The synthesis and polymerisation of some conjugatively extended p-Xylylenes

Martin Fraser Woolley

THE SYNTHESIS AND POLYMERISATION OF SOME CONJUGATIVELY EXTENDED *p*-XYLYLENES

by

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University of Durham

A thesis submitted in part fulfillment of the requirements for the degree of Doctor of Philosophy at the University of Durham

October 1991

Statement of Copyright

Declaration

The work described in this thesis was carried out in the Department of Chemistry at the University of Durham between October 1988 and September 1991. All the work is my own, unless stated to the contrary, and it has not been submitted previously for a degree at this or any other University.

To my family and friends

Acknowledgements

There are a number of people I would like to thank for their encouragement and assistance over the last three years :

(i) Primarily, I must express my gratitude to my supervisor Dr. Gerald Brooke for his tireless enthusiasm and constant support.

(ii) The technical and administrative staff of this department particularly those people involved with nmr, mass spec. and glass-blowing.

(iii) To my Mum and Dad for putting up with me and for financial support.

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(viii) To the barstaff and management of the Swan especially Kate and Gordon, Tammy and Gordon Jr for some belly laughs.

(ix) To the mysterious Dr. Harris I will just say 'undercarriage'.

Abstract

The synthesis and polymerisation of some conjugatively extended *p*-xylylenes

This thesis describes studies directed towards the preparation of new conjugatively extended *p*-xylylenes through *in situ* 1,6- or 1,8-Hoffmann elimination reactions of trimethylammonium salts. The polymers arising from these highly reactive compounds were analysed in order to determine whether or not the extra conjugation had been involved in the polymerisation process. A number of fascinating by-products were also isolated which were useful in determining the structural unit orientation in the related polymer chains.

Chapter 1 highlights the areas of *p*-xylylene chemistry of relevance to the general theme of this thesis.

Chapter 2 describes the *in situ* synthesis and consequent polymerisation of vinyl-extended *p*-xylylene from two different trimethylammonium salts. An in-depth analysis of the polymers and the two cyclic dimers produced is also included.

Chapter 3 describes the *in situ* synthesis and polymerisation of phenyl-extended *p*-xylylene from two different trimethylammonium salts. Once again, an analysis of the polymer structures and the identification of the two cyclic trimers is also included.

Chapter 4 describes attempts to extend the polymerisation reactions of Chapters' 2 and 3 to produce water-soluble precursor polymers from bis-sulphonium salts.

Chapter 5 describes attempts to synthesise novel polymeric materials from fluorinated monomers.

Chapter 6 gives experimental details for Chapters 2-5.

Martin Woolley (October 1991)

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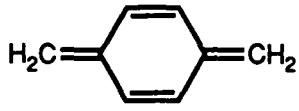
Chapter One

Introduction

1.1 *p*-Xylylenes

1.1.1.Background

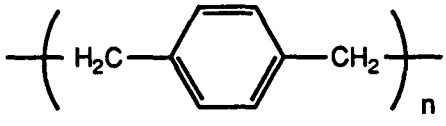
It was as early as 1945 that Soviet theoreticians first discussed[1] the *p*-xylylene structure [1], mentioning it again in a further paper[2] the following year.



[1]

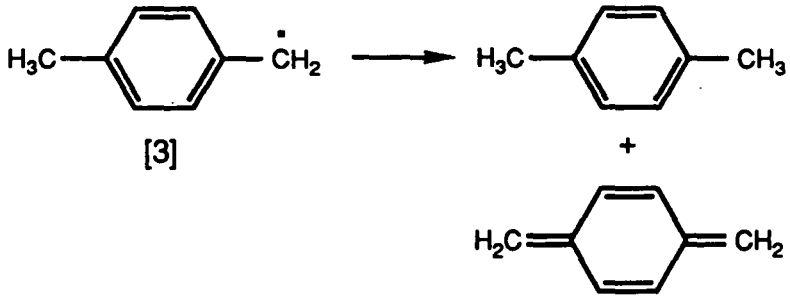
It was indicated then and confirmed later by Coulson et al[3] that the energy difference between the singlet and triplet states of the molecule was very low and that the free valence of the terminal methylene carbons of the molecule in its ground state were very high. This suggested that *p*-xylylene [1] should be a highly reactive molecule.

The initial evidence for the existence of *p*-xylylene was provided by Szwarc[4], who, studying the flash pyrolysis of *p*-xylene under reduced pressure, found that a polymer, assumed to be poly(*p*-xylylene)[2] was produced as a film some distance from the decomposition zone, which suggested that *p*-xylylene was being produced as a volatile reactive intermediate.



[2]

It was presumed that the *p*-xylene first gave the mono-radical [3] which was then converted to *p*-xylylene either by disproportionation[5] [Scheme 1a] or decomposition[6] [Scheme 1b].

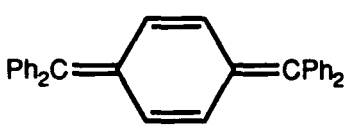


[3] (a)

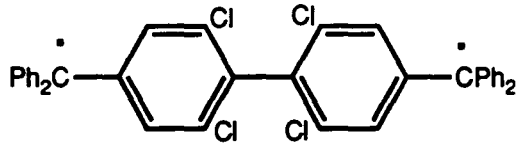
[3] (b)

Scheme 1 *The conversion of monoradical [3] to p-xylylene (a) by disproportionation; (b) by decomposition*

It was not clear whether *p*-xylylene existed in the quinonoid or diradical form. However, the available evidence suggested the quinonoid form since almost all known *p*-xylylenes, e.g [4][7] were diamagnetic. It was only if the stereochemistry of the molecule precluded the possibility of planarity that paramagnetism had been detected e.g [5][8].

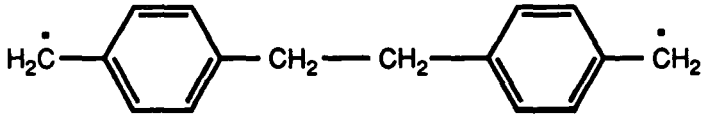


[4]



[5]

Szwarc observed that *p*-xylylene vapour did not polymerise until it condensed[4]. The reason for this lack of vapour phase polymerisation was clear if the mechanism of polymerisation was considered[6]: the first step was a dimerisation to a diradical species [6].



[6]

The central CH_2CH_2 bond of [6] would be relatively weak since the carbon-carbon double bonds have become single bonds leading to two uncoupled electrons and a corresponding loss of binding energy. It was probable that this molecule [6] would revert back to two *p*-xylylene units. However, if four or more units were to combine spontaneously then a comparatively stable compound would be obtained since cleavage of the central carbon-carbon bond would lead to two diradicals that would not be stabilised by xylylene formation. The critical stage in the polymerisation was reached when three or four units were combined. Four or more units were unlikely to meet spontaneously in the gas phase whereas this was much more likely in the condensed phase.

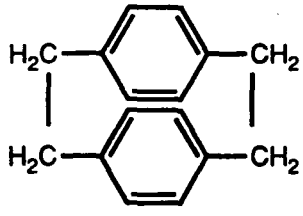
1.1.2. *p*-Xylylene solutions

A convenient method of storing *p*-xylylene was to prepare a solution at -78°C in an inert solvent such as toluene or hexane[9]. The *p*-xylylene was produced through the flash pyrolysis of *p*-xylene and the vapour passed into the well-stirred solvent at -78°C. Obviously the solutions produced contained a large number of impurities and polymerisation of the *p*-xylylene still occurred, albeit slowly, even at this low temperature.

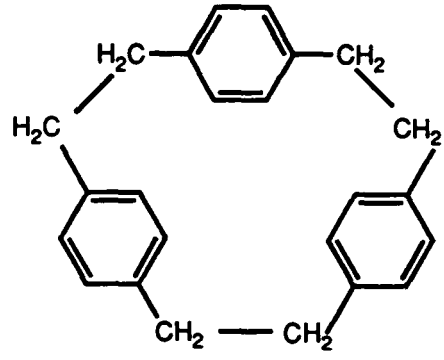
The low temperature polymerisation[10] of these *p*-xylylene solutions was initiated through momentary contact with a 'warm' surface such as a pipette held at room temperature. This contact created diradical n-mers which grew until either all the monomer was consumed or the free radical end groups became trapped in the bulk of the polymer chain. This method has produced polymers with a molecular weight of over $2x10^5$.When the degree of polymerisation exceeded about 20 the polymeric molecules started to precipitate out of solution as a swollen mass. Filtering off this material and drying lead to a polymer which would not reswell or redissolve except at ~300°C in solvents such as benzyl benzoate[11].

Low molecular weight by-products such as cyclo-di-(*p*-xylylene)[7](also called [2.2]paracyclophane), first reported in 1949[12], and cyclo-tri-(*p*-xylylene)[8], first

reported in 1955[13], formed in very high yields through careful control of the reaction conditions [Table 1].[10]



[7]



[8]

Polymerisation at -78°C gave almost exclusively insoluble high molecular weight polymer(92%)[experiment A]. Warming the solution from -78°C to room temperature decreased significantly the yield of insoluble polymer[experiment B]. Diluting the solution considerably before warming to room temperature gave a yield of 93% of cyclo-tri-(*p*-xylylene)[experiment C]. The cyclo-di-(*p*-xylylene) is highly strained[14] and not usually formed very readily. However, dropping a solution of *p*-xylylene at -78°C, slowly into toluene at 100°C, gave a 41% yield of dimer[experiment D], high temperature allowing ring closure to compete with propagation.

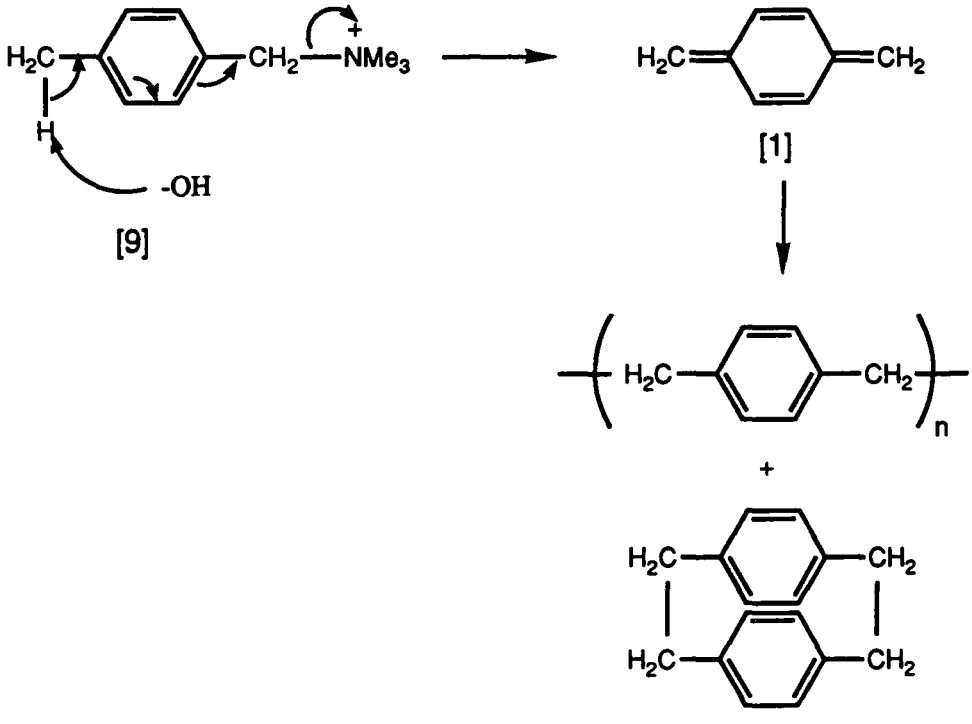
Table 1[10]

Percentage yields of products from four experiments

Experiment	A	B	C	D
Cyclo-di-(*p*-xylylene)	2	1	1	41
Cyclo-tri-(*p*-xylylene)	3	15	93	58
Cyclo-tetra-(*p*-xylylene)	-	0.05	-	-
Soluble polymer mwt ca1600	3	20	-	-
Insoluble polymer mwt ca $2x10^5$	92	64	6	0.5

1.1.3. *p*-Xylylenes from ammonium salts

An alternative method for producing *p*-xylylenes leading to polymeric and dimeric material, was developed by Winberg et al[15a] who found that heating *p*-methylbenzyltrimethylammonium hydroxide [9] at 60-100°C, under reduced pressure, induced a 1,6-Hoffmann elimination reaction and spontaneous reaction of the resulting monomer [1] (Scheme 2).



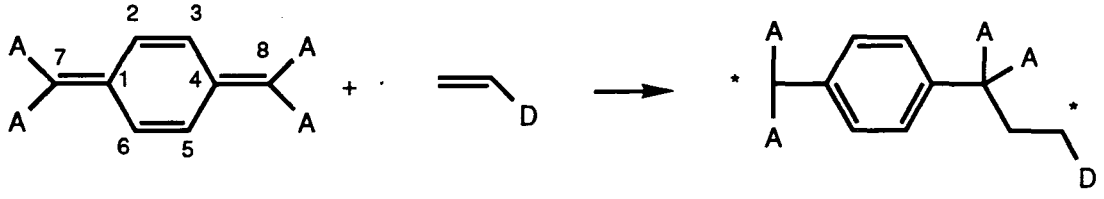
Scheme 2 *1,6-Hoffmann elimination reaction of compound [9]*

This reaction was also achieved by azeotropically drying a hot toluene solution of the hydroxide[15b](a method later improved by Filler et al[16]) and by reacting the ammonium halide with hot concentrated aqueous alkali. The latter reaction was improved and patented in 1985[17].

1.2. Recent Work On Stabilised *p*-Xylylenes

1.2.1. Bond Forming Initiation Theory

p-Xylylenes with electron attracting substituents at the 7- and 8- positions are often obtained as stable compounds and are analagous to electrophilic olefins in that they act as acceptors towards electron-rich olefins. The mechanism of the reaction of *p*-xylylenes with electron-rich olefins has been described[18a,18b] in terms of a 'bond forming initiation theory', the basis of which is that reaction proceeds via a phenylenetetramethylene intermediate which can exist in a diradical [10] or a zwitterionic form [11] (Scheme 3).



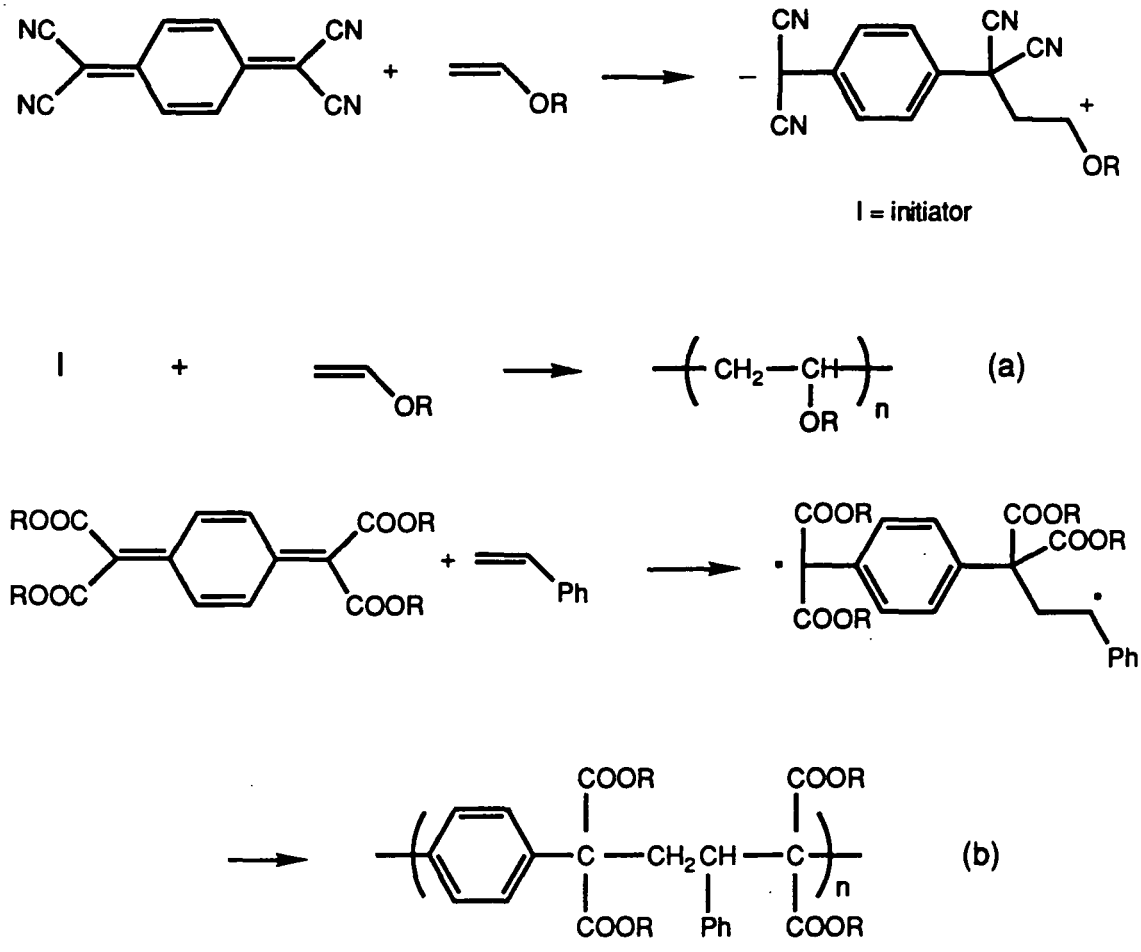
[10] * = ▪

[11] * = + and a matching -

Scheme 3 *The reaction of a tetrasubstituted p-xylylene with an electron-rich olefin to give a phenylenetetramethylene intermediate*

The diradical and zwitterionic forms are not separate but are two extremes of a continuum, the character of the tetramethylene being determined by the nature of the substituents[19a,19b]. It has been proposed that the type of polymerisation can give an idea as to the nature of the tetramethylene since ionic homopolymerisation of the alkene indicates a zwitterionic intermediate which initiates the reaction. A free-radical alternating copolymer, however, can only be formed from a diradical intermediate.

For example, an electron-rich olefin with an alkoxy group(D=OR) combined with a *p*-xylylene bearing cyano groups(A=CN) would favour zwitterions and homopolymerisation of the olefin by a cationic mechanism[20] (scheme 4a), whereas an olefin with an aryl group(D=Ph) combined with a *p*-xylylene bearing ester groups(A=COOR) would favour diradicals and copolymerisation[21](Scheme 4b).



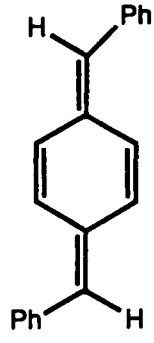
Scheme 4 *Reactions of phenylenetetramethylene intermediate (a)homopolymerisation of the olefin; (b) copolymerisation*

It is not entirely clear why a diradical intermediate cannot initiate radical homopolymerisation or why a zwitterionic intermediate cannot initiate a cationic copolymerisation.

What is clear, from experimental evidence, is that the balance in polar character between a donor and an acceptor monomer is a primary determining factor of the mode of polymerisation.

1.2.2. Homopolymerisations and Copolymerisations

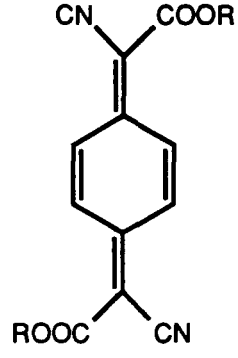
It has long been known that 7,8-diphenyl-*p*-xylylene [12] is a highly reactive monomer[22] and recently a diverse range of tetrasubstituted *p*-xylylenes have been synthesised, principally by Hall et al[23-28] and Iwatsuki et al[29-31], and studies conducted into their homopolymerisations and also their copolymerisations with electron-rich olefins.



[12]

1.2.2.1. 7,8-Bis(alkoxycarbonyl)-7,8-dicyano-*p*-xylylenes [13]

The most reactive of the tetrasubstituted forms of *p*-xylylene have been found to be the 7,8-bis(alkoxycarbonyl)-7,8-dicyano-*p*-xylylenes [13].

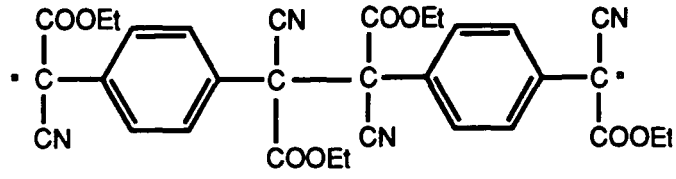


a: R = Me; b: R = Et; c: R=Bu

[13]

Early work[23,29] on 7,8-bis(methoxycarbonyl)-7,8-dicyano-*p*-xylylene [13a] and 7,8-bis(ethoxycarbonyl)-7,8-dicyano-*p*-xylylene [13b] showed that homopolymer isation occurred thermally or with radical or anionic initiators to give soluble polymers.

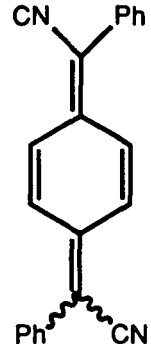
Hall[24] proposed that spontaneous homopolymerisation began with formation of a dimeric diradical [14](c.f ref 6).



[14]

Homopolymerisation of [13] proceeds so readily that copolymerisation with electron-rich olefins was very difficult. Iwatsuki[30] copolymerised [13c] with styrene and with *p*-methoxystyrene in the presence of acetic acid since the acidic conditions blocked the anionic pathway to homopolymerisation and allowed copolymerisation to proceed leading to polymer with molecular weight in excess of $2x10^4$. Hall et al [24] extended this copolymerisation to [13b], forming high molecular weight copolymers with styrene and *p*-methoxystyrene in acidified solution.

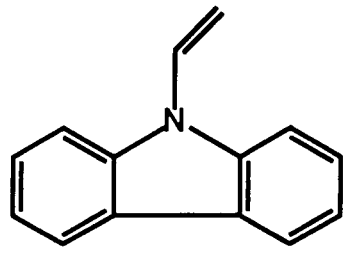
1.2.2.2. 7,8-Bis(diphenyl)-7,8-dicyano-*p*-xylylenes [15]



[15]

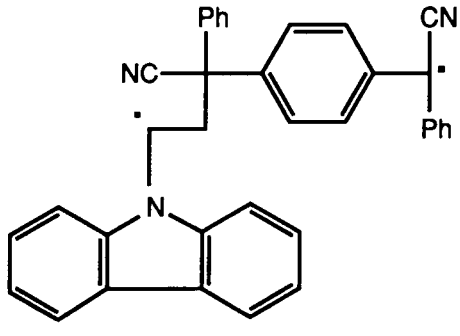
Replacing the alkoxycarbonyl groups with phenyl groups showed the effect the substituents had on the polymerisation of *p*-xylylenes. Compound [15] was obtained[25] as a 1:1 mixture of *cis* and *trans* isomers but whilst compound [13] homopolymerised spontaneously [15] did not, even at 68°C in the presence of the radical initiator AIBN; the lack of reactivity presumably being due to the steric bulk of the phenyl groups. However, copolymerisation of [15] was shown to proceed with *p*-methoxystyrene and *p*

aminostyrene in the presence of AIBN at 65°C[25]. The synthetic route to [15] was later improved[26] and a detailed study of the copolymerisation reactions carried out. It was observed that *p*-methoxystyrene copolymerised with [15] in toluene, 1,2-dichloroethane or nitromethane. However, a stronger donor monomer, N-vinylcarbazole(NVCz)[16] gave different results.

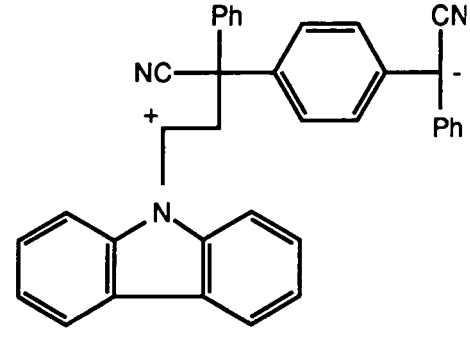


[16]

In the more polar solvents 1,2-dichloroethane and nitromethane, NVCz did not copolymerise with [15]. Instead a homopolymer of NVCz was formed because [15] reacted with NVCz to give a cationic species [17b] which initiated the reaction. In less polar solvents such as toluene, the phenylenetetramethylene exhibited diradical behaviour [17a] and lead to an alternating copolymer.



[17a]

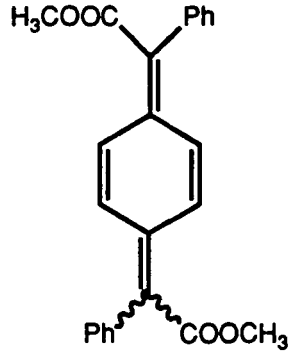


[17b]

Presumably the character of the tetramethylene from *p*-methoxystyrene and [15] was diradical in all solvents due to the reduced electron-donating ability of the styrene and copolymerisation was observed in all cases.

1.2.2.3. 7,8-Bis(dimethoxycarbonyl)-7,8-diphenyl-*p*-xylylenes [18]

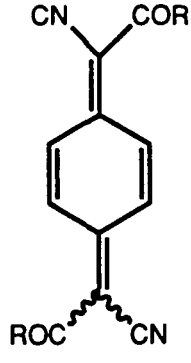
It was found[32] that [18], obtained as a mixture of *cis* and *trans* isomers, did not homopolymerise or copolymerise with styrene, thermally, radically or anionically. This was attributed to the steric strain of the phenyl group in the polymer.



[18]

1.2.2.4. 7,8-Bis(diacyl)-7,8-dicyano-*p*-xylylenes [19]

7,8-Bis(diacetyl)-7,8-dicyano-*p*-xylylene [19a] and 7,8-bis(dibenzoyl)-7,8-dicyano-*p*-xylylene [19b] have also been prepared[31] as stable materials and both compounds homopolymerised in polar solvents to give polymers with molecular weights of $2x10^3$-$2x10^5$.



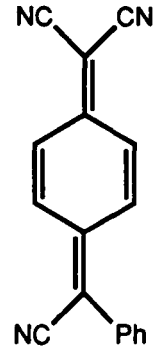
[19a] R = Me
[19b] R = Ph

[19]

Anionic and free-radical initiators worked well but cationic ones did not. Compounds of type [19] also copolymerised with styrene using AIBN in chloroform or dichloromethane.

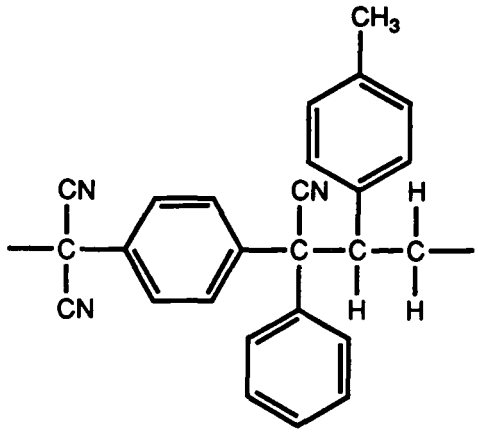
1.2.2.5. 7-Phenyl-7,8,8-tricyano-*p*-xylylene [20]

The first unsymmetrical *p*-xylylene, 7-phenyl-7,8,8-tricyano-*p*-xylylene[20], was reported[27] in1990 and potential copolymerisation of [20] with *p*-methylstyrene was expected to show whether the reaction proceeded by a radical chain mechanism or by radical coupling i.e by chain growth or step growth polymerisation.

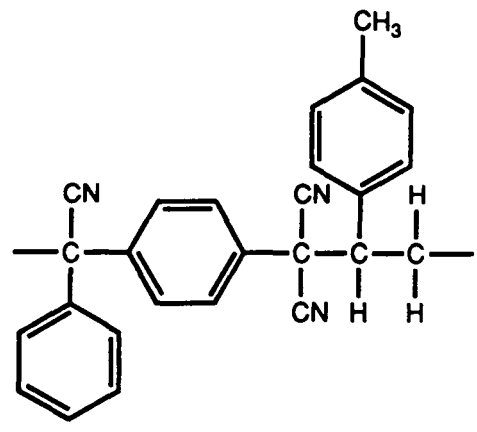


[20]

A 1:1 copolymer was formed and the molecular weight of the copolymer was relatively independent of time and conversion, which is characteristic of chain growth polymerisation.(Once initiated, a chain growth mechanism is rapid with a high DP at the start of the reaction. A step growth mechanism has a much slower propagation rate with high reaction conversion required for high DP). There are two possible alternating structures, [21a] and [21b], that could be produced through the copolymerisation of [20] with *p*-methylstyrene.

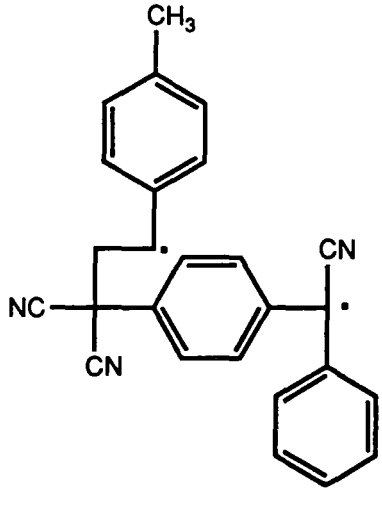


[21a]

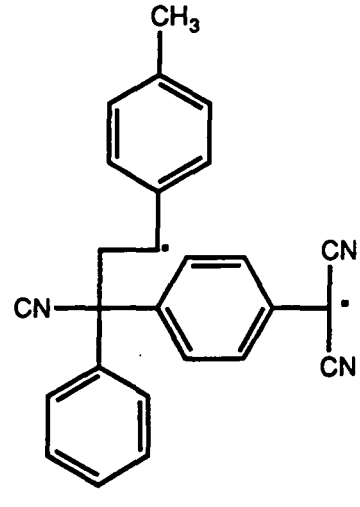


[21b]

The ^{13}C nmr of the copolymer produced was compared with various reference compounds and it was found that [21b] fitted the data better showing that of the two possible phenylenetetramethylene intermediates, [22b] was favoured over [22a].



[22a]

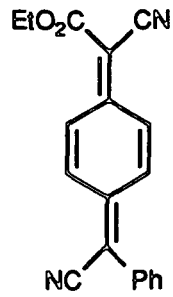


[22b]

This suggested that the intermediate with the lesser steric hindrance at the reactive site was favoured over the intermediate with the more stabilised radical.

1.2.2.6. 7-Ethoxy-8-phenyl-7,8-dicyano-*p*-xylylene [23]

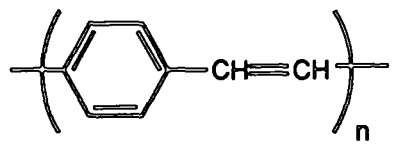
The radical chain addition mechanism was observed again with 7-ethoxy-8-phenyl-7,8-dicyano-*p*-xylylene[28] [23] which copolymerised slowly with styrene, *p* methoxystyrene and *p*-methylstyrene in 1,2-dichloroethane. Once again the molecular weights of the copolymers were found to be independent of time and conversion and were high even at low conversions.



[23]

1.3. Poly(phenylenevinylene)s

The polymerisation of substituted *p*-xylylenes has been extended to produce a class of conjugated polymer known as poly(phenylenevinylene)s (PPV) [24].



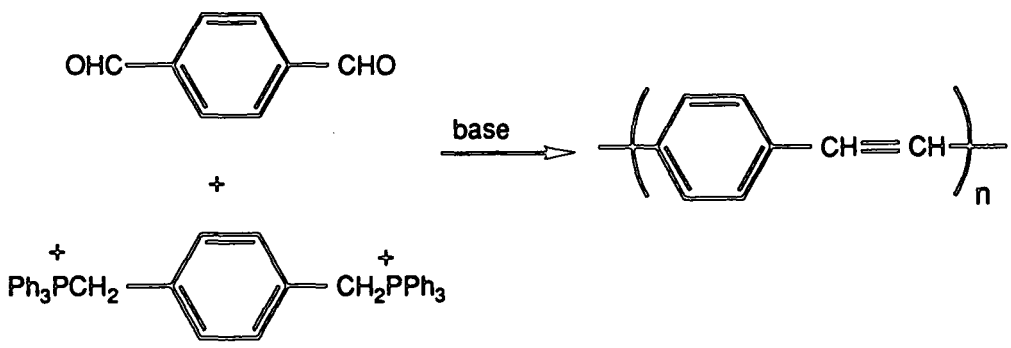
[24]

The development of this synthetic route is described in the following section. This will be followed by a brief discussion of other conjugated polymers and the possibilities for electrical conductivity.

1.3.1. Earlier syntheses of PPV

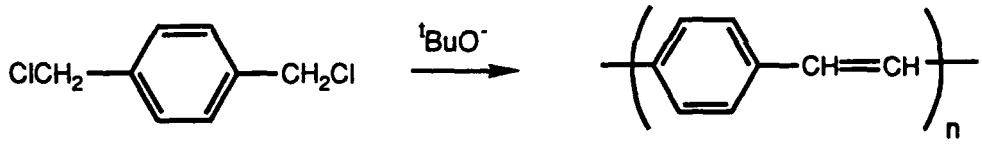
Poly(phenylenevinylene)s were, until recently, only available as low molecular weight, intractable polymers by the following methods:

(i) the Wittig reaction of terephthaldehyde and *p*-xylene(bistriphenyl phosphonium) chloride,[33]



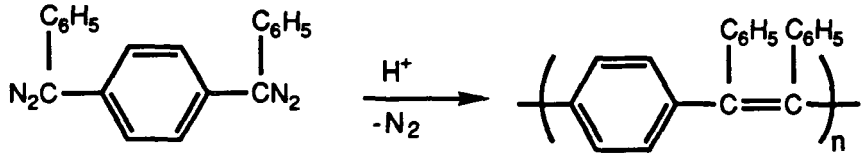
2Cl-

(ii) the dehydrochlorination of α,α'-dichloro-*p*-xylene[34]

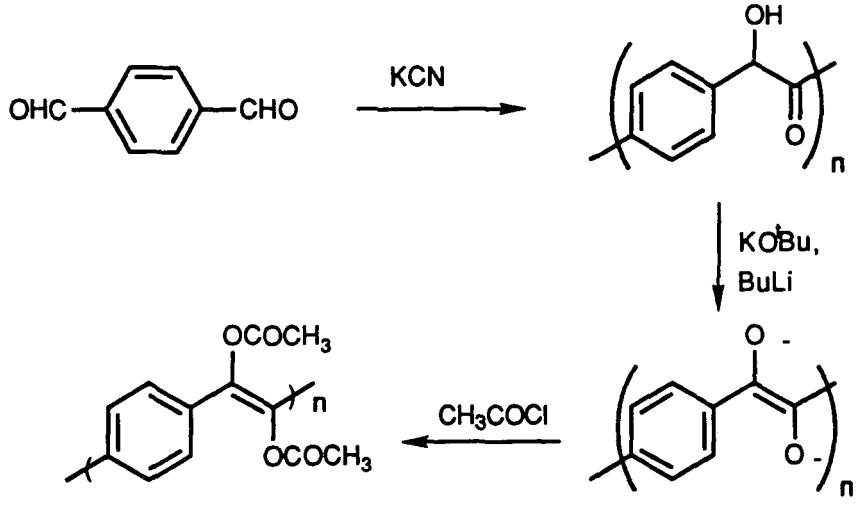


(iii) the electrolytic reduction of α,α,α',α'-tetrabromo-*p*-xylenes[35]

(iv) the polycondensation of bisdiazoalkanes[36]



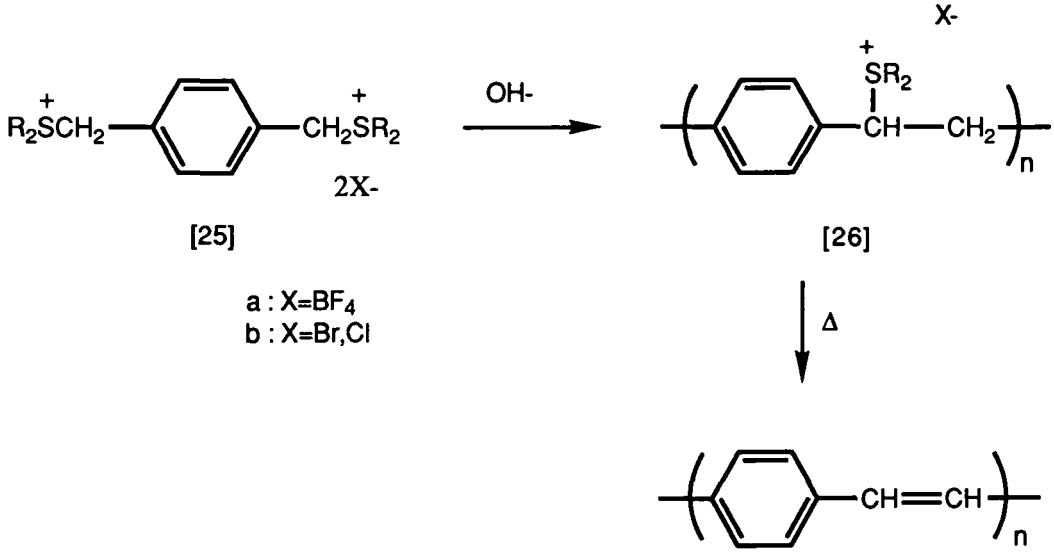
One more recent route to PPV's, an extension of the benzoin reaction, was reported in 1990[37]:



1.3.2. The Precursor Polymer Route

A route to PPVs has now been developed which produces very high molecular weight polymers. The basic principle is that a water soluble precursor polymer is first produced which can be cast into films before being thermally converted to the insoluble, unsaturated PPV. The solubility of the precursor means that precipitation does not occur and hence much higher molecular weights are obtained.

Early attempts to synthesise PPV's from *p*-xylenebis(dimethylsulphonium) tetrafluoroborate [25a] were not very successful[38] leading to insoluble, low molecular weight material. However, later investigations on the halides [25b] by Wessling and Zimmermann[39] yielded high molecular weight, water soluble polyelectrolytes [26] which could be thermally converted to PPV (Scheme 5).



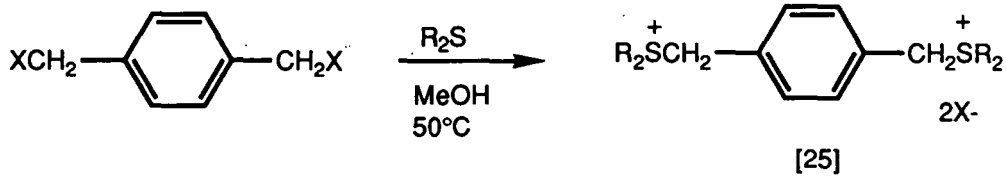
[25] [26]

a : X=BF_4
b : X=Br,Cl

Scheme 5 *The precursor polymer route to PPV*

1.3.2.1. Preparation of bis(dialkylsulphonium) salts

The bis sulphonium salts [25b] are easily synthesised from the corresponding dihalides. The usual method of preparation is to stir the dihalide with an excess of sulphide in methanol or methanol/water at 50°C[40,41,42]. Concentration of this solution leads to an oil from which the solid sulphonium salt (usually a hygroscopic material) is precipitated by treatment with cold acetone .



[25]

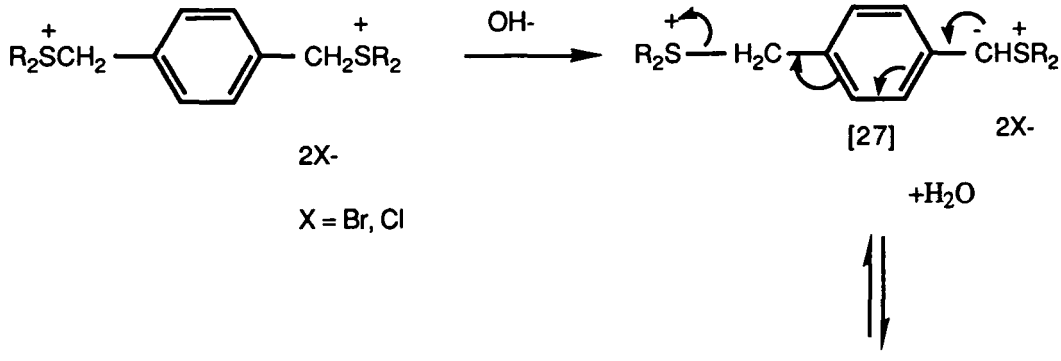
a : X=BF_4
b : X=Br,Cl

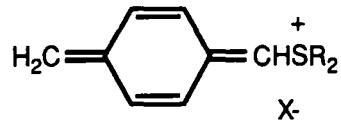
1.3.2.2 Formation of precursor polymer

Preparation of the precursor polyelectrolyte is somewhat more complicated. The success of this step seems to depend on the low reaction temperatures (typically 0-5°C), equimolar base to monomer ratios and the rigorous exclusion of oxygen. Typically, a 0.2M solution of bis-sulphonium salt at 0°C is treated with an equimolar quantity of sodium hydroxide solution. The polymerisations were terminated by the addition of 1N aqueous solutions of hydrochloric acid until neutrality was attained. The resulting solutions or gels were then dialysed for 3 days against deionised water to remove low molecular weight material. Films of the polyelectrolyte were then cast onto glass slides by evaporation of water in vacuo. These films had a slight yellow tinge due to some unsaturation caused by loss of sulphonium groups.

1.3.2.3. Mechanism of polymerisation

The polymerisation mechanism is an unsettled point. It has been proposed that the first step is the formation of an ylid [27] followed by 1,6-elimination of R_2S to form the *p*-xylylene intermediate [28][43](Scheme 6).

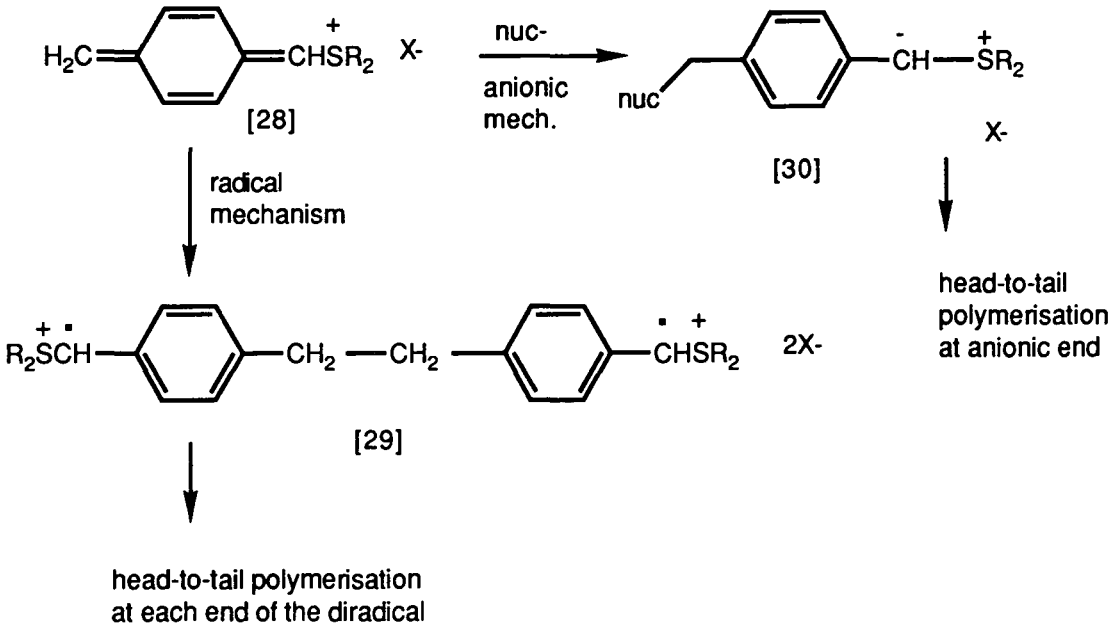




[28]

Scheme 6 *The mechanism of formation of the p-xylylene intermediate [28] in the synthesis of PPV*

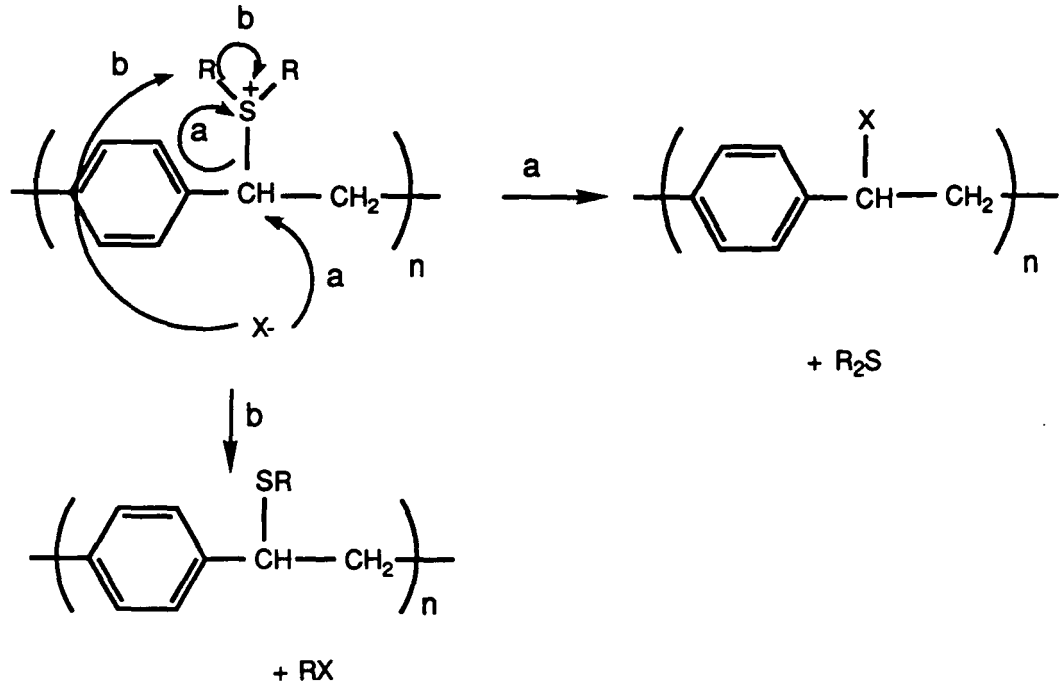
It is at this point that opinions differ, with two mechanisms having been suggested. Wessling[44] has put forward a mechanism, originally suggested by Hatch[43], whereby the *p*-xylylene pseudodiradical polymerises by a free radical mechanism. Initiation to a cationic diradical dimer [29] was given as the first step followed by rapid head-to-tail addition (Scheme 7). This mechanism was disputed, however, in 1988[45] in a paper which suggested that the xylylenes actually polymerise by an anionic chain, rather than a radical chain mechanism (Scheme 7). The authors observed a variety of *p*-xylylene intermediates by spectroscopy but found no evidence of radical formation. The anionic mechanism was more logical in the basic, highly polar conditions which do not normally suit radical mechanisms.



Scheme 7 *The two different mechanisms suggested for polymerisation of the p-xylylene intermediate [28]*

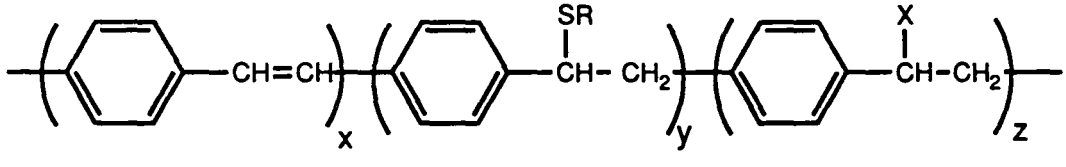
1.3.2.4. Thermal elimination from the precursor polymer

Typical reaction conditions are to heat the precursor film at 240°C in vacuo for 24h. It was usually found[40,41,42,46] that there was some residual sulphur content in the polymer which was explained[44] as being due to an S_N2 reaction of the counter ion with the alkyl sulphide (reaction b in Scheme 8). There was also some residual halogen content thought to be due to reaction a.



Scheme 8 *Side reactions occuring in the thermal elimination of precursor polymer [26] (a) displacement of sulphide by counter-ion (b) abstraction of alkyl group by counter-ion*

At elimination temperatures of between 150 and 250°C the polymer can best be described as a terpolymer [31].

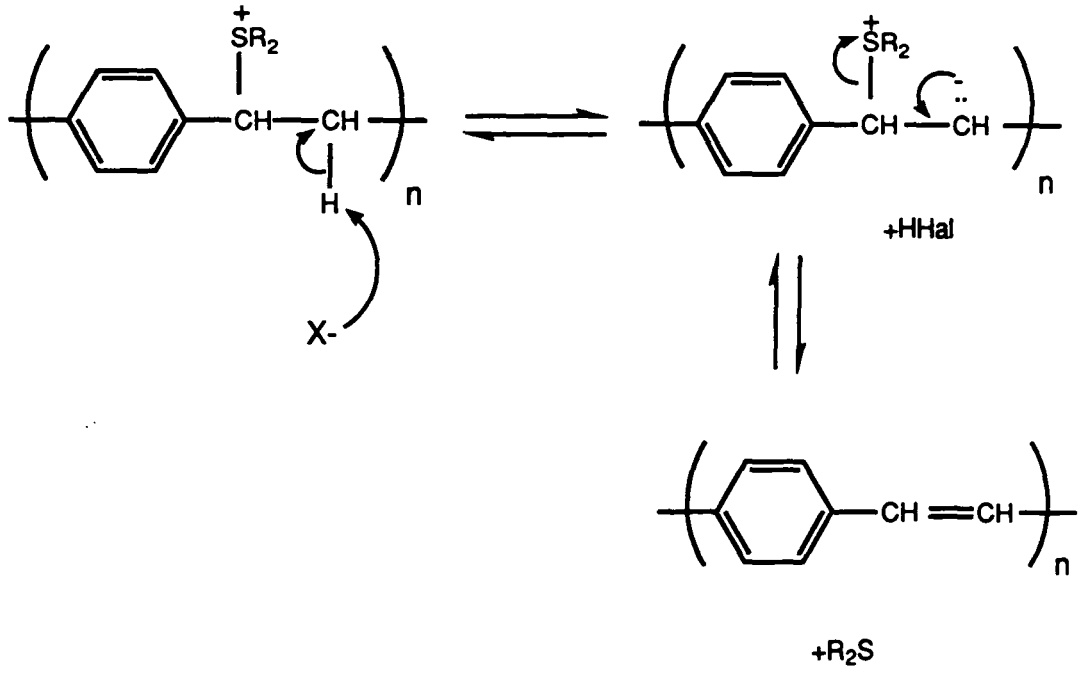


x>>y+z

[31]

Thermogravimetric analysis has shown[42,47] that there are three distinct thermal transition maxima at 106, 360 and 536°C. The major components of the first peak were shown to be due to the loss of the water of hydration, dialkyl sulphide, HCl and alkyl chloride (see reaction b of Scheme 8). The second peak was associated with elimination of alkyl thiol from polymer [31] and the high temperature peak was due to degradation.

