Metathesis ring-opening polymerisation of some heteropolycyclic alkenes: an indirect approach to the synthesis of a new heterosubstituted conjugated polymer

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METATHESIS RING-OPENING POLYMERISATION OF SOME HETEROPOLYCYCLIC ALKENES: AN INDIRECT APPROACH TO THE SYNTHESIS OF A NEW HETEROSUBSTITUTED CONJUGATED POLYMER

by

KEVIN HARPER B.Sc.

Thesis submitted for the Degree of Doctor of Philosophy to
the University of Durham

Van Mildert College,
University of Durham

September 1983

To my parents

ABSTRACT

This thesis consists of four chapters.

The first chapter outlines the origins and objectives of the work reported.

The second chapter discusses olefin metathesis and describes the synthesis, characterisation and investigation of the ring-opening polymerisation of some heterosubstituted cycloalkenes in an attempt to prepare a polymer which would act as a precursor leading to a heterosubstituted conjugated polymer. Keto-substituted derivatives of bicyclo[2,2,1]hept-2-ene were investigated initially and were found to be poor monomers for metathesis ring-opening polymerisation. However, cycloalkenes bearing chlorocarbonate substituents were found to be readily ring-open polymerised by a typical metathesis catalyst system, $WCl_6/SnMe_4$ at 70°C.

The third chapter describes the conversion of the precursor polymer synthesised as described in Chapter Two into a new heterosubstituted conjugated polymer. This new polymer was found to be readily oxidised, and to have similar electrical properties to other poly(acetylene) derivatives bearing electron-withdrawing substituents.

Finally, the fourth chapter describes attempts to synthesise block copolymers by metathesis ring-opening polymerisation using a solvent-free catalyst system.

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MEMORANDUM

The work in this thesis was carried out in the Chemistry Laboratories of the University of Durham between October 1980 and September 1983. This work has not been submitted for any other degree and is the original work of the author except where acknowledged by references.

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CHAPTER ONE

ORIGINS AND OBJECTIVES OF THE WORK REPORTED IN THIS THESIS

1.1 Synthesis of a new polyconjugated system

Conjugated polymers are at present a subject of active research in many academic and industrial laboratories worldwide. The topic involves several scientific disciplines and includes investigations of the synthesis, properties, and uses of such systems. These materials appear to be of great technological potential, and the scope of their applications appears to be exceptionally wide. For example, the simplest conjugated polymer, poly(acetylene),[1] has been shown to be an insulator in its pristine state; chemical modification can convert it to an n- or p-type semiconductor and further reaction leads to a material with conductivity in the metallic range.[2-4] Such behaviour in one material suggests, at least in principle, an enormous applications potential.

One of the most frequently discussed applications is the production of lightweight rechargeable batteries.[5] Much work has been done to develop the use of poly(acetylene) as the electrode material in electrochemical cells. However, since poly(acetylene) is intrinsically an insulating material whose electrical conductivity depends on details of structure, morphology, and purity, its properties have to be modified to produce these elctrodes. Two forms of modification are used, either oxidation or reduction. Oxidation of the polymer backbone can be achieved using electron acceptors such as AsF_5 or iodine, or by electrochemical oxidation.[6] The resulting modified polymer is electrically conducting, with a conductivity which can be as high as $10^3(\Omega cm)^{-1}$ (*cf.* Hg; $10^4(\Omega cm)^{-1}$). Oxidatively modified poly(acetylene) becomes a p-type material, initially containing a series of "holes" or positively charged sites resulting from the radical cations (polarons) created by random oxidation; these species are delocalised along the polymer chain and the odd electrons can combine leaving delocalised cationic species (positive solitons).[7,8] Reduction of the polymer backbone can be achieved using electron donors, such as alkali metals (Li, Na, K).[5] Poly(acetylene) reacts with alkali metal naphthalides in THF solution, producing an n-type material containing a series of radical anions. Stabilisation is again as a result of delocalisation in the conjugated π-system of the polymer. These oxidative or reductive modifications are generally referred to as "doping". However, it has been pointed out by Wegner[9] that this term is really inappropriate since it may be confused with "doping" in the sense used in silicon technology where traces of added impurity have enormous effects, whereas in organic systems the "doping" is achieved by large scale chemical modification.

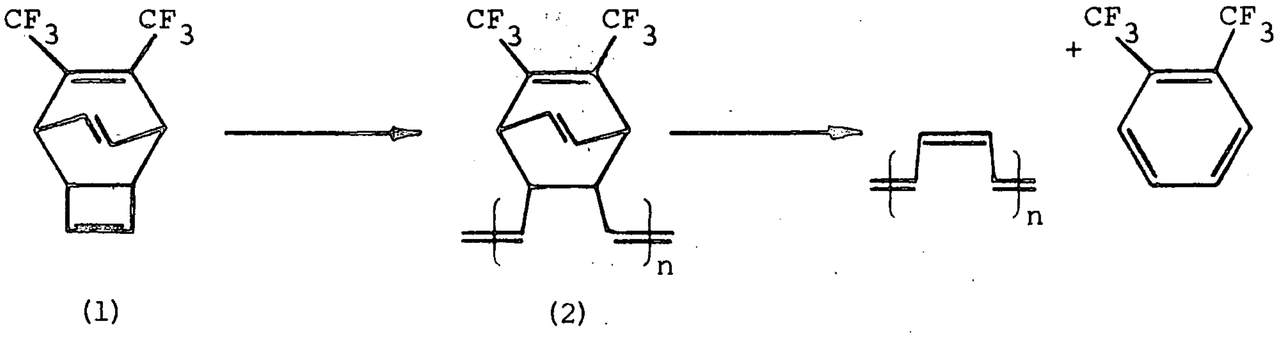
An electrochemical cell may be produced by immersing a piece of p-type material and a piece of n-type material in an electrolyte such as $LiClO_4$ in propylene carbonate or THF.[5] These systems will be reviewed briefly in Chapter Three.

Another oxidising agent which can be used to create p-type poly(acetylene) is molecular oxygen.[8,10,11] Initial uptake of oxygen results in a large increase in conductivity. If oxygen is in excess however, the poly(acetylene) is degraded, and after the initial increase in conductivity there is a marked decrease to insulating levels.[10] This susceptibility of poly(acetylene) to oxidative degradation is a major drawback as far as applications are concerned.

In the discussion above only poly(acetylene) has been considered, however many other polyconjugated systems have attracted interest and some of those which contain heteroatoms appear to be more resistant to oxidative degradation than poly(acetylene) whilst maintaining the interesting electrical properties associated with polyconjugation; examples of this type of material are poly(pyrrole)[12-14] and poly(paraphenylene sulphide).[15-18] There have also been speculations concerning the possibility that heteroatoms covalently bound to the polyconjugated system may act as "internal dopants" with the heteroatom acting as a source of electrons to be delocalised in the polyene sequences.[19]

The aim of part of the work described in this thesis was to investigate this idea by preparing a polyconjugated system having pendant heteroatom substituents, and examining its properties.

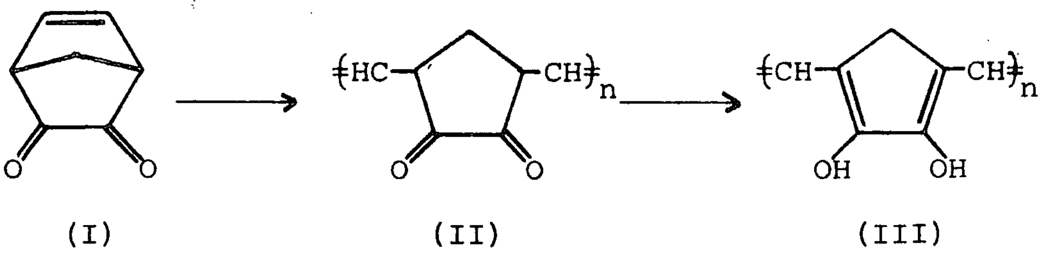
Edwards and Feast[20] have demonstrated that poly(acetylene) can be produced in a novel form using a two-step route via a precursor polymer. The monomer 7,8-bis(trifluoromethyl)tricyclo[4,2,2,0^{2,5}]deca-3,7,9-triene (1) was polymerised by metathesis ring-opening to produce a precursor polymer (2) which could be purified then converted to poly(acetylene) by an allowed thermal elimination, Scheme 1.



Scheme 1

The main advantage of this approach is that the precursor polymer is soluble and may be purified and manipulated by standard techniques, thus circumventing the problems encountered when poly(acetylene) is prepared directly by the polymerisation of acetylene as reported for example by Shirakawa[1] and Luttinger.[21] The direct route utilizes polymerisation at the surface of concentrated catalyst solutions, and since poly(acetylene) is insoluble and infusible the purification and fabrication of the material is difficult. The material produced by the two-step route has a higher purity as judged by pristine conductivity, and a different morphology to conventional poly(acetylene).

The work described in this thesis used the same approach of producing a precursor polymer which can be modified to yield a polyconjugated system. The monomer investigated initially was bicyclo[2,2,1]hept-5-ene-2,3-dione (I). The aim was to ring-open polymerise this monomer to produce a polymer (II) which could be enolised to yield a new polyconjugated system (III) with substituent hydroxyl functions directly attached to the polyconjugated backbone, Scheme 2.



Scheme 2

The questions which needed to be answered were firstly could this diketone (I) be ring-open polymerised by metathesis. Earlier workers[22] have reported that some cyclic and acyclic alkenes containing heteroatoms can undergo metathesis, so the first stage of the scheme may be feasible. The work aimed at answering this initial question is reported in Chapter Two, together with a review of metathesis with particular reference to metathesis of heteroatom-substituted alkenes. Secondly, the conversion of the precursor polymer (II) to the polyconjugated system (III) would have to be accomplished. This would involve keto-enol tautomerism. The polyconjugated system would be formed by locking the diketone precursor polymer into its enol form. There are some examples in the literature[23] of aldehydes and ketones which form stable enols so the second stage of the scheme may also be feasible. The work relating to the conversion of a prepolymer into the polyconjugated system (III) is reported in Chapter Three, together with a brief review of keto-enol tautomerism with particular reference to stabilisation of enols.

1.2 The attempted synthesis of block copolymers via metathesis

A copolymer is formed when two or more different monomers are incorporated into one polymer. In principle, a pair of monomers can lead to an infinite number of different copolymers. The structure and composition of the copolymer obtained depends on the relative reactivities of monomers M_1 and M_2, which also depends on the method of polymerisation. Reactivity ratios r_1 and r_2 can be obtained and provide a measure of the probability of a particular chain end reacting with monomers of its own kind or of the comonomer kind. Four possible cases of chain growth exist for a two monomer system.[24] Figure 1.1 shows these for a radical polymerisation system but the model is valid for other methods of chain-growth polymerisation also.

Growing chain end	Monomer adding	Rate constant	New chain end	Rate
$\sim\sim M_1\cdot$	M_1	$\xrightarrow{k_{11}}$	$\sim\sim M_1\cdot$	$k_{11}[M_1\cdot][M_1]$
$\sim\sim M_1\cdot$	M_2	$\xrightarrow{k_{12}}$	$\sim\sim M_2\cdot$	$k_{12}[M_1\cdot][M_2]$
$\sim\sim M_2\cdot$	M_1	$\xrightarrow{k_{21}}$	$\sim\sim M_1\cdot$	$k_{21}[M_2\cdot][M_1]$
$\sim\sim M_2\cdot$	M_2	$\xrightarrow{k_{22}}$	$\sim\sim M_2\cdot$	$k_{22}[M_2\cdot][M_2]$

Figure 1.1 Chain-end growth in two-component copolymerisation system

Kinetic analysis using a steady state assumption[25-28] leads to a Copolymer Composition Equation, Figure 1.2, which relates the ratio of polymerised monomers $d[M_1]/d[M_2]$ to values of the reactivity ratios, r_1 and r_2, and feedstock ratios $[M_1]$ and $[M_2]$.

$$\frac{d[M_1]}{d[M_2]} = \frac{[M_1](r_1[M_1] + [M_2])}{[M_2](r_2[M_2] + [M_1])}$$

where $r_1 = \frac{k_{11}}{k_{12}}$ and $r_2 = \frac{k_{22}}{k_{21}}$.

Figure 1.2 Copolymer Composition Equation

Values of r_1 and r_2 obtained experimentally have been tabulated extensively for a range of monomers and polymerisation types.

If $r_1<1$ then $\sim M_1^{\cdot}$ prefers to add to M_2 rather than M_1.
If $r_1>1$ then $\sim M_1^{\cdot}$ prefers to add to M_1 rather than M_2.

A random copolymer is formed if $r_1r_2 = 1$, and copolymer composition depends exclusively on feed-stock ratio, Figure 1.3.

$$M_1 + M_2 \longrightarrow \sim M_1M_2M_2M_1M_2M_1M_1 \sim$$

Figure 1.3 Random copolymer

As an example, butadiene is about 1.4 times as reactive as styrene towards free radical polymerisation,[29] and this is reflected in the incorporation ratios of each monomer into the random copolymer produced.

If $r_1 = r_2 \simeq 0$, then an alternating copolymer is produced, Figure 1.4.

$$M_1 + M_2 \longrightarrow \sim M_1M_2M_1M_2M_1M_2 \sim$$

Figure 1.4 Alternating copolymer

Stilbene (1,2-diphenyl ethene) and maleic anhydride copolymerise with absolute regular alternation of units regardless of feed ratio, to produce a 50:50 perfectly alternating copolymer.[30]

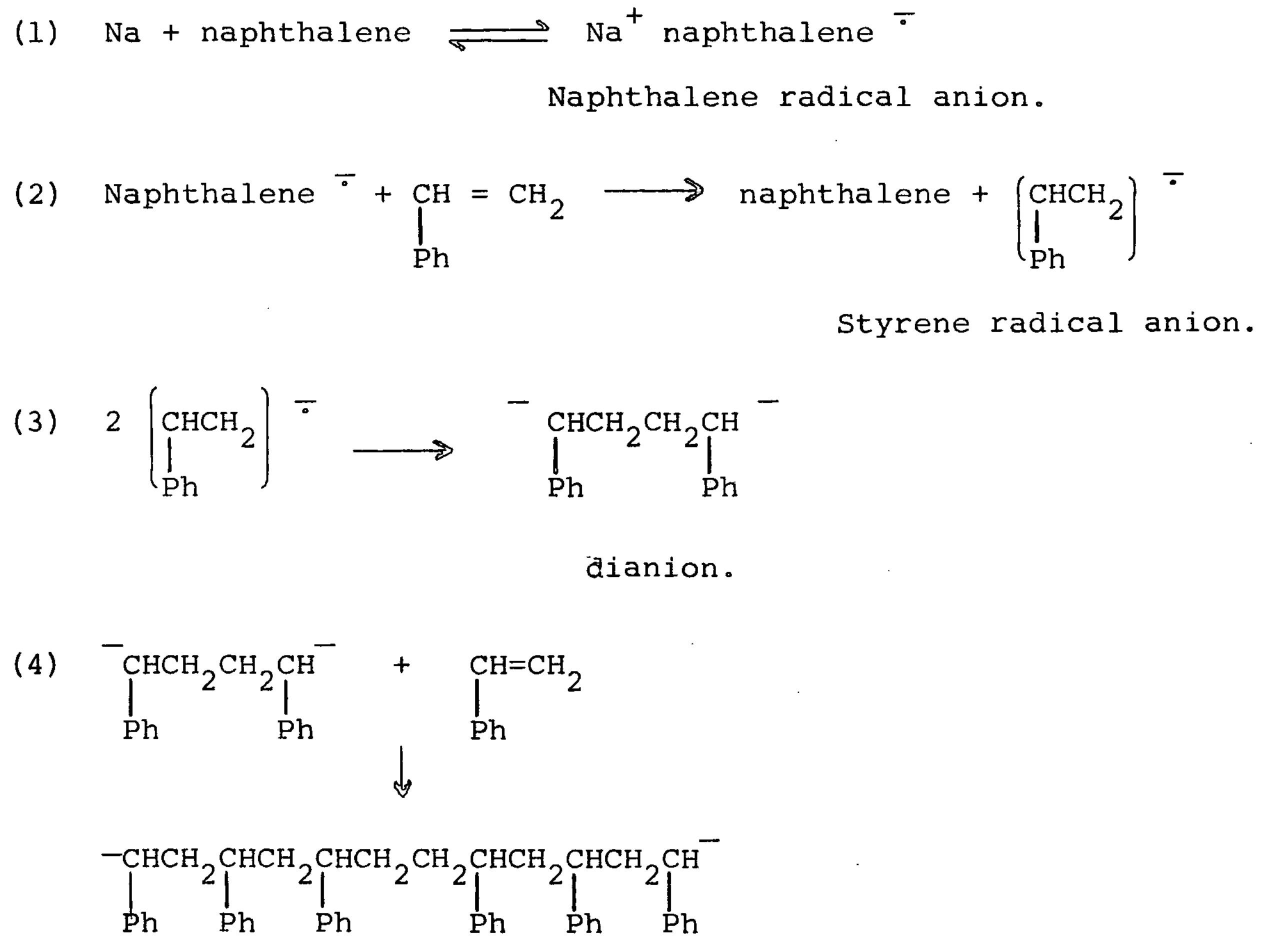
If r_1 and $r_2 \gg 1$, no copolymerisation occurs, rather two homopolymers are produced.

Under special conditions a block copolymer may be produced, in which monomer M_1 is polymerised until the monomer feed is exhausted, then monomer M_2 is added and polymerisation continues, Figure 1.5.

$$M_1 \longrightarrow \sim M_1M_1M_1M_1M_1 \sim + M_2 \longrightarrow \sim M_1M_1M_1M_1M_1M_2M_2M_2M_2 \sim$$

Figure 1.5 Block copolymer

To produce a block copolymer, a "living" system is required - a chain polymerisation system in which there are no chain termination or chain transfer steps. The classic example of a "living" system used to prepare block copolymers was discovered in 1956 by Szwarc.[31] Styrene was polymerised by anionic polymerisation as outlined in Figure 1.6.



(1) $\mathrm{Na} + \text{naphthalene} \rightleftharpoons \mathrm{Na}^{+}\,\text{naphthalene}^{\dot{-}}$

Naphthalene radical anion.

(2) $\text{Naphthalene}^{\dot{-}} + \underset{\mathrm{Ph}}{\mathrm{CH}}=\mathrm{CH_2} \longrightarrow \text{naphthalene} + \left[\underset{\mathrm{Ph}}{\mathrm{CH}}\mathrm{CH_2}\right]^{\dot{-}}$

Styrene radical anion.

(3) $2\left[\underset{\mathrm{Ph}}{\mathrm{CH}}\mathrm{CH_2}\right]^{\dot{-}} \longrightarrow {}^{-}\underset{\mathrm{Ph}}{\mathrm{CH}}\mathrm{CH_2CH_2}\underset{\mathrm{Ph}}{\mathrm{CH}}{}^{-}$

dianion.

(4) $${}^{-}\underset{\mathrm{Ph}}{\mathrm{CH}}\mathrm{CH_2CH_2}\underset{\mathrm{Ph}}{\mathrm{CH}}{}^{-} + \underset{\mathrm{Ph}}{\mathrm{CH}}=\mathrm{CH_2}$$

$$\downarrow$$

$${}^{-}\underset{\mathrm{Ph}}{\mathrm{CH}}\mathrm{CH_2}\underset{\mathrm{Ph}}{\mathrm{CH}}\mathrm{CH_2}\underset{\mathrm{Ph}}{\mathrm{CH}}\mathrm{CH_2CH_2}\underset{\mathrm{Ph}}{\mathrm{CH}}\mathrm{CH_2}\underset{\mathrm{Ph}}{\mathrm{CH}}\mathrm{CH_2}\underset{\mathrm{Ph}}{\mathrm{CH}}{}^{-}$$

Figure 1.6 "Living" polystyrene

Styrene was polymerised by addition of a small amount of Na-naphthalene initiator. When more styrene was added, polymerisation continued. Viscosity measurements indicated that the molecular weight of the polystyrene produced had increased.

When butadiene was added instead of the second batch of styrene, polymerisation took place. No homopolymers could be isolated, and characterisation of the resulting polymer indicated that a block copolymer had been produced.

Block copolymers are of great interest, since they have novel and interesting bulk properties, whilst some of the properties of the individual blocks in the block copolymer are also retained.

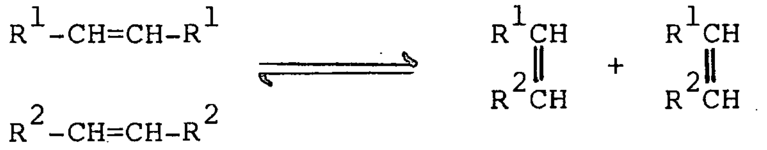
Chapter Four describes attempts to produce block copolymers by ring-opening polymerisation of cycloalkenes using a heterogeneous metathesis catalyst system.

CHAPTER TWO

OLEFIN METATHESIS AND ITS USE IN THE RING-OPENING POLYMERISATION OF SOME HETEROPOLYCYCLIC ALKENES

2.1 Definition of olefin metathesis

Olefin metathesis is a bond reorganisation reaction in which the total number and types of chemical bonds remains unchanged during the transformation of the initial alkenes into equimolar amounts of two new alkenes, as shown in Figure 2.1.



$$\begin{matrix} R^1\text{-CH=CH-}R^1 \\ R^2\text{-CH=CH-}R^2 \end{matrix} \rightleftharpoons \begin{matrix} R^1CH \\ \Vert \\ R^2CH \end{matrix} + \begin{matrix} R^1CH \\ \Vert \\ R^2CH \end{matrix}$$

Figure 2.1

These transformations are induced most commonly using heterogeneous or homogeneous catalyst systems based on tungsten, molybdenum, or rhenium.

2.2 History of olefin metathesis

In 1964, Banks and Bailey[32] discovered that propene was converted into ethene and but-2-ene using a catalyst system comprised of activated molybdenum hexacarbonyl supported on alumina, Figure 2.2.

$$2\ CH_3CH = CH_2 \xrightarrow{\text{catalyst}} CH_2 = CH_2 + CH_3CH = CHCH_3$$

Figure 2.2

The reaction was described by Banks and Bailey as "olefin disproportionation".

Previously, Eleuterio[33] had investigated the reaction of molybdenum oxide on alumina, activated by hydrogen reduction then further reacted with aluminium hydride, with monocyclic, bicyclic, and tricyclic olefins. Polymeric products were obtained in low yield. In the case of cyclopentene, trans-poly(1-pentenylene) was formed with a high degree of stereoregular structure.

The possibility of producing stereoregular polymers from cycloalkenes was further demonstrated in 1963 by Natta and coworkers.[34,35] By varying the catalyst and reaction conditions, cyclobutene was polymerised to predominantly or exclusively cis- or trans-poly(1-butenylene) as shown in Table 2.1. The following year tungsten and molybdenum halides, in combination with organoaluminium compounds, were used to polymerise cyclopentene under mild conditions, demonstrating control of the double bond stereochemistry.[36]

Table 2.1 Cyclobutene polymers by transition metal catalysts.[34,3

Catalyst system	Polymer structure
$TiCl_4/Et_3Al$/n-heptane	Predominantly cis
$TiCl_4/R_3Al$/toluene	Predominantly trans
$MoCl_5/Et_3Al$/toluene	Predominantly cis
$RuCl_3/H_2O$	Mixed cis and trans
$RuCl_3$/EtOH	Trans

In 1967, Calderon and coworkers,[37,38] used for the first time the term "olefin metathesis" for the overall result of the reaction, and showed that the metathesis of acyclic alkenes was possible in the presence of catalysts derived from tungsten hexachloride and an organoaluminium compound similar to those used by Natta for the ring-opening polymersiation of cycloalkenes. This was a significant contribution to the evolution of the metathesis concept, since it confirmed that olefin metathesis of acyclic alkenes and ring-opening polymerisation of cycloalkenes were both cases of a new metal-catalysed reaction known generally as "olefin metathesis".

The olefin metathesis reaction has since been investigated thoroughly, and is still a topic of active research. The range of metathesis catalysts has been extended, its mechanism is now more fully understood, and the scope of its applications is increasing. These aspects, which have been the subject of numerous reviews,[39-46] are dealt with in the following sections of this chapter.

2.3 Olefin metathesis catalyst systems

Although the metathesis of acyclic alkenes and the ring-opening polymerisation of cycloalkenes are governed by a common mechanism, they differ in many chemical, kinetic and thermodynamic aspects. However, for both acyclic and cyclic alkenes, catalysts based on tungsten, molybdenum or rhenium are the most active.

Many different systems have been claimed to be active towards metathesis. Two catagories of catalyst clearly exist, namely heterogeneous catalysts and homogeneous catalysts.

(a) Heterogeneous catalysts

These systems are usually comprised of a high surface area refractory support such as silica, alumina, or titanium oxide, on which the catalyst is dispersed. Typically, an active heterogeneous catalyst is formed by impregnating the support with a catalyst precursor. The active catalyst is formed by thermal decomposition and/or chemical modification of the precursor.[47,48] The most common and most active catalysts are the oxides, sulphides or carbonyls of tungsten, molybdenum or rhenium. The activity of the catalyst is retained by maintaining an inert atmosphere or vacuum. Sometimes a third component acting as a catalyst "activator" or "modifier" is added to reduce side reactions.[49,50] The olefins are passed over the supported catalysts at elevated temperatures (100^{o}-500^{o}C) when catalyst activity and efficiency is maximised.

These catalyst systems, which are of industrial importance,[51] are usually used for the metathesis of acyclic alkenes, when reactants and products are gaseous. They are rarely used to promote the ring-opening polymerisation of cycloalkenes, since separation of the polymeric products from such solid-supported catalysts is difficult. Also, the elevated temperatures which are used tend to degrade the polymers produced. Such problems are overcome using homogeneous catalyst systems.

(b) Homogeneous catalysts

All homogeneous metathesis catalysts consist of a transition metal derivative as the main component. Tungsten, molybdenum or rhenium are the most active metal centres. A second component is often added as cocatalyst to increase the catalytic activity. The most common cocatalysts are organometallic compounds of Group I to IV elements. Sometimes, a third component is also added as a catalyst "activator" or "modifier". Reactions are usually carried out in an inert solvent, between room temperature and 100^{o}C.

These systems can be used together with acyclic alkene or cycloalkene substrates. They are of particular interest to polymer chemists since high molecular weight polyalkenamers can be produced by ring-opening polymerisation of cycloalkenes under relatively mild conditions. Products are easily isolated from the catalytic species by precipitation in a non-solvent; in this process the catalyst is totally deactivated. Homogeneous systems are used immediately after generating the active catalytic species. Their activity is maintained for 24 hours or less, in contrast to heterogeneous systems, which are used industrially for longer periods of time.

Since the number of homogeneous catalyst combinations is endless, the choice of the best catalyst system for the metathesis of a particular alkene is difficult and to some extent an empirical approach still has to be adopted. Thus, although an "educated guess" may be made after careful scanning of the literature, often several systems have to be tried to optimise the reaction conditions.

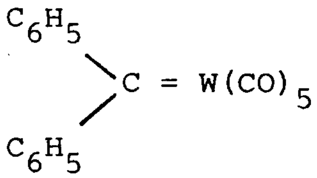
Some typical homogeneous catalyst systems are described in the following three sections.

(i) One-component homogeneous metathesis catalysts

This class of catalysts consists of halides, oxyhalides or stable carbene complexes of the transition metal.

$RuCl_3$, $OsCl_3$ or $IrCl_3$ in ethanol,[52-55] and WCl_6, WBr_6,or $ReCl_5$ [56,57] have been found to be active towards the metathesis of cycloalkenes. Recently, Rudler[58] has ring-open polymerised bicyclo[2,2,1]hept-2-ene using a binuclear tungsten complex.

Stable metal carbenes, whose metal atom is in the zero-oxidation state, have been used to promote ring-opening polymerisations. (Diphenylcarbene) complex (1), as synthesised by Casey,[59] and (phenyl methoxycarbene) complex (2), as synthesised by Fischer,[60] Figure 2.3, have been used to ring-open polymerise cyclobutene and bicyclo[2,2,1]hept-2-ene with high cis-stereospecificity,[61-65] Table 2.2.


(1) Casey Carbene

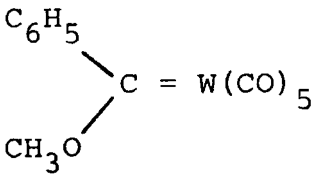
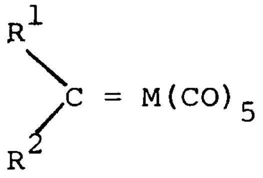

(2) Fischer carbene

Figure 2.3

Table 2.2 Cis-stereospecificity in polymerisation initiated by stable metal-carbene complexes

metal-carbene complex	monomer	% cis content (polymer)
$(CO)_5W{=}C(OCH_3)C_6H_5$	cyclobutene	92
$(CO)_5W{=}C(C_6H_5)_2$	cyclobutene	92
$(CO)_5W{=}C(OCH_3)C_6H_5$	bicyclo[2,2,1]hept-2-ene	95
$(CO)_5W{=}C(C_6H_5)_2$	bicyclo[2,2,1]hept-2-ene	72

Other transition metal-carbene complexes have been developed,[66] Figure 2.4.



$M = W, Cr$

$R^1 = OCH_3, C_6H_5$

$R^2 = CH_3, C_6H_5$

Figure 2.4

The discovery that metal carbene complexes can promote the olefin metathesis reaction was of significance in elucidating the reaction mechanism, as described later.

(ii) Two-component homogeneous metathesis catalysts

The most efficient two-component systems consist of the halide or oxyhalide of the transition metal, activated by an organometallic compound from Groups I to IV. Organotin[67] compounds and organoaluminium[36-38] compounds are particularly effective cocatalysts.

The yield and stereoregularity of polyalkenamers obtained from the metathesis of cycloalkenes in the presence of two-component catalysts depends on catalyst composition, polymerisation temperature,[37, 68-70] type of cocatalyst,[70,71] type of cycloalkene,[65,72] variation of the transition metal to cocatalyst ratio,[70] and monomer concentration.[67] Hence many variables must be considered when optimizing reaction conditions.

(iii) Three-component homogeneous metathesis catalysts

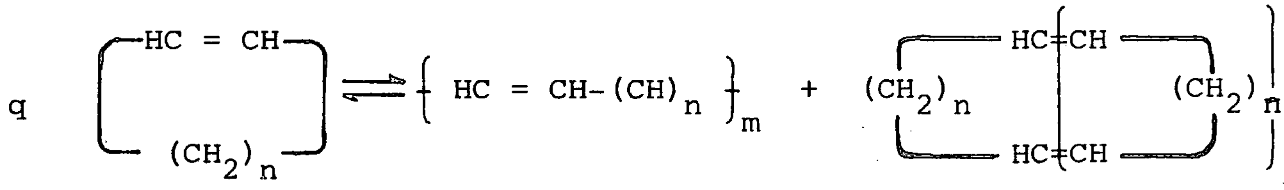
A third component, which acts as a catalyst "activator" or "modifier", is sometimes added to the two-component catalyst systems. The role of the "activator" is to enhance the catalyst activity by increasing the reproducibility of reaction, the stability and solubility of the catalyst, and the rate of polymerisation; to increase monomer conversion, whilst reducing side-reactions.

"Activators" usually consist of oxygen-containing compounds such as alcohols,[38] water,[73] or molecular oxygen[41,73-75]. Recently, 1,2-dichloroethene[76] was used as an activator in the polymerisation of cyclooctene, to produce a low-trans poly-(octenamer). These added components are generally only used in trace amounts, since an excess would totally deactivate the catalysts.

Modifiers are used as "speciality additives" and are added to suppress particular unwanted side-reactions. For example Lewis bases have been used[77-79] to suppress isomerisation or Friedel-Crafts activity; organic bases such as spartein or pyridine have been used[80] to suppress cationic polymerisation.

2.4 The mechanism of olefin metathesis

The transformations which result when acyclic alkenes and cycloalkenes are reacted with metathesis catalysts are summarised in Figure 2.1, (page 12) and Figure 2.5 below, respectively.



(n ≠ 4)

Figure 2.5

Many studies have been undertaken to elucidate the mechanism of olefin metathesis. These are summarised in the subsequent sections.

(a) Transalkylation or transalkylidenation?

There are two possible ways in which the observed products can be formed in the metathesis of acyclic alkenes. These are:

(i) Transalkylation - cleavage of the C-C single bond adjacent to the double bond, Figure 2.6.

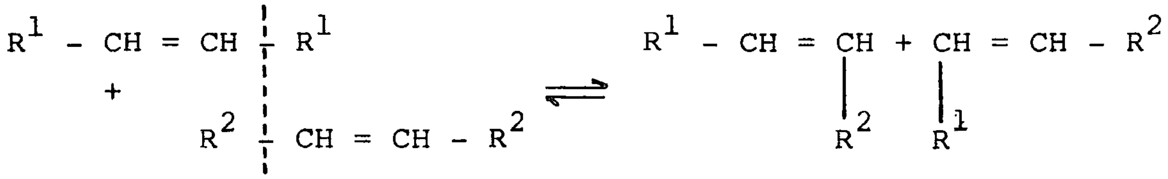


Figure 2.6

(ii) Transalkylidenation - cleavage of the C=C bond itself, resulting in alkylidene moiety exchange, Figure 2.7.

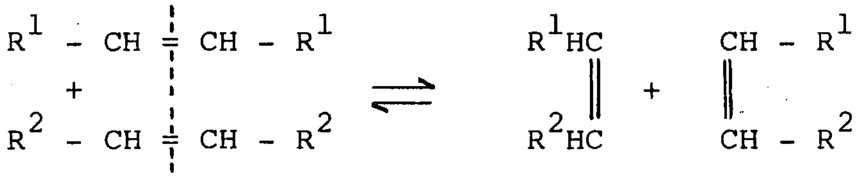
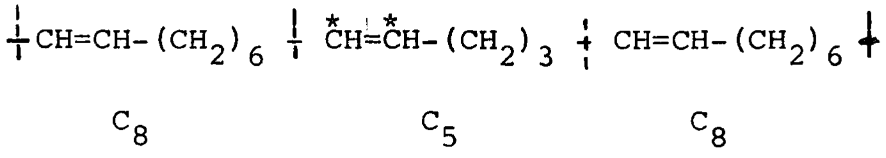


Figure 2.7

The transalkylation scheme was originally proposed by Natta.[68] However, experimental evidence in support of the transalkylidenation scheme was obtained by Dall'Asta and Mortoni.[81,82] This was done by copolymerising cyclooctene with cyclopentene in which the cyclopentene vinyl carbon atoms were labelled with ^{14}C.

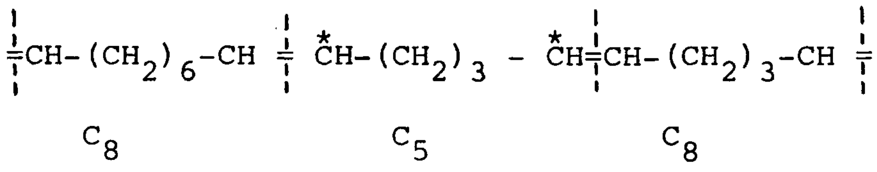
The copolymer structures which would be obtained after a transalkylation process and after a transalkylidenation process are shown in Figure 2.8.

(i)



(i) Transalkylation - allylic bond cleavage.

(ii)



(ii) Transalkylidenation - double bond cleavage.

Figure 2.8 (* denotes ^{14}C-labelling)

Ozonolysis followed by reduction of each of these polymers would produce the glycols shown in Figure 2.9.

(i) $HOH_2C\text{-}(CH_2)_6\text{-}\overset{*}{C}H_2OH + HOH_2\overset{*}{C}\text{-}(CH_2)_3\text{-}CH_2OH + HOH_2C\text{-}(CH_2)_6\text{-}CH_2OH$

(i) Glycol mixture from polymer produced by transalkylation.

(ii) $HOH_2C\text{-}(CH_2)_6\text{-}CH_2OH + HOH_2\overset{*}{C}\text{-}(CH_2)_3\text{-}\overset{*}{C}H_2OH + HOH_2C\text{-}(CH_2)_6\text{-}CH_2OH$

(ii) Glycol mixture from polymer produced by transalkylidenation.

Figure 2.9

The above procedure was performed on the copolymer produced, and labelled ^{14}C atoms were found to be present only in pentane diol.

Supporting evidence was obtained in a similar manner using a cyclobutene/3-methylcyclobutene copolymerisation[83].

Evidence that acyclic alkene metathesis also proceeds via C=C bond cleavage has been obtained using ^{2}D-labelling studies.[38,48,84,85]

(b) Pathway for transalkylidenation

(i) Pairwise mechanism involving quasi-cyclobutane intermediate and tetramethylene transition state

In order to explain alkylidene moiety exchange, several mechanistic routes were conceived. In 1967, Bradshaw[86] proposed a mechanism involving formation of a quasi-cyclobutane intermediate by coordination of two alkenes to the transition metal complex, followed by simultaneous making and breaking of bonds, Figure 2.10.

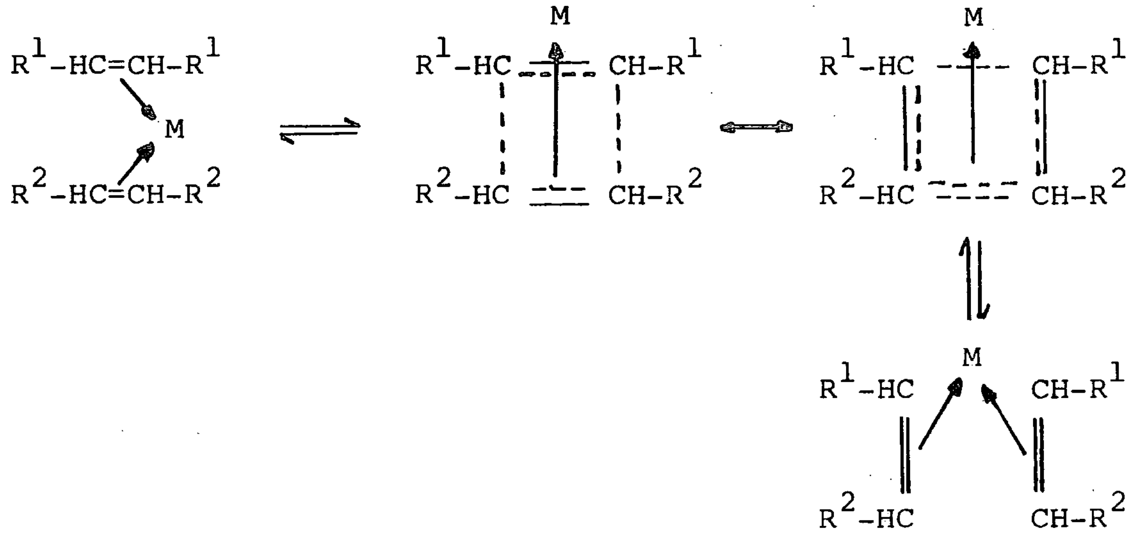


Figure 2.10 Quasi-cyclobutane intermediate, acyclic alkene substrates

This mechanism was adopted by Calderon[37,87] to rationalise polymerisation via a macrocyclization process; this would result in the formation of polyalkenamers if an acyclic alkene impurity interrupted the catalytic cycle to open the macrocycle, Figure 2.11.

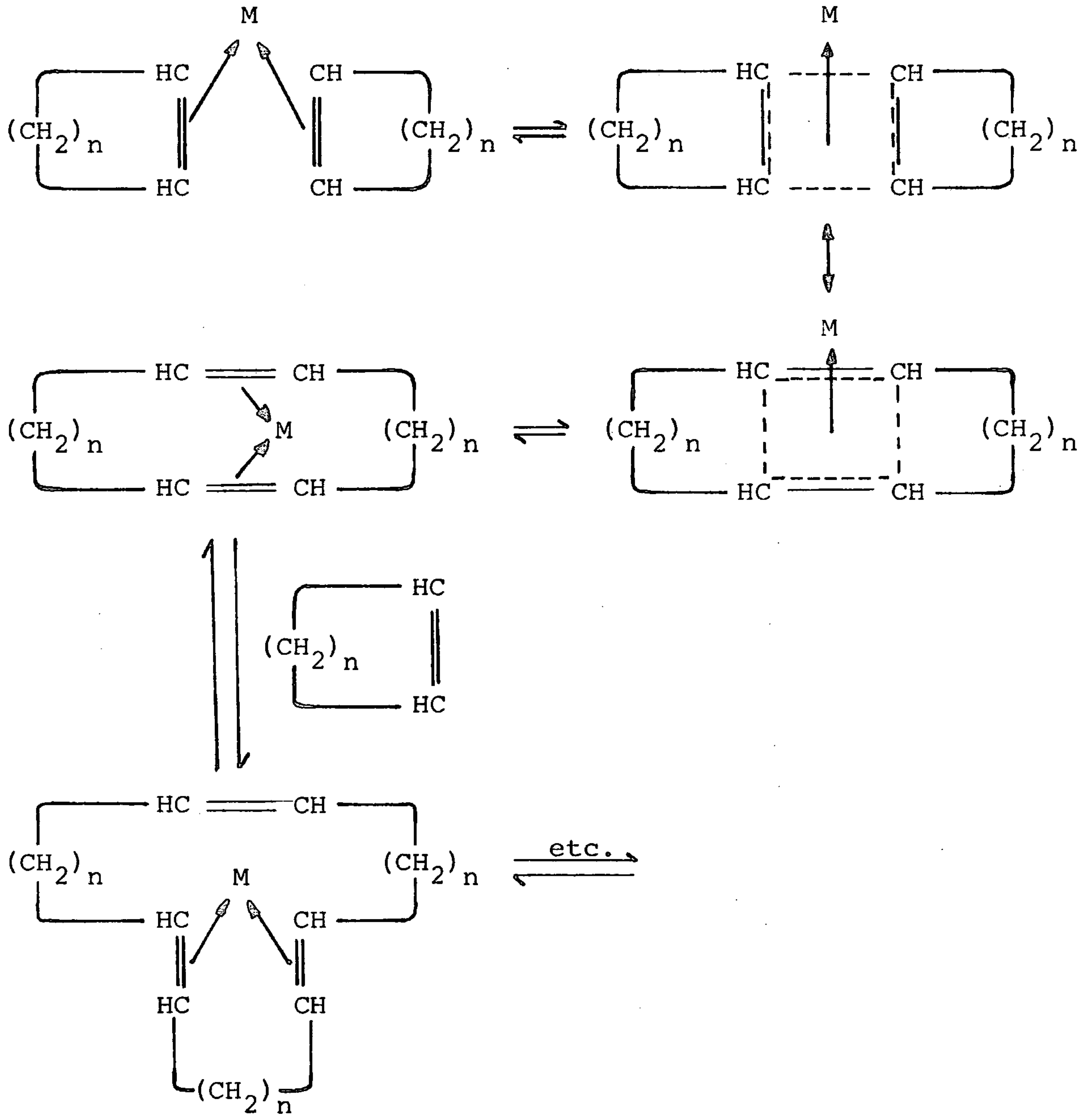


Figure 2.11 Quasi-cyclobutane intermediate, cycloalkene substrates

This mechanism involves concerted $[\pi_{2s} + \pi_{2s}]$ bond fusion which, according to Woodward-Hoffman rules[88] involves a symmetry-forbidden process. The only possible way in which such a mechanism could occur would be if the transition metal has atomic orbitals of the correct symmetry and an available electron pair to switch the symmetry-forbidden process into a symmetry-allowed process.[89]

Since the intermediate in the process is a quasi-cyclobutane, it may be expected that cyclobutanes should be formed as byproducts, or that they may be introduced into the cycle. Efforts to observe this have failed.

This led Lewandos and Pettit to propose an alternative to the quasi-cyclobutane transition state in the reaction, namely the tetramethylene transition state. This results from the C-C σ- and π-bonds concurrently being ruptured, producing a bis-alkene-π-complex which can reorganise to a multi-centre organometallic system, hence avoiding free cyclobutane species.[90]

(ii) Non-pairwise mechanism

An alternative mechanism which was originally proposed by Herisson and Chauvin[91] in 1970 is a non-concerted mechanism involving metal-carbene and metallocyclobutane intermediates - the non-pairwise mechanism, Figure 2.12.

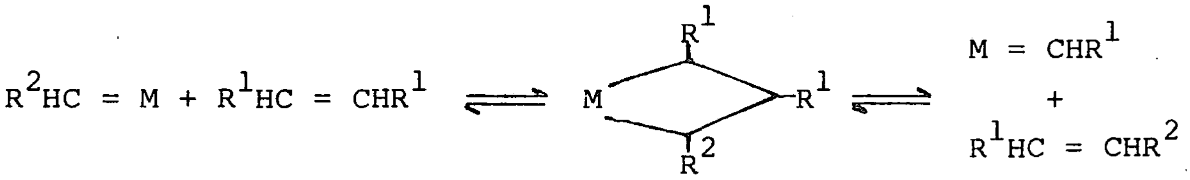


Figure 2.12

This mechanism is readily adapted to rationalise the formation of high molecular weight polyalkenamers from cycloalkenes by chain growth, Figure 2.13.

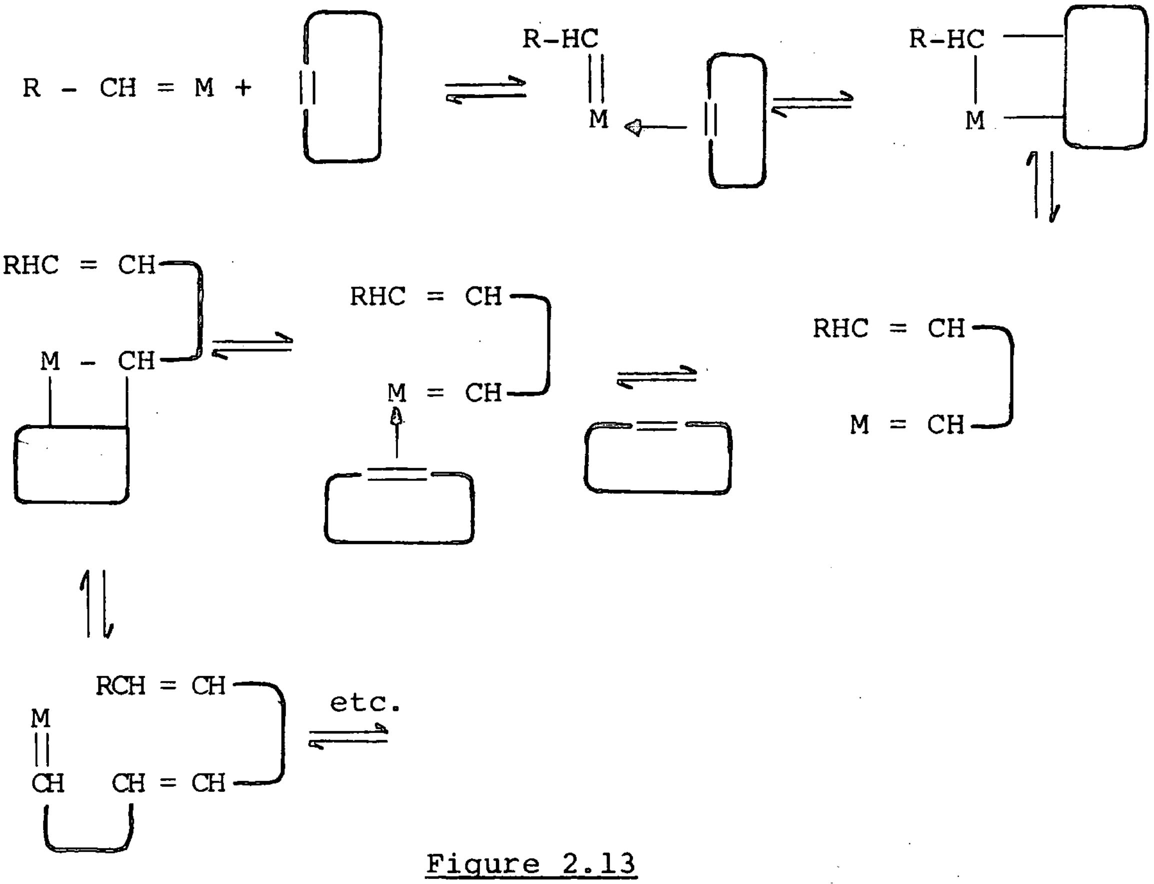


Figure 2.13

This mechanism overcomes the difficulty in the growing macrocycle mechanism proposed earlier, which would need acyclic alkene impurities to open the macrocycle and produce linear polyalkenamers.

Many kinetic studies have been undertaken and these support the metal-carbene chain mechanism. For example, Grubbs *et al*[92] have investigated the metathesis of a mixture of [1,1,8,8-d_4]-octa-1,7-diene and octa-1,7-diene using three different catalyst systems, producing ethene and cyclohexene. The observed ratios of [D_4], [D_2] and [Do] ethene were in agreement with the statistical distribution required by the metal-carbene chain mechanism, and could not be accounted for by the pairwise mechanism.

Studies involving ring-opening polymerisation have led to conclusive evidence that a metal-carbene is involved in the reaction. In 1976, Dolgoplosk[93] reported that small quantities of $PhCHN_2$ with WCl_6 or $MoCl_5$ led to ring-opening polymerisation of cycloalkenes. The formation of a carbene was proposed to rationalise this observation, Figure 2.14.

$$C_6H_5CHN_2 + MX_n \longrightarrow C_6H_5CH = MX_n + N_2 \uparrow \ .$$

Figure 2.14

The discovery that Fischer and Casey carbenes $R_2C = M(CO)_5$ are active metathesis catalysts without the aid of cocatalysts provided conclusive support for the metal-carbene chain mechanism,[61-65] as did work by Ivin and coworkers, described in Section 2.4(c)(ii)(II), Page 30, which rationalises polyalkenamer tacticity and stereoregularity using ^{13}C-nmr spectroscopy.

As in any other chain mechanism, there are initiation, propagation, and termination steps. These have been rationalised as follows.

(c) (i) Metal-carbene initiation

As described in Section 2.3, a variety of different types of catalyst systems promote metathesis. In order to rationalise the formation of the metal-carbene chain carrier, these may be divided into three classes.

Firstly, for solid-supported heterogeneous catalysts such as MoO_3/Al_2O_3 or $WCl_6/AlCl_3$, where there are no cocatalysts, Dolgoplosk[94] proposed a scheme in which a coordinated alkene is converted to a carbene via a 1,2-hydride shift, Figure 2.15.

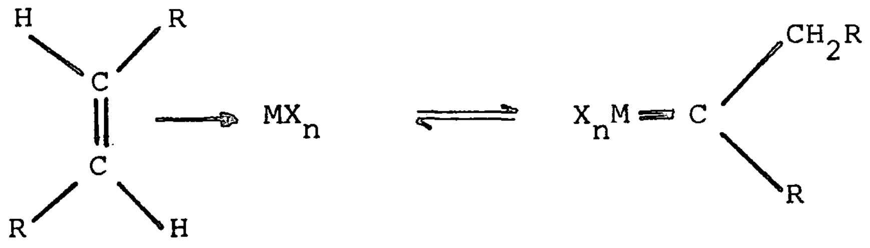


Figure 2.15

In the case of sterically constrained alkenes, the above mechanism would not be possible since the molecule would need to be distorted from planarity. A 1,2-hydride shift via a metal hydride would overcome this problem, Figure 2.16.

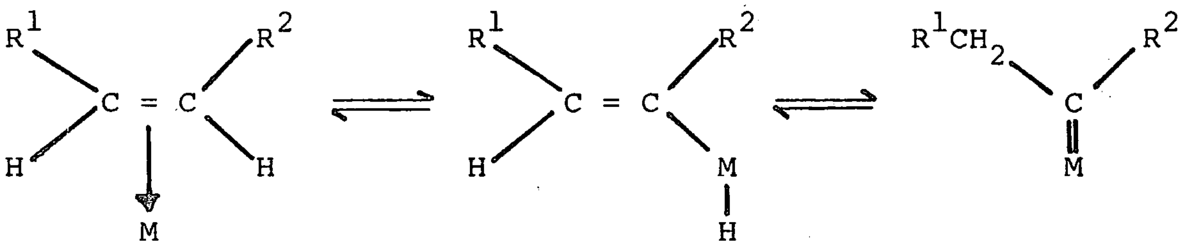


Figure 2.16

Where η^3-allyl formation is possible, the carbene-metal bond may not be formed at all, rather the metallocyclobutane may be formed directly,[95] Figure 2.17.

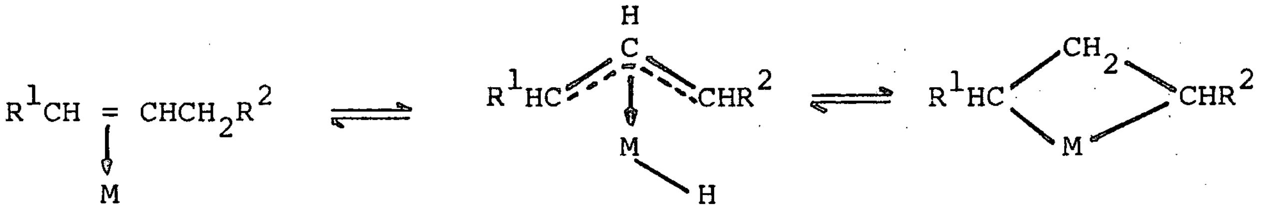


Figure 2.17

Alternatively, a transition metal hydride present initially or formed during reaction may account for carbene formation, Figure 2.18.

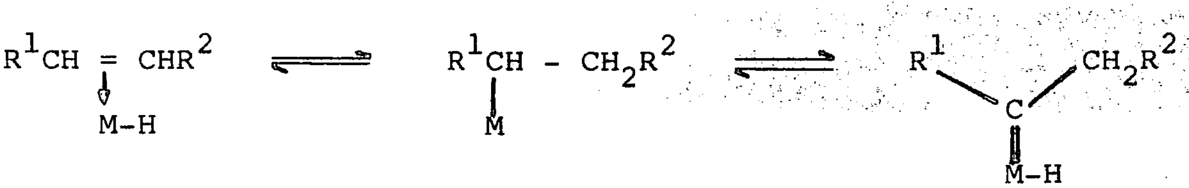


Figure 2.18

The hydride may be formed by an initiation reaction between the transition metal and an oxygen-containing activator, ROH, H_2O or O_2, and may account for the apparent lack of activity in some systems which are scrupulously dried and oxygen-free.[96]

The oxygen containing activator may act in two ways, either via a hydride shift, Figure 2.19, or less likely by a concerted-type reaction, Figure 2.20.

