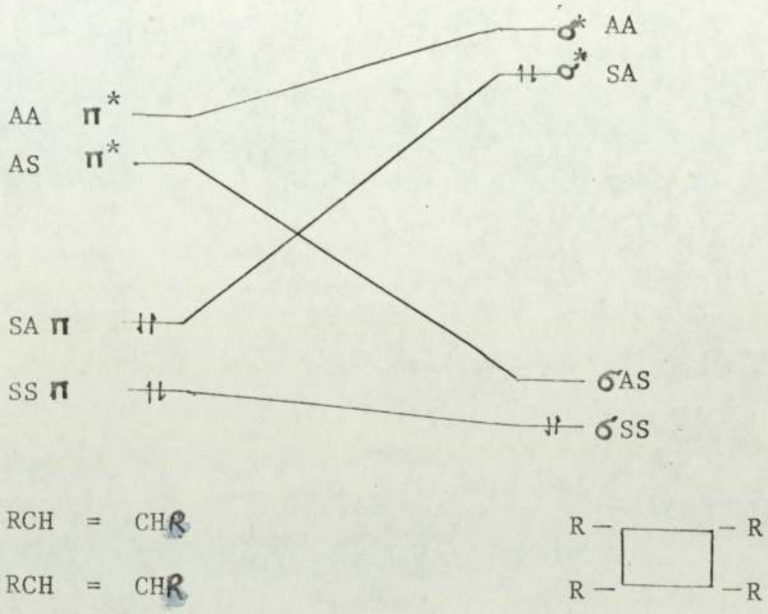
A = Anti symmetrical

In the cyclobutane intermediate the corresponding orbitals are present but from the orbital correlation diagram - fig 1-5 it can be seen that the AS orbital is bonding in cyclobutane and by combination with the SS orbital two sigma carbon-carbon bonds can be formed. The cyclobutane

SA orbital is antibonding.

Fig 1-5

Orbital correlation diagram for a (2 + 2) cycloaddition reaction

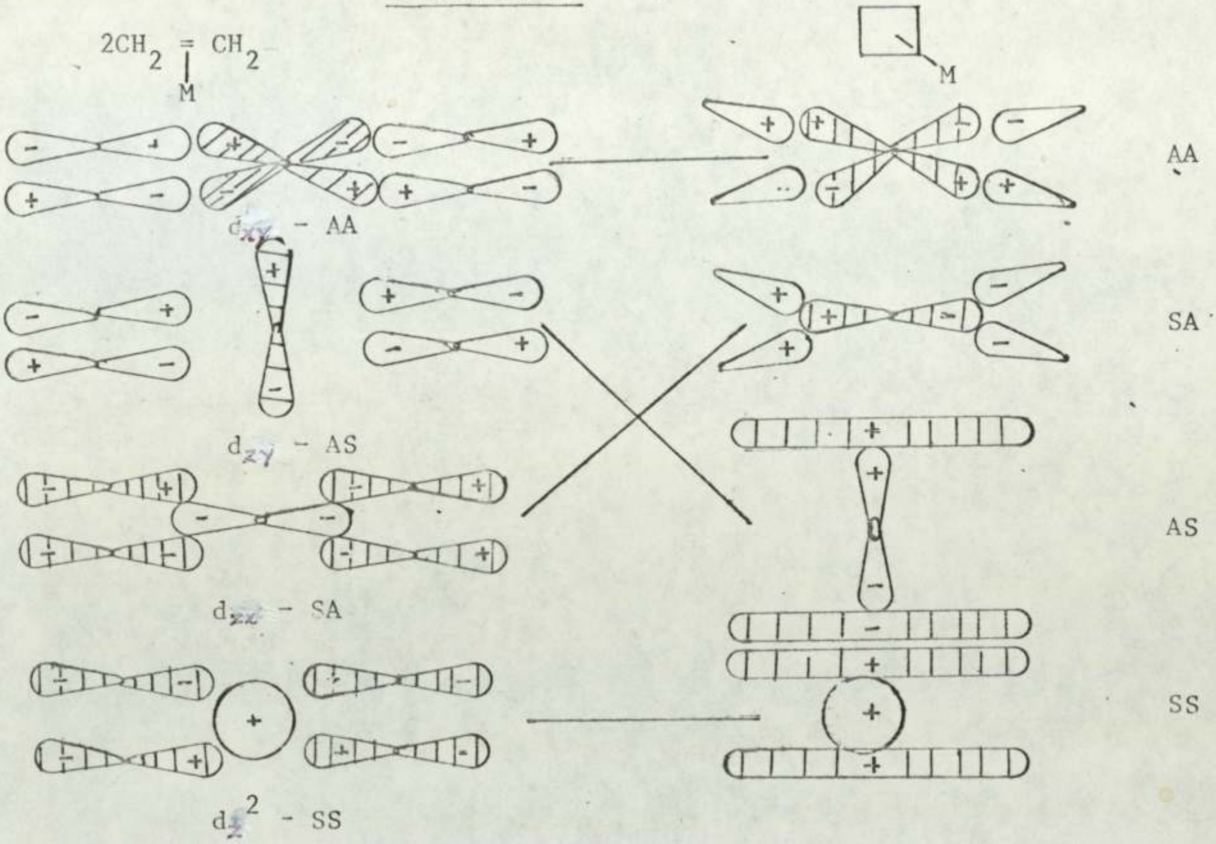


From these diagrams it can be seen that the transformation of the ground state of two ethylene molecules into a ground state cyclobutane must involve the transfer of electrons from one set of orbitals to another set of different symmetry. Such a process possesses a high activation energy and hence in Woodward-Hoffmann terms is symmetry forbidden.

When a catalyst containing a transition metal is present the possible orbital combinations are altered completely. The orbital correlation diagram (fig. 1-5) must be redrawn to include the transformations involving the transition metal d-orbitals. Fig 1-6 shows the effect of the transition metal atom on the orbital combinations, of fig 1-5 for the reactants and also for the'cyclobutane' product.

Fig. 1-6

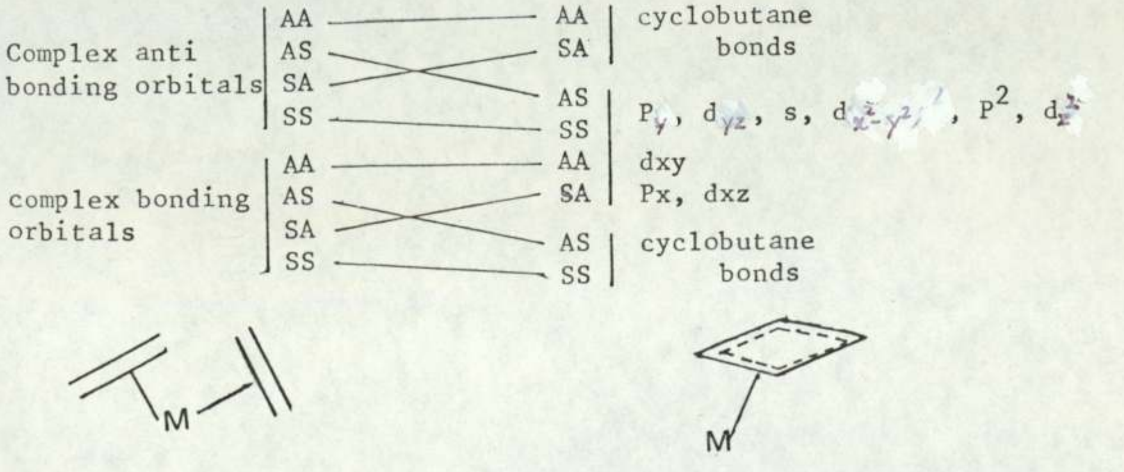
The effect of a transition metal atom on the olefin orbital combinations



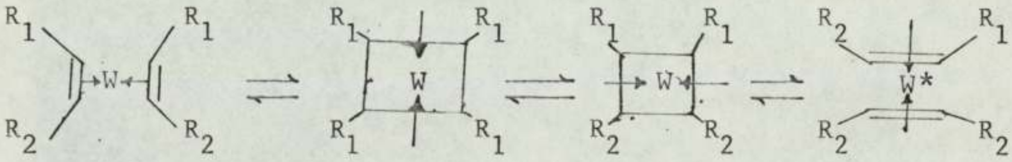
The filled ligand π orbitals of the olefins can interact with empty metal d orbitals of the same symmetry and similarly the empty ligand antibonding π orbitals interact with the filled metal d orbitals having the same symmetry. The new orbital correlation diagram that can then be drawn is shown in fig. 1-7.

Fig. 1-7

Orbital correlation diagram for a (2+2) cycloaddition reaction in the presence of a transition metal atom



A ground state reversible reaction path from cyclobutane to the olefin complex is now available. The shaded areas in fig. 1-6 represent the concentrations of the electron densities in the reactants and products and it can be seen that redistribution of electron density has occurred. The SA π bonding electrons have become metal d electrons and the AS metal d electrons have become σ bonding electrons in the metal co-ordinated cyclobutane ring. It is seen that the metal atom has removed the symmetry restrictions of the cycloaddition reaction by co-ordination to the two olefin molecules. A set of orbital diagrams similar to those in fig 1-5 could be drawn for the other two C-C bonds of the cyclobutane ring which can interact with the metal d orbitals to produce two olefins in which the original alkylidene groups are exchanged to produce - 1-41.



--- 1-41

The transition metal can therefore provide a reaction pathway for the ring opening polymerisation of cyclic alkenes and the metathesis of internal olefins by cleavage of the double bonds in both cases.

(b) <u>The multi-centred species (XIII)</u> - The mechanism involving the cyclobutane intermediate was thought reasonable[40] as an explanation of the gross structural change involved in the cyclic alkene polymerisation and acyclic olefin disproportionation reactions; however to account for the facts that:

(a) no cyclobutane has been isolated from the reaction mixture

(b) cyclobutane has not been found to partake in the metathesis reaction in the presence of metathesis catalysts.

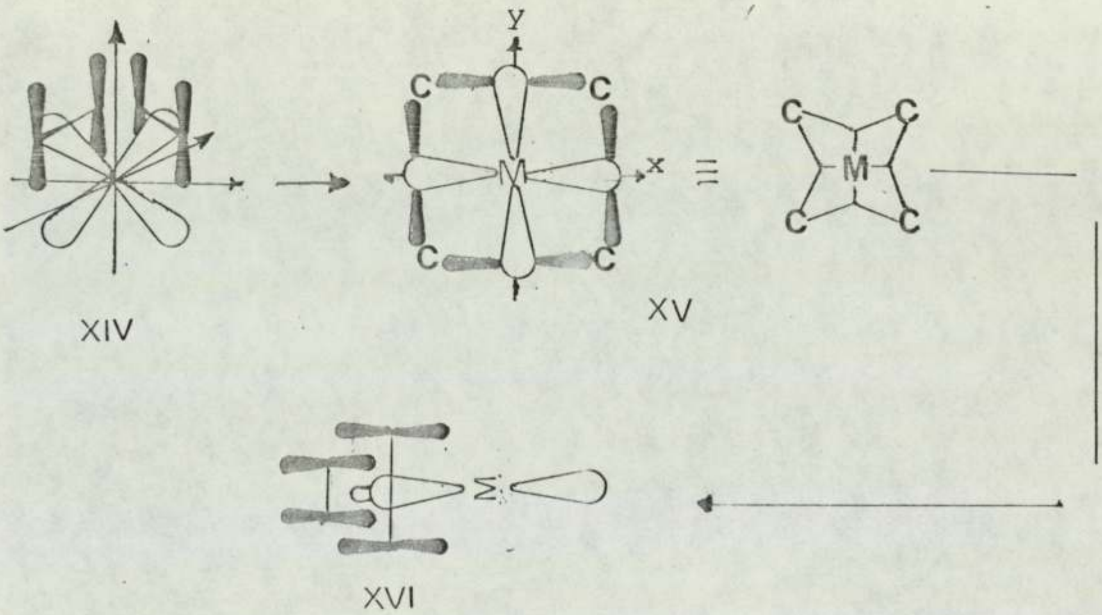
and (c) cyclobutane has no accessible valencies for bonding to metals.

the multicentred species (XIII) was proposed as a possible intermediate by Lewandos and Petit.[49]

It was suggested that the olefin molecules first reacted with the metal to form a bis olefin π complex (XIV) which rearranged to a multi-centred organo-metallic system (XV). Fig 1-8 is a diagrammatic representation of the electron changes that take place in the scheme.

Fig. 1-8

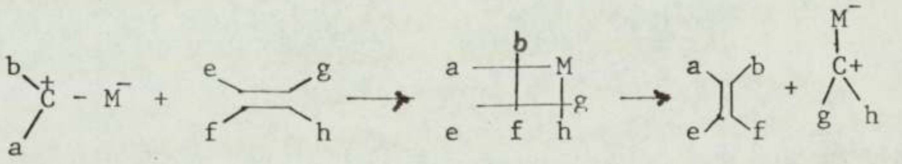
Electron changes in the formation of the multicentred species (XV)



The bonding in XV results from the interaction of a set of metal d atomic orbitals and four methylenic units. Retraction of the system XV along the X axis would reproduce the starting materials whereas separation along the Y axis would lead to the disproportionation or polymerisation products: (XVI).

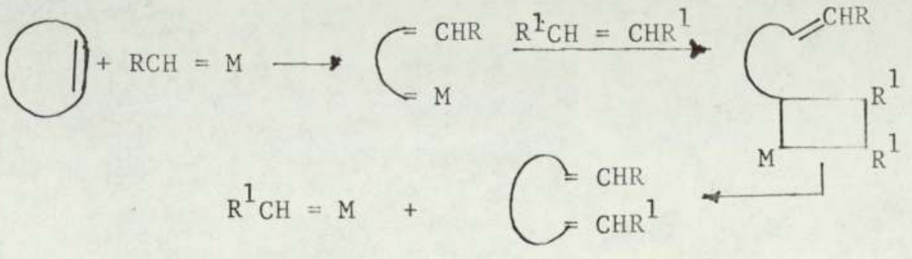
In a manner similar to that described above for the formation of the cyclobutane intermediate, transition metal orbitals interact with olefin orbitals of similar symmetry to provide a pathway for the reaction: however there is a basic difference in the two proposals. In the orbital symmetry pathway provided for cyclobutane formation the initial sigma bonds of the two olefin molecules are untouched and the pi bonds are transformed into the new ∡ bonds thereby forming the cyclic intermediate. In the case of the multi-centred species the carbon-carbon sigma bonds of the initial olefins are broken at the same time as the pi bonds so that a cyclic structure is never actually formed. This dynamic bond formation and breakage is thought to be a more reasonable possibility in the course of a metathesis reaction.

(c) The chain mechanism A recent proposal,[50] as an explanation for the mechanism of the metathesis reaction suggests that neither the cyclobutane intermediate (XII) nor the multicentred species (XIII) is a correct representation of the events. The report proposes that a chain mechanism adequately explains many factors which arise out of olefin metathesis reactions. A scheme is predicted whereby (1-42)



--- 1-42

If this mechanism is applied to the reaction of a cyclic olefin with an acyclic olefin over a tungsten based catalyst the result is: 1-43.



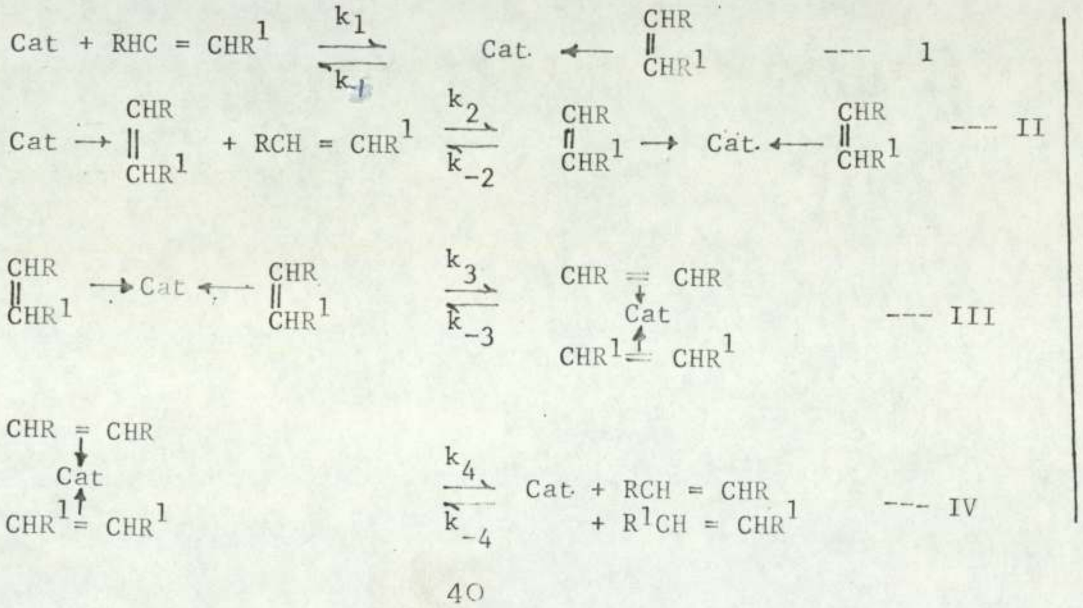
--- 1-43

Since metal carbenes and four membered rings containing metals are known species[51] and also since additions to olefins are common then this proposal requires no unusual theoretical explanations. The theory can be widely applied to make predictions about metathesis reactions in general and also accounts for the high molecular weight polymer which is formed at an early stage in the polymerisation of cyclic alkenes.

1-7 Kinetic treatment of the metathesis reaction A kinetic treatment of the ring opening polymerisation of cyclic alkenes using classical investigation methods has not produced useful results owing to the many experimental difficulties involved in gathering the data. The high rate of polymerisation and the high conversion to polymer at an early stage in the reaction create difficulties in obtaining samples for kinetic studies. It has, however, been possible to obtain kinetic data for the olefin disproportionation reaction using known kinetic study methods and it is possible to apply these results to the polymerisation reaction.

Kinetic studies on the homogeneous disproportionation of pent-2-ene to but-2-ene and hex-3-ene, using tungsten based catalysts, have shown[8,59] that the rate of disappearance of pent-2-ene is first order with respect to the catalyst and has variable order with respect to the olefin. At low olefin to catalyst ratios the order is greater than unity whereas at higher olefin to catalyst ratios the order is approximately unity. The results obtained were interpreted in terms of a mechanism involving stepwise, rapid reversible olefin complexation to the metal followed by a rate determining disproportionation step.

From his work on the disproportionation of cis-2-pentene Hughes suggested[59] that the mechanism (1-44) gave the best fit for his experimental results.



$$\text{Cat} + \text{RHC} = \text{CHR}^1 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \text{Cat} \leftarrow \begin{matrix}\text{CHR}\\ \|\\ \text{CHR}^1\end{matrix} \quad \text{--- 1}$$

$$\text{Cat} \rightarrow \begin{matrix}\text{CHR}\\ \|\\ \text{CHR}^1\end{matrix} + \text{RCH} = \text{CHR}^1 \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} \begin{matrix}\text{CHR}\\ \|\\ \text{CHR}^1\end{matrix} \rightarrow \text{Cat} \leftarrow \begin{matrix}\text{CHR}\\ \|\\ \text{CHR}^1\end{matrix} \quad \text{--- II}$$

$$\begin{matrix}\text{CHR}\\ \|\\ \text{CHR}^1\end{matrix} \rightarrow \text{Cat} \leftarrow \begin{matrix}\text{CHR}\\ \|\\ \text{CHR}^1\end{matrix} \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} \begin{matrix}\text{CHR} = \text{CHR}\\ \downarrow\\ \text{Cat}\\ \uparrow\\ \text{CHR}^1 = \text{CHR}^1\end{matrix} \quad \text{--- III}$$

$$\begin{matrix}\text{CHR} = \text{CHR}\\ \downarrow\\ \text{Cat}\\ \uparrow\\ \text{CHR}^1 = \text{CHR}^1\end{matrix} \underset{k_{-4}}{\overset{k_4}{\rightleftharpoons}} \begin{matrix}\text{Cat} + \text{RCH} = \text{CHR}\\ + \text{R}^1\text{CH} = \text{CHR}^1\end{matrix} \quad \text{--- IV}$$

1-44

Olefin complexation occurred in a stepwise manner and it was found that in general $k_1 \neq k_2$. Step III was the actual disproportionation reaction and step IV represented decomplexation of the product. The complexation and decomplexation steps were thought to be similar to those involved in absorption and desorption on a heterogeneous catalyst surface.

In this kinetic analysis only the first three steps of the reaction are considered and since the experiments were carried out at an early stage in the reaction the reverse of Step III is neglected. Using the simplified notation:

C = catalyst
S = reactant olefin
P = product olefin

the mechanism may be written:

$$C + S \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} CS \quad \text{--- I} \qquad CS_2 \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} CPP_1 \quad \text{--- III}$$

$$CS + S \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} CS_2 \quad \text{--- II}$$

The complexation and decomplexation of the olefin molecules were believed to occur at much faster rates than the disproportionation reaction itself; accordingly the concentrations of the complexes CS and CS_2 could be obtained from the equilibrium expressions for steps 1 and II whereby:

$$k_1 [C] [S] = k_{-1} [CS]$$

and hence: $[CS] = K_1[C][S]$ where $K_1 = \dfrac{k_1}{k_{-1}}$ -- a.

similarly: $k_2 [CS][S] = k_{-2} [CS_2]$

so that $[CS_2] = K_1K_2 [C][S]^2$ where $K_2 = \dfrac{k_2}{k_{-2}}$ -- b.

The rate of disproportionation (R_{dp}) was given by:

$$R_{dp} = k_3 [CS_2] \qquad \text{-- c.}$$

Substituting (b) in (c):

$$R_{dp} = k_3 K_1 K_2 [C][S]^2 \qquad \text{-- --} \qquad d.$$

At a given time 't' it was proposed that:

$$[C] = [C]_0 - CS - [CS_2] \qquad \text{-- --} \qquad e.$$

$$\text{and} \qquad [S] = [S]_0 - [CS] - 2[CS]_2 \qquad \text{-- --} \qquad f.$$

Where $[C]_0$ and $[S]_0$ were the initial concentrations of C and S respectively and $S \simeq S_0$ since the catalyst concentration is lower than that of the olefin. Substitution of these values for [C] and [S] into expressions a and b above will give:

$$[CS] = \frac{K_1 [S]_0 \left[[C]_0 - [CS]_2 \right]}{1 + K_1 [S]_0} \qquad \text{-- --} \qquad g.$$

$$\text{and} \qquad CS_2 = \frac{K_1 K_2 [C]_0 [S]_0^2}{1 + K_1 [S]_0 + K_1 K_2 [S]_0^2} \qquad \text{-- --} \qquad h$$

accordingly the rate of disproportionation (R_{dp_0}) was then given by:

$$R_{dp_0} = \frac{k_3 K_1 K_2 [C]_0 [S]_0^2}{1 + K_1 [S]_0 + K_1 K_2 [S]_0^2}$$

This expression showed the rate of disproportionation to be first order in catalyst concentration at constant olefin concentration. The order with respect to olefin at constant catalyst concentration would be variable. At very high olefin concentrations R_{dp_0} would be expected to approach a zero order dependence on olefin concentration but if $K_1 > K_2$ then even at very high olefin concentration this order would be approximately unity. It was thought from the results obtained that $K_1 > K_2$ which suggested that the mono-olefin complex was more readily formed than the bis olefin complex and indeed this would be as expected if steric hindrance factors are taken into account.

It must be noted that: in step f, although Hughes neglected any significant rate of reformation of the original olefin no account was taken of the small fraction of olefin that would have been converted to product. Accordingly this must reinforce the fact that this treatment could only apply during the initial stages of reaction.

1 - 8 Conclusion

The mechanism of the ring opening polymerisation of cyclopentene resulting in the production of trans polypentenamer is still unclear although a great deal of research has been carried out on it.

The initiation step and the mode of addition of monomer whether to a cyclic structure or to an open chain structure have still not been clearly defined. The following work is concerned with clarifying some aspects of the reaction.

CHAPTER 2

EXPERIMENTAL

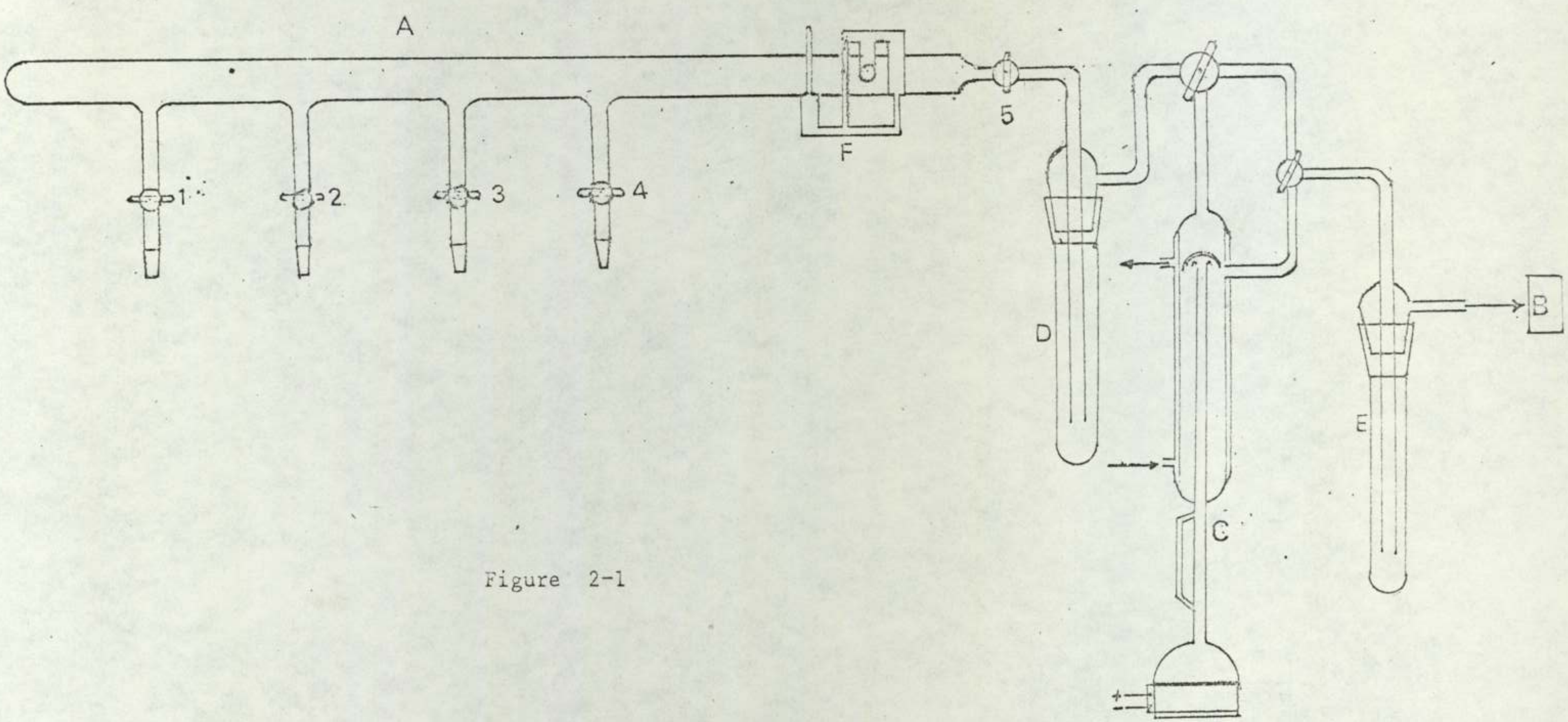


Figure 2-1

2 - 1 Introduction

The materials tungsten hexachloride and aluminium alkyls used in this work are reactive towards traces of impurities such as oxygen and moisture. The experimental procedures adopted had to be rigorous in the exclusion of these; accordingly, wherever possible, all reactions and procedures for the preparation of materials were carried out under high vacuum.

2 - 2 (A) The high vacuum line:

The high vacuum line, shown in fig. 2-1 , consisted of a manifold (A) which was evacuated by a rotary pump (B) assisted by a mercury diffusion pump (C) and two liquid nitrogen cold traps (D,E). Trap D was used to condense the vapours extracted from the manifold and trap E to prevent exhaustion of mercury vapour into the atmosphere. Extending from the manifold were a number of taps with ground glass joints which could be used to attach flasks and other pieces of apparatus to the high vacuum line. Alternatively all glass apparatus could be sealed directly onto the manifold thus obviating the use of taps and joints which were always considered to be potential sources of leakage of air and moisture. The manifold pressure was estimated by use of a "Vacustat" (F).

Solvents and monomers were purified on the high vacuum line by trap to trap distillation procedures.

(B) Distillation of solvents and monomers on the high vacuum line

A round bottomed flask containing the material to be distilled was attached to the high vacuum line manifold at tap I (fig. 2-1); the contents of the flask were frozen with liquid nitrogen and taps 1 and 5 were opened to evacuate the manifold and flask. The manifold was isolated from the evacuation system by closing tap 5 and the material was melted by surrounding the flask with a beaker containing methanol. The gases dissolved in the solvent then passed into the manifold; the

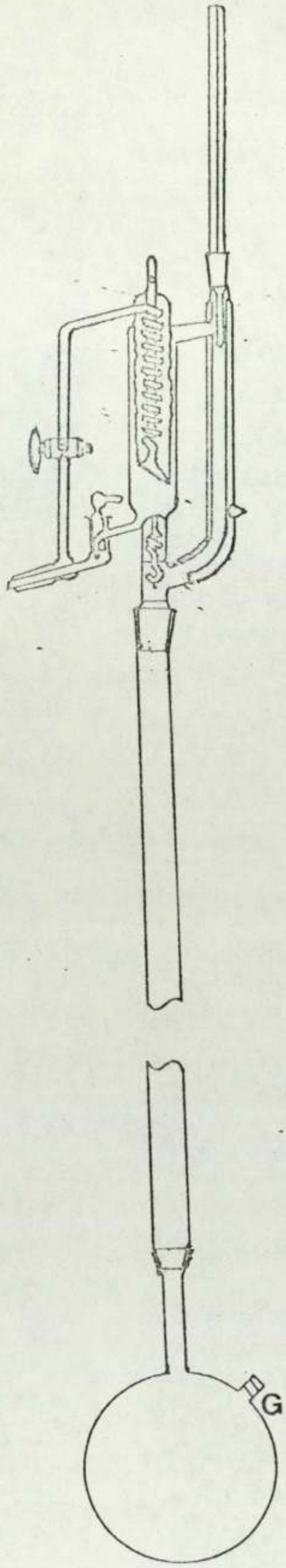


Figure 2-2

flask was refrozen and by opening tap 5 any gases remaining in the manifold were removed. This freeze thaw procedure was repeated until all dissolved gases were removed from the solvent whereupon a 'sticking' vacuum was obtained whenever tap 5 was opened after successive operations.

Tap 1 was then closed and a second round bottomed, clean, dry flask fitted with a 'Subaseal' side arm was attached at Tap 2. The flask was evacuated by opening tap 2 and flame dried under vacuum. When cool the empty flask was surrounded by liquid nitrogen, tap 5 was closed and tap 1 was opened, whereupon the material distilled from flask 1 into flask 2.

2 - 3 Purification of solvents and monomers

Solvents such as toluene and hexane (BDH) contained a large number of impurities and cyclopentene (KOCH - Light) was found to contain trace amounts of an impurity which was known to be cyclopentadiene.

(A) Purification of solvents

All solvents were initially purified by fractional distillation using the equipment shown - fig. 2-2. The apparatus included an insulated six foot column packed with glass beads and heated along its length by an electrical resistance wire. To ensure a good separation of components during the distillation the temperature of the column was controlled by varying the current through the resistance wire. The impure solvent was placed in a 500 ml round bottomed flask attached to the foot of the column and was heated by a thermostatted isomantle. The distillate was collected at the top of the column using the equipment shown - fig.2-2; the 'Jena' column head allowed the reflux ratio to be varied by the drop counting method. The normal reflux ratio was 5:1

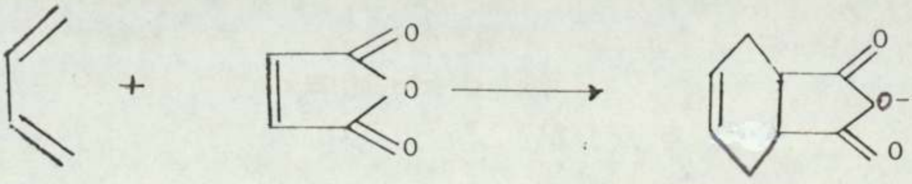
The middle fraction of the distillate was collected and then dried by standing over alumina that had been activated by heating in a furnace at 400^{o}C for four hours. The purity of the collected fraction was checked by gas chromatography and where necessary the distillation operation was repeated until a solvent of very high purity was obtained.

After standing over the activated alumina for 24-48 hours the solvents were distilled under high vacuum into a flask that had a 'Subaseal' side arm. The solvent was finally dried by injecting 1 ml. of aluminium alkyl into the flask through the 'Suba-sealed' side arm (G). The solvent was stored under high vacuum in flask 2 from which it was distilled as required.

(B) Purification of cyclopentene:

Cyclopentadiene present as an impurity in cyclopentene was removed prior to the use of the monomer in polymerisation reactions. Two procedures by which this could be accomplished were available.

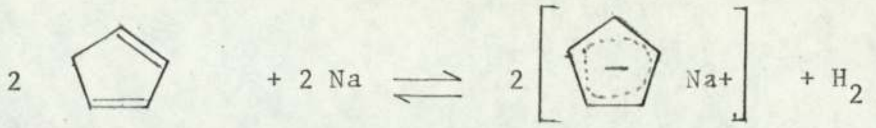
(I) Method 1 Cyclopentene (20g) was refluxed over maleic anhydride (10g) for one hour thereby converting any cyclopentadiene present to an involatile adduct by a conventional Diels-Alder reaction 2-1.



--- 2-1

The cyclopentene was then distilled from the reaction mixture and a G.L.C. analysis of the distillate confirmed the removal of the trace quantities of the impurity. The cyclopentene was initially dried by standing over activated alumina for 24 - 28 hours and finally dried by distillation under high vacuum into a flask with a 'Subasealed' side arm through which 0.5 ml of aluminium alkyl was added.

(II) Method 2 An alternative procedure for the purification of cyclopentene involved the utilisation of the reactivity of cyclopentadiene toward sodium in the following reaction. 2-2



-- 2-2

This reaction could be turned to advantage in this system because cyclopentadienyl sodium acted as a drying agent. Any moisture present in the system was destroyed by the cyclopentadienyl sodium and cyclopentadiene was regenerated. The regenerated cyclopentadiene reacted with more sodium until a slightly green tinge persisted in the solution.

50 ml. of cyclopentene were degassed on the high vacuum line and allowed to stand over sodium wire for 24 hours. In the initial stages when hydrogen was evolved at a significant rate the flask and contents were degassed in the usual manner at regular intervals. The monomer was stored over sodium wire under high vacuum and distilled off as required. Prior to use in polymerisations the removal of cyclopentadiene was confirmed by gas chromatographic analysis.

