BLOCK CO-POLYMERIZATION BY TRANSFORMATION REACTIONS.

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SUMMARY.

The aim of this study was to use the transformation of anionic to metathesis polymerization to produce block co-polymers of styrene-b-pentenylene using WCl_6/PStLi and WCl_6/PStLi/$AlEtCl_2$ catalyst systems. Analysis of the products using SEC and ^1H and ^{13}C NMR spectroscopy enabled mechanisms for metathesis initiation reactions to be proposed.

The initial work involved preparation of the constituent homo-polymers. Solutions of polystyryllithium in cyclohexane were prepared and diluted so that the $[PStLi]_o < 2x10^{-3}M$. The dilution produced initial rapid decay of the active species, followed by slower spontaneous decay within a period of days. This was investigated using UV/visible spectrophotometry and the wavelength of maximum absorbance of the PStLi was found to change with the decay from an initial value of 328nm. to λ_{max} of approximately 340nm. after 4-7 days. SEC analysis of solutions of polystyrene, using RI and UV/visible (set at 254nm.) detectors, showed the UV:RI peak area was constant for a range of polystyrene samples of different molecular weight.

Samples of polypentenylene were prepared and analysed using SEC. Unexpectedly the solutions showed an absorbance at 254nm. which had to be considered when this technique was used subsequently to analyse polymer samples to determine their styrene/pentenylene co-polymer composition. Cyclohexane was found to be a poor solvent for these ring-opening metathesis polymerizations of cyclopentene.

Attempts to produce styrene-b-pentenylene block co-polymers, using a range of co-catalyst systems, were generally unsuccessful as the products were shown to be mainly homopolymers. The character of the polymers did suggest that several catalytic species are present in these systems and mechanisms have been suggested for the formation of initiating carbenes. Evidence of some low molecular weight product with co-polymer character has been obtained. Further investigation indicated that this is most likely to be ABA block co-polymer, which led to a mechanism being proposed for the termination of the polymerization.

KEY WORDS. RING-OPENING METATHESIS POLYMERIZATION,
ANIONIC POLYMERIZATION, CYCLOPENTENE, STYRENE.

To

Allan,

Judith and Rachel.

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LIST OF CONTENTS.

LIST OF FIGURES.

LIST OF TABLES.

GLOSSARY OF TERMS.

[Mt]	transition metal complex.	[W]	tungsten complex.
PStLi	polystyryllithium.	oligo-StLi	oligo-styryllithium.
PSt	polystyrene.	St	styrene.
Cp	cyclopentene.	Pn	pentenylene unit.
L	ligand.	M	monomer.
P_n	polymer chain	c-M_x	cyclic-oligomer.

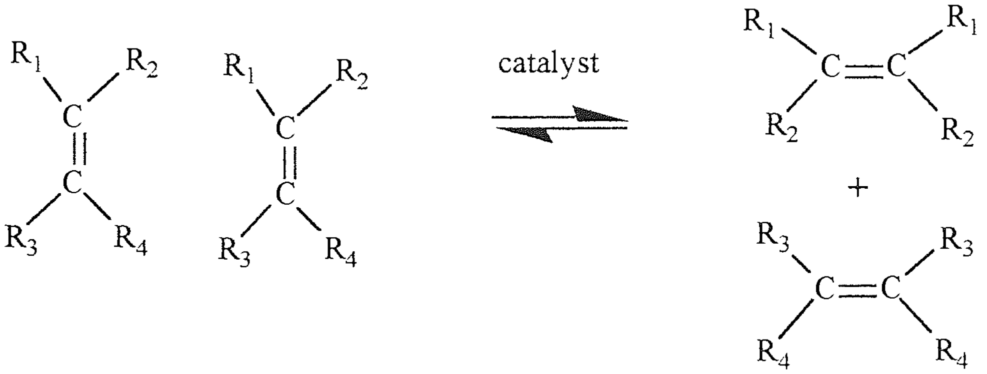
Cp:WCl_6:BuLi	molar ratio of the components in the system.
W:Li or W:Al	molar ratio wrt the concentration of these species.
$M_{wp.}$	peak molecular weight.
$\overline{M}n$	number average molecular weight.
$\overline{M}w$	weight average molecular weight.
HMWP	high molecular weight product.
LMWP	low molecular weight product.

CHAPTER 1.

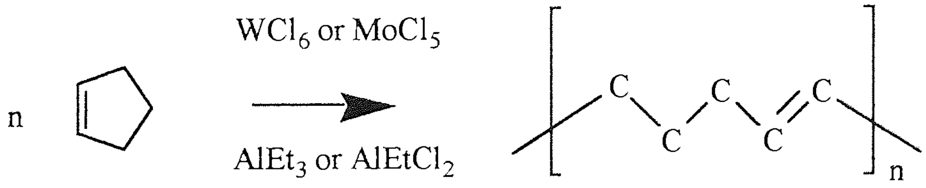
BACKGROUND TO THE STUDY.

1.1 INTRODUCTION.

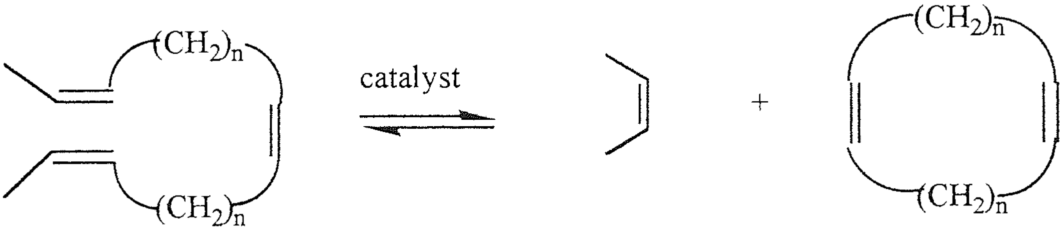
The term metathesis is derived from the Greek and in chemistry it refers to the interchange of atoms between two molecules. The discovery of catalytic metathesis in 1964 can be credited to Banks and Bailey[1], although a non catalytic form of the reaction was reported in 1931 by Schneider and Frohlich[2]. The simplest form of the reaction can be represented by the exchange:



The reactions of cyclic alkenes with metathesis catalysts, discovered by Eleuterio[3] and developed by Natta et al,[4,5] produce high molecular weight polyalkenamers or polyalkenylenes by the process of ring opening metathesis polymerization (ROMP). The reaction of cyclopentene is:



Degradation represents a third application of metathesis, in which a diene or polyene undergoes an intramolecular reaction.



The reactions are generally reversible and with the right catalyst system, equilibrium can be attained within seconds. The catalyst invariably involves a transition metal compound, whose activity is often enhanced by a co-catalyst, which is typically an organometallic compound. A third component is sometimes used as a promoter, these often contain oxygen, e.g. ethanol.

Side reactions that occur during metathesis include alkylation, isomerization, cyclization and double bond addition. However these side reactions can be minimised by the right conditions.

Metathesis can be used to convert inexpensive or over-produced alkenes into more useful homologues. Metathetic precursors are used in analytical chemistry as well as organic and bio-chemical syntheses. The properties of high molecular weight homo- and co-polymers produced by ring opening metathesis vary from elastomers to crystalline solids and several are currently produced commercially.

1.2 HISTORICAL BACKGROUND.

In 1931 Schneider and Frohlich[2] reported that heating propene to 725°C in a silica reaction tube converted it into a mixture of ethene and 2-butene. This symmetry-forbidden reaction is thermally activated but is overall athermal because of the cleavage and then re-formation of a carbon to carbon double bond. The random distribution of products at equilibrium is entropy controlled and so can be attained from either side of the equilibrium.

Banks and Bailey[1] were the first workers to use heterogeneous catalysts in metathesis reactions. They successfully converted acyclic alkenes with 3 to 8 carbon atoms into roughly equimolar amounts of high and low molecular weight homologues, using molybdenum or tungsten hexacarbonyl supported on alumina, at 150°C and 30 atmospheres.

The polymerization of cyclopentene and other cyclic alkenes with the heterogeneous catalyst system of MoO_3/ Al_2O_3, activated by hydrogen at 480°C and then used with $LiAlH_4$ in a benzene suspension, was first recorded by Eleuterio in 1957 and was patented in 1963[3]. In 1960 Truett et al[6] published details of the polymerisation of norbornene (bicyclo(2.2.1)hept-2-ene) using the catalyst system $TiCl_4$ / $LiAl(C_7H_{15})_4$ and demonstrated that the double bonds in the polymer were mainly *trans* and that oxidative degradation of the polymer produced cyclopentane-*cis*-1,3-dicarboxylic acid. However from 1964 the high molecular weight product was more efficiently produced using homogeneous catalyst systems developed by Natta et al.[4,5] The catalyst systems used were molybdenum or tungsten halides or aluminium alkyls and alkyl halides. Natta put forward the theory that the reaction proceded by a transalkylation mechanism involving cleavage of the carbon to carbon single bond α to the double bond.

Calderon[7] adopted the term olefin metathesis when investigating the reaction of acyclic alkenes with the catalyst system WCl_6/ EtOH/ $EtAlCl_2$. He recognised similarities with the polymerization of cycloalkenes and distinguished between two mechanisms, transalkylation and an alternative involving cleavage of the carbon to carbon double bond, called transalkylidenation. Evidence was produced by Calderon [8,9] and then by Dall'Asta and Motroni[10] to show that both types of metathesis proceed by the latter mechanism and this will be discussed later.

The range of substrates and homogeneous and heterogeneous catalyst systems developed for metathesis will also be reviewed. Normally only homogeneous catalyst systems can be used for ring opening polymerization, but these can be one, two or three component systems. The main catalyst is usually a transition metal compound (often a halide) and the co-catalyst is an organometallic species of group I to IV or a Lewis acid. Most systems are very sensitive to oxygen, which in small amounts has been shown to activate the catalyst,[11,12] while in larger quantities is found to destroy catalytic activity.

The kinetics and mechanism of metathesis has been studied extensively since 1967. Bradshaw[13] suggested a four centred cyclobutane intermediate and although it was initially considered to be forbidden by the Woodward-Hoffmann rules of symmetry[14] , Mango et al[15] proposed that the role of the transition metal was to allow such reactions to occur.

In 1970 Herisson and Chauvin[16] proposed a chain mechanism for ring opening metathesis polymerization using homogeneous catalysts. The intermediate species indicated by this mechanism are a carbene and a metallocyclobutane ring and the use of stable forms of these as precursors for metathesis, has led to the acceptance of this propagation mechanism. However possible initiation, transfer and termination reactions during metathesis were less clearly explained.

The kinetic results of different metathesis reactions vary and both first and second order dependence in substrate has been reported. The diverse reaction conditions, which produce a variety of metathesis and other products, give some indication of the number of possible kinetic routes for metathesis and increases the belief that a general theory to explain all systems is unlikely to be advanced.

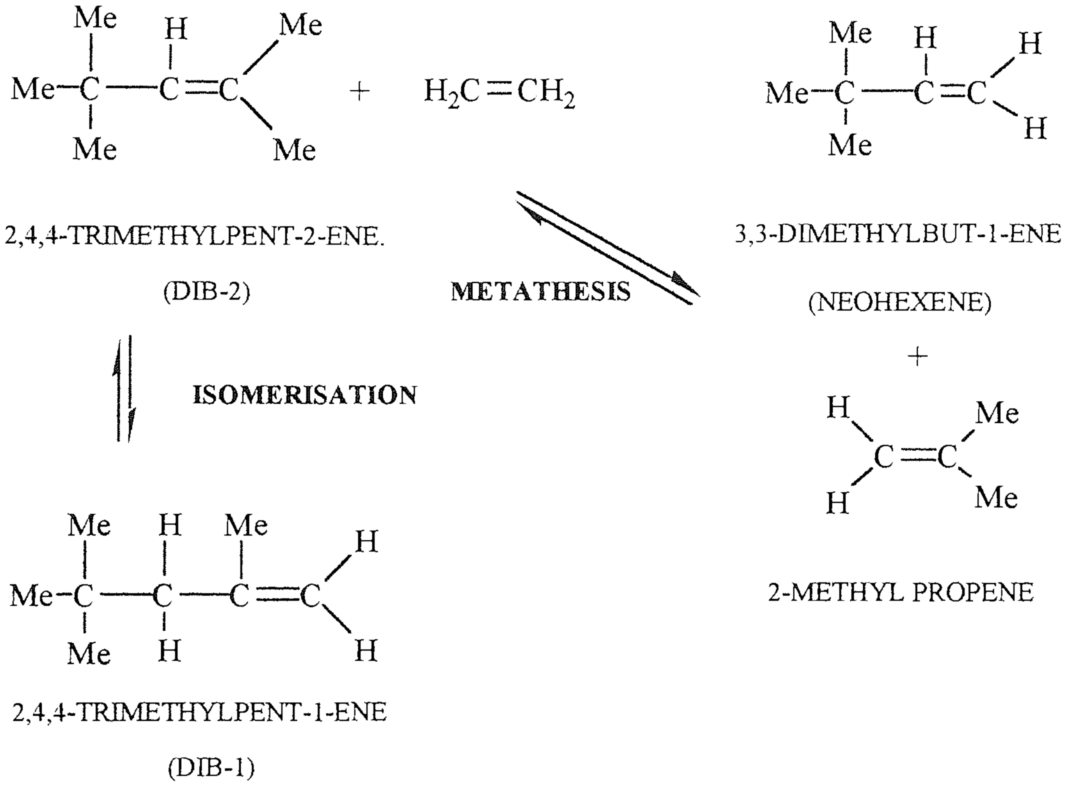
An important development has arisen from the initial work by Tebbe et al[17,18] in 1978-9, a metathesis catalyst was developed from the reaction of titanocene dichloride (dicyclopentadienyltitanium dichloride) and anhydrous aluminium chloride. Grubbs et al used this "Tebbe" compound to produce titanacyclobutanes of strained cycloolefins like norbornene and then by the controlled addition of the monomer, showed that living metathesis polymerization occurred.[19,20]

1.3 INDUSTRIAL APPLICATIONS.

Streck[21] makes the claim that olefin metathesis has found a range of industrial applications wider than any other single reaction. The original researchers were involved in the petrochemical industry[1,2,4,5] and the main developments of metathesis have been in this area. The now defunct Phillips Triolefin

Process[22] was the first major industrial application, converting excess propene into ethene and 2-butene, at temperatures between 370 and 450°C and using WO_3/SiO_2 as the catalyst system. The plant was closed in 1972, but the reverse Phillips process has been operating in Texas since 1985. As with the original process, local plant conditions which produced large quantities of a particular alkene, make the conversion viable.

The conversion of relatively inexpensive olefins into speciality, high purity olefins is typified by the neohexene process developed by Banks et al.[23] This involves the conversion of a commercial mixture of diisobutene (DIB-1 and DIB-2) into 3,3-dimethylbut-1-ene by ethenolysis[24] using a mixture of isomerization and metathesis catalysts.



Only the DIB(2) isomer produces neohexene, the mixed catalyst system of WO_3-/SiO_2/MgO achieves 80 to 85% selectivity for this product, which is used for the synthesis of musk for the perfume industry.

Shell has developed two large scale industrial processes based on metathesis. The Shell Higher Olefin Process (SHOP)[25] is used for the production of linear higher olefins, which are converted into alcohols and then into nonionic detergents by oxyethylation. The Further Exploitation of Advanced Shell Technology or FEAST project[26] has been operating since 1986 and converts cyclic diolefins into α, ω dienes by ethenoloysis using promoted rhenium oxide on alumina as the catalyst.

Ring opening metathesis polymerization has to be economically attractive to compete with other industrial methods of polymer production. This means that relatively high production costs, compared to these other processes, have to be offset either by the use of very cheap monomers, or by the production of speciality polymers or materials with improved processability. Although there has been considerable development work on the production of trans-(1-polypentenylene) or trans-polypentenamer (TPR) as a general purpose rubber by Bayer, Goodyear and other companies,[27,28,29] it has never been produced competitively because of the availability of polybutadiene, polyisoprene, and natural rubber.

A special type of polyoctenamer has been developed[30] and since 1981 "Vestenamer" has been in production as a rubber processing aid used in elastomer blends for gaskets, brake hoses and in some parts of car tyres.

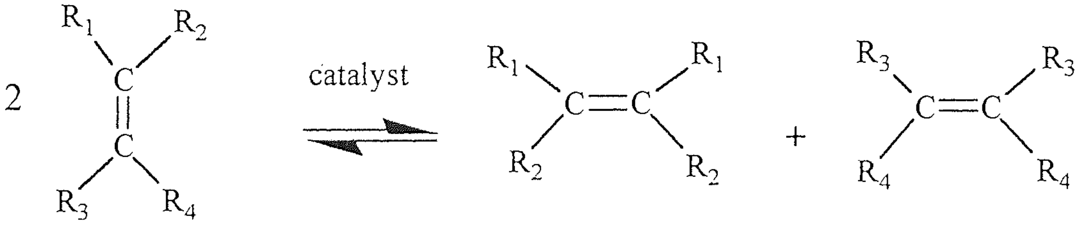
Polynorbornene is the polyalkenamer produced in the largest amounts and the French company CDF-Chemie (now called Orkem) have produced it as "Norsorex" since 1976. The highly strained bicyclic structure of the monomer extends the range of possible polymerization catalysts; the system used is ruthenium chloride, butanol and hydrogen chloride. The two main features of this polymer that make it economically viable are first its thermoplastic behaviour and secondly its ability to absorb up to five times its own weight of extender or plasticizer oil. Vulcanisation of polynorbornene gives it high dynamic damping properties which make it useful in the processing of both noise- and vibration- damping articles.

Polydicyclopentadiene has been produced in Canada since 1985 as "Metton" by PPD-Hercules Inc..[31] The injection moulding process produces a partly crosslinked material in situ and these shaped parts are used as car parts, satellite antenna dishes and the bodies of snow mobiles. More recent reports[32] indicate that this system has been extended to joint ventures in Japan and the Netherlands. The comparative cheapness of the monomer compared to styrene, its relatively easy of isolation from the C_5 steam cracker fraction of petroleum and its availability, as at present only one fifth of the C_5 is taken for chemical use, indicate that there is the potential for expansion of the industrial production of both DCPD homo-and co-polymers.

1.4 SUBSTRATES INVOLVED IN METATHESIS.

1 4.1 ACYCLIC ALKENES.

The catalytic metathesis of linear or branched chain acyclic alkenes as shown in the equation below is entropy controlled producing at equilibrium a mixture of olefins **1**, **2** and **3** in the mole ratio 2: 1: 1.

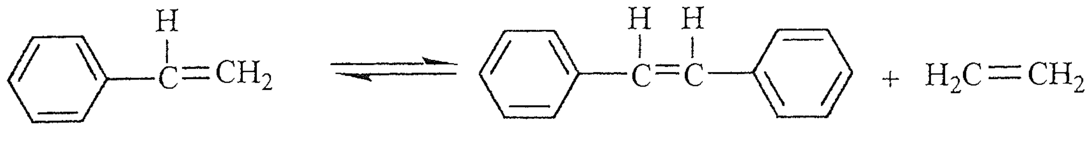


1 **2** **3**

If one of the products is removed, for example ethene, in the metathesis of terminal olefins, good yields of internally symmetrical olefins are obtained. Calderon[33] showed that the degree of substitution on the carbon at the double bond controlled the reactivity of the alkene, he showed a decrease in reactivity:

$$CH_2 = > RCH_2.CH = > R_2CH.CH = > R_2C =$$

However alkenes with bulky groups attached to this carbon, e.g. styrene (CH_2=CHPh), undergo metathesis[34].



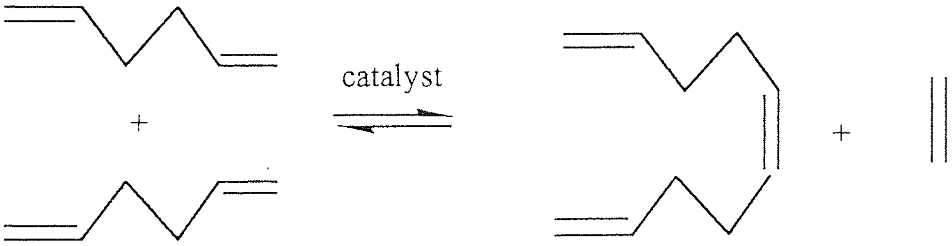
PHENYLETHENE
(STYRENE

1,2 DIPHENYLETHENE
(STILBENE)

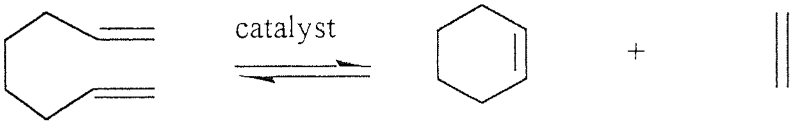
The reverse cometathesis reaction has been the basis of much research, as it represents one stage of a possible industrial process to convert toluene into styrene.[21]

1.4.2 ACYCLIC DIENES AND POLYENES.

Acyclic dienes and polyenes undergo both inter- and intra-molecular metathesis as demonstrated by the following examples investigated by Zeuch et al.[35] 1,5-Hexadiene reacts intermolecularly to produce 1,5,9-decatriene and ethene:



1,7-octadiene forms cyclohexene and ethene by intramolecular cyclisation.



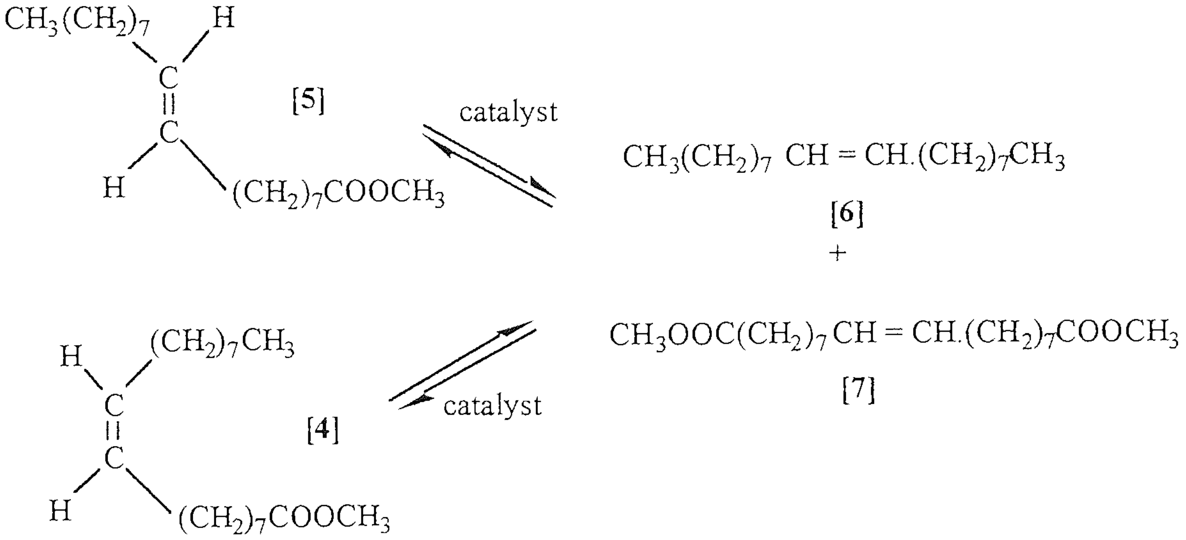
Cross cometathesis between a simple alkene and polyalkenamers causes scission of the polymer and analysis of the fragments can be used to identify monomer sequences in the chain. In the reaction of styrene-butadiene co-polymers with 2-butene, the extent of the double migration during the free radical crosslinking of the butadiene can be determined.[34]

Recently it has been shown[36] that acyclic dienes can under go metathesis polymerization when the catalyst system is Lewis acid free. These acyclic diene metathesis (ADMET) polymerizations are described in section 1.4.5.2.

1.4.3 FUNCTIONALLY SUBSTITUTED ACYCLIC ALKENES.

The metathesis of simple olefins has limited synthetic use but the introduction of a functional group into the alkene molecule greatly increases the potential for novel synthetic pathways. Unfortunately most metathesis catalysts are easily poisoned by polar compounds and Calderon[9] showed that polar groups deactivate the carbon to carbon double bond, so metathesis does not occur if the vinylic hydrogens are replaced by chlorine. However O'Hara and Bradshaw[37] reported that 5-bromo-1-pentene and the 2-pentene do undergo metathesis.

The metathesis of unsaturated esters has been studied extensively since the initial work of van Dam and co-workers in 1972,[38] who reported the selective conversion of methyl oleate (methyl *cis*-9-octadecenoate)[4] and methyl elaidate (methyl *trans*-9-octadecenoate)[5] into equimolar amounts of 9-octadecene[6] and dimethyl 9-octadecene dioate[7]. The catalyst system of WCl_6 /Me_4Sn produced 50% conversion at 110°C in two hours and became recognised as the best homogeneous system for this type of metathesis.

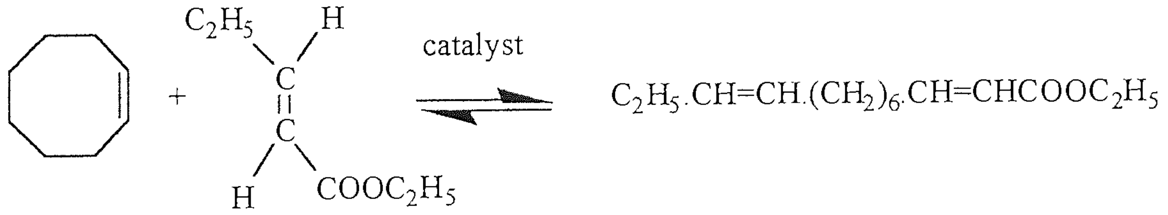


Verkuijlen et al[39] showed that linear unsaturated esters undergo metathesis provided that the carbon to carbon double bond is separated from the ester group by at least one CH_2 group.

Heterogeneous catalyst systems of rhenium oxide on silica-aluminas or boria-aluminas, which owe their activity to the Bronsted acidity of the carriers, have also been used to metathesise functionalised alkenes. They are promoted by small amounts of alkyltin compound and are reported[40] to be less easily poisoned than homogeneous systems, also they have the advantages of easy separation from the system and re-usability. The systems can be used with substrates (e.g. allylacetate, allyl ethers and vinyl chloride) which cannot be metathesised by the homogeneous tungsten-based system.

A recent study[41] of tin-free molybdenum oxide/silica system, developed by a Russian team[42] and involving an activation procedure based on photo-reduction in a CO atmosphere, showed it to have no advantages over the more easily activated Re_2O_7/Bu_4Sn systems, except when considering environmental and occupational safety.

Cometathesis of unsaturated esters with alkenes has been investigated because of possible novel synthetic routes. Verkuijlen[39,43] showed that even methylmethacrylate, which is inactive to self metathesis, reacts with a symmetrical alkene like *trans*-3-hexene producing a precursor for the synthesis of α-methyl β-unsaturated esters and Otton et al[44] have carried out the cometathesis of cyclic alkenes, like cyclooctene, and ethyl 3-pentenoate.



The long-chain linear di-unsaturated mono-esters are biodegradable and have potential use in the surfactant industry.

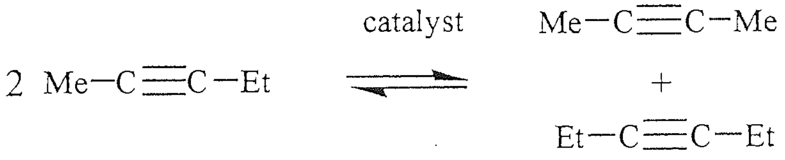
Mol[45] has reviewed the metathesis of unsaturated nitriles[46], amines[47] and ethers[48], which continue to be the subject of much research. More recent summaries of the progress made in several different areas[40,42] emphasise that the problems of low reaction rates and poor stereoselectivity in the synthetic applications remain. However it is important to recognise the number of biologically active organic substances and related compounds that have been produced with the aid of metathesis, insect pheromones and fragances amongst them.

1.4.4 ALKYNES.

The three possible reactions of alkynes with metathesis catalysts will be considered separately.

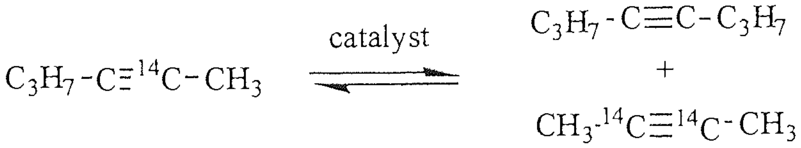
1.4.4.1 Metathesis of Alkynes.

This process occurs mainly with di-substituted alkynes using heterogeneous catalyst systems. Productive metathesis of alkynes was observed by Pennella[49] using 2-pentyne catalysed by WO_3/SiO_2 at 350°C. Some cyclotrimer was also produced[50] but a 53% yield of 2-butyne and 3-hexyne was obtained.



$$2\ \mathrm{Me{-}C{\equiv}C{-}Et} \xrightleftharpoons{\text{catalyst}} \mathrm{Me{-}C{\equiv}C{-}Me} + \mathrm{Et{-}C{\equiv}C{-}Et}$$

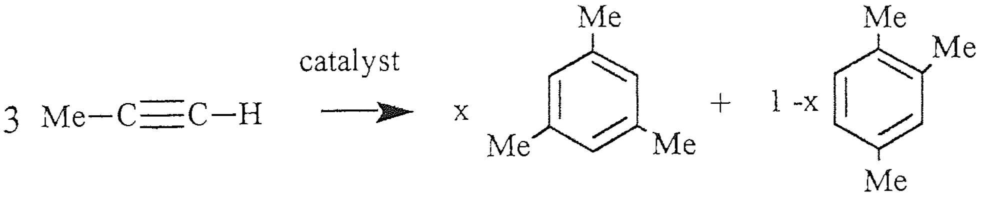
Mortreux has confirmed,[51] by the use of isotopic labelling, that triple bond cleavage occurs in the metathesis reaction.



$$C_3H_7\text{-}C{\equiv}{}^{14}C\text{-}CH_3 \xrightleftharpoons{\text{catalyst}} C_3H_7\text{-}C{\equiv}C\text{-}C_3H_7 + CH_3\text{-}{}^{14}C{\equiv}{}^{14}C\text{-}CH_3$$

1.4.4.2 Cyclisation of Alkynes.

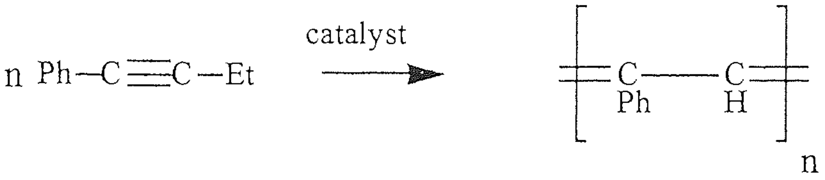
Mono-substituted alkynes do not undergo productive metathesis but 1-propyne, 1-butyne and 1-pentyne all undergo cyclo-trimerization with the heterogeneous catalyst systems of WO_3/SiO_2 at 90°C[46] and MoO_3/SiO_2 at 350°C.



[51] The trisubstituted benzene products are formed by a head to tail linkage of three alkyne units or with one unit reversed.

1.4.4.3 Polymerization of Alkynes.

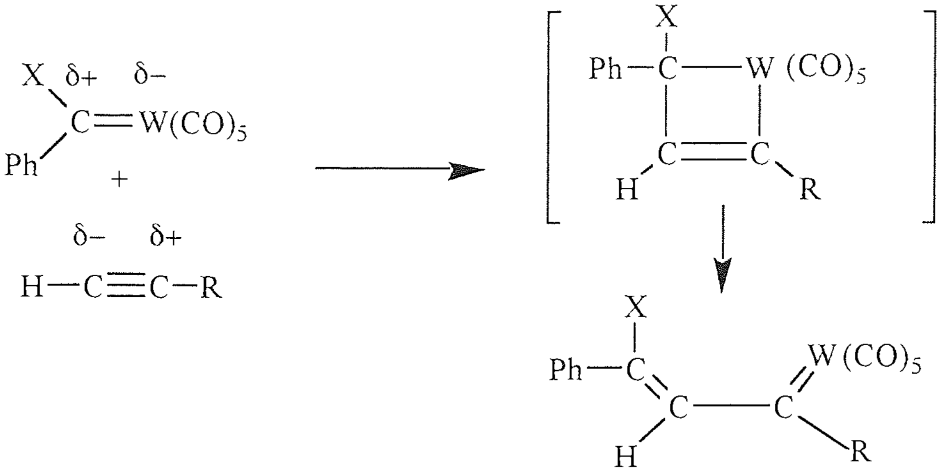
Mono-substituted alkynes either cyclise, usually with heterogeneous catalyst systems, or polymerise, invariably with homogeneous catalyst systems, and these systems also polymerise di-substituted alkynes.



Alkynes can be polymerized by recognized Ziegler-Natta catalysts and the stereo-regularity of the reaction of ethynes with the catalyst system $Ti(OBu)_4/Et_3Al$ producing all *cis*-polymer at -78°C and all *trans*-polymer at 150°C suggests a Ziegler-Natta insertion mechanism for addition polymerisation[52]. However this does not exclude an alternative mechanism using metathesis catalysts.

The isolation and identification of either a transition metal carbene or carbyne, formed from the alkyne, was one of the initial aims in confirming a metathesis -type mechanism. Fischer[53] showed it was possible to form simple adducts of carbenes and alkynes and demonstrated that the alkyne triple bond was converted to a single bond on insertion. Also in 1980 Katz and co-workers[54] used carbenes to initiate the polymerization of mono-, di- and cyclo- alkynes at 60°C. The number average molecular weights of the mono-substituted polyalkynes were significantly higher than those produced with other types of polymerization. There was evidence that phenylethyne could be used as a co-catalyst for metathesis either with the Fischer carbene or with tungsten hexachloride for the polymerization of cycloalkenes[55] and for the metathesis of *cis*-2-pentene[56]. The catalytic activity of the phenylethyne was found to decrease if the concentration was above 1% and analysis of the products by GPC showed co-polymerization had occurred[57]. Amass and Farren[58] reported the production of a soluble block co-polymer when ethyne was added to an active cyclopentene polymerization.

Similar mechanisms for the propagation stages of both alkene and alkyne metathesis polymerization can be proposed. The alkyne reaction progresses via the metallacyclobutene and vinyl alkylidene intermediates with the conversion of the original triple carbon-to-carbon bond into a single bond.

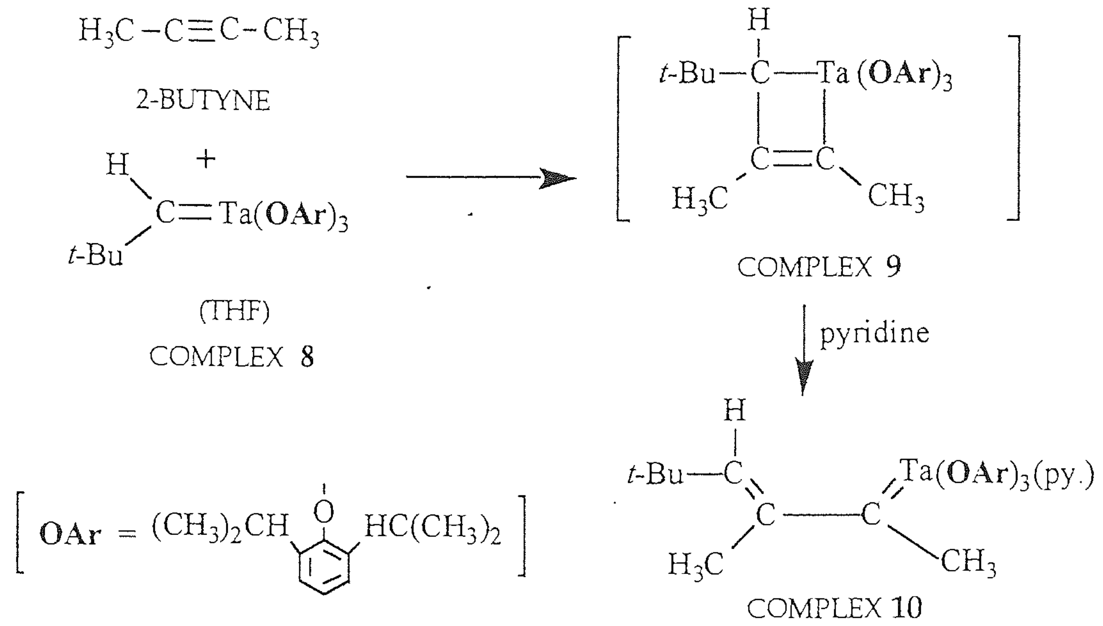


The polarity of the original metal carbene bond, as shown in the reaction sequence, has been confirmed by the effect of substituents on the phenyl group on the rate of reaction.

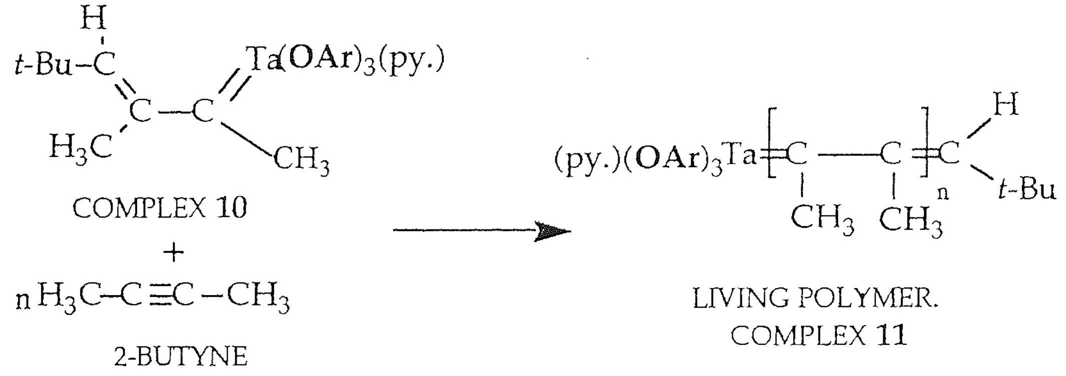
Schrock et al[59] have achieved two further advances in the confirmation of this mechanism.

1. Phenyl-substituted carbenes of tantalum were produced in solutions of THF, (e.g. Ta(CH-t-Bu)(OAr)$_3$ complex 8) and treated with 2-butyne or other di-substitued alkynes to produce the tantalacyclobutene (complex 9). Addition of pyridine induced ring opening to form the vinyl alkylidene complex 10.

   The structure of the final product was elucidated by X-ray study and was shown to be either a highly distorted trigonal bipyramid or a square pyramid.



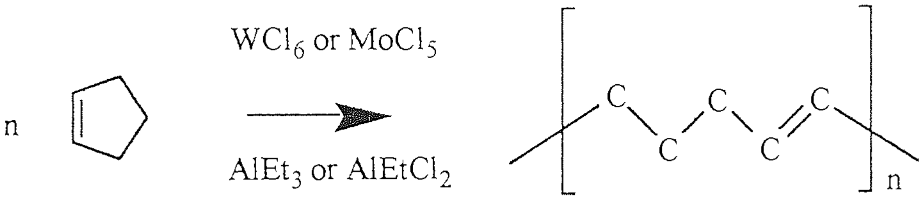
2. The reactivity of this species with carbonyl groups in "Wittig-type" reactions, as well as with alkenes and alkynes, was investigated. The addition of 200 equivalents of 2-butyne to complex 10 produced the living polymer 11, which was cleaved by treatment with benzaldehyde and had a polydispersity of less than 1.05.



1.4.5. CYCLIC AND BICYCLIC ALKENES.

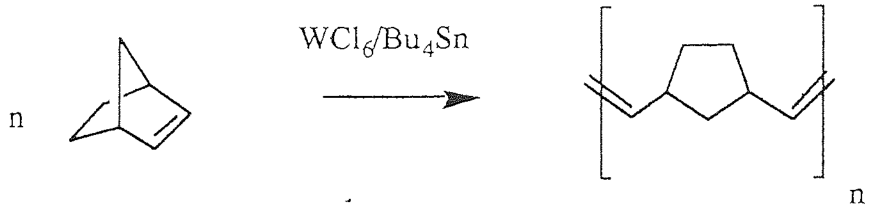
Eleuterio[3] and Truett[6] are credited with the initial discovery of the ring opening polymerisation of cyclic alkenes but Natta et al[4,5,60] first produced reasonable yields of the polymers from unsubstituted cyclic alkenes with 5, 7, 8 and 10 carbon atoms using homogeneous catalyst systems.

Except for cyclohexene, mono-cycloalkenes with four to twelve carbon atoms in the ring have now been successfully polymerised. The products vary in properties from amorphous elastomers to crystalline solids because as Natta showed,[4] the degree of crystallinity is related to the stereochemistry of the polymer and this varies with factors like the catalyst/co-catalyst system used, the ratio of the two and the temperature of the reaction. He found that WCl_6 and Et_3Al produced mainly *trans*-polymer but with $MoCl_5/Et_3Al$ the main product was the *cis*-isomer.



Thermodynamic considerations explain why cyclohexene does not polymerise metathetically. The overall free energy of polymerization has to be negative in the prevailing conditions for polymerization to occur and for cyclic alkenes with 4 and between 8 and 11 carbon atoms, the high level of ring-strain makes the polymerizations pro-enthalpic and this is the dominant factor. However the ring-strain is less for the rings with 5 to 7 atoms and although the overall free energy change for cyclopentene and cycloheptene are still negative, the negligible ring-strain of cyclohexene tips the balance and makes polymerization thermodynamically unfavourable. Alkyl substitution invariably makes the free energy change for polymerization less negative and so the polymerizability of substituted five to seven carbon cycloalkenes is delicately balanced thermodynamically. It is found that very few substituted cyclopentene compounds polymerize.[61]

Bridging groups introduced into the cyclicalkene structure can increased ring strain and make polymerization more favourable. Several strained bicyclic and polycyclic substrates have been investigated but norbornene (bicyclo(2.2.1)-hept-2-ene) and related compounds have generated most interest since the initial work of Oshika[62]. Unlike linear polyalkylidenes the polynobornene does not undergo inter or intramolecular backbiting because steric crowding prevents this.



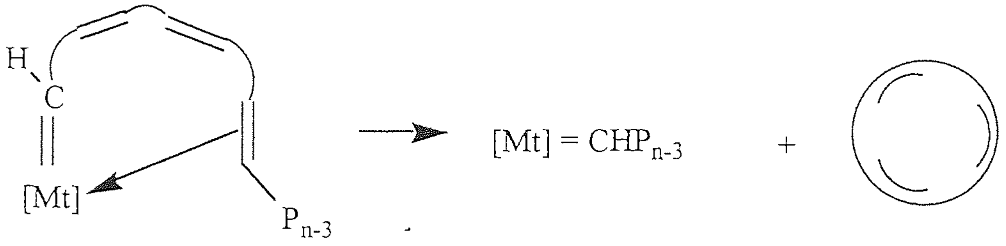
The stereochemistry of propagation is fixed within the structure and Ivin, Rooney and co-workers have shown that the stereochemistry can be tailored from the catalyst system used.[63-65] They also showed that WCl_6, $ReCl_6$and $MoCl_5$ on their own will produce polymeric material from norbornene at ambient temperature and even $EtAlCl_2$ alone causes metathetic ring opening.[66,67]

Calderon[8] was the first to report the formation of oily, low-molecular-weight products during the ring opening polymerization of cyclooctene and 1,5 cyclooctadiene. Separation of these substances and analysis by GLC, GPC and mass spectrometry showed them to contain cyclic oligomers.[68,69] A typical GPC trace from a mixture containing the cyclic oligomers from the reaction of cyclooctene shows a series of peaks of increasing size with elution volume. The phenomenon of the formation of cyclic oligomers occurs with many types of ring opening polymerization.

Chauvin[70] investigated the formation of cyclic oligomers of 1,5 cyclooctadiene and found a continuous series $(C_4H_6)_n$, as if the parent molecule were cyclobutene. The yield of cyclic oligomers, compared to linear polymers, is greatest with low monomers concentrations and this can be related the reactions of the propagating carbene. As will be shown later, the propagation of the linear polymer chain, is thought to be by a second order reaction between the transition metal carbene ($[Mt] = CHP_n$) and the carbon to carbon bond of the monomer (M), which then reform a new carbene:

$$[Mt] = CHP_n \quad + \quad \text{Monomer} \quad \text{--->} \quad [Mt] = CHP_{n+1} \; .$$

However the polyalkylidene has unsaturation along its entire length and when the monomer concentration is low the chances of unimolecular intramolecular backbiting must increase:



Cyclic oligomers for cycloocta-1,5-diene are not just of the series (C_8H_{12}) but also sesquioligomers as though cyclobutene were the monomer. The theory of ring-chain equilibria is quantified by the Jacobson-Stockmayer theory[61] in which the basic assumptions are as follows.

1. The distribution of ring size is determined only by entropy factors because the rings formed are strain-free.
2. End-to-end distances of linear chains obey Gaussian statistics, with no allowance for excluded volume effect. This assumes a random flight model.
3. The probability of ring formation is governed by the frequency of given ring co-incidence.
4. The probability of bond formation is independent of whether co-incident ends are from the same chain or from different ones.

If the polymer chain length is high the formation of cyclic-oligomers (c-M_x) from polymer (M_y) can be represented by the equilibrium reaction:

$$M_y \;===\; M_{y-x} \;+\; c\text{-}M_x$$

The concentrations of M_x and M_{y-x} will be almost the same if the chains are long. The equilibrium constant (K_x) is given by:-

$$K_x = [c\text{-}M_x]$$

and according to the Jacobson-Stockmeyer theory K_x should be proportional to $x^{-2.5}$. The cyclo-oligomers produced by 1,5-cyclooctadiene, cyclooctene and several other cyclic alkenes show resonable agreement with the predicted behaviour especially for the larger ring sizes, where ring strain is absent.

The probability of ring formation decreases with increasing ring size and K_x consists of several components because of *cis/trans* isomers in the rings. Sato[71] used GLC to separate these isomers and NMR studies have revealed that for small rings a higher percentage have *cis* arrangement, 80% *cis* content for C_{16} oligomers, but this pecentage falls for large rings, 52% *cis* content for C_{104} oligomers.

The approach to equilibrium varies depending on the rate constants for the propagation and cyclisation reactions for a particular system. The two extreme cases starting with pure monomer are listed.

1. Polymerization occurs exclusively until virtually all the monomer is used up, then the polymer undergoes intramolecular cyclisation producing the cyclic oligomers until equilibrium is reached. The measurement of the viscosity of the system as a function of time, produces a characteristic maximum intrinsic viscosity in this type of reaction. Cyclopentene has been shown to behave in this way using the efficient catalyst system of WCl_6/ $(i\text{-}Bu)_2AlCl$ in toluene at -20°C[72].
2. The intramolecular cyclisation reaction occurs as soon as the formation of strain-free rings is possible and the production of high molecular weight polymers only starts when the equilibrium concentration of cyclic oligomers is reached. The ring opening polymerization of cyclo-octene at low concentrations in chlorobenzene shows this type of behaviour,[73] when the catalyst system is $WCl_6/EtAlCl_2/EtOH$ and the reaction is carried out at 0°C.

1.4.5.1 Living Polymerization of Bicyclic Alkenes.

The role of carbenes and metallacyclobutane complexes in the metathesis propagation reaction has been established for about twenty years, but more recently work by Tebbe,[17] Grubbs,[19,20] Schrock[74,75] and co-workers led to the production of stable forms of these species, which were able to initiate living polymerization of norbornene. Ring opening metathesis polymerization is generally associated with reactions in which chain termination and chain transfer occur at the same time as propagation and so the molecular weight distributions of the polymers produced, show the products to have broad polydispersities.

Living polymerization was first reported by Ziegler[76] in 1936, who recognised that, in the polymerization of stilbene and styrene initiated by potassium alkyls, chain growth occurred by continuous monomer addition to an active propagating species and no chain termination or transfer occurred. Flory[77] realised that in this type of reaction, if the rate of initiation was comparable to, or faster than, the rate of propagation then a narrow molecular weight distribution would be obtained. Szwarc[78] first demonstrated the effect of introducing additional amounts of monomer to a solution of living polymer. The system was sampled and analysed to show that the molecular weight of the polymer was increasing regularly with further monomer addition and that the polydispersity of the product was less than 1.10. Szwarc adopted the term living polymerization and identified the following characteristics of these systems.

1. The living polymer only grows while there is monomer to feed it but then remains living, so growth will continue if further monomer is added.

2. Although the system (in the absence of impurities and transfer agents) is described as living, the reactive ends can be killed by:

a) spontaneous termination-based on the laws of probabitiy and the conditions of polymerization,

b) killing reactions-when a reagent is added to destroy active ends often intentionally, to introduce an active functional group.

3. The degree of polymerization (DP_n) is the ratio of the total number of moles of monomer added to the total number of moles of unifunctional active ends.

4. If the rate of initiation is very fast, then all the initiator particles are immediately converted to propagating centres and the total number of active ends is equal to the concentration of the initiator. All the polymer

chains will propagate at almost the same rate and to the same degree of polymerization. This is called ideal polymerization and has the following characteristics.

In the absence of transfer and termination only the rate of propagation has to be taken into account, and so the rate of polymerization (R_p) obeys simple pseudo-first order kinetics[79].

$$R_p = k_p \text{[monomer] [active ends]}$$

$$\text{but [active ends]} = \text{[initiator]} = \text{constant}$$

$$\text{thus} \quad R_p = k_{app} \text{[monomer]}$$

Where k_{app} is the 'apparent' pseudo-first-order rate constant and the rate of polymerization decreases linearly with consumption of monomer. The molecular weight distribution (MWD) or polydispersity index (PDI), which is the ratio $\overline{M}_w : \overline{M}_n$ will be of Poisson type.

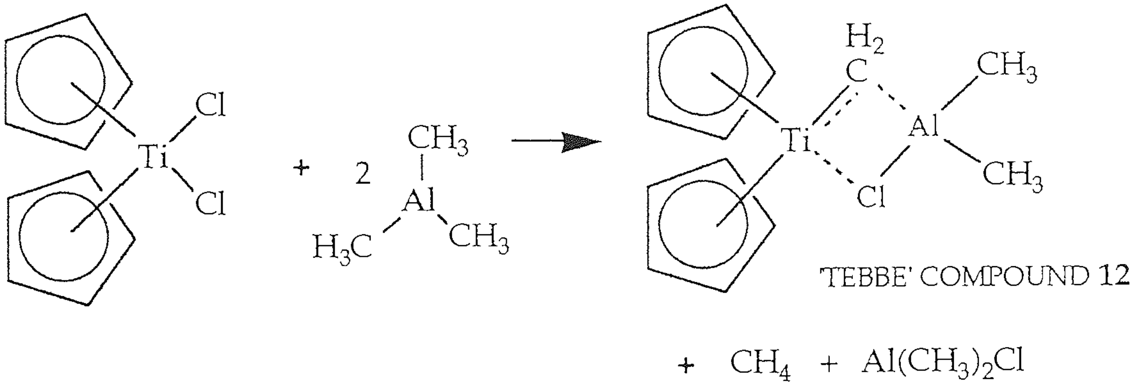
$\overline{M}_w$ = weight average molecular weight of the polymer.

$\overline{M}_n$ = number average molecular weight of the polymer.

For ideal polymerizations $1.01 < \overline{M}_w / \overline{M}_n < 1.10$.

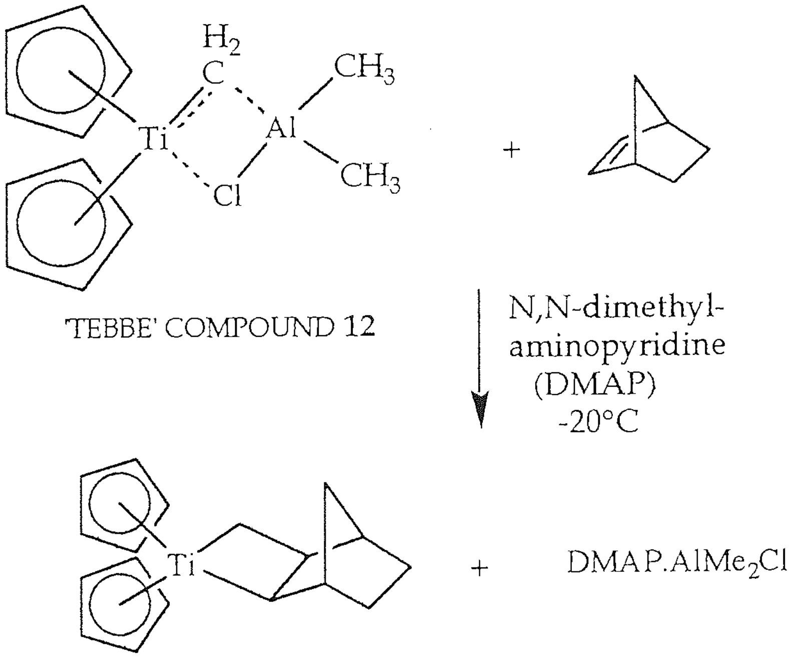
Although Szwarc initially studied anionic polymerizations, any system that has these characteristics is described as living and will show the features of anionic polymerization. The control that can be exercised over these systems makes them very attractive for polymer synthesis, not only for the preparation of homo-polymers of known molecular weight but also because their living character provides the opportunity to make co-polymers. Block co-polymers formed by changing the monomer feed are just one example of this. Extensive work has also been carried out on transformation reactions from one type of living polymerizations to another and this important area will be reviewed.

The first living metathesis polymers were prepared by Grubbs[19,20] using the relatively unreactive titanocylobutanes of norbornene, produced by the reaction of the bicyclic alkene with the bimetallic complexes of titanocene dichloride and trimethylaluminium which was first described by Tebbe[17]. The dark red 'Tebbe' compound 12 ($(\eta^5$-$C_5H_5)_2Ti$-$CH_2AlCl_2Me)$ is formed by the following disproportionation reaction in an inert atmosphere at 25°C over a period of several days.



'TEBBE' COMPOUND 12

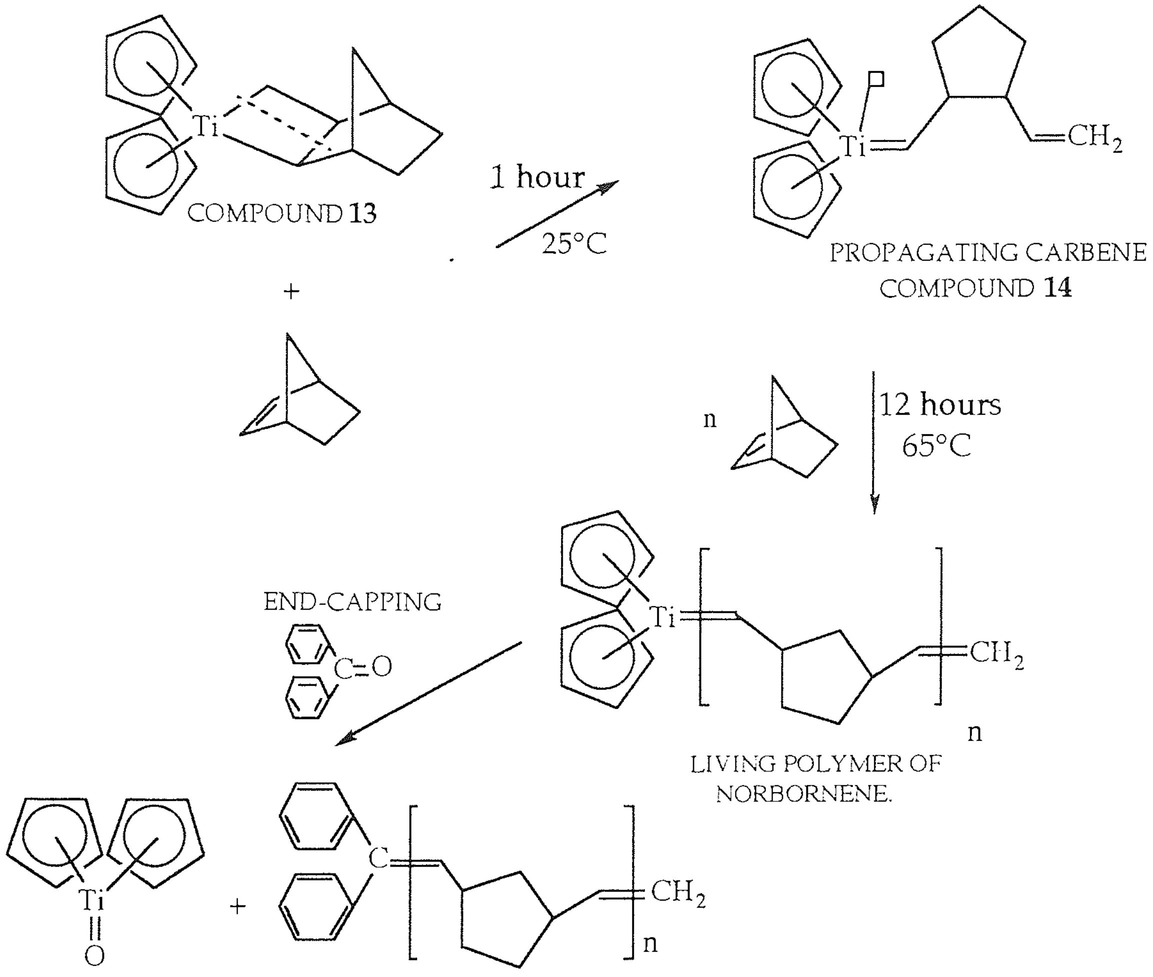
The bis(η^5-cyclopentadienyl) titanacyclobutane derived from norbornene (compound 13) was prepared by the following reaction at -20°C in the presence of the base N,N-dimethylaminopyridine.



'TEBBE' COMPOUND 12

TITANOCENE METALLACYCLOBUTANE
COMPOUND OF NORBORNENE 13

Addition of norbornene and warming to 65°C eventually produces the propagating carbene complex 14, which after this initial induction time, rapidly polymerises with zero order dependence on the monomer concentration.



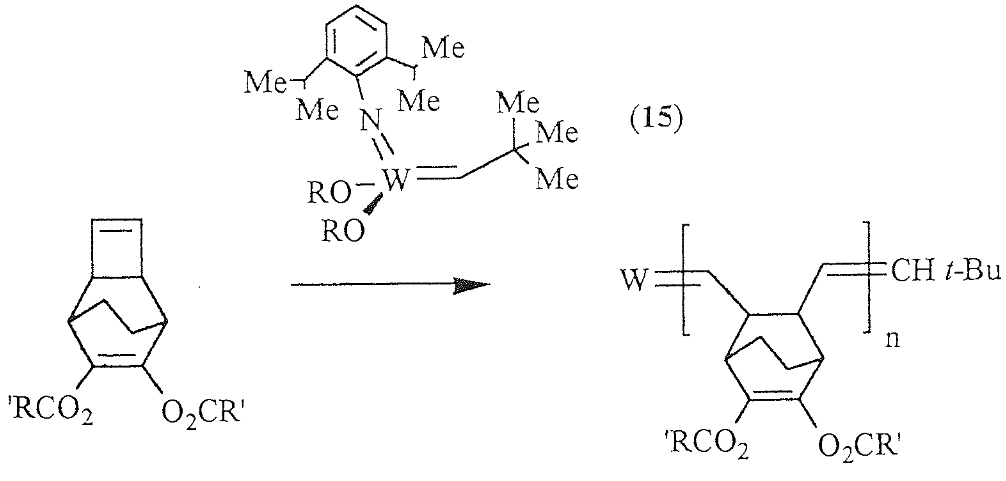
70-100% END-CAPPED POLYMER.

The titanocyclobutane of 3,3-dimethylcyclopropane has more ring strain than compound **13** and has proved a more efficient initiator for the polymerization of norbornene, needing no induction period and forming a product with M_n of 10^4-10^5 and polydispersity less than 1.1. Back-biting and secondary isomerization were not observed and the polymerization ceased on cooling but it was possible to store and re-use the living polymer. Alternatively the polymer was cleaved from the titanium end group by a Wittig-type reaction using benzophenone to obtain over 70% yield of the white amorphous product.

Tantalacyclobutane catalysts, similar to the cyclobutene complexes described in 1.4.4.3, have been prepared by Schrock[74], as well as stable carbenes of tungsten and molybdenum which have been used to produce living polynorbornene.

1.4.5.2 Metathesis Polymerization of Functionalised Monomers.

Schrock et al[75] have reported that the tungsten carbene (ArNWCH*t*-Bu(OR)$_2$ (15), shown in the following reaction, is a catalyst for the polymerization of the functionalised monomer (7,8-bis(acycloxy)tricyclo[4,2,$2^{1,6}$ $0^{2,5}$]deca-3,7-diene, (16) by the reaction involving fission of the highly strained cyclobutene ring to produce polymer (17).

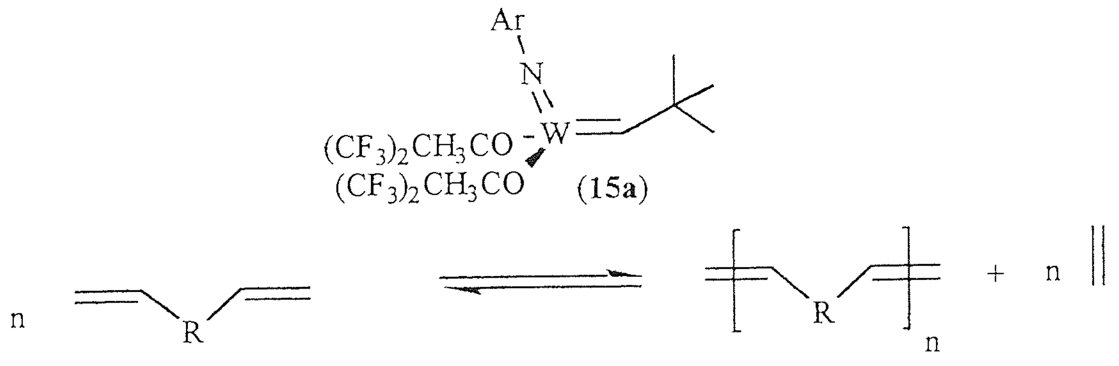

(15)

(16)

(17)

The nature of the alkoxy-ligand attached to the tungsten affects the rate of polymerization. When RO- is *t*-butoxy-, the rate at room temperature is only moderate but as 1,1-bis(trifluoromethyl)ethoxy- there is rapid polymerization at -50°C.

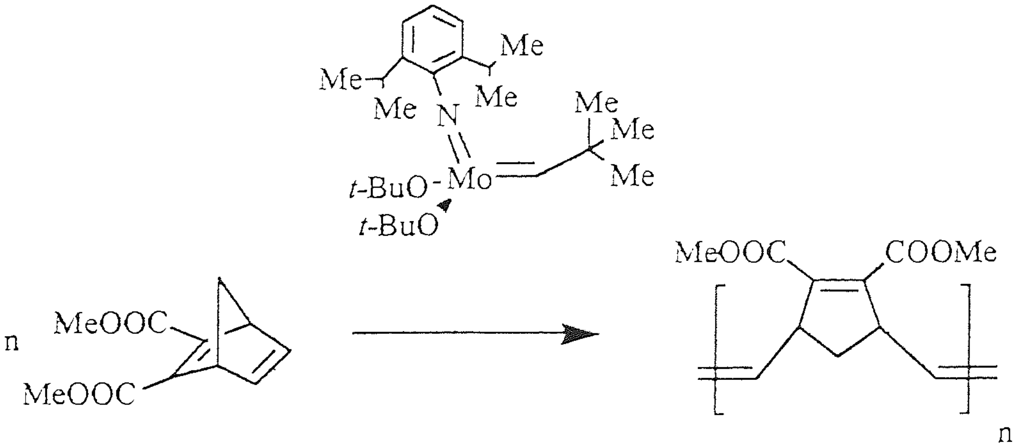
These more reactive tungsten carbenes, which have $-OC(CH_3)_2(CF_3)_2$ (15a) or $-OC(CH_3)_2CF_3$ ligands, have been used by Wagener et al[36,80] and others[81] to polymerize and co-polymerize a variety of acyclic dienes. Acyclic diene metathesis (ADMET) consists of stepwise polymerization in which α,ω dienes (=-R-=) react to form unsaturated polymers and ethene


(15a)

The absence of a Lewis acid avoids vinyl addition reactions and the stepwise polymerization is facilitated by ethene removal. Wagener produced 1,4-polybutadiene, with M_n between 8300 and 14000, from the ADMET polymerization of 1,5-hexadiene at 20-25°C for several hours. Grubbs[82] has reviewed the range of dienes (=-R-=) used, -R- groups include silyl ($-CH_2CH_2Si(Me)_2-$), aromatic ($-CH_2Si(Me)_2\ PhSi(Me)_2\ CH_2-$), ether ($-(CH_2)_3O(CH_2)_3-$), ester $-((CH_2)_8COOCH_2)_2-$) and most recently chloro-carbosilanes ($-CH_2SiClMeCH_2-$).[83]

Nubel et al[84] have successfully carried out acyclic diene polymerizations using more readily available, but equally selective, ADMET catalysts. Ichikawa[85] reported in 1976 that the soluble catalyst system of WCl_6/ $SnMe_4$ and a weak Lewis base such as an alkyl acetate were highly selective metathesis catalysts for acyclic-1-alkenes. The Lewis base was reported to reduce side reactions by neutralising acidic catalyst species. Nubel has used the WCl_6/ $SnMe_4$/ PrOAc catalyst system between 50 and 80°C successfully to produce high purity 1,4-polybutadiene. The product was found to have a lower molecular weight (M_n = 3000) than that produced by the Schrock carbene (15a), but its microstructure was comparable. The process has been extended to cometathesis reactions for the synthesis of α,ω-difunctional telechelic polymers using the same catalyst system but mixing 1,5 -hexadiene and 5-acetoxyl-1-pentene in the ratio 10:1. The product obtained showed some end group functionality.

The molybdenum carbene Mo(CH*t*-Bu)(NAr)(O*t*-Bu)$_2$ has been reported to tolerate monomers with mildly reactive functionalities like esters[86] because it



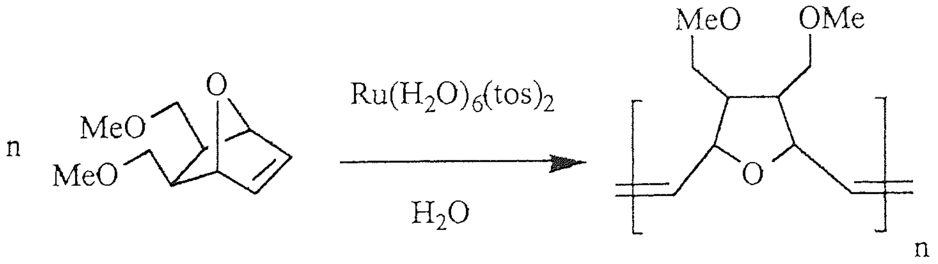
is less oxophilic than the corresponding tungsten compound. The polymerization of 200 equivalents of 2,3-dicarbomethoxy-norbornadiene[87] produced a polymer of polydispersity 1.07.

1.4.5.3 ROMP of Functionalized Monomers in Protic solvents.

The ring opening polymerization is normally carried out in the absence of protic solvents (e.g. water and ethanol) and polar functional groups because, in large amounts, these rapidly deactivate the catalyst system. As early as the 1960's[88] it was shown that, group VIII transition metal compounds of ruthenium, osmium and iridium in the oxidation states II or III, would polymerize highly strained cyclic alkenes, not only in ethanolic solution, but also in aqueous emulsified systems at 20-100°C.

The monomer 7-oxanorbornene deactivates traditional transition metal catalysts[89] but, using ruthenium or osmium complexes in oxidation states II or III, polymerization was found to occur,[90] although long induction periods were required in anhydrous and anaerobic conditions. In an attempt to reduce the induction time by using more rigorous conditions, it was discovered that water was a co-catalyst for the reaction,[91] and there was no decrease in the initial rate of polymerization, even when the water concentration approached 25%.

The catalyst systems, used for the polymerization of 7-oxanorbornene by Grubbs et al, were 1.0M aqueous solution of ruthenium III chloride and $Ru(H_2O)_6(tos)_2$ (tos = *p*-toluene-sulphonate), both these catalysts required an induction time. However recycling the $RuCl_3$ catalyst gradually reduced this time from 35 minutes to 10-12 seconds. The catalyst lost none of its activity and was recycled many times.

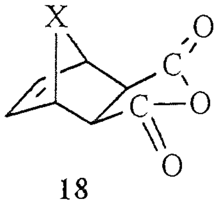


A review of the work[82] carried out on these systems makes the following points.

1. Any termination of the polymerization by hydrolysis must be much slower than propagation.
2. The catalyst $Ru(H_2O)_5(tos)_2$ reacts with one equivalent of monomer to form a Ru^{2+}/ alkene complex which is less than 1% active.
3. Addition of the monomer to the product of 2 produces complete polymerization in 10 seconds at 55°C.
4. The increased activity of the recycled catalyst is thought to involve reduction of Ru^{3+} to Ru^{2+} where applicable and the formation of the monomer/ catalyst complex in situ.

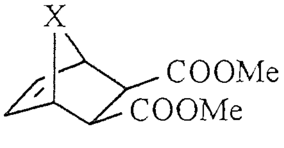
The classical metathesis catalyst systems frequently involved strong Lewis acids and were unable to polymerise functionalised monomers. The new generation carbene and metallacyclobutane compounds of titanium, tantalum, molybdenum and tungsten react under mild conditions and are not very strong Lewis acids so can tolerate polar functional groups. The potential for the production of water soluble polymers and novel ionphoric materials makes this a very important area of research.

A recent contribution to the synthesis of hydrophobically modified water soluble polymers (HMWSP's) using ring-opening metathesis polymerization has been made by Hamilton et al[92]. The catalyst systems $OsCl_3/CH_3OH$ at 100°C and K_2RuCl_5/H_2O at 60°C were used to produce a series of water soluble polymers based on the Diels-Alder adducts (18 and 19) of furan (a) and cyclopentadiene (b).



18

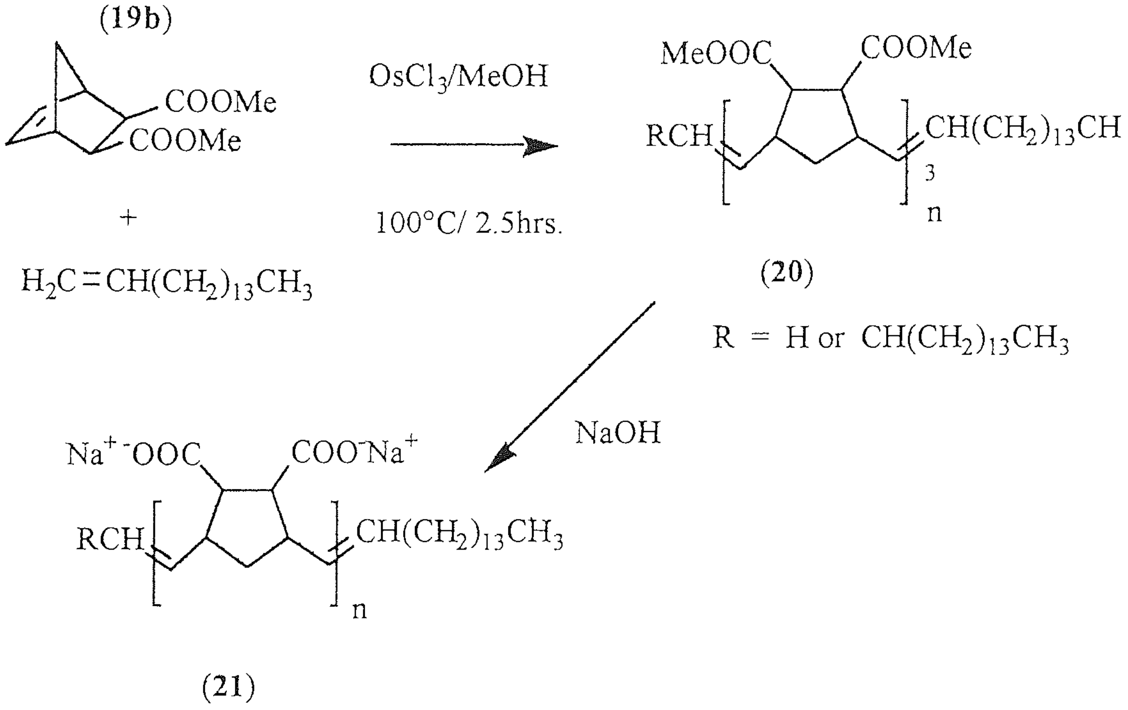
or



19

a) X = O
b) X = CH_2

Three different techniques were used to introduce the hydrophobic functionality co-polymerization with 5-decylbicyclo[2.2.1]hept-2-ene, post-polymerization modification of the acid forms of the polymers with 1-decylamine and chain transfer to 1-hexadecene. A chain transfer polymer was obtained, by pre-mixing the monomer (19b) with a small amount of 1-hexadecene, and after precipitating the polymer (20), it was hydrolysed by prolonged heating with sodium hydroxide to produce the sodium salt (21). After purification water soluble polymers and oligomers with mainly one long chain end group were obtained.



Dilute solution viscometry of the products showed the typical behaviour of polyelectrolytes in water and there was evidence that the hydrophobically modified forms of the cyclopentyl polymers underwent intermolecular association in the semi-dilute region. It is the effect of dilution on the rheological behaviour of polyelectrolytes that has led to their commercial use in the oil and pharmaceutical industries.

1.5 CATALYST SYSTEMS.

The extensive range of metathesis catalyst systems may involve one, two, three or more components. The catalyst mixture may be heterogeneous or homogeneous although some of the latter systems may not be completely homogeneous.

A variety of transition metal compounds produce the main catalyst component. The compounds of tungsten, molybdenum, rhenium and ruthenium are the most common, but seven other group IVA, VA and VIII transition metals have been shown to produce effective catalysts. Catalysts of non transition metals are rare although Ivin et al[66] showed that ethyl aluminium dichloride could be used.

The number of effective catalysts for a particular metathesis reaction is partly controlled by its exothermic character. Exchange metathesis is usually almost athermal so, to attain equilibrium rapidly, only the most active Mo-, W- and Re-based systems are used. Polymerization of slightly strained cyclic alkenes, like cyclopentene also requires highly active catalyst systems and homogeneous systems with moderate temperatures and pressure are normal, although the reactions are sensitive to the particular conditions. Highly strained cyclobutene or bicyclic monomers are readily polymerized by a wider range of catalysts including Ti-, V-, Ru-, Os- and Ir-based compounds. Cross metathesis experiments have shown[93] that it is the initiation reaction which is most sensitive to the catalyst/ alkene reactivity.

Other factors that affect the activity of a particular metathesis system are listed below:

1. The ratio of the components.
2. Pre-treatment procedures, especially for support media of heterogeneous systems.
3. The order of mixing of components.

4. Sequential addition of components or premixing of some components.
5. Delay time for addition procedure.
6. The solvent.
7. Temperature and pressure.

The generally accepted active species for metathesis will be shown later to be a metal carbene or metallacyclobutane formed with the transition metal compound. So the catalyst systems are of three types:

1. Those consisting of a carbene e.g. the Schrock carbene (15) or a metallacyclobutane e.g. bis (η^5-cyclopentadienyl) titanacyclobutane derivative of norbornene (13).
2. Those containing a transition metal compound with an alkyl or allyl group which can readily generate a carbene or can react with an organometallic compound e.g. $EtAlCl_2$ or a Lewis acid e.g. $AlCl_3$ to form a carbene.
3. Those that have no preformed carbene nor an alkyl group in any component. In this case the metal carbene must be generated by a reaction between the transition metal centre and the alkene, e.g. WCl_6/ Ph_4Sn, $PhWCl_3$ or $ReCl_5$.

1.5.1 HETEROGENEOUS CATALYSTS.

These are normally transition metal oxides (e.g. WO_3, Re_2O_7) or carbonyls (e.g. $Mo(CO)_6$) adsorbed on to a high surface area support like alumina or silica. They are mainly used for gas phase alkene metathesis in flow systems at 200 - 400°C. The methods of preparing the system vary from simple mixing and co-precipitation to impregnation or interaction between the support surface and the transition metal compound. Polymer support complexes have also been used, such as polystyrene crosslinked with tungsten complexes[94]. In many cases the support medium has been shown to interact chemically with the transition metal compound and so it is important to identify the material used.

The catalyst systems are activated usually at high temperatures, using gases such as hydrogen, oxygen, carbon monoxide or hydrogen chloride. The physical characteristics of the solid are critical. The surface area, pore size and grain form affect catalytic activity. Chemisorption of oxygen, water or carbon dioxide may irreversibly block the catalytic sites and permanently poison the system.

Molybdenum based heterogeneous systems are particularly useful for the metathesis of linear alkenes and show greater retention of stereochemistry and higher rates than corresponding tungsten systems [95].

The use of co-catalysts and/ or promoters, similar to those discussed in the next section, are common and reference has already been made, in section 1.4.3, to the use of rhenium oxide, supported on silica-aluminas and promoted by alkyltin compounds, for the metathesis of functionalised alkenes[40]. Heterogeneous catalysts are seldom used for ring opening metathesis polymerization.

1.5.2 HOMOGENEOUS CATALYSTS.

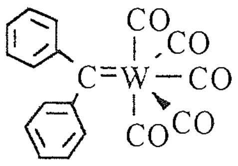
These are used for all types of metathesis reaction and generally produce fewer side reactions because of the relatively mild conditions of temperature and pressure that can be employed. The range of systems and the number of components are daunting but have been extensively reviewed.[82.,93]

1.5.2.1 One Component Systems.

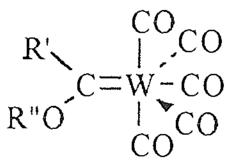
1.5.2.1.1 Carbenes or Alkylidene Complexes.

In 1974 Schrock[96] discovered the first alkylidene complexes in which the metal can be said to have a d^0 electronic configuration, for this he regarded the ligand as a dianion. Since then their preparation has been the study of much research largely because of their catalytic effect on metathesis systems.

The first carbenes used on their own to catalyse metathesis were the 6 coordinated tungsten carbenes known as the Casey compound (22) and the Fischer compounds (23).



(22)



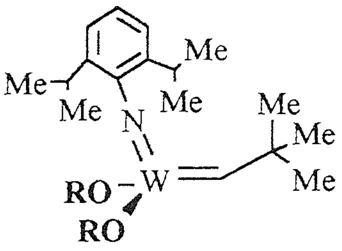
(23)

R' = Ph, R" = Me,
R' = Ph, R" = Et,
R' = Bu, R" = Et.

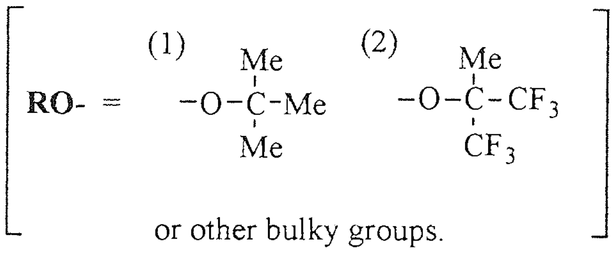
Katz et al[97] used the Casey carbene for the cometathesis of 1-octene and 1-hexene and for the ring opening polymerization of cyclobutene. The reaction was rather slow at room temperature but warming to 50°C produced carbon monoxide and speeded up the reaction. The mechanism proposed for metathesis predicts that the polymers formed from (22) should have $Ph_2C=$ end groups and Katz found UV absorption evidence of this for the polymerization of 1-methylcyclooctene.[98]

The Fischer carbenes react at about 80°C as metathesis catalysts on their own but are reported to be more active when excess $TiCl_4$ is added to them[61], which either facilitates removal of a CO ligand, or forms a more reactive complex. It was stated in 1.4.4.3 that the Fischer carbene $(CO)_5W{=}CPh(OMe)$ polymerizes phenylethyne and this system is also used for the polymerization of cyclopentene, cycloheptene and cyclooctene.[51,52]

Kress[99] has shown that 5 coordinated tungsten carbene complexes of the type $Br_2W{=}CHt\text{-}Bu(OCH_2t\text{-}Bu)_2$ slowly catalyse the metathesis of internal alkenes but again the addition of a Lewis acid greatly increases the reactivity. However 4 coordinated tungsten carbenes of type (24), prepared in dimethoxyethane (DME) show catalytic activity in Lewis acid free conditions.



(24)



$$\textbf{RO-} = \quad (1)\ -O-\underset{Me}{\overset{Me}{C}}-Me \qquad (2)\ -O-\underset{CF_3}{\overset{Me}{C}}-CF_3$$

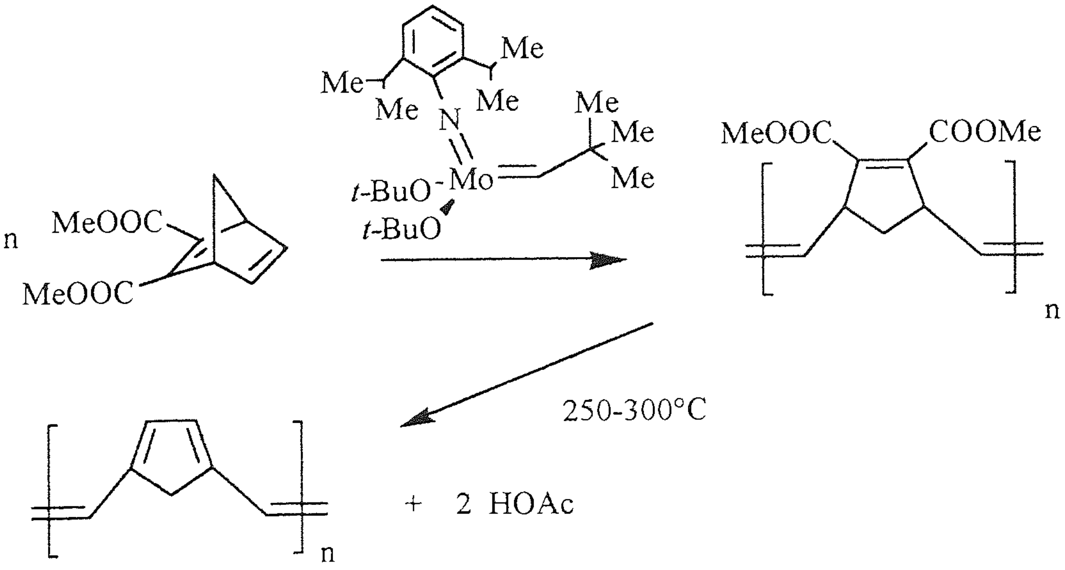
or other bulky groups.

The activity of (**24**) is partly related to the nature of the alkoxy ligands. The very electron withdrawing ligand (2) produces a very reactive metathesis catalyst for *cis*-2-pentene but the *t*-Bu-O- derivative (1) is virtually inactive with this alkene.[82] However the bulkiness of the alkoxy-ligand also affects the reactivity of the carbene.

The catalytic effect of these tungsten carbenes in the polymerization of strained bicyclic alkenes containing functional groups has been mentioned in 1.4.5.2. Even the *t*-BuO- form of (**24**) rapidly produces a living polymer with norbornene[100] with a polydispersity index as low as 1.03, when the degree of polymerization is 500. Cyclopentene is polymerised reversibly by the same catalyst but its PDI is between 1 and 2.

The use of the -O(CH$_3$)(CF$_3$)$_2$ form of (**24**) in acyclic diene metathesis (ADMET) has also been referred to in 1.4.5.2 but this very reactive catalyst also ring opens cyclooctatetraene and mono-substituted cyclooctatetraenes to give "poly(acetylenes)"[101], but chain transfer and the formation of cyclics show the lack of control in this reaction.

