Syntheses of potentially conducting polymers containing fluorine

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SYNTHESES OF POTENTIALLY CONDUCTING POLYMERS CONTAINING FLUORINE

by

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for the degree of Doctor of Philosophy at
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My parents for their continued love and support, Sonia for her love and valued assistance, with the final word going to thank all those people with whom I have spent many enjoyable times in Durham.

ABSTRACT

SYNTHESES OF SOME POTENTIALLY CONDUCTING POLYMERS CONTAINING FLUORINE

The preparation and characterisation of a number of fluorinated monomers capable of electrochemical polymerisation is described. Their electrochemical characteristics and the products of polymerisation are discussed

4,5,6,7-Tetrafluoroisothianaphthene was synthesised and its chemistry investigated. Attempts to electrochemically polymerise this to give a potentially narrow band-gap conducting polymer were generally unsuccessful. Other analogous monomers were also found to be difficult to polymerise by this method.

New fluorinated polyphenylylenevinylene oligomers and polymers have been prepared. In addition, potential routes to high molecular weight polytetrafluorophenylenevinylenes have been being investigated.

Oligomeric poly-2,3,5,6-tetrafluorophenylenevinylenes were prepared *via* a self nucleophilic displacement of the para fluorine in *cis* and *trans* organometallic derivatives of corresponding *cis* and *trans* 1-halo-2-pentafluorphenylethenes.

The attempted preparation of poly 2,3,5,6-tetrafluorophenylene-vinylene *via* two different soluble precursor derivatives is described. 2,3,5,6-tetrafluoro-1,4-xylene-bis(dialkyl sulphonium halides) were prepared with view to the preparation of soluble precursor derivatives of F-PPV. Preliminary work polymerising 2,3,5,6-tetrafluorobenzene-1,4-diethanal with 1,4-dilithium-2,3,5,6-tetrafluorobenzene did provide polyalcohol type precursor polymers to F-PPV, but requires further developement.

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CHAPTER ONE

INTRODUCTION

1. General

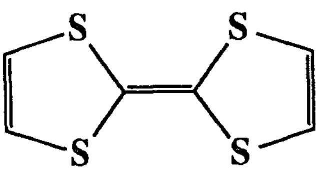
Organic compounds are no longer limited to the realms of being insulators. As one of the foremost areas of research today, organic conductors and electroactive organic solids are set to revolutionise many devices in the modern world. Their inherent advantages over traditional materials- that of structural diversity, ease of fabrication and cheapness- has lead to major commercial interest. This has caused an increased interaction between chemists and physicists to bring many formally separated disciplines of science into close co-operation. Subtle variations in chemical composition can lead to true molecular engineering.

Organic electroactive materials can be catagorised into three classes: charge transfer complexes, organometallic species and conjugated polymeric systems.[1,2,3]

1.1. Charge Transfer Complexes

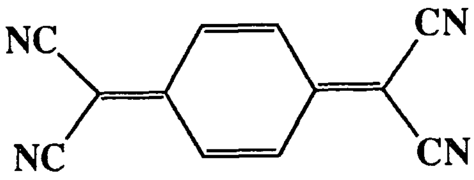
Conducting charge transfer complexes are highly crystalline solid assemblies of two component molecules. They arise by the interaction of one molecule in this binary system (electron donor) with an other (electron acceptor). As prerequisites for conductivity, one or both of these components must be a planar molecule with a delocalised π-electron system and each must crystallise into segregated stacks, one being the electron donor and the other the electron acceptor. Planar molecules and close stacking within the columns should lead to extensive π overlap down the stacks. If the two stacks show partial charge transfer, generating a half filled band (section 1.4.), then high conductivity will be the result.

These highly ordered stacking systems were the first examples of stable, highly conducting organic materials. Their discovery in the 1960's was followed in 1973[4] with the preparation of what is considered to be the model charge transfer system, a 1:1 complex of donor tetrathiafulvalene (TTF) (1) and the acceptor 7,7,8,8-tetracyano-p-quinodimethane (TCNQ) (2). This was found to be metallic in nature, with a room temperature conductivity of $\sigma_{RT} \approx 500$ S cm^{-1}.



TTF

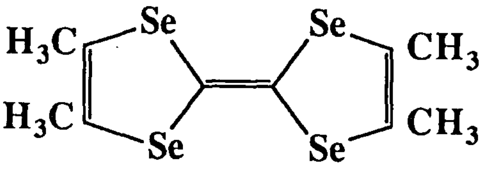
(1)



TCNQ

(2)

The next major breakthrough was the discovery by Jerome et al[5] of superconductivity in the organic compounds of the type (3), the so called Bechgaard salts.



X= PF_6^-, ClO_4^-, ReO_4^-, FSO_3^-, ...

(3)

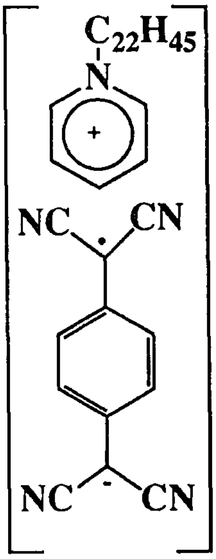
Superconductivity was first discovered in the PF_6^- salt at a temperature of 1 K under a pressure of 1.2 Kbar. Later the ClO_4^- salt was also found to superconduct at 1.2 K but at ambient pressure. Many general reviews on the area of organic metals to superconductivity have been written[6]

Due to the frail crystalline nature of these stacked systems they cannot be bulk processed in the way other organic materials are so have had little interest for industry.

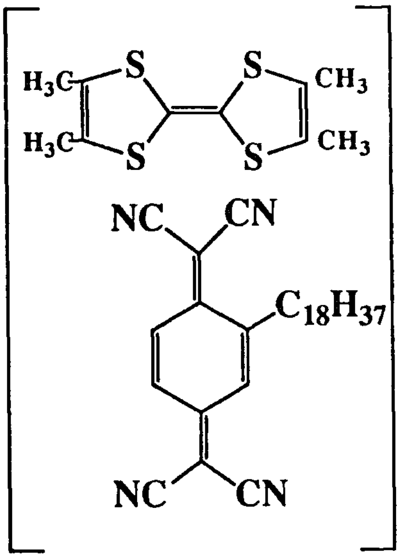
Recent work with potentially major applications in the electronics industry is the formation of very regular planar stacks of donor/

acceptor films using the Langmuir-Bloggett technique of deposition.[7] Derivatives of donors which have either long hydrophobic chains or hydrophilic end groups, can be used to deposit charge transfer films one layer at a time.

Early work was done by Barraud in 1985 on $C_{22}H_{45}$- pyridinium complexes with TCNQ (4) gave films containing crystallised platelets on $(TCNQ^{-})_2$ dimers mostly parallel to the surface.[8] The intrinsic conductivities were very low at $\sigma = 10^{-5} - 10^{-6}$ S cm^{-1} but increased with iodine doping to 0.1 S cm^{-1}.



(4)



(5)

Amphiphilic derivatives of TCNQ and TTF have been synthesised for use in preparing LB films. TCNQ with a $C_{18}H_{37}$ side chain when complexed with tetramethyl-TTF [to give (5)] was found to have a bulk conductivity of 10^{-1} S cm^{-1} without doping*. This complex was also found to be very anisotropic (see section 1.4.2.) with the conductivity perpendicular to the plane being 10^{-13} S cm^{-1}, indicating a favourable orientation of the

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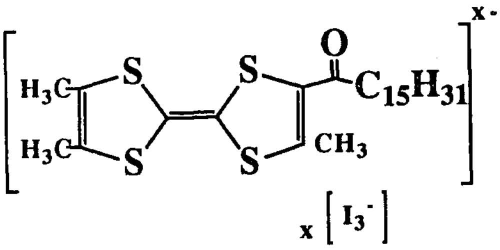
* 'Doping' is of two types: p-doping (involving the loss of electrons- oxidation and n-doping (gain of electrons- reduction)

charge transfer complex by use of the LB technique[9] with the stacks aligning parallel to the plane. Derivatives of TTF have been prepared with one to four side arms. Those with one side arm were found to deposit the best films so gave the higher conductivities. Since TTF itself is hydrophilic, addition of a hydrophobic chain to it generated an ideal molecule for laying a film on water.

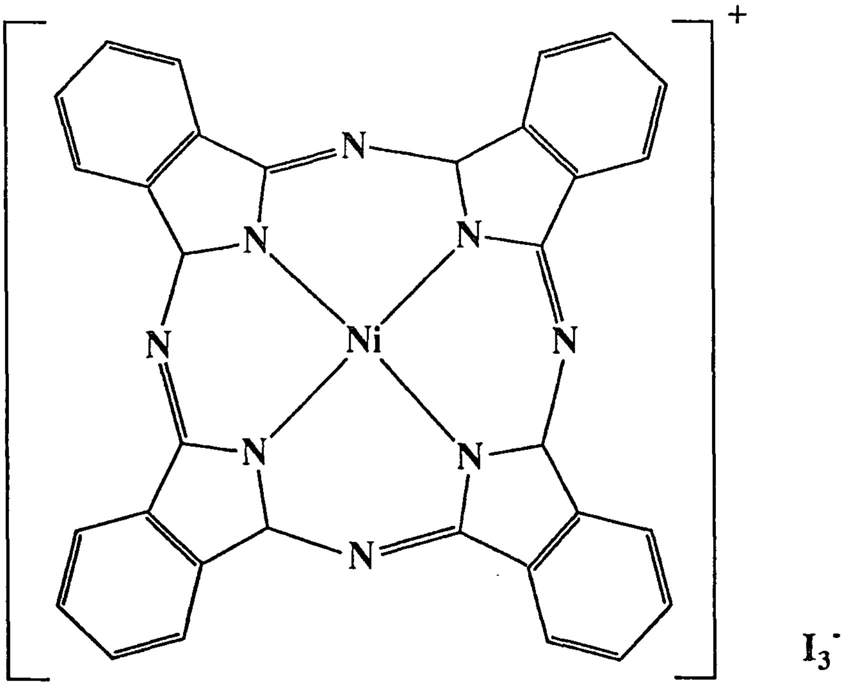


(6)

Deposition of multilayers of (6) on glass gave good LB monolayers.[10] The intrinsic conductivity is $\sigma = 10^{-5}$S cm^{-1}. Upon doping with iodine,the films became firstly highly insulating but as the iodine evaporated, the conductivity rose to a maximum of $\sigma = 10^{-1}$ to 10^{-2} S cm^{-1} after a few hours and was stable at this level for a period of months with a mixed valence system of TTF^{x+} $(I_3^-)_x$ where $x < 1$.

1.2. Metallo-Organic Species

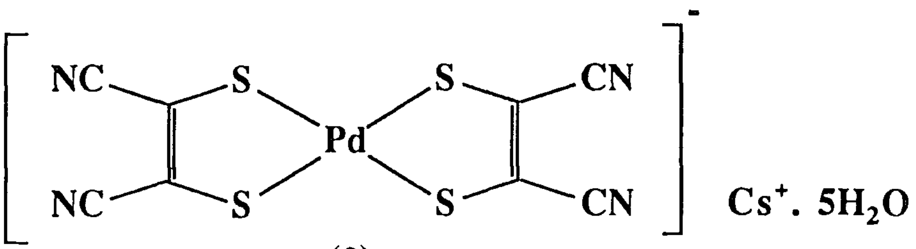
The use of metallocycles in conjunction with electron acceptors yield co-crystallised mixed valence low dimensional conductors. Phthalocyanins, for example, with a nickel metal centre (7), having been partially oxidised with iodine[11,12] are metallic in nature with a conductivity maximum of 5000 S cm^{-1} at 25 K. The charge carriers are associated with delocalised π systems along macrocyclic stacks with small contributions from the iodine chains. Conclusive evidence exists to show that the metallo centre is not required for conductivity. This is shown when the nickel atom is replaced by two hydrogen atoms in the



(7)

phthalocyanin ring[13] and where the product stack exhibits a room temperature conductivity of $\sigma \approx 700$ S cm^{-1}. The metal acts mainly as a template for stacking and also as a binder, holding the cycles in close proximity for maximum orbital overlap

The other major family of organometallic conductors are the metal-dithiolenes. Groups working under Friend and Underhill[14] have studied in particular complexes of the type $Cs(Pd[S_2C_2(CN)_2]_2).5H_2O$ (8).



(8)

This complex has a room temperature conductivity of 5 S cm^{-1} and, unlike many organic metals, remains conducting down to a temperature of 1 K without the application of pressure.

1.3. Conjugated Polymers

From the industrial point of view, polymeric conducting materials are preferred over crystalline solids since they would best fit in with modern industrial processing methods. The approach to conducting polymers has been to generate a polymer backbone with an electronic structure as delocalised as possible. In an ideal world, a fully delocalised orbital system should be conducting. However, no polymer so far prepared is intrinsically conducting when based on carbon for the polymer backbone. All require some form of chemical manipulation to become conducting, usually oxidation or reduction ('doping'). The model polymer for all conjugated systems is polyacetylene[15], structurally the simplest. From this extends a vast array of systems, the major ones being shown in Fig 1. All of these tend to be less conducting than the model PA . In general these systems have not lived up to the expectations of them. Their insolubility and high melting points/low decomposition temperatures means that they cannot be processed in a manner similar to that of other industrial polymers. A large number are also unstable to atmospheric conditions when in a conducting state. However, the conductivities generated are very good for organic systems with a range between 1 and 80,000 S cm^{-1}.

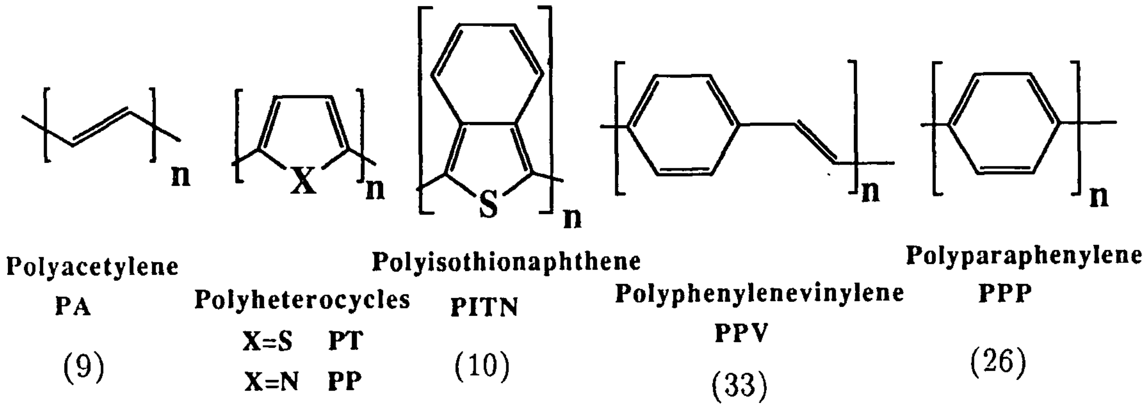


Fig 1

1.4. Physical Aspects: Conductivity Mechanisms

The mechanism of conduction in the various systems is still not fully understood. A number of theories, some contradictory, attempt to explain this property. There is no doubt that the basic concepts of band theory go a long way to providing an explanation of these phenomena, even if in a simplistic manner.

1.4.1. Band Theory of Solids

Despite the availability of a rigorous mathematical approach to the band theory of solids[16], the key to understanding why certain materials conduct can be seen using the band theory of solids. We can imagine the formation of polyenes from ethylene units where as the number of ethylene units incorporated into the system increases, so does the number of filled bonding levels to the extent of band formation (Fig 2).

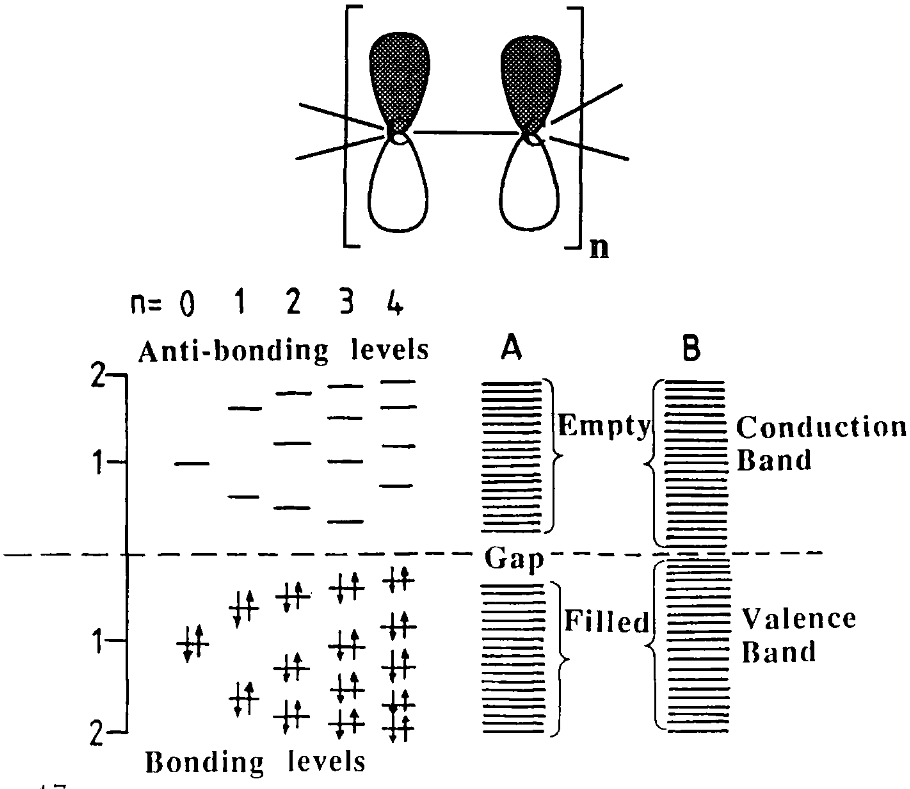


Fig 2[17]

The degree of bond localisation is a major consideration. If the polyene exists with equal carbon-carbon bond lengths, like in benzene, then it will have a half filled continuous band of π Molecular Orbitals (MO's) (B in Fig 2). with a structure comparable to that of metals. If bond alternation exists, then a filled bonding π MO (valence band) and an unfilled antibonding π MO (conduction band) will be generated. These are separated by an activation gap. If this activation gap is large then the material will be an insulator. The extent of filled and half filled π MO's governs the size of the band gap and hence the nature of the polymer (Fig 3).

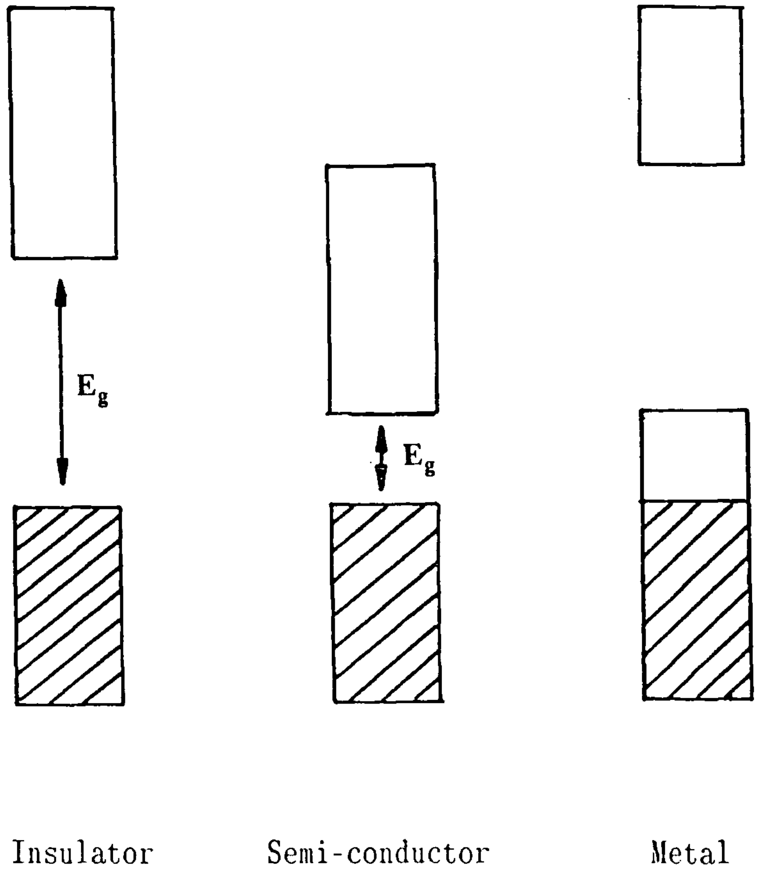


Fig 3 *Band theory for insulators, semi-conductors and metals. The shaded area represents regions with electrons. Eg is the energy gap between the occupied and empty states. Typically, Eg is over 4 eV for an insulator and below 2 eV for a semi-conductor.(Ref 3)*

The build-up of a large array of molecules to form band structures is also applicable to the formation of conducting crystalline solid states (i.e. charge transfer complexes). In these systems, metallic behaviour is associated with partially filled bands in which large numbers of electrons can move the infinitesimally small transition to the higher energy states within the band. This is usually achieved by the application of a potential gradient. The highest occupied state is known as the Fermi level and it is the electrons in the energy states very near to this that are involved in conduction.

The electrical behaviour of metallic conductors and semi-conductors is dependant on temperature. The balance between energy required for the promotion of electrons into the conduction state and that lost during the interaction of electron with lattice vibrations governs this conductivity. Thus as the system is cooled, lattice vibrations decrease which increases orbital overlap in organic systems so conduction in organic metals increases. In semi-conductors, cooling leads to less energy being available to promote electrons from the Fermi level across the band gap so conductivity decreases. Hence in organic metals, cooling makes it easier for a fixed number of charge carriers to move and in semi-conductors leads to a reduction in that number of charge carriers. A partially filled state is essential for conduction in these organic metals.

1.4.2. Conduction in Charge Transfer Salts

The formation of segregated stacks in charge transfer salts is shown schematically in Fig 4.

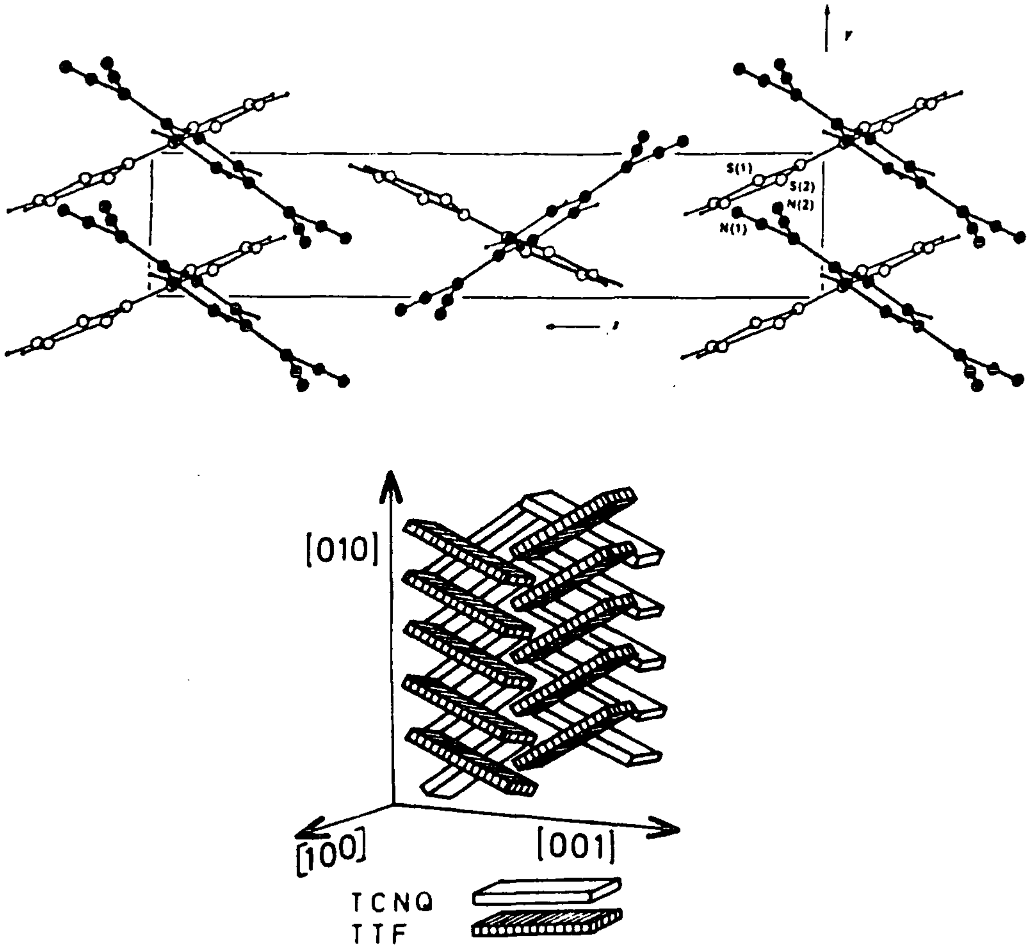


Fig 4. *Top*: *Crystal packing in TTF-TCNQ (Ref 18). Bottom*: *Schematic representation of TTF-TCNQ structure (Ref 6g)*

It is the extensive π overlap between neighbours that leads to the major difference in these organic and metallic conductors. This overlap leads to a highly anisotropic nature where conduction is associated with a preferential direction. Specifically, after partial charge transfer between the stacks, conduction may occur by radical anion formation and subsequent passage along the stack (Fig 5).

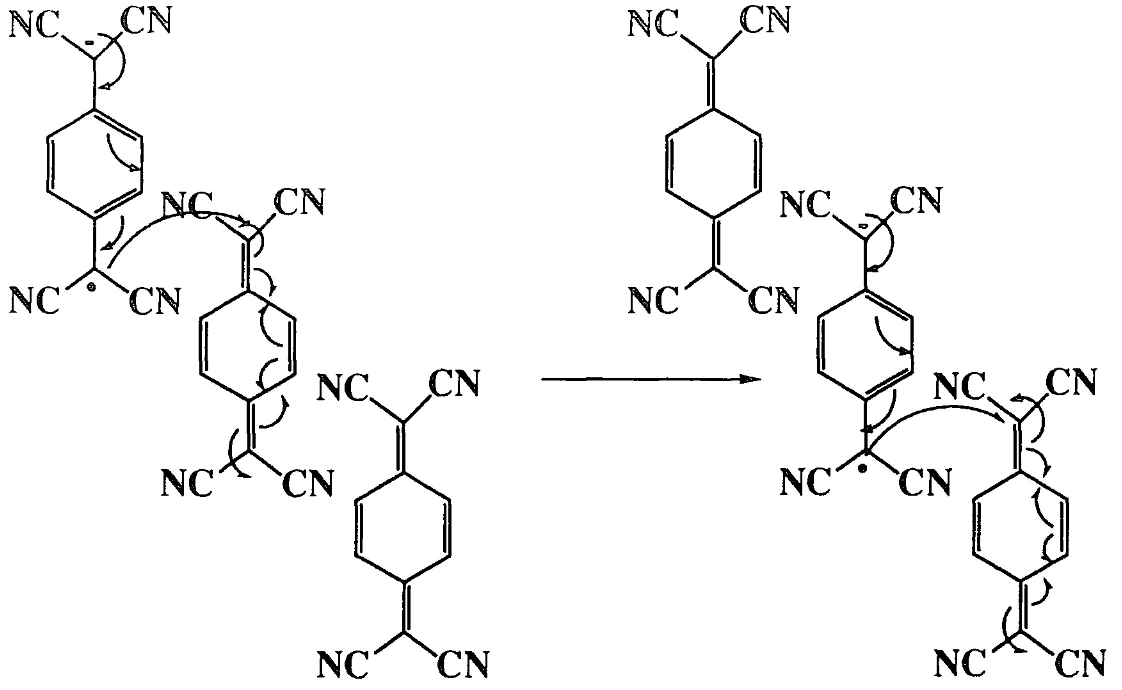


Fig 5. *Charge transfer along stacks.*

1.4.3. Conduction in Polymers

In attempting to rationalise the mode of conduction in polymeric systems, the various forms of charge carriers possible must be discussed.

Soliton Formation

Trans-poly(acetylene)[9] (PA) is unique in organic conductors in that it possesses a degenerate ground state (Fig 6).

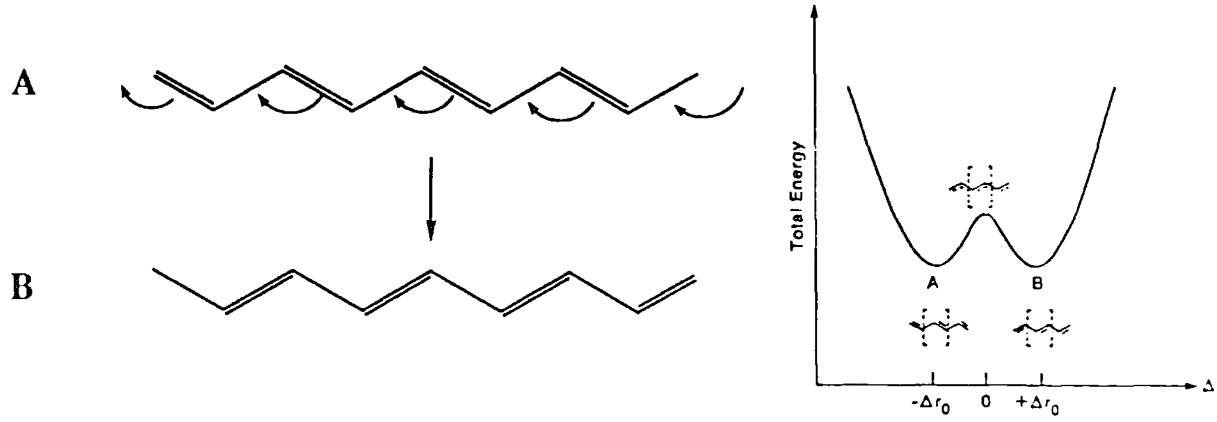


Fig 6. *Degenerate ground states for P.A.(Ref 15,19)*

Upon oxidation or reduction, (p or n type doping respectively), electrons are removed or added respectively to create localised charges called polarons (radical ions). Removal of two electrons creates two polarons of like charge (Fig 7 (b)) which need to be well separated to minimise the electronic repulsions between them. Since PA has a degenerate ground state, bonds can move from state A to state B without loss of energy so no energy input is required to separate the charges thus the process is favourable (Fig 7 (c)). As each charge of the would-be bipolaron is associated with a boundary between two geometrical structures of trans PA of the same energy eg. states A and B, then it is termed a soliton. By definition a soliton has the properties of a solitary wave which can propagate without deformation or dissipation, i.e. no loss of energy or change of form. Three types of soliton can exist (Fig 8).

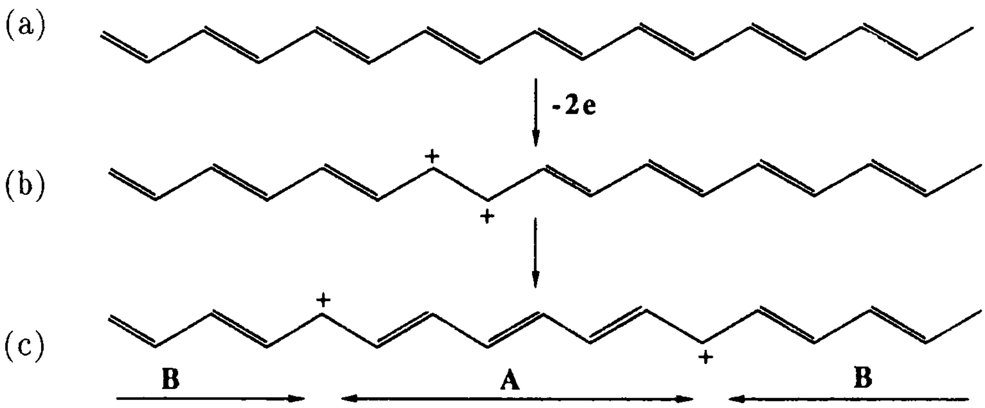


Fig 7 *Illustration of the formation of two charged solitons on trans-polyacetylene (Ref 19)*

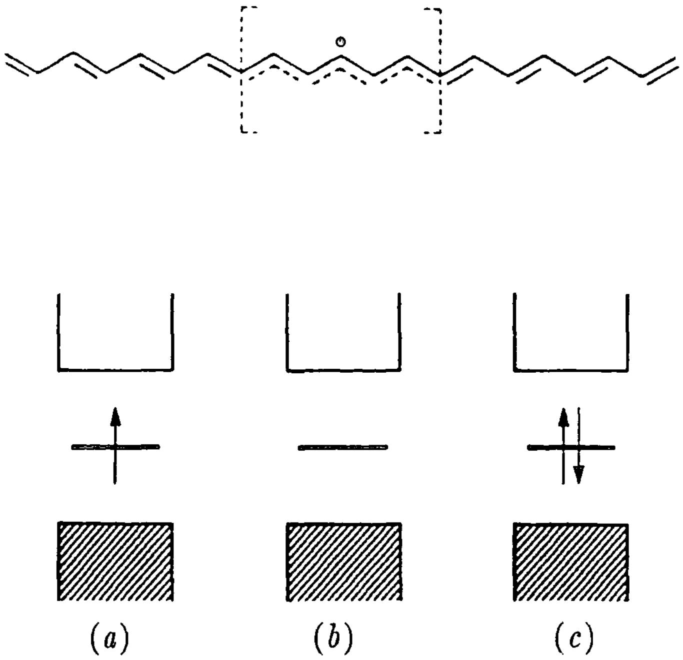


Fig 8. *Top:a schematic diagram of a neutral soliton. (a) a neutral soliton (b) a positive soliton (c) a negative soliton (Ref 19)*

Solitons have an unusual spin/charge relationship in that a neutral soliton is a radical with a spin of 1/2 whereas a charged soliton is spinless.

Polarons

Unlike *trans*-polyacetylene, polyheterocycles and polyphenylenic systems have non-degenerate ground states so cannot generate solitons. However, the removal of one electron from these systems creates, similarly, a polaron and the removal of a second creates two polarons. The energetically favoured species is now a bipolaron which forms by the generation of quinonoid structures within the polymer (Fig 9). This process can be observed by electron spin resonance (e.s.r.) spectroscopy which detects the formation of polarons of spin 1/2 at low doping levels with the subsequent saturation of signal at intermediate levels of doping. The peak signal due to saturation then decreases as the polarons couple to form spinless bipolarons. Thus, highly conductive polymeric systems (intermediate to high doping) observed by e.s.r spectroscopy are found to be spinless, as the charge carriers are spinless bipolarons. This is illustrated schematically in Fig 9.

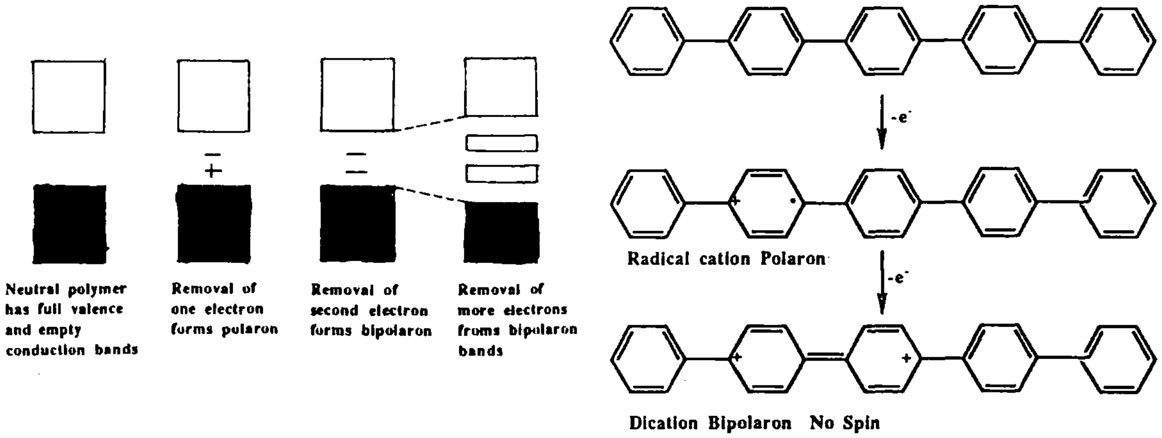


Fig 9. *The band diagram shows increased doping produces bipolaron bands and removes states from both valence and conduction band (Ref 2).*

In addition to e.s.r. spectroscopy, the formation of charge sites can be observed by ultra violet/visible/ near IR (uv/vis/nir) spectroscopy. The uv/vis/nir spectrum observed for most conjugated polymeric systems under discussion are essentially the same in shape. For example, the spectrum of polyisothianaphthene (PITN) (10) (Fig 10). shows a broad absorption with a steep leading edge which peaks and tails off to lower energy. This intrinsic absorption is attributed to the electronic transition between the π-π^* orbitals. Measurement of the energy at the onset of the leading edge gives a value of the band gap directly (E_g).

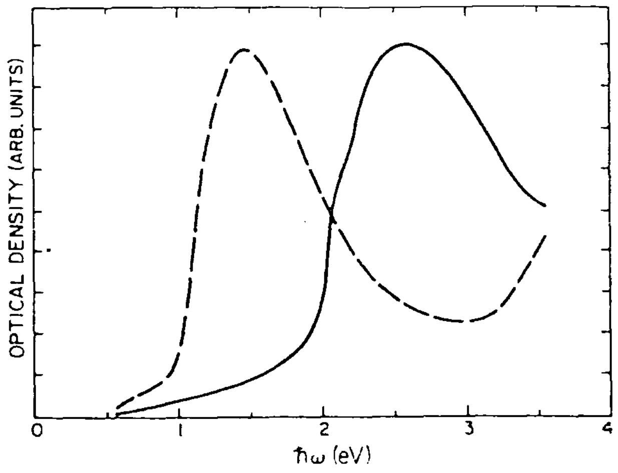


Fig 10. *Absorption coefficients of polythiophene (solid curve) and polyisothianaphthene (dashed curve) (Ref 20)*

Doping affects the electronic spectrum markedly. This is demonstrated by the spectra of polypyrrole[19](Fig 11). At low doping levels, the peaks at 0.7, 1.4 and 2.1 eV are attributed to the presence of polarons. At intermediate levels of doping, the absorption at 1.4 eV disappears which is in agreement with the e.s.r. measurements since this absorption is thought to be associated with the transitions between polarons. At high dopant concentrations, the recombination into bipolarons is seen as two wide optical absorptions at 1.0 and 2.7 eV, which are both below the band width maximum at 3.2 eV. This is again in

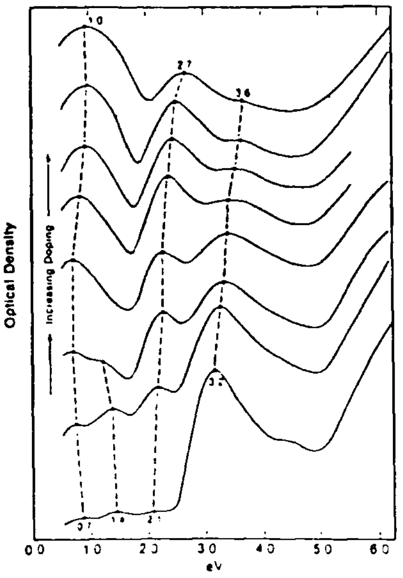
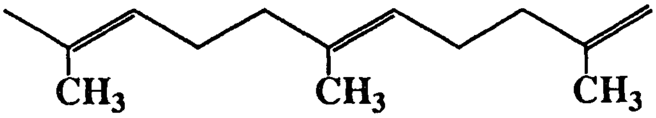


Fig 11[19]

agreement with that expected theoretically. In addition , the bandgap transition has moved to higher energies, 3.6 eV, a value close to that calculated.

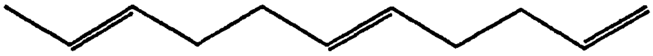
1.4.4. Non-Conjugated Polymers

"A conjugated backbone is not a prerequisite for conducting polymers."[21] Although often thought of as being of paramount importance for conduction, it has been found that conjugation is not necessarily required. A class of polymers with a degree of unsaturation but with appropriate sidegroups has been found to be conducting in a doped state. As such, 1,4-polyisoprene (11) forms a conducting complex with iodine giving a room temperature conductivity of $\sigma_{RT} = 10^{-2}$-10^{-1} S cm^{-1} whereas 1,4-polybutadiene (12) does not conduct. Thus, substituted poly(butadiene)-type backbones may form conducting materials, the effect of electron releasing substituents in (11) stabilising the formation of charge transfer sites in and around the isolated double bond structures.



1,4-*trans*-polyisoprene

(11)



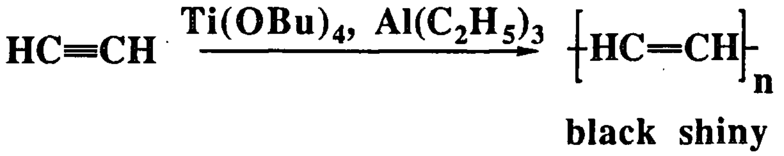
1,4-*trans*-polybutadiene

(12)

Electron transport would then occur via predominantly inter-site hopping. This opens up a new class of conducting polymeric materials and begs the question, how much does the charge transfer mechanism add to the conduction in polymeric organic conductors?

1.5.1. Polyacetylene

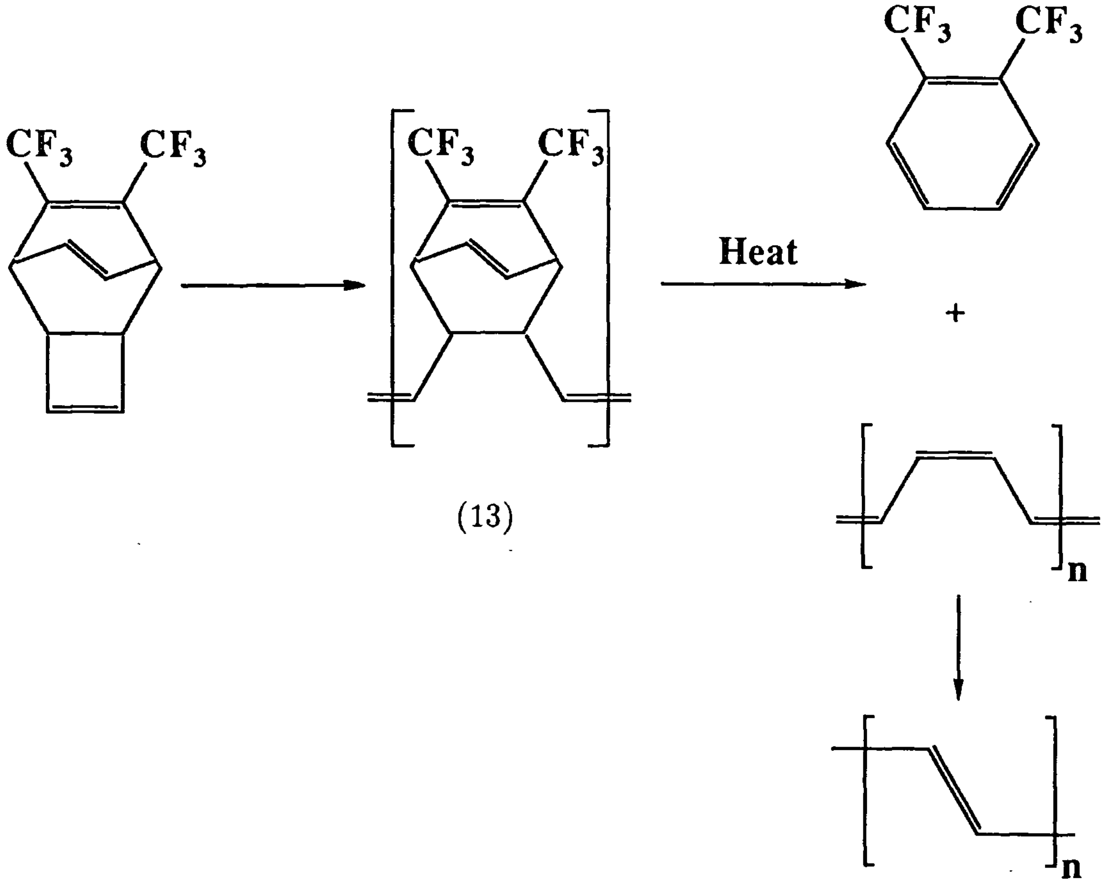
Two major route have been employed to prepare PA. The original preparation was carried out most efficiently by Shirakawa in the 1970's[22] employing a Ziegler catalyst, usually consisting of titanium tetrabutoxide and triethyl-aluminium in an inert solvent, which is exposed to acetylene by blowing it directly onto the catalyst/solvent surface (Scheme 1). The resultant black shiny film floats on the surface and can be removed and washed. Alternatively, a thin film of catalytic solution can be cast onto a glass plate upon which acetylene may be blown to produce a thin layer on an inert support. The layers produced in this manner are seen to be inhomogeneous networks of low density material, the network being built up of separate clusters of compacted PA particles. The overall macroscopic impression however is of a compact film with a metallic lustre. *Trans*-PA is produced exclusively at temperature above 373 K , it being the thermodynamically stable product. Temperatures of 255 K or below are required for *cis*-PA to predominate[1]. From the point of view of fabrication, PA prepared in this manner is unmanageable: it is insoluble, cannot be melt-processed due to its low degradation temperature and is oxidised upon contact with air. These problems were partially overcome by the use of a soluble precursor polymer system developed by Edwards and Feast[23], referred to as



$$HC{\equiv}CH \xrightarrow{Ti(OBu)_4,\ Al(C_2H_5)_3} \underset{\text{black shiny}}{\left[HC{=}CH \right]_n}$$

Scheme 1

the Durham route. This involved the formation of a tricyclic cyclobutene monomer derivative which is subjected to catalytic ring-opening metathesis using a 1:1 ratio of $WCl_6:(C_6H_5)_4Sn$ or $TiCl_4:(C_2H_5)_3Al$, the former giving equal amounts of *cis* and *trans* bonding, the latter giving



(13)

(9)

Scheme 2

predominantly *trans* bonding (Scheme 2). As such, precursor polymers of the general type (13) can be cast into thin films and pyrolysed to give PA of good homogeneity and high purity[24].

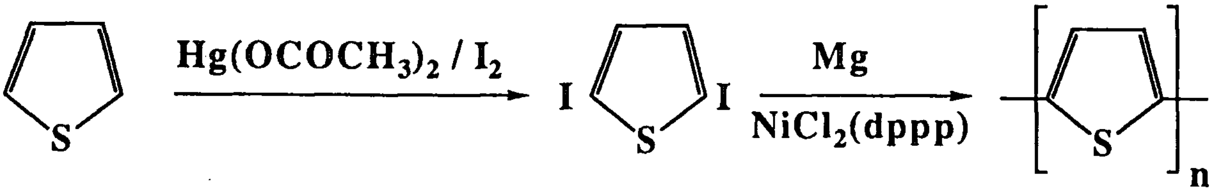
PA has been prepared in various processed forms. Stretch-alignment carried out during the thermal elimination process (13) to (9) increases both the anisotropic nature of the polymer and its overall conductivity. Naarman at BASF[25] produced a stretch-aligned film of PA with copper-like conductivity, σ_{RT}= 80,000 S cm^{-1}. Composite fibres of PA in carrier gels having stretch-aligned conductivities of 6000 S cm^{-1} have been prepared[26] giving PA properties normally associated with polyethylene, ie. flexibility and durability.

1.5.2. Polyheterocycles

Heterocyclic polymers can be considered simply as *cis*-PA units bridged by a heteratom. Their relative chemical stability compared to PA and ease of preparation hold certain advantages. By far the most important bridging heteratom is sulphur to give polythiophene.

Polythiophene

Polythiophene (PT) having sulphur bridging the sp^2p_z carbon chain of cis-PA is relatively stable to air in its p-doped state; the sulphur acts to stabilise the carbocation generated on the chain and the interchain d-orbital overlap aids the electron transfer necessary for conduction. Using 2,5-dihalothiophenes, polythiophene (14) may be synthesised chemically via a catalytic coupling reaction[27,28] to give powder samples of PT having 46-47 thiophene units[29] in 80-90 % yields (Scheme 3).

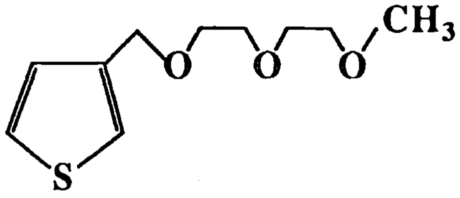


(14)

Scheme 3

The polymer sample exists as a brown/red powder, the preparation from di-iodothiophene giving high purity material which has a conductivity of $\sigma_{RT} = 10^{-9}$ S cm^{-1} and as a pressed pellet doped with AsF_5, $\sigma_{RT} = 14$ S cm^{-1}. This mode of preparation of polymers in general has received renewed attention[27,30].

To prepare films of high molecular weight, electrochemical polymerisation is now chosen as the preferred route[3,31]. The electrochemically-synthesised polymer is obtained in the oxidised (doped) conducting state, the dopant ion being the anion of the supporting electrolyte. De-doping of the polymer can be achieved chemically (exposure to ammonia, hydrazine etc.) or electrochemically to generate the insulating state. Since PT itself was first prepared, recent work has focused on substituent effects[32]. In general, electron donating groups like methyl enhance electrical conductivity: eg. poly(3-methylthiophene) $\sigma_{RT} \approx 100$ S cm^{-1} (cf. PT[33]$\sigma_{RT} = 10\text{-}100$ S cm^{-1}). Recently the trend to synthesise materials that are processable has lead to a large volume of work on soluble polythiophenes. This has involved the synthesis of 3-substituted monomers and making use of the substituent to increase the solubility of the polymer in various solvent systems. A film produced electrochemically using these monomers can then be removed, dissolved and recast into films that retain their conductivity. Alkyl or ether chain substituents have commonly been used to give polymers with conductivities up to $\sigma_{RT} = 1000$ S cm^{-1} for (15)[34]. Extensive literature on these systems is available[35]. Recently some sulphonate polymers (16) have been prepared to form the first water soluble polymeric systems[36].



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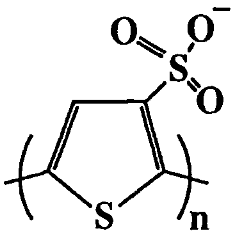
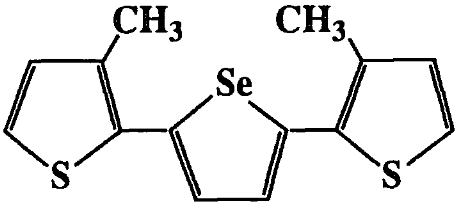


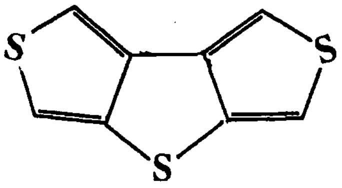
(16)

In a similar manner, polyselenophenes[37,38] and mixed poly(thiophene-selenophene) systems have been prepared. Compared with sulphur, selenium is expected to have increased orbital interaction between adjacent chains due to its larger d-orbitals with the result of an increase in conductivity. However, it is found that polyselenophene itself has a remarkably low conductivity of $\sigma = 10^{-4}$-10^{-3} S cm^{-1}(doped with BF_4^-) even though films of high quality were grown. Conversely, mixed alkylthiophene/selenophene monomers (17) when polymerised produced a film with a high conductivity ranging from 500 - 700 S cm^{-1} [39]. This contrasting behaviour is difficult to explain.



(17)

Other sulphur heterocycles have been polymerised including dithieno[3,4-b:3',4'-d]thiophene (18) which exhibits a bandgap of 1.1 eV[40] and a conductivity of 1.0 S cm^{-1} [41] (when doped with ClO_4^-) existing as a transparent conducting material in thin films.



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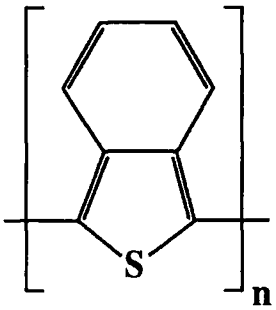
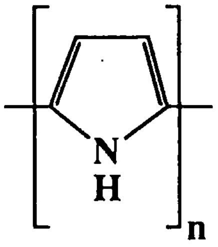


(10)

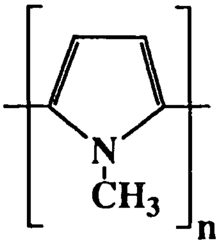
Work on polyisothianaphthene (PITN) (10) and related materials have received a lot of attention in recent years and will be covered in Chapter 2.

Polypyrrole

The historical development of polypyrrole (PP) (19) mirrors that of PT, both having being studied intensively. It was first recognised as a conducting polymer in 1968 by Dall'Olio et al [42] and was prepared by oxidising pyrrole with sulphuric acid, to give a black powder which had a room temperature conductivity of 8 S cm^{-1}. Referred to as "pyrrole blacks", numerous other oxidising reagents have been used[43]. Early work on the electropolymerisation of pyrrole using pyrrole in a 99% aqueous acetonitrile solvent with Et_4NBF_4 as a supporting electrolyte produced good quality films on platinum electrodes[44]. The use of a more nucleophilic solvent or supporting electrolyte prevented film growth (eg. Et_4NBr in acetonitrile). The electrical conductivity of these films (5-50μm thick) ranged from 10-100 S cm^{-1} with the higher values consistently being obtained. Further work showed PP films to be highly thermally stable in a conducting state, with little change in conductivity when heated to 250°C and changing from 100 S cm^{-1} at room temperature to 30 S cm^{-1} when cooled to -193°C [45]. Films of poly-N-methylpyrrole (20) and composite polmers of pyrrole and N-methylpyrrole have also been grown.



(19)



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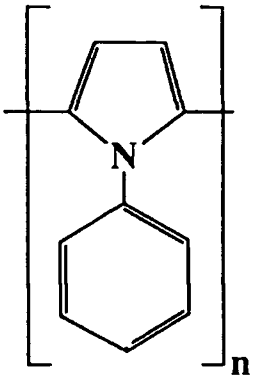


(21)

These generally show a decrease in conductivity with increasing proportions of the N-methylpyrrole monomer to the limit of poly-N-methylpyrrole (20) which exhibited a room temperature conductivity of $\sigma = 10^{-3}$S cm^{-1}. Similar results were found with poly-N-phenylpyrrole (21) where some steric interaction may also occur to push the rings out of planarity (Fig 12).

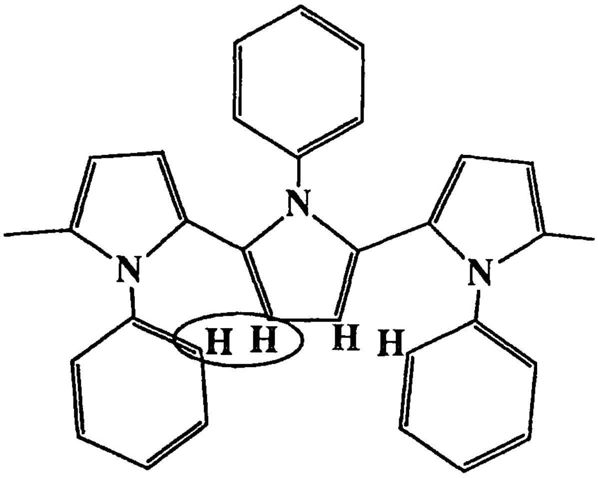


Fig 12

The durability of polypyrroles gave them significant advantages over the then leaders in the area, namely polyacetylenes.

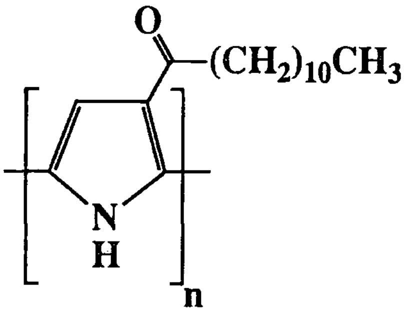
Chemical Synthesis

Recent synthetic approaches have been to chemically prepare PP chemically at interfaces and also to prepare composite materials[46]. Thus, free-standing films of PP were prepared by contact between a 30% aqueous solution of $FeCl_3$ and a 10% solution of pyrrole in benzene over a period of 6 hours. Thin flexible transparent films could be obtained with conductivities in the range of $\sigma = 1 - 30$ S cm^{-1}. The advantages over electrochemical processes are that the reagents involved are of low cost, the process can be applied to large films, water was the main solvent used and the reaction times are short. Composites have been formed by placing polyethylene or rubber latex sheets (0.1 - 0.2 mm thick) at the interface and allowing the pyrrole to permeate the film to come into contact with the oxidising solution. Similar composites with pyrrole absorbed into porous materials such as paper or cloth gave good yields of composite polymer with conductivities up to $\sigma = 50$ S cm^{-1}; for use as anti-static surfaces for example.

Effects of Counter Ion on Planarity

Certain work has focused on improving overall molecular organisation in the polymers, to improve the alignment and hence the anisotropic nature of the films prepared electrochemically. This has involved the use of supporting electrolytes in which the anion is planar, in particular using the toluenesulphonate anion[45b,47]. The resultant films have been studied by X-ray[45b] and neuton-scattering[47] techniques and both show an anisotropic molecular organisation in which the planes of aromatic rings lie parallel to the film surface. The question as to why there are such large differences in molecular packing arrangements of PP films with different counter ions is not a straight forward one. Variations have been correlated with polymerisation temperature and anodic potentials, low temperatures and high potentials leading to an enhancement of both electrical conductivities and molecular anisotropy[45b]. The absence of local anisotropic structures of closely packed rings in any film prepared using SO_4^{2-} or ClO_4^- as counterion indicates a basic difference. It may be simply that a planar anion leads to a planar overall structure, but it has been suggested that at the widely reported molar fraction of dopant (0.33) the toluenesulphonate anion occupies the equivalent volume as the PP chain. This would allow the PP/toluenesulphonate system to form easily an intercalated structure which is not the case for SO_4^{2-} or ClO_4^- [47].

Poly(3-alkylpyrroles) have been studied to a lesser extent than in the PT series. Their development has, however, mirrored them and excellent conductivities have been obtained with useful processability. For example the ketopyrrole (22) exhibits a room temperature conductivity of σ = 360 S cm^{-1} [34].



(22)

The addition of fused aromatic rings to the pyrrole series analogous to the thiophene heterocycles will be covered in Chapter 3.

1.5.3. Poly-para-phenylene's

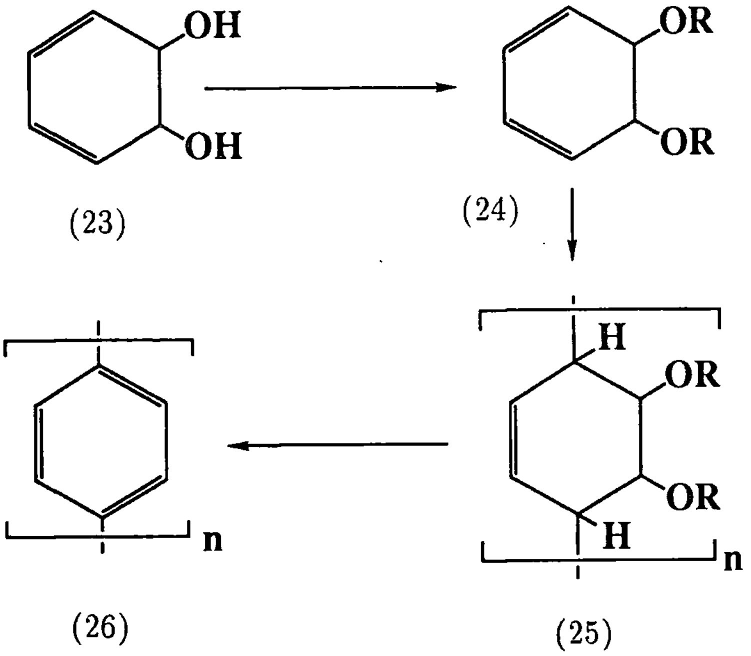
The major poly(aromatic) system, poly-para-phenylene (PPP) has been prepared by various methods. Early chemical methods using either $AlCl_3$ or $CuCl_2$ to couple benzene[48] or more recently polycondensation reactions using dihaloaro-matics in conjuction with magnesium and a transition metal catalyst[49] (eg. $NiCl_2$(dppy)) produced powder or non-flexible films as products. Films produced electrochemically are, however, both flexible and highly conductive due to the increase in molecular weights. Various electrochemical preparations are shown in Table 1

Solvent	Electrolyte	Anode	Conductivity	Observations	Ref.
Nitro Benzene	$CuCl_2$/ $LiAsF_5$	ITO	100	#1	50
Nitro Benzene	BF_3. $O(C_2H_5)_2$	ITO	>1	—	51
SO_2	Bu_4NBF_4	Pt	N/A	#2	52
Benzene	Cetylpyridinium chloride /$AlCl_3$	Pt/ ITO	10^4	#3	53

NOTES: ITO electrode is Indium Tin Oxide.#1 Yellow undoped, Brown doped #2 Electrolysis at -75°C,16 units; -20°C 30 units. Polymerisation in MeCN,$MeNO_2$,CH_2CCl_2 gives 10 units. More linear in SO_2. #3 42% by weight dopant giving empirical formulae of $(C_6H_4)_3AlCl_4$.

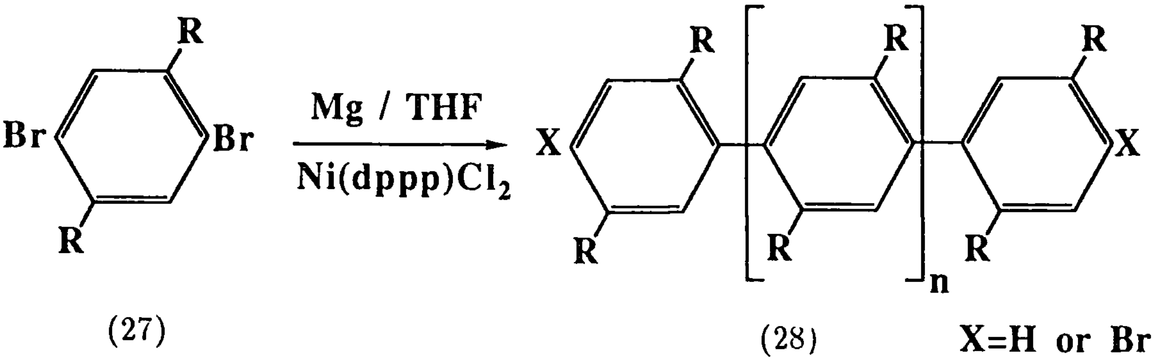
Table 1

Recently, chemical methods have again been used with the move towards making high molecular weight soluble polymeric systems as precursor polymers. The major drawback of early methods was the low degree of polymerisation, typically 10, which lead to the powdery fragile samples. A recent method was devised making use of radical polymerisation of alkyl derivatives of 5,6-*cis*-dihydroxy-cyclohexa-1,3-diene (23), namely (24), to generate the high molecular weight soluble polymer (25)[54]. A cast film of the precursor polymer (25) can be subject to heat treatment to eliminate the alcohol and give a film of PPP (26) or alternatively elimination can be promoted in solution state by addition of a base (N-methylpyrrolidone) to produce a precipitated sample of PPP[54] (Scheme 4).



Scheme 4

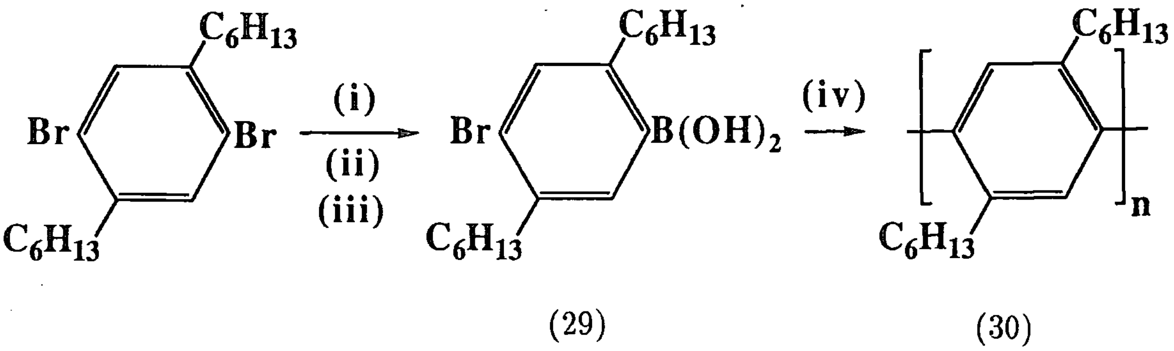
An alternative to this is an extension of the nickel catalysed polycondensation mentioned earlier. Work by Feast et al[55] has taken



Scheme 5

a 1,4-dibromo-2,5-di-n-alkylbenzene (27) and treated it with magnesium and $NiCl_2$(dppy) to give poly(para-2,5-di-n- alkylphenylene)s (28) with a maximum degree of polymerisation of 13 (Scheme 5).

A modification of this route by the same group using a palladium catalysed coupling of 4-bromo-2,5-di-n-hexylbenzene boronic acid (29) gave a soluble product with a much improved degree of polymerisation of approximately 30[56] (Scheme 6).

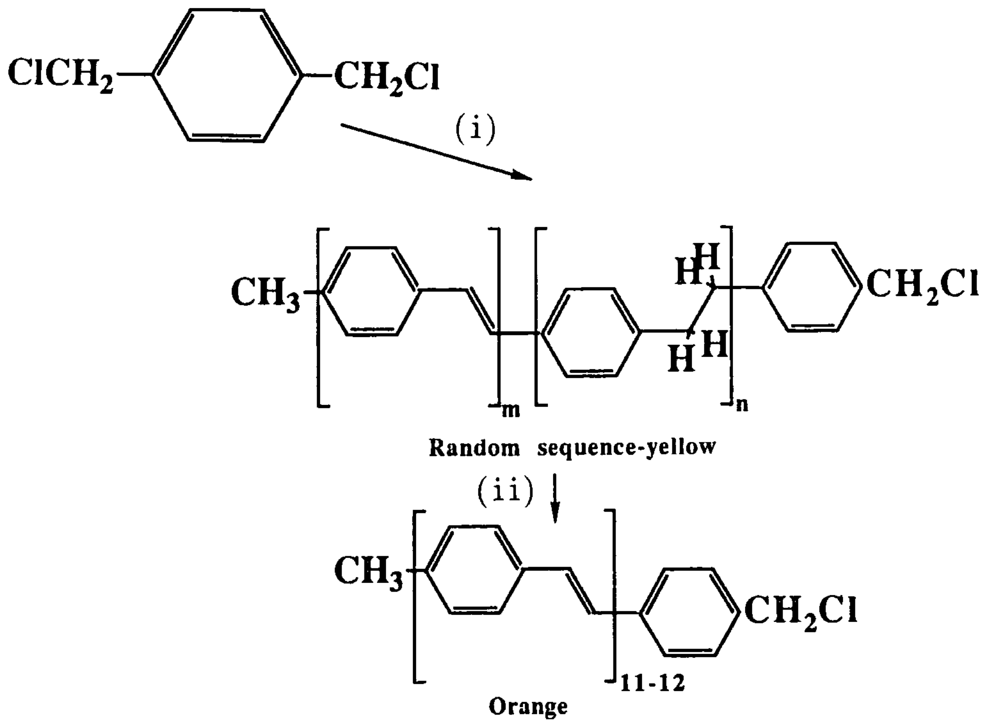


Scheme 6 *(i)* $^{n}BuLi$*, hexane/ether (ii)* $B(OMe)_3$*, ether, -60°C (iii)* $HCl(aq)$ *(iv)* $Pd(PPh_3)_4, C_6H_6, 2M\ Na_2CO_3$

1.5.4. Poly-para-phenylenevinylene's

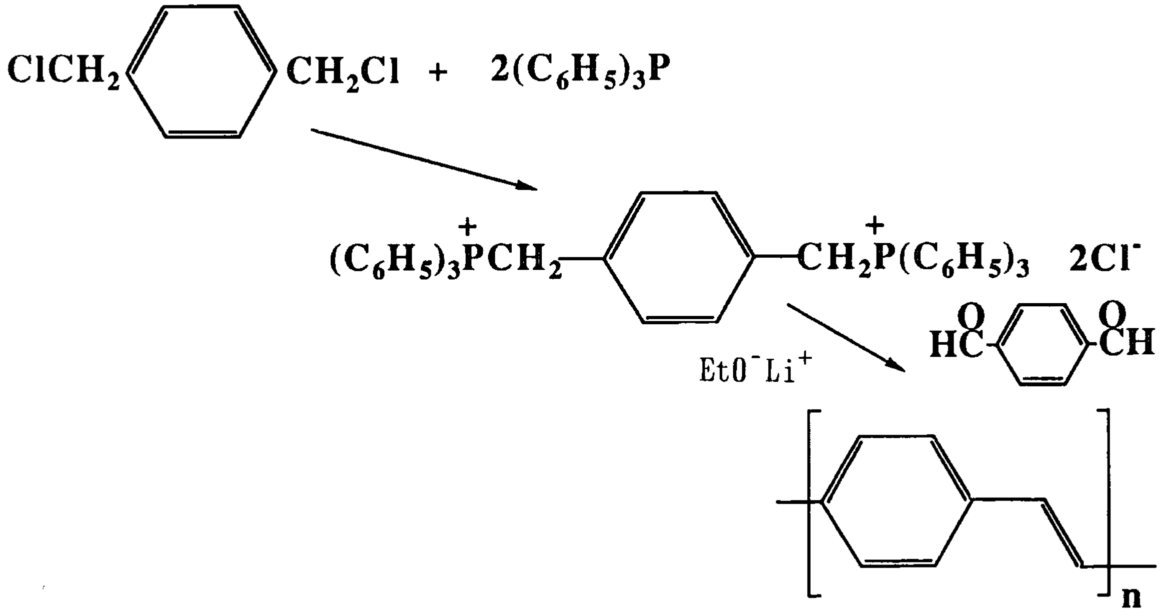
Polyphenylenevinylenes (PPVs), a class of conducting polymers that can be considered to be a cross breed between PPP and PA have been studied extensively. The mixing of aromatic and vinylic characteristics to generate PPV gives it physical characteristics between the two extremes. PPV gains over PA in that it is environmentally stable but its electronic characteristics are less favourable with a band gap of 2.7 eV[57] compared with 1.4 eV for PA and 3.0 eV for PPP.