2 - 4 Preparation of catalyst solutions for use in polymerisation reactions

(A) Purification of tungsten hexachloride and preparation of its solution in toluene:

(1) Commercial tungsten hexachloride: Commercial tungsten hexachloride (BDH) contained oxychlorides of tungsten as impurities. The mixture could be considered to be composed of tungsten hexachloride and tungsten (VI) oxide. Tungsten (VI) oxide present in this mixture was converted to tungsten hexachloride by reaction with hexachloropropene in the following manner, (2-3):

$$WO_3 + 3\,C\,Cl_2 = C\,ClC\,Cl_3 \longrightarrow WCl_6 + 3\,C\,Cl_2 = C\,Cl - CO\,Cl \qquad - 2\text{-}3$$

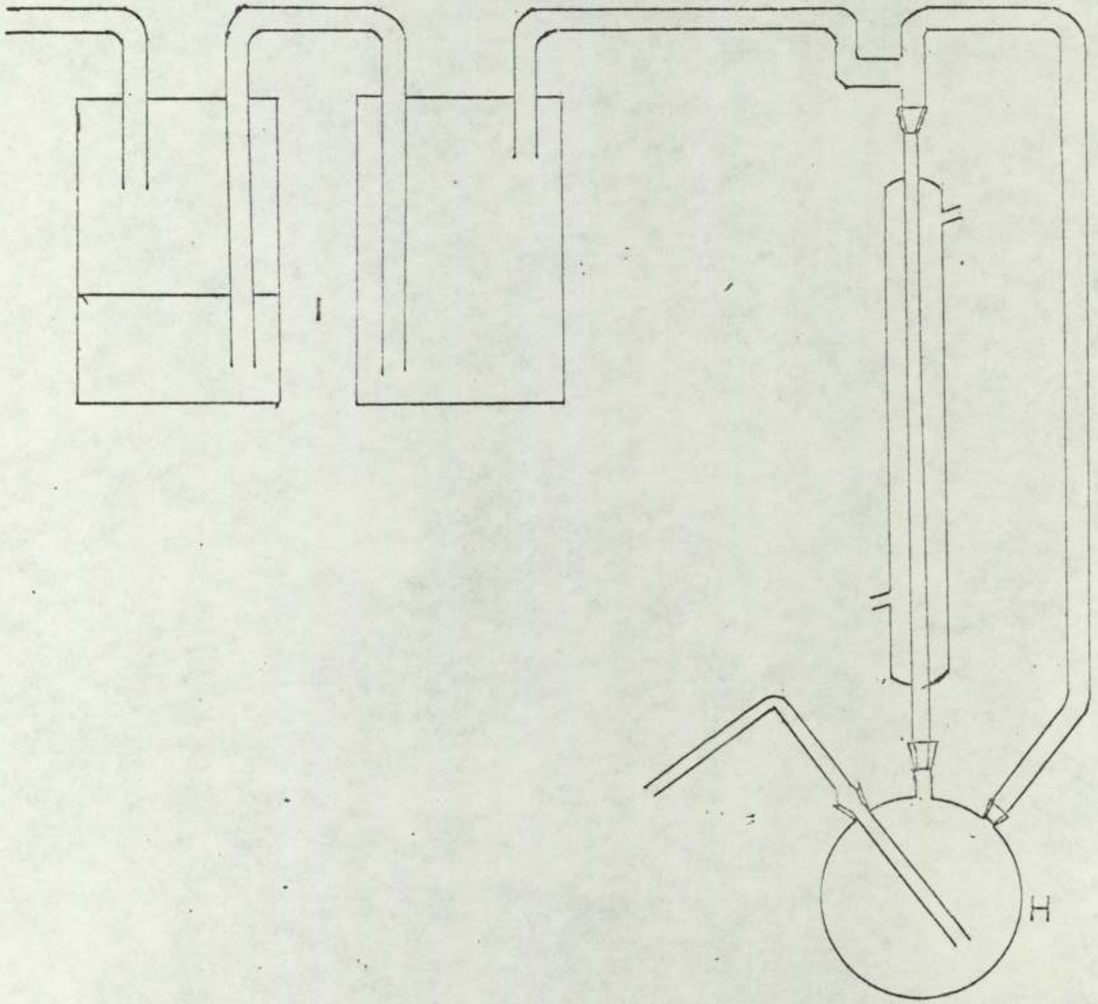


Figure 2-3

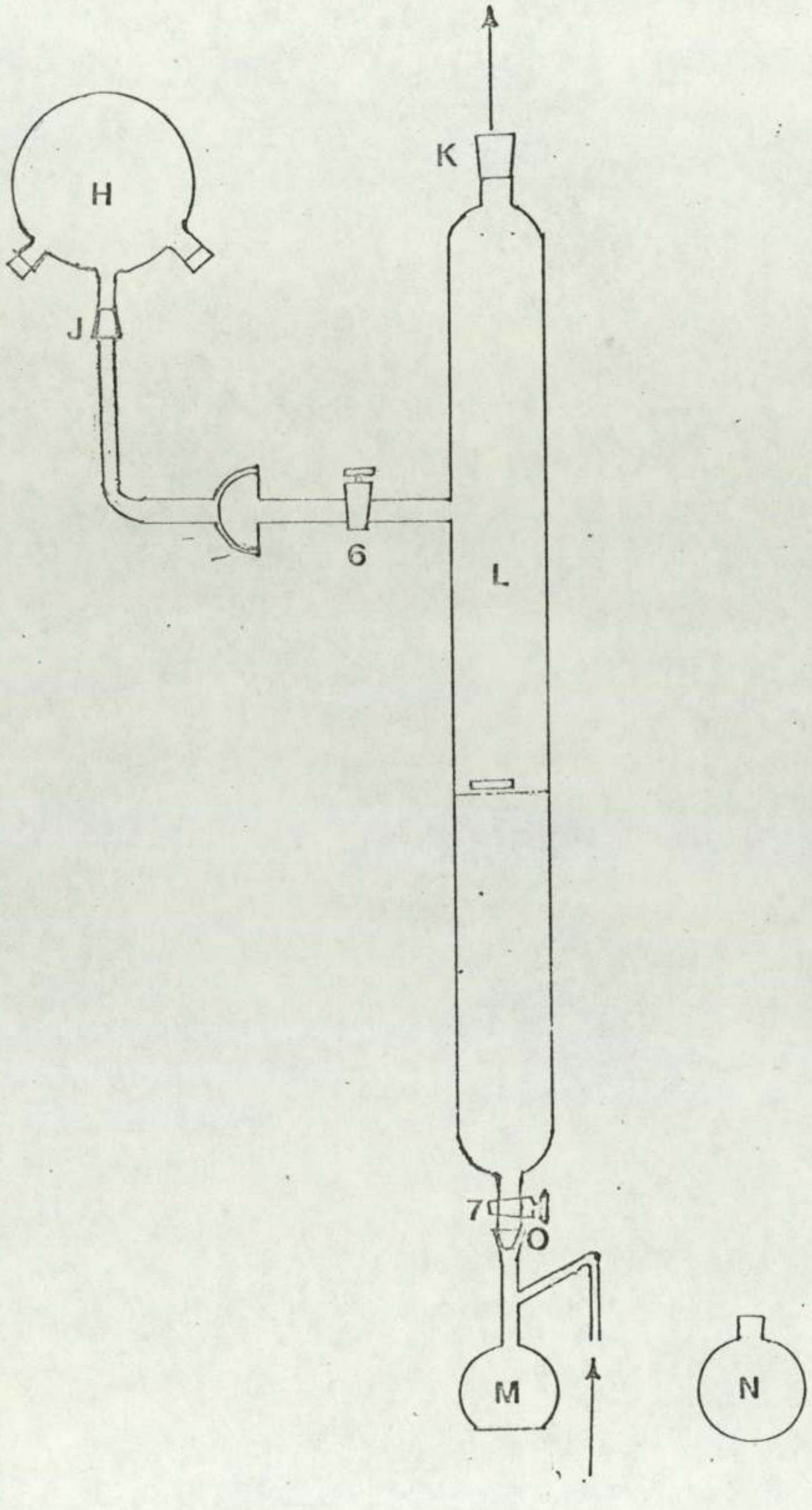


Figure 2-4

Ten grams of commercial tungsten hexachloride and ten ml. of hexachloropropene were refluxed in a clean dry three necked flask (H) - (fig. 2-3). A reflux condenser was attached to one neck and to the other a nitrogen bleed was fixed. A flow of dry nitrogen was maintained through the flask to prevent the hydrolysis of the tungsten hexachloride during the purification. The nitrogen was then passed through a conventional sulphuric acid drying system (I). After one hour the reflux was stopped, the nitrogen inlet and condenser were removed and the flask was stoppered and cooled rapidly in an icebath to produce small crystals of tungsten hexachloride.

The tungsten hexachloride, purified by this method, was washed and made ready for use in polymerisation reactions, as a toluene solution, using the apparatus shown - fig. 2-4. The reflux flask (H) containing the suspension of tungsten hexachloride was attached at J to the apparatus which was connected to the high vacuum line at K. Flask H was immersed in liquid nitrogen and with taps 1, 5 and 6 open and tap 7 closed, the whole system was evacuated and the usual freeze thaw procedure was adopted for the degassing of the contents of flask H. With tap 1 closed the contents of the flask were poured onto the top of the sinter of vessel L. Dry nitrogen was then admitted to the apparatus at tap 1 and the contents of the vessel were filtered into flask M with tap 7 open. The filtrate was discarded and the system was evacuated and pure dry hexane was distilled, from a flask on the line, into the reaction vessel H. The remains of the suspension in flask H were then washed into the vessel L and the suspension of tungsten hexachloride was washed with dry hexane to remove any impurities absorbed on the surface. The suspension was filtered and this washing procedure was repeated five times before the final evacuation of the system to remove traces of hexane. Pure dry toluene was then distilled into flask H and subsequently poured into vessel L. The pure tungsten hexachloride was agitated by a 'Teflon' encased magnetic stirrer

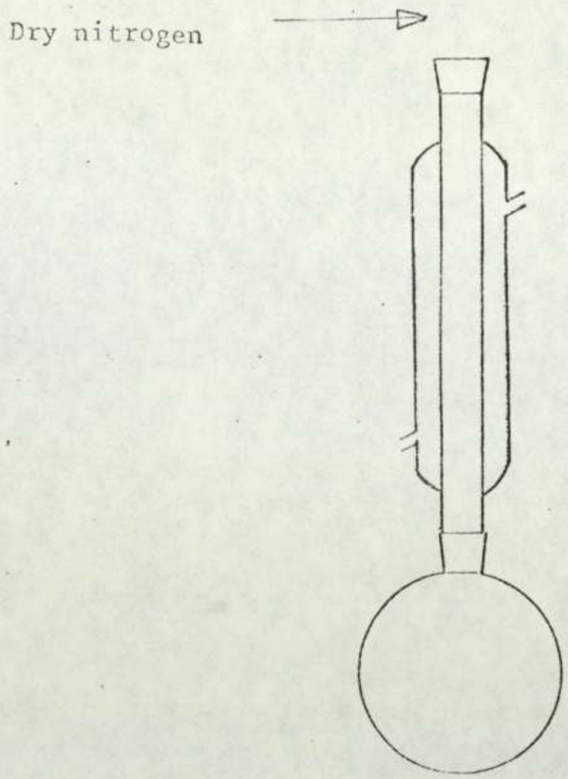


Figure 2-5

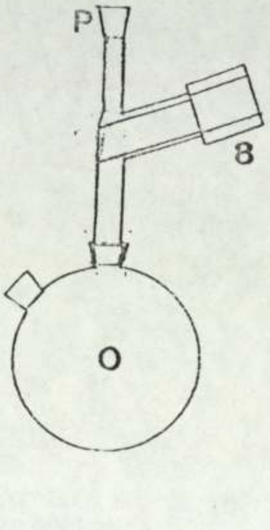


Figure 2-6

and slowly dissolved in the toluene. A clean dry flask (N) was fitted to the apparatus at O and evacuated via tap 7. The solution of tungsten hexachloride was filtered into flask N which was stoppered and stored under nitrogen. Samples of tungsten hexachloride solution could be removed from the flask through the 'Subaseal' stopper by means of a hypodermic syringe.

(II) Pure tungsten hexachloride This was obtained as a sample (BDH) with a degree of purity of 99.90% hence the purification procedure described above was not necessary.

A weighed amount of tungsten hexachloride was placed in a clean dry 100 ml. flask under dry nitrogen. The flask was attached to the high vacuum line, evacuated and immersed in liquid nitrogen; the required amount of toluene was distilled into it from a graduated tube on the high vacuum line. The flask was immersed in methanol, then removed from the high vacuum line under dry nitrogen and immediately stoppered with a 'Subaseal' stopper.

Samples of the tungsten hexachloride solution in toluene were obtained for use in polymerisation reactions using a hypodermic syringe as before.

2-4B Preparation of toluene solutions of tungsten oxychlorides:

Solutions of tungsten oxychlorides of the stoichiometries given below were prepared by refluxing tungstic oxide and tungsten hexachloride in toluene at a temperature of 50°C for one hour.

Tungsten oxychlorides: (1) W_2OCl_{10}
(2) $WOCl_4$
(3) $W_2O_3Cl_6$
(4) WO_2Cl_2
(5) $W_2O_5Cl_2$

To produce the tungsten oxychlorides with the above stoichiometries, as 0.1M solutions in toluene, flasks containing the appropriate amounts of tungsten hexachloride, tungstic oxide and toluene, as shown in table 2-1, were made ready. A nitrogen atmosphere and vacuum distillation techniques were used in this operation to prevent hydrolysis of the tungsten hexachloride.

TABLE 2-1

Quantities of tungsten hexachloride, tunstic oxide and toluene required for the preparation of the tungsten oxychlorides (1-5) above.

tungsten oxychloride required		Vol. toluene mls.	Wt.WCl_6 grams	m.moles WCl_6	Wt.WO_3 grams	m.moles WO_3	molarity of the solution
1	W_2OCl_{10}	20	0.4	1.0	1.16	5	0.1
2	$WOCl_4$	20	0.4	1.0	0.46	2	0.1
3	$W_2O_3Cl_6$	20	0.4	1.0	0.23	1	0.1
4	WO_2Cl_2	40	0.8	2.0	0.23	1	0.1
5	$W_2O_5Cl_2$	50	1.0	2.5	0.10	1.5	0.1

Tungsten hexachloride, tungstic oxide and toluene were refluxed in the ratios given above, for one hour at 50°C, in the apparatus shown - fig. 2-5. Dry nitrogen was blown across the top of the reflux condenser throughout the reflux operation. After one hour the reflux condenser was removed and the flask containing the tungsten oxychloride solution was immediately stoppered with a 'Subaseal' and stored under dry nitrogen. Samples of the solution were withdrawn by hypodermic syringe as required.

(C) Preparation of a toluene solution of aluminium tri isobutyl

The pure aluminium tri-isobutyl obtained from Cambrian chemicals was

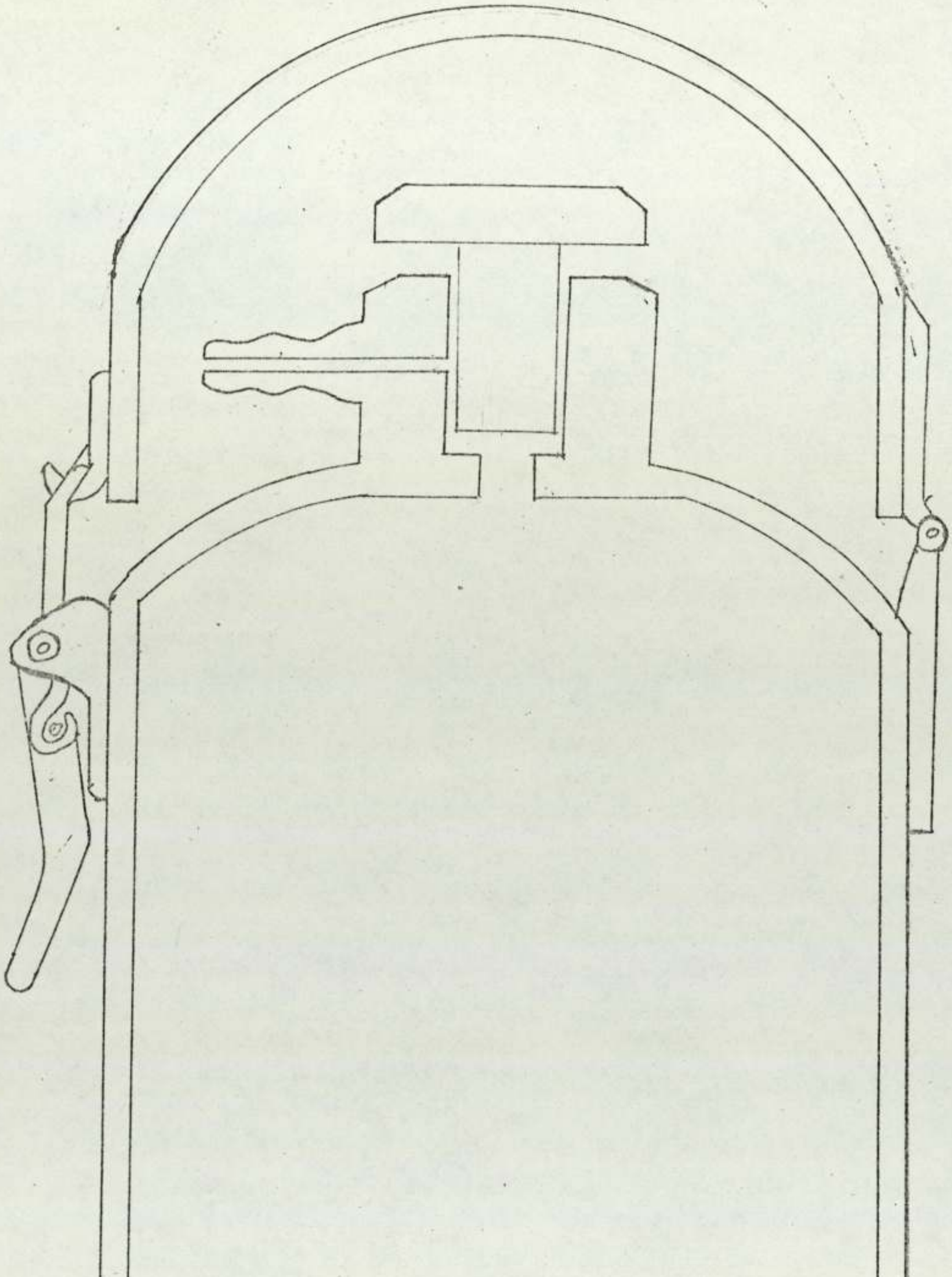


figure 2-7

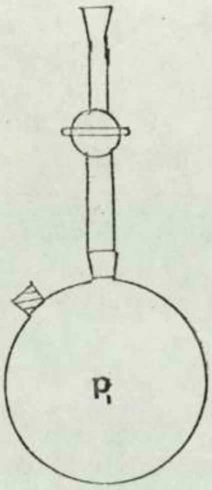


Figure 2-8

used as supplied without further purification. A 0.12M solution of the aluminium tri-isobutyl was prepared in toluene in the round bottomed flask O (fig.2-6) which was fitted with a greaseless tap 8 and a 'Subaseal'.

Aluminium alkyls react explosively with oxidising agents or water and were therefore stored in special containers fig. 2-7. All apparatus used was dried thoroughly and filled with a dry nitrogen atmosphere before allowing any contact with the aluminium alkyl.

Flask O was attached to the high vacuum line at point P and then evacuated and flame dried. 20 mls of dry toluene were distilled into it from a graduated tube on the high vacuum line; the flask was filled with dry nitrogen, tap 8 was closed and the flask was removed from the line. Using a clean dry syringe one ml. of the pure aluminium tri-isobutyl was withdrawn from the container, (fig.2-7) under dry nitrogen, and immediately transferred to the toluene in the flask. Samples of this solution were withdrawn by means of a hypodermic syringe.

2 - 5 Polymerisation procedures

(A) Polymerisations of cyclopentene initiated by the tungsten hexachloride/aluminium tri-isobutyl catalyst system

A 50 ml. round bottomed flask fitted with a 'Subaseal' was attached to the high vacuum line by means of a tap adaptor (fig. 2-8). The required volumes of monomer and solvent were distilled from the storage vessels into graduated tubes and thence into the reaction vessel. The flask was then removed from the high vacuum line complete with the closed tap adaptor and placed in a thermostatted constant temperature bath. After 0.5 hour the required volumes of catalyst solutions were added by syringe through the 'Subaseal'; tungsten hexachloride solution was usually added before the aluminium tri-isobutyl solution.

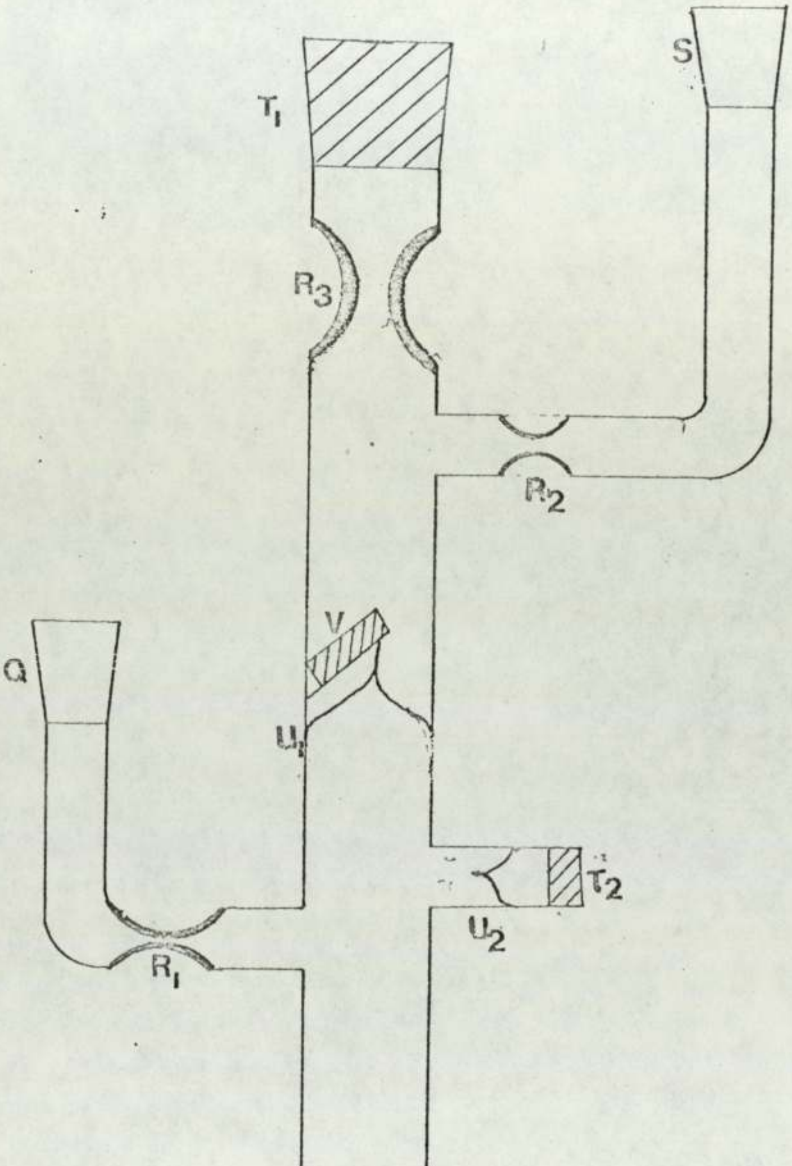


Figure 2-9

The polymerisation reaction could be terminated by the addition of methanol to the reaction flask. The polymer obtained was then purified by successive precipitations from chloroform or toluene solutions using methanol as the non solvent. Alternatively a sample of the polymerisate could be withdrawn from the flask by syringe, injected into a large volume of methanol and the polymer so obtained was purified as described above. The latter method could be used provided the viscosity of the polymerisate was not too high.

(B) Polymerisations of cyclopentene catalysed by tungsten hexachloride alone

The method described above (2.5 A) was used initially for polymerisations employing tungsten hexachloride alone as catalyst but irreproducible results were obtained. Subsequently all polymerisations were carried out in the glass apparatus shown - fig. 2-9. This technique ensured the maintenance of dry, oxygen-free conditions throughout the polymerisation reaction.

The apparatus was attached to the high vacuum line at Q, evacuated and then dried by flame heating. The required volume of cyclopentene was distilled into the compartment from the graduated storage tube on the high vacuum line. Whilst the cyclopentene was still frozen this section of the apparatus was sealed off at point R_1. Point S was then attached to the vacuum line and this section of the apparatus was evacuated and flame dried. The required volume of tungsten hexachloride solution was injected through the 'Subaseal' at point T_1. The tap leading to the high vacuum line was opened and the toluene was removed by distillation under high vacuum into a flask on the line. The final traces of toluene were removed by pumping the system so that solid tungsten hexachloride remained in the top section of the apparatus which was then sealed off at points R_2 and R_3. The apparatus was then

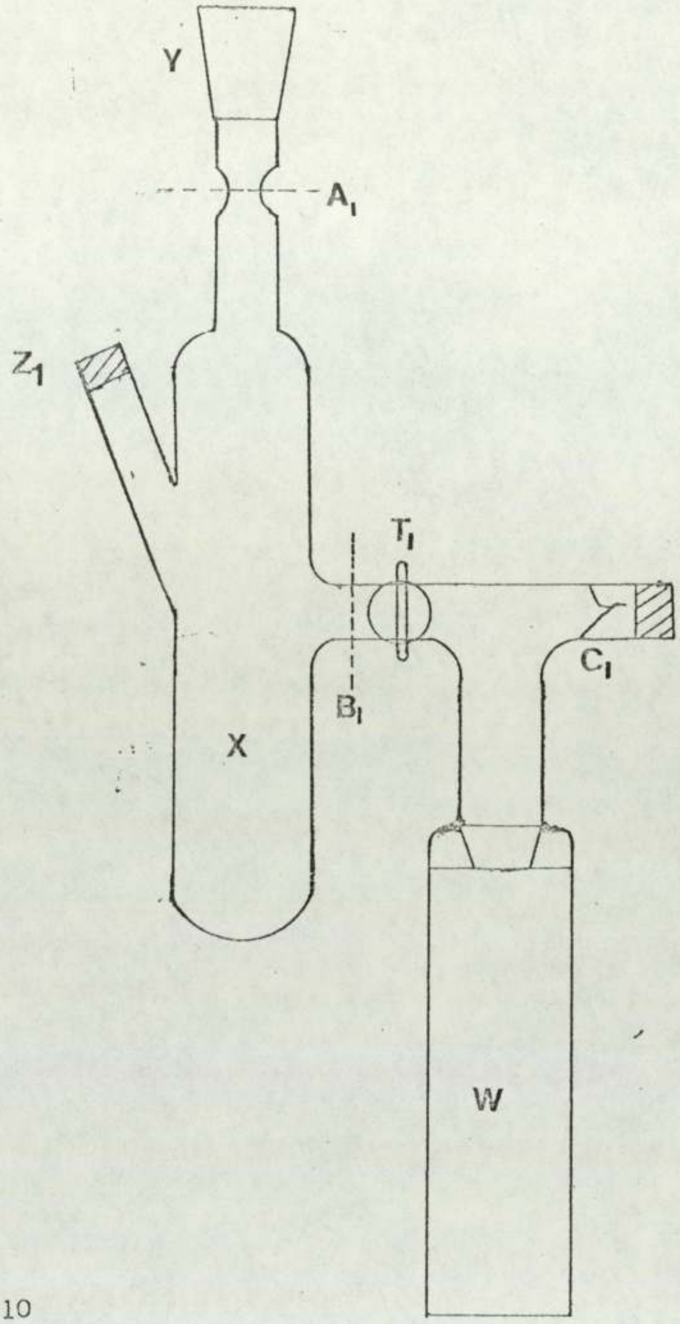


Figure 2-10

immersed in a constant temperature bath for 0.5 hr when the cyclopentene was allowed to interact with the tungsten hexachloride upon breaking the breakseal (U_1) using the glass weight V. The reaction was terminated by breaking the breakseal (U_2) and injecting methanol through the 'Subaseal" (T_2). Alternatively after breaking the breakseal (U_2), dry oxygen was admitted to the apparatus, through the 'Subaseal' T_2, using a hypodermic syringe needle connected to a dry oxygen supply. Methanol was added when termination of the reaction was required.

(C) Polymerisations of cyclopentene catalysed by tungsten oxychlorides

The tungsten oxychlorides prepared by the method described before-2.4B were used to polymerise cyclopentene using the method (B) above with omission of the oxygen addition step.

(D) Spectrophotometric studies of the polymerisation of cyclopentene

The polymerisation of cyclopentene initiated by the reaction of tungsten hexachloride with cyclopentene followed by the addition of oxygen was accompanied by a series of colour changes and hence a study of the spectral changes which occurred during the polymerisation was undertaken.

The apparatus which consisted of a quartz U.V. cell (W) attached to a filling device (X) - (fig. 2-10) - was connected to the high vacuum line at Y, evacuated and then dried by heating gently with a blue flame. The tap leading to the high vacuum line was closed, the required volume of the solution of tungsten hexachloride was injected through the 'Subaseal' at point Z_1. The toluene of the catalyst solution was removed by distillation into a flask on the high vacuum line. The required volume of cyclopentene was distilled into the apparatus from a graduated flask on the line and the apparatus was sealed off at point A_1 whilst the cyclopentene was still frozen. The cyclopentene was then melted and the tungsten hexachloride dissolved in the monomer forming a red/brown solution. This solution was then poured into the quartz cell and isolated from the rest of the apparatus by closing the greaseless tap - (T_1). The isolated U.V. cell and its contents were separated from the filling device (X) by carefully breaking the glass apparatus at B_1. The apparatus (W) was then placed in a constant temperature bath. At regular intervals the cell (W) was removed from the bath and the U.V./visible spectrum was recorded using a Perkin Elmer Sp.137 spectro-photometer with cyclopentene as the reference solvent.

The U.V./visible absorption spectrum of the system was recorded over a period of time after which the breakseal (C_1) was broken and dry oxygen was admitted to the apparatus through the 'subaseal' at C_1. The U.V./ visible spectrum was again recorded at regular intervals after the addition of oxygen.

2 - 6 Methods of analysis

(A) Determination of the concentration of the tungsten hexachloride solution

A gravimetric method for the determination of the concentration of the tungsten hexachloride solution was used because the extinction coefficient for tungsten hexachloride in toluene was unknown.

A 10 ml. sample of the tungsten hexachloride solution was extracted from the flask using a syringe and was injected into distilled water contained in a tared evaporating basin. Tungsten hexachloride was thus hydrolysed to tungstic oxide by 2-4.

$$WCl_6 + 3H_2O \longrightarrow 6HCl + WO_3 \qquad \text{----- 2-4}$$

The remaining water was gently evaporated before the evaporating basin was placed in a furnace at 700°C to ensure complete dryness. After two hours in the furnace the evaporating basin was allowed to cool in a dessicator and then re-weighed. The weight of WO_3 was obtained and hence the concentration of tungsten hexachloride in the original solution was calculated. This procedure was repeated twice to give the readings - table 2-2.

TABLE 2-2

Determination of the concentration of tungsten hexachloride solution

Volume of WCl_6 solution/ml.	Weight of WO_3 obtained on hydrolysis/gram	Concentration of WCl_6/moles l^{-1}
10	0.13	0.057
10	0.129	0.055
10	0.13	0.057

(B) Determination of the oxidation states of tungsten present during polymerisation reactions:

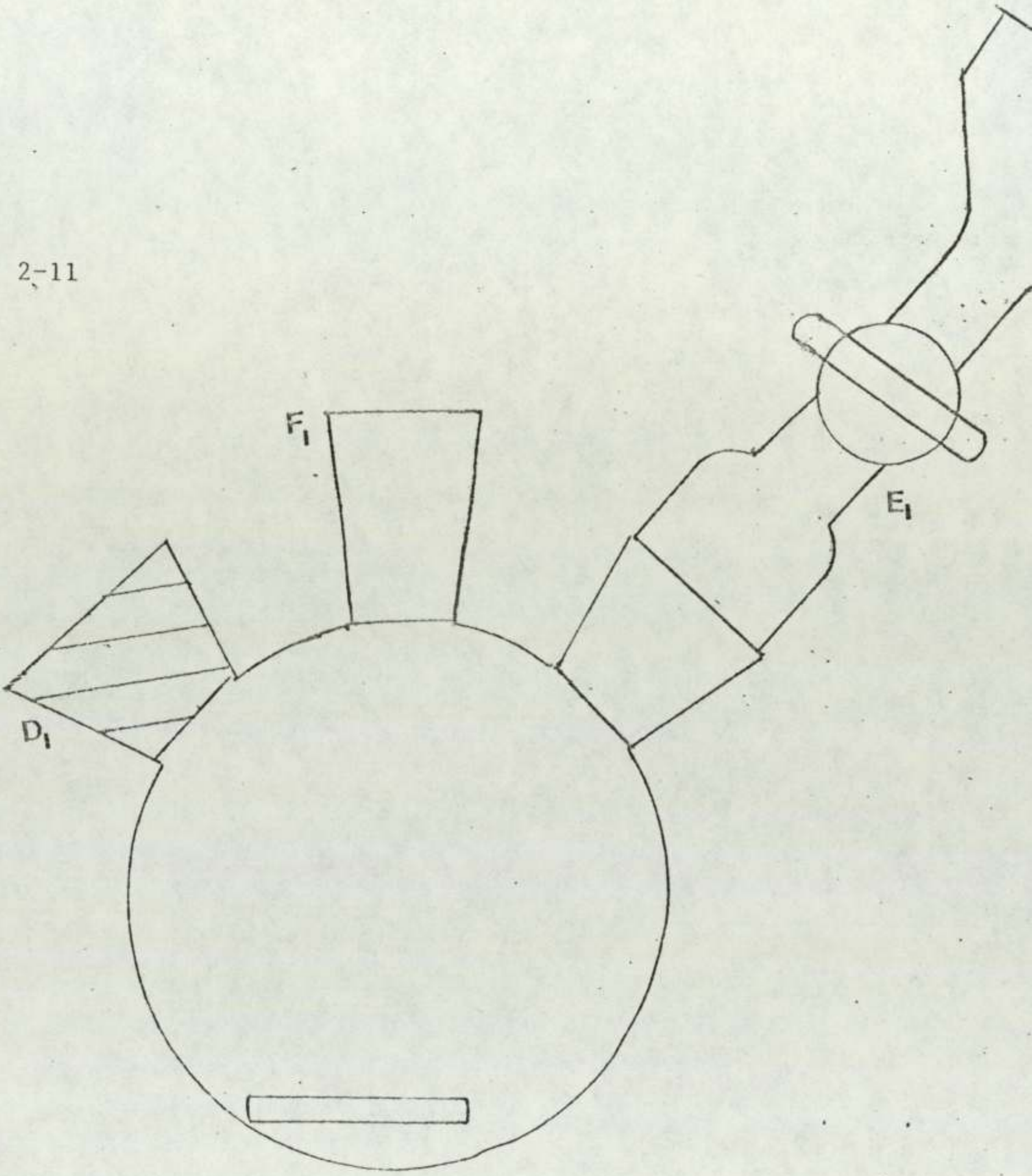
The tungsten atom was known to exist in a mixture of oxidation states during the catalysis of the ring opening polymerisation of cyclopentene. To determine the average value of the oxidation state the tungsten present in lower oxidation states was oxidised to tungsten (VI) by the addition of Potassium permanganate. The amount of standard permanganate used was determined by back titration with standard ferrous ammonium sulphate and the mean oxidation state of tungsten present in the polymerisation reaction was then obtained.

(I) Preparation of standard solutions All solutions were prepared by the procedures described in Vogel, "Textbook of Volumetric analysis".[67]

Potassium permanganate About 3.2 grams of A.R. potassium permanganate were weighed, transferred to a 1500 ml beaker and dissolved in one litre of distilled water. The beaker was covered with a clockglass and the solution was boiled gently for 20 minutes and then cooled. This solution was filtered through a sintered glass crucible, collected and stored in a stoppered, dark brown glass bottle which had been thoroughly cleaned.

This solution of potassium permanganate was standardised using ferrous

Figure 2-11



ammonium sulphate.

Standardisation of the potassium permanganate   9.3 grams of recrystallised ferrous ammonium sulphate was weighed accurately and transferred to a 250 ml. volumetric flask. 200 ml. of distilled water and 5 ml. of concentrated sulphuric acid were added; the salt was dissolved and the solution made up to the mark with distilled water to produce a 0.1N solution of ferrous ions.

25 ml. of this solution were removed with a pipette and added to a 500 ml. conical flask together with 25 ml. of N sulphuric acid. The volume of potassium permanganate required to produce the first permanent pink colour was recorded.

The normality of the potassium permanganate was calculated using the relationship (2-5): it was found to be 0.104N.

$$V_{Fe++} \times N_{Fe++} \rightleftharpoons V_{KMno_4} \times N_{KMno_4} \quad \text{---- 2-5}$$

Preparation of deoxygenated solutions   Deoxygenated solutions of sodium hydroxide and sulphuric acid and a deoxygenated suspension of lead oxide in distilled water were required for the oxidation state determinations.

These were prepared by first boiling the solutions or suspension for 0.5 hr. followed by bubbling white spot nitrogen through them for two hours.

(II) Determination of the change in tungsten oxidation states during the course of a cyclopentene/tungsten hexachloride reaction

A clean dry 250 ml. three necked flask, fitted with a 'Subaseal' (D_1) and an adaptor funnel (E_1) was attached to the vacuum line at point F_1 (fig. 2-11). The apparatus was evacuated and flame dried. The required amount of cyclopentene was distilled into the flask from the graduated tube on the high vacuum line. 2 ml. of .056M tungsten hexachloride solution in toluene were added to the cyclopentene through the 'Subaseal' (D_1). The cyclopentene was allowed to react with the tungsten hexachloride for a predetermined period of time after which the reaction was terminated by the addition to the flask of 25 mls. of deoxygenated, N sodium hydroxide solution which was contained in the stoppered adaptor funnel (E_1). Care was taken to prevent air entering the flask by allowing 2 mls of the sodium hydroxide solution to remain in the funnel. The cyclopentene and toluene in the flask were removed by distillation under high vacuum and 50 mls. of deoxygenated 2N sulphuric acid were then added to the flask from the funnel (E_1). Five ml. of a lead monoxide suspension in deoxygenated distilled water were added through the Subaseal -(D_1)using a hypodermic syringe fitted with a wide bore needle. The solution in the flask was then stirred with a 'teflon' encased magnetic stirrer so that the chloride ions present in the solution following the hydrolysis of the tungsten chlorides were removed as lead chloride. 12.8 mls. of the potassium permanganate solution were added through the funnel (E_1) and after one minute 25 mls. of ferrous ammonium sulphate were added. The flask was removed from the high vacuum line and the resulting solution filtered through a Buchner funnel. The excess of ferrous ammonium sulphate present in the solution was determined by back titration with potassium permanganate solution to the first permanent pink coloration.

The results for the mean oxidation state of tungsten were compared with a blank obtained by adopting the above procedure but excluding the addition of any organic material.

(C) Infra red analysis of the polypentenamer:

The infra red spectra of polymer samples were obtained to determine the relative proportions of cis and trans double bonds in the polypentenamer obtained with varied reaction conditions. The trans double bond absorbs at 10.35 μ and the cis at 13.5 μ

Samples were prepared for infra red analysis by use of the potassium bromide disc method. A 3-5% paste of the polymer solution in chloroform was prepared in potassium bromide and pressed into a disc under vacuum. The disc was then placed in the light path of a Perkin-Elmer infra-red spectrophotometer and the spectrum was recorded.

(D) Measurement of the molecular weight averages of the polypentenamers produced.[64]

Introduction: Methods of measuring molecular weight averages of polymers

Generally low molecular weight compounds are characterised by a precise molecular weight and any deviation from this value is caused by the presence of isotopes of the constituent atoms of the molecule whereas polymers are not so simply described. Methods for the synthesis of high molecular weight polymers give rise to the probability that not all the polymer molecules in a sample of polymer have identical chain lengths. For example during the benzoyl peroxide initiated polymerisation of styrene, polystyryl radicals are formed and a radical of chain length (n) may propagate by the addition of a monomer molecule to form a radical of chain length (n + 1) or terminate to form a dead polymer molecule. Because this is true for all values of the chain length (n) the resultant polymer sample possesses a distribution of molecular sizes and accordingly the application of any physical method for the measurement of the molecular weight of the polymer will yield only an average value.

The most common molecular weights quoted for polymers are the number average molecular weight ($\bar{M}_n$) and the weight average molecular weight ($\bar{M}_w$) where:

$$\overline{M}_n = \frac{\sum_1^\infty N_i M_i}{\sum_1^\infty N_i} \quad - 2.6 \quad \text{and} \quad \overline{M}_w = \frac{\sum_1^\infty N_i M_i^2}{\sum_1^\infty N_i M_i} \quad -- 2.7$$

for a sample of polymer containing N_i molecules of molecular weight M_i. The most convenient method for the routine measurement of a molecular weight average of a polymer sample involves the determination of the intrinsic viscosity (η) of the polymer solution. Application of the Mark-Houwink equation, (2-8),

$$\eta = KM^a \quad - \quad 2\text{-}8$$

will give the viscosity average molecular weight ($\overline{M}_v$) where:

$$\overline{M}_v = \left[\frac{\sum_1^\infty N_i M_i^{1+a}}{\sum_1^\infty N_i M_i}\right]^{1/a} \quad - \quad 2\text{-}9$$

In the case where 'a' approaches 1 the molecular weight obtained is the weight average ($\overline{M}_w$) but in general 'a' lies between 0.5 and 0.8.

The conventional methods for determination of absolute molecular weights, such as ebulliometry and cryoscopy, fail if the molecular weight involved is greater than 40,000 even if equipment of high sensitivity is used. A number of new physical methods have been developed that may be classfied as either absolute or relative. A necessary prerequisite for their application is that the polymer is soluble in a suitable solvent.

