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POLYMER ORIENTED DERIVATIVE CHEMISTRY OF ICOSAHEDRAL CARBORANES.

By Penelope Louise Herbertson B.Sc.
Graduate Society

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A thesis submitted to the University of Durham in candidature for the Degree of Doctor of Philosophy.

September 1995

17 JAN 1996

To Mum and Dad

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DECLARATION

The work described in this thesis was carried out in the University of Durham between October 1992 and September 1995. It has not been submitted, either completely or in part, for any other degree in this or any other University and is the original work of the author except where acknowledged by reference.

Polymer Oriented Derivative Chemistry of Icosahedral Carboranes.

ABSTRACT

Penelope Louise Herbertson B.Sc.

This thesis describes work conducted to incorporate icosahedral carborane units into the backbone of polymers containing para disubstituted benzene rings linked either directly or through ether and ketone functional groups.

It begins with a brief survey of relevant carborane and polymer literature and then describes the synthesis of a range of aryl-substituted carborane derivatives via their copper(I) intermediates. The synthesis and model reactions of a series of diaryl carboranes $RR'C_2B_{10}H_{10}$ (in which R and R' are suitable for polymer synthesis) are described including many previously unknown carborane derivatives. The structures of two carborane derivatives, 1,3,5-tris-1-(2-phenyl-*ortho*-carboranyl)-benzene and 1,12-bis-(4-methyl-phenyl)-*para*-carborane, have been determined by X-ray crystallography.

Chapter 3 describes investigations made into the deboronation of the icosahedral carborane cages to afford more open *nido*- fragments. Many previously inaccessable compounds have been synthesised and are reported.

Chapters 4 and 5 outline the preparation and characterisation of aromatic polymers incorporating the icosahedral carborane cage, linked either through ether and ketone moieties, or via direct arylene bonds. The mass retention properties of the polymers on thermolysis and their potential for incorporation into ceramic-type materials has been probed by evolved gas analysis experiments and solid state NMR studies.

The final chapter describes the synthesis and characterisation of new classes of membranes derived from some of the carborane-containing polymers obtained during the course of this work.

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Abbreviations and Nomenclature:

Bpy	2,2'-Bipyridine
BNCT	Boron Neutron Capture Therapy
DMAc	Dimethylacetamide
DMS	Dimethylsulphide
DMSO	Dimethylsulphoxide
DSC	Differential Scanning Calorimetry
GPC	Gel Permeation Chromatography
M	Molar
NMP	2-methylpyrrolidinone
PPN^+	Bis(triphenylphosphine)iminium
Py	Pyridine
TBDMS	Tertary Butyl Dimethylsilane
TGA	Thermogravimetric Analysis
THF	Tetrahydrofuran
TFSA	Trifluoromethanesulphonic acid
TLC	Thin Layer Chromatography
TMS	Tetramethylsilane

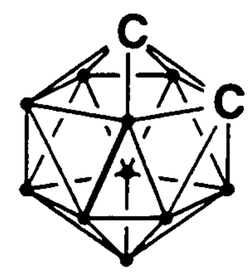
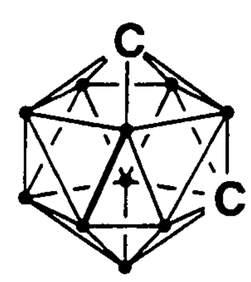
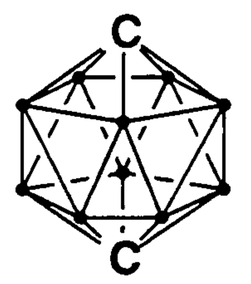
Spectroscopy

IR Infra Red: cm-1 wavenumber; s - strong absorption; m - medium; w - weak; sh. - shoulder.

NMR Nuclear Magnetic Resonance: δ - chemical shift in ppm (parts per million); J - coupling constant (Hertz); s - singlet; d - doublet; t - triplet; m - multiplet.

MS Mass Spectroscopy: EI - electron impact; CI - chemical ionisation; M_r - molecular ion.

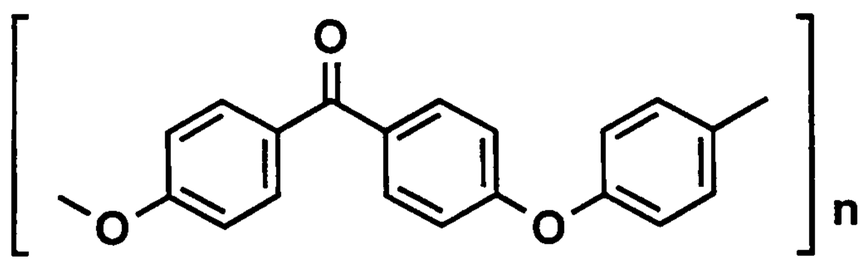
Nomenclature of Carboranes

Full Name	Abreviated Name	Symbols
1,2-dicarba-*closo*-dodecaborane (12)	*ortho*-carborane	
1,7-dicarba-*closo*-dodecaborane (12)	*meta*-carborane	
1,12-dicarba-*closo*-dodecaborane (12)	*para*-carborane	

Carboranes are referred to by their abbreviated names in the text and in most publications. Some Russian literature however uses the term "Barene" to describe the *closo* $C_2B_{10}H_{12}$ cage.

