MECHANISTIC STUDIES OF METATHESIS POLYMERISATIONS

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SUMMARY

Three component catalysts have been used to polymerise cyclopentene by a metathesis ring-opening process. The active catalysts were generated from the reaction of WCl_6 with a metal alkyl and a Lewis acid. The metal alkyl was either LiBu or PstLi and the Lewis acids $AlBr_3$ or $SnCl_4$. The three components were either added separately to a solution of cyclopentene to form the catalyst in situ, or reacted together before the addition. Active systems were produced in all cases, except when LiBu, WCl_6 and $SnCl_4$ were reacted together before addition to monomer.

Detailed studies of the dependence of the activity and decay of the catalyst during polymerisation have been carried out for all systems, using dilatometry as a means of studying the conversion of monomer to polymer. The optimum ratio of catalyst components was found to depend upon the combination used, and whether the components were premixed or added sequentially to the solution. When LiBu was used as the metal alkyl, an optimum molar ratio of W:Li was found to be 1:2. Under the same conditions optimum molar ratio of W:Al was also only 1:2, whereas that of W:Sn was 1:4. This difference was ascribed to a greater ability of $AlBr_3$ than $SnCl_4$ to activate a metal carbene generated by the reaction of WCl_6 and LiBu.

It has been proposed that systems prepared by premixing catalyst components generate the active catalyst by a different route to those in which the catalyst was generated in situ. Molecular weight studies by GPC have shown that the reactions most probably generate more than one active catalyst species, but the molecular weight distribution invariably tends towards an equilibrium distribution. It is considered that the systems studied are reasonable models for the $WCl_6/AlBu_3$ and WCl_6/SnR_4 type.

The use of a PstLi cocatalyst in place of LiBu produced equally complex results. In all cases optimum rates of polymerisation of cyclopentene were increased over those already shown for the bimetallic system WCl_6/PstLi by incorporation of the Lewis acid cocatalyst. Polystyrene block-polypentenamer was always formed as a product, together with various proportions of homopolymers. Materials were analysed using a GPC method. A mechanism for the formation of mixed products has been proposed, and an anionic-to-metathesis transformation reaction suggested for the generation of the transition metal carbene. The role played by the Lewis acid as a complexing agent to activate the reaction has also been suggested.

KEY WORDS: BLOCK COPOLYMERS, CYCLOPENTENE, LEWIS ACIDS, LiBu, STYRENE, TRANSFORMATION REACTION.

To my family

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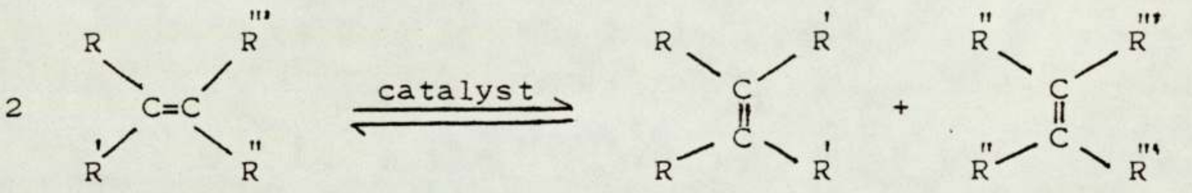
INTRODUCTION

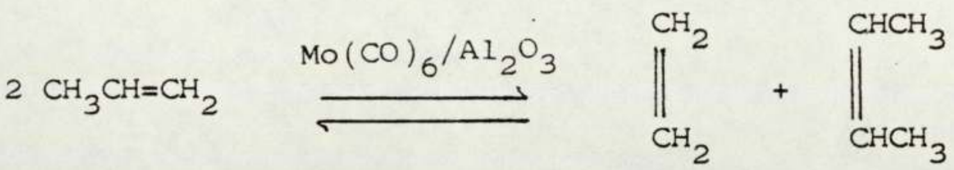
1.1 INTRODUCTION AND HISTORICAL BACKGROUND

Olefin metathesis, formerly known as olefin disproportionation, is a relatively recent development in which the molecules of an olefin are catalytically fragmented at their double bonds and new olefins are formed by recombination of these fragments. This may be described very generally by:-



The non-catalytic disproportionation of olefins dates back to 1931 when Schneider and Frölich(1) converted propene to ethene and 2-butene by heating the propene at 825°C. In 1964 Banks and Bailey(2) discovered that the reaction could be catalysed by the use of alumina supported molybdenum or tungsten hexacarbonyls. The highly selective reaction was carried out at 150°C employing relatively low pressures of 30 atmospheres and equimolar amounts of products were obtained.

The reaction was described by the equation:-



$$2\ CH_3CH{=}CH_2 \xrightleftharpoons{Mo(CO)_6/Al_2O_3} CH_2{=}CH_2 + CH_3CH{=}CHCH_3$$

38% Trans

20% Cis

The name "metathesis" was first used in 1967 by Calderon(3) who employed a homogeneous catalyst system for the first time for this reaction. 2-pentene was converted to a mixture of 2-butene and 3-hexene using a catalyst system comprised of $WCl_6/EtOH/EtAlCl_2$. Calderon(4) simultaneously achieved the metathesis of cycloolefins with the same catalyst system forming polyalkenamers with high selectivity by ring-opening polymerisation. Prior to this Natta(5) had reported the ring-opening polymerisation of cycloolefins using WCl_6/Et_3Al.

Attempts to expand metathesis have been carried out in two directions, investigating the substrate and the catalyst employed. The metathesis reaction has been extended to acetylenes and dienes(6,7) and also to substituted olefins(8).

In order to increase the application of olefin metathesis and ring-opening polymerisation of cycloolefins new heterogeneous and homogeneous catalyst systems were developed, some of which are shown in tables 1.3, 1.4 and 1.5.

Since 1967 the kinetics and mechanism of the reaction have been studied intensively. Bradshaw et al(9) studied the heterogeneously catalysed disproportionation of 1- and 2-butene, suggesting a four-centred cyclobutane intermediate to account for the products. Calderon came to similar conclusions for the metathesis in the homogeneous phase(4) and extended the mechanism to include ring-opening polymerisation(10).

Formation of such cyclobutane rings are forbidden, on the grounds of the Woodward-Hoffman rules of orbital symmetry(11). Mango et al(12) however, suggested that the role played by the transition metal was to allow such reactions to take place. Doubt was first cast on this type of mechanism by Begley and Wilson(13), whose kinetic studies on propene metathesis in the heterogeneous phase implied the reaction followed was first order with respect to substrate, which contradicted the mechanism involving this type of intermediate.

Confusion has arisen over the kinetics of metathesis reactions, with some workers concluding that such a reaction is first order in substrate, whereas others have observed second order dependence. The complexity of the kinetics of ring-opening polymerisation has been pointed out by Amass et al(14,15), so that conclusions drawn from simple studies may be meaningless.

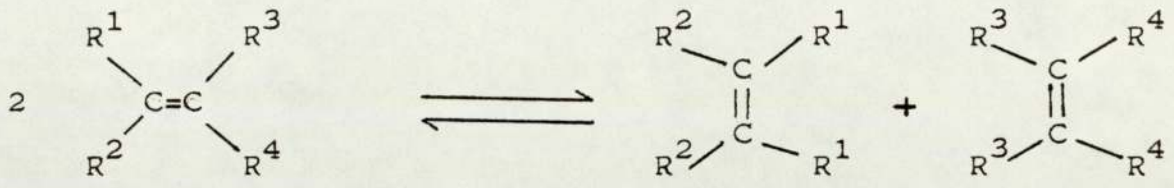
In 1970 Hérisson and Chauvin(16) proposed a chain mechanism for metathesis and ring-opening polymerisation in the homogeneous phase involving carbene intermediates. This type of hypothesis has generated numerous investigations on the mechanism and stereochemistry of the reaction with several workers, resulting in general acceptance of the Hérisson and Chauvin mechanism, although the finer details still remain to be resolved.

The olefin metathesis reaction and ring-opening polymerisation have proved to be of commercial use on an industrial scale such as in the petrochemical industry where olefins such as ethene, propene or butene(17,18) are used to obtain high octane gasoline, high grade mineral oils, monomers or other raw materials. Also the ring-opening polymerisation of cycloolefins has become a simple and economical method of synthesising polyalkenamers with useful properties, chiefly elastomers. Polypentenamer was once considered as a substitute for natural rubber(19,20,21) and polyoctenamer is currently marketed by Chemische Werke Hüls.

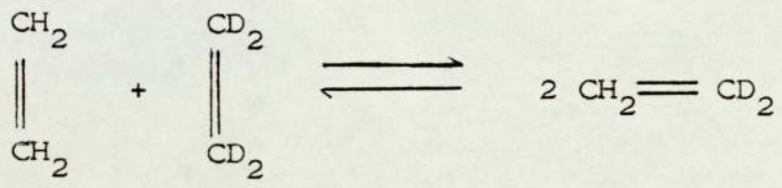
1.2 SUBSTRATES PARTICIPATING IN OLEFIN METATHESIS

1.2.1 Acyclic Olefins

The metathesis of acyclic olefins is a true equilibrium catalysed reaction.



The forward reaction represents simple metathesis and the reverse cometathesis. Approach to the position of equilibrium may be gained from either side of the equation, in which it is possible to form two new olefins or to generate one new olefin. Even symmetrical olefins may be shown to undergo this reaction even though the new products may only involve isomerisation. An example of this type of reaction is the metathesis of ethene which was studied by Olsthoorn(22) in 1972, who cometathesised a mixture of ethene and (d_2) - ethene implying the reaction occurred according to:-



$$CH_2{=}CH_2 + CD_2{=}CD_2 \rightleftharpoons 2\,CH_2{=}CD_2$$

Olefins with a terminal double bond, i.e. α - olefins, produce on metathesis ethene and an internal olefin, but these substrates are characterised by the occurrence of degenerate metathesis. Without recourse to a detailed mechanism of the reaction at this stage degenerate metathesis involves the exchange between the olefin and the propagating species of identical groups. This aspect will be discussed in detail later.

Banks and Bailey(2) studied the disproportionation of propene using a heterogeneous catalyst system, the products being ethene and 2-butene. It was found that the degree of conversion of propene as well as the stereoselectivity in the products is considerably influenced by the nature of the promotor, its concentration on the support and the nature of the support.

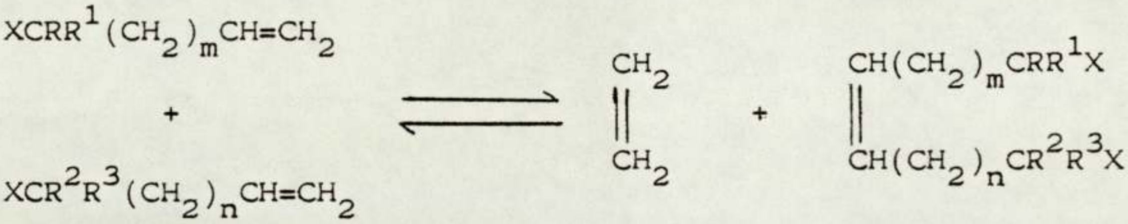
The order of reactivity of the olefin depends on the degree of substitution around the double bond. The order of reactivity for linear olefins is as follows:-

$$R\text{-}CH{=}CH_2 > R\text{-}CH{=}CHR' > RR'\text{-}C{=}CHR'' \gg RR'\text{-}C{=}CR''\text{-}R'''$$

1.2.2. Functionally Substituted Olefins

The metathesis of simple olefins, although interesting, has limited scope for the development of novel synthetic routes. More recently the metathesis reaction has been extended to olefins substituted with such functional groups as halogen, nitrile, acid, ester and amine, giving a new pathway for the synthesis of various mono- and difunctional derivatives of hydrocarbons.

Fridman and co-workers(23) carried out the reaction of allyl and crotyl chlorides and bromides with 5-bromo-1-hexene using heterogeneous catalytic systems. The reaction was also applied to other haloolefins and a general synthetic route to dihaloolefins was recognised:-



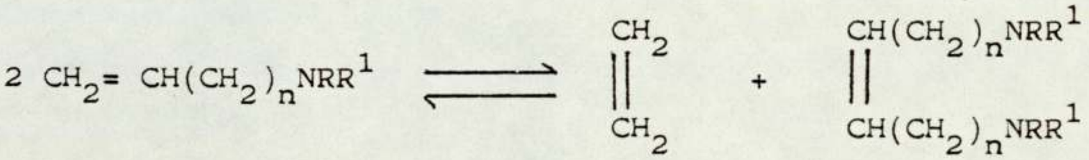
$$\begin{array}{c} XCRR^1(CH_2)_mCH{=}CH_2 \\ + \\ XCR^2R^3(CH_2)_nCH{=}CH_2 \end{array} \rightleftharpoons \begin{array}{c} CH_2 \\ \| \\ CH_2 \end{array} + \begin{array}{l} CH(CH_2)_mCRR^1X \\ \| \\ CH(CH_2)_nCR^2R^3X \end{array}$$

where X = Cl, Br

R = H, Me etc.

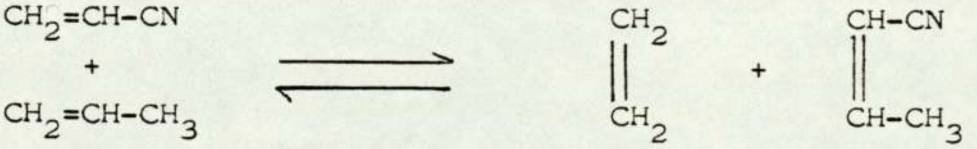
m,n = 0-3

Unsaturated amines were found to produce diamines by metathesis(24).



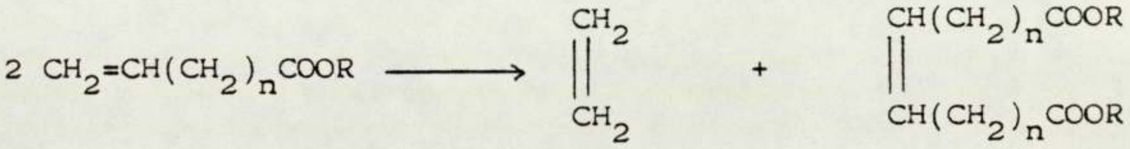
$$2\ CH_2{=}CH(CH_2)_nNRR^1 \rightleftharpoons \begin{array}{c} CH_2 \\ \| \\ CH_2 \end{array} + \begin{array}{l} CH(CH_2)_nNRR^1 \\ \| \\ CH(CH_2)_nNRR^1 \end{array}$$

Acrylonitrile reacts with propene over a silica-supported tungsten oxide catalyst yielding ethene and 1-cyanopropene.



$$\begin{array}{c} CH_2{=}CH{-}CN \\ + \\ CH_2{=}CH{-}CH_3 \end{array} \rightleftharpoons \begin{array}{c} CH_2 \\ \| \\ CH_2 \end{array} + \begin{array}{l} CH{-}CN \\ \| \\ CH{-}CH_3 \end{array}$$

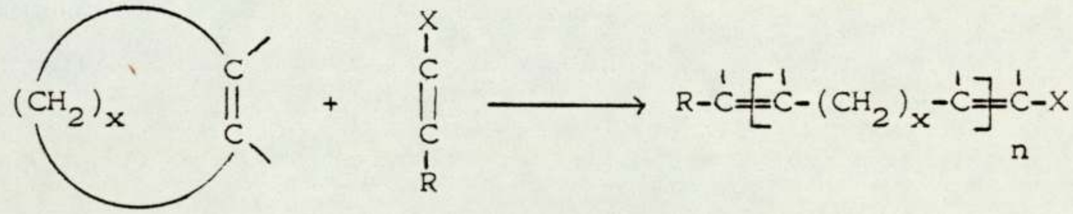
The metathesis of unsaturated esters has attracted much more interest and produces esters of dicarboxylic acids$^{(8)}$.



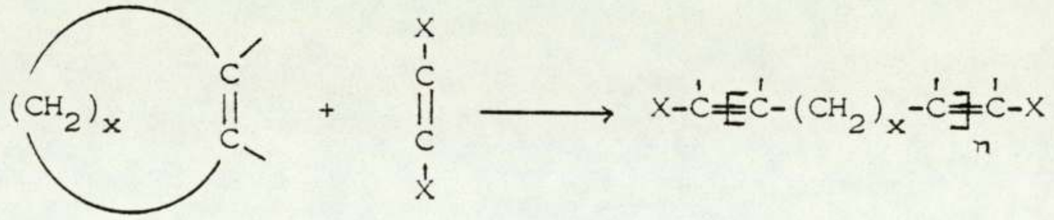
$$2\ CH_2{=}CH(CH_2)_nCOOR \longrightarrow \begin{array}{c} CH_2 \\ \| \\ CH_2 \end{array} + \begin{array}{l} CH(CH_2)_nCOOR \\ \| \\ CH(CH_2)_nCOOR \end{array}$$

The metathesis of unsaturated fatty acids with several carbon-carbon double bonds affords a more complex mixture of products due to intermolecular and /or intramolecular participation of the double bonds forming polymers, mono-carboxylic or dicarboxylic esters and even cycloolefins$^{(25)}$.

Cometathesis reactions with cycloolefins and acyclic olefins lead to linear long chain unsaturated, functionalised olefins as described below:-



When a difunctionalised olefin is reacted with a cyclo-olefin an α,ω - difunctionalised polymer (telechelic) is produced:



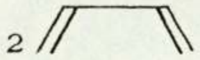
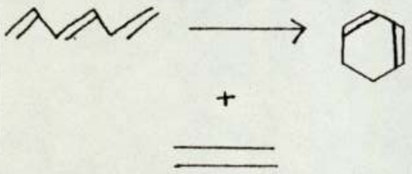
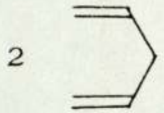
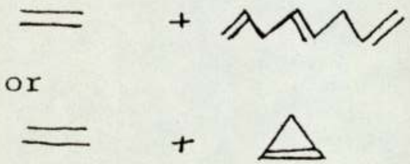
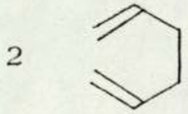
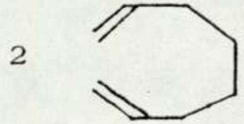
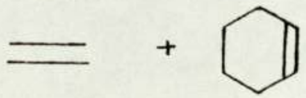
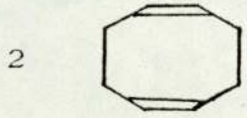
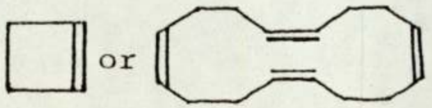
There is however difficulty in finding a suitable catalyst for metathesis and cometathesis involving functionalised olefins, since the functional groups tend to poison the catalyst and high catalyst/substrate ratios are required. Recent work by Amass(26) has suggested that the use of esters of trichloroacetic acid is much more efficient because the electron withdrawing effect of the trichloromethyl group overcomes the catalytic poisoning.

1.2.3. Dienes

Acyclic dienes can successfully undergo the metathesis reaction participating in intermolecular or intramolecular reactions depending upon the relative position of the double bonds. The former case usually applies to short-chain dienes with conjugated or non-conjugated double bonds.

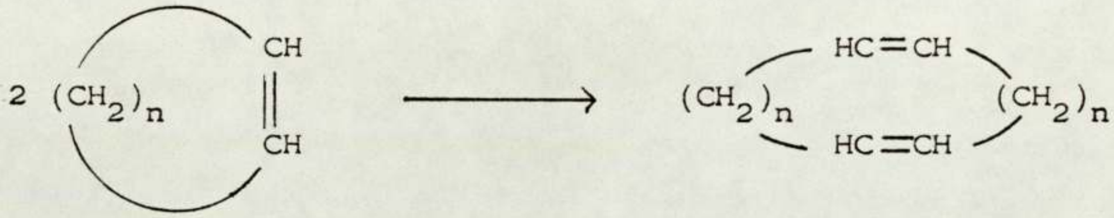
Table 1.1 lists a number of possible reactions of dienes.

Table 1.1 Some metathesis reactions of dienes

REACTANTS	PRODUCTS	REMARKS	REF.
 1,3-Butadiene		The cyclisation reaction could be due to a non-catalysed reaction.	(7)
 1,4-pentadiene		Triene produced through intermolecular reaction, cyclic compound results from reversible intramolecular reaction. Homogeneous cat. suppress side reactions.	(7)
 1,5-hexadiene		Traces of respective tetra-ene and pentene were present in product mixture but intramolecular cyclisation was excluded.	(112)
 1,7-octadiene		1,7,13-tetradecatriene (3%) present in reaction products, main intramolecular course favoured by high stability of cyclohexene.	(10)
 1,5-cyclooctadiene		Trimers also present from intramolecular metathesis. Tendency for cyclobutane to reform into the starting material due to high ring strain.	(10)

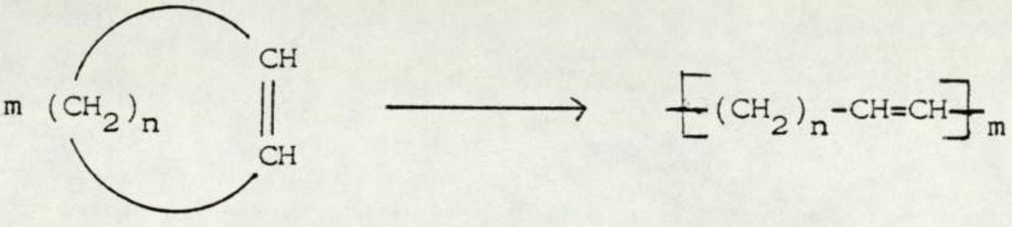
1.2.4. Cycloolefins

The metathesis of cycloolefins represents a different type of reaction. Earlier mechanisms predicted that two cycloolefin molecules would react in such a manner as to yield a cyclic dimer with two double bonds, i.e.:-



The above reaction scheme does not however occur and where such oligomers are found in the product they are generated by modifications of the normal metathesis reaction, i.e. intramolecular metathesis of polyalkenamer.

Polymerisation forming polyalkenamers is a recognised mechanism as illustrated below:-



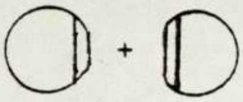
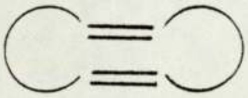
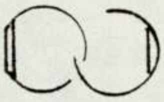
Work was carried out by Natta(5) who formed polyalkenamers from cyclopentene, cycloheptene, cyclooctene and cyclodecene monomers using WCl_6 as catalyst with $AlEt_3$ or $EtAlCl_2$ as a cocatalyst. Eleuterio(27) polymerised cyclopentene by ring-opening in the presence of hydrogen-reduced MoO_3 supported on alumina and activated by $LiAlH_2$ in 1957.

Because of the presence of cycloolefin oligomers and unsaturated macrocycles, as well as the polyalkenamers, it was thought that the ring-opening polymerisation of cycloolefins proceeds by more than one stage, forming initially the cyclic dimer followed by the trimer, etc. These products could then be cleaved by intramolecular metathesis to form cycloolefins and new macrocycles. Recent data suggests the formation of oligomers to be due to cyclodegradation of polyalkenamers. Höcker(28) suggested a back-biting mechanism to account for their presence.

It was reported that catenenes could be obtained during the oligomerisation of cycloolefins in the metathesis reaction if the macrocyclic ring becomes twisted, the outcome being dependent upon the number of half-twists. This report presupposed polymerisation by a quasicyclobutane mechanism and doubt has to be cast on their formation considering the lapse from favour of this mechanism.

Table 1.2 shows several possible structures which could be produced according to the above postulations:-

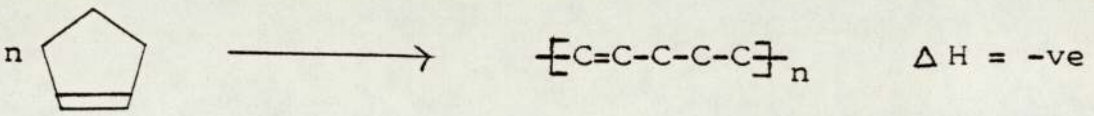
Table 1.2 Oligomerisation products of Cycloolefins

No. ½ Twists (n)	Product	Structure
0	2 cyclolefins	
1	Macrocycle	
2	Catenene	
3	Knot	

The smaller cycloolefins, cyclobutene and cyclopentene are reactive in the presence of polymerisation catalytic systems. Cyclohexene is the only cycloolefin which cannot be easily polymerised to polyhexenamer with the known catalytic systems. This is due to the absence of ring strain energy in its structure. The higher homologues polymerise without difficulty, the ease of polymerisation decreasing with the size of the ring. The most common examples of cycloolefins that show the features of metathesis and ring-opening polymerisation are cyclopentene, cyclooctene and norbornene.

Cyclopentene

Cyclopentene is a strained ring compound and a reactive cycloolefin giving rise to an exothermic polymerisation:-



$$n\ \text{(cyclopentene)} \longrightarrow -\!\!\left[C{=}C{-}C{-}C{-}C\right]\!\!-_n \qquad \Delta H = -ve$$

Eleuterio$^{(27)}$ was the first to polymerise cyclopentene as described earlier, and in later studies Natta and co-workers$^{(5,29,30)}$ obtained low yields of polypentenamer using a series of Ziegler-Natta type catalysts. Nützel$^{(31)}$ and Günther$^{(21,32)}$ used a variety of binary catalyst systems containing metal halides, organometallic compounds and alkali or alkaline earth metals giving a yield of polypentenamer ranging from 21-66%.

Three component catalytic systems were introduced by Dall'Asta and Carella$^{(20)}$ which comprised tungsten or molybdenum compounds, an organometallic compound and oxygen containing compounds such as benzoyl peroxide, t-butyl peroxide, hydrogen peroxide and ethanol. The third component could also be a Lewis-acid type compound such as $AlBr_3$ or $SnCl_4$.

A novel catalyst system based on niobium and tantalum$^{(33,34)}$ produced high yields of polypentenamer with low gel content. Conversely a polymer with 70% gel content was produced using a similar system based on $MoCl_5$(34).

The stereoselectivity of the reaction is very dependent on the catalyst system employed. Molybdenum based catalyst systems favoured production of the cis-isomer(35) as did rhenium based catalysts(36), although the reactivity was reduced in comparison to tungsten based systems which favoured production of the trans-isomer. By replacing the chlorine atoms in WCl_6 by fluorine Oberkirch(37) found that in using $EtAlCl_2$ as the cocatalyst production of cis-polypentenamer rather than the original trans-isomer was favoured. Trans-polypentenamer of between 90-95% yield was produced using WCl_6/C_1-C_6 epoxide/aluminium compound catalyst system in a molar ratio of 1:0.3-10:0.8-15 respectively.

The uses of polyalkenamers are described in section 1.8 and table 1.10 lists the physical and chemical properties of polypentenamer indicating its potential uses for a given isomeric conformation.

Cyclooctene

Cyclooctene has an even greater ring strain than cyclopentene due to non-bonded interactions between axial hydrogen atoms and the monomer consequently polymerises more readily than cyclopentene forming cis- and trans-polyoctenamer. At equilibrium the concentration of monomer is much less in comparison to the corresponding ring-opening polymerisation of cyclopentene, the position of equilibrium lying far over to the formation of polymer.

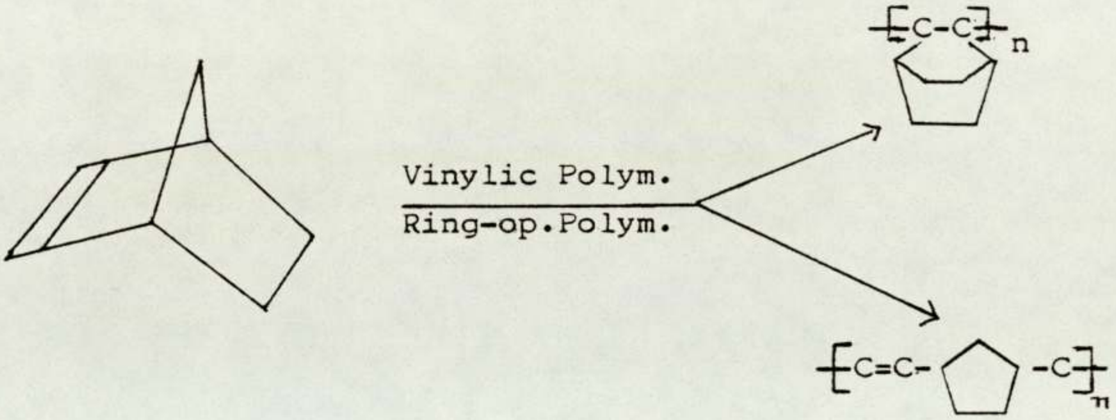
Because of the ease of reaction catalytic activity is not so important. Eleuterio(38) was the first to achieve the ring-opening polymerisation of cyclooctene employing heterogeneous catalyst systems based on chromium, molybdenum, tungsten or uranium oxides, resulting in low yields of chiefly cis-polyoctenamer. Using a homogeneous catalyst system comprising $WCl_6/AlEt_3$ Natta(39) produced high yields of the trans-isomer with relatively high % conversion in comparison to other cycloolefins studied. Calderon and co-workers(10,40) also produced high yields of trans-polyoctenamer using $WCl_6/ROH/RAlCl_2$ catalysts. Other suitable organometallic cocatalysts included $Al(iBu)_3$(41) and BuSn(42), while Lewis acids such as $AlBr_3$(43) were also found to be suitable.

The properties and uses of polyoctenamer are described in section 1.8 and table 1.10.

Norbornene

The polymerisation of norbornene was carried out as early as 1955 by Anderson and Merckling(44) in the presence of a

Ziegler Natta catalyst system formed from $(C_7H_{15})_4LiAl$ and $TiCl_4$. The monomer polymerised irreversibly to give a mixture of saturated and unsaturated products whose structures were not fully elucidated. The ratio of catalyst to cocatalyst was found to be insignificant to the course of the reaction(45), as was the actual catalyst system used.



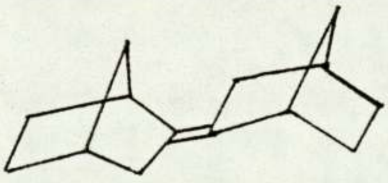
Other cocatalysts such as Grignard compounds, metal alkyl or aryl compounds, metal hydrides and even alkali or alkaline earth metals were also used by the same authors, but in each case lower catalytic activity was observed.

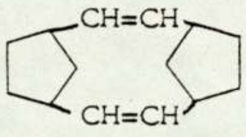
Eleuterio(7) used heterogeneous catalysts comprising Cr,Mo or W oxides reduced with hydrogen and supported on alumina, titania or zirconia to polymerise norbornene by ring opening.

The polymerisation of norbornene to linear polyalkenamers with high molecular weight and uniform structure was carried out by Oshika et al(46) using $MoCl_5$ catalyst in a polar solvent such as CCl_4 or C_6H_5Cl at room temperature to give a polymer with trans-structure at the double bond.

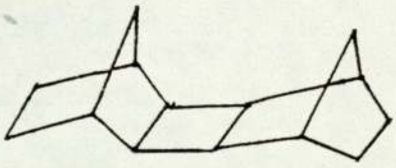
In 1978 Ivin et al(47) reported studies on the ring-opening polymerisation and the formation of oligomers from norbornene catalysed by $EtAlCl_2$ alone. In this respect $EtAlCl_2$ resembles several transition metal complexes which are quite active for ring-opening polymerisation of norbornene but are practically inert for metathesis of less strained olefins and cycloolefins.

Previous to this the same authors described the mechanism of initiation of ring-opening polymerisation of norbornene catalysed by transition metal halides, namely WCl_6, $ReCl_6$ and $MoCl_5$(48). Polymerisation occurred readily at ambient temperatures but only WCl_6 and $ReCl_5$ caused significant formation of the four isometric dimers (a). The dimers (b) and (c), which might have been expected from concerted and non-concerted mechanisms involving pairwise exchange of olefins and carbenes, were never detected.


(a)

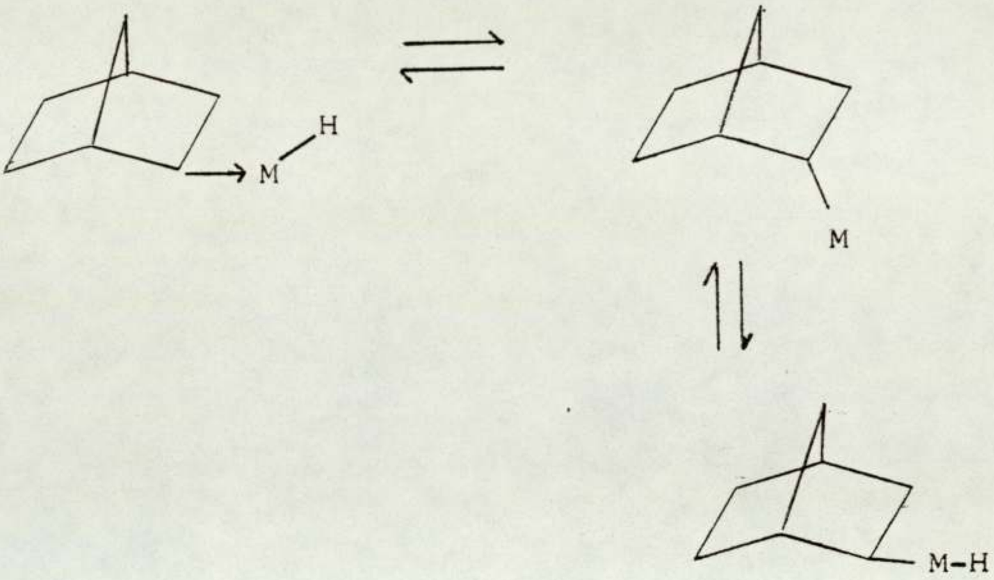


(b)


(c)

In highly reactive cycloolefins such as norbornenes movement of the double bond to exocyclic positions relieves strain.

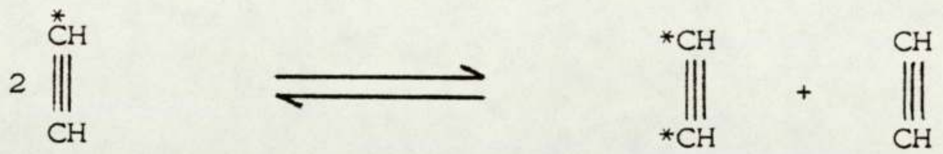
Therefore competition between alkyl reversal to olefin and conversion into carbene, as shown below, is biased in favour of the latter.



As a consequence of this factor, as well as the influence of the reaction, the catalysts capable of ring-opening polymerisation often extend over a wider range of metals than those for metathesis.

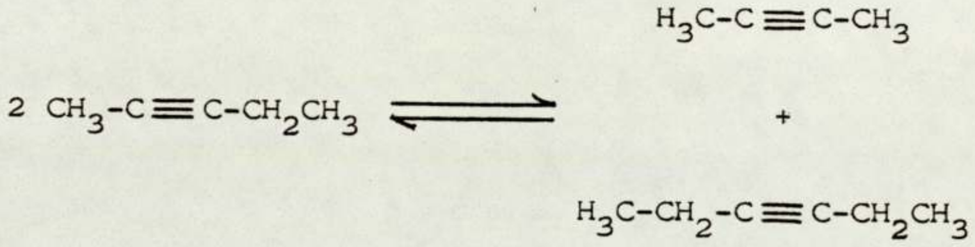
1.2.5 Acetylenes

In 1968 the metathesis reaction was extended to acetylene by Penella, Banks and Bailey(6) following studies carried out by Bauer and Jeffers in 1965 using radioactivity labelled acetylene:



$$2\ \overset{*}{C}H{\equiv}CH \rightleftharpoons {}^{*}CH{\equiv}{}^{*}CH + CH{\equiv}CH$$

Penella and co-workers converted 2-pentyne to 2-butyne and 3-hexyne using heterogeneous catalysts at 200°C to 450°C.

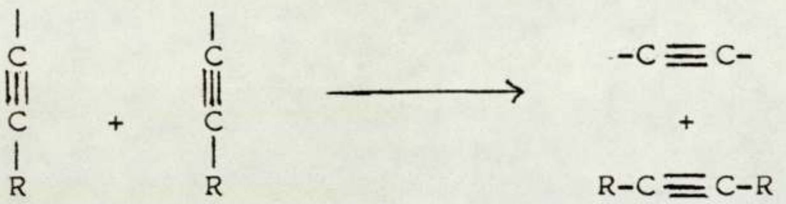


$$2\ CH_3\text{-}C{\equiv}C\text{-}CH_2CH_3 \rightleftharpoons H_3C\text{-}C{\equiv}C\text{-}CH_3 + H_3C\text{-}CH_2\text{-}C{\equiv}C\text{-}CH_2CH_3$$

More recently the reaction has been extended to a larger number of unsubstituted and substituted acetylenes and also to acetylenic derivatives, principally to prepare polyacetylenes.

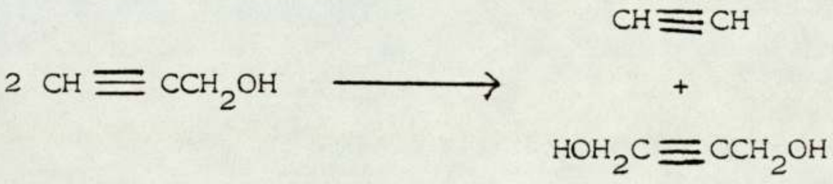
Moulijn and co-workers$^{(49)}$ studied a large number of acetylenes in great detail, using a heterogeneous catalytic system formed from 5.5% WO_3 on silica, and observed dual behaviour of the system between 100°C and 500°C. In most cases cyclotrimerisation of the acetylenes occurred alongside the metathesis reaction, especially for α-acetylenes, β -acetylenes undergoing the metathesis reaction more readily. The yield of metathesis and cyclotrimerisation products depended largely on the reaction conditions employed.

Internal acetylenes symmetrically substituted with alkyl groups are produced from substituted acetylenes:-



Where R=Me, Et, Pr or Ph

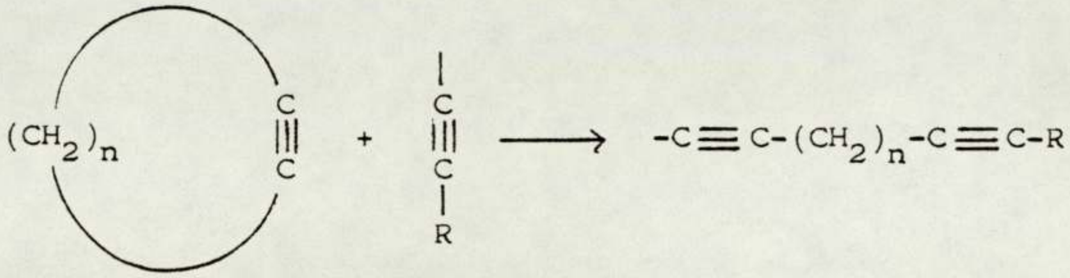
Butyne diol may be prepared from the metathesis of 2-propyn-1-ol:-

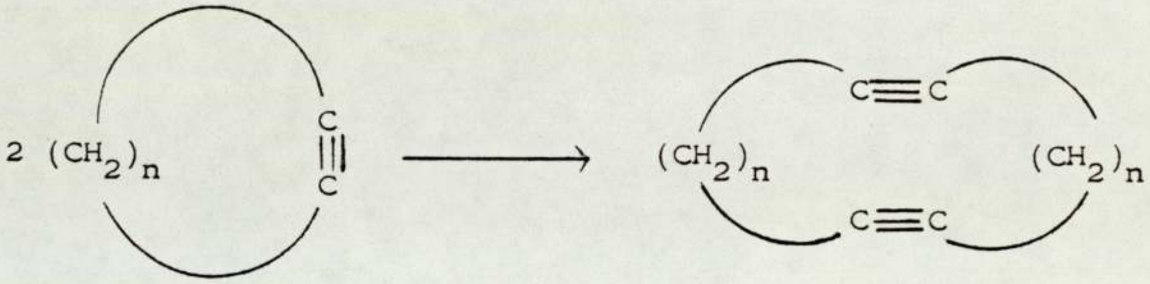


$$2\ CH\equiv CCH_2OH \longrightarrow CH\equiv CH + HOH_2C\equiv CCH_2OH$$

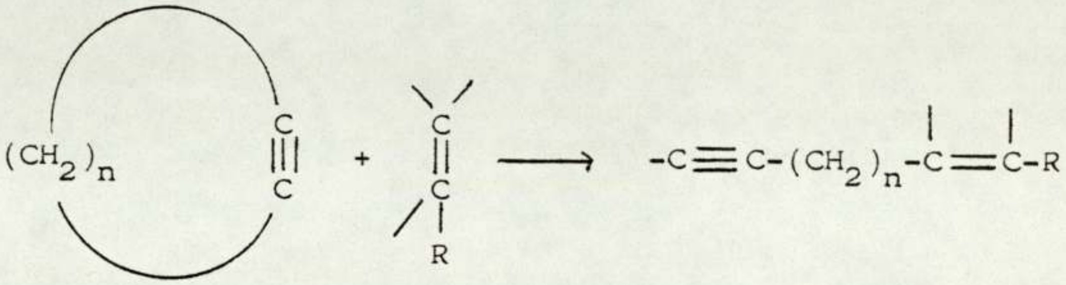
The metathesis of functionally substituted acetylenes affords a pathway to the synthesis of compounds which were previously difficult to prepare by conventional methods. For example the production of disubstituted acetylenes from functionalised 1-phenylbut-1-yne where the functional group is -OH, -COOMe, -Br, -COOH or -CN(50).

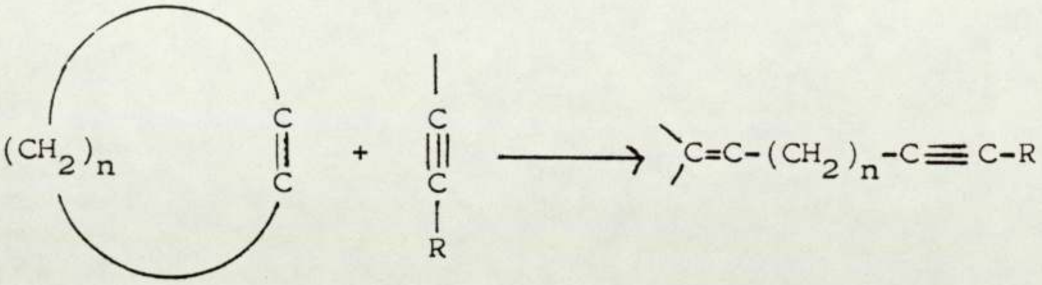
Cyclic diynes and polyynes may be synthesised from the cometathesis of cycloacetylenes with linear or other cycloacetylenic molecules.





With acylic or cyclic olefins it is possible to obtain unsaturated compounds with double and triple bonds in the chains:-





R = alkyl/aryl group

The catalyst systems described for these reactions of acetylenes are all heterogeneous. Homogeneous catalyst systems include $WCl_6/AlEt_3$, $WCl_6/AlEtCl_2$ and $MoCl_5/SnPh_4$.

1.3 CATALYST SYSTEMS

There are numerous heterogeneous and homogeneous catalyst systems which initiate the metathesis reactions of olefins and the ring-opening polymerisation of cycloolefins. The catalytic systems consist of one, two or several components, the main one being a transition metal compound usually containing Mo, W or Re.

For the purposes of simplicity the catalyst will be defined as the transition metal compound and the cocatalyst the metal alkyl or metal halide used in conjunction with these transition metal compounds. It should be realised that the true catalyst must be regarded as the product of some reaction between the components and/or olefins.

1.3.1. Heterogeneous Catalysts

Heterogeneous catalysts are used widely for olefin metathesis rather than for ring-opening polymerisation and consist of a promoter supported on a carrier.

The activity of heterogeneous catalysts, and hence the degree of olefin conversion, depends to a great extent on the surface characteristics of the catalyst. Important physical characteristics include:-

i) surface area - the larger the surface area the greater the activity. Over $100m^2/g$ of catalyst on support is required for all metathesis reactions to obtain a good yield,

ii) pore size - for high activity the average diameter and volume of the pores must be 50-200Å and below $1cm^3/g$ respectively,

iii) form of grain - in general pellets from extrusion or grains from precipitation are used depending on the carrier employed.

Heterogeneous catalysts can lose their activity due to external, physical or chemical factors. The catalysts operate within an optimal temperature and pressure range outside of which the structural properties may change, resulting in the poisoning of the catalyst with polymer or coke which blocks the active centres. Total modification of size and form of the catalyst pores may result in different products.

The chemisorption of traces of oxygen, water or carbon dioxide may block the active catalyst centres, hence precautions must be taken not to subject the reactant mixture to these substances, since regeneration of the active catalyst is virtually impossible once poisoning has taken place.

Several different categories of heterogeneous catalysts will now be discussed.

1.3.1.i. Supported Metal Oxide Catalysts

Catalysts based on metal oxides are the most important for heterogeneous catalysts, especially those of Mo, W or Re deposited on inert materials such as alumina or silica.

The activity of many catalytic systems based on MoO_3 was found to be enhanced by the presence of other metal oxides such as CoO, Cr_2O_3 and TiO_2, but this was usually found to result in an unsatisfactory level of selectivity in the products. The selectivity was found to be greatly improved by the addition of inorganic salts of group 1 or 2 in the Periodic table such as NaOH, KOH and $NaHCO_3$.

WO_3 is among the most highly active catalysts in the metathesis reaction, but temperatures of between $300^{\circ}C$ and $500^{\circ}C$ are normally required. Again the addition of alkali metals was found to enhance the activity, as did Nd_2O_3, Pr_2O_3 or Sm_2O_3.

Many carriers were found to be successful, in many cases the conversion depending on the carrier employed.

Re_2O_7 is a more active promoter at lower temperatures than Mo or W oxides, preferably at a 14-20% ratio to an alumina or silica carrier. Other suitable carriers are oxides of Ti, Zr and Sn giving various conversions.

1.3.1.ii Supported Metal Carbonyl Catalysts

$Mo(CO)_6$ supported on alumina was the heterogeneous catalyst system used by Banks and Bailey(2) when the discovery of the disproportionation of olefins was made. Extensive isomerisation of the reaction products was noted with low conversion, although the use of silica as a support for $Mo(CO)_6$ and $W(CO)_6$ was found to increase the conversion.

1.3.1.iii Supported Metal Salt Catalysts

Common transition metal salts employed as metathesis catalysts include halides, oxyhalides, sulphates and phosphates used alone or in conjunction with organometallic compounds supported on a carrier.

1.3.1.iv Supported Metal Sulphide Catalysts

Sulphides of Mo and W supported on silica or alumina proved to be efficient catalysts for olefin conversion in low concentrations up to 20%(7). Higher temperatures were required for silica supported sulphides than for the alumina equivalents, although at very high temperatures the reactions were accompanied by dimerisation and side reactions.

1.3.2 Homogeneous Catalysts

Homogeneous phase metathesis reactions have an advantage over heterogeneous catalyst systems in that fewer side reactions take place, partly due to the milder temperature and pressure employed. Homogeneous catalytic systems for metathesis and ring-opening polymerisation are of three main types. All contain a transition metal, usually Mo, W or Re, which may be used in combination with an organometallic compound, and in some cases a third component containing oxygen, halogen or nitrogen.

1.3.2.i One Component Catalyst Systems

One component catalyst systems usually consist of a transition metal co-ordination complex. Table 1.3 summarises examples of unicomponent systems employed.

1.3.2.ii Two Component Catalyst Systems (binary)

A binary catalyst system consists of a transition metal salt, usually a halide or a complex, in conjunction with a cocatalyst which is normally a group 1-4 organometallic compound as in Zeigler-Natta type systems, or a Lewis acid as in Friedel-Craft type systems. Examples of each are shown in tables 1.4 and 1.5 respectively.

Table 1.3 Examples of Unimolecular Catalyst Systems

CATALYTIC SYSTEM	SUBSTRATE	REFERENCE
WCl_6	Cyclopentene	(51)
$WOCl_4$	Cyclopentene	(20)
	2-Pentene	(52)
$PhWCl_3$	Cyclopentene	(53)
	2-Pentene	(54)
$Ph_2C{=}W(CO)_5$	Cyclobutene	(55)
	1-Octene + 1-Hexene	(56)
(π allyl)$_4$Zr	Cyclooctene	(57)
(π allyl)MoCl	Norbornene	(58)
$RuCl_3$	Cyclooctene	(59)
$TolW(CO)_3$	4-Nonene	(60)
$MoCl_5$	Cyclopentene	(20)

Table 1.4 Examples of Ziegler-Natta Type Binary Homogeneous Catalyst Systems

CATALYTIC SYSTEM	SUBSTRATE	REFERENCE
$WCl_6/EtAlCl_2$	Cyclobutene	(4)
	1-Decene + 1-Pentadecene	(61)
WCl_6/Ph_4Sn	Cyclopentene	(62)
$WCl_6/nBuLi$	1-Methylcyclobutene	(56)
	1,7-Octadiene	(63)
	2-Pentene	(64)
$WCl_6/LiAlH_4$	Cyclooctene	(65)
	2-Pentene	(66)
$TiCl_4/EtAlCl_2$	1-Octene	(67)
$Mo(NO)_2Cl_2Py_2/Me_3Al_2Cl_3$	1-Octene	(68)
$Mo(NO)_2Cl_2(PPh_3)_2/Me_3Al_2Cl_3$	1-Pentene	(68)
	2-Heptene	(68)
	1-Octene	(68)
$Re(CO)_5Cl/EtAlCl_2$	4-Octene	(69)
	Cyclohexene	(70)
$MoCl_5/Me_3Al_2Cl_3$	1-Pentene	(68)

Table 1.5 Examples of Friedel-Crafts Type Binary Homogeneous Catalyst Systems

CATALYTIC SYSTEM	SUBSTRATE	REFERENCE
$WCl_6/AlCl_3$	Cyclopentene	(20),(71)
	α & β -Olefins	(16)
$WOCl_4/AlBr_3$	Cyclopentene	(16)
	1,5,9-Cyclodecatriene	(43)
	α & β -Olefins	(16)
$MoCl_5/AlI_3$	1,5-Cyclooctadiene	(16)
	1,5,7-Cyclododecatriene	(16)
$(\pi\text{-allyl})_2Ni/AlBr_3$	Cyclopentene	(72)
	Cyclooctene	(72)
	Bicyclo 2.2.1 heptene	(72)
$WBr_5/AlCl_3$	Cyclopentene	(20)
	α & β-Olefins	(16)
$WPhCl_3/AlCl_3$	1,4-Cyclohexadiene	(73)
	2-Butene	(73)
	Ethylcyclopropane	(73)
	Butylcyclopropane	(73)
$MoOCl_2/AlBr_3$	1,5-Cyclooctadiene	(16)
	Cyclododecene	(16)
$Mo(NO)_2Cl_2/AlBr_3$	2-Pentene	(74)

1.3.2.iii Three Component Catalyst Systems

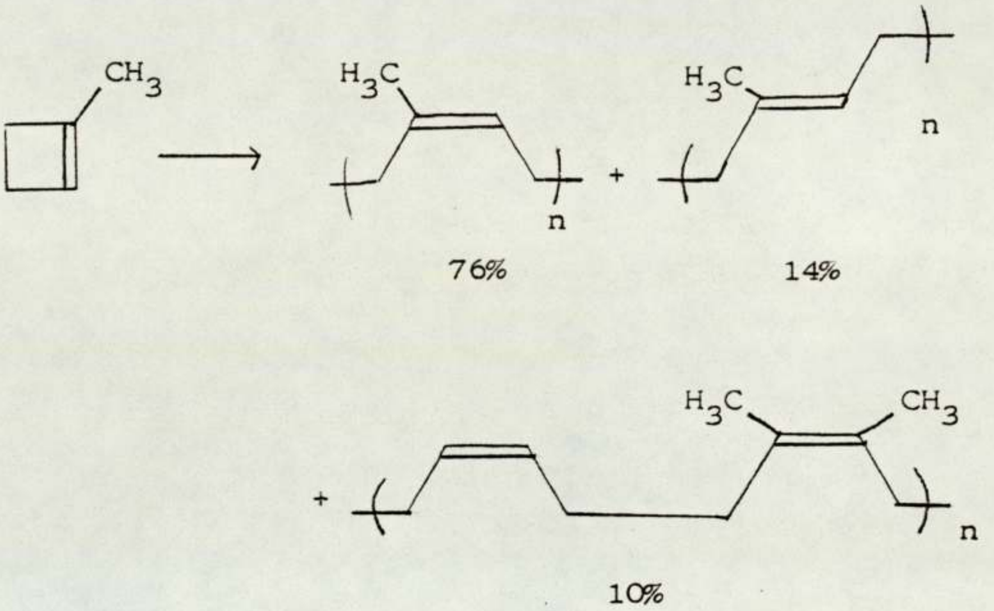
A third component added to binary catalysts acts either as an activator, promoter, stabilizer or inhibitor of side reactions to metathesis reactions and it is found to increase the activity and selectivity, improve the reproducibility and even initiate the polymerisation or control the molecular weight of the polymer in ring-opening polymerisation. The substance is usually an organic compound containing oxygen, halogen, sulphur or nitrogen which readily becomes complexed or reacts with the basic binary system.

Calderon(3) was the first to use a ternary catalyst system in the homogeneous phase for the metathesis of 2-pentene employing a system of $WCl_6/EtOH/EtAlCl_2$ in the ratio 1:1:2(-4) respectively as optimum concentration. This system also proved to be successful for other acyclic(4) and cyclic(42) olefins.

Other third components include CH_3COOH, PhCOOH, H_2O_2, PhOH, HOEtCN and O_2. Pampus and co-workers(33) employed epichlorohydrin and chloroethanol in several procedures to increase the stability of the catalyst systems, forming the trans-configuration of polypentenamer from cyclopentene.

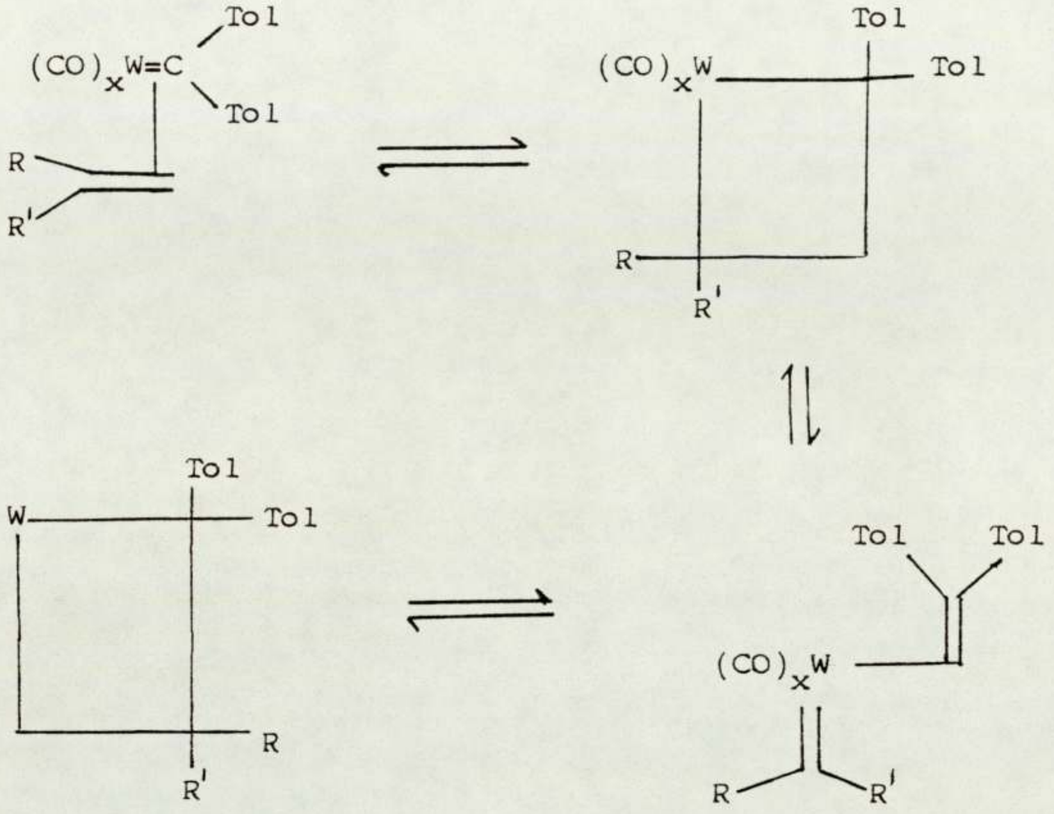
1.3.2.iv Catalysts Based On Carbenes

Katz and co-workers were the first to use a one component carbene catalyst, (diphenylcarbene)pentacarbonyltungsten, for the cometathesis of 1-octene and 1-hexene and for the ring-opening polymerisation of cycloolefins(55) such as 1-methylcyclobutene as shown below:-

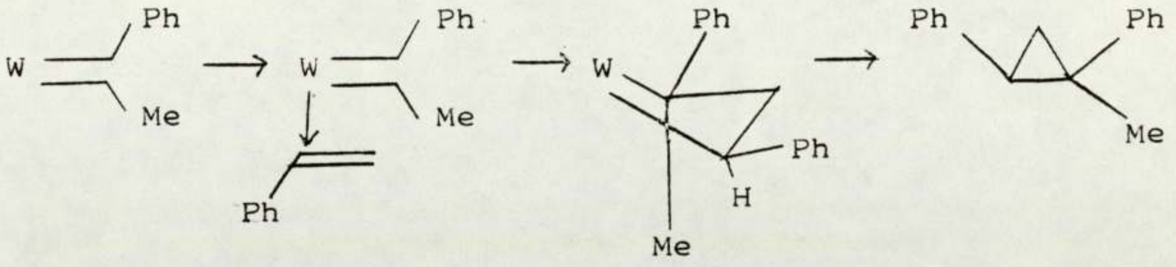


Other complexes of this type used by Katz include (phenylmethoxycarbene)pentacarbonyltungsten(75) and (diphenylcarbene)pentachlorotungsten. The latter was also used by Casey(76) for the cyclopropanation of unsymmetrically substituted olefins.

Using the carbene complex (ditolylcarbene)pentacarbonyltungsten Casey(77) observed the transfer of the ditolylcarbenic ligand to an alkylidene group in the reaction of several olefins.



The cyclopropanation of styrene was carried out by Casey et al(78) using (phenylmethylcarbene)pentacarbonyltungsten which proved to be a very active catalyst. Observations were made that the reactivity towards terminal olefins was greater than for internal olefins. There was also a high selectivity for transfer of the least substituted alkylidene unit of an olefin to the carbene ligand, which helped to explain the structural selectivity found in catalytic olefin metathesis reactions.



Binary catalysts of carbenic complexes of the type $R_4N^+ [M(CO)_5-COR']^-$ were prepared by Kroll and Doyle$^{(151)}$, where M = Mo or W and RR' = Me or Ph. These were used in conjunction with $MeAlCl_2$ or $Me_3Al_2Cl_2$. High conversions were obtained in the metathesis of olefins when the substrates were 1-pentene, 2-pentene, 4-methyl-1-pentene, 1-octene and 1,7-octadiene.

Catalysts containing complexes such as $RR'C{=}M(CO)_5$ (where R = C_3H_5O, CH_3O; R' = CH_3, Ph; M = W, Mo) or $Cl_2(Ph_3P)Pd{=}C(OMe)$–NHPh in conjunction with $AlCl_3$ or $EtAlCl_2$ have also found applications for ring-opening polymerisation reactions by Chauvin et al$^{(79)}$. Using such a system a 70% yield of polypentenamer was obtained from cyclopentene.

1.3.2.v Effects of the Order of Mixing

A factor which can influence the course of the metathesis reaction is the order of addition of the catalyst components to the reaction system. Metathesis active systems are normally produced when the catalyst is added to the olefin solution followed by the cocatalyst and where used the activator. Sometimes activators are premixed with the catalyst or cocatalyst. If however the catalyst and cocatalyst are premixed prior to addition to the reacting olefin (2-pentene) in toluene, Friedel-Crafts alkylation of the solvent may take place in preference to metathesis(80).

In similar fashion when WCl_6 and LiBu are separately added to an olefin in toluene metathesis ensues. Premixing the catalyst and cocatalyst tends again to promote Friedel-Crafts reactions rather than metathesis. Subsequent addition of $AlBr_3$ or $AlCl_3$ to such a reaction has however been shown by Wang et al(81) to restore metathesis activity.

Electron donors, for example aniline, can dramatically alter the course of the reaction depending upon the stage at which they are added to the reaction. If WCl_6 and $EtAlCl_2$ are premixed and then added to an olefin the selectivity towards metathesis is low even if aniline is subsequently added to the system(82). If however WCl_6 and aniline are premixed prior to addition to the olefin and then cocatalyst is added, a highly specific catalyst system for metathesis is produced. It was suggested that in this case aniline acted as a reducing agent and prior to its reaction with $EtAl_2Cl_3$ the tungsten atom was in a lower than maximum oxidation state. More recently triphenylphosphine has been reported to reduce WCl_6 to $WCl_4(PMe_3)_3$ in a sealed tube. It may well be that the reduction of WCl_6 is a crucial step in the generation of a metathesis catalyst when WCl_6 is added to an olefin.

The occurrence of a reaction between WCl_6 and an olefin was used by Amass and Tuck(14) to explain the kinetics of polymerisation of cyclopentene by WCl_6 and $AliBu_3$. The polymerisation rate depended upon the time delay between addition of the catalyst and cocatalyst to the solution of monomer, and reached a maximum at a time that was inversely proportional to the concentration of monomer. Premixing the catalyst and cocatalyst led to an inactive system. It is therefore clear that attempts to explain the initiation of metathesis must take into account the reactions between the catalyst and monomer/substrate.

Dolgoplosk et al(83) observed that for the polymerisation of cyclopentene using the catalyst system $MoCl_3(C_{17}H_{35})_2$/ Et_2AlCl premixing the catalyst components had no effect on the reaction up to a monomer concentration of 7×10^{-3} mol dm^{-3}. Above this however the catalyst was deactivated after a few hours at room temperature.

As well as affecting the rate of reaction the order of mixing can also determine the stereoselectivity of metathesis. Mol et al(84) carried out the metathesis of 2-pentene using catalyst systems consisting of WCl_6 and SnR_4 or Sn_2R_6 as the cocatalyst, where R = Me, Bu, C_8H_{17} or Ph. The dependence of stereoselectivity in such systems on the order of addition was greatest when $SnPh_4$ was used as cocatalyst. If the olefin was added immediately after the addition of $SnPh_4$ to the catalyst the stereoselectivity favoured cis-products.

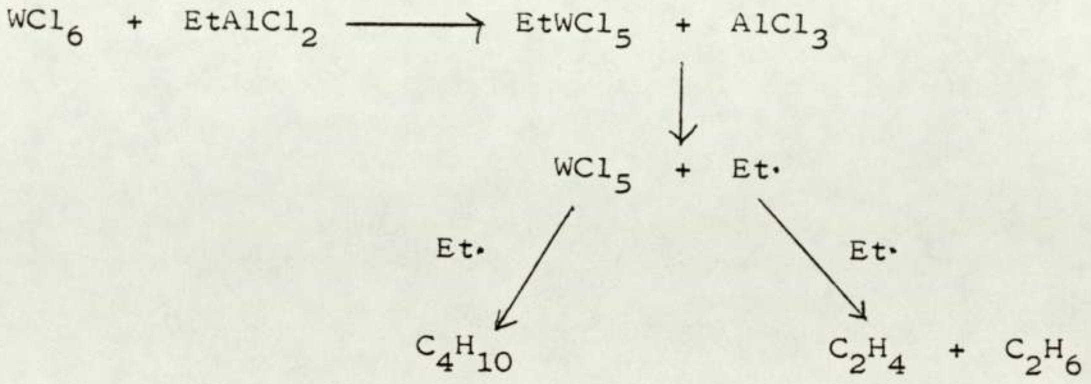
Otherwise the stereoselectivity was similar to other W/Sn systems provided $SnPh_4$ was added after WCl_6 to the olefin.

1.3.2.vi Molar Ratio of Catalyst Components

For most homogeneous catalyst systems the ratio of catalyst to cocatalyst is usually between 1:1 and 1:4. The rate of reactivity or conversion is strictly governed by the molar ratio of the components, having a very narrow band of optimum activity. Wang and Menapace$^{(64)}$ concluded that for the WCl_6/LiBu catalyst system the maximum activity of reaction was observed when the W:Li molar ratio was 1:2 for the metathesis of 2-pentene. This suggested that the role of the cocatalyst might be to reduce W^{VI} to W^{IV} according to:-

$$\begin{tikzcd} WCl_6 + 2\ LiBu \arrow[r] & Bu_2WCl_4 + 2\ LiCl \arrow[d, "\text{olefin}"] \\ & WCl_4(\text{olefin})_2 + R\bullet \end{tikzcd}$$

Calderon$^{(4)}$ also suggested that an optimum 1:2 ratio for W:Al was required for the catalyst system $WCl_6/EtAlCl_2/EtOH$, and postulated the following similar series of reactions to account for this:-

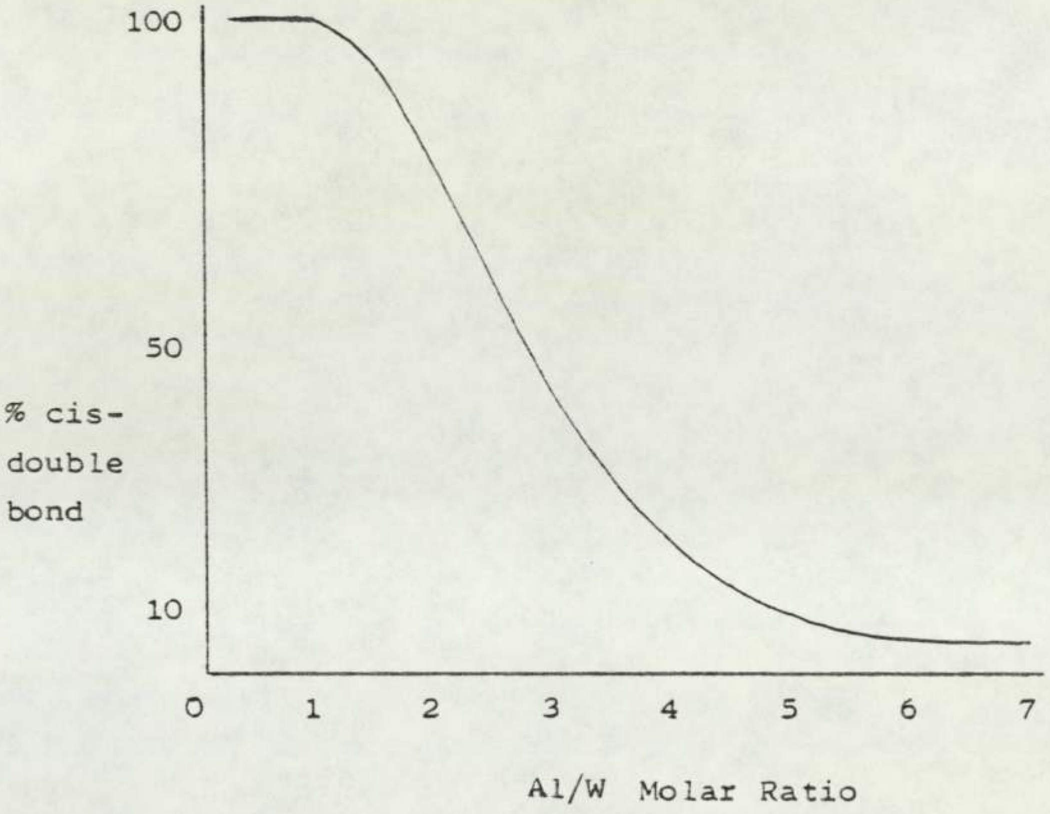


$$\text{i.e.}\quad W^{V} \longrightarrow W^{VI} + W^{IV} + R\bullet$$

For the ring-opening polymerisation of cyclooctene and 3-methylcyclooctene Calderon et al(40) found an optimum catalytic activity of Al:W of 4:1 for $WCl_6/EtAlCl_2$. The same observation was made by Korda et al(85) for the metathesis of 3-heptene using (mesitylene)$W(CO)_3/EtAlCl_2$ as the catalyst system.

These are examples of the effect of molar ratio on catalytic activity, but it is known that in some cases the molar ratio of components may also affect the stereospecificity. Günther et al(86) studied the effect of Al:W ratio on the production of cis- and trans-polypentenamer using a catalyst system comprising $WF_6/Et_2Al_2Cl_3$; the results are shown graphically in figure 1.1 as the percentage of cis-isomer with increasing Al/W molar ratio.

Figure 1.1 The Effect of the Catalyst Molar Ratio on the Stereochemistry of the Product (Polypentenamer)

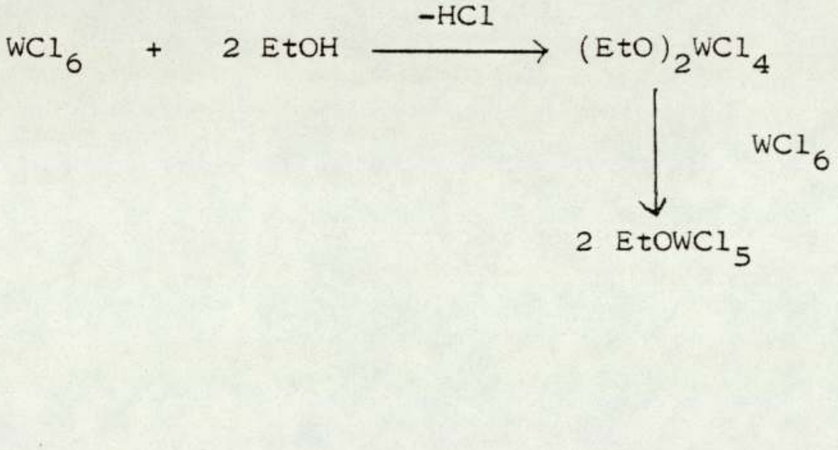


1.3.2.vii The Effect of Solvent

The reactions of metathesis and ring-opening polymerisation in the homogeneous phase generally take place in an adequate solvent which allows solvation of the starting material of the reaction products and and the catalyst complex. The main types of solvent used are non-polar, unsaturated hydrocarbon compounds such as n-heptane and n-octane, non-polar or scarcely polar aromatics such as benzene and toluene and weakly polar chlorinated compounds such as chlorobenzene, chloroform and carbon tetrachloride.

The polarity of the solvent has a significant influence on the ring-opening polymerisation of cycloolefins with catalytic systems consisting of ruthenium, osmium or iridium halides. Natta et al(87) studied the ring-opening polymerisation of cyclobutene using $RuCl_3$ and found that on employing water as a reaction medium an equimolar ratio of the cis- and trans-polybutenamer was obtained, whereas the use of ethanol produced the pure trans-product.

Calderon et al(3) found the catalytic activity of WCl_6 to be increased by the addition of ethanol prior to the organo-aluminium compound. It is believed that species such as WCl_5OEt are formed in a two step process:-



$$\begin{tikzcd}
WCl_6 + 2\,EtOH \arrow[r, "-HCl"] & (EtO)_2WCl_4 \arrow[d, "WCl_6"] \\
& 2\,EtOWCl_5
\end{tikzcd}$$

1.3.2.viii Role of the Cocatalyst

Although the metathesis reaction proceeds in the absence of a cocatalyst its presence greatly increases the activity. The role of the cocatalyst has been interpreted as:-

i) a reducing agent,

ii) an alkylating agent,

iii) a complexing agent, either to the olefins or the transition metal compound, or

iv) to create a vacant co-ordination site that would allow the incoming olefin to complex with the transition metal.

Wang and Menapace(64) favoured the first suggestion concluding that the function of LiBu in the binary catalyst system WCl_6/n LiBu was to reduce the tungsten as mentioned previously. Treatment of WCl_6 with zinc, magnesium or sodium amalgam produced WCl_4 however, which was not a catalytically active species. It would therefore appear that the role of the alkyllithium compound is not simply to reduce WCl_6. The cocatalyst activity of $EtAlCl_2$ in systems containing zero valent tungsten complexes such as (mesitylene)$W(CO)_3$ also indicates that the function of the cocatalyst is not only to reduce the catalyst to an active oxidation state.

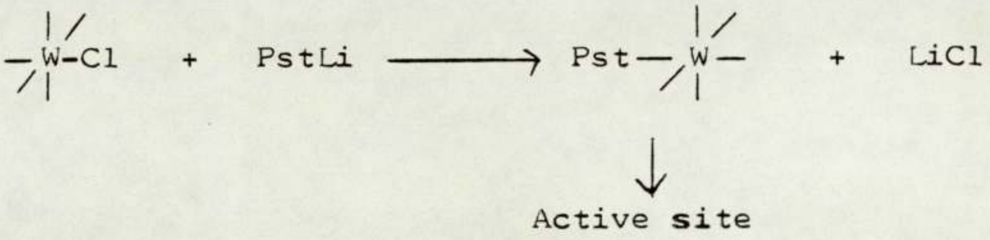
There is certainly evidence in the literature that suggests the active catalyst produced from W^{VI} complexes possesses tungsten in a lower than maximum oxidation state.(43, 88)

But it is not necessarily the role of the cocatalyst to reduce the transition metal to this state, since recent evidence suggests that W^{VI} compounds, particularly WCl_6, may be reduced by electron rich compounds such as phosphines to WCl_4. It is quite conceivable therefore that the olefin is responsible, at least in part, for the reduction of WCl_6 to W^{V} or even W^{IV}. It is then possible to account for the cocatalytic activity of $AlBr_3$, a non-reducing cocatalyst, for the polymerisation of cycloolefins.

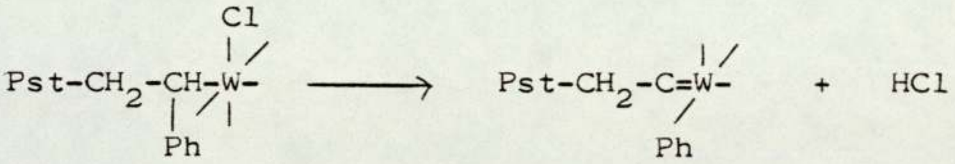
Calderon$^{(89)}$ suggested that the aluminium halides may function as Lewis-acids, reacting with the transition metal compound in an acid-base type equilibrium to provide a co-ordination site for the reacting olefin.

$$WCl_x + AlCl_3 \rightleftharpoons \left[WCl_{x-1}\right]^{+} + \left[AlCl_4\right]^{-}$$

Amass and co-workers$^{(90)}$ studied the production of block copolymers of styrene and cyclopentene by metathesis polymerisation and postulated a mechanism for the formation of the propagating centre, which accounted for the incorporation of the alkyl group of the cocatalyst in the first formed metal carbene. The catalyst system used was a combination of WCl_6 and polystyryllithium which yielded a product that included at least one block copolymer of unknown composition. This gave conclusive evidence that the cocatalyst used in that particular system played an important role in the generation of the active metathesis site in the reaction, and in doing so become an integral part of the first formed propagating species. A mechanism to explain the role of the cocatalyst as an alkylating agent to generate the carbene is shown below:-



This involves the direct substitution of a polystyryl group for a chlorine atom in WCl_6, or more plausibly the product of the reaction between WCl_6 and the olefin:-



Active carbene

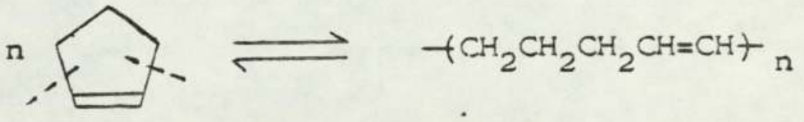
The evolution of HCl was confirmed in later studies by the same authors$^{(91)}$.

1.4 MECHANISTIC PATHWAYS

There are a number of questions regarding the mechanism of olefin metathesis and ring-opening polymerisation which have still to be satisfactorily answered. It may generally be considered that some have already been answered conclusively, but others remain nebulous. The site of cleavage of the olefin or cycloolefin was the first problem to be solved in the elucidation of the mechanism. Having established whether cleavage occurs at a carbon-carbon single or double bond it is then necessary to determine the mechanism of this cleavage and to identify the active species in the reaction. Finally the reactions which lead to the generation of the active species must be elucidated.

1.4.1. Site of Olefin Cleavage

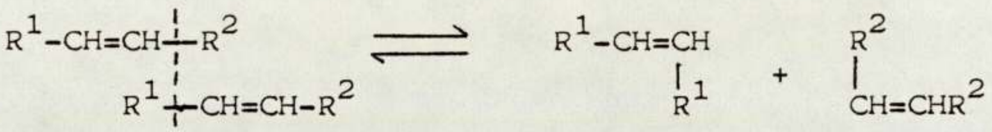
Natta$^{(5)}$ suggested that the metathesis reaction involved cleavage of a carbon-carbon single bond adjacent to the double bond during the polymerisation of cyclopentene, which can be described as:-



However no evidence in support of this mechanism was offered, but it was assumed that since single bonds are generally weaker than double bonds it would be that one which would be cleaved.

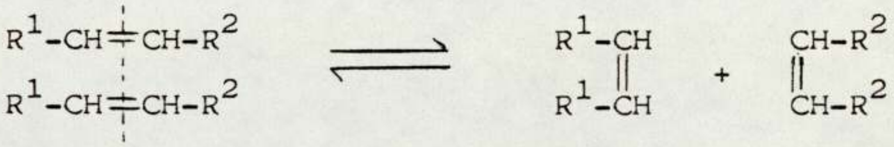
Calderon $^{(4)}$ considered that the metathesis of linear olefins and the ring-opening polymerisation of cycloolefins were examples of the same type of reaction and two alternative routes, transalkylation and transalkylidentation were considered for the process.

Transalkylation would involve the exchange of alkyl groups via cleavage of a carbon-carbon single bond adjacent to the double bond and is analagous to the scheme proposed by Natta$^{(5)}$, i.e.