Until recently, studies on PPV were confined to samples of oligomeric powders derived from dehydrochlorination reactions[58] or Wittig condensations[58,59] (Schemes 7 and 8 respectively). As these oligomers were very insoluble, the degree of polymerisation was very low, usually in the order of 9-11 units.



Scheme 7 *Synthesis of PPV by dehydrochlorination of para-xylylidinedichloride and subsequent pyrolysis. (i) NaH,DMF (ii) 300° C vacuum,3h,(-HCl).(Ref 58)*

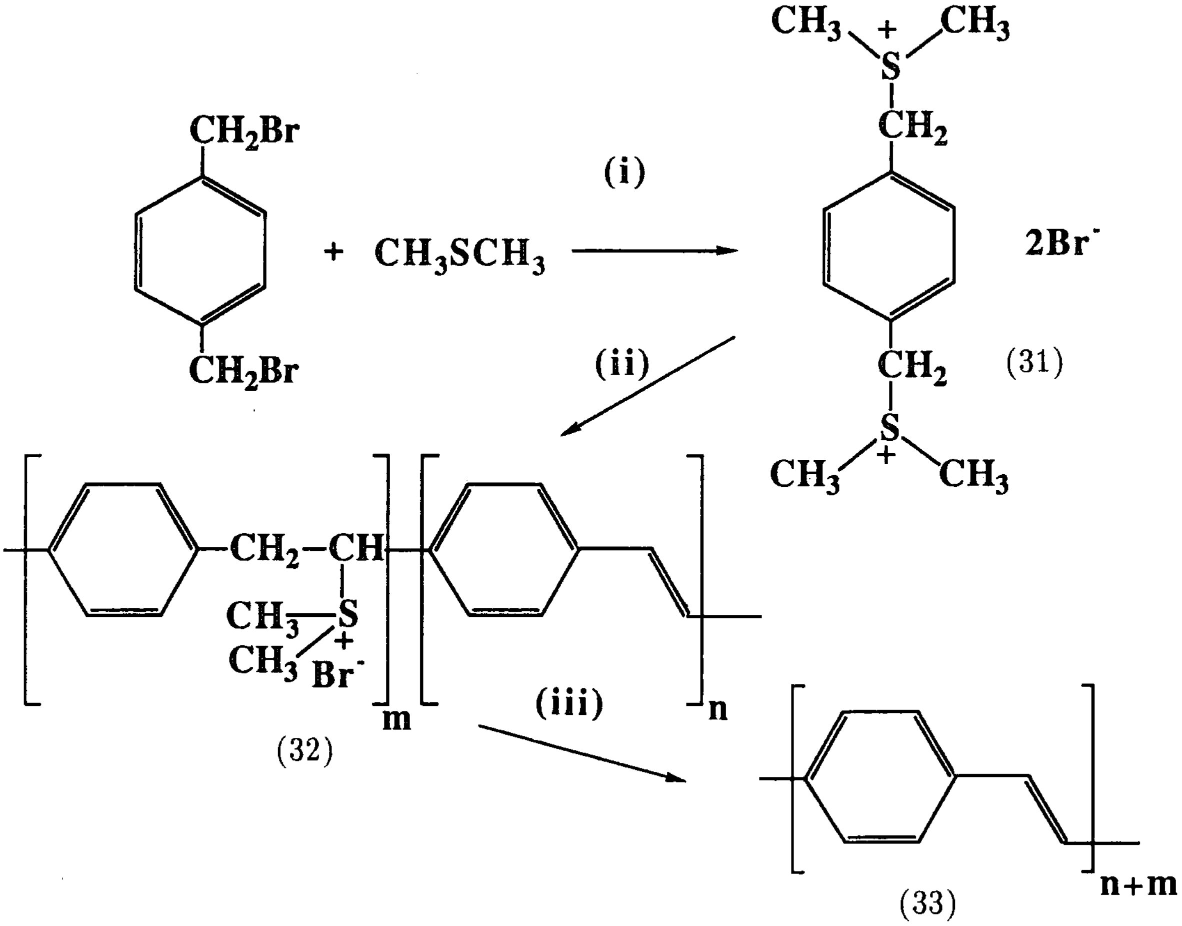
The large number of cis-double bonds produced by Wittig condensations were effectively converted to the *trans* configuration by refluxing with iodine in xylene[58] to give lemon to orange coloured powders. X-ray diffraction studies showed these materials to be amorphous in nature having a pristine conductivity of $\sigma < 10^{-14}$ S cm^{-1}. Surface doping



Scheme 8 *Synthesis of p-xylyene-bis(triphenylphosphonium chloride (Ref 60) and subsequent polymerisation (Ref 58,59).*

of the pressed pellets with AsF_5 was found to increase this to 2-3 S cm^{-1} [58], with halogen doping being ineffective unless carried out for an extended period of time (760 torr for 24 hours at 180°C) which produced conductivities less than $\sigma = 10^{-8}$S cm^{-1} [58].

The limited use of these intractable oligomeric materials lead to PPV being neglected as an electroactive polymeric material. The widespread movement to soluble precursor systems with high molecular weight which can in turn be converted into high molecular weight PPV lead to the emergence of an alternative preparative approach. First demonstrated by Kanbe in 1968[61] as an efficient route to PPV *via* the dimethylsulphonium bromide precursor (32), little has changed in the

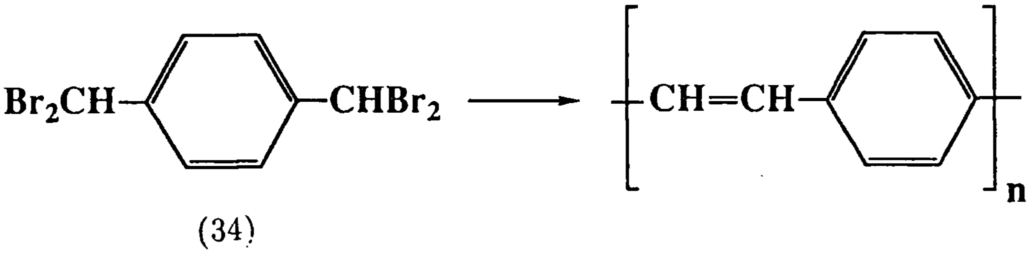


Scheme 9 *Preparation of PPV via soluble sulphonium salt precursor polymer (i) 50 °C, MeOH:H_2O (8:2) (ii) NaOH/0° C (iii) 100-380° C, vacuum.*

synthesis today. Recent work has been involved with the optimisation of reaction conditions to minimise the formation of unsaturated segments within the polymer through premature elimination of dialkylsulphides and hydrogen halides; ie. to keep the m to n ratio large. (Scheme 9) The introduction of unsaturation, seen as an increased colouration of the product, leads to precipitation of the polymer and hence a low degree of polymerisation.

Other studies have looked at the effect of different alkyl groups on the sulphur with respect to the overall polymer yield and the thermal stability of the precursor polymer. These, along with studies relating to the effect of aromatic substitution and film manipulation, will be dealt with in Chapter 5

With the great interest in electrodeposition of polymers present in this field, it is worth noting that an <u>electoreductive</u> synthesis of PPV has been reported from the $\alpha,\alpha,\alpha',\alpha'$-tetrabromo-p-xylene (34) (Scheme 10). Film growth on indium tin oxide coated glass (ITO),Pt,Cu or Ni electrodes in THF or dimethyl ether has been achieved using $Cr(CO)_6$ or $Mo(CO)_6$ to catalyse the system to give thick yellow films of PPV[62].



(34)

Scheme 10

1.6. Fluorinated Systems

Theoretical calculations comparing hydrocarbon PA with poly(fluoroacetylene) (PFA) and poly(difluoroacetylene) (PDFA) (Fig 13) have been carried out by Fukui et al[63]. They have given

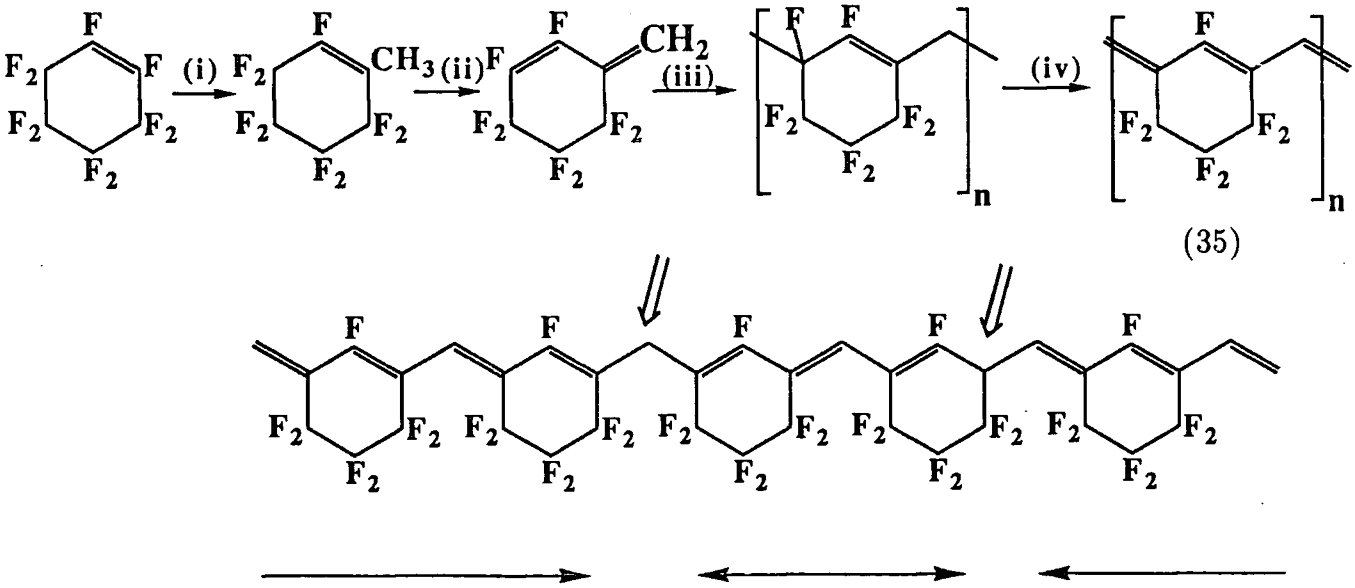
$$\left[\mathrm{CF{=}CH} \right]_n \qquad\qquad \left[\mathrm{CF{=}CF} \right]_n$$

(PFA) **(PDFA)**

Fig 13

rise to some remarkable and interesting conclusions showing that these polymers have the capacity to become intrinsically conducting materials, as well being better conductors than PA when doped with suitable electron donors. The calculations show that the electron affinities of the carbons on the fluorinated backbone become larger in both the cis and trans forms of PA, yet the values of the ionisation potentials are not changed a great deal. Thus, the large electronegative character of fluorine lowers the levels of the lowest unoccupied molecular orbitals (LUMOs) on the carbons and conversely the lone pairs act as electron donors with the effect of raising the levels of the highest occupied molecular orbitals (HOMOs), as is common for fluorinated systems. Since the electron affinities have been increased, the polymer will have a greater capacity to be n-type doped, the LUMOs and HOMOs will become closer together and thus the intrinsic conduct- ivity of PFA and PDFA may be larger than that of PA, and semi- conducting. Later studies using the more reliable *ab initio* Hartree- Fock crystal orbital method of calculation[64] would tend to confirm these ideas. One of the major drawbacks of PA is its instability in air. By using fluorine substituents the band gap should be reduced and a polymer more stable to oxidation be generated. The instability of fluoroacetylene (FA) and di-fluoroacetylene (DFA) monomers[65] makes the preparation of the respective polymers unfeasable via analagous routes to PA although polymerisation to form PDFA has been claimed[66].

Some practical support for these claims is available with the investigation of poly(1,7-7H-heptafluoromethylene-cyclohexenlyene) (35) and comparison with the hydrocarbon analogue. The polymer was synthesised by Feast et al[67] from a precursor polymer using a thermal elimination process eliminating HF (Scheme 11). This elimination process is actually ambiguous in that it can occur as a 1,2-elimination or as a 1,4-elimination with the consequence that saturation may still be present in the product. The authors do note that full elimination may not occur so HF may still be present in the polymer chain. Thus the conductivity values measured may well be due to the slightly doped material rather than the pristine polymer. The results found do suggest

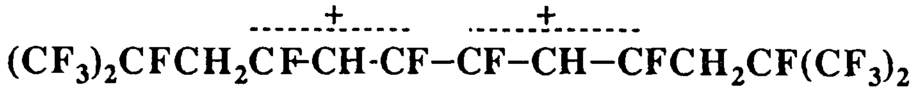


(35)

Scheme 11. *Top: Synthesis of poly(1,7-7H-heptafluoromethylenecyclohexenylene) (i) MeLi/Ether; (ii) NaF/460-480° C /N$_2$ carrier; (iii)radical polymerisation AIBN initiator (Azobisbuteronitrile) (iv) Thermal dehydrofluorination,200° C/10^{-2}mm Hg. Product may have possible saturated units due to ambiguous elimination of HF.*

that Fukui's calculations may be holding true since the conductivity of the converted film is $\sigma = 10^{-4}$-10^{-5}S cm^{-1} compared with pristine PA of $\sigma = 10^{-12}$S cm^{-1} [68]. It was also found that no change in conductivity was observed upon prolonged exposure to iodine vapours indicating considerable stability to oxidation.

It is widely known that fluorine directly attached to a positively charged site ie $^{+}$C-F, is stabilising, whereas fluorines adjacent to the charged site are massively destabilising[65]. Accordingly, much work has been done on long-lived fluorinated carbocations. Recently, work in this area by Chambers et al has lead to the formation of the dication (36)[69] and the preparation of the fluorinated acetylenes (37)



$$(CF_3)_2CFCH_2\overset{+}{CF\text{-}CH\text{-}CF}-\overset{+}{CF-CH-CF}CH_2CF(CF_3)_2$$

(36)

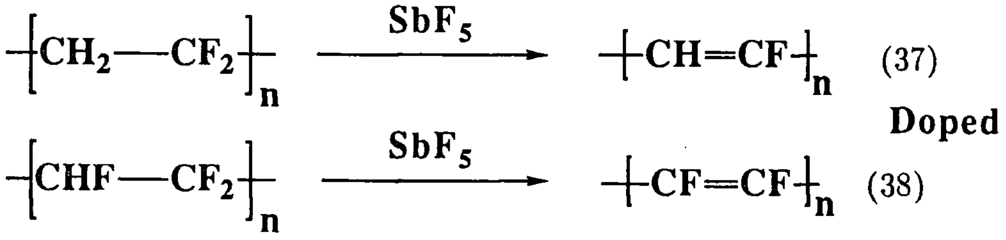
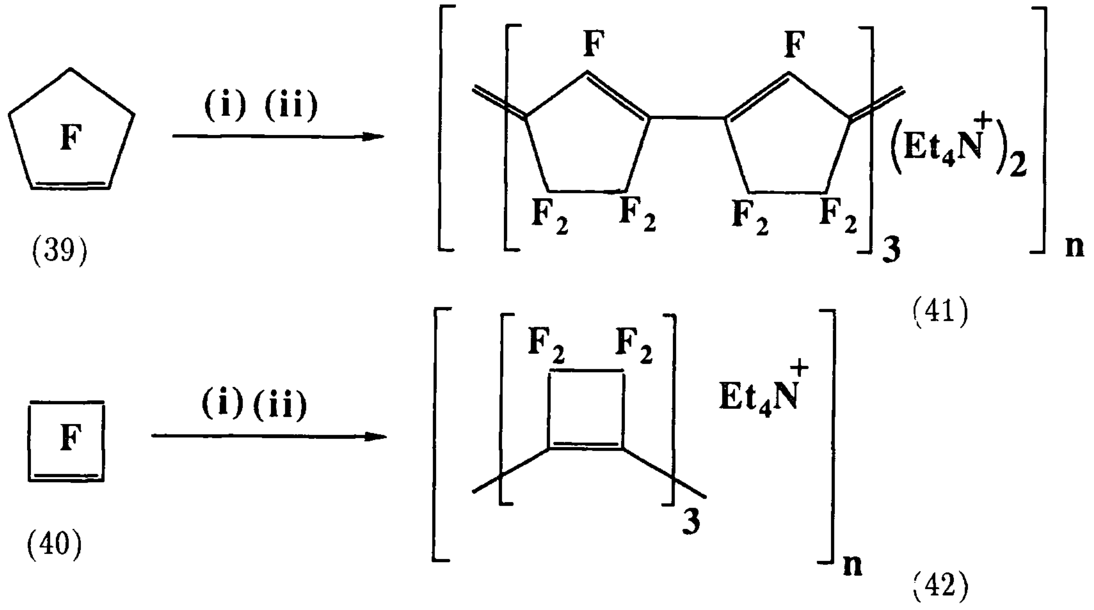


Fig 14. *Extended stable fluorinated conjugated cations*[69,70]

and (38)[70] (Fig 14). Since both these are prepared in the doped state, direct measurement on the pristine polymer was not possible.

Fluorinated polymers with carbanion centres have been synthesised, employing a cathodic (reductive) electro-polymerisation process[71] (Scheme 12). Polymeric crystals (41 and 42) derived from perfluoro-cyclopentene (39) and perfluoro-cyclobutene (40) respectively

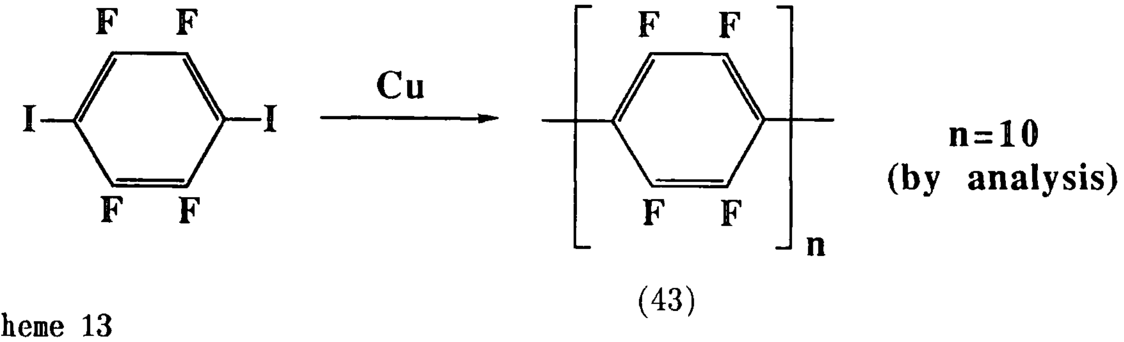


(39) (40) (41) (42)

Scheme 12 *(i) Pt or Hg cathode,divided cell, CH_3CN or DMF with Et_4NBF_4 (ii) -1.9 V SCE*

have been prepared in a doped state with the polymer (41) having a minimum conductivity value of $\sigma = 10^{-3}$S cm^{-1}. It seems therefore that fluorinated polyacetylenic systems can be prepared in both the n-type and p-type doped states.

Poly-para-perfluorophenylene (FPPP) (43) prepared *via* a copper coupling reaction (Scheme 13) has been doped with potassium (K-FPPP) and gives rise to a conductivity of $\sigma = 20$ Scm^{-1}[72], slightly higher than that found for the hydrocarbon analogue at $\sigma = 10$ S cm^{-1}. More interesting is the decrease by an order of magnitude, in the concentration of unpaired electrons observed for K-FPPP. This observation may explain the increase in conductivity since electron transport in PPP's is imparted by bipolarons (radical ion pairs) ie.



(43)

Scheme 13

less polarons observed implies more bipolarons, more charge carriers and hence higher conductivity (See section 1.4.4.). Again, resistance to oxidation was observed with no doping apparent when exposed to AsF_5 or SO_3. One major concern with n-type doping of fluorinated systems is the possible reductive elimination of fluoride ion. In the study of K-FPPP[72], there was no evidence that fluoride ions had been formed since the elimination of fluoride would have lead to the destruction of the polymer.

In conclusion, for fluorinated systems, polymers with slightly higher intrinsic conductivities than their hydrocarbon analogues are expected. Moreover, they should be more resistant to oxidation and hence more susceptable to n-type doping.

CHAPTER TWO

SULPHUR MONOMERS

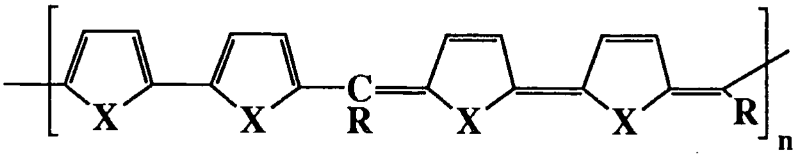
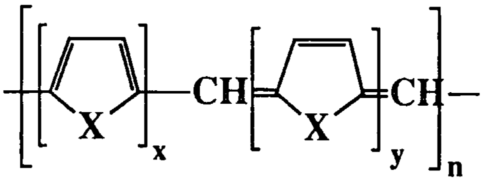
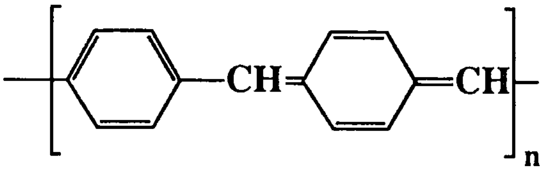
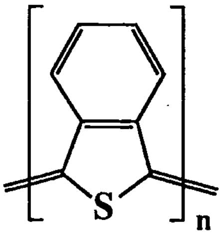
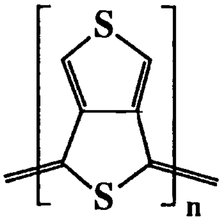
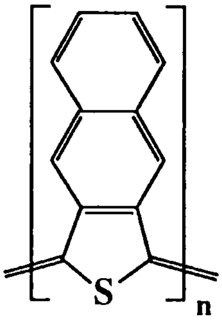
2.1. Introduction

2.1.1. Background

The design of polymeric systems with increased intrinsic conductivities is a major goal (ie. without the need for doping). The preparation of polyisothianaphthene (PITN) (10) by Wudl et al[73] in 1984 which has a band gap of only 1.13 eV sparked off a resurgence of practical and theoretical papers. This reduction of the band gap (E_g) from that of PT (E_g= 2.1-2.2 eV [74]) by approximately 1 eV was attributed to the increased contribution of the quinonoid resonance structure in the case of PITN compared with PT and also due to the increase in coplanarity of PITN compared with PT[75] (Fig 15). The quinonoid structure has increased aromatic nature in the six-membered ring resulting in increased conjugation and delocalisation along the polymer backbone itself. This will have the effect of shortening the inter-ring distance so lower E_g. A number of theoretical investigations have been made into PITN and related compounds[76,77,78] and other systems with narrow band gaps[75,79,80] in which the quinonoid structure may predominate. These include polymer of the type listed in Table 2

AROMATIC **QUINONOID**

Fig 15

	I[80]	E_g = 0.83 eV (expt)
	II[75]	E_g= 0.7 eV (calc)
	III[81]	E_g= 1.17eV (calc)
	IV[76]	E_g = 0.54eV (calc) 1.13eV (expt)
	V[76]	E_g = 1.02eV (calc)
	VI[76]	E_g = 0.01eV (calc)

(44)

Table 2

The availability of many resonance structures, (Fig 16), would be expected to lead to higher stability and more equal bond lengths along the pseudo polyene backbone. Although all these structures are available in the ground state of PITN, they are not degenerate so do not exist equally. Thus like polyheterocycles in general, polarons and bipolarons are the dominant charged species[82] when these materials are doped.

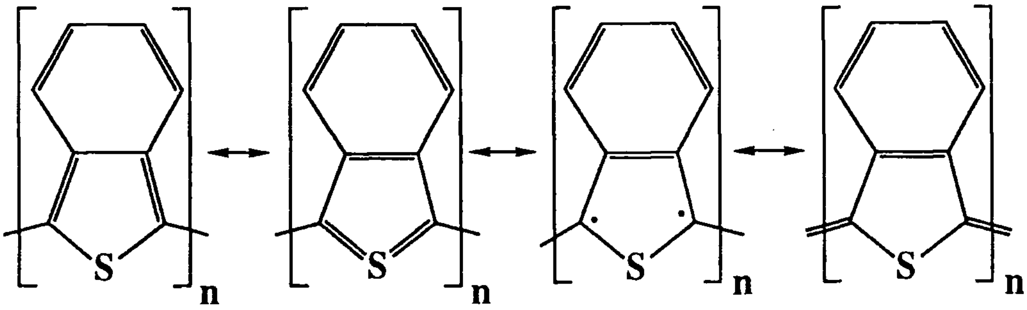
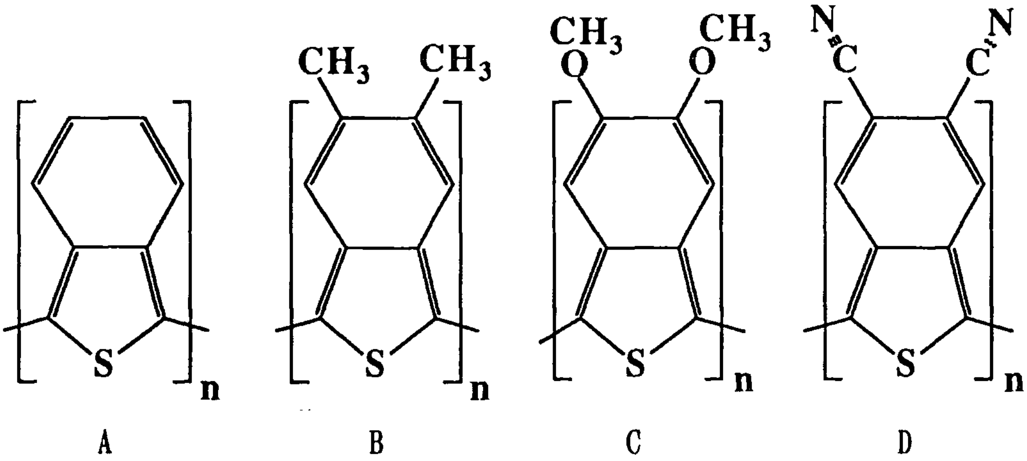


Fig 16

Calculations on PITN have shown it to have a band gap of 0.45 eV (compared with 1.13 eV found experimentally) which is 1.17 eV lower than that calculated for PT in the same theoretical framework. This is in agreement with the 1.0 eV reduction in the band gap found experimentally for that of PT at 2.0 - 2.2 eV to around 1.0 eV for PITN. Calculations went on to show that the addition of a second aromatic ring to give polyisonaphthothiophene (PINT) (44) would give a bandgap of only 0.01 eV, which could represent a major step forward in the search for an intrinsically conducting polymer. It has been pointed out however that factors not accounted for when calculating the band gap may lead to a widening of it. Indeed, there is some doubt as to whether the so called "vanishingly small" band gap predicted by Bredas[76]for PITN does occur. Independent work[79] indicates that the addition of a second aromatic ring may actually increase the bandgap due to a switch over back from the quinonoid to aromatic structure.

The addition of substituent groups onto PITN has also been studied theoretically[77]. Overall, they appear to have very little influence on either the ionization potential of the polymer or its band gap whether electron donating groups or electron withdrawing groups (Fig 17.) are considered. The arguments applied to the fluorine substitution on PA can be applied here with the expected π back donation by the fluorine atoms into the ring and the resultant effect on electron affinities at the carbon centres which may bring about a similar reduction in the band gap as predicted for poly(difluoroacetylene) (Section 1.6). However, no theoretical investigations have been done on fluorinated PITN systems.



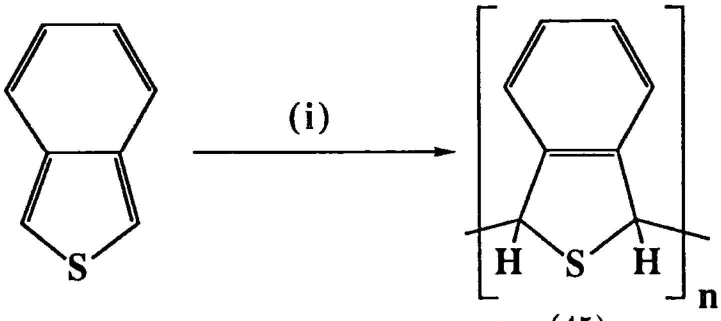
			E_g/eV	IP/eV
A	Poly(isothianaphthene)	PITN	0.54	4.34
B	Poly(dimethylisothianaphthene)	DM-PITN	0.53	4.28
C	Poly(dimethoxyisothianaphthene)	DMO-PITN	0.58	4.31
D	Poly(dicyanoisothianaphthene)	DCN-PITN	0.55	4.43

Fig 17. *Comparison of VEH calculated electronic properties of PITN and derivatives: Band gap and ionisation potentials (Ref. 77).*

2.1.2. Electrochemical preparation of Polyisothianaphthene (10)

PITN has been prepared electrochemically only under very specific conditions. It was found that by using the general conditions of a fresh sample of monomer dissolved in dry acetonitrile with either

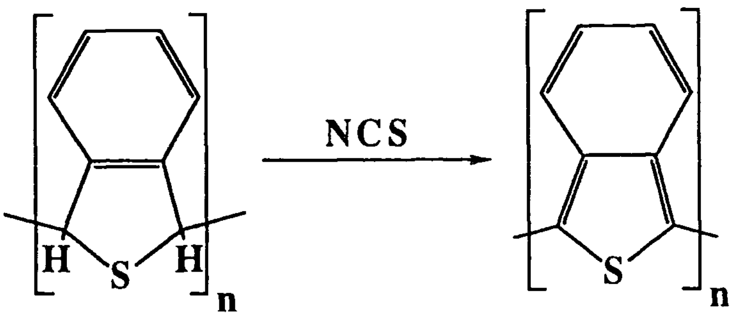
Bu_4NClO_4 or Bu_4NBF_4 as supporting electrolyte ,only a white precipitate formed at the anode upon the application of a voltage[73]. It was further noticed that an initial instantaneous blue film covered the anode prior to the formation of the white precipitate and that the appearance of this precipitate was independent of electrode material, solvent or temperature. Analysis of this material showed it to be poly(dihydroisothianaphthene) (45) (Scheme 14). It was deduced that this was the product of competing cationic polymerisation. To prevent this reaction occurring a species was introduced into the cell that was more nucleophilic than the isothianaphthene to interrupt the propagation step. It was found that halides resistant to oxidation, particularly the tetraphenyl phosphonium and tetraphenyl arsonium chlorides proved ideal whereby no precipitation occurred and a blue black film was deposited. The exact conditions used ie. temperature and applied potentials and cell set-up were <u>not</u> published. It was claimed that doped thin films of PITN have very low optical density in the visible portion of the spectrum, so the material was the first example of a transparent highly conducting polymer (σ = 50 S cm^{-1}).



(45)

Scheme 14. (i) *Electrolysis of ITN in MeCN with Bu_4NBF_4*

The white precipitate of poly(dihydroisothianaphthene) (45) showed a ^1H nmr spectrum in general agreement with the assigned structure (multiplet at 6.6-7.2 ppm, 4 hydrogens and a singlet at 5.0 ppm, 2 hydrogens). Treatment of this polymer with N-chlorosuccinimide (NCS) effected efficient dehydrogenation it to give a product with



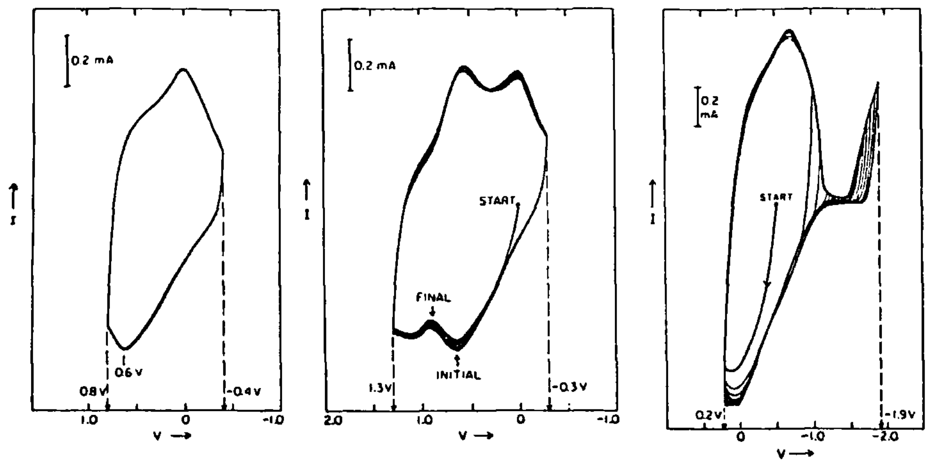
(45)

Scheme 15

an identical infrared spectrum to that of electrochemically produced PITN. $Cl_{0.05}$[82] (Scheme 15).

2.1.3. Physical Aspects

The electronic, electrochemical and optical properties of PITN have been studied extensively[82,83]. The cyclic voltammogram of PITN are shown in Fig 18. Cycles between -0.4 and +0.8 V (SCE) at 40 mV/s as shown in



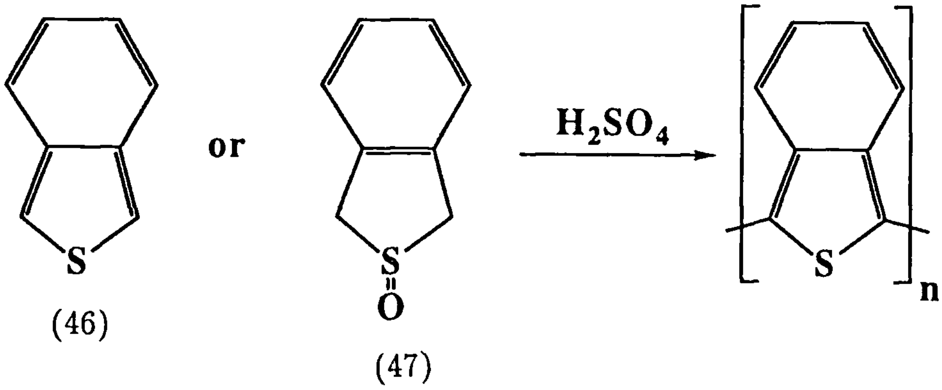
(a) (b) (c)

Fig 18. *C.V.s of PITN* [82]

Fig 18 (a), show a fully reversible redox cycle in that the shape of the curve was unchanged over 60 scans. It was observed that sharp colour changes were associated with the two peaks. For thin films, at +0.6 V on the reduction sweep, the film changed from blue/black (p-doped) to an almost transparent yellow/green colour which at zero V on the oxidation sweep, switched back to the original blue/black. The secondary oxidation seen in Fig 18(b) at +1.1V and reduction at +0.5 V were found to be detrimental to the polymer since the current decayed with each additional cycle thereafter. Fig 18(c) shows the attempts to electrochemically n-type dope PITN. Clearly shown is the irreversible nature with current falling to near zero at -1.4 V before flowing again. This input of charge, however, cannot be removed upon the oxidation scan, so although reduction of the polymer (hence n-type doping) may be occurring at voltages more negative than -1.75 V (vs Ag/Ag^+); the reduced polymer is unstable.

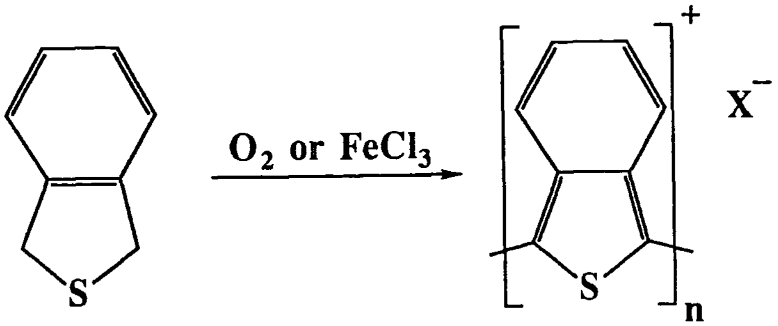
2.1.4. Chemical Preparation of PITN

Powder samples of PITN can be prepared be chemical routes. Commonly isothianaphthene (46) or dihydroisothia-naphthalene S-oxide (47) can be treated with concentrated sulphuric acid to afford a brown



Scheme 16

powder sample of conducting PITN with the empirical formula $(C_8H_4S)(HSO_4)_{0.05}(H_2O)_{0.33}$[73] (Scheme 16). More recently, a convenient procedure to prepare PITN has been discovered directly from 1,3-dihydro-isothianaphthalene (48) saving one or two synthetic steps[84] (Scheme 17). Thus, exposure of (48) to oxygen or to an oxidant formed conductive PITN powder samples with conductivities as high as those previously reported,



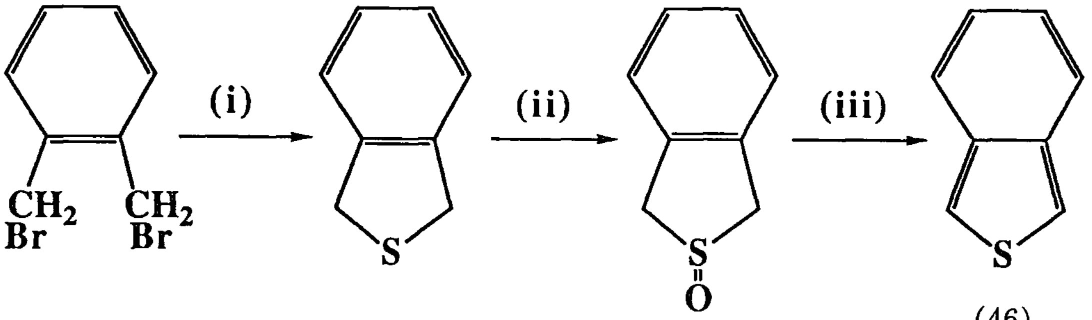
(48)

Scheme 17

of the order of $\sigma = 0.5$ S cm^{-1}.

2.1.5. Preparation of isothianaphthene

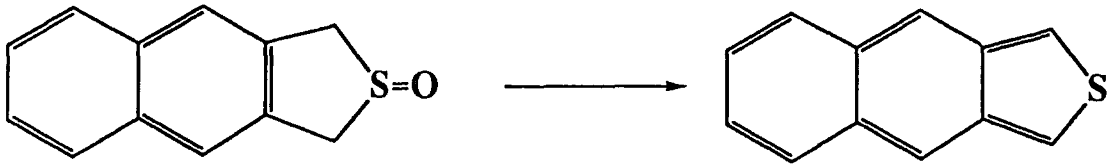
The method used exclusively for the preparation of the isothianaphthene (also known as benzo[c]thiophene) heterocycle (46) was first devised by Cava et al[85] and is outlined in Scheme 18. This synthetic



(46)

Scheme 18. *(i)* Na_2S [86] *(ii)* $NaIO_3$,$MeOH/H_2O$ *(iii)* Al_2O_3/Δ

route has also been applied to the preparation of the naphtho[2,3-c] thiophene (49) but with little success (Scheme 19). However, thermal



(50)

(49)

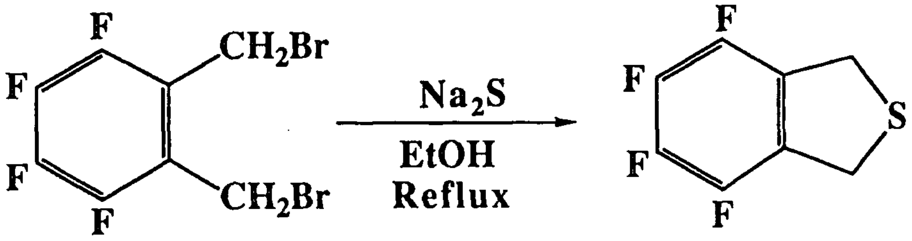
Scheme 19

dehydration of the sulphoxide (50) up an unpacked quartz column at 800°C / 0.3 mm Hg produced good yields of the thiophene (49)[87]. It was trapped in liquid nitrogen and as expected was a yellow very unstable solid.

Isothianaphthene (46) is an unstable material requiring oxygen-free dry-box techniques for efficient handling.

2.2. Synthesis of 4,5,6,7-tetrafluoroisothianaphthene (51)

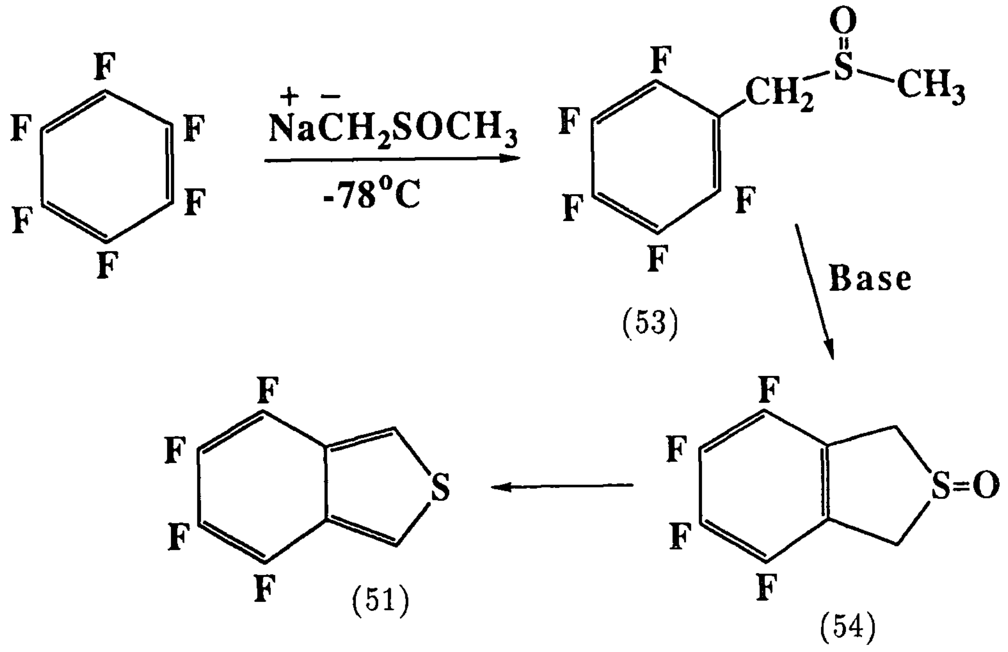
1,3-Dihydro-4,5,6,7-tetrafluoroisothianaphthene (52) has been prepared by Coe et al[88] in a similar manner to the hydrocarbon analogue. The product, obtained only in a 16 % yield, surprisingly was found to be very unstable and so was considered to be unsuitable as the starting material in the synthesis of our target monomer (51) (Scheme 20).



(52)

Scheme 20

A cyclisation reaction using 2,3,4,5,6-pentafluorobenzyl methyl sulphoxide (53) seemed a possible route to generate the cyclic sulphoxide (54) which would require dehydration analogous to the hydrocarbon synthesis to give the tetrafluoroisothianaphthene (51) (Scheme 21). Previous work in our laboratory had produced (53) on a large scale[89,90]. A reference in the literature suggested that the cyclisation would require three equivalents of base[91] to remove the proton on the terminal carbon before cyclisation would occur.



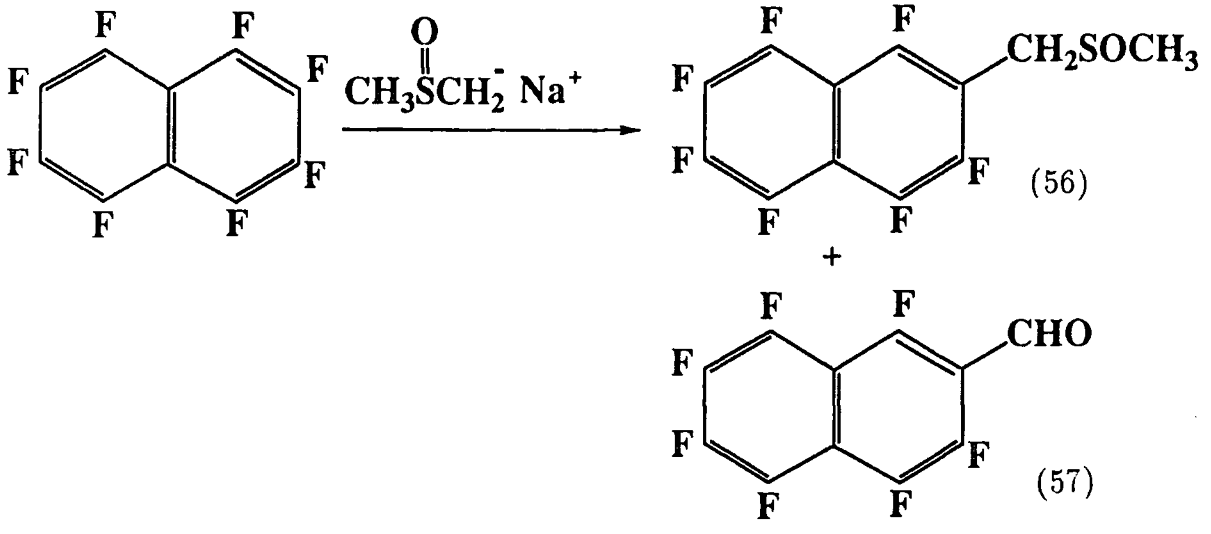
Scheme 21

Preliminary experiments showed that under these conditions, cyclisation and dehydration occurred to give the isothianaphthene derivative (51)[92] in a one pot process.

Therefore, (53) in THF at -78^{0}C was treated with 3 equivalents of butyllithium to give 4,5,6,7-tetrafluoroisothianaphthene (51) (27%). Purification from polymeric material was achieved by first sublimation (25^{0}C/ 5x10^{-3}mm Hg) and chromatography on silica.

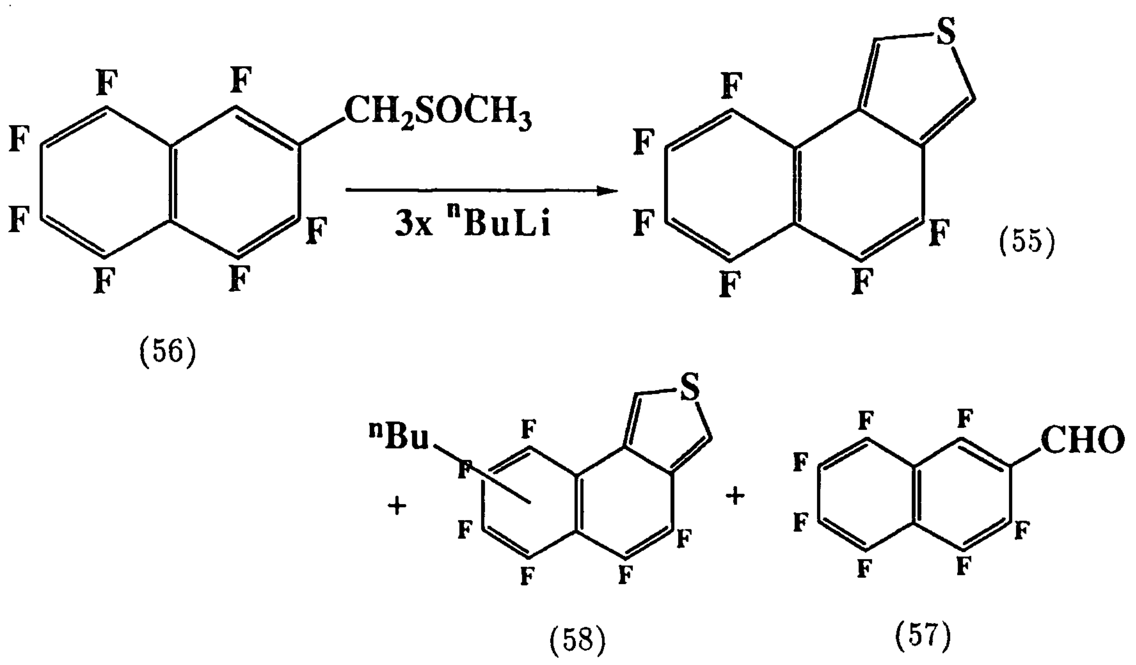
2.3. Synthesis of 4,5,6,7,8,9-hexafluoronaphtho[1,2-c]thiophene (55)

The naphtho-derivative (55) was prepared by an identical route to that of the tetrafluoroisothianaphthene (51). Thus, addition of sodium methylsulphinyl methide to octafluoronaphthalene in THF at -78^{0}C gave 1,3,4,5,6,7,8-heptafluoronaphthalen-2-ylmethyl methylsulphoxide (56) (34%) after sublimation (90^{0}C/ 2x10^{-3}mm Hg), and a side product to this reaction, 1,3,4,5,6,7,8-heptafluoronaphthalene-2-carbaldehyde (57) (7%) (Scheme 22).



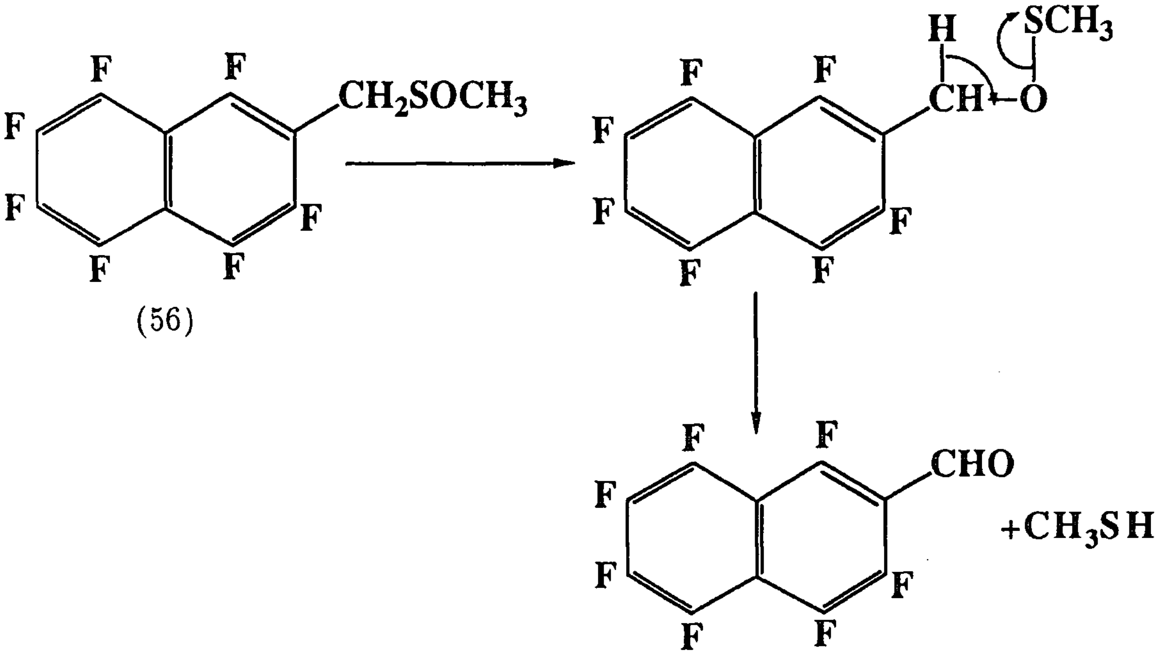
Scheme 22

Again addition of 3 equivalents of butyllithium to (56) in THF at -78^{0}C gave the cyclised product (55) (5%), butylated cyclised product (58) (1-4%) along with 1,3,4,5,6,7,8-heptafluoronaphthalene-2-carbaldehyde (57) (49%) and unreacted starting material (56) (21%) (identified by IR and ^{19}F nmr) (Scheme 23).



Scheme 23

The mechanism for the formation of the carbaldehyde (57) is expected to be analogous to that proposed for the similar formation with the benzyl derivative, with an initial '1,2'-rearrangement to the sulphenate ester followed by a β elimination[90] (Scheme 24).



(56)

(57)

Scheme 24

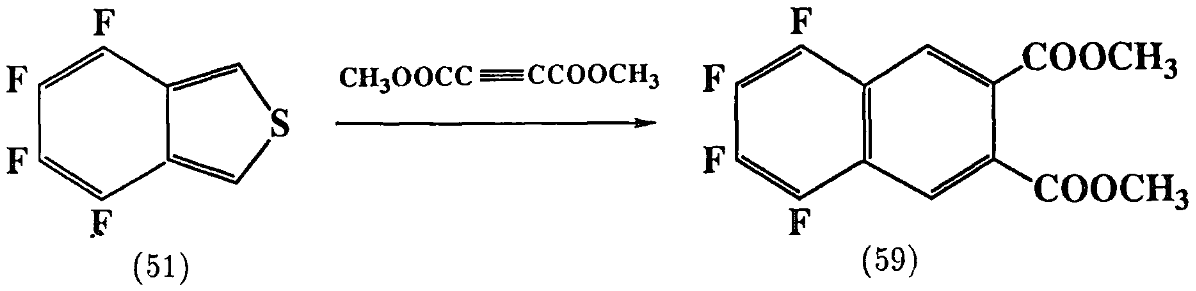
2.4. Reactions of 4,5,6,7-tetrafluoroisothianaphthene(51)

An investigation of the chemistry of (51) was carried out for possible application in synthetic processes.

2.4.1. Diels-Alder Reactions of (51)

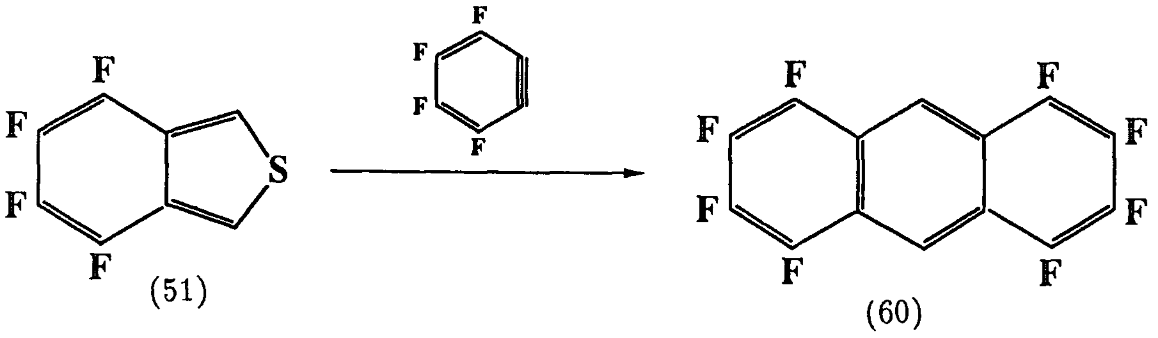
The possible diene activity of (51) was investigated by looking at its involvement in Diels-Alder reactions. It was expected that the presence of fluorinated aromatic ring would generate an electron-poor diene that would have low reactivity with electron-poor dienophiles in particular.

Two reactions were carried out. The first involving the reaction of (51) with dimethylacetylene dicarboxylate (DMAD), was accomplished using neat mixtures at 130°C and gave dimethyl 5,6,7,8-tetra-fluoronaphthalene-2,3-dicarboxylate (59) (84%) after purification by chromatography (Scheme 25).



Scheme 25.

The second reaction involved (51) with tetrafluorobenzyne (prepared at -78°C from bromopentafluorobenzene and butyllithium). Addition of (51) to the tetrafluorobenzyne at -78°C and warming rapidly to room temperature gave 1,2,3,4,5,6,7,8-octafluoroanthracene (60) (21-24%)[93] (Scheme 26).

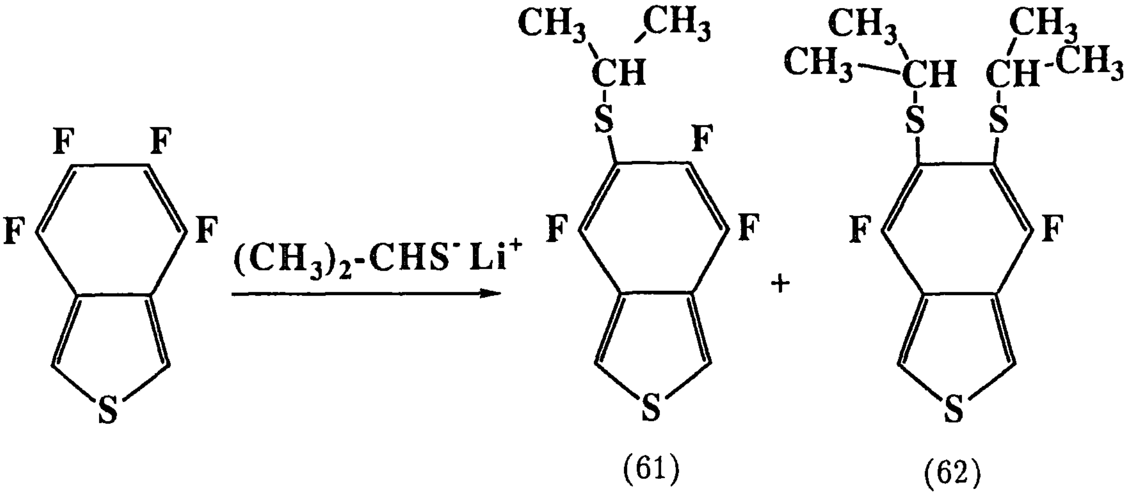


Scheme 26

2.4.2. Nucleophilic substitution reactions

Treatment of (51) with 1 equivalent of lithium isopropylthiolate (prepared from the reaction of isopropylthiol with butyllithium) in THF at room temperature gave 3 products, separated by chromatography: unreacted tetrafluoroisothianaphthene (51) (19%), the monosubstituted

4,6,7-trifluoro-5-(2-propylthio)isothianaphthene (61) (76%) and the disubstituted 4,7-difluoro5,6-(2-propylthio)isothianaphthene (62) (5%) (Scheme 27). These were identified by nmr and mass spectrometry but were found to be too unstable for purification by conventional techniques for microanalysis.



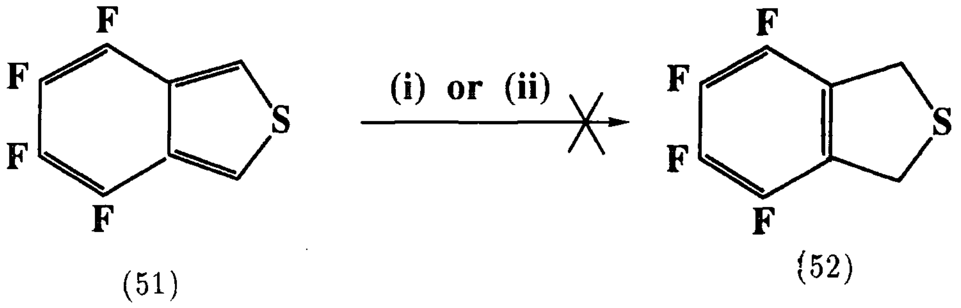
Scheme 27

2.4.3. Attempted Reduction of the thiophene Ring

Reduction of 4,5,6,7-tetrafluoroisothianaphthene (51) to the corresponding 1,3-dihydro-4,5,6,7-tetrafluoroisothianaphthene (52) was attempted *via* two routes. The product (52) was first prepared by Coe et al[88] and surprisingly was found to be a yellow unstable solid.

Treatment of (51) with zinc and trifluoroacetic acid in dichloromethane (1:92:50 ratios respectively) at room temperature gave many complex products whose separation was not worth pursuing. Similar treatment of 4,5,6,7-tetra-fluoroisoindole with coppered zinc in glacial acetic acid had previously given the reduced 1,3-dihydro-4,5,6,7-tetrafluoroisoindole (34%)[94].

An alternative reduction was *via* treatment of (51) in chloroform with triethylsilane and trifluoroacetic acid at 50°C. The tlc. of the product showed three compounds: unreacted (51) (29%) and two unknown products in low yields, the mass spectra of which showed only coupled products (at 412, 392, 280 mass units) with no molecular ion peak for the expected product (at 208) (Scheme 28).



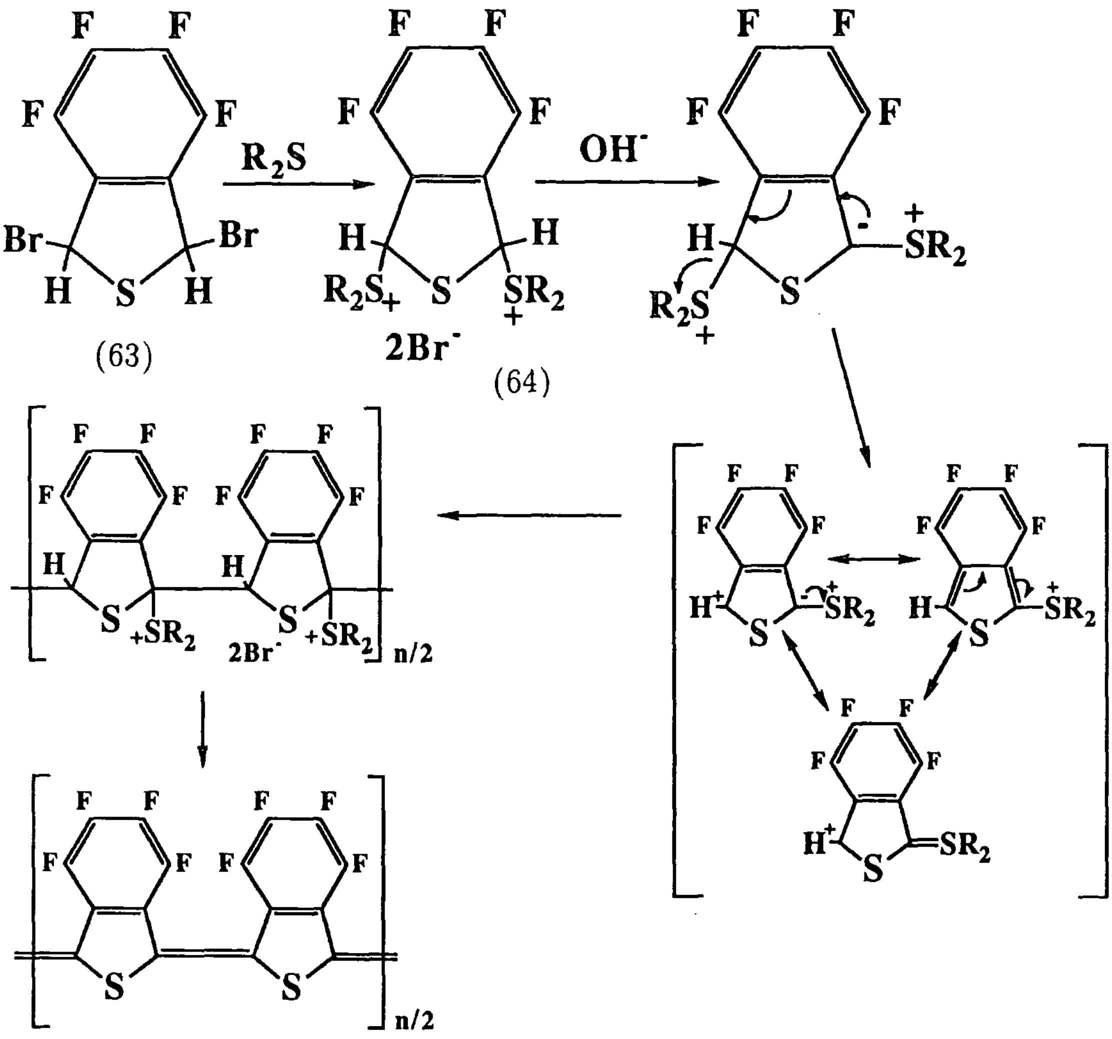
Scheme 28. *(i)* Zn/CF_3COOH *(ii)* $(C_2H_5)_3SiH/CF_3COOH$

Due to the instability of the product (52), it may be formed in low yields but be decomposing. However, even with this in mind, neither of the two preparations attempted seemed promising.

2.4.4. Reaction of (51) with Bromine

It was considered that the precursor to PPV's could be applied to the preparation of poly(tetrafluoroisothianaphthene) *via* a similar precursor polymer (Scheme 29) (see section 1.5.4. or Chapter 5).

The preparation of the dibromide involved treating (51) in dry chloroform with bromine at room temperature to give 1,3-dibromo-4,5,6,7-tetrafluoroisothianaphthene (63) (75%). However, the reaction of (63) with diethyl sulphide under identical conditions to that used for the PPV synthesis, namely in water/methanol at 50°C, lead to no formation of

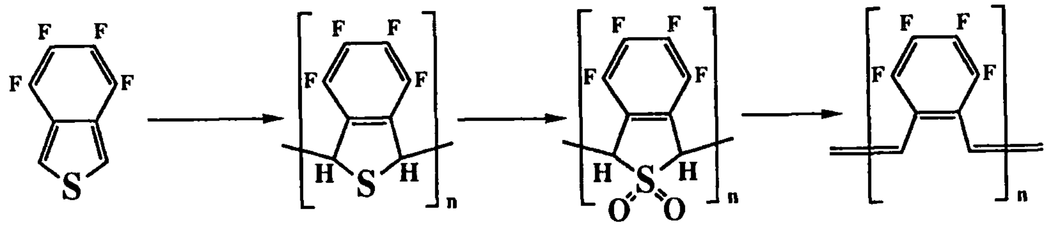


Scheme 29

the expected 1,3-bis(diethylsulphonium bromide)-4,5,6,7-tetrafluoroisothianaphthene (64).

2.5. Potential Route to Poly ortho(tetrafluorophenylenevinylene) (67)

By analogy with the behaviour of isothianaphthene, cationic polymerisation of (51) was expected to lead to a high molecular weight soluble polymer (65). For this to be converted into a fully conjugated material, the sulphur must be extruded. Two methods to achieve this conversion were attempted. In principle, oxidation of the sulphur to the sulphone (66) and thermal elimination of sulphur dioxide (Scheme 30) should provide a route to the poly(ortho-tetrafluorophenylenevinylene) (67).



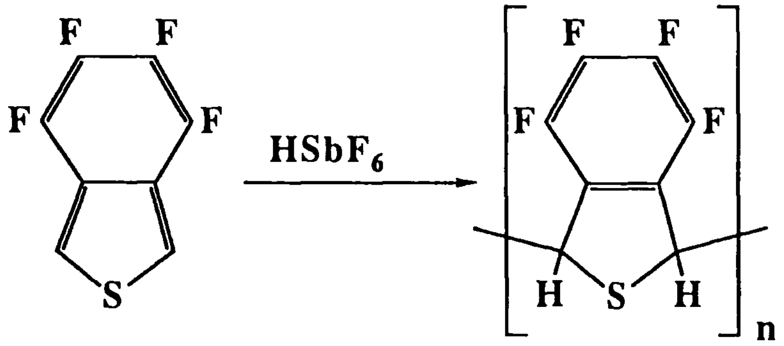
(51) (65) (66) (67)

Scheme 30.

An alternative route was to react the poly(1,3-dihydroisothianaphthene) (65) with trimethyl phosphite in order to create an alternative sulphur leaving group.

2.5.1. Acid Polymerisation of 4,5,6,7-tetrafluoroisothianaphthene (51)

4,5,6,7-Tetrafluoroisothianaphthene (51) in dichloromethane was treated with "magic acid" (SbF_5/HF) for 20 hours. The product slowly went viscous to a point where stirring ceased. The resultant product was dissolved in THF and precipitated into methanol to give a pale yellow solid of poly(1,3-dihydroisothianaphthene) (65) (77%) (Scheme 31).