Polymers

Chemical identifiers of polymers are derived from the polymer structure hence PEEK represents poly(oxy-1,4-phenylene-oxy-1,4-phenylene-carbonyl-1,4-phenylene), (poly(etheretherketone)) and for brevities sake all polymers are referred to using abbreviations.



PEEK

Chapter 1

SURVEY OF RELEVANT LITERATURE (BORON CLUSTERS, POLYMERS AND MEMBRANES)

INTRODUCTION:

This chapter briefly reviews the main areas of chemistry covered in the present work. Much of the background is covered only briefly, with more specialised literature being referenced if required by the reader. The main objectives of the work described in this thesis were the preparation and characterisation of derivatives of icosahedral carboranes that were capable of polymerisation reactions, and the study of oligomeric and polymeric compounds prepared therefrom. This chapter is intended to provide background information about carboranes, about polymers already known incorporating carboranes and about organic polymers (not containing carboranes) related to the types of polymers prepared in the present work. Some of the polymers reported have been fabricated into membranes during the course of this work and a brief background to membrane processes is also given.

1.1. General Chemistry of Boranes:

The first boron hydrides were isolated and characterised by Stock and co-workers[1] in the early 1900's. However this original work was performed before instrumentation for detailed structural analysis was available and although these compounds were initially assumed to have hydrocarbon-like structures, it was recognised that as boron has only three valence electrons, species such as B_2H_6, B_5H_9, and $B_{10}H_{14}$ would be "electron-deficient", with more bonding contacts than electron pairs. However, once their structures were determined in Lipscomb's classic research in the fifties, it was recognised that they could be rationalised using 3 centre, 2 electron BHB and BBB bonds as well as 2 centre, 2 electron BH and BB bonds. It was later evident that their three dimensional structures are formally derived from simple triangulated polyhedra and can be divided into three groups reflecting the number of skeletal bonding electron pairs.[2,3]

1) *closo:* (from the Greek meaning "cage-like"), having the general formula $B_nH_n^{2-}$, and based on a closed n-vertex deltrahedron with each vertex occupied by one boron atom. *Closo*-structures involve n+1 skeletal electron pairs delocalised within the cage, and include species such as $B_6H_6^{2-}$ (octahedral) and $B_{12}H_{12}^{2-}$ (icosahedral).

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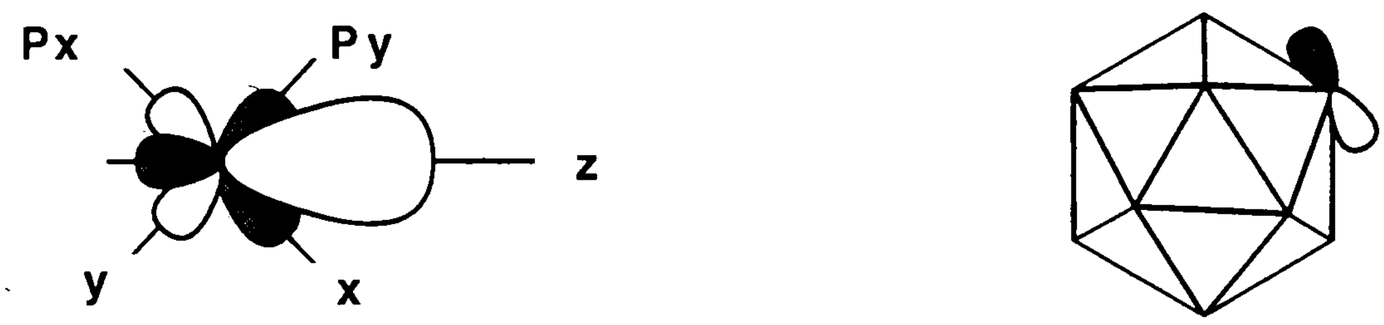
2) *nido:* (from the Latin "nest-like"), having the general formula B_nH_{n+4}, and based on an (n+1) vertex polyhedron with one vertex left vacant. *Nido*-structures involve n+2 skeletal electron pairs, (for example B_5H_9, $B_{10}H_{14}$).

3) *arachno:* (from the Greek meaning "spiders-web"), having the general formula B_nH_{n+6}, with boron atoms occupying n vertices of an (n+2) vertex polyhedron involving n+3 skeletal electron pairs, for example B_4H_{10} and B_5H_{11}.

The skeletal bonding can be understood as follows. Boron has four atomic orbitals available for bonding (2s, $2p_x$, $2p_y$, and $2p_z$), which may hybridise to form two sp-hybrids leaving two p-orbitals. A single sp-hybrid orbital is used to form an exo B-H bond, (a normal two centre/two electron bond from overlap of a hydrogen 1s atomic orbital and a boron sp-hybrid). The remaining sp-orbital points radially towards the centre of the polyhedron. The two p-orbitals available for skeletal bonding lie tangential to the pseudospherical surface of the cluster. Hence each B-H unit provides two electrons and three orbitals to the skeletal cluster bonding.



The z-axis passes through the centre of the cage.

Figure 1.1: *Atomic Orbitals of a Boron or Carbon Atom Involved in Skeletal Bonding*

Carbon is capable of forming two types of mixed hydrides with boron. In the first type, the carbon atom in an organic group is simply attached to a boron cage, via a two centre/two electron bond, thus replacing a B-H bond by a B-C bond.

