The synthesis and characterization of some new unsaturated polymers

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THE SYNTHESIS AND CHARACTERIZATION OF SOME NEW UNSATURATED POLYMERS

by

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Graduate Society

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University of Durham
Department of Chemistry

Conscientiousness is the overcoming

of Bone-idleness

ABSTRACT

The thesis describes investigations into three novel synthetic routes for the preparation of totally conjugated polymers.

The first route involved the attempted photoreductive step-growth polymerization of aromatic diketones with aromatic diols as the first step of a route to poly(arylene vinylene)s. These reactions failed to yield sufficiently high molecular weight polypinacols to merit a continuation of the investigation. The second route examined used the ground state reductive coupling of aromatic diketones utilizing the McMurry reaction. This approach was successful and gave good samples of poly(arylene vinylene)s. The third approach was the thermal and photochemically induced isomerisation of metathesis produced polymers of bicyclofulvenes. Work completed on this project suggests that the products were conjugated polymers.

The products of these syntheses were characterized and electrical conductivity and doping studies were carried out on the new polyconjugated materials.

ACKNOWLEDGEMENTS

This thesis would not have been possible without the aid of many people, above all Dr. W J. Feast to whom I am very grateful for his unfailing supervision, guidance, encouragement and advice. I would also like to express my thanks to the following: my parents for their continual encouragement and interest, Dr. J.H. Edwards for discussions of ideas and much practical advice, Dr. M. Ahmad for helpful explanations and discussions of semiconductor physics and Dr. R.H. Friend to whom I am indebted for allowing me to use the conductivity and doping apparatus at Cambridge.

I would also like to thank the members of the technical staff at Durham particularly Mr. J.A. Parkinson for the g.p.c. data. I must also mention my colleagues in the laboratories for their friendship and good humour, including I.F.A.F. El-Saafin, A.B. Alimuniar, D.S. Richards, V. Tsimis, K. Harper, S. Matuszczak, A.J. Tate and V.J. McNeilly. My thanks go to Mrs. M. Wilson for typing this thesis as well as drawing most of the diagrams.

The author gratefully acknowledges the funding of this work by the Science and Engineering Research Council.

My appreciation goes to my wife Mary for her encouragement and for help with proof-reading, etc. as well as for tolerating being married to a recluse for the last few months.

MEMORANDUM

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

Part of this work has been reported in Polymer Communications, 102, (1983) and has also been presented, by the author, at the Durham Graduate Symposium, April 15, 1983. A further presentation of other parts of these studies is to be made by the author at the Fifth International Symposium on Olefin Metathesis, Graz, Austria, August 22-26, 1983. This will appear in the conference edition of the Journal of Molecular Catalysis.

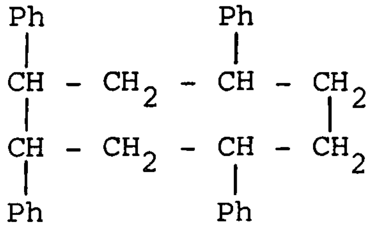
CONTENTS

CHAPTER ONE

BACKGROUND TO THE WORK REPORTED IN THIS THESIS

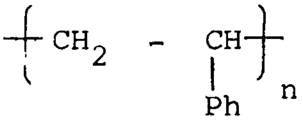
1.1 Introduction

Macromolecules were unambiguously shown to be long chains of valence bonded atoms by Staudinger[1] in 1920 and his theory was subsequently reinforced, mainly by the work of Carothers[2] in the later years of that decade. Previous to this, many polymers had been synthesised as unwanted side products in the flasks of organic chemists. Their macromolecular nature was not appreciated and their structures were usually believed to be cyclic, for example poly(styrene) was represented by the cyclic tetramer shown below:[3]



The behaviour of these compounds in solution was perceived as similar to that of colloids so these structures were held to be weakly physically bonded into colloid size particles by an ill defined, "secondary valence" interaction. Support for this idea as opposed to the long chain alternative was that end groups could not be detected.

Staudinger[1] dismissed these theories and proposed that polymers were composed of chains of molecules totally covalently bonded, for example he represented polystyrene by the now familiar formula shown below:



$$\left(CH_2 - \underset{Ph}{CH} \right)_n$$

Staudinger's ideas are now universally accepted. The reason that the workers of the day could not detect end groups was because the polymer chains they were studying were so long that the end group concentrations were below the limits measurable by the methods of that time.

1.2 Types of Polymerization Processes

The main classes of polymerization process recognized by Carothers were condensation and addition polymerization, subsequent experience has shown this classification to be somewhat limited. Lenz, in particular, has discussed the characterization of polymer forming reactions and emphasised the importance of the mechanism of formation of the polymer, either step-growth or chain-growth.[3] In this thesis examples of both types of polymer formation are described.

(i) Step-Growth Polymerization

Most, but not all, condensation polymerizations occur via a step-growth process. In these reactions difunctional monomers combine eliminating small molecules (CO_2, H_2O, HCl, etc.) in the process. Each combination is a separate step thus they are step-growth polymerizations. In general the scheme is:

$$A - X - A + B - Y - B \longrightarrow \left(X - Y \right) + AB$$

or

$$A - Z - B \longrightarrow \left(Z \right) + AB$$

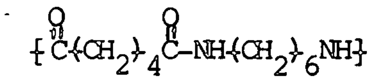
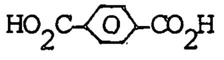
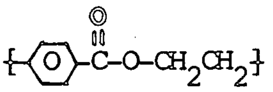
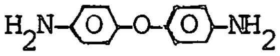
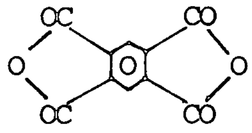
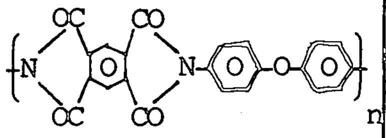
Some industrially important examples are given in Table 1.1.

It can be shown that for condensation polymerization the degree of polymerization (d.p.), that is the number of monomers per polymer chain, is given by,

$$dp = \frac{1}{1-p}$$

where p is the fraction of functional groups which have undergone reaction.

TABLE 1.1 Some Industrially Important Condensation Polymers

PROCESS	MONOMERS	POLYMER REPEAT UNIT	SOME USES
Synthesis of Nylon 6,6	$HO_2C(CH_2)_4CO_2H$ $H_2N(CH_2)_6NH_2$	 $\left[\overset{O}{\overset{\|}{C}}(CH_2)_4\overset{O}{\overset{\|}{C}}-NH(CH_2)_6NH \right]$	textile fibres, tyre cords, engineering materials
Synthesis of poly(ethylene terephthalate)	 $HO-CH_2CH_2-OH$		textile fibres, recording tape, plastic bottles
Synthesis of polyimides	 		thermally stable textile fibres & films

Since the polymerization depends on individual steps, and there are usually other side reactions of the end groups possible, high molecular weights are more difficult to attain than by other types of polymerization. It is evident from the equation that even for a 95% consumption of functional groups a d.p. of only 20 is obtained. Step-growth polymerization requires very high conversion for the formation of genuine high polymers.

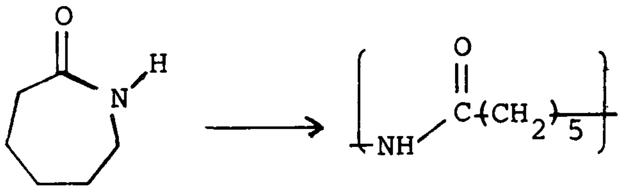
(ii) Chain-growth Polymerization

Addition polymerizations are generally chain reactions in which the molecular weight of the monomer is the same as that of the repeat unit. The d.p.s. obtained are generally very high due to the reactivities of the species involved, conversion from monomer to long chain polymer being rapid (only small concentrations of medium length polymer are present at any time in the process). Some important examples of materials made by chain-growth processes are poly(vinyl chloride), poly(ethylene), poly(styrene) and poly(isoprene).

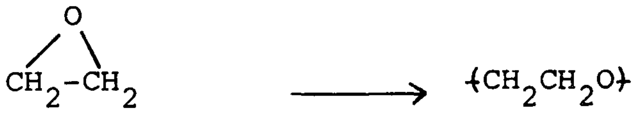
The distinguishing feature of chain growth processes is that the monomer can react only with a reactive species at a polymer chain end. This species may be a radical, a cation, an anion or an organometallic complex. Chain growth processes invariably require at least three types of reaction; namely, initiation, propagation and termination. By contrast step growth polymerization requires only one type of reaction.

(iii) Ring Opening Polymerization

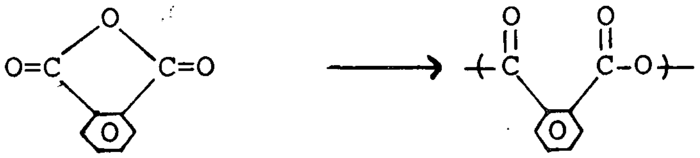
Ring opening addition polymerization can be effected for some cyclic compounds to give polymers identical to those given by non-cyclic condensation polymerizations, for example caprolactam gives nylon 6, which could be regarded as the condensation polymer from 6-aminohexanoic acid.



Other ring opening polymerizations are:

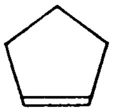


ethylene oxide polyether



phthalic anhydride polyanhydride

Another class of ring opening polymerization utilizes the olefin metathesis reaction, for example the polymerization of cyclopentene to polypentenamer is shown:



$$\xrightarrow[\text{catalyst}]{\text{metathesis}} \;\; -\!\!\!\!\left(CH_2CH_2CH_2-CH = CH \right)\!\!\!\!-$$

A fuller discussion of this type of polymerization, especially as applied to bicyclic monomers, is given in Chapter Four.

1.3 Conjugated Polymers - Syntheses and Electrical Properties

(i) Polymer Syntheses

Polymers having a conjugated carbon-carbon double bond backbone structure have been prepared via a variety of different methods. The following tables summarize these for the polymers poly(acetylene) (Table 1.2), substituted poly(acetylene)s (Table 1.3), poly(p-phenylene) (Table 1.4) and poly(phenylene vinylene) (Table 1.5).

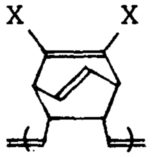
Poly(acetylene) is insoluble, infusible and air sensitive and requires storage and handling in an inert atmosphere. Methods 1 to 3 in Table 1.2 have been used to prepare poly-(acetylene) for measurements of the physical and electronic properties of this material.

The two hydrogen chloride elimination techniques (methods 4 and 5) shown are of doubtful value in that both are almost certain to leave residual saturated units in the chain:

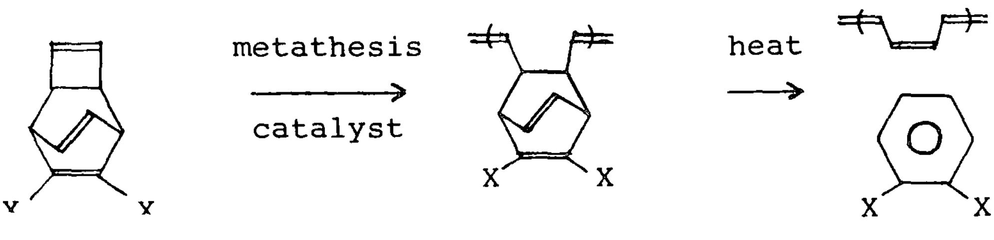
$-CH = CH - CHCl - CH = CH - CH_2 - CH = CH -$ (method 4)

$-CH = CH - CH_2CH_2 -$ (method 5 - dehalogenation).

TABLE 1.2 Some Polyacetylene Syntheses $-(CH = CH)-$

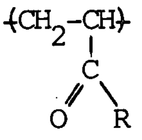
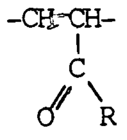
Method	Starting material	Reagents/ conditions	Product	Ref.
1. "Luttinger"	$HC \equiv CH$	Reducing agent (e.g. $NaBH_4$) and group VIII metal compound (e.g. $NiCl_2(Bu_3P)_2$)	Black, trans, along with lower molecular weight orange oils	4
2. Ziegler catalysed ("Shirakawa")	$HC \equiv CH$	TiX_4/MR_n e.g. $Ti(OBu)_4$ and $AlEt_3$	Black. When reacted below -78°C gives all cis, above 150°C gives all trans.	5
3. Elimination of Aromatic unit from a prepolymer		Heat	Black, trans.	6
4. Dehydrochlorination of poly(vinyl chloride)	$-(CH_2CHCl)-$	KOH/heat	Insoluble (in hot dioxane), orange	7
5. Dehydrochlorination of chlorinated poly-(1,4 butadiene)	$-(\overset{Cl}{\overset{\vert}{CH}}-\overset{Cl}{\overset{\vert}{CH}}-CH_2CH_2)-$	Strong base and solvent (e.g. KNH_2 and liquid NH_3)	Black-brown containing 0.8% residual chlorine	8

The Shirakawa method (Ziegler catalysis) can simultaneously provide a film as polymerization is occurring if acetylene gas is passed onto a layer of concentrated catalyst. This is then removed and repeatedly washed with inert solvent. The route of Edwards (method 3) involves prior metathesis formation (from a cyclobutene derivative) of a prepolymer which is then heated under vacuum to remove an ortho-disubstituted benzene and leave poly(acetylene).

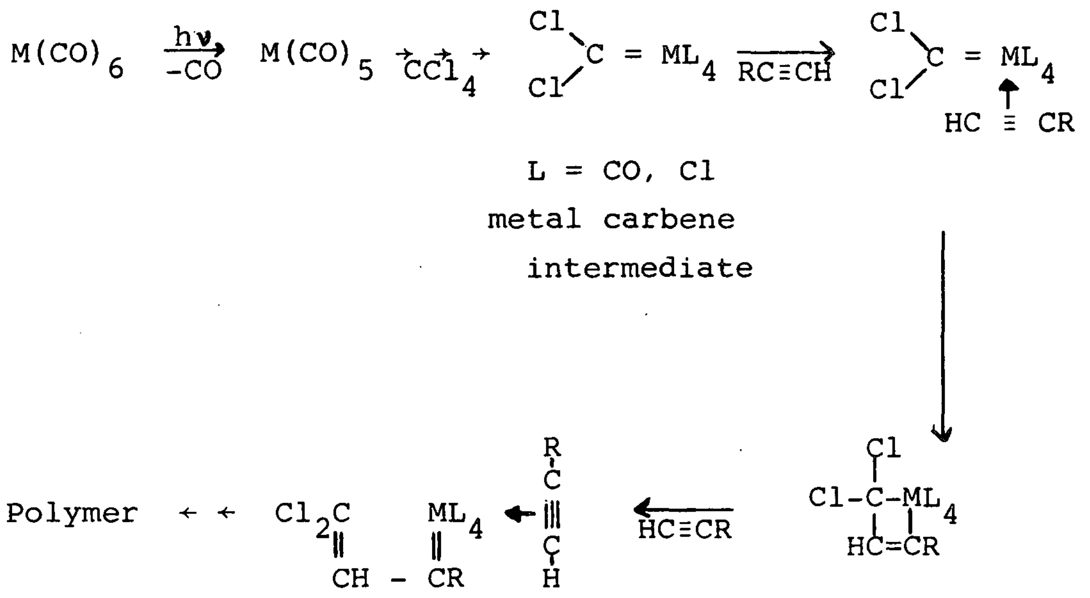


Preparations of substituted polyacetylenes (Table 1.3) generally give soluble polymers.

TABLE 1.3 Some Syntheses of Substituted Poly(acetylene)s $\text{-(}\overset{R}{\overset{|}{C}}H{=}CH\text{)-}$

Method	Starting material	Reagents/ conditions	Product	Ref.
1. "Luttinger"	R-C≡CH R=$CH_3(CH_2)_n$ n=2,3 R=Ph, $CH{=}CH(CH_2)_m$ m=3,4	Reducing agent and group VIII metal compound	Oligomers	9
2. Improved Luttinger	Ph-C≡CH	$RhCl_3/LiAlH_4$	$\bar{M}n$ 5,000, orange-red, 80% crystalline	10
3. Ziegler Catalysed	Ph-C≡CH	$AlEt_3/MR_n$ (e.g. $Fe(acac)_3$ and $Ti(OEt)_4$ where acac= acetylacetonate)	$\bar{M}n$ 6,000-10,000	11
4. Metal carbonyl or aryl metal carbonyl catalysed	Ph-C≡CH	Group VI carbonyl with UV light in CCl_4 e.g. $W(CO)_6$ or $Ar{-}M(CO)_3$ Ar=tolyl, M=Cr, W, Mo	$\bar{M}n$ 100,000 $\bar{M}n$ 12,000	12[a] 12[b]
5. Metathesis Polymerization	Ph-C≡CH R-C≡CH R=aliphatic R-C≡C-R R=phenyl, alkyl	WCl_6 or $MoCl_5$ with cocatalyst (e.g. Ph_4Sn) "	$\bar{M}n$ 92,000 (WCl_6) $\bar{M}n$ 5-8,000 ($MoCl_5$) $\bar{M}n$ up to 10,000 $\bar{M}n$ 1x10^6 for 2-hexyne	13
6. Treatment of poly(vinyl ketones) with active chlorides	 $\text{-(}CH_2{-}\underset{\underset{\displaystyle O{=}C{-}R}{|}}{CH}\text{)-}$	$POCl_3$ or $PSCl_3$	 $-\underset{\underset{\displaystyle O{=}C{-}R}{|}}{C}{=}CH-$ shiny black	14

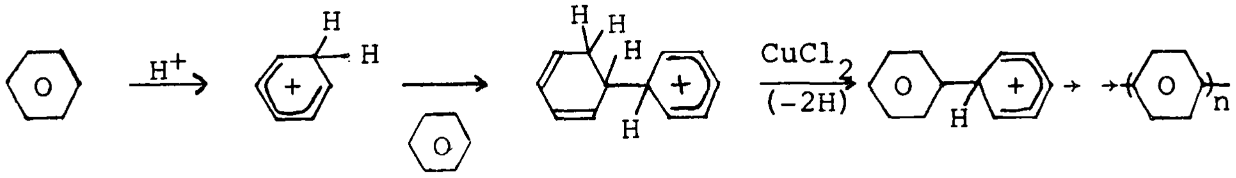
The light induced polymerization of phenyl acetylene described by Masuda *et al* (method 4) gives a high molecular weight product, the mechanism postulated is:



Metal carbene intermediates are also thought to take part in the metathesis polymerizations (method 5) and tungsten carbenes will actually catalyse the reaction. This is consistent with the proposed mechanism of olefin metathesis reactions (see Chapter Four).

Table 1.4 shows some of the many syntheses of poly-(p-phenylene).

Methods 4 and 5 are most often used. The Friedel-Crafts polymerization of benzene (method 4) established by Kovacic has been suggested to have a mechanism involving cationic intermediates:



Syntheses of poly(phenylene vinylene) are given in Table 1.5, poly(arylene vinylene)s which have substituents on the double bond are discussed separately in Chapter Three.

TABLE 1.4 Some Syntheses of Poly(p-phenylene)s 

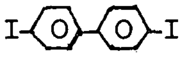
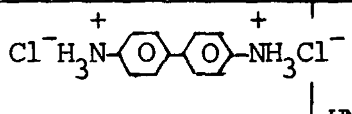
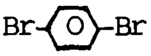
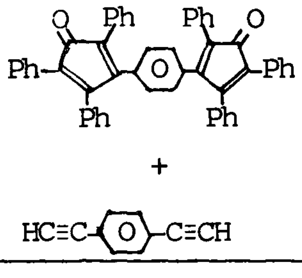
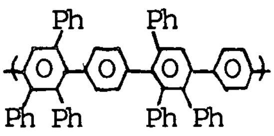
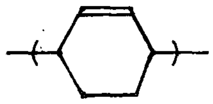
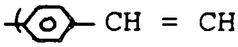
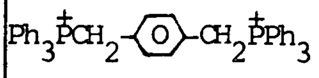
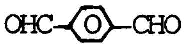
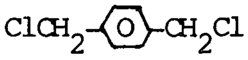
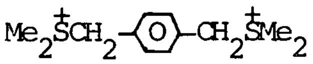
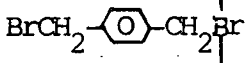
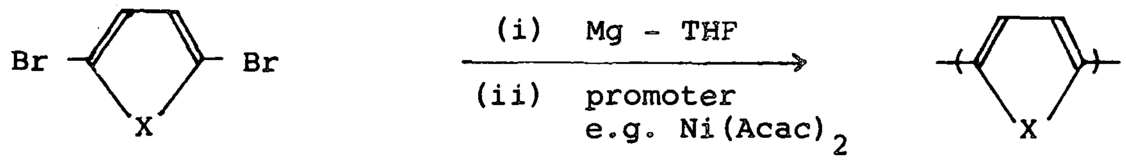
Method	Starting material	Reagents/ conditions	Product	Ref.
1. Wurtz-Fittig Reaction		Na or K	Soluble, low molecular weight (2,000-3,000)	15
2. Ullmann Coupling		Cu	Soluble, low molecular weight	16
3. Diazonium Coupling		HNO_2 then Cu^+	Impure due to -N=N- linkages	17
4. Friedel-Crafts Coupling (oxidative)		$AlCl_3$ with co-catalyst (e.g. H_2O) and oxidizer (e.g. $CuCl_2$, air)	Crystalline, brown, high softening point, low solubility	18
5. Grignard Coupling		Mg/THF then promoter (e.g. $NiCl_2$(bipy) or  bipy=22'bipyridine)	Melting point 550°C (dec.), high degree of polymerization, 20% soluble in hot toluene	19
6. Diels-Alder Addition	e.g. 			20
7. Dehydrogenation of poly cyclohexadiene	 prepared by polymerizing 1,3 cyclohexadiene with a Ziegler catalyst	Dehydrogenating agent (e.g. chloranil, NBS)	High softening point, low solubility	21

TABLE 1.5 Some Syntheses of Poly(phenylene vinylene) [poly(phenylene xylylidene)]. 

Method	Starting material	Reagents/ conditions	Product	Ref.
1. Wittig Reaction	 $2Cl^-$ 	EtLi	Intense yellow, insoluble, $\bar{M}n$ approximately 1,200 (degree of polymerization ∿ 9-10)	22
2. Reductive Coupling		$TiCl_3/LiAlH_4$ in THF	Slightly soluble in chloroform and THF, stable up to 300°C.	23
3. Base catalysed condensation		tBuOK in DMF	Identical to Wittig polymer	24
4. Dehydrochlorination		NaH in DMF or KNH_2 in liq.NH_3	Yellow polymer	25
5. Use of Sulphur Ylides	 $2BF_4^-$ (from  + Me_2S in BF_4^- solution)	aqueous NaOH	Soluble in benzene, $\bar{M}n$, 1,700, 2% residual sulphur	26

The Wittig polymerization is the most frequently reported method of preparation of these polymers (method 1).

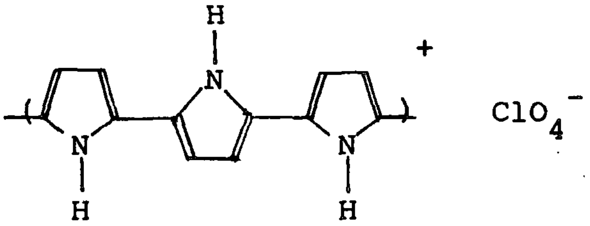
For the synthesis of conjugated bridged heterocyclic polymers two predominant methods have emerged for attaining high molecular weight products. One is by using a Grignard reaction, and is similar to that discussed above for poly(p-phenylene) and is as shown.[27]



X = N-H, N-Me, N-Ph, S

or cis-1,4
dichloro-2-butene

This generally gives black or brown products with low solubility. The alternative method, which has been especially used to prepare poly(pyrrole) is electrochemical polymerization by cathodic or anodic oxidation.[28] A two electrode cell containing a solution of pyrrole and $Et_4\overset{+}{N}\overset{-}{B}F_4$ or ClO_4^- in aqueous acetonitrile is used. A metal-like, amorphous, insoluble film is formed which is said to be relatively stable in air. Its structure is postulated to be,

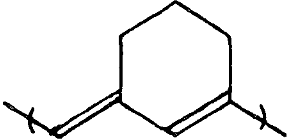


Using the BF_4^- system a 4:1 ratio of pyrrole units to BF_4^- ions is found.

Another conjugated heteroatom containing polymer is poly(p-phenylene sulphide) which is prepared industrially from p-dichlorobenzene and sodium sulphide. The product is called Ryton.

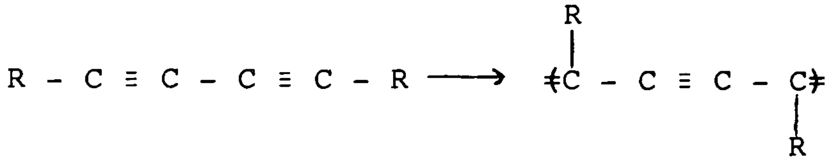
Bridged polyenes can be prepared by homogeneous Ziegler-Natta catalysis of terminal diynes, the best studied being poly(1,6 heptadiyne),[29] this yields a golden-green metallic-looking polymer which can be formed as free standing films.

$HC \equiv C \,(CH_2)_3\, C \equiv CH \longrightarrow$



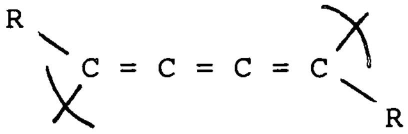
The product is air sensitive and insoluble.

Polymers derived from conjugated diacetylenes also give conjugated polymers but by an entirely different process to the above. Polymerization can be induced in crystals of these diacetylenes (solid state polymerization) by heat, pressure or irradiation;

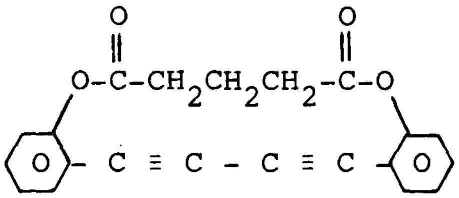


$$R-C\equiv C-C\equiv C-R \longrightarrow \left(\overset{R}{\overset{|}{C}} - C\equiv C - \underset{R}{\underset{|}{C}} \right)$$

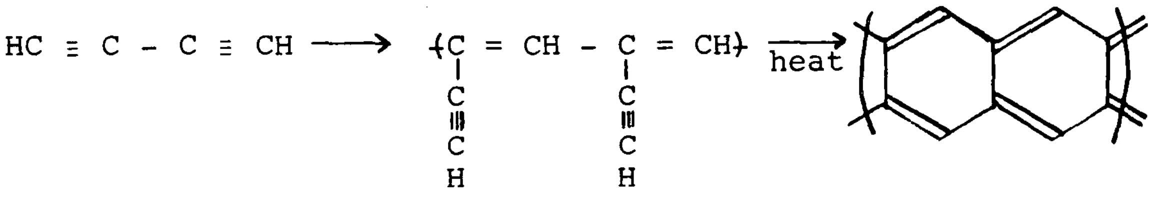
This is believed to be a chain reaction proceeding via the intermediacy of the 1,2,3-triene structure shown below.



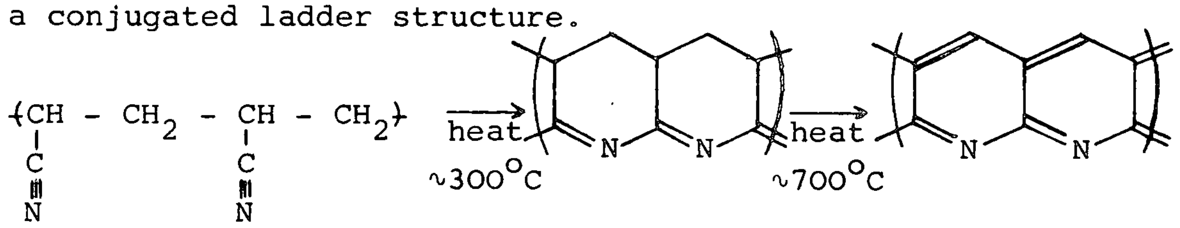
The monomer can be symmetrical or unsymmetrical,[30,31] typical R groups are $-CH_2OH$, $-CH_3$, $-CH_2OCOPh$, $-CH_2OCONHPh$, $(CH_2)_nOCONHCH_2CO_2R'$. Cyclic diynes can also be polymerized in this way,[32] for example the monomer shown.



In the vapour phase a different mechanism can be observed which also leads to conjugated polymers.[33] If butadiyne vapour is left over an inert plastic film, for example P.T.F.E., a coloured coating is observed after about five weeks. Heating induces further internal reaction to give a material for which a ladder-type structure has been proposed.



Other ladder polymers can be produced in similar ways, the most often used is probably the thermal reaction of poly(acrylonitrile) to give what is frequently described as a conjugated ladder structure.



P.A.N. "Orlon Black"

Many similar ladder polymers, some with sulphur or oxygen heteroatoms also in the chain, have been prepared. They are usually brown or black coloured and possess very good temperature resistance properties and high melting points.

(ii) Electrical Properties of Conjugated Polymers

Recently it has been discovered that the electrical conductivities of conjugated polymers can be greatly increased by the addition of electron donors or acceptors, most commonly as gases or in solution by electrochemical means. This has become known as doping, although it must be stressed that the process is not strictly analogous to the more established use of the term to describe additions of elements to semi-metals to modify their conducting behaviour, because the proportion of additive used is far higher in the former case, and the resultant mechanism of conduction is probably also different.

Highest conductivity values have, so far, been found using doped poly(acetylene) whilst promising results have also been found for poly(p-phenylene) and poly(pyrrole). Most of the systems studied have two large problems, one is that they lack "processability", that is, they would be difficult to handle on an industrial scale mainly because of their infusibility and insolubility, the other problem is that most of these polymers oxidize on exposure to air. Studies of more suitable compounds for example, poly(phenylene sulphide) and poly(phenylene vinylene), have been directed towards solving these problems but the attainable conductivities for these alternatives do not yet compete with the above types.

When conjugated polymers are doped a darkening of the colour of the material often occurs. Subsequent exposure to air usually results in a loss of the elevated conductivity so any use made of these systems would require encapsulation of the doped polymer. Obviously many problems need to be overcome before thes polymers can successfully replace metals as conducting materials.

A summarized table of these phenomena is given in Table 1.6.

TABLE 1.6 Behaviour of Conjugated Polymers upon Doping

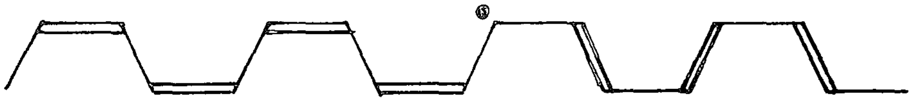
Polymer	Dopant	Uptake	Conductivity before Doping $/\Omega^{-1}\ cm^{-1}$	Conductivity Achieved $/\Omega^{-1}\ cm^{-1}$	Ref.
$(CH)_x$	$SnCl_4$	$CH(SnCl_4)_{0.035}$		360	34
trans $(CH)_x$	I_2	$CHI_{0.20}$	$4.4x10^{-5}$	160	35
	Br_2	$CHBr_{0.23}$	"	0.4	35
	AsF_5	$CH(AsF_5)_{0.10}$	"	400	35
	Ag^+ ($AgClO_4$ or $AgBF_4$)	$CH\ Ag_{0.018}$	10^{-5}	3.0	36
	IBr	$CH(IBr)_{0.12}$	$4.4x10^{-5}$	160	35
	Na	$Na_{0.28}CH$	"	8	35
	Li (electrochemical)			100	37
	MF_6	$(MF_6)_{0.01-0.02}CH$		350(WF_6)	38
	$LiAlH_4$		"	6	39
	H_2IrCl_6	$CH(IrCl_6)_{0.1}$	"	10	40
	$Fe(ClO_4)_3$	$CH(ClO_4)_{0.06}$	"	500	41

TABLE 1.6 (contd.)

Polymer	Dopant	Uptake	Conductivity before Doping $/\Omega^{-1}\ cm^{-1}$	Conductivity Achieved $/\Omega^{-1}\ cm^{-1}$	Ref.
cis $(CH)_x$	I_2	$CHI_{0.25}$	$1.7x10^{-9}$	5	35
	AsF_5	$CH(AsF_5)_{0.14}$	"	560	35
	+3:1 film stretch	$CH(AsF_5)_{0.14}$	"	2000 parallel 200 perpendicular	42
	ICl	$CH(ICl)_{0.14}$	"	5	35
	IBr	$CH(IBr)_{0.15}$	"	400	35
	KI (electrolysis)	$CHI_{0.07}$	$1x10^{-8}$	9.7	43
	nBu_4NClO_4 (electrolysis)	$CH(ClO_4)_{0.065}$	"	970	43
Poly(phenyl acetylene)	I_2	$C\phi{=}CH(I_2)_{0.8}$		$\sim 10^{-6}$	44
	AsF_5	$C\phi{=}CH(AsF_5)_{0.7}$		$>10^{-2}$	44
Poly(p-phenylene)	AsF_5	$C_6H_4(AsF_5)_{0.26}$	10^{-11}	145	45
	Knaphthalide		"	7.2	45
Poly-(pyrrole)	Et_4NBF_4 (electrolysis)	$C_4H_3N(BF_4)_{0.25}$		100	46
	ClO_4^- (electrolysis)	$C_4H_3N(ClO_4)_{0.25}$			28
Poly-(thiophene)	I_2	$C_4H_2SI_{0.32}$	$5.3x10^{-11}$	$3.4x10^{-4}$	27a
	"		$5\ x10^{-11}$	$4\ x\ 10^{-2}$	47
Poly(p-phenylene sulphide)	AsF_5	$C_6H_4S(AsF_6^-)_{0.9}$	10^{-16}	1	48
	"			1	49
	"	$C_6H_4S(AsF_6^-)_{0.78}$		2.7	50
	Na naphthalide			0	48
	K naphthalide			0	49
Poly(p-phenylene vinylene)	I_2			0	51
	AsF_5	$C_8H_6(AsF_5)_{0.92}$	10^{-10}	3	51
Poly(1,6 heptadiyne)	I_2		10^{-12}	$\sim 10^{-1}$	29
	AsF_5		10^{-12}	$\sim 10^{-1}$	29

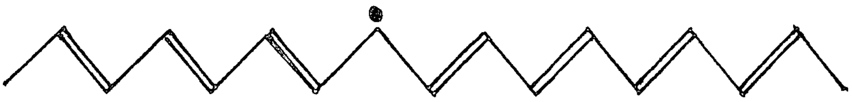
Some theories have been advanced to explain the behaviour described. At present the most popular is that conduction occurs via species on the chain known as solitons or polarons. Let us consider poly(acetylene) first.[52] When formed at temperatures below -70°C this polymer has no odd, unpaired electron spins as witnessed by Electron Paramagnetic Resonance (EPR) studies, it is mostly in its cis-transoid configuration at such temperatures:

When taken above -70°C, spins are detected so a structure can be proposed with free spins on the chain with changes in phase of the double bonds around each radical centre as shown.



cis-transoid trans-cisoid

These free radical centres have been called neutral solitons and are represented by S•. Above 145°C the polymer is mostly in its trans-transoid configuration and spins can be detected, so we now have the structure shown.

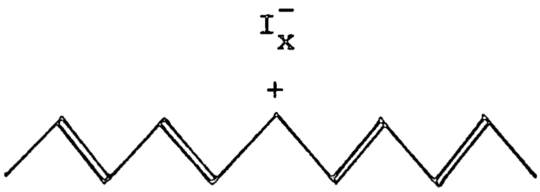


EPR has also shown that S• is more mobile the higher the temperature[†], hence a soliton on trans polyacetylene is more mobile than on the cis forms. Other evidence for S• species is that on standing in inert conditions poly(acetylene) samples become brittle, this is explained in terms of solitons on neighbouring chains combining to form crosslinks.

[†] the higher the mobility the narrower the EPR band width.

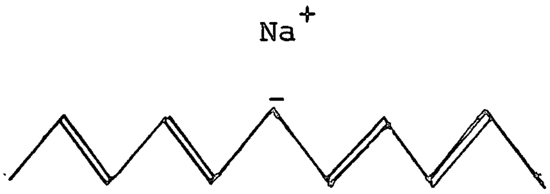
On doping, the electron acceptor (e.g. AsF_5, I_2) or donor (e.g. Na) will complex with the chain endowing a site on the chain with a positive (p-type doping) or negative (n-type doping) charge respectively.

So charged solitons of the types shown below can be envisaged



x = 3 or 5

p-type doping
- conduction via holes

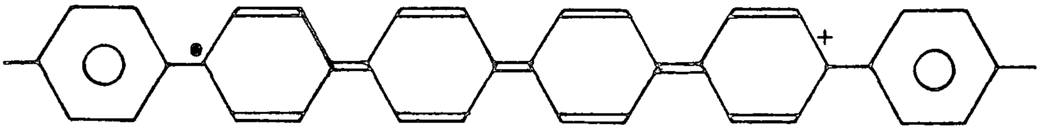


n-type doping
- conduction via extra electrons

Another finding which supports this explanation is that when p-type doped polyacetylene is exposed to ammonia the conductivity decreases to near to the original value. This is due to $:NH_3$ complexing with the carbonium ion on the chain and halting hole mobility.

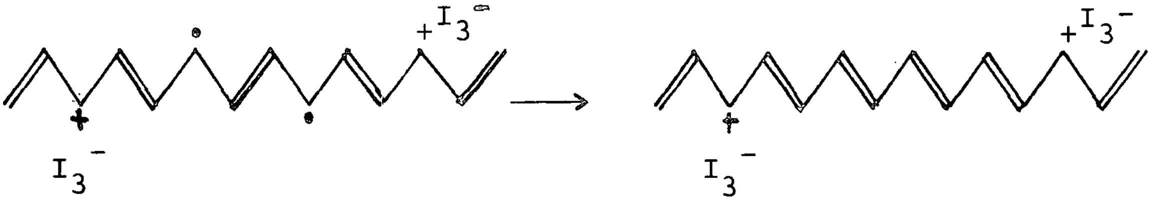
The low conductivities found for substituted poly(acetylene)s, for example poly(phenyl acetylene) and poly(diacetylenes) may be due to the side groups disrupting the planarity of the chain thus reducing the length of conjugation, or the side groups may prevent access of dopants to the backbone thereby hindering formation of charged solitons.

Some doubt has been cast on the soliton model[53] since it is not so easily extended to poly(p-phenylene). A modified theory which involves species known as polarons has been suggested[54] which can be extended to poly(p-phenylene). ESR studies support the proposal that a structure, such as the one shown below, exists in doped conducting forms of this polymer.



A polaron in poly(p-phenylene)

The unpaired electron is delocalized over 2 to 4 phenylene units. In polyacetylene polarons are believed to combine to give charged soliton pairs,[55] so processes probably occur such as that shown below.



Much of the recent research on conducting polymers has been concerned with physical measurements and doping of existing polymers.

The work reported in this thesis describes attempts to prepare novel organic conjugated polymers. The objective of these studies was to use relatively simple synthetic routes capable of yielding high polymers. It was hoped that these polymers could potentially display better properties than existing systems of this type, namely processability and air stability together with good electrical conductivity. Preferably the routes used would involve readily available monomers, catalysts and processes. Although not of immediate importance the factor of cost could be critical in any subsequent technological applications of the products. Another consideration was to try to extend knowledge in the area of correlation between polymer structure and electrical properties.

CHAPTER TWO

ATTEMPTS TO POLYMERIZE AROMATIC DIKETONES BY PHOTOREDUCTIVE COUPLING

2.1 Introduction

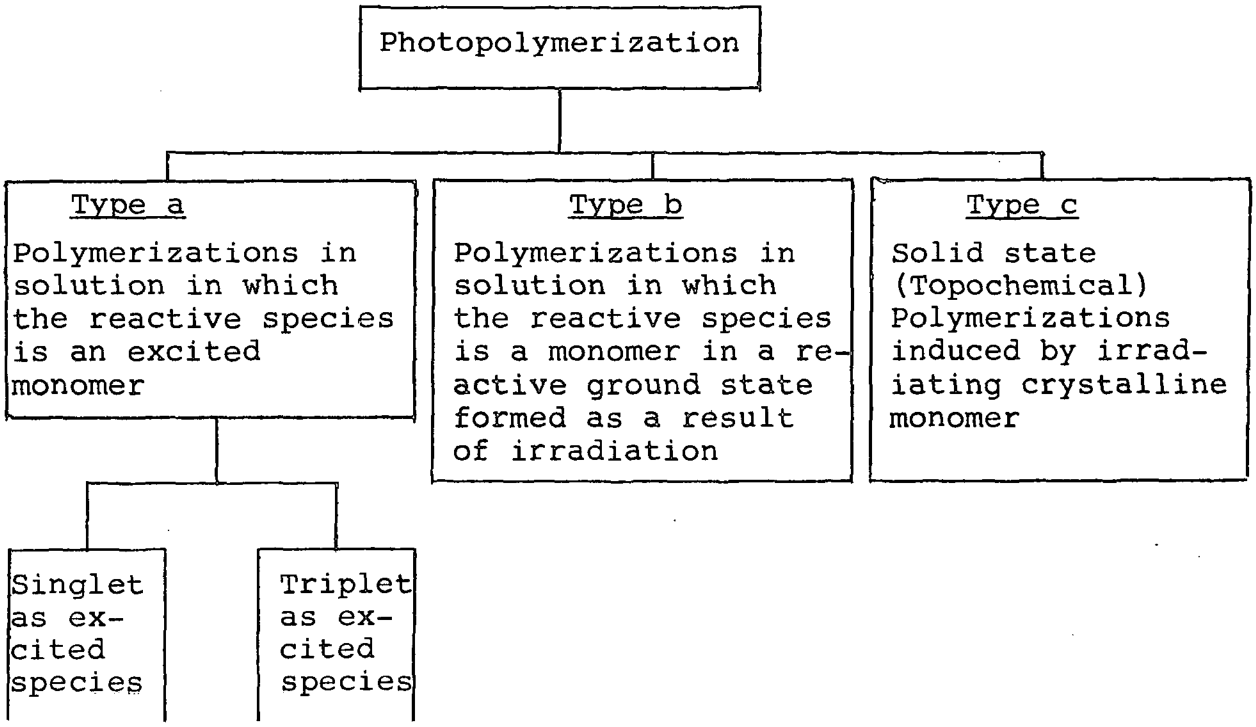
2.1.1 Photopolymerization

(a) Definition

The term photopolymerization is often used when referring to polymerization processes that are initiated by light. Strictly, according to the definition given by De Schryver *et al*,[56,57] this usage is incorrect. Their description is that a photopolymerization is a process in which every chain-propagating step involves a photochemical reaction. That is, the reaction is not merely initiated by light and then proceeds in its absence, rather it needs to be irradiated for the full time of polymerization. Unfortunately it appears that photochemists have not generally acknowledged this classification and the term photopolymerization is still used for both photoinitiated polymerizations and true photopolymerizations.

As well as clarifying the definition of the term photopolymerization, De Schryver *et al* have observed the different classes of reaction which are observed in photopolymerizations. These reaction types are shown schematically below (Scheme 1).

Scheme 1 - Classification of Bichromophore Photopolymerizations



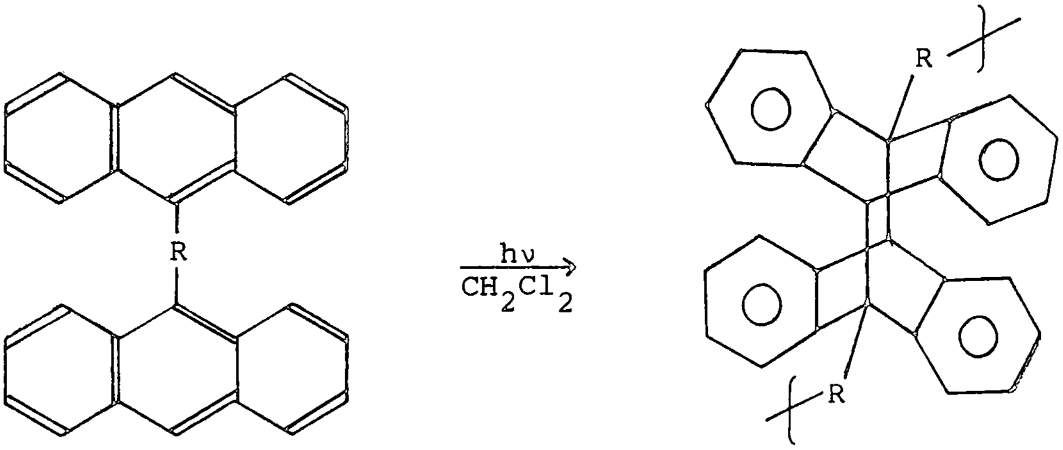
Examples of each type are given below.

(b) Some Examples of Photopolymerizations

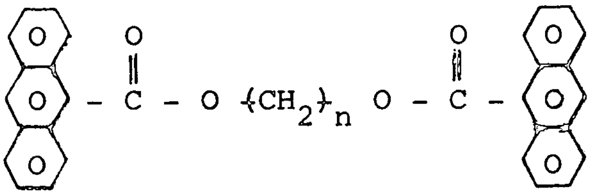
These polymerizations are all extensions of previously discovered analogous, model reactions of the monochromophoric compounds, with most of them intramolecular cyclization is a competing reaction. In many cases the distance apart of chromophores in the monomer is the factor which decides whether cyclization or polymerization will occur.

Type a - Singlet

When irradiated in solution many bisanthracenes polymerize in the manner shown.[56]



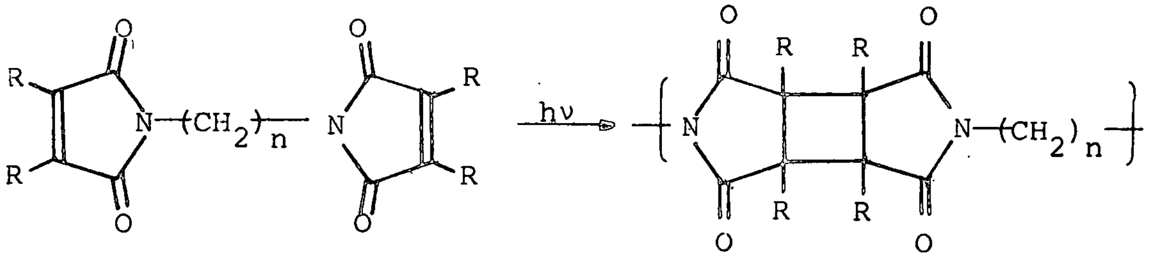
R is usually a long carbonyl containing chain, for example, this monomer:



n = 11,12

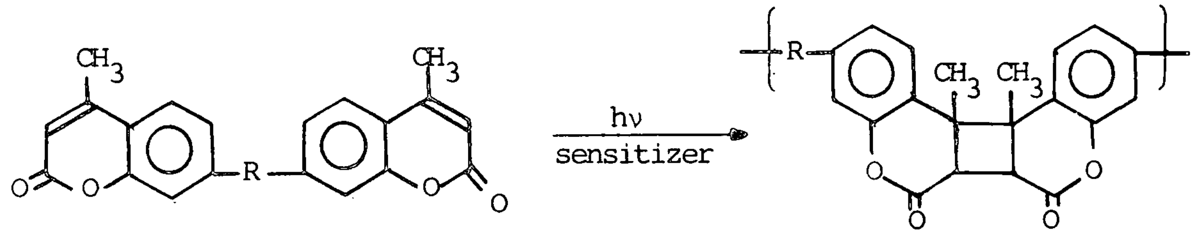
Type a - Triplet

Bis maleimides with the two functionalities linked by an aliphatic chain can polymerize via the triplet excited state.