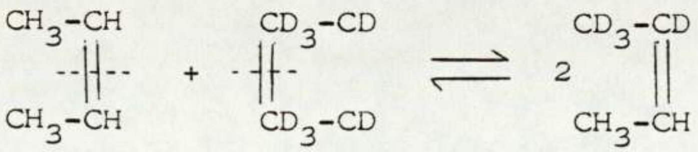
$$\begin{array}{l} R^1\text{-CH=CH-}R^2 \\ \quad R^1\text{-CH=CH-}R^2 \end{array} \rightleftharpoons \begin{array}{l} R^1\text{-CH=CH} \\ \qquad\;\; | \\ \qquad\;\; R^1 \end{array} + \begin{array}{l} R^2 \\ | \\ \text{CH=CHR}^2 \end{array}$$

Transalkylidenation would involve the intermolecular interchange of alkylidene groups by cleavage of carbon-carbon double bonds, described by:-



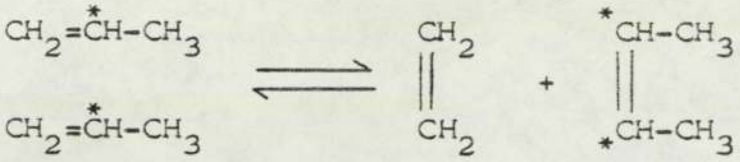
$$\begin{array}{l} R^1\text{-CH=CH-}R^2 \\ R^1\text{-CH=CH-}R^2 \end{array} \rightleftharpoons \begin{array}{l} R^1\text{-CH} \\ \quad\;\; \| \\ R^1\text{-CH} \end{array} + \begin{array}{l} \text{CH-}R^2 \\ \| \\ \text{CH-}R^2 \end{array}$$

Calderon$^{(4, 40)}$ concluded that the latter scheme was the most likely explanation, after carrying out the metathesis of 2-butene and the perdeuterated analogue. The formation of only 1,1,1,2-tetradeuterobut-2-ene complies with the transalkylidenation reaction according to the following scheme:-



$$\begin{array}{l} CH_3\text{-CH} \\ \qquad\;\; \| \\ CH_3\text{-CH} \end{array} + \begin{array}{l} CD_3\text{-CD} \\ \qquad\;\; \| \\ CD_3\text{-CD} \end{array} \rightleftharpoons 2\ \begin{array}{l} CD_3\text{-CD} \\ \qquad\;\; \| \\ CH_3\text{-CH} \end{array}$$

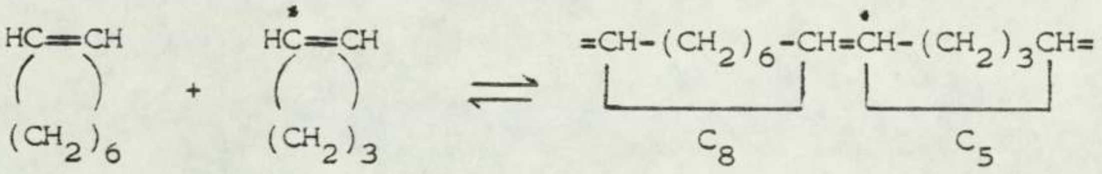
Further evidence to support the transalkylidene mechanism was obtained by Mol(92), who heterogeneously catalysed the metathesis of $[2-^{14}C]$ propene using Re_2O_7 supported on alumina. The products of the reaction were ethene and 2-butene, the former showing no signs of radioactivity and the latter exhibiting a molar radioactivity twice as high as that of the starting material:-



$$\begin{array}{l} CH_2{=}\overset{*}{C}H{-}CH_3 \\ \\ CH_2{=}\overset{*}{C}H{-}CH_3 \end{array} \rightleftharpoons \begin{array}{c} CH_2 \\ \| \\ CH_2 \end{array} + \begin{array}{l} {}^{*}CH{-}CH_3 \\ \| \\ {}_{*}CH{-}CH_3 \end{array}$$

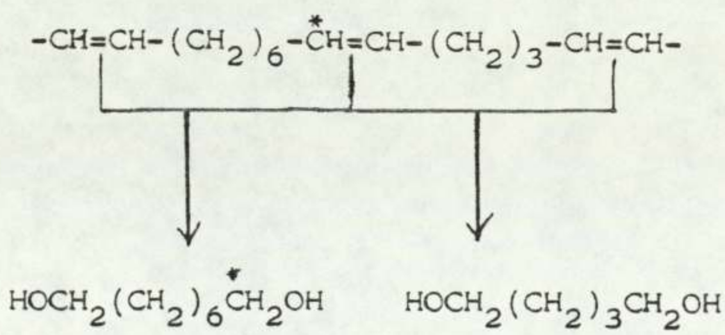
More experiments to support the transalkylidene pathway were carried out by Mol et al(93) using $[1-^{14}C]$ propene and $[3-^{14}C]$ propene. Metathesis of $[1-^{14}C]$ propene produced wholly radioactive ethene, while the use of the $[3-^{14}C]$ analogue led to radioactive 2-butene but non-radioactive ethene. These results were explained by a four-centre mechanism, and it was concluded that the methyl group of the propene molecule is always associated with the same alkylidene fragment throughout the metathesis reaction. Formation of a π-allylic intermediate, common in many transition metal catalysed reactions, was also excluded. Similar results were recorded by Woody, Lewis and Wills(94) in the disproportionation of $[1-^{14}C]$ propene.

The ring-opening polymerisation of cycloolefins can be considered a special case of metathesis transalkylidenation. Confirmation that ring-opening polymerisation proceeds by this route came from work carried out by Dall'Asta and Motroni(95,96), who copolymerised cyclooctene and ^{14}C cyclopentene which was labelled at the double bond using a catalyst system consisting of $WOCl_4/EtAlCl_2$/benzoyl peroxide. A random copolymer was produced which was broken down by complete ozonolysis, the products of which were then reduced to the respective diols. If cleavage of the cyclo-olefin occurred at the double bond the reaction would produce polymer of the following structure:-

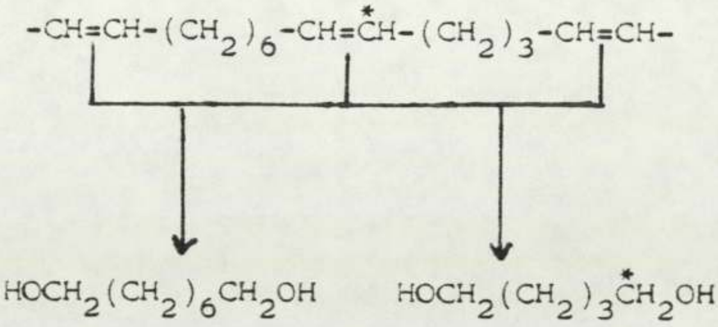


Ozonolysis followed by reduction would lead to 1,8-octanediol $(HOCH_2(CH_2)_6CH_2OH)$ and radioactive 1,5-pentanediol $(HO\overset{*}{C}H_2(CH_2)_3CH_2OH)$.

If polymerisation occurred by ring cleavage at a single bond α to the double bond, polymer units of structures A and B would both result. The ozonolysis and subsequent reduction of these would lead to the products shown.



A



B

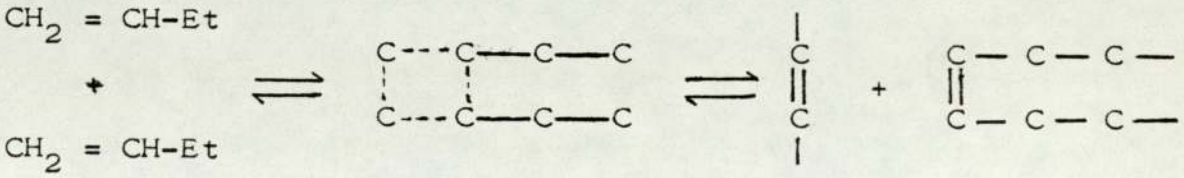
In this case the radioactivity would be equally divided between 1,8-octanediol and 1,5-pentanediol, whereas for transalkylidenation only 1,5-pentanediol would exhibit radioactivity. Thus it could be concluded that the metathesis reaction of cyclic and acyclic olefins proceeds via rupture and reformation of carbon-carbon double bonds. It was however stated at the time of these results that the findings should be limited to the tungsten based catalysts such as rhenium, molybdenum or titanium based Ziegler-Natta systems. Although these catalysts were able to homopolymerise cyclopentene they did not induce the copolymerisation of this olefin with significant amounts of higher olefin. Similarly, the above findings, although valid for low strained cycloolefins, were not automatically extended to high strained olefins such as cyclobutene and norbornene. In fact it was suggested that the non-specificity of the tungsten halide system(67) in the polymerisation of the latter olefins, which simultaneously yield ring-opening and vinyl type polymerisations, may be due to significant differences in the polymerisation mechanism of the two classes of cycloolefins.

1.4.2 Reaction Mechanism

Most of the investigations into the mechanism of olefin metathesis and ring-opening polymerisation of cycloolefins have been directed towards deciding whether the reaction proceeds by a "pairwise" interchange of the carbons between two olefins or through a one-carbon mechanism, implying a carbenic intermediate. Although there is a consensus of opinion which favours the latter mechanism, many experimental observations are hard to explain on this basis.

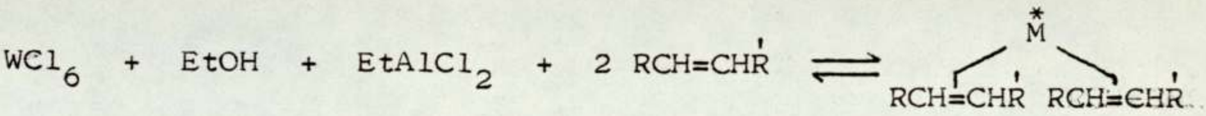
1.4.2.i Quasicyclobutane Model

Bradshaw et al$^{(9)}$ were the first to propose a quasicyclobutane transition state during the disproportionation of 1-butene. The intermediate was deemed to have been formed by a (2+2) cyclisation reaction.



Other investigators including Banks and Bailey$^{(2)}$, Adams and Brandenberger$^{(97)}$ and Crain$^{(98)}$, obtained data from the disproportionation of a number of linear olefins which were interpreted in terms of such a model.

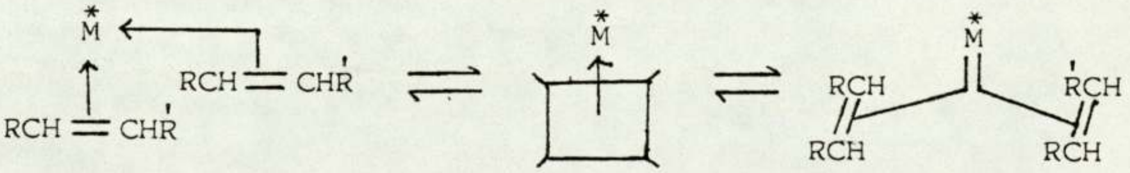
Calderon and co-workers(4,10) subsequently proposed a mechanism for the polymerisation of cycloolefins which involved ring-opening via cleavage of the carbon-carbon double bond and the metathesis of acyclic olefins. For the homogeneous reaction catalysed by $WOCl_4/EtOH/EtAlCl_2$ a pairwise mechanism was conceived, based on the results obtained in the reaction of deuterated-2-butene and but-2-ene and a series of steps was proposed to account for the reaction. It was further proposed that the catalyst components would react in some way, leading to formation of a diolefin-metal complex as described by:-



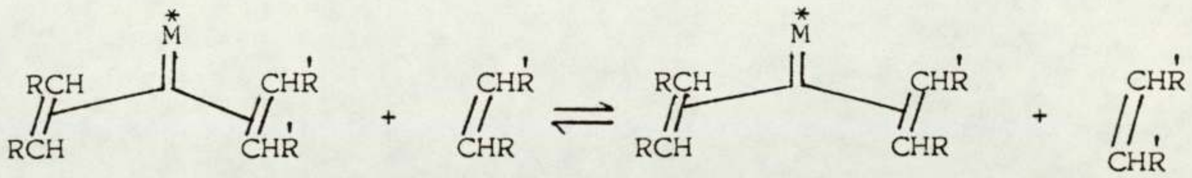
$$WCl_6 + EtOH + EtAlCl_2 + 2\ RCH{=}CHR' \rightleftharpoons \overset{\overset{*}{M}}{RCH{=}CHR'\quad RCH{=}CHR'}$$

where $\overset{*}{M}$ represents the transition metal and the catalytic ligands

Transalkylidenation would then take place via the intermediate formation of a co-ordinated quasicyclobutane, which could cleave to the product olefins still co-ordinated to the transition metal:-



Olefin exchange would take place as one or both of the co-ordinated olefins was replaced by another molecule of reactant:-



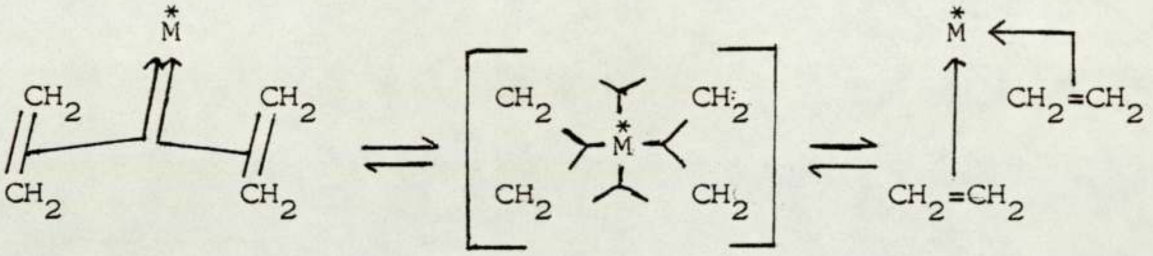
Hughes(99) proposed a similar pairwise mechanism involving a cyclobutane intermediate for the metathesis of 2-pentene with a catalytic system based on molybdenum. By employing the concepts of orbital symmetry Hughes advanced a theoretical interpretation of the proposed mechanism, specifying the role of the transition metal in the cleavage of the bonds from the reacting olefin and leading to the formation of products.

Mango and Schachtschneider(12) formed a quantitative interpretation through the molecular orbital calculations for the pairwise mechanism involving a cyclobutane-type transition state. The Woodward-Hoffmann concepts of conservation of orbital symmetry(11) were extended to the cyclo-addition reaction and correlation diagrams were generated for the formation of the cyclobutane transition state in the presence of transition metals. It was concluded that d-orbitals of the transition metal played an essential role in the process, overlapping the olefin orbital.

Doubt was cast on the validity of this model when cyclobutane , or its complexes as separable intermediates, failed to be identified.

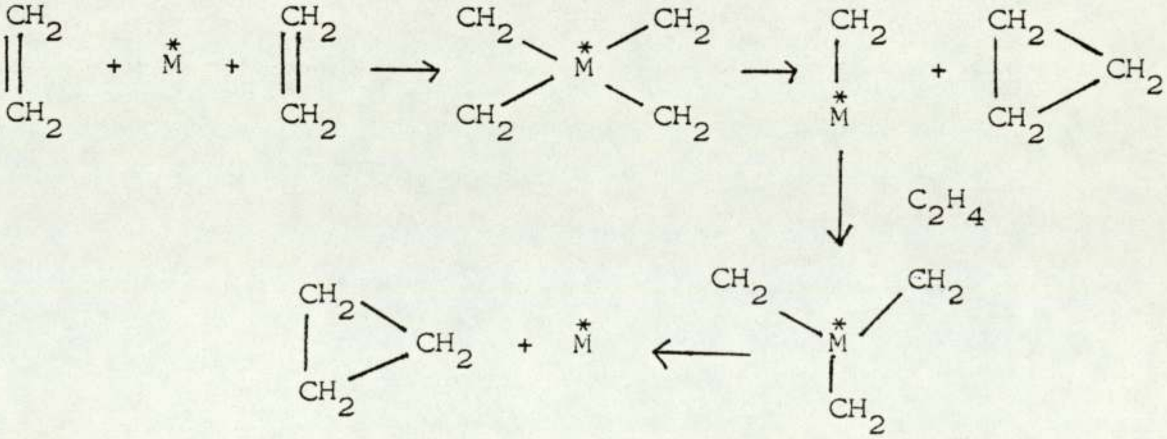
1.4.2.ii Tetramethylene-Metal Complex

Lewandos and Petit$^{(60)}$ proposed a mechanism involving carbene structures and postulated that the symmetry-allowed formation of a four-centred organometallic complex in the reaction:-



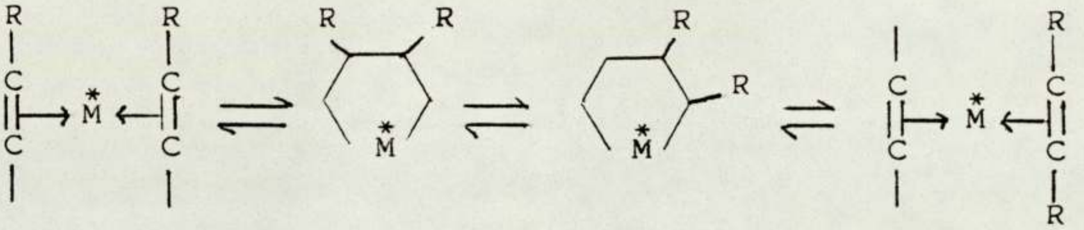
According to this mechanism a diolefin complex of the transition metal forms a four-centred organometallic intermediate rather than a cyclobutane transition state. This intermediate gives rise to the reaction products or the initial diolefin complex through a reversible process.

The tetramethylene-metal complex mechanism has also been used to explain the formation of cyclopropane from ethene in the presence of heterogeneous catalysts:-

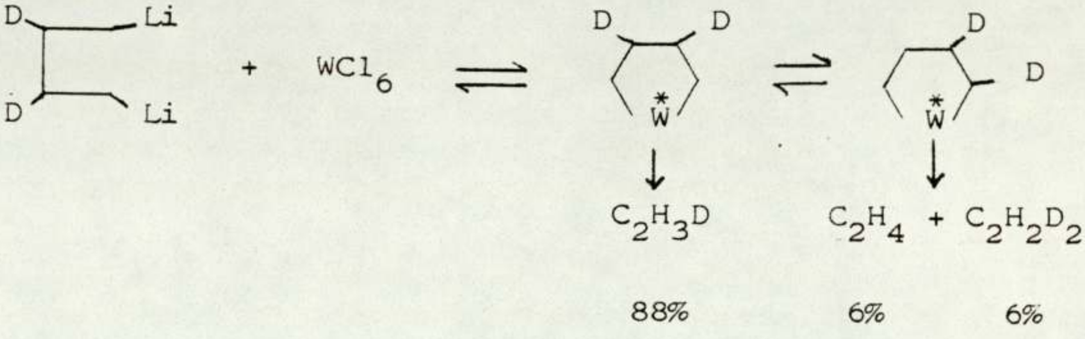


1.4.2.iii Metallacyclopentane Transition Model

Another pairwise mechanism involving the initial formation of a diolefinic complex as a step in the generation of a metallacyclopentane was proposed by Grubbs(63). By rearrangement a new metallacyclopentane was formed which subsequently generated the reaction products. The mechanism for this model may be summarised as:-



The formation of deuterated ethylene from the reaction of 1,4-dilithio-2,3-dideuterobutane was interpreted as evidence for this mechanism:-



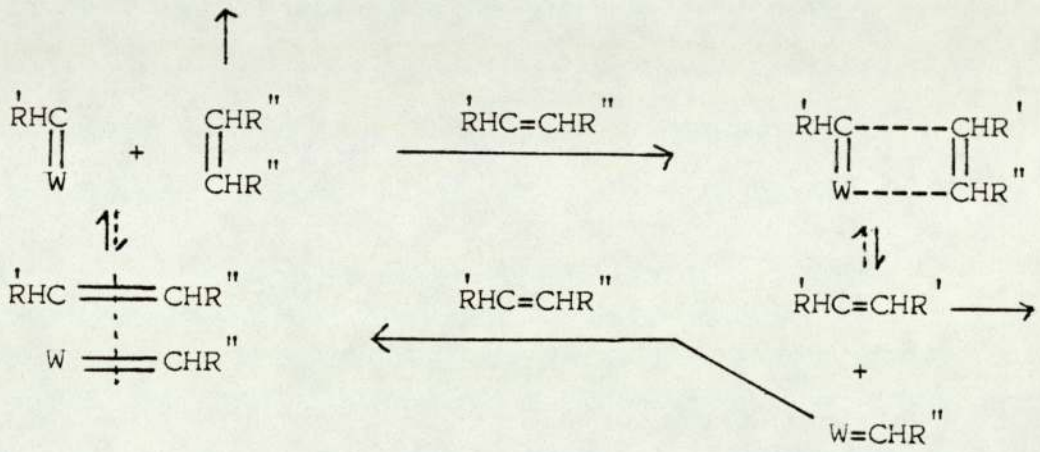
This presupposes that the reactants form the intermediates as shown in the scheme.

The preceding models could be explained readily on a theoretical basis, but there was little conclusive experimental evidence to support them.

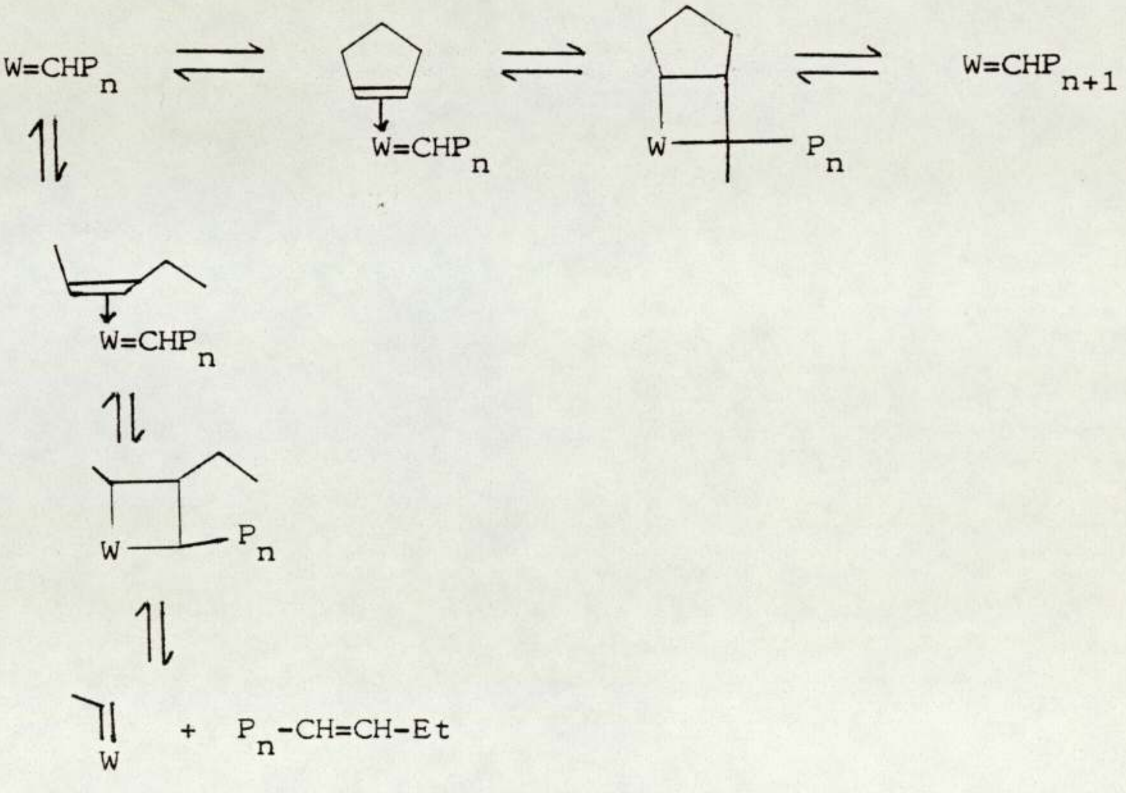
1.4.2.iv Metallacarbene-Metallacyclobutane Mechanism

Introduction and Evidence supporting the Carbene Mechanism

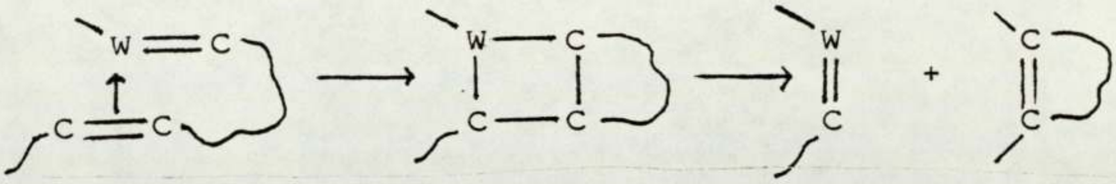
The carbene mechanism was first proposed by Hérisson and Chauvin(16) to explain the oligomerisation of cyclopentene with 2-pentene in the presence of catalytic systems based on tungsten. Reaction of the olefin with a carbene complex of the transition metal was proposed, producing a metallacyclobutane intermediate which then reacted further to generate the products as shown:-



When applied to the reactions of cycloolefins ring-opening of the double bond occurs together with insertion of the cycloolefin unit into the metal carbene. The active species was considered to be equally reactive towards both linear and cyclic olefins. Thus the polymeric carbene generated as a result of propagation could react not only with cyclopentene but also 2-pentene. In the latter case a polymer molecule was produced and a new active carbene complex, thus:-

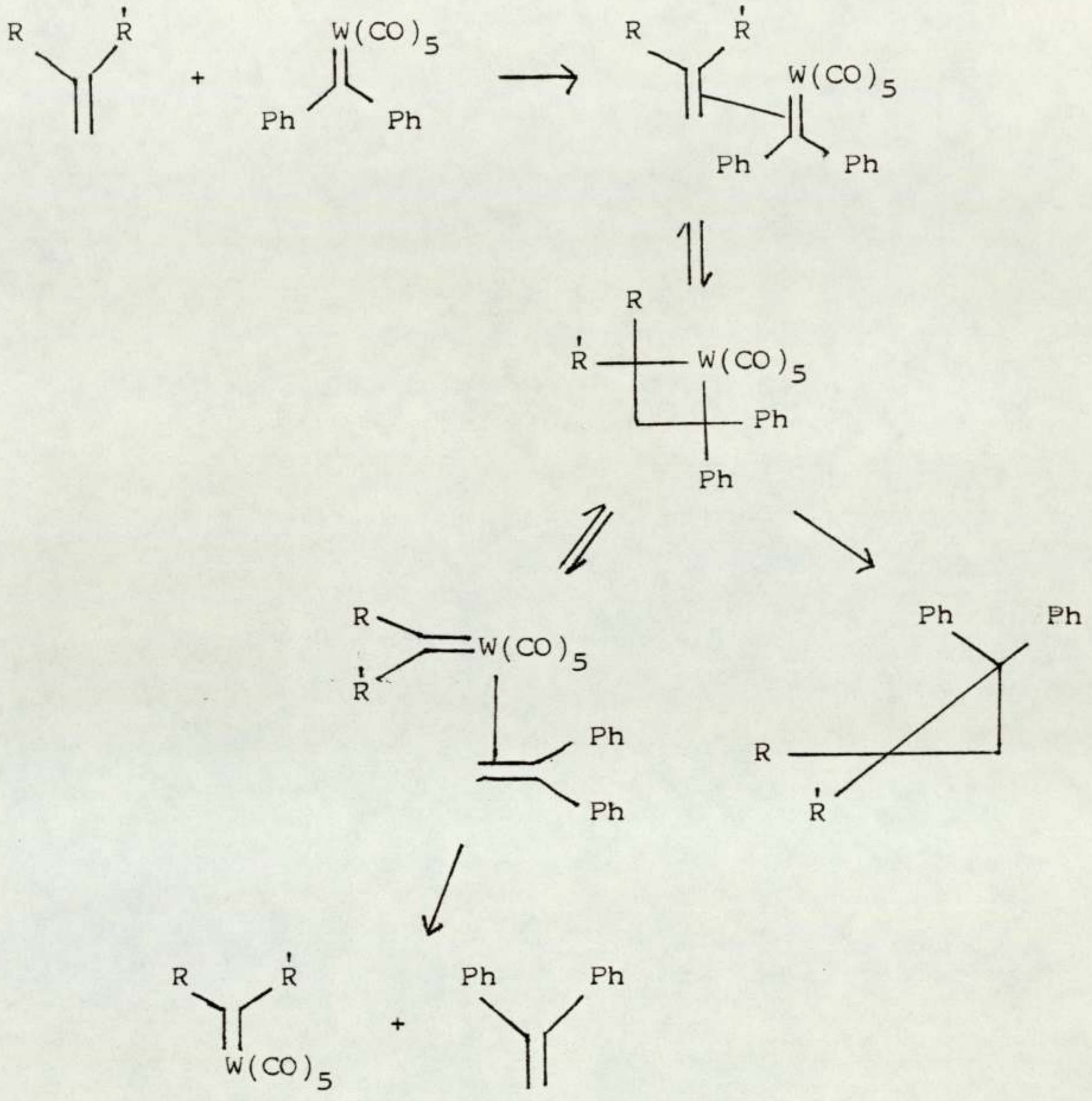


Oligomers can also be formed by an intramolecular reaction, because the carbon-carbon double bond in the polymer chain may also take part in metathesis, thus:-



No attempt was made to explain the reactions leading to the formation of the carbene complex, the product distribution in the cometathesis of α-olefins with cycloolefins, or the fragmentation reaction of cyclic dienes and trienes. Neither did the report explain any features of the system which might lead to an understanding of the kinetics of the reaction. However the proposal was successful in stimulating work which might answer some of the problems of the kinetics and stereochemistry of this kinetic chain process.

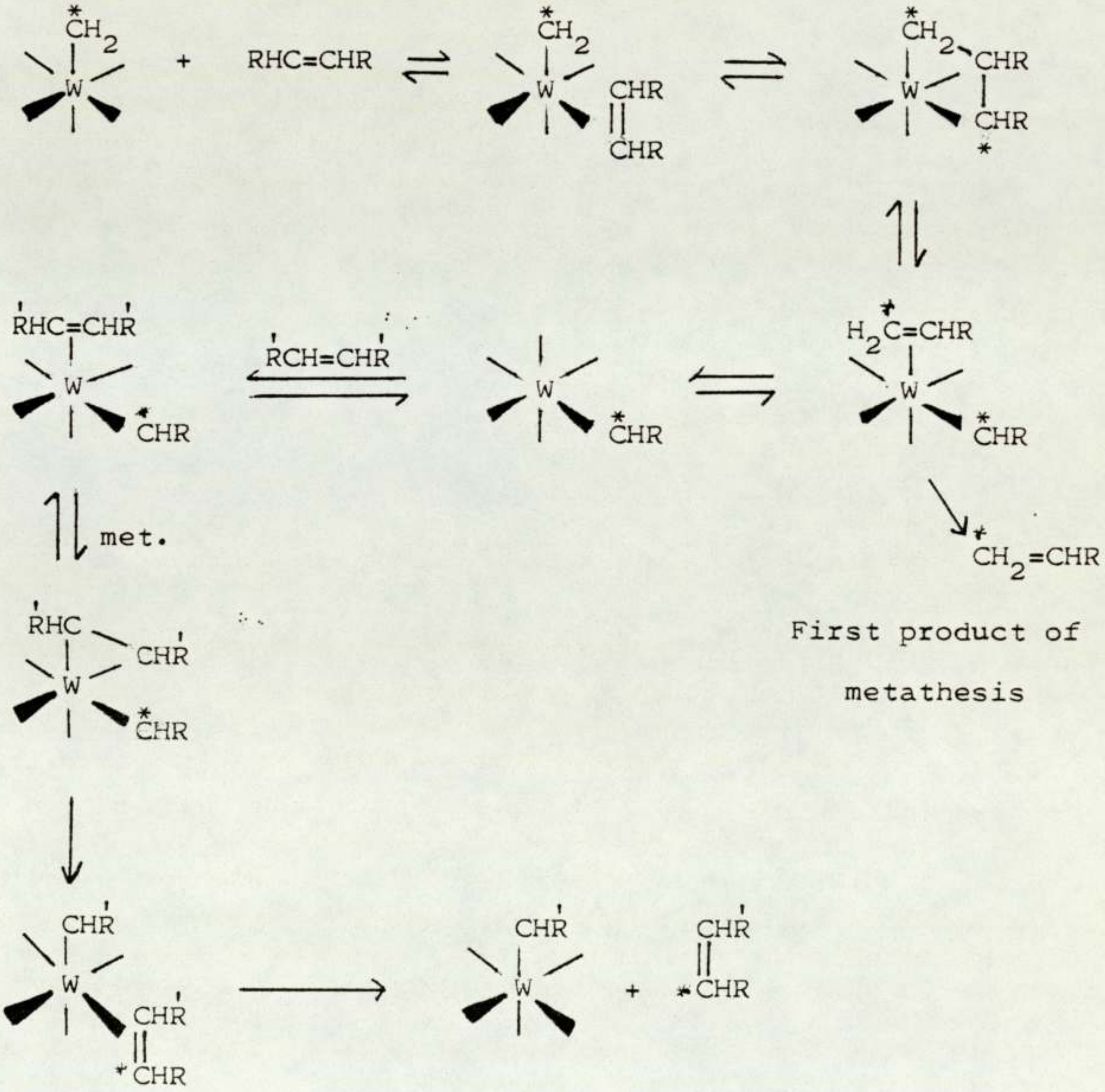
A carbene mechanism was described by Casey and Burkhardt(76) for the transalkylidenation and cyclopropanation occurring in the reaction of olefins with (diphenylcarbene)-pentacarbonyl-tungsten. A metal complex containing both a carbene and a methylpropene ligand was formed which rearranged to a metallacyclobutane. This species then underwent a reductive elimination to give a dimethyl-2,2-diphenyl- and diphenyl-ethene. These products were to be expected from the metallacyclobutane formed, in the one case as a degradation product and in the other as the first product of metathesis. The proposed reaction scheme is as shown:-



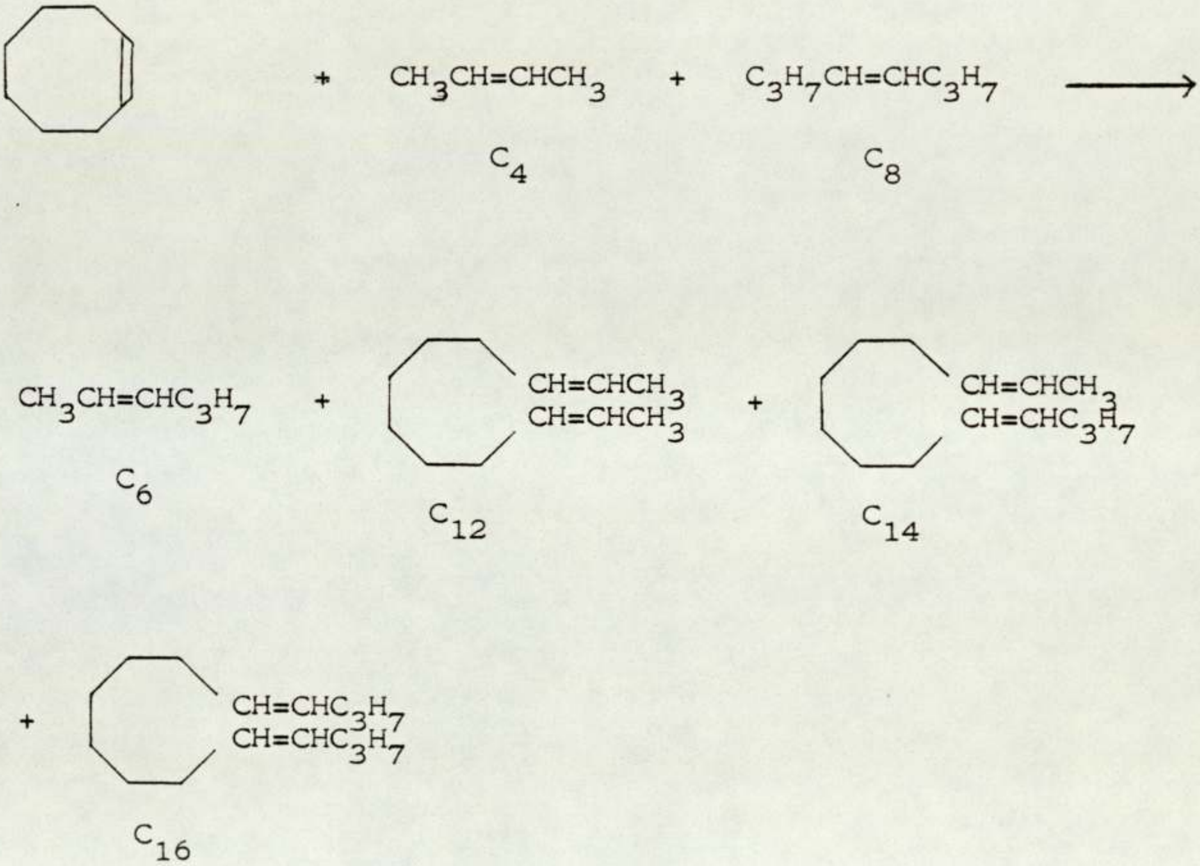
The (diphenylcarbene)-pentacarbonyltungsten was a useful model, in that it is a relatively stable metallacarbene which shows metathesis reactivity.

A similar carbene mechanism was advanced by Muetterties[(100)] for olefin metathesis catalysed by WCl_6 and alkylating reagents such as $ZnMe_2$. The metal carbene formed was proposed to be tungstenmethylene, and the product of the first metathesis reaction of the transition metal carbene was isolated from the products.

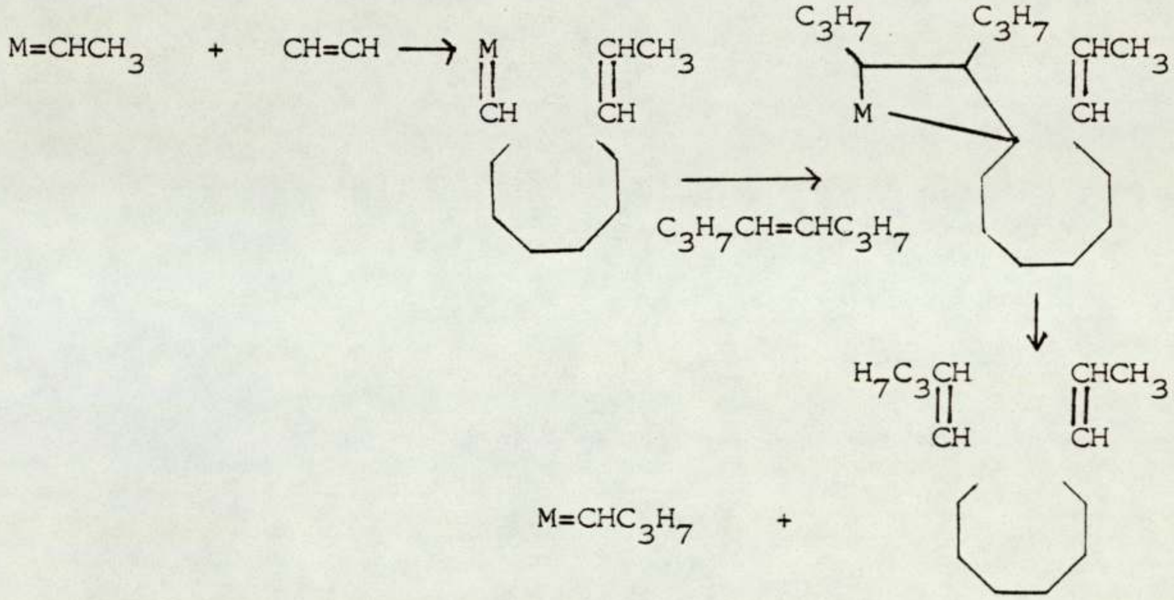
The mechanism for the overall reaction was proposed as follows, with possible sites for interaction of the metal atom in the halide derived from the alkylating reagent starred:-



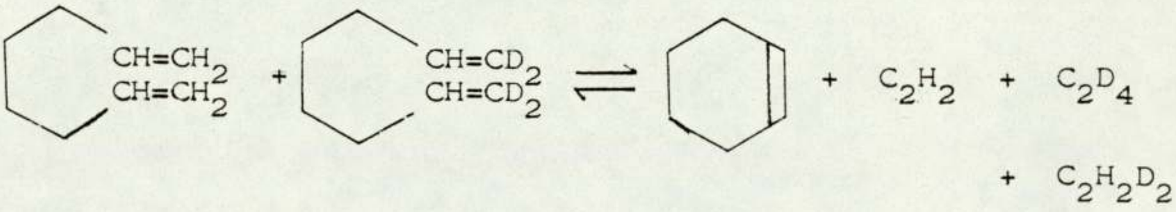
Strong support for the carbene mechanism was supplied by the detailed studies of Katz et al(101) and Grubbs and co-workers(102,103). In order to differentiate between the pairwise models Katz studied the metathesis of cyclooctene with a mixture of 2-butene and 4-octene. The reaction is summarised below:-



It was found that in addition to the product from the cross-metathesis of the linear olefins (C_6), two symmetrical compounds C_{12} and C_{16} were formed along with unsymmetrical C_{14}. For the predicted carbene mechanism the C_{14} product would predominate over the C_{12} and C_{16} for the initial part of the reaction. This was found to be true, but these observations did not rule out the possibility of a pairwise scheme, since it was not known whether the olefin exchange step was rate determining or otherwise. If this was the case a pairwise scheme would also account for the ratio of the reaction products. The indication that the C_{14} diene is a "first" product of metathesis however can only occur if a non-pairwise chain operates such that:-

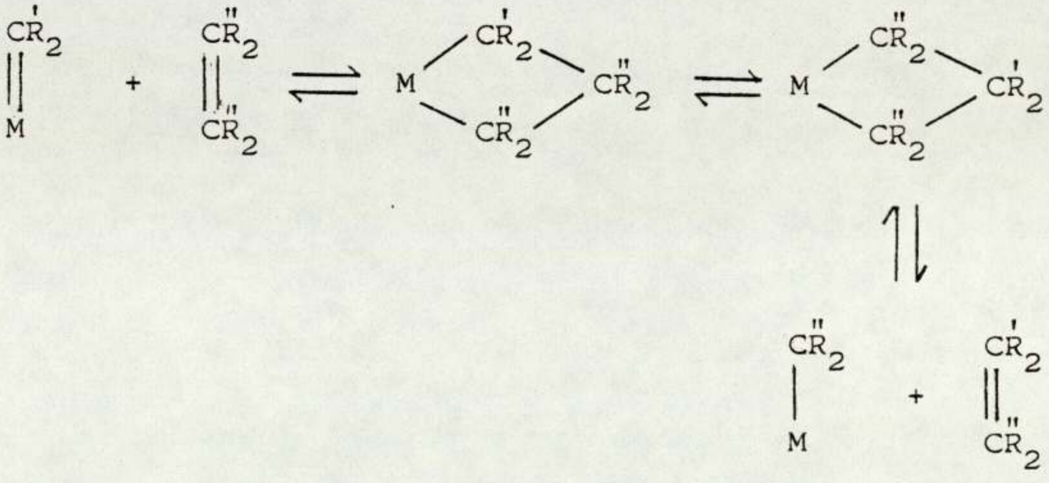


Grubbs studied the metathesis of 1,7-octadiene with the perdeuterated 1,7-analogue as shown below:-



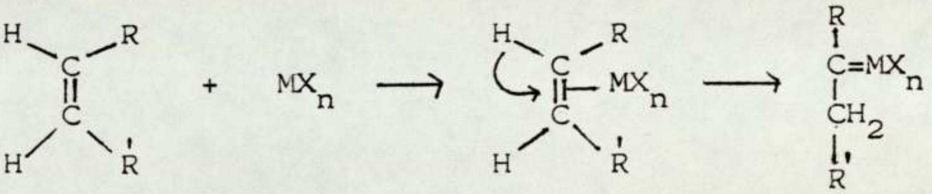
If the reaction had proceeded by a pairwise mechanism the maximum product ratio of d_4: d_2: d_0 would be 1:1.6:1 for a 50:50 mixture of reactants. For a non-pairwise carbene mechanism under non-equilibriating conditions the corresponding ratio would be 1:2:1, and these predictions were observed under experimental conditions , confirming the carbene mechanism above the pairwise scheme.

Puddephatt et al(104) proposed a carbene mechanism for olefin metathesis which did not involve the intermediate formation of a metallacarbene-olefin complex. The direct metallacyclobutane isomerisation has experimental support from the chemistry of substituted platinacyclobutanes, but it remains unclear whether this might occur through a concerted pathway or via a stepwise route involving bond cleavage.

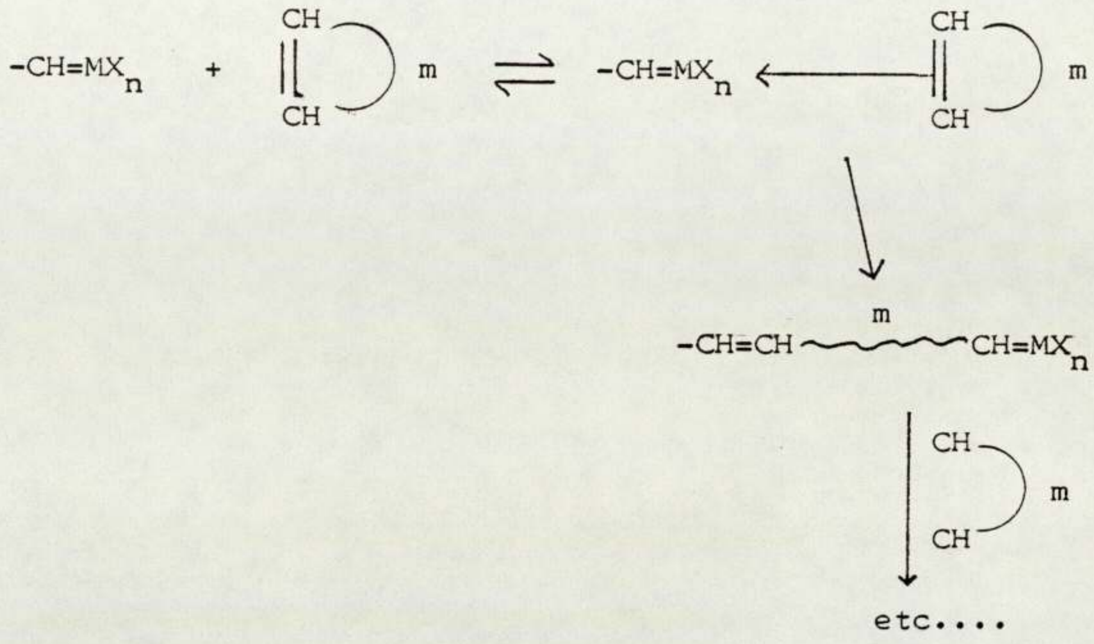


Based on Chauvin's mechanism Basset and co-workers(105,106) proposed a stereochemical control of the co-ordination of the olefin to the metallacarbene moiety. The stereochemical aspects will be discussed in detail later however.

A chain carbene mechanism for the ring-opening polymerisation of cycloolefins was suggested by Dolgoplosk and co-workers(107). It was considered that the chain process of cycloolefin ring-opening involves the participation of active centres which are complexes of carbene with transition metals. It was proposed that the carbene species was formed from reaction of the olefin with the catalyst system, and involved the intramolecular migration of hydrogen in the olefin:-

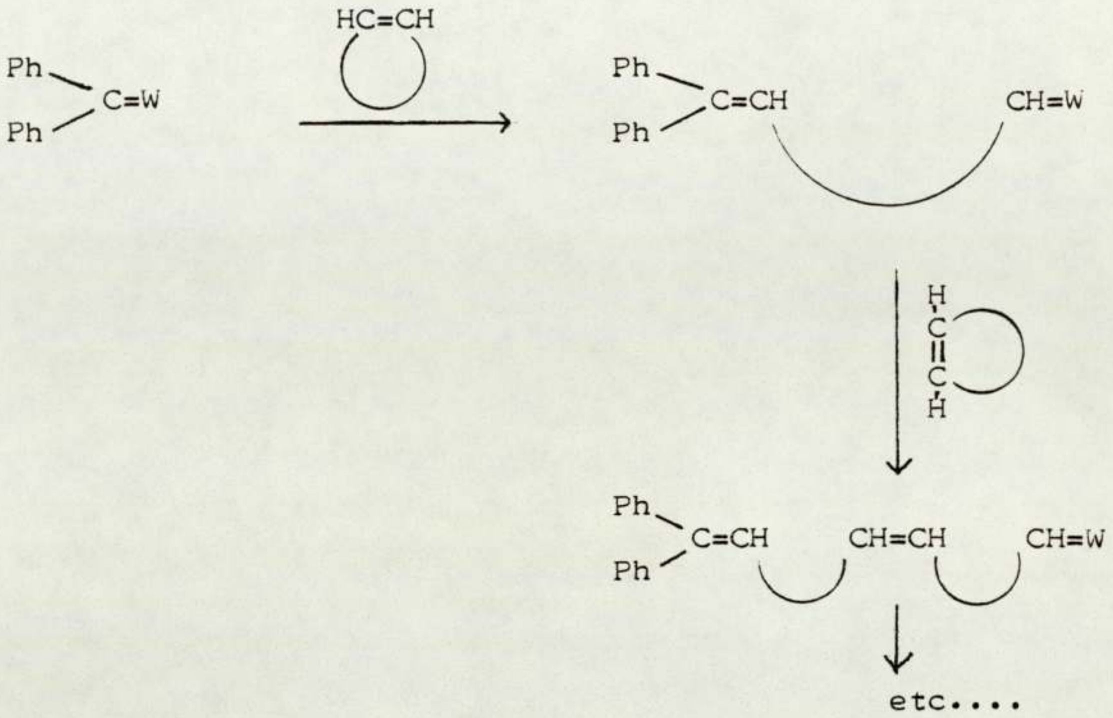


Experimental evidence for the generation of active centres came from the decomposition of phenyldiazomethane under the influence of tungsten chlorides, initiating the polymerisation of cyclopentene and 1,5-cyclooctadiene to high molecular weight polymers. The chain propagation was represented by reversible monomer co-ordination of the cycloolefin to metal, followed by monomer insertion into the chain:-

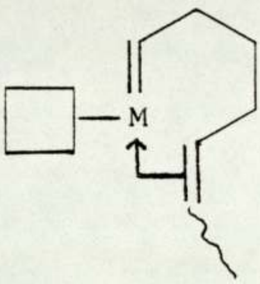


The proportion of oligomeric compounds at low conversion of monomer was found to be small and their formation was associated with cyclisation reactions of the polymer and not with the polymerisation process.

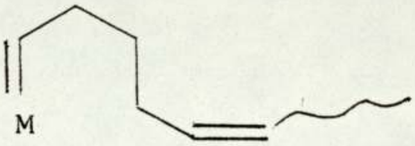
Katz and Acton$^{(55,75)}$ interpreted the mechanism of the polyalkenamer formation from cycloolefins in the presence of the carbene systems $Ph_2C{=}W(CO)_5$ and $Ph(MeO)C{=}W(CO)_5$ through a chain process where the initiation and propagation are attributed to carbene complexes:-



For the ring-opening polymerisation of cyclopentene with cis- and non-specific metathesis catalysts, Calderon and co-workers(108) advanced a bidentate chelating concept involving a multidentate growing chain - (A) for cis-specific catalysts and a non-chelated growing chain, (B) for non-specific catalysts:-

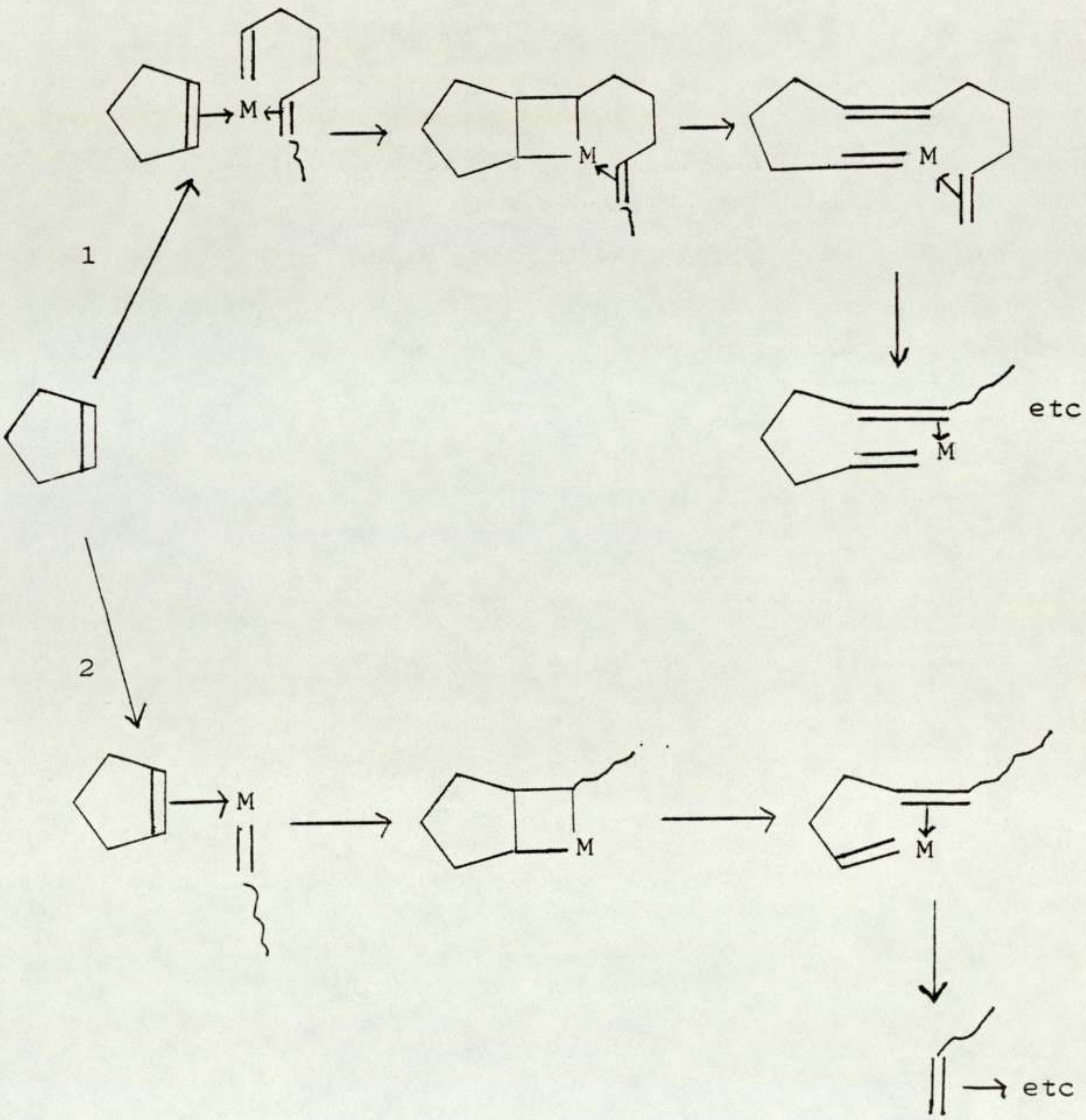


(A)



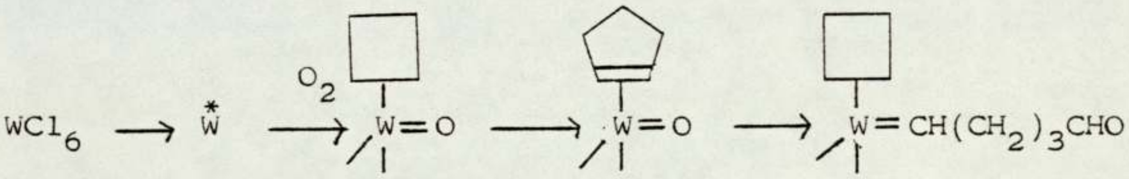
(B)

In the first case the propagation reaction involves a "three ligand sequence", implying simultaneous co-ordination of the carbene, monomer and polymer chain to the metal centre (path 1), and in the second case a "two ligand sequence", involving co-ordination of the carbene and monomer only (path 2).



Based on the steric structure of polyalkenamers Ivin and co-workers(109) postulated the presence of two kinetically distinct species, not in equilibrium with one another, to explain the mechanism of ring-opening polymerisation. This mechanism was interpreted within the limits of the carbene concept as involving metallacarbenes which first co-ordinate then add olefin to give new metallacarbenes and newly formed double bonds. The stereochemical requirements of each of the species has been a subject of considerable debate and will be dealt with in greater detail later.

To account for the oxygen activation of cyclopentene polymerisation in the presence of WCl_6 as a catalyst Amass and McGourtey(110) pointed to the formation of an oxygen ligand as the active species in the initial step responsible for the generation of the carbene chain carrier:-

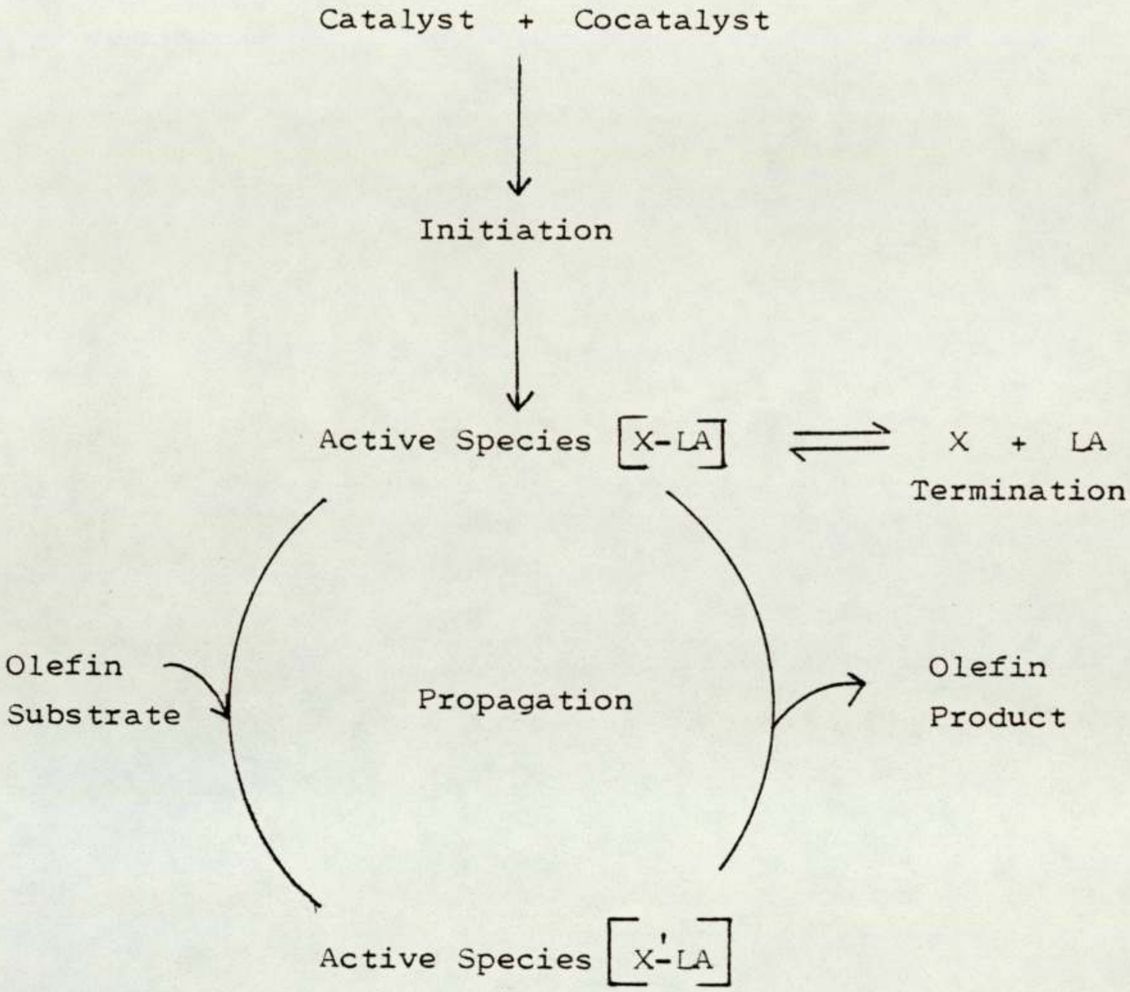


Infra-red spectral analysis of the polymer indicated the presence of a carbonyl group in the chain. The oxygen ligand seems to be essential in the initiation step with this catalyst, but it is not directly implicated in the propagation step.

Although the chain carbene mechanism seems to be correct the metallacyclobutane intermediates proposed do not satisfactorily explain the stereoselectivity of the reaction. Important objections to the simple carbene mechanism were set forth by Verkuijlen$^{(111)}$ based on experimental data obtained in metathesis reactions carried out with the catalyst $WOCl_4/Me_4Sn$. It was observed that the Me_3SnCl derivative of the cocatalyst is essential in maintaining the activity of the system in the metathesis of 10-methyldecanoate or methyloleate; on completely removing Me_3SnCl the catalyst becomes inactive.

The catalyst not only seems to be the source for generating the carbene species in the initiating step, but governs the level of activity in the propagation and termination steps as well. Verkuijlen presented a more comprehensive mechanistic scheme for metathesis reactions induced by bi-component catalyst systems comprising initiation, propagation and termination steps.

This reaction scheme explains several facts encountered in metathesis chemistry, including the ineffectiveness of isolable tungsten-carbene complexes compared to conventional catalysts and the sensitivity of the side reactions:-



Where LA - Lewis acid

X - Transition metal

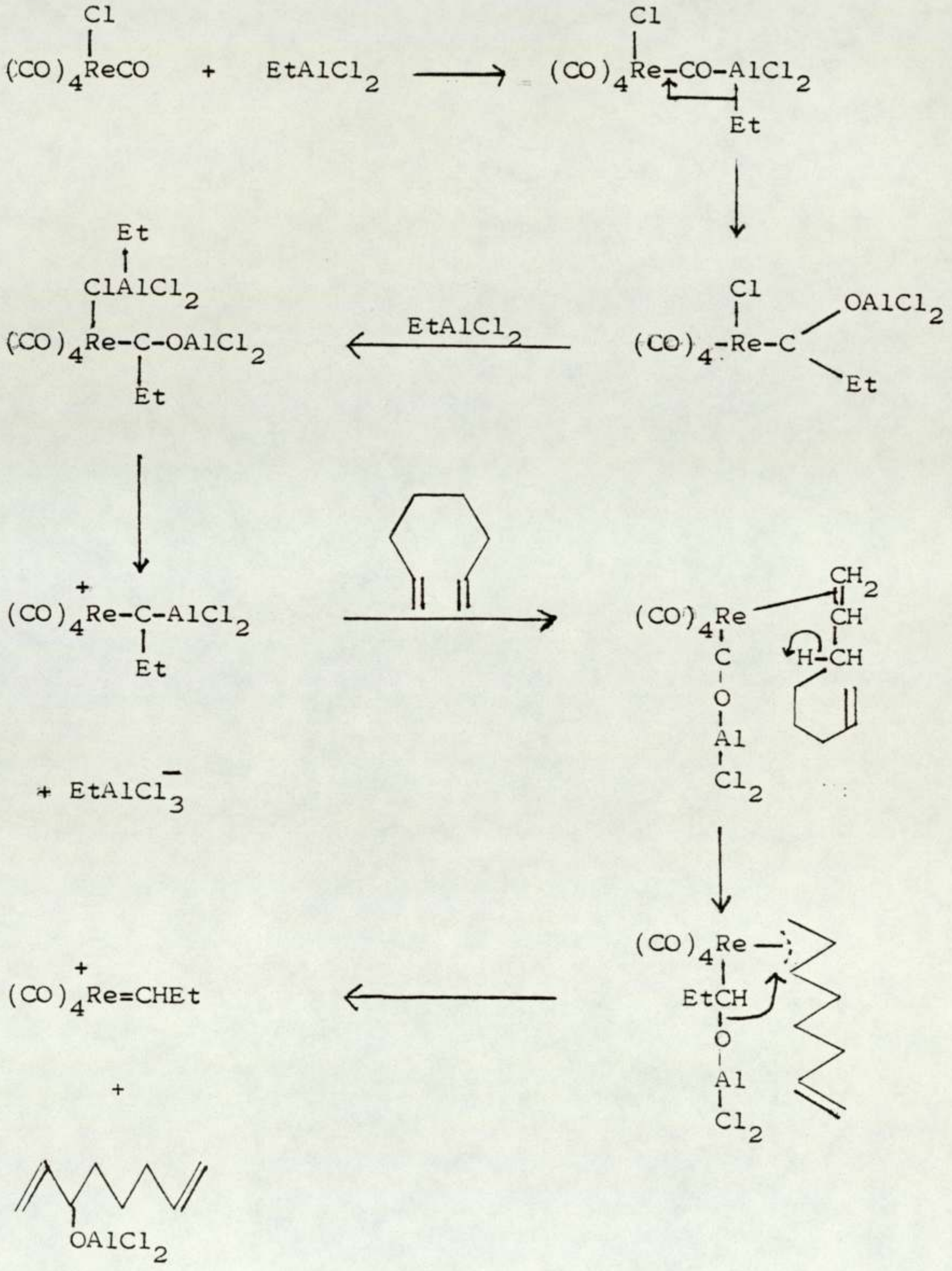
Formation of the Initiating Metallacarbene

If the metallacarbene is to be considered as a propagating centre then questions arise as to the mechanism of generation of the very highly active centre from the catalyst and co-catalyst. Several pathways have been suggested for the formation depending upon the nature of the catalytic system employed.

The majority of homogeneous metathesis catalysts are obtained from tungsten, molybdenum or rhenium halides, or complexes and a metal alkyl. In such systems alkyl transfer readily occurs from the organometallic compound to the transition metal giving rise to alkylated transition metal complexes. α-Hydrogen migration may then occur from an adjacent methylene group to the transition metal, giving rise to an initiating carbene intermediate. It is likely that the carbene complex interacts with the organometallic compounds or the resulting Lewis acid giving a more stable dinuclear compound.

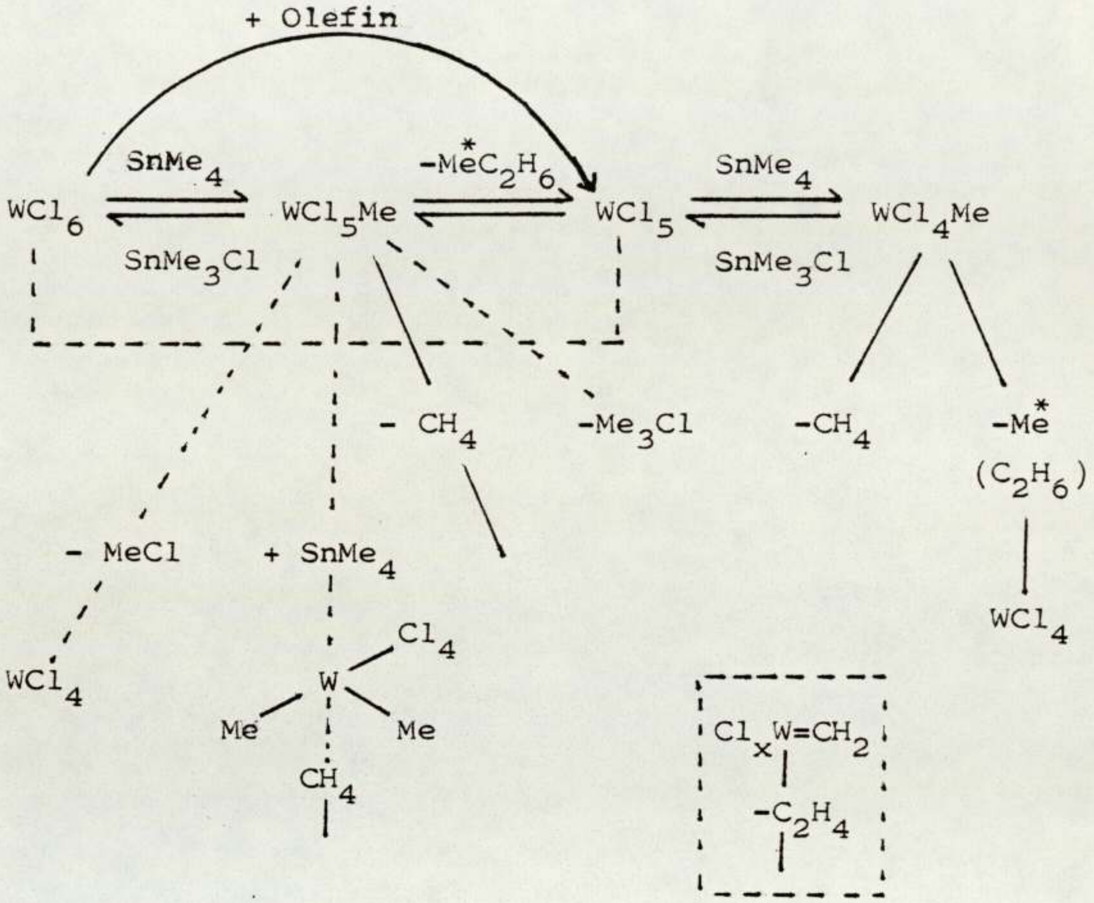
Farona et al(69,113) pointed out different ways of generating the carbene species in binary systems of rhenium or molybdenum carbonyl complexes and organoaluminium compounds. For metathesis reactions promoted by the Re/Al catalyst system the initial carbene must be formed without evolution of gas if a co-ordinated carbene mechanism is operative. This requirement can be met if the initial carbene is formed by attack of an ethyl group on co-ordinated carbon monoxide, followed by exchange of oxygen for hydrogen to create a co-ordinated propylidene molecule. The second site for olefin co-ordination would come about by transfer of chloride from rhenium to aluminium. Considerable evidence supporting this process included the detection of octa-1,7-dien-3-one in the metathesis of 1,7-octadiene which accounted for the transfer of oxygen (from ReCOEt) and hydrogen (from 1,7-octadiene).

The presence of cyclopropane derivatives gave further support to the production of co-ordinated propylidene as the first formed carbene which complied with earlier observations made by Casey and Burkhardt(76) of the type of co-ordinated carbene insertion reaction with olefins. On the basis of these observations the possible mode of production of the first formed carbene was postulated. The reaction scheme proposes two roles for the organometallic compound. In the first step it acts as an alkylating agent, in this case alkylating a carbon monoxide ligand as distinct from displacement of a ligand such as chloride ion. In the subsequent rearrangement of this species the second role of the organometallic is that of a Lewis acid, generating a species that is electron deficient and which will co-ordinate an olefin. The initial products of metathesis would be 1-butene or 1,7-decadiene, depending on the mode of attack of the octadiene. The reaction scheme proposes that the carbon monoxide ligand is sufficiently basic to complex with the Lewis acid. This is not normally the case so that only if the transition metal provides elctron density on the ligand would one expect this facility to be increased. This mechanism has therefore to be approached with scepticism.

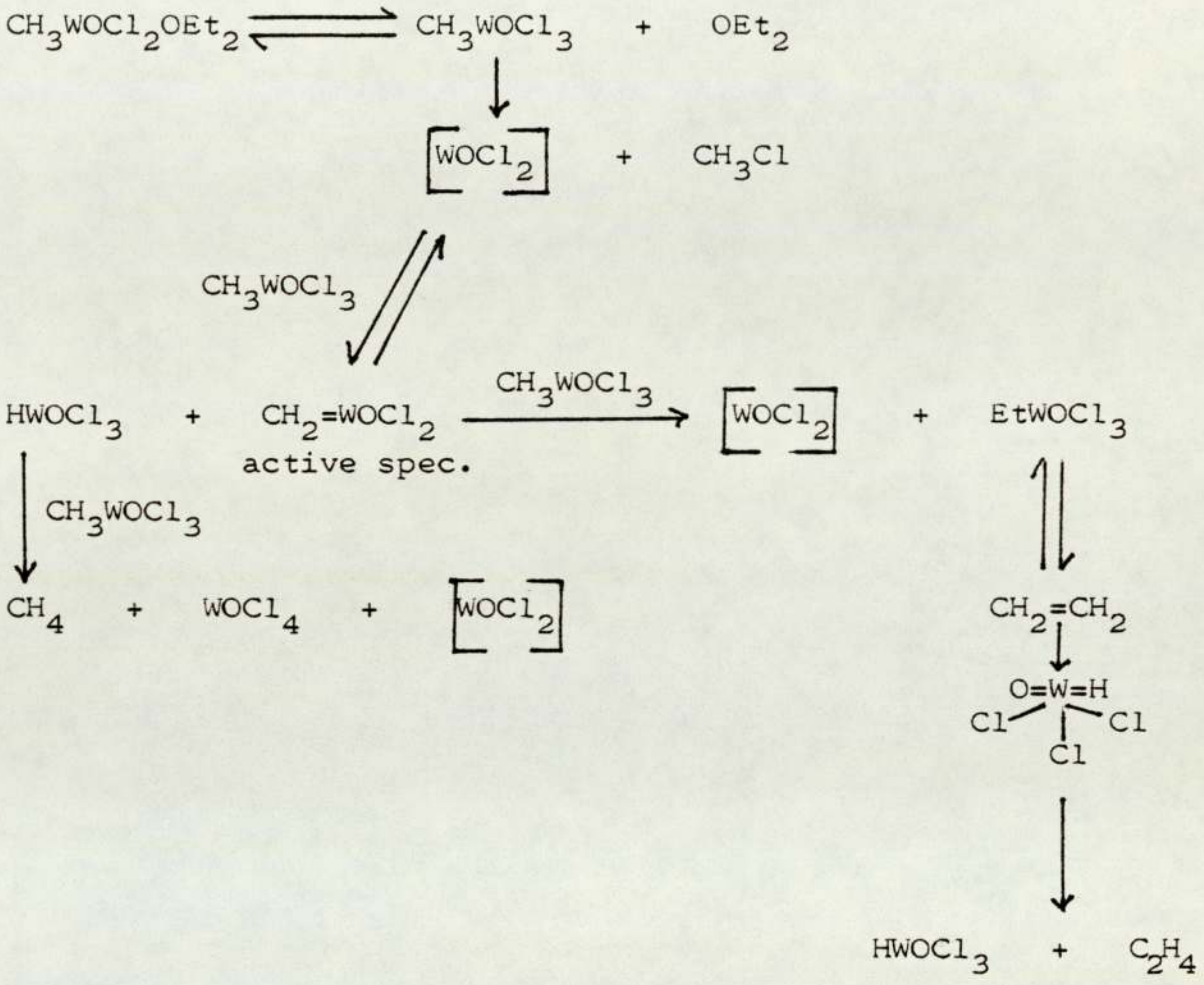


For the binary system Mo(CO)$_5$Py/EtAlCl$_2$, Motz and Farona$^{(113)}$ found that the formation of the initial co-ordinated complex is dependent upon the nature of the solvent. In chlorobenzene the initial carbenes are ethylidene and methylene when employing EtAlCl$_2$ or MeAlCl$_2$ as cocatalysts respectively. However using heptane as the solvent produced co-ordinated propylidene and ethylidene from the corresponding cocatalysts.

A simpler reaction scheme for the generation of the active species was that proposed by Thorn-Cśayni$^{(114)}$ using the binary system WCl$_6$/Me$_4$Sn in kinetic studies on trans-2-pentene. Methylation of the transition metal atom is effected by the cocatalyst, and the tungstenmethyl compound initially formed may subsequently undergo further methylation or eliminate methylchloride. It would appear that the bismethyl derivative was responsible for the formation of the active carbene, but once formed in the presence of 2-pentene two propagating species were produced. The reaction does accept that a number of side reactions may occur which reduce the efficiency of initiation. The scheme is proposed as follows:-

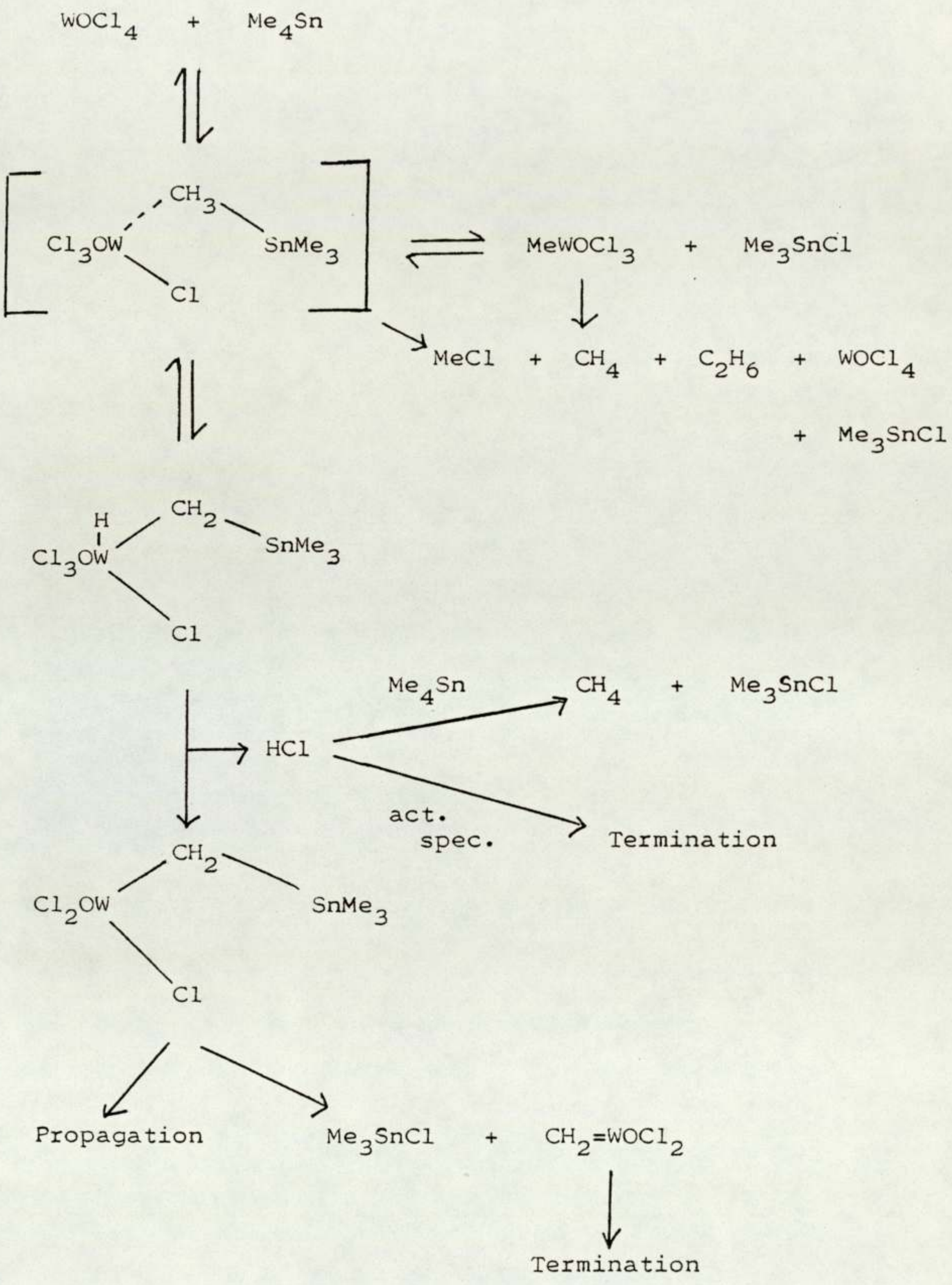


Recent studies by Muetterties and Band$^{(115)}$ on the complex $CH_3WOCl_3.OEt_2$, obtained from the reaction of $WOCl_4$ with Me_2Mg, suggested the intermediate formation of CH_2=$WOCl_4$. The CH_2 fragment was shown to be incorporated into the metathesis products. Production of this intermediate was suggested to be one product of a chain reaction which was initiated by the decomposition of CH_3WOCl_3. The $WOCl_2$ formed in the initial step was the chain carrying species in the sequence of reactions described by:-

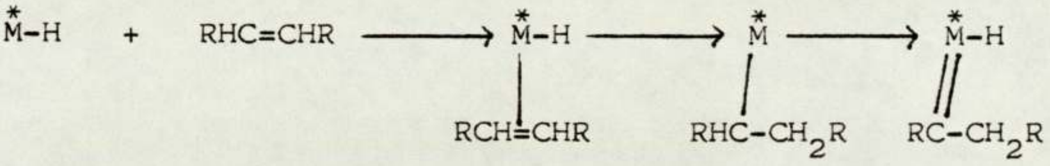


The methylene group of the metathesis active species $CH_2{=}WOCl_2$ was found in products of the first metathesis reaction with 2-pentene as 1-butene and propene.

The formation of methyltungsten derivatives has also been invoked by Verkuijlen$^{(111)}$, who suggested that in metathesis catalysed by $WOCl_4/Me_4Sn$ the active carbene species is a bimetallic co-ordination compound involving the organometallic compound. A scheme for the formation of the active carbene is as follows:-

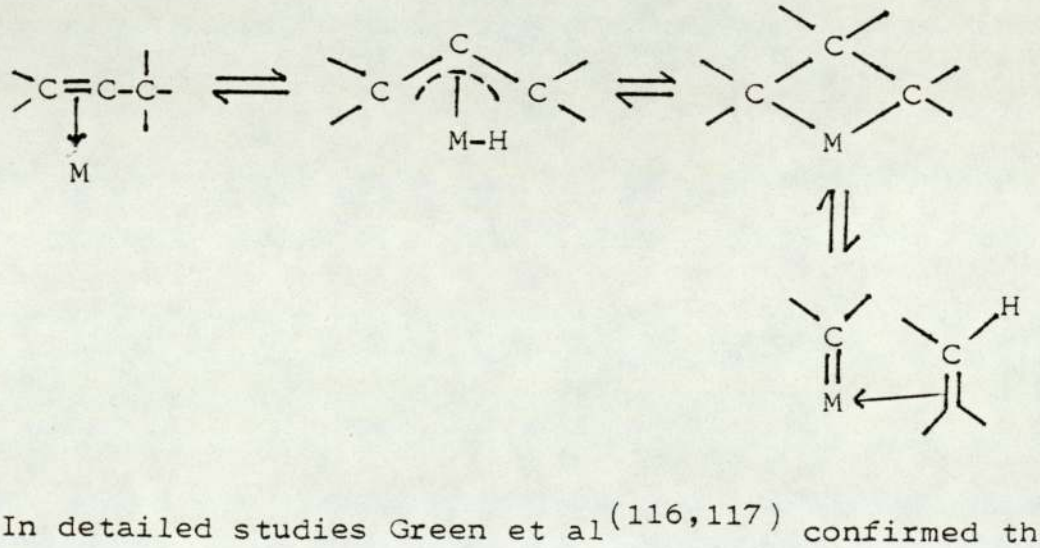

WOCl4 + Me4Sn
CH3
Cl3OW
SnMe3
Cl
MeWOCl3 + Me3SnCl
MeCl + CH4 + C2H6 + WOCl4
+ Me3SnCl
H
CH2
Cl3OW
SnMe3
Cl
Me4Sn
CH4 + Me3SnCl
HCl
act.
spec.
Termination
CH2
Cl2OW
SnMe3
Cl
Propagation
Me3SnCl + CH2=WOCl2
Termination

In the absence of a cocatalyst the carbene species can be a product of the olefin complex and the transition metal. If a hydride is present in the system the olefin complex can lead to an alkyl compound from which the carbene species arises via subsequent hydride α-elimination:-



It was however stressed that the cocatalyst played an important part in activating the carbene towards metathesis.