This thesis is however concerned with a second type of mixed boron-carbon hydride, in which both boron and carbon atoms feature in the "electron-deficient" polyhedral molecular skeleton.

In this type of structure, carbon atoms form an integral part of the delocalised framework, and the present work is focused particularly on the readily accessible and very stable icosahedral $C_2B_{10}H_{12}$ carborane unit.

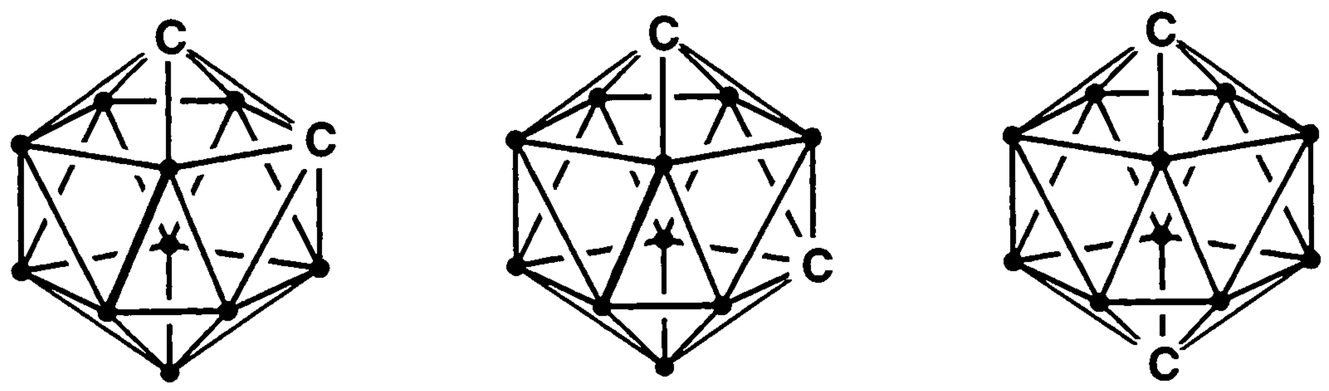
1.2. Carboranes:

Carboranes were first reported in the 1950's[4], in the course of work aimed at the synthesis of higher boron hydrides as potential high energy rocket fuels[5-9]. Their unprecedented polyhedral structures demonstrated the capacity of carbon atoms to bond to as many as six neighbouring atoms simultaneously, forming remarkably stable, chemically robust compounds.

Dicarba-*closo*-dodecaborane ($C_2B_{10}H_{12}$), with 26 skeletal bonding electrons forms an icosahedral structure analogous to $B_{12}H_{12}^{2-}$, in which the skeletal atoms are hexacoordinated. The icosahedral structure of $B_{12}H_{12}^{2-}$ was predicted by Longuet-Higgins and Roberts[10] some years before this anion was first prepared, vindicating the MO arguments they used.

The cage is extremely thermally stable and chemically robust, properties which have been been attributed to its highly delocalised, pseudo-aromatic electronic structure.

There are only three possible isomers of $C_2B_{10}H_{12}$, the 1,2-, 1,7- and 1,12-dicarba-*closo*-dodecaboranes, more commonly known as the *ortho*, *meta* and *para*[11] isomers respectively.



ortho ***meta*** ***para***

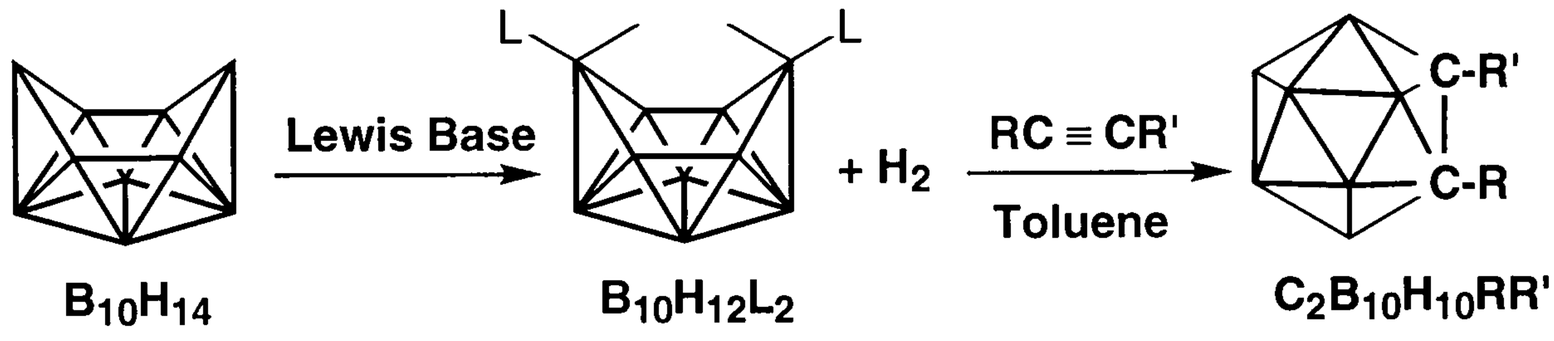
(The *exo* hydrogen atoms, one on each cage atom, are not shown).