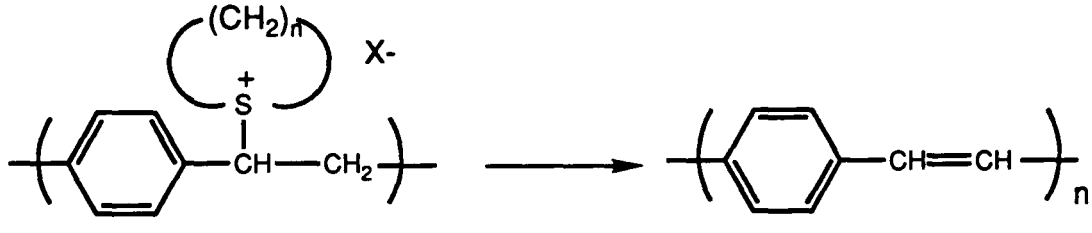
The generally accepted mechanism for the thermal conversion of precursor polymer to unsaturated PPV is via an E1cB elimination reaction (Scheme 9).



Scheme 9 *The mechanism of thermal conversion of [26] to [24]*

1.3.2.5. The Use Of Cyclic Sulphides

A significant advance in the general methodology for producing PPV was made when it was shown[48,49] that polymers from cycloalkylsulphonium precursors [32] had very little residual sulphur or chlorine content after carrying out the elimination reaction. Although cycloalkylene sulphonium groups are obviously less prone to reaction (b) of Scheme 8 it is less clear why reaction (a) does not occur.

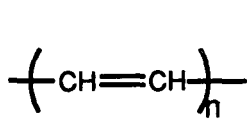


n = 4,5

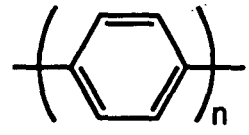
[32]

1.3.3. Electrical Conductivity

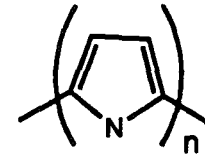
Poly(phenylenevinylene)s are one of a group of polymers that are conjugated and potentially electrically conducting. Other conjugated polymers include: poly(acetylene) [33], poly(phenylene) [34], poly(pyrrole) [35] and poly (thiophene) [36] and this area has been the subject of several extensive reviews[50-64].



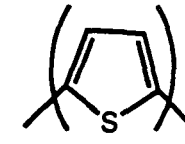
[33]



[34]



[35]



[36]

In order to show how conjugated polymers can be made to exhibit conductivity a very brief discussion of band theory and the conduction mechanism is given below.

1.3.3.1. Band Theory and Conduction Mechanism

Although conjugated polymers are intrinsically insulating materials it is found that treatment with oxidising agents such as iodine or arsenic pentafluoride or with reducing agents such as alkali metals results in dramatic increases in conductivity. For materials such as poly(acetylene)[65] and poly(phenylene vinylene)[40,48] conductivities approaching those of metals have been observed.

Band Theory

The band model for conduction is simply an extension of molecular orbital theory in which two atomic orbitals combine to form a higher energy antibonding molecular orbital and a lower energy bonding molecular orbital. In band theory, N atomic orbitals combine to produce N/2 higher and N/2 lower energy orbitals. The energies of these individual sets of orbitals are so close in energy that they can be thought of as two 'bands' of orbitals; the lower energy orbitals form the valence band and the higher energy orbitals form the conduction band. For a semiconductor or an insulator there is an energy gap, known as the band gap, between the two bands (Fig. 1).

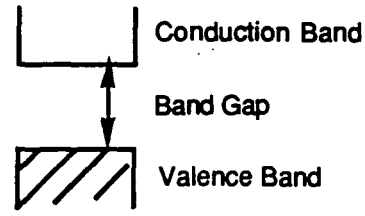


Fig. 1

For a current to flow in the solid there must be orbitals available for electrons to flow to. In a semiconductor the band gap is small and electrons may be thermally excited across it. These electrons are then in the conduction band and are available for conduction whilst holes are left in the valence band and these are also available for conduction(Fig. 2a). In an insulator the band gap is so large it precludes thermal excitation(Fig. 2b) whilst in a metal there is either no band gap or the number of electrons means the highest filled orbital is not at the top of a band leaving orbitals available for conduction (Fig. 2c).

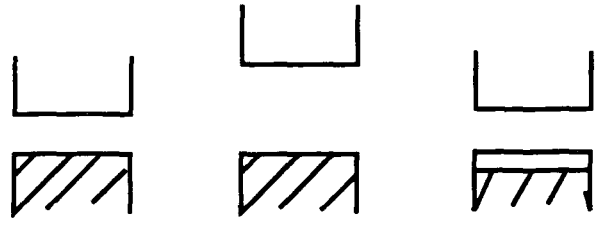


Fig. 2a Fig 2b Fig. 2c

1.3.3.2. 'Doping' of Polymers

The reaction of conjugated polymers with oxidising or reducing agents is often referred to as 'doping' by analogy with the doping of inorganic semiconductors. This term is quite misleading since in the polymer reaction much higher levels of 'dopant' are needed and the chains are actually taking part in a redox reaction; the insulating neutral polymer is actually reduced or oxidised to a polymeric cation or anion with a counter-ion formed from the redox reagent. Nonetheless this reaction is termed 'doping' and by analogy with solid-state physics, the use of an oxidising agent corresponds to p-type doping and that of a reducing agent to n-type doping.

π-Bonded unsaturated polymers are potentially conducting since they have small ionisation potentials and/or electron affinities so electrons can be relatively easily removed or added to form a polymeric ion. In an organic polymer chain it can be energetically favourable for the charge associated with this ion to be localised and for a distortion of the lattice to occur around the charge. This distortion leads to localised electronic states in the band gap due to local upward shift Δe of HOMO and downward shift of LUMO(Fig. 3).

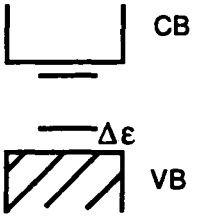
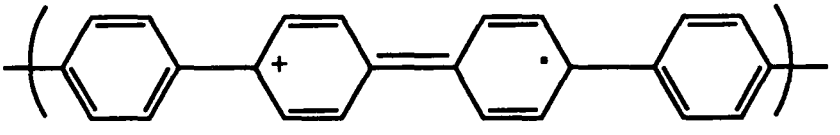


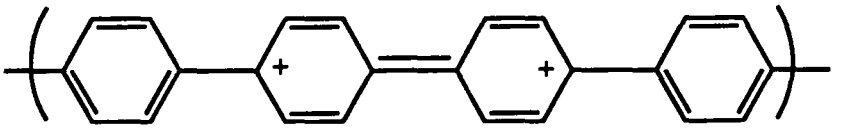
Fig. 3

The oxidation or reduction of the polymer chain involving the loss or gain of one electron leads to the formation of a *polaron* which is simply a radical ion which is localised and associated with a distortion of the lattice; e.g. oxidation of poly(*p*-phenylene) leads to a radical cation and an associated quinonoid form [38].



[38]

Further oxidation or reduction leads to a dication or dianion respectively which is known as a *bipolaron* e.g. [39].



[39]

Poly(acetylene) is a unique case since it has a degenerate ground state[66] because interchange of the double and single bonds leads to two geometric structures corresponding to the same energy (Fig. 4)[64,67].

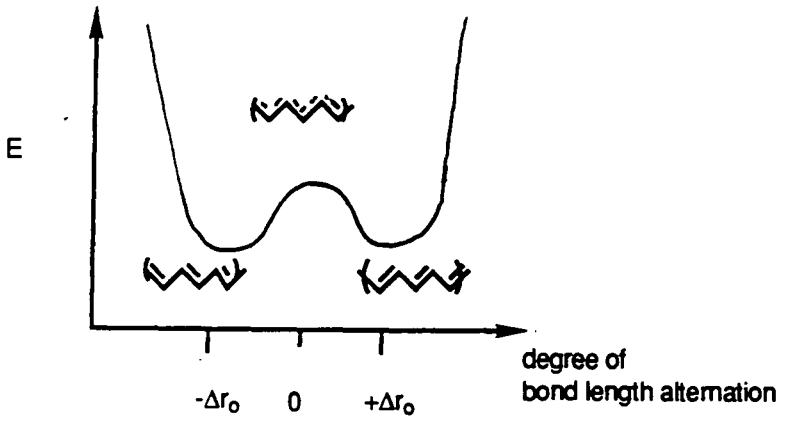


Fig. 4 [64,67] *Total energy curve for an infinite trans-polyacetylene chain as a function of the degree of bond-length alternation Δr.*

When a bipolaron forms in poly(acetylene) the two charges can separate since the geometric structures on either side of the charges have exactly the same energy[66](Fig.5).

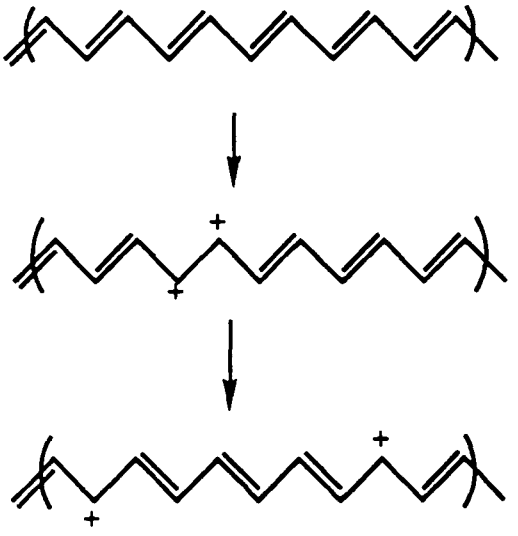


Fig. 5 *Bipolaron formation in polyacetylene*

These isolated ions are termed solitons and lead to a localised electronic level at mid band gap. This level is singly occupied for a neutral soliton, doubly occupied for a negatively charged soliton and empty for a positively charged soliton(Fig.6).

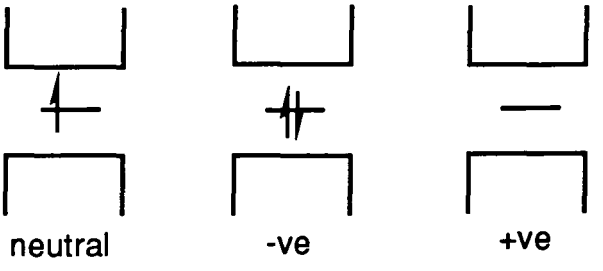


Fig. 6

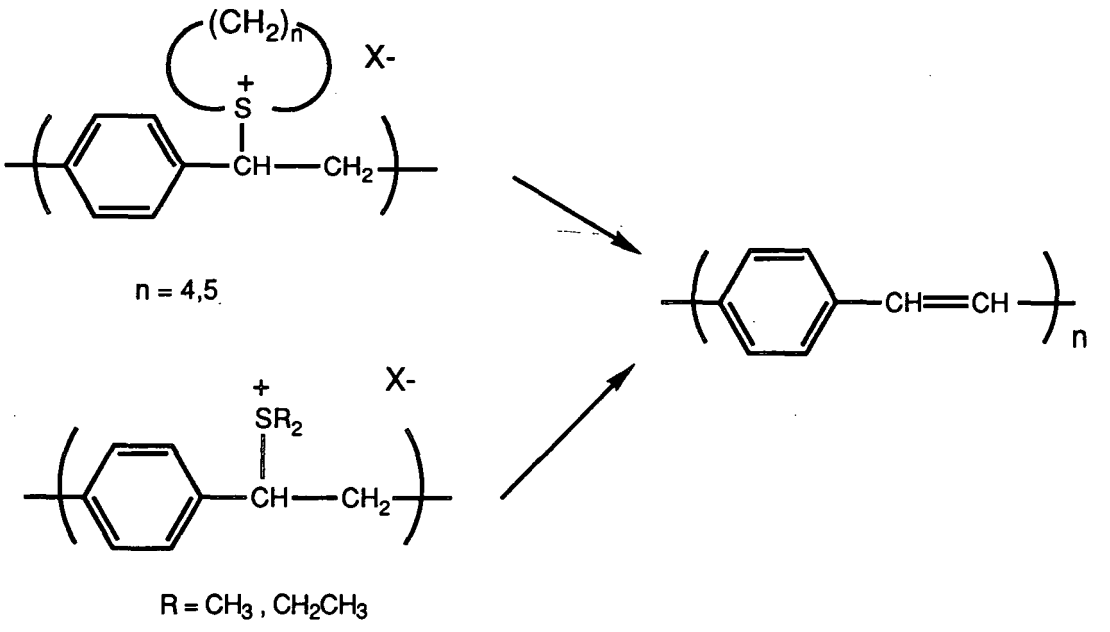
The charge transport process in conducting polymers has not been fully elucidated but it is thought that bipolarons and solitons and not electrons transport the current[67].

1.3.3.3.Electrical Conductivity of Poly(phenylenevinylene)s

As expected undoped PPV behaves as an insulator with a conductivity of 10^{-13}S.cm^{-1} [41]. The conductivity of the doped films depends on a number of factors:

(a) The sulphonium group

It has been shown that the use of cycloalkylene sulphonium salts leads to polymers with higher conductivity than polymers from alkylsulphonium salts (see Table 2). This is presumably because the thermal conversion of [32] to PPV is a much cleaner reaction than the conversion of [26] to PPV as has been discussed previously. The higher degree of conversion to unsaturated units means that the polymer backbone has a greater degree of conjugation and hence should be a better electrical conductor.



(b) The dopant

High conductivities are obtained after doping with AsF_5 or H_2SO_4[40,42] (see Table 2). However, iodine vapour does not enhance the conductivity at all, possibly due to formation of a charge transfer complex between PPV and iodine[40].

(c) Stretching of films

If the polymers are uniaxially stretched during the thermal elimination process then the electrical conductivity is significantly improved in the direction of stretching (Table 2).

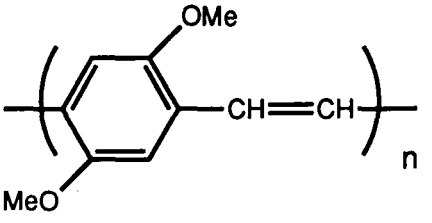
Table 2

Some conductivities of stretched PPV films

Precursor	Conductivity	Dopant	Reference
Me_2S^+ Cl^-	$100 S.cm^{-1}$	H_2SO_4	42
Et_2S^+ Br^-	$38 S.cm^{-1}$(2780)	AsF_5	68(40)
Et_2S^+ Br^-	$10^{-3} S.cm^{-1}$	I_2	40
$(CH_2)_nS^+$ Cl^-	n = 4 ; $44 Scm^{-1}$ n = 5 ; $180 Scm^{-1}$	AsF_5	48

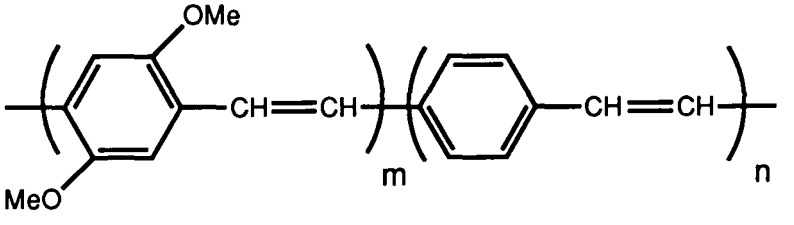
1.3.4. Substituted Poly(phenylenevinylene)s

Poly(2,5-dimethoxyphenylenevinylene) [39], first prepared by a water soluble precursor route in 1985[68], has been found to have higher conductivity, after iodine doping, than PPV itself[69] (Table 3). This was thought to be due to the greater electron donating ability of methoxy compared to a proton which resulted in the formation of a more stable cation radical on reaction with iodine. Unfortunately, although high highly conducting, the poly(2,5-dimethoxy phenylenevinylene) produced could not be drawn and oriented during the elimination process in the same way as PPV could.



[39]

It was found[49,70] that copolymers [40] of 2,5-$(MeO)_2$PPV and PPV not only had higher conductivity than PPV(see Table 3) but that the films could be stretched during thermal elimination much more easily than the 2,5-$(MeO)_2$PPV films.

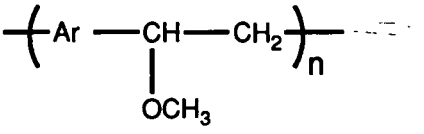


[40]

1.3.5. Organic Solvent Soluble Precursors

A number of poly(arylenevinylene)s including PPV[70], 2,5-$(MeO)_2$PPV[71,72,73] and poly(thienylenevinylene)[71,74,75] have been prepared by a route involving organic solvent soluble precursors. In these reactions after the usual soluble sulphonium salt precursor polymer was formed it was converted to the corresponding *p*-toluenesulphonate salt which was insoluble in water. After extensive drying this material

was dissolved in methanol and stirred for 50h to produce a powdery white precipitate of the polymethyl ether [41].



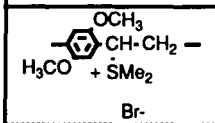
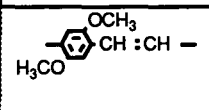
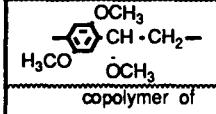
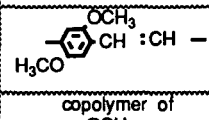
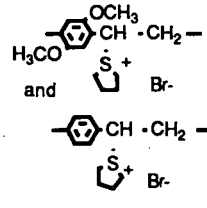
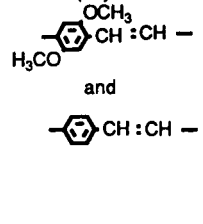
Ar = C_6H_4
$C_6H_2(OCH_3)_2$
C_4H_2S

[41]

Polymers [41] were purified by dissolving in chloroform and reprecipitation into hexane; fibres were spun from chloroform solution which could be drawn and thermally converted to stiff fibres of poly(arylenevinylene)s at ≈200-230°C over 5h in the presence of an acid catalyst (see Table 3).

Table 3

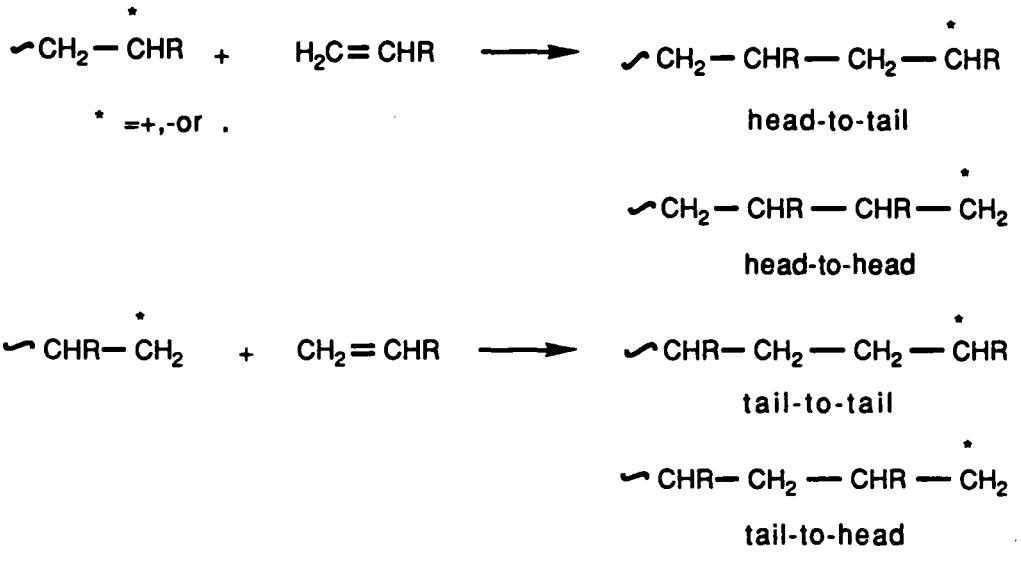
Some further conductivities of PPV films

Precursor	Polymer	Dopant	Conductivity	Reference
		I_2	320Scm^{-1}	68
		I_2	1200Scm^{-1}	73
copolymer of 	copolymer of 	I_2	1500Scm^{-1}	49

1.4. Structural Unit Orientation

When considering the polymerisation of an unsymmetrical monomer unit the polymer structure is dependent on the alignment of each succesive monomer unit with the growing polymer chain. The substituted end of the monomer is termed the head whilst

the unsubstituted end is termed the tail. Clearly three possible linkages can be formed (the head-to-tail and tail-to-head linkages are identical).



The actual structure of the polymer chain is dependant on a number of factors[76]:

(1) *the stability of the new free radical or ion,*

Reaction of the initiator with a monomer unit can lead to either [42] or [43]. Usually the more stabilised [42] is formed because the substituent group R is able to make a more effective contribution to resonance stabilisation. This pattern will be repeated as each succesive monomer unit joins the polymer chain leading to a head to tail polymer.

(2) *steric hindrance,*

The substituent group R offers steric hindrance to the approaching initiator or growing polymer chain thus favouring the initiated monomer [42] and the head to tail polymer.

(3) *electrostatic forces*

The electrostatic interaction between the polymer and the induced dipole in the monomer is important since it means it is favourable for all structural units to be oriented in the same way. This again favours head-to-tail polymerisation.

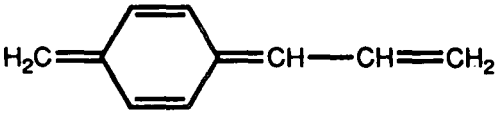
Head-to-tail polymerisation, therefore is usually favoured over head-to-head polymerisation and seems to be an automatic assumption by most authors. Much of the work described in this thesis concerns the polymerisation of unsymmetrical monomers and the different structural possibilities were always considered . Where possible the two types of orientation were identified in the ^{1}H nmr spectra and very often head-to-head linkages were found in quite high proportions.

Chapter Two

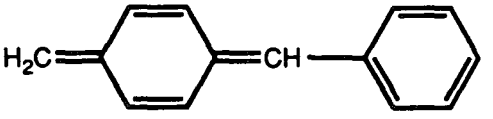
Vinyl-extended *p*-xylylenes

2.1.Introduction

In the first Chapter it has been shown that the polymerisation of *p*-xylylenes can lead to very interesting and potentially useful materials. The new work described in this thesis concerns the effect of extending the conjugation in the *p*-xylylene unit. Two model systems have been studied: vinyl extended *p*-xylylene [44], representing the simplest possible mode for extending the conjugation, which is discussed in this Chapter and phenyl-extended *p*-xylylene [45] which is discussed in Chapter 3.



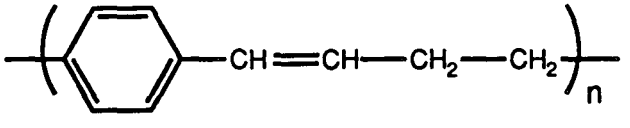
[44]



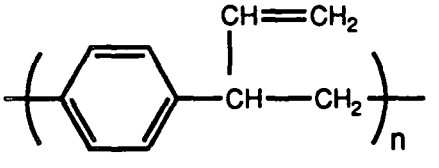
[45]

2.1.1.Vinyl-extended monomer [44]

The monomer [44] is, of course, unsymmetrical and polymerisation could occur head-to-tail in two ways : including the extra conjugation, giving [46], or as *p*-xylylene with a pendant vinyl group, leading to [47].



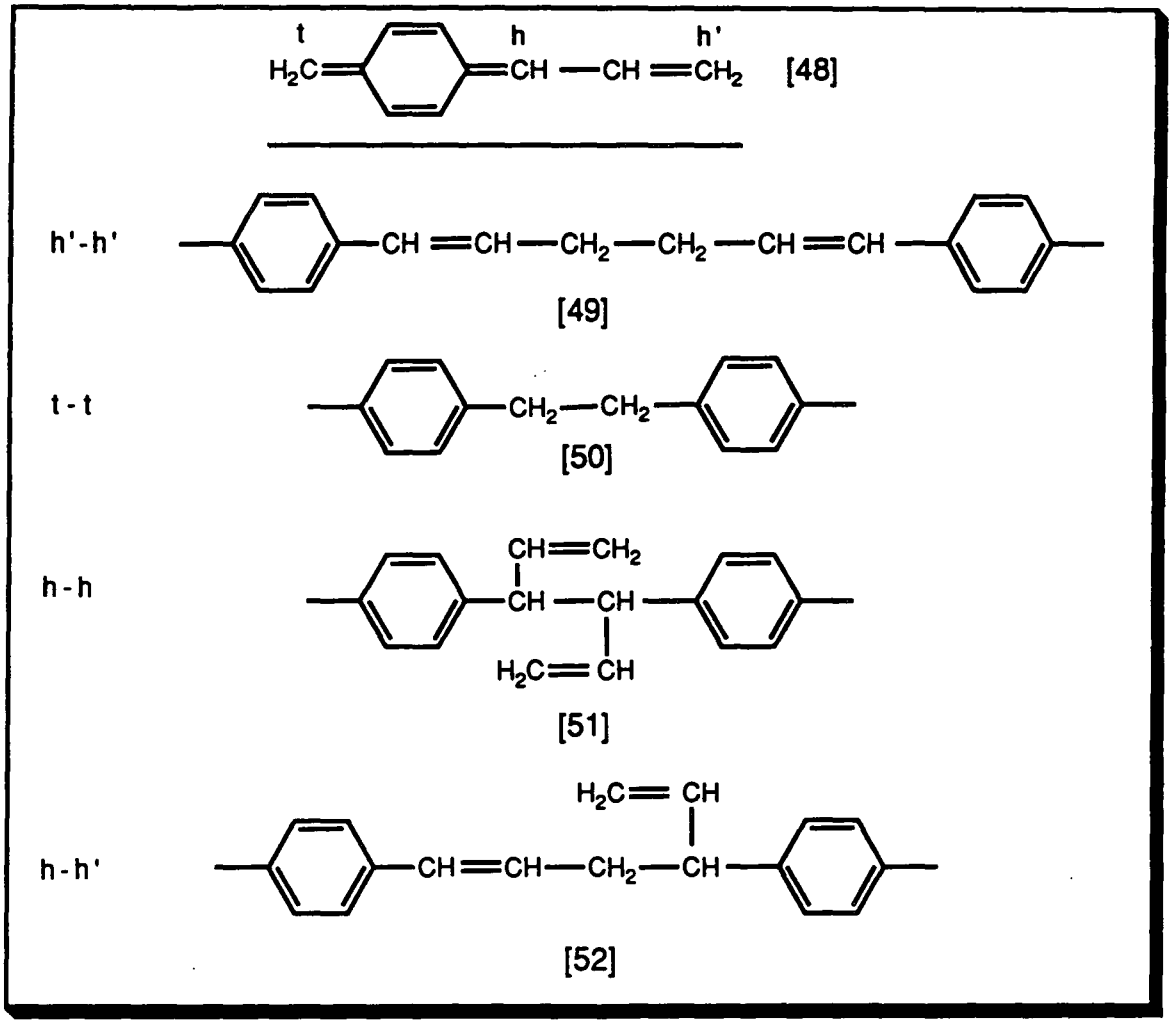
[46]

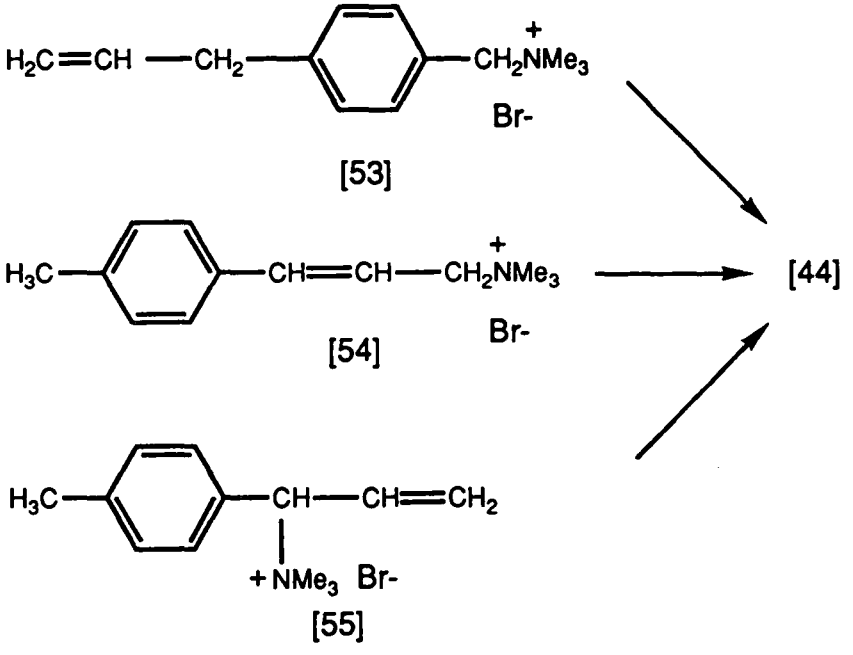


[47]

It is generally assumed that polymerisation will occur in a head-to-tail manner but it is not at all obvious why this should be the case. If the monomer [44] is labelled according to [48] with a tail (t) and two possible heads (h,h') then a number of possible alternative linkages can be drawn out([49],[50],[51],[52]).

Since [44] will be a highly reactive, unstable compound(c.f *p*-xylylene) the actual polymerisations themselves were performed on materials which produced [44] in situ. Three routes to [44] were considered; all three were based on the Hoffmann elimination reaction of quaternary ammonium salts([53], [54], [55]) upon reaction with base (Scheme 10):





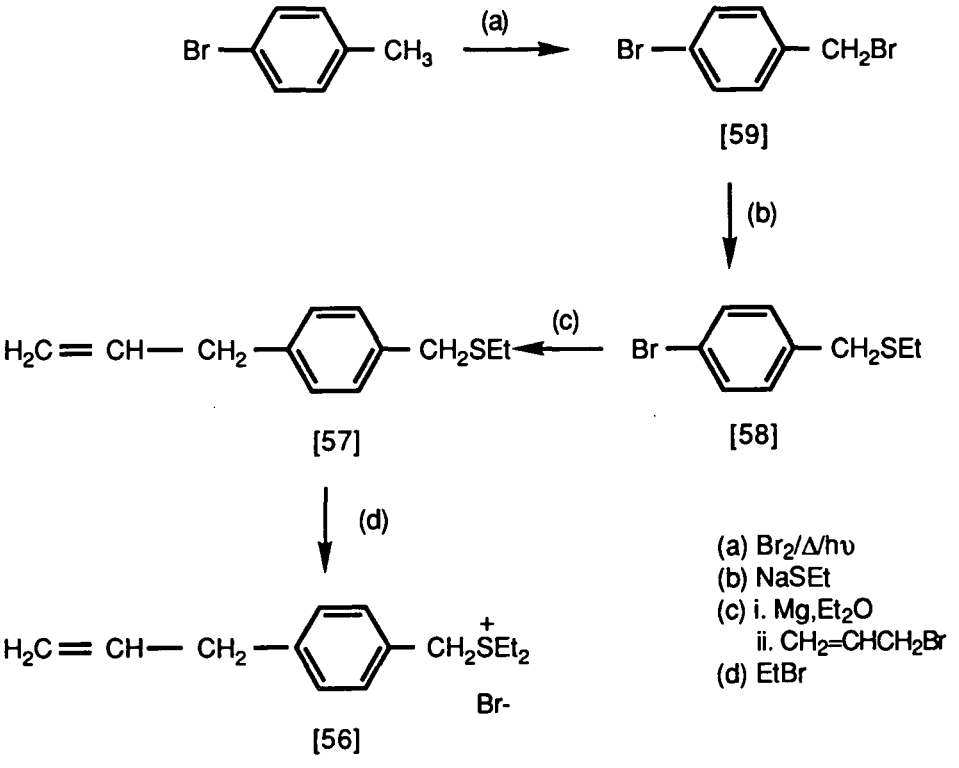
Scheme 10 *Three quaternary ammonium salts which could give [44] through Hoffmann elimination reactions*

In this Chapter the syntheses of the three starting materials will be considered in turn followed by a discussion of the polymerisation reactions and a closer look at some of the interesting products that were obtained.

2.2. Syntheses of starting materials

2.2.1 *p*-Allylbenzyltrimethylammonium bromide [53]

One of the original synthetic strategies conceived to produce the vinyl-extended *p*-xylylene was via a 1,6-Hoffmann elimination reaction on the diethylsulphonium salt [56] prepared by reaction of *p*-allylbenzyl ethyl sulphide with bromoethane; the change to using trimethylammonium salts is explained later. The route to synthesise *p*-allylbenzyl ethyl sulphide which was finally used is shown below (Scheme 11):



Scheme 11 *The proposed synthetic route to [56]*

Step a

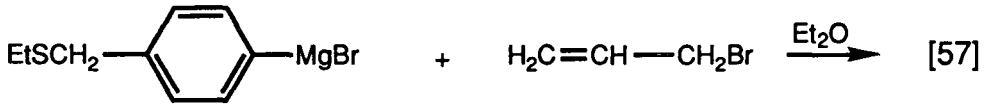
p-Bromotoluene was converted to *p*-bromobenzyl bromide [59] through a photolytically activated reaction with 1 molar equivalent of bromine at 120°C under the light of a 60W bulb[77].

Step b

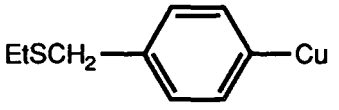
The conversion of *p*-bromobenzyl bromide [59] to *p*-bromobenzyl ethyl sulphide [58] was a straightforward nucleophilic substitution reaction with sodium ethyl thiolate in ethanolic solution.

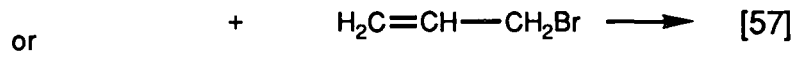
Step c

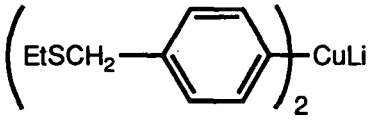
This step took a considerable amount of effort and thus a more detailed explanation is warranted. There are a number of available synthetic routes through which an allyl group may be coupled with an aromatic[78-81] with the obvious method being to react the aryl Grignard reagent with the allylic halide[78] while a more reactive nucleophile would be the organolithium compound[79].



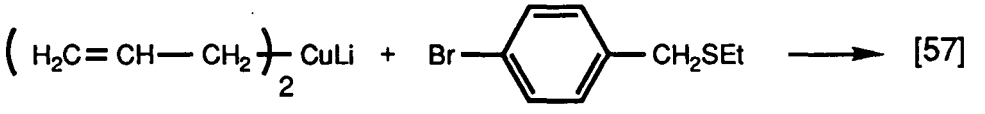
Reaction of an organolithium compound with a copper(I) halide gives an organocopper species, RCu or R_2CuLi depending on the proportions of reagents used, which could couple with allyl bromide[80,81].







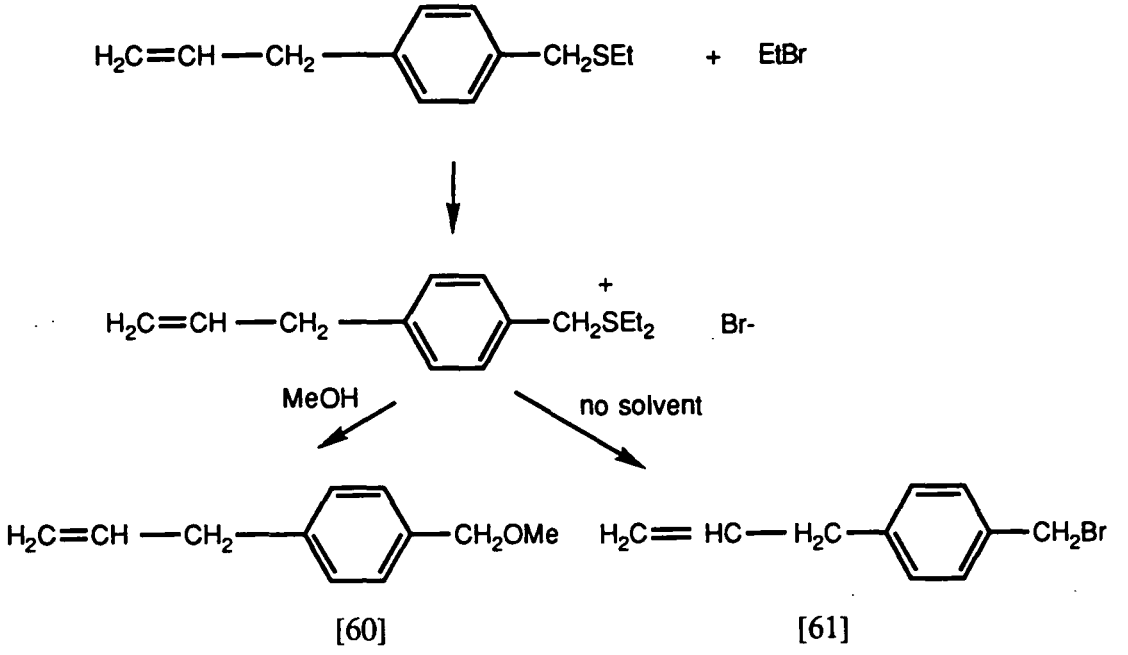
Alternatively lithium diallyl cuprate could be formed and reacted with the aromatic halide but this route would be very indirect as allyllithium itself is difficult to synthesise: the allyltriphenyltin derivative has to be made and converted to allyllithium with phenyllithium[82].



A successful allylation was achieved by reacting the Grignard reagent of *p*-bromobenzyl ethyl sulphide with allyl bromide using a catalytic quantity of copper(I) iodide; compound [57] was obtained in 52% yield.

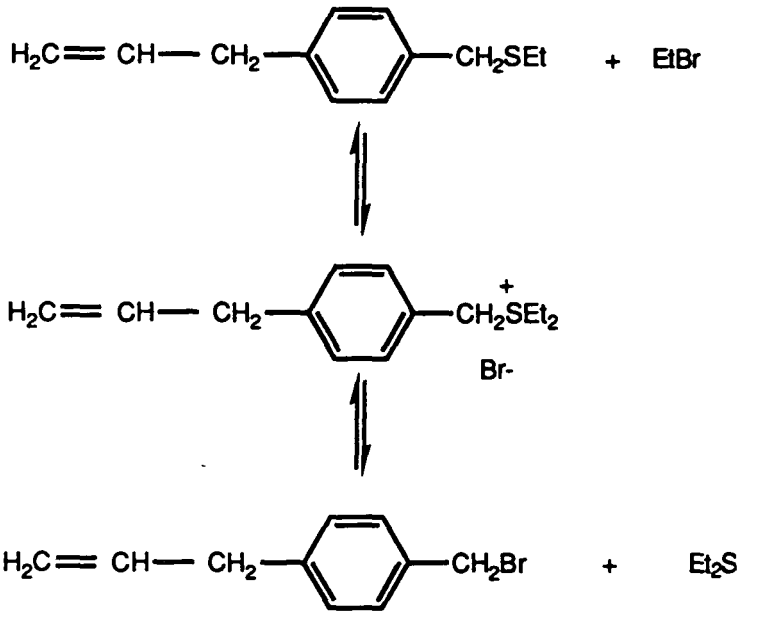
Step d

p-Allylbenzyl ethyl sulphide did not react with bromoethane at its boiling point(37-40°C) under atmospheric pressure so the reaction was attempted in a Carius tube at 110°C. When methanol was used as solvent a mixture of *p*-allylbenzyl methyl ether [60] and *p*-allylbenzyl bromide [61] was obtained but using neat reactants the product was found to be a mixture of starting material and *p*-allylbenzyl bromide [61] which suggested that intermediate salt formation did occur but that the salt was immediately attacked by either methanol or bromide anion in a nucleophilic substitution reaction(Scheme 12).



Scheme 12 *The Carius tube reactions of [57] with bromoethane*

It was observed in the reaction of the neat liquids that increasing the excess of bromoethane resulted in in an increased yield of *p*-allylbenzyl bromide, indicating that the salt was formed in an equilibrium process (Scheme 13).



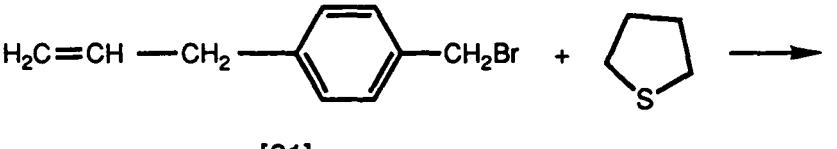
[61]

Scheme 13 *The equilibrium reaction between p-allylbenzyl ethyl sulphide and p-allylbenzyl bromide*

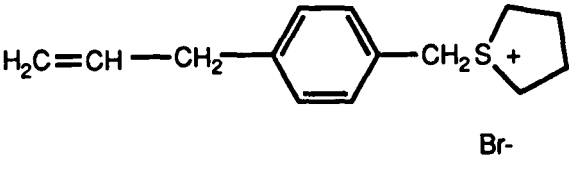
The salt was never observed in this reaction product. Fractional distillation gave *p*-allylbenzyl bromide [61] in 37% yield.

An alternative means of synthesising salt [56] was to react *p*-allylbenzyl bromide [61] with ethyl sulphide. A gel formed which was identified as *p*-allylbenzyl diethylsulphonium bromide by ^{1}H nmr but it would not crystallise.

In an attempt to obtain a solid salt the addition of tetrahydrothiophene to *p*-allylbenzyl bromide [61] produced a white solid almost immediately. The salt *p*-allylbenzyltetrahydrothiophenium bromide [62] was found to be highly hygroscopic and manipulations had to be performed in a glove-bag under nitrogen.



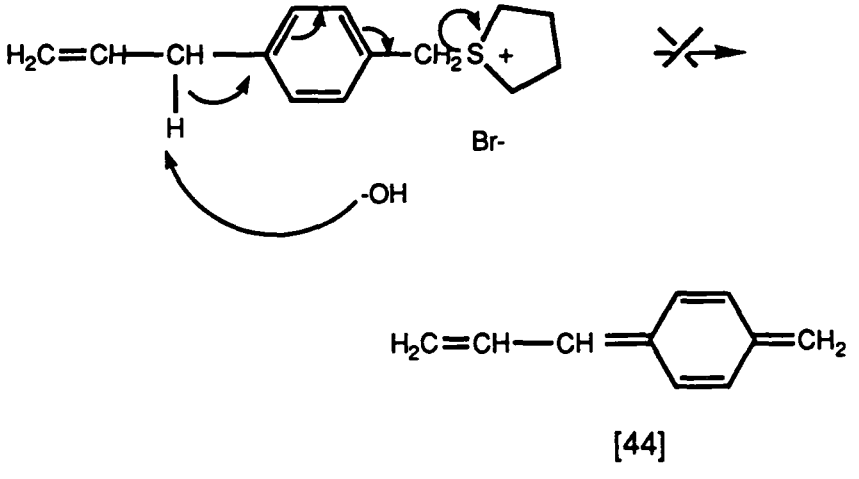
[61]



[62]

An exploratory reaction of this salt [62] with sodium hydroxide solution did not lead to a polymerisation reaction. Instead a mixture of soluble components was produced of which the major product was shown to be *p*-allylbenzyl alcohol through comparison of its infrared with that of an authentic sample.

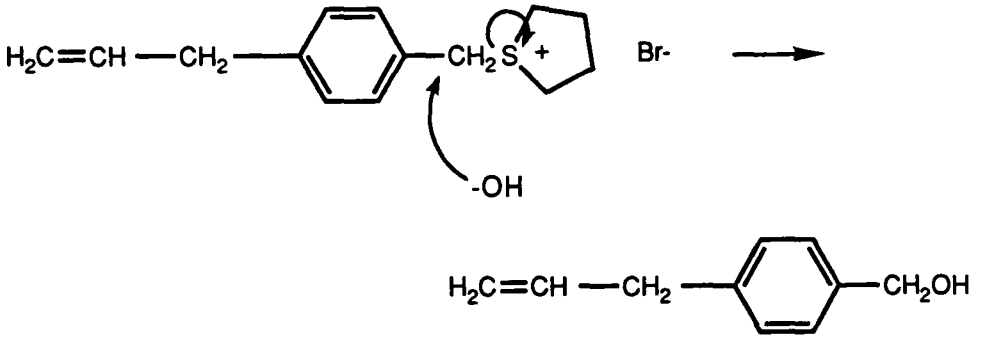
Clearly the desired 1,6-Hoffmann elimination reaction mechanism that had been hoped for under these conditions had not taken place (Scheme 14).



[44]

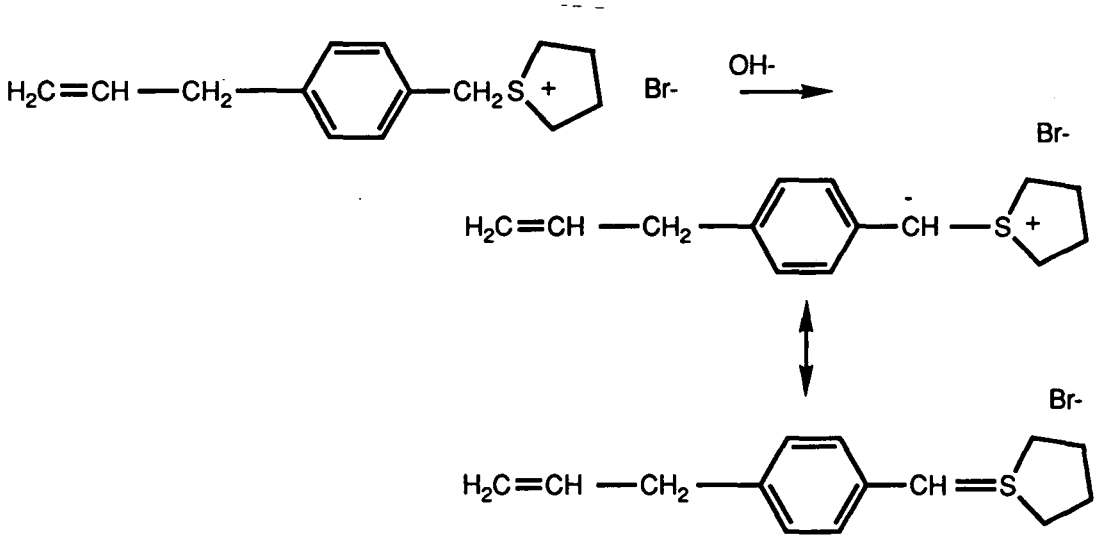
Scheme 14 *The failed 1,6-Hoffmann elimination reaction of [62] which did not give [44]*

Instead the major reaction was the nucleophilic displacement of tetrahydrothiophene by hydroxide ion (Scheme 15).



Scheme 15 *The observed reaction of [62] with hydroxide ion*

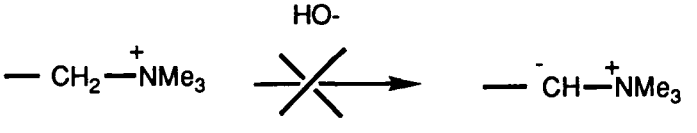
A further complicating factor could be that the benzylic hydrogen in the sulphonium salt may be too acidic for our purposes due to anionic stabilisation by the sulphur d-orbitals (Scheme 16).



Scheme 16 *The resonance stabilisation of the sulphur ylid formed from [62]*

It is significant that there are no reports of unsubstituted *p*-xylylenes synthesised from dialkyl sulphonium salts, in contrast to the precursor polymer route to PPV's described in Chapter 1.

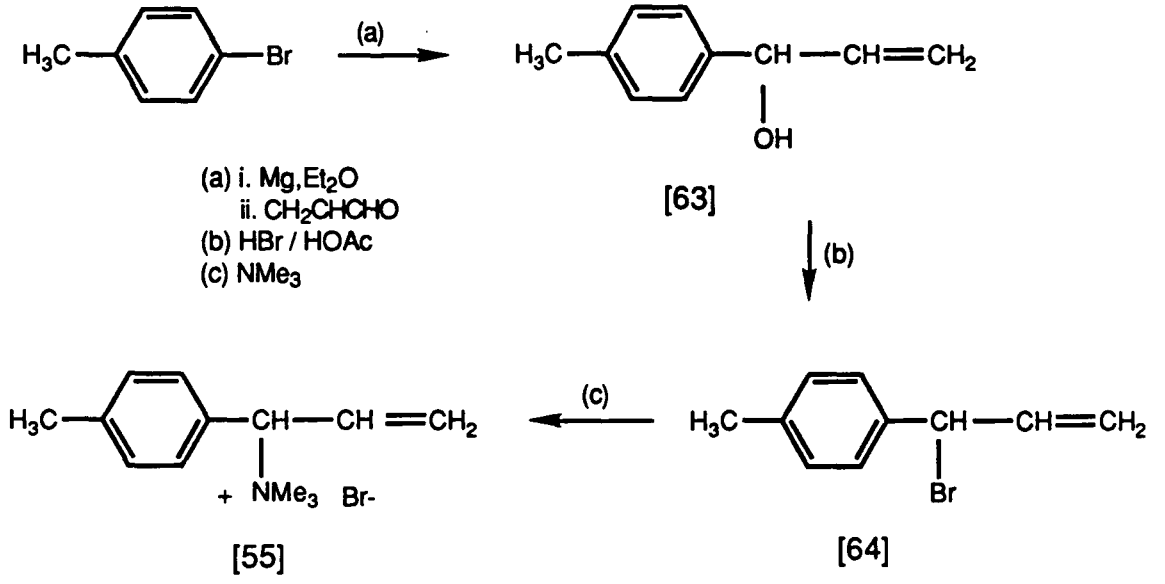
With Winbergs' synthesis of *p*-xylylenes[15] in mind the decision was made to use a tetraalkylammonium salt instead of sulphonium salts as the precursor to the vinyl-extended *p*-xylylene. Nitrogen does not have d-orbitals and so ylid formation is not facile in this system.



p-Allylbenzyltrimethylammonium bromide [53] was readily synthesised by treating an ethereal solution of *p*-allylbenzyl bromide [61] with trimethylamine.