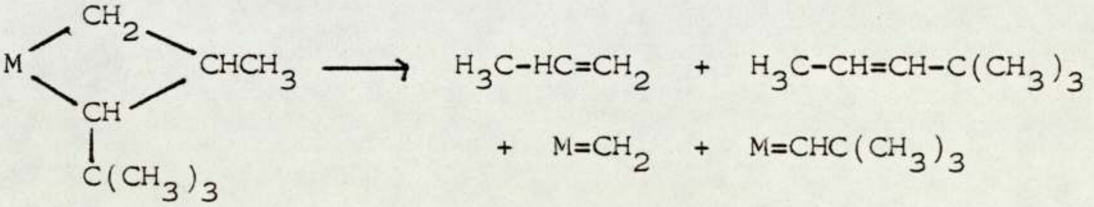
A new method for generation of carbene species in systems which do not have a cocatalyst may derive from π-allylic olefin complexes via a metallacyclobutane intermediate, thus:-

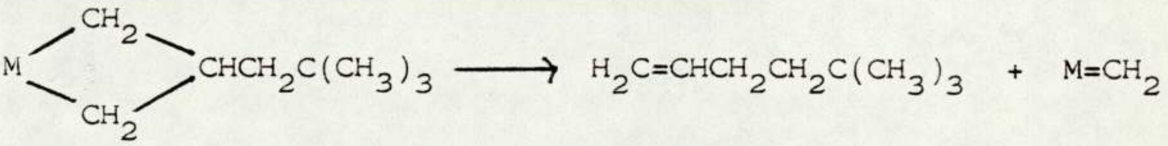


In detailed studies Green et al(116,117) confirmed the formation of metallacyclobutanes in reactions of π-allyltungsten complexes with nucleophilic reagents.

The metallacyclobutanes of tungsten decomposed thermally to cyclopropanes and saturated hydrocarbons, while photochemical decomposition led to olefins with fewer carbon atoms than the initial metallacycle. A photochemically induced $\eta^5 - \eta^3$ shift of an η-cyclopentandienyl ring was thought to provide a suitable vacant site on the metal centre.

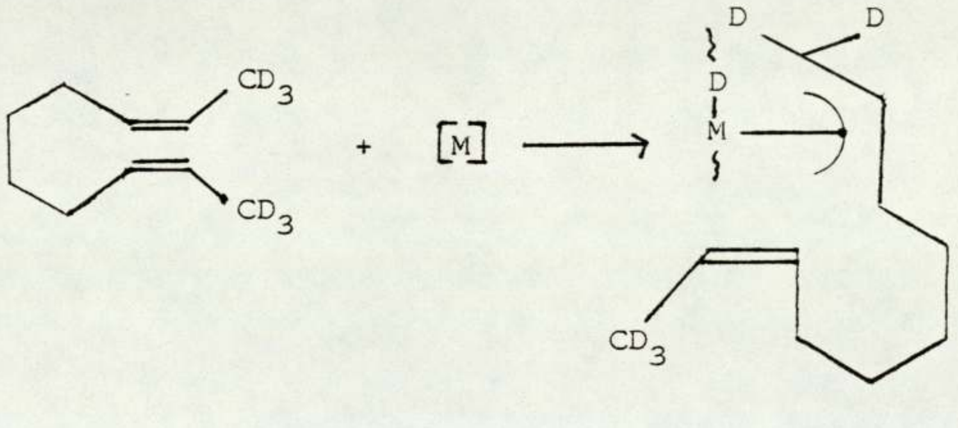
The π-allyl mechanism received significant support from using $Mo(CO)_4$ absorbed on γ-alumina without a cocatalyst, in work reported by Farona and Tucker(70). The metathesis of 2,4,4-trimethyl-2-pentene was carried out, which would show a slow rate of reaction and could isomerize to the 1-ene where the first formed products from either could be predicted. The metallacyclobutanes from starting and isomerized products would be as follows:-



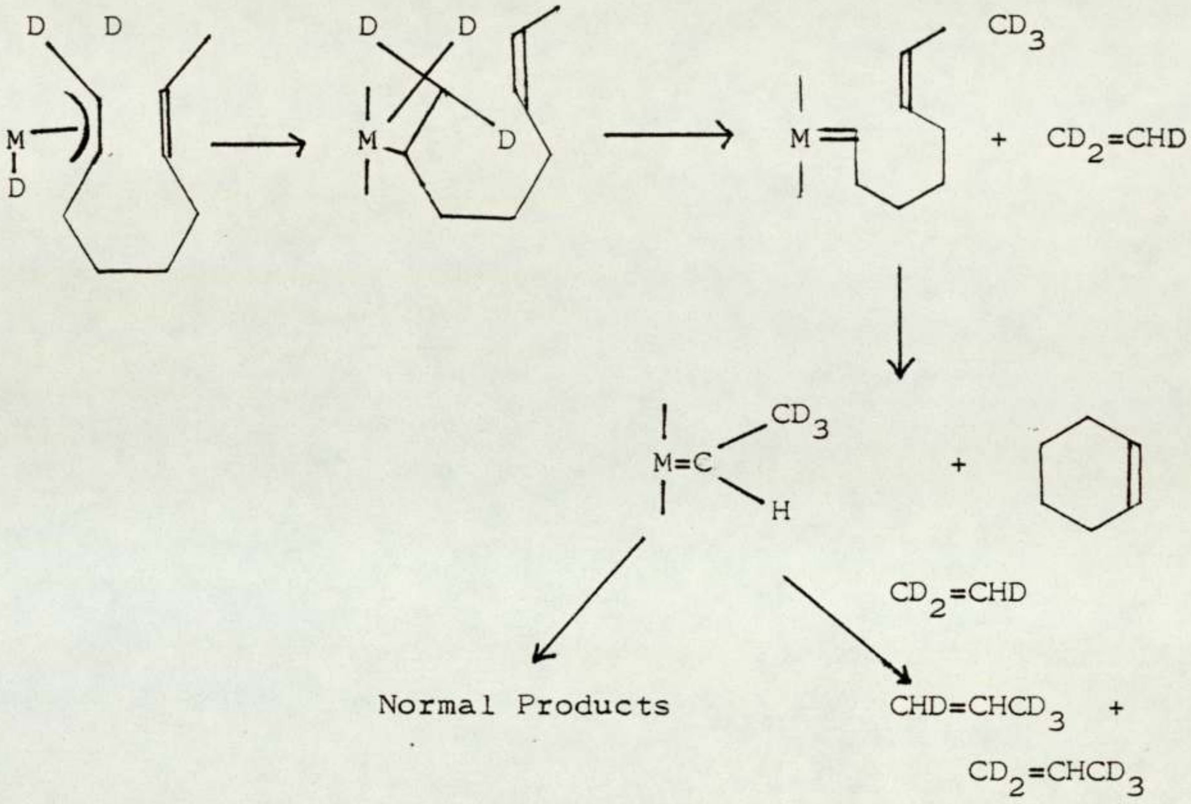


Metathesis of the starting material with $M=CH_2$ gave rise to isobutene and/or 3,3-dimethyl-1-butene as the first formed products. The product mix after a given time included those products as predicted and the absence of branch olefins, ruling out direct formation of the carbene species by the co-ordination of the olefin and subsequent 2,1-hydrogen shift, or by hydride migration from the catalyst and subsequent α -elimination.

Initiation of the starting olefin by a π -allyl complex seems to be in agreement with the isotope effect observed by Grubbs et al(118) for the induction period in the reaction of 2,8-decadiene and 2,8-decadiene-1,1,1,10,10,10-d_6 over $MoO_3/CoO/Al_2O_3$. The work presented suggested that the metathesis of olefins using that particular catalyst system proceeds through a non-pairwise mechanism, but without a cocatalyst there was an induction period, during which the reaction showed a large isotope effect. During this initiation period a π-allyl intermediate was apparently formed, which was the precursor to the active system:-



The conversion of the allylic intermediate to a carbene was presumed to follow the mechanism originally proposed by Green et al(116), i.e.:-

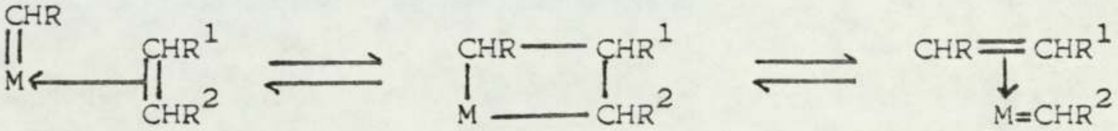


At present there is lack of evidence for the mechanism of generation of metal carbenes in the normal catalyst system, such as $WCl_6/LiBu/AlBr_3$, but work is presently being carried out in order to clarify this.

Nature of the Propagation and Termination Steps

Initially Hérisson and Chauvin(16) suggested a carbene mechanism consisting of an intermediate metallacyclobutane and a metallacarbene as the propagating species. Numerous data seems to support the intermediacy of metallacyclobutanes as the key step in the propagation reaction, as described previously.

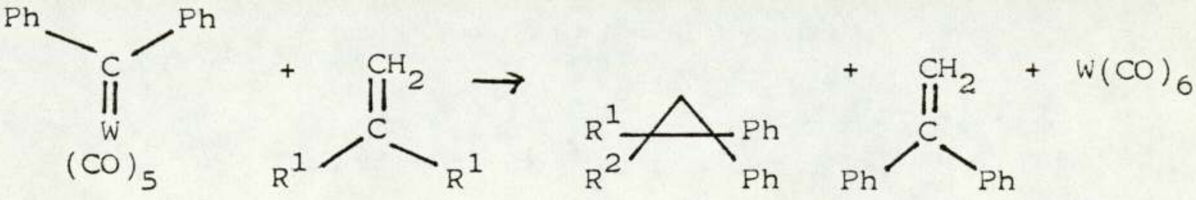
The nature of the chain carrying metallacarbene intermediate has presented problems in the degenerate metathesis of terminal olefins. From deuterium labelling it was deduced that the reaction proceeds either through a $M=CH_2$ complex or through a M=CHR, the latter type being more widely favoured as the chain carrying species.

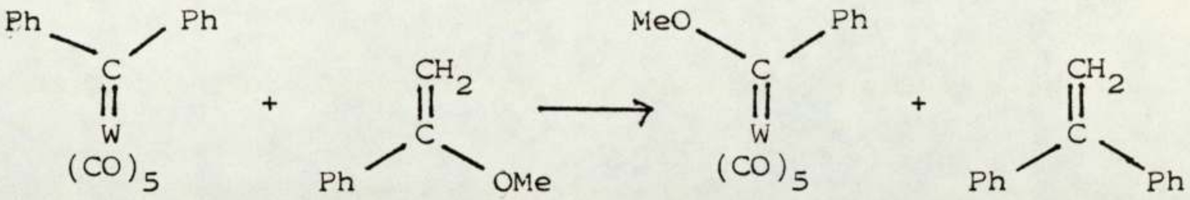


O'Neill and Rooney(119) reported results which were strongly suggestive of carbene participation when they demonstrated that diazomethane decomposed quantitatively to ethene and nitrogen on the sites, which also catalysed the disproportionation of propene on a $CoO/MoO_3/Al_2O_3$ catalyst. Ethene was converted directly to propene at higher temperatures on a $Mo(CO)_6/Al_2O_3$ catalyst, indicating the direct formation of methylene fragments from the initial olefin and their further reaction with it. There are some indications that the termination step in olefin metathesis proceeds by recombination of carbenes from metallacarbene complexes, i.e.

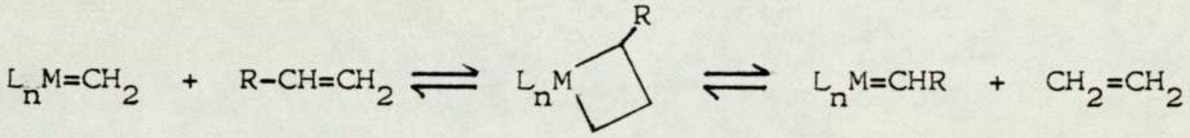
$$2\ L_xM{=}CH_2 \longrightarrow CH_2{=}CH_2$$

Experimental support for such a reaction comes from Schrock(120) for the tantalum-methylene complex and from Casey(121) for tungsten-carbene complexes. Schrock was the first to characterise a transition metal methylene complex by preparing compounds such as $[Me_3CCH_2]_3Ta{=}CHCMe_3$ and $CH_2{=}Ta(C_5H_5)_2Me$ by a route which probably involved α-hydrogen abstraction, and the significant double-bond character of the carbene-metal attachment confirmed by measurement of free energies of rotation. $Ph_2C{=}W(CO)_5$ synthesised by Casey provided a major breakthrough in support of the metallacyclobutane theory by its catalytic activity towards a number of olefins. The products formed probably arose by i) the scission of an olefin with transfer of an alkylidene group to the initial carbene, giving 1,1-diphenylethene and the corresponding propene derivatives respectively, ii) formation of cyclopropanes, and iii) replacement of the diphenylcarbene by new carbenes in the $W\overline{\underline{O}}$ compounds, i.e.





Grubbs and Hoppin(122) correlated the production of ethene in the metathesis of 2,8-decadiene in the presence of $WCl_6/SnMe_4$ or $(Ph_3P)_2\ (NO_2)Cl_2Mo/Me_3Al_2Cl_3$ with metallacarbene dimerization during initiation via dimetallacyclobutanes or bis-(carbene-metal) intermediates:-



More possibilities for termination reactions arise in the metathesis of functionalised olefins. In this case inhibition of the reaction may occur by formation of stable adducts between a functional group and a metallacarbene carrier, or the Lewis acid, used as a cocatalyst.

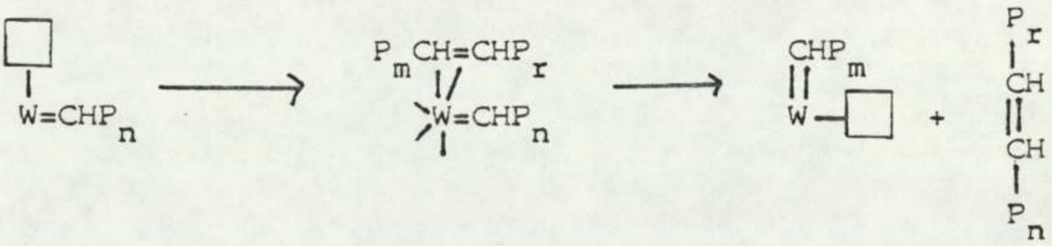
Amass(123) studied the termination reactions in the metathesis polymerisation of cyclic olefins. From kinetic studies of cyclopentene polymerised by $WCl_6/AliBu_3$ it was deduced that olefin metathesis and ring-opening polymerisation of cycloolefins proceeds by kinetic chain reactions, and the rate of polymerisation decreases with conversion of monomer to polymer because the propagating centres were consumed during the reaction.

It was suggested that termination could be considered for this decay, since the reaction recommenced on addition of a second aliquot of catalyst components. Kinetic studies have indicated that the decay of the reaction was second order in active species. However inspection of other polymerisation curves was not in agreement with this postulation and showed that the rate of disappearance of active species was dependent upon the initial rate of polymerisation. To account for this behaviour a bimolecular reaction was assumed, whereby an active tungsten species, W, reacted with a terminated inactive species, thus:-

$$\overset{*}{W} + W_{inactive} \longrightarrow 2\,W_{inactive}$$

producing an acceleration of the rate of termination.

Non-productive metathesis reactions were also assumed to be responsible for removal of active sites from the system. These type of reactions occurred due to the polymer maintaining an activity towards the propagating species and could be as follows:-



Such effects were however estimated to account for only 5% of the active sites.

The Effect of an Organometallic Cocatalyst

As well as its initial role as an alkylating agent and a reducing agent for the transition metal, the cocatalyst may also act upon ligands , creating vacant sites for co-ordination as mentioned previously.

The metathesis catalysts generally have Lewis acid properties, and their role in the reaction largely depends upon the nature of the transition metal and its ligands, cocatalysts, solvent and reaction conditions employed. Numerous Lewis acids attach to halogen, carbonyl or dinitrogen ligands of transition metal complexes. Such adducts were thought to appear in the reductive nitrosation of molybdenum and tungsten chlorides in the presence of $EtAlCl_2$, or in homogeneous catalytic systems based on tungsten and molybdenum halocarbonyl and halonitrosyl, for example:-

$$M(NO)_2L_2Cl_2 \quad + \quad 2\ EtAlCl_2 \rightleftharpoons M(NO)_2L_2Cl_2\cdot 2EtAlCl_2$$

Adduct formation was found to be followed by rapid equilibrium to ion pairs and partial solvation, i.e.

$$\begin{tikzcd}
W(CO)_3Cl_2L_2\cdot 2AlCl_3 \arrow[r, shift left] & \left[W(CO)_3L_2S\right]^{2+} \ \left[AlCl_4\right]^{-}_{2} \arrow[l, shift left] \arrow[d, shift left] \\
 & \left[W(CO)_3L_2S\right]^{2+} \ + \ 2\left[AlCl_4\right]^{-}_{2} \arrow[u, shift left]
\end{tikzcd}$$

It was concluded that on addition of the cocatalyst to the transition metal complexes, two free co-ordination sites may form enhancing the mobility of the other ligands.

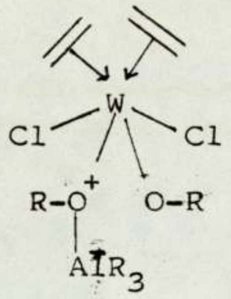
Organoaluminium halides can readily exchange their organic groups with transition metal halides:-

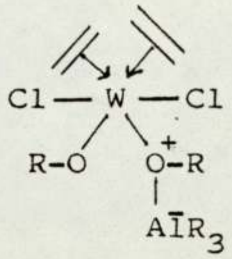
$$WCl_6 + EtAlCl_2 \rightleftharpoons EtWCl_5 + AlCl_3$$

The organocompound thus formed can be further reduced and/or may serve as a source of metallacarbene complex.

Muetterties(100) pointed out that the activity of the WCl_6/MR_n systems varied drastically with the nature of the metal M. He suggested that the organometallic catalyst gives rise to Lewis acids which interact with W complex intermediates through halogen, alkyl and carbene bridges. Consequently active species having M-Cl-W bridge bonding are probably operative in the propagation reaction. For carbene bridges three-centre, two-electron bonds between tungsten, carbon and the second metal would be involved in the active species. These bridged structures may act as chain carriers. The initial interaction of the cocatalyst with the transition metal compound could also be of a bridged nature, wherein α-hydrogen elimination may become a more facile process for the generation of the carbene.

Amass(19) studied the role of $EtAlCl_2$ in ring-opening polymerisations and metathesis reactions of olefins catalysed by WCl_6. It was considered that WCl_6 is reduced to a lower oxidation state halide which is capable of complexing with two olefin molecules. The aluminium compound was then suggested to complex with the tungsten compound to produce a structure as represented below:-

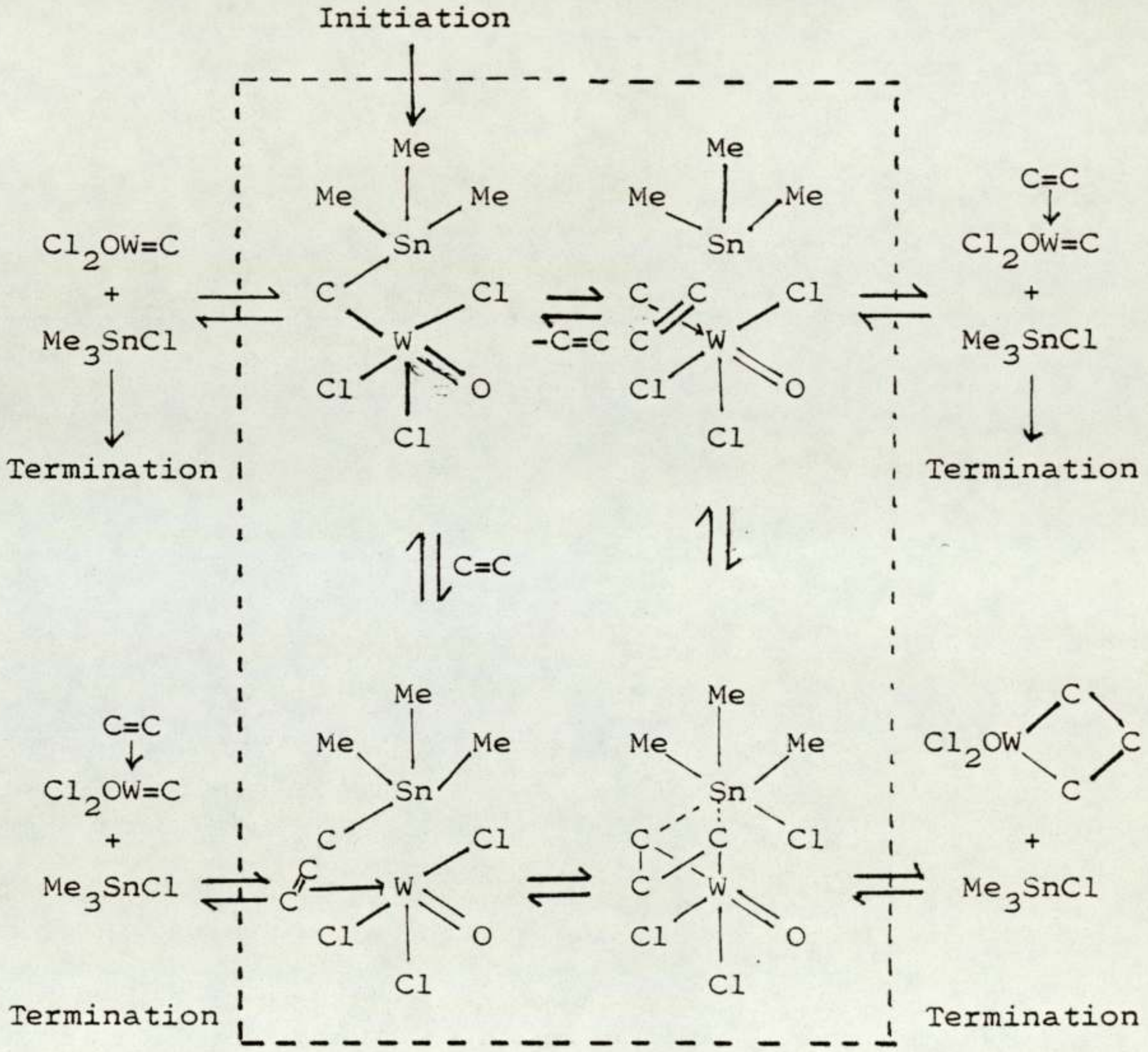




The complexing of aluminium in this manner, or by formation of a W-O-Al bridge, would confer a slightly positive charge on the tungsten atom and subsequently enhance the ability of the transition metal to co-ordinate the reacting olefins.

A possible role for the Lewis acid would be to modify the charge distribution and polarisation of the metal alkyl, alkylidene or alkylidene bond in transition metal complexes. This may have some influence on the formation of the metallacyclobutane transition state, which is dependent on the relative orientation of the carbene ligand.

For the system $WOCl_4/Me_4Sn$ Verkuijlen(111) found that the presence of the cocatalyst derivative Me_3SnCl is essential to maintain the activity of this catalyst system. In consequence a reaction scheme involving dimetallic alkylidene bridged complexes was suggested, with the active participation of the cocatalyst metal atom during all three reaction steps.



The reactions inside the dotted square indicate the propagation stages. In the initiating step Me_4Sn can be a methyl source for the bridged methylene bimetallic complex Cl_2OWCH_2-Me_3SnCl. During proagation the Me_3SnCl takes an active part in the bimetallic bridged carbene complex through its assistance in the metallacyclobutane transition state of the catalytic cycle. The termination products were suggested to be formed from Me_3SnCl reacting with every transient species in metathesis. Only when the Lewis acid is complexed to the carbene is the system active. The distinction between Lewis acid complexing with a ligand and a carbon-tungsten double bond is difficult to perceive.

1.5 STEREOCHEMISTRY

The metathesis of acyclic olefins and the ring-opening polymerisation of cycloolefins are stereoselective. The degree of selectivity depends on the nature of the catalytic system and the reactant olefin used. The reaction conditions may also play a major role in the products formed.

1.5.1 Metathesis of Acyclic Olefins

The first studies on the stereoselectivity of reaction products from metathesis were carried out by Banks and Bailey(2) using a heterogeneous catalyst system. An example of the results is shown in tables 1.6 and 1.7. From these it can be seen that in the reactions of propene and 2-pentene the trans:cis-2-butene ratio was very close to the thermodynamic equilibrium ratio. For the reactions of 1-pentene and 1-butene however the ratio was lower than thermodynamically expected, i.e. the preference for the cis-isomer formation was higher. The trans:cis-2-pentene ratio had values much higher than those for thermodynamic equilibrium.

Table 1.6 Trans:Cis-2-Butene Ratio in the Metathesis Product of Acyclic Olefins

OLEFIN	TEMPERATURE/ °C			
	95	160	200	300
Propene	2.15	1.95	1.78	1.80
1-Butene	0.46	1.24	1.49	1.49
2-Butene	2.31	2.21	2.21	-
1-Pentene	1.00	2.00	-	-
2-Pentene	2.00	1.80	-	1.80
Equil. Ratio	2.40	2.00	1.90	1.70

Table 1.7 Trans:Cis-2-Pentene Ratio in the Metathesis Product of Acyclic Olefins

OLEFIN	TEMPERATURE/ °C			
	95	160	200	300
Propene	-	3.00	3.40	1.80
1-Butene	2.00	2.40	2.40	2.10
2-Butene	3.00	2.60	2.40	-
1-Pentene	1.20	2.20	-	2.10
2-Pentene	3.80	2.70	-	2.20
Equil. Ratio	1.60	1.50	1.40	1.30

Tanaka etal(124) observed that by employing a MoO_3/TiO_3 catalyst system propene underwent the metathesis reaction forming 2-butene in the ratio of 1:6 cis:trans-isomeric form. In contrast to the reaction in the heterogeneous phase that in the homogeneous phase exhibits distinctive stereochemical features. The products formed depend greatly upon:-

i) the purity of the reacting olefin.
ii) the nature of the ligands at the double bond.
iii) the steric environment of the catalyst.
iv) the nature of the transition metal.

The steric course of the homogeneous reaction of pure trans- and cis-2-pentene was initially studied by Calderon et al(4) using the three-component catalyst system $WCl_6EtOH/EtAlCl_2$. The results of these studies are shown in table 1.8 below.

Table 1.8 Metathesis of 2-Pentene showing Molar Ratios of Products

2-PENTENE	Al:W	Conv.	Trans:Cis Ratio		
			2-Butene	2-Pentene	3-Hexene
96% cis	4	9	0.70	0.10	-
"	2	46	2.30	2.10	-
"	1	53	1.90	2.80	-
97% cis	1	40	1.10	0.90	-
"	4	47	1.50	1.60	2.50
"	4	50	2.50	4.50	6.70
100% trans	4	15	1.50	30.00	2.10
"	4	41	2.20	11.50	3.00
"	4	45	2.30	4.50	4.20

It was shown that substantial amounts of both cis- and trans-isomers of 2-butene and 3-hexene were formed initially, whereas the composition of the residual 2-pentene very gradually approached its equilibrium cis- content. It was also noted that initially formed products were somewhat higher in cis- content than the equilibrium values, and the cis:trans-isomer ratio for 2-butene was always different from that for 3-hexene over the entire range of conversions. From these observations three conclusions were drawn:-

i) the isomer content of reaction mixtures can attain thermodynamic equilibrium,

ii) the metathesis reaction is not highly selective in the formation of geometrical isomers,

iii) the metathesis reaction is the principal means of geometrical isomerisation.

The equilibrium cis- content for a given olefin was found to be independent of the structure of the initial olefin, catalyst concentration and the presence of other olefins in the system. The values for the free energy change for the trans- to cis- transformation were found to have a distinct correlation with the steric factors in the structure of the olefin. The dependence on the catalyst for selectivity during the early stages of the reaction reflects slight differences in steric effects in the transition state, due to the difference in requirements of the methyl and ethyl groups of 2-butene and 3-hexene respectively formed in the metathesis of 2-pentene.

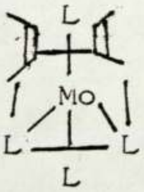
Wang and Menapace(64) observed in comparison that the trans: cis- ratio of the reaction products, from the metathesis of 2-pentene using WCl/LiBu, depends strongly on the steric structure of the initial olefin. This difference in behaviour was attributed to the steric hinderance in coordinating to tungsten atoms for the trans-isomer.

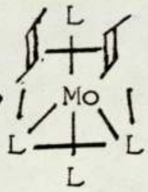
Hughes(99), using homogeneous catalyst systems based on molybdenum complexes, found the metathesis of 2-pentene to be kinetically controlled with respect to stereoselectivity.

For olefin metathesis it is generally observed that the overall stereoselectivity of the reaction products depends significantly on the stereoselectivity of the propagation step. But the initial stereoselectivity at low conversions depends on the stereochemistry of the initiation step and the final stereoselectivity may be drastically changed by the stereochemistry of the termination step.

1.5.2 The Nature of Steric Interactions in Olefin Metathesis

Calderon(4) suggested steric effects in the transition state due to differences in steric requirements of the methyl and ethyl groups in the metathesis of 2-pentene. Thereafter Hughes(99) interpreted the stereochemistry in terms of the pairwise quasicyclobutane mechanism by considering the most stable configurations of the metal-bisolefin complexes, i.e.

cis-2-pentene →  → cis-2-butene + cis-3-hexene

trans-2-pentene →  → trans-2-butene + trans-3-hexene

In general, stereochemical data obtained in heterogeneous metathesis reactions is difficult to interpret owing to competitive secondary reactions occurring. It was found in most cases that the reactions led to a steric composition close to thermodynamic equilibrium. Under kinetic control however cis-stereoisomeric products result predominantly in reactions of lower α - and internal olefins over conventional $MoO_3Al_2O_3$(2).

Stereoselectivity in heterogeneous metathesis reactions could be correlated with steric interactions, assuming as the rate determining step either the complexation of the incoming olefin on the catalyst surface or metallacyclobutane formation. Competitive physico-chemical phenomena such as physical adsorption, chemisorption, bond cleavage and bond rotation may have a significant effect on the overall stereochemistry by the steric interactions involved.

If the initiating metallacarbene species is generated by direct interaction of the starting olefin with the heterogeneous metallic site, significant differences in steric interaction may arise in co-ordination and reaction for cis- and trans- olefins. Several hypotheses have been advanced to account for the stereoselectivities observed in homogeneous olefin metathesis:-

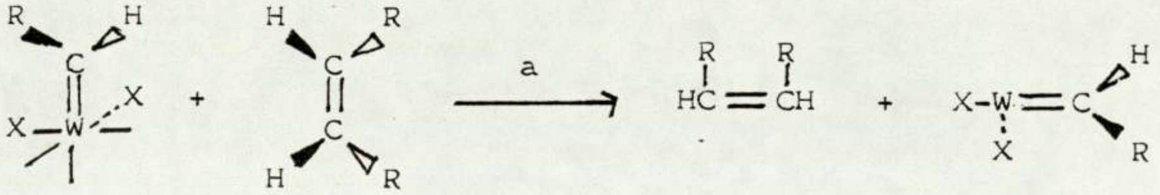
i) steric effects during the co-ordination of the olefin to the metallacarbene,

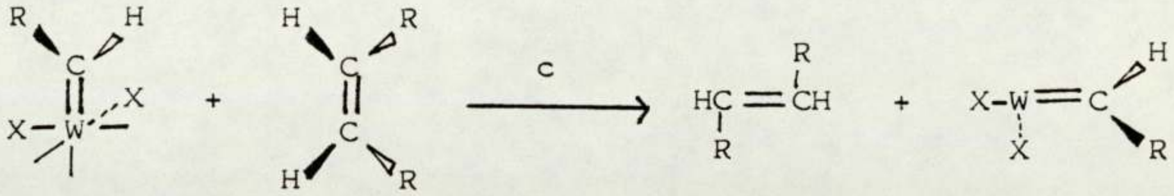
ii) steric directing effects of the ligands on the transition metal,

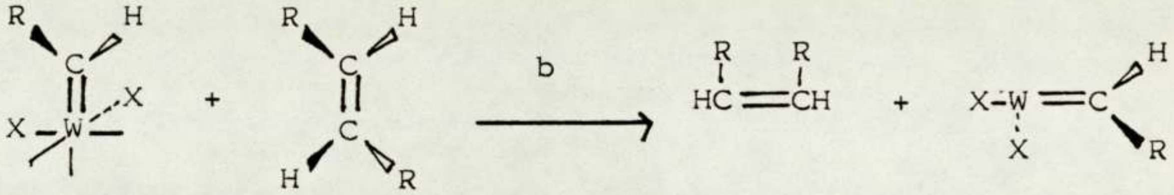
iii) stability of the various conformations of the metallacyclobutane transition state,

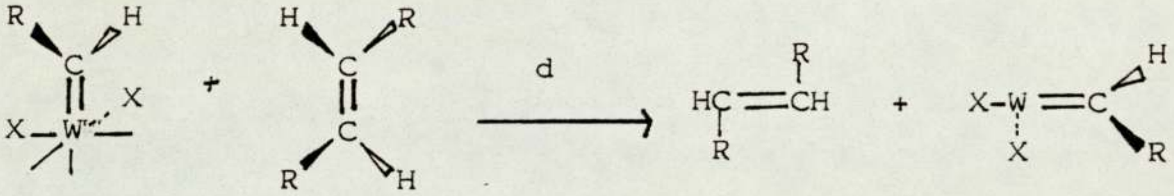
iv) scission of the carbon-metal bond in the metallacyclobutane intermediate, leading to a substituted metallapropyl cation in which the remaining bonds rotate and subsequently reform the matallacyclobutane.

Assuming that complexation is the rate-determining step during the co-ordination of the olefin to the metallacarbene moiety, either interaction between the alkyl group of the co-ordinated carbene and the olefin (a and b), or between the metal and/or its ligands and the alkyl group of the co-ordinating olefin may occur (c and d):-





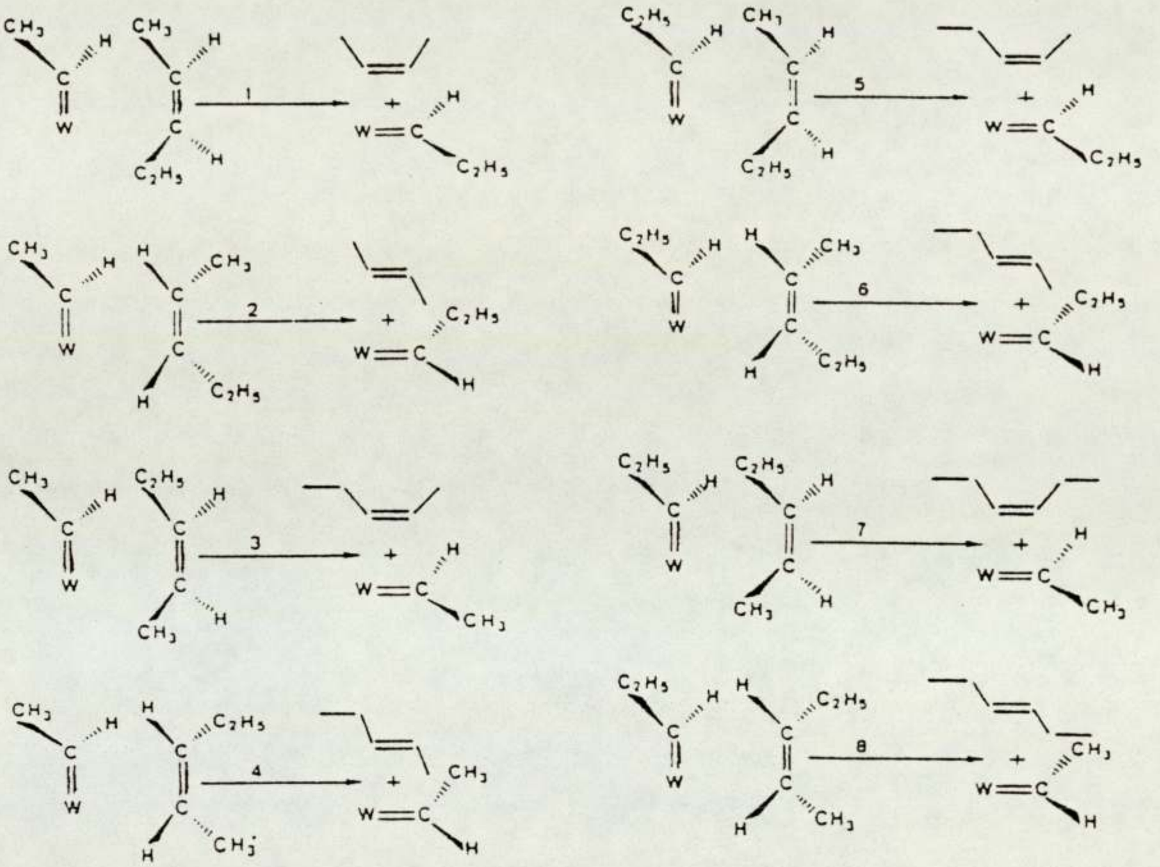




Thus it can be seen that depending upon the nature of the interactions pure cis- and pure trans- olefins can potentially give rise to a mixture of cis- and trans- products.

A stereochemical model for olefin co-ordination, which accounts for the selectivities observed in cis- and trans-2-pentene metathesis, was proposed by Basset and co-workers(105) based on the carbene mechanism of Chauvin(16). In this model they assumed that the carbon of the co-ordinated carbene had sp^2 character with a bond order greater than unity and probably equal to two.

Here the stereochemistry is determined by the geometry of the approach of the olefin, and accounts for degenerate metathesis and cis-trans- isomerisation in olefin metathesis. The reaction of cis-2-pentene in the presence of tungsten carbenes, both ethylidene and propylidene, is shown:-



Routes that provide for cis- and trans- product olefins can be readily defined.

The steric effects due to the ligands co-ordinated to the metal may be relevant to whether the distribution around the metallacarbene may be symmetrical or asymmetrical. In the latter case repulsion occurs between the co-ordinated carbene and the olefin. With a symmetrical ligand distribution the repulsion of olefinic groups is non-stereoselective and both cis- and trans- co-ordination are equally probable, together with a significant decrease of stereoselectivity due to rotation of the carbene around the metal-carbon double bond.

The retention of steric configuration of the starting olefin observed with most tungsten, molybdenum and chromium homogeneous catalysts has been rationalised by Katz(125), Casey(78) and Basset(126,106) in terms of the stability of the possible conformations of the metallacyclobutanes derived from the interaction between co-ordinated olefin and carbene.

In addition to the geometric ligand arrangement around the metallacarbene, the nature of the ligand attached to the transition metal may be relevent to the stereochemistry of the reaction. Two types of ligand are identified, non-stereoselective e.g. the halogens which induce small changes in reaction stereochemistry, and stereoselective e.g. nitrosyl groups which may induce substantial variations in reaction stereochemistry owing to their particular geometry or active presence in the catalyst.

Recently Basset and co-workers(127,128) related the stereoselectivity observed in the metathesis of acyclic and cyclic olefins with the respective energy levels of the co-ordinated olefin and the metallacyclobutane. They showed that when the co-ordinated olefin has a smaller energy level than the intermediate, the stereoselectivity is governed by the energy levels of the two metallacycles. If the energy level is higher however, the products have an equal probability of being cis- or trans-.

The level of lower selectivity in the metathesis of internal olefins obtained with tungsten catalysts, or in the presence of excess metal halides e.g. Lewis acids, was explained by Katz(125) via cleavage of the metal-carbon bond in the metallacyclobutane intermediate and the formation of a metallapropyl cation in which the remaining bonds rotate. Günther(86) supported this theory from the results of increasing the amount of Lewis acid in the metathesis of cyclopentene using tungsten catalysts.

1.5.3. Ring-Opening Polymerisation of Cycloolefins

Here again the catalyst system employed often determines the stereoselectivity.

The steric configurations of the double bonds in polyalkenamers may have cis- or trans- geometries, or alternate in a random distribution:-

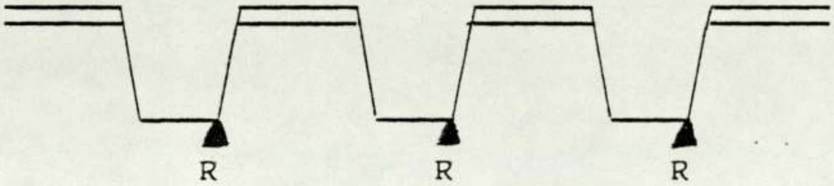
cis- config.

trans- config.

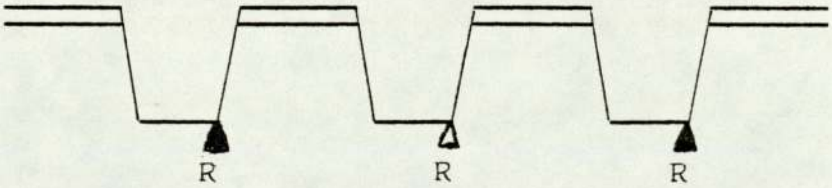
random config.

The stereochemistry of the polyalkenamer determines its physical properties, such as whether it is an elastomer or a plastic.

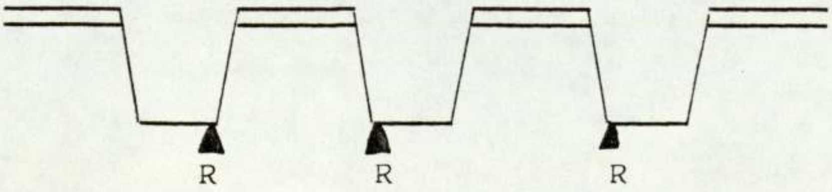
If the polyalkenamers have chiral centres the monomer units may have an isotactic, syndiotactic or atactic relationship:-



isotactic



syndiotactic



atactic

As previously described, within the same binary or ternary catalyst system the cis- or trans- portion of the polymer can be varied by appropriate changes in the molar ratio of the components, the temperature of the reaction, or the solvent employed.

With few exceptions the polymerisation of substituted cyclo-olefins is less stereospecific than that of unsubstituted ones(96). High stereoselectivity is observed however when the substituent is located at the double bond in the presence of the carbenic system $(C_6H_5)_2C{=}W(CO)_5$(56).

Copolymerisations of cycloolefins are generally distinct and less stereospecific than homopolymerisation reactions. Table 1.9 below shows the configuration of cis- and trans- double bonds in a number of copolymers prepared in the presence of $WOCl_6$/benzoyl-peroxide/Et_2AlCl.

Table 1.9 Configuration of Cis- and Trans- Double Bonds in a number of Copolymers

Monomer pair	Monomer composition (molar ratio)	Copolymer composition (molar ratio)	trans: cis Ratio of the double bonds
Cyclopentene cycloheptene	50:50	72:28	75:25
	25:75	44:56	80:20
	10:90	18:82	80:20
Cyclopentene cyclo-octene	50:50	97:3	70:30
	25:75	53:47	65:35
	10:90	13:87	75:25
Cyclo-octene cyclodecene	80:20	85:15	80:20
	50:20	69:31	82:20
	5:95	14:86	70:30

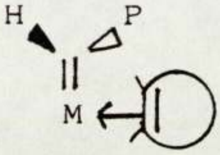
1.5.4 The nature of Steric Interactions in Ring-Opening Polymerisation

Steric interactions significantly occur throughout the course of ring-opening polymerisation reaction. Several factors may be relevant to the steric course of the reaction:-

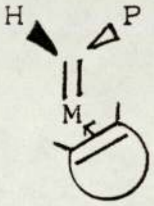
i) the mode of cycloolefin approach to the co-ordination site,
ii) the nature of co-ordination of the cycloolefin,
iii) the geometric configuration of the intermediate metallacarbene,
iv) the steric environment around the transition metal.
v) rotation about the metal-carbon bond,
vi) the mode of addition or insertion of the co-ordinated cycloolefin to the metallacarbene,
vii) steric interactions arising in the transition state of the reaction intermediate,
viii) the steric mode of de-coordination of the newly formed double bond of the polymer chain,
ix) the mode of rupture of the supposed cyclic intermediate,
x) the nature of the transition metal.

Most of the above points are made in the supposition of a metallacarbene mechanism.

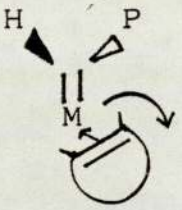
The various modes of olefin approach to the co-ordination site are as shown overleaf:-



parallel approach



orthogonal approach

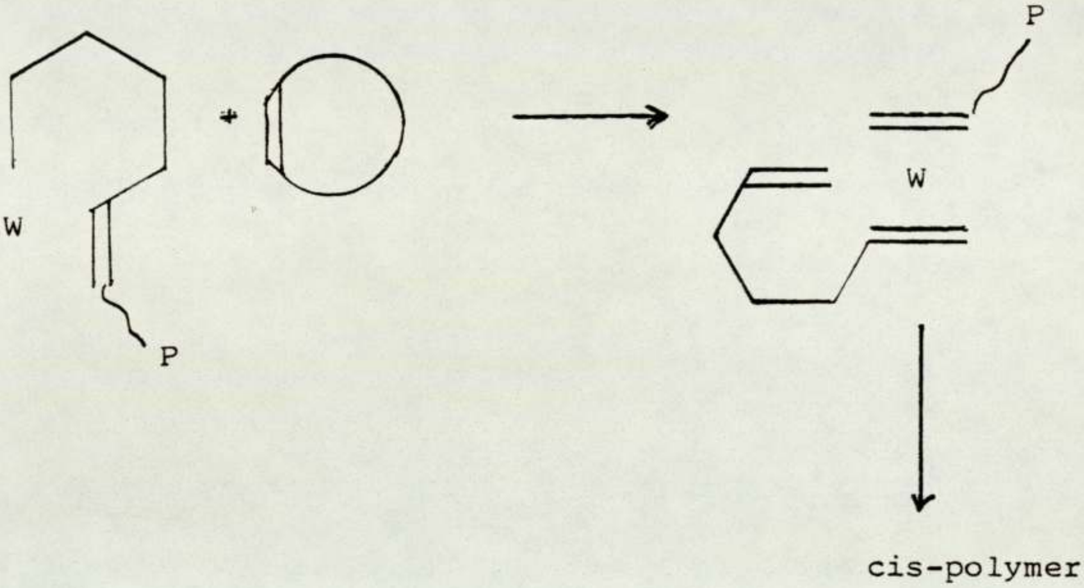


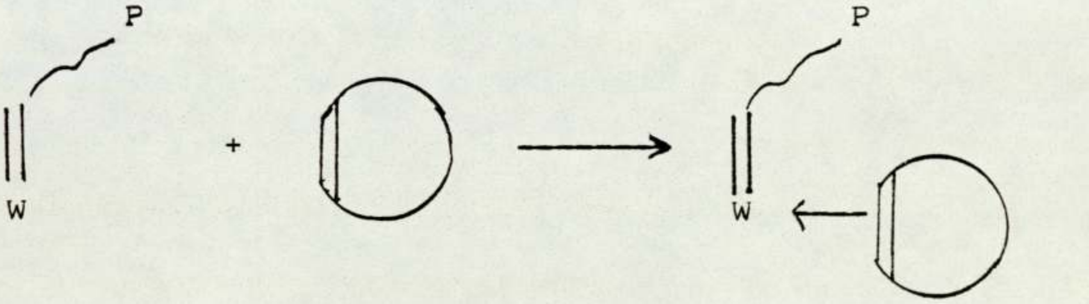
intermediate approach

The mode depends on the geometry of the cycloolefin and the steric environment around the transition metal.

Reaction of the cycloolefin around the carbon-carbon double bond during the co-ordination process is required for positive overlap interaction. Steric interaction of the olefin with metal ligands on the barrier to rotation may render substituted cycloolefins unpolymerisable.

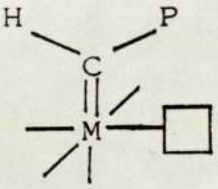
Calderon and co-workers(108,129) recently proposed a chelating concept to explain a high stereospecificity in cyclopentene polymerisation. Here a three-ligand sequence involving simultaneous co-ordination of carbene, cycloolefin and polymer chain leads to highly cis- polymer in the presence of cis- specific catalysts. With trans-specific catalysts a two-ligand sequence involving co-ordination of the carbene and cycloolefin results in trans- polymer:-



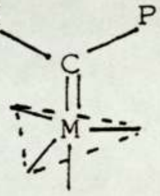


Ivin(130) reported on the effect of steric crowding at the metal site, stating that due to this factor a direct effect is exerted on monomer and the additive co-ordination, resulting in preferential formation of the metallacycle in the cis- or trans- orientation.

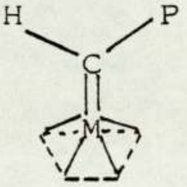
It is presently considered that the configuration around the metallacarbene centre for some active catalyst species such as tungsten is octahedral, having one vacant position cis- to the carbene ligand available for olefin co-ordination(109). The three possible configurations of metallacarbene species are shown below:-



octahedral configuration

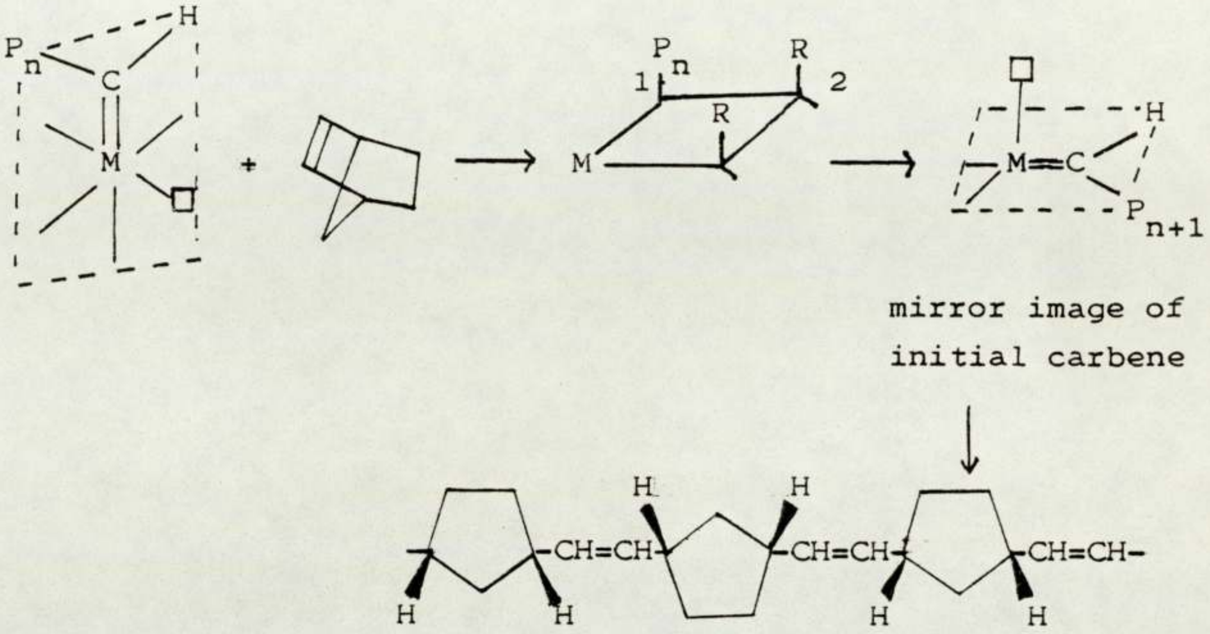


trigonal bipyramidal configuration



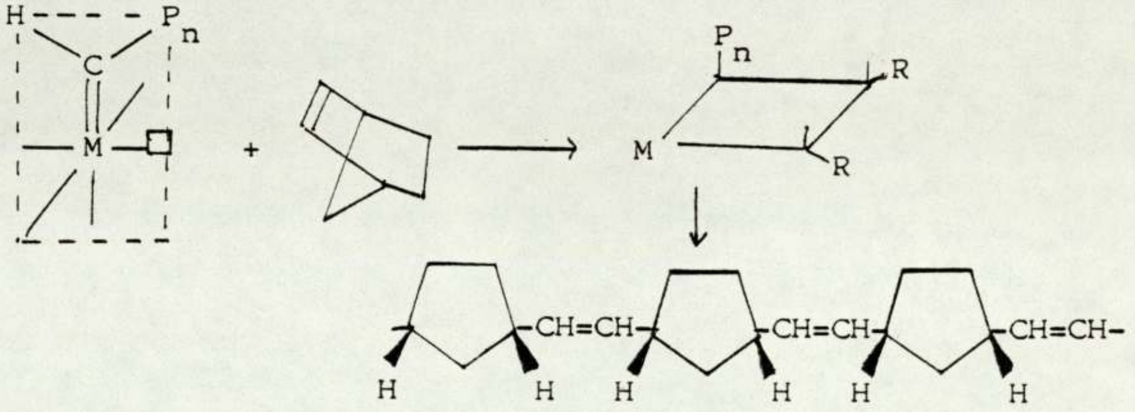
square pyramidal configuration

Co-ordination of monomer to the active centre on the octahedral metallacarbene could result in polymers having cis- or trans- double bonds, depending upon the catalyst system employed. Co-ordination in a cis- manner leads to polymer chains with cis- double bonds derived from a metallacyclobutane in which C_1 and C_2 are cis- with respect to one another.



syndiotactic arrangement

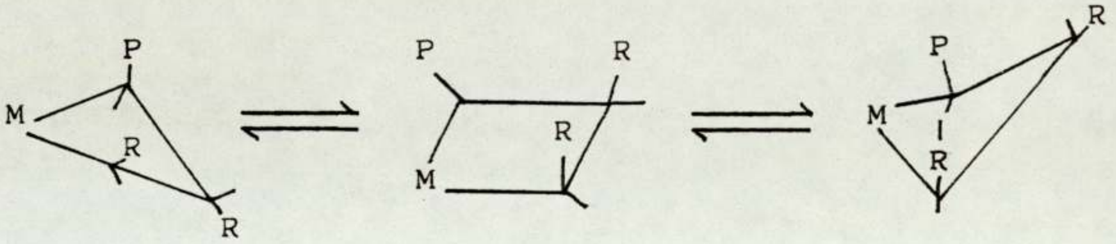
If the co-ordination is trans- however, C_1 and C_2 on the resulting metallacyclobutane are trans- and consequently polymer chains with trans-double bonds are formed:-

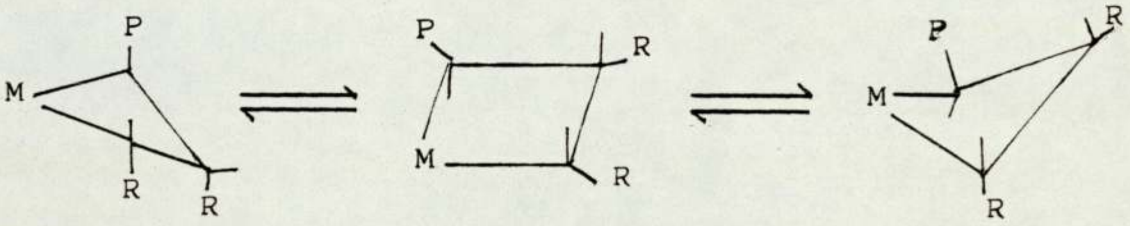


isotactic arrangement

In this case the metallacarbene regenerates itself, thereby resulting in the retention of stereochemistry of the metal-carbene and an isotactic arrangement of cyclopentene rings.

It is generally accepted that to fulfil the maximum overlap requirements monomer addition is of the cis- type. The formation of cis- and trans-double bonds in the polymer was suggested to occur via intermediate cis- and trans- metalla-cyclobutanes in planar and puckered forms:-





The nature of the transition metal in the catalyst seems to be significant for the steric course of ring-opening polymerisation. The more electronegative transition metals and/or oxidation states will prefer to co-ordinate more strongly with the olefin, the carbenic ligand and the unsaturated polymer chain. The reverse applies to the more electropositive transition metals, facilitating conformtional isomerisations.

1.6 THERMODYNAMICS AND MOLECULAR WEIGHT DISTRIBUTION OF POLYALKENAMERS

1.6.1 Olefin Metathesis

Olefin metathesis is a reversible reaction which does not involve any significant structural changes between reactants and products. The enthalpy changes therefore are very small or zero. The free energy change in the metathesis of acyclic olefins is therefore controlled principally by the reaction entropy. For linear acyclic olefins a change of temperature has a small effect on the reaction equilibrium, but for branched olefins the effect is greater because of an increase in reaction enthalpy.

1.6.2 Ring-Opening Polymerisation of Cycloolefins

The ring-opening polymerisation of cycloolefins shows distinct thermodynamic characteristics due to the contribution towards the reaction entropy arising from ring-strain energy of the cycloolefin, and the nature of cycloolefins strongly influences the entropy contribution to the free energy. Although the presence of the double bond makes a minor contribution to the stability of the ring in cycloolefins, the thermodynamic stability may be directly compared with the corresponding cycloalkanes. Small rings (<5 ring atoms) have the lowest stability because of the high ring strain, while cyclohexane possesses the highest stability because of a strain-free conformation. The larger rings show slight instability because of eclipsed conformations and non-bonded interactions between the hydrogen atoms on methylene groups twisted into the centre of the ring.

Natta and Dall'Asta$^{(131)}$ established the dependence of the polymerisation of cycloolefins on the ring strain of small and medium rings, showing a direct correlation for small rings and a dependence on other thermodynamic factors for medium rings. The equilibrium of ring-opening polymerisation reactions is determined by the relative stabilities of the polymer and monomer. The propagation step may be written as an equilibrium reaction thus:-

$$P_n^* + M \underset{k_{-p}}{\overset{k_p}{\rightleftharpoons}} P_{n+1}^*$$

- which represents the addition of a monomer unit to an active polymer species, to form another active species with increased chain length. The equilibrium constant, K, for this reaction is represented by:-

$$K = \frac{k_p}{k_{-p}}$$

At equilibrium the forward reaction rate equals the reverse reaction rate:-

$$K_p \left[P_n^*\right] \left[M\right]_e = K_{-p} \left[P_{n+1}\right]$$

i.e. $$K_p \left[M\right]_e = K_{-p}$$

where $\left[M\right]_e$ = monomer concentration at equilibrium

By rearrangement, $$\frac{K_p}{K_{-p}} = \frac{1}{\left[M\right]_e} = K$$

Since, $$\Delta G = -RT\ln K = \Delta H_p - T\Delta S_p$$

$$= -RT\ln \left(\frac{1}{\left[M\right]_e} \right) = \Delta H_p - T\Delta S_p$$

where ΔH_p and ΔS_p are the enthalpy and entropy changes taking place on polymerisation

Therefore the equilibrium concentration of the monomer is given by:-

$$\ln \left[M\right]_e = \frac{\Delta H_p}{RT} - \frac{\Delta S_p}{R}$$

Calderon(4) was the first to recognise the existence of a thermodynamic equilibrium, demonstrating the initial equilibrium established between the growing chains and the initial monomer, as well as the second ring-chain cometathetical equilibrium between macrocycles and polyalkenamer.

In the polymerisation of cycloolefins, account must not only be taken of equilibrium between monomer and open chain polymer, but also monomer and cyclic oligomers which may be derived from either backbiting of the polymer or polymerisation of monomer. These polymerisation systems show all the thermodynamic features of a true dynamic state of equilibrium between monomer, polymer and cyclic oligomers. The equilibrium distribution of the components depends significantly on temperature and the initial concentrations of each.

1.6.3 Molecular Weight Distribution of Polyalkenamers

It is commonly proposed that the macrocycles obtained in the polymerisation of cycloolefins are produced by a backbiting mechanism as previously discussed. Chauvin(66) showed that a true thermodynamic equilibrium between cyclic oligomers and high molecular weight polymer, without participation of the monomer, is attained for the production of polyoctenamer:-

$$\text{1,5-Cyclooctadiene} \longrightarrow \left[\text{Oligomer} \rightleftharpoons \text{Polymer}\right]$$

It was also found by the same author that the equilibrium oligomer concentration increased with concentration of the reactants when chlorobenzene or heptane were used as solvents instead of benzene. For polypentenamer however a single molecular weight distribution was observed. But Witte and Hoffman(132) found contrasting results from those obtained by Chauvin for the polymerisation of cyclopentene induced by a series of homogeneous catalysts. The resultant polymers showed bimodal distributions, consisting of linear macromolecules and small amounts of cyclic oligomers. The oligomers were formed more slowly than the linear high polymers for the range of concentrations used (10-15%). The molecular weight distribution of the oligomer fraction showed a maximum at a degree of polymerisation of six, broadening to higher molecular weights with increasing reaction time.

Detailed studies by Höcker(28) showed that the initial formation of products in ring-opening polymerisation is kinetically controlled, with distribution being generated gradually. At low conversion oligomers were formed, but with increasing conversion polymeric species were obtained. The oligomeric distribution was found to reach limiting values even though the reaction conditions were varied, such as further additions of catalyst or monomer. Thus the end-state was regarded as being a thermodynamically controlled state. According to the theory of Jacobson and Stockmayer(133), the equilibrium concentration should be nearly independent of the initial monomer concentration. In other words the weight fraction of the material in the form of cyclics should increase with greater dilution up to the so-called cut-off point, i.e. the critical point beyond which linear polymer should be effectively absent.

$$\underset{\text{chain}}{A\text{-}M_y\text{-}B} \rightleftharpoons \underset{\text{chain}}{A\text{-}M_{y-x}\text{-}B} + \underset{\text{ring}}{M_x}$$

$$P_x = \frac{(x_w - 1)}{(x_w + 1)} \approx 1 \qquad (\text{for } x_w \gg 1)$$

where x_w = weight average degree of polymerisation of the linear polymer

$$K_x = \frac{[A\text{-}M_{y-x}\text{-}B]\,[M_x]}{[A\text{-}M_y\text{-}B]} = \frac{[M_x]}{P_x} = [M_x]$$

P_x is the fraction of the equivalent initial monomer converted at equilibrium.

According to the Jacobson-Stockmayer equation relating to such equilibria, the concentration $[M_x]$ of a single species in the distribution is inversely proportional to the 2.5 power of the degree of polymerisation (x). This is only valid however for a constant characteristic ratio C_x (C_∞), according to the following equation:-

$$\left[M_x\right] \approx K_x = (3/2)^{3/2} 1/2N_A (nC_x l^2)^{-3/2} x^{-5/2}$$

where N_A = Avogadros number

n = number of bonds per monomer unit

$$\left[M_x\right] = K_x \propto 1/x^{2.5} \qquad \ln\left[M_x\right] \propto -2.5 \log x$$

Höcker showed that a plot of $\ln\left[M_x\right]$ against log x was a straight line with a slope -2.5.

For the metathesis polymerisation of cyclopentene Amass and Zurimendi(123) concluded that there existed two distinct phases to the reaction, the initial stage being kinetically controlled and the latter being thermodynamically controlled, eventually leading the sysytem to equilibrium. The dependence of composition of polymer on ageing time of catalyst indicated the presence of more than one active species in the system, producing varying molecular weight polymers. This suggests a kinetically controlled molecular weight distribution, the rate of polymerisation being dependent on the ratio of catalyst components and the ageing time. The final composition of each polymer was however found to be irrespective of the initiating system, reaching a thermodynamic equilibrium.

1.7 KINETICS

The kinetics of metathesis and ring-opening polymerisation reactions have not been fully elucidated at the present time. Initial studies were carried out in the heterogeneous phase, although these were found to disagree among themselves and with results obtained in the homogeneous phase.

1.7.1 Metathesis in the Heterogeneous Phase

Most kinetic studies were based on the metathesis of propene with various catalytic systems comprised of transition metal oxides. The results of these investigations are divergent, with some corresponding to a unimolecular Rideal-type kinetic model and others to a bimolecular Langmuir-Hinshelwood model.

Begley and Wilson(13) obtained an equation for the rate constant for the metathesis of propene using a WO_3/SiO_2 catalyst system at temperatures ranging from 600-800°C at various pressures. The results indicated first order kinetics and were explained by a Rideal-type model, which is based on the hypothesis of the interaction of an adsorbed molecule and a gas-phase molecule. At lower pressures however, the rate constants were higher than expected, possibly because of a change in the linear gas velocity in the catalyst bed. In contrast to these results Lewis and Wills(142), using a $WO_3/MoO_3/Al_2O_3$ catalyst, showed that initial rates of propene disproportionation were well correlated by a rate expression, based upon a Langmuir-Hinshelwood mechanism in which the controlling step in the reaction is assumed to be a dual site surface reaction. The difference in observations was thought to be due to a different catalyst system, lower temperature and pressure conditions in the latter case, and two different types of reactor being used to obtain the data.

Numerous factors are involved in the heterogeneous phase reaction, all of which may be rate-determining:-

i) diffusion of the reactants over the catalyst surface,

ii) adsorption of the reactant by the active centres,

iii) reaction of the adsorbed molecules on the catalyst surface,

iv) desorption of the reaction products from the active centres,

v) diffusion of the reaction product from the catalyst surface.

The rate controlling step may conceivably depend on the system, so that it can be difficult to distinguish between Rideal and Langmuir-Hinshelwood models.

1.7.2 Metathesis in the Homogeneous Phase

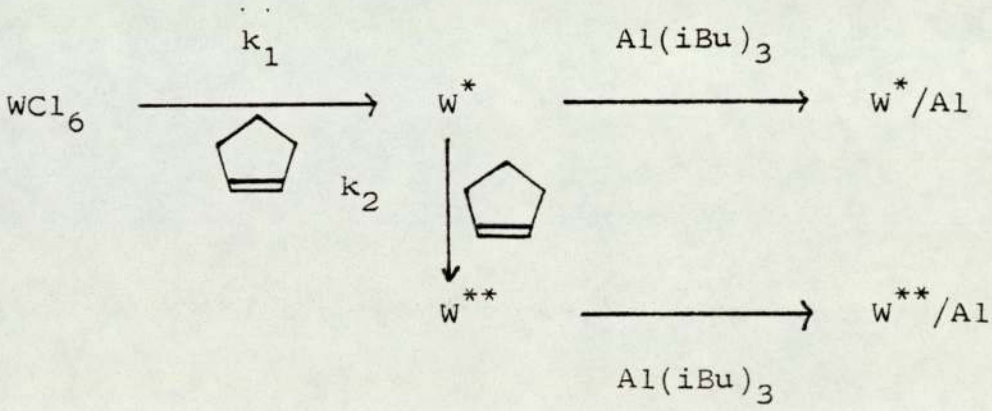
Detailed kinetic studies on 2-pentene metathesis were performed by Basset and co-workers(105) and it was found that the initial rates of cis-trans isomerisation, and the metathesis of 2-pentene, were in agreement with the proposed mechanism of co-ordination of the internal olefin on the two different metallacarbene moieties. The mechanism was simply based on the fact that since the co-ordinated carbene has a high barrier to rotation, the stereochemistry will depend mostly on the geometry of approach of the incoming olefin. The kinetic data obtained related to the respective rates of eight elementary steps occurring at low conversion, and a mathematical model was derived which accounted for the linear relationship observed between trans/cis—C_5, since competition existed between cis-trans isomerisation of the starting olefin and productive metathesis.

1.7.3 Kinetics of Polymerisation of Cycloolefins

The main kinetic data reported on ring-opening polymerisation came from homogeneous catalytic systems using cyclopentene, cyclooctene, cyclooctadiene and norbornene.

Initially it was proposed that the ring-opening polymerisation of cyclopentene with WCl_6 based catalyst systems showed kinetics corresponding to a first-order rate equation. Amass and Tuck(14) agreed with these observations with respect to the catalyst concentration, but concluded that the order with monomer concentration was more complicated, the initial rate of polymerisation being first order in monomer concentration only.

The kinetics of polymerisation were complicated by the fact that the catalyst WCl_6 may also react with the monomer to generate intermediates, probably reduced oxidation states of tungsten, which then reacted with the cocatalyst to generate two sites of different activities towards polymerisation. The following scheme of reactions was proposed to account for these observations:-



It was found that the rate of polymerisation depended upon the time interval between the addition of catalyst and co-catalyst, and the maximum rate of polymerisation was observed after a time interval, t_{max}, which was given by the equation:-

$$t_{max} = \frac{1}{(k_1 - k_2)[M]_0} \ln \frac{k_1}{k_2}$$

where $[M]_0$ = initial monomer concentration

It was shown experimentally that:- $t_{max} \propto \frac{1}{[M]_0}$

The initial rate of polymerisation, R_{p0}, was then represented by the kinetic equation:-

$$R_{p0} = k_p [W^*/Al]_0 [M]_0$$

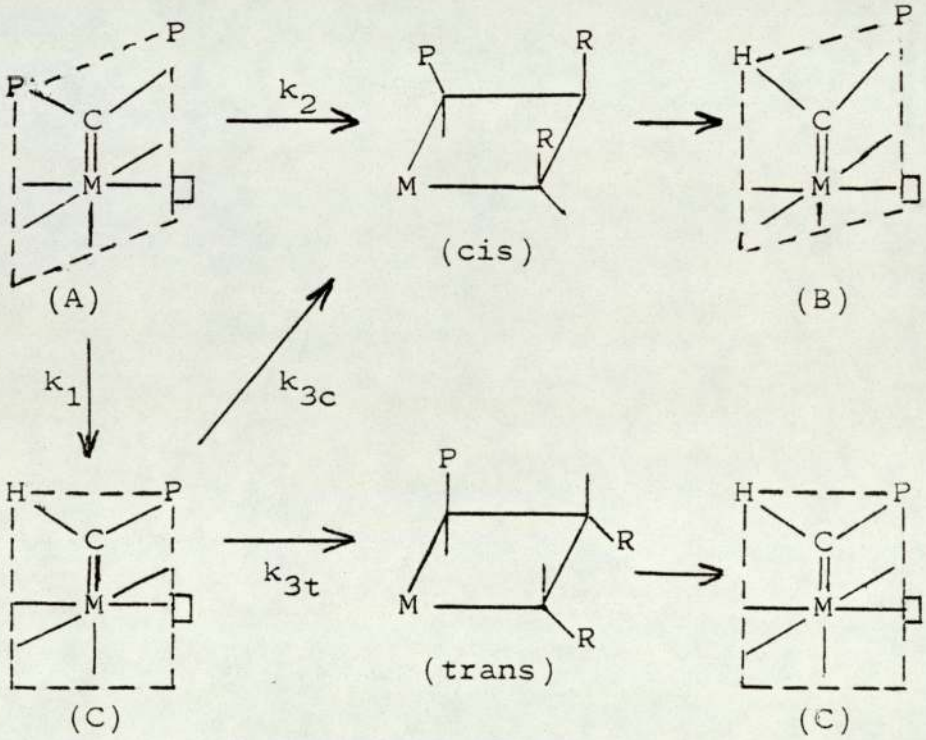
The ratio $[W^*/Al]_0$ depended upon the interval between additions of catalyst and cocatalyst.

Recent investigations by Amass(15) have indicated that the rate of propagation decreases faster than can be accounted for by consumption of monomer alone during the polymerisation of cyclopentene. It was inferred that the decrease in polymerisation rate was a second order reaction with respect to the concentration of active species, which was destroyed during polymerisation by some termination reaction:-

$$W^* + W^* \longrightarrow \text{Polymer} + 2\,W_{inactive}$$

Moreover the deactivated catalyst would destroy those sites still propagating, so that the rate of termination accelerated.

A refined kinetic treatment was developed by Ivin et al(109) for the interpretation of the propagation mechanism for cyclopentene, norbornene, norbornadiene and their derivatives on the basis of the structure and stereochemistry of the resulting polymers. In the experiments with norbornene and its derivatives the effects of dilution and temperature on the fraction of cis- double bonds σ_c were relatively small. Hence it was generally necessary to change the catalyst system in order to achieve a wide range of σ_c values. But in the ring-opening polymerisation of cyclopentene this was done by changing the catalyst/cocatalyst ratio or by raising the temperature. It was supposed that the effect of increasing temperature accelerated the interconversion of metallacarbene species more than the propagating reactions. Thus, from the following scheme:-



The following equation was developed by applying the steady-state approximation:-

$$\frac{\sigma c}{\sigma t} - \frac{k_{3c}}{k_{3t}} = \frac{k_{3c}}{k_{3t}} \frac{k_2}{k_1} \left[M\right]$$

At high temperatures, $k_2 \left[M\right] \ll k_1$, therefore:-

$$\frac{\sigma c}{\sigma t} = \frac{k_{3c}}{k_{3t}}$$

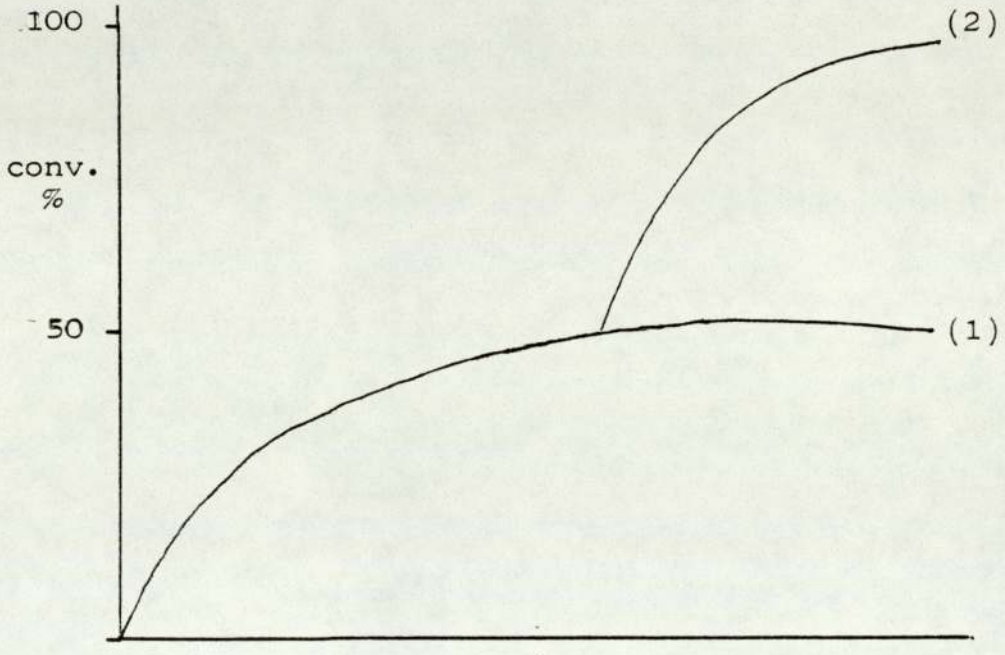
Above $20^{o}C$ $^{k}3c/k_{3t}$ approximated to 0.1 and was independent of temperature. A plot could then be traced of ln $^{k}2/k_{1}$, which is proportional to $\ln\left[(\sigma c/\sigma t)-(^{k}3c/k_{3t})\right]$ against 1/T. This gave a straight line from which E_2-E_1, the difference in activation energies for the reactions with rate constants k_2 and k_1, was calculated to be 55 kJ mol^{-1}

The question remained as to the nature of the structure into which the configurations (A) and (B) could relax, and to the mechanism involved. Relaxation to (C) would not be expected because it would involve hindered rotation about the metal-carbene bond. The rate of relaxation relative to the rate of propagation appeared to be determined by the extent of d-orbital occupancy around the central metal ion. It was concluded that at least two d-electrons were required for the formation of the metal-carbene bond.

The kinetics of polymerisation of cycloolefins have received little attention and are not well defined. Höcker(143) and

Reimann(144) investigated the kinetics of cyclooctene polymerisation using several catalysts. The orders of reaction with respect to catalyst and monomer concentrations were found to vary between one and two, depending upon the catalyst system employed. The authors proposed a pronounced kinetic control of reaction products in the early stage of the reaction. At high initial monomer concentration immediate formation of polymer occurs, while at low concentration the homologous series of oligomers is first formed and eventually the polymer. The concentration of oligomers increases as the reaction progresses, reaching a maximum and decreasing as polymer is formed. Fig. 1.2 shows the time conversion curve of 1.5-cyclooctadiene polymerisation with $WCl_6/Al(iBu)_3$ catalyst system.

Fig. 1.2 <u>Polymerisation of 1.5-Cyclooctadiene</u>



Curve (1) represents the initial addition of catalyst and curve (2) indicates further catalyst addition. It was found that polymerisation did not proceed to the equilibrium concentration of the monomer, but on addition of new catalyst during the polymerisation the reaction proceeded at a higher rate. The decrease in reaction rate was caused by the significant consumption of active species. Similar effects were shown by Amass and co-workers(15) for the polymerisation of cyclopentene.

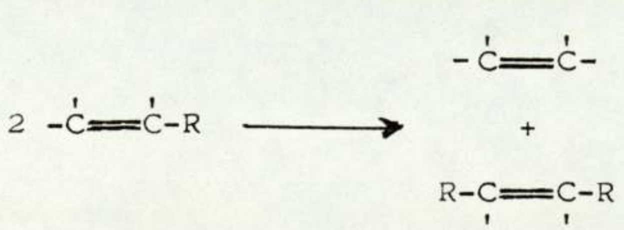
The form of ring-opening polymerisation studies strongly depends on the nature of the stereoisomer of the cycloolefin substrate and the type of catalyst used. Using a system comprising $WCl_6/EtOH/EtAlCl_2$ Riebel(145) found that cis-cyclodecene reacted at a higher rate than the corresponding trans-isomer. The same finding came from Reif and co-workers(143) for the reaction of cyclooctene (although in this case the cis-isomer was the only one studied) and cyclododecene, which was available as a mixture of cis- and trans-isomers. Here it was found that the cis-isomer was consumed faster than the trans-isomer. On using the catalyst system $WCl_6/SnMe_4$ however, the behaviour of the two isomers was reversed, i.e. the trans-isomer reacted faster than the cis-isomer.

The cis/trans ratio of the polyalkenamers obtained depended greatly upon the catalyst employed and it is possible to obtain all cis-polypentenamer and high trans-polypentenamer by using appropriate catalysts, e.g. $WCl_6/SnEt_3/Et_2O$ and $WCl_6/LiBu$ respectively.

1.8 PRACTICAL APPLICATIONS OF METATHESIS AND RING-OPENING POLYMERISATION OF CYCLOOLEFINS

Soon after its discovery, metathesis reaction in the heterogeneous phase was used in industry to prepare olefins which were needed for petrochemistry, organic chemistry and the polymer industry. The ring-opening polymerisation of cycloolefins resulted in the synthesis of polyalkenamers, some of which possessed elastomeric properties which were useful in the rubber industry. Olefin metathesis has more recently been employed as a route to synthesising natural products such as pheromones and substituted acetylenes.