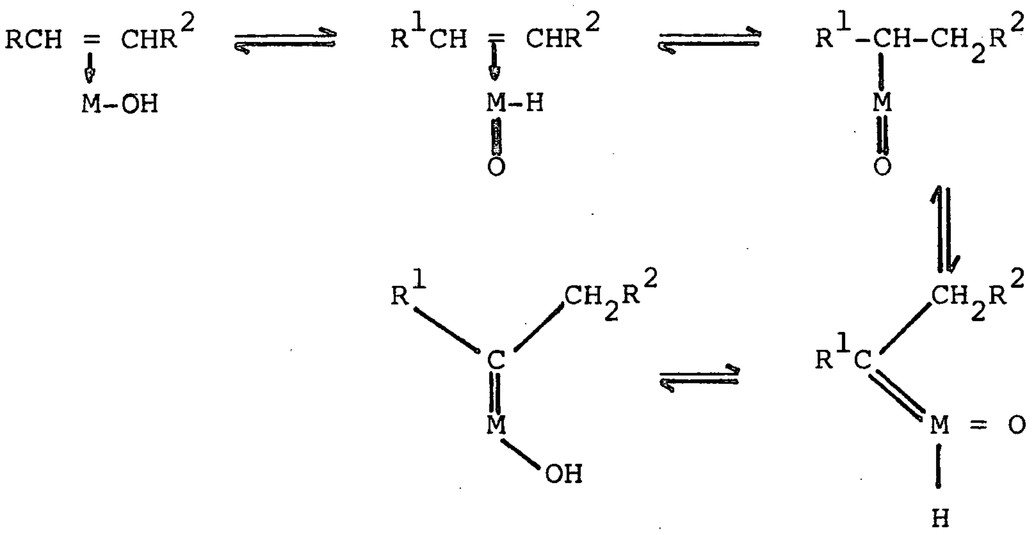


Figure 2.19

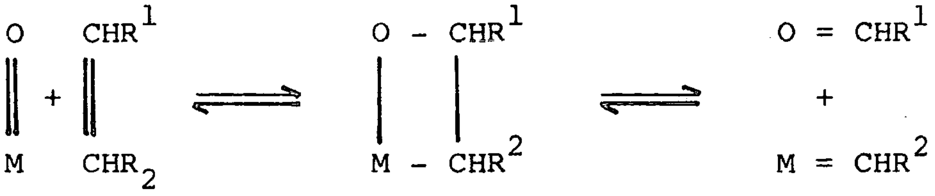
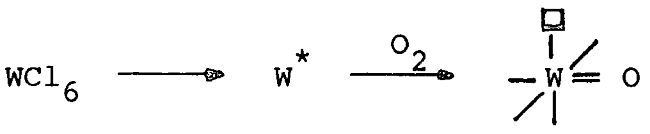


Figure 2.20

Formation of such an M=O species has been proposed by Amass[73,74] for reactions which do not contain metal alkyl cocatalysts, Figure 2.21.



* = activated tungsten species.

□ = vacant site.

Figure 2.21

Secondly, for systems containing a transition metal catalyst together with an organometallic cocatalyst, metal-carbenes are believed to be formed via σ-bonding of the organic ligand of the cocatalyst to the transition metal. Muetterties[97,98] observed methane formation from the reaction of $(CH_3)_2Zn$ and

WCl_6, Figure 2.22. No deutero-methane was obtained when the reaction was carried out in a deuterated solvent.

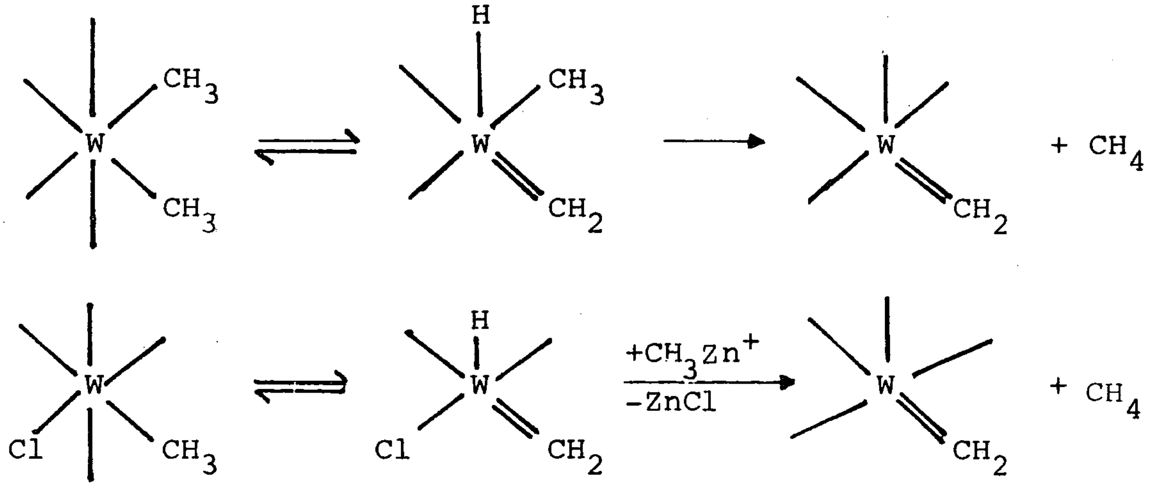


Figure 2.22

By contrast, Grubbs[99] observed CD_4 and $CD_2=CD_2$ generation from a reaction between WCl_6 and $(CD_3)_4Sn$, Figure 2.23.

$$WCl_6 + (CD_3)_4Sn \longrightarrow CD_4 + CD_2 = CD_2 + \text{W-Cat.}$$

Figure 2.23

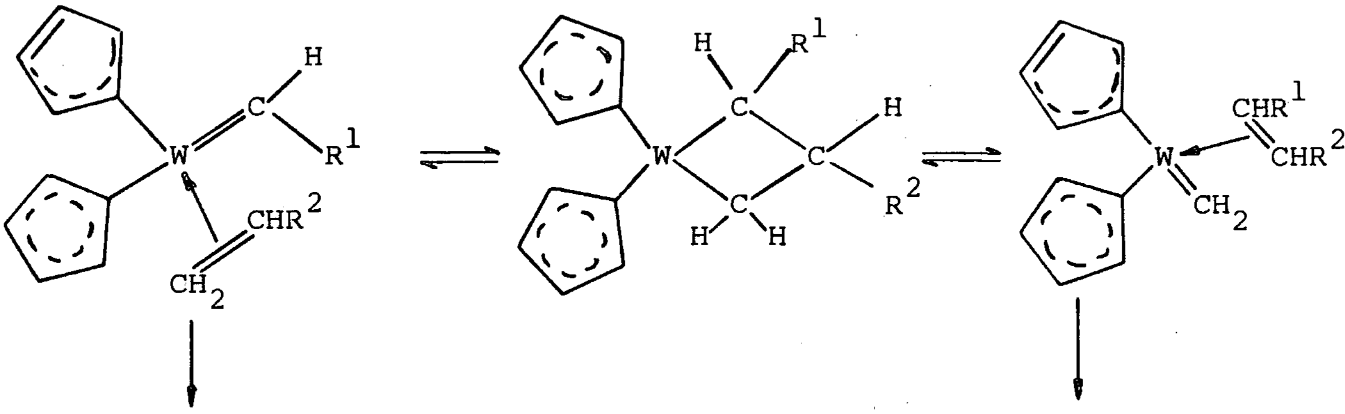
These observations taken together are strong support for the hypothesis set out in Figure 2.22.

Finally, Fischer and Casey carbenes are stable metathesis catalysts without the addition of cocatalysts.

(ii) Propagation step: Metal-carbene to metallocyclobutane interconversion

(I) Reaction of a stable metallocyclobutane

The propagation step in the olefin metathesis reaction involves metal-carbene to metallocyclobutane interconversion. Evidence that metallocyclobutanes are involved has recently been obtained by Green.[100] A stable metallocyclobutane of tungsten was isolated and photolysis or thermolysis yielded an alkene and a metal carbene, Figure 2.24.



$Cp_2[W]{=}CHR^1 + CH_2{=}CHR^2$ $Cp_2[W]{=}CH_2 + CHR^1{=}CHR^2$

(Cp = cyclopentadiene ligand)

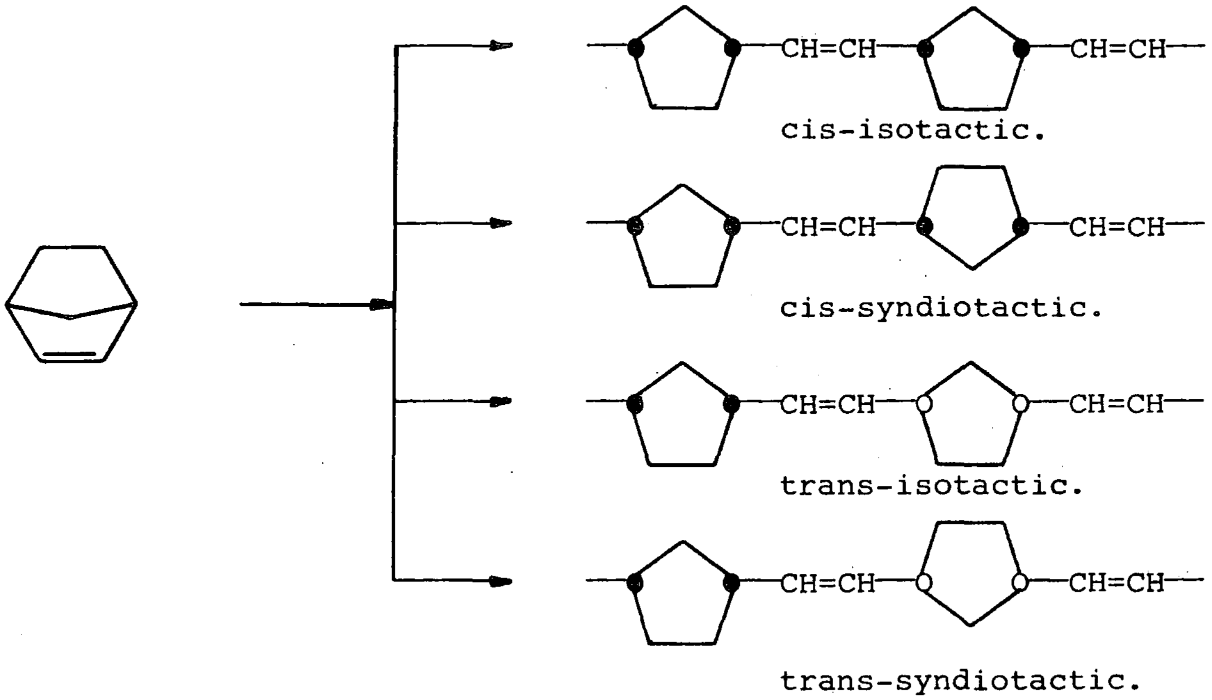
Figure 2.24

(II) Tacticity and stereoregularity studies of polyalkenamers

In the ring-opening polymerisation of cycloalkenes by metathesis it has been observed by infrared and ^{13}C-nmr spectroscopy that both cis and trans C=C bonds can be formed in the polymer chain, and that the relative proportions alter depending upon the catalyst system used, and on temperature.

For example, the catalyst system $WF_6/EtAlCl_2$ converts cyclopentene to almost 100% cis-poly(1-pentenylene),[101] whereas $WCl_6/EtOH/EtAlCl_2$ produces 84% trans double bonds.[102] With WCl_6/tetraalkylsilane, cyclopentene is polymerised to 100% cis-poly(1-pentenylene) at -78°C to -20°C, but to 80% trans-poly(1-pentenylene) at 30°C.[103]

For polycyclic alkenes, in addition to differing cis and trans content, ring tacticity must be considered. Thus for bicyclo[2,2,1]hept-2-ene, four different chain tacticities could be produced, Figure 2.25.



● = C-H bond out of plane of page.

O = C-H bond into plane of page.

Figure 2.25 <u>Tacticity in polymers derived from bicyclo[2,2,1]hept-2-ene</u>

For a monomer which lacks the symmetry of bicyclo[2,2,1]hept-2-ene isomerisation can also occur via head-head, tail-tail, or head-tail (abbreviated to HH, TT and HT) linkages. The situation is complicated and for example, Figure 2.26 shows the possible polymers derived from a single pure enantiomer of endo-5-methylbicyclo[2,2,1]hept-2-ene.

It is clear that ring-opening polymerisation of this specific monomer to give a cis-isotactic assembly requires a HTHT sequence, whereas a cis-syndiotactic assembly requires a HHTT sequence; a trans-isotactic assembly requires a HHTT sequence, whereas a trans-syndiotactic assembly requires a HTHT sequence. Ivin and coworkers have used detailed analysis of ^{13}C-nmr spectra to investigate the stereoregulation of a wide range of different catalyst systems. This was made possible by use of resolved

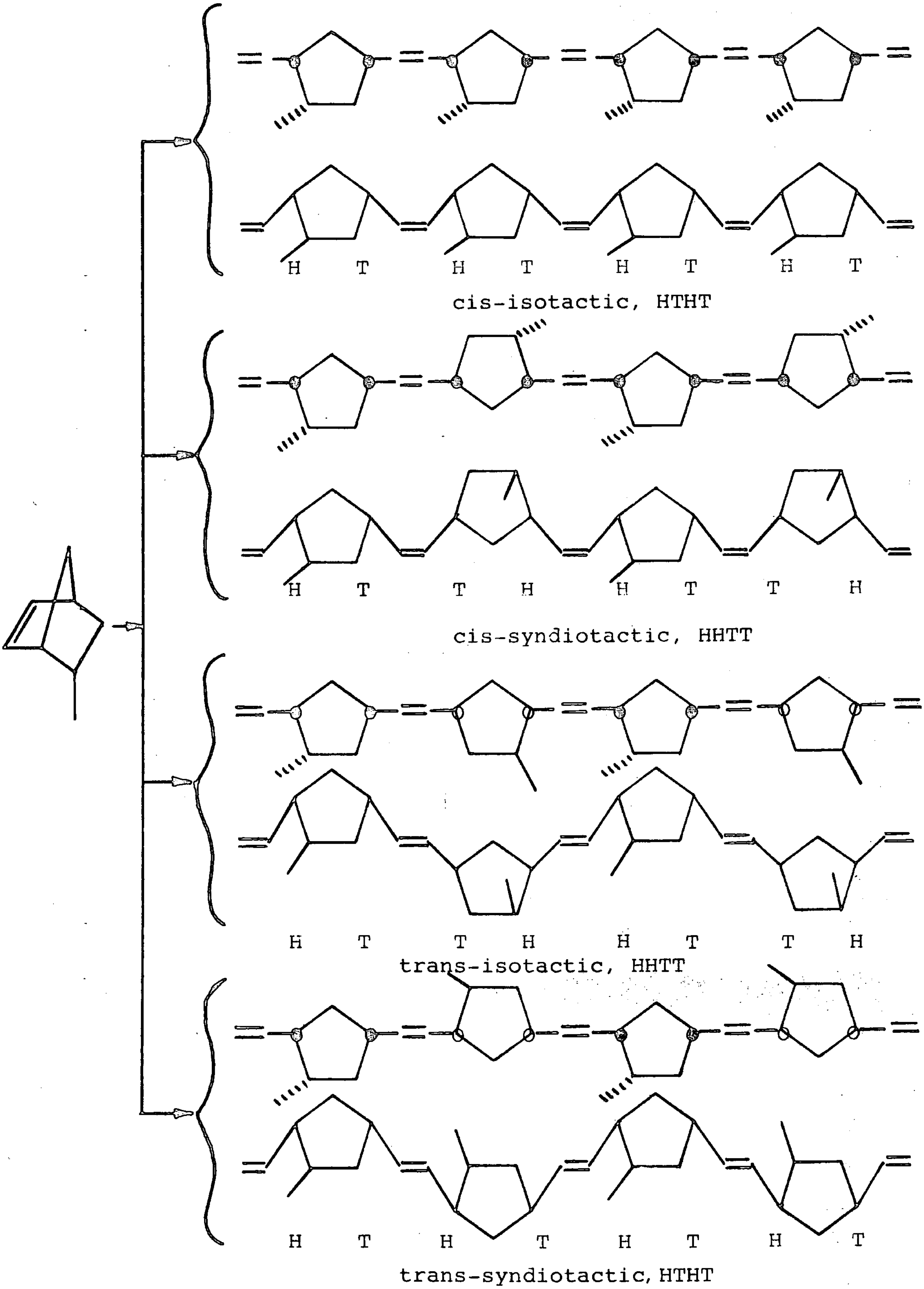
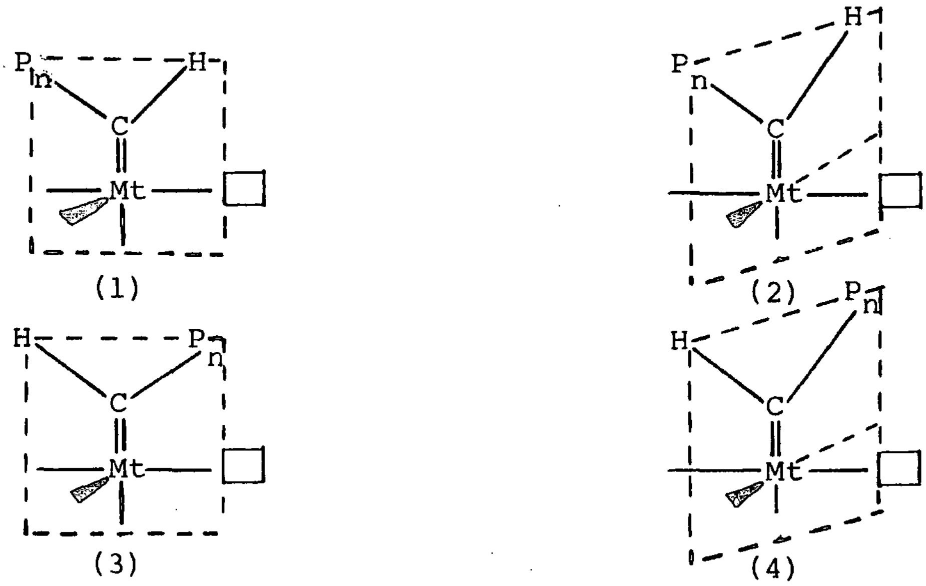


Figure 2.26 Possible assembly modes for a single pure enantiomer of endo-5-methylbicyclo[2,2,1]hept-2-ene

monomers and a knowledge of substituent shift effects which allowed clear distinction between HHTT and HTHT sequences in polymers which had largely cis or trans vinylene units.[104-111] In this analysis, polymerisations using racemic monomers have to be regarded as copolymerisations.

Ivin and coworkers have produced a mechanistic model to rationalise the observed results. This work has allowed them to develop a satisfactory account of the mechanism of stereoregulation in metathesis polymerisation, and why cis/trans double bond content changes with temperature.

Present understanding of the non-pairwise mechanism assumes reaction takes place via a transition metal carbene. Although the oxidation state and symmetry of the active transition metal complex are not known, it is assumed that the active complex, like many other transition metal complexes, has octahedral symmetry. Its structure may be represented as [Mt]=CHP$_n$, where P$_n$ is the polymer chain and Mt the metal centre. Since the incoming ligand coordinates to the active complex it is assumed that one of the octahedral sites is vacant. The carbene ligand in the complex may have one of four possible orientations with respect to the vacant site □, as shown in Figure 2.27.



(1) (2) (3) (4)

Figure 2.27

Forms (2) and (4) are mirror images, designated P_l and P_r. (1) and (3) are symmetrical forms with respect to the geometry defined by C-P_n, C-H and □, but are unlikely to occur on steric grounds.[104]

Since the exo-side of a bicyclo[2,2,1]hept-2-ene derivative is less hindered sterically,[112] it is assumed that the monomer coordinates from this side. Coupling of the monomer may occur in two ways according to the relative positions of the bridging methylene (C_7) of the monomer and the polymer chain, P_n, i.e. whether they are on the same side (syn) or on opposite sides (anti). Since there are also two possible positions of the polymer chain, (2) and (4), there are a total of 4 different propagation processes. Figure 2.28 shows one mode of addition, and its stereochemical consequence.

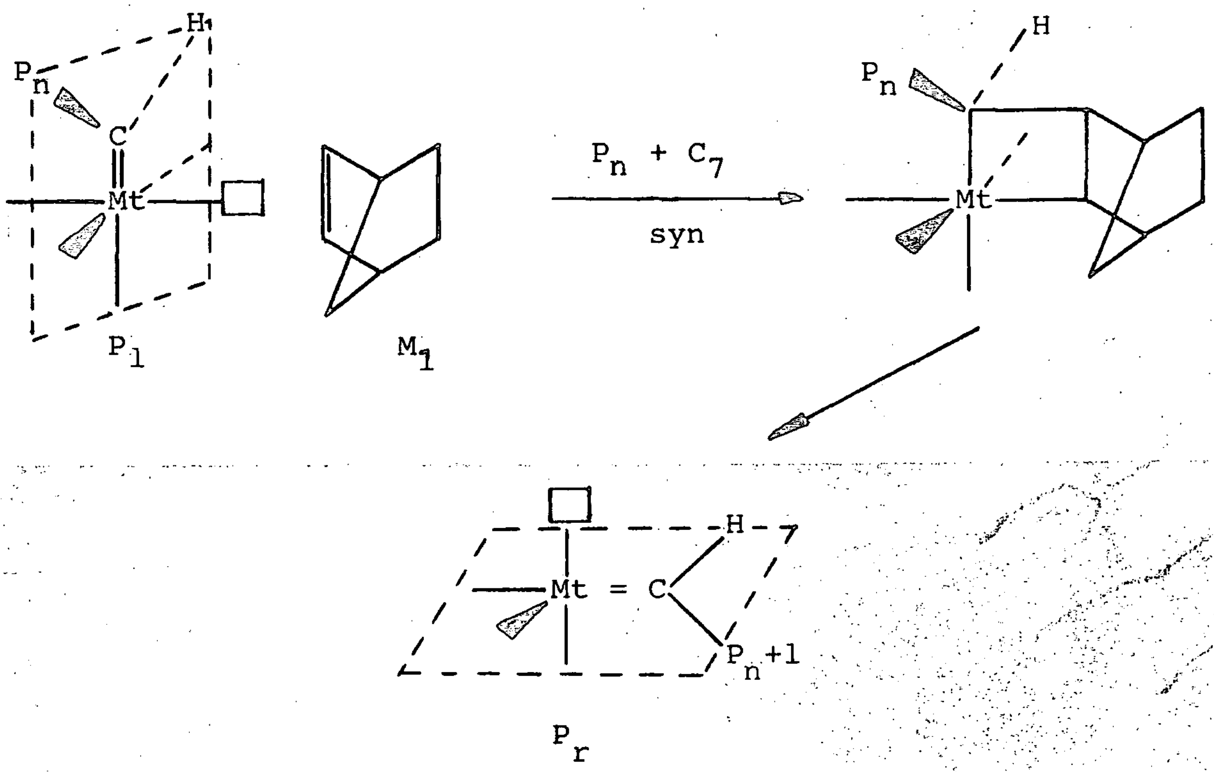


Figure 2.28

The stereochemical consequences for all possibilities are summarised in Table 2.3.

Table 2.3 Stereochemical consequences of different assembly modes

No.	Assembly mode	Double-bond form
(i)	$P_l + M_l \longrightarrow P_r$	Cis
(ii)	$P_r + M_r \longrightarrow P_l$	Cis
(iii)	$P_l + M_r \longrightarrow P_l$	Trans
(iv)	$P_r + M_l \longrightarrow P_r$	Trans

From the table it can be seen that an all cis-polymer results from propagation processes (i) and (ii) occurring in strict alternation, assuming that the propagating complex is conformationally immobile. A fully syndiotactic polymer results if monomer adds with the (C_7) bridgehead and polymer chain P_n always in a syn relationship. This result can be shown best using molecular models, but has been represented diagrammatically in Figure 2.29.

An all-trans polymer would result from the repetition of propagation process (iii) or (iv). If the propagating complex is conformationally immobile, addition of monomer with bridgehead, (C_7), and polymer chain, P_n, always on opposite sides of the complex would result in an isotactic polymer.

If the complexes P_l and P_r are racemised in some way before addition of every monomer unit, an atactic polymer would be formed, independent of cis and trans content.

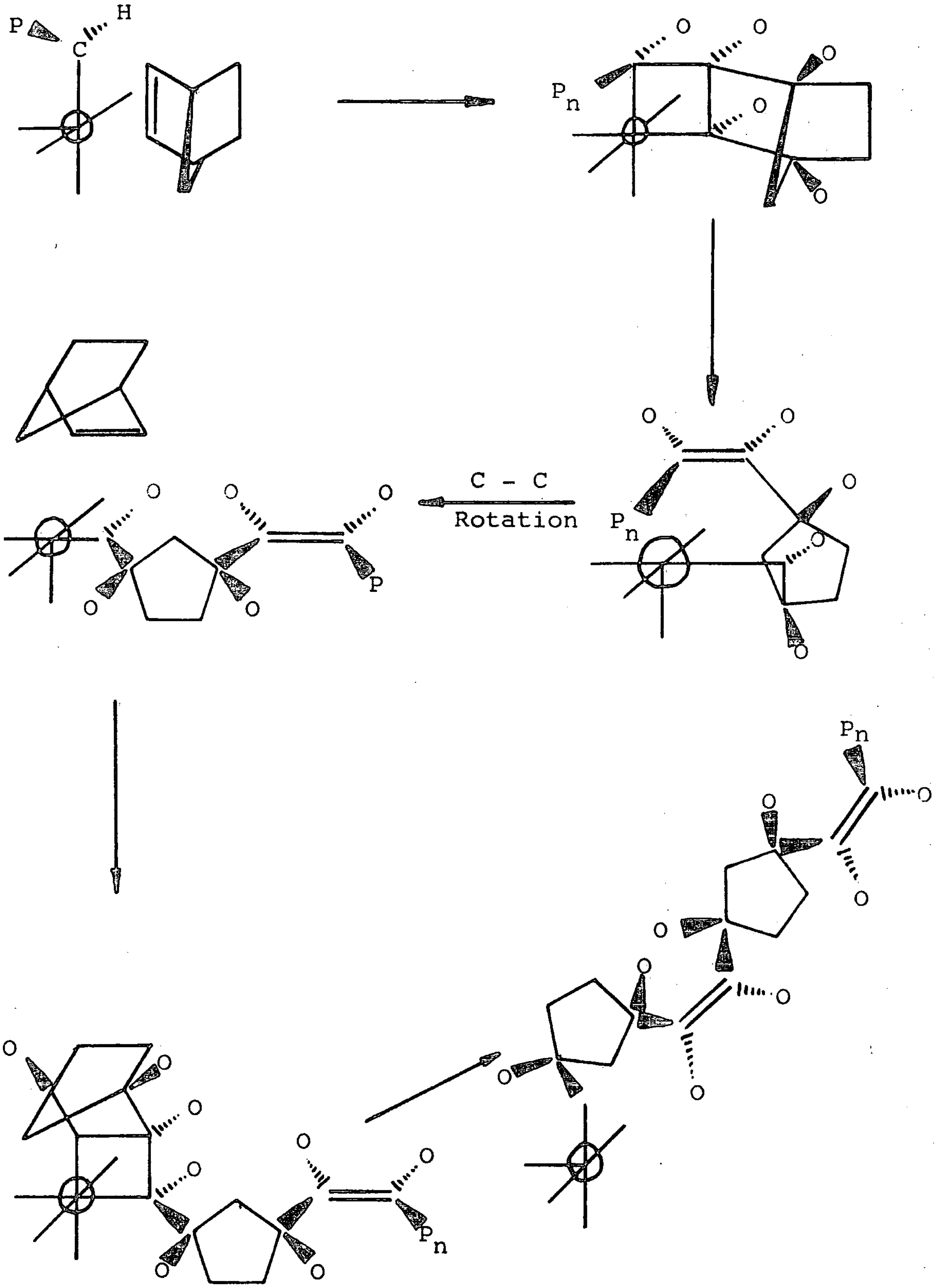


Figure 2.29

In Ivin's use of ^{13}C-nmr spectroscopy to investigate the validity of the model, bicyclo[2,2,1]hept-2-ene was first investigaged and showed no fine structure in its vinylic ^{13}C-nmr resonances, so (+)-exo-5-methyl bicyclo[2,2,1]hept-2-ene was used. When this monomer was polymerised using $ReCl_5$, an all-cis polymer was produced, which was fully syndiotactic, in support of the model. A 74/26 cis/trans polymer was prepared from the same monomer and this contained mainly syndiotactic cis junctions and isotactic trans junctions.

Using $RuCl_3$/cyclooctadiene as the catalyst system, a high-trans polymer was produced (11/89 cis/trans). However, this polymer was found to be atactic, not isotactic as expected.

This result was accounted for in the model by assuming that when a high-trans polymer is produced, the conformations (2) and (4) which are immobile in the production of the all-cis polymer, no longer remain distinct; rather there is total relaxation before every addition of monomer, either into equal proportions of P_l and P_r or into some kind of symmetrical structure, designated Ps to which the monomer units add as M_l or M_r with equal probability. Ps may not necessarily be the octahedral species (1) or (3), but may be a square pyramidal or trigonal bipyramidal complex containing no formal vacant position.

Also, polymers containing 35-80% cis double bonds were found to contain blocks of cis double bonds containing blocks of trans double bonds, rather than a random mixture of cis and trans double bonds. This suggests that the two postulated propagating species, P_l/P_r and Ps are kinetically distinct, so that for a high-cis polymer the formation of a cis or trans double bond depends on the structure of the previously formed double bond. High-trans polymers contain random cis and trans double bonds reflecting the total relaxation to Ps before addition of every monomer unit.

The kinetic relationship was summarised and is shown in Figure 2.30.

$$\begin{tikzcd}
P_1(Pr) + M \arrow[r, "k_2"] \arrow[d, "k_1"'] & Pr(P_1) & (cis). \\
Ps \arrow[ru, "+M", "k_{3c}"'] \arrow[r, "+M", "k_{3t}"'] & Ps & (trans).
\end{tikzcd}$$

Figure 2.30

The model also accounts for the variation in cis-content with temperature. $WCl_6/(CH_2=CHCH_2)_4Si$ produces 100% cis-poly(1-pentenylene) when cyclopentene is polymerised at -80°C to -20°C, but 20% cis-poly(1-pentenylene) at 30°C.

At low temperature, relaxation process k_1 is negligible, and propagation proceeds via k_2 to give an all-cis polymer. However, if $E_1>E_2$ (the activation energies for processes 1 and 2 in Figure 2.30) a temperature will be reached where $k_1>>k_2[M]$ and propagation proceeds entirely by addition to Ps. If $k_{3t}>k_{3c}$ the formation of trans double bonds is favoured. (E_1-E_2 was calculated to be 55kJ/mol).

$ReCl_5$ and $Ph_2C=W(CO)_5$ presumably give all-cis polymers of bicyclo[2,2,1]hept-2-ene at room temperature, since then $k_1<<k_2[M]$. In support of this it was shown that dilution or an increase in temperature caused a decrease in cis-content.

With iridium and rhodium-based catalysts, atactic polymers result, indicating $k_1 >> k_2[M]$.

The reason for the different behaviour of different catalyst systems was postulated as being connected with the extent of dπ-pπ bonding of the ligands in the complex. If dπ-pπ bonding is strong, the relaxation process to Ps is slow, especially if a change of symmetry is involved.

This area of research is currently very active and new data is continually being added; however, the model proposed has so far accounted satisfactorily for the information available.

(iii) Termination steps

Termination of the olefin metathesis reaction can occur by destruction of the active species by impurities, or by a side-reaction. A common reaction of carbenes is cyclopropene formation, and this is a plausible chain termination step, Figure 2.31.

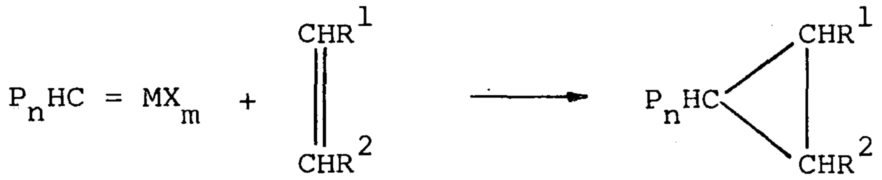


Figure 2.31

A second common carbene reaction involves hydrogen migration, and termination via this process is illustrated in Figure 2.32.

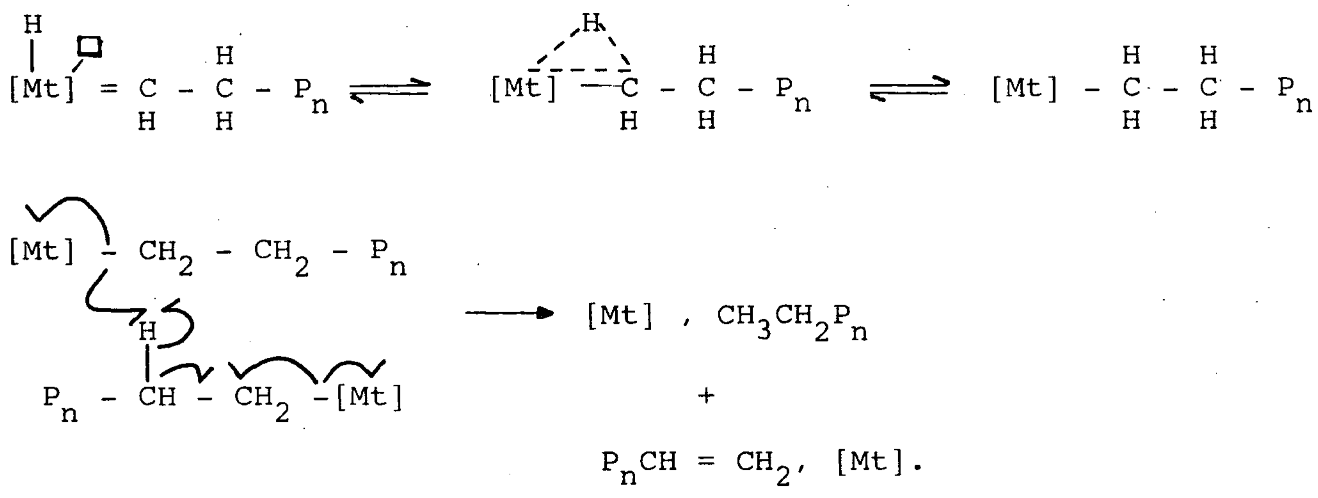


Figure 2.32

Chain transfer via a backbiting process is also possible and accounts for the observation of cyclic products in some cases.

As mentioned earlier, excess oxygen or moisture, or any impurity in the reactants or solvents totally destroys metathesis activity.

2.5 Applications of the olefin metathesis reaction

(a) Synthesis of unsaturated polymers

Monocyclic alkenes from C_4 to C_{12} with the exception of cyclohexene[32] undergo ring-opening polymerisation to produce poly(alkenylenes). The properties of the resulting polymers vary from amorphous elastomers to crystalline materials, depending on the structure of the repeat unit and double bond configuration.

As described previously, by choosing the appropriate catalyst system, polymer stereoregularity can be controlled, as in Ziegler-Natta polymerisation. Unlike Ziegler-Natta polymerisation however, unsaturation is maintained along the polymer chain, hence a totally new class of polymers has arisen.

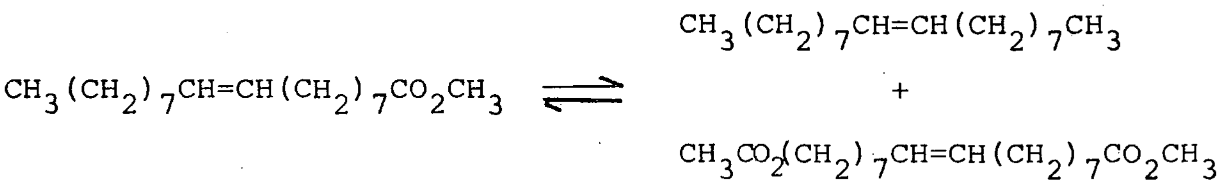
Some poly(alkenylenes) which have commercial potential are trans-poly(1-pentenylene)[42,113,114] for tyre manufacture, poly(4-cyano-1,3-cyclopentylene vinylene)[115] as a thermoplastic resin, poly(1,3-cyclopentylene vinylene) and poly-(1-octenamer). The latter two polymers were commercialised under the trade names Norsorex[116] and Vestenamer 8012R.[117]

(b) Metathesis of substrates bearing polar groups

The metathesis of substrates bearing polar functional groups is a relatively new venture. Until recently, most metathesis catalysts could not withstand the poisoning effect of electronegative atoms such as O, N or S. However, in 1972, Boelhouwer[118] and coworkers discovered a new generation of catalyst systems capable of tolerating a wide variety of functional groups. Since 1972, a large number of substrates have been metathesised, with interesting potential applications in such areas as perfume chemistry, insect control via pheromone synthesis, flame and oil-resistant elastomers and speciality plastics.

(i) Functionalised acyclic olefins

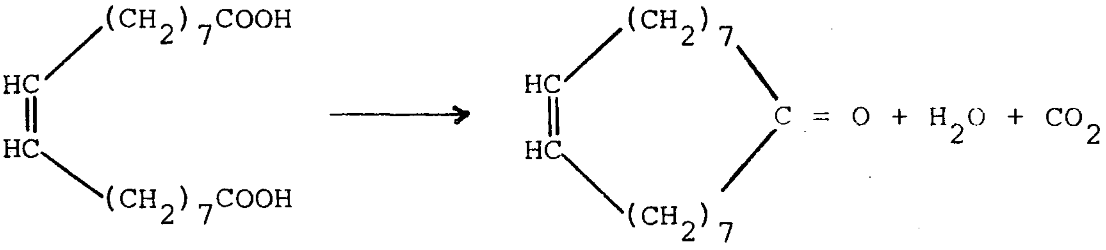
In 1972, Boelhouwer[118] reported the metathesis of methyl oleate (cis isomer) and methyl elaidate (trans isomer) with an homogeneous catalyst system based on $WCl_6/SnMe_4$ in a 1/1·4 molar ratio. Reaction took place at 70^{o}C with an ester/W ratio of 33/1. 49% and 52% conversion was obtained for the cis- and trans-isomers respectively, Figure 2.33.



$$CH_3(CH_2)_7CH{=}CH(CH_2)_7CO_2CH_3 \rightleftharpoons \begin{array}{c} CH_3(CH_2)_7CH{=}CH(CH_2)_7CH_3 \\ + \\ CH_3CO_2(CH_2)_7CH{=}CH(CH_2)_7CO_2CH_3 \end{array}$$

Figure 2.33

Other esters were also metathesised by this system.[119,120] The reaction is of importance commercially since the products may be used as precursors for the production of perfumes. For example, olive oil, consisting mainly of the triglycerides of oleic acid produces the glyceride of 9-octadecene-1,18-dioic acid from which civetone, a musk oil, is obtained after saponification, acidification, low temperature crystallisation and intramolecular condensation of the free acid,[121] Figure 2.34.



Free acid. Civetone.

Figure 2.34

Boelhouwer reported that related catalyst combinations such as $WCl_6/(C_2H_5)_4Sn$, $WCl_6/(C_4H_9)_4Sn$, WCl_6/Ph_4Sn and $MoCl_5/Ph_4Sn$ were inactive towards metathesis of these substrates. The unique activity of $SnMe_4$ as cocatalyst is not fully understood.

In 1976 additional catalyst systems which are effective for the metathesis of olefins bearing polar functional groups were reported by Nakamura. WCl_6 or $(C_2H_5O)_2MoCl_3$ with Et_3B cocatalyst were used at 178°C to convert cis-9-octadecenyl acetate to 1,18-diacetoxy-9-octadecene and 9-octadecene,[122] Figure 2.35.

$$\mathrm{CH_3(CH_2)_7CH{=}CH(CH_2)_7CH_2OAc} \rightleftharpoons \begin{array}{c} \mathrm{AcOCH_2(CH_2)_7CH{=}CH(CH_2)_7CH_2OAc} \\ + \\ \mathrm{CH_3(CH_2)_7CH{=}CH(CH_2)_7CH_3} \end{array}$$

Figure 2.35

Nakamura subsequently reported that WCl_6, $MoCl_5$, $Mo(OC_2H_5)_2Cl_3$, and $W(CO)_6$ with $(CH_3)_3Al_2Cl_3$ cocatalyst were active towards the metathesis of fatty acid esters, as well as alkenyl nitriles, ketones, ethers, amides and oxysilanes.[123]

$WCl_6/(CH_3)_3Al_2Cl_3$ catalysed the reaction summarised in Figure 2.33 in 20-25% yield at 28°C, using a mole ratio of ester/W/Al of 30/1/2.

Cross metathesis of oleyl acetate and 5-decene, Figure 2.36, occurred in 26% yield. A small amount of homometathesis products were also produced.

$$\begin{array}{c} \mathrm{CH_3(CH_2)_7CH{=}CH(CH_2)_7CH_2OAc} + \mathrm{CH_3(CH_2)_3CH{=}CH(CH_2)_3CH_3} \\ \downarrow \\ \mathrm{CH_3(CH_2)_3CH{=}CH(CH_2)_7CH_2OAc} \end{array}$$

Figure 2.36

7-Tetradecene should also be formed in this reaction but its presence was not reported. Its cis-isomer is an insect pheromone.

$WCl_6/(CH_3)_3Al_2Cl_3$ was active towards the metathesis of olefins substituted with N,N-dialkylamide, nitrile, p-methoxyphenyl and keto-groups, as reported earlier. Reactions were undertaken using an olefin /W/Al molar ratio of 15/1/3 but the yields obtained were only 2-10%, and consequently the reactions are of little value.

The systems were inactive towards the metathesis of unsaturated carboxylic acids, alcohols, primary amines, and unsubstituted carboxyamides.

In parallel to Boelhouwer's work, related systems such as $WCl_6/C_2H_5OH/C_2H_5AlCl_2$, Re_2O_7/Al_2O_3, $WCl_6/(C_2H_5)_3Al_2Cl_3$ and $WCl_6/(C_2H_5)_3Al$ were found to be inactive towards these substrates.

Basset and coworkers[124] have found that amino-olefins, such as allyl amine and the N,N-dimethyl derivative fail to undergo metathesis, but that unsaturated quaternary ammonium salts were active towards metathesis at 25°C, using zero-valent molybdenum and tungsten catalysts activated with molecular oxygen, Figure 2.37.

$$CH_2 = CHCH_2\overset{+}{N}(CH_3)_3Br^- \rightleftharpoons \begin{array}{c} CH_2 = CH_2 \\ + \\ Br^-(CH_3)_3\overset{+}{N}CH_2CH = CHCH_2\overset{+}{N}(CH_3)_3Br^- \end{array}$$

Figure 2.37

The systems used were olefin/(mesitylene)$W(CO)_3/C_2H_5AlCl_2/O_2$ in a 20/1/24/80 ratio and olefin/$Mo(NO)_2Cl_2[P(Ph)_3]/C_2H_5AlCl_2$ in a 20/1/24 ratio. Yields were 8-23%.

Boelhouwer[125] has reported that the heterogeneous catalyst system $Re_2O_7/(CH_3)_4Sn$ is active towards the metathesis of methyl-4-pentenoate at 50°C, producing 4-octene-1,8-dioic acid dimethyl ester and ethylene in 51% yield. A ratio of olefin/Re/Sn of 219/6/1 was used, the degree of selectivity was >99%, and the system was found to be inactive without $Sn(CH_3)_4$.

(ii) Functionalised cycloalkenes

When polar functional groups are substituents in cycloalkenes, they inhibit metathesis less than for acyclic alkenes. Release of ring strain provides a significant driving force for these reactions to proceed and may compensate for any inhibition due to substituents.

Bicyclo[2,2,1]hept-2-ene containing various functional groups have been ring-open polymerised by metathesis to prepare polymers of the general type shown in Figure 2.38.

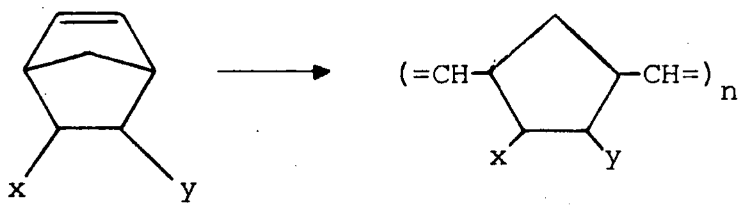


Figure 2.38

From 1965 to 1970, polymerisations of this type were carried out in protic solvents (alcohol, water) using iridium, ruthenium or osmium-based catalysts. Derivatives containing ester,[126-128] hydroxy,[128] chlorine,[129] alkoxy,[130] and imide[126] functionalities were used as substrates.

These were effectively emulsion polymerisations. Reactions were carried out in an alcoholic medium in which the monomer and transition metal catalyst were dispersed either using an emulsifier[128] at 50°C, or by refluxing the reaction mixture.[129] Alternatively the reaction was carried out in a sealed ampoule at 90°C.[126,127,130]

The most effective catalysts were $RuCl_3.3H_2O$ and $(NH_4)_2IrCl_6$.

The alcoholic medium was believed to play an important part as a reducing agent in these reactions. Yields were found to be negligible if no reducing agent was present. Presumably the active species is a low-oxidation state transition metal species.

Since the discovery of Boelhouwer's catalyst system in 1972, homogeneous catalyst systems based on WCl_6 have been employed to ring-open polymerise bicyclo[2,2,1]hept-2-ene derivatives substituted by ester,[130-138] nitrile,[134,136,137,139,140,142,144] amide,[136,137,141] imide,[132,136,137,143] chlorine,[142] anhydride,[136,137] alkoxy[145,146] and pyridyl[136,137] functional groups. Monomer/tungsten ratios employed were as high as 2000/1 typical for polymerisations of unsubstituted substrates. Alkyl aluminiums were used as cocatalysts. Reaction temperatures from 15°C to 70°C were used. Catalyst modifiers were employed to increase metathesis activity. These contained polar groups such as alcohols, peroxides, epoxides, acetals, $Ti(OR)_4$, $FeCl_3$ and $Al(OR)_3$.[136,137] The polymers produced are potentially of commercial interest hence most of the references cited are from patent literature.

Other functionally substituted bicyclo[2,2,1]hept-2-ene derivatives which have been ring-open polymerised include fluorinated derivatives,[147-149] examples of which are shown in Figure 2.39 and aryl-substituted derivatives,[150] Figure 2.40. Catalysts consisted of WCl_6 or $MoCl_5$ together with organotin cocatalysts.

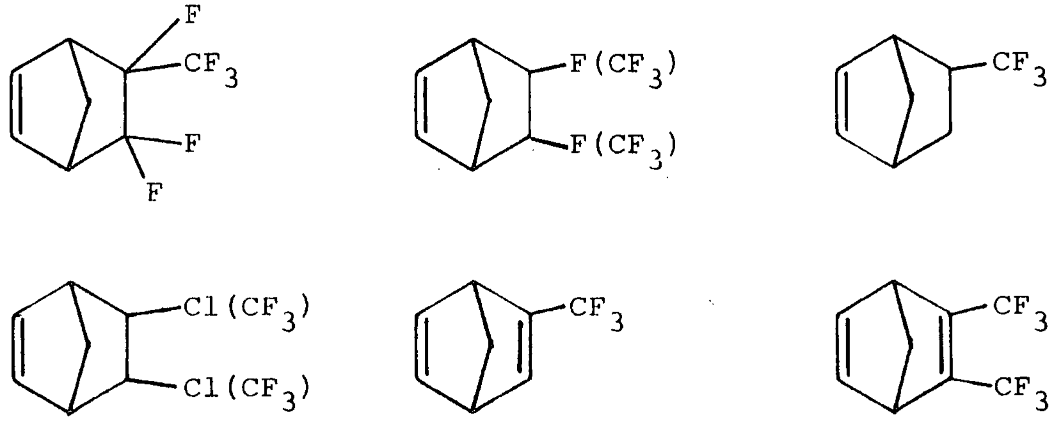


Figure 2.39

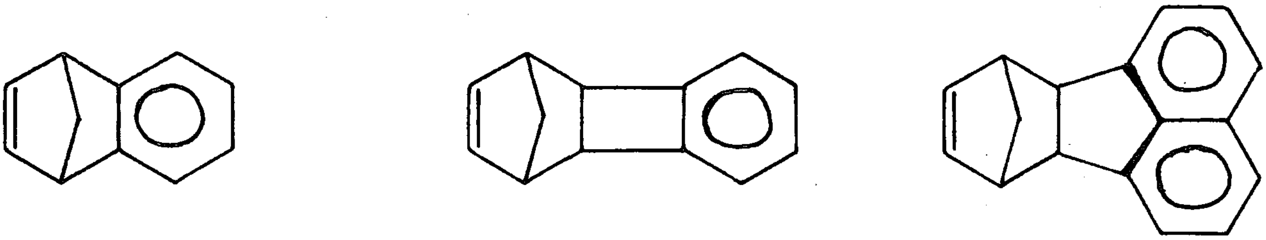


Figure 2.40

Recently Streck[117] reported new silicon-containing polymers, and new tin-containing polymers which appear to have interesting bacteriocidal properties. Two of the monomers used are shown in Figure 2.41.

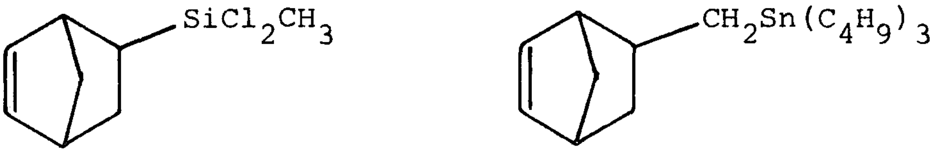


Figure 2.41

Other polyalkenamers, containing pendant ester groups were produced by Ast.[151] Adducts of bicyclo[2,2,1]hepta-2,5-diene, 1,5-cyclooctadiene, and 1,5,9-cis, trans, trans-cyclo dodecatriene with ethyl diazoacetate, Figure 2.42, undergo ring-opening polymerisation using $WCl_6/SnMe_4$

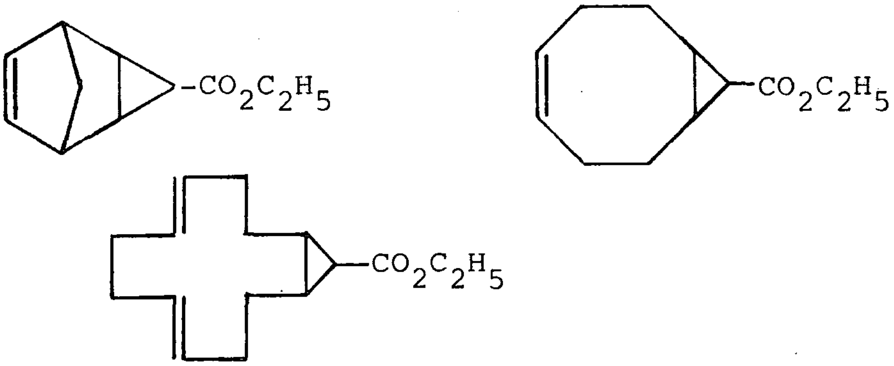


Figure 2.42

Katz[63,65] recently reported that 1-methylcyclobutene and 2-methyl bicyclo[2,2,1]hept-2-ene ring-open polymerise, Figure 2.43. Reaction of a substrate undergoing metathesis at a substituted double bond is rare, although it has also been reported that the exceptionally strained 1,2-dimethylcyclopropene is ring-opened by $(\pi\text{-allyl})_2PdCl_2$ in ether at $0^{o}C$,[152] Figure 2.44.

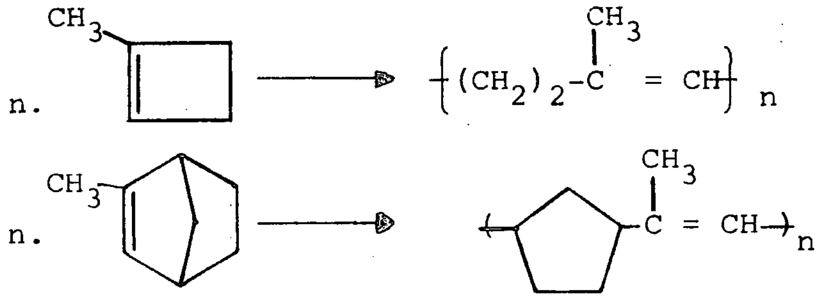


Figure 2.43

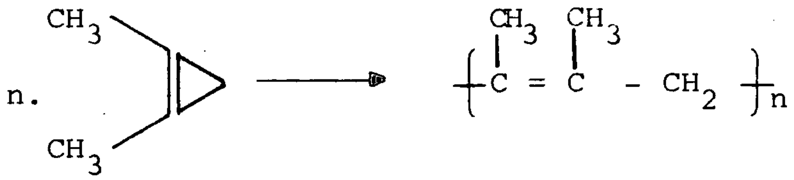


Figure 2.44

If the double-bond substituent is chlorine, however, reaction is prevented. This is exemplified by the ring-opening polymerisation of 1-chloro-1,5-cyclo octadiene[153] which yields a perfectly alternating copolymer of butadiene and chloroprene via metathesis exclusively at the unsubstituted double bond, Figure 2.45.

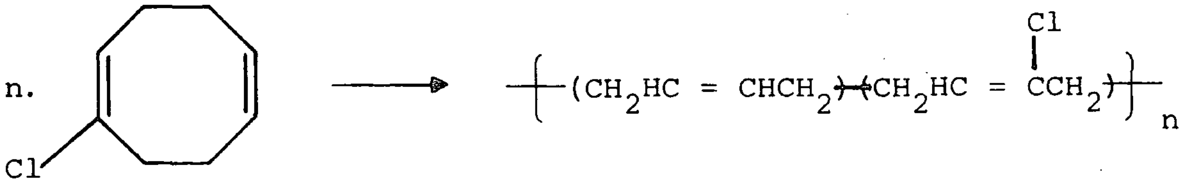


Figure 2.45

Similarly 1-methyl-1,5-cyclooctadiene[154] yields a perfectly alternating copolymer of butadiene and isoprene.

5-methylcyclooctene[155] yields a perfectly alternating terpolymer of butadiene, ethylene and propylene, Figure 2.46.

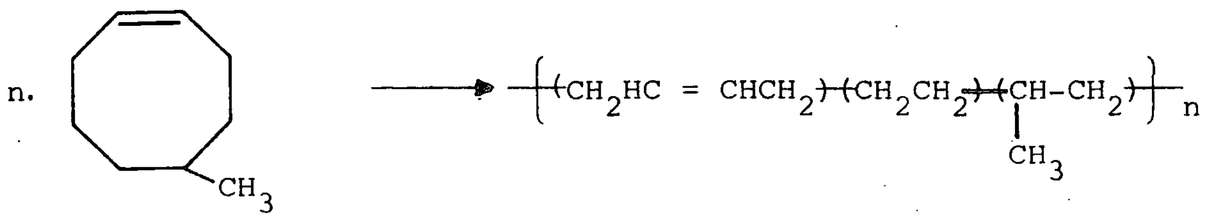


Figure 2.46

The inhibitory effect of a chlorine-substituent at the double bond was confirmed by Bell.[156] Ring-opening polymerisation and copolymerisation of the Diels-Alder adduct of 1,5-cyclooctadiene and hexachlorocyclopentadiene occurred via reaction at the unsubstituted double bond, Figure 2.47. The resulting polymers were found to be thermally stable flame- and oil-resistant materials.

