To my father and the
memory of my mother.

BLOCK COPOLYMER FORMATION BY TRANSFORMATION REACTIONS

Denis Gregory

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SUMMARY

The ring-opening polymerisation of cyclopentene catalysed by the premixed and unmixed bimetallic catalyst system WCl_6/LiBu has been studied dilatometrically. These studies show that both the premixed and unmixed catalyst systems show similar catalystic properties. The rate of polymerisation shows a maximum at a catalyst/monomer ageing time of less than 2·0 minutes, which is roughly comparable to the results obtained for the polymerisation of cyclopentene catalysed by $WCl_6/Al(iBu)_3$.

The rate of polymerisation increases with increasing monomer or tungsten concentration but the rate falls dramatically to zero after 8 minutes reaction time at high monomer (and possibly catalyst) concentrations. Also, as the cocatalyst concentration increases, the initial rate of polymerisation appears to increase accordingly but, after a few minutes, the reactions performed at high cocatalyst concentrations fall and the rate of polymerisation appears to show a maximum at a W:Li molar ratio of 1:2.

Studies on the polymerisation of cyclopentene catalysed by WCl_6/PSt-Li show that the resultant products contain copolymers of polypentenamer/polystyrene and therefore demonstrate the importance of the role played by the cocatalyst in metathesis reactions.

Model compound studies suggest that the metallocarbene initiator is formed by a alpha hydrogen migration from the cocatalyst to the transition metal catalyst; the reaction is believed to be covalent rather than ionic.

Work performed at PERME Waltham Abbey has shown the possibility of synthesising substituted amines of the form R_xN, where R = poly(tetramethylene oxide) and x = 1,2 or 3. The yield of the trisubstituted amine may be dramatically increased by performing the reaction in the presence of a proton sponge.

KEY WORDS: METATHESIS, RING-OPENING POLYMERISATION, CYCLOPENTENE
TRANSFORMATION REACTION.

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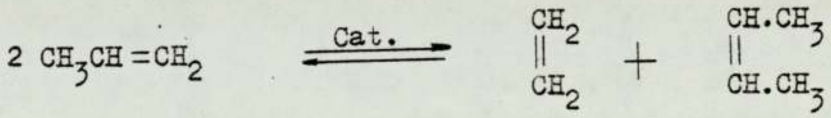
LITERATURE SURVEY

1.1 INTRODUCTION

Perhaps one of the most interesting and potentially useful industrial and synthetic reactions reported within the last twenty five years is that of olefin metathesis. Banks and Bailey$^{(1)}$ first reported the reaction as an olefin disproportionation reaction in 1964 after investigating the catalytic activity of molybdenum hexacarbonyl heterogeneously supported on alumina; they found that equimolar amounts of ethene and butene were produced from propene.



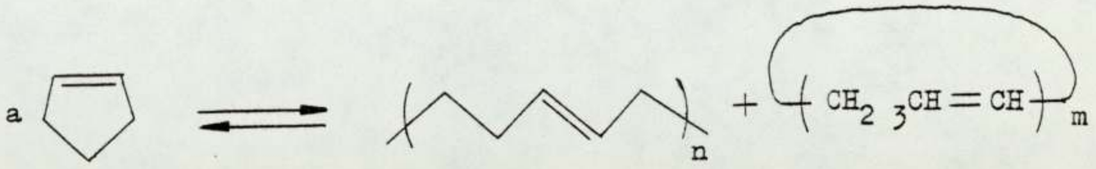
$$2\ CH_3CH=CH_2 \overset{Cat.}{\rightleftharpoons} \begin{matrix}CH_2\\ \|\\ CH_2\end{matrix} + \begin{matrix}CH.CH_3\\ \|\\ CH.CH_3\end{matrix}$$

Much earlier, whilst studying the formation of aromatics from aliphatic hydrocarbons, Schneider and Frolich$^{(2)}$ announced a non catalytic counterpart of this reaction wherein ethene and butene were produced by heating propene to 725°C in a silica reaction tube.

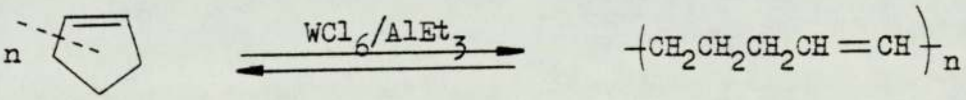
In 1967 Calderon$^{(3,4)}$ first reported the use of homogeneous catalysts for olefin metathesis and it became clear that the metathesis of alkenes is essentially an athermal, entropically controlled reaction. The catalytic rupture and reformation of carbon-carbon double bonds results at equilibrium in a statistical redistribution of the alkylidene entities, and in the reaction:

$$2\ R_1CH=CH.R_2 \rightleftharpoons R_1CH=CH.R_1 + R_2CH=CH.R_2$$

this equilibrium can be approached from either side. Whilst the metathesis of acyclic olefins results in the production of new linear olefins, cylcoolefins undergo ring-opening at the double bond to yield a mixture of macrocycles, polyenes and polymers.

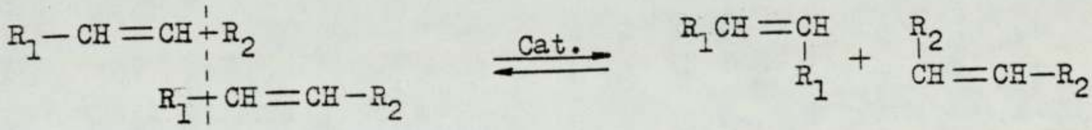


Prior to these reports by Calderon(4), Natta had reported the ring-opening polymerisation of cyclic olefins by the catalyst $WCl_6/AlEt_3$ and suggested that polymerisation occurred by cleavage of the sigma bond adjacent to the double bond, e.g.(5)



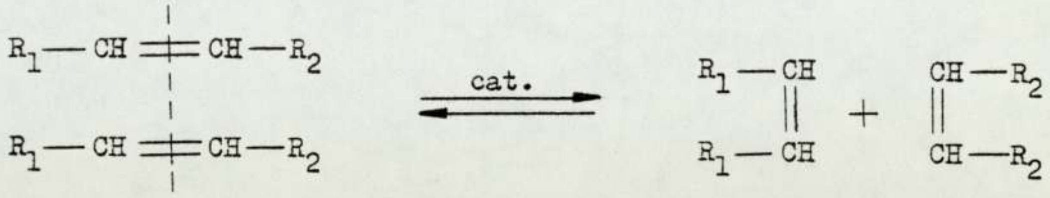
Calderon(4) was later to show that both the metathesis of linear olefins and the ring-opening polymerisation of cyclic olefins were examples of the same reaction. Two alternative routes were considered for the exchange process, transalkylation and transalkylidenation.

Transalkylation



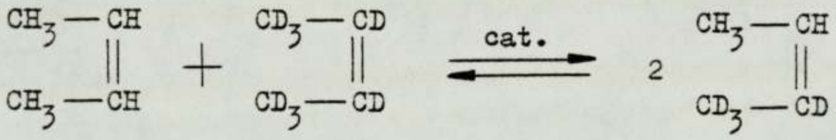
Transalkylation would involve the interchange of alkyl groups via scission of the carbon-carbon single bond α to the double bond; this mechanism is analogous to that suggested by Natta(5) to account for the ring-opening polymerisation of cyclopentene.

Transalkylidenation

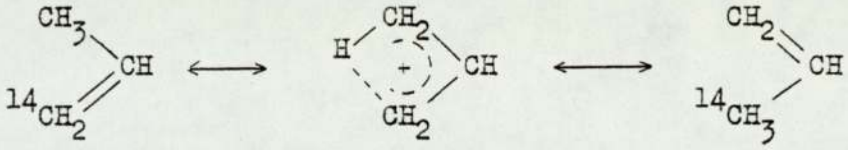


Intermolecular interchange of alkylidene groups by cleavage of the carbon-carbon double bond would result in transalkylidenation.

To distinguish between these two possibilities, Calderon(4,6) analysed the products formed in the metathesis of but-2-ene and perdeutero-but-2-ene catalysed by the homogeneous system $WCl_6/EtOH/EtAlCl_2$. The only olefin produced was 1,1,1,2-tetradeuterobut-2-ene consistent with the transalkylidenation scheme. Thus the reaction could be summarised by:



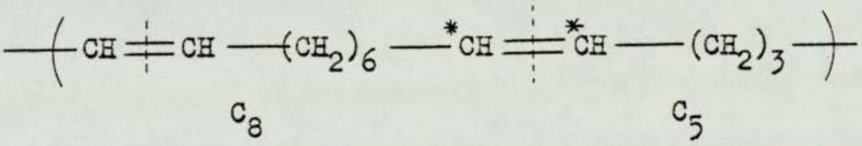
Further evidence supporting the transalkylidenation scheme came from the metathesis of [2-^{14}C] propene over a heterogeneous catalyst of rhenium oxide supported on alumina. An ethylene sample free from ^{14}C was produced in the reaction(7,8). The metathesis of [1-^{14}C] propene(9) and [3-^{14}C] propene(10) yields products which are in accord with the transalkylidenation scheme - provided that there is no double bond migration through a π allylic intermediate.



Additional work by Dall'Asta and Motroni(11,12) was able to confirm that the ring-opening polymerisation of cyclic olefins also proceeds by a transalkylidenation route.

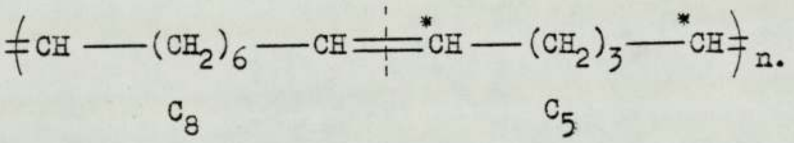
Cyclopentene, ^{14}C labelled at the double bond, and cyclooctene were copolymerised using the catalyst system $WOCl_4/EtAlCl_2$/benzoyl peroxide.

If cleavage oleavage occurred in a position α to the double bond then the resulting polymer would have the following structure:



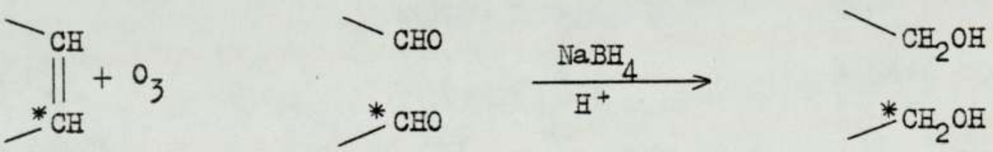
$$-\!\left(\mathrm{CH}\overset{\vdots}{=}\mathrm{CH}-\underset{C_8}{(\mathrm{CH_2})_6}-\overset{*}{\mathrm{C}}\mathrm{H}\overset{\vdots}{=}\overset{*}{\mathrm{C}}\mathrm{H}-\underset{C_5}{(\mathrm{CH_2})_3}-\right)\!-$$

whereas cleavage at the double bond would produce a polymer having the structure shown below:



$$\left(\mathrm{CH}-\underset{C_8}{(\mathrm{CH_2})_6}-\mathrm{CH}\overset{\vdots}{=}\overset{*}{\mathrm{C}}\mathrm{H}-\underset{C_5}{(\mathrm{CH_2})_3}-\overset{*}{\mathrm{C}}\mathrm{H}\right)_n.$$

Upon ozonoloysis and reduction of the ozonides



the products of the reaction were:

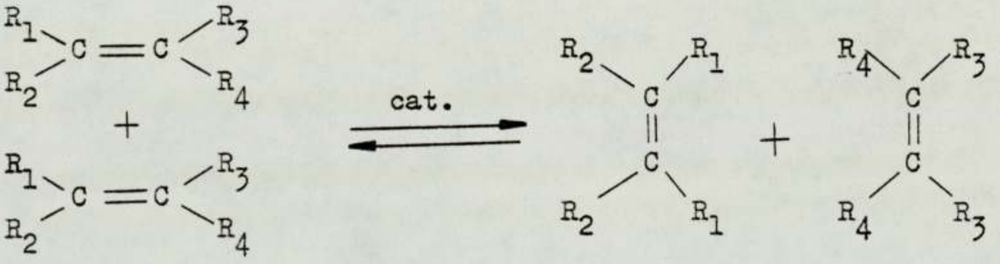
$\mathrm{HOCH_2(CH_2)_6CH_2OH}$	1,8-octanediol
$\mathrm{HO\overset{*}{C}H_2(CH_2)_3\overset{*}{C}H_2OH}$	1,5-pentanediol

The radioactivity was found solely in the pentanediol thus confirming that the ring-opening polymerisation of cycloolefins, like that of linear olefins, occurs via cleavage across the double bond in agreement with the transalkylidenation scheme.

1.2 SCOPE OF THE REACTION

1.2.1. Acyclic olefins.

A wide variety of acyclic mono-olefins and mixtures of olefins, both linear and branched, have been found to undergo catalysed metathesis. Thus, a terminal or internal acyclic olefin will react to give rise to symmetric internal olefins.

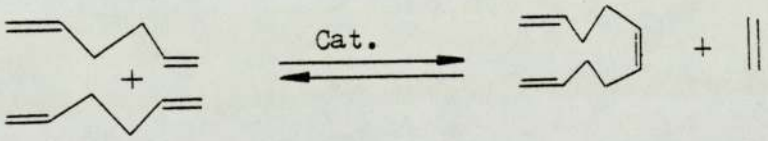


The removal of ethylene during the metathesis of terminal olefins leads to the production of high yields of the internal symmetric alkene.

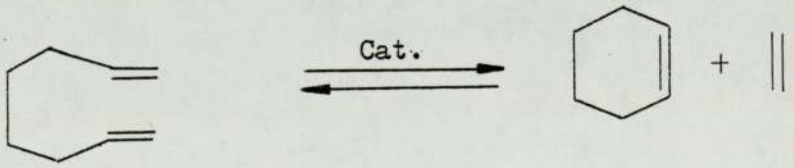
Calderon(13) has shown that steric factors, particularly the degree of substitution of the carbon atom at the carbon-carbon double bond, control the reactivity of the carbon-carbon double bond towards metathesis. This was demonstrated by the decrease in the rate of metathesis along the series $CH_2= \; > \; RCH_2CH= \; > \; R_2CHCH= \; >$ $R_2C=$.

Acyclic olefins, substituted with bulky cycloalkyl, cycloalkenyl or aryl groups, have also been reported to undergo metathesis, e.g. styrene may be converted into ethene and 1,2-diphenylethene (stilbene)(14).

Direct substitution of vinylic hydrogens by chlorine(4) has been shown to deactivate the double bond towards metathesis, although halogen substitution away from the double bond has no such deactivating affect, e.g. 5-bromo-pent-1-ene reacts normally with pent-2-ene(15). The metathesis of acyclic alkadienes and higher polyenes may involve both inter and intramolecular processes. An example of an intermolecular reaction is the conversion of 1,5-hexadiene into 1,5,9-decatriene and ethene(16).



1,7-octadiene may undergo intramolecular metathesis to yield cyclohexene and ethene(16).



Even conjugated dienes may participate in the metathesis reaction; buta-1,3-diene and propene yield ethene and penta-1,3-diene over a tungsten oxide-silica catalyst at 538 °C(17).

Cross metathesis between simple acyclic olefins and polymers containing carbon-carbon double bonds results in low molecular weight products and provides a means of establishing monomer sequence distributions in polymers. Thus the reaction between but-2-ene and styrene-butadiene copolymers allows the determination of the extent of double bond migration during the free radical cross-linking of butadiene(18).

The first commercially viable process using metathesis chemistry was the conversion of propene to polymerisation grade ethene and high purity butene in the 'Phillips Triolefin Process'(19). Unfortunately, as the economic climate and the availability of propene changed, the plant became unprofitable and was shut down after six years operation. It has however, now been reopened to produce high purity but-1-ene as a comonomer for linear low-density polyethylene production(20).

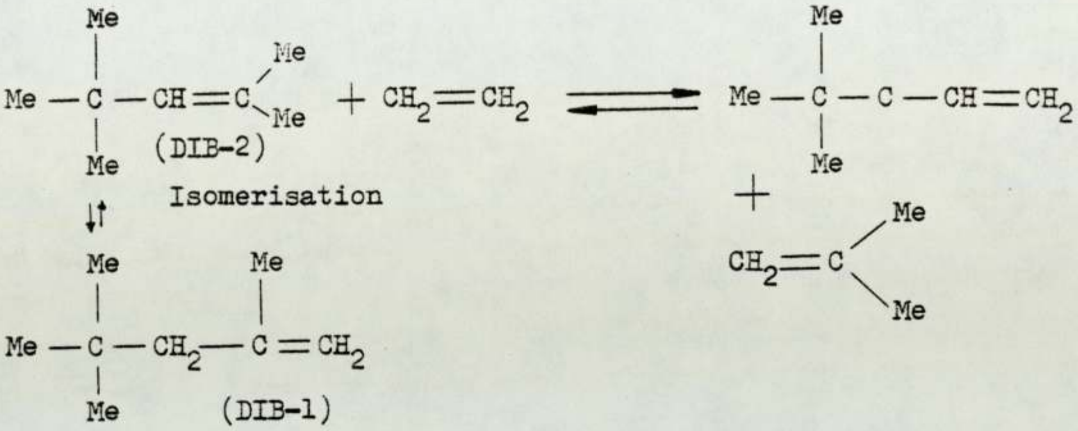
Of recent commercial interest is the Shell Higher Olefin Process (SHOP) which produces extremely pure, even numbered carbon content linear α olefins, e.g. C_{10}- C_{20} and selected ranges (C_{11}-C_{14}) of internal olefins(21). The SHOP plants are two stage in operation. Stage 1 is the oligomerisation of ethene to longer chain alkenes followed by double bond isomerisation from the α position using a metathesis type catalyst.

$$R-CH=CH_2 \rightleftharpoons R_1-CH=CHR_2.$$

The resultant olefins can then be tailored to the desired compounds by a metathesis reaction; the yields are about 10-15wt% of the desired detergent range olefin (C_{11}-C_{14}) per pass.

Another commercial interest lies in the Neohexene process(20) which involves the synthesis of 3,3-dimethylbut-1-ene from the cometathesis of diisobutylene and ethene.

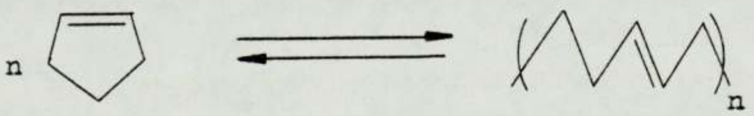
Commercial diisobutylene is a mixture of 2,4,4-trimethylpent-2-ene (DIB-2) and 2,4,4-trimethylpent-1-ene (DIB-1). The effective utilization of the neohexene process requires the conversion of DIB-1 into DIB-2 which is then metathesised to the product. The neohexene process requires an undisclosed dual catalyst system, which is prepared by mixing an isomerisation catalyst with a metathesis catalyst.



A commercial plant built in 1980 has a supply capacity of 1,400,000 Kg of neohexene.

1.2.2. Cyclic olefins

Whilst the metathesis of acyclic olefins generates new linear alkenes, the ring-opening polymerisation of unsubstituted cyclo-monoolefins leads to polymers with unsaturated repeat units$^{(12)}$.

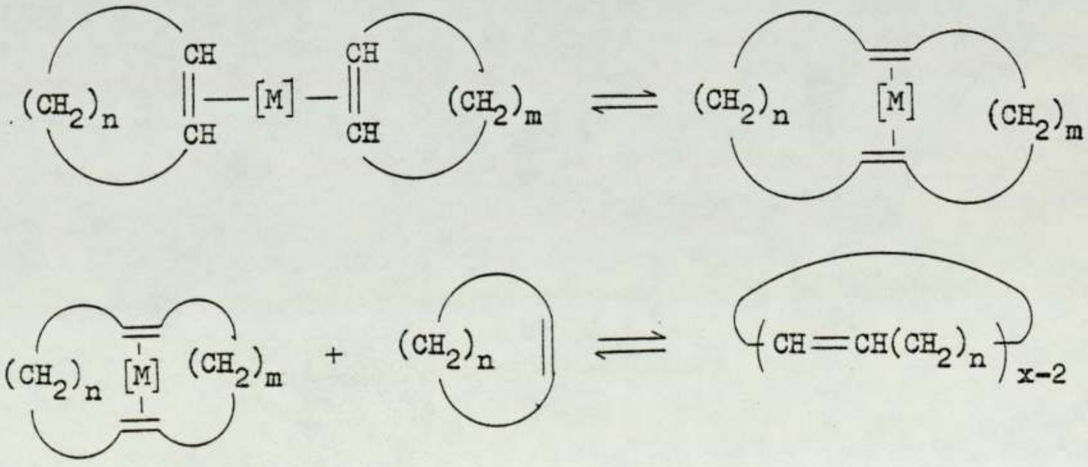


Natta et al$^{(5)}$ demonstrated that the monomers cyclopentene, cycloheptene, cyclooctene and cyclodecene, when exposed to catalyst combinations derived from WCl_6 and either Et_3Al or Et_2AlCl undergo ring-opening polymerisation to their respective polyalkenamers. Prior to Natta's disclosure, Eleuterio$^{(22)}$ announced that cycloolefins undergo ring-opening polymerisation in the presence of a catalyst derived from hydrogen reduced molybdenum oxide supported on alumina and subsequently activated by lithium aluminium hydride.

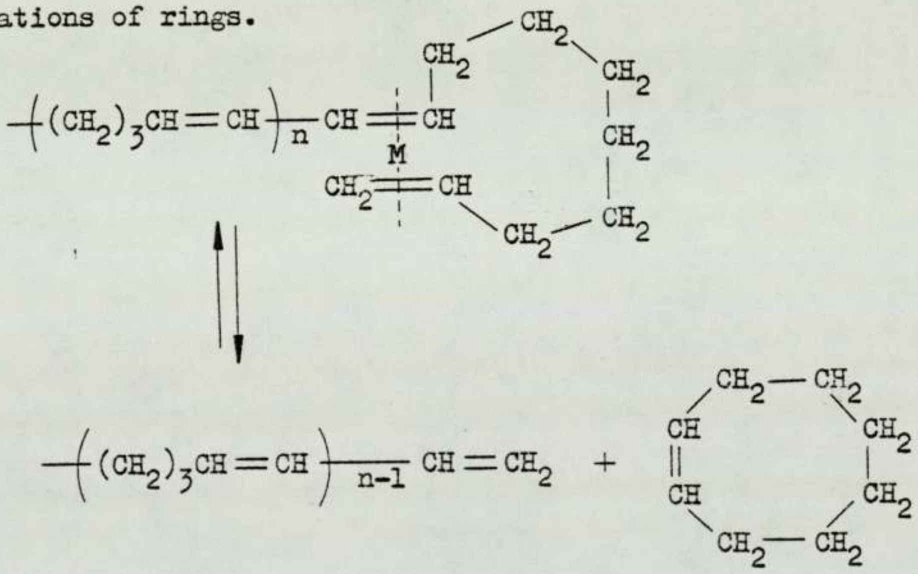
Although the ring-opening polymerisation of cyclic olefins was known for many years, it was not until the pioneering work of Scott(23) and Wasserman(24) that it was realised that such polymerisations were extensions of the olefin metathesis reaction.

From a study of the polymerisation of cyclooctene and cycloocta-1,5-diene, Calderon(6) established the presence of both high and low molecular weight materials in the product polymer. Low molecular weight species were isolated by selective extraction procedures and were shown by mass spectroscopic analysis to be macrocycles and multiplets of the parent compounds(25). Molecular weight distributions of polymers obtained from the ring-opening polymerisation of cyclo-olefins often show bimodal character.

Early metathetic reaction schemes(25) suggested that the transalkylidenation reaction of cyclic olefins would yield cyclic dienes and then larger macrocyclic polyenes as later reaction products, as shown below:



Hughes(26) suggested that trace amounts of acyclic olefins would account for the linear polymers by cross metathesis reactions. Careful analysis of the cyclic oligomers formed in the metathesis of different cycloolefins proved however that the molar concentrations of the oligomers reach entropically controlled values. Hocker(27) suggested that these equilibrium conditions were explained in terms of a back-biting mechanism and that the application of the Stockmayer equation for ring-chain equilibria could predict the relative concentrations of rings.



Following the disclosure by Amass and coworkers that the ring-opening polymerisation of cyclopentene by $WCl_6/2Al(iBu)_3$(28) involves at least two catalytically active species, they proposed that the bimodal molecular weight distribution results from the presence of two kinetically independent metathesis species in the initial stages of the reaction(29). Later however the equilibrium conditions are attained.

With the exception of cyclohexene, cyclic olefins from C_4 to C_{12} yield polyalkenamers which vary in properties from amorphous elastomers to crystalline materials. The degree of crystallinity is related to the proportion of cis to trans double bonds in the polymer which itself is a feature of the metathesis catalyst used(30). High cis polypentenamer has good low temperature characteristics which allows it to be competitive with other more expensive low temperature elastomers such as silicone rubber; trans polypentenamer compares favourably with natural rubber, particularly since it has a glass transition temperature of about-80 °C and a melting point just above room temperature.

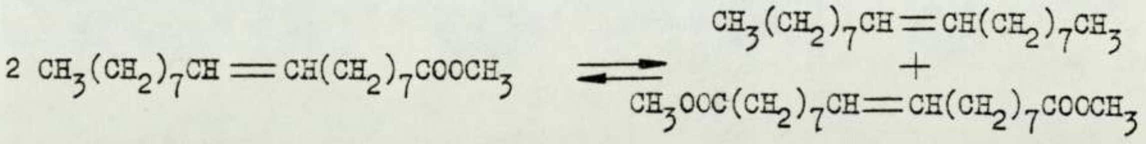
An important reaction which offers great synthetic and commercial value is the cross metathesis between cyclic olefins and ethene to produce α,ω-diolefins.

Calderon has published an excellent review on the ring-opening polymerisation of cycloolefins(31).

1.2.3 Functionally Substituted Olefins

In principle, the metathesis of functionalized alkenes provides new routes to the synthesis of complex olefins, but unfortunately most metathesis catalysts are easily poisoned by polar compounds so that only a few cases of the metathesis of functionalized olefins have been reported. Calderon first reported that polar groups deactivate the carbon-carbon double bond towards metathesis; substition of vinylic hydrogens by chlorine deactivates the double bond towards metathesis, though halogen substituted alkenes can participate in metathesis, e.g. 5-bromopent-1-ene reacts with pent-2-ene(15).

The first report of the successful metathesis of an acyclic functionally substituted olefin was made in 1972 by Van Dam et al(32), who were able to metathesize long chain unsaturated fatty acid esters with the catalyst system $WCl_6/Sn(CH_3)_4$. They reported the selective conversion of methyl oleate (methyl-cis-octadec-9-encate) into octadec-9-ene and dimethyloctadec-9-enedioate.



$$2\ CH_3(CH_2)_7CH{=}CH(CH_2)_7COOCH_3 \rightleftharpoons \begin{array}{c} CH_3(CH_2)_7CH{=}CH(CH_2)_7CH_3 \\ + \\ CH_3OOC(CH_2)_7CH{=}CH(CH_2)_7COOCH_3 \end{array}$$

The reaction was carried out at 343 K in chlorobenzene and gave a 2:1:1 ratio of starting materials and products. They also reported the metathesis of other unsaturated fatty acid esters, such as methyl erucate and methyl undec-10-eneoate$^{(33)}$. The metathesis of functionally substituted olefins generally require very high catalyst: olefin ratios, usually within the range 1:100 to 1:10.

Verkuijlen et al$^{(34)}$ have systematically investigated the influence of an ester substituent on the metathesis reactivity of the double bond. Using the catalyst system $WCl_6/Sn(Me)_4$, the metathesis of low molecular weight unsaturated acid esters of different chain lengths was studied and it was concluded that effective metathesis can occur only if the ester group and the carbon-carbon double bond are separated by at least one methylene group.

Whilst the metathesis of olefinic esters yields products with internal double bonds, the cometathesis of unsaturated esters offers great synthetic utility, since the products are ω-terminally unsaturated esters$^{(35)}$. For instance, cometathesis of methyl oleate with hex-3-ene gives, in addition to the products of self metathesis, dodec-3-ene and methyl dodec-9-enoate. Conversions of 33% of the methyl oleate after 10 hours at 60°C with the catalyst $WCl_6/Sn(Me)_4$ were recorded.

Alternatively, cycloolefins may react with unsaturated esters to prepare long chain linear di-unsaturated mono-esters. An example is the cometathesis of cyclooctene and ethylpent-3-eneoate to yield ethyltrideca-3,11-dieneoate with the catalyst $WCl_6/Sn(Me)_4$(36).

Laval et al(37) have reported that olefinic amines cannot undergo metathesis unless they are transformed into quaternary ammonium salts, e.g.

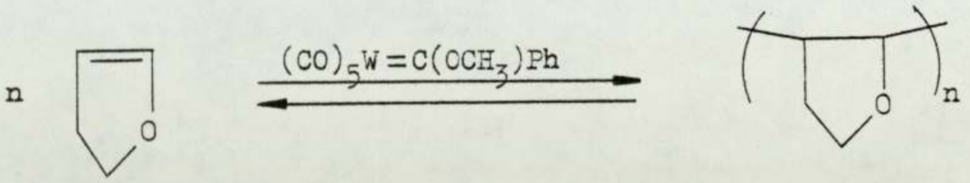
$$2\ CH_2=CHCH_2N(CH_3)_3Br \rightleftharpoons CH_2=CH_2 + \left(Br(CH_3)_3NCH_2CH=\right)_2$$

Later, Nouguier(38) reported that secondary amines can undergo metathesis to give the expected diamine. Using the catalyst system $W(CO)_3$/mesitylene/$EtAlCl_2$ activated with molecular oxygen they recorded conversions in the range of 10-42% for $1 \leqslant n \leqslant 9$, at 25°C, with a maximum for $n = 3$. The fact that the overall yield passes through a maximum for $n = 3$ has been tentatively explained by an intramolecular stabilisation of the metallocarbene intermediate by the amine ligand, thus increasing the lifetime of the catalyst(27).

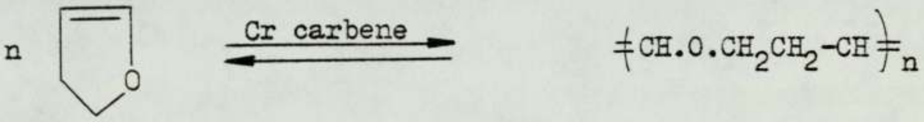
Although the metathesis of unsaturated nitriles is difficult to achieve, Bosma(39) has recently reported the cometathesis of $CH_2 = CH(CH_2)_nCN$, where n is 1,2,3 or 4, with hept-3-ene. The reaction was catalysed by $WCl_6/Sn(Me)_4$. It was found that the order of reactivity was $n = 2 > n = 1 > n = 3 > n = 4$ and that the heptene showed higher reactivity towards cometathesis with the nitrile than towards self-metathesis.

Ast et al(40) have reported the metathesis of unsaturated ethers using the catalyst system $WCl_6/Sn(Me)_4$. They showed that vinyl and allylic ethers do not react metathetically, and further, the minimum number of methylene groups between the ether and double bond which is necessary for metathesis is 2.

Recently, Hocker$^{(41)}$ and coworkers have reported the polymerisation of 2,3-dihydrofuran with tungsten and chromium carbenes. With $(CO)_5W{=}C(OCH_3)Ph$ dihydrofuran (DHF) yields a polymer upon UV irradiation which is free of double bonds.



With $(CO)_5Cr{=}C(Ph)_2$ and $(CO)_5Cr{=}C(OCH_3)Ph$ DHF rapidly reacts to yield a polymer with the structure of poly(oxy-1-buten-1,4-ylene).



They also demonstrated the metathesis of butyl vinylether and ethylpropenyl ether with $(CO)_5Cr{=}C(OCH_3)Ph$ as catalyst.

$$\begin{matrix} CH_3CH{=}CHOCH_2CH_3 \\ + \\ CH_2{=}CHO(CH_2)_3CH_3 \end{matrix} \rightleftharpoons \begin{matrix} CH_3CH{=}CHO(CH_2)_3CH_3 \\ + \\ CH_2{=}CHOCH_2CH_3 \end{matrix}$$

The metathesis of functionalized olefins has been reviewed by Mol$^{(42)}$.

1.3 CATALYSIS SYSTEMS

All known effective catalysts for olefin metathesis contain a transition metal and may be divided into two groups - heterogeneous$^{(43)}$ and homogeneous$^{(44,45)}$.

Heterogeneous catalysts are generally transition metal oxides deposited on a high surface area ($>200m^2/g$) support - typically silica or alumina.

Homogeneous catalysts are derived from a transition metal halide or coordination complex and a non transition metal compound. The most widely used cocatalysts are organoaluminium compounds - preferably the mono or dialkylchlorides or sesquichlorides. Other organometallic compounds such as alkyl lithium or Grignard reagents as well as the non organometallic derivatives lithium aluminium hydride, sodium borohydride, aluminium trichloride and oxygen are also effective.

1.3.1 Heterogeneous Catalysts

Typical heterogeneous metathesis catalysts are based on the oxides or carbonyls of molybdenum, tungsten or rhenium. Other materials that may be used are the sulphides of tungsten and molybdenum and the oxides of indium, lanthanum, niobium, osmium, ruthenium, rhodium, tantalum, tellurium and tin, although their catalytic activities are much lower than those catalysts based on the oxides of tungsten and molybdenum. The various refractory materials used as supports include the oxides of silicon, aluminium, thorium, zirconium and titanium; the phosphates of aluminium, zirconium, titanium, magnesium and calcium, and the mixed oxides of some of these elements may also be used.

1.3.1.1. Supported Oxide Catalysts

Prior to metathesis, supported oxide catalysts required activation which is usually achieved by passing a stream of dry nitrogen, oxygen, air, or an inert gas over them at temperatures ranging from 100 to 400 °C. It is believed that at these elevated temperatures some chemical interaction may occur between the promotor and the support; condensation reactions may take place with the desorption of water and other polar or chemically active materials which are otherwise reported to be catalyst poisons.

Incorporation of alkali or alkaline earth metal ions(46,47) and controlled base treatment may enhance the selectivity of supported systems towards metathesis at the expense of other reactions, such as olefin isomerisation, catalysed by these systems. In general, silica based catalysts require higher operating temperatures than those based on alumina and consequently exhibit greater resistance to catalytic poisons such as alcohols, water and other polar molecules (48).

The activity of WO_3-SiO_2 catalysts gradually increases for some time after reaction with olefins. This induction period can be shortened or even eliminated by controlled treatment with reducing gases such as CO or H_2, though prolonged treatment causes deactivation(49).

Spectroscopic investigations of the heterogeneous catalysts WO_3-SiO_2 and MoO_3-Al_2O_3 which had previously been treated with CO or H_2 revealed the formation of reduced metal species(50,51). This has been confirmed by Giordano et al(53,54) who have suggested that the metathetic activity of MoO_3-Al_2O_3 is related to the concentration of Mo^{V} species in the catalyst. The Mo^{V} species were believed to exist as bis molybdenyl species formed by the reduction of the tetrahedral

Mo^{VI} species to tetrahedral Mo^{V} species.

Many supported metal oxide catalysts become deactivated through prolonged use by the accumulation of carbon deposits on the surface of the catalysts. It is possible to regenerate the catalyst by treatment with oxygen at elevated temperatures which burns off the coke deposits.

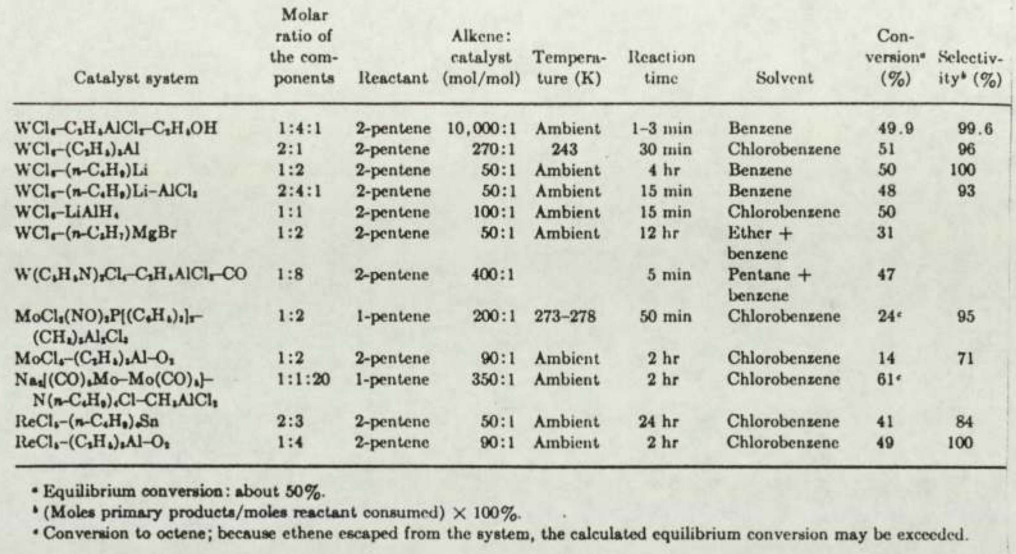
1.3.1.2 Supported Metal Carbonyl Catalysts

Generally, these catalysts require much lower temperatures (110°- 140 °C) for activation than the supported oxide catalysts(55,56). Unfortunately these catalysts become deactivated in air due to the formation of WO_3. This necessitates the use of high vacuum conditions or an inert atmosphere during activation. During activation, the catalysts lose some carbon monoxide ligands to produce sub-carbonyl species e.g. $Mo(CO)_{6-x}$ where $1 > x < 6$.

1.3.2. Homogeneous Catalysts

Natta and coworkers were the first to report the use of homogeneous catalysts (WCl_6/Et_3Al) for the ring-opening polymerisation of cyclopentene, although its significance to the olefin metathesis reaction was not appreciated(5). Subsequent studies have revealed a wide range of homogeneous catalyst systems that exhibit metathetic activity, some of which are shown in Table 1.1(57).

Table 1.1 Typical examples of catalyst systems for the homogeneous metathesis of pentene.



Catalyst system	Molar ratio of the components	Reactant	Alkene: catalyst (mol/mol)	Temperature (K)	Reaction time	Solvent	Conversion[a] (%)	Selectivity[b] (%)
WCl_6–$C_2H_5AlCl_2$–C_2H_5OH	1:4:1	2-pentene	10,000:1	Ambient	1–3 min	Benzene	49.9	99.6
WCl_6–$(C_2H_5)_3Al$	2:1	2-pentene	270:1	243	30 min	Chlorobenzene	51	96
WCl_6–$(n\text{-}C_4H_9)Li$	1:2	2-pentene	50:1	Ambient	4 hr	Benzene	50	100
WCl_6–$(n\text{-}C_4H_9)Li$–$AlCl_3$	2:4:1	2-pentene	50:1	Ambient	15 min	Benzene	48	93
WCl_6–$LiAlH_4$	1:1	2-pentene	100:1	Ambient	15 min	Chlorobenzene	50	
WCl_6–$(n\text{-}C_3H_7)MgBr$	1:2	2-pentene	50:1	Ambient	12 hr	Ether + benzene	31	
$W(C_5H_5N)_2Cl_4$–$C_2H_5AlCl_2$–CO	1:8	2-pentene	400:1		5 min	Pentane + benzene	47	
$MoCl_2(NO)_2P[(C_6H_5)_3]_2$–$(CH_3)_3Al_2Cl_3$	1:2	1-pentene	200:1	273–278	50 min	Chlorobenzene	24[c]	95
$MoCl_5$–$(C_2H_5)_3Al$–O_2	1:2	2-pentene	90:1	Ambient	2 hr	Chlorobenzene	14	71
$Na_2[(CO)_5Mo$–$Mo(CO)_5]$–$N(n\text{-}C_4H_9)_4Cl$–CH_3AlCl_2	1:1:20	1-pentene	350:1	Ambient	2 hr	Chlorobenzene	61[c]	
$ReCl_5$–$(n\text{-}C_4H_9)_4Sn$	2:3	2-pentene	50:1	Ambient	24 hr	Chlorobenzene	41	84
$ReCl_5$–$(C_2H_5)_3Al$–O_2	1:4	2-pentene	90:1	Ambient	2 hr	Chlorobenzene	49	100

[a] Equilibrium conversion: about 50%.

[b] (Moles primary products/moles reactant consumed) × 100%.

[c] Conversion to octene; because ethene escaped from the system, the calculated equilibrium conversion may be exceeded.

One of the main factors governing the activity of homogeneous catalyst systems is the molar ratio of the catalyst to cocatalyst. For the catalyst system WCl_6/LiBu there is a marked dependence of reactivity upon the catalyst/cocatalyst ratio, the greatest activity is found for a 1:2 molar ratio for the metathesis of pent-2-ene. This optimum ratio was attributed to the reduction of W^{VI} to W^{IV}. Similarly, some tungsten-based catalysts which use aluminium cocatalysts produce an optimum activity at a W:Al ratio of 1:2 (e.g. WCl_6/EtOH/$EtAlCl_2$)(59) whilst WCl_6/$EtAlCl_2$ exhibits maximum activity at a W:Al ratio of 1:4 for the metathetic polymerisation of 3-methylcyclooctene(6). It is probable that W^{VI} is reduced to W^{IV} by the cocatalyst, yet the exact nature of the W^{IV} is unknown. Tungsten tetrachloride, prepared in-situ by the reduction of W^{VI} by zinc, magnesium or sodium amalgams, has been shown to be metathetically inactive(60,61,13) so that the operation of the metathesis active species is not easily understood from these studies.

1.3.2.1. Effect of the Order of Mixing

It is usual to add catalyst and then cocatalyst to the reacting olefin in order to produce metathesis in a conventional reaction system. The effect of varying this order upon the course and reactivity of the system can be very dramatic and in many cases leads to alternative reactions. Addition of pent-2-ene to a premixed system of $WCl_6/EtAlCl_2$ in toluene results in rapid Friedel Crafts alkylation of the solvent, whereas preparation of the catalyst by the addition of WCl_6 and then $EtAlCl_2$ to the olefin results in metathesis(62,63).

$$\text{Olefin} + WCl_6 \xrightarrow[\text{Toluene}]{EtAlCl_2} \text{Metathesis products}$$

$$WCl_6 + EtAlCl_2 \xrightarrow[\text{Toluene}]{\text{Olefin}} \text{Friedel Craft Alkylation of toluene.}$$

In addition to the order of mixing the catalyst components, work carried out in these laboratories has shown that the initial rate of the ring-opening polymerisation of cyclopentene, catalysed by the $WCl_6/Al(iBu)_3$ system is dependent upon the time interval between the addition of catalyst and cocatalyst to the cycloolefin(31). Amass and coworkers (64) have shown that the time (t_{max}) to reach the maximum rate of polymerisation of cyclopentene depends upon the concentration of the monomer according to the following relationship:

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

To explain these results they proposed the existence of at least two species which exhibit different degrees of metathetic activity(31,64); that of greater activity reacts rapidly to produce a lesser active species.

Besides affecting the rate of reaction, the order of mixing of the catalyst components has been shown to affect the stereoselectivity of metathesis(65). Cis and trans pent-2-ene were metathesized into but-2-ene and hex-3-ene by the catalyst systems consisting of WCl_6 and R_4Sn or R_6Sn_2 as the cocatalyst ($R = Me, Bu, C_8H_{17}$ or Ph). The dependence of the cis/trans ratio of the product alkenes on the nature of the cocatalyst was studied along with the effect of the time interval between the addition of the cocatalyst to the WCl_6/olefin solution. The cocatalyst $Sn(Ph)_4$ showed a selectivity which differed from that induced by the other cocatalyst when the reacting olefin was added immediately after the cocatalyst. However, when the catalyst and cocatalyst were allowed to react for some time before the olefin was added, the resulting stereoselectivity was similar to that induced by the other catalyst systems. It was suggested that during the reaction at least two catalyst structures are formed. The first prevails in the early stages of the reaction between WCl_6 and $Sn(Ph)_4$ and induces a stereoselectivity which differs from that induced by WCl_6 and other cocatalysts. The second catalyst structure prevails when the catalyst and cocatalyst are allowed to react together for longer times and induces a stereoselectivity which is comparable with that induced by WCl_6 and other cocatalysts. The first structure might be formed immediately upon addition of any of the cocatalysts to WCl_6 and dissappears very quickly by further reaction except when the cocatalyst $Sn(Ph)_4$ is used. An alternative explaination is to assume that the first structure is only formed when $Sn(Ph)_4$ is used as a cocatalyst.

1.3.2.2. Enhancement of Catalytic Activity

The catalytic activity of WCl_6 based metathesis catalysts may be increased by controlled treatment of WCl_6 with aprotic materials such as ethanol, phenol, water or hydroperoxides prior to the addition of an organometallic cocatalyst. If excess of the oxygen containing material is added, the cocatalyst activity is destroyed.

When ethanol reacts with WCl_6 there is a stoichiometric release of hydrogen chloride along with the formation of WCl_5OEt(13). Hocker and Jones(66) have reported that the formation of WCl_5OEt is in fact a two step process.

$$WCl_6 + 2\ C_2H_5OH \xrightarrow{-HCl} (C_2H_5O)_2WCl_4$$

$$(C_2H_5O)_2WCl_4 + WCl_6 \longrightarrow 2\ C_2H_5OWCl_5$$

The activity of the premixed WCl_6/LiBu catalyst system can be inreased at least 100 fold by the addition of $AlCl_3$ (Li:W:Al = 2:1:1)(67) and indeed WCl_6 may itself be activated towards metathesis by this Lewis acid(4). Aluminium halides are not likely to function as reducing agents, unlike the organoaluminium cocatalysts, and it may be possible that the alkene itself reduces the transition metal catalyst complex. For example, 2-chloro and 2,3-dichloronorbornene were identified among the volatile products formed during the ring-opening polymerisation of norbornene(68).

Treatment of a number of molybdenum compounds with nitric oxide prior to the addition of an organoaluminium cocatalyst yields molybdenum nitrosyl species which have enhanced metathesis activities (16). Reaction of $[MoCl_3(PhCO_2)_2]$ with nitric oxide thirty minutes before the addition of the cocatalyst $[Me_3Al_2Cl_3]$ produces a catalyst that gives a 60% yield of oct-4-ene from pentene(69) after 17 minutes. Without the nitric oxide, this catalyst effects only 0·8% conversion of pent-1-ene after one hour.

Carbon monoxide increases the catalytic activity of metathesis catalysts derived from Group VI metal halide complexes and organoaluminium compounds. It has been found that $[WCl_4(C_5H_5N)_2]$ /$EtAlCl_2$ under an atmosphere of carbon monoxide exhibits a very different catalytic activity from the same system under argon(70). If some catalyst systems are over exposed to carbon monoxide they are deactivated; for example $WCl_3[C_2H_4\cdot(PPh_3)_2]_2$/$EtAlCl_2$ is converted into $W(CO)_6$.

1.3.2.3. Molar Ratio of Catalyst Components

For most homogeneous catalyst systems, the ratio of catalyst to cocatalysts are small intergers, i.e. 1:2, 1:4 or 2:3 (see Table 1.1). Following the disclosure by Wang and Menapace(58) that the catalyst system WCl_6/LiBu exhibits maximum activity for a W:Li molar ratio of 1:2 for the metathesis of pent-2-ene, many workers concluded that the role of the cocatalyst was the reduction of W^{VI} to W^{IV}; the reduced tungsten species would then react with the olefin to produce a tungsten olefin complex (as shown below) which was thought to be a bis olefin complex.

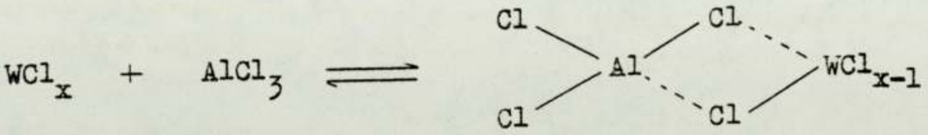
$$\begin{tikzcd}
\mathrm{WCl_6} + 2\ \mathrm{LiBu} \arrow[r] & \mathrm{Bu_2WCl_4} + 2\ \mathrm{LiCl} \arrow[d, "\mathrm{Olefin}"] \\
 & \mathrm{WCl_4(olefin)_2} + \mathrm{R\cdot}
\end{tikzcd}$$

By analogy with classical Ziegler Natta catalysts, Calderon(4,13) postulated the following series of reactions to account for the W:Al ratio of 1:2 for the catalyst $\mathrm{WCl_6/EtOH/EtAlCl_2}$

$$\begin{aligned}
\mathrm{WCl_6} + \mathrm{EtAlCl_2} &\longrightarrow \mathrm{EtWCl_5} + \mathrm{AlCl_3} \\
\mathrm{EtWCl_5} &\longrightarrow \mathrm{WCl_5} + \mathrm{Et\cdot} \\
2\ \mathrm{Et\cdot} &\longrightarrow \mathrm{C_2H_4} + \mathrm{C_2H_6} \\
2\ \mathrm{Et\cdot} &\longrightarrow \mathrm{C_4H_{10}}.
\end{aligned}$$

and then disproportionation of W^{V} to W^{VI} and W^{IV} leading to the generation of the active site. The formation of ethene and ethane (in addition to ethyl chloride) during the reaction of $\mathrm{WCl_5OEt}$ and $\mathrm{EtAlCl_2}$ has been confirmed experimentally, though this does not necessarily confirm the presence of ethyl radicals as predicted by Calderon.

Calderon has also suggested that $\mathrm{AlCl_3}$, whenever present, plays an active role in the metathesis catalyst and proposed two alternate schemes to account for this. The presence of $AlCl_3$ formed during the reaction between the tungsen catalyst and the organoaluminium cocatalyst (previous page) may give rise to associations via μ -chloride bonds (equation 1.1) or even an acid-base type equilibrium (equation 1.2).



(1.1)

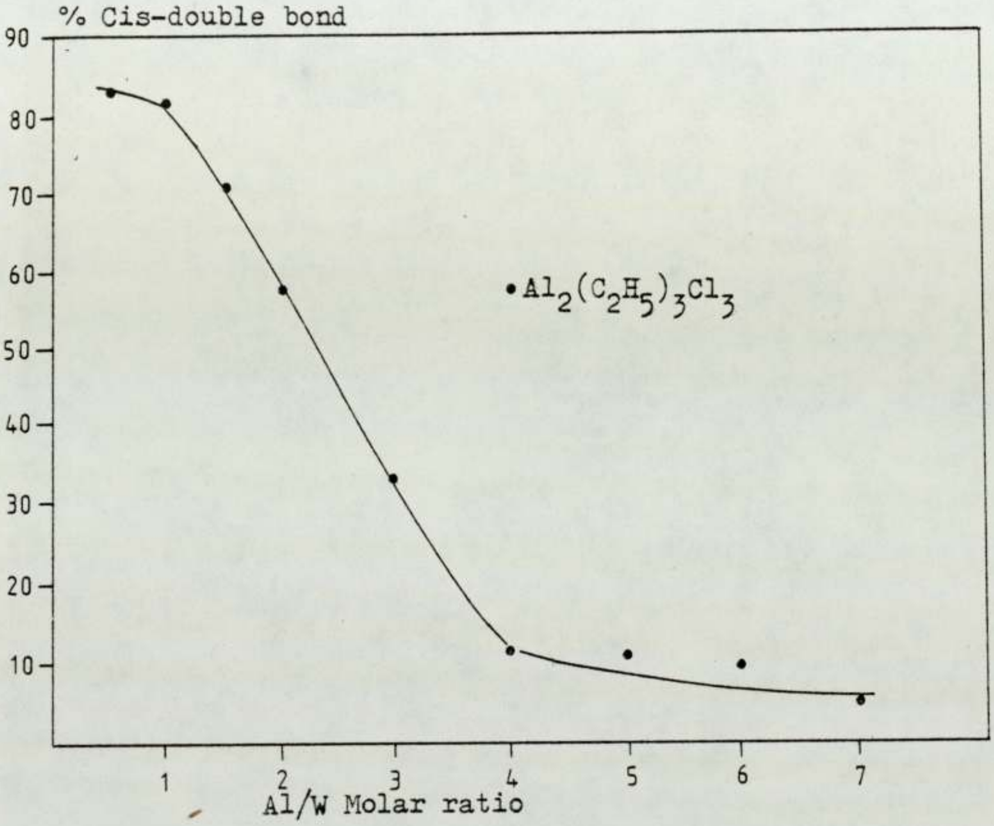
$$WCl_x + AlCl_3 \rightleftharpoons WCl_{x-1}^{+} + ALCl_4^{-} \qquad (1.2)$$

This second alternative though seems very unlikely in non polar environments.

Direct evidence for the significant involvement of $AlCl_3$ during metathesis comes from the work by Wang and Menapace(67). They demonstrated that the activity of the binary catalyst system WCl_6/LiBu can be increased by at least 100 fold if an equimolar amount of $AlCl_3$ is added to the reaction system - pentene/WCl_6/LiBu.

The nature of the organometallic cocatalyst also affects the stereostructure of polymers obtained from the ring-opening polymerisation of cycloolefins. Gunther et al(71) found that a tungsten hexachloride/$AlEt_3$ catalyst produced a trans polypentenamer whereas tungsten hexachloride/$Na_2W(C_6H_5)_5$ produces a cis polymer. They also observed that using a $WF_6/Al_2Et_3Cl_3$ catalyst a continuous variation in the cis:trans ratio of a polypentenamer sample could be achieved by varying the aluminium:tungsten molar ratios in the catalyst.

Fig. 1.1 Polypentenamer microstructure as a function of W/Al ratio.