Absolute methods give the molecular weight directly from mathematical expressions containing only universal constants such as the gas constant or Avogadro's number together with easily determined material constants such as density, refractive index etc. The most important absolute methods are; determination of the osmotic pressure, ultracentrifugation and light scattering. These methods require considerable expenditure in equipment and are therefore not freely available. Therefore chemical methods e.g. end group analysis are still widely used in spite of their limitations.

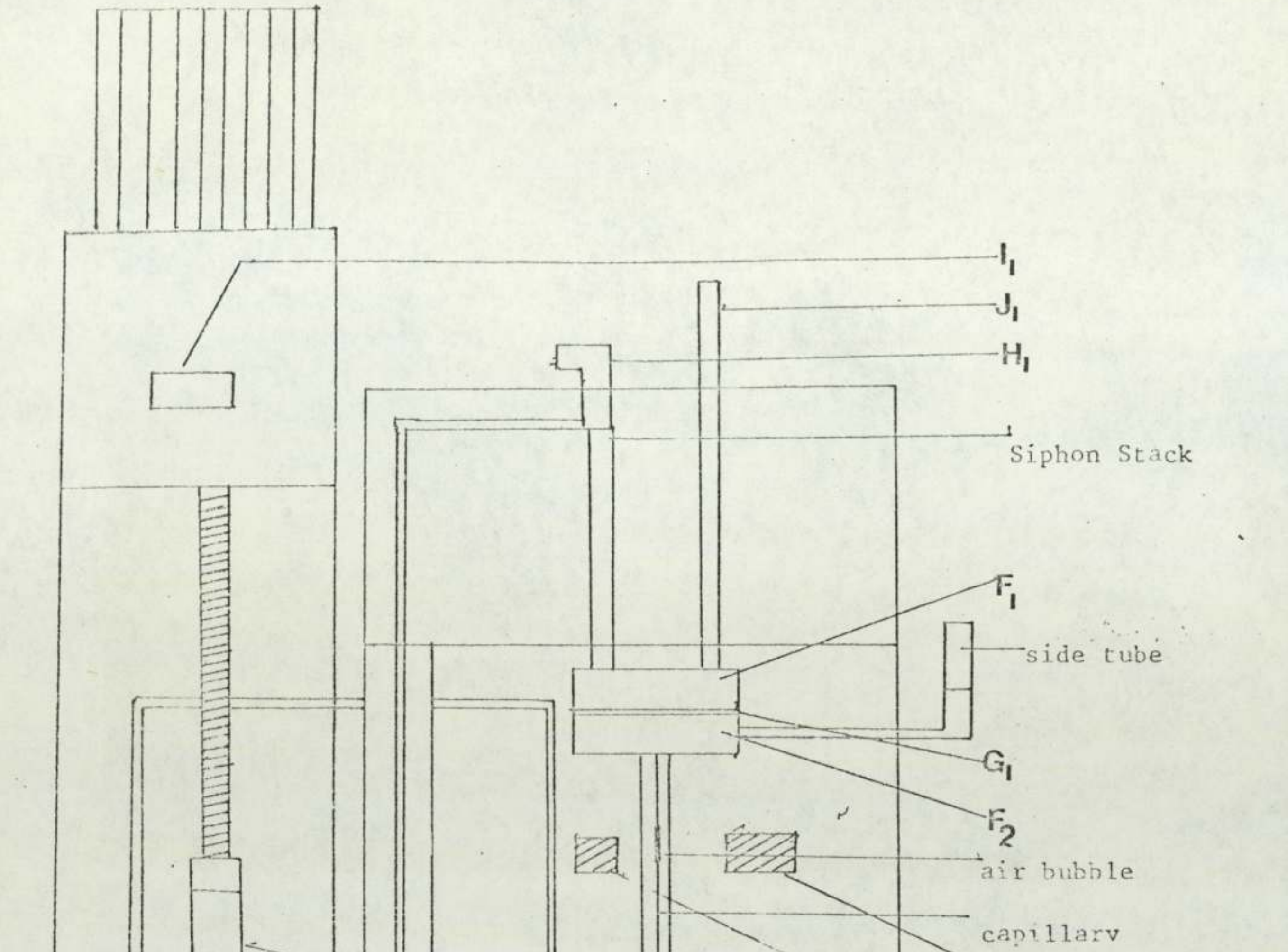

I_1
J_1
H_1
Siphon Stack
F_1
side tube
G_1
F_2
air bubble
capillary
light
photocell
solvent cup
control unit

FIGURE 2-12

Light scattering and ultracentrifugation give a measure of the weight average molecular weight ($\overline{M}_w$) whilst osmometry and end group analysis methods measure the number average molecular weight, ($\overline{M}_n$).

Relative methods for determination of molecular weights involve measurement of some property that is clearly dependent upon the molecular weight such as the viscosity of a dissolved polymer in viscometry or the elution volume of a polymer solution in gel permeation chromatography. Such measurements can only be evaluated if an experimental calibration curve has been determined by reference to some absolute method.

(I) Determination of number average molecular weights ($\overline{M}_n$) by use of high speed membrane osmometry

The use of the Mechrolab High Speed Membrane Osmometer[66] was regarded as the most useful method for determination of the number average molecular weights of the polypentenamers produced.

A schematic representation of the osmometer is shown - fig. 2-12: it comprised a cell consisting of two compartments (F_1F_2) which were separated by a semi-permeable membrane (G_1). The semi permeable membranes used were usually constructed of polymeric materials such as rubber, cellulose acetate or polyvinyl alcohol which were impermeable to species below ~20,000 M.wt. The lower half of the cell was filled with the solvent for the polymer and was connected to a solvent cup by means of a capillary tube and flexible pipe. Trapped in the capillary tube was an air bubble approximately 1 cm. long so that when solvent moved across the membrane in the osmotic process the bubble was carried up the capillary tube. The upper half of the cell could contain either polymer solution or pure solvent.

Solutions of the polymer in toluene were prepared so that their concentrations were approximately 1.0, 0.5, 0.25 and 0.125% by weight/volume. Pure solvent was first placed in the sample stack and by use of the syphon control (H_1) the meniscus was drawn down to the graduation mark; the apparatus was allowed to attain equilibrium which was maintained for a period of five minutes, at which time the air bubble in the capillary tube was in the path of a light beam which was focussed on a photomultiplier detector. The height of the solvent cup at equilibrium (h_1) was measured on the digital panel (I_1). The solvent was replaced by a fresh sample of pure solvent so that the average value for the solvent cup height could be obtained.

The solvent in the upper half of the cell was then replaced by a sample of the least concentrated polymer solution and after 30 seconds the meniscus was drawn down to the top of the capillary, in the sample stack (J_1), by use of the syphon control (H_1). This operation was repeated twice using fresh polymer solution of the same concentration after which the sample stack was refilled with the polymer solution and the meniscus was drawn down to the graduation mark as before. The chemical potential of the solvent in the upper half of the cell was then different from that in the lower half which caused solvent to move across the membrane. When this happened the bubble trapped in the capillary tube moved out of the light path which then caused a servo-motor to be activated so that the level of the solvent cup was lowered until the bubble was again in the light path i.e. at equilibrium. In effect a hydrostatic pressure equal to the osmotic pressure of the solution was applied to the solution side of the cell to prevent movement of the solvent across the membrane. The height of the solvent cup (h_2) was measured on the digital panel and an average value was obtained by repeating the entire procedure four times. The osmotic pressure of the solution (π) was then (h_1 - h_2) cms. of solvent.

The operation was repeated using solutions of increasing concentrations in turn and the osmotic pressure (Π) of each of these solutions was obtained.

Values of $\bar{M}_n$ were obtained by constructing a plot of Π/C against C and extrapolating to zero thus obtaining the value of Π/C_0 which was substituted in 2-10.[61]

Experimental data for the determination of the number average molecular weights

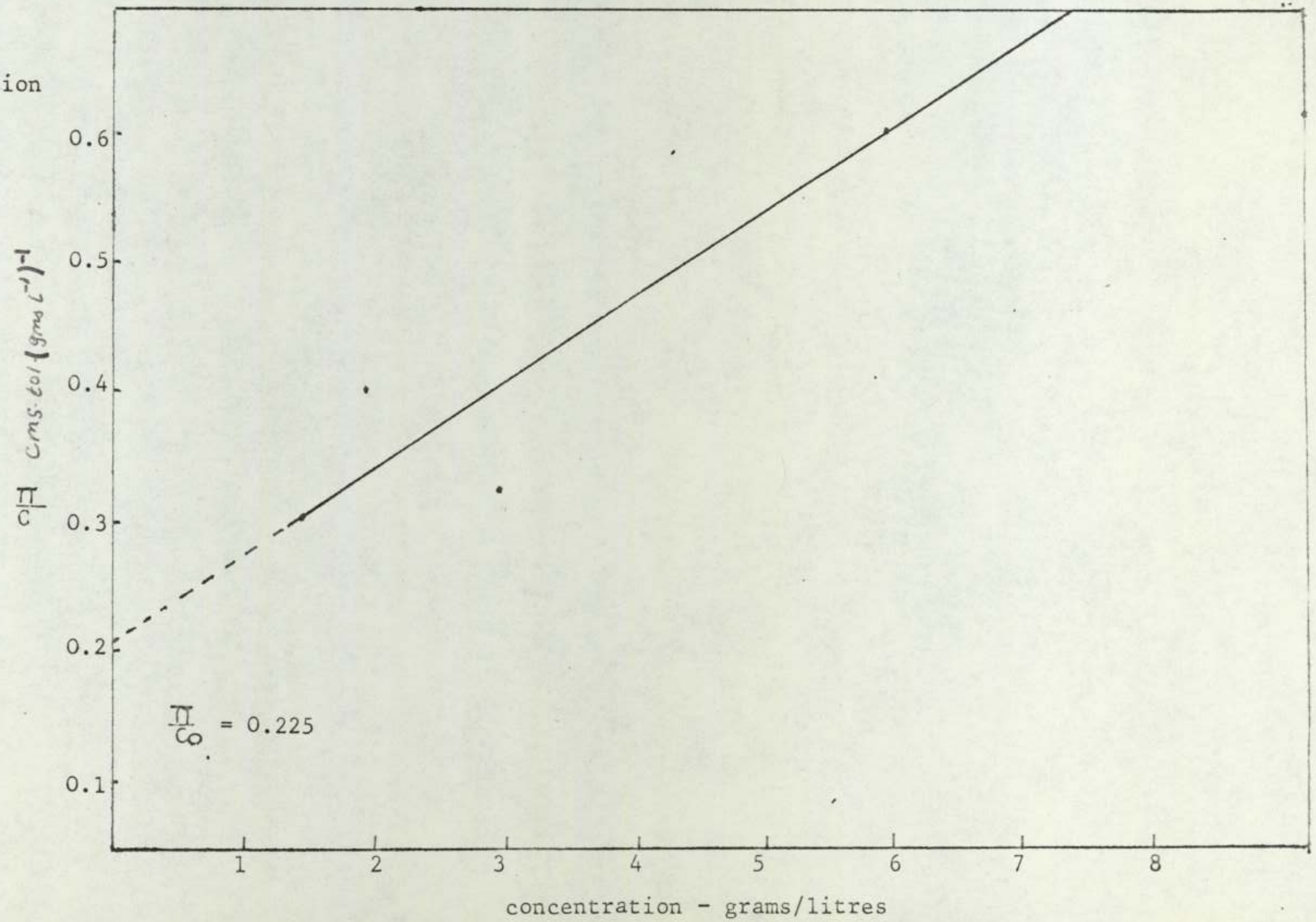
Samples of polypentenamer for molecular weight studies were obtained at various times during two series of polymerisations which were carried out at 25°C using a cyclopentene/toluene concentration of 50/50V/V and a catalyst concentration such that the W:Al:Cp was 1:2:1000. The first series of polymerisations included the addition of 0.02 gram of cis-2-pentene per gram of cyclopentene. The percentage yields in both these series of polymerisations are given in tables 3-1, and 2.

Specimen calculation of the number average molecular weight of a polymer sample

Four solutions, of concentrations 0.1 - 1% (wt%) of the polymer sample produced in the polymerisation (table 3-1) after a polymerisation time of ten minutes were prepared in toluene. The osmotic pressure (Π) of these solutions were determined using the High Speed Membrane Osmometer. A

Figure 2-13

Dependence of π/C on concentration for polypentenamer samples



plot was constructed of π/C vs. concentration – grams/litre and by extrapolation to zero the value of π/C_o was obtained – fig.2-13.

The value of $(\frac{\pi}{C_o})$ was found to be 0.225 in this instance. The value of $\overline{M}_n$ was determined by substitution of this value of $(\frac{\pi}{C_o})$ into eqn. 2-10

$$\frac{\pi}{C_o} = \frac{RT}{\overline{M}_n} \qquad \text{-- \quad --} \qquad 2\text{-}10$$

where: π = the osmotic pressure
C = the concn. grams/litre
R = the gas constant – lt.at.deg^{-1} mole^{-1} = 8.205×10^{-2}
T = the absolute tmeperature – 25^{o}C i.e. 298^{o}K
$\overline{M}_n$ = the number average molecular weight.

The value of R must be converted to pressure units of cms. of toluene which is accomplished by multiplying by a factor – 1026/0.862.

where: atmospheric pressure = 1026 cms H_2O
density of toluene = 0.862 gm/cm3

to give a value of $R = 8.205 \times \frac{1026}{0.862} = 97.8$ lt.cm. tol^{-1} deg^{-1} mole^{-1}.

Therefore where: $\pi/C_o = 0.225$
then by substitution in 2-10: $\overline{M}_n = 1.31 \times 10^{5}$

This procedure was repeated for all the polymer samples thereby obtaining their $\overline{M}_n$ values.

II <u>Determination of the molecular weight distributions of polypentenamer samples by gel permeation chromatography.</u>

The separation of the polymer molecules by gel permeation chromatography took place in a column filled with a porous crosslinked polystyrene gel which was constructed so that it contained a distribution of pore sizes which were as close as possible to the molecular size distribution of the polymer molecules encountered. It is possible to assign to each pore size a size of solute so that polymer molecules with a size greater than this are excluded from the solvent within that pore whereas polymer

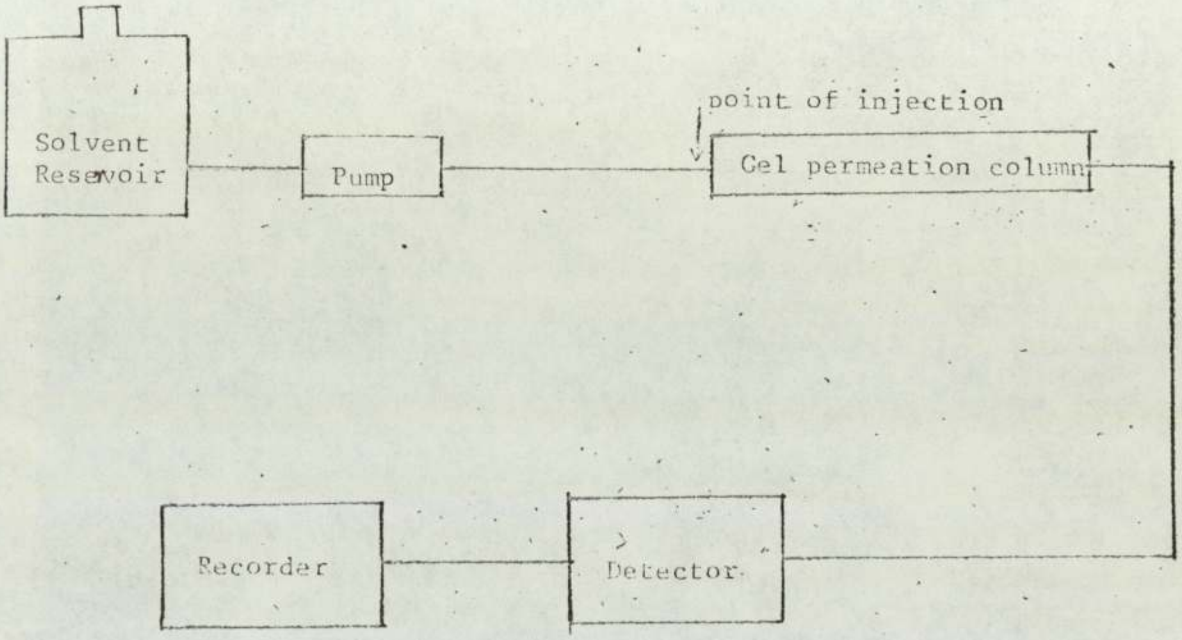

Solvent Reservoir
Pump
point of injection
Gel permeation column
Detector
Recorder

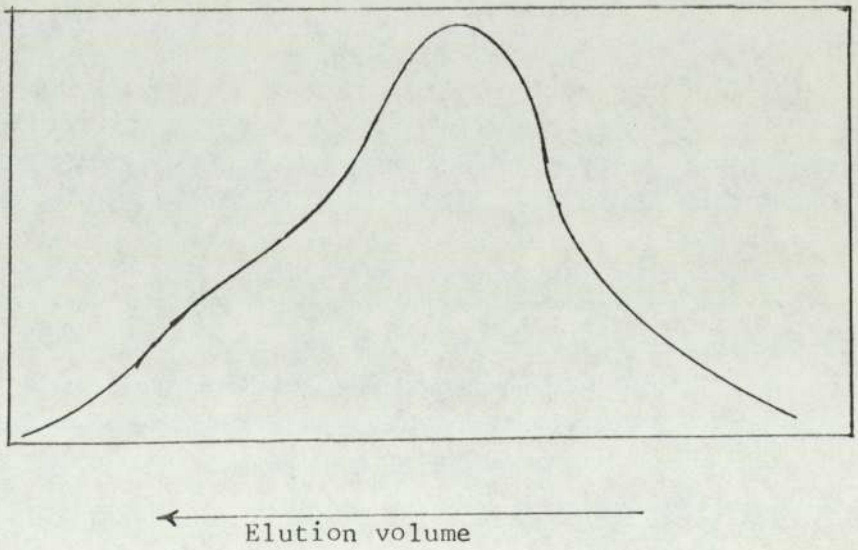
Figure 2-14

molecules with that size and less can permeate the pore.

A sample of polymer was injected onto the top of the column (fig.2-14) through which solvent was pumped at a controlled rate which was of such a value that the pressure across the column did not exceed 30 p.s.i.g. The solvent eluted the polymer molecules from the column so that the polymer was separated according to the size of the molecules with the larger molecules being eluted first.[65] The eluted solution passed from the column to a differential refractometer detector system and the change in refractive index was recorded as a function of elution volume. A typical elution curve obtained is shown - fig. 2-15.

figure 2-15

Elution curve obtained from gel permeation chromatographic analysis of a polypentenamer sample



At any particular elution volume molecules of a precise molecular weight can be expected to be eluted from the column thereby providing information regarding the distribution of molecular weights in a polymer sample.

Gel permeation chromatography theory[63]

The theory underlying the principle of gel permeation chromatography is still in a preliminary stage of development. The elution volume, Ev, for a particular molecular size is composed of two parts as shown by 2-11

$$E_v = E_i + K_d E_p \qquad --- \qquad 2\text{-}11$$

where: E_i = The volume of solvent contained outside the pores in the column gel packing.

E_p = The volume of solvent contained in the pores of the gel.

K_d = The distribution coefficient.

For a polymer of molecular weight M_i the column volume allowed depends on its size. K_d increases as the molecular weight decreases; where K_d is the volumetric distribution coefficient between the total internal volume, E_p, and that part of it which is accessible to a given solute - ($E_{i\,acc}$).

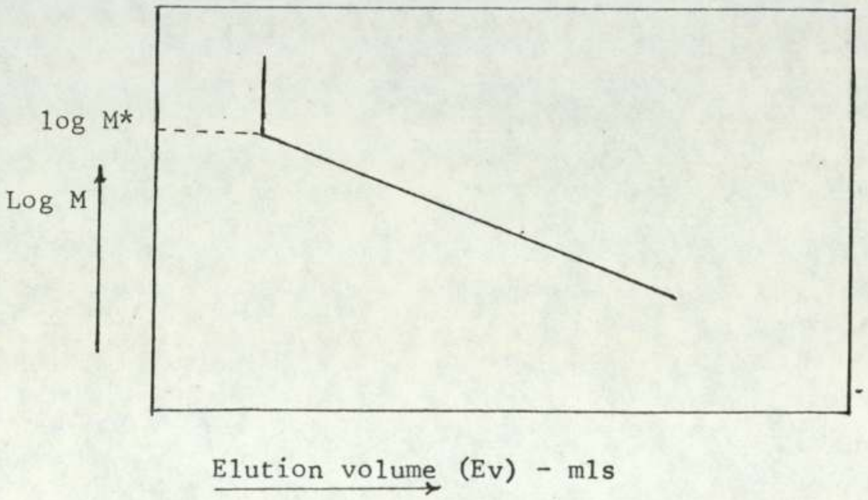
$$\text{Hence:} \quad K_d = \frac{E_{i\,acc}}{E_p} \qquad -- \quad -- \quad 2.12.$$

If K_d is small the total elution volume is small hence large molecules are eluted first.

If a plot is constructed (fig. 2-16) of elution volume against log.M.

Figure 2-16

Molecular size limitation of a gel permeation chromatographic column as determined from a plot of Ev vs. Log Molecular weight

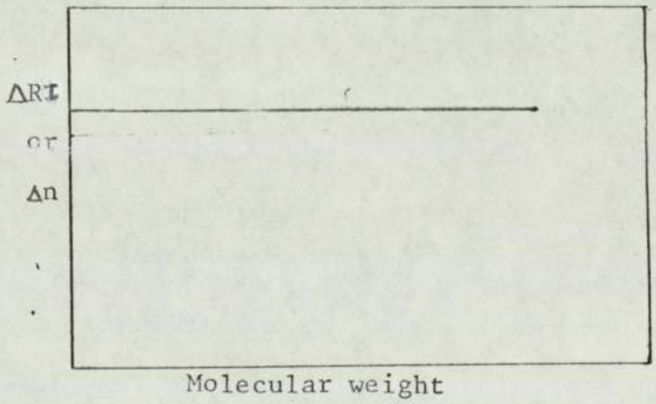


For molecules of size larger than M* and where K is constant and equal to zero then: $E = E$ which results in elution of this size of molecule and larger immediately after injection. There is therefore a relationship between elution volume and molecular weight.

The detection device used in gel permeation chromatography is a differential refractometer and hence to provide a meaningful chromatograph the refractive index must only depend on molecular concentration and not on the size of the molecules so that for a constant concentration of polymer the plot - fig. 2-17 - can be obtained.

Figure 2-17

Plot of refractive index of a polymer solution with varied molecular weight

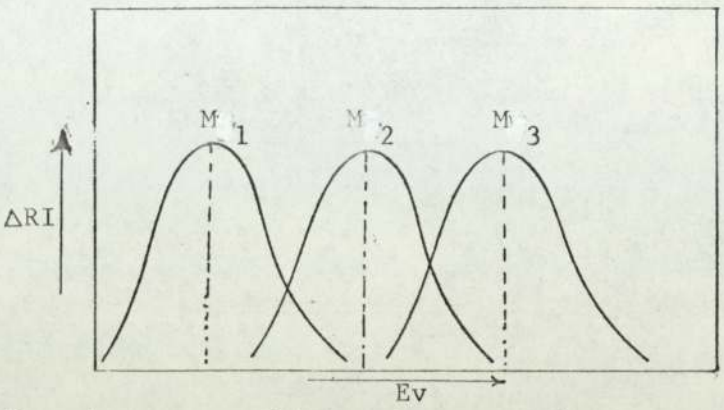


This means that the refractive index of a solution of polymer with a molecular weight of 100,000 at a concentration of C grams/litre must be equal to that of a solution of a polymer with a molecular weight of 200,000 at the same concentration.

Calibration of a chromatographic column for a particular polymer is carried out by injecting mono-dispersed samples of the polymer with a range of molecular weights to give the corresponding elution curves. A typical series of these elution curves is shown - fig. 2-18.

Figure 2-18

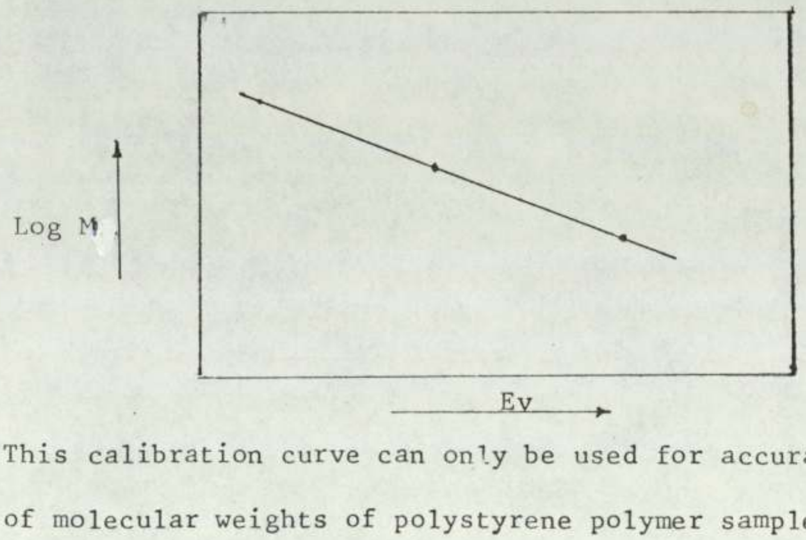
Elution curves of a series of mono dispersed samples of polystyrene



A calibration curve of log molecular weight vs elution volume can then be constructed - fig. 2-19.

Figure 2-19

Calibration curve of a gel permeation chromatographic column for polystyrene



This calibration curve can only be used for accurate determinations of molecular weights of polystyrene polymer samples. It can, however, be used to give an approximate value of the molecular weights of polypentenamer samples since coil extension is quite similar in many polymers: this being the limitation since the exclusion of randomly coiled molecules, in dilute solutions, from the gel is a function of their hydrodynamic volumes which varies with polymer type and also with the solvent used. (see section 3-3B)

The elution curve itself provides useful information since the general molecular size distribution in a polymer sample can be obtained by inspection of its shape when the components of the sample have been separated sufficiently.

Experimental technique   Solutions of 0.25% (wt%) of the polypentenamer sample were prepared in chloroform. 2 mls of each of these solutions was injected in turn onto the high pressure liquid chromatographic columns by means of the valve and loop injection system. Separation of the polymer molecules occurred along 4 x 3 ft, 10^4 Å styragel columns with chloroform as solvent and a differential refractometer detection system.

Calibration of the columns was carried out for polystyrene by injecting 0.25% (wt%) chloroform solutions of polystyrene standards onto the columns to obtain their elution curves.

CHAPTER 3

Studies on the polymerisation of cyclopentene initiated by a tungsten hexachloride/aluminium tri-isobutyl catalyst system

3-1 Molecular weight studies on polymer produced when cyclopentene is polymerised by W/Al based catalysts

Introduction - A great deal of information concerning the mechanism of a polymerisation process may be obtained from a study of the degree of polymerisation, in a given system, as a function of conversion of monomer to polymer and the nature of the molecular weight distribution of the polymer produced.

The types of molecular weight dependencies that are found in some typical polymerisation systems are summarised below.

(i) Anionic addition polymerisation of styrene:

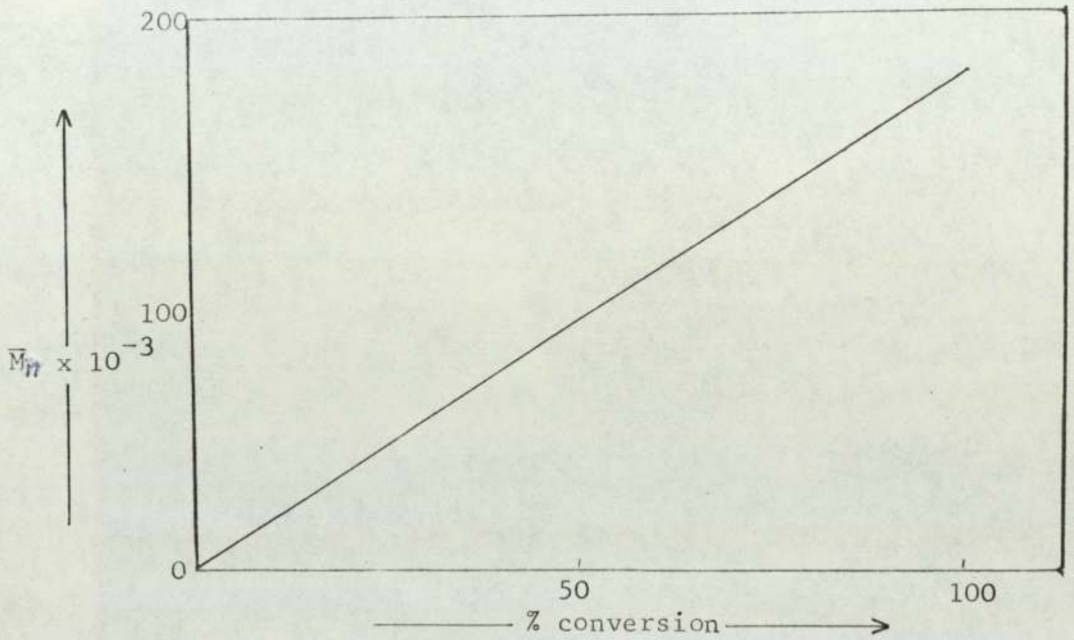
The anionic addition polymerisation of styrene initiated by sodium napthalide in tetrahydrofuran has been characterised as a living polymerisation. The polymer formed has a narrow molecular weight distribution $\left(\frac{\bar{M}_w}{\bar{M}_n} \leq 1.1\right)$ since the rate of initiation in this polymerisation system is very fast compared to the rate of propagation. Accordingly the active sites for the polymerisation are formed instantaneously on the addition of the initiator to the monomer so that throughout the polymerisation the propagating polymer chains have identical chances to add monomer in all the propagation steps. Since no termination or transfer reactions are present in this polymerisation the degree of polymerisation increases with the extent of reaction and the molecular weight distribution is of the Poisson type. An increase in the number average degree of polymerisation with time is found since - 3-(1):

$$\overline{DP}_n = 2\left[\frac{[M]_o - [M]_t}{[I]}\right] \quad \text{--} \quad \text{--} \quad 3\text{-}1$$

where $[M]_o$ and $[M]_t$ represent the initial concentration of monomer and its concentration at any time (t) respectively. The dependence of number average molecular weight on polymerisation extent for a living polymerisation system is shown - figure 3-(1).

Figure 3-1

Dependence of polymer number average molecular weight on the % conversion of monomer to polymer[69]



(ii) Free radical addition polymerisation:

The free radical polymerisation of a vinyl monomer is characterised by the following general kinetic scheme - 3-2.

$$\left.\begin{array}{lll} \text{Initiator} & \xrightarrow{k_d} & 2\,R^{\bullet}_{o} \\ R^{\bullet}_{o} + M & \xrightarrow{k_i} & M^{\bullet}_{n} \end{array}\right) \text{Initiation}$$

$$M^{\bullet}_{n} + M \xrightarrow{k_p} M^{\bullet}_{n+1} \qquad \text{Propagation} \qquad 3\text{-}2$$

$$M^{\bullet}_{n} + M^{\bullet}_{m} \xrightarrow{k_t} \text{Polymer} \qquad \text{termination}$$

\+ Transfer reactions.

The degree of polymerisation in a free radical process is kinetically controlled by the termination steps. The kinetic chain length is given by 3-3:

$$\nu = \frac{k_p^{\,2}\ [M]^2}{2k_t\ R_p} = \left[\frac{[k_p]^2}{2f\ k_d\ k_t}\right]^2 \times \frac{[M]}{[I]^{\frac{1}{2}}} \qquad \text{---}\quad 3\text{-}3$$

which in the absence of transfer reactions is related to the number average molecular weight ($\overline{M}_n$). The lifetime of a propagating radical (except in an emulsion polymerisation) is relatively short - $\sim 10^{-3}$ seconds- and within this time a particular radical has undergone a sufficient number of propagation steps for polymer of high molecular weight to be produced. Accordingly for a free radically initiated polymerisation of a vinyl monomer a plot of $\overline{DP}_n$ as a function of time or conversion should show an increase that is due only to a fall in the rate of polymerisation with conversion. The molecular weight distribution is again of a monomodal type so that $\frac{\overline{M}_w}{\overline{M}_n} \simeq 1.5$ or $\frac{\overline{M}_w}{\overline{M}_n} \simeq 2.0$ when transfer reactions are present.

(iii) Linear condensation polymerisations

In a linear condensation polymerisation system such as the strong acid catalysed condensation of a ω-hydroxy carboxylic acid the molecular weight dependencies are different from those found in a free radical or an anionic addition polymerisation.[61] The synthesis of polymer in a condensation polymerisation system is achieved by means of a series of independent condensation reactions. In the early stages of the reaction monomer is consumed to form polymer of low number average molecular weight and as the reaction proceeds the low polymers first formed condense further with the result that the number average molecular weight increases. Thus the monomer disappears almost completely during the initial stages of the polymerisation.

At any time 't' when the fractional conversion of acid to ester groups is P, then; 3-3.

$$\frac{1}{1-P} + \text{const.} = kC_0t \qquad \text{--} \qquad \text{--} \qquad 3\text{-}3$$

where is the rate constant for the condensation reaction. At this fractional conversion, P, the number average degree of polymerisation, $\overline{DP}_n$, is given by - 3-4

$$\overline{DP}_n = \frac{1}{1-P} \qquad \text{--} \qquad \text{--} \qquad \text{--} \qquad 3\text{-}4$$

and the weight average degree of polymerisation $\overline{DP}_w$ by 3-5.

$$\overline{DP}_w = \frac{1+P}{1-P} \quad \text{---} \quad \text{---} \quad 3\text{-}5$$

The polycondensation of an ω-hydroxy acid is accordingly characterised by:

(1) An increase in number average degree of polymerisation with conversion; and

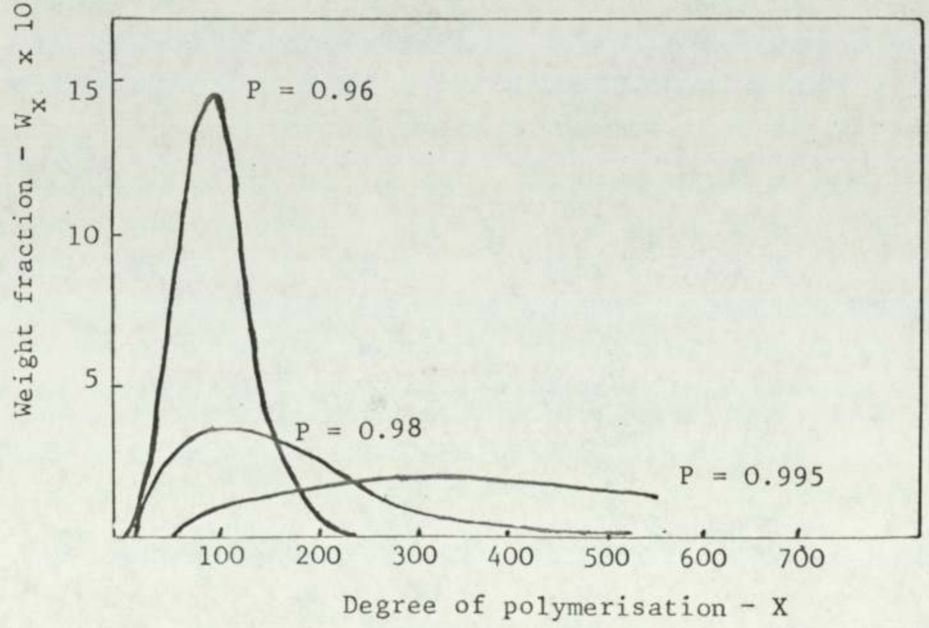
(2) An increase in the breadth of the molecular weight distribution with conversion of monomer to polymer as measured by 3-6.

$$\frac{\overline{DP}_w}{\overline{DP}_n} = \frac{1+P}{1} \quad \text{--} \quad \text{--} \quad 3\text{-}6$$

This information is shown graphically in figure 3-2 where it can be seen that the molecular weight distribution is of a monomodal type at all stages during the polymerisation.

Figure 3-2

Weight fraction distribution curves for linear condensation polymerisation at different values of fractional conversion (P)



3 - 2 Exploratory work on the polymerisation of cyclopentene:

The polymerisation of cyclopentene was carried out by the method described in section 2-5A.

Cyclopentene and toluene (together with cis-2-pentene when used) were distilled into the reaction flask which was allowed to reach thermal equilibrium in a thermostat bath and the required volumes of tungsten hexachloride and aluminium tri-isobutyl solutions were then added in turn. After predetermined times samples of polymerisate were removed from the vessel and the polymer precipitated and purified or alternatively the polymerisation was terminated by the addition of wet chloroform followed by precipitation of the polymer in methanol.

The results of these polymerisation reactions are summarised in figures 3- (3-7).

Infra-red spectra of the polypentenamers produced in these polymerisations were obtained for each set of reaction conditions and conversion times. It was found that the spectra produced did not vary appreciably; a typical example is shown - figure 3-8. Trans double bonds, absorbing at 10.35μ are seen to predominate in the polymer whereas the cis form, absorbing at 13.8μ is present to a small extent.

These results indicated that the most satisfactory system for the study of the molecular weight characteristics of the polymer produced in the cyclopentene polymerisations initiated by the tungsten hexachloride/ aluminium tri-isobutyl system was that wherein:

Molar ratios - Cyclopentene: tungsten: aluminium - 1000:1:2
Temperature - 25°C
[Cyclopentene] - 5.65 mole l^{-1}
Solvent - Toluene

Under these conditions the rate of polymerisation and the equilibrium conversion of monomer to polymer were such that a wide range of samples could be obtained for the study of the molecular weight changes during the polymerisation.