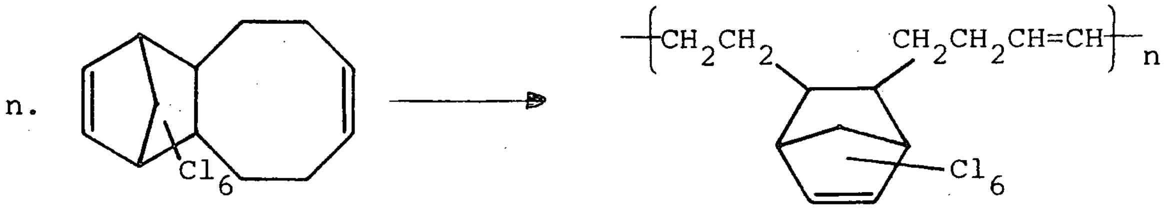


Figure 2.47

(c) Miscellaneous applications

(i) Polysilapentenamer and polygermapentenamer

Heterocyclic cyclopentenoid compounds containing silicon[48,157] and germanium[158] have been reported to undergo ring-opening polymerisation to produce polymers containing heteroatoms in the polymer backbone, Figure 2.48.

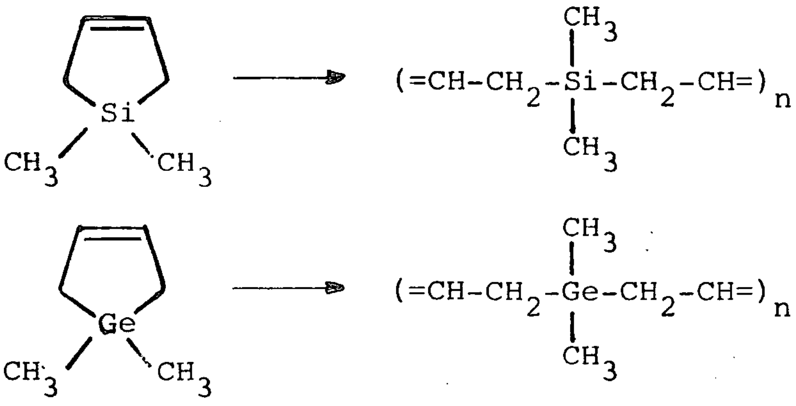


Figure 2.48

(ii) Ring-opening polymerisation of a lactone by metathesis

The naturally occurring lactone, ambrettolide, was ring-open polymerised[159] using the $WCl_6/SnMe_4$ catalyst system and a mole ratio of lactone/W/Sn of 50/1/5 at 90°C, producing a high molecular weight unsaturated polyester in 80% yield, Figure 2.49.

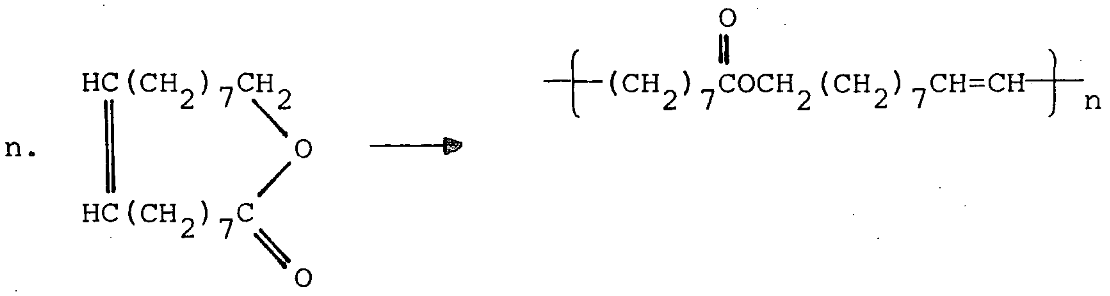


Figure 2.49

Interesting rubbery copolymers were also produced using cyclopentene, cyclooctene, and 1,5-cyclooctadiene as comonomers.

(iii) Synthesis of macrocycles

The metathesis of cycloalkenes under conditions of high monomer dilution produces macrocyclic compounds in high yields.[160-162] The reaction is of commercial importance since the products are the basis of musks and perfumes. For example Wideman[163] reported the dimerisation of cyclooctene to produce cyclohexadeca-1,9-diene whose ketone is a musk-oil, Figure 2.50.

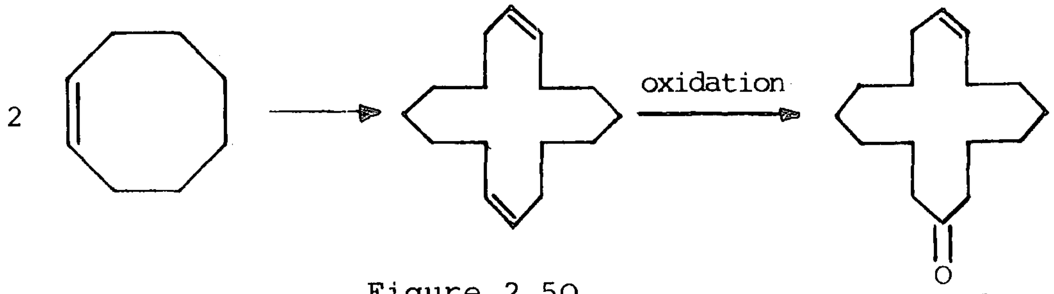


Figure 2.50

Catenanes[164,165] have also been produced by metathesis of cyclododecene using $WCl_6/EtAlCl_2/EtOH$ in hexane. C_{24}, C_{36},

C_{48}, C_{60} and C_{72} homologues were identified by mass spectroscopy. The mechanism for their production is believed to involve an intramolecular metathesis reaction, a 360° macrocyclic ring twist, then a further intramolecular metathesis reaction, Figure 2.51.

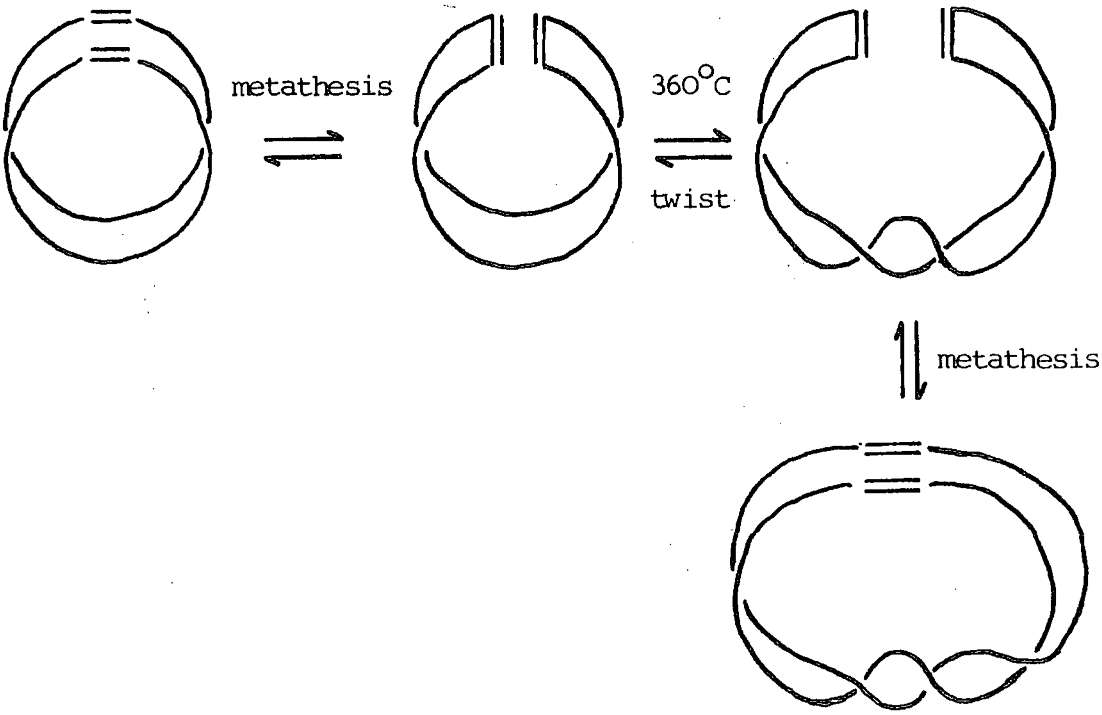


Figure 2.51

(iv) Polymer degradation and characterisation by cross-metathesis with acyclic alkenes

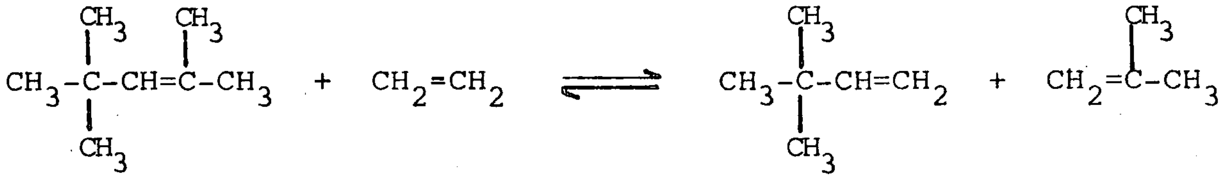
The cross-metathesis of acyclic alkenes with cycloalkenes produces oligomeric products. Their molecular weight depends upon the ratio of acyclic alkene to cycloalkene in the reaction.[166-172]

Cross-metathesis reactions have also been used in the characterisation of unsaturated polymers.[173-183] The polymers are degraded to yield oligomers which are characterised giving information about the unsaturated linkages in the polymer.

(v) Acyclic alkenes

Banks[184,51] has reported a recent industrial use of metathesis in the large scale production of acyclic alkenes. The first example of this was the "Triolefin process" developed by the Phillips Petroleum Company, converting propene which is cheap and abundant, into high purity ethene and linear butenes.

The "neohexene process" provides a second example. In this process, diisobutene (2,4,4-trimethylpent-2-ene) is cross-metathesised with ethene to produce neohexene (3,3-dimethyl but-1-ene) and isobutene (2-methyl propene), Figure 2.52.



$$CH_3-\overset{CH_3}{\underset{CH_3}{C}}-CH=\overset{CH_3}{C}-CH_3 + CH_2=CH_2 \rightleftharpoons CH_3-\overset{CH_3}{\underset{CH_3}{C}}-CH=CH_2 + CH_2=\overset{CH_3}{C}-CH_3$$

Figure 2.52

An heterogeneous catalyst system based on WO_3 supported on a mixture of SiO_2 and MgO is used. Neohexene is an important intermediate in the perfume industry. For example, a bicyclic synthetic musk 7-acetyl-1,1,3,4,4,6-hexamethyl tetralin may be obtained from neohexene as shown in Figure 2.53. Such bicyclic musks have excellent odour and fixative properties, and simulate macrocyclic musks. They are produced from inexpensive raw materials, are colourless, and have exceptional stability towards alkali(soap) and light.

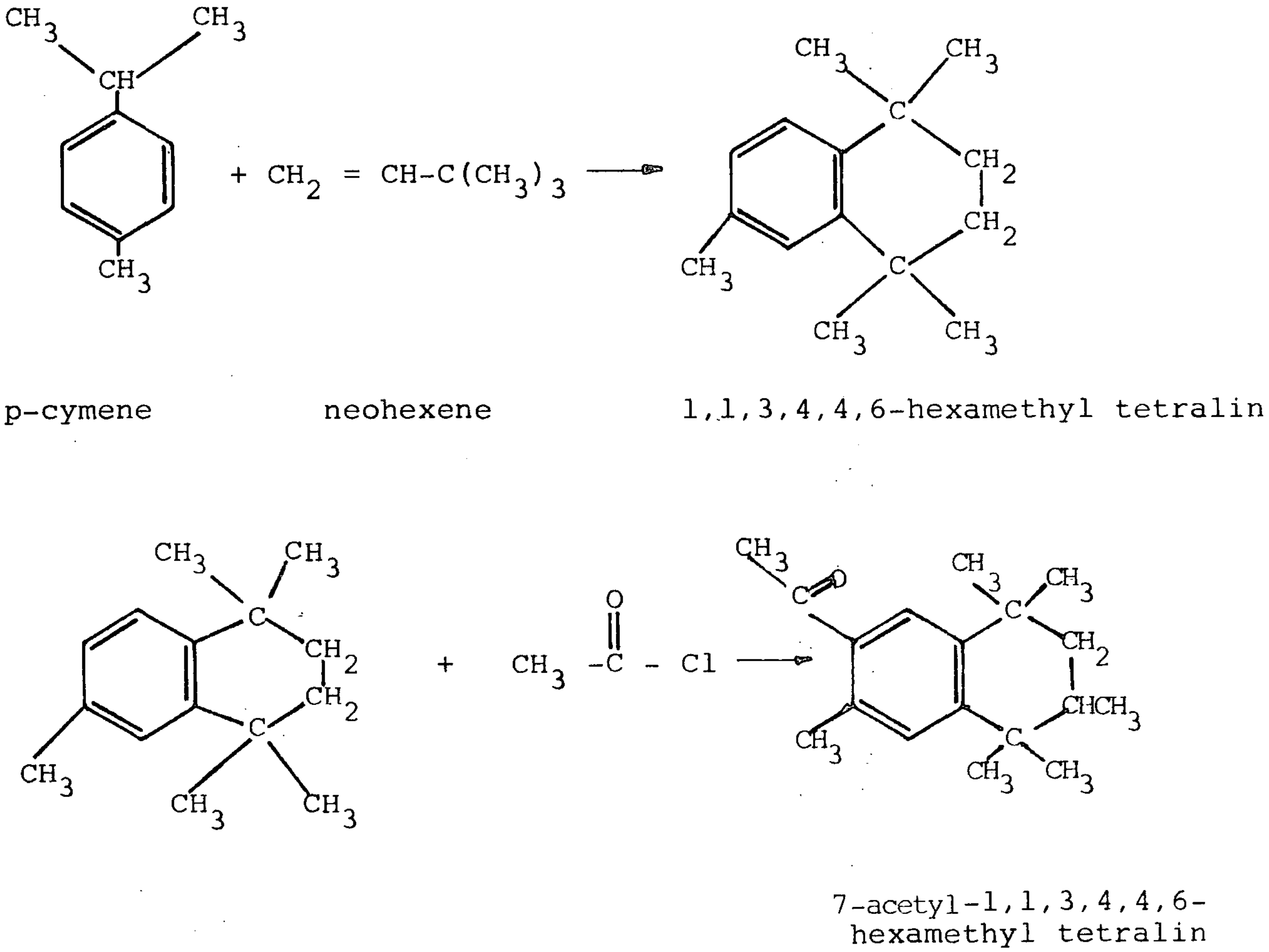
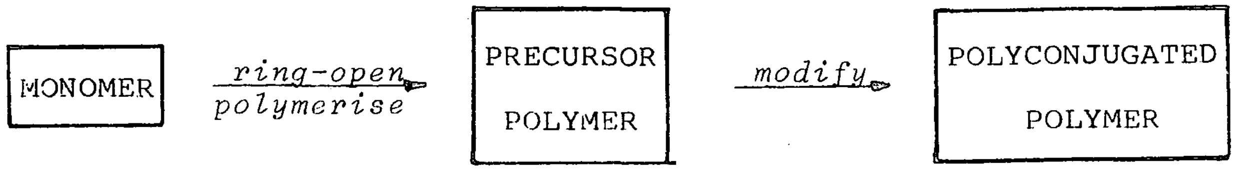


Figure 2.53

2.6 Preparation, characterisation and investigation of the ring-opening polymerisation of some heterosubstituted polycyclic alkenes

(a) Introduction

The aim of this part of the author's work was to investigate the use of metathesis ring-opening polymerisation of hetero-substituted cycloalkenes to prepare a precursor polymer which could be converted into a polyconjugated system by a simple and quantitative modification, Scheme 3.



Scheme 3

The precursor polymer should ideally be processable (soluble, or melt-processable) to allow its manipulation into the desired physical form (self-supported film, fibre, etc.). Conversion to the polyconjugated material should ideally occur quantitatively using a simple one-step modification.

For the reasons summarised in Chapter One, the monomer investigated initially was bicyclo[2,2,1]hept-5-ene-2,3-dione (I).

(b) Synthesis of bicyclo[2,2,1]hept-5-ene-2,3-dione (I).

This monomer (I) was synthesised by a 4-step route originally reported by H.-D. Scharf and coworkers,[185-190] Figure 2.54.

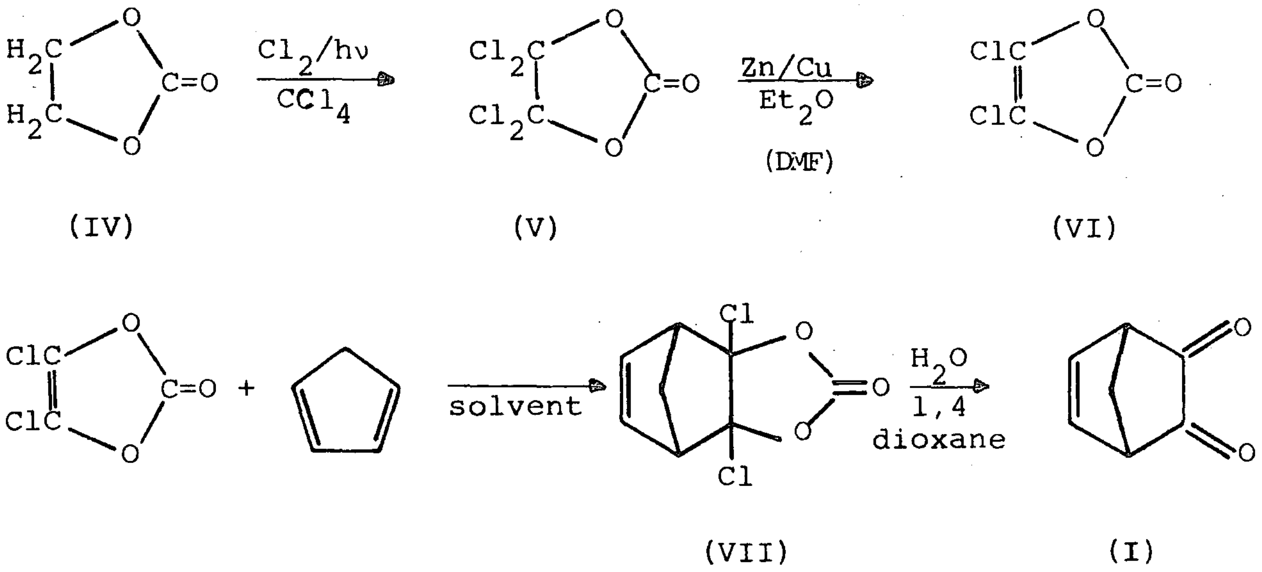


Figure 2.54 Synthesis of bicyclo[2,2,1]hept-5-ene-2,3-dione

Ethylene carbonate (1,3-dioxolan-2-one,(IV)), a cheap and commercially available material, was chlorinated in a reaction using Cl_2 in CCl_4 and initiated by UV-light[191] to give the tetrachloro derivative, 4,4,5,5-tetrachloro-1,3-dioxolan-2-one, (V). This was reacted with a Zn/Cu couple in diethyl ether containing a catalytic amount of DMF[186,192] resulting in partial dechlorination to produce dichlorovinylene carbonate (4,5-dichloro-1,3-dioxol-2-one, (VI)). The thermal Diels-Alder reaction of this weak dienophile with cyclopentadiene in CCl_4 produced the endo-1:1 adduct, endo-3a,7a-dichloro-3a,4,7,7a-tetrahydro-4,7-methano-1,3-benzodioxol-2-one, (VII). Adduct (VII) was hydrolysed in a 1,4-dioxane/water medium to yield bicyclo[2,2,1]hept-5-ene-2,3-dione (I), which is both air and light sensitive. A great deal of care was needed in order to obtain a sample pure enough for investigation of its metathesis polymerisability.

(c) Characterisation of compounds (V), (VI), (VII) and (I)

After each stage of the reactions leading to bicyclo[2,2,1]hept5-ene-2,3-dione (I), intermediate products were purified as described in the experimental section, and were fully characterised by mass spectroscopy (Appendix B), infrared (i.r.) spectroscopy (Appendix C), ^{1}H-n.m.r. and ^{13}C-n.m.r. spectroscopy.

Table 2.4 shows ^{1}H-n.m.r. shifts for compounds (VII) and (I) measured relative to TMS in $CDCl_3$. (Relative peak intensity in parentheses).

Table 2.4 ^{1}H-N.m.r. shifts for compounds (I) and (VII)

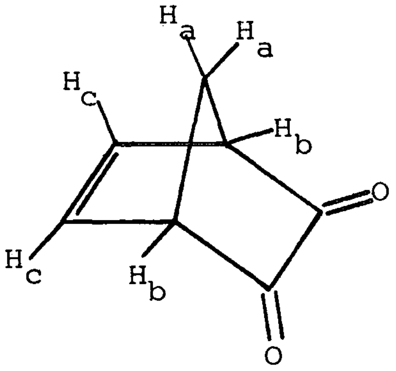
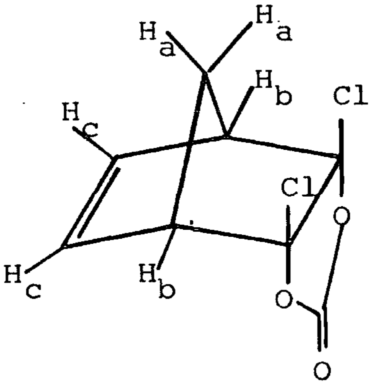
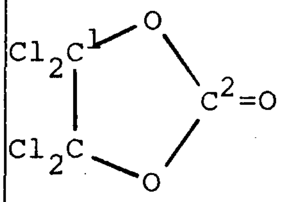
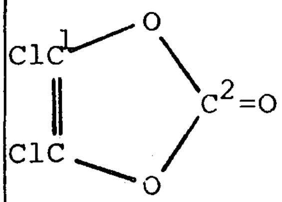
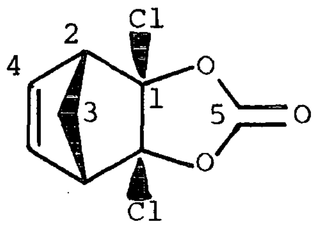
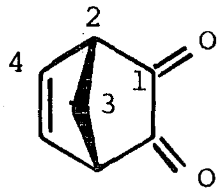
Compound		^{1}H-N.m.r. shifts (δppm.)		
		Ha	Hb	Hc
	(I)	ABq. δ_A 3.00 δ_B 2.43 J_{AB} 10Hz (2)	3.31s (2)	6.51s (2)
	(VII)	2.09 (unresolved multiplets) (1)	3.50 (1)	6.23 (1)

Table 2.5 shows the ^{13}C-n.m.r. shifts for compounds (V), (VI), (VII) and (I) measured relative to TMS in $CDCl_3$.

Table 2.5 ^{13}C-N.m.r. shifts for compounds (V), (VI), (VII) and (I)

Compound	^{13}C-N.m.r. shifts (δppm.)		
	Nucleus	Functionality	Shift
 (V)	C^1	$-\underline{C}Cl_2$	113.79
	C^2	$-\underline{C}=O$	143.16
 (VI)	C^1	$=\underline{C}Cl$	125.74
	C^2	$-\underline{C}=O$	147.05
 (VII)	C^3	$-\underline{C}H_2$	44.78
	C^2	$\rightarrow\underline{C}H$	56.74
	C^1	$-\underline{C}-Cl$	107.16
	C^4	$-\underline{C}=C-$	135.36
	C^5	$-\underline{C}=O$	149.39
 (I)	C^3	$-\underline{C}H_2$	43.38
	C^2	$\rightarrow\underline{C}H$	51.18
	C^4	$-\underline{C}=C-$	137.45
	C^1	$-\underline{C}=O$	195.39

(d) Attempted ring-opening polymerisation of bicyclo[2,2,1]hept-5-ene-2,3-dione(I)

The ring-opening polymerisation of (I) was attempted using Boelhouwer's catalyst system,[118] $WCl_6/SnMe_4$, at 70°C (mole ratio $WCl_6:SnMe_4:(I)$ of 1:2:50) since this is regarded as the most active catalyst system for the metathesis of alkenes bearing polar functional groups. No polymer was produced in any of several attempts.

(e) Attempted copolymerisation of (I) with bicyclo[2,2,1]hept-2-ene (norbornene).

In order to determine whether or not the diketone (I) is a catalyst poison, a copolymerisation with bicyclo[2,2,1]hept-2-ene (norbornene) was attempted. The reaction was performed at room temperature using a mole ratio $WCl_6:SnMe_4:(I)$:norbornene of 1:2:12:232. A small amount of polymer was isolated. Characterisation by i.r. analysis of a film cast from chloroform indicated that this was pure poly(norbornene). (4% yield with respect to input norbornene). This result suggests that the diketone (I) is an extremely poor monomer for metathesis ring-opening polymerisation. However, it does not totally poison the catalyst since some polymer was obtained.

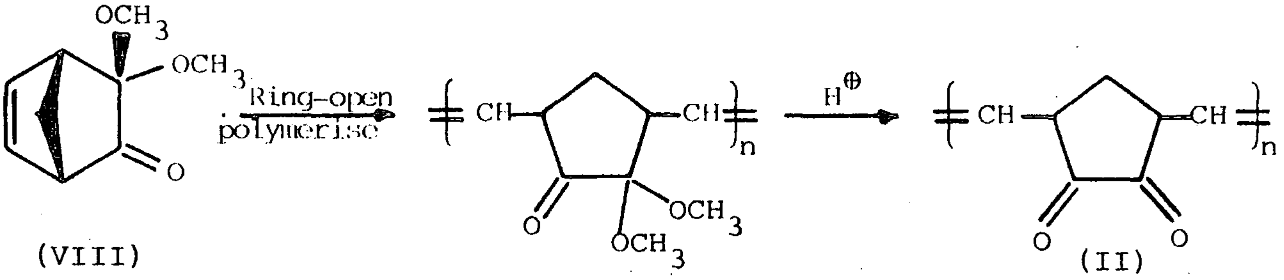
(f) Possible explanation for the poor polymerisability of bicyclo[2,2,1]hept-5-ene-2,3-dione(I)

Some studies have been made of unsaturated α-diketones using a combination of photoelectron spectroscopy and molecular orbital calculations[193] in an attempt to determine the extent of the interaction between the non-bonding orbitals of the α-dicarbonyl group and the neighbouring π-orbitals. The conclusion of these studies is that there is a significant through-bond interaction between the electronegative oxygen atoms and the π-electrons of the double bond. This results in a reduced donor capacity (increased Ionisation Potential) for the π-electrons of the double bond unit and hence accounts for the reluctance of the monomer (I) to enter into homo- or co-metathesis polymerisation. An alternative explanation is that one or other of the carbonyl groups interacts more strongly with the active transition metal carbene than the C=C bond to form a stable metalloheterocyclobutane which is unable to take part in the propagation step of the polymerisation. A third possible explanation is that both carbonyl groups coordinate to the transition metal in which case the monomer may be regarded as a bidentate oxygen ligand.

Several other heterosubstituted derivatives of bicyclo[2,2,1]hept-2-ene were synthesised and their metathesis polymerisability was determined.

(g) Synthesis and characterisation of 3,3-dimethoxy bicyclo[2,2,1]-hept-5-ene-2-one, (VIII).

This potential monomer (VIII) was synthesised by methanolysis of the 1:1 adduct (VII). As discussed by Scharf,[187] there is an equilibrium between the diketone (I) and the dimethoxy ketone (VIII), Figure 2.55; hence ring-opening polymerisation of compound (VIII) may provide an indirect route to polymer (II), Scheme 4.



Scheme 4

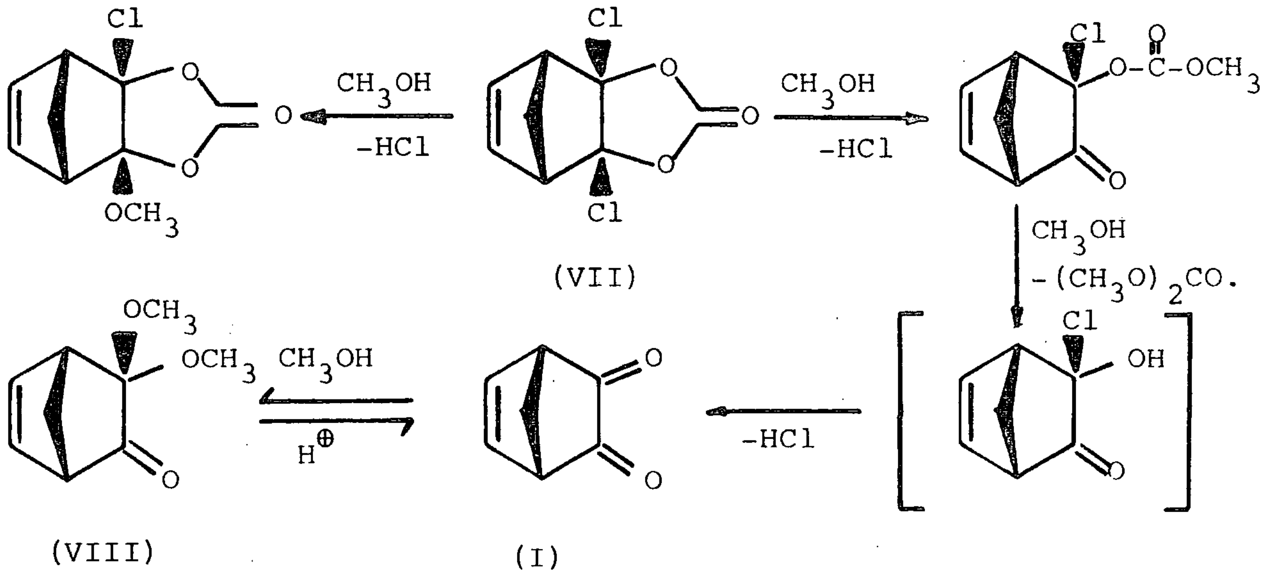


Figure 2.55

Table 2.6 shows the ^{1}H-n.m.r. shifts for compound (VIII) measured relative to TMS in $CDCl_3$ (Relative peak intensity in parentheses).

Table 2.6 ^{1}H-N.m.r. shifts for compound (VIII)

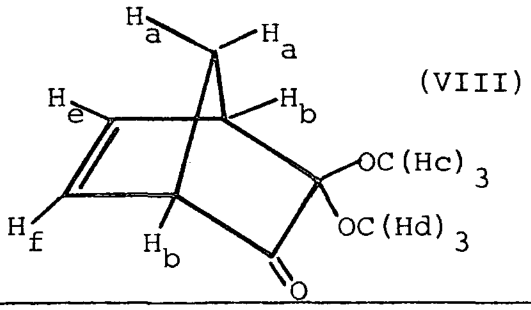
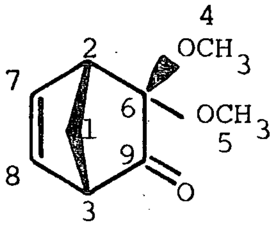
Compound	^{1}H-N.m.r. shifts (δppm.)					
	Ha	Hb	Hc	Hd	He	Hf
	2.30q broad (2)	3.07m broad (2)	3.34s (3)	3.40s (3)	6.19m (1)	6.32m (1)

Table 2.7 shows ^{13}C-n.m.r. shifts for compound (VIII) measured relative to TMS in $CDCl_3$.

Table 2.7 ^{13}C-N.m.r. shifts for compound (VIII)

Compound	^{13}C-N.m.r. shifts (δppm.)		
	Nucleus	Functionality	Shift
 (VIII)	C^1	$-\underline{C}H_2$	44.39
	C^2	$\rightarrow\underline{C}H(C(OCH_3)_2)$	46.08
	C^3	$\rightarrow\underline{C}H(C=O)$	49.84
	C^4	$-O\underline{C}H_3$	50.23
	C^5	$-O\underline{C}H_3$	53.48
	C^6	$-\underline{C}(OCH_3)_2$	97.28
	C^7	$-C=\underline{C}-$	132.49
	C^8	$-\underline{C}=C-$	138.60
	C^9	$-\underline{C}=O$	204.88

(h) Attempted ring-opening polymerisation of 3,3-dimethoxy bicyclo[2,2,1]hept-5-ene-2-one (VIII)

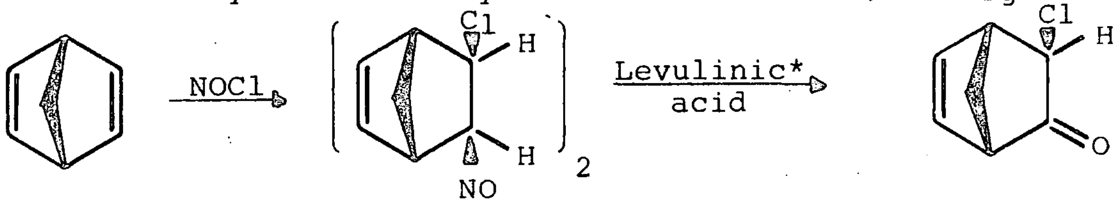
The ring-opening polymerisation of compound (VIII) was attempted with $WCl_6/SnMe_4$ at 70°C and also with $MoCl_5/SnMe_4$ at 70°C using mole ratios $WCl_6(MoCl_5):SnMe_4:(VIII)$ of 1:2:100. No polymerisation occurred in any of several attempts.

(i) Attempted copolymerisation of (VIII) with norbornene

The copolymerisation of (VIII) with norbornene was attempted at room temperature using a mole ratio $WCl_6:SnMe_4:(VIII)$:norbornene of 1:2:57:108. The solution gelled after several hours stirring and the polymer produced was isolated. Characterisation by i.r. analysis of a film cast from chloroform indicated that this was poly(norbornene) alone. (10% yield with respect to input norbornene).

(j) Synthesis and characterisation of exo-3-chlorobicyclo[2,2,1]-hept-5-ene-2-one, (IX)

Synthesis of compound (IX) was accomplished by a 2-step route initially described by Meinwald and Baker,[194] Figure 2.56.



(IX)

* Systematic name, 4-oxo-pentanoic acid

Figure 2.56

Bicyclo[2,2,1]hept-2,5-diene (norbornadiene) was treated with nitrosyl chloride, generated *in situ* using isopentylnitrite and concentrated hydrochloric acid, at 0°-5°C. The adduct produced, which exists as a dimeric species in the solid phase, was hydrolysed to exo-3-chloro-bicyclo[2,2,1]hept-5-ene-2-one(IX) using 4-oxo-pentanoic acid.[195]

Table 2.8 shows the ^{1}H-n.m.r. shifts for compound (IX), measured relative to TMS in $CDCl_3$ (relative peak intensities in parentheses).

Table 2.8 ^{1}H-N.m.r. shifts for compound (IX)

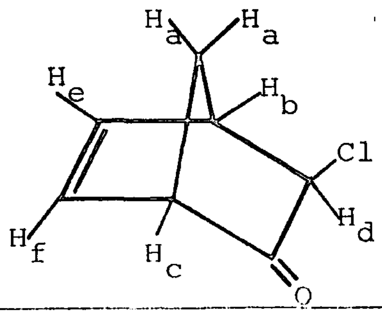
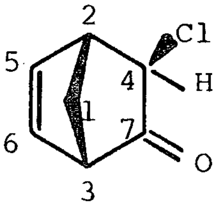
Compound	^{1}H-N.m.r. shifts (δppm.)					
	Ha	Hb	Hc	Hd	He	Hf
 (IX)	Ab$_q$ δ_A 2.51 δ_B 2.28 J_{AB} 10Hz (2)	3.08s Broad (1)	3.25s Broad (1)	3.86d J 3Hz (1)	6.25m (1)	6.51m (1)

Table 2.9 shows the ^{13}C-n.m.r. shifts of compound (IX) measured relative to TMS in $CDCl_3$.

Table 2.9 <u>^{13}C-N.m.r. shifts for compound (IX)</u>

Compound	^{13}C-N.m.r. shifts (δppm.)		
	Nucleus	Functionality	Shift
 (IX)	C^1 C^2 C^3 C^4 C^5 C^6 C^7	-$\underline{C}H_2$ —▷$\underline{C}H(CCl)$ —▷$\underline{C}H(C=O)$ -C-Cl -C=$\underline{C}$- -$\underline{C}$=C- -$\underline{C}$=O	46.13 47.95 52.89 53.67 133.35 140.24 204.84

(k) Attempted ring-opening polymerisation of exo-3-chlorobicyclo[2,2,1]hept-5-ene-2-one(IX)

The ring-opening polymerisation of compound (IX) was attempted using a mole ratio WCl_6:$SnMe_4$:(IX) of 1:2:100 at 70°C. No polymer was produced in any of several attempts.

(l) Attempted copolymerisation of (IX) with norbornene

The copolymerisation of (IX) with norbornene was attempted at room temperature. A mole ratio WCl_6:$SnMe_4$:(IX):norbornene of 1:2:15:85 was used. The solution gelled after a reaction time of only 10 minutes and the polymer produced was isolated. Characterisation by i.r. analysis of a film cast from chloroform indicated that this was pure poly(norbornene). (95% yield with respect to input norbornene).

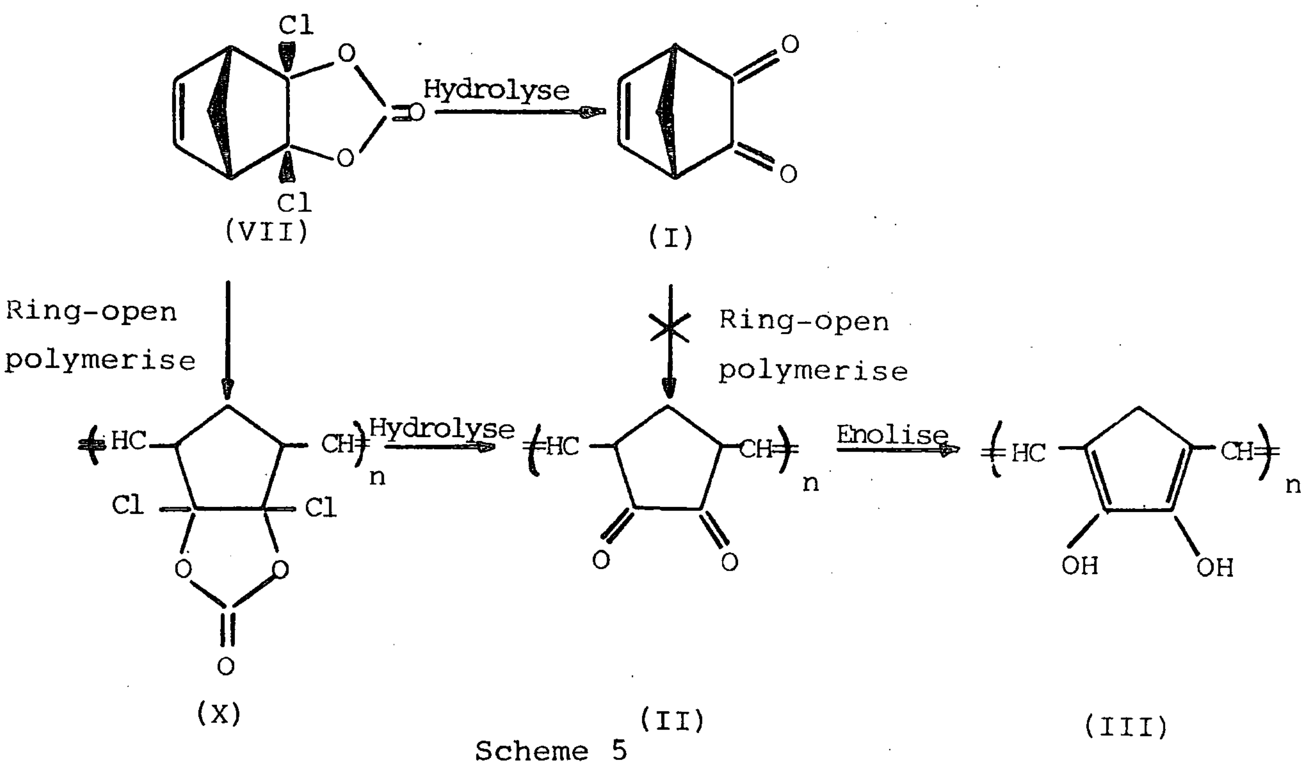
These results indicate that 2- and/or 3-keto substituents suppress the polymerizability of norbornene derivatives, although it appears that the exo-chlorine substituent in (IX) may have prevented coordination between the carbonyl group and the transition metal carbene since almost all of the norbornene was polymerised in the copolymerisation attempt even though compound (IX) itself was not incorporated.

Since all attempts to synthesise polymer (II) from 2- or 3-keto substituted norbornene derivatives were unsuccessful, an alternative approach to the synthesis of this polymer by an indirect route was investigated, as described in the following section.

2.7 (a) Ring-opening polymerisation of endo-3a,7a-dichloro-3a,4,7,7a-tetrahydro-4,7-methano-1,3-benzodioxol-2-one (VII). Investigation of an indirect route to polymers (II) and (III)

The preparation of the polymer derived from monomer (VII), and its use as a precursor for the production of polymers (II) and (III) was investigated. Since the hydrolysis of monomer (VII) produces the diketone (I) an analogous conversion may occur for polymer (X) to produce polymer (II) and hence polymer (III), as shown in Scheme 5.

The ring-opening polymerisation of the 1:1 adduct (VII) was attempted, using a mole ratio WCl_6:$SnMe_4$:(VII) of 1:2:242, at 70°C. After an induction period of 45 minutes a fawn solid began to precipitate out of the reaction medium. This product (polymer (X)) was isolated and fully characterised by elemental analysis, i.r. spectroscopy, ^{1}H-n.m.r. and ^{13}C-n.m.r. spectroscopy (yield 35%).



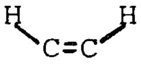
Scheme 5

(b) Characterisation of polymer (X) derived from the 1:1 cyclopentadiene:dichlorovinylene carbonate adduct (VII)

(i) I.r. spectroscopy

Polymer (X) is soluble in dry acetone or THF. Free-standing films of this polymer were produced upon spin-casting in a pyrex cylinder. The transmission i.r. spectrum of the film (Appendix C) contained bands at 3670 cm^{-1} (C=O overtone), 3040, 3005 cm^{-1} (=C-H), 2940, 2875 cm^{-1} (-C-H), 1835 cm^{-1} (C=O), with very strong absorptions in the fingerprint region (1240 cm^{-1} to 890 cm^{-1}, particularly due to C-O stretching modes), 775 cm^{-1} (-C-Cl) and 750 cm^{-1} (cis $\overset{\text{H}}{\diagdown}\text{C=C}\overset{\text{H}}{\diagup}$ out-of-plane bending modes). These frequencies are slightly different from correspondingly assigned bands in the spectrum of monomer (VII) shown in Table 2.10 for comparison.

Table 2.10 I.r. absorption frequencies for monomer (VII) and polymer (X)

I.r. absorption frequencies (cm^{-1})		Assignment
Monomer(VII)	Polymer(X)	
3620	3670	-C=O stretch overtone
3085,3005	3040,3005	=C-H stretch
2955,2880	2970,2940,2875	-C-H stretch
1860sh, 1825	1895sh, 1835	-C=O stretch
1235,1225,1105, 1070,1000, 970,920 880	1240,1215,1160 1105,1045,1010 980,955,925 890	Fingerprint bands including C-C, C-O stretching modes.
790,785	775	-C-Cl stretch
765,740,715	750,720	 out-of-plane bending modes

These assignments indicate that polymer (X) is the ring-opened polymer of monomer (VII), poly(6,8-(1,5-dichloro-2,4-dioxa-3-keto)bicyclo[3,3,0]octylenevinylene). The changes in the observed i.r. absorption frequencies for the monomer and polymer are consistent with the structural assignments; for example, the vinylic =C-H stretching mode occurs at lower frequency in the polymer which is consistent with relief of ring strain on polymerisation.

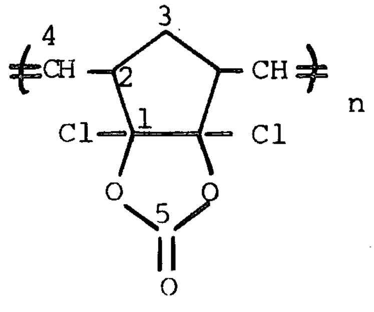
(ii) ^{1}H-N.m.r. spectroscopy

The ^{1}H-n.m.r. spectrum of polymer (X) was recorded in d_6-acetone and shows 3 broad absorptions centred at δ5.37, δ3.16 and δ1.60 relative to external TMS (ratio 1:1:1), due to olefinic, tertiary and bridgehead protons respectively. The corresponding absorptions in the monomer occur at δ6.23, δ3.50 and δ2.09, hence on ring-opening polymerisation an upfield shift occurs consistent with relief of ring strain.

(iii) ^{13}C-N.m.r. spectroscopy

The ^{13}C-n.m.r. spectrum of polymer (X) is shown in Figure 2.57(a). Figure 2.57(b) shows its DEPT (Distortionless Enhancement by Polarization Transfer) spectrum which distinguishes between methylene, tertiary, and quaternary carbon atoms. ^{13}C-n.m.r. shifts and their assignments for polymer (X) are given in Table 2.11.

Table 2.11 ^{13}C-N.m.r. shifts for polymer (X)

Polymer (X)	^{13}C-N.m.r. shifts (δ ppm.)		
	Shift	Integral	Assignment*
 (X)	147.00	1.45	5
	127.81	7.11	4c
	127.20	8.84	4t
	107.71	3.46	1
	54.23	2.65	2
	53.81	1.31	
	50.01	12.48	
	33.88	4.91	3t
	32.72	3.51	3c
	32.10	0.88	

* c=cis, t=trans.

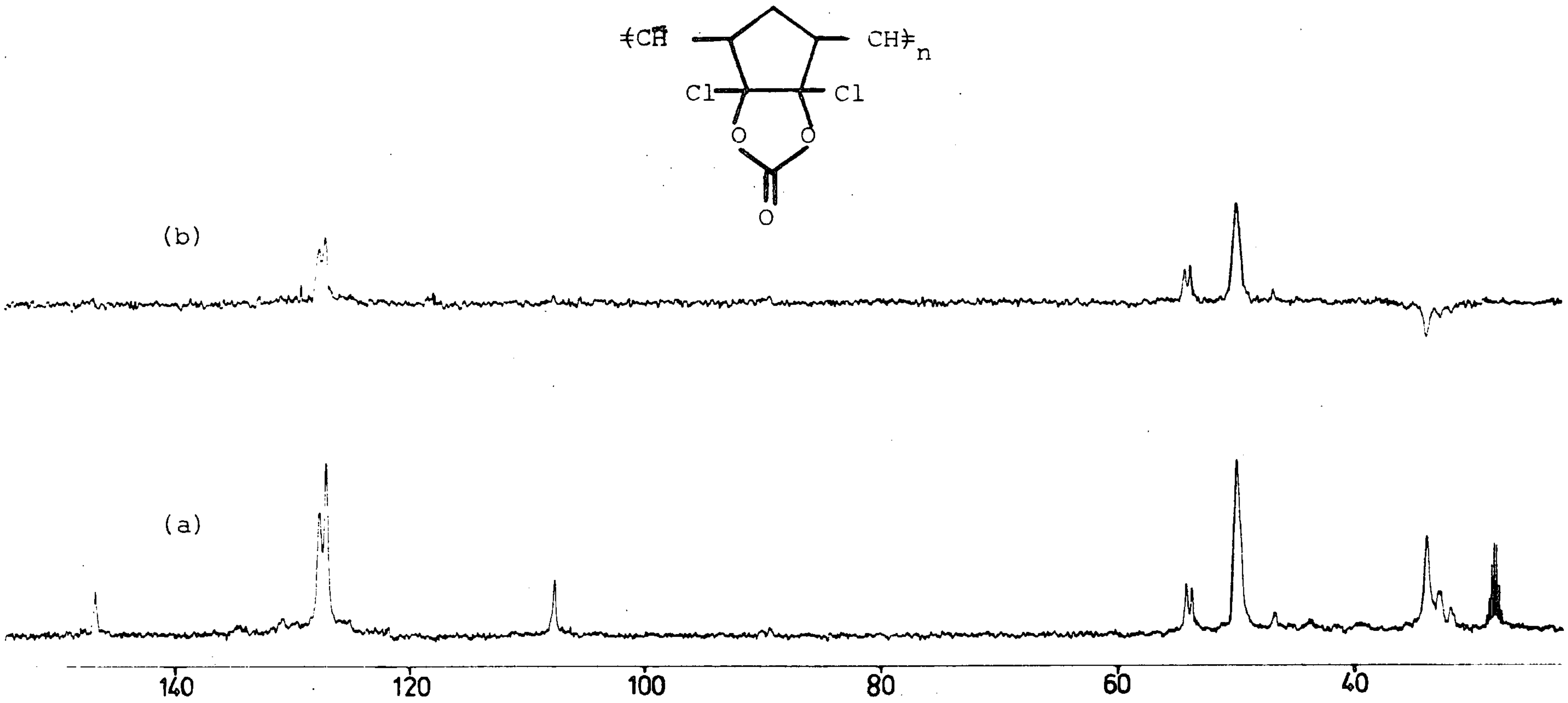


Figure 2.57 ^{13}C-N.m.r. spectrum (a), and DEPT spectrum (b), of polymer (X)

The spectrum of this polymer has proved difficult to unambiguously assign, and the discussion presented below represents the best analysis the author was able to produce.

The carbonyl carbon (5), and the C-Cl (1) are assigned unequivocally by comparison with the ^{13}C-n.m.r. shifts of monomer (VII); also since these absorptions are due to quaternary carbons they do not appear in the DEPT spectrum. The major olefinic resonance is split into two components presumably due to cis(127.81 ppm) and trans (127.20 ppm), the 0.61 ppm separation being typical for cis/trans vinylene carbons. From the integrals of these absorptions the relative proportion of cis and trans double bonds is calculated as:

$$\text{cis content, } \sigma c = \frac{4c}{4c+4t} = 45\%$$

The polymer was made using $WCl_6/SnMe_4$ at 70°C, and this value of σc is as expected for such a catalyst system; however, it has to be acknowledged that there are several unassigned low intensity absorptions in the vinylene region.

The saturated -C-H and $-CH_2$ units are unambiguously identified with the aid of the DEPT facility (see Figure 2.57 (b)); however a complete analysis of these signals is elusive. If we consider the possible assembly modes for the polymer we have four situations analogous to those drawn for poly(norbornene) (see Figure 2.25). Ivin[107] has carried out a detailed analysis for the poly(norbornene) case but if we assume a simple analogy between the spectra for poly(norbornene) and that of polymer (X) the analysis of cis vinylene content derived from the integrated intensities of vinylene, tertiary and methylene carbon signals gives values of 45, 76 and 72% respectively. These results are clearly not internally consistent and consequently a simple analogy between the case of poly(norbornene) and polymer (X) cannot be sustained. A process of empirical fitting of the integrated intensities for the methylene carbon signals suggests that the lowest field signal (33.88 ppm.) should be assigned to methylene in trans sequences, with the two other signals (32.72 and 32.10 ppm) assigned to methylenes in cis sequences. This assignment gives 47% cis vinylene content which compares favourably with the 45% deduced from the vinylene carbons themselves which are the signals assigned with most confidence. Examination of molecular models suggests that the methylene units in cis syndiotactic or isotactic sequences are considerably more crowded than those in trans sequences of either tacticity, and that for the cis cases the environmental differences for the syndiotactic and isotactic situations are significant; such a rationalization is, of course, rather tentative. When we turn to the tertiary carbons attempts to make assignments becomes even more uncertain; it may be that the polymer is essentially atactic with the methine carbons coalescing in the large broad peak at 50.01 ppm; the small resolved peaks at 53.81 and 54.23 ppm may be the consequence of small stereoregular blocks or structural irregularities. Such irregularities are a distinct possibility since, as discussed later, this polymer is very susceptible to hydrolytic degradation and there was generally a delay between its preparation and the recording of its spectrum. Partial degradation may also account for the low intensity signals in the vinylene region. These assignments tend to suggest that the polymer is assembled in an essentially random manner.

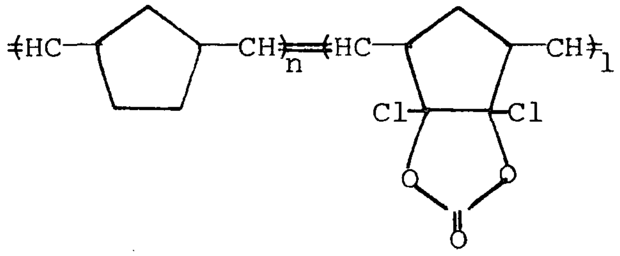
(c) Copolymerisation of endo-3a,7a-dichloro-3a,4,7,7a-tetrahydro-4,7-methano-1,3-benzodioxol-2-one(VII) with norbornene

The copolymerisation of compound (VII) with norbornene was accomplished at room temperature using a mole ratio $WCl_6:SnMe_4$:(VII): norbornene of 1:2:125:143. The reaction medium began to gel after a reaction time of 10 minutes, and the reaction was quenched after 40 minutes. A polymer was isolated in 33 weight % yield based on the combined makes of initial monomers. The polymer was characterised by elemental analysis, i.r. spectroscopy, ^{1}H-n.m.r. and ^{13}C-n.m.r. spectroscopy, which confirmed that a copolymer (copolymer (XI)) had been produced.

(d) Characterisation of copolymer (XI)

(i) Elemental analysis

The experimental elemental analysis figures were used to calculate the copolymer composition. The postulated structure is:



From the experimental % Cl, which is the most reliable figure, the effective molecular mass of the copolymer was calculated:

$$\frac{2 \times 35.453}{\text{Effective molecular mass}} = \frac{11.15}{100}$$

Effective molecular mass = 635.93.

The molecular masses of monomer (VII) and of norbornene are 221.04 and 94.16 respectively. Assuming that copolymer (XI) contains one unit from monomer (VII) for n units from norbornene,

$$n = \frac{635.91 - 221.04}{94.16} = 4.41$$

Using this value of n, C and H elemental analysis figures were calculated and compared with those found experimentally, see Table 2.12. The agreement was reasonable but C and H figures were a little low so the elemental analyses were re-calculated for n=5 which resulted in a somewhat improved fit to the experimental data.

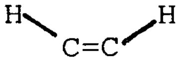
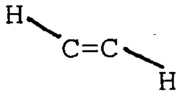
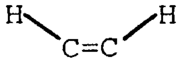
Table 2.12 Elemental analysis figures for copolymer (XI)

Copolymer (XI)	Elemental analysis (%)			
	C	H	Cl	O
Experimental	75.50	9.03	11.15	4.32
calculated (n=4.41)	73.41	7.88	11.15	7.55
calculated (n=5)	74.61	8.09	10.25	6.94

(ii) I.r. spectroscopy

A free-standing film of copolymer (XI) was spun cast from chloroform. Its i.r. spectrum is shown in Appendix C. The presence of both monomer units is clearly demonstrated. Comparison with the i.r. spectra of the homopolymers of monomer (VII) and norbornene enables absorptions due to each monomer unit incorporated to be assigned as summarised in Table 2.13.

Table 2.13 I.r. absorption frequencies for copolymer (XI)

Frequency (cm^{-1})	Functionality	Source*
3000	=C-H stretch	A and/or B
2945,2910,2865	-C-H stretch	mainly A
1840	-C=O	B
1460,1445,1405	 rocking vibration	A (B weak)
1235,1205,1170,1145, 1105,1085,1040,1010 920	Fingerprint region including C-C, C-O modes	B
965	 out-of-plane bend	A
775-720	-C-Cl stretch  out-of-plane bend	B B/A

*A = Poly(norbornene) units; B = poly(6,8-(1,5-dichloro-2,4-dioxa-3-keto)bicyclo[3,3,0]octylenevinylene) units.