1.3.2.4. Nature of Soluble Catalysts

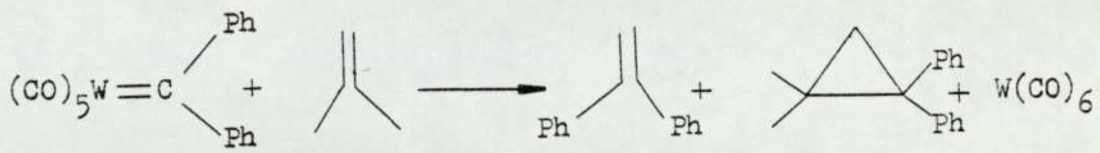
Doubt has recently been cast on the precise nature of some tungsten based homogeneous catalyst systems. Muetterties and Busch(72) have reported the presence of solids in the catalyst systems WCl_6/EtOH/ $EtAlCl_2$, $WCl_6/2EtAlCl_2$, WCl_6/2LiBu and WCl_6/R_2Zn. If the premixed catalyst system WCl_6/2LiBu is filtered, then the colourless filtrate yields no metathesis products with cis pent-2-ene, whilst the solids showed a catalytic activity nearly as high as the standard, unfiltered reaction system. Wolovsky and Nir(73) have however reported conflicting evidence to that of Muetterties, by demonstrating that it is the soluble fraction of the $WCl_6/EtAlCl_2$ system that is responsible for the metathesis of cyclodecene.

Basset and coworkers(74) have made a systematic study of the stereochemistry of cis pent-2-ene using a range of both homogeneous and also heterogeneous alumina supported catalysts. They concluded that the stereoselectivity of metathesis is indepedent of (i) the electronic effects of the ligands coordinated to zerovalent precursor complexes of the type $W(CO)_5L$ ($L = CO$, $P(nBu)_3$, PPh_3); (ii) the number of coordination sites or the steric hindrence of the ligands occuping these sites; (iii) the oxidation state of the precursor complexes (W^6 , W^o), for homogeneous catalysts. The heterogeneous catalysts do however appear to be of greater regulating capacity than similarly structured homogeneous systems. It has therefore been suggested that it may be possible to solve the controversy about the homogeneous nature of some catalyst systems by studying the stereoselectivity of those catalyst systems and comparing with known homogeneous and heterogeneous systems.

1.3.2.5. Carbene Based Metathesis Catalysts

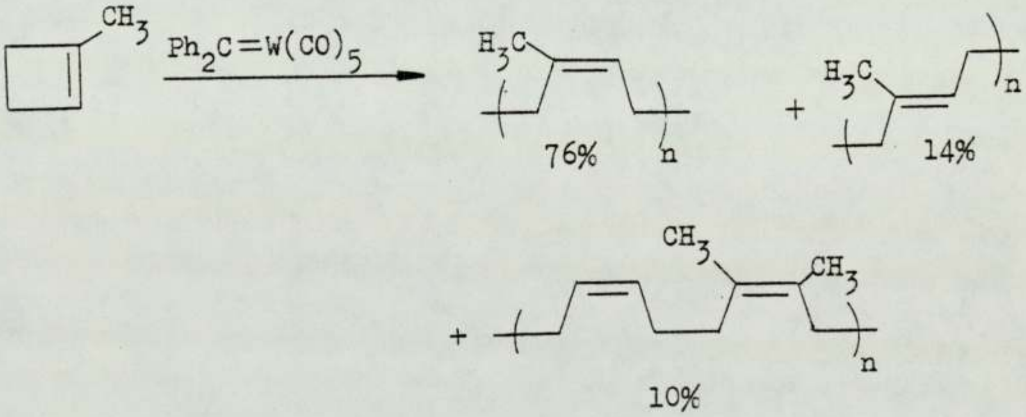
Although metathesis catalysts can be conveniently classified as either heterogeneous or homogeneous, this classification has no relationship to any proposed mechanistic scheme.

Following the suggestion by Herisson and Chauvin(75) that olefin metathesis may involve metallocarbenes, Cassey and Burkhardt(76) synthesised (diphenylcarbene) pentacarbonyltungsten (0) and studied its reaction with 2-methylpropene.



They found that the formation of the products, especially 1,1-diphenylethene and 1,1-dimethyl-2,2,-diphenylethene were in total agreement with the proposed metallocarbene/metallocyclobutane scheme suggested by Herisson and Chauvin.

Katz(77,78,79) verified the use of (diphenylcarbene)pentacarbonyltungsten (0) as a metathesis catalyst in its reaction with unsymmetrically substituted ethylenes and 1-methylcyclobutene.



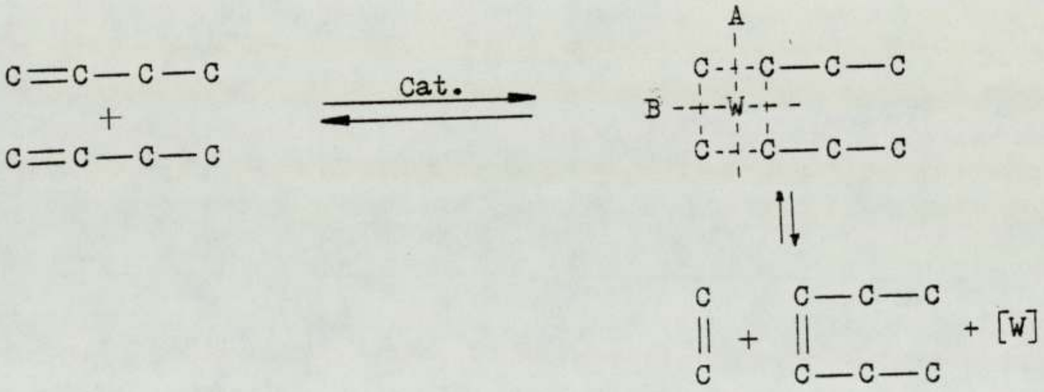
Other carbenes have been used in metathesis, notably Fischers carbene (80). (Phenylmethoxycarbene)pentacarbonyltungsten (0) initiates the metathesis of norbornene at 60 °C to produce a yield of 53% polynorbornene after 6 days.

1.4 MECHANISMS

Concurrent with the development of homogeneous metathesis catalysts, Calderon was able to demonstrate that olefin metathesis occurred by an alkylidene redistribution reaction. Following this announcement, many researchers attempted to describe the mechanism of redistribution; one of the earliest of these mechanisms was that suggested by Bradshaw et al(46).

1.4.1 Quasicyclobutane Model

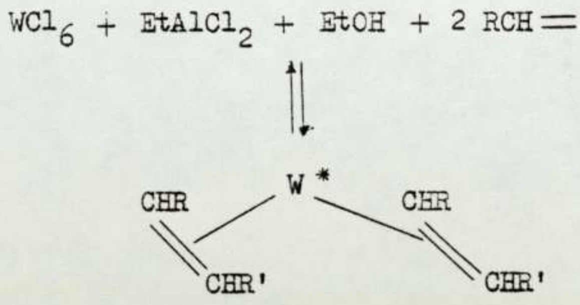
Olefin dismutation of n-butenes over a heterogeneous catalyst derived from cobalt, molybdenum and aluminium oxides was studied by Bradshaw et al(46) who proposed that metathesis occurred via a coordinated quasi-cyclobutane intermediate formed by the correct alignment of the carbon atoms of the double bonds of the reacting olefins; as shown in scheme below.



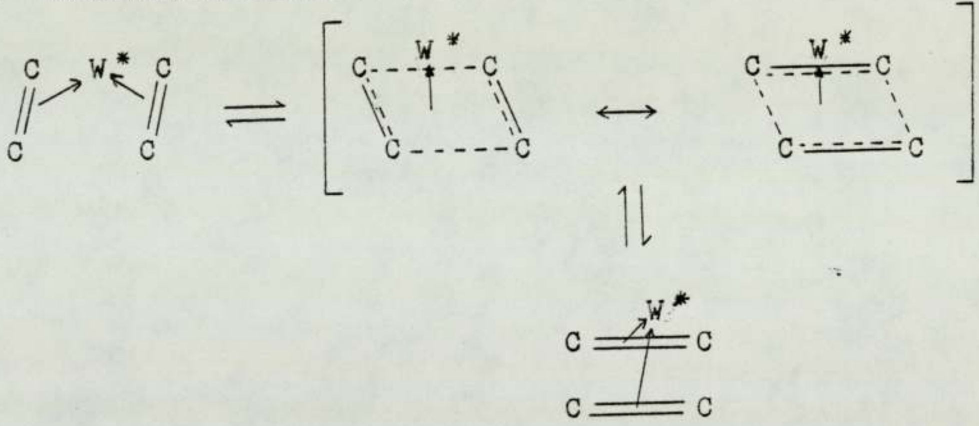
Cleavage along axis A leads to the production of two new olefins (productive metathesis) whilst cleavage across axis B regenerates the starting olefins (degenerate metathesis).

In order to characterise the quasicyclobutane model more fully Calderon suggested a series of reactions(13) as shown below:

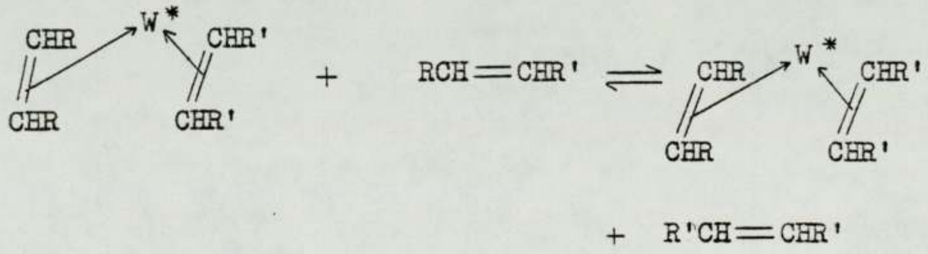
(i) Olefin coordination



(ii) Transalkylidenation



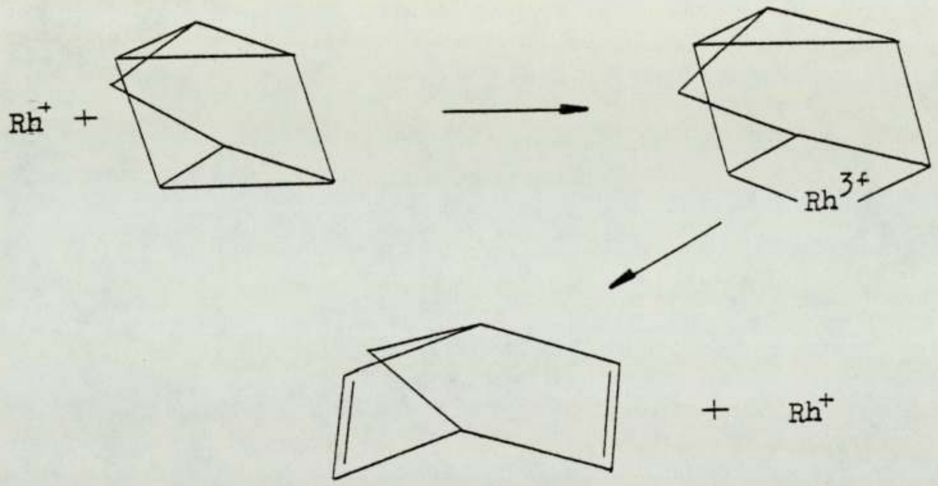
(iii) Olefin exchange



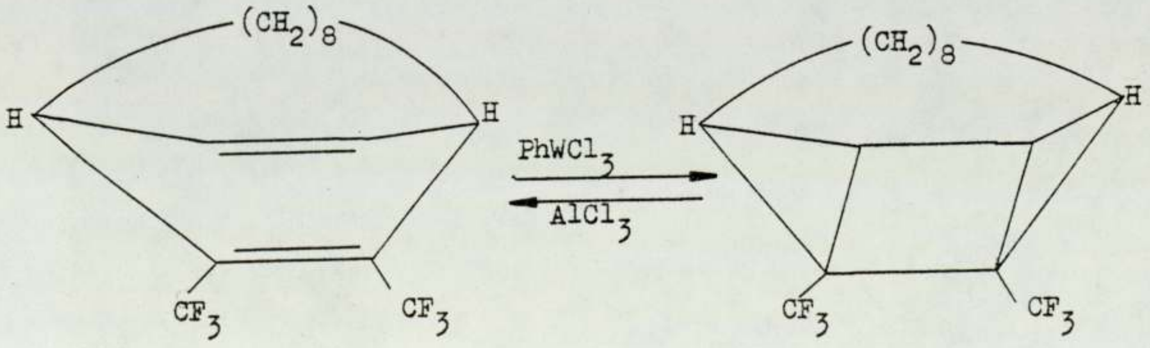
where W * represents the active species.

Concerted (2 + 2) pericyclic reactions in the absence of a catalyst are symmetry forbidden according to the Woodward Hoffmann rules(81).

However, Mango and Schachtschneider suggested that a transition metal system of the prerequisite energy might provide an orbital pathway to allow reaction to proceed. An example of such is the conversion of quadricyclene to norbornadiene which is thermally forbidden but is catalysed by $Rh_2(CO)_4Cl_2$(84) at ambient temperatures. However, it would now appear that this reaction proceeds in the following stepwise manner(85):



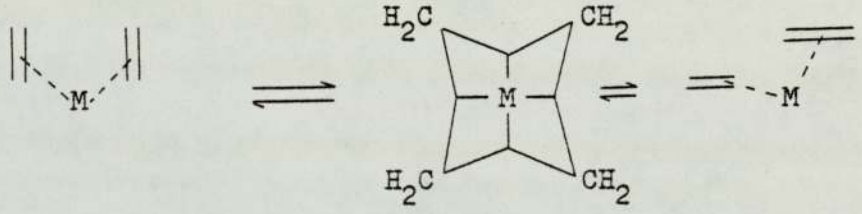
and is not strictly a counterpart of the quasicyclobutane scheme. Additional evidence to support the quasicyclobutane model arose from the conversion of a non conjugated diene into a cyclobutane derivative using a common metathesis type catalyst(86).



Since ethylene and cyclobutane do not equilibriate in the presence of metathesis catalysts the mechanism governing the quadricyclene conversion is now believed not to explain metathesis.

1.4.2 Tetramethylene-Metal Complex Model

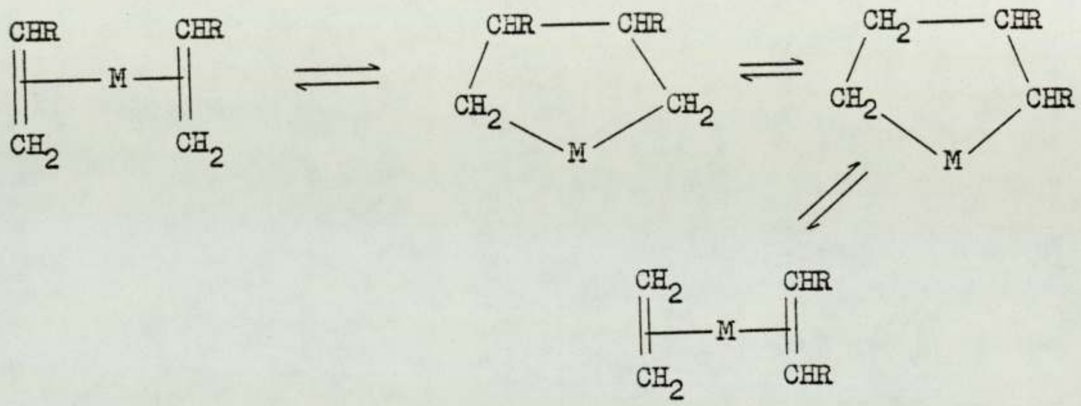
Whilst the quasicyclobutane model successfully predicts the nature of the products for most metathesis reactions and has sound theoretical justifications, a failure to identify cyclobutane or its complexes as separable intermediates in the metathesis of ethene casts some doubt on the validity of this model. To overcome this problem, Lewandos and Petit(87) suggested that metathesis involved the production of a tetramethylene-metal complex in which the olefins exist as ligands attached to the transition metal catalyst by way of four carbon-metal sigma bonds.



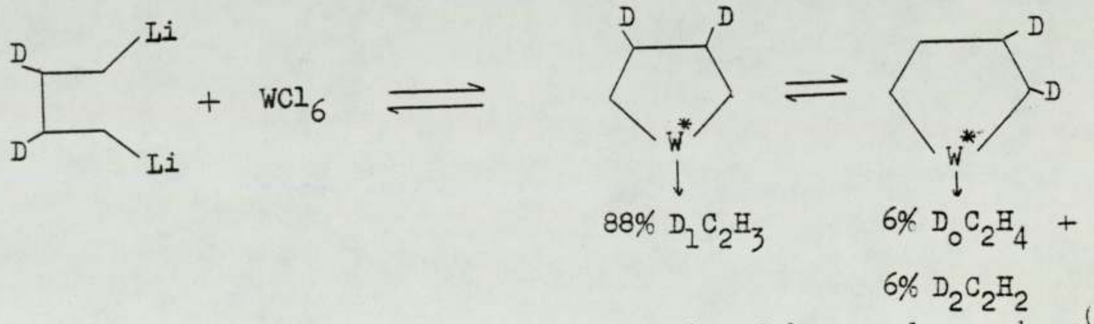
The tetramethylene model has also been treated theoretically and is based on a set of molecular orbitals built up from sp^3 carbon hybrid orbitals and the appropriate metal orbits.

1.4.3 Pairwise Non Concerted Scheme

Although the preceding models could be explained readily on theoretical grounds, there was little direct experimental evidence to support them. Therefore, following the pioneering work of Fisher(88) and Katz(89) on the rhodium catalysed rearrangement of strained carbocyclic systems, Grubb et al proposed a non-concerted pairwise exchange of alkylidenes via a metallocyclopentane intermediate(90).

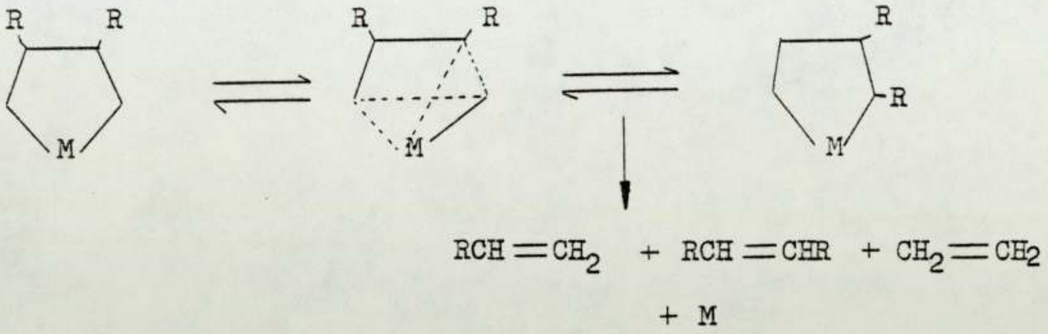


Their proposals were largely based on the observation that WCl$_6$ reacted with 1,4-dilithio-2,3-dideuterobutane giving deuteroethylenes.



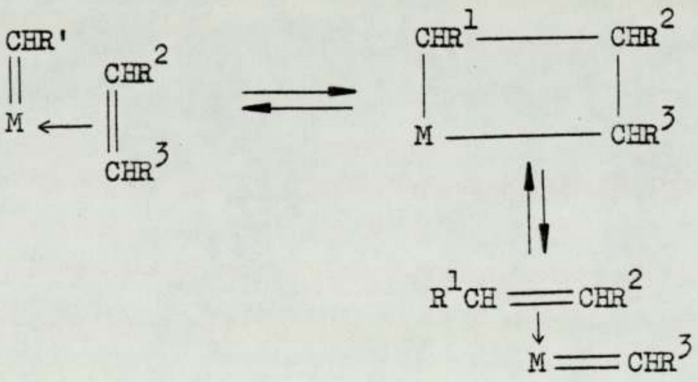
Supporting evidence for this scheme arose when Osborn and coworkers(91) demonstrated that Ir(norbornadiene)$_3$Cl contained a five membered metallocycle which yielded norbornadiene dimer upon refluxing with triphenylphosphine.

From a study of the geometry of bis (triphenylphosphine) tetramethylene platinum (II) Grubbs(92) proposed a possible third step to account for the rearrangement of the metallocycle to yield metathesis products.

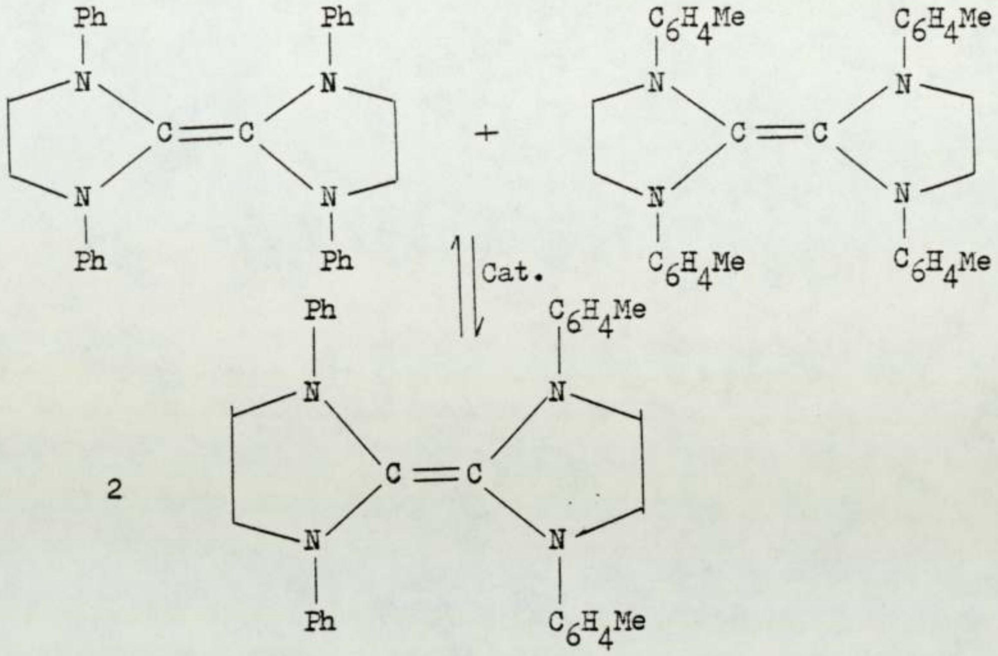


1.4.4. Metallocarbene-Metallocyclobutane Model

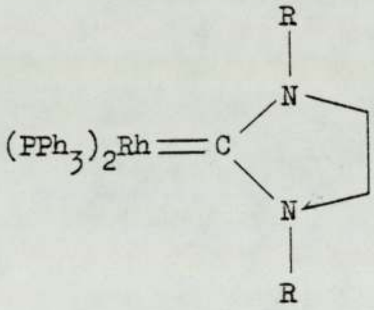
In order to explain the ratios of telomers from the cross metathesis of cyclopentene and pent-2-ene, Herisson and Chauvin(75) proposed a metallocarbene-metallocyclobutane mechanism which may be summerised as:



This scheme was also independently proposed by Lappert and coworkers (93) who had shown that electron rich olefins undergo metathesis with Rh^{I} catalysts at high temperatures.



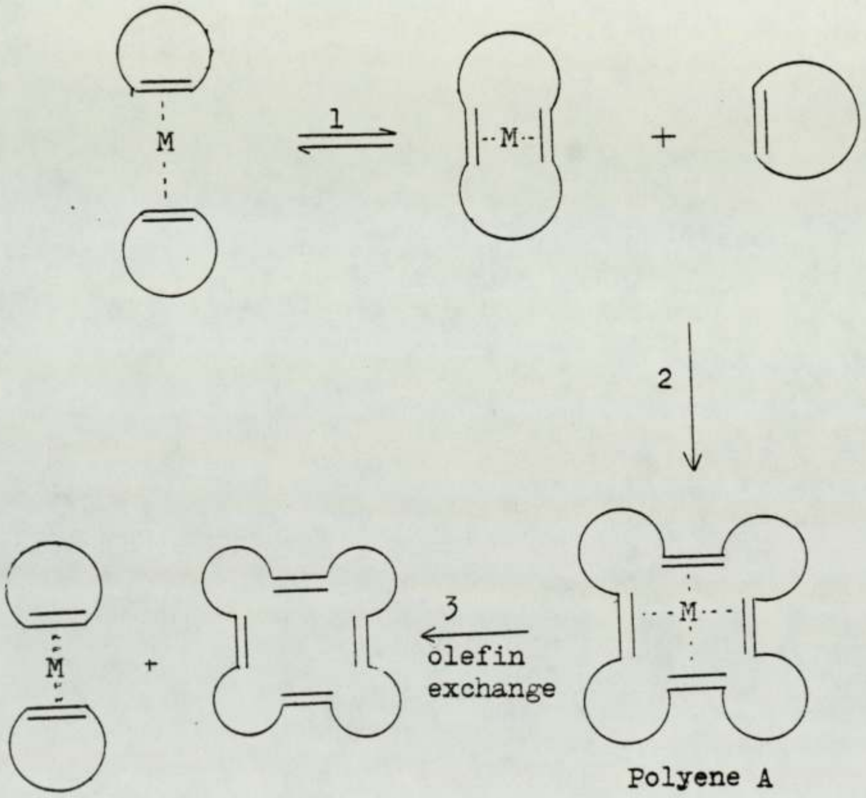
A rhodium carbene complex (I) was isolated and shown to act as a catalyst in the above reaction.



(I)

1.4.4.1. Evidence supporting the carbene mechanism

Dolgoplosk(94,95) has suggested that evidence supporting the carbene mechanism arises from the production of high molecular weight polymer from the metathesis of cyclic olefins at low reaction times by an efficient chain propagation mechanism. If, however, the transalkylidenation step (step 2 in the scheme below) is much faster than olefin exchange, the production of high molecular weight polymers at low reaction times can be explained in terms of the Calderon model.

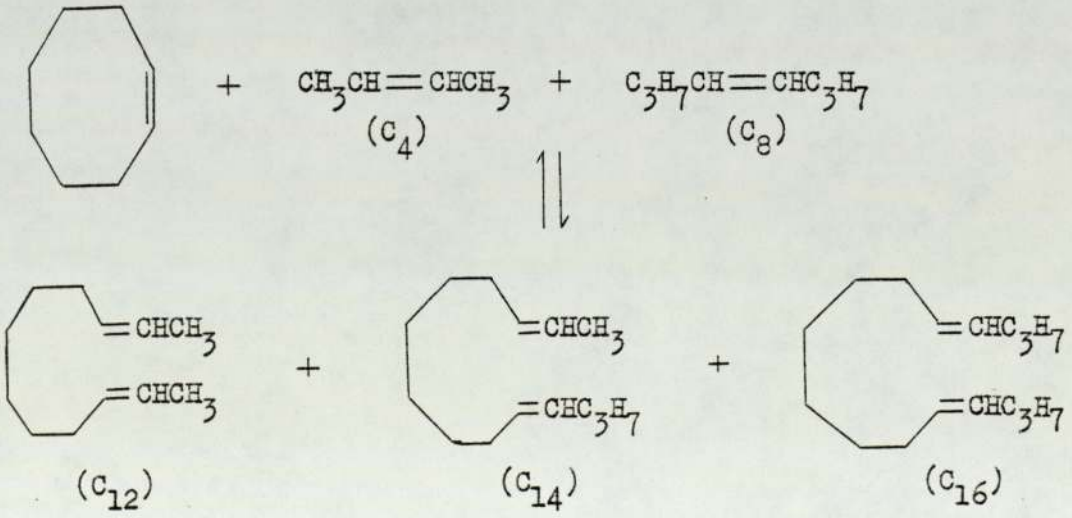


If step 2 is much faster than step 3 then there would be a very rapid build up of the macrocyclic polyene A before olefin exchange (step 3) terminates the step. If olefin exchange occurred at a similar rate as step 2 then the macrocyclic polyene would only contain a few monomer units and so the polymers produced would possess low molecular weights.

Further evidence supporting a carbene chain mechanism was provided by Dolgoplosk(94,95) who showed that high molecular weight polymer can be obtained from the metathesis of cyclopentene using a catalyst of diazomethane with either $MoCl_5$ or WCl_6. The diazomethane was believed to breakdown at the surface of the transition metal catalyst to produce a methylene carbene ($:CH_2$) which would initiate metathesis. This contention was supported by O'Neill and Rooney(96) who found that diazomethane decomposes quantitatively to ethylene and nitrogen on the $CoO.Mo_2O_3.Al_2O_3$ active sites which also catalyse the metathesis of propene.

The clearest evidence for the metallocarbene mechanism was supplied by Cassey(76) when he found that (diphenylcarbene)pentacarbonyltungsten (0), $Ph_2C{=}W(CO)_5$, yields metathesis type products with a variety of olefins (see Section 1.3.2.5).

In order to differentiate between the pairwise and non-pairwise models, Katz and McGinnis(97) investigated the reaction between cyclooctene, but-2-ene and oct-4-ene.

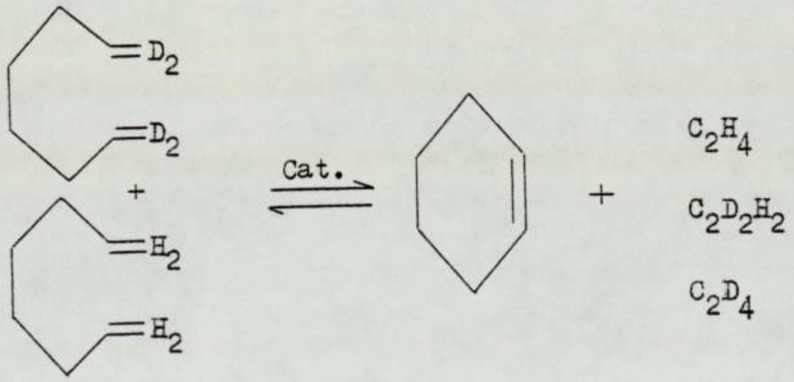


$$+ \quad CH_3CH{=}CHC_3H_7$$

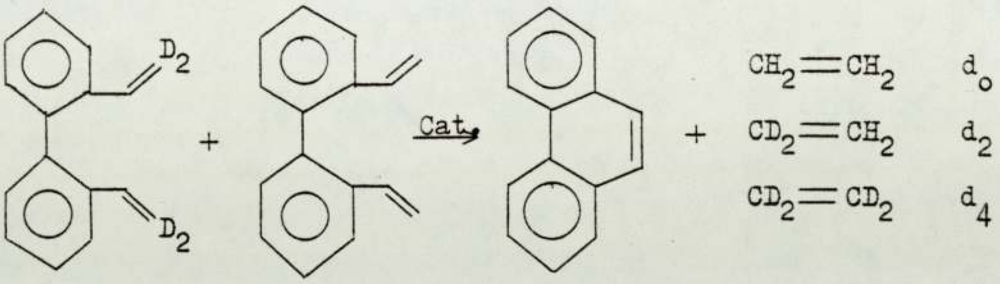
(C_6)

If the carbene mechanism were to hold, then the unsymmetrical (C_{14}) product should predominate over the (C_{12}) or (C_{16}) products by at least a factor of 2 during the early stages of the reaction. Although the amount of the (C_{14}) product was significantly higher than that of the (C_{12}) or (C_{16}) products these experiments do not preclude the pairwise scheme, since if the rate determining step was olefin exchange then the pairwise scheme can account for the ratio of the reaction products.

To avoid these problems, Grubbs et al(98) studied the metathesis of 1,7-dienes, whereby the products could not equilibriate in secondary reactions; as shown in the scheme below.



Since cyclohexene does not undergo further metathesis, the ratio of d_4:d_2:d_o products can be calculated exactly for both pairwise and non-pairwise mechanisms under non equilibrating conditions. For a 1:1 mixture of the d_4 and d_o 1,7-diene system, the pairwise mechanism would produce a 1:1·6:1 mixture of d_4:d_2:d_o products while a carbene mechanism predicts a product ratio of 1:2:1. The observed product ratios were those predicted by the carbene mechanism i.e. 1:2:1. Further experiments(99) using labelled 2,2'-divinylbiphenyl, under non equilibrating conditions, also yields the same results as above.



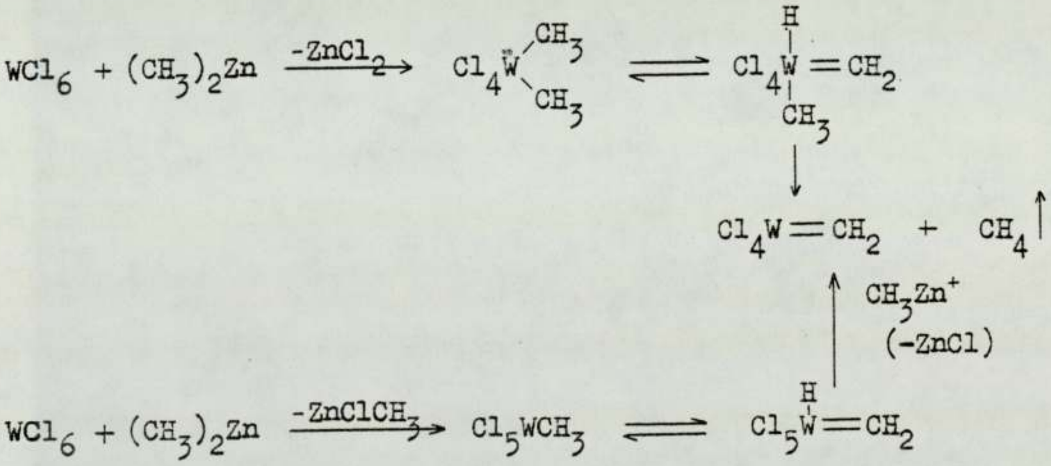
When equal amounts of deuterated and undeuterated 2,2'-divinylbiphenyls were combined with either molybdenum or tungesten catalysts, the ratios of the undeuterated, dideuterated and tetradeuterated ethylenes after about 1% reaction were found to be approximately 1:2:1 (24% d_o, 48·7% d_2 and 25·9% d_4), while the divinylbiphenyl precursers were still 1:0:1. The amount of isotope scrambling in the remaining divinylbiphenyls was measured at about 1%. The disparity could not be ascribed to rapid scrambling of the ethylenes after their initial formation since metathesis of undeuterated divinylbiphenyl in the presence of trans-1,2-dideuteroethylene did not give appreciable amounts of monodeuterated ethylene.

1.4.4.2 Generation of Carbenes

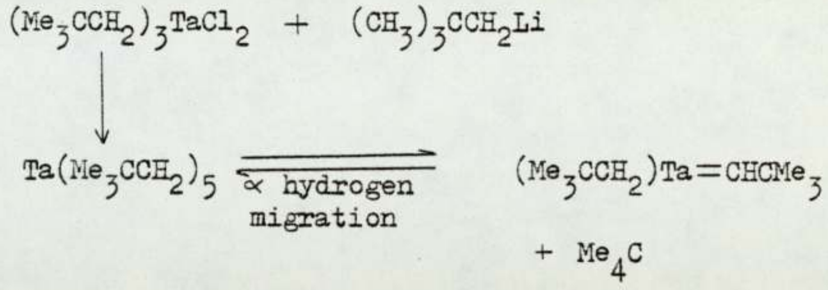
Although it is now widely accepted that olefin metathesis proceeds via a metallocarbene-metallocyclobutane intermediate, the generation of these carbenes has not been fully explained. Because of the diversity of metathesis catalysts it is not possible to provide a single unique model to explain the formation of metallocarbenes in these systems. It is therefore convenient to consider heterogeneous and homogeneous catalyst systems separately.

1.4.4.3 Catalysts Activated by Organometallic Cocatalysts

One of the earliest schemes to explain the generation of metallocarbenes in the olefin metathesis reaction stemmed from the observed evolution of methane from the reaction between tungsten hexachloride and dimethyl zinc. Muetterties(100) proposed two alternate routes to the synthesis of the metallocarbene, both are shown below.

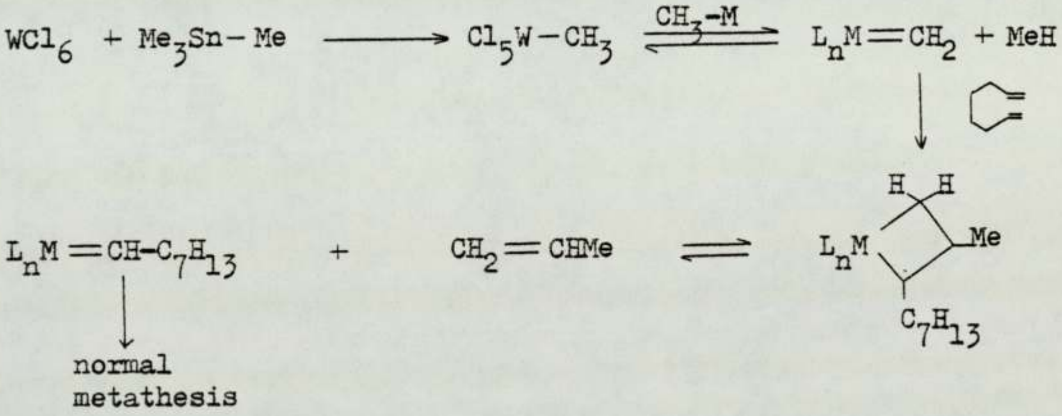


Muetterties suggested that the metallocarbene would be formed in a series of reactions, involving the addition of an alkyl group to the transition metal followed by an α hydrogen abstraction. The existence of a $CH_3{-}W \rightleftharpoons CH_2{=}W{-}H$ equilibrium by migration of a α hydrogen to the tungsten metal has recently been demonstrated by Green and Cooper(101). Additional evidence supporting the generation of metallocarbenes appeared with the isolation of an alkylidene tantulum complex by Schrock(102,103).



$$\begin{array}{l}(Me_3CCH_2)_3TaCl_2 + (CH_3)_3CCH_2Li \\ \downarrow \\ Ta(Me_3CCH_2)_5 \underset{\text{migration}}{\xrightleftharpoons[\alpha\ \text{hydrogen}]{}} (Me_3CCH_2)Ta{=}CHCMe_3 + Me_4C\end{array}$$

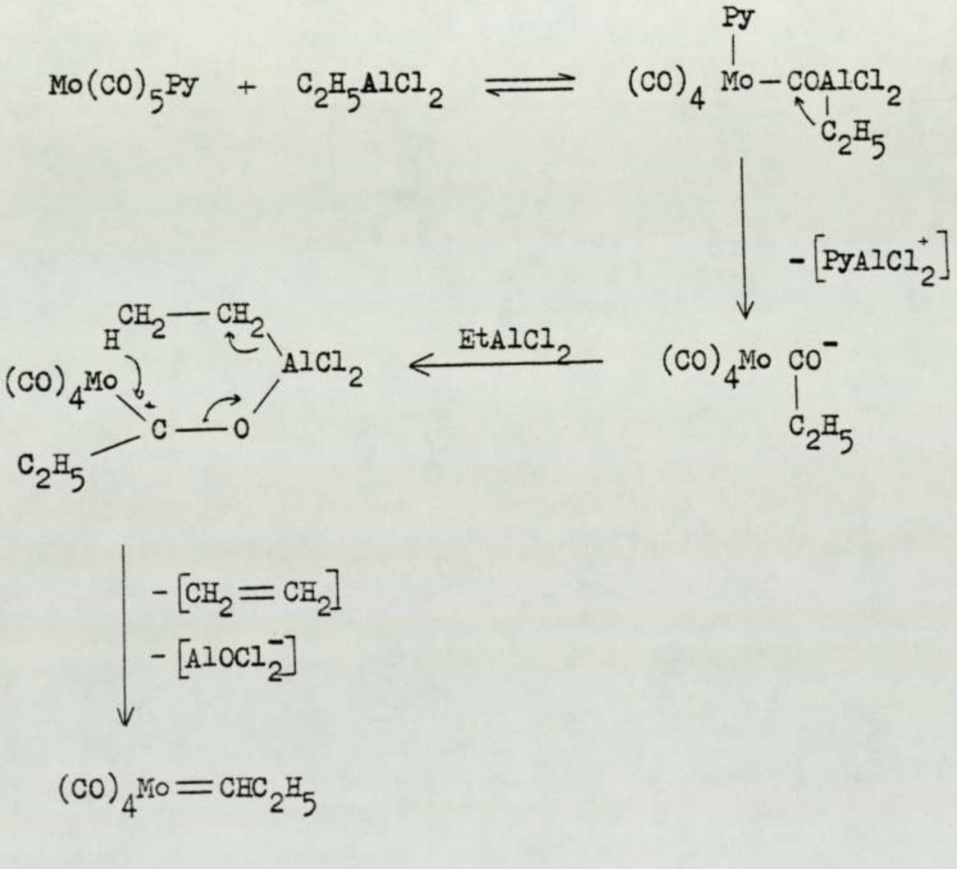
The initial production of propene from the metathesis of deca-2,8-diene eith either Me_4Sn/WCl_6 or $(Ph_3P)_2(NO)_2Cl_2Mo/Me_3Al_2Cl_2$ was also taken as evidence for the generation of metallocarbenes by an α hydrogen abstraction route, as shown below.(104).



Deuterium labelling experiments(105) involving $(CD_3)_4Sn$ and $(1,1,1,-10,10,10,d_6)$ 2,8-decadiene confirmed that propene is indeed the first formed olefin, and its structure indicated that the methylidene and ethylidene moieties originated from the $(CD_3)_4Sn$ and $(1,1,1,-10,10,10,d_6)$-2,8-decadiene, respectively.

Dolgoplosk(106) has reported the generation of a tungsten carbene from the reaction between Me_3SiCH_2Li and tungsten hexachloride; again the carbene species is probably formed by an α hydrogen migration mechanism.

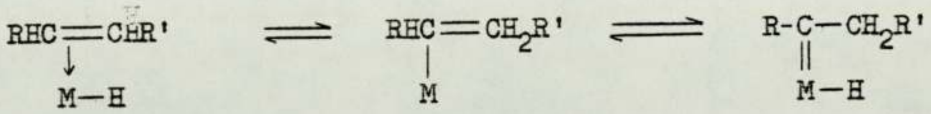
An alternatate route to the formation of the metallocarbene has been proposed (107) for the $RAlCl_2/Re(CO)_5Cl$ and $RAlCl_2/Mo(CO)_5Py$ systems in order to explain the presence of minor amounts of 1,7-octadiene. The key step is the insertion of a CO ligand in the $R-AlCl_2$ bond followed by the following series of steps as shown below:



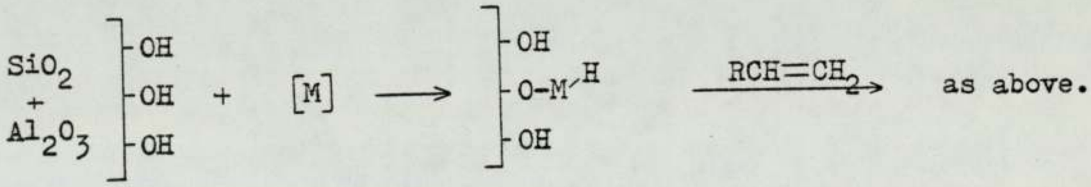
Whereas the formation of metallocarbenes can be reasonably accounted for when using catalysts activated by organometallic cocatalysts, pathways for carbene formation in systems that do not employ organometallics are in most cases still unresolved.

1.4.4.4. Catalysts without Organometallic Cocatalysts

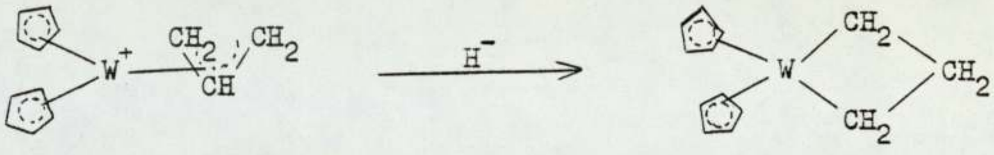
Following a report that metal hydrides were responsible for the ring-polymerisation and dimerisation reactions of norbornene catalysed by several transition metal halides Laverty et al(108) proposed a possible role for hydrido-metal complexes in metathesis.



The carbene arises by a β -hydrogen addition of a metal hydride to the olefin followed by an ∝ -hydrogen elimination. There are numerous possible sources of the hydride, such as water, hydroxyl ligands on the support, and traces of acid produced in the preparation of the catalyst complex(109). A similar reaction could be the major initiation step for supported catalysts with a siloxyl or aluminium alkoxide group providing the initial proton(110).

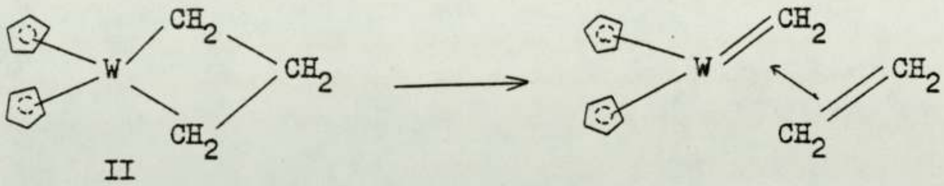


Green and coworkers(111) demonstrated that metallocyclobutanes can be produced by the reduction of $Cp_2W(allyl)^+$ complexes.



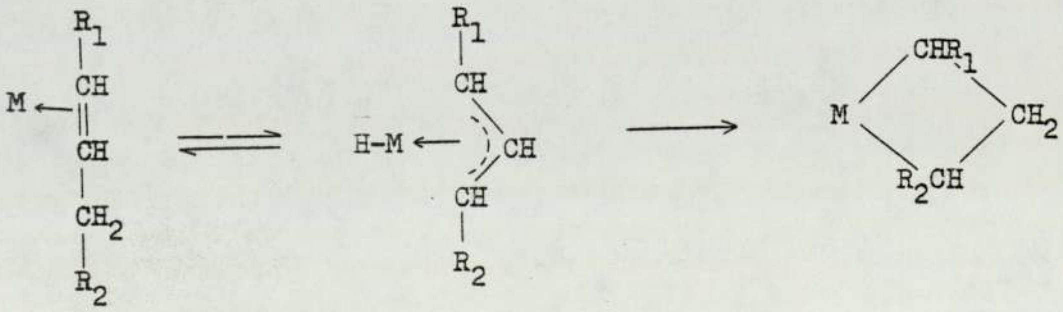
II

The metallocyclobutane (II) undergoes photolytic decomposition to yield ethylene and some methane(112).



II

Osborn and Green's elegant results are instructive, but their relevance to metathesis must be qualified. Until actual catalytic activity with the respective complexes is demonstrated, it remains uncertain whether this chemistry indeed relates to olefin metathesis. If relevant to metathesis, their work provides a basic reaction wherein an olefin and a metal exclusively may produce the initiating carbene-metal complex by a simple sequence of π-complexation followed by a hydride shift. The π-allyl-metal hydride entity thus formed may rearrange into a metallocyclobutane via a nucleophilic attack of the hydride on the central atom of the π-allyl species:



This scheme implies that ethylene cannot generate the starting metallocyclobutane; hence, it will be inert to self metathesis. Indeed, Olthoorn and Tucker (113) found that it was necessary to pre-expose the catalyst system Re_2O_7/Al_2O_3 to higher olefins such as propene or but-1-ene before they could appreciably metathesize C_2H_4 with C_2D_4.

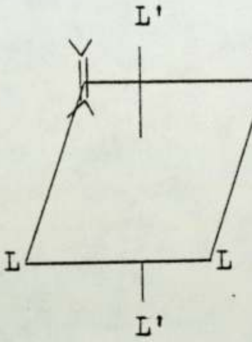
1.5 KINETICS

Whilst the kinetics of the heterogeneously catalysed metathesis of linear olefins has been studied in detail, only a few reports have appeared dealing with the kinetics of homogeneous sytems.

1.5.1 Kinetics of Acyclic Metathesis Reactions

In a series of papers, Zuech et al (16) reported that nitrosyl complexes of molybdenum and tungsten $L_2Cl_2(NO)_2M$ (where M = Mo or W and L = Ph_3P, C_5H_5N, Ph_3PO) when treated with alkylaluminium chlorides exhibit metathetic activity. The activity of the nitrosyl complexes depends on the nature of the metal and the ligand. Catalysts containing tungsten are less active than the analogous molybdenum compounds. The $(C_5H_5N)_2Cl_2(NO)_2Mo$ complexes showed the highest selectivity.

The kinetics of the homogeneous disproportionation of pent-2-ene were investigated, using the catalyst $(C_5H_5N)_2Cl_2(NO)_2Mo/EtAlCl_2$. The order of the reaction was determined as unity with respect to the catalyst and variable with respect to the olefin; at a low olefin concentration the order is 1·7 while at a high olefin concentration the order changes to 0·7. The activation energy was found to be 54·9 KJ mole^{-1}. To explain these observations, Zuech suggested that the catalyst is a zerovalent molybdenum species and metathesis occurs via a molybdenum-diolefin complex, shown below:

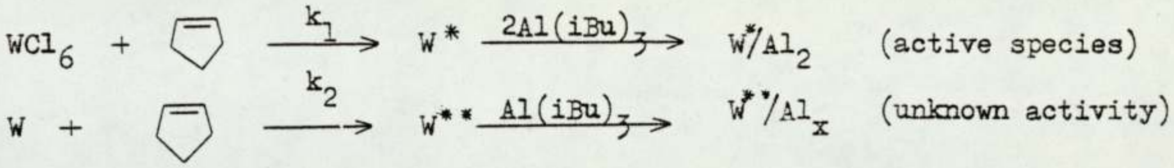


At present the identies of L and L' are not known.

1.5.2 Kinetics of Ring-Opening Polymerisation Reactions.

The kinetics of the ring-opening polymerisation of cycloolefins in the presence of homogeneous metathesis catalysts has also been reported$^{(114)}$.

Amass and Tuck$^{(28)}$ have studied the rate of polymerisation of cyclopentene catalysed by the bimetallic catalyst $WCl_6/Al(iBu)_3$. They observed a strong dependence of the rate of polymerisation and the time delay (ageing time) between the addition of the catalyst components WCl_6 and $Al(iBu)_3$ to a solution of cyclopentene, and suggested the following reactions to account for their observations.



They described a term t_{max} which was defined as the ageing time of WCl_6 with cyclopentene that produced the maximum rate of polymerisation when the cocatalyst was added. From an analysis of the proposed reactions they formulated a kinetic scheme which agreed with the observation that there was a reciprocal relationship between t_{max} and the initial monomer concentration.

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

The initial rate of polymerisation $(Rp)_o$ was reported to be first order with respect to monomer and first order with respect to catalyst concentration.

$$(Rp)_o = Kp \left[W/Al\right]_o \left[CP\right]_o$$

Subsequent work on the ring-opening polymerisation of cyclopentene by $WCl_6/Al(iBu)_3$ (67), suggested that the greater the initial rate of polymerisation, the faster is the decay of the rate of polymerisation. To account for this behaviour, a series of bimolecular termination reactions was postulated.

$$W^* + W^* \xrightarrow{k_{t1}} 2\,W_{inactive}$$

$$W^* + W_{inact.} \xrightarrow{k_{t2}} 2\,W_{inactive}$$

where W^* = active species and

$W_{inactive}$ = the product of the termination reaction.

If the initial concentration of the active species is $[W^*]_o$ and at any time t the fraction of active species is α, then $[W^*]$ $\alpha\,[W^*]_o$, and

$$\frac{-d\,[W^*]}{dt} = k_{t1}[W^*]^2 + k_{t2}[W^*][W_{inact}]$$

$$= [W^*]_o^2 \left\{ k_{t1}\alpha^2 + k_{t2}\alpha\,(1-\alpha)\right\} .$$

Solution of this differential equation gives :

$$\alpha = \frac{k_{t2}}{k_{t2} - k_{t1}\ \ (1 - \exp k_{t2}[W^*]_o\,t)}$$

If the propagation reaction can be represented kinetically as a simple bimolecular reaction then:

$$Rp = k_p\,[M]\,\alpha\,[W^*]_o \qquad \text{and} \qquad \frac{dRp}{dt} \propto \frac{d\alpha}{dt}$$

$[M]$ = monomer concentration

k_p = propagation constant.

$$\therefore \quad Rp = \frac{k_p [M] [W^*]_o k_{t2}}{k_{t2} - k_{t1} (1 - \exp k_{t2} [W^*]_o t)}$$

This equation predicts that the rate of polymerisation at any time during the course of a polymerisation decreases in a complex exponential manner.

1.5.3 Productive and Degenerate Metathesis

Depending on the catalyst used(115) degenerate metathesis of linear alk-1-enes can be at least 100 times as fast as productive metathesis. Molybdenum catalysts are usually very efficient for productive metathesis of terminal olefins, whereas tungsten complexes are not, even though they are often very active for internal olefins. One possible explanation is that metal-carbenes combine selectively with terminal olefins, according to equation (A)

$$R'CH{=}M + R^2HC{=}CH_2 \longrightarrow R'CH{=}CH_2 + R^2CH{=}M \qquad (A)$$

$$R'HC{=}M + R^2HC{=}CH_2 \longrightarrow R'CH{=}CHR^2 + H_2C{=}M \qquad (B)$$

rather than equation (B), but this selectivity varies with the metal, the chain reaction terminating after a limited number of cycles.

This was verified by Katz et al(116) who investigated the cross-metathesis of $[1,1-{}^2H_2]$ oct-1-ene and hex-1-ene. They measured the ratio of rate constants for the formation of oct-1-ene and $[1,1\text{-}^2H_2]$ hex-1-ene, as shown in Table 1.2.

$$\begin{array}{l} CH_3(CH_2)_5CH{=}CD_2 \\ \quad + \\ CH_3(CH_2)_3CH{=}CH_2 \end{array} \rightleftharpoons \begin{array}{l} CH_3(CH_2)_5CH{=}CH_2 \; + \\ CH_3(CH_2)_3CH{=}CD_2 \; + \\ CH_3(CH_2)_5CH{=}CH(CH_2)_3CH_3 \; + \\ CH_3(CH_2)_5CH{=}CH(CH_2)_5CH_3 \; + \\ CH_3(CH_2)_3CH{=}CH(CH_2)_3CH_3 \\ \quad + \; CH_2{=}CD_2 \end{array}$$

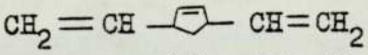
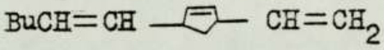
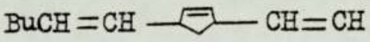
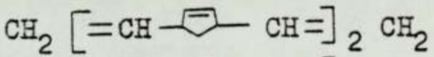
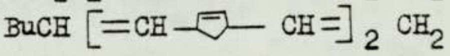
Table 1.2 Productive versus degenerate metathesis of terminal olefins for a variety of catalyst systems.