2.2.2 The attempted synthesis of α-(*p*-tolyl)allyltrimethyl ammonium bromide [55].

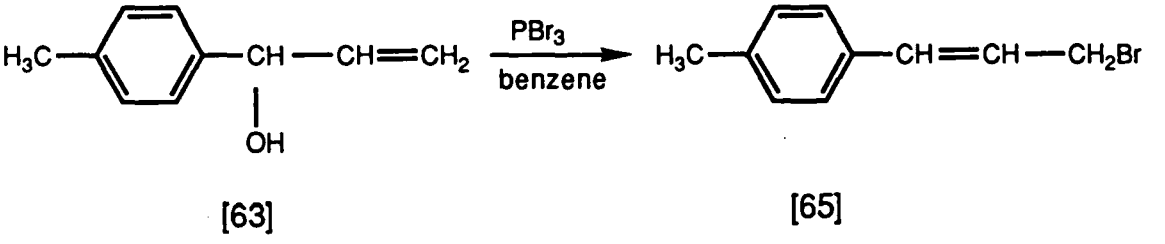
The synthesis of the salt [55] was expected to be fairly straightforward from the synthetic route shown in Scheme 17.



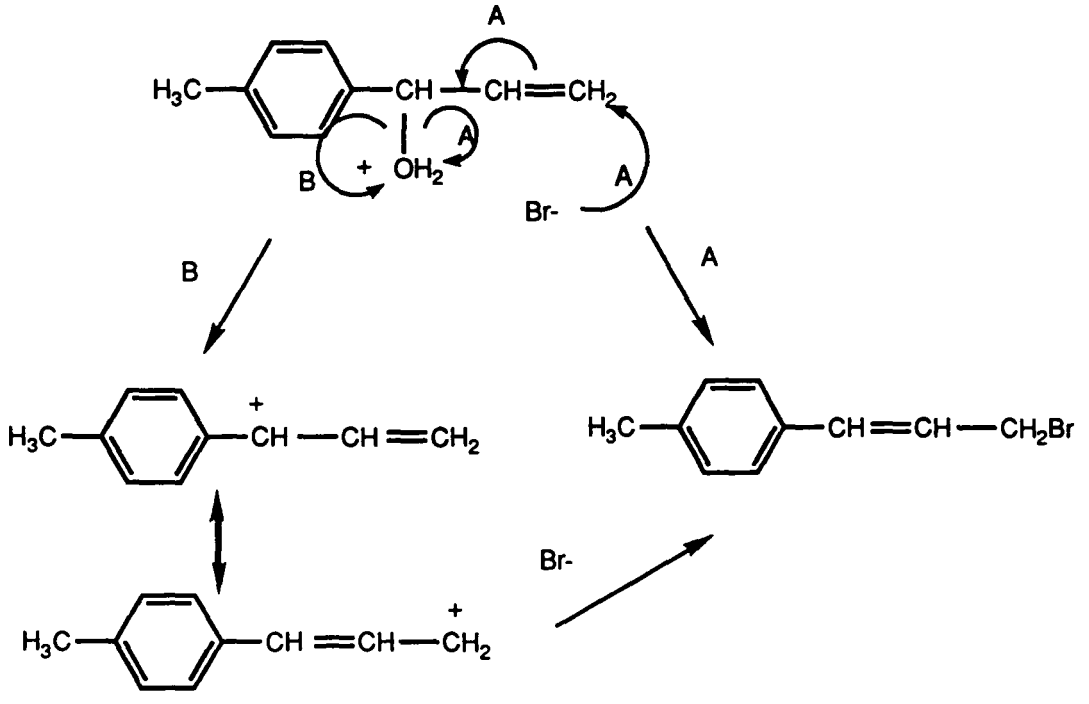
Scheme 17 *The attempted synthetic route to [55]*

The Grignard reaction of *p*-bromotoluene with acrolein is a literature preparation of α-(*p*-tolyl)allyl alcohol [63] and proceeded in 50% yield[83]. A literature survey revealed no references to α-(*p*-tolyl)allyl bromide [64] but one reference suggested a route to α-phenylallyl bromide[84]. It was claimed that refluxing α-phenylallyl alcohol with phosphorus tribromide in anhydrous benzene produced α-phenylallyl bromide.

When α-(*p*-tolyl)allyl alcohol was reacted with phosphorus tribromide in anhydrous benzene, α-(*p*-tolyl)allyl bromide was not produced. Instead the product was identified, through comparison with an authentic sample, as *p*-methylcinnamyl bromide [65].



The mechanism of the conversion of [63] to [65] presumably begins with a protonation of the alcohol [63]. This intermediate can interact with a bromide ion in two ways(Scheme 18).



Scheme 18 *Two mechanistic pathways for conversion of [63] to [65] A : S_N2' B : S_N1'*

The fact that no α-(*p*-tolyl)allyl bromide was produced shows that reaction via pathway A occurs i.e.S_N2' mechanism.

Burton and Ingold reported that reaction of α-(*p*-tolyl)allyl alcohol with cold HBr in acetic acid also produced [65][83]. In the present work this reaction gave pure compound in 58% yield.

2.2.3. *p*-Methylcinnamyltrimethylammonium bromide [54]

Treatment of an ethereal solution of *p*-methylcinnamyl bromide [65], described in the previous section, with trimethylamine produced *p*-methylcinnamyltrimethyl ammonium bromide as a white solid almost immediately.

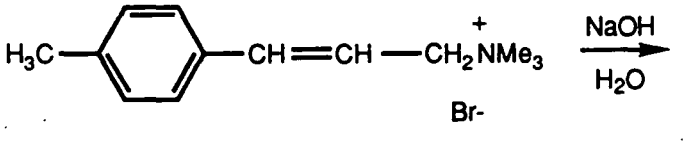
2.3. Polymerisation Reactions of Vinyl-Extended *p*-Xylylenes

The two salts, *p*-allylbenzyltrimethylammonium bromide [53] and *p*-methyl cinnamyltrimethylammonium bromide [54], have been used as starting materials for polymerisation reactions which have been carried out under two different sets of conditions . The first method was simply to add an aqueous solution of the salt dropwise to a refluxing solution of sodium hydroxide which was essentially the method described by Winberg et al for the polymerisation of *p*-methylbenzyltrimethyl ammonium bromide[15]. The second method was to convert the bromide salt to the hydroxide salt and to decompose it in a refluxing azeotropic mixture of toluene and water[16].

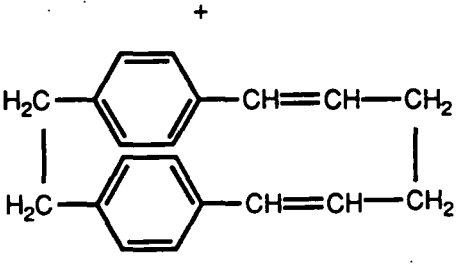
2.3.1. Method 1

2.3.1.1. Using *p*-methylcinnamyltrimethylammonium bromide [54].

A solution of *p*-methylcinnamyltrimethylammonium bromide [54] was added dropwise to a hot, concentrated solution of sodium hydroxide producing a polymeric material mainly insoluble in organic solvents which after extraction with hot dichloromethane represented a 57% yield. The soluble extracts were purified by column chromatography to yield the cyclic dimer [66](5%).



[54]

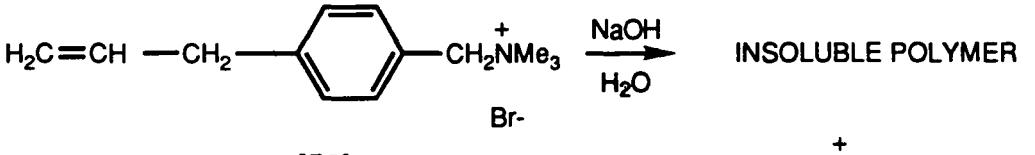


[66]

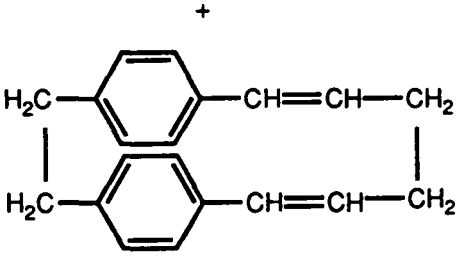
The cyclic dimer was identified by its ^1H nmr and mass spec (see 2.3.1.3.). An analytically pure sample was not obtained at this stage.

2.3.1.2. Using *p*-allylbenzyltrimethylammonium bromide [53]

A solution of *p*-allylbenzyltrimethylammonium bromide [53] was added dropwise to a hot, concentrated solution of sodium hydroxide immediately producing an insoluble, leathery solid which seemed to 'soak up' solvents such as chloroform or tetrahydrofuran in an almost sponge-like fashion.(Removal of the last traces of solvent from this insoluble polymer was very difficult which explains the unreasonably high yield quoted in the experimental (130%!).) Extraction of this solid, which was largely insoluble in organic solvents, in a Soxhlet apparatus with hot dichloromethane produced a small amount of a soluble organic product which after purification by column chromatography on silica and recrystallisation from carbon tetrachloride was identified as the same cyclic dimer [66] (6%) of the vinyl-extended *p*-xylylene [44] that was obtained in 2.3.1.1.



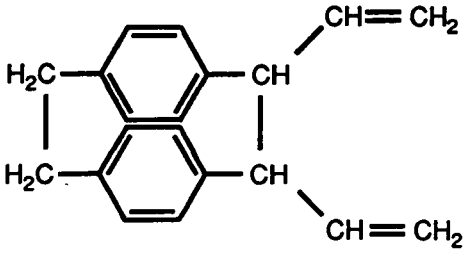
[53]



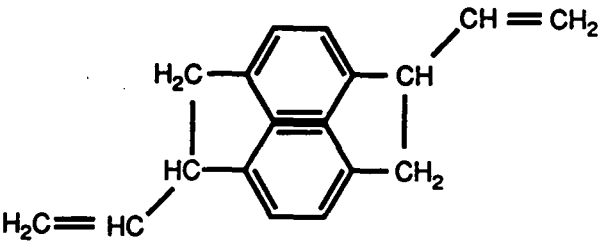
[66]

2.3.1.3. Identification of dimer

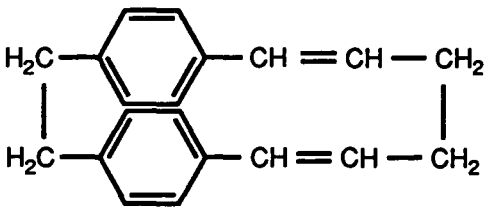
The initial evidence for [66] having a dimeric structure was the mass spectrum which showed a molecular ion of 260. There are six possible cyclic dimers that correspond to this mass [67],[68],[69],[70],[71] and [72].



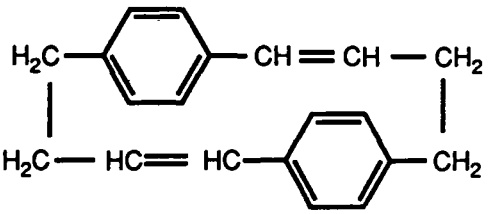
[67]



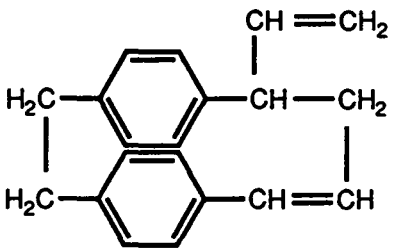
[68]



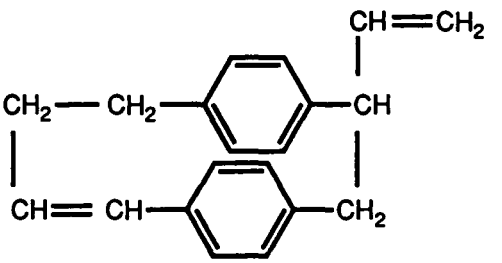
[69] (=[66])



[70]

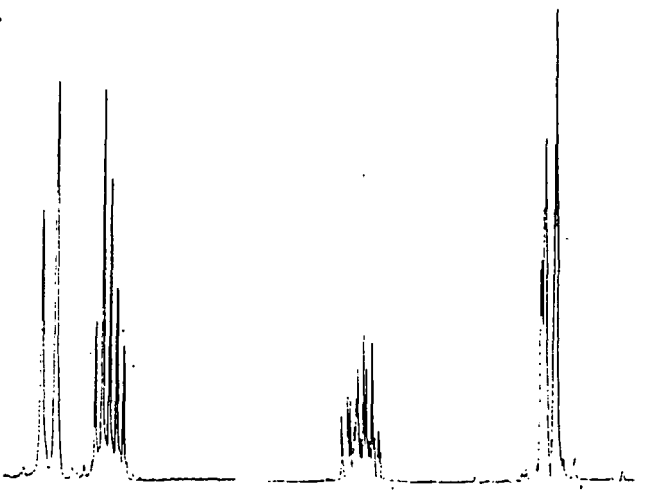


[71]



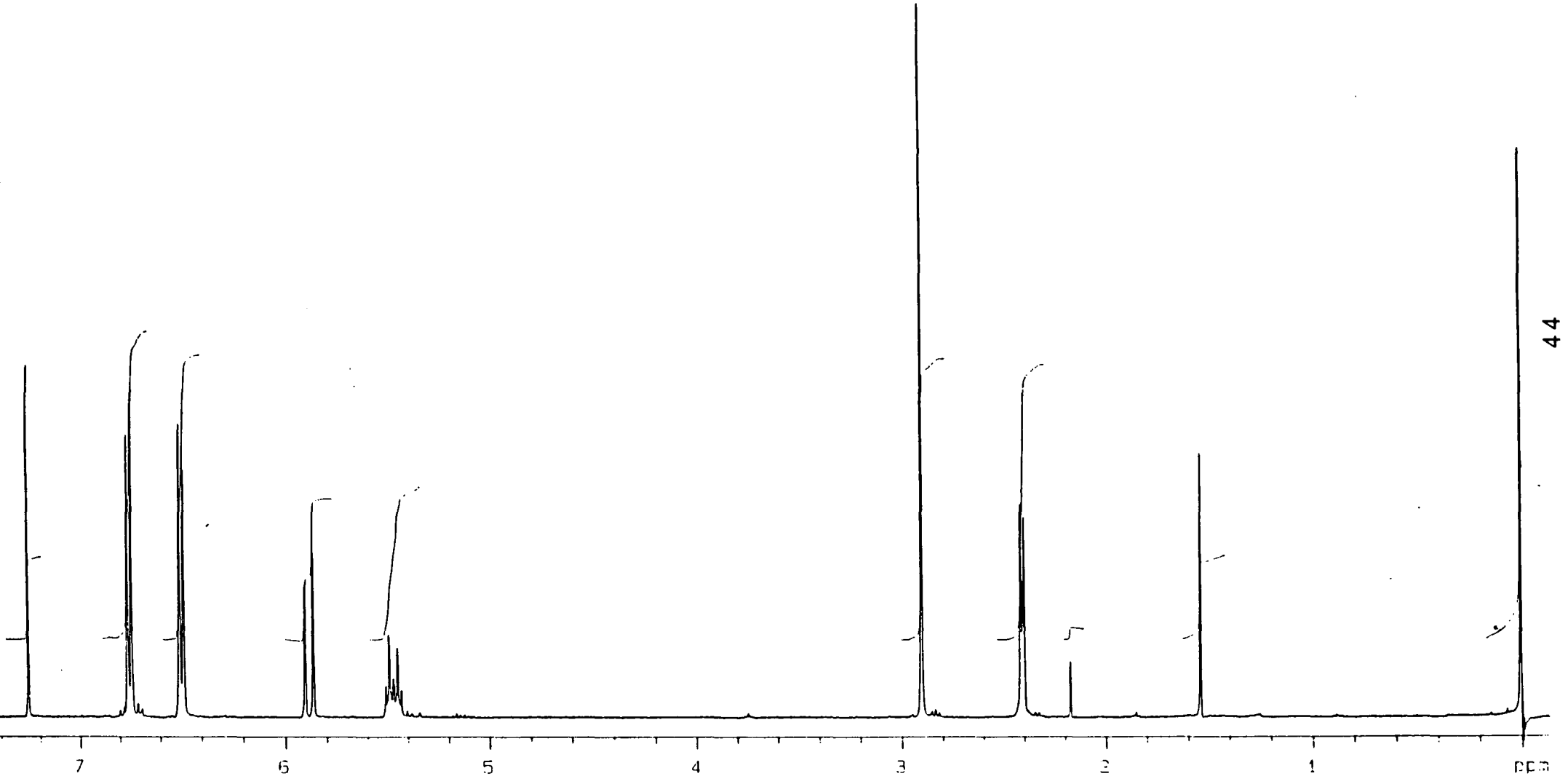
[72]

The simplicity of the ^{1}H nmr (Fig. 7) shows quite clearly that the dimer contains a cinnamyl [73][85] and not an allyl system [74][86], ruling out the possibility of [67],[68],[71] and [72].



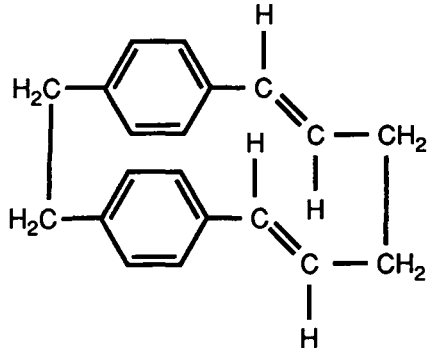
[73] [74]

Fig 7 *400MHz ^{1}H nmr of cyclic dimer [75]*



Therefore, the only feasible dimeric structures are the head-to-head and head-to-tail structures [69] and [70].

The ^1H nmr (Fig 7) shows two methylenic proton peaks: a multiplet at 2.41ppm and a singlet at 2.95ppm. The singlet can only be present in structure [69] since it has a plane of symmetry and the benzylic methylene peak would not exhibit coupling with its identical neighbour. The coupling constant of the doublet at 5.90ppm (16Hz) showed that the cyclic dimer had a *trans-trans* structure [75].



[75]

It is clear, then, that the cyclic dimer [75] E,E-[6,2]-paracyclophan-1,5-diene was a result of a head-to-head coupling. It could be that the benzene rings and double bonds were stacked one above the other leading to $\pi-\pi$ interactions and subsequent stabilisation. It is not claimed that [75] is the only cyclic dimer produced since, although the spot corresponding to [75] was the most intense, the TLC of the crude mixture was very complex and there is the distinct possibility that the other dimers may have been formed in small proportions.

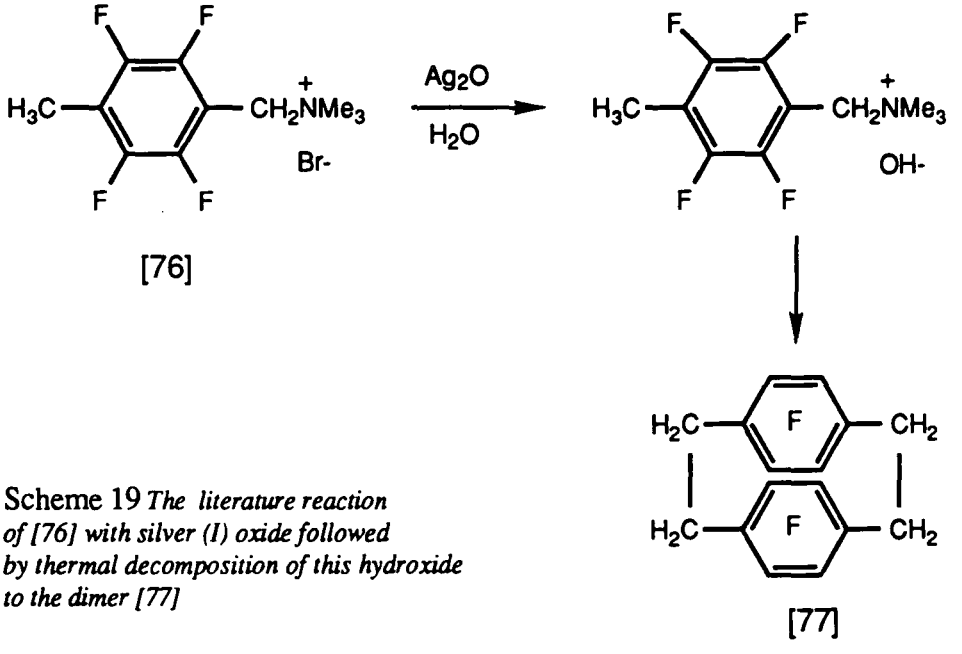
2.3.1.4. Discussion

The two experiments described above had two implications. Firstly, the structure of the cyclic dimer suggested that in the accompanying polymer head-to-head linkage of the monomer units could occur since both products are assumed to involve the common intermediate [44] and, also, secondly, it suggested that the vinyl group may be included in the polymerisation process through extended conjugation.

2.3.2. Method 2

Although the results obtained in Method 1 were very suggestive it was unsatisfactory overall since polymeric material soluble in organic solvents was not obtained; soluble material was essential for an analysis of its structure.

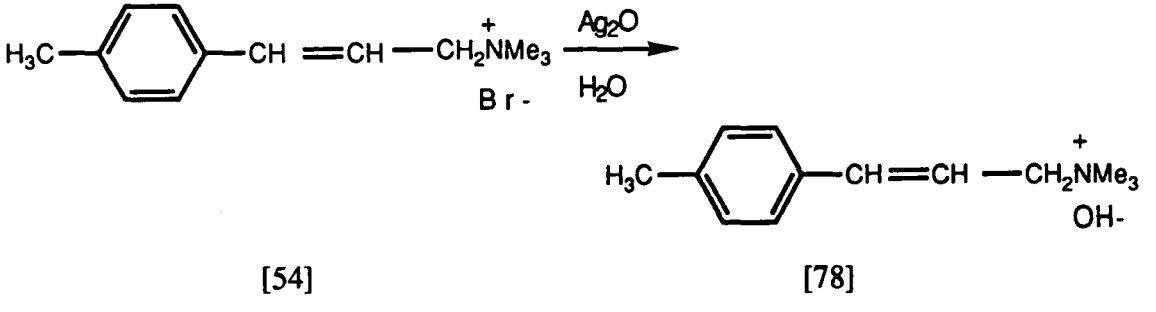
The second method followed in these polymerisation processes was first reported by Filler et al in 1986[16]. The original paper described the conversion of *p*-methyltetrafluorobenzyltrimethylammonium bromide [76] to the corresponding hydroxide with silver(I) oxide and the decomposition of this hydroxide to give a 42% yield of the [2.2]-paracyclophane [77] (Scheme 19).



Scheme 19 *The literature reaction of [76] with silver (I) oxide followed by thermal decomposition of this hydroxide to the dimer [77]*

2.3.2.1. Using *p*-methylcinnamyltrimethylammonium bromide [54]

Reaction of [54] with freshly prepared silver(I) oxide in aqueous solution gave after filtration a clear solution which was assumed to be [78].

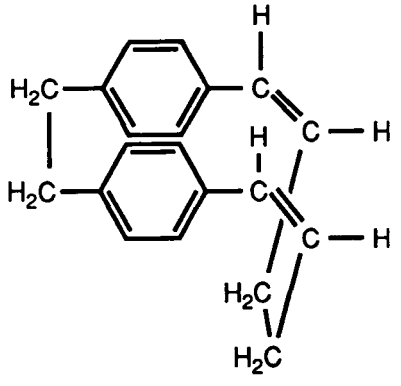


This clear solution [78] was mixed with toluene and a small amount of phenothiazine as a polymerisation inhibitor. Continuous extraction of water over 5h using a Dean and Stark apparatus produced a small amount of insoluble organic material which was filtered from an orange solution. The solution was concentrated to give a polymeric-looking material which was Soxhlet extracted with light petroleum (b.pt. 80-100°C) to leave a greyish polymeric material and, on removal of solvent from the extracts, an orange liquid. The polymeric material was dissolved readily in THF and was purified by reprecipitation from methanol.

2.3.2.2. Oligomeric materials

The orange liquid from the Soxhlet extracts of the polymer produced from [54] produced a white solid when triturated with cold light petroleum(b.pt.80-100°C). After recrystallisation, ^{1}H nmr and mass spectrometry showed the solid was the same dimer [75] that had been obtained previously by Method 1.

Column chromatography of the remaining complex mixture on alumina allowed one further component to be isolated. The mass spectrum again showed a molecular ion of 260 which indicated another cyclic dimer of the vinyl-extended *p*-xylylene. The ^{1}H nmr of the impure sample showed a remarkable similarity to the spectrum of E,E-[6,2]-paracyclophan-1,5-diene [75]. The multiplicity and intergrations of the peaks were identical but the chemical shifts were, in certain cases, quite different. The coupling constant of the doublet at 6.4ppm was 11.25Hz which showed that the material was the Z,Z-[6,2]-paracyclophan-1,5-diene [79].



[79]

2.3.2.3. Analysis of polymer

The ^1H nmr of the polymer is shown in Fig. 8 with the peaks labelled a-j for reference purposes. As usual in the spectrum of a polymer the peaks, particularly g-j, are somewhat broadened leading to oversimplified splitting patterns. It was suspected from the shifts that b,c,d,e and f represented alkenic protons whilst g-j represented protons on saturated carbons.

In order to decipher this complex spectrum two techniques were employed; decoupling experiments were performed on the 'alkenic' resonances (b-f) and then a COSY spectrum was run which gave information on the structure as a whole.

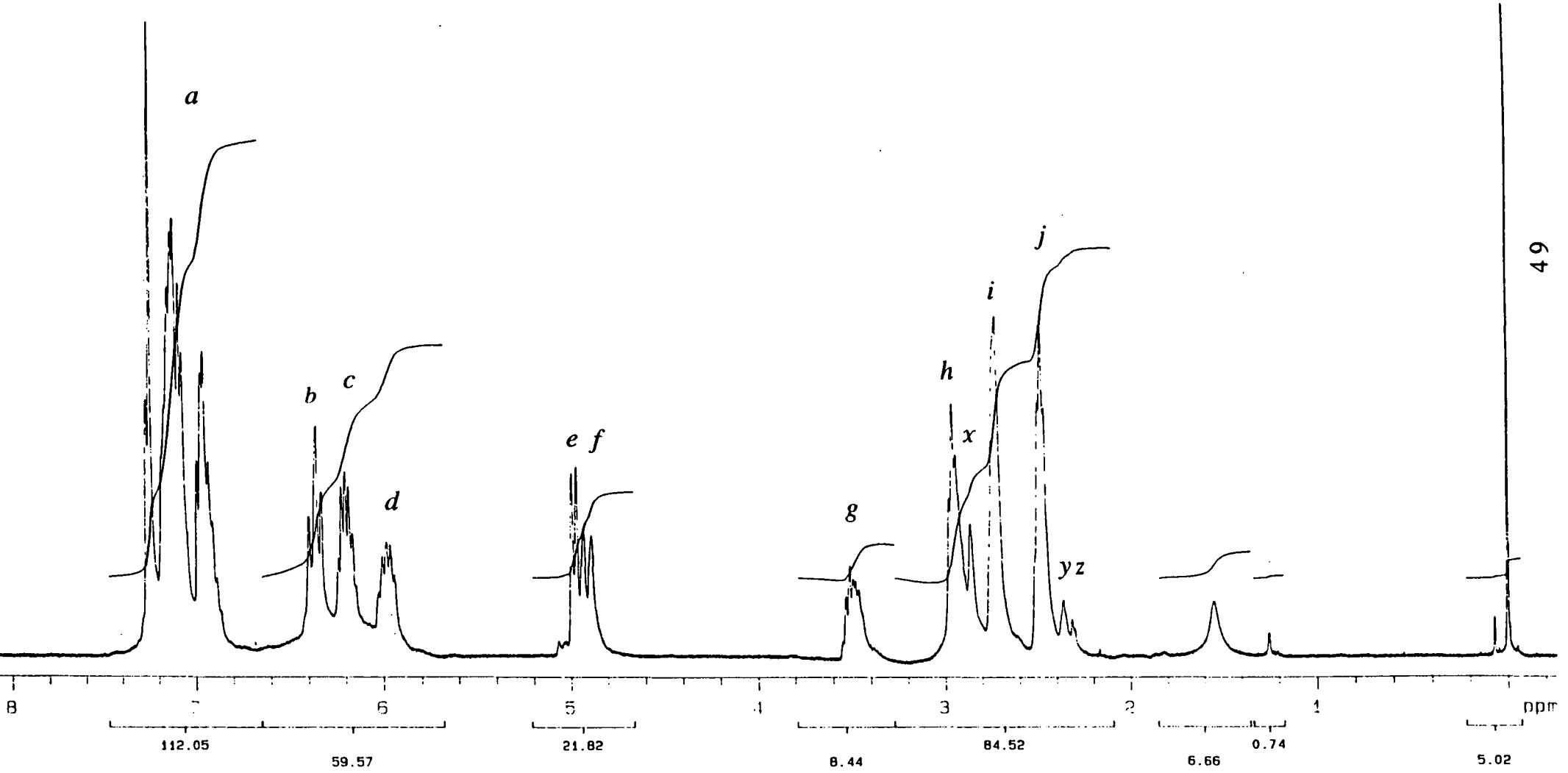
Decoupling Experiments

Two very significant structural features were identified through these experiments:

(i) *Peaks b and c were the protons of a cinnamyl system (ArC<u>H</u>=C<u>H</u>-C).* When peak b was decoupled the only peak affected was c and vice versa. This was not unexpected since the peak integrations showed a ratio of 1:1 between b and c and the splitting patterns and shifts of the peaks were very similar to previously synthesised cinnamyl systems. Moreover the analogy showed that b represented the proton nearer the benzene ring.

(ii) *Peaks d,e and f were the three protons of an allyl system (C<u>H</u>$_2$=C<u>H</u>-C).* When peak d was decoupled it affected only e and f whilst the decoupling of f simplified d. This suggested that d represented the alkenic C<u>H</u> of *C-C<u>H</u>=CH$_2$* whilst e and f represented the two geometrically different protons <u>H</u> of the *C<u>H</u>$_2$=CH* . The relative integrations of d,e and f were found to be 1:1:1 and the splitting patterns and shifts corresponded well with known allylic systems.

Fig 8 *The 400MHz spectrum of the polymer from the reaction of p-methylcinnamyltrimethylammonium bromide by Fillers' method*



COSY Data

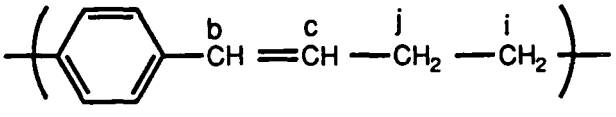
The above experiments gave information about the alkenic peaks (b-f) and clearly showed that polymerisation incorporating the extended conjugation had occurred(because of the presence of cinnamyl groups as found in [46]) but did not rule out or confirm the presence of any of the structural units possible ([46],[47],[49]-[52]) as the aliphatic peaks (g-j) remained unassigned. The COSY spectrum, shown in Fig 9a and 9b, provided a great deal more information about the polymeric structure and this is summarised below:

(i) It was confirmed that the proton of b was coupling with the proton of c and with no other protons.

(ii) As well as coupling with the proton of b the proton of c was coupling with j.

(iii) The protons of j were coupling with i as well as with c but with no others.

This data (i),(ii) and (iii) proved that peaks b,c,j and i were part of a cinnamyl unit [46] though the integrated spectrum was not strictly accurate because of poor resolution and possible overlapping absorptions.



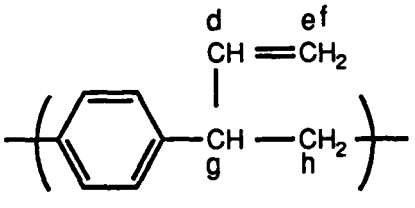
[46]

(iv) The protons of e and f were coupling with d only.

(v) The proton of d also coupled with g in the aliphatic region of the spectrum.

(vi) The proton of g was also coupling with h.

The data in (iv),(v) and (vi) in conjunction with the integrated spectrum proved that peaks d,e,f,g and h corresponded to the unit [47].



[47]

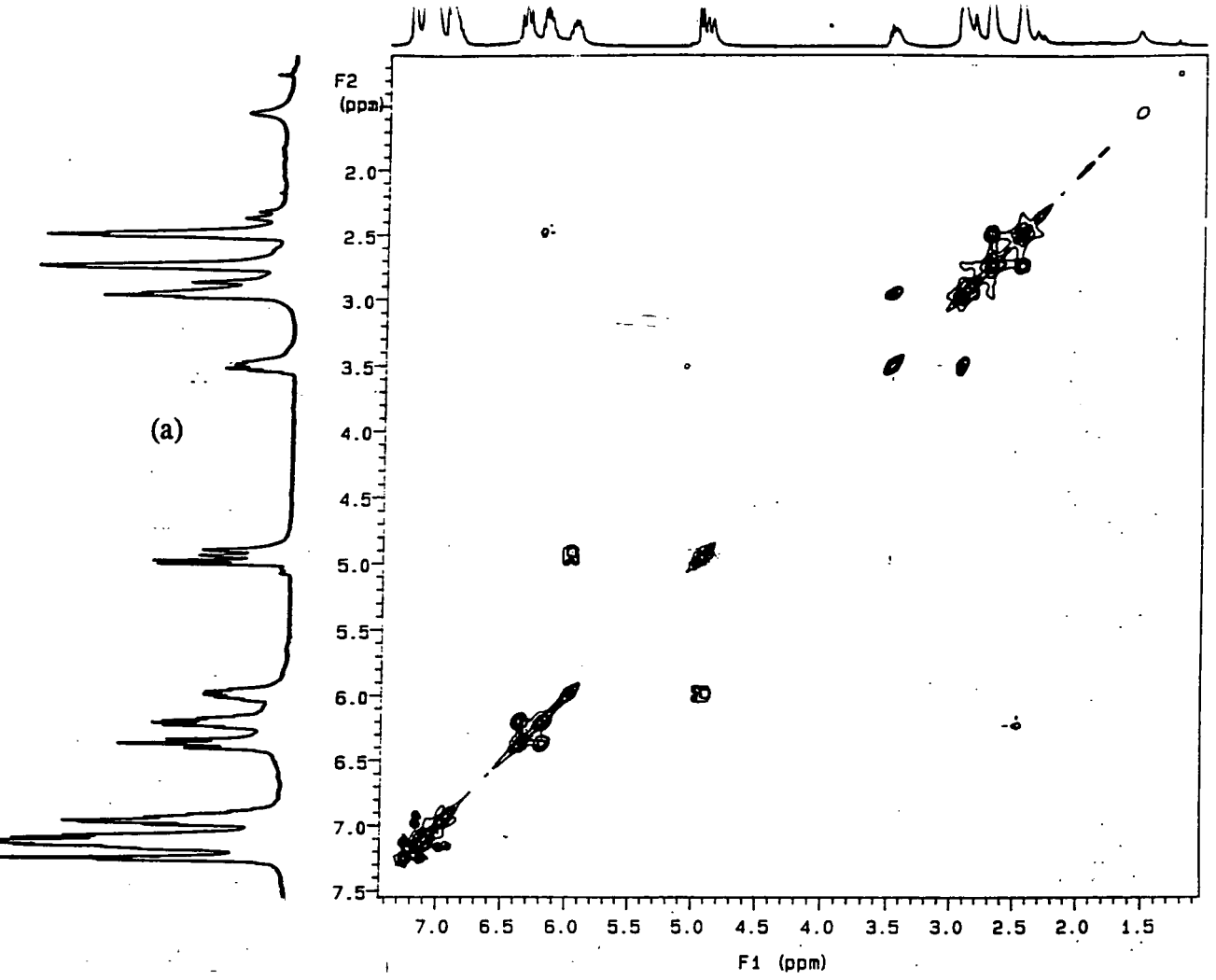
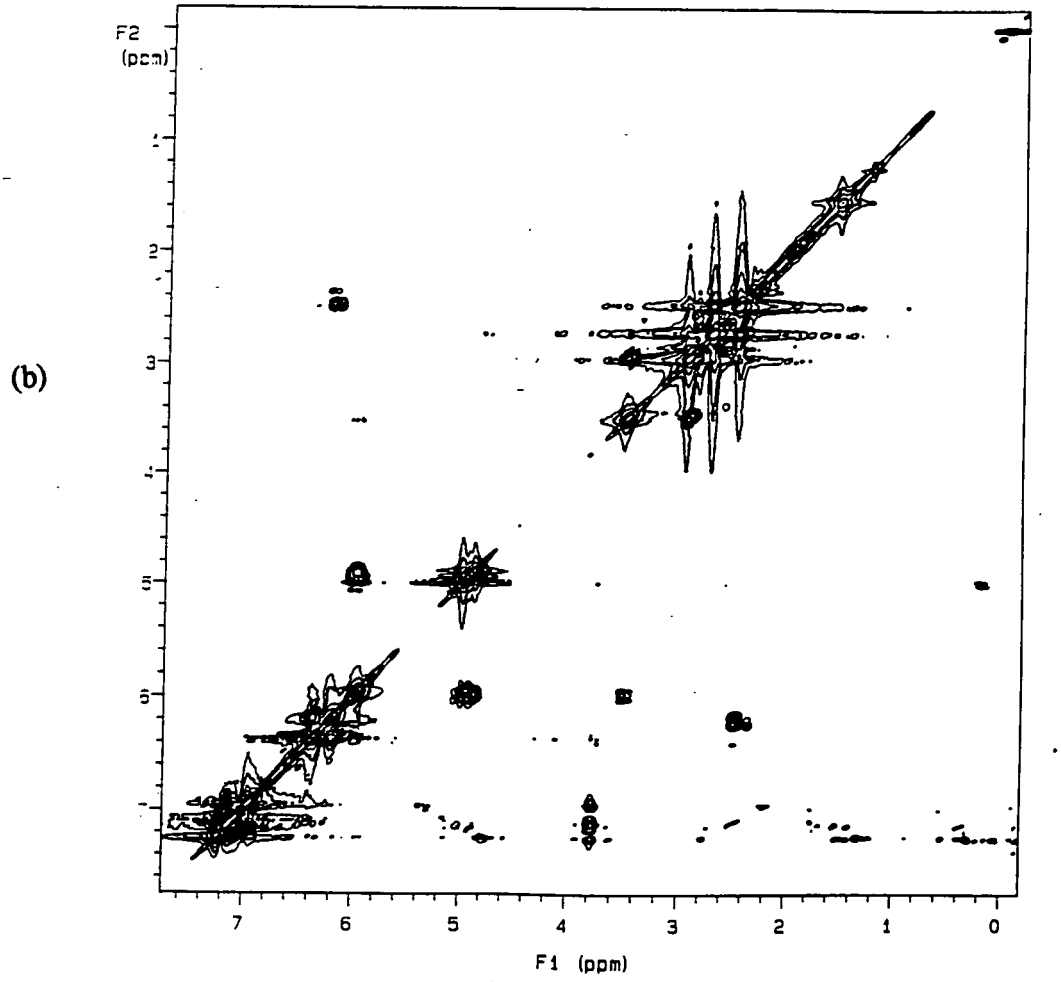
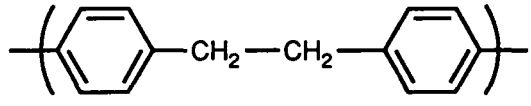


Fig. 9 *The COSY spectrum of polymer [80]: (a) normal spectrum (b) more intense*



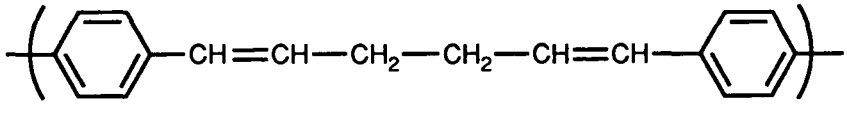
Thus the COSY spectrum showed that the polymer chain consisted of two basic units [46] and [47], which were shown by the integrations to be in a ratio of 1.8:1. None of the other four possible polymer structures fitted the COSY spectrum.

Although the bulk of the polymer structure was clearly aligned in a head-to-tail fashion there were a few smaller peaks which were unassigned and could be due to head-to-head or tail-to-tail units. The cyclic dimers [75] and [79] obtained from the same monomer precursor [44] incorporated structural features which would be found in tail-to-tail unit [50] and head-to-head unit [49]. Whether the comparatively rigid structure of the dimers *can* be used as an appropriate model for assigning ^{1}H nmr resonances in free moving polymer structures is uncertain. Nevertheless, it was clear that the peak in the spectra of the dimers corresponding to the protons H of the C_6H_4-CH_2-CH_2-C_6H_4 unit at 2.9ppm was present in the polymer spectrum and is labelled peak x. It would appear that peak x represents the tail-to-tail unit [50].



[50]

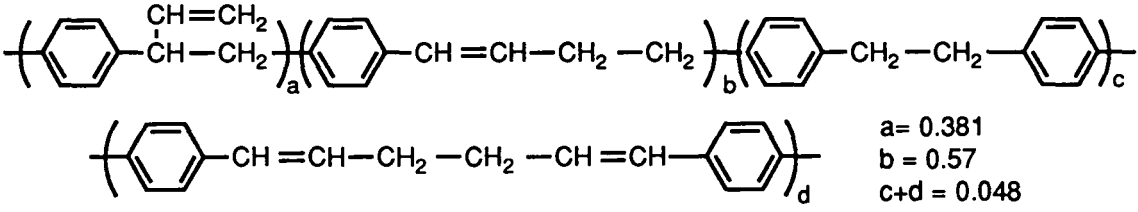
The peak in the spectra of the dimers corresponding to the protons H of the CH=CH-CH_2-CH_2-CH=CH unit was found at 2.4ppm in the E,E dimer [75] and at a lower frequency (2.0ppm) in the Z,Z dimer [79]. The two small peaks, labelled y and z , in the spectrum of the polymer at 2.4ppm and 2.3ppm could represent head-to-head units of type [49] with the shift difference being due to the conformation of the double bonds.



[49]

Obviously if the head-to-head unit [49] is present then alkenic resonances of the type ArCH=CH should also be observed. It is reasonable to suggest that these are obscured by resonances b and c, which also explains the higher than expected integrations

observed for these peaks(see decoupling expts). If the amount thought to correspond to the head-to-head unit is subtracted from the integrals of b and c, then it is found that the units [46] and [47] are actually present in the ratio 1.5:1. Through a comparison of the integrals of peaks x and h the ratio of head-to-tail to tail-to-tail units was found to be ~8:1 which represents a proportion of more than 10% of tail-to-tail(and therefore head-to-head) units. It is possible (though unlikely from consideration of steric effects) that units of the type [51] (due to head-to-head polymerisation as a *p*-xylylene with a pendant vinyl group) could also be present but it is likely that the relevant resonances are obscured by peaks d,e,f and g. It is not possible to ascertain the presence of units of the type [52] from the nmr data. Differential scanning calorimetry was performed in order to determine whether the polymeric material was a mixture of homopolymers with more than one glass transition temperature(T_g) or one copolymer with one T_g. Since only one T_g was observed (see Appendix 3) the polymeric backbone was deduced to be that shown in [80].



[80]

The polymer was analysed by gel permeation chromatography which showed a molecular(M_n) weight of 1.44×10^4 representing a DP of c.a.111.

2.3.2.4. Using *p*-allylbenzyltrimethylammonium bromide [53].

The polymerisation of this salt was performed by this method twice; the first polymerisation involved the use of phenothiazine, following Fillers' methodology[16], as a polymerisation inhibitor whilst in the second polymerisation phenothiazine was omitted.

i. With added phenothiazine

A solution of *p*-allylbenzyltrimethylammonium bromide [53] was converted to the hydroxide using silver(I) oxide. The clear hydroxide solution was mixed with toluene and trace phenothiazine and heated under reflux whilst water was continuously removed

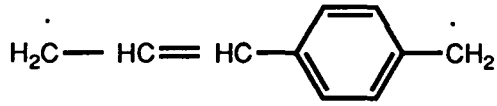
with a Dean and Stark apparatus. Unfortunately, polymeric material insoluble in organic solvents was obtained which amounted to a yield of 30%. The remaining material was shown by ^1H nmr to be 95 parts E,E-[6,2]-paracyclophan-1,5-diene [75] and 3 parts Z,Z-[6,2]-paracyclophan-1,5-diene [79]. After column chromatography on alumina pure E,E dimer was obtained (67%), a remarkably high yield.

ii. Without phenothiazine

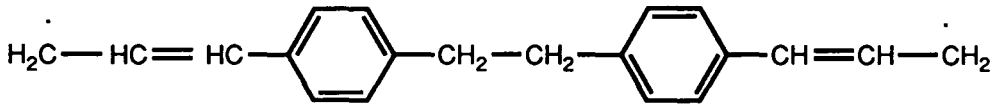
The previous experiment was repeated exactly except that no polymerisation inhibitor was used. It was hoped that a polymeric material soluble in organic solvents might be obtained by this method which could have been compared with that obtained using *p*-methylcinnamyltrimethylammonium bromide. However, a polymeric material insoluble in organic solvents was again obtained which represented a 40% yield. The remaining soluble material was shown by ^1H nmr to be entirely the E,E-dimer [75], thus representing a 60% yield.

2.4. The isomerisation of E,E-[6,2]-paracyclophan-1,5-diene [75].

It was reported by Gorham in 1966 that the cyclic dimer of *p*-xylylene, [2.2]-paracyclophane [7], was converted by vacuum phase vapour pyrolysis at 600°C to high molecular weight linear poly(*p*-xylylene)[87]. It was presumed that [7] was cleaved to form two molecules of *p*-xylylene which spontaneously polmerised on condensation. Since a dimer [75] had also been obtained in high yield from some of the experiments described above there was an obvious interest in seeing whether a high molecular weight polymer of our conjugatively extended *p*-xylylene could be similarly obtained. It was thought that the anticipated intermediate [83] would be likely to lead to a polymer chain containing a greater proportion of cinnamyl units than that obtained in 2.3.2.2. There was also a mechanistic question to be answered: if the polymerisation proceeded via a diradical dimer intermediate such as [84] then a significant amount of head-to-head polymerisation would be expected, whereas if a double cleavage to two monomeric diradical units [83] took place then a similar polymer to that obtained previously [80] might be expected.



[83]



[84]

E,E-[6,2]-paracyclophan-1,5-diene was placed in sublimation zone [A] of the apparatus shown in Fig. 10 which was warmed to about 200°C thus subliming the dimer into the pyrolysis zone [B], held at 580°C. The product collected as a yellowish oil in zone [C].

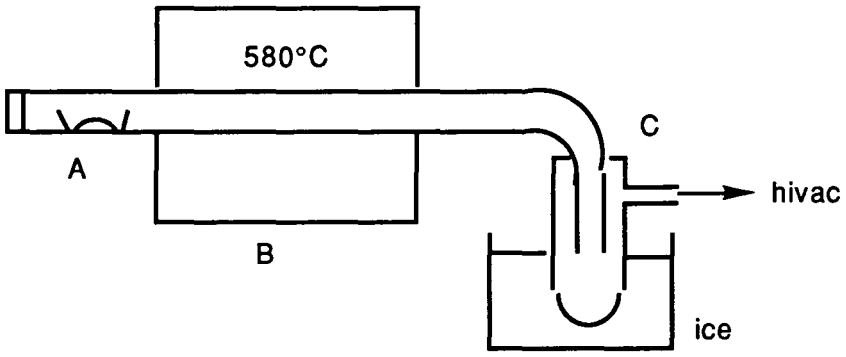


Fig 10 *Vacuum phase vapour pyrolysis equipment*

Analysis of this oil showed the E,E dimer had been entirely converted to the Z,Z dimer [79] by the pyrolyis which indicated that [79] was the thermodynamically more stable of the two isomers. The product was purified by sublimation and recrystallisation from light petroleum. A further pyrolysis using a temperature of 700°C in zone [B] gave similar results.

2.5. Discussion

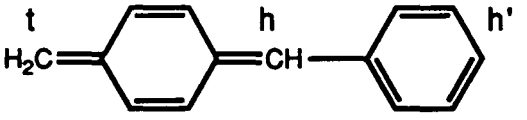
The vinyl-extended *p*-xylylene has been approached from two different salts : [53] and [54]. It must be noted that whilst a polymer soluble in organic solvents was obtained using [54] only insoluble polymer was obtained using [53] despite the fact that identical reaction conditions and reactant concentrations were employed. Presumably, the insoluble polymer from [53] was of a higher molecular weight or had undergone cross-linking to a greater extent than the polymer from [54] but no explanation as to why this should be the case could be tendered. The polymer obtained from [54] was shown to consist of two types of units [46] and [47] showing that the extra conjugation of the vinyl-extended *p*-xylylene was, at least partly, included in the polymerisation process.

Chapter Three

Phenyl-extended *p*-xylylenes

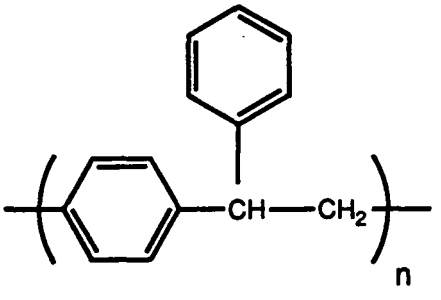
3.1. Introduction

In Chapter Two it was shown that a vinyl-extended *p*-xylylene could be polymerised to some extent through the extra conjugation. In this Chapter the polymerisation behaviour of the unsymmetrical phenyl-extended *p*-xylylene (7-phenyl-*p*-xylylene) [45] will be considered.