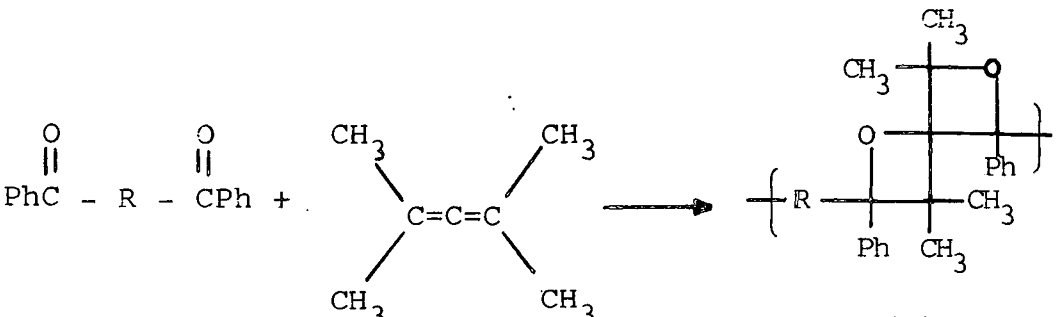
Monomers with R as alkyl or bromine[57] give highest degrees of polymerization when n = 9-11, alternatively R can be chlorine[58] in which case n = 8-10 are optimum chain lengths for polymerization. For the latter type benzophenone sensitization is required.

Biscoumarins undergo a similar polymerization when light and a sensitizer are used,[59] again four-membered rings are formed on polymerization.



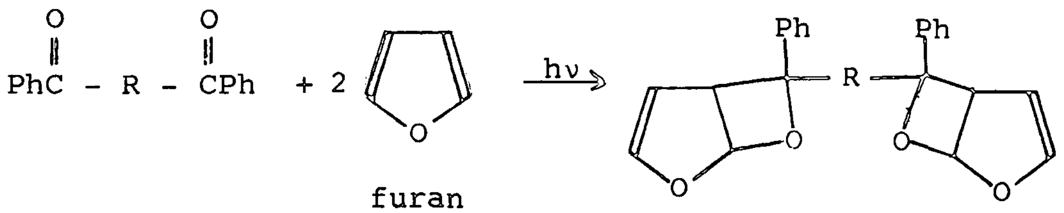
for example R = $-O\overset{O}{\overset{\|}{C}}\,(CH_2)_n\,\overset{O}{\overset{\|}{C}}O-$ n = 10-12

Another example of type a (triplet) is the copolymerization of diketones with conjugated dienes, this utilizes the Paterno-Büchi reaction.[60] This has been successful in forming polymers with the monomers shown below.

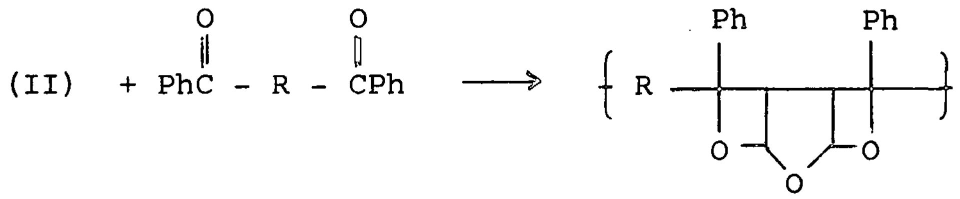


(I)

Tetramethylallene



(II)



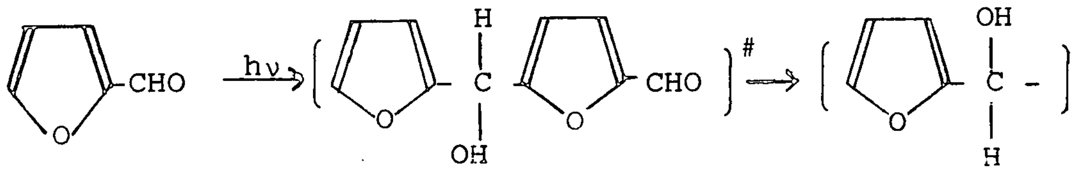
(III)

(I) and (III) were the predominant repeat units but these polymerizations are hampered by competing processes, for example hydrogen abstractions.

For a further example see reference 61.

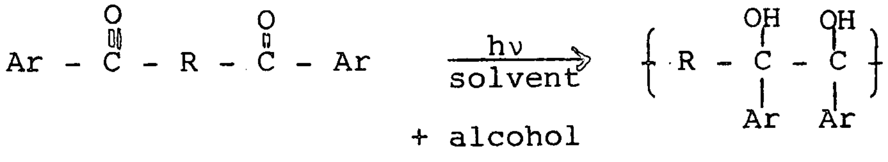
Type b

An example of this type is the photopolymerization of liquid 2-furaldehyde.[62] The reaction is believed to proceed via reactive dimers formed after monomer excitation.

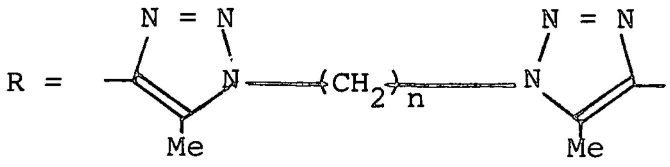


"hot dimer" + some furoin units

Another example is the formation of polypinacols on irradiation of diketones in the presence of a hydrogen donor.[63]



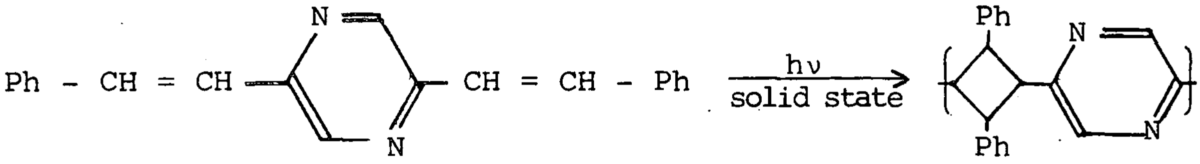
Polymerization is particularly successful where R is $-\text{Ar}\{\text{CH}_2\}_n\text{Ar}-$ or a bisketotriazole, i.e.



Type c

These have been observed in four-centre photopolymerizations of bisolefins. Characteristics of these reactions are that the polymer structure replicates that of the monomer crystal. When the monomers are irradiated in solution it is found that cyclization usually occurs. This is because in the crystalline state the chromophores are held in suitable positions for polymerization to occur whereas this situation does not occur in solution.

There are many examples of bisolefins undergoing this reaction, a few variations are shown with reference numbers to the relevant literature.



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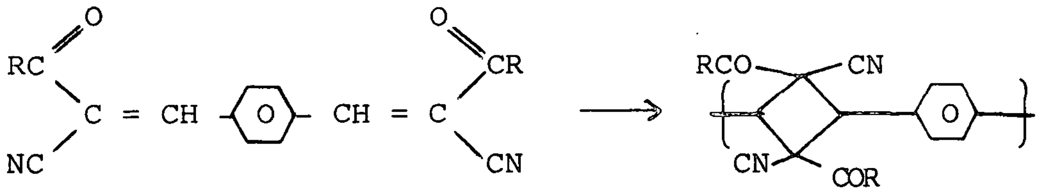

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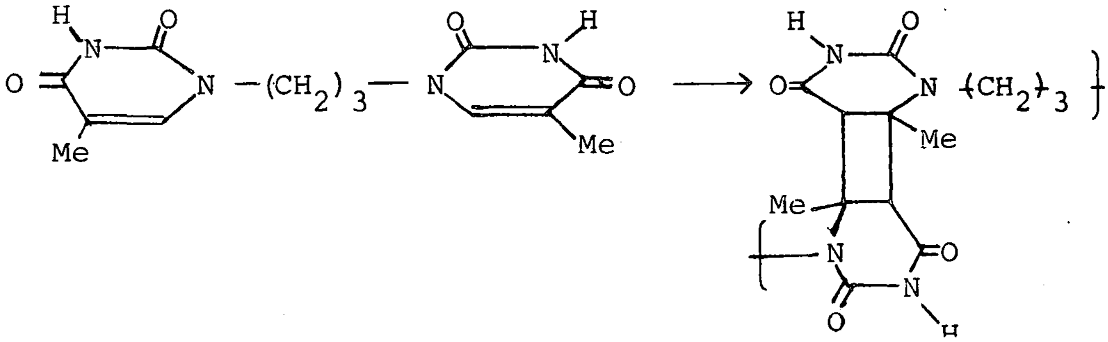

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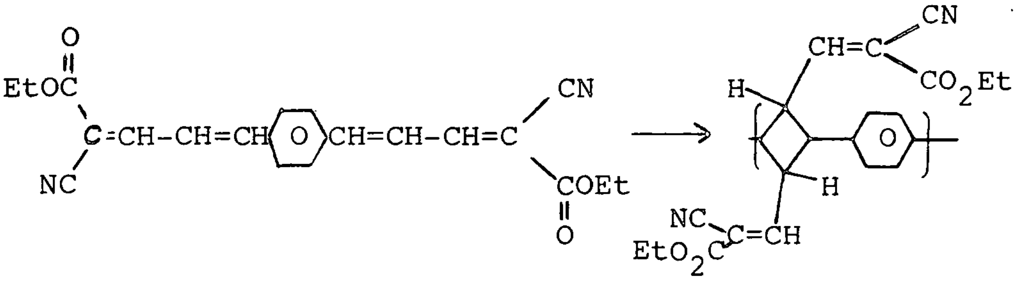

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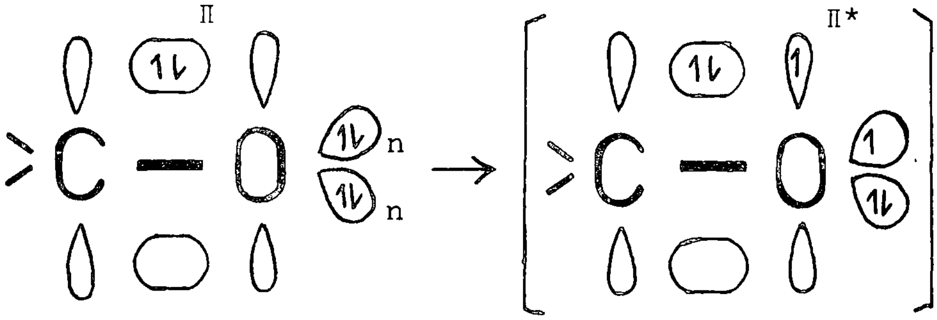
2.1.2 Photopolymerizations of Diketonic Compounds

(a) Carbonyl Photochemistry

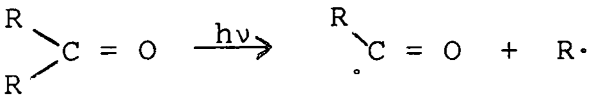
Most carbonyl photochemistry occurs via $n \rightarrow \pi^*$ excitation to a triplet state.



An electron from an oxygen lone pair is excited to a p orbital, the resultant singlet excited state undergoes intersystem crossing very easily to the triplet state and a species electronically and reactively similar to an alkoxy radical is produced. In compounds where there is conjugation with the carbonyl group the $\pi \rightarrow \pi^*$ transition can become the lowest excitation path.

The photochemical reactions of ketones can be classified in three groups.

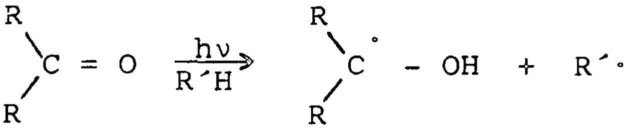
(i) Norrish Type I cleavage:

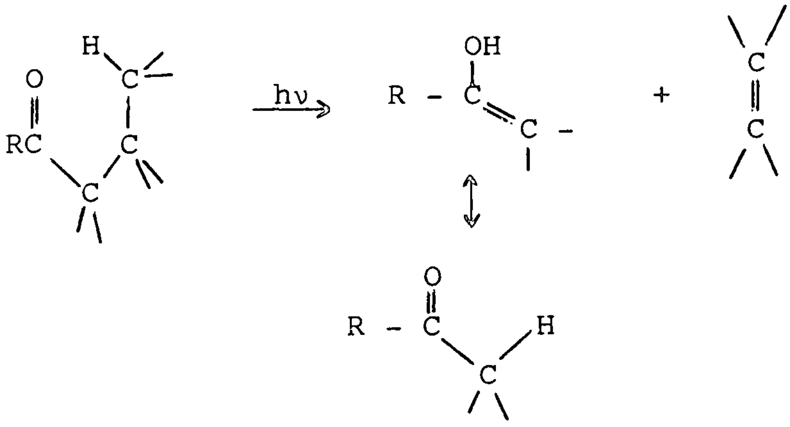


$$R_2C=O \xrightarrow{h\nu} R\dot{C}=O + R\cdot$$

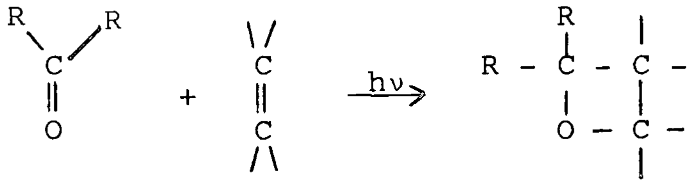
The ketone cleaves homolytically at one of its C-C bonds.

(ii) Norrish Type II hydrogen abstraction, this can occur intermolecularly or intramolecularly.





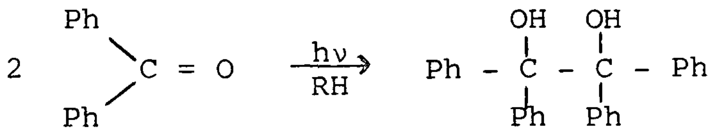
(iii) Cycloaddition, this forms an oxetane.



The type of reaction which is relevant to the studies described in this chapter is intermolecular hydrogen abstraction.

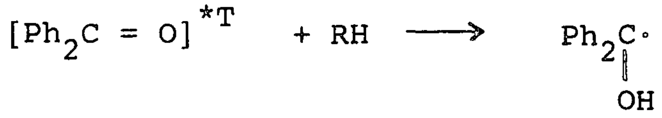
(b) Photoreduction of Aromatic Ketones

Benzophenone can be photoreductively coupled to produce pinacols if a hydrogen donor is present.[68]



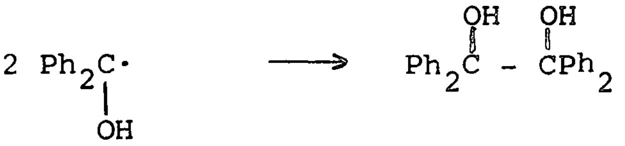
The important steps of the mechanism are shown below.

$$Ph_2C=O \xrightarrow[\text{Absorption}]{h\nu} \underset{\text{Singlet Excited State}}{[Ph_2C=O]^{*S}} \xrightarrow[\text{Intersystem Crossing}]{} \underset{\text{Triplet Excited State}}{[Ph_2C=O]^{*T}}$$



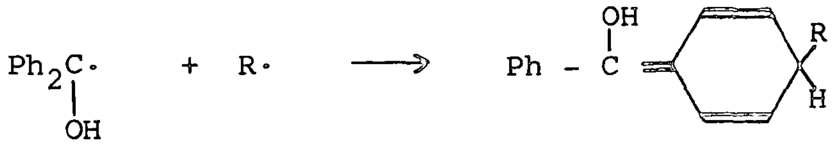
$$[Ph_2C=O]^{*T} + RH \longrightarrow Ph_2\underset{\displaystyle OH}{\underset{|}{C}}\cdot$$

(1)



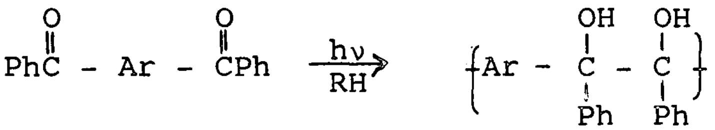
$$2\ Ph_2\underset{\displaystyle OH}{\underset{|}{C}}\cdot \longrightarrow Ph_2\overset{\displaystyle OH}{\overset{|}{C}}-\overset{\displaystyle OH}{\overset{|}{C}}Ph_2$$

The ketyl radical intermediates are believed to combine in the solvent cage after spin flipping of one radical's free electron. A side reaction which leads to the observed yellow colour during irradiation is thought to produce the structure shown below.



This intermediate is removed by further reactions which convert it back to (1).

For aromatic diketones it is clear that this reaction has the potential to lead to polypinacols.

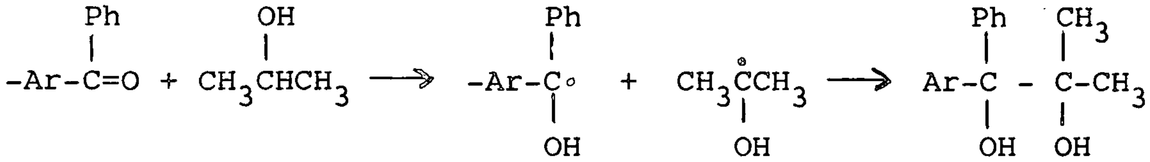


$$Ph\overset{\displaystyle O}{\overset{\|}{C}}-Ar-\overset{\displaystyle O}{\overset{\|}{C}}Ph \xrightarrow[RH]{h\nu} \left\{Ar-\underset{\displaystyle Ph}{\underset{|}{\overset{\displaystyle OH}{\overset{|}{C}}}}-\underset{\displaystyle Ph}{\underset{|}{\overset{\displaystyle OH}{\overset{|}{C}}}}\right\}$$

This reaction has been carried out using two different types of hydrogen donor, aliphatic alcohols such as propan-2-ol and benzhydryl alcohols.

(c) Diketone Photoreduction with Aliphatic Alcohols

A major disadvantage of this technique is that the alcohol hydrogen donor becomes a potential pinacol forming radical itself. This results in some chain termination and thus degrees of polymerization attained are limited. The alcohol most often used is propan-2-ol and steps such as that shown below are possible.



$$-\mathrm{Ar}-\overset{\mathrm{Ph}}{\overset{|}{\mathrm{C}}}=\mathrm{O} + \mathrm{CH_3}\overset{\mathrm{OH}}{\overset{|}{\mathrm{C}}}\mathrm{HCH_3} \longrightarrow -\mathrm{Ar}-\underset{\mathrm{OH}}{\underset{|}{\overset{\mathrm{Ph}}{\overset{|}{\mathrm{C}}}}}\cdot + \mathrm{CH_3}\underset{\mathrm{OH}}{\underset{|}{\overset{\bullet}{\mathrm{C}}}}\mathrm{CH_3} \longrightarrow \mathrm{Ar}-\underset{\mathrm{OH}}{\underset{|}{\overset{\mathrm{Ph}}{\overset{|}{\mathrm{C}}}}} - \underset{\mathrm{OH}}{\underset{|}{\overset{\mathrm{CH_3}}{\overset{|}{\mathrm{C}}}}}-\mathrm{CH_3}$$

Reports of polymerizations of aromatic diketones using aliphatic alcohol hydrogen donors are summarized in Table 2.1. All utilized a long (more than 1 hr.) irradiation period.

TABLE 2.1 Photopolymerizations of Aromatic Diketones using an Aliphatic Alcohol as Hydrogen Donor

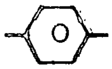
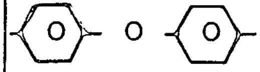
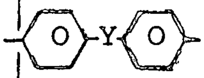
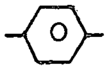
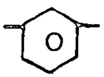
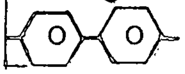
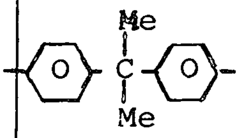
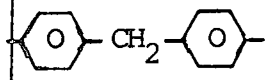
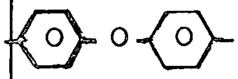
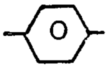
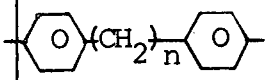
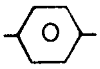
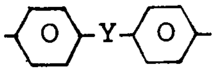
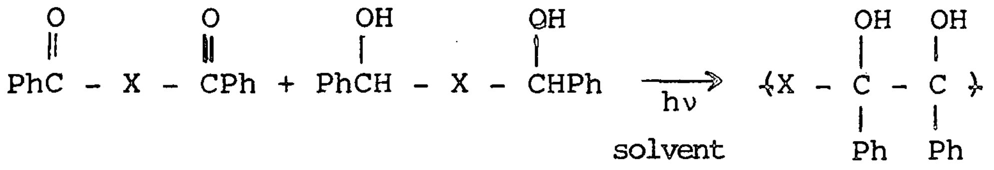
X in $\mathrm{Ph\overset{O}{\overset{\|}{C}}-X-\overset{O}{\overset{\|}{C}}Ph}$	Irradiation Solvent(s)	Degree of Polymerization(dp) or Viscosity(η) of Product	Ref.
	3:1 benzene-isopropanol	dp∿5	69
	isopropanol or mixtures of it with THF or benzene	dp 2.91	70
		dp 1.89	
		dp 2.80	
 Y -S-	1:1 benzene-isopropanol at reflux	η 0.10	71
-O-		η 0.30	
$-CH_2-$		η 0.25	
$-CH_2CH_2-$		η 0.45	
		η 0.04	
		η 0.24	
		no polymerization	

TABLE 2.1 (contd.)

X in $\mathrm{Ph}\overset{O}{\overset{\|}{C}}-X-\overset{O}{\overset{\|}{C}}\mathrm{Ph}$	Irradiation Solvent(s)	Degree of Polymerization(dp) or Viscosity(η) of Product	Ref.
	3:1 benzene-isopropanol	dp 171	72
	"	η 0.23	
	5:1 benzene-isopropanol	η 0.27	
	"	η 0.06	
 $\underline{n}$ 1	2:1 dichloromethane isopropanol	dp 70	73
6		dp 32	
8		dp 23	
10		dp 35	
	1:1 benzene-isopropanol	dp 16.6	74
		dp 4.5	
 $\underline{Y}$ -O-		dp 8.9	
$(CH_2)_n$			
$\underline{n}$ 1	) (3:1-4:1 benzene	dp 2.5(38.8)	
2	) -isopropanol)	6.9(9.4)	
3	)	5.7(10.8)	
4	)	8.3(18.2)	
5		20.9	
6		23.0	
10		25.0	
	benzene : isopropanol		75
	14 : 1	dp 14.8	
	9 : 1	15.0	
	5 : 1	14.1	
	4 : 1	16.5	
	2 : 1	9.7	
	1 : 1	7.7	

(d) Diketone Photoreduction using a Dihydrol as Hydrogen Donor

In this type of polymerization the hydrogen donor is a difunctional alcohol and itself actually becomes a part of the repeat unit.

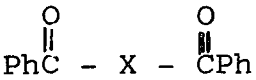
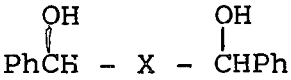
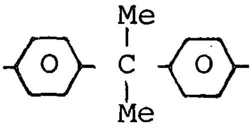
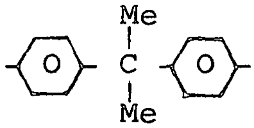
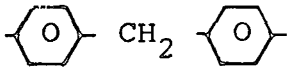
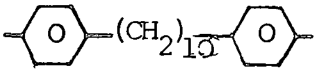
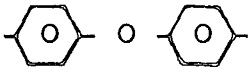
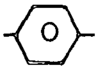


$$\mathrm{Ph}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}} - \mathrm{X} - \overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\mathrm{Ph} + \mathrm{Ph}\overset{\mathrm{OH}}{\overset{|}{\mathrm{C}}}\mathrm{H} - \mathrm{X} - \overset{\mathrm{OH}}{\overset{|}{\mathrm{C}}}\mathrm{HPh} \xrightarrow[h\nu]{} \text{-}\!\!\left(\mathrm{X} - \underset{\mathrm{Ph}}{\underset{|}{\overset{\mathrm{OH}}{\overset{|}{\mathrm{C}}}}} - \underset{\mathrm{Ph}}{\underset{|}{\overset{\mathrm{OH}}{\overset{|}{\mathrm{C}}}}} \right)\!\!\text{-}$$

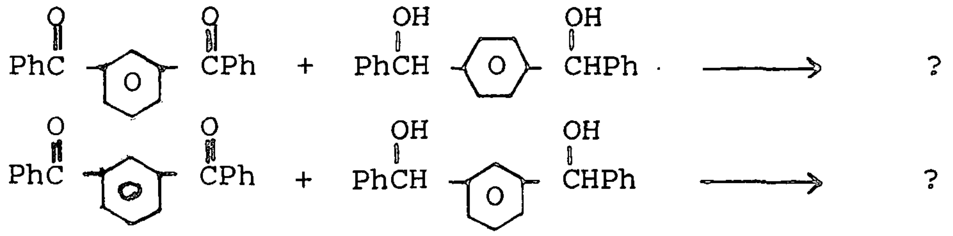
solvent

If the two X groups are different copolymerizations can be effected. This polymer forming method was by De Schryver *et al.*[72] Their results with the X groups containing aromatic groups (they also successfully polymerized monomers with triazole units in these positions) are summarized in Table 2.2.

TABLE 2.2 Diketone - Dihydrol Polymerizations Reported by De Schryver *et al*[72]

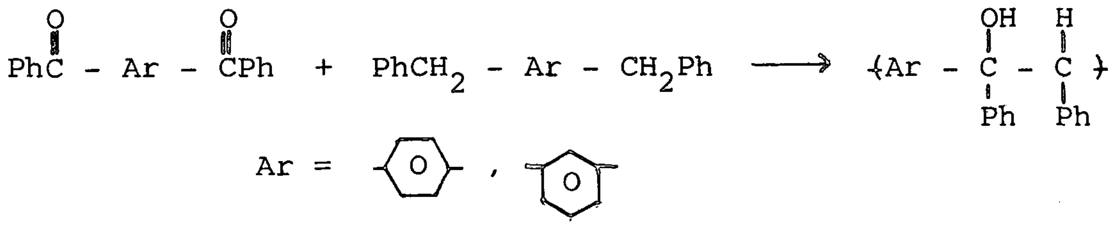
Monomers		Polymer Properties
X in diketone  $\mathrm{Ph}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}} - \mathrm{X} - \overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\mathrm{Ph}$	X in dihydrol  $\mathrm{Ph}\overset{\mathrm{OH}}{\overset{|}{\mathrm{C}}}\mathrm{H} - \mathrm{X} - \overset{\mathrm{OH}}{\overset{|}{\mathrm{C}}}\mathrm{HPh}$	
		dp 430
"		η 0.18
"		dp 102
"		η 0.21
"		η 0.08

The reaction was attempted unsuccessfully in these laboratories by Batey[75] using the monomer mixtures shown below.

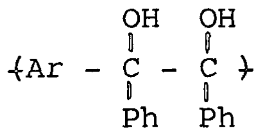


The conditions of reaction tried were, (i) in benzene at room temperature, (ii) in refluxing benzene and (iii) in acetonitrile in which (unlike for (i) and (ii)) the dihydrol is completely soluble. In all three cases a yellowing of the solution occurred but no significant polymerization occurred. This was monitored by a negligible change in the infrared spectrum of the recovered material as compared to an unirradiated monomer mixture, especially the carbonyl peak which would be expected to disappear on polymerization.

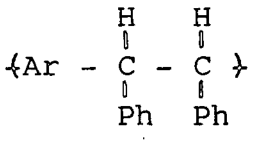
A related study in these laboratories by Spanomanolis[76,77] investigated the similar reaction shown.



This gave low molecular weight products as well as units in the chain corresponding to benzopinacol and tetraphenylethane.



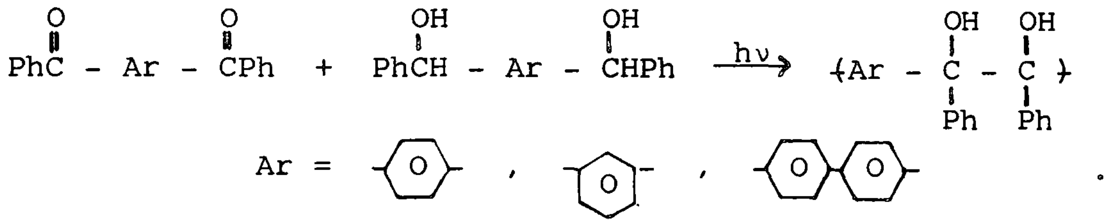
$$\left(Ar - \underset{Ph}{\overset{OH}{C}} - \underset{Ph}{\overset{OH}{C}} \right)$$



$$\left(Ar - \underset{Ph}{\overset{H}{C}} - \underset{Ph}{\overset{H}{C}} \right)$$

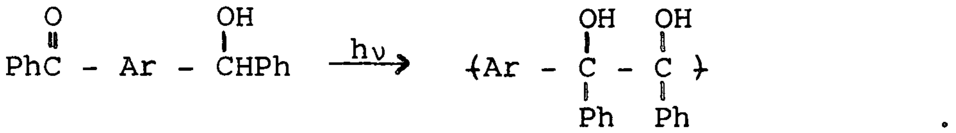
(e) Aims of this Study

The aims of this work were to repeat Batey's attempts to polymerize mixtures of conjugated aromatic diketones and dihydrols and to investigate the reaction more fully. We believed that it should be possible to carry out the polymerization successfully, under the right conditions. The projected polymerization is:



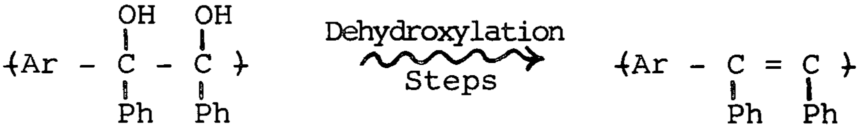
$$PhC(=O)-Ar-C(=O)Ph + PhCH(OH)-Ar-CH(OH)Ph \xrightarrow{h\nu} -\!\!(Ar-C(OH)(Ph)-C(OH)(Ph))\!\!-$$

If this was unsuccessful this variation was to be tried:



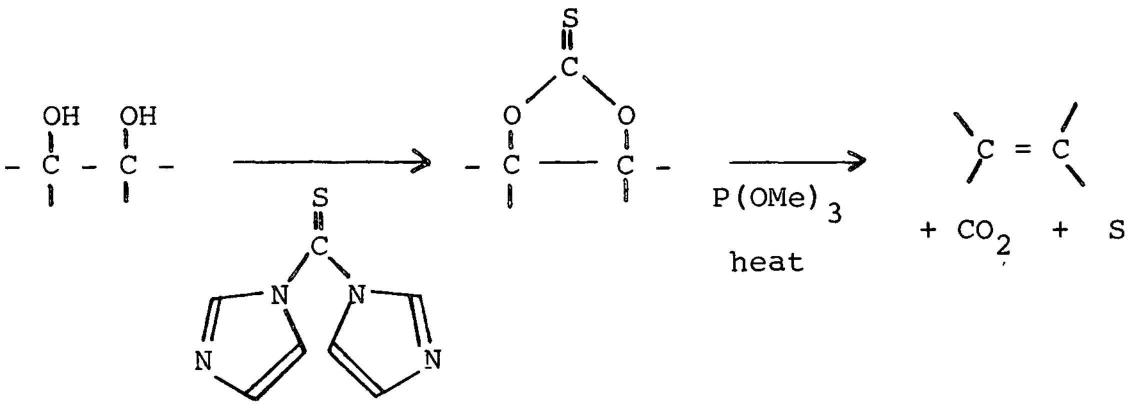
$$PhC(=O)-Ar-CH(OH)Ph \xrightarrow{h\nu} -\!\!(Ar-C(OH)(Ph)-C(OH)(Ph))\!\!-$$

Assuming that high polymers of this type could be formed the subsequent work planned was to dehydroxylate the polymer to yield a polyconjugated system.



$$-\!\!(Ar-C(OH)(Ph)-C(OH)(Ph))\!\!- \xrightarrow[\text{Steps}]{\text{Dehydroxylation}} -\!\!(Ar-C(Ph)=C(Ph))\!\!-$$

A number of possible, short routes are given in the literature for this step. As will become apparent, our studies were not able to reach this stage, so a detailed review of all possible methods is not presented here but an example is shown.[78]

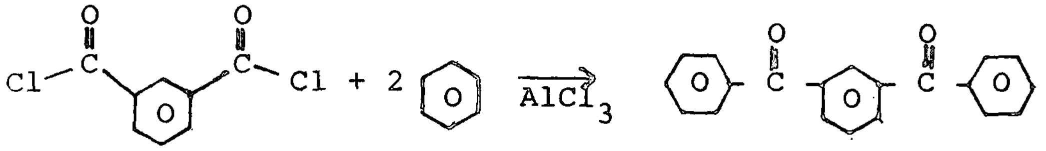


The first step goes virtually quantitatively on treatment of the diol with thiocarbonyldiimidazole then CO_2 and S are eliminated by use of trimethyl phosphite. Using hydrobenzoin a 92% yield of stilbene was obtained.

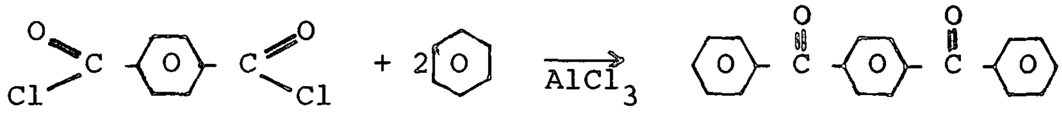
2.1.3 Synthesis of Monomers

(i) Diketones

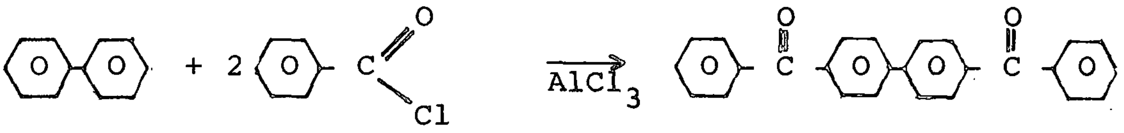
These were prepared by Friedel-Crafts acylation reactions.



m-dibenzoylbenzene



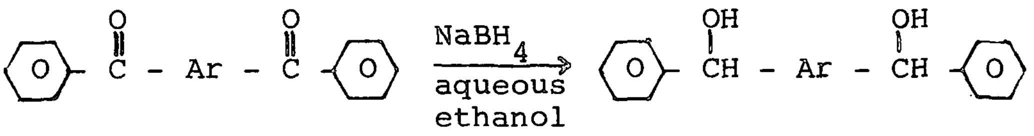
p-dibenzoylbenzene



p,p′-dibenzoyl diphenyl

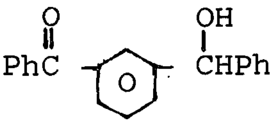
(ii) Bishydrols

These were prepared by sodium borohydride reduction of the diketones.



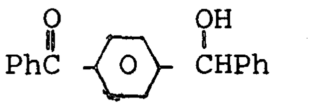
(iii) Ketohydrols

These compounds proved very difficult to prepare in a pure enough state for photochemistry to be carried out with them.



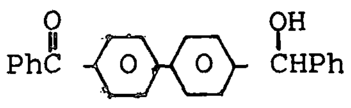
m-benzoyl benzhydrol

"m - AB"



p-benzoyl benzhydrol

"p - AB "



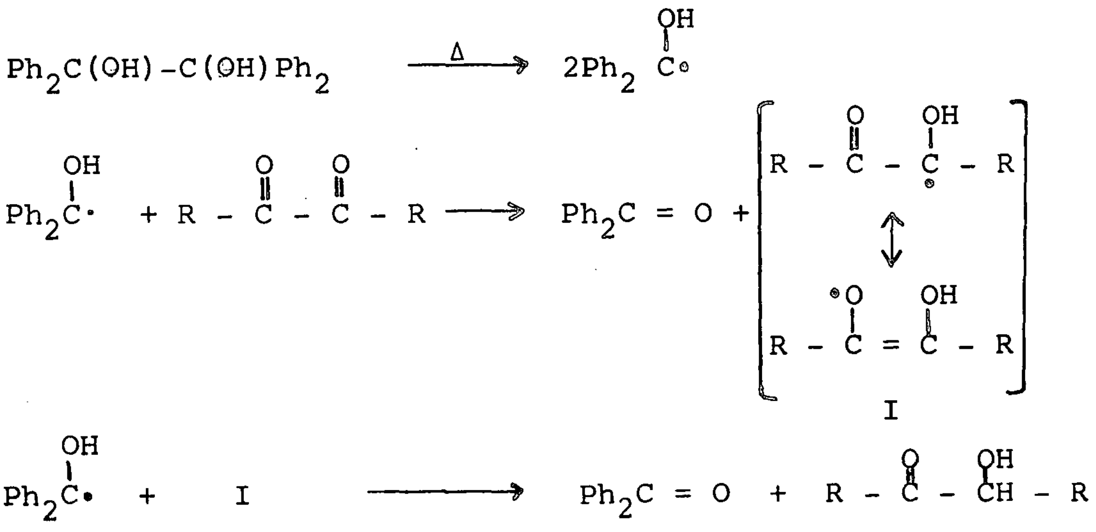
p-benzoyl p′benzhydryl diphenyl

" diphenyl - AB"

All three were oils of low tractability, they could not be recrystallised and attempts to vacuum distil them were unsuccessful, resulting in black residues. It was found that repeated "dry column" chromatographs were the most effective way of removing impurities.

Two methods were used to prepare these compounds in crude form. One involved partial reduction of diketones with sodium borohydride and utilized the procedure of Bertoniere,[79] only very small yields of pure product were eventually obtained after purification. The more effective method was an extension of a reaction discovered by Rubin and Ben-Bassatt,[80] whereby α-diketones can be reduced to α-hydroxy ketones. Since p-dibenzoylbenzene and p,p´-dibenzoyl diphenyl are conjugated between the carbonyl groups it was recognised that these α-diketone vinylogues could also undergo the reaction.

The procedure involves formation of radicals by heating the diketone with excess benzopinacol, which cleaves homolytically and initiates the reaction by acting as a hydrogen donor. The mechanism postulated for α-diketones by Rubin and Ben-Bassatt is as shown.



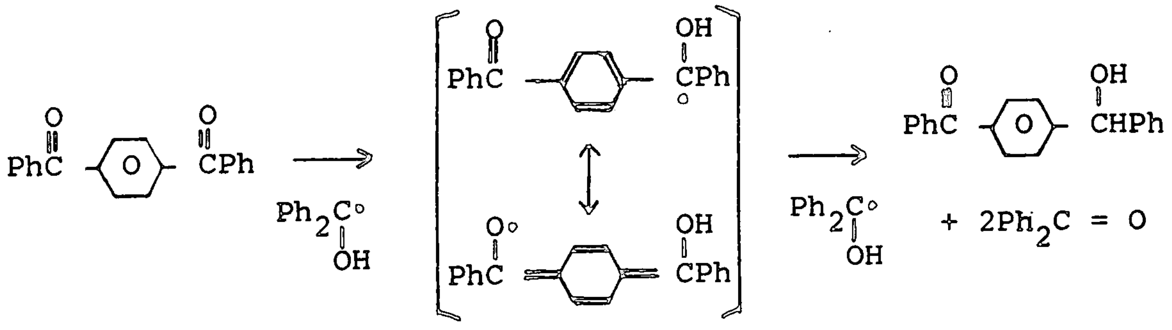
$$Ph_2C(OH)-C(OH)Ph_2 \xrightarrow{\Delta} 2Ph_2\overset{OH}{\overset{|}{C}}\cdot$$

$$Ph_2\overset{OH}{\overset{|}{C}}\cdot + R-\overset{O}{\overset{\|}{C}}-\overset{O}{\overset{\|}{C}}-R \longrightarrow Ph_2C=O+\left[\begin{array}{c} R-\overset{O}{\overset{\|}{C}}-\overset{OH}{\overset{|}{\underset{\cdot}{C}}}-R \\ \updownarrow \\ R-\overset{\cdot O}{\overset{|}{C}}=\overset{OH}{\overset{|}{C}}-R \end{array}\right]$$

I

$$Ph_2\overset{OH}{\overset{|}{C}}\cdot + I \longrightarrow Ph_2C=O + R-\overset{O}{\overset{\|}{C}}-\overset{OH}{\overset{|}{C}H}-R$$

Extending this to p-dibenzoylbenzene a similar scheme can be proposed:



This reaction was successfully used to prepare p-benzoyl benzhydrol and p-benzoyl p′-benzhydryl diphenyl.

2.2 Experimental

(i) Diketone Preparations

(a) m-Dibenzoylbenzene

The procedure of Spanomanolis[77] was followed, isophthaloyl chloride (Aldrich) was purified by two reduced pressure distillations, the distillate (50g) was dissolved in sodium-dried benzene (500 ml) with vigorous stirring. Finely-ground aluminium chloride (50g) was added in small portions to the stirred solution over a period of 5 hours. The reaction mixture was then refluxed for 6 hours during which time the colour of the mixture changed from yellow to brown. This was then hydrolysed by pouring into 3l of 10% HCl/ice-water. The orange organic layer was extracted with benzene (2x250ml), each extract was washed with 1 l. water to remove all aluminium salts. The combined extracts were boiled for 1 hour with decolourizing charcoal yielding a pale-yellow solution; after evaporation of solvent an orange oil remained which deposited white crystals on standing. Repeated recrystallizations from cyclohexane yielded pure meta-dibenzoylbenzene (15g, 21%) as colourless needles and correct m.pt. 102°C (lit.103-4° [74]) with correct infrared spectrum (Appendix 1, No.1). The n.m.r. spectrum showed resonances at δ7.6, 8.0 and 8.3 (aryl hydrogens). Found: C 84.2%, H 5.0 %, calculated, C 83.9%, H 4.9 %.

(b) p-Dibenzoylbenzene

1. Terephthaloyl Chloride

Pure thionyl chloride was freshly obtained by distillation from a 7:1 (v,v) mixture of the supplied reagent (B.D.H.) with quinoline. A three necked 500ml flask fitted with a dropping funnel carrying a $CaCl_2$ guard tube, mechanical stirrer and condenser ($CaCl_2$ tube) was used. Thionyl chloride (120ml) was added to finely-ground terephthalic acid (86.5g) over 20 minutes with stirring, copious fumes of HCl and SO_2 were evolved. After refluxing for 24 hours the excess thionyl chloride was distilled from a water bath and then the last traces were removed by rotary evaporation. The product was recrystallized twice from Ligroin (petroleum ether 100-120°) giving terephthaloyl chloride (46.6g, 44%).

2. p-Dibenzoylbenzene

The method of Higgins *et al*[70] was used. Finely-ground aluminium chloride (56g) was added to a solution of terephthaloyl chloride (35g) in benzene (280ml) over a 1 hour period. This mixture was stirred for half an hour then refluxed for three hours. After cooling, the solution was mixed slowly with 1½ l. 10% HCl/ice-water, the benzene was evaporated leaving a suspension of a white-yellow solid which was collected by filtration. After successive washings with 5% potassium carbonate, 5% hydrochloric acid and water, the product was dried at 130°C then recrystallized from carbon tetrachloride, decolourized with decolourizing charcoal in benzene, then recrystallized once more from carbon tetrachloride to give p-Dibenzoylbenzene (12.8g, 26%) as colourless needles m.pt. 161° (lit 159-160° [74]) and correct infrared spectrum (Appendix 1, No.2). The n.m.r. spectrum showed two peaks at $\delta 7.4$ and $\delta 7.8$ (aryl hydrogens). Found: C 84.3%, H 5.1 %, calculated, C 83.9%, H 4.9 %.

(c) p,p´-Dibenzoyl diphenyl

The method of Andrews[74] was used. Powdered aluminium chloride (344g) was added to benzoyl chloride (208ml, Aldrich) in a three necked flask fitted with a mechanical stirrer and a condenser. Diphenyl (80g, B.D.H.) was added in portions to the stirred solution over 1 hour. The reaction mixture darkened, it was heated to 80-90°C on an oil bath and left stirring for 5 hours at this temperature, HCl gas was evolved. The black-brown mixture was then slowly mixed with 21 5% HCl/ice-water and left standing overnight. The yellow solid obtained was collected by filtration, washed with 5% potassium hydroxide and then water. After drying at 130°C the product was recrystallized from toluene three times to give p,p´-Dibenzoyl diphenyl (38g, 20%) as white platelets, m.pt. 213.5-215.0° (lit. 214.5-215.5[74]). The infrared spectrum is given (Appendix 1, No.3) and the n.m.r. spectrum showed two peaks at $\delta 7.75$ (doublet) and $\delta 7.5$ (aryl hydrogens). Analysis C 85.8%, H 5.7 %, calculated C 86.2%, H 5.0 %.

(ii) Bishydrol Preparations

Since only m-bisbenzhydrol was used in subsequent studies only its preparation is described.

m-Bisbenzhydrol

m-Dibenzoylbenzene (60g) was dissolved with heating and stirring in aqueous ethanol (250ml water:550ml ethanol) in a three necked 1 l. flask. Sodium borohydride (16g) was added slowly as a solid over 1 hour with nitrogen purging to remove the hydrogen gas evolved. After stirring at room temperature for 30 minutes the mixture was refluxed for 1½ hours. After cooling, 300ml of 10% hydrochloric acid was added slowly to destroy excess borohydride. On standing, the product appeared from the solution as white crystals. This was recovered by filtration and recrystallised twice from isopropanol-water to give, after drying over P_2O_5, m-Bisbenzhydrol (23g, 39%) as white powdery crystals m.pt. 148-150°. The infrared spectrum is given (Appendix 1, No.4). An n.m.r. spectrum revealed peaks at $\delta 7.15$ (aryl hydrogens), $\delta 5.65$ (methine protons), $\delta 1.8$ (hydroxyl hydrogens), the integrated peak intensities were equal to the expected 7:1:1 within the accuracy of the electronic integrator. Analysis C 82.8%, H 6.2 %, calculated C 83.3%, H 5.6 %.

(iii) Ketohydrol Preparations

(a) m-Benzoylbenzhydrol (m-AB).

The first attempt to prepare m-AB utilized partial reduction of the diketone with borohydride. Since one molecule of sodium borohydride will reduce four carbonyl groups, the reaction was first tried using a molar ratio of 1 $NaBH_4$:4 diketones.

m-Dibenzoyl benzene (7.15g) was dissolved in aqueous ethanol (245ml ethanol:100ml water) and sodium borohydride (0.237g) was slowly added, with stirring and nitrogen purging, over half an hour. The solution was then refluxed with stirring for two hours. After quenching with aqueous acid about half of the ethanol was removed by rotary evaporation and the flask left in a refrigerator overnight. Yellow-white crystals appeared, these were collected by filtration and after drying an infrared spectrum showed that this was unreacted diketone. After rotary evaporating the filtrate to dryness a yellow syrup remained. Repeated attempts to recrystallize the product with ethanol and cyclohexane only resulted in a yellow oil settling out of the solution. Using benzene-hexane white crystals were obtained which upon subsequent analysis proved to be m-bisbenzhydrol. Evaporation of the filtrate left a yellow oil. Recrystallization attempts from cyclohexane-ethanol, isopropanol, isopropanol-water, acetonitrile and methylene chloride were made but proved to be unsuccessful, the result either being an "oiling-out" or no precipitate being formed.

The oil was recovered and thin layer chromatography carried out using the diketone and bisbenzhydrol as reference compounds, the eluent was 10% methylene chloride - 90% chloroform. This gave the Rf values tabulated below.

Sample	Average Rf value(s)
m-dibenzoyl benzene	0.64
m-bisbenzhydrol	0.09
Yellow oil product	0.20, 0.62

The low intensity spot at 0.20 was assigned to m-AB and indicated that the required product was present in very low yield.

A different method which would give a much improved yield was required. The procedure of Bertoniere[79] was attempted.

To m-dibenzoyl benzene (10g) dissolved in tetrahydrofuran (300ml) was added well-ground sodium borohydride (1g). This was left stirring at room temperature overnight (a previous attempt using a 2 hrs. reaction time resulted in a recovery of an unacceptably high amount of starting material). 10% sulphuric acid (200ml) was added, the product which precipitated was recovered by filtration and recrystallized from ethanol-water to give unreacted diketone. The filtrate was taken, evaporated and run twice down short columns (9cm) of silica gel using 10% methylene chloride:90% chloroform as eluent.

A very small amount of pure m-AB was obtained as a pale yellow oil. Recrystallizations from methanol were unsuccessful. There was just enough sample for an n.m.r. spectrum which revealed peaks at δ7.1-7.8 (4 peaks, most intense at δ7.2 - aryl protons), δ5.85 (hydroxyl H) and δ2.4 (methine H) with integration ratio of 15:1:1 (calculated value 14:1:1).