Catalyst System	K_n/K_p
$Mo(NO)_2Cl_2(PPh_3)_2/Me_3Al_2Cl_3$	26·5 ± 6·1
$Ph_2CW(CO)_5$	75·2 ± 3·6
$WCl_6/LiBu^n$	80·0 ± 7·8
WCl_6/Ph_3SnEt	103· ± 20
$WCl_6/EtCH/EtAlCl_2$	155 ± 33

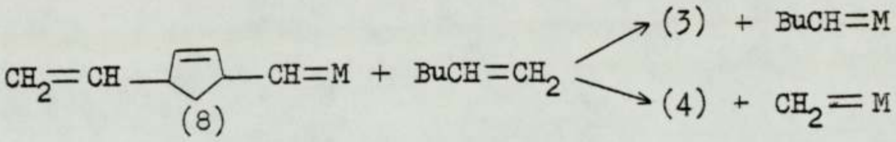
Where K_n is the rate constant for non productive metathesis and K_p is the rate constant for productive metathesis.

Further evidence supporting the claim that the RCH=M metallocarbene is the propagating species in degenerate metathesis came as a result of the work by Ivin et al$^{(117)}$ on the cross metathesis of norbornadiene with hex-1-ene and cyclopentene with oct-1,7-diene. The products of the former reaction are shown in Table 1.3.

Table 1.3 The products of the reaction between norbornadiene and hex-1-ene

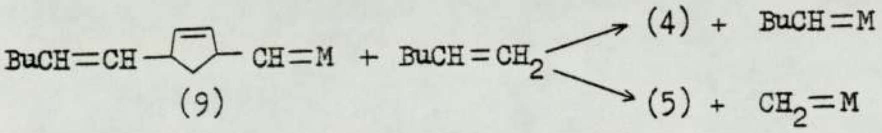
	Products	Yield %
1	$CH_2{=}CH_2$	2·0%
2	BuCH=CHBu	0·0%
3		0·2%
4		57·0
5		2·5
6		0·1
7		38·0

The products (3), (4) and (5) will be formed by the reactions of metallocycles (8) and (9) with hex-1-ene, in one of two ways.



(A)

(B)



(C)

(D)

The relative proportions of (3), (4) and (5) are consistent either with Ka/Kb = 23, (8)/(9) = 0·0035 or with Ka/Kb = 0·0035, (8)/(9) = 23. If the ratio (8)/(9) reflects the proportions of $CH_2{=}M$ and BuCH=M, this means that if the former is correct, BuCH=M and (9) would be the dominant chain carriers, while if the latter is correct $CH_2{=}M$ and (8) would be dominant, with Kb>> Ka.

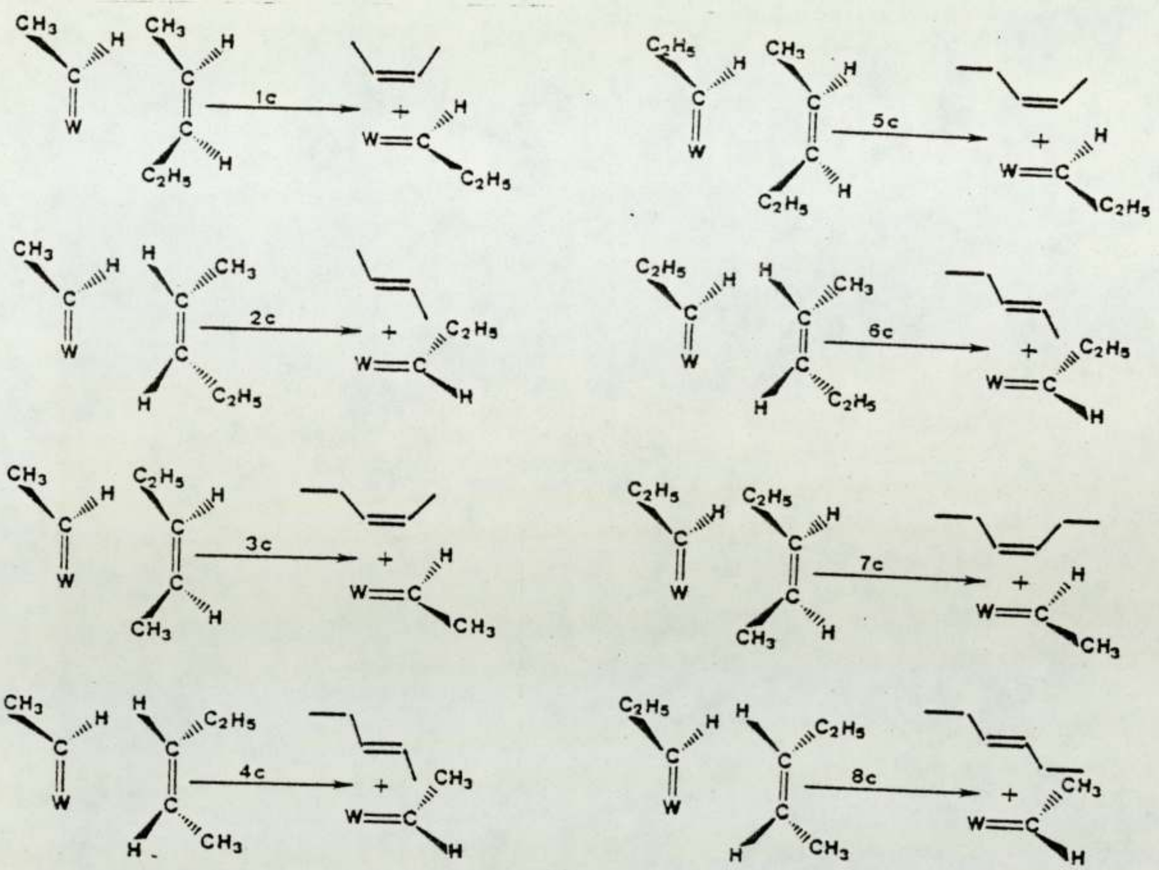
The fact that the quantities of (1) and (5) are very similar may be interpreted to mean that $CH_2{=}M$ is formed almost exclusively by reaction (D) and consumed by (4), rather than by addition of norbornadiene, since the percentage of (3) is very small. The substituted metallocarbene, BuCH$=$M is therefore the major chain carrier. Similar arguements when applied to the cross metathesis of cyclopentene with oct-1,7-diene also support this hypothesis.

1.6 STEREOCHEMISTRY

The metathesis of acyclic olefins can be regarded as a combination of three concurrent reactions: formal or productive metathesis, degenerate metathesis and cis-trans isomerisation.

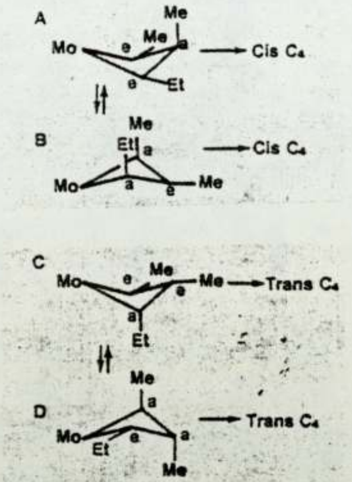
To account for cis-trans isomerisation of the starting olefin as a probable alternative route to the metathesis reaction, Basset and coworkers(118,119) proposed a model in which the stereochemistry of the products was only determined by the geometry of approach of the olefin.

If there are two, equally probable, metallocarbene moieties: $W{=}CHCH_3$ and $W{=}CHCH_2CH_3$ then there are four possibilities of coordination of the starting olefin for each carbene-tungsten moiety. These eight reactions are the only ones which occur at very low conversions and are shown on the next page. The mathematical equations derived from this kinetic model when applied to the initial stages of cis-pent-2-ene metathesis, indicate that a linear relationship could be observed by plotting the ratio of trans/cis but-2-ene concentrations against the ratio of trans/cis pent-2-ene; this was in good agreement with the experimental results.

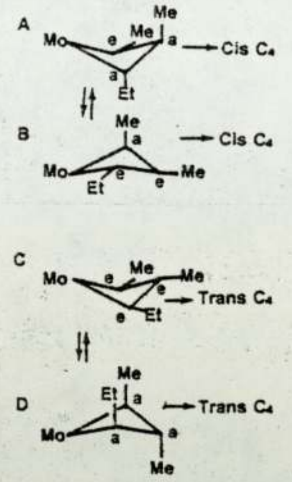


Since there is a linear relationship for the trans/cis ratios of the products of the reaction, steric factors are not important in determining the cis or trans approach of the olefin with respect to the metallocarbene or its reaction once it is coordinated; however there is a slight preference for the cis approach.

The metathesis of cis olefins yields predominantly cis olefins whilst the metathesis of trans olefins yields predominantly trans olefins. Since retention of configuration is higher for trans olefins than for cis olefins, the explanation for this retention may lie in the conformation of the metallocyclobutane transition state. Leconte and Basset(120) outlined the following possible metallocyclobutanes involved in the metathesis of cis-pent-2-ene (left) and trans-pent-2-ene (right).



Various transition states occurring in cis-2-pentene metathesis



Various transition states occurring in trans-2-pentene metathesis

This model shows that the following interactions could be present in a metallocyclobutane intermediate:

(l) 1-2 equatorial-axial or axial-equatorial interactions

(ll) 2-4 repulsive interaction between an axial substituent in the 2 position and the transition metal or its ligands

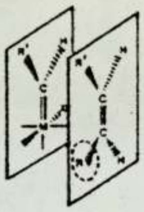
(lll) 3-4 interactions, and

(lV) 1-3 diaxial interactions.

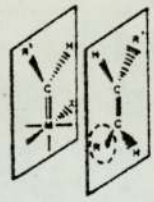
Only the 1-3 or 3-4 interactions are able to supply a satisfactory explanation for the retention of configuration.

For the 1-3 diaxial interaction the most favoured metallocarbene is the one with one methyl and one ethyl group in the 1-3 diequatorial positions and this leads to a cis-C_4 olefin. In the case of trans-pent-2-ene metathesis, the favoured metallocarbene is the one with three substituents - two methyl and one ethyl group - in the 1-2-3 triequatorial position, this leads to a trans-C_4 olefin.

The possible 3-4 interaction is able to account for retention of configuration if an asymmetric ligand distribution around the metallocarbene is assumed; representative configurations for reactions of cis and trans olefins are given below.



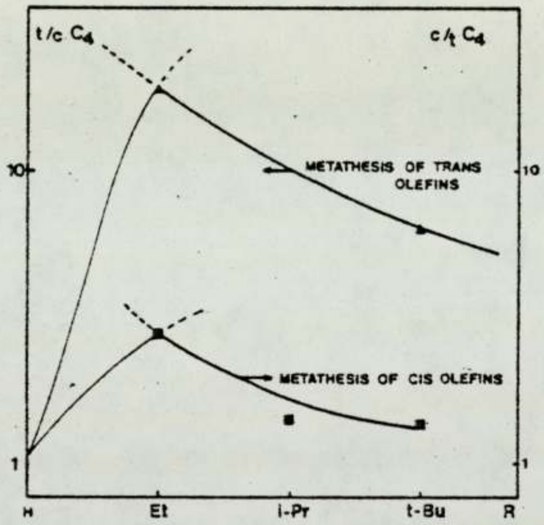
Cis favoured coordination
of a cis olefin



Trans favoured coordination
of a trans olefin

This model predicts that by increasing the size of the R group of a cis or trans olefin RCH═CHR' there should be a progressive increase in the stereoselectivity of the reaction. It has, however, been shown(121) that on increasing the size of R above a certain minimum value decreases the stereoselectivity of the reaction. This is shown diagramatically overleaf.

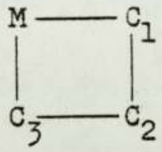
These results may be explained in terms of a change in the rate determining step in a kinetic scheme. As the size of R increases above a certain minimum value, besides the 1-3 diaxial interaction, another type of repulsive interaction occurs, during coordination and/ or reaction, between the R group of the olefin and the transition metal and/or its ligands. With a symmetric ligand arrangement around the metallocarbene, this repulsion is nonstereoselective: whether a cis olefin coordinates and/or reacts in a cis or trans position to the metallocarbene will be equally probable. The same applies to a trans olefin. Besides, it is possible that the bulkiness of the olefin makes the transition state more difficult to be reached, favouring rotation of the carbene about the metal-carbene double bond - which would also result in a decrease in stereoselectivity.



Influence of R on the stereoselectivity of cis-and trans- $RCH=CHCH_3$ (molybdenum based catalyst).

It has been known for a long time that the nature of the transition metal affects the stereoselectivity of metathesis. For Group VI metals, the order of activity for formal metathesis is Cr<<Mo<W and the observed stereoselectivities with cis- or trans- pent-2-ene follows the reverse order i.e. Cr> Mo>>W, chromium being the most stereoselective.

The rather weak stereoselectivities observed with tungsten-based catalysts may be explained as follows(122). In the transition state (I) the M—C_1 and M—C_3 bond lengths would increase from Cr to W, which would increase the C_1 - C_3 distance and decrease any 1 - 3 repulsive interactions.

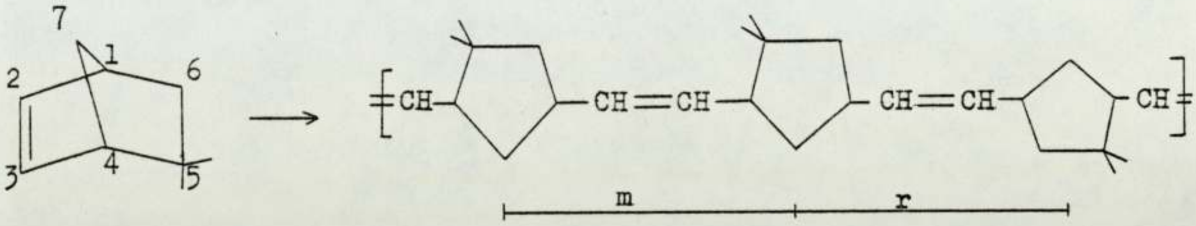


(I)

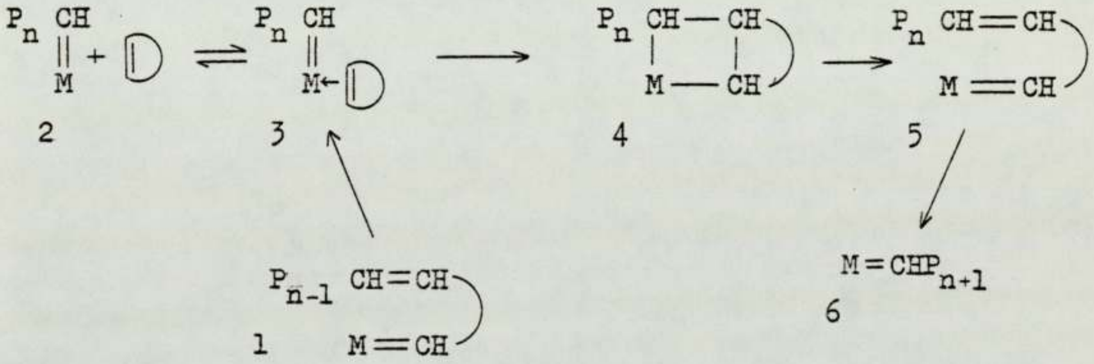
Whilst it is possible to explain many of the stereochemical features of a metathesis reaction by invoking a puckered metallocyclobutane intermediate it was not until comparitively recently that these ideas began to be tested.

Quantum mechanical ab initio calculations on the structure of the titanocyclobutane $Cp\overline{TiCH_2CH_2CH_2}$ have suggested that the metallocycle is planar(123). X ray studies by Grubbs et al(124) on the titanocylcobutane $Cp_2\overline{TiCH_2CHRCH_2}$ also indicate that the metallocycle complex may be planar; when isolated these titanocyclobutane complexes exhibit a moderate degree of activity and stereoselectivity towards metathesis. Basset et al(125) have extended the work by Goddard(123) on the theoretical structure of titanocyclobutanes to include substituted metallocyclobutanes. Using extended Huckel calculations on a six coordinate metallocyclobutane complex $Cl_4\overline{MCHR_1CHR_2CHR_3}$ ($M=Cr,W$; $R_1=CH_3$; $R_2=H,CH_3$; $R_3=H,CH_3,C_2H_5$) they found that the presence of the substituents favours a puckered conformation of the metallocyclobutane. If these studies can be confirmed by x ray analysis then at last it may prove to be possible to examine the role played by the structure of the metallocyclobutane on the stereochemistry of the metathesis reaction.

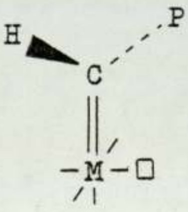
Investigations of the ring-dyad tacticities of polymers obtained from the ring-opening polymerisation of optically active 5,5-dimethylbicyclo [2.2.1] hept-2-ene (DMBNE) have shown the importance of the stereostructure of the propagating metallocarbene in determining the final structure of the products of a metathesis reaction(126).



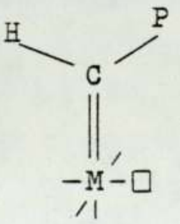
Ivin proposed a series of reaction steps to account for the propagation of the polymerisation reaction as shown below.



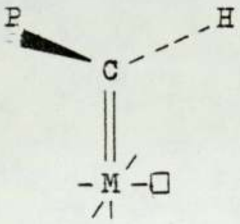
By assuming that the metallocarbene (3) could have either chiral forms P_r and P_l or an achiral form P_s (shown below) Ivin was able to explain many of the observed stereochemical features of the polymerisation reaction.



$3P_r$



$3P_s$



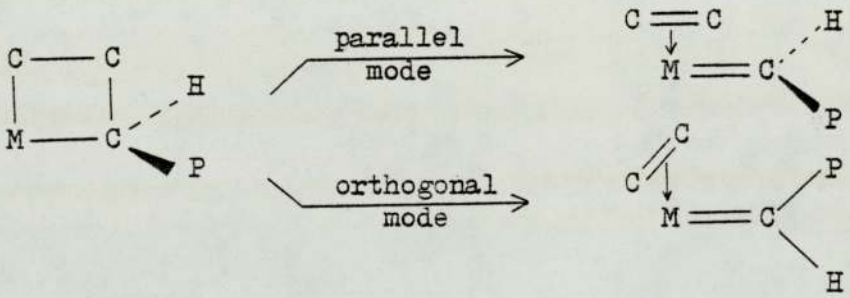
$3P_l$

Ivin's scheme predicts that if no racemization occurs during polymerisation then $(\sigma_r)_c = (\sigma_m)_t = 1$; for partial racemization then $(\sigma_r)_c = (\sigma_m)_t = 0{\cdot}5 - 1{\cdot}0$ and if total racemization then $(\sigma_r)_m = (\sigma_m)_t = 0{\cdot}5$.

where $(\sigma_r)_c$ = fraction of r dyads with respect to cis double bonds
and $(\sigma_m)_t$ = fraction of m dyads with respect to trans double bonds.

These predictions are in accord with the results obtained by ^{13}C NMR investigations of polymers of DMBNE. Unfortunately, this scheme was unable to account for several other stereochemical features and so, in a later paper$^{(127)}$, Ivin proposed two further postulates to account for these problems.

He assumed that the metallocycle (4) could rupture in either of two ways



and that the displacement reaction (1 + M ⟶ 3) is favoured when the coordinated double bond is cis. Using these two postulates he was able to account for cis/trans blockiness in polymers of norbornene, polymers in which the tacticity is independent of monomer concentration and also the variation of cis content of the polymer with different catalyst systems.

1.7 TRANSFORMATION REACTIONS

1.7.1 Copolymers

Copolymers are formed when two chemically distinguishable monomers are allowed to polymerise together to produce a polymer containing both types of monomer unit. There are four possible resultant polymers from the copolymerisation of monomers A and B; random, alternating, block and graft:

-ABBAAABABB-	random (statistical)
-ABABABABAB-	alternating
$-(AAA)_n-(BBB)-$	block
-AAAAXAAAAAA- B B B B	graft

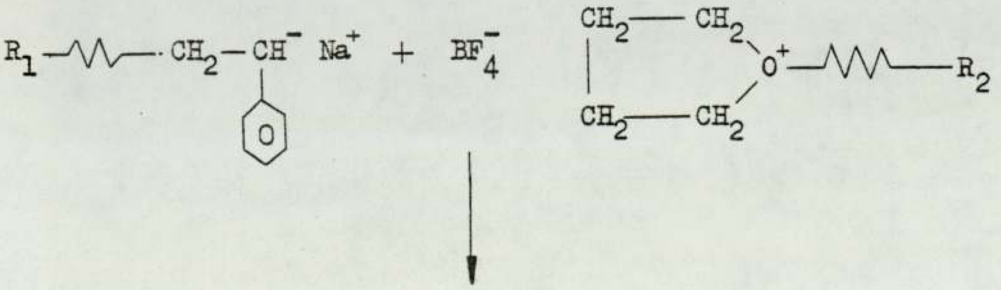
The different types of copolymer can be produced by varying the initial polymerisation conditions to those which allow only the required type of copolymer to form i.e. block copolymers of styrene-butadiene may be synthesised by the sequential anionic polymerisation of styrene and butadiene. Alternatively the monomer composition may be adjusted to produce only one type of copolymer i.e. an alternating copolymer is may be synthesised from the copolymerisation of an azeotropic mixture of styrene and diethylfumarate.

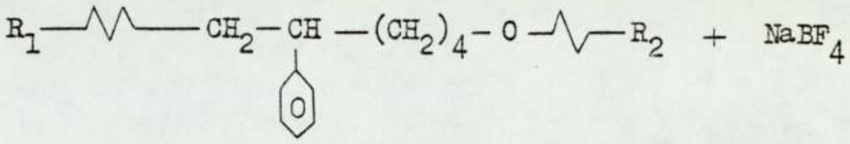
1.7.2 Block Copolymers

A great boost was given to the synthesis of block copolymers following the discovery of living anionic polymerisation by Szwarc et al(128). The synthesis of ABA poly(styrene-b-butadiene) stems directly from his pioneering work and involves the sequential anionic polymerisation of the component monomers. Unfortunately the combinations of monomers which may be converted into block copolymers by sequential anionic polymerisation techniques is severely limited. For example, singly or doubly functional "living" polystyrene initiates the polymerisation of ethylene oxide to give AB or ABA block copolymers, respectively, but the alkoxide ion thus generated is too weak a nucleophile to initiate in turn the polymerisation of styrene(129). It would therefore seem that the range of attainable block copolymers would be greatly extended if a convenient process were to be devised which would allow two, different polymers, synthesised by different mechanistic routes, to be coupled together. Perhaps the simplest scheme would then involve the mutual termination of both anionic and cationic living systems by a direct coupling reaction.

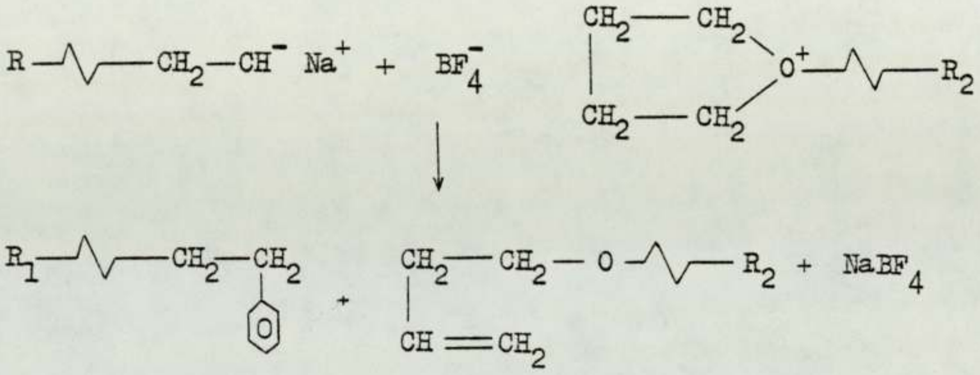
1.7.2.1 Block Copolymers by Direct Coupling Reactions.

Living poly(tetramethylene oxide) can be prepared by the cationic polymerisation of tetrahydrofuran (THF) under conditions where the rate of self-termination is very slow compared to the rates of initiation and propagation. Living poly(THF) can then couple with living polystyrene to yield block copolymers(130).

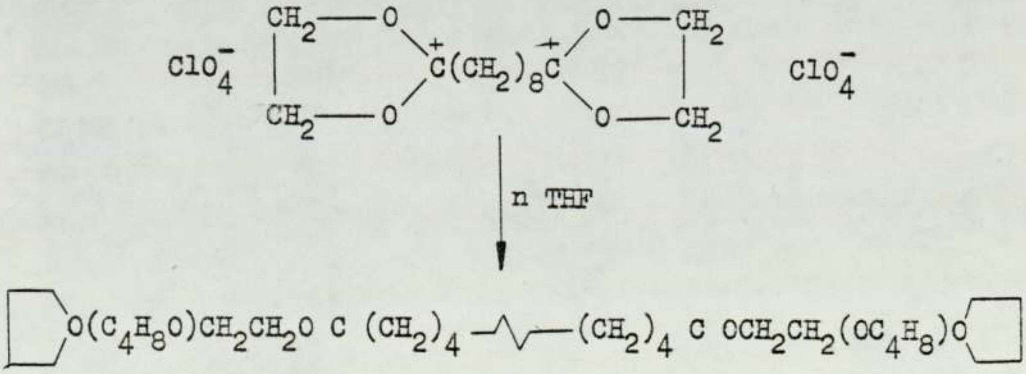




Unfortunately this reaction is complicated by a second type of termination reaction i.e. proton transfer from the cationic to anionic end, thus limiting the practicability of the coupling reaction.



Multiblock copolymers of polystyrene and poly(THF) have been prepared by analogous coupling reactions$^{(131)}$. Dicationic living poly(THF), prepared by reacting 2,2-octamethylene bis-1,3-bioxolenium perchlorate with tetrahydrofuran, reacts with dianionic living polystyrene (prepared from ∝methylstyrene tetramer initiator) to produce block copolymers of the type poly(tetrahydrofuran-b-styrene)$_x$.



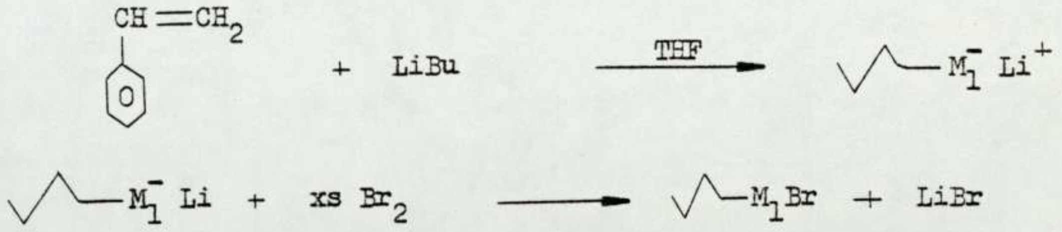
Later work$^{(132)}$ has shown that anions may also cleave polyethers by nucleophilic attack at the C-O linkages, and when the cation is derived from poly(THF), this is the predominant reaction, so that efficient linear block copolymer formation through the mutual termination of anionic and cationic species is unlikely.

1.7.3 Transformation Reactions

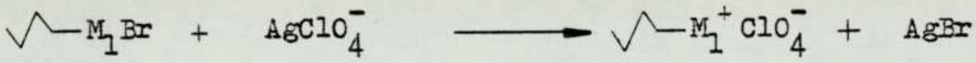
An alternative route to the synthesis of block copolymers might involve a process by which the mechanism of propagation could be changed after polymerisation of the first monomer to one best suited to the propagation of the second. Such reactions have been called transformation reactions(133) and the process devised to prepare block copolymers using them would necessarily have a minimum of 3 stages: (i) Polymerisation of monomer A by mechanism I, capping of the propagating end with a stable but potentially reactive functional group; (ii) isolation of polymer A, dissolution in a solvent suitable for mechanism II and addition of monomer B; (iii) reaction, or change of conditions, to transform the functionalized end into propagating species II which will polymerise monomer B by mechanism II. Ideally the intermediate should be sufficiently stable to allow isolation and protracted storage.

1.7.3.1 Anionic to Cationic Transformation Reactions

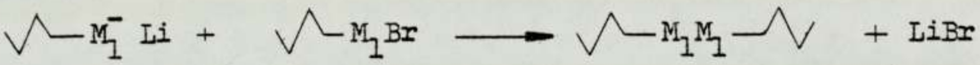
Block copolymers of poly(styrene-b-tetrahydrofuran) have been prepared by anionic to cationic transformation reactions(134, 135). Polysytryl lithium, synthesised by the anionic polymerisation of styrene in THF, is end capped by terminating the living anion with excess bromine.



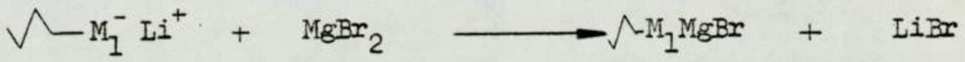
Silver salts (such as $AgClO_4$ or $AgSbF_6$) react with the halogen terminated polystyrene to generate polymeric carbenium ion which then initiates the cationic polymerisation of THF(136); the carbenium ion thus generated is stabilised by the ClO_4^- or SbF_6^- counter ion.



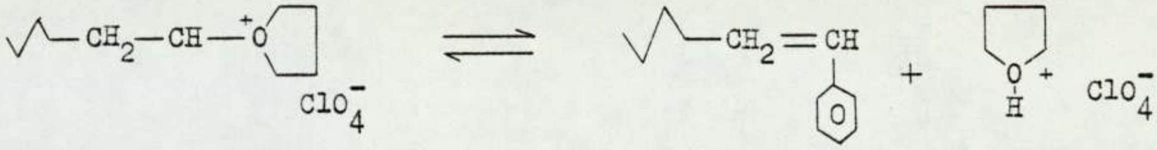
Unfortunately, the production of bromine capped polystyrene is complicated by side reactions, in particular Wurtz coupling reactions which reduce the efficiency of end capping.



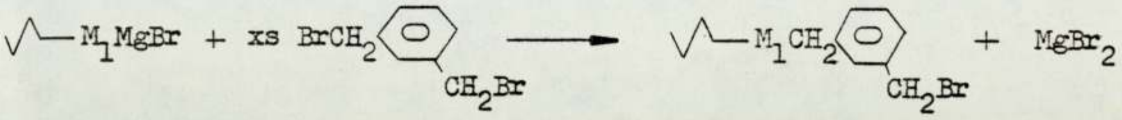
The efficiency of the end capping process has been improved by treating the living anion with magnesium bromide to produce a polymeric Grignard which may then be used in the transformation reaction(137).



Alongside the production of block copolymer there is a small but significant amount of free polystyrene which arises from β elimination from the initially formed oxonium ion.



The β elimination reaction can be prevented by terminating the polymeric Grignard with m-xylyene dibromide.



The advantages of end-capping with a dibromide are three fold, since i) the method can be applied to both vinyl and diene monomers, (ii) the reactivity of the bromide is independent of the nature of the polymer chain to which it is attached, and (iii) no β elimination can take place.

1.7.3.2 Anionic to Free Radical Transformation Reactions

One of the earliest attempts at anionic to free radical transformation reactions arose from the study of the reaction between living anionic polymers with molecular oxygen to generated terminal hydroperoxide functional groups$^{(138)}$.

$$\sim\!\sim M_1^-\,Li^+ \;+\; O_2 \longrightarrow \sim MOO^-\,Li^+ \xrightarrow{H^+} \sim\!\sim MOOH$$

Block copolymers of poly(styrene-b-methylmethacrylate) may then be formed in the reaction between methyl methacrylate and polystyrene hydroperoxide in the presence of ferrous sulphate.

The formation of the hydroperoxide is complicated by a competing side-reaction which is minimized by performing the reaction in a large excess of oxygen.

$$\sim\!\sim\!\sim MOO^- \, Li^+ \; + \; \sim\!\sim\!\sim M^- \, Li^+ \longrightarrow 2 \sim\!\sim\!\sim MO^- \, Li^+$$

An alternative route to polymers having free radicals at their terminal ends involves the decomposition of polymers terminated with lead or mercury salts. Lead tetraalkyls react with silver salts to generate alkyl radicals which can then promote free radical polymerisation of a second monomer(139).

$$R_4Pb \; + \; AgX \longrightarrow R_3PbX \; + \; [RAg] \longrightarrow R\cdot \; + \; Ag\downarrow$$

Polystyryl lithium reacts with a trialkyl lead halide to yield a polymeric lead adduct.

$$\sim\!\sim\!\sim M_1^- \, Li^+ \; + \; R_3PbX \longrightarrow \sim\!\sim\!\sim MPbR_3 \; + \; LiX$$

The lead adduct can then be isolated, purified, redissolved in an appropriate solvent and a second monomer (methyl methacrylate) added before decomposing the lead adduct by the slow addition of silver perchlorate to produce poly(styrene-b-methylmethacrylate) block copolymers. The yields of block copolymer obtained are very low, usually about 5% though the yield can be significantly improved by complexing the silver salts initially with 18C6 crown ethers(140) prior to their addition to the polymer lead adduct. Because the crown ether slows down the rate of free radical production the radical lifetime is increased and more efficient block copolymer formation results.

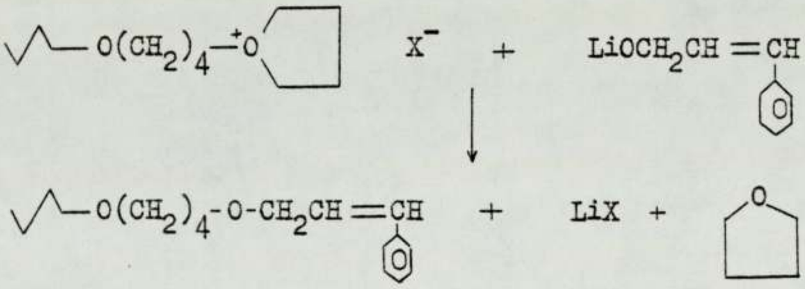
The adducts obtained from the termination of polystyryl lithium with mercuric salts have also been used to initiate the free radical polymerisation of methyl methacrylate to produce block copolymers of poly(styrene-b-methyl methacrylate)(141).

$$\sim M_1^- \, Li^+ + HgX_2 \longrightarrow \sim M_1HgX \xrightarrow{\sim M_1Li} \sim M_1HgM_1\sim$$

Both mono and diadducts are thermally unstable and decompose to yield polymer radicals when refluxed with a solution of methyl methacrylate, the free radicals produced initiate the polymerisation of methyl methacrylate to yield block copolymers though the radicals formed from the diadduct are prone to coupling processes via a radical cage recombination reaction.

1.7.3.3 Cationic to Anionic Transformation Reactions

Living poly(tetrahydrofuran) reacts with lithium cinnamate to yield an adduct possessing a terminal styryl group.



Addition of lithium butyl to the adduct creates a terminal anion which upon addition of styrene engenders anionic polymerisation to produce block copolymers of the type poly(tetrahydrofuran-b-styrene).

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1.7.3.4 Anionic to Ziegler-Natta

Ziegler-Natta polymerisations can be envisaged to occur through a series of sequential steps begining with the reduction of titanium IV with aluminium alkyls.

$$TiCl_4 + R_3Al \longrightarrow RTiCl_3 + R_2AlCl$$

$$RTiCl_3 \longrightarrow \beta\ TiCl_3 + R\cdot$$

$$\beta\ TiCl_3 + R_3Al \longrightarrow RTiCl_2 + R_2AlCl$$

$$RTiCl_2 + C_2H_4 \longrightarrow RTiCl_2C_2H_4 + RCH_2CH_2TiCl_2$$

Replacement of the R groups of the aluminium alkyl with polymer chains suggests another route to the synthesis of block copolymers via Ziegler-Nattta reactions. Aluminium chloride reacts with polystyryl lithium to give partially and fully alkylated products.

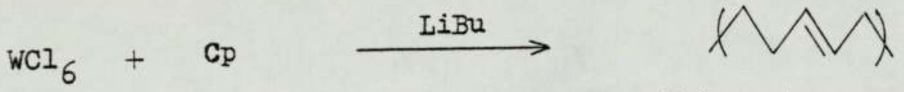
$$\sim\!\!\sim M_1^- Li^+ + AlCl_3 \longrightarrow \sim\!\!\sim M_1AlCl_2 \dashrightarrow (\sim\!\!\sim M_1)_3Al$$

Using the substited aluminium halide in a typical Ziegler-Natta system ($TiCl_4$ or $TiCl_3$) with ethene or propene has led to indications of block copolymer formation.

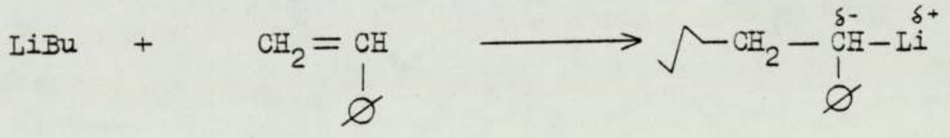
1.7.3.5 Metathetic Transformation Reactions

The metathesis of linear and cyclic olefins is now believed to be initiated and propagated by metallocarbene/metallocyclobutane intermediates. In recent years there has been much work directed at attaining an understanding of how these intermediates are formed and how they direct the course - both kinetically and stereochemically - of the metathesis reaction. Most of this work has concentrated on the role played by the transition metal catalyst and has tended to ignore the role played by both the cocatalyst and the reactant olefin in the metathesis reaction. Whilst the presence of a cocatalyst may be necessary to help generate a metathetically 'active species' it is not at all certain whether it plays any further role in such reactions. If the presence of the cocatalyst - or its derivatives - could be detected in the products of a metathesis reaction then the importance of the role played by the cocatalyst would be demonstrated.

An interesting, but as yet, unexplored route to investigating such reactions is by a anionic to metathetic transformation reaction. For example, the ring-opening polymerisation of cyclopentene can be initiated by the catalyst system WCl_6/LiBu and the LiBu cocatalyst may also initiate the anionic polymerisation of styrene to produce a living polymer, polystyryl lithium. This living polymer may then be used as a cocatalyst in the original ring-opening polymerisation reaction.



Polypentenamer (PPT)



$$LiBu + CH_2{=}\underset{\varnothing}{\underset{|}{CH}} \longrightarrow \sim CH_2-\underset{\varnothing}{\underset{|}{\overset{\delta-}{C}H}}-\overset{\delta+}{Li}$$

Polystyryl lithium (PSt Li)

$$WCl_6 + Cp \xrightarrow{PSt\ Li} \text{New products}$$

If such reactions are feasible, then analysis of the products of such reactions would enable the reaction pathways taken by the cocatalyst throughout the metathesis reaction to be studied.

1.8 SCOPE OF THIS WORK

The application of the homogenous catalyst system WCl_6/LiBu to the metathesis of linear olefins is well known, though its use in ring-opening polymerisation reactions of cycloolefins is less well documented. By studying this catalyst system and its derivatives when used to catalyze the ring-opening polymerisation of cyclopentene, it was hoped that previous results using different catalyst systems i.e. $WCl_6/Al(iBu)_3$, would be confirmed and also, that new insights into the nature of the catalyst/cocatalyst/monomer interactions could be investigated.

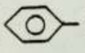
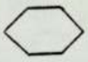
Work carried out at PERME Waltham Abbey was primarly to confirm that proton sponge could be used successfully to push the $RNH_3X \rightleftharpoons RNH_2 + HX$ equilibrium to the right and so provide an easy and efficient means of synthesing trisubstituted amines of the type R_3N where R = poly-(tetramethylene oxide).

CHAPTER 2

EXPERIMENTAL WORK

Table 2.1 shows the chemicals used in this project, their sources and properties.

Table 2.1 List of Chemicals

Material Abbrev.	Formula	Source	Mol. Wt.	MP	BP	Density
Cyclopentene (CP)		Aldrich	68·12	-135	44·2	0·772
Toluene	 CH_3	BDH	92·15	-95	110·6	0·867
Tetrahydrofuran THF		Fissons	72·12	-108	67	0·889
Cyclohexane		Fissons	84·16	6·5	80·7	0·775
Styrene	 CH.CH_2	BDH	104·16	-30·6	145·2	0·906
∝-Methylstyrene	$\phi CCH_3.CH_2$	BDH	118·18	-24·3	163·4	0·908
Tungsten hexachloride	WCl_6	Aldrich	396·6	275	346·7	3·52
Butyl lithium	LiBu	Aldrich	-	-	-	-
Norbornene		Aldrich	94.17			

All information is taken from the Handbook of Chemistry and Physics, 62nd edition, 1981-1982.

2.1 VACUUM TECHNIQUES

Many of the catalyst components used in olefin metathesis reactions are extremely sensitive to air and moisture. There are two general techniques for handling such unstable materials, blanket and vacuum techniques. Blanket techniques usually necessitate manipulations in a nitrogen glove box which are unfortunately unreliable and subject to leakages, for this reason vacuum techniques were preferred to the former.

2.1.1 The Vacuum Line

The vacuum line shown in figure 2.1 consisted of a main manifold which was evacuated by an Edwards rotary pump aided by a mercury diffusion pump. Liquid nitrogen cold traps were used a) to condense any organic vapour leaking from the main manifold into the mercury diffusion pump, and b) to prevent organic and mercury vapours escaping into the laboratory. Pressure as low as 10^{-4} mm Hg could be maintained for prolonged periods in this equipment. The pressure inside the system was estimated by use of a vacustat gauge.

2.1.2 Degassing Solvents

In order for solvents to be distilled under vacuum the solvents first had to be degassed. A flask similar to that shown in figure 2.2 containing the solvent to be degassed was connected to the main-manifold at (B) and was gradually cooled by immersion in liquid nitrogen. When the solvent had frozen, the flask was evacuated by opening tap (H). When a high vacuum was attained, tap (C) was closed and the solvent was allowed to thaw by immersing the flask in

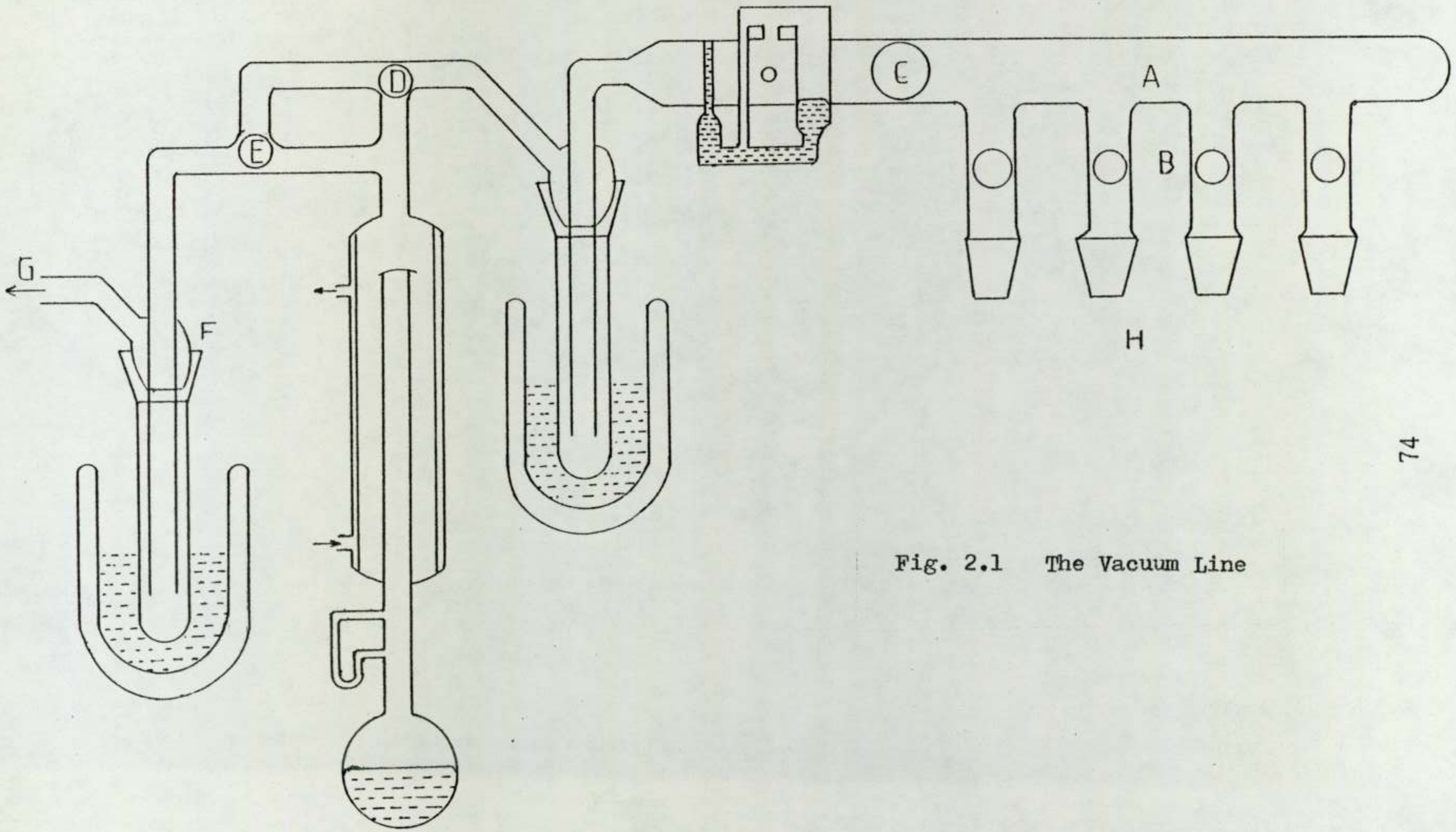


Fig. 2.1 The Vacuum Line

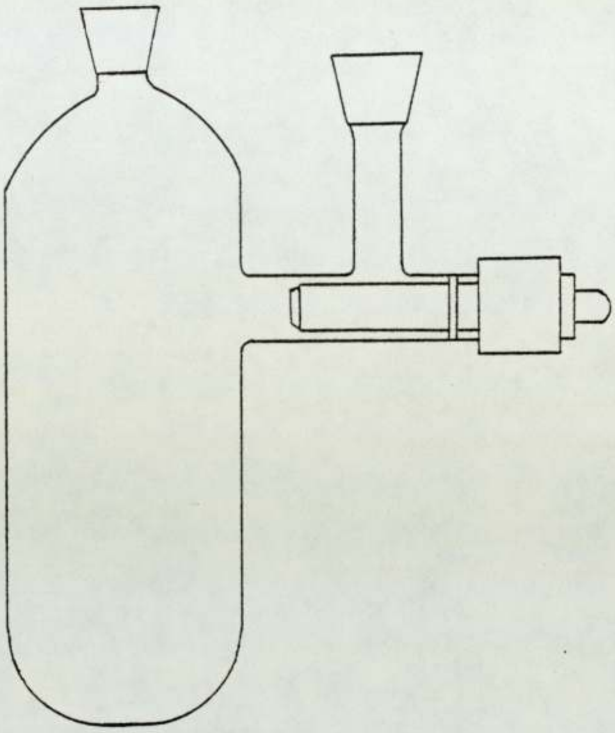


Fig. 2.2 Apparatus for storing dried solvents

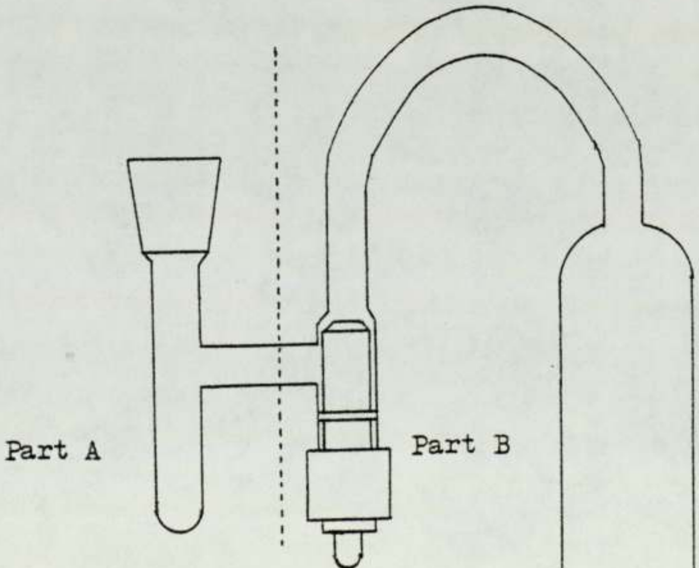


Fig. 2.3 Apparatus used for storing catalyst solutions

methanol. Gas trapped in the frozen solvent was then released and equilibrated in the atmosphere above the solvent. The solvent was refrozen before tap (C) was then again opened until a high vacuum was obtained. This process of freezing and thawing was repeated until a high vacuum was observed between freezing and thawing processes.

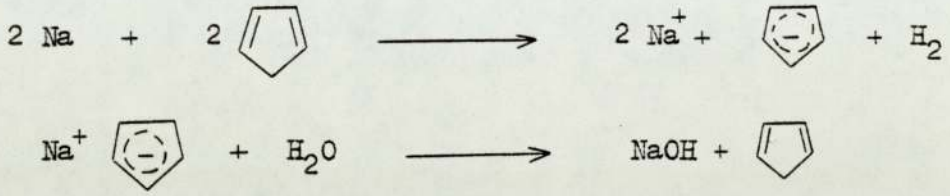
2.1.3 Trap to Trap Distillation

Prior to vacuum distillation, the solvent to be distilled was degassed as described in section 2.1.2. The flask containing the degassed solvent was connected to the main manifold of the vacuum line via tap (H). A second flask was also connected to the vacuum line and evacuated. Once a high vacuum had been obtained in the system, both the empty receiver flask and the main manifold were flamed to remove the last traces of moisture from the interior surfaces of the equipment. After allowing the empty flask to cool to room temperature the flask was further cooled in a Dewar containing liquid nitrogen. Tap (C) of the main manifold was then closed and tap (H) opened to allow solvent to distil from the warm flask to the liquid nitrogen cooled flask. To facilitate distilation, the flask containing the solvent to be distilled was often warmed with a beaker of warm water.

2.2 PURIFICATION AND DRYING OF MATERIALS

2.2.1 Cyclopentene

The main impurities in cyclopentene are water and cyclopentadiene which can destroy the catalyst components used in olefin metathesis. Both of these impurities can be removed by slivers of freshly cut sodium metal in an elegant series of reactions.



When sodium metal was added to cyclopentene, a golden brown residue of cyclopentadienyl sodium formed on its surface. After 24 hours the dry cyclopentene was distilled on to fresh sodium to ensure the complete removal of impurities. The monomer was then stored under vacuum in a flask such as that shown in fig. 2.2 from which it was distilled when required.

Procedure 2

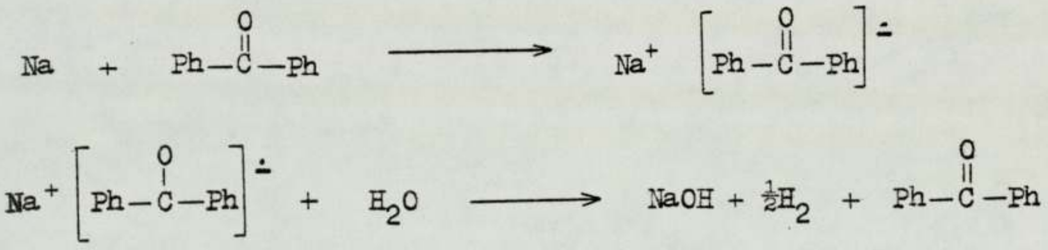
If a little cyclopentadiene is present in the monomer, as shown by the amount of golden residue on the sodium in the flask, no further drying is achieved by subsequent distillation of the monomer on to fresh sodium. Complete drying in these cases was achieved by distilling the monomer under high vacuum from sodium metal on to activated alumina where it was stored under vacuum until required.

2.2.2 Toluene

Toluene was fractionally distilled from sodium pellets through an electrically heated 2 metre fractionation column filled with glass beads. The first 70cm^3 of distillate from the initial 1·5 dm^3 of solvent was discarded and the subsequent distillate (between 200 - 300 cm^3) was collected for further drying.

2.2.2.1 Procedure 1

Toluene was dried over slices of sodium and a small amount of benzophenone in a flask similar to that shown in fig. 2.2. After 24 hours the blue/green solution was degassed and distilled into a second flask also containing slivers of fresh sodium and benzophenone. Within 24 hours the solution had turned deep blue due to the formation of a sodium benzophenone complex - indicating the toluene was completely dry. The toluene was then stored under vacuum and distilled from this flask when required. The drying agent acts by way of the following sequence of reactions.



$$Na + Ph-\overset{\overset{O}{\|}}{C}-Ph \longrightarrow Na^+\left[Ph-\overset{\overset{O}{\|}}{C}-Ph\right]^{\dot{-}}$$

$$Na^+\left[Ph-\overset{\overset{O}{|}}{C}-Ph\right]^{\dot{-}} + H_2O \longrightarrow NaOH + \tfrac{1}{2}H_2 + Ph-\overset{\overset{O}{\|}}{C}-Ph$$

A freshly regenerated sodium surface ensured that efficient drying was achieved.

2.2.2.2 Procedure 2

Whilst the above procedure for drying toluene was very efficient if the initially supplied toluene was reasonably dry, drying was not achieved if the toluene was very wet. In these circumstances the initial drying was achieved by pouring the toluene (about 200 cm^3) on to activated alumina (5-10g) in a flask similar to that shown in figure 2.2. Subsequent drying was accomplished by degassing the dry toluene and distilling, under vacuum, on to freshly activated alumina. The toluene was stored over the alumina, under vacuum, until required.

2.2.3 Cyclohexane

The main impurities in cyclohexane is cyclohexene. These olefin impurities were removed by refluxing about 100 cm^3 of the solvent with 1-2g of tungsten hexachloride under a nitrogen atmosphere. After refluxing for 30 minutes the cyclohexane was distilled under vacuum into a flask (fig. 2.2) containing approximately 5g of activated alumina. The cyclohexane was stored over the alumina under vacuum until required.

2.2.4 Tetrahydrofuran

Tetrahydrofuran was supplied by Fisson Limited and stabilised with 0·1% quinol. About 2 dm^3 of the THF was refluxed, under nitrogen, with sodium naphthalide (0·1 mole) until the deep green colour had been established for 30 minutes. The THF was then distilled under nitrogen and collected in a 250 cm^3 burette. The first 200 cm^3 of the distillate was discarded and the remainder collected as required and used immediately.