FIGURE 3-3

Dependence of conversion of cyclopentene to polypentenamer upon temperature for a cyclopentene/toluene ratio of 50/50 v/v

$[WCl_6]$ = 11.15 m.moles l^{-1}

$[AliBu_3]$ = 22.36 m.moles l^{-1}

$[CP]$ = 5.65 moles l^{-1}

Solvent = toluene

Molar ratio W:Al:Cp - 1:2:500

Temperature

X = 25°C

O = 30°C

□ = 35°C

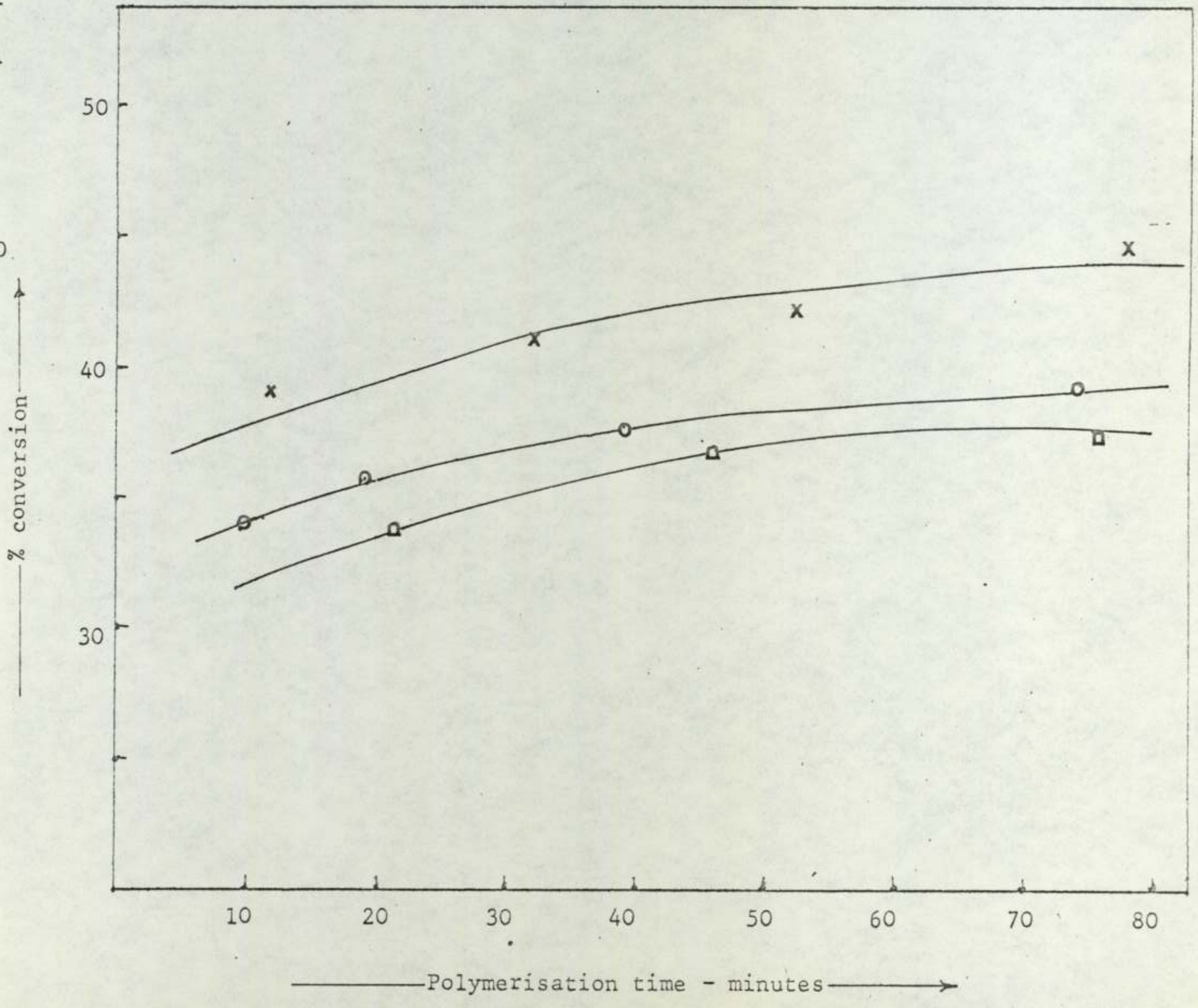


FIGURE 3-4

Dependence of conversion of cylopentene to polypentenamer upon temperature for a cyclopentene/toluene ratio of 50/50 v/v

$[WCl_6]$ = 5.60 m.moles l^{-1}

$[AliBu_3]$ = 11.20 m.moles l^{-1}

$[CP]$ = 5.60 moles l^{-1}

Solvent = toluene

Molar ratio W:Al:Cp - 1:2:1000

Temperature

X = 25°C

O = 30°C

□ = 35°C

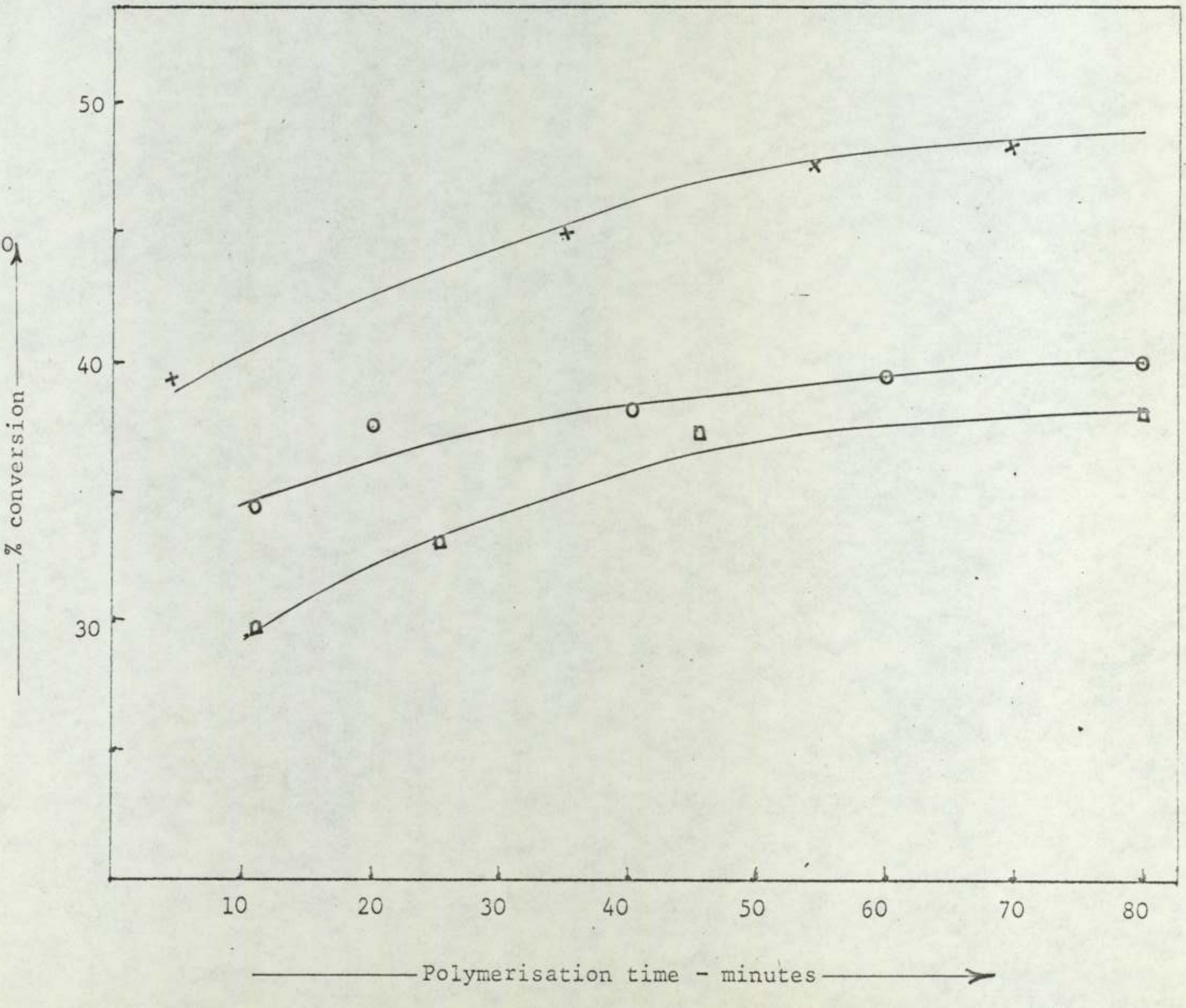


FIGURE 3-5

Dependence of conversion of cyclopentene to polypentenamer upon temperature for a cyclopentene/toluene ratio of 50% v/v

$[WCl_6]$ = 2.80 m.moles l^{-1}

$[AliBu_3]$ = 5.6 m.moles l^{-1}

$[CP]$ = 5.6 moles l^{-1}

Solvent = toluene

Molar ratio W:Al:Cp - 1:2:2000

Temperature

X = 25°C

O = 30°C

◻ = 35°C

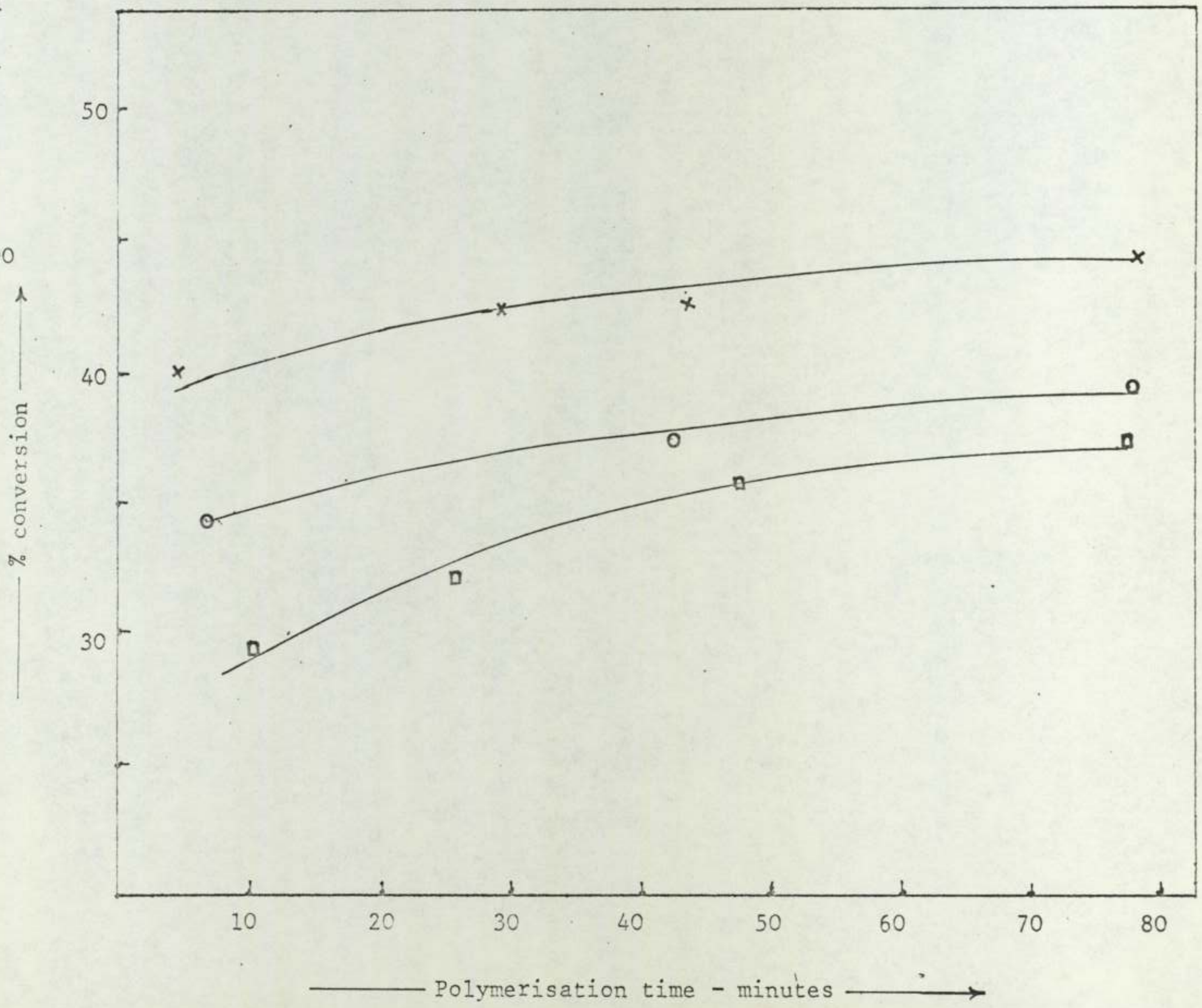


FIGURE 3-6

Dependence of conversion of cyclopentene to polypentenamer on the initial cyclopentene/toluene volumetric ratios (V/V)

$[WCl_6]$ = 5.6 m.moles l^{-1}

$[AliBu_3]$ = 11.2 m.moles l^{-1}

$[CP]$ ≃ 5.60 moles l^{-1}

Solvent = toluene

Molar ratio W:Al:Cp - 1:2:1000

Temperature

X = 25°C

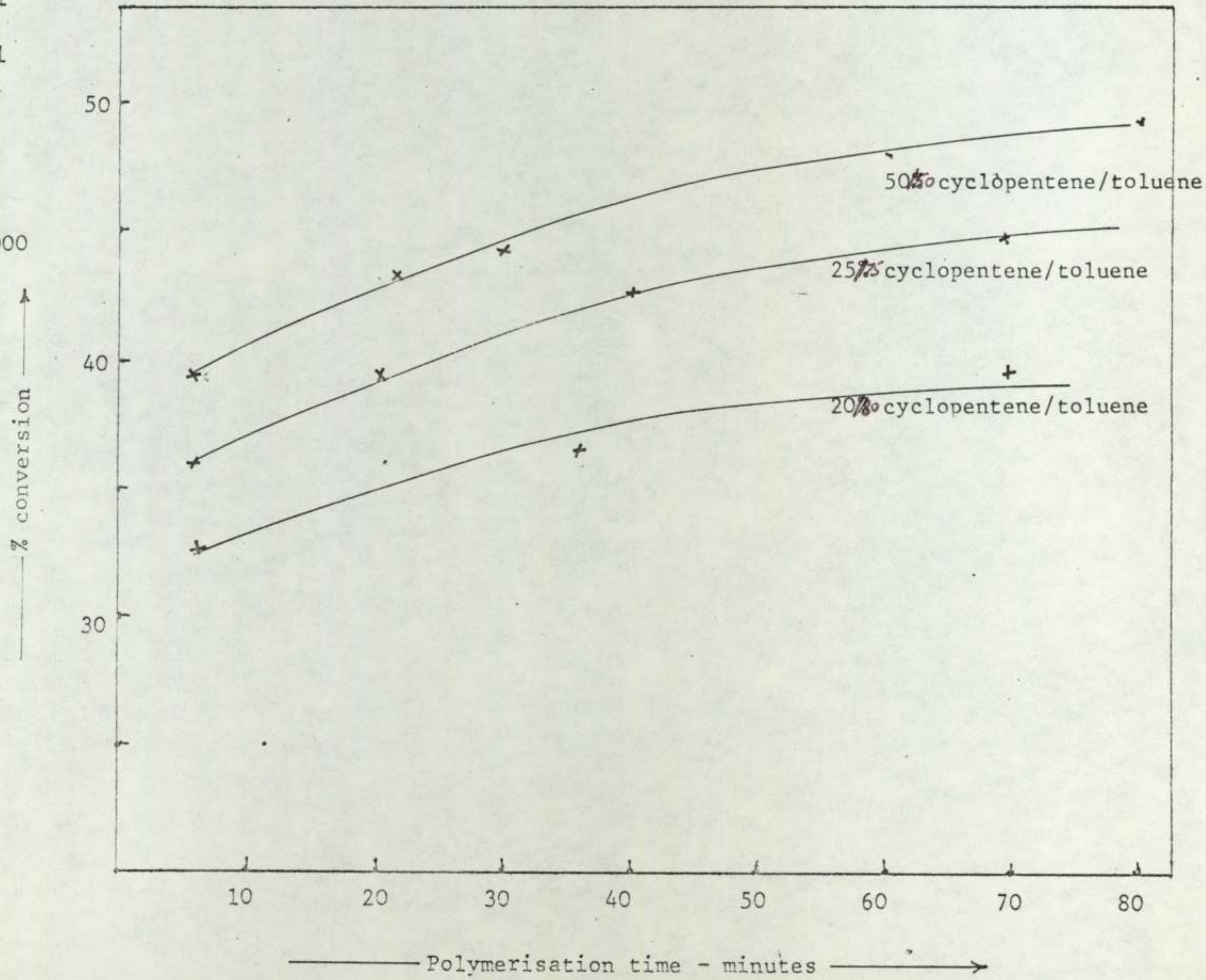


FIGURE 3-7

Dependence of conversion of cyclopentene to polypentenamer on temperature in the presence of cis-2-pentene

$[WCl_6]$ = 5.60 m.moles l^{-1}

$[AliBu_3]$ = 11.2 m.moles l^{-1}

$[CP]$ = 5.6 moles l^{-1}

cis-2-pentene 5.6 m.moles l^{-1}

Solvent = toluene

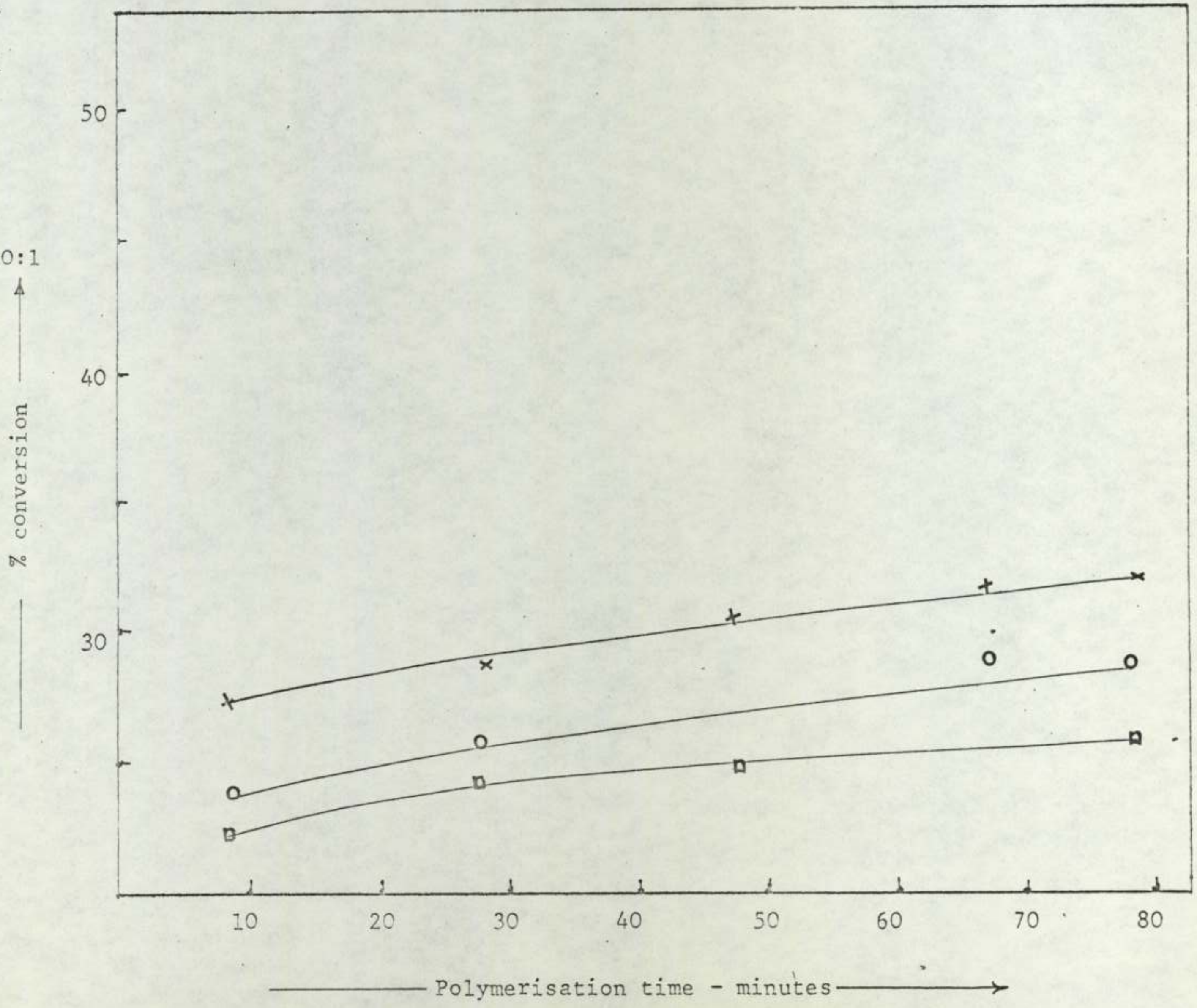
Molar ratio W:Al:Cp - 1:2:1000:1 :cis-2-pentene

Temperature

X = 25°C

O = 30°C

□ = 35°C



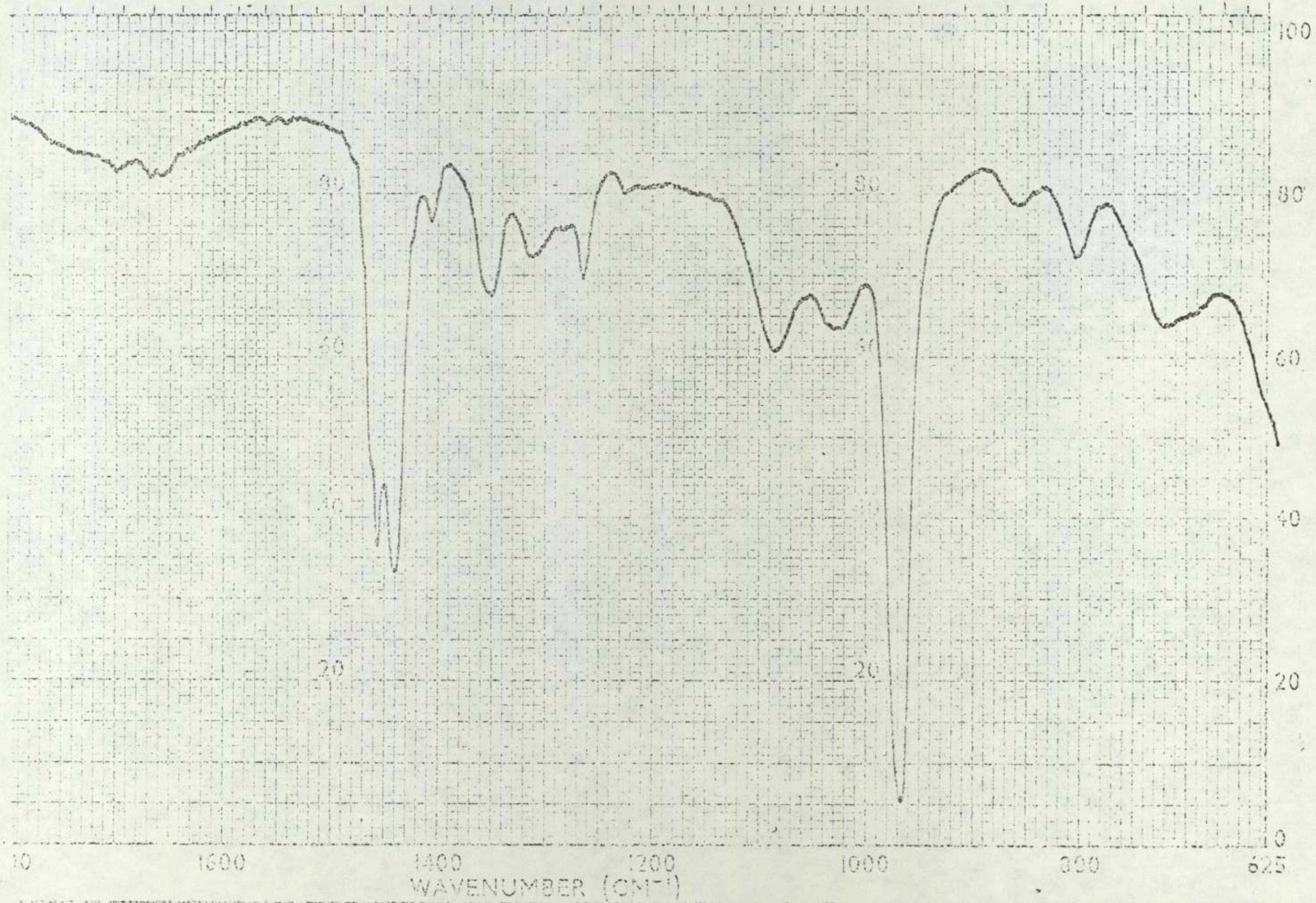


FIGURE 3-8

Infra Red spectrum of polymer produced in the polymerisation of cyclopentene initiated by W/Al catalyst

3 - 3 Molecular weight changes during the polymerisation of cyclopentene

(A) Number average molecular weight changes:

Samples of polypentenamer were obtained during the course of the polymerisation of cyclopentene initiated by the tungsten hexachloride/ aluminium tri–isobutyl catalyst system with the reaction conditions selected above (3-2). Thus, cyclopentene was polymerised at 25°C as a 50/50V/V solution in toluene using a tungsten: aluminium: cyclopentene molar ratio of 1:2:1000. Whenever cis-2-pentene was included a molar ratio of cyclopentene: cis-2-pentene of 1000:1 was employed. The addition of tungsten hexachloride to the solution of cyclopentene preceded the addition of aluminium tri-isobutyl.

After purification of the polypentenamer samples, by successive precipitations in methanol from chloroform solutions, the number average molecular weights of the polymers were determined by osmometry using the Mechrolab High Speed Membrane Osmometer. 1-0.25% (w/%) solutions of the polymer samples were prepared in toluene and the osmotic pressure (π) was determined for each as a function of concentration at a temperature of 25°C. From a plot of π/C VS.C for each sample the value of $(\pi/C)_{c=o}$ was obtained by extrapolation of the curve to zero concentration. By insertion of the value of $(\pi/C)_{c=o}$ into 2-10;

$$\frac{\pi}{(C)}_{c=o} = \frac{RT}{\overline{M}_n} \quad \text{--} \qquad 2\text{-}10$$

the values of $\overline{M}_n$ were obtained for each polymer sample. This procedure is described in 2-6D.

The percentage conversion with time of these two polymerisation series are shown in tables 3-1 and 3-2.

TABLE 3-1

Percentage conversions of cyclopentene to polypentenamer for the conditions given

Polymerisation time/hours	% conversion
0.16	21.6
0.25	21.6
1.00	23.0
3.00	27.0
5.50	27.0
24.00	27.0
72.00	27.0

cyclopentene/toluene -- 50/50 V/V
cyclopentene:W:Al - molar ratios -- 1000:1:2
[cis-2-pentene] -- .02 gram cis-2-pentene/gram of cyclopentene
temperature -- 25°C

TABLE 3-2

Percentage conversion of cyclopentene to polypentenamer for the conditions given

Polymerisation time/minutes	% conversion
5	37
10	41
30	45
40	46
60	48
120	55

cyclopentene/toluene - 50/50 V/V
Cp:W:Al molar ratios - 1000:1:2
temperature - 25°C

Samples of these polymers were prepared in toluene solutions, for use in the High Speed Membrane Osmometer, to determine the values of their number average molecular weights from readings of the osmotic pressure of their solutions, at concentrations of 0.1 to 1% (wt%), using the method described above.

Figure 3-9

Dependence of $\overline{M}_n$ on the extent of conversion of monomer to polymer in a cyclopentene polymerisation

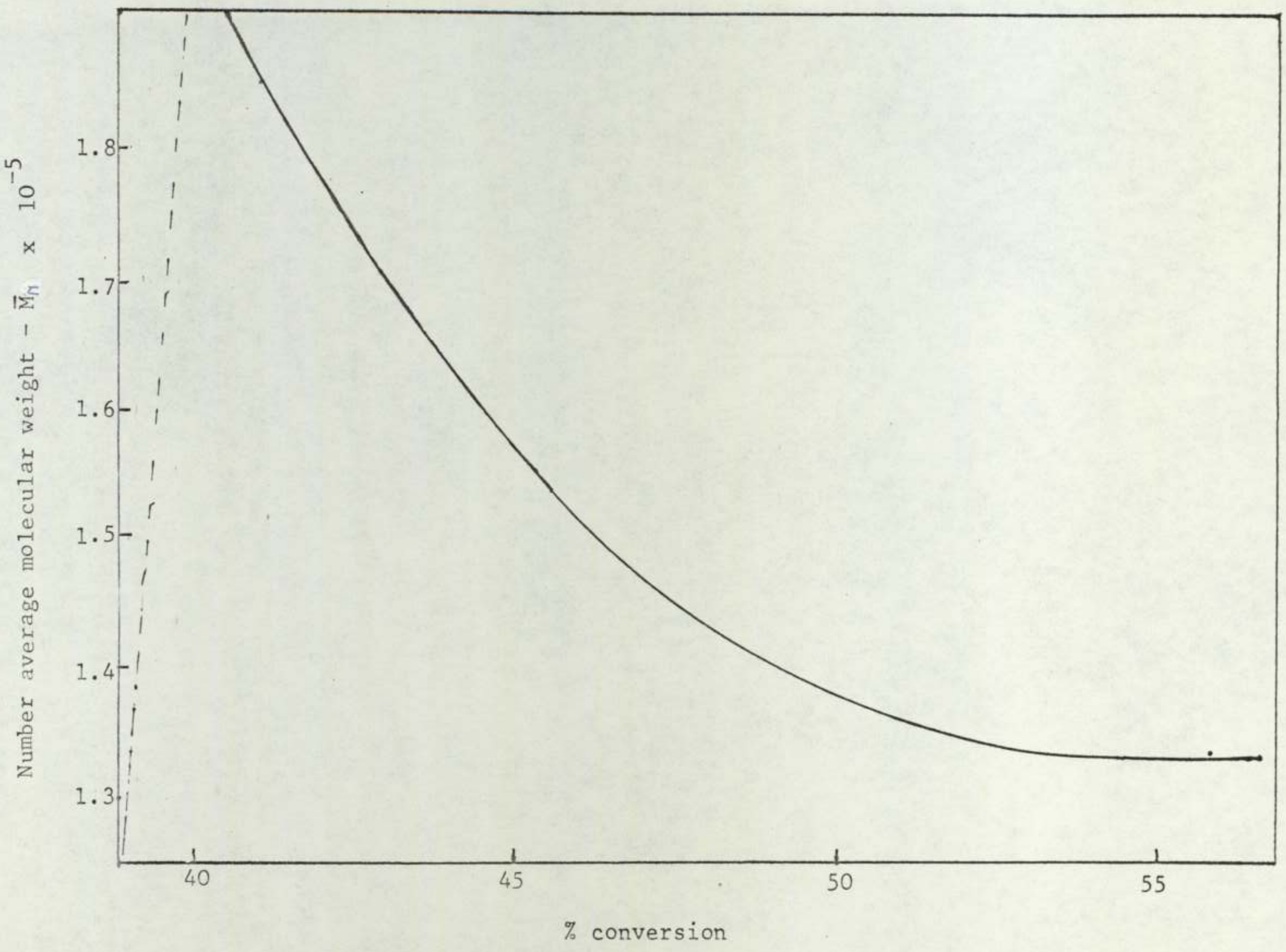


Figure 3-10

Dependence of $\overline{M}_n$ on the extent of conversion of monomer to polymer in a cyclopentene polymerisation in the presence of cis-2-pentene

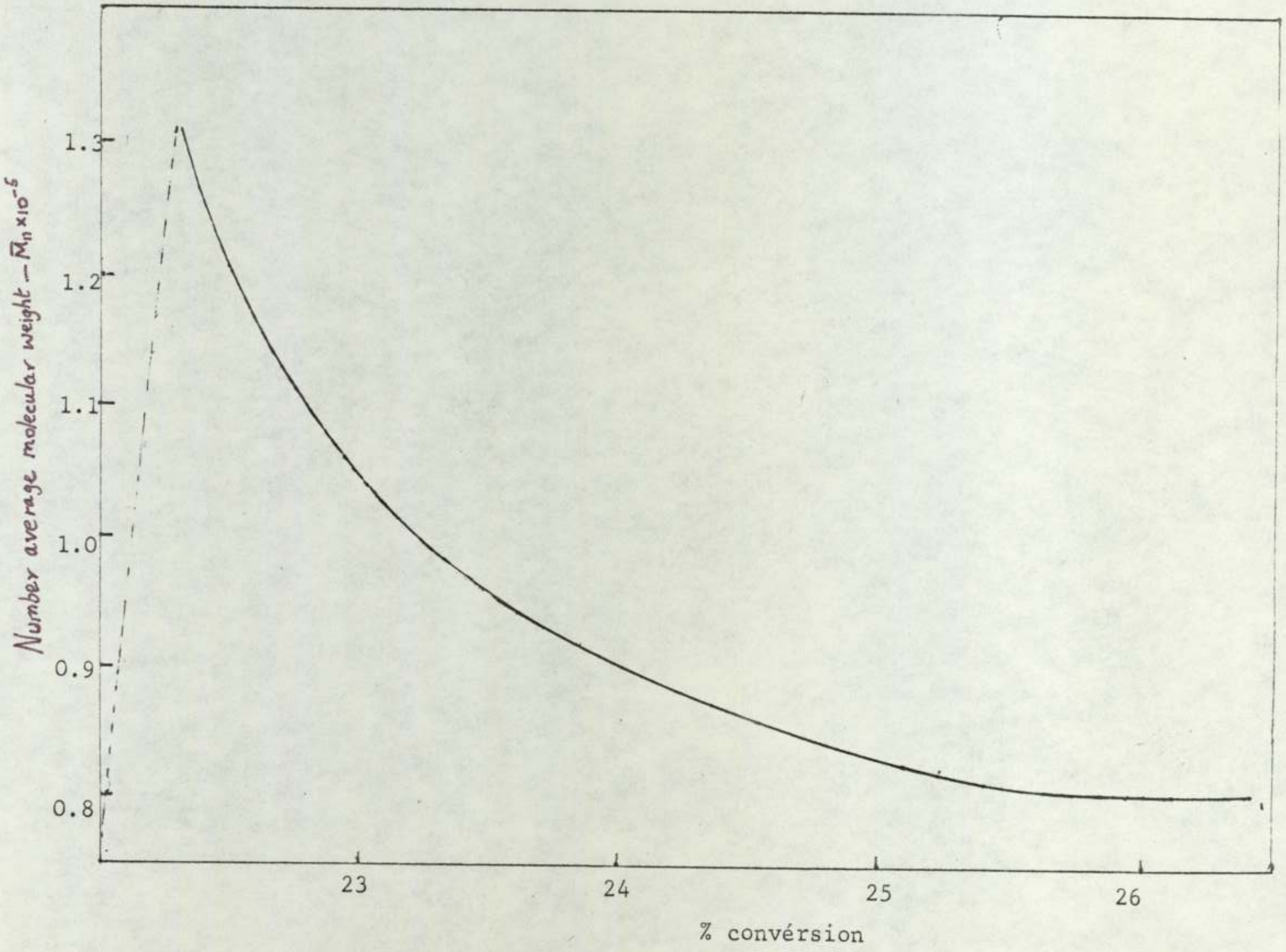
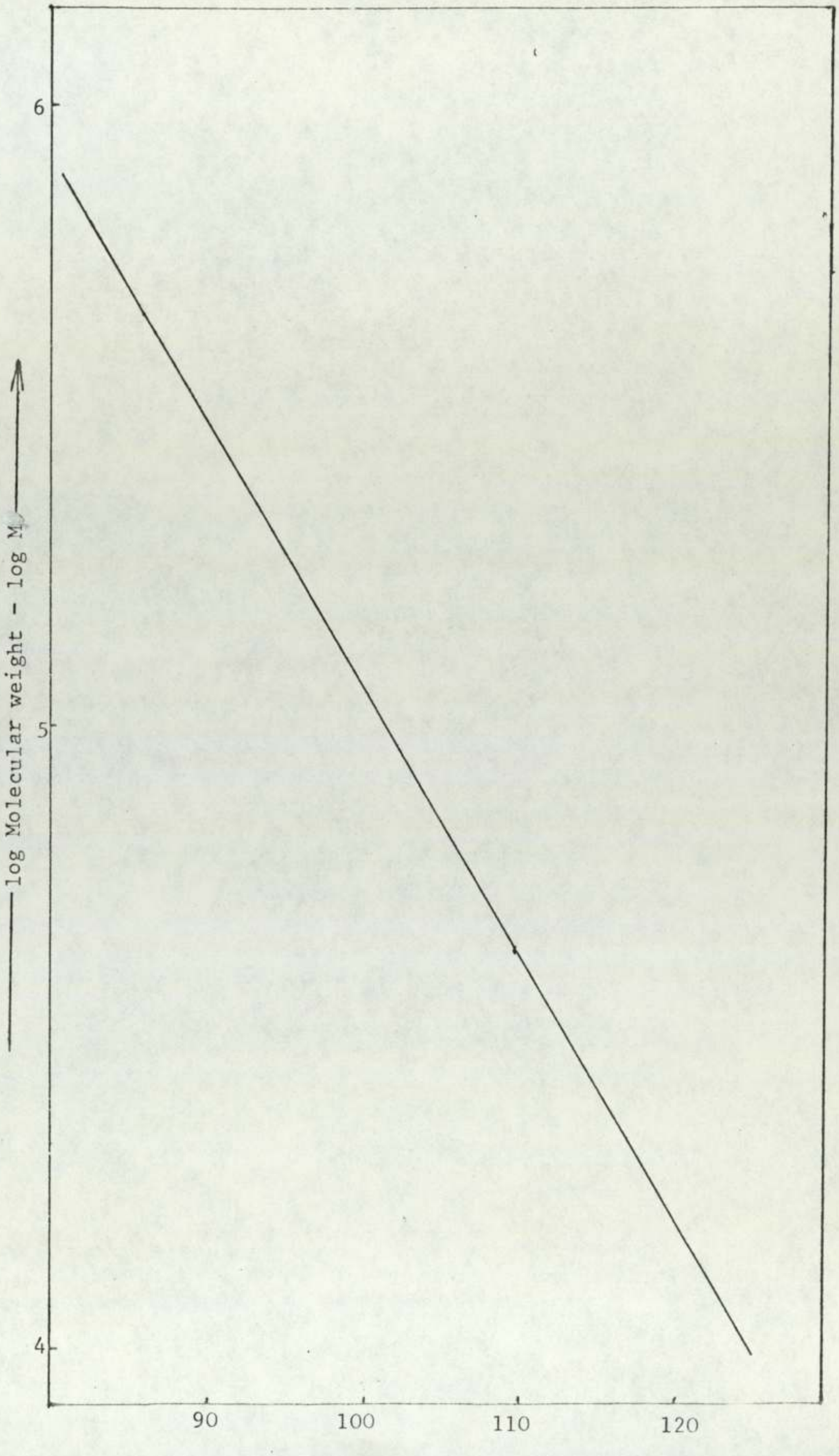


Figure 3-11

Calibration curve for the gel permeation chromatographic columns - dependence of elution volume on the molecular weights of polystyrene standards



Figures 3-9 and 10 show that during the initial stages of the polymerisations a rise in number average molecular weight ($\overline{M}_n$) occurred which was followed by a decrease to a limiting value. When cis-2-pentene was present the maximum value of $\overline{M}_n$ (1.31×10^5) was lower than that observed for the polymerisation of cyclopentene alone (1.95×10^5) which is consistent with the fact that cis-2-pentene acted as a chain transfer agent. It is apparent from a comparison of figures 3-9 and 3-10 that cis-2-pentene did not affect the overall kinetic behaviour of the polymerisation of cyclopentene which at first sight did not appear to fall into any of the three classes described in section 3-1.