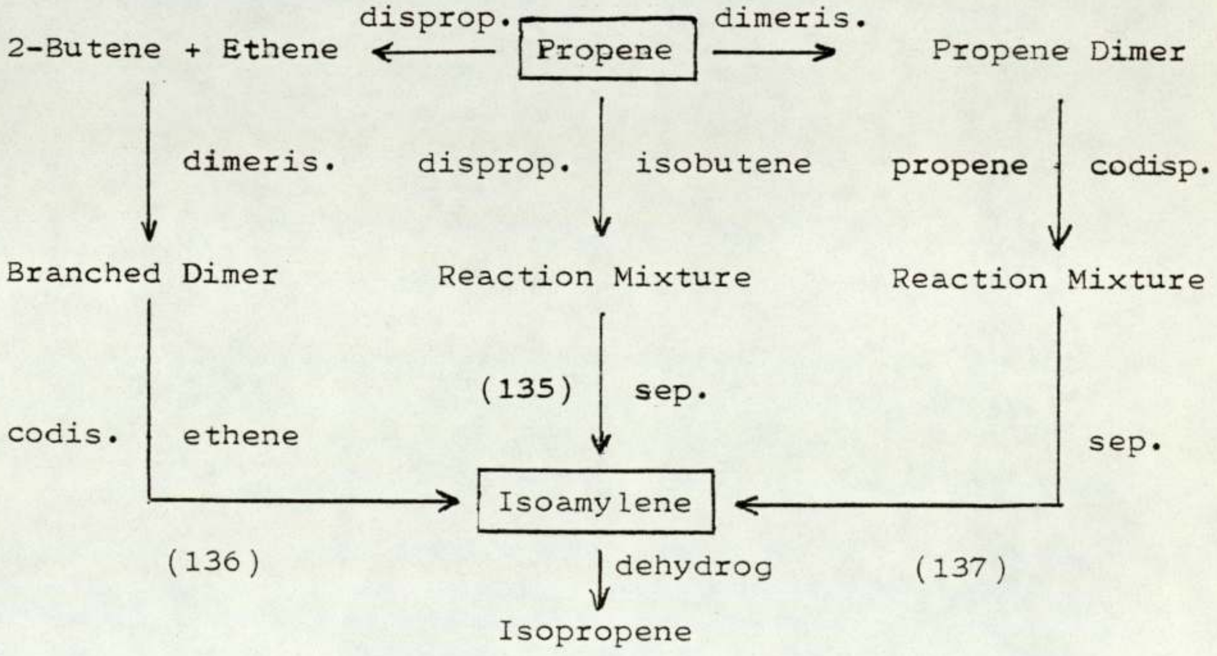
A recent industrial use of metathesis developed by Shell(134) is the Shell Higher Olefin Process, otherwise known as the SHOP process. This involves the production of high purity linear olefins (C_{10}-C_{20}) and selected ranges of internal olefins (C_{11}-C_{14}). The initial stage is the oligomerisation of ethene to form olefins of C_4-C_{20}, which are then partially separated in a fractionating column followed by isomerisation to αolefins. Internal olefins result from the disproportionation of these olefins, while through metathesis β-olefins yield 2-butene and an internal olefin.



$$2\ -\overset{|}{C}{=}\overset{|}{C}-R \longrightarrow \begin{array}{c} -\overset{|}{C}{=}\overset{|}{C}- \\ + \\ R-\underset{|}{C}{=}\underset{|}{C}-R \end{array}$$

The Triolefin Process(17) was the first industrial process used for the synthesis of olefins which involved the disproportionation of propene to ethene and 1-butene. The latter product is 90% of the trans-isomer and used as a starting material for gasoline synthesis, or as a comonomer in polyethylene production after first being converted to high purity 1-butene. Butadiene may also be synthesised from 2-butene via dehydrogenation. A variation of the Triolefin Process produces a mixture of hexene, heptene and octene, which can be used in the oxo-alcohol synthesis for the production of PVC plasticizers.

Isoamylene is a valuable starting material for the polyisoprene rubber industry and can be synthesised via the metathesis reaction in several ways. The methods employed are summarised in the schematic diagram below:-



Propene is used as the starting material for many industrial processes, including higher acyclic olefin production, such as 5-decene and C_{11}-C_{15} acyclic olefins, using a series of disproportionation, isomerisation and fractionation steps. Phillips(135) also developed a similar process for the production of C_{12}-C_{16} olefins from propene or butenes.

Branched acyclic olefins have many applications in the petrochemical industry and can easily be obtained from butene and ethene(138) through metathesis.

The manufacture of polyalkenamers has been mentioned in previous sections and the properties of this will now be discussed in greater detail. Polyalkenamers are polymers with a number of important elastomeric properties, e.g.,

i) low glass transition temperatures,
ii) low melting points,
iii) high rates of crystallisation,
iv) a high molar mass, which permits easy processing,
v) a chain structure which results in high flexibility and the ability to be vulcanised with sulphur.

The most useful polyalkenamers are the cis- and trans-isomers of polypentenamer and polyoctenamer. Table 1.10 lists some properties of these materials and gives a comparable view of their attributes.

Polyalkenamer	M.P/^{o}C	GTT/^{o}C	Compounding and Processing Properties
Trans- Polypentenamer	18	-97	Low crystallinity at room temperature increases resistance during processing. Easily compounded without premastication. Can be loaded with carbon black and oil without losing properties. Easily vulcanised with S to form products of high tensile strength and modulus. Very low permeability to air, with high ageing resistance and stability with respect to UV and ozone.
Cis- Polypentenamer	-41	-114	Compound exhibits poor elastomeric properties due to low melting point and glass transition temperature. Difficult to compound at room temperature, but has great ability between 80-100^{o}C. Physisico-chemical properties improve at lower temperatures but this restricts utilization, though still regarded as a competitor of rubber.
Trans- Polyoctenamer	73	-	Crystallisation rate lower than for cis-isomer, but has high viscosity at room temperature; low at processing temperatures. Good processing properties exhibiting good physical properties after vulcanisation. Usable in a wide range of rubbers, using S, peroxides or other cross-linking agents.
Cis- Polyoctenamer	18	-108	Although melting point is the same as for trans-polypentenamer, crystallisation rate at room temperature is higher. Processing properties poor, particularly below 100^{o}C. Can be compounded with fillers, ingredients and oil between 100-120^{o}C, but quality mixes poor. Not easily vulcanisable.

Table 1.10 Comparison of the Properties of Polyalkenamers

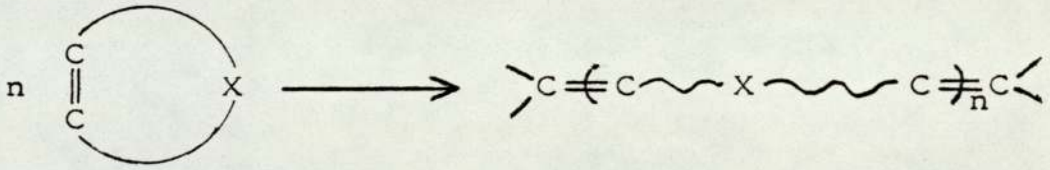
Substituted polyalkenamers, which are of great interest because of their elastomeric properties, include those obtained from 3-methylcyclooctene, 3-phenylcyclooctene and 3-methylcyclodecene. Poly(norbornene) and its alkyl-substituted derivatives offer a large class of polyalkenamers with potential utility as elastomers.

Through metathesis it is possible to obtain polyalkenamers with microstructures of block polymers, graft polymers or branched polymers. Copolymers are formed by the metathesis of two chemically distinguishable monomers. The types which could possibly result from two monomers A and B are:-

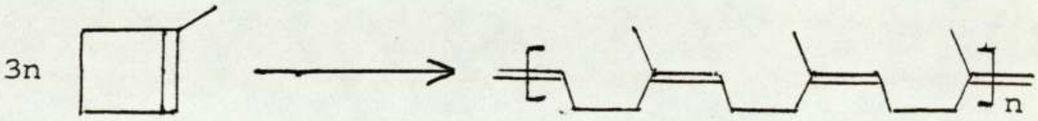
$-(AAAAA)_n-(BBBBB)_n-$	Block copolymer
-ABBAABABAAABBABABB-	Random copolymer
-ABABABABABABABABAB-	Alternating copolymer
-BBBBBBBXBBBBBBBBBB- A A A A A	Graft copolymer

Scott and Calderon(139,140) obtained AB-type block copolymers from polyoctenamer and polydodecenamer, as did Pampus(33) in the reaction between polypentenamer and polybutenamer or butadiene-styrene copolymer. Graft copolymers are obtained through co-metathesis between a polymer with an unsaturated side chain and a cycloolefin or other unsaturated polymer. Scott and Calderon(139,140) and Pampus(33) were among chemists to work on the synthesis of graft copolymers. Copolymers are produced as a means of obtaining a polymer with substantial improvement on the initial polyalkenamer properties.

The metathesis reaction is of great importance for the conversion of heterocyclic compounds to unsaturated linear polymers containing the hetero-atom in the chain via ring-opening polymerisation:-



This application of metathesis polymerisation is very important for synthetic organic chemistry. Olefin metathesis has found a recent use in the preparation of natural compounds with uncommon structures. The first application of this type was the synthesis of poly(isoprene) from 1-methylcyclobutene by Katz and co-workers(56):-

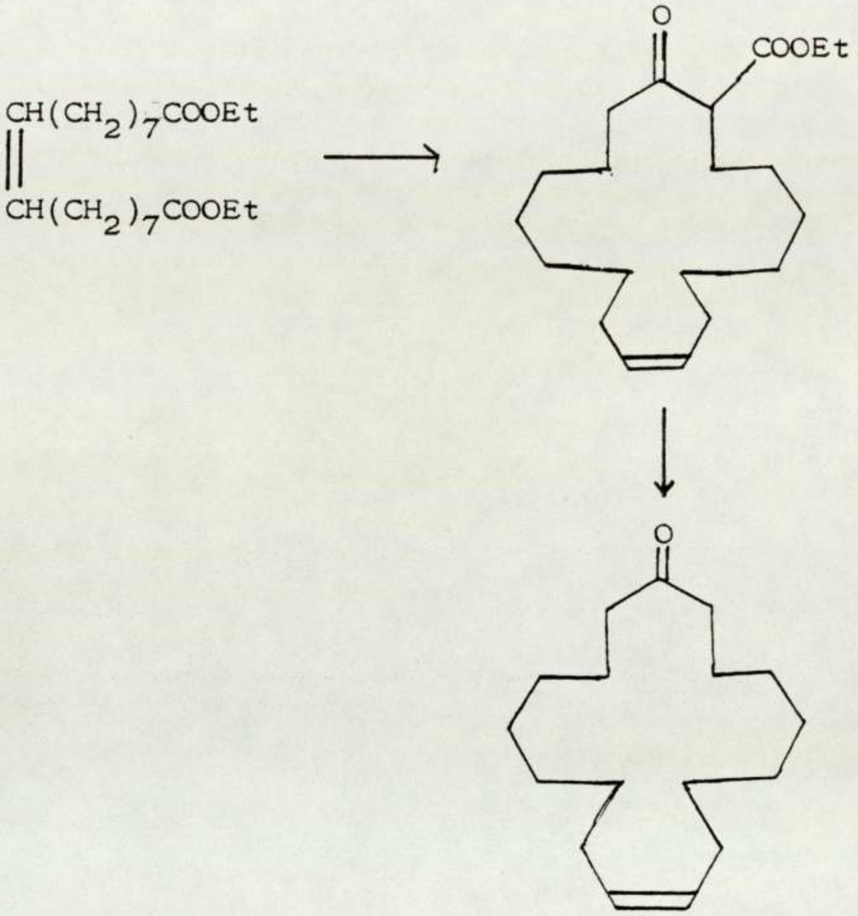


Pheromones are another class of natural compounds which are easily obtainable through metathesis, and recently much more work has been carried out on the topic. Table 1.11 lists a number of pheromones synthesised via olefin cometathesis:-

Table 1.11 <u>Pheromone Synthesis via Olefin Metathesis</u>

Pheromone	Starting Olefins	References
9-Tricosene	1-Decene + 1-Pentadecene	(141)
	1-Decene + 2-Hexadecene	(141,61)
	9-Octadecene + 1-Pentadecene	(141,61)
	9-Octadecene + 2-Hexadecene	(141,61)
13-heptacosene	1-Tetradecene + 2-Hexadecene	(141)
13-Nonacosene	1-Tetradecene + 2-Octadecene	(141)
14-Nonacosene	1-Hexadecene + 2-Octadecene	(141)
2-Methylheptadecene	4-Methyl-1-pentene + 1-Tetradecene	(141)
2-Methyl-7-octadecene	1-methyl-1-octene + 1-Dodecene	(141)
7,8-Epoxy-2-methyloctadecene	1-Methyl-1 octene + 1-Dodecene	(61)

Civetone (cyclo-9-heptadecanone), used in the perfume industry, is obtained by ketocyclisation of 9-octadecene-1, 18-dioate, which was produced by the metathesis of ethyloleate, as shown overleaf:-


CH(CH$_2$)$_7$COOEt
CH(CH$_2$)$_7$COOEt
O
COOEt
O

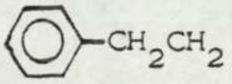
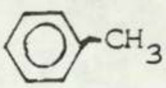
CHAPTER 2

EXPERIMENTAL WORK

2.1 MATERIALS USED

Table 2.1 shows a list of chemicals used during the course of this project, their sources and properties.

Table 2.1 List of Chemicals

Chemical	Form	Source	M.Wt.	M.Pt. °C	B.Pt. °C	Density $g\ cm^{-3}$
Aluminium Bromide	$AlBr_3$	BDH	267.00	97.0	-	3.205
Lithium-butyl	C_4H_9Li	Aldrich	64.06	-	-	0.680
Cyclo-hexane		Fisons	84.16	6.6	80.7	0.775
Cyclo-pentene		Aldrich	68.12	-135.0	44.2	0.772
Styrene		BDH	104.16	-30.6	145.2	0.906
Tetrahydro-furan		BDH	72.11	-108.0	66.0	0.886
Toluene		BDH	92.15	-95.0	110.6	0.867
Tin Tetra-chloride	$SnCl_4$	Aldrich	260.50	-33.0	114.1	2.226
Tungsten hexa-chloride	WCl_6	Aldrich	396.60	275.0	346.7	3.520

2.2 GENERAL TECHNIQUES

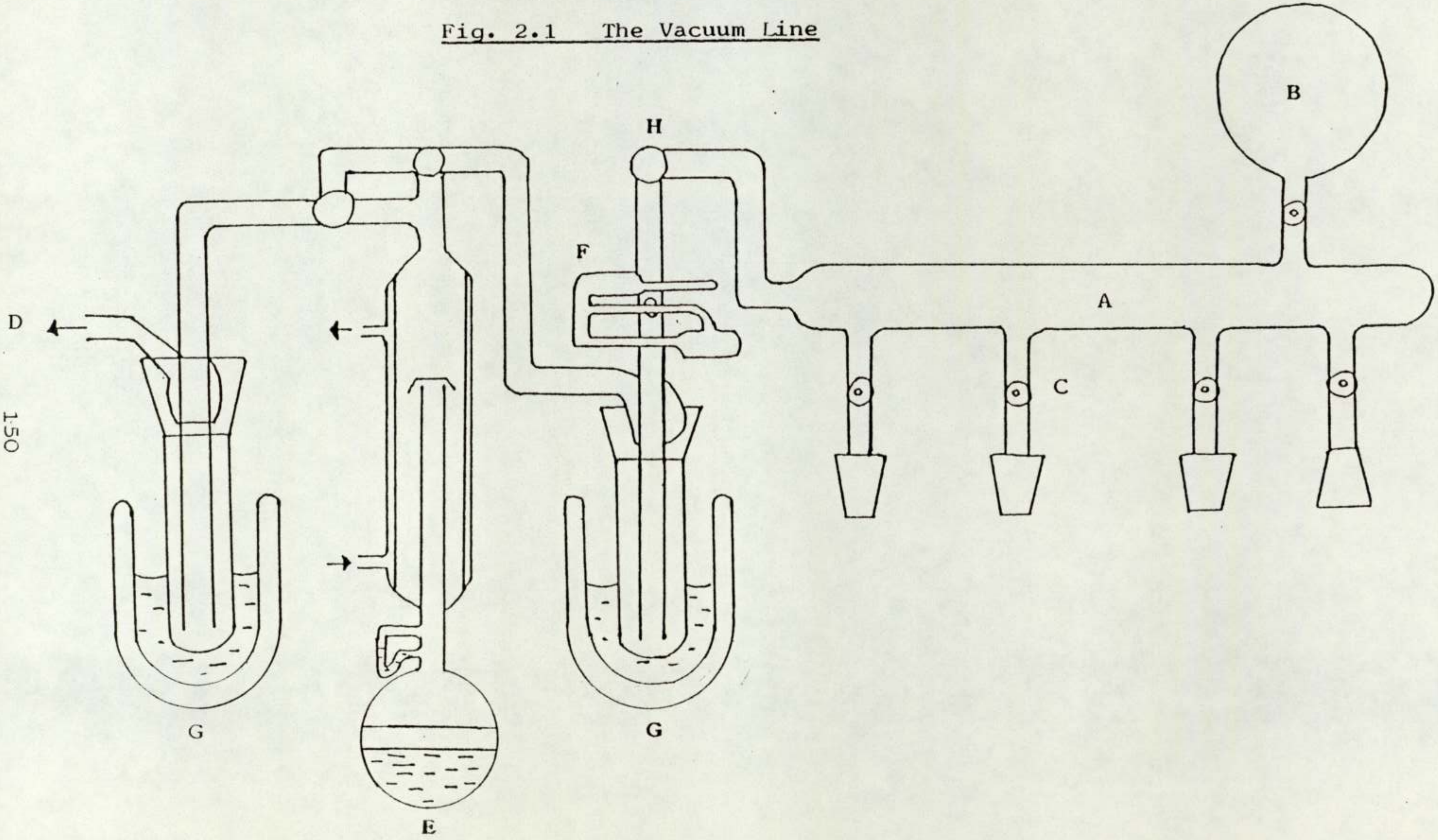
All the catalyst components used in this project were extremely sensitive to air and moisture. It was therefore necessary to prepare the catalyst solutions and carry out the polymerisations either under vacuum or in an atmosphere of nitrogen, in order to exclude these impurities as far as possible.

2.2.1 Vacuum Techniques

2.2.1.i The Vacuum Line

The vacuum line is shown in fig. 2.1 overleaf. The apparatus consisted of a main manifold (A) with an adjoining bulb (B) to increase the internal volume, which aided degassing of material, together with four greaseless taps (C) with joints for the attachment of pieces of apparatus. The manifold was evacuated using an Edwards rotary vacuum pump (D) in conjunction with a mercury diffusion pump (E), thereby achieving a pressure as low as approximately 10^{-5}mmHg estimated by a vacustat (F). Liquid nitrogen traps (G) were situated either side of the mercury pump to condense any organic and mercury vapours from the manifold and diffusion pump respectively.

Fig. 2.1 The Vacuum Line



2.2.1.ii Freeze-Thaw Degassing of Solvents

A high vacuum was produced with bulb (B) open to the manifold and the flask containing solvent (fig. 2.2) attached to the line with its tap closed. A Dewar flask filled with liquid nitrogen was placed around the flask, causing the contents to freeze. The tap on the solvent flask was then opened, thus evacuating the vessel whilst its contents were frozen. When a vacuum had been formed once more the main tap (H) was closed and the solvent allowed to thaw, thus evacuating both flasks and manifold. The degassing process was repeated until no further difference in vacuum was observed between freezing stages of the freeze and thaw processes.

2.2.1.iii Trap to Trap Distillation

A flask containing degassed pure monomer or solvent and a clean dry receiving flask were attached to the manifold, which was then evacuated. The receiving flask was flamed under vacuum and on cooling immersed in liquid nitrogen. With the manifold isolated from the pumping system and bulb(B) the contents of the monomer/solvent flask were allowed to gently distil into the receiving vessel. The rate of distillation was controlled by the greaseless taps, but warming the distilling solution was sometimes found to be necessary in order to facilitate the process.

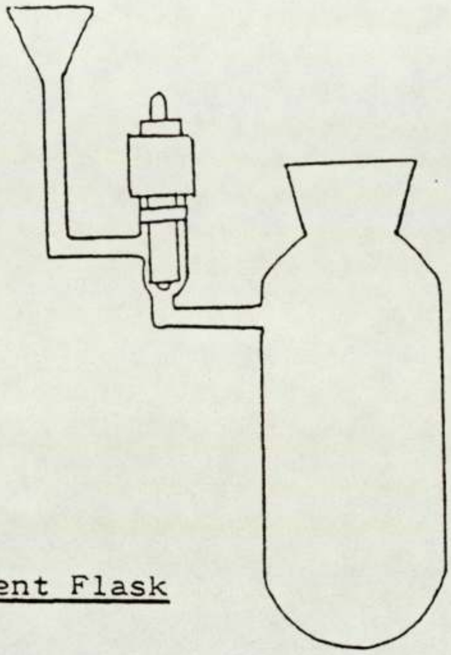


Fig. 2.2 Solvent Flask

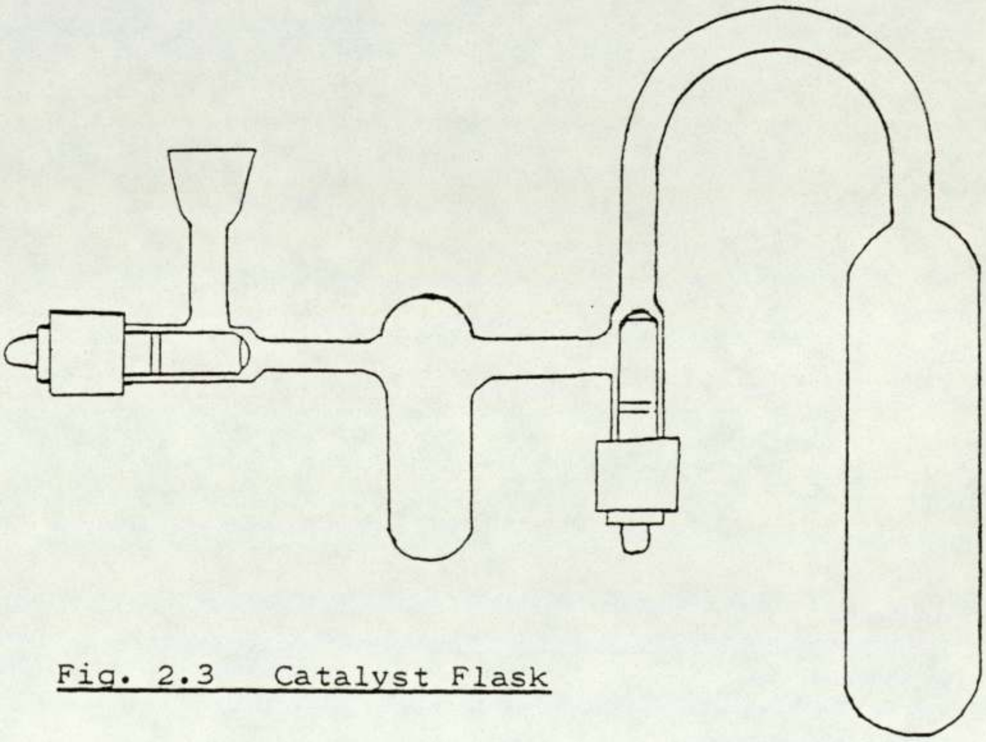


Fig. 2.3 Catalyst Flask

2.2.2 Treatment of Glassware

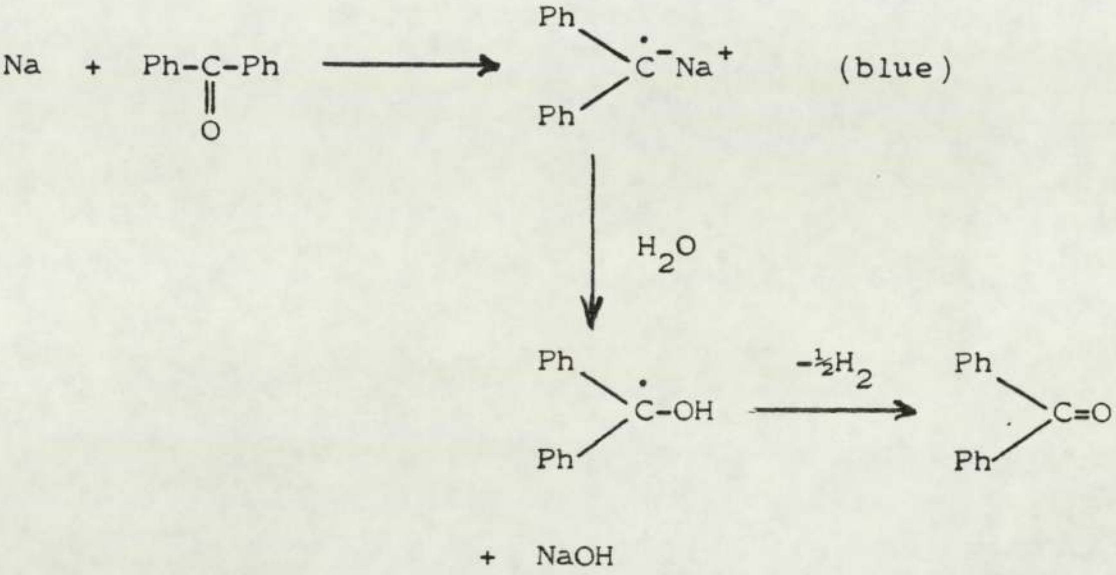
All the glass apparatus, apart from the vacuum line, was cleaned very effectively by soaking overnight in a concentrated solution of sodium hydroxide and ethanol. The cleaning solution also removed high vacuum silicone grease from around the joints. The apparatus was then washed with copious amounts of water and dried in an air oven at 240°C.

The apparatus was evacuated on the vacuum line prior to use, flame dried as an added precaution and allowed to cool under vacuum. After removal from the oven the syringes were left to cool in a dessicator containing powdered calcium chloride.

2.3 PURIFICATION, DRYING AND STORAGE OF MATERIALS

2.3.1 Toluene

Because toluene has a relatively high water content it was refluxed over sodium for two hours and pure toluene then removed by fractional distillation. The pure distillate was maintained over calcium hydride powder in a stoppered flask for at least two days, before distilling into another flask containing slices of freshly cut sodium and approximately 10g benzophenone. The solvent was degassed to remove the hydrogen evolved, and when completely dry a deep blue solution was produced. This colour resulted from the production of a sodium benzophenone complex, which will only develop in a completely dry environment and hence acts as an indication of the solvent's dryness:-



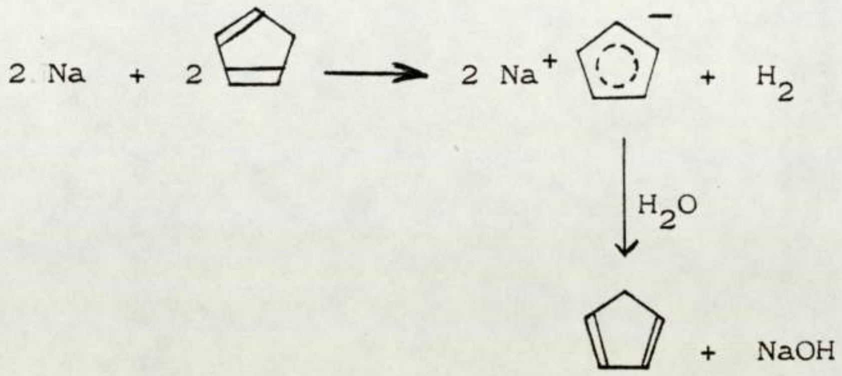
2.3.2 Cyclohexane

Crude cyclohexane was dried over calcium hydride, followed by sodium and benzophenone in the same manner as for toluene.

2.3.3 Cyclopentene

The main impurities in cyclopentene are known to be water, cyclopentanol and cyclopentadiene, all of which are capable of deactivating the catalyst components.

Initially the cyclopentene was left for 24 hours over slices of freshly cut sodium, under a nitrogen atmosphere contained in a flask as shown in fig. 2.2. The sodium acted to remove traces of water, as well as complexing with the cyclopentadiene to form a surface golden residue, according to:-



The degassed monomer was then distilled into a clean, evacuated flask containing sodium and benzophenone in order to ensure complete dryness.

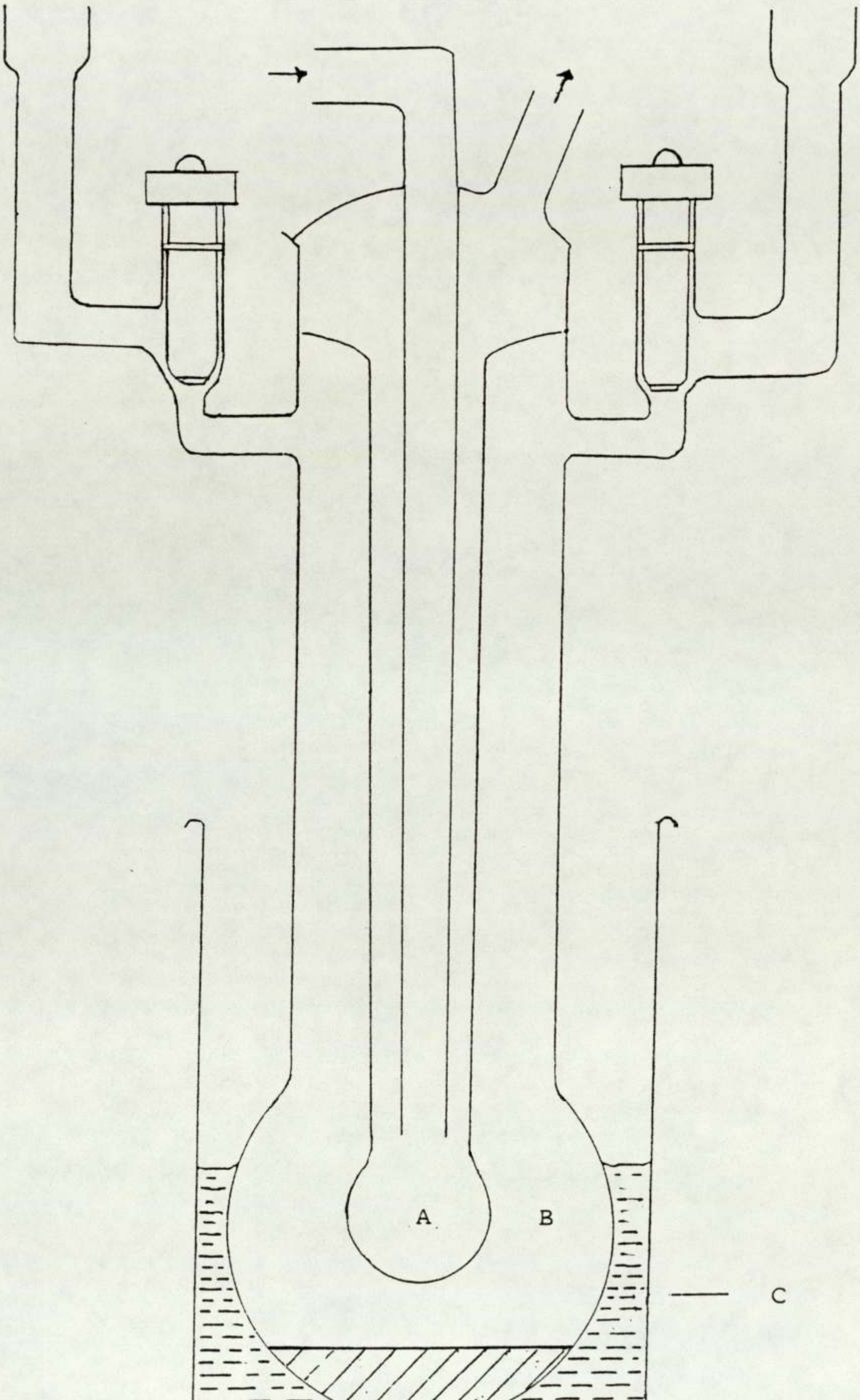
2.3.4 Styrene

Commercial styrene contains 10-15ppm t-butyl catechol to inhibit thermally initiated polymerisation. This inhibitor was removed by washing three times with approximately one third of its own volume of 10% sodium hydroxide solution, then twice with distilled water. The wet monomer was then dried as for cyclohexane and stored under vacuum in a solvent flask at low temperature (4°C) until required.

2.3.5 Tungsten Hexachloride

Pure tungsten hexachloride was initially obtained by sublimation on to a 'hot finger', using the apparatus shown in fig. 2.4 for the sublimation of aluminium bromide. The oxychloride impurities remained on the walls of the vessel. This technique proved to be generally unsatisfactory however,

Fig. 2.4 Sublimation Unit



hence 'Gold Label' tungsten hexachloride supplied by Aldrich, which had a nominal purity of 99.98%, was employed. This was provided in a sealed ampoule and transferred to a catalyst storage flask as shown in fig. 2.3. The procedure was carried out in a nitrogen filled 'dry-box' which contained phosphorus pentoxide in order to absorb moisture from the atmosphere, and the ampoule was opened inside the dry-box for the transfer of its contents to the storage flask.

2.3.6 Aluminium Bromide

The main impurity in aluminium bromide is iron(111) bromide, which also sublimes under vacuum and had therefore to be removed prior to the sublimation process. This was achieved by initially heating aluminium bromide together with pieces of aluminium foil in the sublimation unit (B), while passing cold water through the finger (A). Volatile iron (111) bromide reduced to involatile iron(11) bromide, which does not reoxidise in the presence of foil. When all the iron(111) bromide had been visibly reduced the water passing through the finger was gradually cooled, whilst the contents in the flask continued to be heated. Pure aluminium bromide, seen as white crystals, sublimed on to the finger.

2.3.7 Tetrahydrofuran

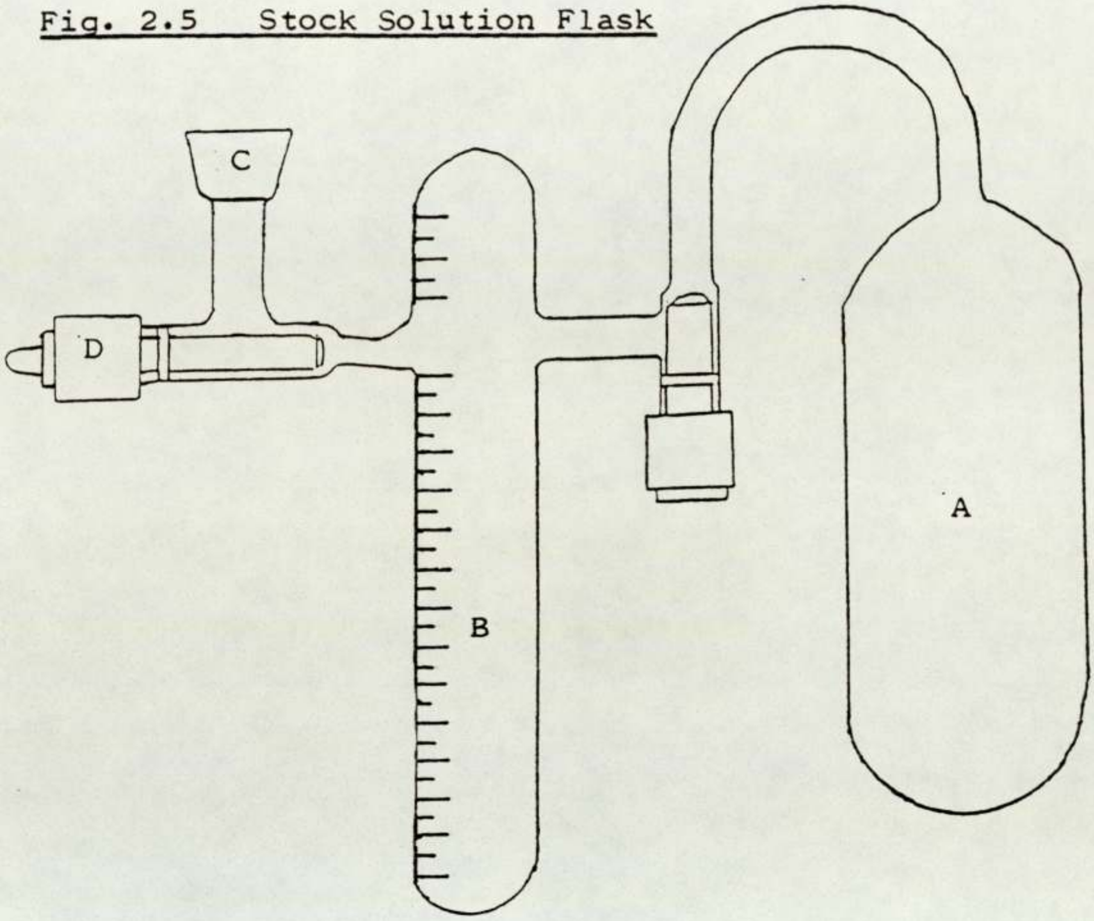
HPLC grade THF was supplied by BDH for gel permeation chromatography (GPC) studies. Due to the expense of this highly pure solvent it was necessary to distil used solvent after recycling through the GPC apparatus several times. Prior to distillation it was essential to remove any peroxides, which tend to form on standing and present an explosion hazard. This was achieved by shaking each litre of solvent with 20cm^3 of a ferrous salt solution made from 60g ferrous sulphate dissolved in 6cm^3 of concentrated sulphuric acid and 110cm^3 of water.

2.4 PREPARATION OF SOLUTIONS

2.4.1 Stock Solution (Cyclopentene/Cyclohexane)

An approximate 30% by volume stock solution of cyclopentene in cyclohexane was prepared by distillation in turn of the dry components into compartment (A) of the vessel shown in fig. 2.5, weighing after each addition in order to determine the concentration of the resulting solution. The graduated centre bulb (B) aided the accurate transfer of solution from the main flask (A), thus minimising wastage. The solution was removed from the flask by passing a stream of nitrogen through joint (C) and removing tap (D), thereby allowing the syringe and needle access to the solution, while the remainder was maintained under vacuum in (A). Alternatively it was possible to pour the required amount of monomer solution from (B) by direct attachment of the vessel to a receiving flask at joint (C), after initial evacuation of the entire apparatus.

Fig. 2.5 Stock Solution Flask



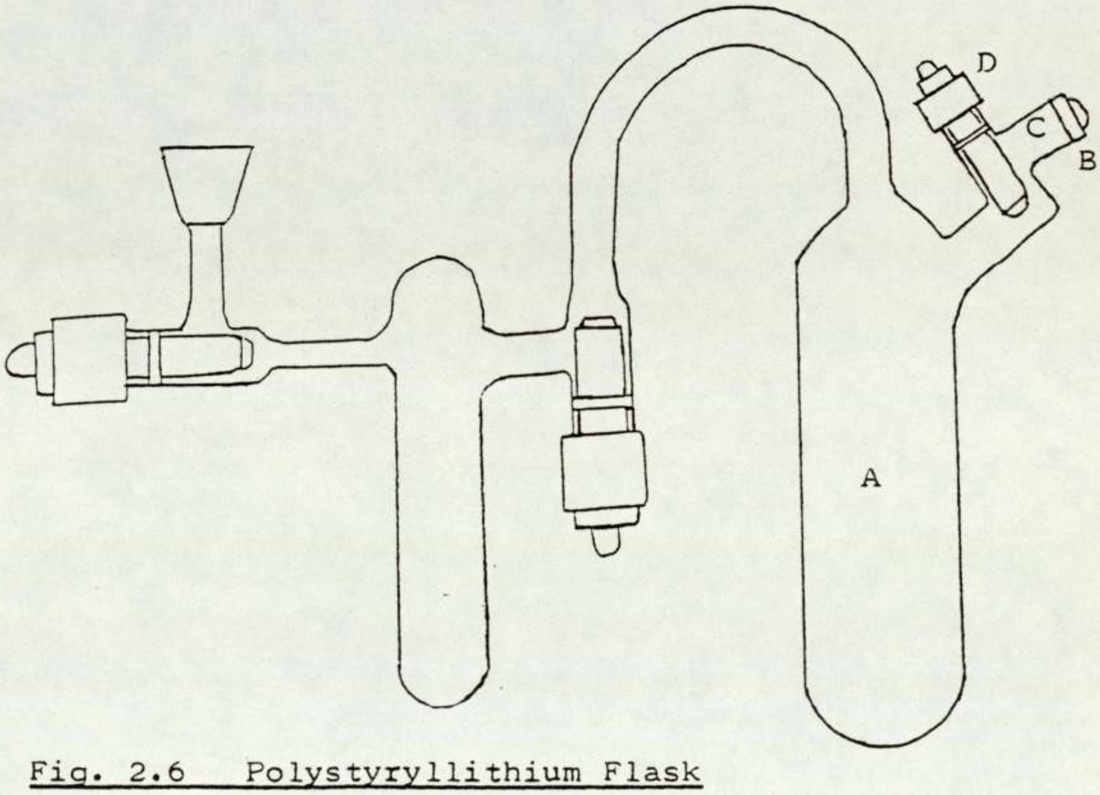


Fig. 2.6 Polystyryllithium Flask

2.4.2 Tungsten Hexachloride

A solution of tungsten hexachloride was prepared by transferring a known weight (approx. 2.5g) of the pure crystals from the storage flask into a clean and dry catalyst flask in a nitrogen filled dry-box, as previously described. Dry cyclohexane was then distilled under vacuum on to the crystals, producing a dark red solution of tungsten hexachloride. The weight of solvent used was in the order of $140cm^3$, giving a molar concentration of solution of approximately $4.5x10^{-2}$. It was very important to establish the accurate molarity of the solution because the rate of polymerisation depended upon it, and the weight of each material was therefore measured to three decimal places on an accurate balance.

2.4.3 Aluminium Bromide

Since aluminium bromide does not readily dissolve in cyclohexane it was necessary to prepare a solution in dry toluene. The sublimation finger, with the pure aluminium bromide crystals adhering to it, was transferred to a pre-weighed catalyst flask in the dry-box. This was reweighed in order to determine an accurate mass of aluminium bromide, evacuated on the vacuum line, and pure dry toluene distilled into the flask producing a bright yellow solution.

If the solution was left unprotected against the light a dark oily residue was seen to form and settle at the bottom of the flask. The production of the residue was inhibited if the vessel was covered with black tape, although its presence was not considered detrimental to the metathesis polymerisation reactions.

2.4.4 Tin Tetrachloride

Tin tetrachloride, as supplied by Aldrich, is in liquid form. A solution in cyclohexane was prepared by distilling the solvent into an evacuated catalyst flask, then weighing prior to the introduction of tin tetrachloride via a syringe and needle under nitrogen in the fume cupboard.

2.4.5 Polystyryllithium (PstLi)

The apparatus used for the preparation of polystyryllithium is shown in fig. 2.6. This was evacuated and styrene followed by cyclohexane, in a ratio of approximately 1:10, were distilled into the main flask (A); the amounts being determined by weight difference. Secondary lithiumbutyl of predetermined volume was injected into the area (C), with tap (D) closed, via a subaseal (B). The apparatus and contents were immersed in a water bath at 5°C and allowed to equilibriate to the same temperature prior to permitting the lithiumbutyl to mix with the monomer and solvent. The low temperature employed, and the use of secondary rather than n-lithiumbutyl, were measures taken to ensure production of material with a narrow molecular weight distribution. The solution was then left in a bath of water at 60°C for two days in order to polymerise, turning red/orange in colour, indicative of a living polymer.

2.4.6 Lithiumbutyl Solution

As supplied by **Aldrich** n-lithiumbutyl is a 1.6M solution in cyclohexane with a secondary analogue of 1.4M solution. Colourless solutions were made in cyclohexane as described for tin tetrachloride solution, but tended to turn pink with age. This was possibly due to aromatic impurities in the solvent undergoing a form of metallation reaction.

2.5 EXPERIMENTAL TECHNIQUES

2.5.1 Dilatometry

Dilatometry is a technique used to measure the contraction or expansion of liquids or solids during a chemical reaction. During polymerisation a contraction of material is usually observed, as there is an increase in density while monomer is converted to polymer.

2.5.1.i Description of the Dilatometer

Fig. 2.7 shows the dilatometer used in this project. Evacuation of the apparatus was possible at joints (H) and (I),

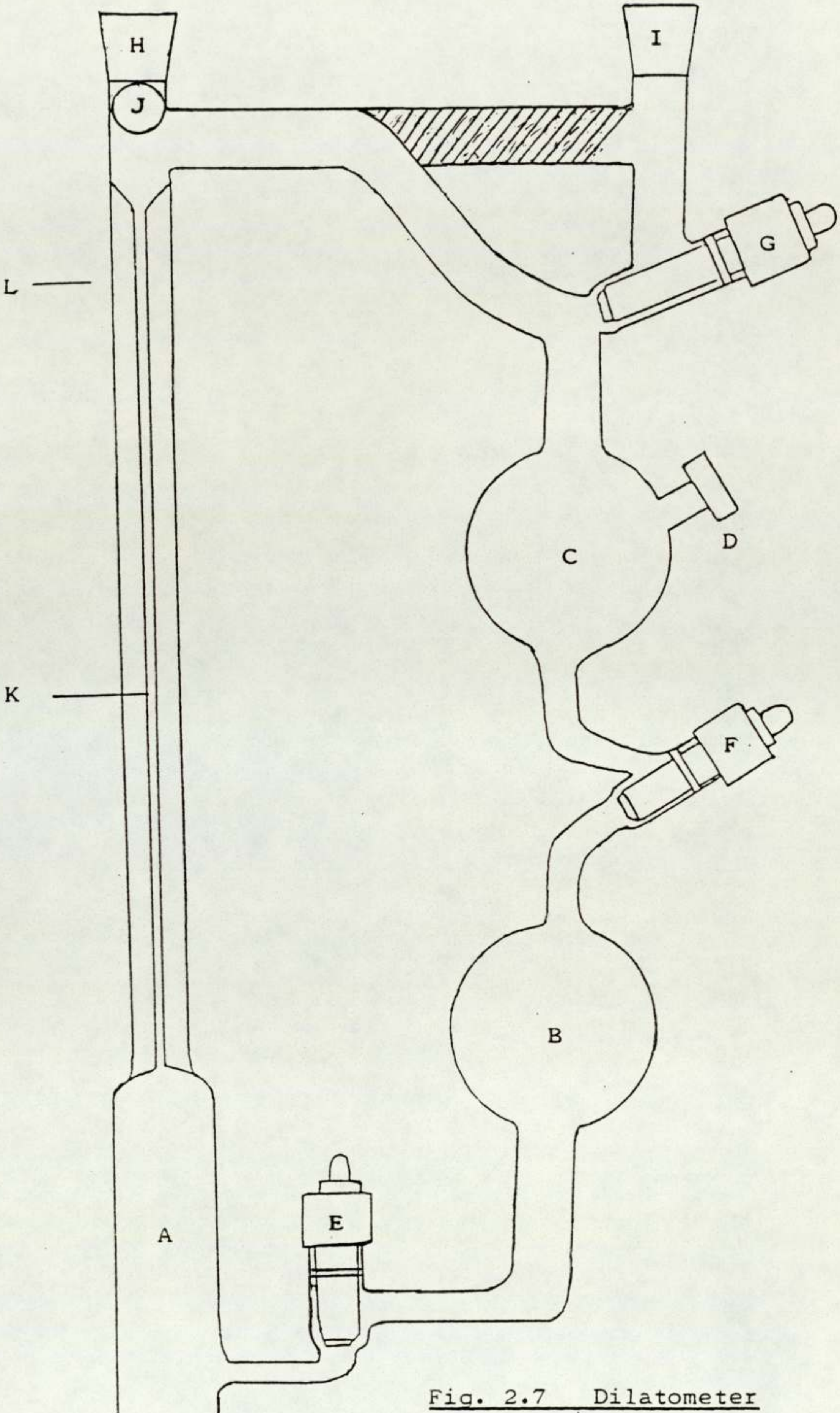


Fig. 2.7 Dilatometer

and taps (E), (F), (G) and (J) were opened or closed in accordance with the particular experiment being carried out. Reactants were injected into bulb (C) via a B17 subaseal at joint (D). The design of the dilatometer was such that reactions involving premixed catalyst components could be performed by isolating the monomer in bulb (B), while premixing other components in bulb (C) prior to addition.

2.5.1.ii Principles of the Dilatometer

The overall rate of polymerisation, $-d[\mathrm{cp}]/dt$, may be calculated from the decrease in height of the meniscus in the capillary (K) during the reaction. If the meniscus moves from point x to point y on the capillary, the decrease in volume (ΔV) would be:-

$$\Delta V = \pi r^2 \Delta h$$

where Δh = distance from point x to y

r = radius of the capillary

For m grams of monomer to polymerise to m grams of polymer contraction in volume would be:-

$$\Delta V = V_p - V_m$$

$$= \frac{m}{\rho p} - \frac{m}{\rho m} = m\left(\frac{\rho m - \rho p}{\rho p \ \rho m}\right)$$

where V_p = volume of polymer

ρp = density of polymer

V_m = volume of monomer

ρm = density of monomer

If ΔM is the number of moles of monomer polymerised, then:-

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

where M_m = molecular weight of monomer

By rearranging:-

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

Assuming that the volume of the dilatometer (v) is much greater than the total volume change, then any variation in monomer concentration $\Delta [M]$ can be approximated to:-

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

$$= \frac{\pi r^2 \Delta h}{v M_m} \left(\frac{\rho_p \; \rho_m}{\rho_m - \rho_p} \right)$$

$$= K \Delta h \text{ moldm}^{-3}$$

Hence the rate of polymerisation is proportional to $^{\Delta h}/_{\Delta t}$ since:-

$$R_p = \frac{-d[M]}{dt} = \frac{\Delta h}{\Delta t} \times K$$

For this project:-

i) The radius of the capillary (r) = 0.092cm

ii) The volume of bulb (A) and the capillary of the dilatometer up to the mark (L) = $0.0211 dm^3$ (v)

iii) Density of cyclopentene (ρm) = $0.7728 gdm^{-3}$(146)

iv) Density of polypentenamer (ρp) = $0.8700 gdm^{-3}$(146)

v) Relative molecular mass of cyclopentene (M) = 68.12g

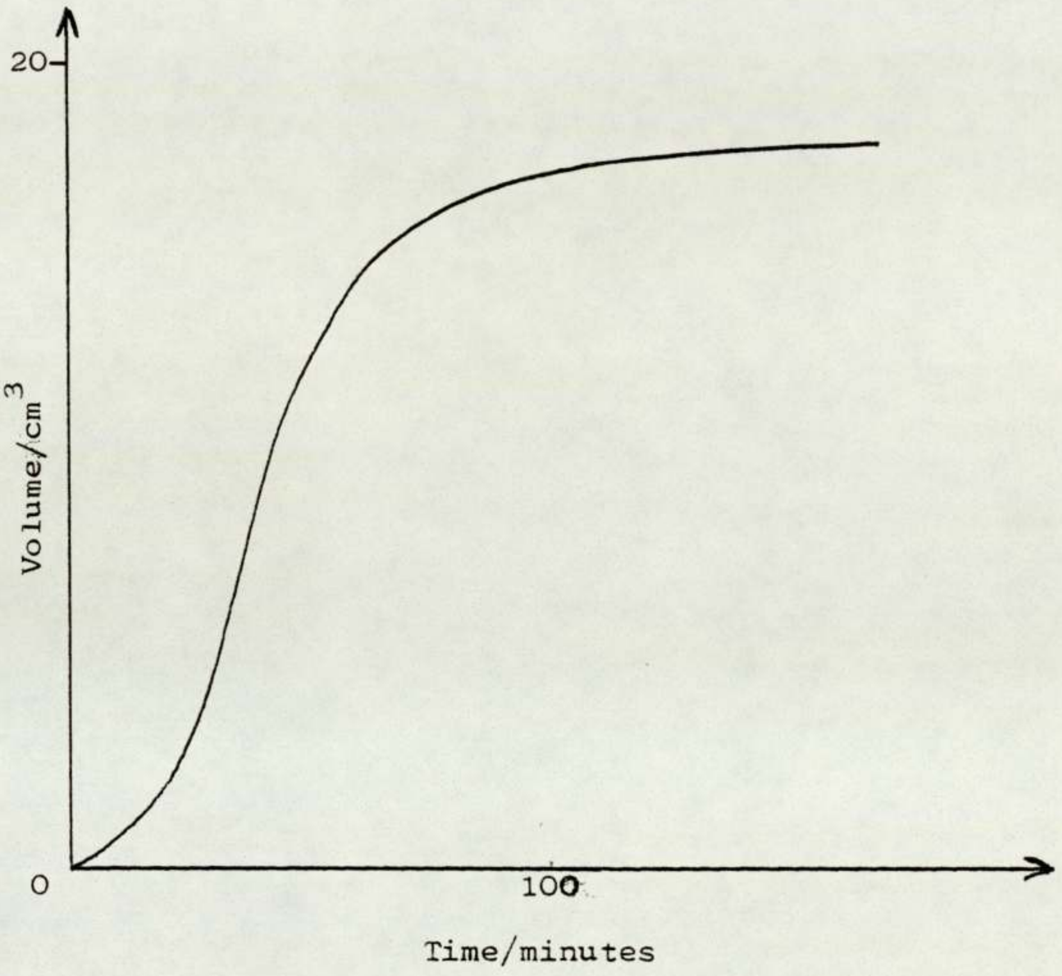
$$\therefore \quad K = \frac{\pi r^2}{Mv}\left(\frac{\rho_p \, \rho_m}{\rho_p - \rho_m}\right)$$

$$\underline{K = -0.130 \text{ moldm}^{-4}}$$

2.5.1.iii <u>Treatment of Data</u>

Using the equation relating Δv to Δh, the rate of polymerisation can be measured from a plot of Δh against reaction time Δt. A typical polymerisation curve is shown in fig. 2.8, from which it can be seen that the rate of polymerisation $d\Delta h_{/\Delta t}$ is not constant.

Fig. 2.8 Typical Dilatometry Curve



2.5.1.iv Dilatometer Experiments

a) Sequential Addition Catalyst Experiments

The dilatometer was flamed out while attached to the vacuum line and allowed to cool to room temperature. Both the dilatometer and reactants were then left to equilibriate thermally in a water bath at 25°C (± 0.1°C) prior to the reaction. After removal from the bath, $25cm^3$ of monomer solution was injected via subaseal (D) into bulb (B) of the dilatometer, whilst tap (E) remained closed. Predetermined volumes of solutions of the catalyst components for a given molar ratio were also added by syringe, with predetermined time intervals between each addition. When the last reactant had been added, the dilatometer and contents were returned to the constant temperature water bath, noting the time of commencement of reaction while opening tap (E), thus allowing the reacting polymerisation mixture into bulb (A) and up capillary (K) to the marked level (L). When all bubbles had been expelled tap (E) was closed, and the height of the meniscus in the capillary determined at regular intervals by a cathetometer.

When the final reading had been taken polymer was obtained by emptying the dilatometer contents into a small round-bottomed flask, evacuating the solvent/unreacted monomer on the vacuum line. The residual polymer was immediately dissolved and stored as a solution in THF to avoid oxidative cross-linking.

b) Premixed Catalyst Experiments

The monomer solution was introduced as previously described. Tap (F) was closed and the catalyst components to be premixed were simultaneously introduced into bulb (C) of the dilatometer, the apparatus then shaken to ensure effective mixing. After a given premixing time the resultant solution was added to the monomer solution in bulb (B), the dilatometer filled and the conversion-time curve determined as described before.

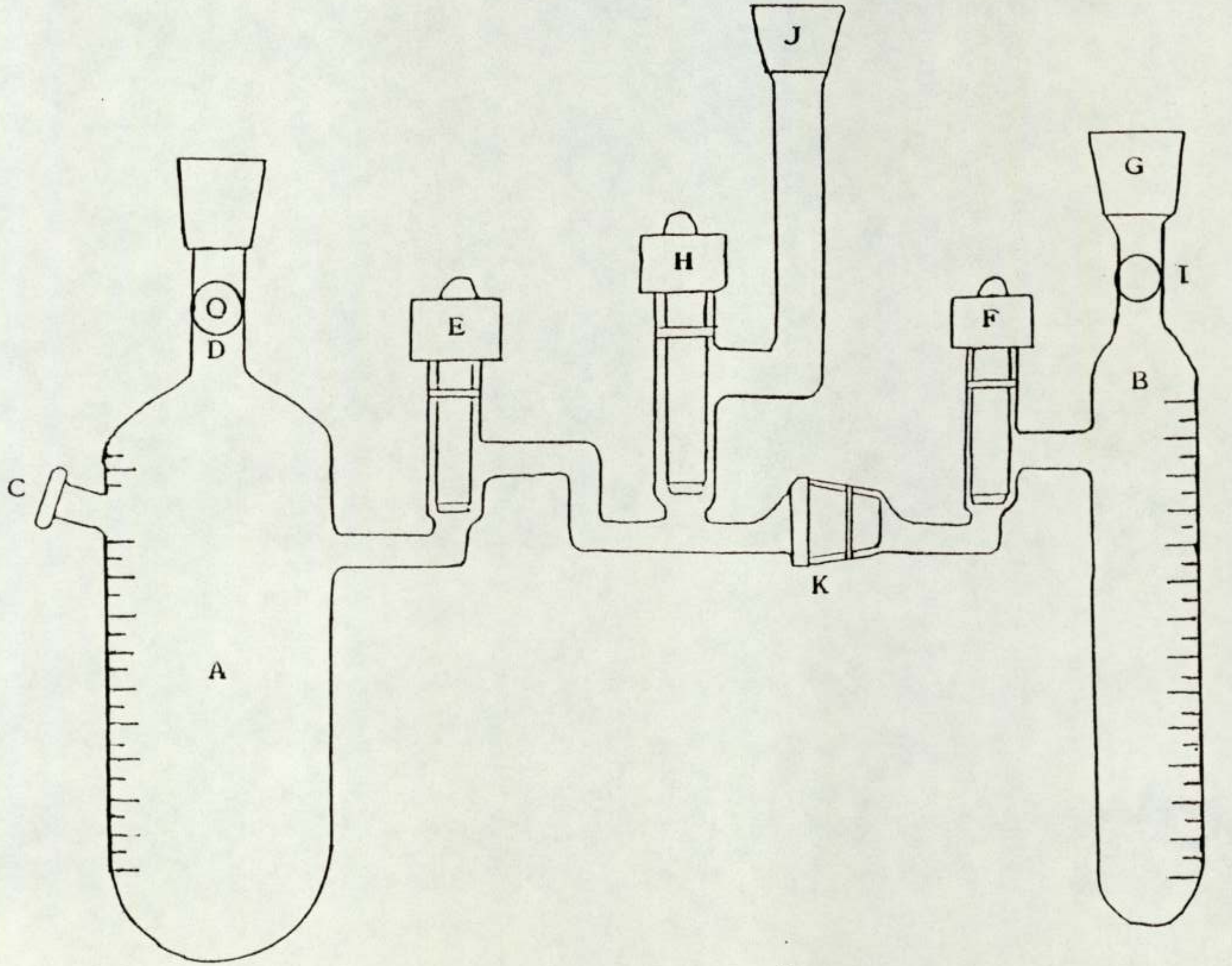
2.5.2 Polymerisate Sampling Procedure

A number of experiments carried out dilatometrically were repeated in a reaction flask, as shown in fig. 2.9, which was specifically designed to separate polymer samples during the course of polymerisation. Samples taken at regular intervals were analysed by GPC, and the progress of polymer/copolymer formation could be followed by comparing ultra violet (UV) and refractive index (RI) analyses.

The polymerisation unit was flamed prior to use and evacuated through tap (H), then allowed to cool to room temperature under vacuum. All taps were now closed and 25cm^3 of monomer solution introduced into the main flask (A) via subaseal (C). Predetermined volumes of the catalyst solutions were also added by syringe. If necessary, premixing of catalyst components could be carried out in a nitrogen-filled syringe. The reaction mixture was thoroughly mixed after each addition.

When all components had been introduced, polymerisation commenced and the reaction time noted from the addition of the last component. At intervals of 5, 15, 30, 90 and 120 minutes and also 24 hours from the start of the reaction, 5cm^3 of polymerisate was transferred under vacuum into flask (B). Taps (E) and (H) were now closed, isolating the sample

Fig. 2.9 Polymerisation Unit



in (B) from the remainder of the reacting mixture. About $5cm^3$ of 'wet' chloroform was allowed into (B) through tap (I) to dilute the polymer solution and terminate the reaction. The two halves of the apparatus were separated, the contents of (B) poured into methanol and the polymer precipitated. The sample was dried in a vacuum oven and re-dissolved in THF to give a 2% solution in preparation for GPC analysis.

The apparatus was now reassembled, cleaned with chloroform to remove traces of polymer from its walls, then flushed with acetone. When clean and dry the apparatus could be evacuated via tap (J) and the sampling section and mid-region of the apparatus flame-dried. In this way samples of polymerisate could be taken from section (A) without contamination of the main solution.

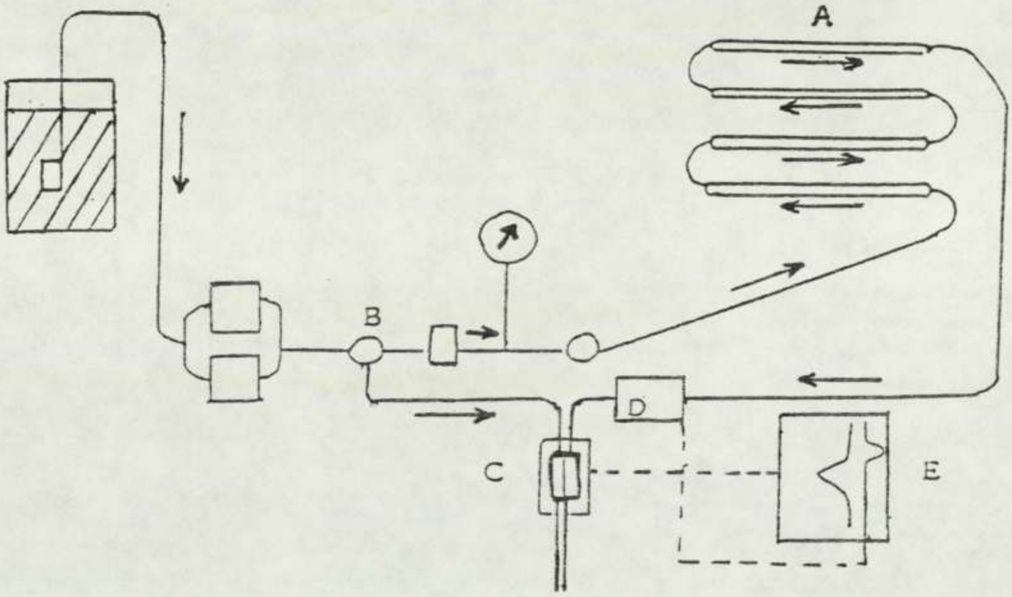
2.6 ANALYTICAL TECHNIQUES

2.6.1 Gel Permeation Chromatography (GPC)

2.6.1.i Principles of the GPC

GPC is one of the most important techniques for the determination of molecular weights and molecular weight distributions of polymer samples. A schematic diagram of a gel permeation chromatograph is shown in fig. 2.10.

Fig. 2.10 Gel Permeation Chromatograph



The principal components of a gel permeation chromatograph are:-

i) a stationary phase (cross-linked porous gel),

ii) a mobile phase (solvent for the polymer),

iii) an injector system (valve and loop),

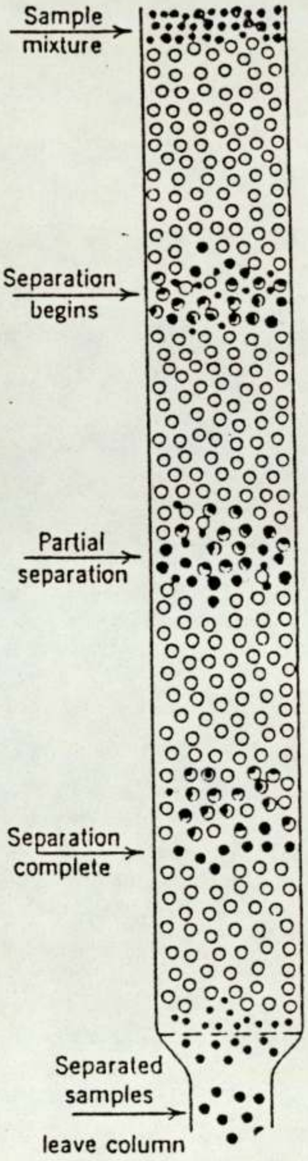
iv) a detector (differential refractometer and UV detector).

The object of GPC is to separate a sample of polymer into its component fractions, according to their size. A stationary phase is packed within a series of columns (A) and solvent is pumped at a constant rate (1 cm^3 min^{-1}) through the columns. The stationary phase is a cross-linked polymer which swells when solvent is introduced to form a gel. The gel is constructed so that pores are on the surfaces of the particles. There is a range of pore sizes and the gel particles are 10μm in diameter. The latter are surrounded by solvent (interstitial solvent), while pure solvent is contained within the pores.

A sample of the polydisperse polymer may be introduced at the inlet of the column using valve and loop (B) injector system. Because solvent is being continuously pumped through the column, the polymer will be transported by the solvent. Polymer molecules will be accomodated in the interstitial solvent and will also permeate the pores, providing the pores are large enough to accomodate them. Small polymer molecules are able to enter the pores for a greater proportion of time than larger ones. Consequently larger polymer molecules will elute from the column first, followed progressively by molecules of lower molecular weights. Fig. 2.11 shows the principle of separation of molecules by GPC according to their size.

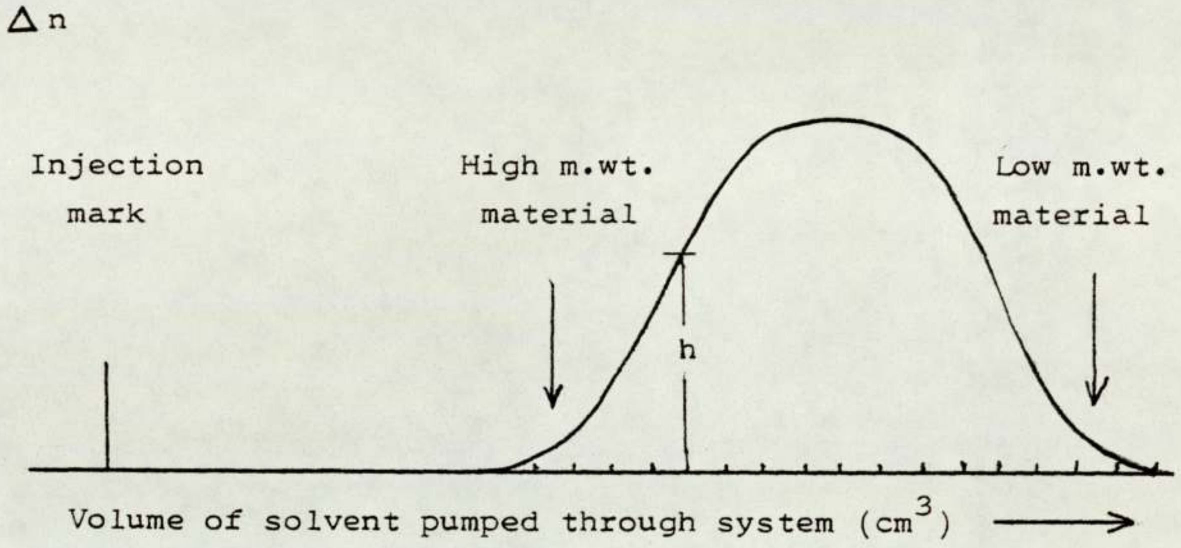
It is essential to detect the polymer in solution as it elutes from the base of the column. A differential refractometer (C) is usually used for this purpose, but in this project it was used in conjunction with an ultra-violet detector (D). The differential refractometer continuously monitors the refractive index (RI) of the eluting solution and compares it with the RI of the pure solvent. Any difference (Δn) generates a deflection on the chart recorder (E) which is proportional to the concentration of eluting polymer at that time; i.e. weight of polymer per unit volume.

Fig. 2.11 Principle of Separation of Polymer Molecules down a GPC Column



A typical gel permeation chromatogram is shown in fig. 2.12.

Fig. 2.12 Typical Gel Permeation Chromatogram



The UV detector can be one of two types, fixed or variable wavelength. Both measure the UV absorption of polymers containing chromophoric groups along the backbone of the polymer chain, or as end groups. The variable wavelength detector has the advantage that the wavelength may be set to maximum wavelength of a chromophore by 'tuning in' to a particular absorption for that specific group. The simultaneous use of both detectors is advantageous in the study of copolymers, especially if one of the blocks contains a UV absorbing chromophore. This project has been principally concerned with the study of anionic-to-metathesis transformation reactions. In this case the use of polystyryllithium as a cocatalyst might lead to the incorporation of a polystyrene block as an end group in polypentenamer. Presence of a UV chromophore in the high molecular weight polymer can be deduced from the UV detector response for that material and used to confirm or disprove its presence.

2.6.1.ii Calibration of GPC Equipment

In order to estimate average molecular weights it must first be determined how the molecular weight of eluted polymer varies over the range of elution volumes. For this purpose samples of polystyrene, of very narrow molecular weight distribution and known molecular weights, were injected into the column in turn. The volume of solvent pumped through the column, which was required to elute polymer of a specific molecular weight, could thus be measured and the calibration curve plotted for columns used is shown in fig. 2.13. By comparing retention volumes of different polymers it is possible to obtain a polystyrene equivalent molecular weight for most linear polymers in solution.

2.6.1.iii Treatment of Experimental Data

The average molecular weights may be calculated as follows:-

By definition, $\bar{M}_n = \frac{\Sigma NiMi}{\Sigma Ni}$ and $\bar{M}_w = \frac{\Sigma NiMi^2}{\Sigma NiMi}$

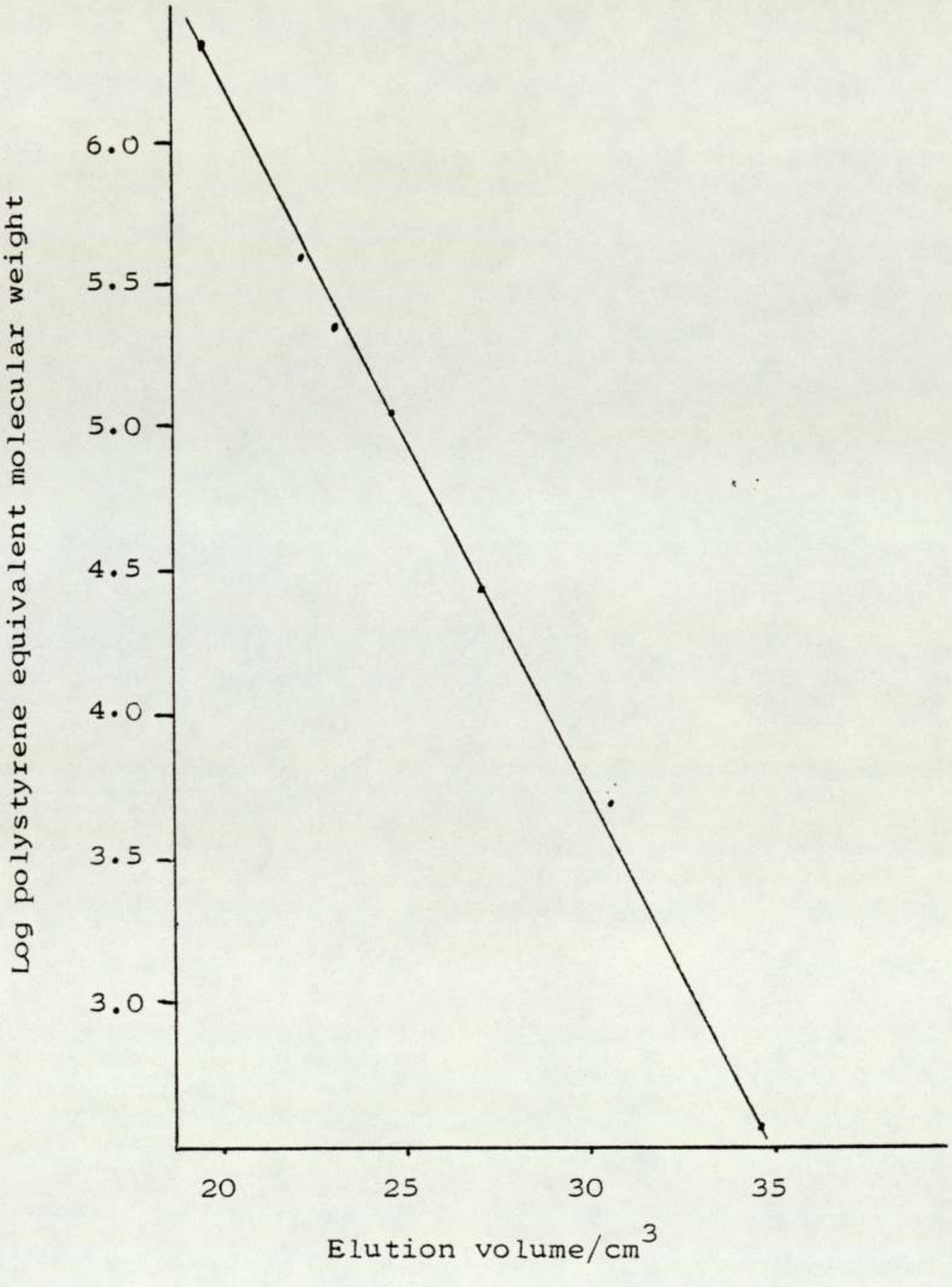
where $\bar{M}_n$ = number average molecular weight

$\bar{M}_w$ = weight average molecular weight

Mi = molecular weight of a given molecule

Ni = number of molecules of molecular weight in a given sample

Fig. 2.13 Calibration Curve for the GPC Equipment using Polystyrene Standards in THF



If Wi is the weight of polymer of molecular weight Mi in a given fraction, then,

$$Ni = \frac{Wi}{Mi}$$

therefore, $\bar{M}_n = \frac{\sum Wi}{\sum Wi/Mi}$ and $\bar{M}_w = \frac{\sum WiMi}{\sum Mi}$

Since the RI response (hi) is a measure of the concentration of polymer of molecular weight Mi, then Wi may be substituted by hi, therefore,

$$\bar{M}_n = \frac{\sum hi}{\sum hi/Mi} \quad \text{and} \quad \bar{M}_w = \frac{\sum hiMi}{\sum Mi}$$

2.6.1.iv Description of the GPC Equipment used

'Hypergrade' THF was used as the solvent, and 2% solutions of polymer were made up in the solvent for analysis.

The instrument used was a Waters model 6000 fitted with four 10 μl PL gel columns of exclusion limits 10^2, 10^3, 10^4 and 10^5 Å. 100 μl of polymer solution was loaded into the loop and injected. The difference in RI was detected by a Waters model R401 differential refractometer, and the UV absorbance by an Applied Chromatography Systems Ltd. UV detector. The resulting chromatograms were recorded on Servoscribe potentiometric chart recorders.

CHAPTER 3

POLYMERISATION STUDIES USING LiBu COCATALYST

3.1 INTRODUCTION

The bimetallic homogeneous catalyst system (WCl_6/LiBu) has been used extensively for olefin metathesis studies. Wang and Menapace(64) showed an optimum molar ratio for W/Li of 1:2 for the metathesis of 2-pentene, and similar results have been reported by Gregory(147) for the ring-opening polymerisation of cyclopentene. It has also been reported that the time delay between additions of WCl_6 and LiBu to a solution of cyclopentene determined the rate of ring-opening polymerisation reaction. The optimum time interval was found to be two minutes over a range of concentrations of cyclopentene and catalysts.

The bimetallic system (W/Li) has yielded a considerable quantity of useful information concerning the initiation mechanism of ring-opening polymerisation. Gregory(147) has shown that the alkyl group associated with the lithium compound is instrumental in generation of initial carbene. Most bimetallic systems are not based on lithium alkyls as the cocatalyst however, but typically aluminium or tin compounds. In order to study the role these metal alkyls play in the generation of a carbon complex it would be useful to undertake investigations with their polystyryl equivalents, such as polystyrylaluminium. The direct synthesis of polystyryaluminium compounds is however difficult to achieve, and an indirect route, such as the reaction of polystyryllithium with $AlBr_3$, may therefore be used.

It was thought that investigation of the W/Al catalyst system would require the generation of polystyrylaluminium bromide by the reaction of $AlBr_3$ and PstLi, or by using a three-component catalyst system such as WCl_6/PstLi/$AlBr_3$ and thus generate the cocatalyst in situ. Before studies of this and similar systems could be undertaken however, knowledge of the behaviour of the similar but simpler WCl_6/LiBu/$AlBr_3$ system seemed desirable.

The optimum catalyst ratios and times for sequential additions were determined and compared with the corresponding bimetallic system (WCl_6/LiBu). Experiments were also carried out to determine the effect of premixing the two cocatalysts. The rates of polymerisation were studied, also the molecular weight changes of the products with reaction time.

3.2 PRELIMINARY EXPERIMENTS

One major reason for carrying out preliminary experiments was to develop the experimental technique, as this form of polymerisation requires techniques which are new to the average worker. Another reason was because initial studies gave an indication of the colour changes expected for a particular active system, and an increase in viscosity of the polymerisate confirmed that polymerisation was in fact occurring. Inactive systems were recognised principally by failure of the reactants to become viscous, which could be confirmed later by the absence of polymer precipitating in methanol.

Experiments were carried out in bulb (A) of the polymerisation apparatus shown in fig. 2.9, and the time allocated for each reaction was four hours. In a typical polymerisation experiment 2.4cm^3 WCl_6 (4.29×10^{-2}mol dm^{-3}) was added to 25cm^3 cyclopentene solution (4.1 mol dm^{-3}), followed two minutes later by 1.3cm^3 LiBu solution (1.57×10^{-1}mol dm^{-3}). The solvent used was dry toluene, and according to Gregory this system should have produced very high activity towards the ring-opening polymerisation of cyclopentene. Although the colour changes were comparable, little increase in viscosity was observed, and only a small amount of precipitate formed on pouring the polymerisate into methanol. The dry product was weighed after each polymerisation and compared with other systems for a given reaction time of four hours.

Similar experiments were carried out using dry cyclohexane as solvent, and the studies were extended to a trimetallic catalyst system using $AlBr_3$ as a second cocatalyst.

Table 3.1 summarises some of the results obtained from these preliminary studies. Toluene appeared to inhibit the reaction and was replaced by dry cyclohexane in further experiments. This solvent was selected because it was much easier to dry than toluene, but as $AlBr_3$ is not soluble in cyclohexane, toluene was used as solvent for that particular cocatalyst.

Table 3.1 Typical Results from Preliminary Experiments

Catalyst System	Solvent	% Conversion
WCl/LiBu	Toluene	18
WCl_6/LiBu	Cyclohexane	48
WCl_6/LiBu/$AlBr_3$	Cyclohexane	62

Total dryness of the solvent was the main problem encountered throughout these studies. The blue complex developed over sodium and benzophenone was a good indication of the dryness (wet solvents were green or colourless), but confirmation came from colour changes during actual polymerisation reaction. If any component in the system was not completely free from moisture, the brown productive system would turn blue and be non-productive.

3.3 DILATOMETRIC STUDIES OF THE RING-OPENING POLYMERISATION OF CYCLOPENTENE USING WCl_6/LiBu

A series of dilatometric experiments was carried out as described in Section 2.5.1

3.3.1 Determination of Optimum Catalyst/Cocatalyst Ratio

In a typical polymerisation reaction, 1.4cm^3 WCl_6 solution (4.55×10^{-2} mol dm^{-3}) was added to 25cm^3 cyclopentene (2.52 mol dm^{-3}), followed by 0.8cm^3 LiBu (7.67×10^{-1} mol dm^{-3}). In each experiment the interval between catalyst and cocatalyst additions was two minutes. Because volumes of catalyst, or more particularly cocatalyst solutions might vary over a series of experiments, total volume of the polymerisation solution was maintained constant by adding a predetermined volume of dry cyclohexane to the monomer solution prior to adding the catalyst and cocatalyst solutions.

A red/brown solution resulted from the addition of WCl_6 (dark red) to the monomer solution, producing a brown polymerisate on addition of LiBu. The reacting solution was observed to increase in viscosity with time.

Figs. 3.1 and 3.2 show a series of polymerisation conversion time curves (for decrease in meniscus height) obtained for various WCl_6 and LiBu concentrations at constant cyclopentene concentrations.

As a finite time was taken to fill the dilatometer it was not possible to accurately measure the rate of polymerisation at very short reaction times. The meniscus height was measured two minutes after polymerisation commenced, then at regular intervals, thus enabling the required time curves to be drawn.