2.2.5 Styrene

Styrene contains 10-15 ppm of t-butyl catechol to prevent thermally initiated polymerisation. The catechol was removed by washing 100 cm^3

of styrene 3 times with 30 cm^3 quantities of 10% sodium hydroxide solution; the monomer was then rinsed several times with distilled water. The wet styrene was dried initially over anhydrous sodium sulphate for 24 hours and then stored over ground calcium hydride in a flask similar to that shown in fig. 2.2. After 24 hours the styrene was degassed and distilled on to freshly ground calcium hydride and stored under vacuum until required.

2.2.6 Norbornene

Norbornene was supplied as a crystalline solid in a narrow-necked bottle. The bottle containing the norbornene was placed in a water bath at 60 °C and after allowing the monomer to melt, the norbornene (100 cm^3) was poured into a flask (fig. 2.2) containing 2-5g of activated alumina. Once the norbornene had solidified, the flask was sealed and evacuated on the vacuum line. This flask was then transferred to a water bath at 60 °C and left for 24 hours. The monomer was then allowed to solidify and the flask containing the norbornene was connected to the vacuum line and evacuated. The monomer was stored in this way until required.

2.2.7 α Methyl Styrene

α methyl styrene is stabilised with 10 ppm of a catechol. The inhibitor was removed by washing 100 cm^3 of the monomer 3 times with 30 cm^3 quantities of a 10% sodium hydroxide solution. The monomer was then rinsed with distilled water and subsequently dried over anhydrous sodium sulphate. Complete drying was achieved by pouring the monomer on to crushed calcium hydride and after 24 hours distilling under vacuum, on to newly crushed calcium hydride.

2.2.8 Tetramethylethylenediamine

Tetramethylethylenediamine was fractionally distilled and the middle fraction collected. This fraction was then dried over activated alumina, and stored under vacuum until required.

2.2.9 Activated Alumina

About 200 cm^3 of chromotagraphic grade alumina was heated in a furnace to 550°C for at least 16 hours. After allowing the alumina to cool in the furnace, it was then stored in an oven at 160°C until required.

2.2.10 Tungsten Hexachloride.

Tungsten hexachloride normally has trace impurities of tungsten oxychloride ($WOCl_4$) and tungsten oxydichloride (WO_2Cl_2) which readily sublime under vacuum as tungsten oxychloride.

$$WCl_6 + WO_2Cl_2 \rightleftharpoons 2\,WOCl_4$$

Tungsten hexachloride was therefore purified by vacuum sublimation on to a hot finger. A small quantity of tungsten hexachloride (about 1·0g) was placed in the bulb of the apparatus shown in figure 2.4. After evacuation, the bulb of the apparatus was immersed in an oil bath at 120°C. By circulating hot water the hot finger was maintained at between 70–80°C; at this temperature tungsten hexachloride sublimed on to the hot finger whilst the impurities sublimed on to the cooler parts of the flask walls above the oil level. The purified tungsten hexachloride was then transferred, under nitrogen, to glass ampules which were then evacuated and sealed.

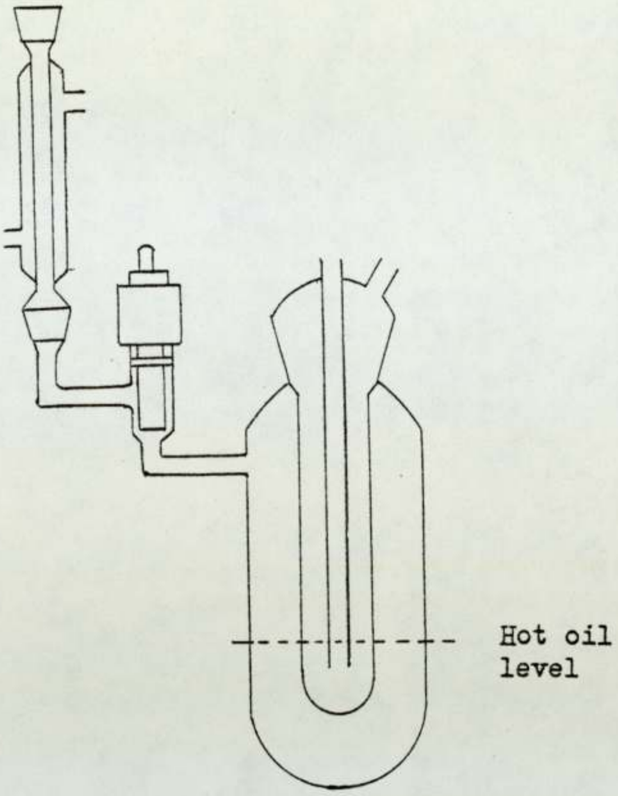


Fig. 2.4 Apparatus used for the purification of tungsten hexachloride

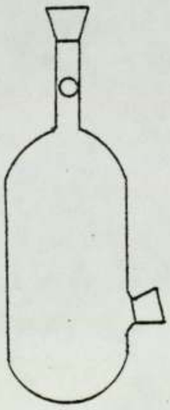


Fig. 2.5 Catalyst premixing vessel

2.3 PREPARATION OF SOLUTIONS

2.3.1 Tungsten Hexachloride

A known amount of purified tungsten hexachloride (usually about 0·3g) was introduced, under nitrogen, into the flask shown in fig. 2.3. The flask was then evacuated and warmed lightly to sublime off any remaining tungsten oxychloride impurities. On cooling, the required amount of toluene was distilled under vacuum into the flask to produce a solution with a tungsten hexachloride concentration of about $1{\cdot}5\times10^{-2}$ mol. dm^{-3}. The volume of solvent distilled was determined by weight difference.

2.3. Lithium Butyl

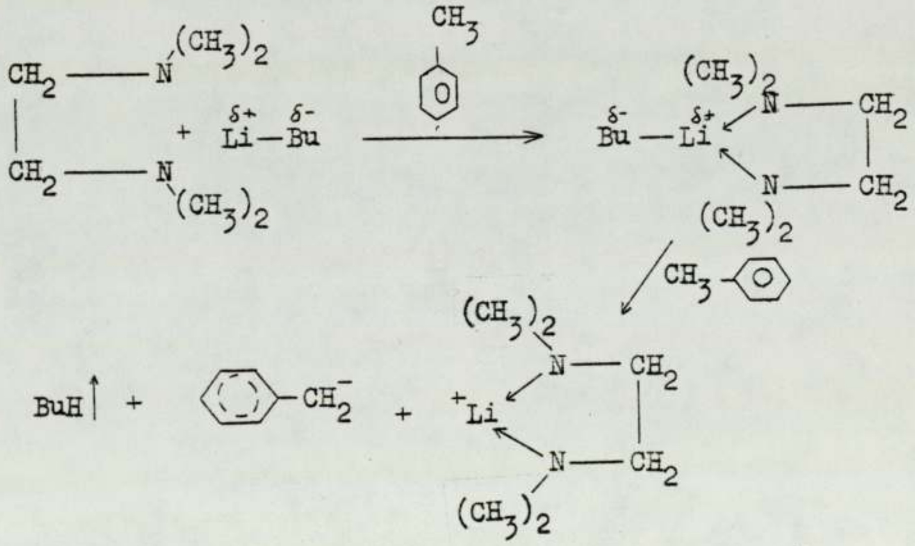
A known amount of pure dry toluene (about 60 cm^3) was distilled under vacuum into a clean dry flask as shown in fig. 2.3. After purging part A of the flask with oxygen-free dry nitrogen, the tap was removed whilst keeping a slow stream of nitrogen flowing through the flask. Lithium butyl (supplied as a hexane solution 1.7 mol. dm^{-3}) was then injected by syringe into part B of the flask to produce a toluene solution of lithium butyl with a concentration of about 1.5×10^{-1} mol dm^{-3}.

2.3.3 Polystyryl Lithium

A solution of styrene (4.4g) in cyclohexane (about 40g) was prepared by sequential vacuum distillation of the monomer and solvent in to a flask (fig. 2.2). Lithium butyl (7.72×10^{-2} mol. dm^{-3}) in hexane was added to the styrene solution as described in section 2.3.2. Once the tap was replaced, the flask was immersed in a hot water bath at 60°C and left for 24 hours. The clear solution gradually turned orange-yellow which is typical of the polystyryl anion in non-polar solvents. The polystyryl lithium concentration was 7.72×10^{-2} mol. dm^{-3} and the average degree of polymerisation ($\overline{DP}_n$) was calculated to be ten.

2.3.4 TMEDA/LiBu solution

A solution of tetramethylethylenediamine ($1{\cdot}7 \times 10^{-2}$ mol) in toluene (56 cm^3) was prepared by sequential vacuum distillation of the two components into a flask similar to that shown in fig. 2.3. Lithium butyl (1.7×10^{-2} mol) was then added to the flask by the procedure outlined in section 2.3.2. The solution immediately turned pale yellow on addition of the lithium butyl and became a very dark red within 60 seconds. The red colour was due to the benzyl anion which is stabilised by the lithium cation.



The final concentration of the benzyl anion was 2.48×10^{-1} mol. dm^{-3}.

2.4 EXPERIMENTAL TECHNIQUES

2.4.1 Dilatometry

2.4.1.1 Principles of dilatometry

During the ring-opening polymerisation of cyclopentene there is a gradual change in the density of the system since the polymer produced has a density greater than that of the monomer. This change in density of the polymerising system is revealed as a gradual volume contraction which may be measured dilatometrically.

Since a dilatometer has essentially the same construction as a thermometer, all dilatometric polymerisation studies must be conducted at a constant temperature. Also, any variation in temperature within the system would affect the rate of polymerisation, and so all reactions were carried out in a temperature controlled water bath. If an exothermic reaction is to be studied dilatometrically then corrections must be made to allow for the effect of the rise in temperature on the observed rate of reaction. Fortunately very little heat is evolved during the ring-opening polymerisation of cyclic olefins such as cyclopentene and so no corrections were necessary to obtain an accurate rate of polymerisation.

2.4.1.2 Treatment of data

A dilatometer is filled so that the capillary contains a thread of polymerising solution. During the course of the polymerisation the meniscus in the capillary of the dilatometer will move from point A to point B, see fig. 2.5.

The change in volume (ΔV) associated with the complete polymerisation of m grams of monomer then becomes:

$$\Delta V = V_p - V_m$$

which is related to the densities of the monomer and polymer by:

$$= \frac{m}{P_p} - \frac{m}{P}$$

where V_p = volume of m grams of polymer / dm^3
V_m = volume of m grams of monomer / dm^3
P_p = density of polymer g/cm^3
P_m = density of monomer g/cm^3

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

$$\Delta V = \Delta M . M_m \left(\frac{P_m - P_p}{P_p . P_m} \right)$$

where M_m is the molecular weight of the monomer.

$$\Delta M = \frac{\Delta V}{M_m} \left(\frac{P_p . P_m}{P_m - P_p} \right)$$

Since the volume of the dilatometer (V) is usually much greater than the change in total volume = (ΔV) then the change in concentration of the monomer is:

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

ΔV may be related to the change in height of the meniscus (Δh) by:

$$\Delta V = \pi r^2 \Delta h \qquad \text{where } r = \text{radius of the capillary in cm.}$$

Then:

$$\Delta[M] = \frac{\pi r^2 \Delta h}{V M_m}\left(\frac{P_p \cdot P_m}{P_m - P_p}\right) = K \Delta h$$

The dependence of Δh on polymerisation time is measured from a plot of Δh against reaction time (Δt).

The rate of polymerisation (R_p) may be obtained since:

$$Rp = \frac{-d[M]}{dt} = \frac{\pi r^2}{VM_m}\left(\frac{P_p \cdot P_m}{P_m - P_p}\right)\frac{\Delta h}{\Delta t}$$

The density of cyclopentene monomer is 0·774 g/cm^3 and that of the polymer is 0·87 g/cm^3.

2.4.1.3 Dilatometry Experiments

Two types of dilatometer were used to study the rate of ring-opening polymerisation of cyclopentene. The second dilatometer was primarily used to study pre-mixed catalyst polymerisation reactions and copolymerisation reactions as it gave more reproducable results.

2.4.2 Dilatometer A

A solution of cyclopentene in toluene (2.50 mol. dm^{-3}) was stored, under vacuum, in a flask similar to that shown in fig. 2.8. This flask was connected to the dilatometer shown in fig. 2.6 via the greaseless joint (D'). The dilatometer was then connected to the vacuum line through tap (C) and the whole system evacuated and flamed. On cooling the dilatometer and closing taps (C') and (A'), 15·0 cm^3 of the monomer solution was introduced into the main bulb of the dilatometer by opening tap (G''). Tap (B') was closed and the flask containing the monomer solution was disconnected from the dilatometer. The catalyst components were then added sequentially to the monomer solution by injection through the suba seal (E'). The dilatometer was removed from the vacuum line and after opening tap (A') the polymerisate was allowed into the reaction bulb and the capillary tube of the dilatometer. Tap (A') was closed and the dilatometer placed in a constant temperature water bath. The polymerisation reaction was followed with a cathetometer by measuring the change in position of the meniscus in the capillary tube of the dilatometer.

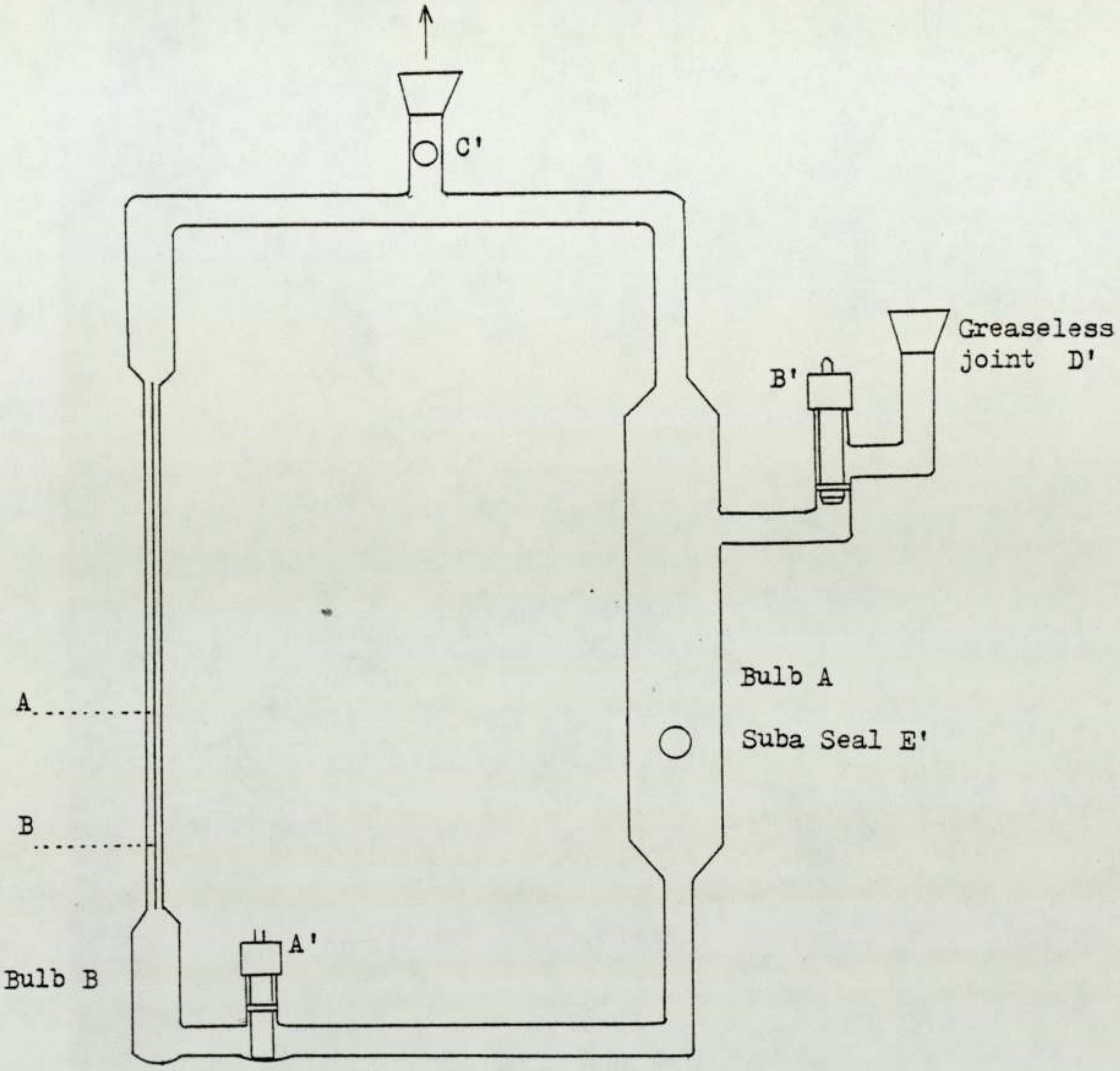


Fig. 2.6 Dilatometer A used for the determination of the rate of polymerisation of cyclopentene catalysed by the unmixed catalyst system WCl_6/LiBu

2.4.2.1 Premixed catalyst experiments

When Wang and Menapace first reported the use of the catalyst system WCl_6/LiBu for the metathesis of pent-2-ene, they added the catalyst components sequentially to the olefin. Later experiments showed that modified premixed catalyst systems (i.e. olefin/WCl_6 + LiBu/$AlBr_3$) also showed metathetic activity. This led to a study of the effect of premixing WCl_6 with LiBu and investigating its effect on the rate of polymerisation of cyclopentene. All experiments were performed using the dilatometer described in section 2.4.2 except the catalyst components were premixed in the correct molar ratios prior to their addition to the monomer. The premixed catalyst was prepared using the flask shown in fig. 2.5. This flask was evacuated and flamed. After cooling to room temperature the catalyst components were added sequentially by syringe to the flask and after the required premix ageing time, the catalyst was added to the monomer solution in the dilatometer by syringe. The rate of polymerisation was followed as described in section 2.4.2.

2.4.3 Dilatometer B

Whilst dilatometer A gave very reliable and reproducable results when the catalyst components were added sequentially to the monomer solution this was not the case when the premixed catalyst was studied. This arose because of the difficulty in transferring accurately the correct amount of the premixed catalyst solutions by syringe to the dilatometer from the premix flask shown in fig. 2.5. These problems were overcome by preparing the premixed catalyst solution in the dilatometer before its addition to the monomer.

A flask shown in fig. 2.8 containing monomer solution was connected

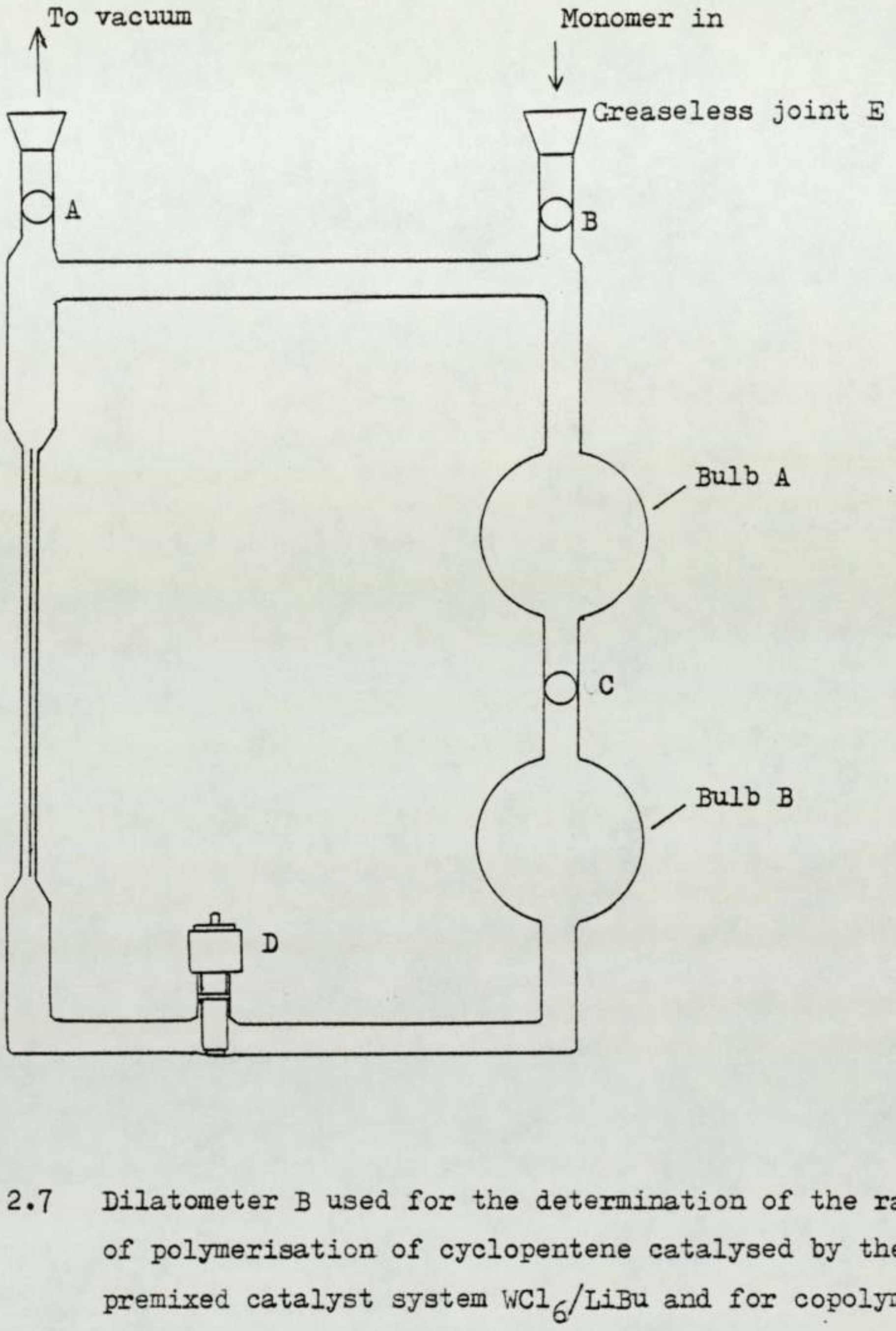


Fig. 2.7 Dilatometer B used for the determination of the rate of polymerisation of cyclopentene catalysed by the premixed catalyst system WCl_6/LiBu and for copolymerisation experiments

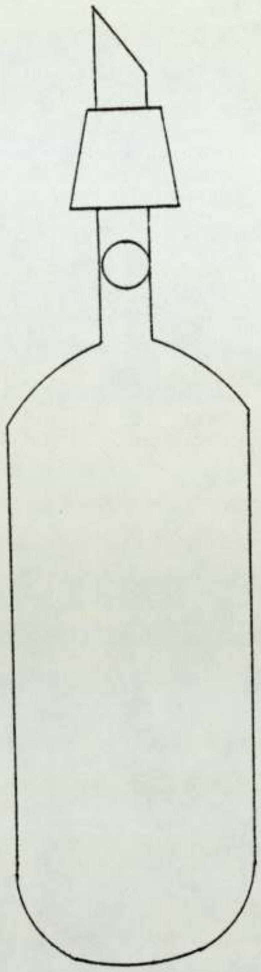


Fig. 2.8 Monomer solution storage flask

via the greaseless joint (E) to the dilatometer shown in fig. 2.7. The dilatometer was then connected to the vacuum line through tap (A) and evacuated and flamed. After cooling, taps (A), (C) and (D) were closed and 15·0 cm^3 of the monomer solution was allowed into bulb A of the dilatometer. Tap (B) was then closed and the monomer flask carefully removed. The required amount of tungsten hexachloride solution was then added to bulb A by syringe transfer. After the required ageing time, the cocatalyst (lithium butyl) was added to bulb A and the polymerising solution allowed into the reaction bulb and capillary tube of the dilatometer. On closing tap (D) and placing the dilatometer in a water bath at 25°C, the rate of polymerisation was followed as described for dilatometer A.

2.4.3.1 Premixed Catalyst Experiments

The dilatometer and monomer flask were assembled as described in section 2.4.3., evacuated and flamed. Monomer solution (15·0 cm^3) was then allowed into bulb B of the dilatometer and tap (C) closed. The monomer flask was removed after closing tap (B). The catalyst and cocatalyst were then sequentially introduced into bulb A of the dilatometer and allowed to react together for a premix ageing time. Tap (C) was then opened and the contents of bulb (A) were allowed to react with the monomer solution; the polymerisate was then poured into the reaction bulb and capillary tube of the dilatometer. Tap (D) was closed and after placing the dilatometer in a water bath, the position of the capillary meniscus was followed by means of a cathetometer.

2.4.4. Polymerisation Reactions

2.4.4.1 Polymerisation of Cyclopentene using a WCl_6/LiBu - TMEDA Catalyst System

The nature of the interaction between the cocatalst and the monomer/catalyst species is not understood. It was hoped that by changing the nature of the covalent lithium-alkyl bond to a more polar species then some insight into this interaction could be gained. This led to the development of the cocatalyst LiBu/TMEDA in which the the lithium -alkyl bond is ionic and the species exist as ion pairs.

The polymerisation of cyclopentene using the catalyst system WCl_6/LiBu-TMEDA was studied dilatometrically. The cocatalyst mixture LiBu/TMEDA (1:1 molar ratio of components) was prepared as described earlier in section 2.3.4. All dilatometric experiments were performed using dilatometer B as outlined in section 2.4.3.

The reaction conditions used were: tungsten: lithium molar ratio 1:1, lithium: TMEDA = 1:1, and an ageing time of 2 minutes. The monomer to tungsten ratio's were varied between 2000:1, 1500:1 and 1000:1.

2.4.4.2 Metathesis of Cyclopentene using WCl_6 /poly α methylstyrene

The generation of a metallocarbene from catalyst containing a organometallic cocatalyst is believed to occur by the migration of a hydrogen atom from an alkyl group to the transition metal catalyst. These ideas may be tested experimentally by producing a cocatalyst which does not contain any α hydrogens and observing how this effects the metathesis reaction. The reaction system studied was cyclopentene/WCl_6/poly α-methylstyryl lithium.

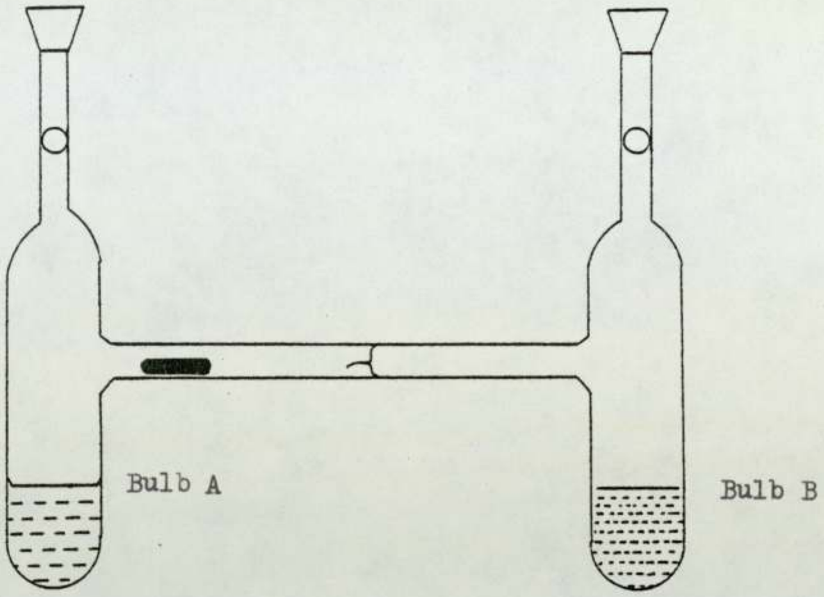


Fig. 2.9 Copolymerisation flask used for the reaction of cyclopentene with WCl_6/ poly α methylstyrene

Fig. 2.10 Norbornene polymerisation flask.

The polymerisation reaction was carried out in the flask shown in fig. 2.9. Pure dry ∝ methylstyrene (0·02 mol) was distilled, under vacuum into bulb A of this flask. Lithium butyl (3.4×10^{-4} mol) was then added to the ∝ methylstyrene by purging bulb A with dry nitrogen and, after removing tap A, the lithium alkyl was added by syringe through tap A. The tap was then replaced and the bulb sealed at C using a hot flame after freezing the contents of bulb A in liquid nitrogen. The whole flask was then placed in a water bath at 60°C for 24 hours to allow the styrene to polymerise.

The flask was removed from the water bath and allowed to cool. The flask was then attached to the vacuum line and bulb B evacuated and flamed. On cooling, 0·15 mol of cyclopentene was distilled into the bulb and after disconnecting the flask from the vacuum line, tungsten hexachloride solution (1.5×10^{-4} mol) was added to the monomer as described in section 2.3.3. The contents of bulb B were then frozen in liquid nitrogen and the flask sealed at D using a hot flame. Once the flask had warmed to room temperature, the flask was shaken so that the glass rod broke the break seal and the poly ∝ methylstyrene was allowed to mix with the monomer/catalyst solution. This reaction mixture was then left for at least 24 hours and then the contents of the flask poured into methanol by breaking open the flask.

2.4.4.3 Norbornene polymerisation

Norbornene was stored, as a solid, over activated alumina in a flask similar to that shown in fig 2.2. A solution of norbornene in toluene (about 1.1 mol. dm^{-3}) was prepared by sequential vacuum distillation of the monomer (≈ 0·7g) and solvent into the flask shown in fig. 2.10. Prior to distillation, the flask containing the norbornene was warmed to 60°C by immersing it in hot water. This allowed the solid monomer to melt and so be distilled under vacuum. Tungsten hexachloride solution was added to the norbornene solution by syringe and the reaction terminated after 30 minutes by pouring the products into 50 cm^3 of cold methanol. The precipitated polymer was redissolved in chloroform, reprecipitated in methanol and dried at room temperature in a vacuum oven.

2.4.4 Synthesis of Polypentenamer Copolymers

About 70 cm^3 of a 2.2 molar cyclopentene solution in toluene was prepared by successive vacuum distillations of monomer and solvent in to a flask similar to that shown in figure 2.11. Catalyst solution was transferred to the monomer solution by syringe through the suba seal. Polystyryl lithium was then added by syringe to the reaction mixture after an ageing time (t_{mix}).

Samples of the polymerisate were collected after pre-determined reaction times using the side-arm device shown in fig. 2.12. The reaction vessel (fig. 2.11) was connected to the side-arm device through the greaseless glass joint (D). The whole system was connected to the vacuum line and evacuated by opening tap (C). After evacuation, tap (C) was closed and the whole system gently removed from the vacuum line. Tap (B) was then opened and about 5-10 cm^3 of the polymerisate was poured into the side-arm device. Tap (B) was then closed and the side-arm device removed by opening tap (C) and gently easing it off the polymerisation flask. The polymerisate collected in the side-arm device was poured into 25 cm^3 of cold methanol and the copolymer

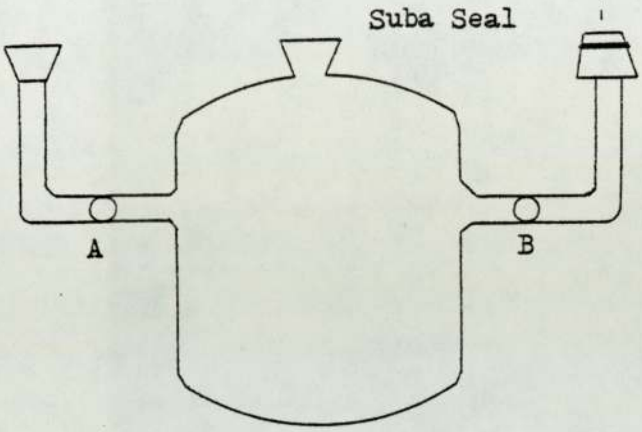


Fig. 2.11 Copolymerisation reaction vessel

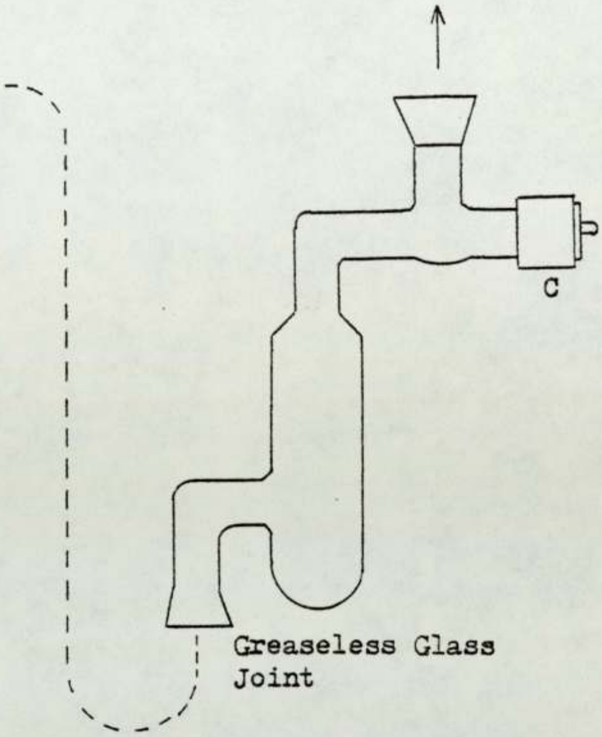


Fig. 2.12 Side-arm device

precipitated. This procedure was repeated to allow all the copolymer samples produced at different reaction times to be collected. All copolymer samples were dissolved in a small amount of hexane and sealed in glass ampules, until they were ready to be analyzed by dual-detector gel permeation chromatography.

2.4.5 Dilatometric Studies of the Copolymerisation Reaction

A solution of polystyryl lithium was prepared in bulb B of dilatometer B (fig. 2.7) by the sequential addition of styrene and cyclohexane (0·89 cm^3; $3{\cdot}74 \times 10^{-4}$ mol. of styrene) and lithium butyl (0·52 cm^3; $3{\cdot}75 \times 10^{-5}$ mol. of lithium butyl) by syringe. Tap (C) was then closed and the dilatometer was placed in a water bath at 60°C for 24 hours. During this time a pale orange/yellow solution of polystyryllithium was formed. After removing the dilatometer from the water bath, it was connected to the vacuum line and assembled and used as described in section 2.4.3.

2.5. ANALYTICAL TECHNIQUES

2.5.1 Gel Permeation Chromatoghraph

Gel permeation chromatography (gpc) is a technique used to separate polymer molecules according to their random coil dimensions in solution. Separation occurs in a column (or series of columns) filled with beads of a rigid porous 'gel' of highly crosslinked polystyrene. As a polymer solution flows past the beads, polymer molecules diffuse into the internal pore structure of the gel; the extent of diffusion is governed by the size of the polymer molecule and the pore-size distribution in the gel. Larger molecules can enter only a small fraction of the internal portion of the gel, or are completely excluded; smaller molecules penetrate a larger fraction of the internal pores of the gel. Larger molecules, therefore, spend less time inside the gel and so are eluted more quickly from the column. Smaller molecules spend more time inside the pore structure of the gel and so elute more slowly from the gpc column.

After emerging from the column, the polymer solution passes through a series of detectors which produce a response which is proportional to the concentration of the polymer in solution. If this response is plotted against retention time (fig. 2.13) then the familiar gpc chromatogram is obtained.

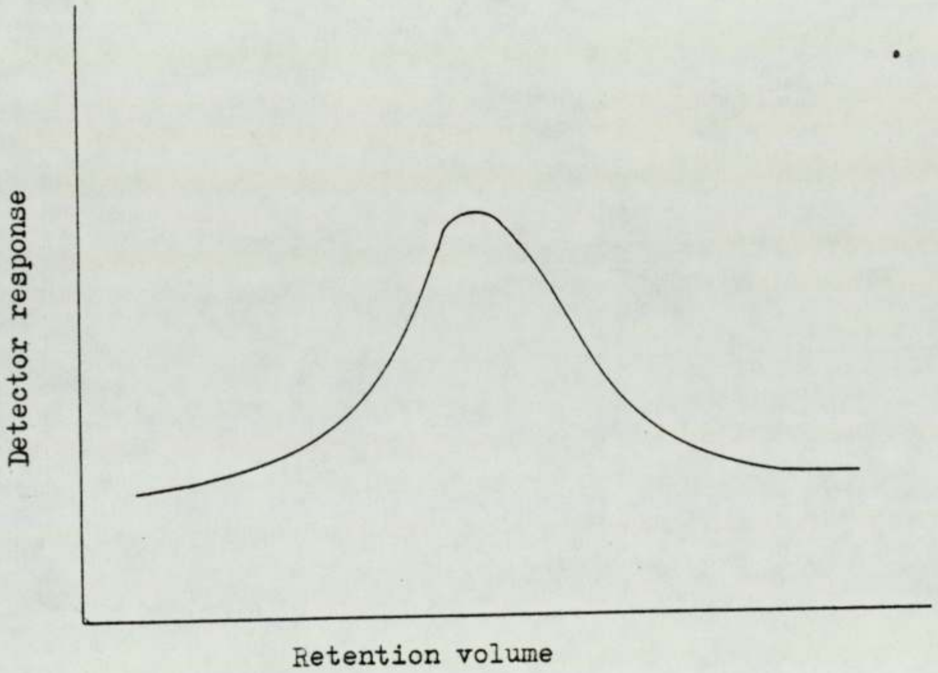


Fig. 2.13 Typical gpc chromatogram for a high molecular weight polymer.

Since there is no complete theoretical understanding of the relationship between molecular size and elution rate of a polymer solution through a gpc column, the chromatogram shown in fig. 2.13 provides only a qualitative description of the molecular size (and in most cases molecular weight) distribution of the polymer in solution. Quantitative information can be obtained by calibrating the series of gpc columns with a series of narrow dispersed polystyrenes of different known molecular weights. This results in a plot of log. molecular weight (polystyrene) against retention time (volume). By comparing retention volumes of different polymers it is possible to obtain a polystyrene equivalent molecular weights for most linear polymers in solution.

2.5.2. Gpc Detectors

Most gpc equipment is fitted with either a ultra violet (UV) detector or a differential refractometer (RI) detector or nowadays both are fitted.

The UV detector measures the UV absorbtion of polymers containing chromophoric groups along the backbone of the polymer chain or polymers having chromophoric end groups. The UV detector can be either of two types: fixed wavelength or variable wavelength. The cheapest detector is the fixed wavelength detector which usually operates at 254 nm wavelength, since this is a characteristic absorbtion of phenyl groups. Variable UV detectors have the facility to tune the detector to a particular wavelength and so achieve optimum detection of a UV absorbing polymer.

Refractive index detectors function by detecting changes in refractive index between a sample of the pure solvent and a sample of the polymer solution eluting from the gpc columns. This detector therefore produces a response which is proportional to the amount of polymer eluting past the detector and is independent of the nature of the polymer in solution.

The use of dual detector (UV and RI) gpc is now becoming increasingly common for the analysis of block copolymers, especially if one of the polymer blocks contains a UV absorbing chromophore. Comparison of both the UV and RI traces of such a gpc chromatogram of a block copolymer enables any increase in molecular weight of the UV absorbing polymer to detected.

2.5.3 Experimental

2.5.3.1 Gpc analysis of copolymers

All gpc chromatograms recorded in this thesis (except chapter 7) were produced in a Du Pont 870 series liquid chromatography system. The detectors used were UV and RI detectors. The polymer samples were introduced as a 2% solution of the polymer in THF by a Waters Associates model 710B Wisp autosampler. Data collection and analysis were performed by a Trivector Systems Limited, Trilab III Laboratory data system. Columns used were 10^5, 10^4, 10^3 and 10^2 Å porosity from Polymer Laboratories 10 PL gel. All chromatograms were obtained at 40 °C. The chromatography system was automatically calibrated after every 10 samples using a series of narrow disperse polystyrene samples of known molecular weights. The molecular weight standards used were 110,000; 24,000; 11,900; 2,900; and 920. All standards were from Polymer Laboratories.

CHAPTER 3

KINETIC STUDIES

3.1 INTRODUCTION

The kinetics of the ring-opening polymerisation of cyclopentene catalysed by the bimetallic system $WCl_6/Al(iBu)_3$ have been thoroughly studied in these laboratories. Amass and Tuck(328) have reported that the rate of polymerisation of cyclopentene shows a maximum at a 1:2 molar ratio of W:Al and found that the initial rate was dependent on the time delay (ageing time) between the addition of WCl_6 and subsequently $Al(iBu)_3$, to a solution of cyclopentene.

Similar results have been reported for the metathesis of linear olefins with the catalyst system $WCl_6/LiBu$. Wang and Menapace showed that the reaction system shows greatest activity at a W:Li molar ratio of 1:2 when the catalyst components were added sequentially to the alkene, pent-2-ene.

Since both catalyst systems seem to show similar features to each other, it was hoped that a study of the catalyst system $WCl_6/LiBu$ and its application to the ring-opening polymerisation of cyclopentene might provide further insights into the nature of the polymerisation of cyclopentene.

3.1.1 Polymerisation of Cyclopentene by the Catalyst System $WCl_6/LiBu$

The polymerisation of cyclopentene initiated by the catalyst system $WCl_6/LiBu$ was studied using dilatometry. These experiments were carried out as described in section 2.4.2 and 2.4.3.

3.1.2. The Effect of Ageing Time on the Rate of Polymerisation of Cyclopentene using the Catalyst System WCl_6/LiBu

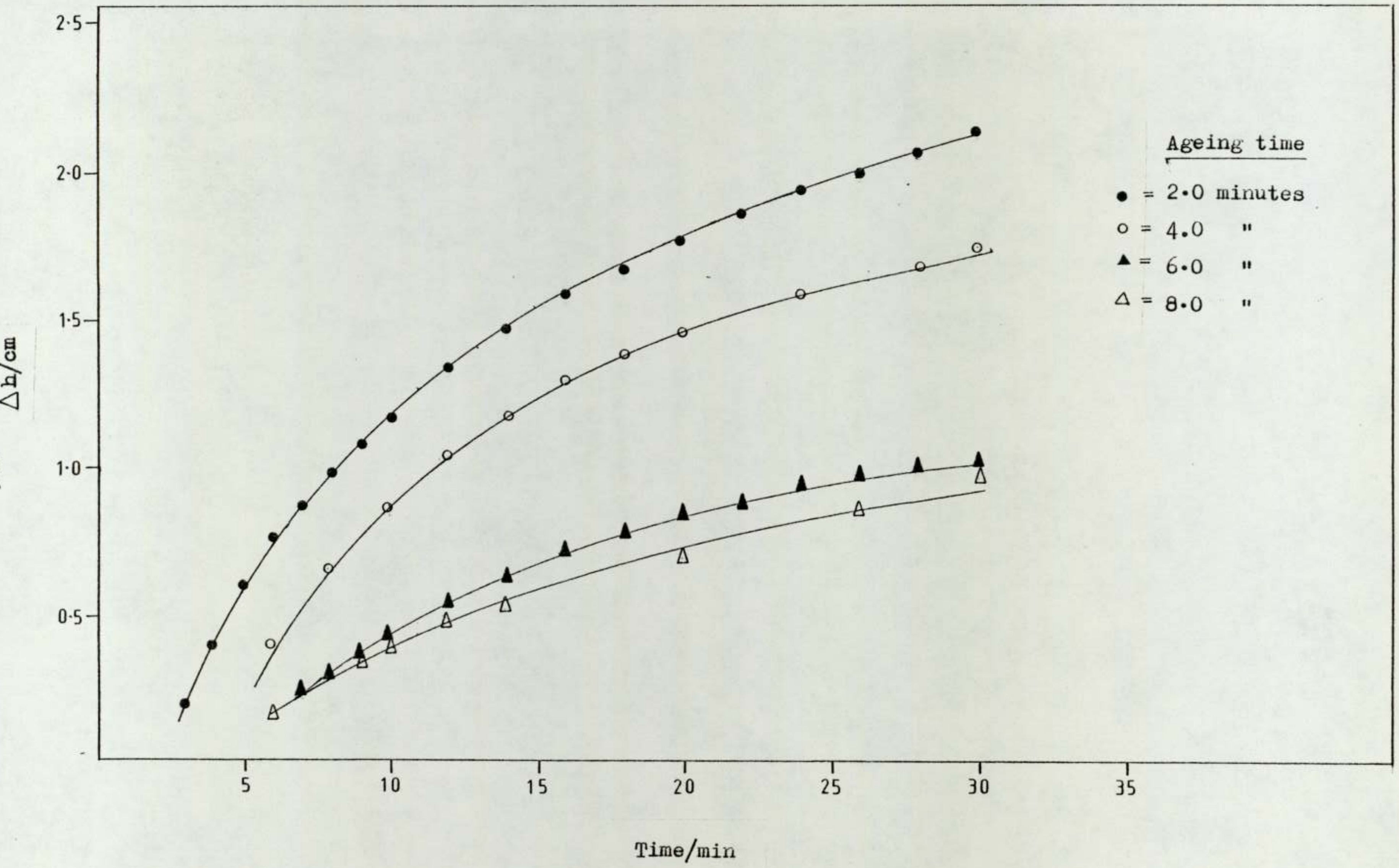
In a series of experiments the time delay (ageing time) between the addition of WCl_6 and LiBu to a solution of cyclopentene was varied and its effect on the rate of polymerisation studied.

In a typical polymerisation reaction 0·64 cm^3 of a solution of WCl_6 in toluene ($2{\cdot}94 \times 10^{-2}$ mol. dm^{-3}) was added to 15·0 cm^3 of the monomer solution (2·50 mol. dm^{-3} of cyclopentene in toluene) held in bulb A of dilatomer B (fig. 2.7). There is an immediate reaction and the blue WCl_6 solution turns reddish brown. After the required ageing time, 0·53 cm^3 of a solution of LiBu in toluene ($3{\cdot}75 \times 10^{-2}$ mol. dm^{-3}) was added to the monomer/catalyst solution. The polymerisate was then poured into the main reaction bulb and capillary tube of the dilatometer, tap (D) was then closed, and after placing the dilatometer in a water bath, the rate of polymerisation followed by a cathetometer.

Typical polymerisation conditions used were: monomer concentration = 2·50 mol. dm^{-3}; cyclopentene: tungsten: lithium molar ratio = 2000: 1: 2; and the ageing times studied were 2, 4, 6 and 8 minutes.

Figure 3.1 shows a series of polymerisation curves obtained at various ageing times.

Fig. 3.1 Dilatometric polymerisation curves of cyclopentene at various ageing times



Analysis of the curves shown in fig. 3.1 suggest that in all the experiments there appears to be an initially fast rate of polymerisation which gradually falls with increasing reaction time and which may attain a steady value beyond 30 minutes.

A clearer understanding of these polymerisation curves may be obtained by plotting the initial rate of polymerisation against reaction time. Unfortunately, because of the difficulty in filling the dilatometer bulb and capillary tube with the polymerisate it was not possible to obtain accurate measurements of $\Delta h/\Delta t$ at low reaction times. Instead, accurate rates of polymerisation were calculated after a common polymerisation time of 4 minutes. These values are tabulated in table 3.1 which shows the rate of polymerisation of cyclopentene at four minutes reaction time, for a series of different ageing times.

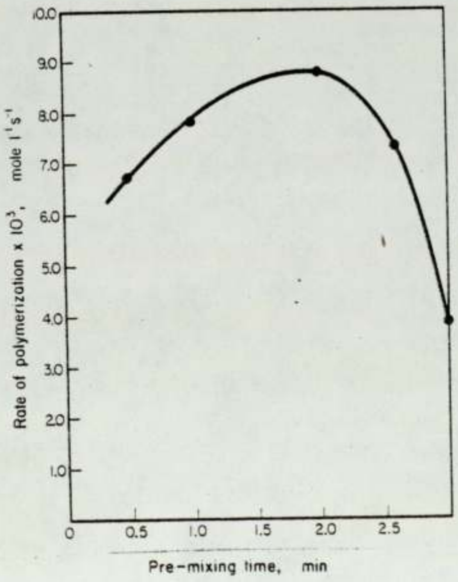
Table 3.1 The rates of polymerisation of cyclopentene at a reaction time of 4 minutes, for a series of ageing times.

Ageing time in minutes	Rate of Polymerisation $\times 10^4$/mol. dm^{-3} s^{-1}.
2	4.24
4	1.47
6	1.44
8	3.38

The figures shown in table 3.1 suggest that there is a much faster rate of polymerisation at an ageing time of 2 minutes; this rate falls to a minimum at an ageing time between 6 and 8 minutes. Experiments performed using ageing times greater than 8 minutes were not reliable and so are not considered in this work.

Similar studies have been performed in these laboratories on the ring-opening polymerisation of cyclopentene catalysed by WCl_6/ $Al(iBu)_3$. The results obtained from these studies indicate that the initial rate of polymerisation is greatest at an ageing time of 2.0 minutes. This can clearly been seen in fig. 3.2 where the initial rate of polymerisation of cyclopentene catalysed by WCl_6/ $Al(iBu)_3$ is plotted against ageing time.

Fig. 3.2 Dependence of the rate of cyclopentene polymerisation on pre-mixing time(28)



The results displayed in table 3.1 suggest that the maximum rate of cyclopentene polymerisation would be obtained if the monomer/catalyst solution had been allowed to 'age' for an ageing time between 0 and 2 minutes before the addition of the cocatalyst. Unfortunately, this prediction could not be tested because of the difficulty in transferring such small quantities of catalyst and cocatalyst to the dilatometer and still maintain a dry system. For this reason, it was found to be impracticable to age the monomer/catalyst solution for less than 90 seconds and for this reason there are no results reported at ageing times of less than 2 minutes.

The increase in the rate of polymerisation of cyclopentene at an ageing time of 8 minutes has not been successfully confirmed and this result remains suspect. If this result is indeed suspect then the trend shown in table 3.1 is in accord with the results shown in fig. 3.2 for the polymerisation of cyclopentene catalysed by WCl_6/$Al(iBu)_3$.

3.2. Effect of Varying the W:Li Molar Ratio on the polymerisation of Cyclopentene

Wang and Menapace have studied the metathesis of pent-2-ene initiated by the catalyst system WCl_6/LiBu. They found that at high olefin to tungsten ratios (i.e. 50:1) the greatest rate of metathesis was observed at a W:Li molar ratio of 1:2. Amass et al have also shown that the rate of polymerisation of cyclopentene is dependent upon the catalyst: cocatalyst molar ratio for unmixed catalyst systems i.e. WCl_6/$Al(iBu)_3$.

This led to an investigation of the effect of the W:Li molar ratios on the rate of polymerisation of cyclopentene by the unmixed catalyst system WCl_6/LiBu.

The polymerisation reaction were studied using dilatometry as outlined in section 2.4.2. The concentrations of monomer and tungsten were kept constant and the tungsten to lithium molar ratio varied at an ageing time of 2 minutes.

In a typical polymerisation reaction 0·89 cm^3 of a WCl_6 solution ($2{\cdot}09 \times 10^{-2}$ mol. dm^{-3}) was added to 15·0 cm^3 of the monomer solution (2·50 mol. dm^{-3}) held in bulb A of dilatometer B. This produced a monomer:tungsten ratio of 2000:1. There was an immediate reaction between the catalyst and the monomer and the resulting solution was reddish-brown. After an ageing time of 2 minutes the required amount of the lithium butyl cocatalyst ($7{\cdot}09 \times 10^{-2}$ mol. dm^{-3}) was added to the monomer/catalyst solution to produce a W:Li ratio of 1:1, 1:2, 1:3 or 1:4. The brown polymerisate was then introduced into the main bulb and capillary tube of the dilatometer and the rate of polymerisation followed by a cathetometer, after first placing the dilatometer in a water bath at 25°C. Because of the difficulty in filling the dilatometer bulb quickly and transferring the dilatometer to the water bath, it was not possible to follow the first 90 seconds of the polymerisation reaction so that the initial rate of polymerisation could not be determined.

Fig. 3.3 shows a series of polymerisation curves obtained by dilatometry at different W:Li molar ratios at constant monomer and tungsten concentrations.