Figure 1.2: *The Icosahedral Carboranes*

All three isomers exist as white, sublimable solids, which decrease in melting points from *ortho*- to *meta*- to *para*-carborane, reflecting a corresponding decrease in polarity in the same order.[12-15]

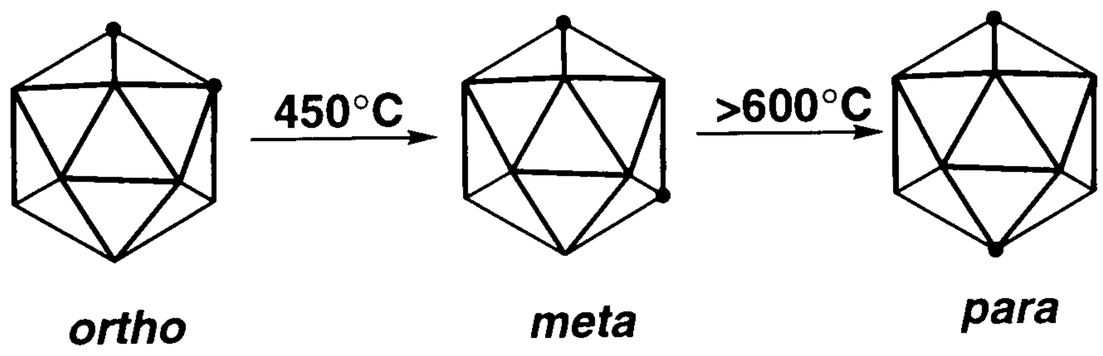
1.3. Synthesis of Icosahedral Carboranes:

Ortho-carborane may be prepared by reaction of acetylene with decaborane in the presence of a Lewis base such as acetonitrile or dimethylsuphide.[13] Decaborane is substituted at the 6 and 9 positions, with loss of H_2, to form the bis-ligand species $B_{10}H_{12}L_2$, which in turn reacts with acetylene to form the *closo*-cage carborane.[16]



The use of substituted acetylenes can lead to the appropriately substituted *ortho*-carboranes,[16-22] although acetylenes containing carboxylic acid or alcoholic functionalities cause degradation of the decaborane cage.[13,16,18,19] This reaction has been used in the present work to synthesise a variety of *ortho*-carborane derivatives and is discussed more fully in chapter 2.

Meta- and *para*-carborane and their derivatives can be prepared by the thermal isomerisation of their ortho isomers. The reaction temperature required depends on the particular substituents and in the case of *meta*-carborane derivatives often exceeds 400°C.[23] Therefore, only very stable, unreactive substituent groups can be used in the preparation. Moreover some groups suppress isomerisation at temperatures below the degradation temperature of the cage.[24]



The *meta*- isomer may also be produced in small amounts (ca. 16%) during the pyrolysis of *nido* CB_5H_9, although this method is not suitable for routine preparation of the compound.[25]

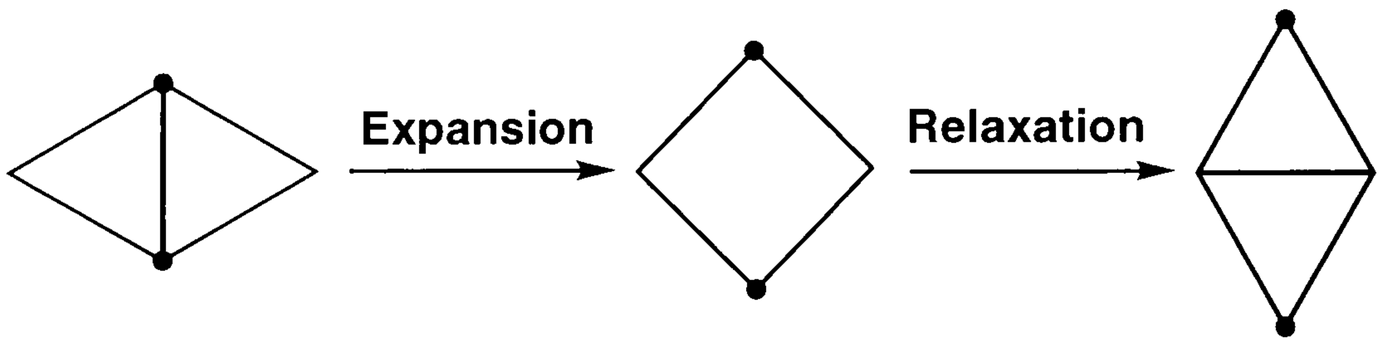
Due to the very high temperatures (ca. 650°C)[26] required to isomerise *meta*-carborane to *para*-carborane, this route is not practical to produce aryl and other derivatives of *para*-carborane, although *para*-carborane itself may be produced, along with considerable cage degradation, by thermal isomerisation of *meta*-carborane.

Both thermal isomerisations may be reversed by the reduction of *meta*- and *para*-carborane to their corresponding dianions $C_2B_{10}H_{12}^{2-}$ using sodium in liquid ammonia. Rearrangement of these dianions and subsequent oxidation regenerates the neutral *ortho* - or *meta*- species respectively.[27-30]

1.4. Isomerisation Mechanism:

Various theories concerning the mechanism for the thermal isomerisation of icosahedral carboranes have been proposed. Lipscomb[31] proposed a diamond-square-diamond rearrangement (dsd), suggesting that the isomerisation from *ortho*- to *meta* -carborane may occur via a cuboctahedral intermediate[32] but this proposal could not explain the formation of the *para* carborane isomer.[33]

This mechanism was later generalised[34] to include a variety of polyhedral species in which certain pairs of adjacent triangular faces open into squares and later rejoin as triangular faces.