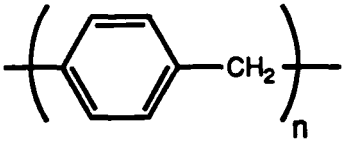


[45]

If we again make the unsubstantiated assumption that the polymerisation will take place only in a head-to-tail manner then two polymer backbones could be obtained: [85] with the phenyl group as a passive substituent; and [86] where the phenyl group is intimately involved through conjugative interaction with the rest of the molecule. In the latter case only the *para* position is considered as a new reactive centre.

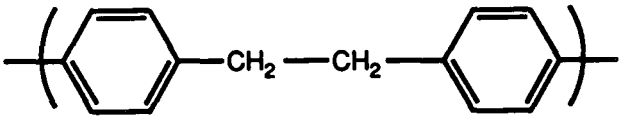


[85]

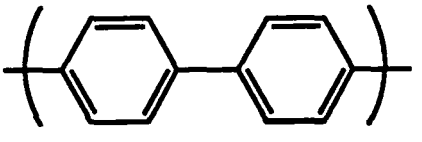


[86]

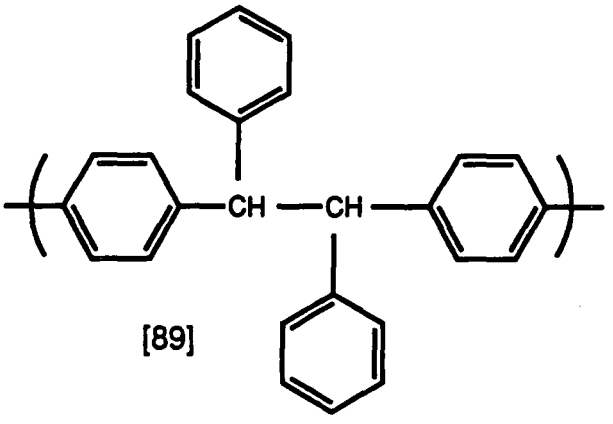
If head-to-head and tail-to-tail linkages also occur the following additional structural features will be present in the polymer.



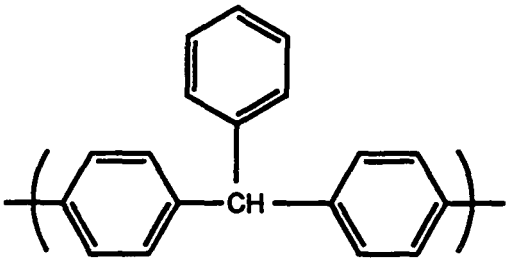
[87]



[88]

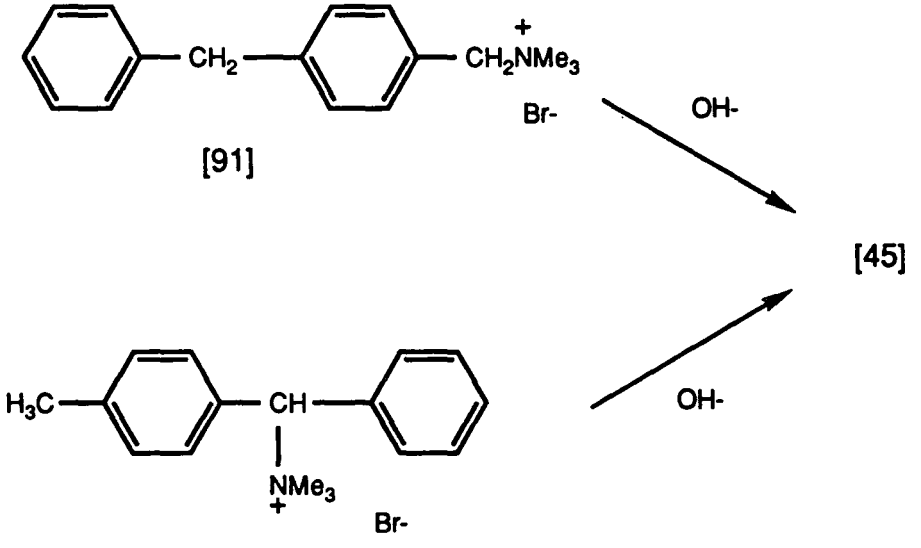


[89]



[90]

Once again [45] was expected to be a highly reactive material and so the polymerisation reactions were performed on materials which lead to its production *in situ*. Two trimethylammonium salts [91] and [92] were synthesised, which, upon reaction with base, were expected to give [45] through 1,6-Hoffmann elimination reactions.



[91]

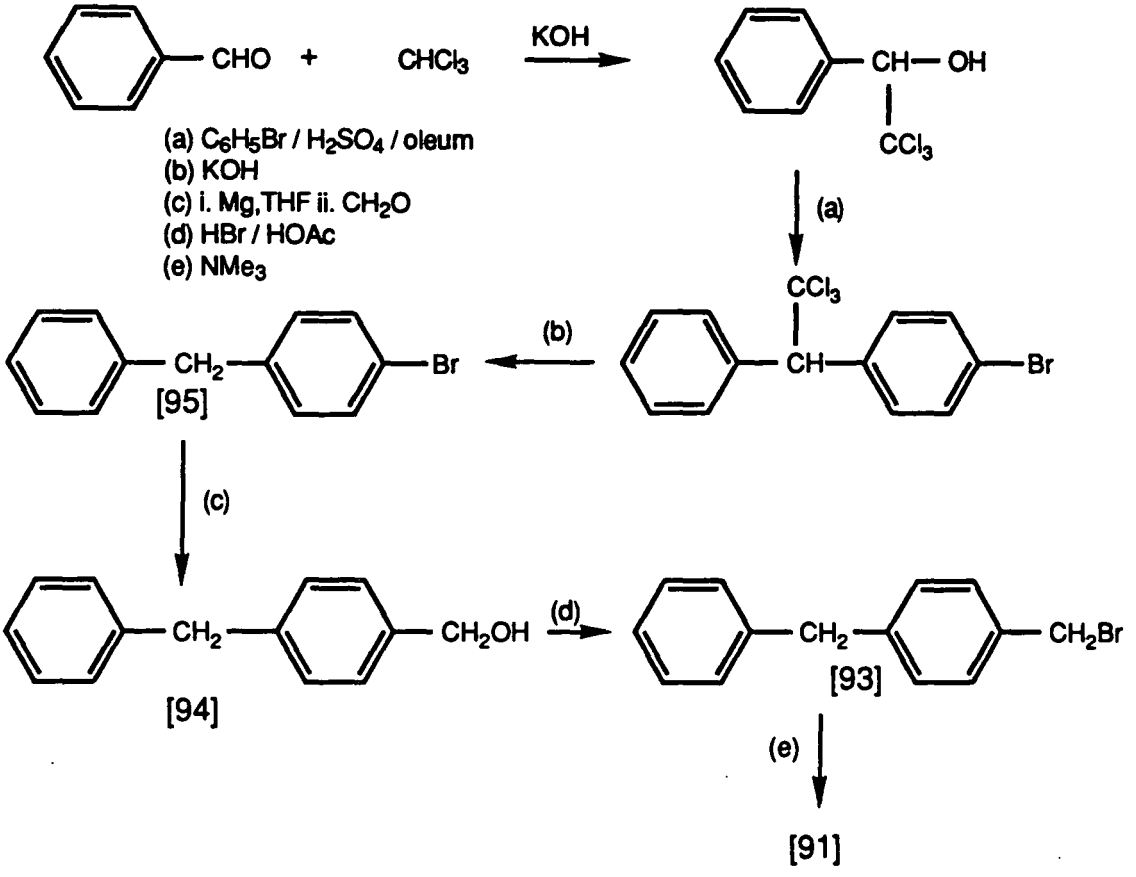
[92]

This Chapter will detail the syntheses of the two salts [91] and [92] followed by a discussion of the polymerisation reactions and detailed analyses of the interesting products that were obtained.

3.2. Syntheses of Salts

3.2.1. *p*-Benzylbenzyltrimethylammonium bromide [91]

The reaction of the hydroxide (related to this compound) on heating was reported in a communication in 1957 by Bersch[88]. However, the synthetic route to the salt [91] was not described. The route used in the present work is shown in Scheme 20 which is based on the literature synthesis of *p*-benzylbromobenzene[89][95].

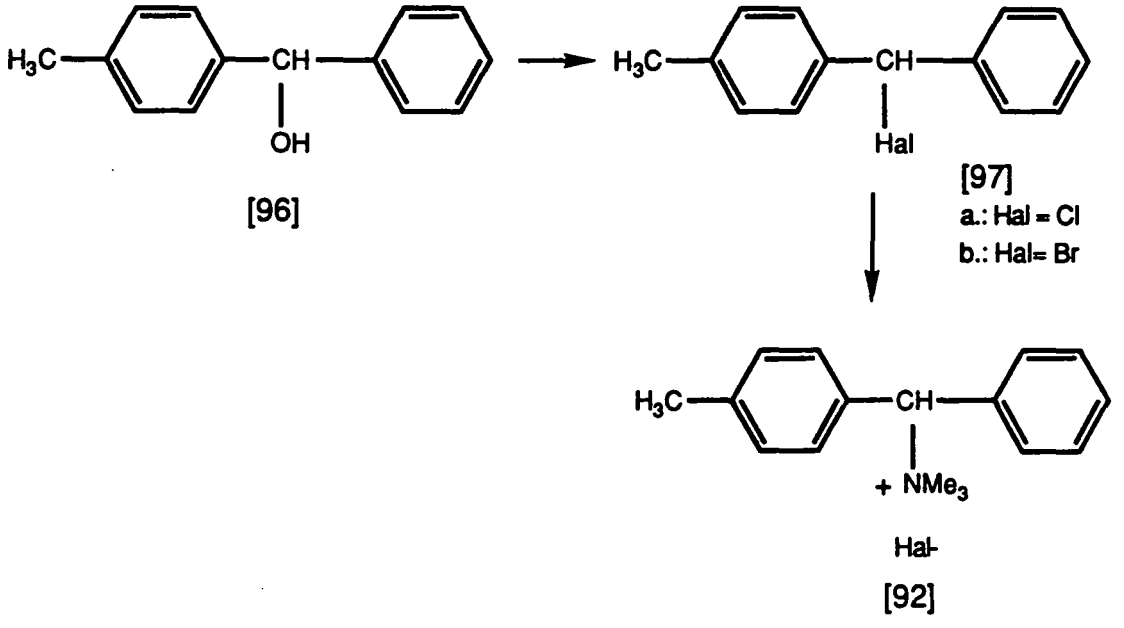


Scheme 20 *The synthetic route to [91]*

The Grignard reagent formed from [95] was reacted with formaldehyde to produce *p*-benzylbenzyl alcohol [94] in 60% yield. *p*-Benzylbenzyl alcohol [94] was converted to *p*-benzylbenzyl bromide [93] using 45% HBr in glacial acetic acid and the salt [91] was produced by treating an ethereal solution of [93] with trimethylamine under nitrogen.

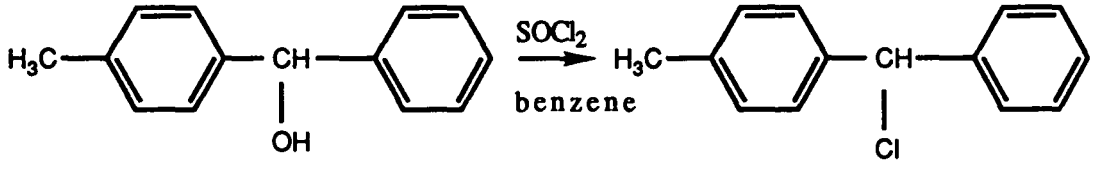
3.2.2. *p*-Methylbenzhydryltrimethylammonium bromide [92]

The synthetic route to [92] was based on the conversion of *p*-methylbenzhydrol [96] to the corresponding halide [97] (Scheme 21).



Scheme 21 *The synthetic route to [92]*

p-Methylbenzhydryl chloride [97a] was produced by refluxing [96] with thionyl chloride in dry benzene. However, the chromatographically pure compound obtained through column chromatography on silica using dichloromethane as elutant did not react with trimethylamine.

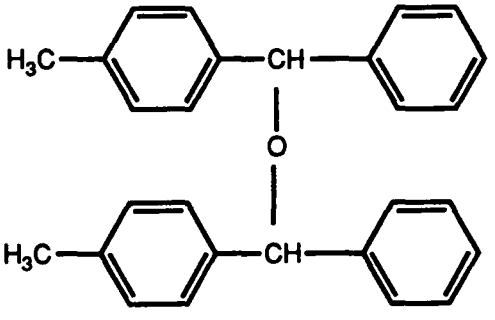


[96] [97a]

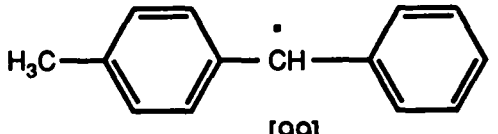
The bromide [97b] was then synthesised by warming *p*-methylbenzhydryl alcohol [96] in a 45% solution of HBr in glacial acetic acid. Gas chromatography showed the distillate was 94% pure and the further purification neccessary was expected to be fairly straightforward. Three methods of purification have been attempted and these will be described separately as unexpected transformations of the bromide took place.

(i) Column Chromatography On Silica

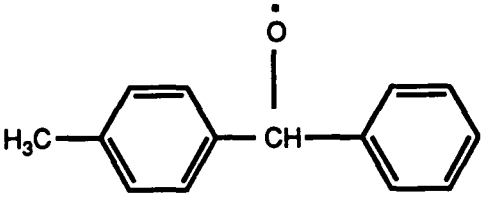
Thin layer chromatography of the crude bromide [97b] showed the presence of three components using dichloromethane as elutant: a fast moving component which was assumed to be the bromide; a slow component which appeared to be the alcohol and a slightly faster moving component than the alcohol. As the mixture was flushed onto the preparatory column of silica a deep orange-brown colouration was observed which did not move appreciably throughout the separation. The fastest moving component was isolated fairly easily as an extremely viscous colourless oil which solidified only after 1 month in methanol solution at -18°C. The 400MHz ^1H nmr spectrum of this product showed that it was di(*p*-methylbenzhydryl) ether [98]. The elemental analysis was correct for this compound and the mass spectrum showed strong peaks at 181 and 197 corresponding to the fragments [99] and [100].



[98]

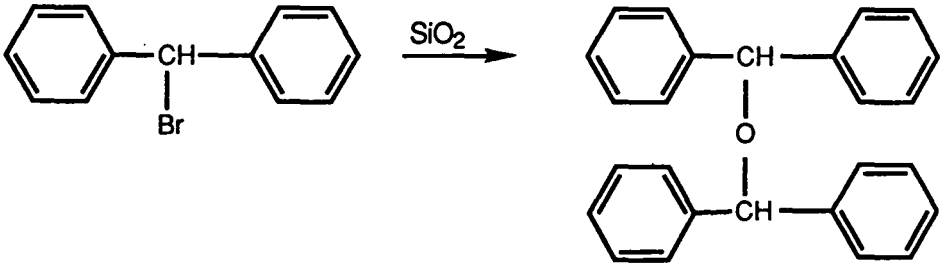


[99]



[100]

In order to test the generality of this simple ether-forming reaction, commercially available benzhydryl bromide was treated under the same conditions and gave the ether [98a] in 78% yield[90].



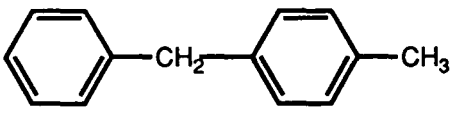
[98a]

(ii) Column Chromatography On Alumina

Column chromatography of the crude bromide [97b] on alumina gave the ether [98] as the fastest moving component identified by a comparison of its infrared spectrum with that of an authentic sample; the next component was the bromide [97b] and the slowest moving component was the alcohol [96]. Clearly the bromide had been partially hydrolysed but presumably the lower acidity of the alumina compared to silica lead to a lower yield of the ether (47% for the silica reaction c.f 13% on alumina).

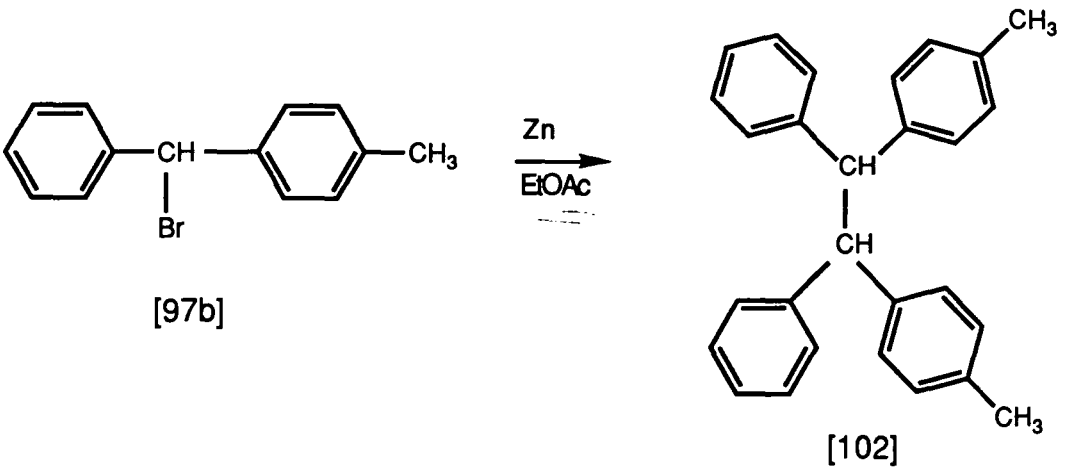
(iii) Distillation Through A Fischer-Spahltrohr Unit

Careful fractional distillation of the crude bromide [97b] at 1.0mmHg pressure gave 4-methylphenylphenylmethane [101] as the distillate rather than the bromide. The hydrocarbon was identified by elemental analysis, mass spectroscopy and ^1H nmr. The distillation flask contained much black polymeric material on completion of the distillation. Presumably the bromide had lost a bromide anion leaving a carbocation intermediate which picked up a hydride ion to give [101].



[101]

p-Methylbenzhydryl bromide [97b] was converted to 1,2-di(*p*-tolyl)-1,2-diphenylethane [102] using zinc[91] (Scheme 22). The hydrocarbon was used as a model for chemical shift assignments in interpreting nmr data(see later).



[97b] [102]

Scheme 22 *The synthesis of [102]*

p-Methylbenzhydryltrimethylammonium bromide [92] was prepared as an analytically pure material by treating an ethereal solution of the impure bromide [97b] with trimethylamine, leaving the mixture to stand under nitrogen for 6 days and washing the salt with diethyl ether.

3.3. Polymerisation Reactions Of Phenyl-Extended *p*-Xylylenes

The two salts [91] and [92] were both converted to hydroxides using silver(I) oxide and on reaction by Fillers' method[16] both gave polymeric materials soluble in organic solvents, accompanied by significant side products. The formation of polymer from the two salts will be described separately followed by a comparison of the results.

3.3.1. Using *p*-benzylbenzyltrimethylammonium bromide [91]

The crude product obtained by following Fillers method[16] was extracted in a Soxhlet apparatus for 18h using light petroleum (b.pt. 80-100°C) and the polymeric material that was left in the thimble was dissolved in tetrahydrofuran and reprecipitated into methanol. After two further reprecipitations the white spongey material was dried in vacuo at 50°C for 8h (the polymer is discussed later). The remaining material that had been Soxhlet extracted from the polymer was a very complex mixture. However, through column chromatography on alumina using various solvents two compounds [103] and [104] (see p.70) were isolated in 36% and 11% yields respectively and both were shown to be cyclic trimers: the mass spectra of both compounds showed molecular ions of 540 but both ^{1}H nmr spectra were very complex. There were found to be six theoretical cyclic

trimeric structures possible (without considering enantiomers) and so in order to explain the complex nature of the ^1H nmrs a detailed discussion is merited.

3.3.1.1. Elucidation of the cyclic trimer structures

The basic monomer unit of the trimeric structure is the α-phenyl-*p*-xylylene diradical (Fig 11).

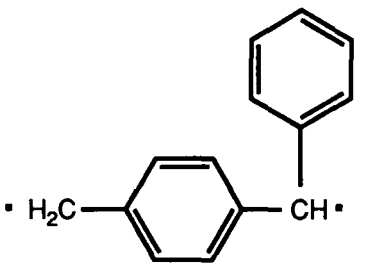


Fig 11 *The monomer unit 7-phenyl-p-xylylene*

For an unsymmetrical monomer unit there are two possible basic cyclic trimeric structures: [105] where three units are joined head-to-tail and [106] where three units are joined in any other order. If the trimers are represented as irregular hexagons i.e. long monomeric units linked by short bonds the possible basic structures which can be drawn out are shown in Fig 12.

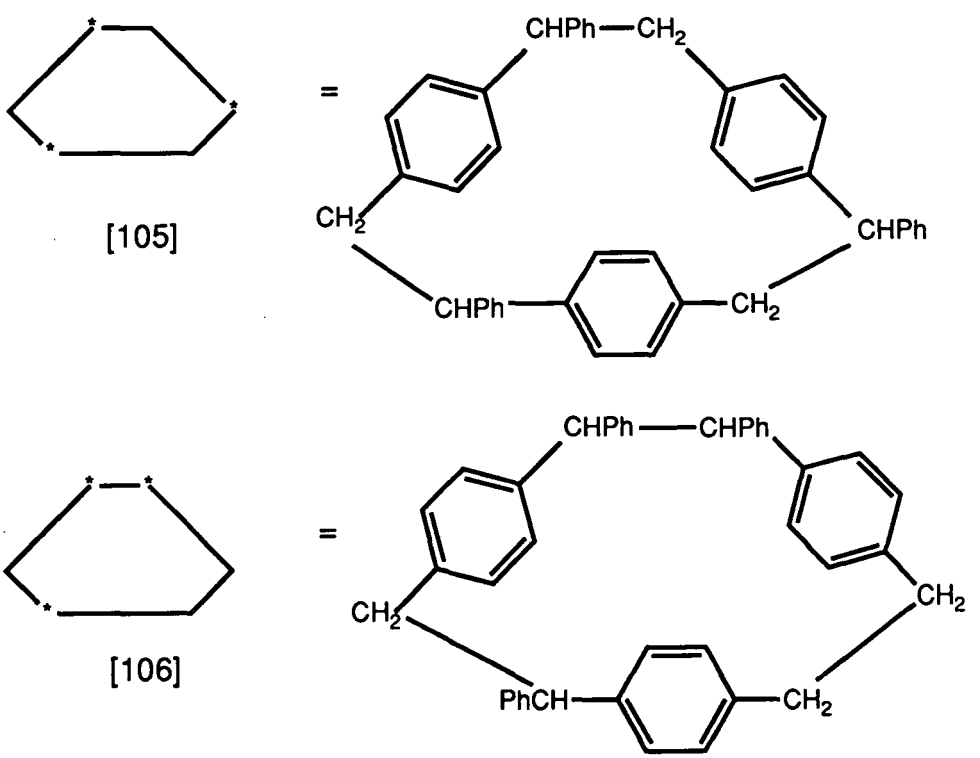


Fig 12 *The two basic cyclic trimeric structures*

However, the α-phenyl group can be either 'up' or 'down' which leads to the following alternatives for each basic structure; only *one* enantiomer is given in each case for simplicity though, in reality, both enantiomers will be present (i.e. all entities will be racemates) (Fig 13).

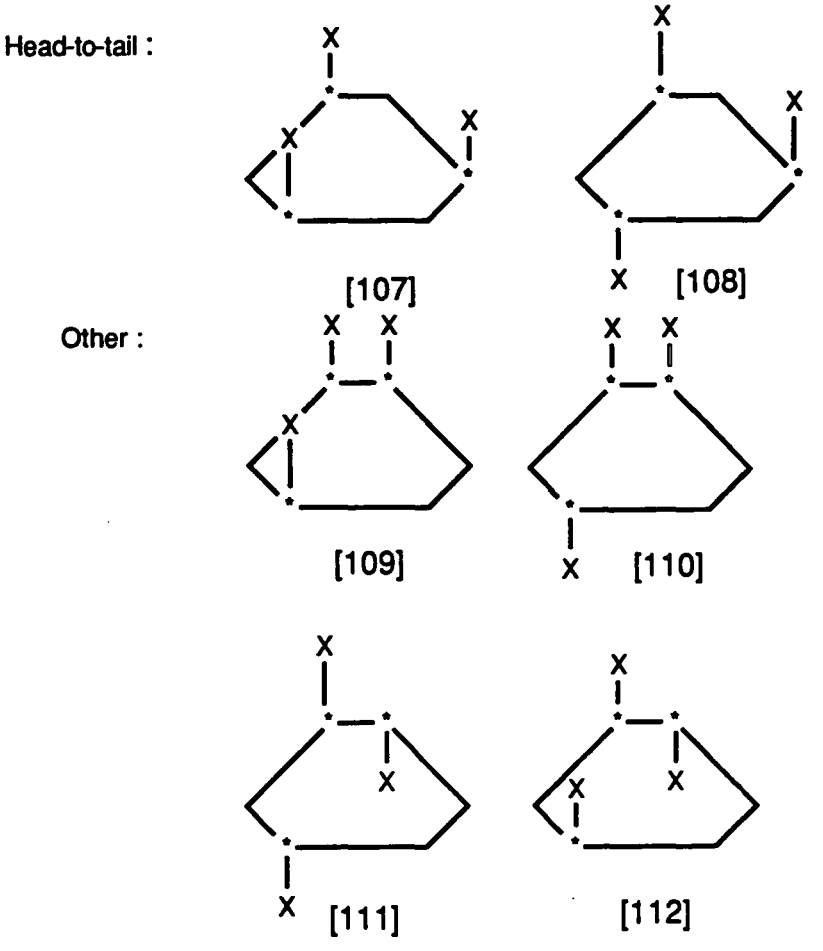


Fig 13 *Theoretical cyclic trimeric structures once the stereochemistry of the pendant phenyl groups is considered*

The 500MHz ^{1}H nmr of the cyclic trimer [103] is shown in Fig 14.

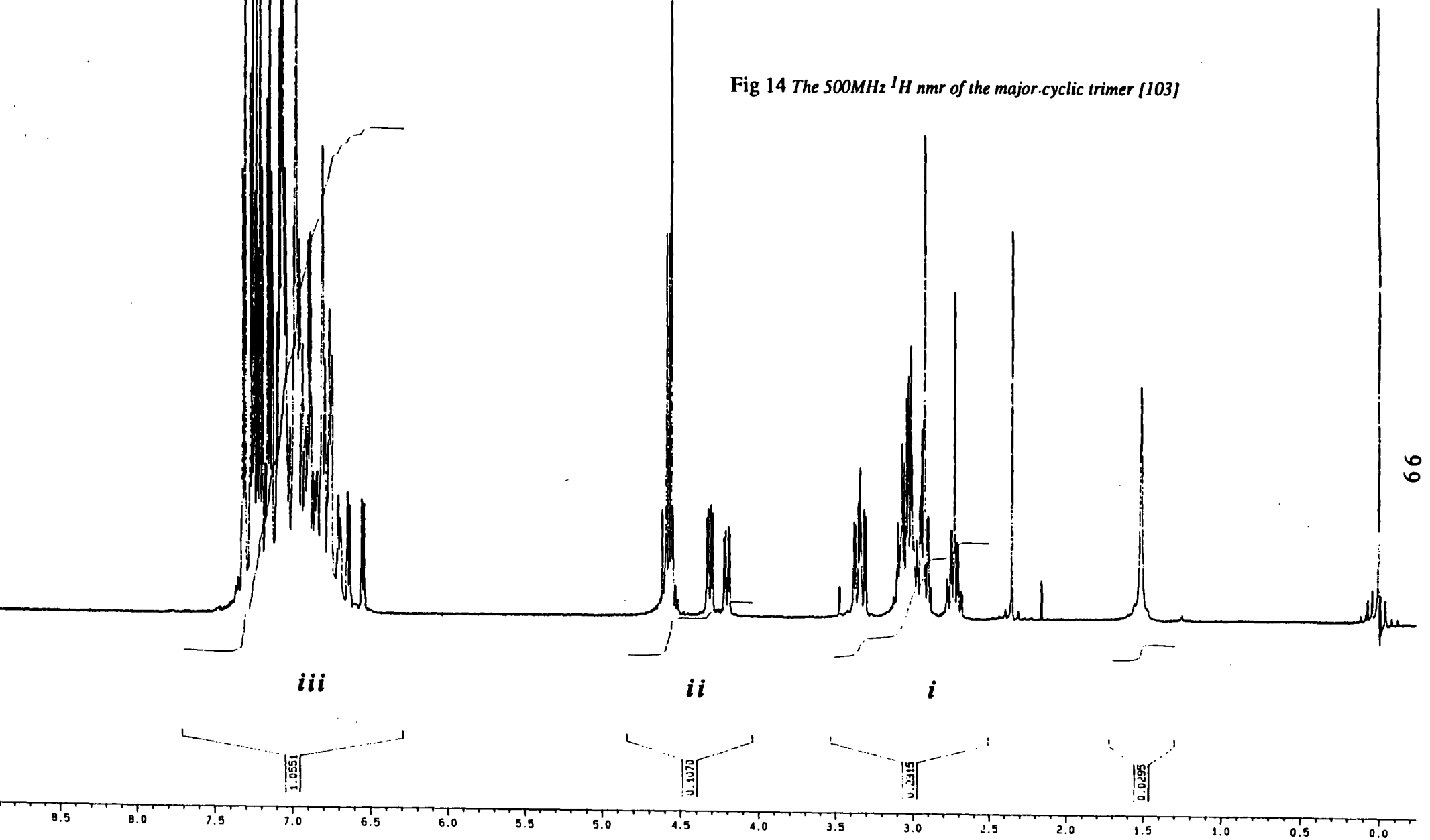
(a) The spectrum can be divided into three distinct regions :

(i) 2.5-3.5ppm

(ii) 4.0-5.0ppm

(iii) 6.5-7.5ppm

Fig 14 *The 500MHz ^1H nmr of the major cyclic trimer [103]*



The integrations of these three regions show relative values of (i):(ii):(iii) = 2:1:9 which clearly shows that :

(i) is due to $C\underline{H}_2$ groups

(ii) is due to $C\underline{H}(C_6H_5)$ groups

and (iii) is due to C_6H_5 and C_6H_4 groups

(b) The expanded spectrum (Fig 15) shows that in region (ii) there is an AB system (rel. integration 18) and an overlapping singlet (rel. integration 13) at ca 4.6ppm (peak B) and two doublets of doublets at 4.3(rel. integration 8.5, peak C) and 4.2ppm (rel. integration 7, peak D) respectively. Peak B is due to the two protons in two different -$C\underline{H}(C_6H_5)$-$C\underline{H}(C_6H_5)$-environments, the chemical shifts of which are very close to the related protons at 4.72ppm found in the model compound 1,2-di-(*p*-tolyl)-1,2-diphenylmethane [102], and peaks C and D are due to one proton in two different $C\underline{H}(C_6H_5)$-CH_2-environments. (This is confirmed by a comparison of the integration of B (31) relative to C and D (15.5)).Therefore the spectrum is due to an inseparable mixture of two isomers which have a head-to-head(and therefore a tail-to-tail) union of the unsymmetrical monomer unit [45] as represented by the basic structure [106].

There are four possible diastereomers with the basic structure [106]; two with syn orientated phenyl groups [109] and [110] and two with the phenyl groups anti [111] and [112]. Each pair of diastereomers will display very similar chemical shifts of the AB systems in $C\underline{H}(C_6H_5)$-$C\underline{H}(C_6H_5)$ but it is not possible at present to distinguish between them. However, what is clear is that in [103] there are two isomers present in the ratio 1.3:1 (average of 18/13 and 8.5/7).

(c) Proton decoupling experiments and a COSY spectrum (Fig. 16) enabled further assignments to be made. The multiplet E was a pair of overlapping doublets of doublets: the one centred at 3.362ppm coupled with the doublet of doublets C whilst the the other at 3.326ppm coupled with the doublet of doublets D. Therefore the protons at C and D (marked $\underline{H}$) in each $C\underline{H}(C_6H_5)$-CH_2 unit are associated with the corresponding protons (marked $\underline{H}$) in E of the structural unit $CH(C_6H_5)$-$C(\underline{H})H$-.

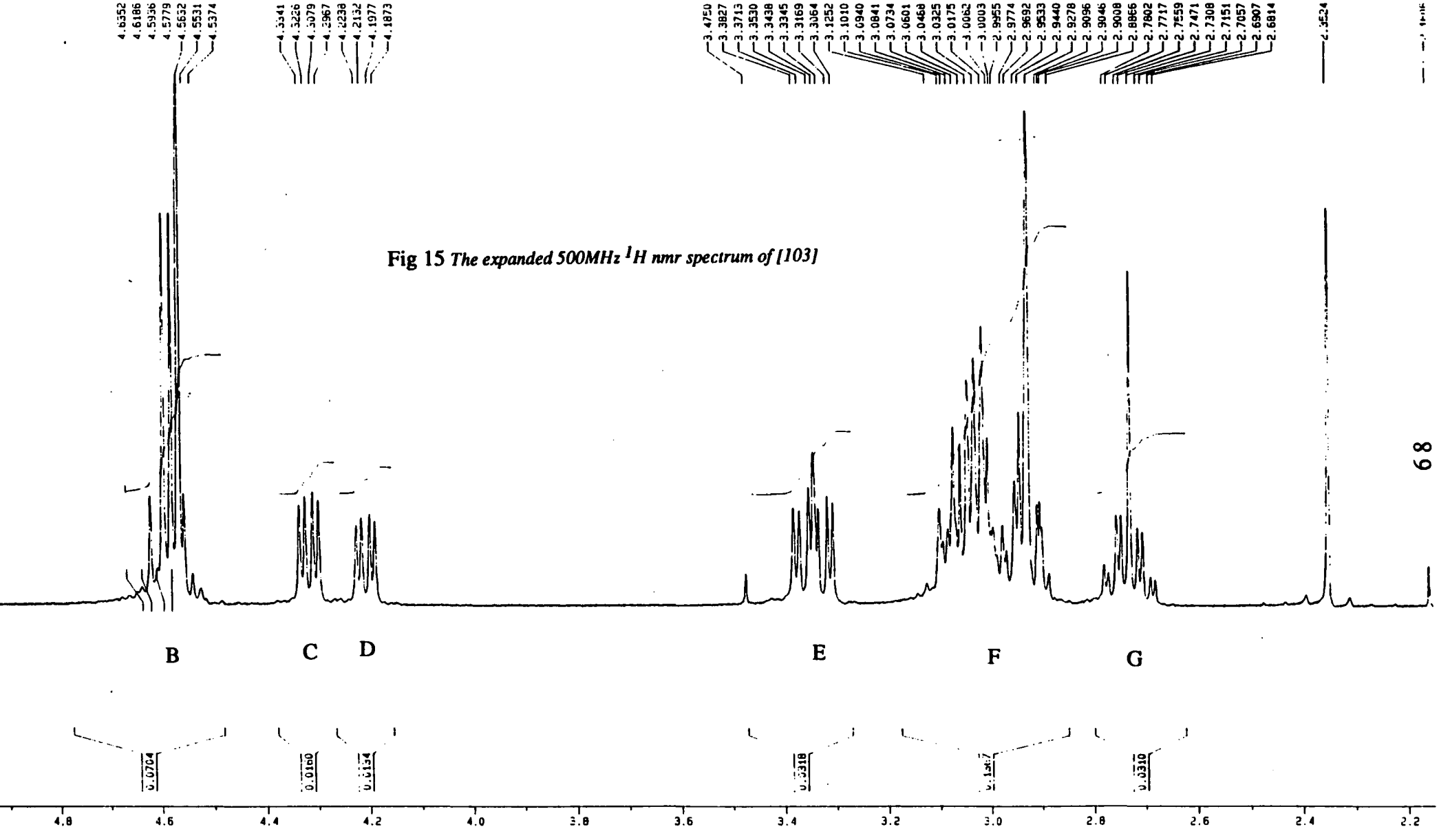


Fig 15 *The expanded 500MHz ^{1}H nmr spectrum of [103]*

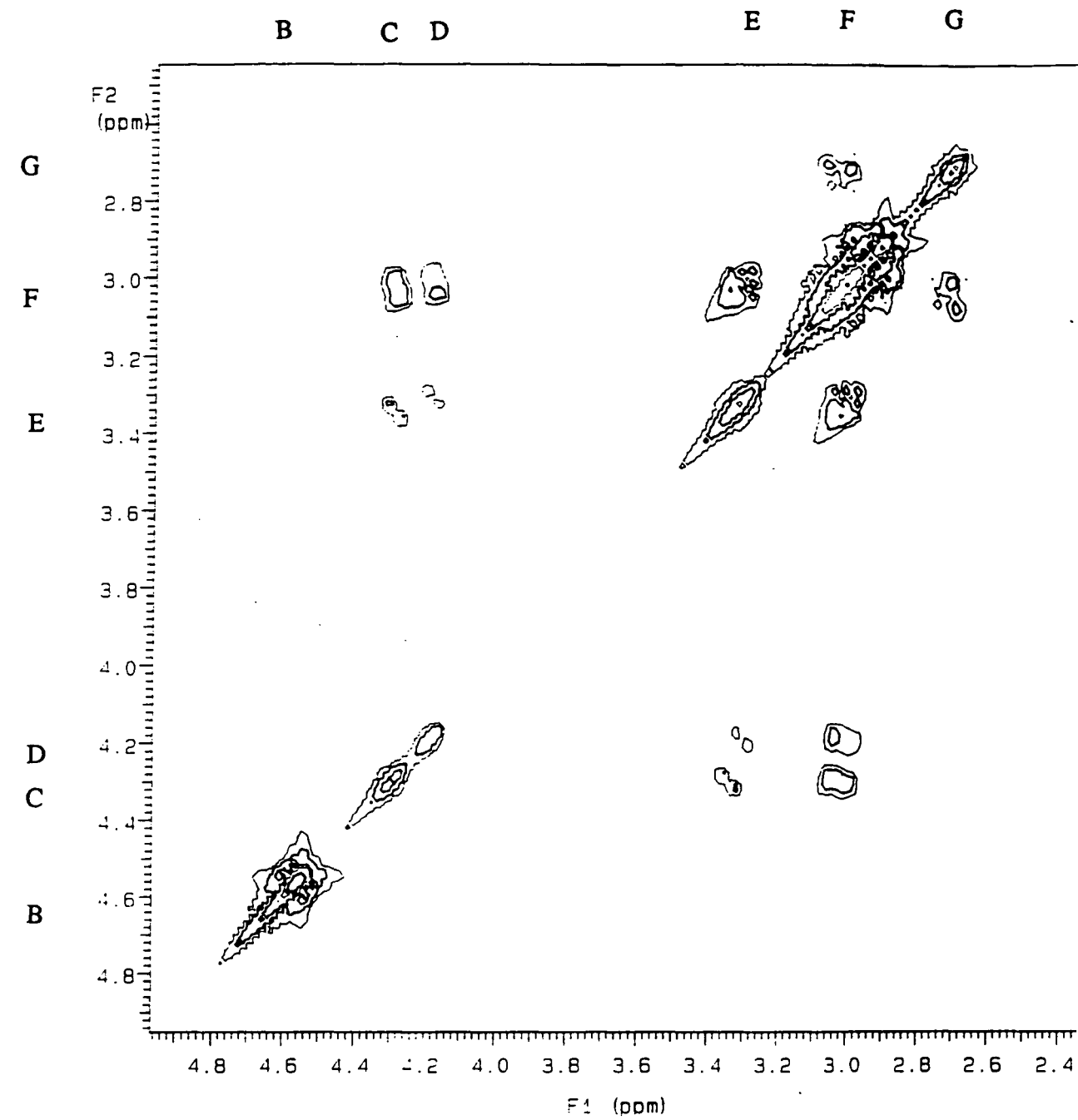


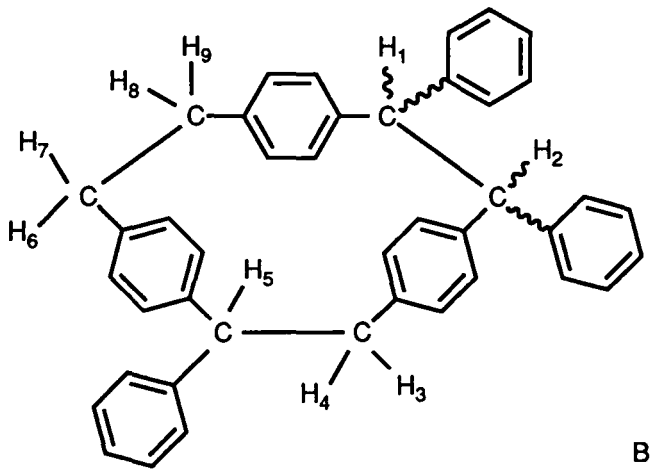
Fig. 16. *The COSY spectrum of major cyclic trimer [103]*

The multiplet G due to overlapping absorptions from one proton from each of the two isomers coupled only with protons in the broad region F. The relative integration of G confirmed it as the H in the CH_2-C(H)H unit in each isomer.

The broad region F therefore is due to the four protons H in the following structural units which were present in each of the two isomers:

CH_2-C(H)H and $CH(C_6H_5)$-C(H)H.

The above observations allow the following two structures (Fig.17) to be drawn and the labelled protons to be assigned to peaks in the ^1H nmr spectrum.



B = H_1, H_2, H_1', H_2'
C = H_5
D = H_5'
E = H_3, H_3'
F = H_4, H_4', H_6, H_6', H_7, H_7', H_8, H_8'
G = H_9, H_9'

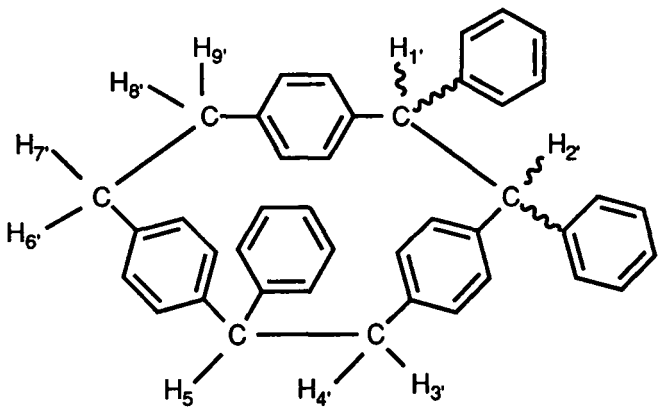


Fig. 17 *The two diastereomers present in [103] showing labelled protons*

(d) ^{1}H-^{13}C heteronuclear correlation (see Appendix 4) enabled labelled carbons to be assigned to peaks in the ^{13}C nmr (Fig. 18).

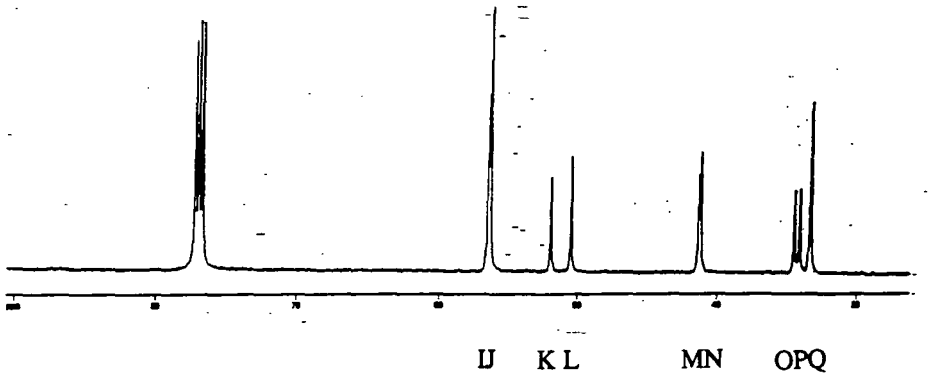
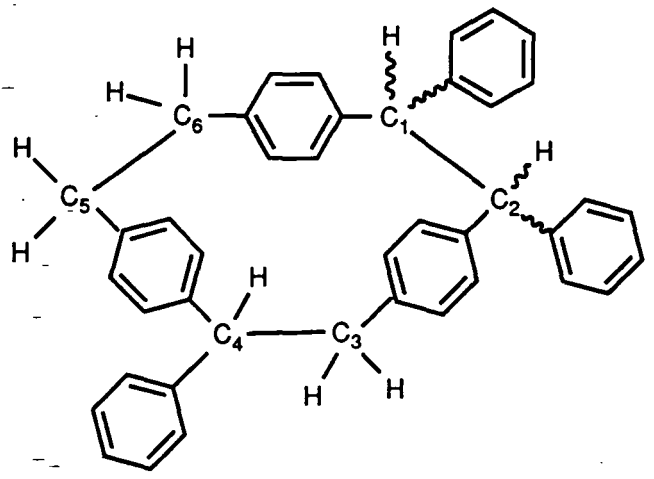


Fig. 18 *^{13}C nmr of cyclic trimer [103]*



I, J = C_1, C_1', C_2, C_2'
K = C_4'
L = C_4
M, N = C_3, C_3'
O, P, Q = C_5, C_5', C_6, C_6'

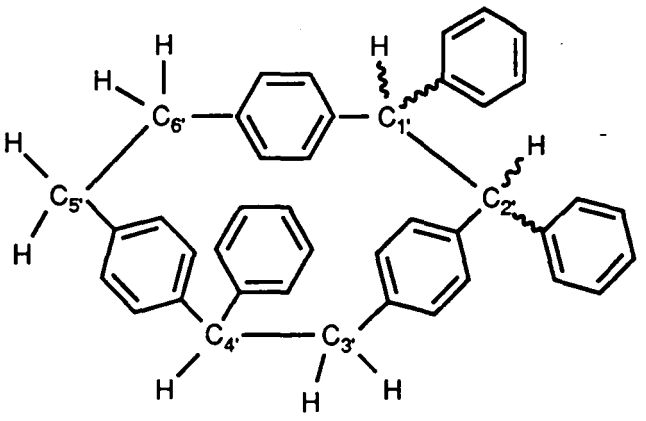
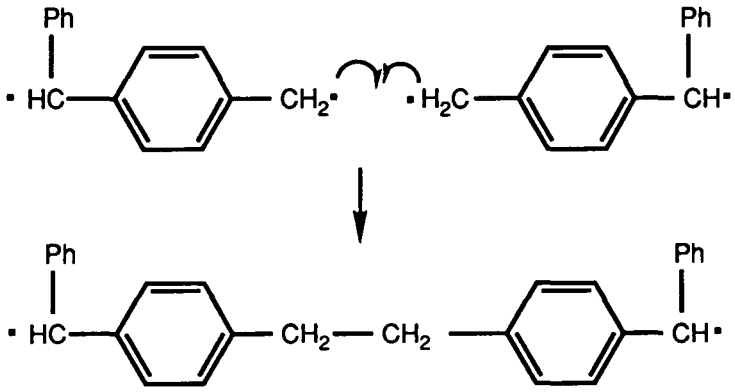


Fig.19 *The two diastereomers present in [103] showing labelled carbons*

The 500MHz ^1H nmr spectrum of the minor cyclic trimer [104] (expanded aliphatic region shown in Fig.20) was very similar to that of the major cyclic trimer [103] showing that it too had the same basic structure [106] with a head-to-head structural unit. Again two isomers were shown to be present in the mixture this time in the ratio 2:1. The most obvious difference however was the chemical shift of the two AB systems due to the $C\underline{H}(C_6H_5)C\underline{H}(C_6H_5)$ unit in the region 5.15-5.35ppm (c.f 4.60-4.66ppm for [103]); this must be due to the different configurations of the protons in the two pairs of isomers {in one pair they are syn [109] and syn [110] and in the other, anti [111] and anti [112]}. Due to the absence of model compounds, no stereochemistry could be assigned to the components of compounds [103] and [104] (Compound [104] is equivalent to [103] but with the opposite orientation in the head-to-head unit). The head-to-head $(C_6H_5)C\underline{H}C\underline{H}(C_6H_5)$- unit clearly has a marked effect on the protons in the head-to-tail ($CHPh\text{-}CH_2$) unit ; so much so that two isomers differing *only* in the stereochemistry of the head-to-tail linkage can easily be identified in the ^1H nmrs of both [103] and [104].

In a sense it is not surprising that both isomers have the unsymmetrical trimeric structure. The monomeric unit can be thought of as having a small methylenic end and a large benzhydrylic end so when two of these units combine it will be sterically favourable for the two small ends to interact producing the dimeric diradical shown.



Interaction of this dimeric unit with a third monomer unit would then produce an unsymmetrical cyclic trimer whichever end interacted first.