(b) p-Benzoylbenzhydrol (p-AB)

This was prepared by an extension of the method of Rubin and Ben-Bassat.[80]

p-Dibenzoylbenzene (1.31g) and benzopinacol (3.35g) were mixed with decalin (25ml) and the mixture heated on an oil bath at 165°C for thirty minutes. After cooling, the orange-yellow solution was poured into 150ml hexane fraction in order to remove decalin, a yellow oil settled out. The solvent was decanted off and the oil dissolved in methylene chloride and reprecipitated by adding dropwise to hexane (100ml). This procedure was repeated and the product was then dried under vacuum.

A thick, yellow oil with n.m.r. peaks at δ7.6-6.8 (aryl H's), δ5.7 (hydroxyl proton) and δ3.85-3.55 (methine hydrogen) and integration ratio of 14.7:1:1 (calculated for p-AB 14:1:1) and infrared spectrum (Appendix 1, No.5) was obtained.

(c) p-Benzoyl, p'-Benzhydryl diphenyl (diphenyl-AB)

The benzopinacol-induced reduction method is also applicable to the preparation of this monomer and it was successfully used.

Dibenzoyl diphenyl (4.25g) and benzopinacol (8.5g) were added to decalin (50ml), the mixture was refluxed for three hours. Part of the decalin (*ca.*40ml) was then removed by distillation and the residual solution separated on a silica column (41 x 2.5cm) using carbon tetrachloride as the initial eluent.

Movement of the fractions down the column was very slow but separation was good. After 7 litres had been eluted chloroform was gradually added to bring the eluent to an 8% level of chloroform. This was found to be the optimum mixture; when more chloroform was added the slowest moving band (diol) began to gain on the AB band. Prior to the diphenyl-AB band coming out of the column the eluent was changed back to carbon tetrachloride and the product slowly eluted.

After drying, p-Benzoyl, p′-benzhydryl diphenyl (2.06g, 41%), straw-yellow solid, m.pt 33^{o}, was obtained with an infra-red spectrum which is given (Appendix 1, No.6) with mass spectrum parent ion $^{m}/e$ 364. This was soluble in acetone, acetonitrile and diethyl ether, slightly soluble in toluene cyclohexane and insoluble in hexane fraction. The n.m.r. spectrum showed peaks at δ7.2-8.1 (aryl protons), δ5.85 (hydroxyl hydrogen) and δ2.55 (methine protons) with integration ratio 20:1:1 (calculated 18:1:1). Thin layer chromatography showed the presence of only one component using chloroform (Rf 0.66±0.04) and benzene.

The above spectral and analytical evidence proves that the product was pure diphenyl AB.

(iv) Photochemical Irradiations

For these experiments samples were irradiated as in previous studies in these laboratories.[74,75,76]

Irradiation of monomer solutions was effected using a Rayonet 204 photochemical reactor fitted with 350nm lamps. Pyrex vessels were used and the solvent was benzene or acetonitrile. Benzene was purified by refluxing over sodium metal for a minimum of three hours, then distilling through a Vigreux column onto activated molecular sieve under dry nitrogen. Acetonitrile was distilled from phosphorus pentoxide through a Vigreux column then the distillate redistilled onto activated molecular sieve under dry nitrogen. The solvents were stored under dry nitrogen.

Prior to all irradiations the solutions were either streamed with dry nitrogen for 30 minutes or degassed by at least three freeze-thaw evacuation cycles to remove traces of dissolved oxygen.

(a) Irradiations of Diketones with Bisbenzhydrols (AA - BB Systems)

The meta substituted monomers were first investigated (m-dibenzoylbenzene and m-bisbenzhydrol).

(i) Acetonitrile as the Solvent

All solutions were irradiated as described above, the results are given in Table 2.3.

TABLE 2.3 Photochemical Irradiations of m-dibenzoylbenzene and m-bisbenzhydrol in Acetonitrile

Tube No.	Irradiation Time/hrs.	Concentration of diketone /M	Concentration of dihydrol /M	Appearance of solution after reaction	Product after solvent removal
1	2.5	0.10	0.10	a	x
2	4.5	0.10	0.10	a	x
3	18.5	0.10	0.10	a	x
4	97.5	0.50	0.50	b	y
5	97.5	0.10	0.10	a	y
6	97.5	0.01	0.01	a	y

a. Yellow solution, no precipitate or undissolved substances.

b. Yellow solution with suspended undissolved dihydrol.

x. Yellow powder.

y. Orange solid.

Infra-Red Analysis of Products

This method is a very convenient monitor of reaction since the peak due to the strong carbonyl stretching frequency in the infrared spectrum should disappear as reaction proceeds. High polymer should show a hydroxyl peak and no carbonyl peak. The infrared spectra of the products of all irradiations are all very similar and show the same characteristic differences as compared to a spectrum of unirradiated monomer mixture. Appendix 1, spectra 7 and 8 show these two traces. The following differences are evident:

1. reduction in size of the alkyl CH str peak at 2880 cm^{-1},
2. broad OH str centred at 3500 cm^{-1} as compared to 3250 cm^{-1} for unirradiated material,

3. slight reduction in C=O str peak at 1645-50 cm^{-1} which is more pronounced for the products of tubes 4 and 5.

Thin layer chromatograms of the products were run on silica using 10% methylene chloride -90% chloroform. The results were as shown in the table below.

Tube number or compound	Average Rf values	Comments
m-dibenzoylbenzene	0.51	
m-bisbenzhydrol	0.08	
1	0 ⟶ 0.21, 0.50	lower spot long and intense
2	0 ⟶ 0.19, 0.34, 0.48,	lower spot long and intense and high peak faint
3	0 ⟶ 0.20, 0.40, 0.51,	

Re-irradiation of 0.25g of the product of tube 5 was carried out in 10ml acetonitrile for 137 hours. The infrared spectrum obtained of the recovered product showed little change (Appendix 1, No.9).

(ii) Irradiation in Benzene

The results of these irradiations are given in Table 2.4

TABLE 2.4 Photochemical Irradiations of m-Dibenzoylbenzene and m-Bisbenzhydrol in Benzene

Tube No.	Irradiation time/hrs.	Concentration of diketone /M	Concentration of dihydrol /M	Appearance of solution after reaction	Product after solvent removal
7	114	0.50	0.50	c	z
8	114	0.10	0.10	d	z
9	114	0.01	0.01	e	z

c. bright orange solution over a lot of white solid (undissolved hydrol),
d. bright orange solution with some undissolved hydrol,
e. yellow solution with a little white solid,
z. yellow-orange solid.

Infrared spectra were obtained of recovered solids which showed the same characteristics (Appendix 1, spectrum 9) as those discussed above for acetonitrile irradiations. The thin layer chromatography results were also similar giving a spread spot from Rf 0 to about 0.20 then individual faint spots at around 0.40, 0.50 and 0.80.

Attempts to extract the higher end of the molecular weight range by adding solvents to the solid products only resulted in an extract with the same infrared spectrum.

Since the intended reaction had failed to proceed using the meta dibenzoylbenzene-bisbenzhydrol system, it was thought unlikely that the para or diphenyl analogues would behave any differently, and thus polymerizations of these monomers were not attempted.

(b) Irradiations of AB Monomers

pBenzoylbenzhydrol

A 0.05M solution of pbenzoylbenzhydrol in acetonitrile was irradiated for 93½ hours (350nm). A yellow solution was obtained with a small amount of white powdery sediment.

After solvent removal and vacuum line drying the infrared spectrum of the product (Appendix 1, No.10) showed similar features to those shown by the products of AA-BB irradiations, that is, movement of the hydroxyl peak to higher wavenumber

(3550 cm^{-1}) and partial reduction of the carbonyl peak at 1650 cm^{-1} as well as some loss of CH alkyl at 2875 cm^{-1}.

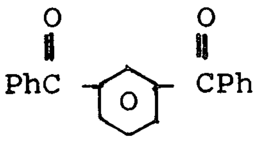
pBenzoyl p′Benzhydryl Diphenyl

A 0.10M solution of the title compound in acetonitrile was irradiated for 45 hours. The colourless solution was perceived to have developed a very pale yellow colour and a small amount of a fine, powdery precipitate had appeared.

After solvent removal and vacuum line drying an infrared spectrum of the whole of the recovered sample was as shown in Appendix 1, No.12. Once again there is a shift of the hydroxyl OH str peak, from 3420 to 3460 cm^{-1} as compared to the monomer spectrum, as well as a negligible reduction in the carbonyl stretching peak size.

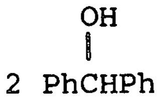
(c) Irradiations of Difunctional Monomers with Model Compounds

To try to find possible reasons for the failures of all the above polymerizations m-dibenzoyl benzene and m-bisbenzhydrol were irradiated with the monofunctional compounds benzhydrol and benzophenone respectively.



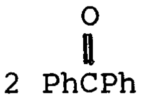
I

+



$2\ \mathrm{Ph}\overset{\mathrm{OH}}{\overset{|}{\mathrm{C}}}\mathrm{HPh}$

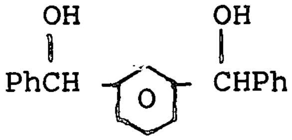
II



$2\ \mathrm{Ph}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\mathrm{Ph}$

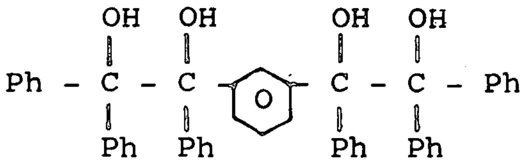
III

+



IV

The product expected for successful pinacolization is the structure shown below:



The irradiation results using benzene and acetonitrile were as shown in Table 2.5.

TABLE 2.5 Irradiations of Difunctional Monomers with Monofunctional Compounds

Tube No.	Solvent	Irradiation Time/hrs	Mixture Concentrations	Appearance after irradiation	Infrared Carbonyl stretch peak
10	Acetonitrile	69	0.05M I 0.1M II	f	Negligible carbonyl reduction
11	Acetonitrile	69	0.05M IV 0.1M III	f	some carbonyl consumption
12	Benzene	92	0.05M I 0.1M II	g	Near complete C=O consumption
13	Benzene	92	0.05M IV 0.1M III	h	Negligible C=O consumption

f. Yellow solution,

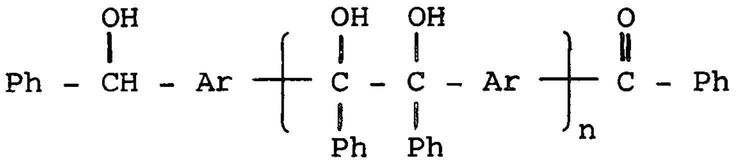
g. Pale yellow liquid with much white precipitate,

h. Dark yellow solution, a little yellow-white precipitate.

2.3 Discussion

The irradiations of AA-BB and AB monomer solutions did not give polypinacols of high molecular weight. The evidence of infrared spectroscopy and thin-layer chromatography shows that the products contain some oligomers but that most of the starting material remains unreacted even after prolonged irradiation.

The t.l.c. investigations often showed a new spot at a higher Rf value than that of either of the monomers, this is probably due to residual solvent (acetonitrile) which was difficult to eliminate completely. In all cases the diketone and dihydrol spots were observed in the t.l.cs. of the products with the diketone at a higher Rf value, but the dihydrol spot was often merged with a smeared-out spot running from Rf 0 to about 0.2. This spot is interpreted as being due to oligomers; the higher the Rf the lower the degree of polymerization and the nearer the structure is to that of the diketone. So oligomers of the form shown below are probably present in the products.



$$\mathrm{Ph - \overset{OH}{\overset{|}{CH}} - Ar} \left(\mathrm{\underset{Ph}{\underset{|}{\overset{OH}{\overset{|}{C}}}} - \underset{Ph}{\underset{|}{\overset{OH}{\overset{|}{C}}}} - Ar} \right)_n \mathrm{\overset{O}{\overset{\|}{C}} - Ph}$$

The number n is almost certainly a single figure.

The infrared spectra of the recovered products were compared with the spectra of the starting materials and were in agreement with the rationalization of the t.l.c. results. Thus, a small reduction of intensity of the carbonyl stretching peak and small alterations in the hydroxyl and CH stretching peaks were observed.

In looking for possible reasons for the failure of these monomers to photopinacolize to high polymers it is necessary to consider the mechanistic details of the reaction and to compare the systems investigated here with those that were successfully polymerized by De Schryver *et al*.

As discussed earlier, the essential steps in the photopinacolization reaction are: firstly, formation of an excited species which has alkoxy radical character, secondly, abstraction of a hydrogen by this species to give a ketyl radical and thirdly, radical-radical combination forming new bonds. With the model compound benzophenone the $n \rightarrow \pi^*$ triplet excited state is efficiently formed and the subsequent reactions occur in virtually quantitative yield.[81,82] However, with other systems $\pi \rightarrow \pi^*$ excited states may be predominant and such states are not active in hydrogen abstraction. There are several examples of aromatic carbonyl compounds which show this behaviour, for example 1-naphthaldehyde and 2-acetonaphthone.[83] In both these cases the $n \rightarrow \pi^*$ band is submerged in the $\pi \rightarrow \pi^*$ band and neither compound can be photoreduced to pinacol.

In the systems successfully polymerized by De Schryver *et al* the aromatic ketone units in the difunctional monomers were invariably separated by a saturated linking group. By contrast, in the systems studied here, since the objective of the work was to synthesise conjugated systems, the linking unit between the two carbonyls was a meta or a para phenylene. The question which has to be answered is therefore if the $n \rightarrow \pi^*$ triplet state of such compounds can be efficiently populated. In the ultra-violet spectrum of benzophenone there is a weak absorption at λ_{max} 333nm (ε=160) which is assigned to the formally forbidden

$n\rightarrow\pi^*$ transition which is resolved from the intense $\pi\rightarrow\pi^*$ band at λ_{max} 253nm (ε=18,000). These spectroscopic observations are consistent with detailed photophysical investigations which established that the lowest excited state of benzophenone is the $n\rightarrow\pi^*$ triplet. De Schryver's diketones exhibit similar characteristics, the $n\rightarrow\pi^*$ triplet is the lowest excited state and the $n\rightarrow\pi^*$ and $\pi\rightarrow\pi^*$ bands are resolved. For m-dibenzoylbenzene the $n\rightarrow\pi^*$ absorption occurs at 333nm (ε=250) and $\pi\rightarrow\pi^*$ at 252nm (ε=28,000) and for p-dibenzoylbenzene these transitions occur respectively at 335nm (ε=420) and 264nm (ε=29,000), these peaks are resolved whereas for p,p′-dibenzoyl diphenyl the $n\rightarrow\pi^*$ is submerged under the $\pi\rightarrow\pi^*$at 300nm (ε=36,000).[74] Consequently it is not unreasonable to assume that the lowest excited state has $\pi\rightarrow\pi^*$ character for the latter compound, whereas the other two monomers would be expected to undergo the reaction although the results indicate that this was at best an inefficient process under the conditions examined.

When the work had reached this stage an alternative route to the desired polymers began to show considerably more promise and the author's efforts were directed to this new approach which is discussed in detail in Chapter Three. However, some further experiments were carried out using the mixtures of potential reactants shown on p. 48. The results were difficult to understand and appear to be inconsistent. Both 2:1 mixtures would be expected to yield the same products but the irradiation of a mixture of benzhydrol and m-dibenzoylbenzene, in a 2:1 ratio, resulted in carbonyl consumption whereas for the reaction of a mixture of benzophenone and m-bisbenzhydrol, in a 2:1 ratio, only a very small amount of carbonyl loss was observed.

This might mean that the bisbenzhydrol is an inefficient hydrogen source, which, if true, is difficult to rationalize. That it is possible to photoreduce m-dibenzoylbenzene is demonstrated, (as has been proved before using isopropanol as the hydrogen source).

A further possibility is that the required excited state is quenched or undergoes an alternative reaction. In all these reactions yellow colours were developed during irradiation which are probably due to similar species to the yellow intermediate discussed earlier (page 28).

A complete understanding of the inefficiency of pinacolization of compounds such as m-dibenzoylbenzene would require a better understanding of the basic photophysics of these molecules with a view to investigating alternative methods of efficiently populating the $n \rightarrow \pi^*$ triplet state. One way may be to irradiate at the long wavelength edge of the ultra violet absorption spectrum. A detailed investigation may allow polymerization to a higher d.p. for these systems to become more available. This is likely to be especially true for m-dibenzoylbenzene and the AB monomers since these monomers are not as subject to the $\pi \rightarrow \pi^*$ excitation pathway as the completely conjugated diketones p-dibenzoylbenzene and p,p′-dibenzoyl diphenyl.

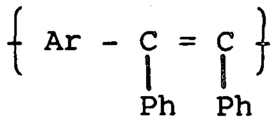
CHAPTER THREE

CARBONYL REDUCTIVE COUPLING AS A GROUND STATE ROUTE TO POLY(ARYLENE VINYLENE)S

3.1 Introduction

3.1.1 Objectives of these Studies

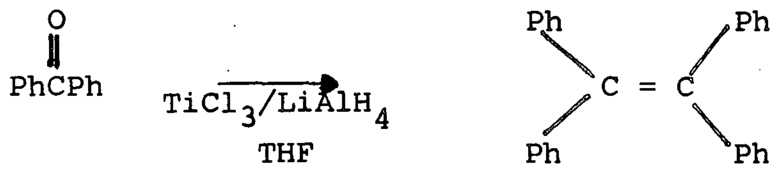
The aims of the work reported in the previous chapter had failed to be realised, that is photopolymerization to give poly(pinacol)s which could be modified to poly(arylene vinylene)s (I).



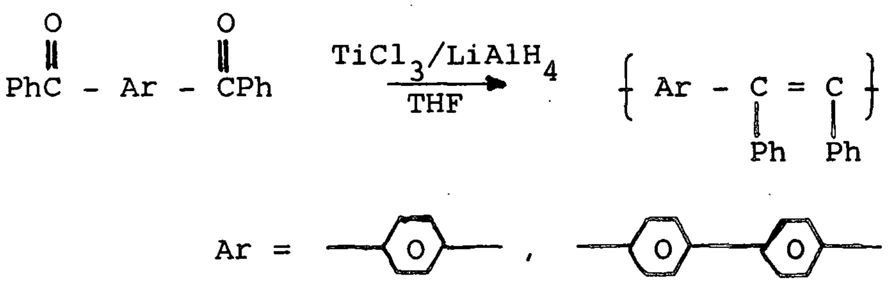
$$\left\{ Ar - \underset{Ph}{\underset{|}{C}} = \underset{Ph}{\underset{|}{C}} \right\}$$

(I)

Another route is available for synthesis of polymers with the structure (I) which is based on the model reaction shown below.



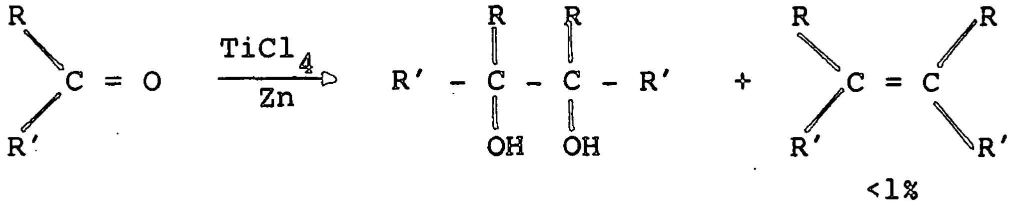
This reaction was first reported by McMurry and Fleming[84] and has become known as the McMurry reaction.[85] It is performed under nitrogen and high yields of alkenes can be obtained. Our proposed extension of this reaction to the formation of poly(arylene vinylene)s is shown below.



Polymers of this general type have been reported to be semi-conductors and/or photoconductors. Our objectives were to prepare polymers of this type and to examine their properties.

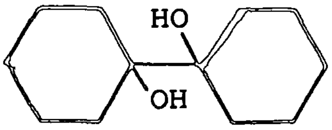
3.1.2 Reductive Coupling of Carbonyl Compounds Induced by Low Valent Titanium

In 1973 it was reported, by two research groups, that titanium salts, in combination with reducing agents, could couple carbonyl compounds to pinacols or alkenes.[86,87] Mukaiyama *et al*[86] described the preparation, in high yields, of pinacols from aldehydes and ketones using a reagent prepared from $TiCl_4$ and zinc at -10^oC.



R, R' = H, Me, Ph, $PhCH_2CH_2$

Tyrlik and Wolochowicz[87] found that treatment of benzophenone, acetophenone and benzaldehyde with $TiCl_3 . 3THF$ and magnesium resulted in good yields of the alkenes. Cyclonexanone was also subjected to this reagent and gave the diol shown below.



In 1974, McMurry and Fleming, in what has become one of the most cited papers on this reaction,[84] reported up to 95% yields of alkenes from reductive coupling of carbonyl compounds such as benzophenone, fluorenone, benzaldehyde and alicyclic ketones using a reagent derived from the reaction of $TiCl_3$ with lithium aluminium hydride in THF. They found that the reaction proceeds through the intermediacy of the pinacols.

(a) Reagents used for Reductive Coupling

The reagents which promote carbonyl coupling are usually composed of a metal salt and a reducing agent, these react together and form a low valent metal complex which is the active species for the coupling. The metal salt is most often a chloride of titanium although some tungsten compounds have also been shown to be active. Reductants used include lithium aluminium hydride,[84] lithium,[88] potassium,[85] magnesium,[85] a zinc-copper couple[89,90] and some other transition metals. The combination of titanium trichloride and lithium aluminium hydride has so far proved to be the most potent coupling system. The solvent most commonly used is tetrahydrofuran, although using other ethers and glymes the reaction is successful.[85] Benzene, cyclopentadiene, hexane, furan, thiophene, pyridine and anisol were tried as solvents for $TiCl_3$ based coupling systems and all were shown to be unsuitable.[85]

Activated titanium metal has also been tried[91,92] and found to be a very strong coupling agent for alicyclic ketones to alkenes, aryl ketones were over-reduced to hydrocarbons.[91] The Ti^0 complex bis(benzene) titanium $(PhH)_2Ti$ in THF gave good yields of olefins from benzophenone and acetone.[93]

Mixtures of titanium (IV) chloride with transition metals or metal amalgam reductants have been shown to be effective reductive coupling agents.[86,94,95]

Dams *et al*[96] have recently investigated the activities of other metal chlorides for carbonyl coupling. They used lithium aluminium hydride as the reductant in THF and compared the yields of tetraphenylethene from benzophenone with different metal chlorides. They found with $TiCl_3$ a 90% yield, 33% with WCl_6 and 18% for $MoCl_5$. With $ZrCl_4$, $NbCl_5$ and VCl_6 yields of about 10% were given whilst catalysts derived from the chlorides of Mg, Co, Ni, Fe, Cu, Cr, Zn, Mn, Sn, Al, Hf and Ta all failed to yield any tetraphenyl ethene.

In other studies, low valent tungsten and molybdenum complexes from reduction of WCl_6 or $MoCl_5$ with lithium aluminium hydride[97] or butyllithium[98] have been shown to be active. With these reagents olefin yields are not as high as those attainable for titanium based systems, this is particularly true for aliphatic ketone couplings.

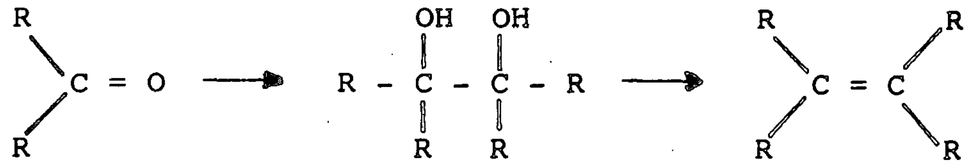
Corey *et al*[94] have developed mild coupling agents capable of giving good yields of pinacols and not continuing the reduction to alkenes. The most effective of these is $TiCl_4$ and Mg amalgam which can reduce aryl and aliphatic ketones to pinacols in good yields, cyclopentadienyl titanium trichloride ($CpTiCl_3$) with $LiAlH_4$ is also suitable for this conversion.

It has recently been found[99] that aqueous alkaline titanium (III) can also induce pinacolization in moderate to good yields although this reaction can be complicated by cleavage of the resultant pinacol under the basic conditions required.

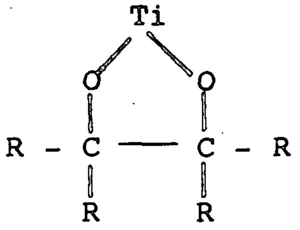
(b) Mechanism

(i) Titanium Based Coupling Agents

There is strong evidence that the reaction proceeds via a pinacol intermediate.

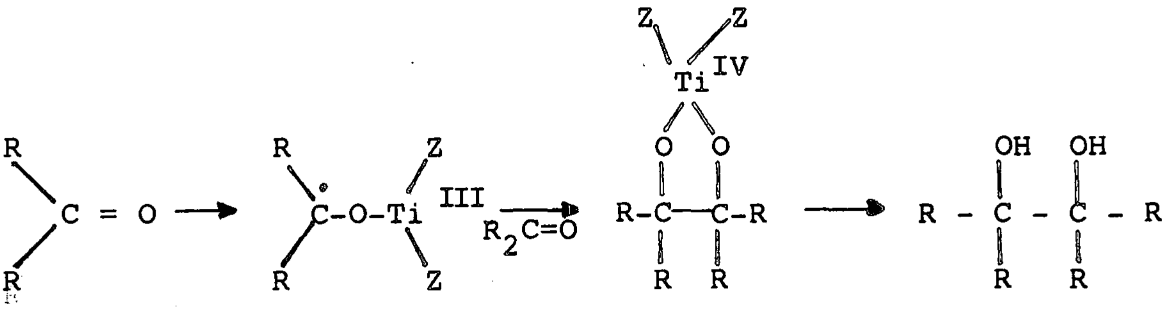


McMurry and Fleming's early studies of this reaction showed that after partial reaction pinacols could be isolated, and subjecting pinacols to the same reaction conditions yielded the corresponding olefins. These findings were confirmed by the results of Mukaiyama *et al*, Tyrlik and Wolochowicz, and Corey *et al*. McMurry's initial suggestion[84] was that an intermediate of the structure (II) was involved.



(II)

This would be formed after initial combination of ketyl radicals and would convert to the alkene by a step-wise or concerted mechanism, consequently involvement of a Ti^{II} species was implied. Corey[94] proposed that the formation of pinacols proceeded via the route shown in scheme 1 involving a Ti^{IV} intermediate (III).

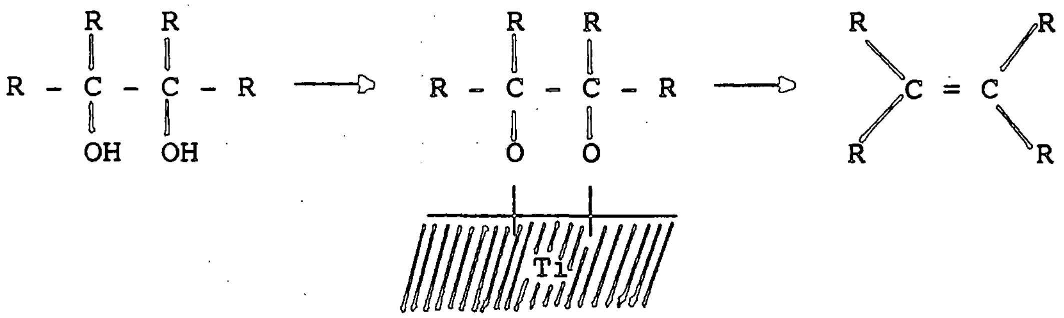


(III)

Scheme 3.1

Compounds with the structure (III) have been isolated in other studies, thus they are plausible intermediates.

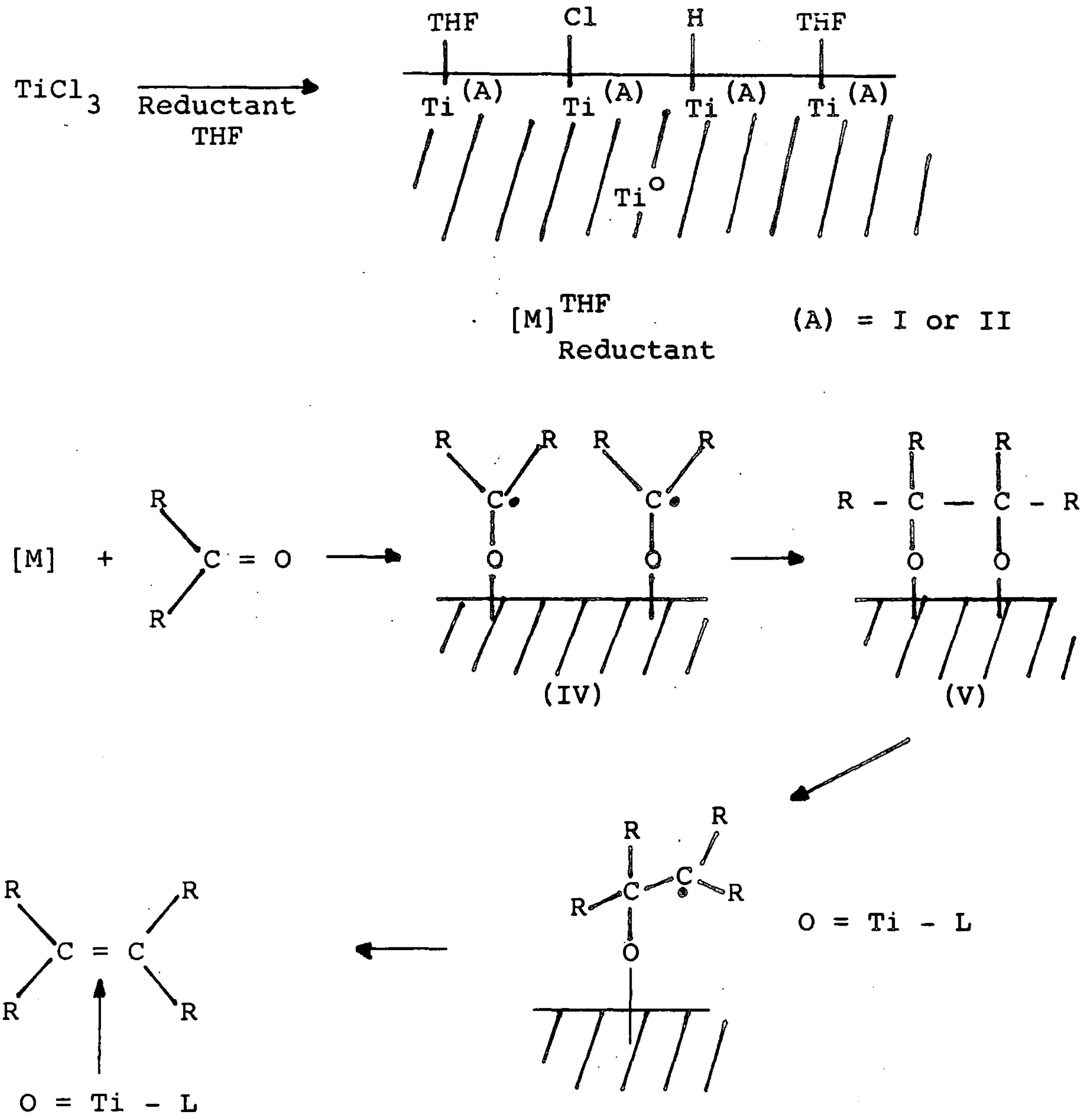
Evidence opposing mechanisms involving five-membered ring intermediates was given by McMurry *et al*[89] who found that cyclic 1,2 diols, when subjected to reductive coupling conditions, gave approximately equal yields of alkene from both their cis and trans forms at the same rate. These parameters would be expected to be different for the two isomers if a five-membered ring intermediate was involved. The proposed mechanism was as shown in Scheme 3.2.



Scheme 3.2

The pinacol forms two bonds to active titanium particles (rather than two bonds to one atom), these particles were identified in the reagent slurry by scanning electron microscopy. Cis and trans diols would both form complexes to the active surface, and presumably the rate determining step must be either the formation of the first oxygen to titanium surface bond or the cleavage of the complex.

Dams *et al*[85] have recently verified and elaborated McMurry's suggestion by detailed e.s.r. studies of the active reagent and optimization of the reaction conditions. The active species is denoted as [M] and found to be e.s.r. inactive, as would be expected for particles of zero valent titanium. The model they propose is that [M] exists as particles of titanium metal with higher valencies present at the surface and the mechanism suggested is shown in Scheme 3.3.

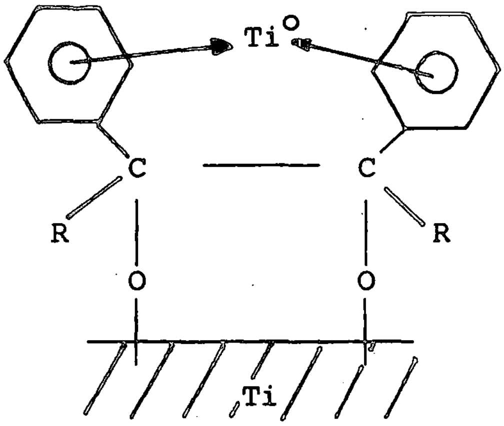


L = ligand e.g. Cl, THF

Scheme 3.3

The above mechanism explains why pinacols are isolated in incomplete reductive coupling, (V) would give a pinacol on hydrolysis in the work-up procedure. Severely hindered ketones do not couple but form secondary alcohols, in this case (IV) cannot dimerize for steric reasons so hydrogen atoms will probably be abstracted from the reductant.

For non-hindered aliphatic ketones a mixture of the E and Z isomers is formed with the E usually predominant (when there is a choice). Lenoir and Burghard[100] have shown that if the difference in enthalpies between the E and Z isomers is less than 5 Kcal mol^{-1} an E and Z mixture is formed but when it is more than this value the E isomer is formed exclusively. For aromatic ketones the Z isomer is often found to be the major isomeric product, this has been explained by Leimner and Weyerstahl[95] as due to complexation of Ti^o species with the aromatic rings in the titanium pinacolate intermediate similar to the bonding in the compound $(PhH)_2Ti$ itself.

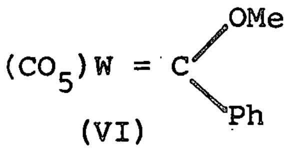


This constraint imposes Z-stereochemistry on the intermediate, which is retained on cleavage from the active surface.

(ii) Tungsten Based Reagents

Tungsten reagents are not as widely used for reductive coupling as are titanium systems because they tend to give lower yields of alkenes. Sharpless *et al*,[98] in 1972, found that WCl_6 and butyllithium in THF is an active system for carbonyl couplings. They called the reaction deoxygenation and proposed that the mechanism was the reverse of that of double-bond oxygenation reactions.

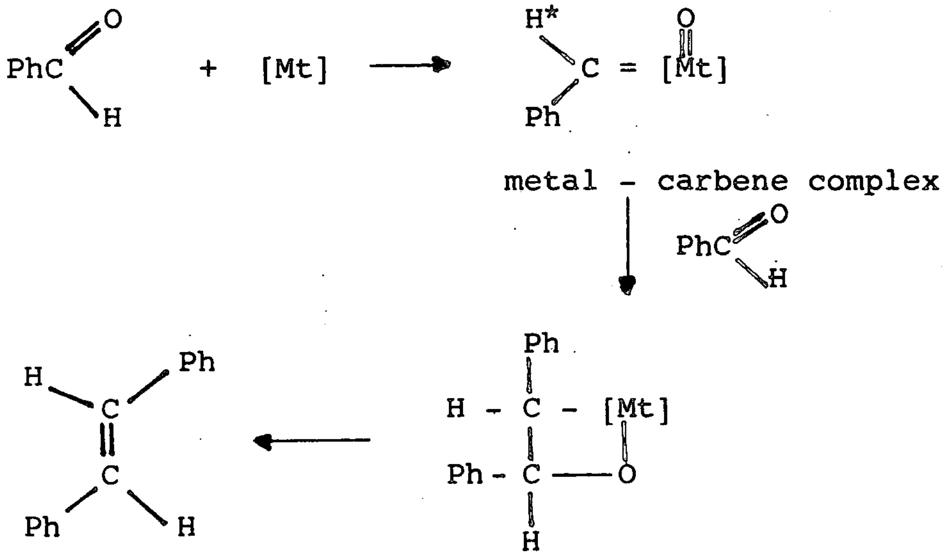
The reaction has since been shown to proceed via a tungsten carbene intermediate by Fujiwara *et al.*[97] This proof is based on four findings; (1) carbene traps (olefins) yielded cyclopropanes under the reaction conditions, (2) carbene precursors, e.g. diazo compounds, will couple with carbonyls under the reaction conditions to give olefins, (3) tungsten carbenes, for instance the one shown below (VI), will couple with carbonyls under the conditions to give alkenes and (4) proton n.m.r. has detected peaks due to the proton H* shown on the metal carbene in Scheme 3.4 (which shows the proposed mechanism of Fujiwara *et al* for benzaldehyde coupling).



(VI)

Mt halide + reductant ⟶ [Mt]

(where [Mt] = lower valent W or Mo with appropriate ligands)



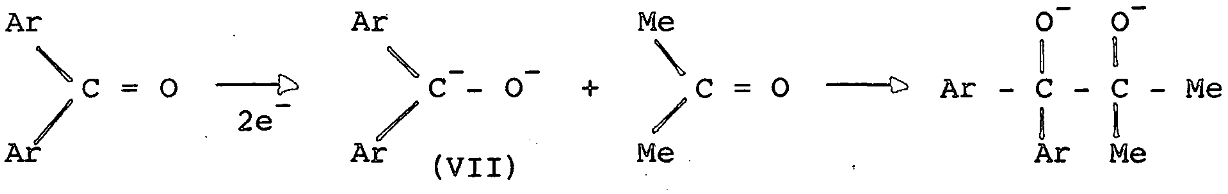
Scheme 3.4

Similar tungsten-carbene four-centre mechanisms have been proposed for other tungsten catalysed reactions, for example olefin metathesis.[101]

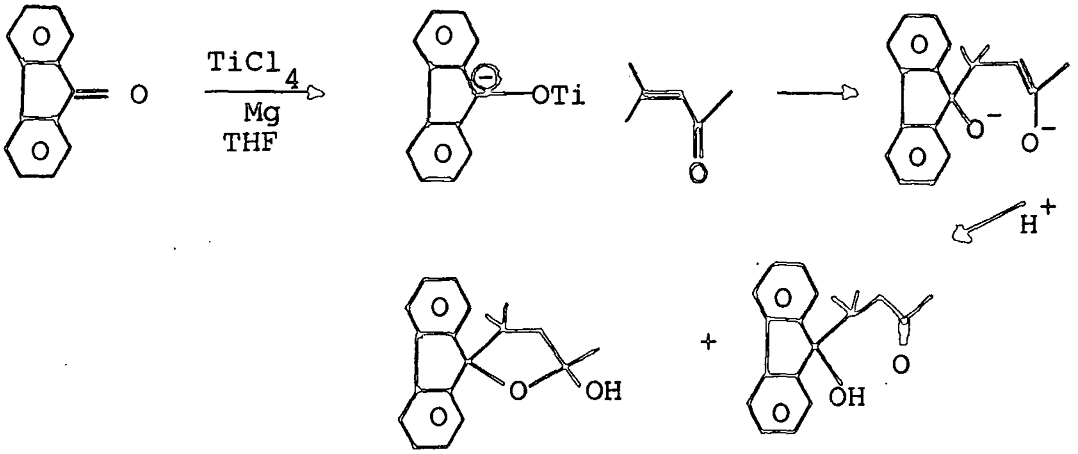
(c) Applications

McMurry coupling has become a standard organic procedure for preparation of diols and alkenes from carbonyl compounds. As McMurry *et al* have recognized,[89] the overall process is a reverse ozonolysis. Many substituted alkenes which are difficult or expensive to prepare in other ways are easily accessible by this reaction.

Mixed couplings are also synthetically useful since they often give the mixed product as the major component. McMurry *et al*[102] found that by using a 4:1 mixture of acetone and an aryl ketone the mixed product only was obtained and even with a 1:1 ratio good yields of mixed product were still given. Self-coupling of aryl ketyl radicals in mixed couplings was surprisingly low and the mechanism shown below was proposed to account for this observation.



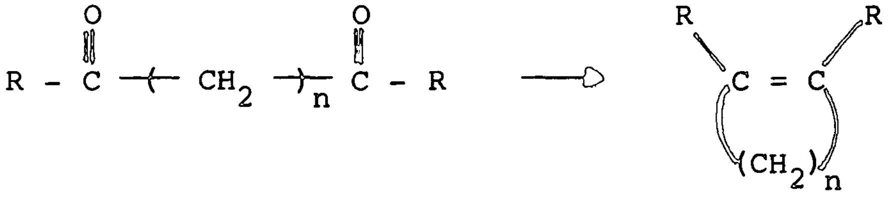
The greater stability of (VII) for aromatic ketones as opposed to aliphatic ketones was suggested as the reason why these undergo mixed couplings so well whilst aliphatic ketones yield statistical mixtures of self-coupled and mixed products. The participation of (VII) has been borne out by a recent study[103] of mixed coupling between fluorenone and mesityl oxide where the structures of the final products suggest that the fluorenone carbanion is first formed and subsequently attacks the double bond of mesityl oxide (Scheme 3.5).



Scheme 3.5

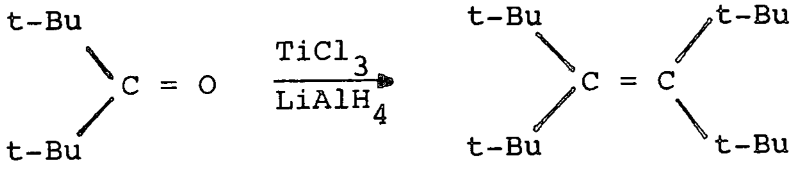
Mixed pinacols have been prepared in up to 75% yields using the reagent systems of Corey *et al.*[94]

Another very useful application of the reaction is for synthesis of cyclic alkenes from dicarbonyl compounds.

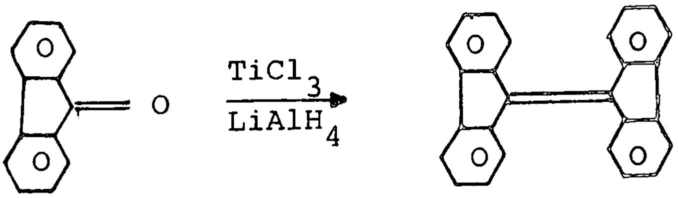


This can be achieved with $TiCl_3$ and $LiAlH_4$ with refluxing for a long period[104] or by using high dilution and a reagent based on $TiCl_3$ and zinc-copper couple.[105] Rings with n=1 to 16 can all be prepared in reasonable yields by these methods. Cyclic pinacols have also been prepared, using the reagent systems of Corey *et al*, in up to 90% yields.[94]

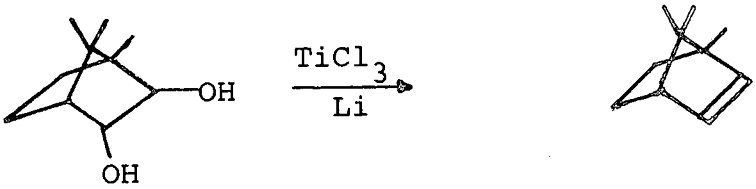
Some other interesting examples of the scope and utility of the reaction are given below.



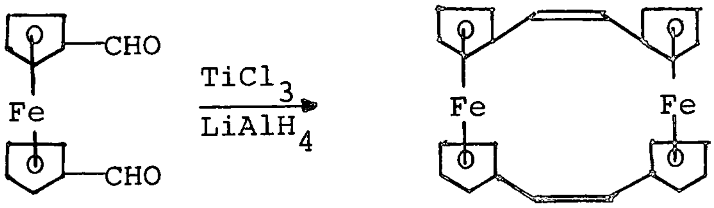
Ref.106



Ref.84

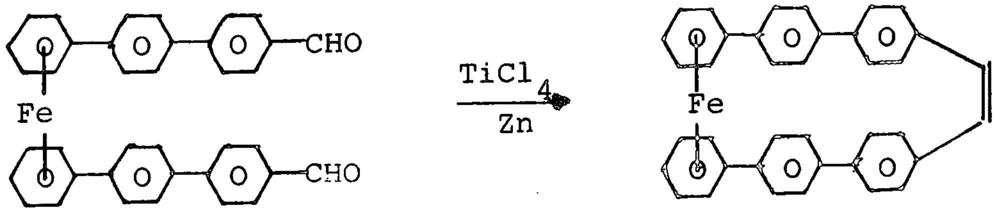


Ref.89



Ferrocenophane 1,13 diene

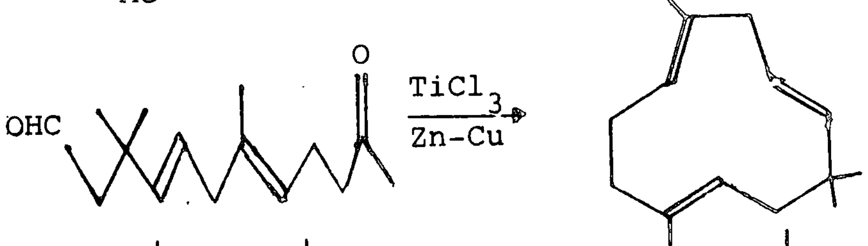
Ref.107



Ref.108

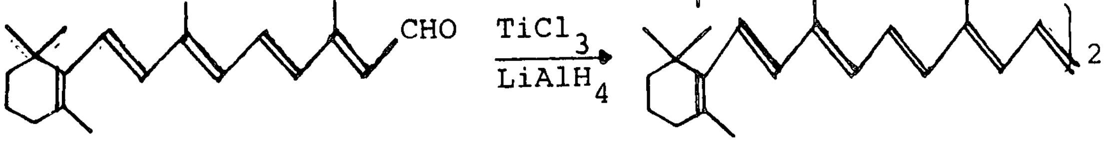
Biphenyl ferrocenophane

Ref.104



Ref.109

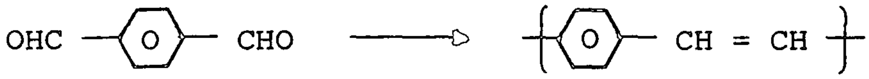
humulene



Ref.84

β-carotene

One further application of the McMurry reaction is to the polymerization of dicarbonyl compounds. It is evident that monomers for reductive coupling polymerizations must be non-cyclizable, that is, the two carbonyl functionalities must be fixed in positions where they cannot form cyclic olefins. To the author's knowledge only one report has appeared of a polymerization of this type. This paper,[23] by Indian workers, describes the polymerization of terephthalaldehyde using $TiCl_3$ and $LiAlH_4$ to give poly(p-phenylene vinylene).

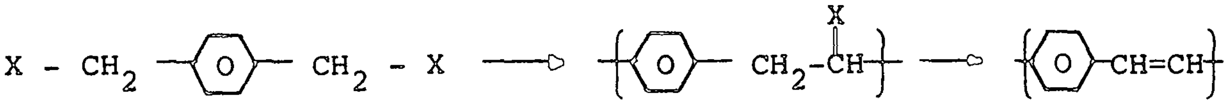


3.1.3 Poly(arylene vinylene)s

Poly (p-phenylene vinylene) itself has most often been prepared by use of the Wittig reaction or by alternative elimination reactions (Table 1.5, methods 1 and 4). The applications of these and other reactions to the synthesis of other poly(arylene vinylene)s are discussed below.

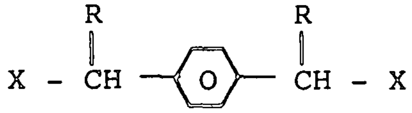
(a) Synthesis

Many of the early syntheses of poly (p-phenylene vinylene) were achieved by base treatment of α,α'-disubstituted xylene where the substituents were good leaving groups.