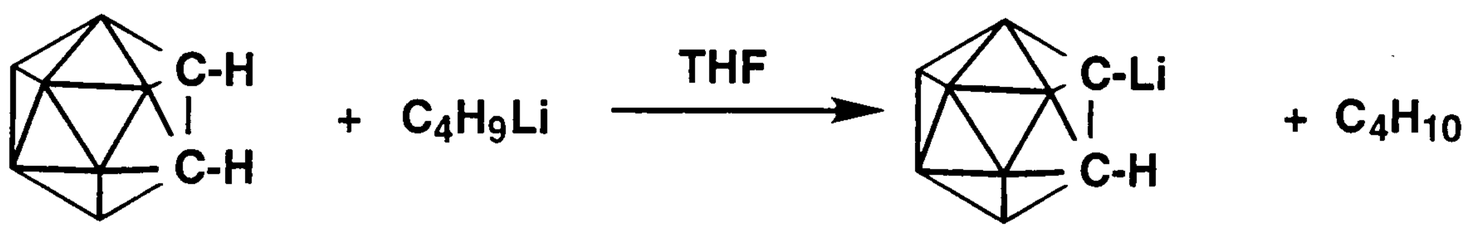


Various other mechanisms have been proposed for the thermal rearrangement of the icosahedral carboranes and the reader is referred to more detailed reviews.[23, 35-38]

1.5. Carborane Derivatives:

Functionality can be introduced at the carbon atoms of carboranes by using substituted acetylenes as previously mentioned. In addition the carborane cage is electron-withdrawing with respect to substituents at its carbon atoms, and therefore hydrogen atoms terminally attached to these carbon atoms are mildly acidic. Hence metallation at these positions using organolithium[39] or Grignard[40] reagents affords versatile precursors to a variety of derivatives and hence an extensive organic chemistry has been developed for the icosahedral carboranes.

For synthetic purposes the C-monolithium and C,C'-dilithium carborane derivatives are widely exploited. C-monolithiated derivatives of *ortho- meta-* and *para*-carborane may be formed[39,40-43] by reacting the carborane with an equivalent amount of butyllithium or phenyllithium in diethylether or THF at room temperature or below.



By using an excess of the organometallic reagent C,C'-dilithiated carboranes are readily obtained.

The rate of the reaction with butyllithium to form the corresponding lithiated carborane decreases in the order $o > m > p$ in agreement with the observed decreasing order of acidity in the C-H hydrogen atoms.[44]

This reaction has its limitations in that it requires the substituent to be unreactive. However, an Ullmann-type coupling reaction utilising carboranyl copper species has been developed and is discussed in more detail in chapter 2.

A varied derivative chemistry at the boron atoms of the cage also exists, and metallation of the boron of all three of the carborane isomers using $Hg(CF_3CO_2)_2$[45] or $Tl(CF_3CO_2)_3$[46] gives metal derivatives that form valuable precursors to a whole range of boron-substituted carboranyl derivatives.

Although the carborane cage is highly resistant to chemical attack, Hawthorne and co-workers[47-49] demonstrated that the unit could be degraded by strong oxidising agents and by bases such as methoxide ion or alkyl amines, with removal of the most electropositive boron atom (- that adjacent to the two carbon atoms in the cage) affording the open nido-cage fragment anion $C_2B_9H_{12}^-$. These anions and their derivatives are highly reactive and are discussed in more detail later (Chapter 3.).

$$C_2B_{10}H_{12} + 2\,CH_3O^- + 2\,CH_3OH \longrightarrow H_2 + B(OCH_3)_4^- + C_2B_9H_{12}$$

A huge derivative chemistry of the metallocene-like *nido* carboranyl fragments has since been developed and is discussed in more detail in various reviews.[50-52]