Functionalised norbornenes are polymerized by the molybdenum equivalent of (**24**) i.e. Mo(CH-*t*-Bu)(N=Ar)(O*t*-Bu)$_2$ (see section 1.4.5.2) and one of the many potential uses for a functionalised polymer of this sort is as a precursor to an unsaturated system.[59]



The role of the solvent is important in these systems, as it has been found that 5-cyanonorbornene is not polymerised by this molybdenum catalyst in a non-coordinating solvent like toluene, but in THF the same system produces rapid polymerization of 200 equivalents of monomer with a PDI of 1.05. The role of the THF is not fully understood but competition between solvent and the functionality for the metal may inhibit the latter reaction, or a bulk solvent effect may keep the polar group pointed away from the metal. Involvement of the THF in the ring opening propagation step is another possibility.

1.5.2.1.2 Metallacyclo-butane/-butene Complexes.

Metallacyclobutane complexes are a second recognized propagating species in metathesis reactions. Reference has already been made in section 1.4.5.1 to the preparation of the 'Tebbe' compound (CpTi(μ–CH$_2$)(μ-Cl)AlMe$_2$), from this, Tebbe produced the first stable metallacyclobutene with diphenylethyne[102], using the basic properties of THF. Grubbs et al[103] prepared metallocyclobutane complexes of alkenes (e.g. 4,4 dimethyl-1-hexene and norbornene), using initially a 4-vinylpyridine/styrene co-polymer as the base but eventually using, the more effective and more easily removed base, 4,N,N dimethylamino-pyridine.

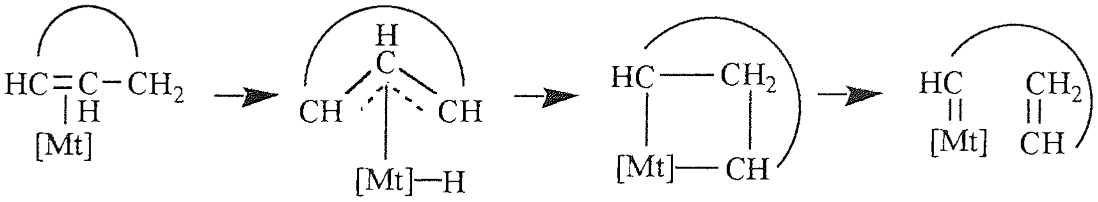
The ability of the titanacyclobutanes of norbornene and 3,3 cyclopropene, to produce the ring opening polymerization of norbornenes, is associated with their relative stability. The lack of inter- or intra-molecular reactions between the growing polymer and the intermediate carbenes results in the living character of the polymer. These catalyst systems can only be used with other strained ring hydrocarbon alkenes because of the reactivity of titanium towards functionalised monomers. The other disadvantage is the relatively high temperatures (≈ 50°C) needed for ring-openening.

The other isolable metallacyclobutane complexes that have been prepared, which are most useful for metathesis reactions, are those of tantalum, tungsten and molybdenum. However they have been less frequently used as metathesis catalysts than their associated carbenes and have not extended the range of possible metathesis or polymerization reactions.

1.5.2.1.3 Transition Metal Halides.

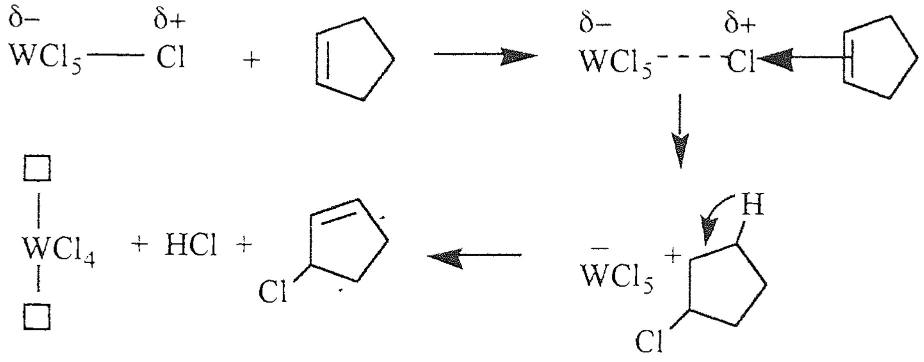
A few transition metal halides (e.g. $WOCl_4$ and $ReCl_5$) have been shown to polymerize strained ring alkenes without the need of a co-catalyst, although other one component systems (e.g. $MoOCl_5$ and WCl_6) show improved catalytic power with aging and this may be attributed to the co-catalytic effect of traces of water or oxygen.

The initiating species in these systems is not fully understood but must involve interaction between the alkene and transition metal compound. A mechanism, of the type shown in the following scheme, gives a good explanation of the initially formed products of the metathesis of certain acyclic alkenes on supported molybdenum oxide catalysts[104] but, whether it applies to the ring opening polymerization reactions of cyclic alkenes, using transition metal complexes with no alkyl group, is open to question. The mechanism involves the reaction between an empty coordination site on the transition metal and an alkene to form a metal-π complex. The allyl system is established and migration of an allylic hydrogen produces the initial metallacarbene.



Other workers[105] have identified stereoselective chloroalkanes as products of the reactions of transition metal halides and alkenes, for example cyclopentene and molybdenum(V) chloride produce a 66% yield of *cis*-dichlorocyclopentane and only 1% of the *trans*-isomer, while the metal chloride is reduced.

A study of the WCl_6/cyclopentene system by Amass et al[106] led to the following mechanism being proposed for the reaction between halide and cyclopentene.



☐ represent 2 vacant co-ordination sites

The factual basis for this was that the oxidation state of the tungsten was known to decrease when cyclopentene was added to tungsten hexachloride[29] and interaction between a 1: 1 mole ratio of the two had been established.[107] The product then showed first order decay in excess cyclopentene and amongst the products of this reaction were hydrogen chloride and 3-chloropentene.

It is possible that the initial reduction of the transition metal facilitates the co-ordination of the monomer, leading to the formation of a carbene.

1.5.2.2 Two Component Systems.

Co-catalysts consisting of organometallic compounds of group I to IV metals (e.g. BuLi, $EtAlCl_2$, R_3Al, R_4Sn where R = Me, Bu, Ph etc.) or Lewis acids (e.g. $AlCl_3$, $AlBr_3$) are used, with transition metal halides, to increase catalytic activity. The possible roles of the co-catalyst are as follows.

1. Provision of an alkyl ligand at the transition metal, which results in the formation of a carbene, by reductive elimination.
2. Complexing agent to the olefin or the transition metal compound modifying the electron density of either.
3. Reducing agent for the transition metal to open up a coordination site for the alkene.

Several workers[108,109] suggested that the organometallic co-catalysts (e.g. $SnMe_4$, Me_2Zn) provide an alkylating species for the transition metal and this is followed by α-hydrogen loss. Methane was detected in the early stages of these reactions so the inference was that a catalytically active carbene was also formed.

$$WCl_6 \; + \; SnMe_4 \; \text{--->} \; Cl_5WMe$$

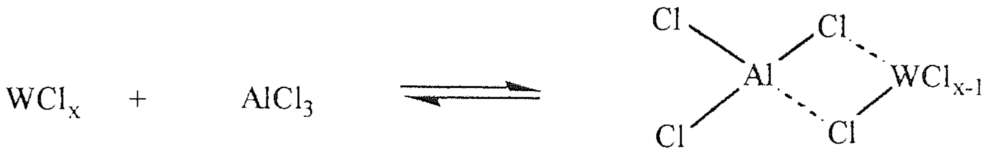
$$2\,Cl_5WMe \; \text{--->} \; Cl_4W = CH_2 \; + \; CH_4 \; + \; WCl_6$$

Bencze[110] showed that WCl_6 and Ph_4Sn react to form $PhWCl_3$, which is a metathesis catalyst, but obviously cannot disproportionate directly to become the active centre.

The activating ability of aluminium co-catalysts has been shown to be[111]

$$EtAlCl_2 > Et_2AlCl > Et_3Al$$

which is the order of electron accepting ability and this must be the reason that strong Lewis acids like aluminium bromide also activate metathesis. Calderon[33] proposed two intermediates to explain this, the first involves μ-chloride association between the tungsten halide and the co-catalyst.

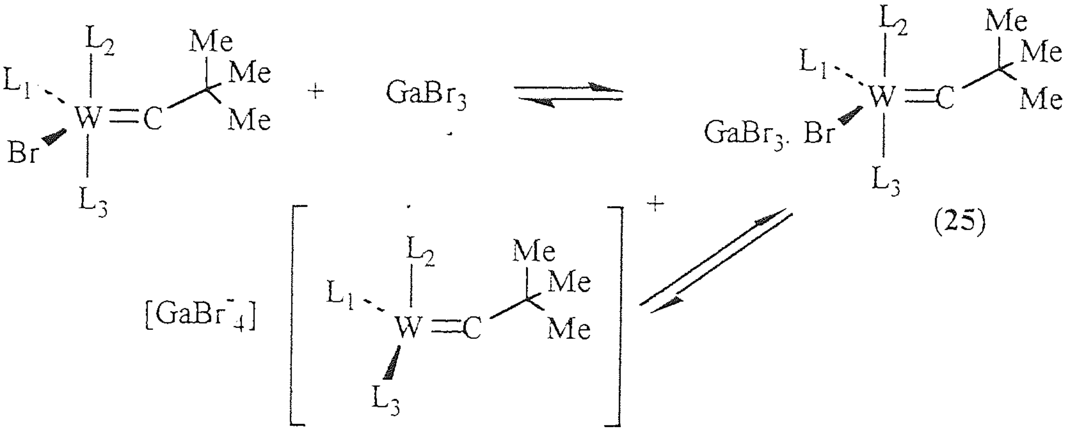


The second involves the acid-base equilibrium, although the environment is non-polar.

$$WCl_X \; + \; AlCl_3 \; \rightleftharpoons \; WCl^{+}{}_{X-1} \; + \; AlCl^{-}{}_4$$

Kress[99] has investigated the effect of Lewis acids (e.g. AlX_3, GaX_3) on the metathetic activity of the five-co-ordinated tungsten carbenes of the type $BrL_1L_2L_3W(CH\text{-}t\text{-}Bu)$. The rate of metathesis of internal alkenes with this type of catalyst is slow but with $GaBr_3$ a highly active catalyst is produced.

NMR studies of the system show the formation of $GaBr_3$ adducts of neopentylidene complexes, containing at least one bromide ligand (25) and also a cationic species (26). Also the equilibrium constant, for the formation of the cationic species, was shown to increase with increasing ligand π donor strength, which will stablise the cationic charge.



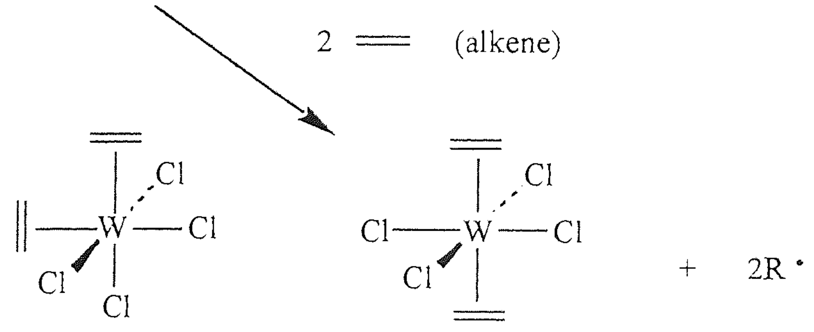
(25)

(26)

X-ray crystallographic characterisation, of similar stable five co-ordinate tungsten complexes and $GaBr_3$, show the existence of μ-associated dimers of the sort mooted by Calderon. These adducts are likely to be the precursors to the four co-odinated cationic complex (**26**), which are active metathesis catalysts.

The function of the organometallic co-catalyst as a reducing agent was related by Wang[112] to the maximum activity of the WCl_6/LiBu system when a W: Li ratio of 1: 2 is used. The following reaction was proposed.

$$WCl_6 + 2LiR \longrightarrow R_2WCl_4 + 2LiCl$$

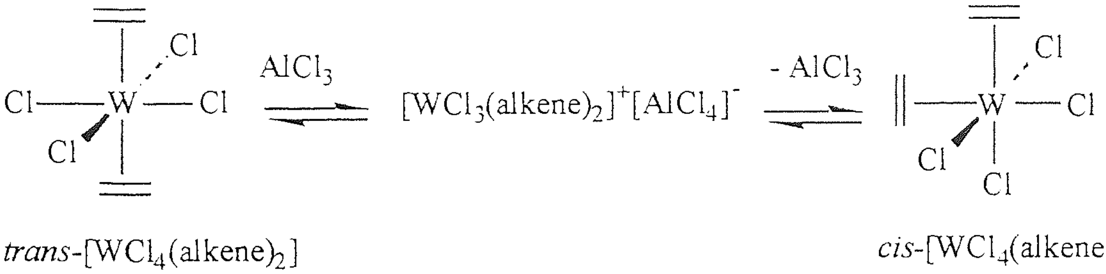


cis-$[WCl_4(alkene)_2]$ *trans*-$[WCl_4(alkene)_2]$

The reducing action of other co-catalysts and the importance of the catalyst to co-catalyst ratio will be discussed in section 1.5.3.1.

1.5.2.3 Three Component Systems.

The use of two co-catalysts, an organometallic compounds like butyllithium and a Lewis acid, e.g. aluminium bromide, has improved the rate and yield in some systems[8,112]. It is thought that aluminium halides cause rapid isomerisation of the reduction isomers, postulated in the previous section, from trans-$WCl_4(alkene)_2$ to the more active cis-$WCl_4(alkene)_2$.[113]



An alternative third component can be used, which may function as an activator, a promoter or as a stabiliser to inhibit side reactions. These may be oxygen, sulphur, halogen or nitrogen containing organic compounds although pure oxygen or hydrogen have been used.

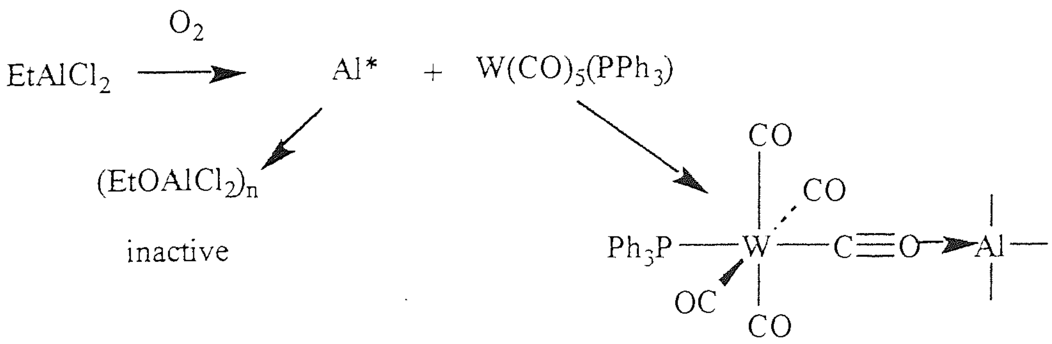
Quaternary ammonium salt (e.g.Bu_4NCl), tertiary amines and other nitrogen containing compounds are frequently used as the third reactant. In the ring opening polymerization of dicyclopentadiene, using $TiCl_4/AlEt_3/NEt_3$, Winstein[114] has shown that, a tertiary amine to $TiCl_4$ ratio of 4: 1, minimises the addition polymerization reaction. In the metathesis of 1,7-octadiene Bu_4NCl is added to the catalyst system, $Mo(CO)_5(py)/RAlCl_2$, and is thought to stabilise the intermediates forming the initiating carbene.[115]

The use of nitric oxide and carbon monoxide as third components has been demonstrated[116,117] and both seem to involve coordination to the transition metal. Several molybdenum complexes showed a marked increased catalytic activity, when exposed to NO for thirty minutes, before the addition of the co-catalyst $Me_3Al_2Cl_3$ and pentene. The catalyst system $WCl_4(py)_2/EtAlCl_2$ (py = pyridine) is more active in an atmosphere of carbon monoxide than under argon. It has been shown that over-exposure can deactivate these catalyst, for example $[WCl_3(C_2H_4.(PPh_3)_2)_2/EtAlCl_2]$, in excess CO, becomes inactive $W(CO)_6$.

Calderon [7,8] first reported the use of oxygen containing additives, when he used the WCl_6/ $EtAlCl_2$/ EtOH catalyst system for the metathesis of acyclic alkenes. For most systems oxygen or oxygen containing compounds only have a beneficial effect in controlled amounts and four main effects have been postulated.

1. To create or help create a vacant site on the transition metal for alkene complexation.
2. To act as a ligand to the transition metal producing a more active catalyst centre.
3. To react with the organometallic compound, which promotes its reaction with the transition metal compound.
4. To help re-oxidation of the active centre that has been previously reduced by the co-catalyst and/ or the alkene.

Haines[118] proposed that the increased metathetic activity of the catalyst system, $W(PMePh)_4(NO)_2$/ $EtAlCl_2$, in the presence of oxygen was caused by the creation of a vacant or a potentially vacant site by the removal of the organic ligand on the tungsten as its oxide. Basset[119] suggested an alternative role for the $EtAlCl_2$ co-catalyst, which involves activating the ethyl aluminium dichloride to the species Al* before it is oxidised. The Lewis acid properties of the Al* species can decrease the electron density on the tungsten catalyst, $W(CO)_5(PPh_3)$, by complexing the lone pair on the oxygen of one carbonyl group. The shift in electron density could then enable the transition metal to co-ordinate with the alkene.



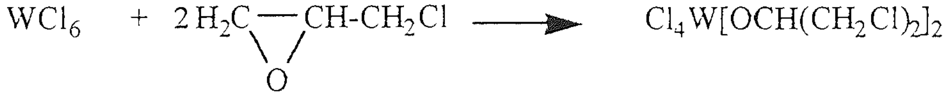
Calderon and his co-workers showed that controlled addition of ethanol, water, phenol, acetic acid or other protic solvents to WCl_6, prior to addition of the organoaluminium chloride, increased the catalytic activity of the system[7,9]. Both the reaction of water and ethanol with tungsten hexachloride were shown to produce stoichiometric amounts of HCl.[33]

$$WCl_6 + H_2O \longrightarrow 2HCl + WOCl_4$$

$$WCl_6 + EtOH \longrightarrow HCl + Cl_5WOEt$$

Unsurprisingly such compounds as $WOCl_4$, $W(OPh)_4$ and $W(OPh)_6$ have been shown to be metathesis catalysts[16,120] and Khodzhemirov[111] has shown that WCl_6 and alcohols undergo displacement reactions to form other alkoxy-tungsten chlorides e.g. $WCl_2(OEt)_3$

Pampus[121] proposed the formation of alkoxide ligands when epoxides are used to promote WCl_6.



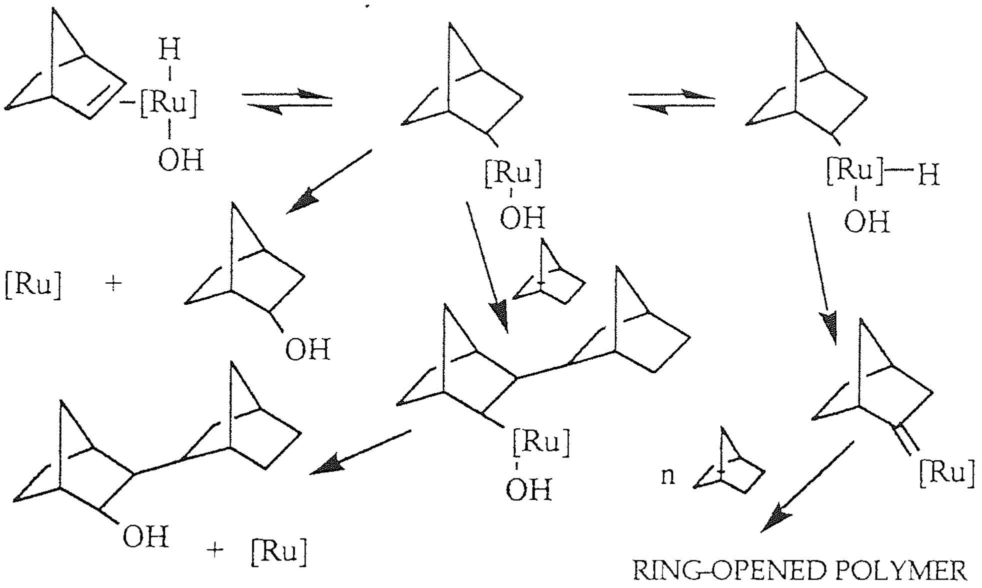
$$WCl_6 + 2\,H_2C\underset{O}{-}CH\text{-}CH_2Cl \longrightarrow Cl_4W[OCH(CH_2Cl)_2]_2$$

The role of the alcoholic or phenolic component may be to upset the highly symmetrical structure of the octahedral WCl_6 and Hoecker[122] has proposed that this facilitates chlorine-alkyl exchange with the organo-aluminium co-catalyst.

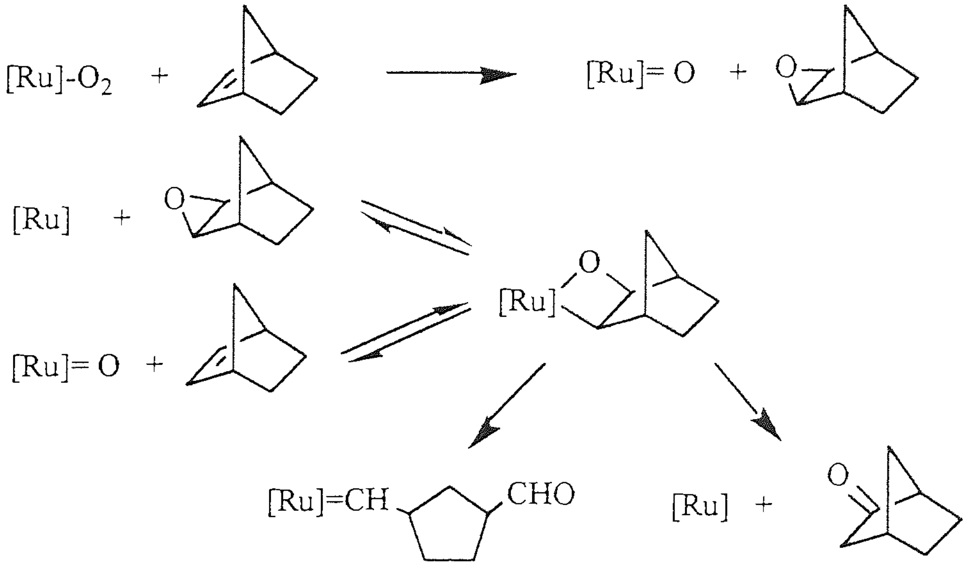
Schrock[59] has suggested that at least one oxo-ligand may be crucial for keeping the metal in the d^0 configuration, he assigned to the carbene or alkylidene complexes, which are the most common precursors to metathesis. The reaction of water or oxygen leads to the formation of oxo-complexes and will be beneficial in small amounts.

The unusual behaviour of compounds of the group VIII transition metals, ruthenium, osmium and iridium, in catalysing the ring-opening metathesis of highly strained cyclic alkenes, usually norbornene and its derivatives, in ethanolic or aqueous solutions, was mentioned in 1.4.5.3.

The production of low molecular weight secondary alcohols, as a side reaction, led Laverty[123] to propose this mechanism for the production of an initiating carbene, from a species with a [Ru]-H bond, for which he showed IR and NMR evidence.



However the initiation may well involve traces of oxygen, as bubbling the gas through solutions of norbornene in chlorobenzene containing the catalyst $RuCl_2(PPh_3)_2(py)_2$, increases the rate of polymerization by a factor of 100. The presence of the products norbornanone and the epoxide of norbornene led Ivin[93] to propose a mechanism involving a metallaoxacyclobutane as an intermediate to the initiating carbene.



1.5.3 FACTORS THAT AFFECT METATHESIS CATALYST SYSTEMS.

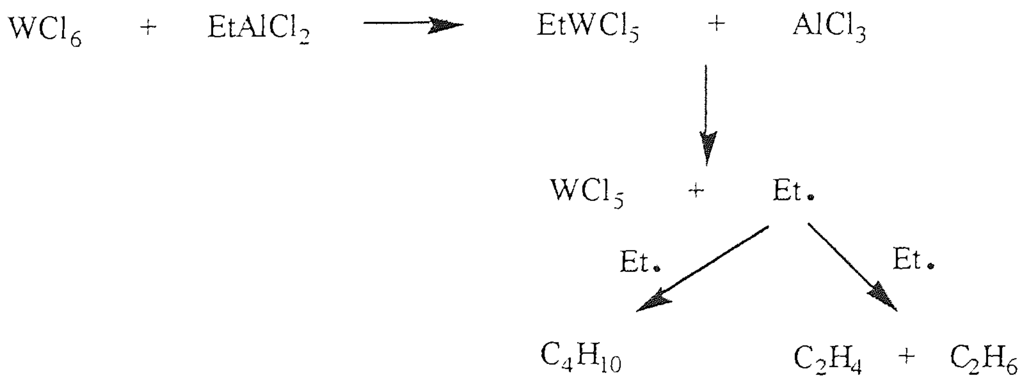
The range of variables in a metathesis system, not just the number and nature of the catalyst components but also such factors as those listed in section 1.5, makes them extremely complicated to interpret. A few of the conditions, which may significantly alter the nature of the products and/or the rate of the reaction, will be reviewed.

1.5.3.1 Ratio of Reactants.

The ratio of transition metal complex to alkene can vary considerably but it is usually of the order of 1: 10^2. In ring-opening metathesis the relative catalyst concentration is usually less than 10^{-3} indicating a typical chain mechanism.

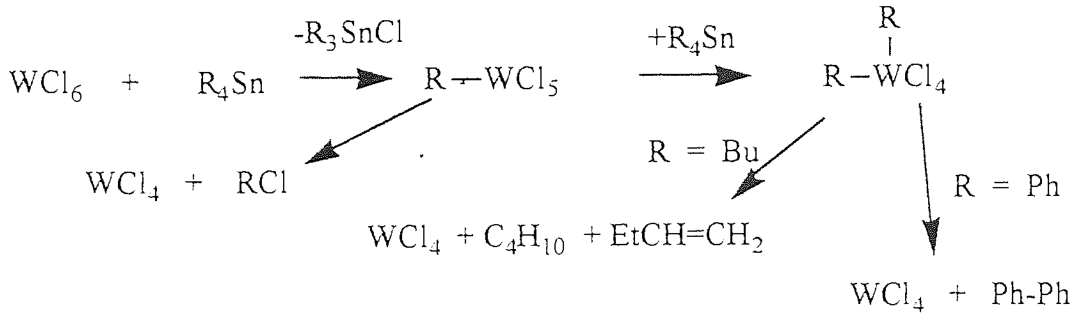
The ratio of the catalyst components has been found to be important and reference has been made in section 1.5.2.2 to the maximum activity of the WCl_6/LiBu system at a ratio of 1:2. This was related by Wang et al[112] to the reduction of the tungsten complex to a $WCl_4(alkene)_2$ intermediate. The improved metathetic activity produced by the addition of a Lewis acid, as a third component, has also been mentioned[8,112] and an optimum ratio of W: Li: Al of 1: 2: 1 was reported. This would support the theory of Calderon, that a 1: 1 association of $WCl_6$and AlX_3 occurs, as discussed in 1.5.2.2.

Calderon found the optimum ratio of 1: 2 for W: Al in the $WCl_6/EtAlCl_2/EtOH$ catalyst system[33] and proposed the following series of reactions.



It was suggested that the WCl_5 would either undergo further reduction to WCl_4, or the W(V) would disproportionate, to W(IV) and W(VI).

Ichikawa[124] proposed the following reducing action of W(VI) to W(IV) in the $WCl_6/2R_4Sn$ system:



The reductive elimination reactions shown produce WCl_4 but it has been recognized that WCl_4, obtained by the reduction of WCl_6 with hydrogen, or prepared in situ, is not a metathesis catalyst. However if $AlCl_3$ is added to the WCl_4, prepared by these methods, a highly active catalyst is produced.

Other optimum W: Al activities have been identified, including a ratio of 1: 4 for $WCl_6/EtAlCl_2$, for the both the ring opening polymerization, of cyclooctene and 3-methylcyclooctene,[8] and for the metathesis of 3-heptene using $(mesitylene)W(CO)_3/EtAlCl_2$.[125] There seems to be a narrow band of optimum activity for the catalyst: co-catalyst ratio of between 1: 1 and 1: 4, which produces the maximum rate of reaction and the highest percentage conversion.

1.5.3.2 Order of Mixing.

The order of mixing is generally found to be most critical for athermal metathesis reactions and least important for ring-opening polymerization of highly strained cyclic alkenes. The time taken for the catalyst system to reach maximum activity is also an important criterion influencing the order of mixing. The $WCl_6/EtAlCl_2$ system reaches maximum activity rapidly and so the alkene is usually added before the co-catalyst but highly strained bicyclic alkenes, like norbornene, undergo rapid polymerization even when WCl_6 and $AlEtCl_2$ are pre-mixed and then the monomer is added. However with moderately strained cyclic alkenes, like cyclopentene, the sequential addition of monomer and WCl_6, followed by the $AlEtCl_2$ is needed to produce high molecular weight polymer. It has been postulated that the norbornene system requires only a trace of active catalyst to produce rapid poymerization.[126]

The WCl_6/AlX_nR_{3-n} catalyst system has been shown to be particularly sensitive to the order of component addition and also to aging time. It has been known for some time that if the two are pre-mixed and then added to an acyclic alkene in toluene solution, no metathesis occurs, but there is Friedel Craft alkylation of the solvent.[127] Similarly the pre-mixing of WCl_6 and LiBu and addition to a toluene solution of alkene promotes the Friedel Craft reaction, but both systems generate metathesis if WCl_6 is first added to the alkene. Wang et al used the co-catalysts $AlCl_3$ or $AlBr_3$ and LiBu and found that even when WCl_6 and LiBu were pre-mixed and added to the alkene, metathesis could be produced by the subsequent addition of $AlCl_3$ or $AlBr_3$.[113]

The same workers investigated the action of electron donors (e.g. aniline) on the system $WCl_6/EtAlCl_2$.[128] Pre-mixing these two and then addition of alkene produces little metathesis even when aniline is subsequently added. However mixing the WCl_6 and aniline, then adding the alkene and finally the $AlEtCl_2$, results in metathesis. An initial reducing action of the base on the WCl_6 has been mooted.

The immediate change in oxidation state of the WCl_6 when cyclopentene is added to it, mentioned in section 1.5.2.1.3, suggests the cyclopentene is itself capable of reducing the WCl_6 to WCl_4 and the alkene prevents this producing a polymeric species, incapable of acting as a metathesis catalyst, by coordination at the vacant sites.[106] Amass et al also reported, that if Al(*i*-Bu)$_3$ or LiBu are used as co-catalysts for the metathesis of cyclopentene, the initial rate of polymerization is dependent on the time interval between the addition of the catalyst and the co-catalyst to the cycloalkene. They have shown[107] that, the aging time required to produce the maximum initial rate of polymerization (t_{max}), depends on the initial concentration of the monomer $[M]_0$ and the rate constants (k_1 and k_2), for the production of two different metathetically active species. The following relationship was proposed:

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

To explain the observed results it was suggested that, the production of an initial, reactive species for metathesis was followed by its conversion into a less active species.

Catalyst systems that require time to develop their activity, benefit from pre-mixing. $MoCl_2(py)_2(NO)_2/Et_3Al_2Cl_3$ (py = pyridine) requires an hour to reach maximum activity and the best results are obtained by pre-mixing the two and then adding the alkene.[120] Several molybdenum systems seem to need this incubation time but Dolgoplosk[129] found that the polymerisation of cyclopentene, using the $MoCl_3(C_{17}H_{35}COO)_2/Et_2AlCl$ catalyst system, gave the same yield if the monomer was added before the co-catalyst, or after a delay of several hours but subsequently the catalyst concentration was found to be critical. Catalyst concentrations of more than $2x10^{-2}M$ were found to be inactive after two hours and this was attributed to over-reduction of the molybdenum.

1.5.3.3 Photochemical Effects.

The activity of metathesis catalysts has been induced or increased by exposure to irradiation, initially a mercury lamp was used. Guenther first noticed the enhancing effect of irradiating WCl_6 solutions, before using them with the co-catalyst $(i\text{-}Bu)_3Al$, for the ring-opening polymerization of cyclopentene.[121] The effects were divided by Tanielian[130] into photoassisted reactions, in which the alkene is present from the start, and photocatalysed reactions, in which it is added only after the catalyst system has been irradiated. Sometimes a period of incubation of the catalyst system is required and this is called a modified photocatalyzed reaction.

Krausz[131] showed that 2-butene undergoes both photo-assisted and -catalyzed reactions to produce an equilibrium mixture of the *cis* /*trans* isomers with $W(CO)_6/CCl_4$. A comparison of the two shows that irradiation continuously regenerates the catalytic species. Solutions of the carbene $Ph(MeO)C{=}W(CO)_5$ in CCl_4, for the polymerization of cyclo-1,5-octadiene, become active when irradiated by uv, but heating to 50°C has the same effect.[132] Kress[133] has shown that a metal carbene is generated by the loss of Me_4C from the catalyst system $(Me_3CCH_2)_3WBr(O)/AlBr_3$.

Tanielian's work on the $W(CO)_6/CCl_4$ system shows the dramatic effects of aging.[130] Short irradiation times of less than 3 minutes produced a very active species for the metathesis of 2-pentene, with over 40% conversion being achieved within an hour, the half-life of this species was only a few hours. When the irradiation time was longer than an hour, slower conversion occurred but the half-life of the less active species was much longer. The exact structures of two different active moieties, have not been determined but the presence of transient species, e.g. $W(CO)_5$, $W(CO)_5Cl$ and $W(CO)_4Cl_2$, has been suggested because the initiating carbene, $[W]{=}CCl_2$, is known to be formed (see section 1.6.2.2.4). Over a period of time, irradiation of the $W(CO))_6/CCl_4$ system, releases nearly all the carbon monoxide, suggesting the two active species could be different forms of $Cl_2C{=}WCl_m(CO)_n$.[93]

1.5.3.4 Solvent Effects.

The solvent used in homogeneous metathesis must allow solvation of the catalyst system and the reactants, although Muetterties and Busch[134] reported the presence of suspended solids in the $WCl_6/EtOH/EtAlCl_2$, $WCl_6/2EtAlCl_2$ and $WCl_6/LiBu$ catalyst systems.

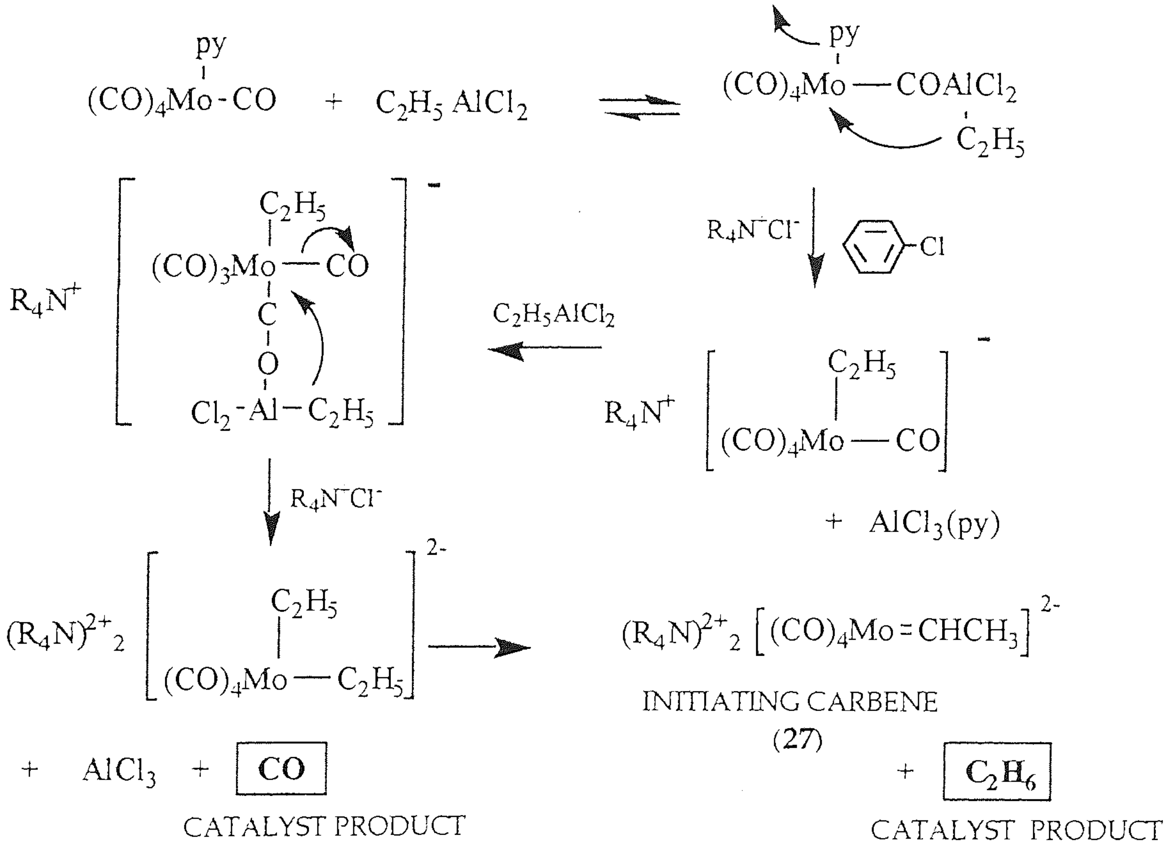
The main type of solvents used are non-polar or slightly polar compounds including linear alkanes (e.g. heptane), aromatic hydrocarbons (e.g. toluene) and chlorinated compounds (e.g. chlorobenzene and tetrachloromethane). The effect of protic solvents on conventional catalysts systems and the special solvent conditions of group VIII transition metal catalyst systems, for the ring-opening polymerization of cyclic alkenes, have already been mentioned.

There has been little systematic research on the effect of different solvents on the course of metathesis. However the nature of the solvent can be shown to have an effect on the reaction between both the catalyst components and the first formed products of the metathesis reaction.

The catalyst mixture $Mo(CO)_5(py)/EtAlCl_2/Bu_4NCl$ produces carbon monoxide and ethane on mixing in chlorobenzene but when the solvent is heptane, the gas is almost entirely ethene. When the systems are used to metathesise 1,7-octadiene a difference in the initiating carbene is indicated.

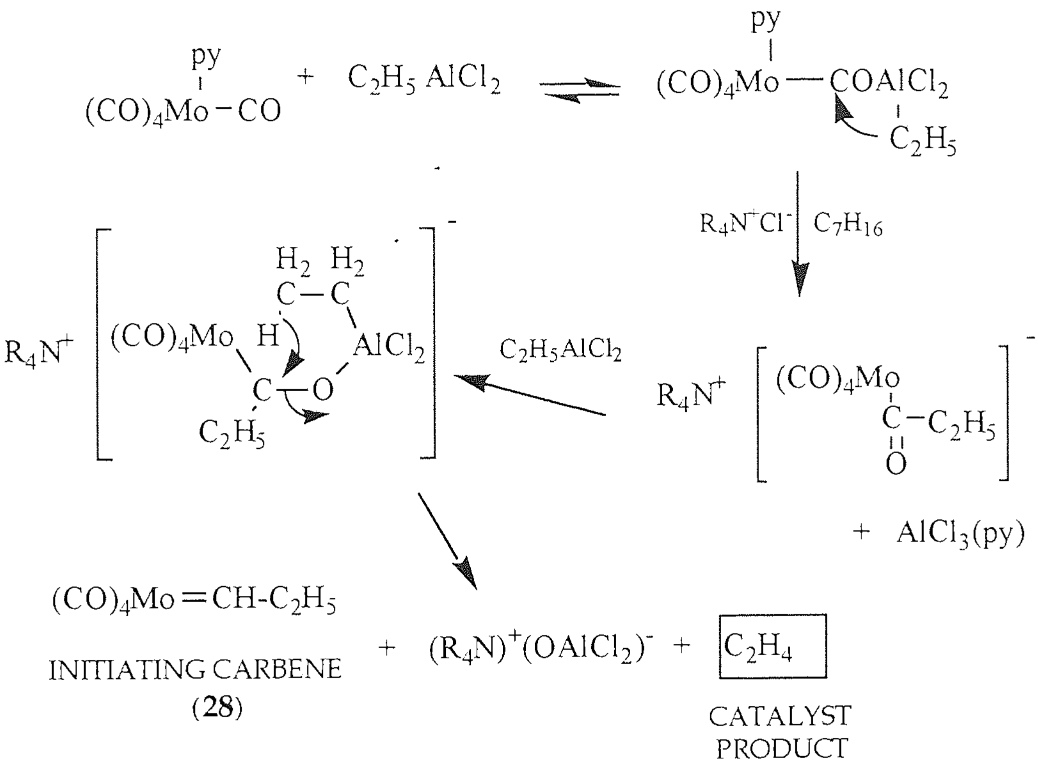
SCHEME 1.5.1. THE EFFECT OF SOLVENT ON THE CATALYST SYSTEM

(1) In Chlorobenzene.



In chlorobenzene propene is an initial product, suggesting the initiating carbene is [Mo]=CHMe, but in heptane, 1-butene is evolved, indicating that the carbene [Mo]=CHEt initiates the metathesis. Motz et al[115] therefore proposed two reaction schemes and scheme 1.5.1 is the proposed mechanism in (1)

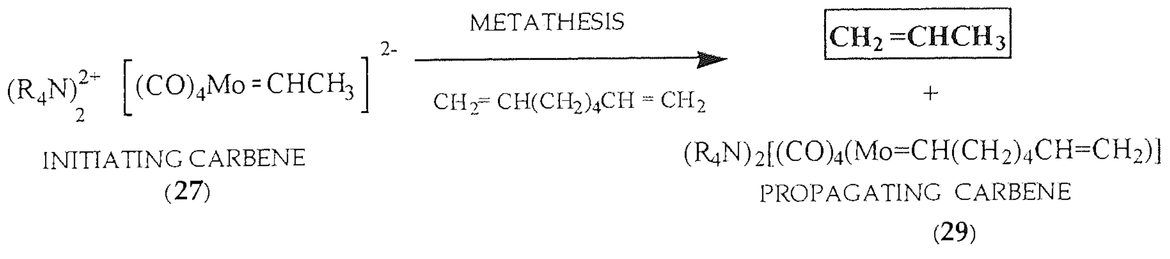
(2) In Heptane.



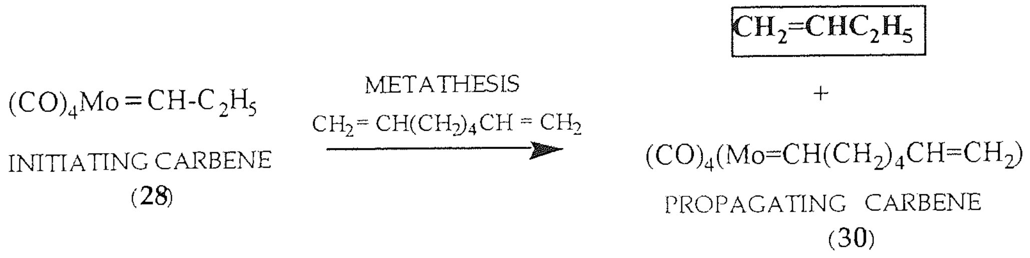
chlorobenzene and (2) heptane. The metathesis in the two solvents has been rationalised in the scheme 1.5.2., which not only indicates different initiating carbenes but also shows different molybdenum oxidation states in the two solvents.[115]

SCHEME 1.5.2. THE INITIAL PRODUCTS OF THE METATHESIS OF CARBENES 27 AND 28 WITH 1,7-OCTADIENE IN DIFFERENT SOLVENTS.

(1) In Chlorobenzene



(2) In Heptane



1.5.3.5 Factors that Affect the Stereochemistry of the Product.

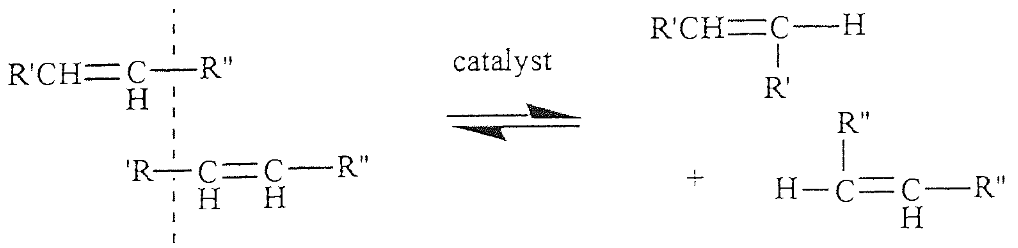
The nature of the catalyst system, the ratio of the catalyst to co-catalyst and the temperature of the reaction are just some of the factors that affect the microstructure of the products of metathesis. Much research has been carried out on the stereochemistry of the first formed products of metathesis because preferential steric arrangements provide useful information about the mechanism of the reaction. One of the problems of this approach, with acyclic alkenes, is that, unless the stereo-selectivity is very high initially, secondary metathesis produces an equilibrium mixture of *cis-* and *trans*-isomers, although the rate at which this is attained varies considerably.

The stereo-specificity of the ring-opening polymerization of monocyclic-alkenes can also be established from the initial products but secondary metathesis is again a problem. However, bicyclic systems, like norbornene, are not susceptible to inter- or intra-molecular back-biting because of steric crowding in the polymer chain. This means they have the stereo-specificity fixed into the chain as it propagates and the implications of this will be considered separately.

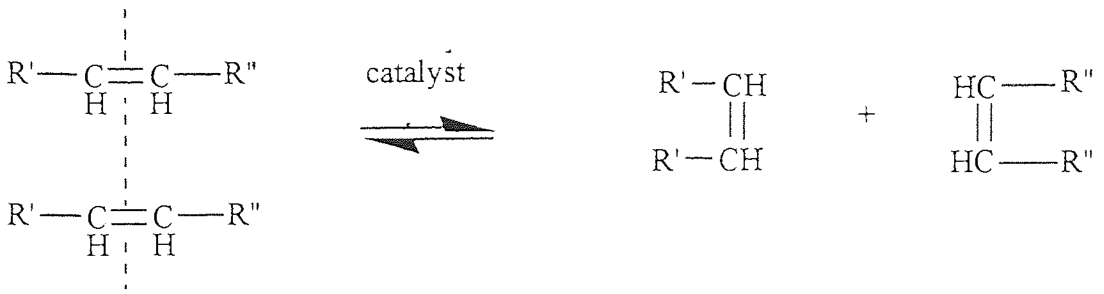
1.6 MECHANISM OF METATHESIS REACTION.

1.6.1 SITE OF ALKENE CLEAVAGE.

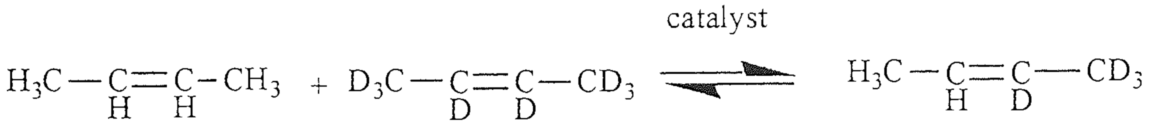
Calderon[8] initially recognized two possible mechanisms for alkene bond scission to produce the metathesis reaction. Transalkylation, a mechanism also proposed by Natta[5], involves cleavage of the carbon to carbon single bond α to the double bond and alkyl-group exchange.



Transalkylidenation was the term adopted for scission of the carbon-to-carbon double bond, which involves exchange of alkylidene groups.



Calderon used the reaction between 2-butene and perdeuterated-2-butene to distinguish between these two possibilities.



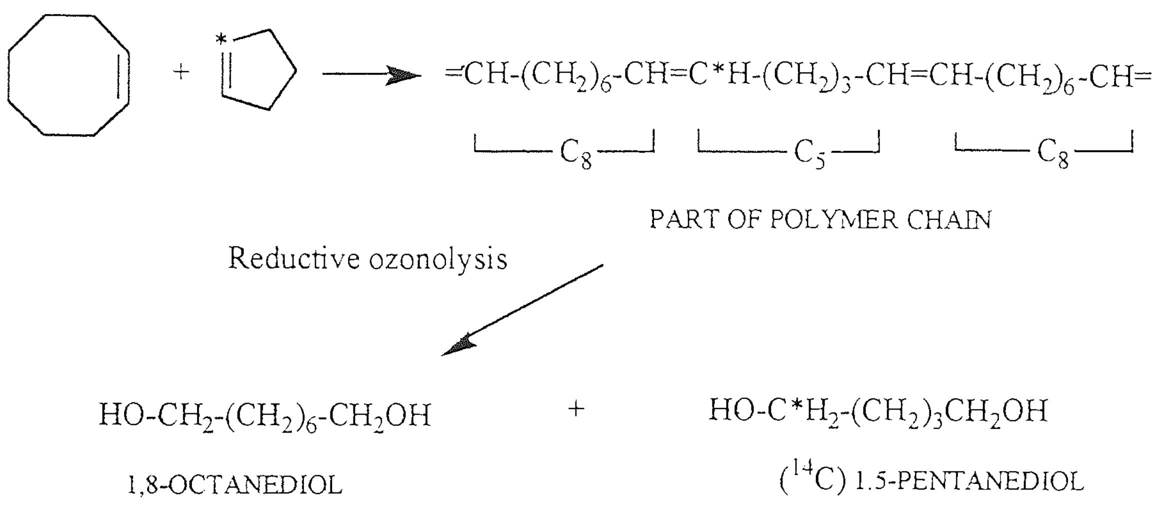
$$H_3C-\underset{H}{C}=\underset{H}{C}-CH_3 + D_3C-\underset{D}{C}=\underset{D}{C}-CD_3 \xrightleftharpoons{\text{catalyst}} H_3C-\underset{H}{C}=\underset{D}{C}-CD_3$$

31 **32** **33**

The equilibrium mixture was found to contain only 31, 32 and 33 in the molar ratio 31 : 32 : 33 of 1:1:2. As 33 was the only product, the transalkylidenation reaction was occurring, because cleavage of the α-single bond would produce a mixture of partly deuterated 2-butenes. Although Calderon initially thought ring-opening polymerization was a special form of metathesis, his subsequent research and that of Dall'Asta and Motroni,[10] demonstrated that the same double bond cleavage was involved. Dall'Asta demonstrated this using the co-polymerization of cyclooctene and cyclopentene, which was isotopically (^{14}C) labelled at the double bond. The random co-polymer was broken down using reductive ozonolysis to cleave the double bonds and produce diol fragments that could be analysed.

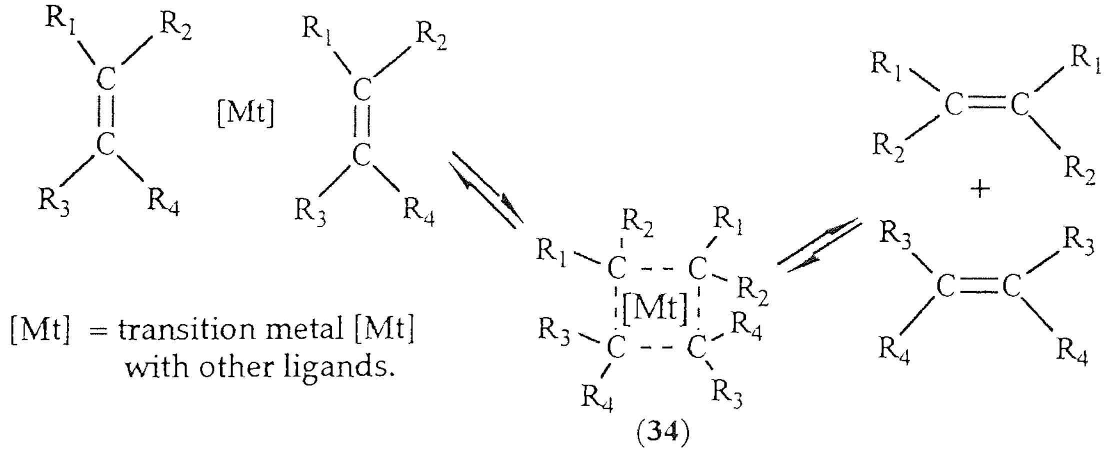
The polymer formed by ring cleavage at the double bond would be expected to contain C_8 units, with no ^{14}C, and C_5 units, which all contain one ^{14}C atom, and therefore only one C_8 and C_5 diol would be produced. Transalkylation would produce a radio-active form of both diols, as well as a non-active form. Radiochemical analysis showed that all the radioactivity was in the 1,5-

pentanediol, which confirmed the carbon-to-carbon double bond scission mechanism for polymerization too.



1.6.2 REACTION MECHANISM.

1.6.2.1 Pairwise Mechanism.



[Mt] = transition metal [Mt] with other ligands.

(34)

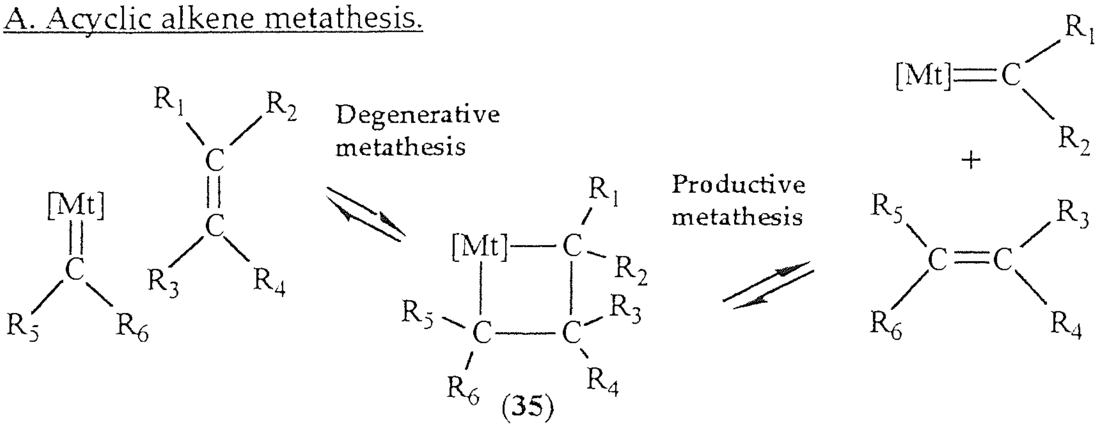
The original mechanisms proposed for metathesis involved species like the "bis-olefin-metal-complex" suggested by Calderon and the "quasi-cyclo-butane-ring", shown as the intermediate (34) in the sequence above, put forward by Bradshaw. Theoretical support for a pairwise mechanism was provided by Mango et al[15], who suggested that the transition metal d orbitals removed the symmetry restrictions, which, according to the Woodward-Hoffman rules of symmetry, would make simultaneous making and breaking of a carbon-to-carbon double bond thermally forbidden. Calculations and orbital symmetry considerations predicted that, in the coordination sphere of the metal, the reaction would proceed with a low activation energy.

1.6.2.2 Kinetic Chain Mechanism.

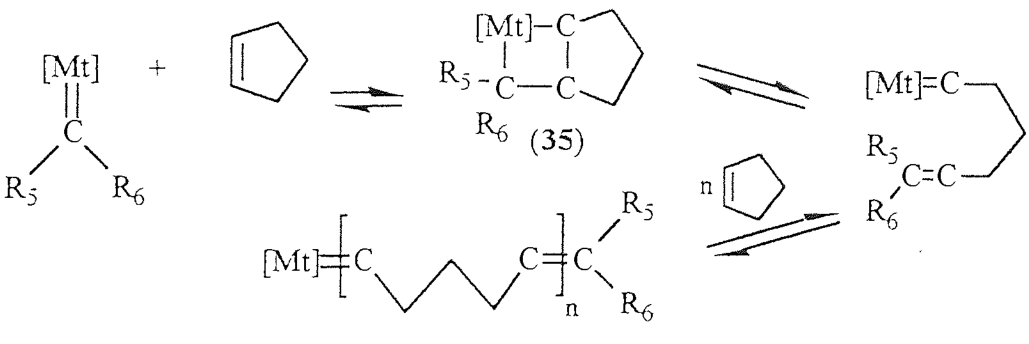
Although there was continuing support in the 1970's for the pairwise mechanism, in 1970 Herisson and Chauvin[16] put forward an alternative kinetic chain mechanism. This has now become accepted for the vast majority of metathesis catalyst systems. The propagating species is a metal carbene (e.g. $[Mt]=C(R_5)R_6$), formed in some way from the catalyst/substrate system, and this produces exchange of the alkylidene groups by the formation of a transient metallacyclobutane ring (35). Productive or degenerative fission then occurs to reform a carbene and an alkene, as the scheme 1.6.1 shows for all three types of metathesis.

SCHEME 1.6.1 FOR KINETIC CHAIN MECHANISM.

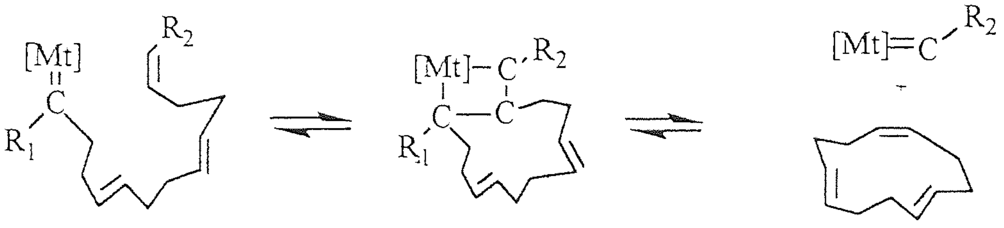
A. Acyclic alkene metathesis.



B. Ring-opening metathesis polymerization of cyclic alkenes.

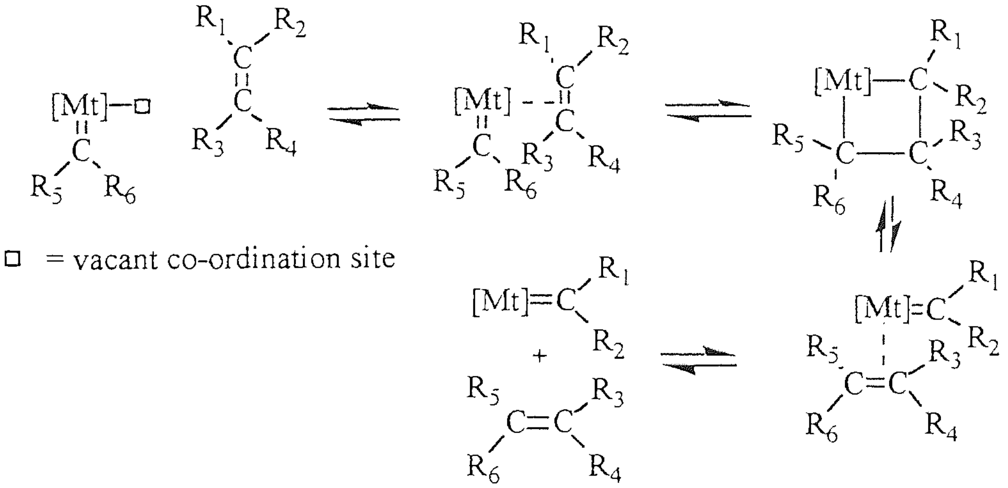


C. Intramolecular back-biting producing cyclic oligomers.



(35)

The production of the metallacyclobutane was explained in two ways. The most common[135,136] involved the coordination of the monomer with the transition metal, using a vacant coordination site adjacent to the carbene to form a metal π complex and this resulted in formation of the very reactive four-membered ring. The metallacyclobutane ring then cleaved to give productive or degenerative metathesis but in either case a carbene and an alkene are reformed. The decoordination of the alkene regenerates the carbene.



□ = vacant co-ordination site

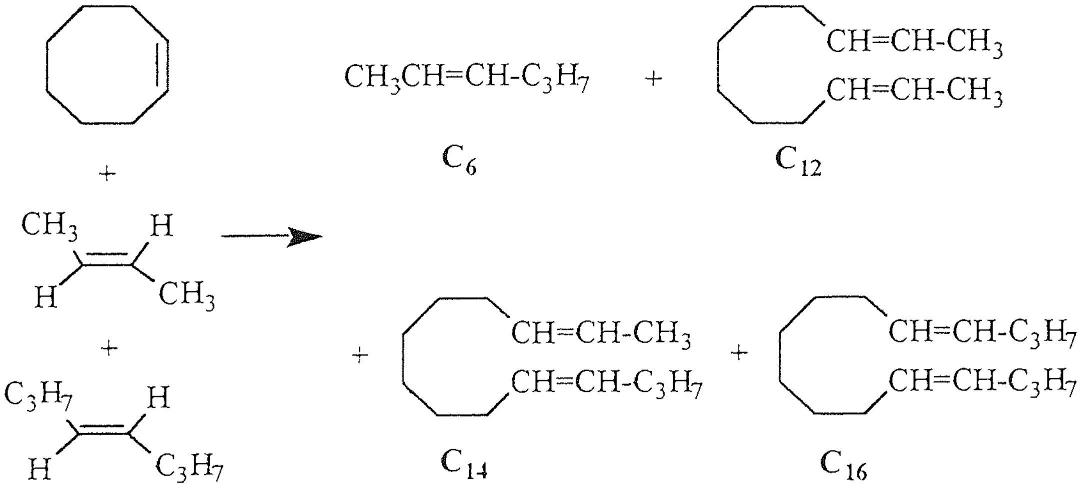
Katz[137] proposed an alternative route to the metallacyclobutane ring. He assumed a dipolar attack by the carbene, and as a π-complex is not specified as an essential element of the mechanism, a vacant transition metal coordination site is not essential. Katz mooted electrophilic character for the carbene carbon but Gassman[138] proposed that it was nucleophilic based on carbene 'trapping' experiments with Michael acceptors, such as ethyl acrylate.

The need for a vacant coordination site has now been accepted as a result of studies by several workers, for example the metathesis of 4-nonene by the catalyst toluene-$W(CO)_3$ was prevented by using a closed system to inhibit the loss of carbon monoxide,[139] and ligand exchange in stable carbenes (e.g. $(CO)_5W=CPh_2$), under relatively mild reaction conditions, was suppressed at low temperatures, as was the the metathetic activity.

The demise of the pairwise mechanism as an accepted route to metathesis has arisen from lack of supporting evidence e.g. no cyclobutanes have been isolated from metathesis reactions and cyclobutanes do not inter-convert with alkenes and metathesis catalysts. However there is a considerable body of knowledge to support the kinetic chain mechanism and some of this will be reviewed.

1.6.2.2.1 Cross Metathesis Reactions.

Cross metathesis reactions were initially devised by Herisson and Chauvin[16] as the basis of their kinetic chain hypothesis and although supporters of the pairwise route developed a "sticky olefin" mechanism to account for the observations, the results of the double cross-metathesis reactions of Katz[140] in 1977 confirmed the former explanation. The experiment involved the reaction between cyclooctene and a mixture of 2-butene and 4-octene using the catalyst system $MoCl_2(NO)_2(PPh_3)_2/Me_3Al_2Cl_3$ in chlorobenzene at 20°C.



The four metathesis products originate as follows: C_6 from the cross metathesis of the linear alkenes, C_{12} and C_{16} from the symmetrical cometathesis of the cyclooctene with 2-butene and 4-octene respectively and C_{14} from an asymmetrical reaction. A pairwise mechanism would predict that initially the ratio of C_{14}: C_{12} and of C_{14}: C_{16} would be zero. Katz found that the initial product ratio, extrapolated back to zero time, was 4.05 + 0.05 for the *cis*-isomers and 4.11 + 0.09 for the *trans*-reactants, which is close to the predicted ratio of 4.0 for the metal carbene mechanism. Grubbs[141] carried out a series of cross-metathesis reactions with α,ω-dienes using undeuterated and deuterated 1,7-octadiene and the experimental results clearly supported the carbene mechanism.

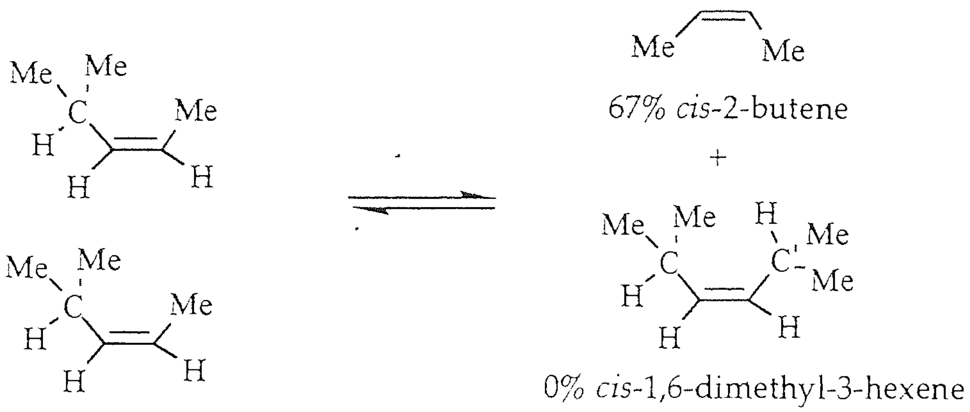
When non-symmetrical alkenes undergo metathesis, the ratio of the first formed products shows that there are some preferred orientations of the alkene at the active site, particularly when terminal alkenes are involved.

1.6.2.2.2 Stereochemical Evidence.

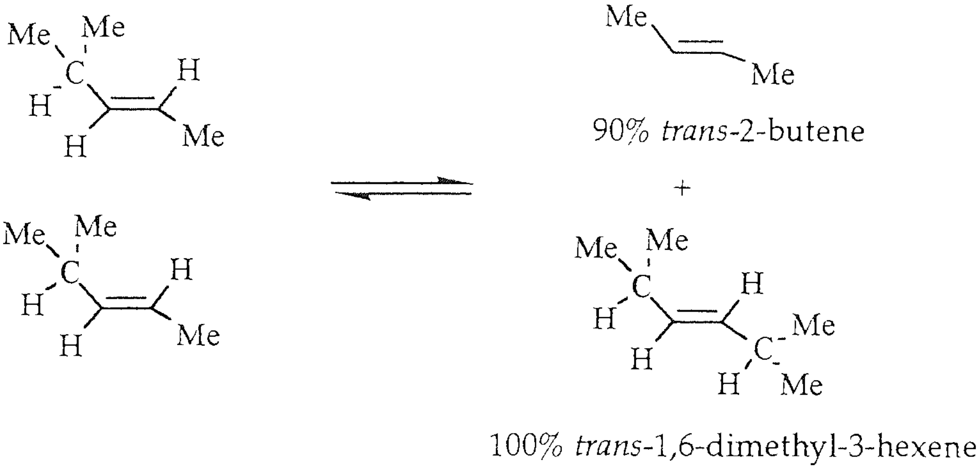
A consequence of the pairwise mechanism for alkylidene exchange is that two *cis*-alkenes produce either both *cis*- or both *trans*- alkenes and two *trans*-reacting molecules would do the same. So the *trans*/*cis* ratio in the product molecules should be the same. Several experiments were shown to produce differing amounts of the isomeric forms but Ofstead[142] produced the most convincing results. Using the catalyst system $WCl_6/Bu_4Sn/2Et_2O$, he carried out the metathesis of both *cis*- and *trans*- 4-methyl-2-pentene.

The percentage of the two products, with each configuration, is not the same and although the 2-butene tends to have the same configuration as the reactant used, the production of only the *trans*- form of 1,6-dimethyl-3-hexene, with both reactants, is best explained by the carbene mechanism. Three-dimensional diagrams showing the different equatorial and axial arrangements of possible metallacyclobutane ring intermediates for the reaction help to explain the final mix of stereo-isomers.

Metathesis of *cis*-4-methyl-2-pentene



Metathesis of *trans*-4-methyl-2-pentene



1.6.2.2.3 Evidence from Ring-opening Polymerization.

The main features of ring-opening polymerization of cyclic alkenes (e.g. cyclopentene) were introduced in section 1.4.5 but the relevance of some experimental observations of the system will be summarised here.[93]

1. The product usually consists of a high molecular weight fraction, with a molecular weight $>10^5$, and a low molecular weight fraction, containing a series of cyclic oligomers.
2. Above a certain minimum monomer concentration, an equilibrium will eventually be established between the monomer, the cyclic oligomers and the high molecular weight polymer.
3. When the monomer concentration is below a specific critical value, no high molecular weight polymer is formed, only oligomers. Above this value, the

concentration of oligomer at equilibrium, is almost constant and so the proportion of high molecular weight product increases with increasing monomer concentration.

4. Both oligomers and high molecular weight polymer are formed concurrently although one reaction may be favoured over the other.
5. The relative proportions of cyclic oligomers form a continuous, declining series, initially and at equilibrium .
6. The relative amount of catalyst to monomer is extremely low, [catalyst]/[monomer]$<10^{-5}$ is common and can be lower. This is a good indication of a chain mechanism.
7. If acyclic alkenes are present in the reaction mixture the molecular weight of the polymer is reduced considerably and if sufficient acyclic alkene is used, there is evidence of these alkylidene species, as polymer chain end groups. Indeed chain transfer agents are now used extensively to produce telechelic species with two end group functionalities to the linear polymer.
8. Cycloalkenes undergo ring opening cross-metathesis with acyclic alkenes. However is has been shown that the viscosity/molecular weight ratio of the high molecular weight polymer, made from pure cyclopentene and from, cyclopentene/1-butene mixtures, are identical. This is further evidence of linear chains in the polymer, allowing for the possibility of acyclic alkene traces causing chain transfer even in the pure cyclopentene system.

As shown in section 1.4.5 the Jackobson-Stockmayer theory[61] of ring-chain equilibria has been applied successfully to some ring-opening systems. A simple pairwise mechanism would have several features that do not tally with these observations.

1. The molecular weight would increase regularly as the size of the cyclic oligomers increases, as observed in condensation polymerizations.

2. The relative proportion of the different cyclic oligomers would change with the reaction time.

3. The series of cyclic oligomers, produced by cycloocta-1,5-diene (referred to in 1.4.5), would be expected to favour the series $(C_4H_6)_x$, where x is even, initially but in fact does not.

1.6.2.2.4 Evidence from Initial Products.

The role of the co-catalyst was discussed in section 1.5.2.2 and examples were given in which the organometallic co-catalyst provided an alkylating species for the transition metal complex. The products of the catalyst reaction indicate carbene formation e.g. $Cl_4W{=}CH_2$ from the $WCl_6/SnMe_4$ system.[108,109] The $WCl_6/SnMe_4$ catalyst system has been used by many workers and results indicate that the two possible reactions of the proposed carbene with non-symmetrical alkenes, like 2-pentene, are equally probable. However the amounts of initial products are of the order of 3-20% of the WCl_6 used. Wastage of the catalyst, by this type of reaction, has been proposed.

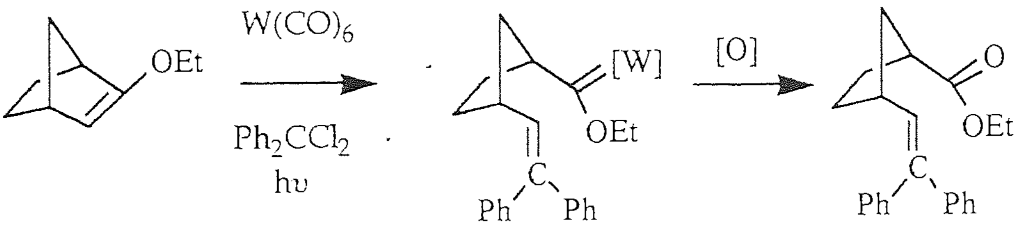
$$[W]{=}CH_2 \text{ ----> } [W] + 1/2\, C_2H_4$$

Thorn-Csanyi[143] used the same catalyst system but added ether as a third component and traces of 1-pentene. There was an initial slight evolution of propene but after two hours the propene was produced in stoichiometric amounts. This was explained in terms of the relative inactivity of the initial carbene with a second more active species forming slowly.

The $WCl_6/SnMe_4$ system must undergo α-H elimination to form the carbene and methane, from [W]-Me, but the $WCl_6/SnEt_4$ and $WCl_6/SnBu_4$ systems produce ethene and 1-butene by β-H elimination.

$$[W]\text{-}CH_2CH_3 \text{ ----> } [W]\text{-}H + CH_2{=}CH_2$$

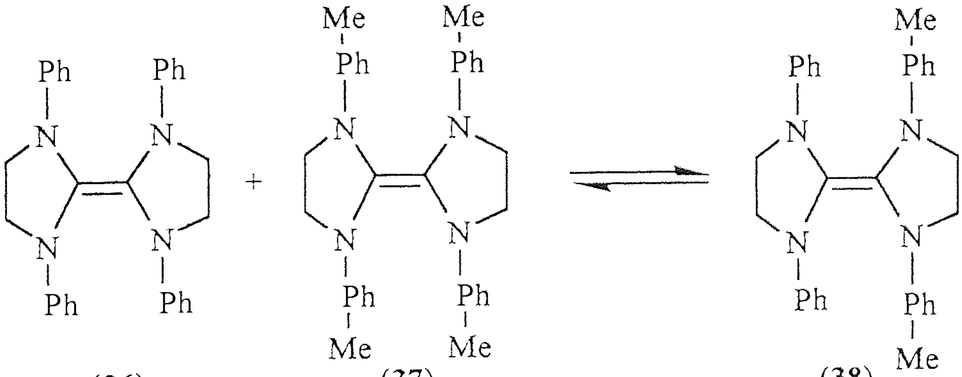
Carbene ligands have been shown to be generated in the $W(CO)_6/Ph_2CCl_4$ and $W(CO)_6/Ph_2CCl_2$ catalyst systems, after photolysis, because the products of the ring-opening metathesis of 2-ethoxynorbornene, were found to have $=CCl_2$ and $=CPh_2$ end groups respectively.[144]



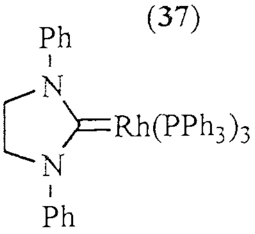
The detection of such end groups has been carried out in several acyclic systems but for the polymerization of cyclic alkenes the only examples of end group characterisation involve using a known carbene as the original catalyst.[98]

In section 1.5.2.1.3, the π-allyl route to the metallacyclobutane ring was used to explain the formation of carbenes by the direct interaction of the alkene with the transition metal complex. Although heterogeneous molybdenum systems have been used in this work,[104] the mechanism accounts for the products and it has also been shown that ethene and perdeuterated ethene do not undergo metathesis exchange with these catalyst systems. As ethene cannot form a π-allyl complex, it cannot produce the carbene by this mechanism.

1.6.2.2.5 Reactions of Isolable Carbenes with Alkenes.



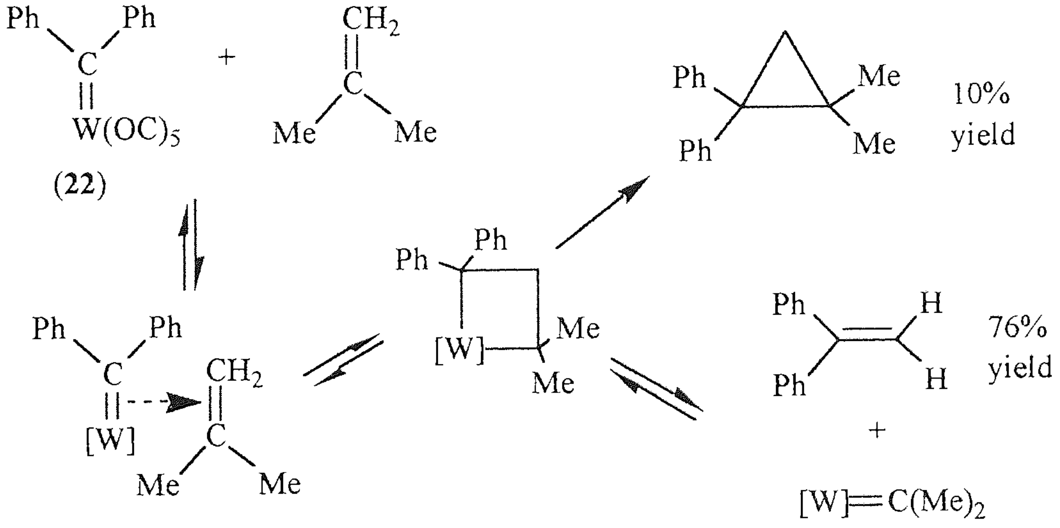
(36) (37) (38)



(39)

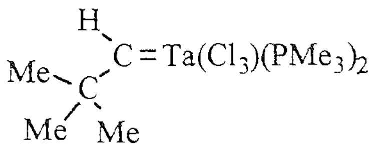
The use of stable carbenes as metathesis catalysts, either on their own or with co-catalysts, has been covered in section 1.5.2.1.1 but the first carbene to be isolated, as an intermediate in a reacting metathesis system, was synthesised by Cardin et al[145] in 1972. They were investigating the metathesis of electron-rich tetrakisamino ethenes (**36**, **37** and **38**) using the rhodium catalysts $RhCl(PPh_3)_3$ and $RhCl(PPh_3)_2Cl$ at high temperatures and isolated and characterised rhodium I carbenes of the form of **39**.

Carbenes can react with alkenes in three different ways metathesis, homologation and cyclopropanation. Cyclopropanation was found to be a side reaction when Casey first investigated the reactivity of the carbene (**22**) with 2-methyl-1-propene. A mechanism involving a metallacyclobutane ring explains the formation of both products. There is some change in the nature of the tungsten coordination during the reaction because Casey recovered $W(CO)_6$, at the end of the experiment, as 45% of the tungsten containing species.

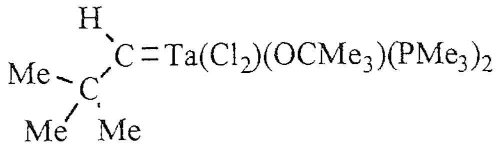


There is evidence that the cyclopropanation reaction is favoured if the alkene has a polar group attached to it. Casey showed that ethoxyethene reacts with carbene (**22**) at 37°C to produce a product mixture of only 11% $Ph_2C{=}CH_2$ and 65% of the cyclopropane compound.

Homologation can also occur exclusively or, with slight changes to the nature of the carbene and/or the alkene used, as well as metathesis. Rocklage[146] investigated the metathesis of 1-butene, with the tantalum carbene **40** and found that only homologation occurred with equal amounts of the two possible products. However the replacement of one -Cl ligand in complex **40** by the *t*-butoxy- ligand (carbene **41**) increased the electron density on the tantalum and the course of the reaction was modified.



$(Me_3)CCH=[Ta'] = $ (**40**)



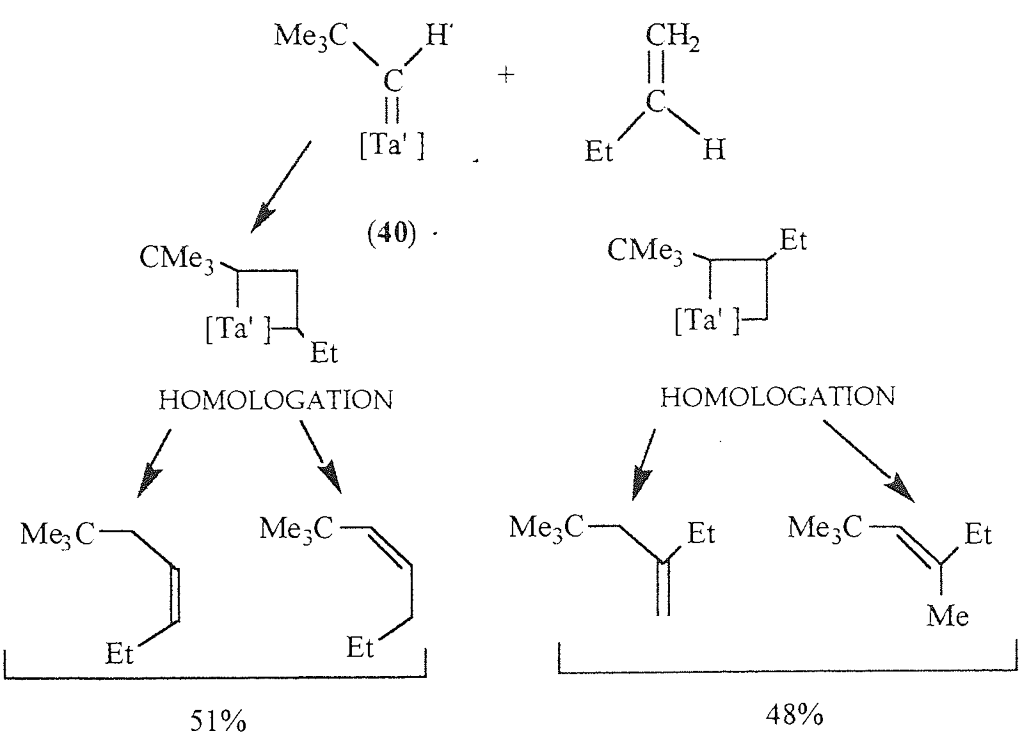
$(Me_3)CCH=[Ta''] = $ (**41**)

Schemes 1.6.2 and 1.6.3 show the different courses of the two systems and again the intermediate metallacyclobutane ring can account for the products. In the scheme 1.6.2 the carbene (**40**) shows no preferential orientation for the alkene to the carbene and four different C_9 products are formed by β-H migration. The two unstable metallacyclobutane rings break down and produce only homologation.

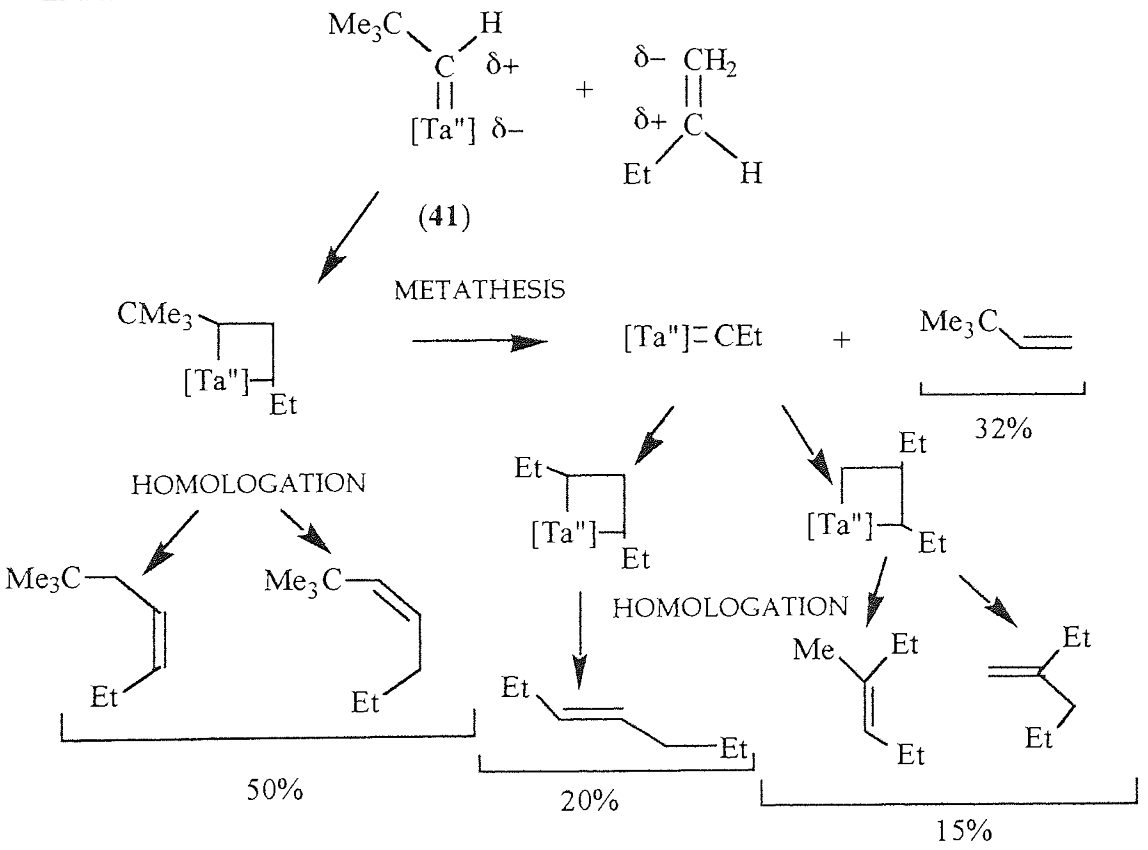
In scheme 1.6.3, the carbene (**41**) and 1-butene have a preferred mode of addition, and the metallacyclobutane ring can break down by homologation or metathesis. However the [Ta″]=CHEt carbene, produced by the metathesis reaction, showed no preferred orientation with respect to the alkene and the two metallacyclobutanes formed only break down by homologation. So both permanent ligands and the nature of the alkylidene affect the carbene/alkene reaction, the main effect was considered by Schrock[147] to be polarity of the metal-carbene bond, with the *ter*-butoxy ligand increasing the electron density of the metal by donation from the oxygen lone pairs.