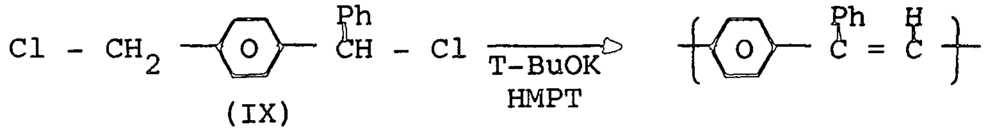


X = $-\overset{+}{S}R_2$[26,110], $-Cl$[25,111], $-\overset{+}{N}Me_3$[112]

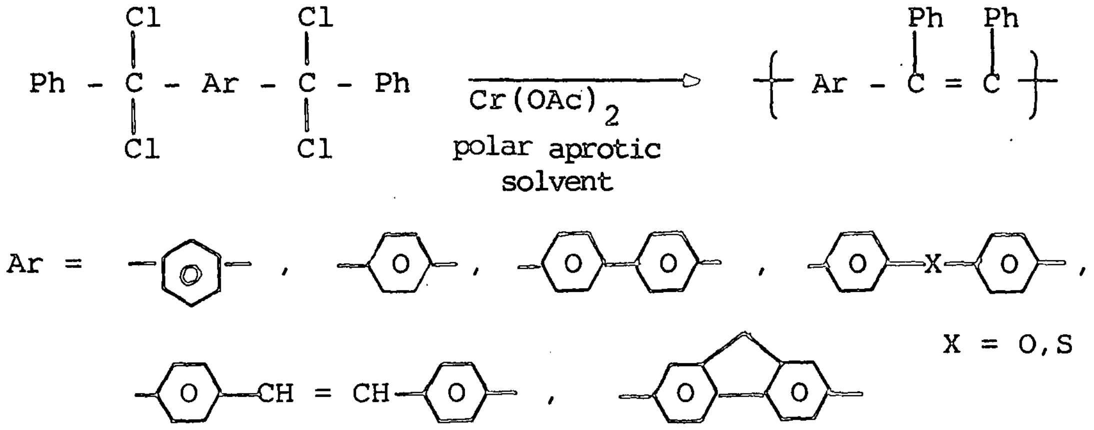
By extension, use of monomers of the type shown below should lead to substituted poly(arylene vinylene)s.



This approach has been shown to be successful by Hörhold *et al* who found, for example that dehydrochlorination of the compound (IX) gave a polymer with d.p.35.[113]

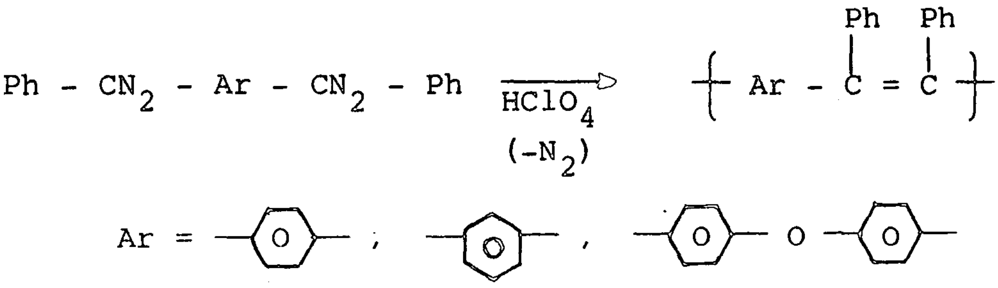


The soluble product had no residual chlorine, as shown by elemental analysis. These workers have extended the technique to dechlorination polymerization as shown below.[114]



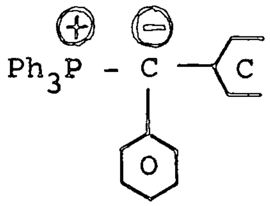
Transparent polymers were obtained with $\overline{M}n$ values between 6,000 and 20,000.

Some similar polymers have been prepared by elimination of nitrogen from bisdiazo monomers as shown below.[117]

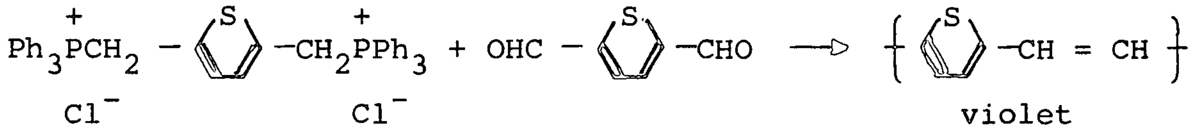


A d.p. of 19 was obtained for the p-phenylene linked polymer.

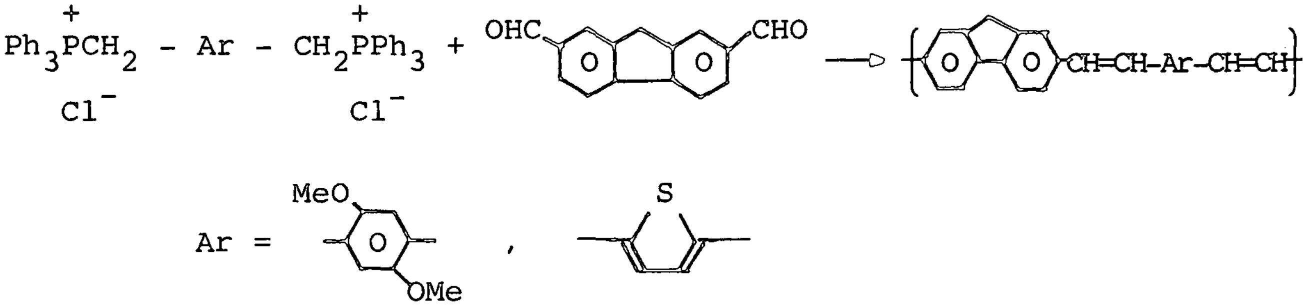
The Wittig reaction (Table 1.5, method 1) would be unlikely to produce such poly(arylene vinylene)s because an ylide such as that shown below would probably be too stable to attack the carbonyl moiety:



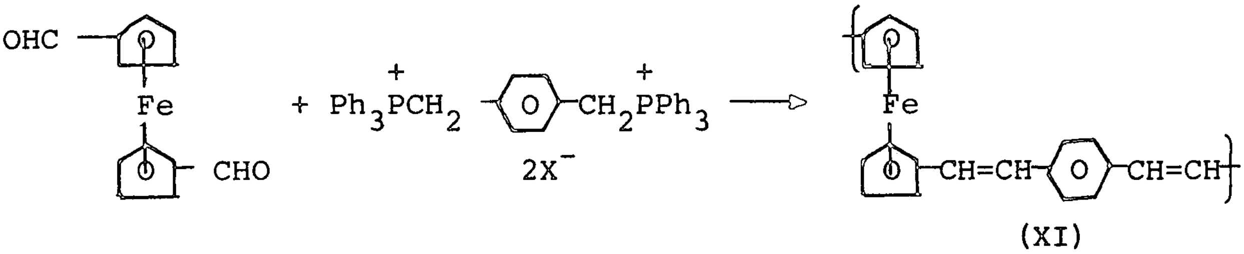
However the reaction has been used to prepare poly(arylene vinylene)s with hydrogens on the double bond by Kossmehl *et al.*[115] Some examples are given below.



(X)

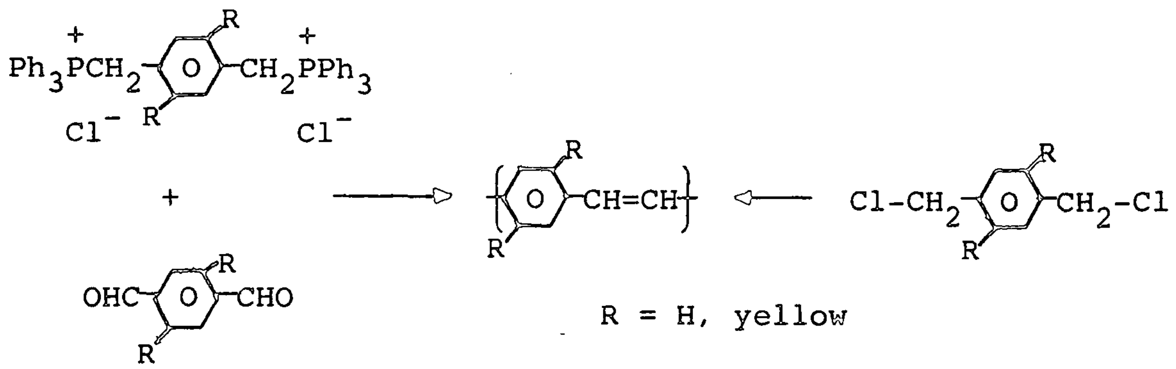


This reaction has recently been used to prepare poly(ferrocenylene vinylene phenylene vinylene):[116]



(XI)

Ring-substituted poly(p-phenylene vinylene)s can be prepared by either dehydrochlorination or Wittig polymerization of the ring-substituted precursors.[25]



R = H, yellow

= CH_3, yellow

= OMe, red

Poly(p-phenylene vinylene) has been prepared by reductive coupling,[23] no reports have appeared before the studies reported in this chapter of the extension of this reaction to the preparation of substituted poly(arylene vinylene)s.

(b) Physical Properties of Poly(arylene vinylene)s

(i) Poly(p-phenylene vinylene)

Poly(p-phenylene vinylene) is a strongly yellow-coloured, insoluble, infusible and heat resistant material.[23] Its electrical conductivity has been measured by various workers and samples prepared by different routes display different properties. Thus, a sample prepared by Wittig polymerization gave a value of $2x10^{-14}\Omega^{-1}cm^{-1}$,[118] material produced by a dehydrochlorination route gave $10^{-15}\Omega^{-1}cm^{-1}$ (at 400K in the dark)[25] and polymer obtained by reductive coupling gave a value of $1.28 \times 10^{-8}\Omega^{-1}cm^{-1}$ [23] for the electrical conductivity of this polymer.

Wnek *et al* have studied the AsF_5 doping of this polymer[51] as prepared by the Wittig method and reported the conductivity to be $\sim 10^{-10}\Omega^{-1}cm^{-1}$ for a d.p. of about 8 (as determined by elemental analysis). On doping with AsF_5 the conductivity increased as shown in Table 3.1, this was accompanied by a colour change of the polymer from yellow to brown. Doping with iodine was unsuccessful, this finding is analogous to studies of poly(p-phenylene) doping. It is thought that iodine is not a strong enough electron acceptor to interact with these polymers.

TABLE 3.1 Conductivity of AsF_5 Doped Poly(p-Phenylene Vinylene)[51]

AsF_5/wt.%	$\delta/\Omega^{-1}cm^{-1}$
5.6	4.3×10^{-5}
8.9	1.3×10^{-3}
16.4	6.2×10^{-2}
57.0	~ 3

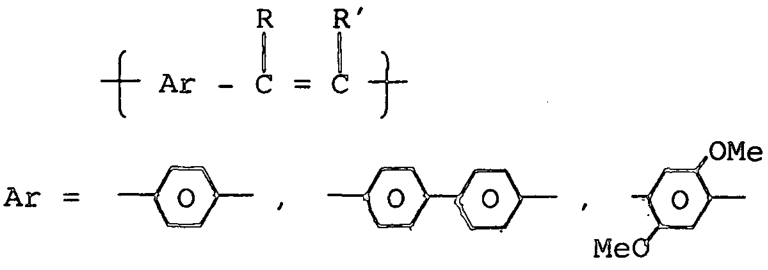
Addition of ammonia to the AsF_5 doped polymer resulted in reversion of the conductivity to that of an insulator. E.p.r. measurements showed that the undoped polymer contains no unpaired electrons but on initial exposure to AsF_5 an e.p.r. signal develops which broadens on longer exposure.

Poly(p-phenylene vinylene) is also a photoconductor, that is, its conductivity increases when it is exposed to light. The excitation energy for photoconduction is 2.35eV[25] and is the same as the calculated energy of the $\pi \rightarrow \pi^*$ transition for the polymer.

(ii) Other Poly(Arylene Vinylene)s

In contrast to poly(p-phenylene vinylene), most other poly(arylene vinylene)s are soluble, thus easier characterization and investigation of their properties is possible.

Hörhold *et al* have extensively studied the photoconductivity properties of polymers with the repeat units shown below.



$$\left[Ar - \overset{R}{C} = \overset{R'}{C} \right]$$

R, R' = H, Ph

Their dark conductivities are of the order of $10^{-14}\Omega^{-1}cm^{-1}$,[113] excitation energies are between 2.45 ⟶ 2.75 eV.[119] Photoconduction is thought to result from the formation of radical ions during the photoconduction process and these then act as charge carriers.[120,121] The series of polymers shown above display a range of excitation energies and it is found that the lower the optical excitation energy for the material the greater is the photocurrent[121] and the longer the wavelength that its absorption edge reaches the more sensitive it is for photoconduction.[122] The sensitivity and spectral range can be improved by addition of sensitizers, some examples are 2,2',4,4'-tetranitrodiphenylmethane,[123] 2,4,7-trinitrofluorenone,[124] pyrylium salts,[124] bis(cyanostyryl)benzenes[124] and picrates.[125] Hörhold *et al* have prepared combinations of poly(arylene vinylene) with a sensitizer and plasticizer cast onto a backing from a suitable solvent to give highly sensitive, photoconducting, transparent layers. These systems were tested by charging the layer to a positive or negative potential then exposing to light. Typically the charge reaches half its value in 1 second[126] indicating that a conduction mechanism is created on light exposure. On charging the systems in the dark then exposing to light through a transparency and developing and fixing, images were obtained.[127]

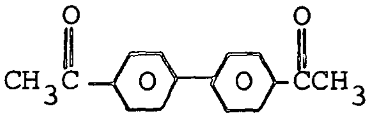
These results show that these systems could be of use as electrophotographic recording or copying materials.

The author was unable to find any report of the effect of chemical doping on the electrical conductivity of these vinylene substituted poly(arylene vinylene)s prior to the work reported in this chapter, however some systems with hydrogens on the double bond have been investigated. Kossmehl *et al* have treated poly(thiophenediyl) (X) with iodine and AsF_5 in solution. They found that the conductivity increases by six orders of magnitude on iodine treatment,[115] in fact the polymer was treated with iodine in order to convert it to its all-trans form and the doping effect was accidentally observed, similar results were obtained on AsF_5 treatment, the highest conductivity attained was $0.02\ \Omega^{-1}cm^{-1}$.[128] Poly(ferrocenylene vinylene phenylene vinylene) (XI) has been found to have a conductivity of $10^{-12}\Omega^{-1}cm^{-1}$ before doping; on iodine doping a value of $10^{-4}\Omega^{-1}cm^{-1}$ was attained.[116] AsF_5 doping was ineffective for this polymer.

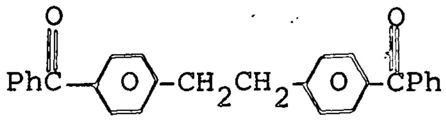
3.2 Experimental

(a) Preparation of Monomers

The preparations of p-dibenzoylbenzene, m-dibenzoylbenzene and p,p′-dibenzoyl diphenyl are described in Chapter Two pp.37-39 Other monomers used were terephthalaldehyde, p,p′-diacetyl diphenyl (XII) and p, p′-dibenzoyl 1,2 diphenyl ethane (XIII).



(XII)



(XIII)

Terephthalaldehyde was obtained from stores, purified by recrystallization from water and dried under vacuum. (XII) and (XIII) were used as previously prepared by Andrews.[74] The infra-red spectra of these monomers are given in Appendix 1, Nos. 13-15.

(b) Reductive Couplings - The Model Reaction

In the studies described here, titanium trichloride and lithium aluminium hydride were used as obtained (Aldrich) and stored under dry nitrogen. Dry THF (distilled from potassium metal) was used as the solvent for all coupling attempts. It was necessary to firstly attempt the model reaction as a check on the technique used, suitability of catalysts and the dryness of solvent and nitrogen supply.

Successful reductive coupling of benzophenone to tetraphenylethene was achieved using a molar ratio of one benzophenone to two $TiCl_3$ and one $LiAlH_4$. A dry nitrogen atmosphere was maintained during the reaction and the established coupling procedure was carried out as follows.

A slurry of titanium trichloride (2.81g) in tetrahydrofuran (30 ml) under dry nitrogen was prepared in a three-necked flask equipped with a nitrogen inlet and a magnetic stirrer follower. The flask was cooled to 0°C and lithium aluminium hydride (0.35g) added. Effervescence occurred and the mixture rapidly changed colour from purple to black. After stirring at 0°C for 30 minutes a condenser was fitted and the solvent refluxed for one hour. Benzophenone (1.65g) was then added and the solution left to stir at room temperature overnight. After stopping the reaction by the slow addition of 2N HCl (40 ml) the product was extracted with chloroform (3 x 10 ml). The combined extracts were dried ($MgSO_4$), filtered and evaporated to dryness. The product was obtained pure by column chromatography using a 25 x 2 cm column packed with silica (Kieselgel 60), eluting with 1:1 60-80 petroleum ether - chloroform.

After removal of solvent from the appropriate column fractions, tetraphenylethene (1.31g, 87%) was obtained with correct infra-red spectrum (Appendix 1, No. 16).

Dams *et al*[85] have reported a 90±5% yield (after chromatography) for this reaction which, in their studies, corresponded to a 99% yield as determined by U.V. spectrophotometry of the final reaction mixture. So our result was comparable to this and meant that polymerizations utilizing this reaction procedure could be tried. Dams *et al* also found that a molar ratio of one benzophenone to one titanium trichloride to a half lithium aluminium hydride resulted in a similar yield of alkene but in the author's hands this was not realised in any of four separate attempts, yields of only 40 to 50% tetraphenylethene were obtained, after column chromatography, as well as significant amounts of benzopinacol.

(c) Polymerizations

The general procedure for all polymerization attempts was as described below. A molar ratio of 2 $TiCl_3$ to 1 $LiAlH_4$ to ½ diketone was used and a dry nitrogen atmosphere was maintained throughout the polymerization period.

Titanium trichloride (2 x moles) was placed in a three-necked flask fitted with a nitrogen inlet and magnetic stirrer follower. The operation was carried out using a glove box under dry nitrogen. The flask was sealed and transferred to the nitrogen line and THF (20-60 ml) added. This solution was cooled with stirring to 0°C and lithium aluminium hydride (x mole) slowly added; effervescence occurred and the colour of the solution rapidly turned to black. After stirring for 30 minutes the flask was fitted with a condenser and the mixture refluxed for 1 hour. The diketone (½ x mole) was then added and the stirred slurry kept at reflux for a period of not less than 16 hours.

The reaction was quenched by the slow addition of 2N HCl (20-60 ml). It was found that polymers could best be recovered by addition of chloroform at this stage followed by removal of the organic solvents by rotary evaporation, granular precipitates were given by this technique. The product was collected on a sinter, washed with water, dried and reprecipitated with appropriate solvents and non-solvents. The product was then dried under vacuum. The degree of conversion of monomer to polymer could be judged by comparing the size of any residual carbonyl stretching peak in the infra-red spectrum with that of the monomer. In most cases no carbonyl peak remained. Hydroxyl stretching peaks were more often observed in these spectra, probably due to residual polypinacol units and reduced chain ends.

The amounts of reactants used in the polymerization attempts are given in Table 3.2, this is followed by the details of the results of the individual reactions.

TABLE 3.2

Monomer	Run No.	Weight of Monomer/g	Weight of $TiCl_3$/g	Weight of $LiAlH_4$/g	Reflux Time
Terephthalaldehyde	1	0.345	1.60	0.195	16 hrs.
p-Dibenzoylbenzene	2	0.894	1.93	0.237	16 hrs.
	3	0.449	0.97	0.119	5 days
p,p´-Dibenzoyl diphenyl	4	0.539	0.92	0.113	16 hrs.
	5	2.36	4.02	0.495	16 hrs.
	6	1.99	3.41	0.417	5 days
m-Dibenzoylbenzene	7	1.29	2.80	0.343	24 hrs.
p,p´-Diacetyl diphenyl	8	0.793	2.06	0.253	4 days
p,p´-Dibenzoyl diphenyl 1,2 ethane	9	1.55	2.47	0.303	16 hrs.

(i) Terephthalaldehyde

A yellow powder was obtained from attempted polymerization of this compound. The product was insoluble in chloroform therefore purification by reprecipitation was not possible. After drying, the infra-red spectrum showed peaks at 3,550-3,100 (residual pinacol and chain end hydroxyl groups), 3,005 (aryl C-H stretch), 2,900 (CH alkyl stretch, possibly traces of residual THF), 1,590 (aryl C=C stretch), 1,500, 1,350-1,430, 1,180, 1,040, 960, 830, no carbonyl stretching frequency remained.

This indicates that essentially no monomer remained, thus polymerization has occurred, but that there were probably pinacol units remaining in the polymer. Rajaraman *et al*[23] also reported the formation of an insoluble yellow powder by this reaction.

(ii) p-Dibenzoylbenzene

During the polymerization attempts on this compound the black catalyst solution was observed to change to a deep-red colour a short time after addition of the monomer. For the shorter term reaction (run 2) this colour remained until the reaction was terminated whilst for the longer one (run 3) the colour had changed to black after three days of the five-day reflux period. In both cases yellow powders were obtained, reprecipitation from THF into methanol was unsuccessful for the product of run 2 - a tractable precipitate could not be formed. The product of the longer reflux was reprecipitated using methanol and petroleum ether to give a yellow solid (0.36g) with infra-red spectrum as given (Appendix 1, No.17) which shows a strong hydroxyl stretching band as well as a residual carbonyl peak at 1650cm^{-1}. Thus, complete carbonyl consumption had not occurred even after 5 days of reflux, it also appeared that there were many pinacol units or hydroxyl chain ends in the product causing the large hydroxyl peak. The infra-red spectrum of the product from the 16 hr. reaction shows similar features but the hydroxyl and carbonyl stretching peaks are stronger in the infra-red.

(iii) p,p′-Dibenzoyl diphenyl

Reductive couplings of this monomer resulted in a yellow, granular solid product which after reprecipitations from chloroform into methanol (twice) resulted in about 80% by weight (for example run 5, 1.95g, 82.6%) of a product displaying the infra-red spectrum shown at Appendix 1, No.18. This shows that all the carbonyl functionalities have been consumed and only a small amount of hydroxyl stretching is observed probably due to reduced chain ends. An alkyl stretching peak appears in the spectrum, it was found that by repeated reprecipitations (4-6 times) from petroleum ether and methanol (alternately) out of chloroform this peak gradually disappeared, hence, it can be assigned to residual THF in the polymer.

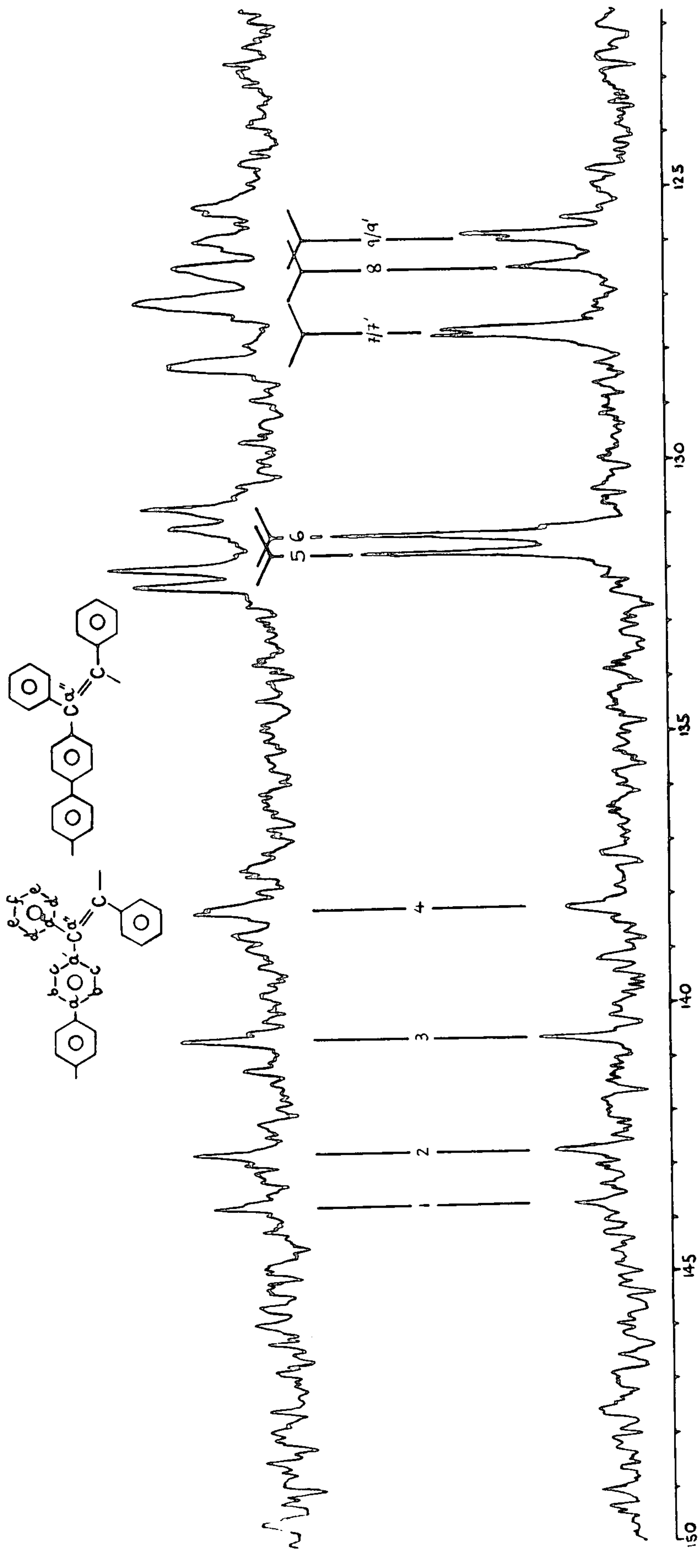
It was found that free-standing, transparent, yellow films could be formed from the product by spin-casting under reduced pressure from chloroform, an infra-red spectrum of a film sample is given (Appendix 1, No.19). A high resolution infra-red spectrum was obtained of a film sample, using a Perkin Elmer 580B, this was first checked using a polystyrene film. The peak positions of poly(p,p′-diphenylene diphenyl vinylene) were given as 3074.0, 3051.1, 3023.0(s), 1944.4(w), 1908.2(w), 1799.9(w) 1596.4, 1574.2(w), 1493.0(s), 1442.1, 1394.9, 1261.3, 1180.6(w), 1154.6(w), 1109.6, 1072.5, 1028.7, 1003.4(s), 974.7, 913.1, 806.2(s), 765.5, 697.2(s), 647.0(w), 628.0, 617.4(w), 573.2 and 470.8 cm^{-1} with errors of ±0.8 cm^{-1}. Brittle fibres of up to 1cm in length could be drawn from the polymer melt. The ^{1}H-n.m.r. spectrum showed one main peak at δ7.0 with shoulders to either side (aryl protons). Elemental analysis gave, for the 16 hr. refluxed product C 91.32% H 5.10% and for the 4 day refluxed product C 92.7% H 6.29%, calculated for poly(p,p′-diphenylene diphenyl vinylene) C 94.5% H 5.5%. The low carbon values may well have been due to the residual THF (C 66.78%);

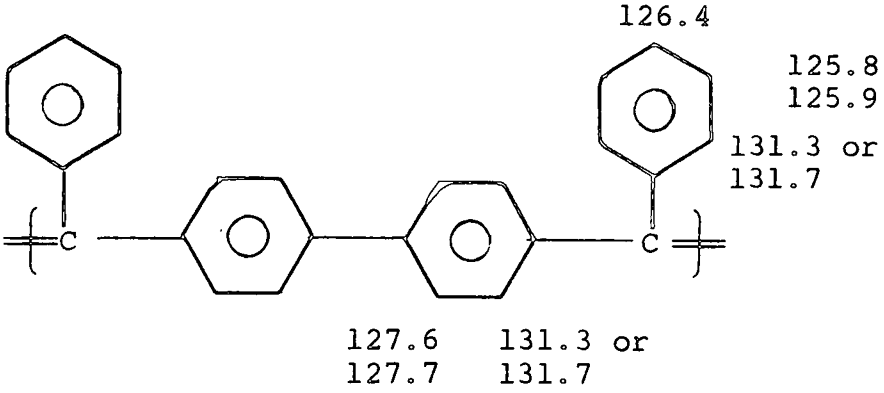
however prolonged pumping of the polymers under vacuum resulted in no change in the elemental analyses. A carbon 13 n.m.r. spectrum of the polymer was obtained; the author is grateful to Dr. I. Sadler of Edinburgh University for these measurements. The spectrum was recorded in $CDCl_3$ along with an off-resonance spectrum, which identifies the carbons carrying a hydrogen since these appear as doublets in the off-resonance spectrum. Figure 3. shows these spectra. Off-resonance is the upper trace.

It is difficult to make absolutely unambiguous assignments for a spectrum of this quality although it is a considerably better resolved spectrum than those reported previously by Hörhold *et al* for a series of poly(arylene vinylene)s.[114(c)]

Signals 1,2,3 and 4 are associated with a-type environments as shown on the diagram, that is, carbons not bearing hydrogen. Of these, the highest field signal is broader (partially resolved in the off-resonance spectrum) which might possibly be due to vinyl carbons in cis and trans environments. Examination of the repeat unit for the polymer with a trans vinylene unit (Fig.3. implies that if there is free rotation about the carbon-carbon single bonds there are only five environments for carbons bearing hydrogen. It is clear from the spectrum that there are indeed five main signals (5-9) but two of these (7 and 9) are resolved into doublets, this observation can not be unambiguously interpreted but is consistent with doubling of environments by restricted rotation and/or the presence of cis and trans isomeric repeat units. Provisional assignments of the observed signals are shown below.

FIGURE 3.1





The assignments are in general agreement with those proposed by Hörhold *et al*[114(c)] although the spectra available to these workers were very poorly resolved.

The molecular weight, conductivity and photophysical measurements of this polymer are described in Section 3.2 (d) 1-3.

(iv) m-Dibenzoylbenzene

The polymerization attempt with this monomer gave a yellow product after reprecipitation from chloroform into methanol, the granular solid was dried (1.04g, 80.6% by weight) and had the infra-red spectrum given, Appendix 1, No.20. This shows a slight residual carbonyl peak at 1610-1680 cm^{-1} and a weak, broad hydroxyl stretching band as well as a weak alkyl stretch at 2,900 - 3,000 perhaps indicating residual THF. Elemental analysis gave C 86.69% H 5.9%, calculated for poly (m-phenylene diphenyl vinylene) C 94.5%, H 5.5%. These observations indicate that a low molecular weight telomeric product has been produced, a low d.p. polymer of this type would have a significant amount of oxygen at the chain ends, this is probably why the analysis gave a low carbon value (as well as the lowering effect of traces of THF). The product was not film-forming.

The molecular weight measurements of this product are discussed in Section 3.2 (d) 1.

(v) p,p´-Diacetyl diphenyl

The product from this reaction, after reprecipitation from THF into methanol, was a white solid (0.55g) which was not film-forming. The infra-red spectrum shows (Appendix 1, No. 21) a strong hydroxyl stretching peak as well as a small residual carbonyl peak similar to that observed for the product of m-dibenzoyl benzene polymerization. As well as the aryl C-H stretch at 3010 cm^{-1} there is also a rather strong peak centred at 2910. Again, this is probably due to residual THF, enhanced by the fact that the reprecipitation was performed from THF itself. Prolonged vacuum line pumping did not reduce the intensity of this peak.

(vi) p,p´-Dibenzoyl diphenyl 1,2 ethane

This reaction gave, after reprecipitation from chloroform into methanol, a pale green solid (1.41g, 90% by weight). It was found that on dissolving in THF a small amount of powdery, white precipitate remained, this was removed by filtratio and the solution reprecipitated into methanol giving a pale yellow solid. This was dried and found to have an infra-red spectrum (Appendix 1, No.22) which showed no residual carbonyl stretching frequency, a weak hydroxyl stretch peak as well as a peak due to alkyl stretching, probably from residual THF (again the last reprecipitation was performed from THF). The elemental analysis gave C 86.98%, H 6.39%, calculated for poly(p,p´-diphenyl 1,2 ethane diphenyl vinylene), C 93.9%, H 6.1%. The carbon value is probably low because of residual THF in the polymer and also because a low d.p. has probably resulted. The product was not film-forming.

The molecular weight measurements of this polymer are given in Section 3.2(d) 1.

In these polymerizations it was found that it was often difficult to remove the last traces of THF from the products. Prolonged pumping under vacuum had no detectable effect. For poly (p,p′-diphenylene diphenyl vinylene) it was found to be possible to remove the solvent by repeated reprecipitations.

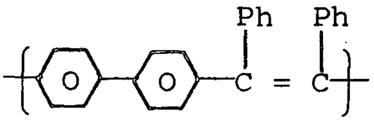
The polymerization itself is not always successful, many more runs than those reported above were carried out but resulted in products with the characteristics of lower molecular weight analogues of the above, for example, strong residual carbonyl stretching peaks in the infra-red spectra.

(d) Further Characterization of Polymers

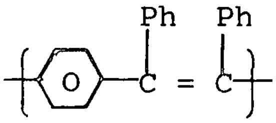
1. Molecular Weight Measurements

Molecular weight determinations were made on the polymers derived from p,p′-dibenzoyl diphenyl, m-dibenzoylbenzene and p,p′-dibenzoyl diphenyl 1,2 ethane. The repeat units proposed for these polymers are shown below.

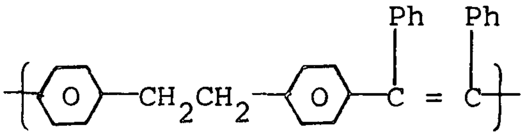
In this section polymer (XIV) poly (diphenylene diphenyl vinylene), will be referred to as PBV, similarly polymer (XV), poly (m-phenylene diphenyl vinylene), as PMV and polymer (XVI), poly (diphenyl 1,2 ethane diphenyl vinylene), as PEV.



(XIV)



(XV)



(XVI)

Two techniques were used for the molecular weight measurements, gel permeation chromatography and vapour pressure osmometry.

Gel permeation chromatography is a technique by which molecules are separated on the basis of their hydrodynamic volume , which is, the volume of the coiled chain of one polymer molecule. This is affected by the stiffness of the chain and the interactions of the polymer with solvent. The sample is dissolved and passed through a gel permeation column which is packed with a gel which retains smaller hydrodynamic volume molecules in its pores. These pores are of such a size as to preclude the retention of larger molecules so that these emerge first from the end of the column. Thus the final trace obtained, by ultra violet or refractive index detection of the eluting solvent will show a curve with the largest molecules represented at the front end of the trace. From this curve the average molecular weight of the polymer can be calculated.

The column is first calibrated using monodisperse standards of a well characterized polymer then the sample is run through the column and the trace obtained analysed in the following way. The area under the curve is divided into i equally spaced points and the calibration graph, previously obtained of elution volume versus molecular weight is consulted to give the equivalent molecular weight values of each of the i points. The formulae shown below are then used to obtain $\overline{Mw}$ and $\overline{Mn}$ values for the polymer.

$$\overline{Mn} = \frac{\Sigma NiMi}{\Sigma Ni}$$

$$\overline{Mw} = \frac{\Sigma NiMi^2}{\Sigma NiMi}$$

$$\text{Polydispersity} = \frac{\overline{Mw}}{\overline{Mn}}$$

where $\overline{Mw}$ and $\overline{Mn}$ are the weight average and number average molecular weights and Ni is the number of molecules with the i th molecular weight value. $\overline{Mw}$ is sensitive to the amount of high molecular weight molecules present whilst $\overline{Mn}$ is affected by low molecular weight material in the sample. Ni is calculated from the height of the curve at the ith point. The polydispersity value is an indication of the molecular weight distribution, the larger the value the wider the spread of d.p.s. In these studies monodisperse polystyrene standards were used to calibrate the elution volumes, the eluent was distilled, degassed THF.

The traces obtained of the poly(phenylene vinylene)s all showed a leading peak which was large and broad followed by sharper peaks corresponding to telomeric units. Ultra-violet detection was used, a typical trace is shown in Fig.3.2.

The molecular weight determinations were calculated on the area under the main front peak which was extrapolated to the base line as shown by the dotted line on Fig.3.2. When

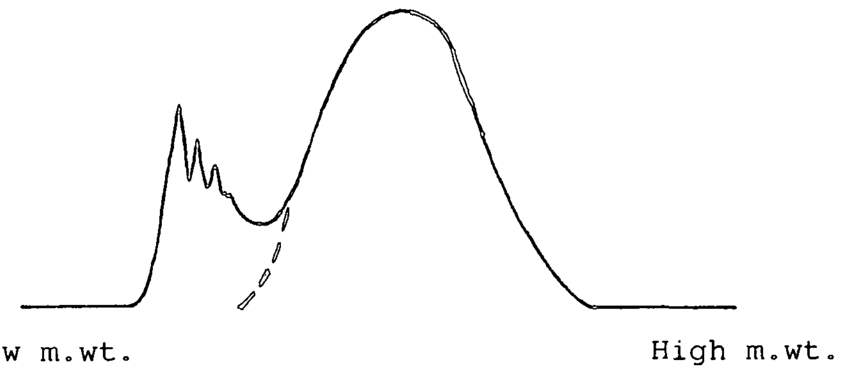


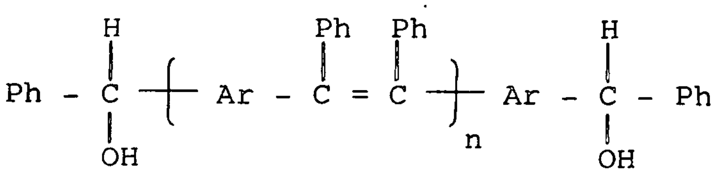
Figure 3.2

the samples were rerun with some added monomer a new peak appeared at a lower molecular weight value than any peak in the product's trace. The exception was PMV which already showed a very weak peak at the elution volume of m-dibenzoylbenzene. The results of these molecular weight analyses are given in Table 3.3.

Table 3.3 Gel Permeation Chromatography Results Calculated Against Polystyrene Standards in THF

Sample	$\overline{Mw}$	$\overline{Mn}$	Polydispersity	d.p.
PBV (16 hr.reflux)	73,800	37,300	2.0	113
PBV (4 day reflux)	125,900	36,100	3.5	109
PMV	3,790	1,650	2.3	7
PEV	13,500	6,000	2.3	17

There was good agreement between the extrapolated molecular weights of the telomer components and the calculated values, if one assumes these molecules to have the structure shown below.



$$Ph-\overset{H}{\underset{OH}{C}}-\left[Ar-\overset{Ph}{C}=\overset{Ph}{C}\right]_n-Ar-\overset{H}{\underset{OH}{C}}-Ph$$

For example for PBV (16 hr. reflux) the extrapolated values for the three distinguishable tail peaks are 770, 1,000 and 1,410; for n = 1-3 the calculated values are 696, 1,026 and 1,356.

Vapour pressure osmometry is a technique by which number average molecular weights can be determined by measuring the change in vapour pressure induced in a solvent by a small amount of dissolved sample. The effect on vapour pressure is best found by measuring the temperature difference between pure solvent and the solution under the same conditions. This is achieved by placing a drop of solvent and a drop of solution on adjacent thermistors in an atmosphere of the solvent vapour, and measuring the difference in evaporation from each drop (which induces cooling at the thermistor). The apparatus consists of a thermostatted chamber which is saturated with the solvent vapour and has two thermistors mounted inside it. Directly above these there are two droppers - from one, pure solvent drops can be produced and through the other drops of solution are produced. The thermistors are connected to a Wheatstone Bridge circuit, this gives a deflection, (ΔR), on a gauge on the instrument, when two drops of different evaporation rates are placed on the thermistors.

The instrument was firstly calibrated using a range of concentrations of benzil, this gives the instrument constant, denoted as K. The ΔR values of three different concentrations of each polymer were then measured and the number average molecular weight calculated by the formulae shown below.

$$\overline{Mn} = \frac{K}{\lim_{C \to O} \Delta R/C}$$

$$\lim_{C \to O} \Delta R/C = \frac{\Sigma C^2 \Sigma \Delta R/C - \Sigma C \Sigma \Delta R}{n \Sigma C^2 - (\Sigma C)^2}$$

The term C is concentration and n is the number of concentrations measured, in this case 3. The calculated results are given in Table 3.4, the solvent was chloroform (Analar).

Table 3.4 V.p.o. Molecular Weight Results

Sample	$\overline{Mn}$	d.p.
PBV (16 hrs. reflux)	4,150	12.6
PBV (4 day reflux)	4,530	13.7
PMV	1,810	7.1
PEV	1,860	5.2

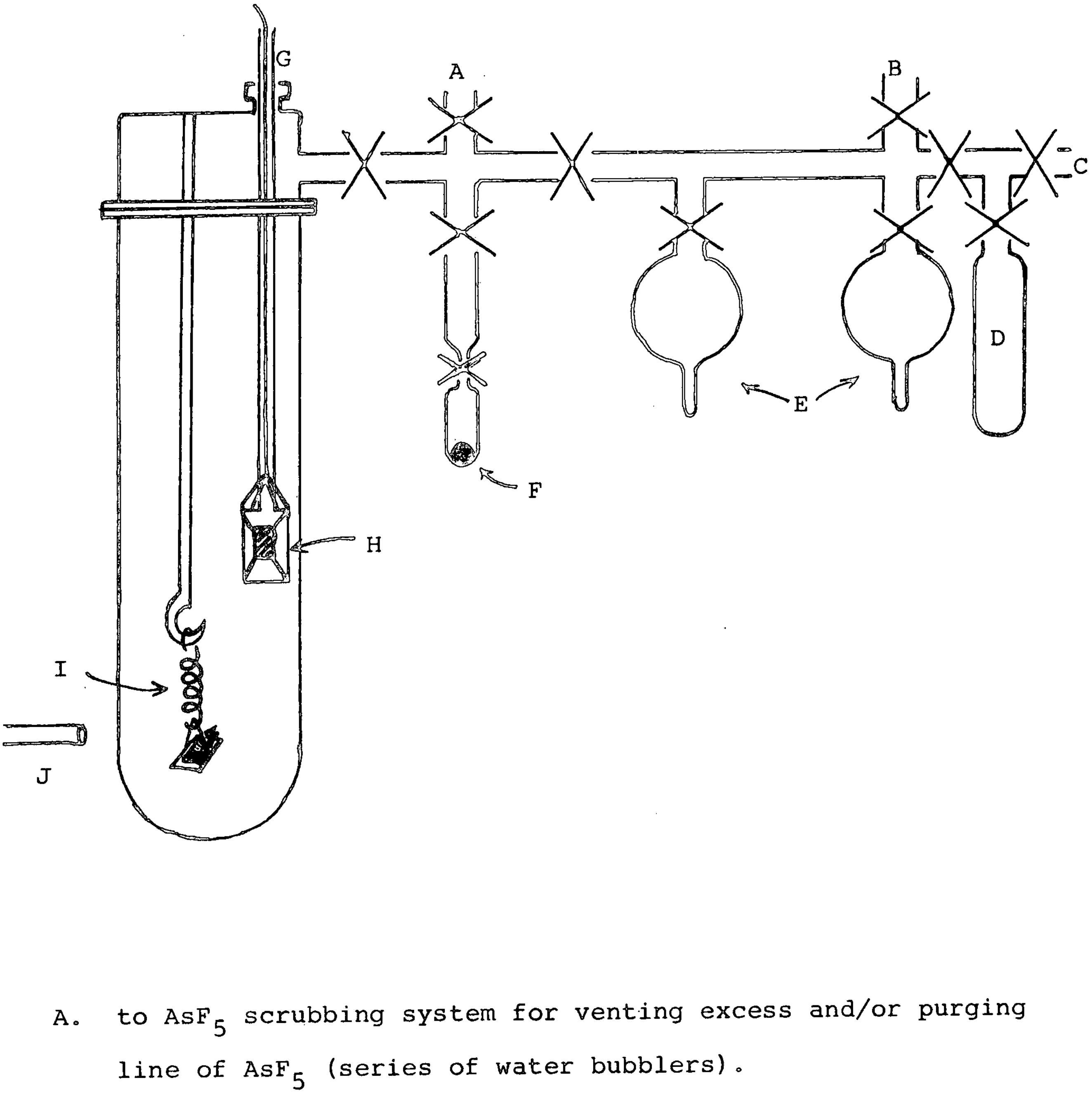
This "molecule counting technique" includes the telomers found on g.p.c. analysis as well as any contaminating THF residue.

2. Electrical Conductivity Studies of PBV

The electrical conductivity and related properties of PBV (4 day reflux) were studied by the author using equipment at the Cavendish Laboratories of Cambridge University. Residual THF was first removed from the polymer by six reprecipitations from chloroform alternately out of 60-80 petroleum ether and methanol.

The effect of arsenic pentafluoride doping of a PBV film was examined by use of the apparatus shown in Fig.3.3.

Figure 3.3 Doping Apparatus at Cambridge University



A. to AsF_5 scrubbing system for venting excess and/or purging line of AsF_5 (series of water bubblers).

B. to pressure gauge

C. to dry nitrogen line and vacuum pump

D. AsF_5 cylinder

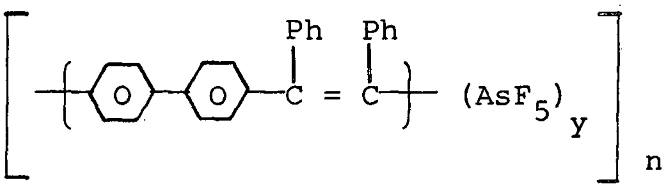
E. cold traps

F. iodine crystals

G. to electrometers
H. sample of film with 4 gold-paint connections
I. spring holding sample on a pan
J. vertical travelling microscope.

This equipment allows the weight gain and electrical conductivity of the material to be monitored simultaneously.

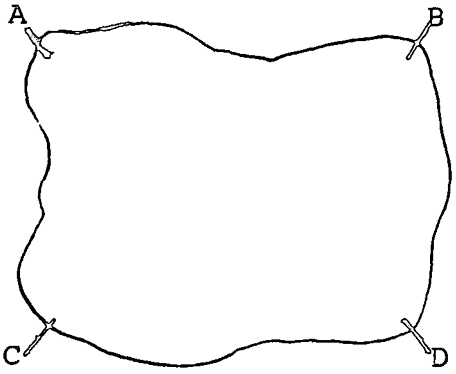
The spring had been previously calibrated and found to give an extension of 1.72mm mg^{-1}. The sample, before AsF_5 was introduced, extended the spring by 6.13mm so the initial weight was 3.56mg. Percentage weight gain is similarly easily found. The doped polymer can be represented by the formula shown below.



The term y is given by the equation shown below.

$$y = \frac{\text{Weight of } AsF_5 \text{(weight gain)}}{\text{Initial weight of film}} \times \frac{\text{mol.wt. of repeat unit}}{\text{mol.wt. } AsF_5}$$

The principle of the conductivity measurements is based on the theory of Van der Pauw[129] which describes a method for finding the resistivity of an arbitrary-shaped, flat sample. This requires four low-resistance contacts to be placed around the circumference of the sample. The sample must be of uniform thickness, for the PBV film obtained by spin casting this requisite is satisfied. Consider a uniform sample, as shown below, with points A, B, C and D as the points of contact.



Let I(AB) x V(CD) = R1

I(BC) x V(AD) = R2

where I = current and V = potential difference and the R values are the resistances between the contacts, known as two-terminal resistances. Van der Pauw's equation is:

$$\frac{\rho}{d} = \frac{\Pi}{2\ln 2} (R_1 + R_2) f \left(\frac{R_1}{R_2} \right)$$

where ρ is resistivity and d is the sample thickness. Assuming density $\sim 1\text{g cm}^{-3}$, d was found to be $\sim 15\mu\text{m}$. Conductivity (σ) is the inverse of resistivity.