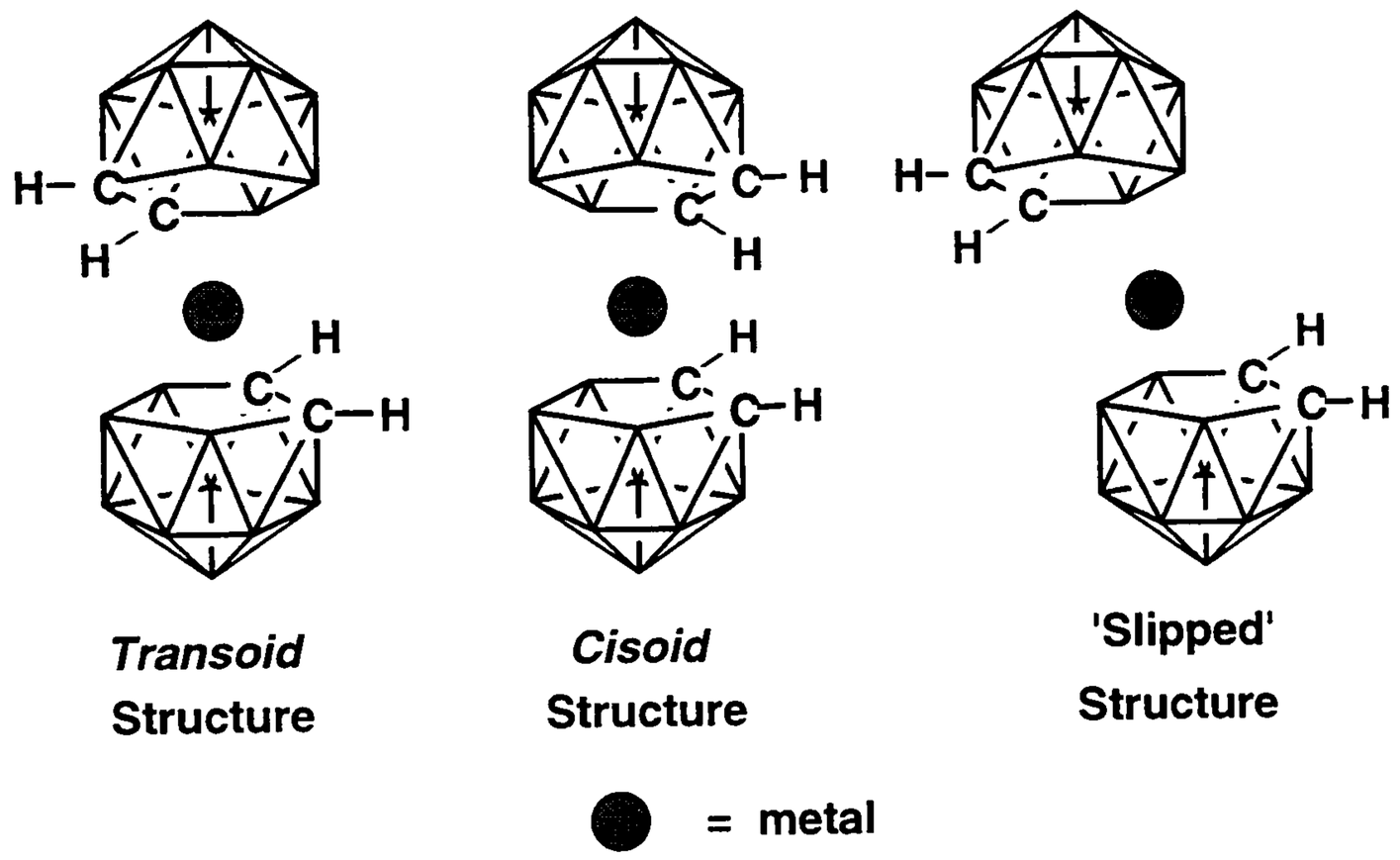


Figure 1.3: *Carborane-containing Metallocenes*

1.6. Potential Applications of Carboranes.

Despite the cost of the icosahedral carboranes, their thermal and chemical properties make them uniquely suitable for several specialised applications. These include the incorporation of large numbers of boron atoms into tumour-seeking drugs for boron neutron capture therapy (BNCT).[53]

The isotope ^{10}B, which occurs in 20% natural abundance, has an unusually high neutron capture cross section, the third highest of any element. Therefore all ^{10}B-containing compounds have potential applications as neutron shields.[54]

BNCT is based on functionalising species rich in ^{10}B to bind preferentially to target cells without contamination of surrounding tissues. Irradiation with thermal neutrons causes the release of highly energetic species with a flight distance within the dimensions of a cell, as boron degrades according to the reaction below.[55,56]

$$^{10}_{5}B + ^{1}_{0}n \longrightarrow ^{11}_{5}B^{*} \longrightarrow ^{7}_{3}Li + ^{4}_{2}He + 2.28MeV$$

Malignant cells can be destroyed by such a method while the surrounding area remains unaffected. The high boron content of icosahedral carborane derivatives makes them potential compounds for BNCT. For example, studies conducted on a "Venus flytrap" type compound, containing ^{57}Co, held tightly between the faces of two covalently bridged carborane ligands, have shown excellent potential for radioimmunotherapy.[57]