The nature of the alkene does have an effect on both its mode of addition to the carbene and the nature and rate of any subsequent reaction. It has been shown that the carbene $Ph_2C=W(CO)_5$ and the alkenes of the type $CH_2=CR'R''$ produce mainly $Ph_2C=CH_2$,[148] showing that steric factors influence the nature of the metallacyclobutane ring. The effect of substituents, on the carbons of the double bond, on the rate of metathesis has been investigated using $(MeC_6H_4)_2C=W(CO)_5$ with 1-pentene, 2-methylpropene and *cis*-2-butene at 70°C[149] and the relative rates were in the ratio 49: 10: 1.

SCHEME 1.6.2



SCHEME 1.6.3

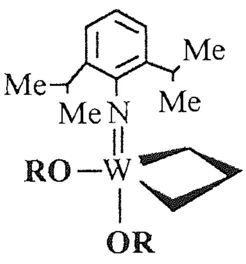


The body of knowledge to support the role of the carbene in metathesis is overwhelming. NMR studies have been used to show their ability to complex directly with carbon to carbon double bonds[150] and the presence of both initiating and propagating carbenes have been detected in the metathesis of 1-butene.[147]

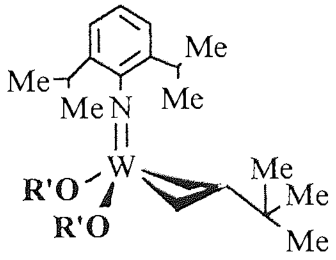
1.6.2.2.6 Reactions of Isolable Metallacyclobutane with Alkenes.

The work of Grubbs[19,20] on the production of stable titanacyclobutanes, which were used to catalyse the ring opening metathesis polymerization of norbornene, has been covered in section 1.4.5.1.

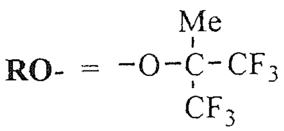
The production of other stable cyclic intermediates of this type has been the subject of much research and has been reviewed by Schrock.[59] The stability of these metallacyclobutanes depends on many factors, as it does for carbenes, and there is X-ray evidence for different structural arrangements. The isolable metallacyclobutanes produced from the four co-ordinated tungsten carbenes described in section 1.5.2.1.1 (e.g.(**24**)) have been shown to have two possible structures. (**42**) is a trigonal bipyramid with a planar metallacyclobutane ring and (**43**) is a distorted square based pyramid having a puckered metallacycle.



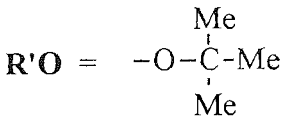
(**42**)



(**43**)



RO- $= -O-\overset{Me}{\underset{CF_3}{C}}-CF_3$

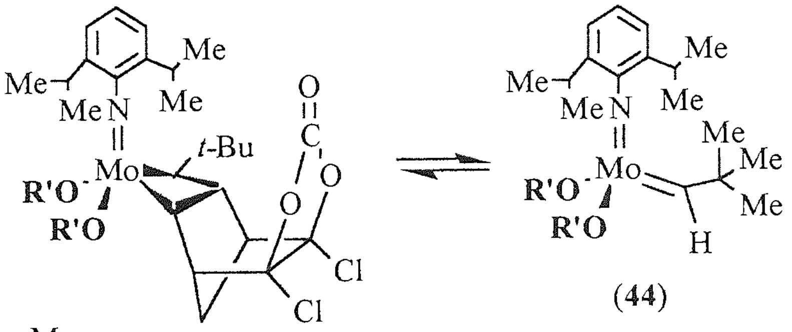


R'O $= -O-\overset{Me}{\underset{Me}{C}}-Me$

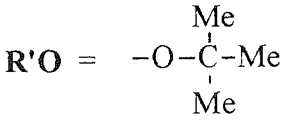
The nature of the alkoxy-groups affects the structure and the reactivity of the complex, as (**42**) is the more stable arrangement with strongly electron withdrawing groups (-**OR**) attached to the metal. The electon donating character of -**OR'** favours the structure (**43**) but renders it less reactive than (**42**) to metathesis exchange.

Isolable metallacycles of tantalum, tungsten and molybdenum have been less frequently used as ring-opening metathesis polymerization catalysts, than their associated carbenes. The $(ArO)_3TaCHPhCH_2CH$*t*-Bu metallacycle can produce living polymerization of norbornene, if the reaction is stopped before complete monomer consumption occurs; because cleavage of the metal carbene chain, with benzaldehyde, produces monodisperse polymer. However with many systems secondary metathesis occurs when the monomer has been consumed and this tends to broaden the molecular weight distribution.

In recent work[87] the carbene (**44**) has been reversibly converted into the metallacycle (**45**). Heating regenerated 50% of the original carbene and the rest converted the monomer into living oligomer.



(44)



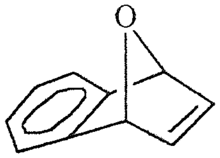
R'O = $-O-\underset{Me}{\overset{Me}{C}}-Me$

(45)

+

LIVING OLIGOMER.

The greater stability of metallacyclobutane complexes with bulky substituents has been recognised and sophisticated molybdacyclobutane complexes have been developed, for the ring-opening metathesis polymerization of functionalised monomers to produce living systems.



(**46**)

Molybdacyclobutane complexes of 7-oxanorbornadienes (e.g. **46**) have been isolated and characterised by X-ray study. This complex produces smooth polymerization of the monomer and polydispersity of the products has been recorded as ≈1.05.

1.6.3 METATHESIS INITIATION.

The evidence for a kinetic chain mechanism for metathesis is overwhelming and the propagation intermediates are well established. The roles of substrate, co-catalyst, promoters and other factors (e.g. the solvent or the use of photoinduction) have been discussed in section 1.5 but some salient features of the effects of these factors on initiation will be summarised. The initiation process is complex as changes to the oxidation state of the transition metal complex, production of one or more vacant coordination sites on the transition metal and formation of the initiating carbene are all involved.

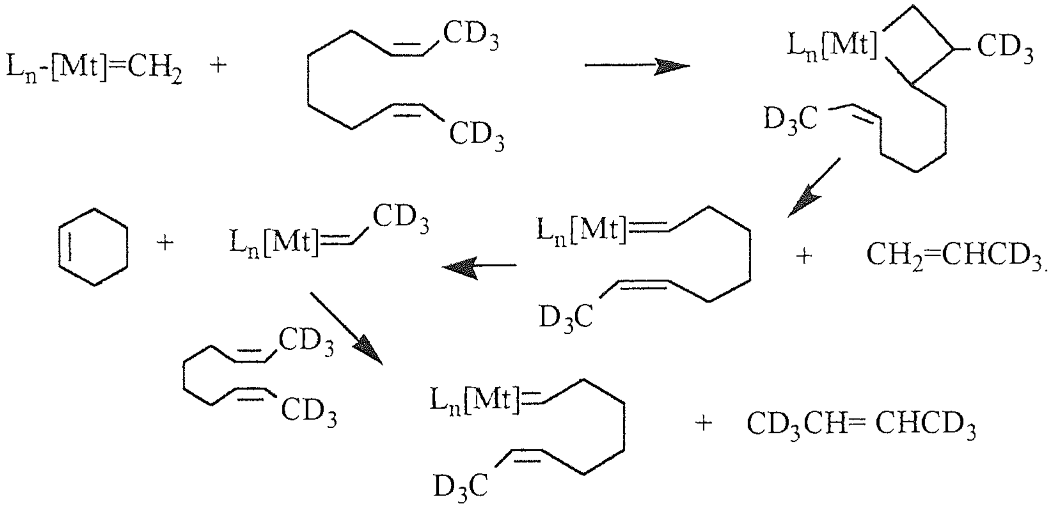
In section 1.5.2.1.3. the production of a carbene from single component catalysts, $WOCl_4$ or $ReCl_5$ and the monomer was considered. The work of Farona et al[104] indicates the formation of metal-π complexes in metathesis reactions of supported molybdenum oxide catalysts and this may be applicable to some homogeneous systems. Evidence has also been quoted for the alkene alone changing the oxidation state of the transition metal complex[29] and producing a vacant coordination site.[107] However this activity may occur simultaneously with similar reactions between catalyst components.

Many examples of the reaction between catalyst components producing the initial carbene have been reported. The evolution of methane from the catalyst mixtures of WCl_6 with both $SnMe_4$[108] and $ZnMe_2$[109] was referred to in 1.5.2.2, and the reaction for the formation of a carbene given. Schrock et al[151] established that methane was also evolved when catalyst systems of the type $L_2(NO)_2Cl_2M$ / $Me_3Al_2Cl_3$ (in which L is neutral organic ligand and M is Mo or W) are pre-mixed and then added to 2,8-decadiene. An initial metathesis product is propene and Grubbs[108] showed that if (1,1,1,10,10,10-D_6) 2,8-decadiene is used then (3,3,3-D_3) propene is formed. In both experiments the expected metathesis products of cyclohexene and 2-butene or (1,1,1,4,4,4-D_6)-2-butene were also formed, as shown by the following reactions.

Catalyst reaction.

$$L_n[Mt] \xrightarrow{CH_3\text{-}[Al]} L_n\text{-}[Mt]\text{-}CH_3 \xrightarrow{CH_3\text{-}[Al]} L_n\text{-}[Mt]{=}CH_2 + CH_4$$

Metathesis reaction.



The production of propene and (3,3,3-D_3) propene are consistent with the initial generation of a metal-methylene compound. Grubbs and Schrock reported the production of stoichiometric amounts of propene, based on the original number of moles of transition metal species. This would suggest a catalyst efficiency close to 100% but in polymerization experiments the degree of polymerization of the polymer obtained indicates a much reduced efficiency.[129] The loss of active carbenes by wastage is referred to in section 1.6.2.2.4.

In section 1.6.2.2.4 mention was also made of end group detection in metathesis, with UV absorption maxima being used to identify $Ph_2C=$ end groups. Ring-opening metathesis of 2-ethoxynorbornene, by the photo-assisted catalyst systems $W(CO)_6/CCl_4$ and $W(CO)_6/Ph_2CCl_2$, established the chain ends $=CCl_2$ and $=CPh_2$. Tanielan[130] suggested that, in the former system, transient species e.g. $W(CO)_5$, $W(CO)_5Cl$ and $W(CO)_4Cl_2$ might result in the formation of the relevant carbene from the co-catalyst.

Farona et al[152] reported the formation of trace products with an extra three carbon fragment when the $Re(CO)_5X/EtAlCl_2$ system was used. An initiating propylenic carbene was deduced to be formed and this was only possible, if ethylation of a carbonyl ligand by the co-catalyst took place, followed by the production of [Re]=CH-CH_2CH_3. Later research by the same workers[135] was mentioned in section 1.5.3.4, which showed a similar effect when the catalyst system $(CO)_5Mo(py)/EtAlCl_2/Bu_4NCl$ was mixed in heptane and used to metathesise 1,7-octadiene. However the use of chlorobenzene as a solvent produced the expected products of an ethylenic carbene. Schemes 1.5.1 and 1.5.2 explain the possible reaction mechanisms.

The reaction of co-catalyst and catalyst must be considered in conjunction with the effect of the substrate not only because of observed efficient metathesis when no alkylating agent is present in the catalyst system e.g. $WCl_6/AlBr_3$,[153] but also because of observations such as those of Basset and co-workers.[154] It was found that pure *trans*-2-pentene failed to undergo metathesis, with the catalyst system $W(CO)_5PPh_3/EtAlCl_2/O_2$ or $W(CO)_3$(mesitylene)$/EtAlCl_2/O_2$, but, if traces of *cis*-2-pentene or a terminal alkene were present, metathesis occurred after an induction period. Pampus,[155] also reported, that *trans*-2-butene did not produce metathesis products with the $WCl_6/MeAlCl_2$ catalyst system although Katz had found no difficulty metathesising *trans*- alkenes with the $Ph_2C=W(CO)_5$ carbene. Basset interpreted this behaviour through steric control of the formation of the initiating carbene. The important alkylating agent for this is the *cis*- form of the substrate or a terminal alkene. The reaction is therefore autocatalytic, as once this species is produced, propagation can proceed using either steric isomer.

The Lewis acid properties of the co-catalyst or a third catalyst component have been used to demonstrate alternative routes to π-complex formation, between the transistion metal complex and the alkene, and the action of promoter, to extend the possible range of reactions, has been adequately covered in sections 1.5.2.2. and 1.5.2.3.

The most recent work on the mechanism of initiation, such as that of Otton[44], Hummel[156], Ceausescu[157] and Farona,[158] has produced evidence of species present in specific reactions during initiation but these and the proposed mechanistic routes are similar to those already discussed.

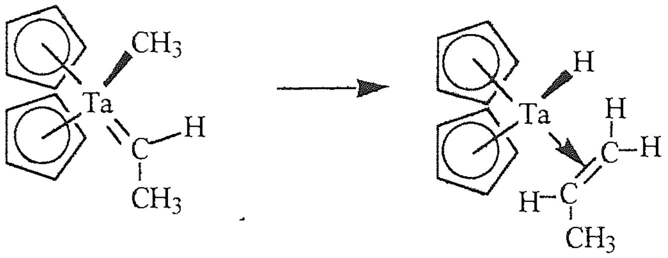
1.6.4 CHAIN TRANSFER AND TERMINATION IN ROMP.

Although recently some ring-opening metathesis reactions have been classified as living polymerizations, the chain mechanism of metathesis polymerizations must include consideration of both chain transfer and termination steps.

The inter- and intra-molecular reactions that occur between the in-chain double bonds of polyalkylidenes, which produce secondary metathesis with characteristic broadening of the polydispersity of the polymer product, have been mentioned, as has the effect of these reactions on the stereochemistry of the product, and the formation of cyclic oligomers. The use of transfer agents, e.g. acyclic alkenes, to control the molecular weight of the polymer is a recognized technique.

Termination reactions can occur either because of the presence of impurities in the system, e.g. oxygen, water or an organic molecule containing a polar group, or from side reactions of the propagating species, when no impurities are present. Several examples of this latter type have been identified.

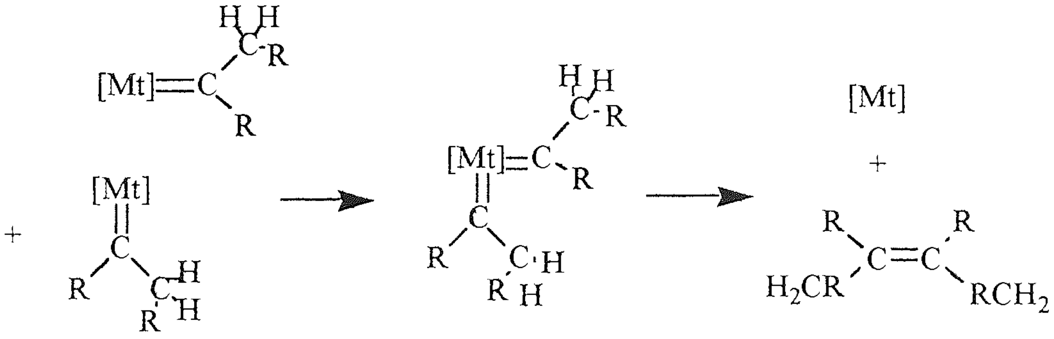
1. Dolgoplosk[159] suggested a first order termination reaction in which a cyclopropane derivative is formed from the metallacyclobutane.. This type of reaction was observed by Casey[135] (see section 1.6.2.2.5) for alkenes containing polar groups and for reactions between model metal carbenes and alkenes.
2. The production of propene in reactions using tantalum carbene initiators, led Schrock[160] to postulate that, the reverse of the initial reaction, between a transition metal complex and an alkene to form the initiating carbene, was occurring and this caused termination by β-H-migration.



3. Dolgoplosk[161] also put forward a mechanism involving the reduction of the transition metal and the formation of a free radical to account for termination.

$$\text{R-CH=WCl}_n \text{ -----> } \text{R-C}^{\cdot}\text{HCl} \quad + \quad \text{WCl}_{n-1}$$

3. Second order termination reactions involving dimerization of the propagating carbene were put forward by Casey[162] and the following general scheme was proposed.



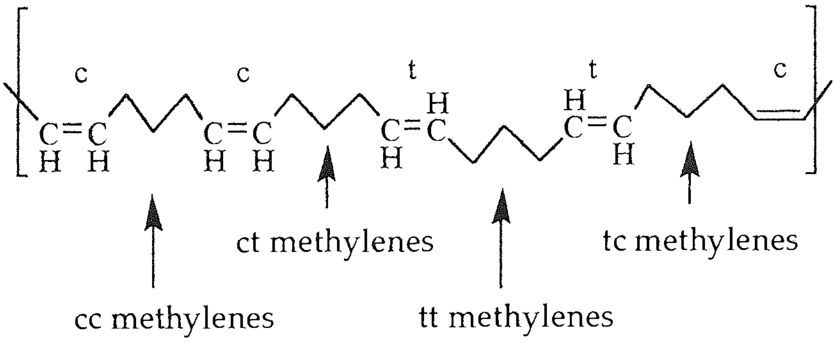
The evolution of ethene from catalyst systems e.g. ($Me_3Al_2Cl_3$/ $Mo(Ph_3P)_2Cl_2(NO)_2$ and Me_4Sn/WCl_6) led Grubbs[108] to suggest that dimerisation of methylene-metal complexes occurred.

1.7 POLYMER MICROSTRUCTURE.

The stereochemistry of the products of metathesis can be a useful guide to reaction mechanisms. Unfortunately the situation is complicated by secondary reactions both in the metathesis of acyclic alkenes and in the ring-opening polymerization, of most mono-cyclic alkenes, which results in the formation of an equilibrium mixture, of *cis*- and *trans*- isomers. During the co-polymerization of cyclopentene and norbornene, for a wide range of initial monomer concentrations, the fraction of *cis*- double bonds (σ_c), related to the polypentenylene containing dyads, was found to decrease with increasing conversion. However the structure of the carbon to carbon double bonds associated with norbornene remained constant with conversion. Therefore the stereochemistry of the polypentenylene is not a reliable source of information, because of secondary metathesis, but the microstructure of polynorbornene is much more satisfactory and has been used extensively to extend the knowledge of the mechanism of ring-opening metathesis polymerization.

The microstructure of the polymer depends on the type of cycloalkene used and three types have been identified.[93]

1. Unsubstituted monocyclic monomers, like cyclopentene, produce only *cis*-(c or z) and *trans*-(t or e) isomers and the arangement of the double bonds nearest to each methylene can be assigned as cc, ct or tt as shown in this section of the polypentenylene chain.

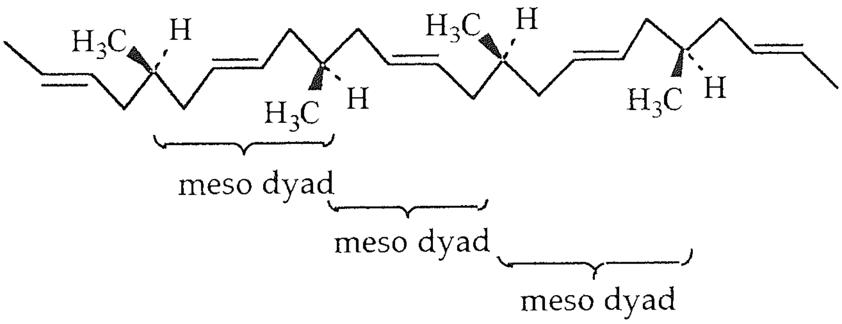


2. Monomers that exist in only one form themselves but produce polymers with chiral centres e,g, 4-methylcyclopentene and bicyclo[2,2,1]-2-heptene (norbornene). The assymetric carbon atoms along the length of these polymers mean that the chains can be divided into dyads and the character of these is related to the symmetry of the double bond, the number of carbon atoms in the dyad and the symmetry of adjacent chiral centres. A dyad is defined as comprising of two methine carbons and a racemic dyad arises from non-superimposable enantiomeric forms of the dyad, a meso dyad is a

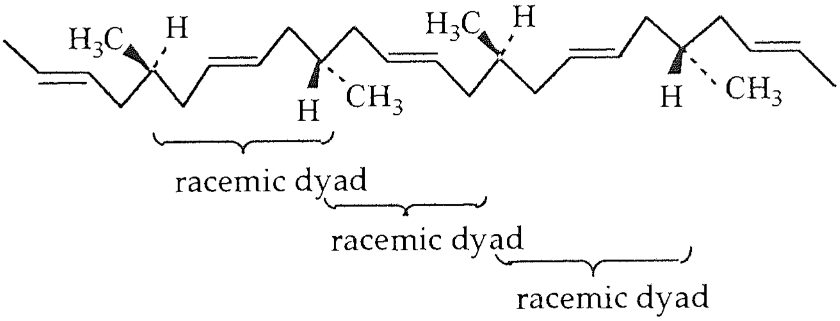
consequence of superimposable mirror forms. The sequence of dyads in the chain indicates the tacticity of the polymer, so all meso dyads result in an isotactic chain and all racemic dyads make the polymer syndiotactic. A random arrangement, or any mixture, makes the polymer strictly heterotactic or atactic, but the percentage character is often quoted

The *cis*- and *trans*- forms of the polypentenylene of 4-methylcyclopentene therefore have both an isotactic and a syndiotactic form. The dyad stretches from one chiral centre to the next and the two forms are shown for the *trans*-4-methylpolypentenylene:

ISOTACTIC *trans*-POLYMER

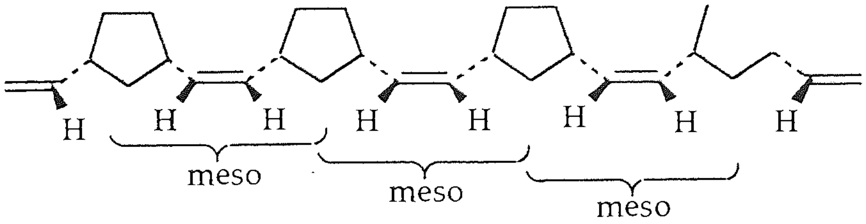


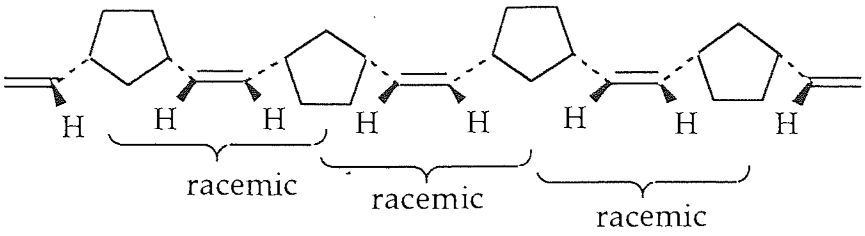
SYNDIOTACTIC *trans*-POLYMER.



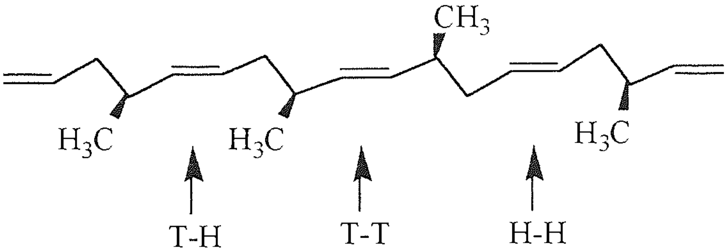
The situation is similar for norbornene but it is the orientation of the in-chain cyclopentane rings, which controls the tacticity. The two forms of the *cis*-form of polynorbornene are shown:

ISOTACTIC *cis*-POLYMER

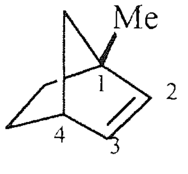



SYNDIOTACTIC *cis*-POLYMER

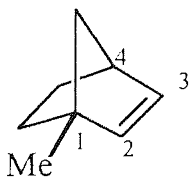
3. Monomers, like 3-methylcyclobutene and 5,5-dimethylbicyclo[2,2,1]hept-2-ene, extend the possible number of isomeric forms as propagation may be of the form head-head(H-H), head-tail(H-T) or tail-tail(T-T) as shown for the *trans*-polymer of 3-methycyclobutene:



Each dyad can be meso or racemic and there is also the option of *cis*- or *trans*-double bonds. Many of the monomers exist in enantiomeric forms and if only one form of the monomer is used in the polymerization then there is correlation between the HH/HT/TT structure and the tacticity. 1-methylbicyclo[2,2,1]hept-2-ene (MNBE) can be used to show this.

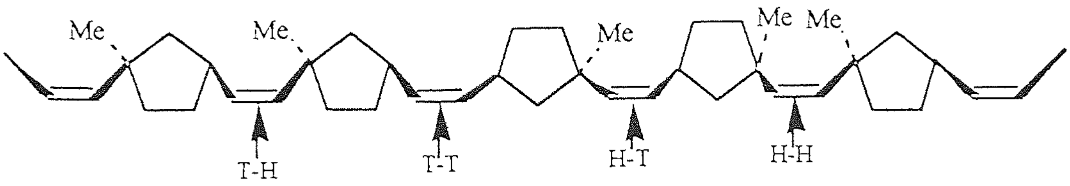


(+)MNBE
(**M**+)



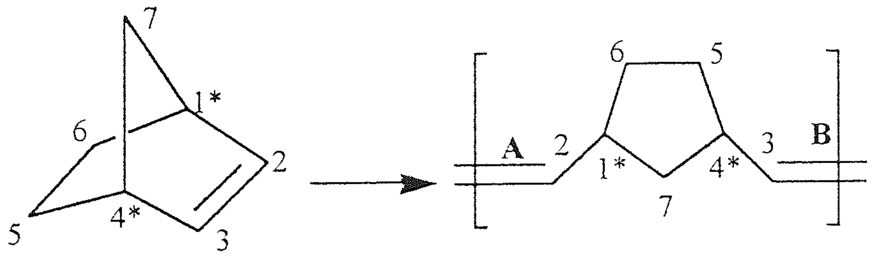
(-)MNBE
(**M**-)

One optically pure form will produce a consistent meso or racemic structure related to the orientation of the monomer units. In the diagram of *cis*-addition, the T-H and H-T sequence produce racemic dyads and the T-T and H-H mode produces meso dyads.



1.7.1 STEREOISOMERISM IN NORBORNENE POLYMERS.

^{13}C NMR spectroscopy is a very useful analytical tool for obtaining information about all three types of dyad in polymer chains, i.e. (1) cc, tt and ct, (2) meso and racemic and (3) H-H, H-T and T-T. The analysis of stereoisomerism in samples of polynorbornene, because of the absence of secondary metathesis, is particularly informative. The diagrams show the rearrangement of the norbornene monomer molecule as it becomes part of the polymer chain.

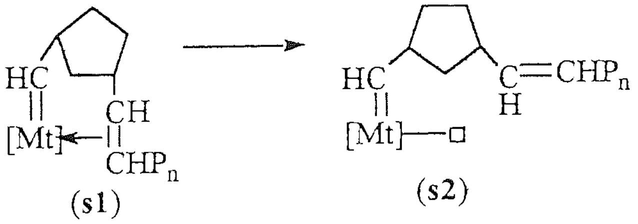


The fraction of *cis*- double bonds can be derived from the intensity of the peaks arising from the carbon atoms in the double bonds (C_2 and C_3), which have chemical shifts, downfield from TMS, of 133.88 for *cis*- and 133.10 for *trans* - double bonds. The chemical shifts for the chiral carbons (C_{1^*} and C_{4^*}) are related, not only to the stereochemistry of the adjacent double bond (bond A for C_{1^*}), but also to that of the next nearest carbon-to-carbon double bond (bond B for C_{1^*}). They produce four peaks with the *cis*A-*cis*B (c,c) and *cis*A-*trans*B (c,t) doublet occurring 5ppm upfield from the *trans*A-*trans*B (t,t) and *trans*A-*cis*B (t,c) pair. The nature of the dyads can be determined not only from these peaks but also from the triple peak, derived from the original bridgehead carbon in the monomer (C_7), which has only three resonances because the (c,t) and (t,c) effects are identical.

If the homopolymer of norbornene is treated as a co-polymer, of *cis*- and *trans*- units, then it is possible to calculate reactivity ratios from the areas of the four peaks assigned to $C_{1'}$ and $C_{4'}$, so $r_t = (t,t)/(t,c)$ and $r_c = (c,c)/(c,t)$, for the *trans-* and *cis-* form respectively[63]. If the double bonds are distributed statistically $r_t.r_c=1$, if $r_t.r_c<1$, then there is a tendency to alternation of the *trans-* and *cis-* forms, and if $r_t.r_c>1$ blockiness would be produced.

Ivin et al[63] studied the polymerization of norbornene with a wide range of catalyst/co-catalyst systems and found the fraction of *cis*-structure (σ_c) varied from 0.2 to 0.8. When $\sigma_c< 0.35$, $r_t.r_c\approx 1$, so the distribution is statistical, for $0.5 <\sigma_c<0.85$, $r_t.r_c>> 1$, showing an increased tendency to blockiness and the presence of at least two distinct propagating species. It has been found that low temperatures, high monomer concentrations and relatively slow rates of polymerization generally increase the tendency to form polymers with a high *cis-* content

Two kinetically distinct propagating species have been proposed by Ivin to account for blockiness.



The species s1 has the double bond, from the last unit addition, still co-ordinated to the metal site and models suggest that its stability is increased by a *cis*-coordinating bond and propagation through an incoming monomer unit favours the formation of another *cis*-arrangement. The species s2 has a vacant site, as decordination has occurred, and does not have the steric constraints of s1, so favouring coordination and insertion of a monomer unit with a *trans-* double bond. An assumption, that all the *trans*-insertions of monomer immediately cause s1 to relax into s2, makes it possible to treat the two propagation sequences kinetically and Ho[64] has shown that the theoretical model produces a similar trend in the relationship between σ_c and $r_t.r_c$, as the experimental observations.

The nature of the transition metal compound alone does not control the microstructure of these polymers. WCl_6 with the co-catalyst $(allyl)_4Sn$ produces high *cis*-content polynorbornene (σ_c= 0.53-0.7) and high blockiness ($r_t r_c$= 5-6). However with Ph_4Sn, σ_c is relatively low (0.41) and $r_t r_c$ is only 1.4, showing almost statistical distribution. Again with the co-catalyst $AlEtCl_2$, the degree of *cis*- double bonds and the blockiness are in the medium range. The presence of a third catalyst component, e.g. ethyl acrylate, can increase the *cis*-content.

Further support for the propagating species (s1), proposed by Ivin for *cis*-addition particularly, has come from the polymerization of cyclopentene, by the $WF_6/EtAlCl_2$ catalyst system at 0°C in chlorobenzene, which has a very high *cis*-content. If transfer agents are used, e.g. 1-pentene, hexa-1,5-diene and octa-1,7-diene, they are relatively ineffective but hepta-1,6-diene, which internally models poly(1-pentenylene), transfers rapidly. Ofstead[142] proposed that the diene could effectively displace the coordinating polymer, when one end of it had become attached to a vacant site.

Other possible spatial arrangements for propagating species have been put forward but as high-*cis* polymer never has a random distribution of double bonds, with any catalyst, it seems likely that the theory of two propagating species of types s1 and s2 is generally applicable.

1.7.2 TACTICITY OF SUBSTITUTED NORBORNENE POLYMERS.

The possible number of stereoisomers of substituted norbornenes e.g. 1-methylbicyclo[2,2,1]hept-2-ene (MNBE) has been discussed in section 1.7. The tacticity, of one optically pure form of the polymer with H-H, T-H and T-T arrangements along the chain, was shown. The ^{13}C NMR spectra of these polymers are extremely complicated, as the arrangement of the repeat units, as well as the *cis/trans* nature of the double bonds, affects the alkenic carbon shift. Experiments show that only the *cis*-H-H arrangement of these units does not occur and a bias of polymerization (B) can be calculated. The bias is a measure of the tendency to repeat head-to-tail placements in the polymerization, which are considered to be the normal arrangement.

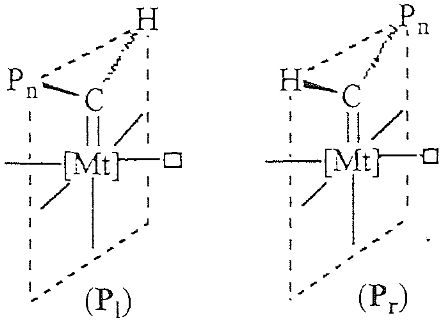
$$B = \frac{\text{H-T} + \text{T-H}}{\text{H-H} + \text{T-T}}$$

The most interesting polymers of this type are those formed by high *cis*-forming catalysts, which show a high bias for H-T arrangements and this results in racemic dyads and a syndiotactic structure.

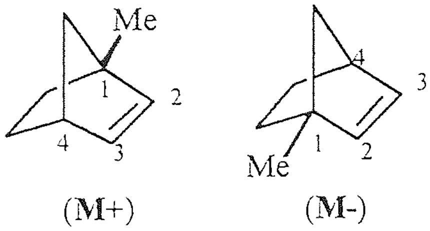
The propagation step for this type of polymerization can be shown to have eight possible arrangements based on the following assumptions: (1) the propagating species can have left- or right- handed forms (P_l and P_r), (2) a norbornene molecule always presents itself in its most favoured orientation, with the five membered unsaturated ring, towards the metal, (3) the substituted norbornene can be orientated to add *cis*- or *trans*- to the carbene, (4) the norbornene derivative has two stereo isomers (M(+) and M(-)) and these can add H-H, H-T or T-T,(5) the configuration of P_l and P_r remains intact between successive propagation steps.

Diagrams of the propagating species, shown with octahedral symmetry, and the optical isomers of MNBE are shown in the diagram on the next page. Scheme 1.7.1 shows one possible mode of addition of the monomer (M+) to the propagating species (P_r) showing that, if the orientation of the monomer is such that C_2 (also regarded as the head (H) of the monomer) becomes attached to the carbon of the carbene, then a *cis*- double bond must be produced and the new propagating carbene must have the orientation (P_l). This means that, a *trans*-double bond will be produced if another M+ monomer adds in the same way. So the most favourable, H-T addition, of one enantiomer produces alternate *cis/trans* double bonds. Therefore all *cis*-HT syndiotactic polymers is produced by alternating co-polymerization of the (+) and (-) forms of the monomer. Scheme 1.7.2 shows the *cis*- addition of M- to the propagating species P_l and Rooney[163] has confirmed that catalysts polymerize racemic mixtures of MNBE to high syndiotactic polymer, but will not polymerize pure

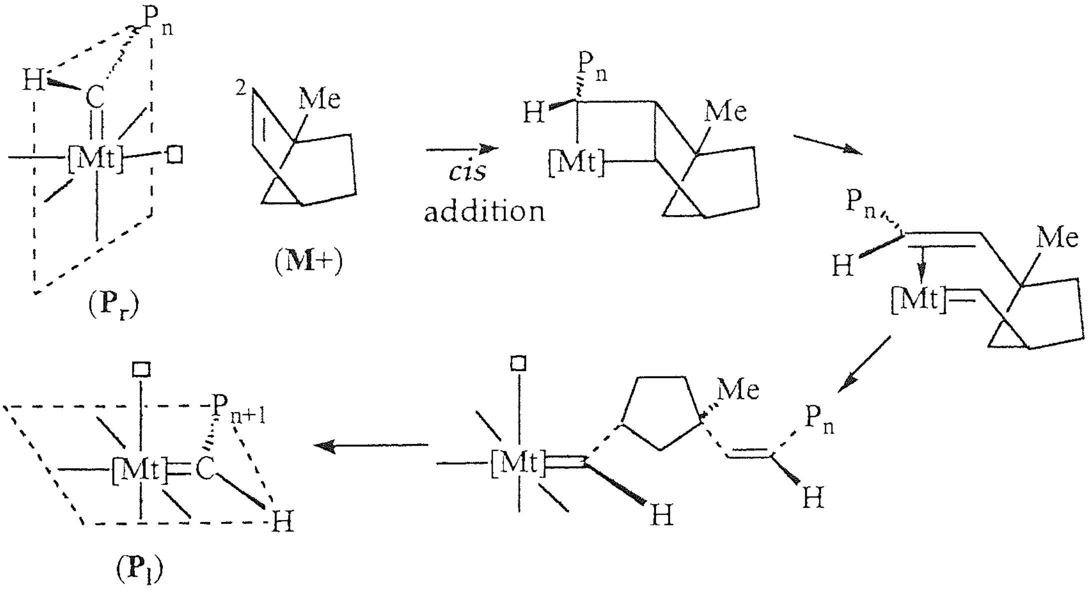
Propagating Species.



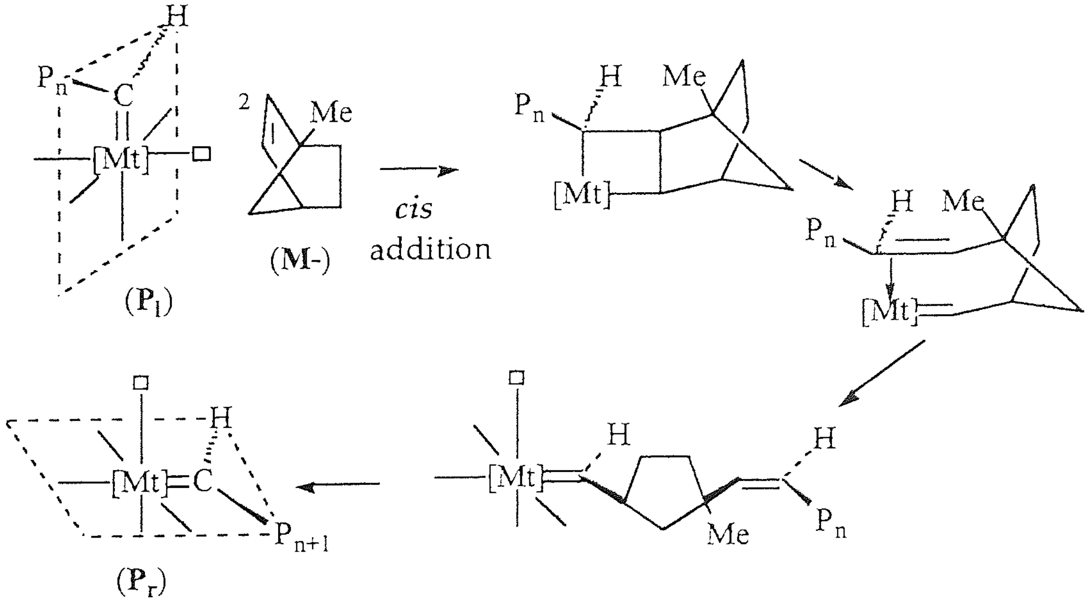
Optical Isomers of MNBE.



SCHEME 1.7.1



SCHEME 1.7.2



enantiomer. The preferential propagation of one form of the monomer by a propagating species also with specific stereochemistry means that they can be regarded as a conjugate pair.

1.8 TRANSFORMATION REACTIONS.

1.8.1 CO-POLYMERIZATION.

When two chemically different monomers (A and B) are allowed to co-polymerize the resulting co-polymer may be one of four distinct types.

1. Random or statistical co-polymers- -AABABBBBAAB-,

2. Alternating co-polymers- -ABABABABA-,

3. Block co-polymers- $-(AAA)_n-(BBBB)_m-$,

4. Graft co-polymers-

-AAAXAAAAXAAAXAA-
B B B
B B B
B B B
B B B

The type of co-polymer produced depends on the initial polymerization conditions, so the formation of alternating and statistical co-polymers depends on the reactivity and composition of the initial monomer feed. For example an alternating co-polymer can be synthesised from an azeotropic mixture of styrene and diethylfumarate

For metathesis reactions, the nature of the catalyst system and the method of mixing can be important too. Ivin[164] has shown that cyclopentene and norbornene produce statistical co-polymers. Most catalyst systems favour norbornene when a high percentage of *cis-* or *trans*-co-polymer is produced. However the catalyst system WCl_6/Ph_4Sn, produces intermediate *cis*-content co-polymer and behaves almost ideally at 20°C, with r_1r_2 close to one, but at -18°C the co-polymer is decidedly blocky with $r_1r_2 = 4.0$..

Block co-polymers can be produced by methods, such as the sequential addition of monomers to a polymerization system. Szwarc's work on living anionic polymerizations,[78] quickly led him to recognize that sequential addition of monomers, like styrene and butadiene, to a catalyst system would produce block co-polymers and that it was possible to control the size of the blocks. Although both mono- and di-functional anionic initiators can be used, to produce either AB or ABA block co-polymers, the range of applications of the technique, using only anionic polymerization, is limited.

Direct coupling of living anionic and cationic propagating species is another synthetic route to block co-polymers. Living cationic poly-(tetramethylene oxide) can be coupled with living anionic polystyrene to produce an AB block co-polymer.[165] Mixing different telechelic oligomers, which react in a stepwise way, can be used to extend the number of the linear blocking arrangements.

The two main areas of interest in this study are linear block co-polymerization and the use of transformation reactions to achieve the product.

1.8.2 TRANSFORMATION POLYMERIZATIONS.

Richards[166] used the term transformation reactions to describe the production of block co-polymers by the polymerization of one monomer by a given mechanism, followed by, appropriate modification of the reactive chain end, and then subsequent polymerization of a different monomer by a second mechanism. Transformation reactions extend the range of monomers that can be linked together allowing polymers with specific properties to be prepared. Co-polymers of glassy polystyrene and elastomeric polyalkenamers, which leads to thermoplastic elastomers, and the alternation of hydrophobic and hydrophilic units, as in the HMWSP's mentioned in section 1.4.5.3, are just two examples of materials that can be produced by the application of this principle.

To simplify the complex synthesis, initial work concentrated on the transformation of living polymers such as cationic to anionic. The complementary, direct coupling reaction of cation and anion produced similar materials although it is not strictly a transformation reaction because sequential polymerization does not occur. One important factor, in the success of this approach, is the control of reaction conditions, which now makes it possible to synthesise living polymers by anionic, Ziegler-Natta, cationic, free-radical, group-transfer and metathesis techniques. The production of a reproducible first segment by living polymerization enables the study of the transformation of the functionality and the reinitiation chemistry, which is often far from ideal.

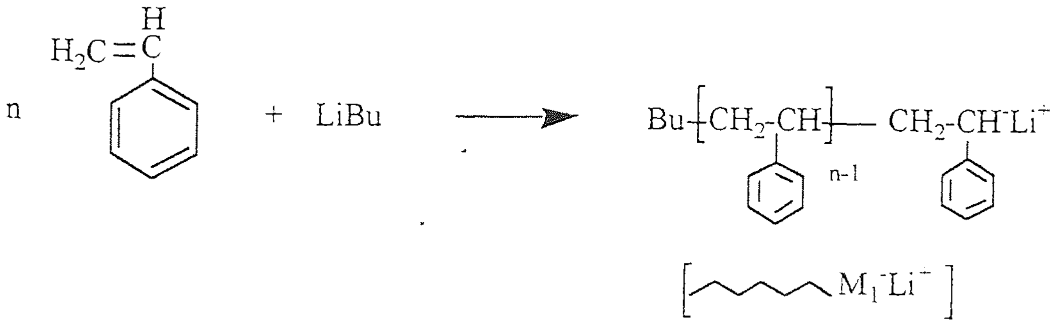
The initial, living polymer can be transformed almost quantitatively, if necessary, using transfer agents, and a wide range of mono- or di-functionalities can be introduced. The main drawback, when the systems move away from living or quasi-living systems, is that control over polydispersity is lost although the increased range of block co-polymer morphologies provides considerable compensation.

1.8.2.1. ANIONIC TO CATIONIC TRANSFORMATIONS.

This was the first type of transformation studied and it is probably the most efficient and well documented. The anionic block is, most frequently, living polystyryl although polybutadienyl, polyisoprenyl and poly(α-methylstyryl) have also been used. THF is the preferred monomer for the cationic section but other cyclic ethers have been used.

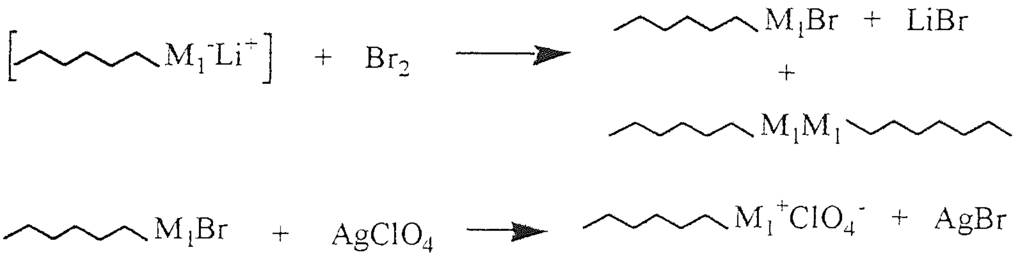
The pioneering work of Richards[166] for the production of poly(styrene-b-tetrahydrofuran) involved the preparation of polystyryllithium in THF using the initiator butyllithium.

Anionic Polymerization.

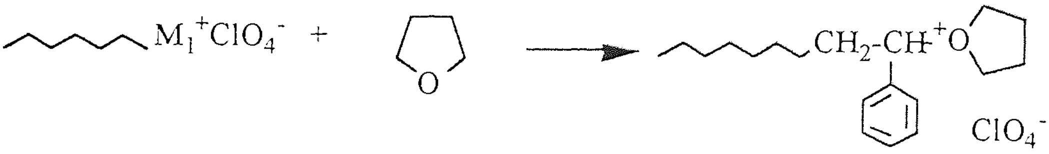


The living polymer was then treated with excess bromine and the bromine terminated product was isolated and purified. Addition of a THF solution of $AgClO_4$ or $AgPF_6$ generated the carbocation or carbenium ion, stabilised by the anion (ClO_4^- or PF_6^-) and silver bromide. Living initiating oxonium ions reacted readily, with the THF, to give co-polymer. The overall conversion was found to be of the order of 60% with Wurtz coupling of polystryllithium and polystyrylbromide being the main side reaction.

End-Capping.

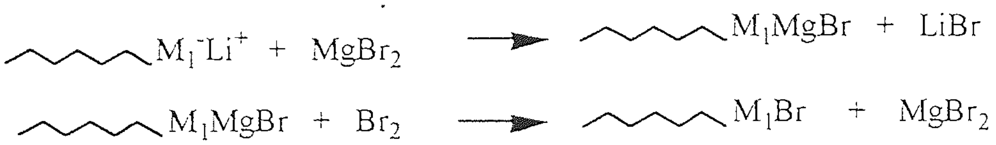


Initiation of Cationic Polymerization.

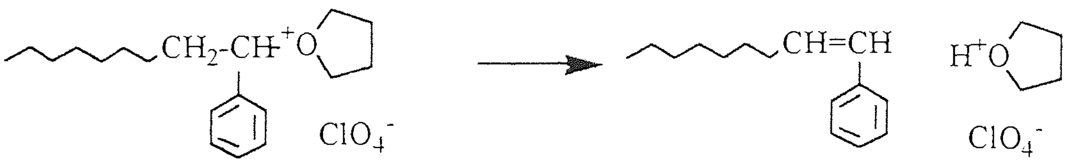


Addition of magnesium bromide, to produce a polymeric Grignard intermediate, overcame the problem as the subsequent reaction with bromine was more controlled and 95% conversion was achieved.[168] The subsequent conversion, to the carbenium ion and then cationic polymerization, showed only 80% efficiency, mainly because of β-hydride transfer in the initiating oxonium ion producing polystyrene. However the polydispersity of the copolymer was characteristically 1.05.

End-Capping via Polymeric Grignard Intermediate.

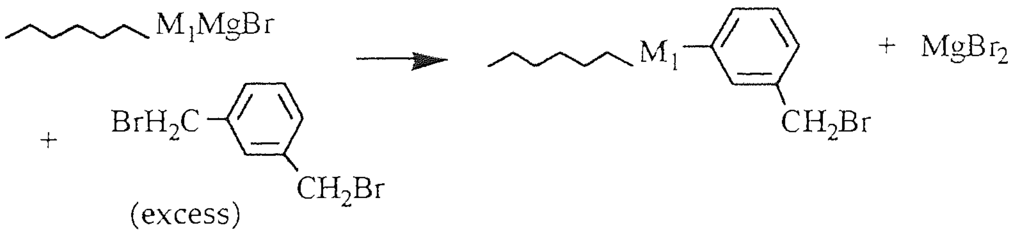


β-Hydrogen Elimination.

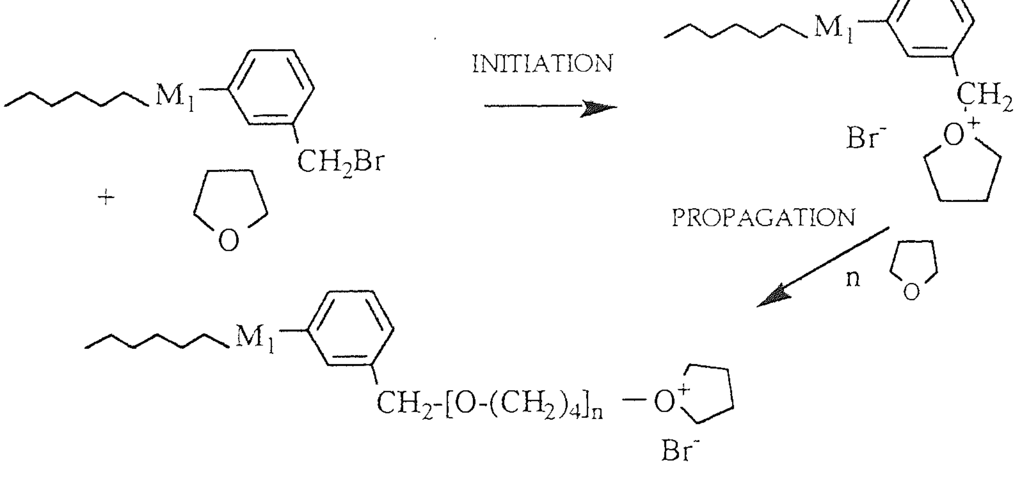


The use of m-xylylene dibromide as the terminant instead of bromine prevented β-hydride transfer because there is no β-hydrogen however no improvement in yield was obtained because of xylylene coupled polystyrene even using the Grignard intermediate.[169]

Adaption of Grignard for Cationic Polymerization.



Cationic Polymerization.

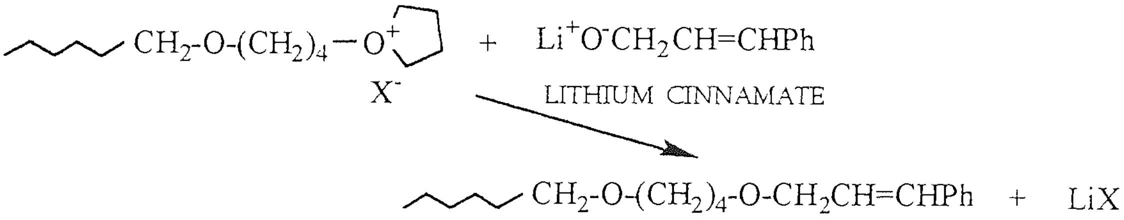


1.8.2.2 CATIONIC TO ANIONIC TRANSFORMATIONS.

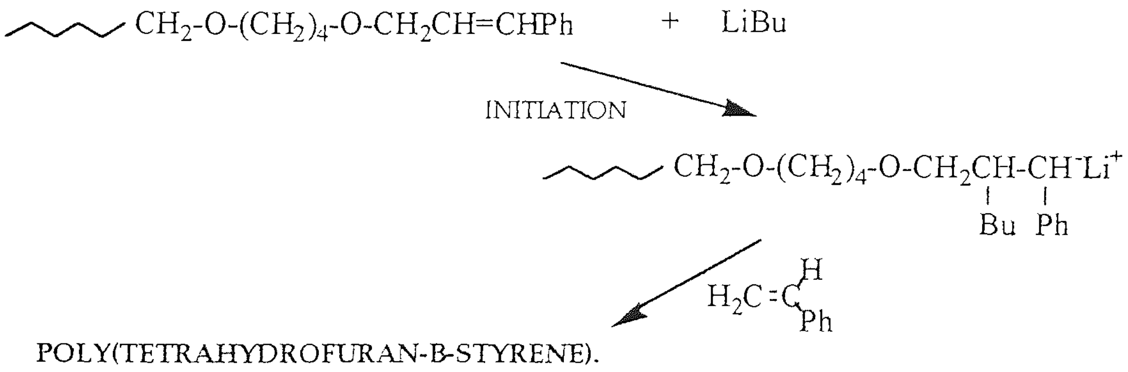
Until recently the only cationic polymer, which could be prepared with the necessary control and termination efficiencies for this type of co-polymerization, was poly(THF). Several different co-monomers have been used to produce the anionic block but styrene is most frequently employed. Poly(THF-b-styrene) has been prepared by terminating the living polymerization of THF with lithium cinnamate, which models styrene as the capping group.

The reaction of this polymeric species with butyllithium, to generate an initiating species for the anionic polymerization, and the subsequent addition of styrene produced about 20% conversion to block co-polymer.[170]

End-Capping Poly(THF).



Anionic Polymerization.



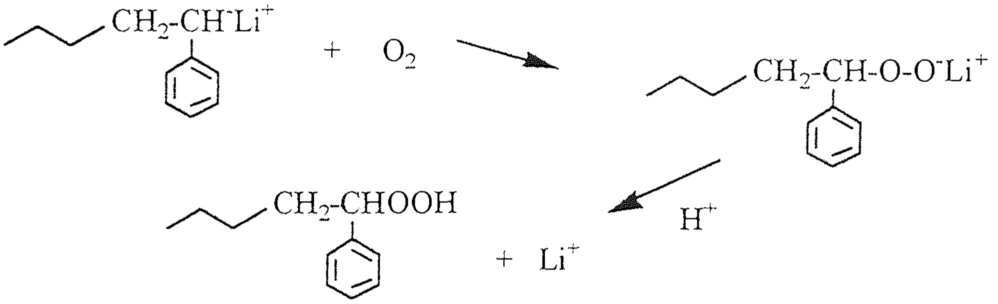
Other transformation routes of this type were postulated using termination of the poly(THF) with primary amines and then metallation using butyllithium to produce a secondary nitranion, which would then act as the initiator for the anionic polymerization. However the overall efficiency showed no improvement on the method outlined above.[171]

1.8.2.3 ANIONIC TO RADICAL TRANSFORMATIONS.

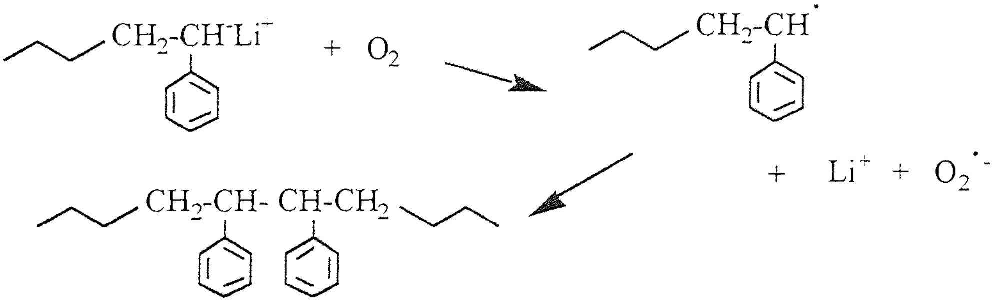
This single electron transformation has been extensively investigated and the wide range of possible monomers, for both the anionic section (e.g. styrenes and dienes) and the free radical segment (e.g. acrylates, methacrylates and many other vinyl monomers), has the potential to be the source of an extremely large number of co-polymers. The living anionic polymerization is terminated to produce a radical precursor (e.g. a hydroperoxide) and this is activated, thermally or by photolysis, to produce the radicals to initiate polymerization.

Mono-functional anionic polymers can produce both AB and ABA block co-polymers as the free radical polymerization can terminate by disproportionation or combination. The use of di-functional anionic segments produces BAB co-polymers by disproportionation and $(AB)_n$ co-polymers by combination termination. This type of transformation therefore produces linear co-polymers with a wide range of morphologies.

End-Capping.



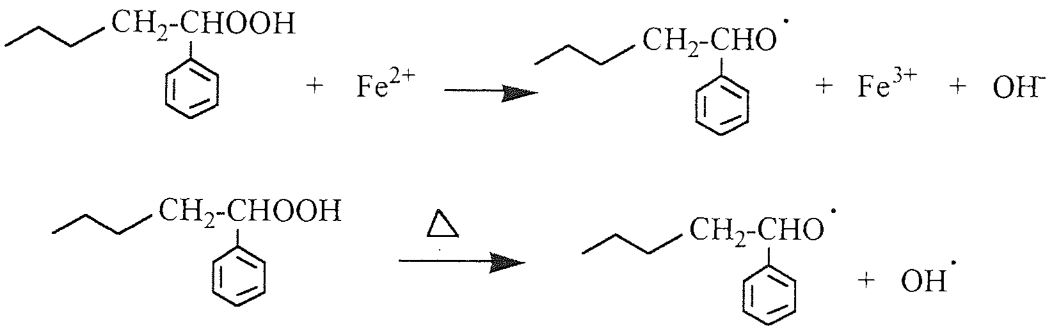
Side Reaction.



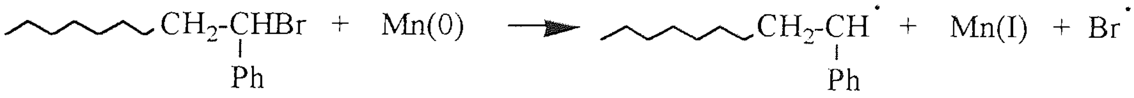
The earliest work on anionic/free radical transformation reactions was carried out by Szwarc,[172] using polystyryllithium, but Brossas[173] repeated the technique, using excess oxygen to minimise the side reactions. The process involved adding oxygen, to the living polymer, to produce the terminal hydroperoxide but keeping the formation of the polystyryl radical, which subsequently dimerises, and the oxygen radical anion as low as possible.

The production of the free radicals was carried out either using iron(II) sulphate or by heating to 150°C. Unfortunately the block co-polymer was not the major product as the hydroxyl radical, produced in both initiation reactions, promotes homopolymerization of the second monomer (methylmethacrylate).

Free Radical Initiation.



Many other techniques have been attempted for this transformation but the most successful so far were developed by Bamford[174] and Eastmond.[175] The anionic living polymer was capped with bromine, as in the anionic/cationic transformation process, which, as has been mentioned is not 100% efficient, but the product can be effectively purified. The polystyrylbromide is then reacted with the active species (Mn(0)) from the irradiation of dimanganese decacarbonyl to generate a radical initiator.

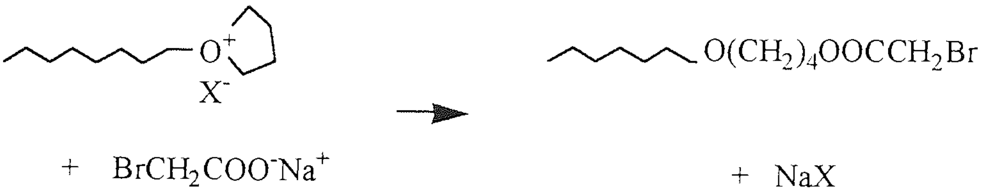


$$\sim\sim CH_2\text{-}\underset{Ph}{CHBr} + Mn(0) \longrightarrow \sim\sim CH_2\text{-}\underset{Ph}{CH^{\bullet}} + Mn(I) + Br^{\bullet}$$

The free radical polymerization of methyl methacrylate, methyl acrylate, ethylacrylate , isoprene and chloroprene has led to the formation of both AB and ABA block co-polymers. 70-80% conversion of homopolymer to block co-polymer has been achieved.

1.8.2.4. CATIONIC TO RADICAL TRANSFORMATIONS.

Again the lack of living cationic systems, other than poly(THF), until recently has reduced the range of synthetic options in this field. Early work was based on the introduction of a functional group (e.g. peroxide or azo-) into the poly(THF) that can be activated in the presence of the second monomer to give the co-polymer. Eastmond[176] has demonstrated that the technique developed for anionic/radical transformations can be adapted for the cationic variation. The termination of living poly(THF) with sodium 3-bromoethanoate is almost quantitative.



The active species, Mn(0), from the irradiation of dimanganese decacarbonyls is used to generate the macroinitiating radicals (poly(THF)$O(CH_2)_4OCOCH_2^{\bullet}$) and the second monomer (e.g. methylmethacrylate) added to achieve high yields of co-polymer.

1.8.2.5. ANIONIC TO ZIEGLER-NATTA TRANSFORMATIONS.

This type of transformation cannot be regarded as simply electron transfer. The co-polymerization can be achieved by modification of the small molecule co-catalyst for Ziegler-Natta polymerization, a trialkyl aluminium, into a polymeric species.

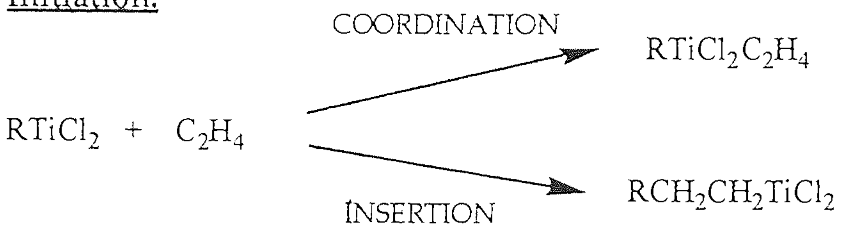
The Ziegler-Natta addition polymerization reactions of alkenes are catalysed by systems like $TiCl_4/R_3Al$ and the stages of the reaction can be represented by the following scheme.[177]

CATALYST REACTION.

Stage 1. $TiCl_4 + R_3Al$ ------> $RTiCl_3 + R_2AlCl$ ------> $\beta\text{-}TiCl_3 + R^{\bullet}$

Stage 2. $\beta\text{-}TiCl_3$ R_3Al -----> $RTiCl_2 + R_2AlCl$

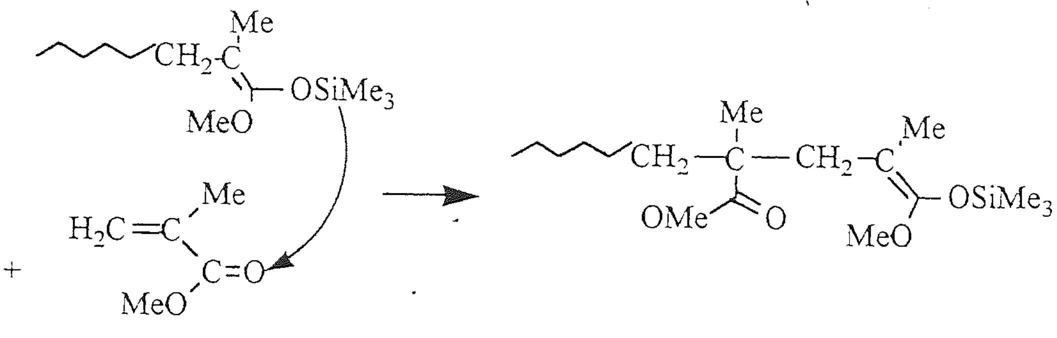
Initiation.



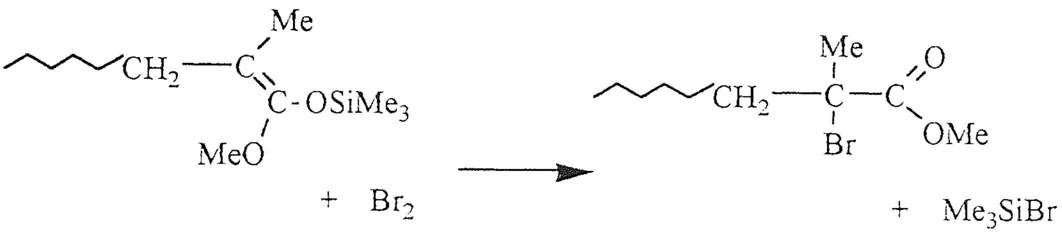
Stage 1 generates the active β-$TiCl_3$ and an alkyl radical which rapidly terminates to inactive products. The active species reacts with more trialkylaluminium to produce $RTiCl_2$, which can initiate polymerization. The reaction of living anionic polymers with aluminium chloride has been successfully used to produce a mixture of polymeric aluminium species and has been reported to produce block co-polymers with ethene when these are used in conjunction with titanium(IV) chloride. Isoprene and styrene have been used to produce the anionic segment and 40% coupling efficiences have been reported. Contamination from homopolymer, produced by termination of the unreacted living chains and from polymeric radicals produced in stage 1 of the catalyst reaction, is a problem. However a lengthy extraction scheme has been devised to isolate the AB polymer.[178]

1.8.2.6. TRANSFORMATIONS INVOLVING GTP.

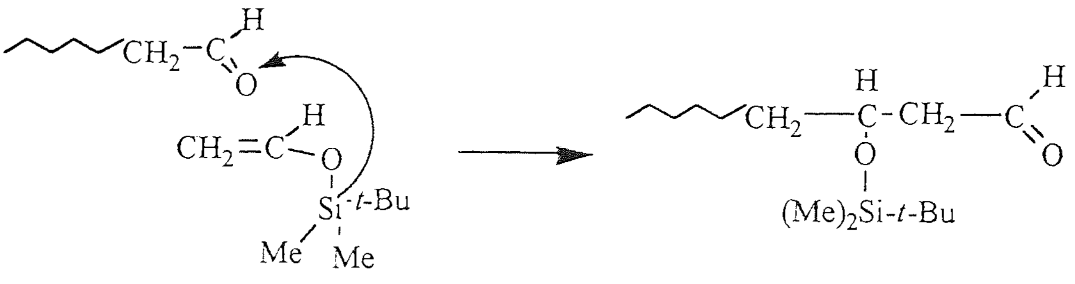
The term 'group transfer polymerization' (GTP) was introduced by Webster et al[179] in 1983 to identify two new polymerization processes. The first is based on the active species silyl ketene acetal, which is present on the terminal unit of the growing polymer chain in such polymers and is transferred to the incoming monomer molecule during propagation. Silyl ketene acetals are trapped enolates and, react with α,β-unsaturated esters and ketones. The standard initiator for this type of GTP is 1-methoxy-1-(trimethylsiloxy)-2-methylpropene, ($Me_2C{=}C(OMe)(OSiMe_3)$(MTS), and the living polymerization of methyl methacrylate has been achieved by this technique, using bifluorides (e.g. tris(dimethylamino)sulphonium bifluoride ($TASHF_2$)) as catalysts.



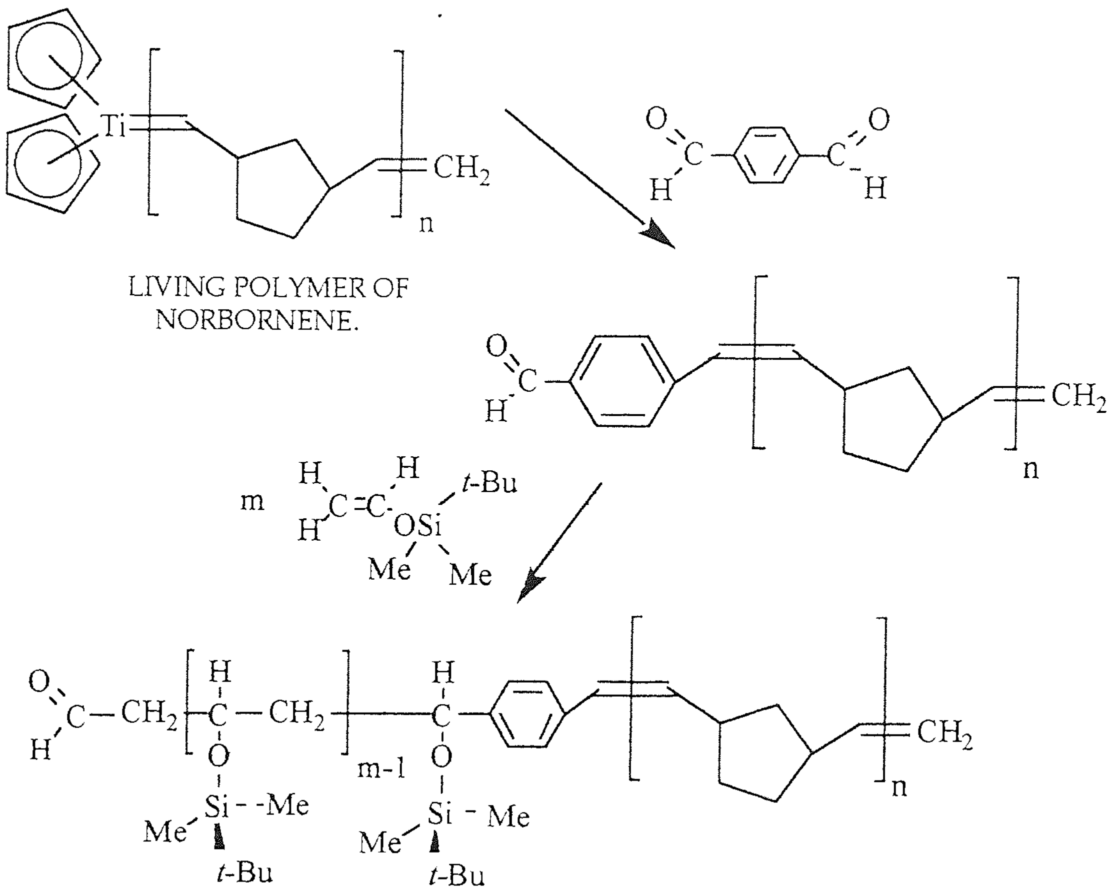
The transformation co-polymerization, of GTP to free radical polymerization, involves converting the active end of polymethyl methacrylate, into bromo-functionality with bromine and then the Eastmond/Bamford technique for initiating free radical polymerization of styrene is used. The AB and ABA co-polymers were contaminated by poly(MMA) but good yields of co-polymer product were obtained.[180]



The second type of GTP involves aldol group transfer polymerization, in which a group attached to the monomer molecule, is transferred to the growing polymer chain. Each unit in the chain, except the active terminal end-group, has the group attached. Aromatic aldehydes are the preferred initiators of aldol GTP and a Lewis acid (e.g. $ZnBr_2$) is the usual catalyst in low concentrations. The polymerization of a silyl enol ether (e.g *t*-butyldimethyl-silylvinyl ether) proceeds to high conversion in dichloromethane.

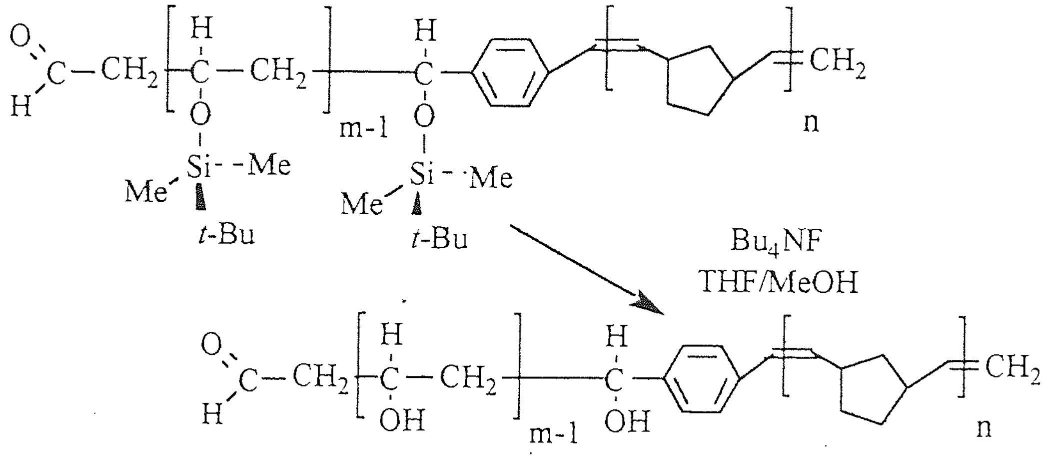


Metathesis to aldol GTP transformations have been carried out to give block co-polymers with low polydispersities. The living ring-opening metathesis polymerization of norbornene using bis(η^5-cyclopentadienyl) titanacyclobutane (13) is described in 1.4.5.1.



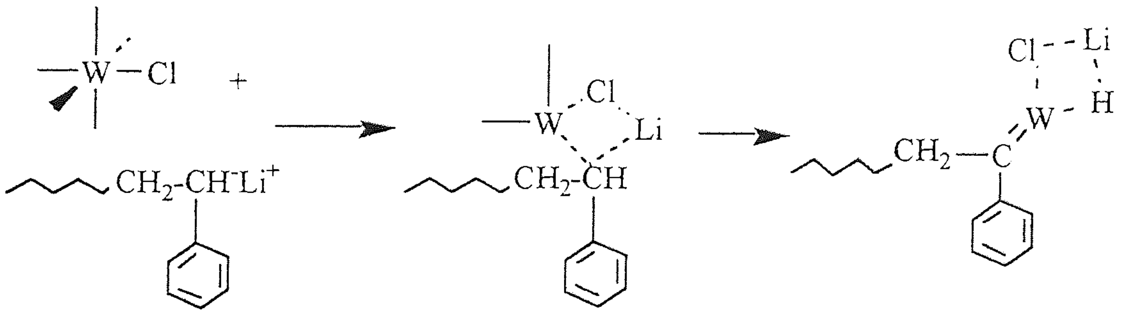
The removal of the titanacyclobutane end groups from the polymer using a nine-fold excess of terephthaldehyde gives polynorbornene with one *p*-formylstyrene end group.[82] This terminal aldehyde group provides the initiator for the aldol GTP of *t*-butyldimethylsilylvinylether. Several AB block co-polymers of this type have been prepared with narrow molecular weight distributions.

Cleavage of the silyl groups from the group transfer section of the polymer is carried out by refluxing the product with tetrabutylammonium fluoride in THF and methanol. The resulting poly(vinylalcohol) is a hydrophilic block and so a hydrophobic / hydrophilic co-polymer has been formed.



1.8.2.7 ANIONIC TO METATHESIS TRANSFORMATIONS.

Living polystyryllithium, prepared by anionic polymerization, has been investigated as a co-catalyst with WCl_6 for the ring-opening metathesis polymerization of cyclopentene by Amass and Gregory[181,182] and there were indications that the polystyrene was incorporated as an end-group into the growing polypentenylene chains. A novel reaction mechanism for the transformation was proposed involving the formation of a bimetallic bridged intermediate to emphasise that the role of the co-catalyst in metathesis is not just as a reducing agent for the transition metal compound.



Thorn-Csanyi[183] investigated the same type of transformation. The catalyst systems of WCl_6/EtOEt or $WOCl_4$ with both oligomers and polymers of living polystyryllithium were used to investigate the ring-opening polymerization of cyclopentene and 1,5-cyclooctadiene. The nature of any metathesis products was investigated using SEC, to separate the fractions, and then IR, UV and ^1H NMR, to characterise the products. It was stated that there was evidence of very short oligo-styrene chains (DP_n= 6) attached to the high molecular weight polypentenylene chains as terminal groups. However when polystyryllithium with 40 or more units of styrene was used, ^{1}H NMR detected only a small percentage of polystyrene terminated polypentenylene chains and a different, unidentified initiating species was suggested.

1.9 SCOPE OF THIS STUDY.

The anionic to metathesis transformation reaction is the basis of this work. The overall aims are to gain more information about the mechanism of the initiation of ring-opening metathesis polymerization reactions, about which there is some dispute, and, given an understanding of such initiation process, to synthesise either AB or ABA block co-polymers.

The original work of Gregory[184] indicates that block co-polymers can be prepared by using polystyryllithium, as a co-catalyst for the ring-opening metathesis polymerization of cyclopentene, with WCl_6 as the catalyst. However there are several areas of the work that warrant further investigation.

Gregory based the WCl_6:PStLi molar ratios upon 100% efficient initiation of styrene polymerization by butyllithium. SEC data on the product indicated that the effective concentration of lithium, as polystyryllithium, in the cocatalyst system was closer to 10% of that expected. Gregory prepared polystyryllithium using butyllithium as initiator, which is a much slower initiator than *sec*-butyllithium, and moreover stored butyllithium as a dilute solution in cyclohexane. Consequently it is possible that the apparent inefficiency of initiation arose from incomplete consumption of the initiator in the preparation of the cocatalyst and the cocatalyst used was actually a mixture of polystyryllithium and unreacted butyllithium. Alternatively the butyllithium solution, being unstable, was more dilute than expected and the overall concentration of lithium consequently less. The initial studies undertaken in this project were therefore directed towards the establishment of the experimental conditions for the preparation of a cocatalyst of known composition and subsequently to assess the stability, or the limit of stability, of the cocatalyst.

Gregory used both RI and UV, set at 254nm, detectors in SEC to analyse the metathesis products, but solely in a qualitative way. Any UV absorbance in the product at 254nm was associated with the presence of polystyrene blocks, because polystyrene shows a strong absorbance at this wavelength. A more detailed approach to the analysis of the products, than that used by Gregory, will be undertaken to establish whether the products are AB or ABA-type copolymers. Such distinction, which may indicate the nature of termination reactions in conventional metathesis polymerization systems, has not previously been attempted.

Having established the effects of reaction conditions on the rate of polymerization, yield and structure of the products of cyclopentene polymerization using as catalyst WCl_6/BuLi and WCl_6/*sec*-BuLi, the range of cocatalysts will be extended to $AlEtCl_2$, $AlEtCl_2$/BuLi and $AlEtCl_2$/*sec*-BuLi. A detailed investigation of the use of PStLi as a cocatalyst for metathesis polymerization will be directed towards solutions to the questions still remaining after the studies carried out by Gregory and those by Thorn-Csanyi, who suggested that the mechanism of initiation depends on the degree of polymerization of the cocatalyst. The successful extension of transformation reactions to anionic to Ziegler-Natta systems relies upon the preparation of polystyrylaluminium compounds from the reaction of polystyryllithium with alkyaluminium halides. Advantage will be taken of these reactions in preparing molecules such as PStAlEtCl and these will be used as alternative cocatalysts for metathesis polymerization.

CHAPTER 2.

EXPERIMENTAL WORK.

2.1 MATERIALS USED.

TABLE 2.1. THE CHEMICALS USED DURING THE PROJECT, THEIR SOURCE AND PROPERTIES .

CHEMICAL	FORMULA	SOURCE	F.W.	M.P./°C	B.P./°C	ρ/ g.cm^{-3}
Butyllithium (1.6M in hexanes)	C_4H_9Li	Aldrich	64.06			0.680
sec-Butyllithium (1.3M in cyclohexane)	$C_2H_5CH(CH_3)Li$	Aldrich	64.06			0.769
Aluminium ethyl dichloride	$(C_2H_5)AlCl_2$	Cambrian Chemicals	127.0	32	115	1.207
Aluminium ethyl dichloride (1.8M in toluene)	$(C_2H_5)AlCl_2$	Aldrich				0.927
Aluminium ethyl dichloride (1.0M in hexanes)	$(C_2H_5)AlCl_2$	Aldrich				0.729
Diphenyl ethylene	$(C_6H_5)_2C=CH_2$	Aldrich	180.25	6	271	1.02
Styrene	$C_6H_5CH=CH_2$	Fluka	104.2	-31	145	0.906
Cyclopentene	C_5H_8	Fluka	68.12	-135	44.2	0.772
Cyclohexane-spectrophotometric grade.	C_6H_{12}	Aldrich	84.12	6.5	80.7	0.779
Toluene-AR grade.	$C_6H_5CH_3$	Fisons	992.14	-93	111	0.867
Absolute ethanol-AR grade.	C_2H_5OH	Fisons	46.07	--118	78	0.790
Tetrahydrofuran (THF)-HPLC grade.	C_4H_8O	Fisons	72.11	-108	66	0.889
Tungsten hexachloride (gold grade).	WCl_6	Aldrich	396.6	275	347	3.52
Tungsten oxy - tetrachloride	$WOCl_4$	Aldrich	341.7	211	227.5	

2.2 GENERAL TECHNIQUES.

2.2.1 VACUUM TECHNIQUES.

Preparatory work was carried out on a vacuum line whenever possible as the catalyst systems are rapidly "killed" by air or moisture. The vacuum line shown in figure 2.1 was used to obtain a high vacuum or to carry out operations under an atmosphere of pure dry argon using the Schlenk technique.

An Edward's rotary pump (A) was used with a mercury diffusion pump (C) to evacuate the manifold (G) and achieve a pressure of approximately 10^{-5}mm of Hg, which was monitored using a Pirani gauge attached at E. Liquid nitrogen traps B and D were placed either side of the mercury diffusion pump to condense any vapours coming from the manifold and/or the diffusion pump. Greaseless tap 1 was opened when the pump was switched off and tap 2 controlled the evacuation of the main manifold. Branches (H_1 and H_3) to the main manifold extended the operations that could be carried out on the line at a given time. Argon was introduced into the line from F by opening tap 3.