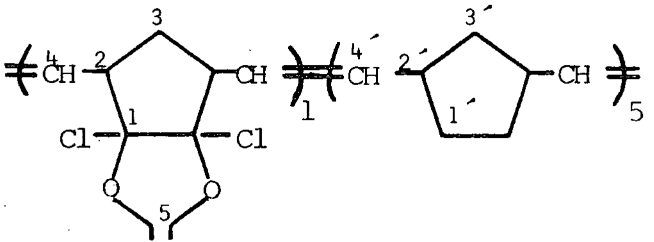
(iii) ^{1}H-N.m.r. spectroscopy

The ^{1}H-n.m.r. spectrum of copolymer (XI) in $CDCl_3$ consists of broad and ill-defined absorptions and is dominated by absorptions due to polynorbornene. The presence of units due to monomer (VII) are hidden. The ^{13}C-n.m.r. spectrum clearly shows that units from both monomers are incorporated, however, as follows.

(iv) ^{13}C-N.m.r. spectroscopy

The ^{13}C-n.m.r. spectrum of copolymer (XI) is shown in Figure 2.58(a). Figure 2.58(b) shows its DEPT spectrum for the 30 to 45 ppm. region. ^{13}C-N.m.r. shifts and assignments for copolymer (XI) are shown in Table 2.14.

Table 2.14 ^{13}C-N.m.r. shifts for copolymer (XI)



(XI)

Shift (δ ppm)	Integral	Assignment*
141.74	15.43	5 (B)
133.74	95.83	4′c,4c (A,B)
132.97	82.12	4′t,4t (A,B)
119.63	14.10	1 (B)
55.57	10.10	2tc + 2tt (B)
50.29	5.26	2cc + 2ct (B)
43.30	54.62	2′tc (A)
43.02	45.10	2′tt (A)
42.67	47.53	3′cc (A)
42.00	43.10	3′tc/3′ct (A)
41.55	10.56	3′ ($\text{B}\underline{\text{A}}\text{B}$)
41.28	22.80	3′tt (A)
40.79	10.56	3′ ($\text{B}\underline{\text{A}}\text{A}$)
38.58	90.64	2′cc (A)
38.33	51.10	2′ct (A)
34.60	29.22	3tc/3tt (B)

Table 2.14 ^{13}C-N.m.r. shifts for copolymer (XI) (contd.)

Shift (δppm.)	Integral	Assignment*
33.07	77.14	1´cc (A)
32.86	61.83	1´ct (A)
32.31	36.23	1´tc (A)
32.14	53.63	1´tt (A)
31.71	9.19	3cc/3ct (B)

*A = poly(norbornene) units' absorption; B = poly(6,8-(1,5-dichloro-2,4-dioxa-3-keto)bicyclo[3,3,0]octylenevinylene) units' absorption.

The copolymer contained 80% poly(norbornene) and the assignment of the main bands by comparison with Ivin's earlier work[107] was relatively straightforward. The presence of components from both monomers, A and B, in copolymer (XI) is clearly shown. The carbonyl carbon 5 (B) and C-Cl carbon 1 (B) are clearly observed at 141.74 and 119.63 ppm respectively. The olefinic resonance is split into 2 components at 133.74 ppm (cis) and 132.97 ppm (trans). From the olefinic resonances 4c and 4t the calculated cis content σc of copolymer (XI) is:

$$\sigma c = \frac{4c}{4c+4t} = 59\%.$$

Absorptions due to carbon 2 are split for both components A and B. For A, 4 absorptions arise at 43.30, 43.02, 38.58 and 38.33 ppm assigned as 2´tc, 2´tt, 2´cc and 2´ct respectively. From these absorptions the calculated cis content is:

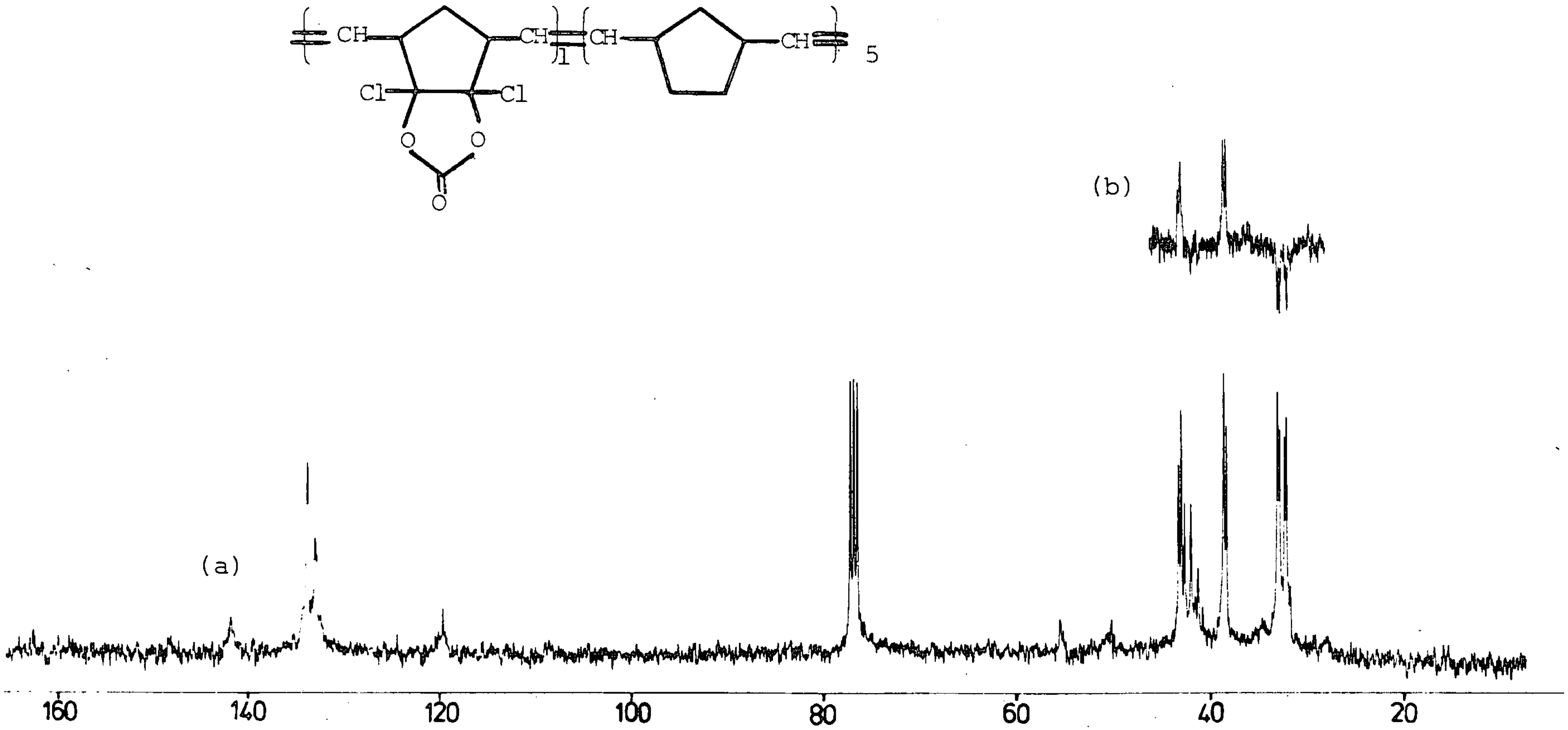


Figure 2.58 ^{13}C-N.m.r. spectrum (a), and DEPT spectrum (b), of copolymer (XI)

$$\sigma c = \frac{2'ct + 2'cc}{2'tt + 2'tc + 2'ct + 2'cc} = 59\%$$

For component B, 2 absorptions are observed due to carbon 2, at 55.57 and 50.29 ppm assigned (2tc + 2tt) and (2cc + 2ct) respectively. From these absorptions the calculated cis content is:

$$\sigma c = \frac{(2ct + 2cc)}{(2tt + 2tc) + (2ct + 2cc)} = 34\%$$

However, in this case the signal to noise ratio is poor and the σc figure cannot be regarded as reliable.

Absorptions due to carbon 3 are split into 3 for component A, at 42.67, 42.00 and 41.28 ppm assigned as 3´cc, 3´tc/3´ct and 3´tt respectively. The calculated cis-content for these absorptions is:

$$\sigma c = \frac{3'cc + 0.5(3'tc + 3'ct)}{(3'tc + 3'ct) + 3'cc + 3'tt} = 61\%$$

Two less intense absorptions also occur in this region at 41.55 and 40.79 ppm. These may be due to carbon 3 in the units of component A which are bound on both sides by component B units (B$\underline{A}$B), or on one side by component B unit (B$\underline{A}$A), i.e. at junctions between the two units.

Absorptions due to carbon 1 in component A occur at 33.07, 32.87, 32.31 and 32.14 ppm and are assigned as 1´cc, 1´ct, 1´tc and 1´tt respectively. The calculated cis content for these absorptions is:

$$\sigma c = \frac{1'ct + 1'cc}{1'tt + 1'tc + 1'ct + 1'cc} = 61\%$$

Two less intense absorptions also occur in this region at 34.60 and 31.71 ppm and these are assigned as 3tc/3tt and 3cc/3ct respectively from component B.

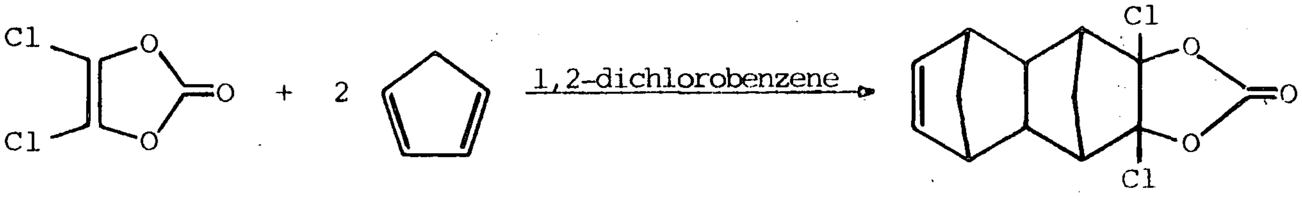
The 4 separate cis/trans content calculations for component A in the copolymer are quite consistent (59-61%) which is convincing for such a complicated system. This cis-content is slightly higher than expected for poly(norbornene) produced using $WCl_6/SnMe_4$ at room temperature.

The ^{13}C-n.m.r. shifts for component B are different to those observed in its homopolymer (X). This suggests that each unit from monomer (VII) is separated by component A units in the copolymer and that the monomer (VII) is incorporated in a random rather than a blocky sense.

2.8 Synthesis, characterisation and ring-opening polymerisation of endo, endo-3a,9a-dichloro-3a,4,4a,5,8,8a,9,9a-octahydro-4,9:5,8-dimethanonaphtho[2,3-d]-1,3-dioxol-2-one (XII)

(a) Synthesis and characterisation of compound (XII)

Compound (XII) was synthesised by the thermal Diels-Alder reaction of 4,5-dichloro-1,3-dioxol-2-one and cyclopentadiene in 1,2-dichlorobenzene, Figure 2.59. The thermal Diels-Alder reaction between these two compounds in carbon tetrachloride produces predominantly the 1:1 adduct (compound (VII)) whereas reaction at a higher temperature gives the 1:2 adduct (XII) as the major product.



(VI)

Figure 2.59

(XII)

The structure and stereochemistry of adduct (XII) had been assigned previously.[187,189] Table 2.15 shows the ^{1}H-n.m.r. shifts for compound (XII) measured relative to TMS in $CDCl_3$. (Relative peak intensities in parentheses).

Table 2.15 ^{1}H-N.m.r. shifts for compound (XII)

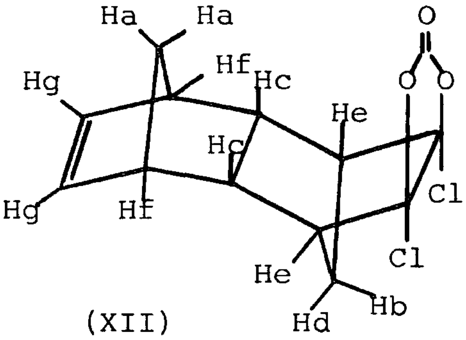
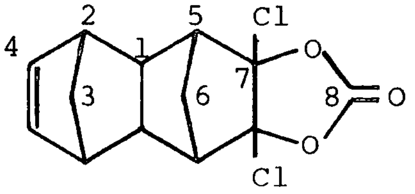
Compound	^{1}H-N.m.r. shifts (δ ppm.)						
	Ha	Hb	Hc	Hd	He	Hf	Hg
 (XII)	1.30 (2)	1.62 (1)	2.41 (2)	2.55 (1)	2.82 (2)	2.93 (2)	5.97 (2)

Table 2.16 shows the ^{13}C-n.m.r. shifts of compound (XII) measured relative to TMS in $CDCl_3$.

Table 2.16 ^{13}C-N.m.r. shifts for compound (XII)

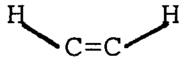
Compound	^{13}C-N.m.r. shifts (δppm.)		
	Nucleus	Functionality	Shift
 (XII)	C^6	$-\underline{C}H_2$	30.93
	C^3	$-\underline{C}H_2$	40.41
	C^1	$\rightarrow\underline{C}H-$	46.91
	C^2	$\rightarrow\underline{C}H-$	53.92
	C^5	$\rightarrow\underline{C}H-$	54.45
	C^7	$-\underline{C}-Cl$	108.25
	C^4	$-\underline{C}=C-$	136.06
	C^8	$\underline{C}=O$	149.31

(b) Ring-opening polymerisation of endo,endo-3a,9a-dichloro-3a,4,4a,5,8,9,9a-octahydro-4,9:5,8-dimethanaphtha[2,3-d]-1,3-dioxol-2-one (XII)

The ring-opening polymerisation of the 1:2 adduct (XII) was attempted using a mole ratio $WCl_6:SnMe_4$:(XII) of 1:2:250 at room temperature. The solution became cloudy after a reaction time of 5 minutes, and a large gelatinous mass of polymer was produced after 10 minutes. This product (polymer (XIII)) was isolated and fully characterised by elemental analysis, i.r. spectroscopy, ^{1}H-n.m.r. and ^{13}C-n.m.r. spectroscopy (yield 49%).

(c) Characterisation of polymer (XIII)

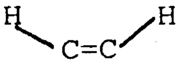
(i) I.r. spectroscopy

Polymer (XIII) is soluble in THF. Free-standing films were produced by spin-casting in a pyrex cylinder. The transmission i.r. spectrum of the film (Appendix C) contained bands at 3670 cm^{-1} (C=O overtone), 3010 cm^{-1} (=C-H), 2950, 2875 cm^{-1} (C-H), 1835 cm^{-1} (C=O), with very strong absorptions in the fingerprint region (1220-885 cm^{-1}, particularly due to C-O stretching modes), 750 cm^{-1} (C-Cl), and at 720 cm^{-1} (cis  out-of-plane bend).

These frequencies are slightly different from correspondingly assigned bands in the spectrum of monomer (XII), shown in Table 2.17 for comparison.

These assignments indicate that polymer (XIII) is the ring-opened polymer of monomer (XII), poly(9,11-(2,6-dichloro-3,5-dioxa-4-keto)tetracyclo[5,5,1,$0^{2,6}$,$0^{8,12}$]tridecylenevinylene).

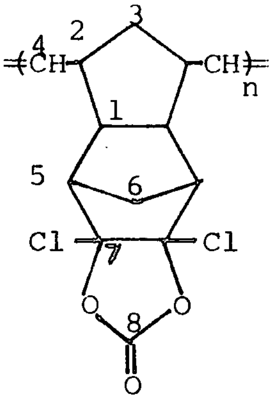
Table 2.17 <u>I.r. absorption frequencies for monomer (XII) and polymer (XIII)</u>

I.r. absorption frequencies (cm^{-1})		Assignment
Monomer (XII)	Polymer (XIII)	
	3670	-C=O stretch overtone
3060	3010	=C-H stretch
2990,2930,2865	2950,2875	-C-H stretch
1830	1835	-C=O stretch
1240,1220,1125 1090,1070,1060, 1010,975,930 915,880	1220 1095,1070 1000,970, 885	Fingerprint bands including C-C, C-O modes
745	750	-C-Cl stretch
700,600	720	 out-of-plane bend

(ii) <u>^{13}C-N.m.r. spectroscopy</u>

The ^{13}C-n.m.r. spectrum of polymer (XII) is shown in Figure 2.60. ^{13}C-N.m.r. shifts and assignments are given in Table 2.18.

Table 2.18 ^{13}C-N.m.r. shifts for polymer (XII)

Polymer (XIII)	^{13}C-N.m.r. shifts (δppm.)		
	Shift	Integral	Assignment
	148.09	17.64	8
	130.59	49.72	4c
	130.21	24.71	4t
	129.45	19.96	4t
	107.46	27.18	7
	54.41	71.46	5
	54.06	16.27	5
	45.01	33.93	2
	44.74	29.95	2
	44.60	48.40	2
	44.13	9.42	2
	44.03	11.09	2
	42.59	9.88	1
	42.37	18.08	1
	40.62	48.77	3
	40.35	10.11	3
	40.21	8.46	3
	32.52	47.02	6

The carbonyl carbon (8), and C-Cl (7), appear at 148.09 and 107.46 ppm respectively. The olefinic region of the spectrum is split into 3 resonances, at 130.59, 130.21 and 129.45 ppm, due to cis/trans isomerism and different polymer tacticities. The trans-absorption appears to have been split into two components at 130.21 and 129.45 ppm. The cis-absorption appears as one component

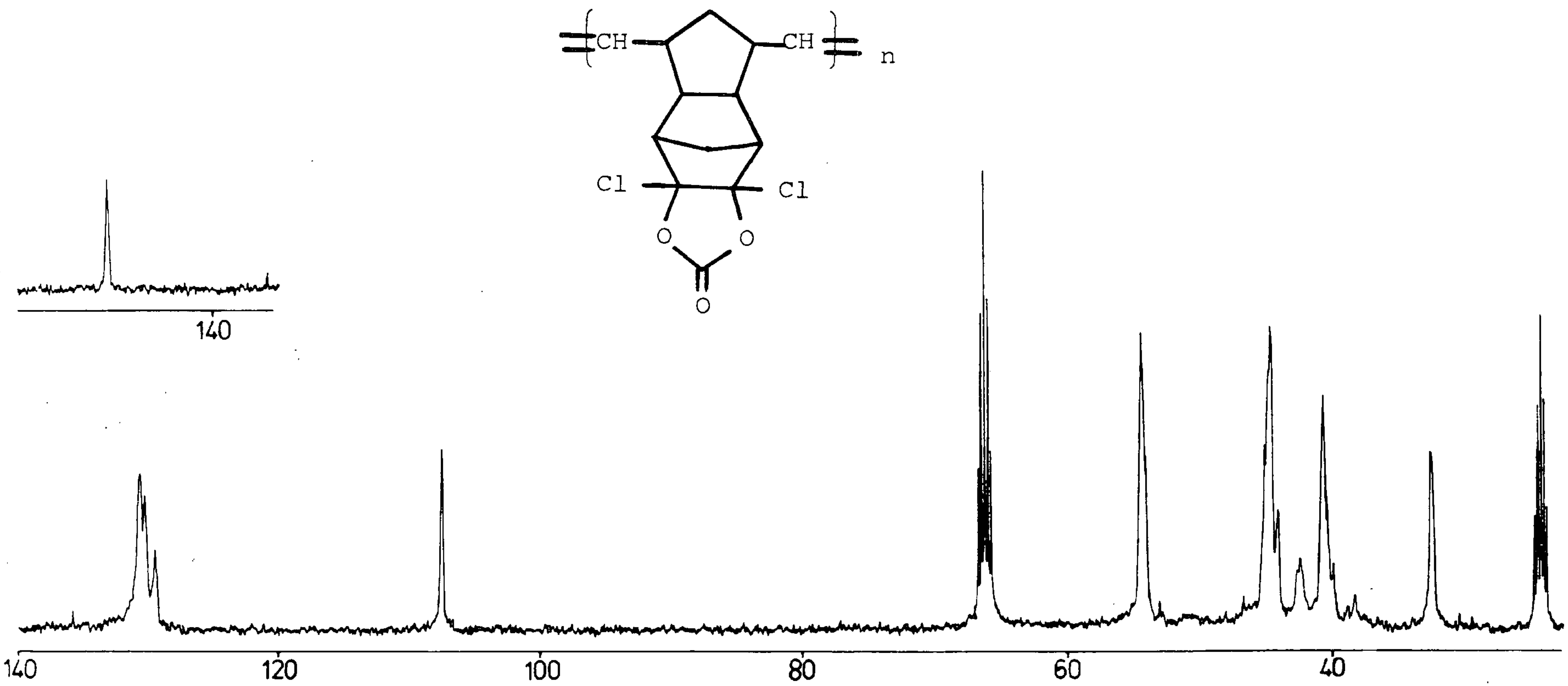


Figure 2.60. ^{13}C-N.m.r. spectrum of polymer (XIII)

at 130.59 ppm. Using these assignments for carbon 4, the calculated cis-content is computed as, $\sigma c = 53\%$, the roughly 50:50 distribution of cis and trans vinylene units being in agreement with expectation for this catalyst system. The absorption due to carbon 6 appears as a singlet at 32.52 ppm. Absorptions at 40.21, 40.35 and 40.62 ppm have been assigned as being due to carbon 3. Two absorptions have been assigned as being due to carbon 1, at 42.37 and 42.59 ppm. Absorptions at 44.03, 44.13, 44.60 and 45.01 ppm have been assigned as being due to carbon 2. Finally, the absorptions at 54.06 and 54.41 ppm have been assigned as being due to carbon 5. (Very weak absorptions at 53.80, 46.66, 39.88 and 38.27 ppm are unassigned).

The fine structure observed in the ^{13}C-n.m.r. spectrum indicates the complexity of the polymer structure. No direct comparison can be made with the ^{13}C-n.m.r. spectrum of poly(norbornene) hence an unambiguous assignment of the fine structure in the regions indicated cannot be made; however, the data appear to be consistent with a random assembly rather than a highly stereoregular structure.

(d) Copolymerisation of endo,endo-3a,4,4a,5,8,8a,9,9a-octahydro-4,9:5,8-dimethanonaptho[2,3-d]-1,3-dioxol-2-one(XII) with norbornene

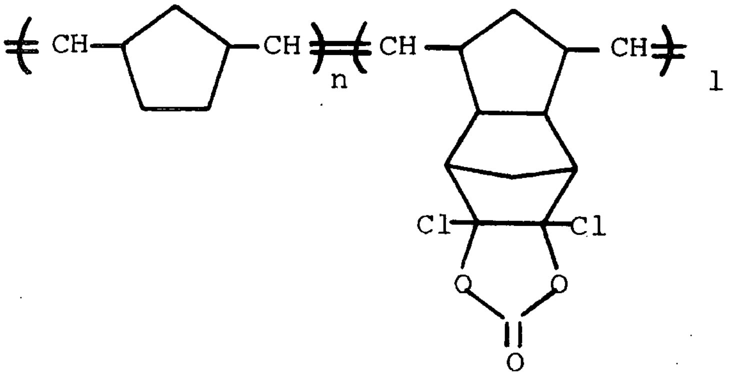
The copolymerisation of compound (XII) with norbornene was accomplished at room temperature using a mole ratio WCl_6:$SnMe_4$:(XII): norbornene of 1:2:75.7:174.3. The polymerisation was instantaneous on addition of the monomer mixture; reaction was quenched after 45 minutes. A polymer was isolated in 92% yield, based on combined masses of monomers. The polymer was characterised by elemental analysis, i.r. spectroscopy, ^{1}H-n.m.r. and ^{13}C-n.m.r.

spectroscopy, which confirmed that a copolymer (copolymer (XIV)) had been produced.

(e) Characterisation of copolymer (XIV)

(i) Elemental analysis

The experimental elemental analysis figures were used to calculate the copolymer composition. The postulated structure is:



From the experimental % Cl, which is the most reliable figure, the effective molecular mass of the copolymer was calculated:

$$\frac{2 \times 35.453}{\text{Effective molecular mass}} = \frac{13.76}{100}$$

Effective molecular mass = 515.3.

The molecular masses of monomer (XII) and of norbornene are 287.15 and 94.16 respectively. Assuming that copolymer (XIV) contains one unit from monomer (XII) for n units from norbornene,

$$n = \frac{515.3 - 287.15}{94.16} = \underline{2.42}$$

Using this value of n, the elemental analysis for C and H were calculated. The figures obtained compare favourably with the values found experimentally as shown in Table 2.19.

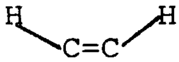
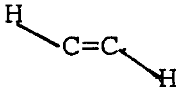
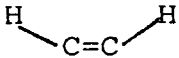
Table 2.19 Elemental analysis figures for copolymer(XIV)

Copolymer (XIV)	Elemental analysis (%)			
	C	H	Cl	O
Experimental	69.19	8.60	13.76	8.45
Calculated (n=2.42)	69.79	7.03	13.76	9.32

(ii) I.r. spectroscopy

A free standing film of copolymer (XIV) was spun-cast from chloroform. Its i.r. spectrum is shown in Appendix C. The presence of both monomer units is clearly shown. Comparison with the i.r. spectra of the homopolymers of monomer (XII) and norbornene enables identification of which absorptions are due to each monomer unit incorporated as shown in Table 2.20.

Table 2.20 I.r. absorption frequencies for copolymer (XIV)

Frequency (cm^{-1})	Functionality	Source*
3000	=C-H stretch	A and/or B
2940,2910,2860	-C-H stretch	mainly A
1840	C=O stretch	B
1480	 rocking vibration	B
1440		A
1220,1140,1095 1070,1000,940 925,890	Fingerprint band including C-C,C-O modes	B
970	 out-of-plane bend	A and/or B
750	-C-Cl stretch	B
720,700,670w	 out-of-plane bend	A and/or B

* A = Poly(norbornene) units ; B = poly(9,11-(2,6-dichloro-3,5-dioxa-4-keto)-tetracyclo[5,5,1,$0^{2,6}$,$0^{8,12}$] tridecylenevinylene)units

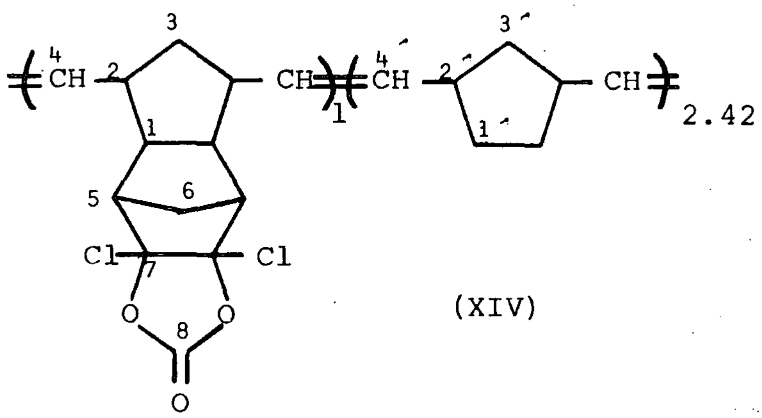
(iii) ^{1}H-N.m.r. spectroscopy

The ^{1}H-n.m.r. spectrum of copolymer (XIV) was recorded in $CDCl_3$. It consists of broad peaks and is dominated by absorptions due to poly(norbornene). The presence of units from monomer (XII) is shown in the δ2.0 to δ3.0 region of the spectrum however; the copolymer spectrum contains fine structure in this region which is absent in the case of pure poly(norbornene).

(iv) ^{13}C-N.m.r. spectroscopy

The ^{13}C-n.m.r. spectrum of copolymer (XIV) is shown in Figure 2.61(a), also shown in its expanded form in Figure 2.62. Figure 2.61(b) shows its DEPT spectrum. ^{13}C-N.m.r. shifts and assignments for copolymer (XIV) are given in Table 2.21.

Table 2.21 ^{13}C-N.m.r. shifts for copolymer (XIV)



(XIV)

Shift (δppm.)	Integral	Assignment*
149.07	7.67	8 (B)
138.00	12.13	4,4'
136.91	18.15	4,4'
134.12	11.06	4,4'
133.92	12.32	4,4'
133.78	29.23	4,4'
133.26	10.11	4,4'

Table 2.21 ^{13}C-N.m.r. shifts for copolymer (XIV) (contd.)

Shift (δppm.)	Integral	Assignment*
132.95	23.40	4,4′
132.78	12.49	4,4′
132.41	3.24	4,4′
130.85	12.71	4,4′
130.56	3.44	4,4′
130.25	6.08	4,4′
129.60	5.01	4,4′
126.84	17.56	4,4′
126.31	4.42	4,4′
126.08	10.63	4,4′
107.74	6.70	7 (<u>B</u>A)
107.58	9.09	7 (<u>B</u>B)
54.42	27.06	5 (<u>B</u>B)
54.23	19.91	5 (<u>B</u>A)
45.14	18.80	
44.85	37.03	2tc (B)
44.38	24.46	2tt (B)
43.27	33.63	2′tc (A)
43.13	9.59	
43.00	31.25	2′tt (A)
42.65	17.42	3′cc (A)
42.31	5.24	
41.98	28.24	3′ct/3′tc (A)
41.66	5.10	
41.25	34.54	3′tt (A)
40.82	8.89	

Table 2. 21 ^{13}C-N.m.r. shifts for copolymer (XIV) (contd.-2)

Shift (δppm.)	Integral	Assignment*
40.60	15.36	2cc (B)
40.32	7.54	2ct (B)
39.28	7.18	
38.85	11.57	
38.56	33.82	2´cc (A)
38.31	21.20	2´ct (A)
33.06	43.36	1´cc (A)
32.85	34.16	1´ct (A)
32.66	16.88	6 (B)
32.30	30.11	1´tc (A)
32.12	35.70	1´tt (A)

* A = poly(norbornene) units' absorption; B = poly(9,11-(2,6-dichloro-3,5-dioxa-4-keto)tetracyclo[5,5,1,$0^{2,6}$,$0^{8,12}$]tridecylene-vinylene) units' absorption.

The fine structure observed in the ^{13}C-n.m.r. spectrum indicates the complexity of the copolymer structure. This is particularly apparent in the vinylene carbon region of the spectrum where at least 16 absorptions occur (12 of relatively high intensity and at least 4 minor peaks). No unambiguous assignment of these has been achieved. There are 3 possible combinations of the two units A and B in a copolymer, AA, AB or BB; each pair of units may be separated by either a cis or trans double bond, and the rings neighbouring each double bond may be in a syndiotactic or isotactic relationship; hence the 12 major vinylic absorptions may be readily rationalised. The remaining minor absorptions present some problems and may

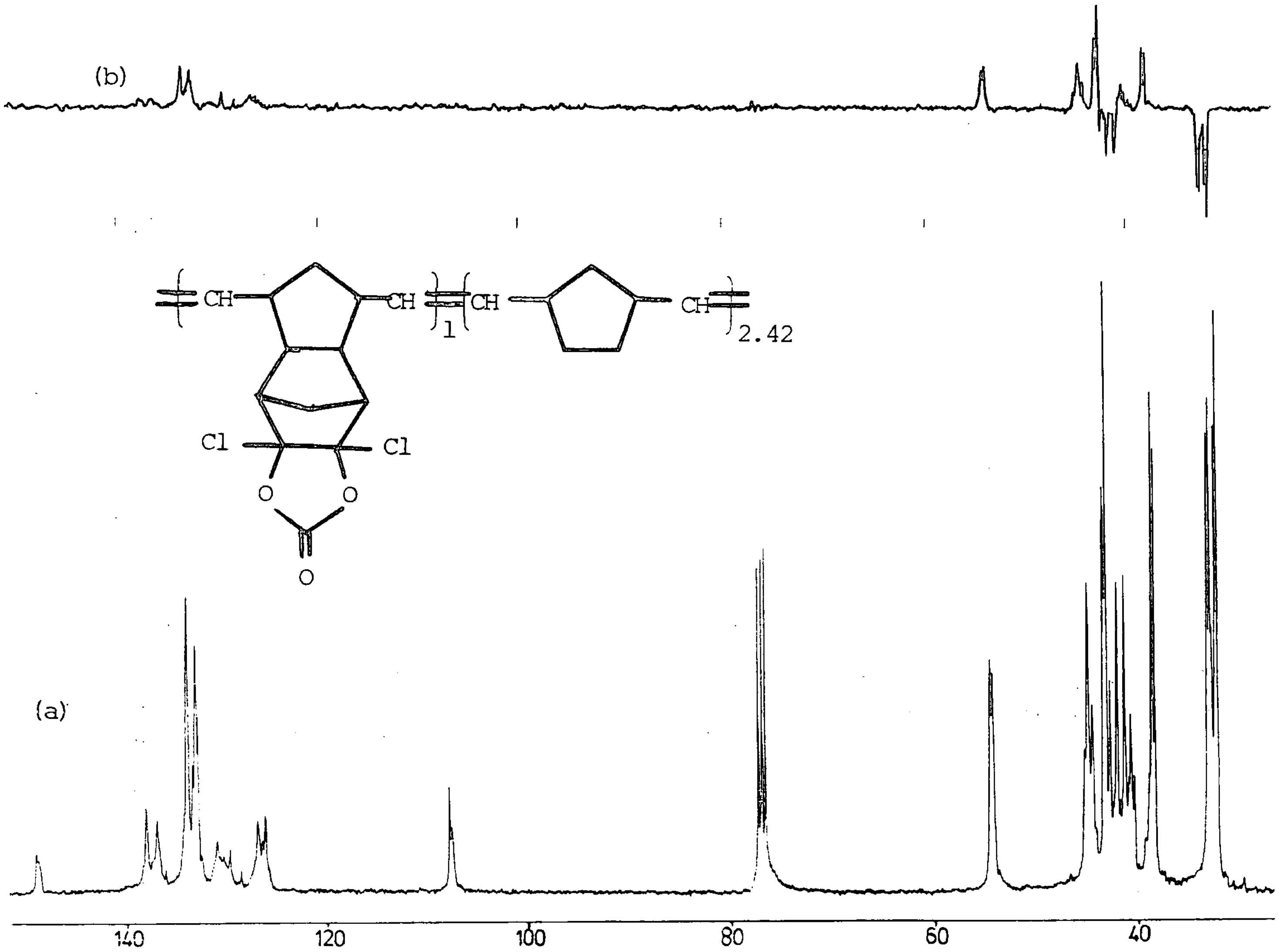


Figure 2.61. ^{13}C-N.m.r. spectrum (a), and DEPT spectrum (b), of copolymer (XIV)

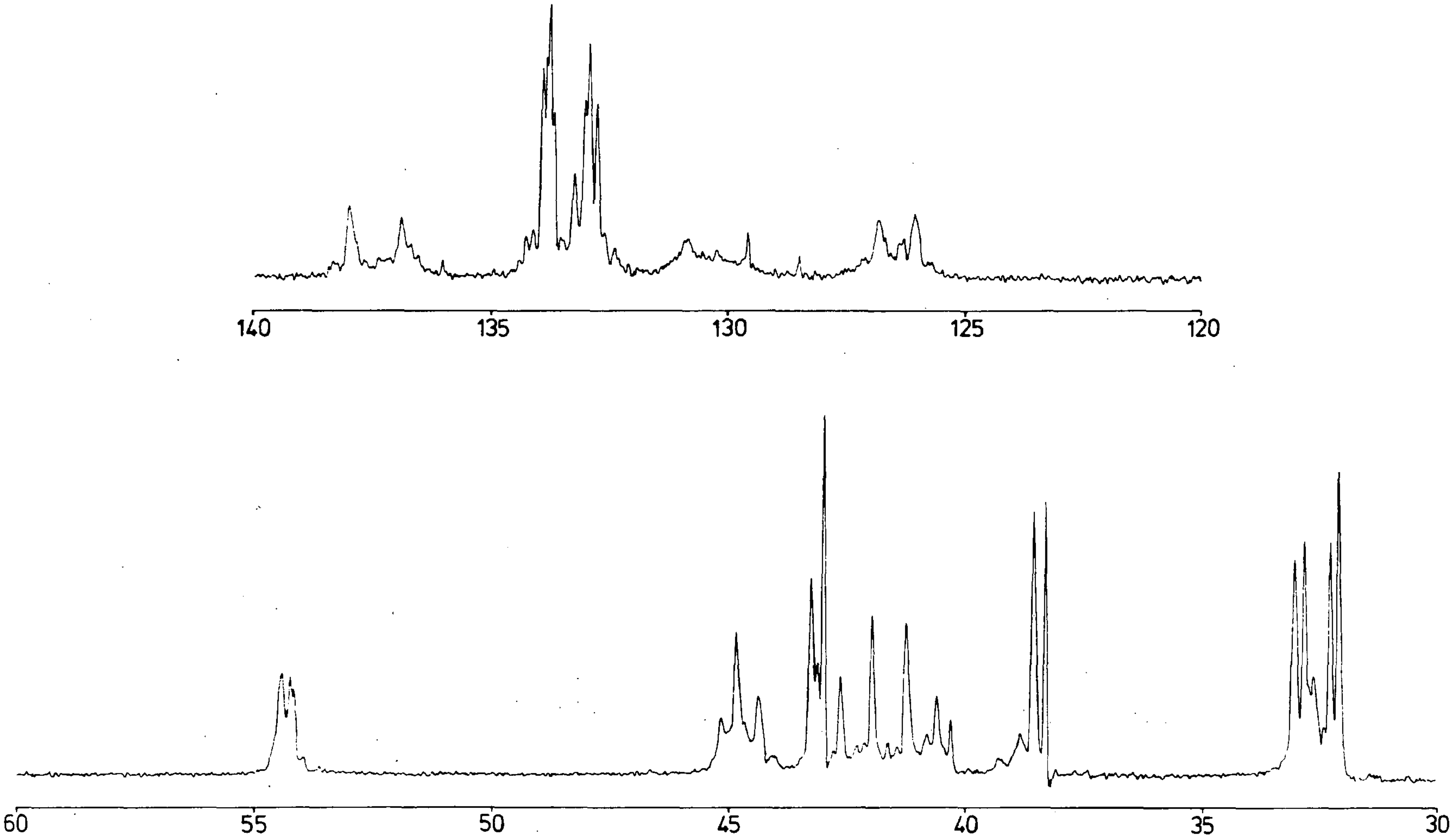


Figure 2.62. Expanded ^{13}C-N.m.r. spectrum of copolymer (XIV)

possibly be due to short blocky sequences or structural irregularities.

Absorptions due to other carbon atoms have been assigned by comparison to the ^{13}C-n.m.r. spectrum of poly(norbornene). The major peaks have been assigned using Ivin's notation.[107] Minor peaks which are seen as shoulders or close neighbours to the major peaks are unassigned in Table 2.21. As in earlier examples, the ^{13}C-n.m.r. spectrum appears to be consistent with an essentially random assembly of monomer units.

2.9 Synthesis, characterisation and attempted ring-opening polymerisation of endo-3a,4,7,7a-tetrahydro-4,7-methano-1,3-benzodioxol-2-one(XV)

(a) Synthesis and characterisation of compound (XV)

Compound (XV) was synthesised by the thermal Diels-Alder reaction of 1,3-dioxol-2-one (vinylene carbonate) and cyclopentadiene in benzene at 180°C in a Carias tube,[196-198] Figure 2.63.

(XV)

Figure 2.63

Table 2.22 records the ^{1}H-n.m.r. shifts for compound (XV) measured relative to TMS in $CDCl_3$ (relative intensities in parentheses).

Table 2.22 <u>^{1}H-N.m.r. shifts for compound (XV)</u>

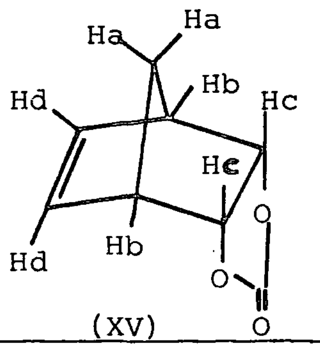
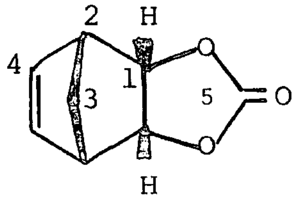
Compound	^{1}H-N.m.r. shifts (δppm.)			
	Ha	Hb	Hc	Hd
 (XV)	Abq δ_A 1.87 δ_B 1.28 J_{AB} 10Hz (2)	3.27m (2)	5.00t J2Hz (2)	6.25t J2Hz (2)

Table 2.23 records the ^{13}C-n.m.r. shifts of compound (XV) measured relative to TMS in $CDCl_3$.

Table 2.23 <u>^{13}C-N.m.r. shifts for compound (XV)</u>

Compound	^{13}C - N.m.r. shifts		
	Nucleus	Functionality	Shift
 (XV)	C^3	$-\underline{C}H_2$	45.76
	C^2	→$\underline{C}$-H	48.74
	C^1	$-\underline{C}$H-O	77.47
	C^4	$-\underline{C}$=C-	131.28
	C^5	$-\underline{C}$=O	152.99

(b) <u>Attempted ring-opening polymerisation of endo-3a,4,7,7a-tetrahydro-4,7-methano-1,3-benzodioxol-2-one (XV)</u>

The ring-opening polymerisation of compound (XV) was attempted with WCl_6:$SnMe_4$ at 70°C, and also with $MoCl_5$:$SnMe_4$ at 70°C, using a mole ratio WCl_6($MoCl_5$):$SnMe_4$:(XV) of 1:2:100. No polymerisation occurred.

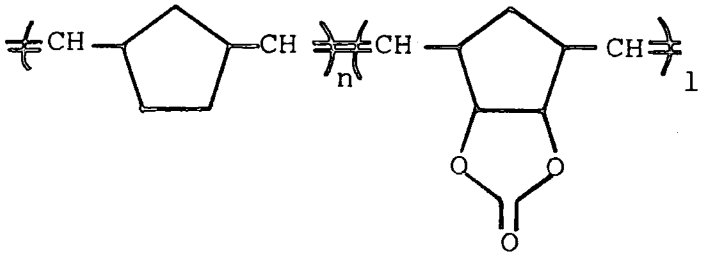
(c) Copolymerisation of endo-3a,4,7,7a-tetrahydro-4,7-methano-1,3-benzodioxol-2-one(XV) with norbornene

The copolymerisation of (XV) with norbornene was attempted at room temperature. A mole ratio WCl_6:$SnMe_4$:(XV):norbornene of 1:2:15.7:84.7 was used. The solution became viscous after a reaction time of 10 minutes; after 45 minutes a large gelatinous mass of polymer had been formed. The polymer produced was isolated in 40% yield based on combined masses of monomers. The polymer was characterised by elemental analysis, i.r. spectroscopy, and ^{13}C-n.m.r. spectroscopy, which confirmed that a copolymer (copolymer (XVI)) had been produced.

(d) Characterisation of copolymer (XVI)

(i) Elemental analysis

The experimental elemental analysis figures were used to calculate the copolymer composition. The postulated structure is:



From the oxygen percentage obtained by difference, the effective molecular mass of copolymer (XVI) may be calculated:

$$\frac{(3\times16)}{\text{Effective molecular mass}} = \frac{3.93}{100}$$

$$\text{Effective molecular mass} = 1221.37$$

The molecular masses of monomer (XV) and of norbornene are 152.15 and 95.16 respectively. Assuming that copolymer (XVI) contains one unit from monomer (XV) for every n units from norbornene, the value of n may be calculated independently from experimental %C and %H figures as n=11.2 and 13.0 respectively.

Experience suggests that the elemental analysis figures for hydrogen are usually less reliable than for carbon; however, the values of n obtained using elemental analysis figures for both elements are in quite good agreement.

This result indicates that the metathesis polymerisability of monomer (XV) is quite low. The dichloro derivative (monomer (VII)) is much more readily polymerised and copolymerised. These results are analogous to those obtained for endo-bicyclo-[2,2,1]hept-5-ene-2,3-dicarboxylic anhydride and its 2,3-dichloro derivative (Figure 2.64). Castner and Calderon showed that endo-bicyclo[2,2,1]hept-5-ene-2,3-dicarboxylic anhydride is very difficult to polymerise by metathesis catalysts[199] (the exo-derivative is readily polymerised), whereas, Lamies Shahada (this Department) has shown that endo-2,3-dichloro-bicyclo[2,2,1]hept-5-ene-2,3-dicarboxylic anhydride is relatively readily polymerised.[200] (In this case the exo-isomer has not yet been investigated).

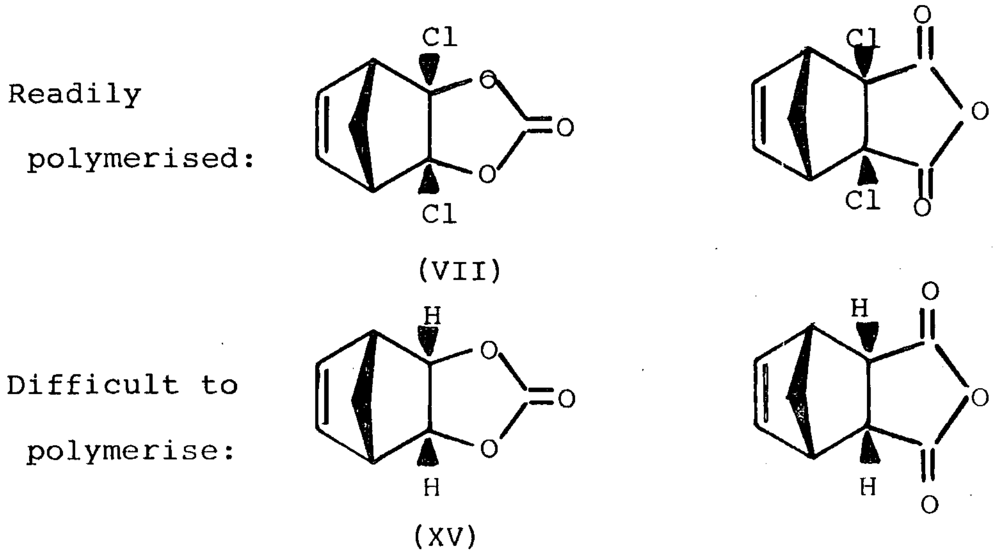


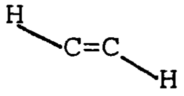
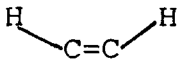
Figure 2.64

No obvious rationalisation for these experimental observations is apparent, and the factors governing the polymerisability of monomers of this type seem to be quite subtle.

(ii) I.r. spectroscopy

A free-standing film of copolymer (XVI) was spun-cast from chloroform. Its i.r. spectrum is shown in Appendix C and contains absorptions from units derived from both monomer (XV) and norbornene. The absorptions from poly(norbornene) units were identified by comparison with the i.r. spectrum of the pure homopolymer. The remaining relatively weak absorptions are assigned to units derived from the ring-opened polymer of monomer (XV), poly(6,8-(2,4-dioxa-3-keto)bicyclo[3,3,0]octylenevinylene), Table 2.24.

Table 2.24 I.r. absorption frequencies for copolymer (XVI)

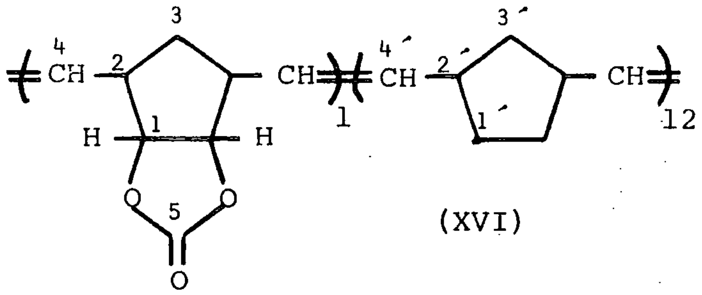
Frequency (cm^{-1})	Functionality	Source*
3000	=C-H stretch	A and B
2940,2910,2860	-C-H stretch	A
1800	-C=O stretch	B
1155,1085	C-O stretch	B
965	 out-of-plane bend	A and B
740	 out-of-plane bend	A and B

* A = poly(norbornene) units; B = poly(6,8-(2,4-dioxa-3-keto)-bicyclo[3,3,0]octylenevinylene) units.

(iii) ^{13}C-N.m.r. spectroscopy

The ^{13}C-n.m.r. spectrum of copolymer (XVI) is shown in Figure 2.65(a). Figure 2.65(b) shows its DEPT spectrum. ^{13}C-N.m.r. shifts and assignments for copolymer (XVI) are given in Table 2.25.

Table 2.25 ^{13}C-N.m.r. shifts for copolymer (XVI)



(XVI)

Shift (δppm.)	Integral	Assignment*
138.54	3.29	5 (B)
138.42	1.68	5 (B)
133.90	16.78	4c
133.75	43.87	4c
132.92	16.50	4t
132.76	13.40	4t
83.39	5.92	1 (B)
43.30	25.88	2´tc (A)
43.02	32.09	2´tt (A)
42.67	23.00	3´tt (A)
42.01	28.20	3´tc/3´ct (A)
41.29	18.08	3´cc (A)
38.59	42.07	2´cc (A)
38.35	22.72	2´ct (A)
33.10	46.43	1´cc (A)
32.89	31.22	1´ct (A)
32.34	35.08	1´tc (A)
32.16	33.53	1´tt (A)

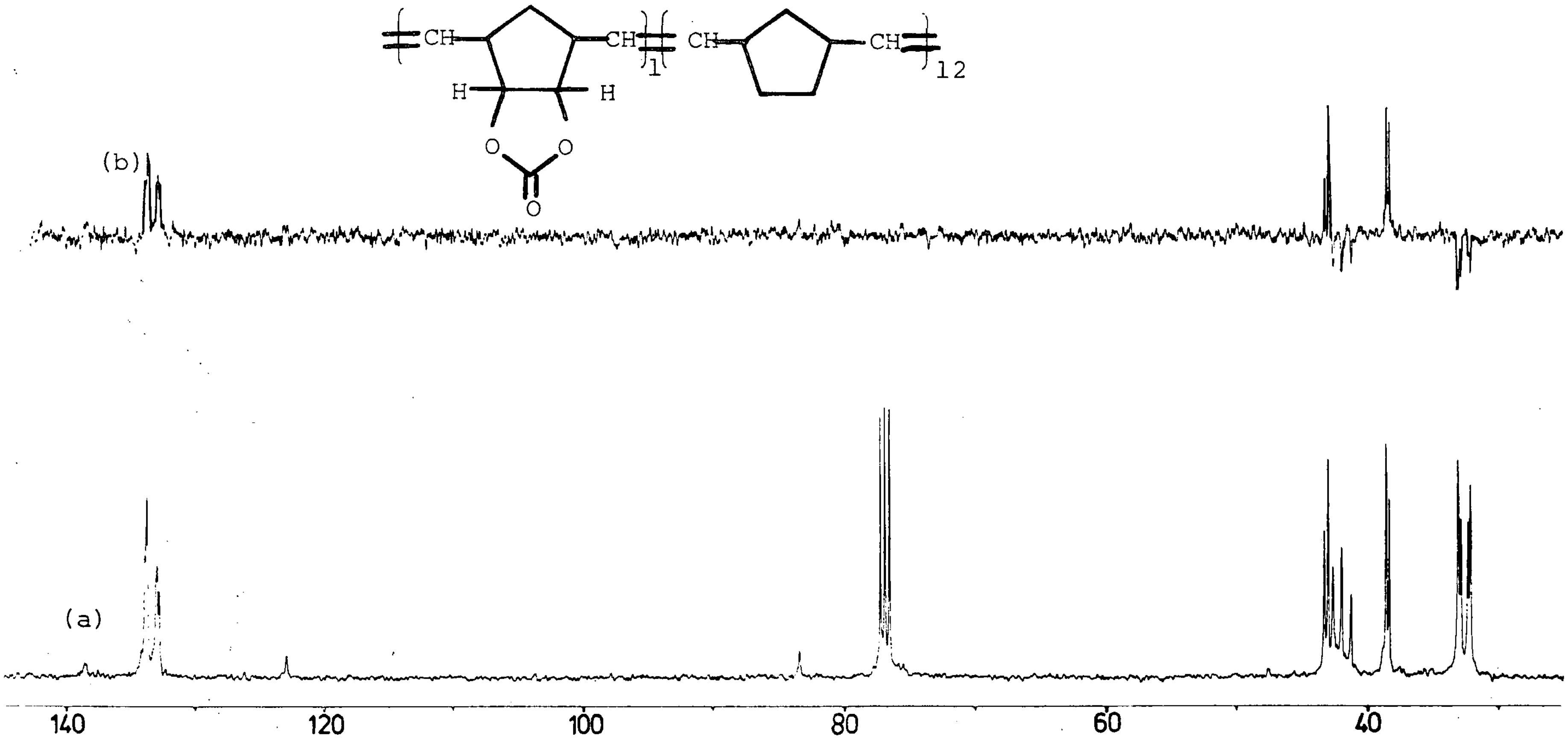


Figure 2.65. ^{13}C-N.m.r. spectrum (a), and DEPT spectrum (b), of copolymer (XVI)

* A = poly(norbornene) units' absorption; B = poly(6,8-(2,4-dioxa-3-keto)bicyclo[3,3,0]octylenevinylene) units' absorption.

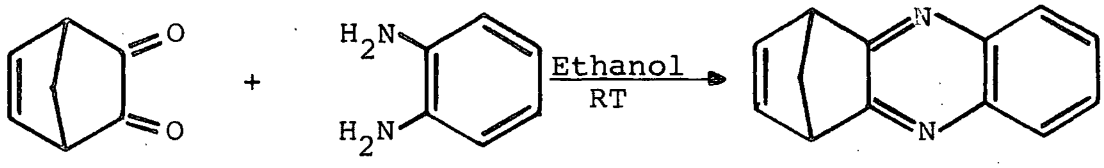
Since the copolymer consists of a 12:1 ratio of poly(norbornene) units (A) to units derived from monomer (XV) (B) the spectrum is dominated by absorptions from the poly(norbornene) component. Only 2 absorptions are clearly visible from the monomer (XV) component, at 138.54, 138.42 ppm due to the carbonyl carbon (5), and at 83.386 ppm due to carbon 1.

In comparison to the ^{13}C-n.m.r. spectrum of poly(norbornene) the olefinic absorptions are again split due to the effect of incorporating monomer (XV) into the polymer; although the incorporation ratio is relatively small, the effect on the spectrum is significant, but not amenable to an unambiguous explanation. Again the spectrum is consistent with a random rather than stereoregular assembly.

2.10 Synthesis, characterisation and attempted ring-opening polymerisation of 1,4-dihydro-1,4-methanophenazine (XVII)

(a) Synthesis and characterisation of compound (XVII)

Bicyclo[2,2,1]hept-5-ene-2,3-dione(I) was synthesised as described in Section 2.6(b). This was reacted with an equimolar amount of 1,2-diaminobenzene (o-phenylenediamine) in ethanol at room temperature to give 1,4-dihydro-1,4-methanophenazine(XVII), Figure 2.66.



(I) (XVII)

Figure 2.66

Table 2.26 shows the ^{1}H-n.m.r. shifts of compound (XVII) measured relative to TMS in $CDCl_3$ (relative intensities shown in parentheses).