(51) (65)

Scheme 31.

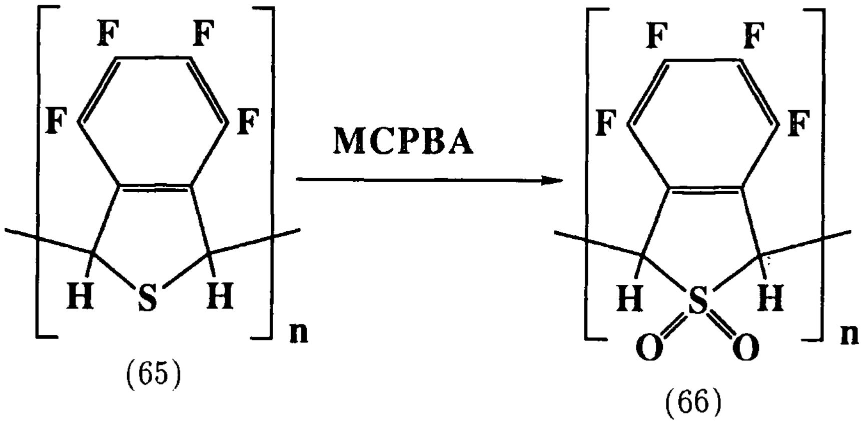
G.P.C. analysis of this gave a polymer weight of 350,000 polystyrene equivalents. Mass spectrometry studies showed that no sulphur was lost from the polymer with patterns for repeating units being observed every

206 units. Simple thermal elimination of sulphur from this was not therefore possible.

2.5.2. **Oxidation of polymer (65)**

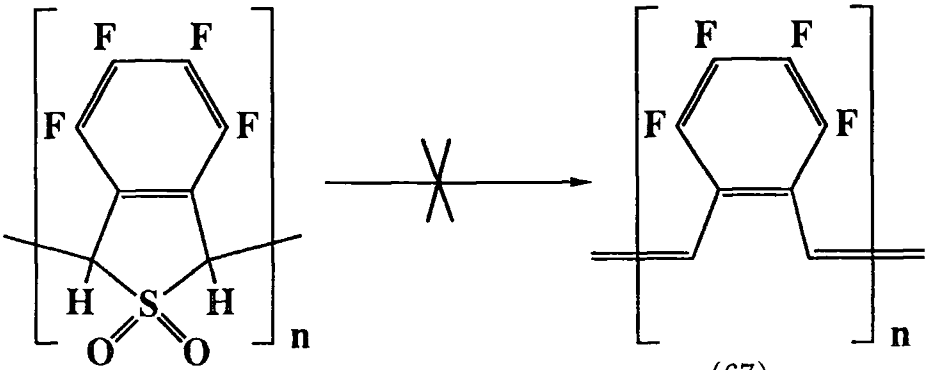
A sample of polymer (65) in ethyl acetate was treated with meta-chloroperbenzoic acid (MCPBA)[96] at 0^oC. A yellow solid appeared after 10 minutes which subsequently redissolved within 1 hour. The yellow solid product was totally soluble in water and was dialysed in water for 3 days to give the anticipated product poly(1,3-dihydroisothianaphthene 2,2-dioxide) (66) (96%) (Scheme 32).

The nmr spectrum of (66) was found to have changed considerably from that of (65) in that only two broad peaks were now present (broad over 15 p.p.m.). The thermal elimination of sulphur dioxide from this polymer was paramount to the formation of the conjugated product. However, studies by mass spectrometry indicated that the elimination of



Scheme 32

SO_2 or SO (no peaks at 62 or 48 mass units) was not occurring and also that no other decomposition of the polymer was either, with only small fragmentation peaks at 61 (CH-SO), 43 (C-CF) and 31 (CF) being present. These results indicated that thermal elimination to form the conjugated polymer (67) was not occurring under these conditions (Scheme 33).



(67)

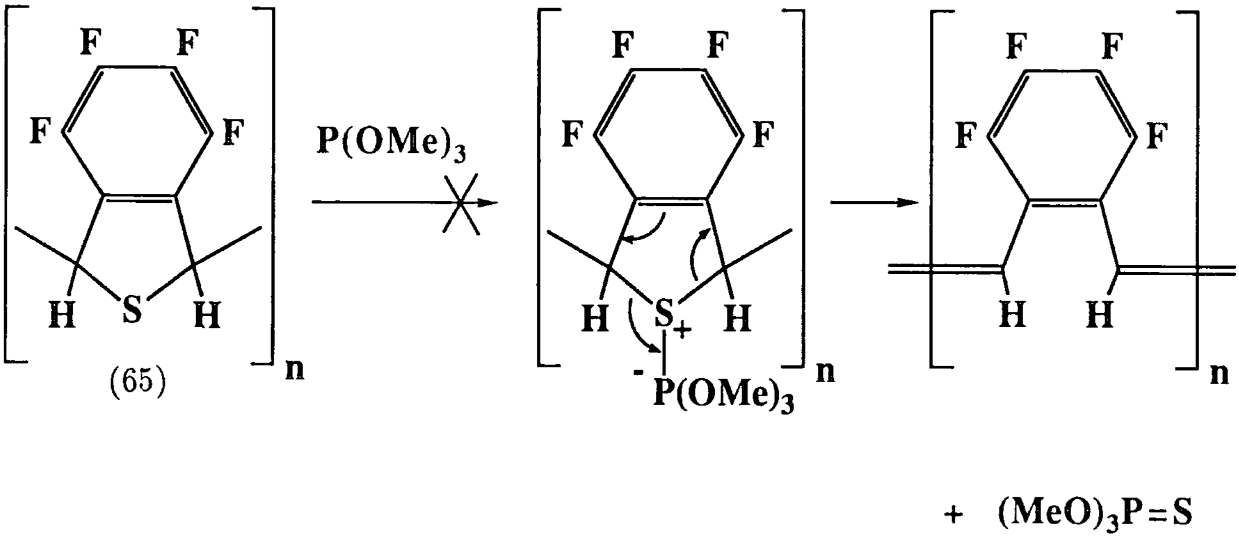
Scheme 33

When a sample of the oxidised polymer (66) was heated at $250^{0}C/2x10^{-3}$mm Hg for 18 h, the product was a black flaky film. This film had a resistivity of >20 MΩ and would seem to be a carbonised decomposed product.

2.5.3. Reaction of (65) with Trimethyl Phosphite[97]

Two criteria must be met for the efficient conversion of (65) to the conjugated polymer (67) by the reaction with a phosphine or phosphite. The first is that all the sulphur sites must react with the phosphite prior to any elimination and the second is that the elimination process must be complete. In order to achieve this, it was important to attempt a synthesis in which no premature elimination occurred in order to avoid the formation of conjugation at an early stage which would directly lead to insolubility of the material, preventing complete reaction of the phosphite with the sulphur sites. It was proposed to carry out the reaction at relatively low temperatures so as to avoid this problem.

The reaction of (65) with 1 equivalent of trimethyl phosphite in acetonitrile at room temperature however lead to no apparent reaction; heating to 50^{0}C also had no effect (Scheme 34).



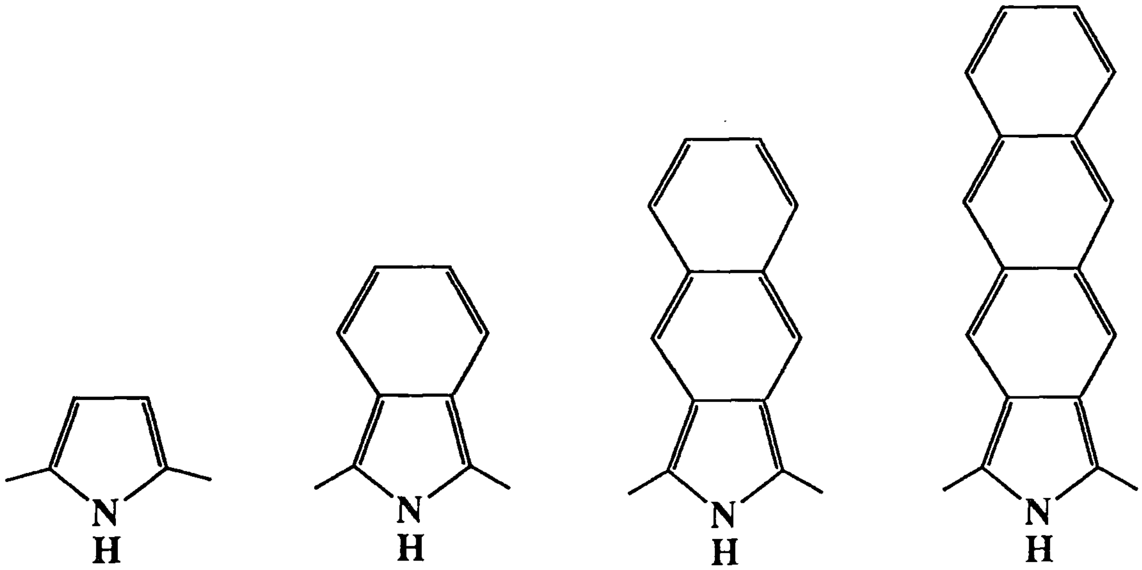
Scheme 34

CHAPTER THREE

NITROGEN MONOMERS

3.1. Introduction

Theoretical calculations by Kertesz[79] on the fused benzene ring derivatives of polypyrrole namely polyisoindole (PII) (68), polyisobenzoindole (PIBI) (69) and polyisonaphthoindole (PINI) (70) have shown two important differences between this series and the sulphur series (Chapter 2), (Fig 19). Firstly, the difference in the energy between aromatic and quinonoid forms of PT is 3.5 Kcal/mol (see 2.1.1.) whereas in PP it is 8.6 Kcal/mol. Secondly[79], the addition of an aromatic ring to pyrrole, in PII (68), introduces significant hydrogen-hydrogen nonbonding repulsions between the hydrogens on the 4-position and those on adjacent nitrogens. These are sufficient enough to increase the intramolecular carbon-carbon bond length (Fig 20). Both these effects help to stabilise the aromatic form of PII.



polypyrrole **PP** (19)

polyisoindole **PII** (68)

polyisobenzoindole **PIBI** (69)

Polyisonaphthoindole **PINI** (70)

Fig 19

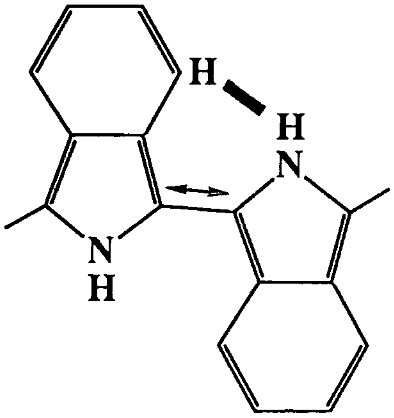


Fig 20

Compensation for the hydrogen-hydrogen interaction can be brought about by twisting the rings out of plane. The non-planar form enjoys a reduction in the inter-ring distance due to a reduced hydrogen-hydrogen interaction but loses out on the resonance conjugation due to this non-planarity. The result is that the two values for the band gap calculated for the planar and the non-planar forms are very close (Table 3).

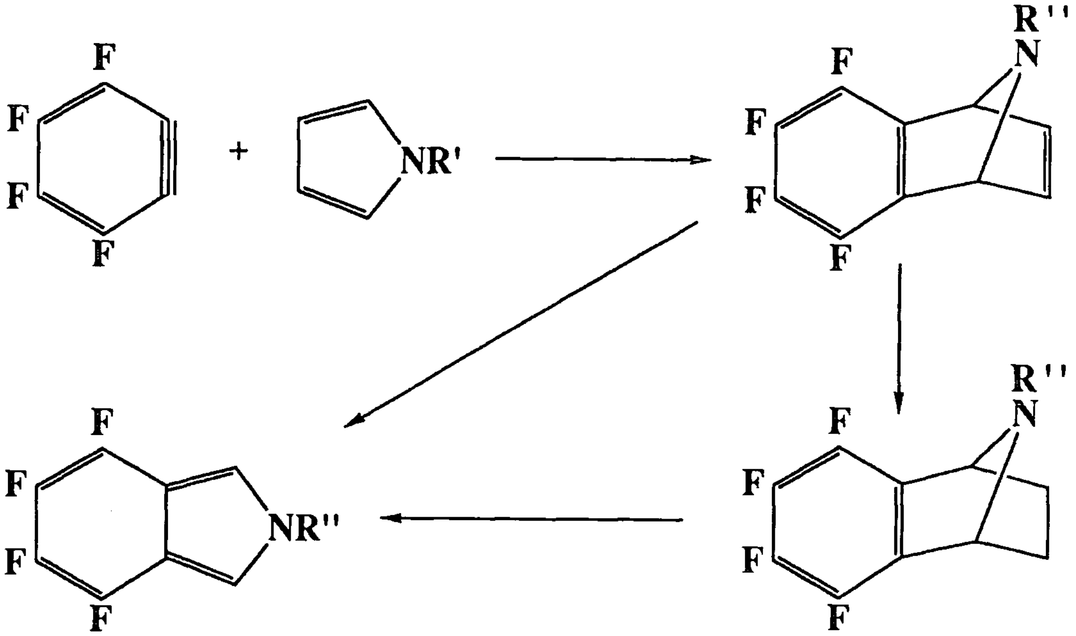
	PP	PII	PIBI	PINI
Planar	2.95	2.02	1.13	0.62
Non-Planar	—	2.10	1.20	0.80

Table 3 *Huckel* E_g *(eV) values of aromatic form of polypyrrole series.*

The addition of one aromatic ring to pyrrole does however force the HOMO to higher energy and the LUMO to lower energy thus reducing the band gap, but this does not outweigh the stabilisation gained by remaining in the aromatic form. Therefore addition of further rings to the system reduces the bandgap further (Table 3) but the crossover to the quinonoid form may not occur at all in the pyrrole series; certainly not at E_g values above that seen for the PT series where this occurs at 1.0 eV.

3.1.1. Synthetic Approach

Preparations for both the tetrafluoroisoindole (71) and the N-methyl-tetrafluoroisoindole (72) have been described[94,98] (Scheme 35). However, no analytical data was given in these reports for any of the products.



R' $=Si(CH_3)_3, CH_3$

(71) R''=H

(72) R''$=CH_3$

(73)

Scheme 35.

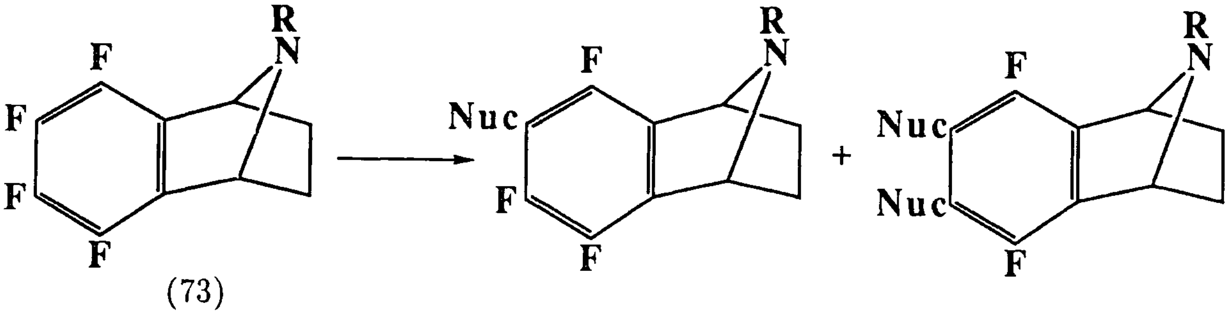
Studies on the hydrocarbon isoindole by nmr have shown that it exists in both the isoindole and the isoindolenine forms (Fig 21). Similar nmr studies on the fluorinated derivative have shown that the effect of the

isoindole **isoindolenine**

Fig 21.

fluorine is to stabilise the o-quinoid structure, in that at 0^0C, the isoindolenine form is almost indetectable[94].

Taking use of the thermolysis precursor (73) to the isoindoles, synthesis of derivatives of these materials may be possible using nucleophilic substitution onto the aromatic ring (Scheme 36).



Scheme 36.

3.1.2. Preparation of the polymers

No preparation of polyisoindole has been reported in the literature. On the other hand, a number of papers have been published on the electropolymerisation of indole and substituted

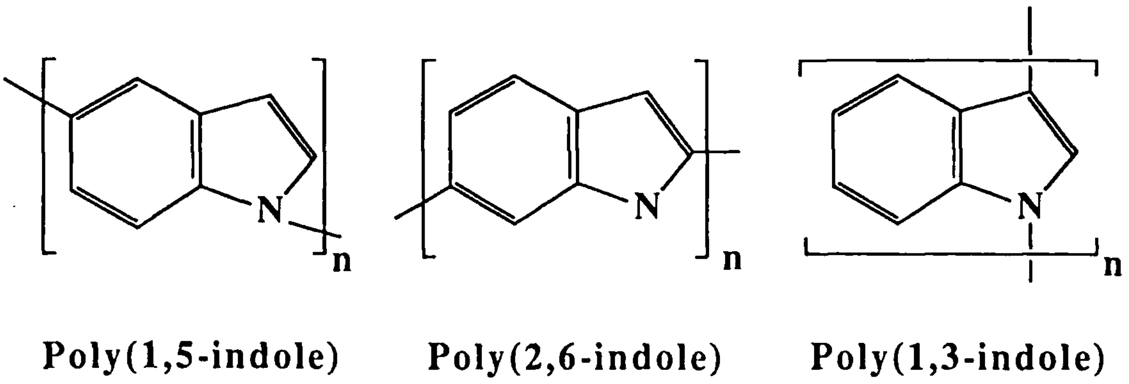


Fig 22.

derivatives[99,100]. The polymerisation of these systems are ambiguous since they can theoretically polymerise via the 1,5; 2,6; or 1,3 positions. The use ofsubstituents to block particular sites has shown that poly(1,3-indole) is the preferred product (Fig 22). Samples prepared electrochemically doped with ClO_4^- had conductivities of $\sigma = 2x10^{-2}$ S cm^{-1} as a pressed pellet sample.

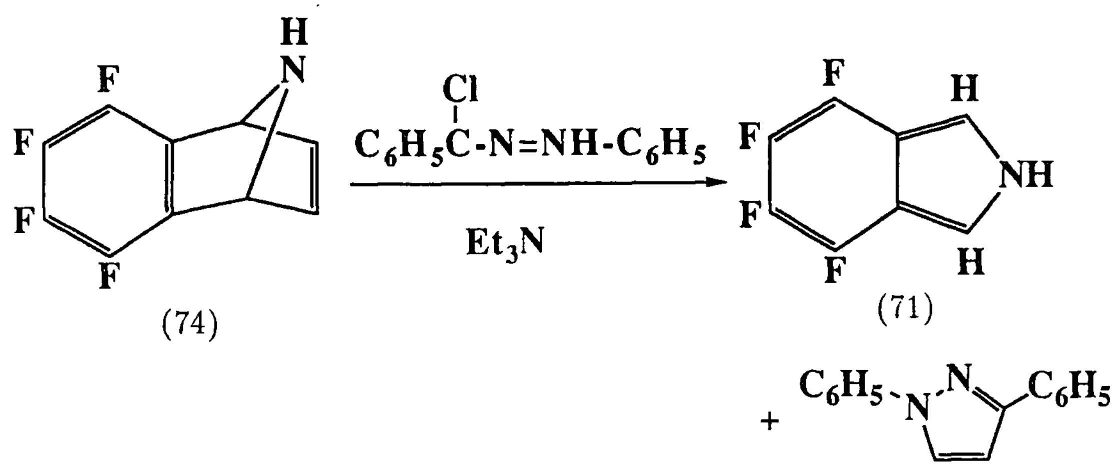
3.2. Synthesis on Monomers

This follows the routes available in the literature with the subsequent preparation of derivatives.

3.2.1. Synthesis of 4,5,6,7-tetrafluoroisoindole (71).

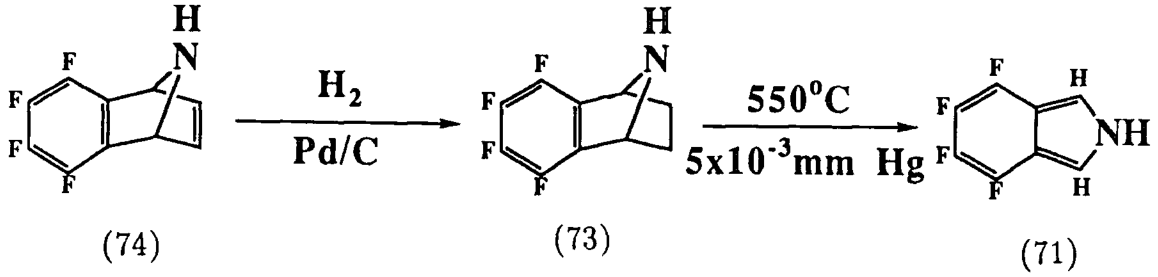
Reaction between N-trimethylsilylpyrrole and tetrafluorobenzyne (generated from bromopentafluorobenzene and butyllithium at -78°C) at temperatures of -78°C to room temperature followed by distillation of the product gave 5,6,7,8-tetrafluoro-1,4-dihydronaphthalene-1,4-imine (74) (40%) in high purity.

Two approaches were made to convert (74) to the required tetrafluoroisoindole (71). The first used the dipolarophile diphenylnitrilimine, made by treating N^1-α-chlorobenzylidene-N^2-phenylhydrazine with base[101], which effected a cycloaddition to (74) followed by a retro-cycloaddition [94] (Scheme 37). This synthesis however gave only low yields (<50%) of the product (Lit.[98] 77%).



Scheme 37.

The alternative route was to first hydrogenate (74) by shaking it in methanol with a palladium/carbon catalyst under 40 p.s.i. H_2 to give 5,6,7,8-tetrafluoro-1,2,3,4-tetrahydronaphthalene-1,4-imine (73) and then to subject this to flash thermolysis at 550°C/ 5×10^{-3}mm Hg according to the method described by Bornstein et al[94] which gave the isoindole (71) in 70-95% yields (Lit.[94] quantitative) (Scheme 38).



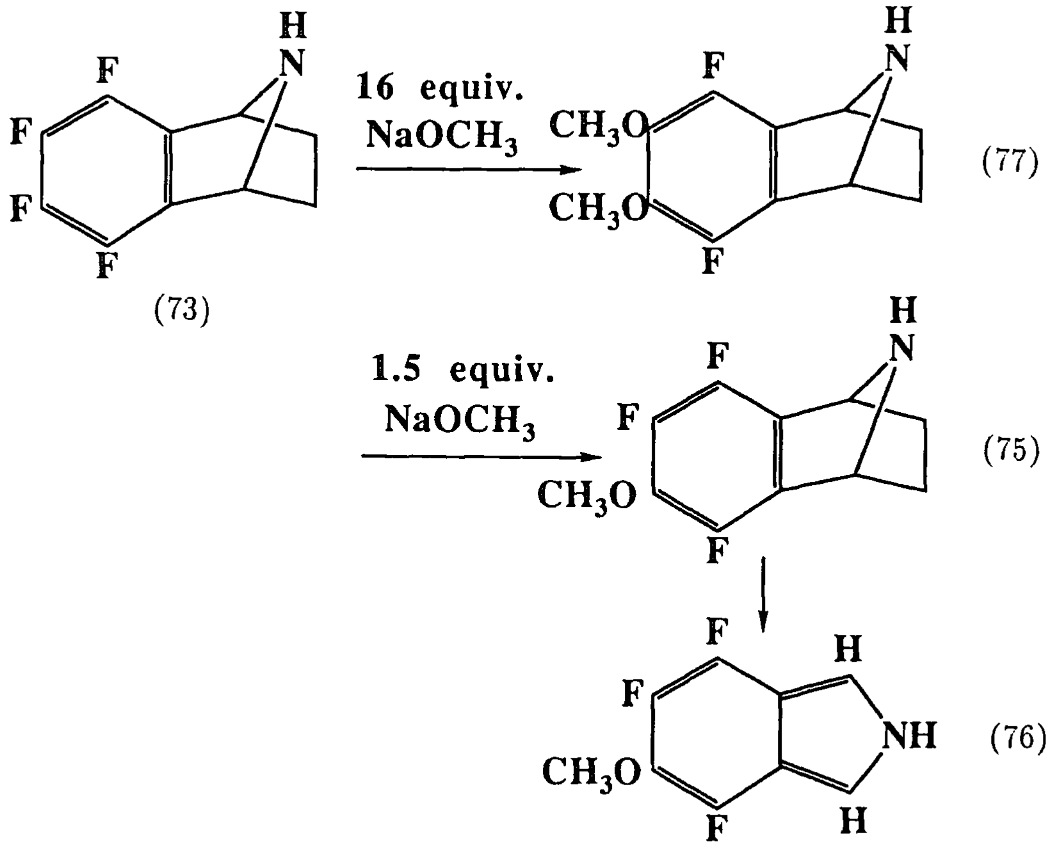
Scheme 38.

3.2.2. Synthesis of N-Methyl-4,5,6,7 -tetrafluoroisoindole (72).

The preparation was identical to that used for the preparation of 4,5,6,7-tetrafluoroisoindole (72) using flash thermolysis to give the final product.

3.2.3. Derivatives of 4,5,6,7-tetrafluoroisoindole (71).

The synthesis of derivatives of (71) was *via* substitution reactions upon the thermolysis precursor (73). Treatment of (73) in THF with 1.5 equivalents of sodium methoxide under reflux gave 5,6,8-trifluoro-6-methoxy-1,2,3,4-tetrahydronaphthalene-1,4-imine (75) (97%). Thermolysis of this product at 550^{0}C/5x10^{-3}mm Hg gave 4,5,7-trifluoro-6-methoxy-isoindole (76) quantitatively (Scheme 39). It was found to be considerably less stable than it's parent (71), decomposing rapidly to a green/black material.

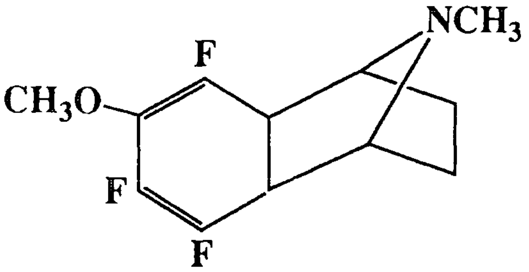


Scheme 39.

Similarly, treatment of (73) with 16 equivalents of sodium methoxide in methanol under reflux gave the disubstituted product 5,8-difluoro-6,7-dimethoxy-1,2,3,4-tetrahydronaphthalene-1,4-imine (77) (93%). No thermolysis of this product was attempted.

3.2.4. Derivatives of N-methyl-4,5,6,7-tetrafluoroisoindole (72).

Similar nucleophilic substitution reactions were carried out on the N-Methyl- derivative. Treatment with 3 equivalents of solid sodium methoxide in refluxing THF gave a 4:1 mixture of the mono- to di-substituted products. Reduction to 1 equivalent of sodium methoxide gave the mono-substituted N-methyl-5,6,8-trifluoro-7-methoxy-1,2,3,4-tetrahydronaphthalene-1,4-imine (78) (87%) exclusively.



(78)

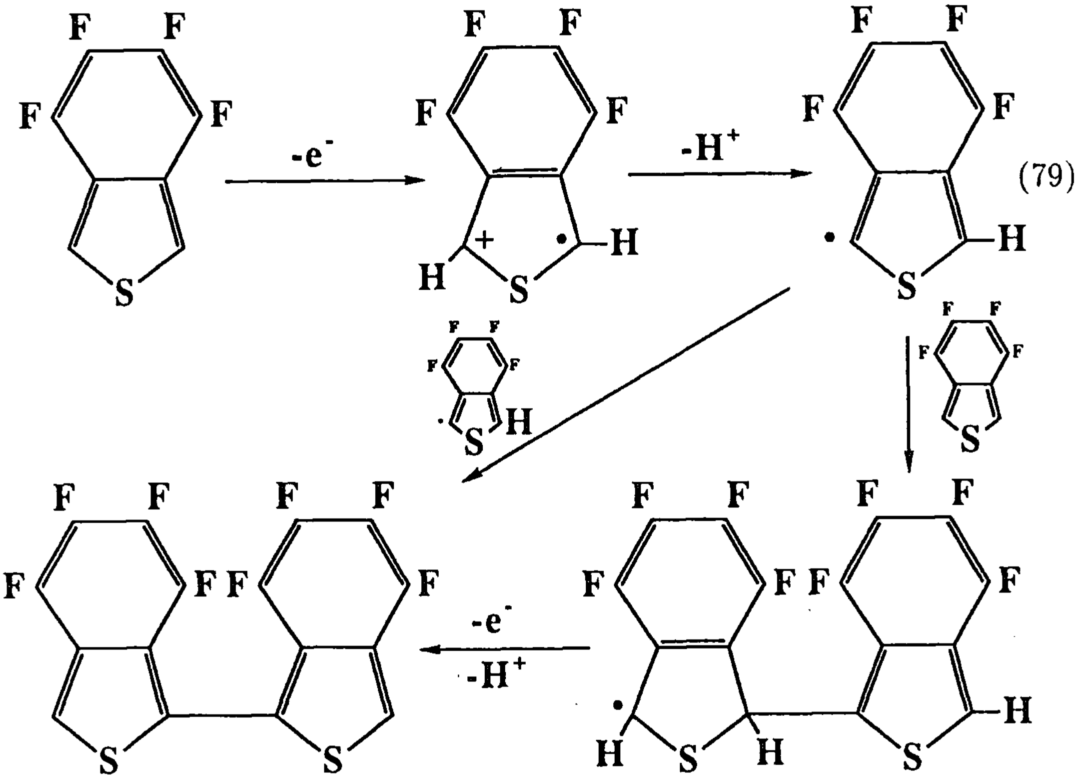
CHAPTER FOUR

ELECTROCHEMISTRY

4.1. Basis of electrochemistry[102]

4.1.1. Mechanism

The polymerisation of all 5-membered ring 6π heterocyclic compounds containing one heteroatom, through the 2 and 5 positions, requires first the anodic oxidation of the monomer followed by a coupling reaction to give an intermediate species. These must then be further oxidised with the subsequent loss of protons to introduce unsaturation into the system in accordance with accepted polymerisation mechanisms. An alternative coupling may be achieved by the simple dimerisation of a radical species of the type (79) in the case of 4,5,6,7-tetrafluoroisothianaphthene (Scheme 40).



Scheme 40. *Electrical Polymerisation of (51)*

The choice of solvent for this reaction is generally governed by the solubility of the monomer, chemical inertness and convenient liquid range, along with the requirements for electrical conductivity and stability to high potentials.

Acetonitrile can be used with both high oxidation and high reductive potentials having a window from +3.4 V to -2.9 V [with respect to the standard calomel electrode (SCE)] and has good solvating power so is generally the most widely used solvent for non-aqueous electrochemical applications.

4.1.2. Cyclic Voltammograms[103]

The oxidation potential of the 4,5,6,7-tetrafluoroisothianaphthene (51) monomer was measured by cyclic voltammetry (C.V.) in acetonitrile with Bu_4NBF_4 as the supporting electrolyte. It was found to oxidise irreversibly with the relatively high peak oxidation potential at +1.51 V (SCE) (Fig 23).

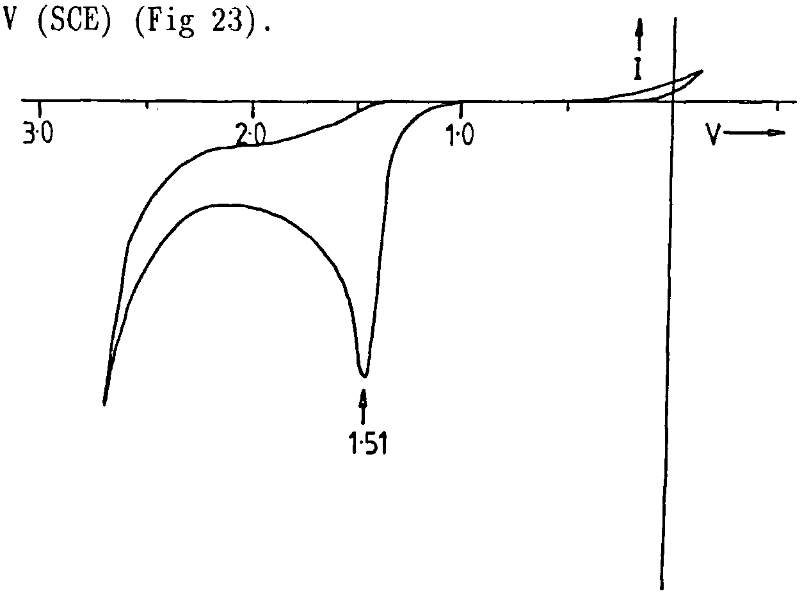


Fig 23. *Cyclic voltammogram of 4,5,6,7-tetrafluoroisothionaphthene*

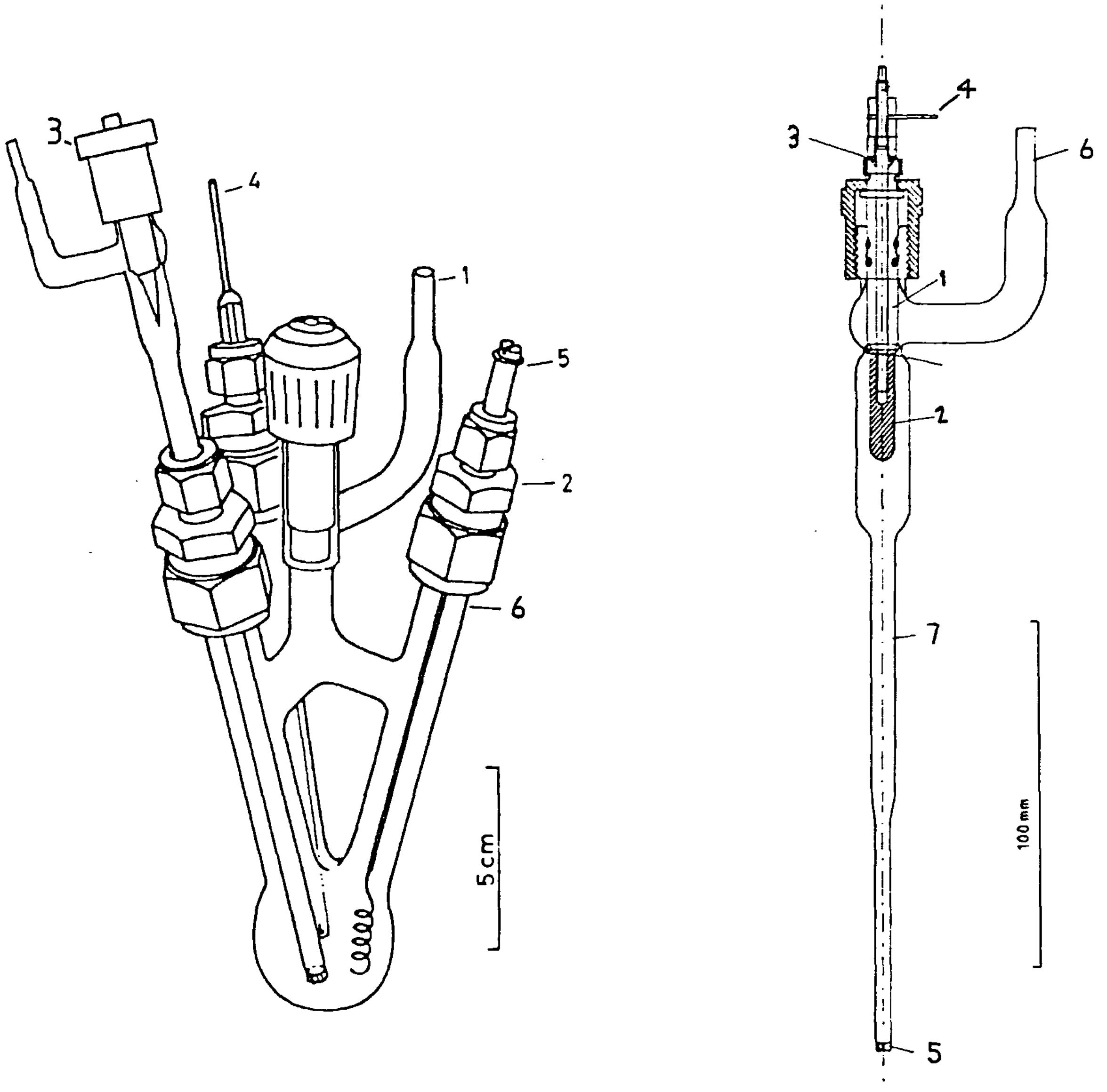
The curve shape was basically the same in structure to those obtained for other monomers of this type. The oxidation potential compares to that of thiophene at 1.46 V[100] and pyrrole 0.60 V[100] (SCE). Thus to polymerise the tetrafluoro monomer (51), a voltage on or above the oxidation potential must be applied. This potential will be considerably above the oxidation potential of water (+0.63V) (SCE) with oxygen present leading to oxidised keto type products [Section 4.2.4.3. (b)]. Thus a policy of rigorous exclusion of both water and air was required.

4.1.3. The Electrochemical Cell

Liquid sulphur dioxide was also intended to be used as a solvent so a cell able to contain a positive pressure was required. Other requirements were to have access to the cell at three points for the positioning of the electrodes with the facility to evacuate the chamber to high vacuum. Various sized cells of the type (Fig 24 A) were used depending on the particular experiment undertaken. All used *Swagelok* fittings on 1/2 and 1/4 inch ground glass.

To minimise contamination by water, the cell was heated at 150^{0}C for 24 h, then for a further 3 h at 50-150^{0}C under a vacuum of 2x10^{-3}mm Hg before it was filled with the monomer and supporting electrolyte [using a glove box (6-10 ppm water)]. The solvent was added and repeatedly degassed by freeze/thaw techniques (except SO_2).

The reference electrode used throughout was a Ag/ Ag^{+} electrode of novel design [104] (Fig 24 B). Contamination between the reference and the cell was reduced by using solutions of the same anion in both the reference solution and the cell solution (ie. use a reference electrode with $AgBF_4$ as theelectrolyte when using Bu_4NBF_4 in the electrolysis cell). **All of the potentials quoted are with respect to the standard calomel electrode (SCE).** The Ag/Ag^{+} reference measured potentials at +0.251 SCE and was rechecked on a regular basis. The SCE potential is +0.6007 (H_2/H^{+}).



A 1. ¹/₄" Ground glass
2. *Swagelock* ¹/₂" to ¹/₄" reducing union
3. Reference Electrode
4. Micro Electrode (Usually Ptlatinum).
5. Auxilliary Electrode
6. ¹/₂" Ground Glass

B 1. Teflon Youngs Tap
2. Silver

3. O-Ring seal
4. Electrical Contact
5. Fine glass sinter
6. ¹/₄" Ground glass
7. ¹/₄" Smooth glass

Fig 24. A: *Three limbed undivided cell typically used for cyclic voltammetry. B: Ag/Ag⁺ reference electrode (ref 104)*

4.1.4. Solvents and supporting electrolytes

All the solvents were dried by recommended techniques[102,105] with HPLC grade acetonitrile being dried from CaH_2 prior to use, SO_2 from P_2O_5 and CaH_2, with the handling of SO_2 being carried out in a stainless steel vacuum line throughout. The common supporting electrolytes of Bu_4NBF_4 (TBATB), Bu_4NPF_6 (TBAHP) and Ph_4PCl were dried by heating at $100^oC/2x10^{-3}$mm Hg for up to 160 h. The pretreatment of other more specialised supporting electrolytes will be dealt with in the main discussion.

4.2. Electro-oxidation of 4,5,6,7-tetrafluoroisothianaphthene (51)

4.2.1. Using a Platinum Anode

Various solvents and supporting electrolytes were used in conjunction with a platinum electrode in order to optimise the conditions for polymerisation of the tetrafluoroisothianaphthene (51).

4.2.1.1. In acetonitrile

The initial electrolysis used a cell set up with TBAHP (0.1M) in acetonitrile as solvent at room temperature with the monomer (0.02M) in conjunction with a platinum anode (25x7mm). The cell used was a divided cell of 20 ml capacity each side separated by a glass sinter.

At a potential of +1.60 V (SCE), no apparent reaction was observed in the anode compartment. As the potential was raised to +1.90 V a red/purple coloured material streamed off the anode. Electrolysis under these conditions for the passage of 10.8 Coulombs of charge (15% extent of reaction assuming 2 electrons per molecule[100] at ≈ 0.5 mA current, 0.3 mA cm^{-2}) lead to a deep blue colour in the anode compartment. By slowly removing the anode from the solvent, it's surface could be seen to lose all of the blue colour that surrounded it with no deposition whatsoever. The blue solution remaining in the anode compartment slowly changed to a deep red solution when left open to the atmosphere (over a period of 3-4 min.) Within the blue solution there was a white/ yellow solid material which dissolved in chloroform washings, but could not be isolated directly.

The change in colour from deep blue to a red solution may be due to the blue material being in an unstable oxidised doped state (p-doped) and that de-doping by some form of atmospheric interaction was occurring.

In order to gain some purification of the crude material from the supporting electrolyte, the product was filtered through a short silica column. This however lead to a large amount of material being retained on the silica and could not be removed from it even after prolonged soaking in various solvents.

4.2.1.2. In sulphur dioxide

Changing the solvent to liquid SO_2 and electrolysing at -20°C lead to very much the same product mixture as that discussed in 4.2.1.1. with the visible formation of white material around the electrode apparent and again overall formation of a deep blue solution. The electrolysis in this case was taken to 50% completion, for the equivalent of 2 electrons per molecule of monomer. The resultant red product mixture was poured into ether from which the supporting electrolyte crystallised out. All the resultant product was totally soluble in common organic solvents.

Most polymers that are highly conjugated are very insoluble. Hence it was evident that either the polymer produced from the electrolysis was a new soluble conjugated material or that it was not the expected conjugated polymer, but one of another type.

The ^{19}F nmr and ^{1}H nmr of the crude product mixture did not show the two broad fluorine peaks that were expected for the polymer (80) (Fig 25) and there were too many proton signals for a product that should essentially contain no protons. Instead, the ^{19}F spectrum obtained indicated the presence of two species; one containing broad peaks in three regions at [-139.1, -139.4], [-141.2 , -153.9] and -154.4 p.p.m. with the other species containing two broad singlet signals at -148.3 and -159.1 p.p.m.. The first series of peaks coincided very accurately with the set of fluorine peaks obtained for the product of acid catalysed cationic polymerisation (65) (See Section 2.5.1.), which is a yellow pale solid which is totally soluble in chlorocarbon solvents.

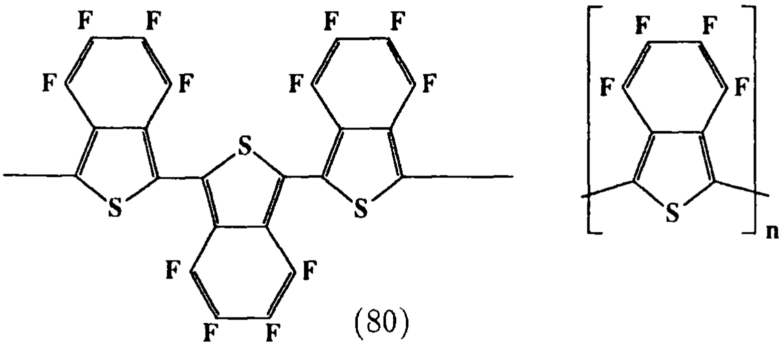
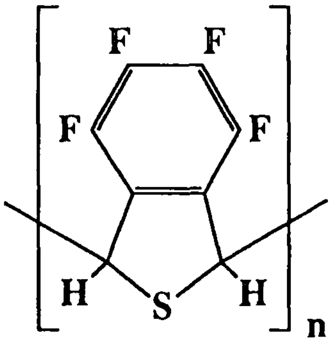

(80)

Fig 25. *Expected conjugated polymer from (51)*


(65)

Extensive chromatography on silica of the electrolysis product with eluants of varying polarity (CCl_4,$CHCl_3$,CH_2Cl_2) brought off streaks of material. This crude chromatographic separation gave a sample of material showing only the two upfield peaks at -148 and -158 p.p.m.. This spectrum fitted in better with that expected for the target polymer (80), but the reasons for its solubility remain unanswered. The nature of this product is discussed in Section 4.3.7..

There are potentially many processes that can occur to prevent a film being deposited on the anode. There may be interactions with the solvent for instance particularly in acetonitrile whose nucleophilicity may lead to reaction with the anodically generated cations reducing their lifetime in solution and preventing reaction with the monomer[100]. In contrast to acetonitrile, liquid SO_2 is good at stabilising these cations particularly since its use also requires low temperatures. This however may lead to termination reactions occurring away from the electrode surface.

4.2.1.3. In other solvents

Although unsubstituted polymeric systems such as PITN are generally very insoluble in all solvents, it was thought that a solvent system may be found in which the red material described above may be suitably insoluble. The search for solvents to aid deposition is common for chemists using monomers of the 3-alkyl-thiophene type which are designed to give polymers soluble in solvents other than that in which it is prepared. Solvent mixtures of nitrobenzene and dichloromethane were commonly used for this type of monomer to obtain good film growth. Thus, electrolyses were carried out using the tetrafluoroisothianaphthene (51) initially in nitromethane, nitrobenzene or propylene carbonate solutions. Of these, propylene carbonate was the most promising for film growth with blue material appearing only near the anode and not streaming away. Removal of the electrode, however, destroyed any tentative linkage there may have been between the product and the anode.

Since solvents of relatively high dielectric constants must be used in electrolytic cells (for conductivity) the least polar solvents commonly found in use are THF and dichloromethane (with dielectric constants of 7.3 and 8.9 respectively). However all of these solvents dissolved the red solid found as the product of electrolysis in SO_2, so a solvent mixture with something less polar was required. Since hexane was found to be immiscible with a large number of the highly polar solvents commonly used in electrochemistry, a 25:75 homogeneous mixture with pyridine was used at $0^{o}C$ for the electrolysis of (51) with TBATB. At voltages up to 2.5 V (SCE) at which point the monomer should have been oxidised, no observed reaction had occurred. Oxidation at any higher voltages produced a red film which was found to be that derived from the oxidation of pyridine (by IR). The oxidation of pyridine is at +2.12 V (SCE)[106]

SOLVENT	DIELECTRIC CONSTANT
DMSO	46.7
MeCN	37.5
DMF	36.7
Nitrobenzene	34.8
SO_2	17.6
1,2-dichloroethane	10.4
Dichloromethane	8.9
n-Hexane	1.9

Table 4

The effect of solvent on the polymerisation process did not seem to improve the deposition of material on the anode. Changing the anode composition was the next alternative. Straightforward anode modification was available directly. Since the isothianaphthene could be electropolymerised and deposited onto a platinum anode, then this could be used as an organic-type electrode upon which to deposit the tetrafluoro derivative. Deposition of PITN onto a platinum anode base was accomplished in acetonitrile with LiBr as the supporting electrolyte. This electrode was then transferred to a cell set up for the electrolysis of the tetrafluoro derivative also in acetonitrile with Bu_4NBF_4 as supporting electrolyte. However, immediately after the application of the potential (1.5V SCE) the PITN was stripped from the platinum surface, with no deposition of the fluorinated monomer.

Alternative Anodes

To get good film growth, the interaction between the monomer and the electrode must be reasonably strong (chemisorption). Having removed one electron from a monomer unit, coupling with another will generate a point for chain growth on the anode surface. Generally, but not exclusively, good film growth is usually obtained from monomers that show nucleation loops in their cyclic voltammograms (Fig 26).

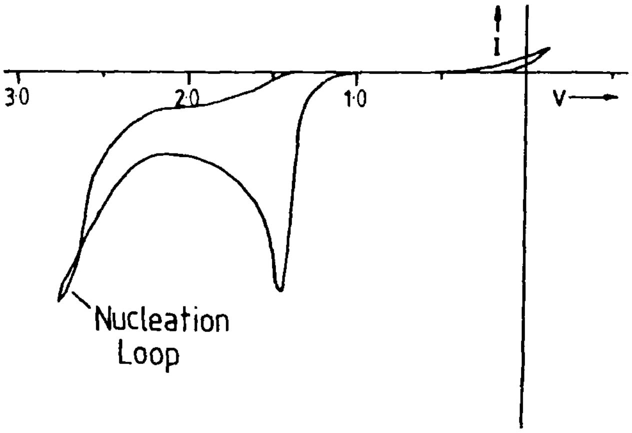


Fig 26. *Cyclic Voltammogram showing a nucleation loop.*

This <u>increase</u> in current on the reductive scan is indicative of charged species attached to the anode surface, thought to be regions of chain growth, giving up their charge. No nucleation loops were observed in the cyclovoltammetric studies of (51) with a platinum anode. Since the presence of nucleation loops is not a pre-requisite for polymer deposition, straight polymerisation reactions were carried out with alternative anodes without the C.V. of the monomer being repeated with the particular anode in use.

4.2.2. Indium Tin Oxide (ITO) anode

Apart from platinum, a very widely used electrode material in non-aqueous electrolysis is tin oxide conducting glass commonly doped into an n-type semi-conductor with antimony or indium. This transparent substrate is commonly used in conjunction with infra-red studies of deposited materials.

A series of experiments were conducted paralleling those using the platinum anode. With use of Bu_4NBF_4 supporting electrolyte in propylene carbonate, again early observations looked as though some interaction was occurring between the blue material forming and the anode but again this dropped off as the electrode was slowly moved. No polymer deposition was observed on the ITO anode in any of the following solvent/supporting electrolyte systems: acetonitrile with Ph_4PCl or Bu_4NF; nitrobenzene with Bu_4NF; propylene carbonate with Bu_4NBF_4; Pyridine with Bu_4NBF_4; pyridine/hexane with Bu_4NBF_4.

4.2.3. Aluminium and Steel anodes.

Both aluminium and steel electrodes were used, again with no deposition occurring. However, both these electrodes were too reactive at the high potentials used to be considered as good candidates.

4.2.4. Gold anode

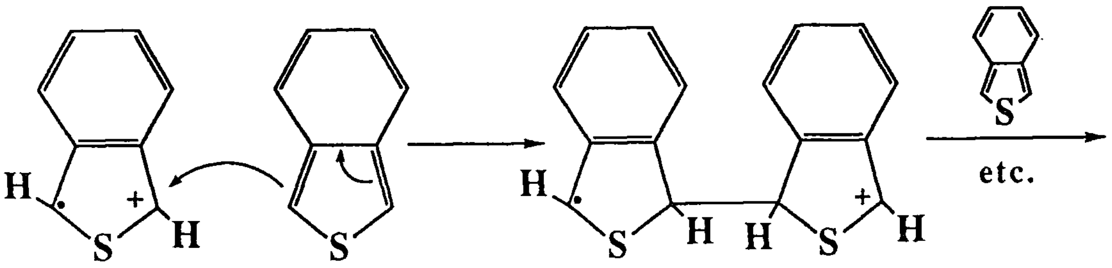
4.2.4.1. With tetrabutylammonium tetrafluoroborate

With a view to getting a highly polished gold surface, an anode composed of gold sputtered onto glass was prepared. This electrode however did not stand up to the rigours of electrolysis, coming away from the glass substrate when current was applied. However, some deposition of a blue film was observed before its final destruction. A more substantial electrode (25x7x0.1 mm) was used under the same conditions but this was found again to be too thin, bending towards the deposited side so destroying the uniform electric field that existed. Increasing the thickness of the electrode further and subsequent electrolysis with Bu_4NBF_4 in both acetonitrile and liquid SO_2 as solvent did give blue deposits on the anode.

It was at this stage that the problem encountered by Wudl et al[73] in the preparation of PITN could be addressed: that of cationic polymerisation.

4.2.4.2. Requirements of supporting electrolytes

Already observed in the electrolysis of the monomer (51) with a platinum anode, is the formation of two species, one of which was identified by its ^{19}F nmr spectrum to be the saturated polymer (65) (by comparison with the product derived from cationic (H^+) polymerisation of (51) (Section 2.5.1.). The difference in the behaviour of the tetrafluoroisothianaphthene (51) and isothianaphthene (46) is that for (46), a white precipitate formed immediately upon the application of a potential to the cell (Scheme 41).



Scheme 41. *Cationic Polymerisation of isothianaphthene (46)*

Thus, electrolysis of (46) in acetonitrile with a non-nucleophilic supporting electrolyte lead to almost exclusive formation of the saturated type of polymer (45). In contrast to this, electrolysis of the <u>tetrafluoro</u>- derivative (51) under the same conditions lead firstly to a crude product that was not exclusively the fluorinated saturated equivalent (65) and secondly, a product that does not precipitate immediately but requires a constant input of charge. The proportion of the saturated polymer (65) to the unknown red material varied from 50-80% (as seen by ^{19}F nmr) This observation implied that cationic polymerisation of the fluorinated derivative was less favoured. This was not unexpected since tetrafluoroisothianaphthene will be a less nucleophilic species compared to the non fluorinated isothianaphthene.

By direct analogy with Wudl's work[73], the use of a nucleophilic species in this reaction should prevent any cationic polymerisation occurring, paralleling Wudl's use of both LiBr and Ph_4AsCl. The requirement was for a nucleophile stronger than the tetrafluoroisothianaphthene (51). However, a very efficient nucleophile may be expected to lead to the formation of the cyclic sulphide (Fig 27).

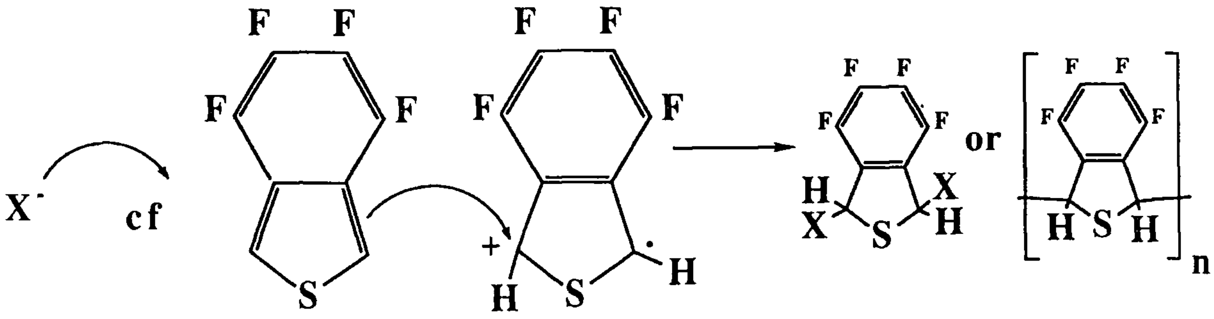


Fig 27.

The second requirement was for a nucleophile that would be stable to the relatively high oxidation potentials required to oxidise the monomer [+1.51 V (SCE)- Section 4.1.2.]. Both bromide (E^0= +1.06 V) and chloride (E^0=+1.36 V) were therefore in principle excluded. The obvious extension was to use a fluoride salt (E^0=+2.85 V). However, repetition of some of Wudl's work did show that in the electropolymerisation of isothianaphthene in acetonitrile with LiBr as the supporting electrolyte, not only was the monomer being oxidised and deposited but also the bromide was being oxidised with the formation of bromine. The final product was found to have a high concentration of bromine present in it giving an empirical formulae of $(C_6H_4SBr)_n$ by micro analysis.

An analogous reaction using Ph_4PCl as the supporting electrolyte for electrolysis of tetrafluoroisothianaphthene (51) in acetonitrile at room temperature gave no product at all and the gold anode was found to be badly etched. No formation of chlorine was visible at the anode but a reaction with it must have occurred. Thus, it was obvious that only oxidation of the chloride was occurring, in contrast to Wudl's findings.

4.2.4.3. Fluoride-containing Electrolytes

Any compound that is to act as a source of fluoride ion for application as a supporting electrolyte must meet two criteria. The compound must be soluble up to 0.1 M solution in the solvent (SO_2 and acetonitrile in particular) and primarily, the compound must be able to be dried to a very high state without decomposing it. Much work has been done on soluble fluoride ion sources and very few of them meet this latter criteria, with many of the common dry fluoride sources, CsF, KF for example,being very insoluble in common solvents. Of the simple inorganic type, AgF is soluble in acetonitrile and can be dried.

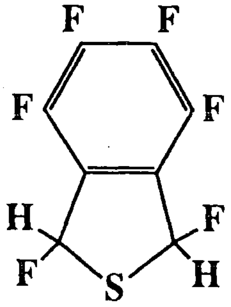
(a) AgF/Acetonitrile

Using AgF in acetonitrile for the electrolysis of the tetrafluoroisothianaphthene (51), no colouration was observed either on the anode or in the anode compartment itself. Using AgF in conjunction with isothianaphthene (46), a very brittle blue lumpy material was deposited on the anode which had within it some white solid indicating that some cationic polymerisation had occurred. In general, the fluoride had prevented cationic polymerisation in (46) but also stopped any deposition of material with the fluorinated derivative.

(b) Tetrabutylammonium fluoride / acetonitrile

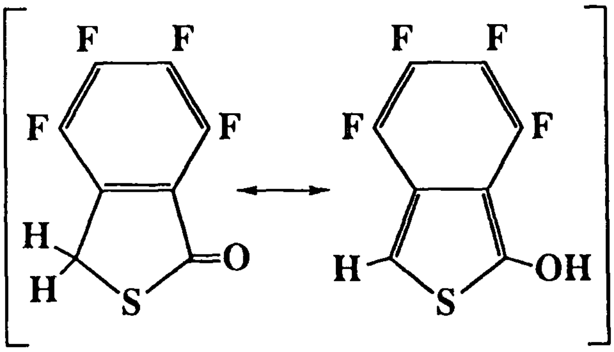
Bu_4NF is bought as a trihydrate. In order to dry it, the temperature must not be raised above 50^oC in a vacuum of greater than 10-1 mm Hg otherwise it decomposes to give the Bu_4HF_2, $CH_2CHCH=CH_2$ and tributylamine[107]. Thus, to maximise drying, a sample was kept under these conditions for 160 h. Even after this treatment, it was estimated that up to 0.1 Moles of water per molecule of salt may still be present. In order to assess its effectiveness at eliminating cationic polymerisation and as an electrolyte, electrolysis of isothianaphthene (46) in acetonitrile was carried out. A good film of polymer on an ITO electrode was produced with no white precipitate observed.

In the electrolysis of the tetrafluoroisothianaphthene (51) under the same conditions with an ITO electrode, no blue colour was produced. Extraction of the anode compartment with dichloromethane and analysis of this extract by ^{19}F nmr and mass spectrometry showed that no product of nucleophilic addition (81) had been formed but that dimers and trimers were present in low concentration, as seen by their presence in the mass spectrum.

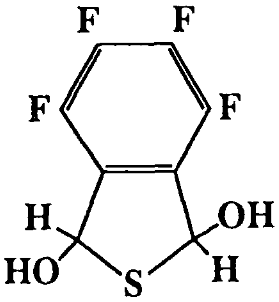


(81)

The mass spectrum also indicated the product of interaction with water in the cell with the formation of (82) and (83) with molecular ion peaks at 222 and 240 mass units respectively.



(82)



(83)

By using a mixture of Bu_4NBF_4 and Bu_4NF in conjunction with the gold anode in the electrolysis of the tetrafluoroisothianaphthene (51), some blue/black deposit was formed. However, the fluoride ion had only been partially successful in preventing cationic polymerisation since some pale yellow material was present on the anode in patches.

An alternative way of drying Bu_4NF by refluxing a solution in dichloromethane with CaH_2 followed by filtration under dry N_2 was carried out[108]. The supporting electrolyte dried in this manner did not change the results of the electrolysis, with some unsaturated polymer (65) still being present (detected by ^{19}F nmr).

(c) CsF/ Bu_4NBF_4/ Acetonitrile

To improve the solubility of the inorganic salts CsF and KF, phase transfer catalysts were used. This was a useful option since some of the supporting electrolytes already described can act as phase-transfer media. Thus, CsF and Bu_4NBF_4 in acetonitrile were used in the electrolysis of the tetrafluoroisothianaphthene (51) with a gold anode. A blue lumpy deposit formed on the anode which could be dissolved with chloroform to give a red solution when exposed to air. The ^1H and ^{19}F nmr spectra of this product showed it to be exclusively the saturated product (65). Phase-transfer of fluoride ion in quantities to prevent the formation of this product had <u>not</u> occurred.

(d) KF/ 18-Crown-6 Ether

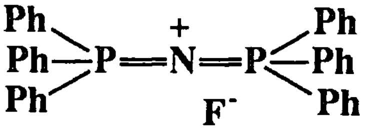
The 18-crown-6 cyclic ether is commonly used to increase the solubility of potassium salts in organic solvents. However, with regard to its use in the electrolysis, its cyclic voltammogram showed a large broad oxidation at +1.0-1.4 V (SCE), so was therefore of little use in a highly oxidative environment such as that used to electo-oxidise the tetrafluoroisothianaphthene (51).

(e) KF/CsF/Sulpholane

Both dry KF and CsF were used in electrolysis experiments of the tetrafluoroisothianaphthene (51) in sulpholane (a common solvent for CsF/KF when used in chemical synthesis). The melting point of sulpholane (+27^{o}C) required the use of elevated temperatures (typically +40^{o}C) for these electrolyses and using a gold anode only soluble products were formed with no deposition of material. Analysis of the products by ^{19}F nmr showed them to be almost exclusively the saturated polymer (65).

(f) PNP^{+}F^{-}/ acetonitrile.

One other fluoride source used was bis(triphenylphosphoranylidene)-ammonium fluoride (PNP^{+}F^{-}) (84). This is prepared by the ion exchange of PNP^{+}I^{-} with AgF in methanol[109]. Purification of this salt was difficult with impurities of silver, iodide and chloride possible. The study of it by cyclic voltammetry showed this contamination to be slight, if at all. However, its use in the attempted electropolymerisation of (51) was without success, the PNPF salt decomposing at the cathode.



(84)

4.2.4.4. CF$_3$COO^{-}Na^{+} as electrolyte and nucleophile

Another nucleophile that was considered as a possible candidate to prevent cationic polymerisation of the tetrafluoroisothianaphthene (51) was sodium trifluoroacetate which has an oxidation potential peak starting at +2.0 V (SCE) and a reduction at -0.82 V (SCE) (by cyclic voltammetry). Electrolysis with this supporting electrolyte (0.04M), monomer (0.1M) in acetonitrile at -20^{o}C at +1.7 to +1.9 V (SCE) gave no observable anode reaction, with no appearance of colour in the solution or on the anode. However, the anode had bubbles coming from it with decomposition of the acid (Kolbe electrolysis presumably giving carbon dioxide and hexafluoroethane).

4.2.4.5. Hydride Sources as nucleophiles

(a) Cycloheptatriene

Removal of hydride ion from cycloheptatriene gives the stable tropilium cation. However, cycloheptatriene has an oxidation peak at +1.30 V , which is lower than the potential used to oxidise the tetrafluoroisothianaphthene (51), so it was not surprising that no polymerisation occurred when it was used in conjunction with Bu_4NBF_4 in acetonitrile at +1.7 V.

(b) Ph_3CH

Triphenylmethane has an oxidation potential starting at +2.30V (SCE),so has a usable potential range wide enough for the electrolysis of the tetrafluoroisothianaphthene (51). With Bu_4NBF_4 (0.05M), Ph_3CH (0.14M) and monomer (0.1M) in acetonitrile with a gold electrode at room temperature (the Ph_3CH crystallised out at temperatures less than 5^{o}C), electropolymerisation at +1.65 V gave a green lumpy deposit which dissolved in chloroform to give a pale red/orange solution whose ^{19}F nmr showed it to be again the saturated polymer (65) :-the product of cationic polymerisation of (51).

(c) Et_3SiH

Triethyl silane acts as a reducing agent for many functional groups[95]. Unfortunately, it has very complex oxidation reactions that occur at the relatively low potentials of +0.7 and +2.3 V (SCE). It was not surprising therefore that no polymerisation of the monomer (51) occurred in its presence under the usual electro-oxidative conditions.

4.2.5. Use of Low Temperatures

Low temperatures were used where possible (typically -20°C) for two reasons. Firstly, low temperatures lower solubilities which improve the chance of deposition on the anode. Secondly, studies by Garnier on the polymerisation of isothianaphthene in acetonitrile solutions showed that while the generation of the saturated polymer (45) predominated under standard conditions of Bu_4NBF_4/ acetonitrile/ room temperature, in agreement with other groups, at -20°C the cationic polymerisation did not occur: PITN was the exclusive product formed[110]. This work has <u>not</u> been confirmed in a publication and was <u>not</u> found to be the case in the studies described in this thesis.

4.2.6. Electrode Pre-Treatment

For all the electrolyses carried out, the platinum and gold electrodes were maintained in a highly polished state. This was achieved by graded mechanical polishing and by manual polishing using fine jewellers rouges. Electropolishing of the platinum electrode[111] was used on some occasions but was found not to improve deposition. Electropolishing of the gold electrode would involve the use of cyanides in the electrolyte with the evolution of HCN during the electrolysis. The improvement in the electrode surface was not thought to warrant the use of such conditions.

All the electrodes were degreased by extraction with refluxing alcohol (iso-propyl alcohol and ethanol) over a period of 24 h.

4.2.7. Nature of the Product

As described earlier, the products obtained from these experiments could be crudely separated by chromatography to give the saturated polymer and a dark red material associated with the two ^{19}F nmr singlets. The ultraviolet/ visible/ near IR spectrum of this latter material showed a λ_{max}= 431-470 nm (2.64-2.87 eV) (depending on experiment) with a band edge at 560 nm (2.20 eV). The material when doped in a solution state with sulphuric acid gave peaks at 490, 750 and 1360 nm (0.91 eV) Fig 28.

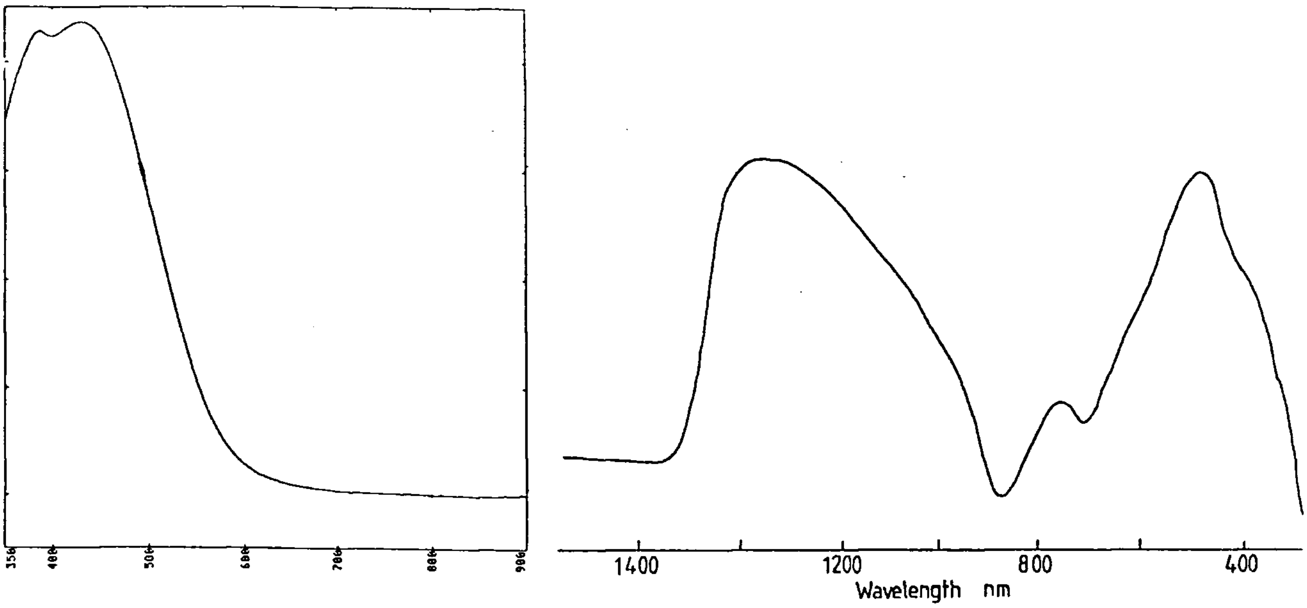
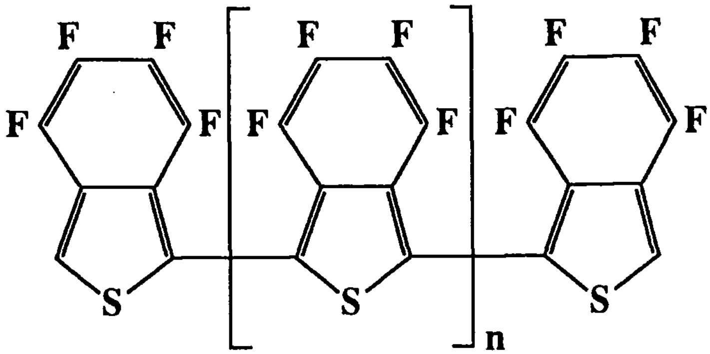


Fig 28. *U.V.s of F-PITN undoped and doped with* H_2SO_4.