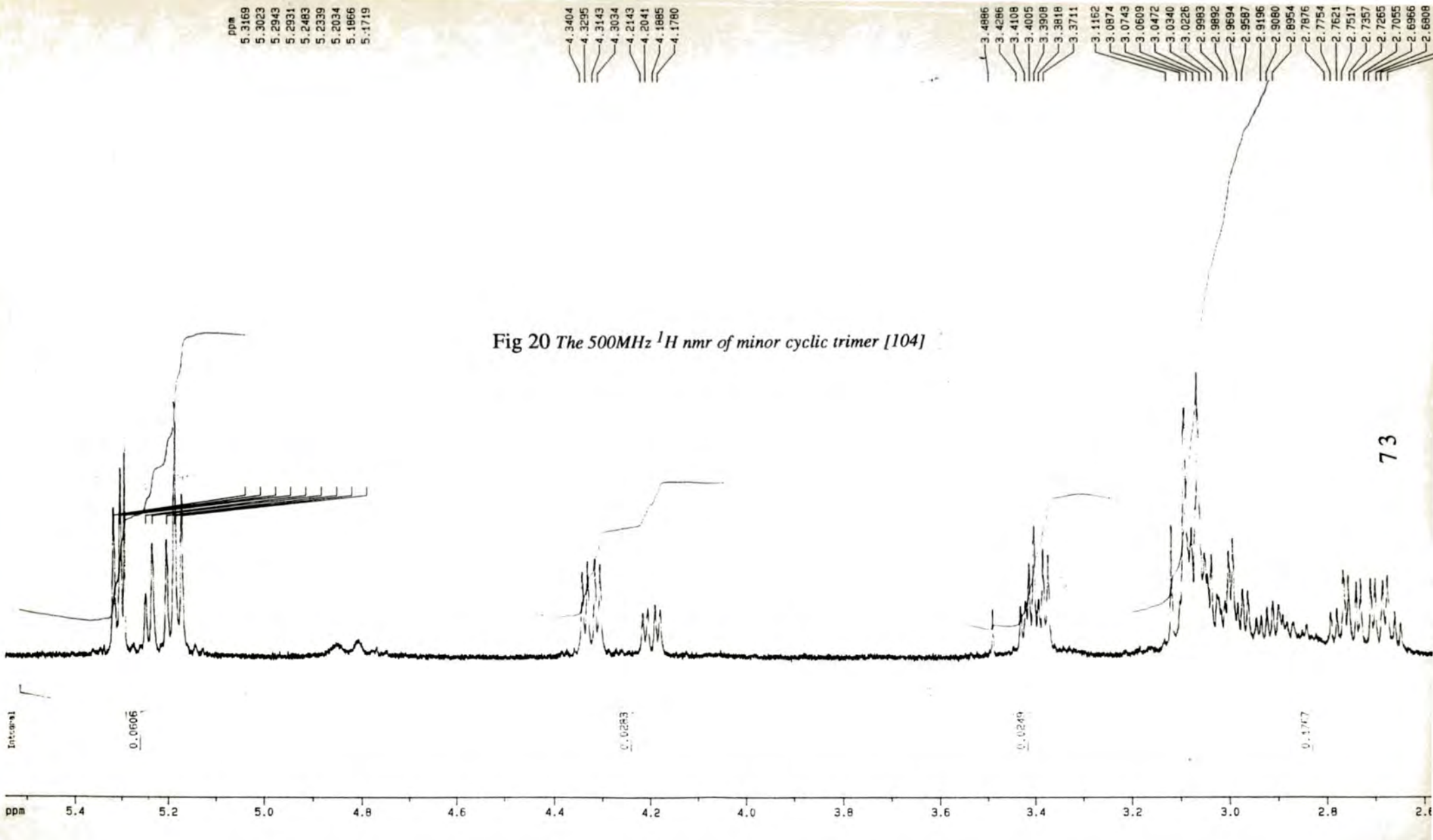
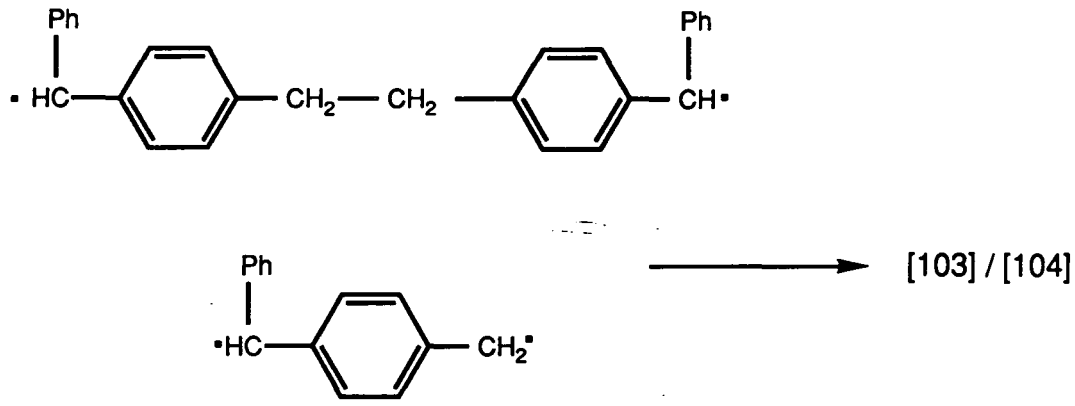


Fig 20 *The 500MHz ^1H nmr of minor cyclic trimer [104]*



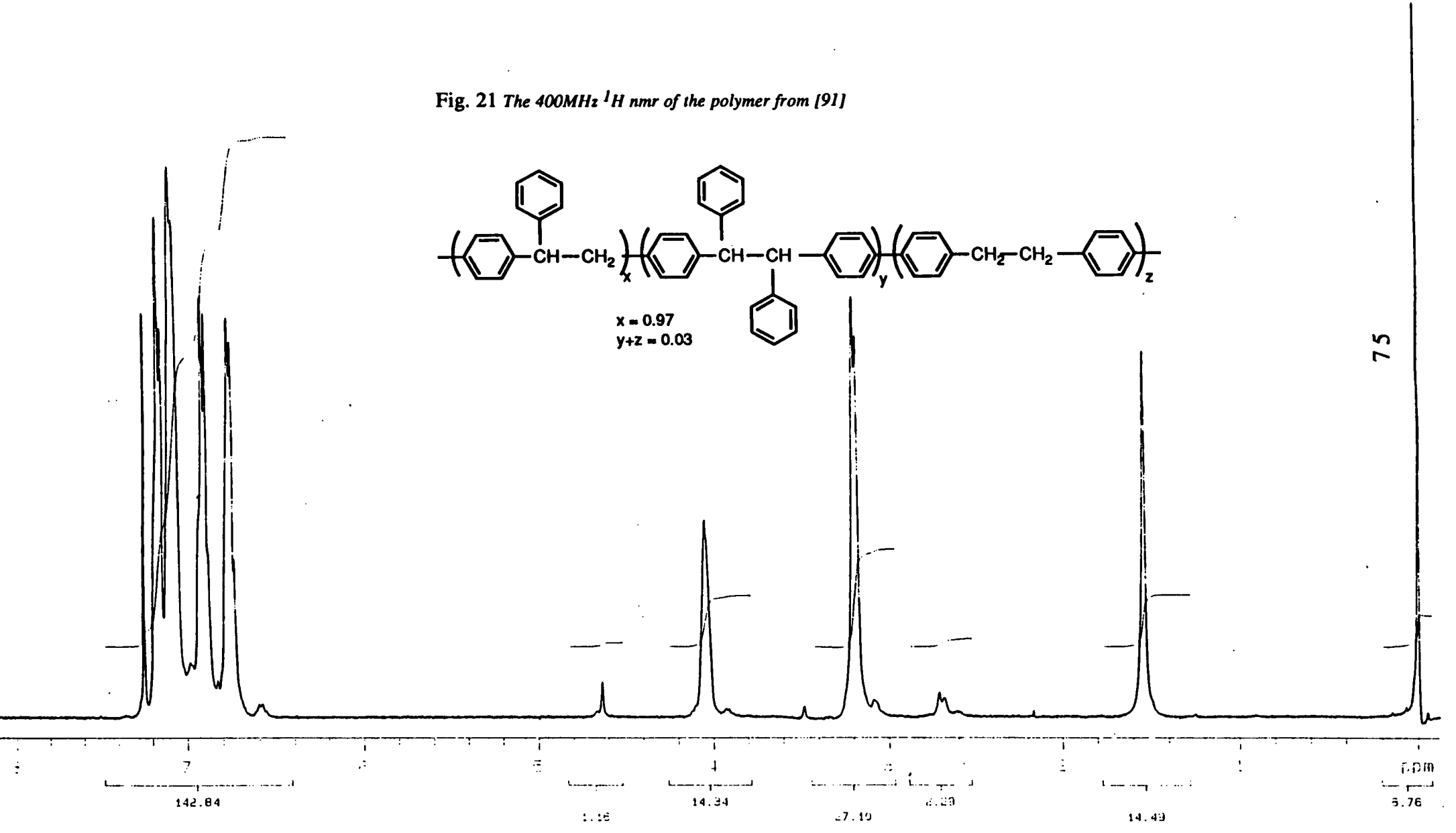
3.3.1.2. Polymeric Material

The average molecular weight M_n of the polymer as determined by gel permeation chromatography was found to be 1.83×10^4 corresponding to a DP of ca 101. The 400MHz ^1H nmr (Fig 21) indicated that the polymer backbone was almost entirely made up of α-phenyl-*p*-xylylene units [85] with peaks at 3.19, 4.05 and 6.74-7.25ppm in a ratio of 2:1:9.showing that head-to-tail polymerisation had occurred. However, several much smaller peaks were observed in the spectrum which were thought to be due to head-to-head and tail-to-tail units. The shifts of head-to-head and tail-to-tail protons were known approximately by referring to the spectra of the cyclic trimers [103] and [104] which contained these units themselves. Thus the peak at 4.64ppm was assigned to a head-to-head unit [89] found in [103] (but not [104]) with the peak at 2.7ppm being assigned to a tail-to-tail unit [87] found in [103] and [104]. Of the other two possible units, [88] and [90], the former would appear in the aromatic region and would not be seen whilst the aliphatic CH in [90] was expected to show a peak at ca 5.55ppm (by comparison with the spectrum of triphenylmethane[92]). It was not present. No assignments could be made to the peaks at 3.05, 3.45 and 3.95ppm. Therefore from the evidence of the integrated ^1H nmr the polymer produced was made up of 97 parts head-to-tail units and 3 parts head-to-head(tail-to-tail) units.

3.3.2. Using *p*-methylbenzhydryltrimethylammonium bromide [92]

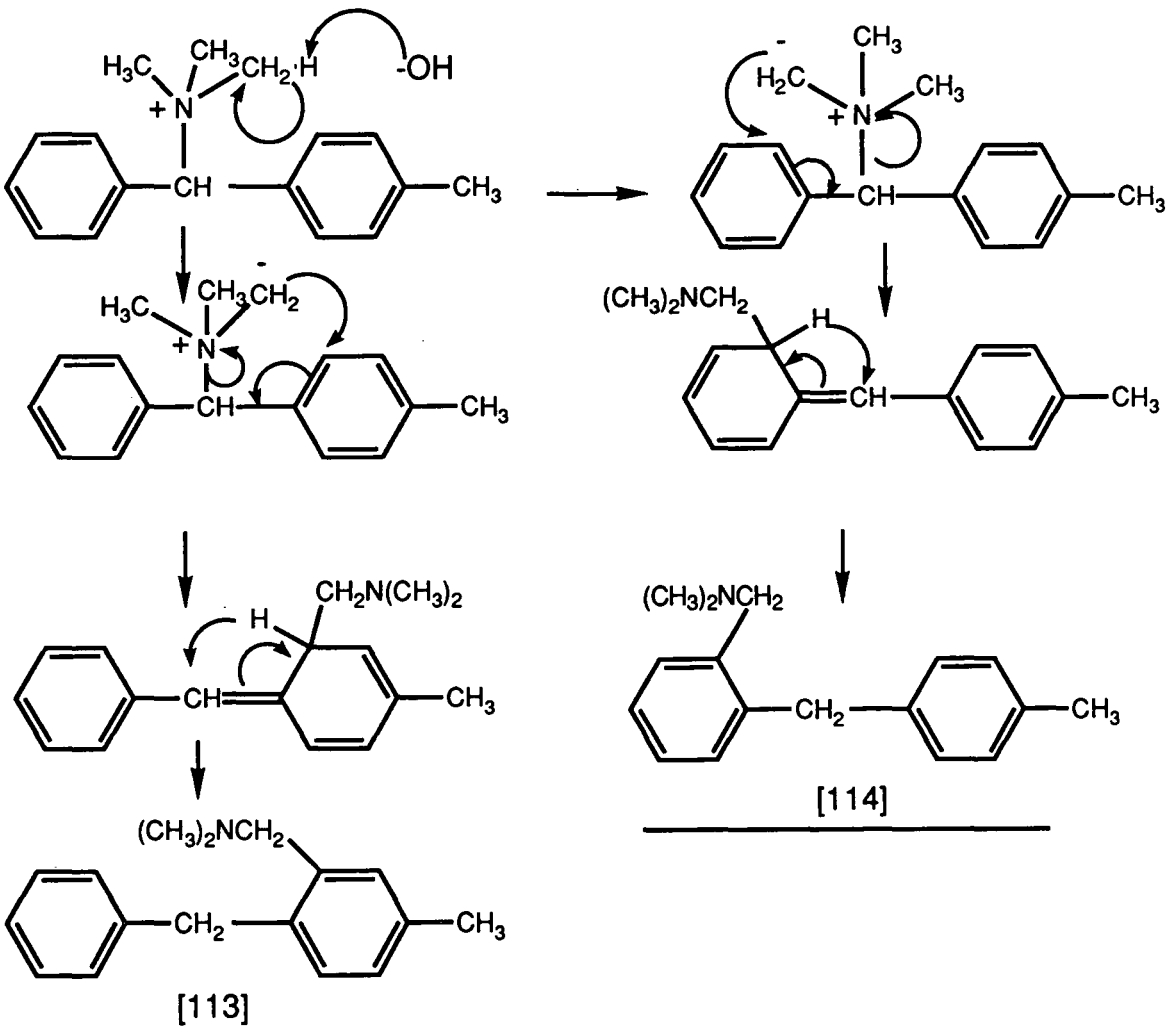
The crude product from the decomposition of the hydroxide derived from the bromide [92] using Fillers' method[16] was extracted in a Soxhlet apparatus for 24h using light petroleum (b.pt. 80-100°C). The polymeric material that remained in the thimble was dissolved in chloroform and reprecipitated by pouring into methanol. After two further reprecipitations the polymer was dried in vacuo at 50°C for 5h.

Fig. 21 *The 400MHz ^1H nmr of the polymer from [91]*



3.3.2.1. Low molecular weight material

The material that had been extracted from the polymer again appeared very complex by TLC but chromatography on alumina separated two compounds in fairly high yields. The major product was a liquid which was purified by distillation and shown to be a mixture of Sommelet-Hauser rearrangement products[93-95] [113] and [114] arising from initial abstraction of an N-methyl proton by hydroxide ion. The gas chromatogram showed two peaks with retention times very close together suggesting two similar compounds and the mass spectrum showed a molecular ion of 239. The ^{1}H nmr indicated three methyl groups rather than four (the tertiary amine methyl groups overlapping), and three methylene groups instead of four, (the diphenylmethylenes overlapping).



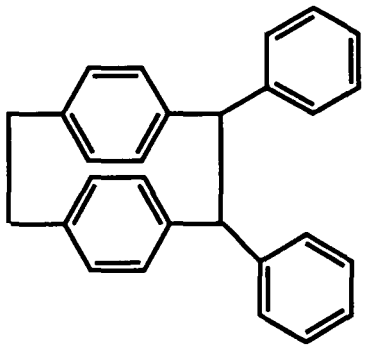
The ^{1}H nmr spectra of the two compounds differed only in the *p*-methyl and benzylic CH_2N shifts. The second major product was identified as the trimer [103] that had been obtained in the previous polymerisation and was obtained in 17% yield.

3.3.2.2. Polymeric material

The 400MHz ^1H nmr spectrum (Fig. 22) indicated that the polymer backbone was again poly(α-phenyl-*p*-xylylene) [85] resulting from head-to-tail polymerisation of the unsymmetrical monomer (96 parts) but there were again some very small peaks which could have been due to head-to-head and tail-to-tail polymerisation (4 parts). Molecular weight determination by gel permeation chromatography gave an average (M_n) of $2.88x10^4$ corresponding to a DP of c.a 159

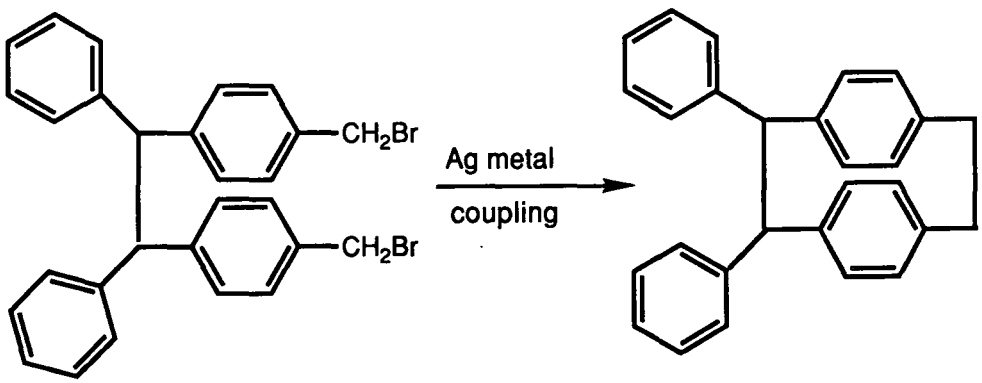
3.3.3. Discussion

In the previously reported reaction of *p*-benzylbenzyltrimethylammonium hydroxide it was reported[88] that the products were a polymer (no details given) and a cyclic dimer [115].

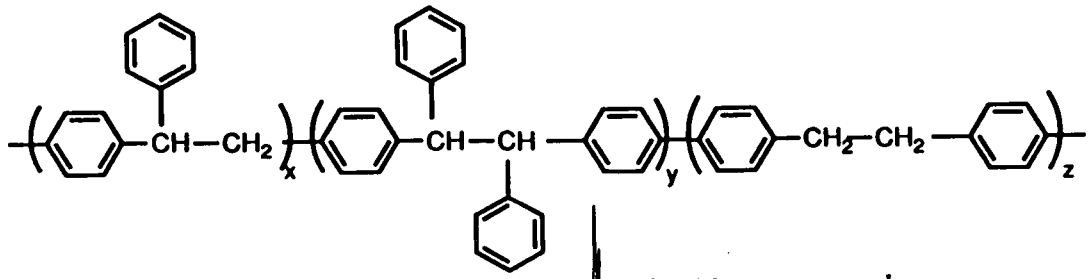


[115]

It was also claimed that silver metal coupling of 4,4-di(α-bromobenzyl)bibenzyl [116] produced an isomer of [115]: [117].



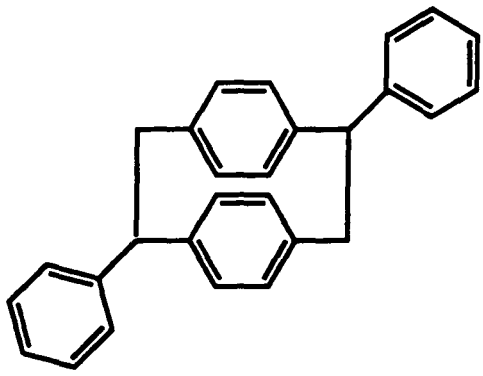
[116] [117]



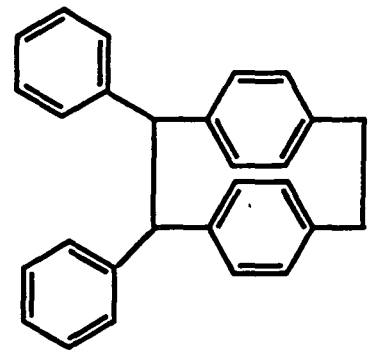
x = 0.96
y+z = 0.04

Fig. 22. *The 400MHz ^1H nmr spectrum of the polymer from [92]*

According to the author (H.W. Bersch[88]) [115] and [117] were the *"trans"* and *"cis"* isomers. However, in a review by Smith[96] it was speculated that the isomers were actually the 1,9-diphenyl [118] and 1,2-diphenyl [117] compounds.



[118]



[117]

The head-to-tail dimer [118] would be sterically if not electronically favoured and Smith has proposed[95] that the pyrolysis of *p*-benzylbenzyl trimethylammonium hydroxide actually produced [118] whilst the silver metal coupling of 4,4-di(α-bromobenzyl)bibenzyl produced [117].

The melting point of the 'dimer' from the polymerisation [118] or [115] (277-279°C) seems to bear an uncanny resemblance to the melting point of the trimer [103] obtained in the reactions described in this work (269-272°C) and it would appear that Bersch actually obtained the trimer [103] from the polymerisation. It is probable that the silver coupling product was in fact the dimer [117] since a much lower melting point (176-178°C) was reported.

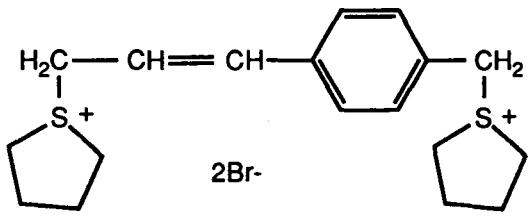
Both *in situ* syntheses of phenyl-extended *p*-xylylene produced the same soluble polymeric product and the trimeric material. It was a little disappointing that polymerisation did not take place through the extended conjugation to give [86] but this was offset by the fascinating by-products that were produced.

Chapter Four

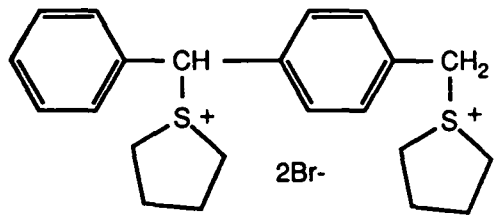
Polymerisations through water-soluble precursors

4.1.Introduction

In Chapters Two and Three the polymerisation behaviour of vinyl- and phenyl-extended *p*-xylylenes was reported. This Chapter concerns the next stage in the work, which was to use bis-sulphonium salts [119] and [120] as a means of producing water-soluble precursor polymers. The syntheses and reactions of these compounds with base will be discussed in two separate sections followed by a comparison and conclusions.



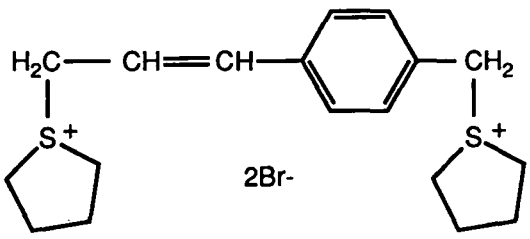
[119]



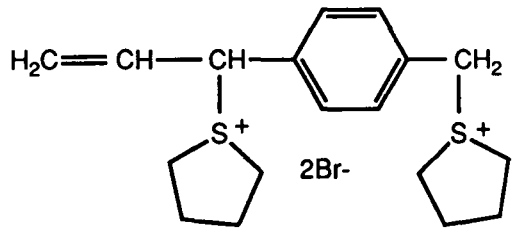
[120]

4.2. *p*-(Tetrahydrothiopheniummethyl)cinnamyltetrahydrothiophenium dibromide

There are actually two conceivable bis-sulphonium salts ([119] and [121]) which could produce a mono-substituted vinyl-extended *p*-xylylene *in situ* through reaction with a base. However, we have previously encountered difficulties in synthesising salts at the α-(*p*-tolyl)allyl position (see Chapter 2) so the synthesis of salt [121] was not attempted.



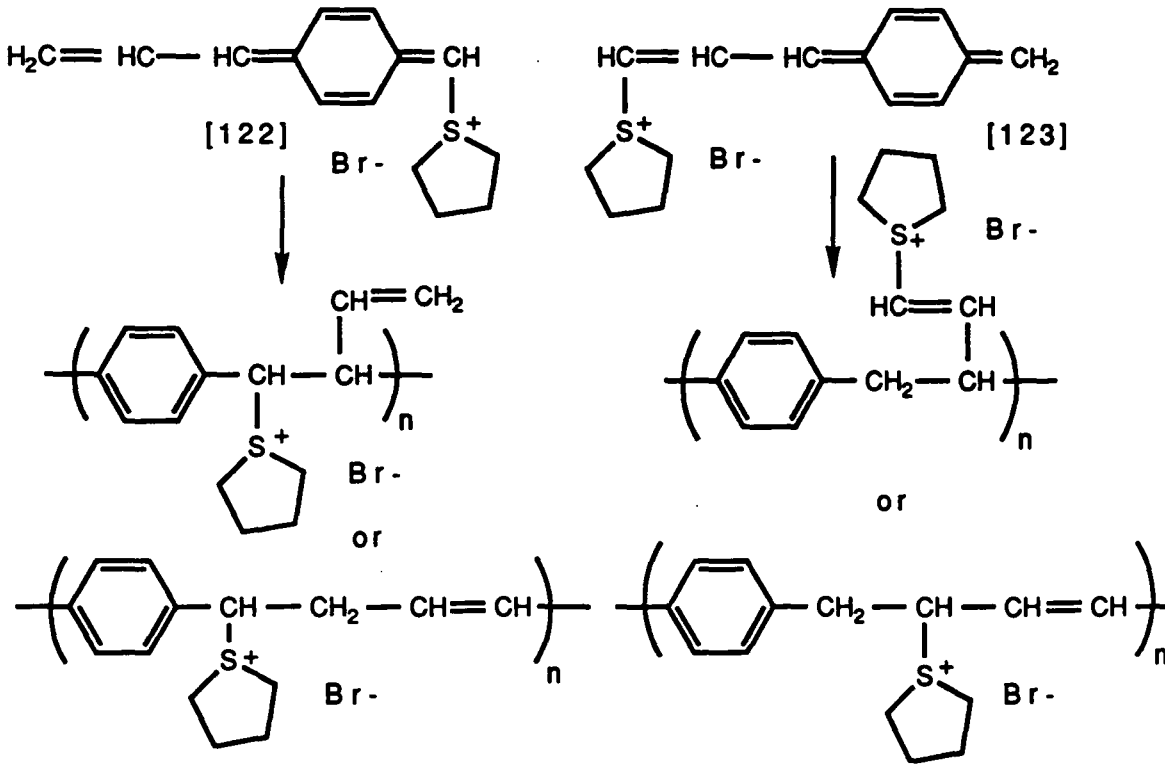
[119]



[121]

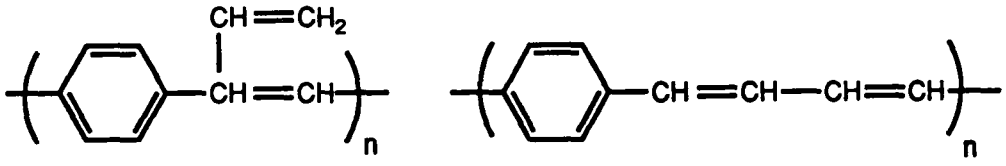
After consideration of the results reported in Chapter 2, which showed the polymer from the vinyl-extended *p*-xylylene consisted of ca 90 parts head-to-tail units,

only head-to-tail polymerisation was considered for the monomers in this section. Thus, the reaction of [119] with base, producing [122] or [123] in situ, can lead to four possible precursor polymers (Scheme 23) and from the results reported in Chapter 2 it would be expected that all four units would be produced.



Scheme 23 *The four possible precursor polymer structures from the vinyl-extended p-xylylene [122]/[123]*

Subsequent thermal elimination of these units would lead to two possible conjugated polymers: [124] which has not previously been reported and [125] poly(*p*-phenylenebutadienylene) which has been synthesised via a Wittig-type reaction by Lapitskii[97] and by Kossmehl[98].

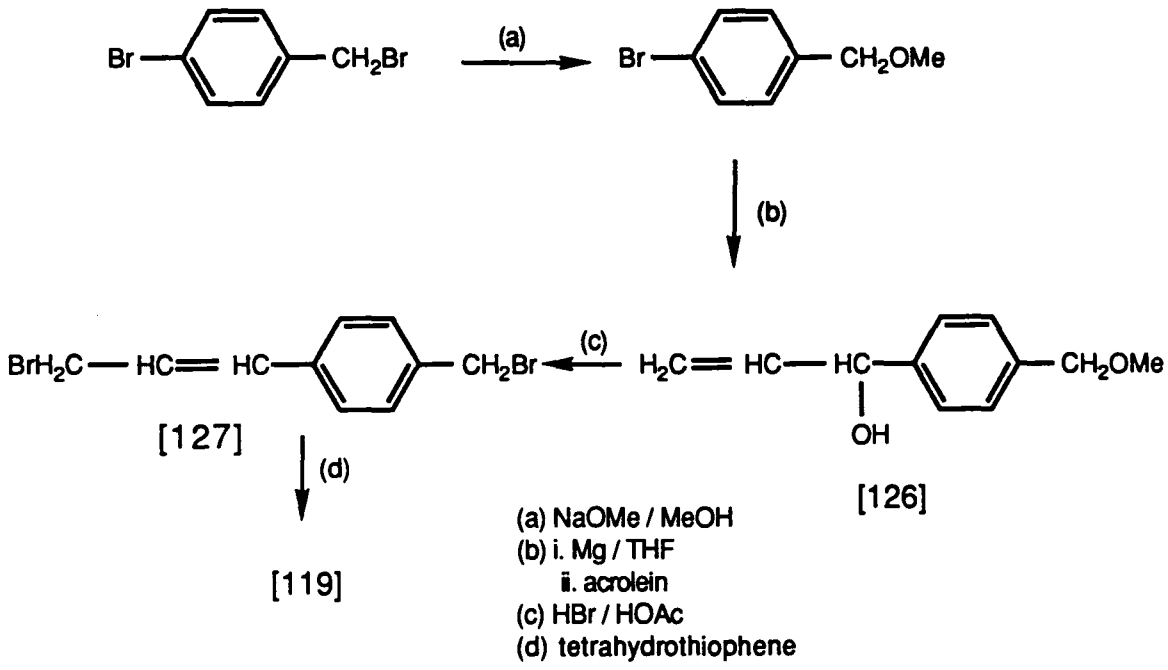


[124] [125]

4.2.1 Synthesis of compound [119]

The synthetic route shown in Scheme 24 was found to be a satisfactory and fairly simple route to [119] starting with commercially available *p*-bromobenzyl bromide.

Treatment of the alcohol [126] with HBr / glacial acetic acid conveniently afforded the dibromide [127] in one step in which the methyl ether had been cleaved and the alcohol had undergone the expected S_N2' reaction (see Chapter 2). A methanol solution of this dibromide with tetrahydrothiophene gave the bis-sulphonium salt [119].



Scheme 24 *The synthetic route to [119]*

4.2.2. Polymerisation reactions using compound [119]

The polymerisation was attempted in two different solvent systems; water and water / methanol :

(a) Formation of the precursor polymer

(i) in water

An aqueous solution of the salt [119] was cooled to 5°C and treated with a pre-cooled solution of sodium hydroxide and after 35 mins quenched with dilute hydrochloric acid. The reaction mixture was a thick yellow suspension at this point and

an attempt to dissolve it up by adding THF was unsuccessful. Centrifugation of the mixture and removal of the supernatant water/THF left a thick gel which was dialysed against deionised water for three days to remove any low molecular weight material. The resultant gel was diluted slightly with THF before a film was cast , dried in vacuo and submitted for elemental analysis (see Table 4). It was found that the sulphur content of the film was virtually zero, suggesting that both sulphonium groups had been lost, but that the bromine analysis was still quite high implying that at least some displacement of tetrahydrothiophene by bromide counterion had taken place.

(ii) In water/methanol

The use of a 2/1 methanol/water solvent system enabled a much lower temperature to be used for the polymerisation reaction and it was hoped that these milder conditions would produce a water-soluble precursor polymer still retaining one of the sulphonium groups. A solution of [119] was cooled to -20°C and treated over 20 minutes with aqueous sodium hydroxide, producing a yellow solution which, after continued stirring over 30 minutes at this temperature, became cloudy. Dialysis of this solution against deionised water/ methanol at room temperature left a thick gel which was cast into a film. The film was dried in vacuo and submitted for elemental analysis, the results of which are shown in Table 4. The sulphur content was much more promising in this film suggesting that the required precursor(s) $(C_{14}H_{17}BrS)_n$ may have been produced. Since the films probably contained some residual moisture, even after drying in vacuo, a better way of assessing the elemental analyses is to compare some of the elemental ratios (see Table 4) ; if the expected and obtained values for S/C, Br/C and Br/S are compared it is clear that they are in fairly good agreement. The observed low values of S/C and Br/C suggest that a measurable number of vinylene units [124] or [125] were formed through elimination reactions which is also suggested by the yellow colour of the films. If the observed Br/S ratio had been found to be much higher than expected it would have suggested that displacement of tetrahydrothiophene by bromide ion had taken place but since the two values were very similar it indicated that this was not a very significant reaction.

Table 4

The elemental analyses of some precursor films derived from [119]

Analysis	C(%)	H(%)	Br(%)	S(%)	S/C	Br/C	Br/S
Found Expt.(i)	56.23	6.57	21.64	<0.97	-	-	-
Found Expt.(ii)	54.33	6.51	22.05	8.52	0.157	0.406	2.59
$(C_{14}H_{17}BrS)_n$ requires	56.57	5.76	26.88	10.79	0.190	0.476	2.50

(b) Thermal elimination reactions carried out on films of precursor polymer

Thermal elimination of those films described above was attempted in vacuo at various temperatures from 170-240°C but even after 3 days at 240°C the elemental analysis showed a high bromine and sulphur content (Table 5). The temperature was not taken any higher since the films were becoming very dark and seemed to be degrading. The best results were obtained through heating the films at 170°C for 7h but even in this case there was found to be a 6.86% sulphur content and a 12.92% bromine content. It is understandable that the bromide counterion may displace the tetrahydrothiophene group under these conditions to produce a polymer with such a high bromine content but less clear why such a high sulphur content was observed. In the reported thermal eliminations of tetrahydrothiophene and HBr from precursor polymer films which produce poly(phenylenevinylene)s these temperatures have been sufficient to reduce the sulphur and bromine content to virtually zero[48,49].

Table 5

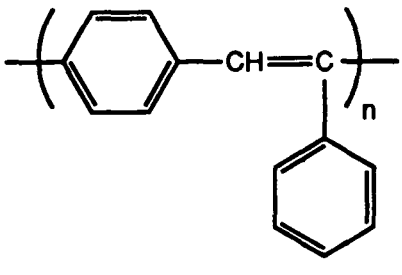
The elemental analyses of some thermally eliminated films derived from [119] {Expt (ii)}

Analysis (X°C/Yh)	C (%)	H (%)	Br (%)	S (%)
160°C/2.5h	69.04	5.89	14.77	7.92
170°C/7h	72.40	6.31	12.92	6.86
240°C/72h	70.61	5.27	—	—
$(C_{10}H_8)_n$ requires	93.71	6.29	—	—

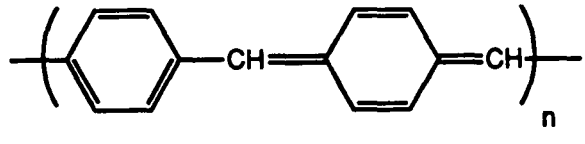
4.3. *p*-(Tetrahydrothiopheniummethyl)benzhydryltetrahydrothiophenium dibromide

The reaction of [120] with base could produce two possible *p*-xylylenes in situ ([128] and [129]) which (if reaction through the conjugatively-extended *p*-xylylene can also take place) could each polymerise in two ways to produce four possible precursor polymer units. (Once again because of the results reported in Chapter 3 only head-to-tail polymerisation has been considered) (Scheme 26).

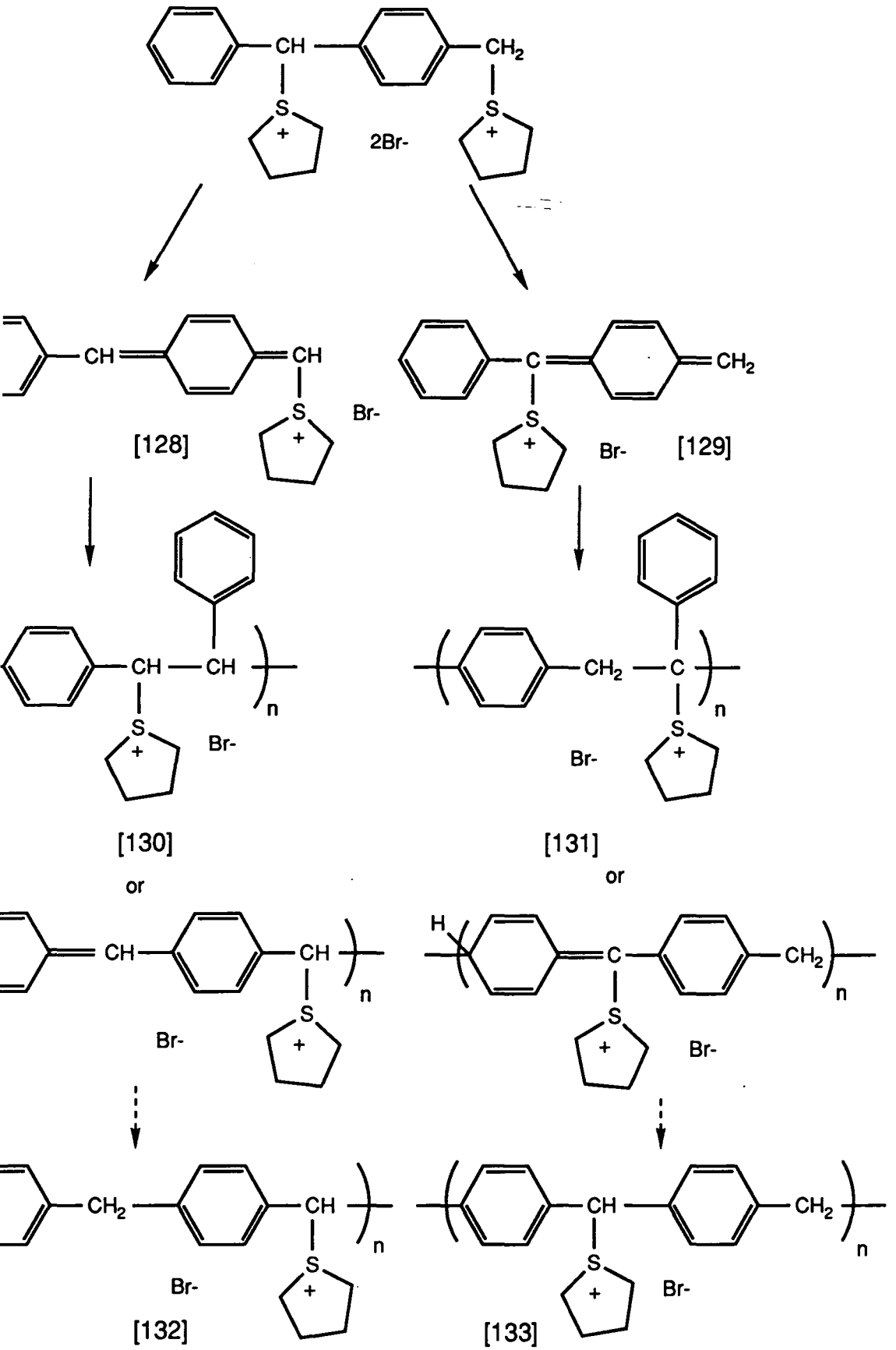
Thermal elimination of the four possible precursors could lead to two possible polymer structures: one [135] a poly(arenemethine) and the other [134] a substituted PPV. Both types of polymer [134] and [135] have been reported and are briefly discussed below:



[134]



[135]

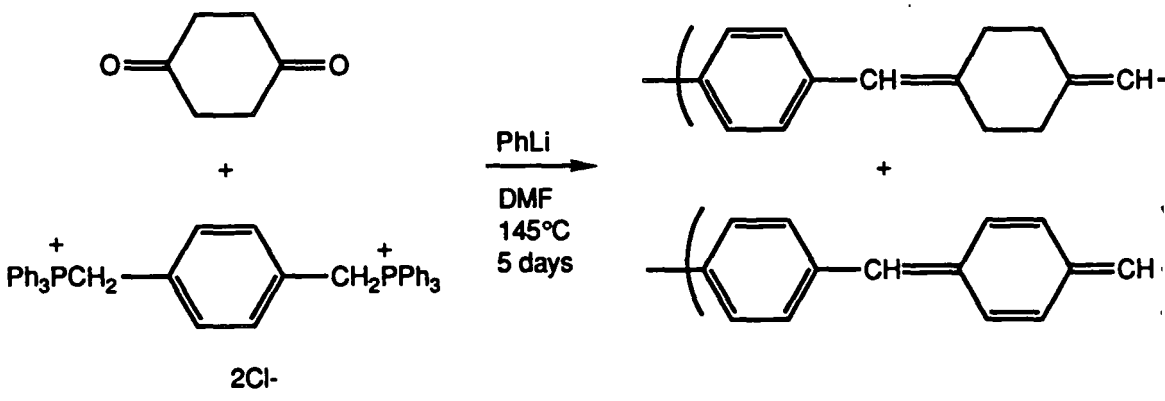


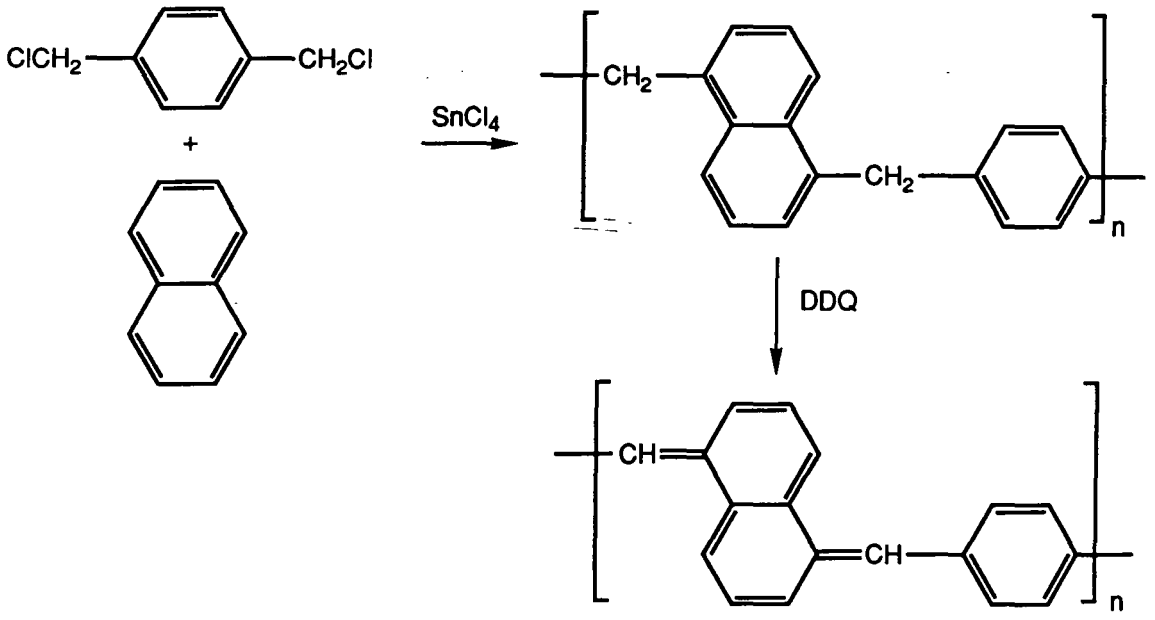
eme 26 *The four possible precursor polymers [130]-[133] which could be produced from phenyl-exrtended p-xylylenes [128] or [129]*

4.3.1. Poly(arenemethines)

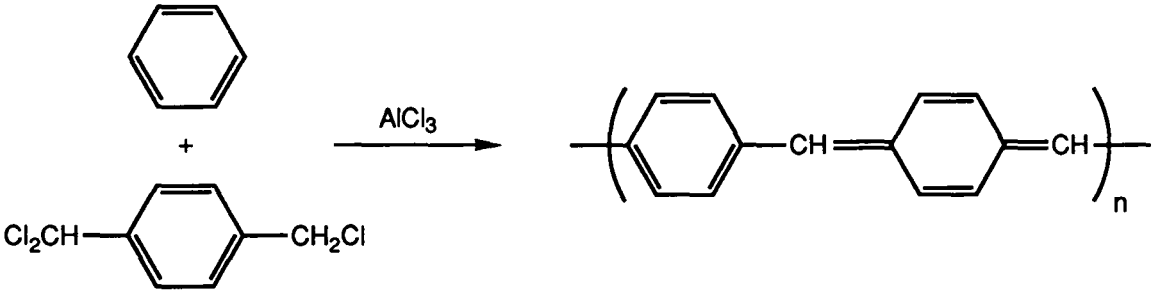
It was originally hoped that polymerisation of α-phenyl-substituted *p*-xylylenes would proceed through the extra phenyl ring to produce the water-soluble precursor polymer(s) [132] and/or [133] suitable for introduction of the extra conjugation. Poly(arenemethines) are a novel and very exciting class of polymer because they are expected to have a degenerate ground state and, by analogy with poly(acetylene), display high conductivity on doping with redox reagents. The exciting possibilities of this polymer were first discussed in a theoretical paper in 1985[99] but a successful synthesis of high molecular weight material has never been achieved. A number of synthetic routes to either the parent compound [135] or a related structure have been claimed.

In 1987 Fernandez and Al-Jumah reported the synthesis of [135] via a Wittig-type reaction followed by partial dehydrogenation[100] and also that of the naphthalene and anthracene derivatives by a $SnCl_4$ catalysed Friedel-Crafts reaction[101].

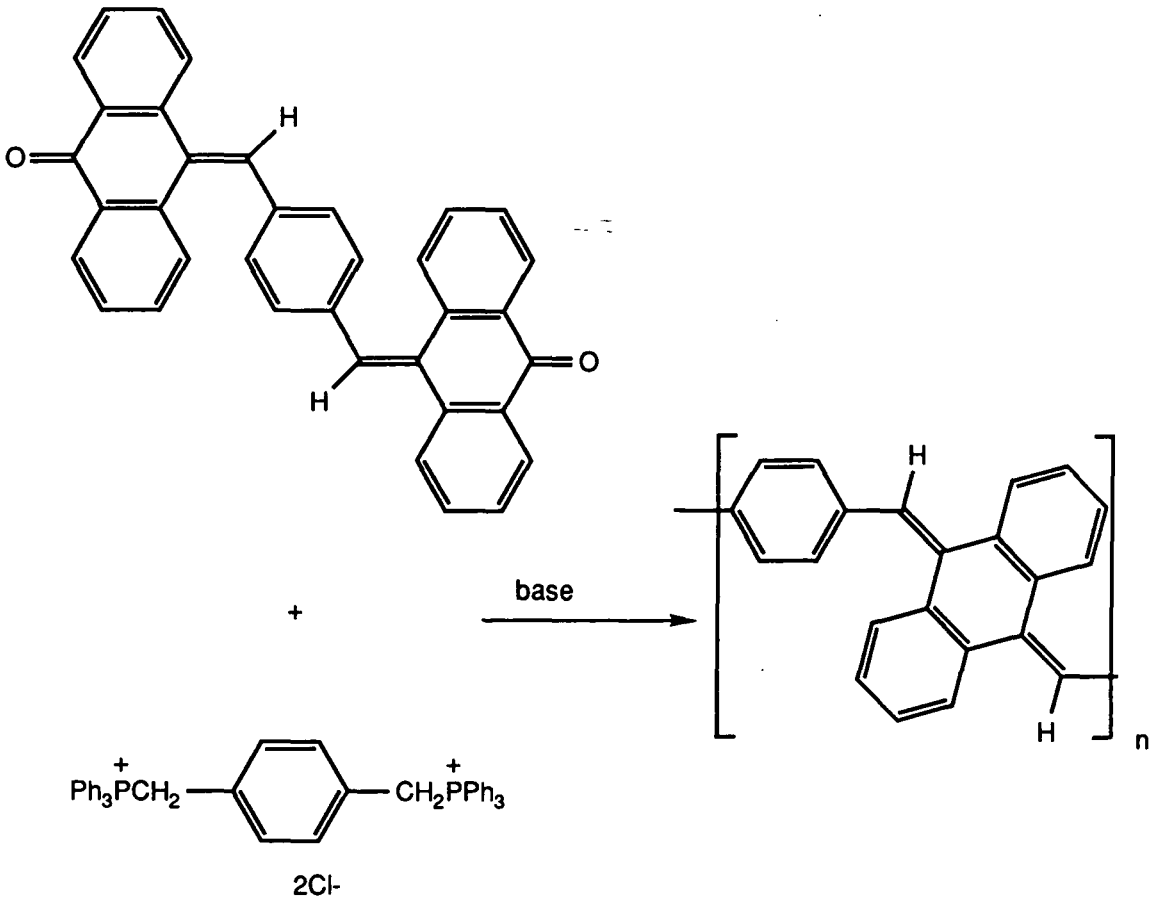




However, attempts to repeat this synthesis of [135] were not successful[102-104] and the claim was later retracted[105]. Jira and Braunling produced a black infusible, insoluble polymer using the Friedel-Crafts reaction of benzene with α,α,α'-trichloro-*p*-xylene[103] and claimed it was [135].



It has been suggested that[106], since 7,8-diphenyl-*p*-xylylene [12] is known to be a highly reactive species[22], the polymer [135] will have similar properties and will be unstable. However, an attempt by Hanack and Dewald to synthesise the more stable dihydroanthracene derivative by a Wittig reaction gave only a poor yield of a polymer with a low conductivity[106].

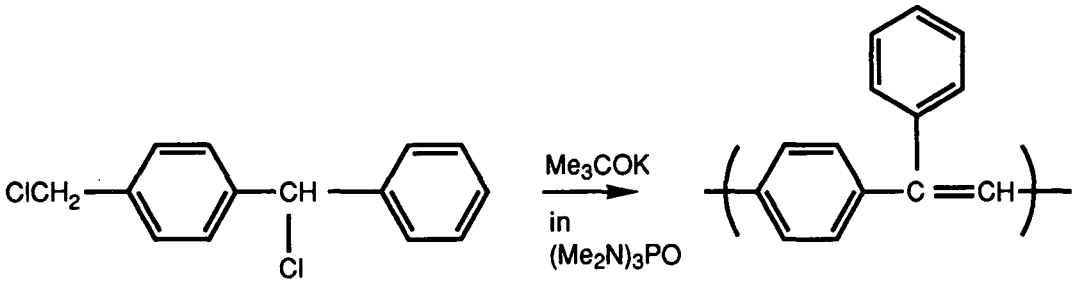


From the results given in Chapter 3 it would be expected that polymerisation of [120] would not include the extra phenyl ring and a mixture of the two precursors [130] and [131] would be obtained.

