# Polymerization of arylcycloalkenes initiated by tungsten hexachloride-tetraphenyltin

El-Saafin, Isam F.A.F.

El-Saafin, Isam F.A.F. (1979) *Polymerization of arylcycloalkenes initiated by tungsten hexachloride-tetraphenyltin*, Durham theses, Durham University. Available at Durham E-Theses Online: http://etheses.dur.ac.uk/8995/

# POLYMERIZATION OF ARYLCYCLOALKENES INITIATED BY TUNGSTEN HEXACHLORIDE-TETRAPHENYLTIN

By

ISAM F.A.F. EL-SAAFIN, B.Sc. (Riyad University)

(Graduate Society)

A thesis submitted for the degree of Master of Science to the
University of Durham
England

1979

بسم الله الرحمن الرحيم

# اهداء

عرفاناً منى بالجميل وبمزيد من الشكر والامتنان
والتقدير اهدى هذه الرسالة لوالدى المرحوم
ولوالدتى ولأخى هشام السعافين

To the memory of my Father,

and for my Mother,

and for my Brother, Hisham El-Saafin

# ACKNOWLEDGEMENTS

First of all I would like to express my deep gratitude to my supervisor, Dr. W.J. Feast, without whose continual help, invaluable advice and helpful discussions, this work would not have been done. Thanks are also due to Dr. R.S. Matthews for recording n.m.r. spectra, Dr. M. Jones for recording mass spectra, and Dr. G.M. Brooke for some discussions.

Assistance from members of the technical staff is greatly appreciated; in particular thanks are due to Mr. D. Hunter for his help and some practical assistance. I also thank my colleagues in Lab. 25 for some discussions and help, and particularly Mrs. E. Duddy for typing this thesis.

I am greatly indebted to every one of my family for their encouragement especially my brother, Hisham El-Saafin, for his generous support and invaluable advice. Finally thanks are due to all of my friends for their encouragement.

## MEMORANDUM

The work reported in this thesis was carried out in the Chemistry Department of the University of Durham between October 1978 and September 1979. This work has not been submitted for any other degree and is the original work of the author except where acknowledged by references.

## ABSTRACT

The work reported in this thesis is concerned with an investigation of the ring-opening polymerization of arylcycloalkenes. The monomers investigated were indene, acenaphthylene and benzonorbornadiene and the catalyst system used was tungsten hexachloride/tetraphenyltin in toluene.

Attempts to ring-open polymerize indene and acenaphthylene are described in Chapter 2. The results suggest that these monomers do not undergo ring-opening polymerization to any appreciable extent with the catalyst system used; however, some ambiguity remains and it may be that a limited amount of ring-opening does occur.

Benzonorbornadiene readily undergoes ring-opening polymerization. Synthesis of the monomer, its polymerization and the characterization of the polymer are described in Chapter 3. Polybenzonorbornadiene is very susceptible to oxidation by atmospheric oxidation.

# CONTENTS

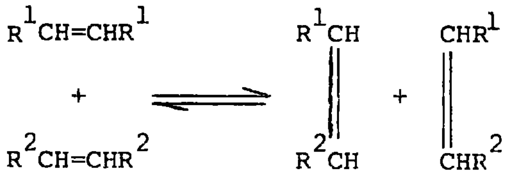
EXPERIMENTAL PART

# CHAPTER 1

## General Introduction and Background

## 1.1. Historical Background of Olefin Metathesis

Olefin metathesis is a bond reorganization reaction characterised by the fact that the total number and types of chemical bonds remain unchanged during the transformation of the initial reactants into two new products as shown in Figure 1.1. When olefins are combined with a variety of catalysts, most commonly containing tungsten, molybdenum or rhenium, they undergo the transformation generalized above. The metathesis reaction of alkenes constitutes a major development in the field of hydrocarbon chemistry in recent years. The versatility of the metathesis reaction not only gives many new pathways for organic synthesis but also offers new openings for the chemical industry. The discovery of the metathesis reaction is also of importance from a theoretical and fundamental point of view, and has contributed to the development of new ideas about reactions of alkenes in the presence of transition metal compounds.



$$\begin{matrix} R^1CH{=}CHR^1 & & R^1CH & & CHR^1 \\ + & \rightleftharpoons & \| & + & \| \\ R^2CH{=}CHR^2 & & R^2CH & & CHR^2 \end{matrix}$$

Figure 1.1.

In 1964, Banks and Bailey[1] reported the first example of the metathesis of linear alkenes, they called the reaction "olefin disproportionation". They demonstrated the equilibrium shown in Figure 1.1., which allows the selective conversion of an unsymmetrical linear alkene into roughly equimolar amounts of higher and lower molecular weight olefins, they used heterogenous catalysts prepared from molybdenum or tungsten hexacarbonyls. This opened the way for the development and study of a very important field of organic chemistry and since then, the metathesis reaction has been extended to other types of alkenes, substituted alkenes, dienes, polyenes, alkynes and, of great importance, cycloalkenes. This last reaction gave rise to a ring enlargement resulting in macrocyclic compounds and eventually polyalkenamers as shown in Figure 1.2. Scott[2] and Wasserman,[3] were the first to

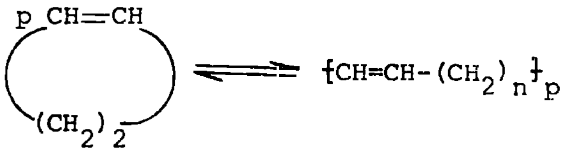


Figure 1.2.

realize that this ring opening polymerization, which had been known for several years, might be a special case of the metathesis reaction.

Instead of the name "metathesis" the term "disproportionation" is frequently applied to the reaction, and sometimes the term "dismutation". For historical reasons the name "disproportionation" is most commonly used for the heterogeneously catalyzed reaction, while the homogeneously catalyzed reaction is usually designated as "metathesis", the name "disproportionation" is correct in the case of the conversion of acyclic alkenes, however, this name is inadequate in most other situations, such as the reaction between two different alkenes, and reactions involving cycloalkenes. The name "olefin disproportionation" was originally used because of the analogy with inorganic disproportionation of metal oxidation states. "Dismutation" is subject to similar objections as an appropriate name for this reaction, whereas the name "metathesis" is not subject to these limitations and therefore is preferred.

In fact the first mention of an olefin metathesis reaction catalysed by a transition metal was the polymerization of bicyclo[2,2,1]hept-2-ene by a mixture of titanium tetrachloride and either ethylmagnesium bromide or lithium tetrabutylaluminium recorded in 1955,[4] but it was not until 1960 that the polymer was shown to be a polyalkenylene.[5]

In 1959 Eleuterio,[6] reported that a catalyst prepared from molybdenum oxide on alumina, activated by hydrogen reduction and further reacted with aluminium hydride, was able to ring-open polymerize a variety of cycloalkenes such as bicyclo[2,2,1]hept-2-ene, tricyclo[5,2,1,$0^{2,6}$]deca-3,8-diene (cyclopentadiene dimer), tricyclo[5,2,1,$0^{2,6}$]dec-8-ene and cyclopentene. In the case of cyclopentene trans-poly(1-pentenylene) was formed with a high degree of stereo-regular structure but only in low yield. In 1963 Dall'Asta and Natta,[7] demonstrated the possibility of producing stereoregular polymers from cycloalkenes using different catalyst systems and reaction conditions, in this work cyclobutene was polymerized to predominantly or exclusively cis- or trans-poly(1-butenylene), several kinds of transition metal catalysts such as $TiCl_4/Et_3Al$/n-heptane, $TiCl_4/R_3Al$/toluene, $RuCl_3/H_2O$, $MoCl_5/Et_3Al$/toluene and $RuCl_3/EtOH$ were used and variation of conditions and catalyst allowed close control of stereo-regularity. In 1964 the same authors[8] investigated tungsten and molybdenum halides in combination with organoaluminium compounds as catalysts, cyclopentene was polymerized by ring-opening under mild conditions, again stereo-selectivity was demonstrated. In 1967 Calderon et al.,[9,10] were the first to use the term "olefin metathesis" for the overall result of the reaction, they converted 2-pentene into a mixture of 2-butene and 3-hexene using a $WCl_6$-$EtAlCl_2$-EtOH catalyst. This result was very important in the evolution of the metathesis concept because it demonstrated that ring-opening reactions and the reactions of acyclic olefins belonged to the same class of reaction and were effected by similar catalysts. Since then a great number of investigations of all aspects of the metathesis reaction have been carried out, and several detailed reviews have been published.[11-24]

## 1.2. The Scope and Applications of the Olefin Metathesis Reaction

The olefin metathesis reaction has been shown to be a very versatile tool for preparation of some valuable hydrocarbons in common demand, and in general for organic chemistry. The applications include: improved utilisation of refinery streams, for example, by converting $C_4$ and $C_5$ alkenes into mixtures containing ethylene and propene together with higher molecular weight products; production of intermediates for flame retardants, stabilisers, perfumes, novel polymers and copolymers; and degradation of polymers.[25]

### 1.2a. Acyclic olefins

The conversion of many acyclic mono-olefins and mixtures of olefins, both linear and branched, has been effected according to the general equation in Figure 1.3., where R represents hydrogen or hydrocarbon groups. Both terminal or internal acyclic olefins can be metathesized in the presence of the appropriate catalyst, the homometathesis reaction of an acyclic α-mono-olefin yields ethylene and a symmetrical internal olefin, the homometathesis reaction of an unsymmetrical internal mono-olefin usually gives two symmetrical internal olefins. The general relationship for acyclic linear olefins is shown in Figure 1.4., where n is the carbon chain length

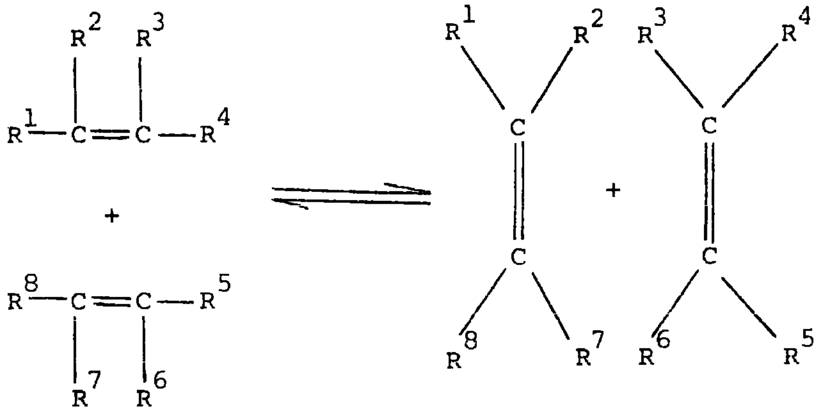


Figure 1.3.

and m is the position of the double bond in the chain, the metathesis of

$$2C_n^m \rightleftharpoons C_{2m}^m + C_{2(n-m)}^{n-m}$$

Figure 1.4.

terminal and internal acyclic mono-alkenes has been reported in great detail.[15,17,18] The metathesis of propylene is an example of this kind of reaction giving ethylene and but-2-ene. Other α-olefins reported to undergo metathesis are 1-pentene,[24,26-30] 1-octene,[26-30] and the non-linear α-olefins 3-methylbut-1-ene,[29] 2-methylbut-1-ene,[30] 4-methylpent-1-ene.[31] Examples of heterometathesis reactions of terminal and internal olefins are the reactions of but-1-ene with but-2-ene,[30] and hept-2-ene with ethylene.[24] Acyclic alkenes can be used in the analysis of polymer microstructure by cross-metathesis, for example the elucidation of microstructure in styrene-butadiene copolymers by reaction with but-2-ene,[32] and the determination of the extent of double bond migration during free-radical cross-linking of butadiene.[33] The metathesis of acyclic olefins substituted with cycloalkyl, cycloalkenyl or aryl groups has been observed,[28] for example styrene is converted to ethylene and 1,2-diphenylethylene;[28] as shown in Figure 1.5.

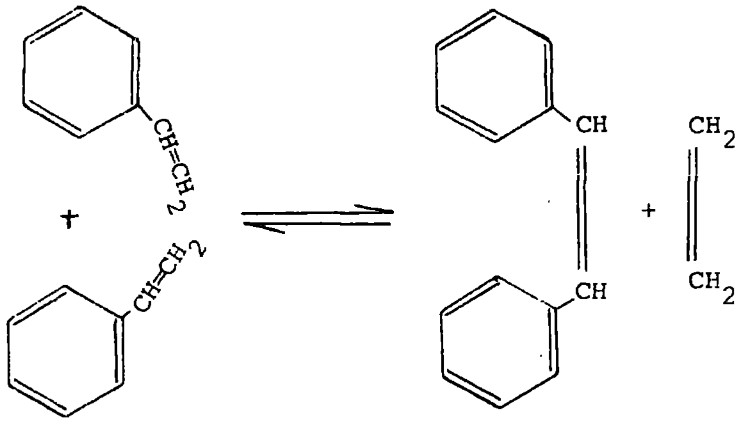


Figure 1.5.

Claderon,[14] reported that the effect of substitution on the ease of participation in the olefin metathesis is given by the series shown in Figure 1.6., indicating steric control of reaction. Unsaturated esters

$$CH_2= \ > \ RCH_2CH= \ > \ R_2CHCH= \ > \ R_2C=$$

Figure 1.6.

have been found to undergo metathesis reaction which opened a new field in synthetic fat chemistry.[34] Alkenes having different functional groups such as -COOR, -OCOR, -OR, -CN, -COR, have been reported to undergo metathesis reactions.[35]

### 1.2b. Acyclic polyenes

Zuech and co-workers,[24] have reported that polyenes or cycloalkenes are formed from the reaction of α,ω-dienes with metathesis catalysts. The reaction follows an inter- or intra-molecular pathway as shown in Figure 1.7., the predominating route being governed by the relative stabilities of ring and chain products. Thus hexa-1,5-diene gives deca-1,5,9-triene and

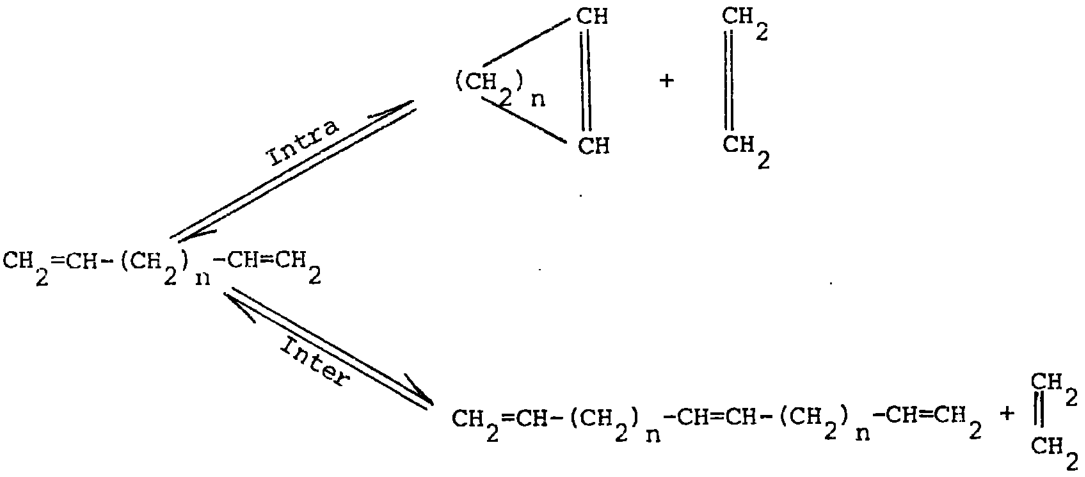


Figure 1.7.

ethylene but no cyclobutene, whereas octa-1,7-diene is almost exclusively converted to ethylene and cyclohexene as shown in Figure 1.8.

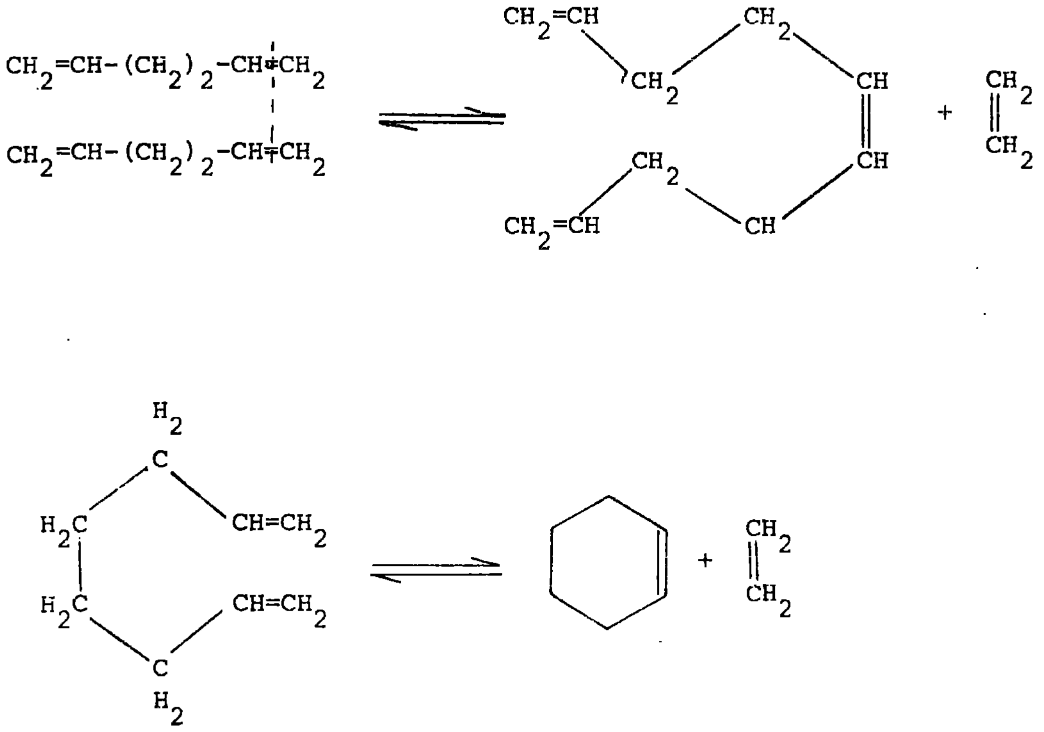


Figure 1.8.

### 1.2c. Cycloalkenes

Many metathesis reactions of cycloalkenes have been reported, they are of particular interest in the synthesis of macrocyclic compounds and polymers. The reaction may be generalized as shown in Figure 1.9. The interesting feature of both kinds of products being that they retain the unsaturation of the monomer, this contrasts with normal telomerization and polymerization where unsaturation is lost. The exact course of reaction depends on the details of monomer structure and reaction conditions.

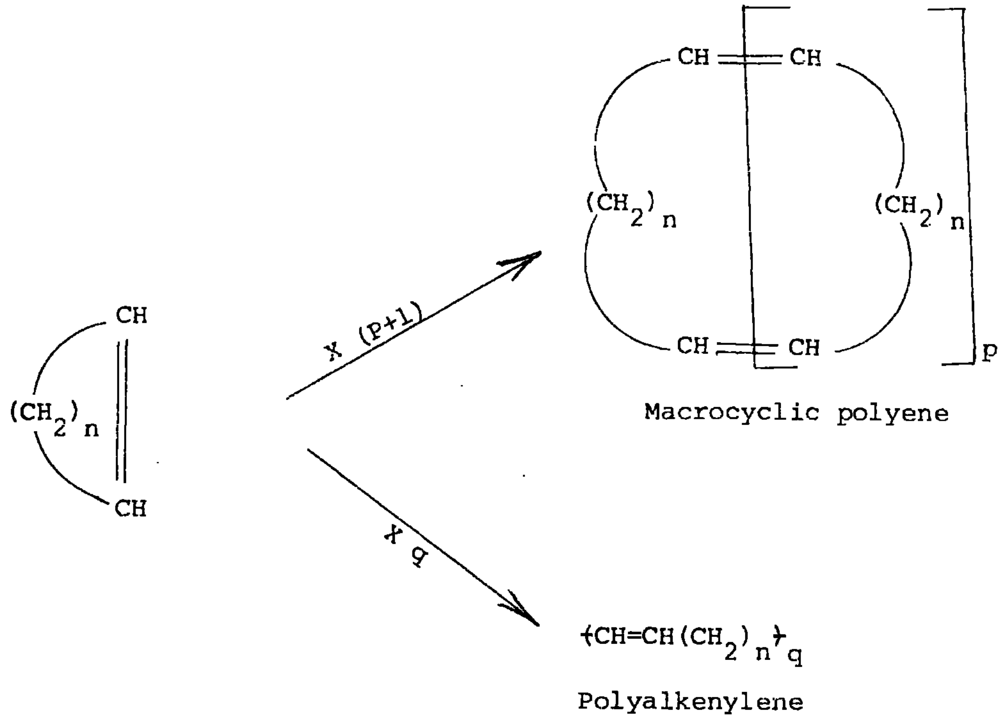


Figure 1.9.

In fact, Anderson and Merckling were the first to realize that Ziegler-type catalysts do polymerize bicyclo[2.2.1]hept-2-ene to a high molecular weight polymer, but they did not disclose either the structure of the polymer or the mode of polymerization.[4] Later, in 1956, Truett, et al.[5] reported that using the catalyst system described by Anderson and Merckling under suitable conditions results in the ring-opening polymerization of bicyclo[2.2.1]hept-2-ene, as shown in Figure 1.10. In 1957 Eleuterio,[6] reported that a variety of cyclo-olefins can polymerize by ring-opening

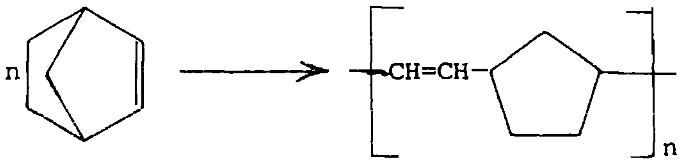
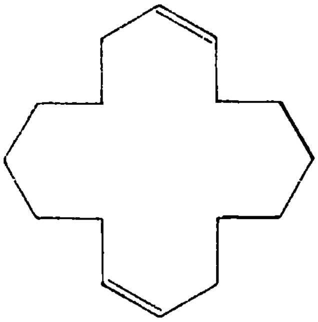
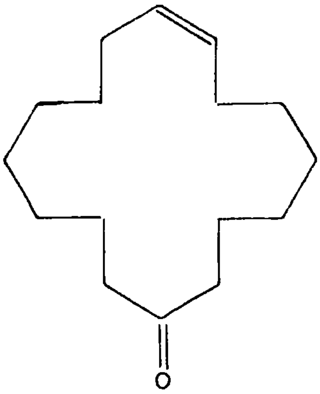


Figure 1.10.

when reacted with catalysts derived from transition metals. All this work did not receive much attention until Natta's group in 1964 reported their successful stereo-specific preparation of polypentenamers in good yields.[8] Mono-cyclic olefins from $C_4$ to $C_{12}$, with the exception of cyclohexene,[11] undergo ring-opening polymerization to yield products which vary from amorphous elastomers to crystalline materials. Ring-opening can be controlled to yield polymers in either a high cis[36] or a high trans[11,38] form, by controlling the temperature. This point is very important in this reaction especially in industry; for example, cis-poly(1-pentenylene)[38] is a low temperature elastomer which could be competitive with the more expensive silicone rubber, trans-poly(1-pentenylene)[26] is a good substitute for natural rubber in the tyre industry, and polymers which are generally gel-free rubbers, have been obtained from cyclopentene,[26,30,34,39,40] cyclooctene,[2,3,26,39,40] cyclododecene,[41,42] and 1,5-cyclo-octadiene.[2] It was shown that the low molecular weight extractable material produced in these reactions could be polymerized to high molecular weight polymer by contact with additional catalyst,[2] and conversely the metathesis of high molecular weight polymers of cycloalkenes at high dilution yielded a mixture of macrocyclic compounds in high yields.[43] Two materials were prepared by this technique; cyclohexadeca-1,9-diene (1), the cyclic dimer of cyclo-oct-1-ene, which when oxidised yielded a ketone (2) with a musk-like odour.[44]



(1)



(2)

Catenanes (interlocked ring systems) can be formed as indicated in Figure 1.11., and evidence for their formation in the metathesis of cyclododecene has been reported.[41,42]

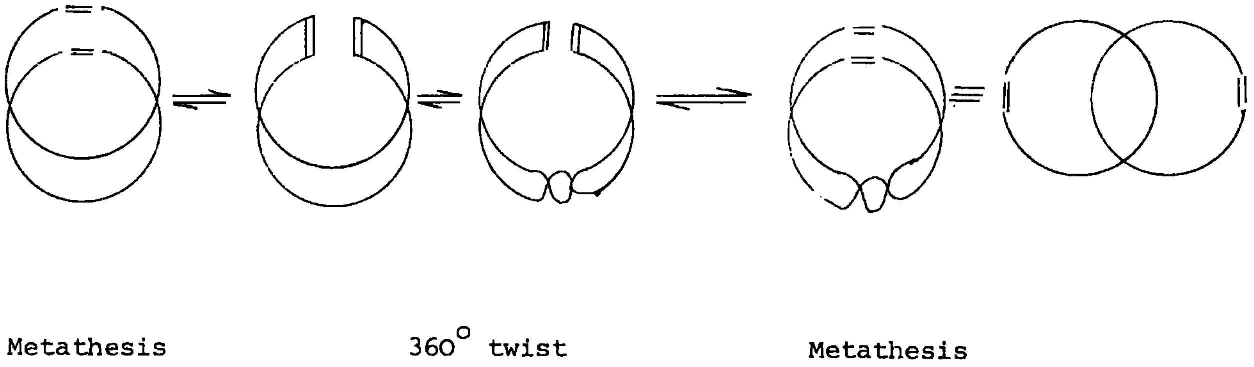


Figure 1.11.

Cyclic dienes, polyenes, as well as mono- and poly-cyclic alkenes, undergo ring opening polymerization. As expected, cyclobutene,[45] cycloocta-1,5-diene, and cyclododeca-1,5,9-triene yield the same polyalkenamer as shown in Figure 1.12.