The material was similarly p-doped with BF_4^- by the addition of the oxidisers $NO^+BF_4^-$ or $NO_2^+BF_4$ to a solution of the red polymer in dichloromethane. The bands in the electronic spectra appeared at slightly higher energy to those found for the polymer in sulphuric acid, probably due to a lower degree of doping. Exposure of a film of the red polymer on glass to AsF_5 (-0.8 barr/ 2h) caused the material to change colour only very slightly to purple with no apparent change in its electronic spectrum indicating that little or no doping had taken place.

It can be expected that a fluorinated polymer may be more easily n-doped than p-doped (see Section 1.6.). Rapid de-doping observed upon the removal of the blue p-doped material from an inert atmosphere into air indicated the instability of the polymer in this p-doped state. n-Type doping can be achieved electrochemically where a film of the polymer to be doped is made into the cathode in a cell containing a suitable counter ion (eg. KBr in acetonitrile would generate a potassium n-doped polymeric system). Alternatively, by treating a film of the polymer with a THF solution of sodium naphthalide, a sodium n-doped polymer would result where the naphthalide radical anion has reduced the polymer. Both these techniques rely on the polymer being insoluble. Since the red material prepared in the experiments described in this Thesis would dissolve in these types of solvent, the methods involving the doping of films are excluded. However, on addition of a THF solution of the polymer to sodium naphthalide in THF, a dark green/ black material appeared which was isolated and repeatedly washed with diethyl ether. This product could not be guaranteed to be free of the sodium naphthalide so was not examined further.

The mass spectrum of the undoped red material suggested the presence of conjugated polymer with peaks increasing in 204 mass units up to 1430 mass units (seven monomer units). The mass spectrum was unusual in that the peaks observed were for units having protons as the end group, thus masses of 206, 410, 614, 818, 1022, 1226 and 1430 were seen (Fig 29). No peaks without these protons were observed indicating the presence of discrete oligomer units in the product rather than fragmentation of a polymer. However, no other experimental observations suggested a mixture of short chained compounds.



205 204 205

Fig 29.

Gell permeation chromatography (G.P.C.) gave a range of molecular weights, which changed from experiment to experiment, with minimum and maximum values of 2000 and 6200 polystyrene equivalents. The value of M_w= 6200 was obtained from the product of a bulk electrolysis of (51) carried out to 50% extent of reaction. From these G.P.C. measurements, it was obvious that high molecular weight material was not being formed. Direct observation of the product showed it not to be viscous, forming a fractured red/ black film when evaporated down.

4.2.8. Conclusions drawn from the Electrolysis Experiments

A number of conclusions can be drawn from the results described above. The deposition of "polymers" from 4,5,6,7-tetrafluoroisothianaphthene (51) can only be accomplished on a gold anode surface, with the carbocations generated at this electrode following one of two pathways to generate two types of polymer. Only one of these polymers can be positively identified, the saturated poly dihydo-4,5,6,7-tetrafluoroisothianaphthene (65). The other material has some characteristics which are not all in agreement with that expected for a highly conjugated polymer. The two broad singlets observed in the ^{19}F nmr at -148 and -158 p.p.m. indicate the type of structure expected. The dark red colour with confirmation from the uv/vis spectrum also indicate a conjugated product. However, a polymer with a molecular weight indicated by G.P.C. of 2000-6200 polystyrene equivalents with this degree of conjugation would almost certainly be insoluble (as are the hydrocarbon analogues). If the presence of the fluorines were acting such as to increase the solubility, then this effect may also be expected to increase the solubility of fluorinated PPV's, which are found to be very insoluble, with solubilities of only milligrams per litre for what would be the equivalent of 7 "thiophene" units for (E)-Ar5 (See Section 6.7.2.).

4.3. Electro Oxidation of 4,5,6,7,8,9-hexafluoronaphthalene-[1,2-c]thiophene (55)

The optimum conditions found for 4,5,6,7-tetrafluoroisothianaphthene (51) were applied to the polymerisation of the naphthalene[1,2-c]thiophene (55).

4.3.1. Cyclic Voltammetry

The C.V. of (51) was run in acetonitrile solution with a platinum working electrode under identical conditions to those used for the tetrafluoroisothianaphthene (51). The curve shape was as expected, with an irreversible primary oxidation wave (Fig 30), as was found for (51). The peak oxidation potential at +1.92V (SCE) was considerably higher than for (51) at 1.51V (SCE). It was noted that this cycle did not decay over repeated scans (40), and that as previously for (51),

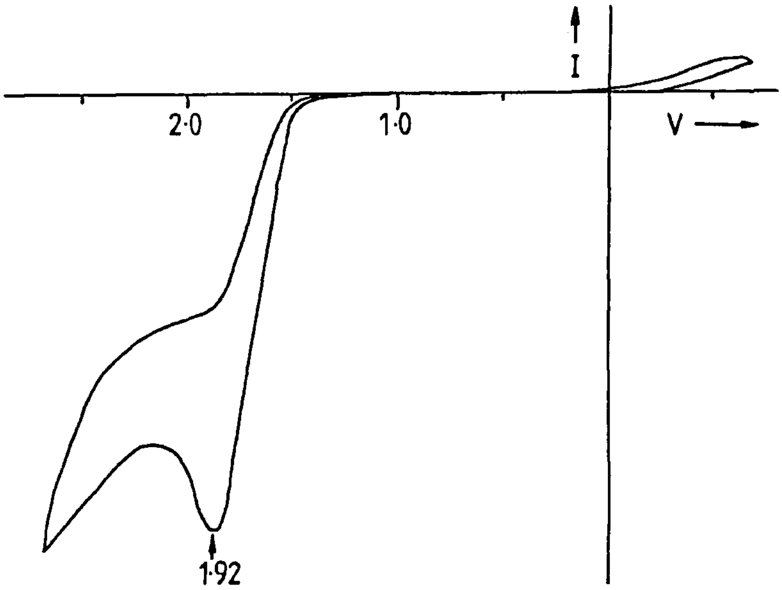


Fig 30. *Cyclic Voltammogram of* (*55*)

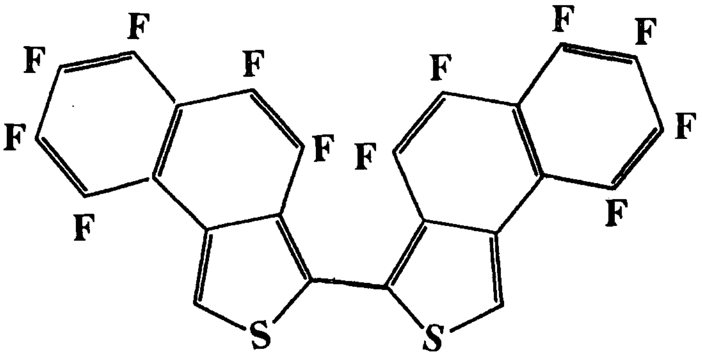
no nucleation loop was observed. At oxidation potentials from +1.85 to +2.70V, dark green material was seen to stream from the anode.

4.3.2. Electropolymerisation of (*55*)

The electrolyte contained 4,5,6,7,8,9-hexafluoronaphtho[1,2-c]-thiophene (55) (0.17M), Bu_4NBF_4 (0.07M) in liquid sulphur dioxide (5 ml). The electrolysis was carried out at -20^{0}C using a gold anode (25x7x2mm), platinum anode (25x7x1mm) parallel to each other at a spacing of 10 mm, with a Ag/ Ag^+reference electrode. The solution was not stirred and the current was applied potentiostatically at 2.00V (SCE). Electrolysis at this potential (average current density of 1.17 mA/cm^2 ; 40% extent of reaction for 2 electrons per molecule) gave an uneven blue/black deposit. Removal of the anode lead to some of the material to come away from the anode as a yellow/orange solid. Some material that stayed on the anode remained in the blue/ black state when handled in a glove box for a period of 5-7 days before turning deep red. The yellow/ orange material was soluble completely in chloroform.

4.3.3. Nature of the Product

The ^{19}F nmr of the yellow/ orange material was found to be very complicated and of little use for characterisation of the material. The mass spectrum showed that it contained unreacted 4,5,6,7,8,9-hexafluoronaphtho[1,2-c]thiophene (55) (m/z 292) and coupled products corresponding to the <u>unsaturated</u> dimer (m/z 582) (85) (negative CI). No further products were observed (ionisation chamber conditions of 300°C/ 10^{-9}mm Hg). Using negative DCI (out of chloroform), higher molecular weight peaks were seen in the region of m/z 872 which indicated the presence of coupled products of the type for the expected trimer.



(85)

4.4. Electro-oxidation of 4,5,6,7-tetrafluoroisoindole (71)

4.4.1. Cyclic Voltammetry

The C.V. of (71) was run in acetonitrile with a platinum working electrode, with Bu_4NBF_4 and the supporting electrolyte. The curve, as previously, showed an irreversible primary oxidation wave (Fig 31.),

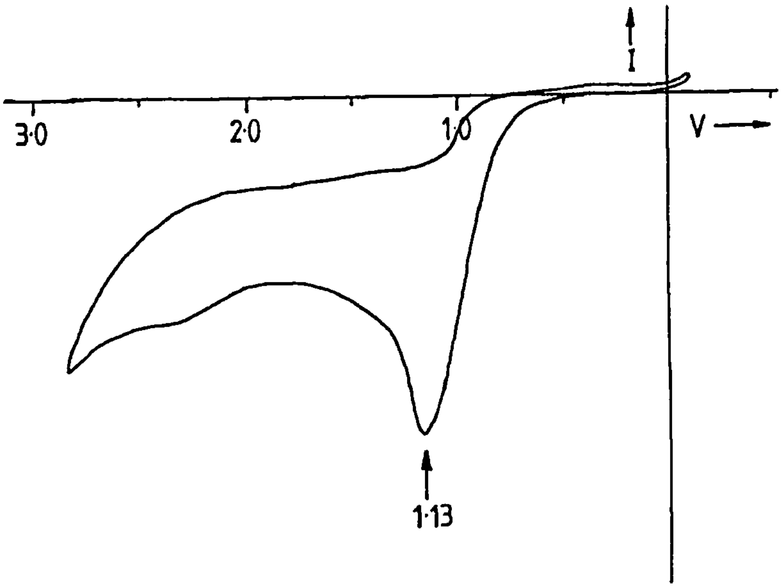


Fig 31. *Cyclic voltammogram of (71)*

with the peak oxidation potential at +1.13V (SCE). Again, no nucleation loop was observed.

4.4.2. Electropolymerisation of (71)

Using the idealised conditions for the electropolymerisation of 4,5,6,7-tetrafluoroisothianaphthene (51), the electrolysis solution contained (71) (0.15M), Bu_4NBF_4 (0.08M) in 5 ml liquid SO_2 or acetonotrile. The solution was cooled to -20^oC and using a gold anode (25x7x2 mm) was electrolysed for the equivalent of 50% extent of reaction with an applied potential of 1.2-1.6 V (SCE). Under these conditions, some blue/ black deposition formed on the anode. This was however very poorly deposited. In some experiments, no deposition occurred.

4.4.3. Nature of Product

The stability of the product from these experiments was difficult to determine since atmospheric oxidation of the monomer 4,5,6,7-tetrafluoroisoindole (71) occurred within 20-30 hours to give a black product (a similar colour to the electrolysis product). The low rate of deposition and the poor quality of sample lead to no true analysis of the product being recorded.

4.5. Electro-oxidation of N-methyl-4,5,6,7-tetrafluoroisoindole (68)

4.5.1. Cyclic Voltammogram

The C.V. of N-methyl-4,5,6,7-tetrafluoroisoindole (68) (Fig 32) shows a more complex curve than that previously recorded for these types of materials. It shows no nucleation loop with a platinum electrode, in agreement with the other potential monomers. The multiple oxidations seen cannot be due to electro-oxidised products since they are present on the first oxidation scan (it is common to see the oxidation potential of any polymer formed in these reactions at lower potentials than that

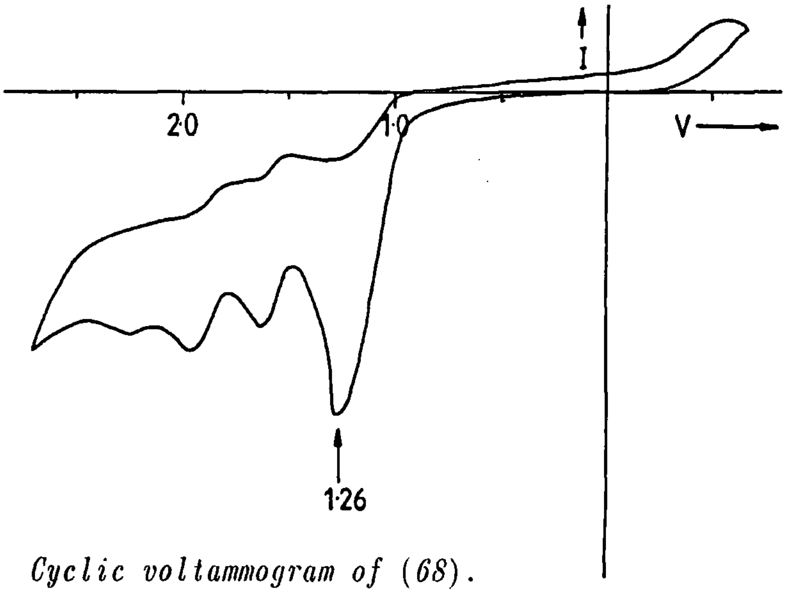


Fig 32. *Cyclic voltammogram of (68).*

of the corresponding monomers). The origin of these peaks must be related to the introduction of the methyl onto the nitrogen.

4.5.6. Electropolymerisation

Electrolysis of a solution containing N-Methyl 4,5,6,7-tetrafluoroisoindole (68) (0.12M), Bu_4NBF_4 (0.10M) using a gold anode in acetonitrile at $-20^{o}C$ at potentials of 1.40-1.80 V (SCE) gave no anode deposition. The solution around the anode turned a green/ yellow colour as the electrolysis progressed, indicating some oxidation of the indole was occurring.

4.5.3. Nature of Product

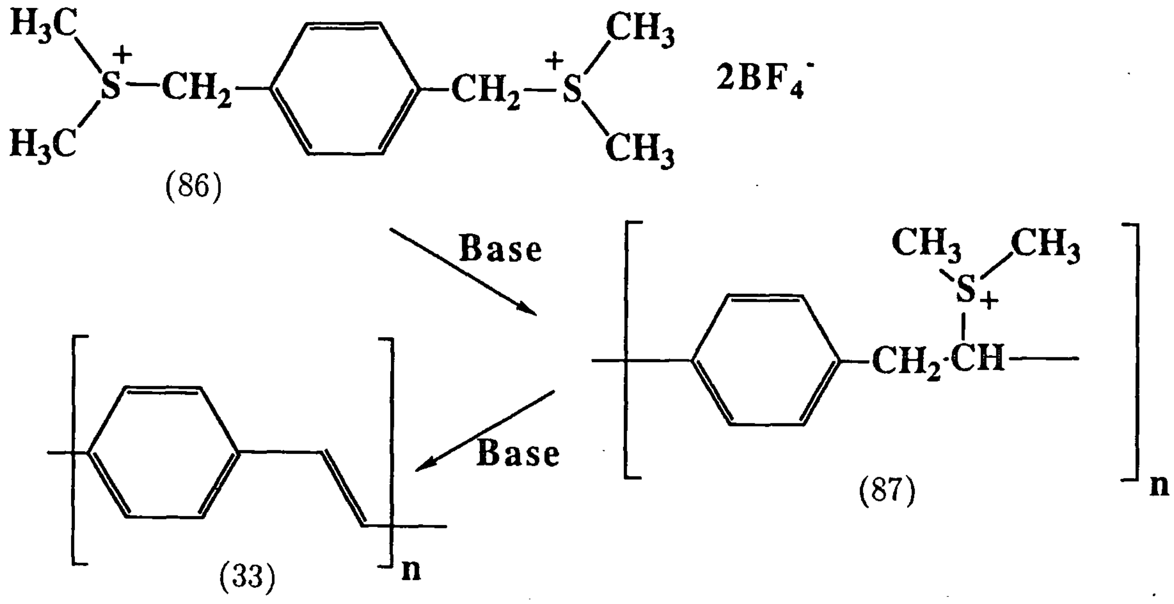
No product from the electrolyte solution could be isolated from the supporting electrolyte, with the crude product from the cell turning green/black upon prolonged exposure to the atmosphere. The complex nature of the C.V. and lack of deposit during electrolysis indicated that this monomer was inappropriate for this type of electrolysis under the conditions used.

CHAPTER FIVE

POLYPARAPHENYLENEVINYLENES *VIA* SOLUBLE PRECURSOR DERIVATIVES

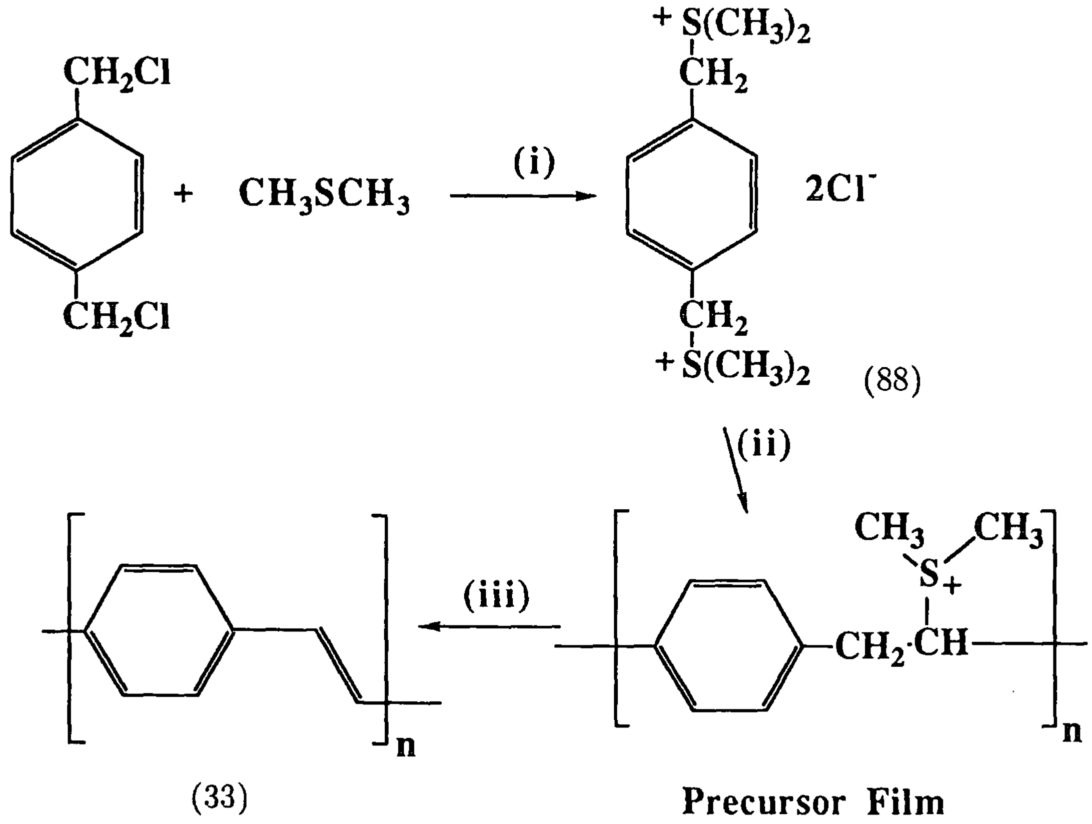
5.1. Preparations

The synthesis of polyphenylenvinylene (PPV) products obtained by Kanbe[61] from the sulphonium salt monomers (86) *via* precursor polymer (82) were oligomeric powders with a degree of polymerisation of about 10 (Scheme 40). The production of low molecular weight products have been attributed, in part, to the use of elevated reaction temperatures (80°C), and the excess base concentration used (3:1 base to monomer). This lead to the partial elimination of dimethylsulphide to form some unsaturated units in the PPV chain, both of which are facilitated by heat and base, so inducing insolubility into the oligomer. The use of sulphonium chloride monomers, low reaction temperatures (0-5°C) and a reduced base to monomer concentration (typically equimolar), gave high molecular weight soluble precursor polymer. Partial oxidation of the polymer backbone, observed as an infra-red band at 1695 cm^{-1} [112], required the rigorous exclusion of oxygen during the polymerisation process. These conditions were adopted by Murase et al[112] to give a greenish/ yellow cast precursor film.



Scheme 42. *Kanbe Synthesis of PPV*

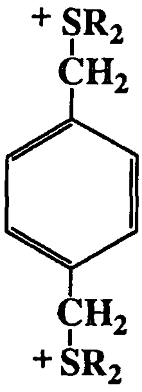
Thermal elimination at 200°C did not remove all of the sulphur present, with temperatures of 300°C required to provide the fully eliminated product, giving pale yellow PPV films. These films showed sharp absorptions at 970 cm^{-1} in the infra-red, (indicating *trans*-configuration in the polymer chain) and conductivities of ≈ 1 S cm^{-1} when doped with SO_3 (Scheme 43).



Scheme 43 *Synthesis and processing of PPV (i) 50° C, methanol /water (8/2); (ii) NaOH, 0° C; (iii) 300-350° C/vacuum*

Gagnan et al[113] optimised the reaction conditions to prepare p-xylylene-bis(dimethylsulphonium chloride) (88) from α,α' - chloro-p-xylylene with excess dimethylsulphide (1.5 equivs) at 50°C in a methanol:water (80:20) solution for 20 hours. Equimolar quantities of monomer and sodium hydroxide (0.2M) were mixed at 0°C for 1 hour and quenched to pH 6.8 with 1M HCl. The clear viscous polyelectrolyte was dialysed for three days against deionised water to remove sodium hydroxide, residual monomer and short oligomers. These conditions are generally adhered to today for the polymerisation process.

The principal derivatives of the bis(sulphonium salt) monomers used for the polymerisation reactions have been dimethyl and diethyl sulphonium chlorides or bromides [(88) and (89) respectively]. Although these produce high molecular weight species, the yields obtained are generally only 10-20% which may be due to undesirable side reactions; in particular nucleophilic substitution on the side chain carbon *α* to the sulphur occurs to a large extent in dimethylsulphonium bromide salts and less so with diethylsulphonium chloride salts and may be responsible for the low yields observed. As a consequence of this, other types of sulphonium salt monomers have been investigated.

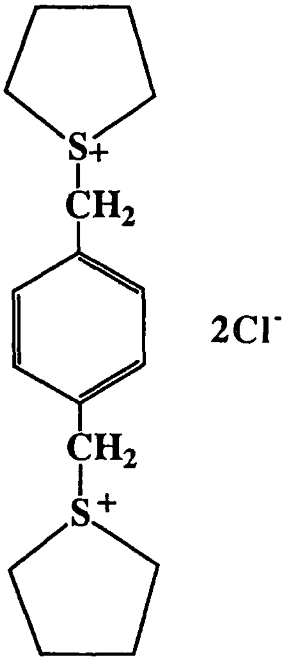


$2X^-$

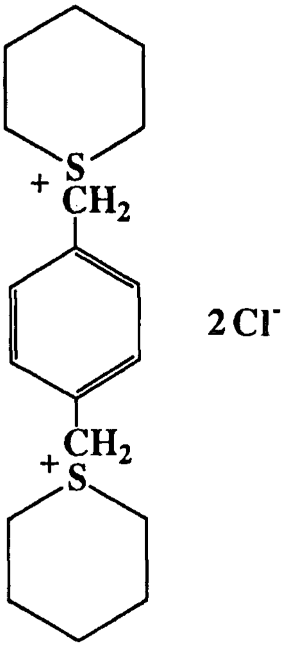
X=Cl R=CH_3 (88)

X=Cl R=C_2H_5 (89)

Lenz et al[114] have compared the sulphonium salts prepared from tetrahydrothiophene (THT) (90) and tetrahydrothiopyran (THTP) (91) with the dimethylsulphonium salts. They found that both the yields and the molecular weights of the polymers derived from the THT sulphonium monomer (90) were considerably higher than those of the dimethyl sulphonium chloride monomer (88), typically 38 - 43%. The THTP sulphonium chloride monomer (91) gave the highest molecular weight, but only in yields comparable to the dimethyl and diethyl sulphonium chloride monomers (88) and (89), at 18%. Both cyclic systems



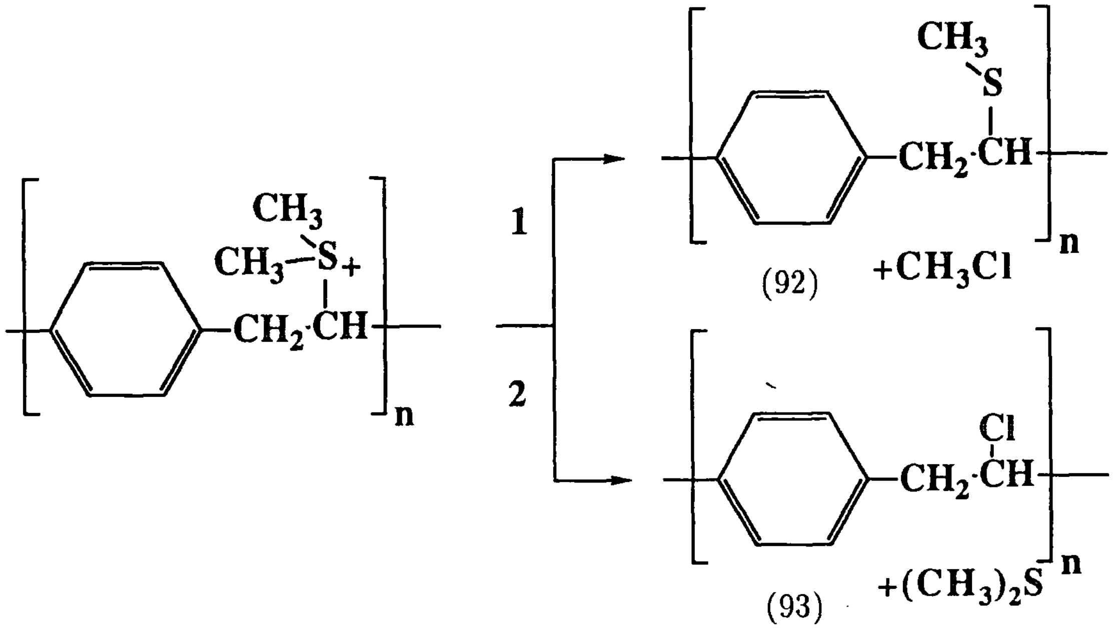
THT (90)



THTP (91)

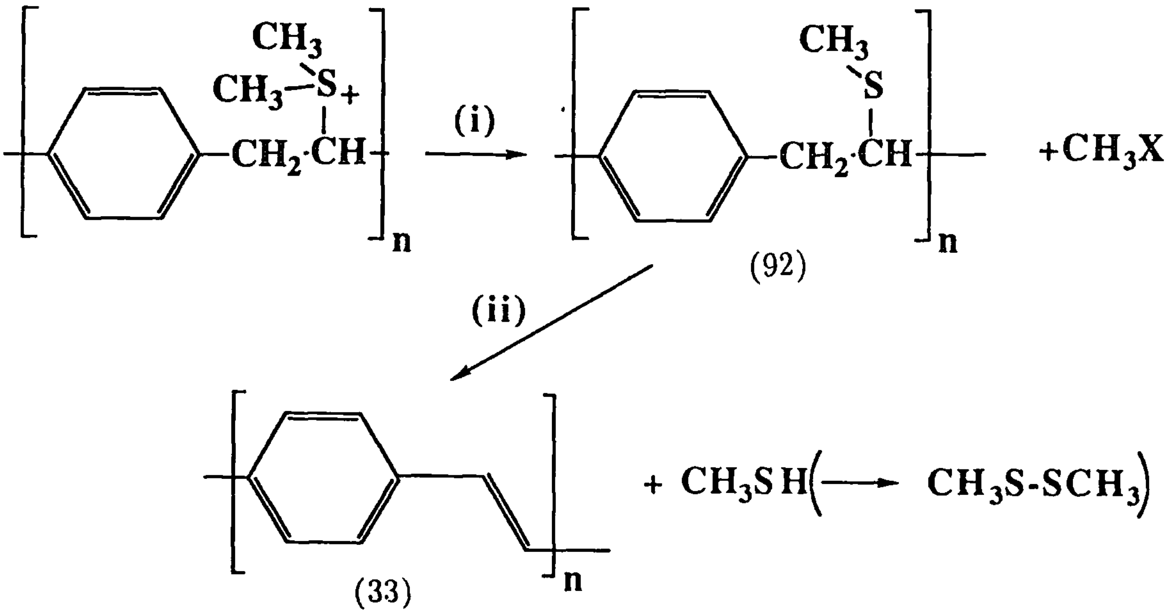
polymerised very rapidly, forming transparent gels within 5 minutes when reacted at a 0.2M concentration with base.

The composition of the polymers was evaluated by elemental analysis after iso-thermal elimination reactions were performed. It was found that the polymers derived from the cycloalkane sulphonium salts (90) and (91) contained very little residual sulphur and chlorine. This was in contrast to the relatively large amounts found for the dialkylsulphonium chloride monomers (88) and (89) under similar thermal elimination conditions. This implied that the elimination reactions of the cyclic sulphide groups to form vinylene units takes place in higher yields than those of the dialkyl groups. This also suggested that competing and undesirable side reactions occur less readily with the cyclic systems. The most likely side reactions are the nucleophilic substitution reactions that form the alkyl sulphide (92) or the alkyl chloride (93) polymers (Scheme 44). These factors permitted better orientation and increased conjugation of the resultant PPV due to fewer irregularities



Scheme 44. *Competing elimination reactions 1: Chloride attack on methyl and loss of chloromethane. 2: Chloride attack on polymer with loss of* Me_2S

in the chain. Hence, higher limiting conductivities were found for the polymers derived from cycloalkyl sulphonium salts, up to 180 Scm^{-1} for the unoriented PPV derived from THTP when doped with AsF_5. It has been shown by direct pyrolysis-mass spectrometry[115] that the instability of the precursor polymer salt, under normal conditions, leads to the sulphide (92), requiring higher temperatures to achieve complete

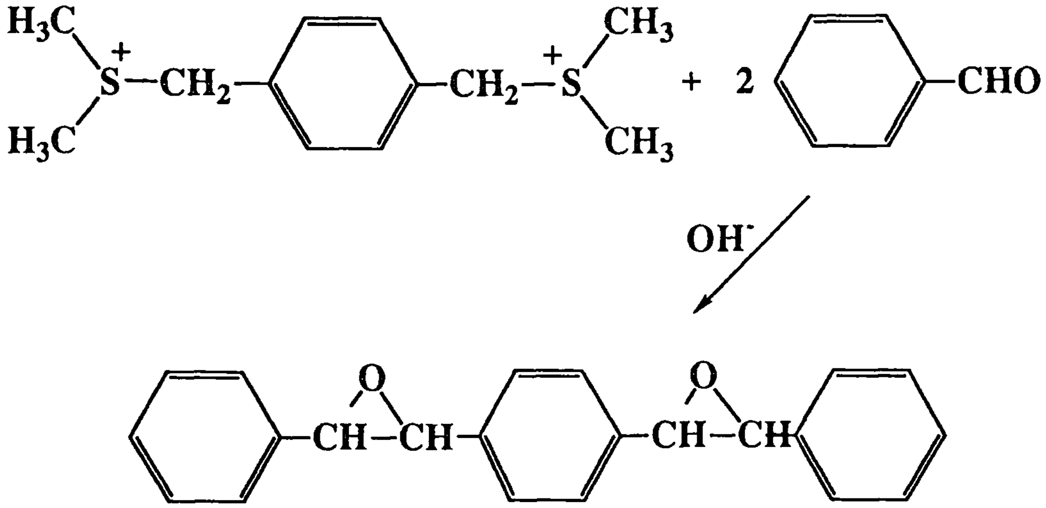


Scheme 45. (*i*) *50°C* (*ii*) *380°C*

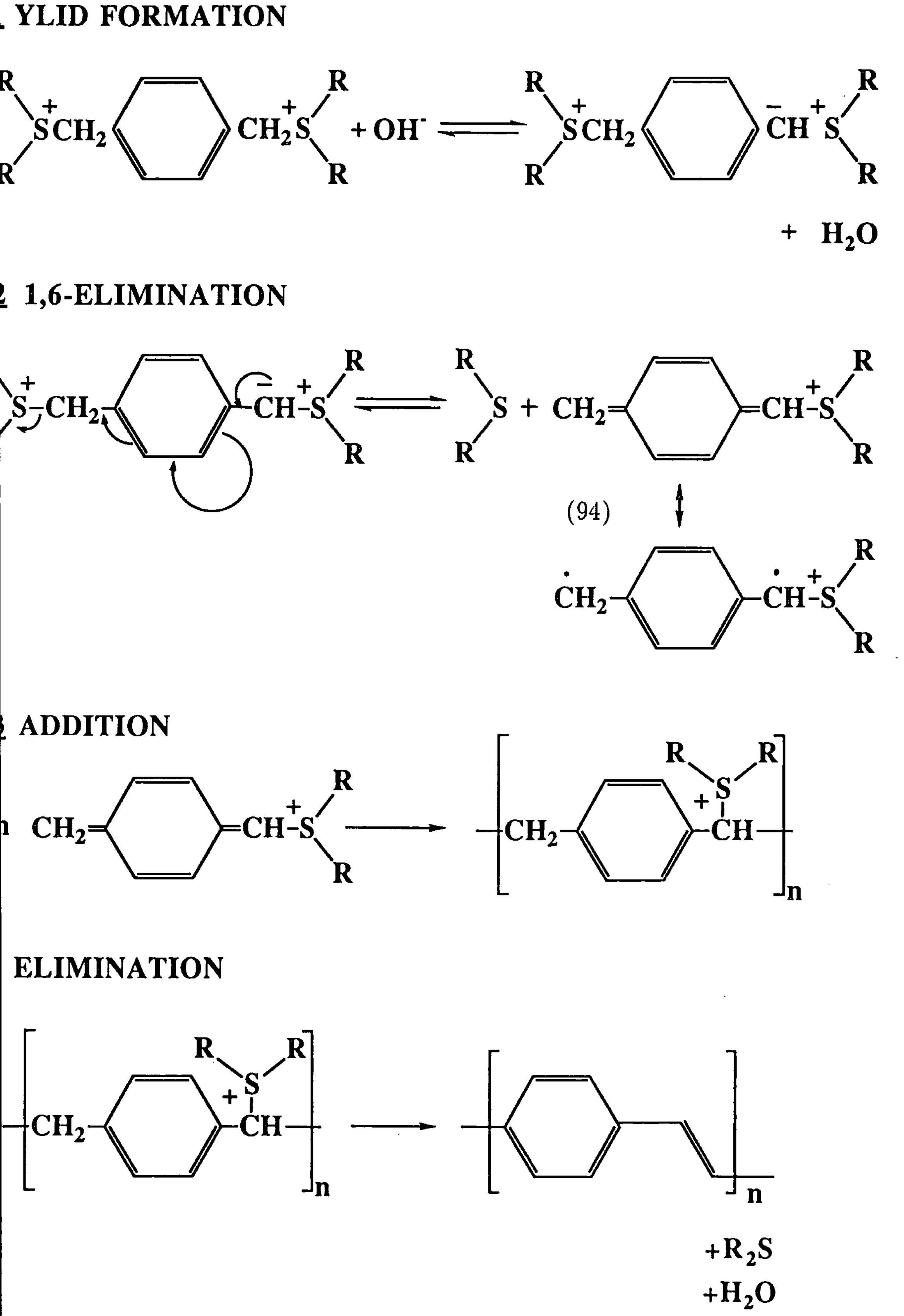
elimination (Scheme 45). If the precursor polymer is kept at low temperatures and is heated gradually to the elimination temperature, only the required elimination of dimethylsulphide and HX occurs.

5.1.1 Mechanism of the Formation of Polyelectrolyte

Wessling proposed a mechanism in which the species (94) is the true monomer (a xylylene pseudo-diradical) (Scheme 46) which polymerises spontaneously by a free radical mechanism. Indeed, addition of a free radical initiator is seen to speed up the reaction. The intermediate ylid has been trapped with benzaldehyde[116] with no polymer formation observed (Scheme 47).



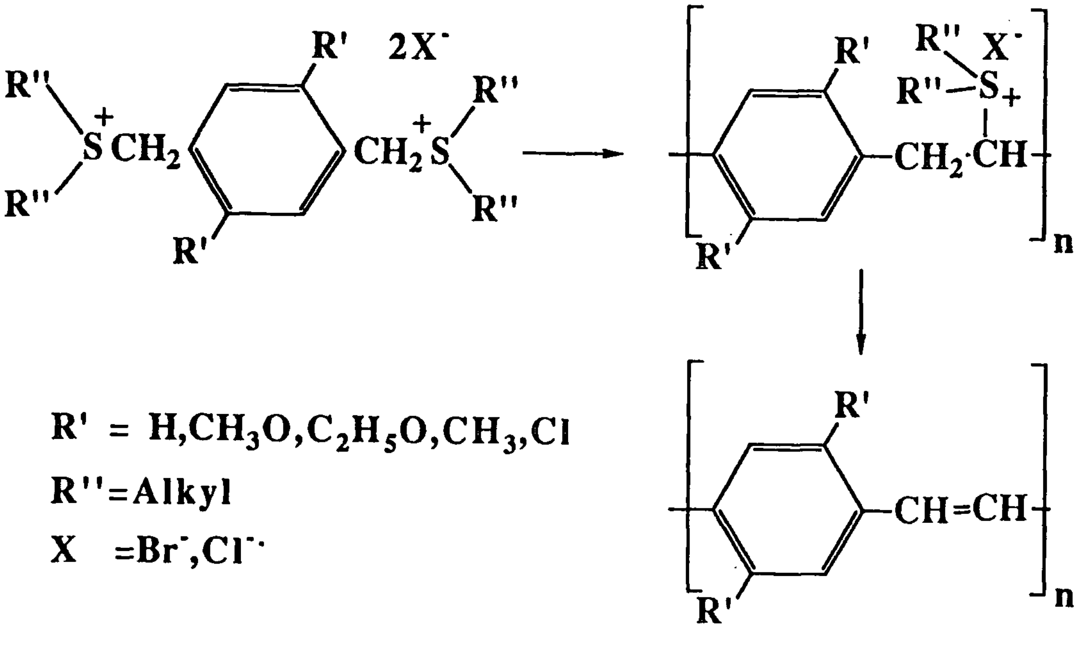
Scheme 47. *Trapping of diradical with benzaldehyde*



Scheme 46. *A Mechanism of base induced polymerisation.*

5.1.2 Substituted Derivatives of PPV

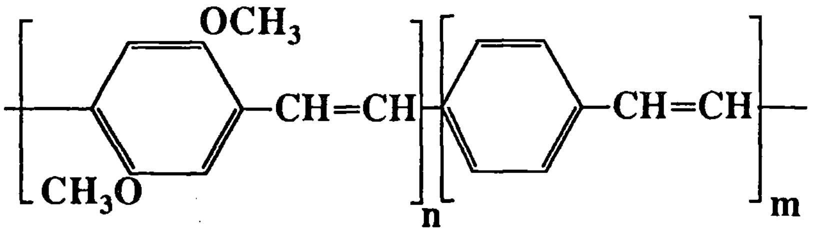
In common with techniques used in polyacetylene formation, the precursor sulphonium halide polymer of PPV can be subject to uniaxial stretching during the thermal elimination process to give aligned systems. In non-substituted PPV, this can lead to the surprisingly large conductivity values at 2780 S cm^{-1} for AsF_5 doping, and 685 S cm^{-1} for SO_3 doping[112,117] for 10-fold stretching. This compares with 10 S cm^{-1} and 100 S cm^{-1} for AsF_5 and H_2SO_4 doping of unstretched films[113]. Stabilization of p-doped polymers by alkoxy-substitution on the aromatic ring of PPV, leads to a lowering of the ionization potential of the polymers, and an increased interaction of the polymer with dopants. Thus, dimethoxy and diethoxy 2,5-disubstituted PPV's were prepared[118] by pyrolysis of the corresponding precursor polymer, to give red transparent flexible films which were air stable (Scheme 48).



R' = $H, CH_3O, C_2H_5O, CH_3, Cl$
R''=Alkyl
X =Br^-, Cl^-

Scheme 48.

The reduction in ionization potential leads to effective iodine doping with a conductivity over 200 S cm^{-1} for unstretched films (Table 5). The substitution also stabilizes the oxidised polymers to atmospheric degradation so that the conductivities remain unchanged over a period of one month. A uniaxially drawn co-polymer with 13% methoxy monomer incorporation (95) doped with iodine showed a constant conductivity of 433 S cm^{-1} over a period of six months[119].



(95)

m/n = 13/87

Dopant studies with AsF_5 show that a maximum conductivity is often not attained until after two weeks exposure, and subsequently decreases to 10^{-4} S cm^{-1} over the following days. This is also seen with SO_3 doping and may indicate a degeneration of the polymer conjugation by some destructive charge transfer when exposed to strong oxidants[120].

Substituted PPV	Conductivity S/cm			
	I_2	SO_3	AsF_5	H_2SO_4
CH_3O - PPV	203 (1.85)	159 (2.00)	68(-)	411(-)
C_2H_5O- PPV	257 (1.17)	43 (0.80)	14(-)	-
H - PPV	2.5×10^{-3}(0.10)	7.7 (0.41)	38(-)	27(-)
CH_3 - PPV	2.1×10^{-4}(0.13)	10^{-4} (—)	-	-

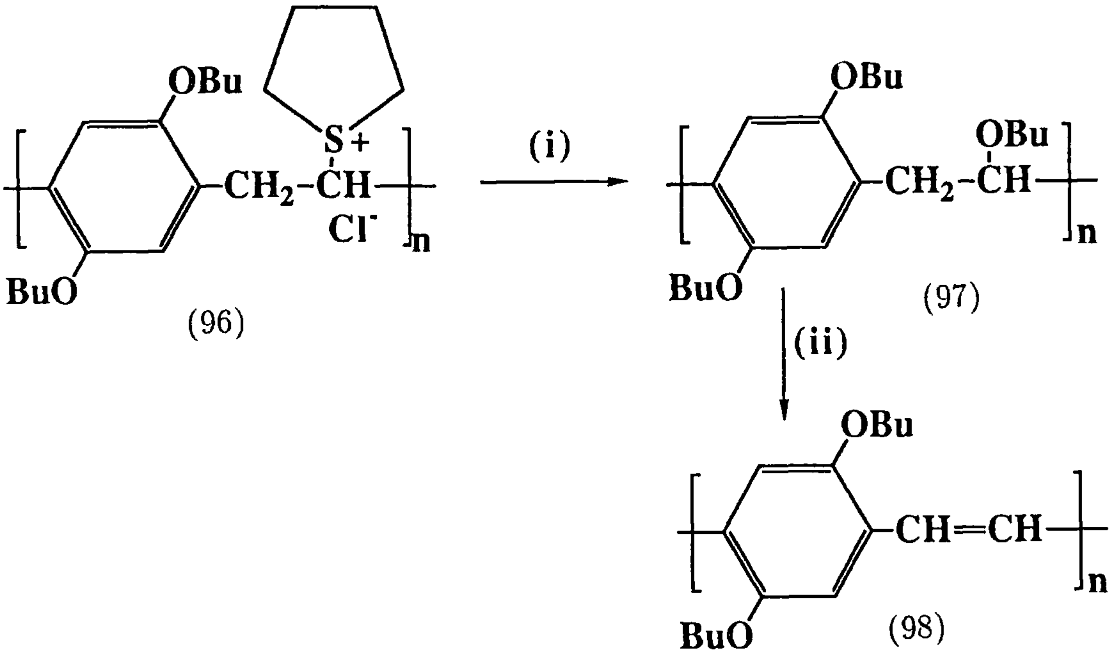
Table 5. *Electrical conductivities of non-stretched PPV films. Concentration of dopant in PPVs (mole/ monomer unit) (Ref. 118)*

The decrease in the ionization potential by alkoxy substitution has made the undoped PPV polymer considerably less stable to oxidation, requiring milder oxidising agents to induce charge transfer, thus generating more stable p-doped polymer. Deformation of planarity in the polymer orbitals was expected upon the introduction of substituent groups, leading to a reduction of electronic delocalisation. This effect, if present at all, is outweighed by the advantages of a lower ionization potential through lowering of the HOMO level, which leads directly to more stable charge carriers upon mild oxidation.

Insight into fluorinated systems may be gained from the observations made on the nature of chlorine substituted PPV[118]. The temperature at which the precursor alkoxy-PPV completely eliminates the dialkylsulphide from the sulphonium salt precursor polymer, is around 100 C^o lower than that for non-substituted PPV. This compares with the precursor chlorine substituted-PPV, which is not completely conjugated with a considerable amount of sulphur still left in the film, even after treatment at 300^oC. Heating to 350^oC or above decomposes the polymer. One may expect a similar trend in the fluorinated analogue.

5.1.3 Alternative Leaving Groups

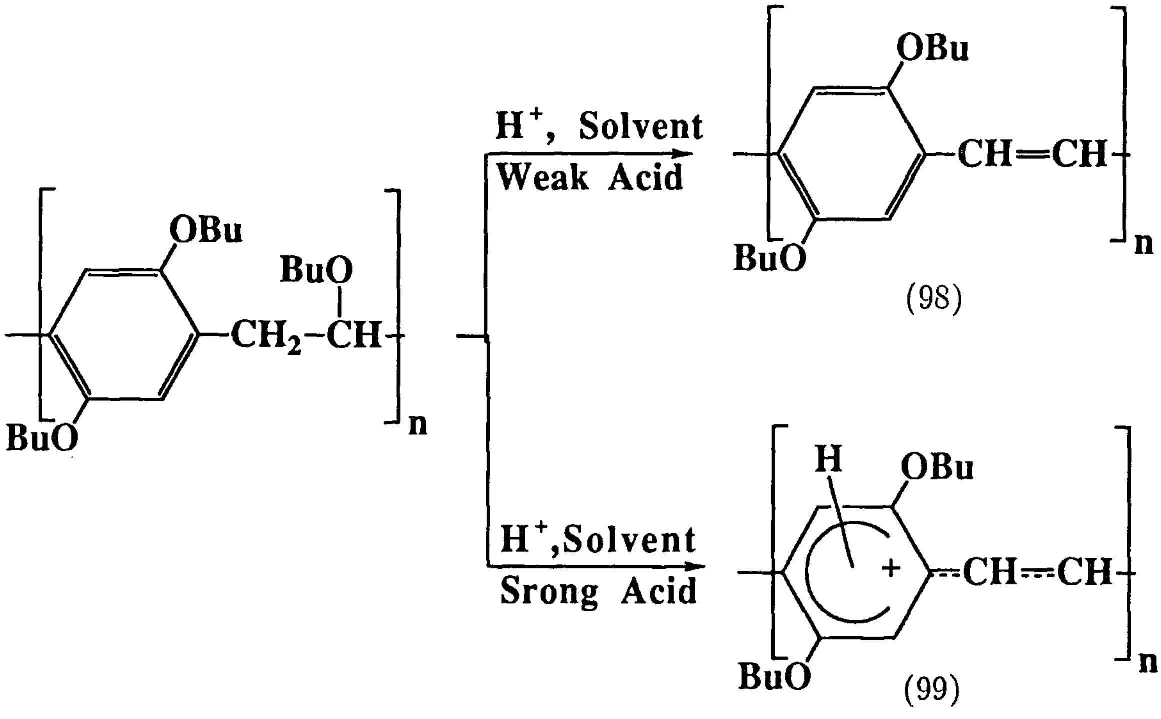
Investigation into soluble precursors and potentially soluble conjugated PPV's lead to the preparation of the butoxy substituted PPV[121]. An interesting derivative was formed when the sulphonium salt polymer (96) of poly(dibutoxyphenylenevinylene) (98) was dissolved in butanol containing a small amount of pyridine as a stabilising agent. It was found that a near quantitative conversion into (97) had occurred (Scheme 49). The polymer (97) was found to be soluble in many organic



Scheme 49. *Conversion of sulphonium polymer (96) to alkoxy polymer (97) and subsequent conversion to substituted PPV (98).*
(i) Butanol, pyridine, room temperature. (ii) 200-250° C/ vacuum.

solvents and could be cast to form a stable highly elastic polymer film. This non-ionic precursor polymer could be converted to the poly(dibutoxyvinylene) (98) polymer by thermal elimination of butanol, at temperatures ranging from 200-250^{o}C under high vacuum.

The elimination could also be accomplished non-thermally. This was found to be catalysed by acids in common organic solvents at room temperature to give solutions of highly conductive polymer (98) (Scheme 50). When acids having a pKa value below 2 are used then the precursor polymer was converted directly into a solution of doped poly(di-butoxyphenylenevinylene) (99).



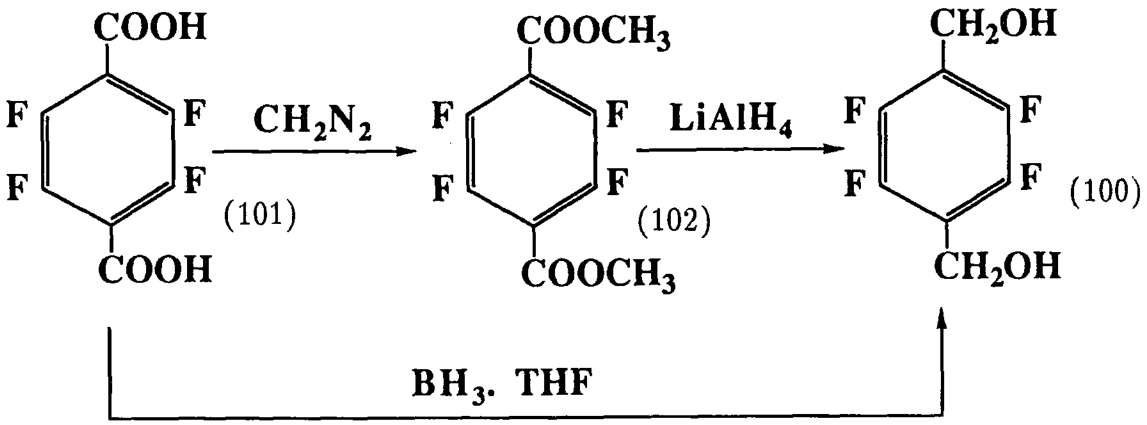
Scheme 50. *Acid catalysed elimination of butanol to give substituted PPV.*

5.2. Present Work: Attempted Synthesis of Poly para-tetrafluorophenevinylene from a Polyelectrolyte

The approach to the synthesis of the precursor sulphonium polyelectrolyte was the same as that used for the hydrocarbon analogues, with the starting *α,α'*-dihalo-tetrafluoro-1,4-xylenes being made from the corresponding tetrafluoroterephthalic acid *via* 2,3,5,6-tetrafluorobenzenedimethanol.

5.2.1. Synthesis of2,3,5,6-tetrafluoro-1,4-benzenedimethanol (100)

Tetrafluoroterephthalic acid (101) was used as the starting material for the 1,4-disubstituted system. To reduce the acid to the corresponding bis alcohol $(100)^{122}$, three routes were attempted (Scheme 51). A $LiAlH_4$ reduction in THF at 40^0 C proved unsuccessful with 60 % unreacted terephthalic acid still present after 20 hours along with complex residues. Therefore, the terephthalic acid was conveniently converted to the dimethyl ester (102) quantitatively using



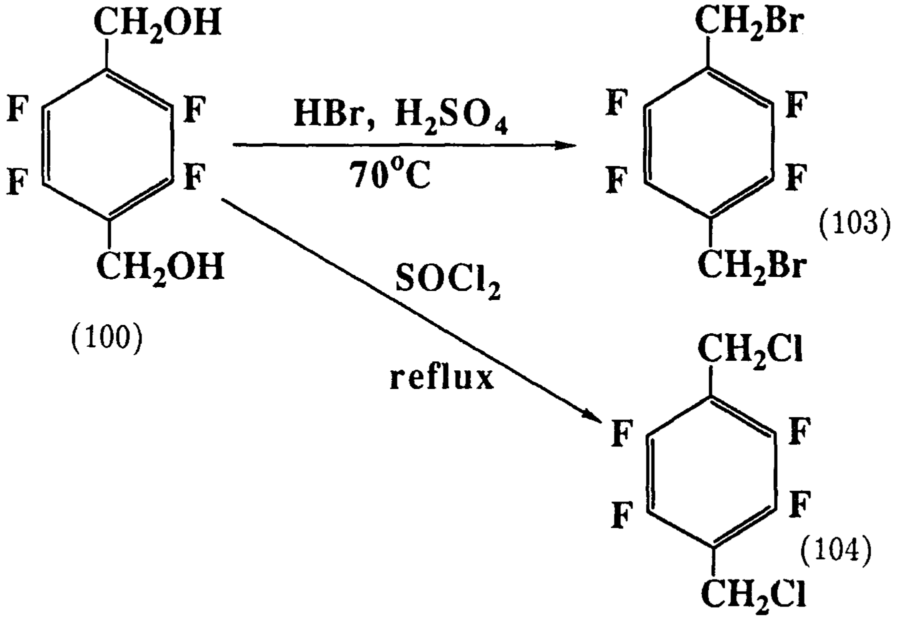
Scheme 51.

diazomethane. The dimethyl tetrafluoroterephthalete was then easily reduced with $LiAlH_4$ at room temperature over 45 minutes to give an almost quantitative yield of (100).

The third and most direct reduction, but the most expensive, was by treatment of the terephthalic acid (101) with borane-tetrahydrofuran complex under reflux for 7 hours. This gave a quantitative yield of (100), as expected for this type of reaction. This route was used in general due to the high yield and the simplicity of the work up.

5.2.2. Synthesis of α,α'-dihalo-2,3,5,6-tetrafluoro-1,4-xylene's

Both the conversion of the dimethanol (100) to the dibromide (103)[123] and to the dichloride(104) were achieved by standard methods (Scheme 52). Treatment of (100) with concentrated hydrobromic acid and concentrated sulphuric acid gave the dibromide (103) quantitatively. Treatment of (100) with thionyl chloride at reflux afforded the



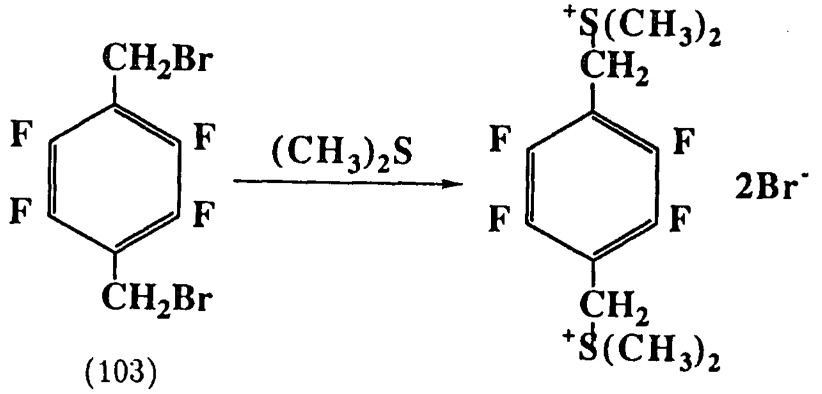
(100) (103) (104)

Scheme 52.

dichloride (104) again quantitatively. Both were white crystalline solid and required very little purification.

5.2.3. Treatment of (103) with Dimethyl sulphide

The conversion of (103) to a bis(sulphonium bromide) derivative (105) requires nucleophilic substitution by the sulphur onto the benzylic carbon atom (Scheme 53). Due to the increased electron



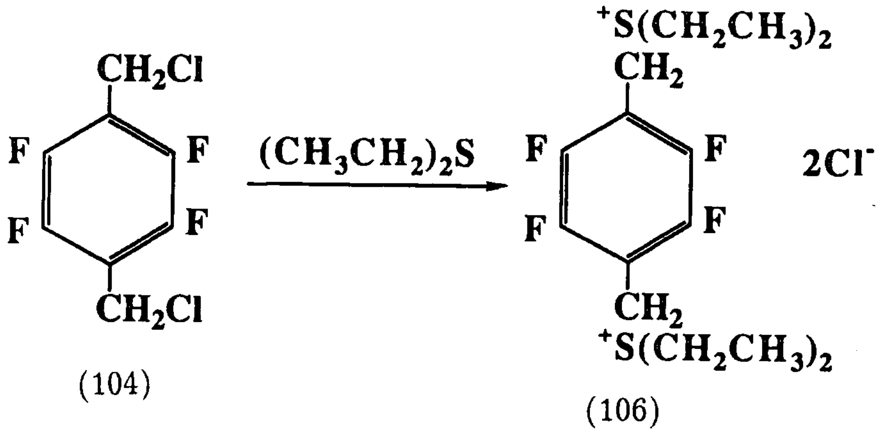
(103) (105)

Scheme 53.

withdrawing nature of a fluoroaromatic system compared with the hydrocarbon derivative, the reaction was expected to occur in a shorter length of time and perhaps give better yields. Treatment of (103) with 2 stoichiometric equivalents of dimethyl sulphide in a methanol/water solvent system (8:2), gave (105) in a 70 % yield.

5.2.4. Treatment of (104) with Diethyl Sulphide

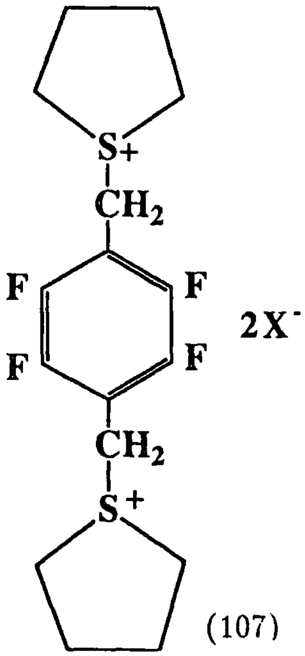
Since, as discussed, both the diethyl and chloride derivatives are to be preferred over the dimethyl and bromide derivatives for polymerisation purposes (section 5.1.), then the bis(diethylsulphonium chloride) (106) was the next target molecule. Treatment of (104) with excess diethyl sulphide in a methanol/ water solvent mixture gave (106) (59 %) (Scheme 54). It was not unexpected that this diethylsulphonium salt, which has a more organic nature than the dimethylsulphonium derivative (105), was more soluble in acetone (its crystallisation solvent) resulting in a lower yield of isolated product.



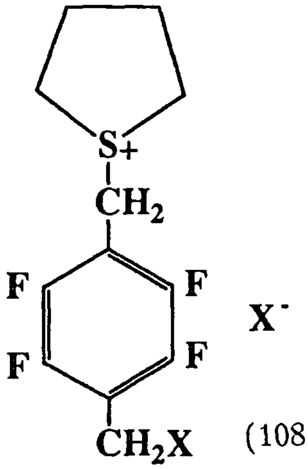
Scheme 54.

5.2.5. Attempted Preparation of the Tetrahydrothiophene (THT) (107) Derivative

Both the α,α'-dichloroxylene (104) and the α,α'-dibromoxylene (103) were treated with THT under similar conditions to those described for the preparation of the dimethyl (105) and the diethyl (106) derivatives. The products from both reactions, when concentrated, were viscous oils, even after prolonged drying under vacuum, which could not be crystallised from any solvent system. The ^{19}F nmr of both products showed two sets of fluorine peaks which clearly indicated that a mixture of the required disubstituted product (107) and of the monosubstituted product (108) were present. No technique could be found to separate these materials and prolonged reaction tine with a large excess of THT gave no major improvement in the yield of the disubstituted material.



(107)

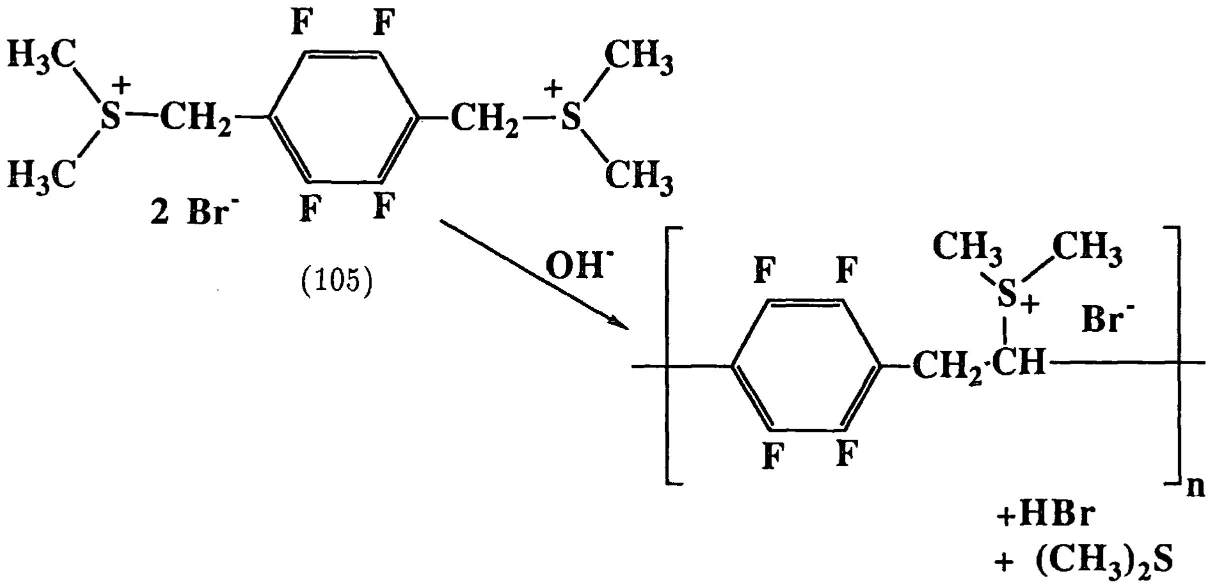


(108)

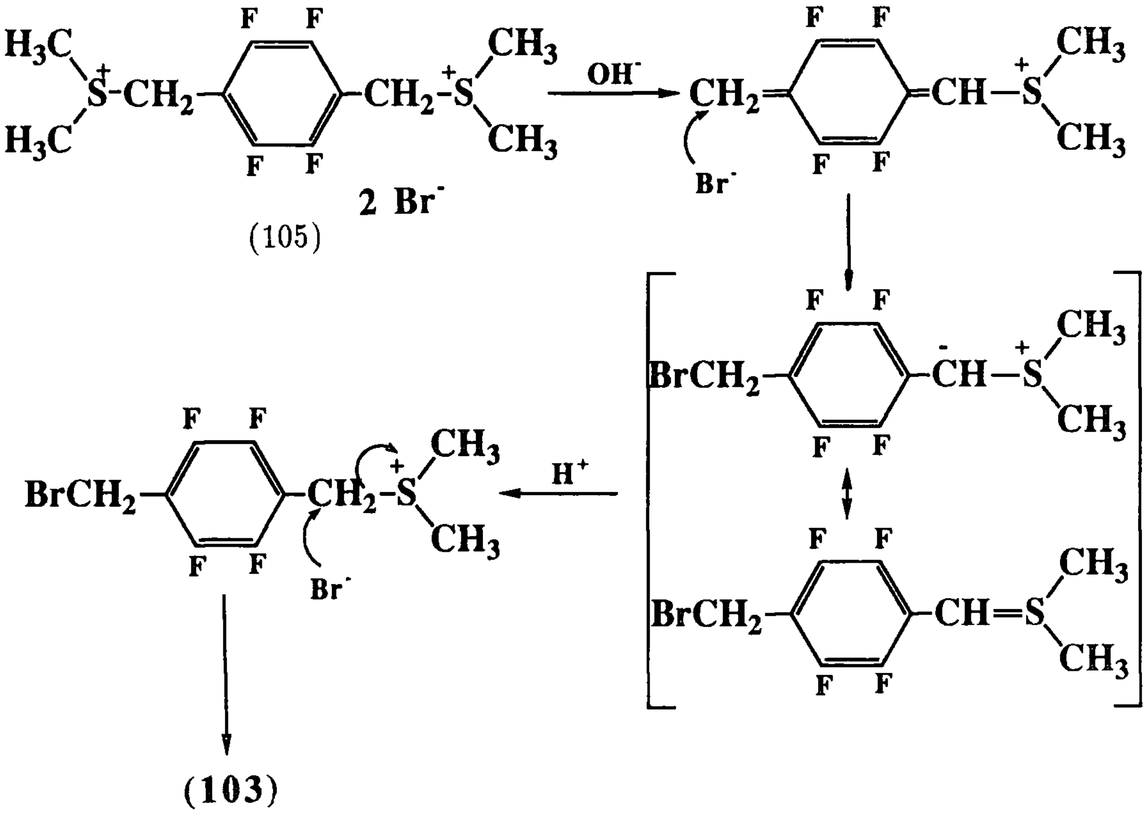
X= Cl^-, Br^-.

5.2.6. Attempted Polymerisation of bis(dimethylsulphonium bromide) (105)

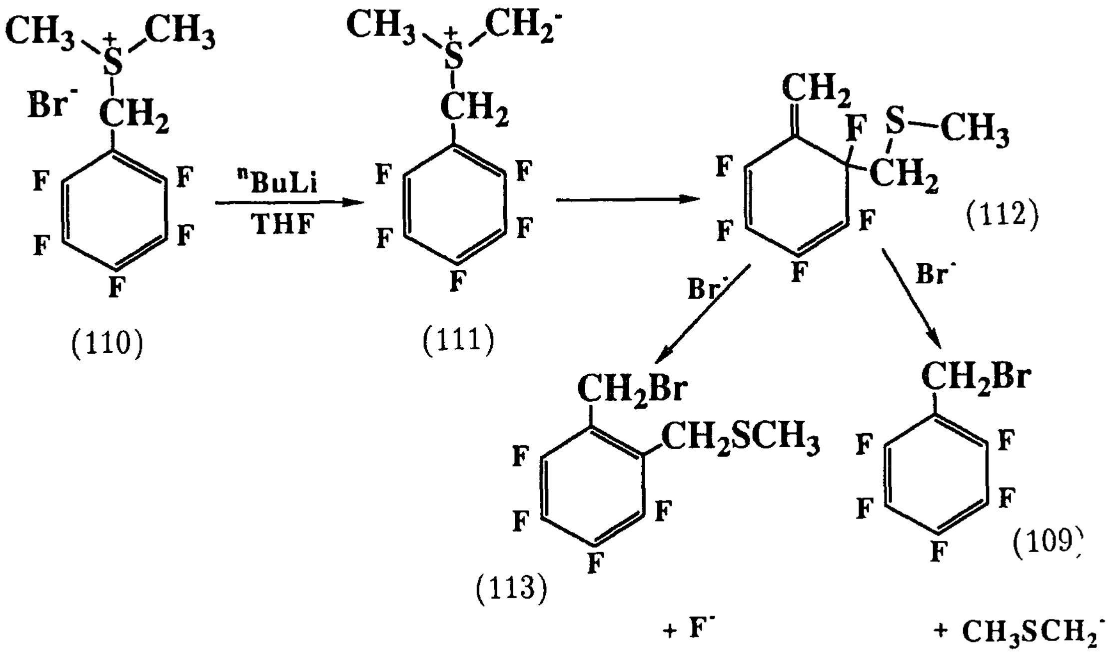
Following the procedure described by Gagnon et al[113], a 0.2M solution of (105) was degassed and cooled to 0°C under nitrogen and treated with a degassed 0.2M solution of sodium hydroxide with a view to making a soluble precursor polymer (Scheme 55). The appearance of a solid was noticed after a period of only 2 minutes. The reaction mixture was maintained at 0°C for 2 hours when it was quenched with 0.5M HCl to pH 6.8. The product was centrifuged to separate off a white solid which was identified as the α,α'-dibromoxylene (103). Some of the α,α'-dibromoxylene had not been completely removed by centrifuging and sublimes out of the remaining aqueous fraction when this was cast into a film and subject to heating under vacuum (80°C/ 2x10^{-3}mm). Overall, compound (103) accounted for 33% of the product, the rest being unidentified. The formation of (103) may be due to one of two processes one of which may be a base promoted decomposition outlined in Scheme 56.



Scheme 55.


Scheme 56.