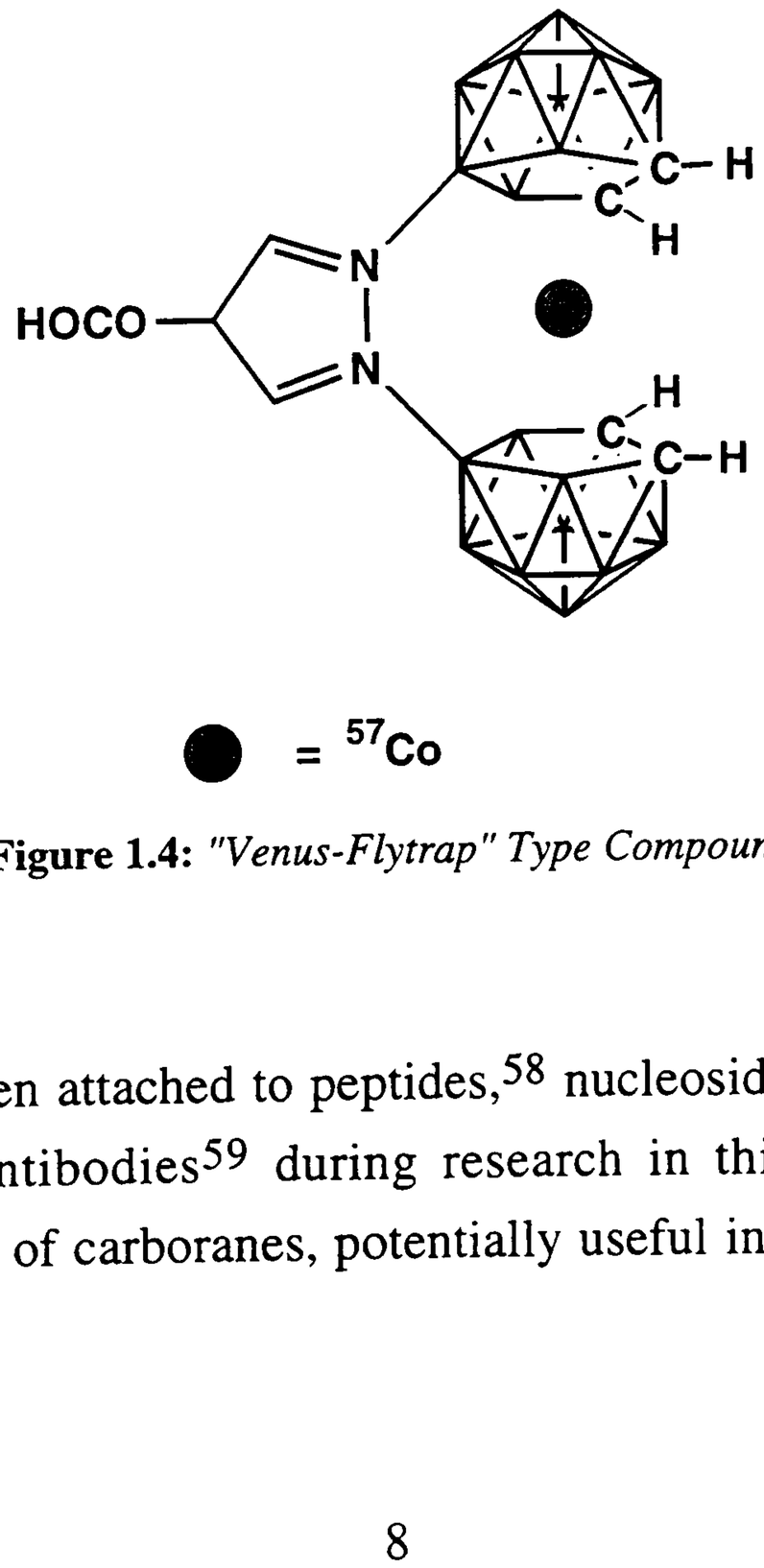


Figure 1.4: *"Venus-Flytrap" Type Compound*

Carboranes have been attached to peptides,[58] nucleosides,[56] porphyrins[59,60] and monoclonal antibodies[59] during research in this area. The neutron screening properties of carboranes, potentially useful in the nuclear industry, have been studied.

The exceptional hydrophobic character and unusual solubility characteristics of carborane ionic derivatives,[61] together with their ability to form potentially ligating *nido* anionic species by treatment with alkali, has led to the use of carborane derivatives in preparing metal complexing agents for solvent extraction, particularly of fissionable metals where neutron capture is desirable,[62] as radiochemical drugs[56] and new catalysts.[63]

An investigation of the non-linear optical properties (NLO) of carborane derivatives, particularly aryl *ortho*-carboranes, has also been carried out recently.[64]

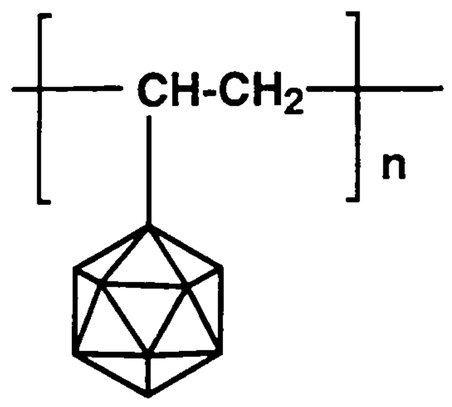
1.6.1. Carborane - containing Polymers:

Much interest in icosahedral carboranes has focused on the incorporation of carborane cages into polymers for high temperature applications.[68]

The relative ease of preparation and chemical stability of icosahedral carboranes has allowed investigators to study their properties in great detail. They were among the first boron hydrides to have promising commercial applications, for example as constituents in high temperature polymers.[69]

Incorporation of the carborane unit into both organic and inorganic polymers has been found to greatly improve the thermal stability of the products compared to the polymers from which they are formally derived. This has been attributed to the electron-withdrawing effects of the carborane cage, with the carboranyl groups behaving as energy sinks and thereby increasing the stability of the neighbouring bonds in the polymeric chain.

All three icosahedral carborane isomers have been incorporated into various polymer categories both as appendages to the polymer chain, for example vinyl carborane,[70,71] and as integral parts in the polymer backbone.