Table 2.26 ^{1}H-N.m.r. shifts for compound (XVII)

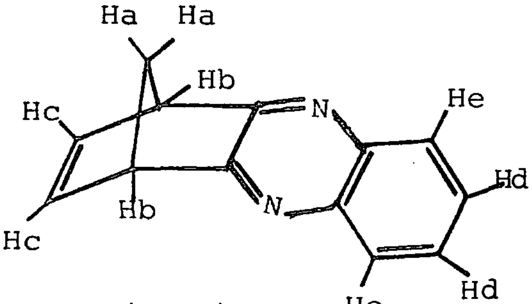
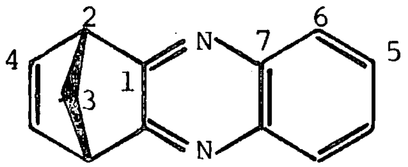
Compound	^{1}H-N.m.r. shifts (δppm.)				
	Ha	Hb	Hc	Hd	He
 (XVII)	ABq δ_A 2.75 δ_B 2.50 J_{AB} 10Hz (1)	3.87d broad (1)	6.78 broad (1)	7.59m (1)	7.77m (1)

Table 2.27 shows the ^{13}C-n.m.r. shifts of compound (XVII) measured relative to TMS in $CDCl_3$.

Table 2.27 ^{13}C-N.m.r. shifts for compound (XVII)

Compound	^{13}C-N.m.r. shifts (δppm.)		
	Nucleus	Functionality*	Shift
 (XVII)	C^3	$-\underline{C}H_2$	49.52
	C^2	→$\underline{C}$H	62.91
	C^5	bz-$\underline{C}$-H	128.29
	C^6	N-C-$\underline{Bz}$	128.55
	C^1	norb-$\underline{C}$=N	139.08
	C^4	-$\underline{C}$=C-	142.07
	C^7	N-$\underline{C}$-bz	166.11

(* Norb = norbornene side of molecule; bz = benzene side of molecule)

When the ^{13}C-n.m.r. spectrum was run initially, only five absorptions were observed, due to carbon atoms bonded to hydrogen. Two further absorptions due to carbon atoms void of hydrogens, carbons 1 and 7, Table 2.27, appeared after the addition of $Cr(acac)_3$, and aided assignments in the above Table.

(b) Attempted ring-opening polymerisation of compound (XVII)

The ring-opening polymerisation of compound (XVII) was attempted using a mole ratio WCl_6:$SnMe_4$:(XVII) of 1:2:152. The catalyst solution became discoloured immediately upon addition of the monomer solution. No polymerisation occurred, which was somewhat surprising since norbornene derivatives carrying pyridyl substituents have been reported to polymerise.[137]

(c) Attempted copolymerisation of compound (XVII) with norbornene

The copolymerisation of compound (XVII) with norbornene was attempted at room temperature. A mole ratio WCl_6:$SnMe_4$:(XVII norbornene of 1:2:37.2:207 was used; no polymer was produced.

These results, particularly the fact that compound (XVII) prevented the ring-opening polymerisation of norbornene during the copolymerisation attempt, indicate that compound (XVII) is a catalyst poison, presumably due to coordination of the nitrogen lone-pairs to the vacant site on the active transition metal carbene.

2.11 Determination of molecular weights of polymer (XIII) and copolymers (XI), (XIV) and (XVI) by GPC

Gel permeation chromatography (GPC) was used to determine the molecular weight of polymer (XIII) and copolymers (XI), (XIV) and (XVI). In this technique a dilute solution of a polymer (0.5% to 1%) in THF is injected into the GPC analyser via a Millipore filter. The solvent stream is split into two components; the injected sample enters one component and is passed through the GPC column to the detector; the second component consists of pure solvent and is used as a reference for the detector. The GPC column contains a gel which separates polymer molecules according to their hydrodynamic volumes. The hydrodynamic volume of a polymer gives a measure of how tightly wrapped a polymer coil is in solution, and is related to the molecular weight since the higher the molecular weight the larger the hydrodynamic volume. High molecular weight molecules have hydrodynamic volumes which are too large to enter the "pores" in the gel of the column, so these interact less strongly with the column and are eluted quickly. Low molecular weight molecules are held within the"pores" of the gel of the column and elute less quickly. The detector used can be of two types, a UV detector is used for molecules which contain strong UV-absorbing chromophores (aromatics); a refractive index detector can be used for any sample,and was used in these determinations. Output from the GPC analyser consists of a plot of elution volume versus peak height hi which gives the relative number of molecules Ni with a molecular weight Mi.

To obtain molecular weights the GPC analyser is calibrated using standard polystyrene samples of known molecular weight. A calibration graph of elution volume versus log molecular weight is obtained.

Molecular weights obtained are the "polystyrene equivalent molecular weights" for the samples, i.e. it is assumed that the polymer coils in the same way as polystyrene. For well characterised polymer systems where solution viscosity has been studied as a function of molecular weight it is possible to use Mark-Houwick K and α values to convert the "polystyrene equivalent molecular weights" to "true molecular weights". However the empirical constants K and α are not known for the samples measured. Nevertheless the values reported can be taken as good estimates of the "true molecular weights".

The GPC output curves of elution volume versus peak height for polymer (XIII) and copolymers (XI), (XIV) and (XVI) are shown in Figure 2.67 (a) to (d).

The number average molecular weight $\bar{M}_n$, weight average molecular weight $\bar{M}_w$, peak-height-maximum molecular weight $\bar{M}_{max}$ and polydispersity $\bar{M}_w/\bar{M}_n$ were calculated for each sample. An example of such calculations for polymer (XIII) is given in Table 2.28.

Table 2.28 <u>GPC results for polymer (XIII)</u>

Elution volume (cm^3)	Peak Height hi (mm)	Mi	Ni = $\frac{hi}{Mi}$ ($x10^3$)	NiMi	NiMi^2
14.5	0	665,349	0	0	0
15	0.5	460,786	0.00109	0.5	230,393
15.5	1.5	319,117	0.00470	1.5	478.675
16	4	221,003	0.01810	4	884,015
16.5	12	153,055	0.07840	12	1,836,670
17	33	105,998	0.31132	33	3,497,952
17.5	80	73,409	1.08978	80	5,872,729
18	94	50,839	1.84896	94	4,778,899
18.5	79	35,208	2.24376	79	2,781,487

Table 2.28 GPC results for polymer (XIII) (contd.)

Elution volume (cm^3)	Peak Height Hi (mm)	Mi	$Ni = \frac{hi}{Mi}$ ($x10^{-3}$)	NiMi	$NiMi^2$
19	70.5	24,383	2.89127	70.5	1,719,052
19.5	57.5	16,886	3.40501	57.5	970,996
20	43.5	11,694	3.71954	43.5	508,732
20.5	30.5	8,099	3.76574	30.5	247,030
21	21.5	5,609	3.83300	21.5	120,597
21.5	14	3,884	3.60394	14	54,384
22	9.5	2,690	3.53121	9.5	25,557
22.5	6.5	1,863	3.48870	6.5	12,110
23	4	1,290	3.09999	4	5,161
23.5	2.5	893	2.79763	2.5	2,234
24	1.5	618	2.42377	1.5	928
24.5	1	428	2.33319	1	428
25	0	296	0	0	0
			44.4891	566.5	24,028,029

$$\overline{Mn} = \frac{\Sigma plimi}{\Sigma Ni} = \frac{566.5}{44.4891 \times 10^{-3}} = 12,733$$

$$\overline{M}_w = \frac{\Sigma NiMi^2}{\Sigma NiMi} = \frac{24,028,029}{566.5} = 42,415.$$

The peak height maximum has an elution volume of 17.85 cm^3.

$\overline{M}_{max} = 56,763.$

$$\text{Polydispersity} = \frac{\overline{M}_w}{\overline{Mn}} = \frac{42,415}{12,733} = 3.33$$

Similar calculations were made for copolymers (XI), (XIV) and (XVI). Table 2.29 gives values of $\overline{Mn}$, $\overline{M}_w$, $\overline{M}_{max}$ and polydispersity for polymer (XIII) and copolymers (XI), (XIV) and (XVI).

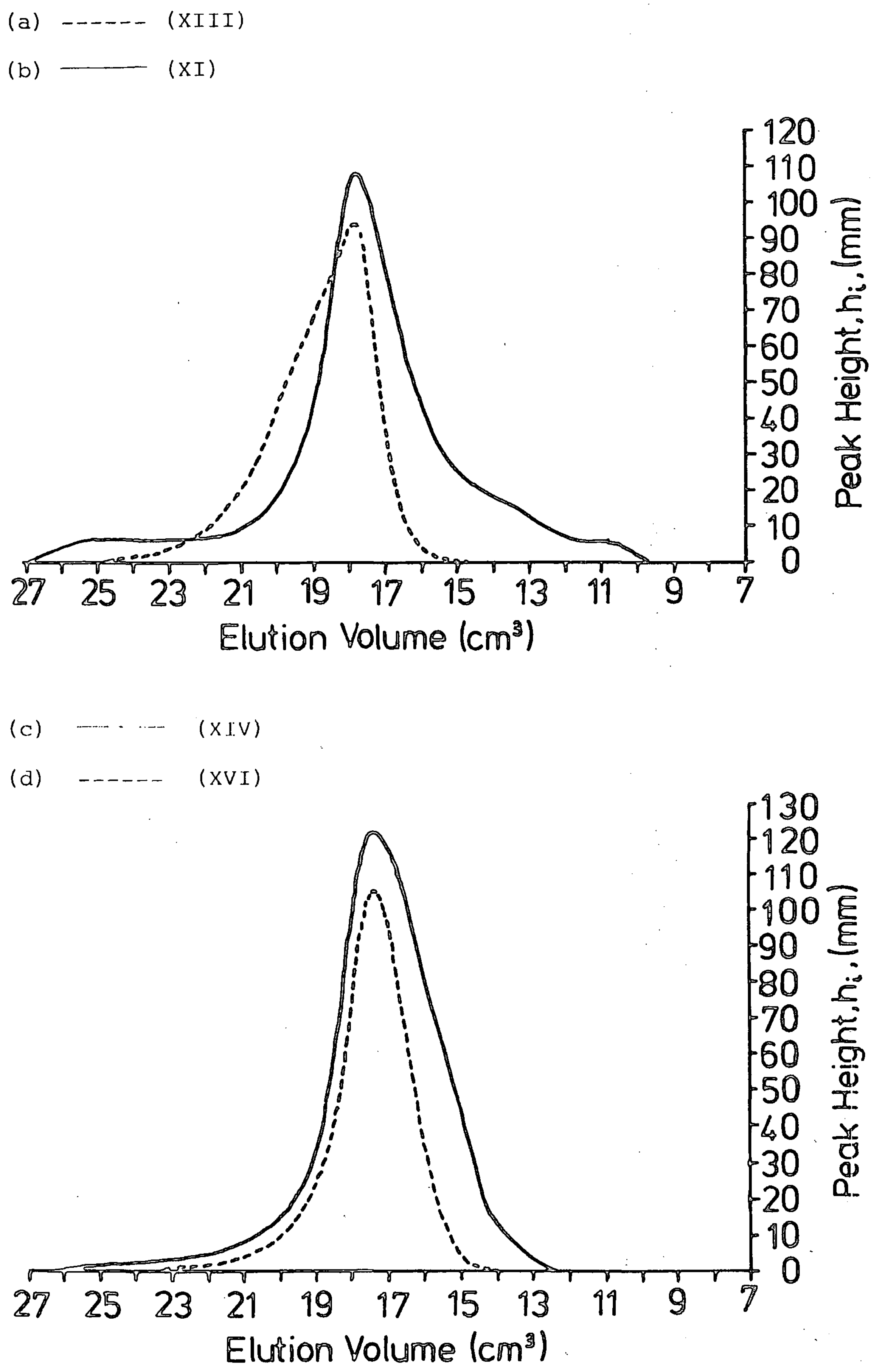


Figure 2.67 GPC output curves

Table 2.29 Molecular weights of polymer (XIII) and copolymers (XI), (XIV) and (XVI)

Sample	$\overline{Mn}$	$\overline{M}_w$	$\overline{M}_{max}$	Polydispersity
(XIII)	12,733	42,415	56,763	3.33
(XI)	5,745	451,478	56,763	78.59
(XIV)	16,804	169,218	73,409	10.07
(XVI)	40,776	94,443	73,409	2,32

Although the peak-height-maximum molecular weight of polymer (XIII) and copolymer(XI), and of copolymers (XIV) and (XVI) are the same, their values of $\overline{Mn}$, $\overline{M}_w$ and polydispersity are very different. In particular for copolymer (XI) a polydispersity of 79 is extraordinarily high, indicating that there is a very wide range of chain lengths from high polymer to relatively low molecular weight telomer in the product. Copolymer (XIV), having a polydispersity of 10 also has an unusually wide range of chain lengths. Polymer (XIII) and copolymer (XVI) however have relatively symmetrical and normal molecular weight distribution curves. Attempts to obtain a GPC curve for polymer (X) were unsuccessful due to its poor stability resulting in the production of a cloudy inhomogeneous solution in THF.

The sample giving the very wide molecular weight distribution is the copolymer formed from norbornene and the 1:1 adduct (VII); the polymer yield was 33% and the monomer incorporation ratio approximately 1:5. By contrast with the homopolymer of (XVI), this copolymer with norbornene gives clear homogeneous solutions in THF, and is also soluble in chloroform whereas the homopolymer of (VII) is insoluble. Thus the solubility characteristics of the material suggest it is a true copolymer and not a mixture of homopolymers. Another standard confirmation of the formation of a random copolymer as opposed to a mixture of homopolymers or a block copolymer is to measure Glass Transition Temperatures; mixed homopolymers and block copolymers show two transitions characteristic of the two phases, whereas true random copolymers give only one Tg value. Unfortunately defective instrumentation has not allowed this measurement to be made at the time of writing.

It is difficult to understand the origins of the extraordinarily wide molecular weight distribution for this copolymer; the GPC trace was reproducible, and it may be that the long tail to the low molecular weight end of the peak is an instrumental artefact or a consequence of unusual interactions between the polymer (possibly degrading slightly) and the gel or the metal tubing, although this seems unlikely.

These results indicate the advantage of GPC over other methods of measuring molecular weights which give a single number as the result. Using GPC the distribution of molecular weights in polymer samples is obtained, which affords a more accurate description of the number and range of chain lengths which make up the sample.

Most of the synthetic work recorded in this chapter was directed to the synthesis of potential precursors of the same system (polymer (III)). The results described above add further data to the delineation of how the polymerisability of hetero-substituted monomers depends on their structures. As was mentioned in the above discussion the factors determining polymerisability appear to be rather subtle and finely balanced and the accumulation of much more data is required before useful generalizations can be drawn. The main objective of this work was not the accumulation of such data, but rather the synthesis of heterosubstituted polyconjugated systems and Chapter Three describes investigations into the use of polymer (X) as a precursor polymer in the preparation of a new heterosubstituted conjugated polymer.

EXPERIMENTAL

2.12 (a) Preparation of 4,4,5,5-tetrachloro-1,3-dioxolan-2-one(V) by the UV-chlorination of 1,3-dioxolan-2-one(ethylene carbonate)(IV)

A 1-litre pyrex chlorination reactor was used for the UV-chlorination of 1,3-dioxolan-2-one. This reactor comprises a 3-necked flanged flask. A medium pressure 100 watt, water cooled Hg lamp was used as the UV source (quartz casing) and was inserted into the central B45 cone. A B19 gas-inlet tube shaped to enable chlorine-gas to be bubbled underneath the UV-source, and a reflux condenser were inserted into the remaining B19 cones. During the chlorination, the reactor was surrounded by aluminium foil, and two more sheets of foil were draped over the front of the reactor to ensure high absorbance of UV-light and to minimise the amount of stray UV-radiation in the laboratory.

Chlorine gas was passed through a cold tap at room temperature into the reactor. Hydrogen chloride gas is produced during the reaction, and this was passed through a Dreschel bottle into a solution of sodium hydroxide held in a 2-litre beaker. The sodium hydroxide solution was stirred magnetically, and gas was passed into this solution via a small filter funnel to prevent suck-back and to ensure an efficient scrubber system. During the chlorination the Dreschel bottle contained colourless HCl gas, and it was assumed that the chlorination was complete when green chlorine gas was observed in this Dreschel bottle.

1,3-Dioxolan-2-one (88g, 1 mole) and Analar carbon tetrachloride (850 mls) were placed into the reactor. The solution was heated to reflux, the UV source was switched on, and chlorine gas was allowed to bubble steadily into the solution.

After completing the chlorination (an average reaction time was 5 hours) the chlorine flow was stopped, and the UV and heat sources were switched off. Dry nitrogen gas was bubbled through the solution to expel excess chlorine into the scrubber.

After cooling to room temperature, the contents of the reactor were poured into a 2-litre separating funnel, and were washed with distilled water (2x250 mls) to remove any remaining dissolved gases. The carbon tetrachloride layer was dried ($MgSO_4$). After filtration carbon tetrachloride was removed using a rotary evaporator, and the remaining pale yellow liquid was vacuum distilled.

The initial fraction containing mainly carbon tetrachloride was discarded. The second fraction, 4,4,5,5-tetrachloro-1,3-dioxolan-2-one (189.6g, 0.84 moles, 84%), a colourless liquid, was collected at 44^{o}-$45^{o}C$, 8mm Hg (Lit[186]: 78^{o}-$80^{o}C$, 35mm Hg; $155^{o}C$, 760mm Hg); Found: C 16.00, Cl 62.57%, calculated for $C_3Cl_4O_3$: C 15.95, Cl 62.79%; i.r. spectrum (Appendix C), ν_{max} 1890cm^{-1} (C=O), 1180, 1040, 1010, 910cm^{-1} (C-O-C), 800, 785cm^{-1} (C-Cl); mass spectrum (Appendix B), high mass 166 ($M-CO_2$); ^{13}C-n.m.r. spectrum as expected, see Discussion.

N.B. It should be noted that we were advised that the product has been reported to be potentially hazardous due to its rearrangement to oxalyl chloride with elimination of phosgene.[201] The rearrangement is catalysed by many substances but particularly by amines.

(b) <u>Preparation of 4,5-dichloro-1,3-dioxol-2-one(VI)(Dichlorovinylene carbonate) by the partial dechlorination of 4,4,5,5-tetrachloro-1,3-dioxolan-2-one(V)</u>

4,4,5,5-Tetrachloro-1,3-dioxolan-2-one was partially dechlorinated using a Zn/Cu couple and a catalytic amount of DMF in diethyl ether, as follows.

(i) Preparation of Zn/Cu couple

Glacial acetic acid (275 mls) was placed in a 1-litre 3-necked round-bottomed flask fitted with a paddle stirrer and reflux condenser. Copper acetate monohydrate (10g) was added with stirring. The solution was heated to reflux, and stirring was maintained for 10-15 minutes to dissolve most of the copper acetate. Heating was stopped allowing the reflux to subside then zinc dust (170g) was added, resulting in an exothermic reaction. The metal was added as quickly as possible, maintaining vigorous stirring. After 1-2 minutes the flask was cooled in an ice-water bath. The reactivity of the couple is dependent upon particle site, and this depends upon the length of time spent in the acid medium. If the metal is reacted for too long, the couple becomes pyrophoric.

After the reaction had cooled (2 minutes) the couple was separated by filtration, washed with glacial acetic acid (500 mls), then with diethyl ether (500 mls). It was used in the partial dechlorination reaction immediately after preparation.

(ii) Partial dechlorination

The Zn/Cu couple was placed in the 1-litre 3-necked round-bottomed flask used for its preparation and fitted with a paddle stirrer, reflux condenser, and dropping funnel. DMF (2 mls) and diethyl ether (500 mls) were added. The ether was heated to reflux, then the heat source was switched off and 4,4,5,5-tetrachloro-1,3-dioxolan-2-one (226g, 1 mole) was added dropwise to maintain the reflux. After the addition was complete, the heat source was reapplied and the reaction mixture was refluxed overnight.

After cooling, the spent couple was separated by filtration, and washed with diethyl ether (250 mls). After drying ($MgSO_4$) and filtering the solution, diethyl ether was removed using a rotary evaporator. The remaining liquid was vacuum distilled to give 4,5-dichloro-1,3-dioxol-2-one(VI) (92.9g, 0.6 moles, 60%), a colourless liquid, b.pt. 56°C, 15-16 mm Hg (Lit[186]: 147°C, 760 mm Hg); Found: C 23.00, Cl 45.70%, calculated for $C_3Cl_2O_3$: C 23.25, Cl 45.76%; i.r. spectrum (Appendix C), ν_{max} 1930, 1875, 1845 cm^{-1} (C=O), 1710, 1685 cm^{-1} (C=C), 1165, 1125, 935 cm^{-1} (C-O-C), 770, 750 cm^{-1} (C-Cl); mass spectrum (Appendix B), high mass 157 (M+2); ^{13}C-n.m.r. spectrum as expected, see Discussion.

(c) Preparation of endo-3a,7a-dichloro-3a,4,7,7a-tetrahydro-4,7-methano-1,3-benzodioxol-2-one(VII) by the thermal Diels-Alder reaction of 4,5-dichloro-1,3-dioxol-2-one(VI) with cyclopentadiene in carbon tetrachloride

4,5-Dichloro-1,3-dioxol-2-one was redistilled under reduced pressure, using a nitrogen bleed, to ensure complete dryness and purity. Cyclopentadiene was freshly prepared by the thermal cracking of its dimer (monomer fraction collected at 40°-42°C).

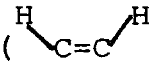
4,5-Dichloro-1,3-dioxol-2-one (52 mls, 72.9g, 0.49 moles) and freshly distilled Analar carbon tetrachloride (140 mls) were placed in a 500 ml 2-necked round-bottomed flask fitted with a condenser and magnetic stirrer. Cyclopentadiene (45 mls, 36.1g, 0.55 moles) was added and the solution was refluxed under nitrogen for 3 hours. After cooling further cyclopentadiene (45 mls) was added followed by a further 3 hour reflux. A final portion of cyclopentadiene (45 mls) was added, and the solution was refluxed for 3 hours.

After cooling, the pale yellow solution produced was distilled under reduced pressure, using a nitrogen bleed, resulting in the removal of excess cyclopentadiene and solvents, to leave an off-white solid. This was purified by multiple recrystallisation (4 times) from cyclohexane, then by sublimation at 70°C,0.1 mm Hg to give endo-3a,7a-dichloro-3a,4,7,7a-tetrahydro-4,7-methano-1,3-benxodioxol-2-one(VII) (68.7g, 0.31 moles, 63.5%) as white crystals, m.pt. 148°C (Lit[187]: 148°C); Found: C 43.59, H 2.50, Cl 32.15%, calculated for $C_8H_6Cl_2O_3$: C 43.47, H 2.74, Cl 32.08%; i.r. spectrum (Appendix C) as expected, Table 2.10; mass spectrum (Appendix B), high mass 221 (M); ^{1}H-n.m.r., ^{13}C-n.m.r. spectra as expected, see Discussion.

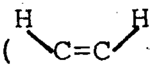
(d) <u>Preparation of bicyclo[2,2,1]hept-5-ene-2,3-dione(I) by the hydrolysis of endo-3a,7a-dichloro-3a,4-7-7a-tetrahydro-4,7-methano-1,3-benzodioxol-2-one(VII)</u>

Endo-3a,7a-dichloro-3a,4,7,7a-tetrahydro-4,7-methano-1,3-benzodioxol-2-one (33.65g, 0.15 moles), 1,4-dioxane (60 mls) and distilled water (120 mls) were placed in a 250 ml 2-necked round-bottomed flask fitted with a condenser and magnetic stirrer. The solution was refluxed for 1 hour, producing a colour change from colourless to dark orange. After cooling, the solution was extracted with diethyl ether (7x50 mls). The extracts were dried ($MgSO_4$), filtered, then diethyl ether was removed using a rotary evaporator. Remaining volatile solvents were removed on a vacuum line (10^{-3}mm Hg), inducing slow crystallization.

After repeated sublimations (3 times) bicyclo[2,2,1]hept-5-ene-2,3-dione(I) was recovered (4.64g, 3.8×10^{-2} moles, 25%) as orange-red crystals, mpt.43°C (Lit[187] 43°C); Found: C 69.73, H 5.18%, calculated for $C_7H_6O_2$:C 68.9, H 4.9%; i.r. spectrum

(Appendix C), ν_{max} 3520 cm^{-1} (C=O overtone), 1760 cm^{-1} (C=O), 1175, 1010 cm^{-1} (C-O), 770 cm^{-1} ( $\overset{H}{\diagdown}C{=}C\overset{H}{\diagup}$ out-of-plane bend); mass spectrum (Appendix B), high mass 122(M); ^1H-n.m.r., ^{13}C-n.m.r. spectra as expected, see Discussion. The product was stored under nitrogen, in the dark.

(e) Preparation of 3,3-dimethoxybicyclo[2,2,1]hept-5-ene-2 one(VIII) by the methanolysis of endo-3a,7a-dichloro-3a,4,7,7a-tetrahydro-4,7-methano-1,3-benzodioxol-2-one(VII)

Endo-3a,7a-dichloro-3a,4,7,7a-tetrahydro-4,7-methano-1,3-benzodioxol-2-one (18.45g, 8.34×10^{-2} moles) and methanol (135 mls) were placed in a 250 ml 2-necked round-bottomed flask fitted with a condenser and magnetic stirrer. The mixture was refluxed for 10 hours under nitrogen. Volatile components were removed using a rotary evaporator to leave a yellow oil. This was replaced in the reaction flask, further methanol (30 mls) was added, and the solution was refluxed for a further 1 hour. After removing volatile components using a rotary evaporator, the remaining yellow oil was distilled under reduced pressure using a B10-distillation apparatus fitted with a 6cm Vigreux column. The first fraction, containing mainly methanol, was discarded. The second fraction, a pale yellow liquid, was collected at 58°C-60°C, 0.1mm Hg (10.37g, 6.17×10^{-2} moles, 74%). The distillate was redistilled using a Fischer-Spaltrohr small concentric tube distillation apparatus (see Appendix A) to produce pure 3,3-dimethoxybicyclo[2,2,1]hept-5-ene-2-one (5.33g, 3.17×10^{-2} moles, 38%), a colourless liquid, bpt.61.5°C, 0.1mm Hg (Lit[187]: 98°C, 10mm Hg); Found: C 64.55, H 7.57%, calculated for $C_9H_{12}O_3$: C64.27, H 7.19%; i.r. spectrum (Appendix C), ν_{max} 3070 cm^{-1} (=C-H), 2990, 2945, 2840 cm^{-1} (C-H), 1755 cm^{-1} (C=O), 1135, 1065, 1045 cm^{-1} (C-O), 775, 705 cm^{-1} ( $\overset{H}{\diagdown}C{=}C\overset{H}{\diagup}$ out-of-plane bend); mass spectrum (Appendix B), high mass 140 (M-CO); ^{1}H-n.m.r., ^{13}C-n.m.r. spectra as expected, see Discussion.

(f) Preparation of exo-3-chlorobicyclo[2,2,1]hept-5-ene-2-one(IX)

(i) Reaction of bicyclo[2,2,1]hepta-2,5-diene with nitrosyl chloride

Freshly distilled bicyclo[2,2,1]hepta-3,5-diene (11 mls, 10g, 0.12 moles), glacial acetic acid (20 mls), 95% ethanol (20 mls) and isopentyl nitrite (27.8 mls, 20g, 0.17 moles) were placed in a 500 ml 3-necked round-bottomed flask fitted with a condenser, paddle stirrer and dropping funnel. After cooling to 0^o-5^oC, a solution of hydrochloric acid (25 mls, 0.25 moles), in 95% ethanol (50 mls) was added over 30 minutes. The solution became dark green immediately, and after 2-3 minutes a white precipitate began to form. The reaction was stirred for a further 15 minutes. The white product produced was filtered and washed with further 95% ethanol (100 mls), then dried on a vacuum line (10^{-3}mm Hg) to give exo,exo-3-chloro-2-nitroso-bicyclo[2,2,1]hept-5-ene (12.57g, 8.0×10^{-2} moles, 66.5%). The white crystalline product exists as a dimer in the solid phase and was used without further purification.

(ii) Hydrolysis of exo,exo-3-chloro-2-nitrosobicyclo[2,2,1]hept-5-ene using 4-oxo-pentanoic acid

Exo,exo-3-chloro-2-nitrosobicyclo[2,2,1]hept-5-ene (10g, 3.16×10^{-2} moles dimer) was placed in a 500ml 2-necked round-bottomed flask fitted with a condenser and magnetic stirrer. 4-Oxo-pentanoic acid (182 mls, 206g) and hydrochloric acid (15 mls, 2N) were added. The solution was heated for 21 hours at 70^o-75^oC.

After cooling, the flask contents were poured into a 2-litre separating funnel, distilled water (650 mls) was added, and this mixture was extracted with diethyl ether (1x350 mls, and 3x100 mls).

After combining extracts, approximately 250 mls diethyl ether were removed using a rotary evaporator. The remaining solution was washed with saturated sodium bicarbonate solution (1x200 mls, and 1x100 mls), then with distilled water (3x100 mls). The extracts were dried ($MgSO_4$), filtered and diethyl ether was removed using a rotary evaporator. The remaining liquid was distilled using a Fischer-Spaltrohr small concentric tube distillation apparatus (see Appendix A) to give exo-3-chloro bicyclo[2,2,1]hept-5-ene-2-one (5.53g, 3.9×10^{-2} moles, 61%), a colourless liquid, bpt. 29^{o}-31^{o}C, 0.01mm Hg (Lit[194]: 78^{o}-80^{o}C, 7mm Hg); Found: C 58.76, H 5.05, Cl 24.53%, calculated for C_7H_7ClO: C 58.95, H 4.91, Cl 24.91%; i.r. spectrum (Appendix C), ν_{max} 3075 (=C-H), 2990, 2950 cm^{-1} (-C-H), 1745 cm^{-1} (C=O), 745 cm^{-1} (C-Cl); mass spectrum (Appendix B), high mass 144 (M+2); ^{1}H-n.m.r., ^{13}C-n.m.r. spectra as expected, see Discussion.

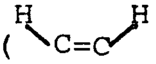
(g) Preparation of 3a,9a-dichloro-3a,4,4a,5,8,8a,9,9a-octahydro-4,9:5,8-dimethanonaphtho[2,3-d]-1,3-dioxol-2-one(XII) by the thermal Diels-Alder reaction of 4,5-dichloro-1,3-dioxol-2-one(VI) with cyclopentadiene in 1,2-dichlorobenzene

4,5-Dichloro-1,3-dioxol-2-one (55.5 mls, 77.5g, 0.5 moles) and freshly distilled 1,2-dichlorobenzene (175 mls) were placed in a 500ml 3-necked round-bottomed flask fitted with a condenser and magnetic stirrer. The solution was heated to reflux under nitrogen. Cyclopentadiene (prepared as in 2.12(c)) (80 mls, 64.2g, 0.97 moles) was added over 1½ hours, followed by a further 1½ hours reflux.

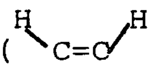
The solution produced was distilled under reduced pressure using a nitrogen bleed, resulting in the removal of excess cyclopentadiene and solvent to leave a fawn solid. This was recrystallised three times from cyclohexane. A small amount of the 1:1 Diels-Alder adduct (compound (VII)) was removed by sublimation at 70°C, 0.1mm Hg. The remaining solid was recrystallised a further three times from cyclohexane to yield 3a,9a-dichloro-3a,4,4a,5,8,8a,9,9a-octahydro-4,9: 5,8-dimethanophtho[2,3-d]-1,3-dioxol-2-one (30.8g, 0.11 moles, 21.5%), as fawn needles, m.pt. 142°C (Lit[187]: 142°C); Found: C 54.73, H 4.39, Cl 24.30%, calculated for $C_{13}H_{12}Cl_2O_3$: C 54.38, H 4.21, Cl 24.69%; i.r. spectrum (Appendix C) as expected, Table 2.17; mass spectrum (Appendix B),high mass 287 (M); ^{1}H-n.m.r., ^{13}C-n.m.r. spectra as expected, see Discussion.

(h) Preparation of 3a,4,7,7a-tetrahydro-4,7-methano-1,3-benzodioxol-2-one(XV) by the thermal Diels-Alder reaction of 1,3-dioxol-2-one with cyclopentadiene

Hydroquinone (0.05g) and 1,3-dioxol-2-one (2.21g, 2.6×10^{-2} moles) were placed in a Carias tube, which was then attached to a vacuum line (10^{-3}mm Hg) and cooled in liquid air. After purging with dry nitrogen, freshly distilled benzene (9 mls) and cyclopentadiene (prepared as in 2.12(c), 2.2 mls, 1.76g, 2.67×10^{-2} moles) were syringed into the tube. The Carias tube was evacuated (10^{-3}mm Hg), sealed, placed in a steel sleeve, and was allowed to warm to ambient temperature before heating to 180°C for 16 hours in a furnace.

After recooling in liquid air the tube was opened by hot-spotting. Benzene solvent was removed by distillation at atmospheric pressure. The product was distilled under reduced pressure. A white solid (3.28g) was obtained at 140°-150°C, 0.5-1.0mm Hg. This was recrystallised twice from 1:1 diethyl ether: hexane to yield 3a,4,7,7a-tetrahydro-4,7-methano-1,3-benzodioxol-2-one (1.31g, 8.6×10^{-3} moles, 34%) as white needles m.pt.113°C (Lit[196-198]: 113°C); Found: C 62.73, H 5.22%, calculated for $C_8H_8O_3$: C 63.15, H 5.26%; i.r. spectrum (Appendix C), ν_{max} 3005 cm^{-1} (=C-H), 3000, 2940, 2880 cm^{-1} (-C-H), 1780 cm^{-1} (C=O), 1165, 1080, 1050 cm^{-1} (C-O), 765 cm^{-1} ( out-of-plane bend); mass spectrum (Appendix B), high mass 153 (M+1); ^1H-n.m.r., ^{13}C-n.m.r. spectra as expected, see Discussion.

(i) Preparation of 1,4-dihydro-1,4-methanophenazine(XVII)

Endo-3a,7a-dichloro-3a,4,7,7a-tetrahydro-4,7-methano-1,3-benzodioxol-2-one(VII), (9.95g, 4.5×10^{-2} moles) was hydrolysed to the α-diketone(I) as described in Section 2.12(d). (The diketone isolated was used without further purification by sublimation). To the impure α-diketone produced, absolute alcohol (125 mls) and 1,2-diaminobenzene (o-phenylene diamine) (4.6g, 4.5×10^{-2} moles) were added, in a 250ml 2-necked round-bottomed flask. Stirring was maintained for 1 hour at room temperature. The 1,2-diaminobenzene slowly dissolved as it reacted. The ethanolic solution was concentrated by rotary evaporation. The product was recrystallised 3 times from ethanol to give 1,4-dihydro-1,4-methanophenazine, (5.12g, 2.61×10^{-2} moles, 58%), as fawn crystals, m.pt. 133°C (Lit[187]: 133°C), Found: C 80.58, H 5.10%, calculated for $C_{13}H_{12}N_2$: C 80.32, H 5.19%; i.r. spectrum (Appendix C), ν_{max} 3060, 3015 cm^{-1} (=C-H), 2965, 2930 cm^{-1} (-C-H), 835, 770, 740 cm^{-1} ( out-of-plane bend); mass spectrum (Appendix B), high mass 196 (M), ^1H-n.m.r., ^{13}C-n.m.r. spectrum as expected, see Discussion.

(j) Ring-opening polymerisations

(i) Reagents

Analar chlorobenzene was purchased from BDH Chemicals Ltd., and was distilled under dry nitrogen from P_2O_5 and used directly as solvent for catalyst and solid monomers. Tetramethyl tin and bicyclo[2,2,1]hept-2-ene were purchased from Aldrich Chemical Company Ltd. and Koch-Light Laboratories Ltd. respectively, and were used without further purification.

Synthesised monomers were purified as described in previous sections immediately before polymerisations and were stored under dry nitrogen. Solid monomers were dissolved in dry chlorobenzene. Liquid monomers were degassed and were used in an undiluted form.

(ii) Preparation of tungsten hexachloride, WCl_6

Tungsten trioxide and hexachloropropene were purchased from BDH Chemicals Ltd. and Koch-Light Laboratories Ltd. respectively, and were used without further purification.

Hexachloropropene (35 mls, 61.8g, 0.26 moles) and tungsten trioxide (3g, 1.3×10^{-2} moles) were placed in a 100 ml 3-necked round-bottomed flask fitted with a gas inlet, condenser, and stopper. The condenser was connected to a bubbler containing heavy white oil, and a dry nitrogen atmosphere was maintained throughout. The reaction mixture was refluxed for 4 hours. The red-brown solution produced was allowed to cool slowly to room temperature inducing crystallisation of tungsten hexachloride.

The condenser was removed and replaced by a sinter connected to a 250 ml 2-necked round-bottomed flask. This flask was connected to a vacuum pump. The solution was filtered through the sinter by careful manipulation of vacuum and nitrogen controls. The tungsten hexachloride crystals isolated were washed with degassed Analar carbon tetrachloride (3x10 mls) then dried on a vacuum line (10^{-3}mm Hg). Steel-blue tungsten hexachloride platelets (3.6g, 9.1×10^{-3} moles, 70%) were obtained and were stored under dry nitrogen in a glove box.

(iii) WCl_6 ($MoCl_5$) solutions used in ring-opening polymerisations

A solution of WCl_6 in dry chlorobenzene (0.01g ml^{-1}) was used in the ring-opening polymerisations. This solution was stored under dry nitrogen, and had a maximum active catalytic life of 3-4 weeks.

Molybdenum chloride, $MOCl_5$ was purchased from Alfa Products Ltd., and was used for ring-opening polymerisations without further purification as a solution in dry chlorobenzene (0.1M).

(iv) General polymerisation procedure

Ring-opening polymerisations were performed in a 50ml 2-necked round-bottomed flask fitted with a magnetic stirrer, a 3-way tap, and either a stopper for room temperature polymerisations, or a condenser and drying tube for polymerisations at 70°C. A dry nitrogen atmosphere was maintained throughout.

A typical polymerisation procedure used is as follows.

A calculated amount of blue-black WCl_6 solution was syringed into the polymerisation flask. Tetramethyl tin cocatalyst (undiluted) was syringed into the polymerisation flask using a microsyringe. A colour change from blue-black to dark chocolate brown was observed. After a catalyst ageing time of 3 minutes the monomer solution was syringed into the polymerisation flask.

Polymerisations were performed either at room temperature or at $70^{\circ}C$ (on an oil bath). The reaction solution remained chocolate brown during successful polymerisations, but was decolourised or became blue in unsuccessful cases.

After the reaction time was complete, polymerisations were terminated by adding Analar methanol or THF (0.5 mls) before pouring the reaction solution into a large excess of polymer non-solvent. Polymers were isolated by filtration and removal of volatiles on a vacuum line (10^{-3}mm Hg) before purification. Purification was accomplished by dissolving the polymer in a solvent, filtering and concentrating this solution, then reprecipitating in a large excess of non-solvent before isolating the purified polymers by filtration and removal of volatiles on a vacuum line.

Specific polymerisation conditions used for the monomers investigated are shown in Table 2.30. This represents a selection of experimental observations. Most experiments were repeated several times and both successful polymerisations and unsuccessful attempts were reproducible.

Table 2.30 Reaction conditions used in ring-opening polymerisations

Monomer mmole	Bicyclo[2,2,1] hept-2-ene mmole	WCl_6 ($MoCl_5$) mmole	$SnMe_4$, mmole	Chloro-benzene, mls[a.]	Reaction temperature, °C	Reaction time, hours	Polymer[b.] yield. %
(I) 3.28	0	0.0655	0.131	2.6 + 2	70	3	0
(I) 0.62	11.7	0.0503	0.1	2 + 2	20	3	4 [c.]
(VIII) 3.03	0	0.0315	0.06	0.3[d.] + 0	70	3.5	0
(VIII) 3.51	0	(0.035)	0.07	0.35 + 0	70	21	0
(VIII) 3.03	5.7	0.0525	0.105	2 + 2	20	4	10 [c.]
(IX) 7	0	0.0702	0.14	2.78 + 0	70	3	0
(IX) 2.4	13.6	0.16	0.32	6.34 + 3	20	0.25	95 [c.]
(VII) 12.2	0	0.0504	0.103	2 + 4	70	2	35 (X)
(VII) 7.87	9	0.063	0.128	2.5 + 3	20	0.75	33 (XI)
(XII) 4.67	0	0.019	0.037	0.74 + 6	20	0.25	49 (XIII)
(XII) 2.96	6.81	0.039	0.078	1.55 + 5	20	0.75	93 (XIV)
(XV) 3.68	0	0.0368	0.0736	1.46 + 3	70	2	0
(XV) 3.49	0	(0.035)	0.07	0.35 + 3	70	21	0
(XV) 1.025	5.66	0.0668	0.133	2.65 + 3	20	0.75	40 (XVI)
(XVII) 7.665	0	0.1	0.2	2 + 8	20	2	0
(XVII) 1.875	10.43	0.05	0.1	1 + 3	20	4	0

a. Catalyst solution + monomer solution.

b. Purification was accomplished using the combination of solvents (named first) and non-solvent given below for each polymer produced:

(X): dry acetone, dry hexane; (XI): chloroform, methanol; (XIII): THF, hexane; (XIV): chloroform, methanol; (XVI): chloroform, methanol.

c. Poly(norbornene) alone. Yield calculated with respect to input norbornene.

d. 0.1M WCl_6 solution used.

(v) Elemental analysis figures for homopolymers (X) and (XIII)

Polymer (X): Found: C 43.54, H 2.87, Cl 31.85%, $(C_8H_6Cl_2O_3)_n$ requires C 43.47, H 2.74, Cl 32.08%;

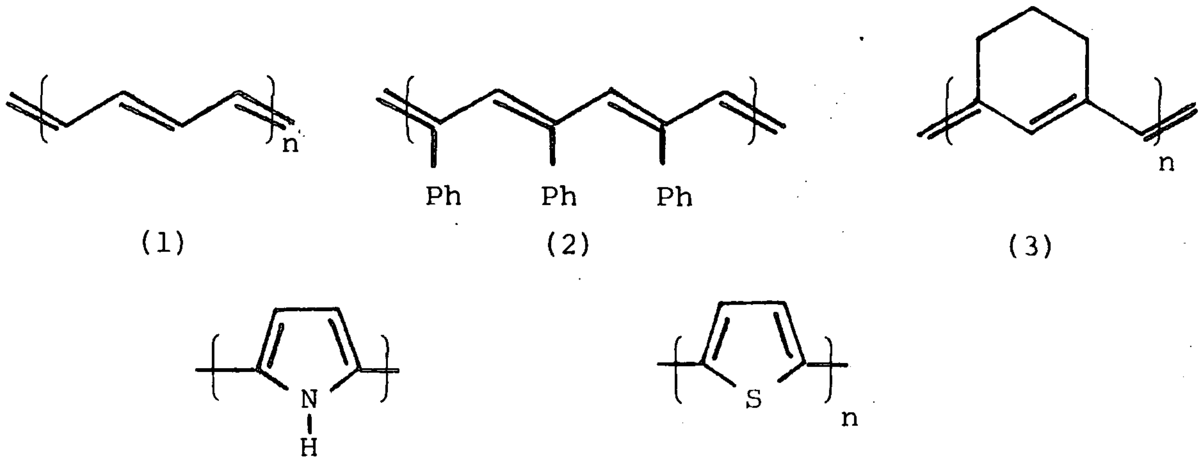
Polymer (XIII): Found: C 56.56, H 4.77, Cl 25.19%, $(C_{13}H_{12}Cl_2O_3)_n$ requires C 54.38, H 4.21, Cl 24.69%.

CHAPTER THREE

SYNTHESIS OF A NEW HETEROSUBSTITUTED CONJUGATED POLYMER

3.1 Introduction

Three main types of conjugated polymers have been synthesised and investigated up to the present time. The first of these is the polyene class of polymers. In this class of polymers the conjugation path simply contains chains of alternating double and single carbon-carbon bonds. Examples are the parent, poly(acetylene) (1), and substituted poly(acetylene)s such as poly(phenyl acetylene) (2), poly(1,6-heptadiyne) (3), poly(pyrrole) (4) and poly(2,5-thienylene) (5) shown in Figure 3.1.

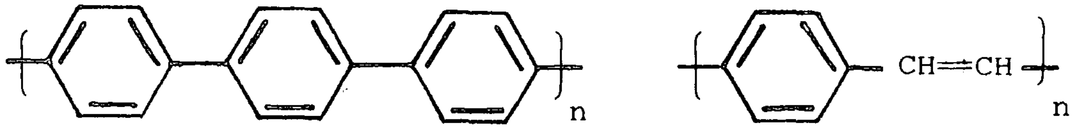


(1) (2) (3)

(4) (5)

Figure 3.1

In the second class the conjugation path contains carbon-carbon double bonds and/or arylene units; examples are poly(p-phenylene) (1) and poly(p-phenylenevinylene) (2), in Figure 3.2.



(1) (2)

Figure 3.2

In the third class the conjugation path contains heteroatoms and arylene units, as in the case of poly(p-phenylene sulphide) (1) and poly(p-phenyleneoxide) (2) in Figure 3.3.

(1) (2)

Figure 3.3

The synthesis, properties and potential applications of these materials are briefly discussed in the following sections.

3.2 Synthesis of conjugated polymers

(a) Poly(acetylene)

In 1974, Shirakawa and Ikeda[1] reported an account of the synthesis of self-supporting films of poly(acetylene) using Ziegler-Natta catalysts. The "Shirakawa technique" involves coating a thin quiescent layer of a concentrated solution of $Ti(OC_4H_9)_4/Al(C_2H_5)_3$ catalyst (Al/Ti, 3 to 4/1) onto the surface of a glass vessel. Acetylene gas is introduced, and this polymerises into thin films of poly(acetylene). At -78^oC, an all-cis polymer is produced. As the polymerisation temperature is increased, or as the film itself is allowed to reach a higher temperature the trans-polymer is produced. An all-trans polymer is produced at 150^oC. It is also observed that if the concentration of the catalyst solution used is less than 3 mmoles/litre in $Ti(OC_4H_9)_4$, a powdered product is formed; this is in agreement with results obtained by Natta and coworkers in 1958 in what was the first reported synthesis of poly(acetylene).[202] Since most applications require films of poly(acetylene), the "Shirakawa technique" was a major contribution to research in the field of conducting polymers. In practice, the key to the rapid development of this field during the mid 1970s was the interaction between Shirakawa and the group of MacDiarmid and Heeger who were already active in the organic semiconductor field.

Alternative catalyst systems for the polymerisation of acetylene had already been reported by Luttinger.[21] These consist of cobalt and nickel salts with $NaBH_4$. Reactions are performed in solvents such as ethanol or water at -80°C to 20°C. At low temperatures a cis-rich film is obtained. As for the poly(acetylene) obtained using the "Shirakawa technique" conversion to trans-poly(acetylene) is accomplished by heating the film. This conversion is slow at room temperature but rapid above 100°C.

The morphology of the poly(acetylene) produced by either of these methods indicates that the films actually consist of a fibrous mat or hard foam which has a density of only 0.3g cm^{-3}. This is considerably lower than the density of 1.2g cm^{-3} expected from crystal packing calculations.[9]

In 1980, a new method for the preparation of poly(acetylene) *via* a percursor polymer was reported by Edwards and Feast.[20] The poly(acetylene) produced using this technique is amorphous rather than foam-like, and has a density of 1.05g cm^{-3}.[203] This work provides a further step forward since the precursor polymer produced is soluble, hence the fabrication problems encountered for poly(acetylene), which is insoluble and intractable, are overcome before the conjugated polymer is actually produced.

(b) Poly(phenylacetylene)

Poly(phenylacetylene) is produced by the polymerisation of phenylacetylene using typical metathesis catalysts. $MoCl_5$ produces the orange-red cis isomer, whereas the brown trans isomer is obtained with WCl_6.[204] Other catalyst systems have been reported to polymerise phenylacetylene, for example $Fe(acac)_3/AlH(^tBu)_2$ and $TiCl_3/AlEt_3$ produce the cis-cisoidal isomer (1) and cis-transoidal isomer (2) as benzene-soluble and insoluble fractions respectively; $TiCl_4/AlEt_3$ and $Fe(acac)_3/AlEt_3$ produce the trans-cisoidal isomer (3),[205] Figure 3.4. Cis-trans isomerisation is observed above 80°C, as in the case of poly(acetylene).

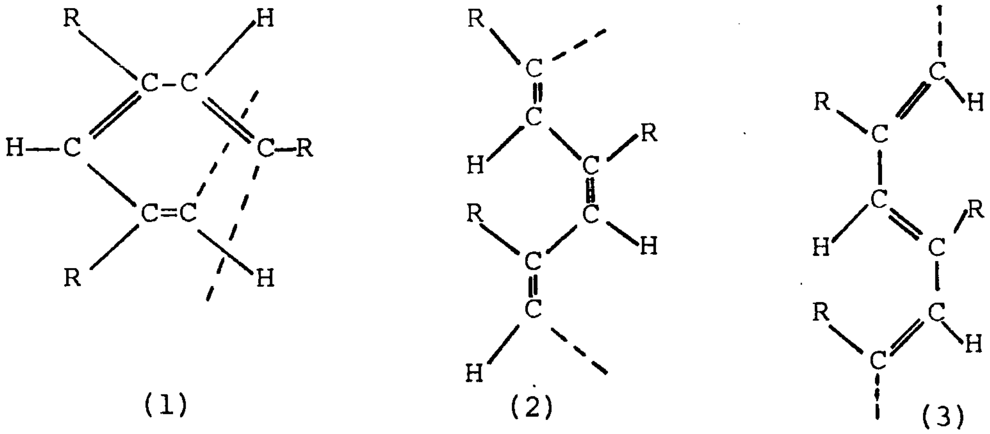

(1) (2) (3)

Figure 3.4

Masuda recently reported the photochemically catalysed polymerisation of phenylacetylene using $W(CO)_6/CCl_4$.[206]

(c) Poly(1,6-heptadiyne)

1,6-Heptadiyne is polymerised to a high molecular weight polymer using Ziegler-Natta catalysts. Free-standing insoluble films are produced using the "Shirakawa technique",[207] Figure 3.5. It is assumed that reaction takes place via a cyclopolymerisation mechanism to produce an amorphous polymer. Stille

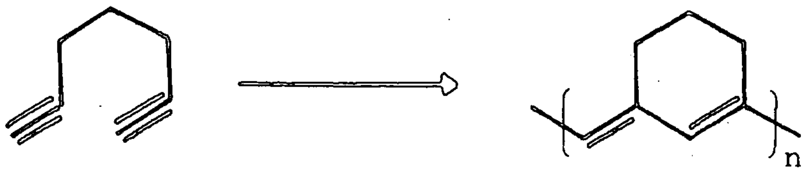


Figure 3.5

previously reported that a soluble polymer is produced using heterogeneous Ziegler-Natta catalyst systems.[208]

(d) Poly(pyrrole)

Poly(pyrrole) is produced by the electrochemical oxidative polymerisation of pyrrole in a solution of acetonitrile containing an electrolyte such as $Et_4N^+BF_4^-$.[12-14] The product, which is formed as a blue-black polymer coating on the anode was shown by elemental analysis to have approximately the stoichiometry shown in Figure 3.6 and is intrinsically electrically conducting (conductivity, $\sigma = 100(\Omega cm)^{-1}$ at 300K).

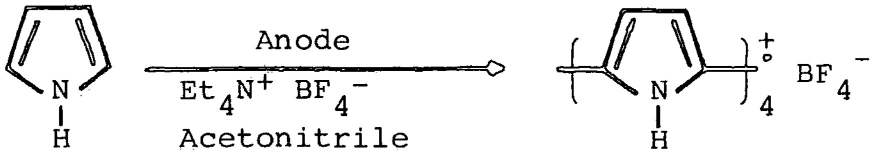


Figure 3.6

Recently Diaz *et al* have investigated the acid catalysed polymerisation of pyrrole in the presence of air; the reaction was carried out in ethanol using dilute sulphuric acid as the catalyst.[209] The product in this case is formed as a yellow film, which slowly darkens to blue-black in air, and which is insulating. It is believed that the conjugated sequences are relatively short since the postulated structure consists of saturated pyrrolidine as well as pyrrole units, Figure 3.7, which accounts for the low electrical conductivity values.

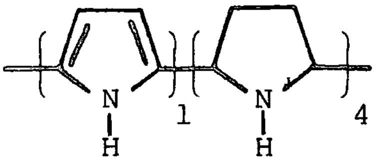


Figure 3.7

This work is in relation to the production of "pyrrole blacks" which occurs during the oxidation of pyrrole using hydrogen peroxide and which has long been known[210-212] but the structures of the products in this case are uncertain. This type of reaction is still in the initial stages of investigation.

(e) Poly(2,5-thienylene)

Poly(2,5-thienylene) is produced in a novel polymerisation reaction utilizing a Grignard reagent. 2,5-Dibromothiophene is reacted with magnesium in THF. This polymerises on addition of $NiCl_2$(2,2'-bipyridine) [213] or $Ni(acac)_2$ [214] to produce an insoluble black amorphous precipitate of poly(2,5-thienylene) Figure 3.8.

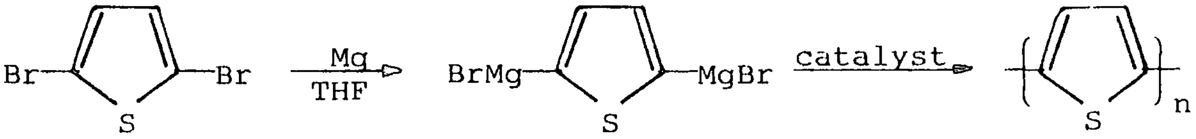


Figure 3.8

(f) Poly(p-phenylene)

Poly(p-phenylene) is obtained in quantitative yield as an insoluble and infusible powder when benzene is polymerised using $AlCl_3/CuCl_2$ (mole ratio 2/1) at 30°C as described by Kovacic.[215,216] The polymerisation proceeds *via* radical cations as indicated in Figure 3.9.[217,218]

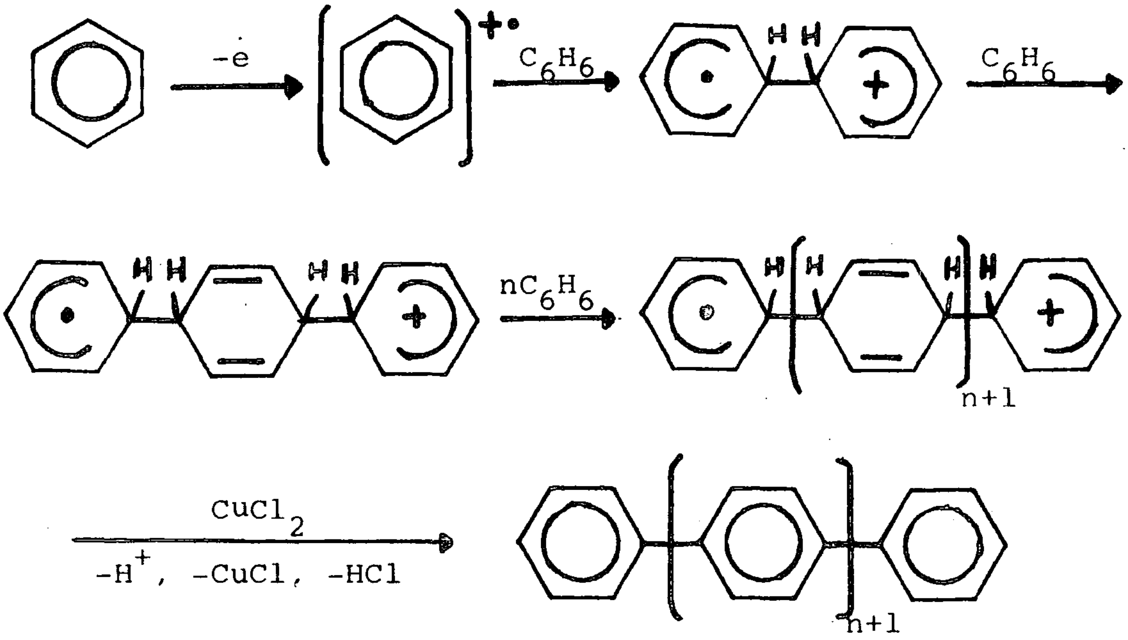


Figure 3.9

The redox potential of oligophenylenes decreases with increasing chain length, hence the units in the polymer produced are further oxidised to radical cation units, Figure 3.10.