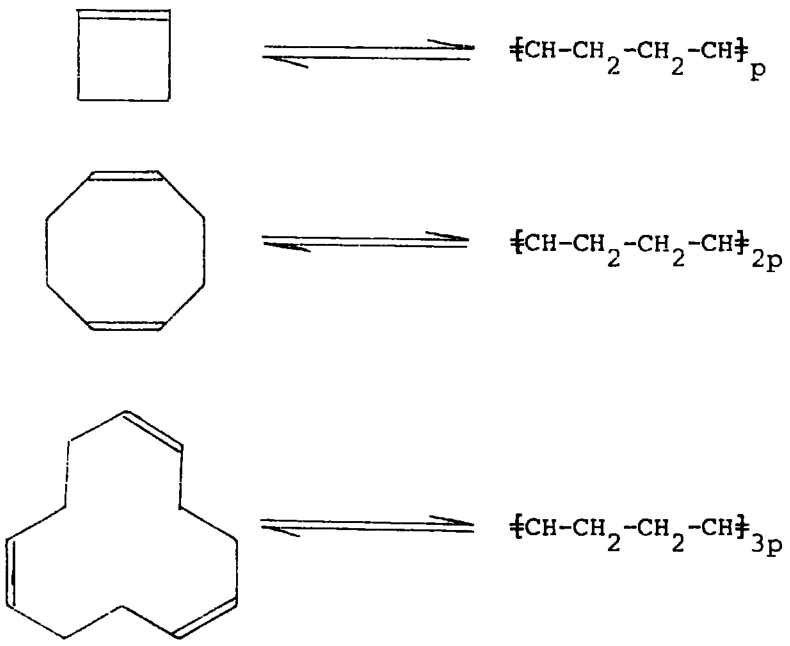


Figure 1.12.

The variety of polymers that can be prepared from cycloalkenes is illustrated by the case of cyclobutene, four different polymers can be obtained as shown in Figure 1.13, depending on the catalyst system and reaction conditions.[13]

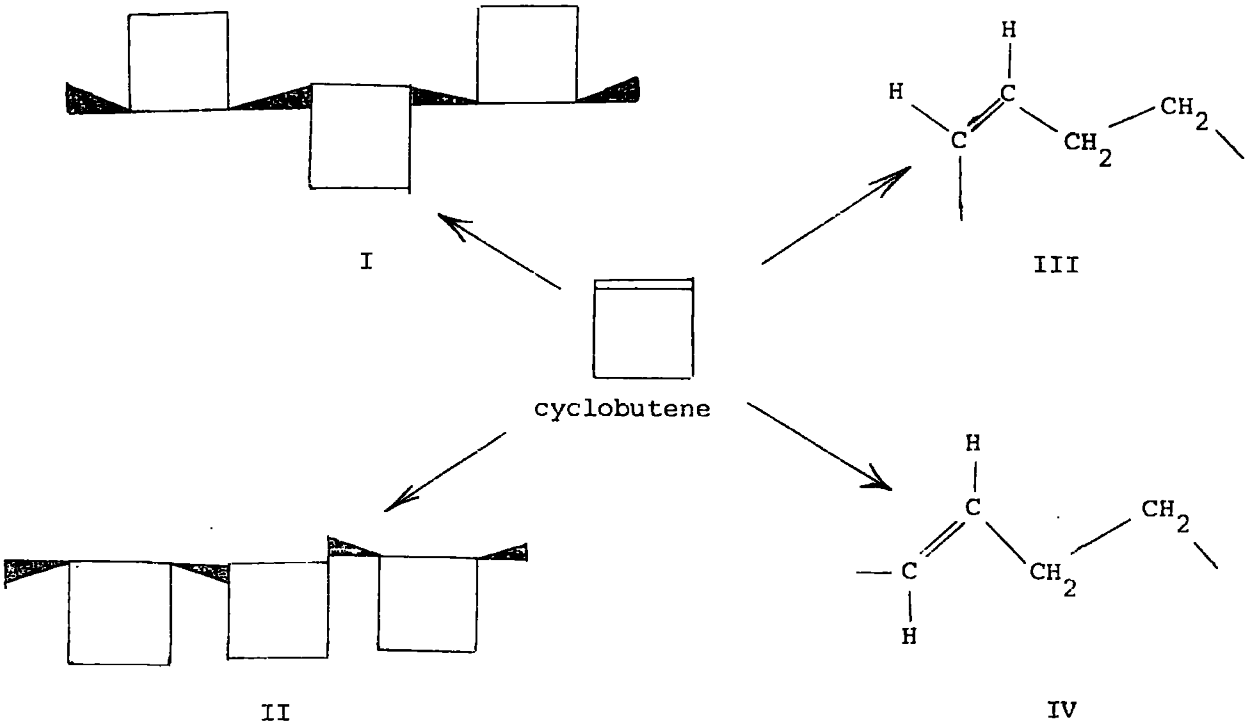


Figure 1.13.

In addition to the examples already mentioned, cycloheptene,[46] cyclodecene,[47] and heterocyclic olefins (such as unsaturated lactones),[48] have been shown to undergo ring opening polymerization.

Cross metathesis of cycloalkenes and polyenes with acyclic alkenes allows the production of α,ω-dienes as shown in Figure 1.14.[26,49,50]

### 1.2d. Alkynes

The metathesis of linear alkynes, such as 1-pentyne, 2-pentyne and 3-hexyne, has been reported.[51-54] The overall reaction was shown to be analogous to the metathesis of acyclic olefins, Figure 1.15.

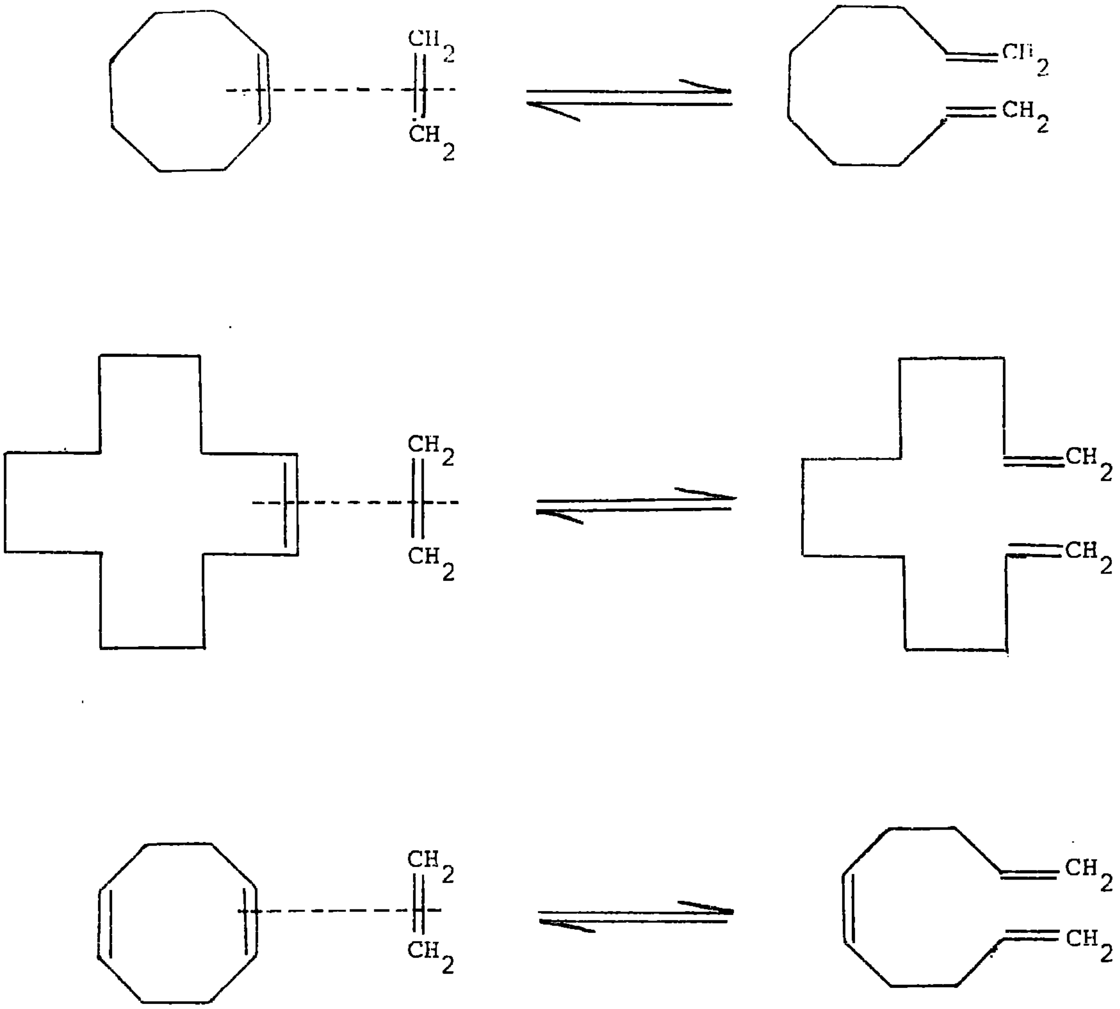


Figure 1.14.

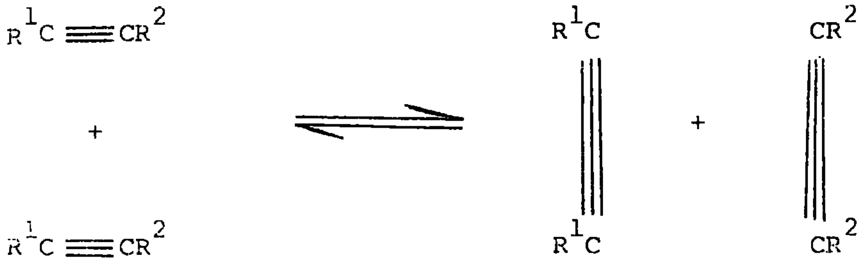


Figure 1.15.

Cyclotrimerization to benzene derivatives is also observed.[55,56] Höcker and Musch,[57] have reported that the oligomerization of cyclodecyne in the presence of $WCl_6$-$EtAlCl_2$-EtOH yielded cyclic compounds of the formula $(C_{10}H_{16})_n$, where n = 1-6.

Tungsten hexachloride and molybdenum pentachloride are very effective in the polymerization of phenylacetylenes at ambient temperatures.[58,59]

## 1.2e. Aryl-substituted olefins

A few examples of the metathesis of phenyl-substituted olefins have been reported,[28,60] and are shown in Figure 1.16.

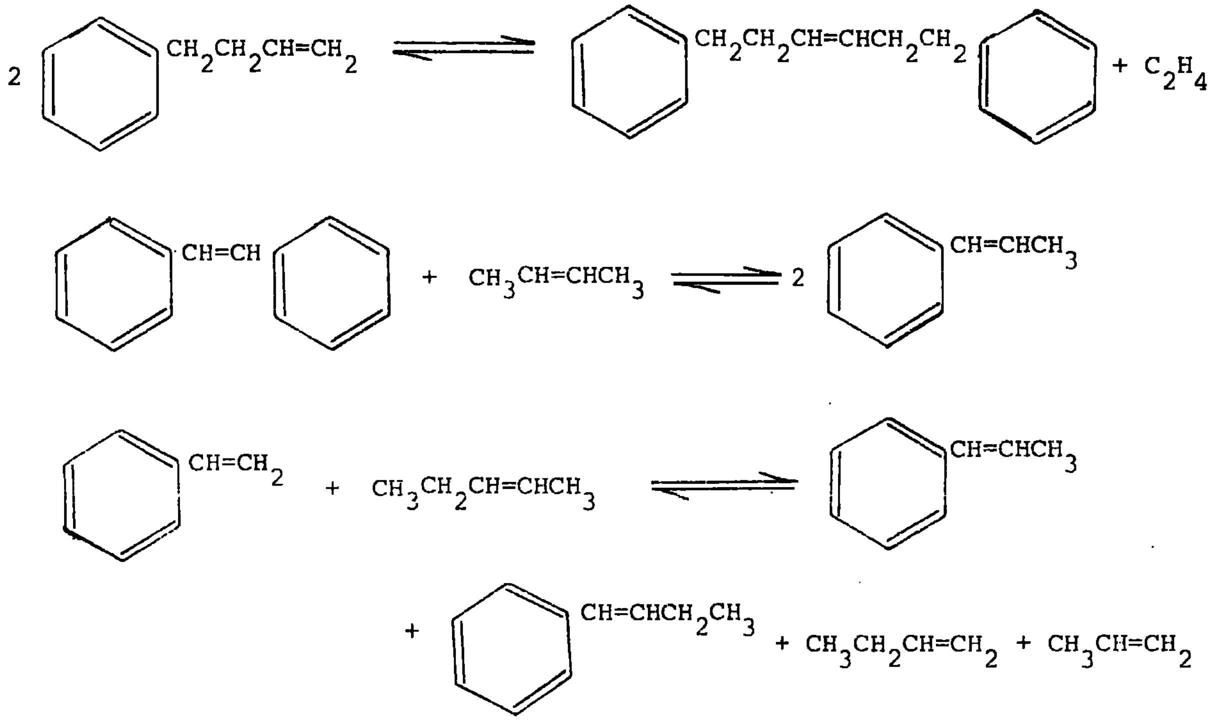


Figure 1.16.

The aromatic system, which is capable of coordinating to low-valent transition metals such as W and Mo, can retard the rate of reaction or deactivate particular catalyst systems.

## 1.3. Olefin Metathesis Catalyst Systems

A wide variety of materials are claimed to be active metathesis catalysts. Metathesis catalysts promote two main types of reaction, namely, ring-opening polymerization of cyclo-olefins and disproportionation reactions of acyclic olefins. Although governed by a common mechanism, these reactions differ in many chemical, kinetic and thermodynamic aspects and this causes different catalyst efficiencies, operating conditions and applicabilities. Almost all the systems contain a transition and a non-transition metal component. The majority of catalyst systems are derived from the group VIA metals, molybdenum and tungsten, the non-transition metal component is more varied but is often a group IIIb or IVb element, particularly aluminum and tin. The nature of the non-transition metal component has a significant effect on catalytic activity, for example, the relative effectiveness of the catalysts obtained from tungsten hexachloride and several alkyl-lithium reagents was found to be n-butyl > s-butyl > t-butyl.[61] Catalysts may be homogeneous or heterogeneous and the generalizations above apply to both groups, for example cocatalysts can promote the activity of both homogeneous and heterogeneous catalysts.[62] The most efficient catalysts for ring-opening polymerizations of cyclo-olefins are composed of halides, oxyhalides or alkoxyhalides of tungsten and organometallic derivatives of aluminium and tin. A second group of metals comprising molybdenum, rhenium, and tantalum also give quite efficient catalysts for ring-opening polymerizations. A third group of metals comprising titanium, zirconium, vanadium, niobium and some lanthanides are of lower catalytic activity and promote metathesis only in some special cases. A very great number of catalysts have been described,[63-70] particularly in the patent literature, and no attempt at a comprehensive survey has been made here.

### 1.3a. Heterogeneous catalysts

In general heterogeneous catalysts consist of transition metal oxides or carbonyls deposited on high surface area supports, such as alumina or silica.

The catalysts derived from oxides and carbonyls of Mo, W and Re have the greatest activity,[1,71,72,73] whilst the remainder of the promoters are less effective,[74] sulphides of Mo and W provide poor catalysts,[74,75] but in special conditions $MoS_2$ alone is quite active.[76]

Olefin metathesis catalyst supports and promoters are listed in Table 1.[15]

Table 1.

Heterogeneous catalyst supports and promoters for olefin metathesis.

| Compounds | Supports | | | Promoters | | |
|---|---|---|---|---|---|---|
| Oxides | Al | Si | Fe | Mo | W | Re |
| | Ni | Zr | Sn | Nb | Rh | Sn |
| | W | Th | SiAl | Te | La | Ta |
| | AlTi | AlTh | MgSi | Os | Ir | |
| | MgTi | | | | | |
| Phosphates | Al | Ti | Ca | | | |
| | Zr | Mg | | | | |
| Carbonyls | | | | Mo | W | Re |
| Sulphides | | | | Mo | W | |

Heterogeneous catalysts can be prepared in different ways; by dry mixing of the individual components, coprecipitation, or impregnation of the supports with substances which decompose at high temperatures to leave the active promoter. The catalysts are sensitive to poisoning by polar compounds.[77] More details have been given by Bailey,[15] and Banks,[18] about analysis of the composition, preparation, activation and regeneration procedures, poisons and catalytic modifications.

### 1.3b. Homogeneous catalysts

Homogeneous catalysts are in many ways similar to the heterogeneous systems discussed earlier; thus, they generally consist of two components, a transition metal derivative and a co-catalyst, sometimes a third component such as an oxygen containing organic compound (e.g. a peroxide or alcohol) or water is also added. Tungsten compounds give the most efficient catalysts for the ring-opening polymerization of cyclo-olefin, and a large number of catalysts are derived from $WCl_6$ combined with suitable cocatalysts. In 1967, Calderon, Chen and Scott,[10] described the first homogeneous catalysts for olefin metathesis, and subsequently greater details about them were provided.[2,78]

Arguments about the exact structure and mode of action of particular catalysts are frequent, and indeed the designation "homogeneous" has been questioned for several systems.[79] The area has been reviewed by Hughes[18] and Dall'Asta.[11] Recent developments include photochemically activated catalysts such as $W(CO)_6$,[80] $WCl_6$,[81] and $TiCl_4$,[82] and the observation that metallocarbenes are active catalysts.[83-85]

## 1.4. Olefin Metathesis Mechanism

The mechanism of the metathesis reaction has been the subject of many investigations and much discussion. Opinions have changed as new evidence was established, and consequently the literature is somewhat difficult to follow since different workers changed their opinions at different times. In discussing the mechanism there are two basic questions to answer:-

(i) What is the overall result of the reaction? That is, which bonds are broken and made during reaction?

(ii) What is the detailed mechanistic pathway by which the overall result is obtained?

## 1.4a. The overall result of reaction

There are two possible reaction schemes which would lead to the observed reaction products:-

(i) A transalkylation scheme, which involves cleavage of a carbon-carbon single bond adjacent to the double bond as shown in Figure 1.17.

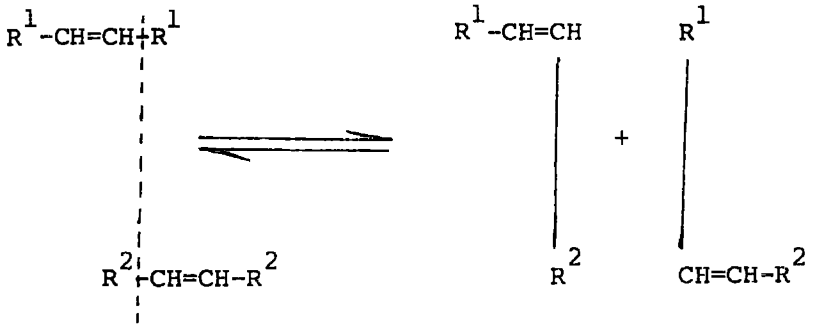


Figure 1.17.

(ii) A transalkylidenation scheme, which involves the cleavage of the double bond itself as a means of alkylidene moiety exchange as shown in Figure 1.18.

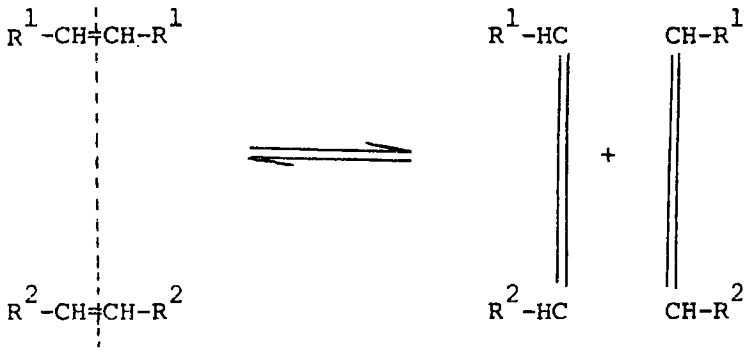
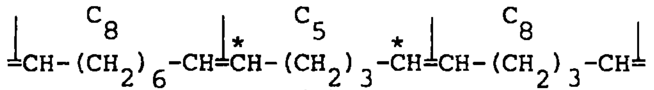


Figure 1.18.

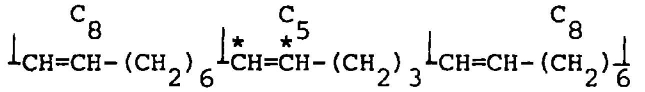
Results from $^{14}C$ isotopic labelling[88,90] and deuterium labelling experiments[2c,10] are completely consistent with a transalkylidenation scheme and excludes a transalkylation. Dall'Asta and Motroni[39,92] have given experimental evidence that in the ring-opening polymerization of cycloalkenes the cleavage occurs at the double bond. By copolymerizing cyclooctene and cyclopentene, in which the cyclopentene double bond was labelled with $^{14}C$, the resulting polymeric units may be (3) or (4) depending on whether cleavage takes place at the double bond or at the carbon-carbon single bond adjacent to the double bond.



$\big|\overset{C_8}{=CH-(CH_2)_6-CH=}\big|\overset{C_5}{\overset{*}{C}H-(CH_2)_3-\overset{*}{C}H=}\big|\overset{C_8}{CH-(CH_2)_3-CH=}\big|$

double bond cleavage

(3)



$\big|\overset{C_8}{CH=CH-(CH_2)_6}\big|\overset{C_5}{\overset{*}{C}H=\overset{*}{C}H-(CH_2)_3}\big|\overset{C_8}{CH=CH-(CH_2)_6}\big|$

allylic bond cleavage

(4)

[*denotes $^{14}C$ labelling]

Ozonolysis of the copolymer followed by reductive cleavage and radiochemical analysis of the resulting diols, showed that all the radioactivity was contained in the 1,5-diol, proving that ring-opening polymerization had proceeded via cleavage of the double bonds.

### 1.4b. The detailed mechanistic pathway

This question is much more complicated and difficult to answer definitely. Several mechanistic proposals have been put forward, and the area is still one of active discussion.

### 1.4b.(i). The intermediacy of a "quasi-cyclobutane"

The first mechanistic rationalization of olefin metathesis was put forward by Bradshaw[86] who proposed that a four-centre or "quasi-cyclobutane" intermediate could be used to rationalize the observed results, this proposal is generalized in Figure 1.19. This idea received quite widespread acceptance and was used by Calderon[2b] to rationalize ring-opening polymerization, the mechanism was assumed to proceed via formation of macrocyclic species as shown in Figure 1.20.

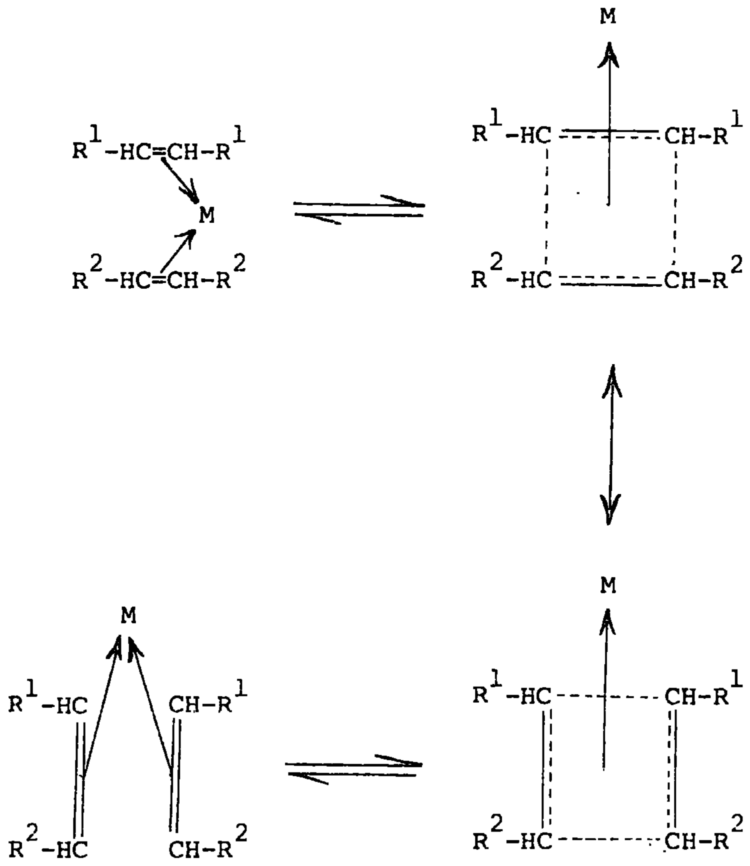


Figure 1.19.