The apparatus was set up with both film samples in place and evacuated. AsF_5 vapour was vacuum transferred in and the conductivity and weight gain were measured over a period of 24 hours. The pressure of AsF_5 was increased in stages. Many readings were taken but the trend of the results is given in Table 3.5 which gives a selection of the readings. During this period the film darkened from yellow green to a dark green colour. After doping the AsF_5 was pumped off and iodine vapour let onto the sample. No change in conductivity or weight occurred over 145 minutes' exposure. The doped samples were then exposed to air, the conductivity decreased rapidly and a

Table 3.5 AsF_5 Doping of PBV

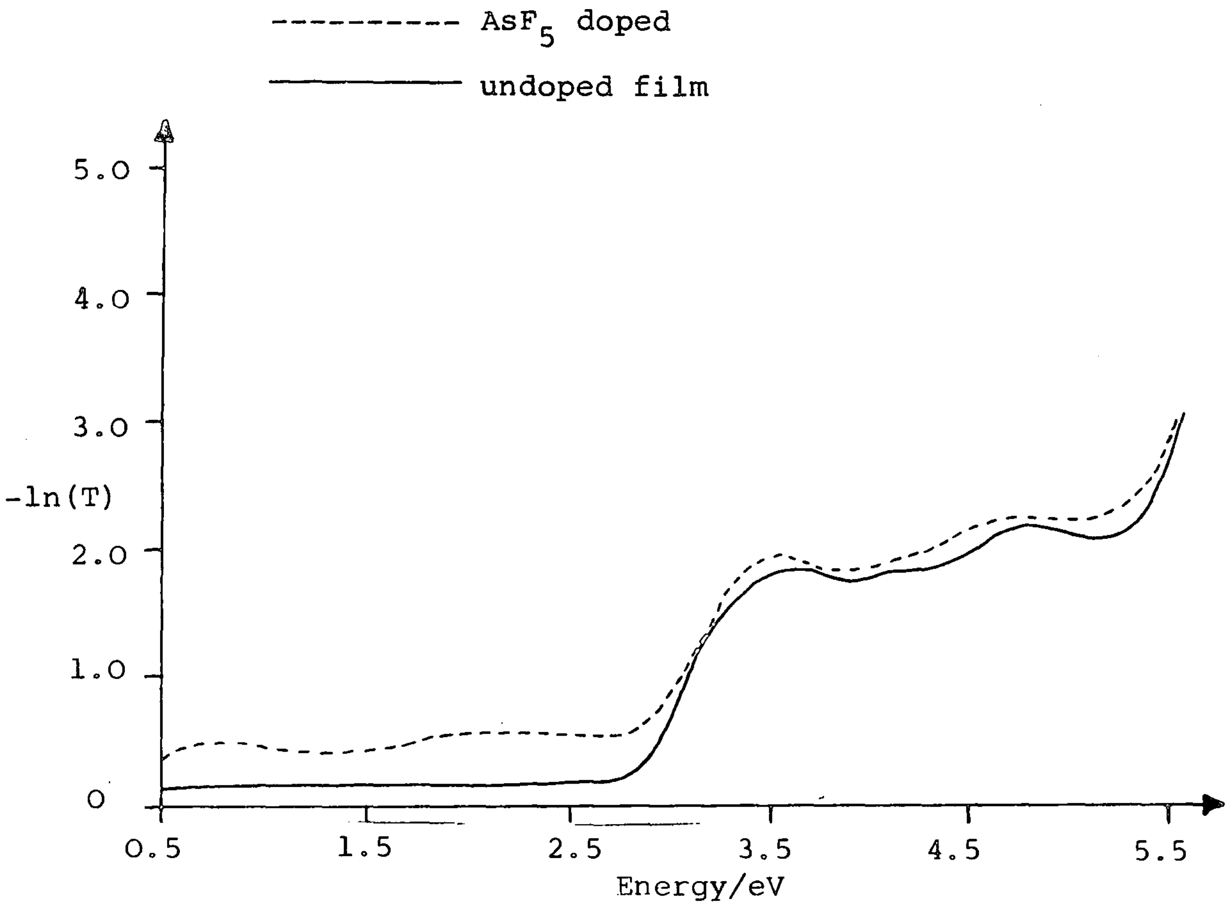
Time (Mins.)	AsF_5 pressure (m bar)	$\sigma(\Omega^{-1}\ cm^{-1})$	% Wt. Gain	y
0	0	6.8×10^{-9}	0	0
1	1	2.7×10^{-7}		
5	3.4	1.7×10^{-6}	1.3	0.03
24	3.4	2.7×10^{-6}	1.3	0.03
102	15	5.3×10^{-6}	2.9	0.05
227	87	1.2×10^{-5}	3.9	0.08
487		2.1×10^{-5}	5.2	0.10
1,492		3.5×10^{-5}		

value of $3.27 \times 10^{-10}\ \Omega^{-1}\ cm^{-1}$ was recorded after ten minutes in air.

Another interesting property of conducting materials is the 'band gap'. On a band model of conductivity in solids, the energy necessary to transfer an electron into the conduction band can be estimated by measuring the minimum energy at which optical absorption occurs, this value is the band gap.

A film of PBV was cast onto the inside of the window of an optical cell, the cell was evacuated and the absorption spectrum recorded. AsF_5 (54 mbar) was then let into the cell and the spectrum run again a few times over the following 24 hours. There were changes in the recorded spectra and these are best seen by comparing the final recorded trace with that of the pure film. The most significant differences are the development of two new, broad peaks centred at 0.8 eV and 2 eV. The main absorption edge appears at about 3 eV. These features are illustrated in Figure 3.4.

Figure 3.4 Optical Spectra of PBV



T = transmittance

3. Photophysical Properties of PBV

It was found that when films of PBV were irradiated by a low power long wavelength U.V. lamp an intense green fluorescence was observed. Samples of the polymer were sent for examination of photophysical properties, to the laboratories of the Royal Institution in London. The results are given below. The author is indebted to Mr. G. Rumbles and Prof. D. Philips for these measurements.

The absorption and excitation spectra were recorded, in dry THF, using approximately 400 mg l^{-1} solutions. These spectra are shown below, Figure 3.5 is the absorption spectrum and Figure 3.6 and Figure 3.7 are the excitation spectra with emission wavelengths 465 nm and 510 nm respectively.

Figure 3.5 PBV absorption spectrum (in THF)

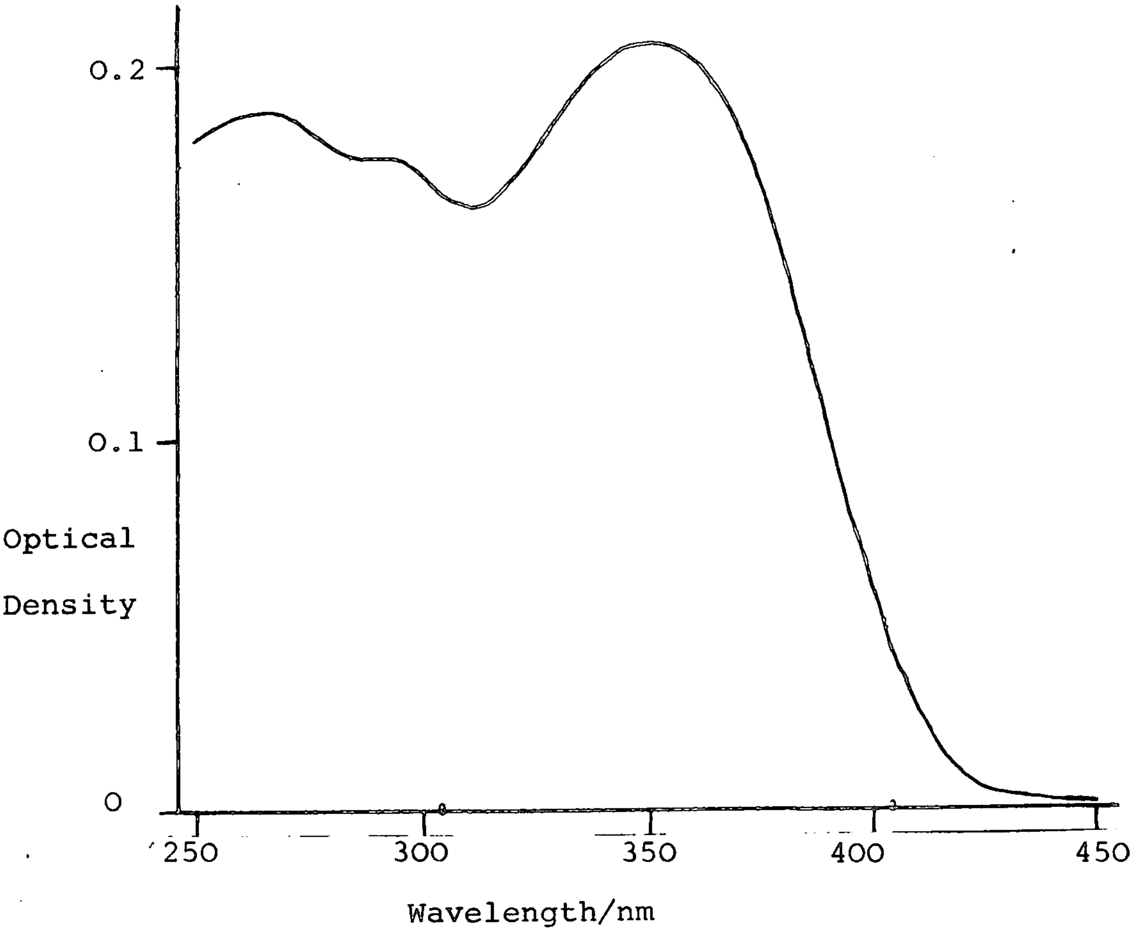


Figure 3.6 Excitation Spectrum of PBV

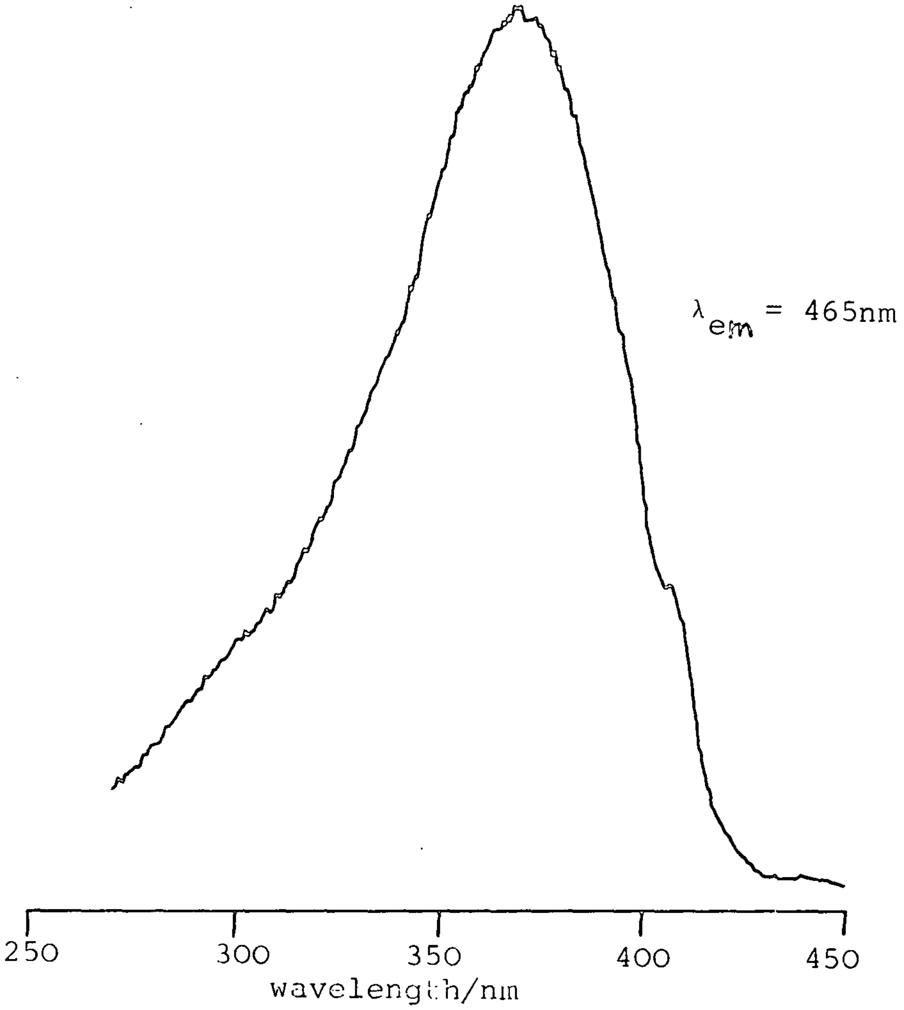
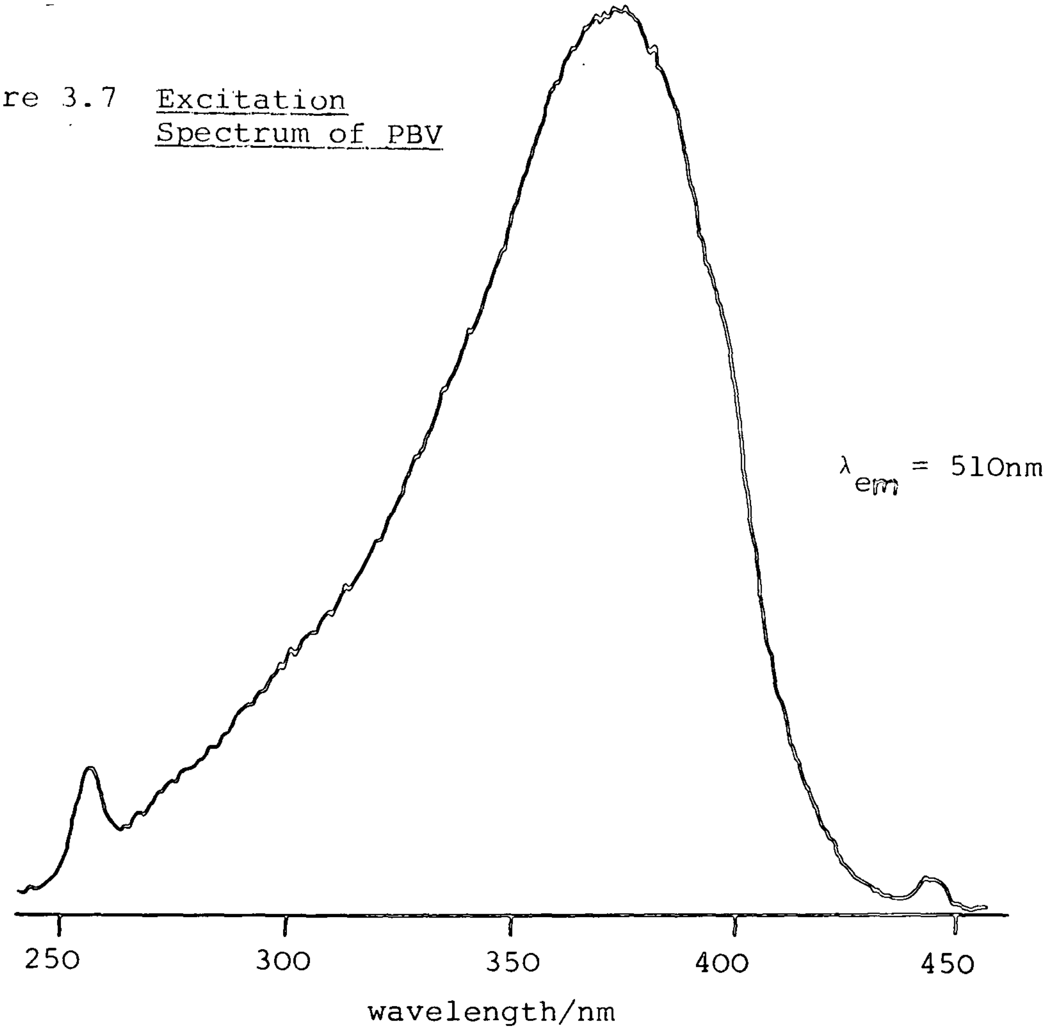


Figure 3.7 Excitation Spectrum of PBV



The peaks in the absorption spectrum at 270nm and 295nm do not appear in the excitation spectra, these are probably due to the telomeric components of the sample (see gel permeation chromatogram).

Eleven fluorescence spectra were recorded in methylene chloride over a range of excitation wavelengths from 257.3-420nm. All showed a strong emission centred at 510nm as well as a smaller accompanying band, due to Raman scattering by the CH bonds of the solvent, which appeared between 280-480nm over the excitation range used (2,980cm^{-1}). In the three lowest excitation wavelength spectra, run at 275.3, 270 and 300nm a weak peak is evident at about 330nm which is again probably due to the telomers. Figure 3.8 shows the fluorescence spectrum recorded with λ_{ex} 360nm, and Figure 3.9 is the spectrum with λ_{ex} 270nm which shows the telomer peak.

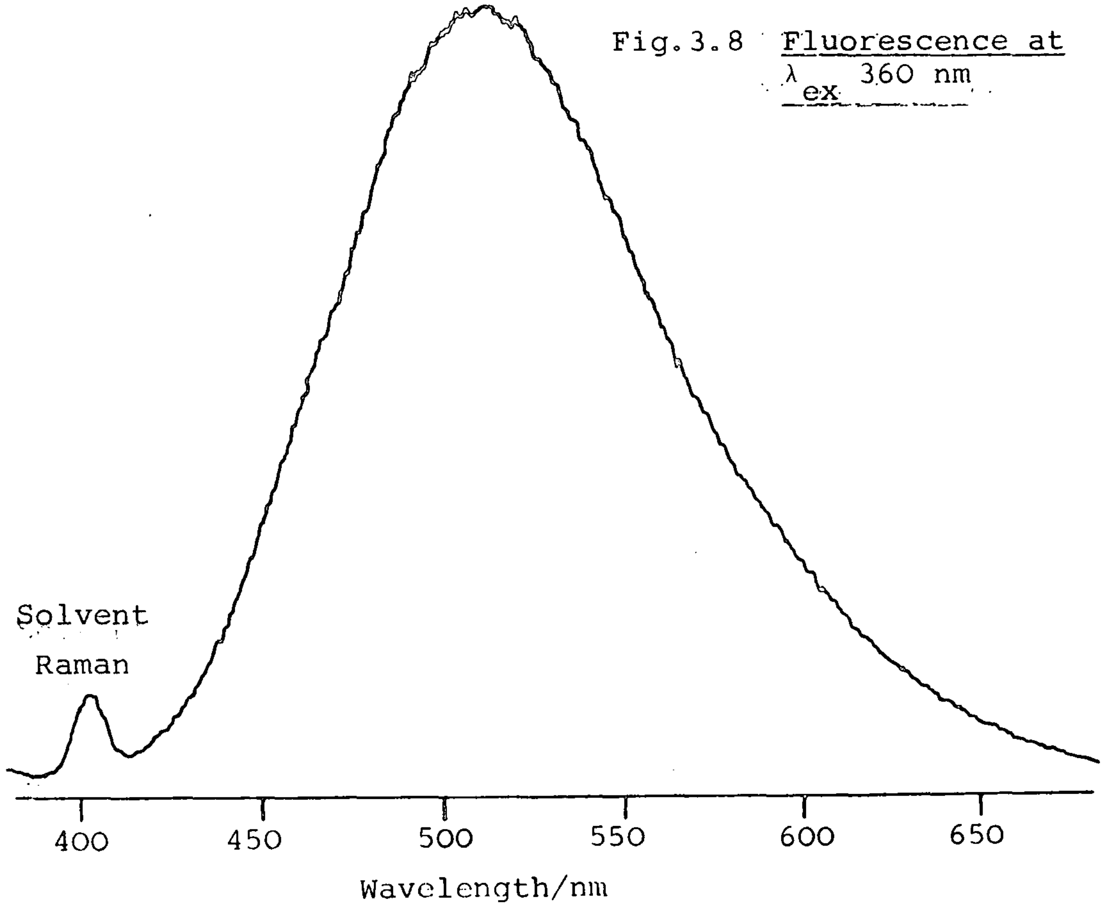
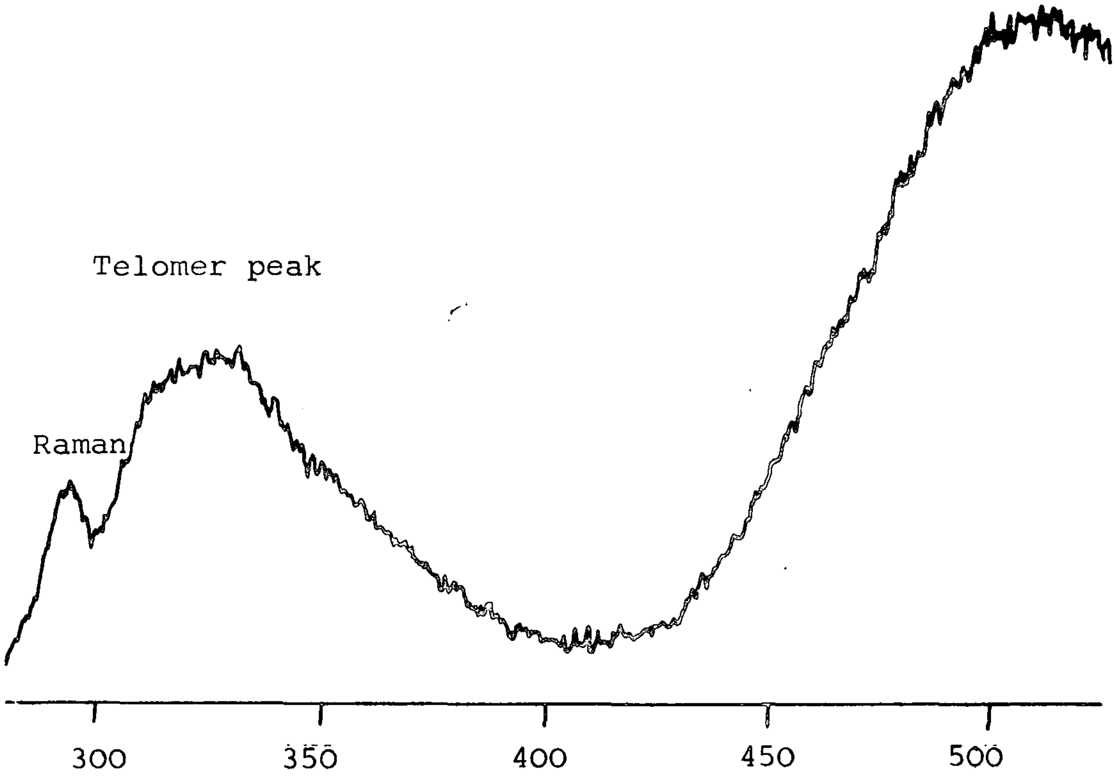


Fig. 3.8 Fluorescence at λ_{ex} 360 nm

Figure 3.9 Fluorescence at λ_{ex} 270nm

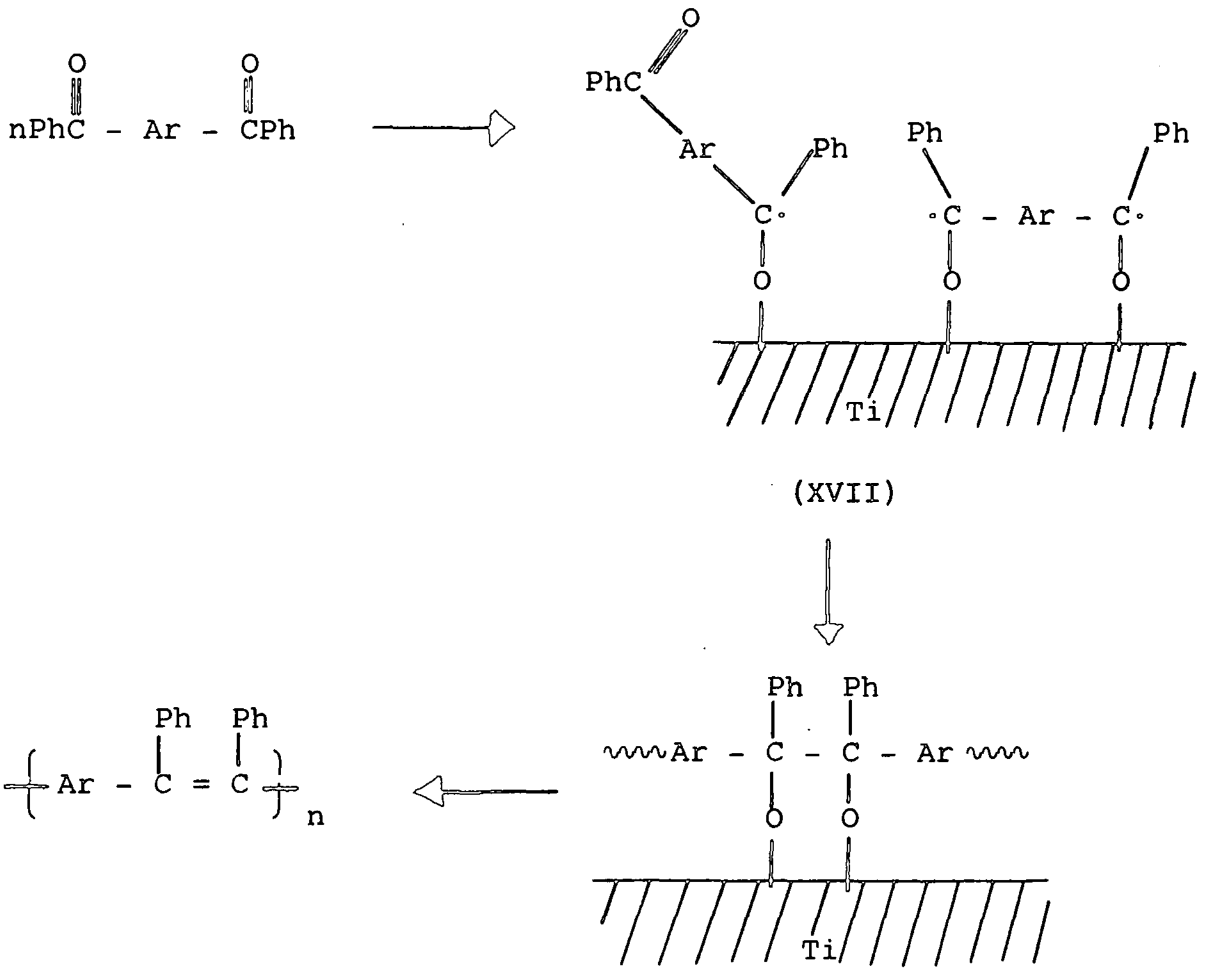


3.3 Discussion

The synthesis of conjugated polymers by reductive coupling of dicarbonyl compounds has been shown to be possible. Genuine polymers can be made although the condition of one component of the reagent system, $TiCl_3$ has been shown to be critical to the attainment of high molecular weights. Even new batches of this compound sometimes failed to give an active reagent mixture. McMurry *et al*[93] have observed that when $TiCl_3$ has deteriorated as a result of contact with air, it begins to fume. This was sometimes observed even for newly acquired $TiCl_3$ samples opened in the glove box. In general, it was found that if the $TiCl_3$ fumed in the glove box, it did not act as an effective coupling agent.

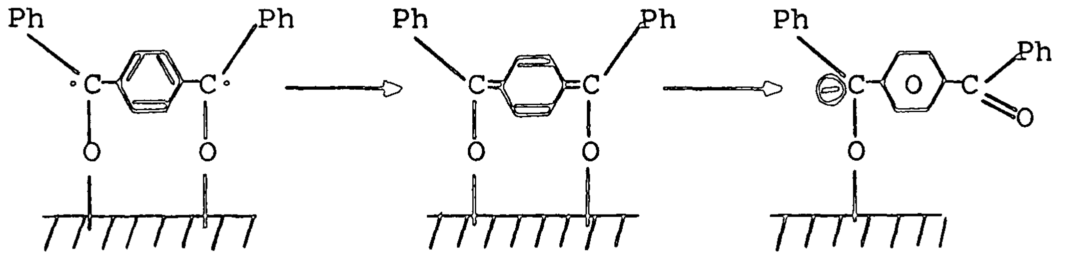
The polymerization of terephthalaldehyde yielded a product which appeared to contain some residual hydroxyl groups, this polymerization has been reported previously.[23] The product was described as a yellow, insoluble powder, our observations confirmed this. The previous workers reported infra-red peaks at 835cm^{-1} (para substituted benzene ring), 976cm^{-1} (out-of-plane CH deformation for a trans ethylenic double bond) and 1620cm^{-1} (stretching for a C=C bond conjugated with aryl groups). The spectrum of our product possessed the peaks at 835 and 960cm^{-1} but no detectable 1620cm^{-1} peak, and in addition there was a weak hydroxyl stretching peak at 3,550-3,100cm^{-1}. This suggests that under our reaction conditions the pinacol only was formed with very little ethylenic double bonding. This may have been due to the variable quality of the $TiCl_3$ because, by this stage in the work, the model reaction had been shown to give a good yield of alkene. By contrast, the failure of p-dibenzoylbenzene to polymerize to the conjugated structure did not seem to be related to the vagaries of the reagent since many polymerizations of this monomer were attempted, only the two most successful (in terms of residual hydroxyl stretching peaks in the IRs) were reported in the experimental section. Furthermore, the reaction was performed at the same time as the successful p,p′-dibenzoyl diphenyl polymerization with the same batch of $TiCl_3$. The reasons for the failure of this monomer to polymerize as successfully as the diphenyl analogue are not obvious. The mechanism of the reaction for mono carbonyl compounds was discussed in Section 3.1, page 61 . Extending this to diketones the processes shown in Scheme 3.6 can be envisaged.

Scheme 3.6 <u>Possible Steps in Diketone Reductive Coupling</u>



(XVII)

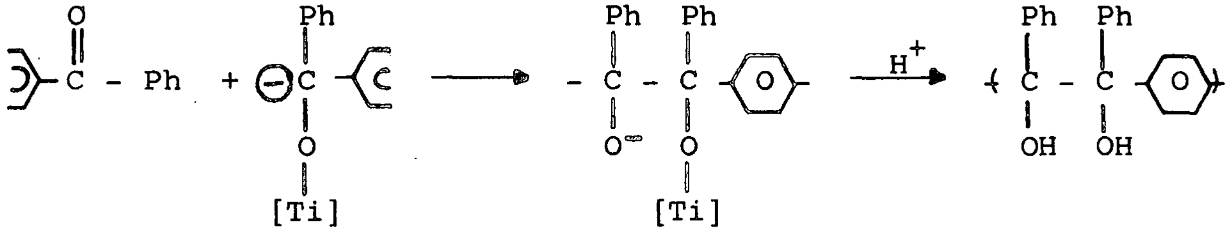
If the existence of molecules bonded to the titanium surface at both functional groups is assumed, as shown in (XVII) above, a possible explanation becomes apparent. For p-dibenzoylbenzene bonded in this way to the catalyst surface two conjugated ketyl species are present. It could be that the electron rearrangement shown below occurs.



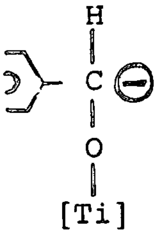
(XVIII)

(XIX)

The species (XIX) is analogous to the carbanion invoked by McMurry *et al* for mixed aryl and aliphatic couplings[102] (see Section 3.1, page64) a similar carbanion has also been shown to be involved in fluorenone couplings.[103] The charge on (XIX) should be stabilized to some extent by the adjacent aromatic rings. This moiety would then be available for nucleophilic attack as shown below, the final step being hydrolysis in the work up.



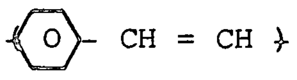
Alternatively the precursor to (XIX) shown above (XVIII) would give p-bisbenzhydrol on hydrolysis which would also account for the large hydroxyl peak observed in the infra-red spectra of the products. For the other monomers polymerized in these studies there is less conjugation between the two functional groups thus analogous structures to (XVIII) and (XIX) are unlikely to be accessible. Terephthalaldehyde gives a better conversion to polymer than p-dibenzoylbenzene, this is probably because the carbanion shown below (XX) would not be expected to be as stable as (XIX).



(XX)

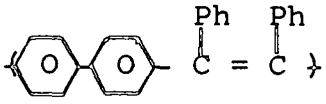
The two molecular weight determination techniques used, provide, between them, an estimate of the true polymer molecular weights. The results obtained by gel permeation chromatography will be overestimates, for two reasons, firstly only the main large peak of each trace was used in the calculations and secondly, the elution volumes were compared directly to poly(styrene) values. It is very unlikely that a polymer with a structure like that of PBV would possess an equivalent hydrodynamic volume to that of poly(styrene). PBV molecules will be rigid and rod-like whilst an average poly(styrene) chain coils up into a spherical shaped particle. Consequently PBV will not be retained in the pores of the gel as well as poly(styrene) thus it will emerge from the column more quickly and give an artificially high value of d.p. However, an idea of the distribution of weights was obtained and any effect of residual THF was negated by using THF as the column eluent. On the other hand vapour pressure osmometry results will have been affected by residual THF since the solvent used was chloroform. This technique will also have accounted for the telomeric components of the samples thus the results given are underestimates of the actual d.ps. of the polymers. In addition the number average molecular weight of a polymer is inherently sensitive to the amount of low molecular weight material in the sample. In any event these results prove that true polymers are obtainable by this method of polymerization. The values of polydispersity obtained by g.p.c. are mostly consistent with those given for other condensation polymers, that is, around 2.

The conductivity and band-gap phenomena observed for the PBV-AsF_5 adduct are typical of a semiconductor material. In the doping studies a very slow uptake of AsF_5 occurred. The resulting conductivity is similar to that found for an equivalent uptake of AsF_5 by poly(p-phenylene vinylene), as reported by Wnek *et al.*[51] This comparison is shown below.



5.6% AsF_5

$\sigma = 4.3 \times 10^{-5}\ \Omega^{-1}\ cm^{-1}$

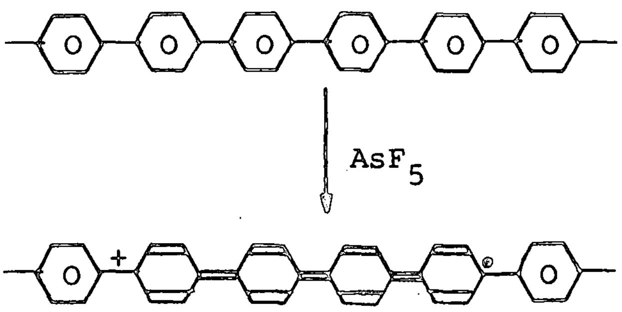


5.2% AsF_5

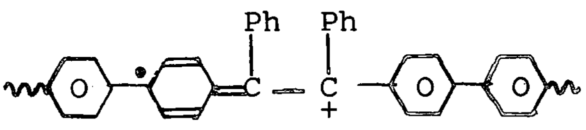
$\sigma = 3.5 \times 10^{-5}\ \Omega^{-1}\ cm^{-1}$

On doping with 57% AsF_5 a value of about 3 $\Omega^{-1}\ cm^{-1}$ was obtained by these workers. The slow rate of dopant uptake for PBV may have been due to the fact that a film sample was used. This will be rather dense, it may prove more effective to dope a pressed powder or solution sample. In view of the initially fast uptake then the slowing of rate of weight gain it is likely that most of the doping has occurred at the surface of the film and after a surface layer of PBV-AsF_5 has formed penetration of more AsF_5 becomes difficult. In this case the value of y would be much higher at the surface than in the interior of the film. On recovering the doped polymer a sample of it was added to chloroform, a yellow solution containing some undissolved brown particles resulted. This observation supports the surface doping proposal, the inner undoped bulk of the material being soluble and giving the yellow colour of the solution whilst the doped surface would be the source of the brown insoluble material. It is not unusual for soluble polymers to become insoluble on doping. Iodine doping had no effect on the AsF_5 doped sample, Wnek *et al* report that iodine does not affect poly(p-phenylene vinylene) conductivity because iodine is not a strong enough electron acceptor to interact with such systems.

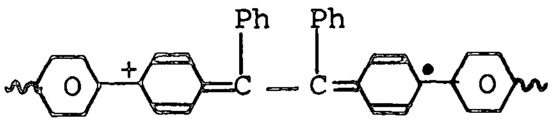
The optical absorption spectrum of the AsF_5 doped polymer shows two new peaks developing at 0.8 eV and 2 eV. The development of similar "mid-gap" bands are observed on acceptor doping of other conjugated polymers although in these cases only one peak develops, for example poly(p-phenylene sulphide) has its main absorption peak at 3.6 eV and a single peak develops at about 1.2 eV on acceptor doping. The observation of two peaks is not so common and suggests that two mid-gap conduction bands are created by doping. As discussed in Chapter One poly (p-phenylene) is thought to become more conducting when the dopant creates polarons by removal of electrons resulting in processes such as that shown below.



For PBV similar processes can be envisaged; but, since the repeat unit has differing structural units, it may be that the radical or cationic entities can be located (trapped?) at different sites. For example, two possibilities for the removal of an electron from the chain are denoted by (XXI) and (XXII) below.



(XXI)



(XXII)

The studies of electrical conductivity upon doping are continuing and it is hoped that improved results will be obtained by solution -phase or pressed-disc doping. With higher uptakes of electron acceptor we believe that an electrical conductivity of up to $\sim 1\Omega^{-1}$ cm^{-1} may be possible. These materials may be potentially useful for applications where semiconductors are currently used, for example in electronic devices.

The photophysical investigations of PBV have revealed a broad fluorescence band centred at 510nm which is responsible for the green colour on shining a UV lamp on samples of the polymer. The weak peaks at shorter wavelengths observed in some of the spectra are probably due to fluorescence of the telomeric components. The fluorescence lifetime could not be determined due to experimental problems but it was thought to be very short, probably less than 50 ps. Measurements of the fluorescence quantum yield were not available to any accuracy but this was found to be very low. Studies on free-standing film samples gave similar results to those measured in solution. All these obtained spectra displayed broad, structureless bands, this is characteristic of large conjugated systems and polymers in general. Low quantum yields and short fluoresence lifetimes are also usually observed for materials of this type. It has been suggested that poly(arylene vinylene)s may be of potential use as photoconductors[114b] although they would need to replace existing systems such as poly(N-vinyl carbazole)-trinitrofluorenone, which is used in electrophotographic applications, for example photocopying machines.

In conclusion, a relatively cheap, new synthetic route to substituted poly(arylene vinylene)s has been developed and shown to give polymers with interesting electrical and photophysical properties. These polymers fulfil some of the requirements lacking in many other conjugated polymers, for example, good solubility and reasonable air stability (films of PBV were left in air for about 1 week before infra-red spectra began to show signs of oxidation occurring) and it is not unreasonable to assume that in any subsequent uses of these polymers addition of anti-oxidants might stabilize them. Due to the brittleness of the films a plasticizer would also be needed if these materials were to be used in film form.

As mentioned, the conductivity work is continuing and different doping methods are to be tried. This is also true for the photophysical studies, determinations of fluorescence lifetime and quantum yield are to be made. Other further work is possible, preparative gel permeation chromatography could be used to isolate the high molecular weight constituents of the samples. For a better idea of the photoconductivity of the polymers, measurements of such parameters as excitation energy for photoconductivity and carrier mobility are required. It would be interesting to compare these values to those obtained by Hörhold *et al* for poly(arylene vinylene)s synthesised by the dechlorination route.

Determination of the stereochemistry of the vinylene double bond would also be of interest in view of the earlier discussed findings of Lenoir and Burghard[100] and Leimner and Weyerstahl[95] (see Section 3.1 p. 62) for aromatic monoketones. This information is not available by infra-red since the double bonds are fully substituted and symmetrical but Raman spectroscopy should be more successful in showing peaks for the double bond and from the wavenumber the stereochemistry should be obtainable, unfortunately this technique was not available at the time of writing.

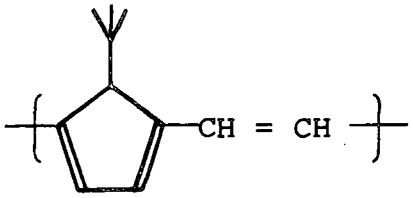
CHAPTER FOUR

SYNTHESIS OF NEW POLYMERS AS PRECURSORS FOR POLYCONJUGATED SYSTEMS BY RING-OPENING POLYMERIZATION

4.1 Introduction

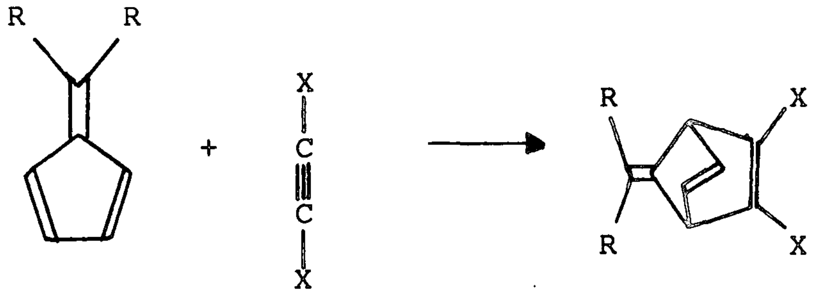
4.1.1 Objectives of this Work

The aims of the studies reported in this chapter were to prepare and characterize conjugated polymers with the repeat unit shown below.



It was hoped that these would display the desirable properties of conjugated systems already discussed in Chapter One. The synthetic route to be used is outlined below.

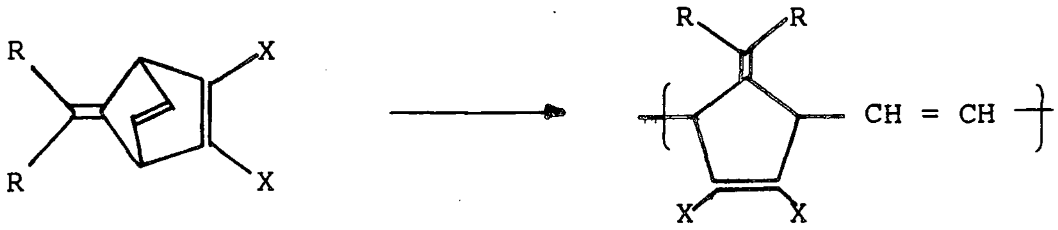
Stage 1 - Preparation of bicyclofulvenes by Diels-Alder addition:



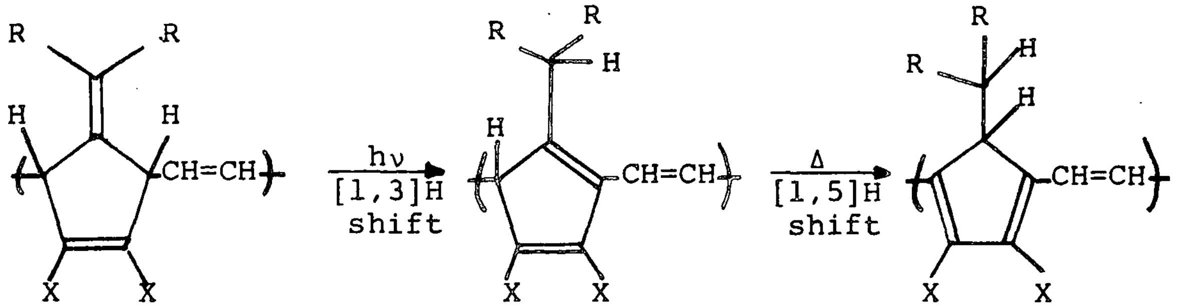
R = Me, Ph

X = CF_3, CO_2Me

Stage 2 - Ring-opening polymerization using a metathesis catalyst:



Stage 3 - Sigmatropic hydrogen shifts induced by light and heat

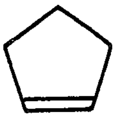


If successful this would be a novel isomerization route to conjugated polymers.

4.1.2 Ring-Opening Metathesis Polymerization

It is well established that cyclic alkenes can be polymerized by use of certain reagents which are effective for metathesis of acyclic olefins. The olefin metathesis reaction and its extension to the polymerization of cyclopentene are shown below.

$$R - CH = CH - R + R' - CH = CH - R' \longrightarrow 2R - CH = CH - R'$$



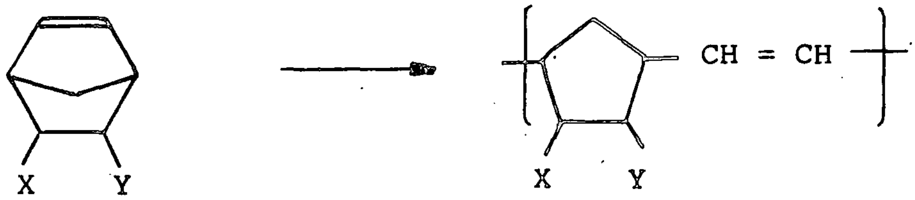
$$\longrightarrow \left(CH_2CH_2CH_2 - CH = CH \right)$$

Catalysts used to effect such transformations can be heterogeneous or homogeneous. Heterogeneous catalysts are commonly comprised of an oxide, sulphide or carbonyl of tungsten, molybdenum or rhenium supported on alumina or silica along with other additives designed to minimise catalyst poisoning. Homogeneous catalysts generally consist of a derivative of tungsten, molybdenum or rhenium often with an added cocatalyst to increase the activity. For cycloalkene polymerizations homogeneous catalysts are generally employed.

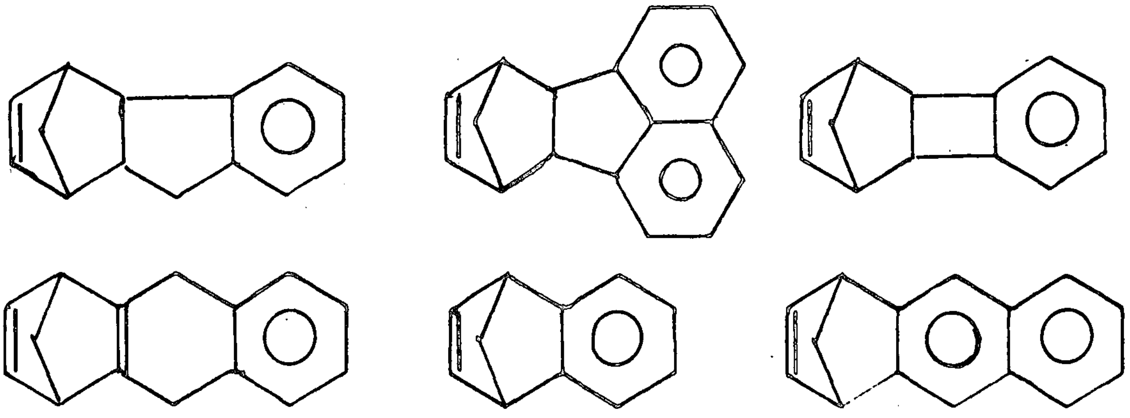
It has been found that four, five, seven, and higher, membered ring cycloalkenes can be polymerized successfully. Three membered rings are more difficult to polymerize whilst cyclohexenes are completely inert to this type of ring-opening.

(a) Ring-Opening Polymerization of Norbornene Derivatives

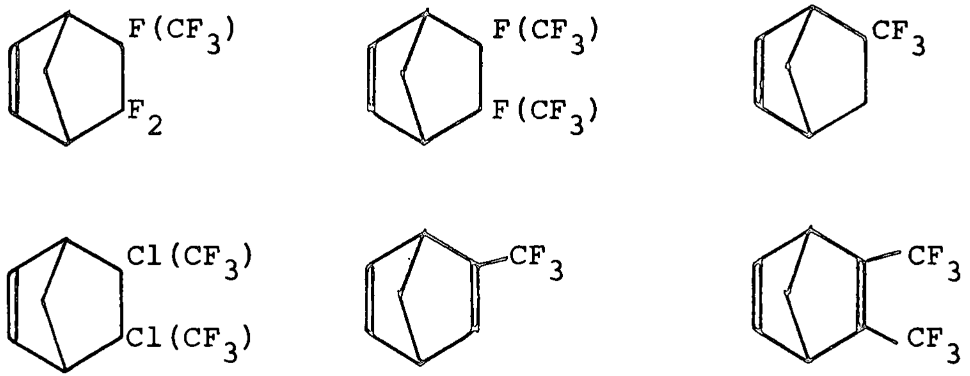
Bicyclo[2,2,1]hept-2-ene, henceforth referred to as norbornene, is easily polymerized by ring-opening due to the resultant release of ring strain. Many 5 and/or 6 substituted derivatives have been polymerized in this way, the reaction is shown below.