2.2.1.1 Freeze-thaw Degassing Processes.

Figures 2.2 and 2.3 show typical solvent flasks with a capacity of approximately 250cm^3, although similar vessels but with an internal volume of only 50-100cm^3 were also used extensively. All liquids were degassed before distillation on the vacuum line. The tap of the vessel was closed before it was attached to the line by evacuating the appropriate part of the system. The liquid was frozen by surrounding the vessel with liquid nitrogen and then its tap was opened until a vacuum had been re-established. The tap was closed while the liquid warmed to room temperature, before the process was repeated

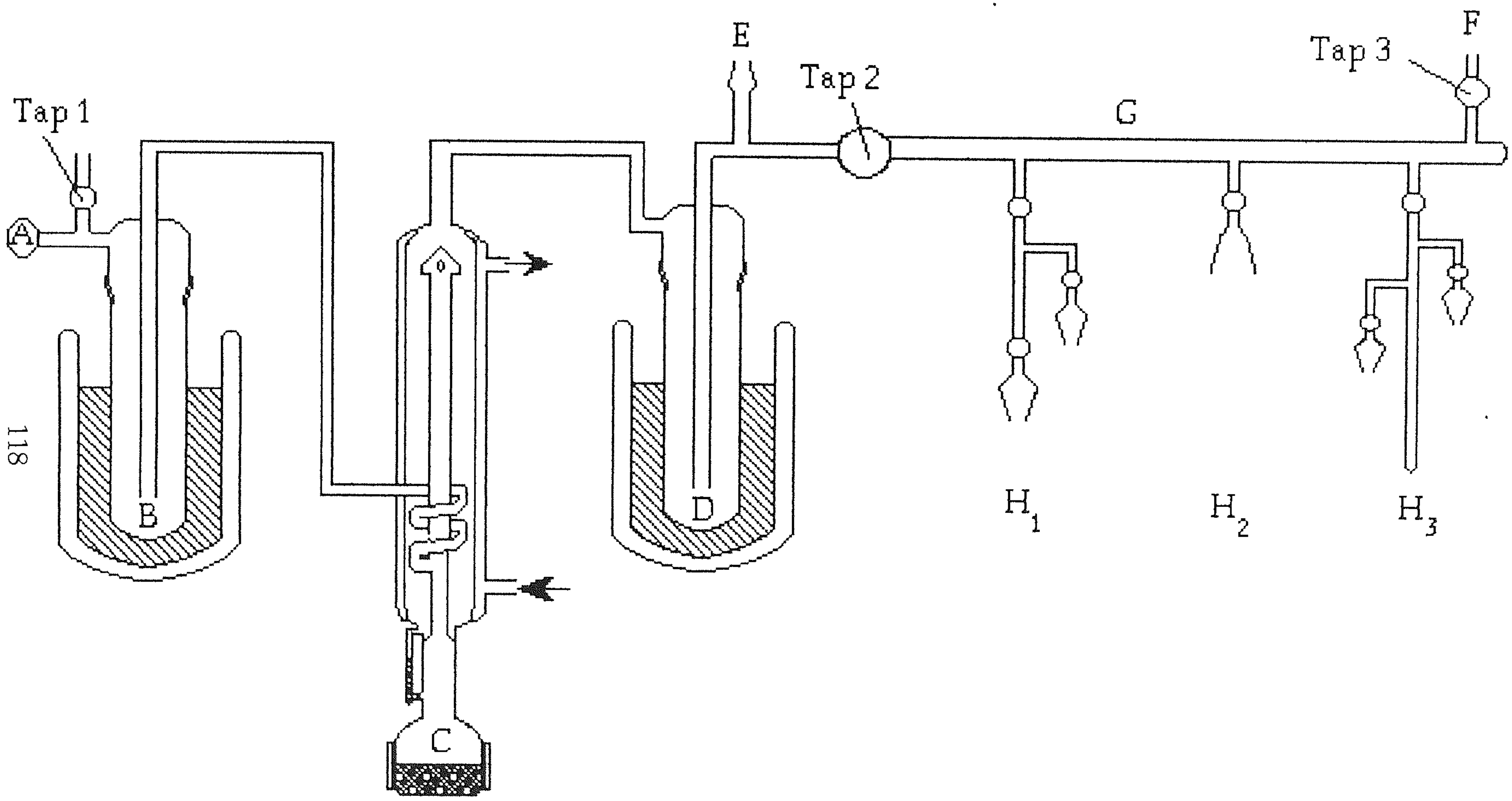


FIGURE 2.1 VACUUM LINE.

FIGURES 2.2 AND 2.3 SOLVENT FLASKS.

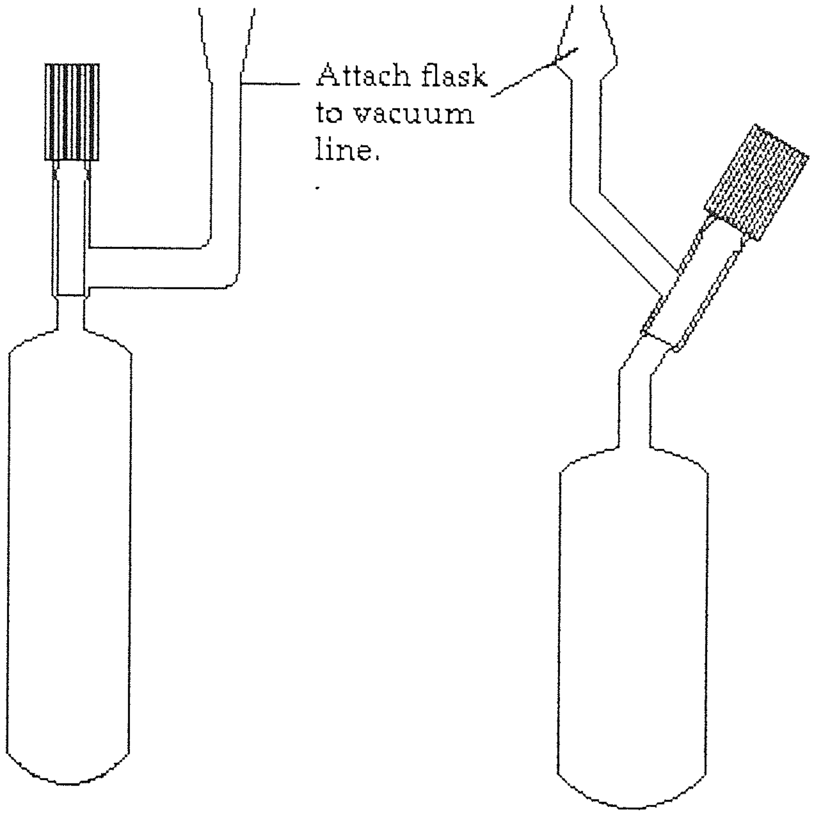
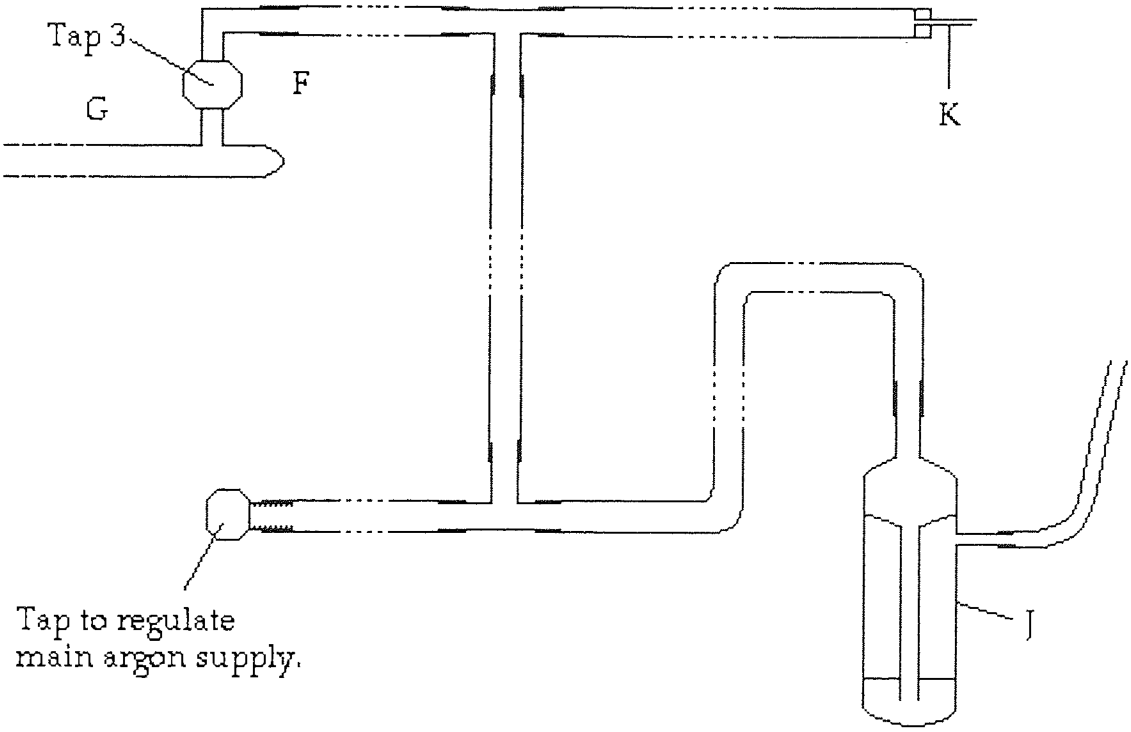


FIGURE 2.4 ARGON SUPPLY TO VACUUM LINE.



until no change in the vacuum was observed, on opening the tap to the frozen liquid.

2.2.1.2 Trap to Trap Distillation.

A flask, containing degassed liquid, and a clean, dry, flamed receiver flask were attached to the line. The cooled receiver flask was surrounded by liquid nitrogen and it and the appropriate section of the line were evacuated and then isolated from the pump. The tap on the flask containing the degassed liquid was opened, in a controlled way, to allow the liquid to distil smoothly into the receiver flask, although heating was needed to distil some liquids.

2.2.2 SCHLENK TECHNIQUE.

The attachment to the line, shown in figure 2.4, was for the transfer of air and/or moisture sensitive reagents under an atmosphere of argon either from reagent bottles or from one reaction vessel to another. The gas lock (J) gave a visual indication of the rate of flow of dry argon from the laboratory supply and allowed the excess gas to escape. Tap 2 in figure 2.1 was closed to isolate the pump from the evacuated manifold and argon was then introduced into the appropriate section by opening tap 3. Vessels held on the evacuated manifold were clamped or clipped securely before passing the argon. Argon was introduced into the vessels by opening the greaseless taps and complete removal of the tap allowed injection into or out of the vessel using clean, dry gas-tight syringes. The small reaction flasks, similar to those shown in figures 2.2.and 2.3, of 50-100cm^3 capacity were designed to enable easy and complete removal of the prepared solutions from the vessels by syringe.

Several reagents were supplied with air/moisture tight seals. The hyperdermic needle (K) shown in figure 2.4 was placed through the seal and the reagent was then removed using a clean, dry syringe.

2.2.3 TREATMENT OF GLASSWARE.

All glassware was rigorously cleaned. The manifold was rinsed out regularly with organic solvents and periodically soaked in decon solution, then rinsed thoroughly with distilled water. The system was then evacuated, flamed and left to hold a vacuum for several hours. All quickfit joints were regularly greased with small amounts of high vacuum silicone grease. Every time the line was used the cold traps were removed, emptied and washed out, the joints to the traps and Pirani gauge were cleaned and re-greased.

Each reaction vessel was cleaned immediately after use with decon solution and when necessary 10% sodium hydroxide solution or chromic acid. Thorough rinsing with distilled water was followed by drying for at least 4 hours at 240°C in an oven. The vessels were then evacuated on the line prior to use, flamed dry and allowed to cool under vacuum. This was also used to test the reliability of the greaseless taps.

Syringes were removed from the oven 10 to 15 minutes before they were needed, assembled and tested, on cooling they were flushed with argon and the appropriate solution before use.

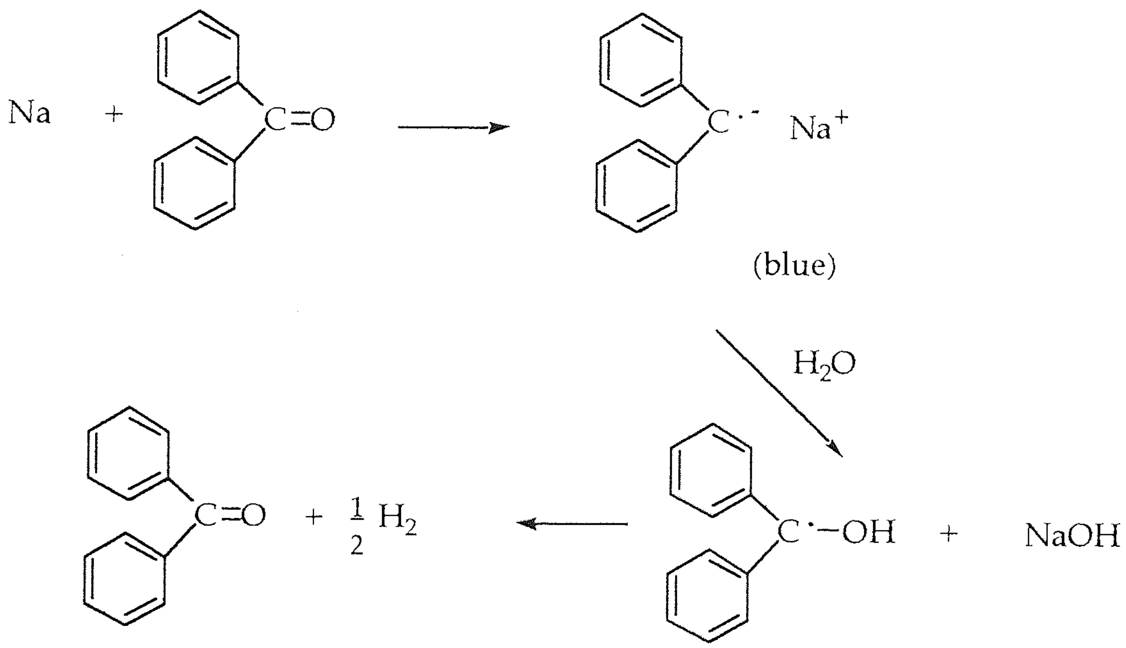
2.3 PURIFICATION, DRYING AND STORAGE OF MATERIALS.

2.3.1 CYCLOHEXANE.

Spectroscopic grade cyclohexane was used in all experiments. It was initially dried over calcium hydride in a closed flask for at least 48 hours, with regular venting of any hydrogen produced. During the first few months of the project the solvent was then degassed and distilled onto a sodium benzophenone melt in an evacuated flask. A deep blue colour, formed by the reaction shown in scheme 1, was taken as an indication of anaerobic, dry conditions

This practice was stopped as complications occurred with the spectroscopic studies, which were traced to benzophenone subliming during trap to trap distillation into the reaction vessel. This happened despite using recommended quantities of benzophenone and an excess of sodium, visible as the shiny silver metal.

SCHEME 2.1



Initially butyllithium or *sec*-butyllithium was used as the replacement drying agent but eventually low molecular weight polystyryllithium was found to be ideal. This orange-yellow, non-volatile, living polymer is immediately destroyed by traces of air or moisture.

2.3.2 TOLUENE.

AR grade toluene was dried over calcium hydride and then distilled onto a sodium/benzophenone melt but as with cyclohexane, polystyryllithium was eventually preferred.

2.3.3 STYRENE.

Commercial styrene contains 0.005% *tert*-butylcatechol to inhibit thermally initiated polymerization. This was removed by standing the styrene over sodium hydroxide pellets for 24 hours. The blue solution was then decanted onto calcium hydride and left for at least 48 hours in a stoppered flask at below -15°C. The mixture was thoroughly degassed and distilled as needed.

2.3.4 CYCLOPENTENE.

The main impurities are water and cyclopentanol both of which would deactivate the catalyst systems. Slices of freshly cut sodium were placed into a clean, dry flask through which argon was being passed. The cyclopentene was injected in and left for 24 hours to form sodium hydroxide and red brown sodium cyclopentoxide. The latter flakes off the sodium leaving a fresh silver surface.

The cyclopentene was degassed and distilled onto fresh slices of sodium, which remain shiny in contact with the colourless solution. Finally the monomer was distilled onto solid polystyryllithium, which had been injected as a dilute solution into the flask and then had all the volatile component removed. A clear red solution confirmed that the cyclopentene was dry and oxygen free.

2.3.5 BUTYLLITHIUM AND *sec*-BUTYLLITHIUM.

Analytical data for each solution supplied by Aldrich proved to be accurate if the samples were kept in the freezing compartment of the refrigerator, dispensed as indicated in section 2.2.2 and covered with fresh "Nesco" film after every injection. A fresh batch of initiator was obtained every 4 to 5 weeks.

2.3.6 TUNGSTEN HEXACHLORIDE.

The gold standard tungsten hexachloride supplied by Aldrich was used. Previous workers[185] had tried unsuccessfully to purify other samples of the solid by sublimation but had found that only this pure form gave reproducible results. The container was put unopened into a Halco dry box and the dark blue solid was dispensed in the box into a pre-weighed argon filled flask. On removal the flask was reweighed and then evacuated on the line.

2.3.7 TUNGSTEN OXYTETRACHLORIDE.

The red powder supplied in a waxed sealed bottle from Aldrich was treated in exactly the same way as tungsten hexachloride.

2.3.8 ALUMINIUM ETHYLDICHLORIDE.

Canisters of aluminium ethyldichloride from previous workers were used in preliminary studies and the pure liquid was removed using the Schlenk technique as previously described in section 2.2.2. To ensure the purity of the co-catalyst and accurate assessment of catalyst mole ratios, fresh 2M aluminium ethyldichloride in toluene and 1M aluminium ethyldichloride in cyclohexane were used. The solutions were treated in a similar way to that described for butyllithium solutions in section 2.3.5.

2.3.9 DIPHENYLETHYLENE.

The pale yellow liquid was dried over calcium hydride for at least 7 days then thoroughly degassed. Known volumes were removed by syringe using the Schlenk technique.

2.3.10 TETRAHYDOFURAN.

HPLC grade THF was used to prepare all solutions for SEC or GPC analysis and was the medium for the analysis.

2.3.11 ABSOLUTE ETHANOL.

Pure ethanol was dried by injecting it under an atmosphere of argon into an empty, clean, dry vessel and adding individual slivers of freshly cut sodium. The small amount of moisture present and the ethanol quickly produced hydrogen. The assumption made was that when several slices of sodium had dissolved completely, the solution should be dry and was ready for degassing.

2.3.12 METHANOL.

GP grade methanol was thoroughly degassed before being used to precipitate the polystyrene and polypentenamer.

2.3.13 OTHER SOLVENTS.

GP grade hexane, chloroform and acetone were used at various stages without special treatment, to dissolve or reprecipitate the polymers.

2.4 PREPARATION OF STOCK SOLUTIONS.

2.4.1 STYRENE.

Solutions of styrene in cyclohexane were prepared of known concentration. Styrene was vacuum distilled into a small, weighed, evacuated flask, which was then re-weighed and the cyclohexane was then transferred in a similar way. Solutions of between 2M and 0.1M were prepared and known volumes were removed by syringe using the Schlenck technique, as they were needed.

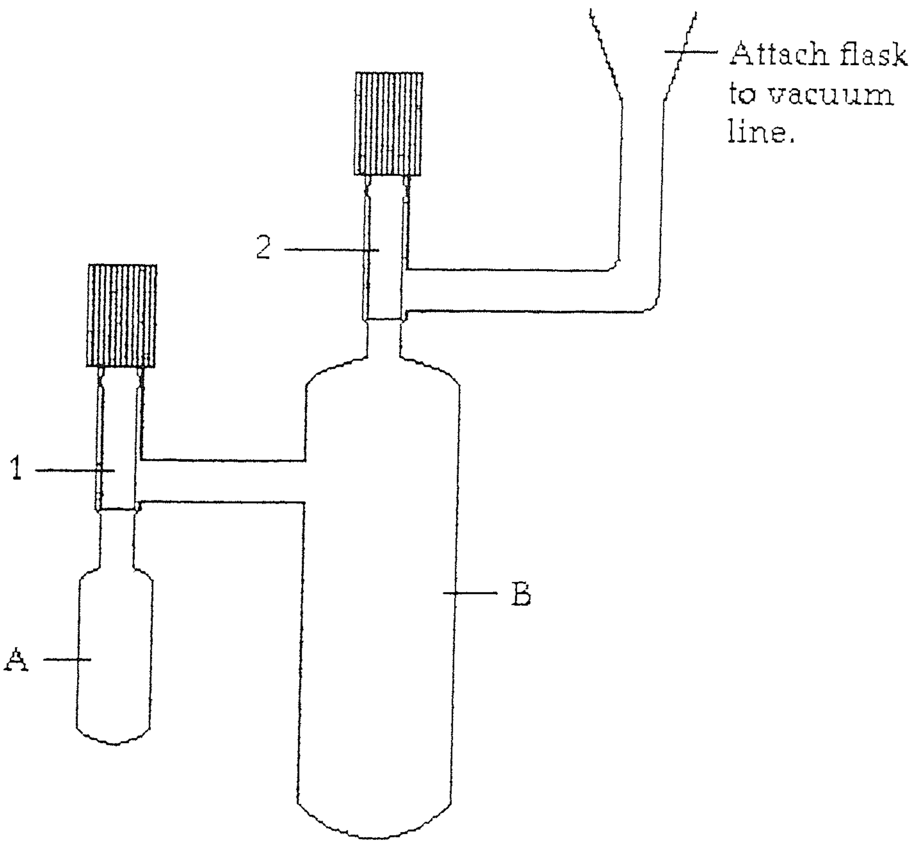
2.4.2 BUTYLLITHIUM AND *sec*-BUTYLLITHIUM.

The standard solutions of these reagents were diluted for some experiments by distilling cyclohexane into a small, weighed, evacuated flask, reweighing and injecting a known volume of the standard solution of the butyllithium under argon as described in 2.2.2. Although the concentration of these diluted solutions were initially found to be close to the theoretical value, spontaneous decay occurred and after 24 hours the activity was much reduced. So all diluted solutions, of these initiators, were prepared immediately before they were used.

2.4.3 POLYSTYRYLLITHIUM.

Stock solutions of "living" polystyryllithium in cyclohexane were prepared in two ways. Firstly known masses of styrene and cyclohexane were distilled under vacuum into a small, weighed evacuated flask or the side-arm of the sort of reaction flask shown in figure 2.5. Then either the standard or freshly diluted solution of *sec*-butyllithium was injected into the solution using the Schlenk technique. In the second method argon was passed into a small, clean, dry flask attached to the manifold of the vacuum line and a known volume of a stock solution of styrene in cyclohexane was injected, followed by a known volume of *sec*-butyllithium solution.

FIGURE 2.5 REACTION FLASK.



The tap to the vessel was carefully closed, the flask was removed from the line and then put in a water bath at 60°C for 3 to 12 hours. The polymerization produces an orange, yellow solution within seconds.

Solutions of 10^{-1} to 10^{-3}M polystyryllithium were prepared and the theoretical degree of polymerization was varied between 5 and 250. The concentration of the solution based on [Li] was confirmed as follows:

1) A sample of the polystyryllithium solution was removed under argon and injected into degassed methanol,

2) The polystyrene was precipitated in excess methanol, filtered, dissolved in acetone, re-precipitated and dried in a vacuum oven for 2 hours at 40°C.

3) A 0.5% (wv) solution of the pure polystyrene in THF was prepared and analysed by SEC.

The value of the number average molecular weight ($\overline{M}_n$) determined by this method provided a check on the concentration of the [Li] in the solution and indicated the accuracy of the experimental technique.

Polystyryllithium in cyclohexane shows no sign of spontaneous decay over several weeks, if the solution has a concentration greater than 10^{-2}M and is kept in dry, anaerobic conditions.

2.4.4 ALUMINIUM ETHYLDICHLORIDE.

Toluene was distilled under vacuum into a small, evacuated, weighed reaction flask, which was then re-weighed. Initially a known volume of aluminium ethyldichloride was removed under argon from a canister by syringe, as previously described in section 2.2.2, and injected into the toluene. Subsequently fresh standard solutions were purchased and diluted when required, as for butyllithium solutions.

2.4.5 TUNGSTEN HEXACHLORIDE.

Solid tungsten hexachloride was transferred to a weighed reaction flask as described in section 2.3.6. The flask was evacuated on the vacuum line, re-weighed, and then a known volume of toluene was distilled into the flask. Dark blue solutions of 0.02M to 0.05M were obtained and their concentrations were checked by titration.

The colour of all the solutions was so intense it was impossible to see if all the solid had dissolved. Analysis of stock solutions involved injecting 1 or 2cm^3 of each under argon into 10cm^3 0.1M degassed sodium hydroxide solution.

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

The blue solution was rapidly hydrolysed to colourless sodium tungstate (VI). The excess sodium hydroxide was then determined by titration with standard hydrochloric acid, which was also used to standardise the original alkali solution.

Table 2.2. shows the concentrations based on the weight of WCl_6 in a given volume of toluene and the corresponding values measured by volumetric analysis.

TABLE 2.2. THE CONCENTRATION OF WCl_6 IN TOLUENE BASED ON WEIGHT/VOLUME MEASUREMENT AND ON VOLUMETRIC ANALYSIS.

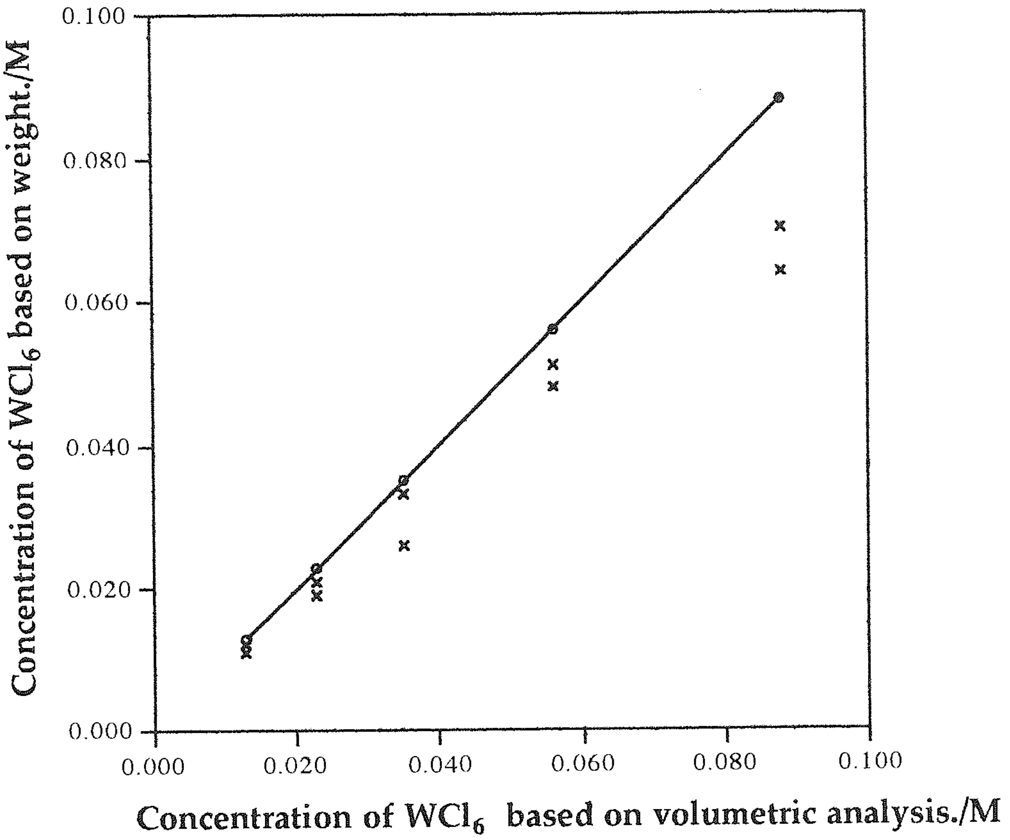
Conc. of $WCl_{6(tol)}$ from weighed amts./M	Conc. of $WCl_{6(tol)}$ from vol. analysis./M	Conc. of $WCl_{6(tol)}$ used in calculations./M
0.013	0.011-0.012	0.01
0.023	0.019-0.021	0.02
0.035	0.026-0.033	0.03
0.056	0.048-0.051	0.05
0.088	0.064-0.070	/

Figure 2.6 shows the correlation between the values and the increasing divergence as the concentration of the WCl_6 increased. This showed that 0.01-0.06M WCl_6 solutions in toluene could be prepared reasonably accurately by the weighing techniques used.

2.4.6 TUNGSTEN OXYTETRACHLORIDE.

Solutions of this dark red solid in toluene were prepared as for tungsten hexachloride. However the low solubility of the solid made it impossible to prepare even 0.02M solutions accurately.

FIGURE 2.6 CORRELATION OF CONCENTRATION OF WCl_6.



× Concentration range of WCl_6 based on titration results compared to concentration based on weight.

o Exact correlation of concentration of WCl_6 values.

2.4.7 CYCLOPENTENE.

Sequential distillation of cyclopentene and either toluene or cyclohexane into a weighed evacuated flask was used to prepare 2-3M solutions.

2.4.8 ALUMINIUM ETHYLDICHLORIDE/BUTYLLITHIUM CO-CATALYSTS.

A range of co-catalyst systems were produced by premixing known molar amounts of aluminium ethyldichloride solution and solutions of butyllithium. In every case the precipitation of lithium chloride indicated a chemical reaction.

A known molar amount of aluminium ethyldichloride solution, from the sources described in section 2.4.4, was injected, using the Schlenk technique, into a small reaction flask or into the sidearm of a vessel of the type shown in figure 2.5. An equivalent molar quantity of butyllithium or *sec*-butyllithium solution was then injected, so that a 1:1 ratio of the co-catalyst components was achieved

2.4.9 CO-CATALYST MIXTURES OF ALUMINIUM ETHYLDICHLORIDE AND POLYSTYRYLLITHIUM.

The appropriate molar amount of aluminium ethyldichloride solution was injected, over argon, into a known molar quantity of polystyryllithium solution, prepared as described in section 2.4.3.

A series of equimolar mixtures of $AlEtCl_2$ and PStLi were prepared using polystyryllithium of different degrees of polymerization. The pale yellow $AlEtCl_2$ was slowly added to the orange solution of PStLi and on shaking the colour of the solution disappeared and a white solid formed. However this sometimes remained as a suspension, when the viscosity of the mixture was quite high. These mixtures were used as the co-catalyst system with the catalyst WCl_6 solution for the polymerization of cyclopentene.

The series of experiments reported in section 5.5.4. required various mole ratios of 0.1M PStLi/cyclohexane to 0.2M $AlEtCl_2$ /toluene, which were prepared using the Schlenck technique and used as co-catalyst systems with WCl_6. The full range used was PStLi:$AlEtCl_2$ of 0.5:1, 1:1, 1.5:1, 2:1 and 2.5:1.

2.4.10 ABSOLUTE ETHANOL.

Degassed, dry, pure ethanol and toluene were distilled into an evacuated small reaction flask attached to the vacuum line to produce a 1M solution of ethanol.

2.5. EXPERIMENTAL TECHNIQUES.

2.5.1 ROMP OF CYCLOPENTENE.

The initial investigations of the ring-opening polymerization of cyclopentene were to establish the effect of reaction conditions on the rate of polymerization, yield and structure of the product using WCl_6 and $WOCl_4$ with a range of co-catalysts and using toluene and cyclohexane as solvents. Three different series of reaction procedures (A, B and C) were followed, all products were precipitated, purified and dried and the yield calculated as a percentage of the cyclopentene used. SEC analyses of 0.5%(wv) solutions of the products in THF were carried out (see section 2.6.1) using an RI detector and a UV/VIS detector set at 254nm. Some samples were also analysed using ^1H and ^{13}C NMR spectroscopy (see section 2.6.3).

2.5.1.1 SERIES A. Sequential Addition of Catalyst and Co-catalyst.

In a typical polymerization approximately 30cm^3 2-3M cyclopentene in toluene were prepared by successive distillations under vacuum into a reaction flask (see figures 2.2 or 2.3), and sufficient 0.02M WCl_6 was injected, over argon, into the monomer solution to give a WCl_6: monomer ratio of 1:500. This ratio was kept constant in all experiments. After a predetermined aging time, the co-catalyst solution (e.g. butyllithium) was injected, over argon, and in a known ratio to the catalyst.

In all experiments the solutions were kept at 25°C until there was an observed increase in viscosity but a maximum of two days was allowed. The product was then precipitated in degassed methanol, dissolved in hexane and reprecipitated in methanol before being dried in a vacuum oven at 25°C for several hours. The yield after the recorded reaction time was calculated and the average molecular weights determined by SEC. The average molecular weights were determined in terms of polystyrene equivalents. Some of the THF solutions formed gels after 4 or 5 days in the solvent and initially this greatly hampered analysis.

2.5.1.1.1 The Effect of Aging time.

Gregory's kinetic studies seemed to confirm the findings of Tuck,[186] that the time delay between addition of the WCl_6 and the co-catalyst, referred to as the 'aging time', affected the rate of polymerization. To find the optimum aging time, a series of polymerizations were carried out using butyllithium in hexanes as a co-catalyst, with a fixed WCl_6:BuLi ratio of 1:2, and aging times of 1, 2, 3, 5 and 10 minutes. The polymerizations were carried out as described above for a known reaction time and the mass of polymer recovered was determined.

2.5.1.1.2 The Effect of WCl_6: Co-catalyst Ratio.

Employing techniques to prevent deterioration of the co-catalyst solutions, the ratio of catalyst to co-catalyst was varied over a wide range using different co-catalyst systems. Butyllithium was used initially but *sec*-butyllithium, aluminium ethyldichloride and 1:1 mixtures of $AlEtCl_2$/BuLi and $AlEtCl_2$/*s*-BuLi solutions (prepared as described in section 2.4.8) were also used. The polymerizations were carried out, as previously described, using a fixed aging time and the monomer to WCl_6 ratio of 500:1.

2.5.1.1.3 The Effect of the Solvent.

As cyclohexane is the preferred solvent for the preparation of the polystyryllithium to be used to co-polymerize cyclopentene, experiments were carried out using cyclohexane, as an alternative solvent for the polymerization. The procedure was modified to prepare solutions of WCl_6 in cyclohexane and 2-3M cyclopentene in cyclohexane. The aging time was kept constant and both butyllithium and aluminium ethyldichloride were used as co-catalysts in a range of catalyst to co-catalyst ratios.

2.5.1.1.4 The Use of $WOCl_4$ as the Catalyst.

Tungsten oxytetrachloride solution in toluene was used as an alternative catalyst for the polymerization of cyclopentene with the co-catalyst butyllithium, using a range of mole ratios, but keeping the other conditions constant for the reaction.

2.5.1.2 SERIES B. Premix Catalyst and Co-catalyst.

A series of experiments were carried out in which the WCl_6-toluene solution was premixed with the co-catalyst solutions (e.g. BuLi, *s*-BuLi or $AlEtCl_2$) and then after a fixed aging time the catalyst mixture was added to the monomer solution.

An evacuated reaction flask of the type shown in figure 2.5 was attached to the vacuum line and tap 1 closed. The approximately 2.5M solution of cyclopentene in toluene was prepared by sequential vacuum distillation into the main vessel B. Argon was then passed into the vessel and tap 1 removed so that both 0.02MWCl_6 solution and the appropriate co-catalyst solution could be injected over argon into the side-arm in a predetermined mole ratio. Taps 1 and 2 were then closed and the flask was removed from the manifold. The resulting catalyst system was then mixed with the cyclopentene solution by opening tap 1. The polymerization mixture was kept at 25°C and left until there were signs of increased viscosity as in series A. The reaction mixture was precipitated, purified and dried as before. The yield was calculated and SEC analysis carried out. The rates of these reactions, the yields and the types of the product were compared with the polypentenylene formed by series A.

2.5.1.3 SERIES C Sequential Addition of Ethanol, WCl_6 and BuLi.

There is frequent reference in the literature to the beneficial effect of small amounts of oxygen containing compounds on the rate of ring-opening metathesis polymerization. The appropriate amount 1M absolute ethanol solution, prepared as described in section 2.4.11, was injected over argon into an approximately 2.5M cyclopentene/toluene solution in a reaction flask. Again using the Schlenck technique, 0.2MWCl_6 and a stock solution of butyllithium were injected with a delay of 2 minute between each addition. The amounts injected were in a predetermined mole ratio for cyclopentene/ WCl_6/EtOH/BuLi. The experiment then proceeded by the method outlined for series A in section 2.5.2.1.

2.5.2 ROMP USING THE CO-CATALYST POLYSTYRYLLITHIUM.

The ring-opening metathesis polymerization of cyclopentene, using WCl_6 as the catalyst and polystyryllithium as the co-catalyst, were carried out to find the optimum conditions for the polymerization. The product was precipitated at a known reaction time, purified and dried to calculate the yield of the reaction. Initially the product was precipitated in degassed methanol, purified and dried as in section 2.5.1.1, so that the whole product mixture could be analysed by SEC. The production of high molecular weight polypentenylene-rich material and low molecular weight polystyrene-rich product was confirmed and the fractional precipitation procedure used by Gregory was then adopted. The yield was calculated from the sum of the masses of the two purified products. The mass of the styrene used was subtracted and the difference was then expressed as a percentage of the original mass of cyclopentene. The subsequent analysis of 0.5%(wv) THF solutions of the purified products was again by SEC as described in section 2.6.1 and by ^1H and ^{13}C NMR spectroscopy as outlined in section 2.6.3..

SEC analysis with both RI and UV/VIS detectors allowed comparison of the UV/RI peak areas obtained for pure polystyrene (used to calibrate the detectors as outlined in section 2.6.1.3) and polypentenylene obtained with the co-catalyst systems mentioned in the 2.5.1 series. The molecular weight values for the metathesis products were obtained in terms of polystyrene equivalents. The homopolymer polypentenylene is reported to show no UV absorbance at 254nm. SEC analysis of the product of the polymerization, using the WCl_6/PStLi catalyst system, would thus show an increase in this absorbance if polystyryl chains had been incorporated into the elastomer as block co-polymer of the type AB or ABA.

2.5.2.1 SERIES A. Sequential Addition of Catalyst and Co-catalyst.

In a typical experiment a solution of polystyryllithium in cyclohexane was prepared over argon, as described in section 2.4.3, in a small reaction flask of the type shown in figure 2.2 (**method 1**) or in the side-arm (A) of a reaction vessel of the type shown in figure 2.5 (**method 2**).

Removal of a known volume of the solution by syringe for SEC analysis, confirmed that complete polymerization had occurred to produce polymer of narrow polydispersity index and provided the molecular weight data needed to calculate the concentration of the polystyryllithium solution accurately. Only solutions of concentration >0.01M PStLi in cyclohexane were used as these showed no signs of spontaneous decay over a period of several weeks.

Method 1. A large flask, of the type shown in figure 2.2, was attached to the vacuum line and evacuated then known amounts of cyclopentene and toluene were vacuum distilled to produce about 30cm^3 2-3M monomer solution. Approximately 0.02M WCl_6/toluene solution was injected over argon to give a cyclopentene:WCl_6 ratio of 500:1 and after 2 minutes aging time the appropriate volume of 0.05M PStLi/cyclohexane was also injected into the reaction mixture. This technique was used with solutions of polystyryllithium which could easily be injected accurately by syringe but some polystyryllithium solutions were too viscous to be syringed accurately.

Method 2. The polystyryllithium was prepared over argon in a flask with side-arm (A) a known mass was removed to be analysed so the number of moles of PStLi remaining was known, tap 1 was kept closed, and the main vessel (B) was evacuated, flamed and allowed to cool under vacuum. The appropriate amounts of cyclopentene and toluene were sequentially distilled under vacuum into (B) and the WCl_6 injected over argon to establish the pre-determined mole ratio and tap 2 was carefully closed. After 2 minutes tap 1 was opened to allow mixing of the two solutions.

The reaction mixture was kept at 25°C until there was an increase in the viscosity or no signs of further reaction. Several methods were utilised to precipitate and separate the mixture of products. Different fractional precipitation techniques were investigated. The polymerization mixture was quenched by adding wet toluene over argon and then poured into hexane, to precipitate the polystyrene (PS) and polystyrene-rich (PSR) product, and filtered. The filtrate was then poured into methanol to precipitate the elastomeric material. The first precipitate was redissolved in acetone and then added to methanol to reprecipitate the PS and PSR product, which was dried in a vacuum oven at 25°C for 2-3 hours. The elastomeric material was redissolved in hexane and precipitated from methanol, this process was repeated three times, and then the product was dried as for the other product. This process was not entirely successful, as when the reaction mixture was viscous, pouring it into the hexane resulted in the insoluble PS and PSR products being held in suspension and they were not removed by filtration. However if the product mixture was poured into acetone first, to precipitate the elastomer which was filtered off and purified as before, and then the filtrate was added to methanol the PS and PSR products are precipitated cleanly and can be easily filtered and purified. This procedure was adopted and the SEC analysis indicated the success of the fractional precipitation.

The system was tested to see the effect of the WCl_6:PStLi ratio, the solvent used and the degree of polymerization of the polystyryllithium on the rate of reaction and the nature of the products. A constant aging time of 2 minutes was used in all the series A experiments.

2.5.2.2 SERIES B. Premix Catalyst and Co-catalyst.

The technique described in 2.5.1.2. was modified so that the catalyst solution of WCl_6 and the polystyryllithium solution were premixed. To provide a comparison with other experiments using PStLi as the co-catalyst, the WCl_6:PStLi ratio of 1:2 was used. 2.5M cyclopentene/toluene solution was prepared by sequential vacuum distillation of the monomer and solvent into the main part B of a reaction vessel (see figure 2.5). The appropriate volumes of 0.02MWCl_6 and 0.05M PStLi (DP_n=20) were injected over argon into the side-arm A. The aging time of the catalyst mixture was varied between 1 and 60 minutes and the solution was then added to the monomer solution in B and treated as before.

2.5.2.3 SERIES C. Sequential Addition of Ethanol, WCl_6 and PStLi.

The method outlined in 2.5.1.3 was extended to the WCl_6/PStLi catalyst system. The preparation of the 2.5M cyclopentene/toluene solution, by vacuum distillation of the two liquids into a reaction flask, was followed by injection of 0.8M absolute ethanol solution in toluene, over argon, in the required mole ratio. After a two minutes aging time, the 0.02M WCl_6 was introduced and after a further two minutes the 0.05M PStLi (DP_n=50) was added, both by syringe over argon and in the appropriate amounts to produce the final mole ratios of cyclopentene: WCl_6:EtOH:PStLi of 500:1:0.5:1, 500:1:1:1 and 500:1:1:2. The treatment of the reaction mixture was then as previously described.

2.5.3 ROMP USING $AlEtCl_2$ /POLYSTYRYLLITHIUM CO-CATALYSTS.

The initial experiments using the $AlEtCl_2$/PStLi co-catalyst system involved preparing the mixture in a 1:1 mole ratio as described in section 2.4.9. The $AlEtCl_2$/PStLi co-catalyst system was prepared either in a small reaction flask (see figure 2.2) or in the side-arm (A) of a reaction vessel (see figure 2.5), by injection under argon. One of the procedures, described in section 2.5.2.1. as **method 1** and **method 2**, was then adopted to polymerize the cyclopentene and to separate and analyse the products. Only the series A polymerization procedure was adopted with these experiments but polystyryllithium with different degrees of polymerization were used and the ratio of WCl_6 to co-catalyst mixture was varied.

To see the effect of a variety of polystyryl/ethylaluminium chloride species on the ring-opening polymerization of cyclopentene, mixtures of PStLi/$AlEtCl_2$ were prepared in different mole ratios (i.e. 0.5:1, 1:1, 1.5:1, 2:1 and 2.5:1). **Method 2** described in section 2.5.2.1. was used to carry out the polymerization. The ratio of W:Al was maintained at 1:1 and the precipitation, purification and analysis of the products was as normal.

2.6 ANALYTICAL TECHNIQUES.

2.6.1 SIZE EXCLUSION CHROMATOGRAPHY.

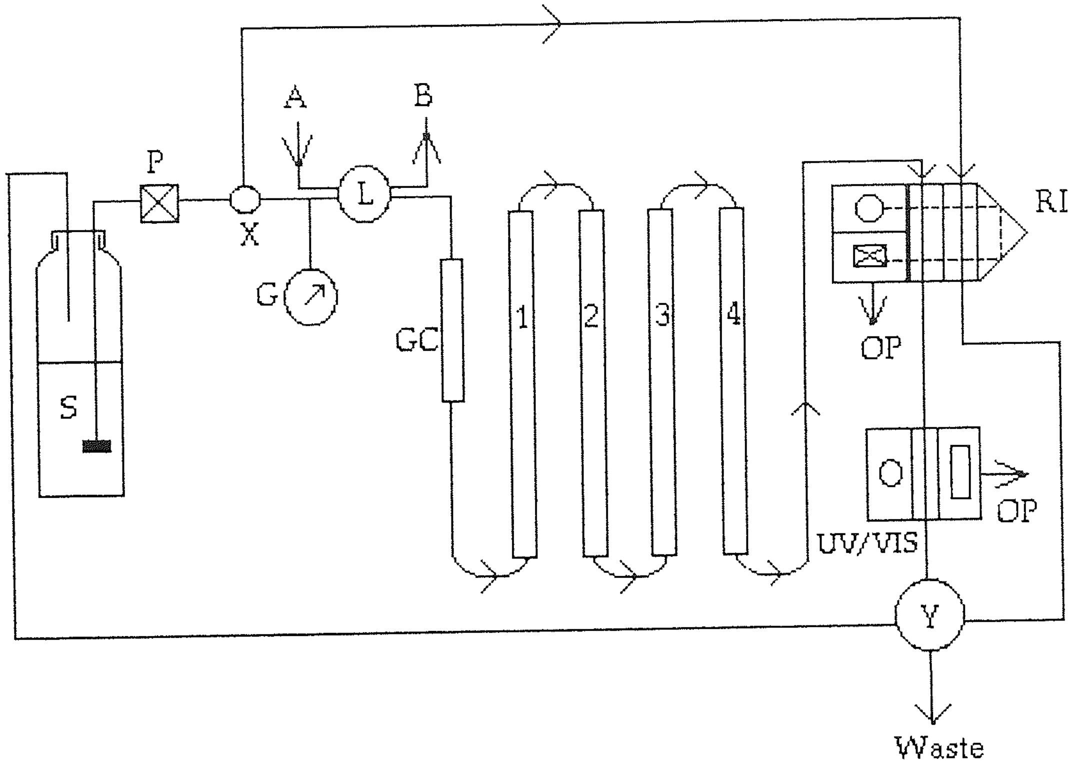
2.6.1.1 Outline of System used.

Size exclusion chromatography (SEC) or gel permeation chromatography (GPC) is a technique for determining the molecular weight and molecular weight distribution of polymer samples. A diagram of the original apparatus used is shown in figure 2.7. SEC involves the separation of a solution of polymer into its component fractions according to size i.e. hydrodynamic volume.

The polymer sample must be soluble in the solvent for the system, which is the eluent or mobile phase. The mobile phase is continuously pumped through the stationary phase, which consists of cross-linked polystyrene beads, packed into one or a series of columns. The beads swell and produce surface pores with a carefully controlled distribution of size. The solution sample is injected into the column and is carried through the system by the eluent. Initially there is a concentration gradient between the solution in the mobile phase and the solvent held in the pores, causing the polymer to diffuse into the porous beads. The smaller molecules are able to permeate a larger number of the available pores than the larger particles. The solvent moves at a constant flow rate and the largest polymer molecules are held up least by the stationary phase and are eluted first.

The system used initially in this project consisted of a Knauer HPLC 64 pump (P), a pre-column (GC), to remove any suspended matter from the solution, and four μ-Styragel columns (1-4) of exclusion limit 10^2, 10^3, 10^4 and 10^5 in series. HPLC grade THF was pumped at $1cm^3$ per minute through the system, which was fitted with a Alltech recycler (Y) to prevent excess waste of solvent. A single mixed bed column (M) replaced the four columns towards the end of

FIGURE 2.7 SCHEMATIC DIAGRAM OF SEC APPARATUS.

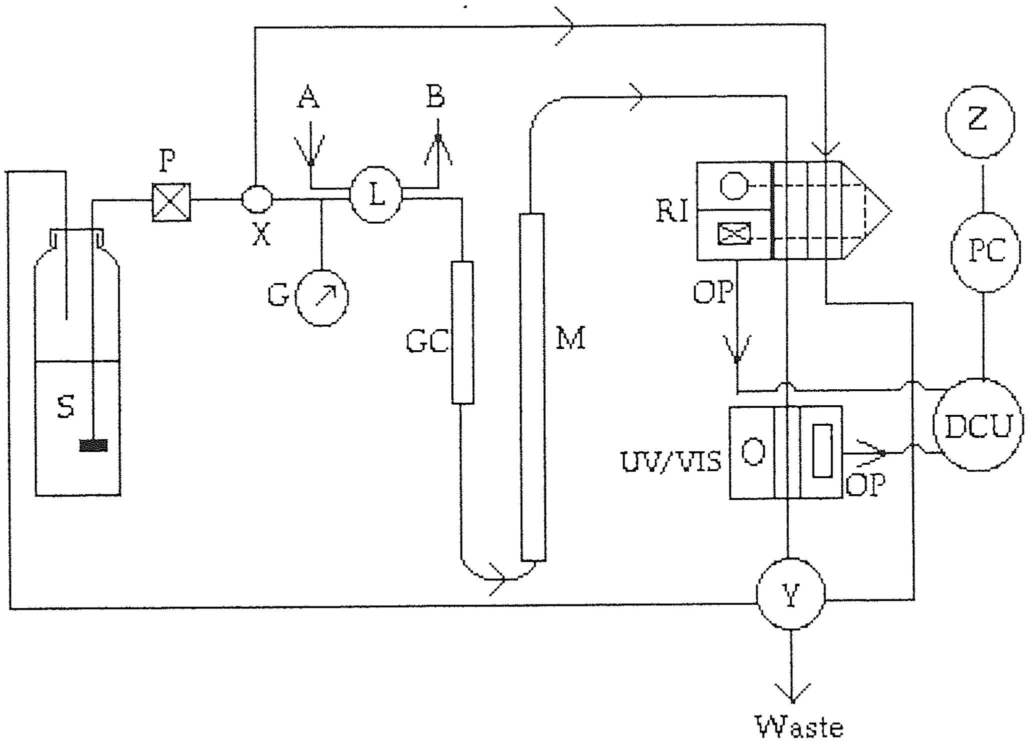


KEY.

S = Solvent reservoir
P = Pump
G = Pressure guage
X = Valve
A = Injection port
B = Waste
Y = Recycler
OP = Output

L = Valve and loop injector
GC = Guard or Pre-column
RI = Refractometer
UV/VIS = Spectrometer set at 254nm.
1 = 10^2 Å Styragel column
2 = 10^3 Å Styragel column
3 = 10^4 Å Styragel column
4 = 10^5 Å Styragel column

FIGURE 2.8 MODIFIED SEC APPARATUS.



KEY.

S = Solvent reservoir

P = Pump

G = Pressure guage

X = Valve

A = Injection port

B = Waste

OP = Output

M = Mixed bed column

L = Valve and loop injector

GC = Guard or Pre-column

RI = Refractometer

UV/VIS = Spectrometer set at 254nm.

Y = Recycler

DCU = Detector control unit

PC = Computer

Z = Printer

the project and this is shown in the modified diagram figure 2.8. 0.5-1.0%w/v solutions of pure dry polymer samples in HPLC grade THF were prepared and injected initially into a 100μl valve and loop injector (L) system. The retention or elution volume (V_r) was recorded from the time the solution was released into the short pre-column. Under controlled conditions of temperature, flow rate and concentration for the same physical system, the retention volume of a polymer sample is a function only of its molecular size.

The eluent is continuously analysed by Knauer differential refractometer (RI) and a Perkin-Elmer LC 85B variable wavelength spectrometer (UV/VIS), connected in series. The former continuously compares the refractive index of the eluent and pure solvent. The UV/visible spectrometer detects chromophoric groups either attached to, or part of the polymer backbone. The spectrometer was set at 254nm a known strong absorbance wavelength of phenyl groups.

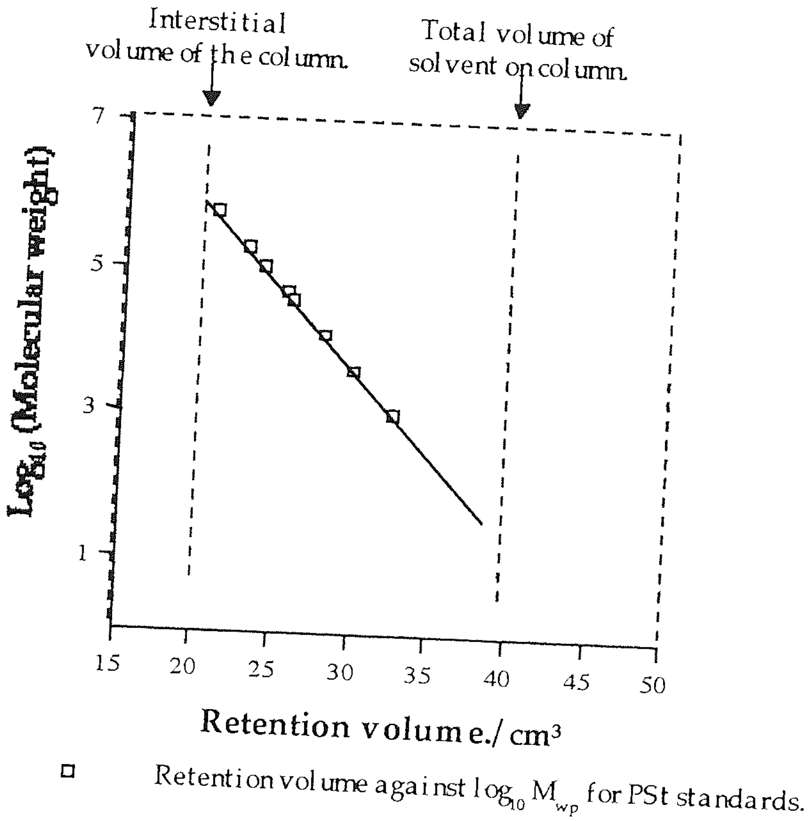
Initially the output of each detector was monitored by a dual-pen chart recorder. The detector response produced a deflection on the chart recorder proportional to the concentration of the solute, measured as weight per unit volume and the deflection for the spectrometer is also dependent on the molar extinction coefficient of the chromophore.

The chart recorder was replaced in later stages of the project by a PCL caliber DCU computerised system. This monitored the response for both detectors simultaneously on a VDU and then, based on reference calibration data, calculated the parameters for each polymer sample automatically.

2.6.1.2 Calibration of SEC for Molecular Weight Determination.

The average molecular weight of a polymer sample can only be calculated if the SEC system has been calibrated using standard samples. A series of polystyrene standards of known molecular weight at the peak (M_{wp}) and narrow molecular weight distribution were introduced into the column in turn and the elution volume at the peak found. Figure 2.9 shows a plot of the retention volume (V_r) against $\log_{10}$ of the known molecular weights of the standards provides a conversion equation to obtain the polystyrene equivalent molecular weight of any polymer sample, between the fixed characteristic limits of the column.

FIGURE 2.9 CALIBRATION OF SEC.



Equation of line. $y = -0.24x + 10.78$

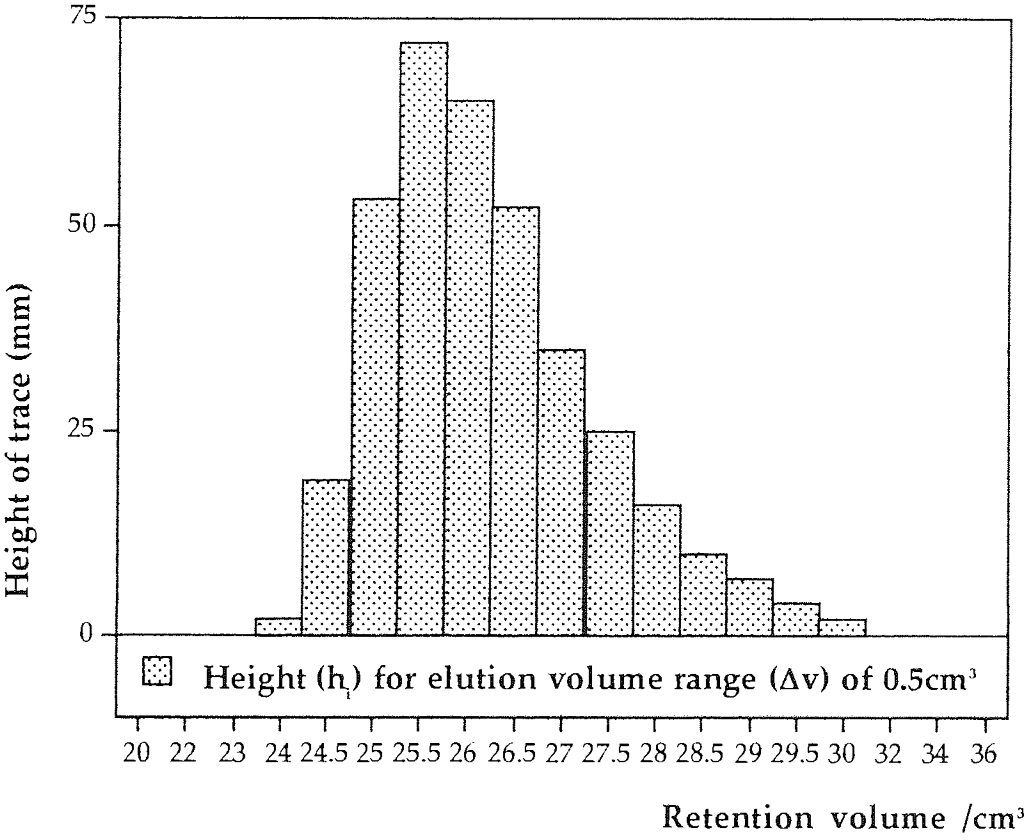
A typical RI chromatograph for a polymer sample is shown in figure 2.10. The interpretation involves recording the deflection height at regular small intervals of the elution volume ($\Delta v = 0.2$ or 0.5cm^3)

$h_i \Delta v = c_i$ but if Δv constant $h_i \alpha c_i \alpha W_i$

c_i = concentration of polymer at retention volume V_{ri}

W_i = weight of polymer at retention volume V_{ri}

FIGURE 2.10 TYPICAL SIZE EXCLUSION CHROMATOGRAPH FOR POLYSTYRENE SAMPLE.



The average molecular weights may be calculated as follows:

By definition

$$\overline{M}n = \frac{\Sigma N_i M_i}{\Sigma N_i} \quad \text{and} \quad \overline{M}w = \frac{\Sigma N_i M_i^2}{\Sigma N_i M_i}$$

where $\overline{M}n$ = number average molecular weight

$\overline{M}w$ = weight average molecular weight

N_i = number of molecules of molecular weight M_i in a given sample

M_i = molecular weight of a given sample.

If W_i the weight of polymer of molecular weight M_i in a given fraction then

$$N_i = \frac{W_i}{M_i}$$

thus $$\overline{M}n = \frac{\Sigma W_i}{\Sigma W_i / M_i} \quad \text{and} \quad \overline{M}w = \frac{\Sigma W_i M_i}{\Sigma M_i}$$

Since RI response is a measure of the concentration of polymer of molecular weight M_i producing a deflection of given height h_i, then h_i can be substituted for W_i and hence

$$\overline{M}n = \frac{\Sigma h_i}{\Sigma h_i / M_i} \quad \text{and} \quad \overline{M}w = \frac{\Sigma h_i M_i}{\Sigma M_i}$$

The M_w at each retention volume is obtained from the calibration curve. The most recent system acquired analyses and interprets the data automatically. The molecular weight distribution or poly dispersity index (PDI) of the sample, is defined by $$PDI = \frac{\overline{M}w}{\overline{M}n}$$

this is also calculated, as is the area under any curve or part of it.

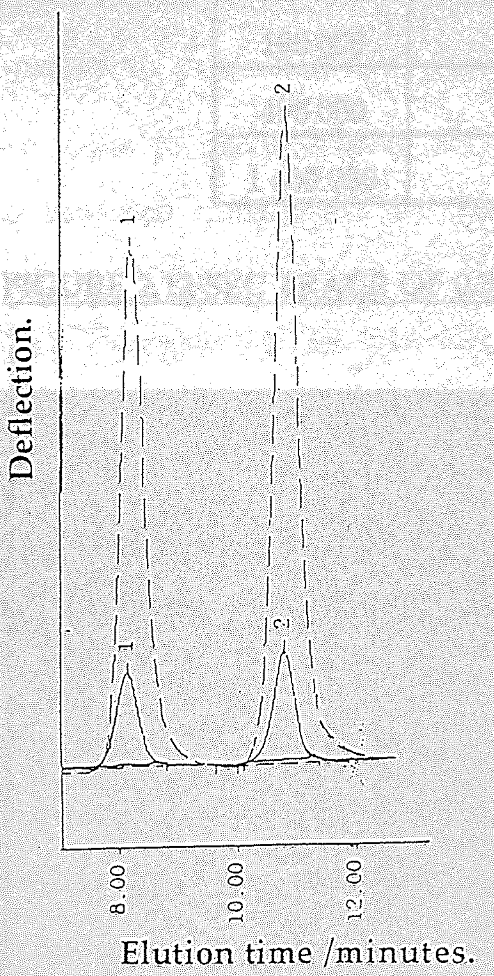
2.6.1.3 Calibration of UV/Visible Detector.

The UV/visible detector had been used by previous workers[184,185] to indicate the formation of some co-polymer when polystyryllithium is used as a co-catalyst for the ROMP of cyclopentene with tungsten hexachloride.

They assumed that pure polypentenamer would show no absorbance at 254nm but any styrene groups attached to the end of the chain would be detected by the high absorbance of the phenyl chromophore at this wavelength.

An attempt was made to quantify the RI:UV/VIS response from the SEC detectors for different polystyrene samples. Figure 2.11 shows the size exclusion chromatograph for a mixture of two standard polystyrene samples with both RI and UV/VIS responses plotted against elution time, because the rate of flow of the mobile phase of THF is 1cm^3 per minute, the retention volume is numerically equal to the elution time.

FIGURE 2.11 SEC TRACE FOR RI AND UV/VISIBLE DETECTORS FOR TWO POLYSTYRENE STANDARDS AS 0.5%(WV) SOLUTIONS IN THF.



KEY.
= RI trace.
= UV absorbance at 254nm.

Peak 1. STANDARD $M_{wp} = 190\,000 g.mol^{-1}$.
M_{wp} from RI trace = $207\,000 g.mol^{-1}$. PDI = 1.10.
M_{wp} from UV absorbance(254nm.)= $170\,000 g.mol^{-1}$.
Ratio of UV:RI peak area = 6.5.

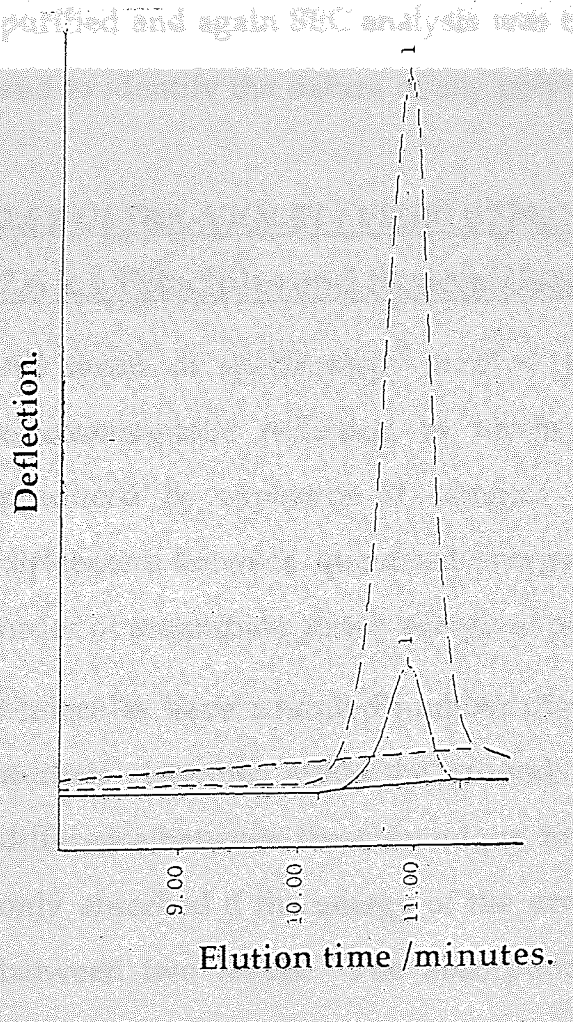
Peak 2. STANDARD $M_{wp} = 1\,200 g.mol^{-1}$
M_{wp} from RI trace = $1\,400 g.mol^{-1}$. PDI = 1.08.
M_{wp} from UV absorbance (254nm.)= $1\,500 g.mol^{-1}$
Ratio of UV:RI peak area = 6.7.

The ratio of the peak areas for the UV/VIS to RI detector was found consistently to be 6.2-6.9. and the values are given in table 2.3. Therefore this ratio is constant for polystyrene samples of different molecular weights within the limits of accuracy possible.

TABLE 2.3 THE RATIO OF UV/VISIBLE TO RI TRACE AREAS FOR STANDARDS OF DIFFERENT MOLECULAR WEIGHT.

M_{wp} /g.mol^{-1}	$\frac{\text{UV/VIS area}}{\text{RI area}}$ from SEC
1 200	6.7
3 000	6.5
28 000	6.4
115 000	6.2
190 000	6.5
495 000	6.9
1 400 000	6.4

FIGURE 2.12 SEC TRACE OF 0.5%(WV) POLYSTYRENE SAMPLE IN THF.



KEY.

= RI trace.

= UV absorbance at 254nm.

Peak 1.

POLYSTYRENE SAMPLE.

Prepared $M_{n(theor.)} = 1040$g.mol^{-1}.

$DP_n = 10$.

M_{wp} from RI trace = 1140g.mol^{-1}.

PDI = 1.08.

M_{wp} from UV absorbance (254nm.) = 1080g.mol^{-1}.

Ratio of UV:RI peak area = 6.5.

Polystyrene sample were then prepared, using known amounts of initiator and monomer, as previously described in 2.4.3. Figure 2.12 shows a SEC plot, which was used to check the initial concentration of the *sec*-butyllithium used and to confirm the consistency of the UV/VIS to RI area for these experimental samples.

Samples of purified polypentenylene, prepared using different initial conditions, were analysed using SEC to determine not only molecular weight characteristics but also to check the UV/VIS absorbance at 254nm. The problems associated with the formation of gels when 0.5% w/v solutions of the metathesis product in THF were left for several days will be discussed later.

Experiments to produce block co-polymerization by ROMP of cyclopentene using tungsten compounds and co-catalysts based on polystyryllithium were carried out using a variety of conditions. The precipitated polymer was purified and again SEC analysis was used to determine molecular weight data and to identify the nature of any polymer containing styrene.

2.6.2 ULTRA-VIOLET / VISIBLE SPECTROPHOTOMETRY.

2.6.2.1 Principles and System Used.

All forms of spectroscopy involve the selective absorption or emission of electromagnetic radiation by atoms or molecules. Electronic spectra are produced by exposure of samples to uv/visible radiation as the energy differences between quantised energy levels of the electrons are of the same order of magnitude as the energy of photons in this region of the spectrum.

Molecules have a limited number of discrete, quantised energy levels available to their electrons, called the ground state and the excited states. The energy difference between these is unique to the particular molecule and radiation is only absorbed if the energy of the exciting photon exactly matches the energy between two levels. The absorption and subsequent re-emission therefore occur at characteristic frequencies for a given compound and can be used to identify it.

The Beer-Lambert law governs the absorption of radiation by an absorbing solute in a non-absorbing solvent.

$$\log_{10}\frac{I_0}{I} = \varepsilon lc = A$$

where: I_0 is the incident intensity

I is the transmitted intensity

ε is the extinction coefficient ($1000 cm^2 mol^{-1}$)

c is the concentration of the absorbant ($mol.dm^{-3}$)

l is the path length (cm)

A is the absorbance

One of the applications of uv/visible spectrometry is the elucidation of the composition of particular metal complex species. The analysis can be carried out continuously and without changing the position of equilibria within the system.

The instrument used was a Pye Unicam SP8-100 uv/visible spectrometer with its own chart recorder. It was possible to scan the absorbance of the species over the uv/visible spectrum or measure changes in absorbance at a given frequency or wavelength with time.

2.6.2.2 Calibration.

The spectrophotometer allowed for the absorbances to be measured against air or against a reference cell. Tests carried out over the range of wavelengths used (600-200nm.) showed that consistent results could be obtained by running the sample cell against air if a blank or reference allowance was made by deducting the absorbance of the solvent at a given wavelength. So a reading for the diluting medium was always taken before each experiment.

2.6.2.3 Experimental.

2.6.2.3.1. UV/Visible Spectrum of PStLi.

The initial investigation involved studying the structure and stability of polystyryllithium as this would be relevant in elucidating its function in the initiation mechanism of ROMP. The apparatus, shown in figure 2.13, was designed, after several modifications to reduce errors caused by loss of activity during dilution or transfer procedures, and procedure 1 was followed.

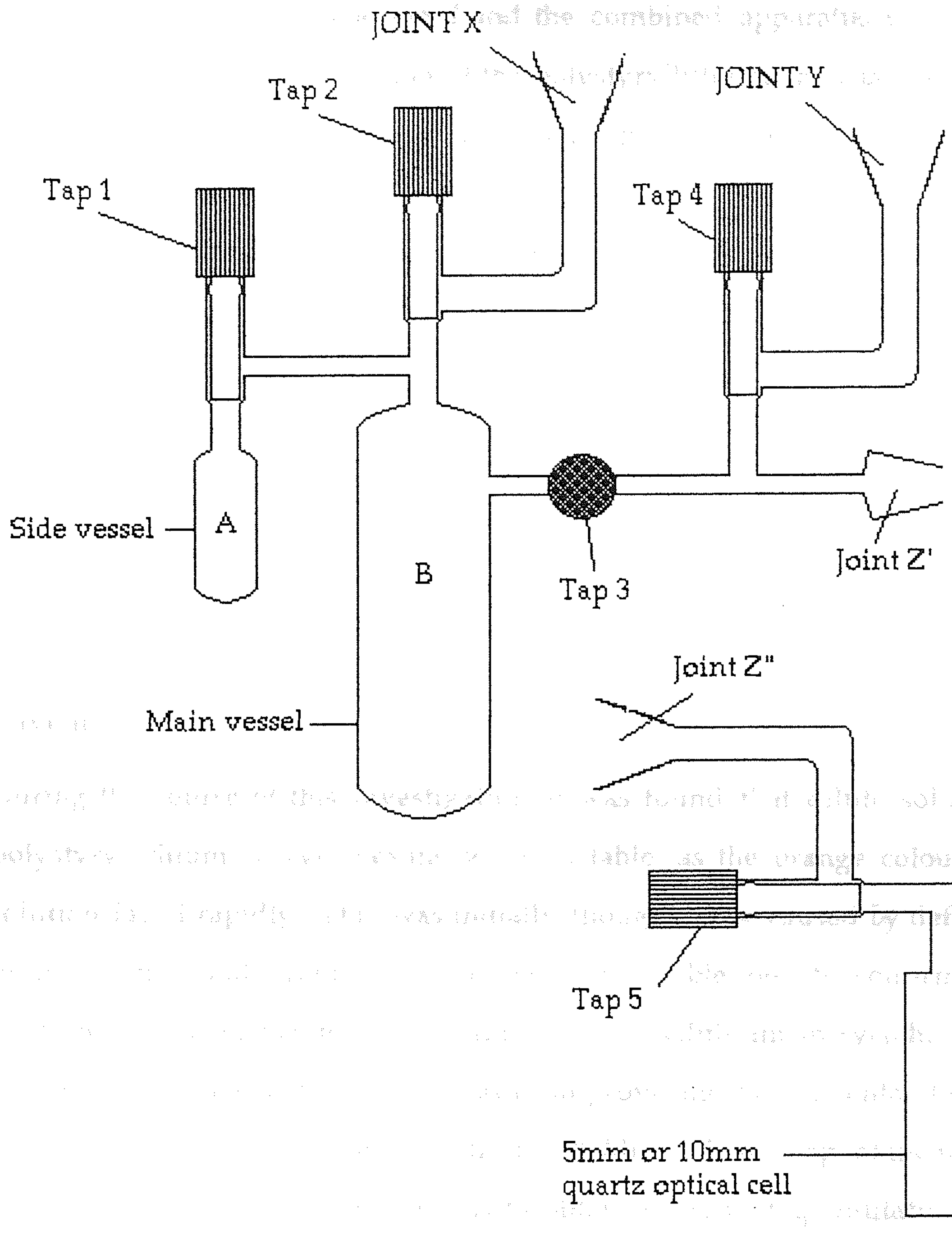
Procedure 1.

The apparatus was attached to the vacuum line using joint X and approximately 0.01M polystyryllithium was prepared in A, as described in 2.4.3. In a typical experiment 0.5cm^3 0.4M styrene solution and 0.5cm^3 0.04M *sec*-butyllithium solution (cyclohexane is the solvent for both solutions) were injected, using the Schlenk technique, into A. Taps 1 and 2 were firmly closed and the apparatus was clamped in a water bath for at least 3 hours to ensure complete polymerization of the styrene.

A known volume of PStLi was removed from A, over argon, and injected into degassed methanol. The styrene was precipitated, purified, dried and analysed using SEC, as described in section 2.4.3. This provided molecular weight data and enabled the accurate concentration of the PStLi solution to be calculated.

The 10^{-2}M PStLi solution was then diluted with cylohexane so that the concentration of polystyryllithium was approximately 10^{-3}M. The main vessel B was evacuated and flamed by attaching it to the vacuum line at X. Pure cyclohexane was distilled under vacuum into B, tap 2 was closed and the vessel was removed from the line. The section with the quartz cell was attached

FIGURE 2.13 INITIAL APPARATUS USED FOR UV/VISIBLE SPECTROPHOTOMETRY.



through joints Z'Z". The combined apparatus was re-attached to the line by joint Y and the whole cell section was evacuated and, apart from the cell the section, flamed. Tap 4 was closed and the combined apparatus was removed from the vacuum line. Dilution of the polystyryllithium in A by the liquid in B was effected by opening tap 1 and then tap 3 was opened so the solution passed into the cell. Taps 3 and 5 were closed and the cell removed and inserted into the spectrophotometer at an ambient temperature of 25 +3°C.

The UV/visible spectrum of the cyclohexane solvent had already been observed, so the UV/visible spectrum of the PStLi solution was recorded from 500 to 200nm. against air and a correction was made for the absorbance of the solvent.

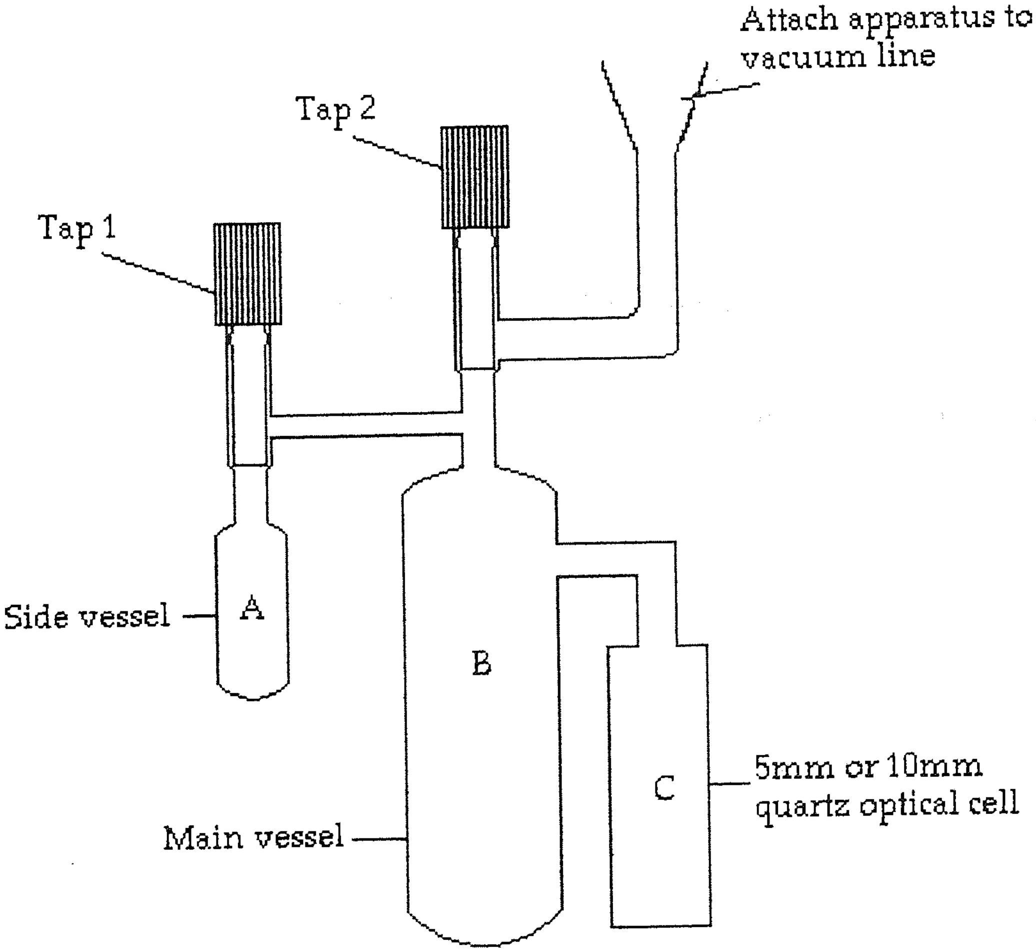
The aim was to find the $\lambda_{max.}$ for the living polymer solution and use this to investigate the nature of the C-Li bond from the known absorption band of the polystyryl anion and that of the lithium polystyryl ion pair in different solvents.[187]

During the course of this investigation it was found that dilute solutions of polystyryllithium in cyclohexane were unstable, as the orange colour of the solution faded rapidly. This was initially thought to be caused by deficiencies in the system and problems obtaining reproducible results confirmed this opinion. However the decay of "living" polystyryllithium in cyclohexane was unreported, so the first objective was to improve the experimental technique used to investigate this system, to try to establish whether spontaneous decay was occurring. The second aim was to obtain consistent quantitative results that could be compared with reports in the literature of spontaneous decay of polystyryllithium in other solvent systems.

2.6.2.3.2. The Decay of PStLi in Cyclohexane.

The detachable cell of the apparatus shown in figure 2.13 was an obvious site at which air might be introduced into the system. Also the transfer of the living PStLi solution through joint Z'Z" might bring the solution into contact with silicon grease that had not been dried. A new apparatus with an integral cell was designed to eliminate any loss of activity in the transfer to the cell (see figure 2.14). The size and shape of the apparatus were dictated by the cell chamber of the spectrophotometer.

FIGURE 2.14 MODIFIED APPARATUS FOR UV/VISIBLE SPECTROPHOTOMETRY.



The attachment of the argon supply to the line shown in figure 2.4 was devised to improve the Schlenk technique. The temperature in the cell compartment of the spectrophotometer could be rigorously controlled at 30±1°C by allowing the instrument to run for 30 minutes before use. The solution was maintained at this temperature between readings by using a thermostatic bath.

Procedure 2.

The apparatus shown in figure 2.14 was used to prepare approximately 0.01M polystyryllithium in A and to distil under vacuum pure cyclohexane into B. The whole apparatus was then placed in a water bath at 30°C. The absorbance of the pure solvent was measured and then dilution of the PStLi to concentrations of 10^{-3}-10^{-4}M was effected by opening tap 1. The modifications to the apparatus reduced the time delay in transferring the apparatus to the instrument so it was possible to record the absorbance at the reported λ_{max} of polystyryllithium in cyclohexane of 328nm as a function of time at 30±1°C. The absorbance of the orange-yellow species over the visible/uv range of 500 to 200nm. was checked periodically during the experiments.

2.6.2.3.3. The Effect of *s*-BuLi on the Decay of PStLi in Cyclohexane.

The spontaneous decay of PStLi was still found to occur. It was decided to investigate the effect of *sec*-butyllithium on the stability of the polystyryllithium by injecting a small volume of standard solution into the cyclohexane in vessel B before diluting the solution.

Procedure 3.

Initial ratios of polystyryllithium to *sec*-butyllithium of 1: 50 to 1: 10 were used. It was noted that the absorbance controls carried out on the cyclohexane/*sec*-butyllithium solutions were unacceptably high compared with the absorbance of the polystyryllithium solutions alone.

Therefore dilute solutions of *sec*-butyllithium were freshly prepared, as previously described in 2.4.3, both for the preparation of polystyryllithium and for injection into these systems. The preparation of approximately 0.05M *sec*-butyllithium, made it possible to prepare solutions of less than 10^{-2}M polystyryllithium initially and these required dilution by a factor of less than 10 to bring the absorbance within the range of the spectrophotometer. The UV/visible spectrum of the dilute *s*-BuLi solutions was observed so that the appropriate correction could be made. The diluted *sec*-butyllithium was injected into the PStLi solution in A immediately before dilution to expose both to the same dilution effects. The decay of solutions with initial polystyryllithium to *sec*-butyllithium ratios of 1:1 -1:10 were studied.

2.6.3 NMR SPECTROSCOPY.

NMR spectroscopy is a powerful technique for characterising the structure of a molecule. The nuclei of most use are ^{1}H and ^{13}C, both of which have an odd number of nucleons and nuclear spin of 1/2 so the nuclei possess a nuclear moment. Atomic nuclei with nuclear spin (I) orientate themselves in 2I+1 ways in the presence of an applied magnetic field (B_o), so ^{1}H and ^{13}C nuclei have two possible orientations with an energy difference (ΔE) between them, given by:

$$\Delta E = h\gamma B_0/2\pi.$$

h = Planck's constant. γ = magnetogyric ratio which is specific to the nucleus.
(measures the strength of the nuclear magnet)

Using the continuous wave method (CW), transitions between the two orientations are induced by applying EMR of radio frequencies. The frequency at which the energy of the applied field is exactly equal to ΔE, is absorbed by the nucleus so that its spin orientation changes. This is called the resonance frequency (ν_0) and is a characteristic of the nucleus and also its particular electron cloud density.

$$\Delta E = h\gamma B_0/2\pi$$

but $\nu_0 = \Delta E/h$. so $\nu_0 = \gamma B_0/2\pi$.

A Bruker AC300 NMR spectrometer was used in these studies. This high field instrument brings the ^1H into resonance at 300MHz (^{13}C at 75MHz). Using the FT NMR technique, a radio signal is applied, as a powerful pulse, over a range of frequencies of the required spectral width. This generates the oscillating magnetic field at right angles to the applied magnetic field (B_0) and the spectrometer monitors the absorbance of all the superimposable resonances, as the signal decays with time because of the various relaxation processes, after the pulse. This is called free induction decay (FID) and it varies for individual nuclei because of local flucuating magnetic fields. Fourier transformation of the FID converts it into a spectrum. This is a much faster and more powerful procedure than the continuous wave (CW) method previously used.

Under the influence of B_0 the electrons produce an opposing induced magnetic field (B_i) which is directly proportional to B_0.

$$B_i = - \sigma B_0.$$

σ is the shielding constant and because B_i affects the total field strength operating on the nuclei it produces a variation or shift in the resonance frequencies of individual protons or ^{13}C nuclei depending on their electronic environment. Tetramethylsilane(TMS) is used as an internal reference compound because it is inert, volatile, non-toxic, cheap and produces only one ^1H and ^{13}C signal. The resonance frequency of TMS (ν_T) is used as a reference for calculating the shift (δ) in the resonance frequency of other nuclei (ν_s).

The samples are dissolved in suitable solvents for the technique (e.g. CCl_4, $CDCl_3$), the internal reference compound added and the tube placed into a probe between the poles of the magnet. The magnet is tuned and the tube is spun to obtain maximum homogeneity before taking the spectrum. A range of frequencies close to the standard resonance frequency of ^{1}H and ^{13}C are examined (e.g. a range of 5000Hz for ^{13}C with a resolution of 0.5Hz) but the spectrum is printed to show the chemical shift (δ) of the resonance frequency of different nuclei caused by their different electron densities. The shift is a dimensionless scale defined by:

$$\delta = \nu_s(\text{Hz}) - \nu_T(\text{Hz}) / \text{ operating frequency (MHz)}.$$

This number is expressed as fractions of the applied field in parts per million (ppm) and the scale is written by convention from right to left with the TMS signal at zero on the right as shown in the following diagram.

low field/high frequency high field/low frequency
<-->
deshielded shielded
δ_C 200 <-->0
δ_H 10 <-->0

CHAPTER 3.

THE STABILITY OF POLYSTYRYLLITHIUM.

3.1 INTRODUCTION.

The extensive use of living polymerization reactions as the first stage in transformation polymerizations has been referred to in section 1.8.2. and the characteristics of these polymers were listed in section 1.4.5.1.. It is the stability of living polymers and the narrow polydispersities that can be attained, using ideal polymerization conditions, which make them useful for transformation polymerizations. The production of a reproducible first segment for the block co-polymer makes it possible to study the characteristics of the transformation reaction itself.