While this mechanism accounts for a large amount of experimental observation, including isotopic labelling studies,[87-90] it has some weaknesses. For example, cyclobutanes might reasonably be expected to be found as by-products, or at least to participate in metathesis reactions; and polyalkenamers might be expected to be cyclic molecules. In fact polyalkenamers frequently consist of a mixture of cyclic and linear molecules. This difficulty was relatively easily overcome by suggesting that the linear polymers arose via interaction of the growing macrocycles with an acyclic alkene, present as an impurity.[91] Alternatively chain termination of a co-ordinated growing polymer macrocycle could be due to migration of the co-ordinated double-bond, accompanied by decomplexation, giving rise to a linear macromolecule having two vinyl end groups, Figure 1.21. On the other hand

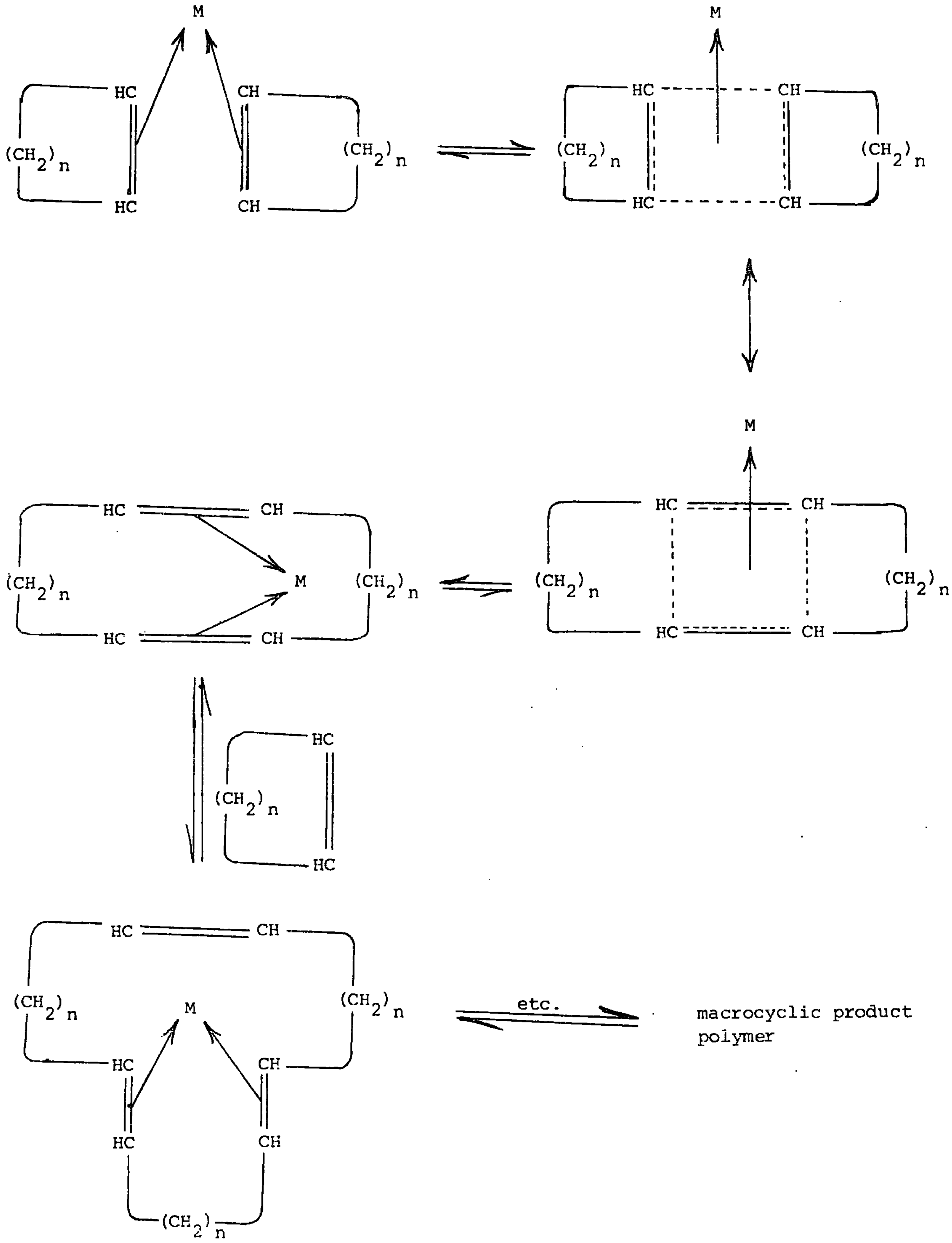


Figure 1.20.

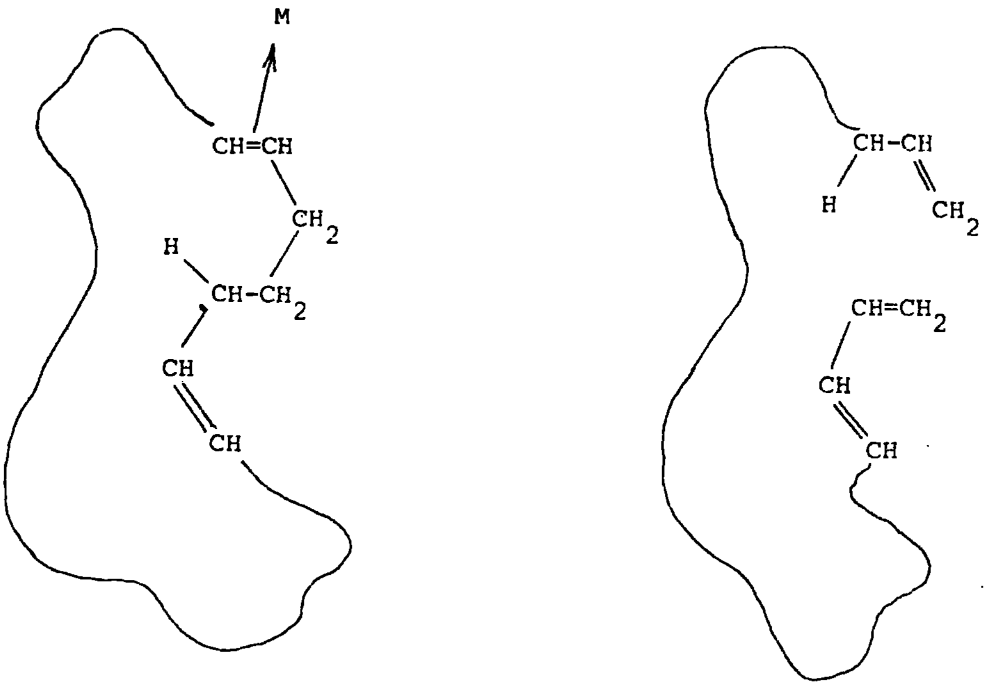
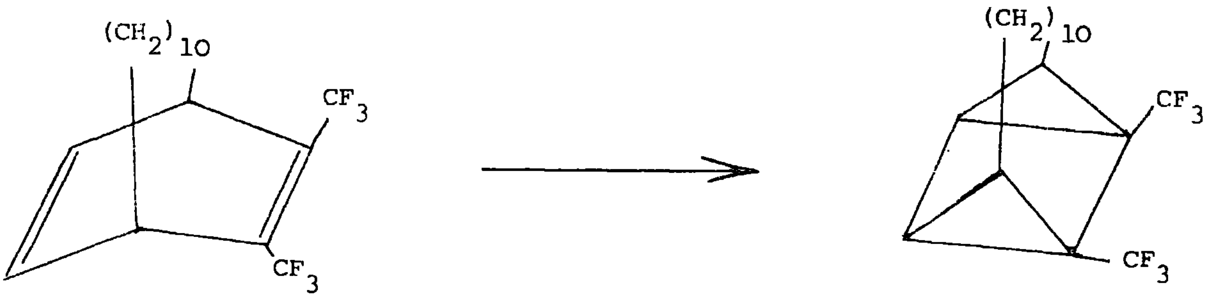


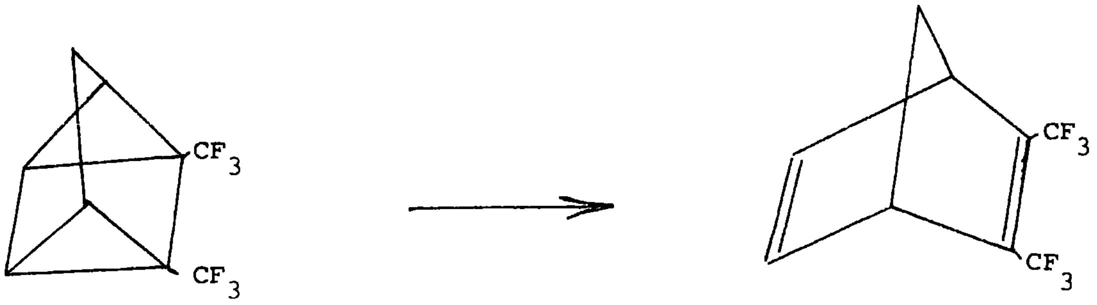
Figure 1.21.

very little evidence for the involvement of cyclobutanes in metathesis has been published, the results of Gassman and Johnson,[93] being the most widely cited. They observed a diene to cyclobutane conversion when compound (5) was reacted with "an accepted metathesis catalyst $PhWCl_3/AlCl_3$", and cyclobutane

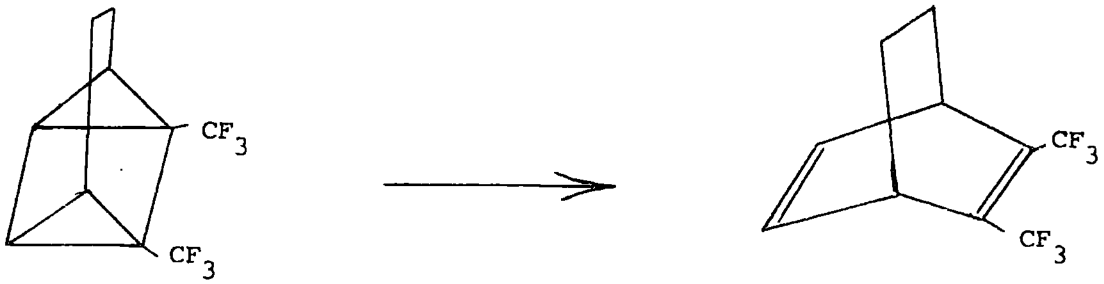


(5) (6)

to diene conversions for compounds (7) and (9) reacting to give (8) and (10) respectively. These authors also reported that the bicyclic dienes were unaffected by their catalyst although it retained its activity for the cyclobutane-diene interconversion even after "normal metathesis activity" had been



(7) (8)



(9) (10)

quenched by the addition of Michael acceptors. Wilson,[94] observed that the bicyclic diene (8) is particularly susceptible to ring-opening polymerization by a range of metathesis catalysts and is even polymerized by pure tungsten hexachloride, this contrasts with its reported lack of reactivity with the $PhWCl_3/AlCl_3$ catalyst and suggests that the interesting cyclobutane-diene interconversions observed with this catalyst have little relevance to the mechanism of the generality of metathesis polymerizations.

It should be noted that ethylene and cyclobutane are not equilibrated in the presence of metathesis catalysts, neither are cyclobutanes formed from simple alkenes nor do they split in the manner required by this mechanism. For these reasons another concerted pairwise exchange mechanism was proposed,[95] this is sometimes called the "tetramethylene transition state hypothesis" and is represented in Figure 1.22. The theoretical implications of these concerted mechanisms have been reviewed by Haines and Leigh.[20]

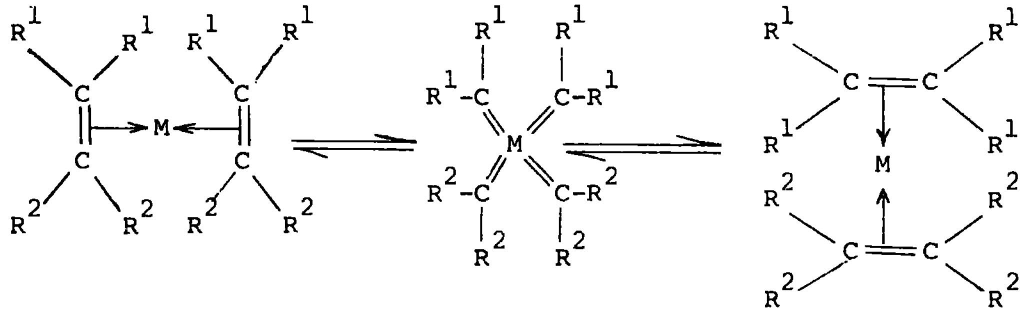


Figure 1.22.

1.4b.(ii). Metallocyclopentanes as intermediates

Although the mechanisms described in the previous section accounted for most of the evidence the weaknesses described made workers look for alternative rationalizations. The observation that $WCl_6$ reacted with 1,4-dilithiobutane in benzene to give a quantitative yield of ethylene,[96] led to the suggestion that metallocyclopentanes might be involved as intermediates in a non-concerted pairwise exchange of alkylidenes in the mechanism for metathesis, such a mechanism is indicated in Figure 1.23. This proposal found less support than the earlier mechanisms and was soon replaced by the currently accepted, non-concerted, non-pairwise mechanism.

1.4b.(iii) Metallocyclobutane and metal-carbene intermediates

The generally accepted mechanism for metathesis involves a reversible reaction between an alkene and metallocarbene to give a metallocyclobutane, as indicated in Figure 1.24. This mechanism was first proposed by Herisso and Chauvin,[97] and was independently put forward by Lappert and co-workers,[98] who had shown that 'electron rich' olefins (11) undergo metathesis with

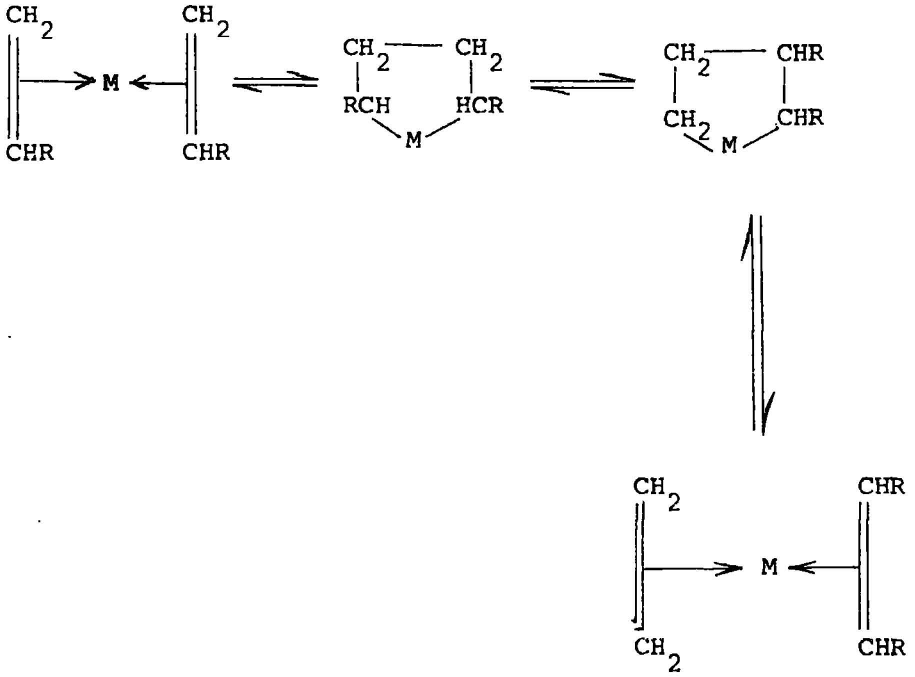


Figure 1.23.

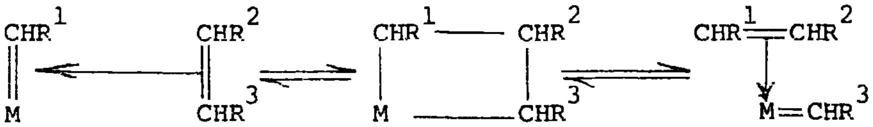
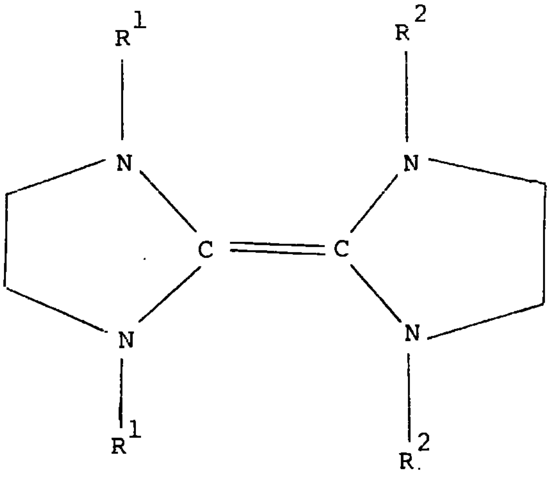


Figure 1.24.

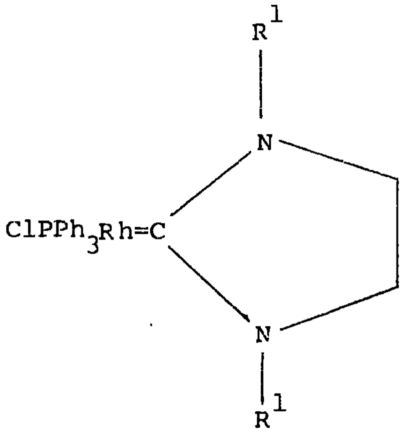
Rh catalysts at high temperatures, they also isolated an intermediate metallocarbene (12) which acted as a catalyst for the reaction.

The metallocyclobutane mechanism accounts for ring-opening polymerization as shown in Figure 1.25.

Polymers are not formed by consecutive macrocyclization (cf. Fig. 1.20), but instead cyclic oligomers are obtained when the carbene end reacts with



(11)

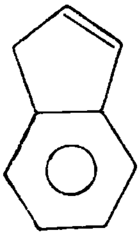


(12)

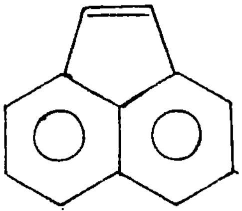
a double bond within the growing polymer chain, Figure 1.26. The evidence supporting the metallocarbene/metacyclobutane mechanism has been reviewed in detail by Roony and Stewart,[12] and recent work by these authors together with, Ivin and Green[99] has led to the suggestion that there is a close mechanistic relationship between Ziegler-Natta polymerization and ring-opening metathesis, this view is summarised in Figure 1.27., and requires a 1,2-hydrogen shift to first generate the active metallo-carbene for the unconventional process.

## 1.5. The Original Question which Initiated the Research Described in this Thesis

Many examples of ring-opening polymerization have been reported, however there is no mention in the literature of the ring-opening polymerization of indene (13). This is a well known monomer for vinyl polymerization and has



(13)



(14)

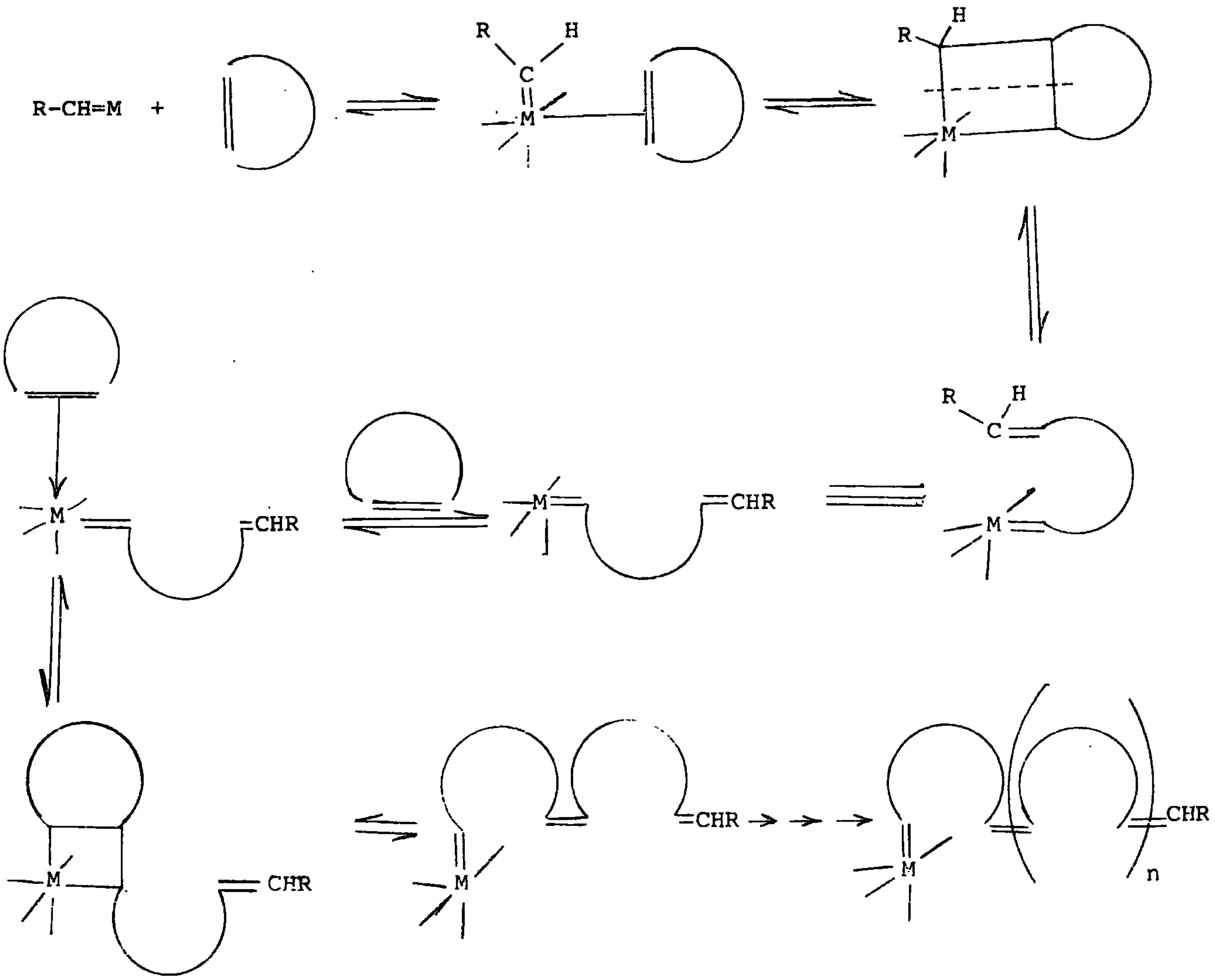


Figure 1.25.

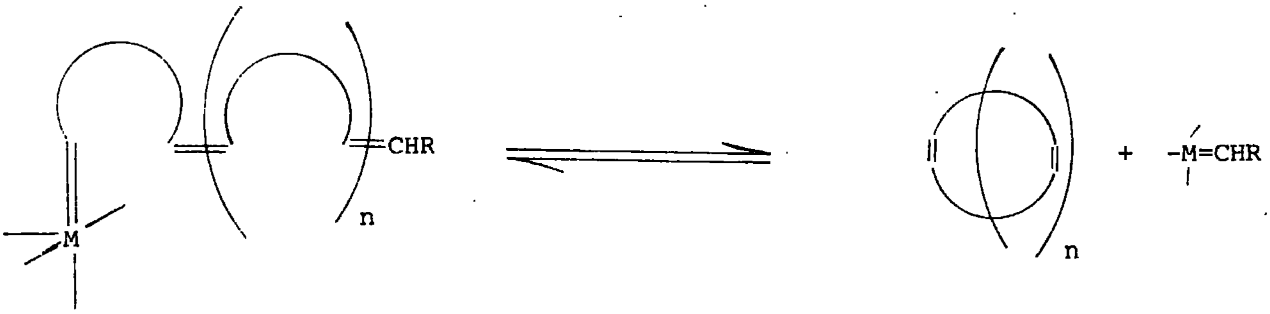
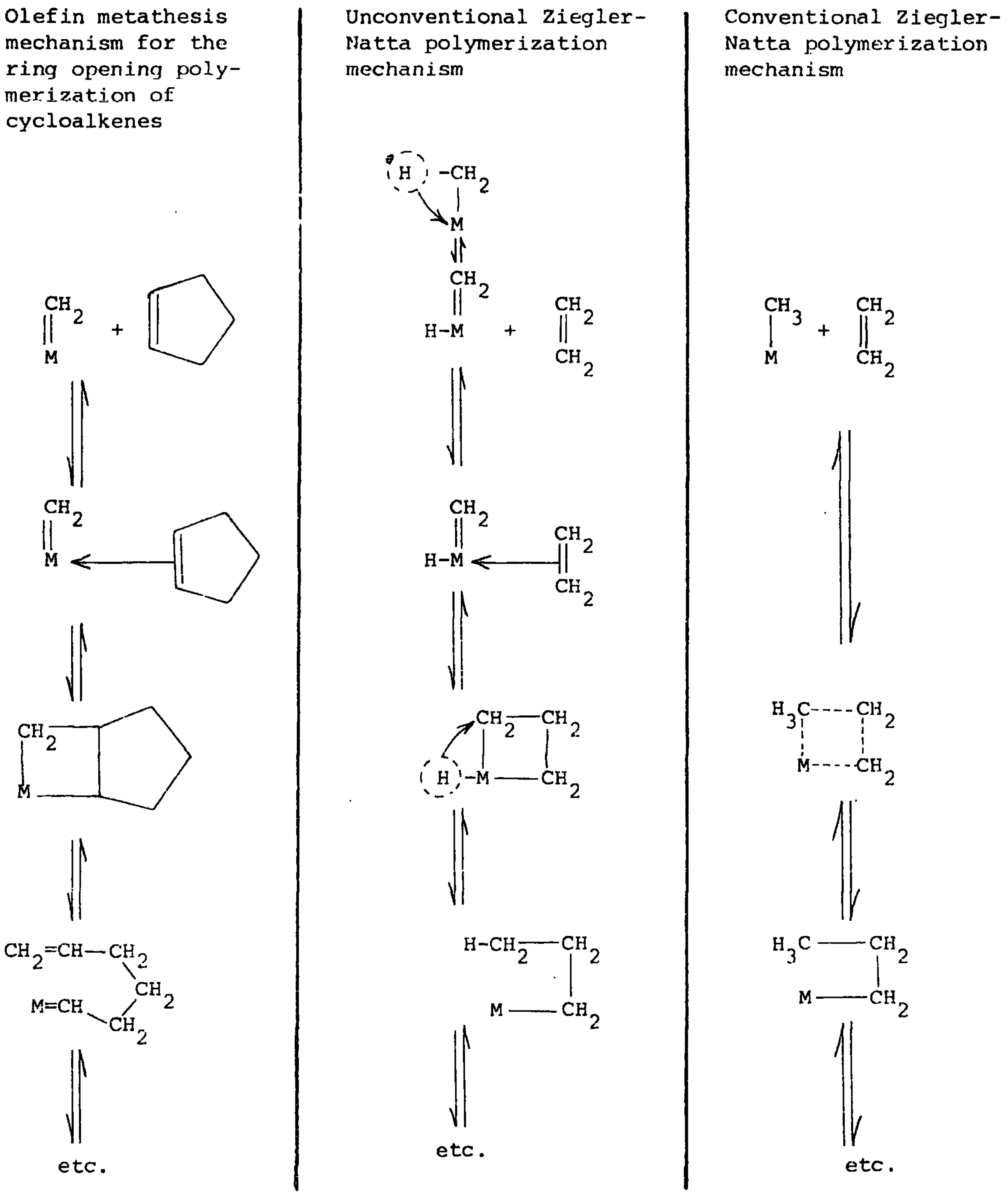


Figure 1.26.