Fig. 3.1 Dilatometric Polymerisation Curves of Cyclopentene at various Catalyst to Monomer Ratios

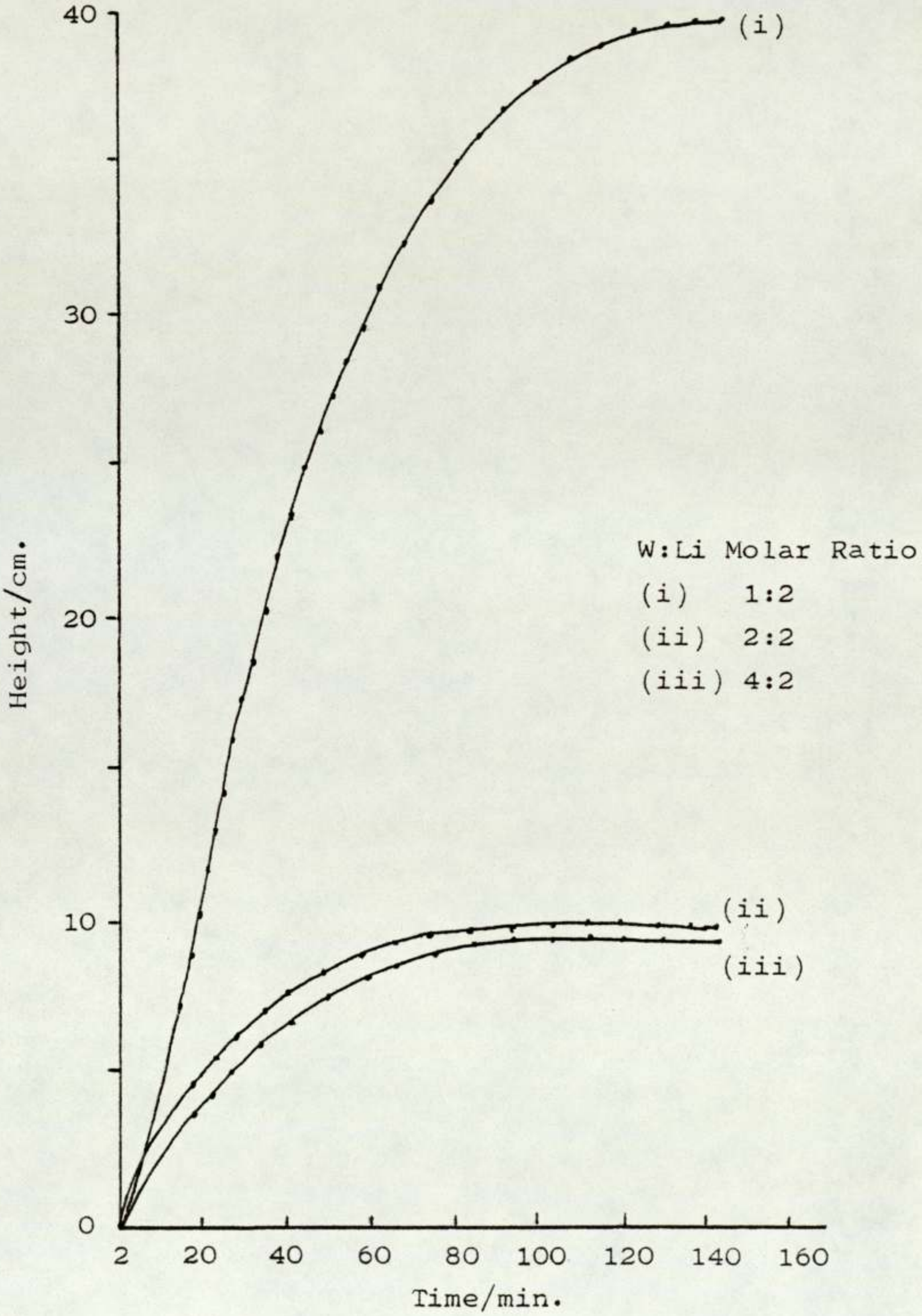
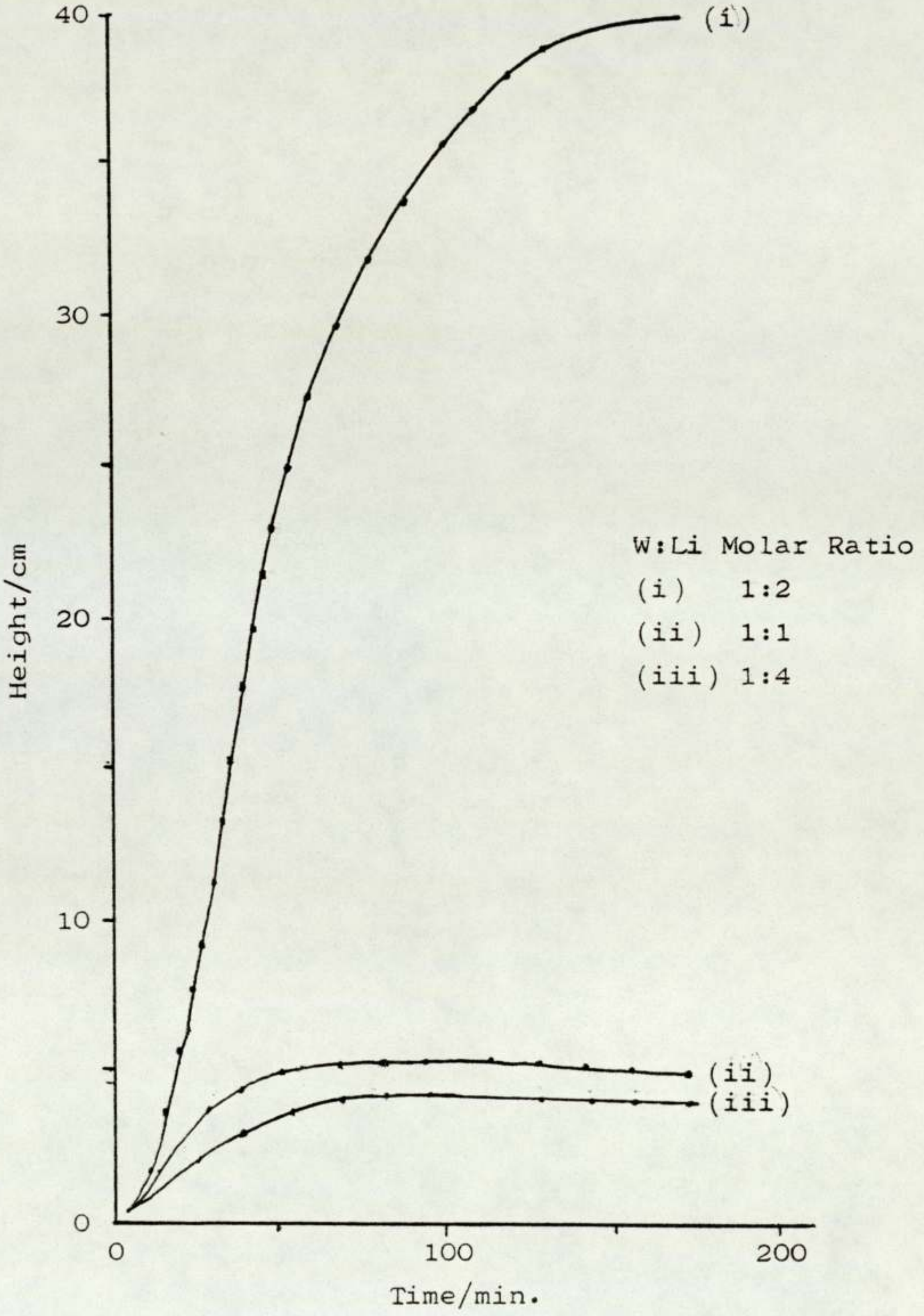


Fig. 3.2 Dilatometric Polymerisation Curves of Cyclopentene at various Cocatalyst to Monomer Ratios

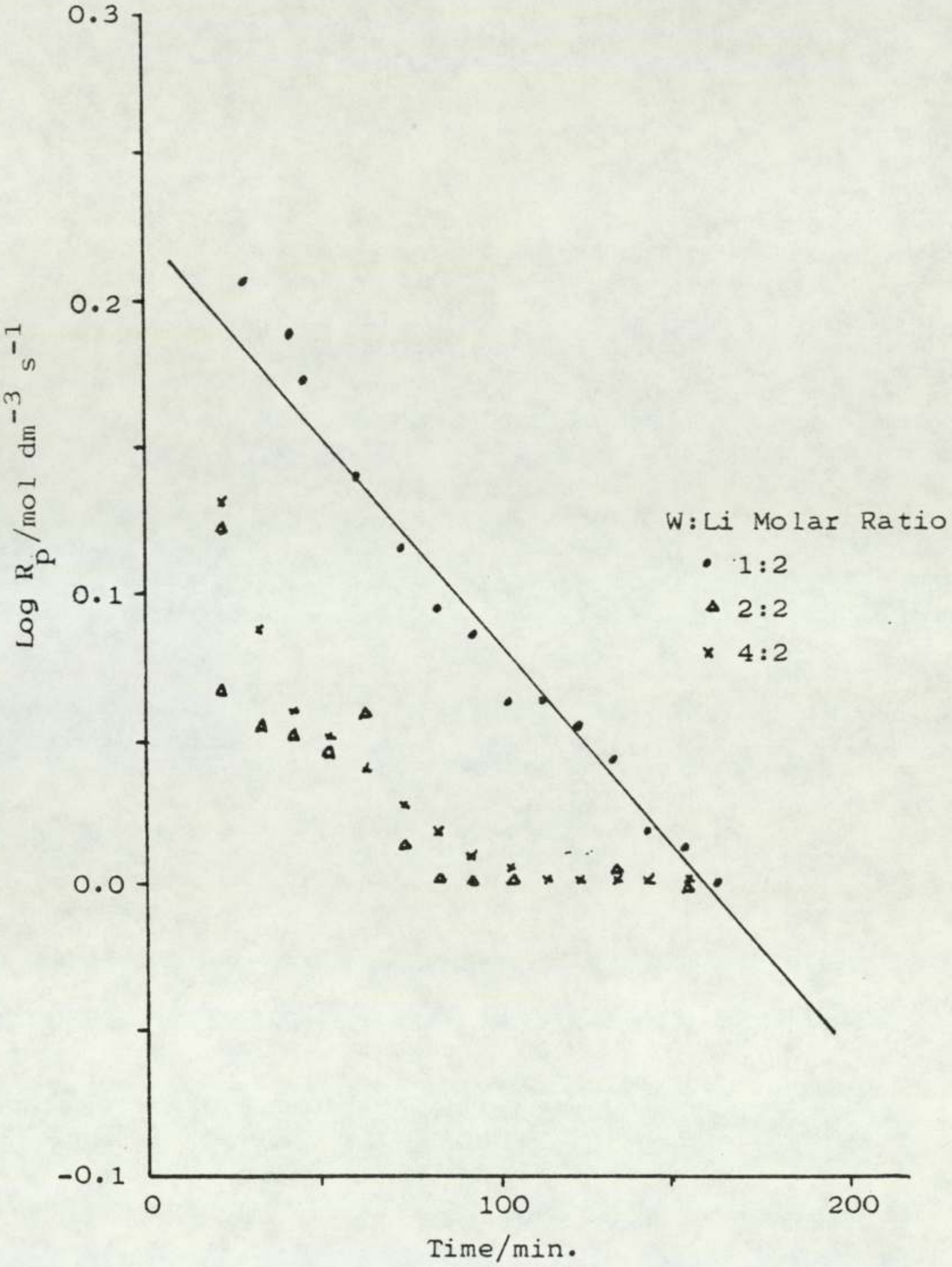


An analysis was made of the polymerisation curves shown in figs. 3.1 and 3.2. Estimates were made of the rates of polymerisation, as a function of time for each at intervals of ten minutes. The system showing optimum activity was characterised by a linear dependence of log R_p on time, as shown in fig. 3.3, but other systems had no simple mathematical relationship.

It is reasonable to assume that the monomer concentration changes significantly over the reaction period, and that this decrease is responsible for the decrease in rate, as the concentration of active species remains constant. When the W/Li ratio is above the optimum 1:2, some kind of deactivation of the active species appears to take place; whereas at lower molar ratios the concentration of active species is presumably lower. In each case the overall rate of polymerisation would be expected to be less than that shown in optimum conditions of catalyst/cocatalyst ratio, and this was observed in practice.

The overall results from this series of experiments are in agreement with those given by Wang and Menapace(64) and Gregory(147), although all systems appeared to be far more active in comparison with those quoted by Gregory.

Fig. 3.3 Dependence of Log R_p^- on Time for Polymerisation of Cyclopentene at various Catalyst to Monomer Ratios



3.4 DILATOMETRIC STUDIES OF RING-OPENING POLYMERISATION OF CYCLOPENTENE - USING WCl_6/LiBu/$AlBr_3$

3.4.1 Dependence of Catalyst Addition Order on Overall Activity of the System

Polymerisation was carried out, in the apparatus shown in fig. 2.8, using a 1000:1:2:2 molar ratio system of cyclopentene/WCl_6/LiBu/$AlBr_3$. In the first reaction (A) 2.6cm^3 WCl_6 (3.55×10^{-2} mol dm^{-3}) was added to 25cm^3 cyclopentene solution (3.68 mol dm^{-3}), followed by 0.3cm^3 LiBu (6.17×10^{-1} mol dm^{-3}) and then 0.6cm^3 $AlBr_3$ solution (3.01×10^{-2} mol dm^{-3}) at two minute intervals. The solvent used was cyclohexane, except in the solution of $AlBr_3$ when toluene was used. 3cm^3 samples of the polymerisate were removed from the system at the predetermined intervals described in Section 2.5.2, and precipitated in methanol. After drying the products were weighed.

The reaction was repeated, changing the order of addition of cocatalyst components - (B).

Table 3.2 shows percentage conversion of monomer with varying reaction times for both systems. The results indicate that conversion of monomer to polymer in ring-opening polymerisation of cyclopentene is not greatly affected by the order of cocatalyst component addition. For the initial rate however, the system appears to have greater activity when LiBu is added to WCl_6 prior to $AlBr_3$.

Table 3.2 Percentage Conversion of Monomer to Polymer with Order of Catalyst Addition

Time of Reaction (mins)	% Conv. (A)	% Conv. (B)
10	29	18
30	47	32
100	61	45
140	61	60
180	61	62
210	60	61
240	62	64

For both polymerisation reactions similar colour changes were observed for addition of WCl_6 to the monomer followed by the cocatalyst. This may imply that in each case the same active species were produced, irrespective of the order of catalyst to WCl_6.

3.4.2 Determination of Optimum Catalyst/Cocatalyst Ratio

Polymerisation reactions were carried out as outlined in Section 2.5.1. Cyclohexane was used as the solvent and the sequence of addition of catalyst and cocatalyst to the monomer was WCl_6, LiBu and finally $AlBr_3$. There was a time delay of two minutes between additions of WCl_6 and LiBu, and a further two minutes before $AlBr_3$ was added. In this series of experiments the concentrations of monomer and WCl_6 were maintained constant at a ratio of 1000:1, while the concentrations of LiBu and $AlBr_3$ were varied, so that W/Li and W/Al molar ratios could be changed independently.

In a typical polymerisation $1.4cm^3$ WCl_6 ($5.61 \times 10^{-1} mol\,dm^{-3}$) was added to $25cm^3$ cyclopentene solution ($3.14 mol\,dm^{-3}$) with $0.8cm^3$ dry cyclohexane then added, followed by $0.9cm^3$ LiBu ($8.72 \times 10^{-2} mol\,dm^{-3}$) and $1.2cm^3$ $AlBr_3$ solution (2.62×10^{-1} $mol\,dm^{-3}$). Figs. 3.4 and 3.5 show conversion-time dilatometry curves for the polymerisation reactions when varying the concentrations of LiBu and $AlBr_3$ respectively. The curves show similar rate patterns to the analogous bimetallic systems (W/Li), but much higher activity is generally observed.

The results indicate that the ratio of catalyst to cocatalyst components is critical with respect to the resultant rate of ring-opening polymerisation. An increase above the optimum concentrations of LiBu or $AlBr_3$ results in an increase in

Fig. 3.4 Dilatometric Polymerisation Curves of Cyclopentene at various Cocatalyst (LiBu) to Monomer Ratios

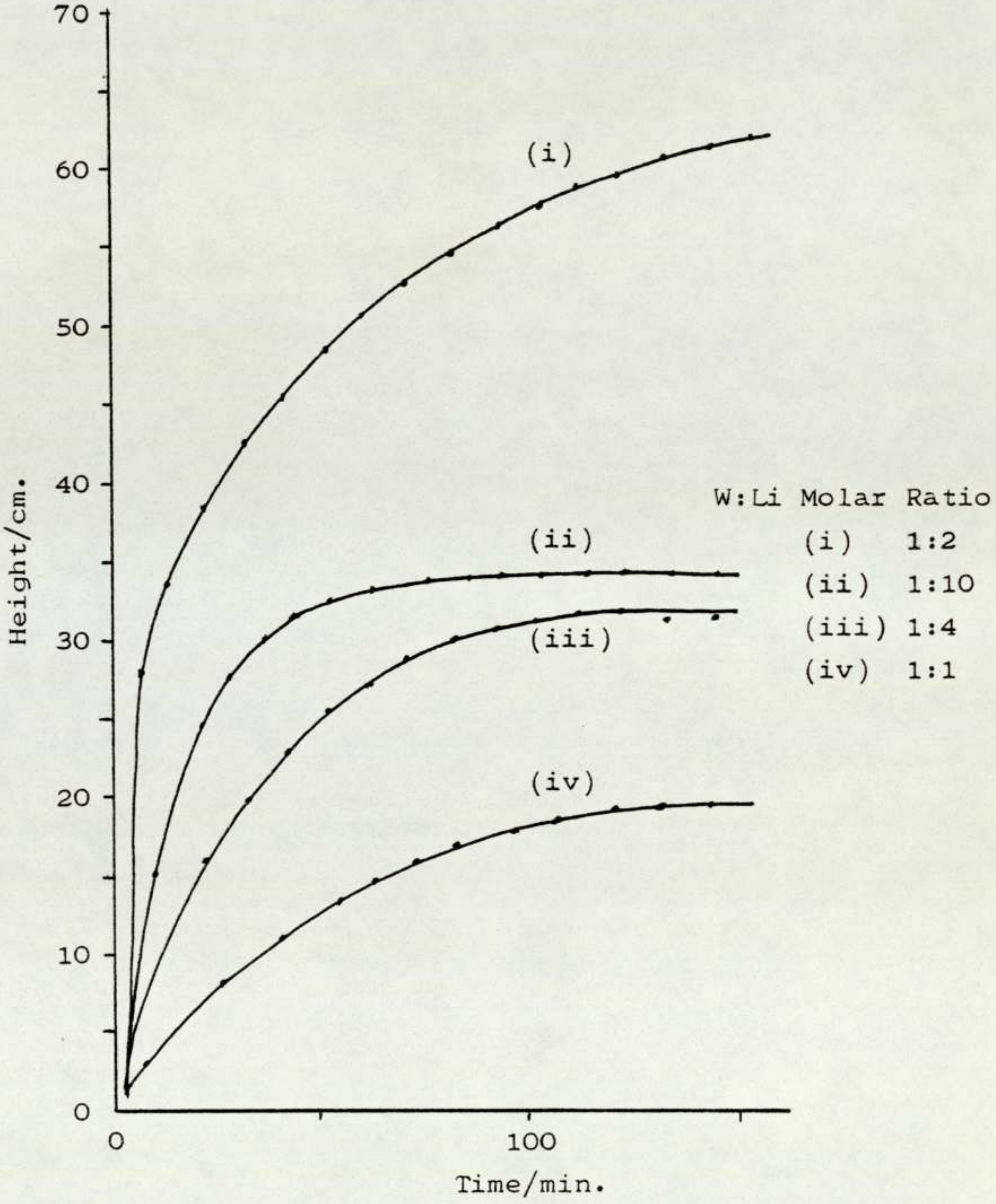
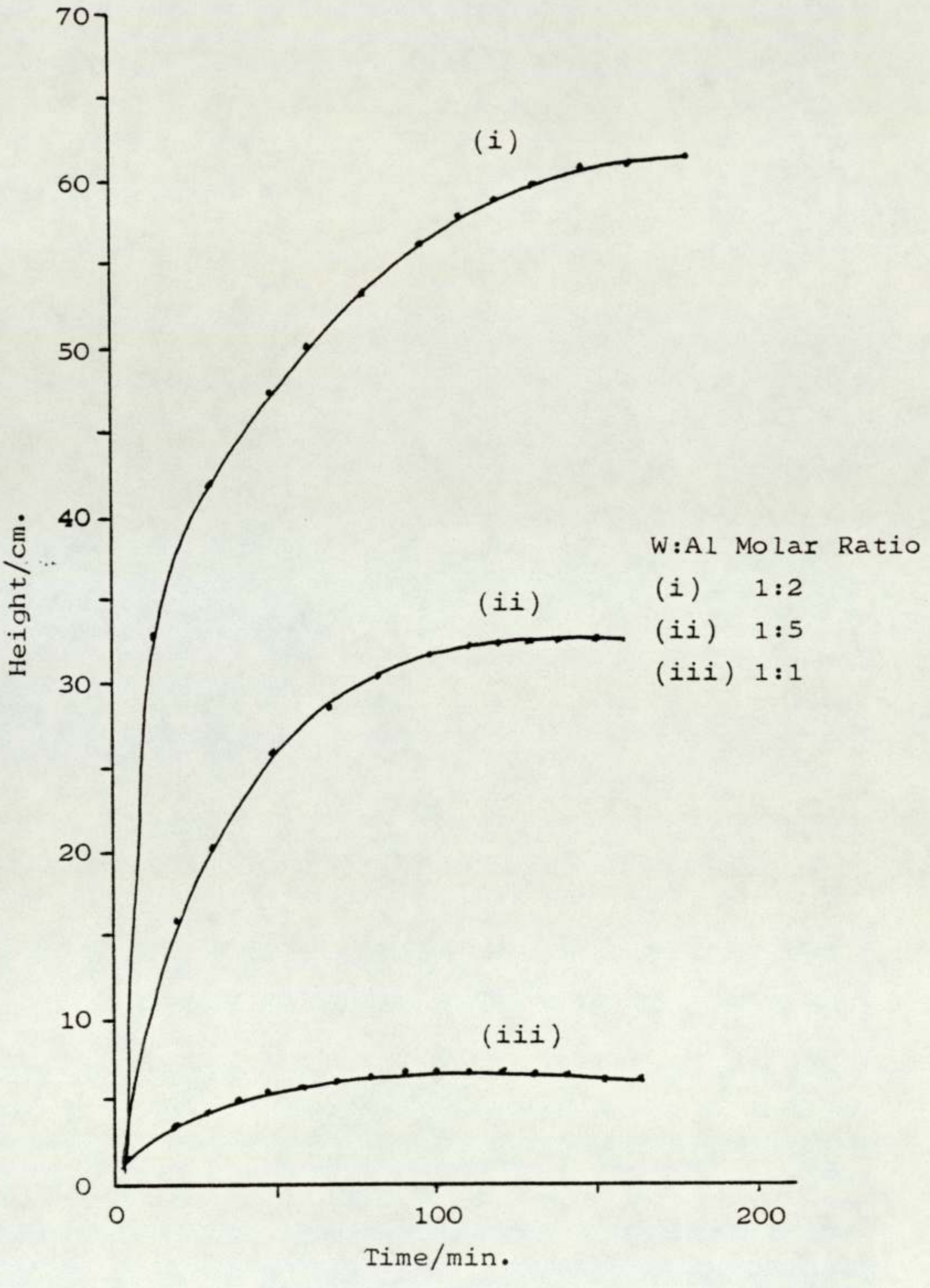


Fig. 3.5 Dilatometric Polymerisation Curves of Cyclopentene at various Cocatalyst ($AlBr_3$) to Monomer Ratios



in the rate of destruction of active centres. Concentrations of cocatalysts below the optimum suggest that the initial production rate of active centres is lower than for the optimum system, and hence the rate of polymerisation is similarly affected.

Figs. 3.6 and 3.7 show the dependence of log R_p on time at various W/Al and W/Li ratios respectively. From fig. 3.7 it can be seen that decay of the rates of polymerisation of cyclopentene for the initial one hundred minutes appears to be similar for low W/Li molar ratios (1:1, 1:2 and 1:4), which possibly indicates the formation of some common active species. But at a higher ratio, W/Li = 1:10, the rate decreases rapidly. After one hundred minutes the rates show a pronounced change when the molar ratio differs from the optimum. From fig. 3.6 it can be seen that variations of $AlBr_3$ concentration above (e.g. W/Al = 1:5) or below (e.g. W/Al = 1:1) the optimum ratio 1:2, appear to produce a non-linear dependence of log R_p on time. This suggests that the rate of decay in such cases is not first order. It would therefore seem that the aluminium compound has a role to play in determining the nature of the termination reaction.

3.4.3 Determination of Sequential Addition Optimum Time of the Catalyst Components

The optimum ageing time for ring-opening polymerisation of cyclopentene catalysed by the bimetallic system WCl_6/LiBu is

Fig. 3.6 Dependence of Log R_p on Time, for Polymerisation of Cyclopentene at various $AlBr_3$ Cocatalyst:Monomer Ratios

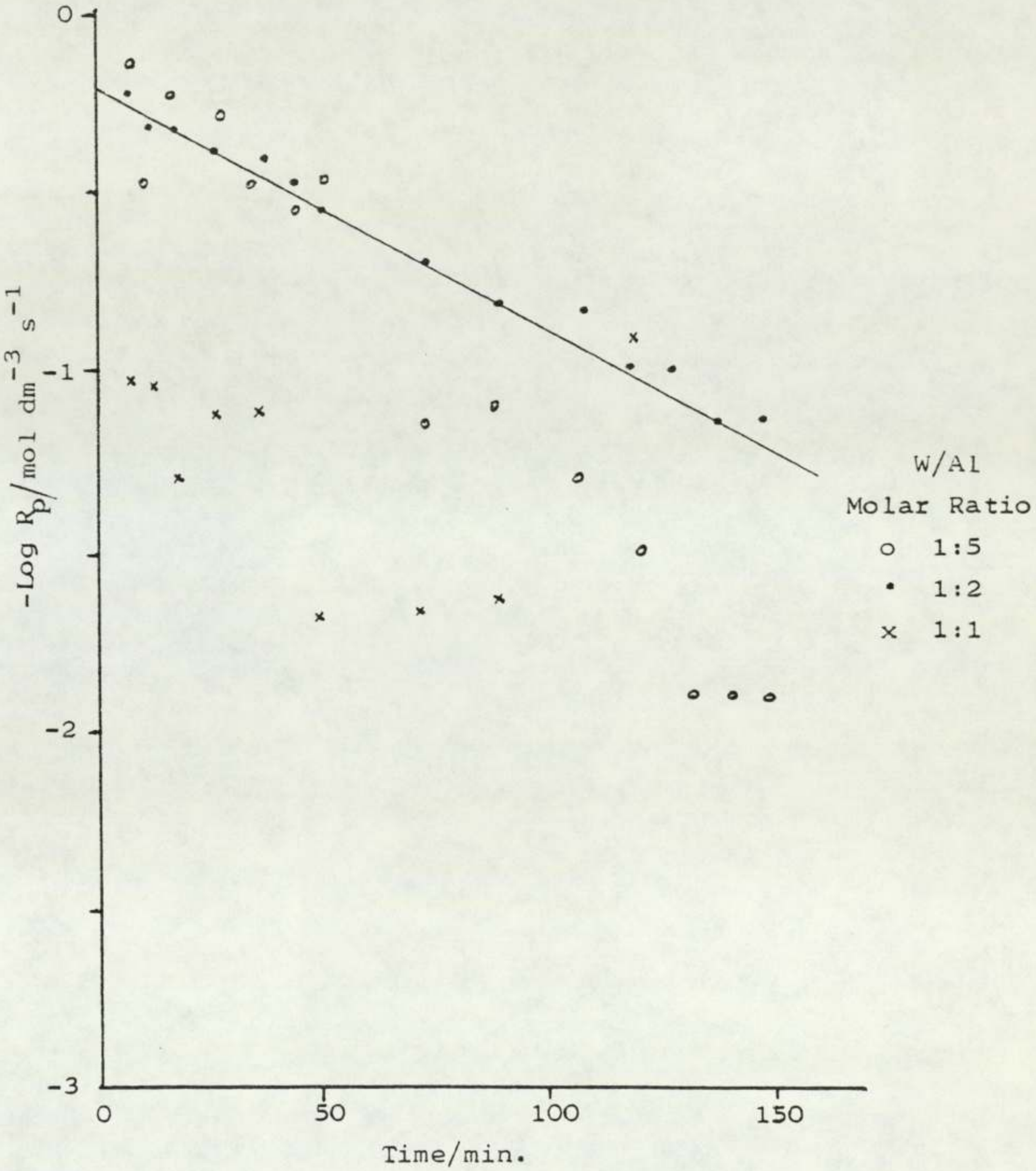
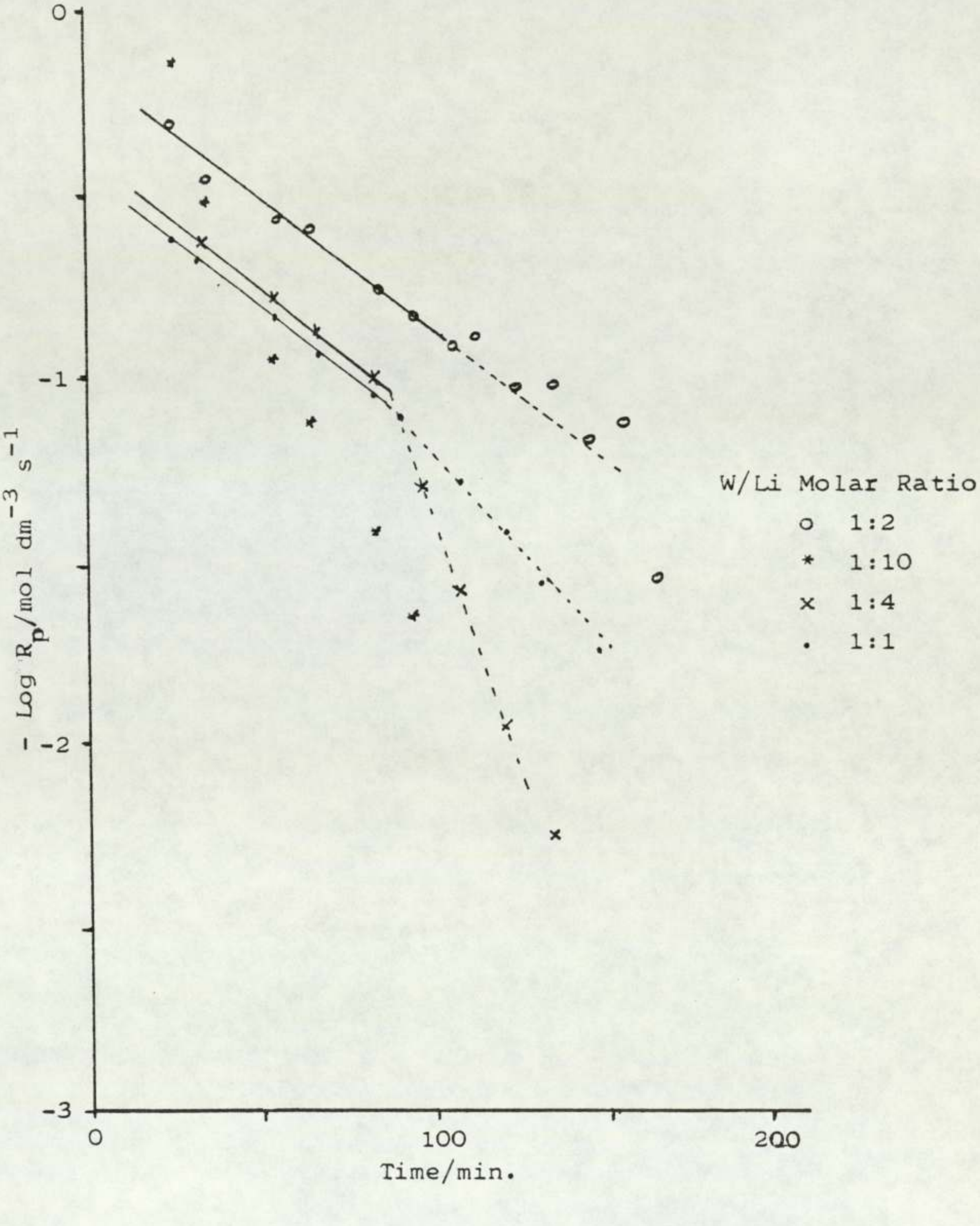


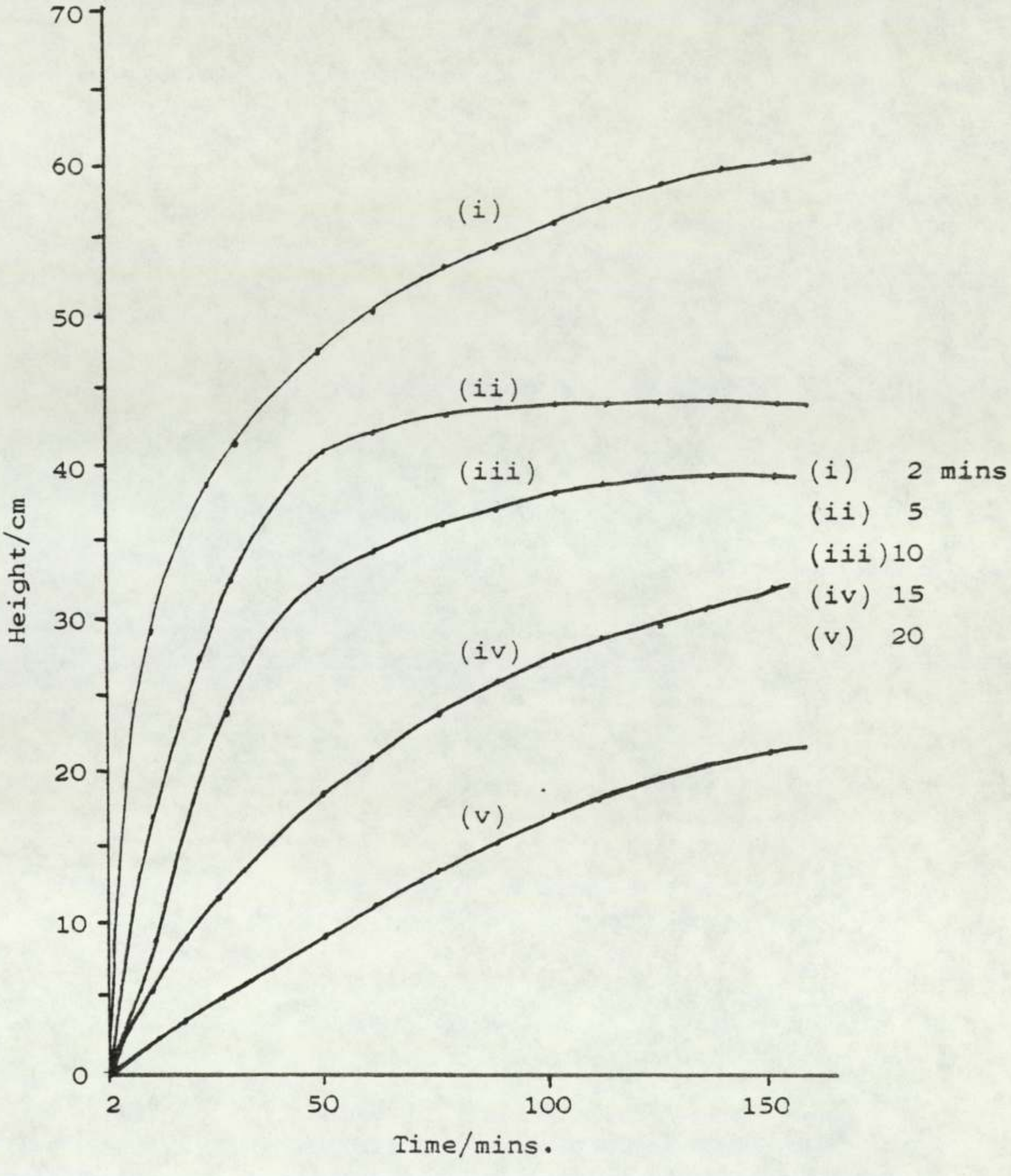
Fig. 3.7 Dependence of Log Rp on Time for Polymerisation of Cyclopentene at various Cocatalyst (LiBu) to Monomer Ratios



two minutes. Amass and Tuck$^{(14)}$ reported similar results using the system $WCl_6/Al(iBu)_3$. It therefore seems feasible to assume the catalyst and monomer react in some way over this period to produce an active species, which may then start to deactivate in the absence of cocatalyst. From the results shown in Section 3.4.1 it may be concluded that the presence of the aluminium compound further activates the polymerisation reaction, possibly by forming a different active species to that formed by the bimetallic system based on WCl_6 and LiBu. It must therefore be assumed that an optimum ageing time also exists for addition of a third component. This was studied dilatometrically, as described in Section 2.5.1, using similar volumes of reactants as in Section 3.4.2, with the optimum catalyst/cocatalyst ratio of 1:2:2. Ageing times used between additions of $AlBr_3$ to the remainder of the reactants were two, five, ten, fifteen and twenty minutes.

Fig. 3.8 shows dilatometer curves for this series of experiments and suggests an optimum ageing time of two minutes. The overall activity decreases with increased ageing time, in particular with long ageing times such as fifteen and twenty minutes. The intermediate curves (five and ten minute ageing times) show a rapid decrease in rate of polymerisation after similar initial rates. The difficulty encountered in the course of these studies was due to the presence of WCl_6 and LiBu as catalyst components prior to

Fig. 3.8 Dependence of Polymerisation of Cyclopentene on Ageing Time of Catalyst Components Sequential Addition



addition of $AlBr_3$, it being known that the concentration of active species formed from these compounds, and hence polymerisation activity, change with time.

One possible explanation for the observations is that $AlBr_3$ further activates the species responsible for WCl_6/LiBu polymerisation in some way, and the instantaneous concentration of the latter species will depend on the $AlBr_3$ addition time, thus determining the initial rate of polymerisation.

3.4.4 Polymerisation Studies of Premixed Catalyst Systems

Premixing of the catalysts is known to affect both the percentage conversion of the starting olefin and the selectivity in metathesis reactions. Wang and Menapace(81) observed that for metathesis of 2-pentene using WCl_6/LiBu/$AlCl_3$($AlBr_3$), the selectivity was increased greatly by premixing catalyst components WCl_6 and LiBu before adding to the monomer. Gregory(147) extended these studies to the ring-opening polymerisation of cyclopentene using a WCl_6/LiBu catalyst system, proving that as in sequential addition experiments optimum activity resulted from a W/Li ratio of 1:2. Little difference in activity was apparent between the premixed and unmixed systems, thus allowing the two systems to be directly compared and indicating that the same species is reponsible for initiation of the ring-opening polymerisation of cyclopentene.

In the course of these studies the effect of premixing LiBu and $AlBr_3$ was investigated.

3.4.4.i Determination of Optimum Catalyst/Cocatalyst Molar Ratio

In a typical polymerisation reaction $1.8cm^3$ WCl_6 (2.61×10^{-2} mol dm^{-3}) was added to $25cm^3$ cyclopentene solution (2.36 mol dm^{-3}), followed two minutes later by a premixed solution of $2.4cm^3$ LiBu (5.00×10^{-2}mol dm^{-3}) and $0.6cm^3$ $AlBr_3$ solution (2.21×10^{-1}mol dm^{-3}) after two minutes ageing time. Throughout the series of experiments the monomer/W ratio was maintained constant at 1000:1, while the concentrations of the cocatalyst components employed were varied to produce a W/Li/Al ratio of 1:1(2,4,10):1(2,4,10). The solvent used was cyclohexane. Fig. 3.9 and fig. 3.10 show the curves obtained from a series of dilatometry experiments on the polymerisation of cyclopentene, catalysed by the premixed catalyst sytem WCl_6/LiBu+ $AlBr_3$ for various concentrations of LiBu and $AlBr_3$ respectively.

From the curves it can be seen that for all ratios of catalyst components used the system is active for the polymerisation of cyclopentene. Generally however, the effect of premixing the two cocatalysts brought about a slight decrease in activity, compared to the analogous system in which the catalyst components were added sequentially. This observation might be explained by a reaction occurring between the two

Fig. 3.9 Dilatometric Polymerisation Curves of Cyclopentene at various Cocatalyst (LiBu) to Monomer Ratios for a Premixed Catalyst System

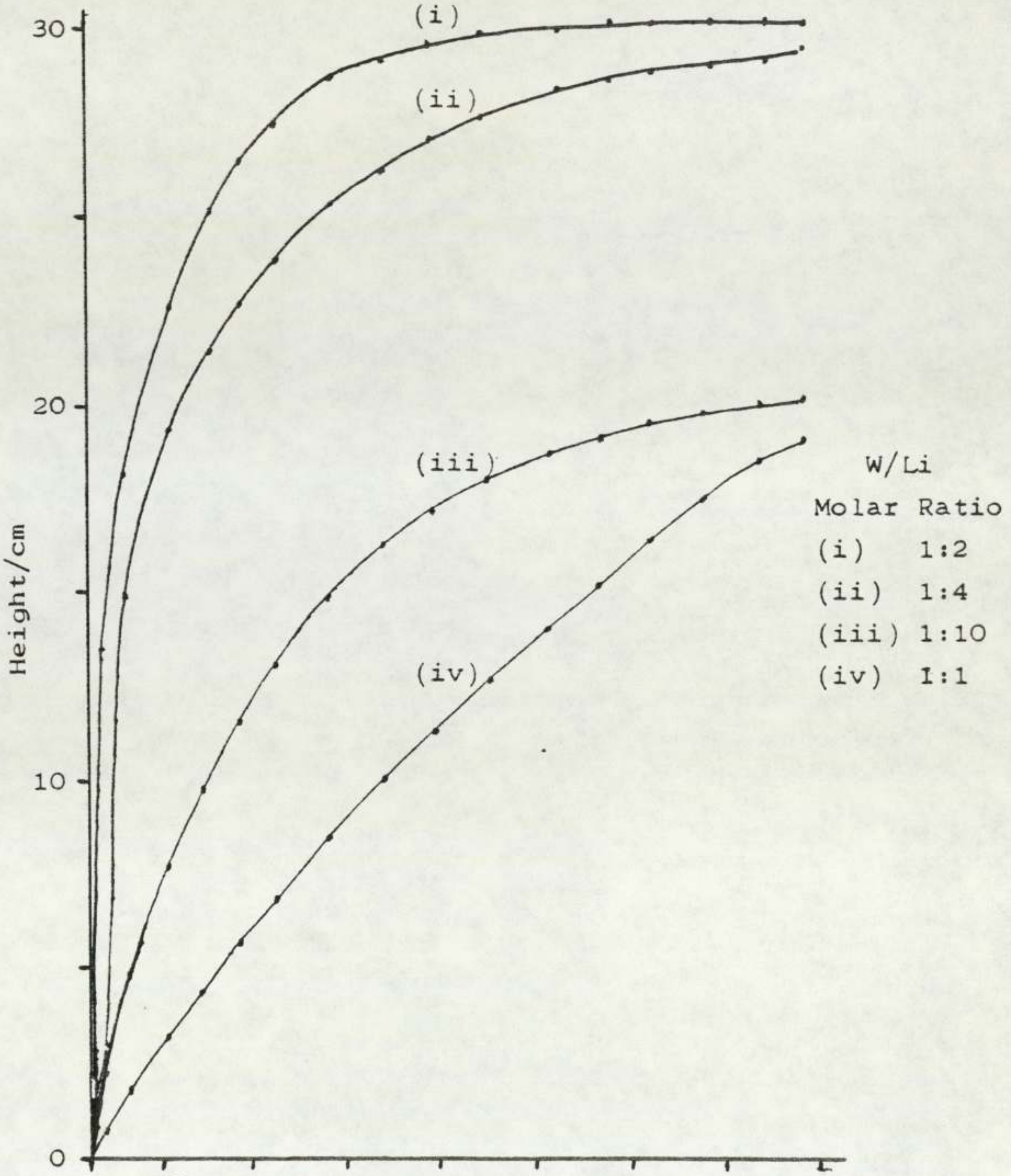
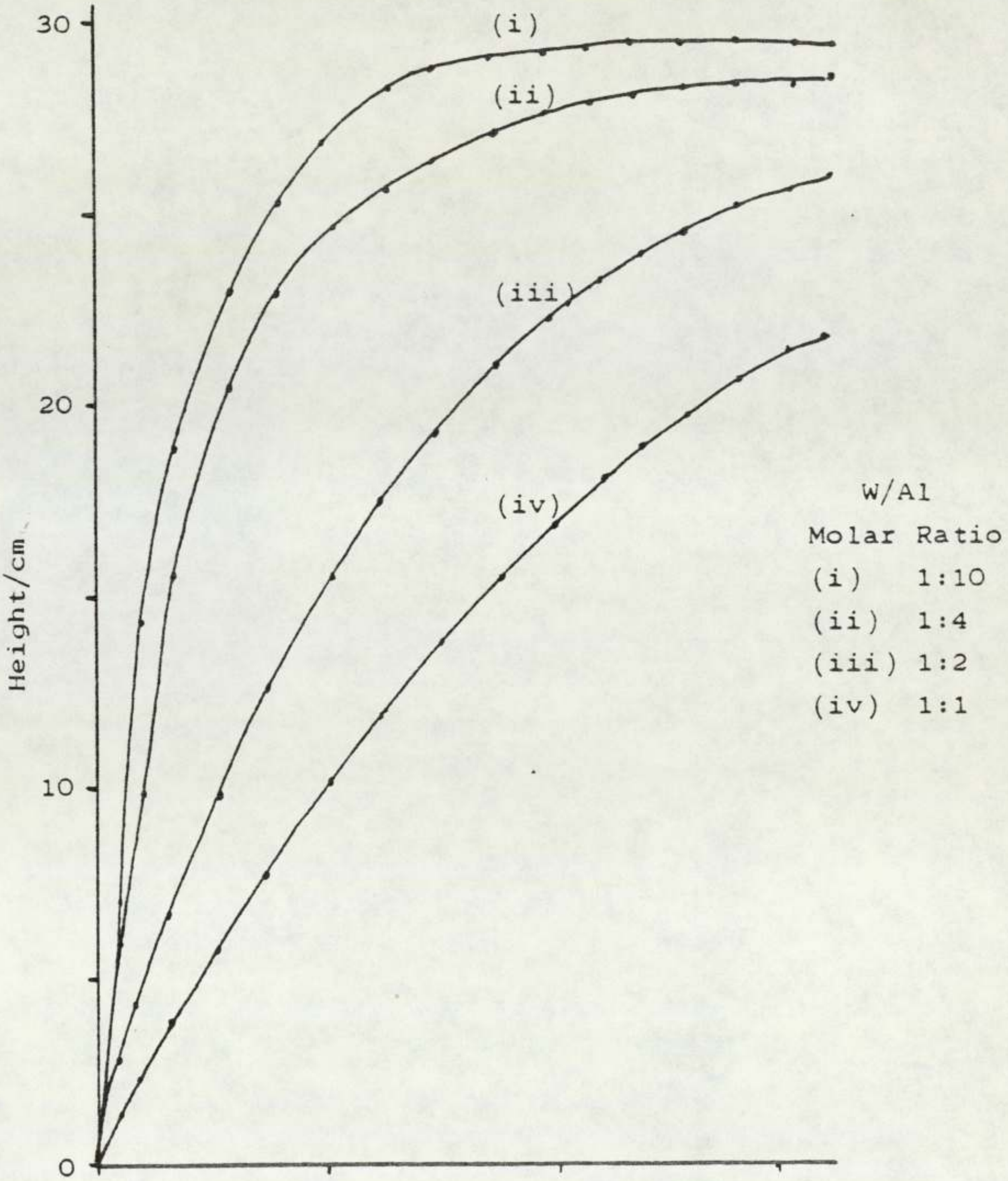


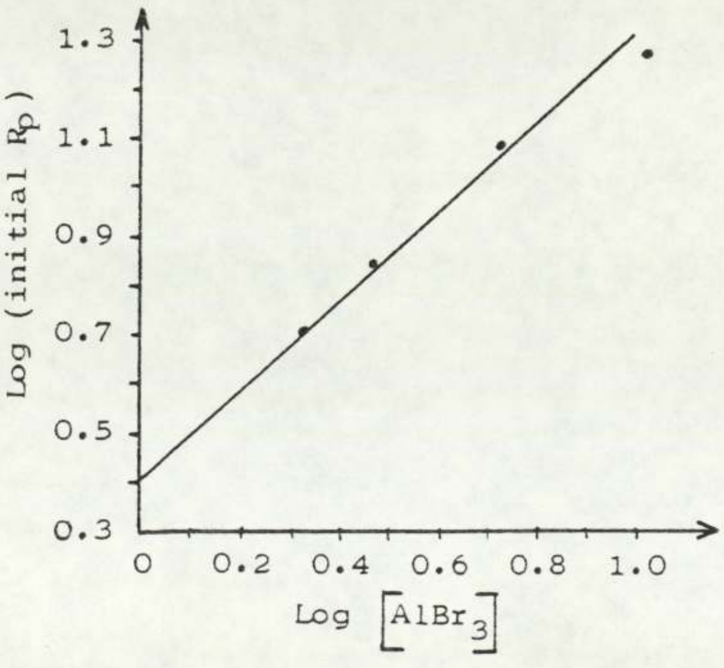
Fig. 3.10 Dilatometric Polymerisation Curves of Cyclopentene at various Cocatalyst ($AlBr_3$) to Monomer Ratios for a Premixed Catalyst System



cocatalysts to form a compound which has less tendency to complex with tungsten compound rather than LiBu alone. Such premixed systems do show a marked change in overall activity and dependence on time, particularly at lower concentrations of cocatalyst components, while for higher cocatalyst concentrations the rates do not appear to fall off so rapidly.

The optimum W:Li ratio was again found to be 1:2 and the rate of polymerisation of cyclopentene was observed to increase with concentration of $AlBr_3$. The former result was anticipated from previous studies, but in the case of dependence on concentration of $AlBr_3$ a linear plot of log (initial R_p) against log $[AlBr_3]$ is obtained with a slope of 1. The order of reaction with respect to the concentration of $AlBr_3$ is therefore 1, and the reaction scheme should take this into account. Fig. 3.11 shows the relationship.

Fig. 3.11 First Order Dependence of $AlBr_3$ on Premixed Cyclopentene Polymerisation



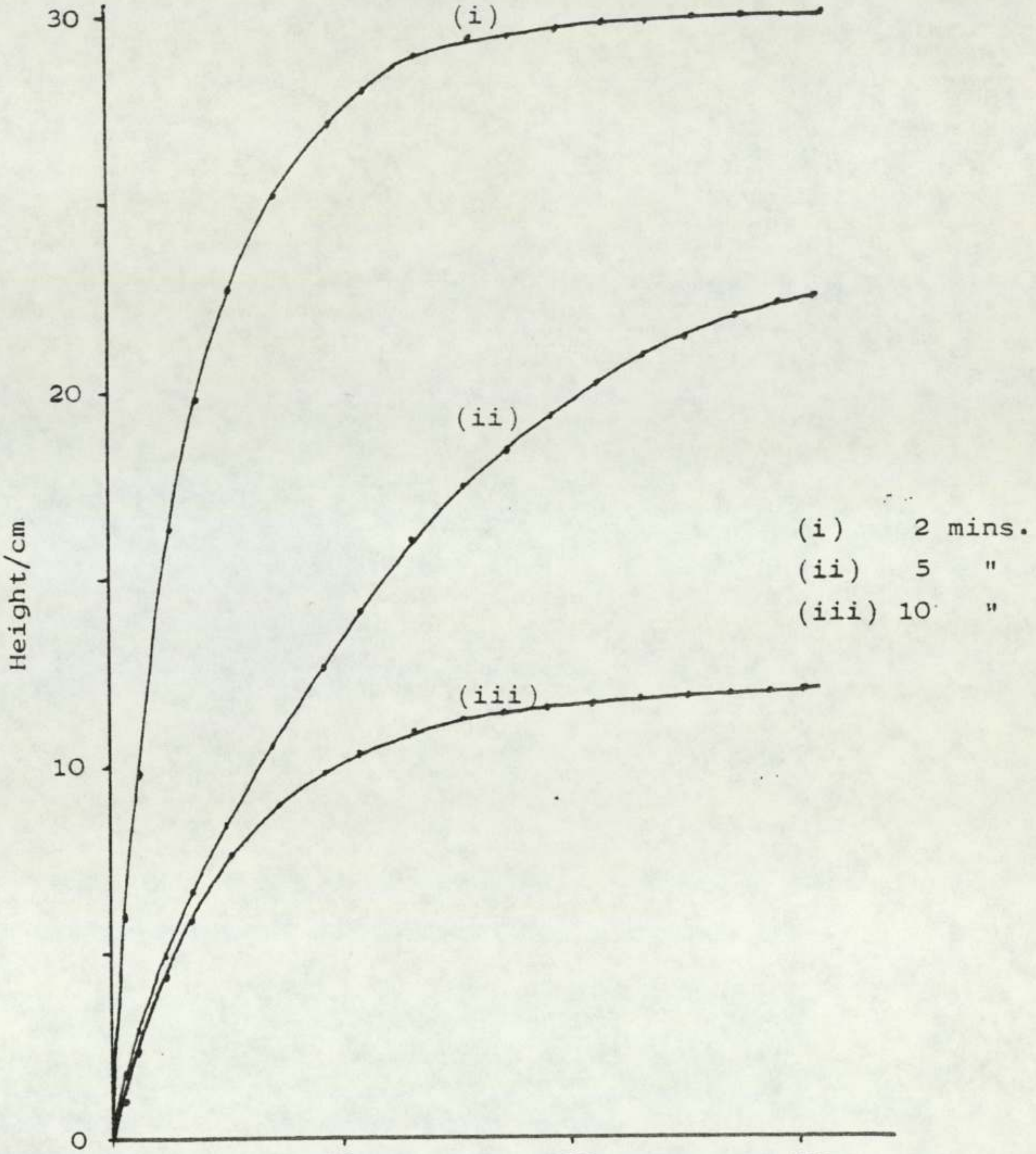
3.4.4.ii Optimum Premix Ageing Time

As with an unmixed catalyst system, the ageing time of the catalyst/monomer and catalyst/cocatalyst are known to affect the rate of polymerisation of cyclopentene; the ageing time of an analogous premixed catalyst system may also influence the rate of polymerisation. This has led to a study of the effect of varying time of reaction between LiBu and $AlBr_3$ on the rate of polymerisation of cyclopentene for the optimum momomer/catalyst ratio, i.e. 1000:1:2:10

The reactions were carried out dilatometrically, as described in Section 2.5.1. The cocatalyst was prepared by allowing $0.2cm^3$ LiBu ($7.91 \times 10^{-1}mol\,dm^{-3}$) to mix with $1.5cm^3$ $AlBr_3$ solution ($2.21 \times 10^{-1}mol\,dm^{-3}$) in a nitrogen-filled syringe for a given period. This was added to $25cm^3$ monomer solution ($2.73\ mol\,dm^{-3}$), containing $1.5cm^3$ WCl_6 solution (4.55×10^{-2} $mol\,dm^{-3}$) which had been added two minutes previously. The premix ageing times studied were two, five and ten minutes and the effect of premix ageing time on the rate of cyclopentene polymerisation is shown in fig. 3.12.

The catalyst activity appeared to decay with the period of premixing LiBu and $AlBr_3$. Fast initial rates were observed in all the sytems, but the reaction seemed to terminate rapidly with aged cocatalyst.

Fig. 3.12 Dependence of Polymerisation of Cyclopentene on Ageing Time of Premixed Cocatalysts Additions



3.4.5 Summary of Cyclopentene Polymerisation by the Catalyst System $WCl_6/LiBu/AlBr_3$

The order of addition of the cocatalysts, LiBu and $AlBr_3$, to the monomer/WCl_6 solution did not appear to affect the overall activity of the polymerising system. The overall rate however, was greatly affected by the molar ratio of the catalyst components, with maximum activity observed for a 1:2 molar ratio of WCl_6/LiBu when the catalysts were added sequentially; similarly when the two cocatalysts were premixed. For the premixed system the rate of polymerisation appeared to accelerate with increasing concentration of $AlBr_3$, but for sequential addition the most active system was produced with a 1:2:2 molar ratio of catalyst to cocatalysts. The ageing time between catalyst addition was also crucial, with polymerisation appearing to lessen in activity with increased ageing time between each addition, irrespective of whether the catalysts were premixed or added to the monomer sequentially.

3.5 DILATOMETRIC STUDIES OF RING-OPENING POLYMERISATION OF CYCLOPENTENE, CATALYSED BY $WCl_6/LiBu/SnCl_4$

Since $AlBr_3$, as a second cocatalyst, increased the rate of polymerisation of cyclopentene when compared with the corresponding bimetallic system, it would be expected that other Lewis acids might have a similar effect. Comparisons may be made of the activities of such systems, which could provide an insight to the requirements of the secondary co-catalyst in its role as an activator for ring-opening polymerisation.

The effect of $SnCl_4$ as a third catalyst component for ring-opening polymerisation of cyclopentene has been studied, the results being directly compared with the corresponding $AlBr_3$ trimetallic system.

3.5.1 Determination of Optimum Catalyst/Cocatalyst Ratio

All the reactions were carried out in a dilatometer, as described in Section 2.5.1. A monomer/WCl_6 ratio of 1000:1 was maintained constant and the molar ratios of WCl_6/LiBu and WCl_6/$SnCl_4$ varied independently.

In a typical polymerisation, 3.1cm^3 WCl_6 (1.49×10^{-2}mol dm^{-3}) was added to 25cm^3 cyclopentene solution (3.15mol dm^{-3}) in bulb (A) of the dilatometer, followed by 1.2cm^3 LiBu (1.37×10^{-2}mol dm^{-3}) and 0.9cm^3 $SnCl_4$ (8.98×10^{-2}mol dm^{-3}), with an interval of two minutes between each addition. On addition of the colourless $SnCl_4$ solution to the brown solution of monomer/WCl_6/LiBu, a change to brown/green was observed. The solution remained brown in colour when $AlBr_3$ was added to a similar system, which indicates that if reactions of $SnCl_4$ and $AlBr_3$ are similar, the surrounding ligands and/or the oxidation state of the transition metal have changed.

Figs. 3.13 and 3.14 show dilatometer curves produced when LiBu and $SnCl_4$ concentrations were varied respectively. The $SnCl_4$ system showed a greater increase in viscosity with reaction than the corresponding $AlBr_3$ system, though according to the dilatometer curve the optimum W/Li molar ratio appeared to be 1:2. This may not be a true representation of concentration resulting from maximum activity, as the 1:1 system from the series became too viscous after eighty minutes for further readings to be taken. The system also showed a great sensitivity to the catalyst concentrations outside the W/Li/Sn molar ratio of 1:2:4, particularly with respect to a concentration of $SnCl_4$. The corresponding $AlBr_3$ system showed a higher tolerance to variation in the catalyst ratio, but for the optimum system (W/Li/Al = 1:2:2) activity was comparable to that of the $SnCl_4$ system (W/Li/Sn = 1:2:4), though in the former case the initial rate of polymerisation appeared to be slightly higher.

3.5.2 Determination of Optimum Time between Sequential Additions of Catalyst Components to the Monomer

Studies were carried out to determine the dependence of polymerisation rate on the time interval between additions of $SnCl_4$ and LiBu. The series of experiments was carried out using the most active catalyst ratio determined from Section 3.5.1. The time delay between additions of LiBu and $SnCl_4$ was varied between two and twenty minutes; fig. 3.15 shows the dilatometry curves resulting from the series

Fig. 3.13 Dilatometric Polymerisation Curves of Cyclopentene at various Cocatalyst (LiBu) to Catalyst Ratios

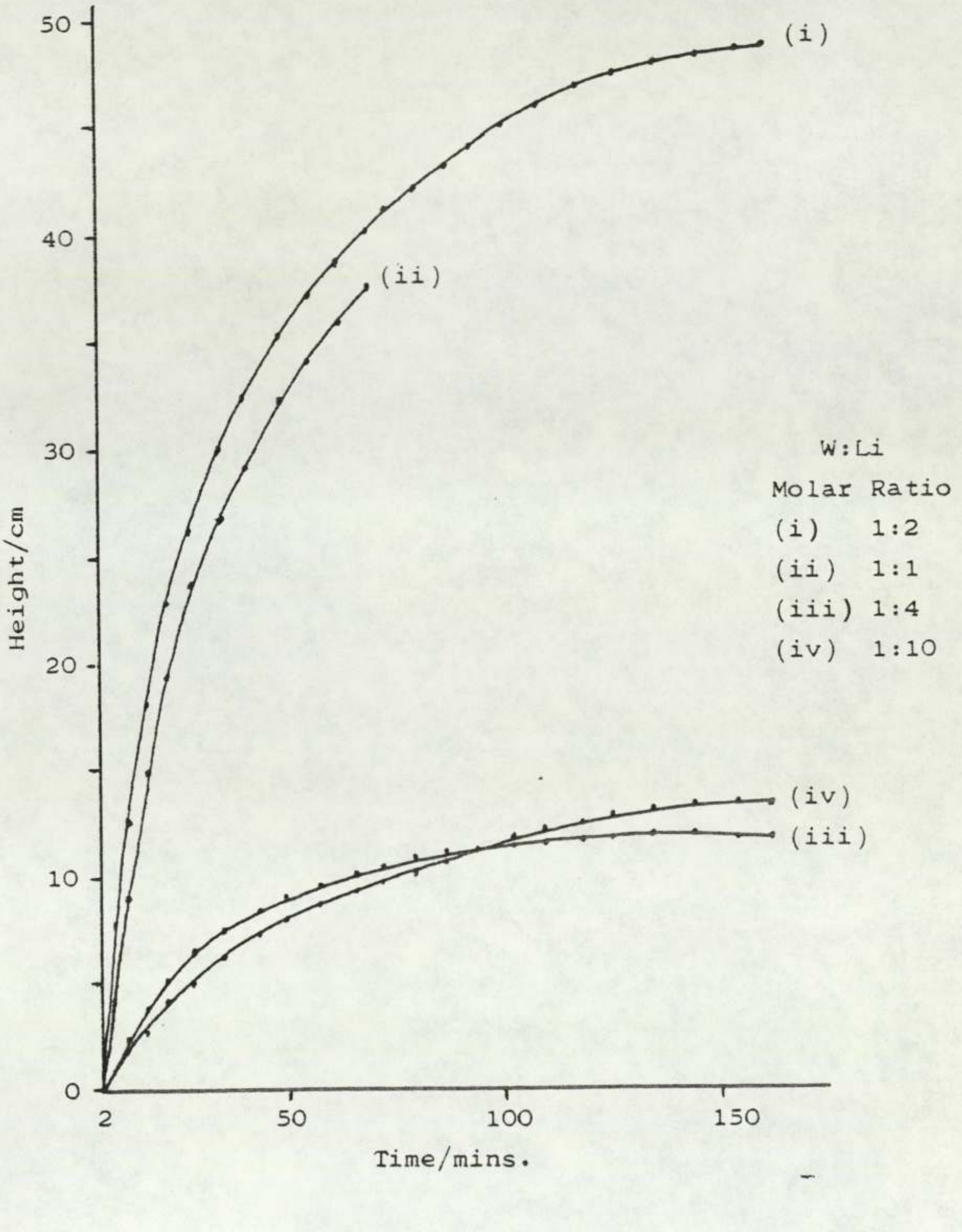


Fig. 3.14 Dilatometric Polymerisation Curves of Cyclopentene at various Cocatalyst ($SnCl_4$) to Catalyst Ratios

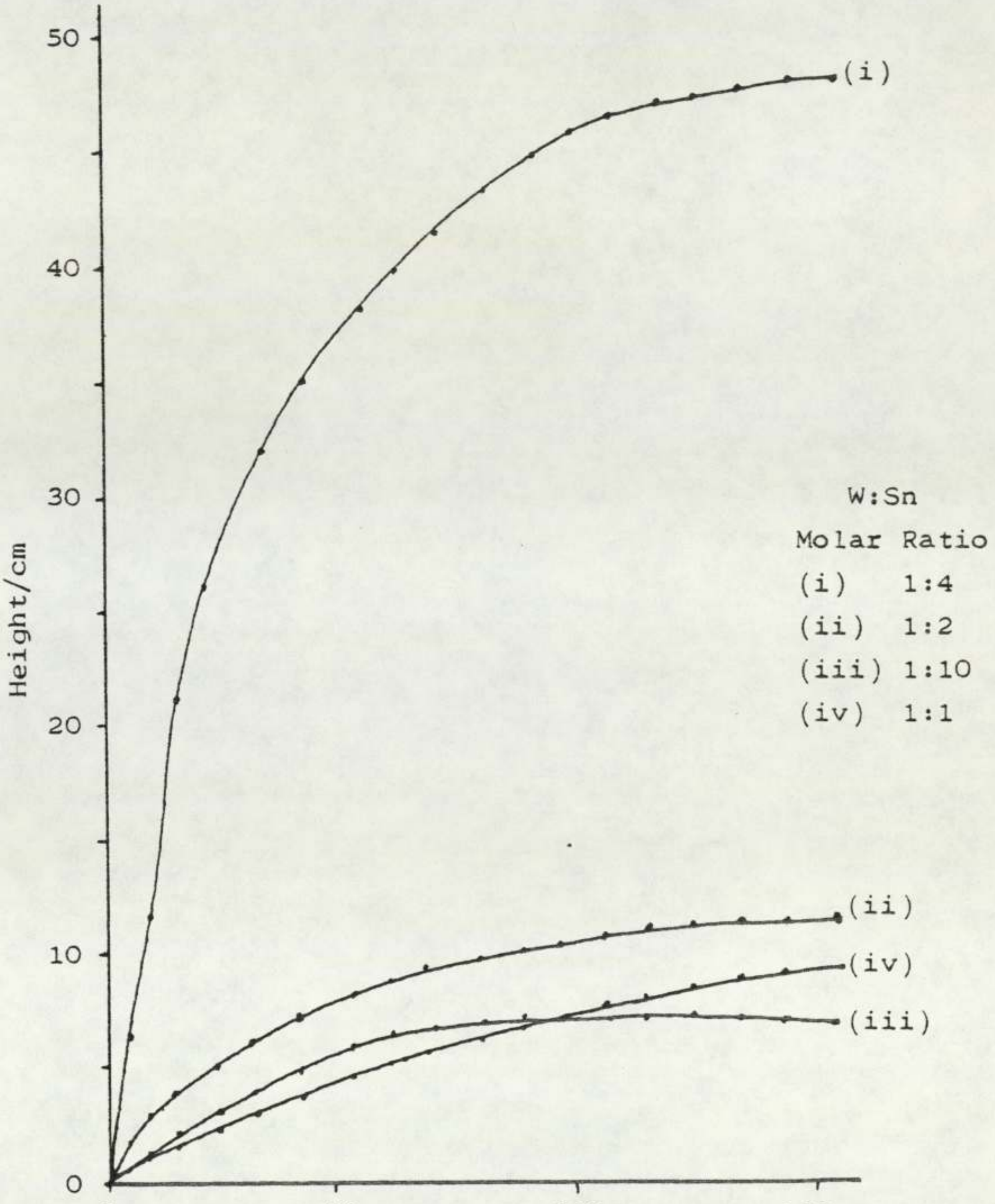
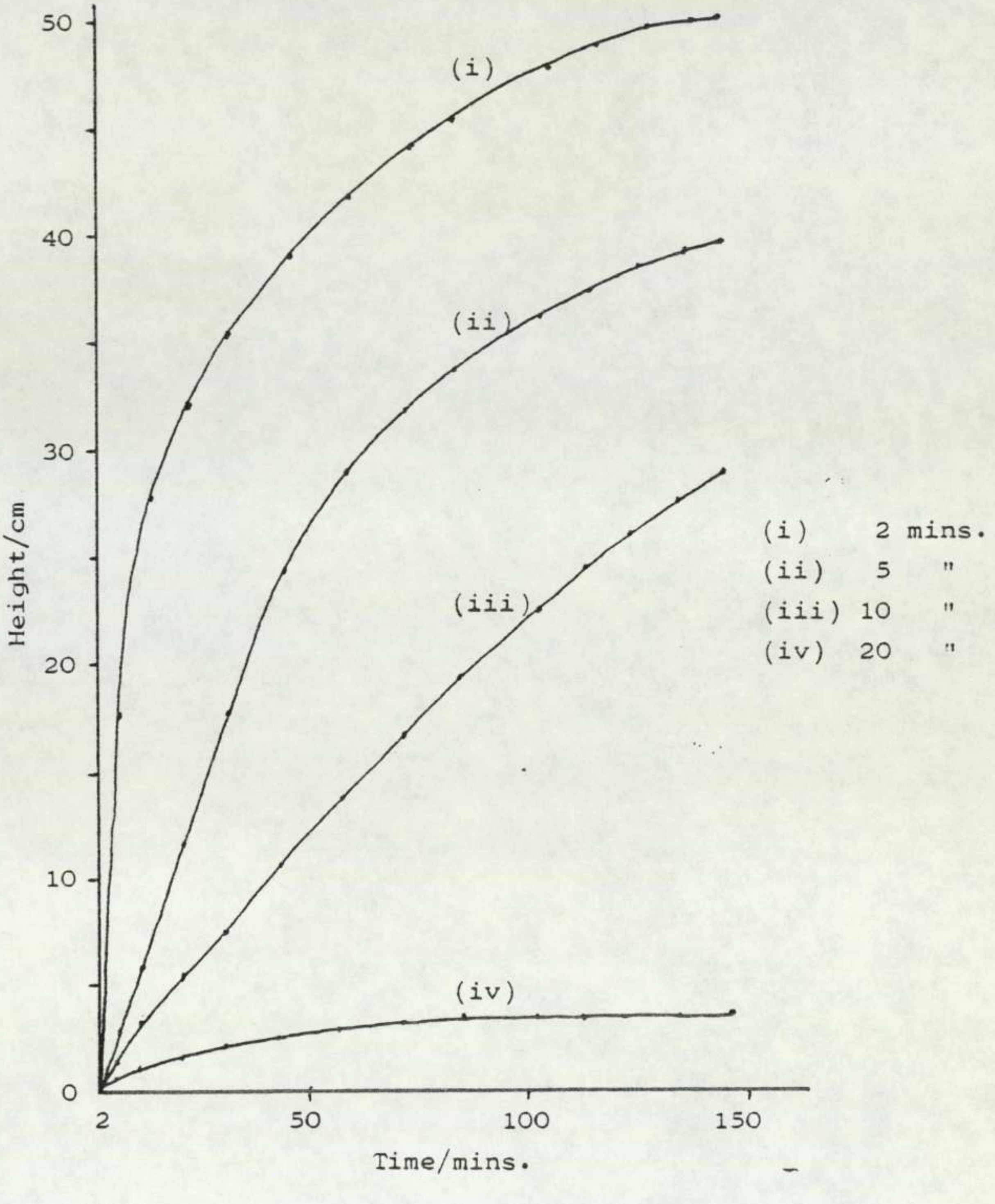


Fig. 3.15 Dependence of Polymerisation of Cyclopentene on Ageing Time of Catalyst Components Sequential Addition



of experiments. These are comparable with those shown in fig. 3.8 for the corresponding $AlBr_3$ system, revealing a steady decrease in activity of the sytem as time delay is increased. Much faster deactivation was also observed in the $AlBr_3$ system, which showed a tendency for greater initial activity for the more prolonged ageing times.

The reaction conditions were such that some polymerisation must have taken place before addition of $SnCl_4$ to the system. By inference from figs. 3.1 and 3.2 the conversion actually achieved is low, even after twenty minutes under bimetallic catalyst conditions. The polymerisation curves should therefore be considered extensions from the appropriate conversion point on the conversion-time curves for the bimetallically initiated polymerisation. As pre-reaction time is increased the subsequent rate of polymerisation decreases, to such an extent that it appears $SnCl_4$ actually 'kills off' the inherent activity of the LiBu system, or the species subsequently generated on addition of $SnCl_4$ has lower activity.

3.5.3 Polymerisation Studies of Premixed Catalyst Systems

A series of experiments was carried out as described in Section 3.4.3, using $SnCl_4$ in place of $AlBr_3$.

3.5.3.i Dependence of Activity of Catalyst Components

In a typical reaction $1.5cm^3$ WCl_6 ($4.55 \times 10^{-2} mol.dm^{-3}$) was added to 25cm^3 monomer solution (2.73mol dm^{-3}), followed two minutes later by a premixed solution of 0.2cm^3 LiBu solution (7.91 x 10^{-1}mol dm^{-3}) and 1.2cm^3 $SnCl_4$ solution (2.35 x 10^{-2} mol dm^{-3}after two minutes of ageing. A constant monomer/WCl_6 molar ratio was maintained throughout the series, and attempts were made to polymerise cyclopentene using various cocatalyst concentrations.

On premixing LiBu with $AlBr_3$ a yellow cloudy solution was produced, which maintained the brown colour of cyclopentene/ WCl_6 when added to it, resulting in an inactive polymerisation system. On premixing LiBu and $SnCl_4$ however, a colourless solution was formed, together with a small amount of precipitate. When the mixture was added to monomer and WCl_6 a pale brown/orange colour resulted and no polymerisation appeared to take place, as the height of liquid in the capillary was unaltered with no apparent increase in viscosity, even after two hours reaction time.

It is possible that an ageing time of two minutes for the premixed components was unsuitable, hence another series of experiments was carried out using the expected optimum catalyst ratio for W/Li/Sn of 1:2:4, with premix ageing times of half, one and five minutes, but all systems appeared to be inactive. $SnCl_4$ does not therefore seem to be a suitable cocatalyst for this particular system, as it reacts with LiBu in such a way as to render it, together with its WCl_6 products, inactive towards polymerisation.

3.5.4. Summary of Cyclopentene Polymerisation by Catalyst System WCl_6/LiBu/$SnCl_4$

When added sequentially, the overall rate of polymerisation appeared to be much more sensitive to changes in cocatalyst (LiBu or $SnCl_4$) to WCl_6 molar ratio and also to times between subsequent additions of each catalyst component to the monomer, compared with the analogous $AlBr_3$ system.

Premixing the two cocatalysts produced a virtually inactive system, whereas there was little effect on the overall rate for the corresponding $AlBr_3$ system when premixed with LiBu.

The existence of an optimum molar ratio of W/Li remains uncertain, although high activity appeared to be achieved at a W/Li/Sn molar ratio of 1:2:4. Experiments carried out in Section 3.5 may not therefore have been under conditions of maximum activity. This fact must be taken into consideration when analysing the results.

3.6 MOLECULAR WEIGHT STUDIES

3.6.1 Introduction

The ring-opening polymerisation of cyclopentene produces polypentenamer, which is readily isolable from unreacted monomer and catalyst components by pouring into methanol -

a precipitate of sticky elastomer is produced which can be analysed by GPC. GPC analysis of polypentenamer was carried out using the differential RI detector rather than UV, as the polymer does not absorb at 254nm. According to Gregory(147) ring-opening polymerisation of cyclopentene using WCL_6/LiBu catalyst does not produce polymers of a normal distribution, but a bimodal molecular weight distribution is shown.

Calderon et al(40) correlated high molecular weight products with linear polymer chains, and the lower molecular weight species with macrocycles, while very low molecular weight products are due to cyclic oligomers. Amass and Zurimendi(15) studied ring-opening polymerisation of cyclopentene catalysed by $WCl_6/Al(iBu)_3$, concluding that the molecular weight distribution and ratio of high to low molecular weight species in the bimodal distribution depended upon the extent of reaction and the pre-reaction time of the catalyst (WCl_6) with cyclopentene. In each case an equilibrium of products was reached after twenty-four hours. A marked similarity was observed for the catalyst system WCl_6/LiBu by Gregory(147); it being concluded that there were two distinct stages to the polymerisation reaction, the initial stage being controlled thermodynamically. The two stages of the reaction were due to the presence of two kinetically independent active species, one capable of producing high molecular weight polymers and the other low molecular weight products. Höcker(143) showed that the relative proportions of high molecular weight to low molecular weight species are governed by the position of equilibrium in the metathesis reaction, while the concentration of cyclic oligomers obeyed the Stockmeyer equation for ring-chain equilibria.

Studies have been made of the molecular weight distribution of polypentenamer produced from cyclopentene using the trimetallic catalyst systems comprising $WCl_6/LiBu/AlBr_3$ and $WCl_6/LiBu/SnCl_4$. The effects of catalyst to cocatalyst molar ratios and the ageing time of cocatalyst reactions have been determined, as well as detailed studies carried out on polymeric species produced during the course of polymerisation using sample techniques. Studies were also carried out on both premixed and sequential additions of catalyst components to the monomer.

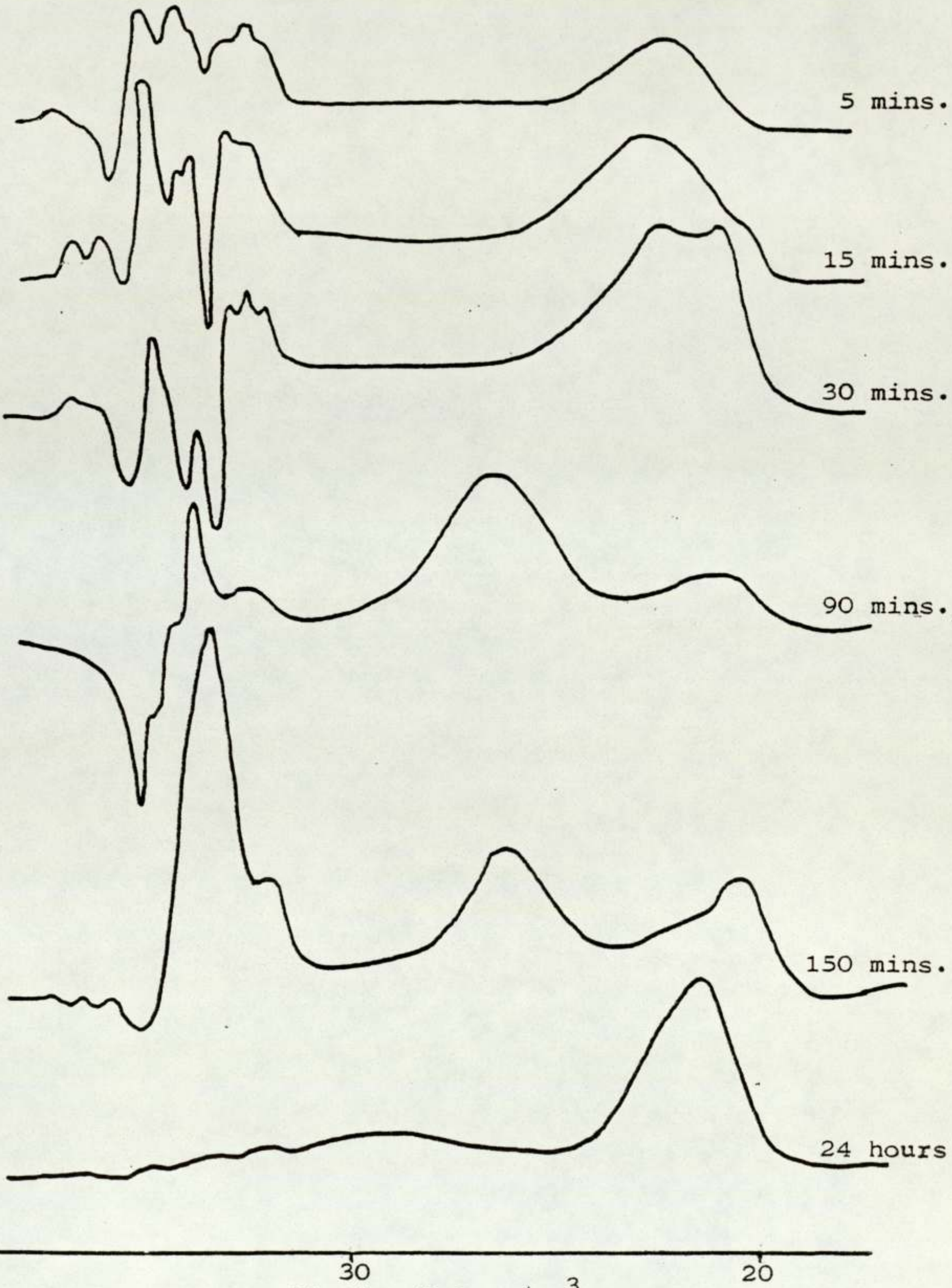
3.6.2 Polymerisation of Cyclopentene by $WCl_6/LiBu/AlBr_3$

GPC studies were carried out, as described in Section 2.5.2, on polymers produced from experiments outlined in Section 3.3 onwards.