In this investigation it was intended that solutions of polystyryllithium in cyclohexane would be used either as the sole co-catalyst, or mixed with $AlEtCl_2$, for the subsequent ring-opening metathesis polymerization of cyclopentene with WCl_6. The ideal conditions for the anionic polymerization of styrene are widely reported and involve the use of *sec*-butyllithium solution as an initiator. At 60°C rapid initiation occurs producing PStLi of narrow polydispersity and complete polymerization occurs within 1 to 3 hours depending on the solvent. The solvent used was cyclohexane, which favours the associated species, and at least 3 hours was allowed for complete polymerization.

In section 2.1.6.3. reference was made to the SEC analysis of the precipitated polystyrene which provided a check on the PDI values of the product and on the [Li] of the solutions. For polymers with narrow molecular weight dispersities to form the mechanism of polymerization should not involve termination or transfer reactions. Figure 2.12 showed that it was possible to prepare PSt of average molecular weight close to the theoretical value and of narrow PDI ($\overline{M}n_{theo.}$= 1040g.mol^{-1}, $\overline{M}n_{act.}$= 1100g.mol^{-1}, PDI= 1.10). It was also found that the SEC analysis of solutions of PSt (0.5%wv) in THF using both UV/visible (set at 254nm.) and RI detectors produced deflection areas that were of a constant ratio. Table 2.3 showed that the UV:RI peak area was between 6.2.and 6.9 for samples of PSt with $1200 \leq \overline{M}n \leq 1\,400\,000$ g.mol.$^{-1}$.

In his review of spontaneous termination in living polymers, Glasse[188] identifies three types of termination for living anionic polymerization reactions; accidental, delibrate and spontaneous. Impurities in the PStLi system (e.g. H_2O, O_2 and CO_2) cause accidental termination by forming dead or dormant polymer. Deliberate termination involves the addition of a reagent to react irreversibly with the living species (e.g. ethanol). However, if despite the most careful precautions to avoid termination, destruction of the living ends still occurs, it is known as spontaneous termination or aging.

As the aging of polystyryllithium solutions in both THF[189.190] and toluene[191,192] has been reported in the literature and the stability of the "living" ends is critical to the production of a block co-polymer with narrow polydispersity index, a check on the "living" character of the initiator system in cyclohexane was carried out.

3.2. UV/VISIBLE SPECTROPHOTOMETRIC STUDIES.

The apparatus shown in figure 2.13 was used and **procedure 1** described in section 2.6.2.3.1 was followed. Approximately 0.01M polystyryllithium was prepared in the side-vessel A and the reaction was maintained at 60°C for at least 3 hours to ensure complete polymerization. A pale orange solution of PStLi formed within a minute and the colour gradually developed. The exact [Li] was determined by the precipitation of a known volume of the PStLi solution and SEC analysis as described in section 2.4.3

The main vessel B was evacuated and flamed by attaching it to the vacuum line at X. A known volume of cyclohexane was distilled under vacuum into B, tap 2 was closed and the vessel removed from the line. The quartz cell was then fitted and the whole apparatus re-attached to the vacuum line at joint Y. The cell section was evacuated and (apart from the quartz cell) flamed, then tap 4 was closed and the apparatus was removed from the line. The PStLi was diluted and the solution was passed into the cell. The cell was isolated and removed from the rest of the apparatus and inserted into the spectrophotometer at the ambient temperature of 25±3°C.

The UV/visible spectrum of the dilute PStLi in cyclohexane was investigated from 200 to 500nm to check its $\lambda_{max.}$. It was found that solutions of $2x10^{-3}M \leq [PStLi] \leq 1x10^{-4}M$ had initial absorbances within the range of the spectrophotometer and the maximum absorbance of the polystyryllithium solution in cyclohexane was at 328nm, as quoted in the literature.[187] However unexpectedly the colour of the solution in the cell was observed to fade over a period of 2-3 hours.

Further investigation of the change in the absorbance of the PStLi at $\lambda_{max.}$ of 328nm. suggested that there was rapid initial decay of the PStLi and then the absorbance decreased more slowly. Improvements to the experimental procedure were implemented to try to eliminate the decay because this lack of stability had considerable implications if solutions of initial $[PStLi] \leq 10^{-2}M$ were to be used as co-catalysts in metathesis polymerisations.

3.2.1. THE DECAY OF PStLi IN CYCLOHEXANE.

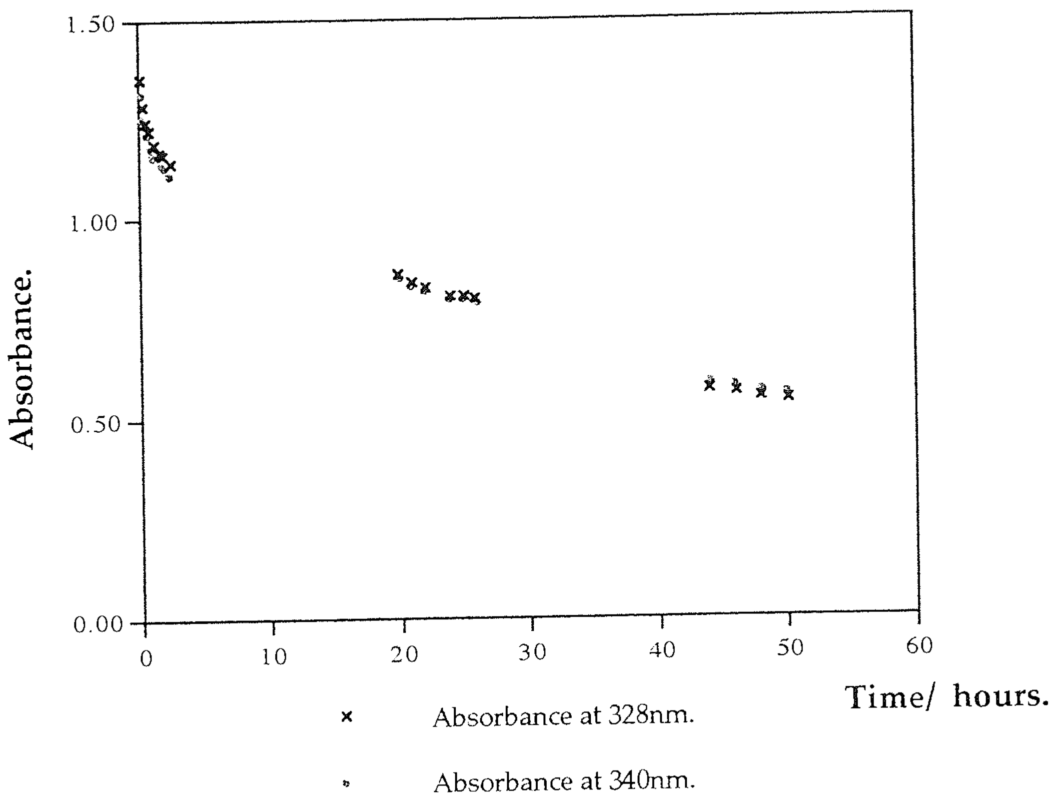
The modifications to the apparatus and the experimental technique were outlined in section 2.6.2.3.2. The detachable cell of the apparatus was an obvious site at which air or moisture might be introduced into the apparatus, both when the dilute solution was transferred to the cell and subsequently through tap 5. This could have caused the observed intial rapid decay of the PStLi and then a slow diffusion related decay. A new apparatus was designed, with an integral cell which would fit into the spectrophotometer, and this is shown in figure 2.14. The method was modified as outlined in **procedure 2.**

Apart from the obvious advantage of having an integral cell in the apparatus, more rigorous initial drying/degassing of the whole apparatus (including the cell) could be applied and, after the preparation of the polystyryllithium solution and distillation of the cyclohexane, the whole apparatus could be put in a thermostatically controlled bath at 30±1°C and the cell could then be maintained at this temperature in the spectrophotometer.

Some of the cyclohexane, distilled into B, was run into the cell C and the absorbance at 328nm. was measured so that a correction could be made to the readings. Tap 1 was then opened and the PStLi was rapidly and thoroughly diluted and a sample run into the cell. Timing commenced at this point and the absorbance of the solution at 328nm. was followed as a function of time. Periodically the spectrum of the solution was also recorded between 200 and 500nm.

Two phenomena were observed, the absorbance of the PStLi at 328nm. still decreased with time and the wavelength at which the species showed maximum absorbance ($\lambda_{max.}$) changed. The spectrum of the PStLi solution

FIGURE 3.1 ABSORBANCE OF PStLi AT 328nm. AND 340n m.

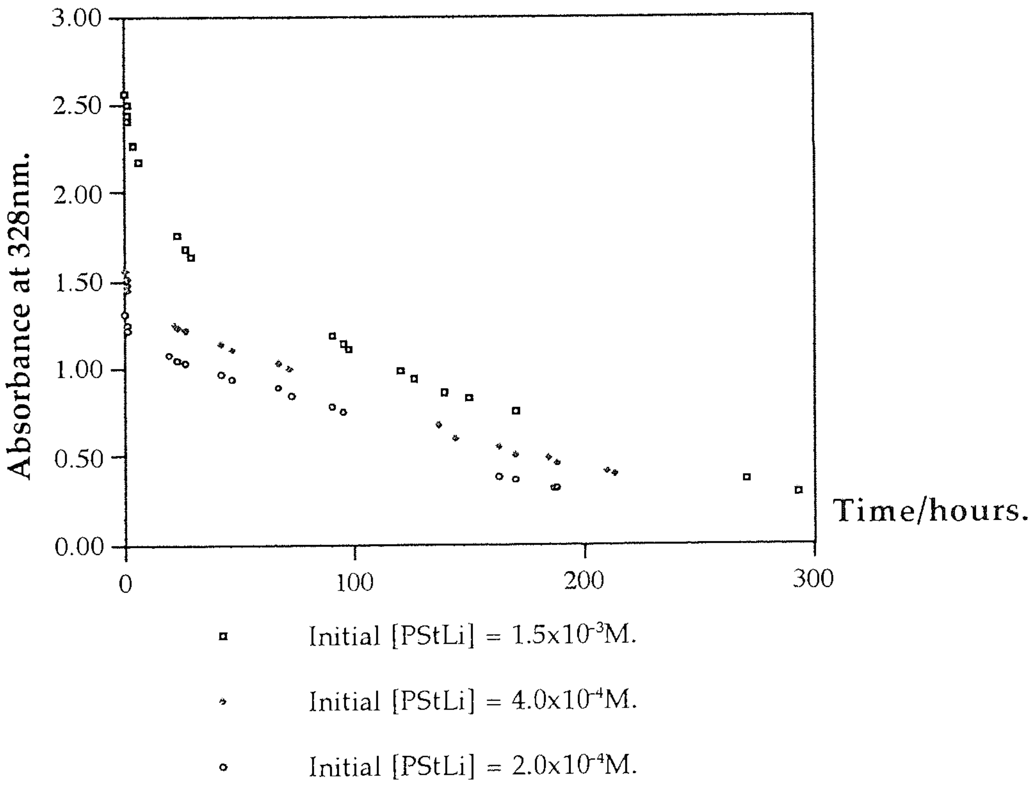


Initial [PStLi] = 4.0x10^{-4} M. M_n = 1000g.mol.$^{-1}$ PDI = 1.1.

showed that $\lambda_{max.}$ moved to a longer wavelength during the decay period. Figure 3.1 shows the absorbance at 328nm. and at 340nm. for a solution of initial [PStLi] of $4x10^{-4}$M for a period of 60 hours. The initial quite rapid decay is still evident and followed by a more gradual aging. The absorbance at 328nm is greater than at 340nm for at least 30 hours but as the graph shows the absorbance at 340nm. eventually exceeds that at 328nm.

The effect of the initial concentration of polystyryllithium ($[PStLi]_0$) on the rate of decay was investigated and shown in figure 3.2, which shows the change in absorbance with time of three solutions of PStLi in cyclohexane ($[PStLi]_0$ are $1.5x10^{-3}$M, $4x10^{-4}$ and $2x10^{-4}$M). Within the limitations of the technique the observations were reproducible and spontaneous decay was observed over the range of concentrations used ($2.0x10^{-3}M>[PStLi]_0>1.0x10^{-4}M$).

FIGURE 3.2 ABSORBANCE OF PStLi AT 328nm.



The decay for the solutions of different [PStLi]$_0$ can be considered in three distinct time intervals. Figure 3.3 shows the decay over the first 30 hours with the initial rate of decay (0-2 hours) appearing to be independent of [PStLi]$_0$ (slope = -0.5 h^{-1}). The period from 2-30 hours showed slower decay, at almost constant rate, which was dependent on [PStLi]$_0$, with the rate of decay for the most concentrated solution (slope A-B = -0.025 h^{-1}) greater than that of the more dilute solutions (slope C-D = -0.010 and E-F = -0.008 h^{-1}). After 30 hours the very slow decay was again independent of the PStLi concentration.

FIGURE 3.3 ABSORBANCE AT 328nm. (0-30 hours).

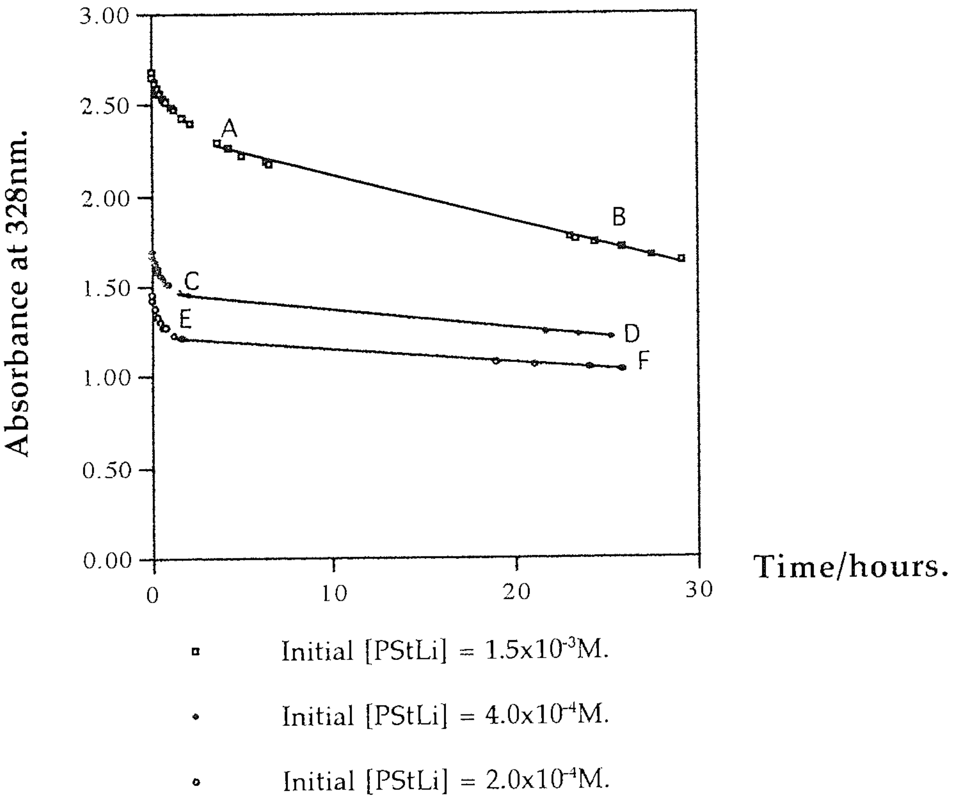


Figure 3.4 shows superimposed UV/visible spectra of the solution of PStLi in cyclohexane over the time of an experiment. The wavelength of λ_{max} for the solution of PStLi in cyclohexane at different reaction times are given in table 3.1 together with the absorbance at λ_{max}. The change in λ_{max} from the reported value of 328nm. for PStLi in cyclohexane to over 340nm. was observed in all the experiments and the data in table 3.1 quantifies the change.

FIGURE 3.4 SPECTRAL CHANGES OF SOLUTION OF 4 X 10^{-4} M POLYSTYRLLITHIUM IN CYCLOHEXANE WITH TIME.

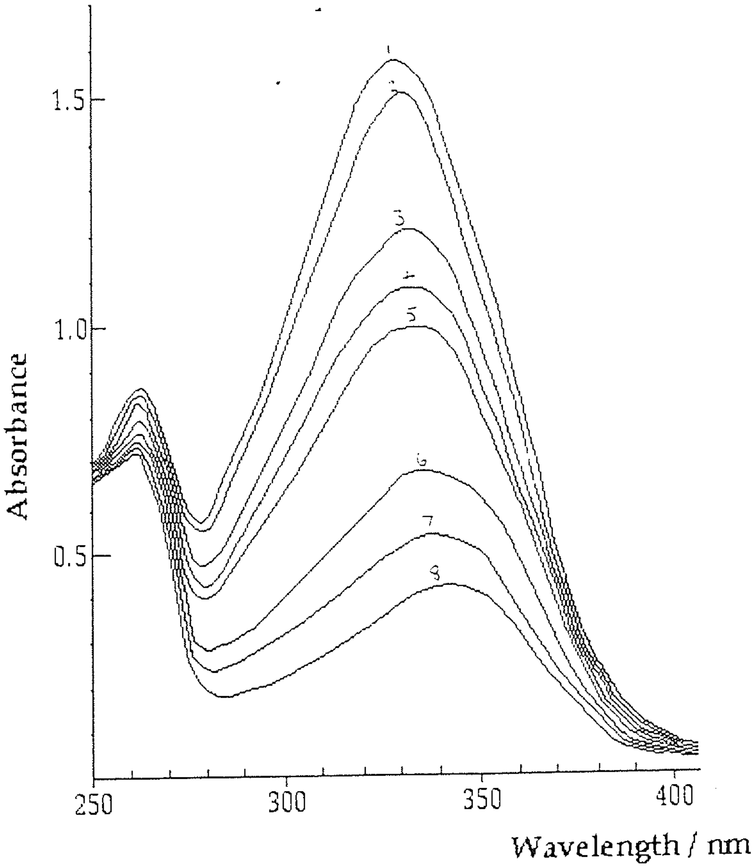


TABLE 3.1. SPECTRAL CHANGES FOR PStLi/CYCLOHEXANE.

Reference.	time/m.	$\lambda_{max.}$/nm.	Absorbance.
1	10	328	1.62
2	50	330	1.52
3	1300	331	1.25
4	2500	332	1.15
5	4000	333	1.03
6	8300	336	0.70
7	9800	339	0.57
8	12700	343	0.45

The broadening of the absorbance peak is noticeable but there is no increased absorbance in the region 400-500nm. which was scanned but not shown in figure 3.4. The peak at 260nm. is the λ_{max} of dead PSt and although this appears to decrease over the reaction decay period there is significant broadening of the peak.

The existence of decay of active centres in every system at the concentrations studied and the reproducibility of the decay seem to indicate that there is some spontaneous aging of the living PStLi in cyclohexane.

λ_{max} can be related to the structure of the PStLi species. In their extensive studies of these polymerizations Bywater et al.[187] reported that addition of THF to solutions of living polymers in non-polar solvents caused a change in the structure of the living species. Kinetic evidence and direct light scattering measurements on solutions of active and deactivated polymer had indicated that association occurred in solutions of PStNa in benzene and cyclohexane. The association disappeared on addition of small quantities of THF and this was attributed to the formation of solvated ion-pairs by complexation with the ether. The change was followed using the UV absorption of the solution which was reported to broaden but showed little change in the position of maximum absorption. They reported also that the UV absorption band observed for PStLi in cyclohexane has λ_{max} of 328nm. and in THF 338nm. In cyclohexane the absorption spectrum is related to the structure of the ion-pair dimers which are the dominant species, in equilibrium with the monomeric form. The following equilibrium therefore lies on the right hand-side.

$$2\mathrm{PStLi}_{(\mathrm{cyclohexane})} \rightleftharpoons (\mathrm{PStLi})_{2\cdot(\mathrm{cyclohexane})} \qquad 3.1.$$

The dimeric species have been found to be resistant to spontaneous decay, termination and transfer reactions and so the living character of the anionic species is maintained. However these present studies would suggest that spontaneous decay may well occur in cyclohexane when $[\mathrm{PStLi}]<2\times10^{-3}\mathrm{M}$

particularly when the solution is formed by rapid dilution of 0.02M solutions. It can be postulated that the initial dilution upsets the equilibrium and produces monomeric PStLi species which are more susceptible to decay than the dimers

3.2.2. THE EFFECT OF *s*-BuLi ON PStLi DECAY IN CYCLOHEXANE.

It has been reported that *sec*-butyllithium forms tetrameric aggregates in cyclohexane[193] and also that when homo-aggregates of different types are mixed hetereo-aggregates or mixed aggregates form as represented by equation **3.2.**[194]

$$(A)_n + (B)_m \rightleftharpoons (AB_x) + (A_2B_{x-1}) + \dots\dots + (A_{y-1}B_2) + (A_yB). \qquad 3.2.$$

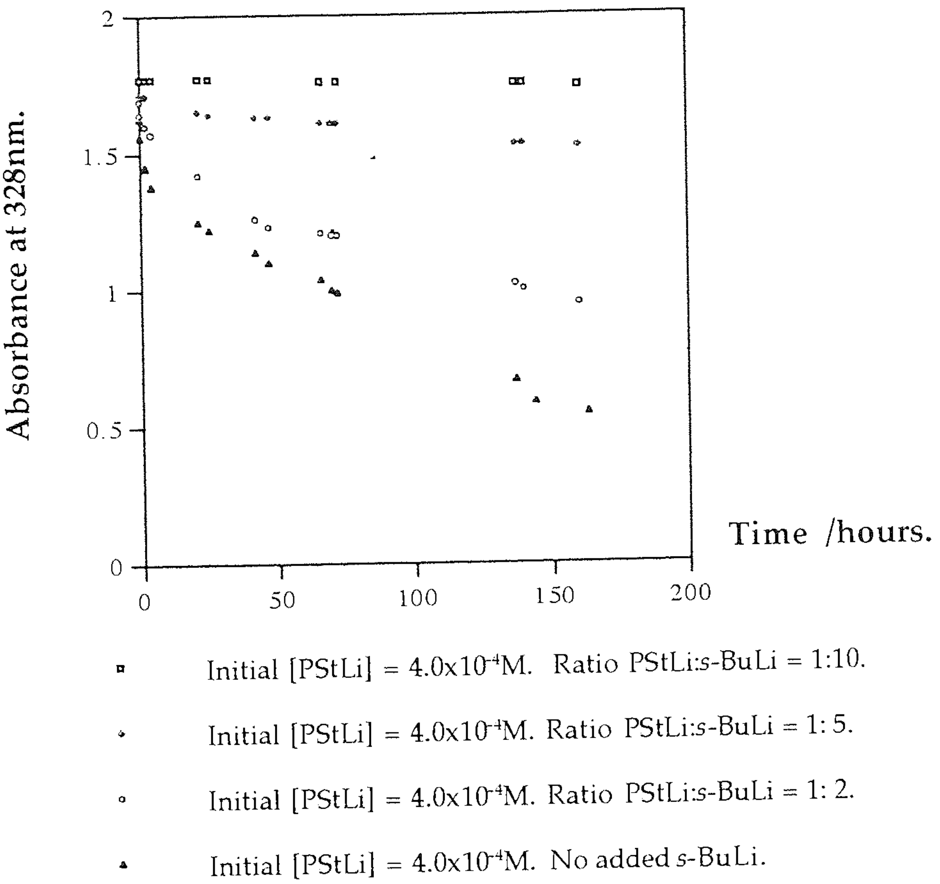
If the decay in the "living" polystyryllithium is related to the formation of monomeric propagating species then reduction of the decay might be achieved by causing such species to aggregate with *sec*-butyllithium.

The effect of *sec*-butyllithium solution on the stability of polystyryllithium in cyclohexane was investigated. **Procedure 3** from section 2.6.2.3.3 was followed. Small volumes of diluted initiator solution were injected into the undiluted polystyryllithium in the side vessel, A, after the polymerization at 60°C. A range of s-BuLi:PStLi ratios (10:1 to 1:1) was investigated. Dilution was then carried out as before and care was taken to use the same initial concentration of PStLi ($[PStLi]_o = 4x10^{-4}$ M) so a direct comparison could be made.

Figure 3.5, which also includes the plot of the decay of polystyryllithium of initial concentration 4×10^{-4} mol dm^{-3} when no s-BuLi initiator was present, shows the effect of added *s*-butyllithium on the rate of decay of polystyryllithium.

The results indicate that the injected initiator has retarded both the initial decay (0-2hours) and the rate of long term decay of the polystyryllithium. A similar trend in the change of λ_{max} with time was observed with the initial value at 328nm. changing to longer wavelengths as the reaction proceeded.

FIGURE 3.5 ABSORBANCE OF PStLi/*s*-BuLi MIXTURES AT 328nm.



3.2.3 Summary.

The changes in the electronic absorption spectra of 'living' species have been used to explain spontaneous decay reactions of PStLi in solvents other than cyclohexane. Two types of reaction have been postulated.

(1) Transformation processes, which involve replacement of the original spectral peak of the "living" polymer end, by another at longer wavelength. This was originally observed in solutions of polystyrylsodium in THF[189] and explained in terms of "isomerization" of the original anion to an allyl carbanion.[195]

(2) Aging by decay reactions, which was attributed initially to spontaneous termination between the living anion and the polar solvent, and again the earliest work showed that solutions of polystyrylsodium and THF decayed to "dead" polymer.[190]

Subsequently it was realised that both types of aging could occur simultaneously and many studies of spontaneous decay reactions have been carried out and several factors, other than solvent, have been identified as influencing the speed of the reaction e.g. photochemical effects, temperature and molecular weight of polymer. There has also been some evidence of decay reactions occurring between polystyryl anions in the presence of non polar aromatic solvents, and some mechanisms have been postulated for these terminations.[191,192]

There was no evidence of a transformation decay in these studies and no reaction between the living end of the polymer and cyclohexane seemed credible. Therefore the explanation of any spontaneous termination in this system seemed to centre on the dissociation of the dimer chain ends

Kinetics studies on the anionic polymerization of styrene by BuLi in cyclohexane show that the rates of initiation and propagation are relatively slow compared to their rates in THF. The kinetics of the reaction in cyclohexane are complex but the reaction is autocatalytic.[196] Most workers conclude that only monomeric ion-pairs in the system can undergo initiation and propagation and that aggregate species are dormant.

As has already been suggested, dilution of the living polystyryllithium may upset the equilibrium represented by equation **3.1** and rapidly increase the number of monomeric ion-pairs. The inabilitiy of cyclohexane to solvate these, may render them susceptible to spontaneous decay because there is no longer any monomer present for them to propagate. The introduction of *sec*-butyllithium into the solution will increase the overall [Li] so dilution would be expected to produce less rapid initial decay, however as figure 3.2 showed the initial rate of decay was found to be almost independent of the initial [PStLi]. Figure 3.5 showed that both the initial rate of decay and that observed between 50 and 150 hours has been reduced. The experiments with PStLi: *s*-BuLi 1:10 and 1:5 showed little loss of activity after 8 days and even accidental decay caused by impurities in the system or diffusion of air into the apparatus seems to have been reduced to a minimum.

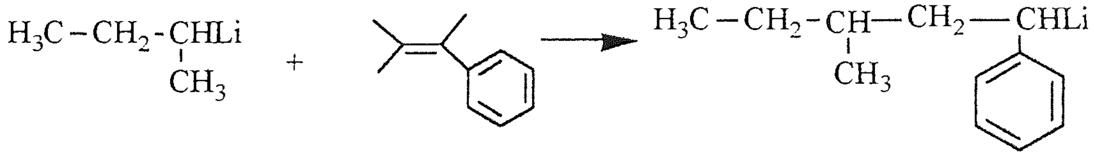
The UV/visible studies have indicated that changes, whatever they are, take place in these living polymer solutions. In order to establish the nature of these changes it was hoped that characterisation of the end-groups might be achieved by some NMR studies and any differences between systems killed immediately after preparation and those allowed to age might be discernible.

3.3. NMR STUDIES OF THE PRODUCTS OF PStLi DECAY.

3.3.1 END-CAPPING PStLi.

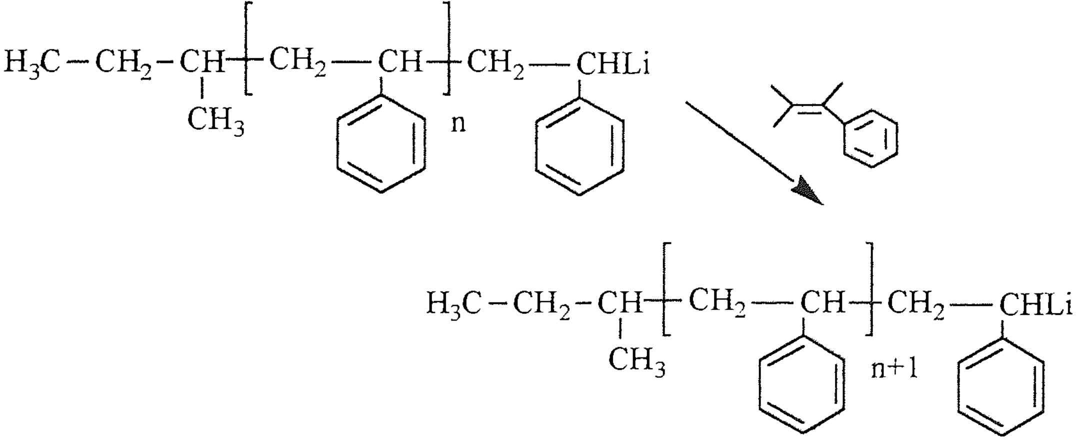
The structure of living polystyryllithium is shown by the equations of initiation (**3.3**)and propagation (**3.4**) of the living anionic polymer.

Initiation.



3.3

Propagation.

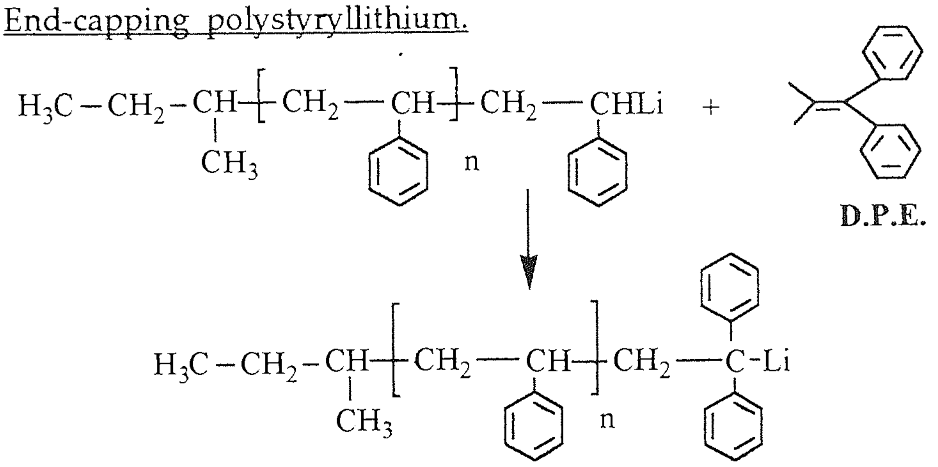


3.4

living polystyryllithium.

Diphenylethylene(DPE) can be used to end-cap PStLi because it will react with the living polymer in a 1:1 mole ratio, as shown in equation **3.5**, but the steric effects of the end group prevent further addition of DPE. Both PStLi and the end-capped product can be killed using degassed methanol as shown in equations 3.6 and 3.7.

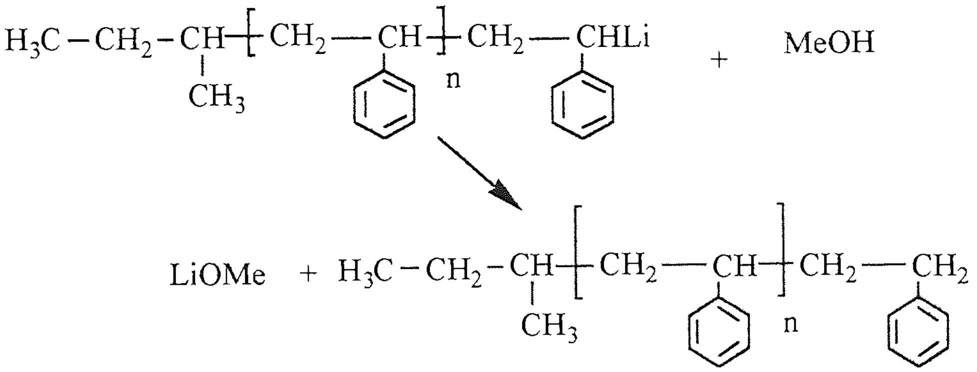
End-capping polystyryllithium.



3.5

end-capped polystyryllithium.

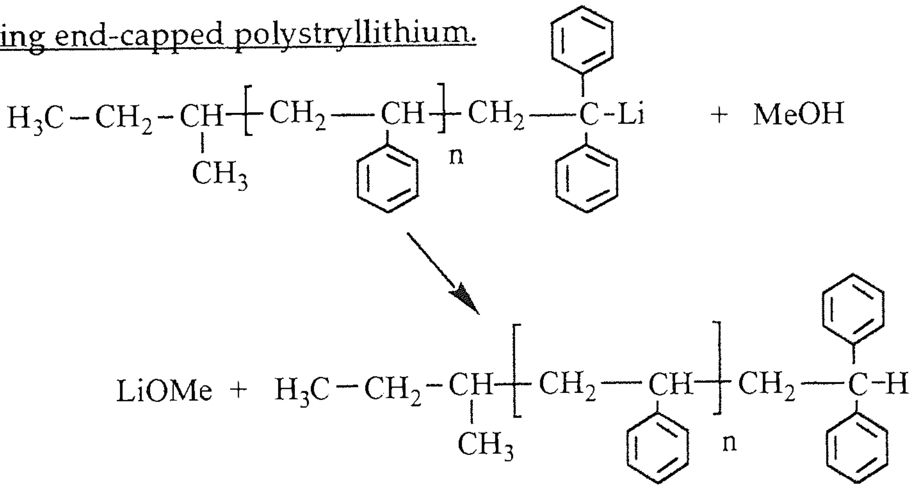
Killing polystyryllithium.



3.6

(47) killed PSt.

Killing end-capped polystryllithium.



3.7

(48) killed end-capped PSt.

The products can be precipitated, purified and dried as before and then analysed by NMR spectroscopy to show that differences in the structure of killed PSt (**47**) and killed end-capped PSt (**48**) are discernable. The ^1H and ^{13}C spectra of **47** and **48** are given in figures 3.6, 3.7, 3.8 and 3.9. and the NMR data are given in tables 3.2, 3.3, 3.4 and 3.5 respectively.

Comparison of the ^1H spectra for **47**and **48** (figures 3.6 and 3.8) showed the following.

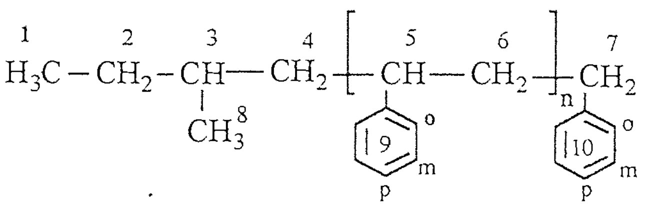
1. The relative low DP_n (6) for **48** increased the area contribution of the end groups and, although the methylene (δ =1.25-2.35ppm) and methine (δ =2.35-3.17ppm) peaks were still difficult to deconvolute the methyl peak area (9.8%) at δ =0.86-1.25ppm could be determined quite accurately. This shows good agreement with the relative number of methyl protons in compound (**48**) (6/62 = 9.7%).
2. The end-capped diphenyl groups in **48** produced an overlap of the aryl methine peaks (δ =6.37-8.04ppm) so the contribution from the terminal phenyl protons could not be calculated independently.
3. The methine proton (7) on the end-capped carbon of **48** could be identified at δ =3.75-4.33 and with peak area 1.1%. The theoretical shift (4.1ppm) and peak area (1.6) for this proton show good agreement. This peak was not present in the proton spectrum of **47**.

The ^{13}C NMR spectra of both **47** and **48** provided little additional information.

3.3.2 THE DECAY OF PStLi DETECTED USING END-CAPPING.

The investigation of the stability of PStLi solutions using UV/visible spectrophotometry limits the concentration range that can be studied. A series of experiments were devised to study the stability of $1x10^{-2}M \geq [PStLi]_{init} \geq 1x10^{-3}M$ using ^1H and ^{13}C NMR spectroscopy.

TABLE 3.2. ^{1}H NMR RESULTS FOR KILLED PST (47).



DP$_n$ = 25. Molecular formula = $C_4H_9(C_8H_8)_{24}C_8H_9$.
= $C_{204}H_{210}$.

Chemical group.	Chemical shift/ppm.	% Area theoretical		% Area from ^{1}H NMR	
methyl ^{1}H (1 and 8)	0.745-0.755	2.9		2.6	
methylene ^{1}H (2)	0.95	1.0		≈0.8	
methylene ^{1}H (4 and 7)	1.02-1.24	1.9	=25.7	≈1.5	=25.7
methylene ^{1}H (6)	1.24-1.83	22.8		≈23.4	
methine ^{1}H(3 and 5)	1.83-2.82	11.9		13.3	
aryl methine ^{1}H(**m** 9 and 10)	6.35-6.98	23.9		23.1	
aryl methine ^{1}H(**o/p** 9 and 10)	6.98-7.65	35.7		35.3	

FIGURE 3.6 ^{1}H NMR FOR KILLED PSt (DP$_n$ =25.)

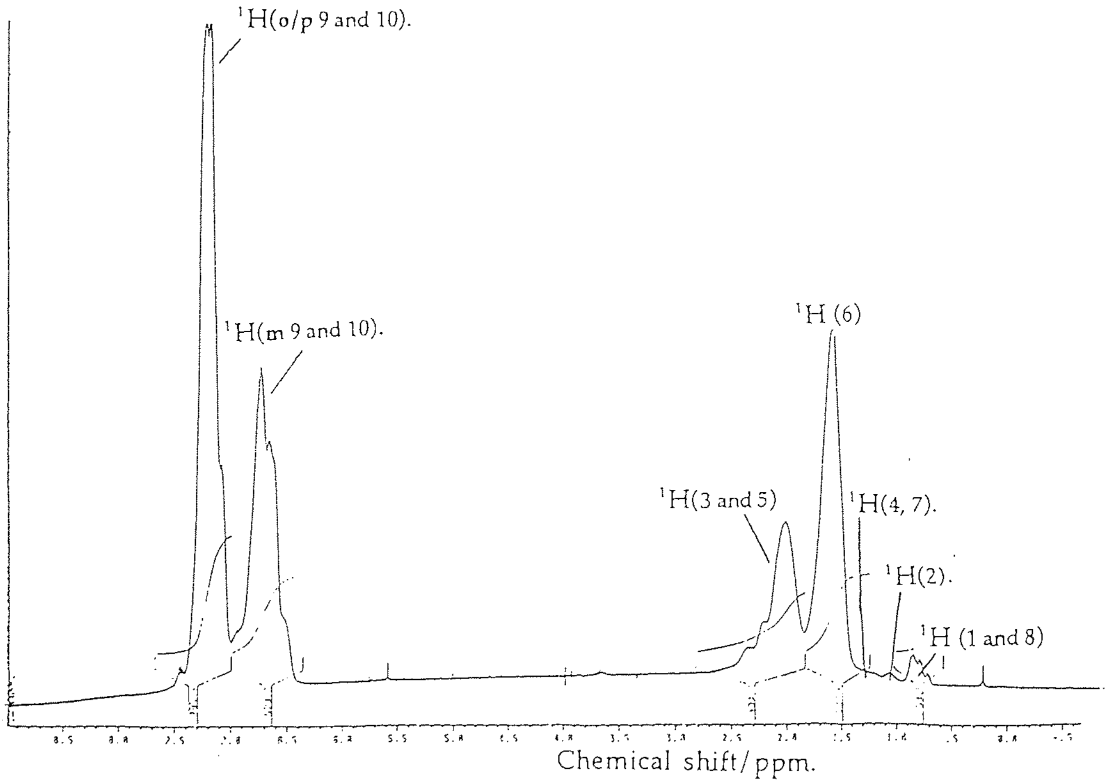
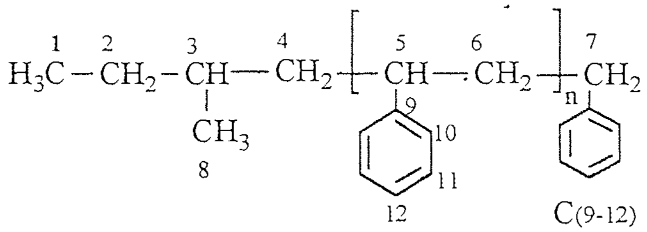


TABLE 3.3. ^{13}C NMR RESULTS FOR KILLED PSt (47).



Molecular formula = $C_{204}H_{210}$.

Chemical group. / + CH_3 or CH and - CH_2 or C.	Chemical shift δ/ ppm.	δ_{theo} for ^{13}C NMR / ppm
Quaternary C peak (C9)	145.05-146.00	148.6
Tertiary CH peak (C11)	127.40-127.92	128.5
Tertiary CH peak (C10 and 12)	125.47-125.62	126.0 and 126.5
Secondary CH_2 peak (C4, and 6)	41.67-46.37	39.1- 47.0
Tertiary CH peak (C5)	40.3	43.5

FIGURE 3.7 ^{13}C NMR FOR KILLED PSt (DP_n =25.)

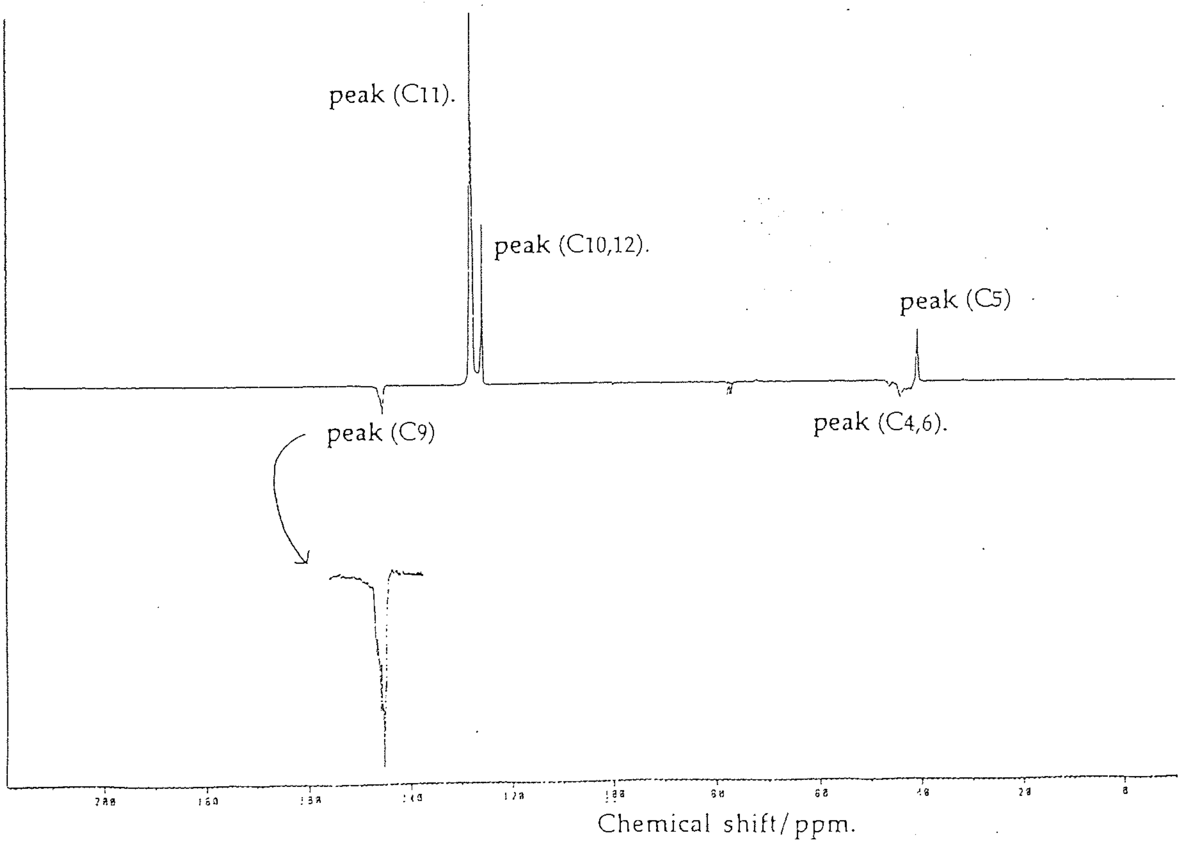
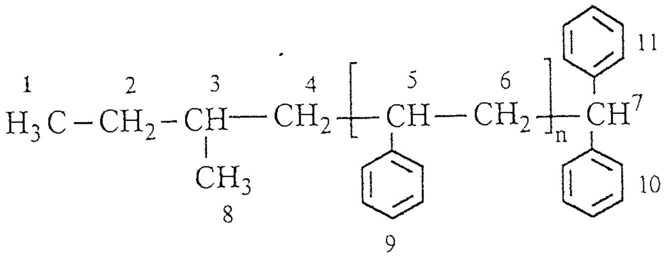


TABLE 3.4. ^{1}H NMR RESULTS FOR KILLED END-CAPPED PSt (48).



DP_n = 6. Molecular formula = $C_4H_9(C_8H_8)_5C_{14}H_{13}$.
= $C_{58}H_{62}$.

Chemical group.	Chemical shift/ppm.	% Area theoretical		% Area from ^{1}H NMR	
methyl ^{1}H (1 and 8)	0.86-1.25	9.7		9.8	
methylene ^{1}H (2)	1.25-1.44	3.2	19.3	≈2.5	21,4
methylene ^{1}H (4)	1.44-1.76	3.2		≈5.0	
methylene ^{1}H (6)	1.89-2.35	12.9		≈13.9	
methine ^{1}H (3 and 5)	2.35-3.17	9.7		11.8	
methine ^{1}H (7)	3.75-4.33	1.6		1.1	
aryl methine ^{1}H (9, 10 and 11)	6.37-8.04	56.0		56.0	

FIGURE 3.8 ^{1}H NMR FOR KILLED END-CAPPED PSt (DP_n = 6.)

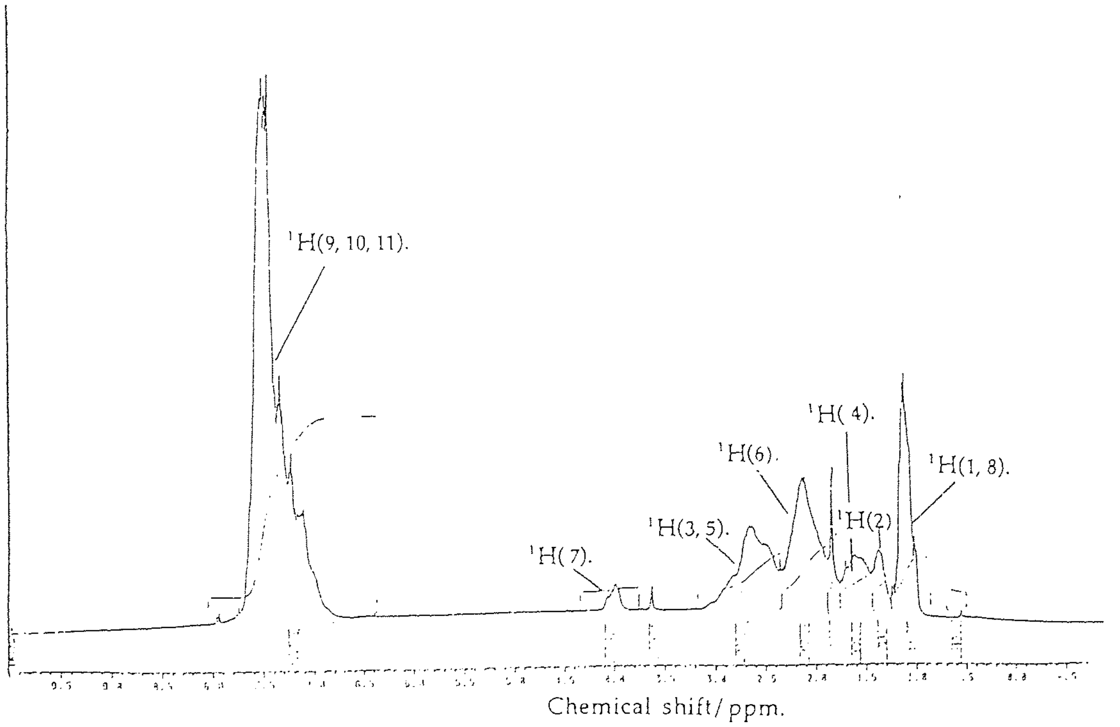
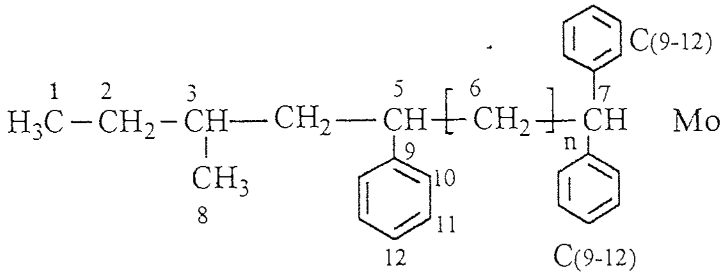


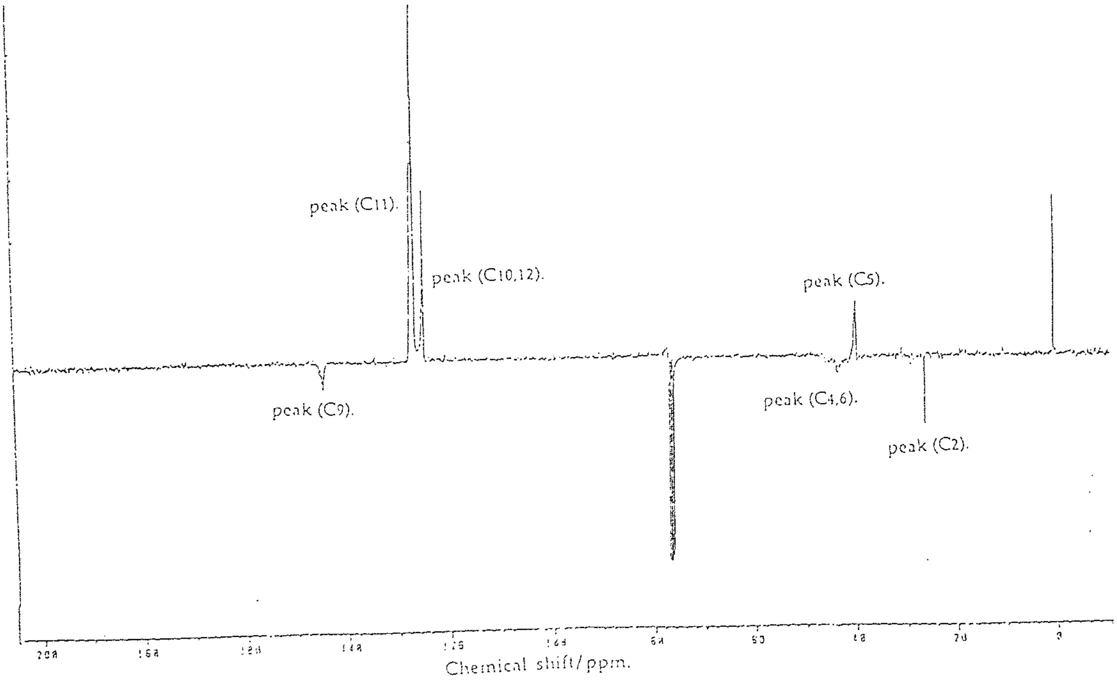
TABLE 3.5. ^{13}C NMR RESULTS FOR KILLED END CAPPED PSt (48).



Molecular formula = $C_{58}H_{62}$.

Chemical group. / + CH_3 or CH and - CH_2 or C.	Chemical shift/ ppm.	δ_{theo} for ^{13}C NMR / ppm
Quaternary C peak (C9)	145.0-145.3	148.6
Tertiary CH peak (C11)	127.3-127.7	128.5
Tertiary CH peak (C10 and 12)	120.8-125.3	126.5-126.0
Tertiary CH peak (C7)	48.8	-
Secondary CH_2 peak (C 4 and 6)	43.4-45.2	46.2-47
Tertiary CH peak (C5)	40.0	43.5
Tertiary CH peak (C3)	31.1	35.3
Secondary CH_2 peak (C2)	26.5	30.3
Primary CH_3 peaks (C8 and C1)	19.5 and 10.7	(20.1 and 11.5)

FIGURE 3.9 ^{13} C NMR FOR KILLED END-CAPPED PSt ($DP_n = 6$).

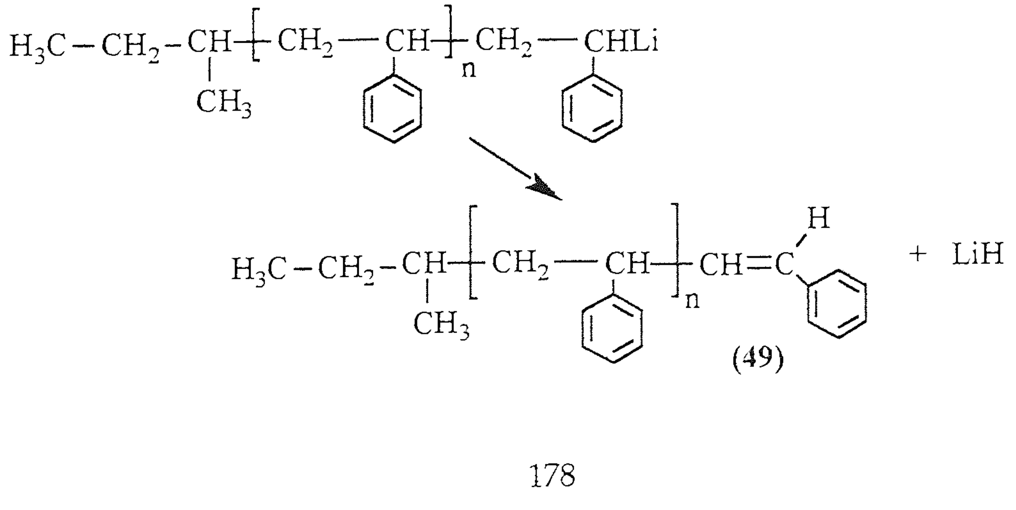


Four solutions of PStLi, within the required concentration range, were prepared using small reaction flasks of the type shown in figure 2.2. 0.1M styrene solutions and freshly diluted solutions of 0.1M *s*-BuLi initiator were injected over argon and kept at 60°C for 3-6 hours. The degree of polymerization was kept low and a value of less than 20 was achieved with all samples. The solutions were kept in a water bath at 30°C for 30 days before excess dry diphenyethylene was injected under argon into each flask. The mixture was then killed by injecting degassed methanol over argon, precipitated, purified and dried in the usual way. The product was analysed by SEC and NMR spectroscopy.

There was little visual evidence that the orange yellow solutions had undergone any decay after 30 days. All four solutions went the characteristic red colour of the diphenyl-end-capped polystyryllithium, shown in equation 3.5 when DPE was added over argon. The addition of excess degassed methanol killed and precipitated the product. Unfortunately only the most concentrated solution ([PStLi] $=1.0\times10^{-2}$M. $DP_n=16$) produced enough solid for it to be reprecipitated twice, using acetone and then methanol, so that, after thorough drying, both SEC and NMR analysis could be carried out.

The aim of this experiment was to investigate the formation of different types of chain end to the polymer. If spontaneous decay of the PStLi occurred, the simplest possible decay reaction would involve the monomeric propagating species:

Spontaneous termination of polystyryllithium.



(49)

3.8

The theoretical ^1H chemical shift for the vinylic methine protons in this product (**49**) is 5.6≤δ≤6.4ppm. Reference to the proton spectra in figures 3.6 and 3.8, shows that both the products **47** and **48** have no ^1H with this chemical shift.

Addition of DPE to the residual PStLi, after 30 days, was to end-cap the polymer (equation **3.5**), which was then killed using methanol (equation **3.7**). The peak at 3.7≤δ≤4.3ppm can be assigned to the terminal methine proton of the killed, end-capped product (see section 3.3.1) so the area of this peak should provide an indication of the relative amount of end-capped product.

Figure 3.10 provides the ^1H spectrum for the product from the decay of [PStLi] $=1.0 \times 10^{-2}$M. (DP_n=16) over 30 days, which was then end-capped with DPE and quenched in methanol. The absence of any protons with chemical shift at 5.6≤δ≤6.4ppm indicated that spontaneous termination by equation **3.6** did not occur and the similarity of figure 3.10 with that of 3.8 is evident so table 3.6 summarises the theoretical and observed NMR data.

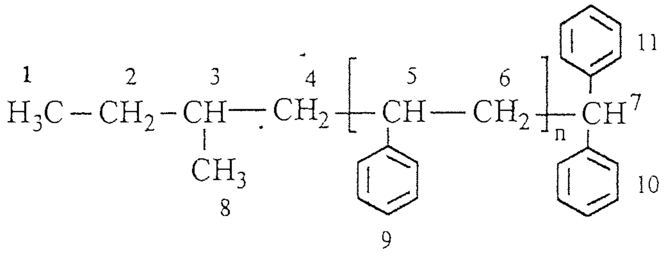
The methine proton (7) of the end capped product at 3.8≤δ≤4.0ppm has a peak area larger than the theoretical value although an impurity peak at δ=3.87 may be responsible. However there is no evidence of a decay product or the decay product may also be capable of adding DPE. This might give rise to a change of shape of the resonance.

3.4 CONCLUSIONS.

This study has highlighted two features of the decay of polystyryllithium in cyclohexane.

1. Rapid decay occurs when 0.01M polystyryllithium in cyclohexane is diluted by a factor of ≥5 and approximately 7% activity is lost after 2 hours.
2. Slow but observable decay of these solutions ($[PStLi]_o < 2 \times 10^{-3}$M) occurs reducing their effective concentration by up to 70% in 7 days.

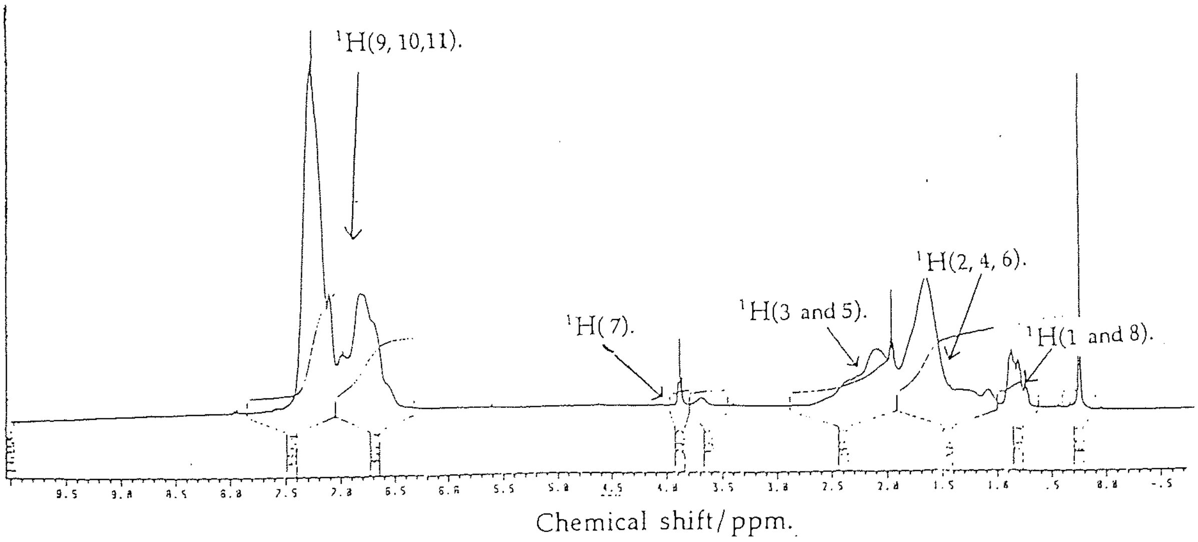
TABLE 3.6. ^1H NMR RESULTS FOR DECAYED, KILLED AND END-CAPPED PSt. (DP_n=16). {assume no decay}.



DP_n = 16. Molecular formula = $C_4H_9(C_8H_8)_{15}C_{14}H_{13}$.
= $C_{138}H_{142}$.

Chemical group.	Chemical shift/ppm.	% Area theoretical	% Area from ^1H NMR
methyl ^1H (1 and 8)	0.60-1.00	4.2	4.2
methylene ^1H (2,4,6)	1.00-1.90	23.9	22.9
methine ^1H (3 and 5)	1.90-2.86	11.2	13.6
methine ^1H (7)	3.77-3.95	0.7	1.1
aryl methine ^1H (9, 10 and 11)	6.30-7.8	56.3	57.0

FIGURE 3.10 ^1H NMR FOR DECAYED, END-CAPPED, KILLED PSt (DP_n=16.).



The implications of these observations for the rest of this study are apparent. The reaction rate for the ROMP involving the catalyst system WCl_6/PStLi should be dependent on the W:Li ratio so precautions must be taken when diluting solutions of PStLi before using them as a co-catalyst. Solutions of [PStLi]$\geq$0.01M were often prepared some days before their use for the metathesis reactions but were diluted immediately prior to use. The rate of reaction for the ring-opening polymerization of cyclopentene, using WCl_6/BuLi as the catalyst system, is known to be affected by the catalyst ratio. Therefore it is essential that the concentration of the co-catalyst is known accurately. The similar potential for spontaneous decay of both BuLi and *s*-BuLi solutions when stock solutions are diluted, makes it essential to prepare these carefully and immediately before to their use as co-catalysts.

CHAPTER 4.

RING-OPENING METATHESIS POLYMERIZATION OF CYCLOPENTENE

PART 1 .

4.1. SERIES A. THE SEQUENTIAL ADDITION OF THE CATALYST AND THE CO-CATALYST.

These experiments were designed to determine the experimental procedures for the ring-opening metathesis polymerization of cyclopentene using mainly tungsten(VI) chloride as the catalyst and a range of co-catalysts. The aim was to find the optimum reaction conditions.

The method outlined in 2.5.1.1 was modified from that used by Gregory,[184] who initially used dilatometric techniques to investigate this system. The use of precipitation techniques and SEC analysis of the product required larger quantities of reactants. It was decided to maintain a cyclopentene to WCl_6 ratio of 500:1 to reduce the need to dilute stock solutions of co-catalyst. Different factors were varied to compare their effect on the rate of polymerization of the cyclopentene and on the yield and structure of the product.

4.1.1. THE EFFECT OF AGING TIME.

The work of Tuck,[186] on the ring-opening polymerization of cyclopentene catalysed by the $WCl_6/Al(iBu)_3$, indicated that, using dilatometry to measure the rate of polymerization, the initial rate of polymerization was affected by aging time. This was defined as the time delay between the addition of the WCl_6 and the $Al(i\text{-}Bu)_3$ to the monomer solution. The aging time varied with the concentration of the cyclopentene and an optimum aging time of two minutes was found for 2.5M cyclopentene solutions.

In a typical experiment 5.5g (0.081moles) of cyclopentene and 15.3cm^3 of toluene were distilled sequentially under vacuum into an evacuated reaction flask (see figure 2.2). 3.2cm^3 0.05M WCl_6 catalyst solution were injected into the monomer solution over argon. After an aging time of 2 minutes, 0.2cm^3 1.6M BuLi was injected over argon. The aging time between the addition of the catalyst solution and the injection of the butyllithium solution was varied from 1 to 10 minutes. The ratio of cyclopentene:WCl_6:BuLi was kept at 500:1:2

and the overall concentration of the monomer solution was between 2.5 and 3.5M.

In all the experiments the dark blue tungsten hexachloride/toluene solution went red/brown when added to the monomer solution and this colour was maintained when the butyllithium solution was injected. All the solutions became more viscous within minutes of adding the butyllithium and after ten minutes reaction time, the mixture was poured into methanol. The supernatent blue solution was decanted off and the elastomer obtained was dissolved in hexane, reprecipitated in fresh methanol, dried and weighed. A 0.5% (wv) solution in THF was prepared and analysed by SEC.

The yield and SEC data obtained for the products are shown in table 4.1.1. and the SEC trace for one of the samples (aging time 2 minutes) for both RI and UV/VIS detectors is shown in figure 4.1.1.

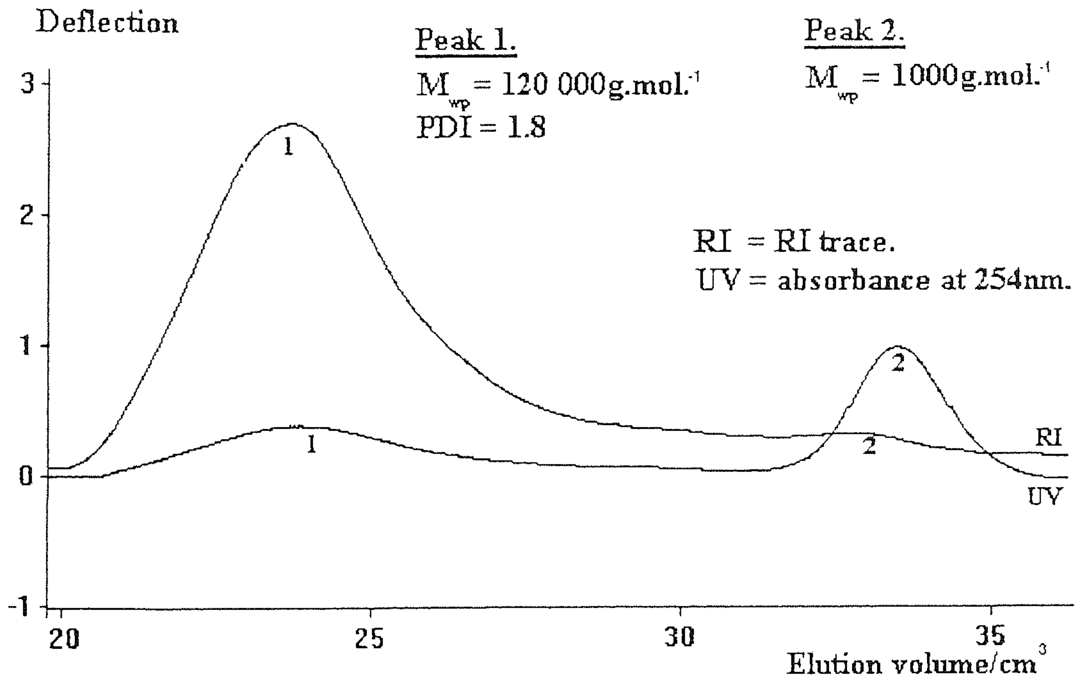
TABLE 4.1.1. SERIES A ROMP OF CYCLOPENTENE WITH DIFFERENT AGING TIMES.

Aging time/mins.	% yield.	(M_{wp})/g.mol.$^{-1}$	PDI.
1	41	130 000	1.7
2	35	120 000	1.8
3	38	160 000	1.8
5	18	130 000	1.9
10	23	140 000	1.8

Concentration of cyclopentene = [Cp] = 3.0M. Cp:WCl_6:BuLi = 500:1:2. Temperature = 25°C.

The yield of reaction is a much less sensitive measurement of the rate of reaction than dilatometry but table 4.1.1. indicates that the amount of polypentenylene formed after 10 minutes is very similar for aging times between 1 and 3 minutes but that delay in co-catalyst addition of 5 minutes or longer reduces the yield considerably. A 2 minute aging time in subsequent experiments, was routinely used between the addition of catalyst and co-catalyst to the monomer.

FIGURE 4.1.1. THE SEC TRACE FOR RI AND UV/VISIBLE DETECTORS FOR PRODUCT WITH AGING TIME OF 2 MINUTES.



The SEC data in table 4.1.1. shows that, within the limits of accuracy of the technique, the molecular weight of the polymeric material is independent of the aging time. An SEC for both detectors is shown in figure 4.1.1. and the RI trace clearly shows the high molecular weight product (peak 1) but the amount of low molecular weight oligomeric material (peak 2) is surprisingly small. However there was a slight but definite absorbance at 254nm. recorded by the UV/VIS detector which warranted further investigation.

4.1.1.1. SEC Analysis of Products from ROMP of Cyclopentene.

The SEC analysis of the products from the ring-opening metathesis of cyclopentene caused problems throughout this part of the project. Other workers report using 1 or 2%(wv) solutions of polypentenylene in THF for this technique but attempts to dissolve the elastomer in THF at these concentrations proved impossible and even some 0.5%(wv) solutions were found to form gels within one week.

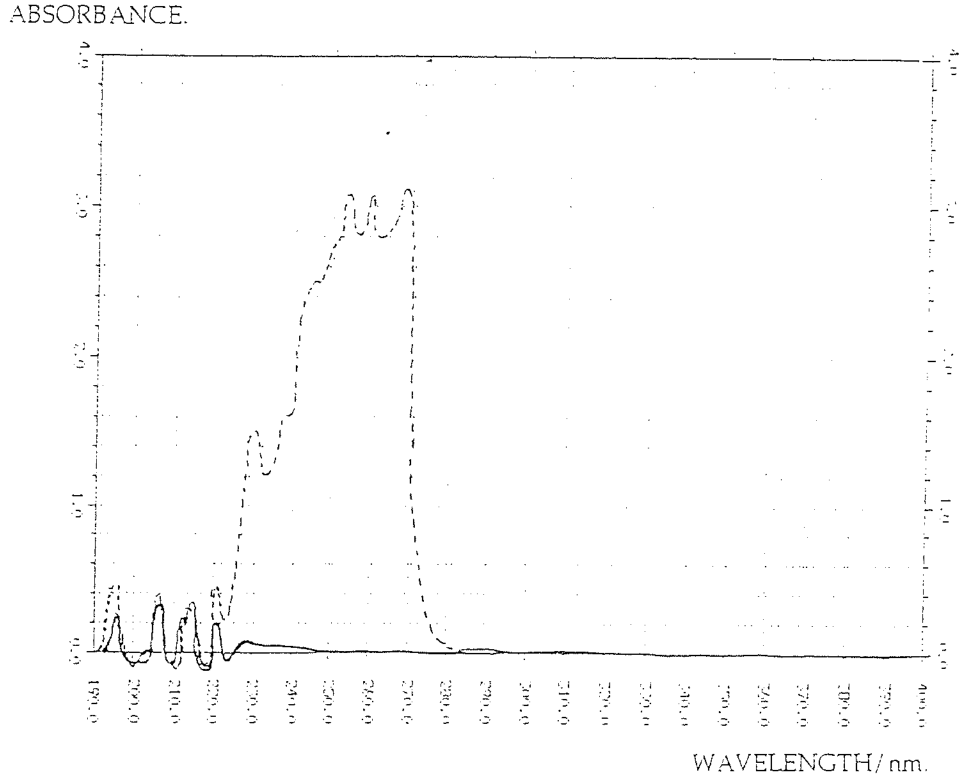
The UV/VIS detector showed negligible absorbance at 254nm when a chart recorder was used to detect absorbance at different elution volumes for samples of polypentenylene. However the subsequent use of automatic data analysis and interpretation has shown, as in figure 4.1.1., that samples have some absorbance at this wavelength, particularly the low molecular weight product. The U V to RI peak area ratio for the high molecular weight polymer was found to vary between 0.01 and 0.5 and this ratio for the low molecular weight material was between 0.5 and 4.0. Attempts to reanalyse some samples were hampered by gel formation.

The UV/VIS absorbance spectra of 0.5 and 2.0%(wv) polypentenylene in THF was recorded from 190-400nm. and compared with that of 0.5%(wv) polystyrene in THF, as shown in figure 4.1.2. This confirmed the high absorbance of polystyrene at 254nm and indicated that the corresponding absorbance of 0.5%(wv) polypentenylene in THF was low. However the 2% solution has a small but significant absorbance at 254nm.

It was concluded that there was some absorbance at 254nm associated with the polypentenylene samples but two additional factors may have increased this. The reprecipitation technique, used to purify the elastomer, was not removing all the transition metal species and this caused absorbance, particularly by complexing with the low molecular weight product, but this absorbance would not be expected to change with time. An alternative explanation could be associated with the gel formation of the solutions which was probably caused

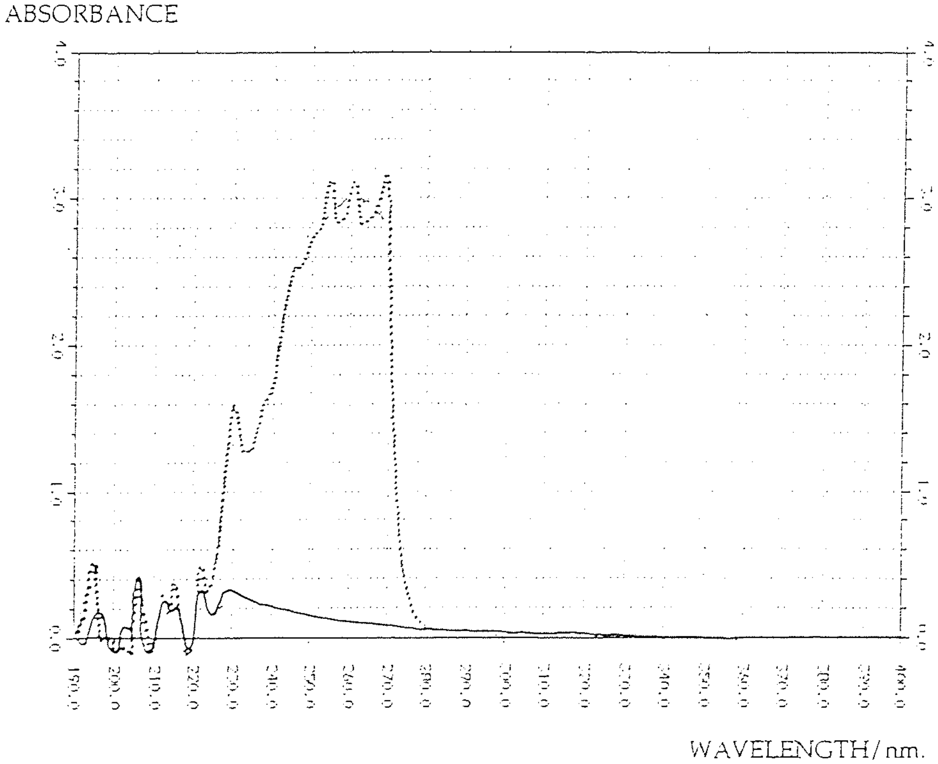
FIGURE 4.1.2. THE UV/VISIBLE ABSORPTION SPECTRA OF POLYSTYRENE SOLUTION AND POLYPENTENYLENE SOLUTION IN THF FROM 190-400nm

(1)



--------	absorbance of 0.5%(wv) polystyrene in THF.
———	absorbance of 0.5%(wv) polypentenylene in THF.

(2).



....	absorbance of 0.5%(wv) polystyrene in THF.
———	absorbance of 2.0%(wv) polypentenylene in THF.

by oxidative crosslinking of the product. SEC analysis of aged samples showed increased absorbance at 254nm. commensurate with extension of the conjugation of double bonds during cross-linking. These results indicated that purification and immediate analysis of polypentenylene was critical.

The purification of the elastomer was subsequently modified. A variety of solvents, besides hexane, were used to redissolve the product (e.g. trichloromethane and toluene). It was found that all had some drawbacks but that hexane was overall the most efficient, the blue colour of the transition metal species was removed after 2 or 3 purification cycles and the dissolution of the elastomer was most effective. The reprecipitation process was extended so that the product was purified three times, although when only small amounts of the elastomer were produced, the procedure had to be modified. Figure 4.1.3. (in section 4.1.2.1.1) is a SEC trace of polypentenylene, precipitated in methanol three times from solutions in hexane and analysed immediately. It shows a reduced, but still significant, absorbance at 254nm.

4.1.2 THE EFFECT OF WCl_6: CO-CATALYST RATIO.

The work of Wang and Menapace[112] on the metathesis of 2-pentene using the WCl_6:BuLi catalyst system shows that the maximum rate of metathesis for a high alkene to tungsten ratio (e.g. 50:1) occurs when the W:Li mole ratio is 1:2. Amass et al have shown that the initial rate of ring-opening polymerization of cyclopentene is dependent on the catalyst:co-catalyst mole ratio for unmixed catalyst systems of $WCl_6/Al(i\text{-}Bu)_3$[186] and WCl_6/BuLi.[184]

4.1.2.1. THE EFFECT OF BUTYLLITHIUM CO-CATALYST RATIOS.

The effect of catalyst to co-catalyst ratio on the ROMP of cyclopentene was studied using the method outlined in 2.5.1.1 for the WCl_6/BuLi system. Care was taken to maintain the effective concentration of the co-catalyst solutions in these experiments. Both butyllithium and *sec*-butyllithium co-catalyst systems were used and the full range is shown in table 4.1.2.

TABLE 4.1.2. THE RANGE OF WCl_6:BUTYLLITHIUM CATALYST SYSTEMS USED FOR THE **SERIES A** ROMP OF CYCLOPENTENE.

Ref.	Co-catalyst system used	Range of WCl_6: Co-catalyst ratios tested
4.1.2.1.1.	BuLi	1: 0.1, 0.2, 0.5, 1.0, 1.5, 2.0, 3.0, 4.0.
4.1.2.1.2.	*sec*-BuLi	1: 0.1, 0.2, 0.5, 1.0, 2.0, 3.0, 4.0.

4.1.2.1.1. The Effect of WCl_6:BuLi ratio on the ROMP of Cyclopentene.

The known instability of the dilute BuLi solutions, was considered to be a factor which might produce inaccuracies in estimating the effective [Li] used in these ring-opening polymerizations. The importance of the W:Li molar ratio in such reactions and the effects on the reproducibility of the polymerization were assessed. In most experiments stock solutions of butyllithium in hexanes, stored as described in section 2.3.5, were used but for some experiments, when W:Li was 1:<1, it was necessary to dilute the stock solutions by the technique outlined in section 2.4.2. The dilute solutions were always prepared and used immediately.

In one experiment 5.6g (0.082moles) of cyclopentene and 14.6cm^3 of toluene were vacuum distilled into an evacuated reaction flask and 4.1cm^3 0.04M WCl_6 catalyst solution were injected over argon. After 2 minutes aging time 0.2cm^3 1.65M butyllithium co-catalyst solution were also injected and the tap was replaced and firmly closed. The cyclopentene:WCl_6:BuLi ratio was therefore 500:1:2 and the overall concentration of the monomer solution was 3.1M.

The dark blue WCl_6/toluene solution went brown on addition to the cyclopentene solution but the colour change on injecting the butyllithium varied. The reaction mixtures which had a WCl_6:BuLi ratio of 1:<1 went red and only showed signs of increased viscosity after several hours. The mixtures with W:Li ratio 1:1 to 1:2 stayed brown when the co-catalyst was added and became viscous within 1 hour. The W:Li ratio of 1:3 produced a red solution which took several hours to become viscous and W:Li ratio 1:4 was also red but showed no increased viscosity after 24 hours and produced no elastomer when poured into degassed methanol.

The yield of the purified dried products was found and 0.5%(wv) solutions in THF were analysed using SEC. Table 4.1.3. shows the data obtained for the high molecular weight product (HMWP) and for the oligomeric material (LMWP) in each experiment.

TABLE 4.1.3. **SERIES A** ROMP OF CYCLOPENTENE USING BUTYLLITHIUM AS THE CO-CATALYST.

W: Li ratio	% yield	Time / h.	M_{wp} for HMWP / g.mol.$^{-1}$	PDI for HMWP.	UV:RI area for HMWP.	M_{wp} for LMWP / g.mol.$^{-1}$
1: **0.1**	2	24	320 000	-	-	1000
1: **0.2**	5	24	200 000	-	-	1500
1: **0.5**	41	24	140 000	1.8	0.3*	2000
1: **1.0**	18	1	150 000	1.6	0.2*	2000
1: **1.5**	30	1	170 000	1.8	0.2*	-
1: **2.0**	66	1	120 000	1.8	0.2*	1000
1: **3.0**	18	24	200 000	2.0	0.2*	-
1: **4.0**	none	24	-	-	-	-

Concentration of cyclopentene = [Cp] = 3.0M. Cp:WCl_6 = 500:1. Temperature = 25°C.
* Values obtained from SEC analysis of aged samples.

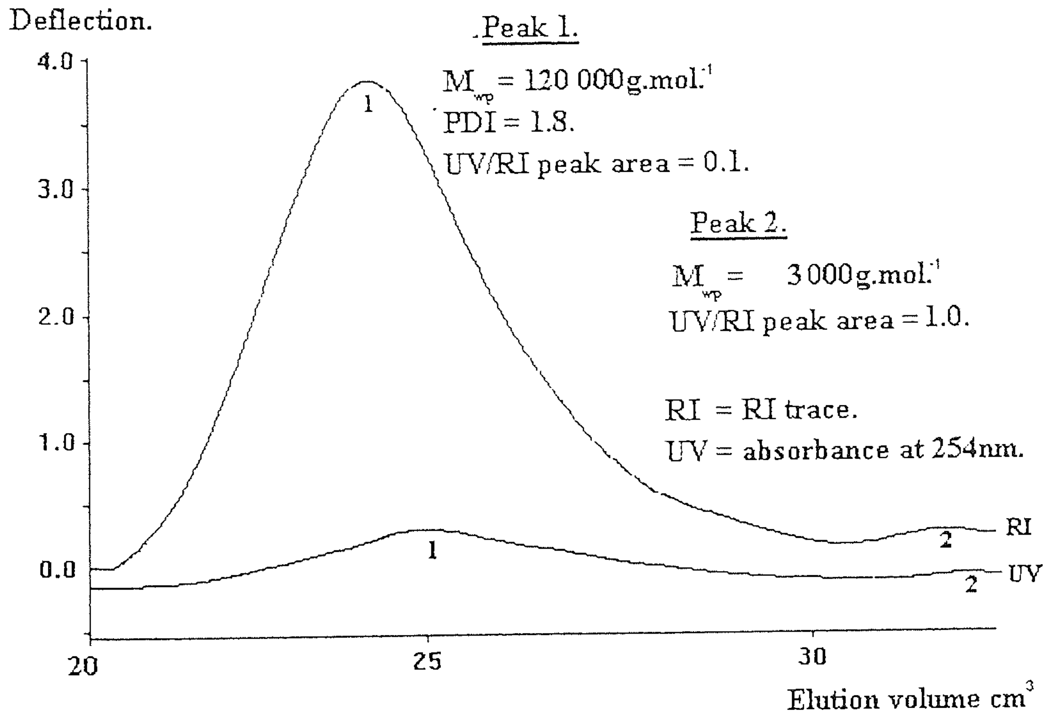
The results showed that the optimum reaction was obtained with a WCl_6: BuLi ratio of 1:2, confirming the results of Tuck[186] and Gregory.[184] When Li:Bu ratios were less than 0.5:1 very low yields were obtained of polymer with very high molecular weight. This would indicate that there were very few active catalytic centres in such systems. High molar concentrations of BuLi (Li:W=>2:1) produced low yields and increased molecular weight of the product compared to the Li:W=2:1 system. Over-reduction of the WCl_6 catalyst may well have caused this effect.

Alkyl metal compounds are known to cause the reduction of transition metal compounds so it is likely that the presence of high concentrations of BuLi reduced the oxidation state of the W to below its most active form and left the effective concentration of metathetically active tungsten species very low.