Olefin metathesis mechanism for the ring opening polymerization of cycloalkenes

Unconventional Ziegler-Natta polymerization mechanism

Conventional Ziegler-Natta polymerization mechanism

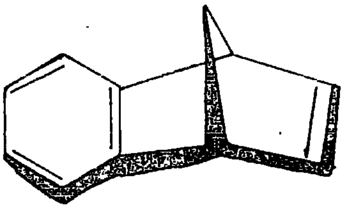
Figure 1.27.

interested polymer scientists for many years both from an academic and commercial point of view, it seemed worthwhile investigating the possibility of making a new polymer from this well known monomer. Indene maybe regarded as a derivative of cyclopentene or cyclopentadiene, another related compound is acenaphthylene (14).

Some preliminary work on the possibility of ring-opening polymerization of indene had been carried out by Wilson in this department and Chapter 2 of this thesis describes a continuation of this work and some work with acenaphthylene as monomer.

The work with indene and acenaphthylene did not lead to ring opened products and this suggested a further question relating to the effect of aromatic units on the polymerizability of potential monomers.

In view of these results, the next project to be examined was the synthesis of other potential monomers containing aromatic units and their polymerization with metathesis catalysts. To-date, one system has been investigated and Chapter 3 describes the synthesis of benzonorbornadiene (15), its polymerization, and the characterization of the product.



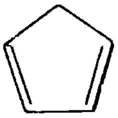
(15)

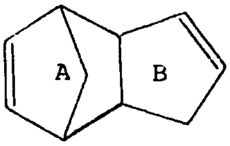
# CHAPTER 2

## Attempts to Polymerize Indene and Acenaphthylene with Metathesis Catalysts

## 2.1. Introduction

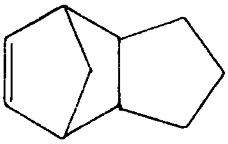
Indene (13), has not been specifically reported to undergo ring-opening polymerization, therefore it was of interest to attempt to polymerize this monomer using olefin metathesis catalysts. Indene maybe thought of as a derivative of either cyclopentadiene or cyclopentene, and it has been reported that conjugated cyclic dienes such as cyclopentadiene (16) do not undergo ring-opening polymerization.[9] Several investigations of the ring-opening polymerization of polycyclic monomers have been reported and dicyclopentadiene (17) is of particular interest in this respect because its structure encompasses two types of unsaturated five membered ring, namely the highly strained bridged ring-A and the fused five membered ring of type B. Oshika and Tabuchi,[100] who investigated the polymerization of dicyclopentadiene by a variety of catalyst systems reported that, this monomer is polymerized exclusively by reaction of the bridged ring A, as shown in Figure 2.1.

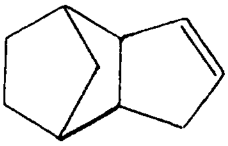

(16)

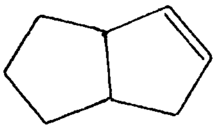


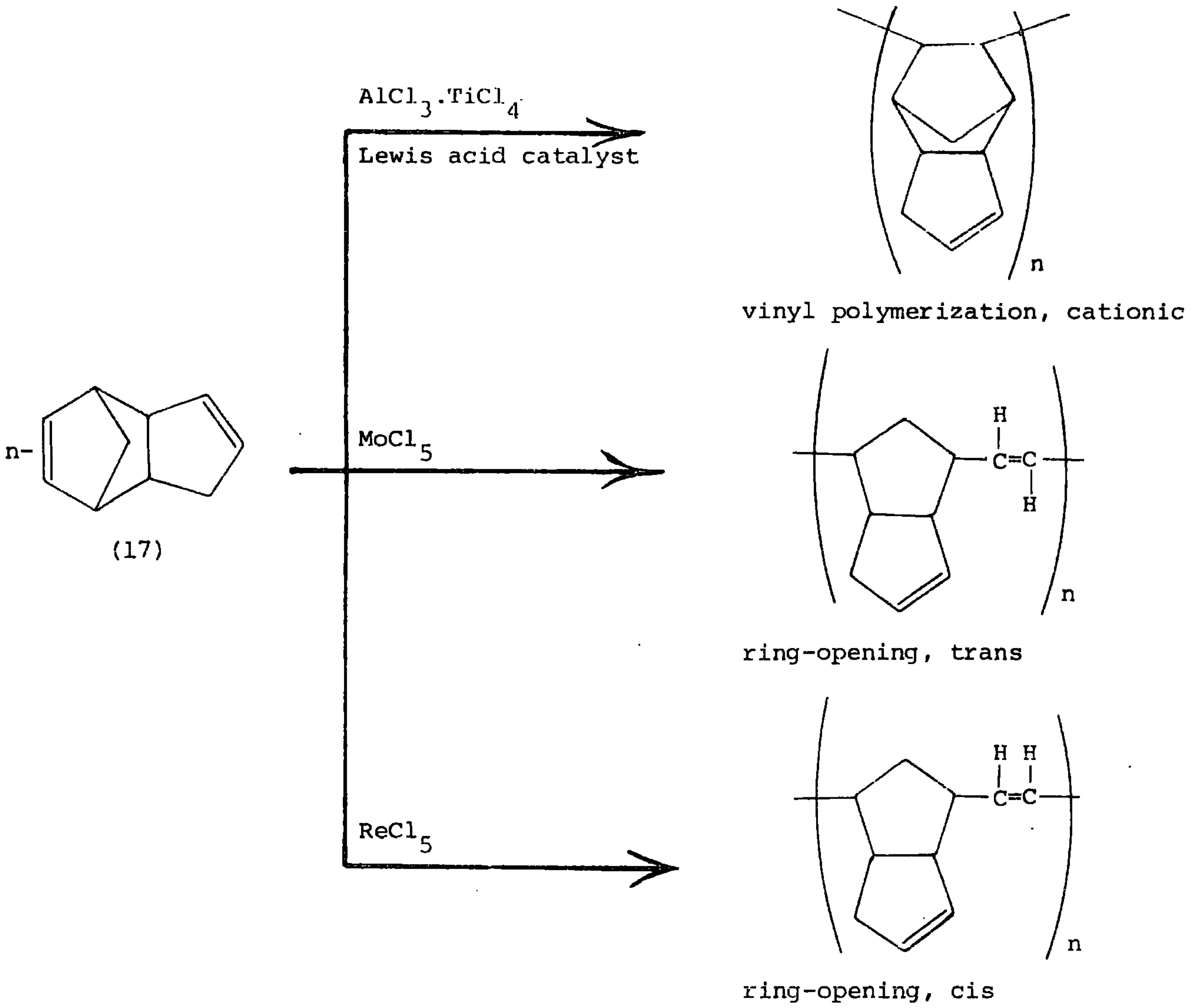
(17)

Eleuterio[6] and Oshika,[100] demonstrated that the isomer of dihydrodicyclopentadiene having the B-ring saturated, tricyclo[5.2.1.$0^{2,6}$]dec-8-ene (18), does undergo ring-opening polymerization. On the other hand, Ofstead and Calderon,[101] have reported that an isomer of (18) with the double bond in the less strained ring, tricyclo[5.2.1.$0^{2,6}$]dec-3-ene (19) and a related compound (20) bicyclo[3.3.0]octene, also possessing a B-type ring do not undergo ring-opening polymerization. These observations would lead one to


(18)


(19)


(20)



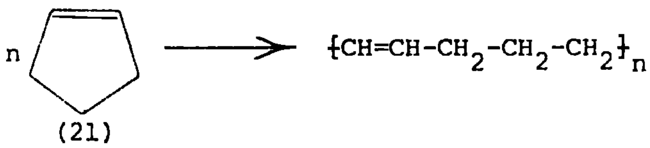
vinyl polymerization, cationic

ring-opening, trans

ring-opening, cis

Figure 2.1.

conclude that fused five-membered B-type rings do not ring-open polymerize under the conditions used. Natta and Dall'Asta,[8] reported that a variety of tungsten or molybdenum based catalysts are very effective for the polymerization of cycloolefins, including those possessing relatively low strain energy such as cyclopentene (21) which polymerized by ring-opening as shown in Figure 2.2. Also

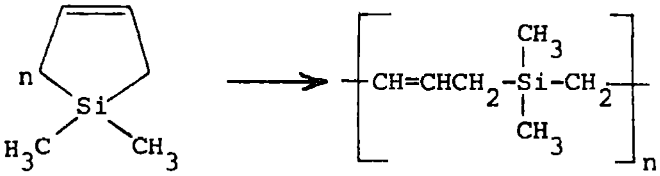


(21)

Figure 2.2.

Gunther et al.[102] reported that some substituted cyclopentenes undergo ring-opening polymerization, for example 3-methylcyclopentene, whereas others, for example 3-isopropylcyclopentene, resisted polymerization.

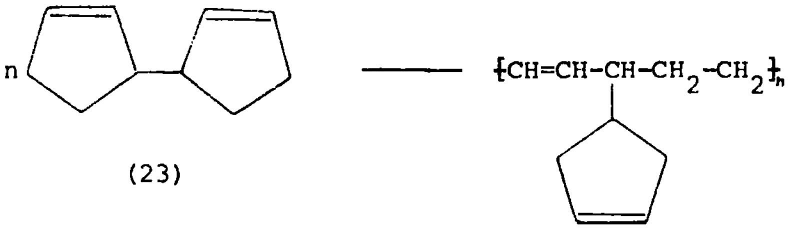
A novel disubstituted five-membered ring, 1,1-dimethyl-1-silacyclopent-3-ene (22), was reported by Lammens and co-workers,[103] to undergo ring-opening polymerization, as indicated in Figure 2.3., and 3,3-bicyclopentene



(22)

Figure 2.3.

(23) was polymerized in low yield to a predominantly soluble product,[101] as shown in Figure 2.4. The overall picture from these literature reports is confusing; for example, it is difficult to understand why 3-methylcyclopentene and 3-cyclopentenylcyclopentene (23) should polymerize whereas 3-isopropylcyclopentene should not.



(23)

Figure 2.4.

Using metathesis catalysts prepared from W or Mo halides and organoaluminium compounds, Dall'Asta and Motroni,[104] reported that bicyclo-[4.3.0]nona-3,7-diene "tetrahydroindene" (24) polymerized by ring-opening. Two possible modes of polymerization exist for tetrahydroindene as shown in Figure 2.5., both of the modes would appear unfavourable, mode A represents the ring-opening of a cyclohexene ring, and cyclohexene has been considered by most researchers to be unpolymerizable, and mode B represents the ring-opening of a fused five membered ring. They proposed that the resulting polymer B was formed from exclusive ring-opening of the five membered ring, which allows the cyclohexene ring in the polymer chain to transform from the boat to the more stable half-chair conformation and the cyclopentene ring to release ring strain, both processes are energetically favourable and it was suggested that these factors were sufficient to render the monomer polymerizable.

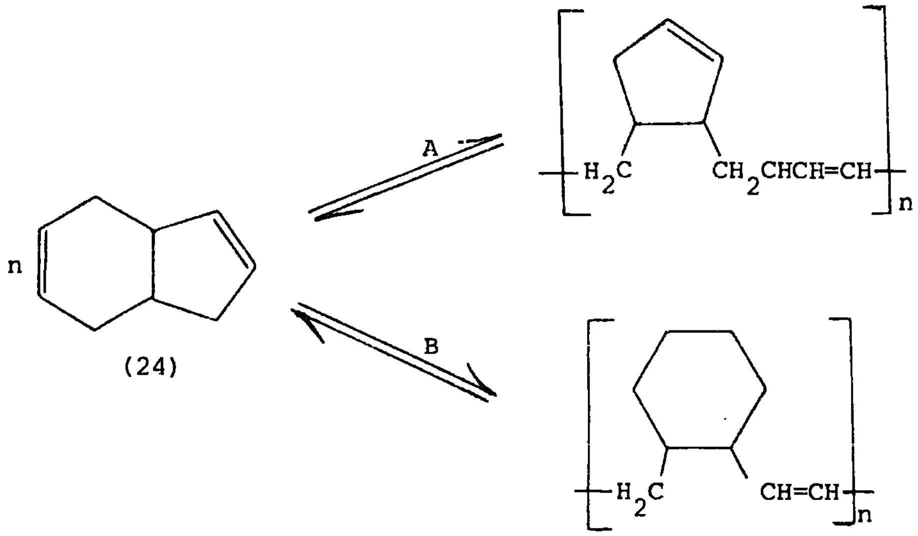


Figure 2.5.

## 2.2. Previous Work on Indene as a Monomer for Polymerization

### 2.2.a. Vinyl polymerization

Indene was first shown to be a polymerizable olefin in 1890.[105] Polymerizations have been achieved using various cationic catalysts such as sulphuric acid, antimony pentachloride and stannic chloride, and also by heating.[106-109] All polymers produced in the early work were of low molecular weight and the repeat unit was as shown in Figure 2.6.

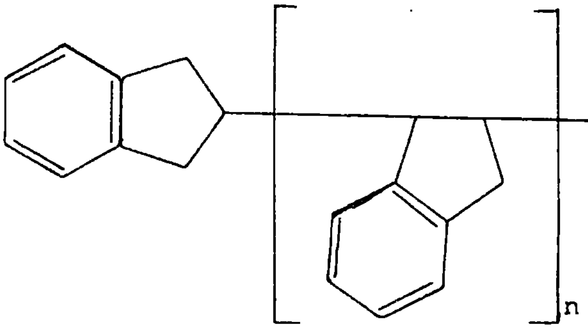


Figure 2.6.

The susceptibility of indene to attack, particularly from cationic reagents is very high, this area has interested many workers and polymerization of indene and its derivatives has been the subject of many investigations.[110,111] The list of Lewis acids which have been used as initiators has been extended to include boron trifluoride and titanium derivatives, low temperature experiments using these two catalysts,[112,113] with and without co-catalysts such as water and hydrogen chloride have produced high polymers with intrinsic viscosities in benzene of upto 2,[114] corresponding to a molecular weight of $\sim 2 \times 10^6$. Also Bhadani and Baranwal,[115-117] have reported the electrolytic polymerization of indene in non-aqueous solvents containing perchlorate and hexachloroantimonate salts.

### 2.2.b. Attempted ring-opening polymerization

Wilson has done some preliminary work to try to polymerize indene by ring-opening using an olefin metathesis catalyst made from tungsten hexachloride and tetraphenyltin. The procedure for polymerization of a cycloalkene using the catalyst system $WCl_6/Ph_4Sn$ used by him was as follows: a reaction vessel containing a magnetic follower was charged with tetraphenyltin (0.148 mmoles) and purged for one hour with dry nitrogen, tungsten hexachloride (0.072 mmoles) dissolved in dried, degassed toluene (7.5 $cm^3$) was injected into the reaction vessel using an air-tight syringe, the mixture was stirred for 12 minutes and the colour changed from blue-black to dark brown.

The reaction was cooled to 0° and the dried, degassed monomer (28.8 mmoles) was injected into the active catalyst mixture using an air-tight syringe, on addition of the monomer to the dark brown active catalyst solution an immediate colour change to deep blue was observed and after 20 minutes there was a detectable increase in viscosity. The reaction was terminated after 3 hours by the addition of a small quantity of methanol and then poured into a five-fold excess of methanol. The white solid powdery material which was precipitated (henceforth referred to as BW-A) was removed by filtration, dissolved in analar toluene, filtered and reprecipitated by addition to excess methanol. The solid material was recovered by filtration and dried under reduced pressure. It was soluble in toluene, chloroform, carbon tetrachloride, methyl ethyl ketone and tetrahydrofuran. This was the only experiment carried out and Wilson examined the product by elemental analysis, i.r. spectroscopy, reaction with bromine, intrinsic viscosity, G.P.C. molecular weight distribution and thermogravimetric analysis. Some of his sample was available for further tests and comparison with materials synthesised in this work.

Elemental analysis confirmed the molecular formula as $C_9H_8$. Wilson suggested that the new polymer (BW-A) might have, at least in part, the repeat unit indicated in Figure 2.7.

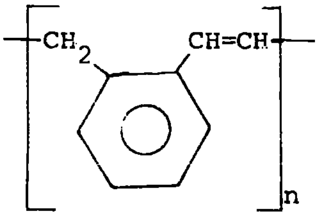


Figure 2.7.

This suggestion was based on a comparison of polyindene BW-A with another polyindene sample BW-B produced by conventional cationic polymerization. Qualitative reaction of solutions of both polyindenes in carbon tetrachloride with a dilute solution of bromine in carbon tetrachloride suggested that unsaturation was present in polymer BW-A to a greater extent than in polymer BW-B.

The intrinsic viscosity of polymer BW-A was determined, the result is given in Table 2 together with the $\bar{M}_n$ and $\bar{M}_w$ determined by G.P.C. analysis, these last two values are compared with those for polymer BW-B.

Table 2.

A comparison of $\bar{M}_n$ and $\bar{M}_w$ for polymers BW-A and BW-B

| Polymer | $[\eta]^a$ dl/g | $\bar{M}_w{}^b$ | $\bar{M}_n{}^b$ | d.p. |
|---|---|---|---|---|
| BW-A | 0.21 | 22920 | 8420 | 73 |
| BW-B | | 3541 | 1671 | 14 |

[a] Solvent methyl ethyl ketone. Determined at 25.00 ± 0.01°.

[b] G.P.C. results through the S.R.C. service of RAPRA.

As can been seen the molecular weight of the two polymers are quite different, polymer BW-A having a molecular weight considerably greater than polymer BW-B. These results certainly indicated that the material made by Wilson was a homopolymer of indene, and the greater molecular weight of BW-A together with its apparent greater reactivity towards bromine are consistent with the suggestion that it contains olefinic units.

A comparison was made between the i.r. spectrum of the polymer prepared using $WCl_6/Ph_4Sn$ catalyst (BW-A) and that prepared by a standard cationic polymerization (BW-B) and the spectra were as shown in Figure 2.8. The only

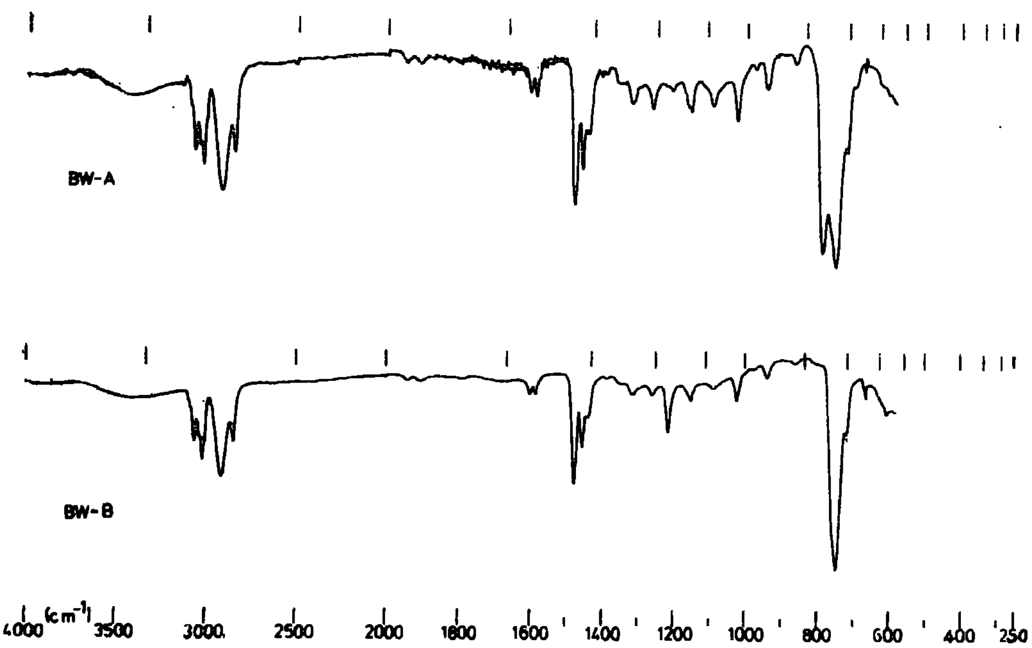


Figure 2.8.

significant difference between the two spectra was the presence of a strong absorption at 790 cm.$^{-1}$ in spectrum BW-A and the absence of such a band in spectrum of cationic polyindene BW-B. Wilson said if the polymer prepared using the catalyst system $WCl_6/Ph_4Sn$ was formed by the ring-opening polymerization of the fused five-membered ring, then it would have the structure shown in Figure 2.7. and the extra absorption at 790 cm.$^{-1}$ might be due to a vibrational mode available to this structure which is not available to conventional polyindene (cf. Figure 2.6.).

Wilson concluded that the material which was produced by the reaction of the active olefin metathesis catalyst system $WCl_6/Ph_4Sn$ on indene, is at least in part the ring-opened polymer.

### 2.3a. Discussion of further work on the polymerization of indene with $WCl_6/Ph_4Sn$ catalyst

The usual procedure for a polymerization of a cycloalkene using the catalyst system $WCl_6/Ph_4Sn$ was used, the dry purified monomer was added to the dark brown active catalyst solution mixture, an immediate colour change to deep blue was observed and the experiment was left overnight with continual stirring. The reaction was terminated after one day by the addition of a small quantity of methanol and then poured into a five-fold excess of methanol, the white solid powdery material which precipitated was dissolved in analar toluene and reprecipitated by addition of methanol. All the polymerizations were carried out under an atmosphere of dry nitrogen, all apparatus was carefully cleaned and dried, and all the transfers of materials and solvents were carried out under an atmosphere of dry nitrogen.

All the polymers which were made in this work appeared to be identical with cationic polyindene of low molecular weight. The i.r. spectra of the polymers produced did not show the absorption at 790 cm.$^{-1}$ (Appendix A(I)) which was originally detected in Wilson's polyindene BW-A. The materials were examined by elemental analysis, confirming the molecular formula as $C_9H_8$; and by G.P.C., which demonstrated that the products were of relatively low molecular weight (e.g. $\bar{M}_n \sim 1400$, $\bar{M}_w \sim 6700$). That the d.p. was low was also evident from the infrared spectra of these products since the terminal $\rangle C{=}CH-$ stretching absorption could be detected at 1610 cm.$^{-1}$ When the infrared spectrum of Wilson's polyindene (BW-A) was re-recorded it showed that the extra band at 790 cm.$^{-1}$ which was present when the spectrum of the freshly prepared sample was originally recorded had disappeared (Appendix A(II)), the time between the recordings of the two spectra was about one year. It is possible that Wilson's polymer had some ring-opened units and some cationic polyindene units and could be represented as shown in Figure 2.9., and for one reason or another this polymer structure had changed with the passage of time possibly to reform the five-membered ring.

Unfortunately, in the repetition of Wilson's work the present author has been unable to produce a polymer sample with the same infrared spectrum as BW-A despite repeated careful attempts. The nature of sample BW-A was carefully

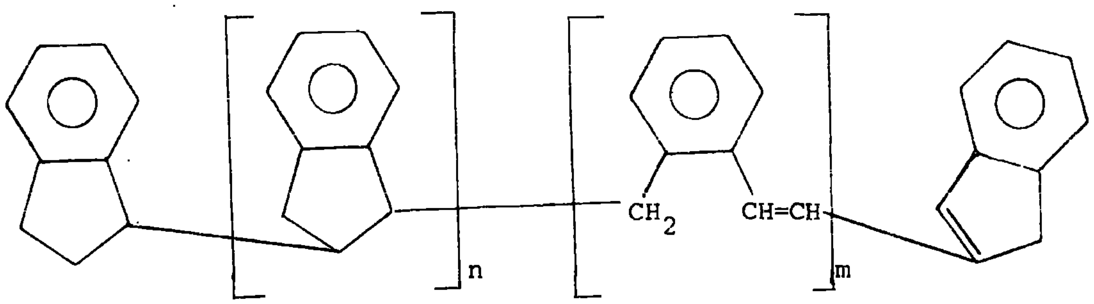
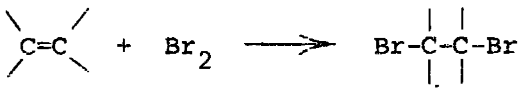


Figure 2.9.

examined and in the next section attempts to measure the amount of unsaturation by bromination are described.

### 2.3b. Quantitative analysis for unsaturation using bromine addition

For the purposes of this work it was necessary to find out if it was possible to use the bromine addition reaction quantitatively as well as qualitatively for the samples of interest here. The Shell-method[118] was selected for this analysis, this method is based on the reaction of the olefinic compound with an excess of bromine under standard conditions. The excess bromine, after reaction, is determined iodometrically and it is assumed



$$>C=C< \; + \; Br_2 \longrightarrow Br-\overset{|}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}-Br$$

that one double bond is equivalent to one bromine molecule.

There are a number of possible difficulties in the application of this method,[119] first of all there may be oxidation and destruction of the molecule; the second kind of difficulty which may cause low results, is precipitation of partially brominated products; and the third type, which may cause high results, is displacement of certain groups such as COOH, $SO_3H$, CHO, and substitution reactions as shown in Figure 2.10.

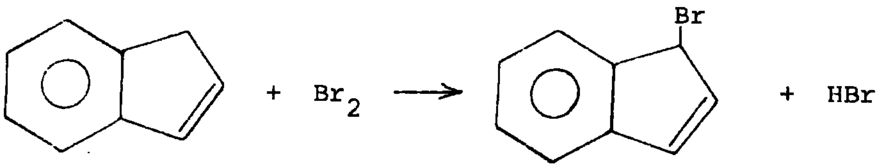


Figure 2.10.

In order to check the applicability of the method it was necessary to carry out experiments on unsaturated compounds of known composition, and clearly, the more closely such compounds resembled the polyindenes of interest the more relevant these checks would be.

The actual analytical procedure adopted was to take a weighed amount of standard material, dissolve it in 25 ml carbon tetrachloride, cool the solution in ice for 10 minutes, add the bromine in carbon tetrachloride reagent in 65-70% excess, store in the dark at $0^{o}$ for 10 minutes, then add 15 ml of 20% potassium iodide solution and titrate the released iodine to the starch end point using standard sodium thiosulphate solution. The reagent solutions were standardized daily.[120,121] From the bromine consumed, assuming one double bond is equivalent to one bromine molecule, the percentage reaction was calculated.

First indene, cyclohexene and indane were analysed by this method and the results are summarised below (Table 3). It is clear from these results that reaction with indane is negligibly small and that reaction with cyclic olefins does not go to completion under the conditions used. The average extent of reaction for cyclic olefins was 91% and it was decided that analyses for polymer unsaturation by this method (corrected for the systematic error by dividing by 9.1) would provide a useful estimate of the relative degree of unsaturation of different samples.