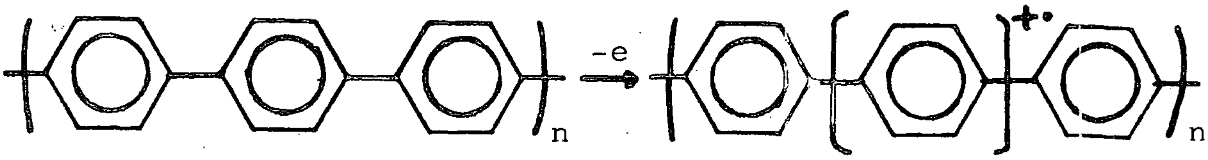


Figure 3.10

The radical cation units are sites for branching, and also account for the spin density of 10^{21} spins.g^{-1} observed for poly(p-phenylene) *i.e.* one unpaired electron for every 8 phenylene units.

In an alternative route, poly(p-phenylene) is prepared *via* a Grignard reaction as used in the preparation of poly-(2,5-thienylene). In this route, 1,4-dichlorobenzene or 1,4-dibromobenzene is reacted with magnesium in THF then the product is refluxed with a transition metal catalyst such as $NiCl_2$(2,2'-bipyridine), $NiCl_2$, $(Ph_3P)_2NiBr_2$, $PdCl_2$(2,2'-bipyridine), $CoCl_2$, $FeCl_3$ or $FeCl_2$,[219-221] Figure 3.11.

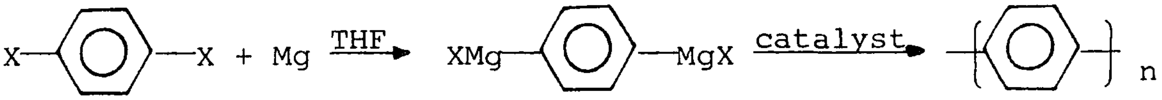


Figure 3.11

Similarly, other poly(arylene) systems such as poly/ (m-phenylene) and poly(2,5-pyridyl) have been synthesised using the corresponding dihalo-aromatics.[219] The polymers produced are reported to be soluble, less coloured than those produced by the Kovacic method, and to have melting points in the region 200° to 550°C.

(g) Poly(p-phenylene vinylene)

Poly(p-phenylene vinylene) is produced by the Wittig reaction between an aryl bisphosphorane and an aromatic biscarbonyl, catalysed by lithium ethoxide in ethanol, Figure 3.12. The

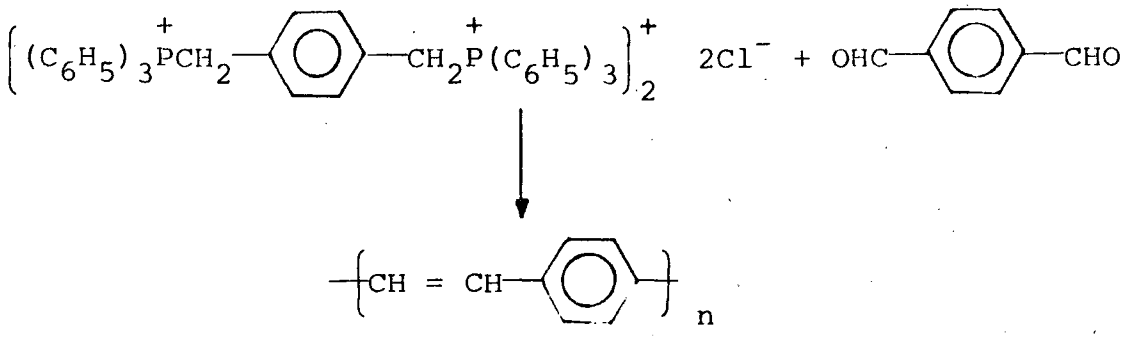


Figure 3.12

product is produced as an insoluble yellow powder, with a relatively low degree of polymerisation (n=9).[222]

Recently Feast and Millichamp[223] have reported the preparation of poly(4,4'-diphenylene diphenylene vinylene) *via* the condensation polymerisation of 4,4'-dibenzoyl biphenyl using $TiCl_3/LiAlH_4$ as the coupling reagent, as shown in Figure 3.13. In this case a much higher degree of polymerisation occurred. Poly(p-phenylene vinylene) has recently been produced in a similar way using terephthaldehyde but in this case the polymer was largely insoluble and consequently incompletely characterised.[224]

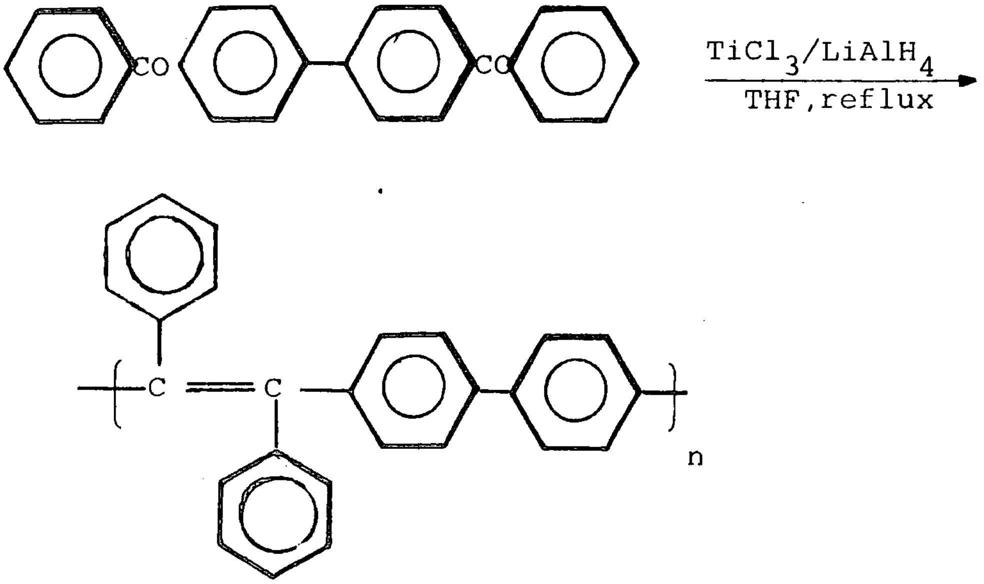


Figure 3.13

(h) Poly(p-phenylene sulphide)

Poly(p-phenylene sulphide) is produced by the reaction between 1,4-dichlorobenzene and sodium sulphide in N-methylpyrrolidone.[15] It is available commercially from the Phillips Petroleum Company under the trade name "Ryton". The product, a white powder, is highly crystalline and precipitates from the reaction. However, poly(p-phenylene sulphide) is soluble in high boiling solvents and melts above 290°C, it is an oxidatively stable material and can be processed more readily than some of the other conjugated systems although high temperatures are required.

3.3 Properties of conjugated polymers

(a) Electrical conductivity

The most remarkable property of conjugated polymers is that when treated ("doped") with electron acceptors or donors their electrical conductivity changes by 10 or more orders of magnitude. In the pristine state these systems generally have conductivities in the insulating range. On "doping" however, their conductivity shows an exponential increase to metallic levels. The conductivities of some conjugated systems before and after doping are shown in Table 3.1.

(b) Conduction mechanism

The conduction mechanism by which the metallic conductivities of "doped" conjugated polymers can be rationalised is not fully understood at the present time. Several postulations have been made in attempts to account for the observed results, particularly for the simplest conjugated system poly(acetylene). One of these is that the high conductivity may arise from the formation of solitons and their interaction with the electron-donor and accept species.[7,8,228,229] It is believed that neutral solitons are formed during the cis-trans isomerisation of poly(acetylene) as shown in Figure 3.14.

Table 3.1 Electrical conductivities of some conjugated systems before and after "doping"

Polymer	"Dopant"	Electrical conductivity $(\Omega cm)^{-1}$	
		Before "doping"	After "doping"
Poly(acetylene)[2-4]	AsF_5	$10^{-9}-10^{-4}$ [a]	560
	Na naphthalide	$10^{-9}-10^{-4}$ [a]	80
Poly(phenylacetylene)[225]	I_2	10^{-12}	10^{-5}
Poly(1,6-heptadiyne)[207]	I_2, AsF_5	10^{-12}	0.1
Poly(pyrrole)[13]	BF_4^-	100[b]	100[b]
Poly(2,5-thienylene)[213]	I_2	5×10^{-11}	3×10^{-4}
Poly(p-phenylene)[226]	AsF_5	10^{-12}	10^4
	K naphthalide	10^{-12}	720
Poly(p-phenylene vinylene)[227]	AsF_5	10^{-10}	3
Poly(p-phenylene sulphide)[16-18]	AsF_5	10^{-16}	1

a. Conversion of cis-poly(acetylene) to trans-poly(acetylene) results in an increase in conductivity from 10^{-9} to 10^{-4} $(\Omega cm)^{-1}$.

b. Poly(pyrrole) as made by Diaz *et al*[12-14] is partially oxidized and is intrinsically conducting.

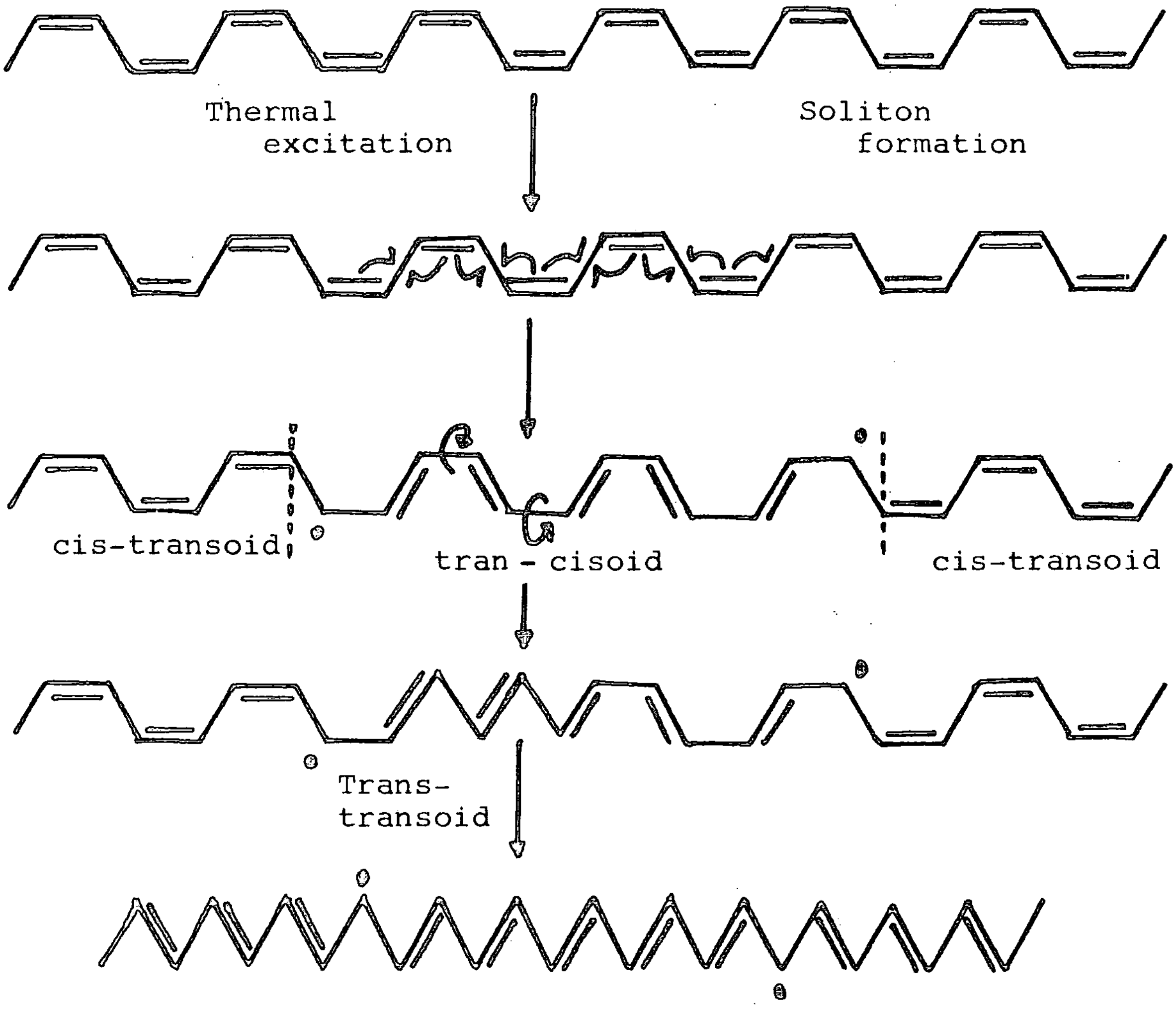


Figure 3.14

The formation of neutral solitons has been studied using e.p.r. spectroscopy,[228] which indicates that the process follows first order kinetics and that the concentration of neutral solitons increases on warming the sample to reach a steady state concentration which does not decrease on recooling the sample.

E.p.r. spectroscopy has also been used to study the mechanism of "doping". Two pathways have been postulated by which iodine "doping" can take place. In the first, electron-accepting iodine converts neutral solitons into positive spinless solitons, Figure 3.15. During this process the concentration

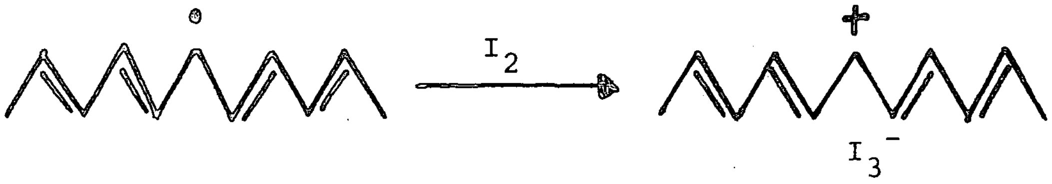


Figure 3.15

of neutral solitons decreases slowly as was observed for very low levels of doping. Hence conductivity in p-type semiconducting poly(acetylene) is due to positive spinless solitons.

In the second stage, iodine reacts with poly(acetylene) directly to produce radical cations, which separate into a neutral soliton and a positive spinless soliton, hence as the level of "doping" increases the radical cation process outlined in Figure 3.16 occurs. Also, interchain migration of the new

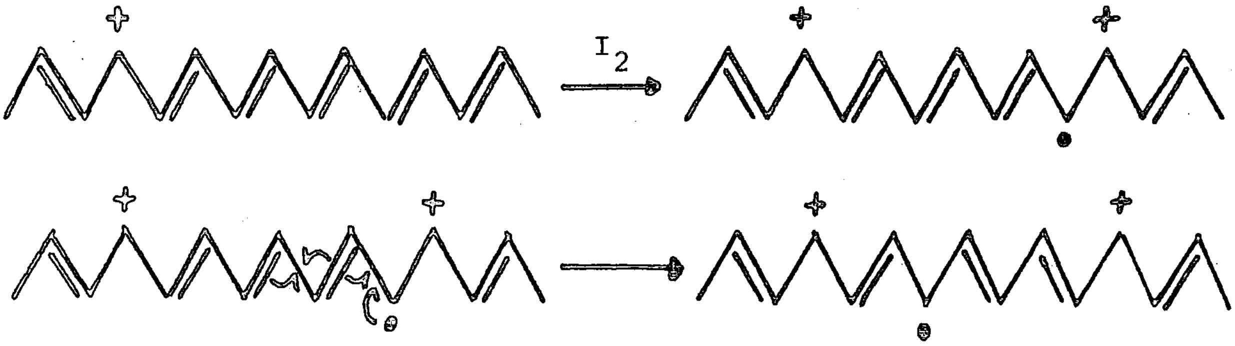


Figure 3.16

neutral solitons produced can occur *via* the dopant acting as a bridge (electron diffraction shows that I_3^- ions are situated between poly(acetylene) chains). At one dopant per two $(CH)_x$ chains a neutral soliton produced on any chain can migrate to and anhilate another neutral soliton on a neighbouring chain. Hence the concentration of neutral solitons decreases precipitously as the level of doping increases above a "threshold" level as observed by e.p.r. spectroscopy, and a corresponding semiconductor to metallic conductivity transition occurs.

The formation of radical cations has been postulated to account for the high conductivity of other conjugated systems.[9] Whether it is the radical cations themselves which are responsible for the high conductivity, or the positive spinless solitons resulting from the separation of the radical cations into a neutral and a positive spinless soliton, then interchain anhilation of neutral solitons producing further positive spinless solitons as postulated for poly(acetylene), is a matter of speculation.

(c) Potential applications of conjugated polymers

Conjugated polymers have a wide range of applications due to the large range of conductivities attainable in these systems from insulating through semiconducting to metallic levels. Two of the potential applications which are creating interest presently are the production of lightweight rechargeable batteries and of solar cells.

Figure 3.17 shows a schematic representation of a poly(acetylene) electrochemical cell.[5,230] The cell is charged

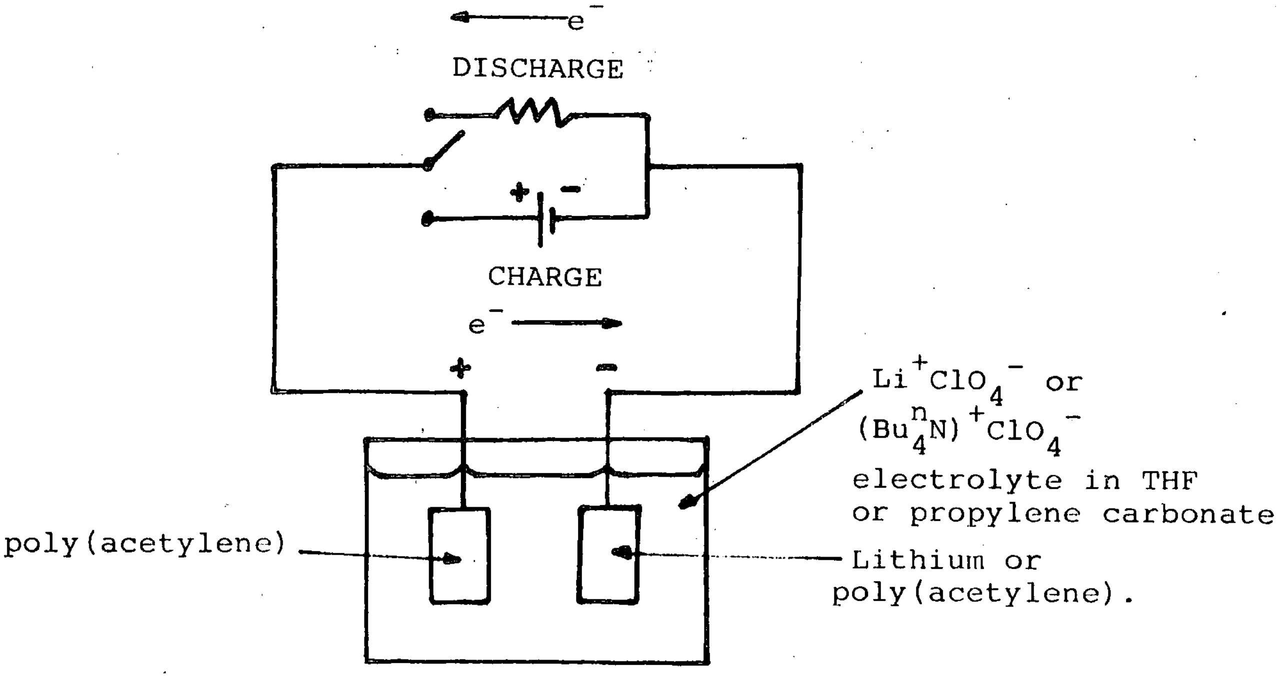


Figure 3.17

by applying a potential across the electrodes resulting in the electrochemical "doping" of the anode,

$$(CH)_x + xy(ClO_4^-) \longrightarrow [(CH)^{y+}(ClO_4^-)_y]_x + xye^- ,$$

where y is the average number of charges transferred per (CH) unit. If the cathode is lithium, the reaction which occurs during "doping" is,

$$xy\ Li^+ + xye^- \longrightarrow xyLi^o.$$

Hence, during charging the overall reaction is,

$$(CH)_x + xy\ Li^+(ClO_4^-) \longrightarrow [(CH)^{y+}(ClO_4^-)_y]_x + xyLi^o.$$

After this reaction, the cell is functional and with a doping level of $y = 0.06$ the open circuit voltage is 3.7V. The corresponding discharge reactions which take place are, at the cathode,

$$xyLi^o \longrightarrow xyLi^+ + xye^-,$$

at the anode,

$$[(CH)^{y+}(ClO_4^-)_y]_x + xye^- \longrightarrow (CH)_x + xy(ClO_4^-)$$

hence overall,

$$[(CH)^{y+}(ClO_4^-)_y]_x + xyLi^o \longrightarrow (CH)_x + xyLi^+(ClO_4^-).$$

Hence the reaction is totally reversible, and the cell is rechargeable and has a much higher power to weight ratio than conventional cells.

Solar cell production using conjugated polymers is still in its infancy, but some reports of the characteristics of these have been made and are encouraging further research. Devices have been made using p-type poly(acetylene) joined to a low work function metal[231-233], or using a p-type poly(acetylene): n-type semiconductor heterojunction.[233] A similar device has also been made by electrochemically depositing poly(pyrrole) film onto n-type GaAs semiconductor.[234] Present research is aimed towards maximisation of the efficiency of these devices which in currently published studies are rather low (∿1%).

(d) The search for new conjugated polymers

The conjugated systems discussed are almost all difficult to manipulate since they are insoluble,(or at best only soluble in high boiling solvents), infusible, and oxidatively unstable, especially when "doped" to metallic conductivity levels, except poly(pyrrole) and poly(p-phenylene sulphide) which are relatively air-stable. The search for new conjugated systems provides an interesting challenge; the next section of this chapter describes the synthesis and properties of a new conjugated polymer.

3.4 Synthesis of poly(4,5-bis hydroxy-1,3-cyclopentadienylene vinylene) (III)

(a) Initial observations

Investigations were made into the use of polymer (X), poly(6,8-(1,5-dichloro-2,4-dioxa-3-keto)bicyclo[3,3,0]octylene vinylene), as a precursor in the synthesis of polymer (III), poly(4,5-bishydroxy-1,3-cyclopentadienylene vinylene) by hydrolysis of the chlorocarbonate group in polymer (X) followed by enolisation, Scheme 5, page 65 .

Initial observations were made on a powdered sample of polymer (X). This darkened slowly from off-white *via* dark green to black on placing in aqueous 0.5M NaOH solution. The black powder produced was washed and isolated, and was found to be insoluble in all solvents tried. Its i.r. spectrum (KBr disc) showed a major absorption in the 2000 to 3600 cm^{-1} region and a further broad band centred at 1575 to 1600 cm^{-1}; absorptions due to unreacted polymer (X) were also present indicating that partial hydrolysis had taken place. In order to try to completely hydrolyse polymer (X) to polymer (III), a sample of polymer (X) was dissolved in Analar acetone producing a pale yellow solution. A few mls of aqueous NaOH solution were added dropwise, resulting in the production of a black precipitate. This was washed, isolated, and analysed by elemental analysis and i.r. spectroscopy. The elemental analysis figures obtained were C 45.0, H 4.1, Na 0%; the figure for carbon is much lower than that calculated for polymer (III), $(C_7H_6O_2)_n$, which requires C 68.9, H 4.9, Na 0%, possibly indicating that air oxidation had taken place. Its i.r. spectrum ((III)·1, Appendix C) contained broad absorptions in the 2000 to 3600 cm^{-1} region (-OH stretch) and centred at 1575 to 1600 cm^{-1} (-OH bend), and the intense carbonyl absorption found in the i.r. spectrum of polymer (X) did not appear in this case. The precipitate was found to be insoluble in organic solvents.

These initial observations suggested that polymer (X) is readily hydrolysed to yield a polymer whose properties (black, insoluble, possibly oxidatively unstable) are similar to other polyene systems.

(b) Synthesis of films of polymer (III)

(i) Preliminary results

Thin, self-supporting films of polymer (X) were spun-cast from dry Analar acetone in a pyrex cylinder. Small samples of film were placed in aqueous 0.5M NaOH solution and in concentrated hydrochloric acid. The alkali-treated film began to darken immediately, changing colour to dark green after 3 minutes and to black after 5 minutes. The film was totally converted to polymer (III) after 3 to 4 hours. The acid-treated film changed colour considerably more slowly. In this case the film was totally converted to polymer (III) after 960 hours (40 days). The hydrolytic conversion of both films could be followed by i.r. spectroscopy, which showed absorptions gradually appearing at 2000 to 3600 cm^{-1} and 1575 to 1650 cm^{-1}, as well as the disappearance of the carbonate carbonyl absorption at 1835 cm^{-1}, and a much diminished band at 750 cm^{-1} (C-Cl). Figure 3.18 (a) to (d) shows the i.r. spectra of polymer (X) at various stages of conversion using concentrated hydrochloric acid.

The i.r. spectrum of the film after total conversion by acid (Spectrum (III).2, Appendix C) is almost identical to that of the alkali treated film (see next section), and that of the black precipitate obtained from acetone solution using alkali (Spectrum (III).1, Appendix C). A slight difference was that the band assigned to -OH bend had its maximum absorption at $\sim$1650 cm^{-1} in the i.r. spectrum of the acid treated film compared to 1575 to 1600 cm^{-1} for the alkali-treated film; however, this absorption was broad in all cases, extending from 1500 cm^{-1} to 1680 cm^{-1}. In all cases, no absorption appeared at 1760 cm^{-1} due to C=O indicating that polymer (II) is produced only as a transient species in the conversion of polymer (X) to polymer (III).

These results indicate that the hydrolysis of polymer (X) to polymer (III) may be accomplished by both acid and alkali,

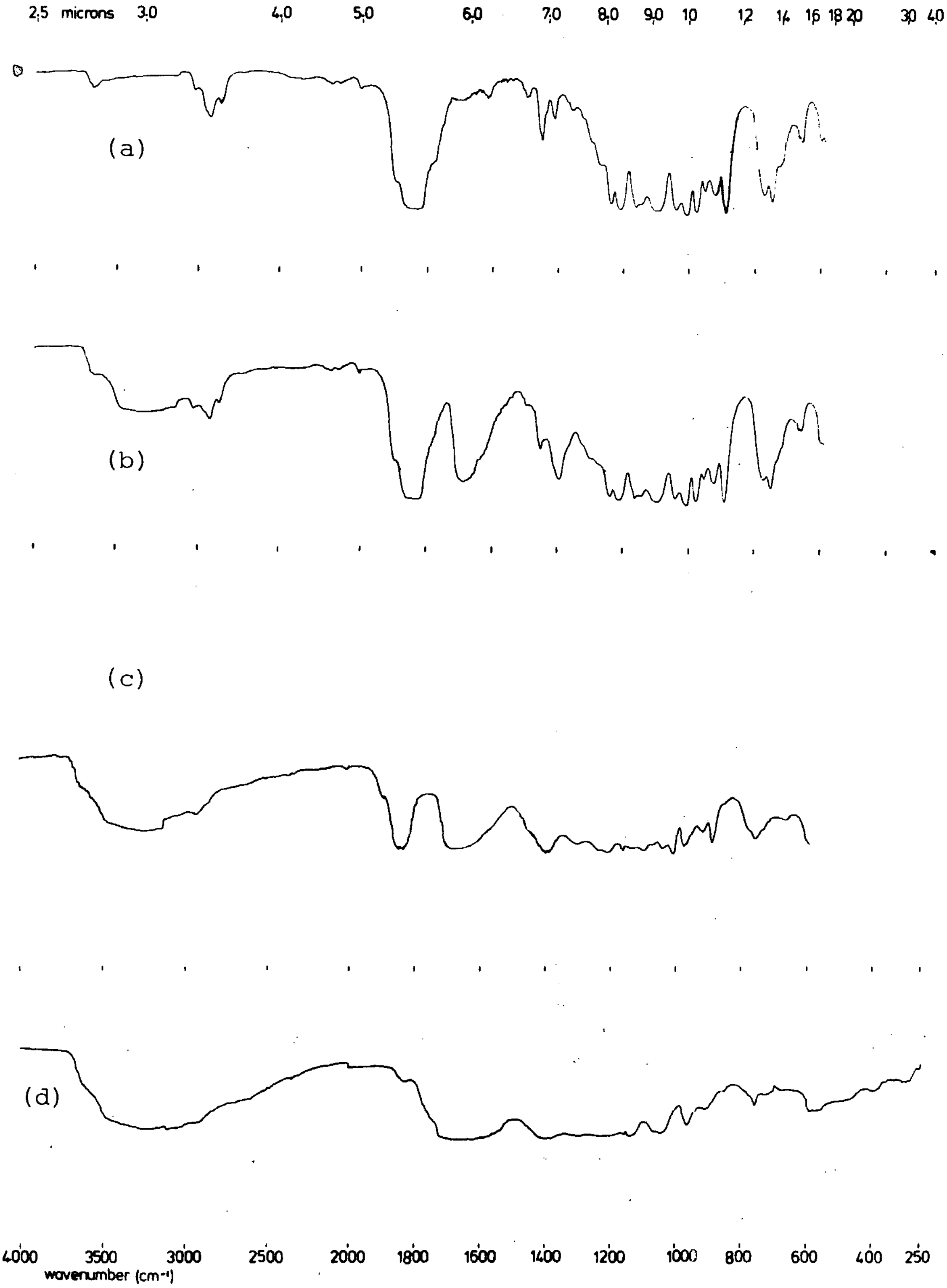


Figure 3.18 I.r. spectra of a film of polymer (X): (a) before treatment, (b) after 126 hours, (c) after 320 hours, (d) after 960 hours in concentrated hydrochloric acid (Polymer (III))

in an analagous manner to the hydrolysis of monomer (VII) to (I) as postulated in Scheme 5, page 65 ; however, in the case of the polymers the equilibrium between the keto and enol forms (polymers (II) and (III)) lies on the enol side.

The elemental analysis results obtained were low in carbon content in these initial conversions, consistent with a ready oxidation of the polymer. An improved conversion procedure was used subsequently as described in the next section (see Experimental).

(ii) <u>I.r. analysis of polymers (X) and (III) using Perkin-Elmer 580B spectrometer</u>

The samples studied in preliminary conversion experiments were found to be readily oxidised, and an improved conversion procedure was adopted to enable synthesis of polymer (III) in a purer form. All manipulations were performed under nitrogen using degassed aqueous 0.5M NaOH solution and degassed distilled water. Using this procedure, a purer sample of polymer (III) was obtained. A Perkin-Elmer 580B infra-red spectrometer was used to record i.r. spectra. This spectrometer is equipped with a Data Station enabling the difference between two spectra to be computed and displayed. Polymer samples were placed in an i.r. isolation cell (see Experimental) enabling a nitrogen atmosphere to be maintained during analysis. Figure 3.19(a) to (d) shows the results obtained. Spectrum (a) is the i.r. spectrum of the precursor polymer; spectrum (b) is the same film after partial conversion using degassed aqueous 0.5M NaOH solution (reaction time 0.5 hours); the difference between (a) and (b) was computed and is shown in spectrum (c); (spectrum (III).3, Appendix C). The film was then totally converted to polymer (III) (5.75 hours in degassed aqueous

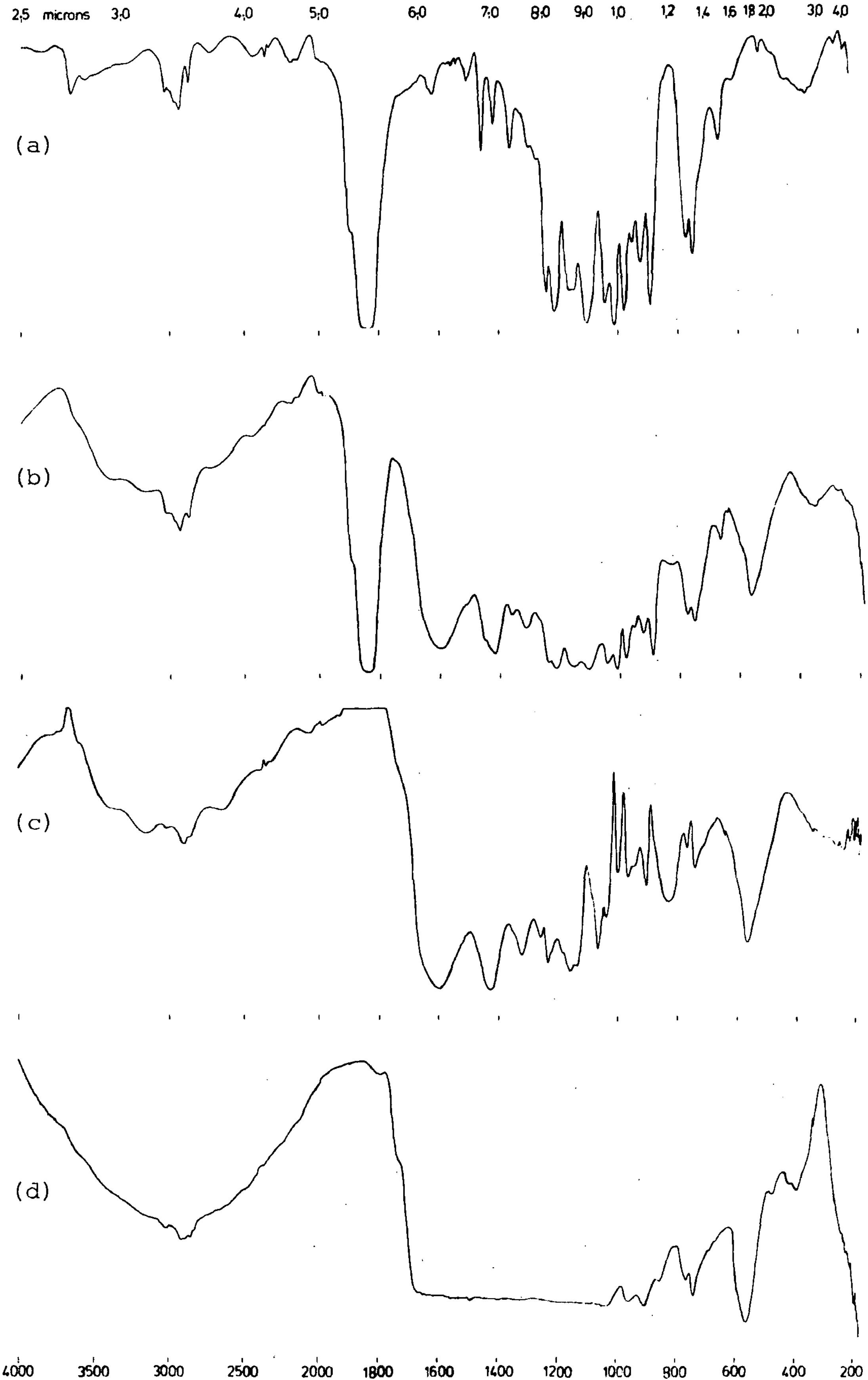


Figure 3.19 I.r. spectra of a film of polymer (X): (a) before treatment, (b) after 0.5 hours in 0.5M NaOH solution, (c) "difference" between spectra (a) and (b), (d) after 5.75 hours in 0.5M NaOH solution

0.5M NaOH solution) and its i.r. spectrum is shown spectrum (d), (spectrum (III).4, Appendix C).

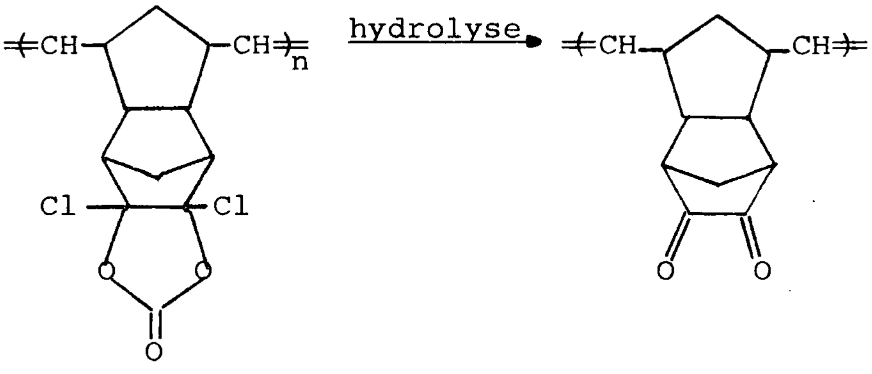
Spectra (c) and (d) are very similar. The resolution in spectrum (d) is lost however, since this sample was very strongly i.r.-absorbing, as expected for a highly conjugated system; spectrum (d) was obtained with the instrument operating at ∿2% transmission.

These samples were also used to obtain electrical conductivity measurements, as described in Section 3.4(b)(vi).

The elemental analysis figures of the totally converted film after i.r. analysis and electrical conductivity measurements had been made were C59.3, H4.8, Na 0%. This film was placed in an air-filled dessicator and after 2 days elemental analysis figures were C 38.6, H 5.0, Na 0%. The results indicate that polymer (III) is extremely sensitive to air oxidation. Similar results were found by Gibson[207] *et al* in the case of poly(1,6-heptadiyne). Oxidation is believed to occur by abstraction of hydrogen atoms from the $-CH_2$ bridges. In the case of polymer (III) the bridging $-CH_2$ is doubly allylic and an analogous abstraction may occur. This leads to a lowering of the elemental analysis figures. The radicals produced can also lead to the production of crosslinks.

(iii) Hydrolysis of polymer (XIII) and attempted hydrolysis of copolymers (XI) and (XIV)

Hydrolysis of polymer (XIII) would result in the production of polymer (XVIII) containing a diketone which is non-enolisable due to the constraints imposed by the bridged 5-membered ring containing the dicarbonyl moiety (Bredt's rule[235]), Scheme 6.



(XIII) (XVIII)

Scheme 6

A thin colourless free-standing film of polymer (XIII) was spun-cast from dry THF. This was placed in aqueous 0.5M NaOH solution for 18 hours. Figure 3.20 (a) and (b) shows the i.r. spectrum of polymer (XIII) before and after treatment with alkali. Yellowing of the film and the appearance of a new i.r. absorption at 1755 cm^{-1} is consistent with Scheme 6, although the rate of hydrolysis is much slower than for polymer (X) and a complete conversion to polymer (XVIII) was not accomplished. This result lends support to the postulate that polymer (III) is produced *via* enolisation. In the case of polymer (III) hydrogens in the keto-isomer (polymer II) are readily enolisable and stabilisation of the enol form may arise due to extension of the π-system during polyconjugation. A discussion of the stabilisation of enols is presented at the end of this chapter.

Attempts were also made to obtain n.m.r. spectroscopic evidence for the structure of the repeat units in polymer (III). Although polymer (III) is totally insoluble, the 1:5 copolymer of (VII) with norbornene, copolymer (XI), is soluble in chloroform. Thin free standing films of copolymer (XI) were cast and

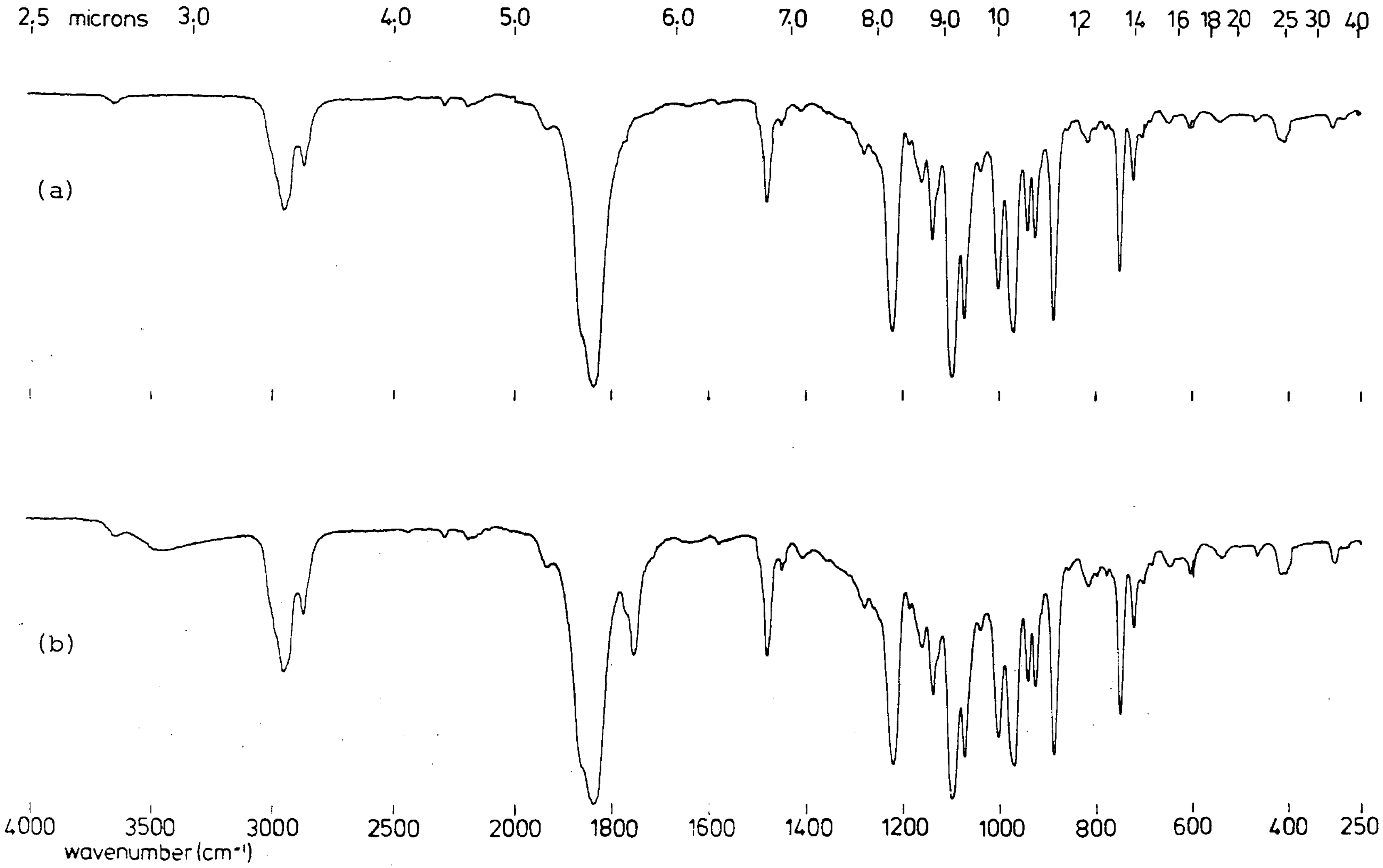


Figure 3.20. I.r. spectra of a film of polymer (XIII), (a) before treatment, (b) after 18 hours in 0.5M NaOH solution

were treated with aqueous 0.5M NaOH solution for several days. I.r. analysis indicated that the chlorocarbonate units in this copolymer were intact after this treatment. This may be as a result of segregation of the poly(norbornene) component (which has the lowest surface free energy[236]) to the surface of the copolymer film, preventing penetration of the alkali to the chlorocarbonate sites. An attempt to hydrolyse this copolymer in solution was not made since the production of an homogeneous solution using chloroform and aqueous solutions is difficult, and since dichlorocarbene is likely to be produced. This would add to the C=C bonds in the copolymer, greatly modifying its structure. A similar attempt to hydrolyse the chlorocarbonate units in a film of the 1:2.42 copolymer of (XII) with norbornene, copolymer (XIV), was also unsuccessful, presumably due to a similar surface effect and due to the low rate of hydrolysis of the polymer (XIII) component.

(iv) Observation of the hydrolysis of polymer (X) using optical microscopy

An optical microscope was used to study the hydrolysis of polymer (X). In this technique a film of polymer (X) was partially hydrolysed in degassed aqueous 0.5M NaOH solution under nitrogen. This was placed in a dry nitrogen glove box and held vertically in a 2½cm x 2½cm aluminium mould using plasticine. An epoxy potting resin was poured into the mould and allowed to solidify. After 1-2 days the resin block was released and the film cross-section was exposed by polishing using 2 grades of "wet and dry" paper. A high polish was finally obtained using a polishing wheel and 3 grades of abrasive powder.

The embedded film was examined using an optical microscope. this instrument is fitted with a 35mm camera attachment enabling the surface of the resin block to be photographed. The photograph obtained is shown in Figure 3.21. Two black surfaces of polymer (III) on the film of polymer (X) can be observed. A calibration slide (10mm in 0.1mm graduations) was also photographed to enable the film thickness to be estimated. The sample had an estimated total thickness of 68.75μm. The thicknesses of the treated surfaces were each approximately 6.25μm. This gives a percentage conversion of ∿18%. The elemental analysis figures obtained for this film were C 45.8, H 2.80, Cl 28.2%. These figures, and the calculated elemental analysis figures of polymer (X) after 16,18 and 20% conversion to polymer (III), are given in Table 3.2.

Table 3.2 <u>Elemental analysis figures for polymer (X) after partial conversion to polymer (III)</u>

% polymer (III) on surface of polymer (X)	Elemental analysis %		
	C	H	Cl
16	45.9	2.92	29.1
18	46.2	2.95	28.7
20	46.5	2.98	28.2
Experimental	45.8	2.83	28.2

This is an example of the kind of measurement attainable by this method. The technique gives a rough estimate of the extent of conversion of polymer films. The method has obvious limitations: the films must be thick enough to withstand the manipulations involved, and the extent of conversion must be low enough to enable the treated and untreated areas to be clearly identified; also, the calibration scale is not very accurate.

A = untreated section (polymer (X))

B = treated surfaces (polymer (III)).

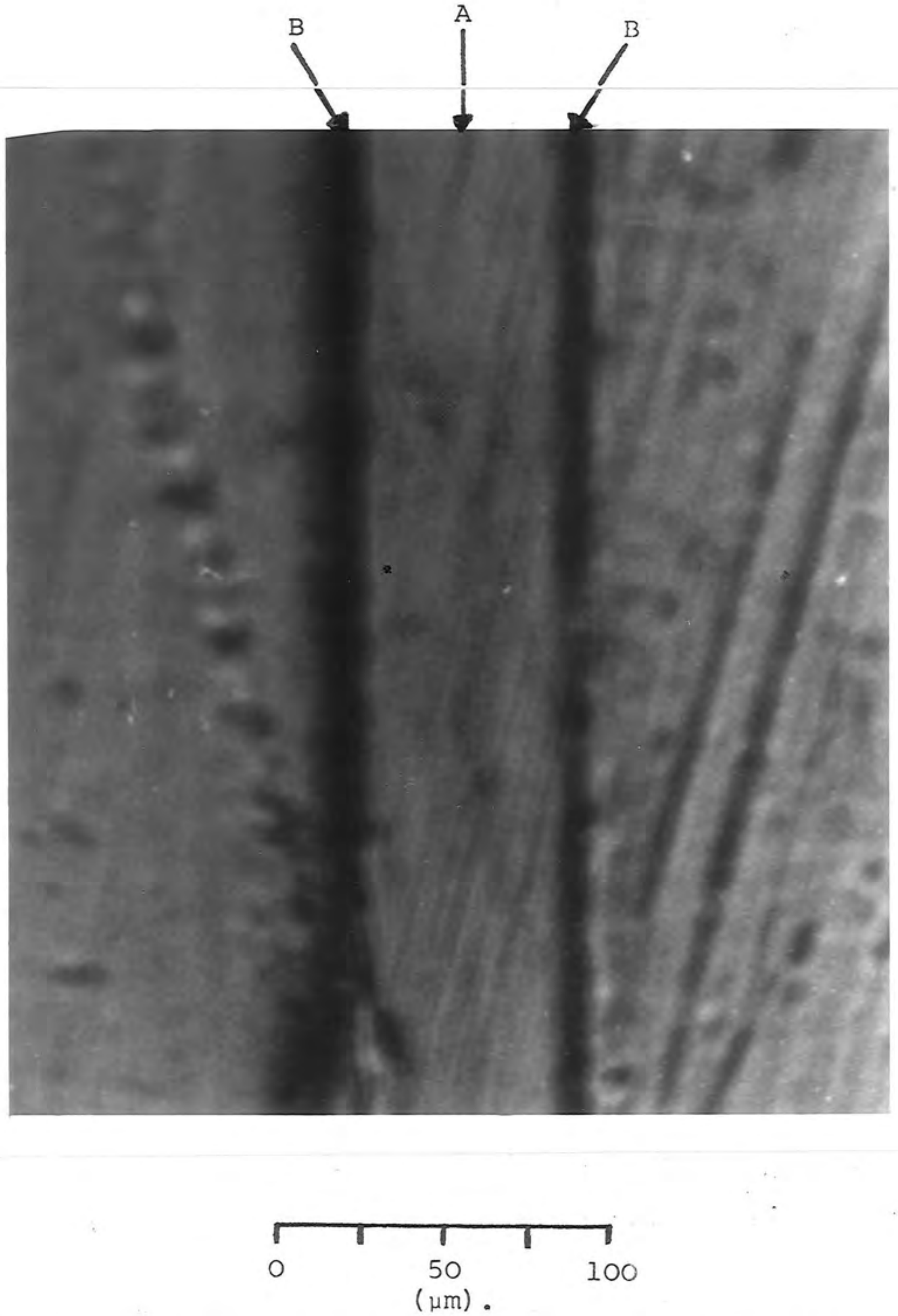
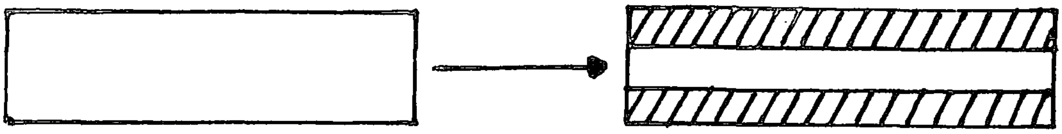


Figure 3.21 Cross-section of a film of polymer (X) after partial hydrolysis to polymer (III).

This experiment demonstrates interesting possibilities for fabrication which can be summarised as shown in Figure 3.22. If the polyconjugated system proved to be a semiconductor which could be doped to a metal, it would, in principle, be possible to fabricate, from one piece of precursor polymer, various types of sandwich structures, for example a metal/insulator/semiconductor sandwich. Such a material might have interesting possibilities in electronic device fabrication. Admittedly this is pure speculation and as will emerge later the electrical properties of the polyconjugated system (III) produced by this route are not particularly encouraging.

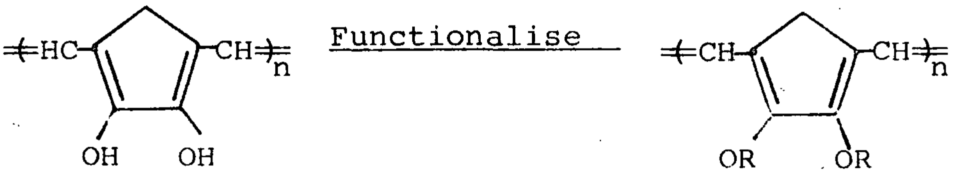


unshaded area = percursor polymer ; shaded area = poly-conjugated system.

Figure 3.22

(v) Attempts to functionalise polymer (III)

Attempts were made to functionalise the -OH groups in polymer (III) to produce further substituted conjugated polymers, Scheme 7. This work was undertaken in the hope of producing products with better handling properties (for example, products which are soluble).



Scheme 7

Initially, powdered samples of polymers (III) and (X) were treated with acetic anhydride and with dimethyl sulphate: 0.5M sodium hydroxide solution (50:50) respectively. I.r. spectroscopic analysis on KBr discs of the recovered polymers showed that no functionalisation had occurred.

In another approach, samples of polymer (X) were dissolved in THF containing trimethyl silyl chloride. It was hoped that polymer (X) could be converted to polymer (III) whilst silating -OH functionalities *in situ* as soon as they were formed. The attempt was made in triplicate, and conversion of polymer (X) to polymer (III) was catalysed by adding a few pellets of sodium hydroxide, a few drops of concentrated hydrochloric acid, and a small amount of triethyl amine in each case. The polymers produced were isolated and i.r.-analysis indicated that polymer (III) had been produced but that silation had not taken place.

Finally, a small piece of film of partially converted polymer (X) was placed in $(CF_3CO)_2O$. The film changed colour to dark red on standing for several hours indicating that some reaction may have occurred. However, when the film was taken out of the $(CF_3CO)_2O$ it became black immediately and its i.r. spectrum was identical with that of polymer (III).

Hence, although the functionalisation of enols is a common reaction in organic chemistry, the heterogeneous nature of these reactions appears to be the most likely explanation for the failure of all attempts to functionalise this polymer which have been tried up to the time of writing.

(vi) Electrical conductivity measurements on polymer films

The electrical conductivity of films of the precursor polymer (X), partially converted polymer, and totally converted polymer (III) (as used for i.r. analysis using the Perkin-Elmer 580B infra-red spectrometer, section 3.4(b)(ii)) were measured using a 4-probe conductivity apparatus. The relationship between voltage, current and resistance is given by Ohm's law,

$$\frac{V}{I} = R.$$

Hence, conductivity $\frac{1}{R} = \frac{I}{V} \quad (\Omega)^{-1}$.

The specific conductivity is defined as,

$$\sigma = \frac{l}{a} \cdot \frac{I}{V} \quad (\Omega\text{cm})^{-1},$$

where l is the distance between the probe tips and a is the area of a probe tip. For the 4-probe apparatus used by the author, $^{l}/_{a} = 31.28\ \text{cm}^{-1}$. Current is passed between the probes using a constant current source and the voltage between them is measured. In order to check the validity of each reading the polarity of the current source is reversed at each current level. The sample should be perfectly ohmic, and the same voltage should be recorded for both polarities, which indicates that a good contact between the probe tips and the polymer film has been made. The measurements were made in a Faircrest glove box under nitrogen containing <2ppm O_2, and <10ppm H_2O; normally levels of 0.6ppm O_2 and 5ppm H_2O were recorded during measurements.

The electrical conductivity of the precursor polymer was found to be too insulating to be measured (i.e. specific conductivity, $\sigma < 10^{-12} (\Omega\text{cm})^{-1}$).

The partially converted polymer (0.5 hrs in degassed aqueous 0.5M NaOH solution) was ohmic; the voltage measurements obtained for this polymer are given in Table 3.3.