The original SEC data for both the M_{wp} and PDI of the HMWP and the M_{wp} of the LMWP were obtained from calculations using traces from a chart recorder and showed negligible absorbance at 254nm. Attempts were made to reanalyse these solutions by SEC using computerised data collection but gel formation in the 0.5%(wv) THF solutions hampered this process. When these gels were extracted with fresh THF, very dilute soluble samples were obtained and fresh SEC data were generated. This analysis showed that, for all samples, the M_{wp} of the high molecular weight fraction (HWMP) had increased, the PDI was much broader than in the original samples and absorbance at 254nm was observed (UV:RI area * in table 4.1.3).

Ideally all the polymerizations above should have been repeated but since most interest was concentrated on the most active system, only the reaction conditions for W:Li = 1:2 were repeated. Figure 4.1.3. shows the SEC trace for a freshly prepared 0.5%(wv) THF solution of the purified product using both RI and UV/VIS detectors. The HMWP (peak 1) has M_{wp} and PDI close to the data recorded in table 4.3., and the LMWP (peak 2) has a M_{wp} of 3000g.mol.$^{-1}$. The ratio of UV:RI peak area is significant but still lower than the ratios recorded on reanalysis of solutions.

FIGURE 4.1.3 THE SEC TRACE FOR BOTH DETECTORS FOR PRODUCT USING WCl_6/BuLi (1:2). CATALYST SYSTEM.



The ^1H and ^{13}C NMR data and spectra of the polypentenylene, obtained from this last polymerization, are shown and discussed in section 4.4 (see tables 4.4.1 and 4.4.2 and figures 4.4.1 and 4.4.2).

4.1.2.1.2.The Effect of WCl_6:*s*-BuLi ratio on the ROMP of Cyclopentene.

Polymerizations were carried out using *sec* -butyllithium as the co-catalyst for the range of WCl_6/*s*-BuLi mole ratios shown in table 4.1.2. Exactly the same procedure was employed as for the BuLi co-catalysed polymerizations except that stock 1.47M *s*-BuLi/cyclohexane solutions were used and diluted as indicated in section 2.4.2, if necessary.

The colour changes during the reaction were similar to those observed using BuLi as the co-catalyst. The brown solutions of cyclopentene/WCl_6 in toluene maintained this colour when *s*-BuLi was injected to give W:Li ratios within the range 1:1 to 1:4. When the final W:Li ratio was 1: <1 the *s*-BuLi injection produced a red solution.

W:Li ratios of 1:0.1 and 1:4 failed to produce any elastomer when the reaction mixture was added to degassed methanol. The products of the other experiments were treated as indicated in 4.1.2.1 and table 4.1.4. catalogues the yields and SEC data for the high molecular weight product (HMWP) and the low molecular weight material (LMWP) in the purified sample.

The results again confirm that the WCl_6:*s*-BuLi ratio of 1:2 in the catalyst system produces the fastest reaction. The molecular weight data were almost identical using a 1: 1, 2 or 3 mole ratio of W:Li. The polypentenylenes formed were of lower molecular weight than those obtained with the same mole ratios of WCl_6:BuLi and the polymerizations were considerably slower.

TABLE 4.1.4. **SERIES A** ROMP OF CYCLOPENTENE USING *sec*-BUTYLLITHIUM AS THE CO-CATALYST.

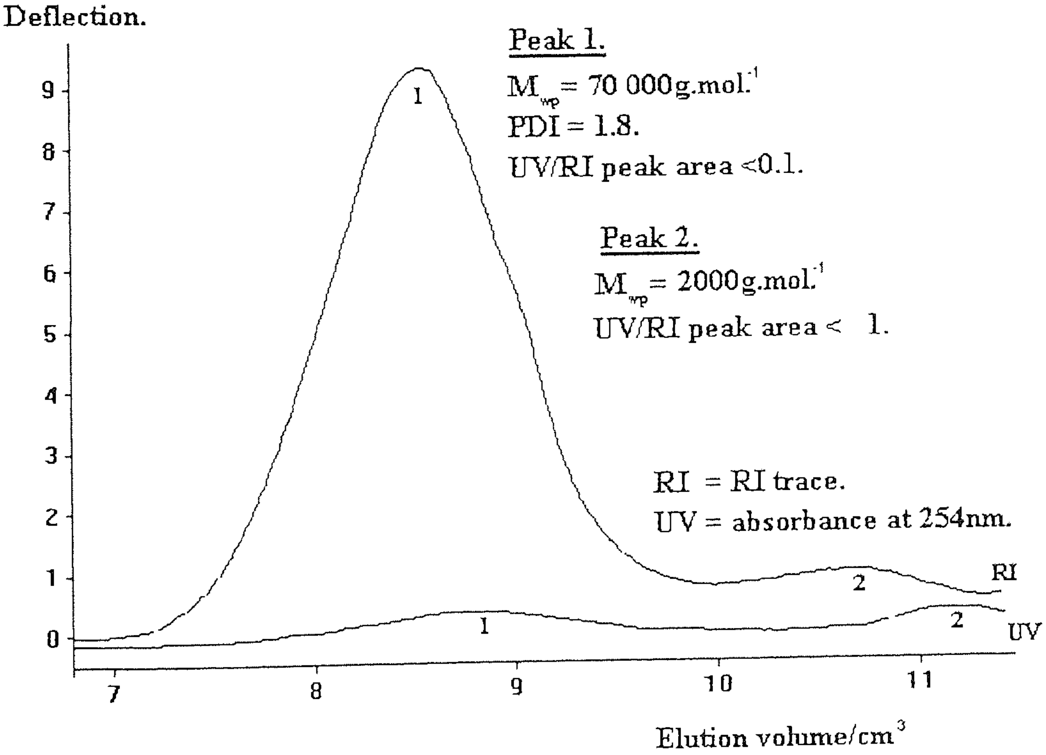
W: Li ratio	% yield	Time / h.	M_{wp} for HMWP / g.mol.$^{-1}$	PDI for HMWP.	UV:RI area for HMWP.	M_{wp} for LMWP / g.mol.$^{-1}$
1: **0.1**	none	-	-	-	-	-
1: **0.2**	1	24	200 000	-	0.1*	1000
1: **0.5**	10	24	200 000	1.7	0.1*	2000
1: **1.0**	30	24	100 000	1.6	0.2*	1000
1: **2.0**	35	1	100 000	1.6	0.1*	2000
1: **3.0**	30	24	70 000	1.7	0.2*	-
1: **4.0**	none	24	-	-	-	-

Concentration of cyclopentene = [Cp] = 3.0M. Cp:WCl_6 = 500:1. Temperature = 25°C.

* Values obtained from SEC analysis of aged samples.

The original SEC analysis indicated negligible absorbance at 254nm., as detected by the chart recorder, and the values of UV:RI peak area given in the table are from the reanalysis of aged samples, as described in section 4.1.2.1.1. A fresh sample of polypentenylene was prepared using the optimum cyclopentene:WCl_6:*s*-BuLi ratio of 500:1:2 and this was precipitated after 10 minutes, purified and dried and prepared for SEC analysis. Figure 4.1.4. shows the resulting SEC trace using both RI and UV/VIS detectors with both HMWP (peak 1) and the LMWP (peak 2).

FIGURE 4.1.4. THE SEC TRACE FOR RI AND UV/VISIBLE DETECTORS FOR PRODUCT USING WCl_6/*s*-BuLi (1:2). CATALYST SYSTEM.



The ^{1}H and ^{13}C NMR spectra of this sample were obtained (figures 4.4.3 and 4.4.4 in section 4.4.) and were identical to those for the polypentenylene prepared using the catalyst WCl_6/BuLi.

These two series of experiments have shown that BuLi is a more active co-catalyst system than *s*-BuLi but both show maximum activity with the catalyst ratio WCl_6:BuLi/*s*-BuLi =1:2. Over the range of [Li] used the M_{wp} decreases to a minimum for the optimum catalyst:co-catalyst ratio of 1:2 and then increases. This can be explained in terms of an increase in the number of propagating centres at the optimum ratio and/or an increase in significant transfer reactions. The other finding has been that the UV absorbance at 254nm. for the polypentenylene samples is not insignificant.

4.1.2.2. THE EFFECT OF ALUMINIUM ALKYLCHLORIDE CO-CATALYST RATIOS.

Richards et al[178] have reported successful anionic to Ziegler-Natta transformation polymerizations based on the anionic species PStLi reacting with $AlCl_3$ to form polymeric aluminium species which act as co-catalysts with $TiCl_4$ to produce block co-polymers of styrene and ethene. One aim of this study was to produce mixtures containing polymeric aluminium species from the reaction of 1:1 mole ratios of $AlEtCl_2$ and PStLi solutions. This mixture and WCl_6 might then be a viable catalyst system for the ROMP of cyclopentene producing block co-polymers. The use of first $WCl_6/AlEtCl_2$ and then the three component $WCl_6/AlEtCl_2/BuLi$ and *s*-BuLi catalyst systems for the ring-opening polymerization of cyclopentene, to find the optimum reaction conditions, was a preliminary stage to the investigation. The range of mole ratios used for each catalyst system is shown in table 4.1.5.

TABLE 4.1.5. THE RANGE OF WCl_6.:ALUMINIUM ALKYLCHLORIDE CATALYST SYSTEMS USED FOR THE **SERIES A** ROMP OF CYCLOPENTENE.

Ref.	Co-catalyst system used	Range of WCl_6: Co-catalyst ratios tested
4.1.2.2.1.	$AlEtCl_2$	1: 0.5, 1.0, 2.0, 3.0.
4.1.2.2.2.	1: 1 ratio $AlEtCl_2$.: BuLi	1: 0.5, 1.0, 2.0, 3.0.
4.1.2.2.3.	1: 1 ratio $AlEtCl_2$.: *s*-BuLi	1: 0.5, 1.0, 2.0, 3.0.

4.1.2.2.1. The Effect of WCl_6:$AlEtCl_2$ ratio on the ROMP of Cyclopentene.

Tungsten hexachloride/aluminium ethyldichloride is recognised as an effective ring-opening metathesis catalyst system and the results of the previous two series of experiments indicated that the optimum rate of polymerization of cyclopentene using WCl_6 and metal alkyl catalyst systems was likely to be 1:2, so the range used for aluminium ethyldichloride as co-catalyst was W:Al of 1: 0.5, 1.0, 2.0 and 3.0.

A stock solution of 0.4M$AlEtCl_2$ was prepared by vacuum distillation of $18.2cm^3$ of cyclohexane into a small evacuated flask, and injection by syringe of $0.8cm^3$ liquid aluminium ethyldichloride ($7.6x10^{-3}$moles) over argon from a canister. The reaction conditions were similar to those described in section 4.1.2.1.1. for WCl_6/BuLi reactions.

The aluminium ethyldichloride solution was pale yellow and when injected, after a time delay of two minutes, into the brown solution of cyclopentene and WCl_6, produced a red solution. An obvious change in the viscosities of the solutions occurred after 2 to 3 hours for W:Al =1:0.5, 20 minutes for ratio 1:1, 10 minutes for ratio 1:2 and 4 to 5 hours for ratio 1:3. So the ratio WCl_6:$AlEtCl_2$ of 1:2 in the catalyst system gave the optimum rate of ring-opening metathesis polymerization of cyclopentene.

When the reaction using W:Al in the mole ratio 1:0.5 was found to be slow, sampling was carried out in the other experiments of the series to gain further information about the polymerization. Samples were removed from the reaction solutions after 20 minutes by extracting some of the mixture, under argon, into a sample bottle containing methanol. A syringe could not be used to remove the solution because of its high viscosity. The remaining mixtures were left for 15 hours before they were finally precipitated, purified and treated as in previous experiments. Table 4.1.6. shows approximate yields calculated for the final product and SEC data for the product at 20 minutes and after 15 hours. Problems with sampling known quantities of the viscous liquid for the

W:Li ratios of 1:1 and 1:2 made it impossible to estimate the yield after 20 minutes for these two polymerizations and the yields after 15 hours were therefore approximate.

TABLE 4.1.6. **SERIES A** ROMP OF CYCLOPENTENE USING ALUMINIUM ETHYLDICHLORIDE AS THE CO-CATALYST.

W: Al ratio	% yield	Time.	M_{wp} for HMWP / g.mol.$^{-1}$	PDI for HMWP.	UV:RI area for HMWP.	M_{wp} for LMWP / g.mol.$^{-1}$
1: **0.5**	75	15h.	130 000	1.9	0.7*	1000
1: **1.0**	-	20m.	140 000	2.5	0.3*	2000
	≈75	15h.	150 000	2.5	0.8*	2000
1: **2.0**	-	20m.	120 000	2.1	0.2*	2000
	≈75	15h.	120 000	2.7	0.6*	2000
1: **3.0**	-	20m.	80 000	1.9	0.3*	hidden
	50	15h.	120 000	3.3	1.0*	hidden

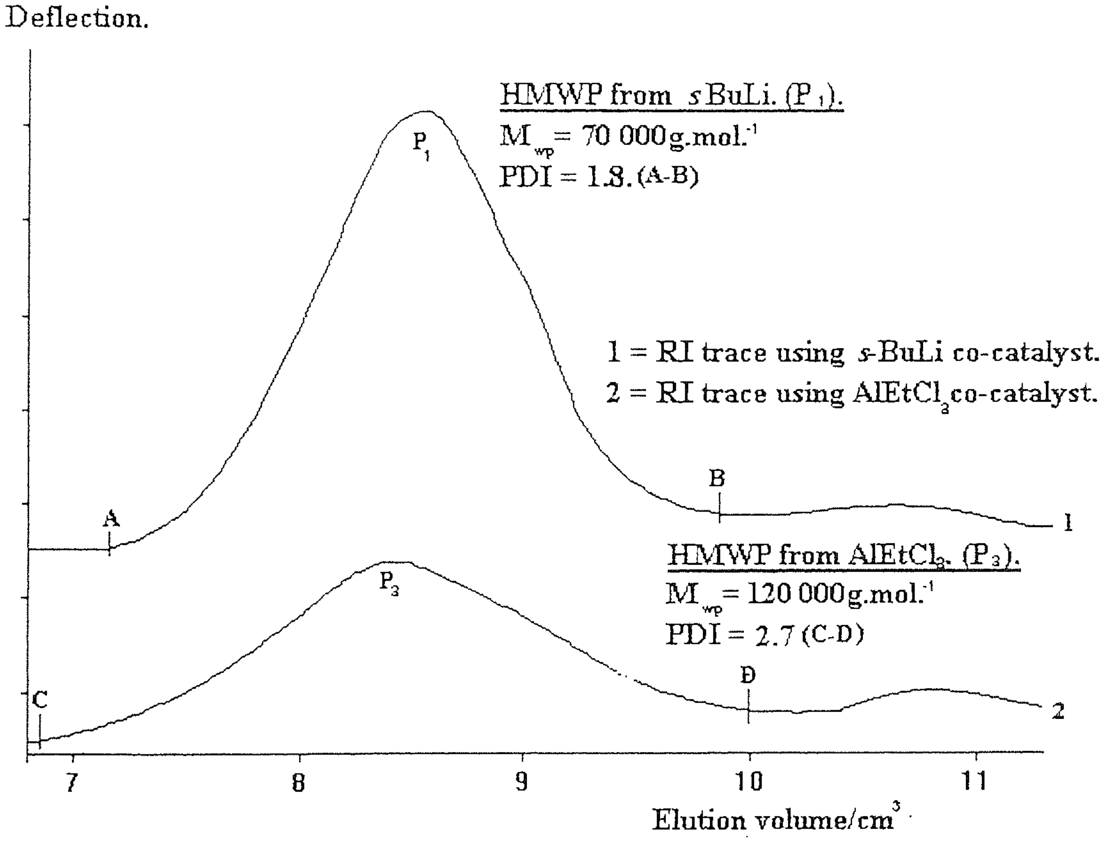
Concentration of cyclopentene = [Cp] = 3.0M. Cp:WCl_6 = 500:1. Temperature = 25°C.

* Values obtained from SEC analysis of aged samples.

The molecular weight of the product after 20 minutes was very similar to that after 15 hours and to that obtained in corresponding experiments using butyllithium as a co-catalyst but the PDI values calculated from the RI traces were much broader. This was most pronounced with the W:Al ratios of 1:2 and 1:3, after 15 hours reaction time, in which the HMWP showed signs of bimodal character. Figure 4.1.5 shows this broader molecular weight distribution by comparing the RI traces from the SEC analysis of two samples using (1)*s*-BuLi. and (2) $AlEtCl_2$ as co-catalysts. In both experiments the catalysts (WCl_6):co-catalyst ratio was 1:2.

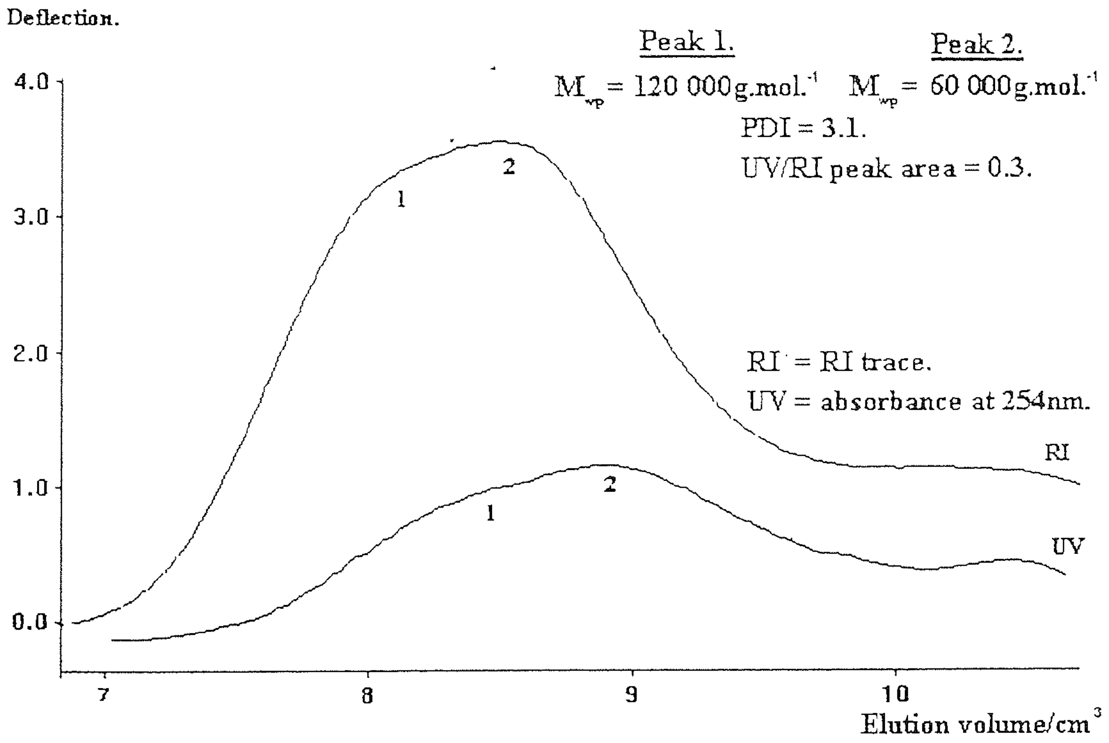
The UV/VIS absorbance was only fully investigated on aged samples for the full co-catalyst range but was even more pronounced for the HMWP obtained using $AlEtCl_2$ as the co-catalyst, than for aged samples using BuLi co-catalysts.

FIGURE 4.1.5. THE SEC TRACES USING THE RI DETECTOR OF THE PRODUCTS USING *s*-BuLi AND $AlEtCl_2$ AS CO-CATALYSTS.



A fresh stock solution of $2MAlEtCl_2$ in toluene was obtained to repeat the reaction with the cyclopentene:WCl_6:$AlEtCl_2$ ratio of 500:1:2. The Schlenk technique was used to inject appropriate volumes of the solution directly from the reagent bottle. The polymerization mixture was precipitated, purified and dried. The SEC trace for the product of the experiment using $AlEtCl_2$ in toluene is shown in figure 4.1.6. using RI and UV/VIS detectors. Very broad, bimodal peaks are discernable and the UV:RI peak area is larger than for other freshly prepared polypentenylene samples.

FIGURE 4.1.6. THE SEC TRACE FOR RI AND UV/VISIBLE DETECTORS FOR PRODUCT USING $WCl_6/AlEtCl_2$ (1:2). CATALYST SYSTEM.



The optimum ratio of catalyst to co-catalyst, is the WCl_6:$AlEtCl_2$ ratio of 1:2. The peak molecular weight of the high molecular weight product is similar to that obtained using BuLi as the co-catalyst but the PDI is broader and some bimodal character is evident in the SEC traces. A comparison of the UV:RI peak areas of freshly prepared and analysed samples shows that the HMWP has a slightly higher ratio (0.3) than for the product using the butyllithium co-catalysts (0.1 for BuLi and for s-BuLi). The ^1H NMR spectrum of this product showed lines which could not be assigned. This and the and ^{13}C spectrum are shown in figures 4.4.5. and 4.4.6 in section 4.4.

4.1.2.2.2. The Effect of WCl_6:$AlEtCl_2$:BuLi ratio on the ROMP of Cyclopentene.

As was stated in the introduction to section 4.1.2.2, this three component systems represent a preliminary stage in an attempt to produce co-polymers of cyclopentene by ring-opening metathesis. To find the optimum reaction conditions the range of component mole ratios given in table 4.1.5 was used.

15cm^3 0.4M aluminium ethyldichloride/cyclohexane solution (6.0x10^{-3}moles), prepared for the experiments described in 4.1.2.2.1., were injected over argon into 3.6cm^3 1.67M BuLi solution (6.0x10^{-3}moles) in a small reaction vessel. This 1:1 mole ratio formed a white precipitate of lithium chloride, which was allowed to settle, and then the supernatent liquid (containing a mixture of aluminium alkyl chlorides) was injected into the approximately 3M cyclopentene/toluene solution, 2 minutes after injecting the WCl_6 solution. The monomer to WCl_6 ratio was kept constant in a series of experiments and the ratios for the catalyst system were varied as follows WCl_6:$AlEtCl_2$:BuLi = 1:0.5:0.5, 1:1:1, 1:2:2 and 1:3:3.

The first two mixtures remained brown after injecting the $AlEtCl_2$/BuLi co-catalyst mixture and became viscous after 1 hour. The mixture with the co-catalyst in the W:Al:Li ratio 1:2:2 was red when the co-catalyst mixture was first injected and turned green and viscous within 30 minutes. The final experiment in the series remained brown when the Al/Li compounds were added and there was little apparent increase in its viscosity even after 24 hours. The products from these experiments were precipitated, purified and dried. The yields and SEC information is given in table 4.1.7.

TABLE 4.1.7. **SERIES A** ROMP OF CYCLOPENTENE USING THE CATALYST SYSTEM WCl_6:$AlEtCl_2$:BuLi IN THE RATIO OF 1: X: X (0.5<X<3.0).

W: Al: Li ratio	% yield	Time. /h.	M_{wp} for HMWP /g.mol.$^{-1}$	PDI for HMWP.	UV:RI area for HMWP.	M_{wp} for LMWP /g.mol.$^{-1}$
1: 0.5: 0.5	40	24	140 000	2.6	0.7*	2000
1: 1.0: 1.0	40	2	150 000	4.2	0.4*	2000
1: 2.0: 2.0	40	1	130 000	>6.5	1.0*	2000
1: 3.0: 3.0	8	24	150 000	5.6	1.0*	2000

Concentration of cyclopentene = [Cp] = 3.0M. Cp:WCl_6 = 500:1. Temperature = 25°C.

* Values obtained from SEC analysis of aged samples.

The fastest rate of reaction was obtained using the catalyst system in the ratio WCl_6:$AlEtCl_2$:BuLi of 1:2:2 and again the peak molecular weights of the HMWP were in the same range as in previous polymerizations. However the SEC trace showed the products had very broad molecular weight polydispersities, particularly when the W:Al:Li ratio was 1:2:2. The peak was distorted but not bimodal. The reanalysis of the aged THF solutions produced an even broader peak for the HMWP, the PDI increased from 4.2 to 6.5 for the W:Al:Bu ratio of 1:1:1, and showed relatively high absorbance at 254nm., the UV:RI peak areas for the HMWP and LMWP for the same polymerization were 0.4 and approximately 1.0 respectively.

The experiment using the W:Al:Li ratio of 1:2:2 was repeated using a stock solution of 2M$AlEtCl_2$ in toluene. The procedure was modified by using an evacuated reaction flask, with a side arm, of the type shown in figure 2.5. Initially tap 1 was closed and 6.4g (0.094moles) of cyclopentene and 15.0cm^3 of toluene were vacuum distilled into section B of the vessel. Argon was introduced into all parts of the vessel and 0.2cm^3 2M $AlEtCl_2$/toluene (4.0×10^{-4} moles) and 0.25cm^3 1.73M BuLi in hexanes (4.3×10^{-4}moles) were sequentially injected into the side-arm A, using the Schlenk technique. Tap 1 was again closed, 6.6cm^3 0.03M WCl_6 (2.0×10^{-4} moles) were injected into the main vessel B and tap 2 was closed, so that the flask could be removed from the vacuum line. 2 minutes later tap 1 was reopened and the co-catalyst mixture was mixed with the solution in B. Precipitation of the mauve polymerization mixture after 20 minutes produced a yield of 16% of the purified elastomer and SEC analysis showed the HMWP had a peak molecular weight of 80 000g.mol.$^{-1}$, which was lower than in the previous experiment using this ratio, the PDI was narrower 2.8 but most significantly the UV:RI peak area was reduced from 1.0 to 0.1.

The ^1H and ^{13}C NMR spectra of the product showed identical structure to the polypentenylene produced using the BuLi co-catalyst systems and are shown in figures 4.4.7 and 4.4.8.

4.1.2.2.3. The Effect of WCl_6:$AlEtCl_2$:*s*-BuLi ratio on the ROMP of Cyclopentene.

This was an extension of the model three component system used in the previous section to compare the optimum reaction conditions. Fresh stock 2M aluminium ethyldichloride/toluene solution was used to prepare the co-catalyst.

The range of WCl_6:$AlEtCl_2$:*s*-BuLi catalyst systems indicated in table 4.1.5 were used. The co-catalyst system was prepared by distilling under vacuum 25cm^3 of toluene into a small evacuated reaction flask and injecting 1.5cm^3 2.0M $AlEtCl_2$ in toluene (3.0×10^{-3}moles) and 2.0cm^3 1.50M *s*-BuLi in cyclohexane (3.0×10^{-3} moles). A white precipitate formed and was allowed to settle from this 1:1 mixture of the Al:Li co-catalyst system (approximately 0.1M with respect to [Al]). The appropriate volume of the supernatent solution was removed by syringe over argon as needed. The procedure was that outlined in section 2.5.1.1. The polymerization precipitation, purification and SEC analysis procedure was followed and the data obtained is shown in table 4.1.8.

TABLE 4.1.8. **SERIES A** ROMP OF CYCLOPENTENE USING THE CATALYST SYSTEM WCl_6:$AlEtCl_2$:*s*-BuLi IN THE RATIO OF 1: X: X (0.5<X<3.0).

W: Al: Li ratio	% yield	Time. / m.	M_{wp} for HMWP / g.mol.$^{-1}$	PDI for HMWP.	UV:RI area for HMWP.	M_{wp} for LMWP / g.mol.$^{-1}$
1: 0.5: 0.5	neg.	20	220 000	2.8	0.3*	2000
1: 1.0: 1.0	56	20	125 000	5.8	0.5*	1500
1: 2.0: 2.0	37	20	110 000	2.0	0.3*	1500
1: 3.0: 3.0	24	20	100 000	1.9	0.3*	hidden

Concentration of cyclopentene = [Cp] = 3.0M. Cp:WCl_6 = 500:1. Temperature = 25°C.

* Values obtained from SEC analysis of aged samples.

The catalyst system (W:Al:Li ratio of 1:0.5:0.5) remained brown when the Al/Li co-catalyst solution was injected into the cyclopentene/toluene mixture, 2 minutes after addition of the 0.04MWCl_6. When the reaction mixture was poured into degassed methanol after 20 minutes there was only enough white elastomer to dry and dissolve in THF to test by SEC. The high molecular weight of the product indicates that there were very few propagating centres present in the polymerization.

In the other three experiments the brown solution of monomer and catalyst went mauve when the co-catalyst solution was injected into the flask and went viscous within 20 minutes. The yield of the elastomer from the W:Al:Li ratio1:1:1 was particularly high but all three reactions produced relatively high yields in 20 minutes. The products had quite broad PDI values but the value for the W:Al:Li ratio of 1:1:1 was exceptionally high, although there was no evidence of bimodality. The molecular weight at the peaks were in the usual range (M_{wp} =100 000-125 000g.mol.$^{-1}$).

The reanalysis of the samples by SEC, for both RI and UV/VIS detectors, a month after the THF solution had been prepared, produced traces showing the usual trends, HMWP with broader PDI and UV:RI peak area of 0.3-0.5. However repeating the experiment with the W:Al:Li ratio of 1:2:2 and produced a yield of 20% of HMWP after 20 minutes reaction time. SEC analysis, on a freshly prepared solution of the product, showed it to have M_{wp} of 100 000g.mol.$^{-1}$, PDI of 2.1 and UV:RI peak area of only 0.1. The NMR spectra of the product were identical to those of previous polypentenylene samples using BuLi as the co-catalyst.

The peak molecular weight of the polymers produced, using all three aluminium co-catalyst systems and with W:Al ratios between 1:1 and 1:3, were remarkably constant. It was found that the ring-opening polymerization of the cyclopentene/toluene solutions, using the three component WCl_6/$AlEtCl_2$ /BuLi or *s*-BuLi catalyst systems, polymerized rapidly using catalyst to co-catalyst ratios between 1:1:1 and 1:2:2.

All three catalyst systems produced polymers with much broader PDI than those obtained using BuLi or *s*-BuLi co-catalyst, in some experiments the PDI was >3.0. In a few cases the HMWP was bimodal, as in figure 4.1.6., the SEC trace for the polypentenylene produced using $WCl_6/AlEtCl_2$ in a 1:2 ratio as the catalyst. The bimodal peak molecular weights of 60 000 and 120 000g.mol.$^{-1}$ may have been produced by propagation at two centres with different activities. However there were other examples of bimodal character, in which the higher peak molecular weight was also twice the lower value. An alternative explanation is that during either the termination reaction or perhaps the killing stage, using degassed methanol, the active polymer chain propagating centres may have dimerized to some extent. This is a well-known feature of oxygen promoted coupling in the termination of polystyryllithium.

Although the absorbances at 254nm. of aged solutions of polypentenylene, using Al-based co-catalysts, were relatively high, particularly for those with broad PDI, freshly prepared THF solutions have similar absorbance to the fresh polymer solutions prepared using BuLi co-catalysts. The SEC traces of some products (as shown in figure 4.1.6), demonstrated high UV/Ri peak area ratio even though analysis was carried out immediately after their preparation.

4.1.3 THE EFFECT OF SOLVENT.

The butyllithium and polystyryllithium solutions are known to undergo slow, spontaneous decay in toluene solution.[191,192] The ring-opening polymerization of cyclopentene has been reported to be successful in cyclohexane[185] and as this is the preferred solvent for the lithium alkyls, the procedure was attempted using cyclohexane as the only solvent.

An attempt was made to prepare $0.02MWCl_6$ in cyclohexane but the red powder remained as a suspension and attempts to dissolve even very small amounts were unsuccessful. So standardised solutions of WCl_6 in toluene were used as the catalyst solution.

The co-catalyst systems and the catalyst:co-catalyst ratios used are summarised in table 4.1.9.

TABLE 4.1.9. THE RANGE OF WCl_6:CO-CATALYST SYSTEMS USED FOR SERIES A ROMP OF CYCLOPENTENE IN CYCLOHEXANE.

Ref.	Co-catalyst system used	Range of WCl_6: Co-catalyst ratios tested
4.1.3.1	BuLi	1: 0.5, 1.0, 1.5, 2.0, 2.5.
4.1.3.2	$AlEtCl_2$	1: 1.0, 2.0..

4.1.3.1. The Effect of the WCl_6: BuLi catalyst ratio on the ROMP of Cyclopentene in Cyclohexane.

The procedure outlined in section 2.5.1.1 was followed. In a typical experiment 6.2g (0.090moles) of cyclopentene and then $20.0cm^3$ of cyclohexane were vacuum distilled into an evacuated reaction flask. $6.0cm^3 0.03M$ WCl_6/toluene ($1.8x10^{-4}$moles) were injected over argon and two minutes later $0.25cm^3 1.6M$ BuLi ($4.0x10^{-4}$moles) were added in the same way. The ratio of the reagents was therefore cyclopentene:WCl_6:BuLi = 500:1:2 and the overall concentration of the monomer soution was 2.6M.

Injecting the WCl_6 solution into the monomer solution in cyclohexane produced an olive green homogeneous solution and, for the W:Li ratios of 1:1, 1:1.5, 1:2 and 1:2.5, addition of the BuLi co-catalyst resulted in a brown mixture forming, which initially separated into two layers. Shaking produced no effect on the homogeneity of the 1:1, 1:1.5 and 1:2.5 W:Li mixtures and after 2 hours the heterogeneous product mixture, which had not increased in viscosity, was shaken before pouring it into degassed methanol. A small amount of white elastomer was obtained from all three reactions on purifiying and drying the product.

The 1:2 mixture of catalyst to co-catalyst remained homogeneous on shaking after 10 minutes and the red/brown mixture became more viscous within 30 minutes. The product was precipitated and purified in the usual way after 2 hours. The mixture with W:Li ratio 1:0.5 separated into two layers in the same way as the others but produced no elastomer when the reaction mixture was poured onto degassed methanol. All the pure products were dissolved in THF and analysed by SEC. The yield and the SEC data is given in table 4.1.10.

TABLE 4.1.10. SERIES A ROMP OF CYCLOPENTENE/CYCLOHEXANE USING BUTYLLITHIUM AS THE CO-CATALYST.

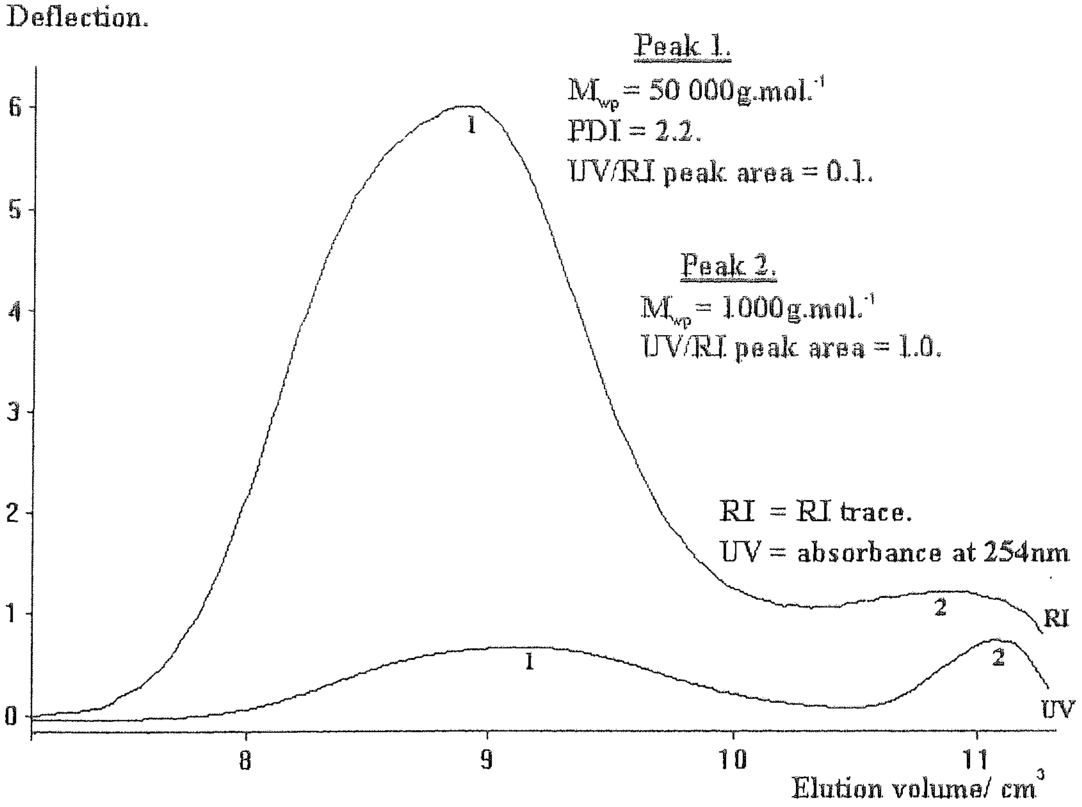
W: Li ratio	% yield	Time /h.	M_{wp} for HMWP /g.mol.$^{-1}$	PDI for HMWP.	UV:RI area for HMWP.	M_{wp} for LMWP /g.mol.$^{-1}$
1: 0.5	none	2	-	-	-	-
1: 1.0	10	2	50 000	2.2	0.1	-
1: 1.5	16	2	50 000	2.5	0.1	1300
1: 2.0	20	2	50 000	2.2	0.1	1000
1: 2.5	neg.	2	80 000	3.6	neg.	1500

Concentration of cyclopentene = [Cp] = 3.0M. Cp:WCl_6 = 500:1. Temperature = 25°C.

* Values obtained from SEC analysis of aged samples.

Comparing these results with those in table 4.1.2., obtained using the same catalyst system but toluene as the main solvent, the lower yields of elastomer obtained in cyclohexane are obvious. Although the W:Li ratio of 1:2 still produced the highest yield (20%), it is much lower than the 66% yield produced in one hour by the same catalyst system in toluene. The SEC trace using both RI and UV/VIS recorders for this ratio is shown in figure 4.1.7. The M_{wp} of the HMWP at 50 000g.mol.$^{-1}$ is also relatively low compared to the 120 000g.mol^{-1} value obtained in reaction with toluene as the main solvent. The PDI values are broader than for the polypentenylene in toluene but the UV to RI peak areas were similar (see figure 4.1.3).

FIGURE 4.1.7 THE SEC TRACE FOR RI AND UV/VISIBLE DETECTORS FOR PRODUCT USING WCl_6/BuLi (1:2). CATALYST SYSTEM.



4.1.3.2. The Effect of WCl_6: $AlEtCl_2$ catalyst ratio on the ROMP of Cyclopentene in Cyclohexane.

The co-catalyst solution of 0.4M $AlEtCl_2$/cyclohexane was prepared by vacuum distillation of cyclohexane and injection, over argon, of liquid $AlEtCl_2$ from a canister as described in section 4.1.2.3. An evacuated reaction flask was attached to the vacuum line and 6.1g (0.09moles) of cyclopentene and 18.0cm^3

of cyclohexane were distilled. Using the Schlenk technique 6.0cm^{3}0.03M WCl_6 ($1.8x10^{-4}$ moles) were injected into the monomer solution and two minutes later 0.9cm^3 0.4M $AlEtCl_2$/cyclohexane ($3.6x10^{-4}$ moles $AlEtCl_2$) was added. The ratio of the catalyst system was therefore 1:2 and the experiment was repeated using W:Al ratio of 1:1.

The olive green solutions of monomer and WCl_6 in cyclohexane went brown when the 0.4M$AlEtCl_2$/cyclohexane was added but neither became more viscous and when the solution were pured into degassed methanol, after 2 hours, no elastomer was precipitated.

It was concluded that cyclohexane was not a satisfactory solvent either for the tungsten hexachloride or for the ring-opening polymerization and it was decided to use toluene as the solvent in all subsequent experiments.

These experiments demonstrate the dramatic effect the solvent can have on the polymerization. The butyllithium co-catalyst is known to exist as aggregates in non-polar solvents (in cyclohexane it forms hexamers).[194] Although the colour change on the addition of BuLi to the cyclopentene/WCl_6 mixture indicates the formation of a new species (probably a W/alkyl species), the polar character of this might also result in the formation of dimers, or other aggregates, whose strong association in cyclohexane, gives rise to their reduced activity as propagating centres. Aromatic solvents produce a lower degree of association between species with permanent dipoles and this may account for the increased rate of polymerization of cyclopentene in toluene compared to cyclohexane solution.

4.1.4 THE USE OF $WOCl_4$ AS THE CATALYST.

There are many references in the literature to the use of $WOCl_4$ as an effective metathesis catalyst. The orange red solid was obtained from Aldrich and put unopened in the Halco dry box. It was dispensed, in the dry box, into a preweighed, argon filled, small reaction flask, similar to that shown in figure 2.2. The closed flask was removed from the box, weighed and attached to the vacuum line and degassed. 0.10g of $WOCl_4$ ($3.2x10^{-4}$moles) was in the flask and 20.4 cm^3 of toluene was vacuum distilled into it. The red solution still had a yellow precipitate after mechanical shaking overnight and several hours in the ultrasound bath to encourage dissolution. The calculated concentration of 0.015M was therefore estimated as 0.01M for the subsequent experiments.

A series of experiments with different mole ratios of $WOCl_4$:BuLi were carried out using the procedure of 2 minute sequential addition of the catalyst and co-catalyst solutions as outlined in section 2.5.1.1. The W:Li ratios attempted were 1: X in which $0.2<X<2$.

The orange solution of $WOCl_4$/toluene maintained its colour when added to the monomer solution and in all the experiments the mixture went green when the BuLi was injected over argon. The solutions remained with the same viscosity over a period of two days and were then precipitated, producing a very small amount of product, after purification and drying,. The yield and SEC analysis results are given in table 4.1.11. The general failure of these experiments led to the repetition of those with W:Li of 1:1 and 1:2 and the results are included in the table along with the SEC data obtained from 0.5%(wv) THF solutions of the purified products.

An attempt to dissolve $WOCl_4$ in cyclohexane produced a red suspension and it was impossible to assign an accurate concentration to the solution. The polymerization was tried using $WOCl_4$:BuLi ratios of 1:1, 1:2 and 1:3 and the same technique as before, using toluene as the solvent for the cyclopentene. After 24 hours the three reaction mixtures were each poured into degassed methanol. Only the mixture with W:Li =1:1 produced any elastomer, there was a relatively large 15% yield of product but SEC analysis showed the M_{wp} to be only 15 000g.mol.$^{-1}$.

TABLE 4.1.11. SERIES A ROMP OF CYCLOPENTENE USING THE CATALYST SYSTEM $WOCl_4$: BuLi IN THE RATIO OF 1: X (0.2<X<2.0).

W: Li ratio	% yield	Time / h.	M_{wp} for HMWP / g.mol.$^{-1}$	PDI for HMWP.	UV:RI area for HMWP.	M_{wp} for LMWP / g.mol.$^{-1}$
1: 0.2	3	48	330 000	2.8	-	slight
1: 0.5	2	48	220 000 20 000	-	-	slight
1: 1.0	2	48	240 000 15 000	-	-	slight
1: 1.0	3	24	210 000	2.5	-	slight
1: 2.0	none.	48	-	-	-	-
1: 2.0	1	48	600 000	2.3	-	-

Concentration of cyclopentene = [Cp] = 3.0M. Cp:WCl_6 = 500:1. Temperature = 25°C.

The failure of this series of reactions may be caused by the relative insolubility of the $WOCl_4$ but the purity of the $WOCl_4$ may be an additional factor. As both the purity and effectiveness of the WCl_6 catalyst had been demonstrated already, it was decided that this was the most efficient catalyst for subsequent work.

4.2. SERIES B. PREMIXING THE CATALYST AND THE CO-CATALYST.

The effect of premixing the components of the catalyst system (WCl_6/$Al(i\text{-}Bu)_3$) before adding the resulting mixture to cyclopentene solution was found by Tuck to produce no high molecular weight polymer when investigated by dilatometry. Zurimendi[107] investigated this system using calorimetry and he reported that, with a premix aging time of 1 minute, a very exothermic reaction occurred which reached zero rate after 3 minutes. SEC analysis showed that no high molecular weight product had been formed but low molecular weight material was present. Common features in the IR spectrum of polypentenylene and this product led to the conclusion that oligomers of cyclopentene were formed. In this current series of experiments the effects of premixing the catalyst/co-catalyst sytems, WCl_6/BuLi, *s*-BuLi and $AlEtCl_2$, were investigated by comparing the yields of product over a range of catalyst to co-catalyst ratios and, using SEC analysis, the nature of the product.

The range of premixed catalyst systems is summarised in table 4.2.1. In all the experiments a reaction flask of the type shown figure 2.5 was used and the procedure outlined in section 2.5.1.2 was followed. The final product was precipitated, purified and dried. The yield was used as a measure of the activity of the catalyst and 0.5%(wv) solutions in THF were analysed using SEC, to determine any change in the relative amount of oligomeric material.

TABLE 4.2.1. THE RANGE OF PREMIXED CATALYST CO-CATALYST SYSTEMS USED FOR SERIES B ROMP OF CYCLOPENTENE.

Ref.	Co-catalyst system used	Range of WCl_6: Co-catalyst ratios premixed.
4.2.1	BuLi	1: 0.2, 0.5, 1.0, 1.5, 2.0, 3.0.
4.2.2	*sec*-BuLi	1: 0.2, 0.5, 1.0, 2.0.
4.2.3	$AlEtCl_2$	1: 1 using various solvent systems.

4.2.1 The effect of the premixed WCl_6:BuLi ratio on the ROMP of cyclopentene.

In a typical experiment the reaction flask was attached to the vacuum line and 5.5g (0.081 moles) of cyclopentene and 20.1cm^3 of toluene were distilled into the main vessel. Argon was passed into the flask and tap 1 was removed and 5.2cm^{3}0.03M WCl_6(1.6×10^{-4} moles) and 0.2cm^{3}1.6M BuLi(3.2×10^{-4}moles) were injected into the side-arm. Both taps were closed and 1 minute after the catalyst system had been mixed, it was introduced into the monomer solution through tap 1. The ratios cyclopentene: WCl_6:BuLi were 500:1:0.5 and the [cyclopentene] 2.5M. The experiment was repeated using the range of ratios W:Li of 1:0.2 to 1:3.0.

The premixing of the catalyst components produced a brown heterogeneous mixture with a brown precipitate clearly visible. When these systems were added to the monomer solution different colour changes occurred. The W:Li ratios of 1:0.2 and 1:0.5 went red and the latter mixture became slowly more viscous and was very viscous after 18 hours. The W:Li ratio of 1:0.2 was less viscous after a similar time but on opening the flask to precipitate the polymer traces of air were introduced into the system and this produced a very viscous red product.

Catalyst systems employing higher Li:W ratios remained brown when the premixed catalyst system was added to the cyclopentene in toluene. The W:Li ratio of 1:1 became viscous within 30 minutes and was precipitated after an hour but the other mixtures were precipitated after 18 hours with viscosities similar to the original mixtures. Table 4.2.2 shows the estimated yields and the results of the SEC analysis of the products.

TABLE 4.2.2. **SERIES B** ROMP OF CYCLOPENTENE USING PREMIXED WCl_6:BuLi AS THE CATALYST SYSYTEM.

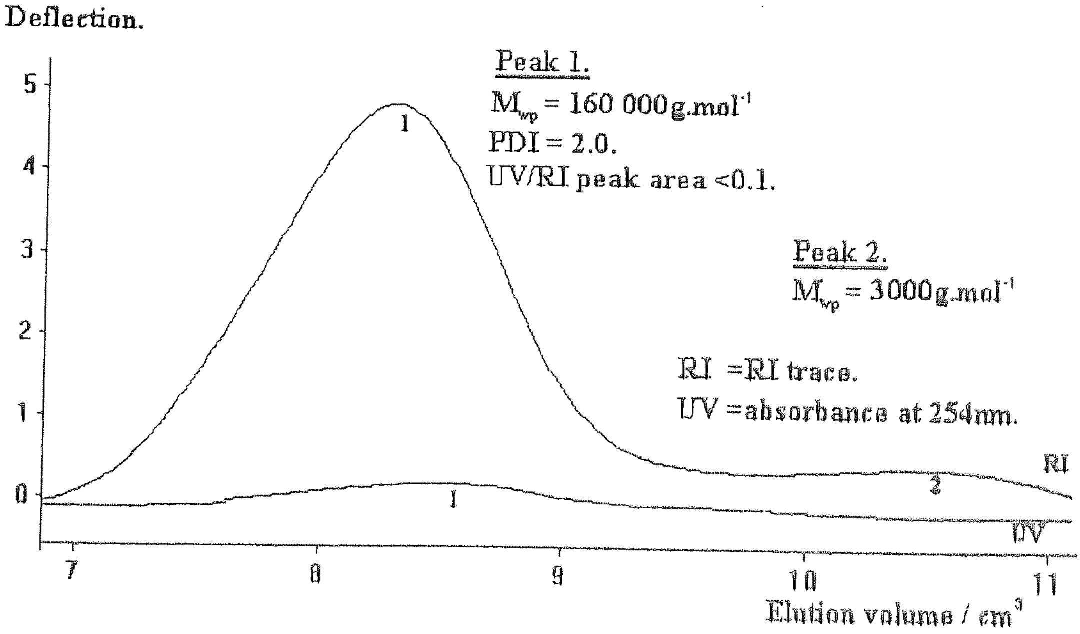
W: Li ratio	% yield	Time /h.	M_{wp} for HMWP /g.mol.$^{-1}$.	PDI for HMWP.	UV:RI area for HMWP.	M_{wp} for LMWP /g.mol.$^{-1}$.
1: 0.2	30	18	1 000 000	2.2	-	-
1: 0.5	30	18	500 000	2.4	-	2000
1: 1.0	47	1	120 000	1.6	negligible	1000
1: 2.0	5	18	180 000	-	negligible	4000
1: 3.0	10	18	200 000	-	negligible	3000

The very high molecular weight polymers obtained from the W:Li 1:0.2 and 1:0.5 may have been caused in part by rapid polymerization of the active centres on exposure to air at the end of the experiment. Loftipour[106] reported that dramatic increases in viscosity occurred when WCl_6/cyclopentene systems were exposed to air.

The W:Li ratio of 1:1 produced the highest observable rate. The HMWP of products from W:Li = 1:1, 1:2 and 1:3 all had M_{wp} similar to those obtained by the same catalyst ratio in series A (see table 4.1.2.1). However the SEC trace for the 1:2 and 1:3 ratios showed relatively large amounts of the LMWP. These samples were analysed using pen and chart recorder and there was negligible absorbance at 254nm. The overlap of the two peaks made it impossible to calculate the polydispersities accurately.

The experiment with the premixed WCl_6:BuLi catalyst system, in the ratio 1:1, was repeated at a later date so that it could be compared with the results for the original polymerization and analysed using the computerised data collection, for both RI and UV/VIS detectors. The brown polymerization mixture went viscous within 15 minutes and was precipitated after 30 minutes. After purification and drying a yield of 20% was obtained and the SEC analysis of the 0.5%(wv) solution in THF is shown in figure 4.2.1.

FIGURE 4.2.1 THE SEC TRACES FOR BOTH DETECTORS FOR THE PRODUCT USING PREMIXED WCl_6/BuLi (1:1). CATALYST SYSTEM.



The ^{1}H and ^{13}C NMR spectra of the product (figures 4.4.9 and 4.4.10) were very similar to those obtained from series A experiments with this catalyst system although the ^{13}C spectrum showed differences in the micro-structure the polypentenylene samples, with a slightly higher fraction of *cis*-double bonds (see section 4.4). The relatively large amount of oligomeric material observed in some of these experiments, with premixed catalyst systems, was not evident in this product. However the low absorbance at 254nm. was noticeable (YV:RI peak area<0.1).

4.2.2 The effect of the premixed WCl_6:*s*-BuLi ratio on the ROMP of cyclopentene.

The procedure described in 2.5.1.2 was followed using the ratios of WCl_6:*s*-BuLi given in table 4.2 and similar quantities to those quoted in 4.2.1. The purified products were obtained and analysed by SEC.

The brown, premixed catalyst systems had a slight precipitate. When added to the monomer solution the colour was unchanged and the mixture appeared homogeneous in all cases. The mixtures, with the W:Li ratios of 1:0.2 and 1:2.0, showed no increase in viscosity and only the former produced a precipitate when the reaction solutions were added to degassed methanol after 24 hours. The other two reaction mixtures became viscous with the catalyst mixture of W:Li of 1:1 again increasing in viscosity in the shortest time.

TABLE 4.2.3. SERIES B ROMP OF CYCLOPENTENE USING PREMIXED WCl_6:*s*-BuLi AS THE CATALYST SYSYTEM.

W: Li ratio	% yield	Time /h.	M_{wp} for HMWP /g.mol.$^{-1}$.	PDI for HMWP.	UV:RI area for HMWP.	M_{wp} for LMWP /g.mol.$^{-1}$.
1: 0.2	4	24	440 000	2.7	-	-
1: 0.5	11	3	260 000	2.5	-	2000
1: 1.0	45	1	80 000	2.2	-	1000
1: 2.0	none	24	-	-	-	-

The results are shown in table 4.2.3. The relative amounts of oligomeric material were not significantly different from that obtained in series A experiments and there was no absorbance detected by the chart recorder at 254nm. The W:Li ratio 1:1 again produced the fastest reaction for these premixed systems. The HMWP for this ratio has a lower M_{wp} (80 000g.mol.$^{-1}$) than the values (160 000 and 120 000g.mol.$^{-1}$) obtained using WCl_6:BuLi in the ratio 1:1 in series B. Similar trends were found in series A experiments.

These WCl_6/butyllithium premixed catalyst systems did not produce a significantly different product mixture from that obtained by sequential addition and so the repetition of these experiments and further analysis of the products by SEC, using the computerised data collection system, was considered to be unnecessary.

4.2.3. The effect of solvent on the ROMP of cyclopentene using premixed WCl_6:$AlEtCl_2$ in the ratio 1:1.

The previous experiments had indicated that the ratio of WCl_6:co-catalyst of 1:1 in the premixed catalyst system produced the most rapid polymerization in terms of the yield and observed increase in viscosity. In this series the co-catalyst $AlEtCl_2$ was premixed with WCl_6 in a 1:1 ratio and the reaction was carried out using first toluene and then cyclohexane as the main solvent.

In the first experiment the co-catalyst solution of 0.4M$AlEtCl_2$/cyclohexane, prepared as described in 4.1.2.2.1 from liquid $AlEtCl_2$ in a canister, was premixed with the WCl_6 in a 1:1 ratio and the method outlined in 2.5.1.2 was adopted. The premixed catalysts formed a red solution and when this was added after 1 minute to the 3M cyclopentene in toluene, the solution darkened and became viscous within five minutes and solid after 25 minutes. The extraction and purification of the product was extremely difficult because of its low solubility.

In a similar experiment cyclohexane was used as the solvent for the monomer. The other conditions were maintained and 0.3cm^3 0.4M $AlEtCl_2$/cyclohexane

(1.2x10^{-3} moles) and 4cm^3 0.03M WCl$_6$/toluene (1.2x10^{-3} moles) were premixed and added to 4.2g (0.061 moles) of cyclopentene in 14.8cm^3 cyclohexane. The red premixed catalyst mixture went brown and only slightly more viscous after 30 minutes. The solution was poured into degassed methanol and the precipitate was treated and analysed as normal. The results of yield and SEC analysis are given in table 4.2.4.

TABLE 4.2.4 SERIES B ROMP OF CYCLOPENTENE IN DIFFERENT SOLVENTS USING PREMIXED WCl$_6$: AlEtCl$_2$ IN THE RATIO 1:1 AS THE CATALYST SYSYTEM.

Solvent for 1:1 ratio	% yield	Time / m.	M$_{wp}$ for HMWP /g.mol.$^{-1}$.	PDI for HMWP.	UV:RI area for HMWP.	M$_{wp}$ for LMWP /g.mol.$^{-1}$.
toluene	>30	30	1 600 000	3.3	0.4	2000
cyclohexane	18	30	100 000	2.3	0.1	1000

FIGURE 4.2.2. SEC TRACES FOR BOTH DETECTORS USING PREMIXED WCl$_6$/AlEtCl$_2$ (toluene)(1:1). CATALYST SYSTEM.

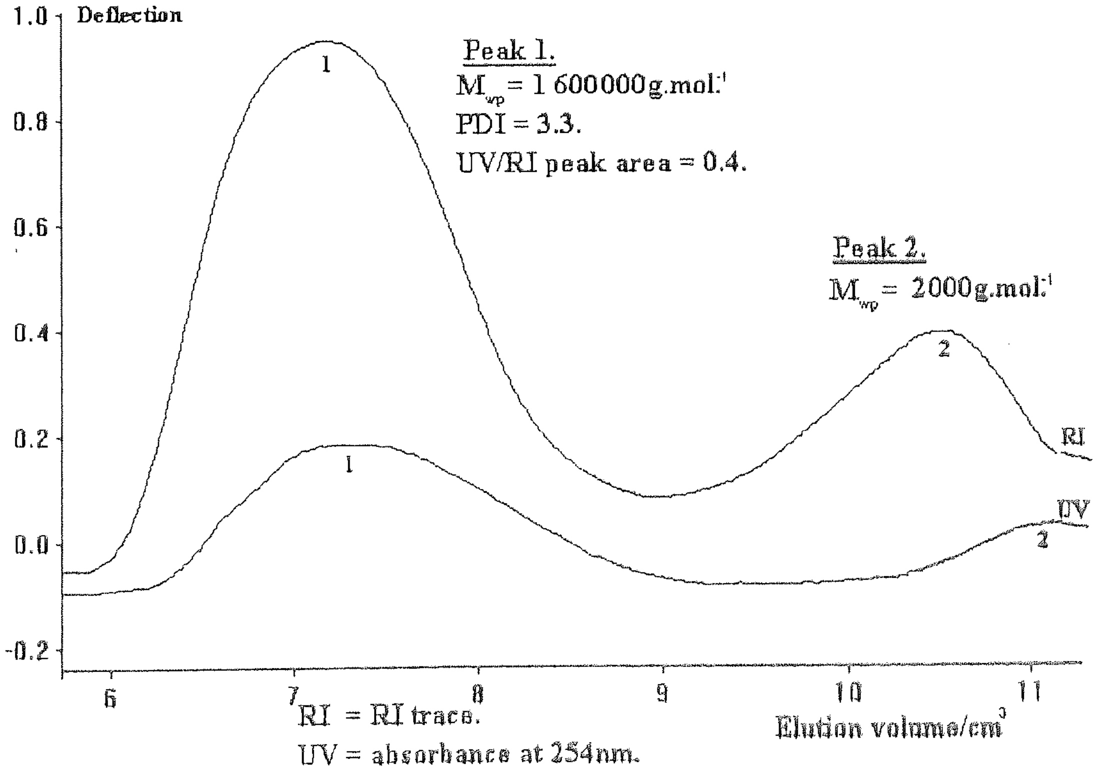
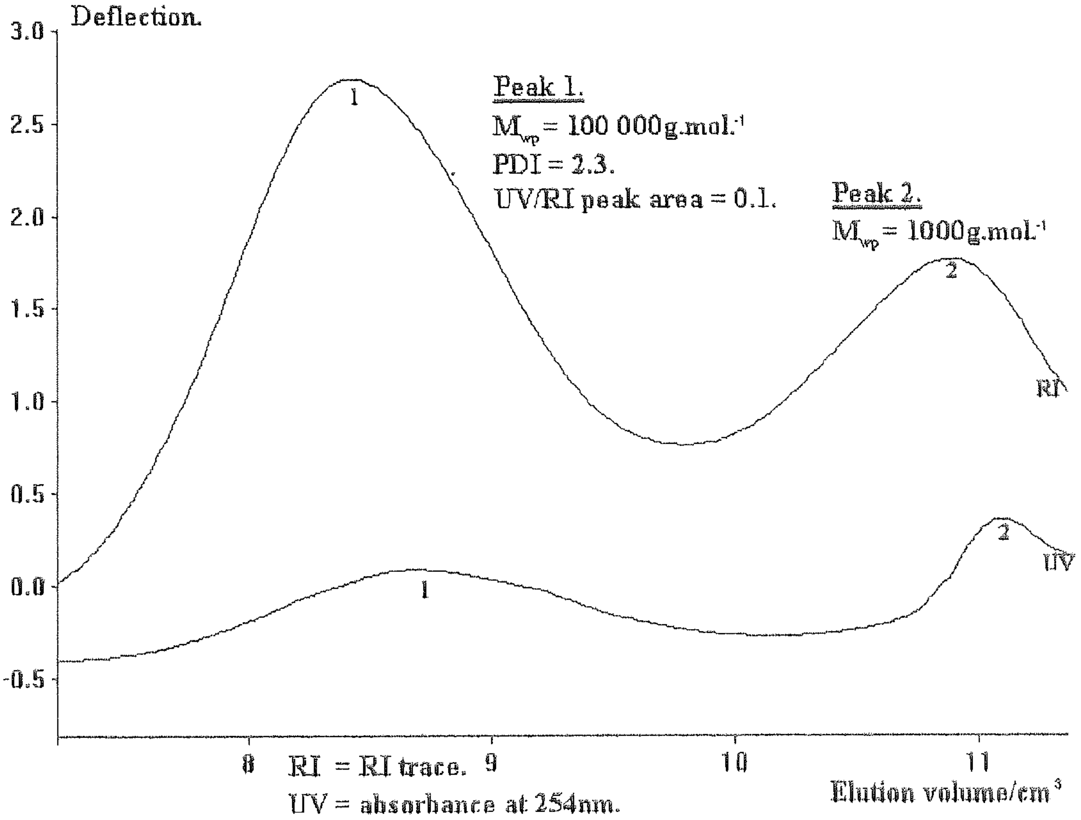


FIGURE 4.2.3. SEC TRACES FOR BOTH DETECTORS USING PREMIXED $WCl_6/AlEtCl_2$ (cyclohexane)(1:1). CATALYST SYSTEM.



Figures 4.2.2 and 4.2.3 show the SEC traces using UV/VIS and RI detectors for both products. The premixed $WCl_6/AlEtCl_2$ system in toluene not only reacted very rapidly but also produced polymer of extremely high peak molecular weight, broad PDI and relatively high absorbance at 254nm.. The relatively large amount of LMWP was evident in the SEC trace. Surprisingly the same catalyst system in cyclohexane also produced both high and low molecular weight material although series A experiments with this catalyst/solvent system had been unsuccessful.

The successful polymerization produced by these premixed catalyst system was unexpected. Tuck[186] and Zurimendi[107] had found that the premixed $WCl_6/Al(iBu)_3$ catalyst system produced only low molecular weight material with cyclopentene. It was decided these experiments should be repeated with both solvent systems using fresh $2MAlEtCl_2$/toluene solution as the co-catalyst.

The addition of the premixed $WCl_6/AlEtCl_2$ catalyst system to 3M cyclopentene in cyclohexane produced no polymer when the reaction mixture was poured into degassed methanol after 2 hours. When the same premixed catalyst system, in the ratio 1:1, was added to 3M cyclopentene/toluene it produced a very small amount of elastomer (about 2% yield) after the same reaction time. The HMWP had a M_{wp} of 80 000g.mol.$^{-1}$ and the value for the LMWP was about 1000g.mol.$^{-1}$. The absence of high molecular weight polymer was in accordance with the findings of Tuck and Zurimendi. A full analysis of the oligomeric material would require a different technique to purify the product, which Zurimendi found to be an oily liquid.

The purity of the liquid $AlEtCl_2$ was questioned as the rapid polymerization, using the premixed catalyst system, could not be reproduced using other sources of the co-catalyst. Partial oxidation of the aluminium compound may account for its ability to polymerise the cyclopentene so rapidly. Only stock solutions of $AlEtCl_2$ were used in subsequent work.

4.3. SERIES C. THE SEQUENTIAL ADDITION OF ETHANOL,THE CATALYST (WCl_6) AND THE CO-CATALYST.

The beneficial effect of small amounts of oxygen containing additives in metathesis catalysis systems was first recognized by Calderon[7,8] for $WCl_6/AlEtCl_2$ catalysts. A few experiments were carried out using the procedure outlined in section 2.5.1.3 in order to compare the yield of polypentenylene obtained with those achieved in series A and B and to analyse the product using SEC as before and to assess the potential use of oxygen activators in the W/Li catalyst system.

The WCl_6:EtOH:co-catalyst ratio was 1:1:1 and only BuLi and *s*-BuLi were used as co-catalyst. In the first of these experiments 7.4g (0.11moles) of cyclopentene and 23.5cm^3 of toluene were vacuum distilled into a reaction flask. The Schlenk technique was used to inject 0.25cm^3 0.8M (2.0×10^{-4} moles) ethanol/toluene into the monomer solution and then after a delay of 2 minutes $10cm^3$ $0.02MWCl_6$ ($2.0x10^{-4}$ moles) and $0.15cm^3$ 1.6MBuLi ($2.0x10^{-4}$ moles) were added by syringe.

The presence of the ethanol in the monomer solution meant that, when the dark blue WCl_6/toluene solution was injected, the solution went red. Addition of the BuLi or *s*-BuLi solution produced a red/brown mixture and both had increased in viscosity when they were added to degassed methanol after 2 hours. The yield and SEC data is given in table 4.3.1.

TABLE 4.3.1. DATA FOR SERIES C ROMP OF CYCLOPENTENE USING THE CATALYST SYSTEM: WCl_6: ETHANOL: BuLi OR s- BuLi.

W:EtOH:Li ratio/co-cat	% yield.	Time /h.	M_{wp} for HMWP /g.mol.$^{-1}$.	PDI for HMWP.	UV:RI area for HMWP.	M_{wp} for LMWP /g.mol.$^{-1}$.
1:1:1BuLi	21	2	90 000	2.6	negligible	1000
1:1:1*s*-BuLi	48	2	80 000	2.2	negligible	1000

The reaction rate of these experiments was not significantly different from that obtained without the ethanol. There was insufficient time to repeat these experiments and analyse the product using the computerised data collection system.

Table 4.3.2 summarises the results obtained, using the three different procedures, for the WCl_6/BuLi and the WCl_6/*s*-BuLi catalyst systems using a 1:1 ratio. The values quoted are not the fastest reactions for series A but provide a direct comparison of the 1:1 catalyst ratio. They show that all three systems produce reactions of similar rate and product composition. The addition of ethanol did not dramatically increase the rate of polymerization and the ratio of oligomer to high molecular weight polymer was similar in all three series using butyllithium co-catalysts.

TABLE 4.3.2. TO SHOW THE YIELD AND SEC DATA FOR THE PRODUCTS OF ROMP CYCLOPENTENE/TOLUENE BY WCl_6: BuLi AND *s*-BuLi IN THE RATIO 1:1 USING **SERIES A,B** AND C.

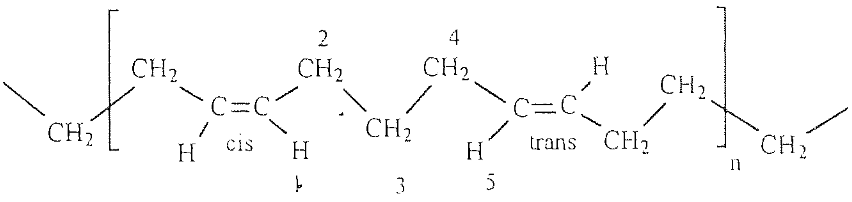
Series / co-catalyst.	% Yield	Time / h.	M_{wp} for HMWP / g.mol^{-1}.	PDI for HMWP	M_{wp} for HMWP / g.mol^{-1}.
A / BuLi	18	1	150 000	1.6	2000
B / BuLi	47	1	120 000	1.6	1000
C / BuLi	21	2	90 000	2.6	1000
A /*s*-BuLi	30	24	100 000	1.6	1000
B /*s*-BuLi	45	1	80 000	2.2	1000
C /*s*-BuLi	49	2	80 000	2.2	1000

4.4 NMR ANALYSIS OF THE POLYPENTENAMER.

^{1}H and ^{13}C NMR spectroscopy was used, as described in section 2.6.3, to obtain more information about the structure of the polypentenylene product of these ROMP reactions. The microstructure of metathesis polymers was discussed in section 1.7. Cyclopentene is an unsubstituted, monocyclic monomer and so only produces *cis*-(c) and *trans*-(t) stereoisomers. The nature of the double bonds affects the chemical shift (δ) of the methine protons (1 and 5) and also the ^{13}C resonance for the trigonal carbons (1 and 5). The stereo-chemistry of the alkene bonds either side of the methylene groups affects their ^{13}C signal and the different dyad structures for both the α or allylic CH_2 (2 and 4) and β CH_2 (3) are shown in the diagram 4.1.

The chemical shift for the alkene protons is only slightly different for *cis*- (δ= 5.42ppm) and *trans*- ($\delta = 5.48$ppm) double bonds and the ^{1}H spectrum in figure 4.4.1 shows an overlap of these peaks ($5.2 \leq \delta \leq 5.5$ppm). The methylene protons of polypentenylene are α^1H(2,4) at $\delta \approx 2.0$ppm. and β^1H(3) at $1.27 \leq \delta \leq 1.48$ppm.

TABLE 4.4.1. ¹H NMR FOR POLYPENTENYLENE (WCl_6/BuLi CATALYST).



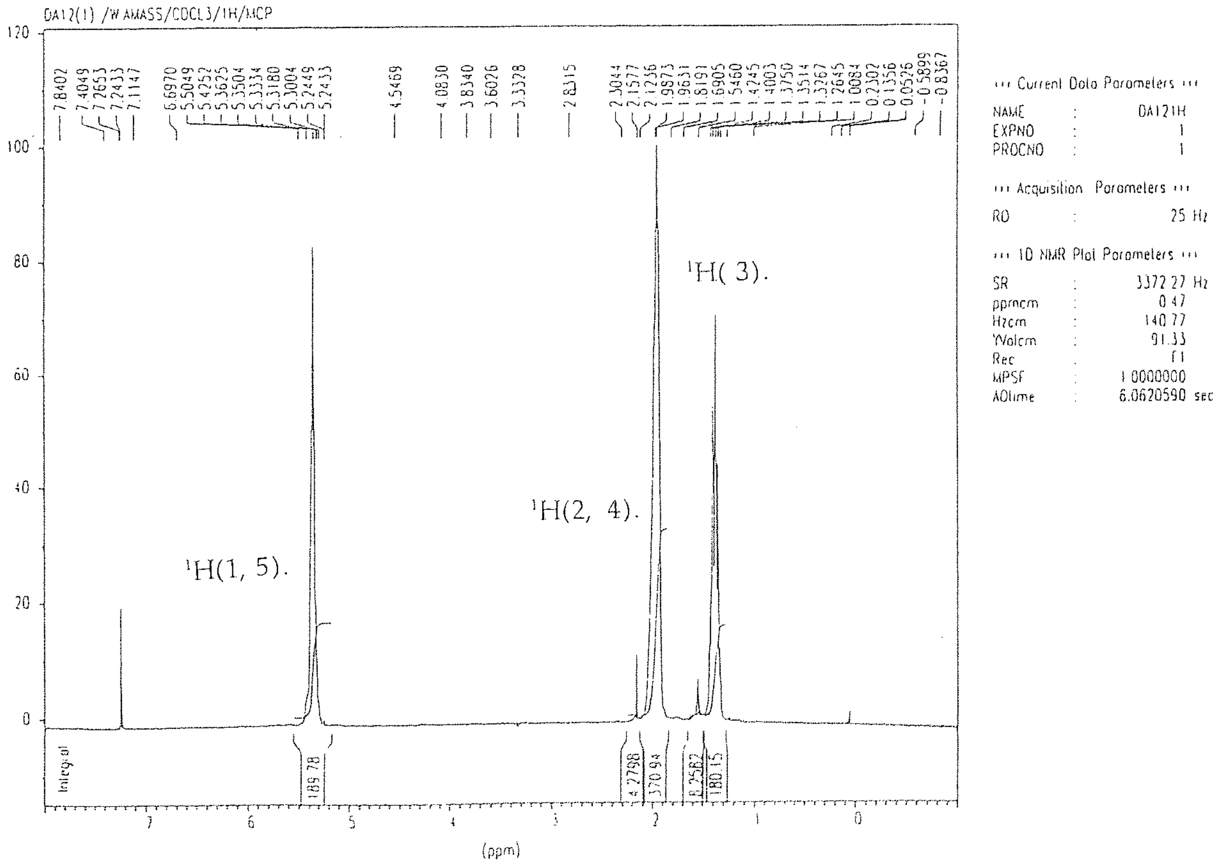
Section of polymer chain M_n = 120 000g.mol^{-1}.

Empirical formula = [CH-$(CH_2)_3$-CH]

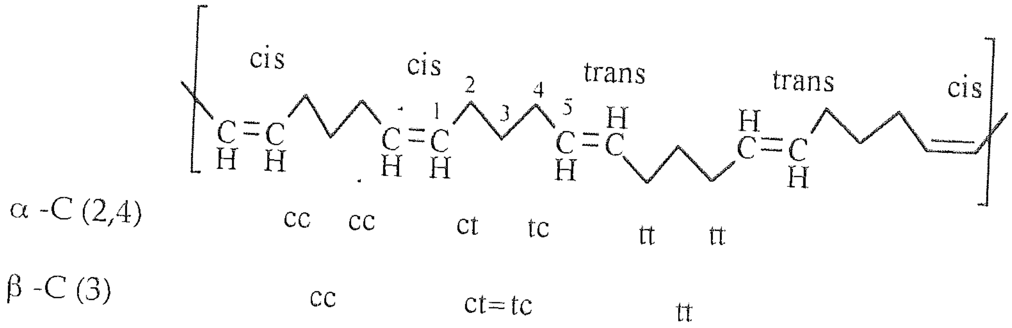
= [C_5H_{10}].

¹H type.	$\delta_{theo.}$/ ppm	$\delta_{act.}$/ ppm.	% Area theoretical.	% Area from ¹H NMR
methine ¹H (*cis*-1)	5.42	5.17-5.55	25	25.6
methine ¹H (*trans*-5)	5.48			
methylene ¹H (2, 4)	2.30	1.84-2.19	50	50
methylene ¹H (3)	1.51	1.27-1.48	25	24.3

FIGURE 4.4.1. ¹H NMR FOR POLYPENTENYLENE.



Methylene dyad structure.

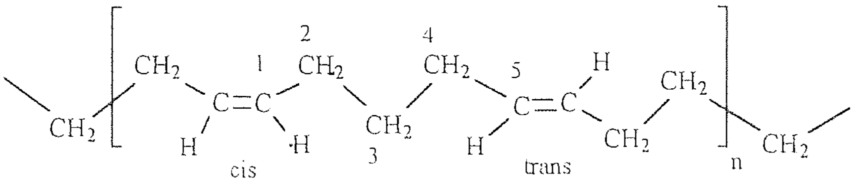


4.1

The ^{13}C NMR spectrum of polypentenylene has been used by Ivin et al[63] to investigate the *cis/trans*-structure of the polymer formed using different metathesis catalysts. The trigonal carbons of a *cis*-double bond come into resonance about 1ppm. downfield (δ =128ppm) relative to the signal from the same carbon of the *trans*-isomer (δ =129ppm) as seen in figure 4.4.2. The relative intensity of the peaks can be related to the fraction of *cis*-double bonds (σ_c). The σ_c is 0.19 in this sample.

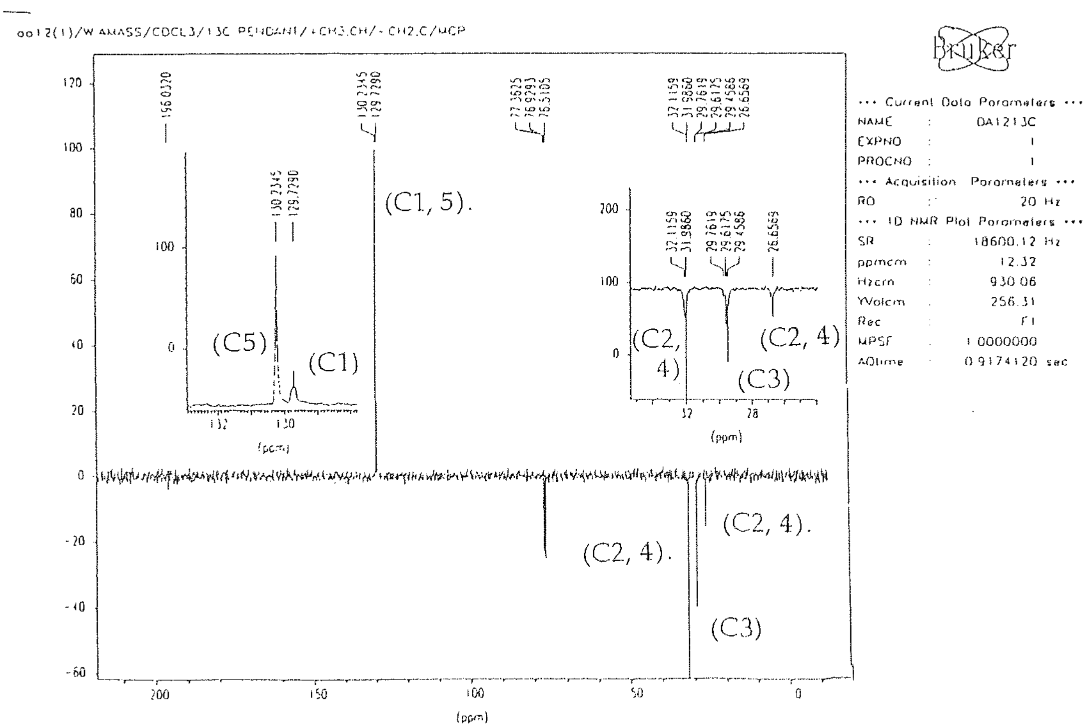
The splitting of the signal for the α and β C atoms is even more pronounced. The allylic-C(2) adjacent to a *cis*-double bond comes into resonance 2-3 ppm. downfield (δ=27ppm.) of the β C(3) (δ=29-30ppm.). The influence of the dyad structure (see **4.1**) produces two lines for the (cc) and (ct) arrangements for the α C. If the allylic-C(4) is next to a *trans*-double bond it has a chemical shift a further 2-3 ppm upfield (δ=32ppm.). Again (tt) and (tc) dyads produce splitting and figure 4.4.3 shows the two peaks. The β C(3) is affected equally by the stereochemistry of the alkene linkages either side and three peaks are produced (tt at 29.6ppm., tc=ct at 29.7ppm. and cc at 29.8ppm.), all are evident in figure 4.4.3. The dominance of the *trans*-alkene structure in the polypentenylene produced using WCl_6/BuLi is again evident from the relatively low intensity of the cc peaks compared to the tt peaks. It must be remembered that secondary metathesis reactions occur and so the structure of product formed after a long period yields little information about the ring-opening addition but this product was precipitated after only ten minutes reaction time.

TABLE 4.4.2 ^{13}C NMR FOR POLYPENTENYLENE (WCl$_6$/BuLi CATALYST).



^{13}C identity./ + CH_3 or CH and - CH_2 or C.	δ_{theo}/ ppm.	δ_{act}/ ppm.
Trigonal *trans* CH (C5)	128.9	130.2
Trigonal *cis* CH (C1)	127.8	129.7
Allylic (tc, tt) CH_2 (C2 or 4)	32.2, 32.1	32.1, 32.0
(cc,ct,tt) CH_2 (C3)	29.8, 29.7, 29.6	29.8, 29.6,29.5
Allylic (cc, ct) CH_2 (C2 or 4)	26.9, 26.8	26.8, 26.7

FIGURE 4.4.2 ^{13}C NMR FOR POLYPENTENYLENE (WCl$_6$/BuLi CATALYST).



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Hzcm      :         930.06
YValcm    :         256.31
Rec       :             F1
MPSF      :      1.0000000
AQtime    :   0.9174120 sec
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The NMR spectra of polypentenylene, shown in figures 4.4.3 to 4.4.6, are from samples produced using the two component catalyst systems WCl_6/*s*-BuLi and WCl_6/$AlEtCl_2$ respectively. The structure of the polymer and the fraction of *cis*-double bonds (σ_c=0.20) are almost identical to that of the polypentenylene formed using BuLi as the co-catalyst. However the ^1H spectrum from the polymer produced using $AlEtCl_2$ as the co-catalyst, has resonance peaks that cannot be easily interpreted, particularly in the methylene resonance region ($1.6<\delta<1.8$ppm). The spectra for the polypentenylene obtained using the three component catalyst systems (WCl_6/$AlEtCl_2$/BuLi or *s*-BuLi) (see figures 4.4.7 and 4.4.8) were identical to those produced from two component W/Li catalyst systems.

Finally the polymer from the series B experiment, to prepare polypentenylene by premixing WCl_6/BuLi and described in section 4.2.1, was analysed and the proton and ^{13}C spectra are shown in figure 4.4.9 and 4.4.10. Although the structures are identical the σ_c at 0.30 is significantly higher.

FIGURE 4.4.3. ^{1}H NMR FOR POLYPENTENYLENE (WCl$_6$/*s*-BuLi CATALYST).

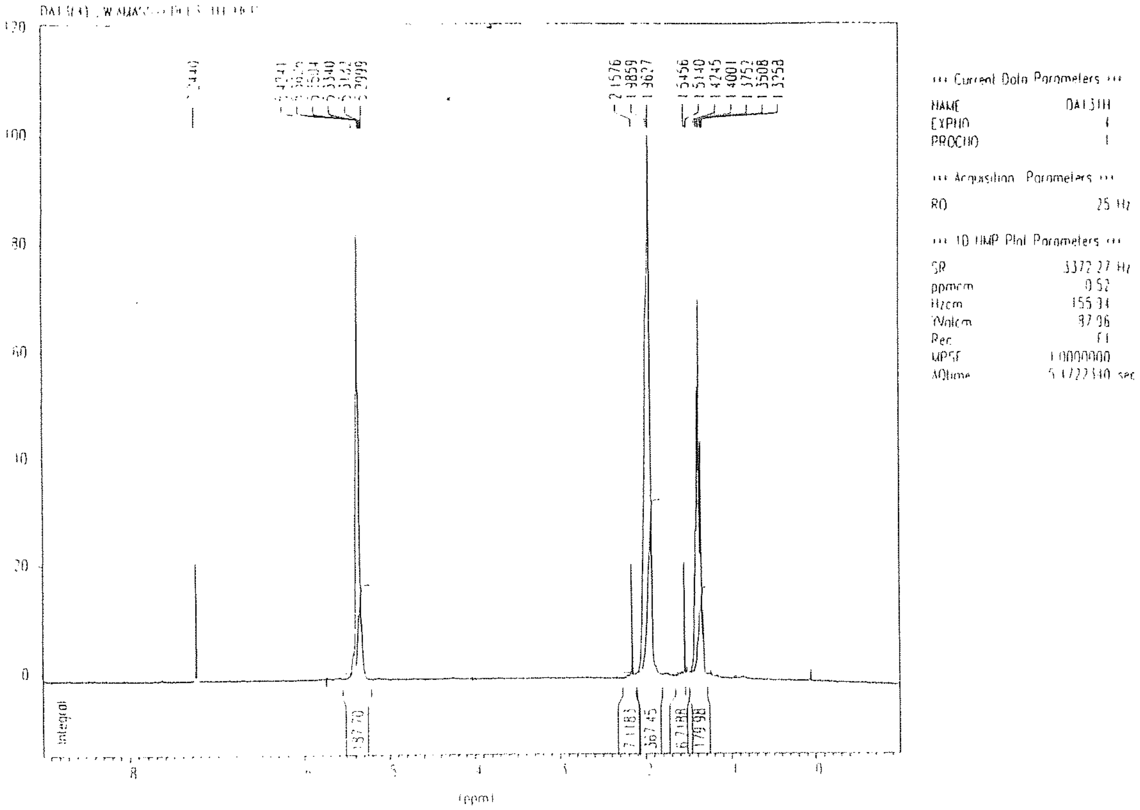

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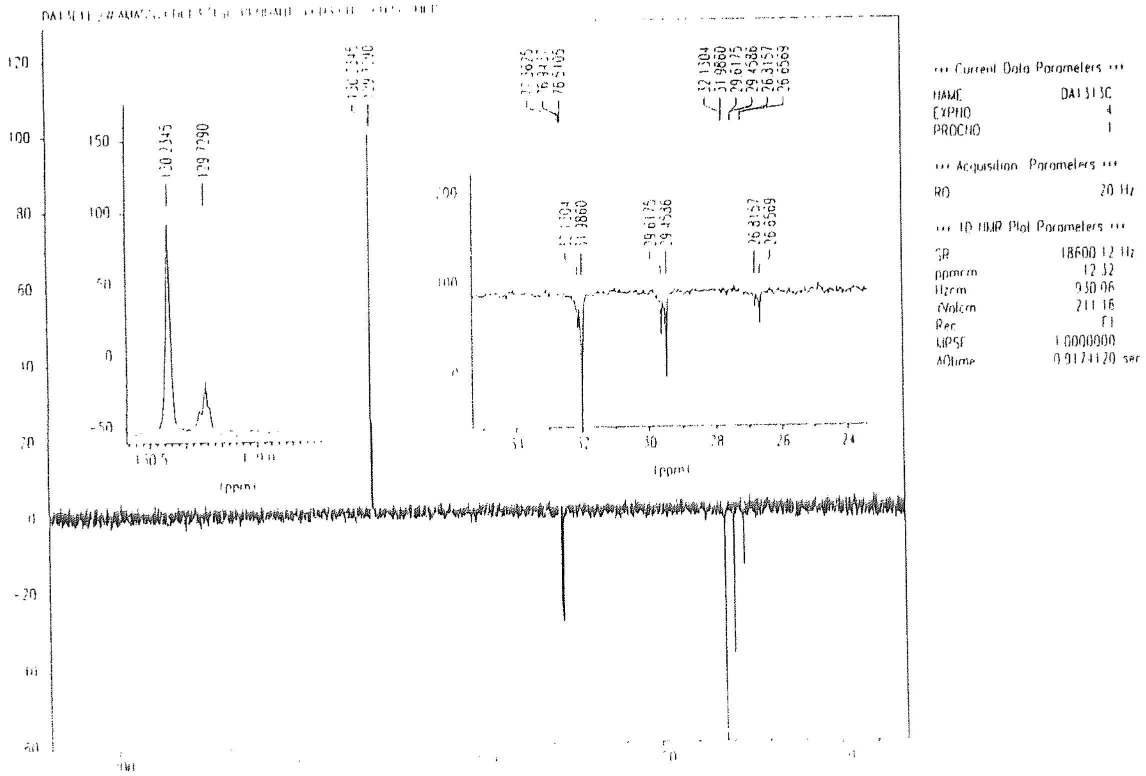
FIGURE 4.4.4 ^{13}C NMR FOR POLYPENTENYLENE (WCl$_6$/*s*-BuLi CATALYST).