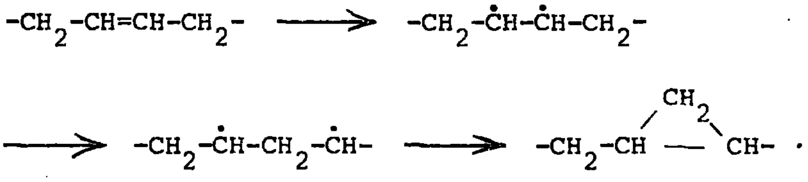
Table 3.

Reaction of unsaturated compounds of known structure with bromine in carbon tetrachloride at $0^{o}$, using the Shell method.[118]

| Compound | % Reaction | Average |
|---|---|---|
| Indene | 89.8, 91.7, 92.9, 89.7, 90.9<br>91.8, 91.1, 89.2, 91.2, 90.5 | 90.9 |
| Cyclohexene | 90, 95 | 92.5 |
| Indane | 1.4, 1.6, 1.8 | 1.6 |

The next step involved the analysis of some unsaturated polymer samples, and the results obtained are shown in Table 4. The polybutadienes used were commercial samples, they were all reputedly 1,4-polybutadienes.

Sample 1 had a random distribution of cis and trans double bonds, sample 2 had an all cis configuration and samples 3 and 4 were copolymers with respectively 5 and 23 mole-% of styrene. It can be seen that for samples 1 and 2 the corrected percentages of reaction are less than the theoretical 100% calculated for a pure poly-1,4-butadiene structure. This is quite a reasonable result since it is known that polybutadienes generally contain a proportion of saturated units formed by cyclization reactions during polymerization or as a result of subsequent photo or thermal reactions, for example:-



$$-CH_2-CH{=}CH-CH_2- \longrightarrow -CH_2-\dot{C}H-\dot{C}H-CH_2-$$

$$\longrightarrow -CH_2-\dot{C}H-CH_2-\dot{C}H- \longrightarrow -CH_2-CH\overset{CH_2}{\overline{\phantom{xx}}}CH- \cdot$$

Thus, the measured amount of unsaturation is expected to be lower than the theoretical ideal. The result for copolymer sample 3, which is expected to resemble samples 1 and 2, is also satisfactory. Sample 4, which contains relatively more styrene gave a corrected result which was a little higher than the value calculated on the basis of the quoted composition, it may be that the quoted composition is slightly inaccurate or that this copolymer undergoes significant substitution reactions at the benzylic C-H bond. Sample 5 was a poly(4-trifluoromethyl-1,3-cyclopentylene vinylene) prepared by Wilson (this department), in this case the corrected value for the percentage reaction is close to the theoretical value, cyclization reactions being much less likely in this relatively immobile structure. These results gave a measure of confidence in the method, as a semi-quantitative analytical procedure and the next step was to apply it to the analysis of various polyindene samples, the results are summarised in Table 5 for samples 1 and 2 produced respectively

Table 4.

Reaction of unsaturated polymers with bromine in carbon tetrachloride at 0°.

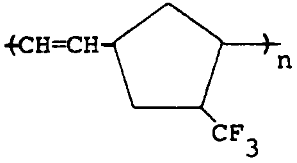
| No. | Polymer | % Reaction | | | |
|---|---|---|---|---|---|
| | | Measured | Average | Corrected | Calculated |
| 1 | Polybutadiene (random cis/trans) | 84 | 84 | 92 | 100 |
| 2 | Polybutadiene (all cis) | 78, 78 | 78 | 86 | 100 |
| 3 | Styrene/butadiene co-polymer (5% styrene) | 78, 78 | 78 | 86 | 91 |
| 4 | Styrene/butadiene co-polymer (23% styrene) | 60, 62 | 61 | 67 | 63.5 |
| 5 |  | 94 | 94 | 103 | 100 |

Table 5.

Reaction of polyindene with bromine in chloroform at 0°.

| No. | Polymer | % Reaction | | D.P.[a] | $\frac{100}{D.P.}$ |
|---|---|---|---|---|---|
| | | Measured | Corrected | | |
| 1 | Polyindene (cationic) by $H_2SO_4$ | 18.9, 16.8 | 20 | - | - |
| 2 | Polyindene (thermal) | 20.1 | 22 | 5 | 20 |
| 3 | Polyindene ($WCl_6$ + $Ph_4Sn$) this work | 17.8 | 20 | 12 | 8 |
| 4 | Polyindene ($WCl_6$ + $Ph_4Sn$) BW-A | 23.2, 23.8 | 26 | 73 | 1.4 |

[a] By G.P.C. analysis.

by cationic and thermal initiation we expect a polyindene with the structure shown in Figure 2.6.; for such a polyindene there is only one double bond available to react with bromine per chain and the percentage reaction with bromine is related to the degree of polymerization by the expression:-

$$\% \text{ Reaction} = \frac{100}{\text{D.P.}}$$

The agreement between the measured value of percentage reaction and that calculated from D.P. values will only be good where the product polymer has the structure shown in Figure 2.6. Degrees of polymerization were obtained by G.P.C. measurements for samples 2, 3 and 4; and from its mode of preparation sample 1 is expected to be a low D.P. product and the measured percentage reaction with bromine would indicate a D.P. of about 5. Agreement between measured and calculated values for sample 2 is good. When we consider sample 3 and 4 produced using the metathesis catalyst we find that the measured percentage reaction with bromine is far greater than would be expected on the basis of structure 2.6., by a factor of 2½ times for sample 3 (produced in this work) and 18½ times for sample 4 (prepared by Wilson).

A reasonable conclusion from these measurements would be that the polymers produced, both in this work and by Wilson, using the $WCl_6/Ph_4Sn$ catalyst contain significantly more units which can react with bromine than the conventional polyindenes. This is, of course, consistent with some ring-opening having occurred. However both the analytic method and the d.p. results obtained from G.P.C. analysis cannot be regarded as totally reliable, and the fact that both the infrared and $^{13}C$ n.m.r. spectra of conventional cationic polyindenes and the products from the $WCl_6/Ph_4Sn$ initiated reactions are identical underlines the uncertainties which remain concerning the true structure of these products.

In view of these uncertainties it was decided to attempt metathesis polymerization of indene under conditions where the intervention of cationic mechanisms could be rigorously excluded.

### 2.3c. Attempts to polymerize indene using the catalyst system tungsten hexachloride and tetraphenyltin in the presence of organic bases.

After the ambiguous results from the attempts to polymerize indene by ring-opening using the catalyst system tungsten hexachloride and tetraphenyl tin, it was decided that in view of the high susceptibility of indene to cations it was necessary to exclude anything which might lead to cationic polymerization, such as moisture or any other source of protons. Tungsten hexachloride is very susceptible to reaction with water and despite all precautions it seemed

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

unlikely that the last traces of water could be removed and so, as the next best procedure, addition of organic bases to remove HCl was investigated.

Previous workers have shown that norbornene is particularly susceptible to ring opening polymerization,[122,123] in this work norbornene was polymerized by $WCl_6/Ph_4Sn$ as a check on the technique used, the catalyst was found to be very active for this monomer.

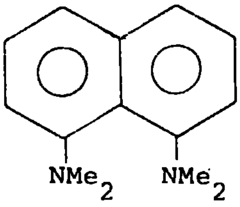
It has been reported that metathesis catalysts modified by addition of several amines show increased activity in ring cleavage in the polymerization of norbornene.[124,125] Oshika and Tabuchi,[100,126] have reported that the addition of a tertiary amine to the polymerization system remarkably increased the polymerization rate and the molecular weight without making any change in the microstructures of the products, also the addition of the base 30 minutes after the reaction had started increased the rate of the polymerization. Tsujino and Saegusa,[127] have examined the effects of various bases on the polymerization of norbornene using some metathesis catalysts, they found that secondary and tertiary amines, dioxane, dibutyl sulphide, pyridine and pyridine derivatives were highly effective in increasing the activity of the $AlEt_3/TiCl_4$ (2.5/1) system in ring-opening polymerization, while the addition of bases such as triethylamine to the system $AlEt_3/TiCl_4$ (1/1) decreased the catalytic activity. The catalyst activity grew higher as the amount of amine was increased and, in this work, caused a considerable change in the microstructure of the polymer.[127] It was also reported that these ternary catalyst systems which were shown to be quite effective for ring-opening polymerization of norbornene, were inactive for the polymerization of olefins such as ethylene and propylene. Kothari and Tazuma, reported that pyridine completely inhibits the disproportionation activity of the $WCl_6/EtAlCl_2$ catalyst system.[128]

The literature examples given above illustrate that the effect of bases on the activity of metathesis and Ziegler type catalysts is difficult to predict, in some cases activating and others deactivating, the effect depending not only on the catalyst system but also on the monomer being polymerized.

Several different organic bases were used in attempts to polymerize indene in the absence of protons, and several different reaction procedures were tried. First of all an aliphatic tertiary amine, triethylamine, was used. This strong base was added to the catalyst system both before the monomer and, in a separate experiment, after the reaction had proceeded for 30 minutes. The active catalyst was generated by mixing at room temperature in most cases, and in some cases the $WCl_6/Ph_4Sn$ mixture was refluxed prior to addition of other reagents. No polymers were formed in most of the reactions using triethylamine as base, usually a residue of tetraphenyltin was recovered. In the case where the base was added 30 minutes after the reaction had started, a very small amount of cationic polyindene was formed, showing that triethylamine stopped the reaction and the rate of cationic polymerization in the presence of the $WCl_6/Ph_4Sn$ catalyst was very slow.

The second base used was pyridine. When a small quantity of pyridine was added to the catalyst system before the indene, a mixture of cationic polyindene and tetraphenyltin was recovered. When pyridine was used in higher concentration for the polymerization of norbornene, no polymers were formed and tetraphenyltin was recovered; the polymerization of the same monomer with the same catalyst system in the absence of pyridine was very successful giving the ring-opened polymer in high yield. These results indicate that even the weak base pyridine effectively suppresses the activity of this catalyst system.

The last base investigated was 1,8-bis-(dimethylamino)-naphthalene, proton sponge (25), this compound has a very high proton affinity. Proton sponge



(25)

was added to the catalyst system both before the monomer addition and, in another experiment, 30 minutes after the reaction had started. The catalyst system was generated either by room temperature mixing or refluxing. In most experiments tetraphenyltin was recovered and no polymers were formed, but in the experiment where the proton sponge was added after 30 minutes, a small amount of cationic polyindene was formed. Addition of proton sponge to the catalyst system completely suppressed the polymerization of norbornene. In summary it was found that 1,8-bis-(dimethylamino)-naphthalene, like pyridine and triethylamine, suppressed all catalytic activity for the $WCl_6/Ph_4Sn$ system used in this work.

In a last attempt to polymerize indene using the catalyst system $WCl_6/Ph_4Sn$, the active catalyst solution was added in three separate portions to the reaction, in this case a good yield of cationic polyindene was formed. The results of these experiments are summarised in Table 6 for indene monomer and in Table 7 for norbornene monomer.

## 2.4. Conclusions

All the attempts to polymerize indene exclusively by ring-opening polymerization were unsuccessful with the catalyst system $WCl_6/Ph_4Sn$, it was found that bases destroyed the catalyst activity completely both for cationic polymerization of indene and ring-opening polymerization of norbornene. There remains some ambiguity and it may be that in some cases a limited amount of ring opening of indene does occur, although this cannot be regarded as proved. The related system acenaphthylene was also briefly examined (see Experimental part), this monomer gave only vinyl polymerization with $WCl_6/Ph_4Sn$ system with no evidence for ring-opening.

Table 6

The polymerization of indene using $H_2SO_4$, heating, $WCl_6/Ph_4Sn$ and $WCl_6/Ph_4Sn$ with organic bases

| No. | Monomer amount (ml) | Catalyst | | Catalyst[a] solvent (ml) | Time of catalyst refluxing | Base[b,c,d] | Base amount | Time of base addition | Wt. of the re-covered material (g) | Nature of recovered material | Elemental analysis | | I.r. spectrum no. in Appendix A |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | | | | | C% | H% | |
| 1 | 20 | 3 drops of conc. $H_2SO_4$ | | - | - | - | - | - | 2.1 | Cationic polyindene | 90.45 | 7.20 | III |
| 2 | 20 | Heating | | - | - | - | - | - | 2.33 | Cationic polyindene | 91.04 | 8.53 | IV |
| | | $WCl_6$ (g) | $Ph_4Sn$ (g) | | | | | | | | | | |
| 3 | 20 | 0.04 | 0.08 | 30 | - | - | - | - | 0.7 | Cationic polyindene | 92.21 | 7.38 | I |
| | | 0.06 | 0.13 | 40 | | | | | | | | | |
| 4 | 20 | 0.06 | 0.14 | 40 | - | - | - | - | 2.0 | Cationic polyindene | 90.86 | 7.82 | VI |
| | | 0.06 | 0.12 | 30 | | | | | | | | | |
| 5 | 40 | 0.43 | 0.9 | 80 | - | b | 1 ml | 5 min. before the monomer | 0.6 | $Ph_4Sn$ | - | | VII |
| 6 | 20 | 0.08 | 0.17 | 70 | - | b | 2 ml. | 30 min. after the monomer | 0.1 | Cationic polyindene | 87.83 | 7.27 | VIII |
| 7 | 30 | 0.64 | 1.20 | 60 | - | c | 1 ml | 5 min. before the monomer | 1.00 | Mixture of $Ph_4Sn$ and cationic | - | | IX |
| 8 | 20 | 0.07 | 0.16 | 80 | - | d | 0.15 g | 5 min. before the monomer | 0.04 | $Ph_4Sn$ | - | | X |
| 9 | 20 | 0.09 | 0.18 | 60 | 10 min. | d | 0.16 g | 10 min. before the monomer | 0.05 | $Ph_4Sn$ | - | | XI |
| 10 | 20 | 0.07 | 0.16 | 60 | - | d | 1.5 g | 30 min. after the monomer | 0.07 | Cationic polyindene | 84.86 | 8.02 | XII |

[a] T-toluene; [b] triethylamine; [c] pyridine; [d] 1,8-bis-(dimethylamino)-naphthalene.

Table 7

The polymerization of norbornene using $WCl_6/Ph_4Sn$ and $WCl_6/Ph_4Sn$ with organic bases

| No. | Monomer (g) | Monomer solvent[a,b] (ml) | Catalyst | | Catalyst solvent[a,b] (ml) | Time of catalyst refluxing | Base[c,d] | Base[c,d] amount | Time of base addition | Wt. of recovered material (g) | Nature of recovered material | I.r. spectrum number in Appendix A |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | $WCl_6$ (g) | $Ph_4Sn$ (g) | | | | | | | | |
| 1 | 12.8 | 40T | 0.41 | 0.88 | 60T | - | - | - | - | 12.5 | Polynorbornene ring-opening | XIV |
| 2 | 11.14 | 40P | 0.25 | 0.51 | 70P | - | c | 130 ml | With the monomer solution | very small | $Ph_4Sn$ | XV |
| 3 | 16.76 | 60T | 0.37 | 0.63 | 70P | - | c | 70 ml | With the monomer soln. | very small | $Ph_4Sn$ | XVI |
| 4 | 10.0 | 5P | 0.30 | 0.60 | 60T | - | c | 5 ml | With the monomer soln. | very small | $Ph_4Sn$ | XVII |
| 5 | 11.36 | 40T | 0.29 | 0.54 | 60T | - | d | 0.54 g | Direct after the monomer addn. | very small | $Ph_4Sn$ | XVIII |
| 6 | 7.92 | 40T | 0.04 | 0.10 | 50T | 10 min. | d | 0.09 g | With the catalyst soln. in the same time | very small | $Ph_4Sn$ | XIX |
| 7 | 9.43 | 40T | 0.07 | 0.18 | 50T | 5 min. | d | 0.18 g | 2 min. before the monomer addn. | very small | $Ph_4Sn$ | XX |

[a] T-toluene

[b] P-pyridine

[c] Pyridine

[d] 1,8-bis-(dimethylamino)-naphthalene

# EXPERIMENTAL PART

## 2.5. Catalysts

### 2.5a. Reagents

Hexachloropropene and tetraphenyltin were used as purchased from Koch-Light Laboratories Ltd. Tungsten trioxide was used as purchased from BDH Chemicals Ltd., carbon tetrachloride was purchased from BDH, and degassed.

### 2.5b. Preparation of anhydrous tungsten hexachloride

Hexachloropropene (35 ml) and tungsten trioxide (3 g) were placed in a 100 $cm^3$, 3-necked, round-bottomed flask, fitted with an air-condenser which was attached to the dry nitrogen line. A sinter filter tube was attached to the flask and its exit was also attached to the dry nitrogen line, the mixture was refluxed for four hours. The resultant reddy-brown solution was allowed to cool slowly to room temperature, tungsten hexachloride crystals were formed under the solution. The condenser was removed from the reaction flask, which was closed immediately with a glass stopper, another 250 $cm.^3$, 2-necked, round-bottomed flask, was fitted to the end of the sinter tube attached to the reaction flask, and the other outlet of this flask was attached to a vacuum pump and with careful manipulation of the reaction flask and the pressure in the system the crystals were filtered from the solvent. The tungsten hexachloride crystals were washed several times with degassed carbon tetrachloride taking care to maintain an atmosphere of dry nitrogen or a vacuum. The crystals were evacuated for three hours on the vacuum line to remove traces of chlorocarbons, the tungsten hexachloride (3.4 g, 66%) obtained was steel-blue in colour.

## 2.6. Polymerizations

### 2.6a. Reagents

Indene was purchased from Hopkin and Williams Ltd., shaken with $P_2O_5$, filtered and purified by fractional distillation from calcium hydride and stored in an atmosphere of dry nitrogen. Toluene was purchased from BDH Chemicals Ltd., purified and dried over sodium wire and distilled directly into the reaction flask. Dry triethylamine was provided by Mr. B. Hall (this department). Pyridine was purchased from Hopkin and Williams Ltd., purified by fractional distillation twice over potassium hydroxide and then over calcium hydride. 1,8-bis-(dimethylamino)-naphthalene was provided by Dr. K.B. Dillon (this department). Acenaphthylene was purchased from BDH Laboratories Ltd. Norbornene was purchased from Aldrich Chemical Co. Ltd.

### 2.6b. The polymerization of indene initiated by conc. sulphuric acid

Purified indene (20 ml) was injected in the reaction vessel which contained a magnetic follower, three drops of concentrated sulphuric acid were added to the liquid, immediately a red solid was formed and the solution colour changed to yellow. The experiment was left overnight, the solution became viscous and red in colour, the solution was dissolved in toluene and washed with water. Part of the toluene was evaporated (Rotavap) and the product precipitated by dropwise addition to a five-fold excess of petroleum spirit (40-60), the white material was removed by filtration and dried under vacuum for four hours (2.1 g. Found: C, 90.45; H, 7.2%; $C_9H_8$ requires C, 93.06; H, 6.94%).

### 2.6c. Polymerization of indene by heating

Purified indene (20 ml) was injected into the reaction vessel which contained a magnetic follower. The liquid was heated at 150°C using oil bath, the experiment was left under these conditions for one week, the initially colourless liquid changed to yellow and became viscous, the liquid was added dropwise to a five-fold excess of petroleum spirit. The precipitated material was removed by filtration and dried under vacuum. A white powdery material was found (2.3 g, $\bar{M}_n$, 630, d.p. 5 by G.P.C. analysis, Found C, 91.04; H, 8.53%).

### 2.6d. The polymerization of indene using tungsten hexachloride and tetraphenyltin as catalyst system

The reaction vessel containing a magnetic follower was charged with tungsten hexachloride (0.04 g) dissolved in dried toluene (30 ml) by injection into the reaction vessel using an air-tight syringe, tetraphenyltin (0.08 g) was added to the mixture. An atmosphere of dry nitrogen was maintained throughout the experiment. The mixture was purged with dry nitrogen and stirred for ten minutes, the colour changed from blue-black to dark brown, the dried purified monomer (20 ml) was injected into the active catalyst mixture using an air-tight syringe, an immediate colour change to dark blue was observed. The reaction was left with continual stirring overnight, the viscosity of the reaction mixture did not increase detectably.

The reaction was terminated by the addition of a small quantity of methanol, followed by the addition to a five-fold excess of methanol. The precipitated material was removed by filtration, dissolved in analar toluene and reprecipitated in excess methanol. The material was a white powder (0.7 g), ($\bar{M}_n$ 1420, d.p. 12 by G.P.C. analysis, found: C, 92.21; H, 7.38%).

NOTE: The same procedure was used for the polymerization in which the catalyst system was added to the reaction mixture in three portions. The first portion at the beginning of the polymerization, the second portion after 20 minutes of reaction and the third after four hours. A white powder was formed (2.0 g, found: C, 90.86; H, 7.82%), it was shown to be cationic polyindene by i.r. spectroscopy.

### 2.6e. The ring-opening polymerization of norbornene using tungsten hexachloride and tetraphenyltin as the catalyst system

A reaction vessel containing a magnetic follower was charged with tungsten hexachloride (0.41 g) dissolved in dried toluene (60 ml) by injection into the reaction vessel using an air-tight syringe, tetraphenyltin (0.88 g) was then added to the mixture. The mixture was stirred for ten minutes, the colour changed from blue-black to dark brown. The monomer (12.8 g) was dissolved in dry toluene (40 ml) and this solution was added to the catalyst mixture, there was an immediate colour change to deep blue with traces of dark brown.

After one minute the viscosity of the reaction mixture had increased and one minute later the reaction mixture became solid. The solid was dissolved in analar toluene and precipitated by the addition to a five-fold excess of methanol.

The material, which was a red powder (12.5 g) was shown to be poly-(1,3-cyclopentylene vinylene) by infrared spectroscopy (Appendix A, VII).

### 2.6f. The attempted polymerizations of indene and norbornene using organic bases with the catalyst system tungsten hexachloride and tetraphenyltin.

The same procedure described above was used and the results are listed in Table 6 and 7.

### 2.6g. The polymerization of acenaphthylene using concentrated sulphuric acid as initiator

Acenaphthylene (1.31 g) and analar toluene (60 ml) were placed in a 250 $cm^3$, 1-necked, round-bottomed flask. Concentrated sulphuric acid (6 drops) was added, the colour changed from yellow to blue-green. The reaction mixture was left for 3 hours with stirring. The product was precipitated by addition to a five-fold excess of methanol, recovered by filtration and dried under vacuum for four hours.

The product, polyacenaphthylene (0.55 g, 42%; found, C, 91.2; H, 6.71%; $C_{12}H_8$ requires C, 94.70; H, 5.30) was a reddy-green colour and was identified by infrared spectroscopy (Appendix A, XXI).

### 2.6h. The polymerization of acenaphthylene using tungsten hexachloride and tetraphenyltin as the catalyst system

The reaction vessel containing a magnetic follower was charged with tetraphenyltin (0.07 g), tungsten hexachloride (0.03 g) dissolved in dried toluene (20 ml) was injected into the reaction vessel using an air-tight syringe. The mixture was stirred for ten minutes and the colour changed from blue-black to dark brown. The monomer (0.86 g) was dissolved in 25 ml of dried toluene to give a yellow solution, this solution was injected into reaction vessel using an air-tight syringe, the colour changed during three hours to deep blue. After 3 hours the reaction was terminated by addition of a small quantity of methanol, followed by the addition to a five-fold excess of methanol. The precipitated material was removed by filtration and dried under vacuum for four hours.

The white-yellow product, polyacenaphthylene (0.62 g, 72%, found: C, 92.44; H, 6.78%), was shown to be cationic polyindene by infrared spectroscopy (Appendix A, XXII).

## 2.7. Analysis for Unsaturation by Bromine Addition

### (a) Reagents

Analar bromine and potassium iodide were purchased from Hopkin and Williams Ltd.; sodium thiosulphate was purchased from Fisons Analytical Reagents; cyclohexene, chloroform, indane, standard potassium iodate (0.01070 g per ml.), carbon tetrachloride and starch were purchased from BDH Chemicals Ltd.; polybutadiene (cis-trans), polybutadiene (cis), styrene/butadiene copolymers were obtained from Professor D.T. Clark's ESCA group's collection of standard polymers, poly(4-trifluoromethyl-1,3-cyclopentylene vinylene) and polyindene (BW-A) were provided by Dr. W.J. Feast.

### (b) Preparation of the reagents

Reagents were prepared according to the usual methods in analytical chemistry,[120,121] as follows:-

### (b)i. Preparation of (0.2N) bromine reagent

Analar bromine (5.5 ml) 17.2 grams was dissolved in one litre of carbon tetrachloride using a one litre graduated flask.

### (b)ii. Preparation of potassium iodide solution 20%

Potassium iodide (20 g) was dissolved in distilled water and completed to 100 ml using a graduated flask.

### (b)iii. Preparation of starch indicator

One gram of soluble starch was dissolved with 100 ml cool distilled water to form a slurry, the slurry was added regularly to 90 ml boiled distilled water with continual stirring. The solution was transferred to a stoppered flask.

(b) iv. Preparation of (0.1N) sodium thiosulphate solution

Sodium thiosulphate ($Na_2S_2O_3.5H_2O$, (25 g)) was dissolved in freshly boiled and cooled distilled water. Sodium carbonate (0.1 g) was added, the solution was diluted to 1 litre, transferred to a dark bottle and standardised after 24 hours.

(c) Standardisation of thiosulphate solution by standard potassium iodate (0.01070 g per ml).

Standard potassium iodate (10 ml) was pipetted into a conical flask, potassium iodide (1.0 g) was added followed by sulphuric acid 2N (15 ml). The titration was made with sodium thiosulphate solution (0.1N) to a faint straw colour, indicator (1 ml) was added and the titration was continued to the starch end point. The measurement was repeated until three consecutive titration agreed within 0.1 ml.

Illustrative calculation

The end point was 29.1 ml.

$$KIO_3 + 5KI + 3H_2SO_4 \equiv 3I_2 + 5K_2SO_4 + 3H_2O$$

The equivalent wiehgt of $KlO_3$ is $\frac{1}{6}$ of its formula weight.