3.6.2.i Sampling Sequential Additions of Catalysts

Samples of polymers taken during the course of polymerisation of cyclopentene, using $WCl_6/LiBu/AlBr_3$ as the catalyst system in a molar ratio of 1:2:2, were analysed by GPC. Fig. 3.16 shows RI analyses for samples taken after five, fifteen,

Fig. 3.16 GPC Chromatograms of Polypentenamer at Various Intervals of the Reaction



thirty, ninety and 150 minutes, also twenty-four hours of reaction time. An analysis of these chromatograms for quotation of reasonable $\overline{Mw}$ and $\overline{Mn}$ values was not attempted in this case, because such values appeared to be meaningless. It is obvious that molecular weight changes occurring during the course of polymerisation were very complex, but it would seem that despite these changes the molecular weight distribution after twenty-four hours was that of a typical polypentenamer. The polymer had a bimodal molecular weight distribution with a high molecular weight portion, together with a low molecular weight component which included oligomeric material.

Comparative analyses of all other chromatograms in fig. 3.16 show signs of progressive change with reaction time. The percentage conversion-time curve for a polymerisation under these reaction conditions is shown in fig. 3.4. During the initial period, i.e. up to approximately fifty minutes, the rate of polymerisation is rapid. Chromatograms of polymers obtained during this period show a significant presence of oligomers; a series of peaks appearing between elution volumes of $34cm^3$ and $40cm^3$.

According to the chromatograms the initially formed polymer showed a peak at an elution volume of $22.5cm^3$ for reaction times of five, fifteen and thirty minutes, with a shoulder gradually appearing at a volume of $20.5cm^3$. The latter persisted for considerable reaction times, whereas the former was slowly replaced by a peak corresponding to polymer of much lower molecular weight, i.e. the peak occurring at $28cm^3$ and $29cm^3$ on the chromatograms for ninety and 150 minute samples. There is some evidence that this material was also present during the first thirty minutes of reaction time, but only to a minor degree.

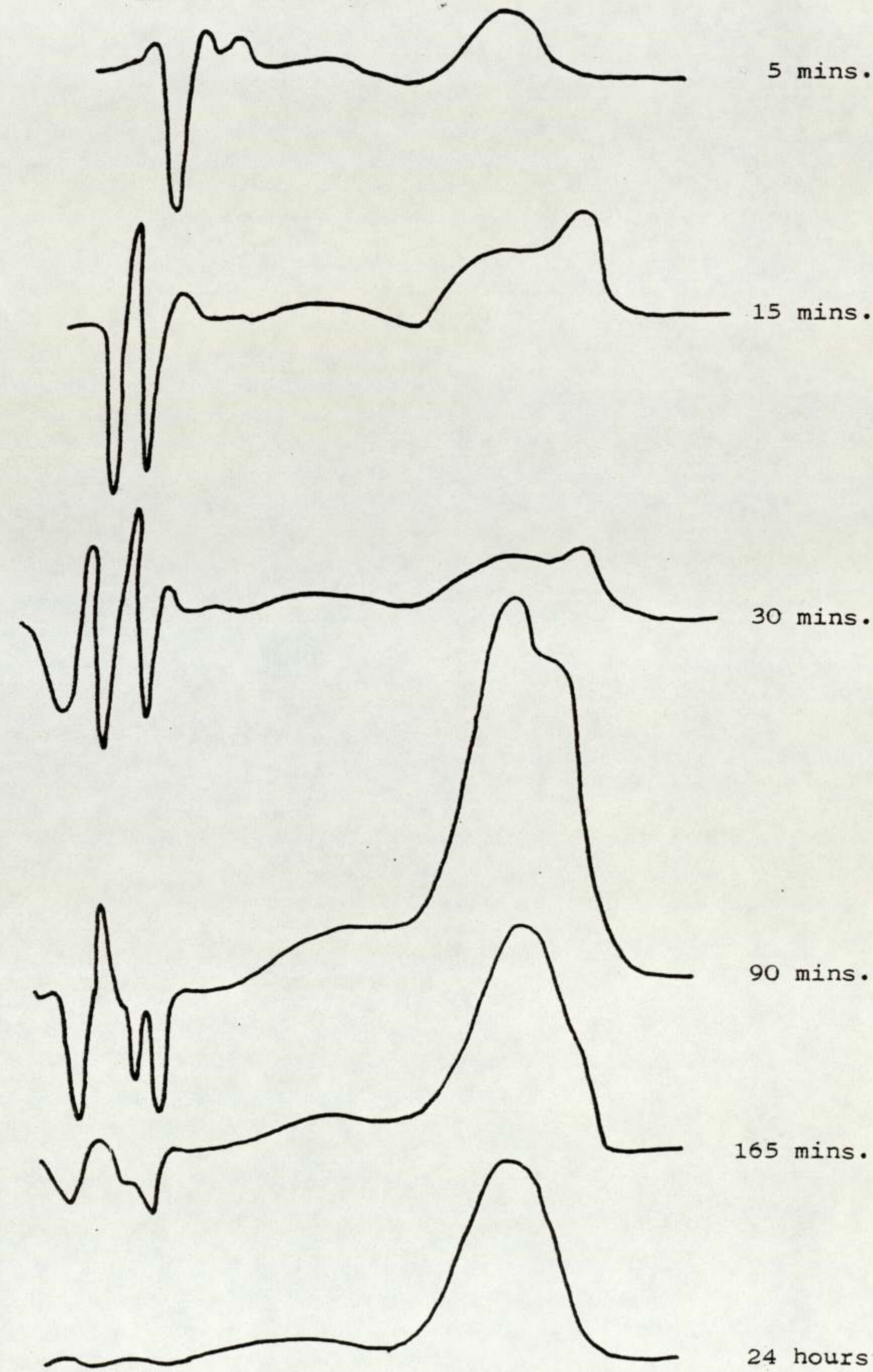
It seems unlikely that only one type of propagating species was present for the whole reaction period. A more probable explanation, taking into account the conversion-time curve, is that a number of species are responsible for the polymerisation and depolymerisation processes which undoubtedly occur in the system.

3.6.2.ii Sampling Premixed Additions of Cocatalysts

Fig. 3.17 shows the GPC traces (RI response) for samples of polymer obtained during the course of polymerisation of cyclopentene, using WCl_6 and a premixed solution of LiBu and $AlBr_3$ as the catalysing components. The values of $\bar{M}n$ and $\bar{M}w$ for these polymers were not considered useful. Dramatic changes in molecular weight distribution were observed throughout the course of the reaction, but after twenty-four hours a bimodal distribution, typical of polypentenamer, was obtained as for the sequential addition system (fig. 3.16).

Although the chromatograms changed with reaction progression in the premixed system, positions of peaks did not appear to alter greatly, particularly between fifteen and 165 minutes.

Fig. 3.17 GPC Chromatograms of Polypentenamer at Various Stages of the Polymerisation Process



After five minutes polymerisation time a high molecular polymer with an elution volume of 23.8cm^3 and a lower molecular weight species (elution volume of 31cm^3) was observed. The latter species was seen to increase in concentration during the course of the reaction. After a reaction time of fifteen minutes the higher molecular weight peak elution volume of 23.8cm^3 shifted slightly to a lower volume of 22.4cm^3, but displayed a shoulder at 20.3cm^3. But this may not have been a true shift, as the resultant peak is obviously a superimposition of two others. After thirty minutes the pattern had remained constant, but at ninety minutes the proportions of the higher peaks were changed. The peak from the polymer which had eluted at 22.4cm^3 far exceeded that of the shoulder peak, which had diminished by the end of the series at twenty-four hours.

A significant presence of oligomers was observed between 36.5cm^3 and 40cm^3, particularly for the first ninety minutes. As with the sequential catalyst addition, they had almost disappeared after twenty-four hours.

A comparison of results from this series, with those shown in fig. 3.16 for the unmixed system, suggest that in both cases more than one catalyst species is likely to be responsible for the polymerisation of cyclopentene. But in the former system the extent of depolymerisation is less marked.

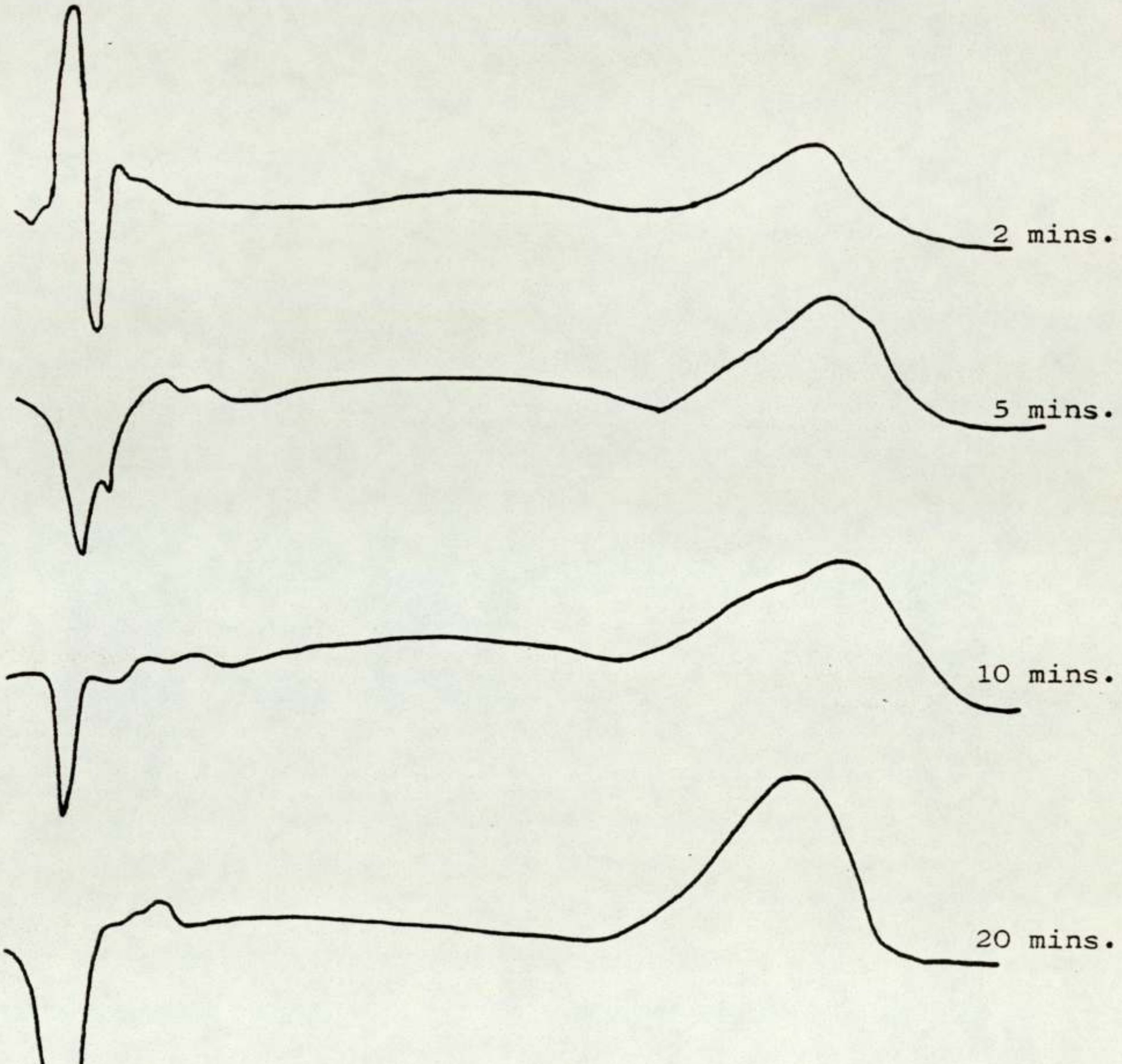
3.6.2.iii Dependence of Molecular Weight Distribution on Time of Sequential Catalyst Additions

Fig. 3.18 shows RI GPC chromatograms of polypentenamer produced after three hours, when time between addition of LiBu and $AlBr_3$ to a solution of monomer and catalyst was varied from two to twenty minutes.

The chromatograms showed similar molecular weight distributions, with a main peak at elution volume of about $20cm^3$ and a low molecular weight species peaking in the region of $28cm^3$. From fig. 3.8 it may be seen that optimum rate of polymerisation occurred when the time delay was two minutes, but fairly high activity was also observed for ageing times of five and ten minutes. Molecular weights of the higher molecular weight products, obtained for ageing times of two, five and ten minutes, were observed to increase slightly with greater time delay. Polymers for five and ten minutes developed a shoulder at an elution volume of $17.6cm^3$, which is very close to the exclusion limit of the columns used.

During the period between additions of LiBu and $AlBr_3$ it is quite probable that the lower activity bimetallic system (WCl_6/LiBu) has caused the polymerisation of cyclopentene. The amount of polymer resulting from this polymerisation would be expected to increase with delay time, while the shoulder occurring at higher molecular weight appears to increase in intensity from two to five and five to ten minutes. Addition of $AlBr_3$ either converts this bimetallic

Fig. 3.18 GPC Chromatograms of Polypentenamer Produced at Various Delay Times of $AlBr_3$ addition to Monomer/WCl_6/LiBu Solution



system into a more active catalyst, or quite independently generates a highly active catalyst. In either eventuality the resulting polymerisation is responsible for polymer with a slightly higher elution volume, but surprisingly, polymer produced in the initial period remained without further reaction. It would appear that if systems of this type are left for a long period, the complex molecular weight distribution slowly reverts to the bimodal type.

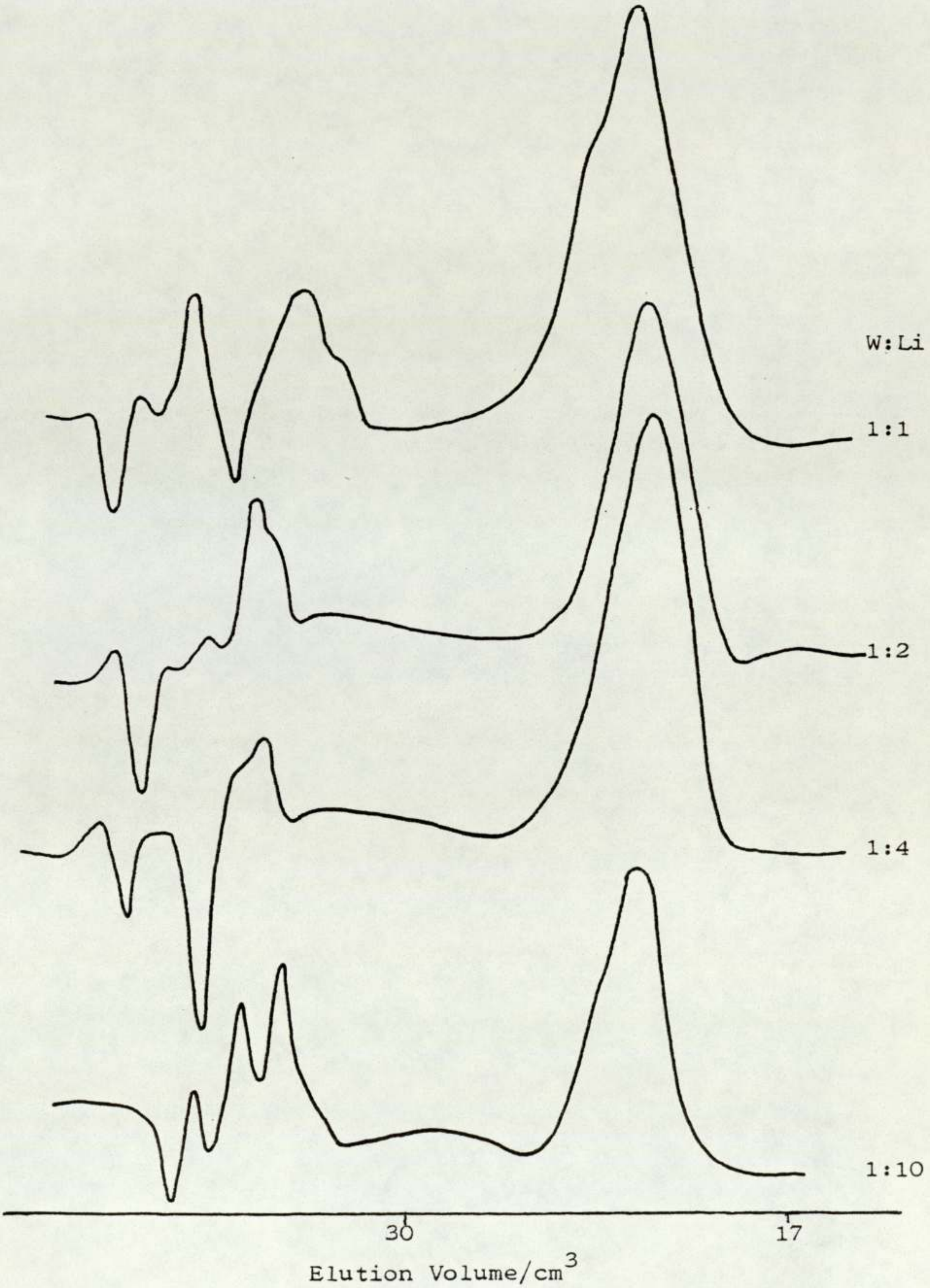
After a time delay of twenty minutes, polymer eluting at 21.2cm^3 was produced as a high molecular weight species with no shoulder visible at the peak. This was most probably a product of cyclopentene polymerisation catalysed by the bimetallic system WCl_6/LiBu alone, since an addition of $AlBr_3$ after this period did not significantly affect the rate of polymerisation (fig. 3.8).

A low concentration of oligomers was observed between 31.5cm^3 and 40cm^3, the distribution of which changed with ageing time.

3.6.2.iv Dependence of Molecular Weight Distribution on Molar Ratios of Catalyst Components

It was apparent from studies carried out in Section 3.4.2 that the rate of polymerisation of cyclopentene is greatly influenced by the molar ratios of the catalyst components used. Fig. 3.19 shows gel permeation chromatograms of polypentenamer produced from a series of experiments in which the

Fig. 3.19 Gel Permeation Chromatograms of Polypentenamer at Varying Cocatalyst (LiBu) to Catalyst Molar Ratios



the molar ratio of LiBu to WCl_6 was varied, but a molar ratio of monomer/WCl_6/$AlBr_3$ maintained at 1000:1:2. The curves show typical bimodal distribution, the major peak of which did not appear to vary significantly with LiBu concentration. However considerable changes took place in the relative concentrations and distributions of oligomer. At low LiBu concentration (W/Li = 1:1) the major peak was observed at an elution volume of $22cm^3$, corresponding to a polystyrene molecular weight of 6×10^5. The presence of a slightly lower molecular weight species was indicated by the shoulder at $24.2cm^3$. On increasing the concentration of LiBu from a W/Li molar ratio of 1:1 to 1:4 the high molecular peak shifted slightly to a lower elution volume of $21.2cm^3$. At the ratio of 1:10 however, the polymer assumed the same elution volume as for the 1:1 material, again with a slight hint of a shoulder at high elution volume. These variations may be considered minor, as they are probably within experimental error.

The system having a molar ratio of 1:2 for W/Li was found to be the most active according to previous studies, while the chromatogram for polypentenamer produced was the only one to show the presence of a very high molecular weight peak at an elution volume of $18.1cm^3$. This species was also shown in fig. 3.16 after 150 minutes reaction time, but later found to disappear aftertwenty-four hours, when the system appeared to reach equilibrium.

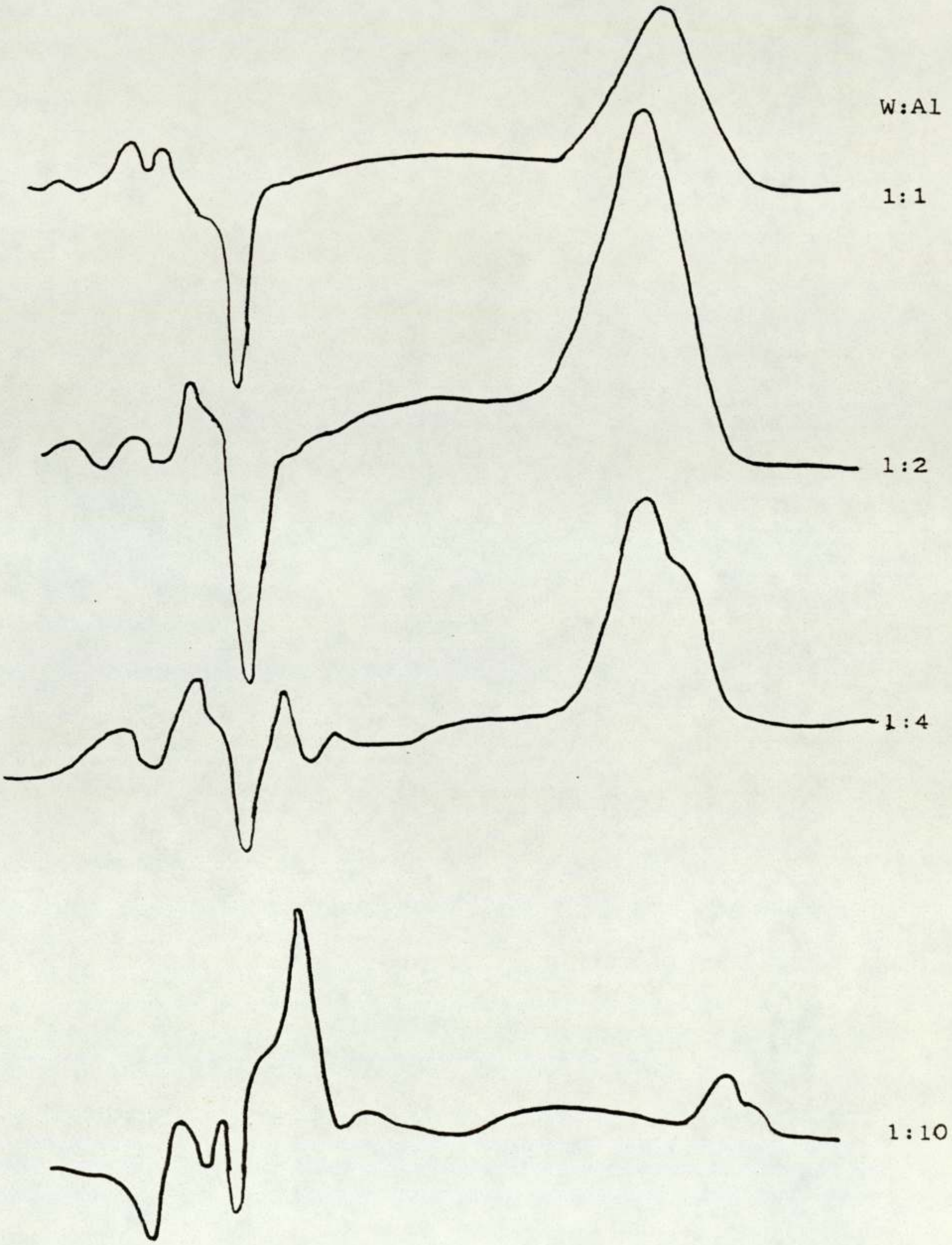
The presence of lower molecular weight polymer eluting at $29cm^3$ was visible for all concentrations of LiBu used, as with all delay times, but appeared to increase significantly with added concentration of LiBu.

The oligomer distribution observed between elution volumes of $33.5cm^3$ and $40cm^3$ varied considerably with LiBu concentration, appearing to be in all cases of very high concentration. But it is difficult to draw any concrete conclusion from this significance, because complete recovery of the oligomeric material is not easily achievable.

Fig. 3.20 shows a series of RI chromatograms of polypentenamer produced by using a WCl_6 catalyst and LiBu/$AlBr_3$ premixed cocatalyst system over a range of $AlBr_3$ concentrations. As experienced with the unmixed system (fig. 3.19), a change in cocatalyst molar ratio in a premixed system, in this case $AlBr_3$, also had an effect on the overall molecular weight of the polypentenamer produced. At the lowest W/Al molar ratio of 1:1 a single peak in the high molecular weight region was observed at an elution volume of $24.2cm^3$ (polystyrene molecular weight of 3×10^5), and with a lower molecular weight peak at $28/29cm^3$, similar to all previous systems. At the optimum ratio of 1:2, the major peak eluted slightly later at $24cm^3$, but unlike the analogous unmixed system there was no trace of polymer at $18cm^3$.

At higher W/Al molar ratios (1:4, 1:10) the major peak was bimodal. A peak at $24.6cm^3$ elution volume was again present,

Fig. 3.20 Gel Permeation Chromatograms of Polypentenamer at Varying Cocatalyst ($AlBr_3$) to Catalyst Molar Ratios for a Premixed Catalyst System



but in this instance with a higher molecular weight shoulder at 23.8cm^3 (polystyrene equivalent molecular weight of 3.5 x 10^5). For the 1:10 system a bimodal peak was observed at both 21.0cm^3 and 22.2cm^3. These peaks were of much less significance however than the corresponding peaks at lower concentrations of $AlBr_3$. This was possibly a result of over-reduction of the catalyst at high $AlBr_3$ concentration, leaving principally the species which generates only low molecular weight polymer and oligomers.

3.6.3 Polymerisation of Cyclopentene Catalysed by WCl_6/LiBu/$SnCl_4$

GPC analyses were carried out on the products of polymerisation studies described in Section 3.5, using $SnCl_4$ as a second cocatalyst in place of $AlBr_3$.

3.6.3.i Dependence of Polypentenamer Molecular Weight Distribution on Molar Ratios of Catalyst Components

The polypentenamer produced, as analysed in fig. 3.21, was obtained by using a W/Sn molar ratio of 1:4, found to be the optimum from previous studies. The chromatograms in fig. 3.22 are of polymer produced by using a W/Li molar ratio of 1:2 at a variety of $SnCl_4$ concentrations. Figs. 3.21 and 3.22 show the molecular weight distributions after a reaction time of three hours.

Fig. 3.21 Gel Permeation Chromatograms of Polypentenamer at Various Cocatalyst (LiBu) to Catalyst Molar Ratios

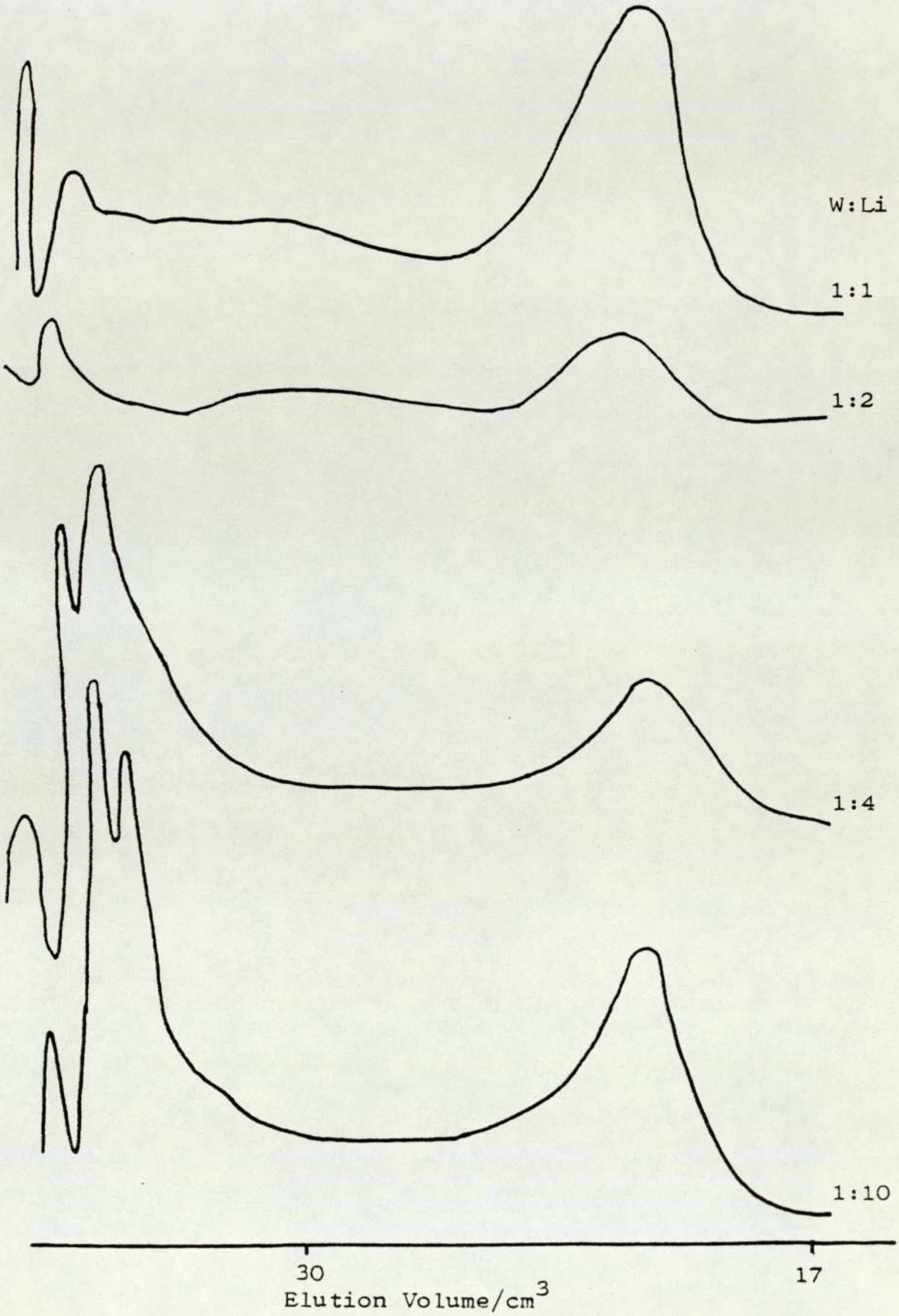
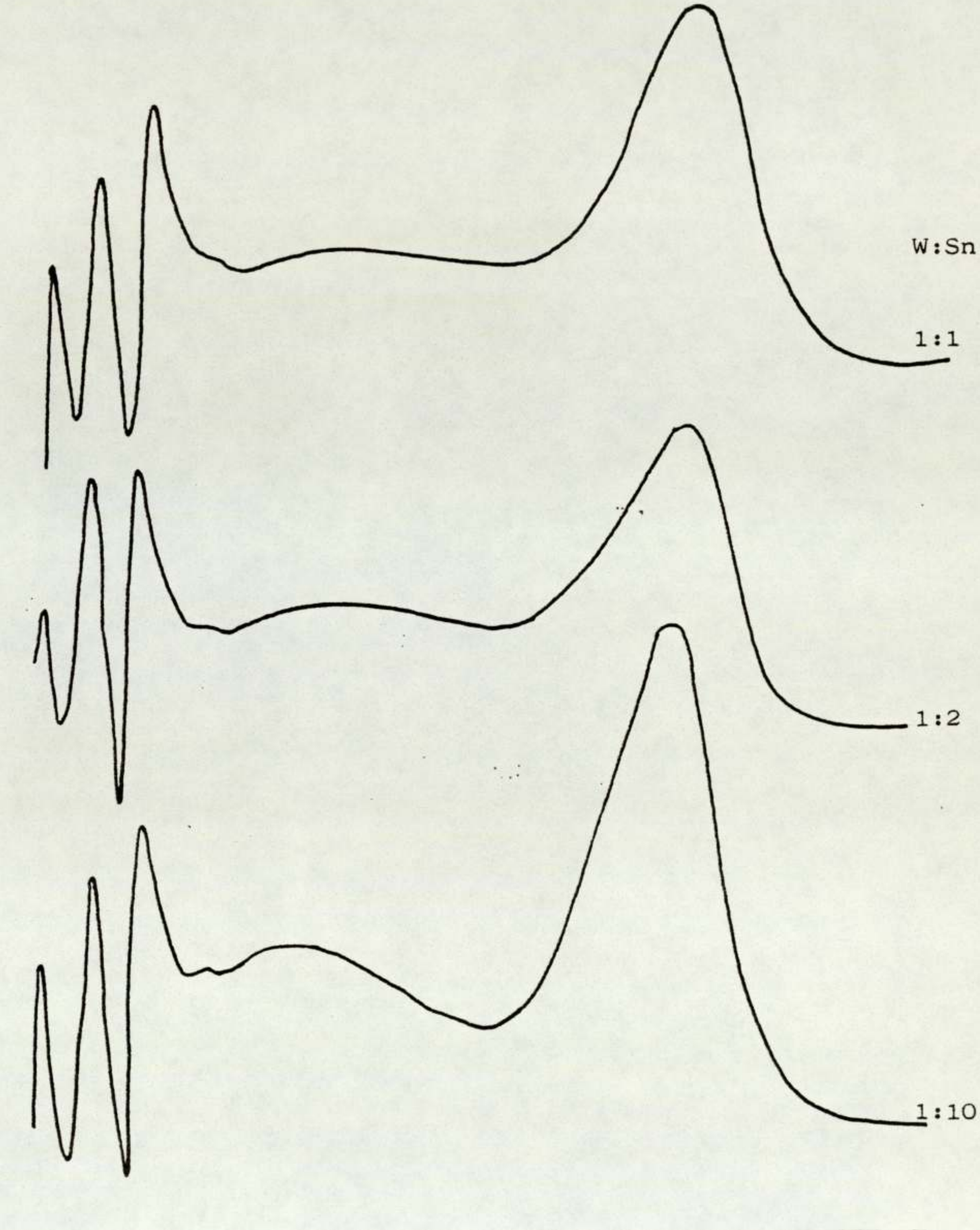


Fig. 3.22 Gel Permeation Chromatograms of Polypentenamer at Various Cocatalyst ($SnCl_4$) to Catalyst Molar Ratios



Unlike the $AlBr_3$ system, a bimodal polypentenamer distribution appeared to occur only for low concentrations of LiBu (fig. 3.21), while at higher molar ratios (W/Li = 1:4, 1:10) only a single high molecular peak was observed, which eluted at a volume of $21.7cm^3$ (polystyrene equivalent molecular weight of 6×10^5). Oligomers of similar molecular weight distributions were present in each of the systems. For the 1:1 system it was observed that a high molecular weight polymer eluted at a volume of $21.2cm^3$, together with the typical lower molecular weight species at $29.6cm^3$. A similar bimodal pattern was produced for the 1:2 W/Li system, but the higher molecular weight peak had shifted to a higher elution volume of $22.0cm^3$. In both systems the presence of oligomeric material was less marked than for systems of higher LiBu concentrations.

Fig. 3.22 shows the effect of varying the concentration of $SnCl_4$ on the molecular weight distribution of the polymers produced. The high molecular weight polymer eluted as a single peak between $21.8cm^3$ and $22.1cm^3$, corresponding to a polystyrene equivalent molecular weight of 5.5×10^5 and seeming to be independent of the $SnCl_4$ concentration used. A lower molecular weight species eluting at a volume of around $30.0cm^3$ was apparent in all cases, being observed to increase in intensity with greater concentration of $SnCl_4$. The oligomer concentration and distribution were identical, apparently irrespective of the molar ratio of catalyst to $SnCl_4$ employed.

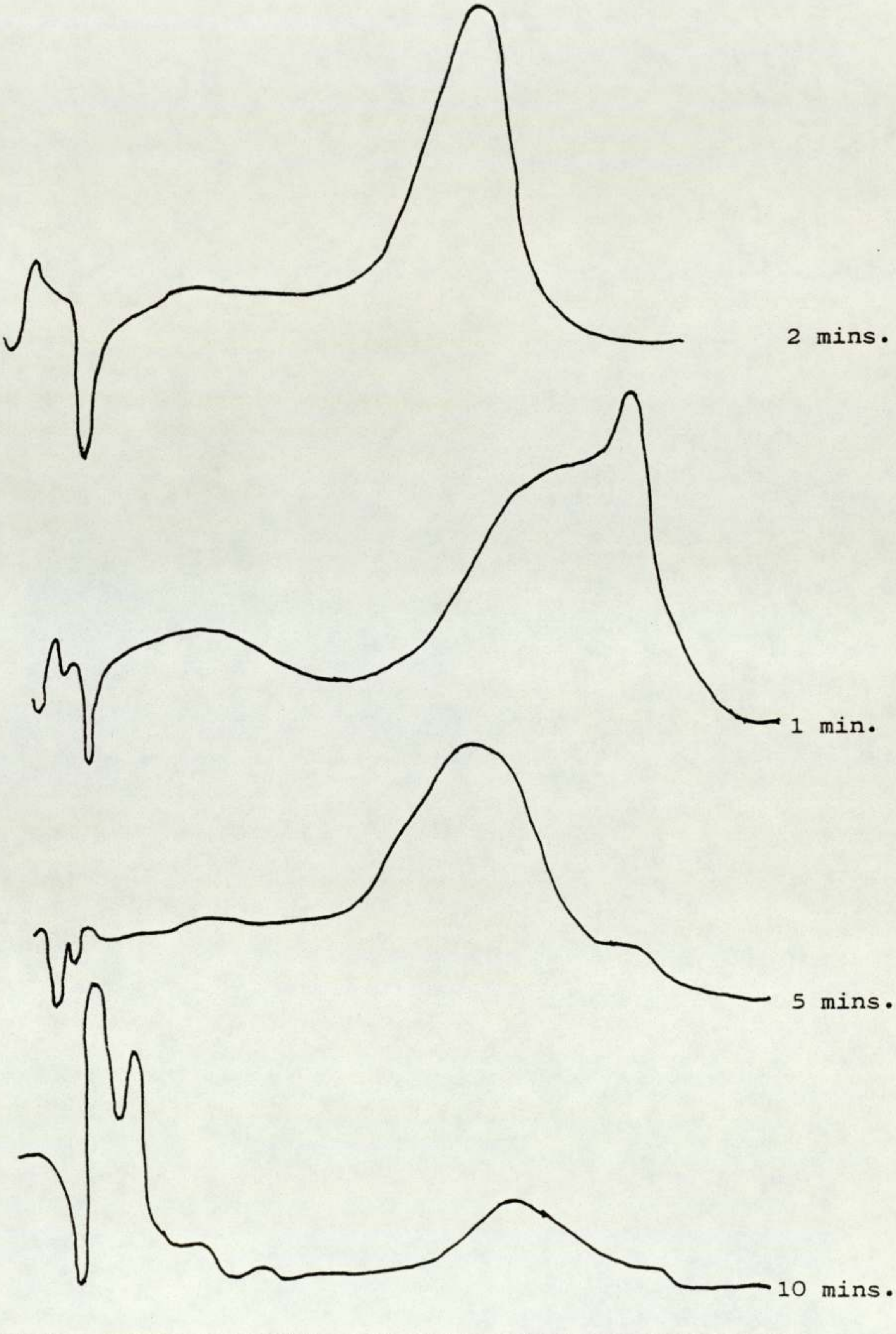
From these results it may be concluded that although the rate of polymerisation varies significantly with molar ratios of catalyst components (fig. 3.14), the overall molecular weight distribution of the products does not differ greatly, except for the oligomer concentration dependence on LiBu molar ratio. It may have been that after a reaction time of three hours the system has reached an equilibrium, which would account for these observations. Further studies of the course of polymerisation from sampling techniques are required to confirm this possibility.

3.6.3.ii Dependence of Polypentenamer Molecular Weight Distribution on Delay Times of Catalyst Components Addition

From Section 3.6.2, the time delay between addition of $AlBr_3$ to a solution of monomer/WCl_6/LiBu was found to drastically effect the molecular weight distribution of polypentenamer produced. Fig. 3.23 shows gel permeation chromatograms (RI response) for the analogous $SnCl_4$ system, using the pre-determined optimum molar ratio of catalyst components for monomer/W/Li/Sn of 1000:1:2:4.

From Section 3.5.2, the optimum time delay for addition of $SnCl_4$ was found to be two minutes. The appropriate chromatogram shows the polypentenamer species thus produced having a typical bimodal molecular weight distribution, with some oligomers also present. It appeared from fig. 3.23 however,

Fig. 3.23 RI Chromatograms at Various Delay Time Additions of $SnCl_4$ to a Solution of Monomer/LiBu/WCl_6



that above and below this optimum the distributions were somewhat more complex. If $SnCl_4$ was added one minute after LiBu, the resulting polypentenamer showed complicated high molecular weight peaks at 20.6cm^3 and 22.6cm^3 elution volumes, which appeared to superimpose each other. The five minute delay chromatogram showed a similar distribution, but with a significantly decreased proportion of polymer at 20.6cm^3. The other high molecular weight peak in this case eluted at 25.1cm^3, which was higher than for a two minute delay, with optimum polymer at 23.4cm^3. A pattern was observed from the three chromatograms with respect to the major peak, with a decrease in molecular weight of polypentenamer apparently resulting from increased time delay of $SnCl_4$ addition. The lower molecular weight polymer eluting at a volume of around 31.8cm^3 was maintained constant up to a five minute delay time, with low oligomer concentration distribution not varying greatly. For a ten minute delay period however, the change in oligomer concentration distribution was marked, with the high molecular peak appearing at an elution volume of 23.4cm^3 (corresponding with the two minute delay species), with an even higher molecular weight polymer of elution volume 20.1cm^3.

From these results it appears that the time interval of co-catalyst ($SnCl_4$) addition to the monomer significantly affects the overall molecular weight distribution of the polypentenamer produced, comparing directly with the analogous $AlBr_3$ system. This was to be expected, as the catalytically active species is likely to be different for each system. With a delay time of one minute the active catalyst will probably be predominantly trimetallic (W/Li/Sn), but after ten minutes the bimetallic system (W/Li) will have initiated the polymerisation process, possibly changing to another active species on addition of $SnCl_4$ and thus produce a variation in overall molecular weight distribution for the final polymer.

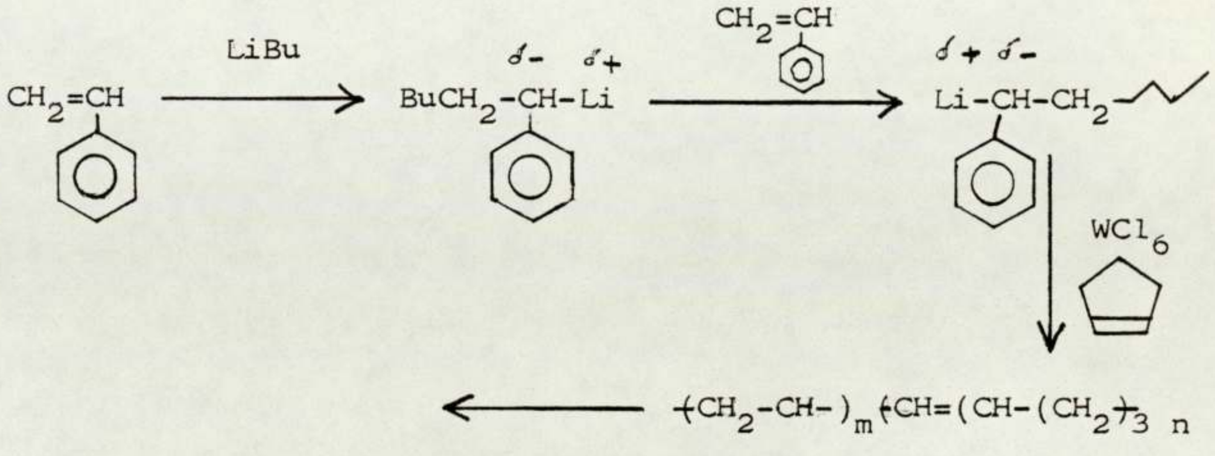
CHAPTER 4

POLYMERISATION STUDIES USING PstLi COCATALYST

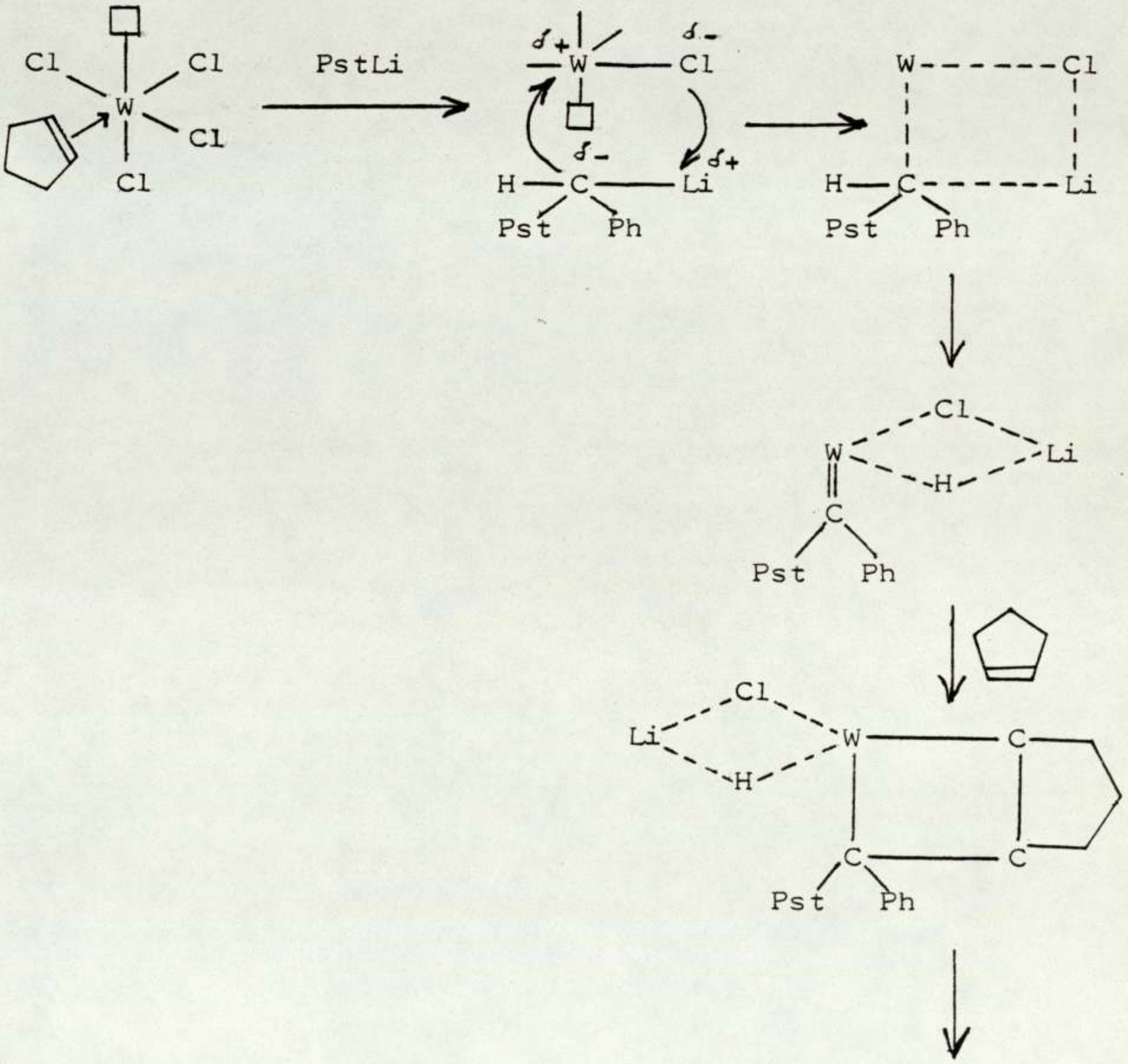
4.1 INTRODUCTION

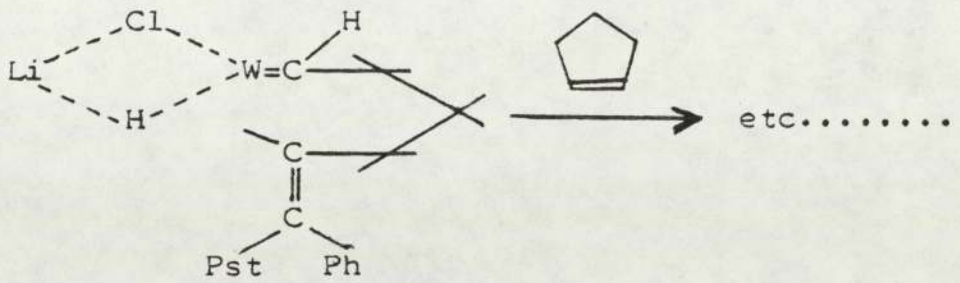
In the previous chapter the homogeneous trimetallic system $WCl_6/LiBu/AlBr_3$ ($SnCl_4$) was studied extensively for the ring-opening polymerisation of cyclopentene. Although the kinetics of the reaction can be observed from results of these studies, little clarification of the mechanism was possible concerning the role of the cocatalyst components. It has been proposed that the organometallic cocatalyst donates an alkyl group to the transition metal compound, which subsequently rearranges by way of an α-hydrogen reaction to yield a metallacarbene which is an active species for olefin metathesis and ring-opening polymerisation. The nature of the alkyl to transition metal bond has been ignored until recent studies by Gregory(147) for the ring-opening polymerisation of cyclopentene have been undertaken.

In experiments using the $WCl_6/LiBu$ bimetallic system, it was shown that the alkyl group was directly involved in the generation of propagating metallacarbene, as it was found that the alkyl group became associated with the final metathesis products. Rather than using labelled LiBu the alkyl group was replaced by an inert chromophore which could be detected by a GPC UV detector. Polystyryllithium (PstLi), produced from the anionic polymerisation of styrene by LiBu, was used for this purpose and the formation of block copolymers of polystyrene/polypentenamer was observed.



The proposed mechanism for the formation of block copolymers was as follows :-





Although at this stage the mechanism can only be regarded as a possible route to the generation of the initial carbene, it does not indicate that the reaction is covalent rather than ionic, or that the cocatalyst requires a transferable α-hydrogen atom.

The above results confirm the possibility of an anionic to metathetic transformation reaction, and this project has been concerned with the extension of these studies by using a trimetallic system. The ring-opening polymerisation of cyclopentene was attempted using the catalyst systems WCl_6/PstLi/$AlBr_3$ and WCl_6/PstLi/$SnCl_4$ to determine the effect of Lewis acids, which are often components in metathesis polymerisation.

4.2 POLYMERISATION OF CYCLOPENTENE USING WCl_6/PstLi/$AlBr_3$

A series of experiments similar to those described in Section 3.4 was carried out, using a solution of PstLi in place of LiBu as a cocatalyst component.

4.2.1 Dilatometric Determination of Optimum Catalyst/ Cocatalyst Molar Ratios

The solvent used in this series of experiments was cyclohexane and the order of addition of catalyst components to the monomer was as described in Section 3.4, i.e. WCl_6, PstLi and $AlBr_3$. The solution of PstLi was prepared as described in Section 2.4.5 and from analysis of the GPC RI trace the number average molecular weight ($\overline{M}_n$) was found to be 1.33×10^4, while the weight average molecular weight ($\overline{M}_w$) was 2.52×10^4 and the polydispersity ($\overline{M}_w/\overline{M}_n$) 1.9. The time delays between additions of PstLi and WCl_6, and between $AlBr_3$ and PstLi, were two minutes in each case. The colour changes observed for each catalyst addition to the monomer were similar to those for the corresponding LiBu system. The WCl_6:monomer molar ratio was maintained constant at 1:1000, but concentrations of PstLi and $AlBr_3$ were varied so that the W/Li and W/Al molar ratios could be changed independently.

In a typical polymerisation $1.3cm^3$ WCl_6 solution (8.69×10^{-2} $mol\,dm^{-3}$) was added to $25cm^3$ monomer solution ($4.52 mol\,dm^{-3}$), followed by $4.7cm^3$ PstLi ($2.39 \times 10^{-2} mol\,dm^{-3}$) and $1.1cm^3$ $AlBr_3$ solution ($2.23 \times 10^{-1} mol\,dm^{-3}$). At the end of each reaction (approx. three hours duration) solvent was evacuated from the polymerisate and the residue dissolved in chloroform prior to reprecipitation of the polymer in methanol. The precipitated polymer was then dried in a vacuum oven and 2% (w/v) solutions in THF were prepared for GPC analysis.

Figs. 4.1 and 4.2 show conversion-time dilatometry curves for the polymerisation reactions, varying independently the concentrations of PstLi and $AlBr_3$ respectively. The curves show similar patterns to corresponding LiBu curves, as seen from figs. 3.4 and 3.5, but lower activity is generally observed. The conditions for maximum activity (W/Li/Al = 1:2:5) produced a rate of polymerisation and decay similar to that for the analogous WCl_6/LiBu system without Lewis acid. In the present system no such dramatic changes in properties occurred on changing concentrations of cocatalyst.

The effects of the concentrations of LiBu and $AlBr_3$ on the maximum rate of polymerisation, plotted as $\Delta h/\Delta t$, are shown in figs. 4.3 and 4.4. In the case of each component there appears to be a concentration at which maximum activity occurs. It would therefore seem that these ratios control the oxidation states (PstLi would be expected to be an effective reducing agent) and the nature of the ligands surrounding the transition metal, as $AlBr_3$ is a powerful Lewis acid.

4.2.2 Determination of Sequential Addition Optimum Time of the Catalyst Components

In all the experiments carried out so far, optimum times between additions of LiBu to WCl_6 and $AlBr_3$ to WCl_6/LiBu/monomer were two minutes. A similar series of experiments was carried out, as described in Section 3.4.3, in order to

Fig. 4.1 Dilatometric Polymerisation Curves of Cyclopentene at various Cocatalyst (PstLi) to Catalyst Ratios

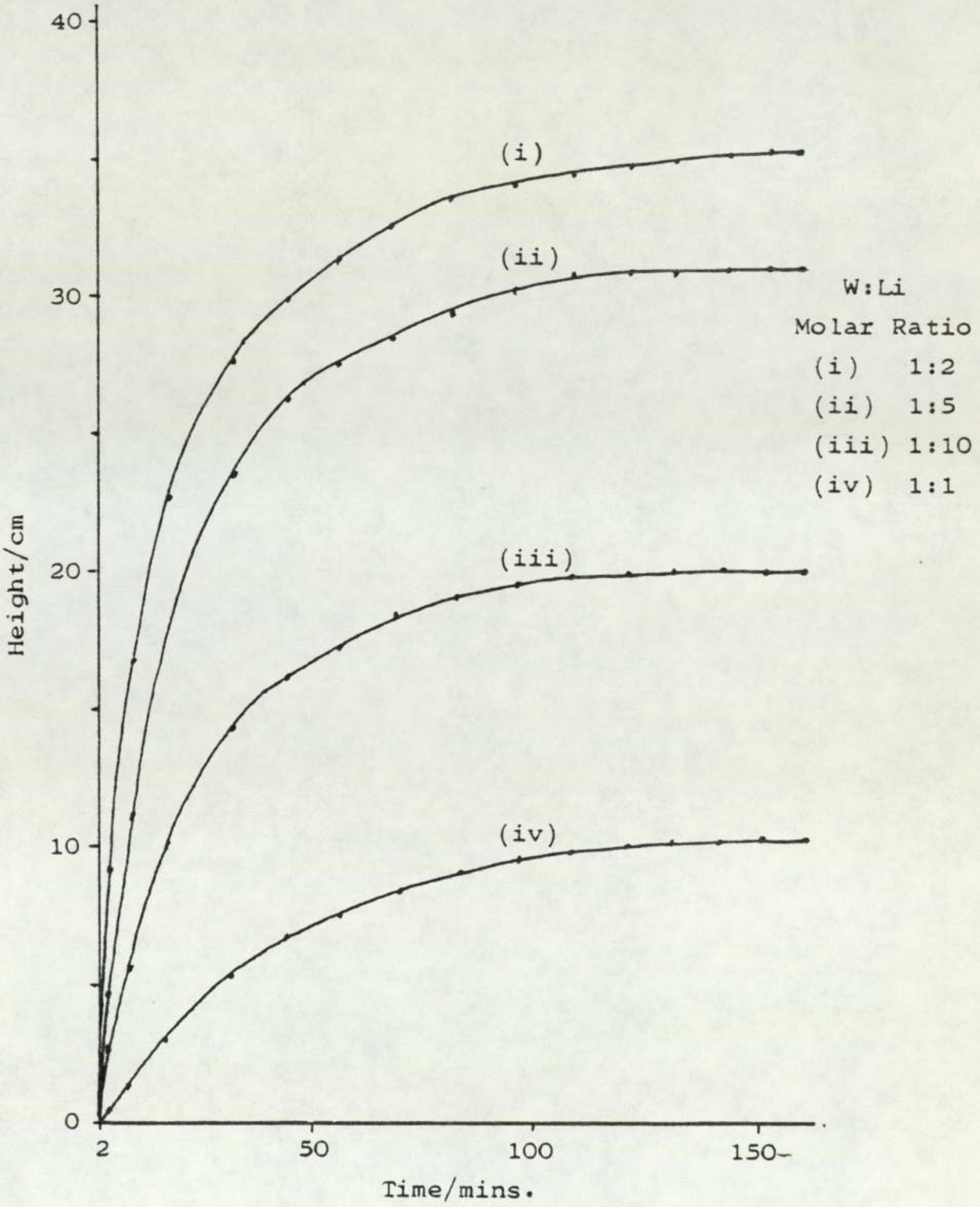


Fig. 4.2 Dilatometric Polymerisation Curves of Cyclopentene at various Cocatalyst ($AlBr_3$) to Catalyst Ratios

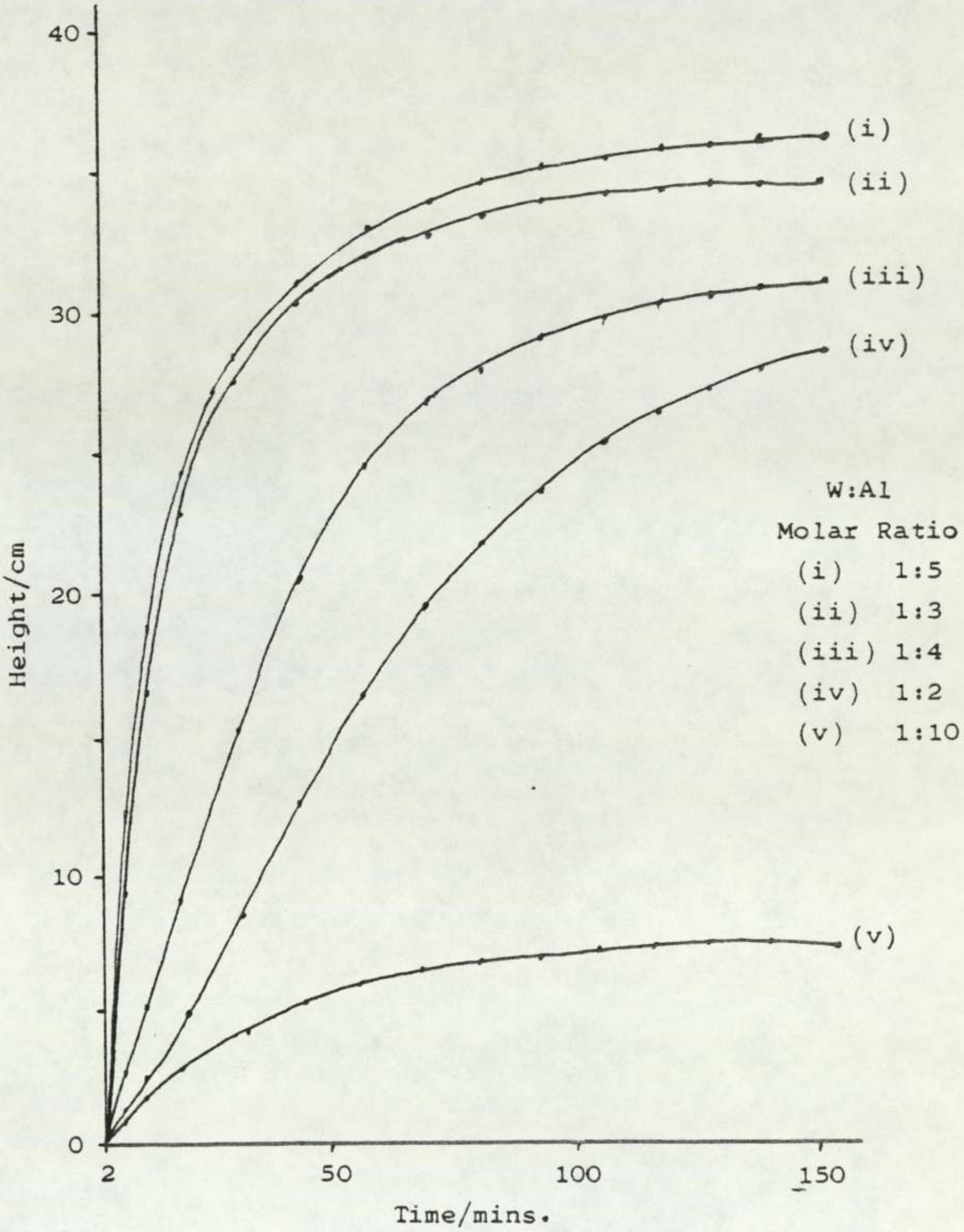


Fig. 4.3 Dependence of Cyclopentene Polymerisation Rate on W:Li Molar Ratio

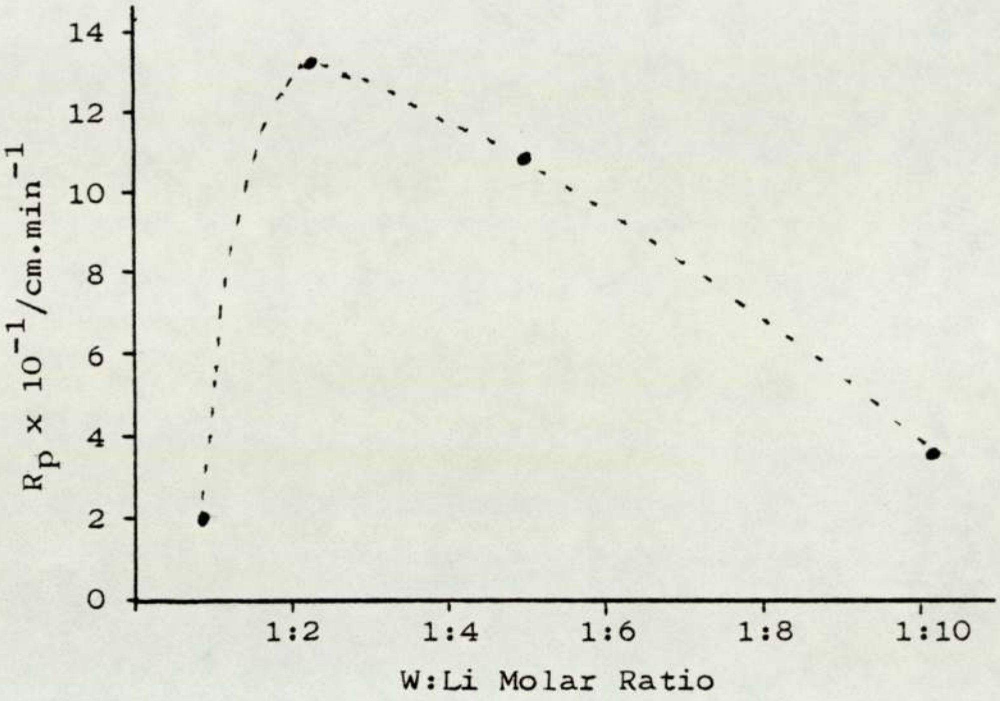
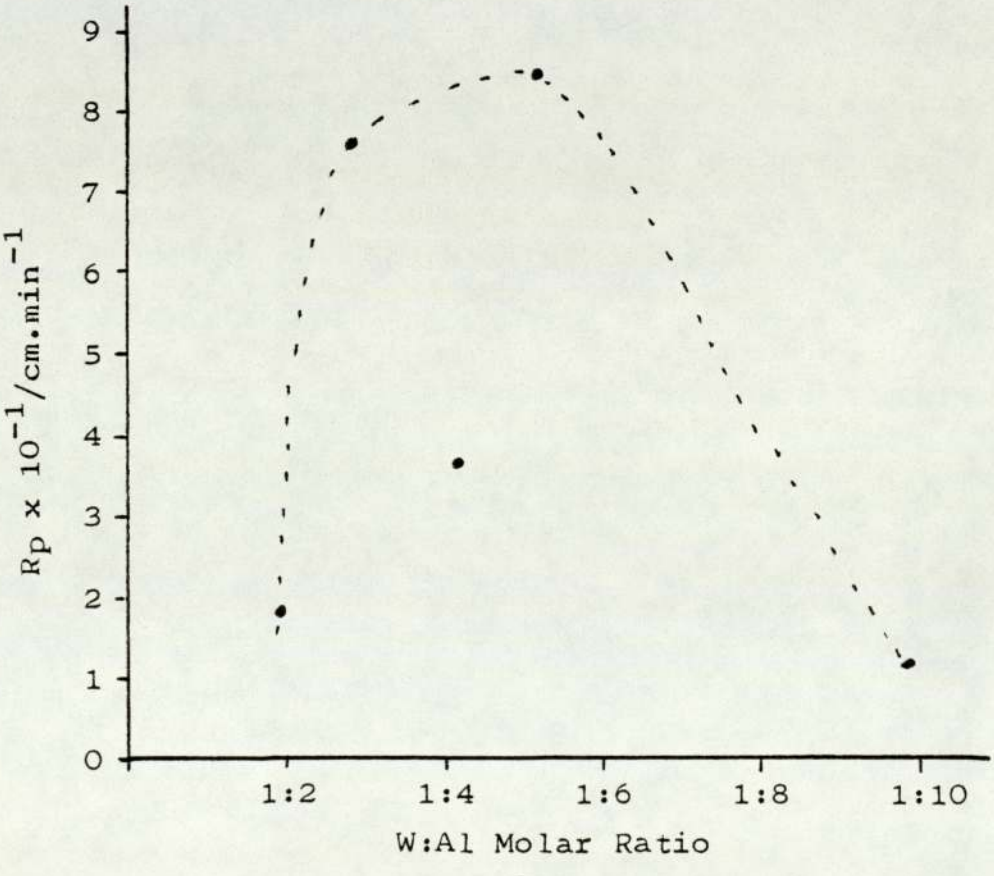


Fig. 4.4 Dependence of Cyclopentene Polymerisation Rate on W:Al Molar Ratio



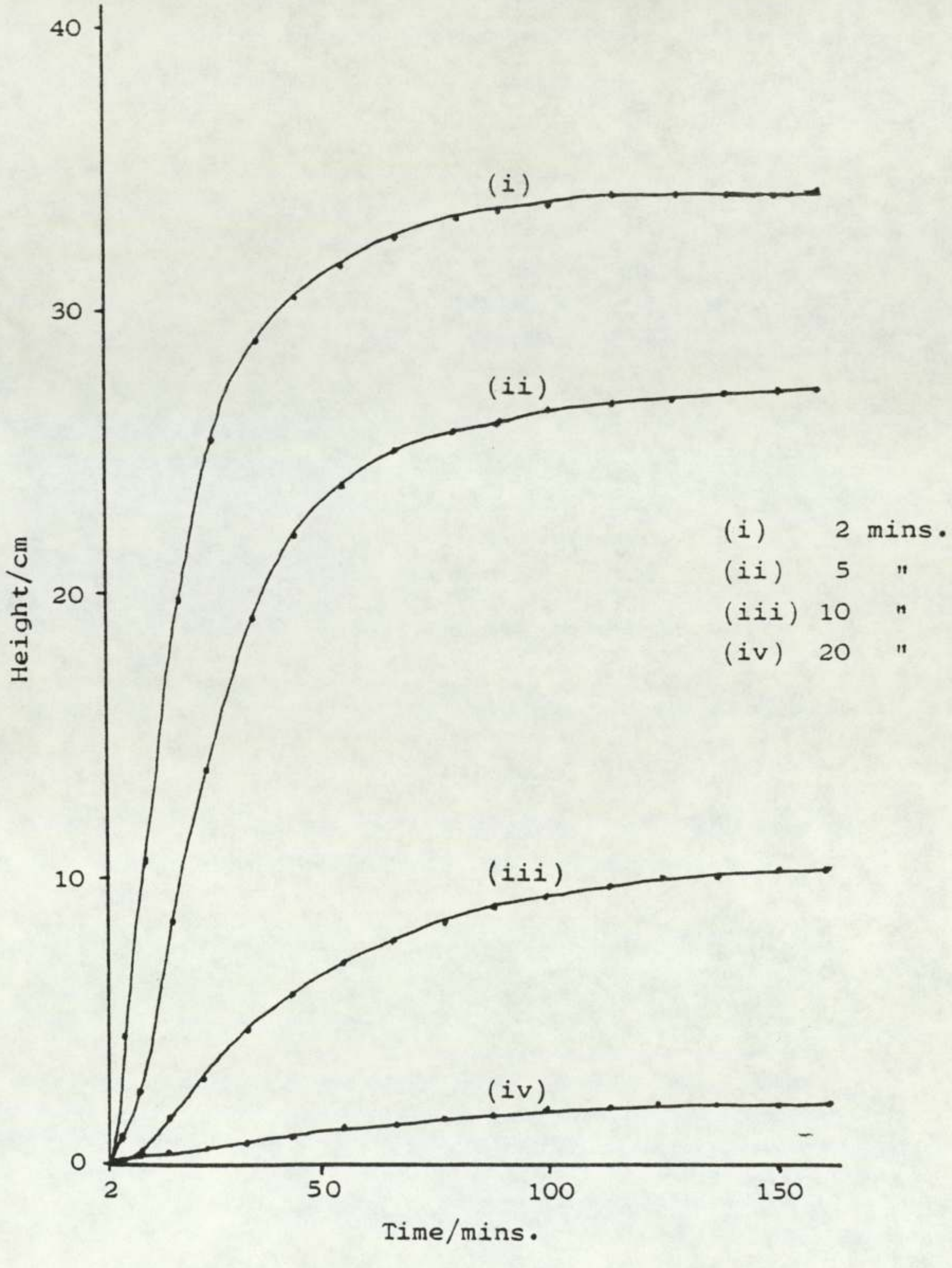
determine the optimum ageing times of additions of WCl_6, PstLi and $AlBr_3$ to cyclopentene. The monomer:W:Li:Al ratio of 1000:1:2:5 was maintained constant and cyclohexane used as the solvent. $6.2cm^3$ WCl_6 solution ($1.49 \times 10^{-2}mol\,dm^{-3}$) was added to $25cm^3$ cyclopentene solution in a dilatometer, followed two minutes later by $1.5cm^3$ PstLi solution ($1.26 \times 10^{-1}mol\,dm^{-3}$). The addition of $2.1cm^3$ $AlBr_3$ solution ($2.21 \times 10^{-1}mol\,dm^{-3}$) to the remainder of the reactants was made at varying intervals of between two and twenty minutes.

Fig. 4.5 shows the conversion curves from this series of experiments, and once again it appears that the catalyst activity decays steadily for additions of the second co-catalyst of more than two minutes ageing time. Further studies are required to determine the activity for much lower ageing times, i.e. below two minutes, in order to establish whether a maximum rate of polymerisation exists. Comparison with curves produced from the analogous LiBu system (fig. 3.8) shows a similar dependence on ageing time. The apparent inactivity of the PstLi system however, after an ageing time of twenty minutes, indicates that at this stage the bimetallic system (WCl_6/PstLi) has formed a species which is not activated by addition of $AlBr_3$, since the rate of polymerisation at the point of addition approaches that without it.

4.2.3 Polymerisation Studies of Premixed Catalyst Systems

Studies of trimetallic premixed systems involving PstLi have

Fig. 4.5 Dependence of Polymerisation of Cyclopentene on Ageing Time of Sequential Addition of Catalyst Components to the Monomer



not previously been undertaken. Gregory(147) carried out experiments to determine the optimum ageing time for the ring-opening polymerisation of cyclopentene, catalysed by the bimetallic catalyst system WCl_6/PstLi, suggesting that a greater rate of polymerisation occurs at an ageing time of six minutes. Presumably a reaction takes place between WCl_6 and PstLi during this period, to produce an active species which reaches maximum concentration at this time.

Studies have been made of the effect of premixing the two cocatalysts, $AlBr_3$ and PstLi, before addition to the WCl_6/monomer solution. On addition of PstLi (orange) to $AlBr_3$ (yellow), a cloudy pale yellow solution resulted, indicative of a reaction occurring between the two. On addition of this premixed solution to WCl_6/monomer (brown) the resultant mixture assumed a pale brown appearance.

4.2.3.i Determination of Optimum Catalyst/Cocatalyst Molar Ratios

In a typical polymerisation reaction 1.8cm^3 WCl_6 (2.61×10^{-2} mol dm^{-3}) was added to 25cm^3 cyclopentene solution (2.36mol dm^{-3}), followed two minutes later by a premixed solution of 1.6cm^3 PstLi (1.84×10^{-2}mol dm^{-3}) and 0.6cm^3 $AlBr_3$ (2.21×10^{-1} mol dm^{-3}). The PstLi and $AlBr_3$ solutions were allowed to react for two minutes before addition to the reactant monomer and catalyst mixture. The monomer:WCl_6 molar ratio was maintained constant at 1000:1 and the W/Li and W/Al molar ratios were varied independently, with cyclohexane used as the solvent. Figs. 4.6 and 4.7 show the conversion curves obtained from the series of reactions achieved by varying the concentrations of PstLi and $AlBr_3$ respectively. From the curves it may be seen that for all ratios of catalyst components the system has very low activity for the polymerisation of cyclopentene when compared with the unmixed system. The shapes of the curves do however follow a similar rate pattern in all cases, i.e. a faster initial rate followed by a rapid decay after approximately fifty minutes. The analogous LiBu based trimetallic system showed a slight decrease in activity for the premixed cocatalyst system, compared with that obtained by adding catalyst components sequentially. For both sequential addition of cocatalysts and premixing lithium compound with $AlBr_3$, the catalyst activity appeared higher when using LiBu rather than PstLi as cocatalyst.

This latter observation might be explained by a reaction occurring between the two cocatalysts PstLi and $AlBr_3$ and/or reaction with WCl_6. The activity of the resulting catalyst depended on whether the tungsten atom bore a Bu or Pst group. From the results however, the system showed that optimum activity was produced with a W/Li/Al molar ratio of 1:2:5. For the corresponding LiBu system the ratio was 1:2:10, though the $AlBr_3$ concentration was not necessarily the optimum, as the rate of polymerisation of cyclopentene was observed to increase with increased $AlBr_3$ concentration, while a W/Al

Fig. 4.6 Dilatometric Polymerisation Curves of Cyclopentene at various Cocatalyst (PstLi) to Catalyst Ratios for a Premixed Catalyst System

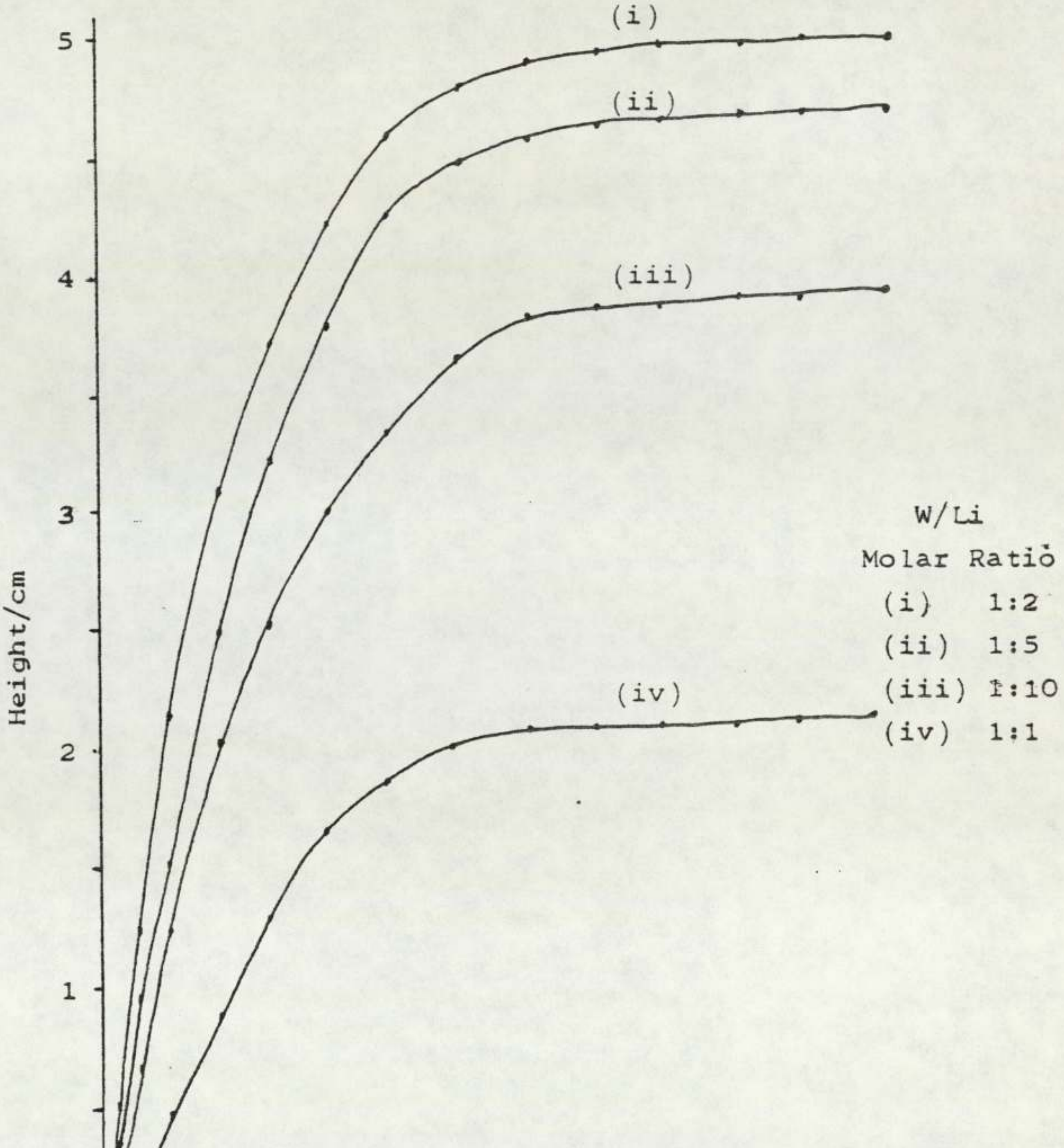
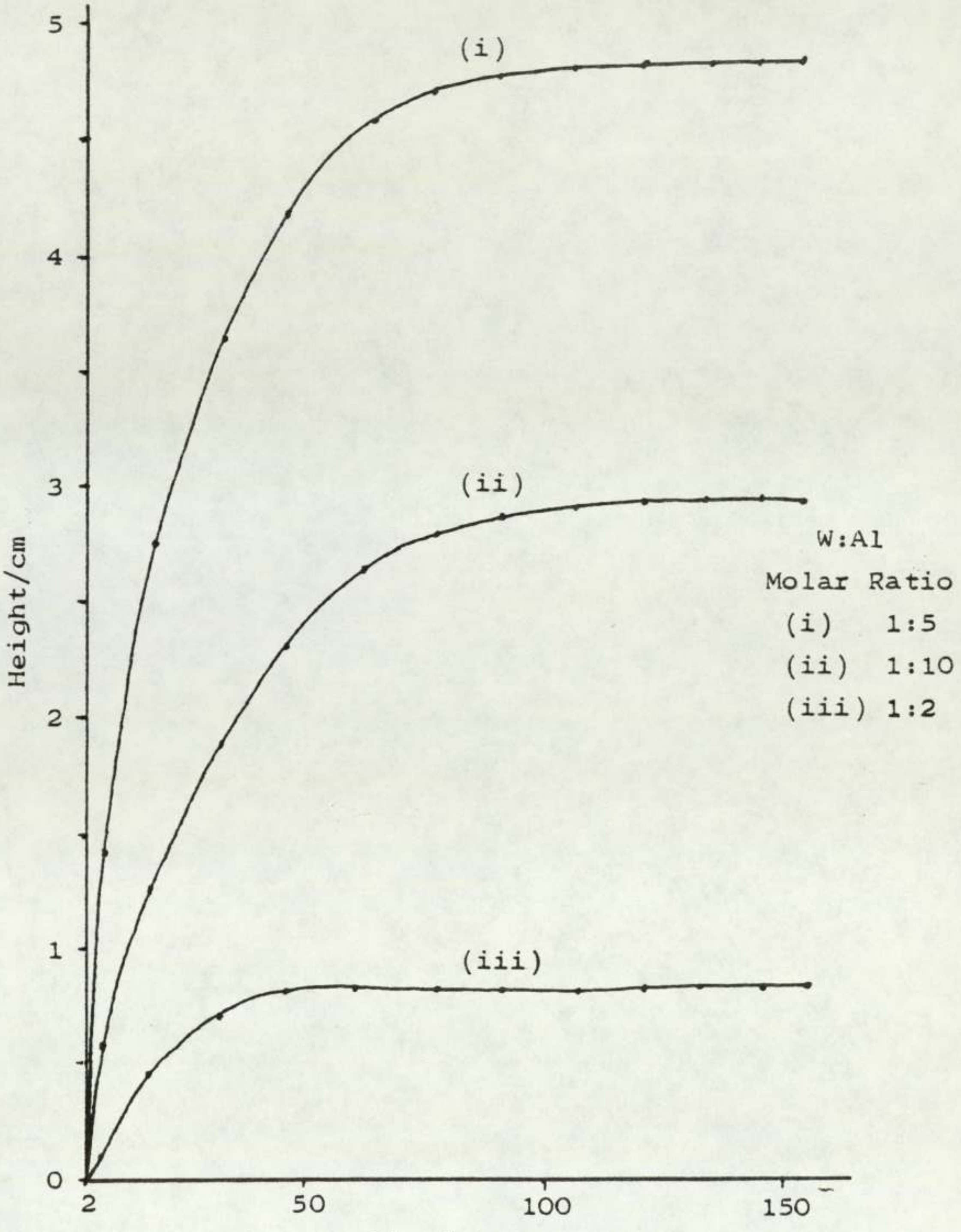


Fig. 4.7 Dilatometric Polymerisation Curves of Cyclopentene at various Cocatalyst ($AlBr_3$) to Catalyst Ratios for a Premixed Catalyst System



molar ratio of 1:10 was the highest studied for that particular series of experiments. From this series however, as all curves are very close together and show little polymerisation activity, it remains uncertain whether a true optimum molar ratio of catalysts exists. The concentration of $AlBr_3$ does not have such a dramatic effect in this case.