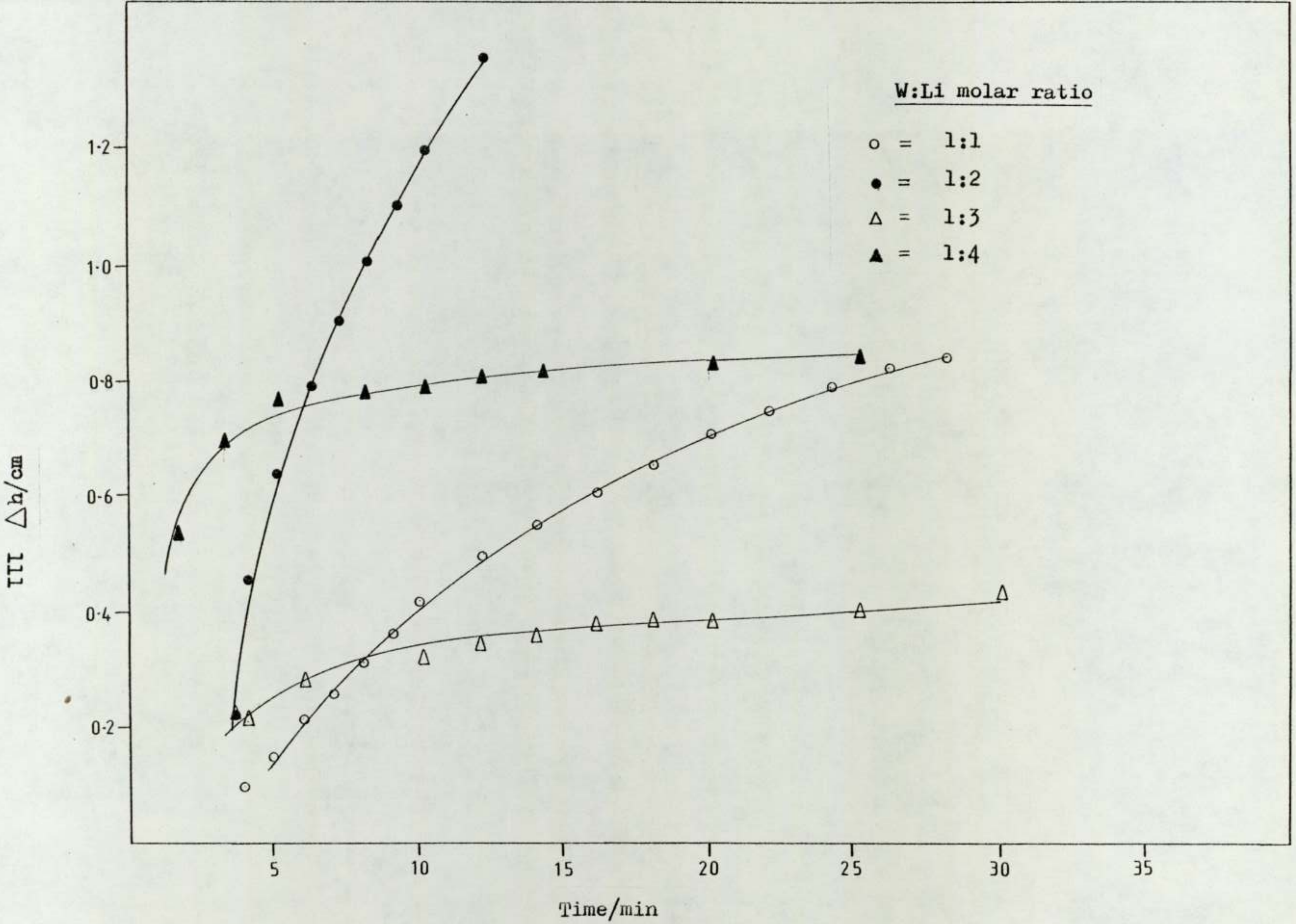


Fig. 3.3 Dilatometric polymerisation curves of cyclopentene for various W:Li molar ratios

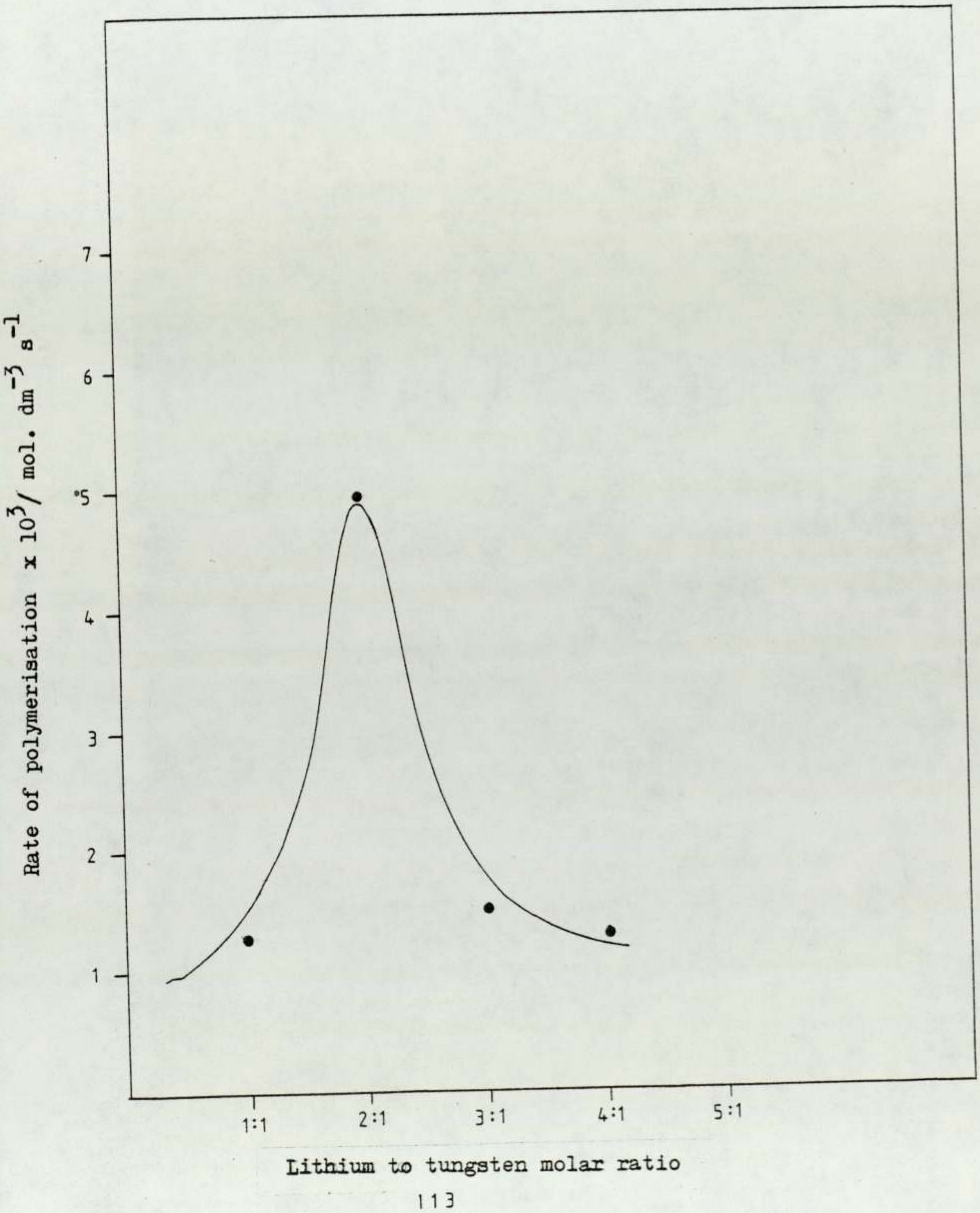
These curves show that the polymerisation of cyclopentene catalysed by WCl_6/LiBu displays a very complex kinetic behaviour.

During the early stages of the polymerisation reaction there is a fast initial rate of polymerisation which slows as the reaction proceeds. This decrease in the rate of polymerisation appears to be greatest at higher cocatalyst concentrations. This suggests that the lithium butyl, apart from being essential to help generate the metathetically active species, is also involved in termination reactions which slow the rate of polymerisation.

Whilst it is not possible to determine the initial rate of polymerisation of cyclopentene catalysed by WCl_6/LiBu from these curves, it appears that during the initial stages of the polymerisation the steepest curves occur at higher Li:W ratios i.e. 1:3 and 1:4 and may be associated simply to an increase in the cocatalst concentration. These results seem to contradict those obtained by Wang and Menapace which suggest that for the same catalyst system the catalyst showed greatest activity at a Li:W molar ratio of 2:1.

If, however, the rate of cyclopentene polymerisation is determined after a fixed polymerisation time (say 4 minutes) then the greatest rate of polymerisation occurs at a Li:W molar ratio of 2:1 as shown in fig. 3.4. This is in total agreement with the results obtained by Wang and Menapace since they analysed the products of the metathesis of pent-2-ene after a reaction time of 1 minute. If they had obtained reaction products at very short reaction times it is possible thet they may have observed the same dependence of rate of reaction on cocatalyst concentration that has been described above.

Fig. 3.4 Dependence of the rate of polymerisation of cyclopentene on W:Li molar ratio



3.2.1 Effect of Monomer:Catalyst Ratio on the Rate of Polymerisation of Cyclopentene

Olefin metathesis reactions which are catalysed by homogeneous catalysts are generally performed using high monomer to catalyst ratios. This is to ensure that high yields of the reaction product are obtained at low reaction times and also to avoid problems associated with trace impurities in the catalyst which may otherwise show detrimental effects at low catalyst concentrations.

Alternatively, ring-opening polymerisation reactions of cyclo-olefins catalysed by homogeneous catalyst systems are usually performed at low monomer to catalyst ratios. It was therefore instructive to investigate the effect of varying the monomer to catalyst ratio on the polymerisation of cyclopentene by an unmixed catalyst of WCl_6/LiBu.

The rate of polymerisation was studied dilatometrically as previously outlined in section 2.4.3.

In a typical polymerisation reaction 1·4 cm^3 of tungsten hexachloride solution (2.69×10^{-2} mol. dm^{-3}) was added to 15·0 cm^3 of the monomer solution held in bulb A of the dilatometer. After an ageing time of 2 minutes 0·67 cm^3 of lithium butyl solution ($1{\cdot}14 \times 10^{-1}$ mol. dm^{-3}) was added to the monomer/ catalyst solution. The polymerisate was then transferred to the main bulb and capillary tube of the dilatometer and, after placing the dilatometer in a water bath, the rate of polymerisation was followed using a cathetometer. Under these conditions the monomer concentration was maintained constant at 2.50 mol dm^{-3} and the W:Li molar ratio kept at 1:2. In the experiment above, the monomer to catalyst ratio was 1000:1, other ratios studied were 500:1 and 250:1, the amounts of the catalyst and cocatalyst solutions added to the monomer were adjusted accordingly.

Fig. 3.5 shows a series of polymerisation curves obtained from the polymerisation of cyclopentene at different monomer to catalyst ratios at constant monomer concentration.

At high monomer to tungsten ratios (i.e. 1000:1) the polymerisation proceeded with only a gradual dimunition in the rate as the reaction continued. The reaction was still continuing slowly after 30 minutes reaction time. At low monomer to tungsten ratios there was a much faster initial rate of polymerisation, so fast that it could not be accurately followed dilatometrically under the experimental conditions used. This initial rate very rapidly decreased and after a reaction time of about 8 minutes the polymerisation reaction had appeared to stop.

This decrease in the rate of polymerisation as the polymerisation proceeded could be due to a decrease in the monomer concentration, the concentration of the catalytically active species, or both.

The rate of decrease of Rp cannot solely be attributable to a fall in monomer concentration since the yield of polymer obtained from these polymerisation experiments is of the order of a few percent. It seems therefore that the decrease of Rp must be due to the presence of termination reactions which destroy the metathetically active species.

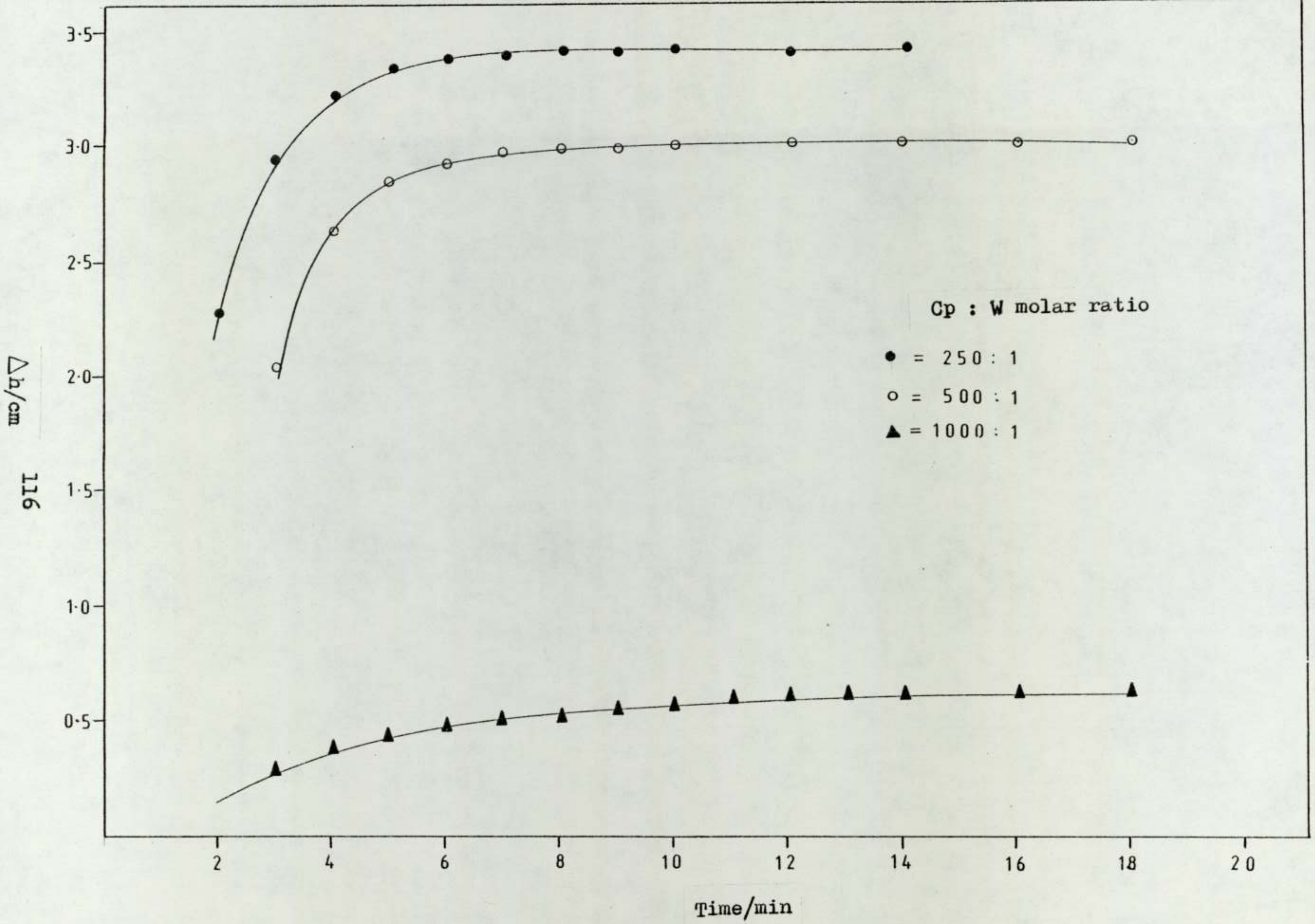


Fig. 3.5 Dilatometric polymerisation curves of cyclopentene at various monomer to catalyst ratios

These results are analogous to those obtained in the work carried out by Amass and Zurimendi(64) on the polymerisation of cyclopentene by $WCl_6/Al(iBu)_3$. They suggest that the active species are removed in a series of reactions:

$$W^* + W^* \xrightarrow{k_t} 2\,W_{inactive}$$

$$W^* + W_{inactive} \xrightarrow{k_{t2}} 2\,W_{inactive}$$

where W^* is the active species and $W_{inactive}$ the product of the termination reaction.

3.3 The Heterogeneous Nature of the WCl_6/LiBu/Cp System

In a conventional metathetic ring-opening polymerisation reaction, catalyst is added to the monomer prior to the addition of the cocatalyst. Immediately the cocatalyst is added to the monomer/catalyst solution the reaction solution becomes viscous indicating that the polymerisation reaction has started. The majority of metathesis catalysts used for the polymerisation of cycloolefins remain clear and homogeneous throughout the polymerisation. This is not the case when the catalyst system WCl_6/LiBu is used for the ring-opening polymerisation of cyclopentene.

There is an immediate reaction when the deep blue catalyst solution (WCl_6 in toluene) is added to the monomer solution. The product of the reaction is a reddish brown solution which shows no obvious sign of metathetic activity although several workers have reported that such systems are weakly active. There is a further reaction when the cocatalyst is added to the monomer/catalyst solution and the resulting solution turns brown and becomes viscous.

At high monomer to tungsten ratios (i.e. 2000:1) this brown solution appears to remain homogeneous for 10 - 15 minutes before a small quantity of brown/black precipitate forms and collects at the bottom of the reaction flask even at high concentrations of monomer. The main bulk of the polymerising solution remains homogeneous.

At much lower monomer to tungsten ratios (i.e. 500:1 or 250:1) the addition of the cocatalyst to the catalyst/monomer solution immediately produces a large quantity of brown/black precipitate which quickly settles to the bottom of the reaction flask. The solution above the precipitate appears colourless.

3.4 Premixed Catalyst experiments

It has been known for a long time that the order of addition of the catalyst components to an olefin in a metathesis reaction may dramatically affect the nature of the ensuing reactions. Addition of pent-2-ene to a premixed catalyst system of $WCl_6/EtAlCl_2$ in toluene has been reported to produce a rapid Friedels Craft alkylation of the toluene almost exclusively, whereas preparation of the catalyst in the presence of the olefin results in a rapid metathesis reaction.

Premixing of the catalyst components is also known to affect both the percentage conversion of the starting olefin and the selectivity of the metathesis reaction. If WCl_6 and LiBu were premixed for 10 minutes before the addition of pent-2-ene and $AlCl_3$ or $AlBr_3$ then the selectivity of the reaction was much higher than that observed in the non-premixing experiments(67). These results promted an investigation of the ring-opening polymerisation of cyclopentene by the premixed catalyst system WCl_6/LiBu.

3.4.1 Effect of the W:Li Molar Ratio on the Metathesis of Cyclopentene

Studies of the ring-opening polymerisation of cyclopentene catalysed by the premixed catalyst system WCl_6/LiBu were performed using dilatometer B as previously outlined in section 2.4.3.

In a typical polymerisation reaction 0·26 cm^3 of the cocatalyst solution ($7 \cdot 09 \times 10^{-2}$ mol. dm^{-3} LiBu in toluene) was added to 0·89 cm^3 of a tungsten hexachloride solution (2.09×10^{-2} mol. dm^{-3} WCl_6 in toluene) held in bulb A of the dilatometer. After a premix ageing time of 2·0 minutes the premixed catalyst solution was allowed into 15·0 cm^3 of the monomer solution (2·50 mol. dm^{-3}, 3.75×10^{-2} moles of cyclopentene) held in bulb B of the dilatometer. The polymerisate was then poured into the main bulb and capillary tube of the dilatometer and, after placing the dilatometer in a water bath, the reaction followed by means of a cathetometer.

Throughout the whole series of experiments the monomer and tungsten concentrations were maintained constant; Cp = 3.75 x 10^{-2} moles , WCl_6 = 1.86 x 10^{-5} moles, the monomer to tungsten ratio was 2000:1. The amount of the cocatalyst added was varied to produce a Li:W ratio of 1:1, 2:1, 3:1 and 4:1.

Figure 3.6 shows the curves obtained from a series of dilatometry experiments on the polymerisation of cyclopentene catalysed by the premixed catalyst system WCl_6/LiBu, for a series of Li:W ratios.

Again, because of the difficulties in filling the dilatometer bulb quickly and transferring the dilatometer to the water bath it was not possible to measure the rate of polymerisation at very short reaction times and therefore it was impossible to determine the initial rate of polymerisation. Instead the rate of polymerisation was calculated at a reaction time of 4 minutes and these values have been plotted in figure 3.7.

These curves (fig. 3.6 and 3.7) show that after a short reaction time the greatest rate of polymerisation is obtained at a Li:W molar ratio of 2:1. These results agree with those obtained for the polymerisation of cyclopentene catalysed by the unmixed catalyst system WCl_6/LiBu and those results obtained by Wang and Menapace from studies of the metathesis of pent-2-ene by the same unmixed catalyst system.

Surprisingly, Wang and Menapace also found that the metathesis of pent-2-ene was dependent not only on the W:Li ratio, but that variations in this ratio was only important at olefin:tungsten

Fig. 3.6 Dilatometric polymerisation curves of cyclopentene at various W:Li ratios for the premixed catalyst system $WCl_6/LiBu$

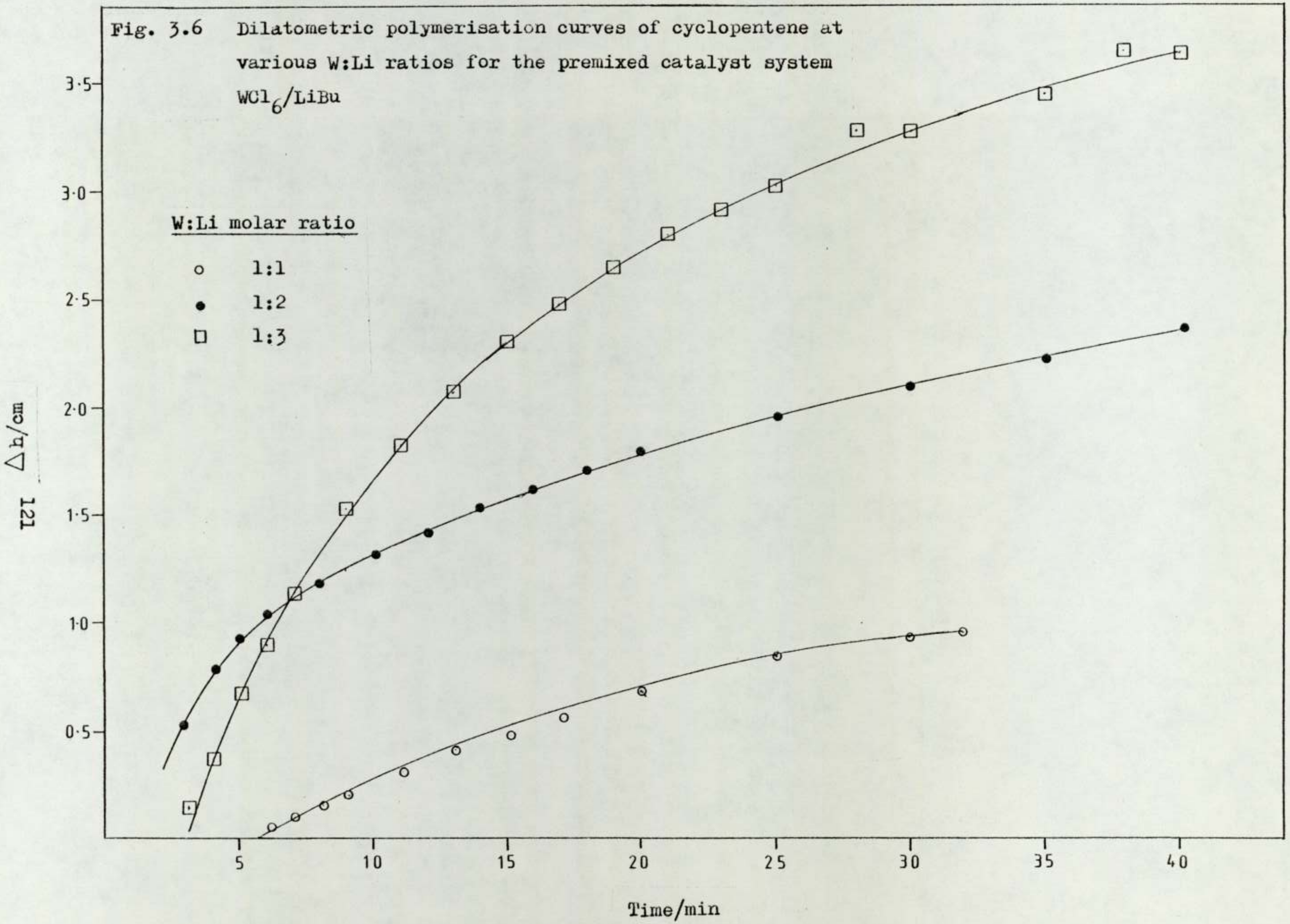
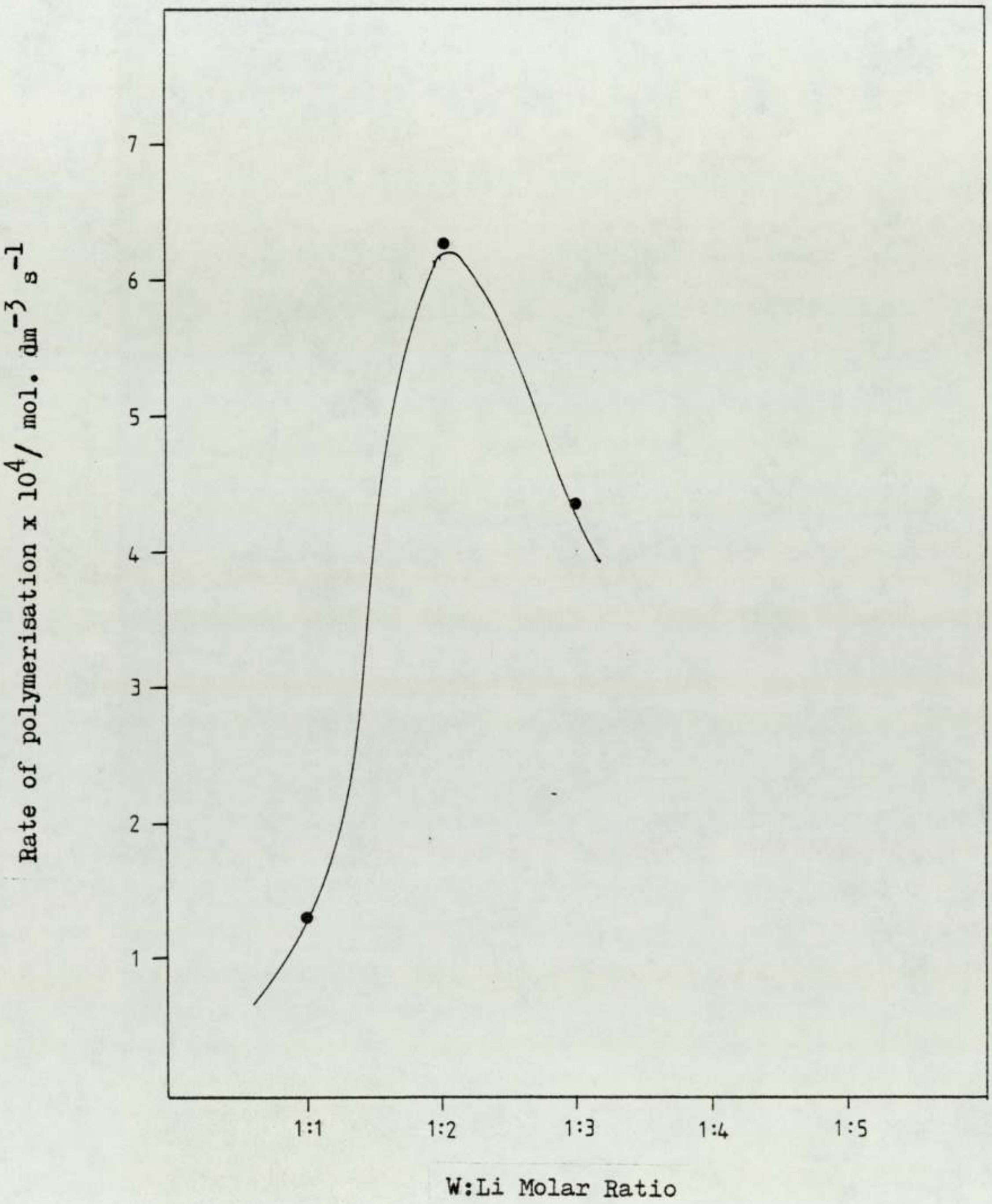


Fig. 3.7 Dependence of the rate of polymerisation of cyclopentene on W:Li molar ratio



ratios of 50:1. At other olefin: tungsten ratios i.e. 100:1, variation of the Li:W ratio between 0·5 to 15 to 1 had little or no effect on the reaction. This is in contrast to the ring-opening polymerisation of cyclopentene, where the effect of the W:Li ratio on the rate of polymerisation was marked even at monomer to catalyst ratios of 2000:1.

A comparison of the polymerisation of cyclopentene catalysed by the unmixed and premixed catalyst system WCl_6/LiBu (fig. 3.1, table 3.1 and fig. 3.6 and 3.7) reveals several interesting features.

(1) there is a maximum rate of polymerisation after a reaction time of 4 minutes at a W:Li ratio of 1:2 for both unmixed and premixed catalyst systems.

(2) The magnitude of these maximum rates of polymerisation (at equivalent reaction times) are approximately equal at corresponding W:Li molar ratios for both types of catalyst system.

(3) The maximum rate of polymerisation (at 4 minutes reaction time) decreases as the lithium butyl cocatalyst concentration increases for both catalyst systems.

This decrease in the maximum rate of polymerisation with increasing cocatalyst concentration is surprising and suggests that an excess of the cocatalyst might interfere with the metathesis reaction possibly by coordinating with the metathetically active species and sterically inhibiting the metathesis reaction. It is well known that, in non-polar solvents, lithium butyl can exist as either tetramers and/or hexamers and that this can dramatically effect the kinetics of, for example, anionic polymerisation reactions initiated by lithium butyl.

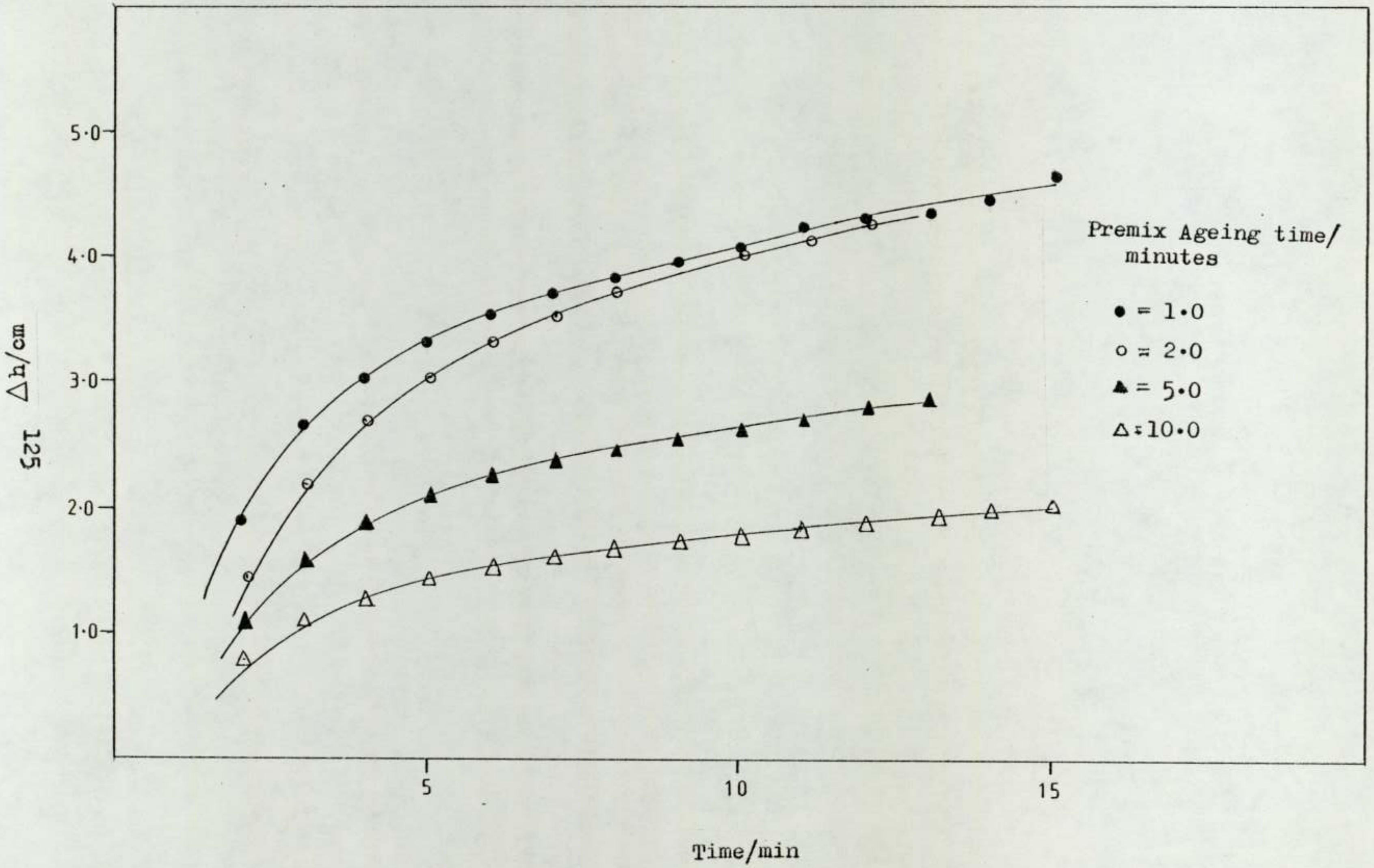
3.4.2 Effect of the Premix Ageing Time on the Polymerisation of Cyclopentene

Premixed catalyst systems are prepared by allowing the catalyst components to react with each other for a definite reaction time (premix ageing time) before their addition to the monomer solution. Since for a unmixed catalyst system, ageing time of the catalyst/monomer is known to dramatically effect the rate of polymerisation of cyclopentene, the premixed ageing time of a premixed catalyst system may also influence the rate of polymerisation of cyclopentene. This has led to a study of the effect of varying the premix ageing time on the rate of polymerisation of cylcopentene for two different monomer concentrations.

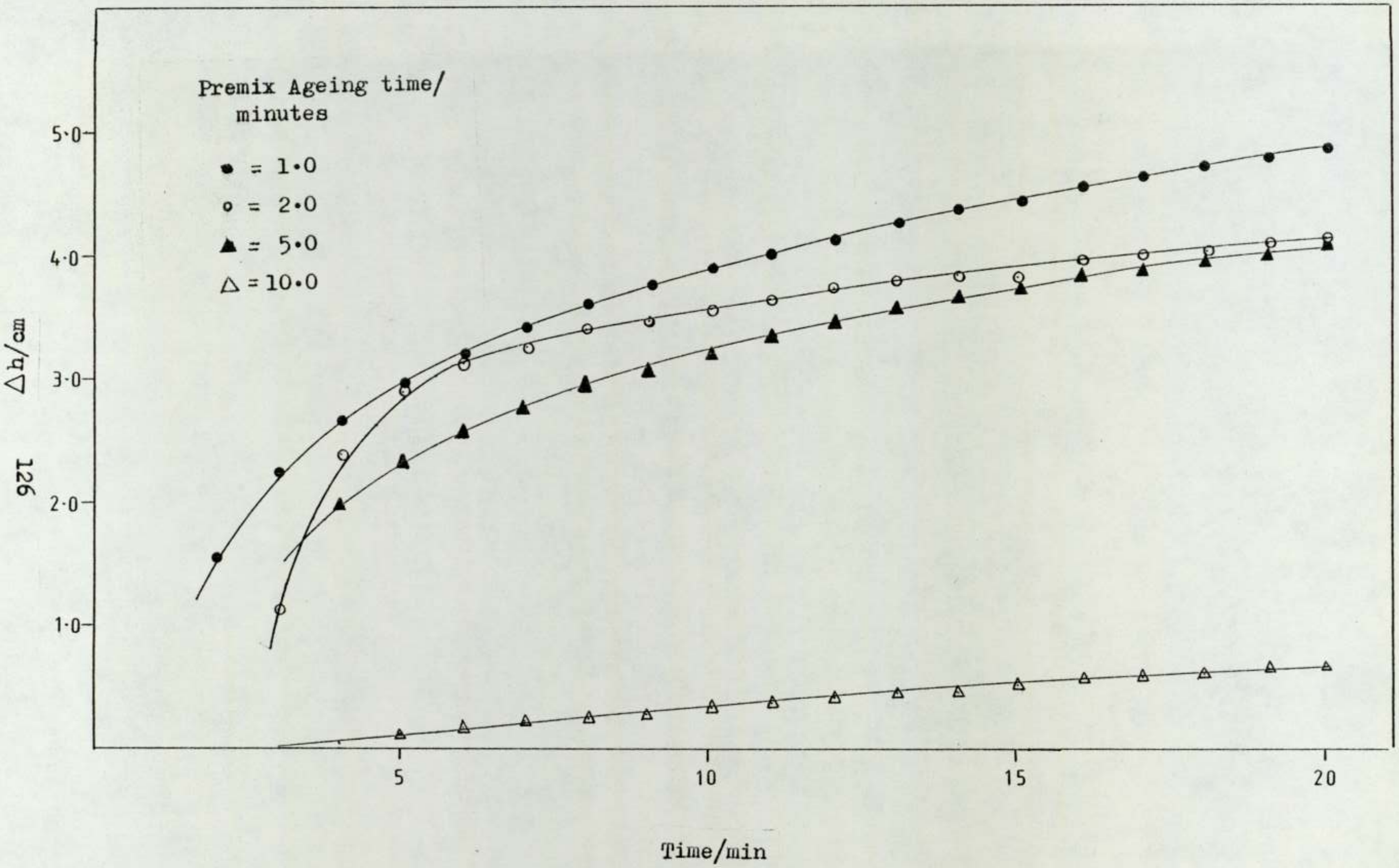
The polymerisation reactions were studied dilatometrically using dilatometer B as outlined previously in section 2.4.3.

The catalyst was prepared by allowing 3.70 cm^3 of tungsten hexachloride solution ($1{\cdot}6 \times 10^{-2}$ mol. dm^{-3}) and lithium butyl (1cm^3 of a $1{\cdot}14 \times 10^{-1}$ mol. dm^{-3} solution) to react together within bulb B of the dilatometer. After the prerequisite premix ageing time the catalyst solution was poured into $15{\cdot}0$ cm^3 of the monomer solution held in bulb B of the dilatometer (monomer concentration = 3.94 mol. dm^{-3})

Fig. 3.8 Dilatometric polymerisation curves of cyclopentene (3·94 mol. dm^{-3}) using the premixed catalyst system WCl$_6$/LiBu at various premixed ageing times



using the premixed catalyst system WCl_6/LiBu at various premixed ageing times



and after the polymerisate had been poured into the main bulb and capillary tube of the dilatometer, and after placing the dilatometer into a water bath, the reaction was followed by means of a cathetometer. The reaction conditions used were: monomer: tungsten ratio = 1000:1 and tungsten:lithium ratio of 1:2. The premix ageing times studied were 1, 2, 5 and 10 minutes.

The same procedures were adopted when the monomer concentration was increased to 4.55 mol. dm^{-3} except the amounts of catalyst and cocatalyst solutions used were 4.26 cm^3 and 1.20 cm^3 respectively. The concentrations of the catalyst and cocatalyst were the same as described previously. Again, the premix ageing times studied were 1, 2, 5, and 10 minutes.

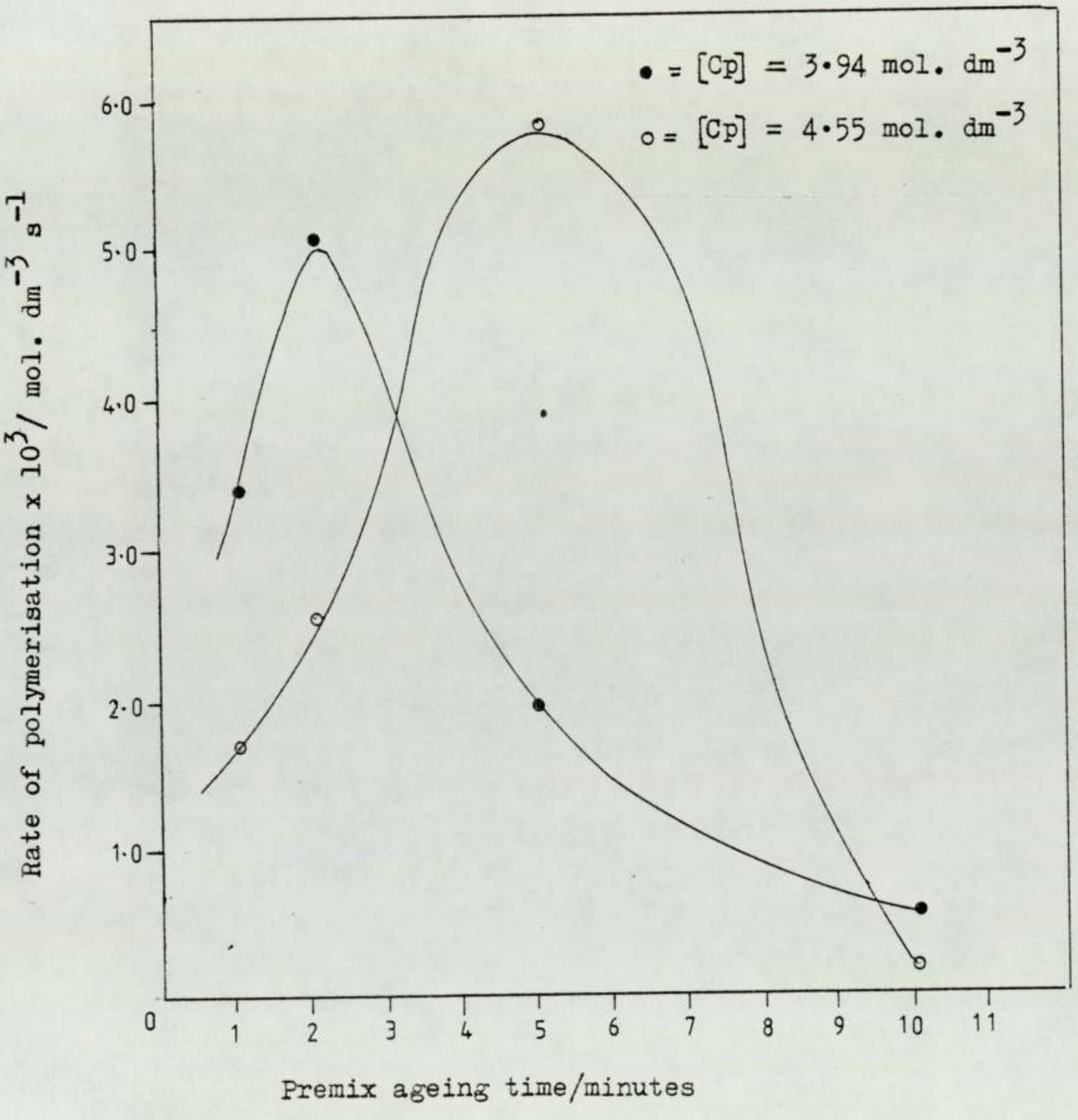
The effect of premix ageing time on the rate of polymerisation of cyclopentene for the two different monomer concentrations (i.e. 3.94 and 4.55 mol. dm^3) are shown in figures 3.8 and 3.9 respectively.

Both sets of curves show similar features (i) a very fast initial rate of polymerisation which slows down very rapidly within a few minutes reaction time, and (ii) the rate of polymerisation is dependent on the premix ageing time of the catalyst components

This second feature is more readily shown in fig. 3.10 where the rate of polymerisation at 4 minutes reaction time is plotted against premix ageing time.

These curves (fig. 3.10) suggest that the maximum rate of polymerisation at 4 minutes reaction time is dependent on both the premix ageing time of the catalyst components and also the initial monomer

Fig. 3.10 Rate of polymerisation of cyclopentene against premix ageing time.



concentration. This latter observation is totally unexpected and needs further investigation before it can be regarded as generally true. That the maximum rate of polymerisation appears at a premix ageing time of 2.0 minutes (for an initial monomer concentration of 3.94 mol. dm^3) is in total agreement with the results obtained from similar unmixed catalyst systems at lower monomer concentrations and also for different unmixed catalyst systems (e.g. $WCl_6/Al(iBu)_3/Cp$).

CHAPTER 4

POLYMERISATION STUDIES

4.1 INTODUCTION

The olefin metathesis reaction can be catalysed by either heterogeneous or homogeneous catalyst systems though it is now believed that the propagating species in each case is a metallocarbene/ metallocyclobutane intermediate. The synthesis of these propagating species, especially in homogeneous systems, has received much attention in recent years. Unfortunately most of these studies have ignored the role of the cocatalyst as a component in a metathetically active species. Rather, the cocatalyst is usually assigned a minor role in the synthesis of these 'active species' some of these roles include: i) acting as a reducing agent for the transition metal catalyst, ii) behaving as a Lewis acid which coordinates with the transition metal catalyst, and iii) acting as an alkylating agent to generate an intermediate which subsequently rearranges to produce the metallocarbene propagating species.

Current models favour the latter hypothesis by which an organometallic cocatalyst donates an alkyl group to the transition metal catalyst which subsequently loses an α - hydrogen to yield a metallocarbene which then initiates olefin metathesis.

How the cocatalyst, especially the alkyl group, becomes associated with the transition metal catalyst has not yet been studied experimentally. It may, for example, be directly involved in the generation of the propagating metallocarbene and so eventually become associated with the final metathesis products. Alternatively, the cocatalyst may help to generate the metallocarbene by some alternate route and so not become involved with the final metathesis products.

These possibiliteis may be investigated by labelling the cocatalyst by some convenient means and detecting the presence - or absence- of the labelled cocatalyst in the final products of a metathesis reaction.

The metathetic ring-opening polymerisation of cyclopentene by the catalyst system WCl_6/LiBu provides a convenient metathesis reaction to study since the products of the reaction -polypentenamer- are readily isolable from the reaction products. For such a reaction system, there are two convenient techniques available for labelling the lithium butyl cocatalyst used. Radioactive isotopes of carbon (^{14}C) or hydrogen (^{3}H) may be substituted into the cocatalyst and detected in the final products of the metathesis reaction by a scintillation detector. Alternatively, the alkyl group of the cocatalyst may be replaced by an inert chromophore which could be detected in the metathesis products by a fluorescence or ultra-violet detector. Chromophoric labelling was preferred since the products of the polymerisation reaction may be separated by gpc and analyzed by both refractive index and ultra-violet detectors.

Lithium butyl can initiate the anionic polymerisation of styrene to living polystyryl lithium which may then be used as the chromophore labelled cocatalyst in the ring-opening polymerisation of cyclopentene. Whilst the ring-opening polymerisation of cyclopentene by the catalyst system WCl_6/polystyryl lithium has not previously been reported, experiments in these laboratories by Mathews et al(142) have suggested that the reaction is feasable.

Analysis of the products of the reaction by infra-red and ultraviolet spectroscopy and C,H analyses suggested that copolymers were formed during the polymerisation reaction though the formation of an intimate polymer blend could not be precluded.

It was hoped that the use of gpc equipped with dual detectors (RI and UV) would be able to resolve these doubts and so provide a method for probing the role played by the cocatalyst in metathetic polymerisation reactions.

4.1.1 Polypentenamer

The ring-opening polymerisation of cyclopentene catalysed by WCl_6/LiBu has been studied dilatometrically as outlined in section 2.4.3. The products of this polymerisation reaction was a white sticky elastomer, polypentenamer.

In a typical polymerisation reaction, 0·64 cm^3 of a WCl_6 solution (2·94 x 10^{-2} mol. dm^{-3}) was added to 15·0 cm^3 of monomer solution (2·50 mol. dm^{-3}) held in bulb A of dilatometer B. After an ageing time of 2 minutes 0·53 cm^3 of the cocatalyst (3·75 x 10^{-1} mol. dm^{-3}) was added to the monomer/catalyst solution. The polymerisate was immediately poured into the main bulb and capillary tube of the dilatometer. After a polymerisation time of 30 minutes the polymerisate was poured into 50 cm^3 of cold methanol and the polymer precipitated. The polymer was then redissolved in a small quantity of chloroform and reprecipitated in 25 cm^3 of cold methanol, filtered and dried in a vacuum oven overnight at 25°C.

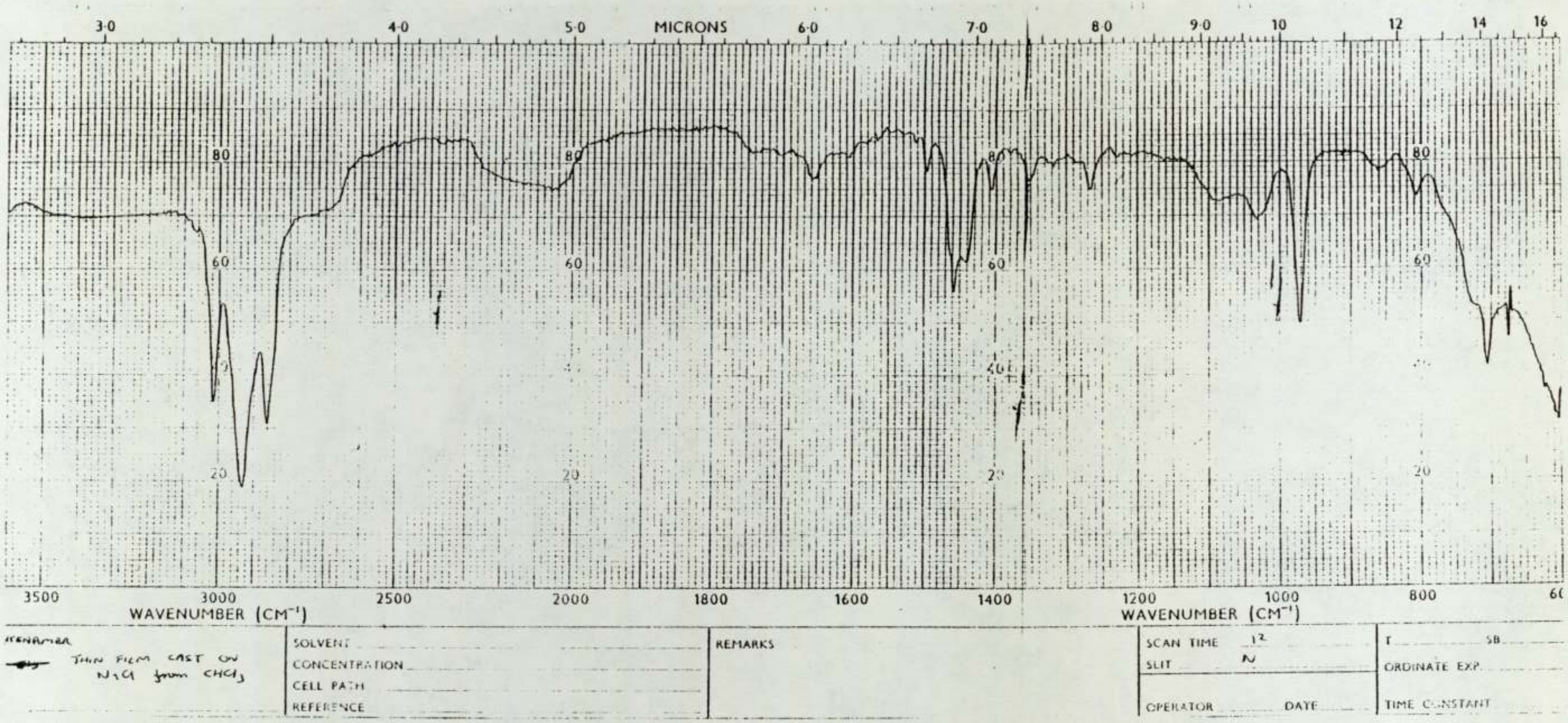


Fig. 4.1 Typical infra red spectrum of polypentenamer

A small amount of the dried polymer was dissolved in chloroform and cast as a thin film on a sodium chloride plate by evaporation of the concentrated polymer solution.

The film was then examined by infra-red spectroscopy. Figure 4.1 shows a typical infra-red spectrum of polypentenamer obtained from the polymerisation of cyclopentene initiated by the catalyst system WCl_6/LiBu. This spectrum shows bands at 7.12μ and $13\cdot8\mu$ which are typical of cis-vinylene bonds and bands at $10\cdot35\mu$ which is typical of trans double bonds in polypentenamer and polyalkenamers in general.

4.1.2 Copolymers

Investigations into the ring-opening polymerisation of cyclopentene by a variety of catalyst systems reveals many features of the active species responsible for the polymerisation reaction. Unfortunately, such studies have so far provided only a partial understanding of the role played by the cocatalyst in such polymerisation reactions. This led to an investigation of the products of the polymerisation of cyclopentene by a catalyst system which contained a cocatalyst which was labelled by a chromophore. The reaction system studied was the polymerisation of cyclopentene initiated by WCl_6/ polystyryl lithium.

In a typical polymerisation reaction approximately $4\cdot0$ cm^3 of WCl_6 solution ($1\cdot7 \times 10^{-2}$ mol. dm^{-3}) was added to 70 cm^3 of a cyclopentene solution (2.2 mol. dm^{-3}) held in a flask as described in section 2.4.4. After an ageing time of 2 minutes $1\cdot8$ cm^3 of the polystyryl lithium cocatalyst ($7\cdot72 \times 10^{-2}$ mol. dm^{-3}) was added to the monomer/ catalyst solution. Samples of the polymerisate were collected at

3, 7, 15, 30 and 60 minutes reaction time by the procedure outlined in section 2.4.4. A 20 cm^3 fraction of the polymerisate was poured into cold methanol and a white sticky polymer precipitated. This material was dissolved in chloroform and hexane added dropwise to the polymer solution. After the addition of a few drops of hexane, polymer began to precipitate. This polymer was collected by filtration, dissolved in chloroform and reprecipitated by adding hexane. An infra-red spectrum was obtained of the hexane insoluble polymer cast as a thin film on a sodium chloride plate and is shown in fig. 4.2.

The remaining filtrate was then added to cold methanol and a white polymer precipitated. This material was dissolved in hexane, and reprecipitated from methanol, filtered and dried in a vacuum oven at 25 °C. This polymer was cast from a concentrated chloroform solution as a thin film on a sodium chloride plate and an infrared spectrum obtained, this is shown in fig. 4.3.

The infra-red spectrum of polystyrene obtained from the polystyryl lithium cocatalyst is shown in fig. 4.4.

Both spectra shown in fig. 4.2. and 4.3 show peaks characteristic of polypentenamer (10·35 μ and 6.8 μ) and polystyrene (16·35 μ), which suggests that both materials may be copolymers. Although these materials may in fact be intimate polymer blends, the precipitation procedure ought to have removed, particularly from the hexane soluble material, any homopolystyrene. However, it is possible that (i) the hexane soluble material is a mixture of polypentenamer and polypentenamer-rich copolymer and (ii) the hexane insoluble material is a mixture of polystyrene and styrene-rich copolymer.