In 10 ml of $KlO_3$ there is 0.1070 g and it was equivalent to 29.1 ml of the sodium thiosulphate solution.

$$I_2 + 2Na_2S_2O_3 \equiv 2NaI + Na_2S_4O_6$$

$$\therefore \quad KlO_3 \equiv \frac{2}{3} Na_2S_2O_3$$

$\therefore$ 29.1 ml of sodium thiosulphate solution $\equiv \frac{0.1070 \times 6}{214}$ equivalents

$\therefore$ 1 litre of sodium thiosulphate solution has $\frac{0.1070 \times 6 \times 1000}{214 \times 29.1}$ = 0.1031

Then the sodium thiosulphate solution normality is 0.1031N.

### (c) i. Standardisation of the bromine/carbon tetrachloride reagent using standard sodium thiosulphate solution (0.1031N)

The reagent was standardised daily as follows: carbon tetrachloride (25 ml) and distilled water (100 ml) were measured out in a glass-stoppered flask and cooled in ice bath for 10 minutes with continual stirring, reagent (20 ml) was added and the flask was stored in the dark at 0° with continual stirring for a further 10 minutes, potassium iodide solution 20% (20 ml) was then added. The released iodine was titrated against standard sodium thiosulphate solution to the starch end point.

## 2.8. The General Method for Determination of Unsaturation by Reaction with Bromine in Carbon Tetrachloride

The same procedure was used for all samples. A small amount of the sample was dissolved in carbon tetrachloride (sometimes in chloroform if the sample did not dissolve in $CCl_4$) (25 ml) in a glass-stoppered flask, water (100 ml) was added and the flask was cooled in an ice bath with continual stirring for 10 minutes. The $Br_2/CCl_4$ reagent in 65 to 70% excess (usually about 20 ml) was added and the flask was then stored in the dark and kept in the ice-bath with continual stirring. 10 minutes after the addition of the reagent, potassium iodide solution 20% (20 ml) was added and the liberated iodine was titrated with sodium thiosulphate solution to the starch end point.

### (a) Results and calculations

One example is given as illustration of the calculation:-

(i) Sodium thiosulphate solution - 0.1031N.

(ii) $Br_2/CCl_4$ reagent - 0.1758N.

(iii) Weight of the sample (indene) - 0.100 g.

(iv) Titre of thiosulphate required - 19.0 ml.

The amount of bromine at the beginning of the reaction was:-

$$\frac{20 \times 0.1758 \times 79.92}{1000} \quad \text{i.e. } 0.2810 \text{ g}$$

The amount of bromine which remained after the reaction was:-

$$\frac{19 \times 0.1031 \times 79.92}{1000} \quad \text{i.e. } 0.1566 \text{ g}$$

Thus, the reaction used 0.2810 - 0.1566 = 0.1244 g of bromine.

On the basis of 1 mole of bromine per reacting double bond the bromine consumed was equivalent to:-

$$\frac{0.1244 \times 116.154}{159.84} \text{ g}$$

i.e. 0.0904 g of indene, thus the % reaction observed was:-

$$\frac{0.0904 \times 100}{0.1} = 90.4\%$$

# CHAPTER 3

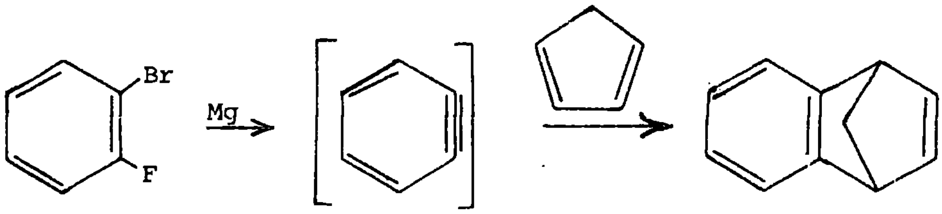
## The Synthesis and Ring-opening Polymerization of Benzonorbornadiene

## 3.1. Introduction

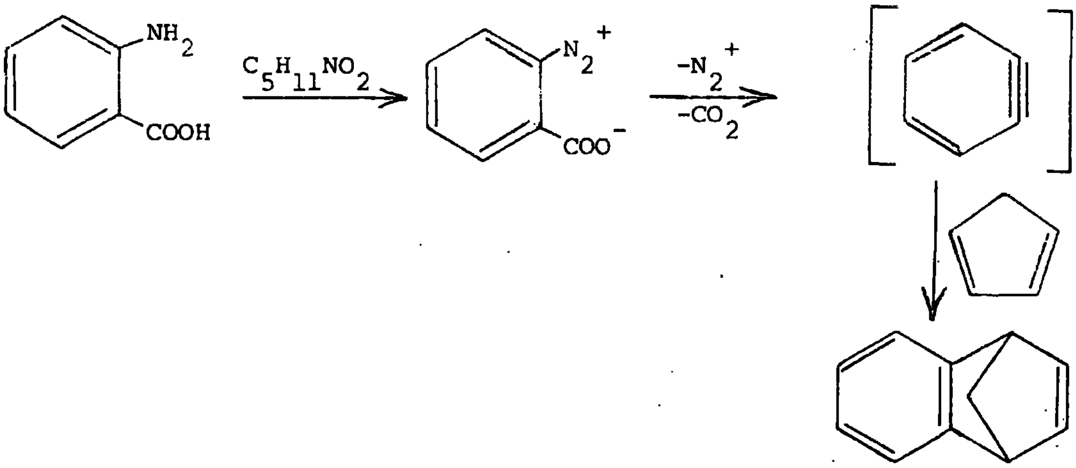
In this chapter the synthesis of benzonorbornadiene and the reaction of this monomer with tungsten hexachloride/tetraphenyltin catalyst are described. The reasons for undertaking this work were given at the end of the previous chapter.

## 3.2. The Synthesis of Benzonorbornadiene

Benzonorbornadiene (15) was first described in 1958,[129] ortho-bromofluorobenzene was reacted with magnesium and the resulting benzyne trapped with cyclopentadiene to give (15). Although this is an effective synthesis the starting material is expensive and for the purposes of this work it was decided to generate benzyne from the reaction of anthranilic acid with amylnitrite.[130]



(15)

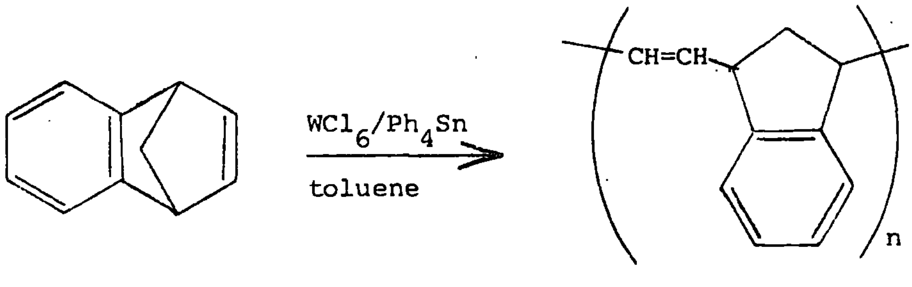


This route has previously been described, and the procedure used in this work involved only small changes from the published method.[131] Monoglyme solutions of the reagents were added to refluxing monoglyme at approximately equal rates, the first formed diazonium salt decomposed immediately and the resulting benzyne was trapped with cyclopentadiene. This method avoids any risk of isolating the explosive diazonium salt.[131] Full details of the preparation and purification of monomer (15) are given in the Experimental Section.

## 3.3. The Ring-opening Polymerization of Benzonorbornadiene Using the Catalyst System Tungsten Hexachloride and Tetraphenyltin

The usual procedure for the ring-opening polymerization of a cycloalkene was followed using the catalyst system $WCl_6/Ph_4Sn$ in toluene. On addition of benzonorbornadiene (1 ml) to the dark brown active catalyst system in (30 ml) toluene an immediate colour change to dark blue was observed, the solution viscosity increased rapidly and the mixture became a jelly like mass after five minutes. This result was like that observed for the polymerization of norbornene, and in fact polynorbornene has a remarkably high capacity for absorbing hydrocarbon solvents. The experiment was repeated using 2 ml of monomer and 125 ml of toluene and the polymerization was terminated by addition of 5 ml of methanol after 30 minutes, at this stage the mixture was viscous but had not yet solidified; this procedure made the isolation of the polymer easier. The reaction product, a blue sticky material, was dissolved in chloroform, the resulting solution was partially evaporated to give a viscous solution which was added dropwise to a large excess of methanol, the product which precipitated was recovered by filtration. The product was then reprecipitated four times using the same solvent/non-solvent combination, and was finally dried for 48 hours under vacuum to give a pale yellow solid in 79% yield.

This product was shown to be the expected ring-opened polymer (16) of benzonorbornadiene by a combination of elemental analysis, spectroscopic examination, G.P.C. analysis and chemical tests described in the next section.



(16)

## 3.4. Characterization of Polybenzonorbornadiene

The elemental analysis of the fresh sample of polymer (16) was unsatisfactory giving C, 87.5; H, 7.6% whereas the calculated figures for the polybenzonorbornadiene are C, 92.9; H, 7.1%; the analysis was repeated after two days and gave C, 86.6; H, 7.7%. At this stage it was realized that the structure (16) contained a tertiary carbon hydrogen bond which is both allylic and benzylic and would therefore be expected to be particularly susceptible to oxidation. The first product of oxidation would be expected to be a peroxide,[132] so a solution of the polymer in chloroform was tested for peroxides using acidified potassium iodide solution (2%), the mixture turned brown after a few minutes and a blue colouration was obtained on addition of starch solution indicating that peroxide units were present. Another sample of (16) 0.1 g was dissolved in 35 ml chloroform and oxygen was allowed to bubble through the solution for 18 hours, then the solvent was removed, the recovered polymer was a darker yellow than the initial material, elemental analysis gave C, 73.64; H, 6.94%, clearly the product was very susceptible to oxidation.

The infrared spectra of the fresh polymer and the highly oxidized sample were compared (Appendix A, number XXV and number XXVI respectively). The oxidized material showed a much more intense band at 3400 cm.$^{-1}$ which presumably arises from OH and OOH groups; also there were changes in the relative intensities in the aliphatic CH stretching region (2850 - 2970 cm.$^{-1}$); the band at 1710 cm.$^{-1}$, assigned to carbonyl stretching, had increased intensity and other small changes in the low frequency part of the spectrum were observed.

The U.V. spectra of benzonorbornadiene, fresh polybenzonorbornadiene and the highly oxidized sample of polybenzonorbornadiene were also compared. The monomer showed no significant absorption above 285 nm, whereas both the fresh and oxidized samples of the polymer showed a series of overlapping bands extending out to 350 nm, a comparison of the extension coefficients for the long wave length bands in the spectra of the two polymer samples is given on the following page.

| Band Position (nm) | Extinction Coefficient | |
|---|---|---|
| | Fresh Sample | Oxidized Sample |
| 292 | 670 | 490 |
| 303 | 600 | 360 |
| 325 | 140 | 110 |
| 350 | 15 | 15 |

The ESCA spectra of the polymer samples were recorded by Dr. A. Dilks (this department). For the fresh sample an oxygen content of approximately 10% was indicated which compares with the 5% oxygen content indicated by elemental analysis, these results are consistent since ESCA is a surface sensitive technique and the precipitated polymer would be expected to be most highly oxidized on the outer surfaces of the particles. The ESCA spectrum of the more highly oxidized sample indicated an increased oxygen content but also indicated the presence of chlorine, presumably derived from solvents. This preliminary ESCA investigation thus confirms that even the fresh polybenzonorbornadiene has undergone considerable surface oxidation.

Thus these three spectroscopic techniques are consistent with the suggestion that polybenzonorbornadiene is rapidly oxidized by molecular oxygen. A possible mechanism for this process is indicated in Figure 3.1. on the following page.

In fact the evidence of the peroxide test is consistent with the proposed formation of peroxides; infrared spectroscopy indicates -OOH and/or -OH as well as carbonyl groups in the oxidized polymer; and the ultraviolet spectral measurements indicate an unsaturated system which absorbs at longer wavelength than the monomer, conjugated systems such as those given for proposed intermediate (18) and/or its dehydration products would be expected to absorb at longer wavelength. The rationalization proposed in Figure 3.1. indicates only the first steps in the oxidation process, all the proposed intermediates

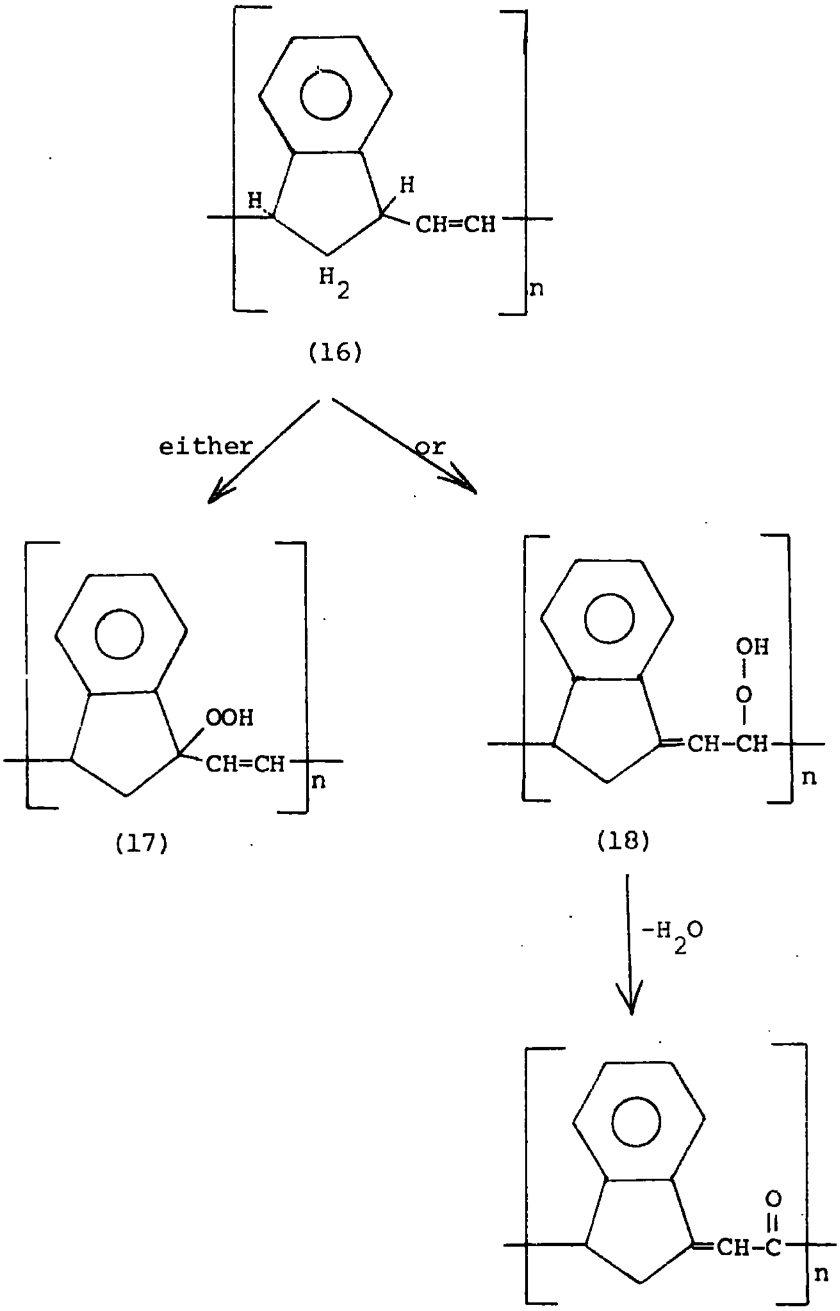
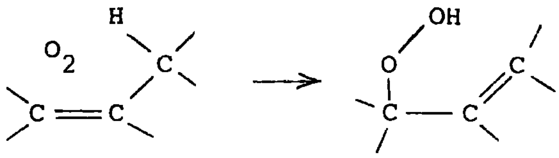


Figure 3.1.

drawn would be expected to undergo further reaction and the overall result will be complex, the spectroscopic examination carried out can only be regarded as preliminary and the available data do not justify an attempt at a more detailed analysis.

The very ready oxidation of polybenzonorbornadiene may make it an interesting test material for studying oxidation processes. For example, oxidation at allylic C-H bonds may occur by way of singlet or triplet oxygen as shown below in Figure 3.2. In the case of polybenzonorbornadiene a singlet mechanism would lead exclusively to formation of (18) as the first step, whereas a triplet mechanism would give both (17) and (18). If an unoxidized polymer can be prepared it should be possible to distinguish between (17) and (18) spectroscopically and, if the hypothesis indicated in Figure 3.1. is proved correct in future work, the relative proportions of (17) and (18) formed in the first step may provide useful information about polymer oxidation processes.

(a) Singlet mechanism:



(b) Triplet mechanism:

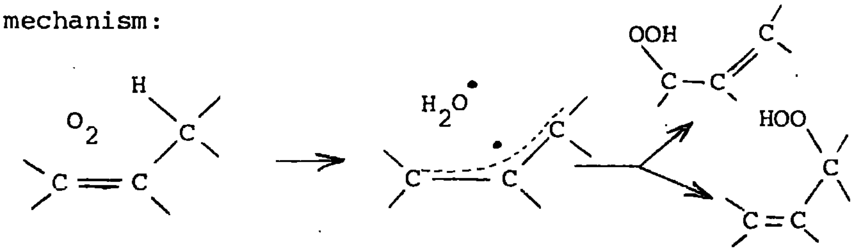
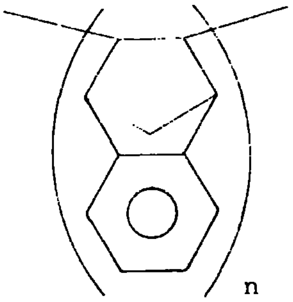


Figure 3.2. Oxidation at allylic C-H

Although the data analysed so far are consistent with the initial formation of ring-opened polybenzonorbornadiene they do not prove that the polymer has the proposed structure. Polymerization of benzonorbornadiene could give rise to a vinyl polymer (19) as well as the expected polymer (16), a polymer with structure



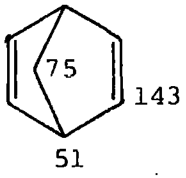
(19)

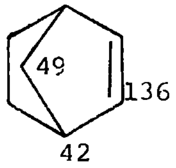
(19) would not be expected to be so easily oxidized as the actual product. However convincing structure proof was provided by nuclear magnetic resonance spectroscopy.

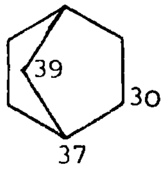
In the $^1$H n.m.r. spectra of structure (16) four aromatic, two vinylic, two methine and two methylene signals would be expected; whereas structure (19) would be expected to give rise to four aromatic, four methine and two methylene signals. The $^1$H n.m.r. spectrum of the freshly prepared polymer showed signals which were only consistent with the structure (16), with broad resonances at 7.2 (aromatic), 5.6 (vinylic), 3.9 (methine) and 1.5 p.p.m. (methylene) in the relative intensity ratio 2:1:1:1. The spectrum was recorded at 90 MHz and the chemical shifts are referred to external tetramethylsilane. The $^1$H n.m.r. spectrum of benzonorbornadiene (15) shows two multiplets in aromatic region at 7.22 and 6.9 p.p.m., the vinylic protons occur at 6.77 p.p.m. with the methine and methylene signals at 3.86 and 2.25 p.p.m. respectively.

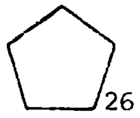
The $^{13}$C n.m.r. of the monomer (15) and the fresh prepared polymer were recorded as solutions in $CDCl_3$ at 22.635 MHz using tetramethylsilane as internal reference. The prediction of shift in $^{13}$C n.m.r. spectroscopy is complicated and small changes in structure can result in very large changes in shift. Before discussing the spectra of (15) and (16) it is necessary to consider the observed shifts for related systems:[133]

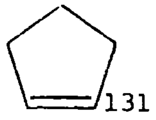
## $^{13}$C n.m.r. chemical shifts in five membered ring systems



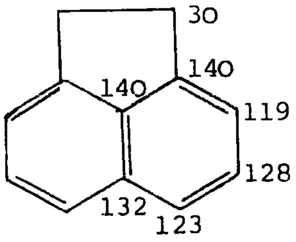


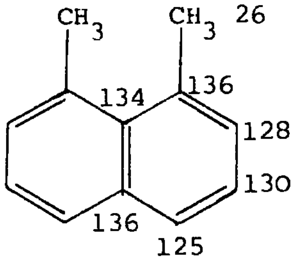


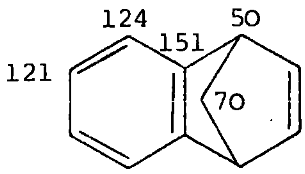




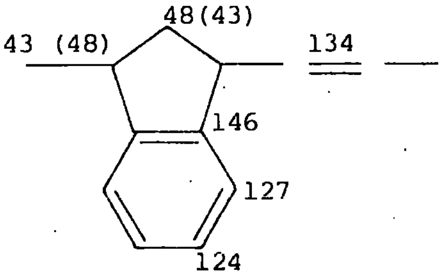
The quoted chemical shifts are in p.p.m. downfield from tetramethylsilane, it can be seen that for all types of carbon decreasing ring strain results in an upfield shift. A similar effect is seen in the two structures shown below, thus all the signals for the carbons in the five membered ring are shifted to higher field in the unstrained analogue 1,8-dimethylnaphthalene. In this last example it is also interesting to note that the aromatic carbons not initially part of the five membered ring experience a downfield shift in the less strained system. In the spectrum of benzonorbornadiene six signals are seen; the highfield







signals at 50 and 70 p.p.m. are assigned to the methine and methylene carbons by analogy with the data given above; the bridging aromatic carbons give a low intensity signal as expected by analogy with other aromatic systems[133] and are assigned to the signal at 151; the two other aromatic signals at 121 and 124 are similarly assigned leaving the vinylic signal at 143. The spectrum of the freshly prepared polymer also showed six signals at 43, 48, 124, 127, 134 and 146 p.p.m. The first point to note is that this spectrum is only consistent with structure (16) because there are two aliphatic and four aromatic and vinylic signals, structure (19) would require three aliphatic and three aromatic signals. By analogy with the data given above an assignment of the observed signals can be made as shown below, all the observed shift changes are consistent with the trends discussed above, although the assignment is not totally unambiguous particularly for the aliphatic carbons. The vinylic carbons signal appeared to be partially resolved into a doublet, most ring-opening polymerizations with $WCl_6/Ph_4Sn$ give an approximately equal amount of cis and trans double bonds along the polymer chain,[94] the partial resolution of the vinylic carbon signal suggest that this also occurs in the ring-opening polymerization of benzonorbornadiene.



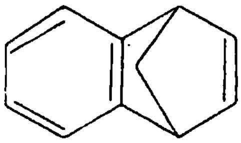
The G.P.C. analyses of both freshly prepared polymer and the highly oxidized sample were carried out at the Rubber and Plastics Research Association (Shawbury).

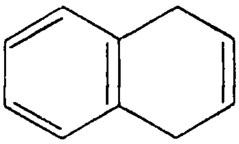
Some difficulty was encountered because, although both samples were totally soluble in chloroform the available instruments used only tetrahydrofuran and the freshly prepared polymer did not dissolve completely in this solvent. However, from the traces obtained it is clear that the freshly prepared sample is a genuine high polymer with a very low proportion of low molecular weight material; the maximum of the observed G.P.C. peak occurred at a polystyrene equivalent of $\bar{M}_n \sim 20,000$ It seems reasonable to assume that the THF insoluble fraction is of high molecular weight. On the other hand, the highly oxidized sample was completely soluble in THF and its G.P.C. peak had a maximum at a polystyrene equivalent of $\bar{M}_n \sim 13,000$; the peak was very broad with tails into both the low molecular weight (3-500) and high molecular weight (100,000) regions. This last result is consistent with extensive chain fragmentation during the oxidized polymer.

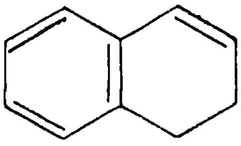
## 3.5. Conclusions and Suggestions for Further Work

The evidence represented above shows that benzonorbornadiene is polymerized by ring-opening in the presence of a metathesis catalyst prepared from tungsten hexachloride and tetraphenyltin. A further confirmation of this conclusion could be obtained by preparing the vinyl polymer of benzonorbornadiene, possibly by a radical or cationically initiated route, and comparing it with the ring opened product obtained in this work.

Since it is clear that norbornadiene undergoes ring-opening polymerization whereas it is unclear whether indene does or does not undergo ring opening (even in part) it might be of interest to examine some related structures so that, for example, reactivity in the series shown below could be compared.







It is clear that the presence of an aromatic ring does not inhibit ring-opening polymerization by a typical metathesis catalyst, however, if indene polymerization is to be re-examined a catalyst active in basic media will probably be required, or at least a neutral material with low Lewis Acid activity, both options seem unlikely to be realized.

# EXPERIMENTAL PART

## 3.6. Reagents

Dicyclopentadiene was purchased from Koch-Light Laboratories Ltd., amylnitrite was purchased from Hopkin & Williams Ltd., dry monoglyme was kindly provided by Mr. B. Hall of this department.

### 3.6a. Cyclopentadiene

Cyclopentadiene was prepared by thermal cracking of dicyclopentadiene. A one-necked round-bottomed flask (1 l.) was quarter-filled with dicyclopentadiene, and an unlagged vigreux column (50 cm) was connected via a still-head carrying a thermometer, and a water-condenser to a receiver flask. The distillation flask was heated strongly using an electric heater. The dicyclopentadiene boiled vigorously and liquid gradually ascended the column, the product (cyclopentadiene) distilled in the range 40° - 45° and was used without further purification. When necessary it was stored in the deep freeze (-20°) and under these conditions it could be kept for several days.