(B) Gel Permeation Chromatography studies

A calibration curve for the gel permeation columns used was obtained by injecting 0.25% chloroform solutions of polystyrene standards onto the columns and recording their elution volumes. The dependence of elution volume on peak molecular weight is shown graphically in figure 3-11:

The constants (K and a) of the Mark-Houwink equation that relates the molecular weight (M_v) of a polymer to the intrinsic viscosity (η) of its solution i.e. 3-7

$$[\eta] = KM^a \qquad \text{-- \quad --} \qquad 3\text{-}7$$

may be used as an indication of the thermodynamic interaction between the polymer and solvent. These constants are dependent upon the polymer, solvent and temperature and whereas reliable values of the constants are to be found in the literature for solutions of polystyrene in chloroform, no such values are available for polypentenamer in chloroform solution. Accordingly it was not possible to adopt the Universal Calibration Procedure for the construction of a calibration curve for polypentenamer (M_1) from the calibration curve for polystyrene (M_2) for the set of gel permeation columns used; where - 3-8:

$$\log M_1 = \frac{1}{1+a_1} \log \frac{K_2}{K_1} + \frac{(1 + a_2)}{(1 + a_1)} \log M_2 \qquad - 3\text{-}8$$

Well characterised narrow molecular weight distribution fractions of polypentenamer were likewise unavailable and hence the number average and weight average molecular weights could not be obtained from the gel permeation chromatographs of the polypentenamers and compared with the data obtained from osmometry.

Figures 3-12 and 3-13 show typical chromatographs of the polymers obtained from samples taken, after various reaction times, from the polymerisation of cyclopentene using $WCl_6/Al(iBu)_3$ as a catalyst. The chromatographs were obtained by injecting 2 ml. of polymer solution onto a set of columns as described previously.

Figure 3- 12

Elution curves of polymer samples obtained in cyclopentene polymerisations after conversion times of 5,30 and 60 minutes

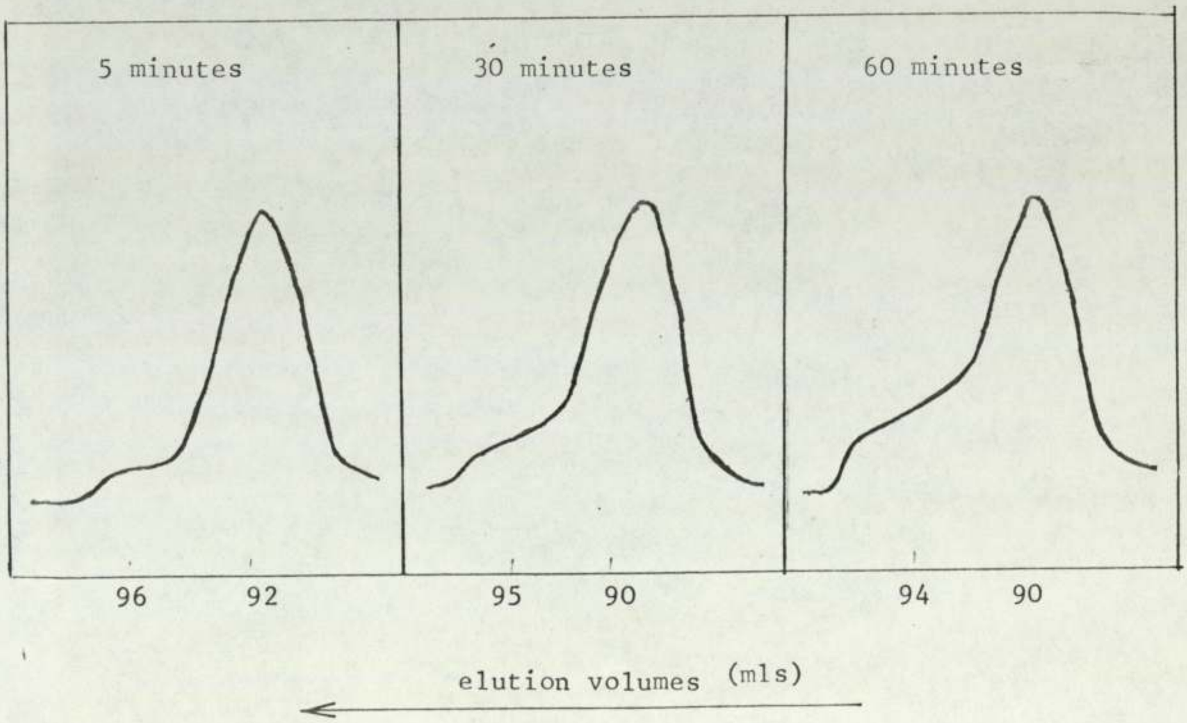
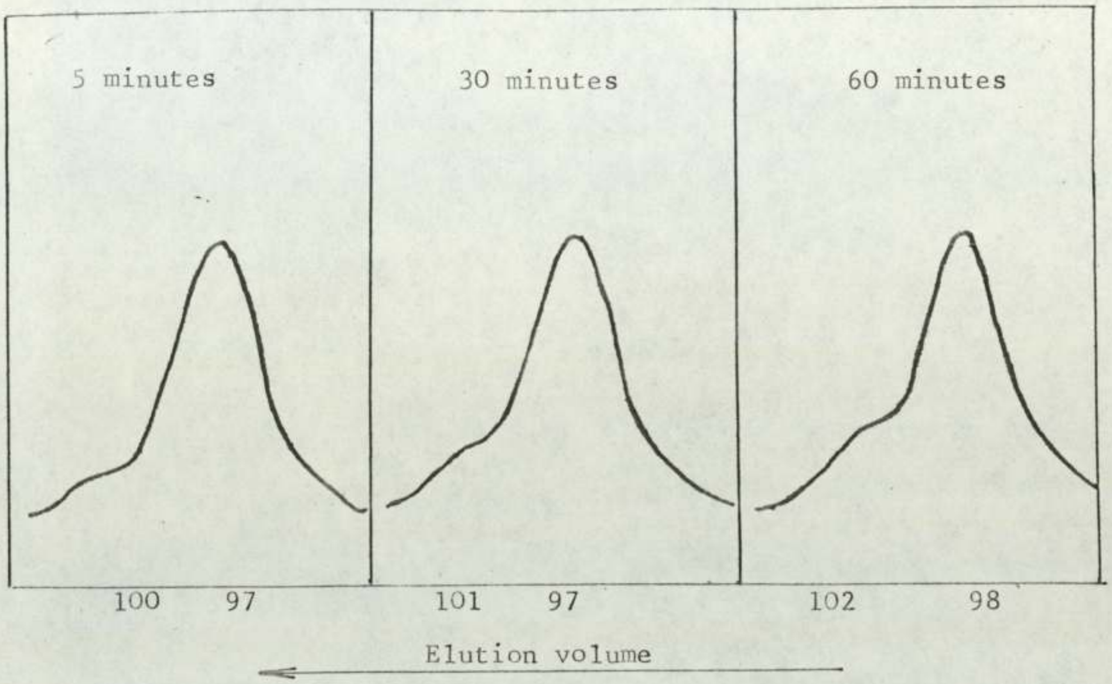


Figure 3-13

Elution curves of polymer samples obtained in cyclopentene polymerisations, in the presence of cis-2-pentene, after conversion times of 5,30 and 60 minutes



Inspection of the chromatographs shown that they were all bimodal in nature for a series of polymerisations carried out in the absence (figure 3-12) or the presence of cis-2-pentene (figure 3-13). Although the molecular weight averages ($\bar{M}_w$ and $\bar{M}_n$) could not be calculated for the series of samples, certain features of these curves are worthy of note. Tables 3-3 and 3-4 show the dependence of the peak elution volumes of the high (EV_1) and low (EV_2) molecular weight materials produced during the polymerisations

Table 3-3

Dependence of elution volume of polymer samples on conversion to polymer in cyclopentene polymerisation

Polymerisation time minutes	% conversion	EV_1	EV_2	$R = \frac{\text{area of } EV_1 \text{ peak}}{\text{area of } EV_2 \text{ peak}}$
5	40	92	96	6/1
10	41	92	96	5/1
30	45	90	95	4.5/1
40	46	90	95	4/1
60	48	90	94	3/1
120	56	89	94	3/1

Molar ratio: Cyclopentene: W:Al - 1000:1:2
Cyclopentene/Toluene - 50/50 V/V
Temperature - 25°C

Table 3-4

Dependence of elution volume of polymer samples on conversion to polymer in cyclopentene polymerisation in the presence of cis-2-pentene

Polymerisation time hours	% conversion	EV_1	EV_2	R= $\frac{\text{area of } EV_1 \text{ peak}}{\text{area of } EV_2 \text{ peak}}$
0.1	21	97	100	6/1
0.5	25	97	101	4.5/1
1.0	26	98	102	4.5/1
3.0	26	98	102	4/1
5.5	25	100	102	4/1
24.0	26	98	99	4/1
72.0	26	98	99	4/1

Molar ratio - cyclopentene: cis-2-pentene: W:Al - 1000:1:2
cyclopentene/toluene - 50/50 V/V
Temperature - 25°C

Attempts were also made to compare the amounts of high and low molecular weight materials by planimetrically determining the areas under the two chromatographic peaks. This information is also shown in tables 3-3 and 3-4 but should be treated with reservation because large errors were involved in the estimation of the shapes of the individual chromatographs.

Table 3-5 shows the results of gel permeation chromatography studies on cylopentene polymerisations at varied initial cyclopentene molar ratios. The gel permeation chromatographs were again bimodal in nature and the elution volumes together with the area of the distribution curves measured by planimetry are shown.

Table 3-5

Dependence of elution volumes of polypentenamer samples on initial cyclopentene/catalyst molar ratios

Cyclopentene Moles l^{-1}	% conversion	EV_1	EV_2	R= $\frac{\text{area of } EV_1 \text{ peak}}{\text{area of } EV_2 \text{ peak}}$
5.6	38	90	95	4/1
5.0	30	91	97	4/1
4.2	30	90	97	4/1
2.8	25	92	97	3.6/1

Polymerisation time - 10 minutes
$[WCl_6]$ - 5.8m mole l^{-1}
$[Al(iBu)_3]$ - 11.6m mole l^{-1}
Solvent - Toluene.

It would appear from the results in tables 3-3 and 3-4 that:

(1) the positions of the peaks in the chromatographs were approximately constant for a given series of samples taken from a polymerisation after various conversion times;

(2) within the limits of their determination the ratio of high to low molecular weight material decreased during the course of the polymerisation; and

(3) cis-2-pentene shifted both peaks to a lower molecular weight range when included as an additive in the system but does not alter observations (1) and (2).

3 - 4 Oxidation state of tungsten during the course of the polymerisation

Whenever tungsten hexachloride was added to cyclopentene in the course of these polymerisations a blue solution was formed which immediately turned to reddish brown. If aluminium tri-isobutyl was added at this stage the colour changed to a deeper brown and the viscosity of the solution increased rapidly indicating that polymerisation had occurred. If aluminium tri-isobutyl was not added and the cyclopentene/tungsten hexachloride system was allowed to stand the solution became clear and a dark oily precipitate was formed on the bottom of the reaction vessel after a time of 0.5 - 1 hour. It was thought that the colour changes and the precipitate formation were due to the formation of complexes between the cyclopentene and the tungsten in which the tungsten atom existed in oxidation states other than tungsten (VI).

To investigate these phenomena a study of the changes in the oxidation state of tungsten in the tungsten hexachloride/cyclopentene system was carried out by application of the titrimetric method described in 2-6B. Although this method of oxidation state determination was capable of producing accurate data it did have several disadvantages: (1) Since a complicated procedure was involved great care had to be exercised at each stage to prevent admission of air or moisture to the reaction vessel since the presence of these would result in irreproducibility of results; and (2)-whereas values of tungsten oxidation states could be obtained for the tungsten hexachloride/cyclopentene system it was not possible to extend the technique to determine these in the cyclopentene/tungsten hexachloride/aluminium tri-isobutyl system since the presence of the polymer formed upon addition of the aluminium tri-isobutyl prevented accurate end point determinations.

Values of the changes in the oxidation state of tungsten were obtained in the tungsten hexachloride/cyclopentene system when;

(1) The tungsten/cyclopentene molar ratio was varied and and reaction time was constant; and

(2) the tungsten/cyclopentene molar ratio was kept constant and the reaction time was varied.

The tungsten oxidation state data obtained for the conditions in (1) and (2) above are shown in tables 3-6 and 3-7 respectively.

Table 3-6

Dependence of tungsten oxidation state on the tungsten/cyclopentene molar ratios in the tungsten hexachloride/cyclopentene system

$[WCl_6]$ / m moles	[cyclopentene] / moles	Molar ratio W/Cp	Mean oxidation state
0.12	0	---	6.0
0.12	0.06	500:1	5.5
0.12	0.12	1000:1	4.9
0.12	0.18	1500:1	4.6
0.12	0.24	2000:1	4.0

Temperature - 25°C
Reaction time - 2 minutes

Table 3-7

Dependence of tungsten oxidation state on the time of reaction in the tungsten hexachloride/cyclopentene system

$[WCl_6]$ m moles	[cyclopentene] moles	Reaction time minutes	Mean oxidation state
0.12	0.12	0.5	5.3
0.12	0.12	2.0	4.8
0.12	0.12	10.0	4.5
0.12	0.12	20.0	4.5
0.12	0.12	30.0	4.5

Temperature - 25°C
Reaction time - varied
Tungsten hexachloride/cyclopentene molar ratio - 1000:1

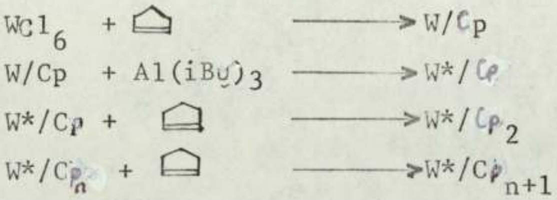
The above data show that the tungsten mean oxidation state, when tungsten hexachloride has reacted with the cyclopentene, does not have an integral value. After a reaction time of ten minutes, when the cyclopentene/tungsten hexachloride molar ratio is 1000:1, the mean tungsten oxidation state had decreased to a limiting value of 4.5 (table 3-7). The value of this lower limit is dependent upon the cyclopentene/tungsten molar ratio since it is observed (table 3-6) that at the higher cyclopentene/tungsten molar ratio of 2000:1 the lower limit of the mean oxidation state is 4.0 which is reached after a reaction time of two minutes.

The dependence of the oxidation state on the cyclopentene/tungsten molar ratio is not clear but it can be deduced that in cyclopentene polymerisations the tungsten atom was present as a mixture of oxidation states. This fact is consistent with the suggestion that the polymerisation of cyclopentene, initiated by the tungsten/aluminium based catalyst and producing a polymer with a bimodal molecular weight distribution, proceeds as two independent polymerisation reactions each initiated by separate, active tungsten species. These species may result from complex formation between the cyclopentene and the tungsten atom in different oxidation states followed by reaction with the aluminium tri-isobutyl (see section 3-5)

3 - 5 Discussion

The polymerisation of cyclopentene may be compared with some conventional polymerisation systems described earlier in this chapter (3-1) and mechanisms can be postulated which differ in their expected dependencies of molecular weight on either reaction time or conversion of monomer to polymer.

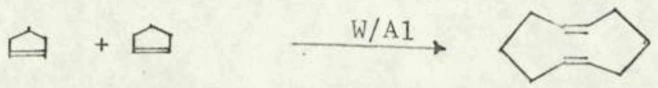
In the absence of cis-2-pentene if the mechanism proposed has the general nature-(3-9):



3-9

when no transfer or termination reactions are invoked then the polymerisation of cyclopentene might be expected to show similarities to the polymerisation of styrene initiated by sodium napthalide in which the number average molecular weight increases linearly with conversion. Furthermore the introduction of a transfer agent into the polymerisation might be expected to have a substantial effect upon the polymerisation producing a series of polymers within which the molecular weight distribution broadens with conversion of monomer to polymer. To account for the bimodal molecular weight distribution of the polymers obtained, two active species with different rate constants could be postulated provided that there was no rapid equilibrium between them.

A general mechanism similar in nature to the polycondensation polymerisation may also be postulated (3-10) if:

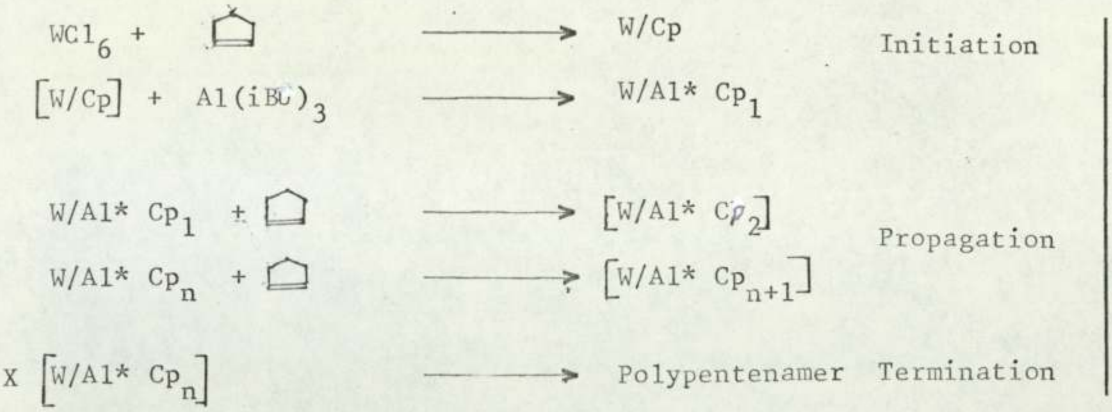


$$\begin{aligned} \text{i.e.}\qquad & Cp + Cp \xrightarrow{W/Al} (Cp)_2 \\ & (Cp) + Cp \xrightarrow{W/Al} (Cp)_3 \\ & (Cp)_2 + (Cp)_2 \xrightarrow{W/Al} (Cp)_4 \\ & (Cp)_m + (Cp)_n \xrightarrow{W/Al} (Cp)_{n+m} \end{aligned} \qquad 3\text{-}10$$

It may be envisaged that the complex formed from the reaction of aluminium tri-isobutyl with tungsten hexachloride acts as a catalyst in all stages of the polymerisation. Such a mechanism would suggest that all double bonds of the polymer would maintain their activity throughout the polymerisation reaction and that there would be a linear increase in the number average molecular weight with conversion of monomer to polymer resulting in the formation of a macrocyclic polymer. If such a mechanism were to apply it would be difficult to propose a means by which a bimodal molecular weight distribution could be obtained.

Both the preceding mechanisms may be discarded in favour of a kinetic chain mechanism because the dependence of number average molecular weight of the polymer on the conversion of monomer to polymer is inconsistent with either the living system or the ring expansion mechanism.

A kinetic chain reaction involving a first progagation step may be invoked to describe the behaviour of the polymerisation of cyclopentene because the positions of the peaks in the molecular weight distribution curves remained constant during the course of a polymerisation, a feature also of the free radical initiated polymerisation of vinyl monomers. Such a scheme is shown below (3-11).



3-II

It is not at present obvious whether the propagating species (W/Al*Cp$_n$) had a short or long lifetime and whether the termination reaction was a first or a second order process.

During the course of the polymerisation the ratio of high molecular weight to low molecular weight material changed significantly. The increased significance of low molecular weight material at high conversions can account for the decrease in number average molecular weight that occurred during the course of the polymerisation. Obviously it would have been advantageous to have been able to compare the values of the number average molecular weight obtained by osmometry with the values obtained by gel permeation chromatography but this was not possible because the columns could not be calibrated for polypentenamer.

The decrease in number average molecular weight has been described also by Chauvin et al[68] for the polymerisation of cyclooctene using metathesis catalysts and it was suggested by these workers that the polymerisation was followed by a degradation process. If such a degradation process was random in nature a skewing of the molecular weight distribution to the lower end should have occurred and a bimodal molecular weight distribution need not have been produced. However it is possible to account for the bimodal molecular weight distribution of polypentenamer by postulating that two independent catalyst species (W_1 and W_2) were present in the system, polymerising the cyclopentene with rates of polymerisation of $R_{\rho 1}$ and $R_{\rho 2}$ respectively. The two catalysts would then polymerise cyclopentene independently of one another to produce a polymer that had a molecular weight distribution that was the sum of two individual distributions. It is proposed that both polymerisation processes should be of a kinetic chain type. If, however, the peaks in the gel permeation chromatographs are to maintain constant elution volumes, the ratio of the rates of polymerisation should change during the course of polymerisation; otherwise the ratio $\dfrac{\int_o^t R_{\rho 1}\, dt}{\int_o^t R_{\rho 2}\, dt}$ will be constant and the number average molecular weight will not decrease with conversion. If there are two propagating species then the overall rate of polymerisation (R_ρ) will be given by 3-12.

$$R_\rho = R_{\rho(1)} + R_{\rho(2)} \qquad \text{--} \qquad \text{--} \qquad 3\text{-}12$$

The natures of the propagating reactions in the polymerisation are unknown but they may be described by the general kinetic equations 3-13 and 3-14:

$$R_{\rho(1)} = k_{p(1)} [\mathrm{Mon}]^a \left[W_{(1)}\right]^b \qquad \text{--} \quad \text{--} \quad 3\text{-}13$$

$$R_{\rho(2)} = k_{p(2)} [\mathrm{Mon}]^{a^1} \left[W_{(2)}\right]^{b^1} \qquad \text{--} \quad \text{--} \quad 3\text{-}14$$

where $W_{(1)}$ and $W_{(2)}$ represent the propagating species in the polymerisation of cyclopentene. To account for the change in the ratio $\dfrac{\int_o^t R_{\rho(1)}\, dt}{\int_o^t R_{\rho(2)}\, dt}$

either:

(1) $a \neq a^1$ if the ratio $W_{(1)}/W_{(2)}$ remains constant or

(11) $\dfrac{W_{(1)}}{W_{(2)}}$ changes during the course of the polymerisation.

If the orders of polymerisation with respect to monomer differ for each reaction, then this should be reflected in a dependence of the molecular weight distribution on the initial concentration of monomer. Table 3-5 shows the dependence of the molecular weight distribution upon initial monomer concentration as determined by the gel permeation chromatographs of the polymer samples obtained. It is observed that the ratio of the areas under each molecular weight distribution curve is effectively constant for each concentration of monomer and hence the orders of the propagation reactions (3-11) may be considered to be identical with respect to monomer concentration and the change in molecular weight distribution as expressed by $\frac{\int_0^t R_{p(1)}\,dt}{\int_0^t R_{p(2)}\,dt}$ considered to be caused by a change in the ratio $\frac{W_{(1)}}{W_{(2)}}$

The study of the oxidation state of tungsten during the course of its reaction with cyclopentene suggested that tungsten existed, in the polymerisation, as a mixture of oxidation states. If tungsten was present in two active oxidation states, $W_{(x)}$ and $W_{(y)}$, a reaction scheme can be constructed (3-15) wherein:

$$\begin{array}{lcl} Cp + W\,(V1) & \longrightarrow & W(x) + W(y) \\ W(x) + Cp & \longrightarrow & W^*(x) \\ W(y) + Cp & \longrightarrow & W^*(y) \\ W^*(x) & \xrightarrow{Al(iBu)_3} & W(1) \\ W^*(y) & \xrightarrow{Al(iBu)_3} & W(2) \\ W_1 + Cp & \longrightarrow & \text{Polymer (1)} \\ W_2 + Cp & \longrightarrow & \text{Polymer (2)} \end{array} \qquad 3\text{-}15$$

CHAPTER 4

Investigation of the activity of a tungsten hexachloride-oxygen catalyst in the polymerisation of cyclopentene

Introduction

A bimetallic catalyst system based upon tungsten and aluminium is capable of polymerising cyclopentene to trans polypentenamer giving conversions of monomer to polymer of the order of 70% together with a high rate of polymerisation.

The role of the catalyst components in the polymerisation mechanism is not clear but it is thought that the tungsten atom acts to co-ordinate cyclopentene monomer to form co-ordination complexes which can be represented by - $W(Cp)_x$. The subsequent addition of aluminium to the system results in rapid polymerisation. It is thought that the aluminium reacts with the tungsten/cyclopentene complex to form a tungsten species (W_1), possibly a tungsten carbene, which can undergo reaction with monomer to produce polymer.

The high rates of polymerisation noted in the above system were difficult to measure by dilatometry. It was therefore decided to investigate the possibility of determining the rate by the use of a cone and plate viscometer, using the increase in the viscosity of the polymerisate as a measure of the rate of polymerisation. During preparations for these experiments solutions of tungsten hexachloride in cyclopentene were made up in ground glass stoppered flasks. It was discovered, when the tungsten hexachloride/cyclopentene solution was left overnight, that polymerisation had occurred. This event led to the investigation of the ability of tungsten hexachloride alone to polymerise cyclopentene and it was hoped that this could also lead subsequently to clarification of the role played by the aluminium in the bimetallic catalyst system.

4.1 Polymerisation of cyclopentene initiated by tungsten hexachloride alone

The polymerisation of cyclopentene initiated by tungsten hexachloride alone was carried out at 25°C by the method described in 2-5A using the apparatus shown - figure 2-8. Two mls of a 0.06M toluene solution of tungsten hexachloride were added to 0.12 moles of cyclopentene in the reaction vessel (P_1) so that the cyclopentene:tungsten molar ratio was 1000:1. The polymerisation was allowed to proceed for a predetermined time after which it was terminated by the injection of methanol into the polymerisate. The polymer was then obtained by precipitation of the polymerisate in methanol and was purified by successive precipitations in methanol from chloroform solutions. The percentage conversions of monomer to polymer for a series of such polymerisations in which the reaction time was varied is recorded - table 4-1.

Table 4-1

Dependence of conversion of monomer to polymer on polymerisation time

Polymerisation time (hrs)	Percentage conversion
0.5	1.0
1.0	1.5
5.0	1.8
12.0	2.0
24.0	2.0

Temperature - 25°C
$[WCl_6]$ - 5.6×10^{-3} moles l^{-1}
[Cyclopentene] - 5.6 moles l^{-1}

Films of polypentenamer samples were cast, on evaporating dishes, from chloroform solutions and the infra-red spectra of the polymer samples were obtained by the method described in section 2-6C. A typical spectrum for a sample of polypentenamer obtained in this series of polymerisations is shown - figure 4-1 - and it is seen that the polymer spectrum showed the absorptions characteristic of polypentenamers which contained predominantly trans double bonds (i.e. the 10.35μ absorption band).

These results indicated that tungsten hexachloride alone would polymerise cyclopentene to produce trans polypentenamer by a ring opening mechanism in a similar manner to the bimetallic catalyst systems but that the conversion of monomer to polymer was very low even after long reaction times. A complicating feature of this system was that during the course of these tungsten hexachloride initiated polymerisations inconsistent results were obtained wherein conversions to polymer were sometimes found to be far greater than those average values shown in table 4-1. The range of yields from supposedly similar reactions is shown in table 4-2.

Table 4-2

Dependence of conversion of monomer to polymer on unknown parameters

Polymerisation time (hours)	Percentage conversion
0.5	1
0.5	6
0.5	60
0.5	32
0.5	2

Temperature - 25°C
$[WCl_6]$ - 5.6×10^{-3} mole l^{-1}
[Cyclopentene] - 5.6 moles l^{-1}

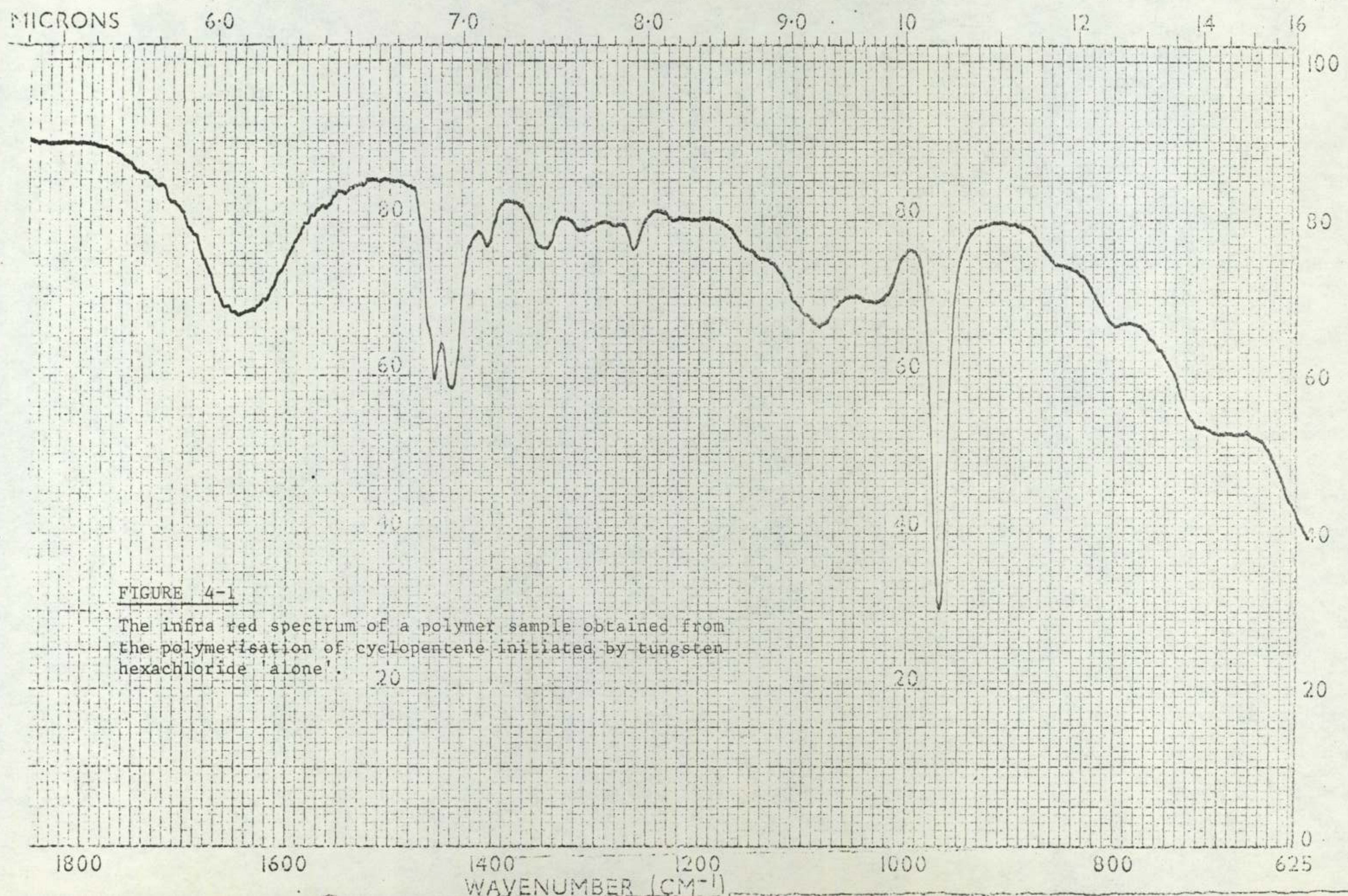


FIGURE 4-1

The infra red spectrum of a polymer sample obtained from the polymerisation of cyclopentene initiated by tungsten hexachloride 'alone'.

The apparatus used in the above polymerisations was very simple in nature consisting only of a flask fitted with a greaseless tap and 'Suba-seal' side arm and it was felt that the apparatus was susceptible to leakages which might have introduced potential impurities into the system. Accordingly, the effect of the addition of dry oxygen to the cyclopentene/tungsten hexachloride system was investigated using apparatus that was leak proof and sealed under vacuum.

4-2 Polymerisation of cyclopentene initiated by tungsten hexachloride and activated by oxygen

The polymerisation of cyclopentene initiated by tungsten hexachloride alone was carried out using the high vacuum apparatus shown in figure 2-9 by the method described in section 2-5B. Two mls of a 0.06 molar solution of tungsten hexachloride in toluene were added to 0.12 mole of cyclopentene contained in the reaction vessel to produce a tungsten hexachloride:cyclopentene molar ratio of 1:1000. The apparatus was sealed from the vacuum line at the appropriate constriction and reaction was allowed to proceed at 25°C for a predetermined time. Normally during this period the intensity of the colour of the brown solution of tungsten hexachloride reduced and often a brown oily precipitate formed which would indicate that some reaction took place between tungsten hexachloride and cyclopentene. After a predetermined reaction time. oxygen, which had been dried by passage through columns of activated molecular sieves and alumina, was admitted to the reaction vessel. An immediate reaction took place in which the oil redissolved to form a caramel solution in cyclopentene and polymerisation commenced. The polymerisation was allowed to proceed for a period of one hour after which it was terminated by the injection of methanol into the polymerisate. The polymer obtained was purified as in 4-1. The reaction time before oxygen addition was varied and the percentage conversion of monomer to polymer recorded - table 4-3.

Table 4-3

Dependence of conversion of monomer to polymer on the tungsten hexachloride/cyclopentene reaction time before oxygen addition

Time of reaction before oxygen addition-hours	Percentage conversion one hour after oxygen addition
0.1	8
0.5	8
1.0	12
12.0	21
24.0	30
48.0	42
72.0	42

Temperature - $25^{o}C$
$[WCl_6]$ = 5.6×10^{-3} mole l^{-1}
[Cyclopentene] = 5.6 mole l^{-1}

The results in table 4-3 would suggest that during the reaction of cyclopentene with tungsten hexachloride at room temperature the conversion of the tungsten hexachloride to a species that could be activated to the polymerisation of cyclopentene by oxygen is complete after 48 hours. A series of polymerisations was then carried out to study the change in conversion with time in this catalytic system.

A series of reaction vessels were prepared in which the concentration of tungsten hexachloride was maintained constant at 5.6×10^{-3} moles l^{-1} in bulk cyclopentene and the cyclopentene in each was allowed to react with the tungsten hexachloride for 50 hours. Oxygen was then admitted to each tube and the resultant polymerisation allowed to proceed in each for different periods before methanol was added to terminate the polymerisation. The change in conversion with time is shown in table 4-4.

Table 4-4

Dependence of conversion of monomer to polymer on reaction time after the addition of oxygen to the tungsten hexachloride/cyclopentene system.

Reaction time after addition of oxygen - minutes	Percentage conversion
1	23
5	23
10	28
30	30
60	40
120	42

Temperature - 25°C
Time of reaction before oxygen addition - 50 hours
$[WCl_6]$ - 5.6×10^{-3} moles l^{-1}
[Cyclopentene] - 5.6 moles l^{-1}

Structure of the polypentenamer produced in the WCl_6/oxygen/cyclopentene system

The polymers obtained in the above experiments were cast into films and were analysed by infra red spectroscopy. A typical spectrum is shown in figure 4-2. The polymer again showed the absorbance of a polypentenamer with peaks at 10.35μ (trans $\supset C = C \subset$) and 13.19μ (cis $\supset C = C \subset$).

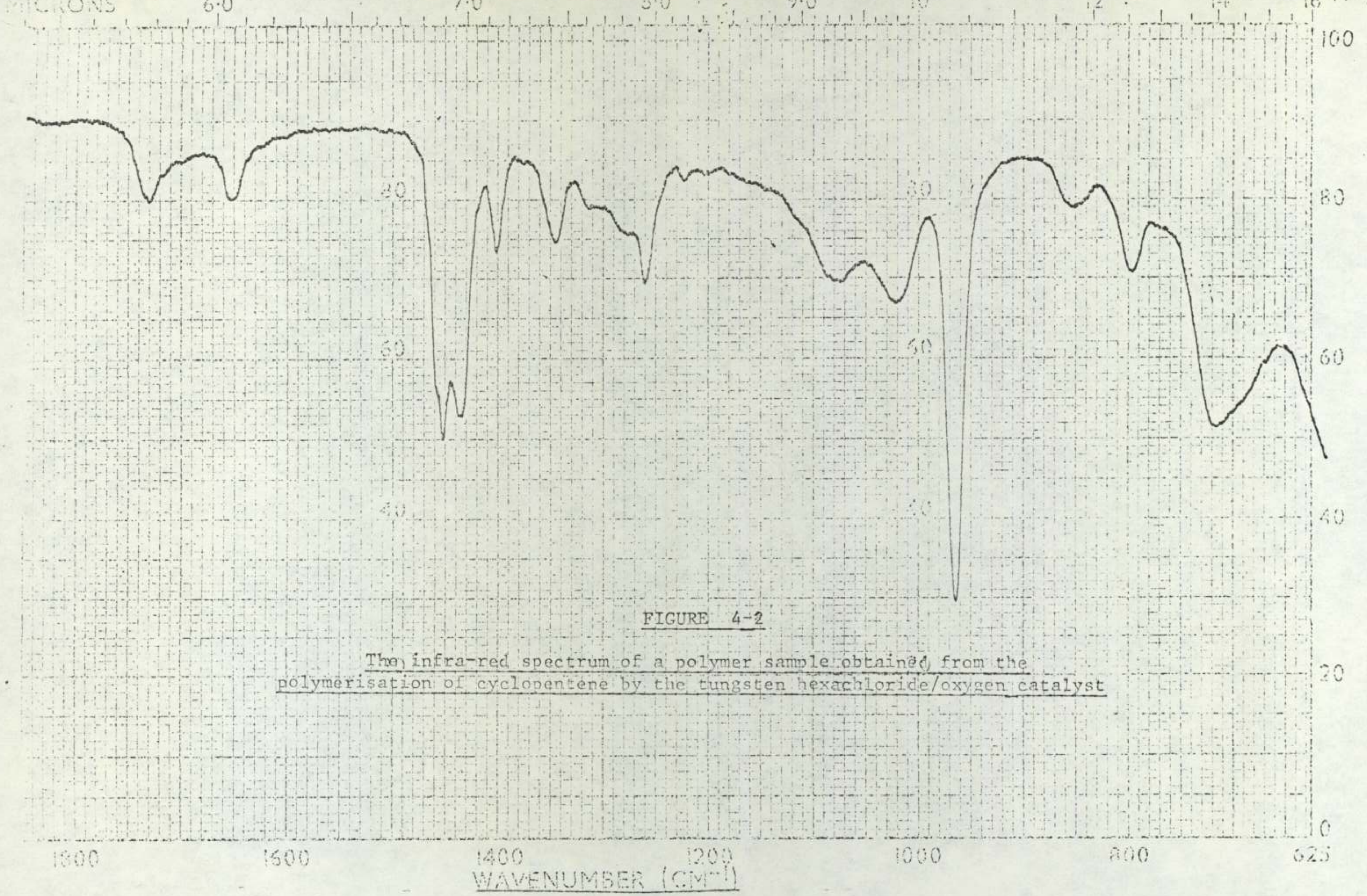
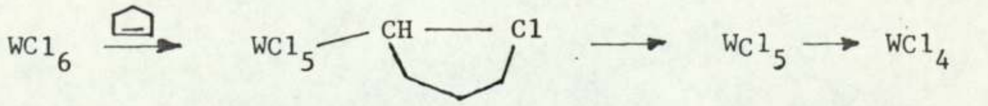


FIGURE 4-2

The infra-red spectrum of a polymer sample obtained from the polymerisation of cyclopentene by the tungsten hexachloride/oxygen catalyst

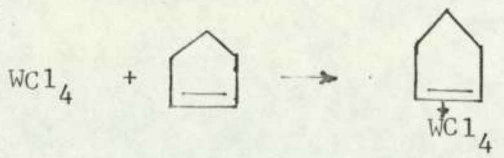
From the foregoing results it can be concluded that the polymerisation of cyclopentene can be initiated by catalysts that do not contain metal alkyls. It was thought that possibly some aluminium was included in the polymerisation system since aluminium tri-ethyl had been used to dry the cyclopentene prior to its use in these polymerisations; however if the relative vapour pressure of cyclopentene at room temperature - 500mm - is compared with that of aluminium tri-ethyl - 10^{-2}mm it can be calculated that the highest possible molar ratio of cp:Al in the polymerisation as a result of distillation would be approximately 50,000:1. This would not be sufficient to catalyse the reaction. Furthermore a drying agent - Butyl Lithium-was used to dry the cyclopentene prior to its use in these polymerisations and this did not affect the yields obtained. Having discounted any possible source of contamination in the system it is therefore reasonable to assume that the catalyst is monometallic.