Brooke et al[124] observed a similar formation of 2,3,4,5,6-pentafluorobenzyl bromide (109) (32%) in addition to 4 other products from 2,3,4,5,6-pentafluorobenzyl(dimethyl sulphonium bromide) (110) when treated with butyllithium in THF (Scheme 57). The mechanism to account for the formation of (109) involved first the formation of the ylid (111) which underwent a [2,3]-sigmatropic rearrangement to give (112). The more likely decomposition of this is to (113) with the far more efficient loss of fluoride. However, compound (113) appeared in only a 2.5% yield, with the major product (109) requiring the suprising loss of $CH_3SCH_2^-$. An alternative route to (109) is a self decomposition of (110) but this has been shown not to take place (in neutral solution). A reduction in the acidity of the alkyl proton or a reduction in the nucleophilicity of the halide may reduce the formation of the α,α'-dibromoxylene (103) to ensure that the proton removed by addition of base is the benzylic one. This was the case



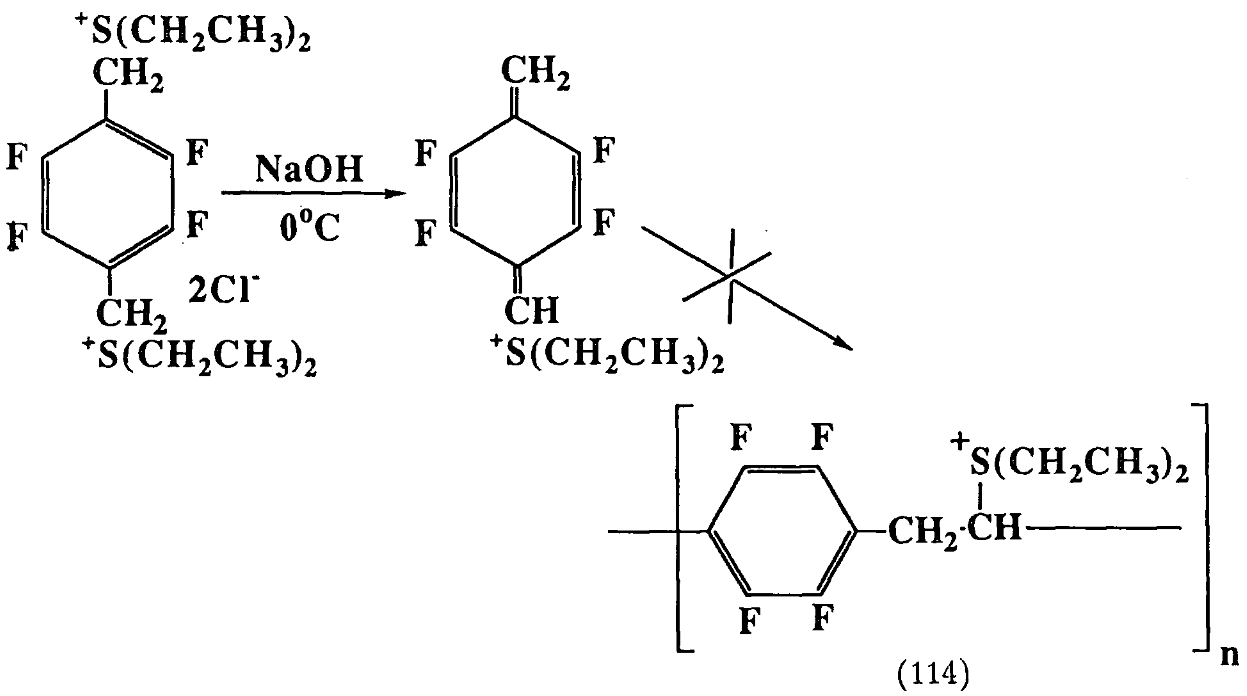
Scheme 57.

when (110) was prepared with fluoride as a counter ion and was treated with $CH_3SOCH_2^-Na^+$ [124] since non of the nucleophilically substituted products were found. The derivative of the bis-salt that may satisfy similar requirements is the bis(diethylsulphonium chloride). The proton α to the sulphur on the ethyl group is less acidic than the proton in a methyl group, and the chloride is less nucleophilic than the bromide.

5.2.7. Polymerisation of bis(diethylsulphonium chloride) (106)

The polymerisation of (106) was attempted in both water and methanol using either NaOH or the organic bases triethylamine and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU). The use of methanol was in order to increase the solubility both the monomer and resultant polymer. It may also lead to the formation of the methoxy derivative (see section 5.1.3.) All the reactions were carried out in degassed solvents under a nitrogen atmosphere.

Treatment of a 0.05M aqueous solution of monomer (106) at 0^{o}C with 0.1M NaOH lead to no observable colour change which indicated a very low concentration of the ylid. After 30 minutes the pH was adjusted to pH 6.5 to quench the reaction. Dialysis in water of this crude reaction product gave a solution which was colourless and could be repeatedly evaporated to dryness and re-dissolved. A film was cast from this solution which was heated under vacuum up to 260^{0}C/3x10^{-3}mm Hg for 24 hours. However, no colour change was observed indicating that conjugation had not been introduced by a thermal elimination process. These observations indicated that polymer (114) had not formed (Scheme 58).



(114)

Scheme 58.

With a monomer concentration of 0.2M at 0^{o}C in an aqueous solution, treatment with 4M NaOH lead to an immediate dark/green colour. The reaction was terminated after 8 minutes by addition of dilute HCl (short reaction times have been shown to give better polymer yield[114]). In comparison to the reaction using a 0.05M monomer solution, this later reaction required very little dilute HCl to adjust the pH to 6.5, indicating that in this reaction, compared to the first, a large percentage of the base had been used up. After dialysis, evaporation of the solvent at less than 25^{o}C to avoid thermal elimination reactions, lead to a yellow/orange film that could not be re-dissolved in any common solvent, which suggests that a large amount of conjugation had been introduced.

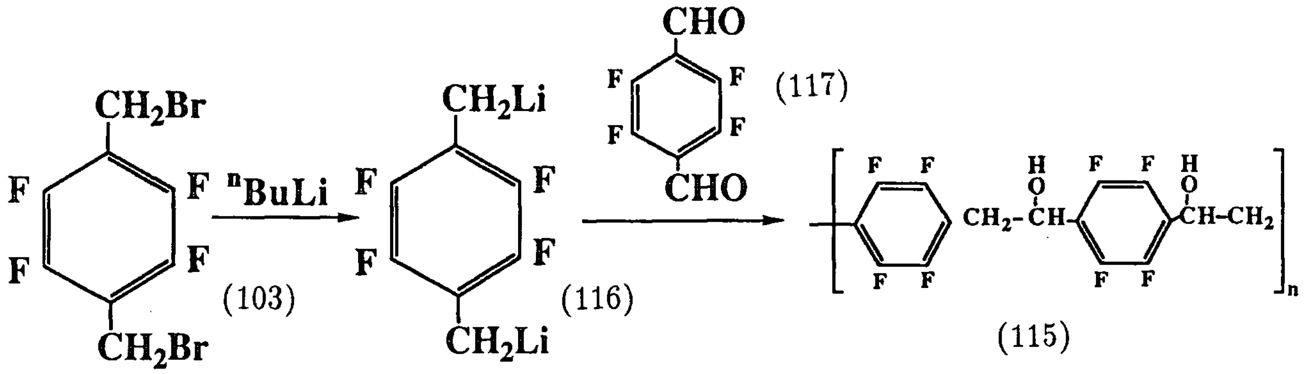
At a concentration of 0.5M for the monomer and 0.5M for the base, a more controlled reaction was achieved. The appearance of a green colouration in the solution indicated the formation of ylid type intermediates, the reaction being terminated after one hour by the addition of dilute acid. The ^{1}H and ^{19}F nmr's of this crude product after dialysis in water were very complex in nature, not showing the peaks expected for the required polymer. A film of this crude yellow/ brown product cast onto a silica plate was subjected to heat under a vacuum of 3x10^{-3}mm Hg. Increasing the temperature in stages up to 350^{o}C lead to no distinct change in colour of the film, which remained overall brown in colour. It was again observed that any film cast could not be redissolved if left in a dry condition for more than two hours. Micro analysis of film after heat treatment were generally in agreement with the expected values for F-PPV except for the nitrogen content. C, 55.62 (req 55.19%); H, 1.52 (req. 1.16%); N, 0.75% (req. 0%).

In a methanol solution at -10 to 0^{o}C , treatment of a 0.06M solution of the monomer with triethylamine over a period of 1.5 hours lead to no colour change indicating no ylid formation. Under the same conditions, treatment with DBU lead to the formation of a green solution within 5 minutes. Dialysis of this solution in methanol after neutralisation gave as products a yellow solution and a yellow solid (23 %). The yellow solution was also cast into a film and subjected to treatment at 300^{o}C / 3x10^{-3}mm Hg to give a product again brown in colour, with an analysis showing considerable nitrogen, indicating possible amine incorporation. C, 55.54 (req. 55.19%); H, 1.63 (req. 1.16%); N, 1.05 (req 0%).

5.3. Attempted Synthesis of Polypartetrafluorophenylenevinylene from a Soluble Polyalcohol

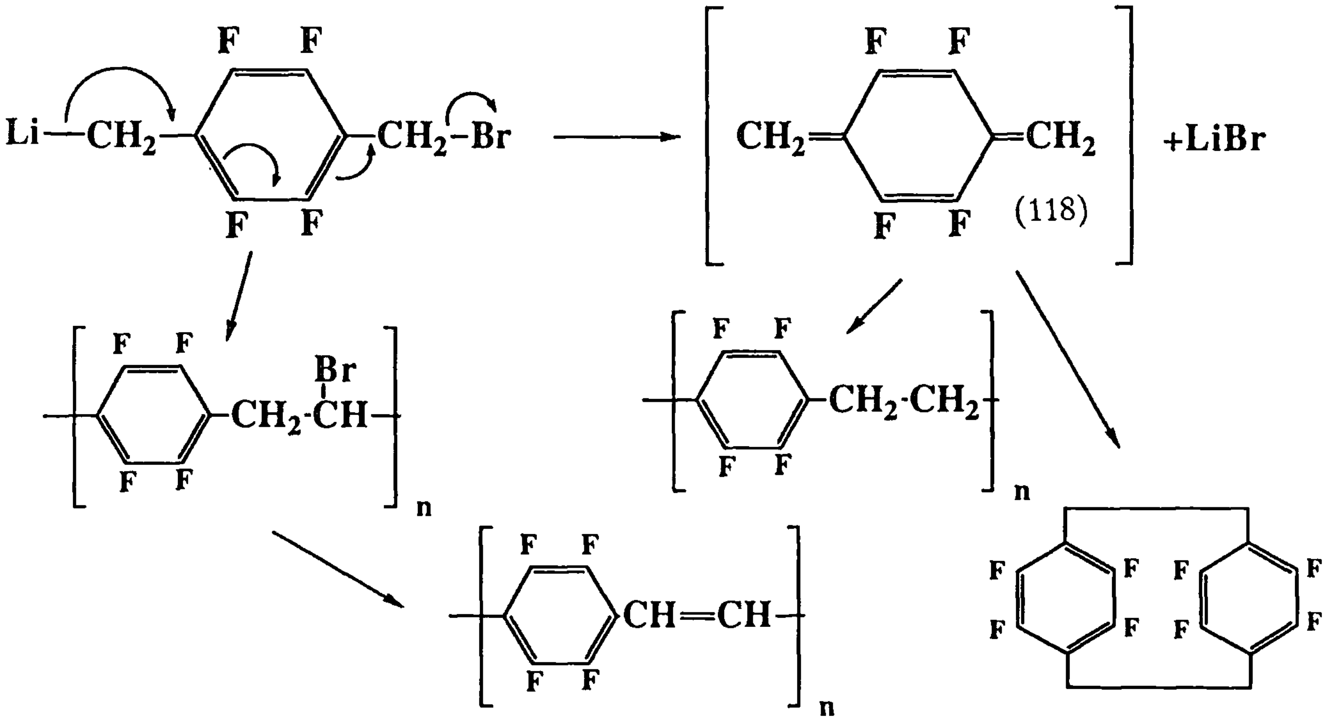
5.3.1. Approach to the Synthesis of the Polyalcohol (115)

Two methods of approach were considered. The first was to use the already prepared α,α'-dibromo-1,4-xylene (103) as a precursor to the dilithium reagent (116) which on reaction with the dialdehyde (117) would lead to the required polymer (115) (Scheme 59).



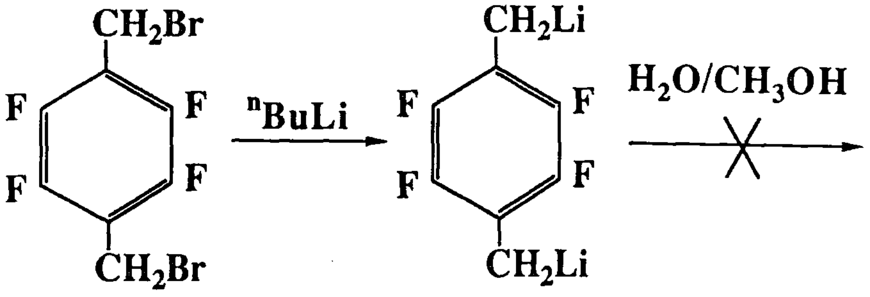
Scheme 59.

However the metallation of (103) was a cause for concern for a number



Scheme 60.

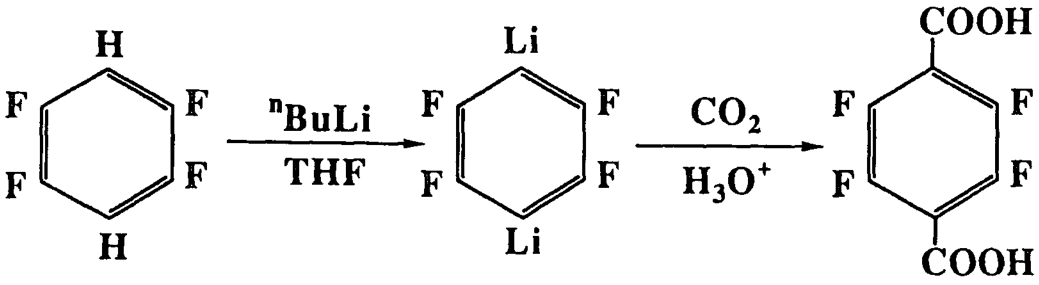
of reasons including the likely generation of the para-xylylene species (118) by the elimination of LiBr . This could then itself undergo polymerisation and cyclisation reactions (Scheme 60). In order to test these ideas, the α,α'-dibromo-1,4-xylene (103) was treated with butyllithium (2 molar equivalents) in THF and then quenched with a methanol/water mixture. No 2,3,5,6-tetrafluoro-p-xylene was isolated indicating that the di-lithioxylene (116) was not formed so a second synthetic scheme was considered.



(103)

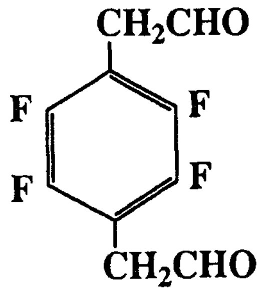
Scheme 61.

Tamborski et al[125] made use of the 1,4-di-lithiated tetrafluorobenzene (119) to generate the tetafluoroterephthalic acid (Scheme 62) from 1,2,4,5-tetrafluorobenzene. Starting with this di-nucleophile, the complementary monomer was the dialdehyde (120).



(119)

Scheme 62.



(120)

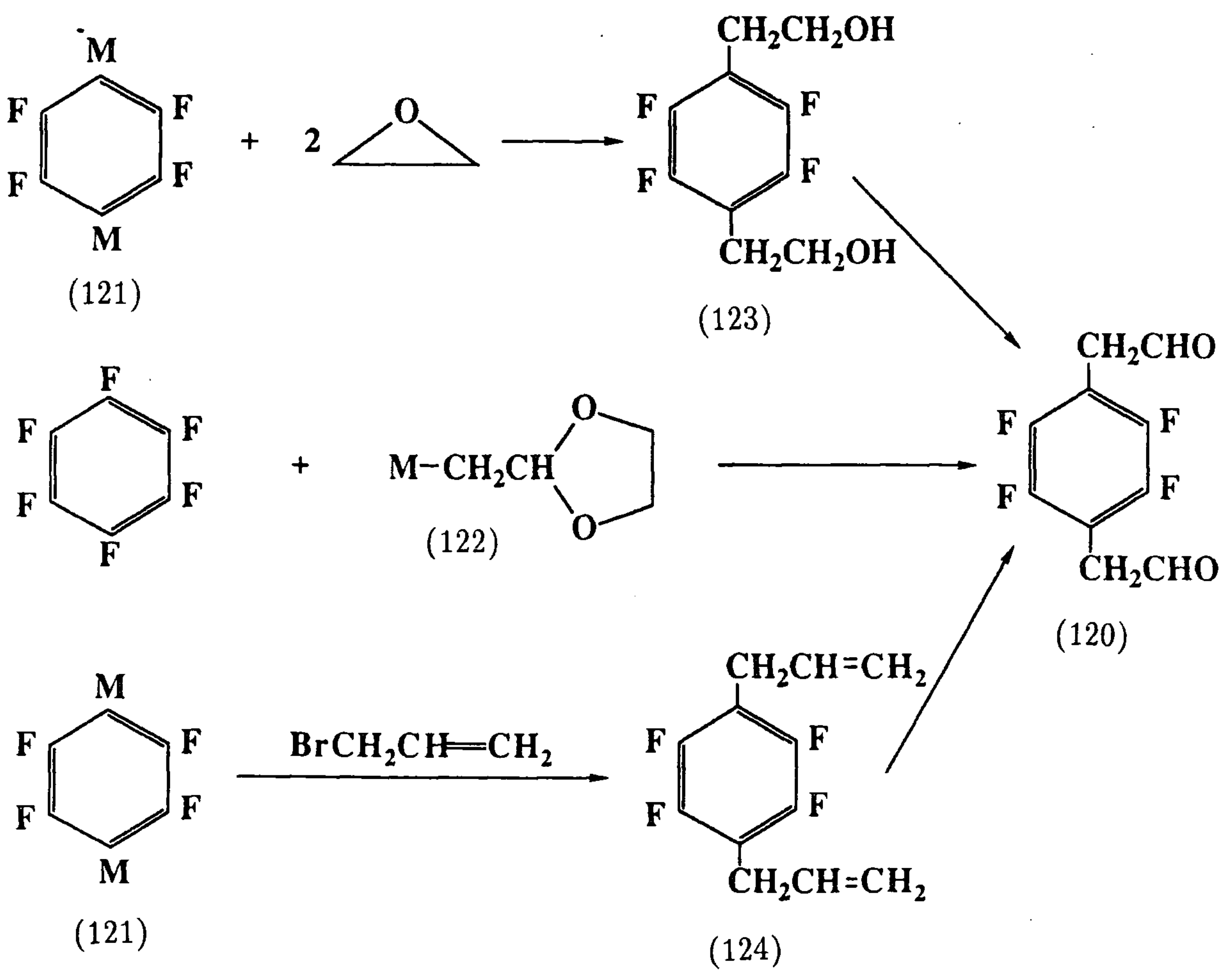
The synthesis of (120) can be approached from a number of precursors.

5.3.2. Synthesis of 2,3,5,6-tetrafluorobenzene-1,4-diethanal (120)

5.3.2.1 Approach to Synthesis

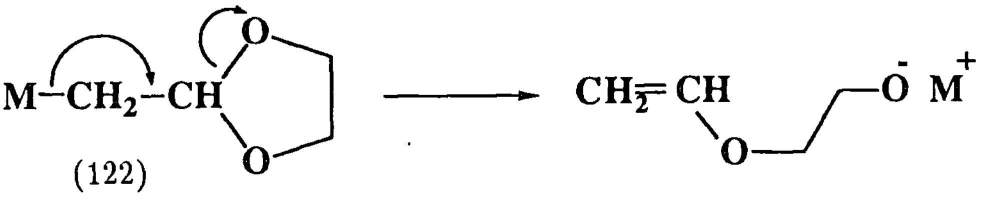
Three routes were considered for the synthesis of (120). The reaction of a bis-organometallic compound of the type (121) (Scheme 63) with ethylene oxide followed by the oxidation of the di-alcohol (123) to (120) could provide a two step route. Although the preparation of the di-alcohol may be relatively high yielding, this route relies on the efficient oxidation of two alcohol groups to their corresponding di-aldehydes. This cannot be expected to go in yields greater than 80% per group, 65% overall[126].

A second route could involve the use of a double nucleophilic substitution reaction onto hexafluorobenzene. The nucleophile that would give the most direct route is an acetal of the type (122). This would give direct access to the target molecule (120) but relies on the preparation of a suitable organometallic reagent (122) -unknown at the present time.



Scheme 63.

[such a derivative would be expected to decompose readily *via* an elimination reaction (Scheme 64)].



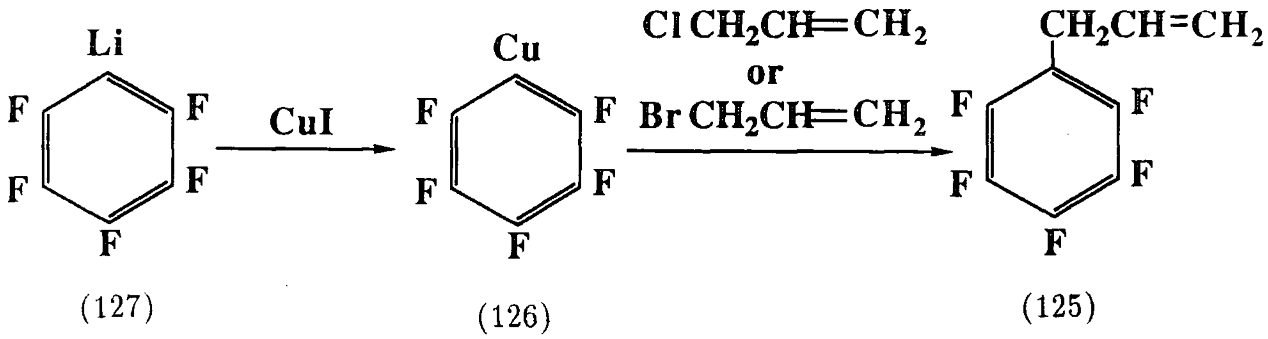
Scheme 64.

The preparation of any di-substituted product by nucleophilic substitution has the inherent problem of purification of the mono- from the di-substituted products.

The third route considered involves the coupling of allyl bromide with the same bis-organometallic compound discussed earlier (121) to prepare the di-allyl compound (124) which should be convertible into (120) by an oxidative cleavage of the double bond. The simplicity of this route made it the most favoured.

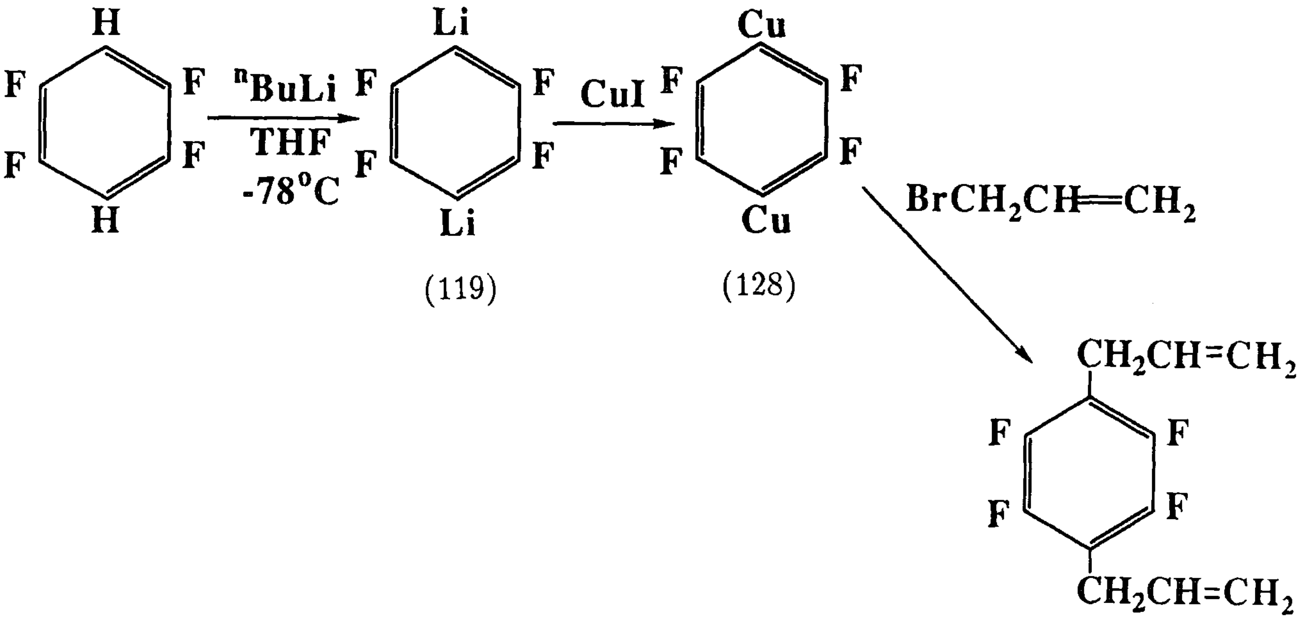
5.3.2.2. Synthesis of 1,4-diallyl-2,3,5,6-tetrafluorobenzene (124)

The type of coupling required to form (124) was used by Jukes et al[127] to form allylpentafluorobenzene (125), by preparing first the organocopper reagent (126) from the organolithium compound (127) and treating this with allyl bromide or allyl chloride to give (125) in yields of 68% and 60% respectively (Scheme 65).



Scheme 65.

For the synthesis of 1,4-di-allyl-2,3,5,6-tetrafluorobenzene, a one pot reaction sequence seemed appropriate. Generation of the di-lithium complex (119) at -78°C according to Tamborski[125] with subsequent addition of anhydrous copper(I) iodide and stirring at -78°C for 4 hours to generate (128) was followed by the addition of an excess of freshly distilled allyl bromide. The solution was stirred for a further 20 hours a room temperature to give the di-allyl product (124) in a 74-80% yield after distillation at 50°C/0.01mm Hg (Scheme 66). If the solution was allowed to warm to room temperature before the addition of the allyl bromide, a black coagulated material appeared



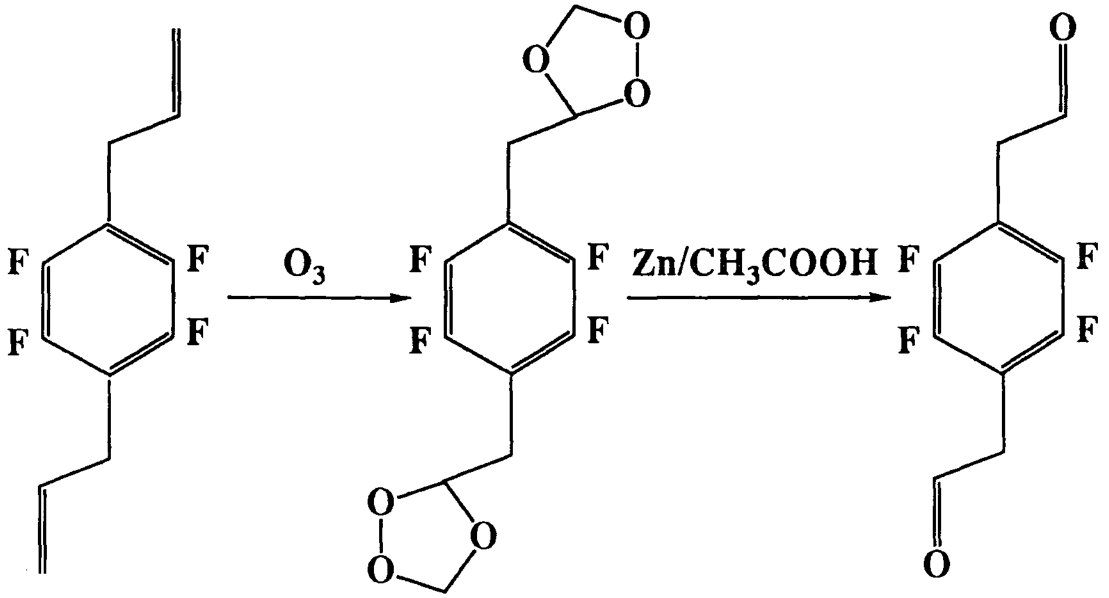
Scheme 66.

to separate leaving a colourless solution, which, when treated with the allyl bromide,gave a considerably lower yield of (124) , 30-50%.

5.3.2.3. Convertion of (124) to 2,3,5,6-tetrafluoro-1,4-benzene-diethanal (120)

A number of methods to oxidatively cleave double bonds exists. The required cleavage to give aldehydes exclusively can be accomplished by the action of osmium tetroxide[13] in 75-80% yields, osmium tetroxide/ sodium periodate in 65-90% yields[128] and ozonolysis essentially quantitatively; the latter procedure was most convenient.

Treatment of (124) with ozone at -20°C in dichloromethane gave the characteristic blue ozonide colour. Quantifying the flow rate of ozone was carried out by the normal procedure of bubbling ozone though a KI solution and titrating an acidified sample against sodium thiosulphate. Attempts to treat (124) with a quantitative amount of ozone so as not to effect over-oxidation of the sample lead to only partial conversion to the di-aldehyde (120). This was due to the incomplete reaction of ozone with the substrate, which was confirmed



(124)

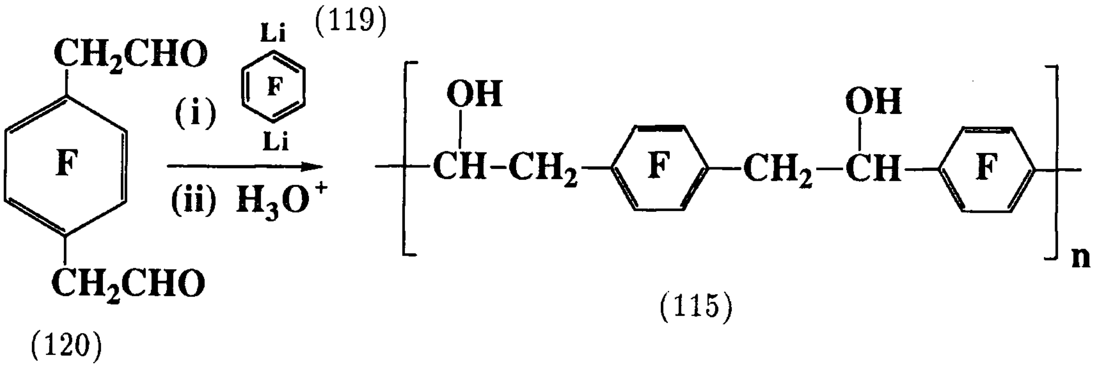
(120)

Scheme 67.

by the attachment of a KI bubbler to the exit pipe. Therefore, most of the ozonolysis reactions of (124) were carried out with an excess of ozone with no obvious over-oxidation being observed. The work-up of the ozonide with zinc dust and acetic acid was initially disappointing with a very complex mixture of products being formed. This was thought to be due to the sodium bicarbonate extraction used to remove the acid. By extracting repeatedly with water instead, only the dialdehyde (120) was isolated in 60-75% yields. This yield is comparable to the expected for this work up[129] (Scheme 67).

5.3.3. Polymerisation reaction of (120) with (119)

The polymerisation reaction of (120) with (119) was carried out by the addition of 2 stoichiometric equivalents of BuLi to 2,3,5,6-tetrafluorobenzene at -78°C, to generate a solution of the di-anion (119), which was treated with a THF solution of (120). Stirring at -78°C for 0.5 h saw the formation of a deep purple slightly gellified solution, which after work up and evaporation gave a yellow powdery solid and



Scheme 68.

a pale yellow film, both of which were soluble in common solvents (methanol, chlorosolvents and ether) and also soluble in water (Scheme 68). The ^{19}F nmr of the crude product was very complex and of little analytical value. The film was subsequently separated from the powder, and subject to heat treatment at $250^0C/3x10^{-3}$mm Hg for 24 hours. Under these conditions, no change in colour was apparent. However, heating the film up to $300^0C/3x10^{-3}$mm Hg lead to a change to an orange/ brown film. It was noted during the low temperature polymerisation reaction that some precipitation occurred. In order to stabilise the poly alkoxide in solution and hence minimise the precipitation, two variations to the above reaction were made. Firstly, the di-potassium salt was generated from the di-lithium salt by addition of potassium t-butoxide after the metallation process. Secondly, the anion stabiliser tetramethylethyldiamine (TMEDA) was added to the reaction mixture. However, neither of these variations of the reaction improved the yield of high molecular weight polymer.

CHAPTER SIX

OLIGOMERIC PARATETRAFLUOROPHENYLENEVINYLENES

6.1. Introduction

Oligomeric para phenylenevinylenes and closely related compounds have been studied[58,59b,129]. Some of these are shown in (Table 6) along with their corresponding conductivities; all exhibit massive increases in conductivities as they are doped. The introduction of vinyl groups into conjugated systems increases the conductivity (compare examples B and E in which the conductivity increases by the power of 10.), not surprisingly, since PA is a better conductor than PPP. Moreover an all *trans* structure also appears better for conduction than systems that contain the *cis* configuration. The fact that high molecular weights are not required for any of these systems to be doped to conducting states supports the case for a charge-transfer system of conduction, It must also be remembered that the conductivities measured are of powder samples which will be undoubtedly doped only on the periphery. The major source of resistance may well be the intergrain boundaries as opposed to any charge transfer resistance. Since normal charge transfer systems of the TTF/TCNQ type require bond alternation (conjugation), planar molecules and efficient close stacking for conduction, then these may also be the requirements for conduction in oligomers. Crystallisation of these materials may afford the close stacking to provide samples with improved charge transfer and higher conductivity.

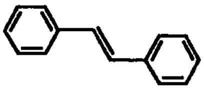
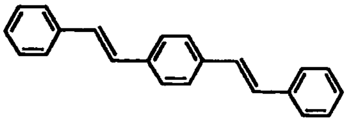
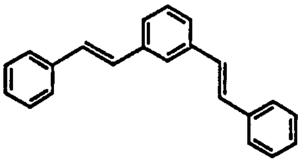
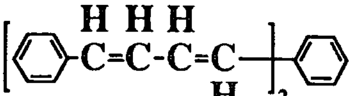
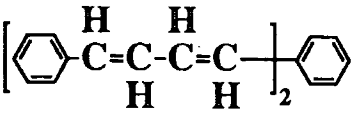
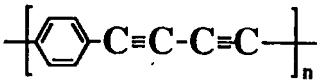
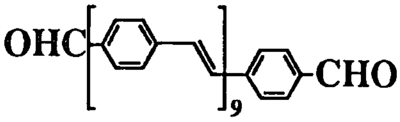
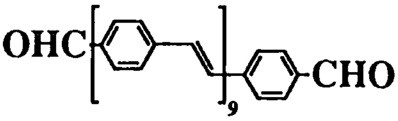
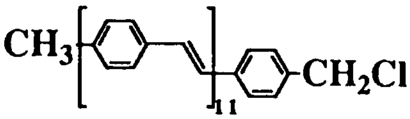
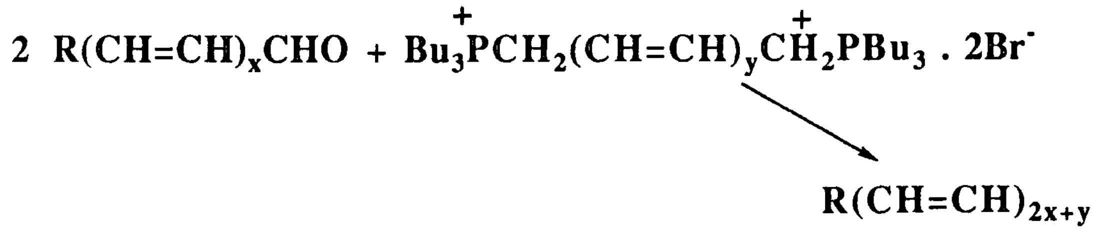
Compound	Synthetic Method		AsF_5 Uptake Mol / Mol. Unit	Conductivity $S\ cm^{-1}$	
				Undoped	Doped
	A		0.195	$<10^{-9}$	$3.2x10^{-6}$ [129]
	B	Grignard	0.36	$<10^{-9}$	$1.1x10^{-4}$ [58]
	C	Wittig	-	$<10^{-12}$	$<10^{-12}$ [58]
 cis trans	D	Wittig	0.23	-	$2.8x10^{-5}$
 trans trans	E	Wittig	0.42 0.37	$<10^{-8}$ $<10^{-8}$	$1.3x10^{-3}$ [58] $5.2x10^{-4}$ [129]
	F	Oxidative Coupling	0	0	$<10^{-12}$
 cis trans	G	Wittig	0.12 [58] Torr AsF_5	-	$1.2x10^{-2}$
 all trans	H	Wittig		-	$3.0x10^{-1}$
 all trans	I	Dehydro-chlorination	0.30	-	$1.2x10^{-1}$

Table 6

6.1.1. Polyenes

Work on regular structured polyenes by Spangler et al[130] has lead to some interesting conclusions. Preparation of these intermediate length polyenes up to n = 10 by Wittig type reactions (Scheme 69) provides samples in the all *trans*-configuration which are very air-sensitive in both the solid and solution state. These can be doped with SbF_5 or iodine to first the polaron then the bipolaron states, as seen by esr spectroscopy, with a corresponding instantaneous change in the ultra-violet spectrum with the removal of the π-π^* transition and the introduction of absorption maxima of lower energy analogous to the formation of mid-gap states in oxidatively doped PA. For the phenyl terminus polyene with n = 10, a bad gap of $E_g \approx 2.3$ eV was found [131]. It has been proposed that 150 - 200 ethylene units would be required to observe PA characteristics but 10-15 double bonds have been found to be equivalent to 100 or more units[131].

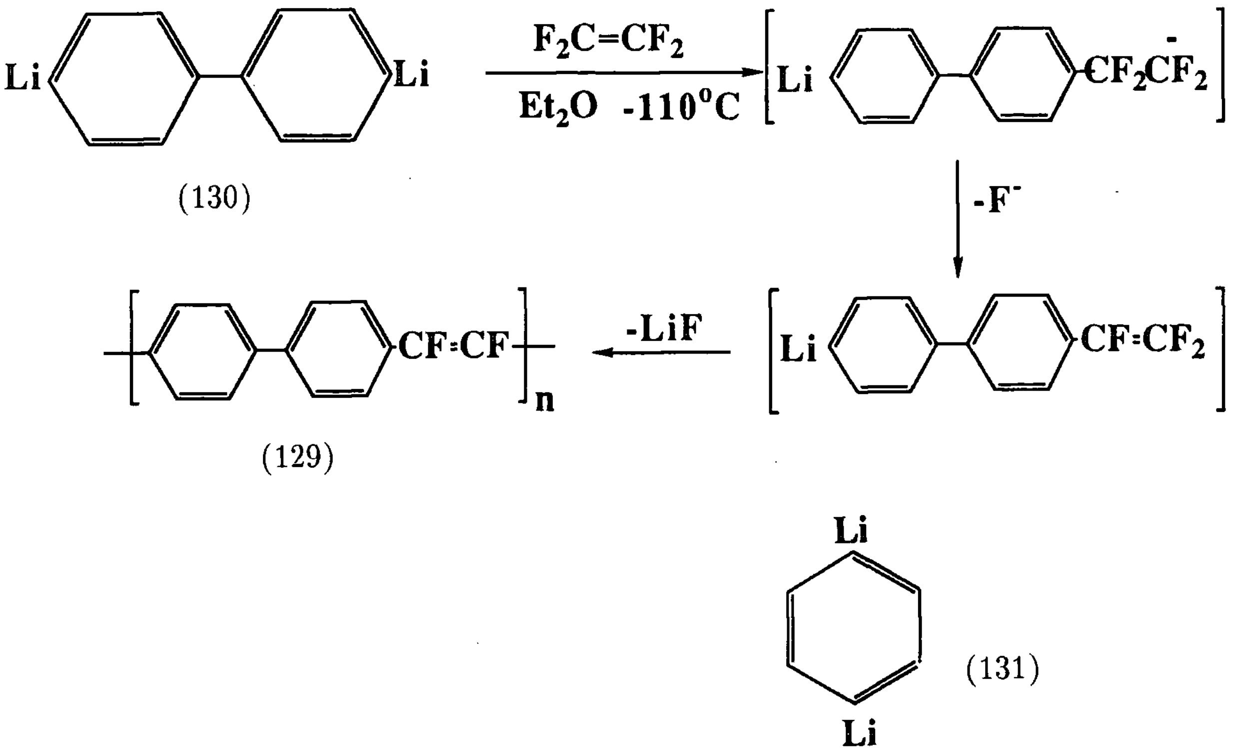


$$2\ R(CH{=}CH)_xCHO + Bu_3\overset{+}{P}CH_2(CH{=}CH)_yCH_2\overset{+}{P}Bu_3\ .\ 2Br^- \longrightarrow R(CH{=}CH)_{2x+y}$$

Scheme 69.

6.1.2. Polyarylenedifluorovinylenes

Utilising a novel polymerisation reaction, poly(biphenylene-difluorovinylene) (129) has been prepared[132] (Scheme 70). Thus di-lithiation of 4,4'-dibromobiphenyl to give (130) and its reaction with tetrafluoroethylene at -110°C in diethyl ether for 3 hours



(130)

(129)

(131)

Scheme 70.

resulted in the formation of a bright yellow solid. After extensive extractions, the micro analysis indicated a chain length of n ≈ 15. The electrical conductivity of a pressed pellet of (129) was $\sigma = 5\mathrm{x}10^{-9}\mathrm{S\ cm}^{-1}$. This increased to $\sigma = 1.7\mathrm{x}10^{-4}\mathrm{S\ cm}^{-1}$ by exposing the powder to 250 Torr of AsF_5 for 1 hour prior to pressing. The reaction of para-dilithiobenzene (131) with tetrafluoroethylene resulted in only a low yield of uncharacterised product due to a low yielding formation of (131)

6.1.3. Role of Oligomers

The generation of highly delocalised charge states in simple oligomers may have application in modelling electroactive materials in extended π systems and also in the design of oligomers or polymers for the increasingly important non-linear optical applications. To this end, the preparation of characterised oligomeric materials does play a role in the field of electroactive materials.

6.2. Synthesis of Paratetrafluorophenylenvinylenes

The aim of this work was to prepare and fully characterise both the *cis* and *trans* paratetrafluorophenylenevinylene oligomers containing up to six or seven aromatic units. The approach was to utilise the property of fluoroaromatic compounds to undergo nucleophilic substitution of fluorine by preparing a species that can contain both a nucleophilic centre and a site for nucleophilic displacement of fluorine. These prerequisites are found in organometallic compounds derived from *cis* and *trans* 1-bromo-2-pentafluorophenylethene (Fig 33).

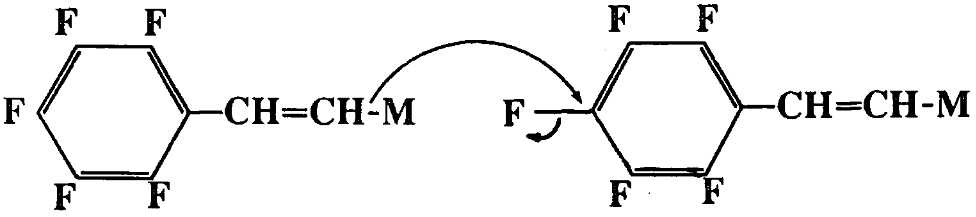
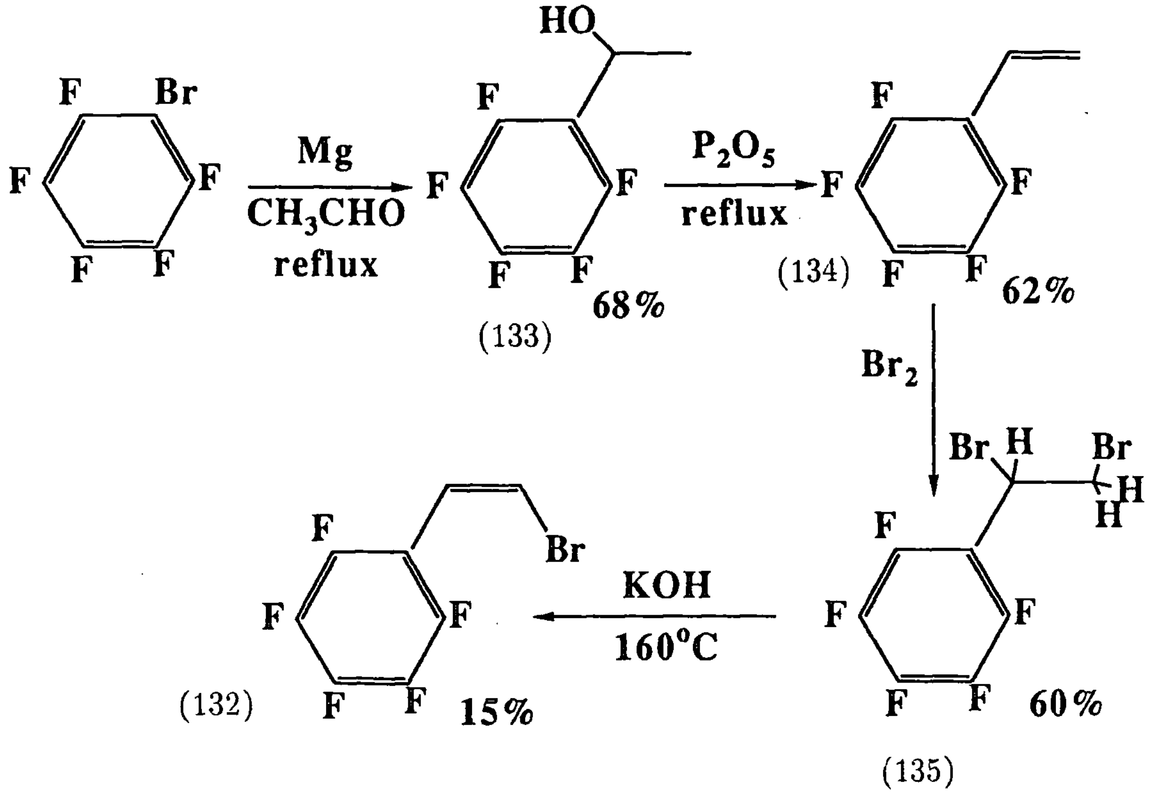


Fig 33.

6.3. Preparation of (Z)-1-bromo-2-pentafluorophenylethene (132)

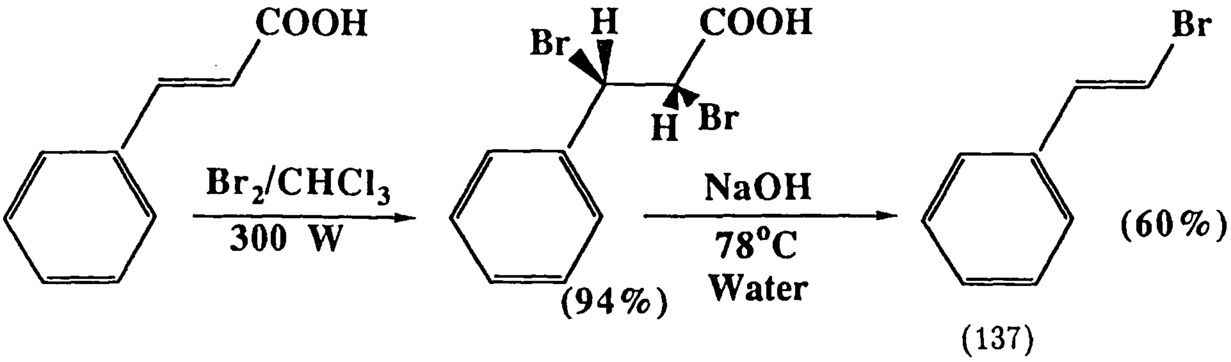
(Z)-1-bromo-2-pentafluorophenylethene (132) was prepared according to literature routes (Scheme 71). Reaction of bromopentafluorobenzene with magnesium in ether under reflux and treatment of the Grignard reagent solution with acetaldehyde at $0^{o}C$ produced 1-(pentafluorophenyl) ethanol (133) (66%, Lit.68%[133]). Dehydration of (133) was achieved by refluxing with P_2O_5 to produce 2,3,4,5,6-pentafluorophenylethene (134) (68%, lit.62%[133]). Treatment of (134) with bromine in ether gave 1,2-dibromo-1-pentafluorophenylethane (135) (Lit. 60%). This dibromo- compound was debrominated with powdered KOH at $160^{o}C$ to give (Z)-1-bromo-2-pentafluorophenylethene (132)[134] purified by fractional distillation.



Scheme 71. *Preparation of (Z)-1-bromo-2-pentafluorophenylethene (132).*

6.4. Preparation of (E)-1-bromo-2-pentafluorophenylethene (136)

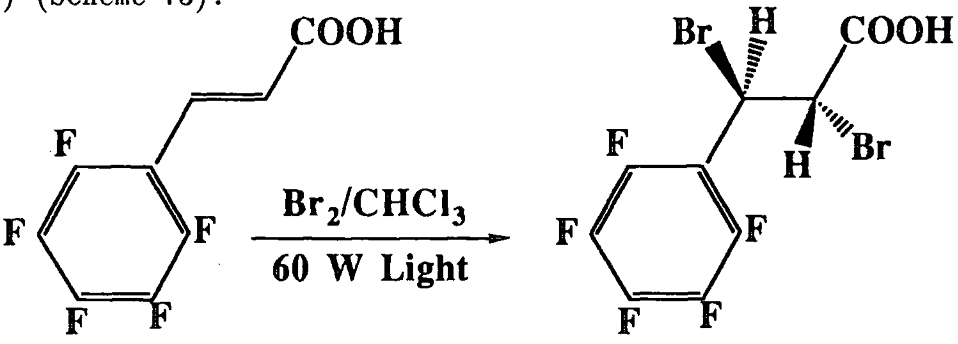
The hydrocarbon (E)-1-bromo-2-phenylethene (137) was prepared by the bromination of cinnamic acid and subsequent base induced elimination of CO_2 and HBr by heating the dibromocinnamic acid in sodium hydroxide to give a 60% yield of (137)[135] (Scheme 72).



Scheme 72.

6.4.1. From 1,2-dibromo-2-pentafluorophenylpropionic acid (138)

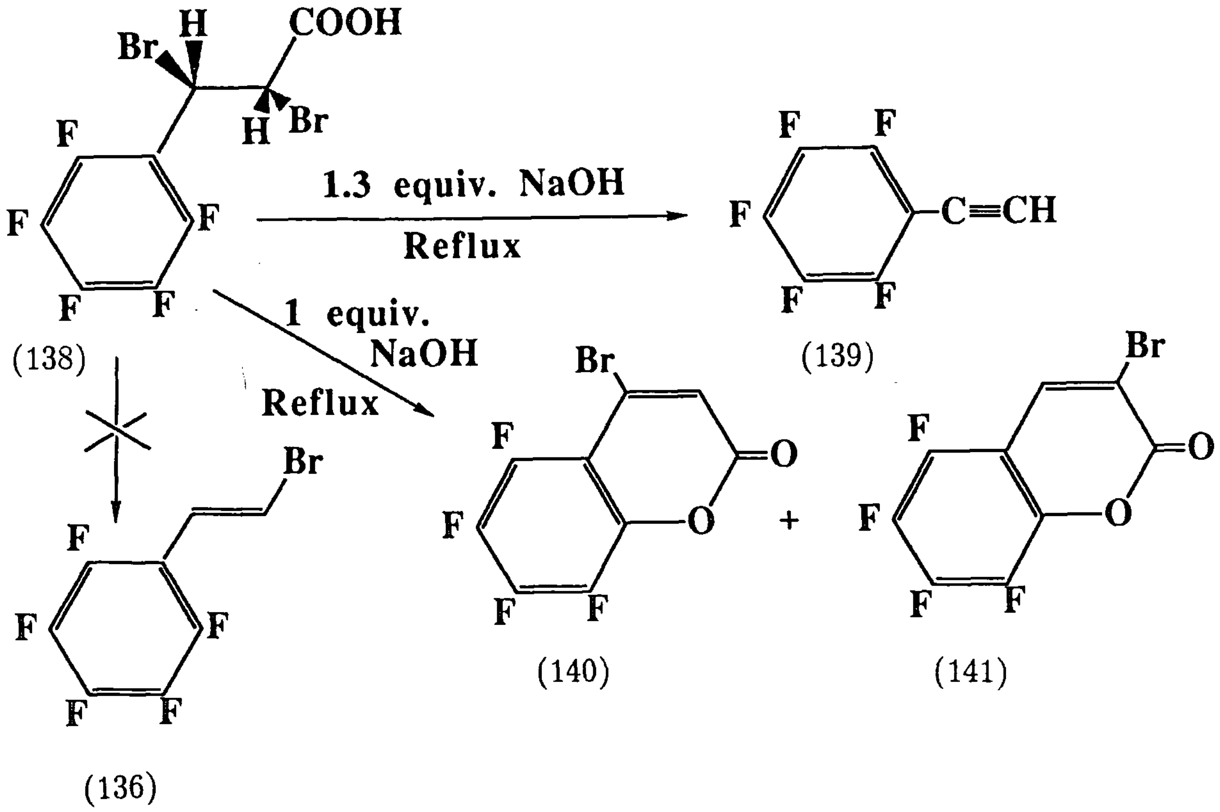
Pentafluorocinnamic acid is an easily available starting material that can be readily brominated by treatment with bromine in chloroform under illumination from a 60W Tungsten lamp to give a quantitative yield of (138) (Scheme 73).



Scheme 73. (138)

The ^{19}F nmr of the resultant material is unusual in that the peaks assigned to the ortho fluorines are broadened over a 350 Hz range at -139.5 and -141.6 ppm.

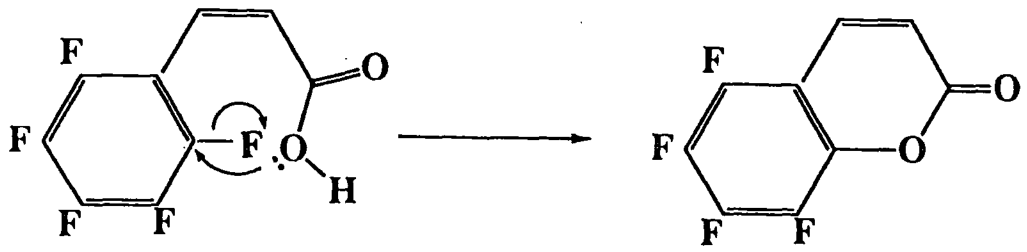
The intended conversion of (138) into the E-bromo styrene (136) was *via* the same base-induced elimination of CO_2 and HBr as that used for the hydrocarbon analogue (Scheme 74). However, the use of excess base (1.3 equivs.) with the fluorinated material to a pH neutral to phenolphthalein (pH 8.2) gave pentafluorophenylacetylene (139) (16%) as the major product and unreacted starting material, as identified by nmr. The yield of (139) may have been considerably higher but for losses which occurred due it's volatility. Reducing the base concentration to an equimolar ratio followed again by heating at 78°C and extraction with dichloromethane under basic conditions gave predominantly unreacted starting materials and a mixture of two cyclised products by t.l.c.. The infrared spectrum of the mixture indicated the presence of carbonyl groups (1735 & 1770 cm^{-1}) with an olefinic stretch at 1655 cm^{-1} and the mass spectrum (EI) showed a molecular ion peak at M^+= 296 and 298 which



Scheme 74.

could be due to isomeric compounds (140) and (141). Due to the difficulty of purification, the mixture of products was not separated. Consequently this method of decarboxylation was not a route to (136) so alternatives were tried.

A related cyclisation was observed by Heaney[136] by heating *cis*-cinnamic acid in aqueous solution (Scheme 75).



Scheme 75.

6.4.1.1. Hunsdieker Reaction on (138) and Debromination

The reaction of the silver salt of a carboxylic acid with bromine is called a Hunsdieker reaction[137] (Scheme 76). This reaction has wide scope for the decarboxylation of straight and branched chained alkyl carboxylic acids to give primary, secondary and tertiary bromides. If R contains unsaturation the reaction rarely gives good

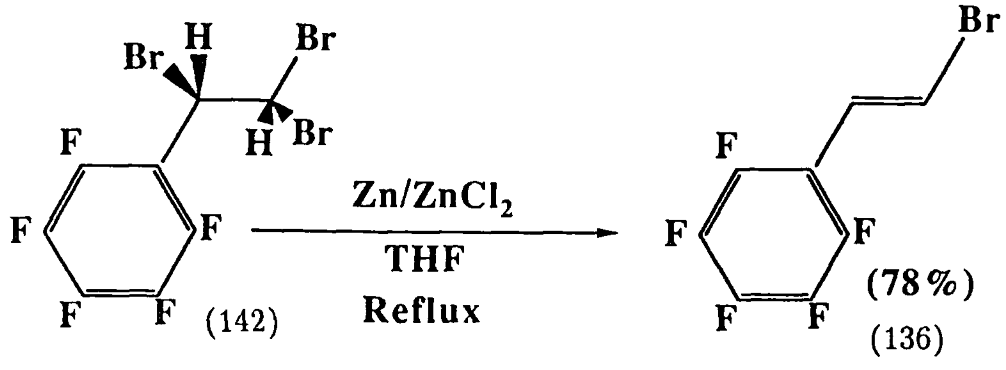
$$RCOOAg + Br_2 \longrightarrow RBr + CO_2 + AgBr$$

Scheme 76. *The Hunsdieker reaction.*

results so (E)-pentafluorocinnamic acid is not a suitable starting material for the target (E)-bromo styrene (136).

However, 1,2-dibromo-2-pentafluorophenylpropionic acid (138) was treated with 1 equivalent of sodium hydroxide and 1.1 equivalent of silver nitrate. The resultant white precipitate was dried for 2 days at 25°C/3x10^{-3}mm Hg to give the silver salt (89%), treatment of which in carbon tetrachloride with a slight excess of bromine gave the tribromide (142) (54%).

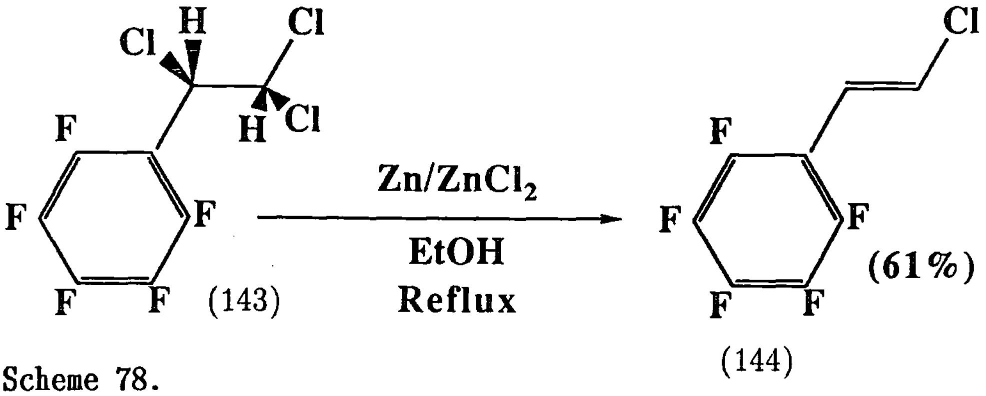
Treatment of (142) with zinc in refluxing ethanol gave approximately 50% of the styrene (136) along with unreacted tribromide (142) (Scheme 77). Changing the solvent to THF afforded a better



Scheme 77.

conversion (78%) over a reaction time of 6 hours, and the product only required straightforward distillation from involatile residues to provide the pure compound. The ^{1}H nmr spectrum for the (E)-bromostyrene (136) showed the two *trans* protons at 7.25 and 7.08 ppm coupled by 14.5Hz which is of the correct order of magnitude for *trans* proton coupling (commonly 12-18 Hz).

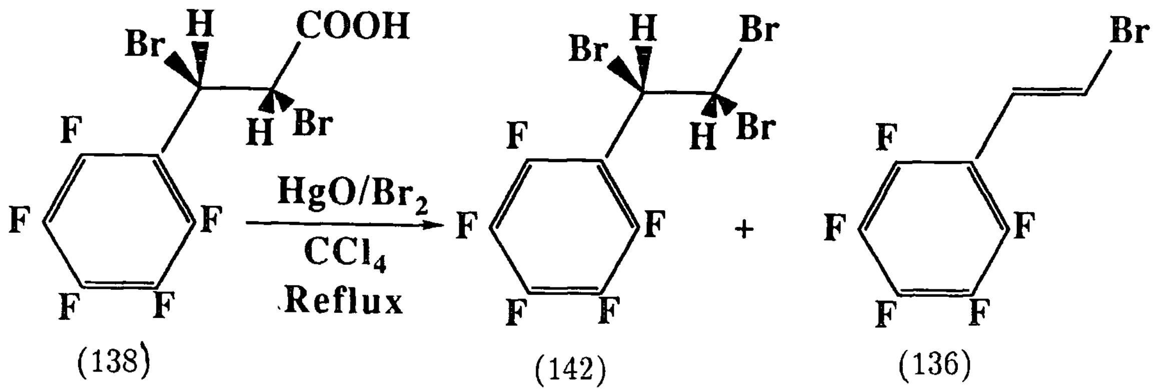
Coe et al[138] de-chlorinated 1,1,2-trichloro-2-pentafluorophenylethane (143) using zinc in refluxing ethanol to give the chlorostyrene (144) stereoselectively in a 61% yield (Scheme 78).



Scheme 78.

6.4.1.2. The Cristol Modification of the Hunsdieker reaction

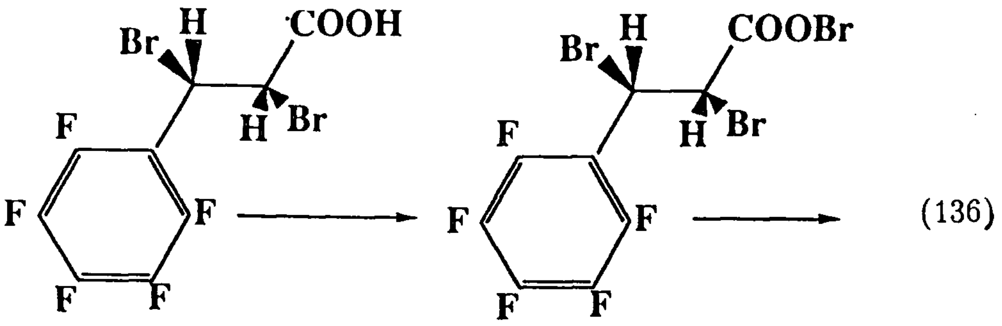
One of the major drawbacks of the Hunsdieker reaction is that the silver salt needs to be very pure and dry to achieve good yields. A more convenient way to perform this reaction is to eliminate the isolation of the intermediate silver salt. Thus, decarboxylation may be accomplished *via* a number of alternative routes including treatment of thallium (I) carboxylates with bromine[139], treatment of the carboxylic acid with lead tetraacetate and lithium bromide[140] and by the use of the acid in conjuction with bromine and mercuric oxide[141]. In the latter case, the Cristol modification of the Hunsdieker reaction, treatment of a slurry of excess red mercuric oxide and aliphatic carboxylic acid in refluxing carbon tetrachloride with bromine in the dark gives the alkyl bromide in 70-90% yields. The reaction is not applicable to benzoic acid, where only poor yields are obtained[141]. Silver oxide may be used instead of the mercuric oxide with light being excluded to prevent polybromination of the sample. Thus, the dibromocinnamic acid (138) in carbon tetrachloride was treated with excess mercuric oxide and bromine and heated under reflux for 4 hours



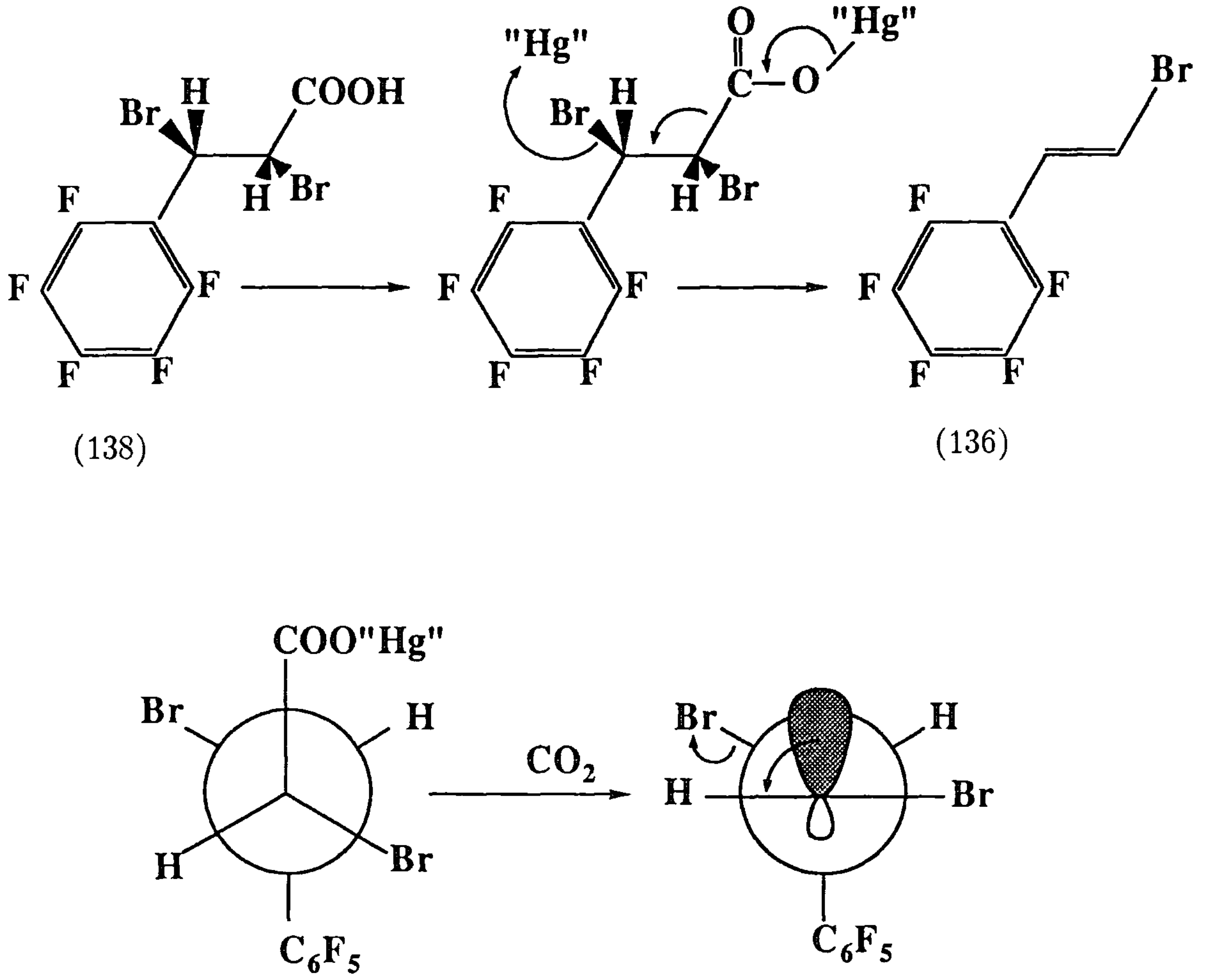
Scheme 79.

in the dark. Two products were obtained which were isolated by chromatography, and found to be the (E)-bromo-styrene (136) (59%) and the expected tribromide (142) (35%) (Scheme 79).

The formation of (136) could be *via* one of two mechanisms. A substitution-elimination reaction by first substitution of bromine before de-bromination, or *via* a loss of CO_2 and HBr. The reaction was repeated without the addition of bromine to gain insight into the mechanism. If the former process was operating then the reaction without the addition of bromine would not give any (E)-bromo-styrene (136) (Schemes 80 and 81).