### 3.6b. The synthesis of benzonorbornadiene

Dry monoglyme (400 ml) was placed in a 3-necked round-bottomed flask (2 l.), the middle neck was fitted with a mechanical stirrer, the second neck was fitted with a dropping funnel containing a solution of amyl nitrite (153.4 ml, 133.45 g, 1.14 moles) in monoglyme (200 ml) and the third neck was attached to a water-condenser which was fitted with a dropping funnel containing anthranilic acid (137 g, 1 mole), cyclopentadiene (164.4 g, 2.5 moles) and dry monoglyme (300 ml). The apparatus was purged with dry nitrogen. The solvent in the flask was heated from a water bath until it refluxed gently, it was stirred continuously throughout the experiment. The components in the two dropping funnels were added to the refluxing solvent in the reaction flask at the same rate. There was considerable evolution of gases and the mixture was kept at reflux throughout the addition which took three hours. After complete addition of reagents the mixture was refluxed gently for one hour, at this stage evolution of gases had stopped and the mixture was oily and dark red to black in colour. The product was vacuum distilled to yield four fractions which were examined by infrared spectroscopy and analytical gas chromatography. The first two fractions (b.r. $27^{o}$ - $79^{o}$/15 mm Hg) consisted of solvent, cyclopentadiene and a trace of benzonorbornadiene, and were discarded. The last two fractions (b.r. $80^{o}$ - $88^{o}$/15 mm Hg) had identical infrared spectra and consisted of benzonorbornadiene together with minor impurities. The last two fractions were combined and fractionated using a Fischer spaltrohr system concentric tube fractionating column (HMS 500, 75 theoretical plates) to give: (i) solvents (6.5 ml, b.r. $48^{o}$ - $82^{o}$/20 mm Hg), identified by i.r. spectroscopy; (ii) a mixture (7.5 ml, b.r. $86^{o}$ - $95^{o}$/23 mm Hg) which on the bases of g.l.c. mass spectroscopy and infrared spectroscopy (Appendix A, number XXIV) appeared to be predominantly amyl alcohol together with traces of solvent, an aliphatic ketone and some benzonorbornadiene; (iii) benzonorbornadiene (15) (35 ml, 42 g, 30% yield, b.r. $96^{o}$ - $98^{o}$/23 mm Hg, found C, 92.95, H, 6.92%, $M_{ms}$(142), calculated for $C_{11}H_{10}$, C, 92.91, H, 7.09%, M, 142) with correct[129] infrared spectrum (Appendix A, number XXIII). This product was shown to be a single component by gas chromatography and G.L.C. mass spectroscopy showed that the peak was homogeneous since the mass spectrum of the leading edge of the peak was identical with that of the trailing edge.

## 3.7. The Ring-opening Polymerization of Benzonorbornadiene Using Tungsten Hexachloride and Tetraphenyltin as the Catalyst System

A reaction vessel containing a magnetic follower was purged with dry nitrogen and charged with tungsten hexachloride (0.26 g) which was dissolved in dried toluene (125 ml), distilled directly into the reaction vessel. Tetraphenyltin (0.52 g) was added to the mixture, a dry nitrogen atmosphere being maintained throughout the experiment. The mixture was stirred for ten minutes, the colour changed from blue-black to dark brown. The monomer (2 ml, 2.4 g) was injected into the active catalyst solution using an air-tight syringe, an immediate colour change to dark blue was observed. The reaction was stirred continually and after 30 minutes the viscosity started to increase. At this stage the reaction was terminated by the addition of 5 ml. of methanol. The reaction product was a blue sticky material which was dissolved directly in 400 ml chloroform; the resulting solution was partially evaporated to give 20 ml of viscous solution which was added dropwise to a five-fold excess of methanol. The yellow precipitated material was recovered by filtration, dissolved in chloroform and reprecipitated in excess methanol four times. The material was dried for 48 hours under vacuum to give a pale yellow solid (1.9 g, 79% yield).

# APPENDIX A

## Infrared Spectra

All spectra were recorded using KBr cells, plates or discs or casting thin films and were run under conditions designated by:-

A - KBr disc

B - thin liquid film

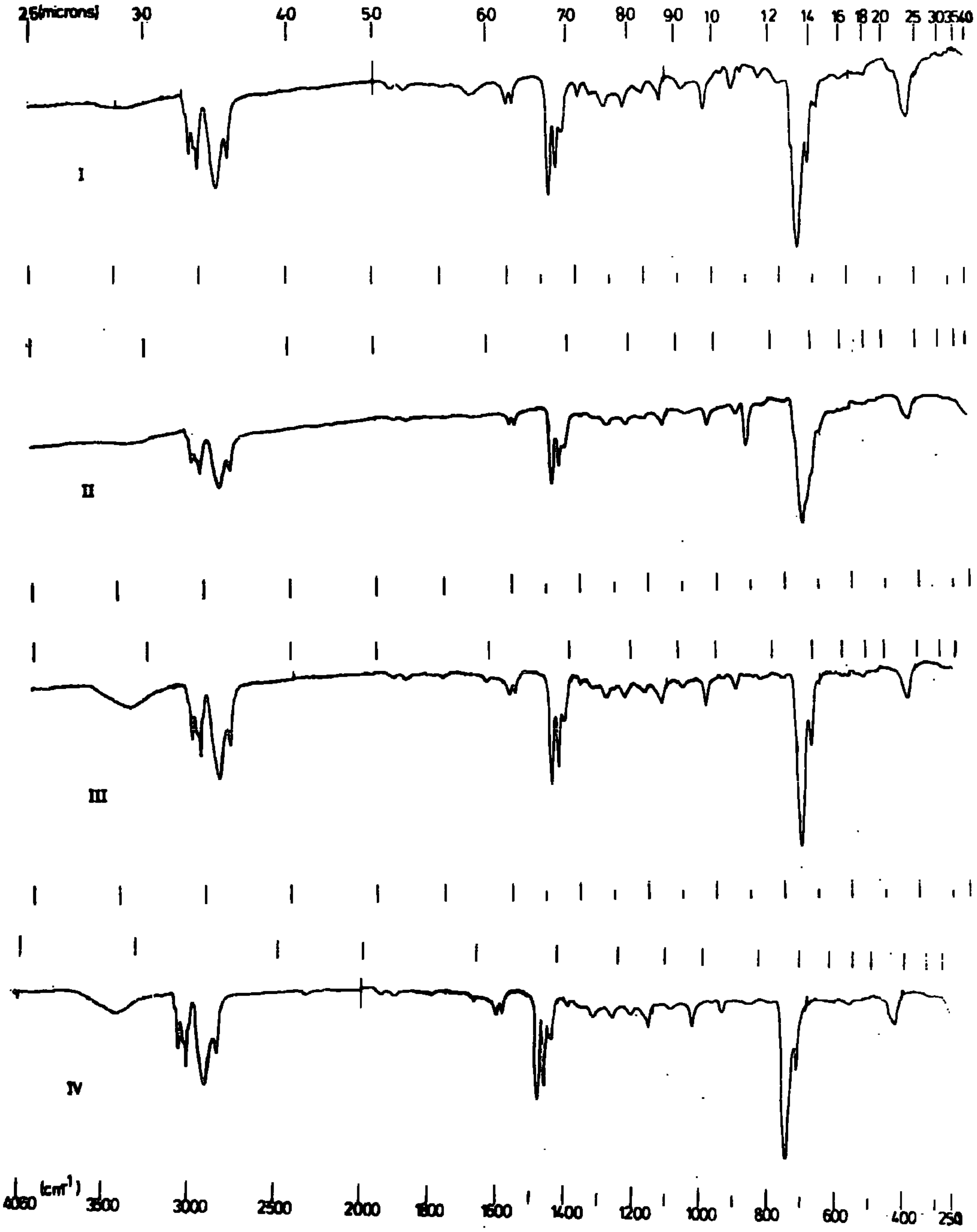
C - thin polymer film

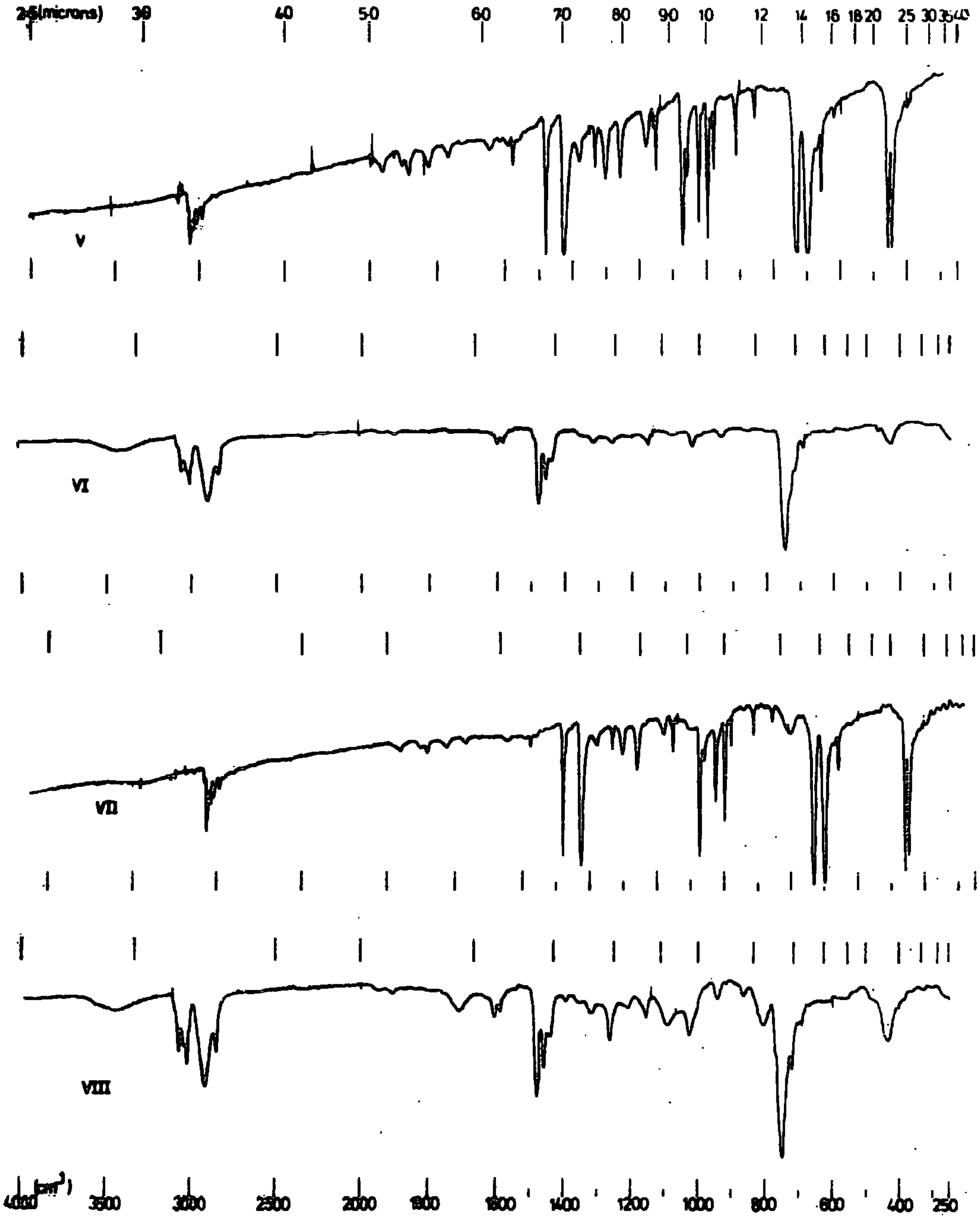
D - casting thin film over mercury

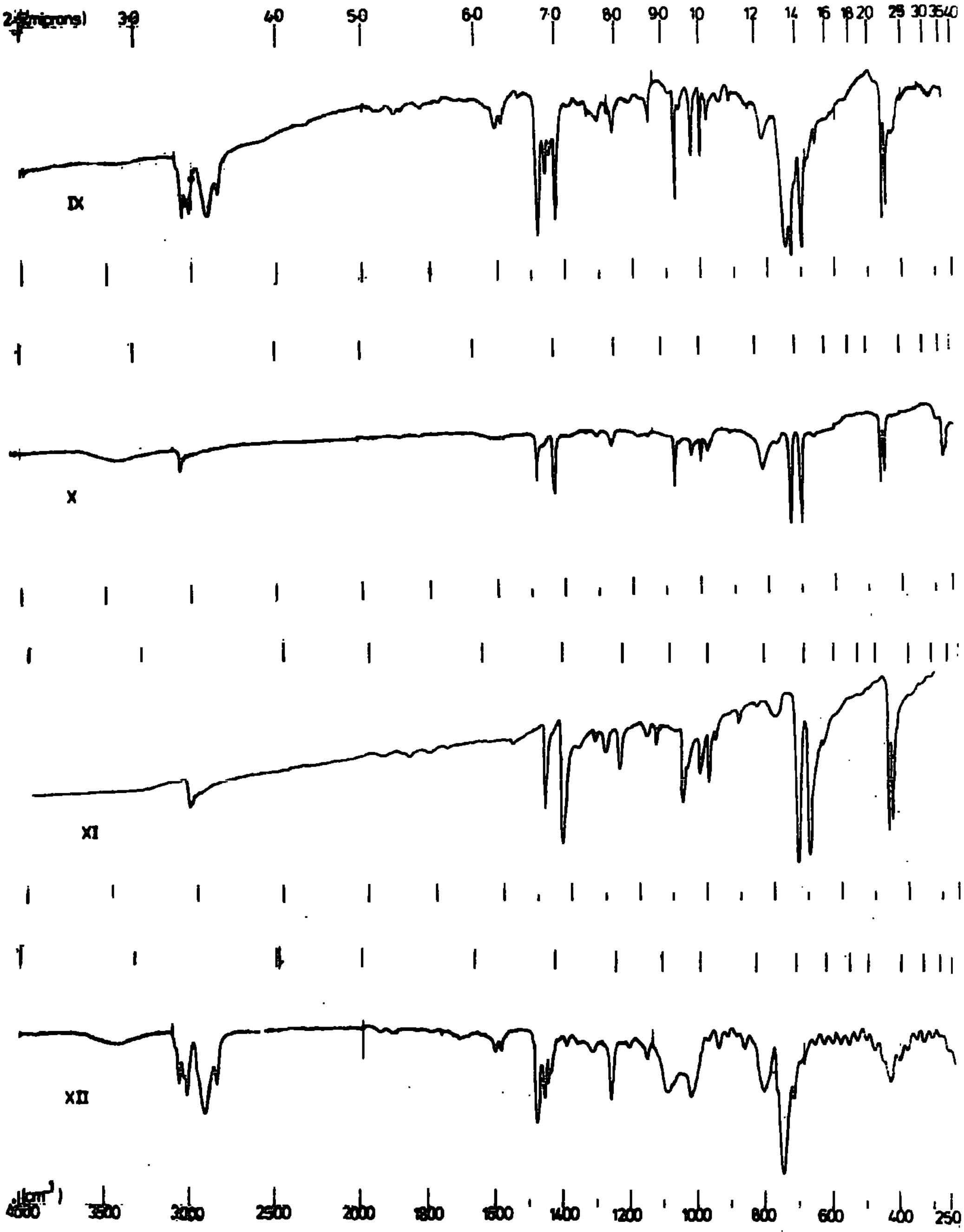
Infrared spectra are given below:-

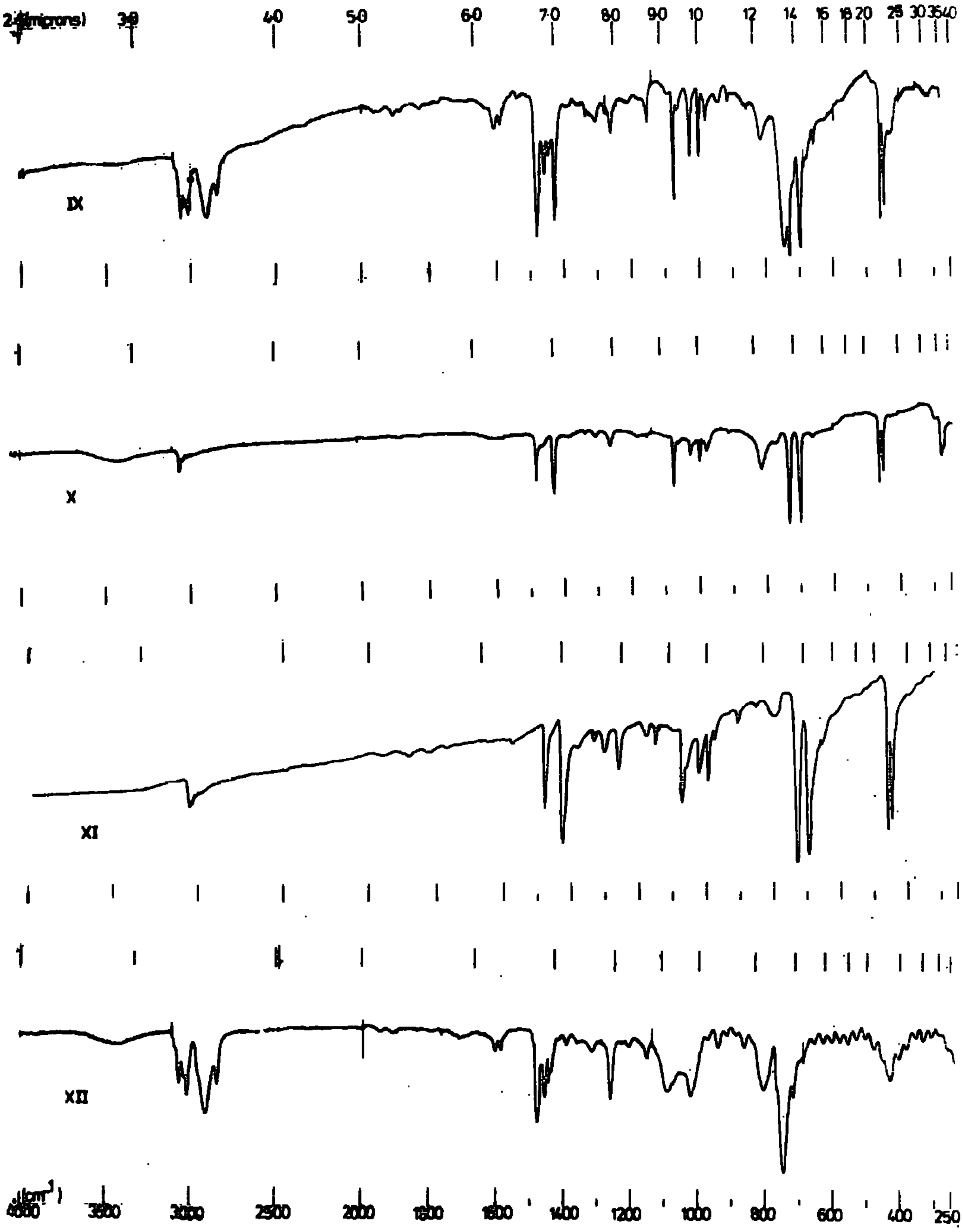
| Spectrum No. | Nature of sample |
|---|---|
| I | Polyindene using the catalyst system $WCl_6/Ph_4Sn$ |
| II | Polyindene (BW-A) see page 37 |
| III | Polyindene initiated by conc. $H_2SO_4$, p.47 |
| IV | Polyindene from heating, p.47 |
| V | Tetraphenyltin as supplied |
| VI | Polyindene using the catalyst system $WCl_6/Ph_4Sn$, addition of the catalyst three times, p.47 |
| VII | Recovered material ($Ph_4Sn$) from the reaction with $WCl_6/Ph_4Sn$ and triethylamine, p.47 |
| VIII | Cationic polyindene using $WCl_6/Ph_4Sn$ and addition of triethylamine after 30 min., p.47 |
| IX | Recovered material by using pyridine as base (cationic polyindene and $Ph_4Sn$), p.47 |
| X | Recovered material ($Ph_4Sn$) from the reaction of indene + $WCl_6/Ph_4Sn$ and 1,8-bis-(dimethylamino)-naphthalene as base, see p.47 |
| XI | Recovered material ($Ph_4Sn$) from the reaction of indene using $WCl_6/Ph_4Sn$ and 1,8-bis-(dimethylamino)-naphthalene as base with refluxing of the catalyst solution, p.47 |
| XII | Polyindene using the catalyst $WCl_6/Ph_4Sn$ and addition of the proton sponge after 30 minutes, p.47 |
| XIII | Norbornene as supplied, see p.48 |

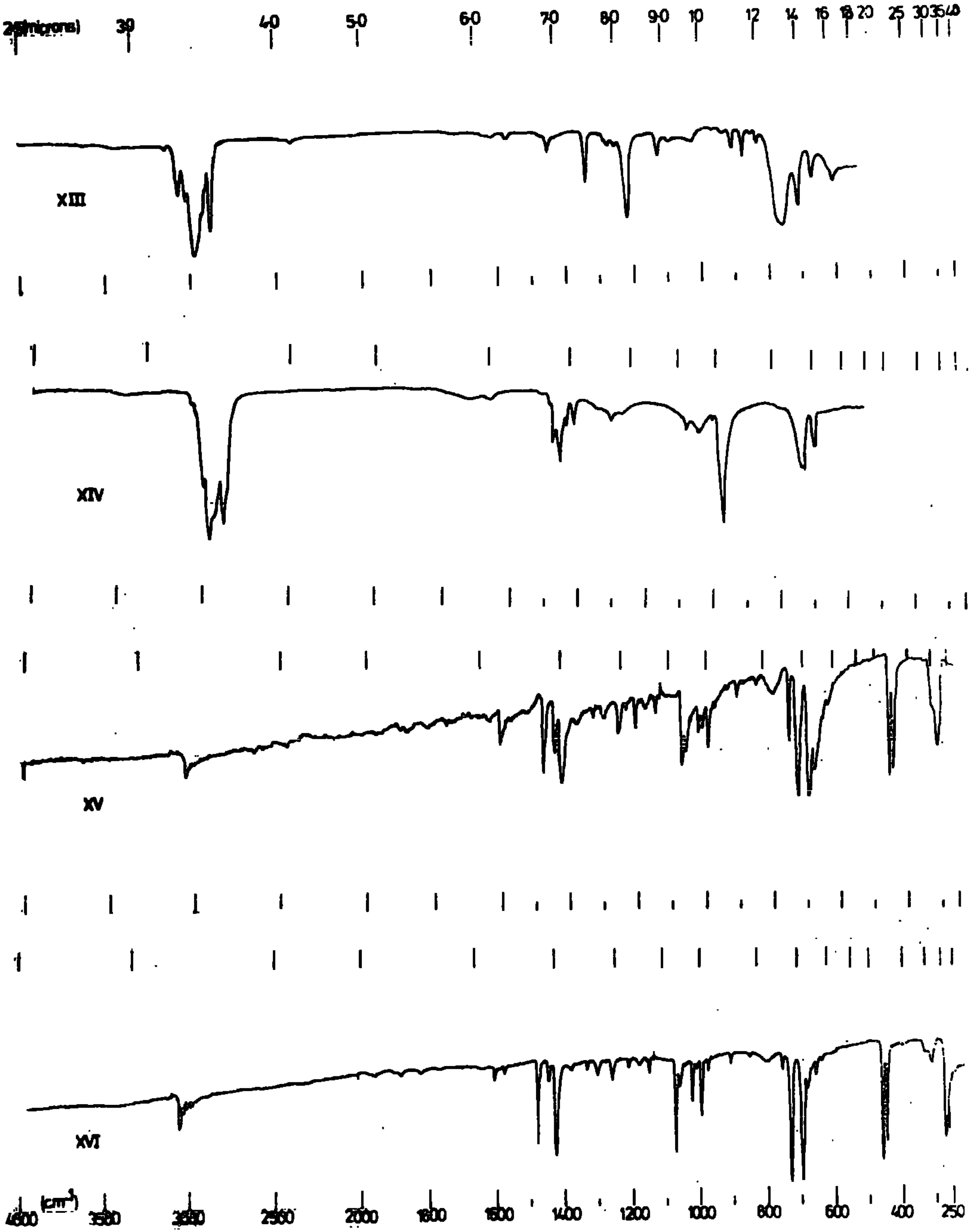
| Spectrum No. | Nature of sample |
|---|---|
| XIV | Polynorbornene from the reaction with $WCl_6/Ph_4Sn$ |
| XV, XVI, XVII | Recovered material ($Ph_4Sn$) from the reaction of norbornene with $WCl_6/Ph_4Sn$ and pyridine as base, see p.48 |
| XVIII | Recovered material ($Ph_4Sn$) from the reaction of norbornene with $WCl_6/Ph_4Sn$ and 1,8-bis-(dimethylamino)-naphthalene) as base |
| XIX | Recovered material ($Ph_4Sn$) from the reaction of norbornene with $WCl_6/Ph_4Sn$ and 1,8-bis-(dimethylamino)-naphthalene as base with refluxing the catalyst solution 10 min., see p.48 |
| XX | Recovered material ($Ph_4Sn$) from the reaction of norbornene with $WCl_6/Ph_4Sn$ and addition of 1,8-bis-(dimethylamino)-naphthalene before the monomer with refluxing the catalyst solution 5 min., see p.48. |
| XXI | Polyacenaphthylene initiated by conc. $H_2SO_4$, see p.52 |
| XXII | Polyacenaphthylene by $WCl_6/Ph_4Sn$, see p.52 |
| XXIII | Benzonorbornadiene b.r. $96^{\circ} - 98^{\circ}/23$ mm Hg |
| XXIV | Mixture from amyl alcohol, traces of solvent, an aliphatic ketone and some benzonorbornadiene distilled between b.r. $86^{\circ} - 95^{\circ}/23$ mm Hg |
| XXV | Polybenzonorbornadiene by the catalyst system $WCl_6/Ph_4Sn$ |
| XXVI | Oxidized polybenzonorbornadiene |