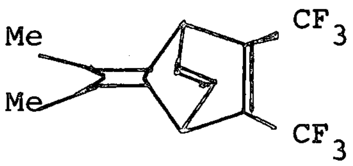
Functional groups incorporated in monomers of this type include esters[130], carboxylic acid,[131] nitrile[130,132], chloromethyl[132,133], amide[130,134], alcohol[131], imide[130,135], aldehyde and keto[130], anhydride[130], pyridyl[130], alkyl[136], phenyl[137] and the aryl substituted derivatives shown below.[138,139,140]



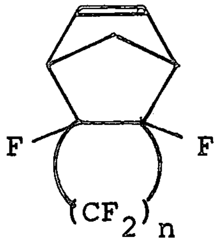
Fluorinated monomers have also been shown to be polymerizable, the monomers shown below were all successfully polymerized in these laboratories.



ref. 142



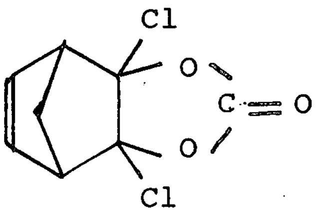
ref. 141



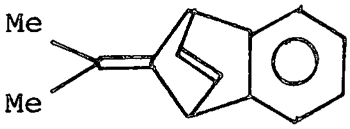
n = 2,3

ref. 143

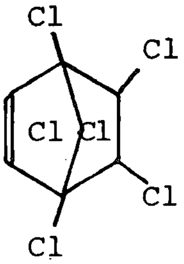
Other norbornene or norbornadiene derivatives which have been polymerized are shown below.



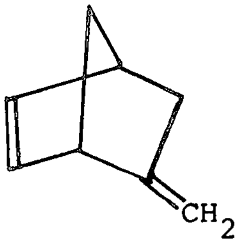
ref. 144



ref. 139



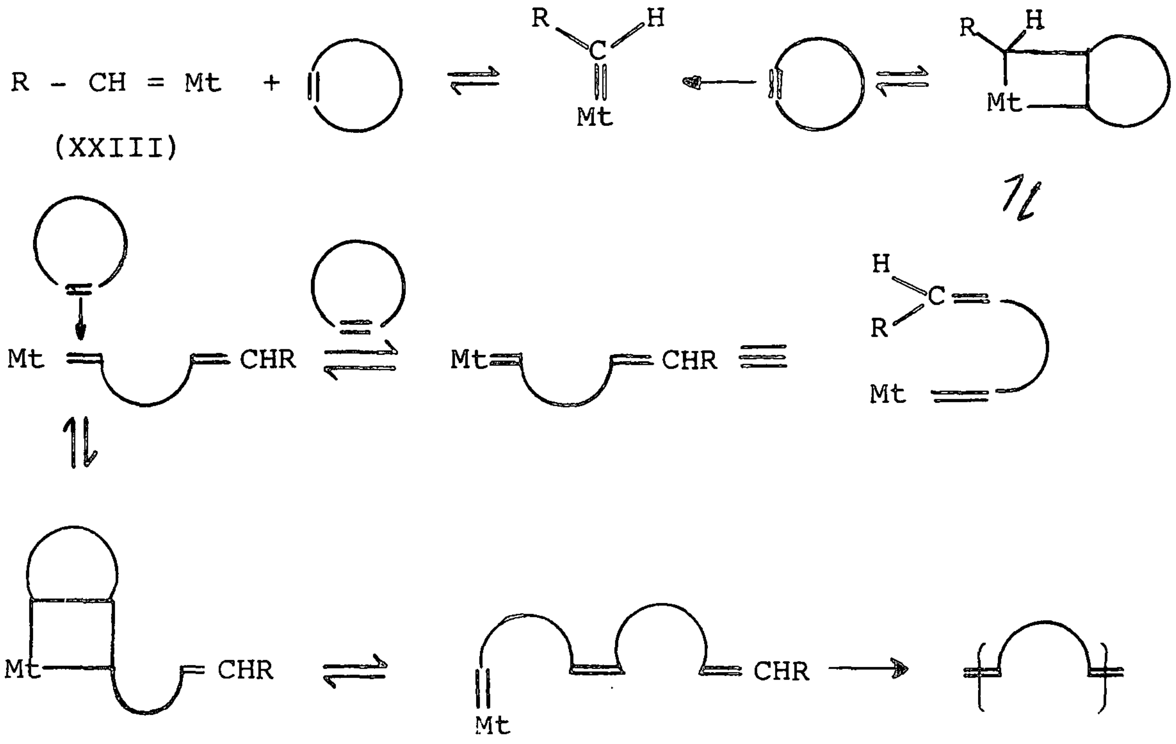
ref. 145



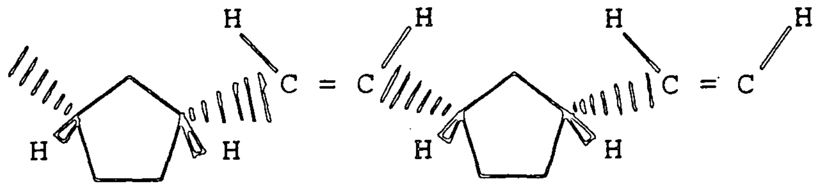
ref. 146

(b) Mechanism of Metathesis Ring-Opening Polymerization

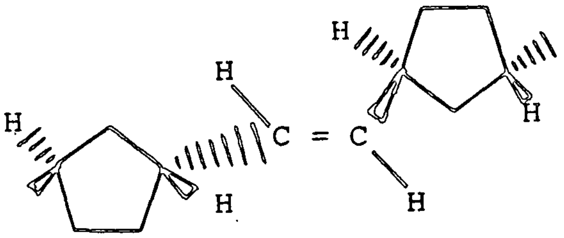
Olefin metathesis is generally believed to occur by a mechanism involving a carbene as the chain carrier and proceeding via metallacyclobutane intermediates[147] as shown below for a monocyclic olefin.



A variety of routes have been suggested to account for the generation of the metal carbene species (XXIII) in the reaction mixture.[101,148] This reacts with a coordinated alkene to form a metallacyclobutane which cleaves to generate another metal carbene species at the chain end. The primary evidence for this mechanism is the fact that metal carbenes themselves can be used as catalysts for the reaction.[149,150] Ivin *et al*[151] have studied the stereochemistries of the polymers produced, for norbornene and some substituted chiral derivatives of norbornene, and have found that for different catalyst systems different stereochemical assemblies occur. For norbornene itself[151] the possibilities are that the double bond can be cis or trans and the ring placement can give rise to different tacticities, two of these possibilities are shown below.

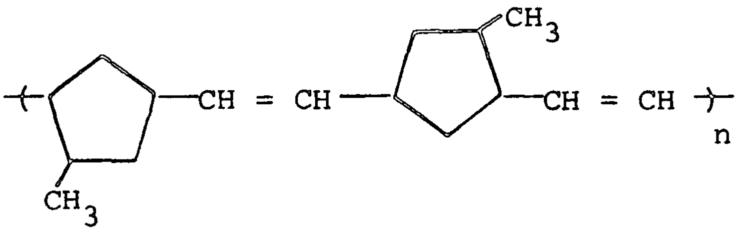


cis - isotactic

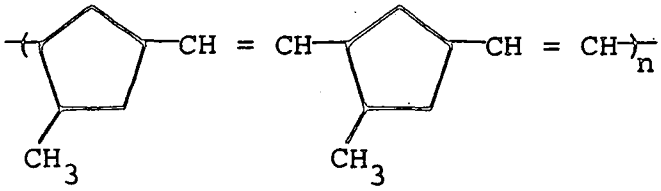


trans - syndiotactic

For unsymmetrical norbornene derivatives such as 5-methyl norbornene further permutations are introduced, the rings can be placed either head-head/tail-tail or head-tail; two possibilities are shown below,[136,152] for polymers derived from an isomer of 5-methyl norbornene.



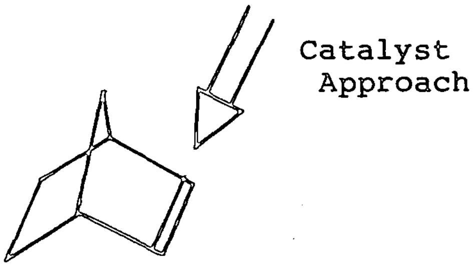
head-head/tail-tail, syndiotactic



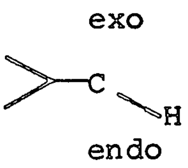
head-tail, isotactic

Ivin *et al* have established the presence of a number of different structural possibilities in polymers produced by metathesis ring-opening using carbon 13 n.m.r. spectroscopy as the structural probe and have identified which catalysts induce a particular stereochemistry in the polymers.[136,151] These workers have postulated[152] detailed mechanisms for these polymerizations. For the case where an immobile (non-rotating) metal carbene is the initiating species the results obtained lead to the conclusion that two types of metal carbene may be present, one is chiral and octahedral and gives cis-syndiotactic stereochemistry, the other is achiral and gives mainly trans polymers. The presence of either type is dependent on the detailed composition of the catalyst system, temperature and monomer concentration.

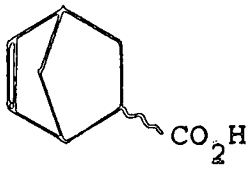
For norbornenyl systems the direction of metal carbene approach to the monomer is believed to be from the exo face as shown below.

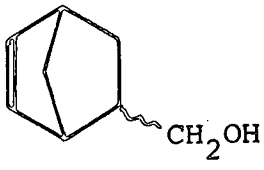


This is consistent with other reactions which occur at the 2,3 bond. For example the results of electrophilic addition may be rationalized by initial approach of the electrophile at the exo face of norbornene, eliminations from norbornanes occur synperiplanar on the exo side of the 2,3 bond and exo attack is preferred for nucleophilic substitutions of 2 substituted norbornanes. It has recently been suggested that in the ground state the C-H bonds at the 2 and 3 positions are bent down into the endo face as shown below, this was suggested as the reason for the preferred exo reactivity of the norbornene double bond.[153]

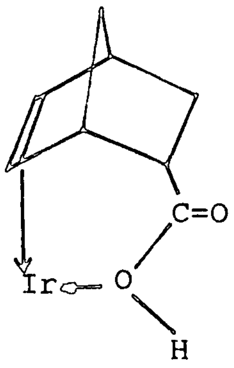


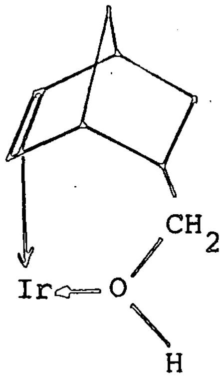
In ring-opening polymerizations of derivatives of norbornene it has been found that some 5-endo substituents inhibit formation of polymer. For example, for the monomers shown below only the exo forms would polymerize using a catalyst of $IrCl_3 . 3H_2O$-ethanol.[131]



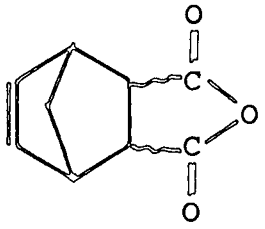


The explanation offered was preferential formation of the complexes shown below.



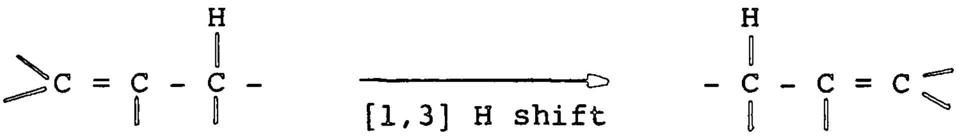


Similar results were found recently[154] for the exo/endo isomers of the monomer shown below.

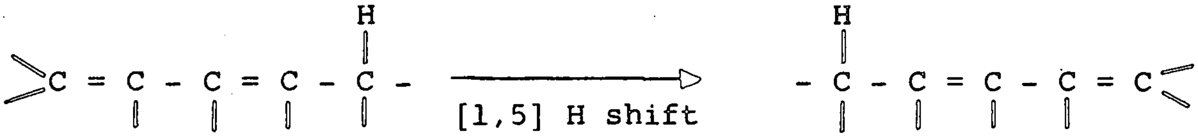


4.1.3 Sigmatropic Migrations of Hydrogen

Uncatalysed migrations of hydrogen atoms along a conjugated system can occur by concerted processes known as sigmatropic rearrangements. For polyenes, the two most commonly observed hydrogen shifts are the [1,3] and [1,5] migrations illustrated below.



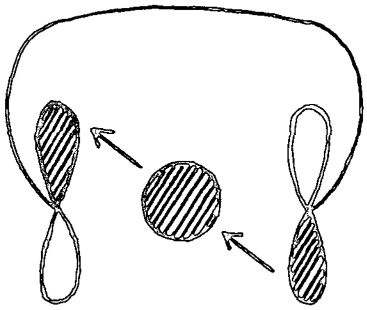
$$>C=\underset{|}{C}-\underset{|}{\overset{\overset{\mathrm{H}}{|}}{C}}- \xrightarrow[\text{[1,3] H shift}]{} -\underset{|}{\overset{\overset{\mathrm{H}}{|}}{C}}-\underset{|}{C}=C<$$



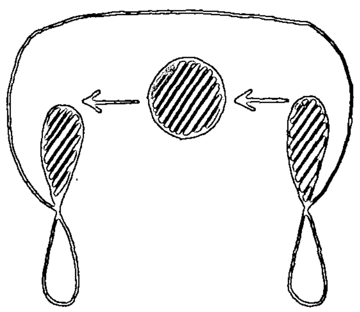
$$>C=\underset{|}{C}-\underset{|}{C}=\underset{|}{C}-\underset{|}{\overset{\overset{\mathrm{H}}{|}}{C}}- \xrightarrow[\text{[1,5] H shift}]{} -\underset{|}{\overset{\overset{\mathrm{H}}{|}}{C}}-\underset{|}{C}=\underset{|}{C}-\underset{|}{C}=C<$$

It is found that the [1,3] shift occurs when energy is supplied by light whilst the [1,5] shift occurs on heating the diene system.

These findings can be rationalized by Frontier Orbital Theory,[155] according to which the migrating hydrogen must move between orbitals with the same phase(sign) of their wave function, and the shift must occur in the highest occupied molecular orbital (HOMO) of the molecule. This can occur in two ways; antarafacially-movement across the π system, or suprafacially-movement along one face of the π system. This is shown below.

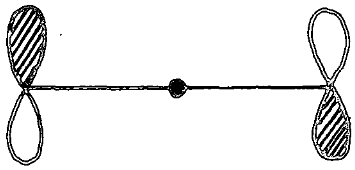


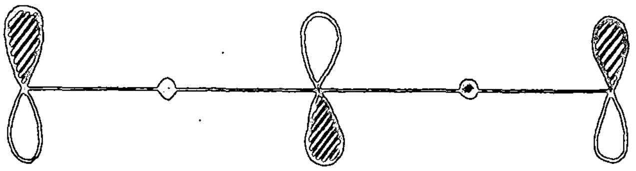
antarafacial
migration



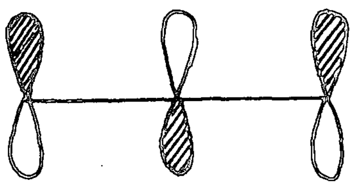
suprafacial
migration

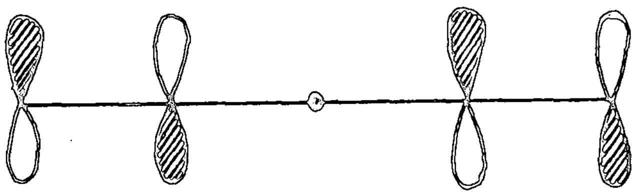
For the propenyl and pentadienyl systems the HOMOs are shown below.





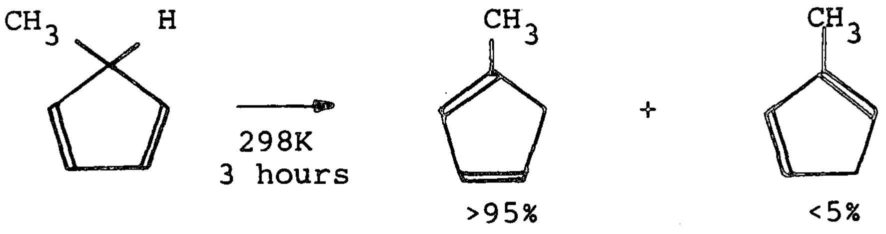
It is evident that for [1,3] shifts an antarafacial process is required whilst for [1,5] shifts the migration must occur suprafacially. However, for a photochemical reaction the excitation of electrons results in occupancy of the orbitals shown below (i.e. the ground state lowest unoccupied molecular orbitals or LUMOs) and thus the stereochemical requirements for migration are reversed.



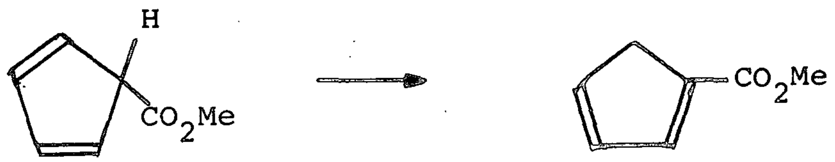


Antarafacial migrations are not common since the transition state required is usually very strained and energetically unfavourable, thus hydrogen shifts usually occur suprafacially. Hence, from the above discussion it is clear that [1,3] shifts will preferentially occur photochemically and [1,5] shifts thermally.

Many thermal [1,5] H shifts have been observed, the type relevant to this thesis is the [1,5] shift in cyclopentadienes. It has been observed, in attempted syntheses of 5 substituted cyclopentadienes, that the products are usually the 1 and/or 2 substituted analogues,[156] this is caused by [1,5] H shifts occurring at the reaction temperatures. 5-Substituted isomers have been prepared at low temperatures but on warming to room temperature the rearrangement occurs. An example is the rearrangement of methyl cyclopentadiene shown below.[156,157]



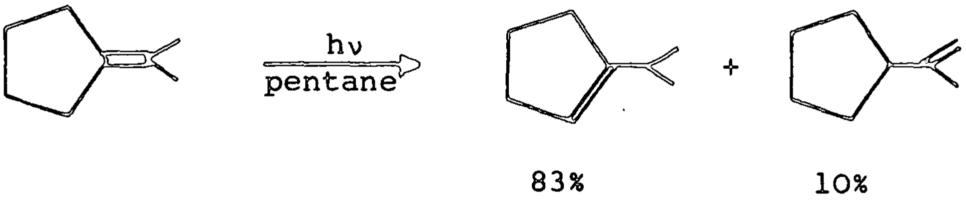
When there are possibilities of the conjugation of the diene being extended the 1 isomer is almost exclusively formed[156] as in the examples shown below.



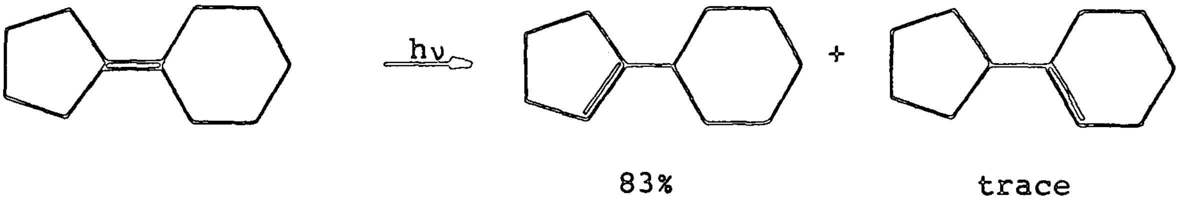
ref.158

ref.159

[1,3] - Photochemical H shifts resulting in the movement of an exocyclic double bond into a ring system have been observed.[160] For dimethyl methylidene cyclopentane an 83% yield of the endo-cyclic alkene was produced as shown below.



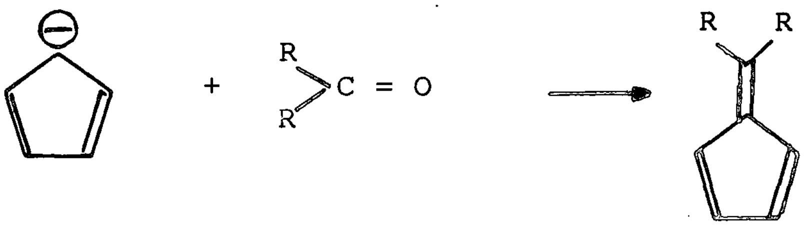
In this example the thermodynamically more stable (substituted) alkene is preferentially formed, however in the example shown below, migration into the five-membered ring rather than the six-membered ring is preferred.



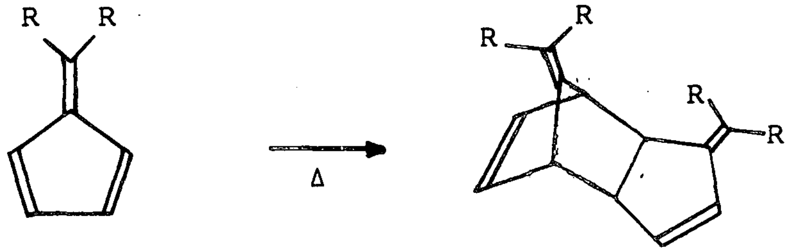
The reason for the preferred migration into the five-membered ring has not been adequately rationalized although it was suggested that in the cyclopentene a low-lying $\pi \rightarrow \sigma^*$ excited state is created due to σ strain and this is responsible for this behaviour.

4.1.4 Preparation of Monomers

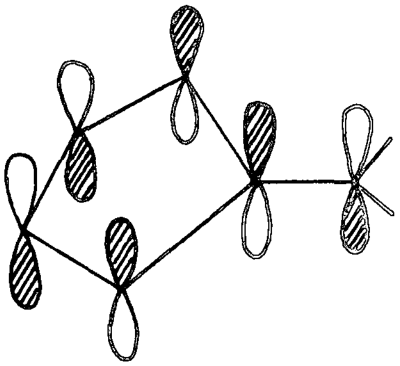
During the course of preparing the monomers for these studies a new method of preparation of 6,6 disubstituted fulvenes was developed. The preparation of these compounds is achieved by condensing the anion of cyclopentadiene with the appropriate ketone as shown below.



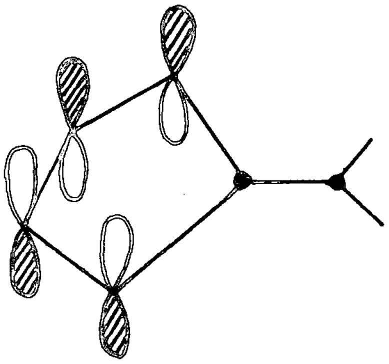
In the established procedure[161] the anion is generated by treatment with sodium in methanol, however, in the author's hands only low yields (∿10%) could be obtained using this method. The modification of this reaction, which was used to produce a 54% yield of diphenyl fulvene, was to use solid sodium methoxide in benzene with added 18-crown-6. The latter reagent acts as a phase-transfer catalyst and presumably makes Na^+ ions more available for cyclopentadiene anion formation. The reaction was carried out at reflux, the time of reflux was found to be critical to the yield obtained, too short a reaction time resulting in reduced yields and too long a heating time giving mainly a compound which was assumed to be the product of dimerisation of the fulvene as shown below.



The monomers for these studies were prepared by Diels-Alder additions of 6,6-disubstituted fulvenes to disubstituted acetylenes. For fulvenes the HOMO and LUMO are as shown below.[162]



LUMO



HOMO

For such cycloadditions suprafacial approach at both attacking points is necessary to avoid highly energetic steric contortions. Frontier orbital theory predicts that supra-supra addition is a thermally allowed process for the addition of fulvenes to acetylenes.

4.2 Experimental

4.2.1 Preparation of Fulvenes

(a) 6,6-Dimethylfulvene

A three-necked flask was fitted with a mechanical stirrer, condenser and dropping funnel. Freshly distilled cyclopentadiene (80 ml) and analar acetone (70 ml) were added and the solution cooled to about -5^{o}C in an ice-salt bath. To this mixture was slowly added a solution of KOH in absolute ethanol (20% w/v, 35 ml) and the mixture was stirred at room temperature overnight. To the resulting black solution was added water (250 ml) and the product was extracted with methylene chloride (2 x 200 ml). The combined extracts were washed with water until the washings were neutral. The deep red-brown solution was dried over sodium sulphate, filtered and the solvent evaporated. The residue was distilled (59-60^{o}C, 10mm Hg) yielding 6,6-dimethylfulvene as a yellow oil (38.2g, 37.1%). The infrared spectrum is given (Appendix 1, No.23).

(b) 6-Methyl-6-phenylfulvene

The method of Kice and Parham[163] was used. A three-necked flask was fitted with a condenser, dry seal, dropping funnel, mechanical stirrer and nitrogen inlet. Absolute ethanol (75 mls) and sodium (5g) were reacted together in the flask and a mixture of acetophenone (24 ml) and cyclopentadiene (16.5 ml) was slowly added with nitrogen purging over a period of 1 hour. The mixture was left to stir for 3 hours at room temperature to give a deep red solution which was added to water (250 ml) and extracted with methylene chloride (2 x 200 ml). The combined organic extracts were washed with water until the washings were neutral and dried (Na_2SO_4), filtered and rotary evaporated to give a deep red oil which was vacuum distilled using a Vigreux column (35cm x 2cm) to give 6-methyl-6-phenyl fulvene (16.61g, 49.4%) with b.pt. 68-72°C, 0.15mm as a light, red oil. The infra-red spectrum is given (Appendix 1, No.24).

(c) 6,6-Diphenylfulvene

As mentioned above, two methods were used for the preparation of this compound; the established procedure[161] and a new method which gives higher yields. The literature procedure is described first.

A three-necked flask containing sodium (15g) in methanol (200 ml) was equipped with two dropping funnels, a two way adaptor fitted with a condenser, dry seal and nitrogen inlet. One dropping funnel was charged with cyclopentadiene (70g) and the other with benzophenone (100g) in methanol (200 ml). The contents of the two funnels were added alternately, with shaking of the flask, over a period of 40 minutes during which time the initially colourless solution changed to deep brown. The mixture was left to stand for 30 minutes then slowly poured into a 1:1 diethyl ether-ice water mixture (1 l) in a 5l separating funnel. The organic layer was removed and the aqueous layer extracted with further ether portions (a total of 700 ml ether). The solvent was removed from the combined organic layers by rotary evaporation leaving a deep red oil. This was purified by dry column chromatography on silica with 60-80 petroleum ether as the eluent. 6,6-Diphenylfulvene (11.8g, 13%) was obtained, after recrystallizing from 60-80 petroleum ether, as red crystals m.pt. 79.5 - 80.5 (lit.[162] 81.5 - 82); found C 94.43%, calculated for $C_{18}H_{14}$, C 93.91% with correct infra-red spectrum (Appendix 1, No.25)

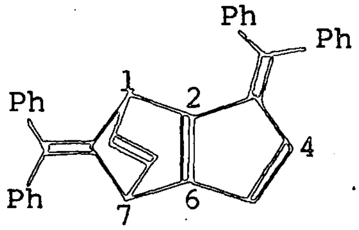
In order to try to improve the yield, the reaction was repeated using absolute (>99%) methanol and the reaction mixture refluxed gently for 1½ hours after all reactants had been added. After column chromatography an 11% yield of 6,6-diphenylfulvene was obtained.

The new method involved the following procedure.

Sodium methoxide (8g) was transferred, in a dry box, to a three-necked flask fitted with an inlet tap. The flask was stoppered, removed from the dry box and attached to a dry nitrogen line. A mechanical stirrer, condenser and dropping funnel containing freshly distilled cyclopentadiene (12.1 ml) were fitted. Benzophenone (20g), benzene (50 ml) and 18-crown-6 (2g) were added to the sodium methoxide in the flask. The diene was slowly added to the stirred mixture over a period of 15 minutes whilst a dry nitrogen stream was maintained. The colour of the solution darkened during this addition to a deep red at the end.

At this point three different reaction conditions were tried for three separate runs. These were (1) overnight stirring at room temperature, (2) refluxing for 15 minutes and (3) refluxing for 2 hours. In each case the products were filtered and the filtrate rotary evaporated to dryness, the product was purified by boiling with decolourizing charcoal in excess 60-80 petroleum ether to give the following results: procedure (1) gave diphenylfulvene (5g, 18.4%) with correct infra-red spectrum; procedure (2) gave diphenylfulvene (13.58g, 54%) with correct infra-red spectrum, and procedure (3) gave a yellow solid after the rotary evaporation stage. Method (2) appears to be the nearest to the optimum conditions for achieving high yields of the product although only the three experiments were carried out.

In procedure (3), the yellow product was probably the dimer of diphenyl fulvene. Similar yellow solids were formed on storage of diphenyl- and methyl, phenylfulvene at room temperature for more than about 2 months and also in recrystallization attempts where the boiling time was more than about 5 minutes. Storage at low temperature (<-15°C) retarded this decomposition. To investigate this, a sample of diphenylfulvene was boiled in 60-80 petroleum ether for 3 hours, the red colour disappeared and a yellow solid precipitated from the solution. After collection by filtration and drying, this material was shown to consist of at least four components by thin layer chromatography. The mass spectrum of this mixture showed the presence of a species with the same m/e as the parent ion of the dimer (460), to higher m/e values four peaks were observed at 476, 492, 508 and 524. These peaks correspond to successive additions of 16 a.m.u. to the m/e 460 peak and must be due to oxidised forms of the dimer. It seems most likely that the dimer is produced by a Diels-Alder reaction to give a structure of the type shown below.



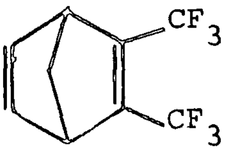
The product has probably been oxidized by air. Air oxidation would be expected to occur easily at the allylic C-H bonds at positions 2 and 6 initially resulting in hydroperoxide groups which would decompose under the conditions of reaction to give hydroxyls. For example, oxidation at position 6 would lead to hydroperoxide units at position 6 and/or 4 depending on whether singlet or triplet oxygen was involved. An infra-red spectrum (Appendix 1, No. 26) showed a hydroxyl peak at 3,450 cm^{-1} and an olefin C=C stretching frequency at 1,650 cm^{-1} as well as a carbonyl stretching peak at 1720 cm^{-1}, this carbonyl function is probably derived from the hydroperoxide formed at position 4. An n.m.r. spectrum of the mixture showed a broad, structureless band at δ6.6-7.9 assigned to aryl and alkene H's, together with a sharp resonance at δ2.12 and a series of overlapping resonances (δ1.2-0.6) with a maximum intensity at δ0.86. For the pristine Diels-Alder dimer of diphenylfulvene the integration ratio for aromatic and alkene hydrogens to aliphatic hydrogens should be 6:1, in the event this ratio was 4.3:1, this discrepancy is consistent with the partial oxidation of the dimer.

4.2.2 Preparation of Diels-Alder Adducts

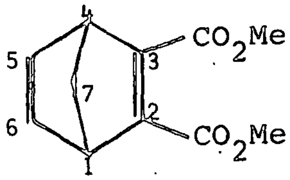
Hexafluorobut-2-yne (HFB) was used as supplied by Columbia Organic Chemicals Co. Ltd. and Fluorochem Ltd. and dimethyl acetylene dicarboxylate (DMAD) as obtained from Aldrich Ltd.

(a) Preparation of the Model Compound

The compounds shown below were the model compounds for these studies.



(XXIV)



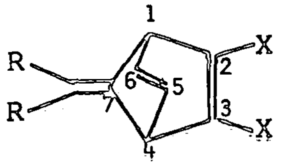
(XXV)

The metathesis polymerization of (XXIV) is well known[142] whereas reports of the polymerization of (XXV) could not be found.

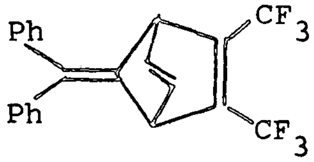
Thus, this monomer was prepared for these studies as described below.

DMAD (7.1g) and benzene (10 ml) were placed in a flask fitted with a condenser and freshly distilled cyclopentadiene (4.1 ml) was slowly added. The mixture was stirred at room temperature for three days by which time the solution was pale yellow. The solvent was removed by rotary evaporation and the residual yellow oil was purified by vacuum distillation at 72-76°C, 0.19mm Hg. The dimethyl ester of bicyclo[2.2.1]hepta-2,5-diene-2,3-dicarboxylic acid was obtained as a yellow oil (5.53g, 54%); its infra-red was consistent with the structure showing bands at 2,820-3,040 (CH str.), 1725(s) (ester C=O str.) and 1640 cm^{-1} (olefinic C=C str.), this is shown in Appendix 1, No.27. The ^1H n.m.r. spectrum showed resonances at $\delta 2.05$ (doublet of doublets, J = 6.8 Hz) assigned to the tertiary hydrogens at C_1 and C_4 coupled with the C_7 methylene which has protons in two different environments, $\delta 3.50$-4.00 (set of peaks including one intense one at $\delta 3.68$ - methyl ester and C_7 methylene protons) and $\delta 6.98$ (vinyl protons) with an integration ratio of 2:8.7:2 (correct value 2:8:2).

The systematic IUPAC names of the alkyne-fulvene Diels-Alder adducts are cumbersome so, for convenience, an abbreviated nomenclature has been adopted in this work. The abbreviation is in two parts, the first part of the name refers to the substituents on the methylidene at the 7 position of the norbornadiene skeleton, and the second part denotes the groups on the 2 and 3 positions which are shown below.

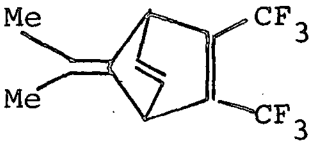


For example 2,3-bis(trifluoromethyl)-7-(diphenyl methylidene)-bicyclo[2.2.1]hepta-2,5-diene(XXVI) is abbreviated as "diPhdiCF$_3$".

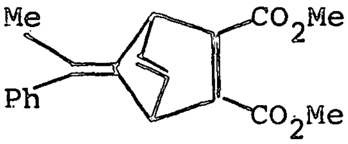


(XXVI)

Two other examples are shown below.



"diMediCF$_3$"



"MePhdiCO$_2$Me"

(b) Preparations of 2,3-Ditrifluoromethyl Monomers

The monomer diMediCF$_3$ was obtained as previously prepared by J.H. Edwards. MePhdiCF$_3$ and diPhdiCF$_3$ were prepared by the general procedure described below.

The appropriate fulvene was placed in a Carius tube and dissolved in benzene. The tube was attached to a vacuum line and HFB was vacuum transferred into it. The tube was sealed and left to stand at room temperature until the red colours had faded to a straw yellow. The tube was then frozen and opened, unreacted HFB was allowed to evaporate and the yellow products were isolated. The reaction conditions, reagent weights, methods of purification and yields are given in Table 4.1.

Table 4.1 Preparations of Ditrifluoromethyl Monomers

Preparation	Fulvene[a] /g	HFB /g	Reaction time/days	Purification procedure	Yield
$MePhdiCF_3$	2.86	3.0	3	v.52-54°C 0.175mm Hg	4.7g 83.4%
$DiPhdiCF_3$	3.93	2.75	6	r.twice (cyclohexane)	2.93g 43.7%

a. about 30 ml benzene was used as solvent

v. = vacuum distilled

r. = recrystallized

Attempts to shorten the reaction times by heating the tubes in a furnace merely resulted in the formation of insoluble yellow solids probably corresponding to the fulvene dimers discussed above.

(c) Preparations of 2,3-Dimethylester Monomers

The compounds $diMediCO_2Me$, $MePhdiCO_2Me$ and $diPhdiCO_2Me$ were synthesised by the general procedure described below.

The appropriate fulvene was dissolved in benzene and DMAD was added. The mixture was gently refluxed until the colour of the solution had changed from red to pale yellow. The solvent was rotary evaporated and the product purified. The reaction conditions, weights of reagents, methods of purifications, and yields are given in Table 4.2.

Table 4.2 Preparations of Dimethylester Monomers

Preparation	Fulvene[a] /g	DMAD /g	Reaction time/hrs.	Purification procedure	Yield
DiMediCO$_2$Me	10.5	19.8	2	r. (benzene-60/80 pet. ether) d. (benzene plus charcoal r. (benzene-60/80 pet. ether)	11.52g 46.9%
MePhdiCO$_2$Me	8.4	10.0	2.5	v. 140-143° 0.1mmHg	11.1g 71.6%
DiPhdiCO$_2$Me	11.5	10.0	4	r. twice (benzene-60/80 pet. ether)	16.7g* 89.9%

* = after one recrystallization

a. about 50 ml benzene was used as solvent

d. = decolourized, other abbreviations as for Table 4.1

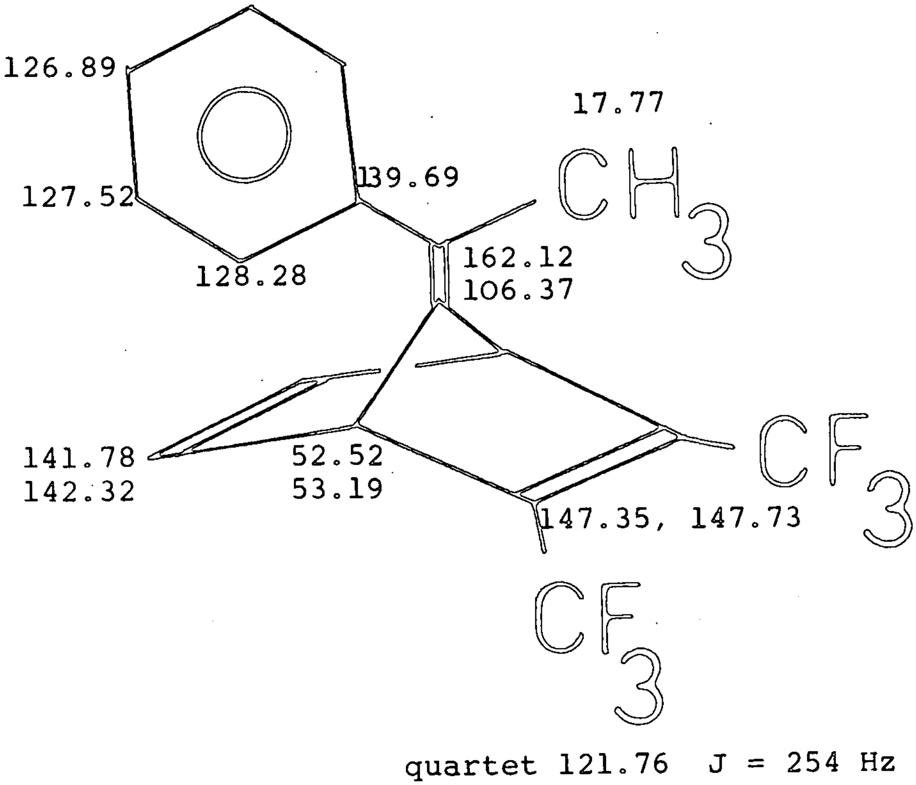
(d) Properties and Characterization of Monomers

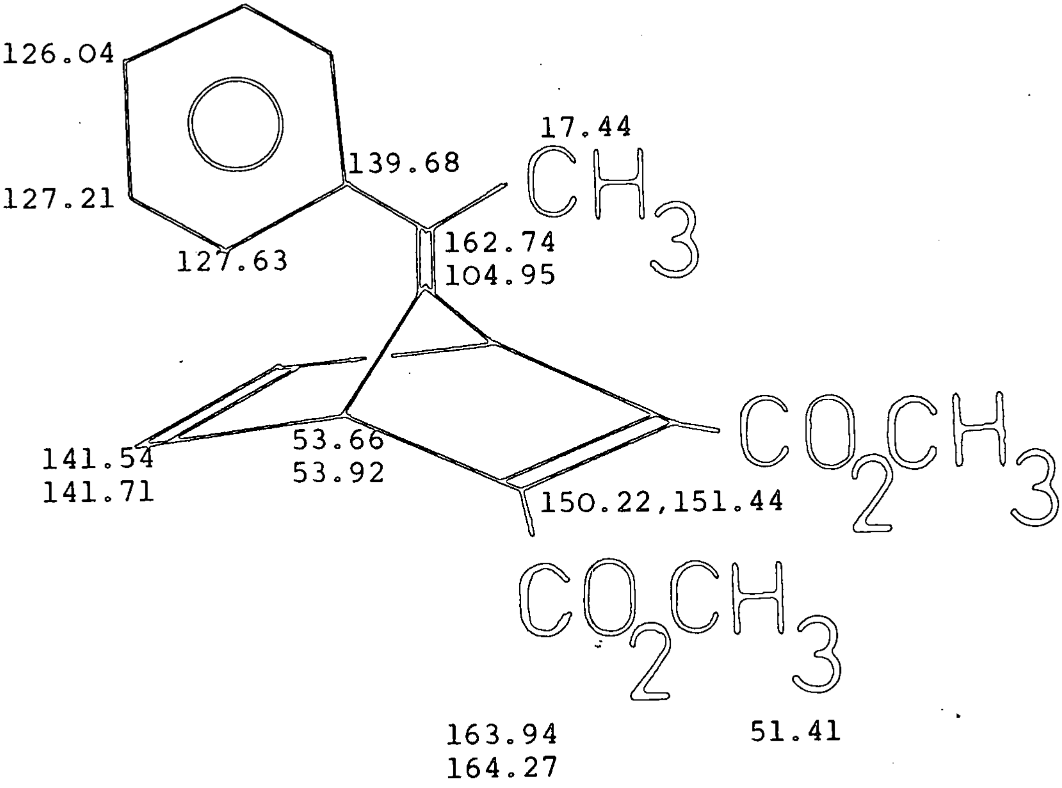
The characterization data of these products are given in Table 4.3.

TABLE 4.3 Characterization of Monomers

Monomer	Sample	Infra red Appendix 1 No.	^{1}H n.m.r. resonances/ppm	n.m.r. integration ratios		Other characterization	Reference
				calculated	found		
DiMediCF$_3$	Colourless crystals m.pt. around room temp.	28					141
MePhdiCF$_3$	Pale yellow oil	29	δ1.88 (methyl H's), δ4.32 - 4.52 (doublet, methine H's) δ 6.98-7.77 (aryl and alkeneH's)	3:2:7	3.6:2:8	^{19}F n.m.r. - one peak at 58.2 ppm (fluorines of the CF$_3$ group). ^{13}C n.m.r. (see below)	
DiPhdiCF$_3$	Colourless crystals m.pt. 83.0-84.0	30	δ4.4 (methine H's), δ6.7 - 7.55 (aryl and alkene H's)	1:6	1:6	Mass spectrum, no parent ion peak but peaks for loss of F, CF$_3$, and CF$_3$ + HC≡CH were present	
DiMediCO$_2$Me	Pale yellow crystals m.pt. 94.5-95.5^{o} (lit.101^{o})	31	δ1.5 (7-methyl H's), δ3.75 (methyl ester H's), δ4.4 (methine H's), δ6.95 (alkene H's)	3:3 :1:1	3:3 :1:1	Elemental analysis Found C67.3% H 7.1% Calculated C 67.7% H 6.5%	164
MePhdiCO$_2$Me	Viscous yellow oil m.pt. around room temp.	32	δ1.86 (7-methyl H's), δ3.80 (methyl ester and methine H's) δ6.90-7.35 (aryl and alkene H's)	3:8:7	3:8:7	^{13}C n.m.r. discussed below	
DiPhdiCO$_2$Me	Colourless crystals m.pt. 138^{o} (lit.139^{o})	33	δ3.8 (methyl ester H's), δ4.5 (methine H's), δ 6.9-7.5 (aryl and alkene H's)	3:1:6	3:1:6		164

^{13}C n.m.r. spectra were obtained of the two methyl phenyl fulvene derived monomers. The assignments are shown below.





4.2.3 Polymerizations

Two metathesis catalyst systems were used in these studies, tungsten hexachloride (as prepared in these laboratories from hexachloropropene and WO_3) with tetramethyl tin (Aldrich) and molybdenum pentachloride (Alfa Products) with tetramethyl tin. All polymerization attempts were carried out under dry nitrogen using freshly distilled chlorobenzene as the solvent. The general procedure was as described below.

Two two-necked flasks, A and B, each fitted with two inlet taps were rigorously dried and attached to a dry nitrogen line. Into flask A was placed a quantity of the monomer (100 molecular equivalents), the flask was flushed with dry nitrogen and then sufficient chlorobenzene added to dissolve the monomer. Flask B was flushed with dry nitrogen then chlorobenzene (approximately 3 ml) and tetramethyl tin (2 molecular equivalents) were added. The solutions in flasks A and B were then degassed by two freeze-thaw and evacuation cycles and both flasks were attached to the nitrogen line. Flask B was allowed to reach the appropriate reaction temperature (after fitting a condenser if necessary) then the metal halide (WCl_6 or $MoCl_5$) was added as a solution in chlorobenzene (1 molecular equivalent). This mixture was allowed to stir until the colour changed indicating that the active species had been generated. For both types of catalyst the colour of the active mixture is brown/red. The monomer solution was then added and the mixture left stirring at the reaction temperature. At the end of the reaction time the catalyst was destroyed by addition of methanol or THF (approximately 5 ml) and the products were recovered by removing solvent on the vacuum line. At this stage it was found that if polymerization had occurred a gelatinous product remained, otherwise an oil or crystalline solid was left. Polymers were purified by reprecipitation. The details of all polymerization runs are given in Table 4.4. An example of the typical scale of the reactions was run 7 where the proportions of reactants were monomer (3.86g), chlorobenzene (5 ml), tetramethyl tin (16 µl) and WCl_6 (0.29 ml of a 0.2M solution). Reactions were usually carried out in parallel with the polymerization of a monomer which was known to be polymerizable as a check on catalyst activity. In these studies norbornene and $diMediCF_3$ were used for this purpose since both polymerize with $WCl_6/SnMe_4$ and $MoCl_5/SnMe_4$.

TABLE 4.4 Metathesis Polymerization Attempts

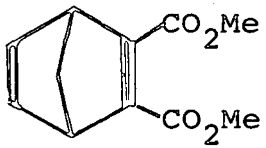
Monomer	Run No.	Catalyst System	Reaction Temperature	Reaction Time	Colour of solution after monomer added	Product
	1	$WCl_6/SnMe_4$	Room	Overnight	brown → green overnight	Yellow oil, with IR spectrum same as that of monomer
	2	"	"	"	red/brown → light green overnight	"
	3	"	"	"	red/brown light yellow instantly	"
	4	"	70°C	"	brown → light yellow overnight	Yellow oil
	5	$MoCl_5/SnMe_4$	Room	1¼ hr.	red/brown throughout	White powder after reprecipitation (THF - methanol). Film former.
$DiMediCF_3$	6	"	70°C	1 hr.	red/brown solution went viscous	White solid after two reprecipitations (chloroform-methanol). Film former.
$MePhdiCF_3$	7	$WCl_6/SnMe_4$	Room	Overnight	black → royal blue overnight	Yellow oil, same IR fingerprint as monomer
	8	"	70°C	"	brown/black throughout	Yellow oil and small amount of white powder
	9	"	"	48 hrs.	"	Yellow oil, same IR as monomer - no white powder.
	10	$MoCl_5/SnMe_4$	Room	Overnight	dark brown → turquoise overnight	Yellow oil, same IR as monomer
	11	"	70°C	35 mins.	brown	Snow white product after reprecipitation (chlorobenzene-methanol) (32% by weight). Film former.

TABLE 4.4 (Contd.)

Monomer	Run No,	Catalyst System	Reaction Temperature	Reaction Time	Colour of solution after monomer added	Product
DiPhdiCF$_3$	12	WCl$_6$/SnMe$_4$	Room	Overnight	red-black → brown – grey overnight	White crystals, same IR as monomer
	13	MoCl$_5$/SnMe$_4$	70°C	2 hrs.	dark brown throughout, became very viscous	Rubbery product insoluble in refluxing organic solvents (acetone, methylene chloride, chlorobenzene, methanol and toluene)
	14	"	"	9 mins.	"	Rubbery yellow gel – slightly soluble in benzene, soluble portion reprecipitated (methanol) to give a fine, white powder
DiMediCO$_2$Me	15	"	"	1½ hrs.	brown throughout	Crystalline solid
	16	"	"	Overnight	"	Crystalline solid, IR similar to monomer
	17	"	"	Overnight	"	Crystalline solid which gave a yellow precipitate when reprecipitated (chloroform-methanol). Difficult to tell from the IR if this was the polymer. Low yield.
	18,19	WCl$_6$/SnMe$_4$	70°C	"	"	Crystalline solid, same IR as monomer

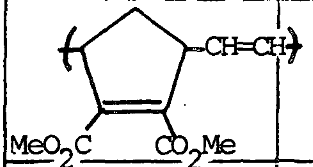
TABLE 4.4 (Contd.)