The initial results of the polymerisations where cyclopentene was thought to be activated by tungsten hexachloride alone were proven inaccurate because the subsequent investigations showed that oxygen was a necessary component in the catalyst system due to the fact that in the sealed system the cyclopentene remained mobile until oxygen was admitted. During the period before addition of oxygen to the system reaction took place between the cyclopentene and the tungsten hexachloride because a precipitate was seen to form. In Chapter 3 the oxidation state of tungsten in contact with cyclopentene is known to fall from its initial value of 6 to some lower non-integral value. It could be suggested that the precipitate is a product of the reduction of the tungsten hexachloride which probably complexed with cyclopentene. This process may involve a two stage process where:



4-1

and:



4-2

The polymers produced by this monometallic system have structures which are essentially the same as that produced by the bimetallic tungsten hexachloride/aluminium tri-isobutyl catalyst system. Therefore it could be concluded that the essential details of the mechanism are identical to that of other metathetic polymerisations. Efforts to confirm this were thwarted since attempts to determine the number average molecular weight of the polymer samples as a function of conversion were unsuccessful because the molecular weight of the samples were too high.

The optimum conversion of monomer to polymer occurred where the tungsten hexachloride was allowed to interact with the cyclopentene for a period of 50 hours before the addition of oxygen to the system, followed by a further polymerisation time of 0.5 - 1 hour. This long period of ageing (50 hours) may be due to the fact that the rate of reactions 4-1 or 4-2 is very low. The species responsible for initiating the polymerisation in the WCl_6/O_2/cyclopentene system is unknown but it was reasonable to assume that a tungsten oxychloride was involved. Hence it was decided to attempt the polymerisation of cyclopentene using tungsten oxychlorides, of varied W:O:Cl stoichiometric ratios, to initiate the polymerisation.

4-3 Polymerisations of cyclopentene initiated by tungsten oxychlorides

Tungsten oxychlorides containing various stoichiometric ratios of W:O:Cl were prepared (2-4(B)). A 0.06 M suspension of tungsten hexachloride in hexane was refluxed with the stoichiometric amount of tungsten oxide (WO_3) to produce:-

$W_2 O Cl_{10}$

$W O Cl_4$

$W_2 O_3Cl_6$

$W O_2Cl_2$

by 4-3

$$yWCl_6 + xWO_3 \text{ —— } W_{y+x} O_{3x} Cl_{6y} \quad \text{----} \quad \text{----} \quad 4\text{-}3$$

The polymerisations of cyclopentene was carried out using the range of tungsten oxychlorides as catalysts at 25°C, in the apparatus described in 2.5b; 0.12m-moles of the tungsten oxychloride were added to 0.12 mole of cyclopentene contained in the reaction vessel, the apparatus was sealed off at the constriction and the polymerisation was allowed to proceed for one hour before it was terminated by the injection of methanol. Oxygen was not allowed to enter the apparatus before the injection of methanol. The polymer was obtained by precipitation and purified by successive precipitations from chloroform solutions. The effect on conversion of monomer to polymer produced by a series of tungsten oxychlorides under the conditions described above is recorded - table 4-5.

Table 4-5

Dependence of the conversion of monomer to polymer on the oxygen content of the tungsten oxychloride

Catalyst	Percentage conversion after one hour
WO_2Cl_{10}	1.0
$WO Cl_4$	16.0
$W_2O_3Cl_6$	10.0
$WO_2 Cl_2$	4.0

[tungsten oxychloride] - 5.6m mole l^{-1}
[cyclopentene] - 5.6 mole l^{-1}

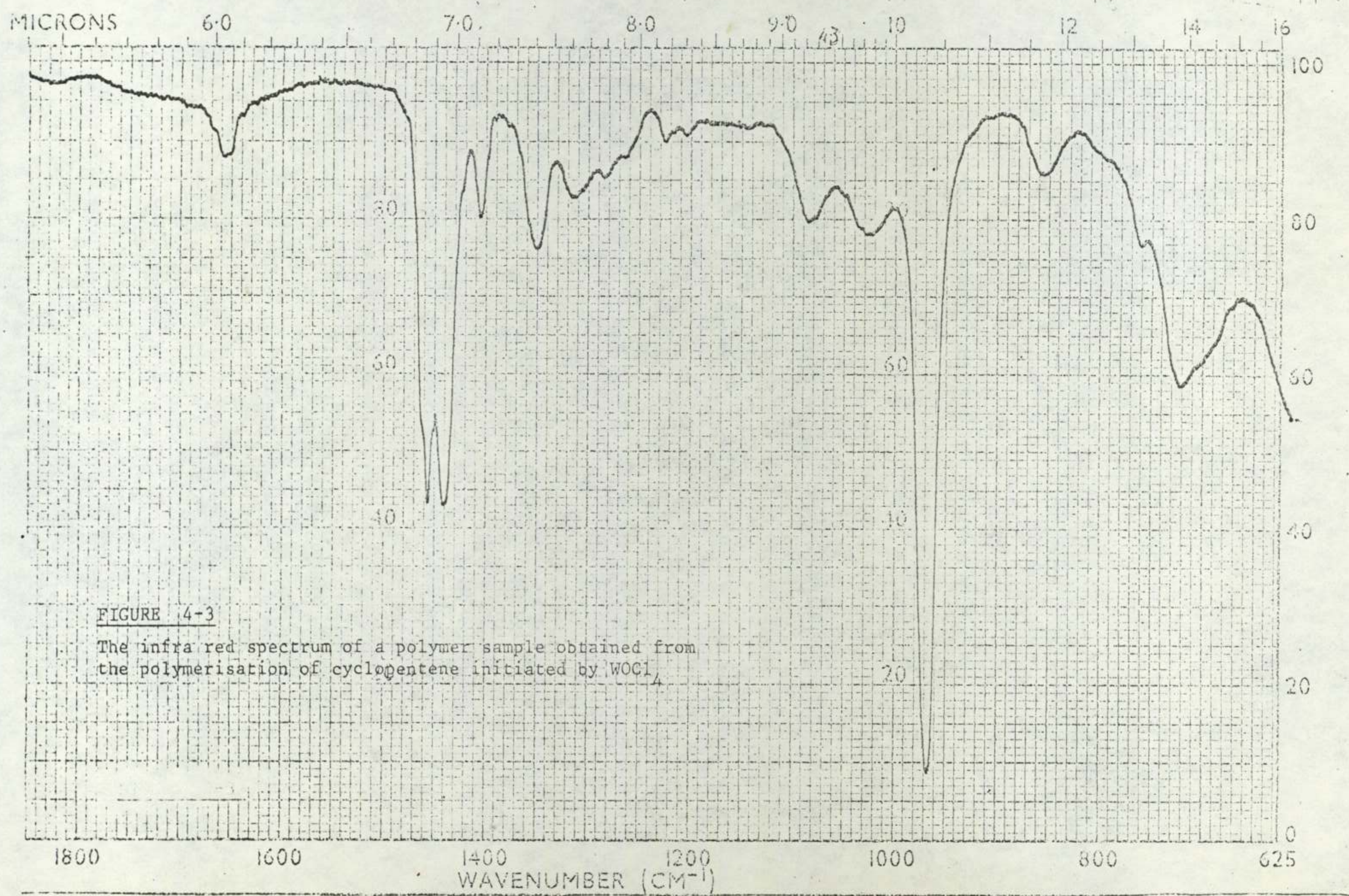


FIGURE 4-3

The infra red spectrum of a polymer sample obtained from the polymerisation of cyclopentene initiated by $WOCl_4$

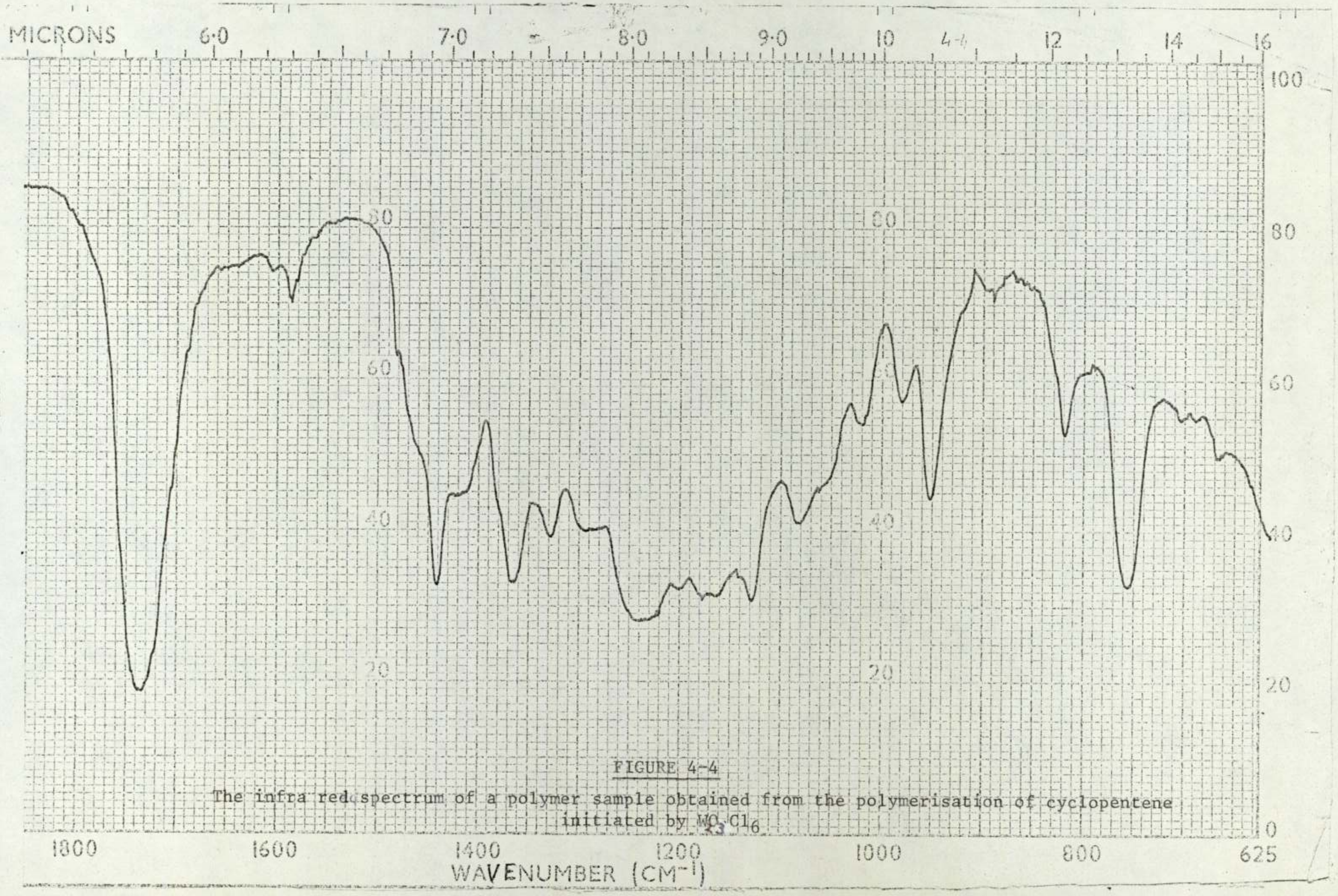


FIGURE 4-4

The infra red spectrum of a polymer sample obtained from the polymerisation of cyclopentene initiated by WO Cl$_6$

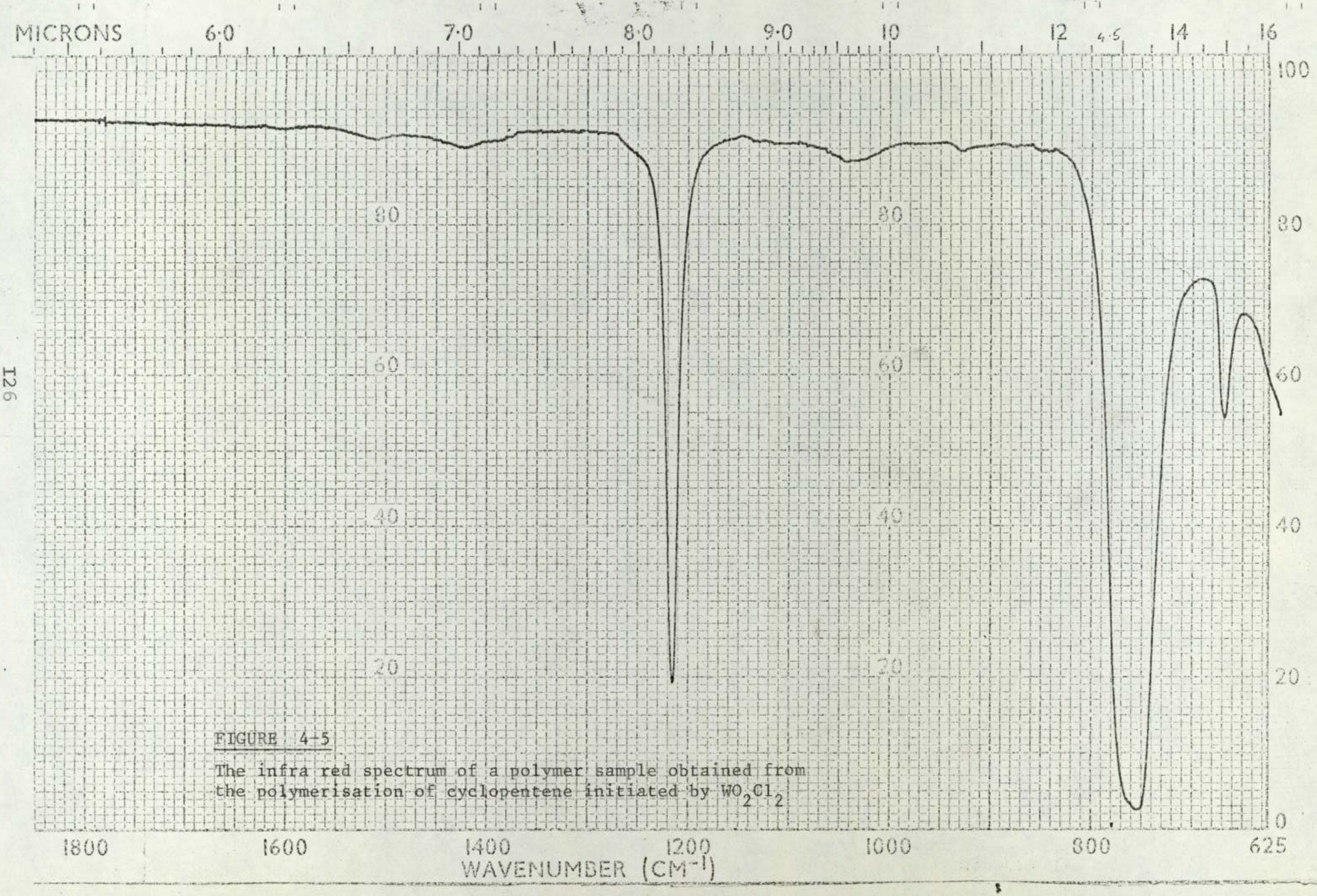


FIGURE 4-5

The infra red spectrum of a polymer sample obtained from the polymerisation of cyclopentene initiated by WO_2Cl_2

The products of the polymerisation of cyclopentene by $WOCl_4$, $W_2O_3Cl_6$ and WO_2Cl_2 were analysed by infra-red spectroscopy; films of the polymer had been produced in the usual manner. An inspection of the absorption bands at 10.35μ and 13.9μ, which are due to the trans and cis $\rangle C = C \langle$ shows that:

(1) $WOCl_4$ produces a predominantly trans polypentenamer (fig.4-3) and (2) WO_2Cl_2 produces a predominantly cis polypentenamer (fig. 4-5).

The ratio $\dfrac{(\text{Log}\frac{I_0}{I})\ 10.5\mu}{(\text{Log}\frac{I_0}{I})\ 13.9\mu}$ for each polymer can be used as a measure of structure as it gives the relative change in the trans/cis ratio in a series of polymers. Using this ratio the trans/cis content of the polymer produced in the WCl_6/O_2 initiated polymerisation (figure 4.2) can be compared (table 4-6) with that produced by the $WOCl_4$, $W_2O_3Cl_6$ and WO_2Cl_2 initiated polymerisations (figures 4-3, 4,and 5 respectively).

Table 4-6

Relative trans/cis content of polymers produced by varied catalyst systems

Catalyst system	$(\text{Log}\ \frac{I_0}{I})_{10.5\mu} / (\text{Log}\ \frac{I_0}{I})_{13.9\mu}$
WCl_6/O_2	9.41
$WOCl_4$	12.00
$W_2O_3Cl_6$	0.66
WO_2Cl_2	0.00

The polymer produced by the $WOCl_4$ initiated polymerisation of cyclopentene is of the same structure relative to that produced by the WCl_6/O_2 catalysed reaction. However, the different rates of polymerisation in the two systems where:

$$^{R}p(\mathrm{WCl_6/O_2}) \gg {}^{R}p(\mathrm{WOCl_4})$$

would suggest that the effect of the addition of oxygen to the cyclopentene/tungsten hexachloride system after fifty hours reaction time is not simply explained by the formation of $WOCl_4$ or any corresponding species.

4-4 Ultraviolet and visible spectroscopic investigations of the cyclopentene/tungsten hexachloride/oxygen system.

Tungsten hexachloride and the products of the reaction with cyclic alkenes were susceptible to hydrolysis which destroyed the catalytic activity of such systems towards the polymerisation of cyclic alkenes. The UV/Visible studies carried out on the catalyst system necessitated the use of apparatus designed to eliminate the problem of hydrolysis because normal stoppered cells were not found to be sufficiently air and moisture-tight for the purposes of these studies. Figure 2-IO shows the apparatus which was developed for use in these experiments.

In order to ascertain a suitable concentration of tungsten hexachloride to be used in these studies an absorption/concentration curve was determined for tungsten hexachloride in cyclopentene;(Figure 4-6).0.1 mole cyclopentene (9 mls) was distilled into the mixing vessel (figure 2.10) and .17 ml of a 0.06 molar solution of tungsten hexachloride in toluene was added by hypodermic syringe. The 1cm. quartz cell was filled with this solution and the apparatus was then placed in the spectrophotometer. The U.V and visible spectrum of the solution was then recorded using cyclopentene as the reference solvent. The spectrum of tungsten hexachloride in cyclopentene showed an absorbance maximum at 510mμ this absorbance maximum having an extinction coefficient of 6.2 l mole^{-1} cm^{-} The absorption spectrum of the solution was recorded immediately after addition of tungsten hexachloride to cyclopentene and then at intervals after the addition when reaction between the components had been allowed to take place at 25°C. After a period of 20 hours dry oxygen was admitted to the system and the absorption spectrum was recorded again. Figure 4-7 shows the spectral changes occurring under the conditions shown in table 4-7.

Table 4-7

Reaction conditions during U.V/visible spectroscopic determinations on the WCl_6/cyclopentene/oxygen system recorded in figure 4-7.

Spectrum	Time (hours)
I	0.1
II	0.5
III	1.0
IV	10.0
V	20.0
VI*	20.0
VII*	21.0

Temperature = 25°C

*Spectra recorded after the addition of oxygen

The U.V./visible spectra in figure 4-7 showed absorbances at 352$m\mu$ and 510$m\mu$ and it was suspected that these absorption bands could be due to the formation of spectroscopically active complexes between the tungsten hexachloride and impurities in the toluene of the catalyst solution. However, when the U.V./visible spectrum of a low concentration solution (.01M) of tungsten hexachloride in toluene was recorded it was observed that neither of these absorption bands were present (figure 4-8). Therefore it was concluded that both of these peaks (figure 4-7) were due to complexes formed between the

FIGURE 4-6

Absorption/concentration diagram for tungsten hexachloride in cyclopentene

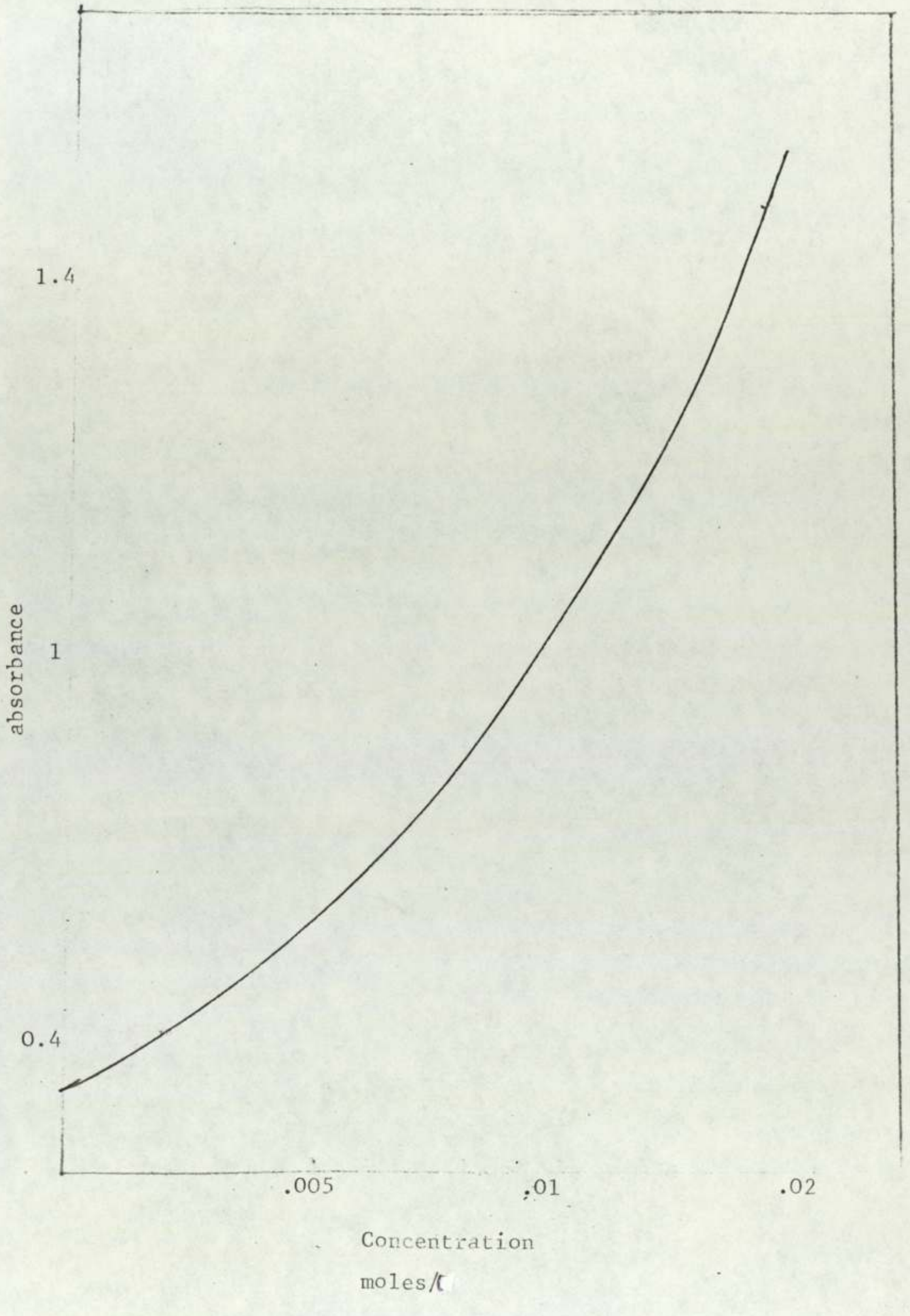


FIGURE 4-7

The ultraviolet/visible spectrum of a tungsten hexachloride/cyclopentene system before and after oxygen addition

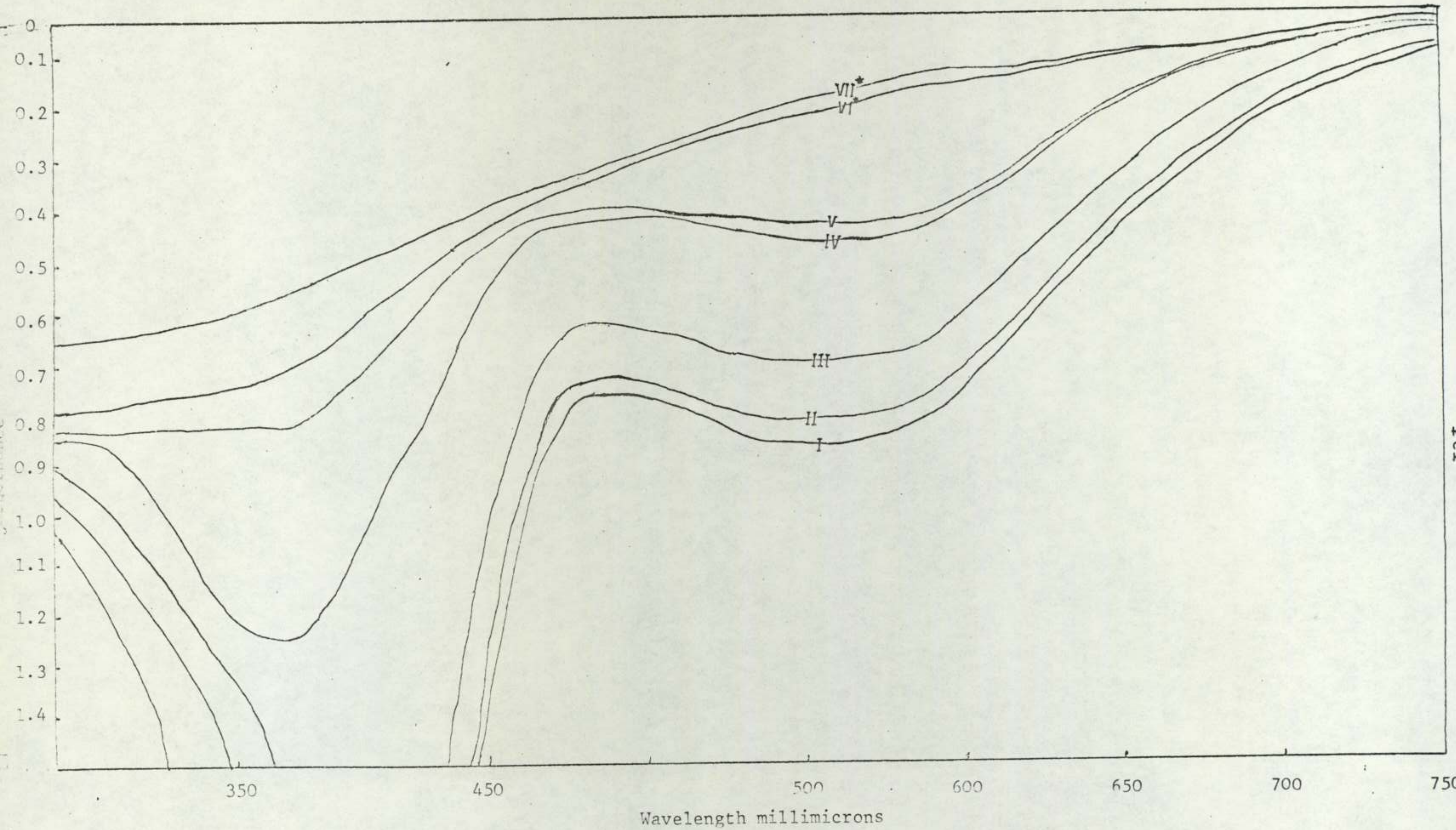
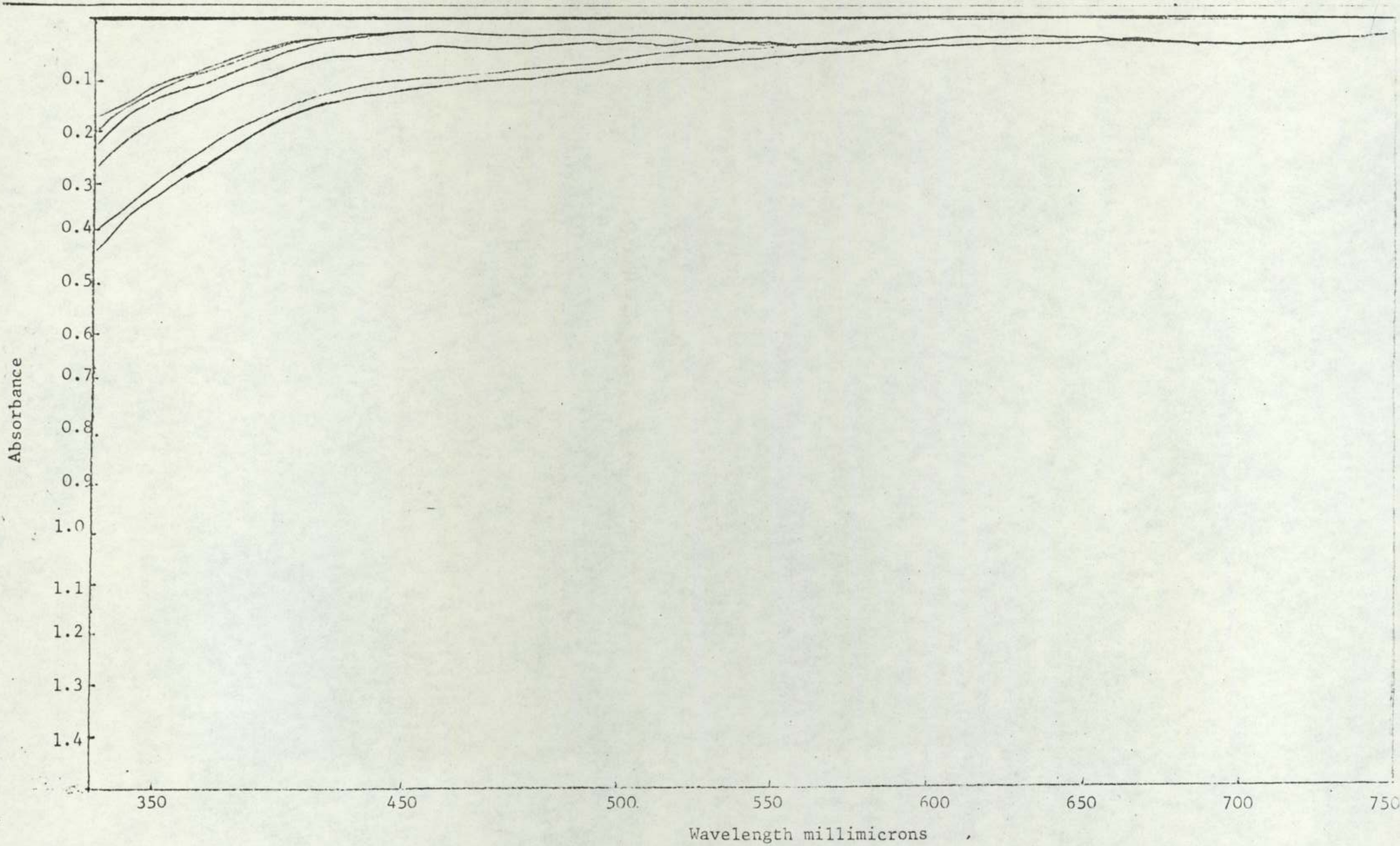


FIGURE 4-8

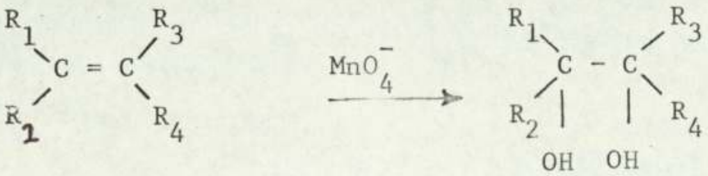
The ultraviolet/visible spectrum of a tungsten hexachloride solution in toluene



tungsten hexachloride and the cyclopentene. The peak at 510mμ decreases in height as a function of time. The colour of a tungsten hexachloride solution in toluene is blue whereas that of tungsten hexachloride in cyclopentene is brown. The brown colour of the solution in the spectrometer cell shows decreases with time which is related to the formation of an oily precipitate at the base of the cell. It could be concluded that the spectrum represents products of reaction between tungsten hexachloride and cyclopentene which are not active species in the polymerisation reaction. The addition of oxygen to the system completely changes the shape of the spectrum so it is probable that the active species in the polymerisation gives rise to spectrum VI* and VII*.

4-5 Determination of the effect of oxygen addition on the tungsten oxidation state when oxygen is added to a tungsten hexachloride/cyclopentene reaction

The determination of the oxidation states of tungsten in the catalyst systems described in the previous chapter was possible because the organic materials used could be removed from the products of hydrolysis by vacuum distillation techniques; side reactions that would lead to the consumption of the oxidising agent ($KMnO_4$)were thus eliminated. It is well known that potassium permanganate will readily oxidise carbon-carbon double bonds to form diols - e.g.



and because the product of the polymerisation of cyclopentene, which contained a high degree of unsaturation, could not be readily separated from the products of the hydrolysis of the catalyst such titrimetric procedures could not be applied in determination of the changes of the oxidation state of tungsten that occurred during the polymerisation of cyclopentene.

However, the applications of metathesis polymerisation catalysts are not confined to the polymerisation of cyclic alkenes since it is believed, with some justification, that the mechanism of linear alkene metathesis reactions is identical to the special case of cyclic alkene polymerisation.[78] It therefore seemed appropriate that the catalyst system - WCl_6/O_2 should be applicable to the metathesis of linear olefins. The resultant changes of oxidation state of tungsten could then be studied because the products of the metathesis reaction could be removed by simple vacuum distillation techniques.

The application of the catalyst system WCl_6/O_2 to the metathetic disproportionation of linear olefins.

A series of reactions were carried out to determine the activity towards the metathetic disproportionation of olefins of the product of the reaction between tungsten hexachloride and the olefin.