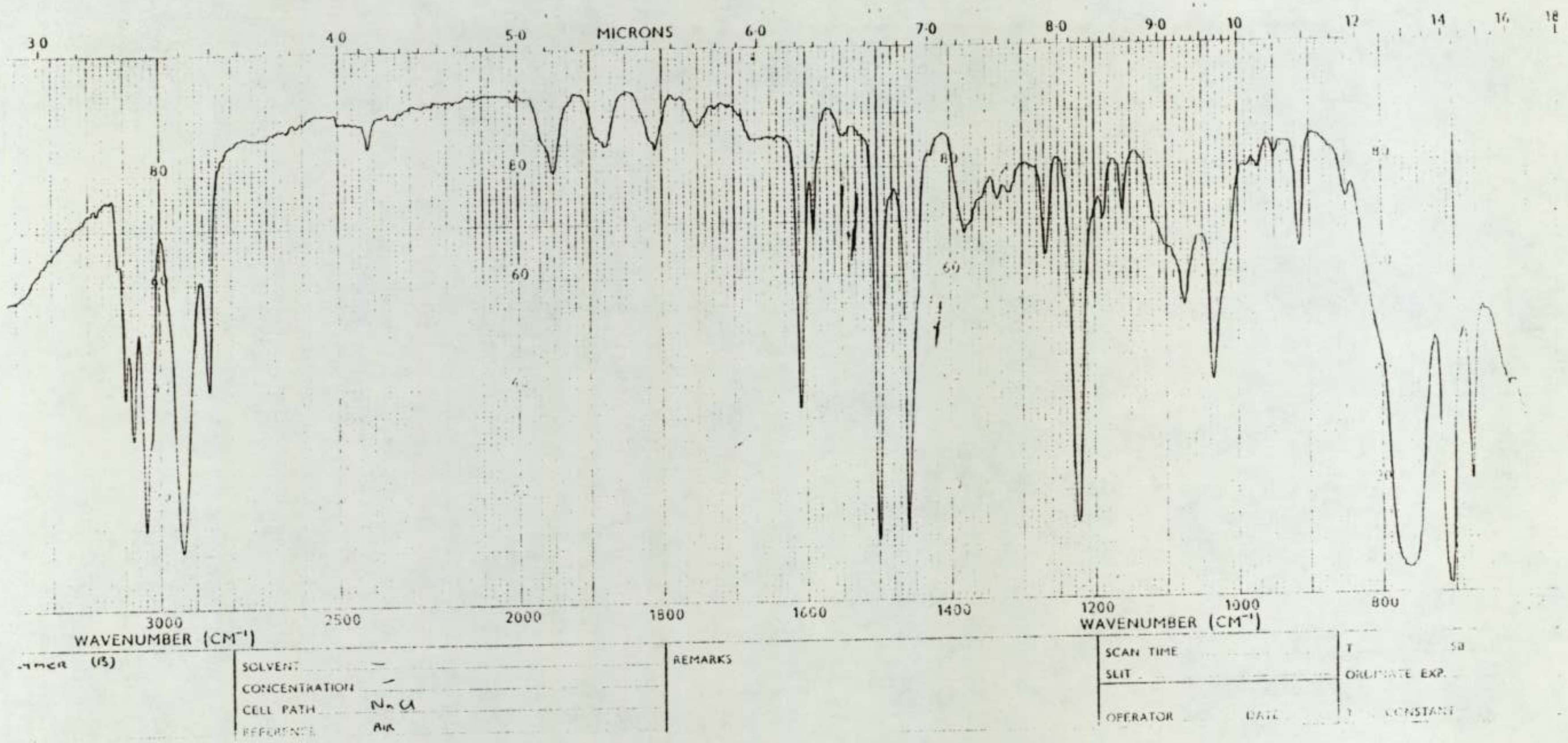
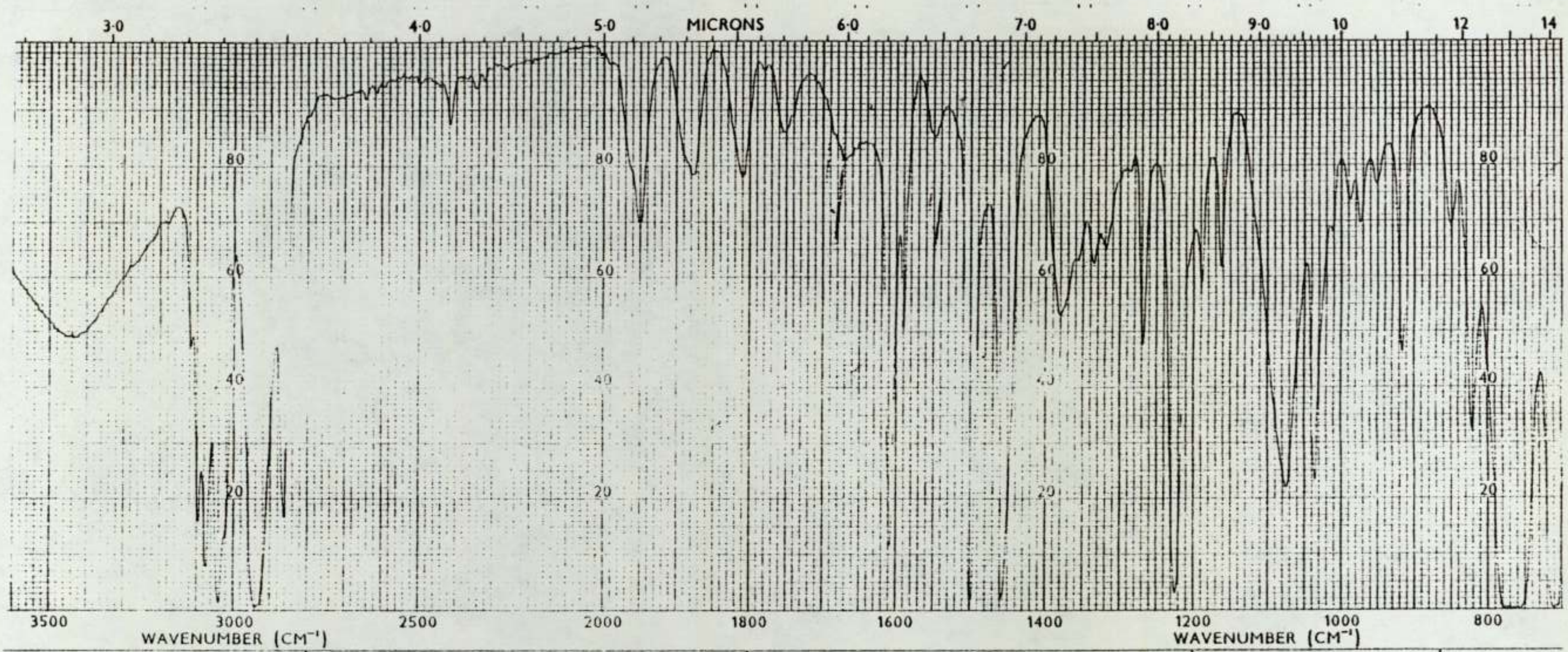


Fig. 4.2 Typical infra red spectrum of the hexane insoluble copolymer



PSC COPOLYMER (A)
CAST FROM $CHCl_3$

SOLVENT —
CONCENTRATION —
CELL PATH NaCl
REFERENCE AIR

REMARKS

SCAN TIME 12 mins
SLIT N
OPERATOR DATE

T S
ORDINATE EXP.
TIME CONSTANT

Fig. 4.3 Typical infra red spectrum of the hexane soluble copolymer

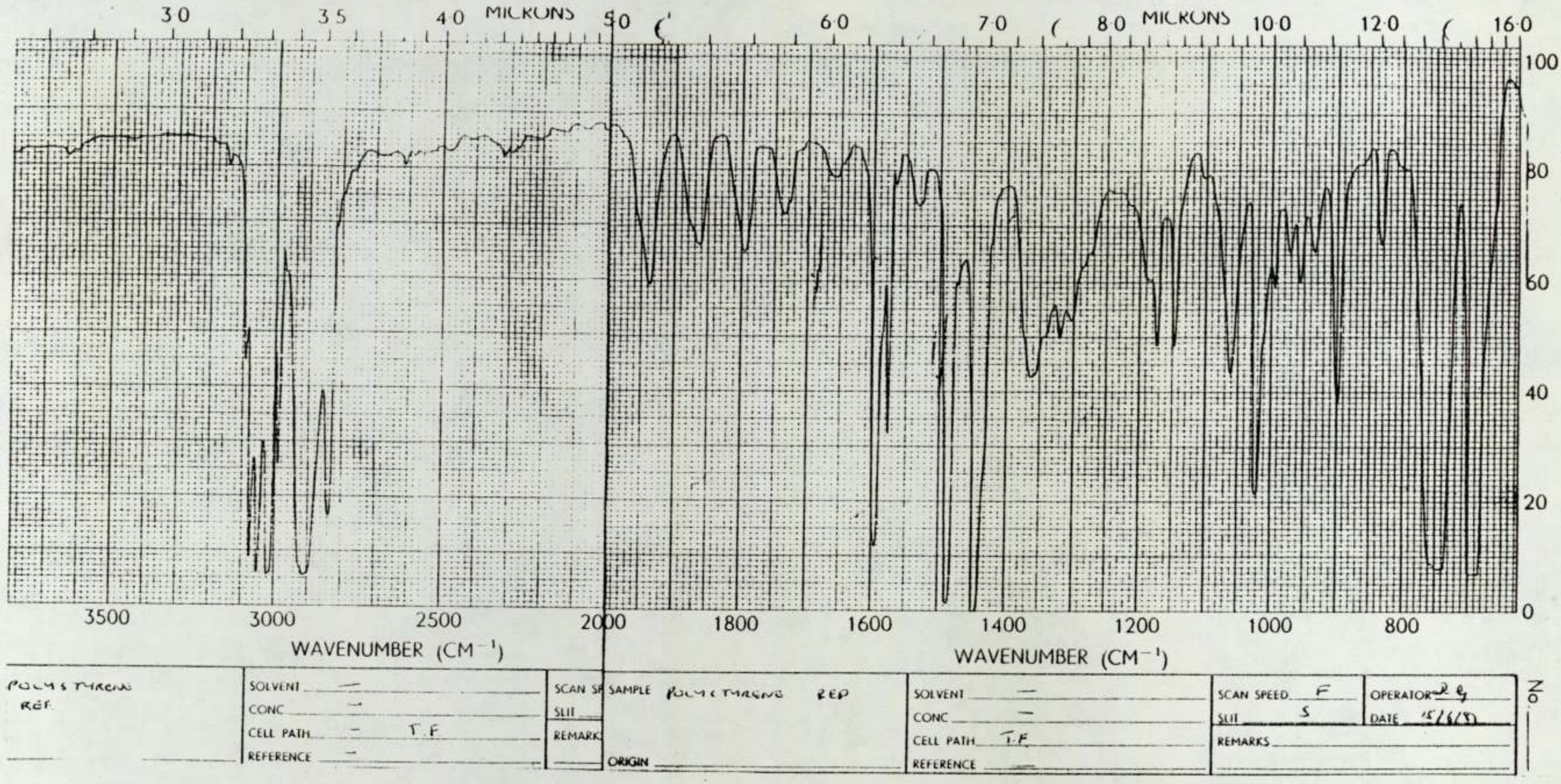


Fig. 4.4 Typical infra red spectrum of polystyrene

If the products are indeed copolymers then the variation in solubility of these materials is probably due to the length of the polypentenamer chain attached to the polystyrene block. As the polypentenamer chain increases in length, then the polystyrene block - which is normally insoluble in hexane - becomes increasingly soluble in hexane and hence the copolymer becomes soluble in hexane.

4.2 MOLECULAR WEIGHT STUDIES

Although the results obtained from both infra-red and solubility studies suggests that the materials obtained from the polymerisation of cyclopentene by WCl_6/polystyryl lithium are copolymers, they may in fact be intimate polymer blends. Unfortunately, these two alternatives can not easily be distinguished by either of the two techniques discussed above. An alternate approach to this problem would be to detect the presence - or absence - of the polystyryl chain in the products of the copolymerisation reaction.

If, during the copolymerisation reaction, the polystyryl block became attached to the growing polypentenamer chain then the molecular weight of the polystyryl block could be expected to increase throughout the copolymerisation reaction. This increase in molecular weight would be detectable by gpc equipped with a UV detector.

4.2.1 Polpentenamer

The ring-opening polymerisation of cyclopentene does not produce polymers having a normal distribution of molecular weight, rather, the products of the reaction possess bimodal molecular weight distributions.

The products of a typical polymerisation reaction initiated by the catalyst system WCl_6/LiBu (as described in section 4.1.1) was analyzed by gpc using a differential refractometer detector. The resultant gpc chromatogram is shown in fig. 4.5.

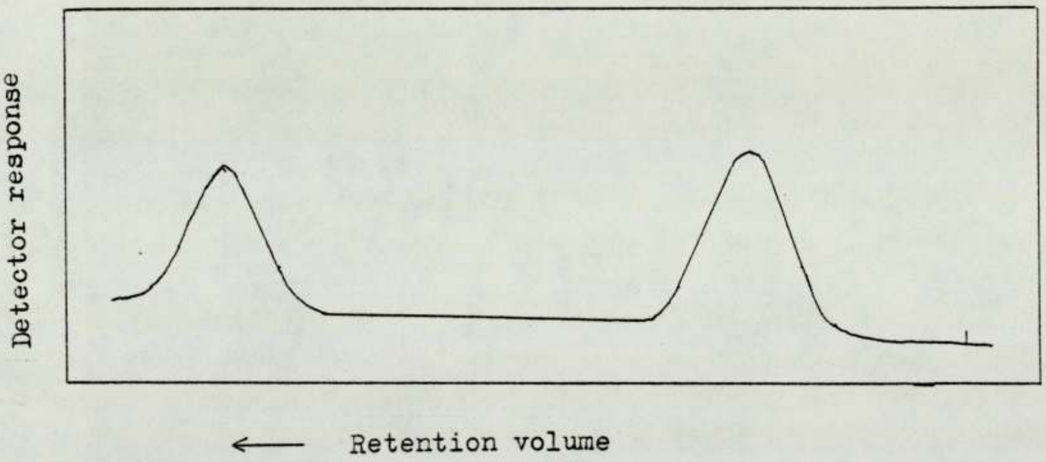


Fig. 4.5 Gpc chromatogram of polypentenamer.

Calderon et al(6) have reported that the high molecular weight products are linear polymer chains whilst the low molecular weight species are macrocycles. Hocker has shown that the relative proportions of high molecular weight to low molecular weight species are governed by an equilibrium the extent of which can be determined by the Stockmeyer equation.

Subsequent work by Amass and Zurimendi(64) has shown that the ratio of high to low molecular weight species, from the ring-opening polymerisation of cyclopentene using the catalyst system $WCl_6/Al(iBu)_3$, depends upon the extent of the metathesis reaction and approaches an equilibrium position within 24 hours. They also found that the ratio of high to low molecular weight species depends upon the ageing time of the catalyst components.

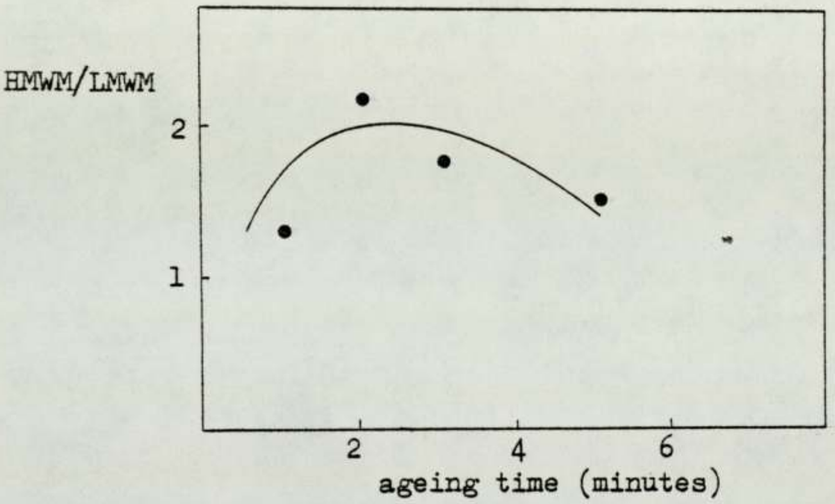
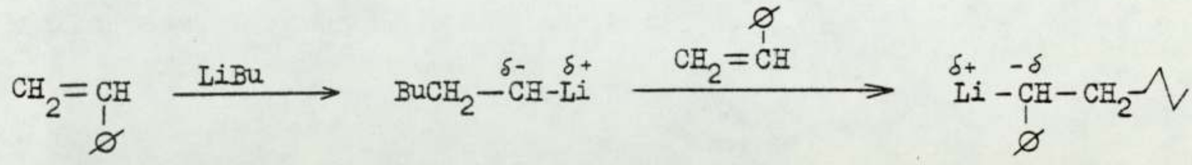


Fig. 4.6 Dependence of polymer composition on ageing time of catalyst.

The molecular weight distribution of polypentenamer obtained from the polymerisation of cyclopentene initiated by WCl_6/LiBu, is also bimodal and is typical of other polyalkenamers obtained from different monomer and catalyst systems.

4.2.2 Polystyryl Lithium Cocatalyst

The anionic polymerisation of styrene in cyclohexane can be initiated by lithium butyl to produce the living polymer polystyryl lithium.



The number average molecular weight of this living polymer is determined by the ratio of monomer to initiator concentrations.

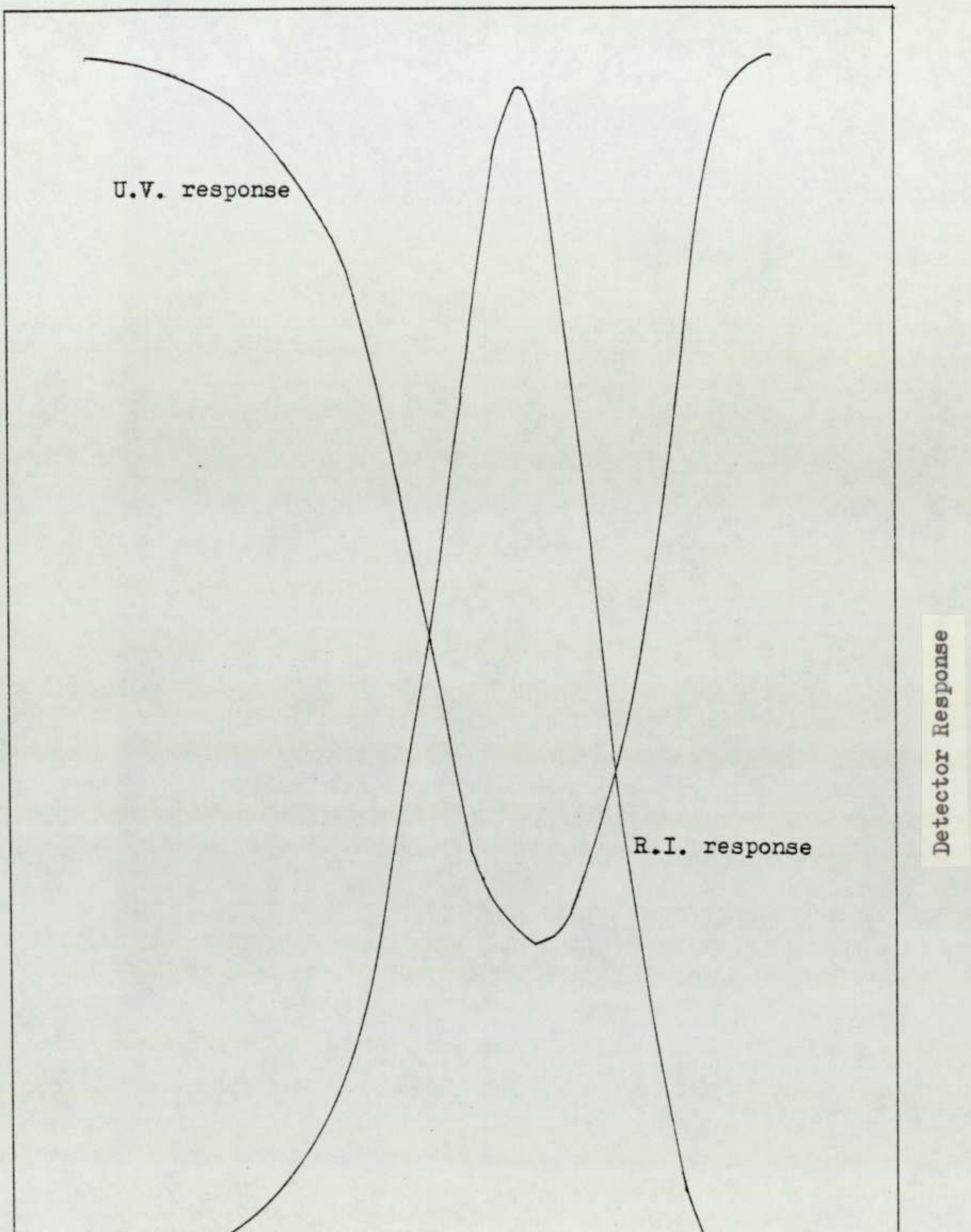
The preparation of the polystyryl lithium cocatalyst has been described in section 2.3.3. A small quantity of this polystyryl lithium cocatalyst was added to methanol and the precipitated polymer dissolved in THF and analyzed by gpc. The resulting UV and RI gpc chromatograms are shown in fig. 4.7.

The retention volume of the eluting polystyrene solution gave a polystyrene equivalent (and therefore a real molecular weight) molecular weight of about 8,000. The expected molecular weight of the polystyryl lithium cocatalyst, based on the relative amounts of styrene and lithium butyl initiator, was about 1,000. The discrepancy between the actual molecular weight (8,000) and the theoretical value (1,000) can be accounted for if some of the lithium butyl initiator was destroyed before it could initiate the anionic polymerisation of styrene.

4.2.3 Molecular Weight Distributions of the Copolymer Material

A typical copolymerisation reaction has been described in section 4.1.2. Samples of the polymerisate were collected after reaction times of 3, 7, 15, 30 and 60 minutes. These samples were added to

Fig. 4.7 Gpc chromatograms of polystyryl lithium



methanol and the precipitated polymer materials dissolved in THF and analyzed by dual detector gpc.

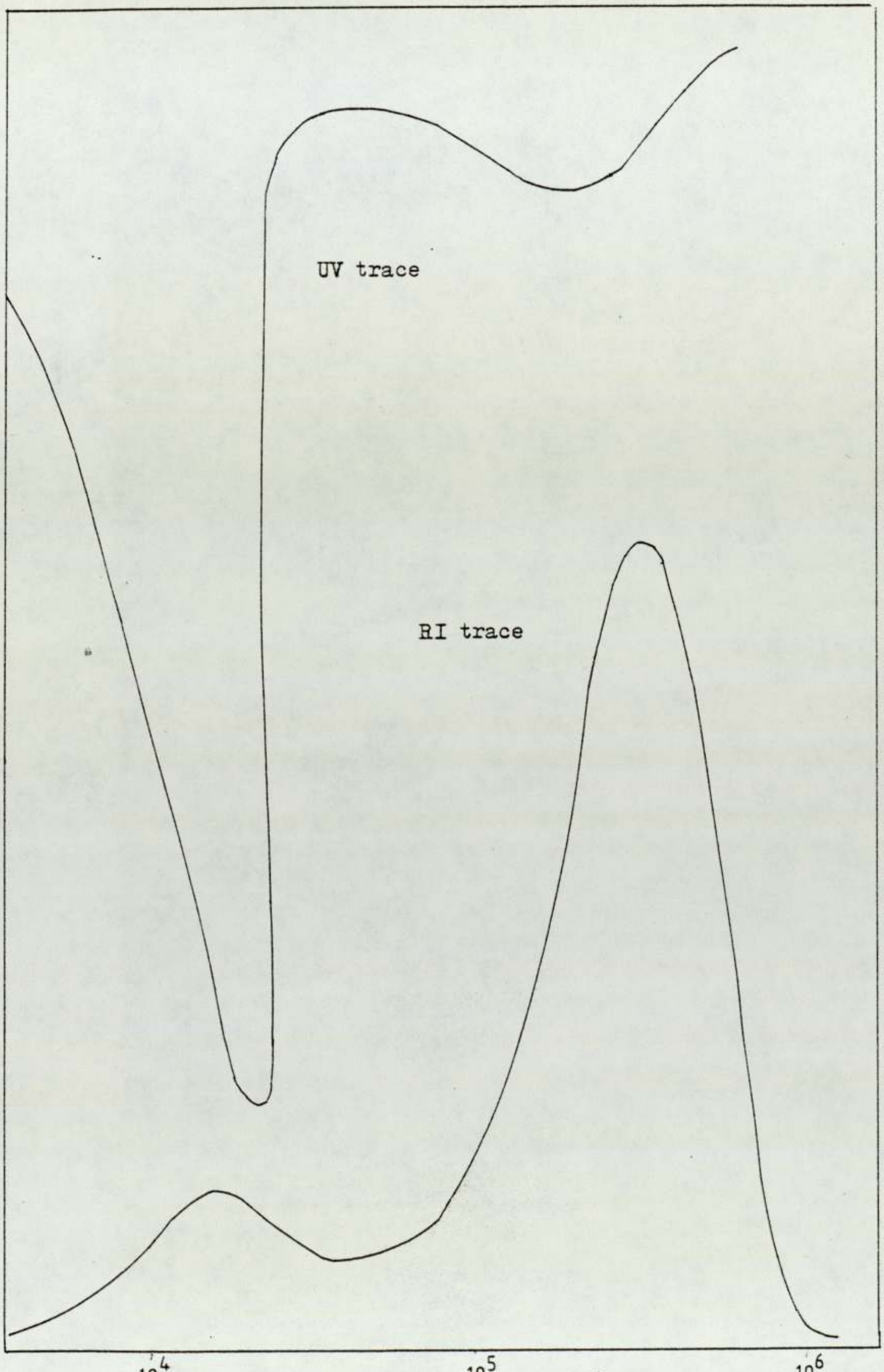
Typical UV and RI gpc traces obtained from the copolymer material (reaction time =3 minutes) are shown in fig. 4.8.

A comparison between the gpc chromatograms (UV traces) of both the copolymer material and the polystyrene blank obtained from the polystyryl lithium cocatalyst (figures 4.8 and 4.7 respectively) show that the copolymer material alone has a bimodal molecular weight distribution. The larger of the two peaks shown in fig. 4.8 (low molecular weight species) has a molecular weight which is approximately equal to that of the polystyrene blank obtained from polystyryl lithium. The other peak in fig. 4.8 (high molecular weight) has a molecular weight which is approximately equal to that of polypentenamer obtained during a normal ring-opening polymerisation reaction.

Since polypentenamer is transparent to UV light at 254 nm wavelength only the increase in the molecular weight of the polystyrene chain is shown in fig. 4.8. This increase in the molecular weight of the polystyrene chains suggests that the polystyryl lithium cocatalyst has, somehow, become attached to the growing polypentenamer chains formed during the copolymerisation reaction. The product of the copolymerisation reaction is therefore almost certainly some form of block copolymer i.e. poly(styrene-b-pentenamer).

The refractive index trace shown in fig. 4.8 also shows a bimodal molecular weight distribution, except the comparitive sizes of the two peaks are different to those of the UV response of the same

Fig. 4.8 Gpc traces (UV and RI) of copolymer material



copolymer material.

The high molecular weight peak is by far the largest of the two peaks and the molecular weight corresponds almost exactly with that of the high molecular weight peak shown in the UV trace in the same figure. The molecular weight of the small peak seen in the RI trace of fig. 4.8 also corresponds to that of the largest peak shown in the UV trace also shown in fig. 4.8.

Since the refractive indes response of the RI detector is proportional to the amount of polymer eluting past the detector, the response curve shown in fig. (RI trace) is mainly due to the polypentenamer fraction of the poly(styrene-b-pentenamer) copolymer.

4.2.4 Effect of Reaction Time on Copolymer Composition

A typical copolymerisation of cyclopentene catalysed by WCl_6/polystyryl lithium has been described in section 4.1.2. As the polymerisation reaction proceeded, samples of the polymerisate were removed (as outlined in section 2.4) at 3, 7, 15, 30 and 60 minutes reaction time. Each sample was added to methanol and the precipitated polymer dissolved in THF and analyzed by dual detector gpc.

Figure 4.9 shows a series of gpc traces (UV response) for a series of copolymer samples collected throughout a copolymerisation reaction (at an ageing time of 6 minutes). Since only the polystyrene content of the copolymer is displayed in these curves, the curves show how the polystyrene composition of the copolymer changes with reaction time.

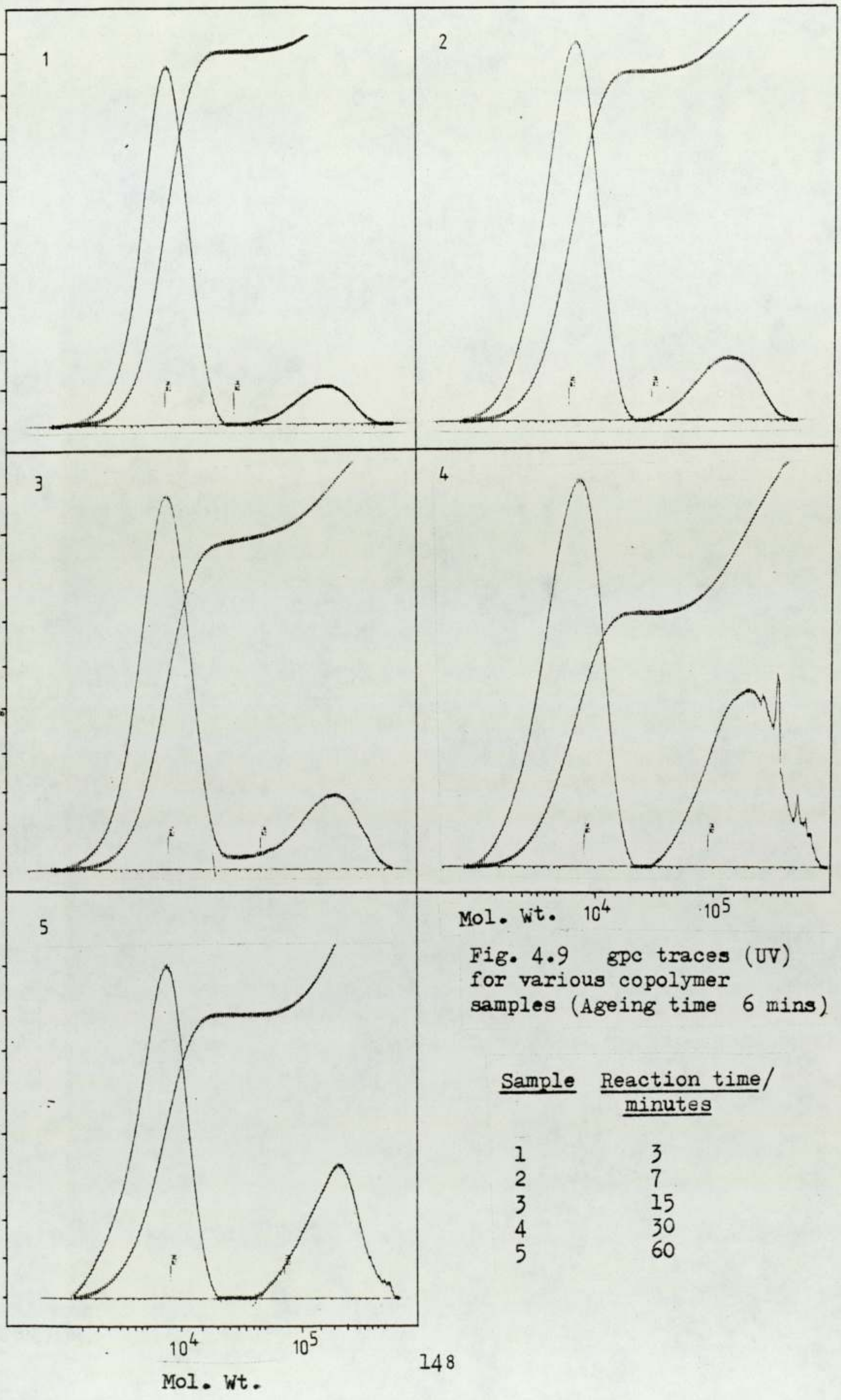


Fig. 4.9 gpc traces (UV) for various copolymer samples (Ageing time 6 mins)

Sample	Reaction time/ minutes
1	3
2	7
3	15
4	30
5	60

As the reaction proceeds the area of the high molecular weight peak steadily increases indicating that more of the low molecular weight polystyryl lithium was being incorporated into the copolymer and hence appears at much higher molecular weights. The rate of incorporation of the polystyryl block into the copolymer is more easily seen in fig. 4.10, where the percentage area of the high molecular weight fraction of the copolymer material is plotted against reaction time.

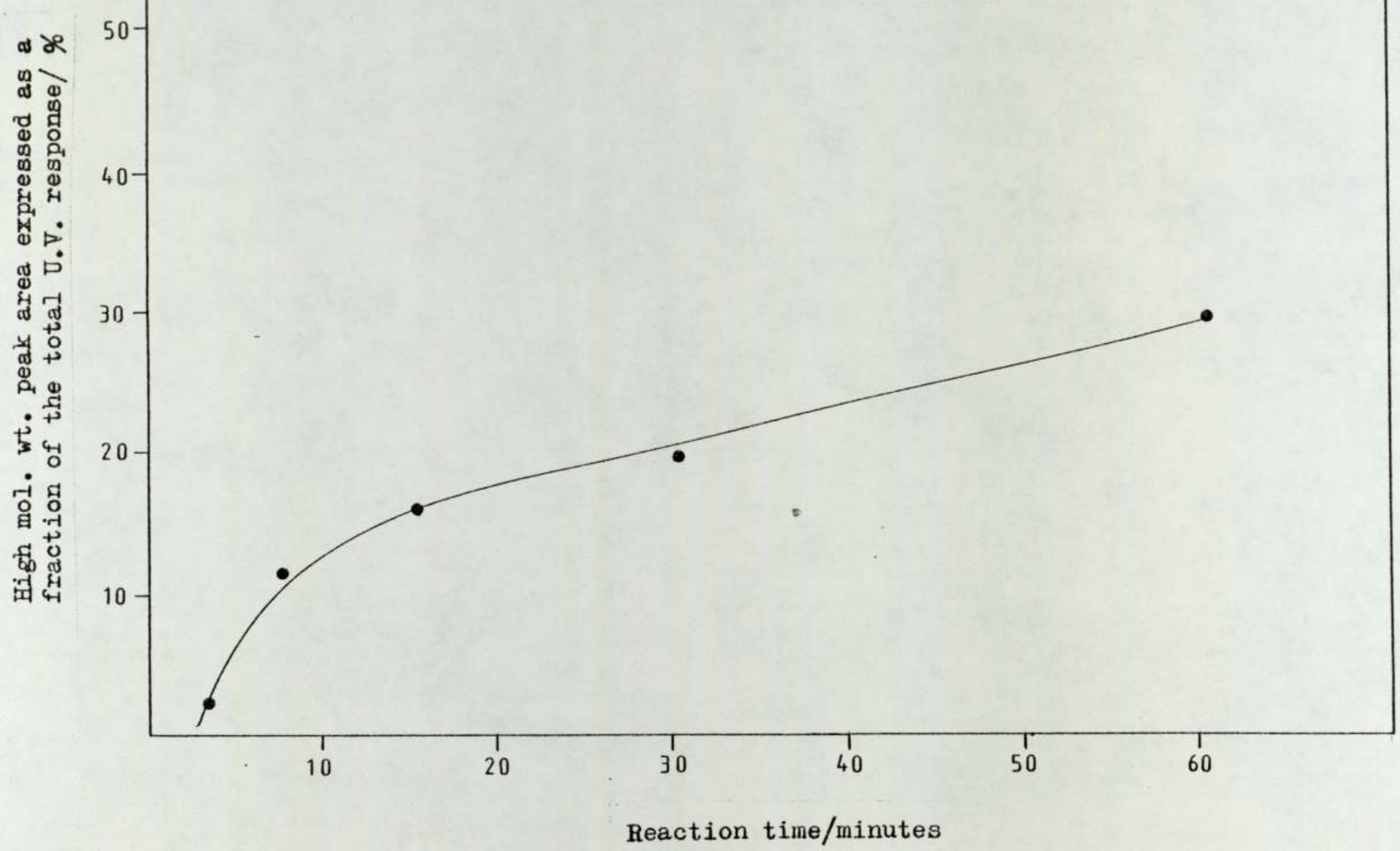
The shape of the curve shown in fig. 4.10 is very similar to the dilatometric curves obtained during the ring-opening polymerisation of cyclopentene catalysed by WCl_6/LiBu and is directly related to the rate of incorporation of the polystyryl lithium cocatalyst into the copolymer.

If the concentration of the polystyrene fraction of the the copolymer was known then it would be possible to obtain approximate values of the rate of incorporation of the cocatalyst into the copolymer and to compare these values with the values of the rate of polymerisation of cyclopentene catalysed by WCl_6/LiBu.

4.2.5 Effect of Ageing Time on Copolymer Composition

Many factors are known to effect the rate of cyclopentene polymerisation catalysed by WCl_6/LiBu, these factors include: (i) the monomer: catalyst ratio, (ii) the catalyst: cocatalyst ratio, and (iii) the ageing time of the monomer/catalyst solution before the addition of the cocatalyst. These factors may also effect the nature of the copolymer composition and so led to an investigation of both the effect of ageing time and also catalyst: cocatalyst ratio on the copolymer composition.

Fig. 4.10 Plot of percentage area of the high molecular weight peak against reaction time (ageing time=2 mins.)



Ageing time.

A typical copolymerisation reaction has been outlined in section 4.1.2. After the addition of the catalyst to the monomer solution there was a time delay (ageing time) before the polystyryl lithium cocatalyst was added to the reaction mixture. Samples of the polymerisate were collected at 3, 7, 15, 30 and 60 minutes reaction time and treated as described earlier. The ageing times studied were 2, 4, 6, 8 and 15 minutes.

The increase in high molecular weight polystyrene content of the copolymer against reaction time, for a series of different ageing times is shown in fig. 4.11.

The similarity between the shapes of these copolymer composition curves and those obtained from dilatometric studies of the ring-opening polymerisation of cyclopentene has already been noted. It can readily be seen that, in all cases, there is a steady increase in the amount of polystyrene incorporated into the block copolymer as the copolymerisation reaction proceeds. Also, the proportion of polystyrene incorporated into the copolymer increases with increasing ageing time.

4.2.6 Effect of the W:Li Ratio on the Copolymer Composition

The W:Li ratio of the catalyst system WCl_6/LiBu is known to dramatically effect both the metathesis of linear olefins and the ring-opening polymerisation of cyclopentene. Whilst the W:Li molar ratio effects the rate of metathesis it is not known if this ratio would also effect the copolymerisation reaction, particularly the copolymer

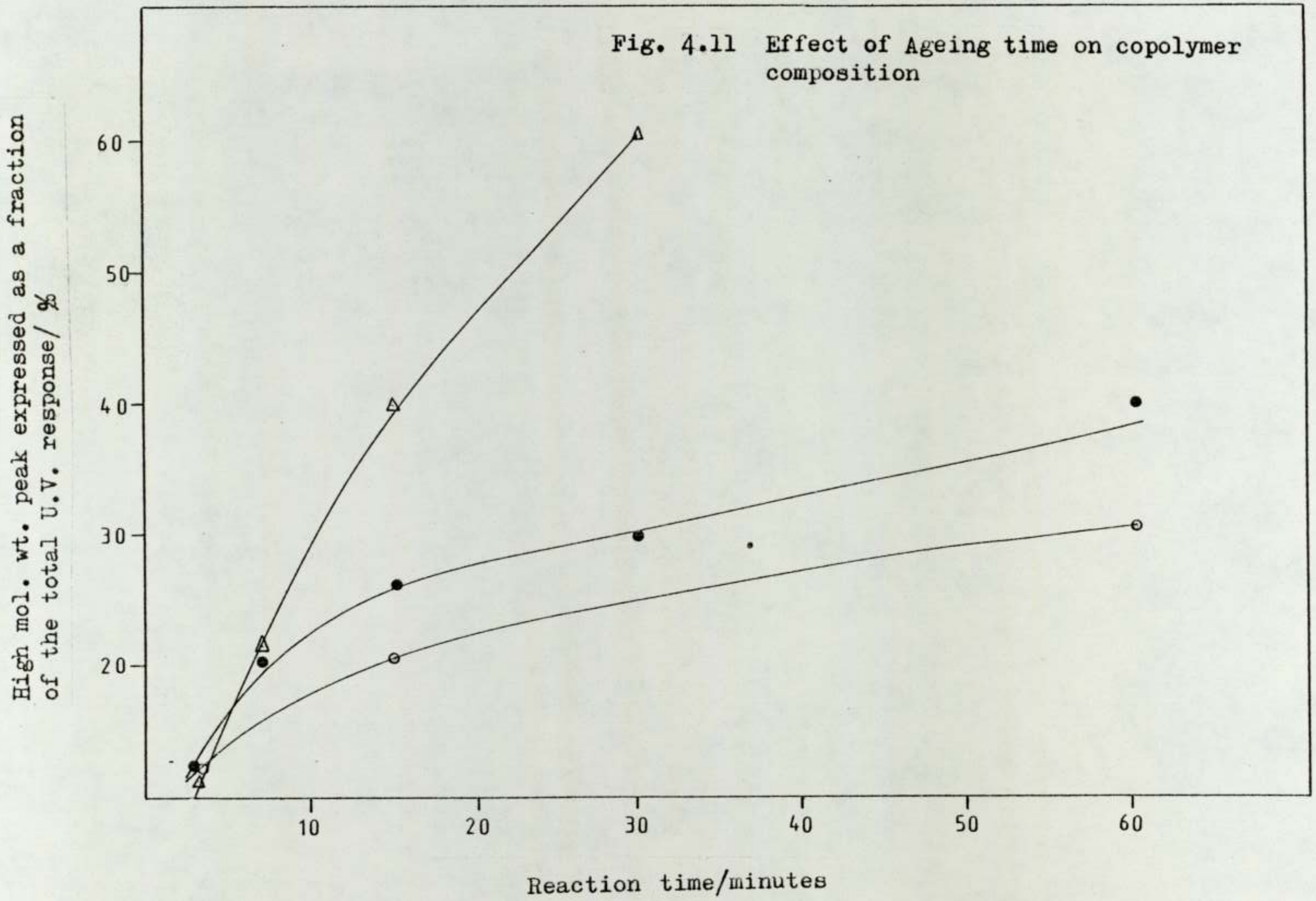


Fig. 4.11 Effect of Ageing time on copolymer composition

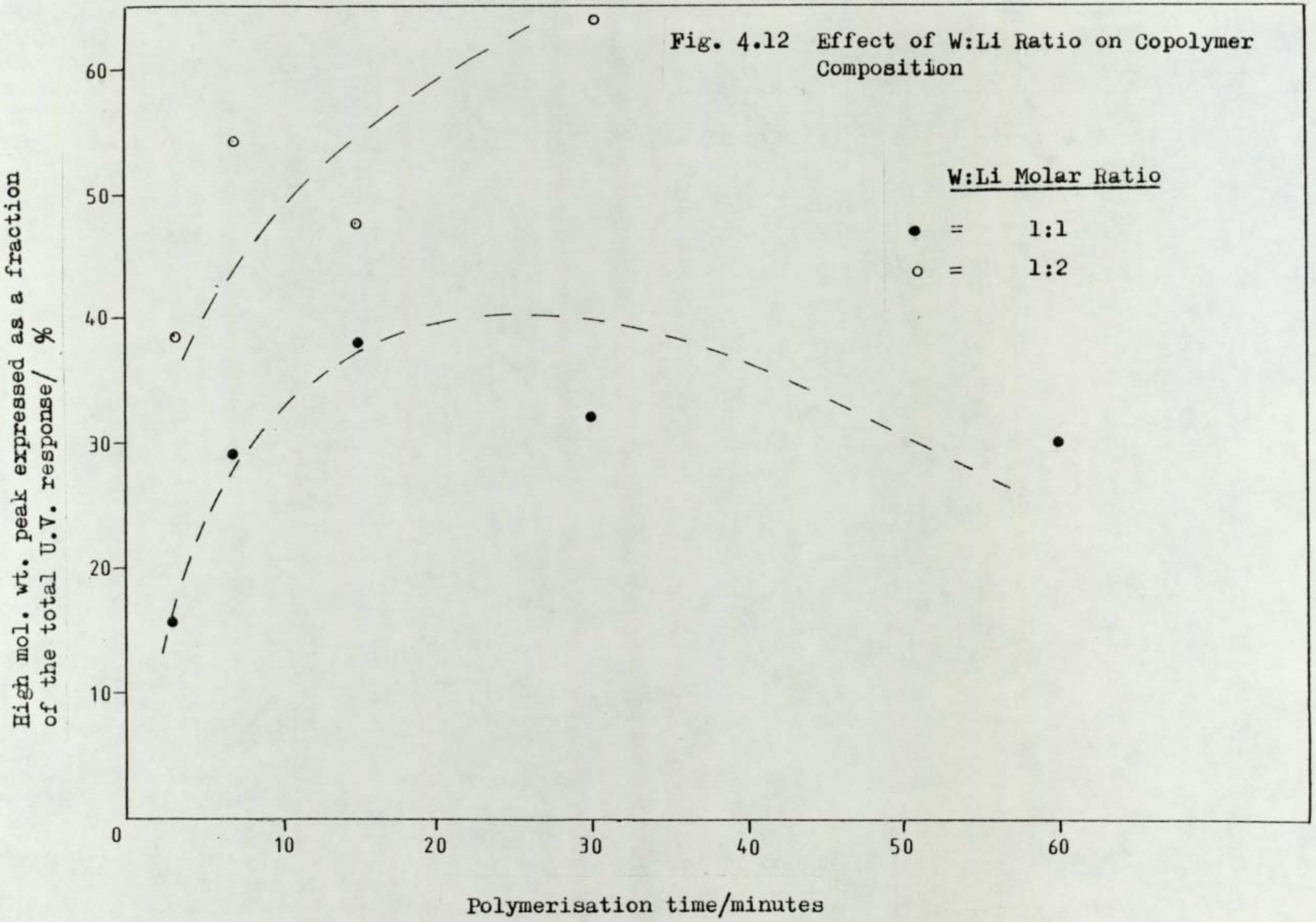


Fig. 4.12 Effect of W:Li Ratio on Copolymer Composition

composition.

A typical copolymerisation reaction has been outlined in section 4.1.2. The monomer and tungsten ratios were maintained approximately constant at 1000:1 and the amount of polystyryl lithium varied to produce the required W:Li molar ratio. The W:Li ratios studied were 1:1, 1:2, 1:3 and 1:4, the monomer concentration was approximately 2.50 mol. dm^{-3}.

Figure 4.12 shows the change in the percentage area of the high molecular weight peak with reaction time for two different W:Li ratios, after an ageing time of 4 minutes - the curves shown are obtained from the UV detector of the gpc equipment. An ageing time of 4 minutes was chosen to be the optimum value because of the difficulty in transferring the viscous polystyryl lithium solution by syringe to the reaction vessel.

Unfortunately,the points do not fall on any simple curve and so no general conclusion can be reached concerning the incorporation of polystyrene into the copolymer for a particular W:Li ratio. It is obvious however that the amount of polystyrene present in the copolymer is greater for a W:Li ratio of 1:2 than for a W:Li ratio of 1:1. These results are analogous to those obtained by Wang and Menapace and also those results reported in this thesis, namely that the efficiency of the WCl_6/LiBu catalyst system is a maximum at a W:Li ratio of 1:2.

4.2.7 Dilatometric Studies on the Copolymerisation Reaction

Previous studies on the copolymerisation system CP/WCl_6/polystyryl lithium have primarily been concerned with demonstrating that block copolymers are formed during the reaction and how a variety of experimental variables influence the synthesis of these copolymers. It is, however, possible to study the polymerisation reaction dilatometrically and hence obtain information concerning the rate of incorporation of the polystyryl lithium cocatalyst into the copolymer. The experimental details have previously been outlined in chapter 2, section 2.4.5.

Figure 4.13 shows the change in height of the meniscus held in the capillary tube of the dilatometer with time for a series of copolymerisation reactions at different ageing times. The curves suggest that the greater rate of polymerisation occurs at an ageing time of 6 minutes.

The results obtained dilatometrically are not in accord with those obtained during the ring-opening polymerisation of cyclopentene by the catalyst system WCl_6/LiBu. In the latter experiments, the greatest rate of polymeriastion (at a reaction time of 4 minutes) occurred at an ageing time of 2 minutes.

This discrepancy between the two polymerisation systems probably represents the slower build up in concentration of the metathetically active species within the copolymerisation reaction. This most likely arises from steric effects because of the large size of the polystyryl chain attached to the lithium atom.

The copolymers obtained during these dilatometric studies were analyzed by gpc and the results obtained are illustrated in fig. 4.14 where the size of the UV response to the high molecular weight

Fig. 4.13 Effect of Ageing Time on the Rate of Polymerisation of the Copolymerisation Reaction.

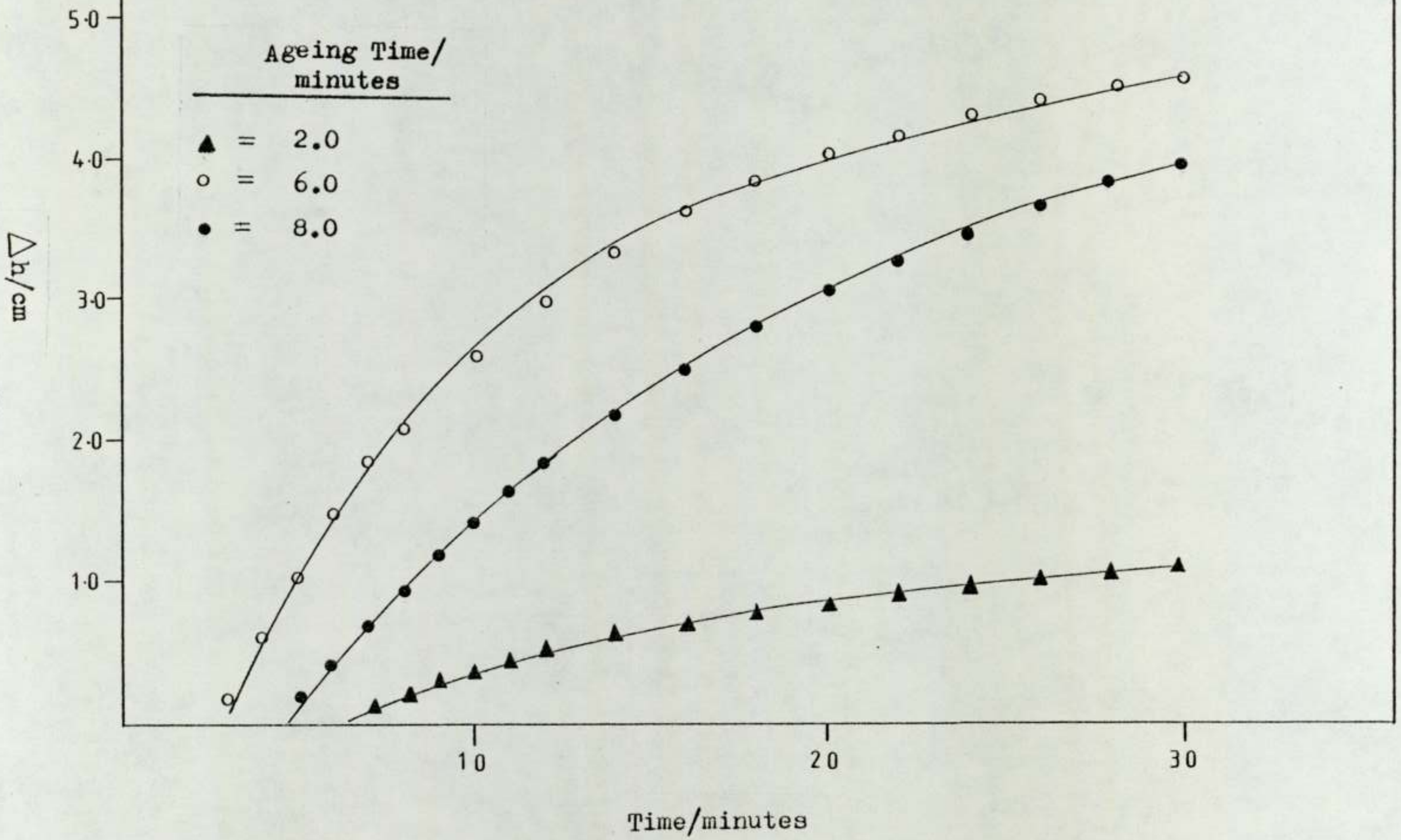
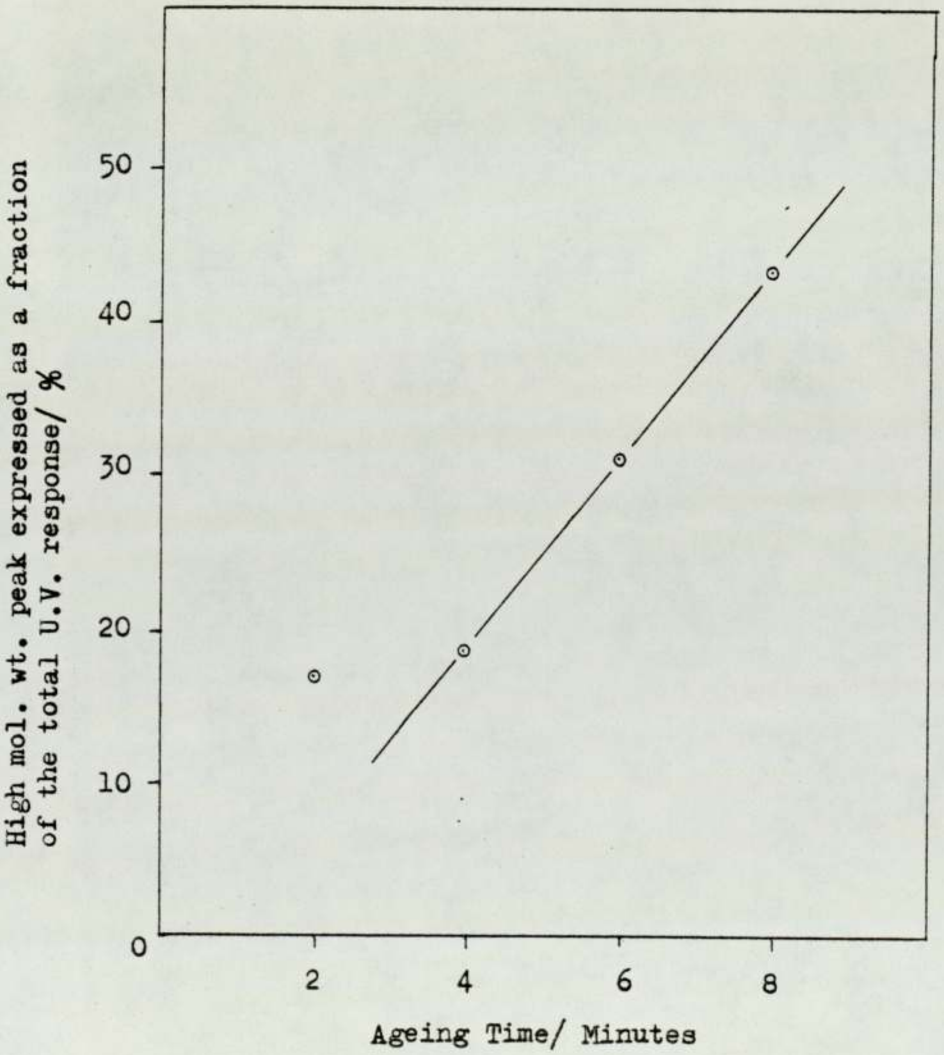


Fig. 4.14 A Plot of Copolymer Composition against Ageing Time for the Dilatometry Samples



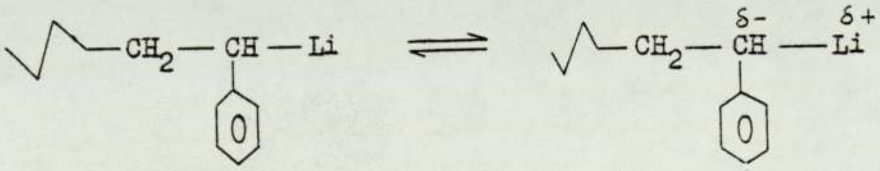
polymer is plotted against ageing time.