Scheme 80. *Generation of Hunsdieker intermediate may be followed by elimination of Br_2 and CO_2 to give (136)*



Scheme 81. *Without the addition of bromine, elimination of HBr & CO_2 may be facilitated by the action of a mercury species*

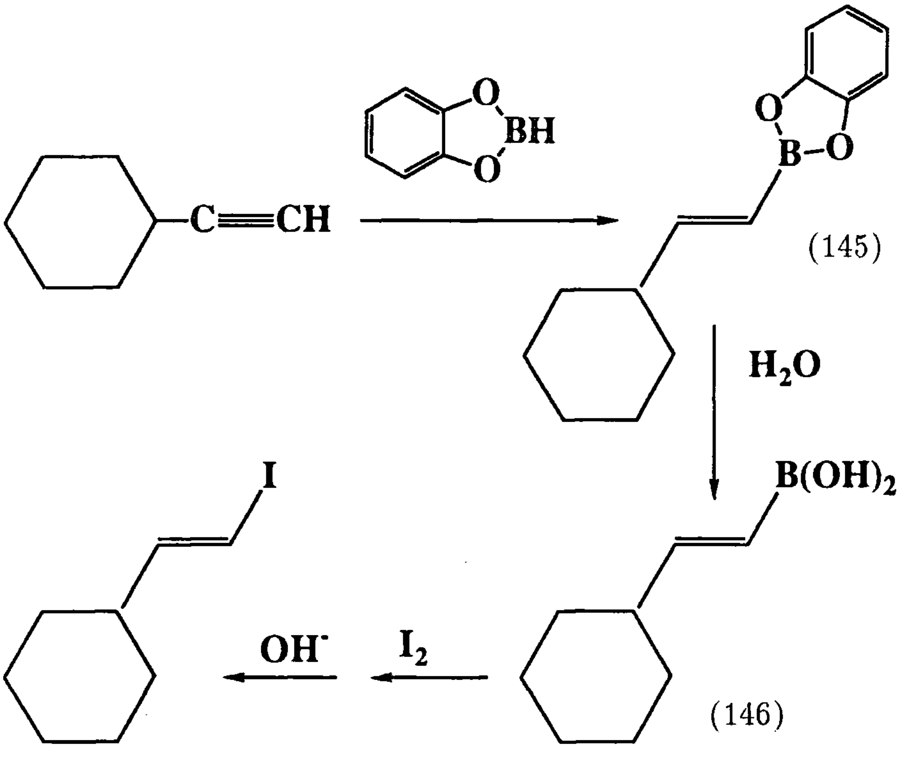
Thus, when the dibromopropionic acid (138) was treated with excess mercuric oxide in carbon tetrachloride under identical conditions to those used previously, yielded a white solid, [unreacted (138)] and a colourless oil identified by nmr as (136) (the (E)-bromo-styrene) , were formed as a mixture (approximately 1:1), indicating that bromine is not a prerequisite for the product (136) to be formed. This reaction was, however very dependant on concentrations and reaction time, so proved less attractive for the purposes of scale up than the original Cristol modification which gave the required (E)-bromo-styrene (136) and the tribromide (142) which could be easily converted to (136)

6.4.2. *Via* Hydroboration:- Introduction

Stereochemical control is one of the major advantages of any synthetic approach involving hydroboration reactions. Their discovery in the late 1950's and subsequent development by Brown[142,143] has lead to the development of many hydroborating reagents useful for addition to double and triple bonds[144].

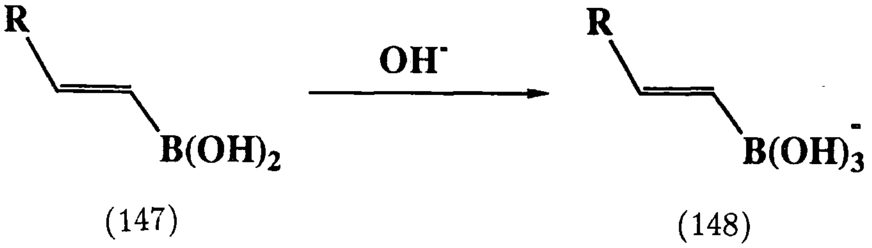
The *cis*-hydroboration of a terminal triple bond stopping at the alkene (ie. one addition only) is most easily achieved using catechol-borane.

For example, the cyclohexylboronic acid (146) [obtained by hydrolysis of the boric acid (145)] can be converted into the *trans*-iodo alkene by simply adding 3 equivalents of sodium hydroxide to a solution in ether at 0^{0}C followed by a slight stoichiometric excess of iodine[145] (Scheme 82). The product was isolated in a quantitative yield, with the iodine colour disappearing almost instantaneously. Brown concluded that



Scheme 82.

since no reaction is observed between the iodine and the free acid (147), it must be the anion produced after the addition of the base, (148), that reacts with the iodine[145] (Scheme 83).



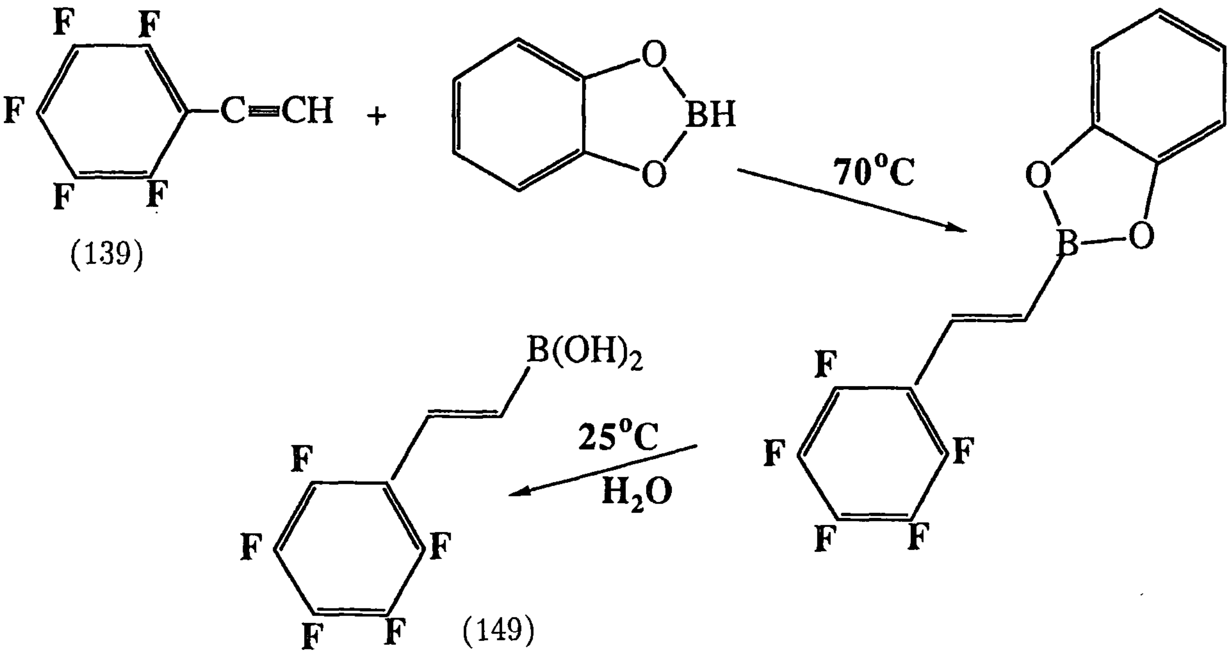
Scheme 83.

Interestingly, similar treatment of (146) with bromine leads to a low yielding mixture of *cis* and *trans* alkenes[146]. No analogous synthesis to the *trans*-bromo alkene has been reported (but see section 6.4.2.3)

However, treatment of the boronic ester (145) with bromine followed by base yields the *cis* vinyl bromide with inversion of the configuration[146]

6.4.2.1. Preparation of (E)-Pentafluorophenylethenylboronic acid (149)

The procedure used successfully to prepare *trans*-cyclo-hexylethenylboronic acid[144] and other alkyl *trans*-alkenes[145], in 90-97% yields was applied to the required precursor 2,3,4,5,6-pentafluorophenylacetylene (139). Freshly distilled catecholborane was added to (139) and the clear neat mixture was heated at 70°C for 3 hours. After cooling the reaction products to room temperature any volatile materials remaining were evaporated under vacuum. This removed any unreacted catacholborane which would otherwise have contaminated the product with boric acid after the hydrolytic work up. The product residues were then hydrolysed with water at room temperature and filtered to isolate (149) (60%) as a white crystalline product (Scheme 84).



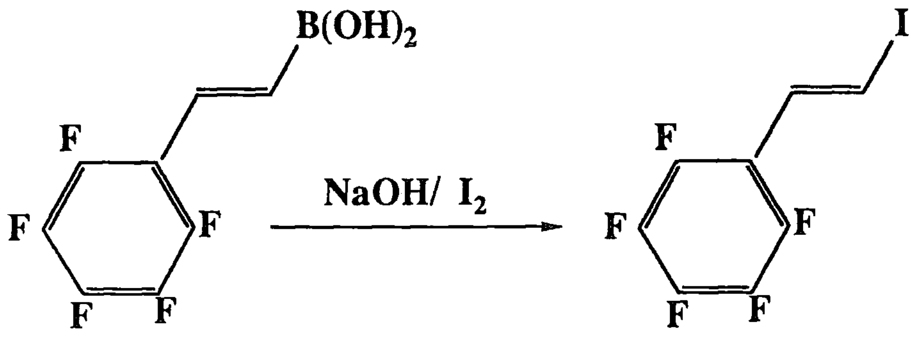
Scheme 84.

The ^{1}H nmr spectrum of (149) showed the two protons at 7.19 and 6.45ppm with a *trans* coupling of 19.0 Hz

6.4.2.2.(E)-1-Iodo-2-pentafluorophenylethene (150)

Following the procedure used previously[145], addition of base to pentafluorophenylethenylboronic acid (149) in ether solution generated a grey precipitate. After treatment with iodine, the colour persisted for half an hour before disappearing to give a negligable (<5%) yield of the styrene (150).

This poor yield lead to a modification of the route, by simply treating the boronic acid (149) with three equivalents of base prior to the addition of any organic solvent. A pale yellow aqueous solution was produced, to which dichloromethane was added. Treatment of this with iodine in dichloromethane over 1 hour lead to an 88% yield of (150) after distillation (Scheme 85).



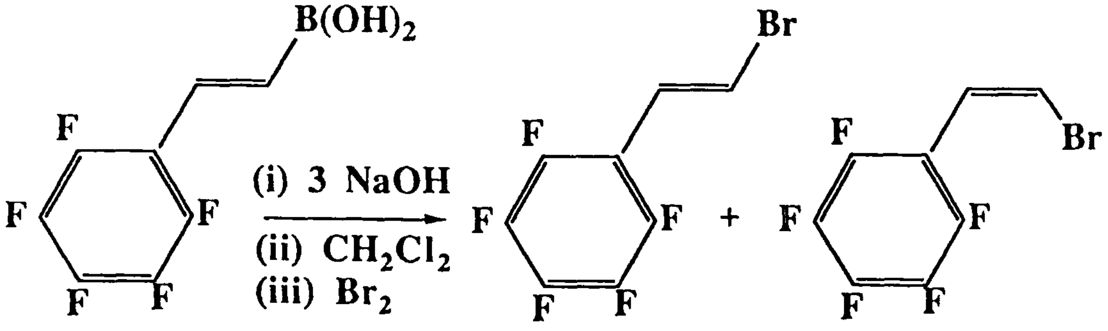
(149) (150)

Scheme 85.

At first there was some concern over the ^{1}H nmr spectrum observed, which showed simply one singlet at 7.41 ppm. Under the limitations of the hardware with a resolution limit of approximately 0.5Hz, no coupling could be seen. Since derivatives (Section 6.7.2.) indicated a *trans* configuration and the infra red showed weak peaks at 1650 and 1590 cm^{-1} for *trans* bonding then it must be assumed that the iodine and the pentafluorophenyl ring are acting to make the two protons accidentally coincidental, so as equivalents, they do not couple.

6.4.2.3.(E)-1-bromo-2-pentafluorophenylethene (136)

The modified route to prepare these (E)-stereochemical type of compound was applied to the formation of the *trans*-bromo derivative (136). Using the same procedure described earlier, (136) was prepared in an 66% yield (Scheme 86).



(149) (136) (132)

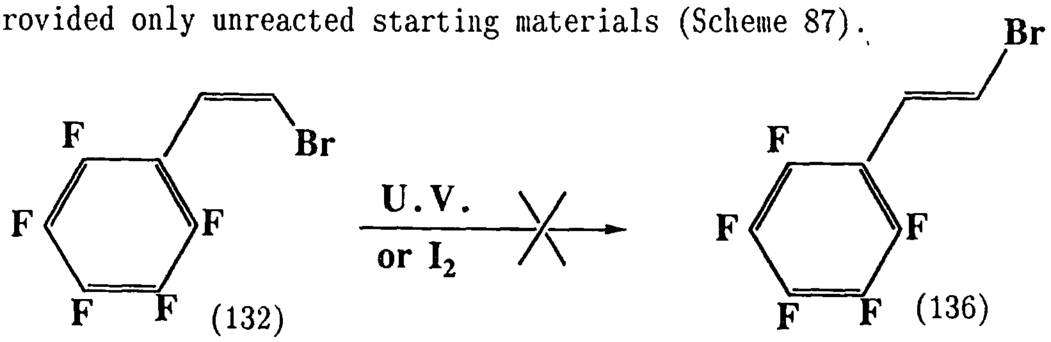
Scheme 86.

The *trans* protons are observed in the ^{1}H nmr spectrum at 7.25 and 7.08 ppm coupled by 14.5Hz. The stereoselectivity of the reaction was evaluated by capillary column G.L.C. and showed a ratio of *trans* 99.4% and *cis* 0.6% which is comparable to that seen in analogous preparations[143].

6.5. Reactions of (Z)-1-bromo-2-pentafluorophenylethene (132)

6.5.1. Attempted *Cis* / *Trans* Isomerisation

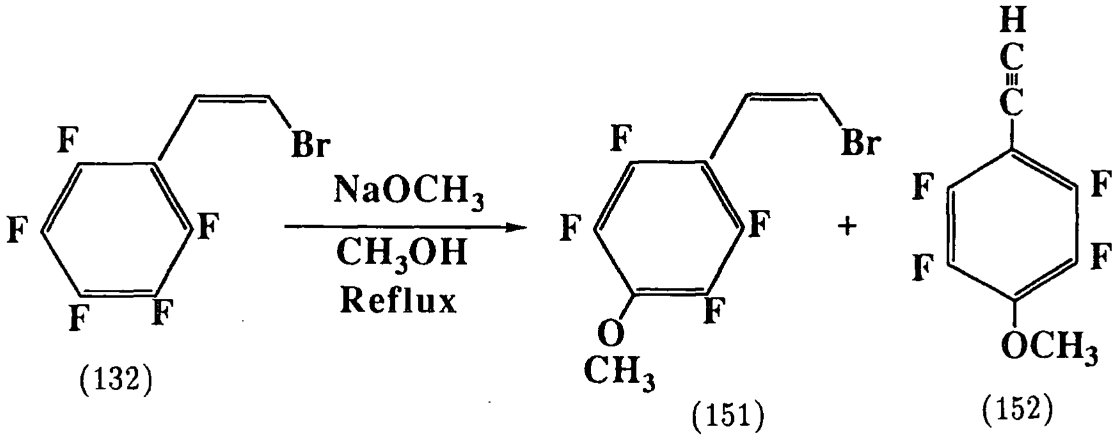
Since the preparation of the (Z)-bromo styrene (132) is considerably easier than the corresponding E-bromo styrene (136), a simple interconversion was considered as an easy route to it. Photochemical isomerisation of the Z-isomer using an medium pressure mercury arc UV source (302, 303, 366, 436 nm maxima) gave only unconverted Z-isomer and polymeric material. Chemical isomerisation involving the addition/ elimination of iodine in refluxing THF again provided only unreacted starting materials (Scheme 87).



Scheme 87.

6.5.2. Nucleophilic Substitution Reactions

The intended new route to poly phenylenevinylene oligomers required nucleophilic substitution of the styrenes (132) and (136) at the para-position. As a model for these reactions, the (Z)-isomer (132) was treated with a variety of nucleophiles. Phenylmagnesium bromide, ammonia and lithium 1-octanethialate all gave little or no substitution products. However with sodium methoxide in methanol under reflux, exclusive para-substitution was observed, by close analogy with the observations of Burdon and Westwood[147] who studied substitution on pentafluorophenylethene. Apart from the para- methoxy substituted product (151) (74%) and unreacted starting material (132) (6%) there

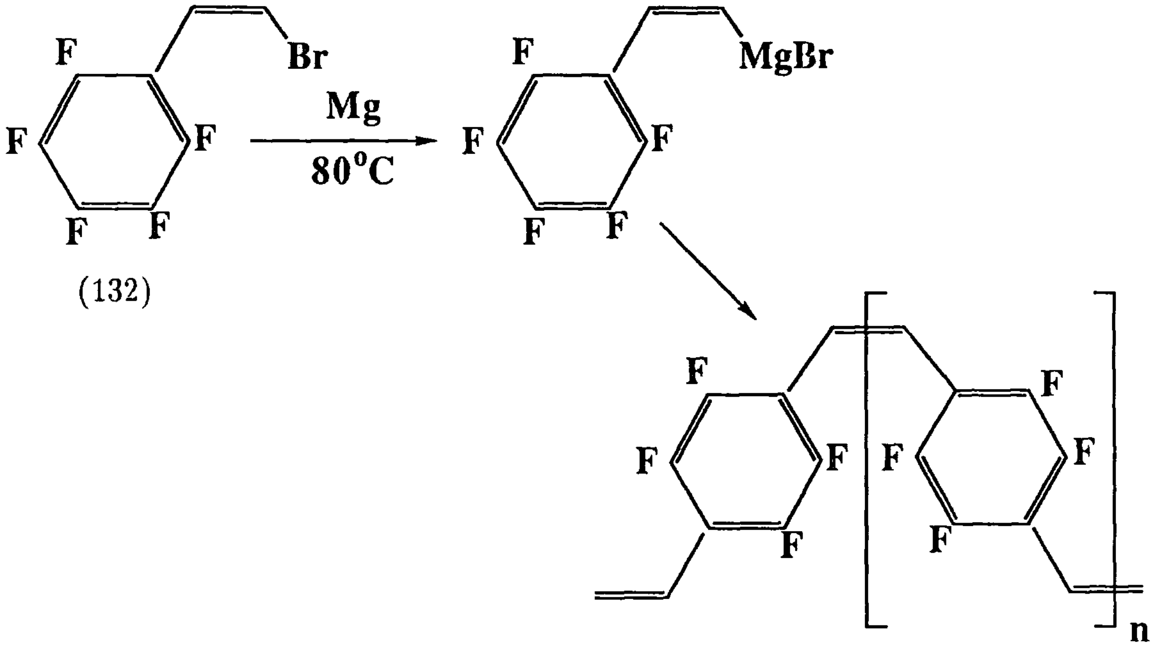


Scheme 88. *Nucleophilic substitution or (132).*

was also formed 2,3,5,6-tetrafluoro-4-methoxyphenylethyne (152) (20%), possibly the product of base induced elimination of HBr from (151) (Scheme 88).

6.5.3. Reaction of (132) with Magnesium

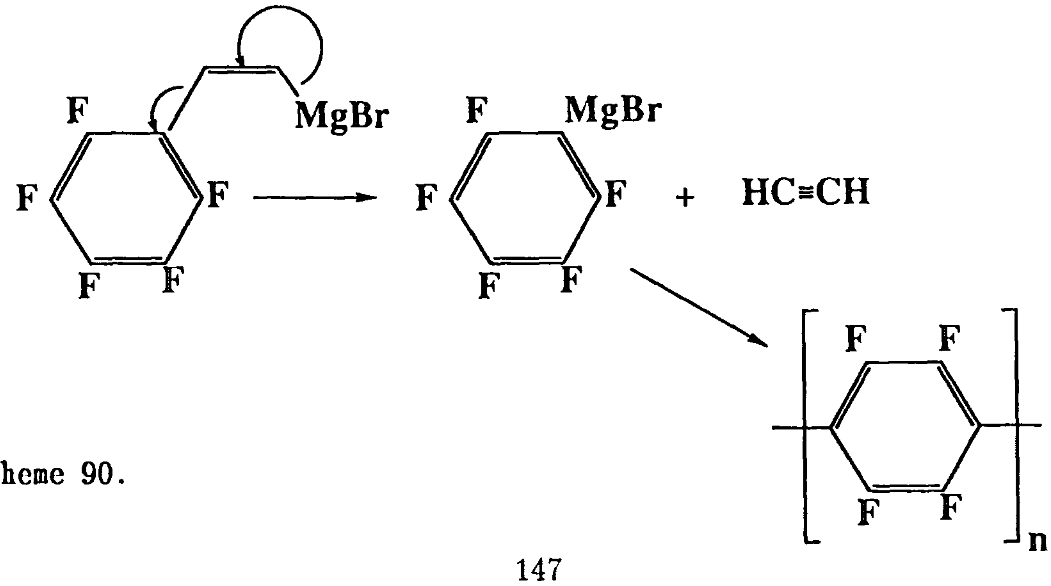
Following the normal procedure for the preparation of Grignard reagents, magnesium in THF was activated with ethylene dibromide at reflux temperature with the subsequent addition of (132). Reflux was maintained over a period of 60 hours and resulted in the formation of a pale brown precipitate which was insoluble in all common solvents and had a melting point in excess of 380°C; it was presumed that this reaction had proceeded according to Scheme 89. However, from direct observation it was clear that the product was contaminated with



(132)

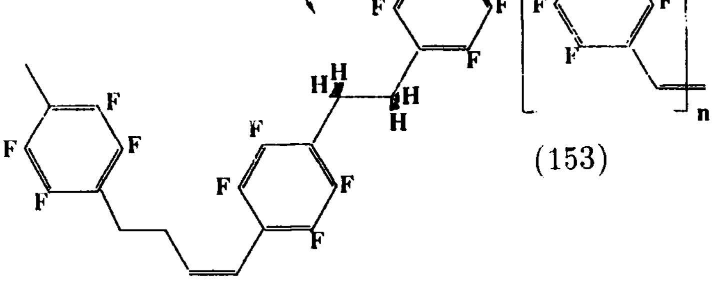
Scheme 89. *Proposed polymer formation via Grignard reaction.*

magnesium that had not been removed by the acid work-up. It was also clear from the pale yellow colour that the material was not a highly conjugated polymer (but see section 6.9.). It was considered possible that the elevated temperature may have lead to the elimination of ethyne and subsequent polymerisation of the accompanying pentafluorophenyl magnesium bromide (Scheme 90). A comparison of the IR of this product was made with that of the material derived from an authentic sample of pentafluorophenyl magnesium bromide in THF which had been allowed to polymerise. Due to the broadness of the absorptions, no conclusion as to the similarity of the materials could be made. The formation of tetrafluorobenzyne from pentafluorophenyl magnesium bromide was also



Scheme 90.

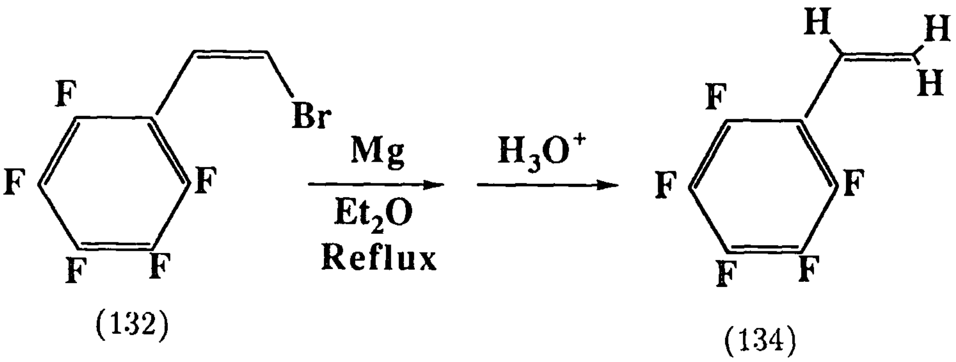
possible which would have lead to an alternative polymer. The Grignard reaction was repeated under milder conditions after activation of the magnesium with ethylene dibromide in THF at reflux; the mixture was cooled to 3^{0}C before the addition of (132) and then stirred for 15 minutes. The majority of the product was found to be unreacted (132). When the reaction was carried out at 20^{0}C, a red colouration was observed indicating the formation of an organometallic complex which disappeared over a period of 40 hours. The product from this reaction was a pale yellow solid which was soluble in many solvents. This was not what was expected for a PPV-type polymer which would be very rigid due to its structure and hence very insoluble. The ^{1}H nmr showed very broad peaks, indicative of a polymeric material, at 6.83, 3.67 and 1.80 ppm. The ^{19}F nmr also showed broad peaks, at -141, -156 and -162 ppm in a ratio of 8:1:2. The structure of these peaks and the solubility of the material indicate possible incorporation of aliphatic CH_2 groups from the ethylene dibromide activating agent into the polymeric material (153) (Scheme 91). The structure of (153) would account for the three proton and three fluorine regions observed. It would also give the



(153)

Scheme 91. *Proposed reaction to form the soluble polymeric material* necessary rotational mobility for the polymer to be soluble. Gell permeation chromatography gave a molecular weight of 6500 polystyrene equivalents.

Although it appeared that a good conjugated polymer was not being formed, it was of interest to discover whether the Grignard reagent was actually forming initially. The failure to react in the manner required may have been due either to the unreactivity of the Grignard towards nucleophilic displacement of fluorine on the aromatic ring or the Grignard reagent not forming at all. Therefore, (132) was added to activated magnesium in diethyl ether and heated under reflux for a 5 minutes and subsequently quenched with dilute sulphuric acid. This gave unreacted (132) (57%) and pentafluorophenylethene (134) (9%) (Scheme 92). The remaining material was soluble polymeric material.



Scheme 92.

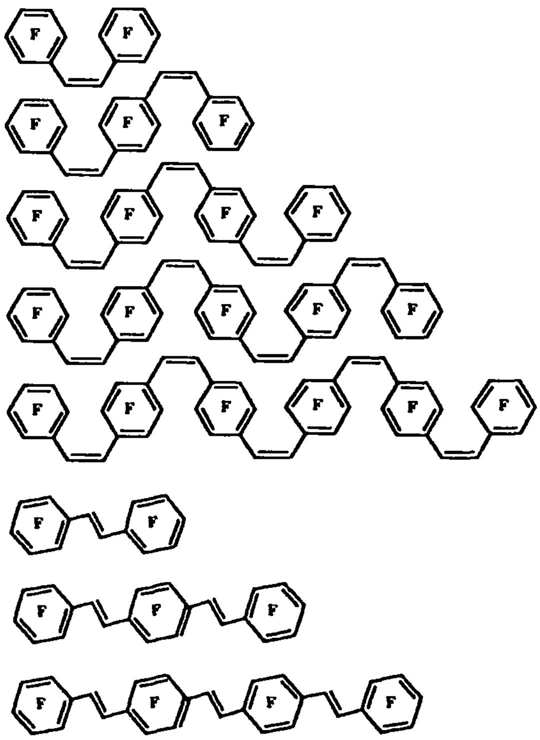
On the basis of these investigations, it was clear that the target F-PPV was not going to be prepared *via* the Grignard route.

6.5.4. Preparation of Oligomeric F-PPV's *via* the Organolithium derivative

Organolithium reagents are more reactive than related Grignard reagents so that following the conversion of (132) to the lithium derivative, subsequent nucleophilic displacement reactions should occur under milder conditions than those using magnesium derivatives.

For the formation of symmetrical oligomeric species, hexafluorobenzene was added to the system to act *via* fluorine substitution as a terminal group.

Note to reader: Due to the complexity of the nomenclature of the oligomeric phenylene vinylenes, the following naming system has been adopted; on the basis of the number of aromatic rings contained in the oligomer and the stereochemistry of them, they will be referred to as shown in Fig 34.



(Z)-Ar2 (156)
(Z)-Ar3 (157)
(Z)-Ar4 (158)
(Z)-Ar5 (159)
(Z)-Ar6 (160)
(E)-Ar2 (163)
(E)-Ar3 (166)
(E)-Ar4 (168)

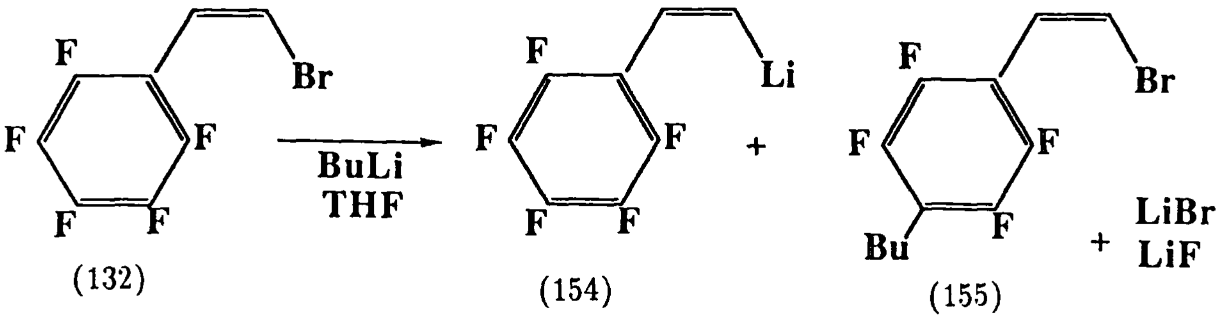
Fig 34.

6.5.4.1 Attempted Lithiation of (132) using lithium metal

Addition of the (Z)-bromo styrene (132) to an excess of lithium in THF at -20°C followed by 160 hours at 20°C gave exclusively unreacted (132); no high molecular weight materials were found. The metallation was also attempted using a lithium/mercury amalgam and with lithium activated with iodine at various temperatures up to reflux in diethyl ether and THF. High molecular weight materials were not formed under any of these conditions.

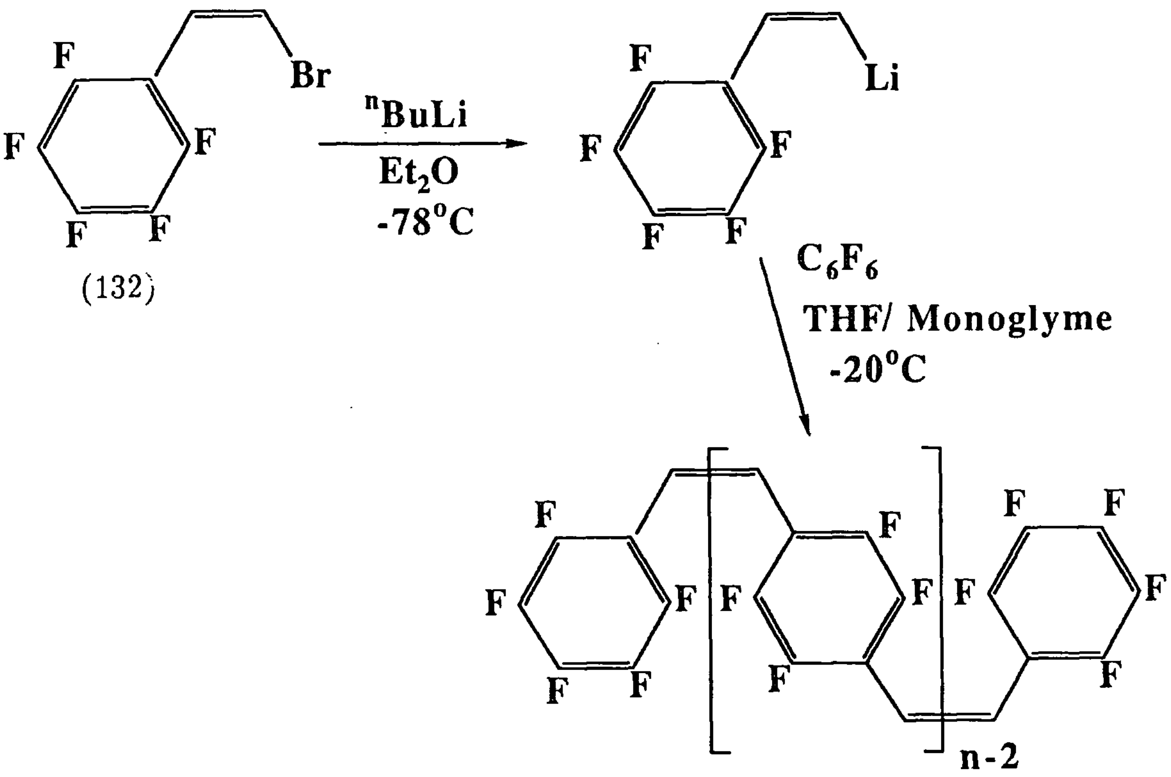
6.5.4.2. Lithiation of (132) using Butyllithium : Preliminary investigations

Problems were expected when using butyllithium to metallate the (Z)-bromo-styrene (132). Since the polymerisation of the lithium derivative relies on the nucleophilic displacement on fluorine from the aromatic ring, then conditions must prevail to favour this process. Specifically, the organometallic species (154) will polymerise most efficiently in THF. However this solvent will however also aid the nucleophilic displacement of fluoride by the butyllithium, so butylation of the starting material can also be expected to give (155) (Scheme 93). In order to avoid this, diethyl ether was chosen



Scheme 93. *Possible products of the reaction of BuLi with (132)*

initially as the solvent in which to carry out the metallation. The later addition of hexafluorobenzene, to provide an end group, and the addition of THF or monoglyme to aid the polymerisation were considered as means to avoid the formation of side products. The metallation process required 2-3 hours to maximise the formation of (154) and as the amount of hexafluorobenzene was varied so the length of the oligomers produced was expected to vary.



Scheme 94.

Thus, treatment of (132) in ether with butyllithium at -78^{0}C over 2.5 hours was followed by the addition of 2 equivalents of hexafluorobenzene. Warming to -20^{0}C for 2 hours before warming to room temperature gave multiple products, which when chromatographed gave (Z)-Ar(2) (*cis*-decafluorostilbene[148]) (156) (18%) and the (Z)-Ar3 (157) (14%) (All yields are with respect to the styrene used) (Scheme 94).

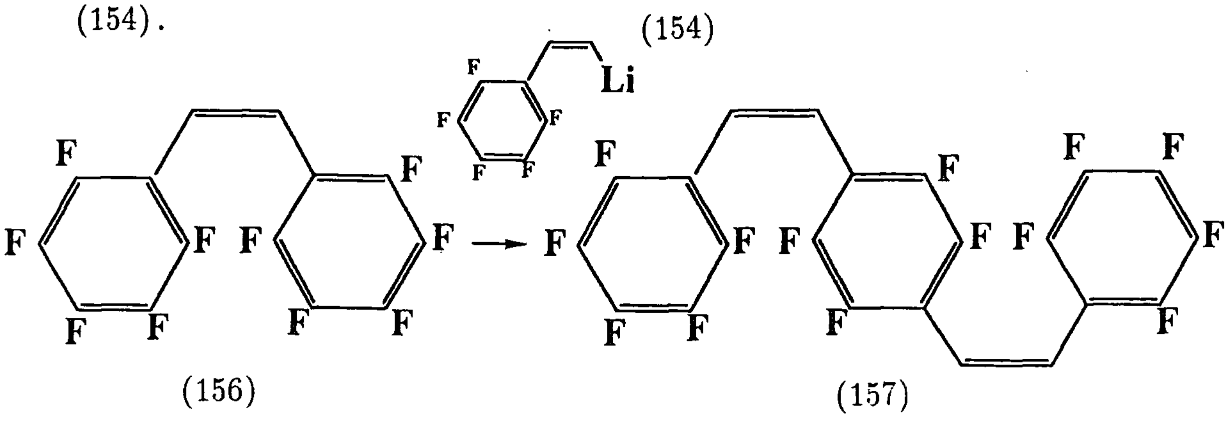
6.5.4.3. Lithiation of (132) using Butyllithium : Preparation of (Z)-Ar2 to (Z)-Ar4

By the addition of monoglyme to the reaction mixture at -78°C prepared in ether as described in section 6.5.4.2. and warming to -20°C, the yields of oligomeric products improved giving the stilbene (Z)-Ar2 (156) (38%,68%), (Z)-Ar3 (157) (17%,30%) and (Z)-Ar4 (158) (1.2%,2%) (yields with respect to styrene and hexafluorobenzene respectively). The remaining material (≈45%) was higher molecular weight material. The yields of the (Z)-Ar3 and (Z)-Ar4 will be higher than these observed, due to some material trapped by the higher molecular weight materials on the top of the chromatography columns. This could be seen by analysis by t.l.c. of this material once removed from the column. Sublimation *in vacuo* was also used as a method of purification but only provided crude separation of the stilbene to tetramer oligomers from the bulk residues. By using a solvent system containing 12% v/v toluene in petroleum ether (bp 40-60°C) for the chromatography, the (Z)-Ar5 (159) was isolated in a pure form. The (Z)-Ar6 (160), however, could only be obtained in an 80% pure state (as seen be ^{1}H nmr) Confirmation of the identity of the (Z)-Ar6 was obtained *via* mass spectrometry showing the molecular ion peak at 1056 mass units. The similarity of the solubilities of (Z)-Ar5 and (Z)-Ar6 meant that multiple chromatography would be necessary to obtain pure (Z)-Ar6.

6.5.4.4. Lithiation of (132) using butyllithium and use of (Z)-Ar2 (156) for Specific Chain Extension

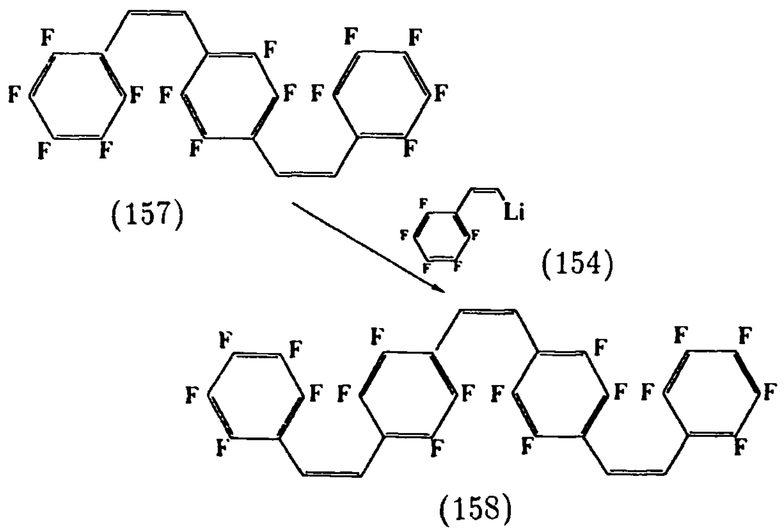
In the reactions described in 6.5.4.2. and 6.5.4.3., hexafluorobenzene was used as a "foundation block" upon which to add the lithiated styrene (154). In a similar manner, it was decided to use (Z)-Ar2

((Z)-stilbene) (156) as a "foundation block" for the addition of (154).



Scheme 95.

The addition of (Z)-Ar2 (156) to a solution of the organometallic reagent (154) prepared in diethyl ether, as previously described, at -78^{0}C, addition of THF followed by 10 hours at -20^{0}C provided the (Z)-Ar3 (157) (6%) after chromatography (Scheme 95). The procedure allowed for a 3:1 excess of bromostyrene (132) to butyllithium to ensure that all the butyllithium had been used up before 2 equivalents of the (Z)-Ar2 (156) was added. On the basis of this yield, it was obvious that the chain extension approach to the formation of the oligomers was not a practicable procedure. A similar experiment using the (Z)-Ar3 (157) as a "foundation block" in order to prepare the (Z)-Ar4 (158) gave a yield too small to isolate (Scheme 96).



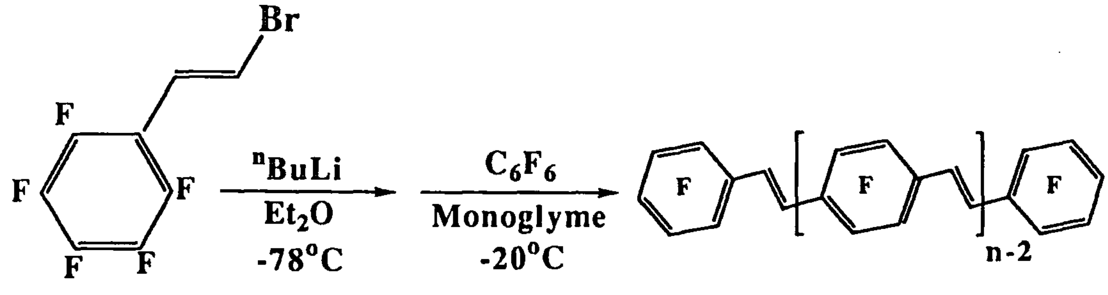
Scheme 96.

In both these reactions some baseline material was seen by chromatography. This may well indicate one reason for the difficulty in obtaining higher yields of the low molecular weight oligomers: the higher oligomers being more reactive towards (154). Specifically, the (Z)-Ar4 (158) may be reacting to form the (Z)-Ar5 (159) faster than it itself is being formed. The limiting factor to this will then be on the basis of solubility.

6.6. Reactions of (E)-1-bromo-2-pentfluorophenylethene (136)

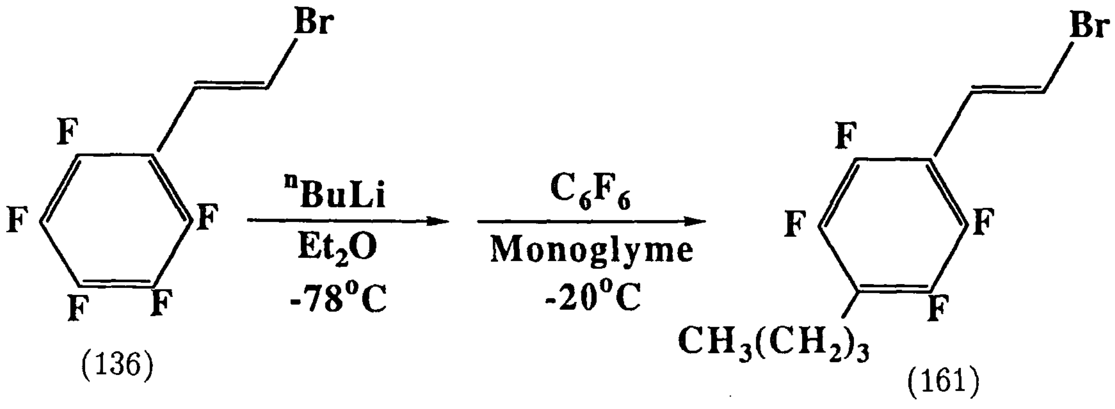
6.6.1. Lithiation of (136) with Butyllithium

Following the successful preparation of the oligomeric *cis* F-PPV's (Section 6.5.4.3.) the synthetic route was applied to the *trans* isomers in an identical manner (Scheme 97). Specifically, the metallation of (136) in ether over a period of 2h at -78^{0}C with butyllithium was followed by the addition of 2.5 equivalents of hexafluorobenzene and 20 ml of monoglyme before warming to -20^{0}C for a further 16 hours. The product mixture was found to contain one major and three minor components, the three minor ones showing up as fluorescent spots on tlc. Separation of the product by chromatography gave only the major product, butylated starting material (161) (>55%) (Scheme 98).



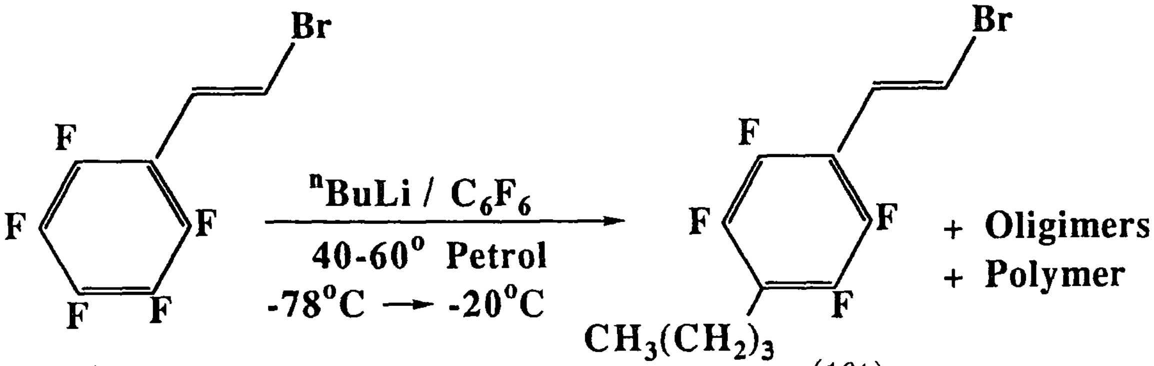
(136)

Scheme 97.



Scheme 98.

The reactivity of the bromine site on the *trans* isomer towards metallation is thus considerably less than the para fluorine site towards nucleophilic displacement, contrasting remarkably with the behaviour of the *cis* isomer. It was expected that using a less polar solvent would reduce the extent of nucleophilic substitution of fluorine but not hinder the metallation reaction; alternatively the use of lithium or magnesium would bring about metallation only. The lithiation reaction was therefore attempted first of all in both petroleum ether (bp 40-60^{0}C) and benzene. The metallation in petrol was carried out at -78^{0}C for 7 hours before addition of 3 equivalents of hexafluorobenzene with subsequent warming to -10^{0}C followed by the addition of THF. An exothermic reaction occurred which increased the temperature to +3^{0}C with a colour change from pale yellow to purple. Purification of the product mixture again gave (161) (27%) along with some oligomeric materials (5%) and baseline polymer, so the method was abandoned (Scheme 99).



(136) (161)

Scheme 99.

The reaction in benzene under similar conditions gave an increased yield of the butylated starting materials.

6.6.2. Reaction of (136) with Magnesium

The reaction between (136) and magnesium when activated with ethylene dibromide or with iodine were quite different. Magnesium in THF was activated with ethylene dibromide after which (136) was added and the mixture heated at 40°C. After 1.5 hours, only unreacted starting material was be isolated. Upon addition of some more ethylene dibromide (4 drops), the solution darkened immediately and an exothermic reaction ensued. A yellow/orange material was isolated which was soluble in many organic solvents. Its ^{1}H nmr spectrum was almost identical to that found for the similar reaction of the *cis* isomer (Section 6.5.3.) , that is, showing a polymeric material containing saturated units indicating the type of structure shown in Fig 35.

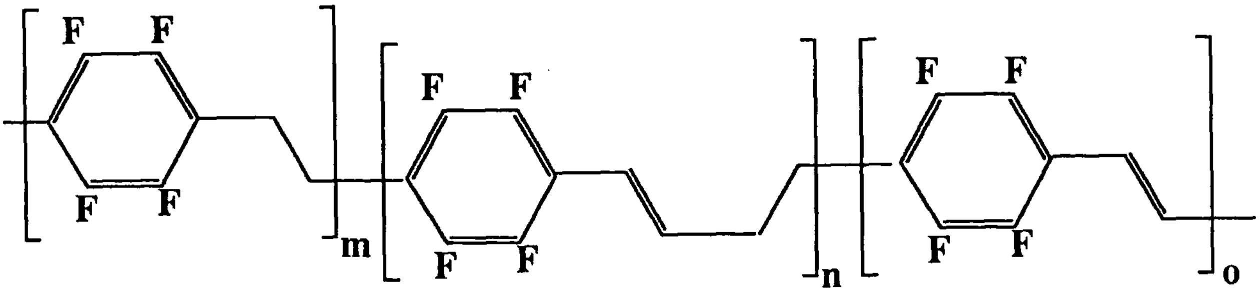
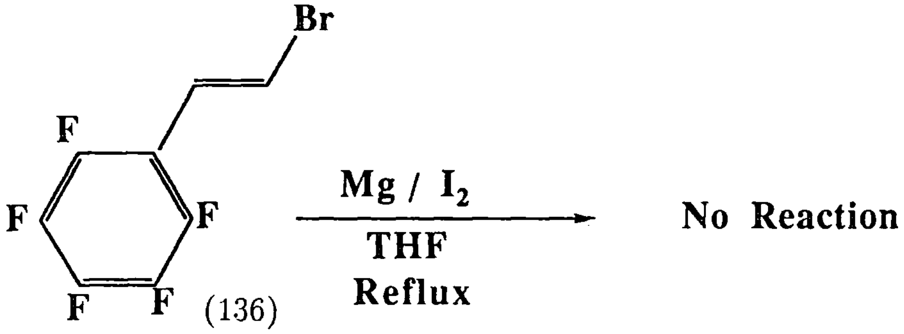


Fig 35.

In contrast, when magnesium in THF was activated with iodine and treated with (136) at 40^{0}C , only unreacted (136) could be isolated on work-up. Heating the mixture under reflux for 8-10 hours with repeated activation with iodine also had no effect on (136) (Scheme 100).

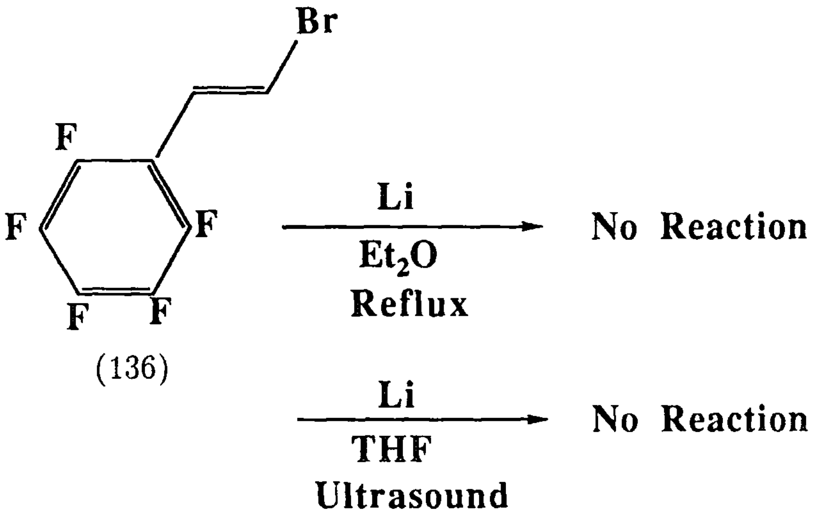


Scheme 100.

These reactions confirmed that the ethylene dibromide again was acting not only to activate the magnesium, but also to react with the bromo styrenes'.

6.6.3. Reaction of (136) with Lithium

In the hope of achieving good metallation and increasing the reactivity of the resultant organometallic material, the reaction of (136) with lithium metal was attempted. Addition of (136) to lithium metal in diethyl ether under reflux conditions gave as products only unreacted (136). With the recent more widespread use of ultrasound in organic synthesis[149], an ultrasound-promoted reaction was attempted. Reaction of (136) with lithium metal in THF at room temperature in the presence of C_6F_6 under ultrasound conditions lead to a faint yellow solution after 3 hours (Scheme 101).



Scheme 101.

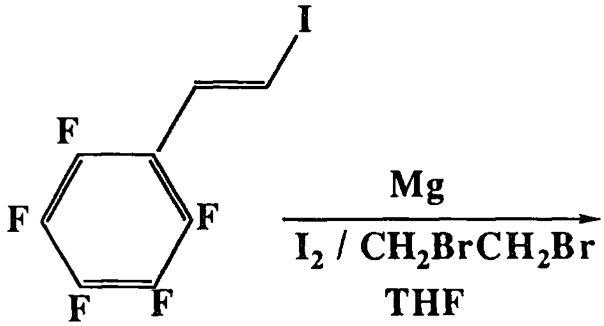
Addition of iodine and a further 58 hours of reaction under these conditions gave a solid brown/red product. This was insoluble in common organic solvents showing infrared bands at 3405(w), 2210(w), 1710(w), 1645(m), 1025(m) and 985 cm^{-1}(s). The very dark colour may be due to the presence of lithium doped FPPV units. Conductivity of this sample (2-probe) was $<10^{-10}$ S cm^{-1}.

6.7. Reactions of (E)-1-iodo-2-pentafluorophenylethene (150)

Since the *trans* bromo-styrene did not appear to be reactive enough for the synthetic procedure envisaged, it was hoped that a move to the more reactive iodine system would be more successful.

6.7.1. Reaction of (150) with magnesium

No difference in reactivity towards Grignard formation was observed between the iodo (150) and the bromo (136) derivatives with the same products as those described in Section 6.6.2. being found.



(150)

Scheme 102.

Both these *trans* halo styrenes seem to be very deactivated compared with the *cis*-bromo-styrene (132).

6.7.2. Lithiation of (150) with butyllithium

Treatment of (150) in diethyl ether at -78^{0}C with one equivalent of butyllithium over a period of three hours followed by warming to -20^{0}C and treatment with C_6F_6 and THF for 1 hour gave a yellow/ lime green fluorescent product. This was found to contain at least seven products (as seen by tlc) of which the first five were efficiently separated by chromatography. They were identified by mass spectrometry and nmr to be oligomers and their butylated derivatives (Fig 36).

(162) (I)

(163) (II)

(164) (III)

(165) (IV)

(166) (V)

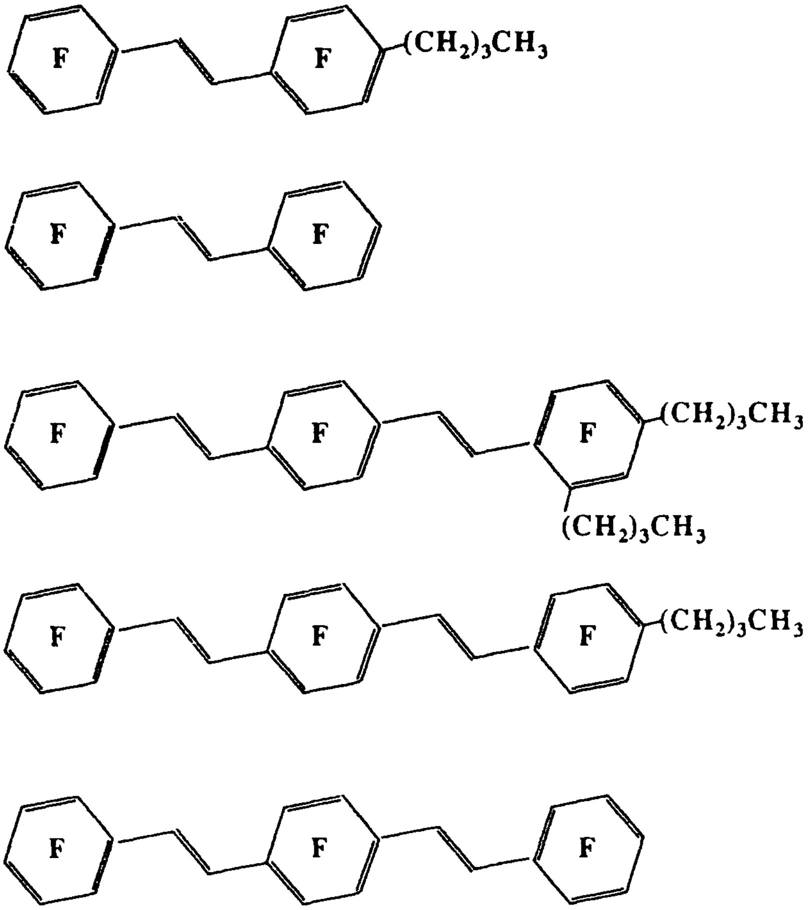
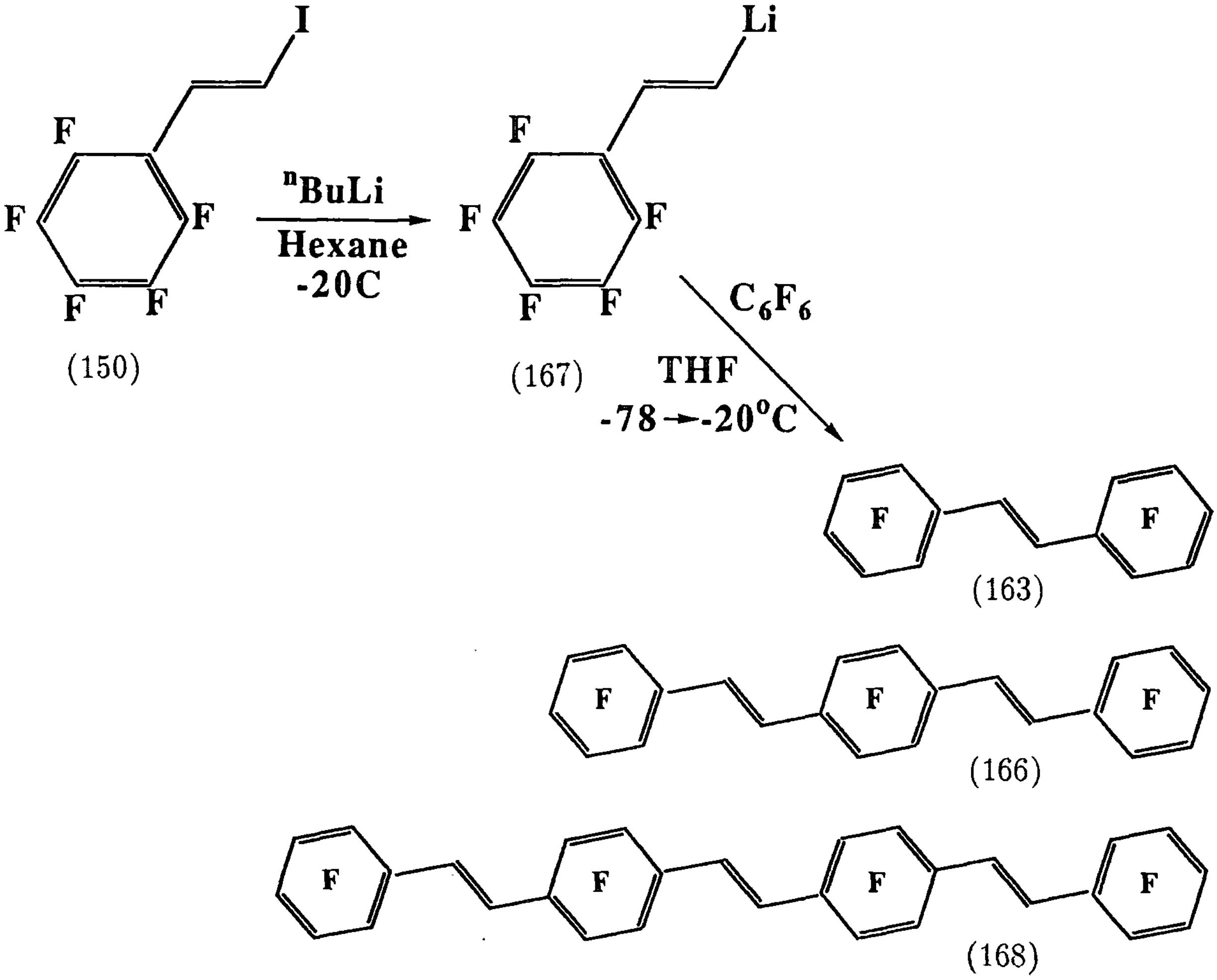


Fig 36.

The difficulties of purification of the oligomers was greatly complicated by the presence of these butylated materials.

The addition of butyllithium to a solution of (150) in hexane at -20^{o}C to minimise butylated products, produced a white precipitate (167) almost instantly. This mixture was stirred for 1.5 hours and was then added <u>to</u> a solution of 5 equivalents of C_6F_6 in THF at -78^{o}C. The total reaction mixture was then allowed to warm to -20^{o}C and stirred for 18 hours, at which point it had turned an ink-blue colour. This mixture was warmed to room temperature and quenched with dilute sulphuric acid to give a beautiful green/yellow fluorescent material which contained multiple products. Using 7 equivalents of C_6F_6 under the same conditions the product was chromatographed and found to contain the (E)-Ar2 (163)^{148} (7%) and (E)-Ar3 (166) (14%) with the majority of the yellow fluorescent material remaining on the top of the column (Scheme 103). The (E)-Ar4 (168) was found in very small yields and was

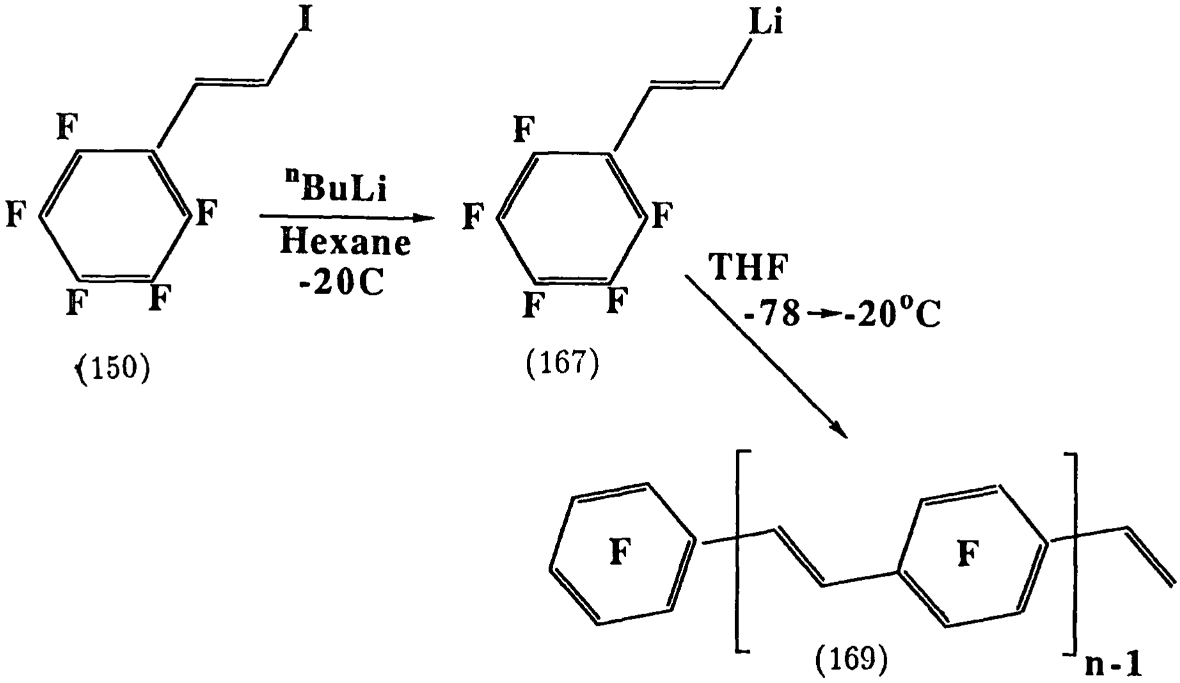


Scheme 103.

contaminated with the (E)-Ar3. All of the *trans* systems were more insoluble than the *cis* series in all solvents and so were inherently more difficult to purify. This lead to the columns being overloaded easily with resultant loss of resolution. The method used to purify the (E)-Ar4, as a last resort, was chromatography at an elevated temperature, using a very low column loading. Upon a lagged column 10 cm in diameter using petroleum ether (bp 60-80^{0}C) as eluant at 45-50^{0}C was placed an 80 mg sample of a (E)-Ar3 and (E)-Ar4 mixture. From this was obtained approximately 5 mg of a yellow solid sample of (E)-Ar4 (168) (<1.0%).

6.7.3. Lithiation of (150) with butyllithium to give high molecular weight material F-PPV (169).

In an attempt to prepare high molecular weight material in which there was no ambiguity about the end groups (C_6F_5 and $-CH=CH_2$), a reaction was carried out under similar conditions to those described in section 6.7.2. but with the omission of C_6F_6 (Scheme 104). The addition of the lithiostyrene (167) to THF at -78°C gave an immediate deep purple colour. After 15 minutes at -20°C, the reaction had gone deep black, followed after 4 hours by the mixture gellifying, indicating the formation of high molecular weight material. The temperature was maintained at -20°C for a further 17 hours before the mixture was quenched with dilute sulphuric acid. The resultant bright yellow product was Soxhlet extracted in two 48 hour cycles with water and ethanol and then with toluene for eight days before being extracted with diethyl ether. The elemental analysis indicated a molecular weight equivalent to 12 or 13 phenylenevinylene units (Table 7).

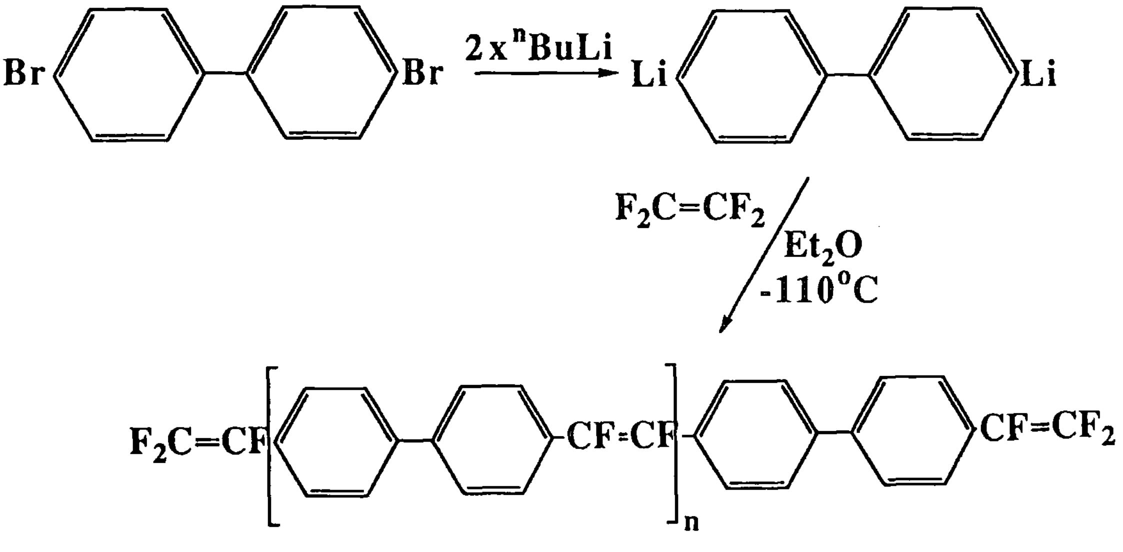


Scheme 104. *Preparation of high molecular weight F-PPV.*

	C / %	H / %	N / %
Extracted Product	54.70	1.61	(2.12)
Required for n = 8	54.41	1.21	
n = 10	54.57	1.20	
n = 20	54.88	1.18	

Table 7

This is of comparable molecular weight to that obtained by Droske et al[132] using a similar nucleophilic displacement reaction to prepare the di-aryl fluorinated vinylene material (129) (Scheme 105).

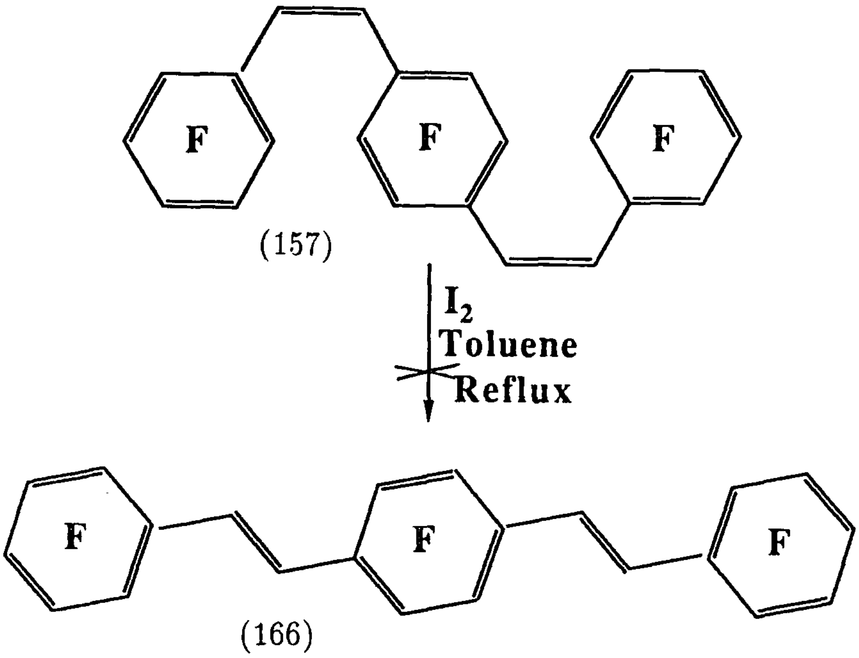


(129)

Scheme 105.

6.8. Attempted Isomerisation of *cis-cis* trimer (Z)-Ar3 (157) to *trans-trans* trimer (E)-Ar3 (166).

Since the *cis*-oligomers are considerably easier to prepare than the *trans*-oligomers, an attempt was made to isomerise the *cis* to *trans* systems. The *cis-cis*-trimer (Z)-Ar3 (157) was heated under reflux in toluene with a few crystals of iodine for 48 hours.



Scheme 106.

The infrared spectrum showed that no isomerisation had occurred (Scheme 106). This is in contrast to the hydrocarbon version in which the polymeric system isomerises under these conditions[59b]. This perhaps reflects the effect of the electron withdrawing nature of the fluorines which reduces the electron density in the double bonds so making electrophilic attack by iodine less attractive. Haszeldine et al. found that a similar attempted isomerisation of *cis*-decafluorostilbene was also unsuccessful[148]

6.9. Comparison of *cis* and *trans* Oligomeric tetrafluorophenylene-vinylenes

All of the *cis*-oligomers described (section 6.5.4.3) gave excellent molecular ion peaks in the EI mode for mass spectrometry, with very little fragmentation (See Fig 37 for an example).