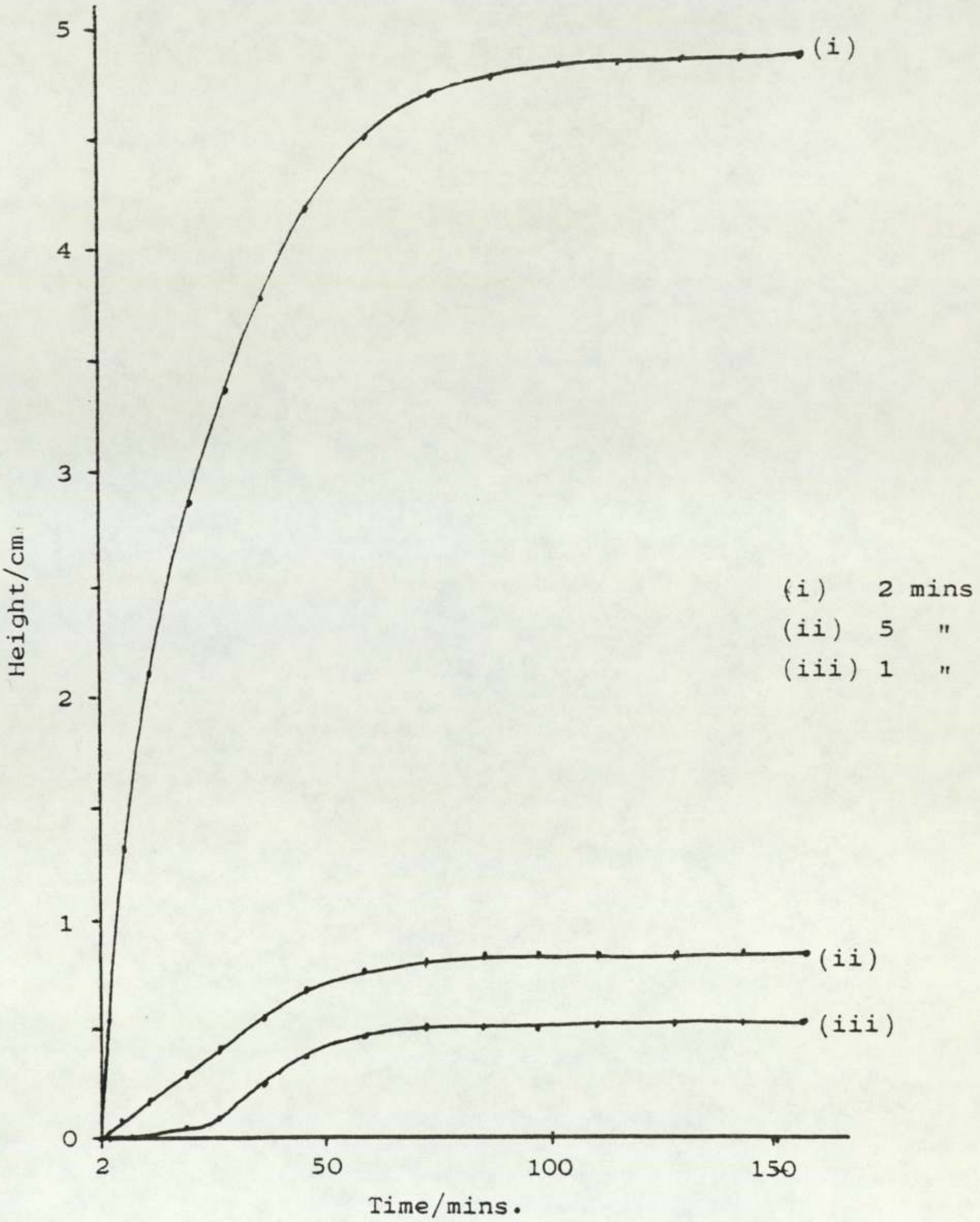
4.2.3.ii Determination of Optimum Premix Ageing Times

Low activity towards cyclopentene polymerisation of the cocatalyst, obtained by premixing PstLi and $AlBr_3$, could have been a product of the time allowed for reaction between the components. Either insufficient time had been allowed for the components to react, or the most active product from a reaction may have decomposed before addition to the WCl_6/monomer solution. A series of experiments was carried out using a constant monomer/W/Li/Al ratio of 1000:1: 2 :5, with varying cocatalyst reaction ageing times from one to five minutes. Fig. 4.8 shows the dilatometer curves resulting from these experiments, and it appears that the system is almost inactive for ageing times other than two minutes. This in turn must suggest that when PstLi reacts with $AlBr_3$ the cocatalyst is a species of short lifetime.

4.2.4 Summary of Cyclopentene Polymerisation by Catalyst System WCl_6/PstLi/$AlBr_3$

The overall rate of polymerisation of cyclopentene appeared

Fig. 4.8 Dependence of Polymerisation of Cyclopentene on Ageing Time of Premixed Addition of Cocatalysts



to be lower than the corresponding LiBu system, particularly when the two cocatalysts were premixed; the resultant activity being similar to that from the bimetallic system WCl_6/LiBu. When added sequentially, maximum activity was observed for a W/Li/Al catalyst molar ratio of 1:2:5, with an interval of two minutes between each addition. But the system was not particularly sensitive to cocatalyst ratios and ageing times close to this range.

Premixing the two cocatalysts produced a system of very low activity, which was highly sensitive to concentration of $AlBr_3$ and ageing time of the cocatalysts. Optimum activity appeared to occur at a W/Li/Al molar ratio of 1: 2 :5, with a premixed ageing time of two minutes.

4.3 POLYMERISATION OF CYCLOPENTENE USING WCl_6/PstLi/$SnCl_4$

Previous studies using the catalyst system WCl_6/LiBu/$SnCl_4$ seemed to produce activity towards cyclopentene polymerisation comparable with that of the corresponding $AlBr_3$ trimetallic system, in which the catalyst components were added sequentially to the monomer. A study was therefore undertaken to investigate the use of PstLi as a cocatalyst in the trimetallic system, using $SnCl_4$ as the second catalyst component.

4.3.1 Dilatometric Determination of Optimum Catalyst/Co-Catalyst Molar Ratios

All the polymerisation reactions were carried out in the dilatometer as described in Section 2.5.1. A monomer/WCl_6 ratio of 1000:1 was maintained constant and the molar ratios of WCl_6/PstLi and $WCl_6/SnCl_4$ varied independently.

In a typical polymerisation, 1.4cm^3 WCl_6 solution (1.49 x 10^{-2}mol dm^{-3}) was added to 25cm^3 cyclopentene solution (3.81 mol dm^{-3}) in bulb (A) of the dilatometer, followed by 3.4cm^3 PstLi (2.39 x 10^{-2}mol dm^{-3}) and 0.6cm^3 $SnCl_4$ solution (1.31 x 10^{-1}mol dm^{-3}) at intervals of two minutes between each. On addition of the colourless $SnCl_4$ to the brown solution of monomer/WCl_6/PstLi, a change to grey/green was observed, in a similar manner to that in the corresponding LiBu system when the change was to a brown/green colour. This indicates that the ligands surrounding the transition metal and/or its oxidation state had been changed by addition of $SnCl_4$.

Figs. 4.9 and 4.10 show the dilatometer conversion-time curves produced when PstLi and $SnCl_4$ concentrations were respectively varied. Here again there was a marked increase in viscosity of the reactant material with time, indicative of rapid polymerisation. But unlike the corresponding LiBu system it was possible to obtain dilatometric curves for all concentrations of cocatalysts studied. Fig. 4.9 shows the optimum PstLi molar ratio with respect to WCl_6 solution as

Fig. 4.9 Dilatometric Polymerisation Curves of Cyclopentene at various Cocatalyst (PstLi) to Monomer Ratios

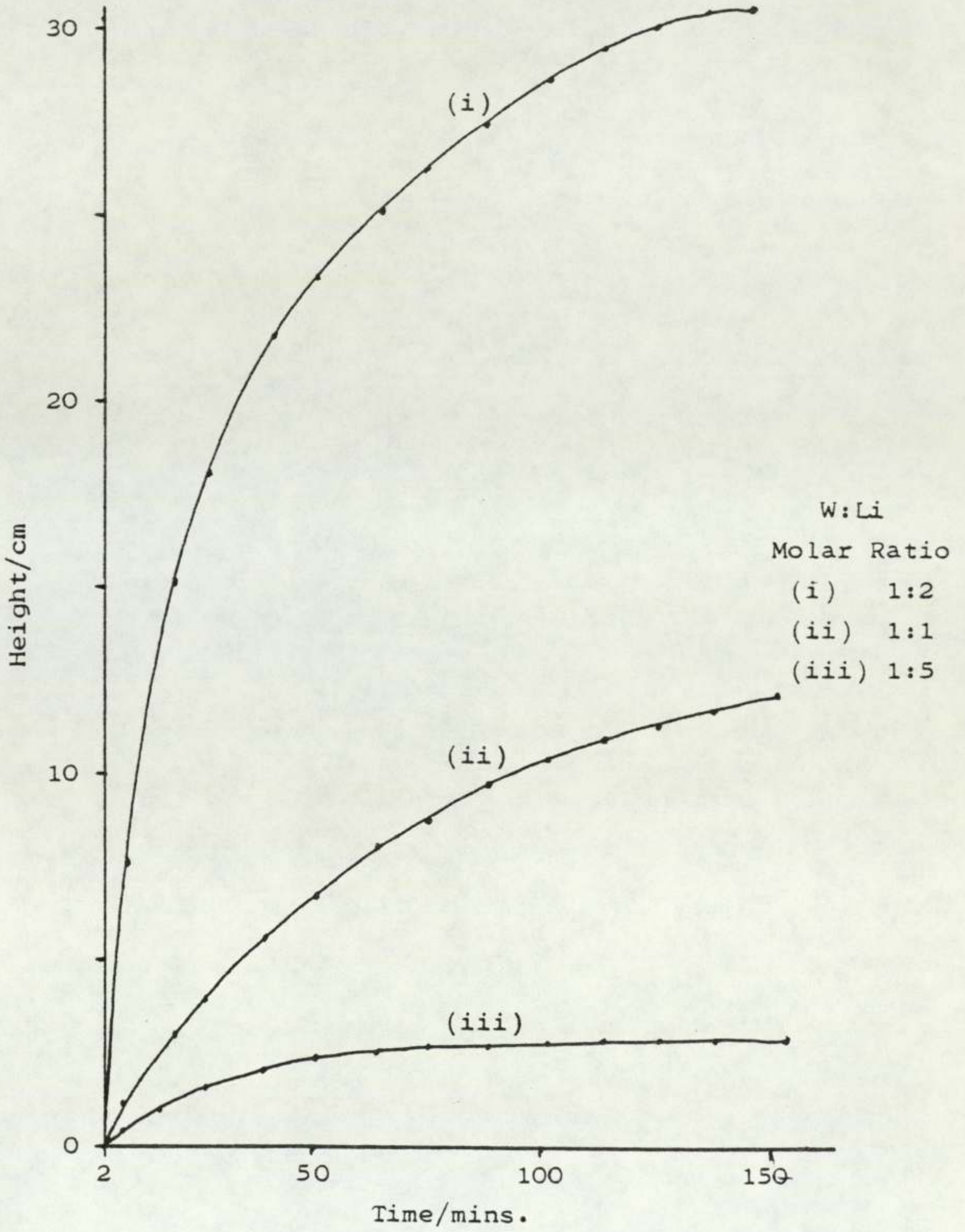
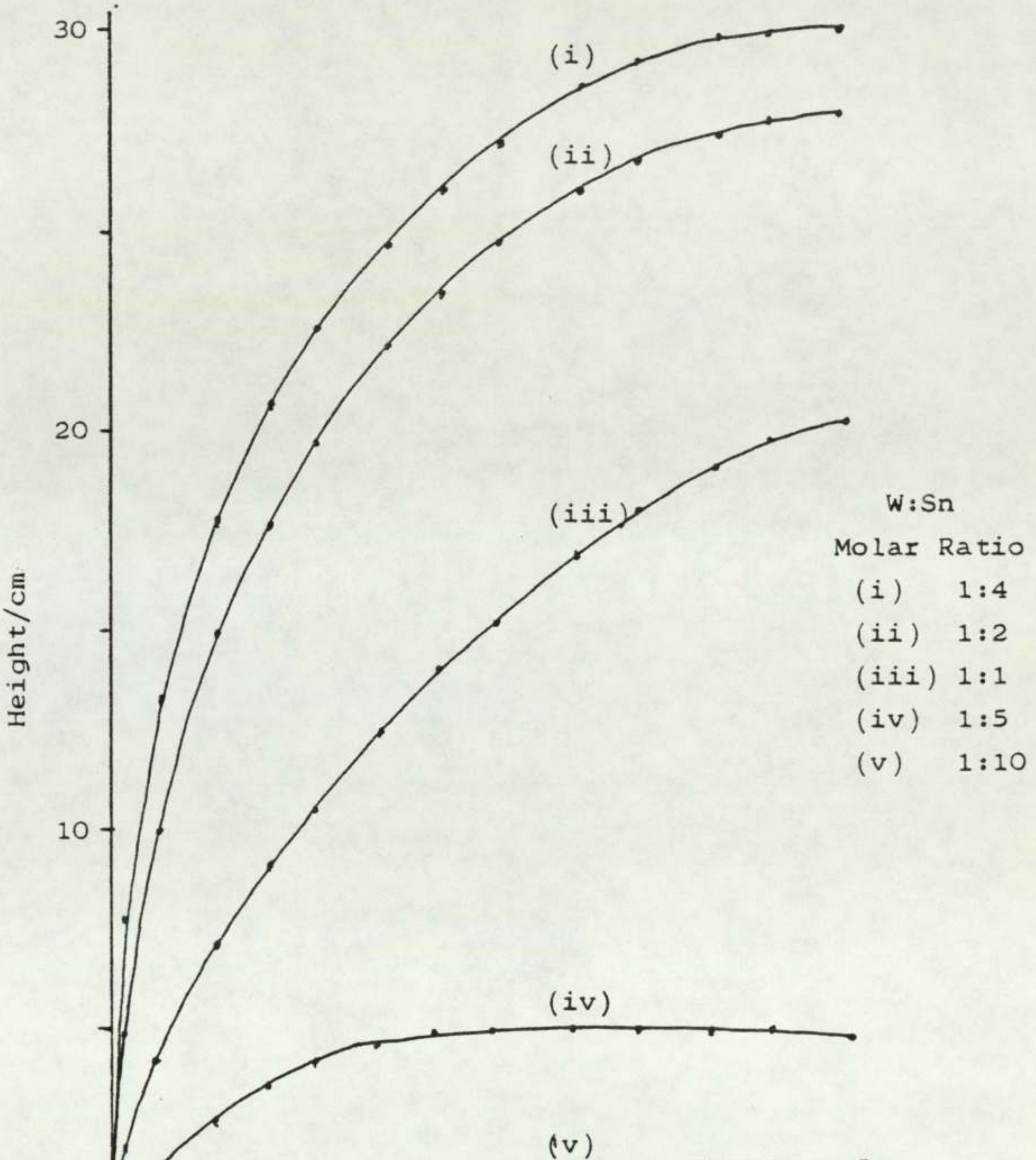


Fig. 4.10 Dilatometric Polymerisation Curves of Cyclopentene at various Cocatalyst ($SnCl_4$) to Monomer Ratios



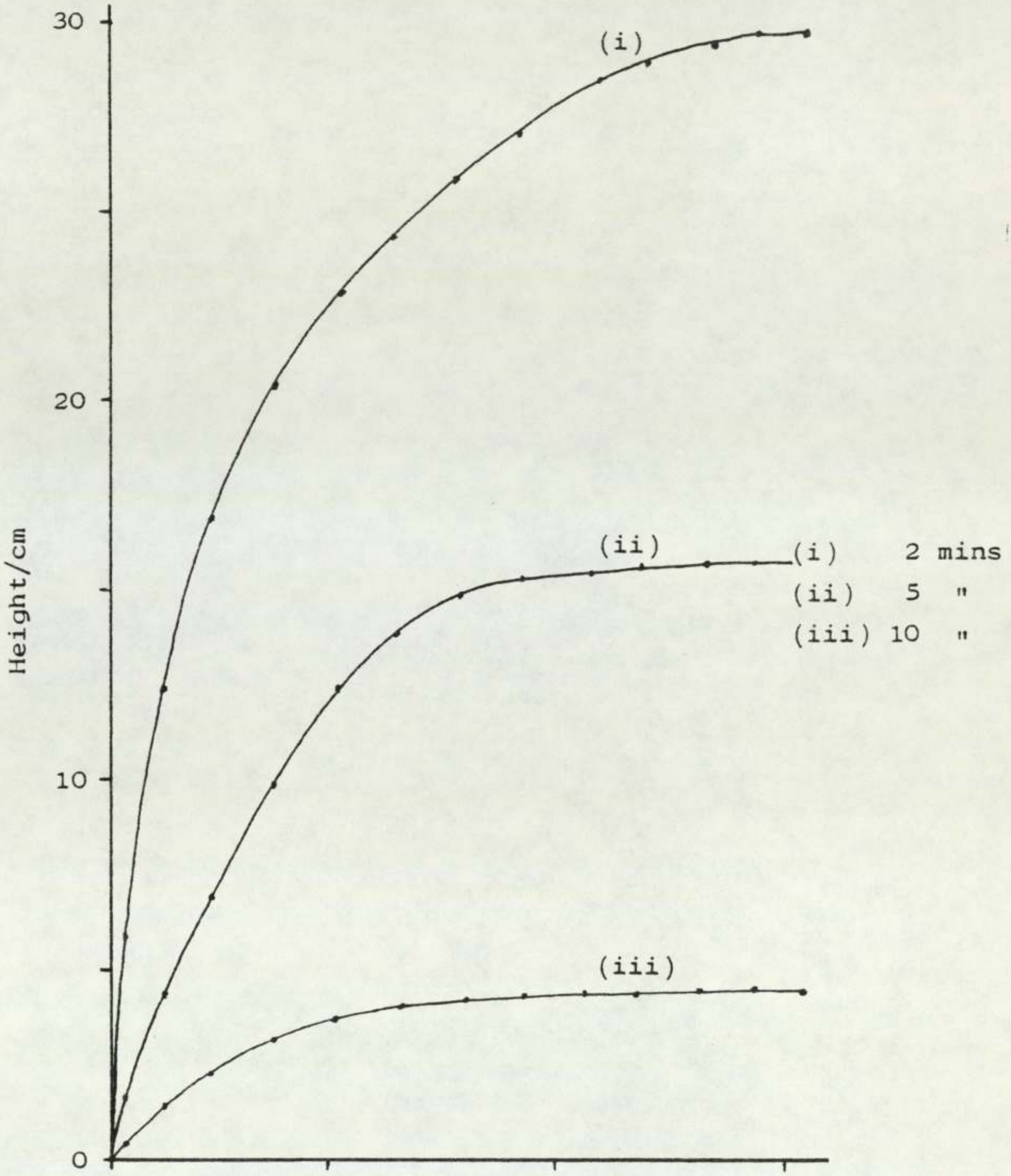
1:2, comparable to the LiBu system, though at lower concentration (W/Li=1:1) the activity decreased rapidly. From Fig. 4.10 optimum W/Sn molar ratio is shown to be 1:4, which compares directly with the analogous LiBu system. Reasonably high activity was shown for the lower W/Sn ratios (W:Sn=1:2,4), but at high concentrations (W:Sn=1:5,10) the initial activity decreased rapidly.

Curves are produced that are similar in shape for both LiBu and PstLi systems, though higher overall activity was apparent in the former case.

4.3.2 Determination of Optimum Time for Sequential Addition of Catalyst Components to the Monomer

Studies were carried out in order to determine the dependence of the rate of polymerisation of cyclopentene on the time interval between additions of $SnCl_4$ and PstLi to the WCl_6/monomer solution. The most active catalyst ratio of W/Li/Sn (1:2:4), as determined from Section 4.3.1, was maintained constant and the time delay between additions of PstLi and $SnCl_4$ varied between two and ten minutes. Fig. 4.11 shows the dilatometer curves for this series of experiments. As with all previous systems a steady decrease in activity of the system is observed with increased time delay. The curves are comparable with the corresponding LiBu curves (fig. 3.15), showing high initial activity at low ageing times (two/five minutes), with rapid deactivation afterwards, particularly for the PstLi system.

Fig. 4.11 Dependence of Cyclopentene Polymerisation Rate on Ageing Time of Sequential Addition of Catalyst Components



The reaction conditions were such that polymerisation could have occurred before the addition of $SnCl_4$ by the WCl_6/PstLi catalyst, but studies of this bimetallic system were not carried out, hence comparisons cannot be made.

4.3.3 Polymerisation Studies of Premixed Catalyst Systems

Premixture of LiBu and $SnCl_4$ was found to produce a system totally inactive towards the polymerisation of cyclopentene. On premixing $SnCl_4$ and PstLi a colourless solution resulted, which turned the dark brown solution of WCl_6/monomer to a pale brown colour. The colour alteration is indicative of a change occurring either in the ligands surrounding the transition metal orin the latter's oxidation state. Polymerisation appeared to be very slow, with little increase in viscosity of the solution, even when left overnight.

4.3.3.i Determination of Optimum Catalyst/Cocatalyst Molar Ratios

In a typical polymerisation, $3.2cm^3$ WCl_6 ($2.83 \times 10^{-2}mol\,dm^{-3}$) was added to $25cm^3$ monomer solution ($3.69mol\,dm^{-3}$), followed two minutes later by a premixed solution of $3.8cm^3$ PstLi ($2.39 \times 10^{-2}mol\,dm^{-3}$) and $1.4cm^3$ $SnCl_4$ solution (1.30×10^{-1} $mol\,dm^{-3}$) of ageing time two minutes. The monomer/WCl_6 ratio of 1000:1 was maintained constant and the concentrations of cocatalyst components employed were varied, to produce a W/Li/Sn ratio of 1:2(4,10):2(4,10). The solvent used was cyclohexane.

Figs. 4.12 and 4.13 show the curves obtained from a series of the dilatometry experiments carried out on the polymerisations of cyclopentene, catalysed by the premixed system WCl_6/PstLi $SnCl_4$, for various concentrations of PstLi and $SnCl_4$ respectively.

From the curves it can be seen that the activity is low in comparison with that for the analogous unmixed system shown in figs. 4.9 and 4.10. The rate of polymerisation appears to be virtually independent of the concentration of PstLi, as in all systems very fast initial rates were observed, followed by rapid decay after approximately one hundred minutes. The maximum activity appeared to occur for a W/Sn molar ratio of 1:4, while activity was lessened by increasing $SnCl_4$ concentration. Further studies are required in order to determine the system's activity at lower molar ratios of WCl_6 to PstLi and $SnCl_4$.

4.3.3.ii Determination of Optimum Premix Ageing Times

The apparently low activity of the premixed catalyst system (PstLi and $SnCl_4$) towards the polymerisation of cyclopentene was possibly due to an ageing time of two minutes proving unsuitable. A series of experiments was therefore carried out using the system of highest activity, as determined from the previous Section (W/Li/Sn = 1:2:4), with cocatalyst premix ageing times of one and five minutes.

Fig. 4.12 Dilatometric Cyclopentene Polymerisation Curves at various Cocatalyst (PstLi) to Catalyst Ratios for a Premixed Catalyst System

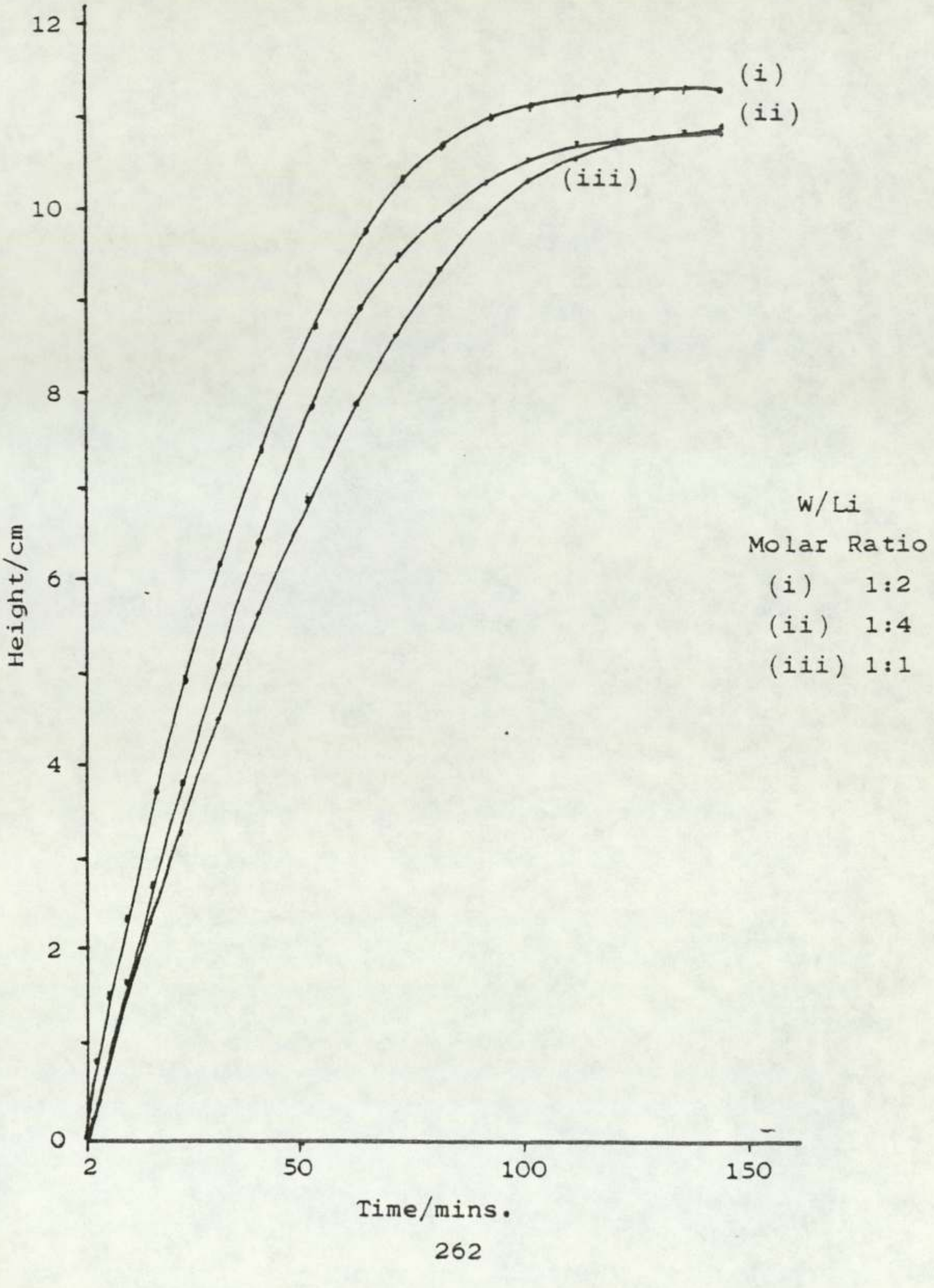


Fig. 4.13 Dilatometric Polymerisation Curves of Cyclopentene at various Cocatalyst ($SnCl_4$) to Catalyst Ratios for a Premixed Catalyst System

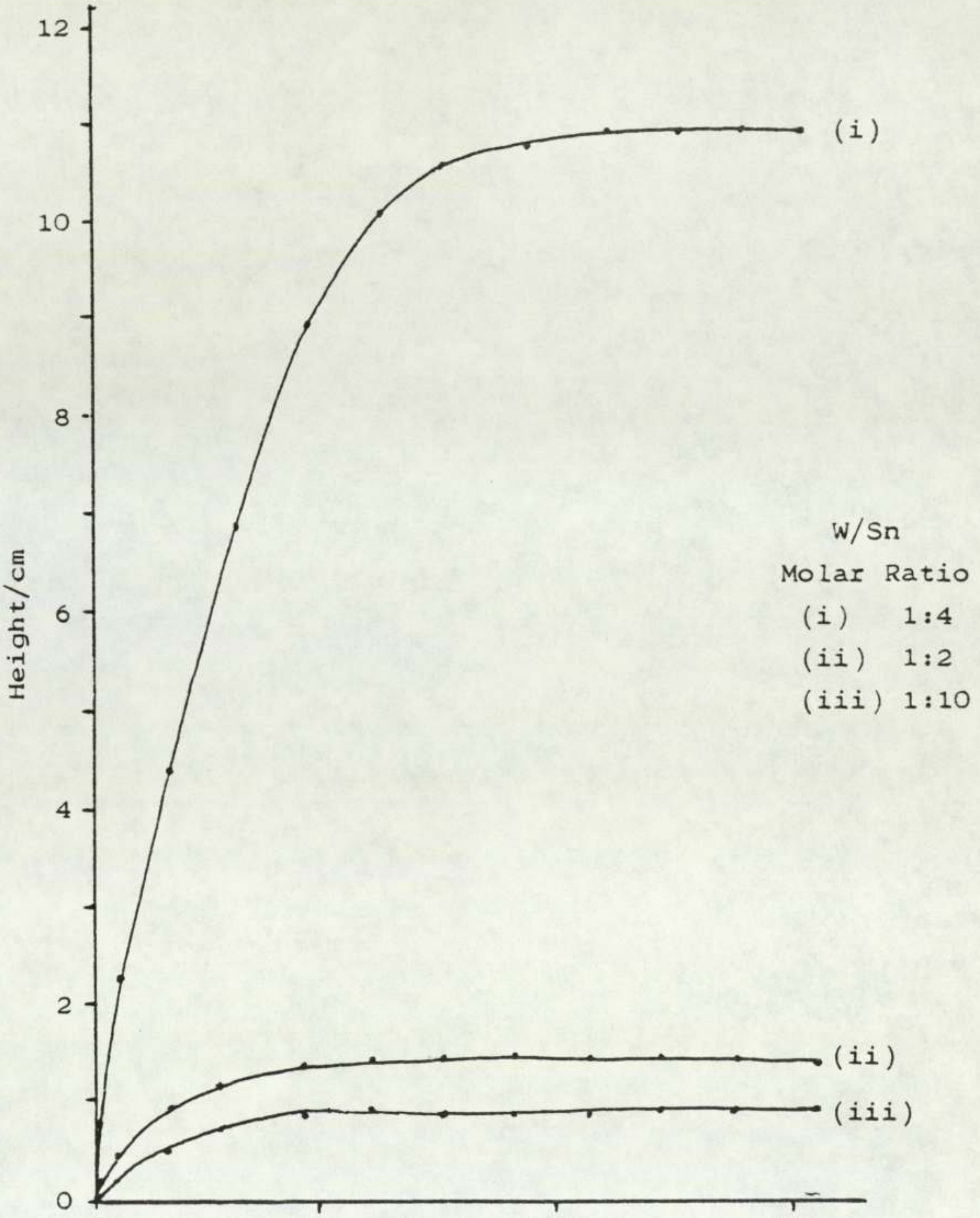


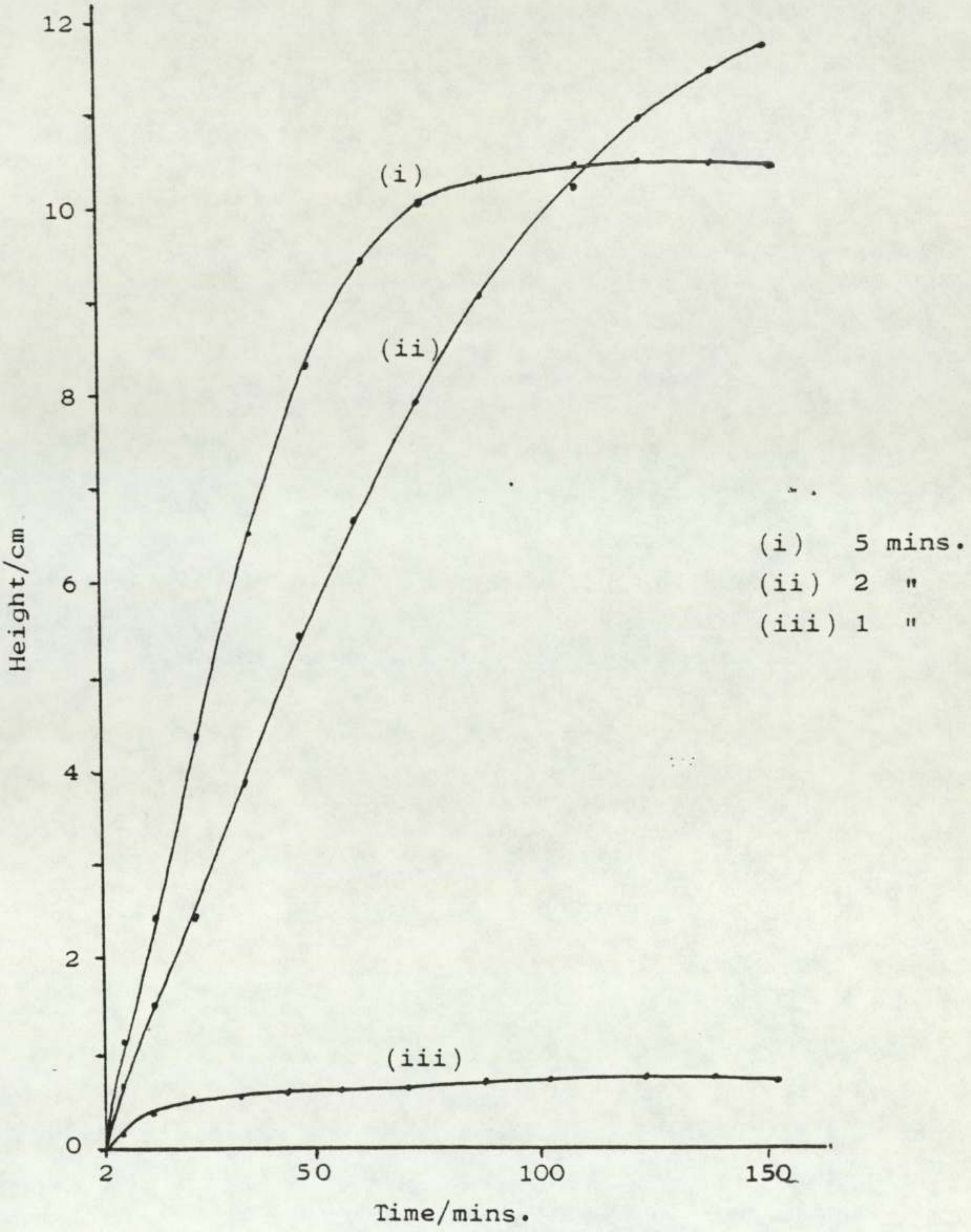
Fig. 4.14 shows the conversion-time curves from these experiments. Very little activity resulted from the premix ageing time of one minute, but for a five minute system activity appeared to increase above that of the two minute system, with a much slower rate of activity decay. Within the five minute period cyclopentene will most likely polymerise by the bimetallic system WCl_6/PstLi, with the active catalyst maintaining activity on addition of $SnCl_4$, resulting in the steady polymerisation of the monomer at a rate differing to that of a trimetallic catalyst system.

4.3.4 Summary of Cyclopentene Polymerisation by the Catalyst System WCl_6/PstLi/$SnCl_4$

When catalyst components were added sequentially the rate of polymerisation was relatively high, showing similar activity to the corresponding LiBu system. An optimum molar ratio of W/Li/Sn of 1:2:4 was shown, with two minute intervals between additions, which correlated with that for the LiBu system. The system showed high tolerance towards variations in the concentration of $SnCl_4$, but to a lesser extent for PstLi deviations.

Premixing the two cocatalysts appeared to halve the activity of the unmixed system, the rate of polymerisation showing great sensitivity to changes in the optimum molar ratio of catalyst components (W/Li/Sn = 1:2:4), and the ageing time (two minutes) of the two cocatalysts.

Fig. 4.14 Dependence of Cyclopentene Polymerisation on Ageing Time of Premixed Addition of the Cocatalysts



4.4 MOLECULAR WEIGHT STUDIES

4.4.1 Introduction

The use of GPC to distinguish between block polymers and homopolymers has been discussed in Section 2.6.1. Previous studies have shown that PstLi cocatalyst in a bimetallic system WCl_6/PstLi plays a significant role in generating the active species for metathesis, i.e. the transition metal carbene(147). Dilatometric studies reported in preceeding sections have shown that Lewis acids, $SnCl_4$ and $AlBr_3$, greatly affect the rate of cyclopentene polymerisation. In deciding the role played by these compounds in the generation of active sites, it would be useful to determine whether the products of the polymerisation reactions are block copolymers of polystyrene and polypentenamer, or mixtures of homopolymers.

The analysis requires the use of the dual detector feature of the gel permeation chromatograph, to establish whether polyalkenamer chains are associated with any polystyrene chains from the cocatalyst.

4.4.2 Analysis of the PstLi Cocatalyst

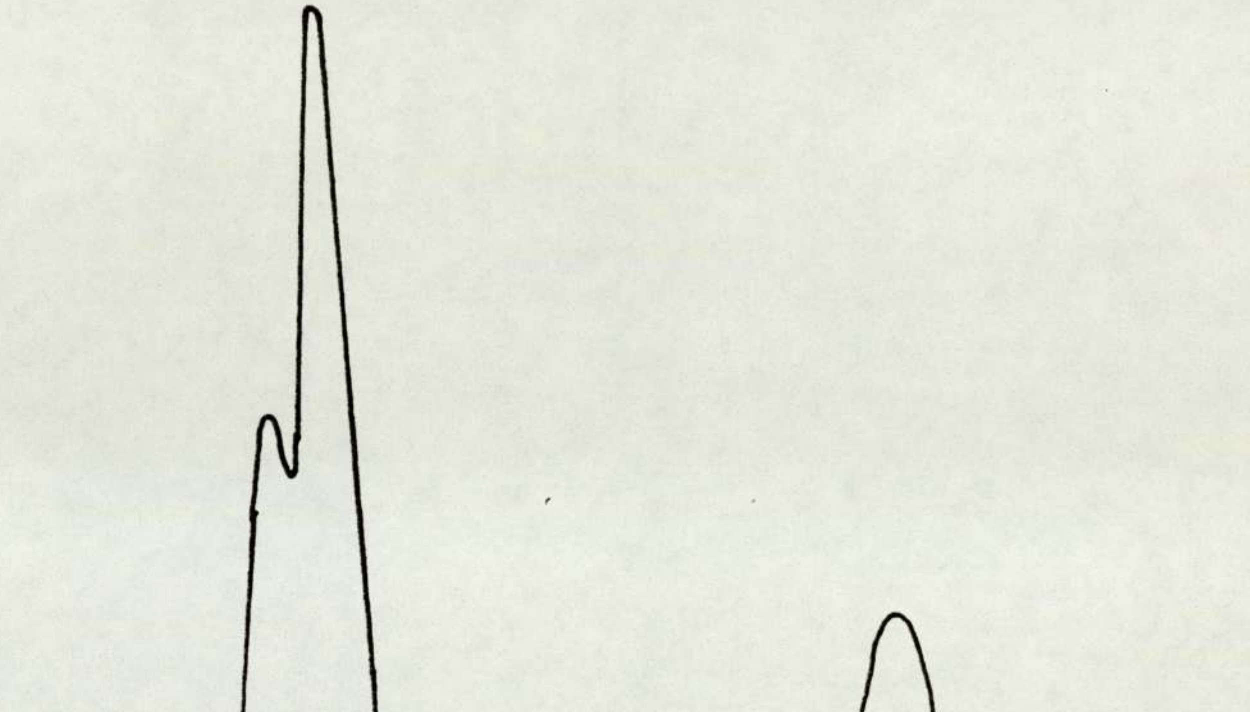
Before any meaningful analysis could be carried out on the products of metathesis the molecular weight average of the PstLi cocatalyst had to be known. A small quantity ($20cm^3$) of PstLi solution, prepared as described in Section 2.4.5, was added to methanol. The resulting polymer was separated, dried and redissolved in THF as a 2% solution suitable for GPC analysis. Fig. 4.15 shows the resultant RI/UV chromatograms of a typical product, a bimodal distribution being observed rather than a single peak. The PstLi cocatalyst prepared by Gregory(147) showed a broader molecular weight distribution. This was obtained from using n-LiBu as the initiator, whereas the current narrower distribution samples were prepared from use of the more reactive initiator s-LiBu. Molecular weight distributions of this type are not uncommon in anionic polymers, arising most probably during destruction of the active sites with methanol. Unless the solvent is purged with nitrogen prior to its addition to the living polymer solution, dissolved oxygen in the methanol will react with the living end of the polymer in such a way producing a polystyryloxy free radical, which combines with another free radical, so doubling the molecular weight.

$$\mathrm{Ps\bar{t}Li^{+}} + \mathrm{O_2} \longrightarrow \mathrm{PstO\cdot} \longrightarrow \mathrm{Pst\text{-}\dot{O}\text{-}O\text{-}Pst\cdot}$$

The values for $\bar{M}n$ and $\bar{M}w$ were found to be 1.33×10^4 and 2.52×10^4 respectively.

By using PstLi as a cocatalyst, Gregory(147) polymerised cyclopentene and produced a copolymer of similar molecular weight to that of polypentenamer obtained during a normal ring-opening polymerisation reaction, using the same bimetallic system. A second peak, contributing to the bimodal

Fig. 4.15 Gel Permeation Chromatograms of Polystyryllithium



molecular weight distribution corresponded with that of the polystyrene blank, from analysis of the cocatalyst.

GPC studies have been carried out on the products formed from ring-opening polymerisation of cyclopentene, catalysed by the trimetallic systems $WCl_6/PstLi/AlBr_3$ and $WCl_6/PstLi/SnCl_4$, to determine the dependence of molecular weight distribution of products on the reaction conditions employed.

4.4.3 Polymerisation of Cyclopentene Catalysed by $WCl_6/PstLi/AlBr_3$

GPC analyses, using both UV and RI detectors, were carried out on samples of polymer produced from experiments in which ratios of catalyst components and delay times of their addition were varied. The products were obtained during the course of polymerisation by sampling, as described in Section 2.5. In all the following chromatograms, the UV response is represented by a dotted line superimposed on the RI response, which is shown as a continuous line.

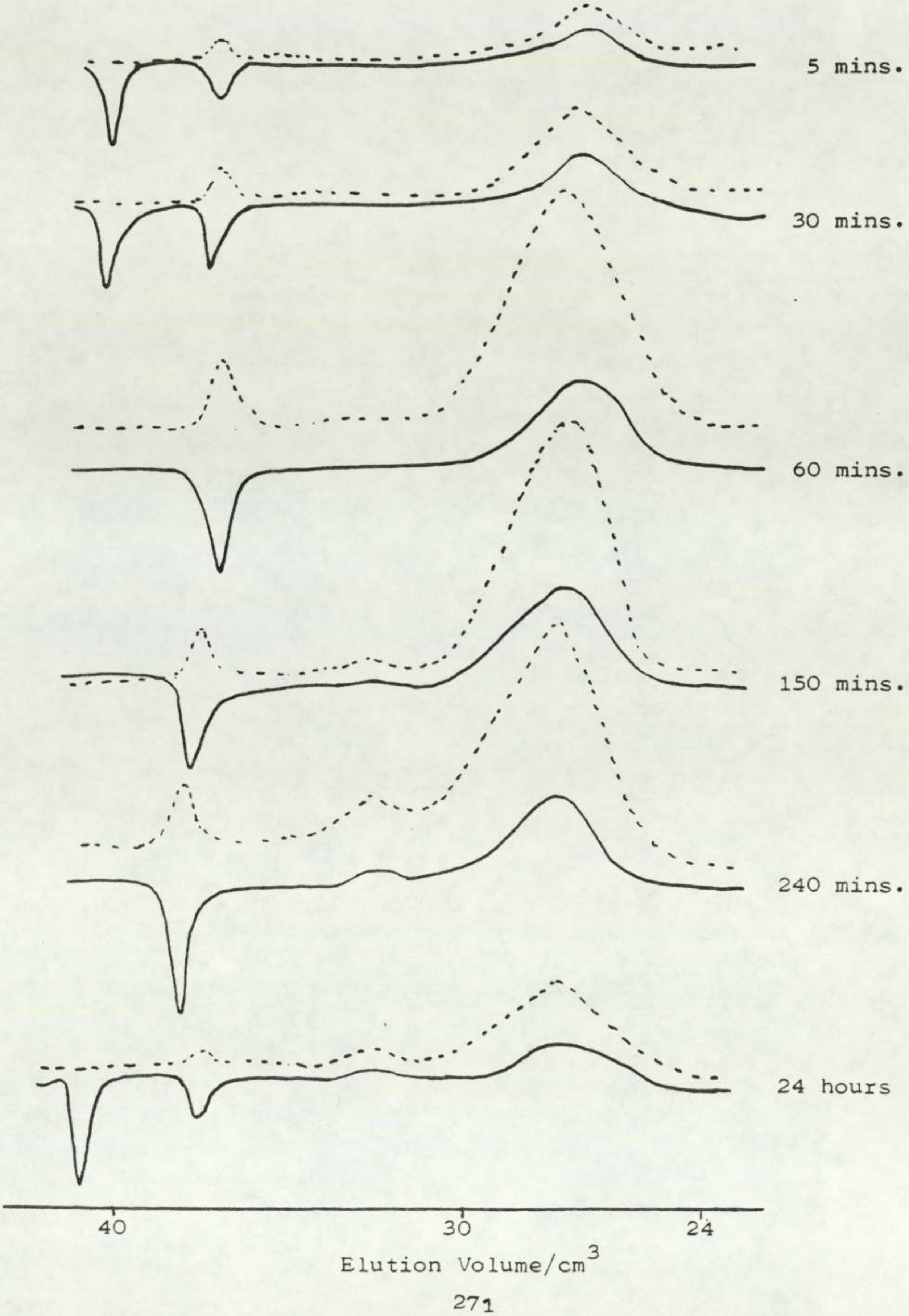
4.4.3.i Sequential Addition of the Catalyst Components

The results from the analogous LiBu system experiments are described in Section 3.6. It was noted that throughout the course of polymerisation, molecular weight distribution changed until equilibrium distribution was reached after 24 hours. Samples of polymer taken during polymerisation of cyclopentene, using WCl_6/PstLi/$AlBr_3$ as the catalyst in a 1:2:2 molar ratio, were analysed by GPC. Fig. 4.16 shows results from these samples taken after five, thirty, sixty, 150 and 240 minutes, and also 24 hours of reaction time.

If the gel permeation chromatograms shown in fig. 4.16 are compared with those obtained from the corresponding WCl_6/LiBu/$AlBr_3$ catalyst system, it is immediately obvious that the former are much simpler. In the early stages of the reaction the product has a molecular weight distribution showing a peak with maximum response at $26.7cm^3$, together with a peak in the low molecular weight region at $35.2cm^3$. A particularly interesting feature of these chromatograms is the combination of UV and RI detector responses.

It has already been shown that polypentenamer does not absorb at 254nm - the wavelength of light used in the UV detector, so the response recorded in the region of $26.7cm^3$, by the UV and RI detectors, must have resulted from the presence of a chromophore in the polymer eluting at that time. A probable explanation is that the latter is a block copolymer of polystyrene and polypentenamer, with the polystyrene segment providing the chromophore which responds to the UV detector. The polymer eluting at $26.7cm^3$ could not have been polystyrene derived from the PstLi cocatalyst, since previous analysis has shown this eluting at $33.5cm^3$.

Fig. 4.16 GPC Chromatograms of Block Copolymer Produced During the Course of Reaction



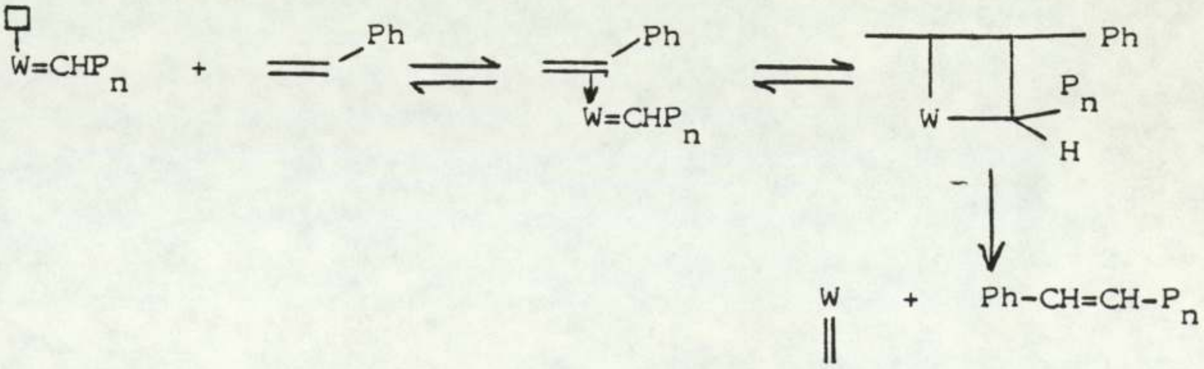
The polymer molecular weight distribution did not change significantly with conversion during the first 60 minutes of polymerisation. The increased significance of a peak between 31.5cm^3 and 35.0cm^3 at long reaction times is almost certainly due to production of polystyrene, which at most will be associated with oligomers of polypentenamer units and derived from random chain scission reactions.

Peaks appearing at 34.8cm^3, which seem to be present as a constant proportion of the product, show some indications ascribed to oligomers, i.e. a negative RI response. But in these cases absorption in the UV suggests the material possesses an aromatic chromophore. Only two sources of such chromophores were present in the polymerisation system:-

i) polystyrene, or unreacted styrene monomer, derived from the PstLi solution,

ii) toluene, which had been used as a solvent for the co-catalyst $AlBr_3$.

If absorption was derived from unreacted styrene present, it could have occurred in a metathesis of a growing polymer chain with styrene, by way of:-



The catalyst was however living PstLi, and it would be reasonable to expect the concentration of free styrene at equilibrium to be extremely low, with depolymerisation of the polystryl anion, before its reaction with $AlBr_3$ or the tungsten compound, not expected. A most likely explanation for the formation of low molecular weight UV absorbing species therefore, is its derivation from the reaction of toluene with either a propagating centre, or with a by-product of the reaction.

From the results it seems probable that only one propagating species was present for the whole reaction period, producing a copolymer of molecular weight between the values for polypentenamer and polystyrene (from the PstLi cocatalyst). Slow depolymerisation with time slightly lowered the molecular weight of the copolymer, possibly with respect to the polystyrene units, since the gradual formation of pure polystyrene was later observed.

Figs. 4.17 and 4.18 show a series of gel permeation chromatograms of polymer samples produced at various concentrations of the PstLi and $AlBr_3$ cocatalysts. From fig. 4.17 it can be seen that the resulting molecular weight distribution at low concentrations of PstLi (W:Li = 1:1), shows an important difference from other products. Two features of the curve are significant:-

i) the block copolymer shows a much lower molecular weight than those formed by higher concentrations of PstLi,

ii) the product also contains polymer which is apparently not a block copolymer, because the peak which appears around 26.5cm^3 does not have a strong UV absorbance associated with it.

A discussion of the polymerisation mechanism may therefore have to take account of the fact that not all metathesis sites, for the ring-opening polymerisation of cycloolefins, necessarily require presence of a metal alkyl to provide a metal carbene. This conforms with a disclosure some years ago by Marshall and Ridgewell$^{(43)}$, that metal alkyl-free systems may be used to initiate ring-opening polymerisation of cyclo-octadiene.

Table 4.1 shows the positions of the major peaks for samples obtained by using varying monomer:catalyst (PstLi) molar ratios.

Table 4.1 Elution Volumes of Polymer produced at various PstLi to Catalyst Molar Ratios

WCl_6:PstLi Molar Ratios	Elution Volume of Peaks/cm^3
1:1	26.5, 29.5, 34.0
1:2	26.2, 31.3
1:5	26.5, 33.3
1:10	26.7, 31.8 - 33.5

Fig. 4.17 GPC Chromatograms of Block Copolymer Produced at Various Concentrations of PstLi

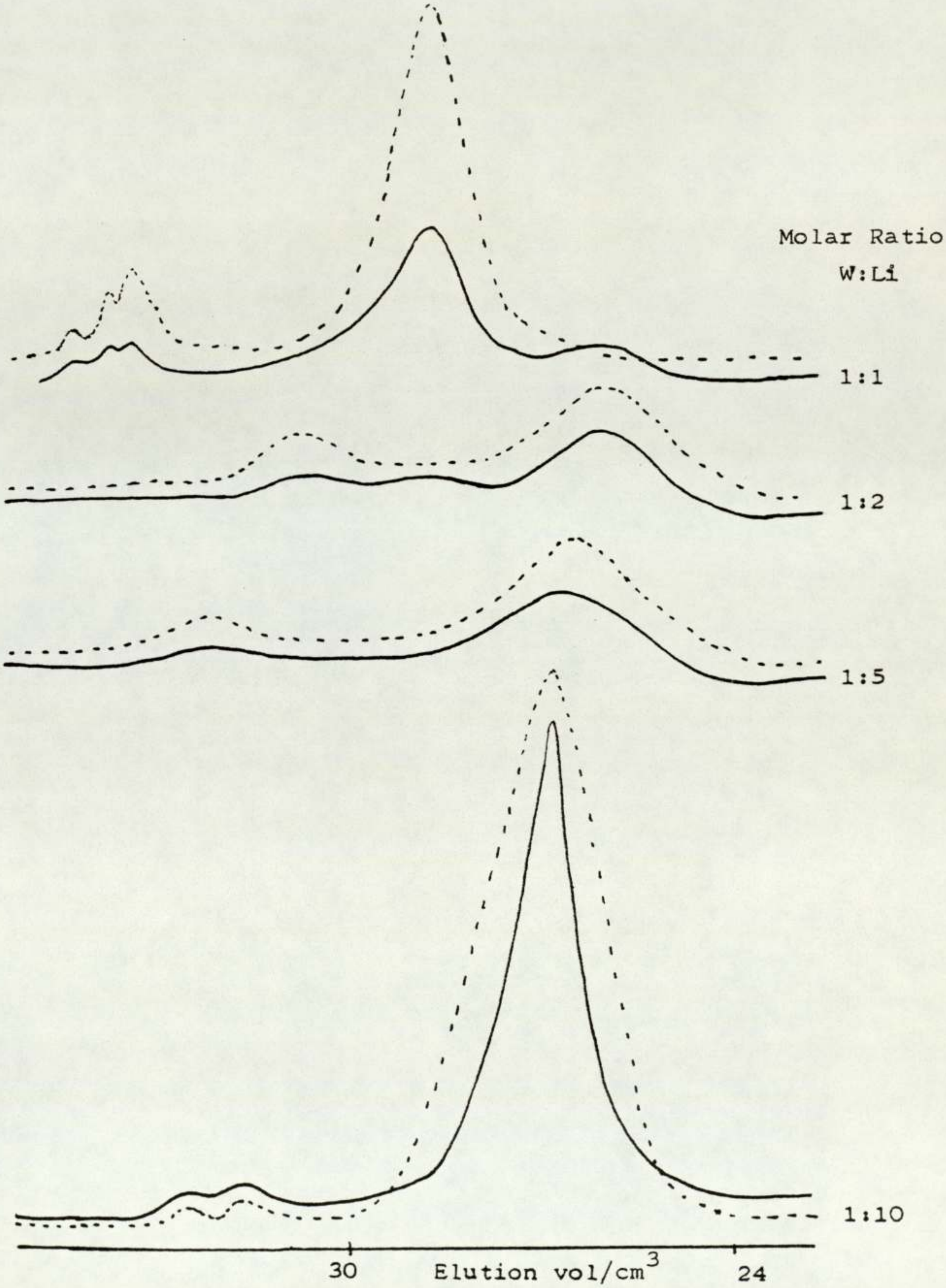
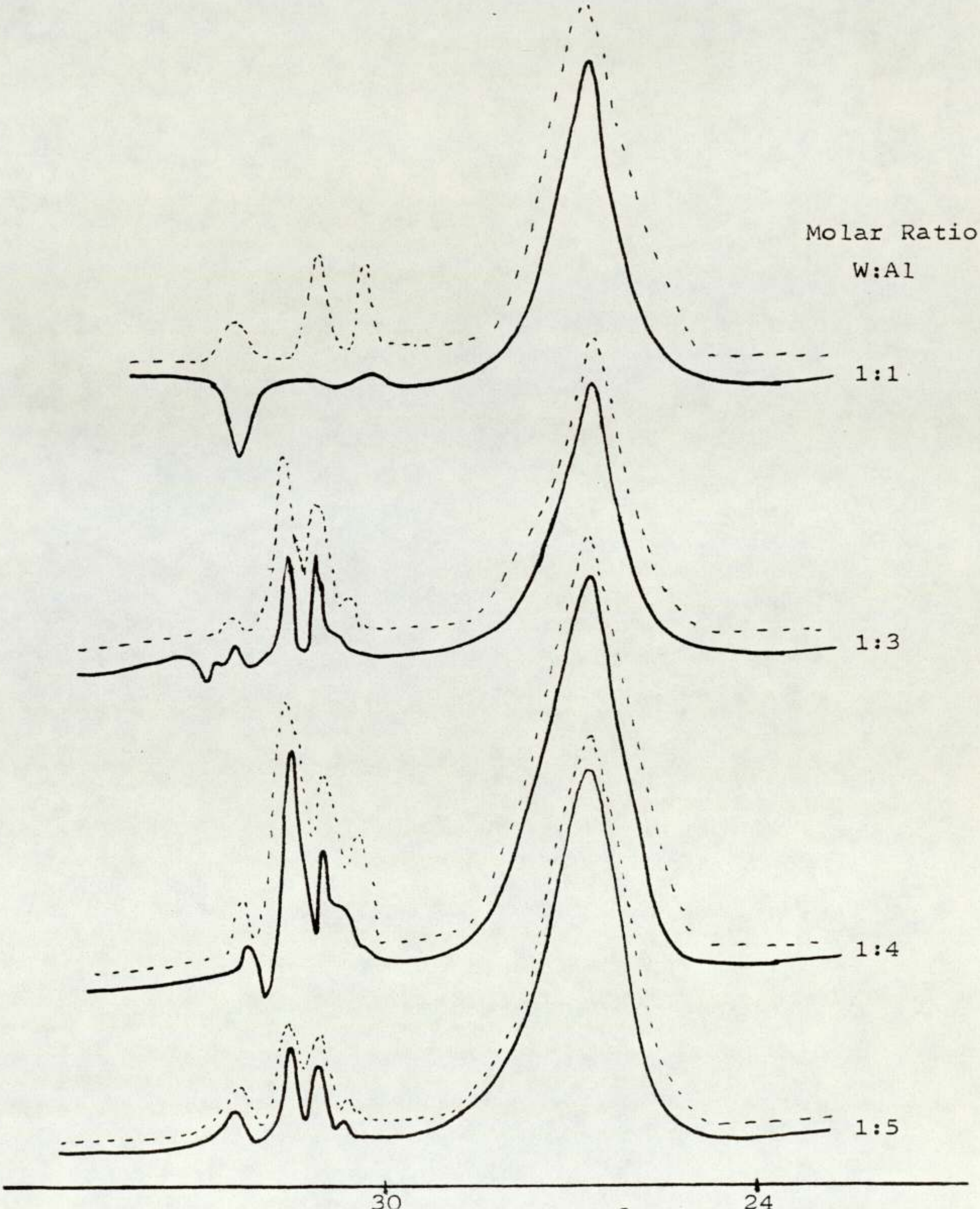


Fig. 4.18 GPC Chromatograms of Block Copolymer Produced at Various Concentrations of $AlBr_3$



As the concentration of PstLi was increased to a W:Li molar ratio of 1:2 and above, the chromatograms were essentially similar in nature. From Table 4.1 it was apparent that positions of the principal peaks did not change significantly with concentration of PstLi, but there was a tendency towards a much sharper molecular weight distribution at higher concentrations.

It should be noted that these chromatograms were recorded at identical attenuations of the detectors, being apparent in each case that the relative heights of the UV and RI peaks increase with greater molecular weight of the block copolymer. This is readily accounted for from the polystyrene proportion of the polymer decreasing with increasing molecular weight.

Fig. 4.18 shows GPC chromatograms of samples obtained from the polymerisation of cyclopentene using WCl_6/PstLi in a molar ratio of 1:2, while varying molar ratio of $AlBr_3$ to monomer (x:1000). It appears that a copolymer was present at an elution volume of 27.6cm^3, totally independent of the concentration of $AlBr_3$. The lower molecular weight species, which were observed after an elution volume of 30.0cm^3, differed slightly and their positions and corresponding polystyrene molecular weights are grouped in Table 4.2.

Table 4.2 Elution Volumes of Polymer Produced at Various $AlBr_3$ to Catalyst Molar Ratios

$WCl_6:AlBr_3$ Molar Ratio	Elution Volume (cm^3)	Polystyrene Equivalent $/10^3$
1:1	30.2	6.0
	30.9	4.5
	32.3	2.2
1:3	30.3	6.2
	30.9	4.5
	31.4	3.3
	32.2	2.4
1:4	30.2	6.0
	30.8	4.7
	31.4	3.3
	32.2	2.4
1:5	30.6	5.2
	31.0	4.3
	31.5	3.2
	32.4	2.0

It appears that some of the figures correspond directly with the elution volume from the polystyrene in polystyryllithium.

From fig. 4.15 it may be seen that polystyrene from the PstLi cocatalyst also elutes at a volume of 32.7cm. Most of the polymer species in the lower molecular weight region of the chromatograms were eluted at volumes between these values (fig. 4.18) and it is likely therefore that the species may be attributed to the polystyrene chain of any unreacted PstLi cocatalyst, the proportion of which is dependent upon the concentration of $AlBr_3$. Although no peaks correspond to an exact multiple of the original polystyrene molecular weight, there appear to be increases of up to almost one and a half times the original weight in all cases. This may be due to continued anionic polymerisation of PstLi under the catalytic conditions employed. The absence of peaks at an elution volume of 32.7cm^3 further supports this theory, as polystyrene chains from the original PstLi appeared to have been completely fragmented, or further polymerised to produce higher molecular weight material. The latter seems more likely, since there is a general trend in that region to produce polymers of increased molecular weight.

It can be seen from fig. 3.18, that the time delay between the addition of $AlBr_3$ to a solution of cyclopentene/WCl_6/LiBu did not appear to greatly affect the molecular weight distribution of polypentenamer. Samples from the analogous PstLi were analysed by GPC and the results are shown in fig. 4.19. The molar ratio of catalyst components found to be the optimum (W:Li:Al = 1:2:2), was maintained constant for these experiments, while time delay between addition of $AlBr_3$ to the remainder of the system was varied between two and ten minutes.

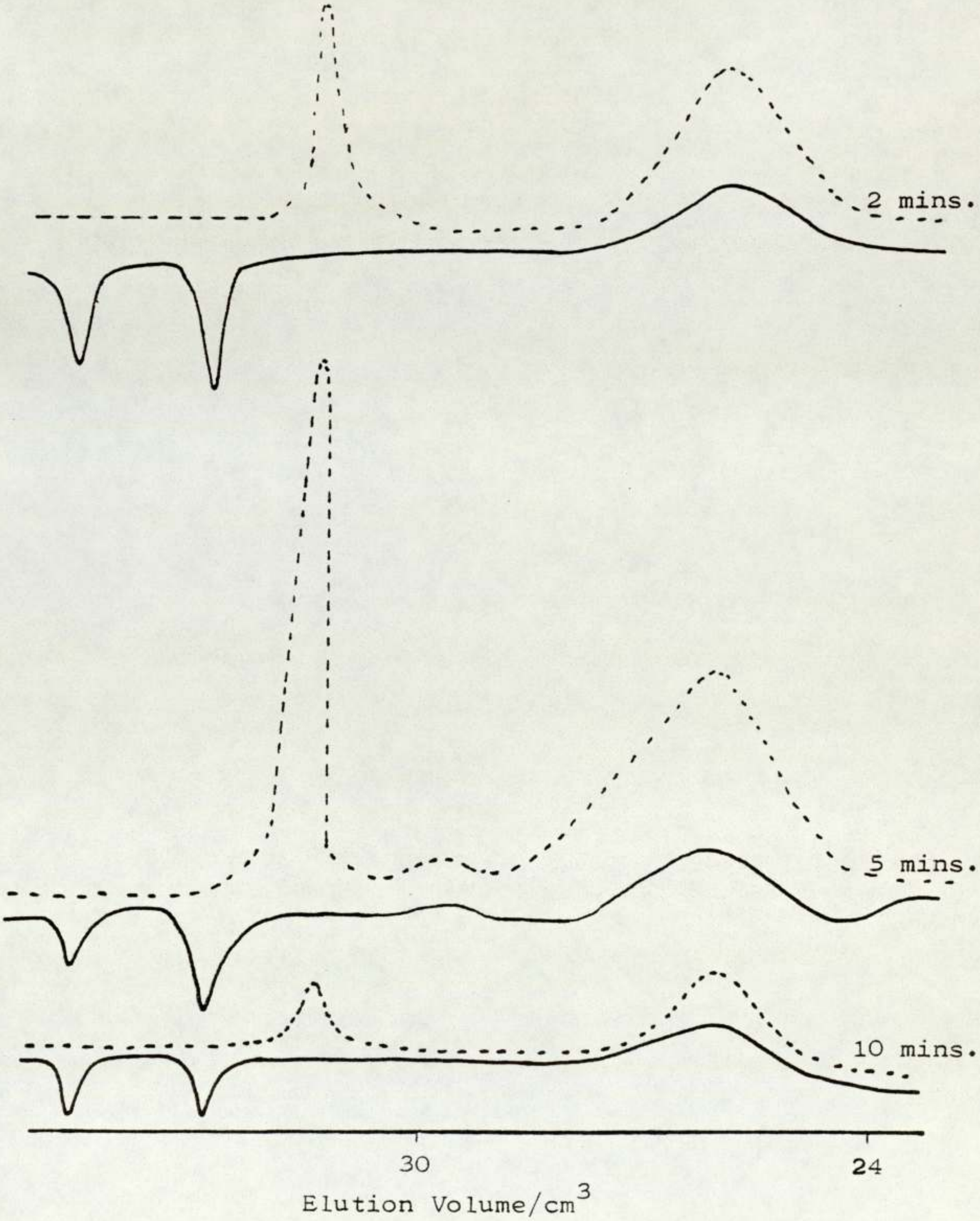
For a two minute delay a single polymeric species was produced, which eluted at a volume of 26.1cm^3. This polymer was present irrespective of the time delay between catalyst addition, unlike the catalyst molar ratio dependence (figs. 4.17 and 4.18), where a slight shift in molecular weight was observed. The oligomer distribution between 31.0cm^3 and 35.0cm^3 also remained constant with time delay. For a five minute delay however, the molecular weight distribution differed, in that a high molecular weight polymer eluted at 23.6cm^3. This was probably due to polypentenamer, as there was no corresponding UV response in this region. A second lower molecular weight species was also observed at 29.7cm^3, which could have been due to polystyrene derived from unreacted and/or deactivated PstLi.

These results are comparable with those from the analogous LiBu system (fig. 3.18), where molecular weight distribution also showed little dependence on delay periods of catalyst additions. It may therefore be inferred that in all cases active catalyst species are the same, though obviously the concentration changes with delay period, as demonstrated by the effect on rate of polymerisation (fig. 4.5).

4.4.3.ii Premixed Addition of Catalyst Components

Fig. 4.20 shows the molecular weight distribution dependence of polymer on concentration of PstLi for a premixed catalyst system. In all cases a bimodal pattern was observed for high molecular weight material, together with a peak corresponding to oligomeric material. Table 4.3 summarises

Fig. 4.19 GPC Chromatograms of Block Copolymer at various Delay Times between Addition of $AlBr_3$ to PstLi



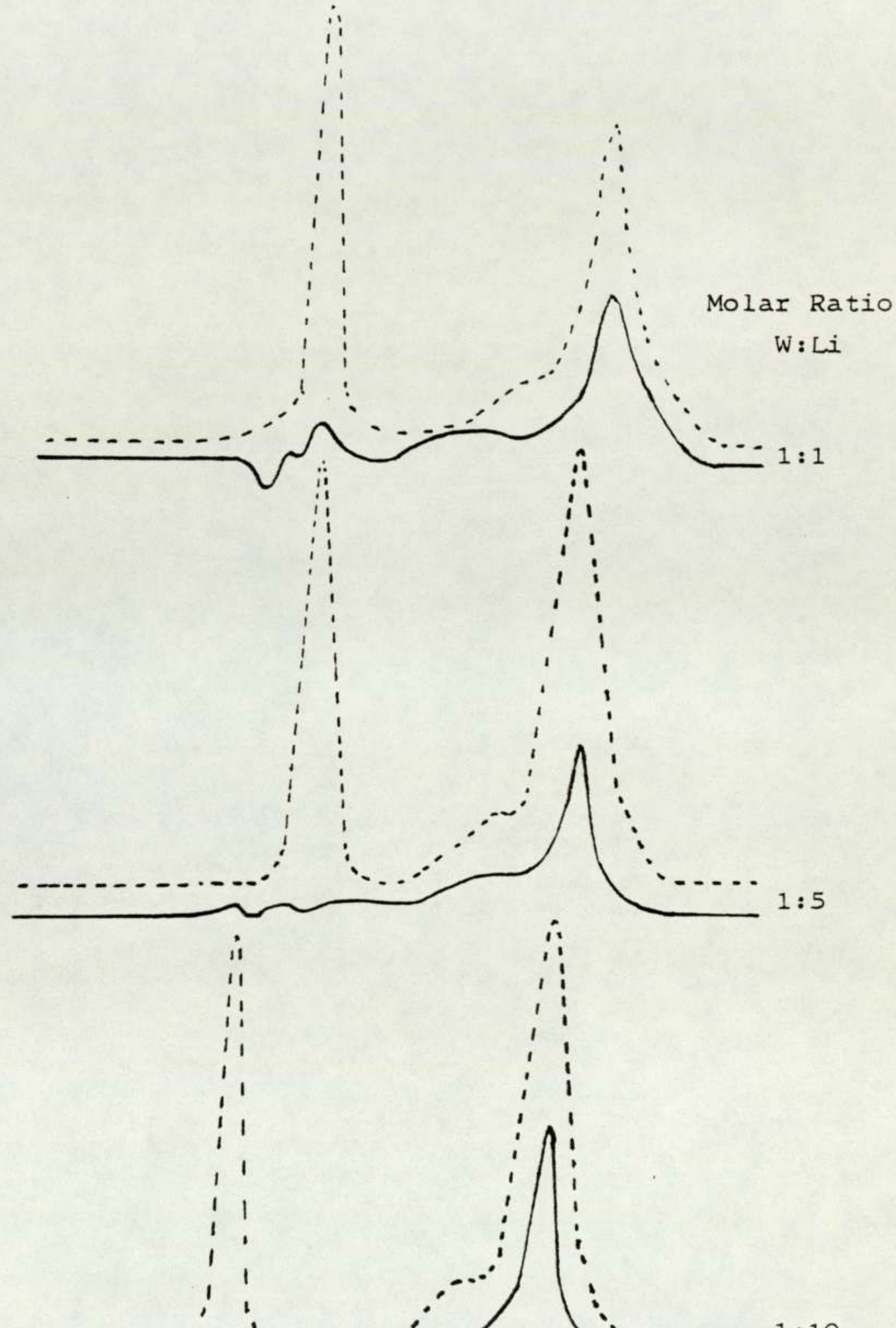
the positions of the peaks and corresponding polystyrene equivalent molecular weights.

Table 4.3 Elution Volumes of Polymer Produced at Various Premixed PstLi Concentrations

WCl_6:PstLi Molar Ratio	Elution Volume (cm^3)	Polystyrene Equivalent/10^3
1:1	26.7	4.5
	28.9 - 30.0	6.6 - 5.6
	32.1	3.5
1:5	26.9	4.2
	29.2 - 29.3	6.4.-.6.5
	32.2	3.3
1:10	28.0	1.6
	30.0 - 30.4	5.6 - 5.4
	33. 0	1.2

From these results it was apparent that high molecular weight polymer decreased in molecular weight with increased PstLi concentration, but retained the same pattern of distribution. Oligomeric material, eluting at around 32.2cm for 1:1 and 1:5 samples, showed virtually the same molecular weight distribution and proportion. But at higher concentrations of PstLi however, a similar progression of high to low molecular weight polymer was observed to that of the analogous unmixed system (fig. 4.17), though in the latter case bimodal activity and oligomer formation was more apparent.

Fig. 4.20 GPC Chromatograms of Block Copolymer at various PstLi Concentrations for a Premixed Catalyst System



These observations may suggest that a different catalytically active species was responsible for the polymerisation processes, depending upon the mode of catalyst addition. Figs. 4.6 and 4.7 show that rates of polymerisation were rapid in both cases, but clearly the resulting products' molecular weight distributions are very dependent on whether the cocatalysts are premixed or added sequentially to the monomer. This is indicative of different propagating species being responsible for the polymerisation reactions.

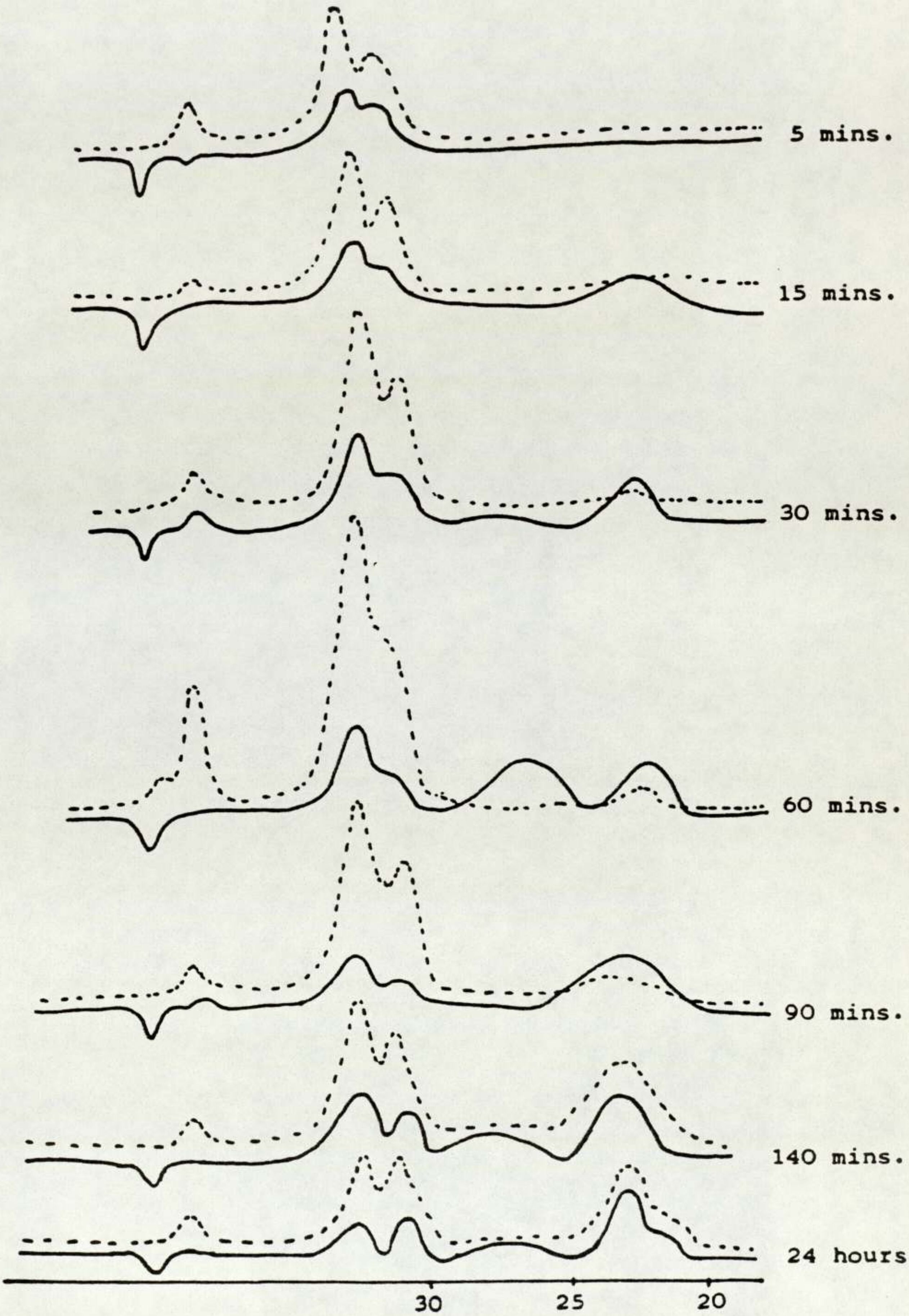
4.4.4 Polymerisation of Cyclopentene Catalysed by WCl_6/PstLi/$SnCl_4$

4.4.4.i Sequential Addition of Catalyst Components

Experiments described in Section 3.4.2.i were repeated and samples taken of the polymerisate produced, using $SnCl_4$ as a second cocatalyst in place of $AlBr_3$. The molar ratios of WCl_6:PstLi:$SnCl_4$ employed were 1:2:4. A general trend was observed as for the $AlBr_3$ system, with a copolymer shift from a molecular weight of 5×10^4 produced after five minutes reaction time, to one of a polystyrene equivalent of 3×10^4 after twenty-four hours. Furthermore, polystyrene which derived from PstLi was present. Fig. 4.21 shows the GPC chromatograms of samples produced by using $SnCl_4$ as second cocatalyst at various reaction times.

From figs. 4.8 and 4.9 it was apparent that the bimetallic

Fig. 4.21 GPC Chromatograms of Polymer produced during the course of Reaction



catalyst system WCl_6/PstLi/$SnCl_4$ showed high activity towards the polymerisation of cyclopentene. Fig. 4.21 shows that polymer was actually formed from a reaction time of fifteen minutes, producing material which had an elution volume of $22.7cm^3$ (3×10^5 polystyrene equivalent molecular weight). This polymer, which revealed evidence of the presence of polystyrene units, was observed in the products throughout the course of reaction, but after thirty minutes another low molecular weight material eluted at $27.8cm^3$ (2×10^4 m. wt.). The latter material was probably polypentenamer, since there was no corresponding UV response.