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%Valcm            211.16
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NPSF           1.0000000
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FIGURE 4.4.5 ^{1}H NMR FOR POLYPENTENYLENE (WCl$_6$/AlEtCl$_2$ CATALYST).

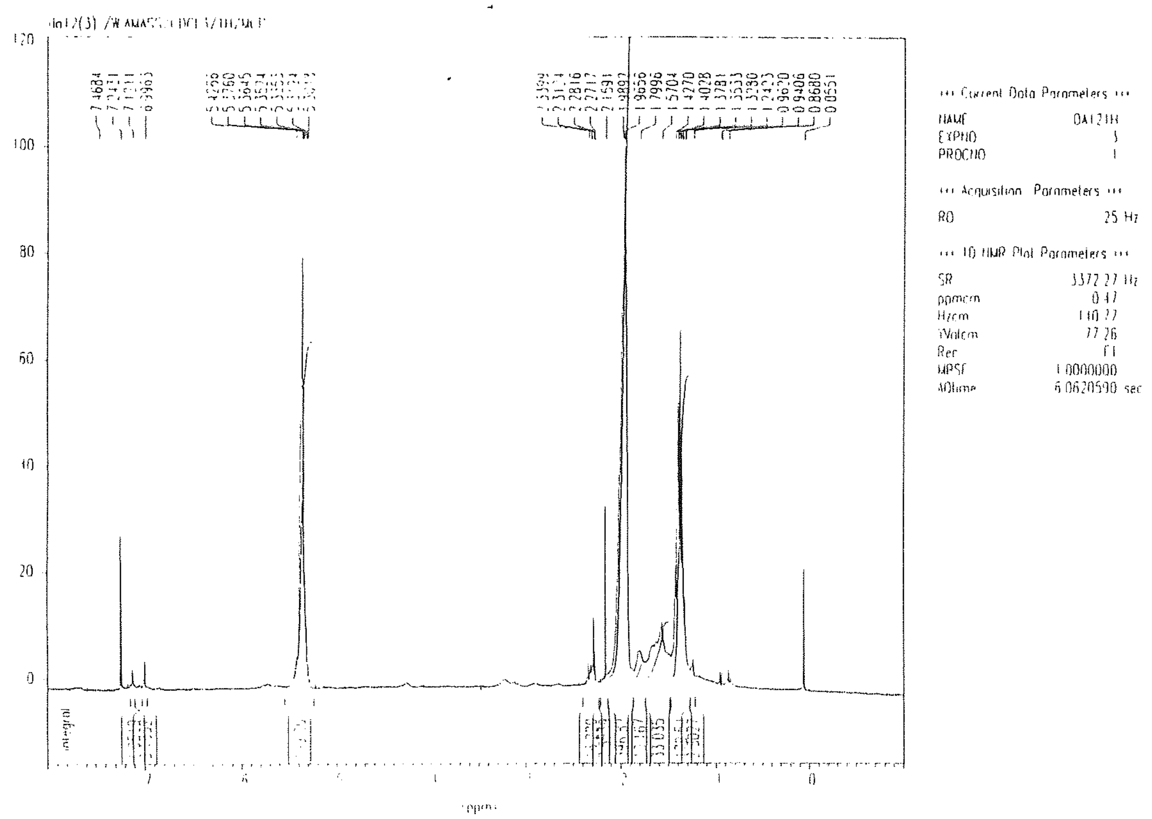


FIGURE 4.4.6 ^{13}C NMR FOR POLYPENTENYLENE (WCl$_6$/AlEtCl$_2$ CATALYST)

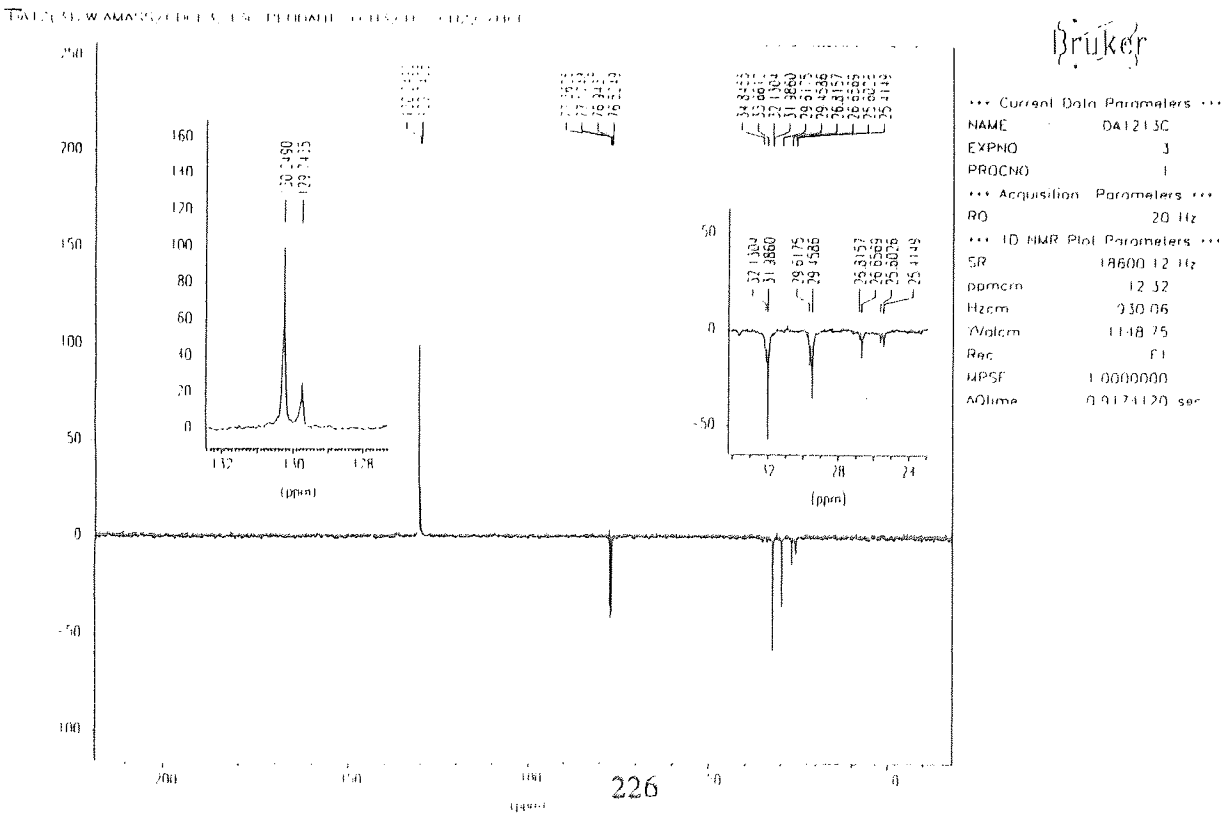


FIGURE 4.4.7 ^{1}H NMR FOR POLYPENTENYLENE (WCl_6/BuLi/$AlEtCl_2$ CATALYST).

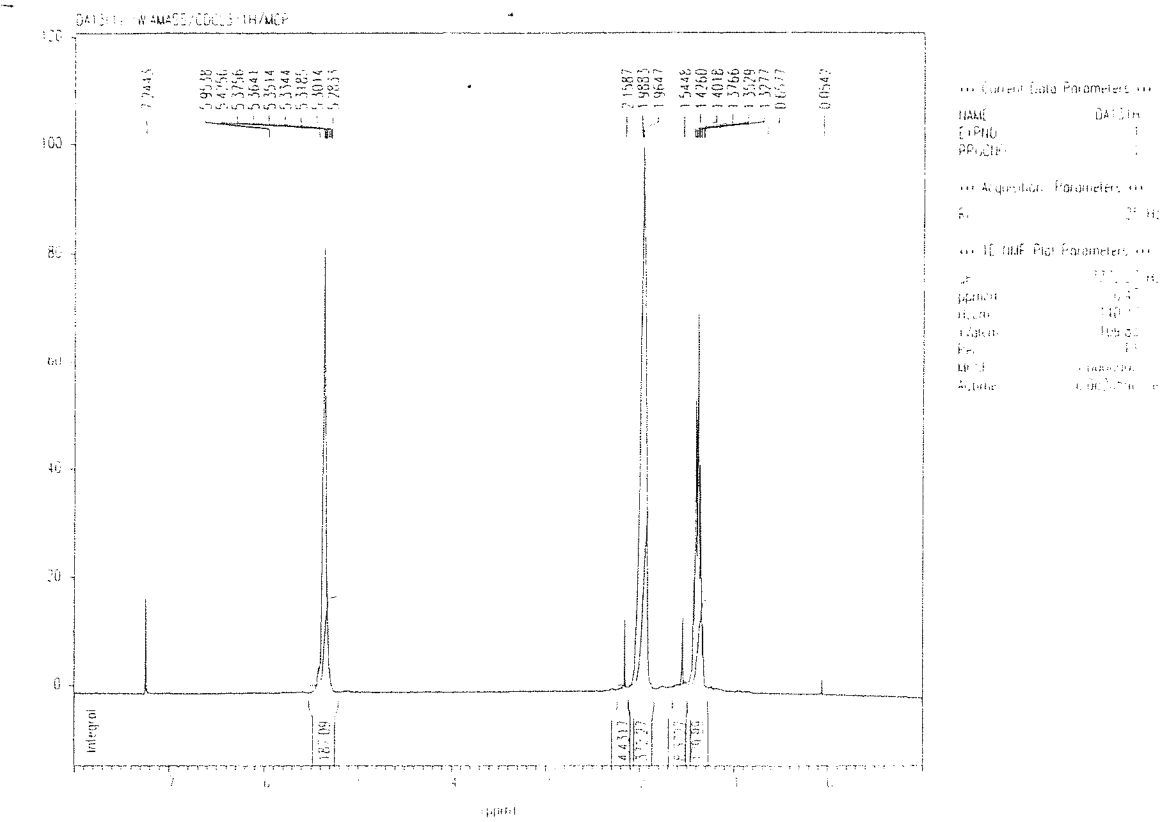


FIGURE 4.4.8 ^{13}C NMR FOR POLYPENTENYLENE (WCl_6/BuLi/$AlEtCl_2$ CATALYST).

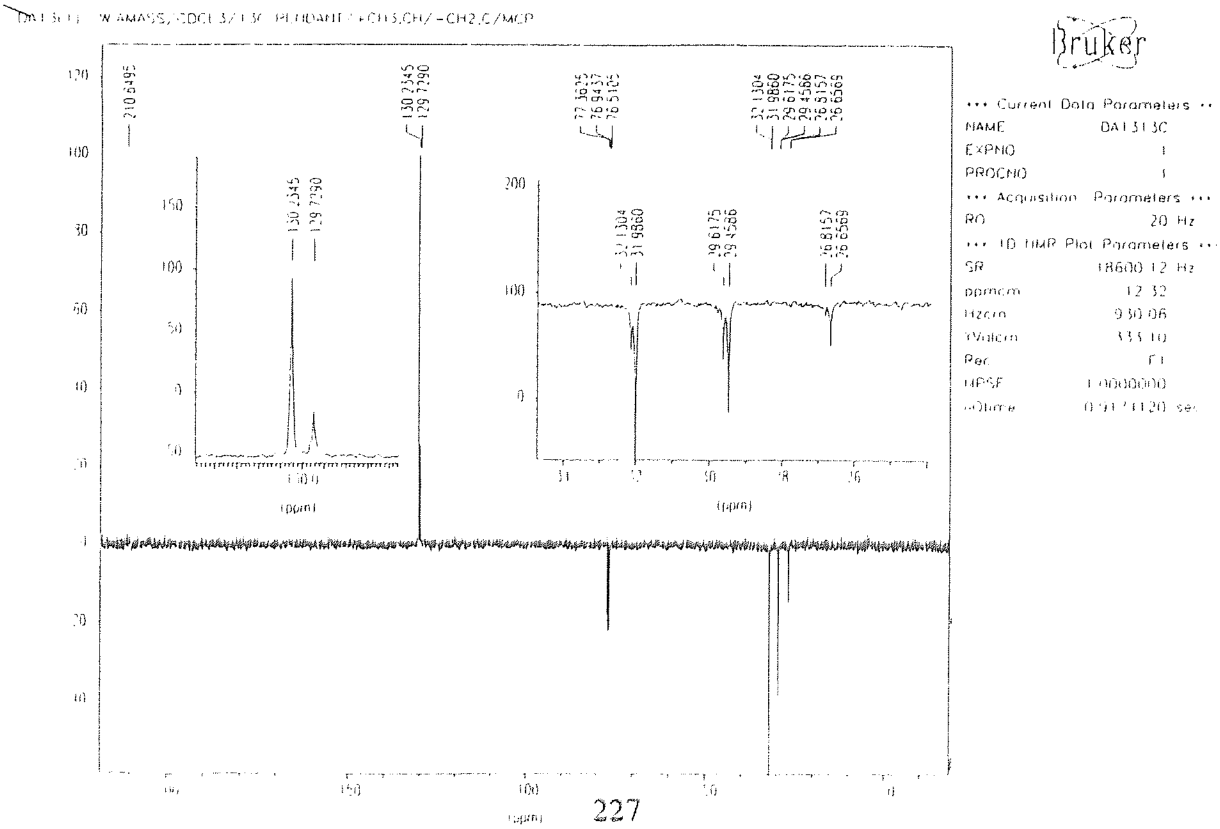


FIGURE 4.4.9. ^{1}H NMR FOR POLYPENTENYLENE-SERIES B (WCl$_6$/BuLi CATALYST).

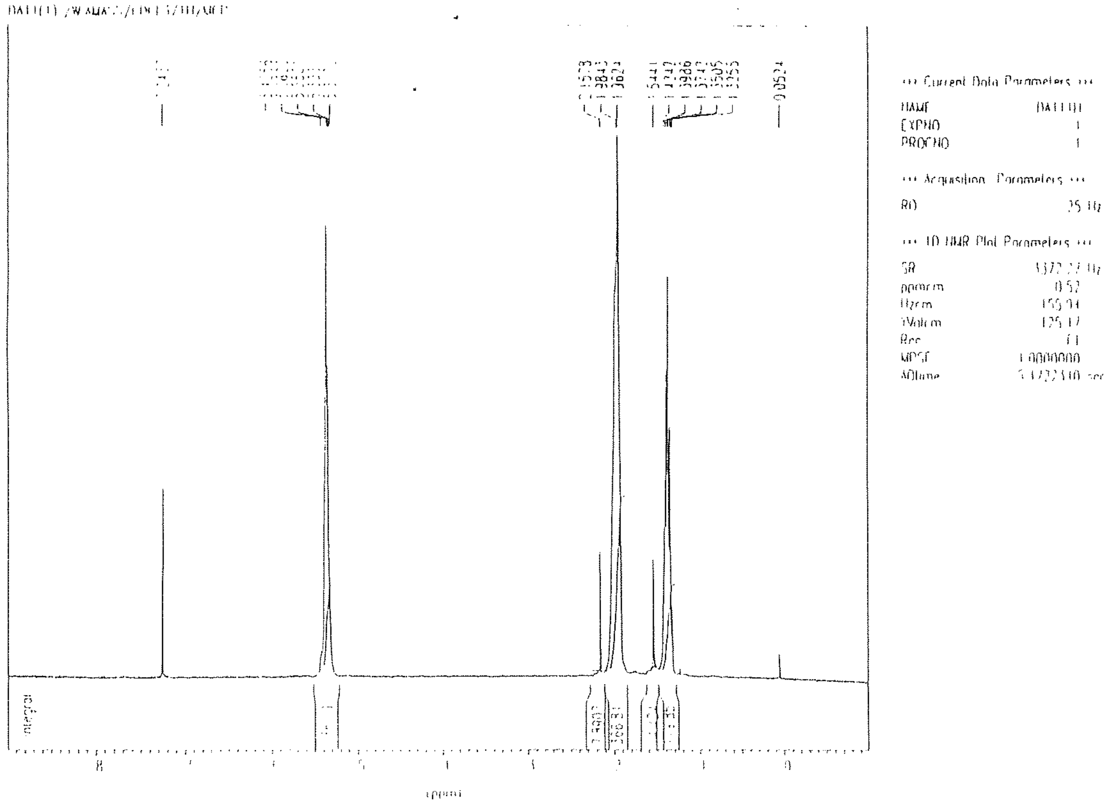
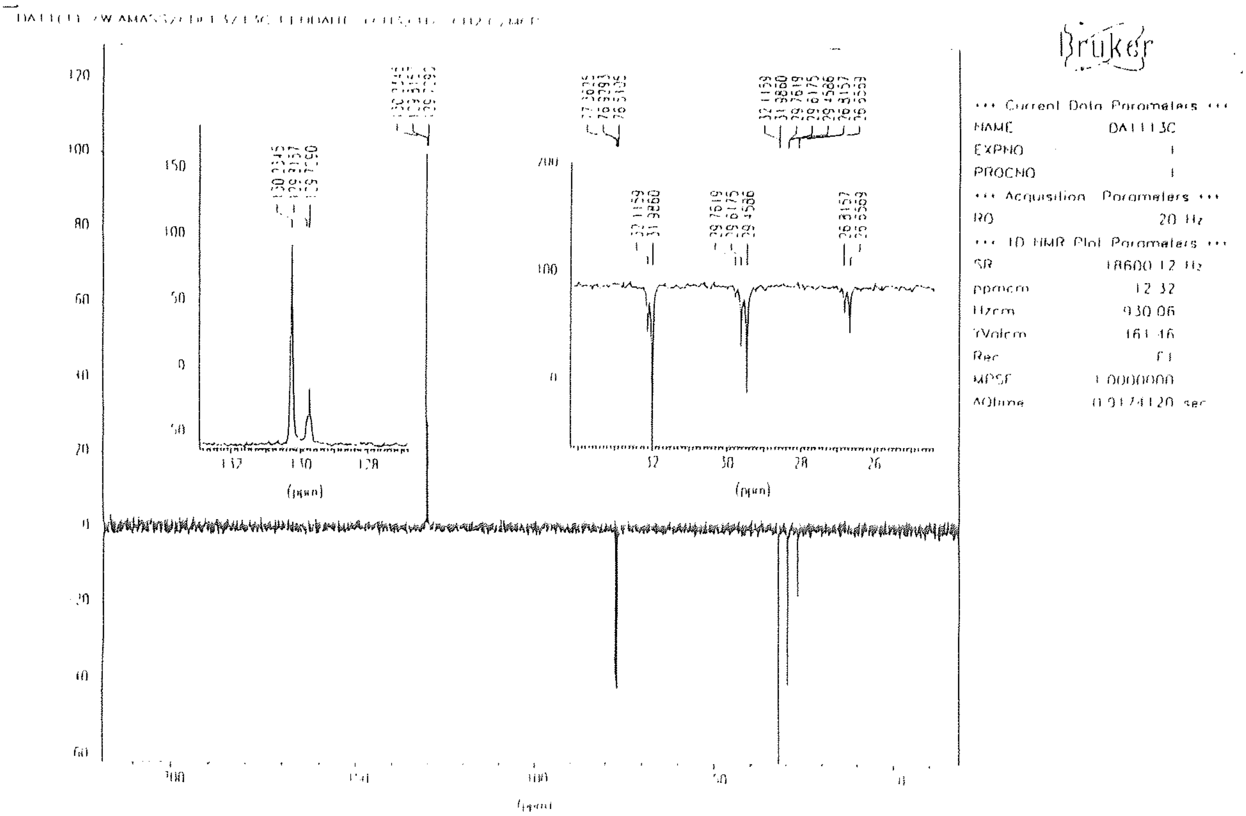


FIGURE 4.4.10 ^{13}C NMR FOR POLYPENTENYLENE SERIES B (WCl$_6$/BuLi CATALYST)



CHAPTER 5.

RING-OPENING METATHESIS POLYMERIZATION OF CYCLOPENTENE

PART 2 .

5.1 ROMP OF CYCLOPENTENE USING WCl_6 AND PStLi.

Gregory[184] reported that the ring-opening polymerization of cyclopentene, using the catalyst system WCl_6/PStLi, resulted in the formation of two products, which were postulated to be block co-polymers. The products were separated by fractional precipitation and analysed by IR spectroscopy and SEC. The SEC analysis also showed that the number average molecular weight of the polystyrene, used as the co-catalyst, was much higher than the theoretical value. However a high molecular weight, polypentenylene-rich material, with UV absorbance at 254nm, was identified and a low molecular weight, polystyrene-rich product was also obtained. The existence of AB or ABA block co-polymers was mooted but the exact nature of the product was not established.

Thorn-Csanyi[183] investigated the same metathesis polymerization using the catalyst systems WCl_6/EtOEt/PStLi and $WOCl_4$/PStLi and separated and characterised the products using first SEC then IR, UV and ^1H NMR spectroscopy. The degree of polymerization of the polystyryllithium was varied and the conclusions drawn were that oligostyryllithium (DP_n<6) was involved in the initiation of metathesis polymerization and was identified as a terminal unit on the polypentenylene chain. However although polystyryllithium (DP_n>30) also acted as a co-catalyst for the ROMP, analysis of the products indicated that polystyrene terminated species were present in only very small amounts, and it was deduced that more than one chain initiation mechanism had occurred.

The aim of this study was to establish the reaction conditions for the optimum rate of polymerization of cyclopentene, using the catalyst system WCl_6/PStLi. SEC and ^1H and ^{13}C NMR spectroscopy were used to analyse the purified, dry products to determine their nature and to provide information about initiation of the metathesis reaction and the propagating carbene. The viability of the transformation from anionic to metathesis polymerization to form block co-polymers could then be assessed.

Polymerizations were carried out using the three procedures outlined in section 2.5.2 (A, B and C) with the catalyst WCl_6 and oligo- or poly-styryllithium co-catalyst, with known degree of polymerization, such that $5<DP_n<250$. After a known reaction time fractional precipitation was used to separate the products. A range of solvent systems were examined to find the best technique for the separation of polystyrene-rich and polypentenylene-rich material.

The calibration of the UV (at 254nm.) and RI deflection areas for the SEC analysis of 0.5% solutions of polystyrene has been described in section 2.6.1.3. The small but significant absorbance of polypentenylene at 254nm, has also been quantified in terms of the UV:RI peak area for both the high and low molecular weight products of the metathesis polymerization. The SEC traces from the polypentenylene products using the WCl_6/PStLi catalyst system were then compared with those from the two homopolymers.

5.2 SERIES A. THE SEQUENTIAL ADDITION OF WCl_6 AND PStLi.

2-3M cyclopentene solutions were polymerized by the sequential addition of the 0.02M WCl_6 catalyst solution and then 0.1M PStLi co-catalyst after a two minute aging time. The polymerization procedure was varied to study the effect of various factors on the rate of polymerization of the cyclopentene and on the yield and nature of the product.

5.2.1. THE EFFECT OF WCl_6:PStLi RATIO.

The ratio of catalyst to co-catalyst of 1:2 has been shown to produce the optimum conditions for the metathesis polymerization of cyclopentene using the range of co-catalysts mentioned in section 4.1.2. The range of WCl_6:PStLi ratios, listed in table 5.2.1., was tested in the same way. The procedure, outlined in section 2.5.2.1 method 1, was followed with a sample of the polystyryllithium being removed for SEC analysis before the metathesis polymerization.

TABLE 5.2.1. THE RANGE OF PStLi SYSTEMS USED FOR **SERIES A** ROMP OF CYCLOPENTENE WITH CATALYST WCl_6:

Degree of polymerization of co-catalyst. (DP_n)	Range of WCl_6:PStLi ratos tested.
20	**1:** 0.25, 0.5, 1.0, 2.0, 3.0.
50-60	**1:** 1.0, 2.0.

In a typical experiment, 5.0g (0.069 moles) of cyclopentene and 20.0cm^3 of toluene were successively vacuum distilled, into a large, evacuated reaction vessel. 3.8cm^3 0.05M (1.8x10^{-4} moles) WCl_6/toluene solution were injected over argon and two minutes later 4.5cm^3 0.08M PStLi/cyclohexane (DP_n=20 and 3.6x10^{-4} moles of Li) were added, by syringe, over argon. The reaction mixture was kept at 25°C until there were signs of polymerization but a maximum of two days was allowed. Care was taken to keep the volume ratio of toluene to cyclohexane in the final polymerization mixture approximately constant in each experiment and to maintain the overall concentration of the cyclopentene between 2.0 and 3.5M. In the example given [cyclopentene] was 2.0M, there was 69% toluene and 13% cyclohexane.

A single product was precipitated by pouring the mixture into degassed methanol under argon. Purification of this involved redissolving the solid in hexane and precipitating in methanol; the process was repeated until a white solid was produced and all the catalyst residues appeared to have been removed. The sample was dried for 2-3 hours in a vacuum oven at 25°C and the polymerization products were identified by SEC analysis, initially using the chart recorder. The UV/RI area was calculated from these traces but this was a relatively inexact operation.

The dark blue WCl_6/toluene solution went brown when added to the colourless cyclopentene/toluene solution, as expected, but the colour change on the addition of the PStLi varied as did the time taken for the mixtures to become viscous. The yields of the high molecular weight product (HMWP) and the SEC data from the purified precipitates are recorded in table 5.2.2 for PStLi (DP_n=20) and for PStLi (50>DP_n>60).

The WCl_6:PStLi ratios of 1:<1 produced red solutions when the PStLi was added and were only slightly viscous when precipitated after 2 days. The low yield and the very high peak molecular weight (M_{wp}) of the high molecular weight product (HMWP) were very similar to those obtained using WCl_6:BuLi ratios of 1:<0.5 recorded in table 4.1.3. The M_{wp} of the low molecular weight product (LMWP) corresponds to that obtained for the polystyrene, but the polydispersity index increased. It was concluded that the products were a mixture of the homopolymers.

The two experiments using the WCl_6:PStLi ratio of 1:1 produced mauve solutions when the PStLi was added and were moderately viscous when they were precipitated in methanol after 24 hours. The reactions in which the W:Li ratios were 1:2 and 1:3 remained brown when the co-catalyst was added. Using the lower molecular weight PStLi co-catalyst both mixtures showed no increase in viscosity when they were precipitated after 24 hours and the low yields reflected this. The WCl_6:PStLi (DP_n=50) of 1:2 became viscous after several hours and when poured into methanol, purified and dried, produced a similar yield to that obtained with the 1:1 ratio.

All the SEC traces showed three characteristic peaks although the relative heights areas varied. Only if the material showed a significant absorbance at 254nm. were attempts made to compare the UV and RI detector response. Given the inaccuracies involved in the estimation of the relative areas of the UV and RI peaks, it was found that simple comparison of the peak height at the maximum responses gave the most reliable data. Overlap of peaks made it impossible to calculate PDI values accurately.

To compare the effect of aging on the THF solutions of these products, with those obtained from the experiments using the BuLi or Al compounds as co-catalysts, some of the solutions were reanalysed using the computerised data collection procedure. The problem of gel formation restricted the number of

TABLE 5.2.2. **SERIES A** ROMP OF CYCLOPENTENE FOR THE CATALYST SYSTEM WCl_6:PStLi IN THE RATIO 1:X (0.25<X<3.0).

Ratio W:Li [$DP_{n(theo.)}$]	PSt data $\overline{M}_n$ [M_{wp}]	[Cp]/mol.dm^{-3}. {%(vv)toluene} (%(vv)cyclohexane)	% yield	Time / h.	M_{wp} for HMWP /g.mol.$^{-1}$	PDI for HMWP	UV:RI area for HMWP	M_{wp} for LMWP /g.mol.$^{-1}$	Type of LMWP peak.	UV:RI area for LMWP
1: 0.25 [20]	2100 [3000]	[2.6] {70} (6)	<1	48	300 000	broad*	slight*	3000	broad	5.6
1: 0.5 [20]	2100 [3000]	[3.4] {62} (8)	2	48	300 000	broad*	slight*	3000	broad	5.5
1: 1.0 [20]	1800 [2200]	[2.5] {73} (5)	21	24	100 000	1.8*	<0.1*	4000 2000	bimodal	≈4.6 ≈5.6
1: 2.0 [20]	1800 [2200]	[2.0] {72} (12)	4	24	40 000	1.7*	0.1*	4000 2000	bimodal	≈6.9 ≈7.7
1: 3.0 [20]	1800 [2200]	[2.0] {71} (13)	2	24	60 000	1.8*	0.1*	4000 2000	bimodal	≈8.2 ≈8.5
1: 1.0 [60]	6000 [6300]	[2.4] {62} (8)	30	24	70 000	broad• ≈1.8	<0.1• 0.2	12000 6000	bimodal	≈4.2 ≈6.8
1: 2.0 [50]	5200 [6000]	[2.0] {69} (13)	30	24	90 000	broad• ≈1.8	<0.1• 0.3	12000 6000	bimodal	≈6.5 ≈7.2

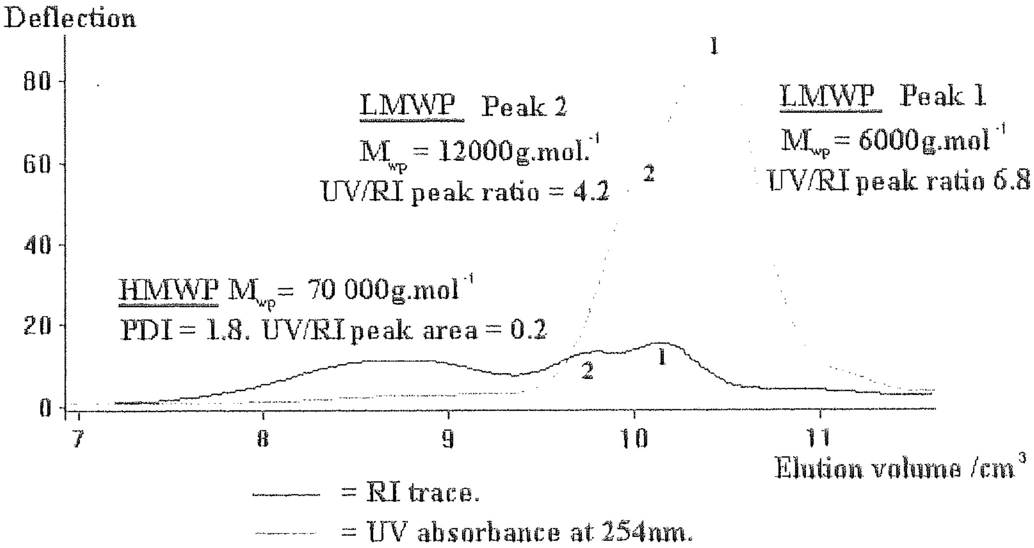
Temperature 25°C. W:Li = catalyst ratio. [$DP_{n(theo)}$] = theoretical number average moecular weight of polystyrene.

$\overline{M}_n$ = number average molecular weight and [M_{wp}] molecular weight at peak for polystyrene. [Cp] = concentration of cyclopentene/mol.dm^3.

* Original SEC data, reanalysis impossible. • Original SEC data, reanalysis possible.

samples that could be reanalysed as indicated in table 5.2.2. A typical SEC trace is shown in figure 5.2.1. for the reanalysis of the W:Li ratio 1:1 (PStLi DP_n= 60).

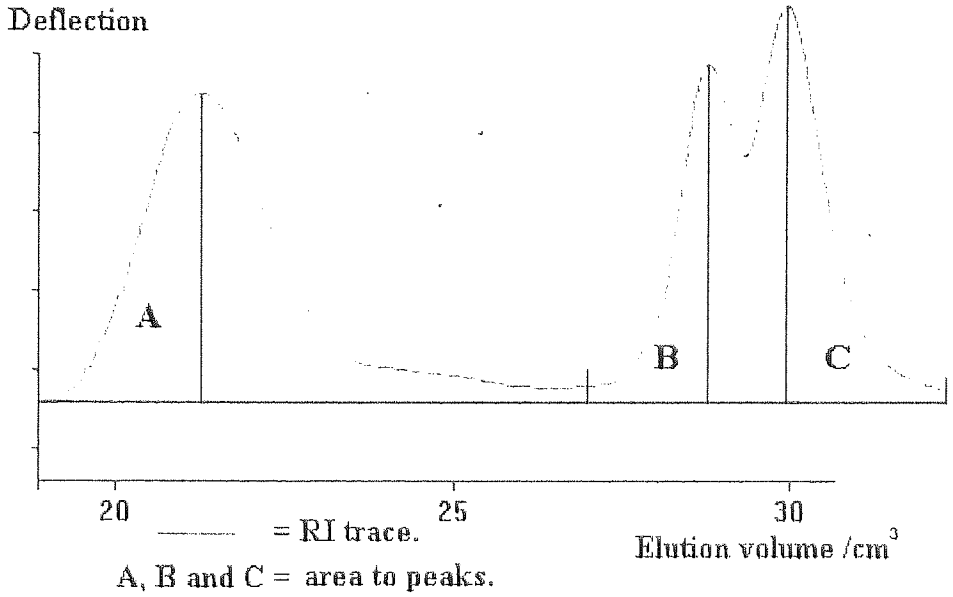
FIGURE 5.2.1. THE SEC TRACE FOR BOTH DETECTORS FOR PRODUCT USING CATALYST WCl_6/PStLi (DP_n = 60) IN RATIO OF 1:1.



The peak molecular weight for the high molecular weight polymers were lower, for the WCl_6:PStLi catalyst system using the ratios 1:1, 1:2 and 1:3, than for the corresponding products using the WCl_6:BuLi catalyst system (see table 4.1.3.). All the HMWP samples showed the same UV activity at 254nm. as the polypentenamer obtained using butyllithium co-catalysts, so the indications were that there was no co-polymerization. Aged THF solutions showed increased absorbance at 254nm as did polypentenylene from previous studies.

The SEC traces of the LMWP were bimodal and the M_{wp} values showed the presence of the original polystyrene (peak 1) and also a product with a molecular weight corresponding to the dimer of the polystyrene (peak 2). The calculation of the UV to RI deflection area was carried out by measuring the areas to the peak, as indicated in figure 5.2.2 (areas A, B and C), for both RI and UV/VIS traces and the assumption was made that the peak distribution was symmetrical. The markers could then be accurately placed using this system and even with overlapping peaks an estimate of the ratios could be found.

FIGURE 5.2.2. SEC RI TRACE TO SHOW PEAK AREA CALCULATION.



These experiments have not clearly identified one optimum catalyst to co-catalyst ratio to produce the best rate of reaction. Both the W:Li ratios of 1:1 and 1:2 were used in the following experiments.

5.2.2. THE EFFECT OF SOLVENT.

The metathesis polymerization of cyclopentene in cyclohexane using WCl_6 with BuLi or $AlEtCl_2$ as co-catalysts had shown reduced reactivity compared to the identical system in toluene (see table 4.1.10.). It was decided to attempt to polymerize cyclopentene with WCl_6 and PStLi using cyclohexane as the main solvent for the monomer.

The experimental procedure is described in 5.2.1, except that cyclopentene and then cyclohexane were sequentially vacuum distilled into an evacuated reaction flask. The required volumes of 0.02M WCl_6 and 0.06M PStLi solutions were injected over argon into the monomer solution, allowing an aging time of 2 minutes. The experiment was carried out using cyclopentene:WCl_6:PStLi (DP_n=20) in the ratios 500:1:1 and repeated using 500:1:2.

Both mixtures went green when the dark blue WCl_6/toluene solution was injected into the 2.5M cyclopentene/cyclohexane solution. Addition of the orange PStLi/cyclohexane solution produced a brown homogeneous mixture but there was no increase in viscosity after 24 hours. The mixture with W:Li ratio 1:1 produced a white, powdery precipitate when poured into methanol, which SEC analysis showed contained only the bimodal peak of the LMWP with M_{wp} of 2200 and 4000g.mol.$^{-1}$. However the solution using the WCl_6/PStLi catalyst mixture of 1:2 produced a more elastomeric product although on purification the yield, compared to the theoretical mass of the polystyrene, was negligible. The SEC trace for the product was similar to that shown in figure 5.2.1 with a HMWP of M_{wp} of 40 000g.mol.$^{-1}$ and the bimodal LMWP as for the 1:1 ratio.

It was decided to extend this series of experiments to test the effect on the rate of reaction of the relative amounts of cyclohexane in the solvent mixture. The mole ratio of WCl_6:PStLi of 1:2 was fixed but PStLi of different degree of polymerization were used, first in solutions with a relatively high percentage of cyclohexane and then using the minimum of this solvent.

TABLE 5.2.3. THE EFFECT OF % CYCLOHEXANE IN THE SOLUTION ON THE % YIELD AND SEC DATA OF THE PRODUCT.

M_{wp} of PSt /g.mol.$^{-1}$	[Cp]/ mol.dm^{3}	% cyclohexane	% yield	time/m.	M_{wp} for HMWP /g.mol.$^{-1}$
2400	3.3	20	3	20	25 000
6000	2.3	48	neg.	120	20 000
8000	2.8	30	9	20	300 000
11000	2.8	34	14	120	110 000
2400	2.9	9	24	20	180 000
6000	1.6	13	30	120	100 000
8000	2.8	16	16	20	1 000 000
12000	3.2	15	25	120	300 000

All the reaction mixtures were quenched with wet toluene and precipitated first using acetone, to separate the elastomeric material, and then methanol, to obtain the polystyrene-rich product. The precipitates were purified, dried and analysed using SEC. The data for the PSt obtained from the co-catalyst solution and the yields and M_{wp} of the HMWP are recorded in table 5.2.3.

The data shows that over a wide range of molecular weights of PStLi the % yield is reduced when the amount of cyclohexane in the solvent is increased. Also the polypentenylene-rich metathesis product has a lower peak molecular weight when there is higher percentage of cyclohexane in the reaction mixture.

5.2.3 THE EFFECT OF THE DP_n OF THE POLYSTYRYLLITHIUM.

In the original plan for this investigation it was hoped that the high molecular weight product of the metathesis of cyclopentene, using WCl_6/PStLi as the catalyst system, would show characteristics of an AB or ABA block co-polymer. The small UV absorbance at 254nm, was therefore disappointing but might be explained by the relatively low DP_n of the PStLi used. If an AB co-polymer is formed and the relative number of UV absorbing phenyl groups is low (e.g.10-50) per polypentenylene chain (M_{wp}>100 000g.mol.$^{-1}$), the absorbance at 254nm per unit mass of product would be expected to be low. It was decided that PStLi of much higher number average molecular weight should be used so that, if any became attached to the end of the polypentenylene chains, the larger number of phenyl groups would increase the measured UV absorbance. Any effect of the number average molecular weight of the PStLi on the M_{wp} of the HMWP would be shown at the same time.

The investigations of Thorn-Csanyi seemed to indicate that the length of the chain in the oligo- or poly-styryllithium affected the nature of the metathesis products. A wide-range of co-catalysts from short chain oligo-styryllithium (10>DP>50) to PStLi chains with DP_n>100 were used. The cyclopentene: WCl_6:PStLi ratio was maintained at 500:1:2 and the percentage of cyclohexane in the solvent was kept to a minimum.

The procedure described in section 2.5.2.1 **method 1** was used when the co-catalyst solution (oligo-StLi DP_n<50) could be injected by syringe over argon. 2.5M cyclopentene/toluene solution was prepared in the reaction flask. 0.05M WCl_6 and two minutes later 0.10M oligo-StLi was injected over argon into the reaction mixture and the tap was firmly closed. At the end of the experiment the reaction mixture in the main vessel was quenched with wet toluene and poured onto acetone to precipitate the elastomer. The filtrate was then poured into methanol to produce insoluble polystyrene-rich products. Both solids were purified and dried, the yield was calculated and SEC analysis carried out.

Because the amount of cyclohexane was kept relatively small, the prepared solutions of PStLi with DP_n>50 were too viscous to transfer by syringe and so **method 2** (see section 2.5.2.1) was used. The polystyryllithium was prepared over argon in the side-arm A of a reaction flask (see figure 2.5). The cyclopentene and toluene were then distilled under vacuum into B and the appropriate amount of WCl_6 injected over argon. After 2 minutes tap 1 was opened to allow mixing of the reaction mixture with the co-catalyst solution.

The blue solution of WCl_6 went the same characteristic red/brown colour in the monomer solution and addition of the co-catalyst produced increased viscosity within 10 minutes, in the brown mixture, in all the experiments with PStLi of DP_n<80. The viscosity of the PStLi itself caused problems when DP_n>100. Several experiments had to be abandoned because the orange solution would not form a homogeneous solution with the monomer/WCl_6 mixture and using more dilute solutions of PStLi, and therefore an increased percentage of cyclohexane, resulted in a drastic reduction in metathetic activity.

The yields and SEC data are given in table 5.2.4. The results for the experiments using PStLi (DP_n>50) are discussed first and then those using oligo-StLi.

TABLE 5.2.4 **SERIES A** ROMP OF CYCLOPENTENE FOR THE CATALYST SYSTEM WCl_6:PStLi ($10<DP_n<250$).

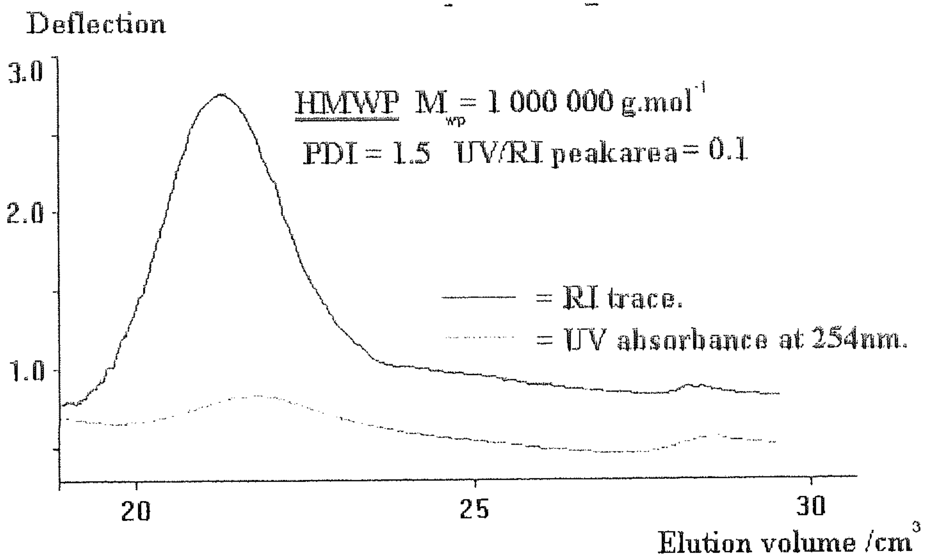
[$DP_{n(theo.)}$]	PSt data $\overline{M}_n$ [M_{wp}]	[Cp]/mol.dm^{-3}. *{%(vv)toluene}* **(%(vv)cyclohexane)**	% yield	Time/ m.	M_{wp} for HMWP /g.mol^{-1}	PDI for HMWP	UV:RI area for HMWP	M_{wp} for LMWP /g.mol^{-1}	Type of LMWP peak.	UV:RI area for LMWP
10	1000 [1100]	[2.8] *{67}* **(9)**	34	20	120 000 60 000, 30 000	2.7 (whole)	0.1	1300	unimodal PDI=2.0	8.6
20	2000 [2300]	[2.9] *{63}* **(9)**	24	20	180 000	2.0	0.1	7000	unimodal PDI=1.3	5.5
50	5200 [6000]	[2.0] *{69}* **(13)**	30	24h.	90 000	1.8*	0.3*	12000 6000	bimodal	≈6.5 ≈7.2
70	7100 [7900]	[2.8] *{54}* **(16)**	16	20	1 000 000	1.5	0.1	18000 8000	bimodal	≈6.0 ≈6.5
100	10400 11000	[3.2] *{49}* **(15)**	25	120	300 000	1.8	0.1	20000 11000	bimodal	≈6.6 ≈7.2
150	15000 [16000]	[2.5] *{42}* **(21)**	8	120	700 000	1.6	0.1	37000 17000	bimodal	≈5.8 ≈8.2
250	26000 [29000]	[2.1] *{11}* **(49)**	neg.	24 h.	>1 000 000	4.9	0.1	60000 30000	bimodal	≈5.4 ≈7.1

Experiments at 25°C. Ratio [W]:[Li] = 1:2. * Reanalysis of SEC data.

5.2.3.1 The catalyst system WCl_6:PStLi (DP_n>50).

The SEC analyses for the reactions using PStLi co-catalyst (DP_n>50) were very similar. The deflections using both RI and UV/VIS detectors are shown in figures 5.2.3. and 5.2.4. for the acetone and methanol precipitates respectively from the reaction using PStLi' (DP_n= 70). They show that the fractional precipitation and purification techniques produced good separation of the polypentenylene-rich and polystyrene-rich material.

FIGURE 5.2.3 SEC TRACES FOR THE POLYPENTENYLENE-RICH PRODUCT (USING WCl_6:PStLi (DP_n=70) AND RATIO 1:2).



The SEC of the acetone-insoluble fraction showed that the HMWP had no increased UV absorbance at 254nm., when compared with the polypentylene samples discussed in chapter 4, and it was concluded that again homopolypentenylene had formed. The ^{1}H and ^{13}C NMR spectra of the HMWP from the polymerization using WCl_6/PStLi(DP_n= 70) were obtained (see figures 5.2.5 and 5.2.6) and compared with those spectra of the metathesis product using BuLi as co-catalysts (see figures 4.4.1 and 4.4.2). The products were structurally identical with the fraction of *cis*-double bonds (σ_c) at the same value of 0.2.

FIGURE 5.2.5 ^{1}H NMR FOR POLYPENTENYLENE-RICH PRODUCT.

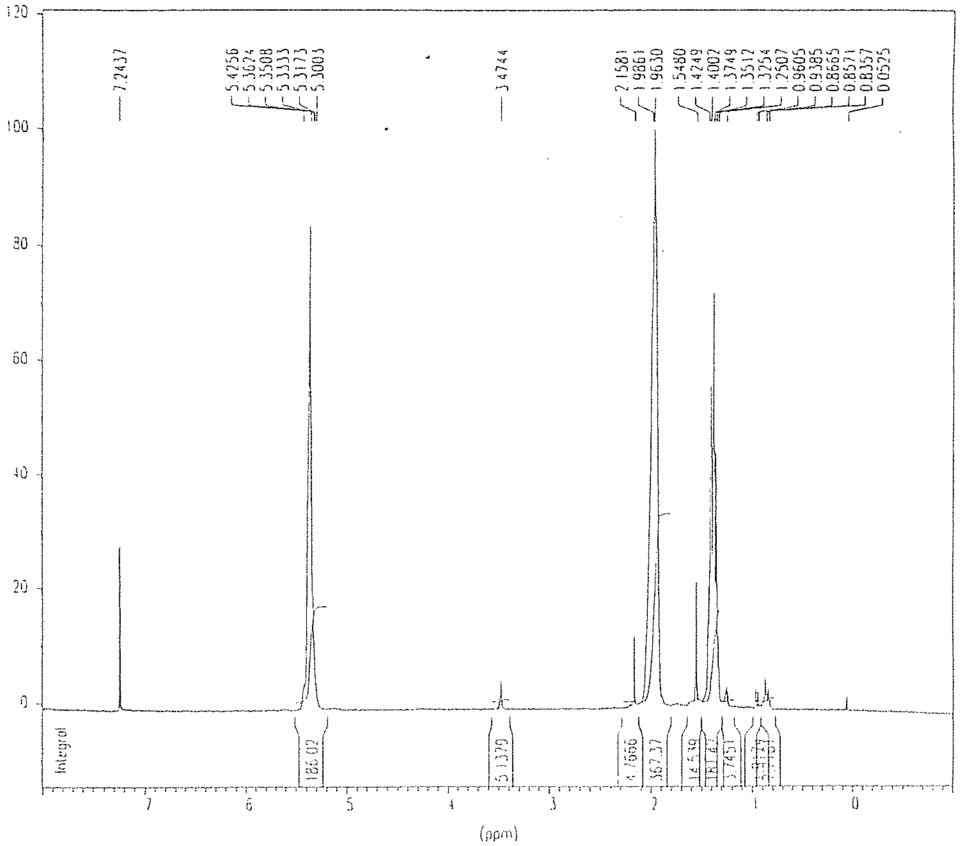
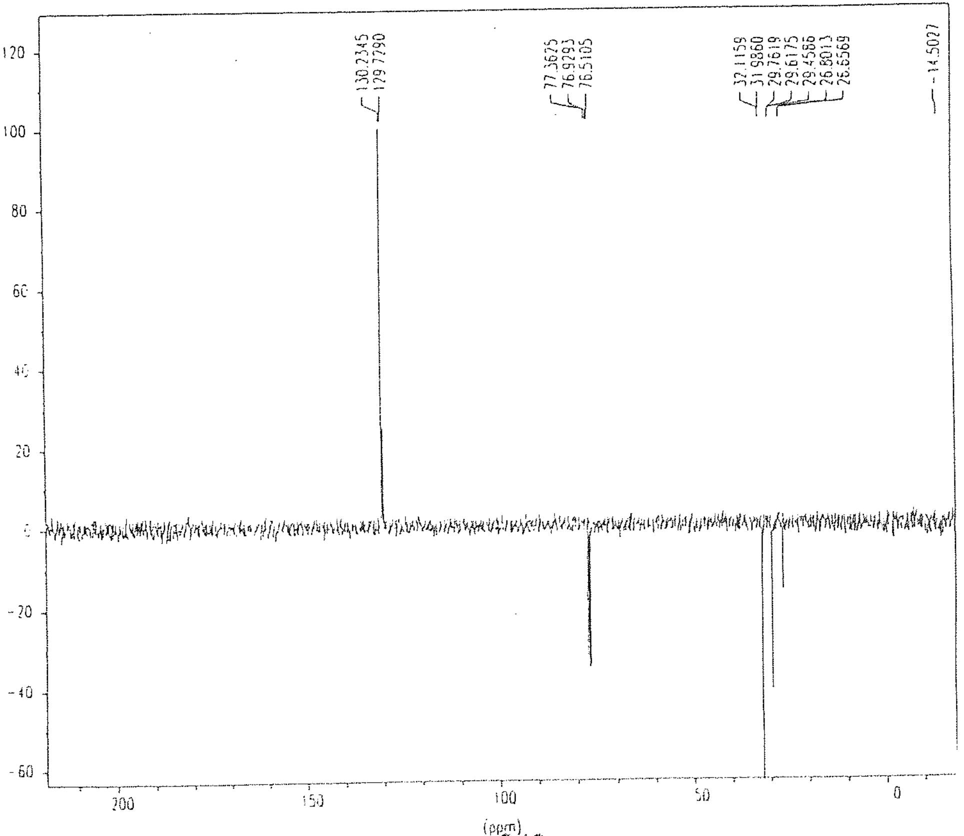
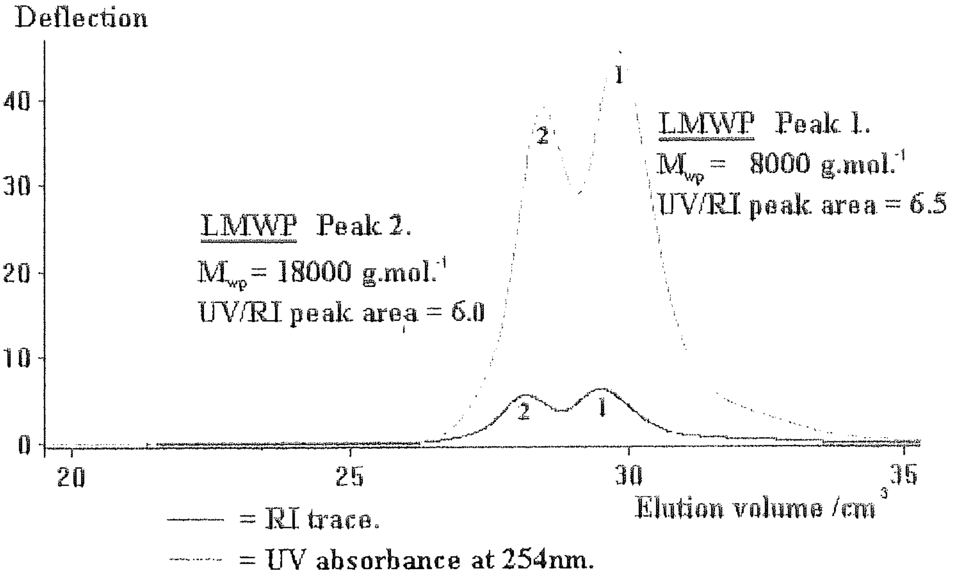


FIGURE 5.2.6 ^{13}C NMR FOR POLYPENTENYLENE-RICH PRODUCT.



There was a decrease in the yield and some increase in the M_{wp} of the HMWP as the number average molecular weight of the PStLi increased. However the problems with the homogeneity of the reaction mixture confused the situation.

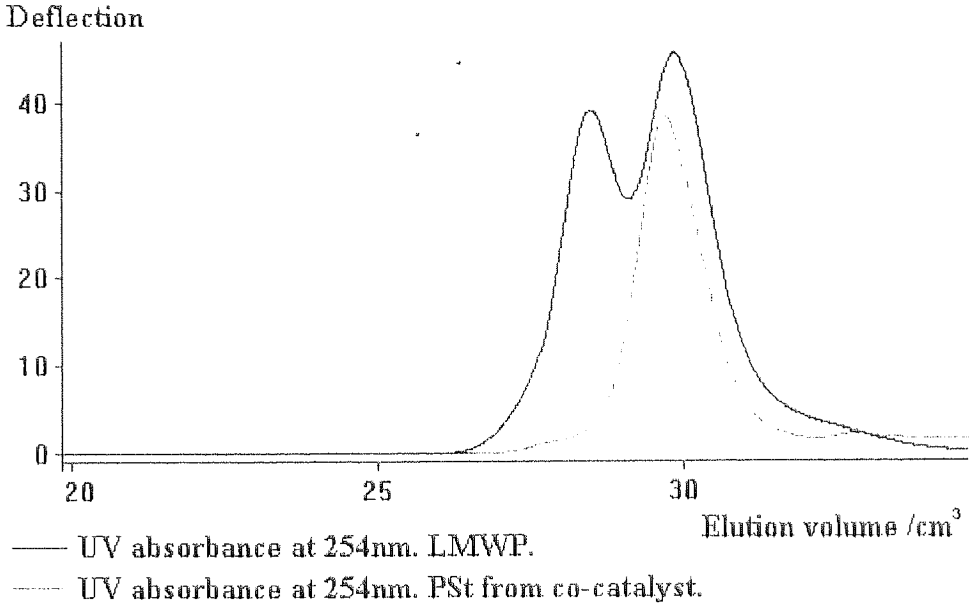
FIGURE 5.2.4. SEC TRACES FOR THE POLYSTYRENE-RICH PRODUCT (USING WCl_6:PStLi (DP_n=70) AND RATIO 1:2).



Analysis of the acetone-soluble product shows that the bimodal LMWP (shown in figure 5.2.4.) has the M_{wp} value of the original polystyrene peak and also that of a dimeric species. Figure 5.2.7. shows an overlay of the UV traces for the polystyrene from the killed co-catalyst and the polystyrene-rich product. There is correlation not only in the M_{wp} but also in the ratio of the UV/RI trace areas (at 6.5) for the species with lower molecular weight.

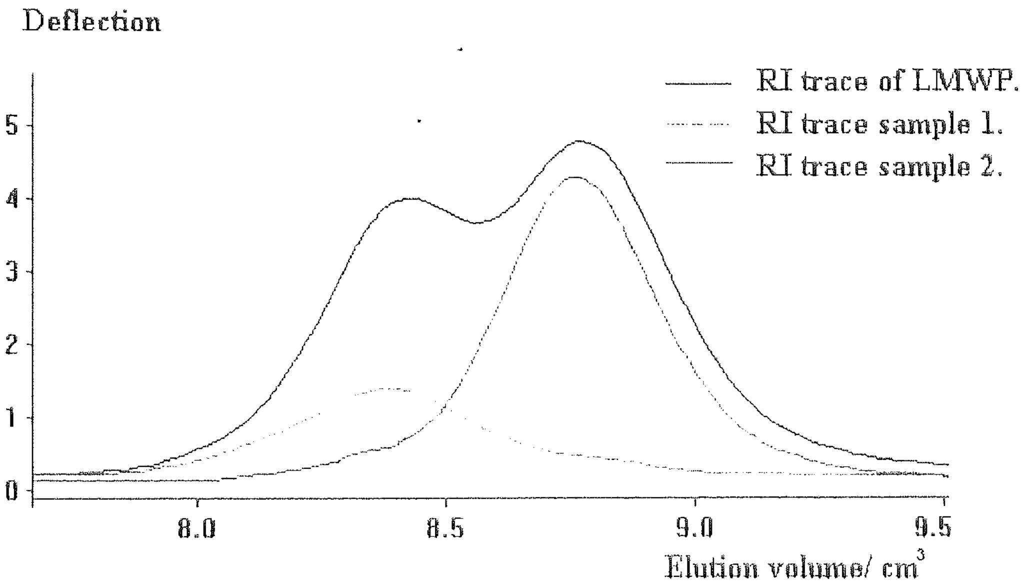
Thorn-Csanyi suggested that the dimeric species was formed by a PStLi coupling reaction catalysed by the WCl_6 and not from coupling of the anionic species in the presence of oxygen when the reaction was terminated. In an attempt to identify the structure of the dimeric species, SEC was used to separate the two LMWP components and then their ^1H and ^{13}C NMR spectra were compared with those of pure polystyrene.

FIGURE 5.2.7 UV ABSORBANCE AT 254n m. FOR LMWP AND PSt FROM CO-CATALYST.



To do this the methanol precipitate from the reaction using PStLi (DP_n=70), shown in figure 5.2.4, was reprecipitated from acetone and methanol three times to remove all traces of polypentenylene material. A 1% (wv) solution of this white powder in THF was run through the single mixed bed SEC column (see figure 2.7). After 7.8 minutes (7.8cm³ elution volume) the RI detector began to show a deflection and the eluent was collected in a sample tube (sample 1), the deflection showed a maximum at 8.4 minutes and then began to fall. At 8.6 minutes there was a second increase in the RI deflection. Allowing 10 seconds for the eluent to pass from the detector to the sample tube, the tube was switched to a new sample tube (sample 2) and this was collected until 10 minutes elution time. The process was repeated 25-30 times over a period of 3 days and samples of the resulting solutions were run through the SEC to check that separation had been achieved and figure 5.2.8, showing an overlay of the RI traces for the original mixture (diluted) and the samples 1 and 2, confirmed that separation had been satisfactorily achieved.

FIGURE 5.2.8 RI TRACES OF LMWP BEFORE AND AFTER SEC SEPARATION.



The THF solutions were then evaporated to dryness and finally dried in a vacuum oven for several hours. The small amounts of white solid in each tube were analysed by NMR spectroscopy and the ^{1}H spectra are shown for samples 1 and 2 in figures 5.2.9 and 5.2.10 respectively. Sample 2 had the ^{1}H NMR spectrum of polystyrene as expected. In the case of sample 1, the ^{1}H NMR showed the expected resonances for polystyrene but in addition it had a signal between chemical shift (δ) 5.12 and 5.19 ppm.. This is a characteristic resonance of methine protons attached to carbon-to-carbon double bonds as found in polypentenylene chains (see table 4.4.1 section 4.4.). So there is some evidence that sample 1 may be a block co-polymer.

Assuming that the NMR spectrum of sample 1 is of co-polymer only, a calculation based on the proton signal areas can be carried out to estimate the number average molecular weight of any AB or ABBA block co-polymer. The M_n of the PStLi co-catalyst is 7100g.mol^{-1} and the ^{1}H NMR spectrum for sample 1 shows that the 5 phenyl/methine protons (^1H_p) produce a combined signal area (A_p) of 373.10. The 2 alkene/methine proton(^1H_m) signal area (A_m) is 80.79.

FIGURE 5.2.9 ^{1}H NMR FOR SAMPLE 1.

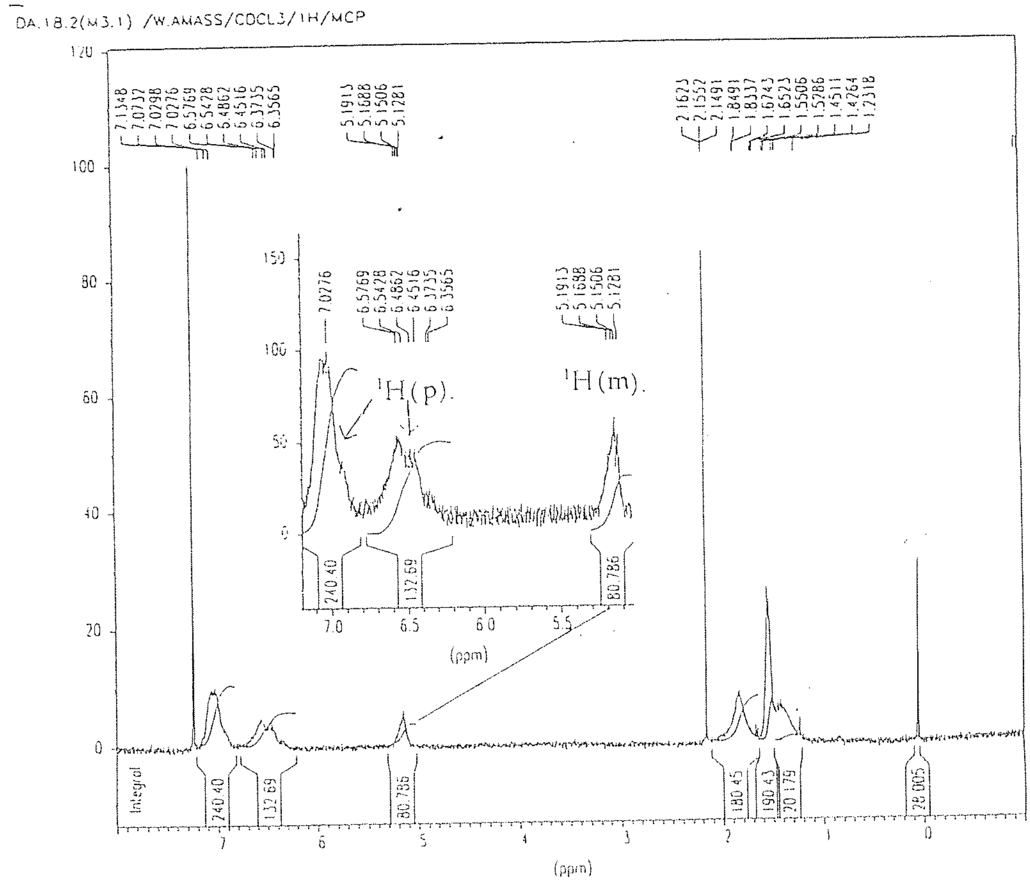
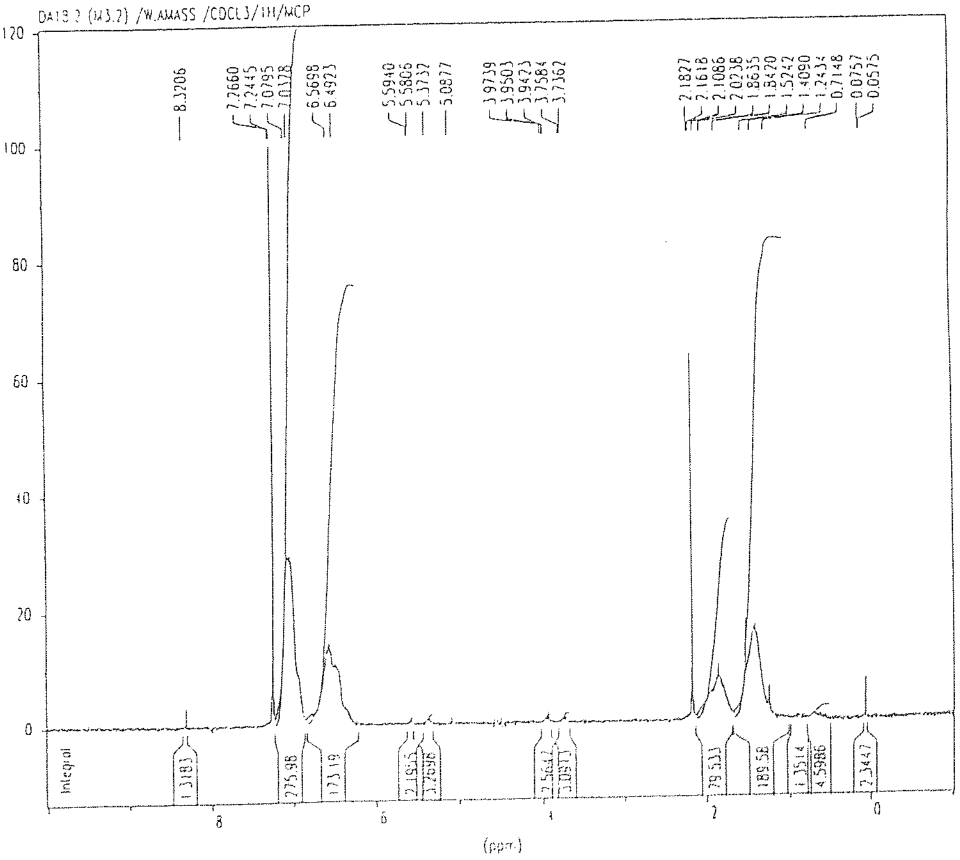


FIGURE 5.2.10 ^{13}C NMR FOR SAMPLE 2.



NMR data.

Area per styrene (St) unit in the chain = $A_p/5$ = 74.6.

Area per pentenylene (Pn) unit in the chain = $A_m/2$ = 40.4.

The relative number of Pn: St units = 40.4: 74.6 = 0.54: 1.

The actual DP_n of the PSt = M_n/ Molecular weight of PSt = 7100/ 104 = 70.

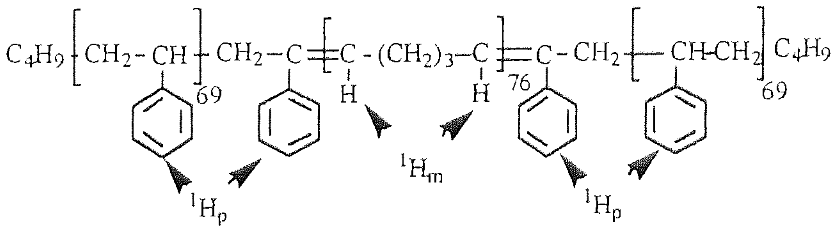
The number of pentenylene units = 0.54 x 70 = 38.

M_n polypentenylene chain = 38 x 68 = 2 600 g.mol^{-1}.

M_n A-B co-polymer $[St]_{70}[Pn]_{38}$ = 9 700 g.mol^{-1}.

M_n A-B-B-A co-polymer $[St]_{70}[Pn]_{76}[St]_{70}$ = 19 400 g.mol^{-1}.

Sample 2 has an observed M_{wp} of 18 000g.mol^{-1} and there is evidence that it contains some polypentenylene material. So the peak molecular weight could correspond to ABBA block co-polymer, of the structure shown below, which would produce a proton NMR with the alkene/ methine ^1H_m ($5.13 \leq \delta \leq 5.19$) to phenyl/ methine ^1H_p ($6.4 \leq \delta \leq 6.6$ and $\delta = 7.0$) signal area (A_m:A_p) in the observed ratio.

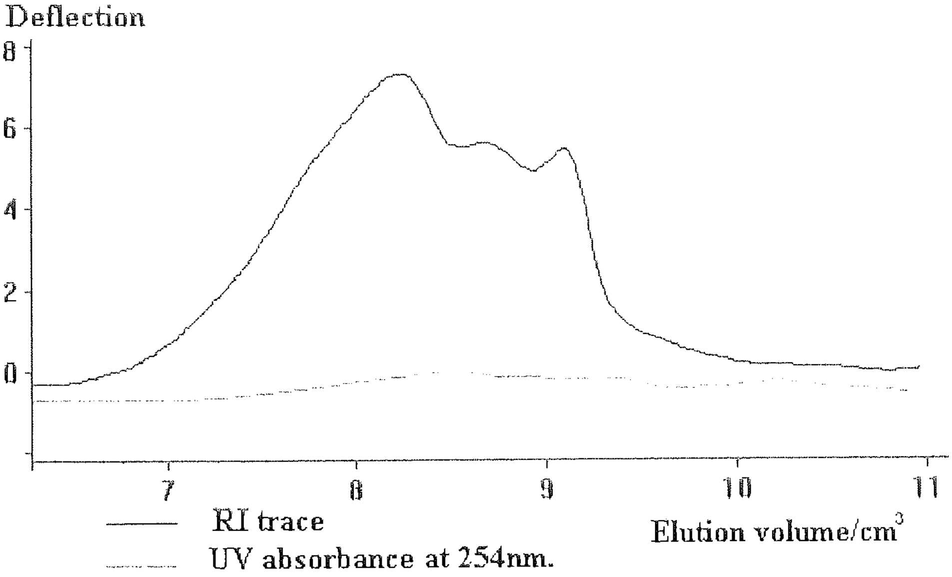


5.2.3.2. The catalyst system WCl_6: oligo-StLi (DP_n<50).

The results of these two experiments were atypical and will be considered separately. The use of very low molecular weight oligo-StLi (DP=10) produced a mixture of acetone-insoluble products. The SEC trace for this HMWP mixture using RI and UV/VIS recorders are shown in figure 5.2.11 and there are three identifiable peaks on the RI trace with peak M_{wp} of 120 000, 60 000 and 30 000g.mol.$^{-1}$. The overall UV to RI deflection area ratio is only 0.1 and the ^1H

and ^{13}C NMR spectra were identical to those shown in figures 4.4.1 and 4.4.2 for pure polypentenylene produced using the WCl_6/BuLi catalyst system. The SEC traces for the acetone-soluble product shows only the oligo-styrene used as the co-catalyst.

FIGURE 5.2.11. SEC TRACE FOR THE POLYPENTENYLENE-RICH PRODUCT (USING WCl_6:PStLi (DP_n=10) AND RATIO 1:2).



The experiment using the olig-StLi (DP_n=20) produced a typical HMWP as shown by its SEC trace but the acetone-soluble material was found, by SEC analysis, to be unimodal and have a M_{wp} of 7000g.mol^{-1}, considerable higher than the number average molecular weight of co-catalyst (2000g.mol^{-1}). Figure 5.2.12 shows the overlay of the RI trace for the two. The UV to RI peak area ratio (5.5) for the LMWP is lower than that of polystyrene.

Again NMR spectroscopy was used to compare the structure of the LMWP and PSt (see figure 5.2.10). The small amount of white solid was reprecipitated twice using acetone and methanol and its ^1H NMR spectrum is shown in figure 5.2.13.

FIGURE 5.2.12. RI TRACES FOR LMWP AND PSt FROM CO-CATALYST.

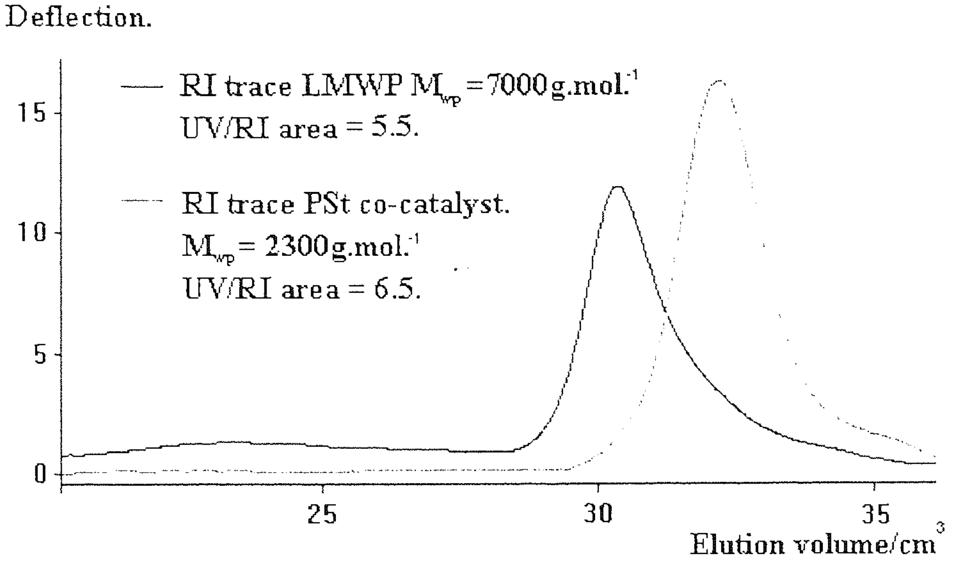
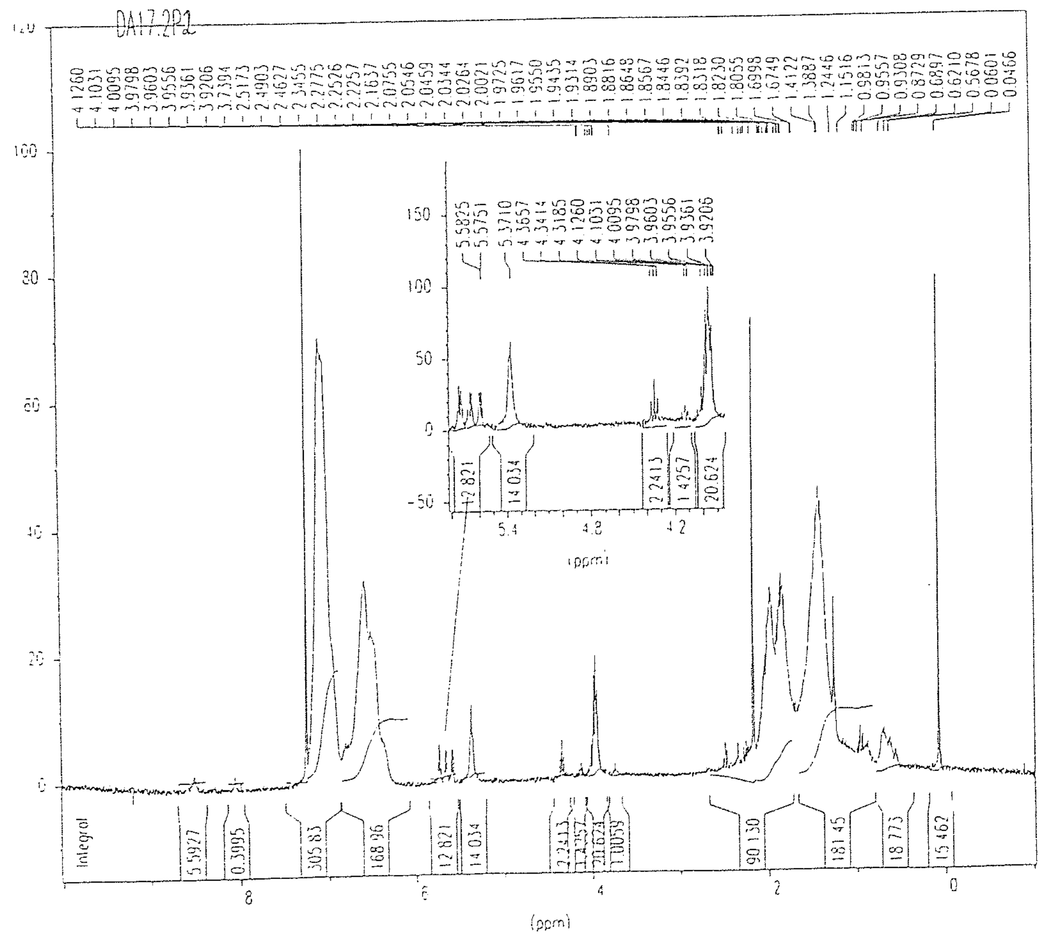


FIGURE 5.2.13. ^{1}H NMR OF LMWP.



The signal at chemical shift 5.37 ppm, which can be attributed to methine protons adjacent to a carbon-to-carbon double bond, indicates some pentenylene bonds in the compound. Assuming this to be co-catalyst an estimate of its structure can be made. The M_n of the PStLi co-catalyst is 2100g.mol.$^{-1}$, the phenyl/methine ^1H_p signal area (A_p) is 474.8 and the alkene / methine ^1H_m signal area is 14.0.

The area per styrene unit = 474.8/5 = 95.0

The area per pentenylene unit = 14.0/2 = 7.0

The relative number of Pn:St units from the NMR = 7.0: 95.0 = 0.074:1.

The actual DP_n of the PSt = M_n/104 = 2100/104 = 20.

The number of pentenylene units (Pn) = 0.074 x 20 = 1.5

M_n AB co-polymer with $(St)_{20}(Pn)$ or $(St)_{20}(Pn)_2$ = 2168-2236 g.mol.$^{-1}$

M_n ABBA co-polymer with $(St)_{20}(Pn)_2(St)_{20}$ or $(St)_{20}(Pn)_4(St)_{20}$ = 4336-4472g.mol.$^{-1}$

The LMWP has M_{wp} of 7000g.mol.$^{-1}$

The calculation assumes that the product is all co-polymer and there is no pure polystyrene in the acetone-soluble material. The signal associated with the phenyl/methine ^1H_p would be affected by the presence of any pure polystyrene but the alkene/methine signal would not. There is some indication that the LMWP again has some co-polymer content.

5.3 SERIES B. PREMIXING THE CATALYST AND CO-CATALYST.

Thorn-Csanyi's report on the use of WCl_6/PStLi as a catalyst system for the ring-opening metathesis of cyclopentene does not specify either the ratio of the catalyst mixture used nor the details of the addition procedure, apart from stating that the PStLi solution was added to the monomer solution and then the WCl_6 was injected into the mixture. Our work with the premixed WCl_6/BuLi, *s*-BuLi or $AlEtCl_2$ catalyst systems had reacted most rapidly using a

1:1 ratio of catalyst to co-catalyst with a two minute aging time for the catalyst components. It was decided to examine this premixing method with the WCl_6/PStLi catalyst mixture but so that a direct comparison could be made, with the results of the experiments described in section 5.2.3, the ratio of WCl_6/PStLi was kept at 1:2 and only the premix aging time was varied.

The method was described in section 2.5.2.2. A 2.5M cyclopentene/toluene solution was prepared by consecutive vacuum distilllation of the liquids into the main vessel B (figure 2.5). 0.10M PStLi (DP_n=20) solution and 0.05M WCl_6 solutions were premixed in a 2:1 mole ratio by injecting appropriate volumes over argon into the side-arm A of a reaction flask. Taps 1 and 2 were closed and after a fixed aging time of 1, 5 or 60 minutes the two solutions were mixed and then treated as in all other experiments.

The premixed catalyst components produced a red homogeneous solution which became browner when added to the monomer solution. The viscosity in all three experiments increased within 15 minutes and they were precipitated after 20 minutes. The yields and SEC data for the acetone-insoluble and -soluble materials are given in table 5.3.

The yield of polypentenylene-rich product, after 20 minutes, for the 1 minute premix time was comparable with that obtained in series A using PStLi of similar DP_n (see table 5.2.4). The yields for longer premix times were lower. The low UV absorbance at 254nm. indicates that HMWP is the homopolymer polypentenylene. The M_{wp} of the samples is overall higher than for the series A equivalent and is particularly high for the mixture which had a premix time of 1 hour.

The LMWP for all three experiments showed bimodal character but the M_{wp} for both was considerably higher than for the PSt obtained from the original co-catalyst solution. This is clearly shown in figure 5.3.1. which is an overlay of the SEC traces for the RI deflection of the PSt from the co-catalyst and the methanol precipitate from the reaction mixture with 1 hour premix time.

TABLE 5.3. **SERIES B** ROMP OF CYCLOPENTENE FOR THE PREMIXED CATALYST SYSTEM

WCl_6:PStLi (DP_n=20) IN THE RATIO 1:2.

Premix time/ m.	PSt data $\overline{M}_n$ [M_{wp}]	[Cp]/mol.dm^{-3}. *{%(vv)toluene}* (%(vv)cyclohexane)	% yield	Time/ m.	M_{wp} for HMWP /g.mol^{-1}	PDI for HMWP	UV:RI area for HMWP	M_{wp} for LMWP /g.mol^{-1}	Type of LMWP peak.	UV:RI area for LMWP
1	2000 [2300]	[3.5] *{75}* **(14)**	25	20	230 000	2.0	0.1	6500 4000	bimodal	≈6.5 ≈7.0
5	2000 [2300]	[3.1] *{60}* (9)	10	20	240 000	1.8	0.1	7000 4000	bimodal	≈6.7 ≈8.5
60	2000 [2300]	[3.1] *{60}* (9)	14	20	500 000	1.9	0.1	6500 4000	bimodal	≈6.0 ≈6.9

Experiments at 25°C.

FIGURE 5.3.1. SEC RI TRACES FOR LMWP AND PSt FROM CO-CATALYST.