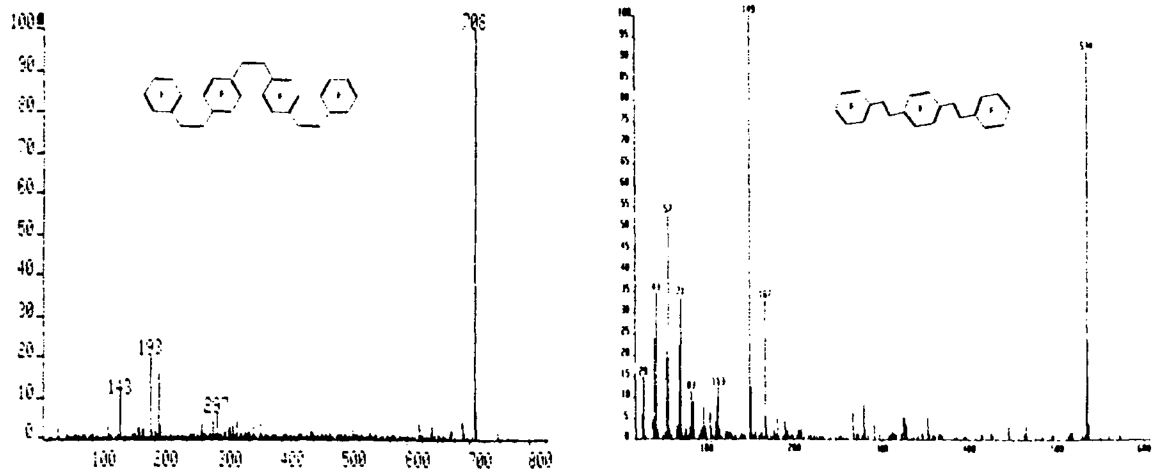


Fig 37.

The ultra violet spectra was very revealing in that no major increase in wavelength of absorption was observed as the oligomer chain-length was increased. This reflects the observation that all the samples are white in colour. This must be a direct result of the *cis* double bond configuration which introduces interactions between the fluorines on adjacent rings which force the structure out of plane thus disrupting the conjugation of the system. This also shows that these systems will be of little use for application as conducting materials. With this in mind, the pale product derived from the Grignard reaction of the (Z)-bromo-styrene (132) (Section 6.5.3.) may be the polymer product required, be it contaminated heavily with magnesium.

The *trans*-oligomers (section 6.7.2.) however, are quite different. (E)-Ar2 is white in colour but is distinctly reflective. (E)-Ar3 is faintly yellow and also reflective, with (E)-Ar4 as the first really yellow coloured oligomer. This is shown more clearly by the uv/vis spectra of these oligomers (Fig 38 and Table 8), with λ_{max} increasing as expected with the increase in chain length.

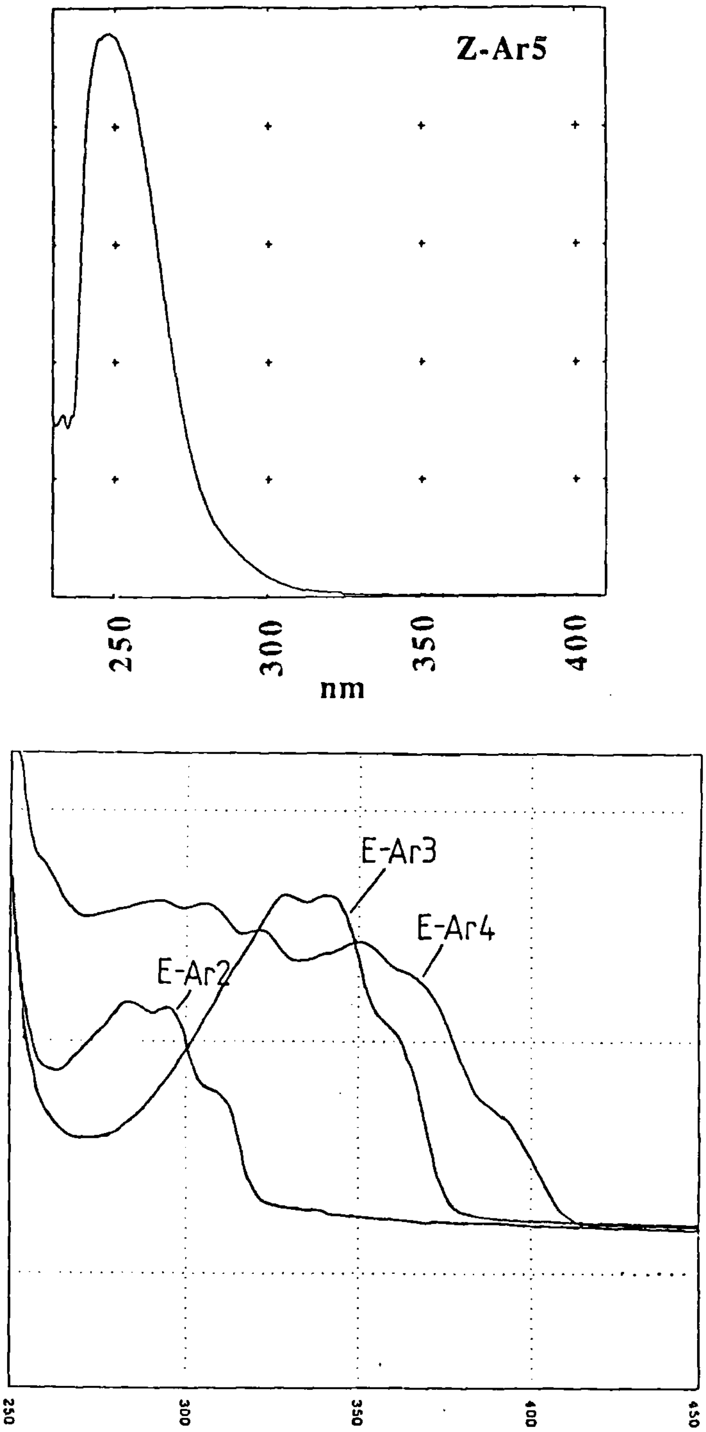


Fig 38.

Compound	Extinction Coefficient	λmax / nm
(Z)-Ar2	7400	241
(Z)-Ar3	24000	246
(Z)-Ar4	40200	244
(Z)-Ar5	40000	248
(E)-Ar2	52650	295
(E)-Ar3	81040	330
(E)-Ar4	—	350

Table 8

Both the *cis* and *trans* systems show excellent ^{1}H and ^{19}F nmr spectra with the build up of peaks corresponding to the central portions of the oligomers as the chain length is again increased.

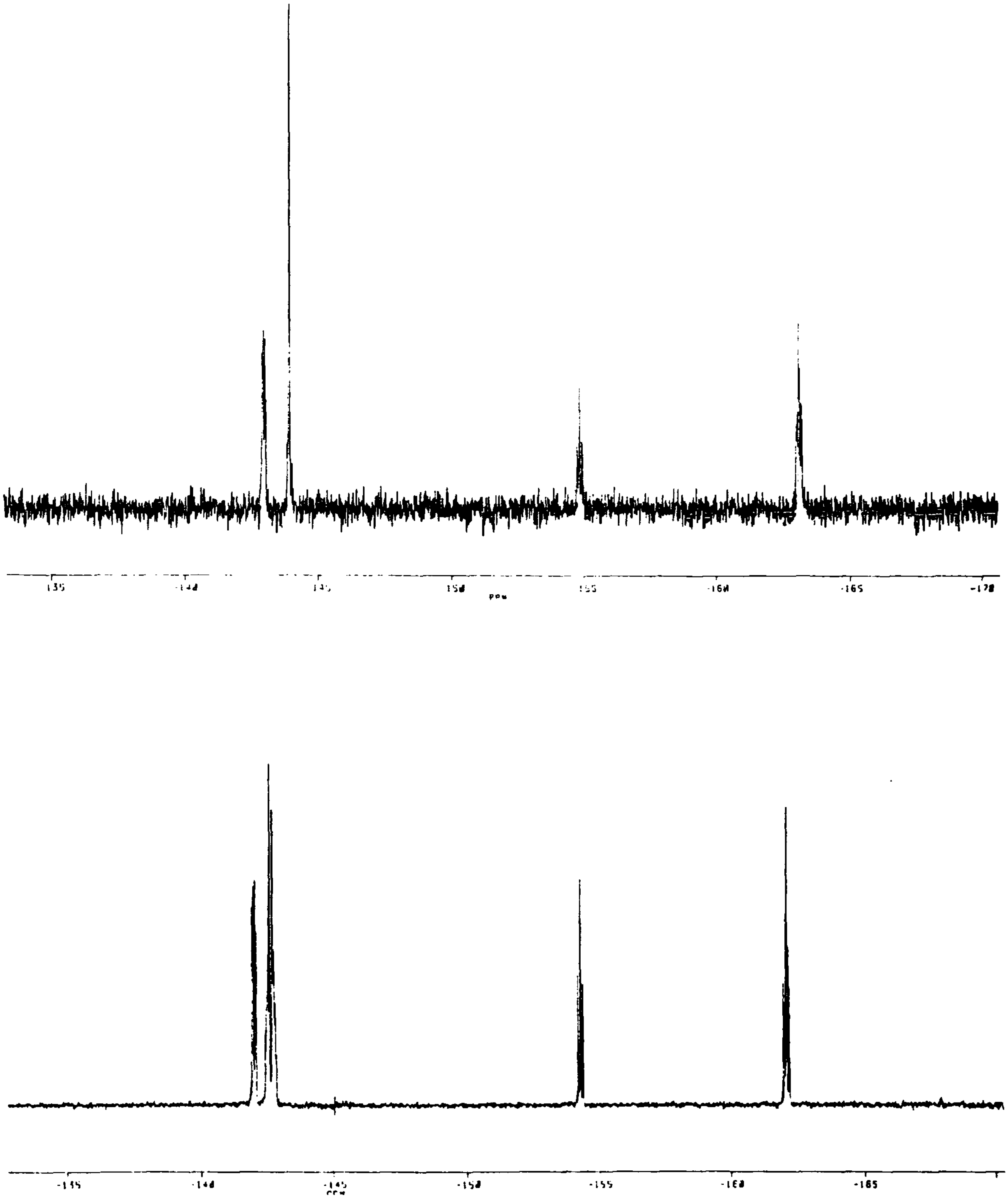


Fig 39. ^{19}F *nmr of Top*: *(E)-Ar3 and Bottom*: *(Z)-Ar3*

6.10. Doping Studies on Oligomeric tetrafluorophenylenevinylenes

The oligomers described were found to be very robust to generally considered to be harsh environments. They cannot be dissolved in large amounts in any normal solvent. They were found not dissolve in hot hydrofluoric acid/ nitric acid mixtures (for analysis purposes), but simply floated as a hydrophobic fluorine containing compound may be expected to. Similarly, exposure to bromine or iodine vapour had no effect on the bright yellow material. Doping with concentrated sulphuric acid was without success. However, when a sample of "high" molecular weight material ($n \approx 13$, section 6.7.3.) which had been pressed into a pellet (13mm diam. x 0.2mm) was exposed to a THF solution of sodium naphthalide, it appeared to "fizz" and disappear into the solution, implying that a reaction had taken place. No doped pellet of polymer could be recovered, and no further doping studies were pursued. All the oligomeric polymers had intrinsic conductivities beyond the range of available instrumentation (with a limit of $\approx 10^{-10}$S cm^{-1}).

CHAPTER SEVEN

EXPERIMENTAL

INSTRUMENTATION

Infrared spectra were recorded using a Perkin-Elmer 457 or 577 grating spectrophotometer. Proton and Fluorine NMR were recorded on a Bruker AC 250 [235.342MHz (^{19}F), 250.133MHz (^{1}H)]. Chemical shifts are expressed in parts per million (ppm) upfield from internal $CFCl_3$ (δ_F) and downfield from internal tetramethylsilane (TMS). Mass Spectra were recorded on a VG 7070E instrument with an ionisation beam energy of 70eV, the ionisation modes as indicated.

Ultraviolet spectra were recorded on a Kontron - Uvikon 930 spectrophotometer in 1 cm quartz cells. Microanalysis were obtained using a Carlo ERBA C.H.N. Elemental Analyser - 1106

Cyclic Voltammetry were carried out using a Bioanalytical Systems Inc. CV-1B current sweep source. Electrolysis were driven by a Cycopel Scientific Ltd. Potentiostat DD 10M/I as the current source.

Appendix I contains details of infra-red spectra.

TECHNIQUES

Volatile materials were handled in a conventional glass vacuum systems or a greaseless glass vacuum system employing Youngs Taps in conjunction with an Edwards E2M2 two stage high vacuum pump.

Silica gel for chromatography was Merck Kieselgel 60 (230-400 mesh); preparative thin layer chromatography was performed on plates (20x20x0.1 cm) coated with Fluka Kieselgel GF 254.

Dialysis was carried out using Visking seamless dialysis tubing (pore size 24 Å, 14 mm diam., McQuilkin)

Commercial compounds and solvents were used as received from the supplier. All chromatography solvents were re-distilled prior to use. Further drying and purification was carried out according to standard procedures[105].

EXPERIMENTAL TO CHAPTER TWO

7.1. Preparations of

7.1.1. 4,5,6,7-Tetrafluoroisothianaphthene (51)

A solution on butyllithium in hexane (105 ml, 1.715 M) was added dropwise over 30 min. to a solution of 2,3,4,5,6-pentafluorobenzyl methyl sulphoxide (53) (14g, 57.3 mmol) in dry THF (250 ml) at -70^{o}C and stirred at this temperature for 3 hr. The solution was warmed with an ice bath, a mildly exothermic reaction being noted at -10^{o}C to -6^{o}C, and was stirred at this temperature for a further 1 hr, after which ice cold sulphuric acid (2 M) was added. The mixture was extracted with ether and the extracts then washed with water, dried ($MgSO_4$) and solvent evaporated *in vacuo* at room temperature to give a dark red oil. Sublimation of the oil at 25^{o}C/5x10^{-3}mm Hg into a Leibig condenser and recrystallisation of the solid (5.1g) from light petroleum gave *4,5,6,7-tetrafluoroisothianaphthene* (51) (3.14g,27%) mp 52-53.0^{o}C (Found: C, 46.83; H, 0.63%; M^+, 206(EI). $C_8H_2F_4S$ requires C, 46.61; H, 0.98 %; M, 206) δ_H($CDCl_3$) 7.87 p.p.m. (1-H/3-H); δ_F($CDCl_3$) -149.1 (4-F/7-F)and -162.8 p.p.m. (5-F/6-F).

7.1.2. 1,3,4,5,6,7,8-Heptafluoronaphthalene-2-ylmethyl methyl sulphoxide (56)

Octafluoronaphthalene (10g,37mmol) in dry THF (160 ml) cooled to -78^{o}C was treated with sodium methylsulphinylmethide in dimethyl sulphoxide (27.5ml, 2.68 M) dropwise for 1 hr and stirred at this temperature for a further 3 hr. Water (60 ml) was added and the mixture was allowed to warm to room temperature. The mixture was extracted with diethyl ether, and the extracts washed with water, dried ($MgSO_4$) and solvents evaporated to give a brown oil. Sublimation at 45^{o}C/ 5x10^{-3}mm Hg removed unreacted starting material (2.25g) and further sublimation at 90^{o}C/2x10^{-3}mm Hg yielded the crude product (4.1g, 34%) which upon recrystallisation from ethanol/ light petroleum (bp 60-80^{o}C) gave

1,3,4,5,6,7,8-heptafluoronaphthalen-2-ylmethyl methyl sulphoxide (56) mp 113.5-114.0°C (Found: C, 43.44; H, 1.36%; M^+, 330. $C_{12}H_5F_7SO$ requires C, 43.64; H, 1.52%; M, 330). $\delta_H(CDCl_3)$ 2.68 (s,CH_3); 4.23 and 4.32 p.p.m. (AB, CH_2), J_{AB}13 Hz; $\delta_F(CDCl_3)$ -118.1 (dd, 1-F), -136.3 (bd,3-F), -143.3 (dt, 8-F), -145.5 and -147.5 (both dt unassigned 4-F, 5-F), -151.9 and -154.5 p.p.m. (both m, unassigned 6-F, 7-F) $J_{1-F,8-F}$68Hz; $J_{4-F,5-F}$55Hz.

Large scale preparations yielded a product which upon sublimation at 50°C/ $5x10^{-3}$mm Hg gave a sublimate containing both unreacted octafluoronaphthalene and *1,3,4,5,6,7,8-heptafluoronaphthalene-2-carbaldehyde* (57) (7%) mp 89-90°C [from light petroleum (bp 40-60°C)] (Found: C, 46.75; H, 0.18%; M^+, 282. $C_{11}HF_7O$ requires C, 46.81; H,0.36%; M, 282). $\delta_H(CDCl_3)$ 10.48 p.p.m. (s, CHO); $\delta_F(CDCl_3)$ -121.6 (dd, 1-F), -140.8 (dm, 4-F), -143.3 (t,3-F), -144.8 and -147.9 (unassigned 4-F, 5-F), -147.7 and -153.7 p.p.m. (both m, unassigned 6-F, 7-F); $J_{1-F,8-F}$72.5 Hz; $J_{4-F,5-F}$58 Hz.

7.1.3. 4,5,6,7,8,9-Hexafluoronaphtho[1,2-c]thiophene (55)

1,3,4,5,6,7,8-heptafluoronaphthalen-2-ylmethyl methyl sulphoxide (56) (2.49g, 7.55 mmol) in dry THF (250 ml) cooled to -78°C was treated with butyllithium in hexane (1.48M, 15.31ml, 22.6 mmol) dropwise over 0.5 hr and stirred at this temperature for a further 4 hr. The solution was warmed to 0°C and dilute sulphuric acid (2M) was added, the temperature being maintained at 0°C. The solution was extracted with ethyl acetate, the extracts washed with water, dried ($MgSO_4$) and solvent evaporated *in vacuo* at 30°C to give a red brown oil. Separation of the crude product by chromatography on silica (13x3.5 cm diam.) using light petroleum (bp. 40-60°C) as eluant gave 4 components: (i) aliphatic hydrocarbons (butyllithium residues), complex (78 mg), (ii) a mixture of isomers of monosubstituted ^{n}butylated naphtho[1,2-c]thiophen (34mg), (iii) *4,5,6,7,8,9-hexafluoronaphtho[1,2-c]thiophene* (55) (0.103g, 4.7%) mp 106-107^{o}C [from light petroleum (bp. 40-60^{o}C)] (Found: C, 49.59; H, 0.55%; M^{+},292. $C_{12}H_2F_6S$ requires C, 49.32; H, 0.68%; M, 292). $\delta_H(CDCl_3)$ 8.43 (q) and 7.85 p.p.m. (dd) (unassigned 1-H, 3-H); $\delta_F(CDCl_3)$ -140.8 (m, 9-F), -145.3 (dm, 6-F), -146.5 (m,4-F); -155.2 (ddt, 5-F), -156.8 p.p.m. (m,overlapping 7-F and 8-F) $J_{5-F,6-F}$66 Hz; and (iv) a lime green component (<5mg)

Elution of the column with ethyl acetate gave a residue (2.1g) which was separated by chromatography on silica (13 x 3.5 cm diam.) using ethyl acetate as eluant to give four components.
(i) 1,3,4,5,6,7,8-heptafluoronaphthalene-2-carbaldehyde (57) (1.059 g) identified by infrared and nmr, (ii) and (iii) unknown mixtures of complex butylated products and (iv) unreacted starting material (56) (0.510g) identified by infrared and nmr.

Reactions of 4,5,6,7-Tetrafluoroisothianaphthene(51)

7.2.1. With Dimethyl acetylenedicarboxylate

Dimethyl acetylenedicarboxylate (DMAD) (2 ml) and (51) (0.2435g, 1.18 mmol) were heated together rapidly under nitrogen by plunging the reaction flask into a hot oil bath at 150^{o}C and then the external temperature was maintained at 130^{o}C for a further 2.5 hrs. Excess DMAD was removed *in vacuo* (30^{o}C/3x10^{-3}mm Hg) and the solid residue was chromatographed on silica (15x3 cm diam.) using dichloromethane as eluant to give *dimethyl-5,6,7,8-tetrafluoronaphthalene-2,3-dicarboxylate* (59) (0.314g, 84%) mp 139.5-140.0^{o}C [from toluene/light petroleum (bp. 60-80^{o}C)] (Found: C, 53.10; H, 2.30%, M^{+}, 316 (EI) $C_{14}H_8F_4O_4$ requires C, 53.16; H, 2.53%; M, 316); $\delta_H(CDCl_3)$ 8.46 (s, 1,4-H); 3.99 p.p.m. (s, 2x CH_3); $\delta_F(CDCl_3)$ -143.6 (5-F,8-F), -149.7 p.p.m. (6-F,7-F).

7.2.2. With Tetrafluorobenzyne

A solution of bromopentafluorobenzene (1.70g, 6.88 mmol) in dry diethyl ether (50 ml) cooled to -78^{0}C was treated with butyllithium in hexane (1.58M, 4.4 ml, 6.92 mmol) and stirred at -78^{0}C for 3 h. The solution was further treated with (51) (0.26g, 1.26 mmol) in dry ether (20 ml), the mixture stirred for 0.5 h at -78^{0}C, warmed to room temperature and stirred for a further 18 h. The solution was acidified, extracted with diethyl ether and the dried ($MgSO_4$) extracts evaporated to give a residue which was chromatographed on silica (15 x 5 cm diam.) using light petroleum (bp 60-80^{0}C) as eluant to give *1,2,3,4,5,6,7,8-octafluoroanthracene* (60) (0.082g, 21%), mp 172-173^{0}C (lit mp 137-139^{0}C^{93}) [from light petroleum (bp. 60-80^{0}C)] (Found: C, 52.41; H, 0.63%; M^+, 322; $C_{14}H_2F_8$ requires C, 52.19; H, 0.63%; M, 322) δ_H($CDCl_3$) 8.86 p.p.m. (s, 9,10-H); δ_F($CDCl_3$) -149.3 (1,4,5,8-F); -155.8 p.p.m. (2,3,6,7-F).

7.2.3. With Lithium 2-propylthiolate

To 2-propylthiol (0.67g, 8.9mmol) in 40 ml THF (dry) at -78^{0}C was added butyllithium in hexane (5.8 ml, 1.585M, 9.19mmol) and the mixture was allowed to warm to room temperature to give the lithium salt (in a concentration of 0.195 M).

To 4,5,6,7-tetrafluoroisothianaphthene (51) (0.18g, 0.88mmol) was added lithium 2-propylthiolate (4.5ml, 0.195M, 0.875mmol) and stirred at room temperature for 70 h (until completion of reaction followed by tlc.). Water was added and the product was extracted with ether to give the crude material (0.23g), which was separated by chromatography on silica (150 x 50mm diam.) to yield unreacted starting material (34mg, 19%), *4,6,7-trifluoro-5-(2-propylthio) isothianaphthene* (61) (0.174g, 76%)

(Found M^+,262; $C_{11}H_9F_3S_2$ requires M, 262); $\delta_H(CDCl_3)$ 7.88 and 7.79 (unassigned 1-H and 3-H); 3.44(septet,-$C\underline{H}(CH_3)_2$), J,6.7Hz; 1.29 p.p.m. (d,-$CH(C\underline{H}_3)_2$), J, 6.7Hz); $\delta_F(CDCl_3)$ -122.1 (4-F); -141.2(6-F)and -151.3 (7-F); and *4,7-difluoro-5,6-di(2-propylthio) isothianaphthene* (62) (14 mg, 5%) (Found M^+, 318; $C_{14}H_{16}F_2S_3$ requires M, 318); $\delta_H(CDCl_3)$ 7.98(s, 1,3-H); 3.60 (septet,-$C\underline{H}(CH_3)_2$), J, 6.7Hz; 1.29p.p.m. (d, -$CH(C\underline{H}_3)_2$) J, 6.7Hz. $\delta_F(CDCl_3)$ -128.7 p.p.m..

7.2.4. With Bromine

4,5,6,7-tetrafluoroisothianaphthene (51) (0.1g, 0.485mmol) in dry chloroform (20ml) was treated with bromine (0.12g, 0.75mmol) and stirred for 18h. Evaporation of the solvent *in vacuo* and separation by chromatography on silica (150 x 50 mm diam.) using petroleum ether (bp 40-60°C) as eluant gave *1,3-dibromo-4,5,6,7-tetrafluoroisothianaphthene* (63) (0.133g, 75%) mp (decomposes) (Found C,26.88; H, 0.22%; M^+, 366; 285 (-HBr) $C_8H_2Br_2F_4$ requires C,26.26; H, 0.55%; M, 366) $\delta_H(CDCl_3)$ 5.30 p.p.m. ; $\delta_F(CDCl_3)$ -155.3(4,7-F); -159.5 (5,6-F).

7.2.5. Cationic polymerisation of (51): Reaction with Magic Acid

To 4,5,6,7-tetrafluoroisothianaphthene (51) (0.51g, 2.47 mmol) in dichloromethane (1ml) was added magic acid (SbF_5/HF) (2 drops). The resultant solution was stirred at room temperature for 20 h after which the viscous oil was dissolved in THF and precipitated into methanol. Filtration of the resultant yellow solid and re-precipitation twice from THF into methanol gave the pure product *poly(1,3-dihydroisothianaphthene)* (65) (77%) (Found C,46.39; H, 1.20%; $C_8H_2F_4S$ requires C,46.61; H, 0.98%). $\delta_H(CDCl_3)$ Three regions, all broad peaks (5.67); (5.55, 5.50, 5.45); and (5.27, 5.24 p.p.m.) ratio 1:2:1 ; $\delta_F(CDCl_3)$ Three regions, broad peaks, (-138.7, -139.1, -139.4); (-140.9); and (-152.9, -153.4 p.p.m.) in a ratio of 1:1:2.

7.2.6. Oxidation of (65).

To (65) (0.035g, 0.17mmol) in ethylacetate (5ml) at 0^oC was added meta-chloroperbenzoic acid (MCPBA) (0.26g of 50-55%, 0.75mmol). The solution was allowed to warm to room temperature and stirred for 10 min. at which point a solid precipitated. After a further 50 min. the now yellow solution was evaporated *in vacuo*, dissolved in water and dialysed with water for 3 days, to give a yellow solid (0.039g, 96%). (Found C, 40.58; H, 0.85%, $(C_8H_2F_4O_2S)_n$ requires C, 40.58; H, 1.61%). δ_F(methanol) -134.2 (s, vbr, 1xF); -155.8 p.p.m.(s, vbr, 1xF) (Broad over 15 p.p.m.)

EXPERIMENTAL TO CHAPTER THREE

Nitrogen monomers : Preparation of:-

7.3.1. 5,6,7,8-Tetrafluoro-1,4-dihydronaphthalene-1,4-imine (74)

A flame dried flask flushed with nitrogen was charged with bromopentafluorobenzene (28.7g, 0.116 mol) in dry diethyl ether (200 ml) and cooled to -78^oC. To this was added, dropwise, butyllithium in hexane (1.16M, 94 ml, 0.12mol) over a period of 1 h and the resultant mixture was stirred at this temperature for a further 3 h, then, also dropwise, was added N-trimethylsilylpyrrole (24.4g, 0.176mol) over 0.5 h and stirred at -78^oC for 1 h. This was then allowed to warm to room temperature and stirred for 18 h, after which distillation at ($56-58^oC/5x10^{-3}$mm hg) gave the product *5,6,7,8-tetrafluoro-1,4-dihydronaphthalene-1,4-imine* (74) (9.827g, 40%). $\delta_H(CDCl_3)$ 6.79(s, CH=CH); 5.04 (s, CH); 2.84 p.p.m. (s, NH); $\delta_F(CDCl_3)$ -144.4 (5,8-F); -159.3 (6,7-F)

7.3.2. 5,6,7,8-tetrafluoro-1,2,3,4-tetrahydonaphthalene-1,4-imine (73)

A solution of (74) (1.04g, 4.65mmol) in dry methanol (100ml) was shaken with 10% palladium-charcoal under a hydrogen atmosphere (35 psi) at 40^oC for 3h. The product was filtered and the solvents evaporated *in* *vacuo* to give a quantitative yield of *5,6,7,8-tetrafluoro-1,2,3,4-tetrahydro-naphthalene-1,4-imine* (73) (0.9861g). mp 40-41^{o}C [from light petroleum (bp. 40-60^{o}C)] (Found: C, 55.58; H, 3.19; N, 6.36% $C_{10}H_7F_4N$ requires C, 55.29; H, 3.22; N, 6.45%) M^+, 189 (EI,CI thermal elimination products). δ_H($CDCl_3$) 7.04(s, NH); 5.19(CH); 2.34(CH_{ax}); 1.44 p.p.m. (m, CH_{equi}). δ_F($CDCl_3$) -143.2(5-,8-F); -155.1 p.p.m. (6-,7-F).

7.3.3. 4,5,6,7-Tetrafluoroisoindole (71)

A sample of (73) (1.43g, 6.6 mmol) was sublimed through a quartz tube (300x20 mm) at 550^{o}C/5x10^{-3}mm Hg the resultant product being collected on a cold finger to yield *4,5,6,7-tetrafluoroisoindole* (71) (0.9g, 72%). mp 134-135^{o}C [from light petroleum (bp 40-60^{o}C)] (Found: C, 50.55; H, 1.40; N, 7.41%; M^+, 189. $C_8H_3F_4N$ requires C, 50.79; H, 1.59; N, 7.41%; M, 189) δ_H($CDCl_3$) 7.36(CH); 9.47 p.p.m. (br, NH). δ_F($CDCl_3$) -150.8 (4-,7-F), -166.7 (5-,6-F).

7.3.4. N-Methyl-5,6,7,8-tetrafluoro-1,4-dihydronaphthalene-1,4-imine (72a)

A flame-dried flask flushed with nitrogen was charged with bromopentafluorobenzene (15.0g, 60.7mmol) in dry diethyl ether (200 ml) and cooled to -78^{o}C. To this was added, dropwise, butyllithium in hexane (1.61M, 50 ml) over a period of 1h and the mixture was stirred for a further 3h, after which freshly distilled N-methyl pyrrole (11.3g, 140 mmol) was added over 0.5 h and stirring was continued at -78^{o}C for a further 0.5 h. The mixture was allowed to warm to room temperature and stirred for 18 h., then acidified with dilute sulphuric acid (2M) and the viscous acid washings were basified with 4M NaOH. The resultant precipitate was filtered off, washed repeatedly with water, and finally sublimed at 45^{o}C/5x10^{-3}mm Hg to yield the product *N-methyl-5,6,7,8-tetrafluoro-1,4-dihydronaphthalene-1,4-imine* (72a) (6.89g, 30.1 mmol).

$\delta_H(CDCl_3)$ 2.15 (s,NCH_3); 4.87(s,CH); 6.96 (s,CH=CH). $\delta_F(CDCl_3)$ -143.8 (d, 5,8-F) $J_{5\text{-}F,6\text{-}F}$16Hz; -157.3 (d, 6,7-F), $J_{6\text{-}F,5\text{-}F}$21Hz.

7.3.5. N-methyl-5,6,7,8-tetrafluoro-1,2,3,4-tetrahydro-naphthalene-1,4-imine (72b)

A solution of (72a) (2.0g, 8.73 mmol) in dry methanol (100 ml) was shaken with 10% palladium-charcoal under a hydrogen atmosphere (36 psi) at 40°C for 3 h. Filtration of the solution and evaporation of the solvent gave only one product *N-methyl-5,6,7,8-tetrafluoro-1,2,3,4-tetrahydronaphthalene-1,4-imine* (72b) quantitatively.

$\delta_H(CDCl_3)$ 1.25(m, CH_{eq}); 2.07 (s, NCH_3); 2.15 (CH_{ax}); 4.43 p.p.m. (CH). $\delta_F(CDCl_3)$ -144.8 (5-,8-F); -156.7 p.p.m. (6-,7-F), $J_{5\text{-}F,6\text{-}F}$20Hz

7.3.6. N-Methyl-4,5,6,7-tetrafluoroisoindole (72)

A sample of (72b) (1.639g, 7.2 mmol) was sublimed through a quartz tube (300x20 mm) at 550°C/5x10^{-3}mm Hg , the product being trapped on a cold finger to yield a white crystalline material *N-methyl-4,5,6,7-tetrafluoroisoindole* (72) (1.302g, 6.41 mmol) mp 155-156°C [from light petroleum (bp 60-80°C)] (Found: C, 53.19; H, 2.63; N, 6.93%; M^+, 203 (EI). $C_9H_5F_4N$ requires C, 53.20; H, 2.46; N, 6.90%; M, 203).

$\delta_H(CDCl_3)$ 3.99 (s, NCH_3); 7.16 p.p.m. (CH). $\delta_F(CDCl_3)$ -151.2 (br, 4-,7-F); -167.5 (5-,6-F).

7.3.7. 5,8-difluoro-7,8-dimethoxy-1,2,3,4-tetrahydronaphthalene-1,4-imine (77)

A solution of (73) (0.3g, 1.38 mmol) in dry THF (50 ml) was treated with sodium methoxide (24 mmol) in methanol (6ml) and heated under reflux for 75 h. Water was added and the reaction mixture extracted with diethyl ether, the extracts dried ($MgSO_4$) and solvents evaporated to give *5,8-difluoro-6,7-dimethoxy-1,2,3,4-tetrahydronaphthalene-1,4-*

imine (77) (0.32g, 93%) mp 86.5-87.0^{o}C [from light petroleum (bp 40-60^{o}C)] (Found: C, 59.31; H, 5.35; 5.57%; M^{+}, 213 (EI decomposition product) $C_{12}H_{12}F_{2}O_{2}N$ requires C, 59.75; H, 5.43; N, 5.80%; M, 213) δ_H(CDCl$_3$) 4.80 (s, 1-,4-H); 3.92 (s, 2x OCH$_3$); 2.22 (s, NH); 2.04 (H$_{ax}$); 1.30 p.p.m. (H$_{eq}$). δ_F(CDCl$_3$) -140.2 (s, 5,8-F).

7.3.8. 5,6,8-Trifluoro-7-methoxy-1,2,3,4-tetrahydronaphthalene-1,4-imine (75)

A solution of (73) (1.0g, 4.61 mmol) in dry THF (40 ml) was treated with sodium methoxide (0.36g, 6.55 mmol) and heated under reflux for 20 h. Sodium hydroxide (100 ml, 0.5M) was added and the product extracted with diethyl ether, dried (MgSO$_4$) and solvents evaporated *in vacuo*. purification by recrystallisation out of chloroform gave the product *5,6,8-trifluoro-7-methoxy-1,2,3,4-tetrahydro-naphthalene-1,4-imine* (75) (1.024g, 97%). δ_H(CDCl$_3$) 4.83 (CH); 3.97 (s, OCH$_3$); 2.26 (s, NH); 2.06 (CH$_{ax}$); 1.28p.p.m. (CH$_{eq}$); δ_F(CDCl$_3$) -139.4 (d, 8-F); -146.2 (t, 5-F); -153.3p.p.m. (d, 6-F), $J_{5-F,6-F}$20Hz; $J_{5-F,8-F}$20Hz..

7.3.9. Thermolysis of 5,6,8-trifluoro-7-methoxy-1,2,3,4-tetrahydronaphthalene-1,4-imine (75).

A sample of (75) (1.0g, 4.37mmol) was sublimed through a quartz tube (300x20 mm) at 500^{o}C/5x10^{-3}mm Hg, the product trapped on a cold finger to yield *4,5,7-trifluoro-6-methoxyisoindole* (76) (97%) (Found M^{+}, 201 (EI); M+1^{+},202 (CI) $C_{9}H_{6}F_{3}NO$ requires M, 201). δ_H(CDCl$_3$) 9.41 (br, NH); 7.29 (CH); 4.01 p.p.m. (s, OCH$_3$); δ_F(CDCl$_3$) -145.1 (d, 7-F); -152.7 (t, 4-F); -162.4 p.p.m. (d, 5-F), $J_{4-F,5-F}$,18Hz; $J_{4-F,7-F}$18Hz. Product too unstable for micro analysis and suffers decomposition upon heating.

7.3.10. N-Methyl-5,6,8-trifluoro-7-methoxy-1,2,3,4-tetrahydronaphthalene-1,4-imine (78)

A solution of (72b) (0.13g, 0.53mmol) in THF (8ml) was treated with sodium methoxide (0.028g, 0.54mmol) and heated under reflux for 60h. Sodium Hydroxide (10ml, 2M) was added and the product was extracted with ether, dried ($MgSO_4$) and solvent evaporated to give the crude product (0.18g). Sublimation ($30^{o}C/5x10^{-3}$mm Hg) and flash chromatography on silica (150x30mm diam.) using ethylacetate as eluant provided a pure sample of *N-Methyl-5,6,8-trifluoro-7-methoxy-1,2,3,4-tetrahydronaphthalene-1,4-imine* (78) (0.158g, 87%). (Found M^+, 215 (EI) $C_{10}H_8F_3NO$ for fragmentation (loss of ethene) requires M, 215) $\delta_H(CDCl_3)$ 4.37 (CH); 3.99 (s,OCH_3); 2.06 (s, NCH_3); 2.12 ($2CH_{eq}$); 1.25 p.p.m. (CH_{eq}). $\delta_F(CDCl_3)$ -139.5 (d, 8-F); -146.3 (t, 5-F); -152.3 (d, 6-F) $J_{5-F,6-F}$,21Hz; $J_{5-F,8-F}$21Hz.

EXPERIMENTAL TO CHAPTER FOUR

7.4.1. Typical Electrolysis Experiment

into an electrolysis cell (capacity 5ml) dried at $100-200^{o}C/3x10^{-3}$mm Hg was placed a gold anode (25x7x2mm), a platinum cathode (25x15x0.1mm) Bu_4NBF_4 (0.1g, 0.05M), 4,5,6,7-tetrafluoroisothianaphthene (51) (0.15g, 0.12M) and dry SO_2 (or acetonitrile) (6ml). All solvents (except SO_2) were degassed repeatedly over a period of 3h. The reference electrode (Ag/Ag^+) was placed in the solution which was cooled to $-20^{o}C$. Electrolysis was then carried out under potentiostatic conditions, with the number of coulombs of charge passed being recorded. Electrolysis was normally carried out to an extent of 15-20% of the total reaction, but depended on the type of product formed.

EXPERIMENTAL TO CHAPTER FIVE

7.5.1 Preparation of 2,3,5,6-Tetrafluoro-1,4-benzene dimethanol (100)[122]

(i) A solution of tetrafluoroterephthalic acid (11.59g, 0.049 M) in diethyl ether (100ml), cooled in an ice/ salt bath, was methylated with excess diazomethane in ether. Excess diazomethane and diethyl ether were removed by distillation to give crude dimethyl tetrafluoroterephthalate (102) (12.97g, 100%), which was used without further purification.

Dimethyl tetrafluoroterephthlalate (102) (1.52g, 5.71 mmol) was added to lithium aluminium hydride (0.31g, 8.2 mmol) in dry THF (100ml) and the mixture was stirred at room temperature for 45 min. Water was carefully added to the mixture which was then acidified (2m H_2SO_4) and the product extracted with diethyl ether to give 2,3,5,6-tetrafluoro-1,4-benzene dimethanol[122] (100) (1.61g, 97%); no purification required.

(ii) A solution of tetrafluorophthlalic acid (18.08g, 76 mmol) in dry THF (50ml) is treated with borane-tetrahydrofuran complex (920ml, 0.407M) and the mixture heated under reflux for 7h. Tetrahydrofuran was removed by distillation, and the residue treated with water and NaOH (2M, 100ml) and extracted with diethyl ether. The combined extracts were dried ($MgSO_4$) and the solvent evaporated to give 2,3,5,6-tetrafluoro-1,4-benzene-dimethanol (100) (15.9g, 76mmol) quantitatively.

7.5.2 *α,α'*-Dibromo-2,3,5,6-tetrafluoro-1,4-xylene[123](103)

A mixture of 2,3,5,6-tetrafluoro-1,4-benzenedimethanol (100) (1.53g, 7.3mmol), hydrobromic acid (10ml) and sulphuric acid (98%, 4ml) was heated at 70°C for 3h. The mixture was poured into water (100ml) and extracted with diethyl ether to give *α,α'*-dibromo-2,3,5,6-tetrafluoro-1,4-xylene[123] (103) (2.40g,98%). mp 118-119°C [from light petroleum (bp 40-60^{o}C)] (Found: C,28.60; H,1.07%; M^{+},334, 336, 338 $C_8H_4Br_2F_4$ requires C,28.60; H,1,2%; M,334, 336, 338) δ_H($CDCl_3$) 4.5 p.p.m. (s,2xCH_2Br); δ_F($CDCl_3$) -142.89 p.p.m.(s,2,3,5,6-F).

7.5.3. Preparation of 2,3,5,6-Tetrafluoro-1,4-xylene-bis(dimethylsulphonium bromide) (105)

A solution of α,α'-dibromo-2,3,5,6-tetrafluoro-1,4-xylene (103) (1.5g, 4.46mmol) in methanol (50ml), water (12ml) and dimethyl sulphide (2.21g, 35.7mmol) was heated at 50^{o}C for 1h. The solution was concentrated by evaporation *in vacuo* then poured into cold acetone to precipitate *2,3,5,6-tetrafluoro-1,4-xylene-bis(dimethylsulphonium bromide*) (105) (1.43g, 70%) mp 176-177^{o}C (from methanol) (Found: C,31.04; H,3.25%; M^{+},460 (DCI) $C_{12}H_{16}Br_2F_4S_2$ requires C,31.32; H,3.5%; M,460) δ_H(D_2O) 4.84(s,2xCH_2) 2.94 p.p.m. (s,4xCH_4); δ_F($CDCl_3$) -137.90 p.p.m(s,2,3,4,5-F).

7.5.4. α,α'-Dichloro-2,3,5,6-tetrafluoro-1,4-xylene (104)

A mixture of 2,3,5,6-tetrafluoro-1,4-benzenedimethanol (100) (8.68g, 41.33 mmol) and freshly distilled thionyl chloride (20ml) was heated under reflux for 5h. Excess thionyl chloride was removed by distillation, the residue treated with potassium carbonate and extracted with diethyl ether. The combined extracts were dried ($MgSO_4$), the solvent evaporated *in vacuo* and the crude product (20.34g) purified by sublimation (55^{o}C/10^{-2}mm Hg) to give *α,α'-dichloro-2,3,5,6-tetrafluoro-1,4-xylene* (104) (9.90g, 97%) mp 77-78^{o}C [from light petroleum (bp 40-60^{o}C)] (Found: C, 38.94; H, 1.44%; M^{+},246,248 $C_8H_4Cl_2F_4$ requires C, 38.90; H, 1.63%; M, 246,248 (based on chlorine isotopes)) δ_H($CDCl_3$) 4.67 p.p.m. (s, 2xCH_2Cl); δ_F($CDCl_3$) -143.2 p.p.m.(s, 4xF).

7.5.5. 2,3,5,6-Tetrafluoro-1,4-xylene-bis(diethylsulphonium chloride) (106)

A solution of (104) (2.83g, 11.5 mmol) in methanol (50 ml), water (12 ml) and diethyl sulphide (8.3g, 92 mmol) was heated at 50°C for 480 h. The solution was concentrated by evaporation *in vacuo* then poured into ice cold acetone to precipitate *2,3,5,6-tetrafluoro-1,4-xylene-bis(diethylsulphonium chloride) dihydrate* (106) (2.90g, 59%) mp (v. broad) (from methanol/acetone) (Found: C, 41.44; H, 6.24% $C_{16}H_{24}Cl_2F_4S_2.2H_2O$ requires C, 41.47: H, 6.09%) $\delta_H(^2H_2O)$ 5.13 (s, 4H, $\underline{CH_2}S(CH_2CH_3)_2$); 3.69 (q, 8H, $CH_2S(CH_2CH_3)_2$), J_{CH_2,CH_3} 7.3Hz; 1.74 p.p.m. (t, 12H, CH_3), J_{CH_3,CH_2} 7.3Hz; $\delta_F(^2H_2O)$ -137.9 p.p.m. (s,4xF).

7.5.6. Typical polymerisation of the bis(sulphonium salts).

A solution of (106) (0.82g, 1.92mmol) in water (20ml), cooled to 0°C was treated with sodium hydroxide (1.92mmol, 0.1932M) and stirred at 0°C for 1 h, neutralised to pH 6.5 with dilute HCl, and dialysed with water for 3 days (by stirring product in a dialysis tube in a conical flask, the water being changed every 6-8 h.

Poly(alcohol) Synthesis: Preparation of:-

7.5.7. 1,4-diallyl-2,3,5,6-tetrafluorobenzene (124)

A solution of 2,3,5,6-tetrafluorobenzene (7.0g, 40 mmol) in dry THF (300 ml) at -78°C was treated with butyllithium in hexane (61.81 ml, 1.51M) and stirred at -78°C for 35 min. Anhydrous copper (I) iodide (19.6g, 0.103 mol) was added and the mixture was stirred at -78°C for a further 4 h. The resultant black suspension was treated with freshly distilled allyl bromide (17.6g, 0.146 mol) at a temperature less than -60°C then allowed immediately to warm up to room temperature, stirring at this temperature for a further 18 h. Addition of diethyl ether and washing with ammonia solution (2x150 ml, 2M) and dilute sulphuric acid

(2M) removed copper salts. The organic phases were dried ($MgSO_4$) and the solvents evaporated *in vacuo* to yield a yellow oil (11.0g). Distillation under reduced pressure provided *1,4-diallyl-2,3,5,6-tetrafluorobenzene* (124) (7.88g, 74%) (bp 50°C/0.08 mm Hg) (Found: C, 62.30; H, 4.32%; M^+, 230 $C_{12}H_{10}F_4$ requires C, 62.60; H, 4.38%; M, 230) $\delta_H(CDCl_3)$ 5.86 to 5.73 (m, $-CH_2C\underline{H}=CH_2$), 4.97 (d, $-CH_2CH=C\underline{H}_2$) J_{CH,CH_2}11.3Hz; 3.34 p.p.m. (d, $-C\underline{H}_2CH=CH_2$), $J_{CH_2,CH}$6.3Hz; $\delta_F(CDCl_3)$ -146.1 p.p.m. (s).

7.5.8. 2,3,5,6-Tetrafluorobenzene-1,4-diethanal (120)

A solution of the diallyl compound (124) (1.52g, 6.61 mmol) in dry dichloromethane (80 ml) at -20°C was treated with 6-7% ozone in oxygen for 120 min. (13.3 mmol ozone passed by KI calibration). The resultant blue solution was carefully added to a mixture of an excess of zinc dust in 50% acetic acid (50 ml) and stirred at room temperature for 1.5 h. The zinc was removed by filtration and the organic phase extracted with water (3x 100 ml), dried ($MgSO_4$) and solvents evaporated *in vacuo* to give *2,3,5,6-tetrafluorobenzene-1,4-diethanal* (120) (1.02g, 66%) mp 161-162°C [from diethyl ether/light petroleum (bp 40-60°C)] (Found C, 51.28; H, 2.72%; M^+, 234 (EI^+) $C_{10}H_6F_4O_2$ requires C, 51.30; H, 2.58%; M, 234) $\delta_H(CDCl_3)$ 9.78 (s, CHO); 3.91 p.p.m. (s, CH_2); $\delta_F(CDCl_3)$ -143.2 p.p.m. (s).

7.5.9. Polymerisation reaction of 2,3,5,6-tetrafluorobenzene-1,4-diethanal (120) with dilithio-2,3,5,6-tetrafluorobenzene (119).

To 2,3,5,6-tetrafluorobenzene (0.2g, 1.33mmol) in dry THF (15ml) at -78°C was added butyllithium in pentane (1.51M, 1.88ml) and the solution stirred for 0.5 h. To this was added the diethanal (120) (0.32g, 1.37mmol) in THF (5ml) (cooled to -78°C before addition *via* a cannula). The resultant mixture was stirred at this temperature for 0.5h before warming to room temperature and stirring for 18h. The product was acidified (40ml, 2M H_2SO_4) and extracted with ether, the organic extracts washed repeatedly with water, and then evaporated. The resultant yellow material was physically separated into a yellow powder (0.4g) and a yellow film (10-20mg). The film was heat treated with a change in colour being observed between 250°C-300°C/ $3x10^{-3}$mm Hg indicating a possible elimination reaction at this temperature.

EXPERIMENTAL TO CHAPTER SIX

Preparation of:-

7.6.1. 1,2-Dibromo-2-pentafluorophenylpropionic Acid (138)

A solution of (E)-2,3,4,5,6-pentafluorocinnamic acid (2.86g, 12 mmol) in dry chloroform (200 ml) was treated with bromine (2.0g, 12.5 mmol) and stirred at room temperature for 1 h under irradiation from a with a 100 W lamp. Evaporation of the solvent and residual bromine *in vacuo* gave *1,2-dibromo-2-pentafluorophenylpropionic acid* (138) (4.73g, 99%) mp 158-159°C [from light petroleum (bp 100-120°C)] (Found: C, 26.99; H, 0.65%; M^+, 398 (DCI) $C_9H_3Br_2F_5O_2$ requires C, 27.16; H, 0.76; M, 398); $\delta_H(CDCl_3)$ 9.21 (br, COO$\underline{H}$); 5.68 (d, CH); 5.14 p.p.m. (d, CH), $J_{1-H,2-H}$11.9Hz; $\delta_F(CDCl_3)$ -139.5 (br) and -141.6 (br) (2x s, 2-,6-F); -151.0 (t, 4-F); $J_{3-F,4-F}$ 21Hz; -160.5 p.p.m. (t, 3,5-F) $J_{2-F,3-F}$21Hz. The effect of the bromine adjacent to the pentafluorophenyl ring is to broaden the ^{19}F nmr signals corresponding to the 2,6- fluorines. This is also seen in the tribromide (142) (7.6.2.)

7.6.2. 1,1,2-Tribromo-2-Pentafluorophenylethane (142)

a) *Via* the Hunsdieker Reaction

1,2-Dibromo-2-pentafluorophenylpropionic acid (138) (15.43g, 38.8 mmol) dissolved in aqueous sodium hydroxide (0.198M, 196 ml, 38.8 mmol) was treated with silver nitrate (7.81g, 45.9 mmol in 100 ml). The precipitate was filtered, washed with cold water and dried *in vacuo* ($20^oC/3x10^{-3}$mm Hg) for 120 h to yield *silver 1,2-dibromo-2-pentafluoro-phenylpropionoate* (17.34g, 89%).

The silver salt (17.34g, 34.4 mmol) was suspended in dry carbon tetrachloride (300 ml), treated with bromine (5.70g, 35.6 mmol) and stirred at room temperature for 30h. The product was filtered through silica and the solvent evaporated. Distillation of the residue gave *1,1,2-tribromo-2-pentafluorophenylethane* (142) (8.1g, 54%) bp 40-$50^oC/3x10^{-3}$mm Hg (Found: C, 22.43; H, 0.36%; M^+, 436, 434, 432, 430; $C_8H_2Br_3F_5$ requires C, 22.17; H, 0.46%; M^+, 436, 434, 432, 430; (based on bromine isotope pattern); $\delta_H(CDCl_3)$ 6.18 (d, CH); 5.61 p.p.m. (d, CH), $J_{1-H,\ 2-H}$10.8Hz; $\delta_F(CDCl_3)$ -140.6 (br) (s, 2,6-F); -151.6 (t, 4-F), $J_{2-F,3-F}$21Hz; -160.7 p.p.m. (td, 3,4-F), $J_{3-F,\ 4-F}$21Hz.

b) *Via* the Cristol Modification

The acid (138) (0.4205g, 1.06 mmol) dissolved in carbon tetrachloride (50ml) was treated with red mercuric oxide (0.196g, 0.90 mmol) and bromine in carbon tetrachloride (0.542M, 1.95 ml, 1.06 mmol) and the mixture was heated under reflux in the dark for 4.5 h. The mixture was filtered, the solvent evaporated *in vacuo* and the residue was separated by flash chromatography on silica (15 x 3.5 cm diam.) using light petroleum as eluant to give two components: (*E*)-*1-bromo-2-pentafluorophenylethene* (136) (0.170g, 59%) (Found: C, 35.06; H, 0.70%; M^+,272,274; $C_8H_2BrF_5$ requires C, 35.20; H, 0.74%; M, 272, 274); $\delta_H(CDCl_3)$ 7.25 and 7.08 p.p.m. (d,2,CH=CHBr); J_{Ha-Hb},14.5Hz. $\delta_F(CDCl_3)$ -142.7 (dd,2,6-F); J,20.7Hz; J,8.5Hz; -154.8(t,4-F) J,20.6Hz; -162.5 p.p.m. (td,3,5-F) J,20.1Hz; J,3.3Hz.; and 1,1,2-tribromo-2-pentafluorophenylethane (142) (0.159g, 35%) bp 40-50°C/ $3x10^{-3}$mm Hg

7.6.3. De-bromination of (142)

A sample of (142) (7.45g, 17.2 mmol) dissolved in dry THF (60 ml) was treated with zinc dust (1.51g, 23.1 mmol) and the mixture heated under reflux for 6 h. The product was filtered, the filtrate acidified (2M sulphuric acid) and extracted with diethyl ether. The combined extracts were dried ($MgSO_4$), the solvents evaporated and the residue distilled to give (E)-1-bromo-2-pentafluorophenylethene (136) (3.65g, 78%) bp 30°C/$3x10^{-3}$mm Hg.

7.6.4 (E)-Pentafluorophenylethenylboronic Acid (149)

Pentafluorophenylacetylene (5.24g, 27 mmol) was treated with freshly distilled catecholborane (3.23g, 27 mmol) and the mixture heated at 70°C for 30h. The reaction products were cooled to room temperature and the remaining volatile materials were evaporated *in vacuo* (25°C/ $5x10^{-3}$mm hg). Hydrolysis of the residual solid (8.34g) by stirring with water over 1.5h followed by filtration gave the white crystalline product *(E)-2-pentfluorophenylethenyleneboronic acid* (149) (3.82g, 60%). mp 163-164°C (from water) (Found: C, 40.26; H, 1.61%; $M+1^+$, 239(CI) $C_8H_4BF_5O_2$ requires C, 40.38; H, 1.69%; M, 238); $\delta_H(^2H_6$ acetone) 7.23(s, $(B(OH)_2)$; 7.19(d,Ha) J_{Ha-Hb} 19Hz; 6.45 p.p.m. (d,H_b) J_{Hb-Ha}, 19Hz: $\delta_F(^2H_6$ acetone) -144.2 (m,2-,6-F); -157.0 (t,4-F), J, 20.4Hz; -164.3p.p.m. (m,3-,5-F).

7.6.5. (E)-1-Bromo-2-pentafluorophenylethene (136) from (E)-Pentafluorophenylethenylboronic Acid (149)

A mixture of (E)-2-pentafluorophenylethenylboronic acid (149) (1.31g,5.22 mmol) dissolved in aqueous sodium hydroxide (2M, 8.5ml, 17 mmol) and dichloromethane (40ml) was cooled to 0^{o}C and treated with bromine (0.833g, 5.52 mmol) in dichloromethane (10ml) and stirred for 1h. The organic phase was separated and the aqueous phase was extracted with dichloromethane. The combined organic phases were dried ($MgSO_4$), the solvent evaporated and the residue (1.7g) was distilled *in vacuo* to give (E)-1-bromo-2-pentafluorophenylethene (136) (bp 30^{o}/ $3x10^{-3}$mm Hg) (1.0g, 66%).

7.6.6. (E)-1-Iodo-2-pentafluorophenylethene(150) from (E)-Pentafluorphenylethenyl boronic Acid (149)

A mixture of (E)-2-pentafluorophenylethenylboronic acid (149) (2.31g, 9.71 mmol) dissolved in aqueous sodium hydroxide (0.1932M, 151ml, 0.029 mol) and dichloromethane (100ml) was cooled to 0^{o}C and treated with iodine (4.0g, 15.7 mmol) in dichloromethane (250ml) and stirred for 18h. The organic phase was separated and the aqueous phase was extracted with dichloromethane. The combined organic phases were dried ($MgSO_4$), the solvent evaporated and the residue (3.06g) was distilled *in vacuo* to give *(E)-1-iodo-2-pentafluorophenylethene* (150) bp 40^{o}C/ $3x10^{-3}$mm Hg (2.68g,88%) (Found: C, 29.75; H, 0.55%; M^+,320; $C_8H_2F_5I$ requires C,30.03; H, 0.63%; M,320) $\delta_H(CDCl_3)$ 7.41 p.p.m.(s) (The two vinylic protons having identical shifts) $\delta_F(CDCl_3)$ -143.6(m,2,6-F); -154.6(t,4-F); -162.5 (m,3,5-F).

7.6.7. Reaction of (Z)-1-Bromo-2-Pentafluorophenylethene (132) with Sodium Methoxide

A solution of (Z)-1-bromo-2-pentafluorophenylethene (132) (1.0g, 3.66 mmol) in dry methanol (50 ml) was treated with sodium methoxide in methanol (10 ml, 0.435M) and heated under reflux for 4 h. The mixture was added to dilute sulphuric acid (50 ml, 2M) and the solution extracted with diethyl ether. The ether extracts were dried ($MgSO_4$) and the solvent evaporated *in vacuo* to give a colourless oil (1.13g) which on analysis by ^1H nmr spectroscopy showed there were two new components and unreacted starting material present in the ratio 73:20:7. The unreacted starting material was selectively removed from the mixture by evaporation *in vacuo* (22^oC/ 5x10^{-3}mm Hg) and the residue was separated by gas liquid chromatography (SE 10% column at 200^oC) to give the major product, an oil, *(Z)-1-bromo-2-(2,3,5,6-tetrafluoro-4-methoxyphenyl) ethene* (151). (Found C, 37.96; H, 1.75%; M^+, 286; $C_9H_5BrF_4O$ requires C, 37.92; H, 1.77; M, 286) $\delta_H(CDCl_3)$ 6.17 and 6.03 (2d, CH=CHBr) $J_{Ha\text{-}Hb}$2Hz; 4.12 p.p.m. (t, OCH_3) $J_{2,4\text{-}F,CH_3}$1.6Hz. $\delta_F(CDCl_3)$ -141.8 (d, 1-F, 5-F) $J_{Ha,\ 1\text{-}F}$24Hz; -158.3 p.p.m. (s, 2-F,4-F) and the minor component *2,3,5,6-tetrafluoro-4-methoxyphenylethyne* (152) mp 54.0-55.0^oC (Found C, 53.26; H, 1.98%; M^+, 205; $C_9H_4F_4O$ requires C, 52.96; H, 1.98%; M, 205) $\delta_H(CDCl_3)$ 4.12 (t, OCH_3) $J_{2,4\text{-}F,CH_3}$1.5Hz; 3.45 p.p.m. (s, CH); $\delta_F(CDCl_3)$ -137.9 (s, 1-F, 5-F); -158.1 p.p.m. (s, 2-F, 4-F).

7.6.8. Grignard Reagent from (132)

The (Z)-bromo-styrene (132) (1.51g,5.53 mmol) was added dropwise to magnesium (0.5g) activated with 1,2-dibromoethane in dry diethyl ether (20 ml) at reflux temperature and heated under reflux for 5.5 min to form a deep red coloured solution. Water was added to the solution at room temperature followed by dilute sulphuric acid (50 ml, 2M) and extraction with ether and subsequent evaporation of the dried ($MgSO_4$) extracts gave a brown/red oil. The oil was fractionally evaporated *in vacuo* (25^oC/5x10^{-3}mm Hg) to give 2,3,4,5,6-pentafluorostyrene (29.3 mg, 2.7%), identified by infrared and ^1H nmr spectroscopy followed by the less volatile unreacted starting material (0.2311g, 15%) identified similarly. The involatile residue (0.341g) was shown to be multicomponented by tlc on silica using ethylacetate /hexane (5/95 v/v) as eluant with the main material being at the baseline.

7.6.9. Polymerisation of the (Z)-bromo-styrene (132) using Magnesium activated with ethylene dibromide

A mixture of magnesium (0.1g, 4.1 mmol) in anhydrous THF (6 ml) activated with 1,2-dibromoethylene at 0°C was treated with (132) (1.0g, 3.66 mmol) dropwise over 10 min and stirred at room temperature for 60 h. The mixture was added to dilute sulphuric acid (25 ml, 2M) and extracted with diethyl ether. The combined extracts were dried ($MgSO_4$) and solvent evaporated to give a yellow solid. This was re-precipitated twice from THF by addition to methanol to give a pale yellow solid (153) (0.61g). The ^1H nmr showed broad peaks at 6.83, 3.67 and 1.80 p.p.m.; ^{19}F nmr broad peaks at -141, -156 and -162 p.p.m.

7.6.10. Reaction of (Z)-2-Pentafluorophenyl-1-ethenyllithium (154) with hexafluorobenzene

A solution of the (Z)-bromo-styrene (132) (1.81g, 6.62 mmol) in dry diethyl ether (20 ml) at -78°C was treated with butyllithium in hexane (4.42 ml, 1.56M) and stirred at -78°C for 2h. Hexafluorobenzene (2.703g, 14.5 mmol) in dry monoglyme (20 ml) was added and the mixture was very rapidly warmed to -20°C and stirred at this temperature for 15h. The mixture was treated at room temperature with sulphuric acid (2M), extracted with dichloromethane, the extracts dried ($MgSO_4$) and the solvents evaporated to yield a crude brown product (2.12g) which was separated by chromatography on silica (15x3 cm diam.) using light petroleum (bp. 40-60°C) as eluant to give three components: (i) (Z)-Ar2 (*cis*-decafluorostilbene) (156) (0.780g, 34%) mp 56.5-57.5°C [from light petroleum (bp. 40-60°C)] (Lit 53[148]) (Found: C, 46.78; H, 0.71%; M^+, 360; $C_{14}H_2F_{10}$ requires C, 46.68; H, 0.56%; M, 360) $\delta_H(CDCl_3)$ 6.02 p.p.m.(s, CH); $\delta_F(CDCl_3)$ -142.2 (dd, 2-F), J 22Hz, J, 8Hz; -154.1 (t, 4-F) J,21Hz; -162.0 (m, 3-F); $\lambda_{max}(CH_2Cl_2)$ 241 nm (ϵ 7400); ν_{max} (olefinic C-H) 2940; (olefinic C=C) 1657 cm^{-1};

(ii) ***(Z)-Ar3*** (157) (0.421g, 30%) mp 163.0-162.5^{o}C [from light petroleum (bp. 80-100^{o}C)] (Found: C, 46.96; H, 0.85%, M^+, 534. $C_{22}H_4F_{14}$ requires C, 49.46; H, 0.76%, M, 534); $\delta_H(CDCl_3)$ 6.07 (s, H_b); 6.02 p.p.m. (s, H_a); $\delta_F(CDCl_3)$ -142.1 (dd, 2-F) J, 21Hz, J, 8Hz; -142.7 (s, 2x 2'-F); -154.3 (t, 4-F) J, 21 Hz; -162.1 p.p.m. (m, 3-F); $\lambda_{max}(CH_2Cl_2)$ 245.7 nm (ϵ 24,000), ν_{max}(olefinic C-H)2920, 2850; (olefinic C=C)1630, 1660 cm^{-1};

(iii) ***(Z)-Ar4*** (158) (0.0563g, 3%) mp 167-168^{o}C [from light petroleum (bp. 100-120^{o}C)] (Found: C, 51.15; H, 0.87%; M^+,708; $C_{30}H_6F_{18}$ requires C, 50.85; H, 0.85%; M, 708); $\delta_H(CDCl_3)$ 6.08 (s, H_b, H_c); 6.03 p.p.m. (s, H_a); $\delta_F(CDCl_3)$ -142.0 (dd, 2-F) J, 22Hz; J, 8Hz; -142.6 (m, 2',3'-F); -154.3 (t, 4-F) J, 21Hz; -162.1 p.p.m. (m, 3-F); $\lambda_{max}(Ch_2Cl_2)$ 243.8 nm (ϵ 40,200). ν_{max}(olefinic C-H) 2920, 2850; (olefinic C=C) 1630, 1655 cm^{-1}.

Strongly retained materials flushed off many columns with methanol were taken up in light petroleum (bp. 80-100^{o}C) and re-chromatographed on silica (15 x 3 cm diam.) using toluene/light petroleum (bp. 40-60^{o}C) (7/93 v/v) as eluant to yield more (Z)-Ar4 and two further products:

(iv) ***(Z)-Ar5*** (159) mp 223-224^{o}C [from light petroleum (bp 100-120^{o}C)] (Found: C, 51.72; H, 0.98%; M^+, 882. $C_{38}H_8F_{22}$ requires C, 51.72; H, 0.91%; M, 882). $\delta_H(CDCl_3)$ 6.07 (s, H_b,H_c,H_d); 6.02 (s, H_a). $\delta_F(CDCl_3)$ -142.6 (dd, 2-F) J, 23Hz, J, 8Hz; -142.6 (m, 2',3',2"-F); -154.3 (t, 4-F) J, 21 Hz; -162.1 p.p.m. (m, 3-F); $\lambda_{max}(CH_2Cl_2)$ 248.0 (ϵ 39,800). ν_{max}(olefinic C-H) 2930, 2860; (olefinic C=C) 1630, 1658 cm^{-1}, and (v) ***(Z)-Ar6*** (160), not pure (ca. 75%), M^+, 1056, M, 1056.

Reactions to form oligomeric F-PPVs'

7.6.11. Lithiation of (E)-1-Bromo-2-Pentafluorophenylethene (136) with butyllithium and reaction with hexafluorobenzene in monoglyme

A solution of (136) (0.40g, 1.47 mmol) in dry diethyl ether (30 ml) at -78°C was treated with butyllithium in hexane (1.58M, 0.93 ml, 1.47 mmol) and the mixture stirred at -78°C for 2 h. Hexafluorobenzene (0.68g, 3.66 mmol) in dry monoglyme (20 ml) was added to the pale red mixture and the resultant deep blue solution was warmed to -20°C. After stirring at this temperature for 16 h, the solution was warmed to room temperature, acidified (2M, sulphuric acid) and extracted with diethyl ether. The combined extracts were dried ($MgSO_4$), the solvent evaporated *in vacuo* and the crude product (0.69g) purified by chromatography on silica (15x5 cm diam.) using light petroleum (bp 40-60°C) as eluant and evaporated onto a cold finger (30°C/ $3x10^{-3}$mm Hg) to give as the major product *(E)-1-bromo-2-(4-n-butyl-2,3,5,6-tetrafluorophenyl)ethene* (161) (0.25g, 55%) as a colourless liquid. (Found: C, 46.52; H, 3.48%; M^+, 311. $C_{12}H_{11}BrF_4$ requires C, 46.33; H, 3.56%; M, 311); $\delta_H(CDCl_3)$ 7.21 (d, Ha) $J_{Ha,Hb}$14.3Hz; 7.11 (d, Hb); 2.71 (t, $C\underline{H}_2CH_2CH_2CH_3$) 1.57 and 1.39 (m, $CH_2C\underline{H}_2C\underline{H}_2CH_3$); 0.94 p.p.m. (t, $CH_2CH_2CH_2C\underline{H}_3$) $\delta_F(CDCl_3)$ -144.5 and -145.7 p.p.m. (both m, 2-,6-F/3-,5-F unassigned).

7.6.12. Reaction of (E)-2-Pentafluorophenyl-1-ethenyllithium (167) with Hexafluorobenzene

A solution of (E)-1-iodo-2-pentafluorophenylethene (150) (1.0g, 3.125 mmol) in dry hexane (30 ml) at -20°C was treated with butyllithium in hexane (2.06ml, 1.52M) and stirred at -20°C for 1 h. The resultant white suspension was added to hexafluorobenzene (4.07g, 21.9 mmol) in dry THF (100 ml) at -78°C over 15 min. and stirred at -78°C for a further 15 min., allowed to warm to -20°C and stirred for 18 h. The mixture was treated at room temperature with sulphuric acid (2M), extracted with dichloromethane, and the combined extracts were filtered to remove a bright yellow insoluble organic product, the filtrate was dried ($MgSO_4$) and solvents evaporated *in vacuo* to give the total overall crude product (0.873g). Sublimation of this product (160°C/5x10^{-3}mm Hg) and separation of the sublimate by flash chromatography on silica (17 x 6 cm diam.) yielded pure fractions of the *trans*-stilbene[148] ((E)-Ar2) (163) (73 mg) and (E)-Ar3 (166) (31 mg). Slower fractions (90 mg) were redissolved in refluxing light petroleum (bp 60-80°C) and subject to separation by chromatography on silica (10 x 7.5 cm diam.) running the column at 45-55°C to yield (E)-Ar3 (166) (80 mg,) and (E)-Ar4 (168) (5 mg). Overall isolated yields based on amount of iodo-styrene used : *trans*-stilbene (73mg, 7.0%), (E)-Ar3 (110mg, 14.0%), (E)-Ar4 (5mg, 0.6%).