Monomer	Run No.	Catalyst System	Reaction Temperature	Reaction Time	Colour of solution after monomer added	Product
$MePhdiCO_2Me$	20	$WCl_6/SnMe_4$	Room	Overnight	brown → green black instantly	Yellow oil with IR same as monomer
	21	$MoCl_5/SnMe_4$	"	2¼ hrs.	brown → yellow after 1 hour	Yellow solid, IR same as monomer
	22	"	70°C	Overnight	dark brown throughout, viscous at end of reaction	White granules after two reprecipitations (THF-methanol and methylene chloride-methanol). Film former. (20% yield by weight).
$DiPhdiCO_2Me$	23	$WCl_6/SnMe_4$	Room	"	brown → green-blue overnight	Product with same IR as monomer
	24	"	"	"	"	"
	25	"	60°C	1½ hrs.	black/blue → brown	Solid with same IR as monomer, m.pt. 133°C (monomer 138°C)
	26	"	"	48 hrs.	"	Solid with same IR as monomer
	27	$MoCl_5/SnMe_4$	70°C	1¼ hrs.	brown throughout	Crystalline solid and small amount of white powder after adding to methanol
	28	"	"	Overnight	brown → dirty green overnight, gel had formed	White solid after reprecipitation (methylene chloride-methanol). Film former. (46% yield by wt.)

4.2.4 Characterization of the Polymers

Characterization data for the polymers are given in Table 4.5.

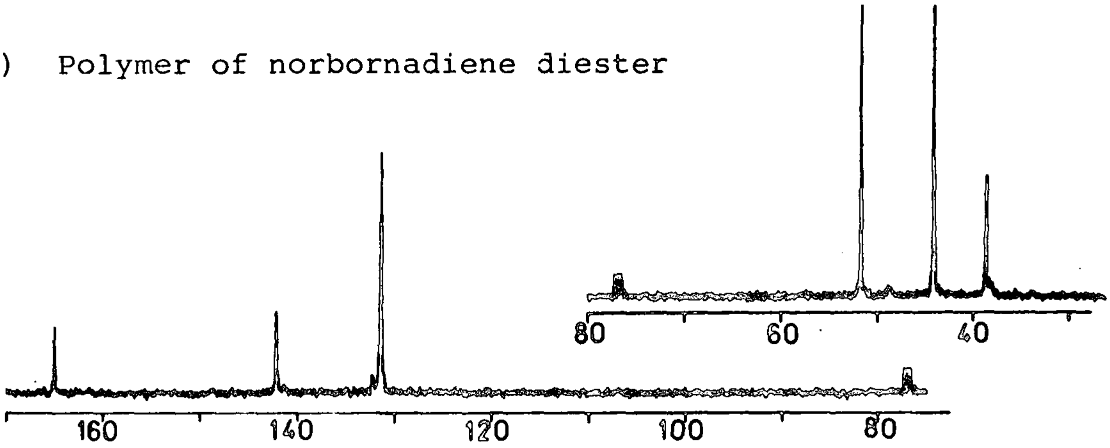
TABLE 4.5 Characterization of Polymers

Polymer	I.R. appendix 1 No.	Elemental Analysis		U.V. Spectrum	Other Characterization
		Found	Calculated		
	34	C63.1% H 5.7%	C63.5% H 5.8%		^{13}C n.m.r. spectrum see below
Poly diMediCF$_3$	35				
Poly MePhdiCF$_3$	36	C62.0% H 3.5% F 34.2%	C61.8% H3.6% F 34.5%		^{13}C n.m.r. spectrum see below g.p.c., see section 5.
Poly diPhdiCF$_3$	37				Only sparingly soluble
Poly MePhdiCO$_2$Me	38	C 72.5% H 6.8%	C 73.6% H 5.8%	242.5nm strong ($\pi\rightarrow\pi^*$ transition) 295nm weak (forbidden $n\rightarrow\pi^*$)	^{13}C n.m.r. spectrum see below g.p.c., see section 5.
Poly diPhdiCO$_2$Me	39	C 77.7% H 5.8%	C 77.4% H 5.4%	238nm (ε168,750) ($\pi\rightarrow\pi^*$)	

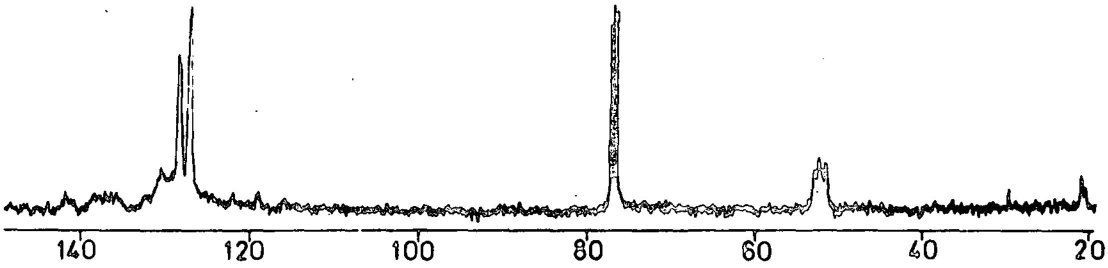
^{13}C n.m.r. spectroscopy is a powerful structural technique for polymers, in the case of these materials, the limited solubility of the products required relatively long accumulation times and consequently only three samples have been run on the high field facility provided by S.E.R.C. at Edinburgh University. The spectra are reproduced in Figure 4.1 and the assignments of the observed resonances are shown in Figures 4.2 to 4.4.

Figure 4.1 ^{13}C n.m.r. spectra of Polymers[(a)]

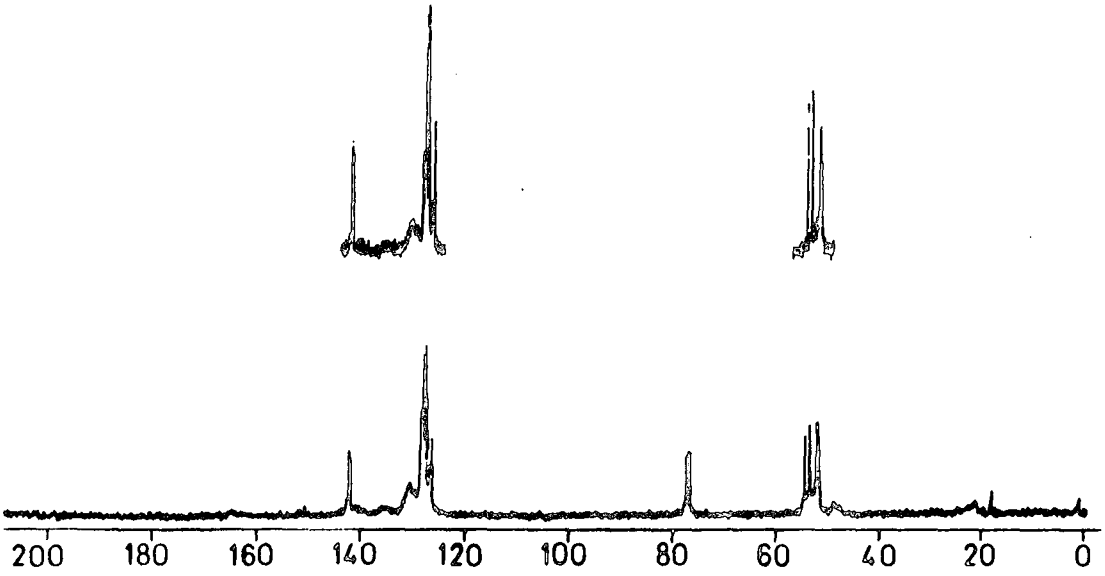
(a) Polymer of norbornadiene diester



(b) PolyMePhdiCF$_3$



(c) PolyMePhdiCO$_2$Me



(a) The solvent was CDCl$_3$ (peak at 76.9 ppm). Shifts are in ppm from TMS.

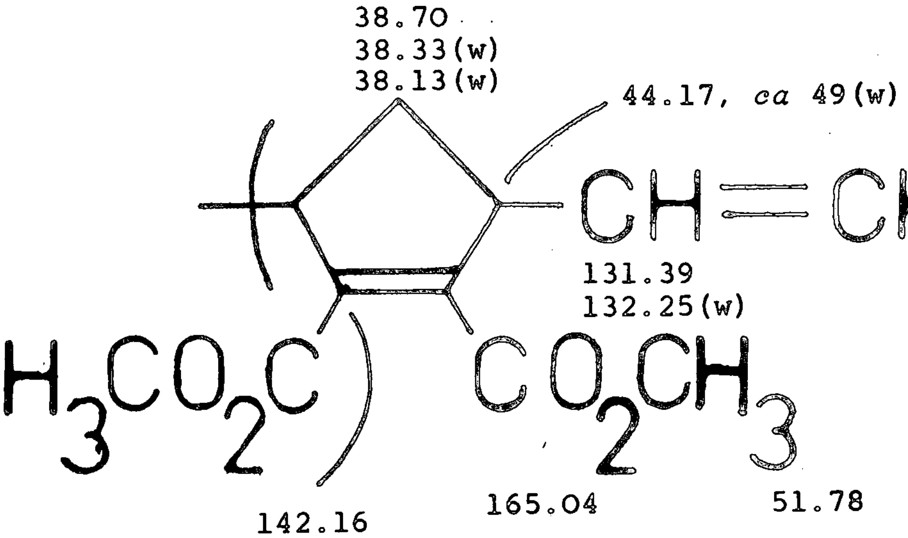


Figure 4.2

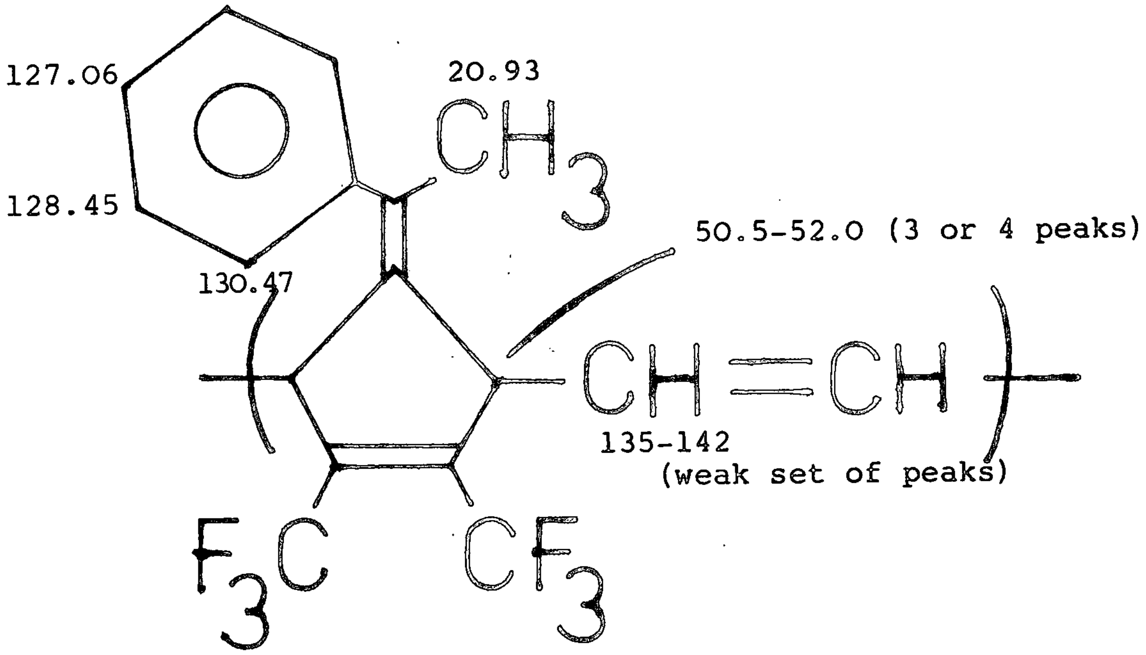


Figure 4.3

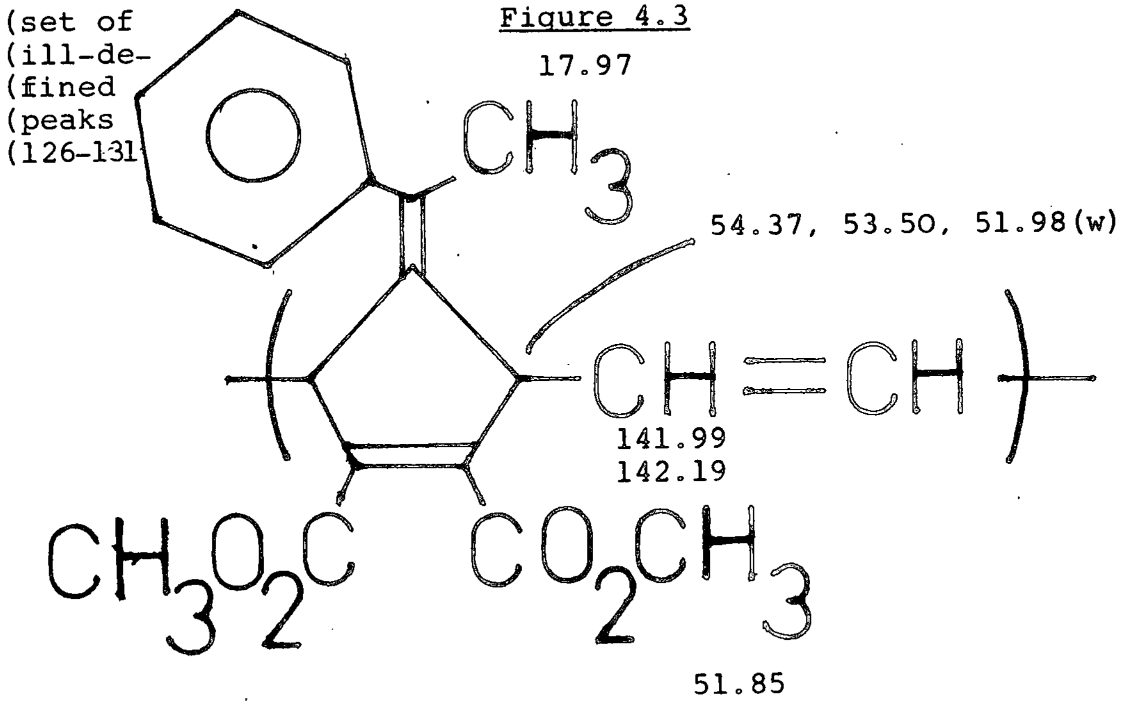
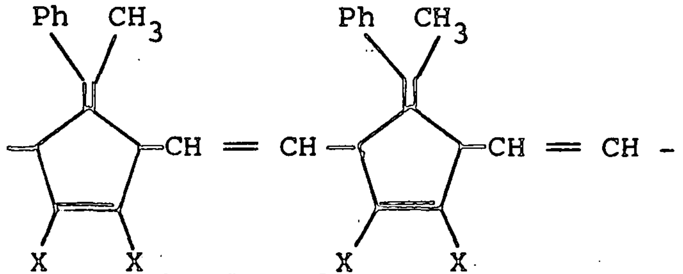


Figure 4.4

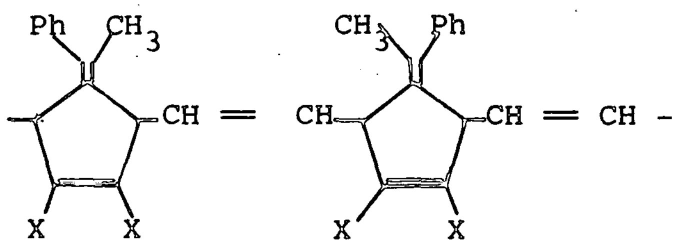
Figure 4.2 shows the assignments for the polymerized model compound, these are based on detailed analyses carried out by Ivin and co-workers[152] and previous workers in this laboratory.[142,143] The intensity ratios for the vinylene carbons bearing hydrogen at 132.25 (cis) and 131.39 (trans) indicate a predominantly (90%) trans stereochemistry, this is confirmed by the methylene resonances at 38.70 (tt), 38.33 (tc) and 38.13 (cc) where the letters in parentheses indicate the stereochemistries of the adjacent vinylene units, in this case the trans content is calculated as 87.5%. The methine carbon signal at 44.17 is assigned to carbons adjacent to trans vinylenes with the methines adjacent to cis vinylenes probably being the weak resonance at *ca.* 49 ppm., unfortunately the computer did not recognize this peak and so it was not integrated. The assignment of a predominantly trans stereochemistry at the vinylene units is also consistent with the relative intensities of the vinyl CH out of plane bending modes in the infrared spectrum. These bands appear at 970 cm^{-1} (trans) and 750 cm^{-1} (cis).

Using the ^{13}C n.m.r. of this polymer it is also possible to deduce that there is probably high stereoregularity because the peak at 131.39 has a shoulder to the high field side indicating two types of tacticity are present.

When turning to the assignments of structure for polyMePhdiCF$_3$ and polyMePhdiCO$_2$Me there is a considerably more involved analytical problem. For the model polymer discussed above there are four possible assembly modes (see introduction, Section 4.1.2 (b)), these are combinations of cis or trans vinylenes with syndio- or isotactic ring placements. The polymers derived from the bicyclofulvene monomers have even more structural possibilities. In addition to vinylene stereochemistry and ring tacticity, the stereochemistry of the substituents at the exocyclic methylidene unit have to be considered. For example, two possibilities with isotactic ring placements are shown below.



head-tail

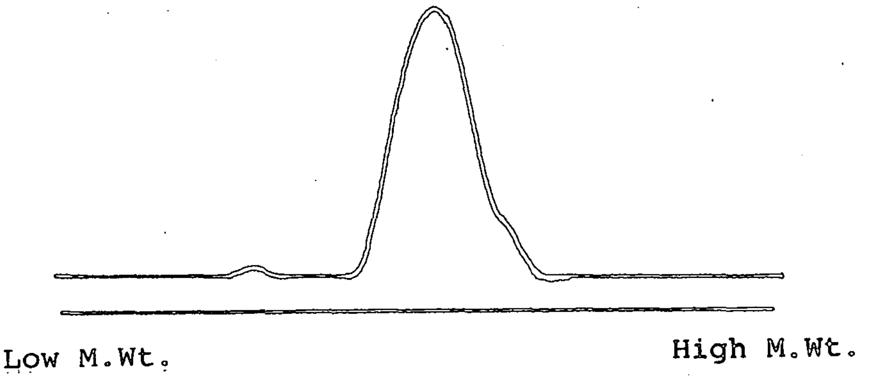


head-head/tail-tail

It proved experimentally difficult to obtain good spectra (Figure 4.1). Resonances for carbons which had no hydrogens attached were not detected under the recording conditions. The sets of peaks found at around 50-55 ppm (aliphatic carbons) and 135-142 ppm (vinylene carbons) were ill-resolved and reflect both the experimental difficulties and the probability that a range of different stereochemistries are present giving rise to the series of overlapping peaks. The best resolved spectrum was that of poly $\text{MePhdiCO}_2\text{Me}$ and in this case a resolved doublet at 142.19 and 141.99 ppm is assigned to the vinylene carbons. Accumulated experience suggests that the normal separation between cis and trans vinylene carbons for such polymers is of the order 0.6-0.8 ppm, the separation in this case is 0.2 ppm suggesting that the polymer is either high cis or high trans with either mixed tacticities or mixed head-tail/head-head isomerism producing this result. Prior to the advent of the ^{13}C n.m.r. method for determining cis/trans vinylene distribution it was common practice to use an infra-red spectroscopic method for determining the stereochemistries of the vinylene units in norbornene derived polymers. This method involves calculating the ratio of the absorbances of the IR peaks at around 965 cm^{-1} (vinylene trans CH out-of-plane bend) and 740 cm^{-1} (vinylene cis out-of-plane CH bend) and matching the value obtained with a correlation curve derived from the standard samples. This method of analysis has to be treated with some caution since the peaks used occur in the rather crowded fingerprint region of the spectrum; however, the results of this approach suggest that the polymers are of high cis content.

4.2.5 Gel Permeation Chromatography of Two of the Polymers

Characterization of the polymers poly MePhdiCF$_3$ and poly MePhdiCO$_2$Me was carried out using THF as the eluent. The other polymers were found to be insoluble in THF and g.p.c. using other solvents was not available. The theory of this technique and the calculations used to obtain molecular weight values are described in Chapter Three. Reproducible traces were obtained with the general shape shown below.



The results were as shown in Table 4.6

TABLE 4.6 Results of Gel Permeation Chromatography

Polymer	Mn	Mw	Polydispersity
PolyMePhdiCF$_3$	61.6x10^4	1.13x10^5	1.84
PolyMePhdiCO$_2$Me	1.11x10^4	3.57x10^4	3.22

Since no absolute molecular weight method has been used this data can only be taken as demonstrating that genuine high polymers have been formed.

4.2.6 Photochemical Irradiations

As a preliminary experiment a free-standing film sample of polyMePhdiCO$_2$Me was mounted in air in a photochemical reactor and irradiated at 254nm for 2¼ hours. No visual change in the film was apparent but an infra-red spectrum showed the development of a weak peak at 3350-3550cm^{-1} (OH str), some oxidation had probably occurred.

A film sample of polyMePhdiCF$_3$ was irradiated inside an evacuated quartz vessel (18 hrs., 254nm). The film developed a slight yellow-grey colour, its infra-red spectrum was indistinguishable from that of the monomer.

Irradiations were also carried out in solution, the general procedure is given below.

The polymer was dissolved in distilled methylene chloride in a quartz tube and the solution degassed by three freeze-thaw cycles. The solution was then irradiated (254nm) for a period of at least 18 hours, during this time the heat of the reactor kept the tube at a temperature of *ca* 50°C. The reaction times and amounts of reactants used are given in Table 4.7.

TABLE 4.7 Solution Irradiations (254nm)

Polymer	Weight of polymer (g)	Amount of CH_2Cl_2 (ml)	Irradiation Time (hrs)
PolydiMediCF$_3$	0.28	28	19
PolyMePhdiCF$_3$	0.10	10	18
PolydiPhdiCF$_3$ (soluble portion)	0.05	15	19
PolydiPhdiCO$_2$Me	1.0	10	114.5

Copper-coloured flakey precipitates were obtained (approximately 10% by weight) for all solution irradiations. The products of the irradiations of polyMePhdiCF$_3$ and polydiPhdiCO$_2$Me were characterized as discussed below.

The product of irradiation of polyMePhdiCF$_3$ gave an infra-red spectrum (Appendix 1, No.40) which was similar to the spectrum of the unirradiated polymer except for a weakening and change in shape of the C=C str. bands at around 1620-1690 cm^{-1}. Elemental analysis gave C60.8%, H4.0% calculated C61.4%, H4.2%. The product was found to be insoluble in methylene chloride, methanol, benzene, cyclohexane, 1,4 dioxan, petroleum ether, acetonitrile, acetone, chloroform, THF, acetic acid, ethyl acetate, pyridine and toluene.

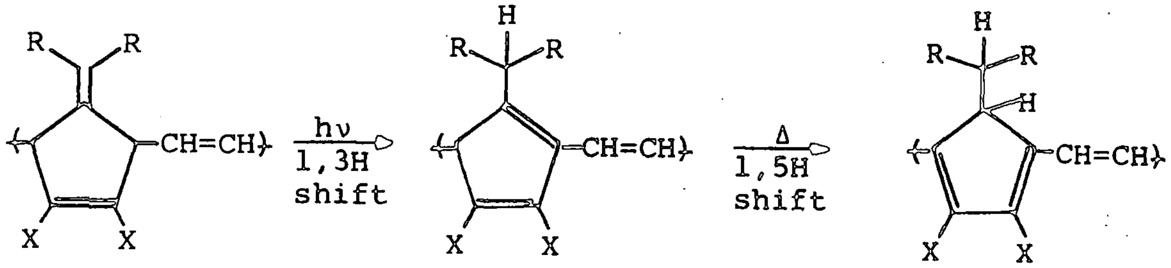
The product of irradiation of polydiPhdiCO$_2$Me was an insoluble product with an infra-red spectrum as given (Appendix 1, No.41). Compared to the spectrum of the unirradiated polymer the olefin peaks at around 1610-1670 cm^{-1} are weaker compared to the carbonyl peaks in both spectra. Analysis gave C66.7% H5.7%, calculated C76.7% H5.6%, the very low carbon value may have been due to the fact that the sample was unfortunately left in air for 3 days before the elemental analysis was performed. As a check the sample was analysed again after a further period of one day's exposure to air giving C62.5% H5.6%.

Conductivity measurements were attempted on the latter product using a four-probe conductivity apparatus. Unfortunately a meaningful reading could not be obtained, either because of bad electrical contacts or because this polymer has a very high resistance and thus an unmeasurably small value of conductivity. A pressed disc sample was left under iodine vapour for 4 hours then pumped under vacuum for 15 minutes to remove excess iodine. The disc increased in weight by 17% indicating that uptake of iodine had occurred, but again a value of conductivity could not be obtained. The product of irradiation of polyMePhdiCF_3 was pressed as a disc in order to carry out conductivity measurements but it was found that discs obtained from this material were very prone to powder when manipulated. Thus strong enough pieces of film could not be obtained for the intended measurements.

4.3 Discussion

Irradiations of the metathesis-produced polymers gave insoluble, copper-coloured, flat, flakey products. The insoluble nature of these materials precluded more detailed characterisation which might have shown, with more certainty, whether the desired poly-conjugated systems had been formed. The properties are indeed in accord with a system of this type, the chain will be held in a flat, planar structure and the colour would be expected to be metallic. Insolubility is also a characteristic of many conjugated polymers. The infra-red spectra of these materials were similar to those of the starting polymers except for some changes in the peaks due to olefinic bands.

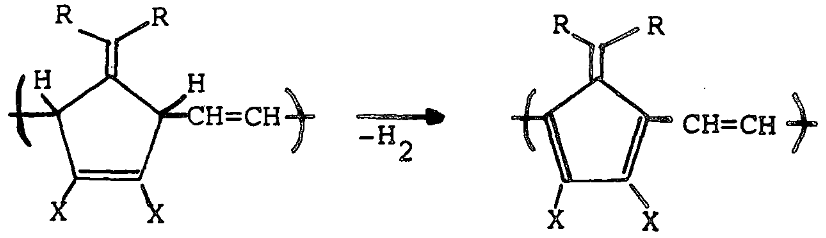
The desired reaction was as shown below.



It appears that the two hydrogen shifts may have occurred, the temperature of solutions during irradiations was about 50°C, it is possible that the second, thermal shift occurred in these conditions. The failure of the polymers to isomerize in the solid state is not unreasonable since the process involves considerable conformational reorganization. For the solution phase irradiations it may be that the precipitating polymer is not completely converted to the conjugated system.

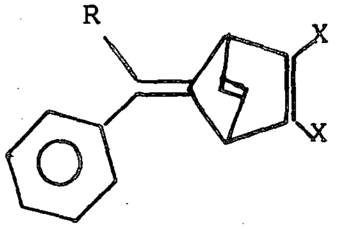
The product of irradiation of polydiPhdiCO$_2$Me appears to be very air sensitive as shown by the elemental analysis results. This may explain why a value of conductivity could not be observed; if the disc was highly oxidized the conductivity may have become too low to measure.

An alternative way to produce a similar polyconjugated system would be by dehydrogenating the metathesis produced polymers as shown below.



However, preliminary attempts using the dehydrogenating reagents palladium on charcoal and dichlorodicyanoquinone (DDQ) failed to effect this transformation.

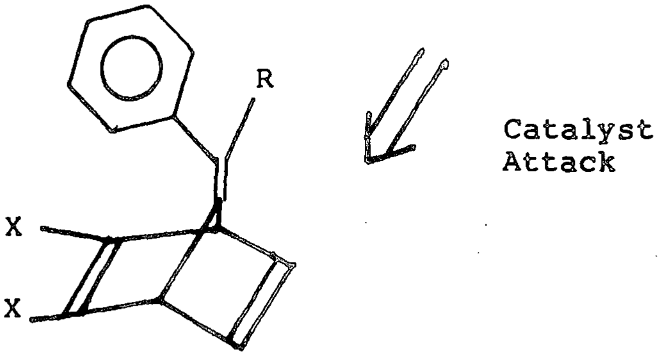
The synthesis of the precursor polymers has uncovered some interesting effects in relation to metathesis ring-opening polymerization. The bicyclofulvene monomers shown below could only be polymerized using the $MoCl_5/SnMe_4$ catalyst system at temperatures above ambient.



R = Me, Ph

X = CF_3, CO_2Me

These monomers could not be polymerized using $WCl_6/SnMe_4$ under the same conditions. This finding is the reverse of the order of activities generally found for tungsten and molybdenum based catalysts. For most cycloalkenes, tungsten systems have been found to be significantly more active and less stereochemically discriminating catalysts than molybdenum systems.[165] The reason in this case for the opposite result may be associated with the fact that the catalyst attack occurs at the exo face of the monomer (see Section 4.1.2(b)) as shown below.

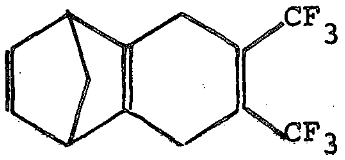


Interference between the approaching catalyst and the groups at the methylidene position may occur, thus a smaller attacking species would have a better chance of reaching the olefinic bond and forming a metallacyclobutane with it. Molybdenum would be expected to form a marginally smaller carbene complex than tungsten. The reason for the failure of polymerization of the 2,3 dimethyl ester of norbornadiene using $WCl_6/SnMe_4$ is not clear. It could be that the catalyst coordinates with the ester groups whilst this effect is not present in the ditrifluoromethyl analogue (which does polymerize with this catalyst). $DiMediCF_3$ appears to be the only monomer of this series which polymerizes with the $WCl_6/SnMe_4$ system.

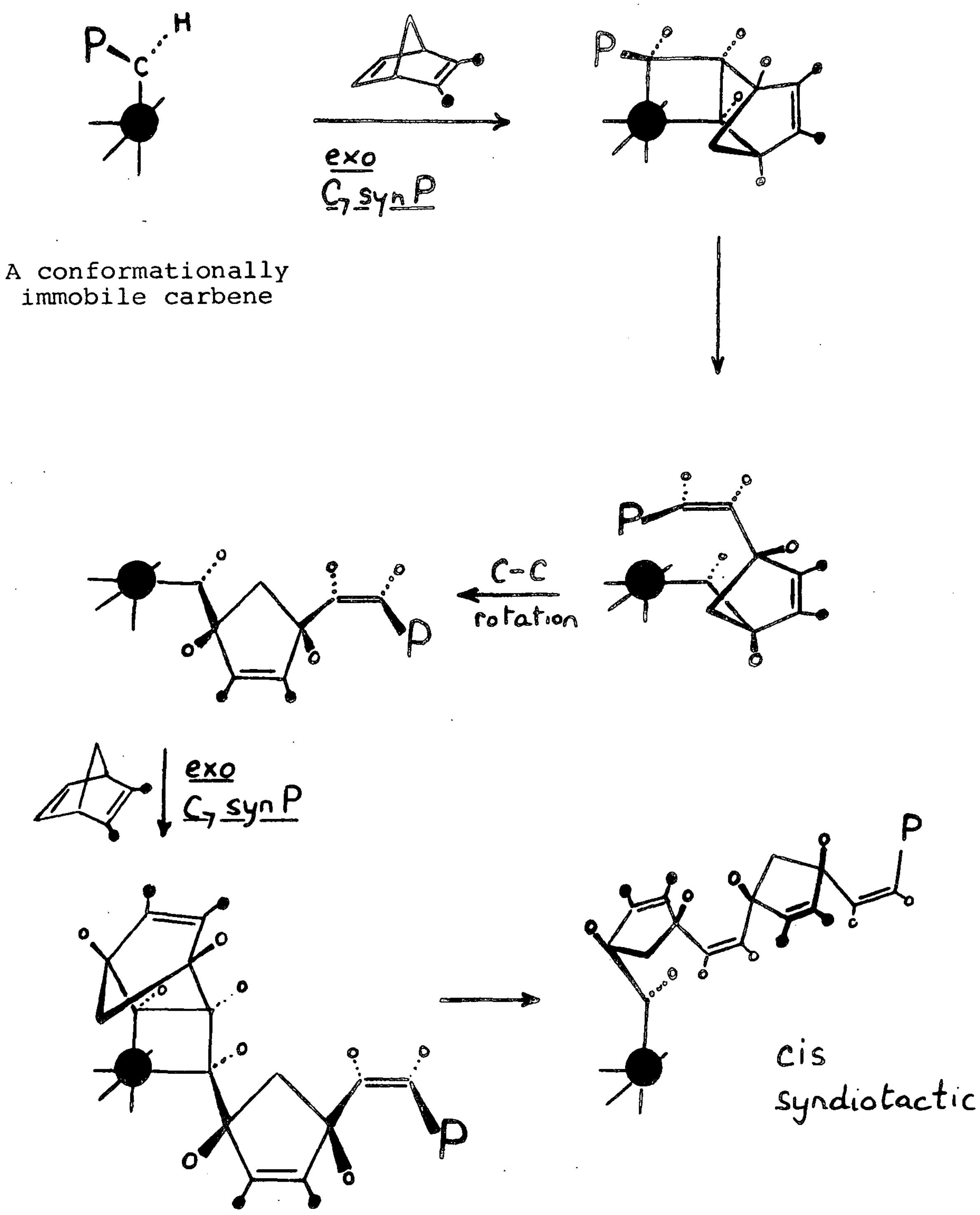
Gel permeation chromatography showed that high molecular weight polymers had been obtained ($\bar{M}n>10^4$). These polymers were all found to be susceptible to air oxidation. Film samples were left exposed to air and after periods of about 8 days infrared spectra showed the development of new peaks at about 3,500cm^{-1} (strong and broad OH str.) and 1,750cm^{-1} (C=O str.). The originally flexible films became yellow and brittle during this oxidation. As an example the spectrum of $polyMePhdiCF_3$ exposed to air and light for 18 days is given (Appendix 1, No.42) for comparison with the spectrum of the freshly made polymer (Appendix 1, No.36).

The infra-red peak observations show that high cis-vinylene polymers were produced from the bicyclofulvene monomers. Metathesis polymerizations carried out above room temperature have previously been found to result in an increase in the trans content of the polymers.[165] Another surprising result was provided by the polymerization of the model compound, the 2,3 dimethyl ester of norbornadiene. Ring-opening polymerization of norbornene and norbornadiene derivatives has been extensively investigated by Ivin and co-workers and by workers in these laboratories. The examples studied to date fit a general pattern in which tungsten-based catalysts yield atactic polymers with a roughly 50:50 distribution of cis and trans vinylenes whereas molybdenum based catalysts give high cis-vinylene syndiotacticity. Ivin has proposed the mechanism shown in Scheme 4.1.

This rationalization requires a conformationally immobile carbene at the molybdenum centre and an approach of the catalyst to the exo face of the monomer in such a manner that the C_7 methylene is syn-disposed towards the polymer chain attached to the carbene carbon. With the model compound used in this study the stereochemistry of the polymer is unambiguously trans-vinylene, this result is in interesting contrast to earlier work. It is also worth noting that other work in these laboratories has recently shown that there is no difference between the results of tungsten catalysed or molybdenum catalysed polymerization of the monomer shown[140] below, both types of catalysts give a 50:50 cis-trans atactic polymer.



Scheme 4.1 Mechanistic steps leading to a Cis-Syndiotactic Ring-opened Polymer



A conformationally immobile carbene

The conclusion from these results are that the monomer structure must have a significant effect on the detailed polymerization mechanism. A possible rationalization can be seen by a consideration of the mechanism of the polymerization (Scheme 4.1, p. 151). It is only necessary to change the relative dispositions of the C_7 methylidene and the polymer chain attached to the metallocarbene to an anti configuration to produce a trans-syndiotactic polymer. It is possible that subtle steric interactions between the monomer and the incoming active centre determine the overall result. What these recent results underline is that the generalizations concerning the polymerization mechanism should be applied with some reservations.

In summary, this route to conjugated polymers does show promise but the products are insoluble and the indications are that they are also quite air sensitive. Such disadvantages apply to most other polyconjugated materials. Unfortunately no measurement of conductivity was possible.

APPENDIX 1

INFRA-RED SPECTRA

Key, k.d. = KBr disc

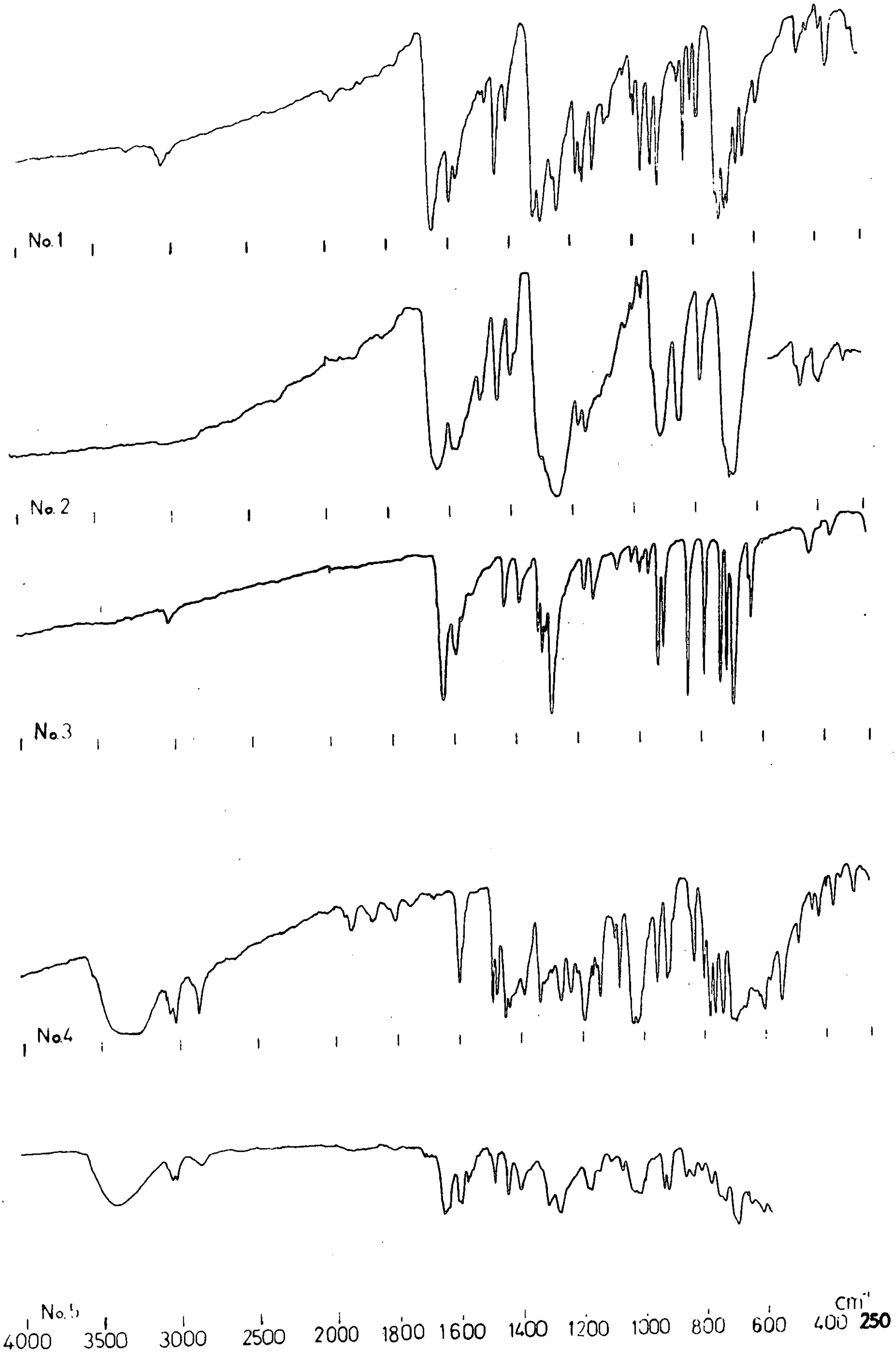
k.p. = KBr plates

n.p. = NaCl plates

1. m-Dibenzoylbenzene k.d.
2. p-Dibenzoylbenzene k.d.
3. p,p'-Dibenzoyl diphenyl k.d.
4. m-Bisbenzhydrol k.d.
5. p-Benzoyl benzhydrol (p-AB) n.p.
6. p-Benzoyl p'-benzhydryl diphenyl (diphenyl-AB) k.p.
7. m-Dibenzoylbenzene/m-Bisbenzhydrol irradiated in acetonitrile k.d.
8. m-Dibenzoylbenzene/m-Bisbenzhydrol, 1:1 mixture k.d.
9. Product of irradiation of m-Dibenzoylbenzene/m-Bisbenzhydrol reirradiated in acetonitrile k.d.
10. m-Dibenzoylbenzene/m-Bisbenzhydrol irradiated in benzene k.d.
11. p-AB irradiated product k.d.
12. Diphenyl-AB irradiated product k.d.
13. Terephthalaldehyde k.d.
14. p,p'-Diacetyl diphenyl k.d.
15. p,p'-Dibenzoyl 1,2 diphenyl ethane k.d.
16. Tetraphenylethene k.p. ($CHCl_3$ smear)
17. Product of p-Dibenzoylbenzene reductive coupling k.d.
18. Polymer from p,p'-Dibenzoyl diphenyl reductive coupling k.d.
19. Film of polymerized p,p'-Dibenzoyl diphenyl.
20. Product of m-Dibenzoylbenzene reductive coupling k.d.
21. Product of p,p'-Diacetyl diphenyl reductive coupling k.d.

22. Product of p,p'-Dibenzoyl diphenyl 1,2 ethane reductive coupling k.d.
23. 6,6 Dimethyl fulvene k.p.
24. 6 Methyl 6 phenyl fulvene k.p.
25. 6,6 Diphenyl fulvene k.d.
26. Decomposition product of 6,6 Diphenyl fulvene k.d.
27. Norbornadiene 2,3 dimethyl ester k.p.
28. DiMediCF$_3$ k.p.
29. MePhdiCF$_3$ k.p.
30. DiPhdiCF$_3$ k.d.
31. DiMediCO$_2$Me k.d.
32. MePhdiCO$_2$Me k.p.
33. DiPhdiCO$_2$Me k.d.
34. Film of polymer of norbornadiene 2,3 dimethyl ester.
35. Poly diMediCF$_3$ - film.
36. Poly MePhdiCF$_3$ - film.
37. Poly diPhdiCF$_3$ k.d.
38. Poly MePhdiCO$_2$Me - film.
39. Poly diPhdiCO$_2$Me - film.
40. Irradiated poly MePhdiCF$_3$ k.d.
41. Irradiated poly diPhdiCO$_2$Me k.d.
42. Poly MePhdiCF$_3$ exposed to air and light for 18 days - film.