Since the UV response only measures the amount of polystyrene incorporated into the copolymer, this curve reflects the increase in the amount of polystyrene incorporated into the copolymer with ageing time. Why there is a steady increase in the polystyrene content of the copolymer with ageing time is unknown?

4.3 Catalyst Studies

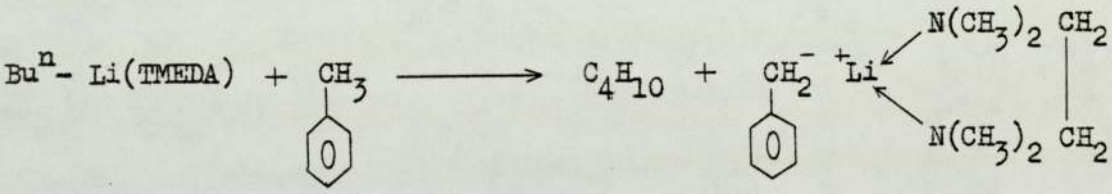
Whilst studies of the metathetic ring-opening polymerisation of cyclopentene using the catalyst system WCl_6/polystyryl lithium show that the cocatalyst plays a direct role in the metathesis reaction, the nature of this role has sc far been unclear. For example, does the cocatalyst become incorporated into the copolymer by some form of polar or non-polar mechanism?

It is well known that both the solvent and gegen-ion have a pronounced influence on the rate of anionic polymerisation reactions and hence they may also exert a similar effect on the copolymerisation reaction. Early experiments using the polystyryl lithium cocatalyst were conducted in a non-polar solvent i.e. cyclohexane. In such non-polar solvents the carbon-lithium bond can be described as a partially polarised covalent bond.

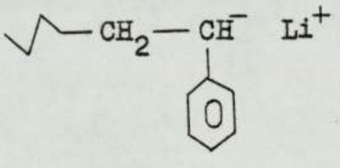


There are two principal techniques usually used to change the polarity of the carbon-lithium bond; i) change the reaction medium to a more polar one i.e. use a more polar solvent or ii) change the gegen ion to engender the production of free-ion pairs. Since it is well known that polar environments adversely effect metathesis reactions the latter technique was preferred during later experiments.

The nucleophilic character of carbon directly bonded to lithium appears to increase when the lithium is coordinated to a base. For example, the n-butyl lithium chelate complex with tetramethylethylenediamine (TMEDA) is a particular powerful metalating agent and at room temperature metalates toluene to give the TMEDA complex of benzyllithium.



The benzyl anion thus produced can be considered to be a model for a polystyryl anion i.e.



A solution of the benzyl anion ($1{\cdot}96 \times 10^{-1}$ mol. dm^{-3}) was prepared by the addition of butyl lithium and TMEDA (1:1 molar ratio) to toluene (as outlined in section 2.3.4). This solution was then used as a cocatalyst in a series of metathetic ring-opening polymerisation reactions. Typical reaction conditions studied were tungsten: monomer ratio 1:1000, tungsten to lithium ratio 1:2 and an ageing time of 2 minutes - further experimental details are given in section 2.4.4.1.

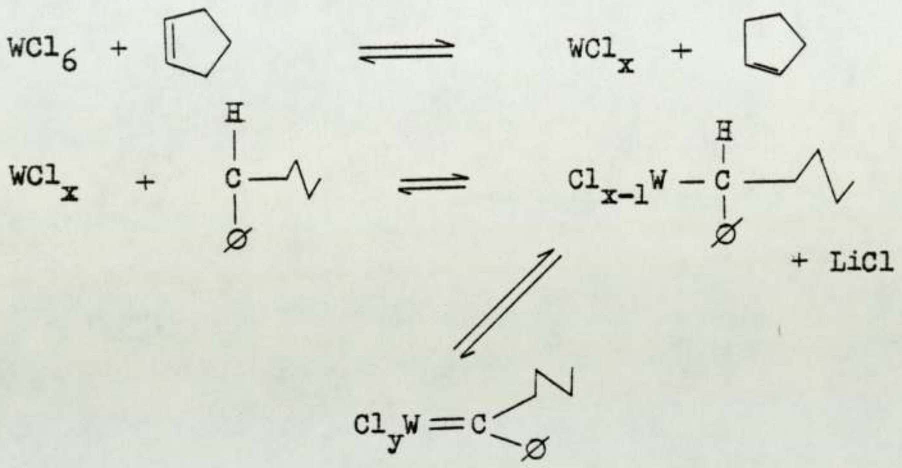
In all the reactions performed there was no observable reaction when the cocatalyst was added to a solution of the monomer and tungsten hexachloride catalyst. In all cases no product was obtained when the reaction solution was added to methanol.

These results suggest that either the TMEDA is interfering with the formation of a catalytically active species - probably by coordinating directly with the tungsten hexachloride - or alternatively, the free-ion pairs present in the cocatalyst are not capable themselves of initiating the production of the catalytically active species.

4.3.1. Alkyl Group Migration Studies

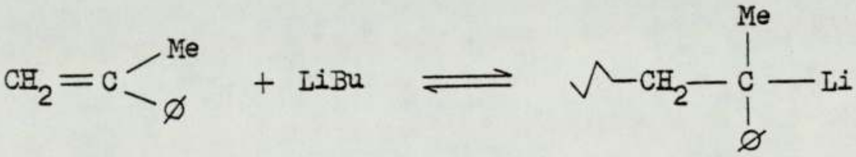
The olefin metathesis reaction and the ring-opening polymerisation of cyclo-olefins have almost unequivacally been shown to proceed by a metallocarbene -metallocyclobutane intermediate. The formation of the initial metallocarbene still remains a mystery for many catalyst systems though the metallocarbene has been envisaged to occur by an α - hydrogen elimination reaction in catalyst systems containing metal alkyl cocatalyst.

The generation of the metallocarbene from the catalyst system WCl_6/ polystyryl lithium/ cyclopentene may then be written thus:



That such α hydrogen elimination reactions are responsible for the generation of the initial metallocarbene from the catalyst system WCl_6/ polystyryl lithium may be investigated by using a substituted polystyryl chain as a cocatalyst, such a cocatalyst would not be able to undergo such hydrogen elimination reactions.

α methyl styrene may be anionically polymerised by lithium butyl to produce poly α methylstyryl lithium.



The resulting substituted polystyryl lithium may then be used as a cocatalyst in the copolymerisation reactions previously studied.

Such experiments have been performed (as previously described in section 2.4.4.2) and in all cases no ring-opening polymerisation reaction has been observed. The addition of the poly α methylstyryl-lithium to a solution of WCl_6/cyclopentene does not give a solution with the characteristic reddish-brown colour of a normal polymerisation reaction and the solution does not become viscous even after 6 days reaction. The products of any reaction do not reveal the presence of any copolymer.

4.4 NORBORNENE POLYMERISATION STUDIES

4.4.1 Introduction

Studies on the ring-opening polymerisation of cyclopentene catalysed system WCl_6/PStLi have revealed the viability of obtaining block copolymers from metathetic transformation reactions. It was the purpose of investigating the polymerisation of norbornene to extend these copolymerisation studies, but first it was necessary to study the norbornene polymerisation reaction.

Norbornene is known to undergo a metathesis like ring-opening polymerisation reaction under very mild conditions and was therefore considered to be an ideal monomer to continue these studies on the metathetic transformation reaction.

4.4.2 The Ring-Opening Polymerisation of Norbornene

Initial studies on the ring-opening polymerisation of norbornene have shown that the reaction may be catalysed by WCl_6 alone, as described in section 2.4.4.3. The monomer concentration was maintained constant at about 1.1 mol. dm^{-3} and the amount of tungsten hexachloride catalyst (2.94×10^{-2} mol. dm^{-3}) varied to produce a tungsten to monomer ratio of $1:10^3$, $1:2 \times 10^3$, $1:4 \times 10^3$ and $1:10^4$.

On the addition of the catalyst to the norbornene solution, the mixture turns a characteristic reddish-brown (typical of a metathesis polymerisation reaction) and the solution becomes very viscous and gel-like within one minute.

The polymers obtained from these reactions were precipitated in methanol, dissolved in chloroform, reprecipitated in methanol and the polymer dried overnight in a vaccum oven at 25°C. The yields of the polymer have been recorded in table 4.1 .

Table 4.1 Norbornene polymerisation studies at various monomer to catalyst ratios

Monomer: Catalyst ratios	Monomer Conc^n mol. dm^{-3}	Yield of Polymer/ %
$10^3:1$	1.42	74.5
$2 \times 10^3:1$	0.95	63.0
$4 \times 10^3:1$	1.13	1.6
$10^4:1$	1.39	1.3

At low monomer to catalyst ratios the amount of polymer obtained is very high i.e. greater than 50%, but by increasing the monomer to tungsten ratio the yield of polymer obtained rapidly falls off to very low values. These results however neglect the wide variation in the monomer concentration and this may well have a pronounced effect on the yields of polymer recorded.

4.4.3 The effect of the W:Li ratio on the Polymerisation of Norbornene

Since the reaction between the monomer and the tungsten hexachloride catalyst is extremely rapid, it is not possible to add the cocatalyst to the polymerising solution (monomer plus catalyst) before it had gelled. The cocatalyst (lithium butyl) was therefore added to the norbornene prior to the addition of the tungsten hexachloride catalyst.

During these experiments the W:Li ratio was varied whilst keeping the monomer concentration constant at about 1.1 mol. dm^{-3},; The W:Li ratio vas varied between 1:1. 1:2, 1:3 and 1:4 whilst the monomer to tungsten ratio was maintained at 1000:1.

The polymers obtained during these polymerisation reactions were precipitated from methanol, dissolved in chloroform and reprecipitated from methanol, and then dried overnight in a vacuum oven at 25°C. The yields of the polymers obtained during these experiments are displayed in table 4.2 .

The results shown suggest that the most efficient catalyst system is obtained with a W:Li molar ratio of 1:2 which is comparable to the kinetic results obtained from the ring-opening polymerisation of

Table 4.2 Yield of Polynorbornene obtained with different W:Li molar ratios

Tungsten: Lithium molar ratio	Yield of Polymer/ %
1:1	13.0
1:2	41.2
1:3	37.5
1:4	33.3

cyclopentene catalysed by the WCl_6/LiBu catalyst system. It seems therefore that the polymerisation of norbornene is comparable to that of cyclopentene when the reaction is catalysed by the WCl_6/LiBu catalyst system. Unfortunately, it was not possible to extend these polymerisation studies to the WCl_6/PStLi catalyst system because of time limitations, but it seems very likely that such studies should prove to be informative and that new types of copolymers would be obtained.

CHAPTER 5

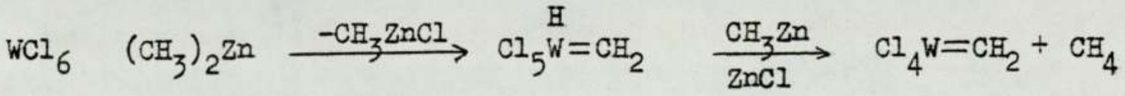
DISCUSSION

5.1 INTRODUCTION

Perhaps one of the greatest challenges to our understanding of the olefin metathesis reaction is that of the precise role played by the catalyst and/or cocatalyst in the metathesis reaction. It is clear from the work of Katz, Grubbs and others(77,91), that the reaction is propagated by some form of metallocarbene/metallocyclobutane intermediate though how these species are formed during the initial stages of the olefin metathesis reaction remains uncertain for most catalyst systems.

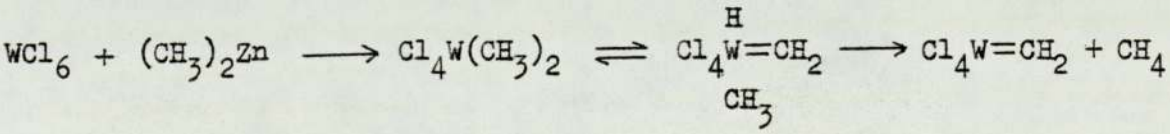
Most studies on the synthesis of the initiating metallocarbene have been primarily concerned with the nature of the transition metal catalyst and its ligands, and have tended to relegate the importance of both the reactant olefin and the cocatalyst as components necessary to promote the generation of the metallocarbene/metallocyclobutane initiating species.

Recent studies have however suggested that the cocatalyst may provide an important role in the metathesis reaction by providing a means to generate a metal-carbon double bond.



$$WCl_6 \quad (CH_3)_2Zn \xrightarrow{-CH_3ZnCl} Cl_5\overset{H}{W}{=}CH_2 \quad \xrightarrow[ZnCl]{CH_3Zn} Cl_4W{=}CH_2 + CH_4$$

or



$$WCl_6 + (CH_3)_2Zn \longrightarrow Cl_4W(CH_3)_2 \rightleftharpoons Cl_4\underset{CH_3}{\overset{H}{W}}{=}CH_2 \longrightarrow Cl_4W{=}CH_2 + CH_4$$

Although such studies provide a partial understanding of the generation of a metallocarbene capable of initiating metathesis, they have so far ignored the role played by the olefin during the formation of such metallocarbene intermediates. There is considerable evidence that suggests that the olefin also plays a significant part in the generation of the metallocarbene during a metathesis reaction.

For example, it is well known that some catalyst/cocatalyst mixtures when prepared in the absence of olefins are not active towards metathesis although they can exhibit metathetic activity when prepared in the presence of an olefin. An example of such is the catalyst system $WCl_6/Al(iBu)_3$ which has been reported to be inactive towards metathesis when the catalyst components are premixed prior to their addition to cyclopentene. If the cocatalyst is added to a mixture of cyclopentene/tungsten hexachloride then an active ring-opening polymerisation reaction ensues.

Alternatively, some catalyst/cocatalyst mixtures seem to exhibit metathetic activity whether they are added sequentially to the olefin or premixed prior to their addition to the olefin. An example of this type of catalyst system (WCl_6/LiBu) has been reported in this thesis.

Since many types of catalyst system seem to show metathetic activity only when prepared in the presence of the olefin (e.g. $WCl_6/Al(iBu)_3$) it is probable to assume that the olefin is directing the course of the 'catalyst reactions' to produce metathetically active species. Similarly, it must not be assumed that since some catalysts exhibit metathetic activity when premixed prior to their addition to the olefin, that such systems are generating a metallocarbene capable of producing metathesis before they are added to the olefin.

One of the primary objectives of the work reported in this thesis is to provide a clearer understanding of the roles played by all the reaction components in a metathesis reaction - in particular, the ring-opening polymerisation of cyclopentene. The initial experiments were designed to yield quantitative data on the kinetics of the ring-opening polymerisation of cyclopentene catalysed by both the unmixed and premixed WCl_6/LiBu catalyst system. Unfortunately during the course of the ring-opening polymerisation reaction a precipitate forms and, if the precipitate is a source of active species, complicates the kinetic analysis of the polymerisation reaction.

There is also substantial indirect evidence to suggest that this precipitate is, in some unknown way, responsible for the rapid decrease in the rate of cyclopentene polymerisation. Since the amount of precipitate produced, and hence its surface area, cannot be controlled in a precise manner, it is not possible to give a precise mathematical description of the concentrations of the metathetically active species.

These problems can to some extent be overcome by comparing and contrasting the rate of polymerisation of cyclopentene which is catalysed by both the unmixed and premixed WCl_6/LiBu catalyst system with that of cyclopentene catalysed by $WCl_6/Al(iBu)_3$. Since the polymerisation reaction initiated by $WCl_6/Al(iBu)_3$ is much cleaner than that produced by WCl_6/LiBu, it is much more amenable to kinetic analysis and so can provide a starting point from which the ring-opening polymerisation of cyclopentene catalysed by WCl_6/LiBu can be understood.

5.2 CATALYST STUDIES

5.2.1 Comparison between various Catalyst Systems

Analysis of the dilatometric curves (fig. 3.1 and fig. 3.8) obtained from the ring-opening polymerisation of cyclopentene catalysed by the unmixed and premixed WCl_6/LiBu catalyst system show that both catalyst systems exhibit similar behaviour. Both sets of curves show a rapid initial rate of polymerisation which subsides to a very slow rate within about 20 - 30 minutes at low monomer and catalyst concentrations (i.e. $[Cp] = 2{\cdot}50$ mol. dm^{-3} and Cp:W = 2000:1).

Apart from producing similar polymerisation characteristics, both types of catalyst system (unmixed and premixed) seem to be influenced in similar ways by a variety of reaction conditions.

After a reaction time of 4 minutes the rate of polymerisation reaction catalysed by both the unmixed and premixed catalyst system shows a maximum at (i) an ageing time or premix ageing time of 2·0 minutes, and (ii) a catalyst to cocatalyst molar ratio of 1:2. Under similar reaction conditions the magnitude of the rates of cyclopentene polymerisation are vary similar, as can be seen from table 5.1.

Table 5.1 Maximum rate of polymerisation for various reaction conditions

Reaction Variable	Value	Rp (max) mol. dm^{-3} s^{-1}
Ageing Time	2·0 mins	4.2×10^{-4}
Premix Ageing Time*	2.0 mins	5.0×10^{-3}
W:Li (unmixed)	1:2	4.8×10^{-4}
W:Li (premixed)	1:2	6.2×10^{-4}

* This value was obtained using a high initial monomer concentration (3.95 mol. dm^{-3} - the other results quoted are obtained from experiments using a 2.50 mol. dm^{-3} monomer solution) and hence the rate of polymerisation is correspondingly larger.

The similarity between the rates of polymerisation of cyclopentene when catalysed by both the unmixed and premixed catalyst systems suggests that the reaction is being initiated (and propagated) by similar active species or by different active species possessing similar kinetic properties. If the former hypothesis is correct, then the species formed during the action of the premixed catalyst system with the monomer solution (shown below) must be similar to that produced by the unmixed catalyst system.

$$WCl_6 + LiBu \longrightarrow X \qquad (5.1)$$

$$X + Cp \longrightarrow \text{Active species (A)} \qquad (5.2)$$

and

$$Cp + WCl_6 + LiBu \longrightarrow \text{Active species (A')} \qquad (5.3)$$

Where A and A' may be similar species or just simply possess similar activities.

If A is very similar to A' then the olefin is an important reactant necessary to promote the generation of the active species and not simply a reagent consumed by the polymerisation reaction.

This result apparently contradicts the hypothesis by Dolgoplosk et al

(94) who have suggested that a metallocarbene may be generated directly from the WCl_6/LiBu catalyst system, as shown below.

$$WCl_6 + 2LiBu \longrightarrow Cl_4W.Bu_2 + 2LiCl$$

$$Cl_4W.Bu_2 \longrightarrow Cl_4W{=}CH.CH_2CH_2CH_3 + BuH \qquad (5.4)$$

The formation of the metallocarbene in equation 5.4 arises from a alpha hydrogen migration form one butyl chain to the other. The occassional formation of gas bubbles during the preparation of the premixed catalyst system (WCl_6/LiBu) lends credence to these ideas.

It is possible that the precipitate observed during polymerisation reactions catalysed by both the premixed and unmixed catalyst system arises from the reduction of the tungsten hexachloride catalyst by the cocatalyst to a variety of insoluble tungsten species.

5.2.1.1 Kinetic Studies of the Polymerisation of Cyclopentene

Dilatometric studies on the polymerisation system Cp/WCl_6/$Al(iBu)_3$ have led Amass and Tuck(28) to suggest that the complex kinetic behaviour of this system could be explained by a simple series of reactions.

$$WCl_6 + Cp \xrightarrow{K_1} W^{*} \xrightarrow{Al(iBu)_3} W^{*}/Al \quad \text{(active species)} \qquad (5.5)$$

$$W + Cp \xrightarrow{K_2} W^{**} \xrightarrow{Al(iBu)_3} \overset{*}{W}{}^{*}/Al \quad \text{(unknown activity)} \qquad (5.6)$$

Analysis of the concentrations of the active species led to equation 5.7 which relate t_{max} to the reciprocal monomer concentration.

$$t_{max} = \frac{1}{[Cp]o} \cdot \frac{1}{(k_1 - k_2)} \cdot \ln\left(\frac{k_1}{k_2}\right) \qquad (5.7)$$

Where t_{max} = Ageing time of WCl_6/Cp to produce a maximum rate of polymerisation

Because of the similarity between the polymerisation of cyclopentene catalysed by either $WCl_6/Al(iBu)_3$ and WCl_6/LiBu (unmixed) it is probable that a similar sequence of reactions may explain some of the kinetic aspects of the ring-opening polymerisation of cyclopentene catalysed by the latter catalyst system, i.e.

$$WCl_6 + Cp \xrightarrow{k_1} W^* \xrightarrow{LiBu} W^*/Li \quad \text{(active species)} \qquad (5.8)$$

$$W^* + Cp \xrightarrow{k_2} W^{**} \xrightarrow{LiBu} W^{**}/Li \quad \text{(unknown activity)} \qquad (5.9)$$

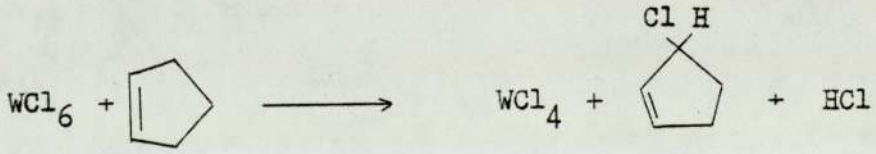
According to these equations the addition of the transition metal catalyst to the monomer produces an active species W^*. These active species are consumed in equation 5.9 to produce a second species which may or may not exhibit metathetic activity. The concentrations of these active species is governed by the relative rate constants k_1 and k_2 and is a maximum after an ageing time t_{mix}. This ageing time is approximately 2.0 minutes for both the $Cp/WCl_6/Al(iBu)_3$ and Cp/WCl_6/LiBu reaction systems. The similarity between the ageing times for both reaction systems implies that the concentrations of the active species are governed by similiar kinetic equations and hence probably similar chemistry. This is almost certainly the case since the first stage of of the polymerisation reaction i.e. the addition of WCl_6 to the monomer solution - is the same for both systems.

5.2.1.2 Catalyst to Cocatalyst Ratios

Whilst Amass and Tuck(28) successfully accounted for the effect of the monomer/catalyst ageing time on the initial rate of polymerisation of cyclopentene catalysed by $WCl_6/Al(iBu)_3$, they were unable to explain other equally important features of the polymerisation reaction, notably the dependence of the rate of polymerisation on the catalyst to cocatalyst ratio.

Further studies have however suggested that it may be possible to explain the dependence of the initial rate of polymerisation on the catalyst to cocatalyst ratio if it is assumed that the production of a metathetically active species is a two stage process.

The reaction between tungsten hexachloride and cyclopentene has recently been shown in these laboratories(145) to produce halogenated cyclopentenes; the reaction has been envisaged to occur as follows:



This reaction shall be considered in more detail in section 5.4.1.

The hydrogen chloride liberated during this reaction (equation 5.7) reacts with one mole of the cocatalyst thus:

$$HCl + Al(iBu)_3 \longrightarrow ClAl(iBu)_2 + BuH \quad \text{or}$$

$$HCl + LiBu \longrightarrow LiCl + BuH$$

both equations producing butane gas.

The quantity of butane gas formed during a typical polymerisation reaction (Cp:W:Al or Li = 2000:1:2; $[Cp] = 2{\cdot}50$ mol. dm^{-3}) is only about $0{\cdot}8$ cm^3 at STP. This amount of gas would probably dissolve in the solvent (toluene) and would therefore be exceedingly difficult to observe under normal reaction conditions.

The second stage of the reaction would then involve the synthesis of the initiating metallocarbene intermediate from the reduced WCl_6 species (i.e. WCl_4) and the remaining cocatalyst. This second reaction (below) is believed to require only one mole of catalyst per mole of WCl_4, and shall be considered in greater detail in section 5.4.1.

$$WCl_4 + Cp \xrightarrow{LiBu} Cl_4W = CH —$$

If both of these hypotheses are correct, then the maximum concentration of the initiating metallocarbene is attained at a catalyst to cocatalyst ratio of 1:2. Unfortunately, this result is only correct if the rates of the initiating reactions (equations 5.7, 5.8 and 5.9) are very rapid so that the final concentration of the metallocarbene is governed by the concentrations of the catalyst and cocatalyst and not by the rate of formation of any of the reaction intermediates.

Since the rate of polymerisation of cyclopentene is a maximum for a W:Li molar ratio of 1:2 only after a few minutes reaction time, the relative rates of equations 5.7 and 5.8 are important in understanding the mechanisms of the polymerisation reaction. No attempt has been made to understand how these equations govern the rate of polymerisation after the first few minutes of the polymerisation reaction.

5.2.2 Premixed Catalyst Systems

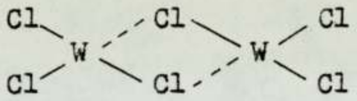
The similarity in the preparation of the reaction systems $WCl_6/Al(iBu)_3/$ Cp and WCl_6/LiBu/Cp (unmixed) allows the two systems to be compared directly. Such a comparison between the reaction systems $WCl_6/$ $Al(iBu)_3$/Cp and WCl_6/LiBu/Cp (premixed) is not possible since the first step in the latter case is the reaction between the catalyst and cocatalyst, whilst in the former, the catalyst is reacted with the monomer solution before the addition of the cocatalyst. Although this means that a similar sequenee of equations cannot be used to describe the formation of the active species in the WCl_6/LiBu/Cp reaction system, it is probable that the species responsible for the initiation of the ring-opening polymerisation of cyclopentene are identical for each reaction system. This follows because of the similarity between the polymerisation curves of cyclopentene produced from the different catalyst systems.

5.2.2.1 Effect of Premix Ageing Time

Since the rate of polymerisation of cyclopentene shows a maximum at a catalyst:cocatalyst premix ageing time of 2·0 minutes, then it follows that the concentration of the metathetically active species is a maximum at this time. This implies that there is a complex series of reactions occuring to generate the metathetically active species. By analogy with the unmixed catalyst system $WCl_6/Al(iBu)_3$, a possible series of reactions may be envisaged as follows:

$$WCl_6 + 2LiBu \xrightarrow{K_1} Cl_4WBu_2 \xrightarrow{Cp} \text{Active species}$$

$$2Cl_4WBu_2 + 2LiBu \longrightarrow$$



2LiCl
BuH
BuBu
$CH_3CH.CHCH_3$

Unfortunately, because of the presence of a precipitate which forms when the catalyst and cocatalyst are mixed together, it was deemed not possible to describe these series of equations mathematically since the precipitate may be responsible for secondary reactions and its surface area (it is that which will determine the extent of any such reactions) cannot be determined.

5.2.2.2 Catalyst: Cocatalyst Ratio

The results obtained in experiment 3.4.1 show that the rate of polymerisation (after a common reaction time) shows a maximum when the catalyst/cocatalyst are premixed in a 1:2 molar proportion. This may be tentatively explained by using equation 5.10 above; the active species responsible for metathesis arising from the reduction of the tungsten hexachloride catalyst. The complex tungsten material formed later may be one of the species responsible for producing the precipitate observed when the catalyst and cocatalyst are first mixed.

5.2.2.3 Termination Reactions

From the results of the ring-opening polymerisation of cyclopentene, catalysed by either the unmixed or premixed catalyst system $WCl_6/LiBu$, it is obvious that the initial rate of polymerisation falls rapidly after only a few minutes reaction time. This decrease in the rate of polymerisation cannot simply be attributed to a reduction in the initial monomer concentration and suggests that some form of termination reactions are occurring to slow down the polymerisation reaction.

Amass and Zurimendi(64) have suggested that the decrease in the rate of polymerisation of cyclopentene catalysted by $WCl_6/Al(iBu)_3$ could be accounted for by the following series of termination reactions.

$$W^* + W^* \xrightarrow{K_{t1}} 2\,W_{inactive} \qquad 5.11$$

$$W^* + W_{inactive} \xrightarrow{K_{2t}} 2\,W_{inactive} \qquad 5.12$$

From an analysis of the concentrations of the active species, they were able to predict that:

$$Rp = \frac{Kp\,[M][W]o\,K_{t2}}{K_{t2} - K_{t1}\,(1 - \exp K_{t2}\,[W]o\,t)}$$

The derivation of this equation is given on page 147. This equation predicts that the rate of polymerisation at any time during the course of a polymerisation decreases in a complex exponential manner. Values of Kp, K_{t1} and K_{t2} have not been estimated.

Although this scheme was developed to account for the termination reactions occuring in the $WCl_6/Al(iBu)_3/Cp$ reaction system, it may also be applied to the $WCl_6/LiBu/Cp$ system.

Modifications of this scheme have recently been proposed to account for the very rapid decrease in the rate of polymerisation of cyclopentene at high monomer concentrations. This new scheme suggests that termination reactions occur in a two stage operation.

$$W_n + M \underset{K_{-1}}{\overset{K_1}{\rightleftharpoons}} W_1 \xrightarrow{Kp} W_{n+1}$$

and

$$Wn + P_m \underset{K_{-2}}{\overset{K_2}{\rightleftharpoons}} W_2 \xrightarrow{K_d} W_m + P_m$$

where W_n is the propagating centre, W_1 and W_2 are active species and P_m is a polymer chain which can continue to act in the reaction.

Using these equations, the rate of polymerisation was described by means of a Michaelis Menten equation. Unfortunately, these theories need further development before they can adequatly describe the ring-opening polymerisation reaction.

5.3 MOLECULAR WEIGHT STUDIES

The ring-opening polymerisation of cyclopentene by a variety of metathesis catalysts produces polymers which possess a bimodal molecular weight distribution (fig. 4.1). Following a study of the polymerisation of cyclopentene catalysed by $WCl_6/Al(iBu)_3$, Amass and Zurimendi(64) suggested that the bimodal molecular weight distribution arose from the presence of two kinetically independent metathetically active species. One of these species was capable of producing high molecular weight polymer (HMWM) and the other(s) capable of producing low molecular weight material (LMWM). They also suggested that the concentrations of these active species could be determined by the ageing time of the catalyst components through a series of termination reactions.

$$W_1 + W_1 \xrightarrow{K_{t1}} 2W_2$$

$$W_1 + W_2 \xrightarrow{K_{t2}} 2W_2.$$

where W_1 is the propagating centre producing high molecular weight polymer and W_2 is the species produced on termination. It is possible that W_2, although inactive towards the production of high molecular weight polymer, may lead to the formation of low molecular weight material.

A plot of the ratios of the areas under the high and low molecular weight peaks, for the $Cp/WCl_6/Al(iBu)_3$ reaction system, shows an initial decrease and then a subsequent increase to an almost constant value - as shown in table 5.2.

Table 5.2 Dependence of molecular weight distribution on ageing time and conversion.

Ageing time/ minutes	Reaction time/ minutes	HMWM/LMWM
1	2	6·9
	6	2·4
	20	1·4
	24 x 60	3·7
2	1·5	10·1
	20	2·3
	50	2·0
	24 x 60	3·7
5	4	4·5
	20	1·6
	50	1·5
	24 x 60	3·7

These figures suggest that there may be two distinct stages to the polymerisation reaction, the initial stage would be kinetically controlled and the later stage, which would be thermodynamically controlled, eventually leading the system to equilibrium. Further, a plot of HMWM/LMWM against ageing time, for a common polymerisation time of say 20 minutes, leads to the plot shown in fig. 5.1.

Because of the marked similarity between the catalyst systems WCl_6/ $Al(iBu)_3$ and WCl_6/LiBu and WCl_6/PStLi, it is possible that similar arguments could be applied to the latter catalyst systems. If this is indeed the case, then a table of HMWM/LMWM against reaction time for either WCl_6/Li or WCl_6/PStLi catalyst system should show an initial decrease and an eventual increase to an equilibrium position.

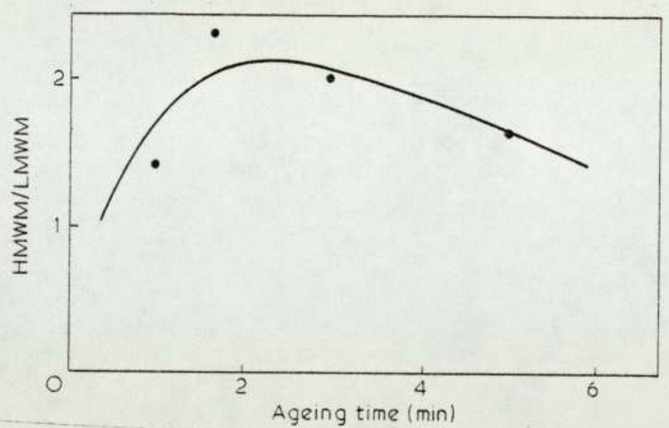


Fig. 5.1 Dependence of polymer composition on ageing time of catalyst.

Table 5.3 Dependence of molecular weight distribution of copolymer samples on ageing time and conversion.

Ageing time/ minutes	Reaction time/ minutes	HMWM/LMWM
4	3 7 15 30	1·5 0·9 1·9 1·3
6	3 7 15 30 45 60	2·8 3·9 4·9 5·1 3·1 3·5
8	3 7 15 30	2·3 3·2 3·4 3·7
15	3 7 15 30	1·0 1·2 2·7 2·5

As table 5.3 shows, this does not, in fact, appear to be the case. Instead, the ratio of HMWM to LMWM appears to increase to a maximum usually after 15 - 30 minutes polymerisation time and then gradually subside. Since the results tabulated in table 5.3 are obtained from the copolymerisation system (i.e. $Cp/WCl_6/PStLi$) these results may not necessarily disagree with the theoretical treatment used for the $Cp/WCl_6/Al(iBu)_3$ system. Rather, the gradual increase in the ratio of HMWM/LMWM up to a maximum probably reflects the relative stabilities of the active species W_1 and W_2. If W_2 were less stable during the copolymerisation reaction than for the ring-opening polymerisation of cyclopentene, then the initial discrepancy can be explained. At the begining of the copolymerisation reaction the ratio of HMWM/LMWM would be determined by the initial concentrations of W_1 and W_2. As the reaction proceeds then the ratios of the concentration of W_1/W_2 would increase and hence the ratio of HMWM/LMWM would also gradually increase. This would be analogous to the first stage of the ring-opening polymerisation of cyclopentene (kinetic control) catalysed by $WCl_6/Al(iBu)_3$. Unfortunately, samples of the copolymerisation reaction were not collected at long reaction times, i.e. 24 x 60 minutes, and so no conclusions concerning the attainment of a thermodynamically determined equilibrium can be justifiably made.

5.4 MECHANISTIC STUDIES

5.4.1 Introduction

Over the past 12 years or so it has become increasingly clear that the metathesis of linear olefins and the ring-opening polymerisation of cycloolefins are initiated and propagated by a metallocarbene/

metallocyclobutane intermediate. Studies performed during the mid-seventies proved that a chain mechanism involving metallocarbenes could provide a theoretical basis for understanding the product ratios fromthe metathesis of deuterated and undeuterated olefin systems. These studies however have ignored the question of how the initiating metallocarbene is formed.

Later studies by Meuterties(72) led to the idea that, for some catalyst systems at least, the metallocarbene was formed by an α -hydrogen migration from an alkyl group attatched to a transition metal of the transition metal catalyst. Again, these studies ignored the role played by the olefin in providing a pathway to the synthesis of the initiating metallocarbene and so provide only a partial understanding of the metathesis reaction.

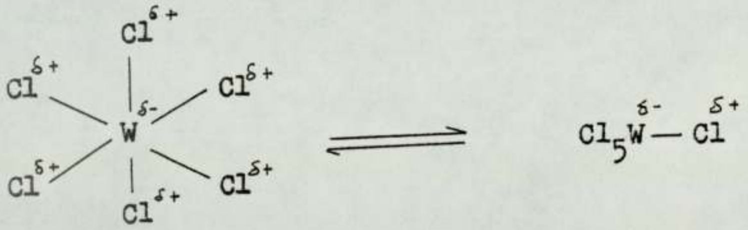
Studies of the ring-opening polymerisation of cyclopentene by a variety of catalyst systems suggest that the formation of the initiating carbene is complex and requires the direct involvement of all three reaction components i.e. cyclopentene, tungsten hexachloride an and the cocatalyst (either $Al(iBu)_3$ or LiBu or even PStLi).

5.4.1.1 Reaction between Tungsten Hexachloride and Cyclopentene

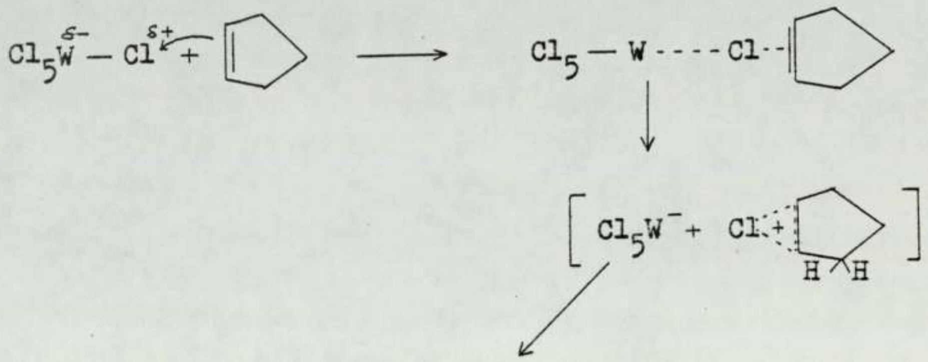
Since the generation of a metathetically active metallocarbene species is likely to be very complex, it is appropriate to study the initiation reaction in various stages. The first stage of the polymerisation reaction is the addition of the catalyst (WCl_6) to a solution of cyclopentene in toluene. If it is assumed that the solvent does not play any role in the metathesis reaction then we can consider the reaction as follows.

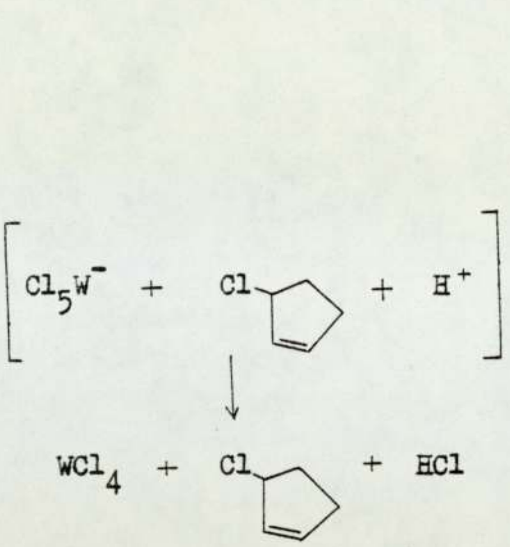
On addition of the blue/black catalyst solution to the monomer solution, there is a dramatic reaction and the resulting solution appears reddish-brown. In order to appreciate this colour change, it is first necessary to consider why tungsten hexachloride is blue.

Since the tungsten has a d^0 configuration, the colour cannot arise from simple electron transitions between the various electronic energy levels. Instead, the colour probably arises from a charge transfer phenomenon between the chlorine atoms and the tungsten metal of tungsten the catalyst.

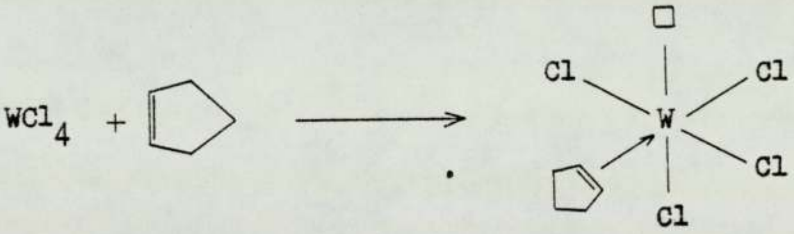


The olefin may then react with the catalyst in the following series of steps:



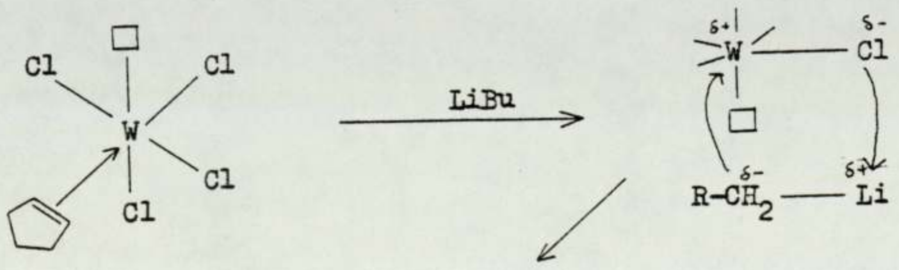


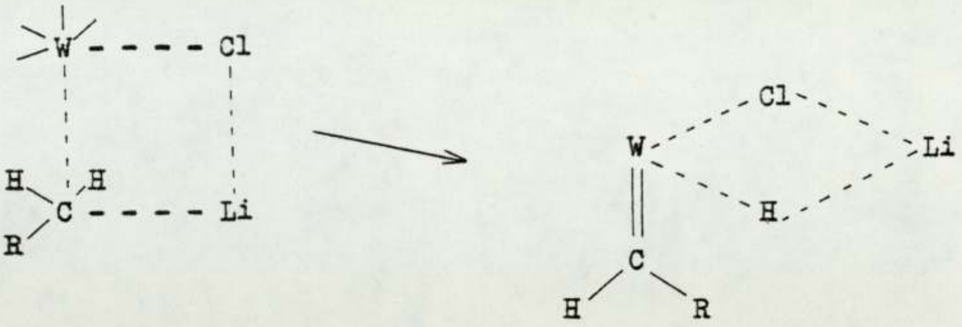
The reaction between the reduced tungsten hexachloride (tungsten tetrachloride) probably produces a complex with the characteristic reddish-brown colour.



Stage 2

The onset of metathesis begins immediately the cocatalyst (LiBu) is added to the solution of monomer and catalyst. The metallocarbene initiating species may be produced from the above intermediates in the following way:

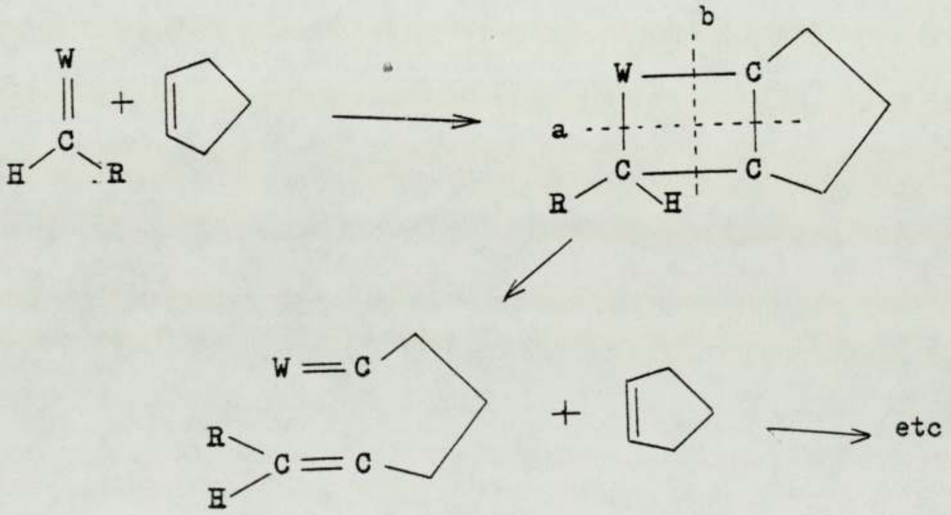




Metallocarbene.

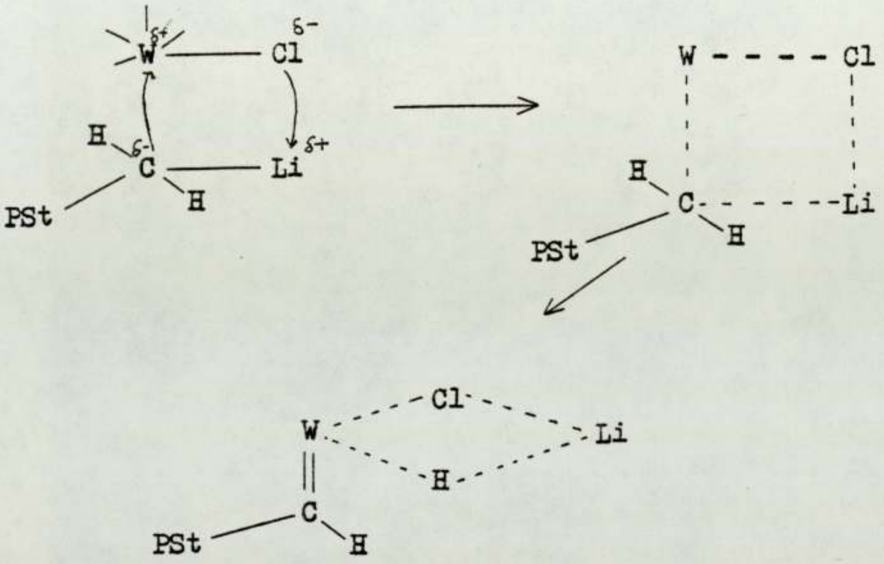
Where R = $CH_3CH_2CH_2$-.

The metallocarbene (above) may then propagate the ring-opening polymerisation of cyclopentene like so:-

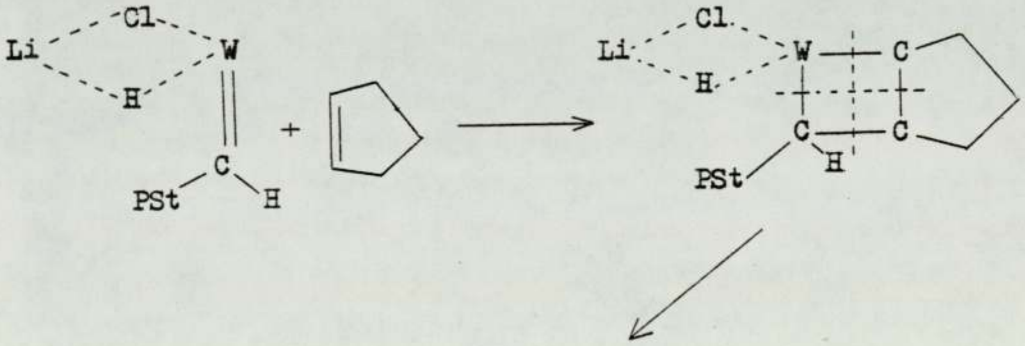


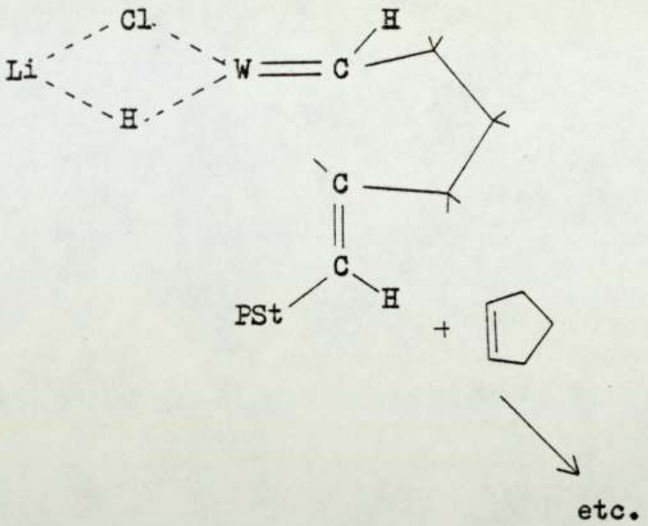
If cleavage across axis a occurs then the polymerisation reaction proceeds normally, whilst cleavage across axis b leads to degenerate metathesis.

The above mechanism may be extended to include substituted cocatalysts such as polystyryl lithium and so explain the formation of block copolymers from such reaction systems.



This polystyrene substituted metallocarbene may then react with cyclopentene to produce copolymers of poly(pentenamer-styrene).





This mechanism agrees with all the tests presented within this thesis, namely that i) the reaction is covalent rather than ionic and ii) the cocatalyst requires an alpha hydrogen which is capable of transfering from the cocatalyst to the transition metal catalyst. It also successfully accounts for the production of block copolymers from reactions such as WCl_6 + Cp + PStLi. Although these tests do not prove the validity of the above mechanism (which would require much more work) they do provide realistically stringent tests to allow the mechanism to be considered as a possible route to the generation of the initial metallocarbene during the first stages of the metathesis reaction. Further, the above mechanism makes it plain that the generation of metathetically active species requires all the reaction components and not simply a reaction between the transition metal catalyst and the monomer, has as been suggested by many workers in the field.

Recently, the presence of chlorinated cyclopentenes have been detected in the reaction products between cyclopentene and tungsten hexachloride, this is even more evidence to support such a mechanism as that shown above.(143)

CHAPTER 6

CONCLUSIONS AND SUGGESTIONS FOR FURTHER WORK

6.1 CONCLUSIONS:

The kinetics of the ring-opening polymerisation of cyclopentene catalysed by either the unmixed or premixed WCl_6/LiBu catalyst system seems to show a remarkable resemblence to that found for the ring-opening polymerisation of cyclopentene catalysed by $WCl_6/Al(iBu)_3$.

The maximum rate of polymerisation is related to both ageing time or premix ageing time of the catalyst/monomer components and, like that for the Cp/$WCl_6/Al(iBu)_3$ reaction system, is greatest after an ageing time (or premix ageing time) of 2 minutes. Likewise, the rate of polymerisation seems to show a maximum, after a reaction time of 4 minutes, at a catalyst: cocatalyst ratio of 1:2 for both the unmixed and premixed WCl_6/LiBu catalyst systems. This is in total agreement with the results obtained for the ring-opening polymerisation of cyclopentene catalysed by $WCl_6/Al(iBu)_3$. These results have been explained by the existence of two competing reactions at the begining of the metathesis reaction. Also, the dependence of the rate of polymerisation with reaction time for different catalyst/cocatalyst ratios suggests that the cocatalyst may be responsible for preventing, by some unknown mechanism, the participation of the catalytically active species from initiating and propagating further polymerisation reactions.

Model studies using polar benzyl ions to mimic the structure of polystyryl lithium have shown that the initiating process is inhibited by either the polar nature of the benzyl ion or that the complexing agent TMEDA interferes with the formation of a catalytically active species. Further, studies using polyαmethylstyrene have shown that the generation of a catalytically active species requires the presence of a cocatalyst which possess an alpha hydrogen atom.

Using the polymerisation system Cp/WCl_6/PStLi, the existence of a anionic to metathetic transformation reaction has been demonstrated. The reaction produced a variety of polymer materials, some of which were copolymers of polystyrene and polypentenamer. The existence of these copolymers demonstrates that the cocatalyst plays a significant role in the metathesis reaction and does not simply act as a reducing agent reducing the transition metal catalyst to an active species which would then initiate metathesis.

6.2 SUGGESTIONS FOR FURTHER WORK

Although the kinetics of the polymerisation of cyclopentene catalysed by WCl_6/LiBu and $WCl_6/Al(iBu)_3$ seem to be very similar, the existence of a brown/black precipitate in the former catalyst system appears to complicate the kinetics of the polymerisation reaction. It is necessary therefore to study the WCl_6/LiBu catalyst system in environments where the polymerisation reaction is homogeneous so that a more complete comparison of this catalyst system with that of $WCl_6/Al(iBu)_3$ can be made so that direct comparisons between the kinetics of both systems are not invalidated. A possible solution to this problem would be to perform the polymerisation reactions in more polar solvents such as chlorobenzene, where the precipitate found in the toluene based systems may be soluble.

Experiments using substituted styrenes (i.e. polyα methylstyrene) suggest that the formation of the initial metallocarbene species requires the presence of a mobile hydrogen atom alpha to the transition metal catalyst. Unfortunately, this may not be the only reason, it is possbile that the methyl group of the substituted styrene may sterically interfere with the generation of the metallocarbene. Although this is highly unlikely, this second hypothesis needs testing. This may be done by using radioactively labelled cocatalysts so that the presence of tritium (^3H) may be detected in the products of a metathesis reaction. This may then finally show that hydrogen atom migrations are responsible for the generation of the initiating carbene species.

Now that it has been confirmed that anionic to metathetic transformation reactions are possible for the polymerisation system Cp/WCl_6/PStLi it would be interesting to extend these studies to other polymerisation systems. A possible example is norbornene/PStLi/WCl_6. The order of addition of the reaction catalysts in this case would be extremely important since WCl_6 alone initiates the ring-opening polymerisation of norbornene within a few seconds. If such transformation reactions are feasible, then further reaction systems may then be studied.

APPENDIX 1

CHAPTER 7

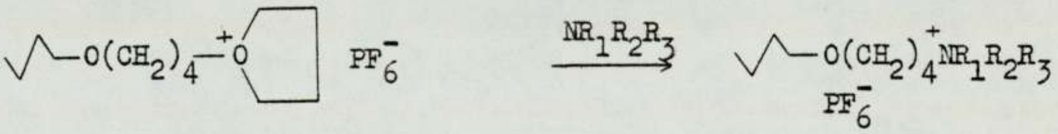
REACTIONS OF LIVING POLY-(TETRAMETHYLENE OXIDE)

7.1 INTRODUCTION

7.1.1 Reactions of Living Poly(tetramethylene oxide) with Amines

Many of the transformation reactions described in chapter 1 (section 1.7.3) have two essential stages: (a) termination of a 'living' polymer with a stable but potentially reactive functional group; and (b) isolation of this material and using it to initiate the polymerisation of a second monomer by a mechanistic route which is different to that used for the first monomer. This first stage has led to a research emphasis into developing new reactive functional groups to enable more transformation reactions to be investigated. One example of this type of research is the termination of living poly(tetramethylene oxide) with various types of amines(144 - 147). These studies may ultimately lead to the development of new block copolymers e.g. poly(tetramethylene oxide-b-vinyl pyridine).