(i) **(E)-Ar2** *trans*-stilbene (163) mp 101-102°C [from light petroleum (bp 40-60°C)] (Lit[148]. 96.5-97.5°C) (Found: C, 46.42; H, 0.80%; M^+, 360 (EI^+) $C_{14}H_2F_{10}$ requires C, 46.68; H, 0.56%; M^+ 360) $\delta_H(CDCl_3)$ 7.32 p.p.m. (s). $\delta_F(CDCl_3)$ -142.3 (m, 2-,6-F); -154.0 (t, 4-F); -162.5 (m, 3-,5-F).

(ii) ***(E)-Ar3*** (166) mp 202.5-203.0°C [from light petroleum (bp 100-120°C)] (Found: C, 49.25; H, 0.98%; M^+, 534 (EI^+) $C_{22}H_4F_{14}$ requires C, 49.46; H, 0.75%; M^+, 534) $\delta_H(^2H_8$ toluene) 7.35 p.p.m. (br, overlapping); $\delta_F(^2H_8$ toluene) -143.0 (m, 2-,6-F); -144.0 (s, 2'-,6'-F); -154.8 (t, 4-F); -163.1 p.p.m. (m, 3-F).

(iii) ***(E)-Ar4*** (168) (Found accurate mass analysis 708.0123 $C_{30}H_6F_{18}$ requires 708.0182) $\delta_H(^2H_8$ toluene) 7.36 p.p.m. (s); $\delta_F(^2H_8$ toluene) -142.9 (m, 2-,6-F); -143.8 (m, 2'-,6'-F/3'-,5'-F unassigned); -154.8 (t, 4-F); -163.1 (bm, 3-,5-F). The remainder of the material was in the bright yellow insoluble material and in the involatile residue from the sublimation.

7.6.13. Poly(2,3,5,6-tetrafluorophenylenevinylene) (169)

A solution of (E)-1-iodo-2-pentafluorophenylethene (150) (1.0g, 3.125 mmol) in dry hexane (10ml) at -20^{o}C was treated with butyllithium in hexane (2.05 ml, 1.52M) and stirred at -20^{o}C for 1h. The resultant white suspension was added to dry THF (40ml) at -78^{o}C and the mixture allowed to warm to -20^{o}C stirring at this temperature for 18h. The blue/black gelatinous product was treated with sulphuric acid (2M) warmed to room temperature and stirred for a further 4h; the bright yellow solid produced was filtered and washed with water. Soxhlet extractions with water (to remove LiF), ethanol, water, ethanol, diethyl ether (48h each) purified the product (0.53g) Further extraction with toluene (200 h) removed any lower molecular weight fractions. See Section 6.7.3. for analysis.

APPENDICES

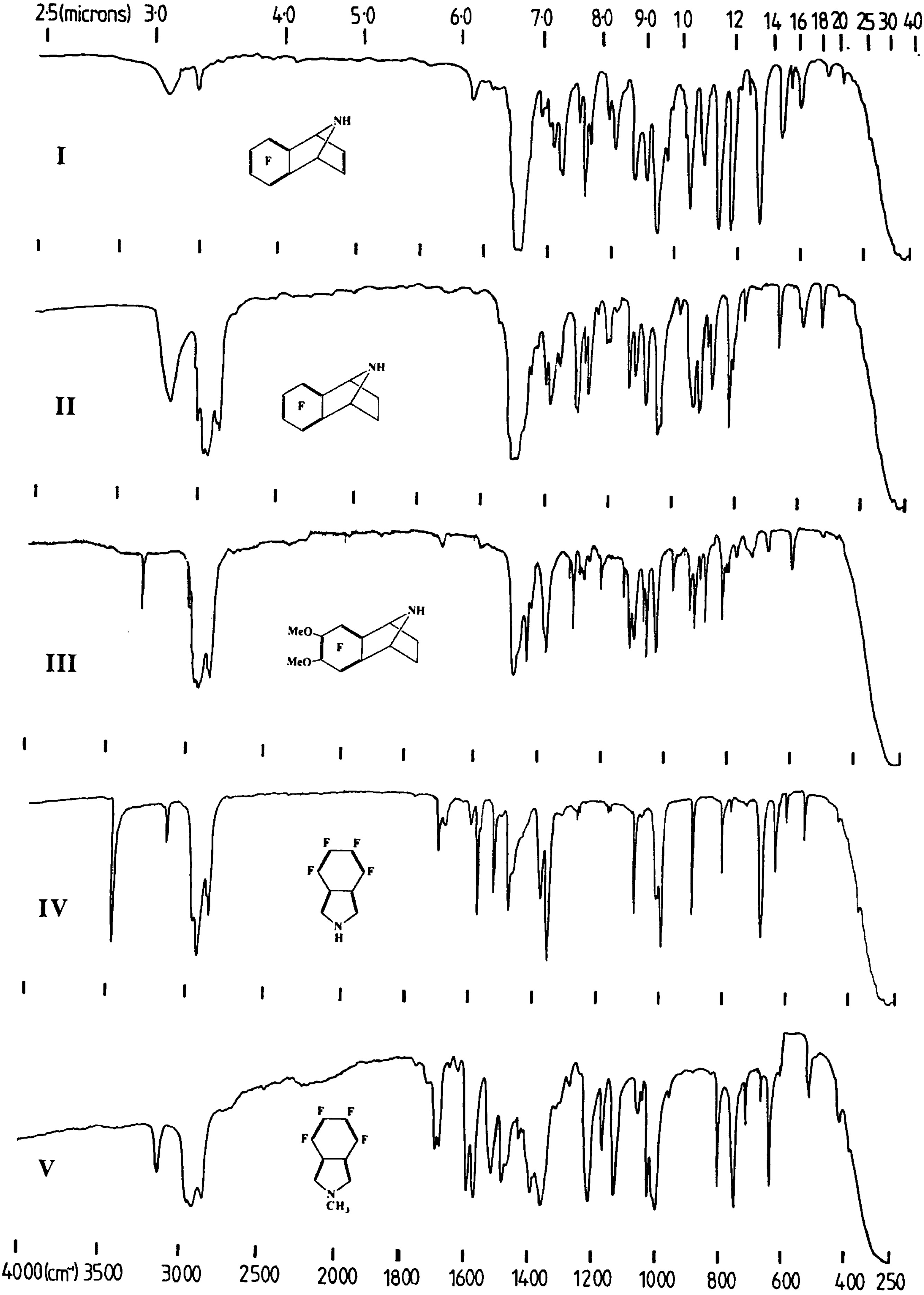
APPENDIX I

INFRA-RED SPECTRA

Samples run as liquid films using KBr plates (L), as a KBr disc (D),as a nujol mull (NM) or as a polymer film (PF).

Compound Number	Name of Compound
I	5,6,7,8-Tetrafluoro-1,4-dihydronaphthalene-1,4- imine (74) (L)
II	5,6,7,8-Tetrafluoro-1,2,3,4-tetrahydronaphthalene-1,4-imine (73) (NM)
III	5,8-Tetrafluoro-6,7-dimethoxy-1,2,3,4-tetrahydronaphthalene -1,4-imine (77) (NM)
IV	5,6,7,8-Tetrafluoroisoindole (71) (NM)
V	N-Methyl-5,6,7,8-tetrafluoroisoindole (68) (NM)
VI	5,6,7,8-Isothianaphthene (51) (NM)
VII	Dimethyl-5,6,7,8-tetrafluoronaphthalene-2,3-dicarboxylic acid (59) (D)
VIII	1,2,3,4,5,6,7,8-octafluoroanthracene (60) (NM)
IX	Poly(1,3-dihydroisothianaphthene) (65) (PF)
X	Poly(1,3-dihydroisothianaphthene 2,2-dioxide) (66) (PF on AgCl)
XI	Polyisothianaphthene (80) (PF)
XII	1,3,4,5,6,7,8-Heptafluoronaphthalen-2-ylmethyl methylsulphoxide (56) (NM)
XIII	1,3,4,5,6,7,8-Heptafluoronaphthalene-2-carbaldehyde (57) (NM)
XIV	4,5,6,7,8,9-Hexafluoronaphtho[1,2-c]thiophene (55) (NM)
XV	8-Butyl-4,5,6,7,9-pentafluoronaphtho[1,2-c]-thiophene (58) (NM)

Compound Number	Name of Compound
XVI	(Z)-1-bromo-2-(2,3,5,6-tetrafluoro-4-methoxy-phenyl)ethene (151) (L)
XVII	2,3,5,6-tetrafluoro-4-methoxyphenylethyne (152) (NM)
XVIII	Polymer Unknown (153) (D)
XIX	2,3,5,6-tetrafluoro-1,4-benzenedimethanol (100) (NM)
XX	α,α'-dibromo-2,3,5,6-tetrafluoro-1,4-xylene (103) (NM)
XXI	α,α'-dichloro-2,3,5,6-tetrafluoro-1,4-xylene (104) (NM)
XXII	2,3,5,6-tetrafluoro-1,4-xylene-bis(dimethylsulphonium bromide) (105) (NM)
XXIII	2,3,5,6-tetrafluoro-1.4-xylene-bis(diethylsulphonium chloride) (106) (NM)
XXIV	1,2-dibromo-2-pentafluorophenylpropionic acid (138) (NM)
XXV	1,1,2-tribromo-2-pentafluorophenylethane (142) (L)
XXVI	(E)-pentafluorophenylethenylboronic acid (149) (NM)
XXVII	(E)-1-bromo-2-pentafluorophenylethene (136) (L)
XXVIII	(E)-1-iodo-2-pentafluorophenylethene (150) (L)
XXIX	(E)-1-bromo-2-(4-n-butyl-2,3,5,6-tetrafluorophenyl)ethene (132) (L)
XXX	(Z)-Ar2 (156) (D)
XXXI	(Z)-Ar3 (157) (D)
XXXII	(Z)-Ar4 (158) (D)
XXXIII	(Z)-Ar5 (159) (D)
XXXIV	(E)-Ar2 (163) (D)
XXXV	(E)-Ar3 (166) (D)
XXXVI	Poly2,3,5,6-tetrafluorophenylenevinylene) (169) (D)
XXXVII	1,4-di(prop-2-enyl)-2,3,5,6-tetrafluorobenzene (124) (L)
XXXVIII	2,3,5,6-tetrafluorobenzene-1,4-diethanal (120) (D)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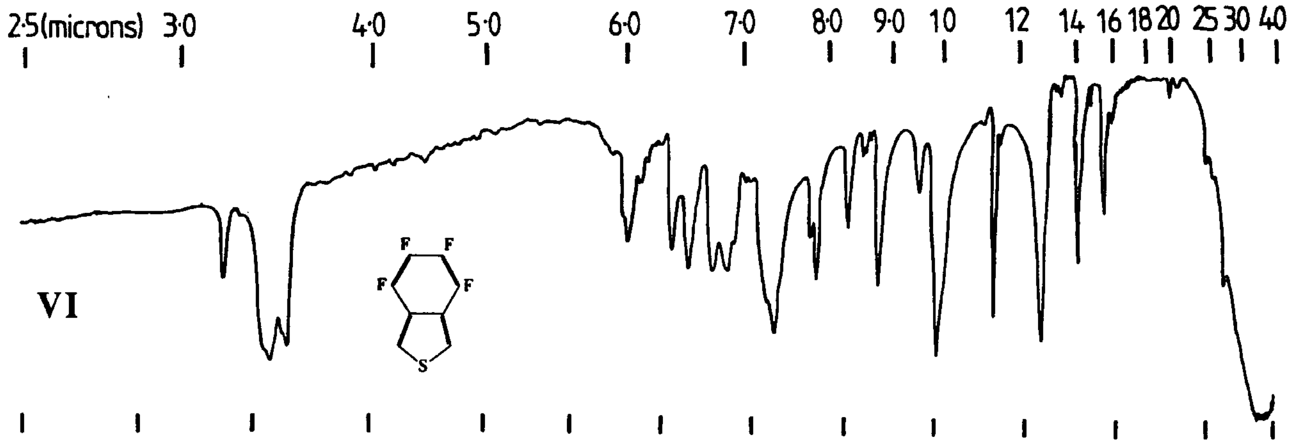
I
NH
F
II
NH
F
III
NH
MeO
MeO
F
IV
F F
F F
N
H
V
F F
F F
N
CH₃
4000(cm⁻¹) 3500 3000 2500 2000 1800 1600 1400 1200 1000 800 600 400 250

VI



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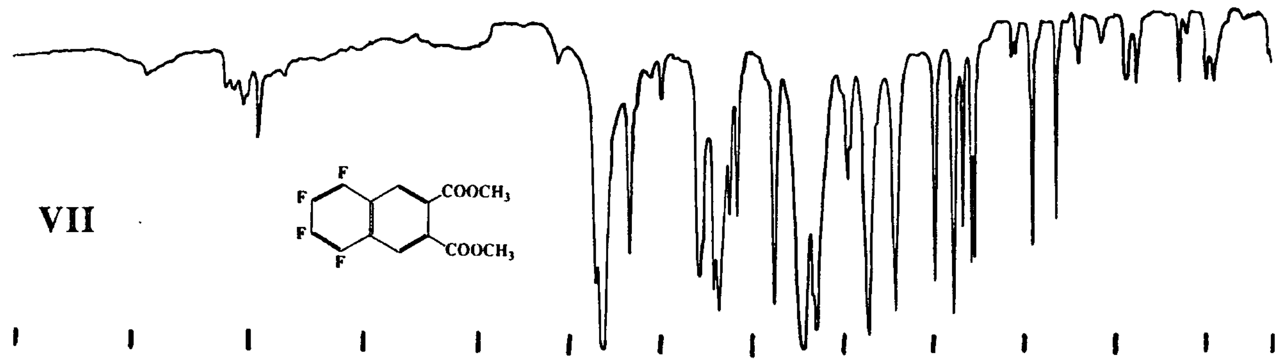

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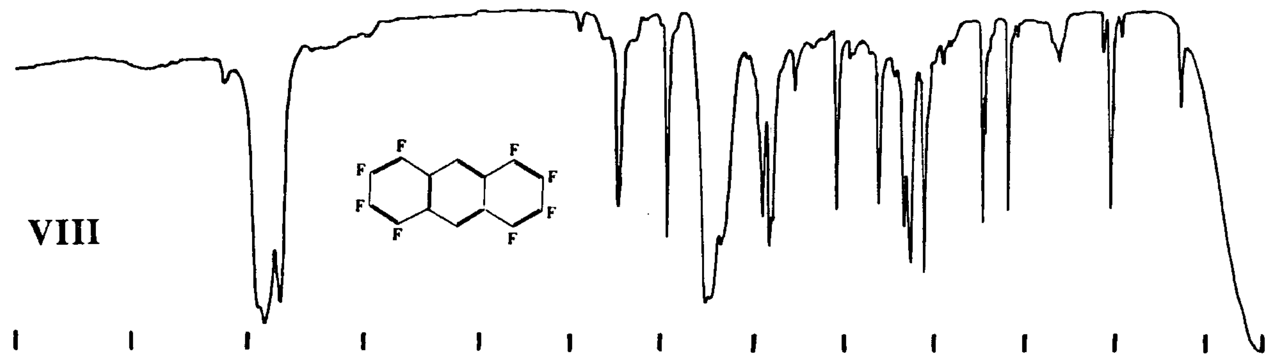

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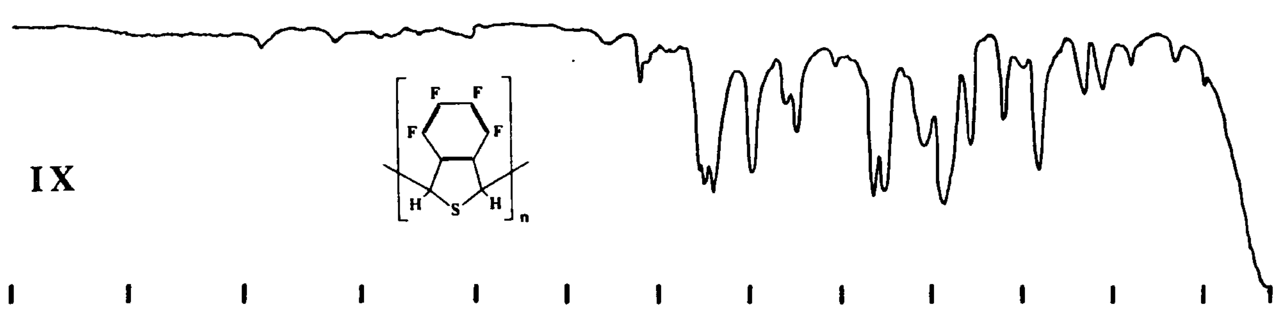

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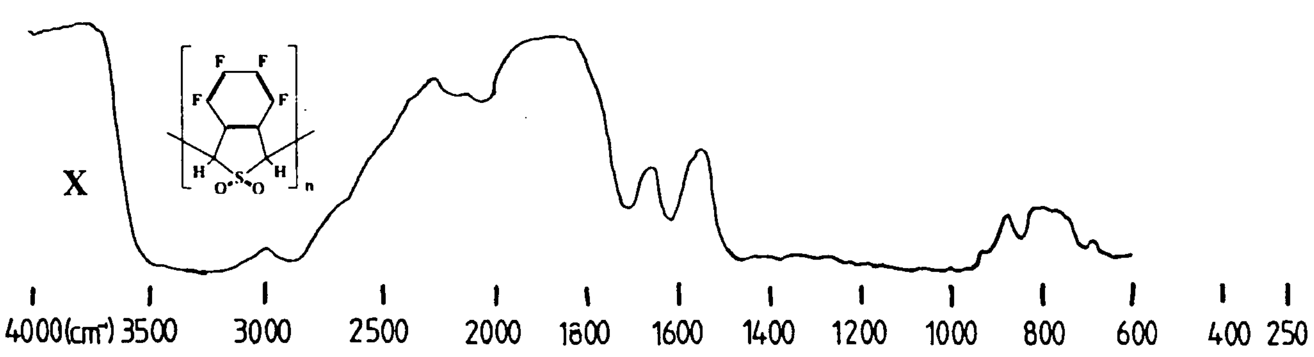

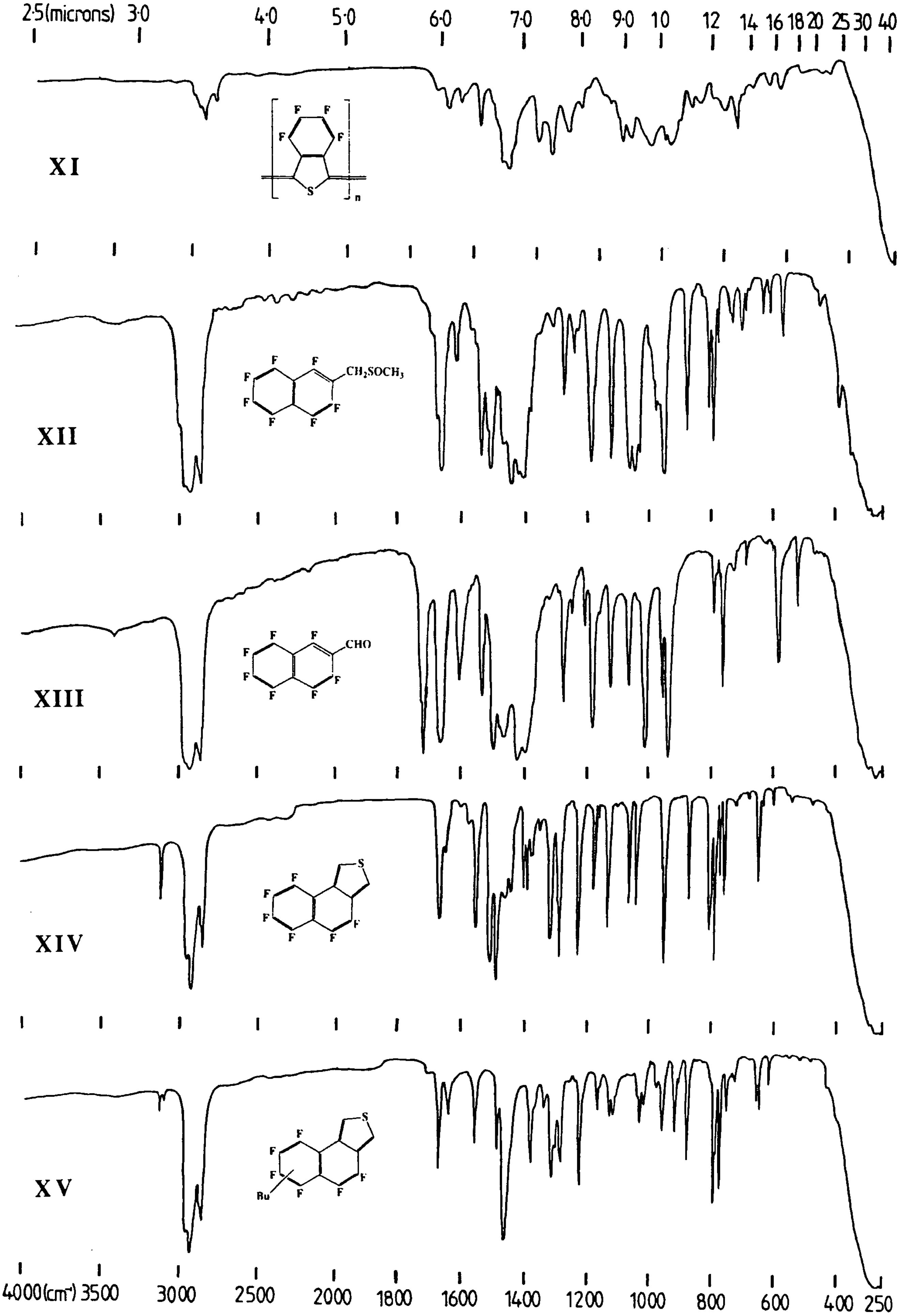
2·5(microns)
3·0
4·0
5·0
6·0
7·0
8·0
9·0
10
12
14
16
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20
25
30
40
XI
F
F
F
F
S
n
XII
F
F
CH₂SOCH₃
F
F
F
F
F
XIII
F
F
CHO
F
F
F
F
F
XIV
S
F
F
F
F
F
F
XV
S
F
F
F
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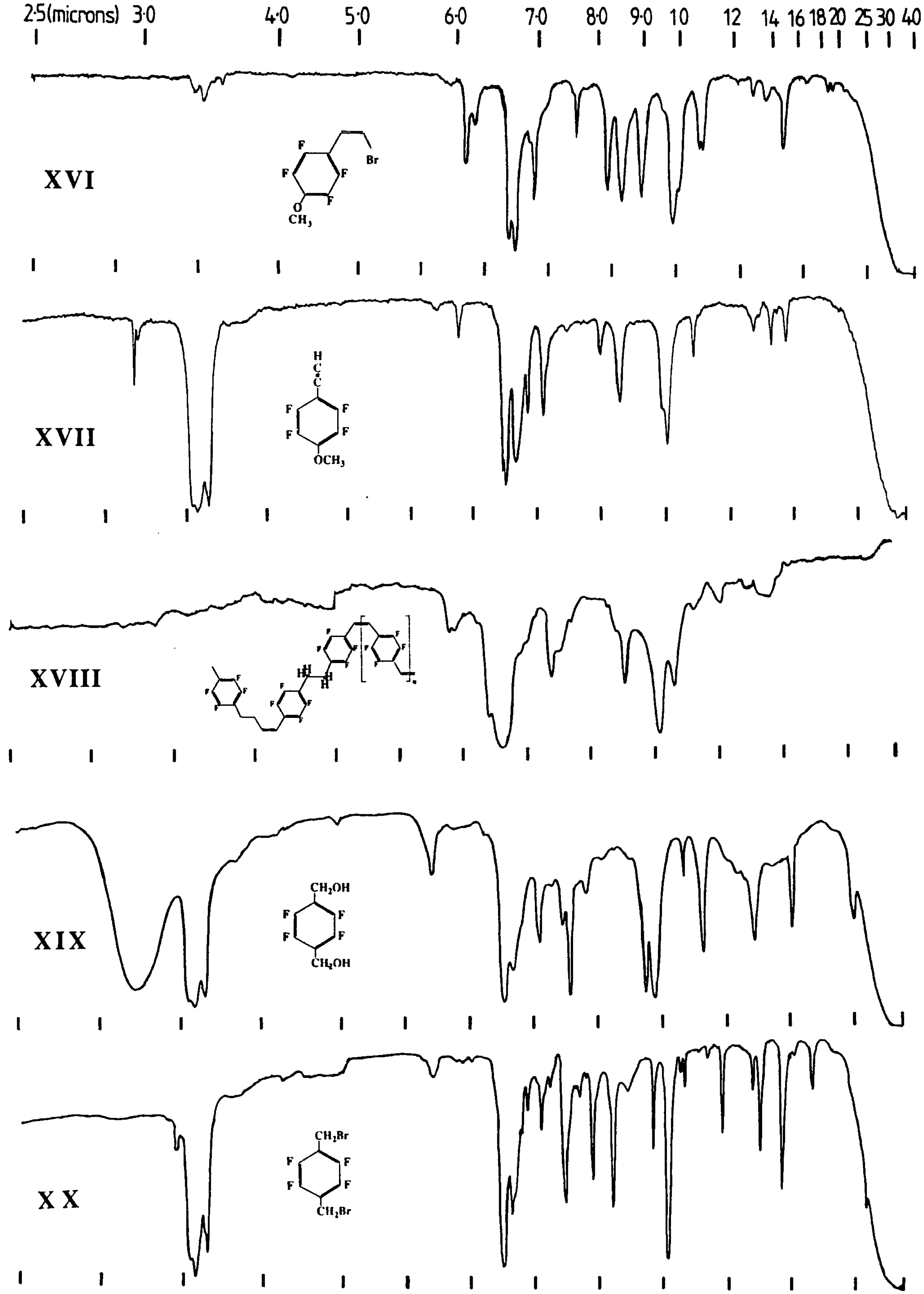
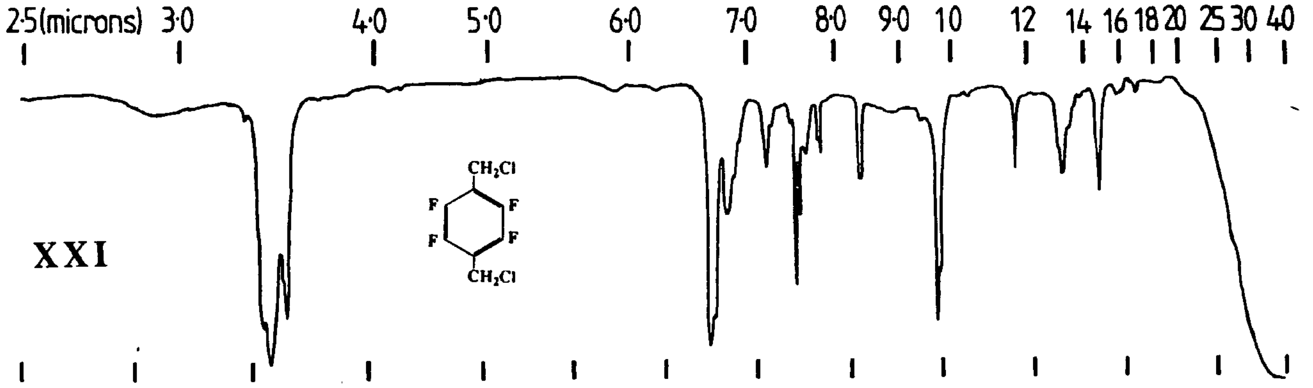
1200
1000
800
600
400
250


2·5(microns) 3·0 4·0 5·0 6·0 7·0 8·0 9·0 10 12 14 16 18 20 25 30 40
XVI
F F F F Br O CH₃
XVII
H C C F F F F OCH₃
XVIII
H H H F F F
XIX
CH₂OH F F F F CH₂OH
XX
CH₂Br F F F F CH₂Br
4000(cm⁻¹) 3500 3000 2500 2000 1800 1600 1400 1200 1000 800 600 400 250



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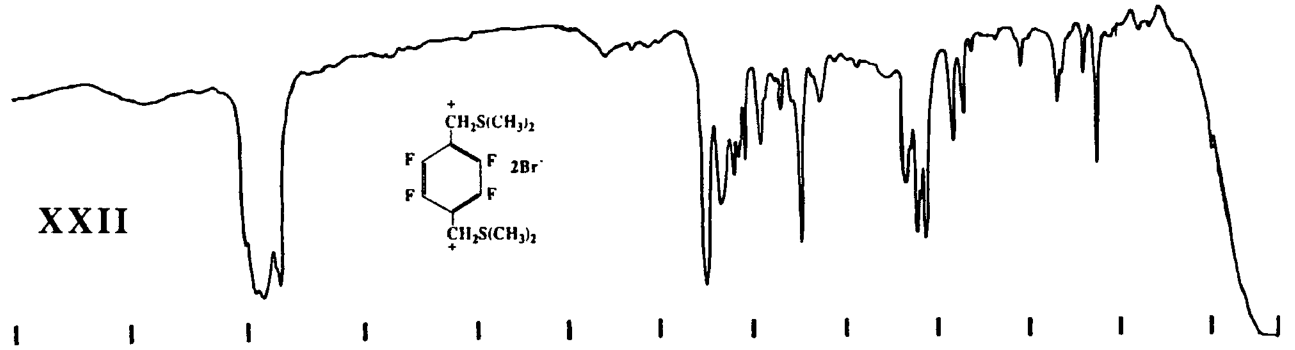

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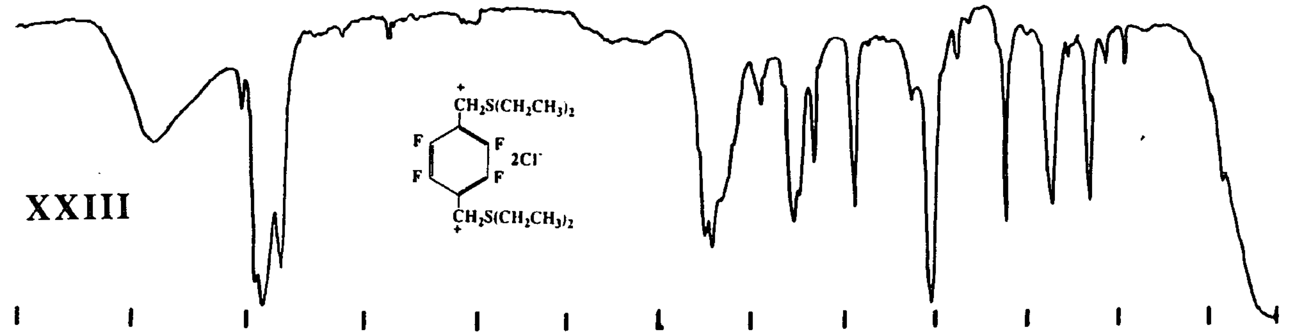

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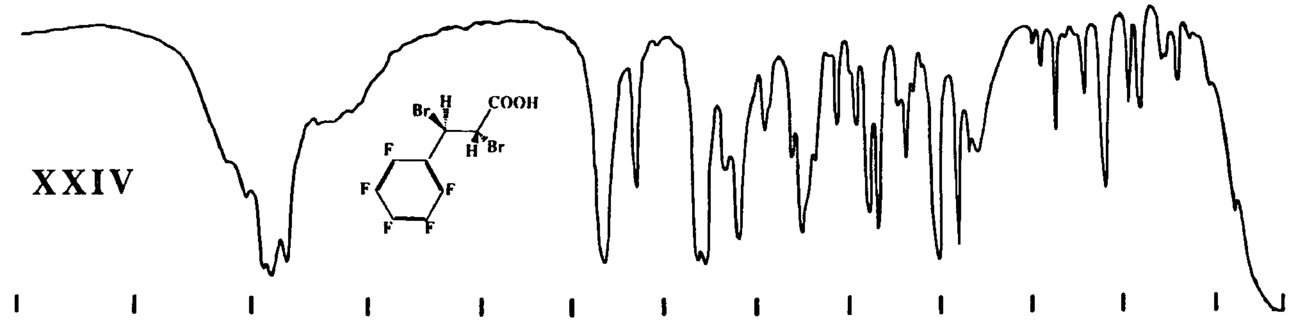

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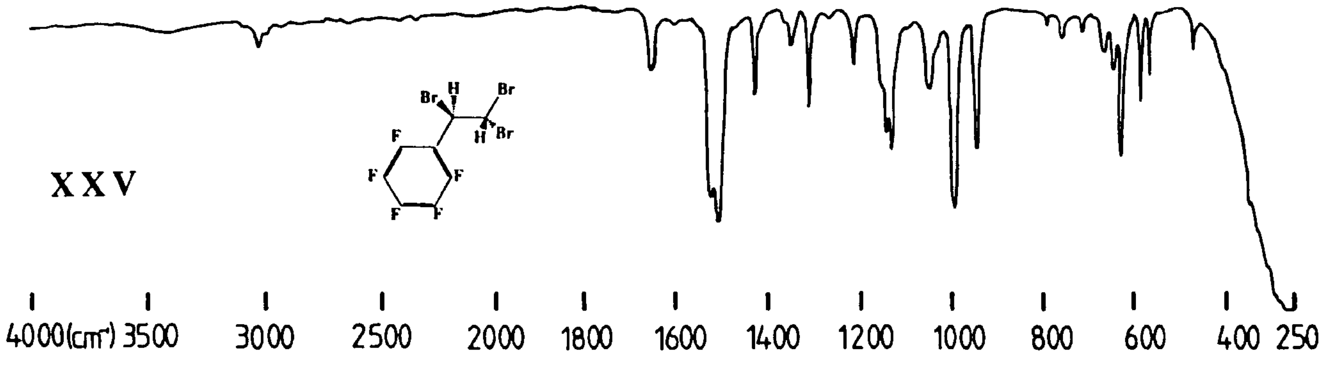

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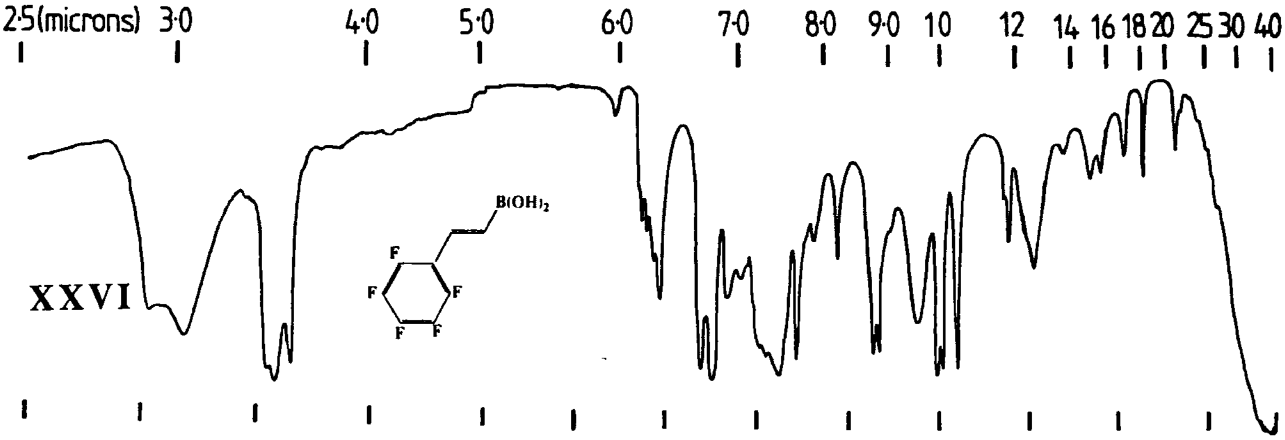

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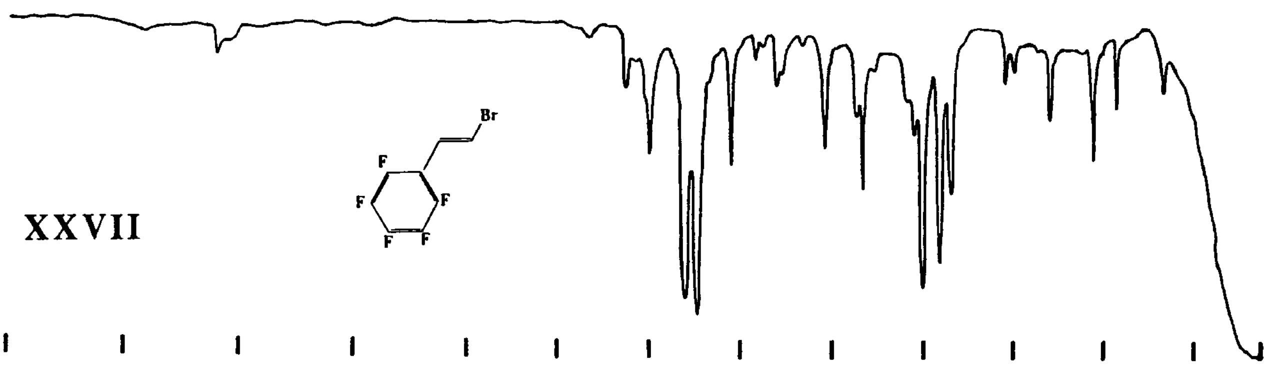

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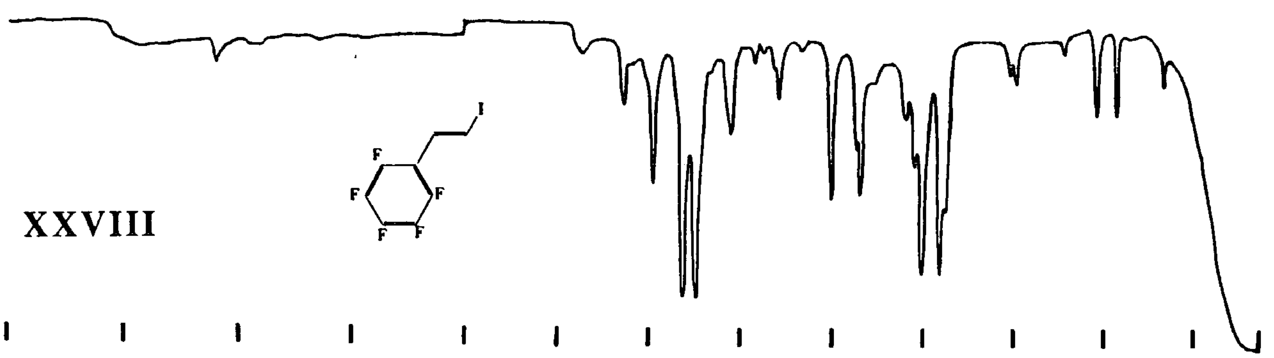

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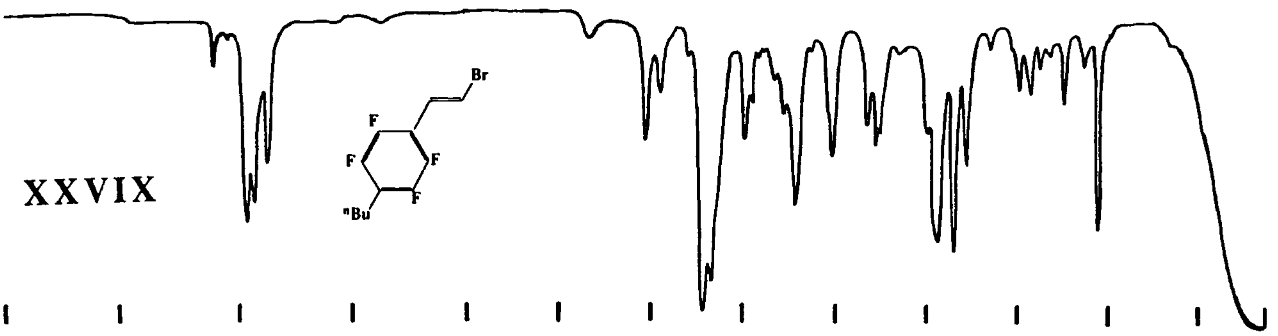

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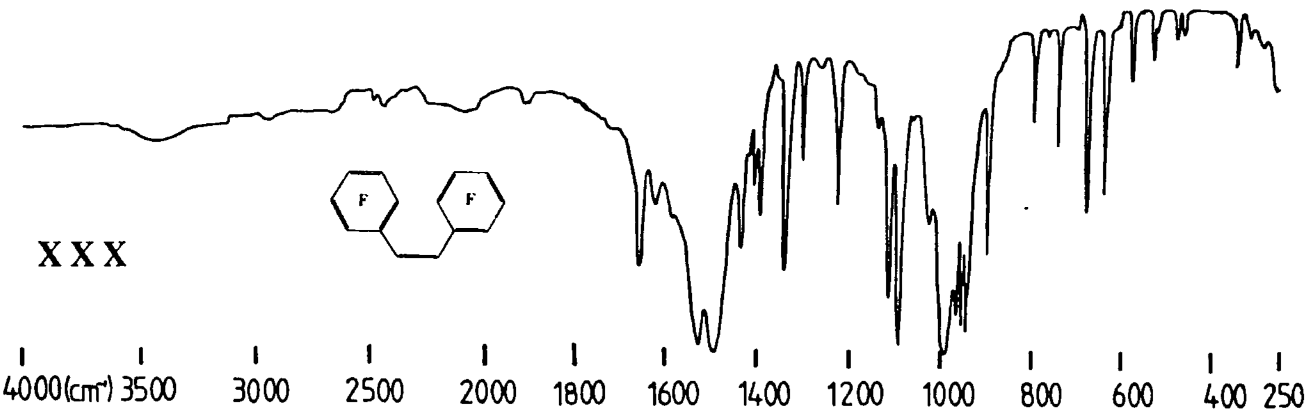

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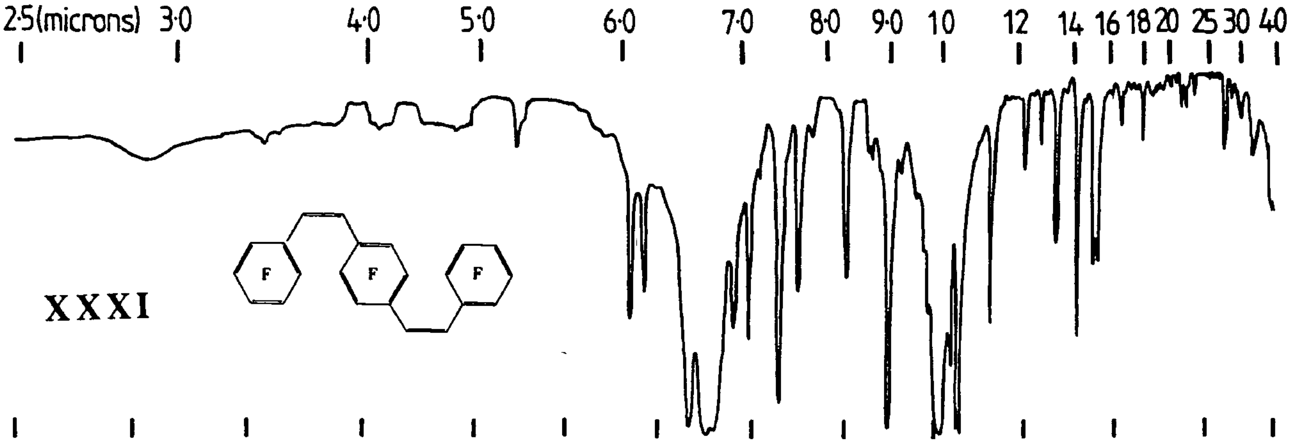

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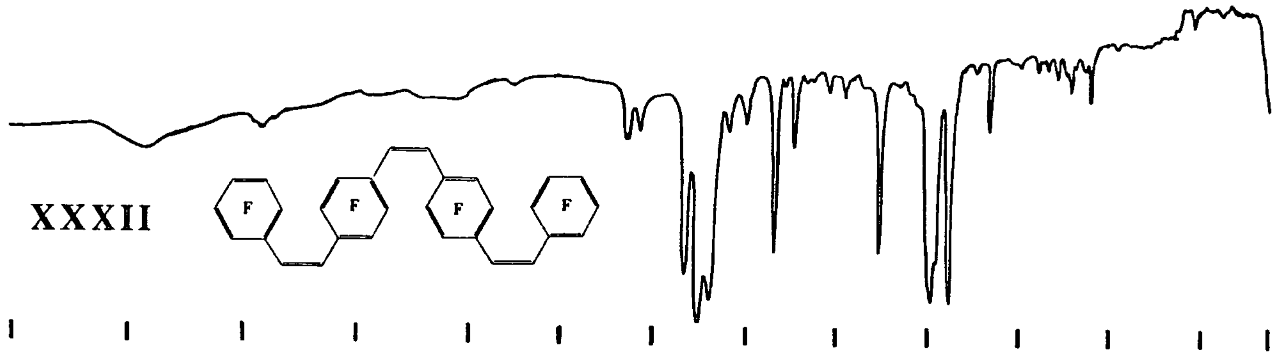

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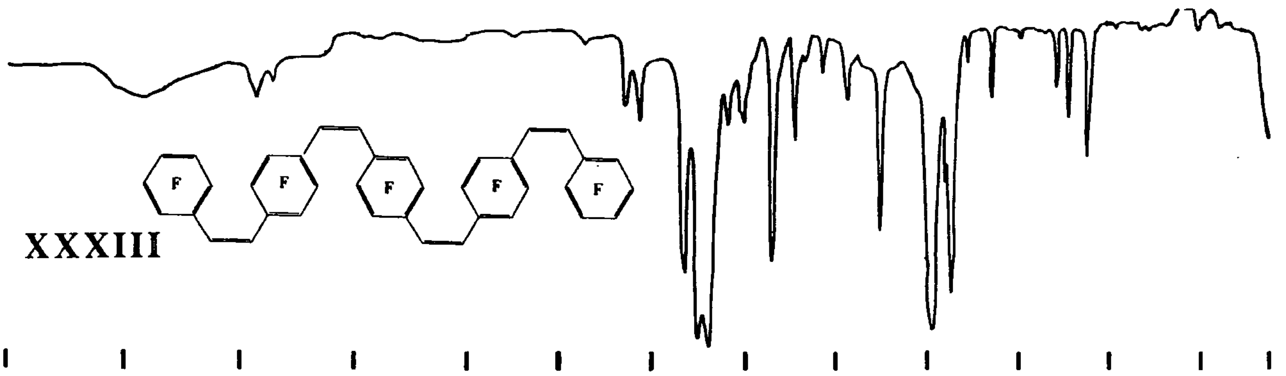

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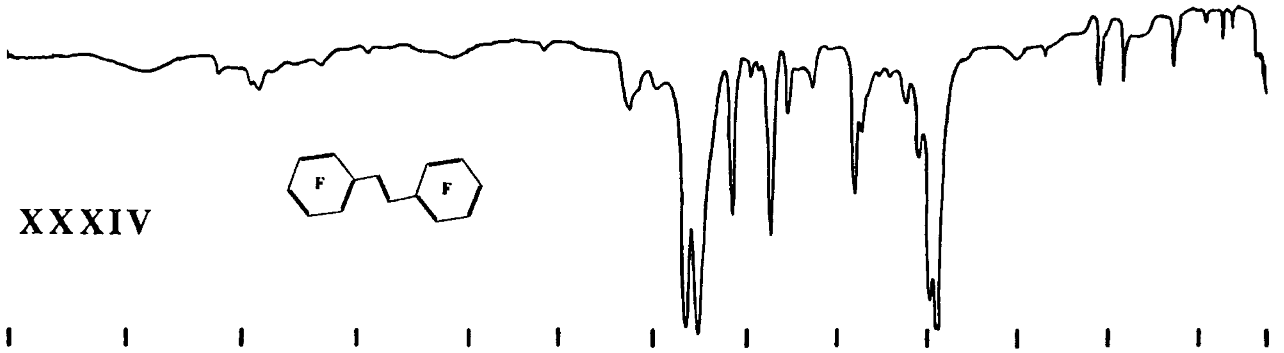

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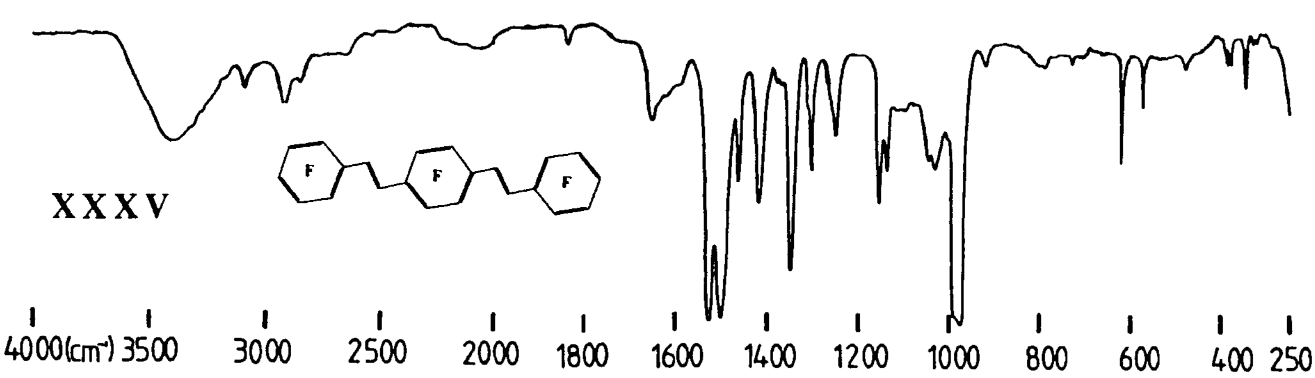

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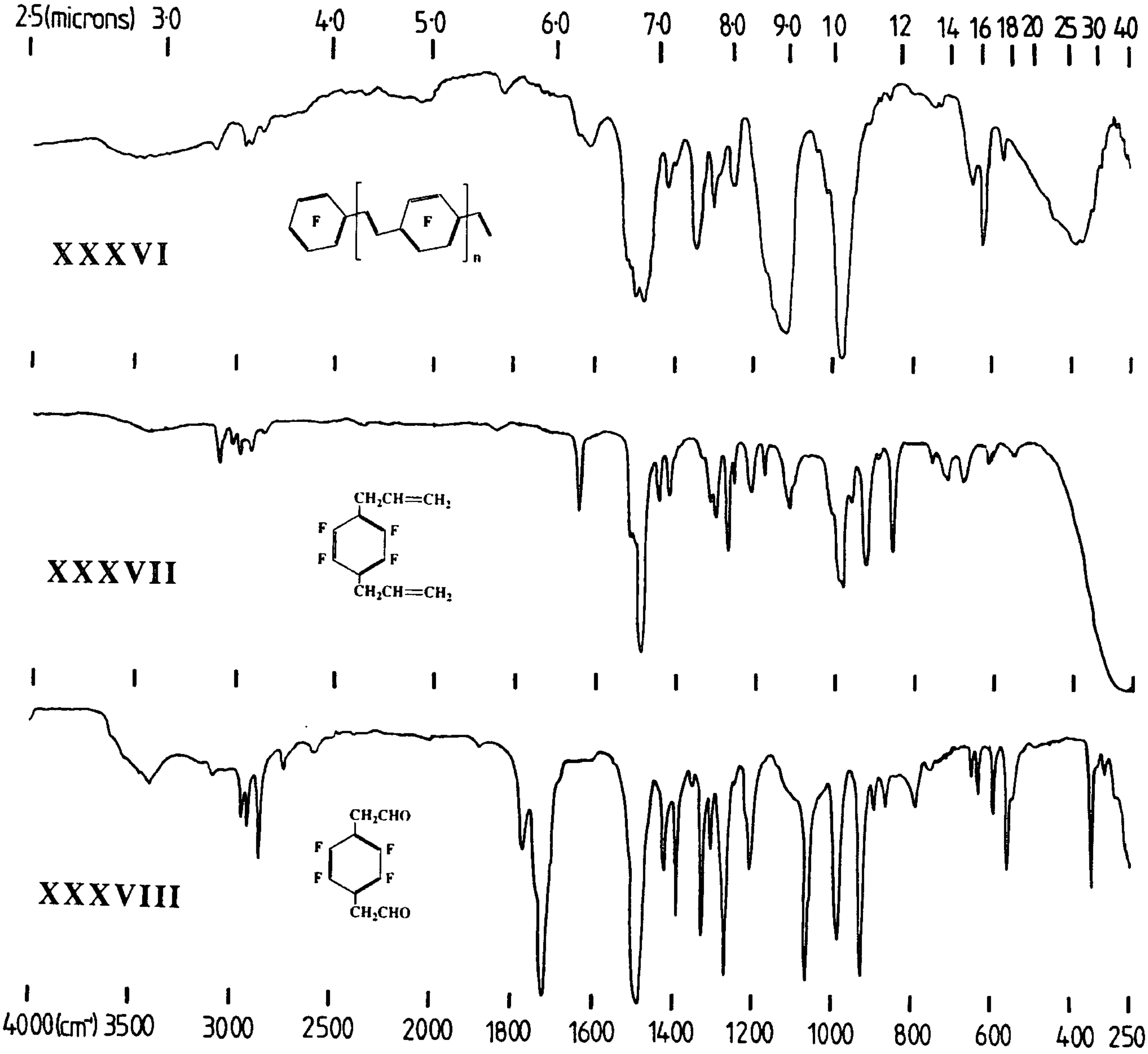

XXXVI

XXXVII

XXXVIII

APPENDIX II - RESEARCH COLLOQUIA, SEMINARS, LECTURES AND CONFERENCES ORGANISED BY THE DEPARTMENT OF CHEMISTRY DURING THE PERIOD: 1986-1989

* - indicates Colloquia attended by author.

29.10.86 Prof. E.H. Wong (University of New Hampshire, U.S.A.), 'Coordination Chemistry of P-O-P Ligands'. (*)

5.11.86 Prof. D. Dopp (University of Duisburg), 'Cyclo-additions and Cyclo-reversions Involving Captodative Alkenes'. (*)

26.11.86 Dr. N.D.S. Canning (University of Durham), 'Surface Adsorption Studies of Relevance to Heterogeneous Ammonia Synthesis'. (*)

3.12.86 Dr. J. Miller (Dupont Central Research), 'Molecular Ferromagnets: Chemistry and Physical Properties'. (*)

8.12.86 Prof. T. Dorfmuller (University of Bielefeld), 'Rotational Dynamics in Liquids and Polymers'.

28.1.87 Dr. W. Clegg (University of Newcastle-upon-Tyne), 'Carboxylate Complexes of Zinc: Charting a Structural Jungle'. (*)

4.2.87 Prof. A. Thomson (University of East Anglia), 'Metalloproteins and Magnetooptics'. (*)

11.2.87 Dr. T. Shepherd (University of Durham), 'Pteridine Natural Products: Synthesis and Use in Chemotherapy'. (*)

17.2.87 Prof. E.H. Wong (University of New Hampshire, U.S.A.), 'Symmetrical Shapes from Molecules to Art and Nature'.

4.3.87 Dr. R. Newman (University of Oxford), 'Change and Decay: A Carbon-13 CP/MAS NMR Study of Humification and Coalification Processes'.

11.3.87 Dr. R.D. Cannon (University of East Anglia), 'Electron Transfer in Polynuclear Complexes'.

17.3.87 Prof R.F. Hudson (University of Kent), 'Aspects of Organophosphorus Chemistry'.

18.3.87 Prof. R.F. Hudson (University of Kent), 'Homolytic Rearrangements of Free Radical Stability'.

6.5.87 Dr. R. Bartsch (University of Sussex), 'Low Co-ordinated Phosphorus Compounds'.

7.5.87 Dr. M. Harmer (I.C.I. Chemicals & Polymer Group), 'The Role of Organometallics in Advanced Materials'. (*)

11.5.87 Prof. S. Pasynkiewicz (Technical University, Warsaw), 'Thermal Decomposition of Methyl Copper and its Reactions with Trialkylaluminium'. (*)

27.5.87 Dr. R.M. Blackburn (University of Sheffield), 'Phosphonates as Analogues of Biological Phosphate Esters'.

24.6.87	Prof. S.M. Roberts (University of Exeter), 'Synthesis of Novel Antiviral Agents'. (*)
26.6.87	Dr. C. Krespan (E.I. Dupont de Nemours), 'Nickel (0) and Iron (0) as Reagents in Organofluorine Chemistry'. (*)
4.11.87	Mrs. M. Mapletoft (Durham Chemistry Teachers' Centre), 'Salters' Chemistry'.
19.11.87	Dr. J. Davidson (Herriot-Watt University), 'Metal Promoted Oligemerisation Reactions of Alkynes'. (*)
10.12.87	Dr.C.J. Ludman (University of Durham), 'Explosives'. (*)
16.12.87	Mr. R.M. Swart (I.C.I.), 'The Interaction of Chemicals with Lipid Bilayers'.
16.3.88	Mr. L. Bossons (Durham Chemistry Teachers' Centre), 'GSCE Practical Assessment'.
7.4.88	Prof. M.P. Hartshorn (University of Canterbury, New Zealand), 'Aspects of Ipso-Nitration'. (*)
13.4.88	Mrs. E. Roberts (SATRO Officer for Sunderland), Talk - Durham Chemistry Teachers' Centre, 'Links Between Industry and Schools'.
18.4.88	Prof. C.A. Nieto de Castro (University of Lisbon and Imperial College), 'Transport Properties of Non-polar Fluids'.
19.4.88	Graduate Chemists (Northeast Polytechnics and Universities), R.S.C. Graduate Symposium. (*)
25.4.88	Prof. D. Birchall (I.C.I Advanced Materials), 'Environmental Chemistry of Aluminium'. (*)
27.4.88	Dr. J.A. Robinson (University of Southampton), 'Aspects of Antibiotic Biosynthesis'. (*)
27.4.88	Dr. R. Richardson (University of Bristol), 'X-Ray Diffraction from Spread Monolayers'.
28.4.88	Prof. A. Pines (University of California, Berkeley, U.S.A.), 'Some Magnetic Moments'. (*)
11.5.88	Dr. W.A. McDonald (I.C.I. Wilton), 'Liquid Crystal Polymers'. (*)
11.5.88	Dr. J. Sodeau (University of East Anglia), Durham Chemistry Teachers' Centre Lecture, 'Spray Cans, Smog and Society'.
8.6.88	Prof. J.-P. Majoral (Universite Paul Sabatier), 'Stabilisation by Complexation of Short-Lived Phosphorus Species'.
29.6.88	Prof. G.A. Olah (University of Southern California), 'New Aspects of Hydrocarbon Chemistry'. (*)
18.10.88	Dr. J. Dingwall (Ciba Geigy), 'Phosphorus-containing Amino Acids: Biologically Active Natural and Unnatural Products'.

18.10.88 Mr. F. Bollen (Durham Chemistry Teachers' Centre), 'The Use of SATIS in the classroom'.

18.10.88 Dr. C.J. Ludman (Durham University), 'The Energetics of Explosives' (*).

9.11.88 Dr. G. Singh (Teesside Polytechnic), 'Towards Third Generation Anti-Leukaemics'.

16.11.88 Dr. K.A. McLauchlan (University of Oxford), 'The Effect of Magnetic Fields on Chemical Reactions'. (*)

2.12.88 Dr. G. Hardgrove (St. Olaf College, U.S.A.), 'Polymers in the Physical Chemistry Laboratory'.

9.12.88 Dr. C. Jaeger (Friedrich-Schiller University GDR), 'NMR investigations of Fast Ion Conductors of the NASICON Type'.

14.12.88 Dr. C. Mortimer (Durham University Teachers' Centre), 'The Hindenberg Disaster - An Excuse for Some Experiments'

25.1.89 Dr. L. Harwood (University of Oxford), 'Synthetic Approaches to Phorbols Via Intramolecular Furan Diels-Alder Reactions: Chemistry Under Pressure. (*)

1.2.89 Mr. T. Cressey and Mr. D. Waters (Durham Chemistry Teachers' Centre), 'GCSE Chemistry 1988: A Coroner's Report'.

13.2.89 Prof. R.R. Schrock (M.I.T.), 'Recent Advances in Living Metathesis' (*).

15.2.89 Dr. A.R. Butler (St. Andrews University), 'Cancer in Linxiam: The Chemical Dimension'. (*)

22.2.89 Dr. G. MacDougall (Edinburgh University), 'Vibrational Spectroscopy of Model Catalytic Systems'.

1.3.89 Dr. R.J. Errington (University of Newcastle-upon-Tyne), 'Polymetalate Assembly in Organic Solvents'.

9.3.89 Dr. I. Marko (Sheffield University), 'Catalytic Asymmetric Osmylation of Olefins'.

14.3.89 Mr. P. Revell (Durham Chemistry Teachers' Centre), 'Implementing Broad and Balanced Science 11-16'.

15.3.89 Dr. R. Aveyard (University of Hull), 'Surfactants at your Surface'.

20.4.89 Dr. M. Casey (University of Salford), 'Sulphoxides in Stereoselective Synthesis'. (*)

27.4.89 Dr. D. Crich (University College London), 'Some Novel Uses of Free Radicals in Organic Synthesis' (*).

3.5.89 Mr. A. Ashman (Durham Chemistry Teachers' Centre), 'The Chemical Aspects of the National Curriculum'.

3.5.89 Dr. P.C.B. Page (University of Liverpool), 'Stereocontrol of Organic Reactions Using 1,3-dithiane-1-oxides'. (*)

10.5.89 Prof. P.B. Wells (Hull University), 'Catalyst Characterisation and Activity'.

11.5.89 Dr. J. Frey (Southampton University, 'Spectroscopy of the Reaction Path: Photodissociation Raman Spectra of NOCl'.

16.5.89 Dr. R. Stibr (Czechoslovak Academy of Sciences), 'Recent Developments in the Chemistry of Intermediate-Sited Carboranes'.

17.5.89 Dr. C.J. Moody (Imperial College), 'Reactive Intermediates in Heterocyclic Synthesis' (*).

23.5.89 Prof. P. Paetzold (Aachen), 'Iminoboranes $XB{\equiv}NR$: Inorganic Acetylenes ?'.

14.6.89 Dr. M.E. Jones (Durham Chemistry Teachers' Centre), 'GCSE and A-level Chemistry 1989'.

15.6.89 Prof. J. Pola (Czechslovak Academy of Sciences), 'Carbon Dioxide Laser Induced Chemical Reactions - New Pathways in Gas-Phase Chemistry'.

28.6.89 Dr. M.E. Jones (Durham Chemistry Teachers' Centre), 'GCSE and A-level Chemistry 1989'.

11.7.89 Dr. D. Nicholls (Durham Chemistry Teachers' Centre), 'Liquid Air Demonstration'.

Lectures organised by Durham University Chemical Society 1986-1989

* indicates those attended by the author

16.10.86 Prof. N.N. Greenwood (University of Leeds), 'Glorious Gaffes in Chemistry'. (*)

23.10.86 Prof. H.W. Kroto (University of Sussex), 'Chemistry in Stars, between Stars and in the Laboratory'. (*)

30.10.86 Prof. D. Betteridge (B.P. Research), 'Can Molecules Talk Intelligently'.

6.11.86 Dr. R.M. Scrowston (University of Hull), 'From Myth and Magic to Modern Medicine'. (*)

13.11.86 Prof. Sir G. Allen (Unilever Research), 'Biotechnology and the Future of the Chemical Industry'. (*)

20.11.86 Dr. A. Milne and Mr. S. Christie (International Paints), 'Chemical Serendipity - A Real Life Case Study'.

27.11.86 Prof. R.L. Williams (Metropolitan Police Forensic Science), 'Science and Crime'. (*)

22.1.87 Prof. R.H. Ottewill (University of Bristol), 'Colloid Science: A Challenging Subject'.

5.2.87 Dr. P. Hubberstey (University of Nottingham), 'Demonstration Lecture on Various Aspects of Alkali Metal Chemistry'.

12.2.87 Dr. D. Brown (I.C.I. Billingham), 'Industrial Polymers from Bacteria'. (*)

19.2.87 Dr. M. Jarman (Institute of Cancer Research), 'The Design of Anti-Cancer Drugs'. (*)

5.3.87 Prof. S.V. Ley (Imperial College), 'Fact and Fantasy in Organic Synthesis'. (*)

9.3.87 Prof. F.G. Bordwell (Northeastern University, U.S.A.), 'Carbon Anions, Radicals, Radical Anions and Radical Cations'. (*)

12.3.87 Dr. E.M. Goodger (Cranfield Institute of Technology), 'Alternative Fuels for Transport'. (*)

15.10.87 Dr. M.J. Winter (University of Sheffield), 'Pyrotechnics (Demonstration Lecture)'. (*)

22.10.87 Prof. G.W. Gray (University of Hull), 'Liquid Crystals and their Applications'. (*)

29.10.87 Mrs. S. van Rose (Geological Museum), 'Chemistry of Volcanoes'. (*)

5.11.87 Dr. A.R. Butler (University of St. Andrews), 'Chinese Alchemy'. (*)

12.11.87 Prof. D. Seebach (E.T.H. Zurich), 'From Synthetic Methods to Mechanistic Insight'. (*)

19.11.87 Prof. P.G. Sammes (Smith, Kline and French), 'Chemical Aspects of Drug Development'. (*)

26.11.87 Dr. D.H. Williams (University of Cambridge), 'Molecular Recognition'. (*)

3.12.87 Dr. J. Howard (I.C.I. Wilton), 'Liquid Crystal Polymers'. (*)

21.1.88 Dr. F. Palmer (University of Nottingham), 'Luminescence (Demonstration Lecture)'. (*)

28.1.88 Dr. A. Cairns-Smith (University of Glasgow), 'Clay Minerals and the Origin of Life'.

11.2.88 Prof. J.J. Turner (University of Nottingham), 'Catching Organometallic Intermediates'. (*)

18.2 88 Dr. K. Borer (University of Durham Industrial Research Laboratories), 'The Brighton Bomb - A Forensic Science View'. (*)

25.2.88 Prof. A. Underhill, (University of Bangor), 'Molecular Electronics'. (*)

3.3.88 Prof. W.A.G. Graham (University of Alberta, Canada), 'Rhodium and Iridium Complexes in the Activation of Carbon-Hydrogen Bonds'.

6.10.88 Prof. R. Schmutzler (University of Braunschweig), 'Fluorophosphines Revisited - New Contributions to an Old Theme'.

21.10.88 Prof. P. von Rague Schleyer (University of Erlangen), 'The Fruitful Interplay Between Calculational and Experimental Chemistry'.

27.10.88 Prof. W.C. Rees (Imperial College), 'Some Very Heterocyclic Compounds'. (*)

10.11.88 Prof. J.I.G. Cadogan (B.P. Research), 'From Pure Science to Profit'. (*)

24.11.88 Dr. R.W. Walker and Dr. R.R. Baldwin (University of Hull), 'Combustion - Some Burning Problems'. (*)

1.12.88 Dr. R. Snaith (University of Cambridge), 'Egyptian Mummies - What, Where, Why and How ?' (*)

26.1.89 Prof. K.R. Jennings (University of Warwick), 'Chemistry of the Masses'.

2.2.89 Prof. L.D. Hall (Addenbrookes' Hospital), 'NMR - A Window to the Human Body'. (*)

9.2.89 Prof. J. Baldwin (University of Oxford), 'Recent Advances in Bioorganic Chemistry of Penicillin'. (*)

16.2.89 Prof. J.B. Aylett (Queen Mary College), 'Silicon-based Chips: The Chemists Contribution'. (*)

23.2.89 Dr. B.F.G. Johnson (University of Cambridge), 'The Binary Carbonyls'.

FIRST YEAR INDUCTION COURSE
OCTOBER 1986

This course consists of a series of one hour lectures on the services available in the department.

1. Departmental organisation.
2. Safety matters.
3. Electrical appliances and infra-red spectroscopy.
4. Chromatography and microanalysis.
5. Atomic absorptiometry and inorganic analysis.
6. Library facilities.
7. Mass spectroscopy.
8. Nuclear magnetic resonance spectroscopy.
9. Glassblowing technique.

RESEARCH CONFERENCES ATTENDED

1. GRADUATE SYMPOSIUM, Durham University, 27th March, 1987
2. GRADUATE SYMPOSIUM, Durham University, 19th April, 1988
3. GRADUATE SYMPOSIUM, Durham University, 17th April, 1989
4. INTERNATIONAL CONFERENCE ON SCIENCE AND TECHNOLOGY OF SYNTHETIC METALS (ICSM '88), Sante Fe, New Mexico, U.S.A., June 26th - July 2nd, 1988.

APPENDIX III - REFERENCES

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