1) alone

and 2) upon the addition of dry oxygen to the reaction mixture. The reactions were carried out as described in section 2.5B. 0.12m mole of dry cis-2-pentene was distilled into the reaction vessel and 0.12m mole of tungsten hexachloride was added before the vessel was sealed off from the vacuum line. The reaction was allowed to proceed at room temperature for 20 hours and an oily precipitate, which was similar in appearance to that produced upon the reaction of cyclopentene with tungsten hexachloride, formed in the tube. The reaction was terminated by the addition of 1ml. of isopropanol that

FIGURE 4-8'

The gas chromatogram of the products of the reaction between cis-2-pentene and tungsten hexachloride

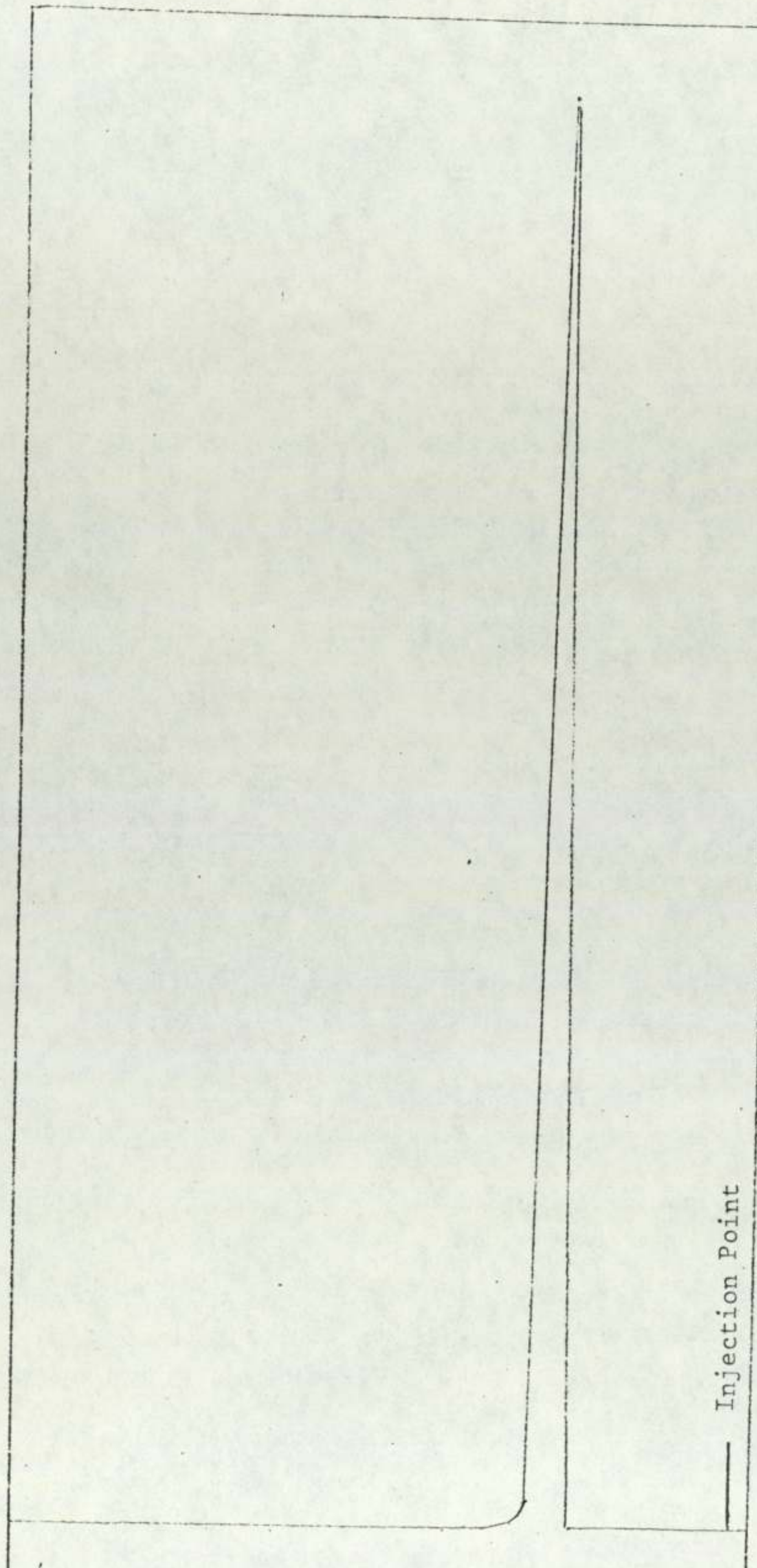


Figure 4-9

The gas chromatogram of the products when cis-2-pentene was reacted with tungsten hexachloride for a period of 0.5 hours followed by the addition of oxygen and a further reaction time of 0.5 hour

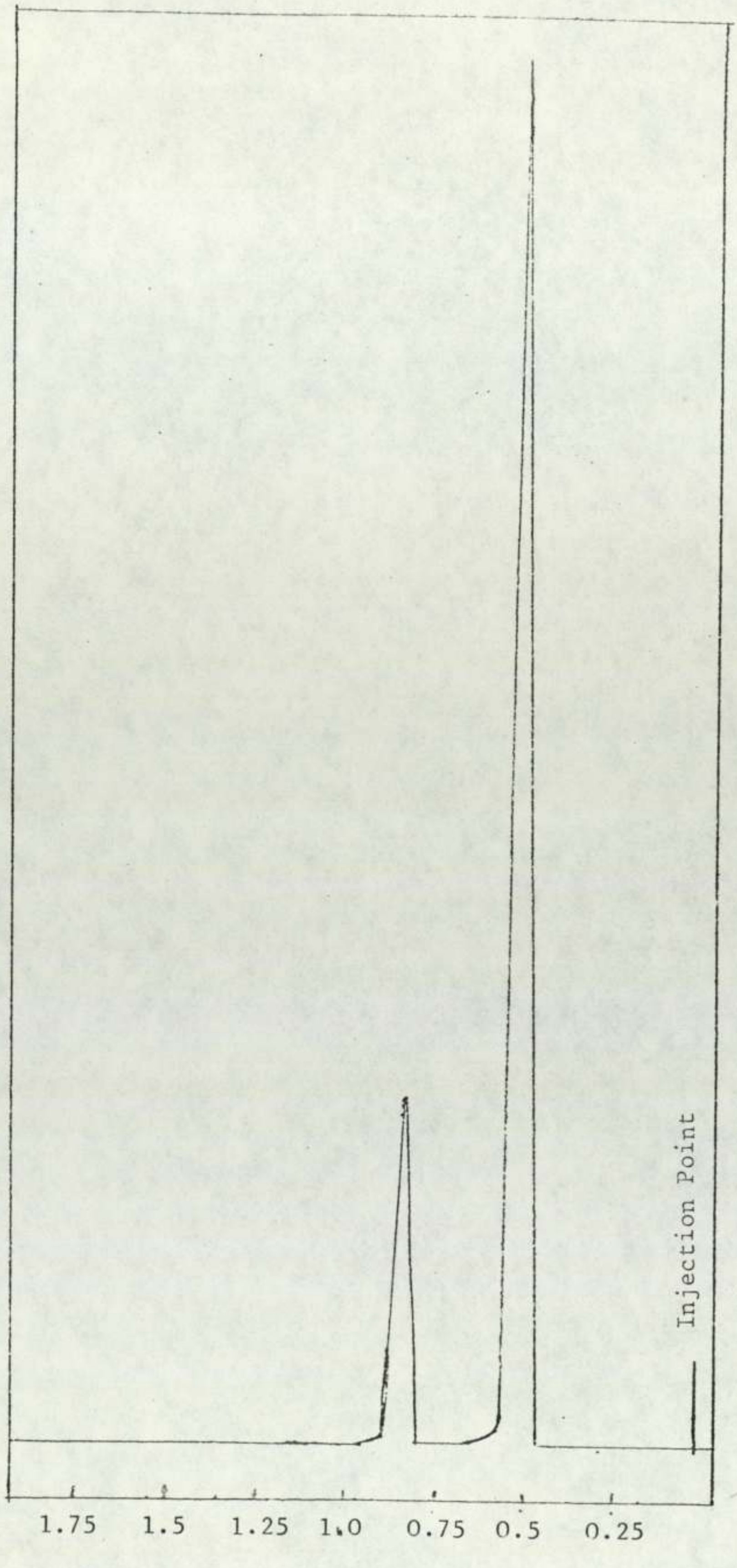
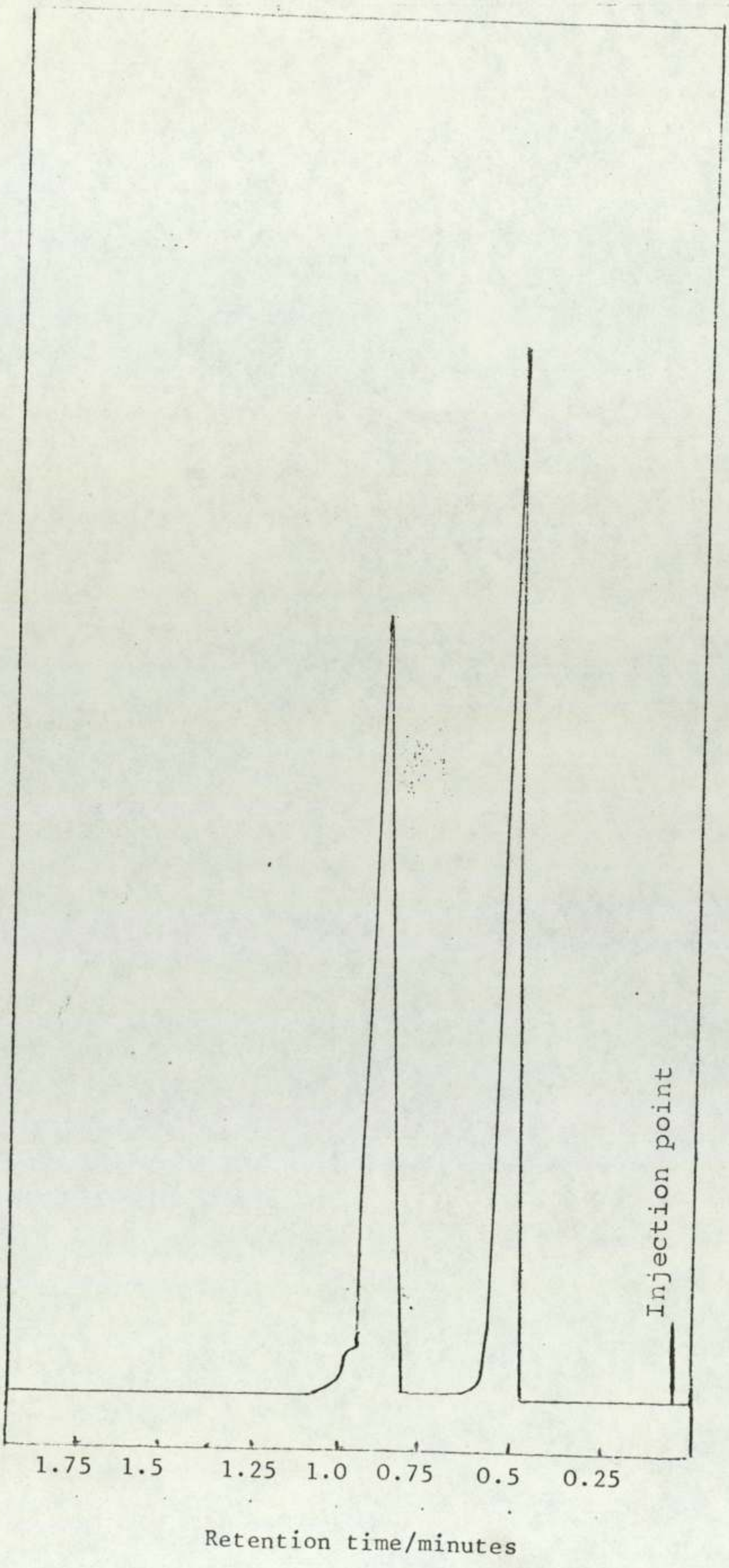


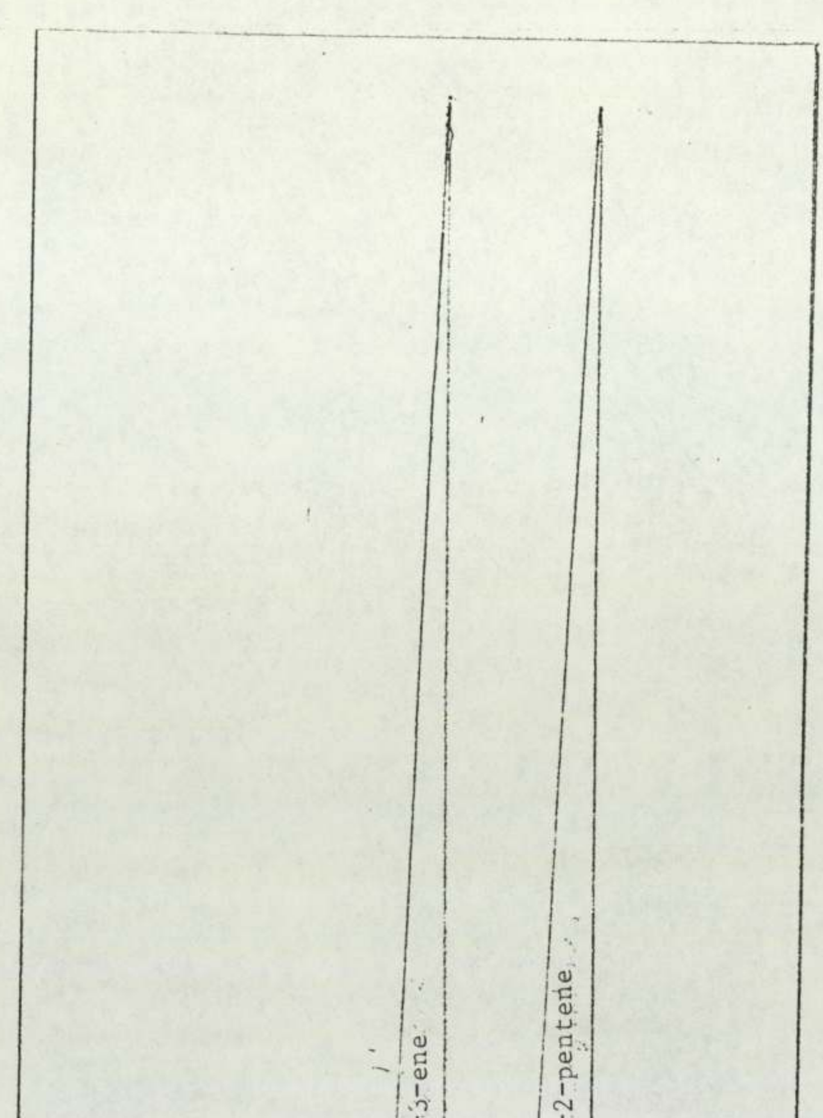
FIGURE 4-10

The gas chromatogram of the products when cyclopentene was reacted with tungsten hexachloride for a period of 24 hours followed by the addition of oxygen and a further reaction time of 0.5 hour.



The gas chromatographic calibration curve for
cis-2 pentene and hex-3-ene

Figure 4-11



was contained in a break seal ampoule and the products of the reaction were analysed by gas chromatography. The gas chromatograph of the products of this reaction, shown in figure 4-8', suggested that no metathesis reaction took place in the absence of oxygen because only the parent cis-2-pentene peak is obtained in the chromatogram - i.e. the products of metathetic disproportionation are absent.

In parallel reactions, with identical conditions, oxygen was admitted to the tube 0.5 and 24 hours after the tungsten hexachloride was added to the olefin. After a further reaction time of 0.5 hour the products were analysed by gas liquid chromatography, and the resultant chromatographs are shown in figures 4-9 and 10. Two peaks are apparent in both these chromatographs. When compared with the already prepared chromatographs of cis-2-pentene and hex-3-ene (figure 4-11) it is seen that these peaks are coincidental.

The metathetic disproportionation of cis-2-pentene should have resulted in the formation of an equilibrium mixture of the two new products - hex-3-ene and but-2-ene - together with the parent cis-2-pentene. The gas chromatograph of such a mixture should therefore have exhibited three distinct peaks.

An inspection of figure 4-8' shows that no disproportionation had occurred because the cis-2-pentene peak alone was present. In figures 4-9 and 10 two peaks were present - corresponding to cis-2-pentene and hex-3-ene when compared with figure 4-11—the standard chromatograph for these two compounds. This suggests that the tungsten hexachloride/oxygen catalyst did initiate the metathetic disproportionation of the acyclic olefin whereas tungsten hexachloride alone did not.

The absence of the third peak in figures 4-9 and 10 corresponding to but-2-ene can be explained by the fact that but-2-ene is a volatile product of the metathetic disproportionation reaction and was lost on transfer of the material from the flask to the column using a syringe that was only suitable for injecting liquids.

Determination of the oxidation states of tungsten in the tungsten hexachloride/cis-2-pentene/oxygen system

The changes in the oxidation state of tungsten in the above system was determined by the titrimetric method described in 2.6B. 2 mls of a 0.06M solution of tungsten hexachloride in toluene were added to 0.12 moles of cis-2-pentene in the reaction vessel. The reaction was allowed to proceed for a predetermined time after which it was terminated by the addition of deoxygenated sodium hydroxide solution. Alternatively oxygen was added to the system and the reaction was allowed to continue for a further period of 0.5 hour after which it was terminated by addition of the sodium hydroxide solution. The volatile reaction products were then removed by distillation followed by addition of 50 mls. of dilute sulphuric acid and 5 ml of a lead monoxide suspension. The flask contents were stirred and 12.8 mls. potassium permanganate were added. The excess potassium permanganate was determined by addition of 25 mls of standard ferrous ammonium sulphate, filtering and back titration of the filtrate with potassium permanganate.

The changes in oxidation state during the metathesis reaction are shown in tables 4.8 and 9.

Table 4-8

Changes in the oxidation state of tungsten with time in the cis-2-pentene/tungsten hexachloride system

Reaction time (minutes)	Mean oxidation state
0	5.8
5	5.8
10	5.4
15	4.9
30	4.9

[Cis-2-pentene] - 5.6 moles l^{-1}
$[WCl_6]$ - 5.6×10^{-3} moles l^{-1}
Temperature - 25°C

Table 4-9

Changes in the oxidation state of tungsten with time in the cis-2-pentene/tungsten hexachloride/oxygen system

Time before oxygen addition - minutes	Mean oxidation state
0	5.4
5	5.4
10	5.1
15	5.1
30	4.8
24 x 60	4.8

[Cis-2-pentene] - 5.60 moles l^{-1}
$[WCl_6]$ - 5.60m moles l^{-1}
temperature - 25°C

Inspection of the data in table 4-8 reveals that the change in the tungsten oxidation state with time in the tungsten hexachloride/cis-2-pentene system is similar to that found in the tungsten hexachloride/

cyclopentene system (chapter 3) which had been assumed in 4-5 above. In both systems the mean oxidation state of tungsten is not an integral number and it decreases to a limiting value with time.

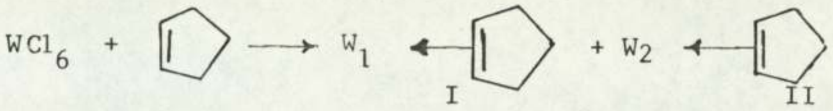
When oxygen was added to the tungsten hexachloride/cis-2-pentene system no dramatic change occurred in the tungsten oxidation state - table 4-9. The oxygen did not oxidise the tungsten atom and hence its role may well have been the conversion of an otherwise inactive tungsten centre to an active site wherein the oxidation state of the atom remained unchanged.

Discussion

The polymerisation of cyclopentene and the metathetic disproportionation of acyclic alkenes could be catalysed by a monometallic catalyst, tungsten hexachloride. Tungsten hexachloride alone, or the complex derived from it and cyclopentene was not the active species in this polymerisation, because such a catalyst system had to be activated by oxygen.

The structure of the polymer produced suggested that the polymerisation of cyclopentene again occurred by a ring opening mechanism and thereby that the active species was present in a similar state to the active species in the bimetallic system based upon $WCl_6/Al(iBu)_3$. The oxidation state of tungsten in the bimetallic system would suggest that the tungsten was present in at least two oxidation states and similar studies on the monometallic system would suggest that even after the addition of oxygen a mixture of oxidation states was present. However, it is not clear whether more than one species would be active in the metathesis reaction because the molecular weights of the polymers produced in the monometallic system were too high to be studied conveniently by gel permeation chromatography or membrane osmometry.

A simple scheme of reactions may be envisaged for the polymerisation system under study.



where (I) and (II) have similar structures to those described in Chapter III. However some reaction must occur wherein one or other of these species is removed from solution because U.V. studies showed that the absorbance at 510mμ decreased with time. The decrease in absorbance at 510mμ was also associated with an increase in the activity of the system towards polymerisation after the addition of oxygen. It is possible that the oxygen reacted with an intermediate species produced from W(I) and/or W(II) to produce a site capable of sustaining a kinetic chain if comparison with the bimetallic system is valid.

CHAPTER 5

General Discussion

5-1 The polymerisation of cyclopentene by the bimetallic W/Al based catalyst

The study of the metathesis of linear alkenes which was initiated by catalysts active in the polymerisation of cyclopentene, led to the conclusion that the ring opening polymerisation of cyclic alkenes was a simple extension of the general olefin metathesis reaction which took place by cleavage of the carbon-carbon double bond. The structure and the mechanism of formation of the transition state complex have not been defined conclusively but the following suggestions have been made to describe this species as:

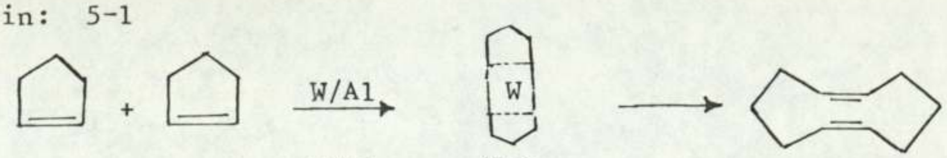
(1) A quasi cyclobutane ring (40)

(II) A multi centred tetracarbene species (49)

and (III) A species containing a tungsten-carbon double bond (50)

Number average molecular weights and molecular weight distribution curves for polymer samples obtained from the ring opening polymerisation of cyclopentene in the presence of the bimetallic W/Al catalyst showed that high molecular weight polymer was formed in the initial stages of the reaction which would suggest that a kinetic chain mechanism might be invoked to describe the propagation step in the polymerisation. An examination of these species in turn as possible intermediates may be made in the light of the probability that a kinetic chain mechanism is required to describe the system.

(I) The quasi cyclobutane ring: A polymerisation scheme incorporating a quasi cyclobutane ring as the transition state can be constructed wherein: 5-1

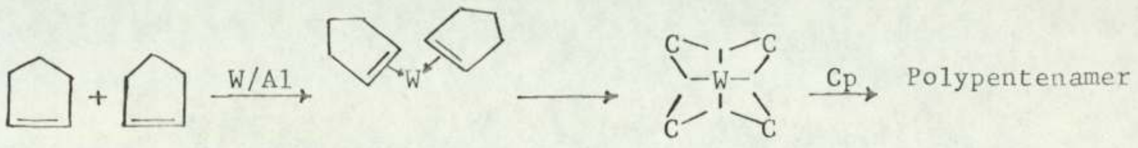


i.e. $Cp + Cp \xrightarrow{W/Al} (Cp)_2$

$$\left.\begin{array}{llll}
(Cp)_2 & + \; Cp & \xrightarrow{W/Al} & (Cp)_3 \\
(Cp)_2 & + \; (Cp)_2 & \xrightarrow{W/Al} & (Cp)_4 \\
(Cp)_m & + \; (Cp)_n & \longrightarrow & (Cp)_{m+n}
\end{array}\right| \quad 5\text{-}1$$

Such a polymerisation scheme, wherein chain growth occurred by the formation of macrocyclics, would mean that all the double bonds of the polymer maintained their activity throughout the polymerisation and the resultant molecular weight dependence would be expected to be similar to that of a condensation type polymerisation (chapter 3) wherein a gradual linear increase in the molecular weight with conversion of monomer to polymer would be found. Since such a molecular weight dependence was not apparent in the ring opening polymerisation of cyclopentene then the suggestion that the transition state complex can be described as a quasi cyclobutane ring must be viewed with scepticism especially if the double bond maintains its activity during the polymerisation.

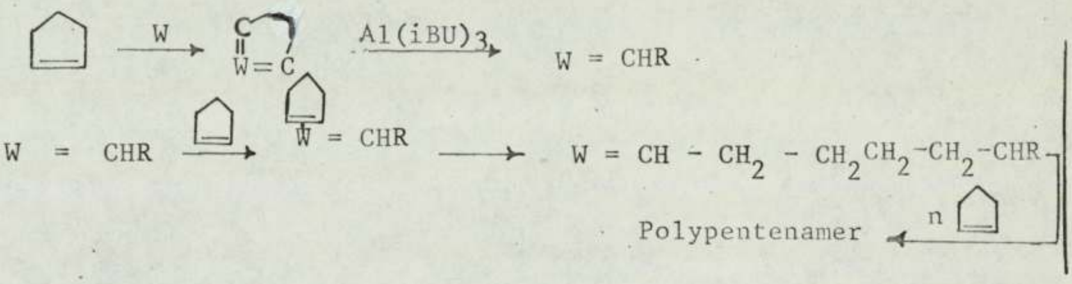
(II) <u>The multi centred tetracarbene species</u>: Two monomer units were considered to coordinate to the tungsten where reaction occurred to form a bis-olefin complex which rearranged to a multi-centred organometallic system. This species then promoted polymerisation by co-ordination of further monomer units (5-2) or polymer chains.



5-2

The essential difference between this proposal and (I) above is that a cyclic structure is never actually formed as an intermediate; instead a dynamic bond formation and breakage occurs. Notwithstanding this basic difference the overall mechanism which could include such a multicentred tetracarbene species would be similar kinetically to 5-2 above leading to a condensation type polymerisation with its associated molecular weight dependence.

(III) <u>The species containing a tungsten-carbon double bond</u>: It was suggested that the cyclopentene molecule reacted with the tungsten atom to form a metallocyclic which could produce a metal carbene in the presence of the aluminium compound. The metal carbene which contains a tungsten to carbon double bond and a vacant co-ordination site may propagate the polymerisation reaction by co-ordination of further monomer units followed by their insertion into the growing chain. The mechanism of these reactions can be illustrated by: 5- 3 -



5-3

Since cyclic organometallic compounds and metal carbenes were well characterised species and also additions to olefins common, this proposal required no unusual theoretical explanations. Furthermore the polymerisation scheme - 5-3 - describes a reasonable kinetic chain process which is in agreement with the molecular weight dependencies found in the present studies. Although the evidence in support of this mechanism is not conclusive it is probably that the polymerisation occurred by formation of the metal carbene followed by co-ordination of monomer to the tungsten atom and insertion into the growing chain.

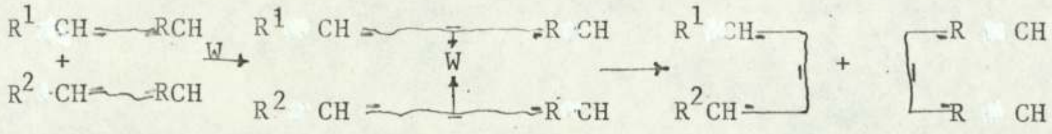
This simple description of the polymerisation mechanism adequately explains the fact that high molecular weight polymer was formed in the initial stages in the reaction. However, as reported in Chapter 3, the initial increase in the number average molecular weight of the polymer was followed by a decrease with time. The gel permeation chromatographic study of the polymer showed that the polymers had bimodal molecular weight distributions. The positions of the peaks in the molecular weight distribution curves which corresponded to low and high molecular weight polymer, remained constant throughout the polymerisation but it was seen by inspection of the curves and by measurement of the area under each peak that there was an increase in the amount of low molecular weight material relative to the amount of high molecular weight material as the polymerisation proceeded. This increased importance of the lower molecular weight polymer fraction explains the fall off in the number average molecular weight of the polymer produced but not how the bimodal molecular weight distribution arose.

Two explanations for this occurrence are feasible: -

(I) the polymerisation system contains two species that are capable of polymerising cyclopentene by two polymerisation reactions with independent rate constants for the propagation and termination reactions;

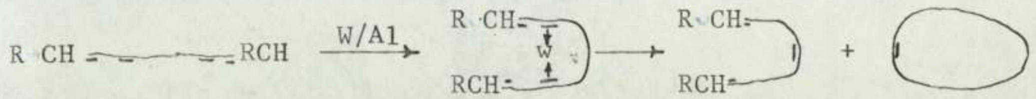
or (II) the polymerisation process occurs and is then followed by a catalytic depolymerisation reaction.

The latter proposal which has been made by Chauvin et al[68] must be considered. If a depolymerisation reaction occurred in polymer which is formed in a kinetic chain process (i.e. open chain polymer) then the type of reactions which would occur can be described by 5-4 and 5-5.



5-4

This type of intermolecular depolymerisation reaction which is random in nature could lead to a broadening of the molecular weight distribution which would however still remain monomodal. If an intramolecular depolymerisation occurred by coiling of the polymer chain on itself then the process could be represented by - 5-5 - whereby:



- 5-5

This would result in the formation of a lower molecular weight open chain polymer together with a lower molecular weight macrocyclic. However since this process would again be random the resultant molecular weight distribution would remain monomodal but would be skewed to the lower molecular weight side. Thus it is unlikely that the bimodal molecular weight distribution of the polymerisation products can be explained in terms of a depolymerisation reaction.

The proposal that two independent propagating species are present in the system is therefore probably correct and it is likely that these could involve the tungsten atom in different oxidation states. This is acceptable since the oxidation state studies (chapter 3) have shown that the tungsten existed as a mixture of at least two oxidation states in the presence of cyclopentene. Without attempting to define the structure of these active species if they are represented by W(I) and W(2) then a simple polymerisation scheme can be constructed wherein: - 5-6.

$$\left.\begin{array}{l} WCl_6 + Cp \longrightarrow W(Cp)_x \xrightarrow{Al(iBu)_3} W(I) \\ \qquad W_1 \longrightarrow W_2 \\ W_1 + Cp \longrightarrow \text{Polypentenamer} \\ W_2 + Cp \longrightarrow \text{Polypentenamer} \end{array}\right| \quad 5\text{-}6$$

It has been proposed (chapter 3) that the ratio $\frac{W_1}{W_2}$ changes during the course of the polymerisation thereby producing a change in the molecular weight distribution as expressed by $\frac{\int^t R_p(1)dt}{\int^t R_p(2)dt}$ and thus leading to the increased importance of the lower molecular weight polymer fraction. The change in the ratio $\frac{W_1}{W_2}$ can be brought about by a process wherein W_1 and W_2 were formed at the outset and subsequently one or other of these produced an inactive species by a process wherein: 5-7

$$\left.\begin{array}{lcl} WCl_6 + Cp & \longrightarrow & W(Cp)_x \xrightarrow{Al(iBu)_3} W_1 + W_2 \\ W_1 & \longrightarrow & \text{inactive species} \\ \text{or } W_2 & \longrightarrow & \text{inactive species} \end{array}\right| \quad 5\text{-}7$$

Alternatively the treatment in 5-6 is possible whereby W_1 is formed at the outset and this subsequently goes to W_2.

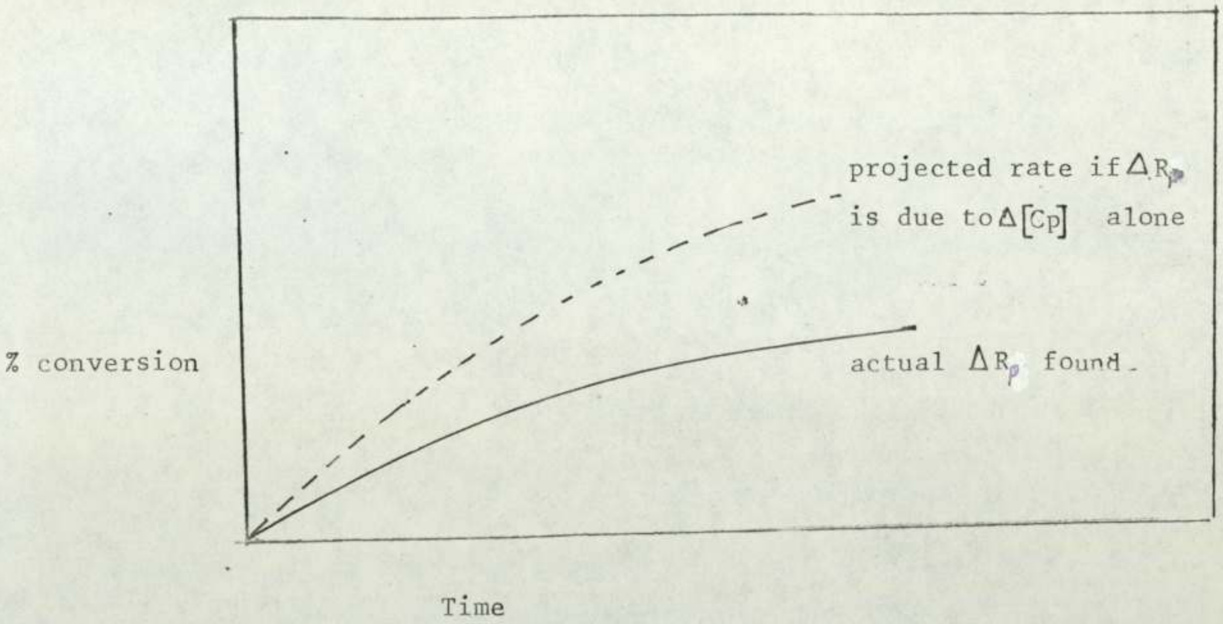
The foregoing reactions merely suggest that one or other of the propagating species was consumed during the course of the polymerisation. Evidence in support of this proposal has been recently revealed[70] wherein recent studies on the polymerisation reaction have shown that:

(1) the rate of polymerisation was found to decrease rapidly with conversion

and (2) the overall decrease in the rate was greater than that which would be expected as deriving from the decrease in monomer concentration during the polymerisation - thus- figure 5-1:

Figure 5-1

Projected and actual conversions with time of cyclopentene to polypentenamer



Therefore the polymerisation of cyclopentene can be achieved by a bimetallic catalyst system by a mechanism which can be tentatively described as a kinetic chain process wherein two species can propagate independent polymerisation reactions to produce a polymer which has a bimodal molecular weight distribution. The role of the tungsten is to provide a site where monomer units can co-ordinate and form a metal carbene by a reaction with the aluminium. Propagation of the polymerisation occurs by co-ordination of further monomer units followed by their insertion into the growing kinetic chain at the metal-carbon double bond. The role played by the aluminium is not well defined but this will be discussed later in this chapter in conjunction with the role of the oxygen in the monometallic catalyst system.

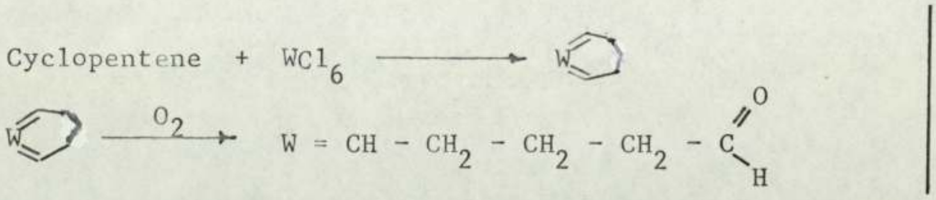
5-2 The polymerisation of cyclopentene by the monometallic WCl_6/O_2 catalyst system

Investigations showed that tungsten hexachloride alone was incapable of polymerising cyclopentene but when oxygen was added to the WCl_6/ cyclopentene mixture a rapid polymerisation ensued. The addition of oxygen was found to be most effective when added to a WCl_6/ cyclopentene mixture which had been allowed to age for a period of ~2 days. During this ageing period the mixture became clear and an oily precipitate formed at the base of the reaction flask indicating that some reaction between the cyclopentene and the tungsten hexachloride had occurred.

Inspection of the infra-red spectrum of the polymer produced, in the WCl_6/O_2/cyclopentene polymerisation system, showed that it had the same structure as that produced in the bimetallic catalysed reaction: i.e. a predominantly trans polypentenamer. It was therefore considered likely that the monometallic system produced polymer by a mechanism which was similar in nature to that proposed for the bimetallic catalysed polymerisation with oxygen acting in a role which was similar to that played by aluminium tri-isobutyl in the latter. The results of the oxidation state studies were consistent with this proposal because it was found that the oxygen did not act to oxidise the tungsten atom after addition to the system.

The oxidation studies (chapter 4) on the monometallic system were carried out using cis-2-pentene instead of cyclopentene because of the difficulties involved in removing the polymer from the mixture after oxygen addition. However the similarities in the oxidation states of tungsten in the WCl_6/Cp system before the addition of aluminium tri-isobutyl (chapter 3) and that of the tungsten in the WCl_6/cis-2-pentene system before the addition of oxygen and indeed the overall similarities between the metathesis of acyclic olefins and the ring opening polymerisation reactions initiated by the same catalyst system suggested that a direct comparison of oxidation state data in the two systems could be made.

The U.V./visible spectroscopic studies on the WCl_6/cyclopentene reaction mixture showed an absorbance at 510 mμ which decreased with time and when oxygen was added to the system the absorbance peak was completely removed. It was believed that the decrease in the 510 mμ absorbance peak with time was linked to the concurrent appearance of the oily precipitate at the base of the photocell and when this is considered alongside the non-oxidising role played by the oxygen a reaction scheme can be suggested such as: 5-8



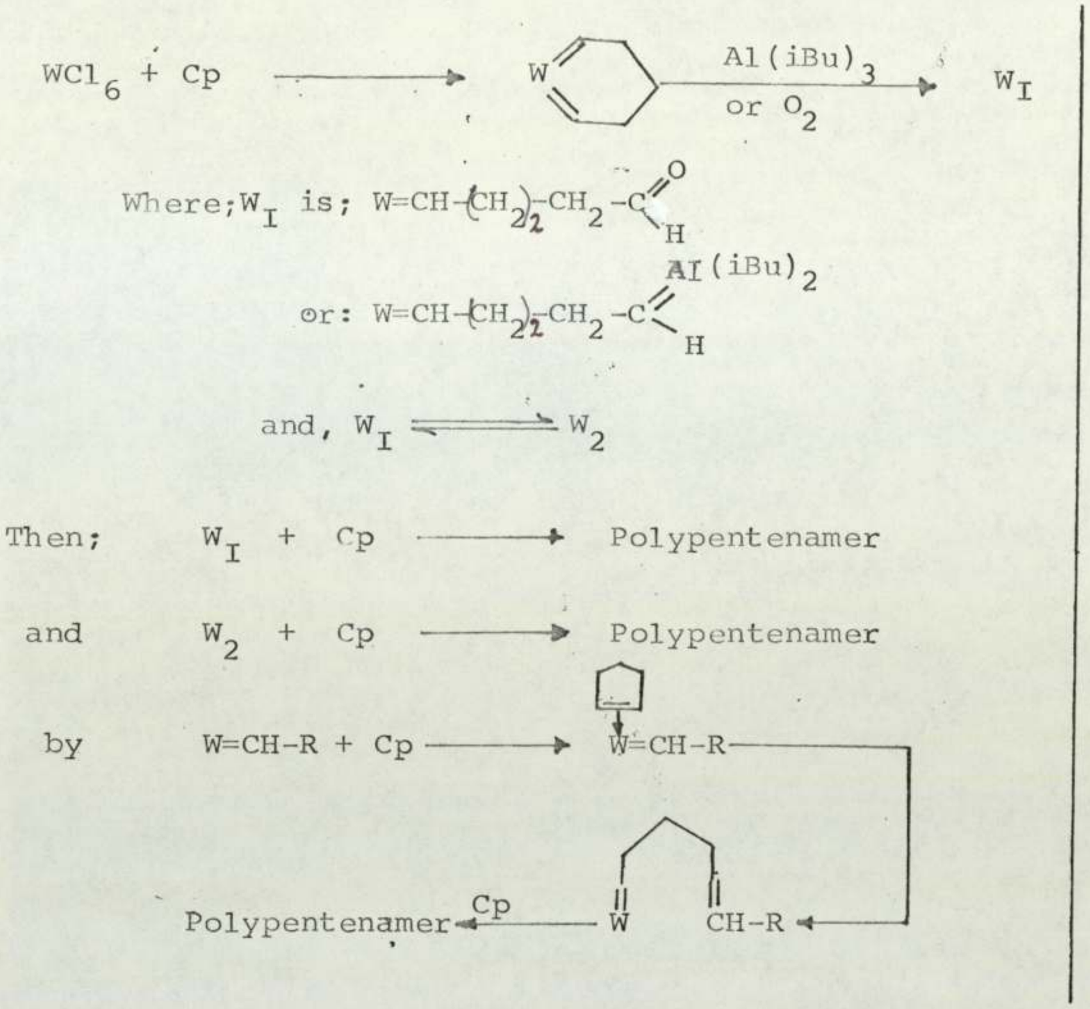
5-8

It was believed that the formation of the cyclic organometallic produced the precipitate at the base of the flask and the role of the oxygen is as shown (5-8). Acting in this manner the oxygen would produce (1) a W = C double bond

and (2) a vacant co-ordination site on the tungsten atom. Thus is it quite feasible that the polymerisation can occur by a process which is similar to that proposed for the bimetallic initiated reaction i.e. by a kinetic chain mechanism wherein the initiation step is the production of a metal carbene and propagation occurs by co-ordination of monomer units to the tungsten atom followed by insertion into the growing kinetic chain.