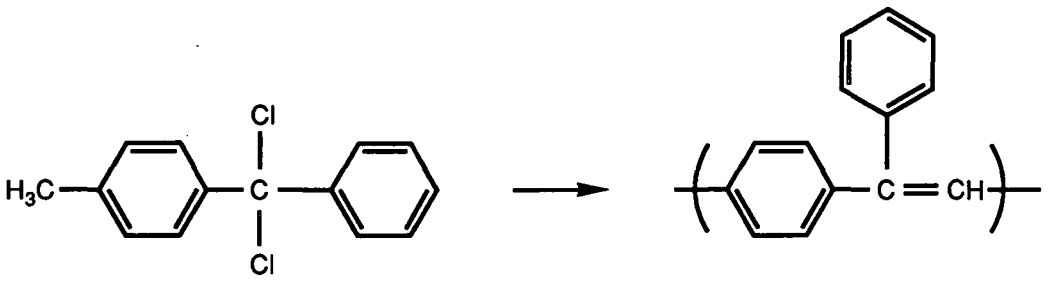
4.3.2. Substituted PPV (compound [134])

The phenyl substituted poly(phenylenevinylene)[134] has been synthesised previously by a variety of methods for use as a temporary coating to protect optical glass against corrosion. Two methods are reported here:

(a) the dehydrochlorination-polycondensation of 4-chloromethylbenzhydryl chloride[107]

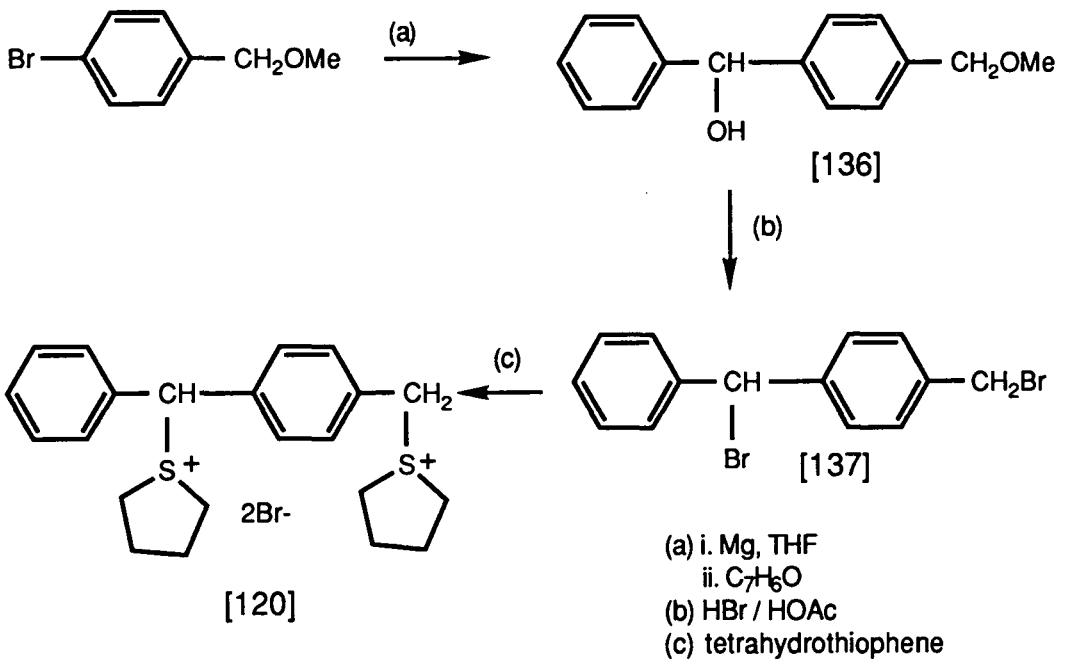


(b) the thermal dehydrochlorination of 4-(α,α-dichlorobenzyl)toluene[108]



4.3.3. Synthesis of [120]

The synthetic route shown in Scheme 27 produced [120] in fairly good yield with *p*-bromobenzyl methyl ether again the starting material: its reaction with magnesium followed by treatment with benzaldehyde gave the alcohol [136] which was converted to the dibromide [137] with HBr in glacial acetic acid. The bis sulphonium salt [120] was obtained by treating a solution of [137] in acetonitrile with tetrahydrothiophene, concentrating the solution in vacuo and precipitating with acetone.



Scheme 27 *Synthetic route to [120]*

4.3.4. Polymerisation reactions using compound [120]

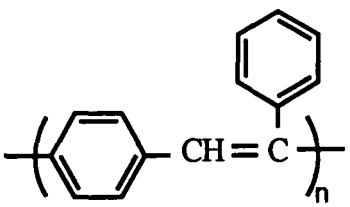
The polymerisation reaction has been attempted in three different solvent systems: water, tetrahydrofuran/water and methanol/water.

(i) In water

Using D_2O as the ^1H nmr solvent caused hydrolysis of the salt, [120] at room temperature so the solid was added to an equimolar solution of sodium hydroxide cooled externally by an ice-salt bath. A deep orange colouration and a precipitate was formed which after quenching with acid and extensive dialysis gave a suspension which dissolved in tetrahydrofuran and was cast into a film. Unfortunately the films produced were too powdery to be of any use which was presumably because the growing polymer chains had come out of solution at a low molecular weight.

(ii) In tetrahydrofuran/water

Since the polymer had exhibited solubility in tetrahydrofuran in (a) this solvent system was used in an attempt to retain a solution throughout the reaction. An ice-cooled solution of [120] treated with sodium hydroxide solution became deep orange then cloudy and finally produced a fine precipitate. After further stirring, quenching with acid and dialysis, the suspension was dissolved in more THF and water and a brittle yellow film cast. The elemental analysis of the vacuum dried film (Table 6) was quite promising showing fairly high bromine and sulphur content in the film. The observed values of S/C and Br/C were again lower than expected presumably due to the formation of some vinylene units [134] and the Br/S ratio was lower than expected which suggested that some displacement of bromide counter-ions by hydroxide ions had occurred.



[134]

(iii) In methanol/water

The methanol/ water solvent system was again used in an attempt to retain polymer solubility throughout the reaction. A solution of the salt in a 2/1 mix of methanol/ water was precooled in a carbon tetrachloride / carbon dioxide bath, treated with an appropriate volume of sodium hydroxide solution and stirred at -20°C for a further 1 hour. Unfortunately the polymer again came out of solution leading to an orange suspension which was dialysed against methanol/water for 2 days. Treatment of the suspension with further methanol afforded a polymer solution which was cast into a film, dried in vacuo and submitted for elemental analysis (see Table 6) which showed very similar results to those found in (b) (above). An attempt was made to precipitate the salt out as the *p*-toluene sulphonic acid species[109] but this was not very successful.

(b) Thermal elimination carried out on films of precursor polymer

Thermal elimination of the precursor films from experiment (iii) was performed at two different temperatures; 170°C and 240°C (Table 7). Once again the elemental analyses in both cases showed high bromine and sulphur content, presumably due to side reactions of the bromide counter-ion with the precursor polymer chain (see Chapter 1).

Table 6

The elemental analyses of some precursor polymer films derived from [120]

Analysis	C (%)	H (%)	Br (%)	S (%)	S/C	Br/C	Br/S
Expt.(ii)	59.35	5.66	16.25	7.40	0.125	0.274	2.20
Expt.(iii)	58.66	5.84	16.41	8.34	0.142	0.280	1.97
$C_{18}H_{19}BrS$ requires	62.25	5.51	23.0	9.23	0.148	0.37	2.49

Table 7

Thermal elimination of precursor polymer films from expt (iii)

Analysis (X°C/Yh)	C(%)	H(%)	Br(%)	S(%)
170°C/12h	75.56	6.33	8.75	6.58
240°C/26h	77.98	5.45	7.55	5.88
$(C_{14}H_{10})_n$ requires	94.34	5.66	--	--

4.4. Discussion

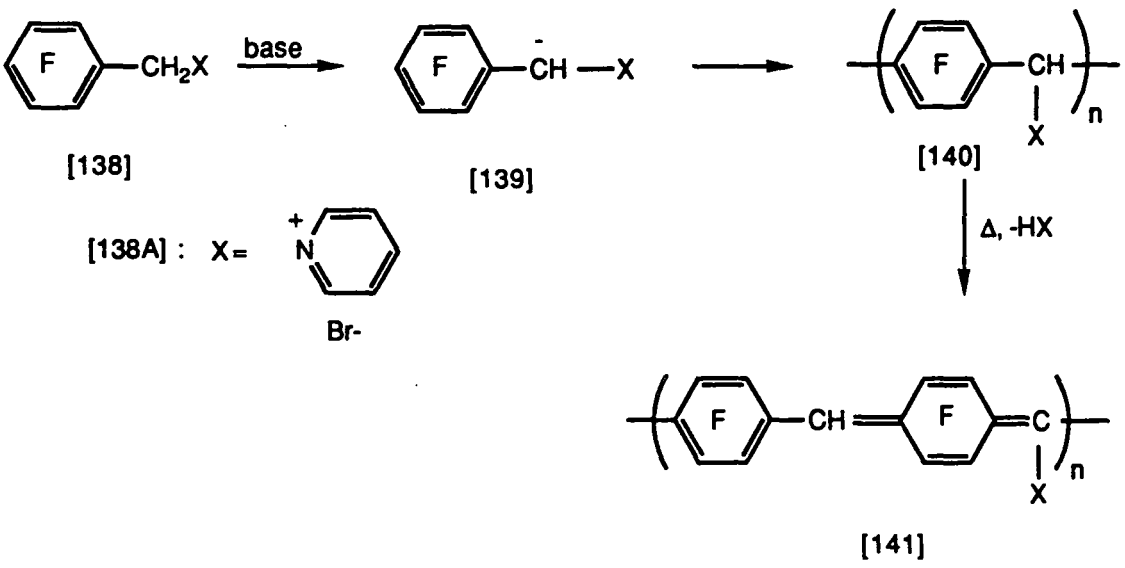
The reactions of salts [119] and [120] with base were fairly successful in that firstly very good films of the 'cinnamyl' type precursor were obtained and also the elemental analyses of both types of precursor film were extremely promising . However, the thermal elimination reactions of these precursor films were not very successful as shown by the elemental analyses obtained. Further analysis of the precursor films was attempted by infrared spectroscopy but the peaks were too broad to be of any real use. This was thought to be due to the poor alignment of the polymer chains[110]; it was thought that stretching of the films during thermal elimination could have improved the infrared spectrum considerably.

Chapter Five

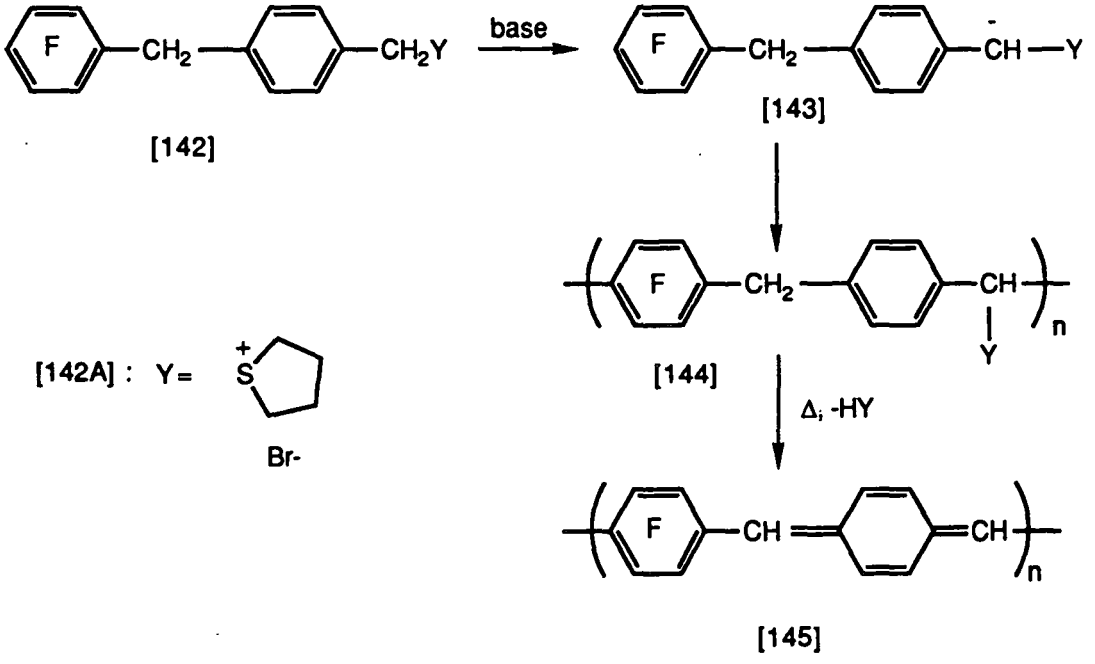
Potential polymerisation reactions of fluorinated salts

5.1 Introduction

The unambiguous syntheses of poly(arenemethides) [135] could be achieved through the use of polyfluoroaromatic precursors arising from the nucleophilic displacement of a *para*-fluorine on a C_6F_5 ring. Two experiments were conceived (Schemes 28 and 29):



Scheme 28



Scheme 29

The displacement of fluoride ion from C_6F_6 by Coreys' reagent dimethyl sulphoniummethylide[111] $Me_2S^+CH_2^- \leftrightarrow Me_2S{=}CH_2$ has been reported[112].

The choice of X and Y moieties are rationalised in the two separate sections below which outline the syntheses and reactions with base of the two salts [138] and [142].

5.2. 2,3,4,5,6-Pentafluorobenzylpyridinium bromide [138A]

There are a number of different salts of type [138] which could have been used in this reaction. The pyridinium salt was finally chosen for the following reasons:

(i) there are no acidic protons in the salt other than the benzylic ones which limited the number of possible complicating side-reactions (c.f. the reaction of 2,3,4,5,6-pentafluorobenzyldimethylsulphonium bromide [containing two possible types of acidic protons] with *n*-BuLi which gave a complex mixture of products and no polymer[112]),

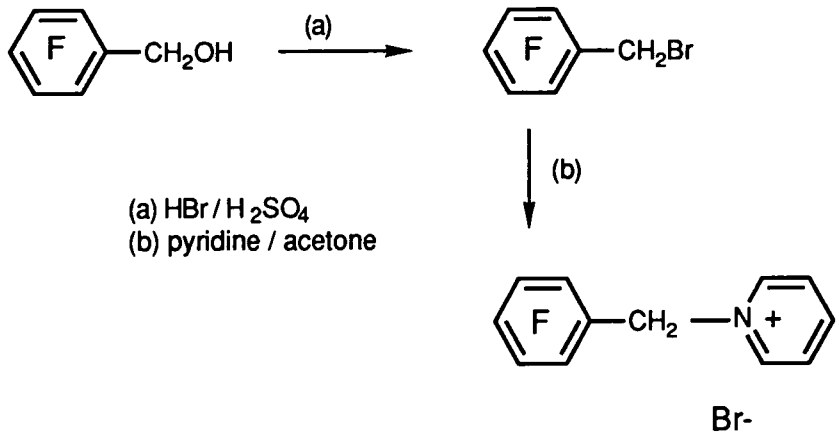
(ii) since nitrogen does not have d-orbitals, the ylid formed from reaction of [138A] with base would not be stabilised in the way the P or S analogues would be and would presumably be more reactive,

(iii) the steric hindrance at the potential reactive site is less than in possible alternatives such as the diphenylsulphonium or triphenylphosphonium salts

and (iv) a literature search revealed a straightforward synthetic route to the compound [138A][113].

5.2.1. Synthesis of compound [138A]

The synthetic route to [138A] was based on the literature preparation of benzylpyridinium bromide[113] and is shown in Scheme 30. The pyridinium salt was produced in 84% yield.



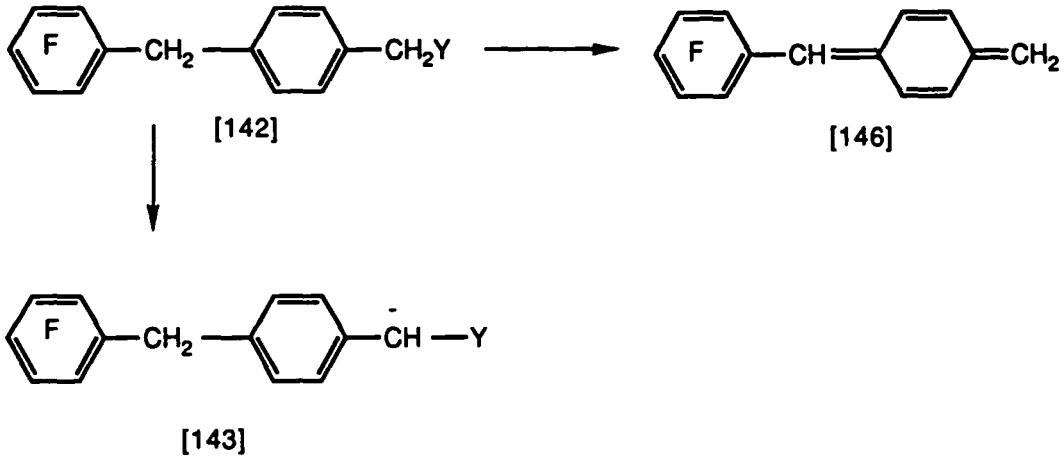
Scheme 30 *The synthetic route to [138]*

5.2.2 Reaction of [138A] with *n*-BuLi

A suspension of [138A] in tetrahydrofuran was cooled to -70°C and treated over 10 mins with *n*-butyllithium in hexane. An immediate indigo colouration, indicative of ylid formation, was observed which after 1 hour at this temperature had given rise to a yellow-brown suspension. This was promising since similar observations had been made in a successful experiment performed by G.M.Brooke and J.A.K.J.Ferguson in 1988[112]. After heating under reflux, quenching with acid and extraction with diethyl ether the aqueous phase was concentrated and dialysed for 48h against deionised water. The ^{19}F nmr of this solution showed five peaks; three corresponding to starting material [138A] and two unidentified peaks whereas the potential precursor polymer [140] would be expected to show only one peak in the spectrum. An attempt to precipitate out any precursor polymer as the p-toluenesulphonic acid species[109] was not successful.

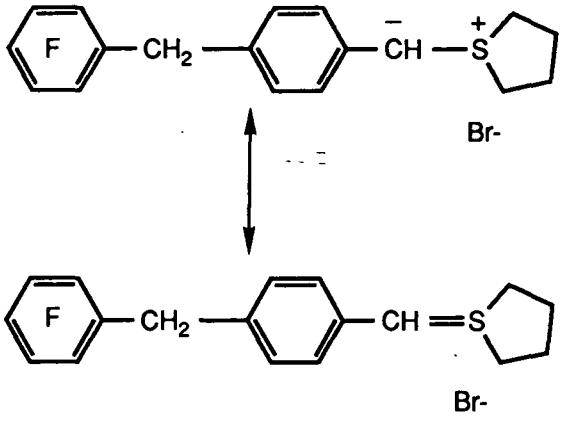
5.3. 2,3,4,5,6-Pentafluorobenzylbenzyltetrahydrothiophenium bromide [142A]

Salts of the type [142] clearly contain two possible acidic sites which could potentially be attacked by base; abstraction of a benzhydrylic proton would lead to a xylylene type species [146] and the desired abstraction of a benzylic proton would give rise to the ylid [143] (Scheme 31).



Scheme 31 *The two potential reactions of compound [142]*

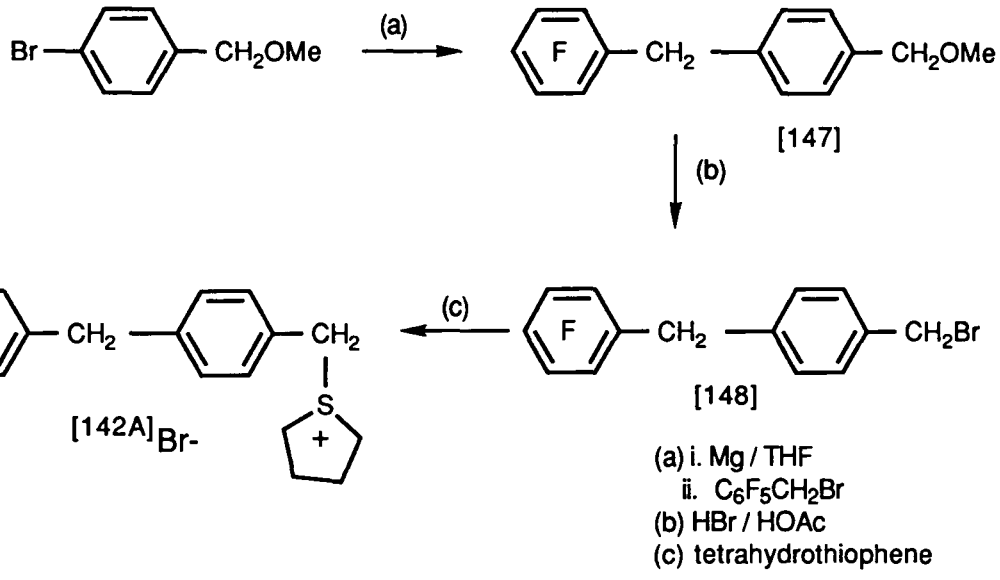
It was argued that the use of a sulphonium group Y would lead to the desired ylid [143A].



[143A]

5.3.1. Synthesis of [142A]

The synthetic route followed is shown in Scheme 32.



Scheme 32 *The synthetic route to [142A]*

The Grignard reagent of p-bromobenzyl methyl ether was reacted with pentafluorobenzyl bromide to give a 23% yield of [147] which was readily converted to [148] using the standard treatment with HBr in glacial acetic acid (86%yield). The conversion of pentafluorobenzylbenzyl bromide [148] to [142A] was effected by treating a methanolic solution of [148] with tetrahydrothiophene an 89% yield being obtained.

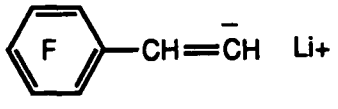
5.3.2. Reaction of [142A] with *n*-BuLi

A suspension of [142A] in tetrahydrofuran was cooled to -70°C and treated with one molar equivalent of *n*-butyllithium in hexane producing an orange suspension which, after stirring overnight, became a clear solution. This solution was heated under reflux for 18h. It had been hoped that the product of the reaction would be a water-soluble precursor polymer [144] but after work-up a white solid was isolated from the organic phase and the aqueous phase was shown by nmr to be free of any fluorinated species. The solid was analysed by ^{19}F nmr which showed three large peaks corresponding to starting material and a collection of smaller peaks at around 145ppm. The desired precursor polymer [144] would be expected to show two peaks in the spectrum whilst the polymer [149] which would arise from the *p*-xylylene type intermediate [146] would show three peaks. Since the nmr appeared to show largely starting material further purification was not attempted.

5.4. Discussion

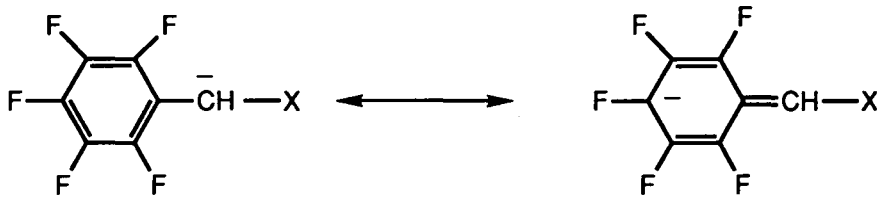
These results were disappointing since it had been hoped that at least low molecular weight poly(arenemethide)s would have been produced. The distinctive colouration of the reaction mixtures on treatment with *n*-butyllithium suggested that the ylids were formed but it would appear that the desired reactions of these ylids did not occur.

Anions such as [150] have been shown to give oligomeric materials through self-coupling reactions[114] but these systems are different from those described in this Chapter since the anion in [150] is not adjacent to the aromatic ring. One possible rationalisation for the unreactivity of the ylids [139] and [143] may be that the extra stabilisation of the adjacent ring system renders the carbanion less nucleophilic.



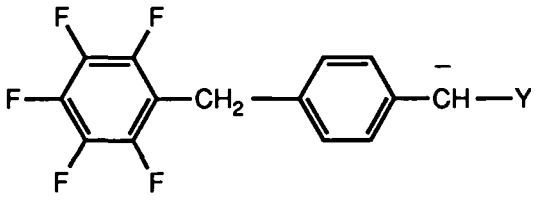
[150]

Another important factor influencing the ease of this nucleophilic displacement reaction is the 'electrophilicity' of the *para*-carbon. The resonance stabilisation of the ylid [139] gives this carbon slight electronegative character δ– and it is consequently much less vulnerable to attack by a nucleophile.



[139]

In contrast, the relevant *para*-carbon in the ylid [143] would not be affected by such resonance stabilisation and the desired nucleophilic displacement reaction was deemed more likely to proceed than that involving [139]. However, the C_6F_5 ring in [143] would be expected to be less susceptible to nucleophilic attack than C_6F_6 itself since C_6F_6 is more reactive towards nucleophiles than $C_6F_5CH_3$ (due to the relative inductive effect of F compared with Me[115]).



[143]

Chapter Six

Experimental

6.1 General

6.1.1 Instrumentation

Infra-red spectra were recorded on Perkin Elmer 577 and 457 grating spectrophotometers using KBr discs, nujol mulls or neat liquids. Absorptions have been abbreviated as : vs(very strong), s(strong), m(medium), w(weak) and br(broad).

Mass spectra were recorded on a VG 7070E Organic Mass Spectrometer.

NMR spectra were recorded on the following instruments and the frequencies listed : Bruker AMX 500 ^{1}H(500.1385MHz), ^{13}C(125.7735MHz); Varian 400MHz ^{1}H(399.952MHz), ^{13}C(100.377MHz); Bruker AC250 ^{1}H(250.13MHz), ^{13}C(62.90MHz), ^{19}F(235.342MHz). The following abbreviations have been made for bond multiplicities : s(singlet), d(doublet), t(triplet), q(quartet) and m(multiplet). Chemical shifts are quoted as δ in ppm with respect to the following references: ^{19}F(upfield from internal $CFCl_3$), ^{1}H(downfield from internal TMS).

Elemental analyses were performed on a Carlo ERBA C,H,N Elemental Analyser 1106.

Gas chromatography was performed on Hewlett Packard 5890 Series II and 5890A gas chromatograms.

6.1.2 Techniques

Volatile materials were handled in a conventional glass vacuum system or a greaseless glass vacuum system employing Youngs taps in conjunction with an Edwards E2M2 two stage high vacuum pump. Gas-liquid chromatography was performed in the range 40-270°C with a temperature gradient of 10°C per minute. Silica gel for chromatography was Merck Kieselgel 60(230-400 mesh). Alumina gel for chromatography was Merck Aluminiumoxid 90(70-230 mesh)(Brockmann activity II-III). Dialysis was carried out using Visking seamless tubing (pore size 24 Å, 14mm diameter, 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.

6.2 Experimental for Chapter Two

6.2.1 Preparation of *p*-allylbenzyltrimethylammonium bromide [53].

i.Preparation of *p*-bromobenzyl bromide [59]

p-Bromotoluene (102g, 0.70mol.), stirred at 120 °C and exposed to the light of a 60W bulb, was treated with bromine (102g, 0.64mol) over 3h and stirring continued for a further 1h. The brown crystalline mass which solidified upon cooling to room temperature (85g) was recrystallised from ethanol to produce *p*-bromobenzylbromide [59] (74g, 50%); m.pt. 61-62 °C(lit.63 °C ; ref. 77)

ii.Preparation of *p*-bromobenzyl ethyl sulphide [58]

Ethanolic sodium ethoxide, prepared by dissolving sodium (4.02g, 0.17mol.) in dry ethanol (100ml) was cooled to 0°C and treated over 15 mins with ethanethiol (13g, 0.20mol.). *p*-Bromobenzyl bromide (42.4g, 0.17mol.) in hot ethanol (50ml) was added with stirring over 30 mins and the mixture heated under reflux for 1h. The cooled mixture was acidified (2M H_2SO_4), extracted with diethyl ether and the extracts dried ($MgSO_4$). Evaporation of the solvent gave the crude product (42.48g) which was distilled to give *p-bromobenzyl ethyl sulphide* [58] (34.3g, 88%) b.pt. 92-95°C(0.08mmHg)

[Found : C, 46.97 H, 4.53% , $C_9H_{11}BrS$ requires C, 46.76 H, 4.80%]

$\delta_H(CDCl_3)$ 0.50(t, $CH_2C\underline{H}_3$), 1.63(q, $C\underline{H}_2CH_3$), 2.92(s, $ArC\underline{H}_2S$), 6.46 and 6.70ppm(AB, $-C_6H_4-$).

iii.Preparation of *p*-allylbenzyl ethyl sulphide [57].

Magnesium (25g, 1.04mol.) in dry tetrahydrofuran (200ml), activated using ethylene dibromide (0.5ml), was treated under nitrogen with *p*-bromobenzyl ethyl sulphide [58] (94g, 0.407mol.) in dry tetrahydrofuran (60ml) over 1h and the mixture heated under reflux for a further 1h. The ethereal Grignard solution was then separated from unreacted magnesium by means of a steel canular. Copper(I) iodide (0.16g, 0.84mol) was added to the Grignard reagent followed by allyl bromide (40ml, 0.462mol) over 40 mins with stirring, a very exothermic reaction taking place. The brown reaction mixture was heated under reflux for 18h. After cooling, the mixture was poured onto water, acidified(2M H_2SO_4) and extracted with diethyl ether. The ether extracts were dried($MgSO_4$) and concentrated by rotary evaporation to give crude product which was

distilled under reduced pressure to give *p-allylbenzyl ethyl sulphide* [57] (40.6g, 52%) b.pt 118-120°C(1.5mmHg)

(Found : C, 75.31 H, 8.40% ; $C_{12}H_{16}BrS$ requires C, 74.94 H, 8.39%)

$\delta_H(CDCl_3)$ 1.26(t, CH_2CH_3), 2.48(q, CH_2CH_3), 3.40(d, $CH_2CH=CH_2$), 3.72(s, $C_6H_4CH_2S$), 5.12(m, $CH=CH_2$), 5.97(m, $CH=CH_2$), 7.16 and 7.28ppm(AB, C_6H_4).

iv.Reactions of *p*-allylbenzyl ethyl sulphide [57] with bromoethane.

a.In methanol.

p-Allylbenzyl ethyl sulphide [57] (1.1g, 5.73mmol), bromoethane (7.1ml, 95mmol) and methanol (15ml) were heated in a sealed tube at 110°C for 21h. The solution was poured into water, acidified (2M H_2SO_4) and extracted with chloroform, the organic extracts being dried ($MgSO_4$) and concentrated by rotary evaporation to give crude product (0.761g). Distillation under reduced pressure produced a two-component mixture shown by GC-MS to be *p*-allylbenzyl methyl ether [60] and *p*-allylbenzyl bromide [61]. Column chromatography on silica using diethyl ether as elutant separated the two components with the major fraction being *p-allylbenzyl methyl ether [60]* (0.32g, 34%) Found M^+162, $C_{11}H_{14}O$ requires M^+162

$\delta_H(CDCl_3)$ 3.29(s, OCH_3), 3.33(d, $CH_2CH=CH_2$), 4.36(s, $C_6H_4CH_2O$), 5.11(m, $CH=CH_2$), 5.95(m, $CH=CH_2$), 7.14 and 7.27ppm(AB, $-C_6H_4-$) .

b.No solvent.

p-Allylbenzyl ethyl sulphide [57] (4.5g, 23.4mmol) and bromoethane (15ml, 0.2mol.) were heated in a sealed tube at 150°C for 50h. The crude product (4.0g, 81%) was distilled through a Fischer-Spahltrohr column to afford *p-allylbenzyl bromide* [61] (1.83g, 37%) b.pt 108-112°C(2.0mmHg) (Found : C, 56.60 H, 5.23% , M^+ 210/212; $C_{10}H_{11}Br$ requires C, 56.90 H, 5.25%, M^+ 210/212)

$\delta_H(CDCl_3)$ 3.34(d, $CH_2CH=CH_2$), 4.42(s, CH_2Br), 5.08(m, $CH=CH_2$), 5.90(m, $CH=CH_2$), 7.15 and 7.28ppm(AB, $-C_6H_4-$).

v.Preparation of *p*-allylbenzyltetrahydrothiophenium bromide [62].

p-Allylbenzyl bromide [61] (0.52g,2.46mmol.) and tetrahydrothiophene (0.32ml, 3.69mmol.) were mixed under nitrogen and within 30 mins a white solid had formed. The hygroscopic solid was washed under nitrogen with light petroleum(b.pt. 40-60°C) and dried in vacuo for 5h to afford *p-allylbenzyltetrahydrothiophenium bromide* [62] (0.5g, 68%) (Found : C, 55.94 H, 6.67% ; $C_{14}H_{19}BrS$ requires C, 56.19 H, 6.40%)

$\delta_H(CDCl_3)$ 2.08(m, $C\underline{H}_2CH_2S$-), 3.10(d, $C\underline{H}_2CH=CH_2$), 3.25(t, $CH_2C\underline{H}_2S$-), 4.37(s, $C_6H_4C\underline{H}_2S$), 4.85(m, $CH=C\underline{H}_2$), 5.69(m, $C\underline{H}=CH_2$), 7.02 and 7.29ppm(AB, -C_6H_4-).

vi.Preparation of *p*-allylbenzyl alcohol.

p-Allylbenzyl bromide [61] (0.34g, 1.59mol.) was treated with sodium hydroxide solution (10ml, 1M, 10mmol.) and heated under reflux for 3h. After pouring onto water (25ml) and acidifying (2M H_2SO_4), the mixture was extracted with diethyl ether, the extracts dried ($MgSO_4$) and concentrated by rotary evaporation to give crude product (0.24g), purified by chromatography on silica using diethyl ether in light petroleum (b.pt 40-60°C) (30%v/v) as elutant to leave *p-allylbenzyl alcohol* (a liquid) (Found : C, 80.84 H, 7.84% ; $C_{10}H_{12}O$ requires C, 81.04 H, 8.16%)

$\delta_H(CDCl_3)$ 2.09(s, OH), 3.29(d, $C\underline{H}_2CH=CH_2$), 4.52(s, -$C_6H_4C\underline{H}_2O$), 5.01(m, $CH=C\underline{H}_2$), 5.86(m, $C\underline{H}=CH_2$), 7.08 and 7.18ppm(AB, -C_6H_4-)

υ_{max}(neat) 3540-3120cm^{-1}(broad, -OH).

vii.Reaction of *p*-allylbenzyltetrahydrothiophenium bromide [62] with sodium hydroxide.

p-Allylbenzyltetrahydrothiophenium bromide [62] (0.61g, 2mmol.) in water (5ml) was treated with sodium hydroxide solution (1M, 5ml) and the solution stirred and heated under reflux for 3.5h. The mixture was poured onto water, acidified (2M H_2SO_4) and extracted with dichloromethane. The organic extracts were dried ($MgSO_4$) and concentrated by rotary evaporation to leave a viscous yellow oil (0.188g). Column chromatography on silica using diethyl ether in light petroleum (b.pt 40-60°C)(30%w/v) as elutant gave *p*-allylbenzyl alcohol(0.0263g, 9%) identified by infra-red comparison with an authentic sample.

viii.Reaction of *p*-allylbenzyl bromide [61] with trimethylamine

p-Allylbenzyl bromide [61] (1.49g, 7mmol.) in diethyl ether (10ml) was treated with trimethylamine (3.0g, 51mmol.) and left standing under nitrogen for 1 week. The white salt produced was filtered and washed under nitrogen with diethyl ether before drying in vacuo for 6h to give *p-allylbenzyltrimethylammonium bromide* [53] (1.36g,71%) a hygroscopic salt (Found : C, 55.76 H, 7.21 N, 4.75% ; $C_{13}H_{20}BrN$ requires C, 57.79 H, 7.46 N, 5.18%)

$\delta_H(CDCl_3)$ 3.41-3.48 overlapping(s, $(C\underline{H}_3)_3N$-)(d, $C\underline{H}_2CH=CH_2$), 5.02(s, $C\underline{H}_2N^+$-), 5.08(m, $CH=C\underline{H}_2$), 5.92(m, $C\underline{H}=CH_2$), 7.25 and 7.58ppm(AB, $-C_6H_4-$).

ix.Polymerisation reactions using *p*-allylbenzyltrimethylammonium bromide [53].

a.Method 1 (ref. 15a)

p-Allylbenzyltrimethylammonium bromide [53] (3.18g, 11.7mmol.) in water (10ml) was added over 30 mins to a refluxing solution of sodium hydroxide (41g, 1.03mol.) in water (55ml) and refluxing continued for a further 15 mins. After cooling the mixture, insoluble polymeric material was filtered off and washed with water before drying in vacuo. Extraction of the polymer in a Soxhlet apparatus with hot dichloromethane allowed insoluble polymer (1.97g) to be isolated (Found: C, 85.32 H, 7.68%; $(C_{10}H_{10})_n$ requires C, 92.3 H, 7.7%). The aqueous filtrate was acidified(2M H_2SO_4), extracted with dichloromethane and all the organic extracts combined, dried ($MgSO_4$) and solvent evaporated to leave 0.17g of a complex mixture (by TLC). Column chromatography of this material on silica (15cm x 3cm) using carbon tetrachloride as elutant enabled one component (0.08g, R_F0.15) to be isolated from the mixture. Recrystallisation from carbon tetrachloride gave *E,E-[6,2]-paracyclophan-1,5-diene [75]* (0.06g, 3.9%) m.pt. 147-150°C.

$\delta_H(CDCl_3)$ 2.42(m, $CH=CH-C\underline{H}_2$), 2.92(s, $C_6H_4C\underline{H}_2$), 5.50(m, $C_6H_4CH_a=C\underline{H}_b$), 5.90(d, $C_6H_4C\underline{H}_a=CH_b$), ($J_{Ha,Hb}$ 16.0Hz) 6.51 and 6.77ppm(AB, $-C_6H_4-$)

υ_{max} (KBr disc) 968cm^{-1}(trans CH=CH bend).

b.Method 2 (ref. 16)

With polymerisation inhibitor.

p-Allylbenzyltrimethylammonium bromide [53] (4.3g, 0.016mol.) in water (120ml) was treated with silver(I) oxide (4.0g, 0.017mol.) (from reaction of silver nitrate with sodium hydroxide) and mechanically stirred for 2.25h. The silver bromide precipitate was filtered and washed with water (40ml) to leave a solution of *p*-allylbenzyltrimethylammonium hydroxide (160ml, 0.1M). This solution was mixed with toluene (175ml) and phenothiazine (0.10g, 0.5mmol.) and mechanically stirred under reflux whilst azeotropically removing water by means of a Dean-Stark apparatus. After 3h all the water had been removed and no more trimethylamine was evolved. The hot toluene solution was filtered to remove insoluble material (0.62g, 30%) and concentrated by rotary evaporation to leave crude product (1.57g). The ^{1}H nmr of this material showed it was a mixture of *E,E-[6,2]-paracyclophan-1,5-diene [75]* (95%) and *Z,Z-[6,2]-paracyclophan-1,5-diene [79]* (3%) (see later) and, surprisingly, no soluble polymer. Column chromatography of a portion of this mixture (0.304g) on alumina using light petroleum (b.pt. 40-60°C) as elutant gave *E,E-[6,2]-paracyclophan-1,5-diene* (0.27g, representing 67% overall yield) m.pt. 147-150°C identified by ^{1}H nmr.

Without polymerisation inhibitor.

p-Allylbenzyltrimethylammonium bromide [53] (5.46g, 0.02mol.) in water (150ml) was treated with silver(I) oxide (8g, 0.034mol.) (from reaction of silver nitrate with sodium hydroxide) and stirred at room temperature for 1.5h. The silver(I) bromide precipitate was filtered off and washed with water (50ml) to leave a solution of *p*-allylbenzyltrimethylammonium hydroxide (200ml, 0.1M). Toluene (150ml) was added and the water removed azeotropically over 3.5h under reflux using a Dean and Stark apparatus. The hot toluene solution was filtered to remove insoluble polymeric material (1.05g, 40%) and the filtrate concentrated by rotary evaporation to leave *E,E-[6,2]-paracyclophan-1,5-diene [75]* (1.58g, 60%) identified by ^{1}H nmr.

6.2.2 The preparation of *p*-methylcinnamyltrimethylammonium bromide [54].

i.Preparation of α-(*p*-tolyl)allyl alcohol [63].

Magnesium (6.0g,0.25mol.) in dry diethyl ether (100ml), activated using ethylene dibromide (0.2ml), was treated under nitrogen with *p*-bromotoluene (43g, 0.25mol.) over 30 mins and the mixture stirred under reflux for a further 1h. After cooling to 0°C, freshly distilled acrolein (14g, 0.25mol.) in dry diethyl ether (50ml) was added over 1.5h and the mixture allowed to warm to room temperature over 3h. The solid yellow mass produced was poured onto a mixture of acetic acid (1M, 300ml) and crushed ice (400ml), the product extracted with diethyl ether and the ether extracts washed with sodium bicarbonate (0.5M) (2x100ml). The extracts were dried ($MgSO_4$) and concentrated by rotary evaporation to give the crude product which was purified by distillation under reduced pressure to give α-(*p*-tolyl)allyl alcohol [63] (19.5g, 52%) b.pt. 57-59°C(0.05mmHg) lit[83]120-122°C(10mmHg) $\delta_H(CDCl_3)$ 2.32(s, CH_3), 2.83(b, -OH), 5.07(m, CH=C$\underline{H}_2$), 5.25(d, C$\underline{H}$(OH)CH=CH_2), 5.97(m, C$\underline{H}$=CH_2), 7.11 and 7.19ppm(AB, -C_6H_4-)

υ_{max}(neat) 3560-3140cm^{-1}(OH).

ii.Preparation of p-methylcinnamyl bromide [65].

α-(*p*-Tolyl)allyl alcohol [63] (5.48g, 37mmol.) was added dropwise to a well stirred, ice-cooled solution of HBr in glacial acetic acid (50g, 30%w/v). After 5 mins the mixture was poured onto water and extracted with diethyl ether. The ether extracts were washed in turn with water (4x25ml), potassium bicarbonate solution (1M, 2x25ml) and then water again before they were dried ($MgSO_4$) and concentrated by rotary evaporation. The crude yellow solid residue (7.44g, 95%) was recrystallised from light petroleum (b.pt. 40-60°C) to give *p*-methylcinnamyl bromide [65] (4.5g,58%) m.pt.59.5-60.5°C (lit[83] 64-65°C)

$\delta_H(CDCl_3)$ 2.32(s, CH_3), 4.13(d, CH_2Br), 6.32(m, $C_6H_4CH_a$=C$\underline{H}_b$), 6.59(m, $C_6H_4C\underline{H}_a$=CH_b) ($J_{Ha,Hb}$ 15.6Hz) 7.10 and 7.26ppm(AB, -C_6H_4-).

iii.Reaction of *p*-methylcinnamyl bromide [65] with trimethylamine

p-Methylcinnamyl bromide [65] (1.44g, 6.82mmol.) in dry diethyl ether (15ml), treated with trimethylamine (3.0g, 50mmol.) was left standing under nitrogen for 21h. The white precipitate was filtered and washed with diethyl ether to leave *p-methylcinnamyltrimethylammonium bromide hemihydrate [54]* (1.0g,53%)(Found: C, 55.76 H, 7.21 N, 4.75% ; $C_{13}H_{20}BrN$ requires C, 57.78 H, 7.41 N, 5.19% ; $C_{13}H_{20}BrN.0.5H_2O$ requires C, 55.92 H, 7.58 N, 5.02%)

$\delta_H(D_2O)$ 2.32(s, CH_3), 3.06(s, $N^+(CH_3)_3$), 3.97(d, $CH=CHC\underline{H_2}N$), 4.81(s, H_2O), 6.29(m, $C_6H_4CH_a=C\underline{H_b}$), 6.91(m, $C_6H_4C\underline{H_a}=CH_b$)($J_{Ha,Hb}$ 15.6Hz), 7.25 and 7.45ppm(AB, -C_6H_4-).

iv. Polymerisation reactions using *p*-methylcinnamyltrimethylammonium bromide [54].

a.Method 1.[15a]

p-Methylcinnammyltrimethylammonium bromide hemihydrate [54] (0.596g, 2.2mmol.) in water (10ml) was added dropwise over 30 mins to a refluxing solution of sodium hydroxide (15g, 0.38mol.) in water (20ml) and refluxing continued for 1.5h. The insoluble polymeric material was filtered off, washed with water and hot dichloromethane and dried in vacuo (0.158g, 57%) (Found : C, 84.21 H, 7.06% ; $(C_{10}H_{10})_n$ requires C, 92.3 H, 7.7%). The aqueous filtrate was acidified (2M H_2SO_4) and extracted with dichloromethane and the combined organic extracts were dried ($MgSO_4$) and concentrated by rotary evaporation to leave crude soluble product (0.12g). Column chromatography of this product on silica using carbon tetrachloride as elutant gave *E,E-[6.2]-paracyclophan-1,5-diene [75]* (0.015g, 5%) as the fastest moving component in a complex mixture (R_F0.15) identified by ^1H nmr and infrared.

b Method 2[16]

p-Methylcinnammyltrimethylammonium bromide hemihydrate [54] (20.51g, 0.076mol.) in water (115ml) was treated with freshly prepared silver(I) oxide (25g, 0.108mol.) (from reaction of silver nitrate with sodium hydroxide) and mechanically stirred for 2.5h. The precipitated silver(I) bromide and excess silver(I) oxide was filtered off and washed with water to give a solution of *p*-methylcinnamyltrimethylammonium

hydroxide (175ml, 0.043M). Toluene (250ml) and phenothiazine (1g, 5mmol.) were added to the solution and water removed azeotropically over 5h under reflux using a Dean and Stark apparatus. The hot toluene solution was filtered to remove insoluble material (0.35g) and the filtrate concentrated by rotary evaporation to leave crude product (11.5g). Soxhlet extraction of this material with light petroleum (b.pt 80-100°C) left polymeric material [80] (2.1g, 22%)) which was dissolved in tetrahydrofuran and reprecipitated into methanol.(Found: C, 87.96 H, 7.39%; $(C_{10}H_{10})_n$ requires C, 92.3 H, 7.7%) M_n $1.44x10^4$, M_w $7.43x10^4$, M_w/M_n 5.15

$\delta_H(CDCl_3)$ 2.49(m, CH-C$\underline{H}_2$-CH_2), 2.73(m, CH-CH_2-C$\underline{H}_2$), 2.98(m, CH-CH-C$\underline{H}_2$), 3.49(m, CH-C$\underline{H}$-CH_2), 4.88(m, CH-CH=C$\underline{H}$(H)), 5.04(m, CH-CH=CH($\underline{H}$)), 5.99(m, CH-C$\underline{H}$=CH_2), 6.21(m, CH=C$\underline{H}$-CH_2), 6.35(m, C$\underline{H}$=CH-CH_2) and 7.15ppm(m, C_6H_4) {see page 53 [80]}

The cooled Soxhlet extracts yielded a white precipitate (3.43g,36%) which was recrystallised from light petroleum (b.pt. 80-100°C) and sublimed twice to give *E,E-[6,2]-paracyclophan-1,5-diene[75]* (2.5g,25%) (Found : C, 92.31 H, 7.78%, M^+ 260.1526, $C_{20}H_{20}$ requires C, 92.26 H, 7.74% , M^+ 260.1565).

$\delta_H(CDCl_3)$ 2.42(m,CH=CH-C$\underline{H}_2$), 2.91(s,$C_6H_4C\underline{H}_2$), 5.49(m, $C_6H_4CH_a$=C$\underline{H}_b$), 5.90(m, $C_6H_4C\underline{H}_a$=CH_b), $J_{Ha,Hb}$ 16.0Hz and 6.63ppm (m, -C_6H_4-); υ_{max} (KBr disc) 968cm^{-1}(trans CH=CH bend).

Column chromatography on alumina of the petroleum soluble material from the Soxhlet extracts using light petroleum(b.pt. 40-60°C) as elutant produced an impure sample of *Z,Z-[6,2]-paracyclophan-1,5-diene[79]* (20mg) identified by ^1H nmr(see below).

v.Pyrolysis of E,E-[6,2]-paracyclophan-1,5-diene [75].

E,E-[6,2]-Paracyclophan-1,5-diene [75] (0.182g, 0.7mmol..) was sublimed at approximately 250°C(0.01mmHg) and passed through a furnace maintained at 580°C into a cool tube held at room temperature. The oily material that collected was sublimed at 40°C and recrystallised from light petroleum to give *Z,Z-[6,2]-paracyclophan-1,5-diene[79]* (Found : C, 91.88, H, 7.54% ; $C_{20}H_{20}$ requires C, 92.26 H, 7.74%) m.pt. 70.5-71.5°C.

$\delta_H(CDCl_3)$1.96(m, CH=CH-C$\underline{H_2}$), 2.87(s, $C_6H_4C\underline{H_2}$), 5.55(m, $C_6H_4CH_a{=}C\underline{H_b}$), 6.34(d, $C_6H_4C\underline{H_a}{=}CH_b$), ($J_{Ha,Hb}$ 11.25Hz), 6.58 and 6.72ppm(AB, -C_6H_4-).

6.3 Experimental for Chapter Three

6.3.1.Preparation of *p*-benzylbenzyltrimethylammonium bromide [91]

i.Preparation of 1-phenyl-2,2,2-trichloroethanol

Benzaldehyde (178g, 1.68mol.) and chloroform (326g, 2.73mol.) were treated with powdered potassium hydroxide (100g, 2.5mol.) and stirred mechanically over 1.5h, the temperature being kept below 10°C. Stirring was continued for a further 1h at room temperature before the mixture was poured onto water (1.5L), acidified (2M H_2SO_4, 60ml) and extracted with chloroform. The organic extracts were washed three times with sodium bicarbonate solution (1M) and with water, dried ($MgSO_4$) and concentrated by rotary evaporation to leave crude product. Distillation under reduced pressure gave 1-phenyl-2,2,2-trichloroethanol (130g, 34%) b.pt. 75-85°C [0.05mmHg] lit.[89]90-100°C[0.5mmHg] $\delta_H(CDCl_3)$ 3.8(s, OH), 5.06(s,CH), 7.31 and 7.51ppm(AB, -C_6H_5-) υ_{max}(neat) 3530-3400cm^{-1}(OH).

ii.Preparation of 1,1,1-trichloro-2-(4-bromophenyl)-2-phenylethane

A mechanically stirred, ice-cooled mixture of 1,1,1-trichloro-2-phenylethanol (30g, 0.133mol.) and bromobenzene (26.5g, 0.168mol.) was treated over 2h with a mixture of sulphuric acid (26.5ml, d1.89) and oleum (8ml, 30%). After stirring for a further 0.5h at 0°C and for 4h at room temperature, the mixture was poured onto ice (300ml) and left overnight. After extraction with diethyl ether, the organic extracts were dried ($MgSO_4$) and concentrated by rotary evaporation to leave crude product (35.2g). Recrystallisation from ethanol gave 1,1,1-trichloro-2(4-bromophenyl)-2-phenylethane(26g, 54%) m.pt. 94-95°C [lit[89] 95-96°C] $\delta_H(CDCl_3)$ 5.03(s, CH), 7.32 and 7.47(AB, -C_6H_4) and 7.35ppm(m, C_6H_5-).

iii.Preparation of *p*-benzylbromobenzene [95].