Table 3.3 4-Probe conductivity measurements for partially converted polymer

I (Amps)	V (volts)			Specific conductivity $(\Omega cm)^{-1}$
	Polarity		Average	
$1x10^{-9}$	+ 1.5	-1.5	1.5	2.1×10^{-8}
$2x10^{-9}$	+ 3.1	-3.0	3.05	2.1×10^{-8}

Table 3.4 gives the electrical conductivity results for the fully converted film, polymer (III).

Table 3.4 4-Probe conductivity measurements for polymer (III)

I (Amps)	V (volts)			Specific conductivity $(\Omega cm)^{-1}$
	Polarity		Average	
$1x10^{-8}$	+ 1.1	-1.1	1.1	2.9×10^{-7}
$2x10^{-8}$	+ 2.2	-2.2	2.2	2.9×10^{-7}
$3x10^{-8}$	+ 3.3	-3.3	3.3	2.9×10^{-7}

Hence on converting the precursor polymer (X) to polymer (III) there is an increase in electrical conductivity from $<10^{-12}$ $(\Omega cm)^{-1}$ to 2.9×10^{-7} $(\Omega cm)^{-1}$. The partially converted polymer has an intermediate value.

A preliminary attempt to "dope" polymer (III) was made by placing a sample in an atmosphere of iodine vapour in a glove box for 22 hours. The conductivity values obtained for this sample are given in Table 3.5.

Table 3.5 4-Probe conductivity measurements for polymer (III) "doped" in iodine vapour

I (Amps)	V (volts)			Specific conductivity (cm)$^{-1}$
	Polarity		Average	
1 x 10^{-7}	+ 0.96	- 1.07	1.015	3.1 x 10^{-6}
2 x 10^{-7}	+ 2.03	- 2.5	2.265	2.8 x 10^{-6}

The results indicate that "doping" is inhomogeneous since the film is not perfectly ohmic. The specific conductivity increases only by one order of magnitude on "doping".

The electrical conductivity of polymer (III) was re-measured after standing in an air-filled dessicator for 2 days. The results obtained are given in Table 3.6. The results indicate that although the film is substantially oxidised its conductivity does not change markedly.

Table 3.6 4-Probe conductivity measurements for polymer (III) after 2 days in air

I (amps)	V (volts)			Specific conductivity (cm)$^{-1}$
	Polarity		Average	
1 x 10^{-9}	+ 0.1326	- 0.1395	0.13605	2.3 x 10^{-7}
2 x 10^{-9}	+ 0.256	- 0.278	0.267	2.3 x 10^{-7}
3 x 10^{-9}	+ 0.375	- 0.395	0.385	2.4 x 10^{-7}

The conductivity results obtained for polymer (III) are similar to other substituted poly(acetylene)s reported recently: in 1982, Gibson and Pochan[237] reported the synthesis of poly(acetylene) derivatives bearing electron-withdrawing groups. Propiolic anhydride was cyclopolymerised using I^- or CNS^- as catalysts to poly(propiolic anhydride) as shown in Figure 3.23.

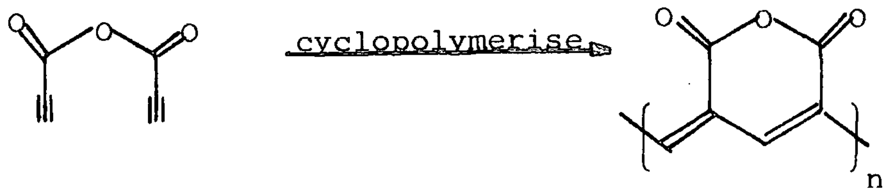


Figure 3.23

The electrical conductivity of this polymer measured in pressed pellet form is 2 x 10^{-14} $(\Omega cm)^{-1}$, and this value changed only by a factor of 2 after the pellet had been placed in an atmosphere of pure oxygen. After "doping" the pellets with iodine the conductivity increased to 5 x 10^{-4} (Ωcm^{-1}). Also, the poly(propiolic anhydride) was hydrolysed, however some decarboxylation also occurred during this process, and a copolymer of poly(propiolic acid) and poly(acetylene) was produced, Figure 3.24.

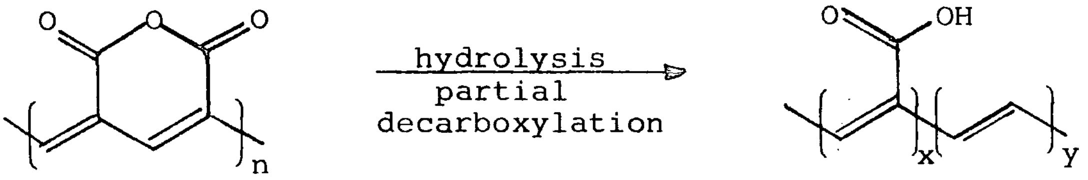
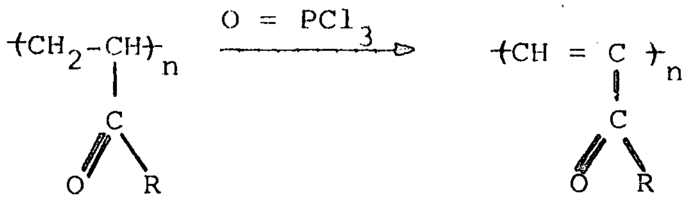


Figure 3.24

The electrical conductivity of this copolymer changed from 10^{-14} to 10^{-5} $(\Omega cm)^{-1}$ on "doping" with iodine.

In the same year, Ogawa *et al* reported that films of poly(alkyl vinyl ketone)s are converted to corresponding poly(acyl acetylene)s on treatment with phosphoryl chloride, Figure 3.25. This appears to be a rather novel dehydrogenation reaction.



(R = methyl or ethyl)

Figure 3.25

The electrical conductivities of the poly(acyl acetylene)s produced were quoted as being in the range 10^{-5} to 10^{-2} $(\Omega cm)^{-1}$ for the ethyl derivative and in the range 10^{-6} to 10^{-3} $(\Omega cm)^{-1}$ for the methyl derivative. These values did not change after standing the films in air. It is believed that the films are spontaneously "doped" by phosphoryl chloride or hydrogen chloride as made, since washing them with cold methanolic triethylamine resulted in a colour change from black to brown and a lower electrical conductivity (10^{-6} $(\Omega cm)^{-1}$); also treatment of the films with iodine vapour resulted in only a slight change in electrical conductivity (less than one order of magnitude).

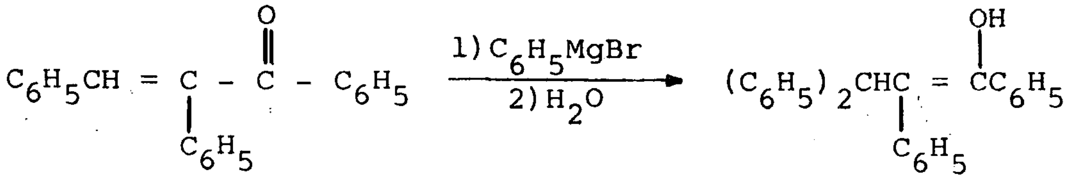
3.5 Conclusions

The aim of this work was to synthesise a new heterosubstituted conjugated polymer via a precursor polymer. The original aim was to metathesis ring-open polymerise diketone (I) then enolise the resulting polymer to produce the polyconjugated system. Diketone (I) was unpolymerisable, hence the endo-1:1 cyclopentadiene:dichlorovinylene carbonate adduct (VII) was ring-open polymerised and the polymer (X) produced was used as the precursor in the synthesis of the desired conjugated polymer.

Electrical conductivity measurements indicated that this new heterosubstituted conjugated polymer is at best semiconducting, hence the initial postulation that the substituent heteroatoms may act effectively as "internal dopants" was not found to be true in this case. This new conjugated polymer was also found to be readily oxidised in contrast to the behaviour of poly(pyrrole), containing nitrogen heteroatom substituents, which is relatively air-stable.

3.6 Keto-enol tautomerism and the stabilisation of the enol tautomer

The rapid and apparently complete enolization which occurs in the formation of polymer (III) might be somewhat surprising at first sight, since it is a widely accepted generalization that keto-forms are more stable than enol-forms. However, while this generalization is true for most simple aliphatic systems, there are many exceptions. Thus, the equilibrium constants for the keto-enol tautomerization of acetaldehyde to vinyl alcohol and acetone to propen-2-ol are 5×10^{-6} and 6×10^{-8} respectively.[239] However in many cases the enol form has been found to be the most stable tautomer, because the keto tautomer is destabilised and/or because the enol tautomer is stabilised. As early as 1906 Kohler[240] isolated a crystalline compound formed by the addition of phenyl magnesium bromide to the unsaturated ketone, shown in Figure 3.26.



$$C_6H_5CH = C(C_6H_5) - C(=O) - C_6H_5 \xrightarrow[2)\,H_2O]{1)\,C_6H_5MgBr} (C_6H_5)_2CHC(C_6H_5) = C(OH)C_6H_5$$

Figure 3.26

In this case conversion to the keto form is rapid in solution. Derivatives containing mesityl groups in place of phenyl groups in the above reaction lead to further stabilisation of the enol tautomer. It would appear that the bulky aryl groups destabilise the keto tautomer whilst conjugation of the double band in the enol tautomer with the aromatic moieties leads to its stabilisation. Many other "hindered" enols of the type $R_1R_2C = C(OH)R_3$ have been produced by Fuson *et al.*[241-45] These enols had a range of stabilities; in some cases the enol form was only observed in solution, sometimes the keto form could not be isolated. Fuson concluded that for a hindered enol with the structure shown in Figure 3.27 the enol tautomer was isolable when B is alkyl or hydrogen and A is a hindered aryl group, or when B is a hindered aryl group and A is aryl, alkyl or hydroxy but not hydrogen.

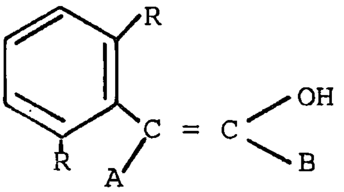
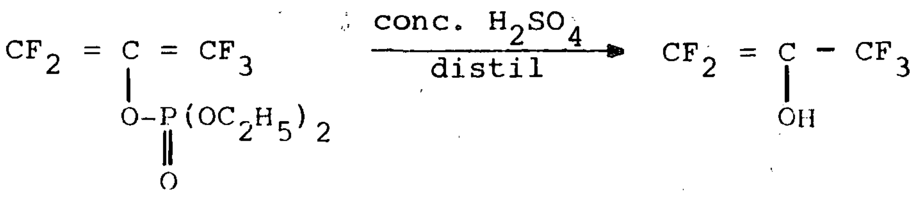


Figure 3.27

Many examples of stable steroidal enols exist. In these the carbon-carbon double bond is usually tetrasubstituted and the hydroxyl group is in a crowded environment.[246] The stability of the enols is accounted for kinetically since in this case the steric constraints of the structure slow down the ketonisation process.

Many examples of enols substituted by fluorine have been reported. The enol of pentafluoroacetone was isolated as a distillable liquid (b.pt. 54° - 55°C) by Becker[247,248] *et al* Figure 3.28.



$$CF_2 = \underset{\substack{|\\ O-\underset{\substack{\|\\ O}}{P}(OC_2H_5)_2}}{C} = CF_3 \xrightarrow[\text{distil}]{\text{conc. } H_2SO_4} CF_2 = \underset{\substack{|\\ OH}}{C} - CF_3$$

Figure 3.28

Several cyclic fluorinated enols have also been isolated,[249,250] Figure 3.29.

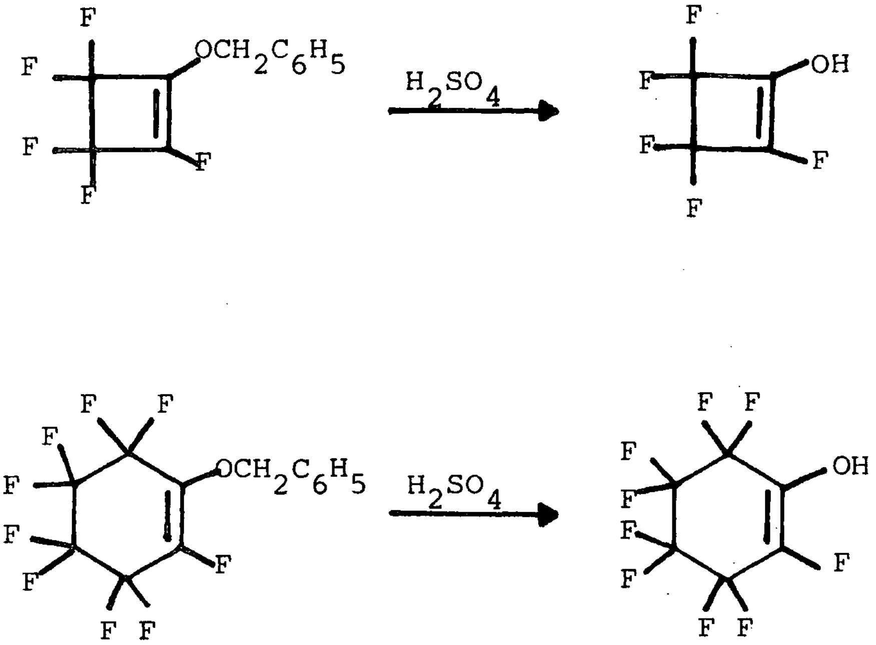


Figure 3.29

Phenols may be regarded as being the enol tautomer of two possible keto forms as shown in Figure 3.30.

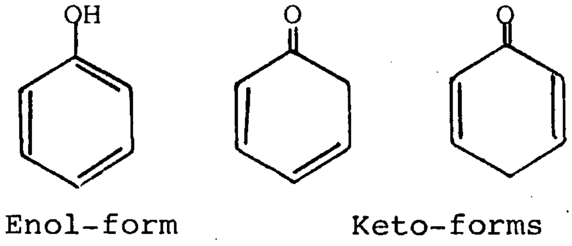


Figure 3.30

The resonance energy gained through aromatization is considerably greater than the bond energy difference which usually favours keto structures in simple ketones. Neither keto-form of phenol has been detected, although the ortho-dihydro tautomer is assumed to be an intermediate in a photochemical reaction reported in 1974.[251] As the number of fused aryl rings is increased the keto tautomers become more stable. Hence for naphthol and 9-phenanthol the keto isomers represented in Figure 3.31 have been observed.

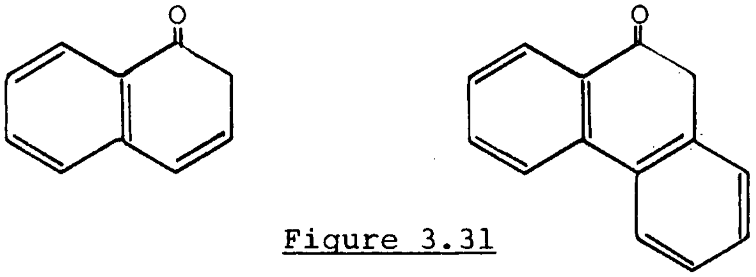


Figure 3.31

In this series the gain in resonance energy achieved through aromatisation is diminished as the number of fused rings is increased hence the energy gap between the keto and enol tautomers is reduced.

Stable enols have also been detected in a range of 1,2-diketones.[252] Cyclopentan-1,2-dione exists as the monoenol. This was determined using dipole moment measurements. The keto and enolic species shown in Figure 3.32 have calculated dipole moments of 4.71 and 2.17 Debyes respectively. The measured dipole moment was 2.21 Debyes.

Figure 3.32

The molecule was found to be planar. The distance between the hydrogen and carbonyl oxygen atom in this case is 2.5Å, hence hydrogen bonding is not believed to occur, and conjugation of the hydroxyl and carbon-carbon double bond is believed to be responsible for the O-H group being held in the plane of the ring. As the ring size is increased in the cycloalkane-1,2-dione series the molecules become more flexible and less planar and the proportion of enol tautomer becomes less, *i.e.* enolization is most favourable when the two carbonyl groups are in a planar cis-configuration.

The spontaneous enolization of polymer (II) to polymer (III) may therefore be rationalized. Thus, if we assume that initial hydrolysis produces the diketone polymer repeat unit shown in Figure 3.33, we would expect on the basis of the behaviour of cyclopentane-1,2-dione and in view of the fact that the process occurs in an aqueous base medium that initial enolization to give the structure shown in Figure 3.34 would be easily accomplished despite the conformational reorganization required. Stabilization of the dienol form consequent on formation of a fully conjugated planar polyene may be the "driving force" for the second enolization step. The stabilization gained by formation of a linear polyene is not easily estimated as compared to the formation of phenols, but may well be quite significant. In this respect it is worth noting that

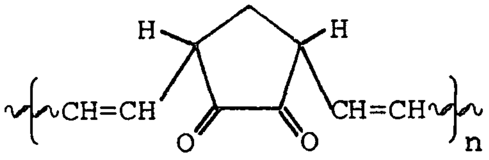


Figure 3.33

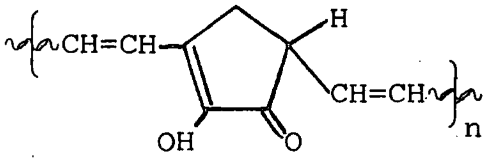


Figure 3.34

the elimination of an aromatic moiety to give poly(acetylene) from polymer (2) in Scheme 1 (page 4) occurs spontaneously at room temperature whereas the monomer (1) in Scheme 1 is indefinitely stable at room temperature. In this instance, the formation of the polyene, poly(acetylene), would appear to be significantly favoured.

EXPERIMENTAL

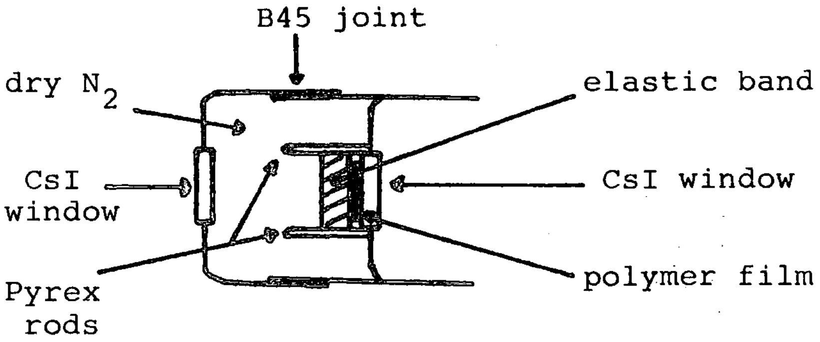
3.7 (a) Preparation of self-supporting films of polymer (III)

Aqueous 0.5M NaOH solution and distilled water were degassed 4 times before use and were stored in 2 x 250ml 2-necked round-bottomed flasks each fitted with a high vacuum tap and stopper. Self-supporting films of polymer (X) were spun-cast from dry acetone in a pyrex cylinder. In a typical hydrolytic conversion a piece of this film was placed in a 50ml 2-necked round-bottomed flask fitted with a high vacuum tap and stopper. After flushing the flask with dry nitrogen degassed aqueous 0.5M NaOH solution (25mls) was poured into the flask *via* a B19 u-joint maintaining a nitrogen atmosphere throughout. The film changed colour *via* dark green to black during hydrolysis to polymer (III). After the desired reaction time (complete conversion of polymer (X) to polymer (III) took 3 to 4 hours) the spent NaOH solution was poured out of the flask *via* a B19 u-joint. Using a similar transfer technique the film was washed repeatedly with degassed distilled water (20ml portions) until the washings were neutral to Universal Indicator Paper. After pouring the final washings from the reaction flask, the flask was evacuated on a vacuum line at 10^{-4} to 10^{-5}mm Hg for at least 10 hours.

The flask containing the converted film, which was dark green with a golden lustre, was placed in a Faircrest glove box under oxygen-free and moisture-free nitrogen (usually $\sim$0.6 ppm O_2 and $\sim$5 ppm H_2O), where further manipulations could be made.

(b) Sample mounting during i.r. spectroscopic analysis of polymer films using Perkin-Elmer 580B infra-red spectrometer

In order to maintain a totally oxygen-free and moisture-free environment during the i.r. spectroscopic analysis of the films, films were mounted in an isolation cell inside the Faircrest glove box. A diagram of the isolation cell used is shown below.



Polymer film mounted inside isolation cell during i.r. spectroscopic analysis

The isolation cell is in 2 parts. The lower part consists of a CsI i.r. window onto which the film was placed and held by an elastic band supported around 3 pyrex rods next to the window. The upper part contains a second CsI window; both parts of the cell fit together to enclose the sample (B45 joint).

(c) Attempted functionalisation of polymer (III)

Reactions were performed under nitrogen in 50ml 2-necked round-bottomed flasks.

In the attempted acetylation a sample of powdered polymer (III) (0.3 to 0.5g) and acetic anhydride (10mls) were placed in the reaction flask. After stirring for several days the sample was filtered through a sinter into a 100ml 2-necked round-bottomed flask connected to a vacuum pump maintaining an inert atmosphere by careful manipulation of vacuum and nitrogen controls, before evacuation on a vacuum line. I.r. spectroscopic analysis (KBr disc) indicated that no reaction had occurred.

A similar procedure was adopted in the attempted methylation. A sample of polymer (X) (0.3 to 0.5g) and 50:50 dimethyl sulphate: aqueous 0.5M NaOH (20mls) were used. (Reaction time 2 hours). In this case the polymer changed colour to black due to hydrolysis by NaOH. The i.r. spectrum of the polymer produced (KBr disc) contained strong absorptions due to -OH stretch (2000-3600 cm^{-1}) and -OH bend (1500-1650 cm^{-1}) together with some absorptions due to remaining polymer (X), at 1835 cm^{-1} etc. (see Chapter Two). Hence no methyllation had occurred.

In the attempted silation reactions samples of polymer (X) (0.3 to 0.5g) were dissolved in THF (20mls). Trimethyl silyl chloride (3mls) was added with either sodium hydroxide pellets (0.5g), concentrated hydrochloric acid (1 ml), or trimethyl amine (1 ml). Observations made were as follows:

(i) In the reaction containing NaOH pellets, the solution became dark brown, and contained a small amount of black precipitate after stirring overnight. The polymer produced was isolated by rotary evaporation of volatiles and evacuation on a vacuum line (10^{-3} mm Hg). Its i.r. spectrum (KBr disc) indicated that this was unreacted polymer (X) containing a small amount of polymer (III). No i.r. absorptions due to $-Si(CH_3)_3$ were observed.

(ii) In the reaction containing concentrated hydrochloric acid the solution became dark green after stirring overnight. A thin film of the polymer produced was spun-cast from solution. I.r. spectroscopic analysis indicated that this was unreacted polymer (X).

(iii) In the reaction containing Et_3N, the solution became dark red containing a white precipitate after stirring overnight. The precipitate was isolated by filtration (sinter filterstick); i.r. spectroscopic analysis indicated that this was Et_3HN+Cl^-. The polymer produced was isolated by rotary evaporation of volatiles and evacuation on a vacuum line (10^{-3}mm Hg). Its i.r. spectrum indicated that a mixture of products had been isolated; i.r. absorptions due to unreacted polymer (X), $Et_3HN^+Cl^-$ and absorption at 1710 cm^{-1} presumably due to an oxidised species were observed. No i.r. absorptions due to $-Si(CH_3)_3$ were observed.

The attempted functionalisation of a film of partially converted polymer (X) was performed by immersing a small piece of this film in $(CF_3CO)_2O$ (15 mls). After several hours the film had changed colour from black to dark red. The film was recovered by decanting excess $(CF_3CO)_2O$ and evacuating the reaction flask on a vacuum line. On removing the sample from solution a colour change to black was observed. The film's i.r. spectrum contained no absorptions due to $-COCF_3$.

(d) 4-Probe electrical conductivity measurements of polymer films

4-Probe electrical conductivity measurements were made on the polymer films using standard procedures. No contact material was used; the probes were simply pressed onto the film surface. Iodine "doping" was accomplished in the Faircrest glove box by leaving a piece of film of polymer (III) in the top of a tube containing a small quantity of iodine crystals for 20 hours.

CHAPTER FOUR

ATTEMPTS TO SYNTHESISE BLOCK COPOLYMERS VIA METATHESIS

4.1 Initial objectives

The initial work on this theme was carried out by Dr. F. Stelzer (Technical University of Graz, Austria), who was a Visiting Research Fellow in this Department from July to September 1980. Dr. Stelzer's aim was to use ESCA to study the formation and propagation of the active species during the ring-opening polymerisation of cycloalkenes via metathesis. However, a solvent-free system was needed to facilitate direct observation using ESCA. The $WCl_6/SnMe_4$ catalyst system was chosen for two main reasons:

(i) This system is easily manipulated using vacuum-line techniques since WCl_6 is sublimable, and $SnMe_4$ is a volatile cocatalyst.

(ii) This system has been found to be the most active metathesis system in conventional polymerisations, and hence was expected to remain active under solvent-free conditions.

Ideally, WCl_6 may be sublimed onto the probe of the ESCA spectrometer. The cocatalyst may then be evaporated and condensed onto the WCl_6, and allowed to react. A volatile monomer such as cyclopentene may then be evaporated onto the active catalyst, and allowed to polymerise. The core energy levels of all the nuclei could be studied by ESCA at each stage of the process and hence the nature of the active sites formed, and the propagating species, during the polymerisation, might possibly be deduced.

4.2 Initial observations

The initial observations were made using a cold-finger apparatus, as shown in Figure 4.1, which may be attached to the vacuum line. A weighed amount of WCl_6 was sublimed onto the cold-finger, followed by $SnMe_4$. The catalyst system changed colour during this process from purple-black to red-brown, and a gas was observed bubbling from the catalyst surface. After evacuating volatile byproducts, cyclopentene was condensed

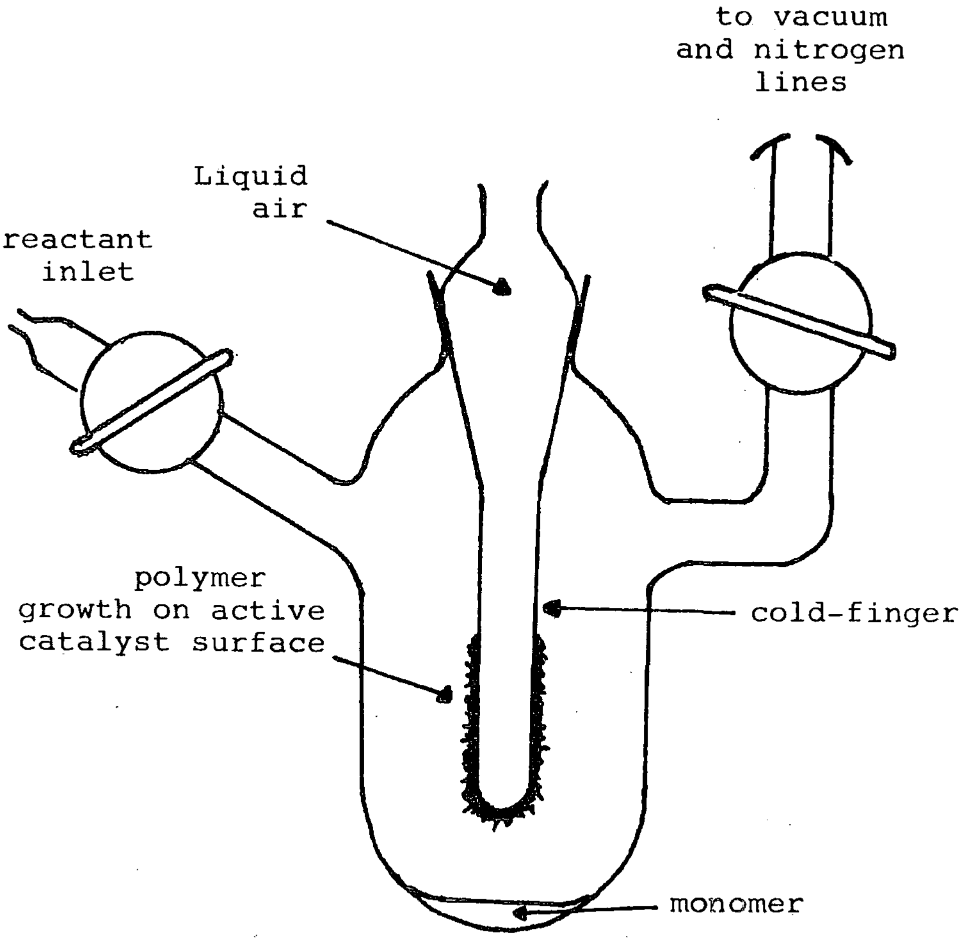
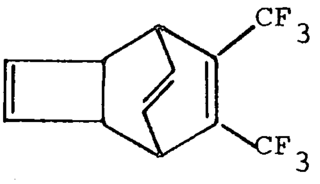


Figure 4.1 Cold-finger apparatus used in solvent-free polymerisations

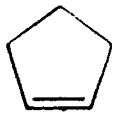
onto the surface of the catalyst, and on warming to room temperature needles of polymer began to grow. Addition of a second amount of cyclopentene after 24 hours resulted in further polymerisation. The system remained active for at least seven days.

These results would seem to indicate that a "living" system had been observed, and initial attempts were made to prepare a block copolymer; two systems were investigated:

(i) Attempted block copolymerisation of 7,8-bis(trifluoromethyl)tricyclo$[4,2,2,0^{2,5}]$deca-3,7,9-triene(A) and cyclopentene (B), shown below.



(A)



(B)

Using the techniques described above, monomer (A) was polymerised. The reaction vessel was kept at room temperature for a maximum of 15 minutes before being stored in a freezer. This allowed sufficient time for polymerisation to take place without converting the polymer resulting from monomer (A) into poly(acetylene). Two successive batches of this monomer were polymerised.

On adding cyclopentene further polymerisation took place. After standing at room temperature for several hours the polymer produced consisted mainly of black poly(acetylene) containing white elastomeric segments of poly(1-pentenylene). An attempt was made to physically separate these segments and elemental results for each were reported as shown in Table 4.1.

Table 4.1 Elemental analysis figures for components in the initial attempted block copolymerisation of monomers (A) and (B)

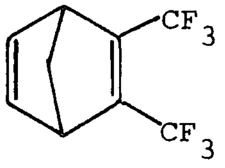
Sample	Elemental analysis (%)	
	C	H
metallic "foam"	78.94	8.76
black elastomer	85.41	14.77
white elastomer	86.41	14.01

Calculated elemental analysis figures for the homopolymers derived from monomers (A) and (B) and for poly(acetylene) are given in Table 4.2.

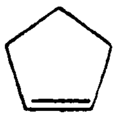
Table 4.2 Calculated elemental analysis figures for homo polymers of (A) and (B) and poly(acetylene)

Sample	Calculated elemental analysis (%)		
	C	H	F
homopolymer of (A)	54.1	3.2	41.7
poly(1-pentenylene)	88.24	11.76	-
poly(acetylene)	92.3	7.7	-

(ii) Attempted block copolymerisation of 2,3-bis(trifluoromethyl)bicyclo[2,2,1]hepta-2,5-diene(XIX) and cyclopentene(B), shown below.



(XIX)



(B)

Monomer (XIX) was polymerised followed by cyclopentene. The resulting polymer was placed in acetone. The acetone-soluble part was separated, and after removal of remaining traces of acetone, the acetone-insoluble part was placed in chloroform. Again the polymer partly dissolved. The elemental analysis figures reported for these polymers are given in Table 4.3.

Table 4.3 Elemental analysis figures for components in the initial attempted block copolymerisation of monomers (XIX) and (B)

Sample	Elemental analysis (%)		
	C	H	F
Acetone-soluble	46.66	2.28	50.0
chloroform-soluble	79.35	10.89	8.98
homopolymer of (XIX) (calculated)	47.4	2.7	50.0

Hence, the acetone-soluble component appeared to be the homopolymer of monomer (XIX) whereas the chloroform-soluble component appeared to be a copolymer.

4.3 Postulations from initial work, and author's aims

From these initial observations it is clear that the catalyst system used is potentially a "living" system since it remains active for at least 7 days. However, the catalyst was in a high localised concentration in comparison to conventional polymerisations. Three possible explanations can be given to rationalise the behaviour of the system.

(a) The system contains active sites which remain active for at least 7 days - a truly "living" system. Using such a system the preparation of block copolymers is feasible.

(b) The system contains an abundance of active sites and potential active sites, so that when one active site is terminated it is immediately replaced, and polymerisation continues at this new site.

Any system in which chain transfer steps are feasible cannot be classed as "living". An attempt to prepare block copolymers with such a system would result in the production of two homopolymers.

(c) The system is behaving as a combination of (a) and (b). In this case, an attempt to prepare block copolymers would result in the production of a mixture of a block copolymer and the two homopolymers.

The aim of the author's work was to distinguish between the above three possibilities.

4.4 Modification of sampling technique

In order to obtain polymer samples from the system used by Dr. Stelzer, the cold-finger apparatus had to be detached from the vacuum line and placed in a glove box where it could be dismantled to allow access to the polymer. Also, catalyst and polymer segments were prone to detach themselves from the cold-finger and fall into the base of the apparatus, hindering further manipulations. Initial work was aimed at overcoming these difficulties. Subsequent polymerisations were accomplished in a 2-necked round-bottomed flask attached to the vacuum line. The cocatalyst and monomers were placed in a second round-bottomed flask which was attached to the line adjacent to the polymerisation flask.

All manipulations could be carried out under vacuum or dry nitrogen using this system. Sampling could be accomplished relatively easily by flushing the polymerisation flask with nitrogen and removing desired amounts of polymer via the side-arm.

The series of solvent-free polymerisations which were accomplished are described and discussed below.

4.5 Cyclopentene polymerisation - an attempt to monitor successive increases in molecular weights

The aim was to polymerise cyclopentene and monitor the molecular weights of the polymers produced. If the system is "living" the molecular weights should sequentially increase on polymerising successive amounts of monomer.

In this attempt, WCl_6 was transferred into the polymerisation flask using a u-tube. The catalyst was dispersed as a solid using a magnetic stirrer. On cooling to -198^oC, the thermochromic behaviour of WCl_6 was observed as it changed colour from lustrous purple to bright red. Tetramethyl tin was syringed into the monomer flask (WCl_6:$SnMe_4$ in a 1:2 ratio). This was degassed several times then vacuum-transferred and condensed onto the surface of the WCl_6 catalyst. On warming the polymerisation flask to room temperature, a reaction took place and bubbles of gas were evolved from the catalyst which became blue/black. After 30 minutes, the polymerisation flask was evacuated to remove volatile byproducts.

Cyclopentene monomer, which had been distilled from CaH_2 to ensure complete dryness, and degassed several times, was vacuum transferred and condensed onto the surface of the catalyst. The catalyst under the layer of the cyclopentene became dark brown, whilst above this layer it remained blue/black. The reaction flask was warmed to -90°C (acetone slush bath) with stirring then gradually to room temperature. At 0°C, the monomer became very viscous. After leaving overnight all the cyclopentene had polymerised.

A small sample of polymer was taken, and an attempt was made to dissolve this polymer in dry toluene containing a small amount of methanol without success.

A second amount of cyclopentene was vacuum transferred into the polymerisation flask. On warming the flask to room temperature, the polymer became swollen, and polymerisation continued. The experiment was left overnight.

A second sample of polymer was taken, and again proved to be insoluble in dry toluene.

The samples were insoluble, even after several days reflux. They became swollen and gelatinous in toluene but an homogeneous solution was not obtained. Various other solvents were tried without success.

Due to the insolubility of the polymers no attempts to measure their molecular weights could be made. However, the polymers were swollen by $CDCl_3$ and 'H-n.m.r. analysis indicated that the polymers were essentially poly(1-pentenylene).

This experiment showed that the ring-opening polymerisation of cyclopentene did occur readily, and that the system is active for several days. However, the polymers obtained appeared to be cross-linked.

4.6 Attempt to prevent cross-linking during the polymerisation of cyclopentene

The above procedure was repeated, but the samples taken after each amount of cyclopentene had polymerised were placed in dry toluene containing 1% 2,6-di^{t}butyl p-cresol, an anti-oxidant, to try to prevent cross-linking which may be due to air oxidation.

The polymers were found to be insoluble, even after prolonged reflux.

4.7 Attempts to prepare a block copolymer

The ultimate proof that a system is "living" is block copolymer synthesis. The monomers chosen in this attempt to prepare a block copolymer were cyclopentene and 2,3-bis(trifluoromethyl)bicyclo[2,2,1]hepta-2,5-diene(XIX).

Wilson[147,148] had shown that monomer (XIX) can be ring-open polymerised using WCl_6/Ph_4Sn. Later work by Alimuniar[149] extended the range of catalysts used to polymerise this monomer using $WCl_6/SnMe_4$. The polymers produced were pale yellow, brittle, and were soluble in acetone or methyl ethyl ketone, Wilson[148] also showed that this monomer (XIX) copolymerises with cyclopentene to produce a copolymer which is soluble in toluene and acetone. The copolymer consisted of monomer (XIX): cyclopentene units in a 2:1 ratio. Poly(1-pentenylene) prepared by conventional polymerisation is soluble in toluene and chloroform, but not in acetone. The combination of cyclopentene and monomer (XIX) appears to be ideal for use in a block copolymerisation experiment since both monomers polymerise readily using $WCl_6/SnMe_4$, and the polymers produced have totally different solubility characteristics. Hence if two homopolymers were produced they could be readily separated, whilst the fractional solubility properties characteristic of block copolymers could also be shown.

The first block copolymerisation attempt was carried out by initially polymerising cyclopentene, as in the previous section. Cyclopentene polymerised readily, and the polymerisation flask was evacuated thoroughly to ensure removal of any unreacted monomer.

Monomer (XIX) was then vacuum transferred and condensed into the polymerisation flask. On warming to room temperature, the poly(1-pentenylene) was surrounded by a pool of monomer (XIX). After leaving the experiment for several days, the monomer (XIX) still had not polymerised and was ineffective at swelling the poly(1-pentenylene).

Monomer (XIX) was recovered and an attempt to dissolve the polymer was made without success.

In the second attempt monomer (XIX) was polymerised first. The rate of polymerisation was much lower than for cyclopentene. However, after 4 days a considerable amount of the monomer had polymerised. Excess monomer was recovered, the system was thoroughly evacuated, and cyclopentene was vacuum transferred and condensed into the polymerisation flask. On warming the flask to room temperature the catalyst changed colour to blue. After 30 minutes the catalyst surface still remained wet with cyclopentene. The polymerisation was terminated at this stage to try to prevent any crosslinking of the poly(1-pentenylene) component.

The polymer was dissolved in acetone containing 1% antioxidant. A small amount of undissolved polymer was recovered by filtration, and the acetone solution was concentrated and added dropwise to hexane to reprecipitate the polymer. The reprecipitation was accomplished with difficulty since the polymer solution in acetone was not very viscous, and the resulting precipitated polymer formed as a sticky material and was isolated by decanting the solution and removing traces of volatiles on a vacuum line.

A film was cast, and i.r. analysis indicated that the polymer was the homopolymer of monomer (XIX) containing antioxidant. No poly(1-pentenylene) component was detected.

Due to the poor dispersion of the catalyst, access of the cyclopentene to the active sites was hindered, since they were well surrounded by the polymer derived from monomer (XIX). If catalyst dispersion could be improved, the active sites may be more accessible to both monomers. Also, crosslinking during cyclopentene polymerisation may be reduced. Hence it was decided to try to improve the polymerisation technique further.

The use of antioxidant, which strongly absorbs in the infra-red, was abandoned to simplify the spectra obtained from the polymers, and in any event all manipulations were conducted under vacuum or a nitrogen blanket.

4.8 Use of perfluoro(methylcyclohexane) as a dispersant medium

WCl_6 was transferred into the polymerisation flask, as in previous polymerisations. Perfluoro(methylcyclohexane) diluent was degassed several times, then syringed into the polymerisation flask. The catalyst was dispersed in the diluent by stirring overnight.

During this process the catalyst became well dispersed but it had changed colour to crimson, presumably due to a reaction with the diluent to produce WCl_nF_{6-n} type species. Tetramethyl tin cocatalyst was degassed and vacuum transferred producing a further colour change of the catalyst to dark brown. Cyclopentene was degassed, then syringed into the flask. Although the cyclopentene was not totally miscible with the diluent the reaction mixture became cloudy and catalyst adhered to the walls of the reaction flask. The mixture was stirred overnight, then poured into a large excess of methanol. No polymer was produced, hence use of this type of diluent did not improve the polymerisation technique, and this approach was abandoned.

4.9 Dispersion of the catalyst using solvent evaporation: vapour-transfer and polymerisation of cyclopentene

WCl_6 was dissolved in dry toluene. The desired quantity of this solution was syringed into the polymerisation flask under nitrogen. The solution was stirred, then toluene was slowly removed by evacuating the flask through a cold trap. This produced a coating of very finely divided WCl_6 in the base of the polymerisation flask. The active catalyst was formed by vacuum transferring tetramethyl tin cocatalyst, as previous.

The desired amount of degassed cyclopentene was frozen at -198°C in the monomer flask. Both flasks were evacuated to 10^{-3}mm Hg pressure, then isolated from the rest of the vacuum line. The monomer was allowed to warm to room temperature.

This allowed transfer of cyclopentene in the vapour phase. As polymerisation began, the partial pressure of cyclopentene was reduced, more cyclopentene evaporated, and the polymerisation continued. After leaving the reaction overnight, all the cyclopentene had transferred and polymerised. Figure 4.2 shows the apparatus used in this technique.

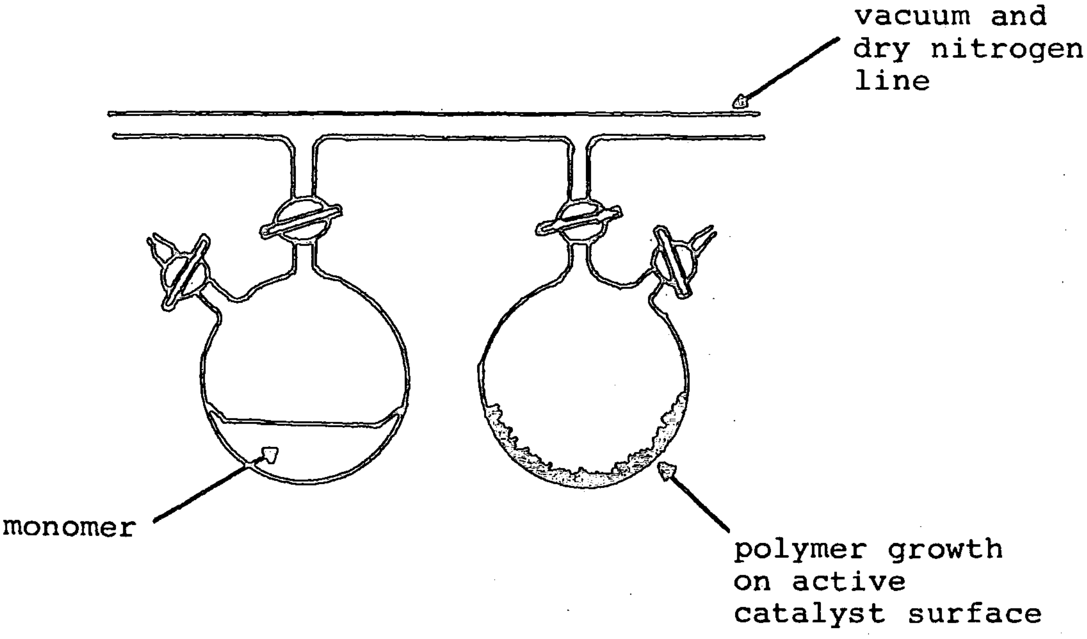


Figure 4.2 <u>Vapour-transfer and polymerisation in solvent-free system</u>

After taking a sample of poly(1-pentenylene) a second amount of cyclopentene was polymerised. A second sample was taken.

Both samples were placed in toluene containing a small amount of methanol. The samples did not dissolve, even after several days reflux.

Using this technique, the active catalyst was well dispersed in the polymerisation flask, and the system remained active for at least 7 days. This technique was adopted in subsequent polymerisations.

4.10 Cyclopentene absorption experiment

The previous polymerisation indicated the very highly active nature of the catalyst system used. In order to make sure that the second amount of cyclopentene had polymerised, and not simply been absorbed in the polymer, a cyclopentene absorption experiment was performed.

A sample of the polymer prepared in the previous polymerisation was isolated by precipitation in methanol, filtration, then prolonged evacuation on a vacuum line. This polymer was placed in a sample tube, weighed, then placed in the polymerisation flask. Cyclopentene was frozen to -198°C in the monomer flask, then allowed to warm to room temperature. After leaving overnight, a small amount of cyclopentene had transferred. On weighing the sample tube, it was apparent that this had been absorbed by the poly(1-pentenylene). The sample tube was replaced in the apparatus, and the polymerisation flask was evacuated for several hours. On reweighing the sample tube, all cyclopentene had been desorbed.

This experiment showed that the "dead" poly(1-pentenylene) readily absorbs cyclopentene but that it also readily desorbs it. In the previous polymerisation the second amount of cyclopentene transferred, was absorbed into the poly(1-pentenylene) which still contained active catalyst, and was subsequently polymerised. The high activity of the catalyst system was hence confirmed.

4.11 Vapour-transfer and polymerisation of bicyclo[2,2,1]hept -2-ene (norbornene)

The vapour-transfer and polymerisation of norbornene was accomplished using the procedures described in Section 4.9. Three successive amounts of monomer were polymerised over a one week period. Samples of polymer were taken between additions of monomer. The crosslinking problems encountered during cyclopentene polymerisations did not occur with norbornene, since the polymers were found to be soluble in chloroform. The polymer which remained at the end of the polymerisation after samples had been removed was also soluble (a small amount of insoluble material was removed by filtration).

The polymers were purified by reprecipitation in methanol. Molecular weight measurements were kindly made by Dr. A.F.Johnson (University of Bradford); the measurements were made by conventional GPC, using chloroform as the eluent since the facility to use chloroform solutions for GPC did not exist in this Department. All molecular weights were found to be high (10,000 to 20,000) but no successive increase in molecular weight for the successive samples of polymers taken was observed.

These results would seem to indicate that although the catalyst system is extremely active, chain-transfer reactions can occur.

4.12 Attempted block copolymerisation of 2,3-bis(trifluoromethyl) bicyclo[2,2,1]hepta-2,5-diene (XIX) and norbornene

A further attempt to prepare a block copolymer was made. The catalyst system was generated using WCl_6 (1.26×10^{-4} moles) and $SnMe_4$ (2.52×10^{-4} moles). Monomer (XIX) (0.42 mls, 0.65g, 2.85×10^{-2} moles) was polymerised from the vapour phase over 7 days. After thorough evacuation of the polymerisation flask, norbornene (o.81g, 8.62x10^{-3} moles) was polymerised from the vapour phase overnight.

The polymerisation flask was thoroughly evacuated. Chloroform (25 mls) and methanol (0.5 mls) were added to the polymerisation flask to swell the polymer. After 1 hour stirring, the flask contents were transferred into a 250 ml 2-necked round-bottomed flask to which chloroform (150 mls) was added. After stirring overnight the solution was filtered. The chloroform solution was concentrated then added dropwise into methanol, which resulted in the precipitation of a white rubbery polymer. The polymer (0.67g) was recovered by filtration. A sample was spun-cast from chloroform, and i.r. analysis of the film (spectrum (XXI), Appendix C), indicated that it was pure poly(norbornene). Volatile components of the methanolic filtrate from the re-precipitation were removed, and an oily residue (0.33g) was recovered. Presumably this consisted of the lower oligomers of poly(norbornene) together with a small amount of unreacted monomer and catalyst residues.

The polymer which was insoluble in chloroform was dissolved in acetone. Reprecipitation into hexane was accomplished to purify the polymer (0.44g). A sample of this material was spun-cast from acetone, and i.r. analysis of the film (Spectrum (XX), Appendix C) indicated that it was pure homopolymer of monomer(XIX).

The mass balances are summarised below in Tables 4.4 and 4.5.

Table 4.4 Monomer-input during attempted block copolymerisation of monomer (XIX) and norbornene

Reactants	Moles	Mole ratio	Mass (g)
WCl_6	1.26×10^{-4}	1	
$SnMe_4$	2.52×10^{-4}	2	
monomer (XIX)	2.85×10^{-2}	226	0.65
norbornene	8.62×10^{-3}	68.4	0.81
Total mass input monomers			1.46

Table 4.5 Polymer output during attempted block copolymerisation of monomer (XIX) and norbornene

Polymers	Mass (g)
chloroform-soluble, methanol-insoluble (poly(norbornene)).	0.67
chloroform-soluble, methanol-soluble (unreacted monomers + oligomers of poly(norbornene)).	0.33
acetone-soluble, hexane-insoluble	0.44
Total mass output polymers	1.44

4.13 Conclusions and suggestions for further work

From the observations made it may be concluded that:

(a) the catalyst system is very active towards ring-opening polymerisation of cycloalkenes. The vapour-transfer and polymerisation technique is convenient for the preparation of such polymer

(b) Out of the three possible rationalisations presented in the initial postulation, the second description is correct. That is, the system contains an abundance of active sites. It seems likely that chain transfer occurs and when an active site is terminated it is replaced by a new site at which polymerisation continues.

Hence the system is not "living", and may not be used to prepare block copolymers.

(c) The initial aim of Dr. Stelzer's work was to study the formation and propagation of the active species during the ring-opening polymerisation of cycloalkenes using ESCA. Such a study could be readily undertaken and may lead to interesting results using the catalyst system developed during this work.

EXPERIMENTAL

4.14 (a) Preparation of 2,3-bis(trifluoromethyl)bicyclo [2,2,1]hepta-2,5-diene(XIX)

Hydroquinone (0.05g) was placed in a Carias tube, which was then attached to the vacuum line (10^{-3}mm Hg) and cooled in liquid air. Hexafluorobut-2-yne (15.6g, 9.6×10^{-2} moles) was vacuum transferred into the Carias tube. After purging with dry nitrogen, cyclopentadiene (prepared as in 2.12(c), 7.95 mls, 6.4g, 9.7×10^{-2} moles) was syringed into the tube. The Carias tube was evacuated, sealed, placed in a steel sleeve and allowed to warm to ambient temperature.

After 24 hours, the Carias tube was recooled in liquid air, then opened by hot-spotting. The liquid remaining was filtered through a sinter, then distilled using a Fischer-Spaltrohr small concentric tube distillation apparatus (see Appendix A) to give 2,3-bis(trifluoromethyl)bicyclo[2,2,1]hepta-2,5-diene (20.6g, 9.1×10^{-2} moles, 95%), a colourless liquid, b.pt. 122°-123° (Lit.[147,148]:110°-112°C); found: C 48.0, H 2.8%, calculated for $C_9H_6F_6$, C 47.4, H 2.7%; with i.r.spectrum (Appendix C) and mass spectrum (Appendix B), high mass 228(M), as expected.

(b) Solvent-free polymerisations

All manipulations were performed under vacuum or dry nitrogen conditions using standard vacuum-line techniques as described in the Discussion.

APPENDIX A

APPARATUS AND INSTRUMENTS

Vacuum system

A conventional vacuum system incorporating a mercury diffusion pump and a rotary oil pump was used for degassing materials, vacuum distillations, removing volatile residues from polymers, etc., and in the polymerisations discussed in Chapter Four.

I.r. spectra

A Perkin-Elmer 457 or 577 Grating Infrared Spectrophotometer was used to record i.r. spectra. A Perkin-Elmer 580B Spectrometer fitted with a Data Station was used for polymer analysis as discussed in Chapter Three.

N.m.r. spectra

The ^{1}H-n.m.r. spectra of monomers were recorded on a Brüker Spectrospin HX 90E or a Varian EM 360L n.m.r. spectrometer. The ^{13}C-n.m.r. spectra of monomers were recorded on the Brüker Spectrospin HX 90E spectrometer. The ^{13}C n.m.r. spectra of polymers were recorded through the SERC n.m.r. service at Edinburgh University, using a Brüker WH 360 spectrometer.

Elemental analysis

Carbon and Hydrogen analyses were obtained using a Perkin-Elmer 240 CHN analyser.

Analyses for halogens and sodium were obtained using a Perkin-Elmer 5000 Atomic Absorption Spectrophotometer.

Distillation of liquid monomers

A Fischer-Spaltrohr small concentric tube distillation apparatus (HMS 500) was used for the distillation of liquid monomers. The apparatus contains a fractionating column with 75 theoretical plates.

Mass spectra

(see Appendix B).

Gel permeation chromatography

Measurements were made using a Perkin-Elmer 601 Liquid Chromatography Apparatus containing 3 PL Gel columns (10^5, 10^3, and 500 Å) supplied by Polymer Laboratories Ltd., and fitted with a Knauer Differential Refractometer detector.

Electrical conductivity measurements

All measurements were made on self-supporting polymer films in a Faircrest glove box containing <2 ppm O_2 and <10 ppm H_2O using a Signatone 4-probe conductivity apparatus, a 225 Constant Current Source (Keighley Instruments Ltd.) and a 616 Digital Electrometer (Keighley Instruments Ltd.).

APPENDIX B

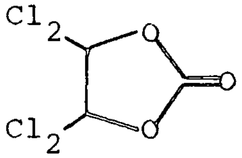
MASS SPECTRA

The mass spectra of the compounds synthesised in the course of this work are tabulated below. Ions are tabulated in a standard form; for example, in compound (V) the designation 119(63%, C_3ClO_3, $M-Cl_3$) indicates that this ion has a mass to charge ratio of 119, its intensity is 63% of the intensity of the base peak of the spectrum, it has provisionally been assigned the formula C_3ClO_3 (the + being understood), and its supposed origin is loss of 3 chlorine atoms from the parent ion (M). The base peak is designated B.

Mass spectra for compounds (VI) and (VII) are chemical ionisation mass spectra recorded at Sunderland Polytechnic; unfortunately, although this allowed the molecular ions to be detected, the output galvanometers were overloaded, hence the relative intensities of fragment peaks in these cases could not be estimated.

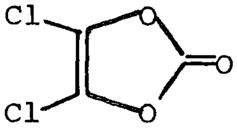
The remainder of the mass spectra were recorded using either an A.E.I. MS9 or a V.G. Micromass 12B mass spectrometer for solid and liquid samples respectively.

(V) 4,4,5,5-Tetrachloro-1,3-dioxolan-2-one



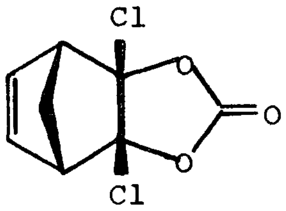
164(0.5%, C_2Cl_4, $M-CO_3$), 145(10%, C_2Cl_3O, $M-CO_2-Cl$), 119(63%, C_3ClO_3, $M-Cl_3$), 117(72%, CCl_3, $M-CO_3-CCl$), 84(31%, C_3O_3, $M-Cl_4$), 82(53%, CCl_2, $M-CO_3-CCl_2$), 63(100%, COCl, B), 56(13%, C_2O_2, $M-COCl_4$), 47(27%, CCl, $M-C_2Cl_3O_3$), 44(5%, CO_2, $M-C_2OCl_4$).

(VI) 4,5-Dichloro-1,3-dioxol-2-one



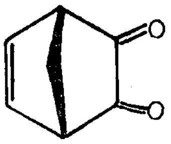
158(M+4), 156(M+2), 154($C_3Cl_2O_3$,M), 119(C_3ClO_3, M-Cl), 84(C_3O_3, M-Cl_2), 82(CCl_2, M-C_2O_3), 63(COCl, M-CO_2-CCl), 56(C_2O_2, M-CCl_2O), 47(CCl, M-CO_2-CO-Cl), 44(CO_2, M-C_2Cl_2O).