See text of Chapter Four for abbreviations used for spectra 28-42.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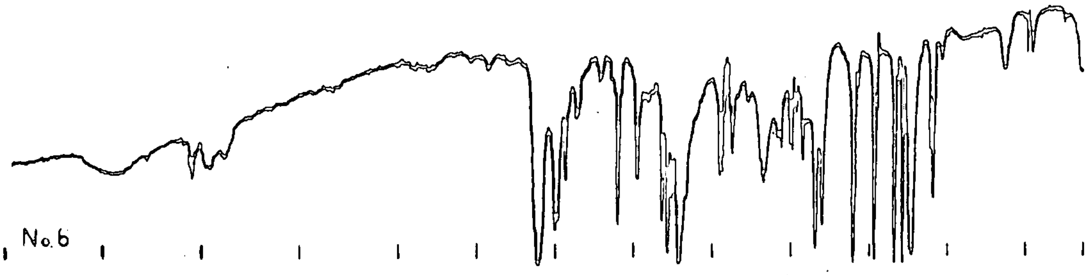
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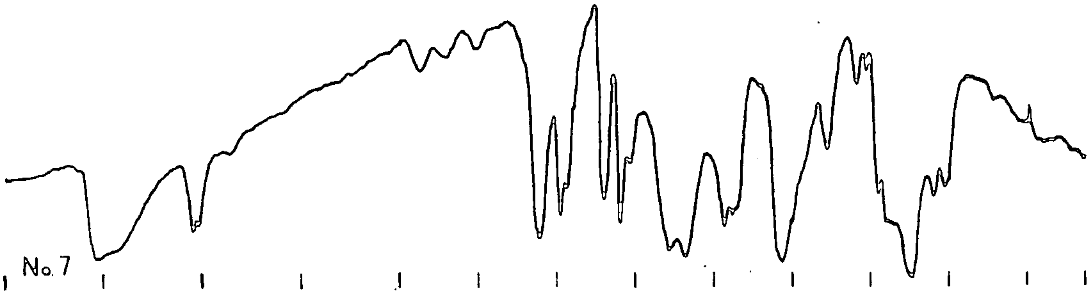
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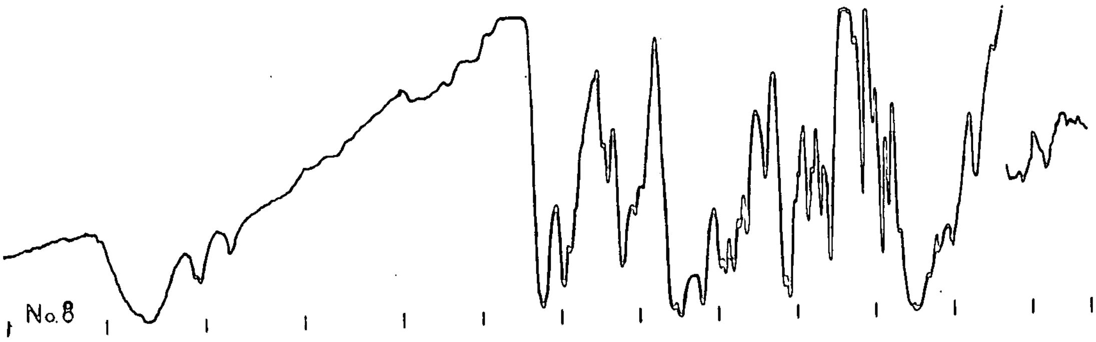
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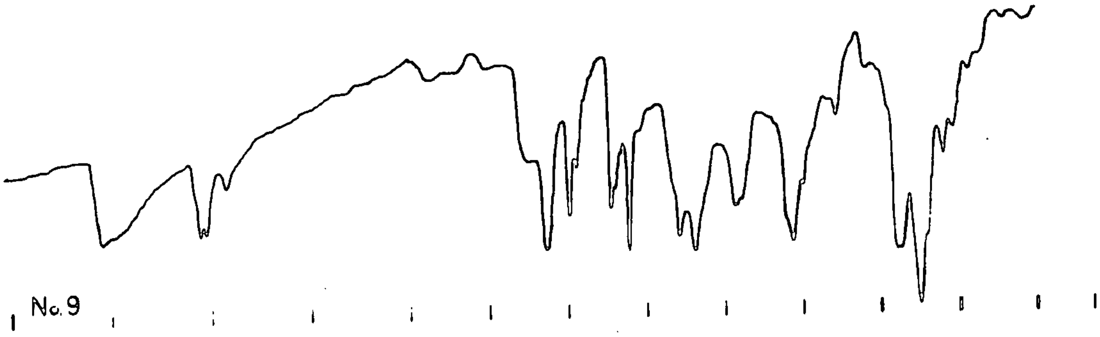
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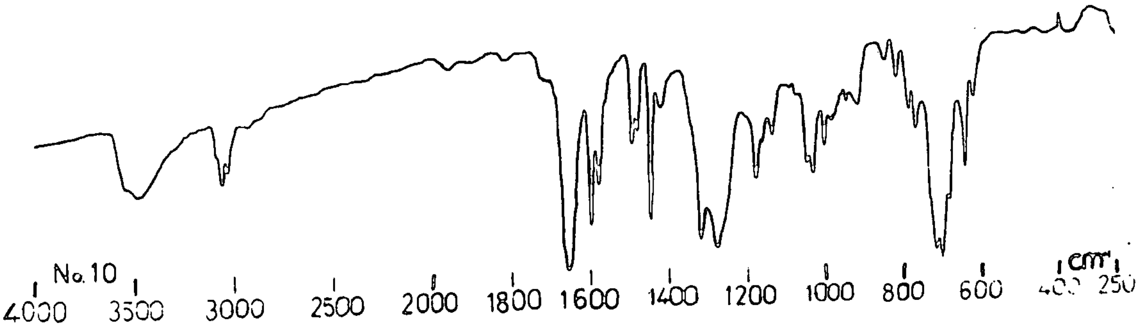
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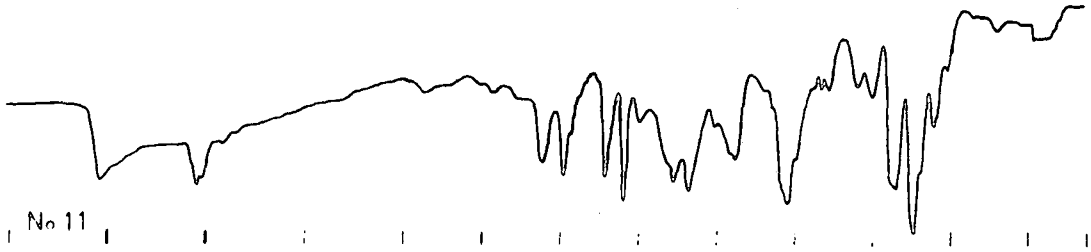
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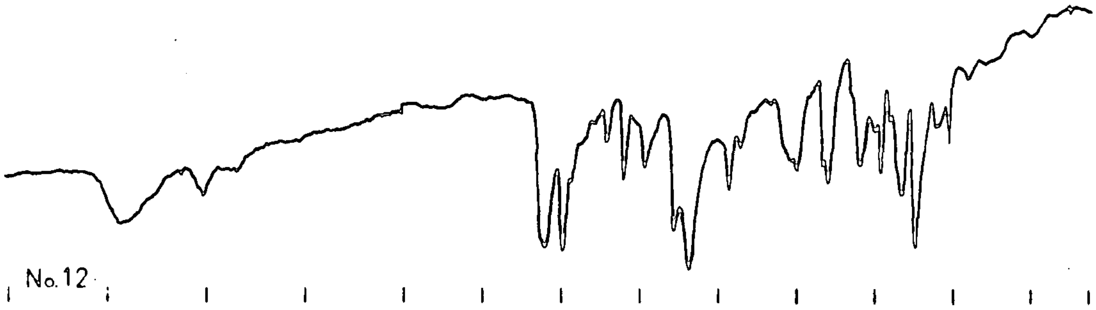
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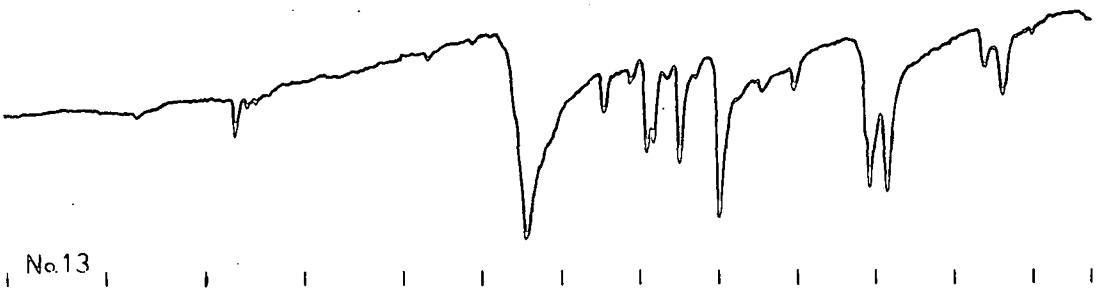
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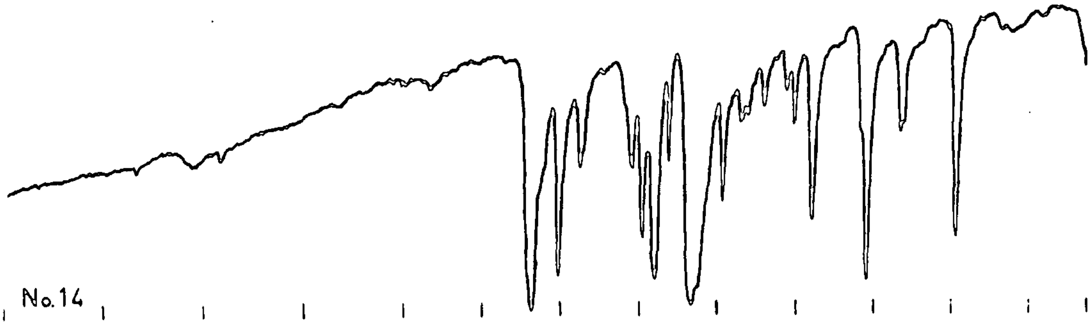
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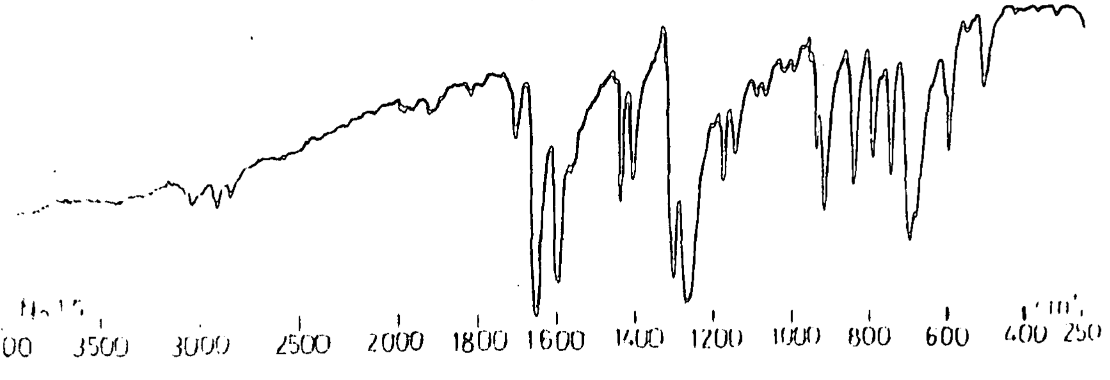
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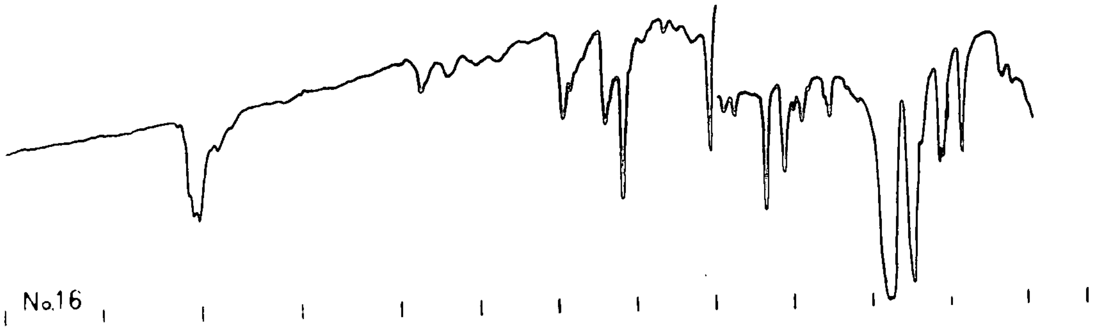

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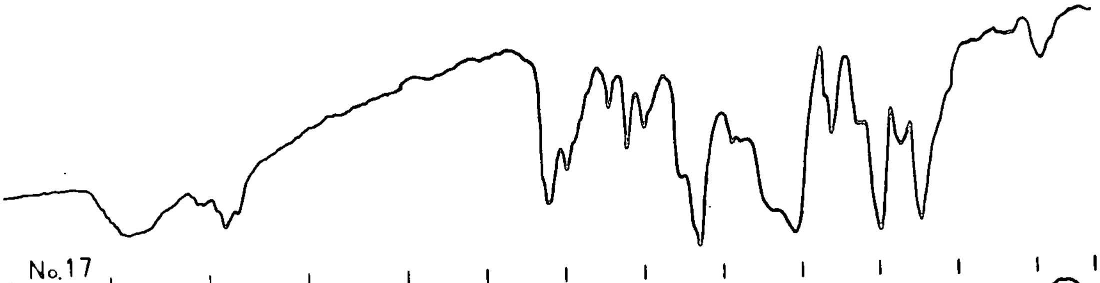

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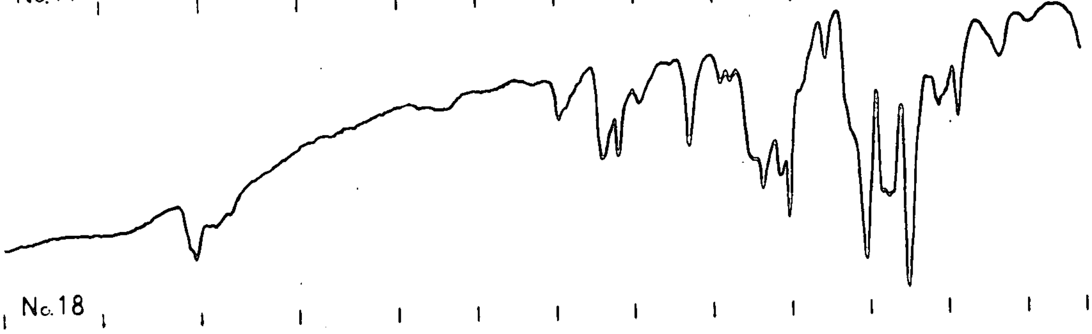

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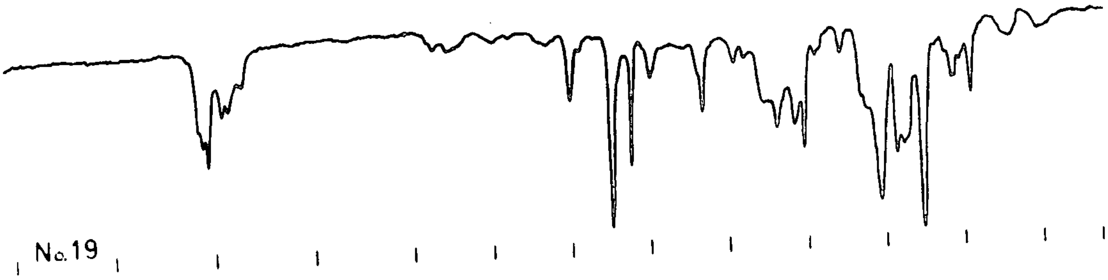

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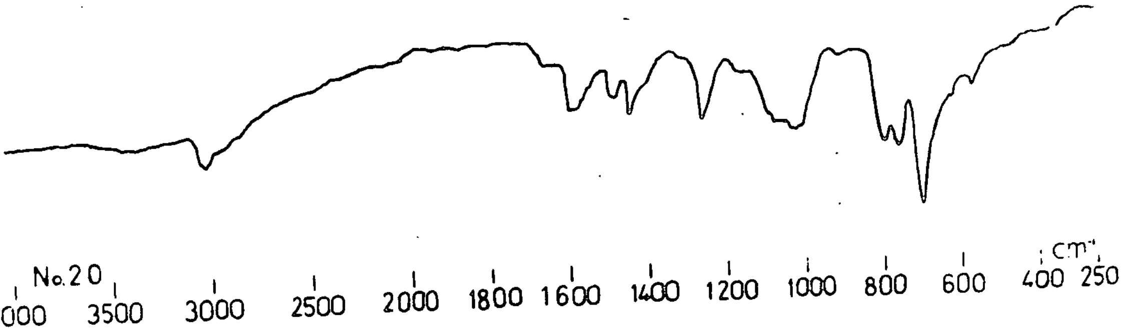

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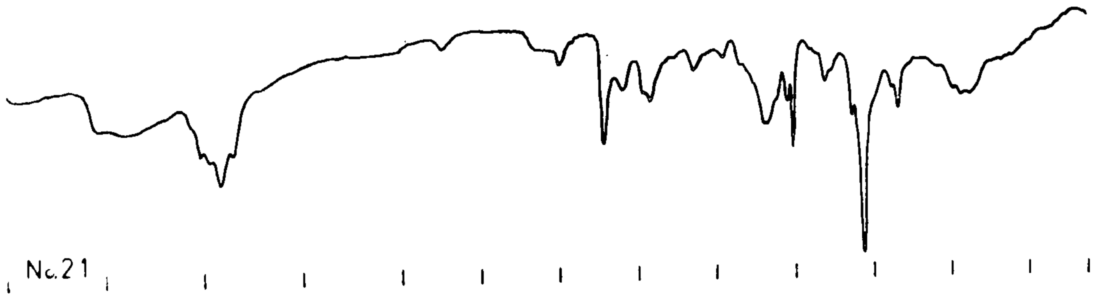

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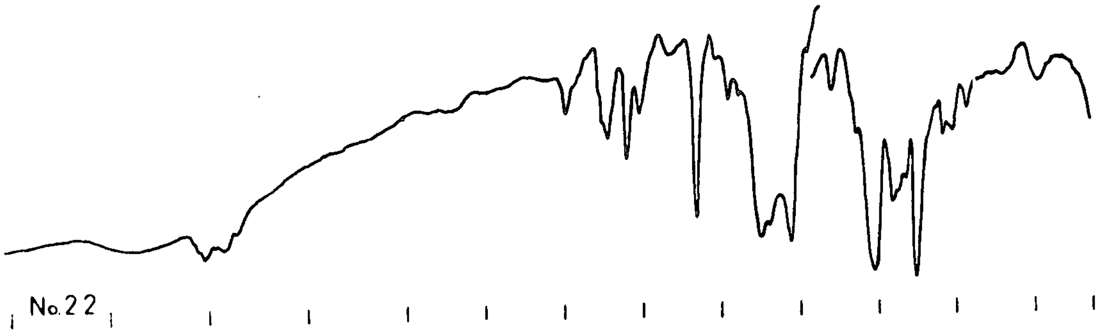

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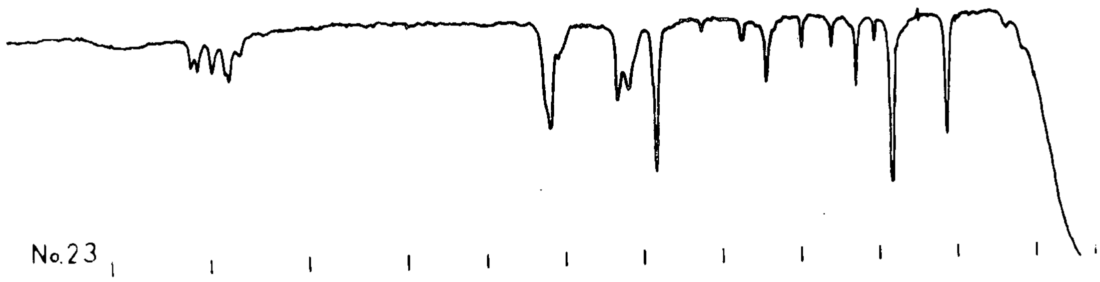

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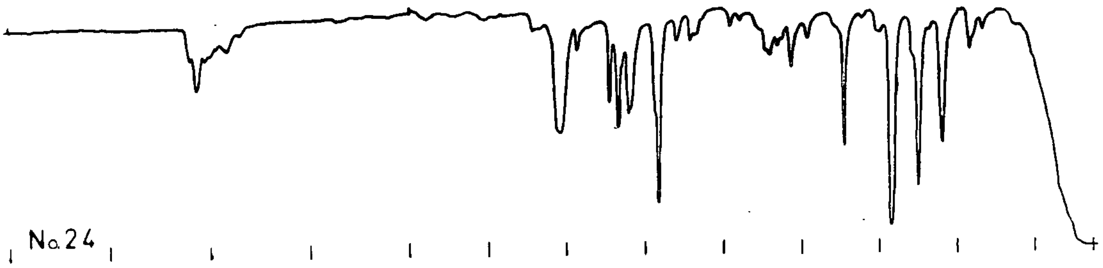

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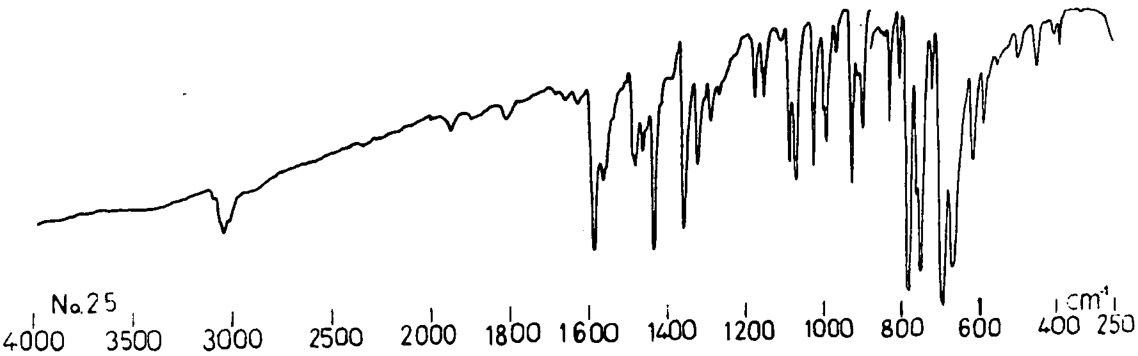

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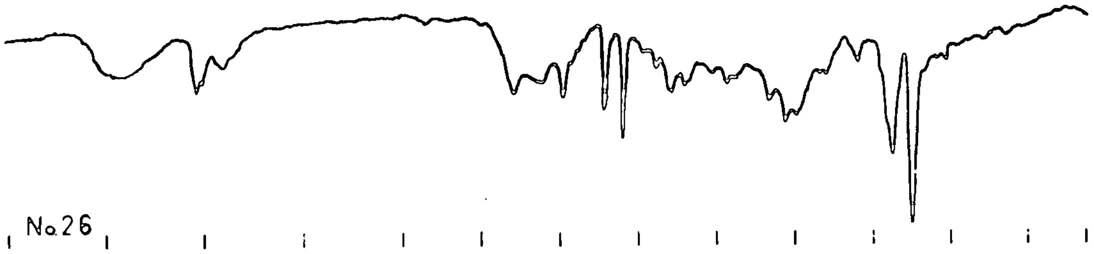
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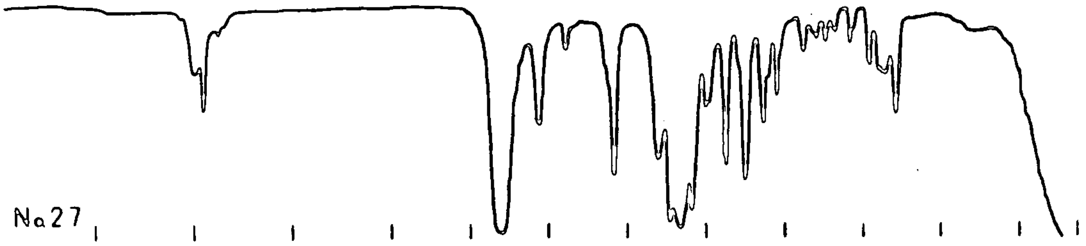
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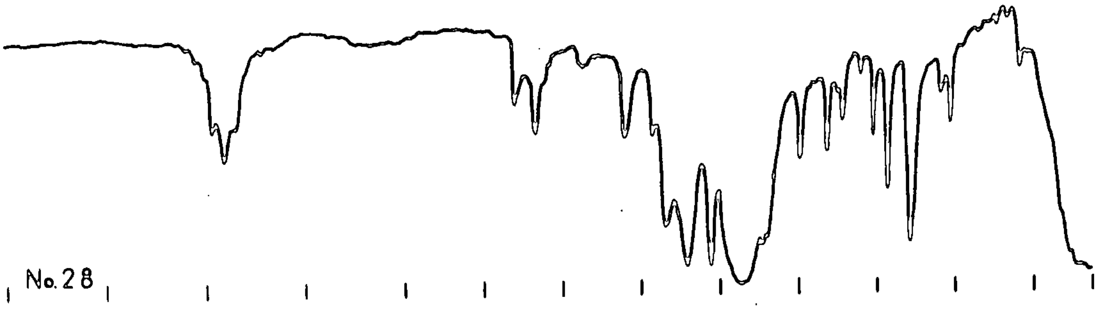
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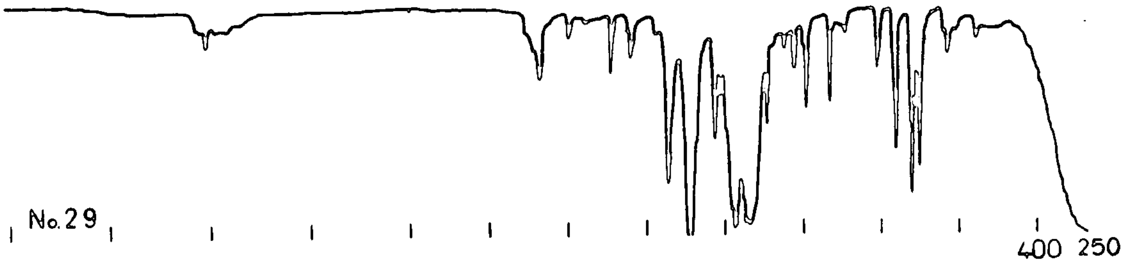
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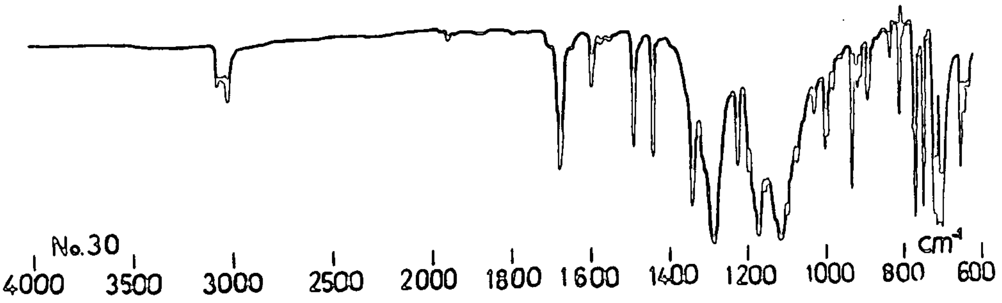
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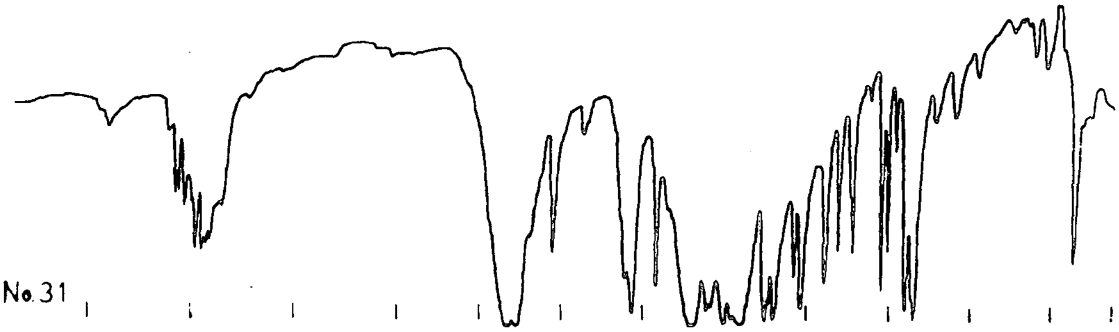
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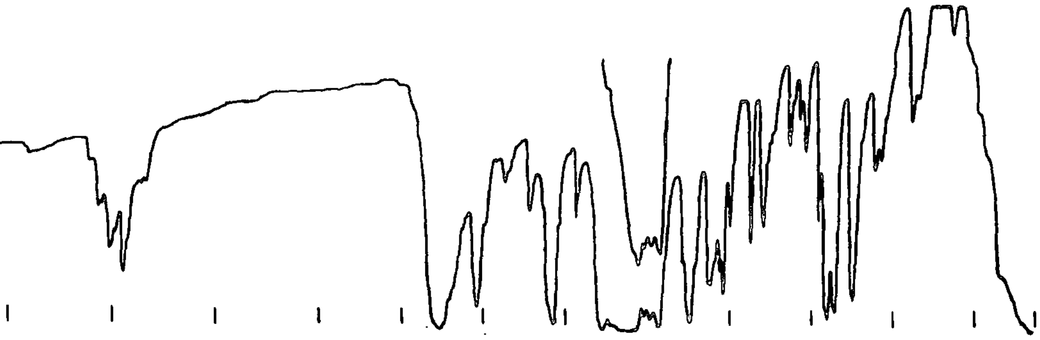
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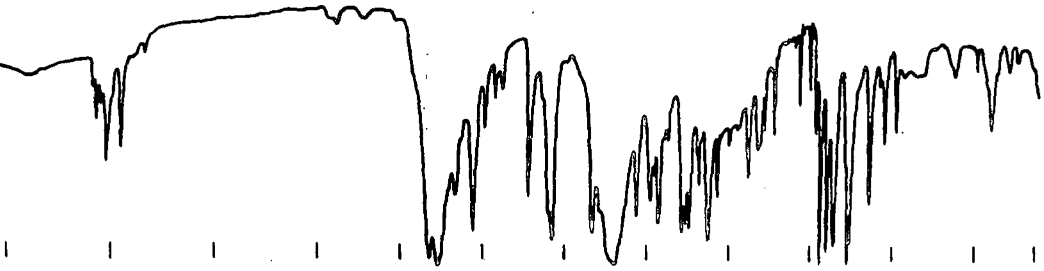
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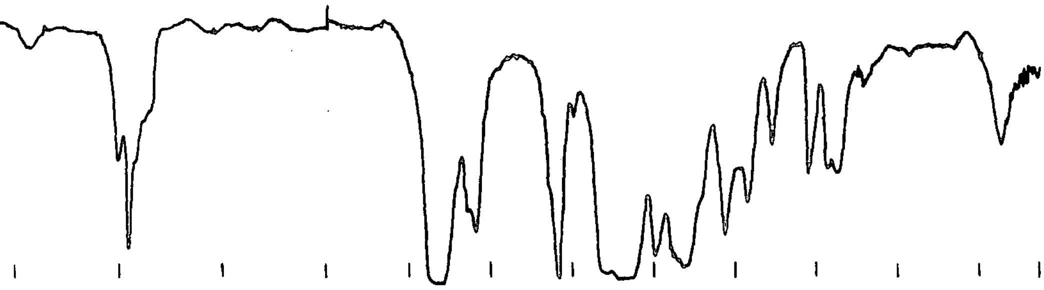
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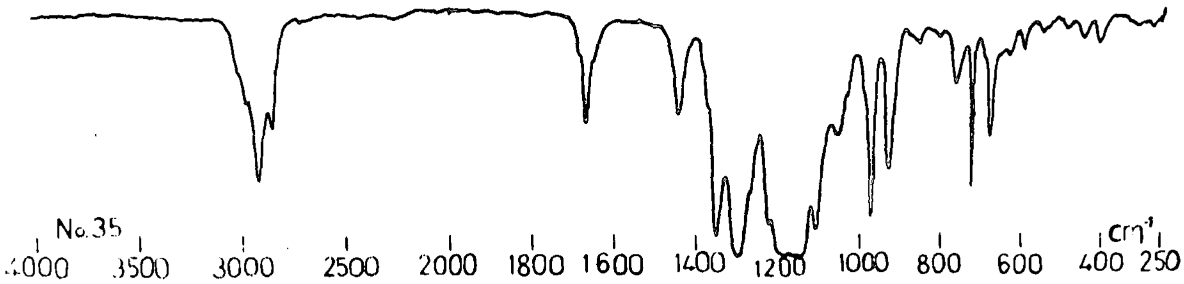
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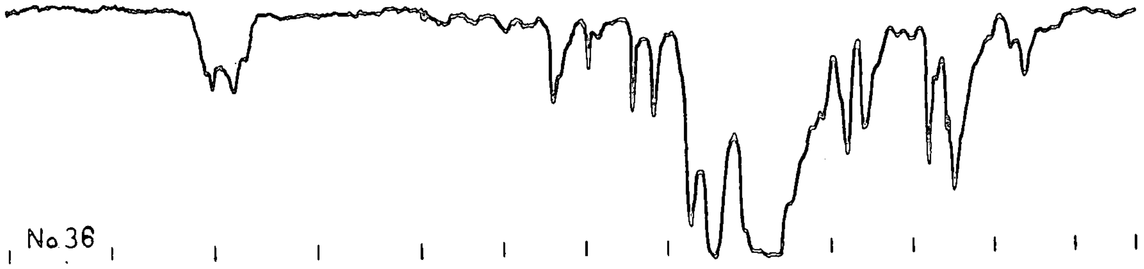

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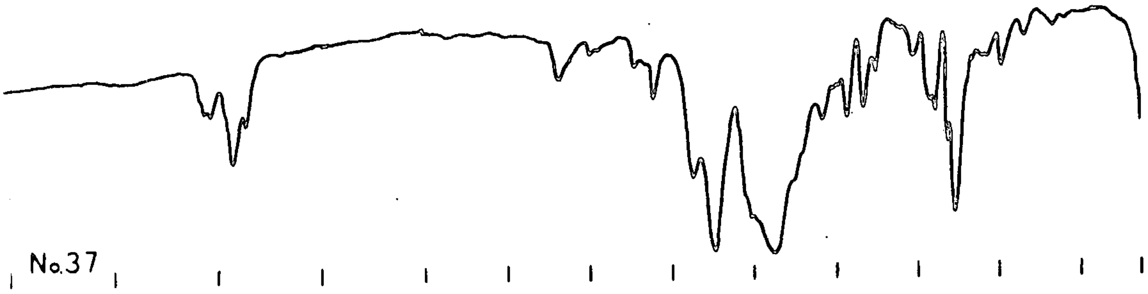

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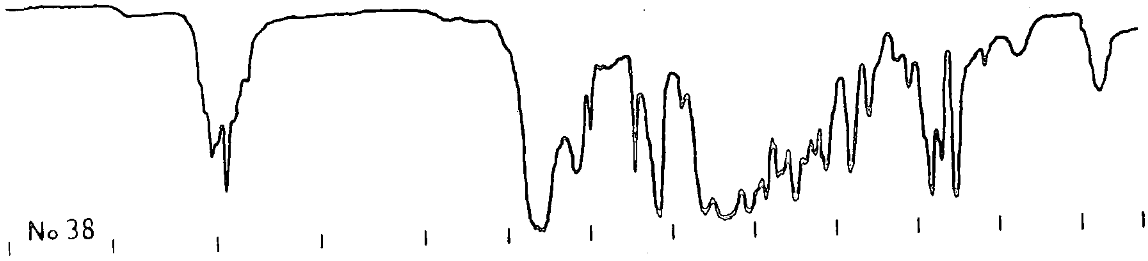

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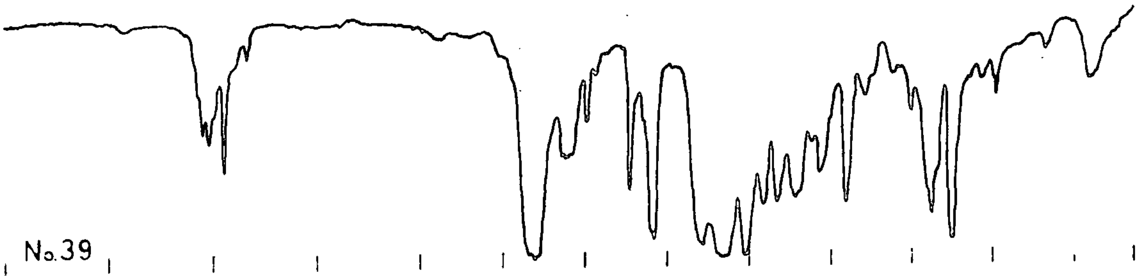

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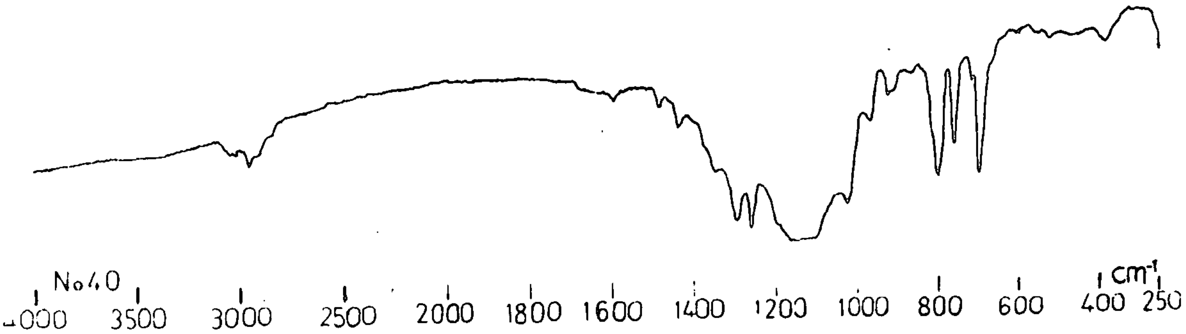

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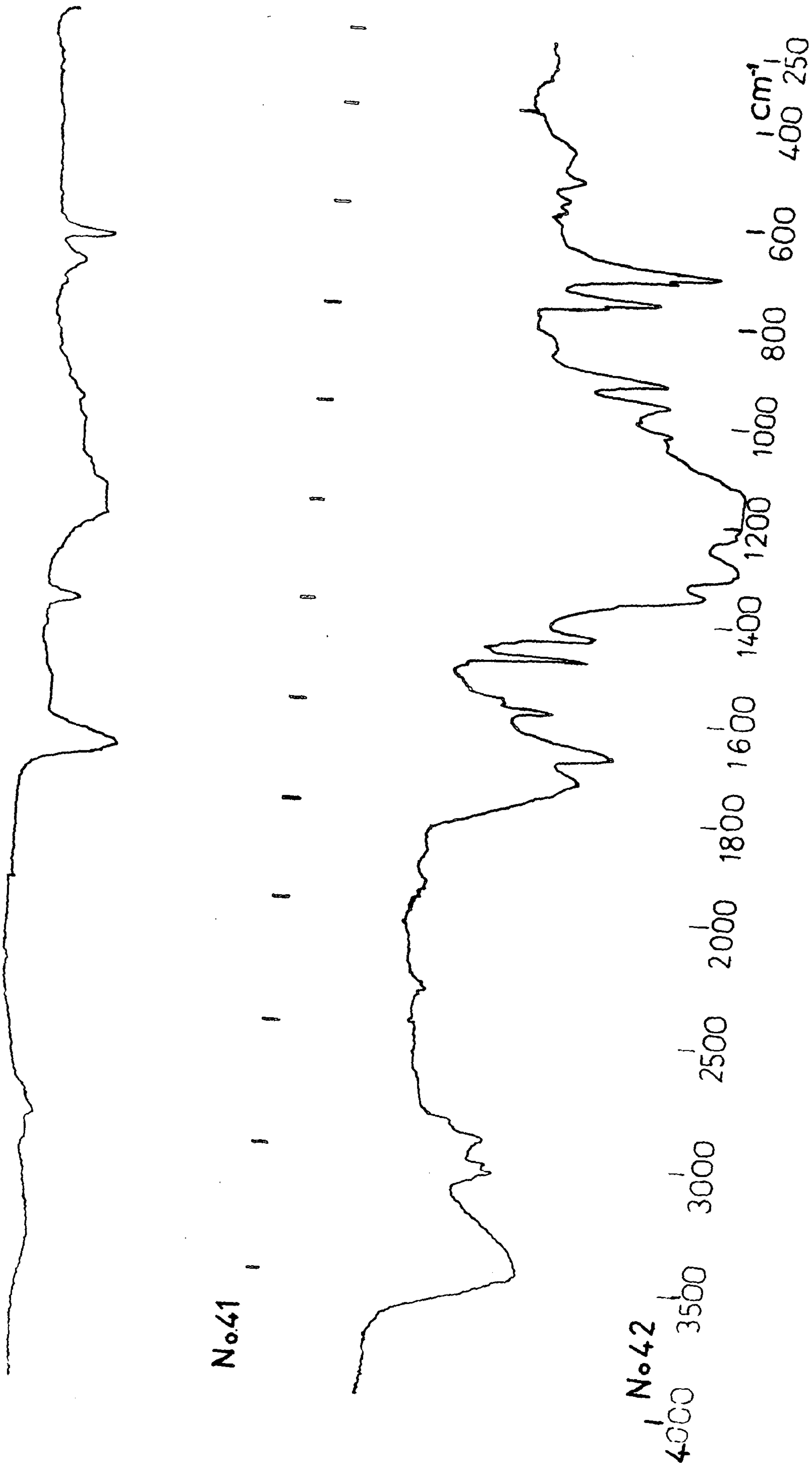
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APPENDIX 2

APPARATUS AND INSTRUMENTS

Infra-red Spectra - were recorded on Perkin-Elmer 457 or 577 grating Infrared Spectrophotometers.

^{1}H and ^{19}F N.m.r. Spectra - were obtained on a Varian EM 360L N.m.r. spectrometer (60 MHz).

^{13}C N.m.r. Spectra - were recorded at Edinburgh University on a Bruker WH360 N.m.r. spectrometer (90.56 MHz).

Gel Permeation Chromatography - was obtained using a Perkin-Elmer 601 Liquid Chromatograph with a Perkin-Elmer LC-55 U.V. detector using PL gel columns (Polymer Laboratories Ltd.)

Elemental Analyses - were carried out with a Perkin-Elmer CHN 240 Elemental Analyser.

Mass Spectra - were recorded on an AEI MS9 mass spectrometer.

Ultraviolet Spectra - were obtained using a Pye Unicam SP8-100 Ultraviolet Spectrophotometer.

APPENDIX 3

RESEARCH COLLOQUIA, SEMINARS, LECTURES AND CONFERENCES

The Board of Studies in Chemistry requires that each postgraduate research thesis contains an appendix listing all research colloquia, seminars and lectures by external speakers held in the department as well as all conferences attended by the author, during the period of research.

Lectures held October 1980 - July 1983

Dr. D. Mass (Salford Univ.) - 'Reactions a Go-Go', 16 Oct.1980.
Prof. T.M. Sugden (Cambridge Univ.) - 'Chemistry in Flames', 23 Oct. 1980.
Prof. N. Grassie (Glasgow Univ.) - 'Inflammability Hazards in Commercial Polymers', 30 Oct. 1980.
Prof. A.G. Sykes (Newcastle Univ.) - 'Metallo-proteins: An Inorganic Chemist's Approach', 6 Nov. 1980.
Dr. M. Gerloch (Cambridge Univ.) - 'Magnetochemistry is about Chemistry', 12 Nov. 1980.
Prof. N.N. Greenwood (Leeds Univ.) - 'Metalloborane Chemistry', 13 Nov. 1980.
Dr. T. Gilchrist (Liverpool Univ.) - 'Nitroso-olefins as Synthetic Intermediates', 19 Nov. 1980.
Rev. R. Lancaster - 'Fireworks', 4 Dec. 1980.
Dr. R. Evans (Brisbane Univ., Australia) - 'Some Recent Communications to the Editor of the Australian Journal of Failed Chemistry', 18 Dec. 1980.
Prof. E.A. Dawes (Hull Univ.) - 'Magic and Mystery through the Ages', 22 Jan. 1981.
Mr. H.J.F. Maclean (I.C.I.Ltd.) - 'Managing in the Chemical Industry in the 1980s', 29 Jan. 1981.
Prof. F.G.A. Stone (Bristol Univ.) - 'Chemistry of Carbon to Metal Triple Bonds', 5 Feb. 1981.
Dr. I. Fleming (Cambridge Univ.) - ' Some Uses of Silicon Compounds in Organic Synthesis', 12 Feb. 1981.
Prof. S. Kettle (Univ. of East Anglia) - 'Variations in the Molecular Dance at the Crystal Ball', 18 Feb. 1981.
Dr. K. Bowden (Essex Univ.) - 'The Transmission of Polar Effects of Substituents', 25 Feb. 1981.
Dr. J.F. Stoddart (I.C.I. Ltd.) - 'Stereochemical Principles in the Design and Function of Synthetic Molecular Receptors', 11 Mar. 1981.
Prof. W.P. Jencks (Brandell Univ., Mass.) - 'When is an Intermediate not an Intermediate?', 17 Mar. 1981.
Dr. J.P. Smith (Int. Tin Research Institute) - 'Organotin Compounds - A Versatile Class of Organometallic Compounds', 18 Mar. 1981.
Dr. W.H. Meyer (RCA, Zurich) - 'Properties of Aligned Polyacetylene' 9 Apr. 1981.
Prof. M. Gordon (Essex Univ.) - 'Do Scientists have to Count?', 7 May 1981.
Dr. J. Rose (ICI Plastics) - 'New Engineering Plastics', 10 Jun.1981.
Dr. P. Moreau (Montpelier Univ.) - 'Recent Results in Perfluoro-organometallic Chemistry', 17 Jun. 1981.
Dr. P. Plimmer (Du Pont) - 'From Conception to Commercialization of a Polymer', 21 Sept. 1981.

Prof. E. Kluk (Univ. of Katowice) - ' Some Aspects of the Study of Molecular Dynamics', 14 Oct. 1981.

Dr. P.J. Cornish (Dunlop Ltd.) - 'What would Life be like without Rubber?', 22 Oct. 1981.

Dr. W. Moddeman (Monsanto Ltd.) - 'High Energy Materials,6 Nov.1981.

Prof. A.I. Scott (Edinburgh Univ.) - 'An Organic Chemist's View of Life in the n.m.r. tube', 12 Nov. 1981.

Dr. W.O. Ord (Northumbrian Water Authority)- ' The Role of the Scientist in a Regional Water Authority', 26 Nov. 1981.

Dr. R.E. Hester (York Univ.) - 'Spectroscopy with Lasers',3 Dec.1981

Prof. I. Fells (Newcastle Univ.) - 'Balancing the Energy Equations' 28 Jan. 1982.

Dr. D. Pethnick (Strathclyde Univ.) - 'Conformational Dynamics of Small and Large Molecules', 10 Feb. 1982.

Dr. D.W. Turner (Oxford Univ.) - 'Photoelectrons in a Strong Magnetic Field', 17 Feb. 1982.

Prof. R.K. Harris (Univ. of East Anglia) - 'N.m.r. in the 1980s', 18 Feb. 1982.

Prof. R.O.C. Norman FRS (York Univ.) - 'Turning Points and Challenges for the Organic Chemist', 25 Feb. 1982.

Dr. P. Banfield (I.C.I. Organics) - 'Computer Aided Synthesis Design: A View from Industry', 3 Mar. 1982.

Dr. R. Whyman (I.C.I. Ltd.) - 'Making Metal Clusters Work", 4 Mar. 1982.

Prof. D.J. Burton (IOwa Univ.) - 'Some Aspects of the Chemistry of Phosphonium Salts and Phosphates', 28 Jun. 1982.

Prof. Neidlein (Heidelberg Univ.) - ' New Aspects and Results of Bridged Annulene Chemistry', 13 Sep. 1982.

Dr. W.K. Ford (Xerox, New York) - 'The Dependence of the Electronic Structure of Polymers on their Molecular Architecture', 27 Sep. 1982.

Prof. H. Suhr (Univ. of Tübingen) - 'Preparative Chemistry in Non-Equilibrium Plasmas', 14 Oct. 1982.

Mr. F. Shenton (County Analyst, Durham) - 'There is Death in the Pot', 14 Oct. 1982.

Dr. C.E. Housecroft (Notre Dame Univ.) - 'Bonding Capabilities of Butterfly-shaped Fe_4 Units', 27 Oct. 1982.

Prof. M.F. Lappert, FRS (Sussex Univ.) - 'Approaches to Assymetric Synthesis and Catalysis using Electron-rich Olefins and Some of their Metal Complexes', 28 Oct. 1982, and 'The Chemistry of some Unusual Subvalent Compounds of Group IV and V Elements', 28 Oct. 1982.

Dr. D.H. Williams (Cambridge Univ.) - 'Studies on the Structures and Modes of Action of Antibiotics', 4 Nov. 1982.

Dr. J. Cramp (I.C.I.Ltd.) - 'Lasers in Industry', 11 Nov. 1982.

Dr. G. Bertrand (Paul Sabatier Univ., Toulouse) - 'Curtius Rearrangement in Organometallic Series: A Route for New Hybridized Species', 15 Nov. 1982.

Prof. F.R. Hartley (R.M.C.S., Shrivenham) - 'Supported Metal Complex Hydroformylation Catalysts', 24 Nov. 1982.

Dr. D.R. Richards, (P.E.R.M.E.) - 'Terminally Functional Polymers - their Synthesis and Uses', 25 Nov. 1982.

Dr. G. Wooley (Trent Poly.) - 'Bonds in Transition Metal Cluster Compounds', 8 Dec. 1982.

Dr. D.C. Sherrington (Strathclyde Univ.) - 'Polymer Supported Phase Transfer Catalysts', 12 Jan. 1983.

Prof. D.W.A. Sharp (Glasgow Univ.) - 'Some Redox Reactions in Fluorine Chemistry', 27 Jan. 1983.

Dr. P. Moore (Warwick Univ.) - 'Mechanistic Studies in Solution by Stopped Flow F.T. n.m.r. and High Pressure N.m.r. Line Broadening', 9 Feb. 1983.

Sir G. Allen FRS (Unilever Ltd.) - 'U.K. Research Ltd.', 10 Feb. 1983.

Prof. A.G. MacDiarmid (Pennsylvania Univ.) - 'Metallic Covalent Polymers: $(SN)_x$ and $(CH)_x$ and their Derivatives', 17 Feb. 1983.

Dr. D. Bloor (Queen Mary College) - 'The Solid State Chemistry of Diacetylene Monomers and Polymers', 2 Mar. 1983.

Prof. A.C.T. North (Leeds Univ.) - 'The Use of a Computer Display System in Studying Molecular Structures and Interactions', 3 Mar. 1983.

Prof. D.C. Bradley, FRS (Queen Mary College) - 'Recent Developments in Organo-Imido Transition Metal Chemistry', 8 Mar. 1983.

Prof. H.G. Viehe (Univ. of Louvain, Belgium) - 'Oxidations on Sulphur', 11 Mar. 1983 and 'Fluorine Substitution in Radical and Biradical Addition Reactions', 11 Mar. 1983.

Dr. I. Gosney (Edinburgh Univ.) - 'New Extrusion Reactions: Organic Synthesis in a Hot Tube', 16 Mar. 1983.

Prof. J. Passmore (Univ. of New Brunswick) - 'Novel Selenium - Iodine Cations', 21 Apr. 1983.

Prof. P.H. Plesch (Keele Univ.) - 'Binary Ionisation Equilibria between two ions and two Molecules. What Ostwald never thought of', 4 May 1983.

Prof. K. Berger (Munich Univ.) - 'New Reaction Pathways to Partially Fluorinated Heterocyclic Compounds', 10 May 1983.

Dr. N. Isaacs (Reading Univ.) - 'The Applications of High Pressures to the Theory and Practice of Organic Chemistry', 11 May 1983.

Dr. T.D. Marder (U.C.L.A.) - 'The Chemistry of Metal-Carbon and Metal-Metal Multiple Bonds', 13 May 1983.

Dr. J.M. Vernon (York Univ.) - 'New Heterocyclic Chemistry involving Lead Tetra-Acetate', 25 May 1983.

Dr. A. Pietrykowski (Warsaw Univ.) - 'Synthesis Structure and Properties of Aluminoxanes', 15 Jun. 1983.

Conferences Attended

(a) 'Advances in Polymer Characterization, an International Symposium', Durham, July 1981.

(b) 'Membranes, A One Day Symposium', Macro Group UK, London. 27 Oct. 1982.

(c) Two 'Graduate Symposia' at Durham University - 21 Apr. 1982 and 15 Apr. 1983 (Presentation given by the Author).

(d) To be attended at time of writing - 'Fifth International Symposium on Olefin Metathesis', Graz, Austria, Aug. 22-26, 1983.

REFERENCES

Key: CA = chemical abstracts

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