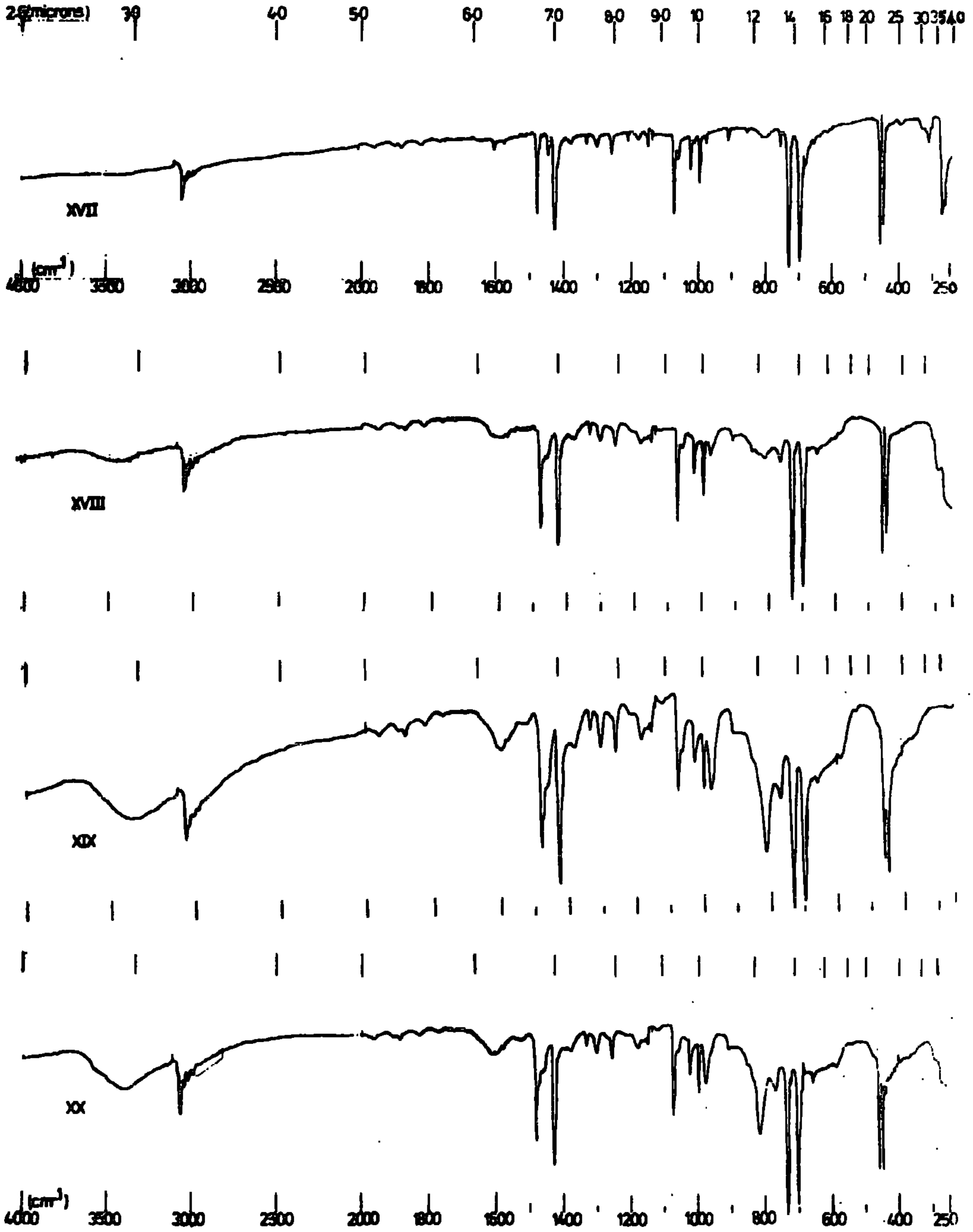

2.5 (microns)
3.0
4.0
5.0
6.0
7.0
8.0
9.0
10
12
14
16
18
20
25
30
35
40
I
II
III
IV
4000
(cm$^{-1}$)
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
400
250

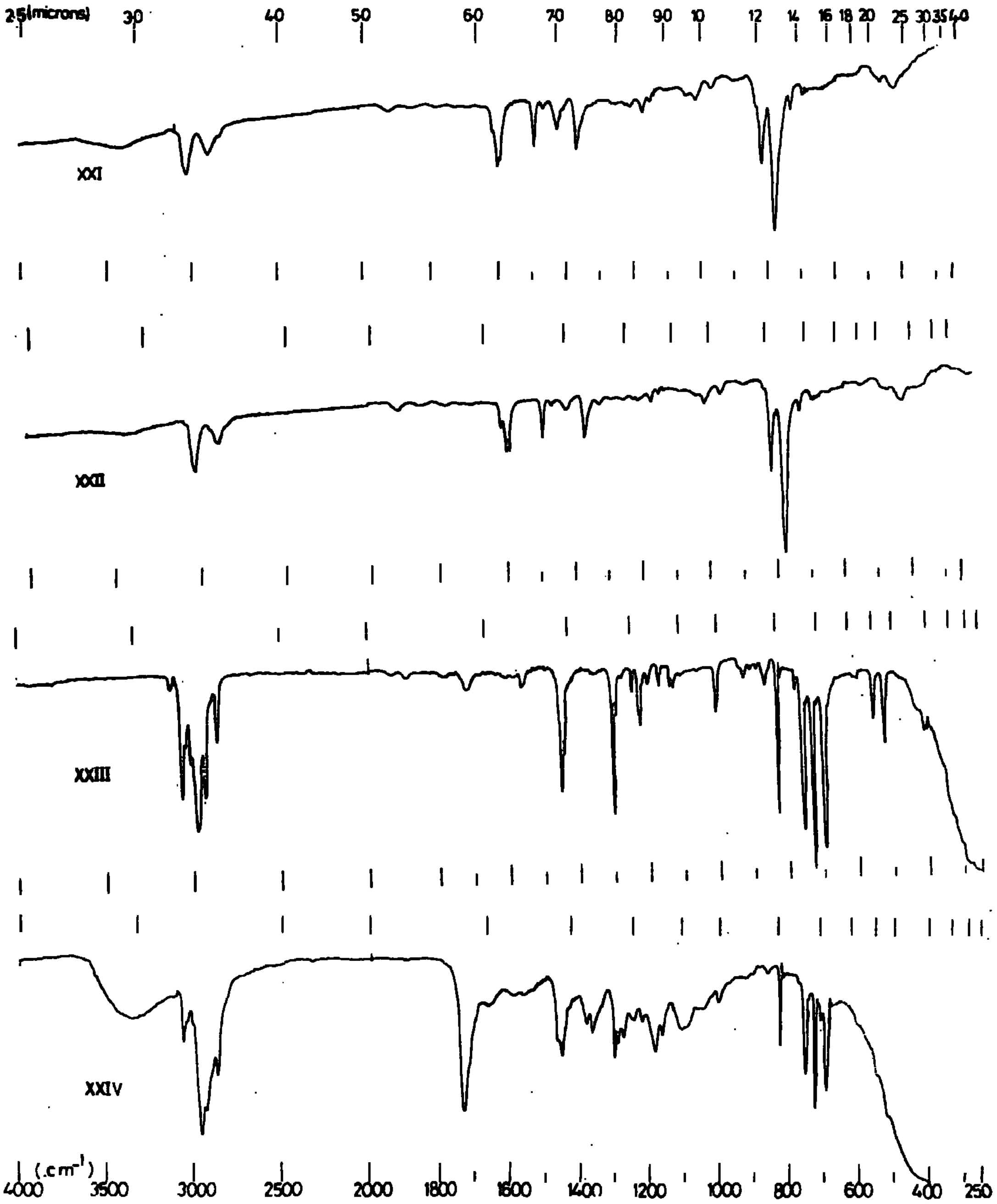

2·5(microns)
3·0
4·0
5·0
6·0
7·0
8·0
9·0
10
12
14
16
18
20
25
30
35
40
V
VI
VII
VIII
4000
(cm⁻¹)
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
400
250

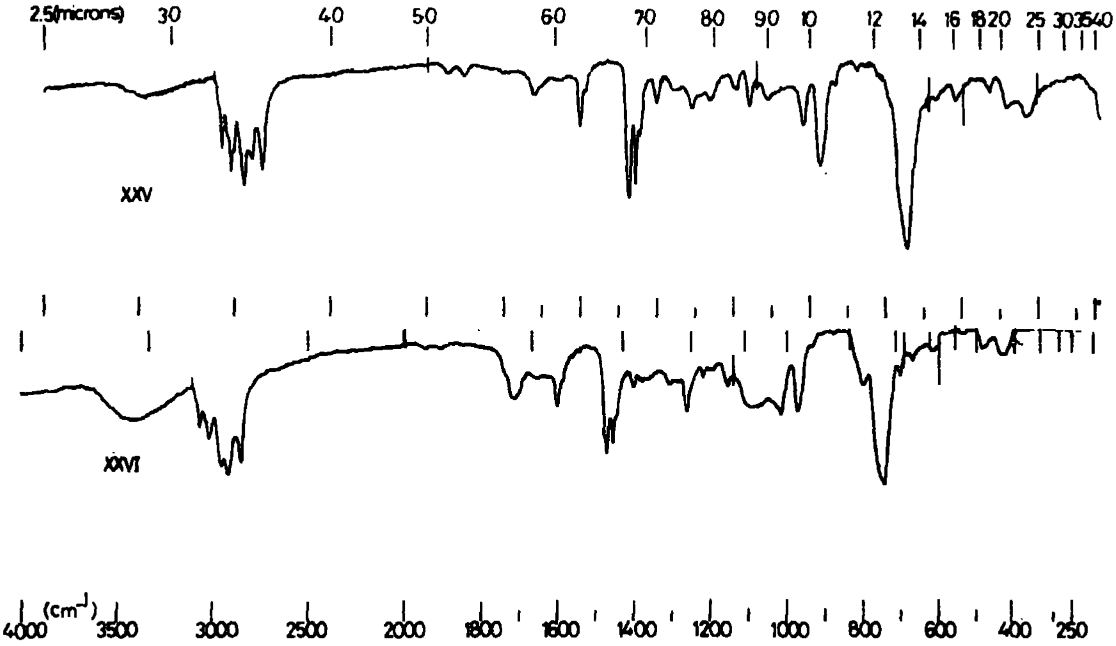

2.5(microns)
3.0
4.0
5.0
6.0
7.0
8.0
9.0
10
12
14
16
18
20
25
30
35
40
IX
X
XI
XII
ν(cm⁻¹)
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
400
250


2·5 (microns) 3·0 4·0 5·0 6·0 7·0 8·0 9·0 10 12 14 16 18 20 25 30 35 40
IX
X
XI
XII
(cm⁻¹) 4000 3500 3000 2500 2000 1800 1600 1400 1200 1000 800 600 400 250


2.5 (microns)
3.0
4.0
5.0
6.0
7.0
8.0
9.0
10
12
14
16
18
20
25
30
35
40
XIII
XIV
XV
XVI
(cm⁻¹)
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
400
250


2.5 (microns)
3.0
4.0
5.0
6.0
7.0
8.0
9.0
10
12
14
16
18
20
25
30
35
40
XVII
(cm⁻¹)
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
400
250
XVIII
XIX
XX


2.5(microns)
3.0
4.0
5.0
6.0
7.0
8.0
9.0
10
12
14
16
18
20
25
30
35
40
XXI
XXII
XXIII
XXIV
(cm⁻¹)
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
400
250


2.5(microns)
30
40
50
60
70
80
90
10
12
14
16
18
20
25
30
35
40
XXV
XXVI
(cm⁻¹)
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
400
250

## REFERENCES

1. R.L. Banks and G.C. Bailey, Ind. Eng. Chem. Prod. Res. Develop., 3, 170 (1964).

2. K.W. Scott, N. Calderon, E.A. Ofstead, W.A. Judy and J.P. Ward, J. Amer. Chem. Soc., 90, 4133 (1968); Adv. Chem. Ser., 91, 399 (1968); A.C.S. Meeting Abs., 155, L54 (1968).

3. E. Wasserman, D.A. Ben-Efram and R.J. Wolovsky, J. Amer. Chem. Soc., 90, 3286 (1968).

4. A.W. Anderson and N.G. Merckling, U.S. Patent 2,721,189 (1955).

5. W.L. Truett, D.R. Johnson, I.M. Robinson and B.A. Montague, J. Amer. Chem. Soc., 82, 2337 (1960).

6. H.C. Eleuterio, U.S. Patent 3,074,918 (1963).

7. G. Dall'Asta, G. Mazzanti, G. Natta and G. Mortoni, Makromol. Chem., 69, 163 (1963).

8. G. Dall'Asta, G. Mazzanti and G. Natta, Angew. Chem., 76, 765 (1964).

9. N. Calderon, E.A. Ofstead and W.A. Judy, J. Polymer Sci., Al, 5, 2209 (1967).

10. N. Calderon, H. Yuchen and K.W. Scott, Tetrahedron Lett., 3327 (1967).

11. G. Dall'Asta, Rubber Chem. Technol., 47, (3), 511 (1974).

12. J.J. Rooney and A. Stewart, Catal., 1, 277 (1977).

13. N. Calderon, J. Makromol. Sci., C, 7, 105 (1972).

14. N. Calderon, Acc. Chem. Research, 5, 127 (1972).

15. G.C. Bailey, Catal. Rev., 3, 37 (1969).

16. M.L. Khidekel, A.D. Shebaldova and I.V. Kalechite, Russ. Chem. Rev., 40, (8), 669 (1971).

17. R.L. Banks, Topics in Current Chem., 25, 39 (1972).

18. W.B. Hughes, Organometal. Chem. Synth., 1, 341 (1972).

19. J.C. Mol and J.A. Moulijn, Adv. Catal., 24, 131 (1975).

20. R.J. Laines and G.L. Leigh, Chem. Rev., 4, 155 (1975).

21. L. Hocks, Bull. Soc. Chim. France, 1894 (1975).

22. R. Streck, Chem. Ztg., 99, 397 (1975).

23. W.B. Hughes, Chem. Tech., 486 (1975).

24. E.A. Zuech, W.B. Hughes, D.H. Kubicek and E.T. Kittleman, J. Amer. Chem. Soc., 92, 528 (1970).

25. W.B. Hughes, Ann. N.Y. Acad. Sci., 295, 271 (1977).

26. E.A. Zuech, U.S. Patent, 3,558,518 (1971).

27. E.A. Zuech, Chem. Commun., 1182 (1968).

28. G. Doyle, Ger. Pat. 2,047,270 (1971).

29. L. Bencze and L. Marko, J. Organometal. Chem., 28, 271 (1971).

30. H. Knoche, Ger. Pat. 2,024,835 (1970).

31. W.R. Kroll and G. Doyle, Chem. Commun., 839 (1971).

32. L. Michajlov and H.J. Harwood, J. Amer. Chem. Soc., Div. Polym. Chem. Preprints, 11, 1197 (1970).

33. W. Ast and K. Hummel, Kautschuk Gummi, 24, 220 (1971).

34. E. Verkuijlen and C. Boelhouwer, Fette. Seifen Anstrichmittel, 11, 444 (1976).

35. R. Nakamura, S. Matsumoto and E. Ecligoya, Chem. Letts., 1019 (1976).

36. F. Hass, K. Nützel, G. Pampus and D. Theisen, Rubber Chem. Tech., 43, 1116 (1970).

37. G. Dall'Asta and P. Scaglione, Rubber Chem. Tech., 42, 1235 (1969).

38. D. Sianesi and G. Caporiccio, Macromol. Chem., 60, 213 (1963).

39. G. Dall'Asta and G. Motroni, Eur. Polym. J., 7, 707 (1971).

40. W.B. Hughes, E.A. Zuech, E.T. Kittleman and D.H. Kubicek, Macromol. Preprints, 11, 1063 (1971).

41. R. Wolovsky, J. Amer. Chem. Soc., 92, 2132 (1970).

42. D.A. Ben-Efraim, C. Batich and E. Wasserman, J. Amer. Chem. Soc., 92, 2133 (1970).

43. N. Calderon, U.S. Patents, 3,439,056 and 3,439,057 (1969).

44. L.G. Wideman, J. Org. Chem., 33, 4541 (1968).

45. G. Natta, G. Dall'Asta and L. Parri, Makromol. Chem., 81, 253 (1965).

46. G. Natta, G. Dall'Asta, I.W. Bassi and G. Carella, Makromol. Chem., 91, 87 (1966).

47. G. Dall'Asta and R. Manetti, Eur. Polym. J., 4, 145 (1968).

48. W. Ast, G. Rheinwald and R. Kerber, Makromol. Chem., 177, 1341 (1976).

49. E.A. Zuech, W.B. Hughes, D.H. Kubicek and E.T. Kitteman, J. Amer. Chem. Soc., 92, 528 (1970).

50. D.M. Singleton, U.S. Pat. 3,530,196 (1970).

51. G.C. Bailey, R.L. Banks and F. Penella, Chem. Commun., 1548 (1968).

52. C. Boelhouwer, J.A. Moulijn and H.J. Reitsma, J. Catal., 25, 434 (1972).

53. M. Blanchard and A. Mortreux, Bull. Soc. Chim. France, 1641 (1972).

54. A. Montreux and M. Blanchard, J.C.S. Chem. Comm., 786 (1974); J. Mol. Catalysis, 1, 101 (1976).

55. A.V. Mushegyan, V. Kh. Ksipterides, R. Kh. Dzhylakyan and G.A. Chukhadzhyan, Armyan. Khim. Zhur., 28, 672 (1975).

56. G.M. Whitesides and W.J. Ehman, J. Amer. Chem. Soc., 91, 3800 (1969).

57. H. Höcker and Musch, Makromol. Chem., 176, 3177 (1975).

58. T. Masuda, K. Hasegawa and T. Higashimura, Makromolecules, 7, 728 (1974).

59. T. Masuda, N. Sasaki and T. Higashimura, Makromolecules, 8, 717 (1975).

60. N. Calderon and H.Y. Chin, U.S. Pat. 3,535,401 (1970).

61. J.L. Wang and H.R. Menapace, J. Org. Chem., 33, 3794 (1968).

62. E.S. Davie, D.A. When and C. Kemball, Chem. Commun., 1430 (1969).

63. J.A. Moulijn and C. Boelhouwer, Chem. Commun., 1170 (1971).

64. R. Nakamura and E.E. Chigoya, Chem. Letters, 273 (1972).

65. A. Uchida, K. Kobayashi and S. Matsuda, Ind. Eng. Chem. Prod. Res. Develop., 11, (4), 384 (1972).

66. T. Takagi, T. Hamaguchi, K. Fukuzmi and M. Aoyama, Chem. Commun., 838 (1972).

67. J. Chatt, R.J. Haines and G.J. Leigh, Chem. Commun., 1202 (1972).

68. P.B. Van Dam, M.C. Mittelmeijer and C. Boelhouwer, Chem. Commun., 1221 (1972).

69. P.B. Van Dam, M.C. Mittelmeijer and C. Boelhouwer, Fette. Seifen. Anstrichm, 76, (6), 264 (1974).

70. R. Nakamura, S. Fukuhara, S. Matsumoto and K. Komatsu, Chem. Letters, 253 (1976).

71. R.L. Banks, U.S. Pat. 3,261,879 (1966).

72. British Petroleum Co. Ltd., Dutch Pat. 6511659 (1966); K.V. Williams and L. Turner, B.P. 1116243 (1968).

73. L.F. Heckelsberg, R.L. Banks and G.C. Bailey, Ind. and Eng. Chem. (Product Res. and Development), 7, 29 (1968).

74. L.F. Heckelsberg, R.L. Banks and G.C. Bailey, Ind. and Eng. Chem., (Product Res. and Development), 8, 259 (1969).

75. L.F. Heckelsberg, U.S. Patent, 3,340,322 (1967).

76. T. Okuhora and K.I. Tanaka, J. Catalysis, 42, 474 (1976).

77. W.H. Davenport, V. Kollonitsch and C.H. Kline, Ind. Eng. Chem., 60, 10 (1968).

78. Goodyear Tire and Rubber Co., South African Patent 671,913.

79. E.L. Muetterties and M.A. Busel, J. Chem. Soc. Chem. Comm., 754 (1974).

80. G.M. Graff and E. McWelis, J. Catal., 38, 482 (1975).

81. N. Calderon "Eighth Leeds-Sheffield Symp. on Coord. Chem. and Catalysis, April 1976".

82. Y. Chauvin, D. Commereuc and D. Cruypelinck, Makromol. Chem., 177, 2637 (1976).

83. P. Casey and T.J. Burkhardt, J. Amer. Chem. Soc., 96, 7808 (1974).

84. J. McGinnis, T.J. Katz and S. Hurwitz, J. Amer. Chem. Soc., 98, 605 (1976).

85. S.J. Lee, J. McGinnis and T.J. Katz, J. Amer. Chem. Soc., 98, 7818 (1976).

86. C.P.C. Bradshaw, E.J. Howman and L. Turner, J. Catalysis, 7, 269 (1967).

87. J.C. Mol, J.A. Moglijn and C. Boelhouwer, J. Chem. Soc. Chem. Comm., 633 (1968).

88. R.L. Banks and G.C. Bailey, J. Catalysis, 14, 276 (1969).

89. F.L. Moody, M.J. Lewis and G.B. Wills, J. Catalysis, 14, 389 (1969).

90. A. Clark and C. Cook, J. Catalysis, 15, 420 (1969).

91. K.W. Scott, N. Calderon, E.A. Ofstead, W.A. Judy and J.P. Ward, Rubber Chem. Technol., 44, 1341 (1971).

92. G. Dall'Asta, Makromol. Chem., 154, 1 (1972).

93. P.G. Gassman and T.H. Johnson, J. Amer. Chem. Soc., 98, 861 (1976), and references therein.

94. B. Wilson, Ph.D. Thesis, Durham University (1978).

95. G.S. Lewandos and R. Pettit, J. Amer. Chem. Soc., 93, 7087 (1971); G.S. Lewandos and R. Pettit, J. Amer. Chem. Soc., 93, 789 (1971).

96. R.H. Grubbs and T.K. Brunck, J. Amer. Chem. Soc., 94, 2538 (1972).

97. J.L. Herisson and Y. Chauvin, Makromol. Chem., 141, 161 (1970).

98. D.J. Cardin, M.J. Doyle and M.F. Lappert, J.C.S. Chem. Comm., 927 (1972); D.J. Cardin, M.J. Doyle and M.F. Lappert, Chem. Rev., 2, 99 (1973).

99. K.J. Ivin, J.J. Rooney, D. Stewart and M.L.H. Green, J.C.S. Chem. Comm., 604 (1978).

100. T. Oshika and H. Tabuchi, Bull. Chem. Soc. Japan, 41, 211 (1968).

101. A. Eilert, E.A. Ofstead and N. Calderon, Makromol. Chem., 154, 21 (1972).

102. P. Gunther, F. Laas, G. Marwede, K. Nutzel, W. Oberkirch, G. Pampus, N. Schön and J. Witte, Angew. Makromol. Chem., 14, 87 (1970).

103. H. Lammens, G. Sartori, J. Siffert and N. Sprecher, Polymer Letters, 9, 341 (1971).

104. G. Dall'Asta and G. Motvoni, Chim. Ind. (Milan), 972 (1968).

105. Kramer and Spilker, Ber., 23, 3276 (1890).

106. G.S. Whitby and M. Katz, J. Amer. Chem. Soc., 50, 1160 (1928).

107. H. Cheradane, P. Sigwalt, C.R. Acad. Sci. Fr., 260, 159 (1965).

108. N.A. Hug, H. Cheradame, P. Sigwalt, Eur. Polym. J., 9, 385 (1973).

109. F. Subira, J.P. Varion, A. Polton, P. Sigwalt, Bull. Soc. Chim. Fr., 12, 2903 (1974).

110. E. Marechal, J. Basselier, P. Sigwalt, Bull. Soc. Chim. Fr., 1740 (1964).

111. A. Mizote, T. Tanaka, T. Higashimura and K. Kobunshi,Ragaku, 23, 78 (1966); Chem. Absts., 64, 17722c (1966).

112. H. Cheradame and P. Sigwalt, Compt. Rend., 260, 159 (1965).

113. A. Potton and P. Sigwalt, Compt. Rend., 265c, 1303 (1967).

114. B. Kouche-Waksman, Mme. Ltka and P. Sigwalt, Compt. Rend., 255, 680 (1962).

115. S.N. Bhadani, P.P. Baranwal, Makromol. Chem., 178, 1049 (1977).

116. S.N. Bhadani, P.P. Baranwal, Makromol. Chem., 178, 2637 (1977).

117. S.N. Bhadani, P.P. Baranwal and Yugalk Prased, Makromol. Chem., 179, 1623 (1978).

118. A. Polgar and J.L. Jungnickel, Organic Analysis, Vol. 1, edited by J. Mitchell et al., Interscience Publishers, New York, p.237 (1956).

119. A.W. Francis and A.J. Hill, J. Amer. Chem. Soc., 46, 2498 (1924).

120. Quantitative Organic Analysis Via a Functional Group, Third Edition, Sideny Siggia, p.296.

121. R. Belcher, A.J. Nutten, Quantitative Inorganic Analysis, Third Edition, 242 (1970).

122. G. Sartori, F. Ciampelli and W. Gamell, Chim. & Ind. [Milano], 45, 1473 (1963).

123. W.L. Truett, D.R. Johnson, I.M. Robinson and B.A. Montage, J. Amer. Chem. Soc., 82, 2337 (1960).

124. T. Tsujino, T. Saegusa, S. Kobayashi and J. Furukawa, Kogys Kugakuzasshi, J. Chem. Soc. Japan, Ind. Chem. Sect., 67, 1961 (1964).

125. T. Saegusa, T. Tsujino and J. Furukawa, Makromol. Chem., 78, 32 (1964).

126. D.A. Edward and G.W.A. Fowles, J. Chem. Soc., 24 (1961).

127. T. Saegusa, T. Tsujino and J. Furukawa, Makromol. Chem., 85, 71 (1965).

128. V.M. Kothar and J.J. Tazuma, J. Org. Chem., 36, 2951 (1971).

129. G. Wittig and E. Krauss, Ber., 91, 895 (1958).

130. L. Friedman and F.M. Logullo, J. Am. Chem. Soc., 85, 1549 (1963).

131. T.F. Mich, E.J. Nienhouse, T.E. Farina and J.J. Tufariello, J. Chem. Education, 45, 272 (1968).

132. B. Ranby and J.F. Rabek in "Singlet Oxygen, Reactions with Organic Compounds and Polymers", Edited by Ranby and J.F. Rabek, John Wiley, Chichester, 211 (1978).

133. G.C. Levy and G.L. Nelson, Carbon-13 Nuclear Magnetic Resonance for Organic Chemists by G.C. Levy and G.L. Nelson, General Electric Corporate Research and Development, Wiley-Interscience, a Division of John Wiley & Sons, Inc., New York-London-Sydney-Toronto (1973).