A role for the aluminium tri-isobutyl in the bimetallic catalyst system can now be postulated since it is likely to act in a manner which is similar to the oxygen in the monometallic system.

If the construction in 5-8 is expanded then a scheme for the polymerisation reaction can be made wherein - 5-9.



5-9

5-3 Molecular orbital treatment of the polymerisation of cyclopentene by tungsten based catalysts.

In the foregoing discussion the polymerisation of cyclopentene was described as a kinetic chain process wherein the initiation step involved the formation of a tungsten carbene species. Co-ordination of monomer to the tungsten atom was then followed by insertion of the monomer into the growing kinetic chain. The bonds formed and cleaved in the polymerisation can be examined in terms of orbitals available. These can be defined as:

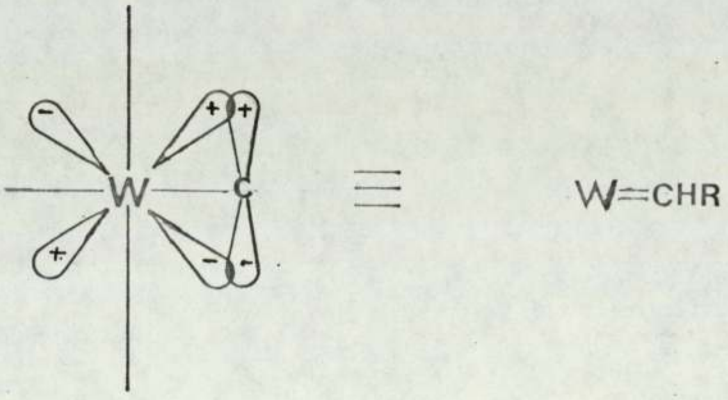
(1) Tungsten - T_{2g}, Eg. orbitals

(II) the $=\mathrm{CH}\diagdown_{R_n}$ double bond - the P_z orbital perpendicular to the plane of the Sp^2 hybrid orbital and (III) the incoming olefin - the π orbital which has the correct symmetry for overlap with the dz^2 orbital of the tungsten atom and an unfilled π^* anti-bonding orbital.

The formation of the tungsten carbene species can be explained by overlap of the d_{xz} orbital of the tungsten atom and the P_z orbital of the carbon atom, both of similar symmetry, thus forming a tungsten to carbon π bond. The tungsten atom, in a reduced oxidation state, contributing one electron as does the carbon atom to form the electron pair bond. This can be represented by figure 5-2.

Figure 5-2

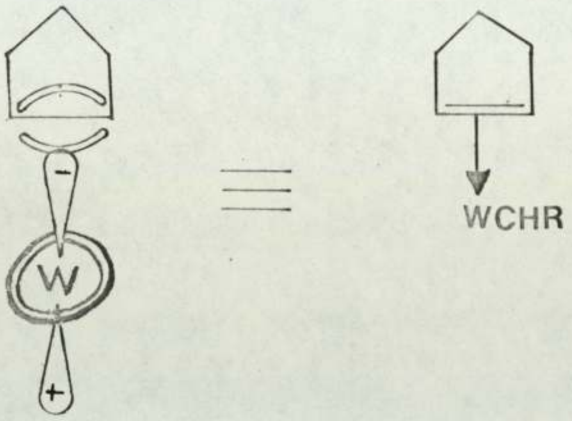
Molecular orbital representation of the formation of the tungsten carbene



The co-ordination of the reacting olefin to the tungsten atom, by analogy to the Ziegler Natta system, can be postulated to occur by overlap of the tungsten dz^2 orbital and the π orbital of the incoming olefin as shown in figure 5-3.

Figure 5-3

Molecular orbital representation of the co-ordination of monomer to the tungsten atom

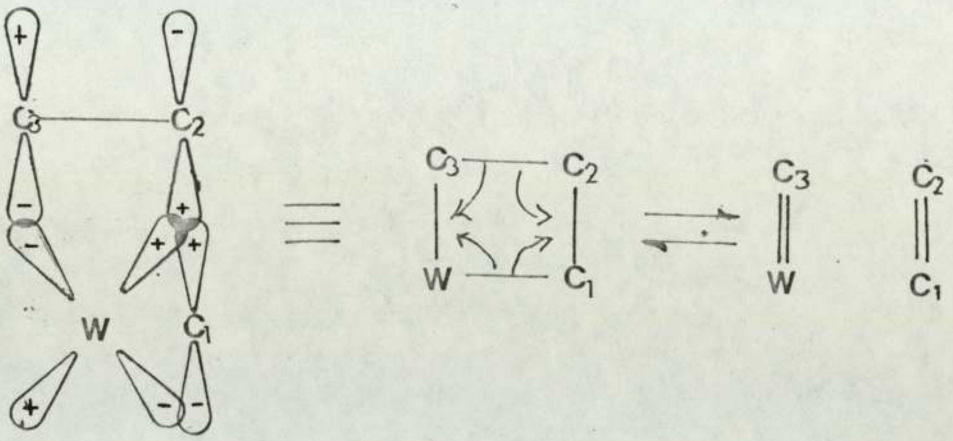


Thus the formation of the tungsten carbene and the mode of co-ordination of the monomer to the tungsten atom can be described in molecular orbital terms.

The olefin also possesses a π^* antibonding orbital that has the correct symmetry for overlap with the d_{xz} orbital of the tungsten atom which in turn can overlap with the P_z orbital of the carbon. A diagramatic representation of the process is shown in figure 5-4.

Figure 5-4

Molecular orbital representation of the insertion of monomer into the kinetic chain at the tungsten-carbon double bond

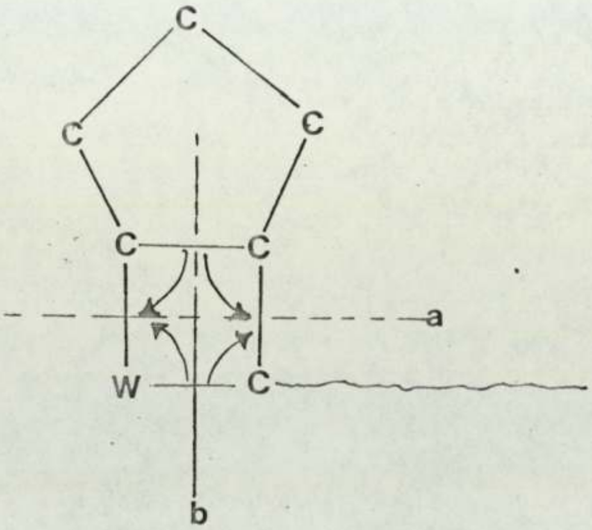


If the carbon atoms are labelled as shown, it can be envisaged that the two electrons forming the π , W=C, bond can be used to form a ∢ bond between C_1 and C_2 and simultaneously the two electrons in the molecular orbital formed from the overlap of the olefin π bond and the tungsten d_z2 orbitals provides electrons for a W-C_3, ∢ bond. The breakdown of the metallocyclic is also shown in the figure and it is assumed that the whole process is of a reversible nature.

In a monomer addition step the process can be represented by figure 5-5.

Figure 5-5

Addition of monomer to the tungsten carbene species - the intermediate involved

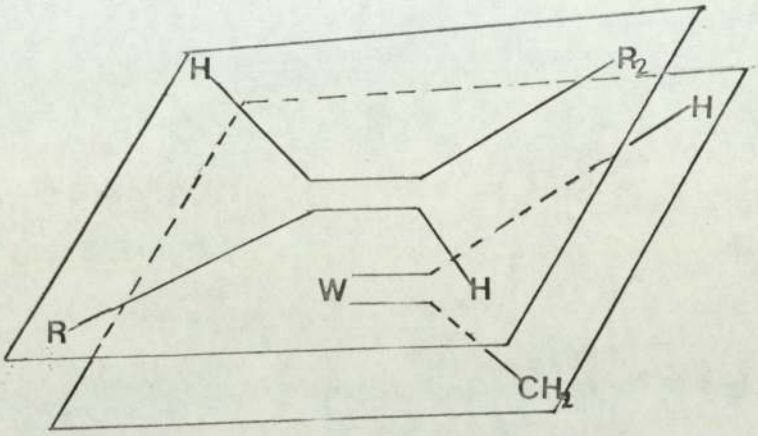


If bond cleavage occurs along the 'a' axis the initial reactants are reproduced however cleavage along the 'b' axis would result in insertion of the monomer unit into the growing kinetic chain and reproduction of a site for further monomer addition.

Having accounted for the mode of formation of the tungsten carbene species and described the olefin addition step it is further possible to explain the polymer structure in terms of steric hindrance factors if the process is represented by figure 5-6.

Figure 5-6

Co-ordination of monomer to the tungsten carbene to produce trans polypentenamer



The plane of the olefin and the plane tungsten carbene are coplanar as shown in figure 5-6. The polymer is produced by the chain mechanism described previously so that the R_2 and the $CH_2^{\cdot}$ groups are trans to each other thus producing the trans polypentenamer.

Thus cyclopentene can be said to be polymerised to trans polypentenamer by a kinetic chain process involving initiation by metal carbene formation and propagation by insertion of monomer at the tungsten to carbon double bond.

CHAPTER 6

Further work

1) It is not clear if the chain growth in the polymerisation of cyclopentene by the catalyst systems, described in this work, occurs by macrocyclic formation or by addition of monomer to an open chain. This could be easily tested in the case of the WCl_6/O_2 catalyst system by the use of radioactive tracer techniques to determine if oxygen is present in the chain. Alternatively other oxidising agents e.g. Cl, S could be tested to determine their ability to activate the polymerisation in the WCl_6/cyclopentene system and subsequent radioactive tracer techniques would provide information on their presence in the polymer chain.

The (radioactive) isotopes O^{18}, Cl^{37}, S^{34} are readily available and this work could be carried out using the polymerisation techniques described in 2-5B.

2) Kinetic studies on the WCl_6/O_2/cyclopentene system could be carried out using the dilatometric techniques. Various concentrations of the W/O_2 catalyst could be used to determine if oxygen is an effective activator when present in very low concentrations.

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APPENDIX I

PUBLISHED WORK

SOME MOLECULAR WEIGHT STUDIES IN THE POLYMERIZATION OF CYCLIC OLEFIN

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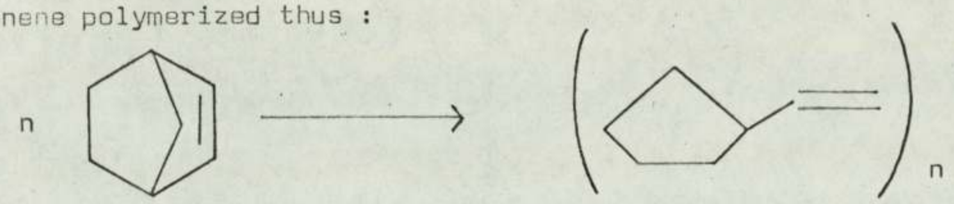
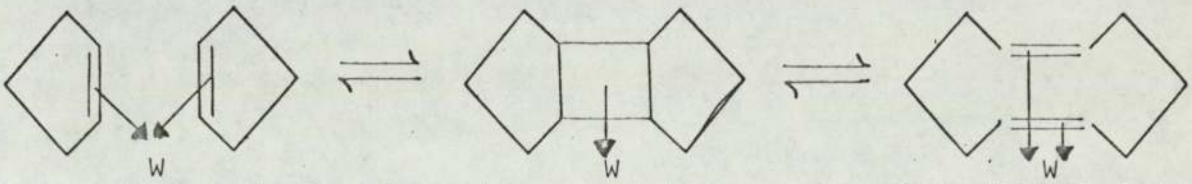
I-INTRODUCTION

The disclosures by Eleuterio (1) and subsequently Natta (2) of W/Al based catalysts for the polymerization of cyclic olefins have stimulated a great deal of industrial and academic research. These catalyst systems are notoriously inefficient leading only to low conversions of cyclopentene to polypentenamer in prolonged reaction times and as such are of no commercial significance even though the polymer produced from cyclopentene has considerable technological advantages over other synthetic rubbers. Interest in the subject of ring opening polymerization gathered momentum when Farbenfabriken Bayer disclosed a series of activators for the polymerization of cyclopentene and overcame many of the commercial disadvantages of the process (3).

Transition metal based catalyst systems form the basis of some extremely interesting research and many mechanisms have been proposed to account for the activity of such catalyst systems. However, it is generally agreed that the mechanism of polymerization by ring opening is different from the polymerization of acyclic α-olefins. Natta (2) first suggested that the ring-opening polymerization of cyclic olefins proceeded by scission of the single bond α to the double bond since norbornene polymerized thus :



However, it was the subsequent work of Calderon et al (4) on the metathesis of olefins which suggested that polymerization proceeded by way of scission of the C = C double bond. It was postulated that the intermediate in a general mechanism is an unstable quasi cyclobutane ring coordinated to a tungsten atom :



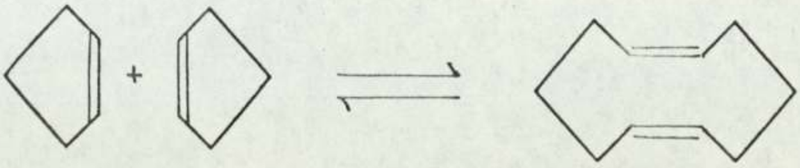
Although a great deal of work has been carried out on the polymerization of cycloolefins the natures of the complexes and propagation steps involved in the polymerization are still unclear.

A great deal of information concerning the nature of a polymerization process may often be obtained from a study of the molecular weights of polymers produced in the process. It is perhaps an appropriate time just to remind ourselves of the types of molecular weight dependences that can be found in polymerization systems. The anionic living polymerization of styrene is characterized by the production of narrow molecular weight distribution polymer

$$\left(\frac{M_n}{M_n} < 1.1 \right)$$

since the rate of initiation in such polymerizations is of the same order as the rate of propagation. Moreover since no termination or transfer reactions are involved in such systems the degree of polymerization increases with the extent of conversion. If termination and transfer reactions are absent in the polymerization of cyclic olefins and the rate of initiation is fast the system might be expected to show molecular weight characteristics similar to those of the anionic living polymerization system.

Some of the general mechanisms proposed for the polymerization of cyclic olefins would suggest that the system should show the kinetic dependences of a typical condensation polymerization since it has been proposed that a double bond may maintain its activity towards metathesis throughout the polymerization and the polymerization may be described by a series of equilibrium reactions :



$$\begin{array}{lcll}
M & + & M & \rightleftharpoons & M_2 \\
M_2 & + & M & \rightleftharpoons & M_3 \\
M_2 & + & M_2 & \rightleftharpoons & M_4 \\
M_n & + & M & \rightleftharpoons & M_n + 1 \\
M_n & + & M_m & \rightleftharpoons & M_{n+m}
\end{array}$$

All these reactions will of course involve the catalyst but they are essentially similar in kinetic nature to the polycondensation systems adequately described by Flory (5). Some essential features of these systems are :

(i) the number average degree of polymerization increases with the extent of conversion as shown in Figure 1 ;

(ii) during the polymerization the molecular weight distribution broadens such that :

$$\bar{x}_n = \frac{1}{1 - p} \qquad \bar{x}_w = \frac{1 + p}{1 - p}$$

where p is the fraction of reactive groups which have been converted.

(iii) it is finally worth noting the shape of a typical distribution curve (Fig. 1) since it is of a mono model type.

The third and final molecular weight dependence to be discussed is that typical of a conventional free radical system wherein such systems :

$$\begin{array}{llll}
\text{Initiator} & \rightarrow & 2R_o^{\cdot} & \left.\begin{array}{l} k_d \\ k_i \end{array}\right\} R_i \\
R_o^{\cdot} + M & \rightarrow & M_1^{\cdot} & \\
M_n^{\cdot} + M & \rightarrow & M_{n+1}^{\cdot} & k_p \\
M_n^{\cdot} + M_m^{\cdot} & \rightarrow & \text{Polymer} & k_t
\end{array}$$

\+ transfer reactions

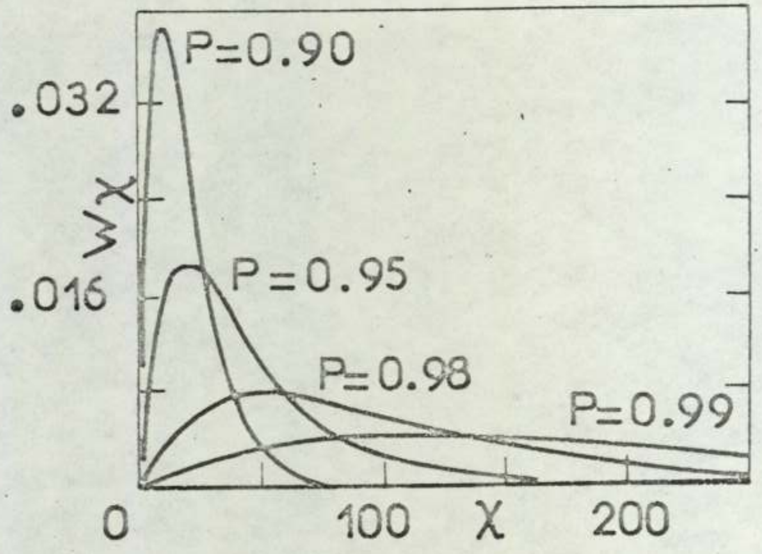


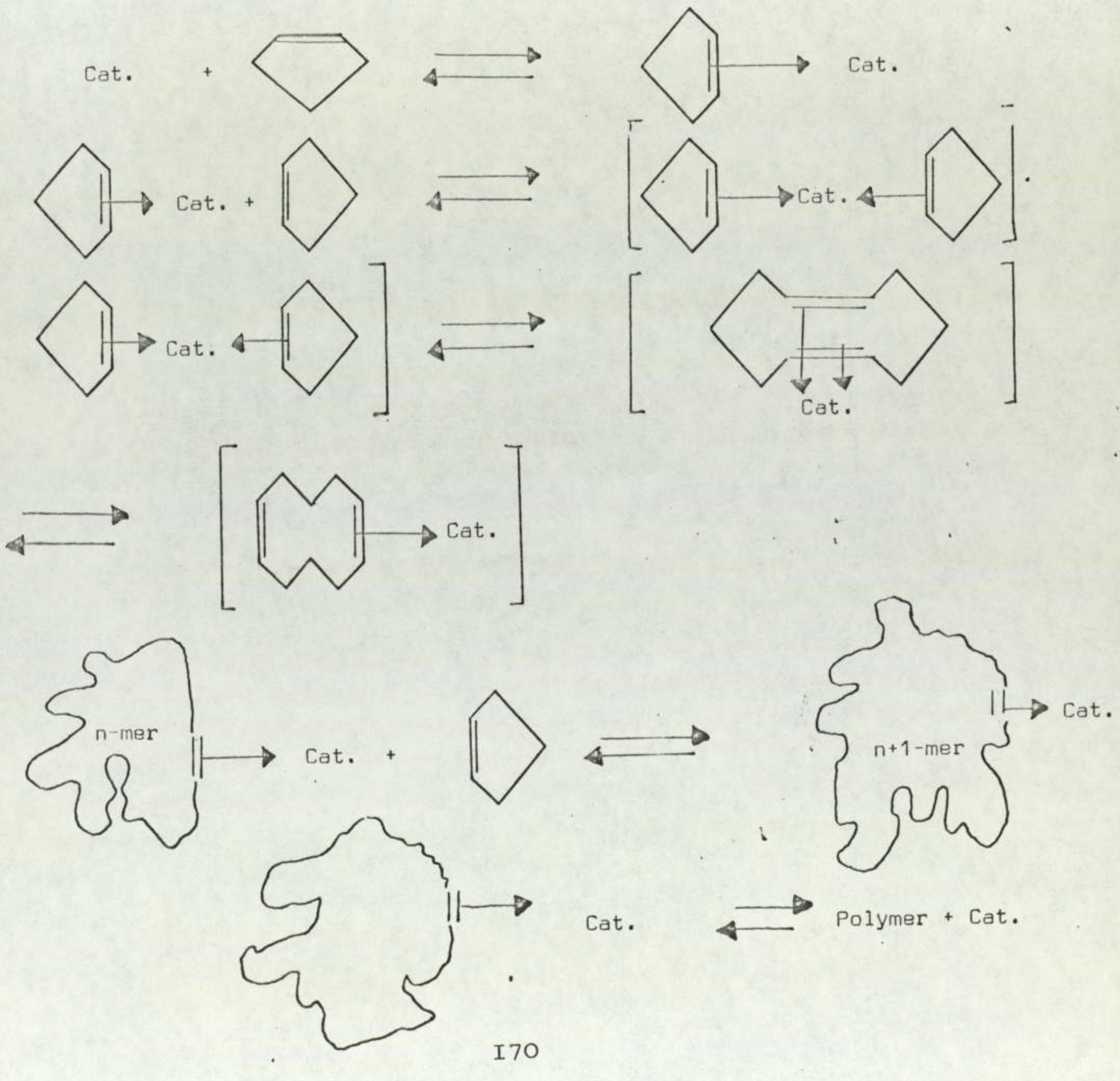
FIGURE 1 : WEIGHT FRACTION OF CHAIN MOLECULES IN LINEAR CONDENSATION POLYMERS FOR SEVERAL EXTENTS OF REACTION

Reproduced from Principles of Polymer Chemistry by P. J. FLORY nlike the condensation polymerization the degree of polymerization of a free radical polymer is kinetically controlled by the termination steps. The kinetic hain length (ν) in such processes is given by :

$$\nu = \frac{k_p^2 \, (M)^2}{2 \, k_t R_p} = \left(\frac{k_p^2}{2f \; k_d k_t} \right)^{1/2} \frac{(M)}{(I)^{1/2}}$$

hich in the absence of transfer is related to molecular weight. The lifetime of propagating radical (other than in an emulsion polymerization) is relatively short (10^{-3} - 10^{-4} sec) and within this period polymer of high molecular weight is produced. Accordingly in the free radical polymerization if $\bar{x}_n$ is plotted against time or conversion any increase is due only to a fall of polymerization with conversion.

If the ring opening polymerization of cyclopentene follows the following sequence :



the molecular weight conversion curves might be expected to be similar to those for free-radical polymerizations if the rate constant k_p is high. It was this reasoning that led us to investigate the dependence of molecular weight on conversion as a step in elucidating the mechanism of polymerization. I would like to stress at this point that our investigations so far have been only of a preliminary nature but we believe that we have some interesting features to report.

EXPERIMENTAL

The solvents and monomer used in these polymerizations were subjected to extremely rigorous drying procedures. Both solvents and monomer (cyclopentene) were dried initially over activated alumina and then distilled under high vacuum into flask containing aluminium triethyl which was used as a final drying agent. Solvent and monomer were then distilled under vacuum into a round-bottom reaction flask. Tungsten hexachloride was prepared by the reaction of hexachloropropene on tungstic oxide :

$$WO_3 + CCl_3 - CCl = CCl_2 \rightarrow WCl_6$$

and used as a solution in dry distilled toluene. Aluminium tri-isobutyl was used as a dilute solution in dry-vacuum-distilled toluene.

POLYMERIZATION OF CYCLOPENTENE

Polymerizations of cyclopentene were carried out in a 25ml round bottom flask fitted with a suba-sealed side arm and a tap. The required volumes of solvent and monomer were distilled under high vacuum into the flask and the catalyst components were added in turn to the flask by hypodermic syringe. The polymerization vessel was maintained at a constant temperature in a thermostat bath. Polymerizations were terminated by addition of water, usually as very wet solvent, and the polymer was precipitated by addition of the solution to methanol.

NUMBER AVERAGE MOLECULAR WEIGHT

Solutions of polypentenamers were prepared in toluene and the number average molecular weights determined using a high speed membrane osmometer.

GEL PERMEATION CHROMATOGRAPHY

GPC traces were obtained using 0.1 - 0.25 % solution of polypentenamer in chloroform which was the solvent in a Waters high speed liquid chromatograph fitted with 2 24ft 10^4 Å styragel column. The effective length of the column could be increased by using the apparatus in a recycle mode.

DETERMINATION OF THE OXIDATION STATE OF TUNGSTEN

Samples of the polymerizate were hydrolysed in NaOH and oxidation state of W determined by titration with $Ce_2(SO_4)_3$ under nitrogen.

RESULTS

All preliminary polymerizations were carried out using a 20 % solution of cyclopentene in toluene as solvent. The catalyst components WCl_6 and $AliBu_3$ were added in order to the solution of monomer in cyclopentene such that the molar ratio W:Al:Cl = 1:2:1000. Samples were obtained for molecular weight measurement either :

a) by carrying out a series of polymerizations under identical conditions for a number of reaction times, or

b) by removing samples of polymer solutions from a reaction vessel at various times during a polymerization.

Although for our purposes this latter technique was the more desirable it was often impossible to follow since the reaction solution became extremely viscous.

The change in number average molecular weight is recorded in figure 2. This figure shows the change in number average molecular weight with time during the course of a typical polymerization. Two features are of particular interest in this slide,

1 - The steep rise in $\overline{M}_n$ during the initial stages of a polymerization is considered to be a real effect and might be correlated with a condensation type mechanism.

2 - An intriguing feature was that this steep rise in $\overline{M}_n$ vs time was followed by a fall in $\overline{M}_n$ with time. At first this effect was found to be rather mysterious since it does not fit the effects found in a free radical, condensation or ionic type of mechanism and it was only subsequent investigations which convinced us that this effect was real.

The measurement of $\overline{M}_n$ and $\overline{M}_w$ molecular weights although desirable has for some time been recognized as having limitations since their measurement alone provides no information concerning the nature of the distribution of molecular weights. However we are fortunate to have at our disposal gel permeation chromatography. To investigate the peculiar $\overline{M}_n$ effects we then decided to obtain GPC traces for the polymers obtained in these experiments.

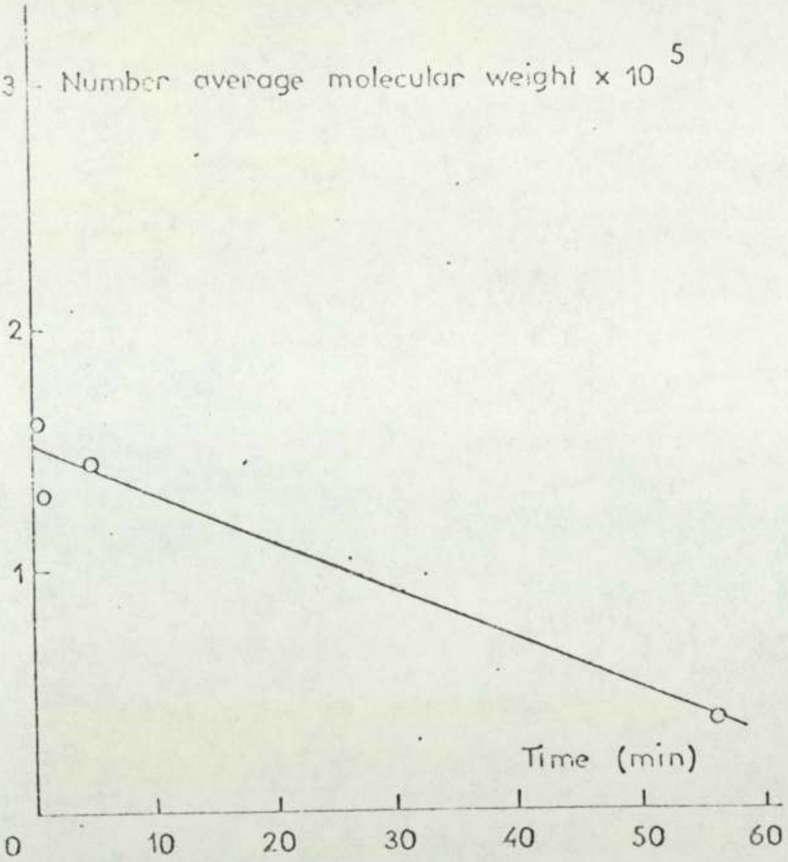
A peculiar effect was immediately apparent when the polymer obtained after 1 hour was investigated. The GPC trace is shown in figure 3. Unlike the polymer obtained in conventional polymerization processes such as free radical, condensation or anionic, a bimodal distribution was obtained. It was then decided that each of the samples obtained in this series of experiments should be analysed by GPC, and of particular interest is the GPC trace obtained for the polymer prepared in the initial stages of the process. A typical GPC trace obtained for polymer after 1 minute is shown in figure 4. Although the polymer again shows a bimodal type distribution, the proportion of the lower molecular weight material is less and this accounts for the observed decrease in $\overline{M}_n$ with time.

Having accounted for the decrease in $\overline{M}_n$ with time one has to ask why the distribution is of the bimodal type found. One could postulate various mechanisms to account for this effect.

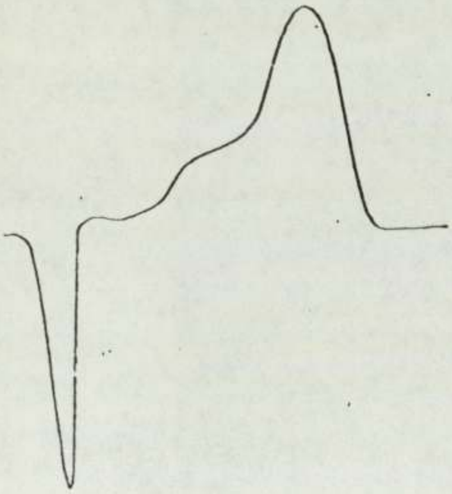
(i) high molecular weight polymer is formed initially and followed by a scission process to form low molecular weight material. One would expect this scission process if it occurs to be a random process resulting perhaps in an increase in the breadth of the distribution which would be expected to remain a monomodal type.

(ii) There may be two types of propagation reactions. If the kinetic parameters of these independent processes are different then one might expect to prepare a polymer which is effectively a mixture of two monomodal distribution polymers. The overall rate of polymerization R_p would be given by :

$$R_p = R_{p(1)} + R_{p(2)}$$



ig. 2 : VARIATION OF NUMBER AVERAGE MOLECULAR WEIGHT WITH TIME



GURE 3 : GEL PERMEATION CHROMATOGRAPH OF SAMPLE AFTER 60 MINS.

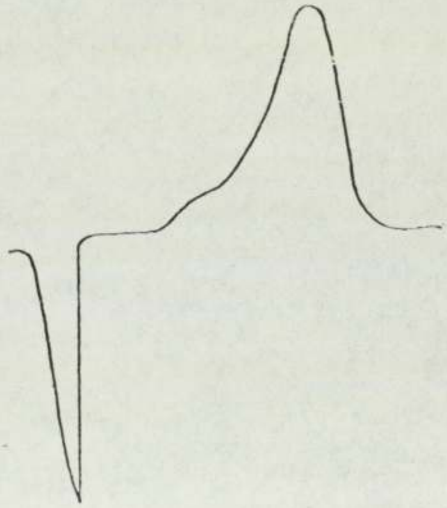


FIGURE 4 : GEL PERMEATION CHROMATOGRAPH OF SAMPLE AFTER 1 MIN

[illegible] One follows the oxidation state of W during the course of a [illegible] experiment when the oxidation state of W is not an integral value [illegible] has shown in table 1. Hence it is possible that W is present in the system as a mixture of oxidation states and this could account for the bimodal distribution. This is similar in fact to Dr Olivé's explanation yesterday of the trimodal distribution found for polymers prepared from a mixture of Ti(IV), Ti(III) and Ti(II). However this alone is not sufficient to account for the observed change in the relative amounts of high to low molecular weight material.

1 - During the course of olefin the (W_x) may change by some type of reaction to inactive state or even the state that produces low m. wt. One would then expect a change in ratio of $R_{p(1)}/R_{p(2)}$ which could cause a change in the nature of the distribution.

2 - It is also possible to suggest that the $R_{p(1)}$ and $R_{p(2)}$ are reactions which have different orders with respect to the monomer, hence if

$$R_{p(1)}\ \alpha (M)^a \qquad R_{p(2)}\ \alpha (M)^b \qquad a < b$$

during the course of the reaction then there will be a change in the ratio of $R_{p(1)}/R_{p(2)}$ determined by the values of a and b. A simple way to test this postulate is to observe the effect of $(M)_{init}$ on the distribution at a particular conversion. This work is in hand at the moment and without being adamant it would appear to bear out these postulates. If this is true then the system poses many more questions than at first thought.

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TABLE 1 : Changes in the mean oxidation state of tungsten during the reactions involved in the polymerization of cyclopentene

Reaction conditions.	Mean oxidation state of tungsten
(1) WCl_6 solution	6.0
(2) WCl_6 + cyclopentene after 1 min	5.1
(3) WCl_6 + cyclopentene after 20 min	4.3
(4) (3) + $AliBu_2OiBu$	4.3
(5) (4) after 2 h	4.4

European Polymer Journal, Vol. 12, pp. 93 to 94. Pergamon Press 1976. Printed in Great Britain.

TUNGSTEN HEXACHLORIDE ALONE AS A CATALYST FOR THE METATHETIC POLYMERIZATION OF CYCLIC OLEFINS

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(*Received* 18 *April* 1975)

Abstract—The polymerization of cyclic olefins may be initiated by tungsten hexachloride alone. The rate of polymerization is less than that normally obtained with bimetallic catalysts but the equilibrium conversion monomer is of the same order.

INTRODUCTION

The polymerization of cyclic olefins to polyalkenamers gives products representing a novel class of polymers obtained by reactions based upon the metathesis of linear olefins. Such reactions are normally catalysed by complexes derived from the reactions of tungsten halides and aluminium alkyls or alkyl halides [1,2], although catalysts based upon other transition metal compounds have been reported. All the catalysts for the metathesis reactions have been reported to be bimetallic systems although it is likely that the role of the aluminium alkyl compound is different from that in a conventional Ziegler–Natta polymerization of α-olefins. Indeed, since the complex obtained from the reaction of tungsten hexachloride and aluminium tribromide [3] is a catalyst for the polymerization of cyclic olefins, it has been suggested that the aluminium compound behaves as a simple Lewis acid in these reactions, rather than producing a transition metal–alkyl bond [4]. We now report that such two-component catalyst systems are not essential for the polymerization of cyclic olefins since tungsten hexachloride alone acts as a metathesis catalyst.

EXPERIMENTAL

Tungsten hexachloride was purified by refluxing the commercial material with hexachloropropene for 30 min. The suspended pure tungsten hexachloride was filtered under vacuum and then washed several times with hexane previously dried by distillation under high vacuum from aluminium triethyl. The pure dry tungsten hexachloride was then dissolved in rigorously dried toluene.

All monomers and solvents used in the experiments were rigorously purified by distillation under high vacuum from aluminium triethyl.

All polymerizations were carried out in 50 ml round-bottom flasks fitted with suba-seals and attached to the high vacuum line by means of a greaseless tap. The required volume of monomer was distilled under high vacuum from aluminium triethyl into the flask. Tungsten hexachloride solution was then added by syringe through the suba-seal and the polymerization allowed to proceed at room temperature for up to 15 hr. Polymer was obtained by precipitation of the polymerizate in methanol and whenever possible the product was purified by further precipitation in methanol from a chloroform solution. The conversion of monomer to polymer was estimated by weighing the product.

RESULTS AND DISCUSSION

The polymerization of cyclic olefins by tungsten hexachloride alone resulted from an observation in these laboratories that bicyclo (221) hepta-1,4-diene polymerized extremely rapidly when tungsten hexachloride solution alone was added to the monomer; much heat was evolved during the polymerization, presumably associated with the rapid release of a large ring strain energy. This prompted us to investigate the susceptibility of other monomers to tungsten hexachloride; the results of these experiments are shown in Table 1, which indicates the equilibrium conversion of monomer to polymer for a series of cyclic olefins.

The polymerization of cyclopentene indicates that even relatively strain-free cyclic olefins may be polymerized by tungsten hexachloride alone. Infra-red analysis of the product (Fig.1) indicates that the polymerization occurs by ring-opening since the spectrum of the polymer shows absorbances at 10·35 and 13·8 μm characteristic of *trans* and *cis* carbon–carbon double bonds. A detailed study of the rate of polymerization of cyclopentene is not yet available. It appears that the rate is somewhat slower than that obtained using a conventional two-component catalyst, although the eventual equilibrium conversion of monomer to polymer is of the same order.

Table 1. Equilibrium yields of polyalkenamers obtained by the polymerization of cyclic olefins using WCl_6 as catalyst

Monomer	Conversion (%)
Cyclopentene	65
Cyclohexene	4
Cycloheptatriene	5
1,4-cyclo octadiene	0
1,3-cyclo octadiene	5
Bicyclo (2,2,1,) hepta 1,4-diene	90

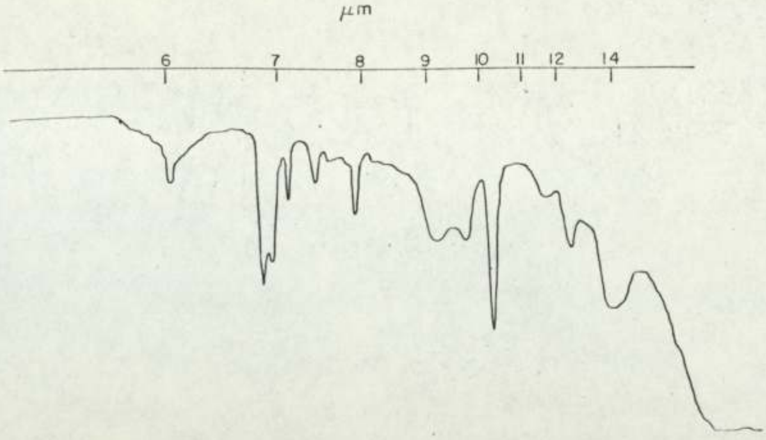
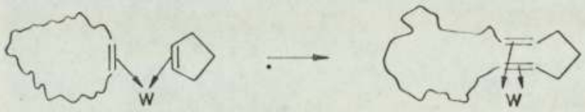


Fig. 1. Spectrum of polypentenamer obtained by polymerization of cyclopentene initiated by WCl_6.

Tungsten hexachloride alone will catalyse the polymerization of cyclopentene to a polypentenamer and presumably the tungsten compound performs the same role as in the bimetallic case and the polymerization takes place via metathesis. A general propagation mechanism can be represented as:



Although not essential for polymerization, the aluminium compound greatly increased the rate of polymerization. The reason for this effect upon the rate could be that these aluminium compounds facilitate the formation of complexes between the cyclic olefin and transition metal atom, when there is formation of a complex between the transition metal and aluminium compounds. It was considered that during the purification procedure an aluminium alkyl might have distilled with the monomer into the reaction vessel, but when lithium butyl was used as a drying agent identical results were obtained.

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