The chromatogram, at sixty minutes reaction time, was anomalous in that the lower molecular weight peak appeared to have slightly increased, now eluting at a volume of 26.6 cm^3. The copolymer, which was present until the end of the reaction, produced a bimodal pattern after twenty-four hours. The absence of polypentenamer in the system after ninety minutes was possibly due to an error, since it appeared later and was associated with the eventual equilibrium products.

Throughout the course of the reaction a double peak, eluting between $31.0cm^3$ and $33.0cm^3$ was present and may have been due to polystyrene from unreacted PstLi. It is possible that the peak at $31.0cm^3$ could otherwise have been due to polystyrene-polypentenamer oligomeric copolymers. Oligomers were also observed in low concentrations during the rapid initial stage of the reaction, i.e. up to thirty minutes, but tended to diminish after twenty-four hours.

The bimetallic $SnCl_4$ system showed great sensivity to variations in PstLi and $SnCl_4$ concentrations, which caused major changes in the rate of cyclopentene polymerisation. Figs. 4.22 and 4.23 show GPC traces of samples produced when molar ratios of WCl_6:$SnCl_4$ (W:Li = 1:2) and WCl_6:PstLi (W:Sn = 1:4) were respectively varied, the products all being taken after a reaction time of 180 minutes.

It can be seen from fig. 4.23 that polystyrene was present at all PstLi concentrations, the peaks eluting between 31.0cm^3 and 33.0cm^3 and thus corresponding to initial polystyrene from the PstLi cocatalyst. At a low W:Li molar ratio (1:1), only polypentenamer, rather than copolymer, appeared to be formed, as the RI response at an elution volume of 24.3cm^3 does not exhibit a corresponding UV absorbance. This result compares directly with the analogous $AlBr_3$ system, where copolymer production only appeared at W:Li molar ratios of 1:2 and above. The sample produced at optimum catalyst ratio (W:Li = 1:2), showed a bimodal copolymer distribution at elution volumes of 23.6cm^3 and 22.1cm^3, and it was also noted that the relative heights of the peaks in the 31.0-33.0cm^3 range were not the same as for the corresponding 1:1 and 1:5 chromatograms.

It is questionable whether these derive from PstLi of polystyrene-polypentenamer oligomeric copolymers. For a W:Li molar ratio of 1:5, neither the presence of polymer nor copolymer was apparent, for only peaks corresponding to

Fig. 4.22 GPC Chromatograms of Polymer produced at Various Concentrations of $SnCl_4$

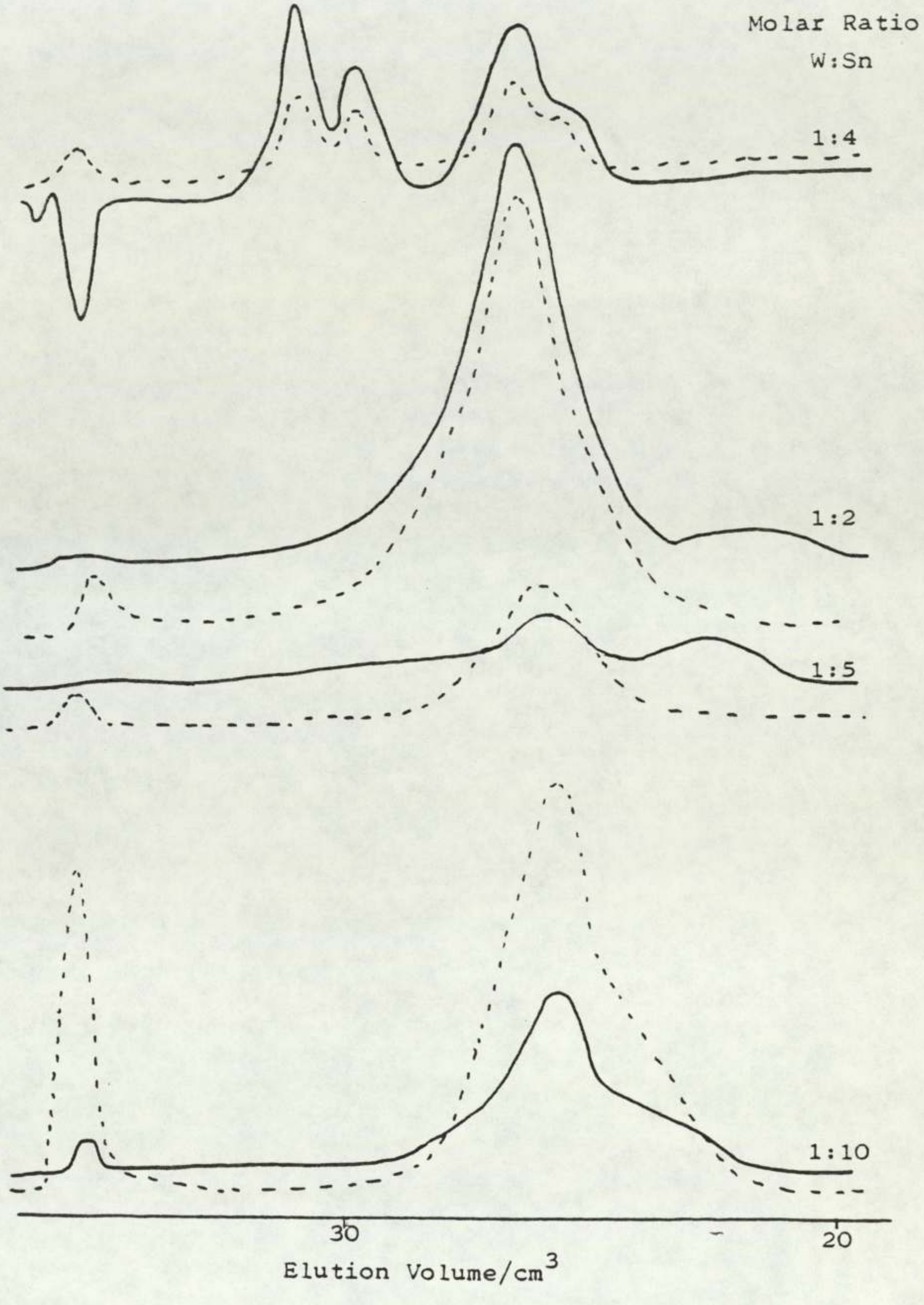
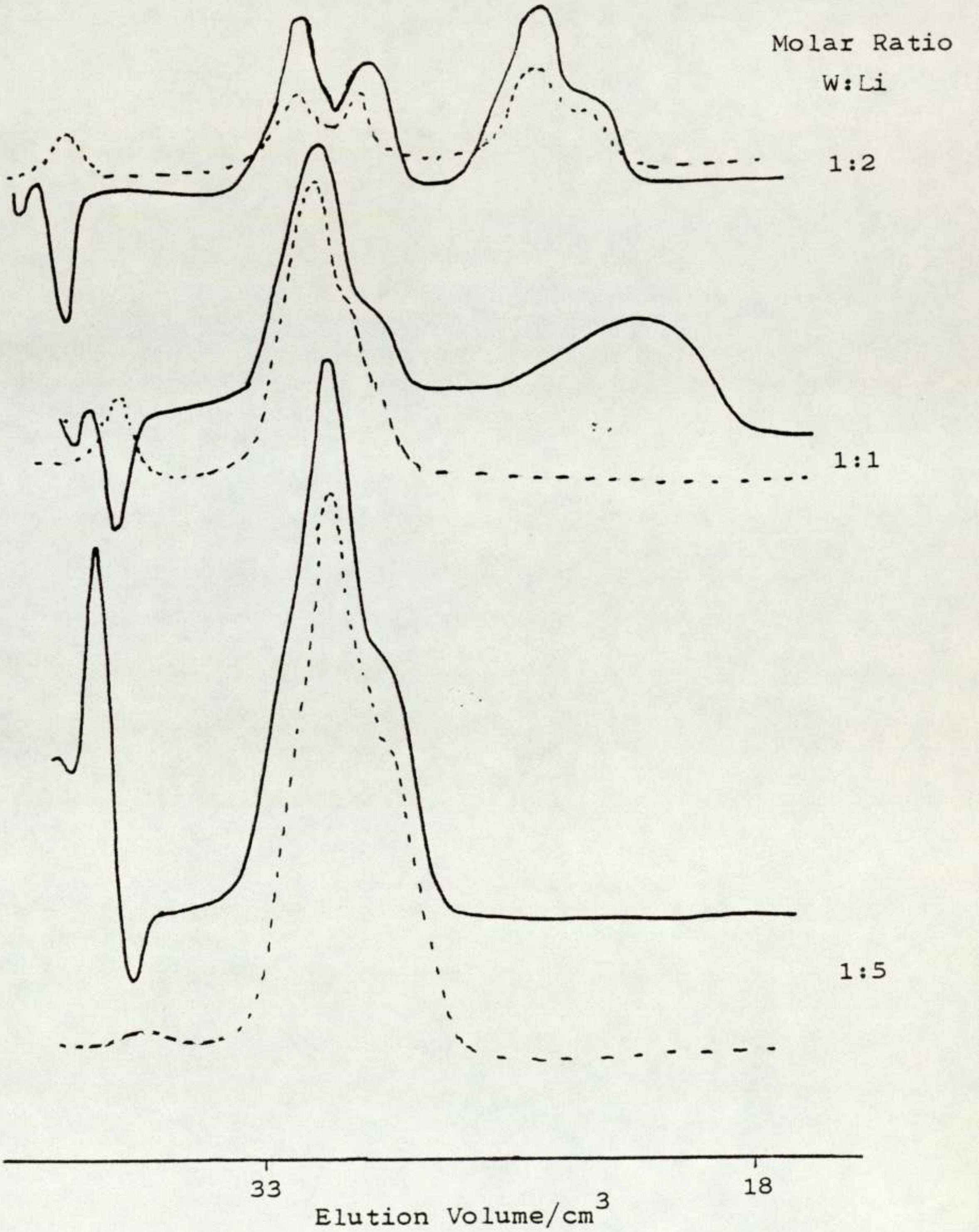


Fig. 4.23 GPC Chromatograms of Polymer produced at various Concentrations of PstLi



oligomeric material were present. The system did in fact show very little activity towards polymerisation of cyclopentene, and it is likely that high concentration of PstLi deactivated the other catalyst components towards metathesis polymerisation.

The dependence of molecular weight distribution on $SnCl_4$ concentration is shown from the chromatograms in fig. 4.22. The analogous LiBu system (fig. 3.22) indicated no particular dependence of the overall distribution on concentration of $SnCl_4$. For the PstLi equivalent system however, changes were observed with respect to copolymer formation. For low concentrations of $SnCl_4$ (W:Sn = 1:2), copolymer eluted at a volume of $26.6cm^3$ (M. wt. 5×10^5) and polypentenamer at $21.2cm^3$ (M. wt. 1×10^6). These products were present for the 1:5 system, with a slight shift of copolymer to higher molecular weight and polypentenamer to a marginally lower value.

For the molar ratio of 1:10, a copolymer peak eluted at a volume of $25.7cm^3$, with a shoulder on the RI response at $23.4cm^3$. This was probably the superimposed product of copolymer and polypentenamer possessing similar weight values. The GPC chromatogram for the W:Sn = 1:4 system differed from the others, showing polystyrene as well as a bimodal copolymer peak between $26.3cm^3$ and $24.7cm^3$.

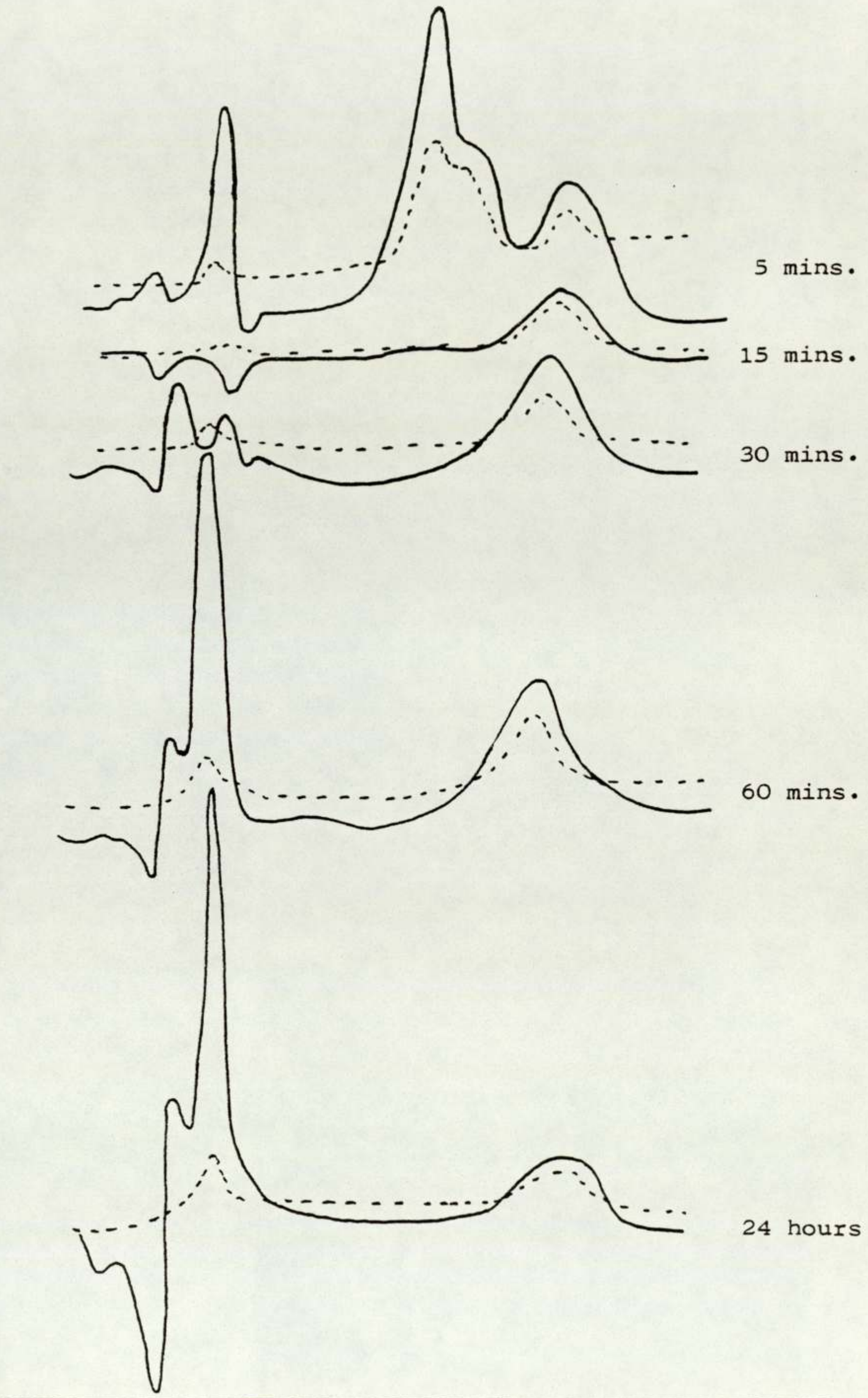
Low concentrations of oligomers were apparent for all systems, particularly at lower concentrations of $SnCl_4$, distribution of which remained constant.

4.4.4.ii Premixed Addition of the Catalyst Components

Premixing LiBu and $SnCl_4$ was found to result in a totally inactive system for cyclopentene polymerisation. When PstLi was used however, polymerisation did occur, but to a much lesser extent than for the sequential addition system.

Fig. 4.24 shows GPC traces of polymer samples produced after given reaction times when PstLi was premixed with $SnCl_4$. The equivalent traces for sequential catalyst additions (fig. 4.21), showed a general progression of low to slightly higher molecular weights of copolymer with time, which is markedly different to the distributions shown in fig. 4.24. After a reaction time of five minutes the sample produced a complex copolymer molecular weight distribution, displaying a very high molecular weight polymer peak at 19.1cm^3, also at 24.3cm^3 with a shoulder at 23.2cm^3. The highest peak showed only a moderate UV absorbance, which could again be ascribed to the fact that the polystyrene segment of the high molecular weight material is a smaller fraction of the overall chain length. Nevertheless the appearance of an absorbance in this region is indicative of block copolymer formation. Oligomers and/or unreacted PstLi were apparent at an elution volume of 33.5cm^3. From the reaction time of fifteen minutes onwards the shouldered peak had disappeared,

Fig. 4.24 GPC Chromatograms of Polymer produced at Various Intervals of Reaction



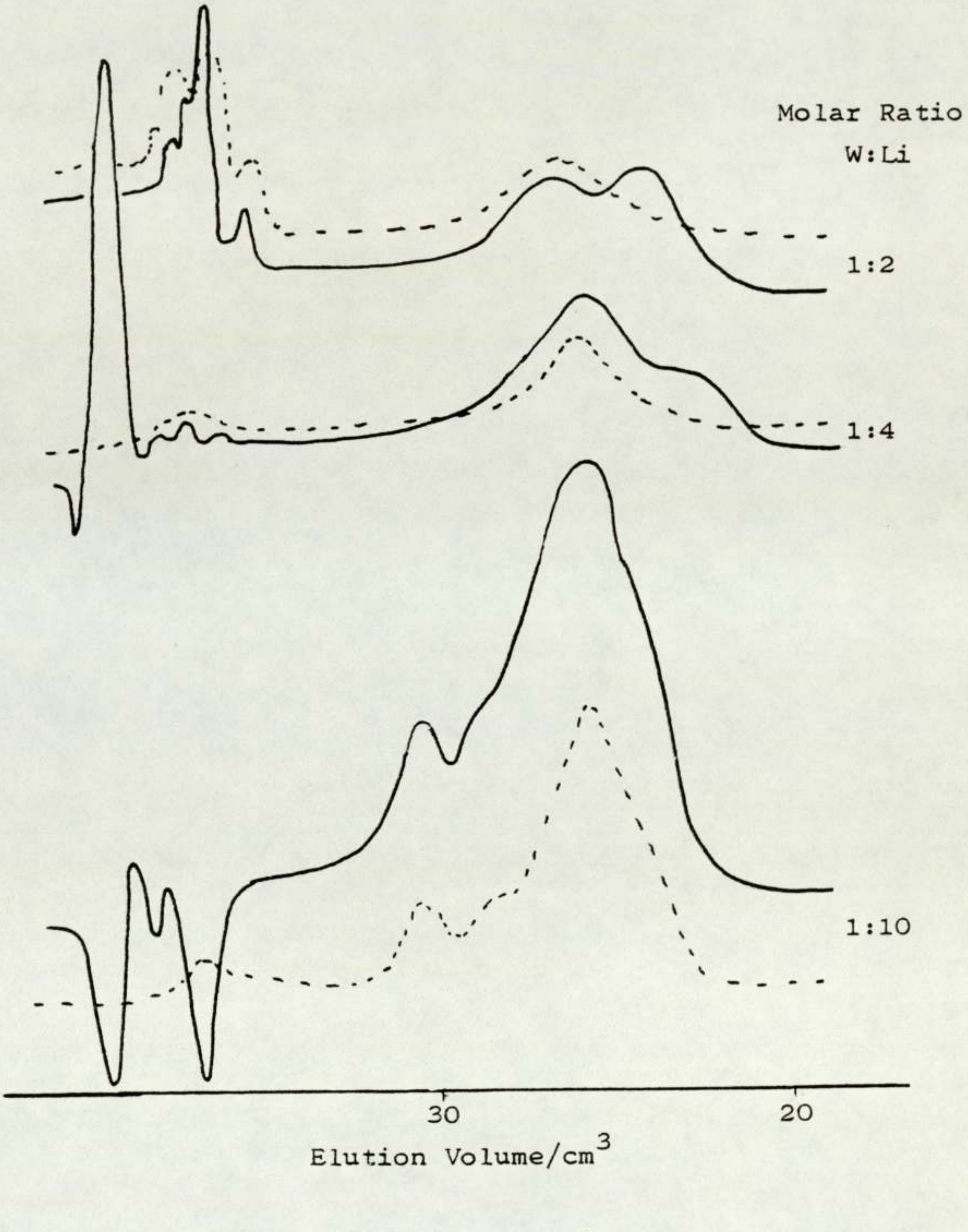
but the higher molecular weight peak gradually decreased in weight with reaction progress, reaching an elution volume of 22.4cm^3 after twenty-four hours. This corresponded to a polystyrene equivalent molecular weight of 4 x 10^5.

The results indicate that at the start of the reaction a number of propagating species are likely to be present, to form several copolymer species by various reactions. Depolymerisation is also apparent in this system, evidenced by formation of copolymer material eluting between 24.0cm^3 and 25.0cm^3 after five minutes, but which later disappeared.

From previous studies it was noted that activity of the premixed cocatalyst system appeared to be virtually independent of PstLi concentration, but was drastically affected by $SnCl_4$ concentration which produced an almost inactive system for molar ratios outside the optimum of W:Sn = 1:4. Fig. 4.25 shows GPC chromatograms obtained for samples produced from various concentrations of PstLi, and although from dilatometry studies activity appears to be independent of these concentrations, the chromatograms show that the molecular weight distribution and the type of polymer produced are greatly affected.

At low PstLi concentrations (W:Li = 1:2,4), polypentenamer was produced together with copolymer, forming a double peak at elution volumes of 26.8cm^3 and 23.4cm^3 for the 1:2 sample

Fig. 4.25 GPC Chromatograms of Polymer produced at Various Premixed Concentrations of PstLi

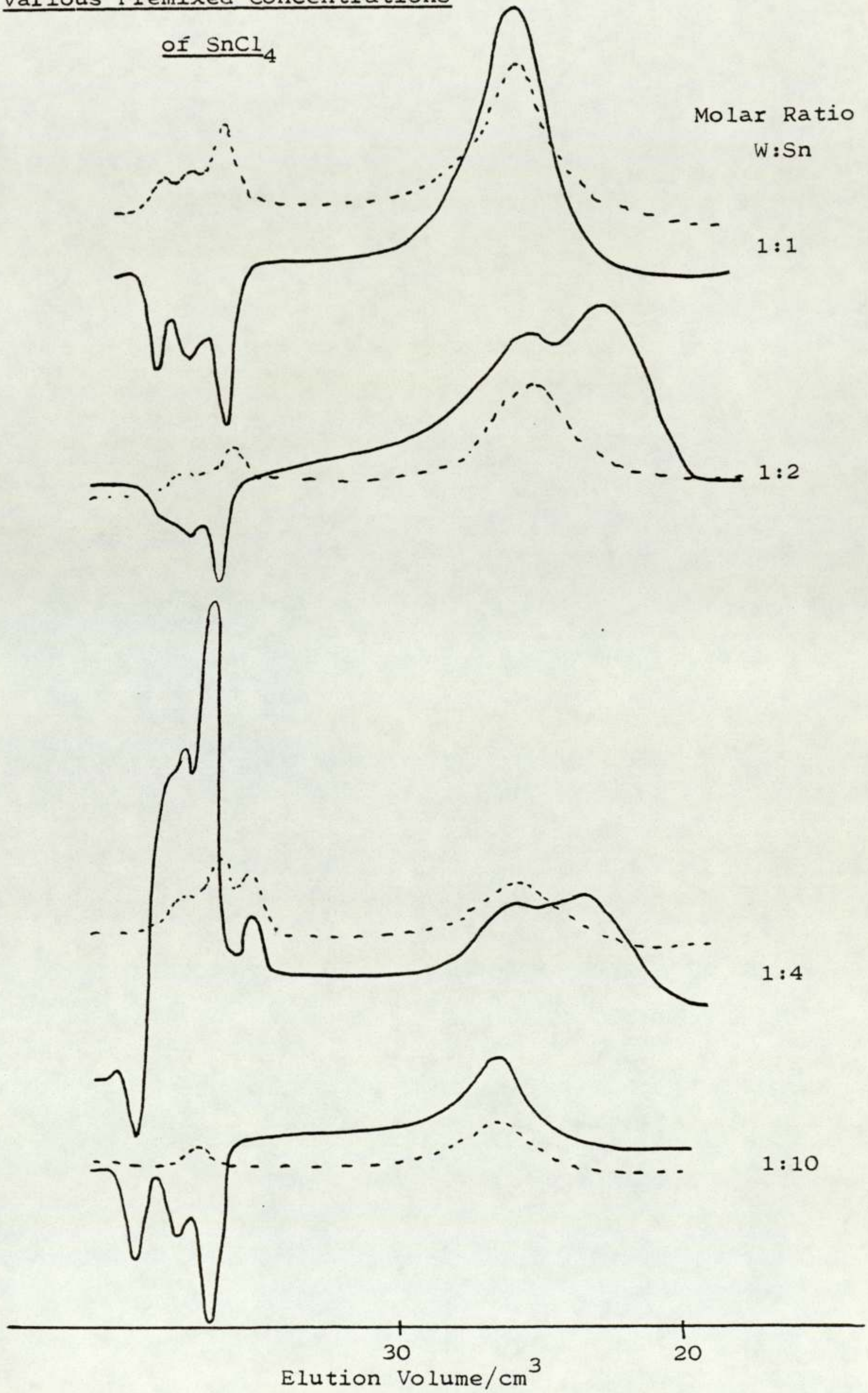


and at 24.6 and 22.1cm^3 for the 1:4 sample. At a very high concentration of PstLi (W:Li = 1:10) no polypentenamer was observed, but the copolymer peak at 24.6cm^3 had been maintained and polystyrene from unused PstLi was apparent at 31.5cm^3. The distribution of oligomers between 34.0cm^3 and 40.0cm^3 was greatly affected by the molar ratio of PstLi to monomer employed.

Fig. 4.26 shows the dependence of molecular weight distribution on concentration of $SnCl_4$ for a premixed cocatalyst system. At a W:Sn molar ratio of 1:1 a single copolymer eluted at a volume of 26.4cm^3, which corresponded to a lower molecular weight species than for the analogous unmixed system. For a molar ratio of 1:2 a double RI response was observed, with a single UV peak appearing in a similar region to that for the 1:1 copolymer. The secondary RI response appeared at an elution volume of 23.2cm^3, showing the presence of homopolypentenamer. This distribution was also present for the 1:4 system, though molecular weight and the proportion of homopolymer had decreased slightly, while that of the copolymer material was marginally increased. At very high $SnCl_4$ concentration (W:Sn = 1:10) the system reverted to a monomodal molecular weight distribution, with copolymer again eluting at 26.4cm^3.

Oligomeric material was apparent in all systems between 35.0 cm^3 and 39.0cm^3. The distribution appeared to markedly vary with $SnCl_4$ concentrations, while molecular weights of the oligomers were lower than usual in all cases.

Fig. 4.26 GPC Chromatograms of Polymer produced, using Various Premixed Concentrations of $SnCl_4$



CHAPTER 5

DISCUSSION

5 DISCUSSION

5.1 INTRODUCTION

Chapters 3 and 4 comprise two very important studies of the metathesis of cyclopentene, the kinetics of the reaction and examination of the molecular weight behaviour of the product polymers for each catalyst system employed by GPC. One of the greatest challenges concerning olefin metathesis is to elucidate the mechanism involved in generation of the active centre, and experiments carried out in this project have been orientated towards a deeper understanding of this. The role of the catalyst and cocatalyst have been of particular interest.

It is widely accepted that the metathesis reaction is propagated by some kind of metallacarbene/metallacyclobutane intermediate. The reactant olefin and cocatalyst employed are believed to play an important role in the generation of this active species. Many catalyst systems only show metathetic activity when generated in the presence of an olefin. An example of this is the system $WCl_6/Al(iBu)_3$, which remained inactive towards polymerisation when the catalyst components were premixed in the absence of cyclopentene(14). $Al(iBu)_3$ added to a mixture of WCl_6/cycloolefin brought about a ring-opening polymerisation reaction however. With other catalysts, active polymerisation systems may result from the premixing of the catalyst components, as described by

Gregory(147) for the bimetallic system WCl_6/LiBu.

It has proved of interest to study the kinetics of polymerisation of cyclopentene using bimetallic catalyst systems based on WCl_6, lithium alkyl compounds - either LiBu or PstLi - and a Lewis acid ($AlBr_3$ or $SnCl_4$). Sequential additions of the catalyst components, as well as premixed additions of the two cocatalysts to the olefin, have shown great diversity in the action of the system, which is largely dependent upon the nature of the cocatalysts and the mode of their addition to cyclopentene and WCl_6.

The molecular weight distribution shows a similar dependence. However in this case an equilibrium tends to be reached after a given period. It is apparent from molecular weight studies of the products that a number of active species are responsible for the polymerisation. The nature of the catalyst and its mode of addition to the WCl_6/cyclopentene mixture appear to determine the system's activity. Kinetic studies of the polymerisation of cyclopentene in this project may have been complicated by the presence of more than one active species in the reacting mixture. The precipitate formed during the reaction may also be a source of active species, or responsible for polymerisation which evidently occurs in certain cases.

5.2 COMPARATIVE CATALYST STUDIES

Gregory(147) studied the bimetallic catalyst system WCl_6/LiBu for the ring-opening polymerisation of cyclopentene. As a starting point for this research some of the reactions were repeated using modified equipment. This was necessary to obtain a valid comparison with experiments carried out using a bimetallic catalyst system.

5.2.1 Polymerisation Studies using an LiBu Cocatalyst

Gregory(147) stated that maximum activity for the ring-opening polymerisation of cyclopentene resulted from a WCl_6:LiBu molar ratio of 1:2, with a two minute interval between the addition of WCl_6 and LiBu to the monomer. Experiments carried out in this project confirmed that maximum activity does indeed occur under these conditions. A value of 3.56×10^{-3} mol dm^3 s^{-1} for the initial rate of polymerisation was obtained using a 1:2 molar ratio for W:Li. This is comparable with rates observed by Gregory for the same system.

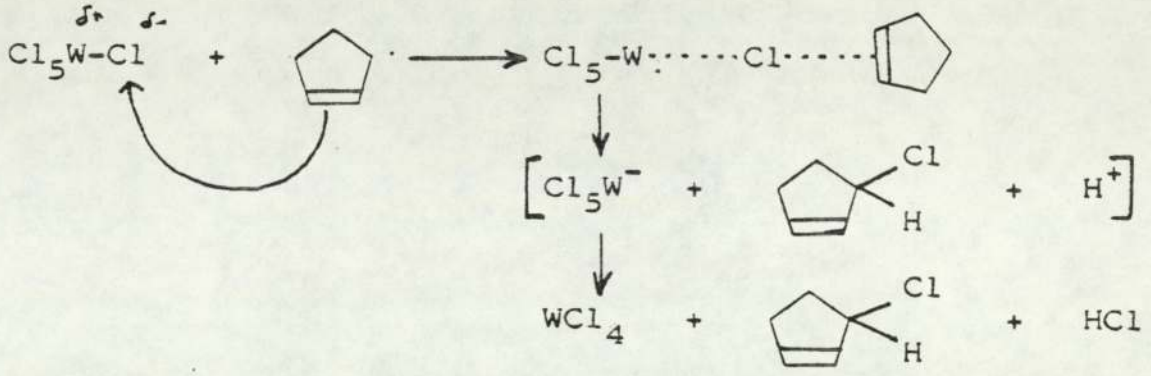
Dolgoplosk(149) suggested the following mechanism for generation of the initiating metallacarbene from catalyst systems of this type:-

$$\begin{array}{l} WCl_6 + 2\,LiBu \longrightarrow Bu_2.WCl_4 + 2\,LiCl \\ \qquad\qquad\qquad\qquad\quad \downarrow \\ \qquad\qquad\qquad\qquad\quad BuH + Cl_4W = CHCH_2CH_2CH_3 \end{array}$$

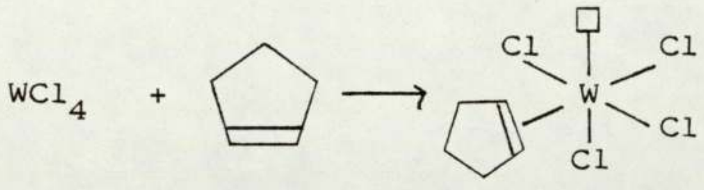
This would explain the W:Li molar ratio of 1:2 proving to be the optimum. A LiBu:WCl_6 molar ratio of less than 2 would result in fewer active centres and hence a slower rate of polymerisation. An Li:W ratio greater than the optimum is likely to bring about very fast initial rates of reaction due to the abundance of propagating species, but would be inevitably followed by a rapid decrease in the rate, due to the depletion of active centres as they reacted with excess LiBu.

Polymerisation curves shown in Fig. 3.2 confirm these postulations. It follows that when the concentration of WCl_6 is increased in the presence of a constant LiBu concentration, the cocatalyst concentration in the system is effectively reduced and hence the activity of the system decreases, as shown in fig. 3.1.

From recent studies of the mechanism of olefin metathesis(150), it is proposed that the following reaction occurs between WCl_6 and cyclopentene:-

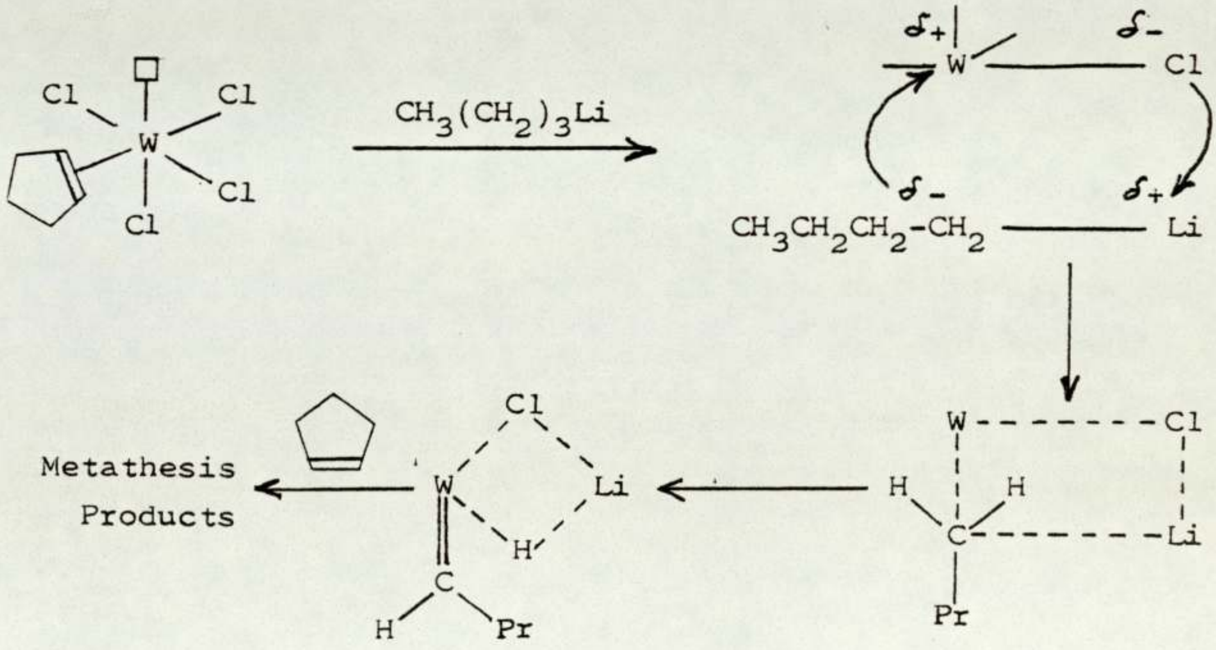


The reduced tungsten compound formed then reacts with cyclopentene to produce a complex having a characteristic brown colour.



(I)

The metallacarbene species results from the reaction of the complex with the LiBu cocatalyst. Initially a complex occurs between cocatalyst and brown complex (I) to form a bridge type complex, which subsequently rearranges itself to produce the propagating metallacarbene, as shown by:-

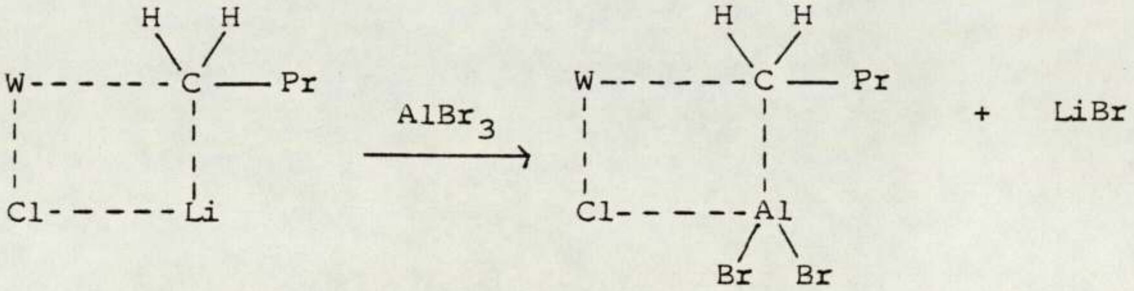


A second cocatalyst is likely to produce a different series of intermediates and the resulting metallacarbene will exhibit an activity towards metathesis, which will depend on its structure. Two secondary cocatalysts have been studied in this project, $AlBr_3$ and $SnCl_4$, both of which display Lewis activity.

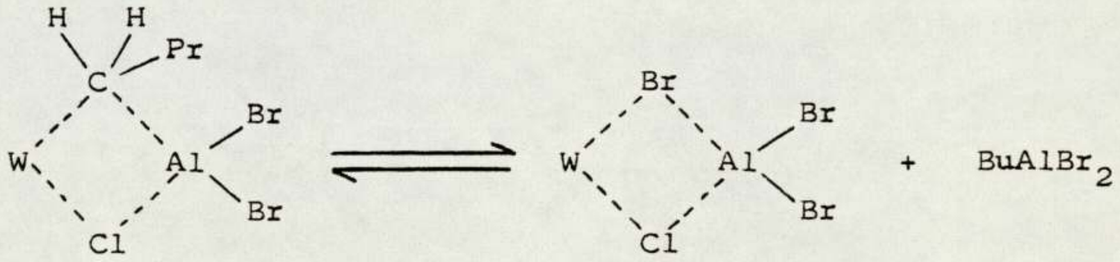
The first observation to be made when using a trimetallic system was that differing colour changes occurred. This suggested that the intermediate complexes produced were of a different nature to those for a bimetallic system. The order of addition of $AlBr_3$ and LiBu to WCl_6/cyclopentene mixture did not appear to affect the system's overall activity, which suggests that either the same species were produced in each case or their activities towards metathesis were similar.

Results from the $AlBr_3$ system showed that an optimum catalyst molar ratio existed for a given interval between the addition of each component. The optimum time of addition for $AlBr_3$ to a mixture of WCl_6/cyclopentene/LiBu was found to be two minutes, with highest activity achieved by using a W:Li:Al molar ratio of 1:2:2. The initial rate of polymerisation for this system was 1.92×10^{-2} mol dm^{-3}s^{-1}, approximately five times greater than the bimetallic equivalent. Fig. 3.5 shows the dependence of cyclopentene polymerisation on the ratio of $AlBr_3$ to WCl_6. It appears that at low concentrations $AlBr_3$ brings about a reduction in the rate of polymerisation, which is increased by subsequent higher concentration. Beyond the optimum however, further addition causes a decrease in rate. This suggests that the structure of the complex changes with $AlBr_3$ concentration.

If it is supposed that during the time of reaction the metallacarbene is produced as previously described prior to addition of the aluminium compound, the following reaction may occur on addition of the second cocatalyst:-

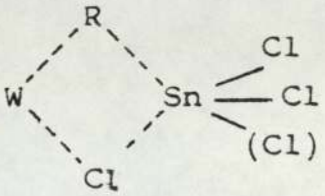


This complex would explain a 1:1 optimum molar ratio for LiBu:$AlBr_3$. The same species may also be produced for a lower concentration of $AlBr_3$, though in this case there would be less active substitution. An excess of $AlBr_3$ may bring about an exchange of the alkyl group by bromine, i.e.:-



The effect of the high concentration of LiBu was not studied at a high concentration of $AlBr_3$, but it is likely that over-reduction by the aluminium compound could have occurred.

Optimum activity for the analogous $SnCl_4$ system resulted from a molar ratio for W:Li:Sn of 1:2:4, with a two minute delay between addition of each cocatalyst as before. The initial rate of polymerisation for this system was 5.69×10^{-3} mol dm^{-3} s^{-1}, showing slightly higher activity than for the corresponding bimetallic system. The Lewis acidity of the second cocatalyst appeared to affect the activity of the system. $SnCl_4$ is a weaker Lewis acid than $AlBr_3$, which could explain why a greater concentration of the former is required to produce the most active system. A Sn:Li molar ratio of 2:1 could be a result of more than one tin atom complexed to the tungsten. It is far more likely however, that a similar complex is formed to the corresponding $AlBr_3$ system, possibly with additional chlorine atoms attached to the tin, i.e. :-

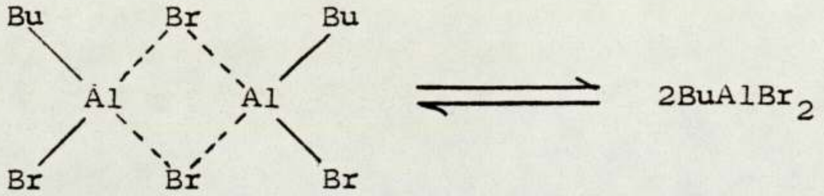


Another part of this research has been to determine the effect of premixing the two cocatalysts. Premixing $AlBr_3$ and LiBu prior to their addition to WCl_6/cyclopentene solution resulted in active polymerisation, but when $SnCl_4$ and LiBu were premixed the system became totally inactive. For the former catalyst system maximum activity was achieved with a W/Li molar ratio of 1:2. The rate of polymerisation appeared to increase with increasing concentration of $AlBr_3$, as illustrated in fig. 3.10. The value of the initial rate of reaction was 7.83×10^{-3} mol dm^{-3} s^{-1}. for optimum conditions, though higher activity may have been caused by using a greater quantity of $AlBr_3$.

When $AlBr_3$ and LiBu were mixed a precipitate was observed, which is probably due to the formation of LiBr :-

$$LiBu + AlBr_3 \rightleftharpoons Complex + LiBr$$

The butylaluminiumbromide complex formed in the reaction is possibly of the following structure:-

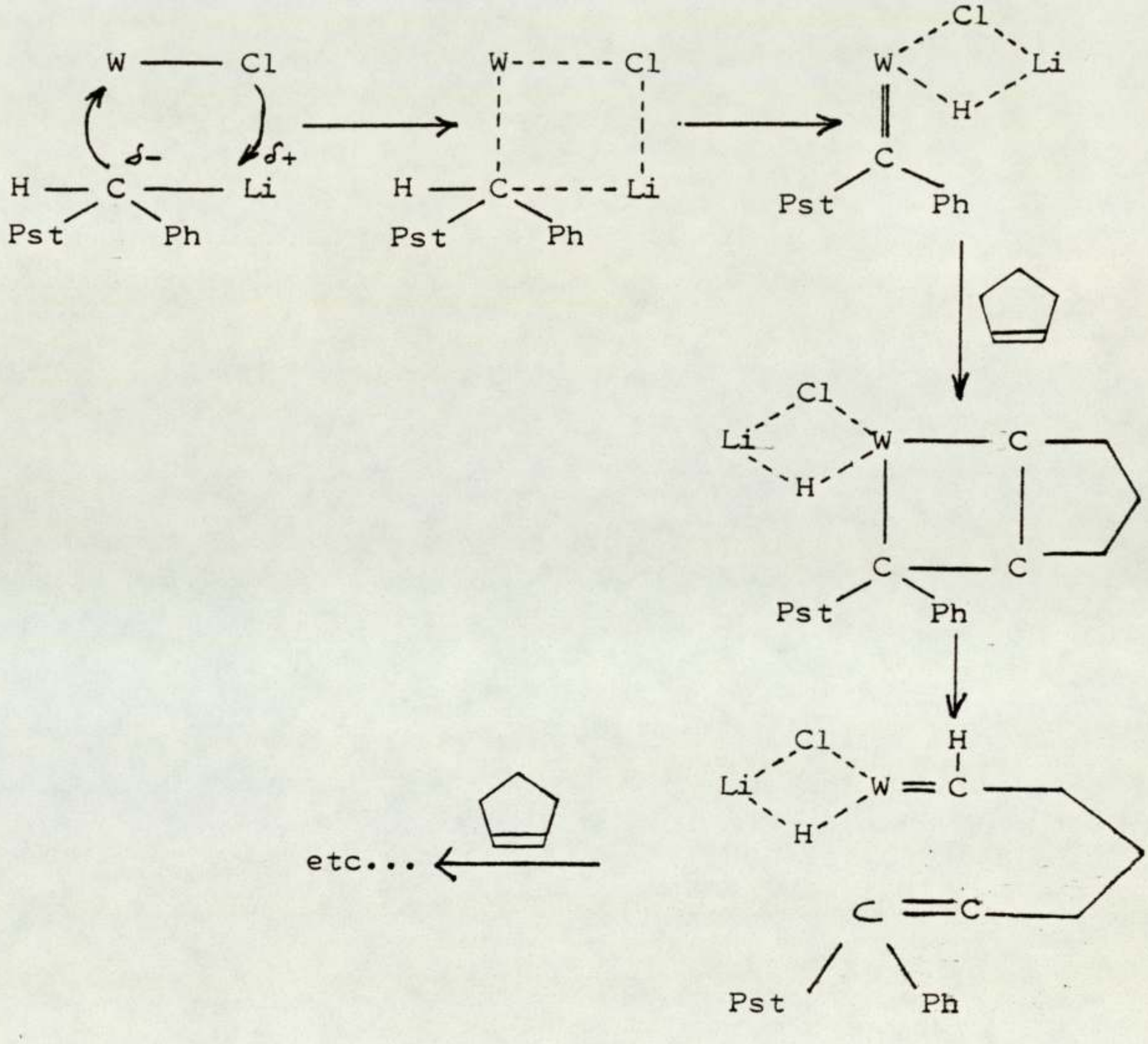


This complex might not be expected to alkylate as readily as the LiBu equivalent, and hence on addition to WCl_6 it will not generate such a highly active system. Slow rates of polymerisation have been observed for such systems, but these are associated with continuous generation of catalyst, which maintains the rate.

The inactivity of a premixed $SnCl_4$ system could possibly be due to the production of unstable butyltinchloride complexes. These may not be sufficiently long lived to activate the WCl_6/ cyclopentene mixture by generation of the metallacarbene.

5.2.2 Polymerisation Studies using a PstLi Cocatalyst

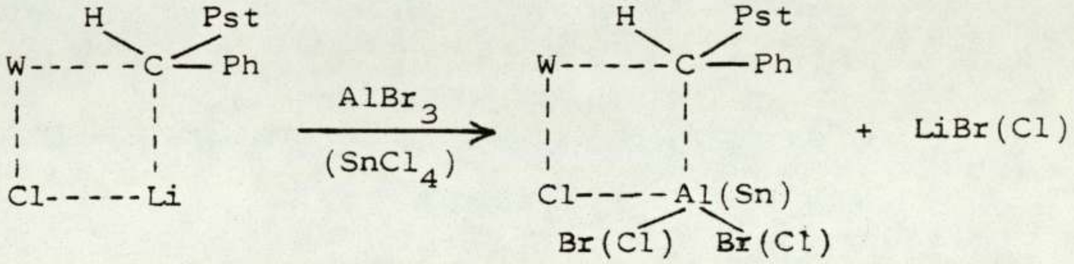
Gregory(147) carried out studies in which PstLi was used in place of LiBu for the ring-opening polymerisation of cyclopentene with WCl_6 as the catalyst. The formation of block copolymers from such reaction systems was explained by the following mechanism:-



This research has extended the studies to include the effects of a second cocatalyst, $AlBr_3$ or $SnCl_4$. Generally much lower polymerisation was observed when using PstLi as a cocatalyst with $AlBr_3$, compared with the corresponding LiBu system (fig. 4.1). For the analogous $SnCl_4$ system however, the unmixed cocatalyst system showed rates comparable with its LiBu equivalent. It was also noted that premixing PstLi and $SnCl_4$ did not result in a totally inactive system, though the rate of polymerisation was very low.

In comparing the rates of polymerisation, it might be expected that catalysts derived from LiBu would show greater activity, because of the bulkiness of the polystyryl group hindering initiation reaction. A more pronounced effect would be expected with an increase in degree of polymerisation of the cocatalysts. This is suggested as an area of future study.

It is reasonable to assume that the effect of introducing $AlBr_3$ or $SnCl_4$ to the initially formed lithium complex would bring about a metal exchange reaction, similar to that described earlier, i.e.:-



Using the bimetallic catalyst system WCl_6/PstLi, Gregory obtained a value for the initial rate of polymerisation of cyclopentene of $4.78 \times 10^{-4} mol\, dm^{-3} S^{-1}$, employing a W:Li molar ratio of 1:2. An increase in activity was found to occur on adding $AlBr_3$ or $SnCl_4$ as a second cocatalyst, giving rates of polymerisation of 1.62×10^{-3} and 1.07×10^{-3} mol dm^{-3} s^{-1} respectively; i.e. almost three and a half and double the initial rates of the bimetallic analogue. The Lewis acid cocatalysts are most likely to displace the lithium atom from the bridging complex, as shown earlier, and these newly formed complexes appear to have greater activity towards the metathesis reaction. Since $AlBr_3$ is a stronger Lewis acid than $SnCl_4$, which in turn is stronger than lithium, it is reasonable to expect complexation with cyclopentene to be more favourable from the aluminium based carbene, as the electrons have been more effectively withdrawn from the transition metal.

The same molar ratio of 1:2 for WCl_6 and PstLi was found to be an optimum in all cases, presumably because the same W/Li complex is formed. The higher $AlBr_3$ concentration required, (W:Al = 1:5), may be to compensate for the reducing effect of PstLi. Optimum $SnCl_4$ concentration (W:Sn) was found to be 1:4, using either LiBu or PstLi as the cocatalyst.

Premixture of the two cocatalysts was found to decrease the activity of the system below that of the corresponding bimetallic analogue. An initial rate of 1.78×10^{-4} mol dm^{-3} s^{-1} resulted from premixing PstLi and $AlBr_3$, and a rate of 3.56×10^{-4} mol dm^{-3} s^{-1} if $SnCl_4$ was the second cocatalyst employed. The results suggest that if PstLi and $AlBr_3$ react to form $PstAlBr_2$ or $PstSnCl_3$, they may not be stable and hence the overall concentration of the active centres may be reduced.

For all the catalysts used it seems that the activity of the system is strongly governed by the time delay of each subsequent addition to the monomer. This factor illustrates the short lives of the complexes formed and the critical periods of their formation to bring about effective ring-opening polymerisation.

5.3 Molecular Weight Studies

Gregory(147) carried out molecular weight studies on the bimetallic catalytic (WCl_6/LiBu, WCl_6/PstLi) polymerisations of cyclopentene. From the results obtained it was concluded that both systems showed bimodal equilibrium distributions of high and low molecular weight products. This compared similarly with results obtained by Amass and Zurimendi(15) in corresponding studies in which the catalyst system WCl_6/$Al(iBu)_3$ was used.

Molecular weight studies have been extended in this project to include bimetallic catalyst systems, and to establish whether a second cocatalyst has any effect on the overall molecular weight distribution of the products.

5.3.1 LiBu Cocatalyst System

Fig. 3.19 shows the molecular weight distribution dependence on the molar ratio W:Li for an umixed system, maintaining the concentration of $AlBr_3$ at optimum level. Since all the chromatograms show similar patterns, it would appear that the nature of the catalyst species is not dependent upon the concentration of LiBu in the system. The slight presence of a lower molecular weight species for a 1:1 molar ratio of W:Li is likely to be the result of a low concentration of active species.

In contrast to these results, a change in concentration of $AlBr_3$ for a premixed cocatalyst system brings about a dramatic alteration in the molecular weight distribution of the products, as shown in fig. 3.20. This is indicative of a dependence of the nature of the catalyst species on concentration of $AlBr_3$. The relative concentrations of the various species which may be present determines the molecular weight distribution, and more particularly the oligomer distribution.

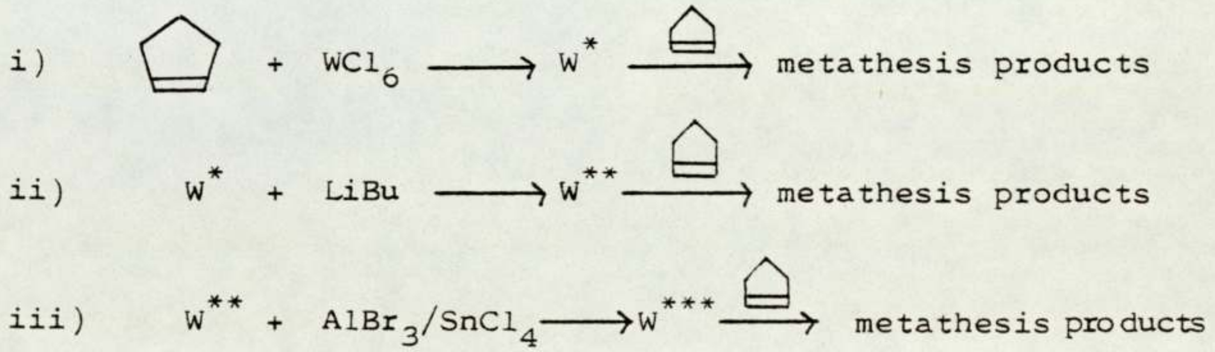
The use of $SnCl_4$ as a second cocatalyst also revealed little dependence of polypentenamer molecular weight distribution on the molar concentration of LiBu, as shown in fig. 3.21. This again implied that the nature of the active species was unaffected by change in concentration of LiBu. The distribution was however greatly affected by the $SnCl_4$ concentration, particularly with respect to the formation of low molecular weight species.

To obtain a clearer understanding of active species formation, molecular weight distribution studies were carried out on products of polymerisation for varying times of third co-catalyst sequential additions to the remainder of the system. The time dependence of such additions for the $AlBr_3$ system shown in fig. 3.18, from which it is clear that the overall molecular weight distribution is not greatly affected by time delay between additions of $AlBr_3$ to WCl_6/cyclopentene/LiBu. The analogous $SnCl_4$ system (fig. 3.23) shows much greater dependence on delay time with respect to both rate of polymerisation and molecular weight distribution of the product polypentenamer. In the case of $AlBr_3$ the active species appears to be formed rapidly when the former is added to a bimetallic system. This species is responsible for the polymerisation of any cyclopentene monomer, and also the metthesis polymer produced from the initial bimetallic catalyst species, as this material disappears on addition of $AlBr_3$.

For the $SnCl_4$ system however, a number of active species seem to be responsible for the polymerisation, the concentration and nature of which depend upon time delay between additions of $SnCl_4$ to cyclopentene/WCl_6/LiBu. Presumably for a ten minute time delay the active species is essentially of a bimetallic nature. The GPC chromatogram of the product from a five minute delay shows a similar molecular weight distribution and it is therefore likely that in both cases the same active species are responsible for the polymerisation.

The presence of a number of products of varying molecular weight indicates the complexity of the system at high delay times. The simple distribution for a two minute delay is indicative of a single active species polymerising the monomer, and since the highest rate of reaction results from this system, the catalyst complex is presumed to have greater activity than that of a bimetallic W/Li species. For a one minute delay time the molecular weight distribution of polymer is of the greatest complexity, since at this stage the bimetallic species is probably still in the process of formation, and part of the polymerisation must inevitably be due to WCl_6 alone.

The progressive formation of tungsten-based active species during the course of reaction may be simplified as shown thus:-



where W^*, W^{**} and W^{***} represent active species

All the results previously described are for systems after a reaction time of 180 minutes. As discussed earlier, these systems tend to reach an equilibrium molecular weight distribution after this time, and in order to acquire a greater understanding of the progress of formation of the active samples were taken from the reaction mixture at intervals.

Fig. 3.16 shows GPC chromatograms of polypentenamer at various intervals from commencement of the reaction, when using $AlBr_3$ sequentially added after two minutes to a mixture of WCl_6/cyclopentene/LiBu. A very complex series of molecular weight changes was observed in both high molecular weight products and oligomers. There appeared to be two distinct stages leading to eventual equilibrium after twenty-four hours; the period between five and thirty minutes, also that between ninety and 150 minutes. Since the corresponding chromatogram after three hours (fig. 3.19) shows a molecular weight distribution similar to the two hour products, it may be assumed that an equilibrium is in fact reached between 150 minutes and three hours. Reference to the corresponding conversion-time curve would tend to agree with this assumption. Prior to reaching equilibrium the reaction mixture contains changing concentrations of the active species W^*, W^{**} and W^{***}. It seems feasible to assume that each is predominantly responsible for a particular stage of the reaction.

Fig. 3.17 shows the molecular weight changes which occur in the polymerisation of cyclopentene for the premixed catalyst system WCl_6/LiBu/$AlBr_3$. The changes are less dramatic than those of the equivalent sequential addition systems (fig. 3.16). Positions of the molecular weight fractions do not vary significantly with conversion, the most notable feature being the appearance and subsequent disappearance of the peak at $21.5cm^3$. For systems of this type it is probable that the catalyst components react together, as described in the previous section, to generate a precursor with only one catalyst species formed. The final molecular weight distribution is typical of a cyclopentene polymerisation and represents a linear-cyclic oligomer equilibrium. During the progression to this state however, the proportions of linear and oligomeric material change, a feature also displayed by the $WCl_6/Al(iBu)_3$ system$^{(14)}$.

5.3.2 PstLi Cocatalyst System

Gregory found that polymerisation of cyclopentene using the bimetallic catalyst WCl_6/PstLi resulted in the formation of block copolymers, comprising polypentenamer and polystyrene units. This instigated further study of the system using a third cocatalyst species $AlBr_3$ or $SnCl_4$. In all cases the formation of block copolymers was also apparent.

Fig. 4.17 shows the dependence of the molecular weight distribution on molar ratio of W:Li for an unmixed system, keeping the optimum concentration of $AlBr_3$ constant. In contrast to the corresponding LiBu system, a dependence of molecular weight distribution on W:Li molar ratio seems to exist, in particular at a low concentration of PstLi, e.g. W:Li= 1:1. For this system the resultant product contained polymer of low molecular weight, and as the concentration of PstLi was increased there was a tendency to form high molecular weight products. The 1:1 system also exhibited different kinetic features, as shown in fig. 4.1, and low molecular weight products must have been produced, as the reaction propagation rate was low compared to that of any termination reactions.

For higher concentrations of PstLi the presence of some unreacted PstLi was evident, most of which would however have been removed during the polymerisation process.

From fig. 4.18 it is clear that production of a block copolymer eluting at 27.6cm^3 was unaffected by the concentration of $AlBr_3$. The lower molecular weight products did however show a complex molecular weight distribution being dependent on this concentration. Although these products could be regarded as oligomeric in nature, it is difficult to determine whether they comprise polystyrene fragments or low molecular weight copolymers. Certainly the response is more complex than would be expected for normal polystyrene.

The chromatograms shown in fig. 4.19 indicate that the delay between the addition of $AlBr_3$ to a mixture of cyclopentene/WCl_6/PstLi does not greatly affect the overall molecular weight distribution of the products. This is comparable with the analogous LiBu system, tending to indicate that the active species is formed very rapidly when $AlBr_3$ is added to the bimetallic catalyst system, thus being primarily responsible for the final molecular weight distribution of the products.

Cyclopentene was polymerised using the optimum concentration of reactants, samples being taken from the system for GPC analyses at given periods. From analysis of chromatograms shown in fig. 4.16, it is obvious that molecular weight distribution is established after five minutes of reaction. The presence of polystyrene after 150 minutes could be indicative of depolymerisation of the copolymer - a phenomenon not observable in the corresponding LiBu system. Unlike the latter system there was no series of complex stages leading to final distribution, unless it occurred within the first five minutes, and an equilibrium molecular weight distribution appeared to be reached between 60 and 150 minutes, before the block copolymer began to fragment. Such features indicate that the PstLi system is much more reactive in nature than the corresponding LiBu equivalent, forming an active species almost immediately after the reactants are mixed.

Fig. 4.20 shows the molecular weight distribution dependence on concentration of PstLi when mixed with $AlBr_3$. In contrast to the unmixed equivalent, little change was again observed with respect to molecular weight distribution, while the copolymer exhibited a bimodal distribution. The high molecular portion of the peak was unusually sharp and associated with a much broader lower molecular weight fraction. The rate curves for this series of experiments (fig. 4.6) show the system had very little activity towards polymerisation. From the GPC traces it may be suggested that, irrespective of the molar concentration of PstLi, the same low activity species were produced in all cases.

Using $SnCl_4$ as a secondary cocatalyst was found to produce activity towards polymerisation, whether added sequentially or premixed with PstLi prior to addition to the monomer.

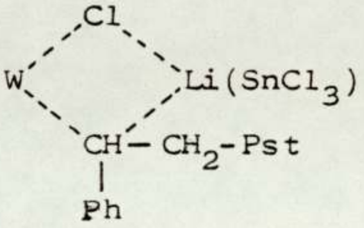
Figs. 4.22 and 4.23 show the dependence of the molecular weight distribution on concentrations of $SnCl_4$ and PstLi respectively, when added separately to the monomer. At high PstLi concentration (W:Li = 1:5) the absence of copolymer is apparent, corresponding to the very low rate of polymerisation for the system as shown in fig. 4.9. Possibly in this case only oligomers were formed, while the metal carbene was produced by a route not involving the metal alkyl. The W:Li molar ratio of 1:1 proved to be anomolous, in that only homopolypentenamer was produced. The same phenomenon was also exhibited for very high or low $SnCl_4$ concentrations, where both homopolymer and copolymer were apparent. Only under optimum catalyst molar ratios was pure copolymer obtained (W:Li:Sn = 1:2:4).

It is therefore suggested that while catalyst concentrations outside the optimum produce a series of active species, to form either homopolymer or block copolymer, only one species will be responsible for polymerisation under optimum conditions, and this is likely to be of the type:-

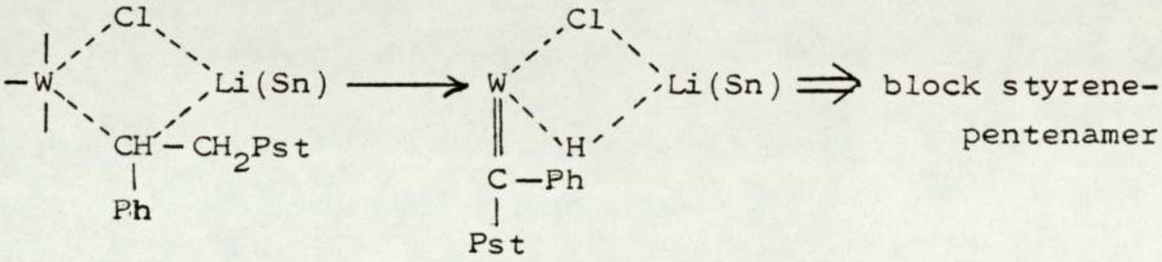
$$Sn(Pst)_x\ Cl_{4-x}$$

The W:Li (1:5) and W:Sn (1:10) systems may be ignored, as very low rates are exhibited under these conditions. The production of homopolymer may well be due to a transfer reaction, under which the chain will fragment by a back-biting mechanism.

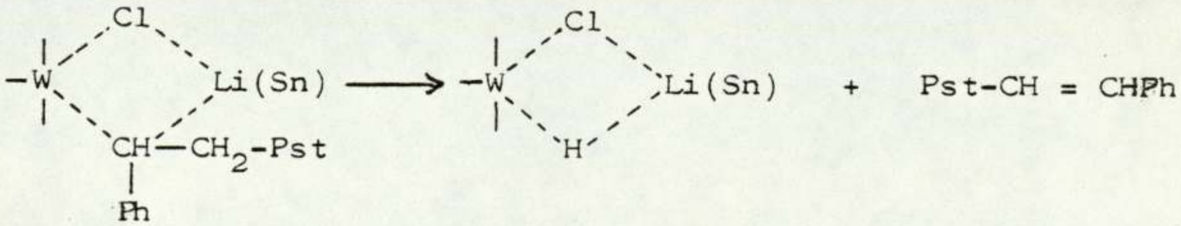
Homopolymer was also apparent in products of the premixed systems (figs. 4.25 and 4.26), though in all cases copolymer was present. The tendency for production of polypentenamer appeared to increase with greater $SnCl_4$ concentration (fig. 4.26), but decreasing PstLi concentration (fig. 4.25). Under these conditions the value of x for the species R_xSnCl_{4-x} would be low. The formation of block copolymers, together with homopolymers, can be postulated to occur in the following manner, it being firstly assumed that the metal alkyl alkylates the tungsten compound, either as PstLi or as polystyryltin chloride, forming:-



This complex may rearrange as previously suggested, to form the precursor to the block copolymer, i.e. :-



Alternatively the complex might decompose in the following manner, by β-hydrogen transfer:-



The product of this decomposition might then generate a propagating carbene by the following route:-

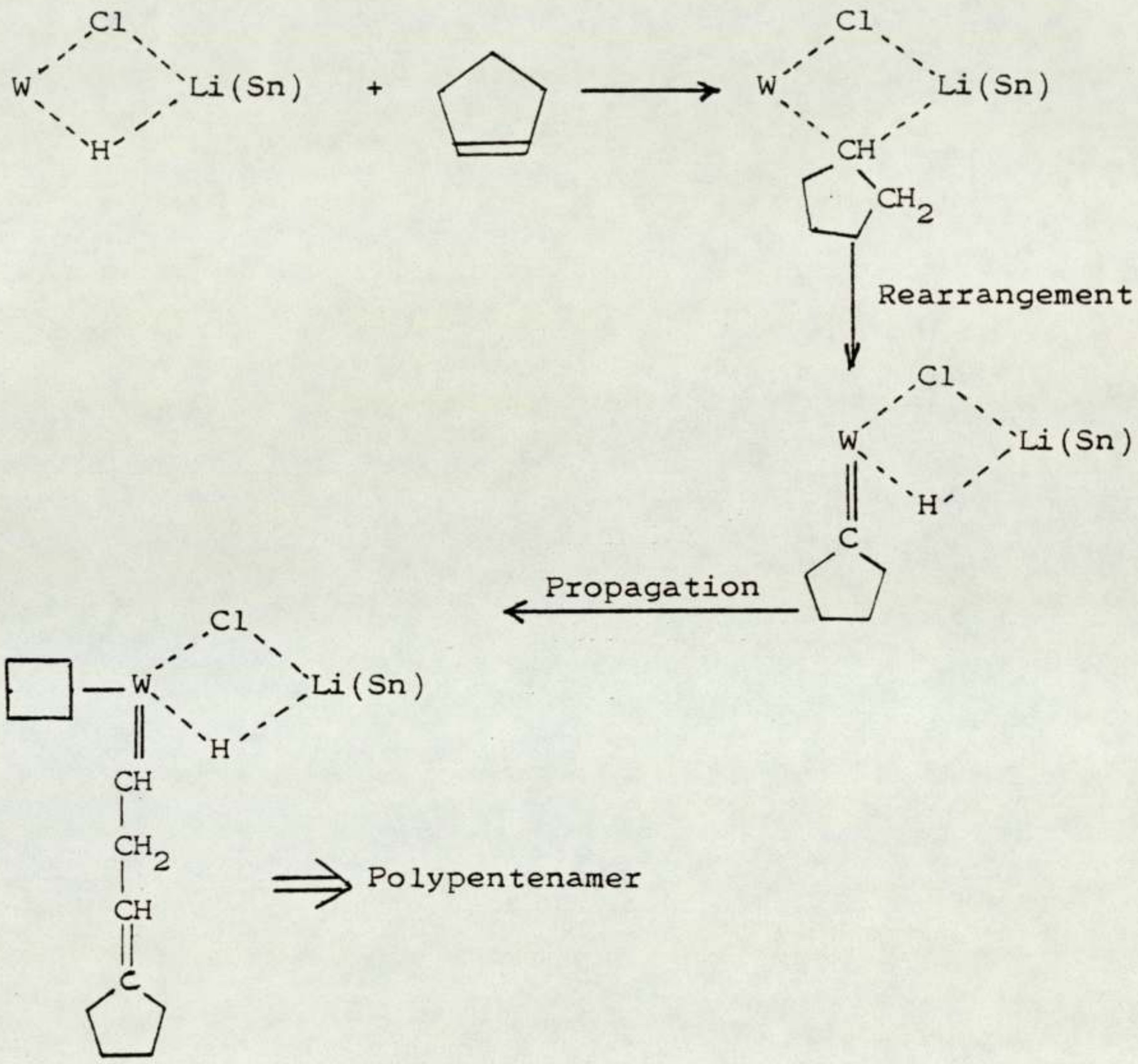


Fig. 4.21 shows GPC traces for samples taken at various stages of conversion. The presence of polypentenamer late in the reaction is indicative of a secondary catalyst generation of the type shown earlier. The analogous premixed system (fig. 4.24) shows similar distribution for the products after fifteen minutes of reaction. The complex distribution shown at five minutes, together with the low activity observed, indicates active species being rapidly produced, consequently deactivated according to:-

$$\text{PstLi} + \text{SnCl}_4 \longrightarrow \text{Cl}_{3-x}\text{Sn} - \text{Pst}_x \longrightarrow \text{deactivation}$$

CHAPTER 6

CONCLUSIONS AND SUGGESTIONS FOR FURTHER WORK

6.1 CONCLUSIONS

From initial studies of ring-opening polymerisation of cyclopentene catalysed by the bimetallic catalyst system WCl_6/LiBu, it is seen that the rate of conversion and optimum molar ratios of catalyst confirm earlier studies obtained by Gregory$^{(144)}$. These in turn correlate with studies of the $WCl_6(AlLiBu)_3$ system by Amass$^{(14)}$, where W:Li molar ratio was found to be 1:2.

The introduction of $AlBr_3$ as a secondary cocatalyst greatly increases the rate of polymerisation if added sequentially to the monomer. As with all systems studied a condition for optimum activity exists. The rate of polymerisation is greatest for a W:Li:Al molar ratio of 1:2:2, with two minute intervals between additions of the cocatalysts to a mixture of cyclopentene/WCl_6. The specific catalyst molar ratio requirement is attributed to the production of a most active aluminium/tungsten complex brought about by an exchange reaction, whereby lithium is exchanged for aluminium.

The use of $SnCl_4$ as a second cocatalyst also brings about an increase in polymerisation rate in comparison to that of the corresponding bimetallic analogue. For this system a higher concentration of $SnCl_4$ (W:Sn = 1:4) is attributed to the fact that $SnCl_4$ has lower Lewis acidity than $AlBr_3$, but in both cases the mechanism of metal exchange is thought to be the same.

Premixing studies of the cocatalysts resulted in moderate activity from the $AlBr_3$ system, but total inactivity when $SnCl_4$ was employed. In the former case the butylaluminium-bromide complex thought to be subsequently produced is not expected to alkylate as readily as its LiBu equivalent, which would explain the lower activity of the system. The high concentration of $AlBr_3$ required, W:Al = 1:10, indicates the difficulty of generating such complexes, and/or continuous generation, due their instability. It is likely that $SnCl_4$ of lower Lewis acidity is unable to generate such complexes that are stable for sufficient duration to bring about the metathesis reaction. But attempted generation must occur, since no activity is exhibited by the WCl_6 alone, while colour changes during the reaction further emphasise this possibility.

Molecular weight studies of polymer samples taken after three hours, under various conditions, show that the molecular weight distribution of polypentenamer has no dependence upon the concentration of LiBu. The concentration of cocatalysts do however greatly affect distributions of polymer and oligomers, which is indicative of various polymer producing active species depending upon molar concentration of the secondary cocatalyst.

As mentioned previously, the molecular weight distribution of polypentenamer tends to reach an equilibrium, but the time required to do this depends upon the nature of the catalyst components. Conversion studies of the products with reaction time show the complexity of this system before an equilibrium is reached, also indicating stages of production of the various active species responsible for polymerisation.

The replacement of LiBu with PstLi, using a bimetallic catalyst system, is an example of an anionic-to-metathesis transformation reaction. The lower activity of the sequential catalyst addition reactions is indicative of the bulkiness of the polystyryl group bringing about a degree of steric hindrance. PstLi proved to be an effective cocatalyst when used in conjunction with either $AlBr_3$ or $SnCl_4$, although only low activity is apparent if premixed with the second cocatalyst. Here again there exists an optimum molar ratio of concentrations of catalyst components at which the polymerisation progresses most effectively. For the $AlBr_3$ system the optimum ratio of W:Al is 1:5, while that for $SnCl_4$ is 1:4. A W:Li ratio of 1:2 is maintained constant for all systems, whether premixed or unmixed.

The mechanism is thought to be analogous to that of the LiBu systems, as the only difference is replacement of the butyl group with the chromophoric polystyryl group. GPC UV/RI analysis shows the formation of block copolymers of polystyrene and polypentenamer, thus demonstrating the role of the PstLi cocatalyst in the metathesis reaction. Also noted is the production of homopolymer, the proportion of which depends upon the activity of the system; generally the lower the activity the more likely production of polypentenamer. Traces of samples taken during the reaction indicate the lower complexity of the PstLi system compared to corresponding LiBu polymerisations, though depolymerisation is much more apparent in these systems.

6.2 SUGGESTIONS FOR FURTHER WORK

More detailed studies of the kinetics of the trimetallic system are required, which may be obtained from closer study of the reactions of WCl_6 during the polymerisation. This is explained more clearly in Appendix I.

TMEDA (NMe_2-CH_2-CH_2-NMe_2) reacts with LiBu to change the electronic structure of LiBu (which is covalent in hexane) to a compound possessing an ion pair (Li^+Bu^-). When this is used with WCl_6 alone the WCl_6/LiBu is inactive as a catalyst system towards the polymerisation of cyclopentene. It would be useful to establish the effect this has on the activity of a three component system. This could be achieved by polymerising styrene in cyclohexane with a mixture of LiBu/TMEDA and using this as the cocatalyst in place of PstLi for the systems described in this thesis.

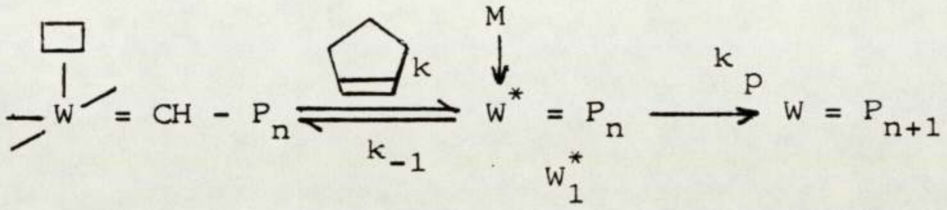
Three other component systems may also be studied, such as WCl_6/LiBu(PstLi)/$SnMe_4$, to determine the activity towards polymerisation of cyclopentene, together with other olefins such as oct-1-ene and oct-2-ene.

Other analytical techniques such as N.M.R. may be used to detect the presence of low molecular weight polystyrene in block copolymers produced by using a PstLi cocatalyst, and in these cases in particular investigation of the structure at the link between the polystyrene and polypentenamer blocks should be made.

APPENDIX I

KINETIC STUDIES

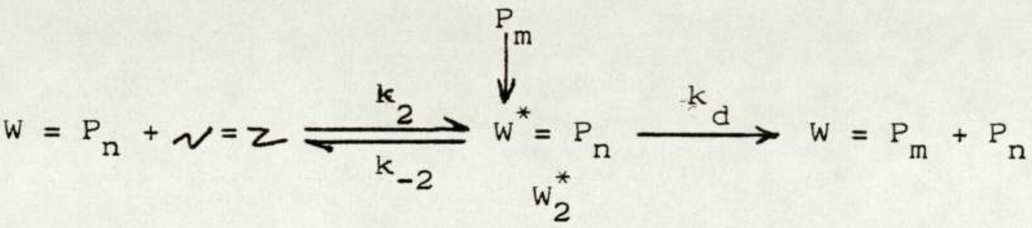
The propagation reaction during metathesis is thought to be:-



where: P_n - Polymer chain of n units
M - Monomer
W_1^* - Active species for propagation

The rate of disappearance of monomer, $\frac{-d}{dt}[M] = k_p[W^* = P_n]$

It is possible that another reaction is taking place whereby polypentenamer, P_m, containing an active double bond can interact with the tungsten atom bringing about a rearrangement reaction, since P_m is incorporated but P_n is released, i.e.



$$W = P_n + \sim = \sim \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} \underset{W_2^*}{\overset{P_m \downarrow}{W^* = P_n}} \xrightarrow{k_d} W = P_m + P_n$$

where: W_2^* - Active species for rearrangement reaction

If the steady state approximation (SSA) is applied in W_1^* and W_2^*, i.e. assuming that the major parts of the reactive intermediates at constant concentration, then:-

$$\text{Total } [W] = [W_1^*] + [W_2^*] + [W = P_n]$$

The rate of production of the initial active species W_1^* is:-

$$\frac{d}{dt}[W_1^*] = k_1[CP][W = P_n] = k_{-1}[W_1^*] + k_p[W_1^*] = 0$$

$$[W_1^*] = \left(\frac{k_1}{k_{-1} + k_p}\right)[W = P_n][CP] \equiv k_1[W = P_n][CP]$$

$$[W_2^*] = \left(\frac{k_2}{k_{-2} + k_d}\right)[W = P_n]\left([CP]_o - [CP]\right) \equiv k_2[W = P_n]\left([CP]_o - [CP]\right)$$

The rate of loss of monomer:-

$$\frac{-d[M]}{dt} = k_p[W_1^*] = \left(\frac{k_p k_1}{k_{-1} + k_p}\right)[W = P_n][CP]$$

$$[W] = k_1[CP] + k_2\left([CP]_o - [CP]\right)[W = P_n] + [W = P_n]$$

$$= [W = P_n]\left(k_1[CP] + k_2\left([CP]_o - [CP]\right) + 1\right)$$

The rate of loss of cyclopentene:-

$$\frac{-d[CP]}{dt} = \frac{k_{1\,p}[CP][W]}{k_1[CP] + k_2\left([CP]_o - [CP]\right) + 1}$$

$$= \frac{k_1 k_p [W][CP]}{1 + k_2 [CP]_o + [CP](k_1 - k_2)}$$

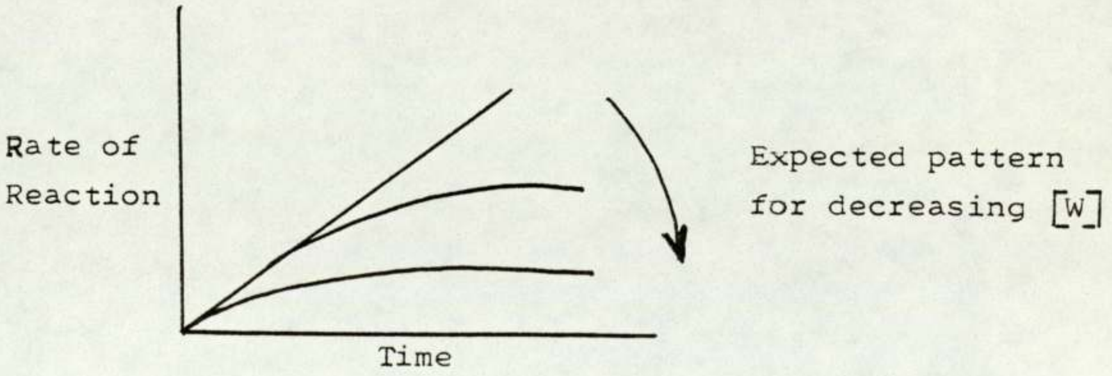
$$- \int_{CP_o}^{CP} \frac{1 + k_2 [CP]_o + [CP](k_1 - k_2) \cdot d[CP]}{[CP]} = k_1 k_p [W] \int_o^t dt$$

$$- \int \frac{1 + k_2 [CP]_o}{[CP]} + (k_1 - k_2) \cdot d[CP] = k_1 k_p [W] t$$

$$- \Big[1 + k_2 [CP]_o \ln [CP] + (k_1 - k_2)[CP] \Big]_{[CP]_o}^{[CP]} = k_1 k_p [W] t$$

$$\therefore \left((1 + k_2 [CP]_o) \ln \frac{[CP]_o}{[CP]} + (k_1 - k_2)([CP]_o - [CP]) \right) = k_1 k_p [W] t$$

Hence from these equations, the concentration of WCl_6 can be observed to change with time. A graph of reaction rate with time will be a straight line if the rearrangement stage is not occurring, but will be a curve otherwise, i.e.



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