Water was distilled from a mixture of diethylene glycol (74.5ml, d 1.118), potassium hydroxide (13g, 0.325mol.) and water (6.8ml) until the internal temperature

reached 180°C. After cooling the mixture to below 100°C, 1,1,1-trichloro-2-(4-bromophenyl)-2-phenylethane (5.25g, 13mmol.) was added and the mixture heated to reflux (175°C) with mechanical stirring for 5h, before finally pouring onto ice (250ml). After extraction with diethyl ether, the organic extracts were dried ($MgSO_4$) and concentrated by rotary evaporation to leave crude product (3.5g). Distillation under reduced pressure gave *p*-benzylbromobenzene [95] (3.0g, 84%) b.pt. 92-98°C[0.05mmHg] (lit[89] 120-130°C[3mmHg] $\delta_H(CDCl_3)$ 3.99(s, CH_2) and a complex multiplet between 7.10 and 7.48ppm(m, -C_6H_4- and -C_6H_5-).

iv.Preparation of *p*-benzylbenzyl alcohol [94].

Magnesium (2.8g, 0.116mol.) in dry tetrahydrofuran (25ml), activated using ethylene dibromide (20 drops), was treated over 0.5h with *p*-benzylbromobenzene [95] (10g, 0.04mol.) in dry tetrahydrofuran (10ml) and heated under reflux for a further 1h. Paraformaldehyde (4.5g, 0.155mol.) was decomposed at 180-200°C and the resulting formaldehyde gas passed over the ice-cooled Grignard reagent through a heated wide bored tube by means of a stream of nitrogen. After stirring at room temperature for 1h the mixture was poured onto ice, acidified (2M H_2SO_4) and extracted with diethyl ether. The organic extracts were dried ($MgSO_4$) and concentrated by rotary evaporation to give crude product (9.4g). After trituration with light petroleum (b.pt. 30-40°C) a white solid was obtained (7.5g) which was recrystallised from light petroleum (b.pt. 30-40°C) to give *p-benzylbenzyl alcohol [94]* (4.6g, 57%) m.pt.44.0-45.0°C (Found: C, 84.48 H, 7.11% ,M^+198 ; $C_{14}H_{14}O$ requires C, 84.81 H, 7.12%, M^+198).

$\delta_H(CDCl_3)$ 1.76(b, OH), 3.97(s, CH_2), 4.62(s, CH_2OH), 7.17 and 7.26ppm(AB, -C_6H_4- and -C_6H_5-); υ_{max}(nujol) 3250cm^{-1}(OH).

v.Preparation of *p*-benzylbenzyl bromide [93]

p-Benzylbenzyl alcohol [94] (4.1g, 0.021mol.) was treated with HBr in glacial acetic acid (30ml, 45%w/v) and stirred at 45°C for 2h. The bulk of the acid was removed in vacuo (0.05mmHg) at room temperature before fractional distillation to give *p-benzylbenzylbromide* [93] (4.8g, 89%) b.pt. 98-102°C[0.05mmHg] m.pt. 35.5-36.5°C[from light petroleum(b.pt. 40-60°C)](Found : C, 64.11 H, 4.88% M^+ 260/262;

$C_{14}H_{13}Br$ requires C, 64.39 H, 5.02% M^+ 260/262); $\delta_H(CDCl_3)$ 3.89(s, CH_2), 4.36(s, CH_2Br), 7.12 and 7.22ppm(AB, C_6H_4 and C_6H_5).

vi.Reaction of *p*-benzylbenzyl bromide [93] with trimethylamine.

p-Benzylbenzyl bromide [93] (0.643g, 2.46mmol.) in dry diethyl ether (10ml) was treated with trimethylamine and left standing under nitrogen for 1 day. The resulting white solid was washed by decantation with dry diethyl ether before drying in vacuo gave *p-benzylbenzyltrimethylammonium bromide* [91] (0.52g, 66%) (Found: C, 63.45 H, 6.92 N, 4.34% ; $C_{17}H_{22}BrN$ requires C, 63.75 H, 6.92 N, 4.37%) $\delta_H(CDCl_3)$ 3.38(s, $N^+(CH_3)_3$), 3.98(s, CH_2), 5.02(s, CH_2N^+) and complex multiplet(incl.7.27 and 7.62 as part of an AB system)7.4ppm(m, -C_6H_4- and -C_6H_5-).

vii.Polymerisation using *p*-benzylbenzyltrimethylammonium bromide [91].

A solution of *p*-benzylbenzyltrimethylammonium bromide [91] (6.39g, 0.02mol.) in water (100ml) was treated with silver(I) oxide (6.8g, 0.03mol.)(from reaction of silver nitrate with sodium hydroxide) and mechanically stirred at room temperature for 2.5h. The silver(I) bromide and excess silver (I) oxide were filtered off and washed with water (20ml) to leave a solution of *p*-benzylbenzyltrimethylammonium hydroxide (120ml, 0.167M). This solution was mixed with toluene(250ml) and phenothiazine(0.25g, 1.26mmol.) before removing water under reflux using a Dean and Stark apparatus. After 2.5h no more water or trimethylamine was evolved and the toluene solution was filtered hot to remove the very small amount of insoluble impurities. The filtrate was concentrated by rotary evaporation to leave crude product (4.32g) which was extracted for 18h in a Soxhlet apparatus using light petroleum (b.pt. 80-100°C). The remaining material (2.19g) was dissolved in tetrahydrofuran and reprecipitated in methanol to give poly(α-phenyl-*p*-xylylene)[85] (1.17g, 32%) M_n $1.83x10^4$, M_w 4.12x104, Mw/Mn 2.26 (Found: C, 91.34 H, 6.75%; $(C_{14}H_{12})_n$ requiresC , 93.29 H , 6.71%); $\delta_H(CDCl_3)$ 2.69(CH_2, tt), 2.72(CH_2, tt), 3.09(CH_2, tt), 3.19(CH_2, ht), 4.05(CH, ht), 4.64(CH, hh) and 6.74-7.25ppm(m, -C_6H_4- and C_6H_5-) [see page 75, fig 21]

The fast moving components of the Soxhlet extracts (1.45g) were isolated by chromatography on an alumina column using ethyl acetate in hexane (10%w/v) as elutant.

These components (1.1g) were further separated by column chromatography on alumina using diethyl ether in light petroleum (b.pt.40-60°C) (5% v/v) as elutant. Two major products were isolated and identified as isomeric structures of the same cyclic trimer, tri(α-phenyl-*p*-xylylene). The faster moving cyclic trimer [103] was purified by recrystallisation from toluene and dried in vacuo at 100°C(1.3g, 36%) m.pt. 269-272°C(Found : C, 93.67 H, 6.68% , M^+ 540 ; $C_{42}H_{36}$ requires C, 93.29 H, 6.71%, M^+ 540) $\delta_H(CDCl_3)$ 2.73 and 2.93(m,$H_{6,7,8,9}$,$H_{6',7',8',9'}$), 3.05(m,H_4,$H_{4'}$), 3.34(m, H_3,$H_{3'}$), 4.20(m, $H_{5'}$), 4.31(m, H_5), 4.58(m, $H_{1,2,1',2'}$) and 7.20ppm(m, C_6H_4 and C_6H_5) [see page 70, fig 17]

$\delta_C(CDCl_3)$ 33.43, 34.17, 34.55($C_{5,5',6,6'}$), 41.23, 41.36($C_{3,3'}$), 50.51(C_4), 51.97 ($C_{4'}$), 56.44($C_{2,2'}$), 56.56($C_{1,1'}$) and 125.88-145.25(C_6H_4 and C_6H_5)

The other cyclic trimer [104] was purified by recrystallisation from ethanol (0.43g, 11%) m.pt. 97-100°C (Found: M^+ 540.2977 ; $C_{42}H_{36}$ requires M^+ 540.2817) $\delta_H(CDCl_3)$ 2.76(m, -C<u>H</u>$_2$-C<u>H</u>$_2$-), 3.02(m, -CHPh-C<u>H</u>(H)-), 3.40(m, -CHPh-CH(<u>H</u>)-), 4.19(m, -C<u>H</u>Ph-CH_2-), 4.32(m, -C<u>H</u>PH-CH_2-), 5.29(m, -C<u>H</u>Ph-C<u>H</u>Ph-) and 7.12ppm(m, C_6H_4 and C_6H_5) .

6.3.2 The preparation of *p*-methylbenzhydryltrimethylammonium bromide [92].

i.Preparation of *p*-methylbenzhydryl bromide [97b].

p-Methylbenzhydrol [96] [Aldrich catalogue name(also *p*-methylphenyl phenyl methanol)](20g, 0.1mol.) was treated with a solution of HBr in glacial acetic acid (120g, 45%w/v) and stirred at 40°C for 3h. The excess acid was removed in vacuo (0.05mmHg) and the crude product distilled (101-106°C/0.05mmHg) to give a liquid (23g) which GC-mass spectrometry showed was a mixture of *p*-methylbenzhydryl bromide [97b](94% GC yield) and *p*-methylbenzhydrol [96]/α-phenyl-*p*-xylene [101](6% GC yield) (Found: C, 66.01 H, 5.13% ; $C_{14}H_{13}Br$ requires C, 64.39 H, 5.02%)

$\delta_H(CDCl_3)$ 2.25(s, CH_3), 6.21(s, CHBr), 7.05 and 7.39(AB, -C_6H_4-) and 7.26ppm(m, -C_6H_5-).

Purification of the *p*-methylbenzhydryl bromide [97b] was attempted as follows:

a.Column chromatography on silica

Crude *p*-methylbenzhydryl bromide [97b](0.613g, 2.34mmol.) was sent through a silica column slowly, using dichloromethane as elutant. The extremely viscous oil that was isolated was identified as di(*p*-methylbenzhydryl) ether [98] (0.42g, 47%) m.pt.69-71°C(from methanol).

(Found: C, 88.51 H, 6.92% ; $C_{28}H_{26}O$ requires C, 88.85 H, 6.92%).

$\delta_H(CDCl_3)$ 2.08(s, CH_3), 5.24(s, CHOCH), 6.91 and 7.20(AB, C_6H_4) and 7.04ppm(m, -C_6H_4- and -C_6H_5-); υ_{max}(neat) 1055cm^{-1}(ether stretch).

b.Column chromatography on alumina

Crude *p*-methylbenzhydryl bromide [97b] (275mg, 1.05mmol.) was passed through an alumina column using ethyl acetate in hexane (2%v/v) as elutant and three fractions were obtained The fastest moving component (R_F0.73) was identified as di(*p*-methylbenzhydryl) ether [98](0.05g) by comparison of its infrared with an authentic sample.

The second component (24mg)(R_F 0.47) was impure *p*-methylbenzhydryl bromide [97b] from its ^1H nmr spectrum. $\delta_H(CDCl_3)$ 2.32(s, CH_30, 6.65(s, CHBr) and 7.32ppm(m, -C_6H_5- and -C_6H_5-).

The most polar component (R_F 0.22) was identified as *p*-methylbenzhydrol [96](150mg) M^+198 , $C_{14}H_{14}O$ requires M^+198.

$\delta_H(CDCl_3)$ 2.29(s, CH_3), 2.47(b, OH),5.70(s, CHO) and 7.23ppm(m, -C_6H_5- and -C_6H_4-).

c.Distillation using a Fischer-Spahltrohr unit.

Crude *p*-methylbenzhydryl bromide [97b](30g, 0.115mol.) was distilled through a Fischer-Spahltrohr column. Instead of bromide being isolated, α-phenyl-*p*-xylene [101] was distilled (10g, 0.06mol.) b.pt. 112-132°C(1.0mmHg)

(Found : C, 92.05 H, 7.54% ; $C_{14}C_{14}$ requires C, 92.26 H, 7.74%)

$\delta_H(CDCl_3)$ 2.27(s, CH_3), 3.90(s, CH_2), 7.05(m, C_6H_5) and 7.15 and 7.21ppm(AB, -C_6H_4-).

p-Methylbenzhydryl bromide [97b] was converted into 1,2-di(*p*-tolyl)-1,2-diphenylmethane [102] as follows:

The bromide (0.25g, 0.96mmol.), zinc (0.5g, 7.7mmol.) and ethyl acetate (5ml) were stirred at room temperature for 18h before the zinc was filtered off and washed with ethyl acetate. The filtrate was concentrated by rotary evaporation to a yellow solid, purified by recrystallisation from ethanol (0.165g, 95%) m.pt. 212-214°C(Found: C, 92.90 H, 7.51% ; $C_{28}H_{26}$ requires C, 92.77 H, 7.23%)

$\delta_H(CDCl_3)$ 2.17(s, CH_3), 4.72(s, CH) and 6.89-7.18ppm(m, -C_6H_4- and -C_6H_5-).

ii.Reaction of *p*-methylbenzhydryl bromide [97b] with trimethylamine.

Crude *p*-methylbenzhydryl bromide [97b](0.685g, 2.62mmol.) in dry diethyl ether (15ml) and trimethylamine (1.07g, 18mmol.), were left to stand under nitrogen for 6 days. The resulting white solid was washed by decantation under nitrogen with dry diethyl ether and dried in vacuo for 3h to give *p-methylbenzhydryltrimethyl ammonium bromide[92]* (0.40g, 48%) (Found : C, 63.82 H, 7.13 N, 4.10% ; $C_{17}H_{22}BrN$ requires C, 63.75 H, 6.92 N, 4.37%).

$\delta_H(CDCl_3)$ 2.39(s, CH_3), 3.50(s, $N^+(CH_3)_3$), 6.99(s, CHN^+) and four multiplets from 7.38-8.18ppm(-C_6H_5- and -C_6H_4-).

iii.Polymerisation using *p*-methylbenzhydryltrimethylammonium bromide.

A solution of *p*-methylbenzhydryltrimethylammonium bromide [92] (4.29g, 0.013mol.) in water (70ml) was treated with freshly prepared silver(I) oxide (3.44g, 0.015g)(from reaction of silver nitrate with sodium hydroxide) and mechanically stirred at room temperature for 1h. The silver bromide and excess silver oxide were filtered off and washed with water to leave a solution of *p*-methylbenzhydryltrimethylammonium hydroxide (100ml, 0.13M). This solution was mixed with toluene (150ml) and phenothiazine (0.18g, 0.90mmol.) and water removed under reflux using a Dean and Stark apparatus. After 3h no more water or trimethylamine was evolved. The hot toluene solution was filtered to remove the small amount of insoluble impurities and concentrated by rotary evaporation to leave crude product (2.67g). Extraction of this product for 24h in a Soxhlet apparatus using light petroleum (b.pt. 80-100°C) left polymeric material (0.305g) further purified by dissolving in tetrahydrofuran and reprecipitating into

methanol. The polymer was identified as poly(α-phenyl-*p*-xylylene) [85](0.30g, 12%) M_w 6.37x10^4, M_n 2.88x10^4, M_w/M_n 2.22 (Found C, 88.27 H, 6.32 ; $(C_{14}H_{12})_n$ requires C, 93.29 H, 6.71%); $\delta_H(CDCl_3)$ 2.69(CH_2, tt), 2.72(CH_2, tt), 3.09(CH_2, tt), 3.19(CH_2, ht), 4.05(CH, ht), 4.64(CH, hh) and 6.74-7.23ppm(m, -C_6H_4- and -C_6H_5-) [see page 78, fig 22]

The remaining non-polymeric material (2.3g) was a very complex mixture of components. Partial separation of components was achieved by column chromatography on alumina using diethyl ether in light petroleum (b.pt.40-60°C)(5%v/v) as elutant. Further column chromatography on alumina using diethyl ether in light petroleum (b.pt.40-60°C)(1%v/v) as elutant isolated three major components. One component, obtained as a liquid, was further purified by distillation ($60°C_{0.05mmHg}$) and identified as a mixture of *2-benzyl-5-methyl-N,N-dimethylbenzylamine [113]* and *2-(4-methylbenzyl)-N,N-dimethylbenzylamine [114]* (0.25g, 8%) (Found : C, 85.10 H, 9.08 N, 5.88% M^+ 239 ; $C_{17}H_{21}N$ requires C, 85.30 H, 8.84 N, 5.85%, M^+ 239) $\delta_H(CDCl_3)$ 2.24(s, $N(CH_3)_2$), 2.34(s, CH_3), 2.37(s, CH_3), 3.37(s, CH_2N), 3.40(s, CH_2N), 4.20(s, $C_6H_5CH_2C_6H_4$-) and 7.29ppm(m, C_6H_5,C_6H_3 and C_6H_4,C_6H_4). The second product was a solid, recrystallised from toluene, and identified as the cyclic *tri(α-phenyl-p-xylylene)[103]* by infrared comparison (0.40g,17%) m.pt. 270-273°C .

The third product was an unidentified luminous green solid which was recrystallised from light petroleum(b.pt.100-120°C)(0.19g) m.pt.174-176°C (M^+398) $\delta_H(CDCl_3)$ 0.224(s), 1.56(s) and 7.07(m); u_{max}(KBr) 3340cm^{-1}(sharp).

6.4.Experimental for Chapter Four

6.4.1.Preparation of *p*-tetrahydrothiopheniummethylcinnamyltetrahydro thiophenium dibromide [119].

i.Preparation of *p*-bromobenzyl methyl ether.

A methanolic solution of sodium methoxide formed by dissolving sodium (9.5g, 0.413mol.) in methanol (300ml) was treated with *p*-bromobenzyl bromide (98g, 0.392mol.) in hot methanol (100ml) over 20 mins. The mixture was then heated under reflux for 18h, and the methanol removed by rotary evaporation. The residues were poured into water, acidified (2M H_2SO_4) and extracted with ether. The organic extracts

were dried ($MgSO_4$) and concentrated by rotary evaporation to leave the crude product which was purified by distillation under reduced pressure to give *p-bromobenzyl methyl ether* (74.5g, 95%) b.pt. 150-152°C[20mmHg] (Found: C, 47.80 H, 4.42 % ; C_8H_9BrO requires C, 47.79 H, 4.51 %); $\delta_H(CDCl_3)$ 3.35(s, OCH_3), 4.37(s, CH_2O), 7.18and 7.44ppm(AB, $-C_6H_4-$).

ii.Preparation of α-[(*p*-methoxymethyl)phenyl]allyl alcohol[126].

Magnesium (4g, 0.166mol.) in dry tetrahydrofuran (60ml), activated with ethylene dibromide, was treated over 15mins with *p*-bromobenzyl methyl ether (5g, 0.0249mol.) in dry tetrahydrofuran (10ml) and the mixture heated under reflux for a further 2h. After cooling the mixture to 0°C, acrolein (1.47g, 0.0263mol.) in dry tetrahydrofuran (10ml) was added over 15 mins and the mixture then stirred at room temperature for 18h. The supernatant liquid was poured into water, acidified (2M H_2SO_4) and extracted with diethyl ether. The organic extracts were dried ($MgSO_4$) and concentrated by rotary evaporation to leave crude product (4.92g). Distillation under reduced pressure gave *α-[(p-methoxymethyl)phenyl]allyl alcohol[126]* (1.64g,37%) b.pt. 83-84°C[0.01mmHg] (Found : C, 73.85 H, 7.77 % M^+178; $C_{11}H_{14}O_2$ requires C, 74.13 H, 7.92% M^+178); $\delta_H(CDCl_3)$ 2.30(b, OH), 3.36(s, OCH_3), 4.44(s, CH_2O), 5.18(d, $CH=CH\underline{H}_{cis}$ and CHO),5.33(d, $CH=C\underline{H}_{trans}H$),6.02(m, $C\underline{H}=CH_2$) and 7.32ppm(m, $-C_6H_4-$); υ_{max}(neat) 3550-3200cm^{-1}(broad,OH).

iii. Preparation of *p*-bromomethylcinnamyl bromide[127].

α-[(*p*-Methoxymethyl)phenyl]allyl alcohol [126](1.64g, 9.2mmol.) cooled in an ice bath, was stirred with HBr in glacial acetic acid (15ml, 45%w/v). After 15 mins the resulting white solid was filtered off, washed with water and dried in vacuo. This crude product (2.23g) was recrystallised from light petroleum (b.pt. 40-60°C) to leave *p-bromomethylcinnammyl bromide [127]* (1.6g, 60%) m.pt. 83.0-83.5°C (Found: C, 41.34 H, 3.49 % M^+288/290/292; $C_{10}H_{10}Br_2$ requires C, 41.42 H, 3.48 %,M^+ 288/290/292)

$\delta_H(CDCl_3)$ 4.15(d, $CH-C\underline{H}_2Br$), 4.48(s, $C_6H_4C\underline{H}_2Br$), 6.40(m, $CH=C\underline{H}-CH_2Br$), 6.62(d, $C\underline{H}=CH-CH_2Br$) and 7.35ppm(m, $-C_6H_4-$).

iv.Reaction of *p*-bromomethylcinnamyl bromide [127] with tetrahydrothiophene

p-Bromomethylcinnammyl bromide [127] (0.183g, 0.63mmol.) in dry methanol (7ml) was treated with tetrahydrothiophene (0.5ml) and stirred at room temperature for 18h. The solution was then concentrated in vacuo and a white solid precipitated out by trituration with dry acetone. The solid was washed by decantation with dry acetone and dried in vacuo to give *p-(tetrahydrothiopheniummethyl)cinnamyl tetrahydrothiophenium dibromide [119]* (0.26g,88%) (Found: C, 46.08 H, 6.04% ; $C_{18}H_{26}Br_2S_2$ requires C, 46.36 H, 5.62%); $\delta_H(CDCl_3)$ 2.14(m, $C\underline{H}_2CH_2S^+$-), 3.36(m, -$CH_2C\underline{H}_2S^+$-), 3.99(d, CH=CH-$C\underline{H}_2S^+$), 4.38(s, $C_6H_4C\underline{H}_2S^+$), 6.25(m, CH=C$\underline{H}$-$CH_2$), 6.85(d, C$\underline{H}$=CH-$CH_2$), 7.37 and 7.47ppm (AB, -C_6H_4-).

6.4.2.Polymerisation reactions using *p*-(tetrahydrothiophenium methyl) cinnamyltetrahydrothiophenium dibromide [119].

a.In water

p-(Tetrahydrothiopheniummethyl)cinnamyltetrahydrothiophenium dibromide [119] (0.30g , 0.64mmol.) in water (1.5ml), cooled in an ice bath , was treated with a pre-cooled solution of sodium hydroxide (0.381M, 1.69ml) and stirred for 35mins before quenching with a solution of hydrochloric acid (0.208M, 0.5ml). The thick yellow suspension was treated with tetrahydrofuran (20ml) before centrifugation and removal of water and tetrahydrofuran by decantation. The suspension became gelatinous and was dialysed for 3 days against deionised water to leave a thick gel which was diluted slightly with tetrahydrofuran (10ml). A film was cast and dried in vacuo for 18h (Found : C, 56.23 H, 6.57 Br, 21.64 S, <0.97% ; $C_{14}H_{17}BrS$ requires C, 56.57 H, 5.76 Br, 26.88 S, 10.79%).

This precursor polymer film was then heated in vacuo at 180°C for 7h to leave a canary yellow film (Found : C, 54.59 H, 7.09 Br, 7.25 S,< 0.72%)

b.In water/methanol

p-(Tetrahydrothiopheniummethyl)cinnamyltetrahydrothiophenium dibromide [119] (0.366g, 0.785mmol.) in methanol/water (2/1v/v, 7.5ml) cooled to -20°C, was treated over 20 mins with sodium hydroxide (0.381M, 2ml). The resulting yellow solution became slightly cloudy and was stirred for a further 0.5h at <-15°C before dialysing for 18h against methanol/water (1:1v/v) at room temperature. Initially a white yellow precipitate appeared but this redissolved with continued dialysis to leave a partly gelatinous solution which was cast into a film on a plastic sleeve (Found: C, 54.33, H, 6.51, S, 8.52, Br, 22.05% ; $C_{14}H_{17}BrS$ requires C, 56.57 H, 5.76 Br, 26.88 S, 10.79%) . The film was heated in vacuo at 170°C (0.05mmHg) for 7h, turning a yellow-brown colour (Found C, 72.40, H, 6.31, Br, 14.77,S, 7.92% ; $(C_{10}H_8)_n$ requires C, 93.71, H, 6.29%)

6.4.3.Preparation of *p*-tetrahydrothiopheniummethylbenzhydryltetrahydro thiophenium dibromide [120].

i.Preparation of *p*-methoxymethylbenzhydryl alcohol [136].

Magnesium (4g, 0.166mol.) in dry tetrahydrofuran (60ml) activated with ethylene dibromide (0.2g, 1.06mmol.), was treated over 15mins with *p*-bromobenzyl methyl ether (5g, 24.9mmol.) in dry tetrahydrofuran (10ml) and the mixture heated under reflux for 2h. After cooling the Grignard reagent to room temperature, benzaldehyde (2.7g, 25.5mmol.) in dry tetrahydrofuran (10ml) was added over 15mins and the solution heated under reflux for 18h. The mixture was then cooled, the supernatant liquid decanted into water, acidified (2M H_2SO_4) and extracted with ether. The organic extracts were dried($MgSO_4$) and concentrated by rotary evaporation to leave the crude product (6.2g) which was purified by column chromatography on alumina using ethyl acetate in hexane (10%v/v) as elutant to give *p-methoxymethylbenzhydryl alcohol [136]* (4.21g, 74%) (a liquid) (Found: C, 78.81 H, 7.11 % ; $C_{15}H_{16}O_2$ requires C, 78.92 H, 7.06 %). $\delta_H(CDCl_3)$ 2.98(d, OH), 3.30(s, OCH_3), 4.37(s, CH_2O), 5.69(d, CHO) and 7.28ppm(m, $-C_6H_4-$ and $-C_6H_5-$).

υ_{max}(neat) 3550-3200cm^{-1}(broad, -OH).

ii.Preparation of *p*-bromomethylbenzhydryl bromide [137].

p-Methoxymethylbenzhydryl alcohol [136] (3.77g, 0.0165mol.) was treated with HBr in glacial acetic acid (25ml, 45%w/v) and the mixture stirred at room temperature for 2h. The excess acid was removed in vacuo at room temperature to leave crude product (5.15g) which solidified and was recrystallised from light petroleum (b.pt. 40-60°C) to give *p-bromomethylbenzhydryl bromide [137]* (4.22g, 75%) m.pt. 50-52°C (Found : C, 49.70 H, 3.50%; $C_{14}H_{12}Br_2$ requires C, 49.45 H, 3.56 %); $\delta_H(CDCl_3)$ 4.47(s, CH_2Br), 6.26(s, CHBr) and 7.35ppm(m, -C_6H_4- and -C_6H_5-).

iii.Reaction of *p*-bromomethylbenzhydryl bromide [137] with tetrahydro thiophene

p-Bromomethylbenzhydryl bromide [137] (0.353g, 1.04mmol.) in acetonitrile (5ml) was treated with tetrahydrothiophene (1ml, 11.3mmol.) and stirred at room temperature for 23h. The solution was then concentrated in vacuo and a white salt precipitated by trituration with dry acetone. After washing by decantation with dry acetone and drying in vacuo for 3h *p-(tetrahydrothiopheniummethyl)benzhydryl tetrahydrothiophenium dibromide* [120]was obtained (0.38g, 71%)(Found : C, 51.30 H, 5.78 % ; $C_{22}H_{28}Br_2S_2$ requires C, 51.17 H, 5.47 %)

$\delta_H(D_2O)$2.18 (m, free THT), 2.56(m, $S(CH_2\underline{CH_2}$-), 3.07(m, free THT), 3.67(m, $S\underline{CH_2}CH_2$-), 4.81(s, $\underline{CH_2}S$), 5.13(s, D_2O), 6.08(s, CHS), 6.17(s, CHOD) and 7.66-8.08ppm(m, C_6H_4 and C_6H_5).

6.4.4.Polymerisation using *p*-(tetrahydrothiopheniummethyl)benzhydryl tetrahydrothiophenium dibromide [120].

a.In water

A solution of sodium hydroxide (1.93ml, 0.381M), cooled in an ice-salt bath, was treated, under nitrogen, with *p*-(tetrahydrothiopheniummethyl)benzhydryl tetrahydrothiophenium dibromide [120] (0.38g, 0.74mmol.). A deep orange colour appeared immediately quickly followed by a precipitate. Stirring was continued for 20 mins and the reaction quenched with dilute hydrochloric acid (0.208M). The suspension was dialysed for 3 days against deionised water before it was dissolved in

tetrahydrofuran (5ml). An attempt was made to cast a film but only a flakey solid was obtained.

b.In tetrahydrofuran/water.

p-(Tetrahydrothiopheniummethyl)benzhydryltetrahydrothiophenium dibromide[120] (0.331g, 0.64mmol.) in tetrahydrofuran (2ml) and water (2ml) was cooled in an ice-bath and treated with ice-cooled sodium hydroxide solution (0.381M, 1.68ml). Immediately the solution became a deep orange colour which became cloudy and lead to a suspension. After stirring for 15 mins the polymerisation was quenched with HCl (0.208M, 0.5ml) and the suspension dialysed against deionised water for 4 days. The solution afforded by the subsequent addition of water (3ml) and tetrahydrofuran (5ml) to the contents of the dialysis tubing was cast into a brittle yellow film (Found: C, 59.35 H, 5.66 Br, 16.25 S, 7.40% ; $C_{18}H_{19}BrS$ requires C, 62.25 H, 5.51 Br, 23.0 S, 9.23%) .

c.In methanol/water

p-(Tetrahydrothiopheniummethyl)benzhydryltetrahydrothiophenium dibromide[120] (0.268g, 0.628mmol.) in methanol/water (2/1 v/v, 6.3ml), precooled in a carbon tetrachloride/CO_2 bath, was treated over 10 mins with sodium hydroxide (0.381M, 1.65ml) and stirred at this temperature for a further 1h. The resulting mixture was dialysed for 2 days against methanol/water (1/1 v/v) before dissolving in more methanol (5ml) and casting a precursor film on a plastic sleeve (Found: C, 58.66 , H, 5.84, Br, 16.41, S, 8.34%; $C_{18}H_{19}BrS$ requires C, 62.25 H, 5.51 Br, 23.0 S, 9.23%) .

6.5.Experimental for Chapter Five

6.5.1.Preparation of 2,3,4,5,6-pentafluorobenzylpyridinium bromide [138A].

2,3,4,5,6-Pentafluorobenzyl bromide (1.38g, 5.28mmol.) in dry acetone (6ml) was treated with pyridine (0.45ml, 5.84mmol.) and heated under reflux for 4h. After cooling to room temperature a white precipitate appeared which was filtered off, washed with dry acetone and dried in vacuo to give *2,3,4,5,6-pentafluorobenzylpyridinium*

bromide[138A] (1.51g, 84%) m.pt. 159.0-161.0°C (Found: C, 41.91 H, 1.99 N, 4.09% ; $C_{12}H_7BrF_5N$ requires C, 42.38 H, 2.07 N, 4.12%)

$\delta_H(D_2O)$ 6.05(s, CH_2), 8.14(t, β-H), 8.63(t, χ-H) and 8.98ppm(d, α-H)

$\delta_F(D_2O)$ -141.9(o-F), -150.81(p-F) and -161.43(m-F).

6.5.2. Reaction of 2,3,4,5,6-pentafluorobenzylpyridinium bromide [138A] with *n*-butyllithium.

A suspension of 2,3,4,5,6-pentafluorobenzylpyridinium bromide [138A] (0.296g, 0.87mmol.) in tetrahydrofuran (10ml), cooled to -70°C, was treated over 10mins with *n*-butylithium in hexane (0.55ml, 1.63M) and stirred at this temperature for 1h. The initial indigo mixture turned to a yellow/brown suspension which was warmed to room temperature and heated under reflux for 18h. The resulting dark brown mixture was poured onto water, acidified (2M H_2SO_4) to pH 4.5 and extracted with diethyl ether. The ether extracts were dried ($MgSO_4$) and concentrated by rotary evaporation to leave crude organic product (0.12g) $\delta_F(CDCl_3)$ 161.52-142.55ppm(unidentified). The aqueous phase was concentrated in vacuo and dialysed for 48h against deionised water before it was concentrated further to leave a yellow-orange solution. $\delta_F(H_2O)$ 161.30(m-F), 150.68(s,p-F), and 141.80ppm(o-F) all corresponding to unreacted starting material and also 144.42(s, unidentified) and 144.19ppm(s, unidentified).

6.5.3.Preparation of *p*-(2,3,4,5,6-pentafluorobenzyl)benzyltetrahydro thiophenium bromide [142A].

i.Preparation of *p*-(2,3,4,5,6-pentafluorobenzyl)benzyl methyl ether [147].

Magnesium (2.5g, 0.104mol.) in dry tetrahydrofuran (30ml), activated with ethylene dibromide, was treated over 15 mins with *p*-bromobenzyl methyl ether (1.77g, 8.81mmol.) in dry tetrahydrofuran (10ml) and the mixture heated under reflux for a further 2h. After cooling and transferring the supernatant liquid to a second flask by canular, the solution was treated over 20 mins with 2,3,4,5,6-pentafluorobenzyl bromide (2.29g, 8.77mmol.) in dry tetrahydrofuran (10ml) and the solution heated under reflux for a further 18h. The solution was then poured into water, acidified (2M H_2SO_4) and extracted with diethyl ether. The dried ($MgSO_4$) ether extracts were concentrated by

rotary evaporation to leave crude product (2.27g). Distillation under reduced pressure gave *p-(2,3,4,5,6-pentafluorobenzyl)benzyl methyl ether [147]* (0.61g, 23%) b.pt. 80°C[0.01mmHg] m.pt. 40.2-41.5°C[from light petroleum(b.pt.40-60°C)] (Found : C, 59.57 H, 3.50 % M^+302; $C_{15}H_{11}F_5O$ requires C, 59.61 H, 3.67%, M^+302); $\delta_H(CDCl_3)$ 3.43(s, OCH_3), 4.09(s, $C_6F_5C\underline{H_2}C_6H_4$), 4.50(s, $C\underline{H_2}O$) and 7.38ppm(m, $-C_6H_4-$).

ii.Preparation of *p*-(2,3,4,5,6-pentafluorobenzyl)benzyl bromide [148].

p-(2,3,4,5,6-Pentafluorobenzyl)benzyl methyl ether [147] (0.10g, 0.331mmol.) was treated with HBr in glacial acetic acid (2ml, 45%w/v) and stirred at room temperature for 0.5h. The excess acid was removed in vacuo to give *p-(2,3,4,5,6-pentafluorobenzyl)benzyl bromide [148]* (0.122g), recrystallised from light petroleum (b.pt. 40-60°C)(0.10g, 86%)m.pt. 81.5-82.0°C(Found: C, 47.59 H, 2.24 % ; $C_{14}H_8BrF_5$ requires C, 47.89 H, 2.30%); $\delta_H(CDCl_3)$ 4.17(s, $C_6F_5C\underline{H_2}C_6H_4$-), 4.63(s, CH_2Br), 7.50 and 7.61ppm(AB, $-C_6H_4-$).

iii..Reaction of *p*-(2,3,4,5,6-pentafluorobenzyl)benzyl bromide [148] with tetrahydrothiophene

p-(2,3,4,5,6-Pentafluorobenzyl)benzyl bromide [148] (0.362g, 1.03mmol.) in methanol (7ml) was treated with tetrahydrothiophene (0.75ml, 8.5mmol.) and stirred at 50°C for 18h. The solution was concentrated in vacuo and a white solid precipitated by trituration with dry acetone. The solid was washed by decantation with dry acetone and dried in vacuo to leave *p-(2,3,4,5,6-pentafluorobenzyl)benzyltetrahydrothiophenium bromide [142A]* (0.402g, 89%) (Found: C, 48.88 H, 3.90% ; $C_{18}H_{16}BrF_5S$ requires C, 49.21 H, 3.67%); $\delta_H(CDCl_3)$ 1.86(m, $C\underline{H_2}CH_2S^+$), 2.78(m, $CH_2C\underline{H_2}S^+$), 3.94(s, $C_6F_5C\underline{H_2}C_6H_4$), 4.38(s, CH_2S^+), 7.12 and 7.25ppm(AB, $-C_6H_4-$).

6.5.4.Reaction of *p*-(2,3,4,5,6,-pentafluorobenzyl)benzyltetrahydro thiophenium bromide [142A] with *n*-butyl lithium

p-(2,3,4,5,6,-Pentafluorobenzyl)benzyltetrahydrothiophenium bromide [142A] (0.20g, 0.45 mmol.) in dry tetrahydrofuran (10ml) was cooled to -70°C and treated with *n*-butyllithium in hexane (0.30ml, 1.63M). The orange suspension was warmed to room temperature during which time the colour became more yellow. After stirring at room temperature overnight a clear, heterogeneous solution was obtained which was heated

under reflux for a further 24h. The solution was concentrated by rotary evaporation and added to water, which was extracted with dichloromethane, the extracts dried ($MgSO_4$) and concentrated by rotary evaporation to leave crude product (0.155g).

$\delta_H(C_7D_8)$ 1.90(m), 3.26(s), 3.73(s), 4.14(s) and 6.78ppm(m)

$\delta_F(C_7D_8)$ 164.30, 158.85, 147.25, 146.91, 146.31, 146.21, 145.80 and 145.72ppm.

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Appendix 1

First Year Induction Courses: October 1988

The 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 infrared spectroscopy
4. Chromatography and Microanalysis
5 .Atomic absorption and inorganic analysis
6. Library facilities
7. Mass spectroscopy
8. Nuclear Magnetic Resonance
9. Glass blowing techniques

Research Colloquia, Seminars and Lectures Organised By the Department of Chemistry.

* - Indicates Colloquia attended by the author

During the Period: 1988-1989

ASHMAN, Mr. A. (Durham Chemistry Teacher's Centre) 3rd May 1989
The Chemical Aspects of the National Curriculum

AVEYARD, Dr. R. (University of Hull) 15th March 1989
Surfactants at your Surface

AYLETT, Prof. B.J. (Queen Mary College, London) 16th February 1989
Silicon-Based Chips: - The Chemist's Contribution

* BALDWIN, Prof. J.E. (University of Oxford) 9th February 1989
Recent Advances in the Bioorganic Chemistry of Penicillin Biosynthesis

* BALDWIN & WALKER, Drs. R.R. & R.W. (Hull Univ.) 24thNovember 1988
Combustion: Some Burning Problems

BOLLEN, Mr. F. (Durham Chemistry Teacher's Centre) 18th October 1988
Lecture about the use of SATIS in the classroom

* BUTLER, Dr. A.R. (St. Andrews University) 15th February 1989
Cancer in Linxiam: The Chemical Dimension

* CADOGAN, Prof. J.I.G. (British Petroleum) 10th November 1988
From Pure Science to Profit

CASEY, Dr. M. (University of Salford) 20th April 1989
Sulphoxides in Stereoselective Synthesis

WATERS & CRESSEY, Mr. D. & T. (Durham Chemistry Teacher's Centre) 1st February 1989
GCSE Chemistry 1988: "A Coroners Report"

CRICH, Dr. D. (University College London) 27th April 1989
Some Novel Uses of Free Radicals in Organic Synthesis

DINGWALL, Dr. J. (Ciba Geigy) 18th October 1988
Phosphorus-containing Amino Acids: Biologically Active Natural and Unnatural Products

ERRINGTON, Dr. R.J. (University of Newcastle) 1st March 1989
Polymetalate Assembly in Organic Solvents

FREY, Dr. J. (Southampton University) 11th May 1989
Spectroscopy of the Reaction Path: Photodissociation Raman Spectra of NOCl

* GRADUATE CHEMISTS, (Polytechs and Universities in North East England) 12th April 1989
Symposium for presentation of papers by postgraduate students

* HALL, Prof. L.D. (Addenbrooke's Hospital Cambridge) 2nd February 1989
NMR - A Window to the Human Body

HARDGROVE, Dr. G. (St. Olaf College U.S.A.) December 1988
Polymers in the Physical Chemistry Laboratory

HARWOOD, Dr. L.(Oxford University) 25th January 1988
Synthetic Approaches to Phorbols Via Intramolecular Furan Diels-Alder Reactions: Chemistry under Pressure

JAGER, Dr. C. (Friedrich-Schiller University GDR) 9th December 1988
NMR Investigations of Fast Ion Conductors of the NASICON Type

* JENNINGS, Prof. R.R. (Warwick University) 26th January 1989
Chemistry of the Masses

JOHNSON, Dr. B.F.G. (Cambridge University) 23rd February 1989
The Binary Carbonyls

JONES, Dr. M.E. (Durham Chemistry Teacher's Centre) 14th June 1989
Discussion Session on the National Curriculum

JONES, Dr. M.E. (Durham Chemistry Teacher's Centre) 28th June 1989
GCSE and A Level Chemistry 1989

* LUDMAN, Dr. C.J. (Durham University) 18th October 1988
The Energetics of Explosives

MACDOUGALL, Dr. G. (Edingburgh University) 22nd February 1989
Vibrational Spectroscopy of Model Catalytic Systems

MARKO, Dr. I. (Sheffield University) 9th March 1989
Catalytic Asymmetric Osmylation of Olefins

McLAUCHLAN, Dr. K.A. (University of Oxford) 16th November 1988
The Effect of Magnetic Fields on Chemical Reactions

* MOODY, Dr. C.J. (Imperial College) 17th May 1989
Reactive Intermediates in Heterocyclic Synthesis

MORTIMER, Dr. C. (Durham Chemistry Teacher's Centre) 14th December 1988
The Hindenberg Disaster - an Excuse for Some Experiments

NICHOLLS, Dr. D. (Durham Chemistry Teacher's Centre) 11th July 1989
Demo. "Liquid Air"

PAETZOLD, Prof. P. (Aachen) 23rd May 1989
Iminoboranes XB=NR: Inorganic Acetylenes

PAGE, Dr. P.C.B. (University of Liverpool) 3rd May 1989
Stereocontrol of Organic Reactions Using 1,3-dithiane-1-oxides

POLA, Prof. J. (Czechoslovak Academy of Science) 15th June 1989
Carbon Dioxide Laser Induced Chemical Reactions
New Pathwats in Gas-Phase Chemistry

* REES, Prof. C.W. (Imperial College London) 27th October 1988
Some Very Heterocyclic Compounds

REVELL, Mr. P. (Durham Chemistry Teacher's Centre) 14th March 1989
Implementing Broad and Balanced Science 11-16

SCHMUTZLER, Prof. R. (Techn. Univ. Braunschweig) 6th October 1988
Fluorophosphines Revisited - New Contributions to an Old Theme

SCHROCK, Prof. R.R. (M.I.T.) 13th February 1989
Recent Advances in Living Metathesis

* SINGH, Dr. G. (Teesside Polytechnic) 9th November 1988
Towards Third Generation Anti-Leukaemics

* SNAITH, Dr. R. (Cambridge University) 1st December 1988
Egyptian Mummies: What, Where, Why and How

STIBR, Dr. R. (Czechoslovak Academy of Sciences) 16th May 1989
Recent Developments in the Chemistry of Intermediate-Sited Carboranes

VON RAGUE SCHLEYER, Prof. P. (Univ. Erlangen) 21st October 1988
The Fruitful Interplay Between Calculational and Experimental Chemistry

WELLS, Prof. P.B. (Hull University) 10th May 1989
Catalyst Characterisation and Reactivity

During the Period 1989-1990

ASHMAN, Mr.A. (Durham Chemistry Teachers' Centre) 11th October,1989
The National Curriculum - an update

BADYAL, Dr J.P.S. (Durham University) 1st November 1989
Breakthroughs in Heterogeneous Catalysis

*BECHER, Dr.J. (Odense University) 13th November 1989
Synthesis of New Macrocyclic Systems using Heterocyclic Building Blocks

BERCAW, Prof. J.E. (California Institute of Technology) 10th November 1989
Synthetic and Mechanistic Approaches to Zieger-Natta Polymerisation of Olefins

*BLEASDALE, Dr. C. (Newcastle University) 21st February 1990
The Mode of Action of some anti-tumour Agents

BOLLEN, Mr.F. (Former Science Advisor, Newcastle LEA) 27th March 1990
Whats New in Satis, 16-19

BOWMAN, Prof. J.M. (Emory University) 23rd March 1990
Fitting Experiment with Theory in Ar-OH

* BUTLER, Dr. A. (St. Andrews University) 7th December 1989
The Discovery of Penicillin: Facts and Fancies

CAMPBELL, Mr. W.A. (Durham Chemistry Teachers Centre) 12th September 1989
Industrial Catalysis- some ideas for the National Curriculum

CHADWICK, Dr. P. (Dept. Physics, Durham University) 24th January 1990.
Recent Theories of the Universe (with reference to National Curriculum Attainment Target 16)

CHEETHAM, Dr.A.K. (Oxford University) 8th March 1990
Chemistry of Zeolite Cages

CLARK, Prof. D.T. (ICI Wilton) 22nd February 1990
Spatially Resolved Chemistry (using Nature's Paradigm in the Advanced Materials Arena)

COLE-HAMILTON, Prof. D.J. (St. Andrews University) 29th November 1989
New Polymers from Homogeneous Catalysis

* CROMBIE, Prof. L. (Nottingham University) 15th February 1990
The Chemistry of Cannabis and Khat

DYER, Dr. U. (Glaxo) 31st January 1990
Synthesis and Conformation of C-Glycosides

FLORIANI, Prof. C. (Lausanne Univ., Switzerland) 25th October 1989
Molecular Aggregates- A Bridge Between Homogeneous and Heterogeneous Systems

*GERMAN, Prof. L.S. (USSR Academy of Sciences) 9th July 1990
New Syntheses in Fluoroaliphatic Chemistry: Recent Advances in the Chemistry of Fluorinated Oxiranes

GRAHAM, Dr.D. (B.P. Research Centre) 4th December 1989
How Proteins Absorb to Interfaces

GREENWOOD, Prof. N.N. (University of Leeds) 9th November 1989
Novel Cluster Geometries in Metalloborane Chemistry

HOLLOWAY, Prof. J.H. (University of Leicester) 1st February 1990
Noble Gas Chemistry

HUGHES, Dr.M.N. (King's College, London) 30th November 1989
A Bug's Eye View of the Periodic Table

HUISGEN, Prof. R. (Universität München) — 15th December 1989
Recent Mechanistic Studies of [2+2] Additions

IDDON, Dr.B. (University of Salford) — 15th December 1989
Schools' Christmas Lecture-
The Magic of Chemistry

JONES, Dr.M.E. (Durham University Teachers Centre) — 3rd July 1990
The Chemistry A Level 1990

JONES, Dr. M.E. (Durham University Teachers Centre) — 21st November 1989
GCSE and Dual Award Science as a Starting Point for A level Chemistry- How Suitable are They?