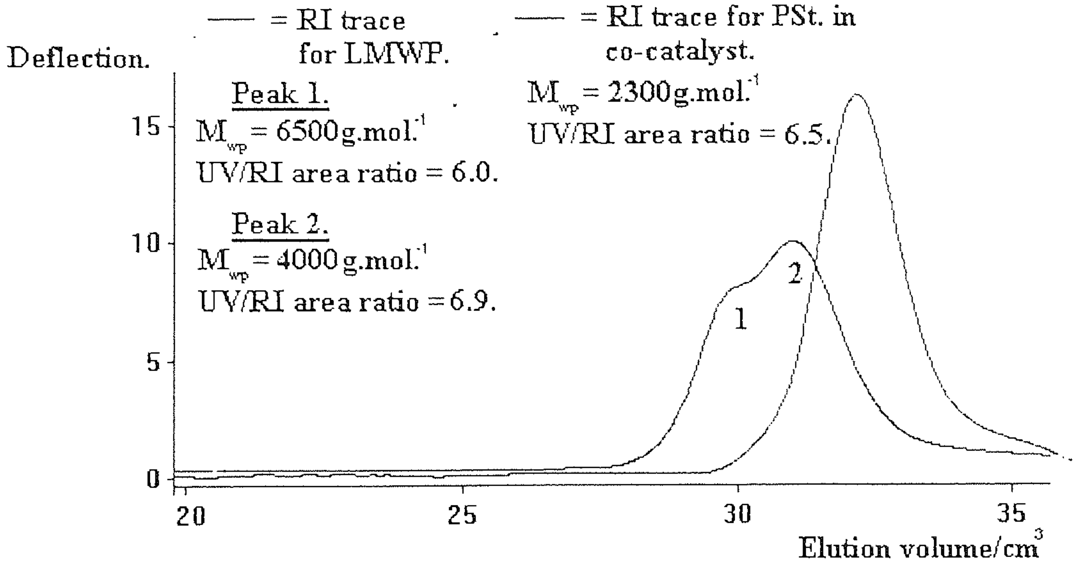
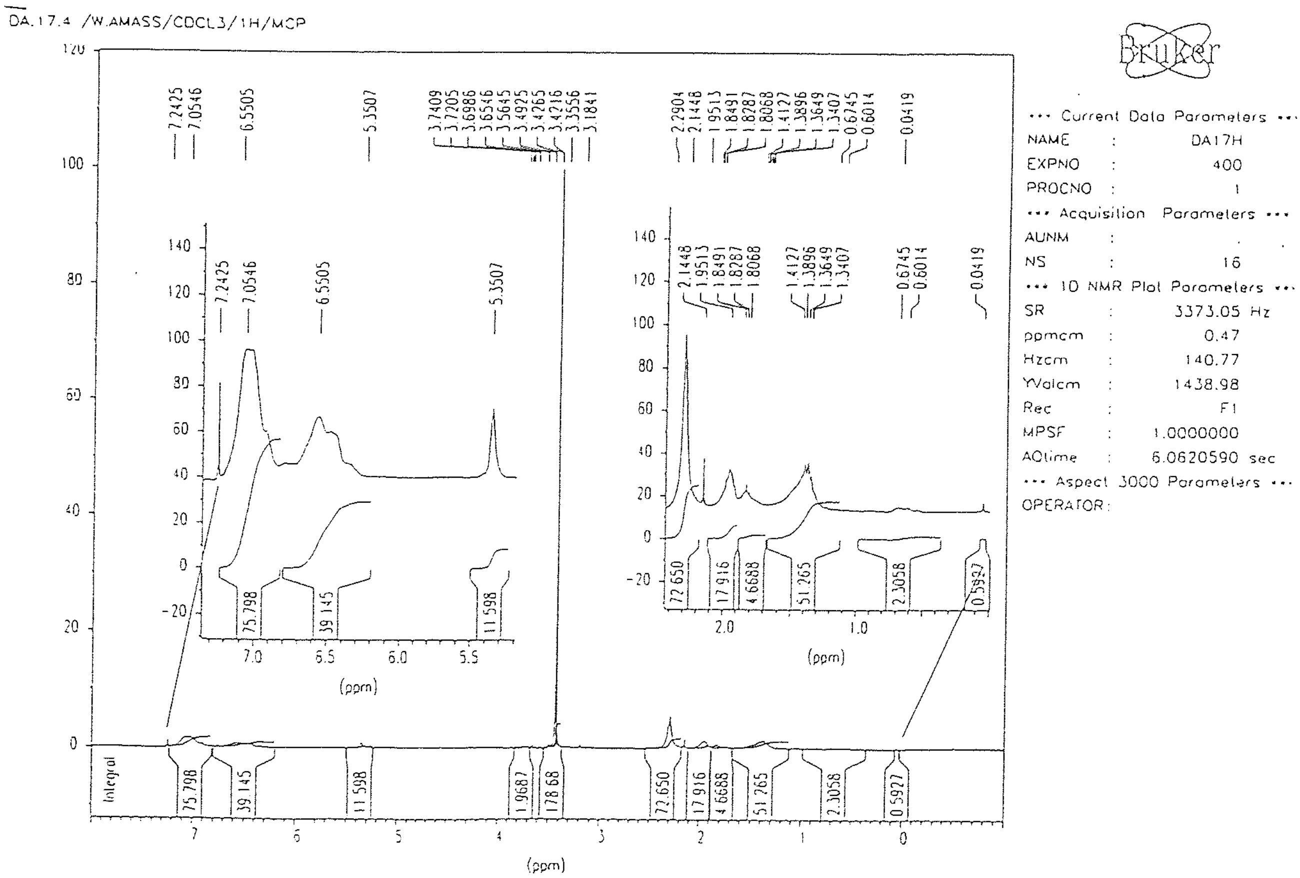


FIGURE 5.3.2. ^{1}H NMR POLYSTYRENE-RICH MATERIAL.



The overlap of the two peaks of the methanol precipitate made separation by SEC, as described in section 5.2.3.1, impossible but the small amount of white solid obtained, on reprecipitating the methanol insoluble material three times, was analysed by ^{1}H and ^{13}C NMR spectroscopy. The ^{1}H NMR spectrum is shown in figure 5.3.2. and again the absorbance peak at δ = 5.3 ppm was an indication of the presence of the CH=CH methine protons found in polypentenylene chains. Hence some block co-polymer may be present in this LMWP. As the product was a mixture of PSt and PSt-rich material no calculation based on the ^{1}H NMR signal areas was possible.

5.4 SERIES C. SEQUENTIAL ADDITION OF ETHANOL, WCl_6 AND PStLi.

A few experiments using absolute ethanol as a third catalyst component were described in section 4.3. and it was decided that the ring-opening polymerization of cyclopentene should be carried out by this method, using PStLi as the co-catalyst.

The ratio of components in the catalyst mixture was WCl_6:EtOH:PStLi of 1:0.5:1, 1:1:1 and 1:1:2. The appropriate volume of 0.8M ethanol/toluene solution was injected over argon into the 2.5M cyclopentene solution and then with two minutes delay time between each injection, the 0.02MWCl_6 and PStLi (DP_n=60) were added over argon by syringe.

The dark blue WCl_6/toluene solution went red when injected into the monomer solution containing ethanol and went dark red when the orange PStLi was introduced. The 1:1:1 mixture showed no increased viscosity after 24 hours and on addition to acetone produced no precipitate. The other two reaction mixtures were quite viscous after 24 hours and produced precipitates with acetone and methanol. The yields and SEC data are shown in table 5.4.

TABLE 5.4. **SERIES C** ROMP OF CYCLOPENTENE FOR THE CATALYST SYSTEM WCl_6:EtOH:PStLi (DP_n=50) IN DIFFERENT RATIOS.

Ratio W:EtOH:Li	PSt data $\overline{M}_n$ [M_{wp}]	[Cp]/mol.dm^{-3}. *{%(vv)toluene}* **(%(vv)cyclohexane)**	% yield	Time/ h.	M_{wp} for HMWP /g.mol^{-1}	PDI for HMWP	UV:RI area for HMWP	M_{wp} for LMWP /g.mol^{-1}	Type of LMWP peak.	UV:RI area for LMWP
1:0.5:1	5300 [5900]	[2.5] *{59}* **(18)**	15	24	100 000	2.3	<0.1	11000 6000	bimodal	≈5.0 ≈6.4
1:1:1	5500 [6100]	[2.5] *{54}* **(20)**	-	-	-	-	-	12000 6000	bimodal	≈5.2 ≈6.8
1:1:2	5700 [6500]	[2.7] *{57}* **(18)**	10	24	85 000	2.5	<0.1	13000 6500	bimodal	≈5.7 ≈6.7

Experiments at 25°C.

The catalyst mixture WCl_6:EtOH:PStLi in the ratio 1:1:1 failed to produce any HMWP but the two reactions with a molar excess of PStLi over the EtOH produced polypentenylene-rich material and LMWP with bimodal character.

Using equimolar amounts of the three components resulted in the ethanol destroying the activity of the WCl_6/PStLi system as a metathesis catalyst and it reduced the effective [PStLi] in the other two experiments. The amount of cyclohexane in the systems was relatively high and this may have had an effect on the yield. The reactions were quite slow, the peak molecular weight of the HMWP was relatively low and the PDI values were broad. There was little advantage in using the ethanol as a third component so no further studies using this method were undertaken.

5.5 ROMP OF CYCLOPENTENE USING WCl_6/$AlEtCl_2$/PStLi.

The anionic to Ziegler-Natta polymerization transformation reactions, referred to in section 1.8.2.5, were achieved by converting the small molecule co-catalyst for Ziegler-Natta polymerizations (aluminium trialkyls) into polymeric aluminium species. Polystyryllithium and aluminium chloride were used to make the mixture of polyaluminium species, which were then used with $TiCl_4$ as the catalyst system for the polymerization of ethene. Block co-polymers were produced with 40% coupling efficiency. This investigation involved preparing a similar mixture of polyaluminium compounds and using them with WCl_6 for the ring-opening metathesis polymerization of cyclopentene, in an attempt to produce co-polymer.

All the experiments involved the series A method of sequential additon of the catalyst components with a two minute aging time between the addition of the $WCl_6$and the co-catalyst system. The main solvent was toluene and the % cyclohexane was kept as low as possible. A co-catalyst mixture of $AlEtCl_2$/PStLi in a 1:1 ratio was prepared and first the effect of different WCl_6:co-catalyst ratios was examined and then the optimum W catalyst:Al co- catalyst ratio was used to see the effect of varying the degree of polymerization of the PStLi on the rate of the metathesis reaction and on the nature of the products.

5.5.1 THE EFFECT OF DIFFERENT WCl_6: CO-CATALYST RATIOS ($AlEtCl_2$: PStLi RATIO = 1: 1).

The method is outlined in section 2.5.3. Equimolar amounts of approximately 0.30M $AlEtCl_2$ solution and orange 0.1M PStLi (DP_n=30) were premixed in a small reaction flask or in the side-arm of a reaction vessel and a white, cloudy mixture formed, indicating that the reaction had produced lithium chloride. Either method 1 or method 2 described in section 2.5.2.1 was then adopted, so an approximately 2.5M cyclopentene/toluene solution was prepared and 0.02M WCl_6 was injected into it over argon. Two minutes later, the appropriate volume of co-catalyst mixture was added by one of the two methods. The polymerization process, the fractional precipitation procedure and the purification, drying and analysis of the products were as described in section 2.5.2.1. The cyclopentene:WCl_6 ratio was kept at 500:1 and the experiment was carried out using WCl_6:co-catalyst ratios of 1:0.5, 1:1, 1:2 and 1:3. The amount of cyclohexane in the reaction mixture was kept as low as possible.

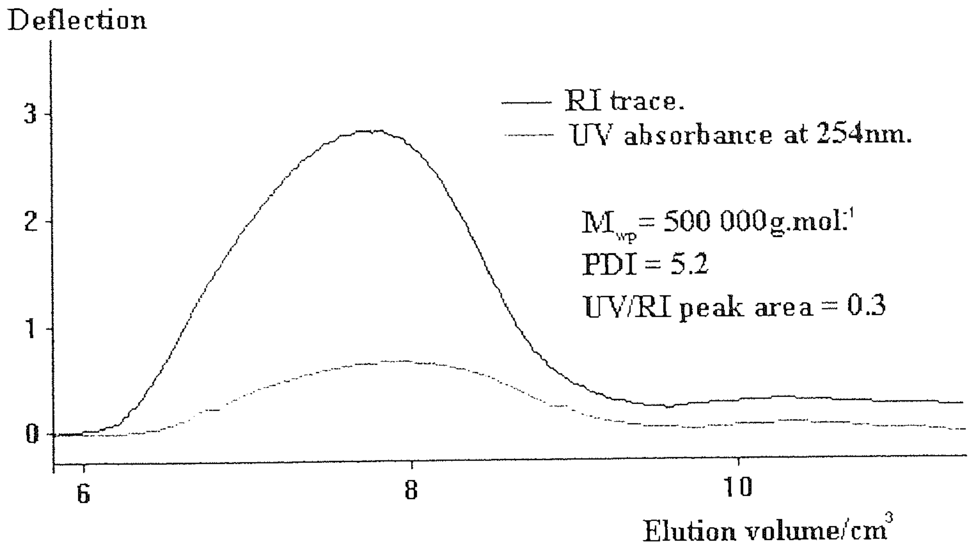
The expected colour change took place when the WCl_6 was added to the cyclopentene solution but the addition of the aluminium co-catalyst mixture produced a red mixture with the ratio 1:0.5 and purple solutions with the other ratios. The 1:1 ratio of WCl_6:(Al/Li) produced the fastest reaction and the highest yield, there was an increase in viscosity within 30 minutes. The other reactions were viscous only after several hours and the catalyst ratios 1:0.5:0.5 and 1:2:2 had very similar reactivities. The yields and SEC data are shown in table 5.5.1. and figure 5.5.1. shows the SEC trace using both detectors for the acetone-insoluble HMWP using the catalyst system WCl_6:$AlEtCl_2$:PStLi in the ratio 1:1:1.

TABLE 5.5.1. **SERIES A** ROMP OF CYCLOPENTENE FOR THE CATALYST SYSTEM WCl_6:$AlEtCl_2$:PStLi (DP_n=30) FOR DIFFERENT MOLE RATIOS.

Ratio W:Al:Li	PSt data $\overline{M}_n$ [M_{wp}]	[Cp]/mol.dm^{-3}. *{%(vv)toluene}* **(%(vv)cyclohexane)**	% yield	Time/ h.	M_{wp} for HMWP /g.mol^{-1}	PDI for HMWP	UV:RI area for HMWP	M_{wp} for LMWP /g.mol^{-1}	Type of LMWP peak.	UV:RI area for LMWP
1:0.5:0.5	3200 [3500]	[2.8] *{71}* **(3)**	30	24	300 000	3.7	0.2	3500	unimodal	6.7
1:1:1	3200 [3500]	[3.3] *{61}* **(10)**	40	3	500 000	5.2	0.2	3600	unimodal	6.8
1:2:2	3200 [3500]	[2.5] *{65}* **(14)**	28	24	(180 000)	5.9	0.3	3900	unimodal	6.9
1:3:3	3200 [3500]	[3.1] *{48}* **(26)**	20	24	600 000	8.1	0.1	3800	unimodal	6.5

Experiments at 25°C.

FIGURE 5.5.1. SEC TRACE FOR BOTH DETECTORS FOR ACETONE-INSOLUBLE PRODUCT FROM WCl_6:$AlEtCl_2$:PStLi CATALYST SYSTEM.



The extremely high peak molecular weights of the HMWP are evident except for the elastomer from the 1:2:2 catalyst mixture. However closer inspection of the RI trace shows, that this extemely broad peak, has its maximum value towards the lower part of the molecular weight range and the weight average molecular weight is 900 000g.mol.$^{-1}$. The broad PDI values (>3.7) are common to other HMWP using Al based co-catalysts (see table 4.16, 4.1.7 and 4.1.8). The UV:RI peak area ratios for the HMWP are relatively high for freshly prepared solutions but the ^1H and ^{13}C NMR spectra for the HMWP (W:Al;Li=1:1:1) are shown in figures 5.5.2 and 5.5.3 respectively and confirm that pure poly-pentenylene has been produced. The acetone-soluble material from all four reactions had an SEC trace identical to that of the PSt used in the co-catalyst.

After this series of experiments had been completed, there were doubts about the purity of the liquid $AlEtCl_2$ used to make the co-catalyst. So no specific comparison of these results with other three component series could be made although the optimum catalyst ratio seems to be similar to that for the other

FIGURE 5.5.2. ^{1}H NMR FOR HMWP (WCl_6:$AlEtCl_2$:PStLi CATALYST SYSTEM).

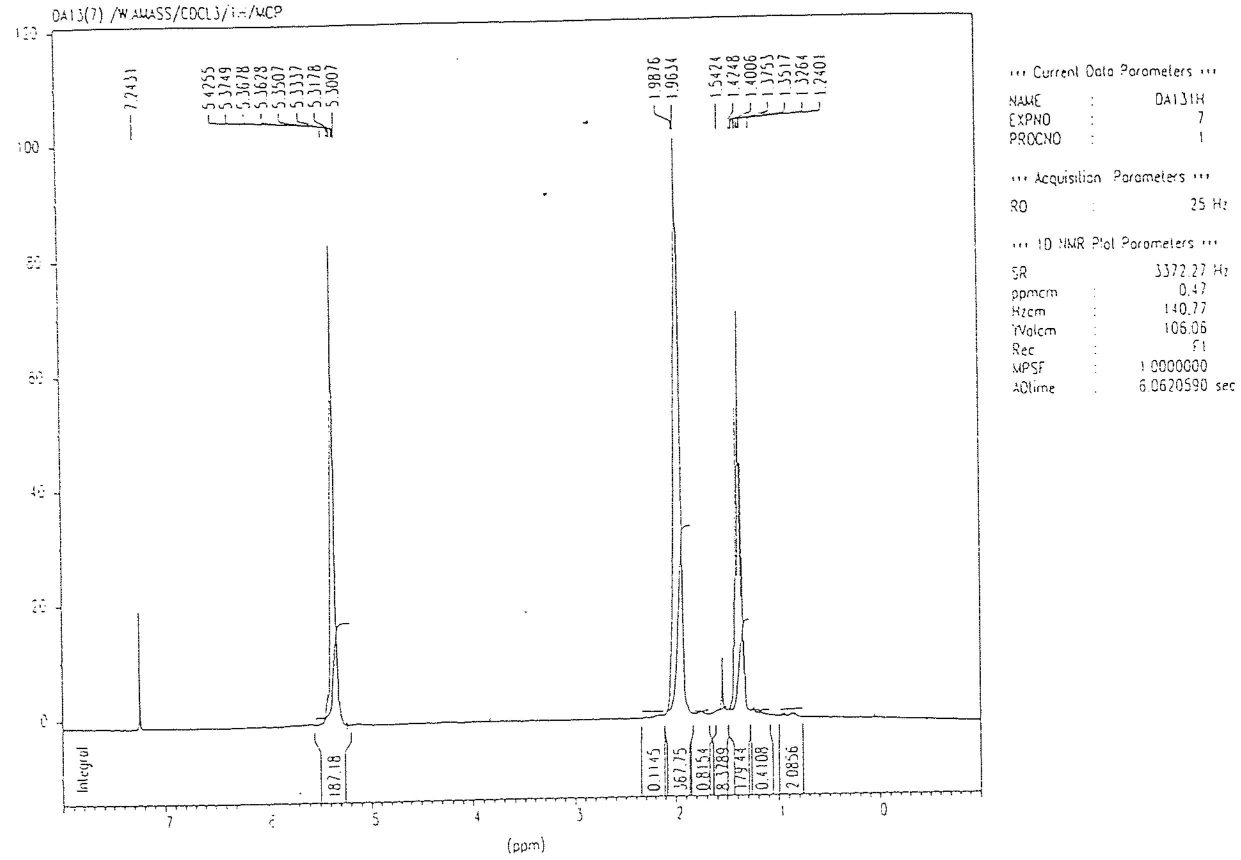
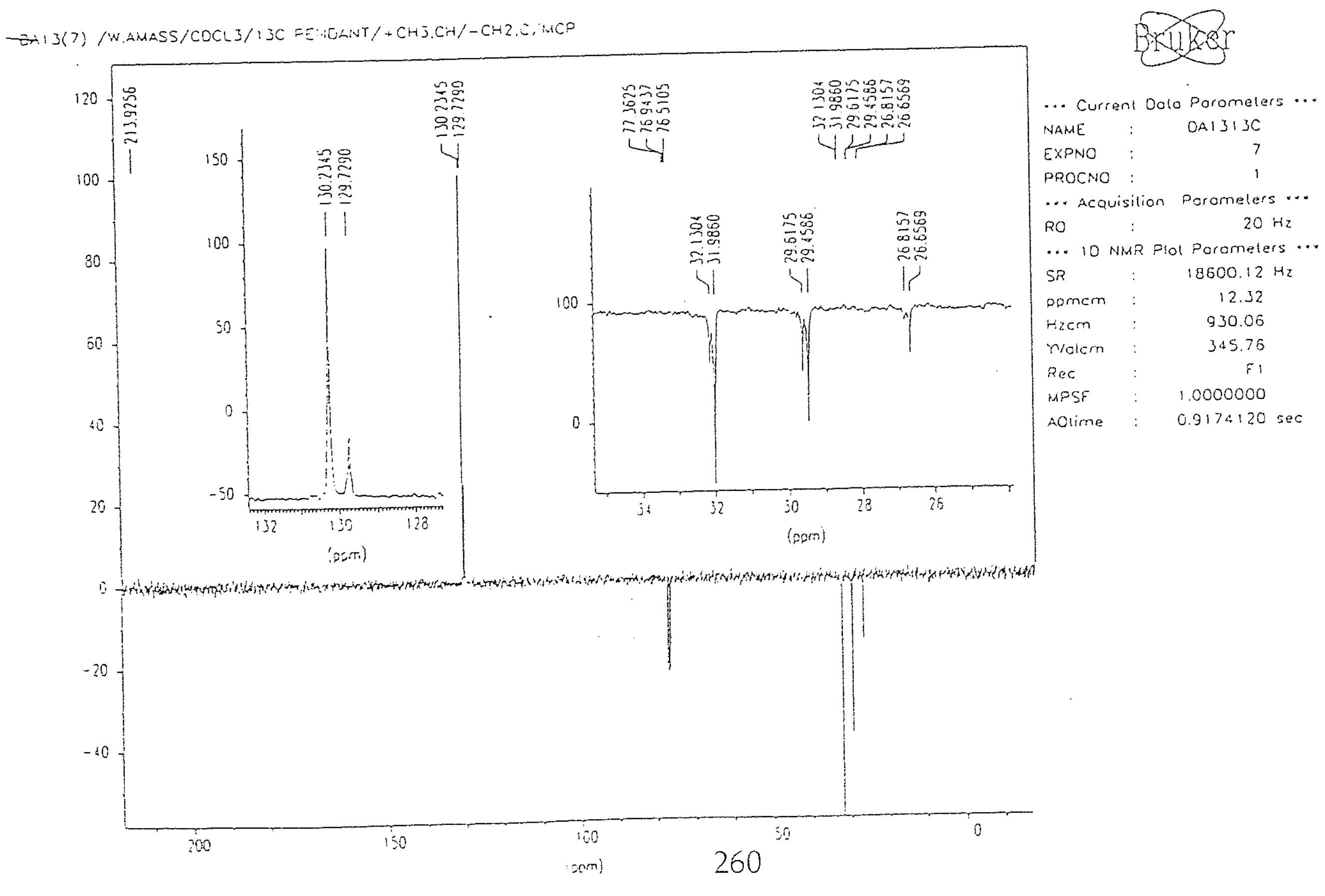


FIGURE 5.5.3. ^{13}C NMR FOR HMWP (WCl_6:$AlEtCl_2$:PStLi CATALYST SYSTEM).



W:Al:Li systems. It was concluded that WCl_6:$AlEtCl_2$:PStLi ratios between 1:0.5:0.5 and 1:2:2 should be investigated for co-catalyst systems containing PStLi (DP_n>50) and oligo-StLi (DP_n<20) and using fresh solutions of $AlEtCl_2$.

5.5.2. THE EFFECT OF HIGH MOLECULAR WEIGHT POLYSTYRYLLITHIUM OVER A RANGE OF CATALYST RATIOS.

The three component WCl_6/$AlEtCl_2$/PStLi catalyst system was used in a range of ratios from 1:0.5:0.5 to 1:2:2 and for PStLi with degree of polymerization between 100 and 125. The procedure was similar to that described in 5.5.1 but a fresh solution of 2M aluminium ethyldichloride/toluene was used and injected over argon into the PStLi solutions (of known DP_n) in the side-arm of a flask (see figure 2.5) so that a 1:1 mole ratio was achieved. **Method 2** (described in section 2.5.2.1) was then adopted and a range of catalyst systems was examined. The yields and SEC data for the ratios investigated, are summarised in table 5.5.2.

The catalyst mixture with W:Al;Li ratio 1:1.5:1.5 produced a mauve reaction solution when the co-catalyst solution was added and was viscous within 10 minutes. The other solutions remained brown/red and were only slightly more viscous when they were precipitated after 24 hours. The reaction with the maximum activity again produced HMWP of very high peak molecular weight (900 000g.mol.$^{-1}$). The M_{wp} of the HMWP for other ratios were no higher than those of the product polymer formed using PStLi (DP_n=30) (see table 5.5.1.) but their PDI values were much narrower (2.5 compared to >3.7). The low UV to RI ratio indicated that only homopolymer of the cyclopentene had been produced. The single peak for the LMWP corresponded to the PSt used in the co-catalyst.

Comparison of the HMWP data from table 5.5.2 with that for the same products from the ROMP of cyclopentene using WCl_6/$AlEtCl_2$/BuLi and

TABLE 5.5.2. **SERIES A** ROMP OF CYCLOPENTENE FOR THE CATALYST SYSTEM WCl_6:$AlEtCl_2$:PStLi ($100<DP_n<140$) FOR RATIOS 1:0.5 TO 1:2.

Ratio W:Al:Li [DP_n theo]	PSt data $\overline{M}_n$ [M_{wp}]	[Cp]/mol.dm^{-3}. *{%(vv)toluene}* **(%(vv)cyclohexane)**	% yield	Time/ h.	M_{wp} for HMWP /g.mol^{-1}	PDI for HMWP	UV:RI area for HMWP	M_{wp} for LMWP /g.mol^{-1}	Type of LMWP peak.	UV:RI area for LMWP
1:0.5:0.5 [100]	11 000 [11 000]	[2.2] *{52}* **(24)**	11	24	240 000	2.5	0.1	11 000	1.1	6.5
1:1:1 [100]	11 000 [11 000]	[2.0] *{55}* **(23)**	6	24	290 000	2.5	0.1	11 000	1.1	6.2
1:1.5:1.5 [125]	12 700 [12 800]	[2.7] *{49}* **(22)**	11	20m.	900 000	2.5	<0.1	13 000	1.1	6.4
1:2:2 [140]	14 000 [14 700]	[2.9] *{40}* **(23)**	6	24	400 000	2.4	<0.1	15 000	1.1	6.3

Experiments at 25°C.

s-BuLi catalyst systems (see sections 4.1.2.2.2. and 4.1.2.2.3) in ratios between 1:1:1 and 1:2:2 can be carried out and a summary is given in table 5.5.3.

TABLE 5.5.3. HMWP DATA FROM ROMP OF CYCLOPENTENE USING WCl_6:$AlEtCl_2$:RLi (R'= Bu, *s*-Bu OR PSt) CATALYST SYSTEMS.

Ratio [W]:Al:RLi [RLi]	PSt data M_n [M_{wp}]	[Cp]/ mol.dm^{-3}. *{% (vv) toluene}* (%(vv)cyclohexane)	% yield	Time / m.	M_{wp} for HMWP / g.mol^{-1}	PDI for HMWP	UV:RI area for HMWP
1:1:1 [BuLi]		[2.7] *{74}* (2)	40	120	70 000	4.2*	0.2*
1:1:1 [*s*-BuLi]		[3.3] *{61}* (10)	56	20	125 000	5.8*	0.5*
1:1.5:1.5 [PStLi]	12 700 [12 800]	[2.7] *{49}* (22)	11	20	900 000	2.5	<0.1
1:2:2 [BuLi]		[2.2] *{77}* (3)	16	20	80 000	2.8	0.1
1:2:2 [*s*-BuLi]		[2.5] *{65}* (14)	20	20	100 000	2.1	0.1
1:2:2 [PStLi]	14000 [14700]	[2.9] *{40}* (23)	6	24h.	400 000	2.4	<0.1

Experiments at 25°C. * Data only determined on reanalysis of aged samples.

The optimum reacting ratio cannot be clearly identified from these results however the very high peak molecular weight of the HMWP using the $AlEtCl_2$/ PStLi co-catalyst is evident. The similarity of the PDI and UV:RI peak areas for freshly analysed samples can also be seen.

Table 5.5.4 compares the data for the HMWP from these experiments with those using only PStLi ($DP_n \geq 60$) as the co-catalyst given in tables 5.2.2 and 5.2.4. There are similarities in the M_{wp} of the two reactions that were particularly fast. The PDI values for the 3 component catalyst mixture are broader than for the WCl_6/ PStLi system and the UV/ RI deflection area for both reactions shows that no polypentenylene-rich co-catalyst has been formed. However the variations in reaction rates, yields and peak molecular weights indicate that

TABLE 5.5.4 HMWP DATA FROM ROMP OF CYCLOPENTENE USING WCl$_6$:AlEtCl$_2$:PStLi OR WCl$_6$:PStLi CATALYST SYSTEMS (PStLi DP$_n$>60).

Ratio [W]: to co-catalyst	PSt data M_n [M_{wp}]	[Cp]/mol.dm^{-3}. *{% (vv) toluene}* (%(vv)cyclohexane)	% yield	Time / h.	M_{wp} for HMWP / g.mol^{-1}	PDI for HMWP	UV:RI area for HMWP
1:1 W:Li	6000 [6300]	[2.4] *{62}* (8)	30	24	70 000	≈1.8	0.2*
1:2 W:Li	7100 [7900]	[2.8] *{54}* (16)	16	20m.	1 000 000	1.5	0.1
1:2 W:Li	10400 [11000]	[3.2] *{65}* (14)	25	2	300 000	1.8	0.1
1:2 W:Li	15000 [16000]	[2.5] *{42}* (21)	8	2	700 000	1.6	0.1
1:1:1 W:Al:Li	11000 [11000]	[2.0] *{55}* (23)	6	24	290 000	2.5	0.1
1:1.5:1.5 W:Al:Li	12700 [12800]	[2.7] *{49}* (22)	11	20m.	900 000	2.5	0.1
1:2:2 W:Al:Li	14000 [14700]	[2.9] *{40}* (23)	6	24	400 000	2.4	0.1

Experiments at 25°C. * UV to RI area ratio only determined on reanalysis of aged samples.

either the reaction conditions are not sufficintly rigorous to achieve reproducible results or that this complex reaction can produce different metathesis propagation centres in which there are several, interdependent factors controlling their production.

5.5.3. THE EFFECT OF LOW MOLECULAR WEIGHT POLYSTYRYLLITHIUM OVER A RANGE OF CATALYST RATIOS.

When the co-catalyst mixture of AlEtCl$_2$:PStLi (DP$_n$=10) in a 1:1 mole ratio was prepared by injecting, over argon, an appropriate volume of 1M AlEtCl$_2$/ cyclohexane solution into the PStLi solution in a small reaction flask, a pale yellow cloudy solution was formed. Method 1 described in section 2.5.2.1 was then followed and after polymerization the mixtures were quenched, poured into acetone and then methanol, reprecipitated, dried and analysed. A range of catalyst systems was tested.

TABLE 5.5.5. **SERIES A** ROMP OF CYCLOPENTENE FOR THE CATALYST SYSTEM WCl_6:$AlEtCl_2$:PStLi (DP_n=10) FOR RATIOS 1:0.5 TO 1:2.

Ratio W:Al:Li	PSt data $\overline{M}_n$ [M_{wp}]	[Cp]/mol.dm^{-3}. *{%(vv)toluene}* (%(vv)cyclohexane)	% yield	Time/ h.	M_{wp} for HMWP /g.mol^{-1}	PDI for HMWP	UV:RI area for HMWP	M_{wp} for LMWP /g.mol^{-1}	Type of LMWP peak.	UV:RI area for LMWP
1:0.5:0.5	1200 [1400]	[2.3] *{78}* (1)	38	1	400 000	2.2	0.2	20 000, 10 000, 3000, 1300	2 bimodal peaks.	4.4 0.4
1:1:1	1200 [1400]	[2.5] *{76}* (3)	20	1	160 000 70 000	2.3	0.1	30 000, 15 000, 3000, 1500	2 bimodal peaks.	5.2 0.8
1:1.5:1.5	1200 [1400]	[2.0] *{79}* (4)	10	1	180 000 90 000	1.8	0.1	20 000, 10 000, 3000, 1500.	2 bimodal peaks.	2.0 0.5
1:2:2	1200 [1400]	[2.2] *{74}* (5)	5	1	230 000	2.6	0.3	1500	unimodal	6.3
1:2.5:2.5	1200 [1400]	[3.0] *{48}* (11)	neg.	1	280 000	3.0	0.1	1500	unimodal	6.3

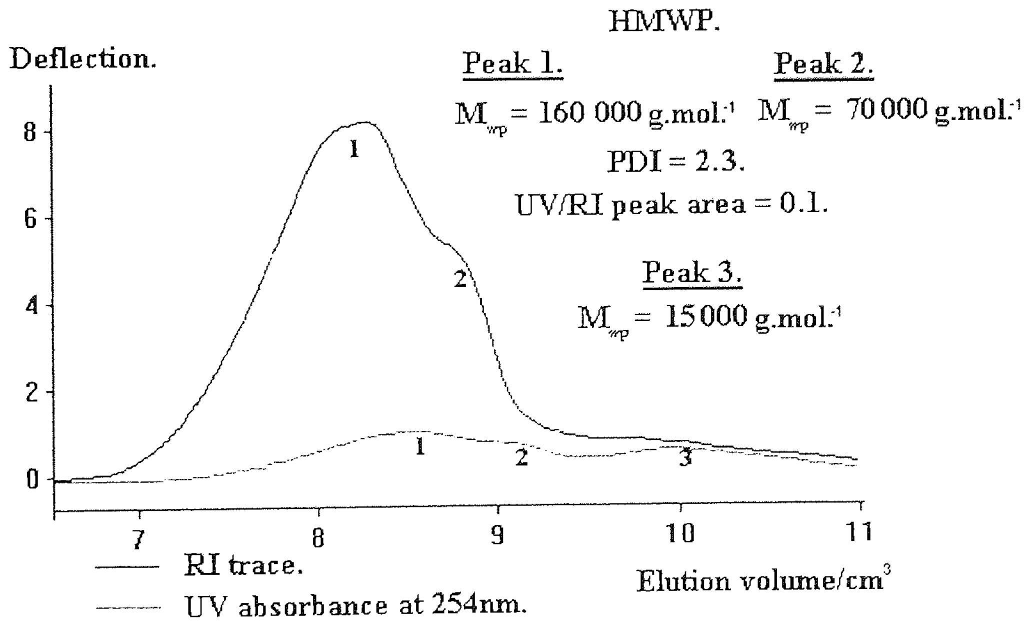
Experiments at 25°C. **LMWP** M_{wp}values underlined are for the principle peaks.

The catalyst mixtures with W:Al:Li of 1:0.5:0.5 to 1:1.5:1.5 went mauve on addition of the co-catalyst and were moderately viscous within an hour. The other two mixture remained brown/red on addition of the co-catalyst solution and were only slightly viscous when they were precipitated. Addition of the acetone filtrate to methanol produced hardly any additional precipitate, in any of the experiments, and so purification was extremely difficult; only sufficient solid was produced for SEC analysis. Table 5.5.5. gives the results for the range of catalyst components used.

The relatively high co-catalyst ratios (WCl_6:co-catalyst<1:2) produced small amounts of two homopolymers. The HMWP had very similar characteristics to the polypentenylene produced using this three component catalyst system with PStLi of longer chain length and the LMWP was just PSt from the co-catalyst.

The results for the systems 1:0.5:0.5≤W:Al:Li≤1:1.5:1.5 were more complex. All these reactions were relatively fast with the 1:0.5:0.5 catalyst ratio producing the highest yield. Figure 5.5.4 shows the SEC traces for the acetone-insoluble

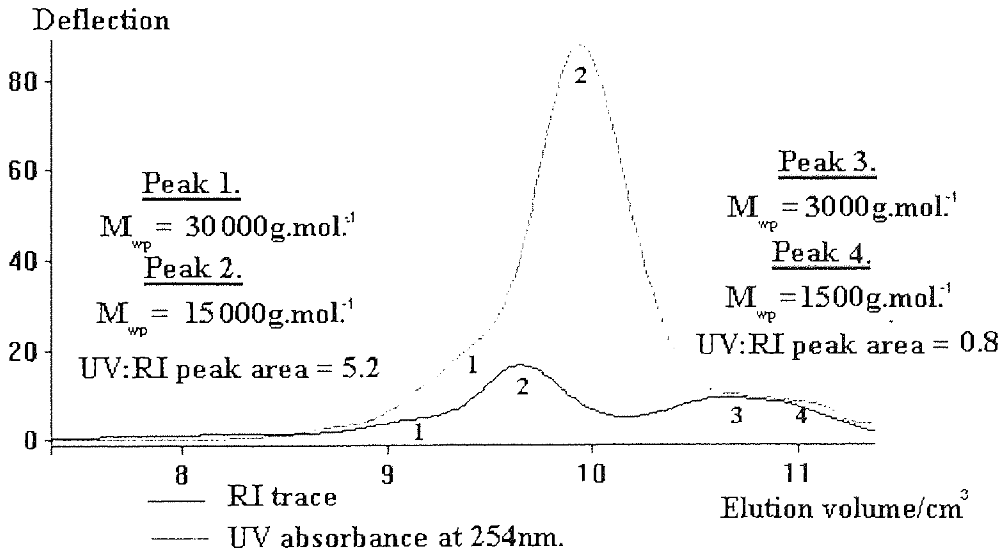
FIGURE 5.5.4. SEC TRACE OF THE ACETONE-INSOLUBLE PRODUCT.



products using the catalyst system WCl_6:$AlEtCl_2$:PStLi (DP_n=10) in the ratio 1:1:1. These SEC traces show a bimodal peak for the HMWP with molecular weights (400 000-70 000g.mol^{-1}), PDI values (1.8-2.3) and UV:RI peak areas (0.1-0.2) in the usual range. However there is also a small amount of material with lower peak molecular weights (30 000-10 000g.mol.$^{-1}$). Attempts to remove this low molecular weight material by reprecipitating the acetone-insoluble material were unsuccessful, the SEC traces continued to show peak 3.

The filtrates from the acetone precipitation, when poured into methanol, produced only minute amounts of precipitate and so limited reprecipitation was possible, involving a single cycle of dissolution in acetone and precipitation in methanol. The SEC analysis of the acetone-soluble material produced the traces shown in figure 5.5.5 for the ROMP of cyclopentene using WCl_6:$AlEtCl_2$:PStLi (DP_n=10) in the ratio 1:1:1 as the catalyst system.

FIGURE 5.5.5 SEC TRACE USING BOTH DETECTORS OF THE ACETONE-SOLUBLE PRODUCT.



The main bimodal peaks of these products had peak molecular weights between 30 000 and 10 000 g.mol.$^{-1}$ and relatively high UV:RI peak area ratios, which was unusual as no previous experiments had produced material with

M_{wp} so much higher than that of the PSt ($\overline{M}_n$=1200g.mol.$^{-1}$) and with such relatively high absorbance at 254nm. The bimodal LMWP peak might be PSt (M_{wp}= 1500g.mol^{-1}) and a dimeric species of PSt (M_{wp}=3000g.mol.$^{-1}$) although, as the UV:RI peak areas were less than 1 and the purification was not thorough, pentenylene-oligomers contaminated by transition metal complexes are another possibility.

The presence of some relatively high molecular weight material in this sample (probably polypentenylene) and possibly low molecular weight oligomers of cyclopentene made any SEC based separation of the material, with peak molecular weight 15 000g.mol.$^{-1}$, impracticable. The ^{1}H NMR spectrum of the fractions would not distinguish between a mixture of polymers and any co-polymer formed.

Comparing these results with the products from the ROMP of cyclopentene using the catalyst system WCl_6/PStLi. Only the ROMP using WCl_6/PStLi (DP_n=10) in the ratio 1:2 (see table 5.2.4.), showed any similarity in the nature of the HMWP, with the SEC showing several peaks but the UV:RI peak area was only 0.1 and the ^{1}H spectrum was of pure polypentenylene. The only evidence of any co-polymer using PStLi as the co-catalyst was in the proton spectra of the purified samples of some LMWP and the peak molecular weight of this was approximately twice the molecular weight of the polystyrene in the co-catalyst.

SEC evidence suggests that using the three component catalyst system, WCl_6/$AlEtCl_2$/PStLi (DP_n=10), there is a very small quantity of material with peak molecular weight approximately ten times that of the number average molecular weight of the polystyrene used (i.e. 10 000-15 000g.mol.$^{-1}$). Traces of this solid can be seen in the SEC of the acetone insoluble product but it is found mainly in the acetone-soluble mixture, suggesting that the material is polystyrene-rich. The small amount of this product available and the SEC evidence of the inadequate separation of the polypentenylene-rich, polystyrene-rich and possibly pentenylene-oligomeric/transition metal complexes made it impossible to investigate this product further.

5.5.4. THE EFFECT OF THE $AlEtCl_2$:PStLi RATIO.

Experiments using the catalyst system $WCl_6/AlEtCl_2/PStLi$ ($DP_n=10$) had produced some materials that might have been co-polymer, when the ratio of catalyst to co-catalyst was 1:<2 and the co-catalyst components ($AlEtCl_2/PStLi$) were in a 1:1 ratio. However the limitations of the technique were such that the co-catalyst mixture might have an excess of one component. We decided to investigate the system keeping the mole ratio of W:Al at 1:1 but changing the relative amount of PStLi. This co-catalyst range was designed to produce a varied mixture of polystyryl/ethylaluminium chloride compounds so that the subsequent effects on the rate of polymerization of cyclopentene and the products of the metathesis could be investigated. The mole ratios of PStLi and $AlEtCl_2$ used and the subsequent theoretical co-catalyst composition are shown in table 5.5.6.

TABLE 5.5.6 TO SHOW THE RANGE OF MOLE RATIOS OF PStLi:$AlEtCl_2$ USED AS CO-CATALYST SYSTEMS.

Mole ratio PStLi:$AlEtCl_2$	THEORETICAL CO-CATALYST.
0.5 : 1.0	$Al(PSt_{10})EtCl : AlEtCl_2 = 1:1$
1.0 : 1.0	$Al(PSt_{10})$.EtCl.
1.5 : 1.0	$Al(PSt_{10})_2Et : Al(PSt_{10})EtCl = 1:1$
2.0 : 1.0	$Al(PSt_{10})_2Et$

In a typical experiment a reaction flask with side-arm (see figure 2.5) was used. 8.2g of cyclopentene (0.12 moles) and 20cm^3 of toluene were distilled under vacuum into the main vessel B. Using the Schlenk technique 1.2cm^3 0.10M PStLi (DP_n=10, 1.2x10^{-4}moles) and 1.4cm^3 0.17M $AlEtCl_2$ (2.4x10^{-4} moles) were injected into the side-arm A and 6.0cm^3 0.04M WCl_6 (2.4x10^{-4} moles) were injected into B. The taps were closed and 2 minutes after the addition of the catalyst to the monomer solution the co-catalyst mixture was run in from the side-arm. The cyclopentene:WCl_6:$AlEtCl_2$:PStLi ratio was 500:1:1:0.5, there was 70% toluene and 3% cyclohexane in the 3M solution.

Injection of the $AlEtCl_2$ into the PStLi solution produced a white cloudy mixture for the ratios Al:Li 1:0.5 and 1:1 but the orange colour of excess PStLi remained for the 1:1.5 and 1:2 mixtures. Addition of the co-catalyst mixture to the cyclopentene/WCl_6 solution produced mauve solutions. The mixtures W:Al:Li of 1:1:0.5 and 1:1:1 became viscous within 10 minutes but the other solutions showed little change in viscosity after 24 hours.. Although all the experiments produced an acetone-insolube product when the filtrates were added to methanol very little polystyrene-rich material was obtained and for the W:Al:Li ratio of 1:1:0.5 there was no precipitate in methanol. Further purification of the acetone-soluble material was limited. The results are summarised in table 5.5.7.

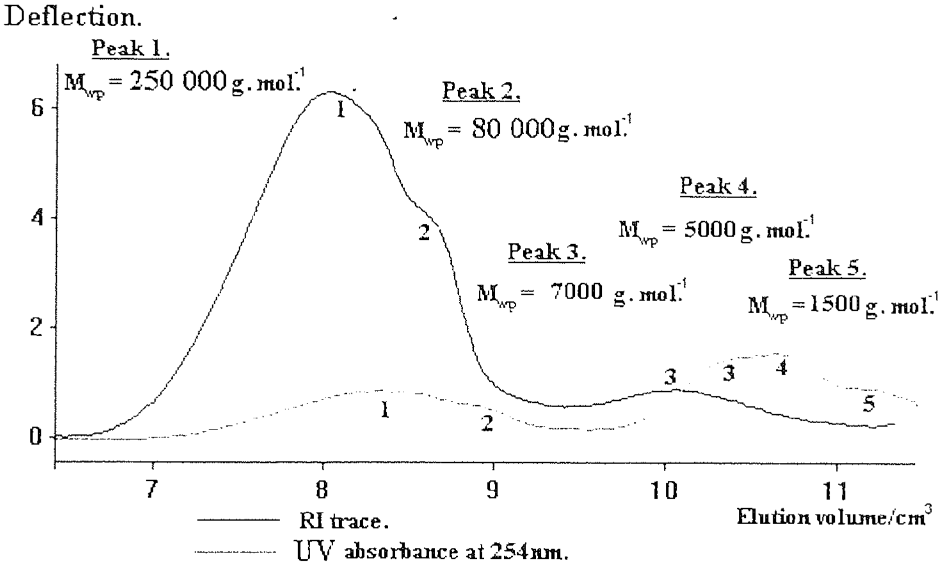
Figure 5.5.6 shows the SEC analysis of the product of the reaction using W:Al:Li of 1:1:0.5 which produced only an acetone insoluble precipitate. The similarity of the traces to the results obtained using W:Al:Li of 1:1:1 and 1:1.5:1.5 (see table 5.5.6 and figures 5.5.4 and 5.5.5) are obvious. The RI trace in figure 5.5.6 shows no evidence of the original PSt used in the co-catalyst but the UV/visible detector, set at 254nm., is very sensitive to phenyl-groups and there were signs of a peak at the expected M_n of PSt (peak 5 with M_{wp}=1500 g.mol.$^{-1}$). After repeated reprecipitation of the acetone-insoluble material, the polystyrene peak could still be detected in the SEC trace and so NMR spectroscopy could not be used to determine the nature of this product which is known to be a mixture of polypentenylene-rich and polystyrene-rich products.

TABLE 5.5.7 **SERIES A** ROMP OF CYCLOPENTENE FOR THE CATALYST SYSTEM WCl_6:$AlEtCl_2$:PStLi (DP_n=10) FOR RATIOS 1:1:0.5 TO 1:1:2.

Ratio W:Al:Li	PSt data $\overline{M_n}$ [M_{wp}]	[Cp]/mol.dm^{-3}. *{% (vv) toluene}* (%(vv)cyclohexane)	% yield	Time/ h.	M_{wp} for HMWP /g.mol^{-1}	PDI for HMWP	UV:RI area for HMWP	M_{wp} for LMWP /g.mol^{-1}	Type of LMWP peak.	UV:RI area for LMWP
1:1:0.5	1200 [1300]	[3.0] *{70}* (3)	20	1	250 000 80 000	2.4	0.1	7000 (5000, 1500)		≈2.2
1:1:1	1200 [1300]	[2.3] *{75}* (4)	20	1	200 000 25 000	3.3	0.1	12 000, 1300	2 peaks	
1:1:1.5	1200 [1300]	[2.2] *{74}* (6)	8	24	160 000 20 000	4.6	0.5	1500.	unimodal	≈2.0
1:1:2	1200 [1300]	[2.2] *{73}* (7)	6	24	170 000 60 000	3.1	0.3	15 000 1500	bimodal	

Experiments at 25°C.

FIGURE 5.5.6 SEC TRACE USING BOTH DETECTORS OF THE ACETONE INSOLUBLE PRODUCT.



In the experiments using mole ratios PStLi≥$AlEtCl_2$ the reactions were much slower, the reducing power of the PStLi may be the cause of this. Acetone-insoluble material and a precipitate in methanol from the acetone filtrate were obtained but there was only a small amount of the latter material. The SEC analyses showed that the HMWP and LMWP were not completely separated by the fractional precipitation technique because again products with peak molecular weight between 60 000 and 15 000 g.mol.$^{-1}$ appeared in both fractions even after reprecipitation.

The UV:RI peak area for some of these species (60 000≥M_{wp} ≥15 000 g.mol.$^{-1}$) were higher than for pure polypentenylene (0.1) and less than that of pure polystyrene (6.4-6.7). However the overlap of these peaks made it impossible to calculate the UV:RI peak area accurately.

The deactivating effect of excess PStLi in the co-catalyst mixture is evident but the variation in the mole ratio of the catalyst components has not produced a simple reaction product or clarified the mechanism for the production of active propagation sites. The complexity of product mixtures is shown by the

SEC traces and must result from different initiation, transfer or termination reactions. Although the homopolymer polypentenylene still seems to be formed most easily by the most active catalyst systems, there is evidence that co-polymer may be produced in small amounts by the $WCl_6/AlEtCl_2/PStLi$ catalyst systems when the oligo-StLi has $DP_n \leq 20$.

CHAPTER 6.

CONCLUSIONS AND FUTURE WORK.

6.1 CONCLUSIONS.

6.1.1 PRODUCT ANALYSIS USING SEC.

In determining the nature of co-polymers, SEC can have a significant role especially if the absorption chatacteristics of the component blocks differ greatly. Gregory[182] and Thorn-Csanyi[183] made use of SEC characterisation in the analysis of materials made by WCl_6/PStLi initiated ring-opening metathesis polymerization of cyclopentene. These workers assumed that pure polypentenylene has no absorbance at 254nm. In this study the UV/visible detector showed negligible deflection when this material was eluted from the column and a chart recorder monitored the response, so such assumptions were not unreasonable. The introduction of a computerised data collection system challenged this basic assumption and therefore a more quantitative approach could be adopted to the contribution of the polypentenylene blocks to the absorbance at 254nm.. The absorbance of homo-polypentenylene at this wavelength was found to be dependent on its method of purification and on the aging of the solutions. A rigorous reprecipitation procedure was adopted and only freshly prepared solutions of polymer when analysed produced reproducible results. However a small, but significant absorbance at 254nm. was still observed in 0.5% (wv) solutions of polypentenylene in THF. The UV/RI peak area was measured as 0.1 in most solutions of homo-polypentenylene. Since Gregory had not taken this fact into account when analysing his material, his assertion that block co-polymers were produced has to be questioned.

6.1.2 ROMP OF CYCLOPENTENE USING TWO COMPONENT CATALYST SYSTEMS.

The series A experiments in this study of ring-opening metathesis polymerization of cyclopentene, involved sequential addition of the WCl_6 catalyst and the co-catalyst (BuLi, *s*-BuLi or $AlEtCl_2$) to 2.5M solutions of cyclopentene in toluene. It was shown that the time between the addition of the catalyst and the co-catalyst (the aging time) affected the rate of reaction. The yield after ten minutes decreased if the aging time was greater than 3 minutes, which is in broad agreement with the findings of Tuck[186] who reported that an aging time of 2 minutes produced the fastest initial rate of ROMP of 2.5M cyclopentene solutions, using the catalyst $WCl_6/Al(iBu)_3$.

A significant feature of the work undertaken in this section was the effect of the solvent on the polymerization. It was unexpectedly found that cyclohexane was a poor solvent for the metathesis reaction. The solubility of WCl_6 in cyclohexane was low and the rate of the ROMP of cyclopentene was slower (20% in 2 hours) compared to the reaction with toluene as the main solvent (66% in 1 hour), using the same catalyst system (WCl_6: BuLi=1:2). The HMWP also had a lower peak molecular weight (50 000g.mol.$^{-1}$) when cyclohexane was the main solvent. The formation of aggregates of species with permanent dipoles in cyclohexane has been mentioned (e.g. $(PStLi)_2$, $(BuLi)_4$) and it may be that the rate of metathesis is retarded because of association of propagating species or their precursors in this solvent. Toluene, with its associated π electron system, is known to produce lower degrees of aggregation in many cases and this could account for the higher rate of metathesis in this solvent.

The SEC traces of the metathesis products showed both high molecular weight material and low molecular weight (oligomeric) products although there were relatively small amounts of the LMWP in most polymerizations. If the ratio of cyclopentene to WCl_6 was maintained at 500:1, the optimum molar ratio of catalyst to co-catalyst was 1:2, using each of the three co-catalysts, BuLi, *s*-BuLi or $AlEtCl_2$. These results were in agreement with the work of Tuck[186], who used the $WCl_6/Al(iBu)_3$ catalyst system, and Gregory[184], using the WCl_6/BuLi catalyst mixture, for the ROMP of cyclopentene.

The peak molecular weights of the high molecular weight polypentenamer and the rates of reaction, using the optimum ratio of catalyst to co-catalyst for all three co-catalysts, were very similar. Typically, using the WCl_6/BuLi catalyst system, there were two significant features; as the Li:W ratio increased to a maximum at the ratio 2:1 so the $M_{wp}$of the HMWP decreased to a minimum. Further addition of BuLi, beyond this ratio, reduced the rate and the produced a significant increase in the M_{wp}. A possible explanation is that as the ratio of BuLi increase to 2:1 the concentration of the active centres increases to a maximum. Further addition of BuLi causes a decrease in this concentration because the tungsten species is reduced to an inactive species. One cannot ignore also the possible effects of transfer reactions, involving butyllithium, on the molecular weight of the product.

The PDI for the polymers produced using butyllithium co-catalysts were relatively narrow (1.6-1.8) but the materials formed using the co-catalyst $AlEtCl_2$ have broader PDI (1.9-2.7). The ratio of the absorbance at 254nm. to the RI deflection area for the purified products, as freshly prepared 0.5% (wv) solutions in THF, was consistently 0.1. The ^1H NMR spectra of the polypentenylene samples gave a good indication of the purity of the high molecular weight polymers. Using BuLi co-catalysts, the samples produced materials with readily interpreted spectra but with $AlEtCl_2$ as the co-catalyst extra peaks were evident in the proton spectra (particularly at the δ of methylene resonance). The ^{13}C spectra showed a relatively low *cis*-carbon-to-carbon double bond content (σ_c=0.2) in the all the polypentenylene samples.

Although all three co-catalysts are recognised alkylating agents, the additional Lewis acid character of $AlEtCl_2$ may account for the observed differences in the PDI and proton spectra of the polymers they produce. The alkylating action is involved in the generation of propagating species for the metathesis and therefore the production of the polypentenylene. However the Lewis acidity may result in the formation of other active propagating species or produce side-reactions e.g. Friedel Craft reactions.

6.1.3 ROMP OF CYCLOPENTENE USING THREE COMPONENT CATALYST SYSTEMS.

No one optimum ratio was found for the three component catalyst systems WCl_6/$AlEtCl_2$/BuLi or *s*-BuLi, the fastest reactions were obtained with the ratios 1:2:2 and 1:1:1 respectively. The peak molecular weights of the HMWP, using these ratios, were within the same range as for the two components systems. Using fresh solutions of $AlEtCl_2$ and the W:Al:Li ratio of 1:2:2, immediate SEC analysis of the products showed them to have PDIs (2.8 and 2.1) which were comparable to the values using $AlEtCl_2$ alone (($1.9<PDI<2.7$).

The characteristics of the polypentenylene were very similar to the product from the two component catalyst system. The UV/RI peak areas from the SEC traces of freshly prepared samples were 0.1 and the proton spectra were identical to those from the products using BuLi as the only co-catalyst. The ^{13}C spectra confirmed that the samples of polypentenylene from all these series A experiments had predominantly *trans*- double bonds (σ_c=0.2).

6.1.4 ALTERNATIVE PROCEDURES.

Series B polymerizations of cyclopentene involved premixing the WCl_6/co-catalyst components before adding them to the monomer solution. The optimum ratio of W:Li for both BuLi and *s*-BuLi was 1:1 and, with an aging time of 2 minutes, these mixtures were the only ones to produce significant amounts of HMWP in this series. The peak molecular weight and PDI of the HMWP, for the optimum catalyst ratio, were in the same range as for the product using method A. The proton spectrum of the HMWP, using premixed WCl_6:BuLi of 1:1, had very few unassigned peaks and the ^{13}C spectrum varied, from that formed by method A, only in an increase in the number of *cis*-linkages (σ_c=0.3).

SEC analysis of the products of several of these polymerizations showed an increased amount of the LMWP. The premixing of the WCl_6/$AlEtCl_2$ catalyst components produced initially an anomalous result but using pure $AlEtCl_2$ (W:Al=1:1) confirmed the findings of Tuck[186], who premixed the components $WCl_6/Al(i\text{-}Bu)_3$, as there was very little HMWP formed.

A limited number of series C experiments, using ethanol as an additive, were carried out but there was no dramatic increase in rate or other significant advantages to the ROMP of using EtOH/WCl_6/BuLi or *s*-BuLi as the catalyst system.

6.1.5 ROMP USING WCl_6/POLYSTYRYLLITHIUM AS THE CATALYST.

The series A experiments extended the catalyst system for the ROMP of cyclopentene to WCl_6/PStLi. The two objectives were to investigate the initiation reaction of the metathesis polymerization and to prepare block co-polymer by anionic to metathesis transformation polymerization.

The optimum conditions for the polymerization using this co-catalyst system were investigated. No one optimum WCl_6:PStLi ratio was found, the ratios 1:1 and 1:2 produced similar yields of polymer. Cyclohexane was again found to be a poor solvent for the metathesis as the rate of reaction, the yield and peak molecular weight of the polymer were reduced by increased amounts of cyclohexane in the reaction mixture.

The products were shown by SEC analysis to be high molecular weight polypentenylene-rich material and low molecular weight polystyrene-rich material. Good separation of these was effected by fractional precipitation, using acetone to precipitate the polypentenylene-rich material (HMWP) and adding the filtrate to methanol to precipitate the polystyrene-rich product. Initially the method adopted by Gregory had been used which involved the addition of hexane to the reaction mixture to precipitate the polystyrene-rich material. It was found that when hexane was added to the quenched solutions, the polystyrene-rich solid was held in suspension and not easily separated from the solution by filtration, so contamination of the polypentenylene-rich product occurred.

For systems using the co-catalyst PStLi (DP_n<70) the yield of the HMWP was not greatly affected by increased length of the PSt chain and the molecular weight of the polypentenylene-rich material was in the same range as for the polymer using the BuLi co-catalyst systems. It was difficult to integrate the highly viscous PStLi (DP_n>100) solutions into the reaction mixture without the addition of relatively large amounts of cyclohexane and so the results were not thought to be reliable and should be reinvestigated by preparing toluene or benzene solutions of PStLi.

6.1.5.1 Character of the High Molecular Weight Product of ROMP.

In all the experiments using PStLi as the co-catalyst, the UV/RI peak area for the HMWP was approx. 0.1 and no greater than that for polypentenylene produced using BuLi or $AlEtCl_2$ co-catalyst combinations. Further, ^1H NMR spectra (see figure 5.2.5) showed that the purified polypentenylene-rich product had no discernible phenyl proton resonance between 6.5 and 7.5ppm, which seems to contradict the evidence from the work of Gregory. Thorn-Csanyi reports that "using oligostyryllithium (average DP_n=6) UV spectroscopic examination of the polymer fraction proved the occurrence of styrene units." No evidence was presented and our studies have shown that these products and pure polypentenylene have the same absorbance at 254nm..

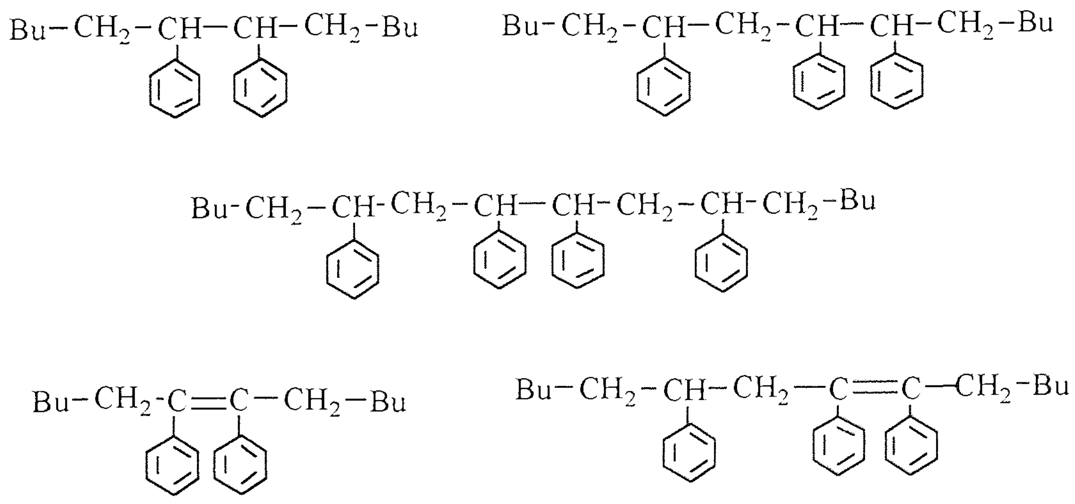
Thorn-Csanyi produced ^1H NMR evidence for the presence of phenyl ^1H, and therefore styrene units, in the HMWP from the ROMP of cyclopentene using WCl_6/(EtOEt)/PStLi(DP_n=300) but calculated that 99% of the polypentenylene chains did not have terminal polystyrene groups. As has been stated there was no evidence of styrene units in the HMWP from any our experiments.

6.1.5.2 Character of the Low Molecular Weight Product from ROMP.

SEC analysis of the polystyrene-rich product generally produced a bimodal peak with the peak molecular weights corresponding to those of the PSt from the killed co-catalyst and a dimer of this species. There is also correlation between the UV/RI peak area ratios (6.3-6.9) of the lower molecular weight species and the polystyrene from the co-catalyst.

Thorn-Csanyi produced SEC evidence that WCl_6 reacts with PStLi (DP_n =30), in the absence of monomer, to form some dimeric species. WCl_6 and oligostyryllithium (DP_n 1 and 2) were mixed and the products were identified, using mass spectrometry, as having the structures shown in scheme 6.1, which consist of dimers with either saturated or in-chain carbon-to-carbon double bonds.

SCHEME 6.1.



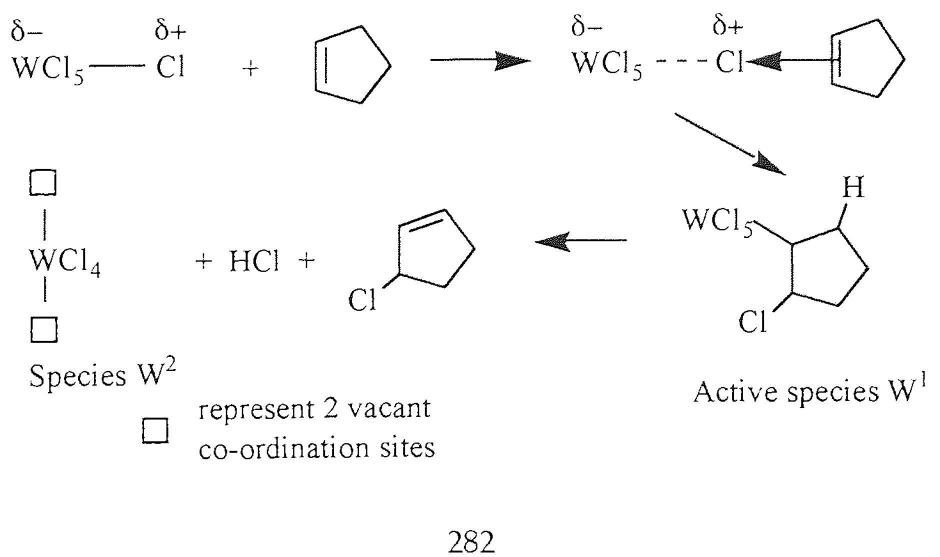
Two observations in our studies, however, seemed to indicate that the LMWP might not just be PSt and its dimer. First the M_{wp} values for the two components of the LMWP did not always correlate with the expected values for the PSt and its dimer (see figure 5.2.4) and sometimes the SEC showed a single peak at M_{wp}>M_n (PSt in co-catalyst) (see figure 5.2.12).

SEC separation of the two LMWPs shown in figure 5.2.4 followed by analysis using proton NMR confirmed that the species with the lower molecular weight was pure polystyrene (figure 5.2.10) but the product with the higher molecular weight had resonance peaks corresponding to methine protons attached to a carbon-to-carbon double bond (figure 5.2.9). The polypentenylene content of this compound could be quantified using the proton resonance areas and the existence of some ABBA styrene-pentenylene block co-polymer proposed.

The LMWP product identified by its SEC in figure 5.2.12 was also found to have alkene proton resonances, from its spectrum shown in figure 5.2.13.

Thorn-Csanyi reports that PStLi was added to the monomer solution before the addition of the WCl_6 catalyst solution and so any dimerisation reaction between the living species and the transition metal compound may occur independently of metathesis. The nature of the saturated dimeric species suggested in scheme 6.1 would render the PSt inactive to metathesis, while the unsaturated dimeric forms could be formed from carbene precursors. It has been shown that ROMP of the cyclopentene occurs despite the interaction of the PStLi and the WCl_6 and so active carbenes must be produced.

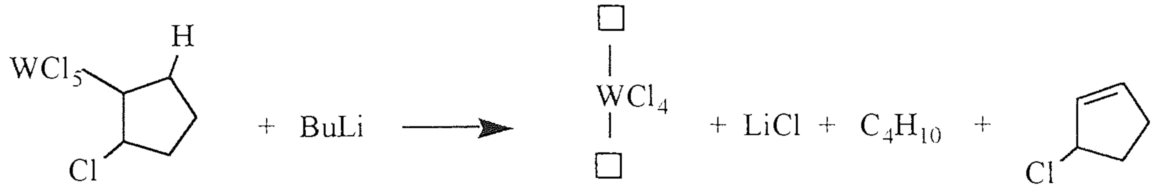
In our studies the series A experiments involved addition of WCl_6 to the 2.5M cyclopentene solution and the colour change (blue to brown) indicated some interaction between the monomer and the transition metal. The reaction between solutions of cyclopentene and WCl_6 in toluene has been studied[105] using UV/visible spectrophotometry and, based on the results and a study of the products of the reaction, a mechanism has been proposed to account for these colour changes.



The production of species W^2 (W(IV)) from the active species W^1 was suggested as the reason for the colour change.

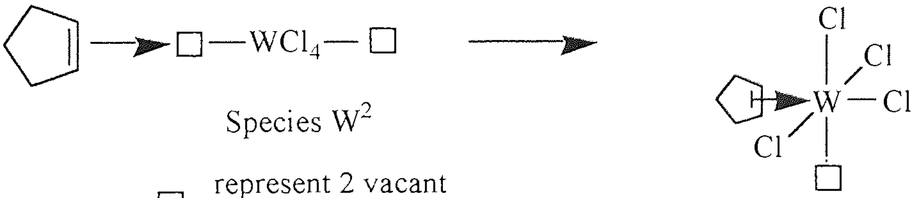
Two theories can be mooted for the action of the metal alkyl co-catalyst, the first would also explain the optimum 1:2 ratio for WCl_6: co-catalyst observed in all the two component systems in series A experiments.

1. The production of W^2 from W^1 would occur at an increased rate in the presence of a metal alkyl which would react in a 1:1 ratio to form butane with BuLi and ethane with $AlEtCl_2$.



W^1 W^2

The reduction of W(VI) to W(IV) (species W^2) is well known in metathesis reactions but cyclopentene plays an essential part. WCl_4 itself is only a low activity metathesis catalyst, however it seems likely that coordination of the monomer to the vacant sites during the course of the reaction sequence prevents the transition metal compound forming the polymeric species $(WCl_4)_n$.



Species W^2

☐ represent 2 vacant co-ordination sites

Species W^3

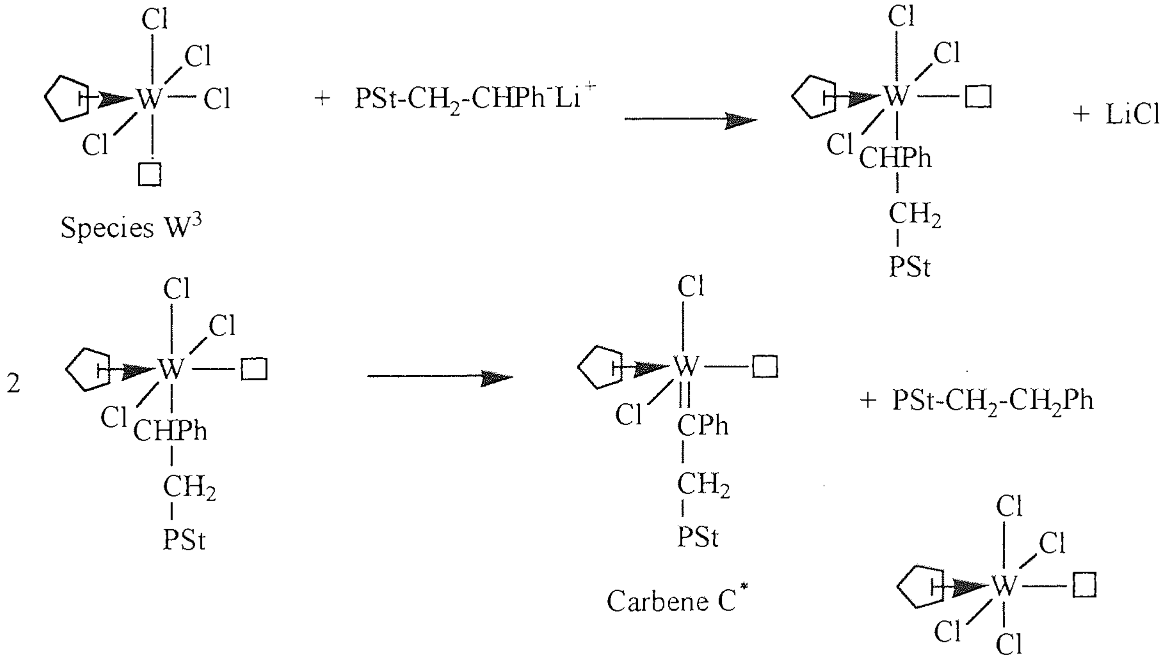
The formation of the propagating carbene may then result from alkylation of the transition metal complex followed by α-hydrogen loss. This type of reaction has been been proposed by several workers[108,109]. The metathesis catalyst system $WCl_6/SnMe_4$ was found to produce methane in the early stages of the reaction so the following scheme 6.2 was proposed which involves alkylation followed by disproportionation.

SCHEME 6.2.

$$WCl_6 + SnMe_4 \dashrightarrow WCl_5Me$$

$$2WCl_5Me \dashrightarrow Cl_4W{=}CH_2 + CH_4 + WCl_6$$

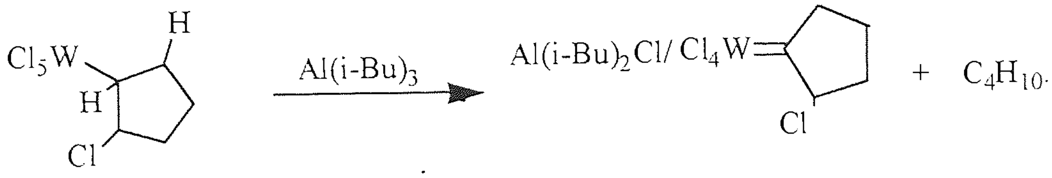
The second mole of co-catalyst (BuLi or $AlEtCl_2$) would be involved in this reaction. Based on evidence that block co-polymers of styrene-pentenylene were formed, by the action of the WCl_6/PStLi catalyst system on cyclopentene, Gregory[181] proposed that PSt-based carbenes could also be produced from alkylation of the species W^3 and put forward a mechanism based on a LiCl co-ordination complex. However an alternative mechanism similar to that in scheme 6.2 is another possibility.



The evidence from this study is that no HMWP block co-polymer was formed but some low molecular weight material may contain polypentenylene and be ABBA block co-polymer formed from propagation of a carbene of the type shown in the above equation (C*). This occurs only to a relatively small extent and ROMP of cyclopentene produces homo-polypentenylene by a much more active and abundant carbene (e.g. C** in the following section).

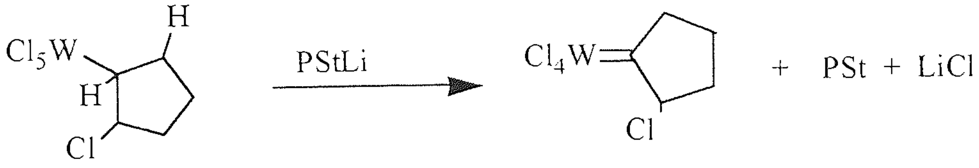
2. Several workers have studied the ROMP of cylopentene, using the $WCl_6/(Al(i\text{-}Bu)_3)$,[106,157] catalyst system and have suggested that the active

species W^1 reacts directly with the Lewis acid by the following mechanism to produce the initiating metallocarbene.



Active species W^1

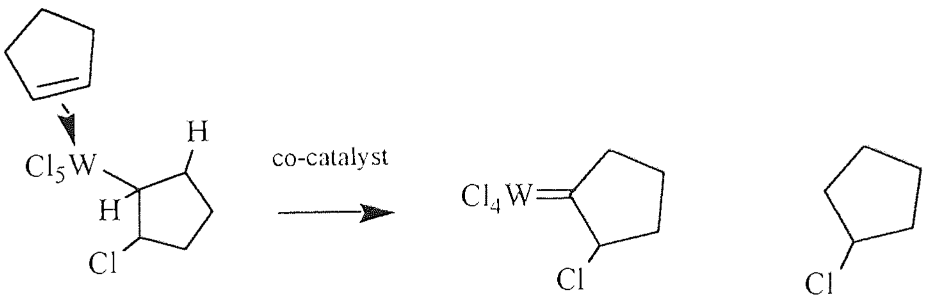
However BuLi and PStLi may be equally effective in producing this carbene (C**) by the following reaction.



Active species W^1

Carbene C**

Alternatively the same carbene may be formed by a catalysed reaction between W^1 and the monomer.



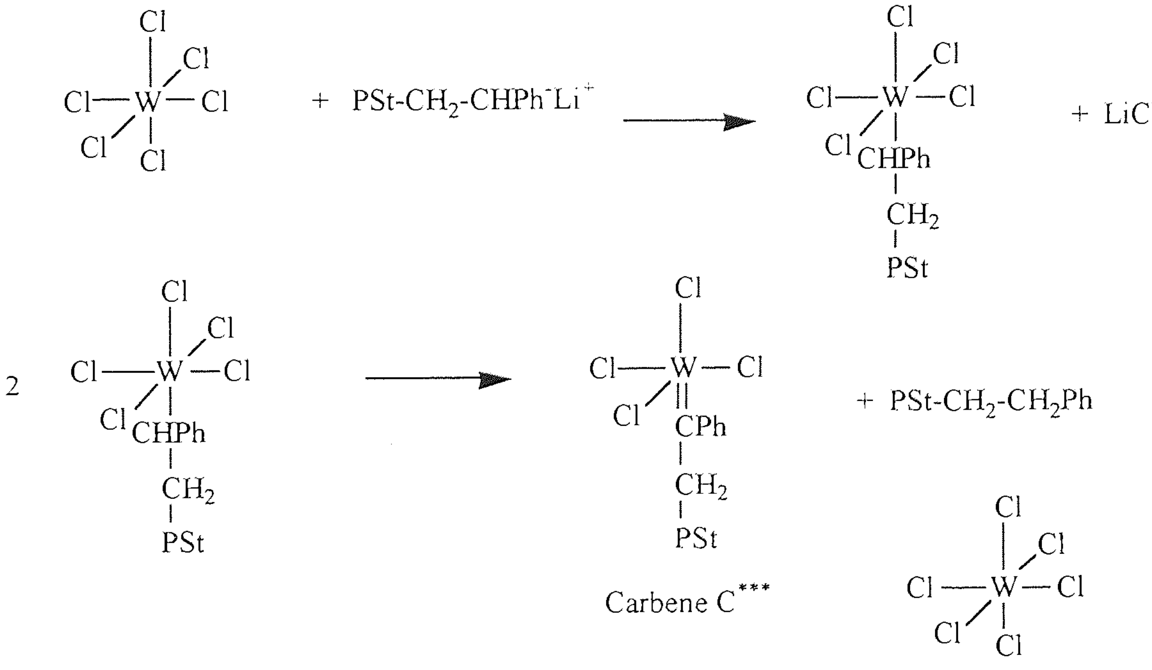
W^1

Carbene C**

The evidence from this study is that homo-polymerization of cyclopentene is the dominant reaction using any of the co-catalysts and the mechanism of initiation does not primarily involve the creation of transition metal alkyls from the catalyst components that go on to form the carbene.

Series B experiments were adapted to investigate the effect of different premixing times on the nature of the products. WCl_6:PStLi(DP_n=20) solutions in 1:2 ratio were premixed for 1, 5 and 60 minutes to asertain if any reaction between the catalyst components inhibited the ROMP. Although the one minute premix time produced the highest yield after 20 minutes, there were similar amounts of HMWP after the 5 and 60 minutes premix time. The peak molecular wights were all high and, for the product with 60 minutes premix time, particularly high (M_{wp}=500 000g.mol.$^{-1}$). This confirms that any reaction between the WCl_6 and the PStLi, as indicated by the colour changes taking place, does not inhibit metathesis. The SEC traces for the LMWP all showed very similar bimodal character (see figure 5.3.1) with the M_{wp} for both being considerable higher (M_{wp}=6500 and 4000g.mol.$^{-1}$) than for the PStLi co-catalyst (M_n=2000g.mol.$^{-1}$). Separation of the two components was not possible but the proton spectrum of the mixture again showed evidence of alkene methine resonance at 5.3ppm.

The evidence of Thorn-Csanyi of a reaction between the catalyst components may well be as a result of the type of alkylation reaction proposed in scheme 6.2 involving PStLi and WCl_6.



Again the carbene (C***) has the potential to produce block co-polymer by metathesis. Analysis of the product indicated that there were two polystyrene blocks per chain and this would result in a triblock co-polymer. The most probable explanation is that the central polypentenylene section is from two shorter polypentenylene blocks joined in the termination and hence an ABBA block co-polymer is formed. Bimolecular termination would not just account for the formation of ABBA block co-polymers but also dimeric species with structures similar to those identified in scheme 6.1.

$$2\ W{=}CHPhCH_2\text{-}PSt.\ \text{----->}\ \text{Products.}$$

Bimolecular termination reactions have been proposed for metathesis reactions by Grubbs[108] and Casey[162] and are known to occur in other polymerization reactions as demonstrated by Olive and Henrici-Olive for Ziegler-Natta catalysed polymerizations.

6.1.6 ROMP USING WCl_6/ $AlEtCl_2$/PStLi.

Only the series A procedure was attempted with this three component catalyst system. Solutions of $AlEtCl_2$ and PStLi were mixed in 1:1 mole ratios and the immediate precipitation of a white solid and the disappearance of the orange colour of the PStLi were taken as an indication that some polystyryl aluminium species had been formed. The initial series of experiments tested the effect of different catalyst ratios on the rate of ROMP of cyclopentene. A 1:1:1 mole ratio of WCl_6:$AlEtCl_2$:PStLi (DP_n=30) produced the fastest reaction. SEC analysis of the products indicated very high peak molecular weights for the HMWP, especially for the product from the fastest reaction (500 000 g.mol.$^{-1}$), relatively broad PDI (>3.7) and relatively high absorbance at 254nm. The ^{1}H NMR spectra confirmed that the HMWPs were pure polypentenylene.

Using both high molecular weight (DP_n>100) polystyryllithium and oligostyryllithium (DP_n<20) no optimum catalyst to co-catalyst ratio was found but the fastest reaction in any series produced very high molecular weight polypentenylene. The PDI values were in the range for polymer produced using Al based co-catalysts and there was the expected small absorbance at 254nm..

The HMWP formed using the oligo-St/$AlEtCl_2$ co-catalyst system had similar characteristics to polypentenylene produced in other experiments but the acetone-insoluble product contained traces of material with peak molecular weight 30 000-10 000g.mol.$^{-1}$ (see figure 5.5.4). The acetone filtrate produced only a slight precipitate which again contained products with M_{wp} between 30 000 and 1000g.mol.$^{-1}$ (see figure 5.5.5). The absorbance at 254nm. of some of this species, with M_{wp}>>M_n of the oligo-styryl co-catalyst, were relatively high (UV:RI peak area 5.2) and between the value expected for pure PSt and polypentenylene. It was not possible to purify the samples and so NMR analysis was not carried out.

In all these experiments achieving the predetermined ratio of the catalyst components was a problem. As this ratio has a dramatic effect on the rate of reaction and is a controlling factor in obtaining reproducible results, it was decided to investigate the effect of different W:Al:Li ratios on the rate of reaction and on the nature of the products. As only experiments with oligo-styryllithium and $AlEtCl_2$ had produced any material that might have been co-polymer, a series of experiments with both excess $AlEtCl_2$ and excess oligo-StLi (DP_n=10) were carried out but the W:Al ratio was maintained at 1:1.

In experiments using an excess of oligo-StLi (W:Al:Li =1:1:>1) a very slow reaction occurred whereas using an exces of $AlEtCl_2$ (W:Al:Li = 1:1:<1) produced HMWP much more rapidly. All the reactions produced minute amounts of material with M_{wp} between 25 000 and 5000 g.mol.$^{-1}$, which also had absorbance at 254nm. which was not that of polystyrene or polypentenylene. These products could not be purified sufficiently to be characterised by NMR spectroscopy.

6.2 FUTURE WORK.

The role of the solvent has been found to be a critical factor in the ring-opening metathesis polymerization. The use of cyclohexane as a solvent for the preparation of the polystyryllithium subsequently caused problems with the metathesis reaction partly because the rate of polymerization was reduced. This may have been caused by the solvent changing the structure of the propagating species. The immiscibility of concentrated solutions of high molecular weight PStLi in cyclohexane with solutions of cyclopentene in toluene was an addition factor. An investigation of the polymerization of cyclopentene with the WCl_6/PStLi catalyst system using only toluene or benzene as the solvent would provide a more rigorous study. Although solutions of PStLi in toluene are known to undergo transfer to solvent, this reaction takes place slowly in the later stages of the polymerization so the PStLi could be synthesised immediately prior to its use. The benefits of toluene as a solvent for this metathesis reaction might then be explained.

The production of the homo-polypentenylene seems to be the dominant reaction for all the different metathesis catalyst systems used. Although the critical effect of the reaction conditions, particularly the catalyst to co-catalyst ratio, has been demonstrated. The three component catalyst system of WCl_6/$AlEtCl_2$/PStLi, using low molecular weight PStLi, seemed to show the most promising evidence of some block co-polymer formation but an investigation based on more accurate control of the ratio of the catalyst components is needed. SEC separation on a larger scale would both simplify and improve product identification.

The range of transition metal catalysts available for the metathesis of cyclopentene is extensive. A study using complexes of rhenium, tantulum or molybdenum and the co-catalyst systems PStLi and $AlEtCl_2$/PStLi might have greater success in promoting the formation of styrene-pentenylene block co-polymers and establish the role of the transition metal, particularly with regards to its oxidation state.

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