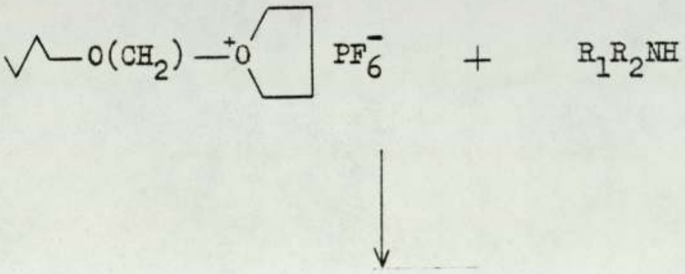
The earliest investigations involved the reactions of living poly-(tetramethylene oxide) with tertiary amines to produce quaternary ammonium salts.

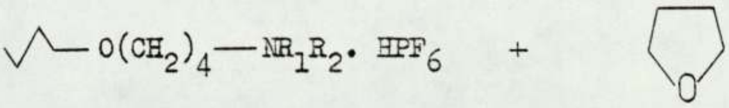


The resultant polymer is stable and was shown not to exchange with any excess oxonium ions present in solution. Analysis of the products of the reaction between living poly(tetramethylene oxide) and either pyridine or poly(4-vinylpyridine) by gpc has shown the termination reaction to be quantitative i.e. one mole of amine terminates one mole of living polymer. The gpc chromatograms of these amine terminated polymers show traces with asymmetric peaks at retention times longer than those obtained with poly(tetramethylene oxide) of the same molecular weight not possessing polar terminal groups. The skew distributions were ascribed to arise from interactions between the ionic terminal group of the polymer and specific polar absorption sites on the gpc columns. The adsorption sites may be carbonyl or hydroxyl groups which are known to develop in small concentrations on cross-linked polystyrene columns on use.

Subsequent work using other tertiary amines has showed that the rate of reaction with the living polymer was controlled by the nucleophilicity of the amine; for heterocyclic amines the order is 4-ethylpyridine > pyridine > isoquinoline > quinoline > acridine, and for aliphatic tertiary amines triethylamine > tributylamine > diethylamine. The reaction of pyridine and aliphatic amines such as triethylamine being complete within a minute or so at -10°C in contrast to the extremely slow addition of acridine.

Further studies involved the synthesis of poly(tetramethylene oxide) with terminal tertiary amine groups by the reaction of living poly(tetramethylene oxide) with secondary amines. The products of the reaction were expected to result in the initial formation of polymers possessing terminal groups which were the acid salts of tertiary amines.

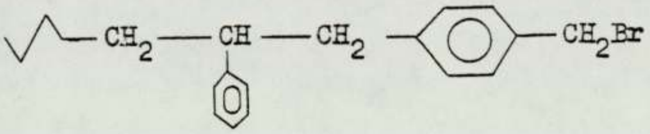




These acid salts could then be reacted with alkali to liberate the free polymer possessing tertiary amine terminal groups.

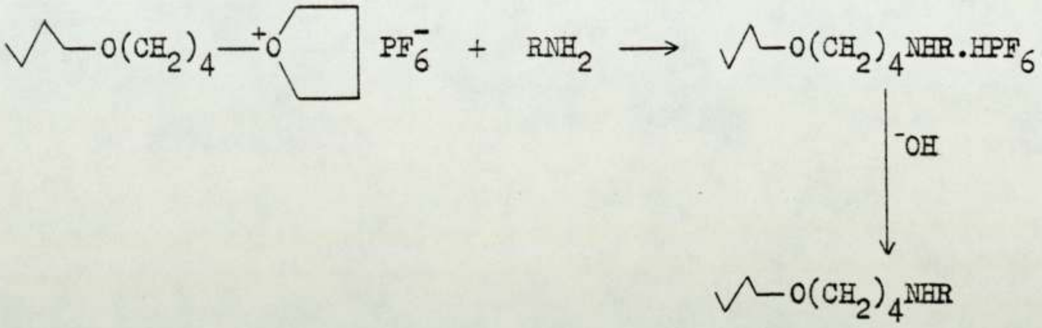
$$\sim O(CH_2)_4-NR_1R_2\cdot HPF_6 \xrightarrow{^-OH} \sim O(CH_2)_4NR_1R_2 \qquad (3)$$

The amines used in these studies were: diethylamine, dicyclohexylamine, piperidene, diphenylamine and carbazole. The reaction of living poly(tetramethylene oxide) with aliphatic amines is rapid but the reaction with aromatic amines is slow. In order to increase the rate of reaction between the aromatic amines and the living polymer, the amine was first converted to its lithium salt by reacting it with butyl lithium. These lithium salts react rapidly with the living polymer to yield polymers with terminal tertiary amine groups. It was found to be possible to convert these polymers containing tertiary amine terminal groups into quaternary ammonium salts by reacting the amine terminated polymer with either living poly(tetramethylene oxide) or bromine-terminated polystyrene. Only polystyrenes terminating as a primary benzyl bromide (structure I) reacted with the amine terminated polymer.



(I)

The reactions of living poly(tetramethylene oxide) with primary amines are potentially more complicated than those involving secondary or tertiary amines. The reaction should, in principle, proceed to produce polymers with secondary amine terminal groups.



(4)

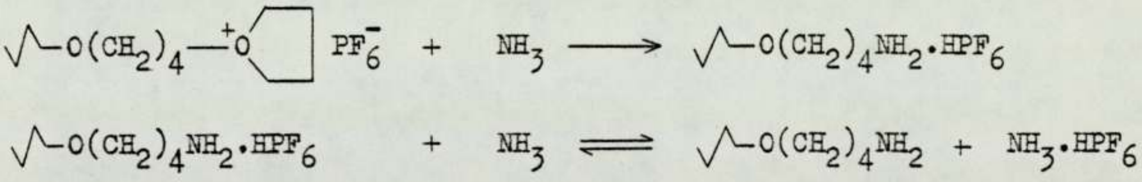
The initial product of this reaction is the acid salt of the secondary amine, and in this form should not be subject to any further electrophilic attact. However, the generated acid may equilibrate between the polymer secondary amine and any unreacted primary amine present.

$$\sim O(CH_2)_4NHR.HPF_6 + RNH_2 \rightleftharpoons \sim O(CH_2)_4NHR + RNH_2.HPF_6 \qquad (5)$$

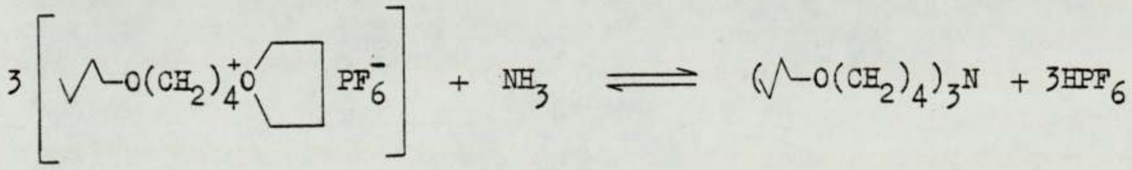
The position of this equilibrium is governed by the relative basicities of the two amines involved, and this in turn could control the course of further reaction with living poly(tetramethylene oxide) since the secondary amine released can undergo further alkylation. The reaction of living poly(tetramethylene oxide) with a series of primary amines has proved the existence of the equilibrium shown in equation (5). Therefore to achieve near quantitative conversion of to the secondary amine a large excess of amine is used and under these conditions almost 100% secondary amine terminated polymer is produced. The form of the unneutralised amine product is dependent on the primary amine used. The product from the reaction of living poly(tetramethylene oxide) with aniline exists as the free secondary amine whilst those from cyclohexylamine and n-butylamine exist as the acid salt. This difference is best explained by the equilibrium shown in equation (5), which for n-butylamine and cyclohexylamine lies well over to the left and for aniline lies well over to the right.

7.1.2 Reactions of Living Poly(tetramethylene oxide) with ammonia

The reaction between living poly(tetramethylene oxide) and ammonia will, like that for other primary amines, be governed by the equilibrium between the resulting acid salt and the free amine terminated polymer.

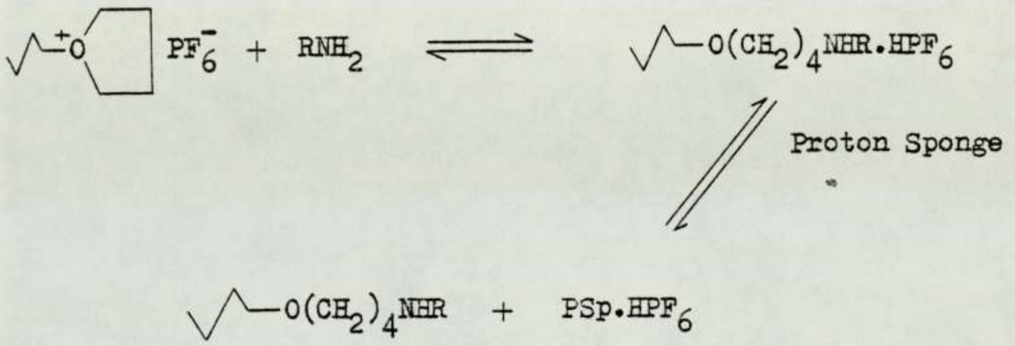


It is the purpose of the present investigation to study this eqiulibrium and to optimise the reaction conditions to achieve the fully alkylated ammonium species, i.e.



Experiments between primary amines and living poly(tetramethylene oxide) have shown that excess base enables a near quantitative amount of the disubstituted amine to be formed. This results since the excess base reacts with any acid salt liberating the free monosubstituted amine, which can then undergo further alkylation reactions with the living polymer , as shown in the equations above.

An alternate approach to using excess base would require alternative means of liberating the free substituted amine from its acid salt. This may be achieved by using proton sponges. Proton sponges are strongly hindered tertiary amines and bicyclic amidines which have a lack of nucleophilicity towards electophiles but may still be used as proton acceptors. The reaction between a primary amine and living poly(tetramethylene oxide) might be envisaged thus:



Where PSp = proton sponge.

7.2 MATERIALS

Tetrahydrofuran (THF), supplied from BDH, was dried and purified by refluxing 2 dm^3 of THF over sodium naphthalene (0·1 mole), under nitrogen, for thirty minutes. The THF was then distilled as required, the first fraction of 200 cm^3 being discarded.

Both silver hexafluorophosphate and p-methylbenzyl bromide were used as received without further purification.

Proton sponge was purified by crystallisation from a water/methanol mixture.

Aniline was purified by drying over potassium hydroxude pellets and fractional distillation from the alkali.

Ammonia was obtained from a cylinder and was dried by liquifying the ammonia over sodium pellets. The ammonia was liquified in a tube cooled by a solid carbon dioxide/acetone mixture.

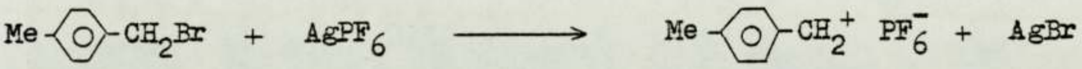
7.2.1 Analysis of amine terminated polymers

All polymer samples were analysed by a Waters Associates model 301 gel permeation chromatograph. The instrument was fitted with both a differential refractometer and a ultraviolet detector operating at 254 nm. High resolution was not necessary in this work, and two Styragel columns with porosities 10^4 and 10^5 were used in series. The mobile phase was THF eleuting at 1 cm^3/minute. Samples were injected from a 1·7 cm^3 loop normally charged with a 0·1% w/v THF solution of the polymer. Polystyrene equivalent molecular weights were obtained by calibrating the instrument with a series of narrow dispersity polystyrene standards (Polymer Laboratories) in THF. These polystyrene equivalent molecular weights may be converted to actual poly(tetramethylene oxide) molecular weights by multiplying by 0·556(148), provided there are no extraneous polymer - column interactions.

7.3 EXPERIMENTAL

7.3.1 Synthesis of Poly(tetramethylene oxide)

About 250 cm^3 of dry THF was placed in a 500 cm^3 three-necked flask, fitted with a nitrogen inlet and outlet, and a suba seal. This flask was cooled in a water/isopropanol/solid carbon dioxide mixture to -15°C and the THF was stirred by a magnetic follower. After equilibration, 0·6g ($3\cdot3 \times 10^{-3}$ moles) of p-methylbenzyl bromide was dissolved in 5 cm^3 of dry THF and added by syringe to the 500 cm^3 flask. Then 0·9g ($3\cdot3 \times 10^{-3}$ moles) of silver hexafluorophosphate, in 5 cm^3 of dry THF, was added to the THF in the 500 cm^3 flask. A pale yellow/white precipitae of silver bromide was formed immediately.



The benzylic cation produced initiates the cationic polymerisation of THF. After one hour the polymerisation was terminated by the addition of 50 cm^3 of methanol. The molecular weight distribution of the polymer was analysed by gpc.

7.3.2. Modification of the Synthesis of Poly(tetramethylene oxide)

Although the poly(tetramethylene oxide) obtained by the procedure outlined above gave gpc traces which showed no sign of interference from the precipitated silver salts, it was decided to separate the living polymer from the silver bromide to prevent any possible interaction between the halide and the proton sponge used in later experiments.

The initial procedure was the same as that used previously. After allowing the THF to polymerise for 1 hour, the reaction mixture was cooled to -25°C and filtered, under a positive nitrogen pressure, through a glass sinter (porosity 3). This resulted in a clear solution of living polymer solution which showed little or no trace of any silver salts. All amine termination reactions described in this work were carried out on such a filtered polymer solution.

7.3.3 Comparison of the Polymerisation of THF with and without Proton Sponge

Living poly(tetramethylene oxide) was prepared by the cationic polymerisation of THF for one hour, as described in section 7.3.2. After this time, 80 cm^3 aliquots of the polymerising solution were transferred, by syringe, to two 250 cm^3 round bottom flasks, A and B, fitted with magnetic followers and suba seals. About 8 cm^3 of the polymerising solution was removed from flask A and terminated with 2-3 cm^3 of methanol. This material was used as a low molecular weight blank. A small amount of proton sponge ($1{\cdot}06 \times 10^{-3}$ mol.) was dissolved in 5 cm^3 of dry THF and added to flask A. This quantity of proton sponge (P.Sp) provided, theoretically, a 1:1 molar ratio of proton sponge to growing polymer chains. The THF in both round bottom flasks was then allowed to polymerise for a further 3 hours; after every hour a 8 cm^3 sample was taken from both flasks and terminated with 2-3 cm^3 of methanol. These samples were then analyzed by gpc.

7.3.4 Reactions of Living Poly(tetramethylene oxide) with Ammonia

A clear solution of living poly(tetramethylene oxide) was obtained by the procedure outlined in section 7.3.2. A 5 cm^3 sample of this polymerising solution was terminated with 2 cm^3 of methanol and used as a low molecular weight blank. About 40 cm^3 aliquots of the polymerising solution ($5{\cdot}3 \times 10^{-4}$ mol. of growing chain ends) were added to two 100 cm^3 round bottom flasks A and B, which were fitted with magnetic followers and suba seals.

An ammoniacal solution of ammonia ($1{\cdot}8 \times 10^{-4}$ mol) in THF was added to both round bottom flasks. The concentration of the ammonia was determined by titration with hydrochloric acid using a congo red indicator. This quantity of ammonia provides, theoretically, a 1:3 molar ratio of ammonia to growing polymer chain ends. About 5 minutes after the addition of the ammonia solution, a solution of proton sponge ($5{\cdot}3 \times 10^{-4}$ mol.) in THF was added to flask B. This quantity of proton sponge gave a 1:1 molar ratio of proton sponge to growing polymer chain ends. Samples of the polymerisate from each flask (5cm^3) were obtained one minute after the addition of the proton sponge to flask B. These samples were added to methanol and then analyzed by gpc.

7.3.5 The Effect of Neutralisation and Precipitation on Amine Terminated Poly(tetramethylene oxide)

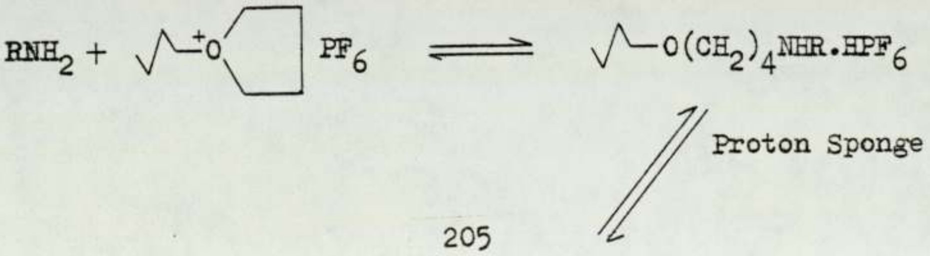
Living poly(tetramethylene oxide) was prepared by the method outlined in section 7.3.2. A 5 cm^3 sample of this polymerising solution was terminated with excess methanol and used as a low molecular weight blank. Then 40 cm^3 aliquots of the living polymer solution were added to two 100 cm^3 round bottom flasks A and B. The flasks had previously been fitted with magnetic followers and suba seals. The polymer in flask A was terminated with an ammoniacal solution of ammonia ($1{\cdot}8 \times 10^{-4}$ mol. of ammonia) in THF, and five minutes later a 8 cm^3 sample from A was added to an excess of methanol. This provided a 3:1 molar ratio of growing polymer chain ends to ammonia.

A solution of proton sponge ($5{\cdot}3 \times 10^{-4}$ mol.) in dry THF was then added to flask B. This gave a 1:1 molar ratio of proton sponge to growing polymer chain ends. Five minutes later 1.8×10^{-4} moles of ammonia in 5 cm^3 of THF was added to the contents of flask B. Five minutes later the contents of Flask B were terminated with 10 cm^3 of methanol.

On addition of the ammonia solution to the living polymer/proton sponge solution (flask B) a white precipitate formed; this precipitate was later shown to be protonated proton sponge. This precipitate was filtered off and the eleunt washed with a solution of sodium methoxide. The basic solution was added to neutralise any acid salts of the primary and secondary amine derivatives. On addition of the methoxide a white precipitate was obtained. This precipitate was filtered, dissolved in THF and analyzed by gpc.

7.3.6 Reactions between Living Poly(tetramethylene oxide) and aniline in the presence of Proton Sponge.

Although the reactions between primary amines and living poly(tetramethylene oxide) have been reported$^{(147)}$, these reactions have not been carried out in the presence of proton sponge. The proton sponge should, theoretically, push the equilibrium reaction (shown below) to the right by removing the acid salt formed and leaving the disubstituted amine.



$$\sim\!\!\sim\!O(CH_2)_4NHR \quad + \quad PSp.HPF_6$$

It is the intention of the following series of reactions to investigate this eqiilibrium and contrast it with that for ammonia and living poly(tetramethylene oxide).

Living poly(tetramethylene oxide) was prepared as described in section 7.3.2. After filtering, a 5 cm^3 sample of the polyerisate was terminated with excess methanol and used as a low molecular weight blank. Three 100 cm^3 round bottom flasks were each filled with 40 cm^3 of the polymerising solution. The flasks had previously been fitted with magnetic followers and suba seals. For convenience , each flask shall be considered in turn, as three separate experiments were conducted simultaneously.

Flask A

A solution of aniline (2.64×10^{-4} mol.) in 5 cm^3 of THF was added to the solution of the living polymer in flask A. This gave a 2:1 molar ratio of growing polymer chain ends to the base. After five minutes a solution of proton sponge ($5 \cdot 3 \times 10^{-4}$ mol.) in THF was added to the above solution and a sample taken five minutes after the addition of the proton sponge. The sample was added to excess methanol and analyzed by gpc.

Flask B

A small sample of the polymerisate in flask B was taken and reacted with excess methanol; this material was subsequently analyzed by gpc and provided a low molecular weight blank for the following experiment. A solution of aniline ($1{\cdot}32 \times 10^{-4}$ mol.) in THF was added to flask B and, after 5 minutes, a sample of this solution was obtained and after terminating in excess methanol, analyzed by gpc. This amount of aniline gave a 4:1 molar ratio of growing polymer chain ends to the added base. Proton sponge (2.64×10^{-4} mol.) in THF was then added to flask B and after about five minutes, a sample was taken and added to 2 cm^3 of methanol. A further quantity of aniline ($1{\cdot}32 \times 10^{-4}$ mol) in THF was added to flask B and after about five minutes a sample obtained for gpc analysis. A further quantity of proton sponge ($2{\cdot}64 \times 10^{-4}$ mol.) in THF was then added to flask B and after 5 minutes a sample was taken for analysis by gpc.

Flask C

A solution of proton sponge ($5{\cdot}28 \times 10^{-4}$ mol.) in THF was added to the polymerisate in flask C. This amount of proton sponge provided a 1:1 molar ratio of proton sponge to growing polymer chain ends. After 3 hours polymerisation a solution of aniline (5.28×10^{-4} mol.) in THF was added to flask C and after about 5 minutes a sample was taken, added to 2 cm^3 of methanol, and subsequently analyzed by gpc. A high molecular weight blank was obtained by allowing some of the original polymerising THF solution to polymerise for a total of 4 hours (1 hour before filtering and 3 more hours) before terminating in methanol.

7.3.7 Comparison between the termination of Living poly(tetramethylene oxide) with either ammonia or aniline

Living poly(tetramethylene oxide) was prepared as described in section 7.3.2 and 40 cm^3 aliquots were then transferred to two 100 cm^3 round bottom flasks containing magnetic followers. The flasks A and B had previously been flushed with dry nitrogen and sealed with suba seals. A small sample of the polymerising solution was added to methanol and this material was used as a low molecular weight blank. Proton sponge ($5 \cdot 28 \times 10^{-4}$ mol.) in THF was then added to the polymerising solutions in both flasks. This produced a 1:1 molar ratio of proton sponge to growing polymer chain ends in both flasks. The solutions in both flasks were then allowed to polymerise for a further 3 hours and, after this time, a small sample from flask A was added to methanol and used as a high molecular weight blank. It is now convenient to consider each reaction flask separately.

Flask A

A solution of ammonia (5.87×10^{-4} mol.) in THF was added to the contents of flask A; after about five minutes reaction a sample of this solution was added to 2 cm^3 of methanol. This amount of ammonia gave a 9:1 molar ratio of growing polymer chain ends to ammonia. This procedure of adding $5 \cdot 87 \times 10^{-5}$ moles of ammonia and subsequently taking a sample of the solution five minutes later was repeated until a total of $1 \cdot 76 \times 10^{-4}$ moles of ammonia had been added. This gave a final 3:1 molar ratio of growing polymer chain ends to added ammonia.

Flask B

A solution of aniline ($1{\cdot}32 \times 10^{-4}$ mol.) in THF was added to the contents of flask B and after five minutes a sample of this solution was obtained and added to excess methanol. The amount of aniline added gave a 4:1 molar ratio of growing polymer chain ends to the added base. This procedure was repeated again, so that the final ratio of growing polymer chain ends to added aniline was 2:1.

7.4 RESULTS AND DISCUSSION

7.4.1 Reactions of Poly(tetramethylene oxide) with Proton Sponge

The initial reaction between living poly(tetramethylene oxide) and primary of secondary amines results in the formation of acid salts of the amine terminated polymer. The acid salt produced may then react with any free amine to liberate the free amine terminated polymer which may in turn react further with any free living polymer to produce amines substituted with more than one polymer chain. The equilibrium between the acid salt and the free amine terminated polymer dictates the extent of substitution of the amine by the living polymer chains. Excess amine may be used to liberate the free polymer from its acid salt though it may be possible to achieve this by using bases which show little nucleophilicity e.g. proton sponges. If this is the case, then proton sponge should not interfere with the cationic polymerisation of THF. This lead to our first investigation of the cationic polymerisation of THF in the presence of proton sponge.

Figure 7.1 shows the gpc curves obtained from the polymerisation of THF as outlined in experiment 7.3.3. Trace A shows the result of polymerising THF in the presence of proton sponge whilst trace B shows poly(tetramethylene oxide) prepared without proton sponge.

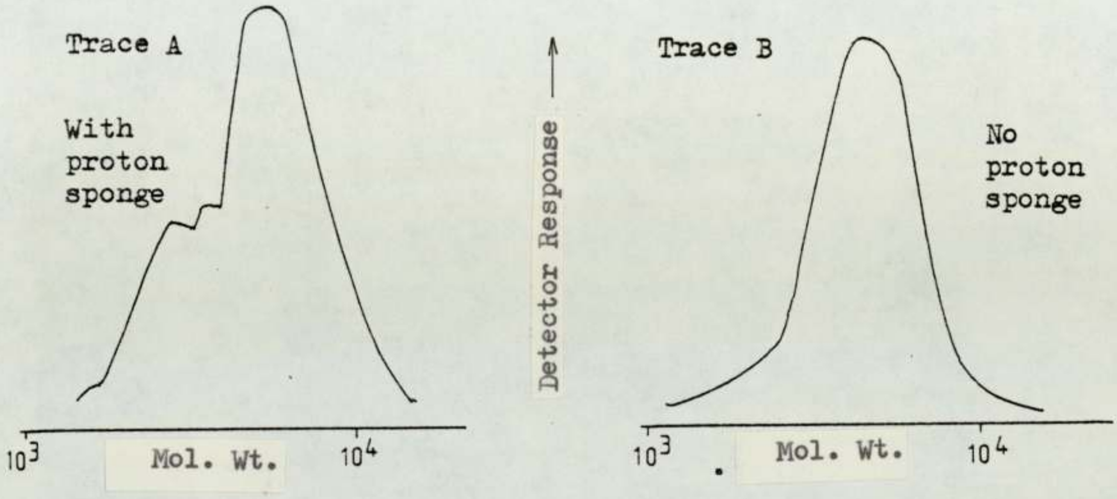


Fig. 7.1 Gpc chromatograms of poly(tetramethylene oxide) after 3 hours polymerisation. The traces are from the refractive index detector.

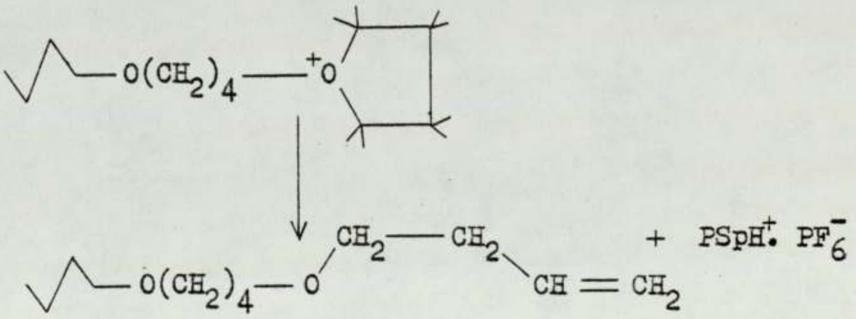
The gpc results for the polymerisation of THF with and without proton sponge are summarised in table 7.1. Living poly(tetramethylene oxide) prepared without proton sponge shows a progressive increase in molecular weight with time. THF polymerised in the presence of proton sponge shows anomolous results. Before the addition of the proton sponge to the living polymer (reaction time equals 1 hour) the growth of the living polymer shows no discrepancy with that of the living polymer contained in the other flask. After the addition of the proton sponge there is a doubling of molecular weight within one hour and very

Table 7.1 Variation in molecular weight of living poly (tetramethylene oxide) with time

Polymerisation time in hours	Mol. Wt (P.St. Eq) No proton sponge	Mol. Wt. (P.St. Eq) Proton sponge
1	3150	3150
2	4320	6490
3	5730	7120
4	7570	7120

little subsequent increase. A comparison of the gpc traces A and B reveals that trace A shows peaks at low molecular weights as well as high molecular weight peaks.

It seems that the reactions of proton sponge with living poly(tetramethylene oxide) are very complicated and it is possible that several different types of reaction are occurring simultaneously. The low molecular weight peak (trace A) might be explained by the proton sponge 'killing off' some growing polymer chain ends by a proton transfer reaction.



It is also possible that the proton sponge forms an ionic association with the positively charged oxygen atom of the growing polymer chain end and that this limits the extent of further polymerisation. This idea also explains the rapid decline in the increase in molecular weight after the addition of the proton sponge to the living polymer. The high molecular weight peak is probably formed by the usual cationic polymerisation of THF, but as the polymerisation continues more and more of the chain ends become associated with the proton sponge and so the increase in molecluar weight gradually slows down and ultimately stops.

7.4.2 Termination reaction of living poly(tetramethylene oxide) with ammonia

Figure 7.2 shows the gpc traces obtained by terminating living poly(tetramethylene oxide) with ammonia; trace A shows the low molecular weight blank which has been methanol terminated. Traces B and C show poly(tetramethylene oxide) which has been terminated with ammonia, with and without proton sponge respectively.

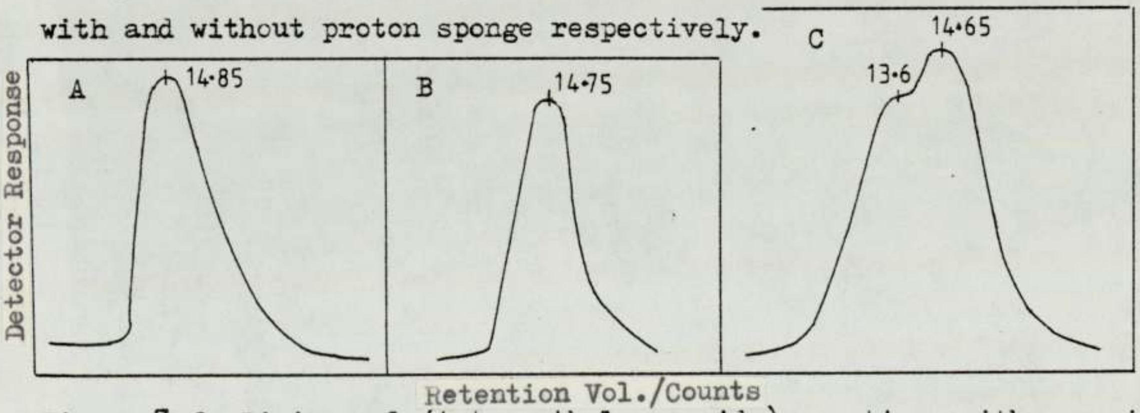


Figure 7.2 Living poly(tetramethylene oxide) reactions with ammonia

All traces are from the differential refractometer detector.

Table 7.2 Variation of molecular weight of poly(tetramethylene oxide) terminated with ammonia

Sample	Retention Vol. in counts	Mol. Wt.(PSt. Eq.)
A	14·85	10,800
B	14·75	11,500
C	14·65	12,300
	13·6	24,000

Table 7.2 summarises the gpc traces obtained in the experiment outlined in section 7.3.4.

After the addition of ammonia to the living polymer there is a slight shift to lower retention volumes (i.e. from 14·85 to 14·75 counts). This increase in molecular weight from 10,800 to 11,500 can be accounted for by the formation of a monosubstitued ammonia and the continued polymerisation of the remaining living polymer. When proton sponge is added to the solution of the living polymer and ammonia, there is a dramatic change in the molecular weight of the resultant polymers. The gpc analysis of this solution shows two peals at 12,300 and 24,000 respectively. The low molecular weight peak correspends to the monosubstituted ammonia and the living polymer which has continued to polymerise. The high molecular weight peak corresponds to about 2.2 times that of the low molecular weight blank. This may imply that the ammonia has been disubstituted; alternatively it may be due to the side reactions between the living polymer and the proton sponge. There was some evidence from experiment

7.4.1 that proton sponge produces an increase in molecular weight of the living polymer. The effect of proton sponge on the living polymer was minimized by terminating the reaction system five minutes after the addition of the proton sponge to the reaction system.

7.4.3 The effect of Neutralisation and Precipitation

All the samples obtained in experiment 7.3.5 were analyzed by gpc and the resulting chromatograms are shown in fig. 7.3.

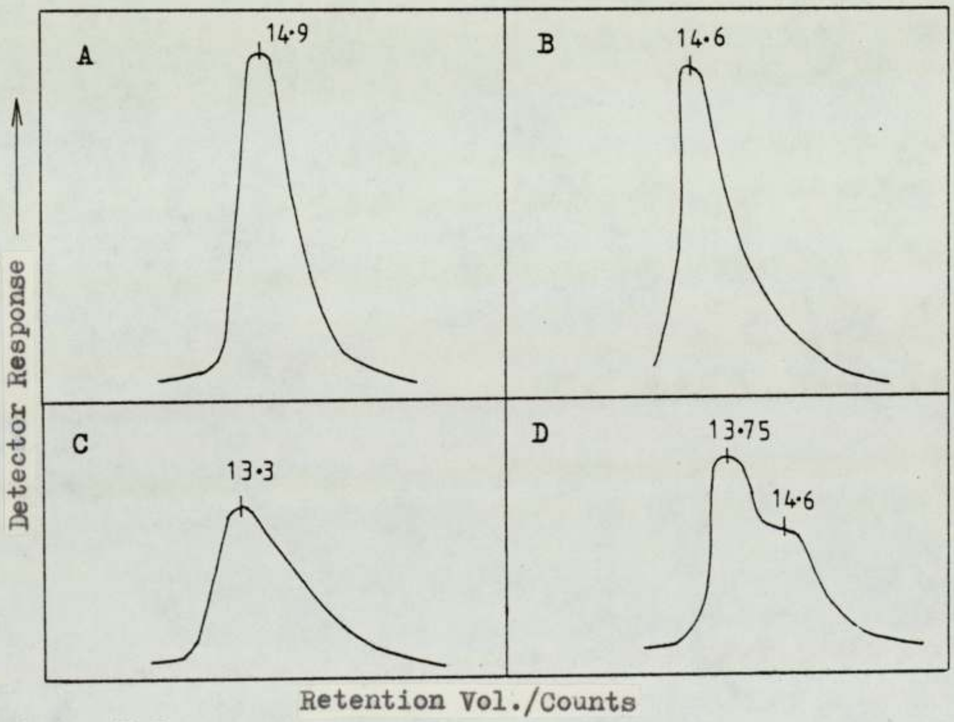


Figure 7.3 Gpc traces of samples obtained in experiment 7.3.5

All traces shown are produced by the differential refractometer detector.

Table 7.3 Tabulated data of the gpc chromatograms obtained in experiment 7.4.5

Sample	Retention Vol. in counts	Mol. Wt. (PSt. Eq)
A	14·9	10,500
B	14·6	12,600
C	13·3	30,000
D	13·75	22,500
		12,600

Sample A shows a symmetrical gpc trace (trace A) which is typical of methanol terminated living poly(tetramethylene oxide). Addition of ammonia to the living polymer solution results in sample B (trace B) having a asymmetric gpc chromatogram. There is also a slight increase in molecular weight from 10,500 to 12,600 when compared to the molecular weight blank (trace A). This shift in molecular weight can be explained by the growth of any residual living polymer and/or the formation of some secondary amine acid salt with the commensurate doubling of molecular weight. The asymmetry exhibited in trace B could be due to the fact that the material is still in the acid salt form.

When proton sponge is added to sample B there is a dramatic change in molecular weight (from 12,600 to 30,000) and the gpc trace (trace C) shows a broad symmetrical peak. The initial conclusion, therefore, is that the proton sponge has reacted with the polymer acid salt the release the primary amine which has then reacted further with living polymer to form the higher substituded amines. The situation could, however, be more complicated than this simple analysis since it has been shown that there is a direct reaction between living poly(tetramethylene oxide) and proton sponge which may also result in significant molecular weight increases.

After washing, two peaks can be resolved, the one at lower molecular weights is at a retention time near that of the blank (trace A) and therefore indicates the presence of some residual primary amine. The large peak, corresponding to a polystyrene equivalent molecular weight of 22,500 suggests that appreciable chain coupling has occurred. This may be explained by further substition of the primary amine with living polymer chains (experiment 7.3.4). This interpretation remains uncertain, however, because the nature of the direct reaction between living poly(tetramethylene oxide) and proton sponge is still unresolved.

7.4.4 Comparison of aniline and ammonia termination reactions

The termination of living poly(tetramethylene oxide) with ammonia and aniline were compared in the following series of experiments. The initial experiments involved the termination of the living polymer with aniline, with and without proton sponge.

7.4.5 Reactions of aniline with living poly(tetramethylene oxide)

7.4.5. Experiment A

Fig. 7.4 shows the gpc chromatograms of the samples obtained from experiment 7.3.6, flask A.

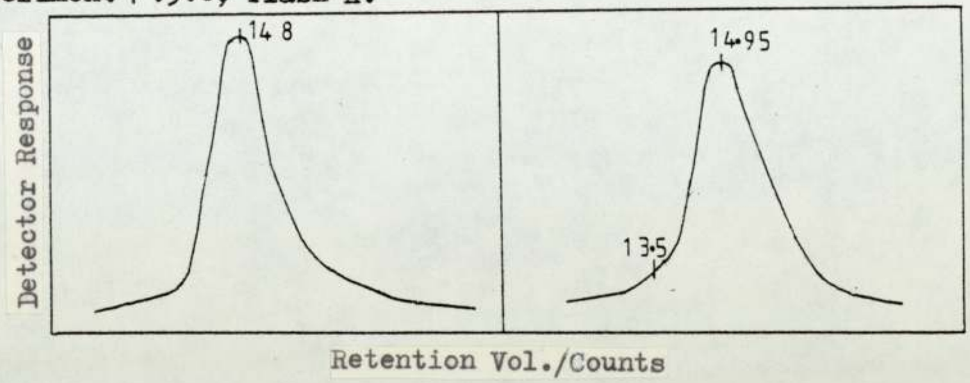


Figure 7.4. Gpc chromatograms of living poly(tetramethylene oxide) with aniline.

Trace A shows poly(tetramethylene oxide) which has been methanol terminated after 1 hour's polymerisation. The low molecular weight tale probably arises from the presence of some dead poly(tetramethylene oxide) resulting from the reaction of the living polymer with contaminents in the system. Trace B reveals two peaks, one at 14·95 counts and the other at 13·5 counts.

Table 7.4 Tabulated data from the gpc chromatograms from experiments 7.3.6.

Sample	Retention. Vol. in counts	Mol. Wt. (PSt. Eq)
A	14·8	11,000
B	14·95	10,000
	13·5	26,000

The small increase in retention time compared with the blank is characteristic of a species with ionic terminal groups. This analysis, however, implies that the polymer remains in the acid salt form even in the presence of the proton sponge. If this is so, then it is understood why the peak corresponds to the monosubstituted secondary amine only and that there is evidence of only a small amount, if any, of the furthersubstituted products. The apparent inactivity of the proton sponge is surprising, but seems to be the only way that these results can be rationalised.

Experiment B

Experiment 7.3.6.B was performed in order to assess if the quantity and order of addition of the aniline to the living polymer had any effect on the degree of substitution of the amine terminated polymer. Fig. 7.5 shows the gpc chromatograms obtained from experiment 7.3.6B.

Trace A shows a sample of the poly(tetramethylene oxide) terminated with methanol after 1 hours polymerisation, and trace B shows the effect shows the effect of adding aniline to the living polymer (4:1 molar ratio of growing chain ends to base).

The results obtained from these experiments have been tabulated in table 7.5 overleaf.

After the addition of the aniline to the living polymer there is a slight decrease in retention time which contrasts with the results obtained in experiment A of this series, where the retention time increased. The low molecular weight tail probably reflects the

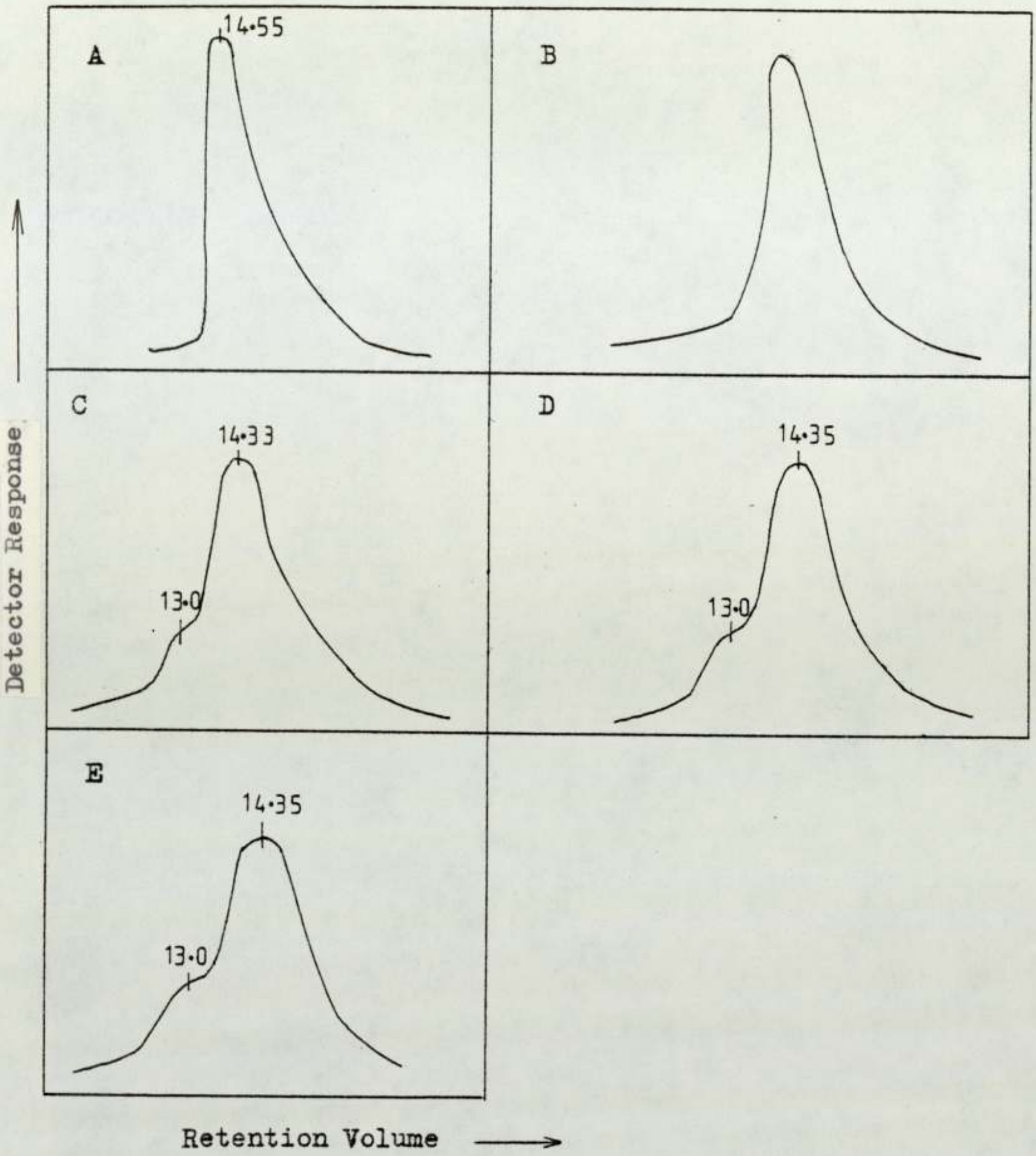


Figure 7.5 Gpc chromatograms obtained from experiment 7.3.6.B

presence of the acid salt and maybe some of the killed polymer. There is a dramatic change in trace C when the proton sponge is added. The large peak at 14·3 counts is probably due to the secondary amine and the smaller peaks implies a greater degree of substitution of the

Table 7.5 Tabulated data from the gpc results obtained from experiments 7.3.6B

Sample	Retention Vol. in counts	Mol. Wt. (PSt. Eq)
A	14·55	13,000
B	14·4	14,500
C	14·33	15,000
	13·0	36,000
D	14·35	15,000
	13·0	36,000
E	14·35	15,000
	13·0	36,000

secondary amine. Again, this may be complicated by side reactions involving the reaction between the living polymer and the proton sponge. Increasing amounts of aniline and/or proton sponge does not seem to effect the retention times of the products nor their amounts. Sample E is very similar to sample C.

Experiment C

The polymerisation of living poly(tetramethylene oxide) has previously been shown to be effected by the addition of proton sponge. In this experiment, the effect of proton sponge on the living polymer is investigated further.

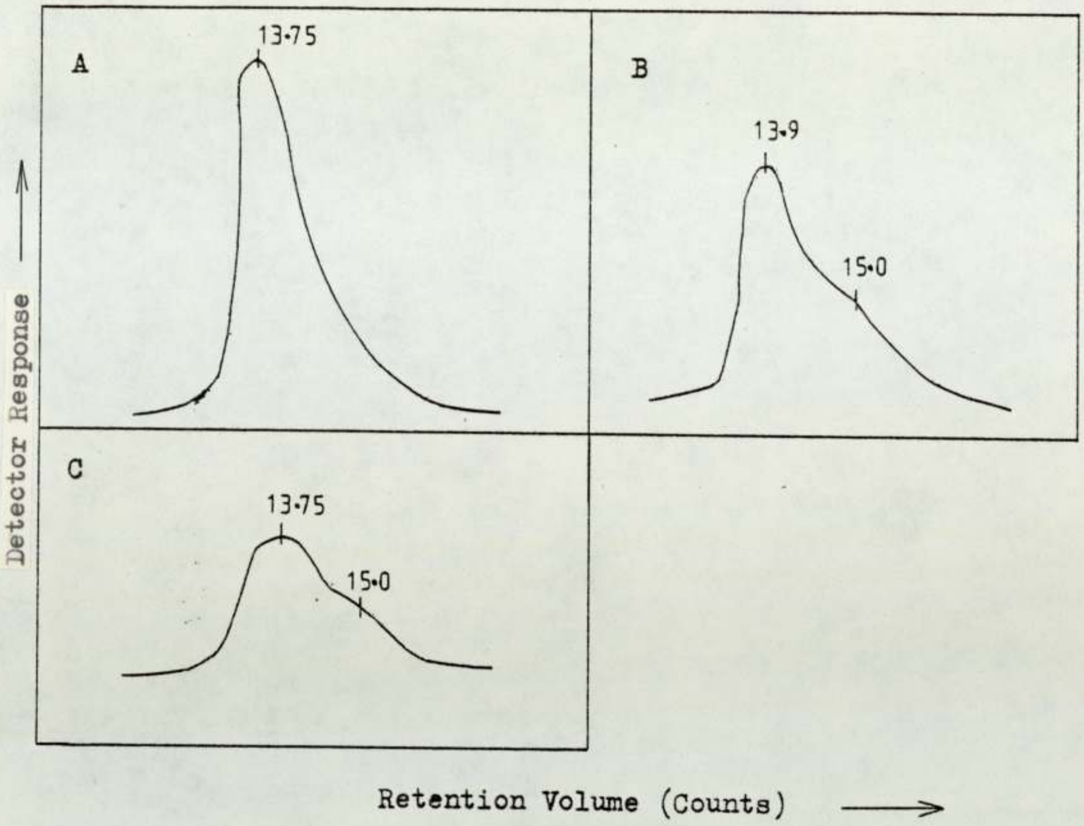


Figure 7.6 The gpc chromatograms obtained in experiment 7.3.6.C

The results of experiment 7.3.6.C are tabulated in table 7.6.
Table 7.6 Results of experiment 7.3.6.C

Sample	Retention Vol. in counts	Mol. Wt. (PSt. Eq.)
A	13·75	22,500
B	13·9	20,000
	15·0	9,700
C	13·75	22,500
	15·0	9,700

Trace A shows the gpc chromatogram of living poly(tetramethylene oxide) which has been polymerised for 4 hours. The addition of proton sponge to the living polymer, which had been polymerised for 1 hour, and then allowed to polymerise for a further 3 hours gives rise to the chromatogram shown in trace B. This trace shows two peaks at 13·75 and 15·0 counts respectively. The peak at 15·0 counts corresponds to the addition of proton sponge to the living polymer, and is in fact comparable with the low molecular weight blank obtained in experiment 7.3.6A (trace A). Thus confirming that the addition of proton sponge does result in the killing of some living polymer; this killing reaction seems to be very rapid.

The large peak at 13·75 counts indicates that some living polymer has continued to polymerise; this peak had roughly the same retention time as that of the high molecular weight blank (trace A).

The addition of aniline to the solution of living polymer and proton sponge resulted in a sample with the chromatogram shown in trace C. This trace is very similar to that shown in trace B; though there is a slight shift of the large peak to a higher molecular weight. This might be due to the formation of the disubstituted amine but this remains uncertain.

7.4.6 Termination Reactions of Living Poly(tetramethylene oxide) with Ammonia.

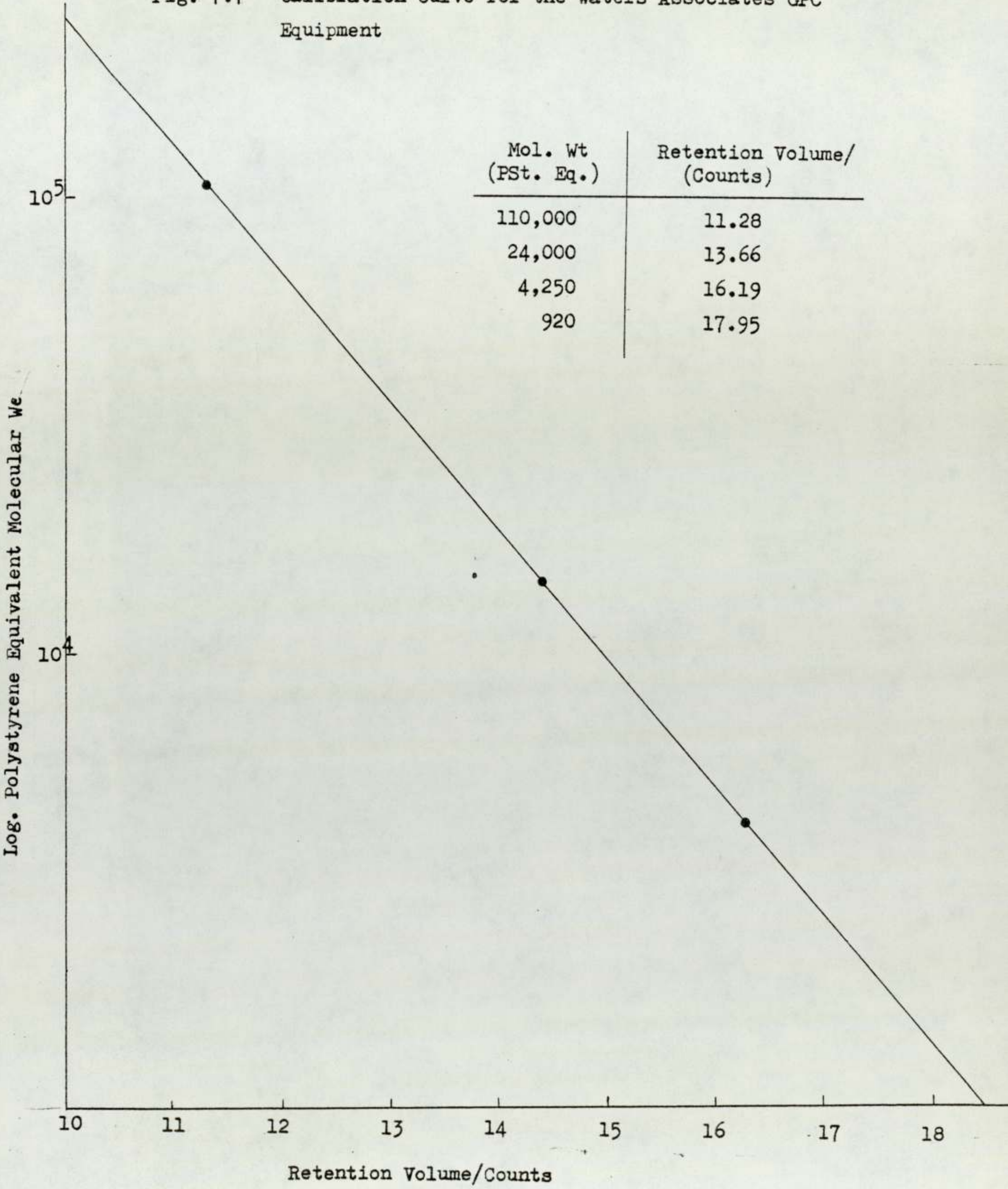
Unfortunately, the experiments using ammonia corresponding to those above produced results which defy analysis and so shall not be considered in this thesis.

7.5 Conclusions

It is clear from the preceeding sections that the reactions of living poly(tetramethylene oxide) with proton sponge are not easily understood. When proton sponge is added to a solution of the living polymer, some of the polymer is terminated, whilst the rest continues to polymerise. This terminated polymer may be coupled so as to produce polymer of much higher molecular weight than the original living polymer. How this coupling reaction occurs is not clear. Experiments performed with aniline have shown that addition of proton sponge to a solution of the living polymer and and aniline produces a slight increase in molecular weight suggesting that any polymer acid salt has been neutralised and the free primary amine reacted further to produce a disubstituted amine. This though remains to be proved. Experiments using methoxide washed terminated polymers has suggested that acid salts of the tertiary amine R_3N (R = poly(tetramethylene oxide)) have been formed.

It is apparent from these studies that the generation of trisubstituted ammonia's cannot be achieved efficiently using a proton sponges directly with living poly(tetramethylene oxide). Any further studies which attempt to continue this work must take this into account and they will probably neutralise any free acid salts (formed in the reaction between the living polymer and ammonia) with excess ammonia. More interestingly, experiments may be conducted where the acid salt is isolated, neutralised with a common base and then used as a free polymer to continue the substitution reactions.

Fig. 7.7 Calibration Curve for the Waters Associates GPC Equipment



Mol. Wt (PSt. Eq.)	Retention Volume/ (Counts)
110,000	11.28
24,000	13.66
4,250	16.19
920	17.95

APPENDIX 2

ABBREVIATIONS

a	Axial
Cp	Cyclopentene
DMNBE	Dimethyl norbornene
e	Equatorial
L	Ligands
M	Transition metal
NBE	Norbornene
PS	Proton sponge
PSt	Polystyryl chain
X	halogen

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