(VII) Endo-3a,7a-dichloro-3a,4,7,7a-tetrahydro-4,7-methano-1,3-benzodioxol-2-one



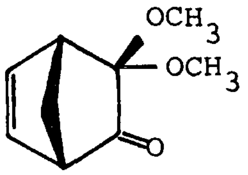
222(M+2), 220($C_8H_6Cl_2O_3$,M), 176($C_7H_6Cl_2O$, M-CO_2), 149($C_8H_5O_3$, M-Cl-HCl), 144($C_6H_5ClO_2$, M-CO-CClH), 142($C_6H_3ClO_2$, M-CO-CH_2-HCl), 123(C_7H_4Cl, M-CO_3-HCl-H), 116(C_5H_5ClO,M-CO_2-CCl-H), 114($C_5H_6O_3$, M-C_3Cl_2), 113($C_5H_5O_3$,M-C_3HCl_2), 106(C_7H_6O, M-Cl_2-CO_2), 78(C_6H_6 M-CO_2-CO-Cl_2), 66(C_5H_6, M-$C_3Cl_2O_3$), 52(C_4H_4, M-$C_4H_2Cl_2O_3$), 40(C_2O, M-$C_6H_6Cl_2O_2$).

(I) Bicyclo[2,2,1]hept-5-ene-2,3-dione



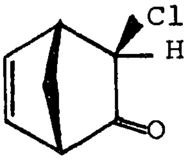
123(1%, M+1), 122(18%, $C_7H_6O_2$,M), 94(10%, C_6H_6O, M-CO), 79(4%, C_5H_3O, M-CO-CH_2-H), 67 (10%, C_4H_3O, M-C_3H_3O), 66(100%, C_5H_6,B), 65(32%, C_5H_5, M-C_2O_2H), 64(4%, C_5H_4, M-$C_2H_2O_2$), 63(9%, C_5H_3, M-$C_2O_2H_3$), 62(6%, C_5H_2, M-$C_2H_4O_2$),61(4%, C_5H, M-$C_2H_5O_2$), 51(7%, C_4H_3, M-$C_3H_3O_2$), 50(6%, C_4H_2, M-$C_3H_4O_2$), 44(2%, CO_2, M-C_6H_6), 40(34%, C_2O, M-C_5H_6O), 39(54%, C_3H_3, M-$C_4H_3O_2$), 38(19%, C_3H_2, M-$C_4H_4O_2$), 37(9%, C_3H , M-$C_4H_5O_2$), 28(49%, CO, M-C_6H_6O), 27(13%, C_2H_3, M-$C_5H_3O_2$).

(VIII) 3,3-Dimethoxy bicyclo [2,2,1] hept-5-ene-2-one



140(71%, $C_8H_{12}O_2$, M-CO), 139(71%, $C_8H_{11}O_2$, M-CO-H), 125(13%, $C_7H_9O_2$, M-CO-CH_3), 110(7%, $C_7H_{10}O$, M-CO-CH_2-O), 109(73%, C_7H_9O, M-CO-OCH_3), 97(16%, $C_5H_5O_2$, M-CO-C_3H_7), 94(39%, C_6H_6O, M-$COCH_3$-OCH_3), 93(45%, C_6H_5O, M-$COCH_3$-OCH_3-H), 82(4%, C_5H_6O, M-CO-$COCH_3$-CH_3), 81(15%, C_5H_5O, M-CO-$COCH_3$-CH_3-H), 79(50%, C_5H_3O, M-$COCH_3$-OCH_3-CH_2-H), 77(20%, C_6H_5, M-CO-OCH_3-OCH_3-H), 67(18%, C_5H_7, M-CO- $COCH_3$-OCH_2), 66(100%, C_5H_6, M-CO-$COCH_3$-OCH_3,B), 65(59%, C_5H_5, M-CO-$COCH_3$-OCH_3-H), 59(90%, $COOCH_3$, M-C_7H_9O), 55(11%, C_3H_3O, M-$C_6H_9O_2$), 40(50%, C_2O, M-$C_7H_{12}O_2$), 39(38%, C_3H_3, M-$C_6H_9O_3$), 28(50%, CO, M-$C_8H_{12}O_2$).

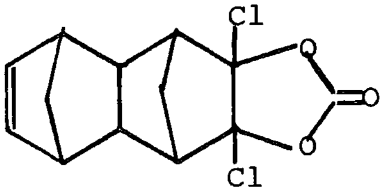
(IX) Exo-3-chloro bicyclo [2,2,1] hept-5-ene-2-one



144(4%, M+2), 142(8%, C_7H_7ClO, M), 113 (2%, C_6H_6Cl,M-CO-H), 107(2%, C_7H_7O, M-Cl), 79(100%, C_6H_7,B), 78(30%, C_6H_6,M-CO-Cl-H), 77(63%, C_6H_5, M-CO-Cl-2H), 66(61%, C_5H_6,M-CO-CCl-H), 63(4%, COCl,

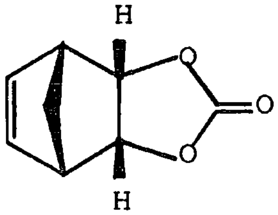
$M-C_6H_7$), 51(31%, OCl, $M-C_7H_7$), 50(5%, CH_3Cl, $M-C_6H_4O$), 40(8%, C_2O, $M-C_5H_7Cl$), 39(30%, C_3H_3, $M-C_4H_4ClO$), 32(8%, CH_3OH, $M-C_6H_3Cl$), 28(34%, CO, $M-C_6H_7Cl$).

(XII) Endo,endo-3a,9a-dichloro-3a,4,4a,5,8,8a,9,9a-octahydro-4,9:5,8-dimethano naphtho[2,3-d]-1,3-dioxol-2-one



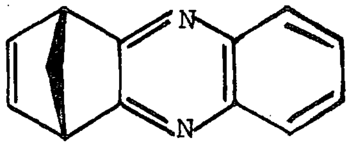
286(1%, $C_{13}H_{12}Cl_2O_3$, M), 198(1%, $C_{10}H_8Cl_2$, $M-CO_3-CH_2-CH_2$), 141(5%, C_7H_6ClO, $M-CO_2-Cl-C_5H_6$), 113(4%, C_6H_6Cl, $M-C_7H_6ClO_3$), 77(12%, C_2H_2OCl, $M-C_{11}H_{10}ClO_2$), 66(100%, C_5H_6, B), 51(4%, ClO, $M-C_{13}H_{12}ClO_2$), 44(3%, CO_2, $M-C_{12}H_{12}Cl_2O$), 40(50% C_2O, $M-C_{11}H_{12}Cl_2O_2$), 39(8%, C_3H_3, $M-C_{10}H_9Cl_2O_3$), 36(3%, HCl, $M-C_{13}H_{11}ClO_3$), 28(6%, CO, $M-C_{12}H_{12}Cl_2O_2$).

(XV) Endo-3a,4,7,7a-tetrahydro-4,7,methano-1,3-benzodioxol-2-one



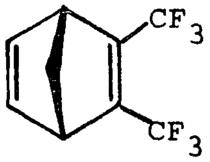
153(1%, M+1), 152(3%, $C_8H_8O_3$, M), 108(1%, C_7H_8O, $M-CO_2$), 107(5%, C_7H_7O, $M-CO_2-H$), 79(93%, C_6H_7, $M-CO_2-HCO$), 77(42%, C_6H_5, $M-CO_3-CH_2-H$), 67(19%, C_5H_7, M-3CO-H), 66(100%, C_5H_6, B), 65(14%, C_5H_5, $M-C_3H_3O_3$), 53(7%, C_4H_5, $M-C_4H_3O_3$), 52(6%, C_4H_4, $M-C_4H_4O_3$), 51(11%, C_4H_3, $M-C_4H_5O_3$), 44(4%, CO_2, $M-C_7H_8O$), 41(6%, CHCO, $M-C_6H_7O_2$), 40(12%, C_2O, $M-C_6H_8O_2$), 39(27%, C_3H_3, $M-C_5H_5O_3$), 29(6%, COH, $M-C_7H_7O_2$), 28(7%, CO, $M-C_7H_8O_2$).

(XVII) 1,4-Dihydro-1,4-methanophenazine



196(2%, M+2), 195(32%, M+1), 194(100%, $C_{13}H_{10}N_2$, M+B), 193(44%, $C_{13}H_9N_2$, M-H), 168(22%, $C_{11}H_8N_2$, M-C_2H_2), 167(9%, $C_{11}H_7N_2$, M-C_2H_3), 166(4%, $C_{11}H_6N_2$, M-C_2H_4), 129(11%, $C_8H_5N_2$, M-C_5H_5), 102(11%, C_8H_6, M-$C_5H_4N_2$), 97(9%, $C_5H_9N_2$, M-C_8H), 76(10%, C_6H_4, M-$C_7H_6N_2$), 75(8%, C_6H_3, M-$C_7H_7N_2$), 66(70%, C_5H_6, M-$C_8H_4N_2$), 65(14%, C_5H_5, M-$C_8H_5N_2$), 63(6%, C_5H_3, M-$C_8H_7N_2$), 51(8%, C_4H_3, M-$C_9H_7N_2$), 50(10%, C_4H_2, M-$C_9H_8N_2$), 40(7%, CN_2, M-$C_{12}H_{10}$), 39(14%, C_3H_3, M-$C_{10}H_7N_2$), 28(15%, N_2, M-$C_{13}H_{10}$).

(XIX) 2,3-bis(trifluoromethyl)bicyclo[2,2,1]hept-2-ene



228(26%, $C_9H_6F_6$, M), 209(7%, $C_9H_6F_5$, M-F), 208(7%, $C_9H_5F_5$, M-HF), 202(24%, $C_7H_4F_6$, M-C_2H_2), 189(10%, $C_9H_5F_4$,M-HFF), 159(100%, $C_8H_6F_3$, B), 133(11%, $C_6H_4F_3$, M-CF_3-C_2H_2), 119(8%, $C_5H_2F_3$, M-$C_4H_4F_3$), 109(22%, C_7H_6F, M-C_2F_5), 69(12% CF_3, M-$C_8H_6F_3$), 66(18%, C_5H_6, M-C_4F_6), 51(10%, CHF_2, M-$C_8H_5F_4$).

APPENDIX C

INFRA-RED SPECTRA

Infra-red spectra are given below. The spectra were recorded under conditions designated by:

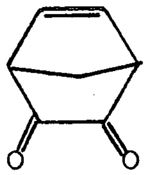
A: KBr. disc

B: thin liquid film (KBr plates)

C: thin polymer film

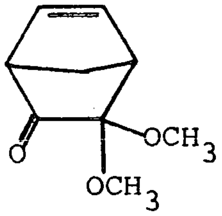
Compounds which have not been reported previously are marked with an asterisk, *eg*(X)*

(I)



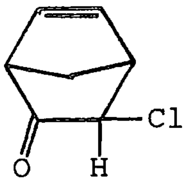
bicyclo[2,2,1]hept-5-ene-2,3-dione (A).

(VIII)



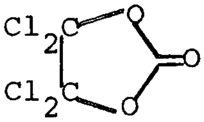
3,3-dimethoxybicyclo[2,2,1]hept-5-ene-2-one (B).

(IX)



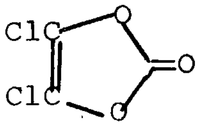
Exo-3-chlorobicyclo[2,2,1]hept-5-ene-2-one (B).

(V)



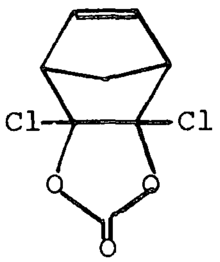
4,4,5,5-tetrachloro-1,3-dioxolan-2-one(B).

(VI)



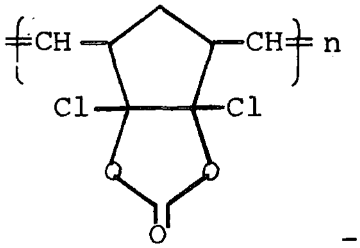
4,5-dichloro-1,3-dioxol-2-one (B).

(VII)



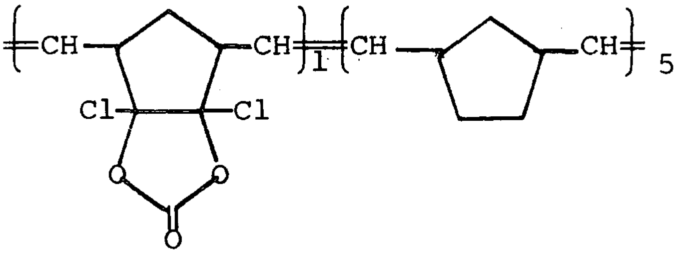
Endo-3a,7a-dichloro-3a,4,7,7a-tetrahydro-4,7-methano-1,3-benzodioxol-2-one (A).

(X)*



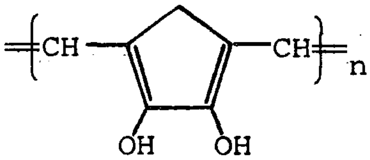
poly(6,8-(1,5-dichloro-2,4-dioxa-3-keto)bicyclo[3,3,0]octylene vinylene) (C).

(XI)*



1:5 poly(6,8-(1,5-dichloro-2,4-dioxa-3-keto)bicyclo[3,3,0] octylene vinylene): poly(norbornene)copolymer (C).

(III)*



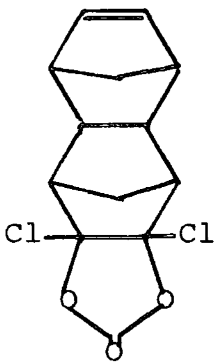
(III).1* poly(4,5-bis hydroxy-1,3-cyclopentadienylenevinylene) precipitant from reaction of aqueous NaOH with polymer (X) dissolved in acetone. (A).

(III).2* poly(4,5-bis hydroxy-1,3-cyclopentadienylene vinylene) film from reaction of polymer (X) with concentrated hydrochloric acid. (C).

(III).3* poly(4,5-bishydroxy-1,3-cyclopentadienylenevinylene) on surface of film of polymer (X) by reaction in aqueous NaOH (C) (see Section 3.4(b)(ii)).

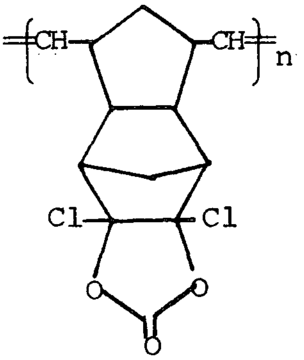
(III).4* poly(4,5-bishydroxy-1,3-cyclopentadienylenevinylene) film from reaction of polymer (X) with aqueous NaOH (C).

(XII)



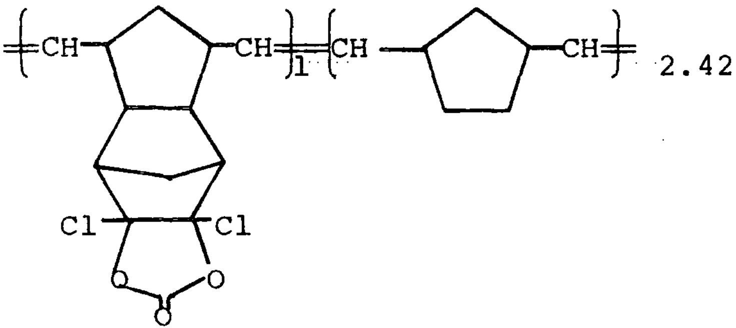
Endo,endo-3a,9a-dichloro-3a,4,4a,5,8,8a,9,9a-octahydro-4,9:5,8-dimethanonaphtho [2,3-d]-1,3-dioxol-2-one (A).

(XIII)*



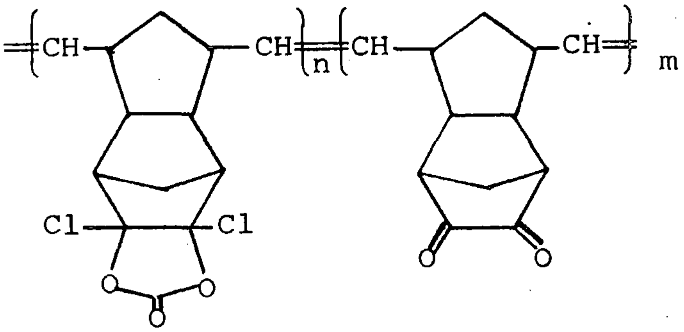
poly(9,11-(2,6-dichloro-3,5-dioxa-4-keto) tetracyclo[5,5,1,$0^{2,6}$,$0^{8,12}$]tridecylene vinylene) (C).

(XIV)*



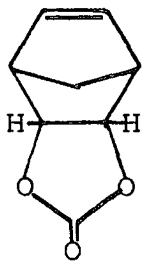
1:2.42 poly(9,11-(2,6-dichloro-3,5-dioxa-4-keto)tetracyclo [5,5,1,$0^{2,6}$,$0^{8,12}$]tridecylene vinylene): poly(norbornene) copolymer (C)

(XVIII)*



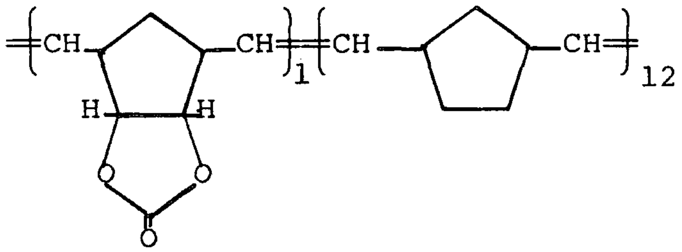
poly(9,11-(2,6-dichloro-3,5-dioxa-4-keto)tetracyclo[5,5,1,$0^{2,6}$,$0^{8,12}$]tridecylene vinylene) after reaction with aqueous NaOH (C).

(XV)



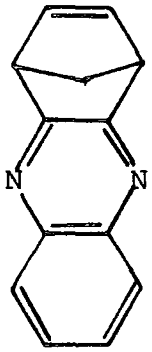
Endo-3a,4,7,7a-tetrahydro-4,7-methano-1,3-benzodioxol-2-one (A).

(XVI)*



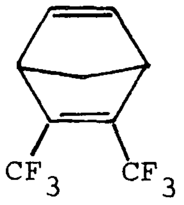
1:12 poly(6,8-(2,4-dioxa-3-keto)bicyclo[3,3,0]octylene vinylene) : poly(norbornene) copolymer (C).

(XVII)



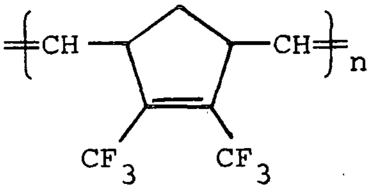
1,4-dihydro-1,4-methanophenazine (A).

(XIX)



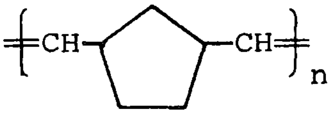
2,3-bis(trifluoromethyl)bicyclo[2,2,1] hepta-2,5-diene (B).

(XX)

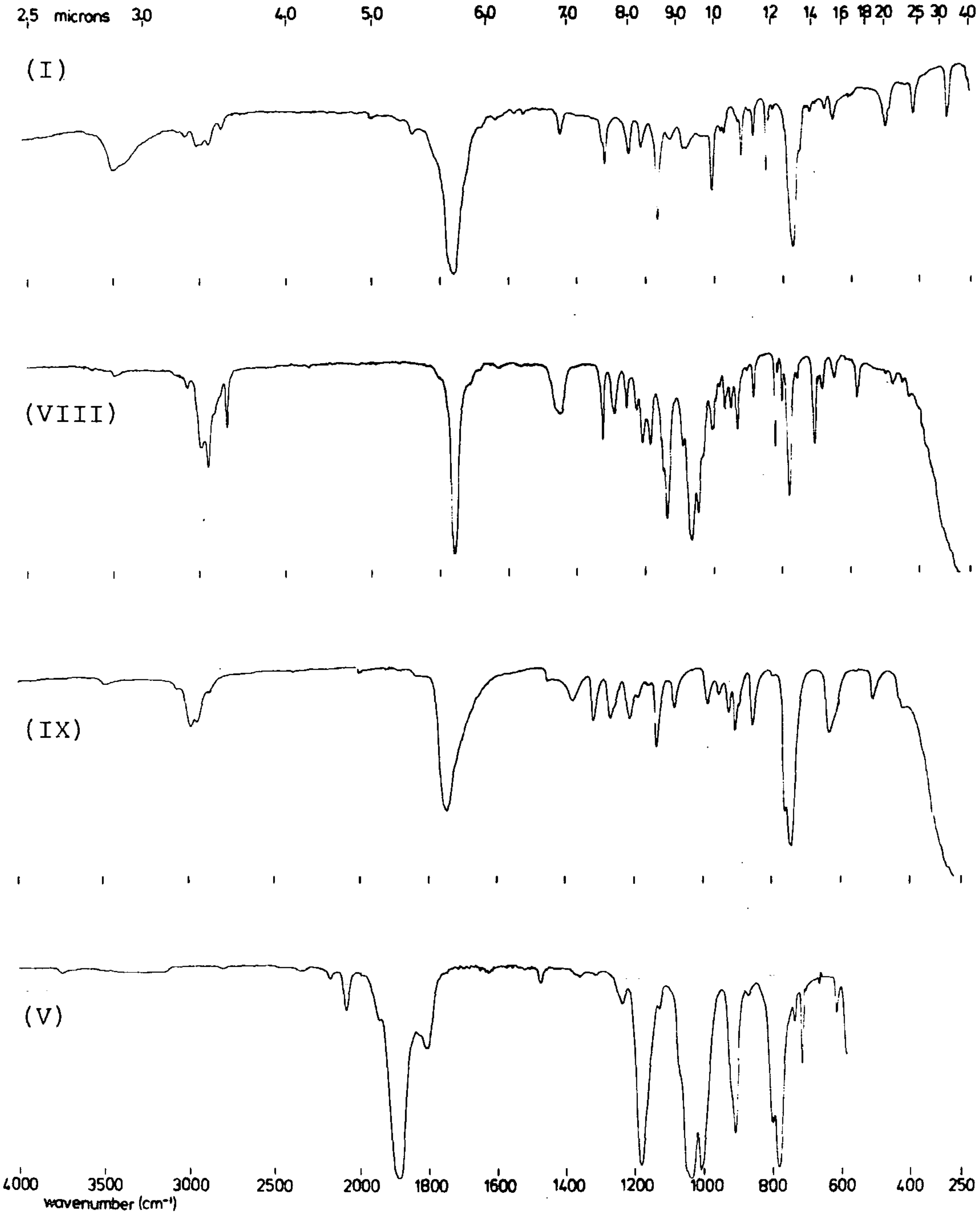


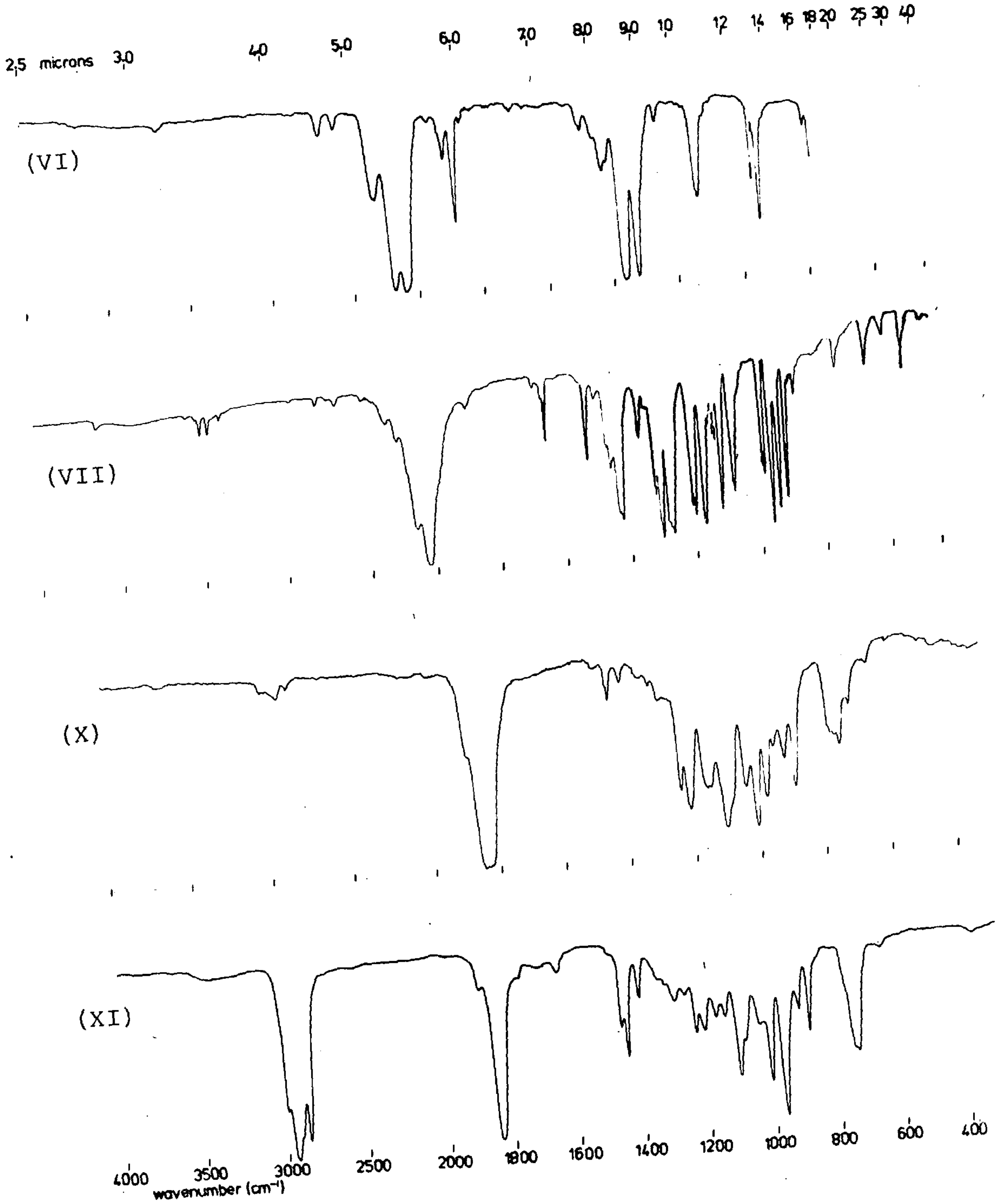
poly(4,5-bis(trifluoromethyl)1,3-cyclopentylenevinylene) prepared by solvent-free polymerisation.

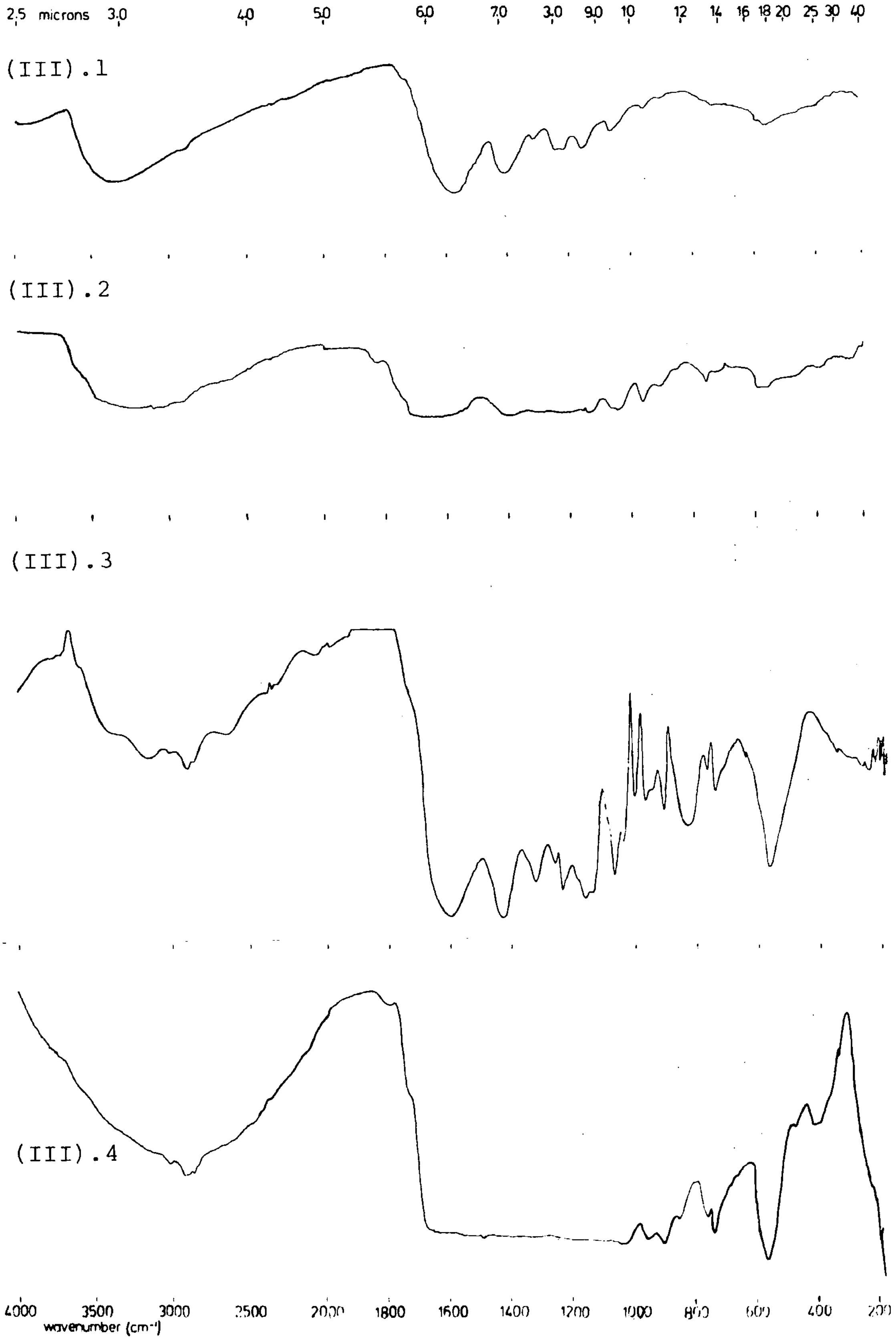
(XXI)

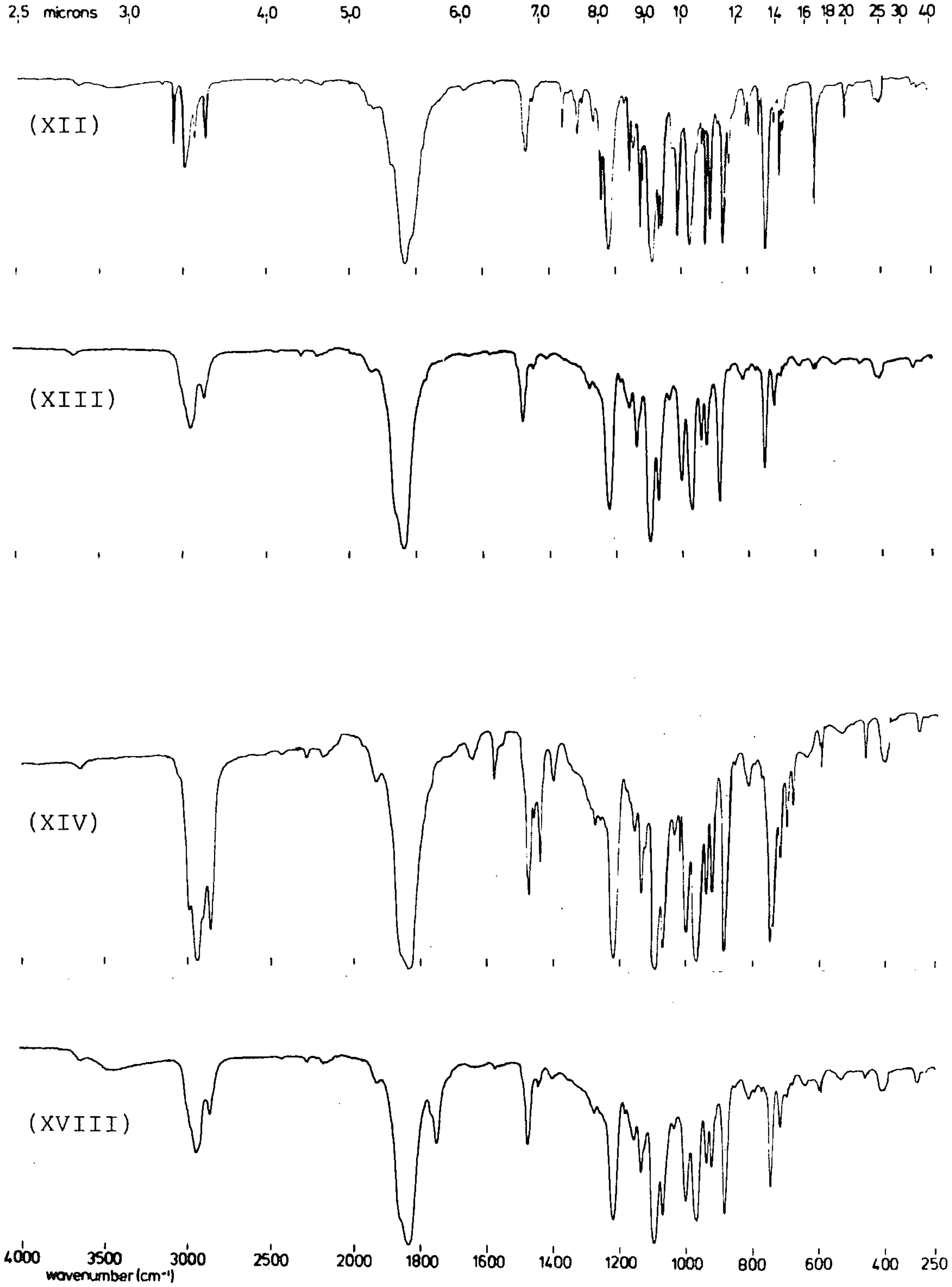


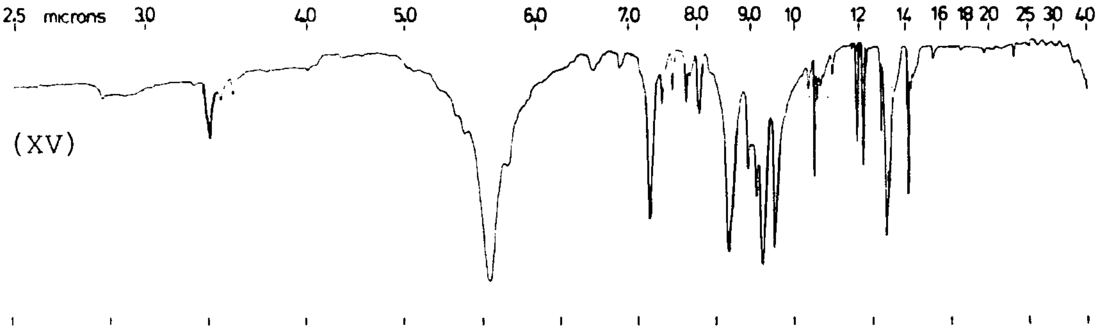
poly(norbornene) prepared by solvent-free polymerisation


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 40
(I)
(VIII)
(IX)
(V)
4000 3500 3000 2500 2000 1800 1600 1400 1200 1000 800 600 400 250
wavenumber (cm⁻¹)

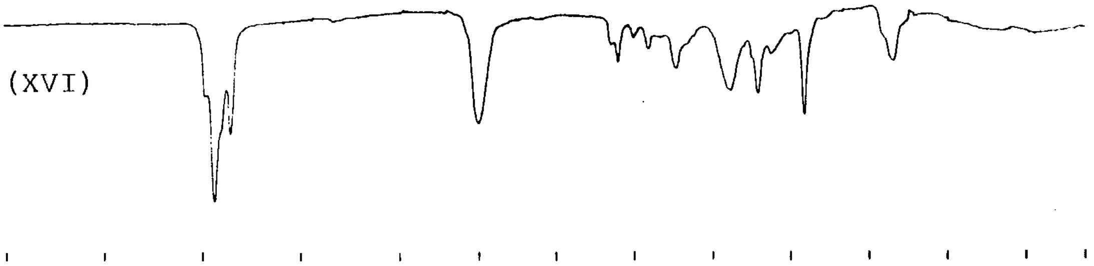

2,5 microns
3,0
4,0
5,0
6,0
7,0
8,0
9,0
10
12
14
16
18
20
25
30
40
(VI)
(VII)
(X)
(XI)
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
400
wavenumber (cm⁻¹)


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 40
(III).1
(III).2
(III).3
(III).4
4000 3500 3000 2500 2000 1800 1600 1400 1200 1000 800 600 400 200
wavenumber (cm⁻¹)


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 40
(XII)
(XIII)
(XIV)
(XVIII)
4000 3500 3000 2500 2000 1800 1600 1400 1200 1000 800 600 400 250
wavenumber (cm⁻¹)

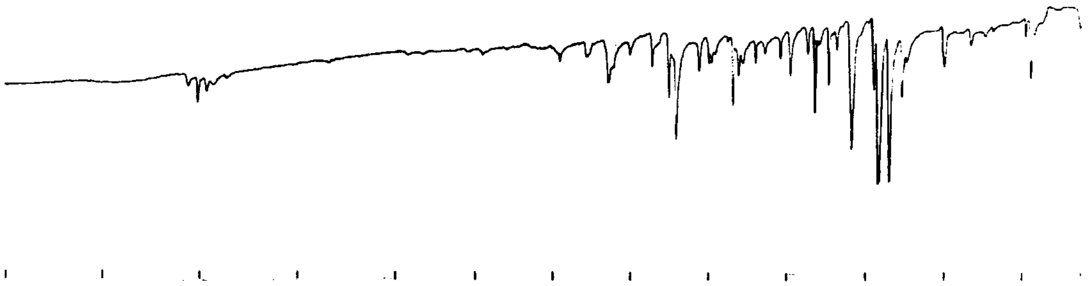


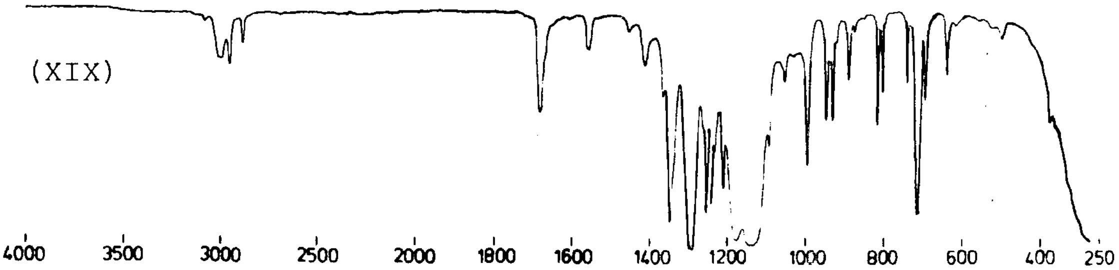
(XV)



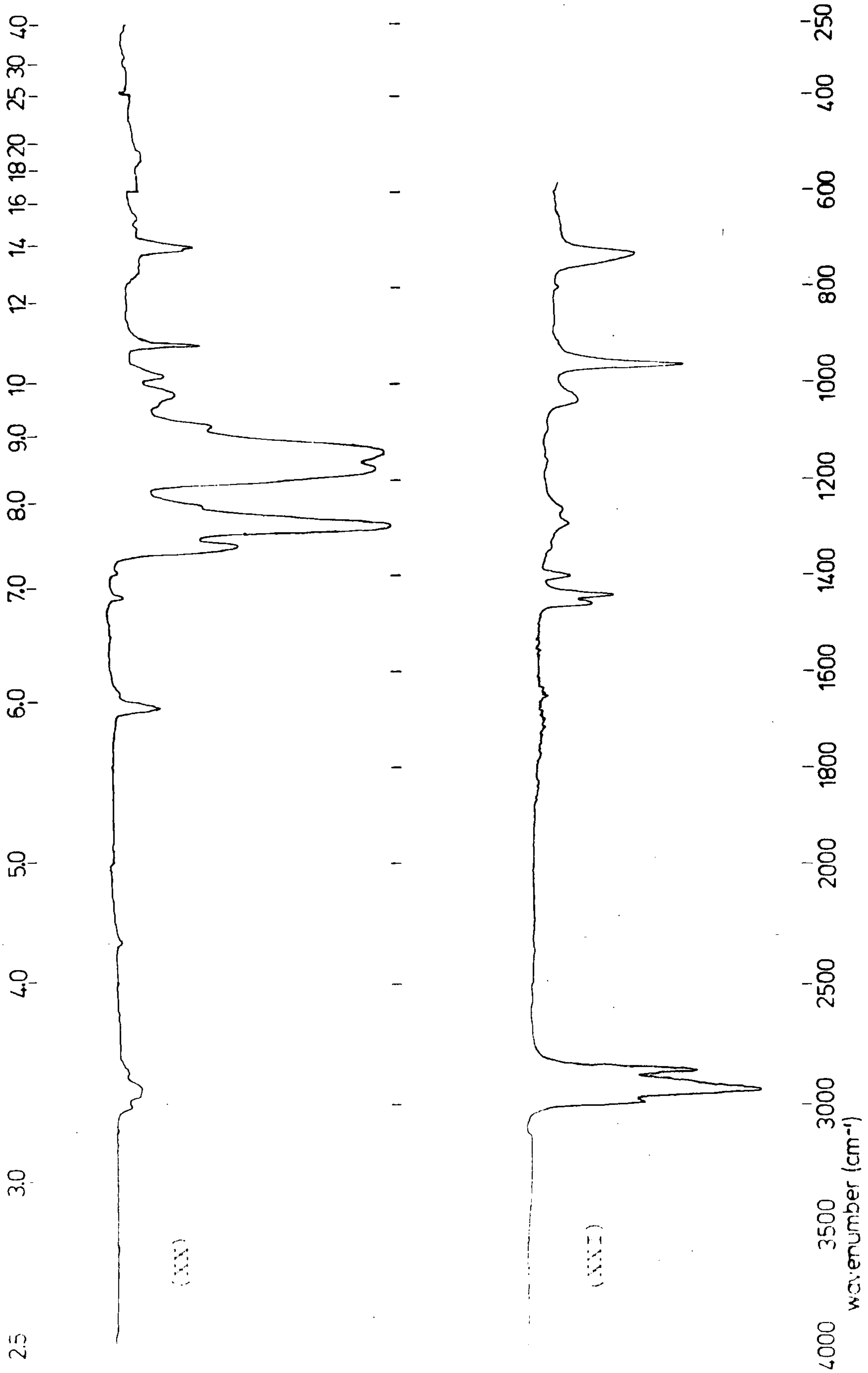
(XVI)

(XVII)





(XIX)


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

APPENDIX D

The Board of Studies in Chemistry requires that each postgraduate research thesis contains an appendix listing:

1. all research colloquia, research seminars and lectures (by external speakers) arranged by the Department of Chemistry since October 1980; and
2. all research conferences attended by the writer of the thesis during the period when the research for the thesis was carried out.

1. Research colloquia, seminars and lectures

7 October 1980

Professor T. Fehlner, 'Metalloboranes Cages or Coordination Compounds?'.

16 October 1980

Dr. D. Mass (Salford University), 'Reactions a Go-Go'.

23 October 1980

Professor T.M. Sugden (Cambridge University), 'Chemistry in Flames'.

30 October 1980

Professor N. Grassie (Glasgow University), 'Inflammability Hazards in Commercial Polymers'.

6 November 1980

Professor A.G. Sykes (Newcastle University), 'Metallo-proteins: An Inorganic Chemist's Approach'.

12 November 1980

Dr. M. Gerloch (University of Cambridge), ' Magnetochemistry is about Chemistry'.

13 November 1980

Professor N.N. Greenwood (Leeds University), 'Metalloborane Chemistry'.

19 November 1980

Dr. T. Gilchrist (University of Liverpool), 'Nitroso-olefins as Synthetic Intermediates'.

4 December 1980

Reverend R. Lancaster, 'Fireworks'.

18 December 1980

Dr. R. Evans (University of Brisbane, Australia), ' Some Recent Communications to the Editor of the Australian Journal of Failed Chemistry'.

22 January 1981

Professor E.A. Dawes (Hull University), ' Magic and Mystery through the Ages'.

29 January 1981

Mr. H.J.F. MacLean (I.C.I. Ltd.) ' Managing in the Chemical Industry in the 1980s.'.

5 February 1981

Professor F.G.A. Stone (Bristol University), 'Chemistry of Carbon to Metal Triple Bonds'.

12 February 1981

Dr. I. Fleming (Cambridge University), 'Some Uses of Silicon Compounds in Organic Synthesis'.

18 February 1981

Professor S. Kettle (University of East Anglia), ' Variations in the Molecular Dance at the Crystal Ball'.

25 February 1981

Dr. K. Bowden (University of Essex), ' The Transmission of Polar Effects of Substituents'.

11 March 1981

Dr. J.F. Stoddart (I.C.I. Ltd.), 'Stereochemical Principles in the Design and Function of Synthetic Molecular Receptors'.

17 March 1981

Professor W.P. Jencks (Brandell University, Massachusetts), 'When is an Intermediate not an Intermediate?'.

18 March 1981

Dr. P.J. Smith (International Tin Research Institute), 'Organotin compounds - A Versatile Class of Organometallic Compounds'.

9 April 1981

Dr. W.H. Meyer (RCA Zurich), 'Properties of Aligned Polyacetylene'.

7 May 1981

Professor M. Gordon (Essex University), 'Do Scientists have to Count?'.

10 June 1981

Dr. J. Rose (I.C.I. Plastic Division), 'New Engineering Plastics'.

17 June 1981

Dr. P. Moreau (University of Montpellier), 'Recent Results in Perfluororganometallic Chemistry'.

21 September 1981

Dr. P. Plimmer (Du Pont), 'From Conception to Commercialization of a Polymer'.

14 October 1981

Professor E. Kluk (University of Kotowice), 'Some Aspects of the Study of Molecular Dynamics - Simple Molecular Liquids'

22 October 1981

Dr. P.J. Corrish (Dunlop Ltd.), 'What would Life be like without Rubber?'.

6 November 1981

Dr. W. Moddeman (Monsanto Ltd., U.S.A.), 'High Energy Materials'.

12 November 1981

Professor A.I. Scott (University of Edinburgh), 'An Organic Chemist's View of Life in the NMR Tube'.

26 November 1981

Dr. W.O. Ord (Northumbrian Water Authority), 'The Role of the Scientist in a Regional Water Authority'.

2 December 1981

Dr. G. Beamson (University of Durham), 'Photoelectron Spectroscopy in a Strong Magnetic Field'.

20 January 1982

Dr. M. Bryce (University of Durham), 'Organic Metals'.

28 January 1982

Professor I. Fells (University of Newcastle upon Tyne), 'Balancing the Energy Equations'.

3 February 1982

Dr. D. Parker (University of Durham), 'Modern Methods for the Determination of Enantiomeric Purity'.

10 February 1982

Dr. D. Pethrich (University of Strathclyde), 'Conformational Dynamics of Small and Large Molecules'.

17 February 1982

Professor D.T. Clark (University of Durham), 'Structure, Bonding, Reactivity and Syntheses of Surfacesas Revealed by ESCA'.

3 March 1982

Dr. P. Banfield (I.C.I. Organic Division), 'Computer Aided Syntheses Design: A view from Industry'.

19 May 1982

Professor R.D. Chambers (University of Durham), 'Fluorocarbanions - Some Alice in the Looking Glass Chemistry'.

28 June 1982

Professor D.J. Burton (University of Iowa), 'Some Aspects of the Chemistry of Fluorinated Phosphonium Salts and Phosphonates'.

13 September 1981

Professor R. Neidlein (University of Heidelberg), 'New Aspects and Results of Bridged Annulene Chemistry'.

27 September 1982

Dr. W.K. Ford (Xerox Research Centre), 'The Dependence of the Electronic Structure of Polymers on their Molecular Architecture'.

14 October 1982

Professor H. Suhr (University of Tübingen), 'Preparative Chemistry in Non-equilibrium Plasmas'.

27 October 1982

Dr. C.E. Housecroft (University of Notre Dame), 'Bonding Capabilities of Butterfly-shaped Fe_4 Units: Implications for C-H Bond Activation in Hydrocarbon Complexes'.

28 October 1982

Professor M.F. Lappert (University of Sussex), 'Approaches to Asymmetric Synthesis and Catalysis using Electron-rich Olefins and some of their Metal Complexes'.

28 October 1982

Professor M.F. Lappert (University of Sussex), 'The Chemistry of Some Unusual Subvalent Compounds of the Main Group IV and V Elements'.

4 November 1982

Dr. D.H. Williams (University of Cambridge), 'Studies on the Structures and Modes of Action of Antibiotics'.

11 November 1982

Dr. J. Cramp (I.C.I. Ltd.), 'Lasers in Industry'.

15 November 1982

Dr. G. Bertrand (Universite Paul Sabatier, Toulouse), 'Curtius Rearrangement in Organometallic Series: A Route for New Hybridised Species'.

24 November 1982

Professor F.R. Hartley (R.M.C.S. Shrivenham), 'Supported Metal Complex Hydroformylation Catalysts: A Novel Approach using γ-radiation'

24 November 1982

Professor G.G. Roberts (University of Durham), 'Langmuir-Blodgett Films'.

25 November 1982

Dr. D.H. Richards (P.E.R.M.E., Ministry of Defence), 'Terminally Functional Polymers - Their Synthesis and Uses'.

8 December 1982

Dr. G. Wooley (Trent Polytechnic), 'Bonds in Transition Metal Cluster Compounds'.

12 January 1983

Dr. D.C. Sherrington (University of Strathclyde), 'Polymer Supported Phase Transfer Catalysts'.

27 January 1983

Professor D.W.A. Sharp (University of Glasgow), 'Some Redox Reactions in Fluorine Chemistry'.

3 February 1983

Dr. R. Manning (University of Durham), 'Molecular Mechanisms of Hormone Action'.

9 February 1983

Dr. P. Moore (University of Warwick), 'Mechanistic Studies in Solution by Stopped Flow F.T. N.M.R. and High Pressure N.M.R. Line Broadening'.

10 February 1983

Professor Sir G. Allen (Unilever Ltd.), 'U.K. Research Ltd.'

17 February 1983

Professor A.G. MacDiarmid (University of Pennsylvania), 'Metallic Covalent Polymers: $(SN)_x$ and $(CH)_x$ and their Derivatives'.

21 February 1983

Dr. R. Lyden-Bell (University of Cambridge), 'Molecular Motion in the Cubic Phase of NaCN'.

2 March 1983

Dr. D. Bloor (Queen Mary College, London), 'The Solid State Chemistry of Diacetylene Monomers and Polymers'.

3 March 1983

Professor A.C.T. North (University of Leeds), 'The Life of Computer Display Systems in Studying Molecular Structures and Interactions'.

8 March 1983

Professor D.C. Bradley (Queen Mary College, London), 'Recent Developments in Organo-Imido-Transition Metal Chemistry'.

9 March 1983

Dr. D.M.J. Lilley (University of Dundee), 'DNA Sequence, Symmetry, Structure and Supercooling'.

11 March 1983

Professor H.G. Viehe (University of Laurain, Belgium), 'Oxidations on Sulphur'.

11 March 1983

Professor H.G. Viehe (University of Lauvain, Belgium), 'Fluorine Substitution in Radical and Biradical Addition Reactions'.

16 March 1983

Dr. I. Goosney (University of Edinburgh), 'New Extrusion Reactions: Organic Synthesis in a Hot Tube'.

25 March 1983

Professor F.G. Baglin (University of Nevada), 'Interaction Induced Raman Spectroscopy in Supercritical Ethane'.

21 April 1983

Professor J. Passmore (University of New Brunswick),'Novel Selenium - Iodine cations'.

4 May 1983

Professor P.H.Plesch (University of Keele), 'Binary Ionisation Equilibria Between Two Ions and Two Molecules. What Ostwald Never Thought Of'.

10 May 1983

Professor K. Berger (University of Munich), 'New Reaction Pathways from Trifluoromethyl-Substituted Heterodienes to Partially Fluorinated Heterocyclic Compounds'.

11 May 1983

Dr. N.I. Isaacs (University of Reading), 'The Applications of High Pressures to the Theory and Practice of Organic Chemistry'.

13 May 1983

Dr. T.D. Marder (University of California), 'The Chemistry of Metal-Carbon and Metal-Metal Multiple Bonds'.

13 May 1983

Dr. R. de Kock (Calvin College, Michigan), 'Electronic Structural Calculations on Organometallic Cobalt Cluster Molecules: Implications for Metal Surfaces'.

25 May 1983

Dr. J.M. Vernon (University of York), 'New Heterocyclic Chemistry involving Lead Tetracetate'.

15 June 1983

Dr. A. Pietrzykowski (Technical University of Warsaw), 'Synthesis, Structure and Properties of Aluminoxanes'.

22 June 1983

Dr. D.W.H. Rankin (University of Edinburgh), 'Floppy Molecules - The Influence of Phase on Structure'.

5 July 1983

Professor J. Miller (University of Campinas, Brazil), 'Reactivity in Nucleophilic Substitution Reactions'.

2. Research Conferences

(a) Advances in Polymer Characterisation. An International Symposium, Durham, July 1981.

(b) The Fourth International Symposium on Olefin Metathesis, Belfast, Northern Ireland, September 1981.

(c) The Fifth International Symposium on Olefin Metathesis, Graz, Austria, August 1983.

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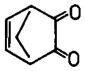
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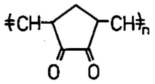
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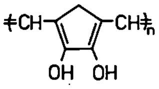
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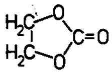
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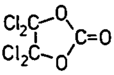
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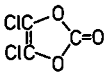
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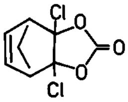
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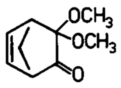
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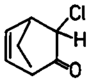
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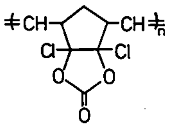
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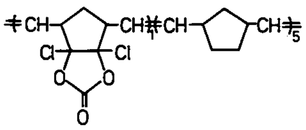
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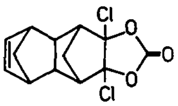
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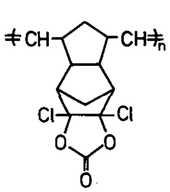
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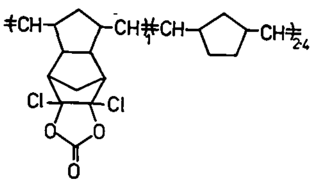
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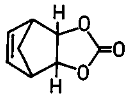
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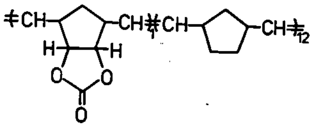
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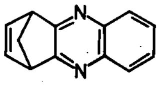
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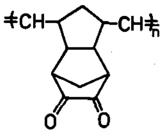
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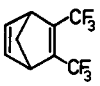
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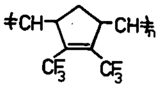
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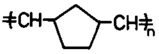
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