JOHNSON, Dr. G.A.L. (Durham University Teachers Centre) — 8th February 1990
Some Aspects of Local Geology in the National Science Curriculum (Attainment Target 9)

KLINOWSKI, Dr.J. (Cambridge University) — 13th December 1989
Solid State NMR Studies of Zeolite Catalysts

* LANCASTER, Rev. R. (Kimbolton Fireworks) — 8th February 1990
Fireworks - Principles and Practice

LUNAZZI, Prof. L. (University of Bologna) — 12th February 1990
Application of Dynamic NMR to the Study of Conformational Enantiomerism

* PALMER, Dr. F. (Nottingham University) — 17th October 1989
Thunder and Lightning

* PARKER, Dr. D. (Durham University) — 16th November 1989
Macrocycles, Drugs and Rock'N'Roll

PERUTZ, Dr. R.N. (York University) — 24th January 1990
Plotting the Course of C-H Activations with Organometallics

* PLATONOV, Prof. V.E. (USSR Academy of Sciences) 9th July 1990
Polyfluoroindanes: Synthesis and Transformation

* POWELL, Dr.R.L. (I.C.I.) 6th December 1989
The Development of CFC Replacements

POWIS, Dr. I. (Nottingham University) 21st March 1990
Spinning off in a Huff: Photodissociation of Methyl Iodide

RICHARDS, Mr. C. (Health and Safety Exec., Newcastle) 28th February 1990
Safety in School Science Laboratories and COSHH

* ROZHKOV, Prof. I.N. (USSR Academy of Sciences, Moscow) 9th July 1990
Reactivity of Perfluoroalkyl Bromides

* STODDART, Dr.J.F. (Sheffield University) 1st March 1990
Molecular Lego

SUTTON, Prof. D. (Simon Fraser Univ., Vancouver) 14th February 1990
Synthesis and Applications of Dinitrogen and Diazo Compounds of Rhenium and Iridium

THOMAS, Dr.R.K. (Oxford University) 28th February 1990
Neutron Reflectometry from Surfaces

THOMPSON, Dr. D.P. (Newcastle University) 7th February 1990
The Role of Nitrogen in Extending Silicate Crystal Chemistry

During the Period 1989-1990

ALDER, Dr. B.J. (Lawrence Livermore Labs., California) 15th January 1991
Hydrogen in all its Glory

* BELL, Prof. T. (SUNY, Stoney Brok, U.S.A.) 14th November 1990
Functional Molecular Architecture and Molecular Recognition

* BOCHMANN, Dr. M. (University of East Anglia) — 24th October 1990
Synthesis, Reactions and Catalytic Activity of Cationic Titanium Alkyls

BRIMBLE, Dr. M.A. (Massey University, New Zealand) — 29th July 1991
Synthetic Studies Towards the Antibiotic Griseusin-A

* BROOKHART, Prof. M.S. (University of N. Carolina) — 20th June 1991
Olefin Polymerizations, Oligomerizations and Dimerizations using Electrophilic Late Transition Metal Catalysts

BROWN, Dr. J. (Oxford University) — 28th February 1991
Can Chemistry provide Catalysts Superior to Enzymes

BUSHBY, Dr. R. (Leeds University) — 6th February 1991
Biradicals and Organic Magnets

* COWLEY, Prof. A.H. (University of Texas) — 13th December 1990
New Organometallic Routes to El;ectronic Materials

CROUT, Prof D. (Warwick University) — 29th November 1990
Enzymes in Organic Synthesis

DOBSON, Dr. C.M. (Oxford University) — 6th March 1991
NMR Studies of Dynamics in Molecular Crystals

GERRARD, Dr. D. (British Petroleum) — 7th November 1990
Raman Spectroscopy for Industrial Analysis

HUDLICKY, Prof. T. (Virginia Polytechnic Institute) — 25th April 1991
Biocatalysis and Symmetry Based Approaches to the Efficient Synthesis of Complex Natural Products

* JACKSON, Dr. R. (Newcastle University) — 31st October 1990
New Synthetic Methods: α-Amino Acids and Small Rings

KOCOVSKY, Dr. P. (Uppsala University) 6th November 1990
Stereo-Controlled Reactions Mediated by Transition and Non-Transition Metals

LACEY, Dr. D. (Hull University) 31st January 1991
Liquid Crystals

* LOGAN, Dr. N. (Nottingham University) 1st November 1990
Rocket Propellants

* MACDONALD, Dr. W. A. (I.C.I. Wilton) 11th October 1990
Materials for the Space Age

* MARKHAM, Dr. R. (ICI Pharmaceuticals) 7th March 1991
DNA Fingerprinting

PETTY, Dr. M. C. (Durham University) 14th February 1991
Molecular Electronics

PRINGLE, Dr. P. G. (Bristol University) 5th December 1990
Metal Complexes with Functionalised Phosphines

PRITCHARD, Prof. J. (Queen Mary College, London) 21st November 1990
Copper Surfaces and Catalysts

SADLER, Dr. P. J. (Birbeck College, London) 24th January 1991
Design of Inorganic Drugs : Precious Metals, Hypertension + HIV

SARRE, Dr. P. (Nottingham University) 17th January 1991
Comet Chemistry

SCHROCK, Prof. R. R. (M.I.T.) 24th April 1991
Metal Ligand Multiple Bonds and Metathesis Initiators

SCOTT, Dr. S. K. (Leeds University) 8th November 1990
Clocks, Oscillators and Chaos

SHAW, Prof. B. L. (Leeds University) — 20th February 1991
Syntheses with Coordinated, Unsaturated Phosphine Ligands

* SINN, Prof. E. (Hull University) — 30th January 1991
Coupling of Little Electrons in Big Molecules. Implications for the Active Sites of (Metalloproteins and other) Macromolecules

* SOULEN, Prof. R. (South Western University, Texas) — 26th October 1990
Preparation and Reactions of Bicyloalkenes

WHITTAKER, Dr. B. J. (Leeds University) — 28th November 1990
Two-Dimensional Velocity Imaging of State-Selected Reaction Products

Appendix 2 : Infrared spectra

(liq = liquid film; KBr = KBr disc; nuj = nujol mull; thin film = film of polymer from a polymer solution)

1. *p*-Bromobenzyl ethyl sulphide [58] (*liq*)
2. *p*-Allylbenzyl ethyl sulphide [57] (*liq*)
3. *p*-Allylbenzyl methyl ether [60] (*liq*)
4. *p*-Allylbenzylbromide [61] (*liq*)
5. *p*-Allylbenzyl alcohol (*liq*)
6. Product of reaction of *p*-allylbenzyltetrahydrothiophenium bromide with sodium hydroxide (*liq*)
7. E,E-[6,2]-Paracyclophan-1,5-diene [75] (*KBr*)
8. α-(*p*-Tolyl)allyl alcohol [63] (*liq*)
9. *p*-Methylcinnamyl bromide [65] (*nuj*)
10. Polymeric material from thermal reaction of *p*-methylcinnamyltrimethyl ammonium hydroxide (*thin film*)
11. Z,Z-[6,2]-Paracyclophan-1,5-diene [79] (*KBr*)
12. 1-Phenyl-2,2,2-trichloroethanol (*liq*)
13. 1,1,1-Trichloro-2-(4-bromophenyl)-2-phenylethane (*nuj*)
14. *p*-Benzylbromobenzene [95] (*liq*)
15. *p*-Benzylbenzyl alcohol [94] (*nuj*)
16. *p*-Benzylbenzyl bromide [93] (*liq*)
17. Polymeric material, poly(α-phenyl-*p*-xylylene), from thermal reaction of *p*-benzylbenzyltrimethylammonium hydroxide (*thin film*)
18. Tri(α-phenyl-*p*-xylylene)[103] (*KBr*)
19. Tri(α-phenyl-*p*-xylylene)[104] (*KBr*)
20. *p*-Methylbenzhydryl chloride [97a] (*liq*)
21. Di(*p*-methylbenzhydryl) ether [98] (*liq*)
22. *p*-Methylbenzhydryl bromide [97b] (*liq*)
23. 1,2-Di(*p*-tolyl)-1,2-diphenylmethane [102] (*KBr*)

24. Polymeric material, poly(α-phenyl-*p*-xylylene), from thermal reaction of *p*-methylbenzhydryltrimethylammonium hydroxide (*liq*)

25. 2-Benzyl-5-methyl-N,N-dimethylbenzylamine [113] and 2-(4-methylbenzyl)-N,N-dimethylbenzylamine [114] (*liq*)

26. α-[(*p*-Methoxymethyl)phenyl]allyl alcohol [126] (*liq*)

27. *p*-Bromomethylcinnamyl bromide [127] (*KBr*)

28. *p*-Methoxymethylbenzhydryl alcohol [136] (*liq*)

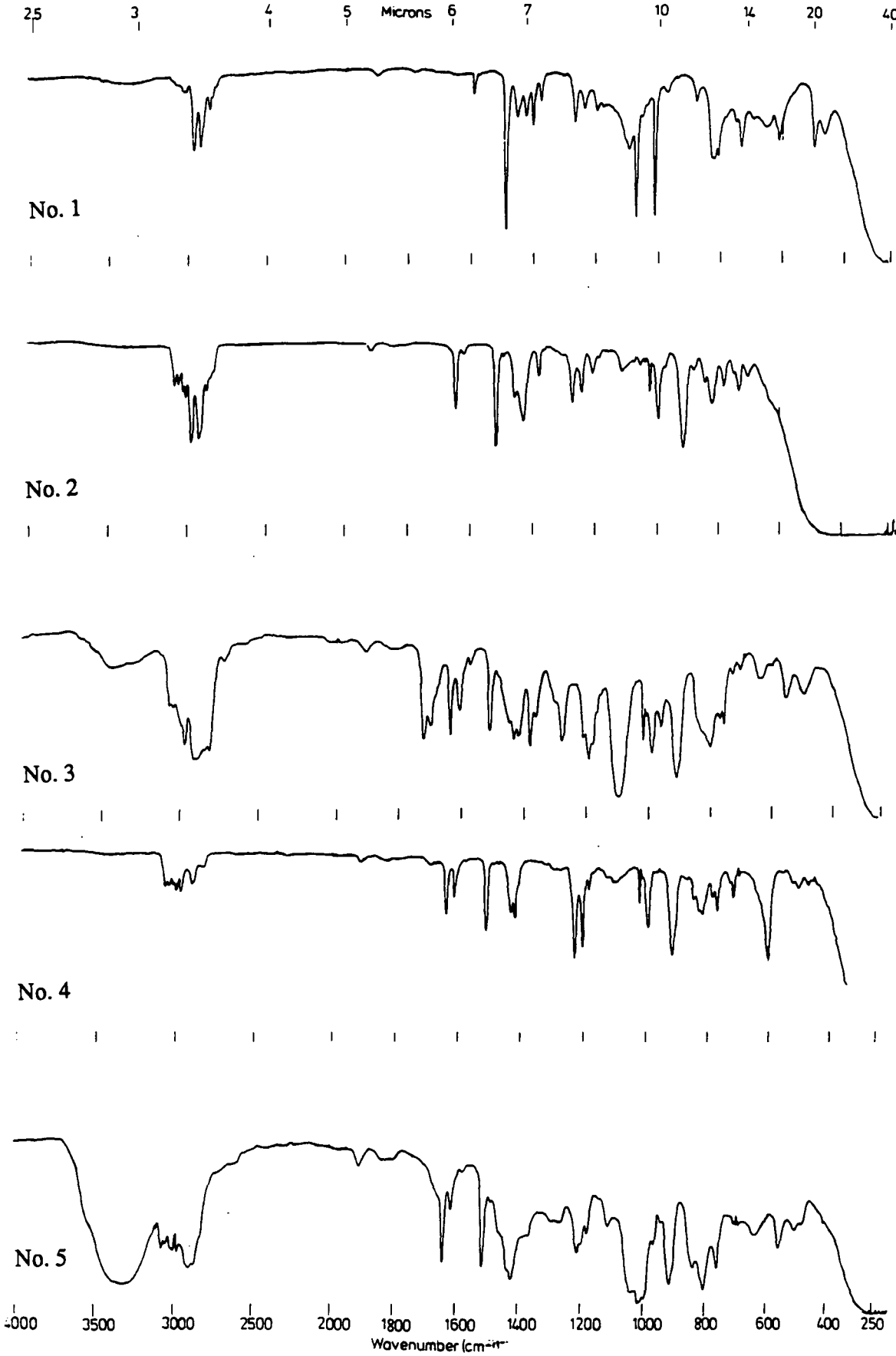
29. *p*-Bromomethylbenzhydryl bromide [137] (*KBr*)

30. 2,3,4,5,6-Pentafluorobenzylpyridinium bromide [138A] (*nuj*)

31. 2,3,4,5,6-Pentafluorobenzylbenzyl methyl ether [147] (*nuj*)

32. 2,3,4,5,6-Pentafluorobenzylbenzyl bromide [148] (*KBr*)

33. Unidentified luminous green product from the thermal reaction of *p*-methyl benzhydryltrimethylammonium hydroxide. (*KBr*)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3
4
5
Microns
6
7
10
14
20
40
No. 1
No. 2
No. 3
No. 4
No. 5
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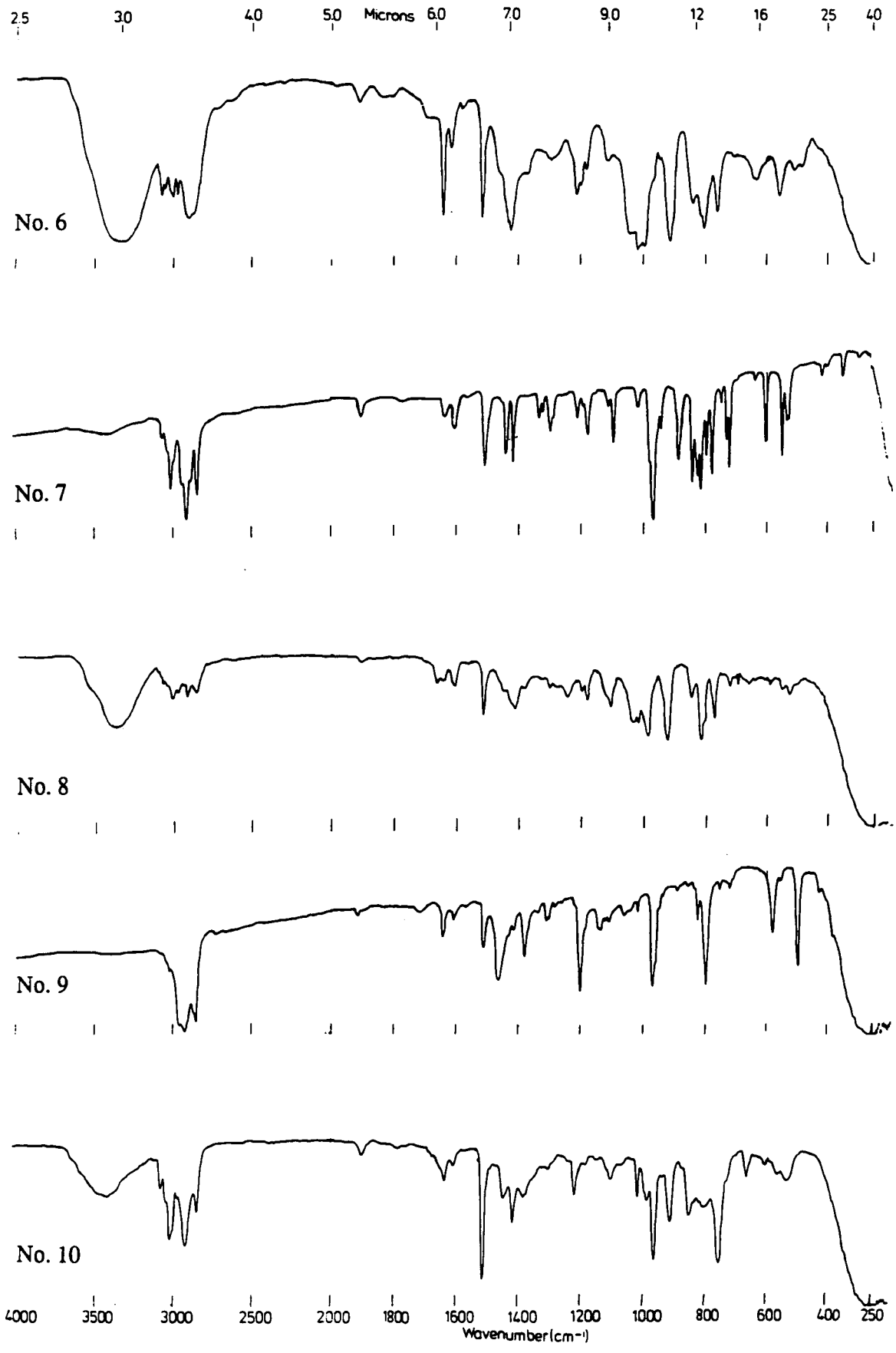
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
400
250
Wavenumber (cm⁻¹)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3.0
4.0
5.0
Microns
6.0
7.0
9.0
12
16
25
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No. 6
No. 7
No. 8
No. 9
No. 10
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3000
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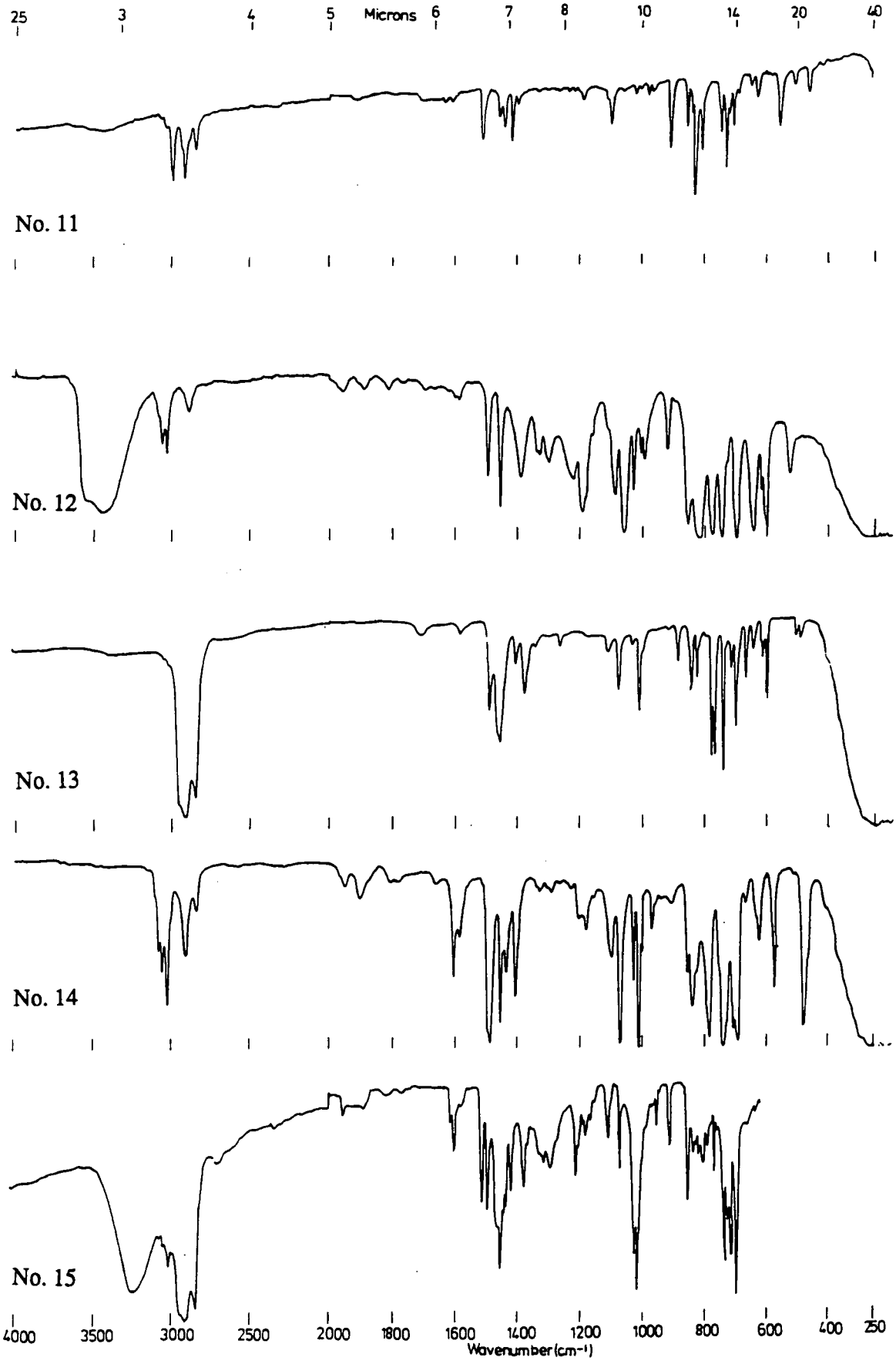
2000
1800
1600
1400
1200
1000
800
600
400
250
Wavenumber (cm⁻¹)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No. 13
No. 14
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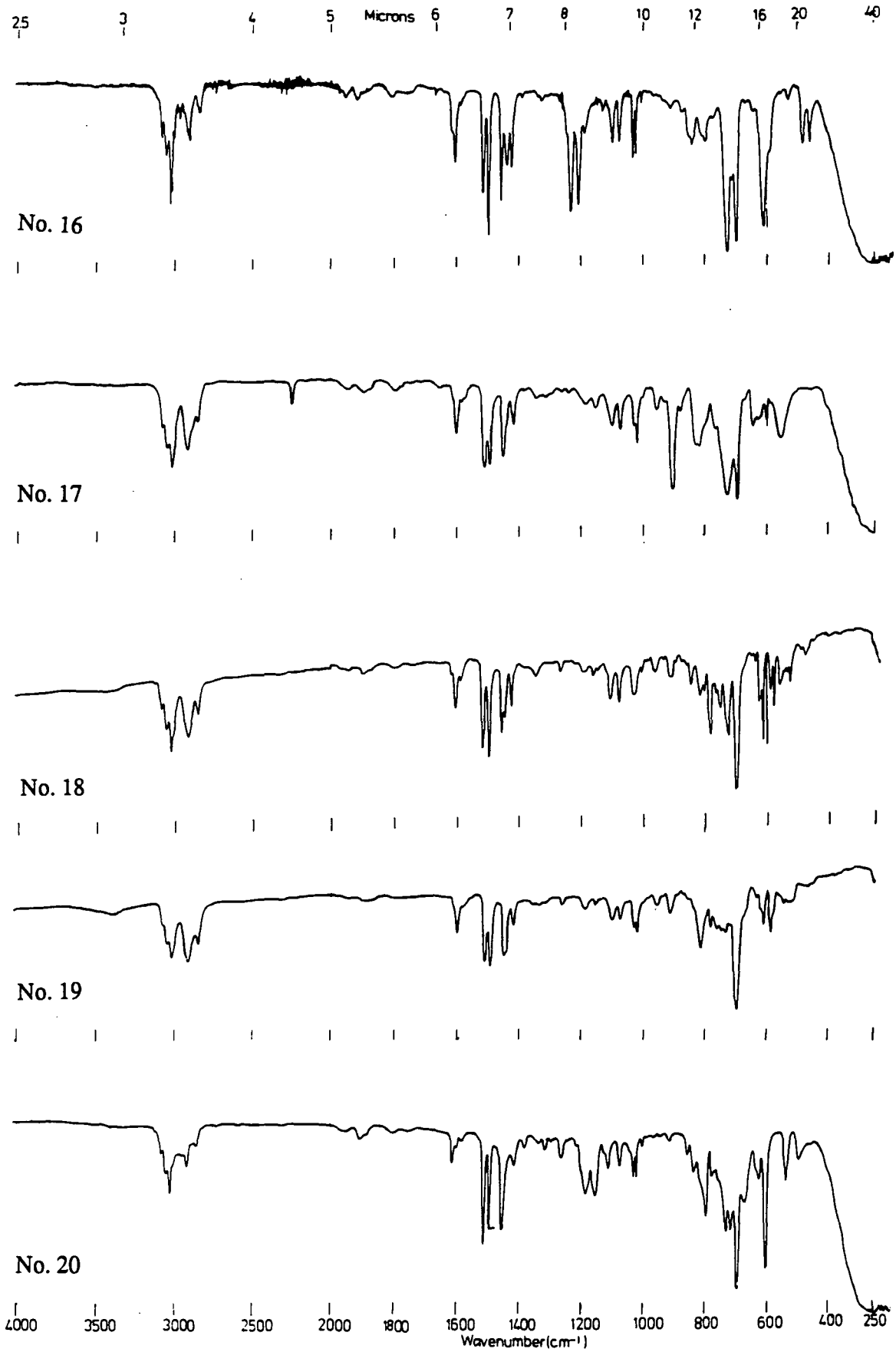
Wavenumber (cm⁻¹)


2.5
3
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Microns
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8
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12
16
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40
No. 16
No. 17
No. 18
No. 19
No. 20
4000
3500
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2000
1800
1600
1400
1200
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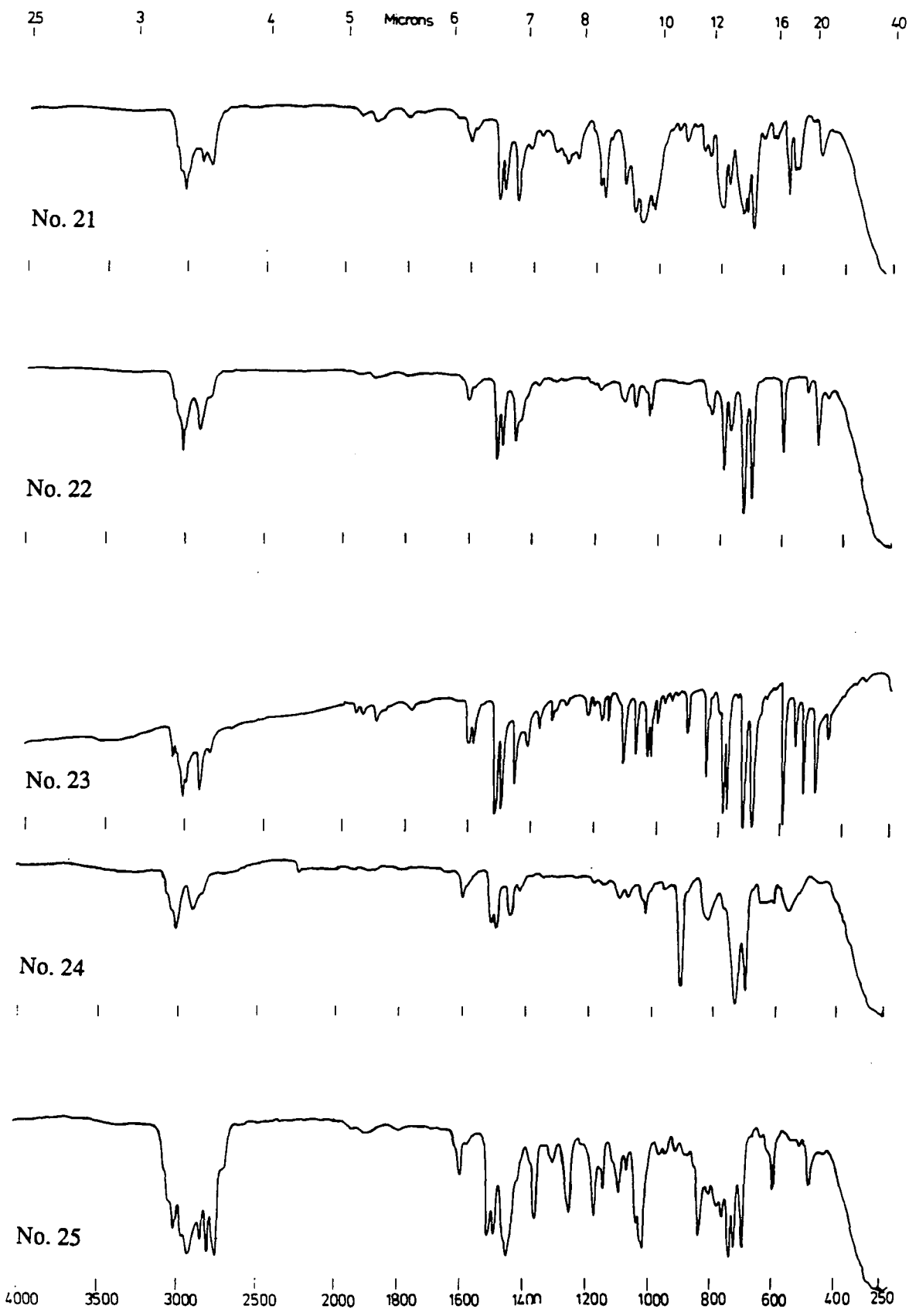
600
400
250
Wavenumber (cm⁻¹)


25
3
4
5
Microns
6
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8
10
12
16
20
40
No. 21
No. 22
No. 23
No. 24
No. 25
4000
3500
3000
2500
2000
1800
1600
1400
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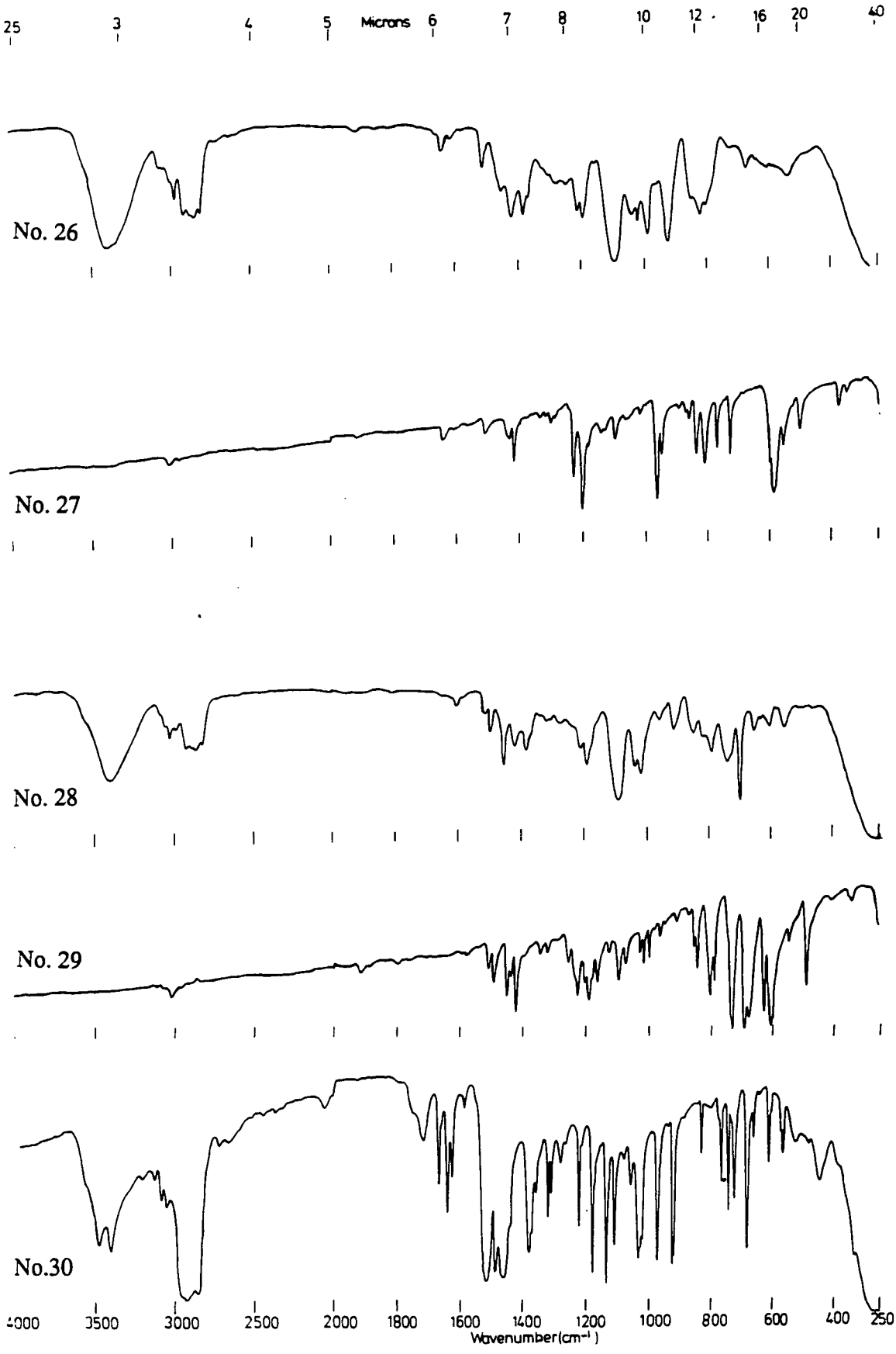
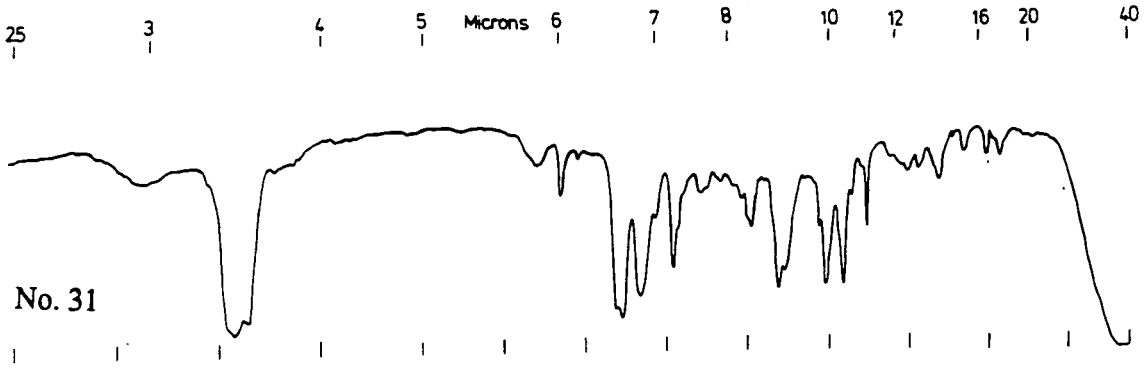
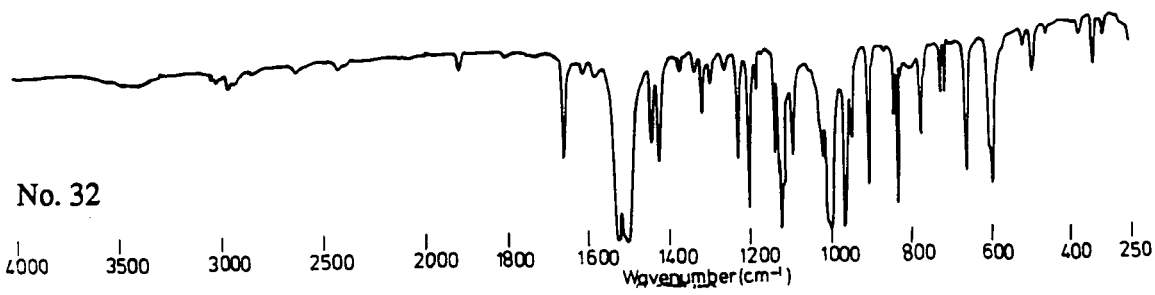
400
250

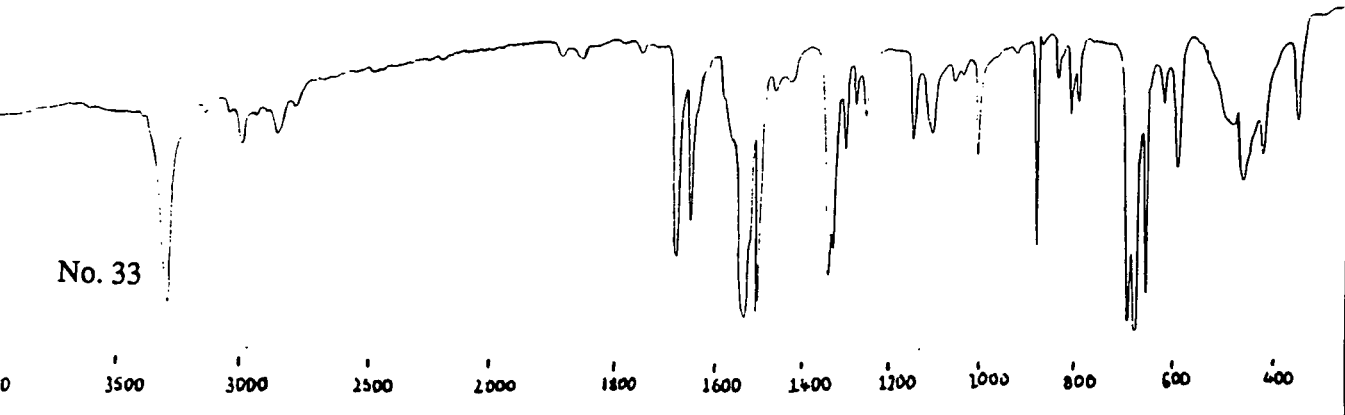

25
3
4
5
Microns
6
7
8
10
12
16
20
40
No. 26
No. 27
No. 28
No. 29
No.30
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
400
250
Wavenumber(cm⁻¹)



No. 31

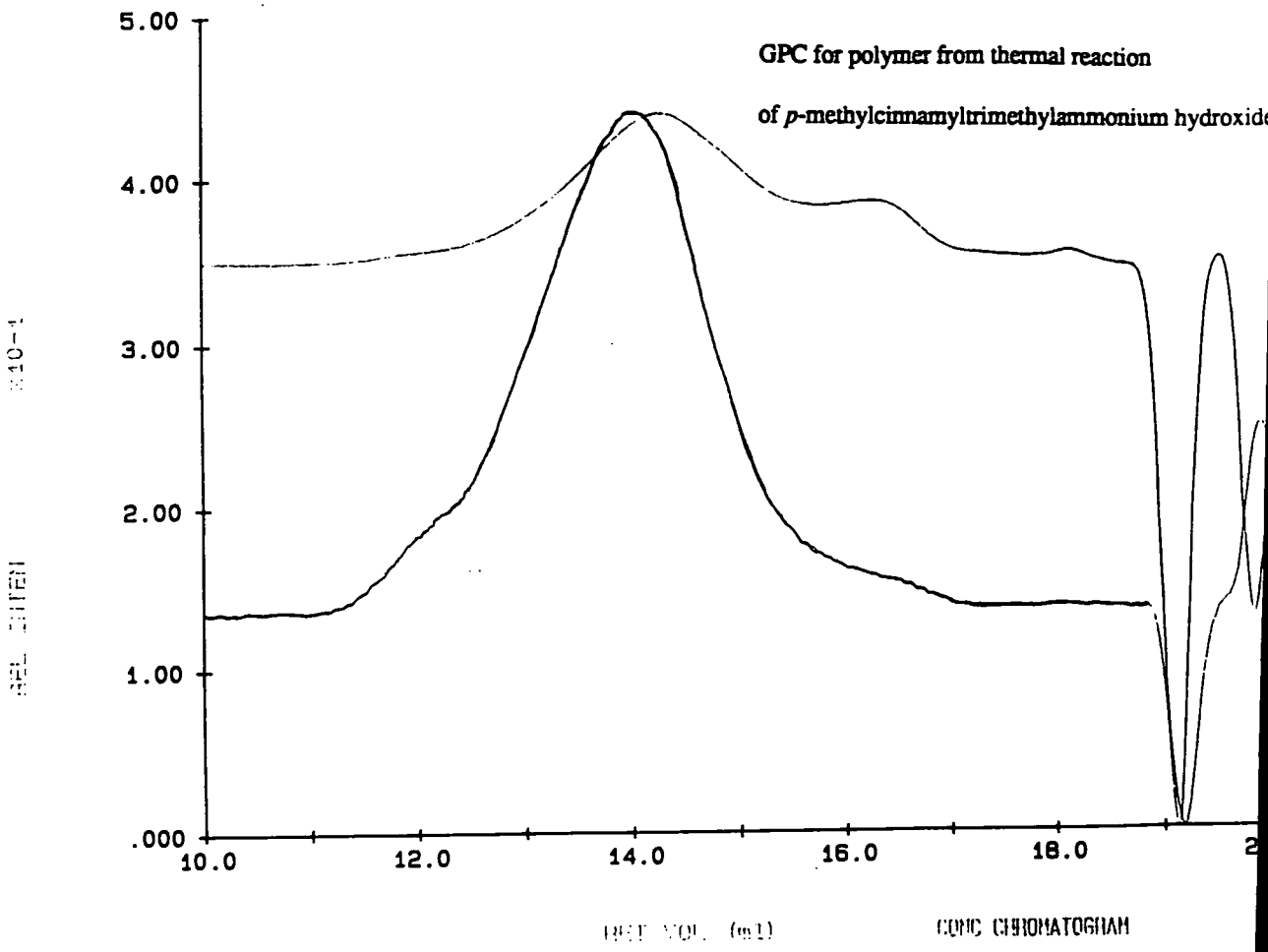


No. 32

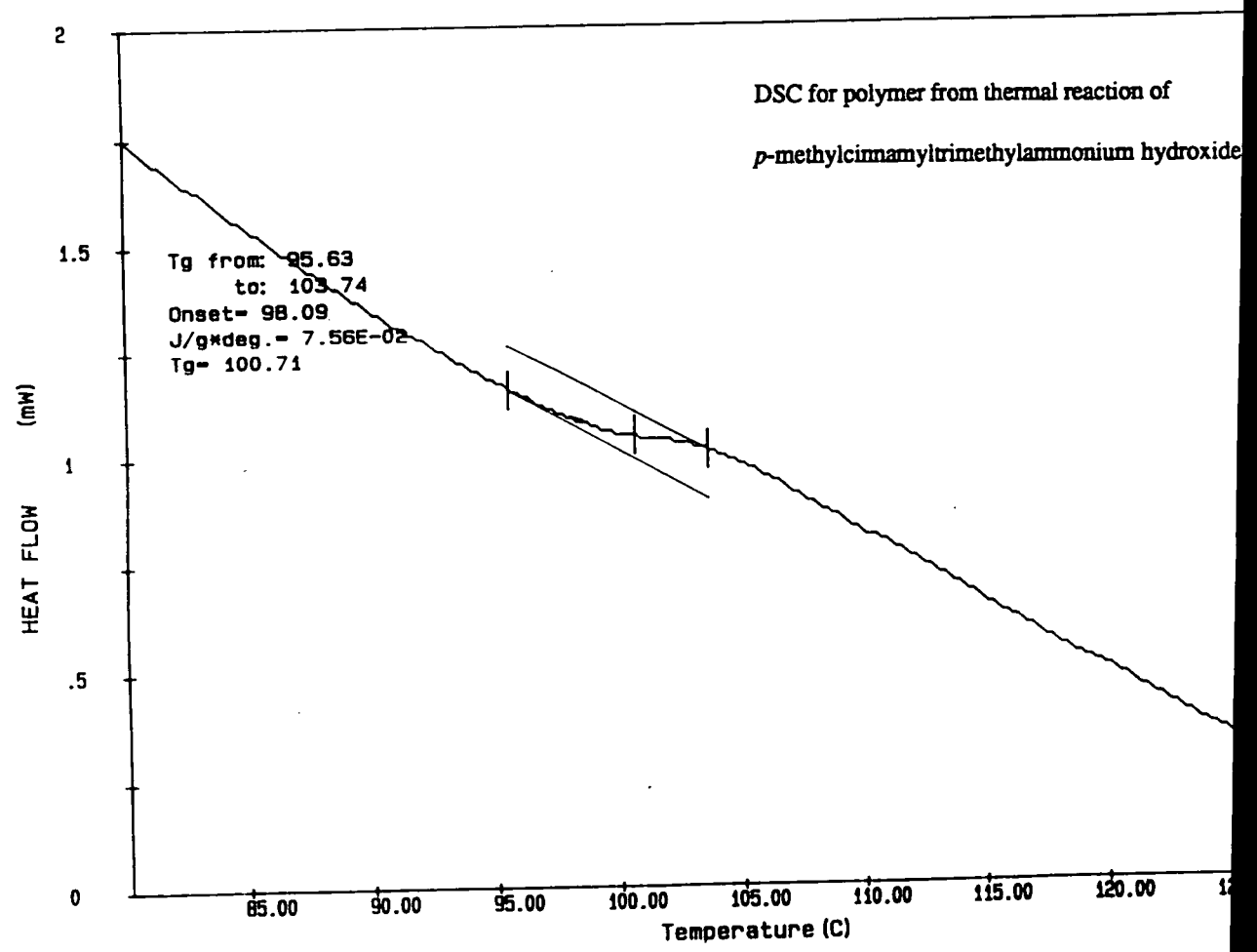


No. 33

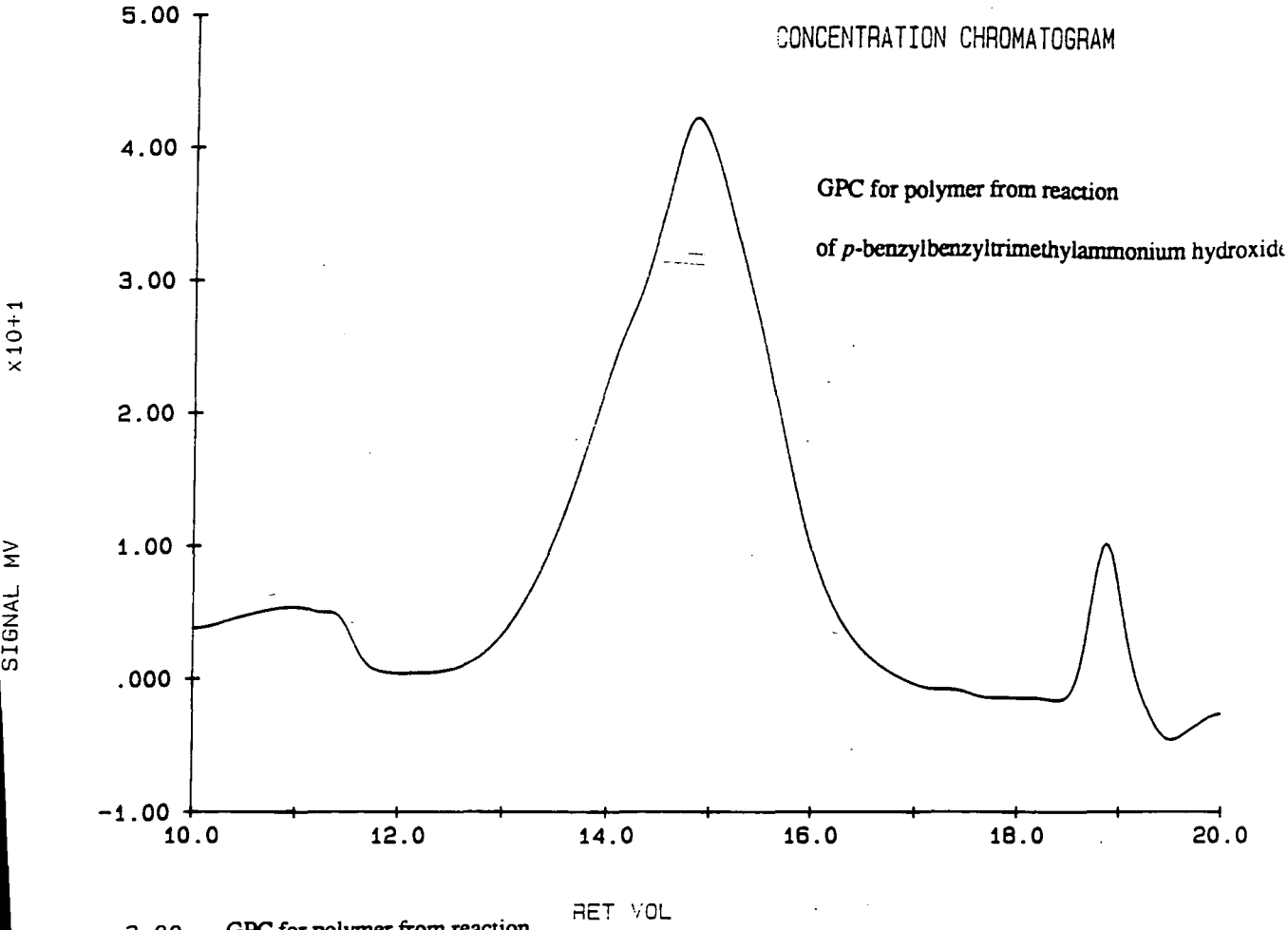
Appendix 3 : GPC and DSC data

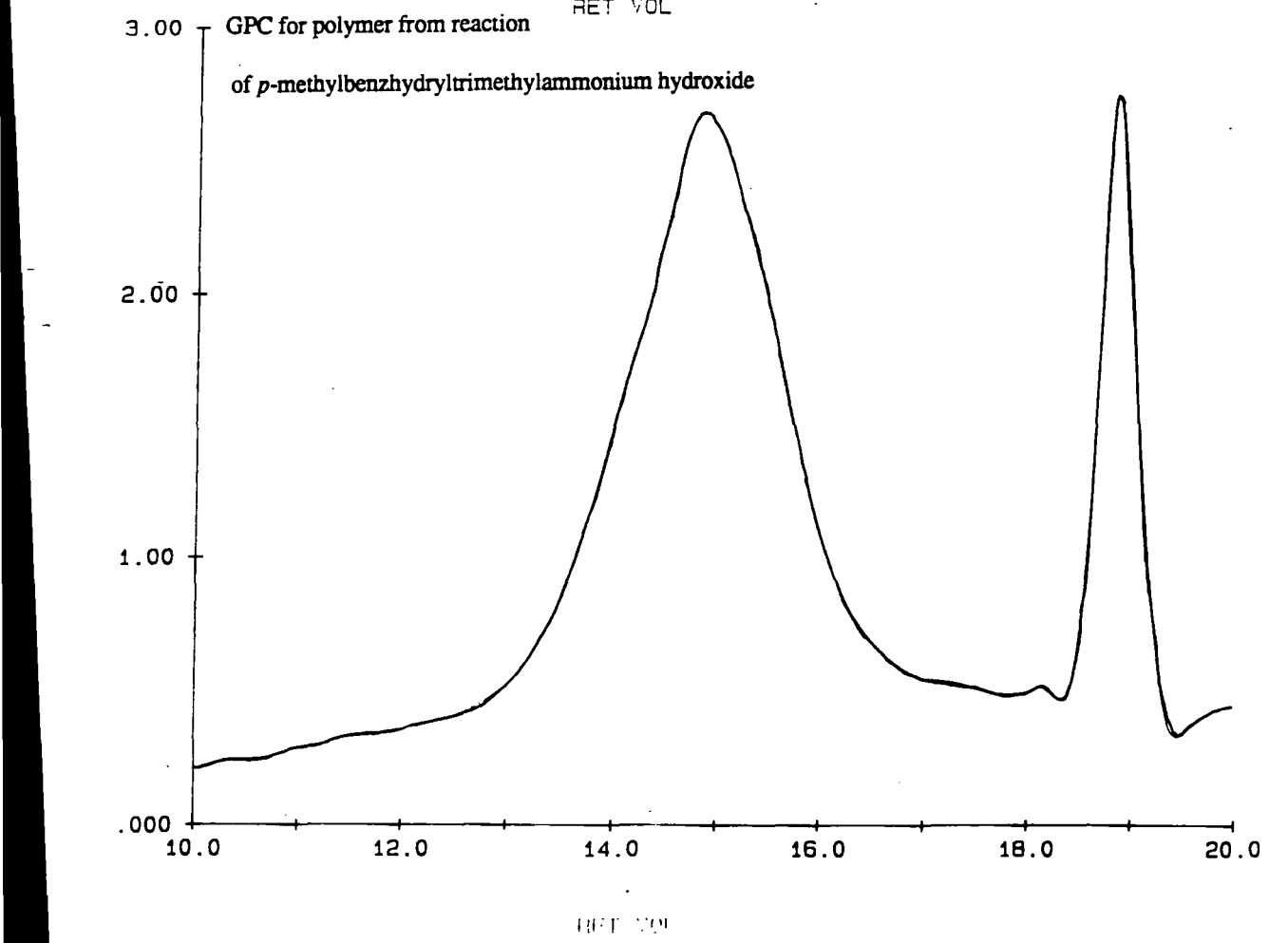


GPC for polymer from thermal reaction of *p*-methylcinnamyltrimethylammonium hydroxide



DSC for polymer from thermal reaction of *p*-methylcinnamyltrimethylammonium hydroxide


CONCENTRATION CHROMATOGRAM
GPC for polymer from reaction
of p-benzylbenzyltrimethylammonium hydroxide
5.00
4.00
3.00
2.00
1.00
.000
-1.00
x10+1
SIGNAL MV
10.0
12.0
14.0
16.0
18.0
20.0
RET VOL


GPC for polymer from reaction
of p-methylbenzhydryltrimethylammonium hydroxide
3.00
2.00
1.00
.000
10.0
12.0
14.0
16.0
18.0
20.0

Appendix 4

^{1}H-^{13}C Heteronuclear correlation spectrum of the cyclic trimer [103]