To date numerous polymer systems containing the carborane unit have been synthesised including polyester,[66] polyformal,[67] polyurethanes[68] and polysiloxanes,[69] most exhibiting extraordinary properties, being resistant to degradation by heat and oxidation under conditions in which conventional organic counterparts undergo degradation.[72] The siloxanes are probably the most successful of all of the carborane-containing polymers to date, and are more commonly known as Dexsils.[73]

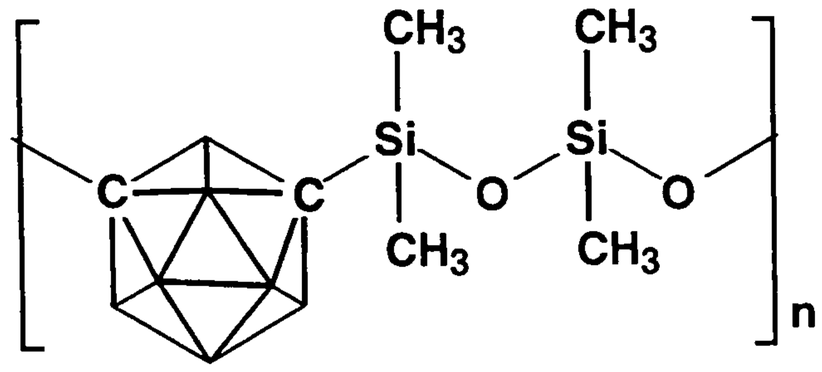
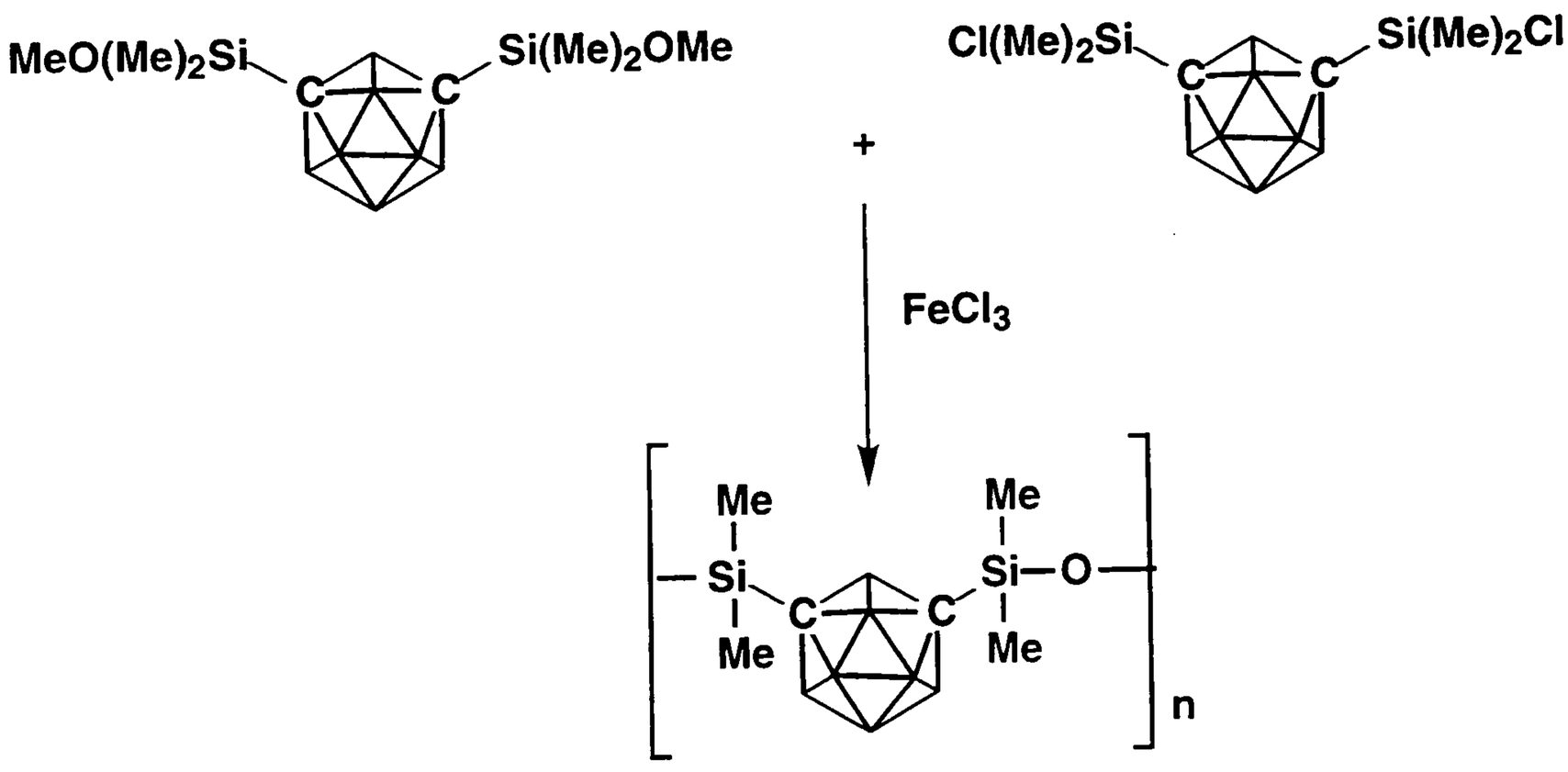


Figure 1.5: *Dexsil 200*

These are heat resistant elastomers, with a range of properties depending on the actual composition of the polymer molecule. They are produced by the condensation polymerisation of 1,7-bis-(chlorosilyl)-*meta*-carborane with 1,7-bis-(chlorosilyl)-*meta*-carborane derivatives, alklychlorosilanes, or alkylchlorosiloxanes in the presence of a catalyst such as $FeCl_3$.



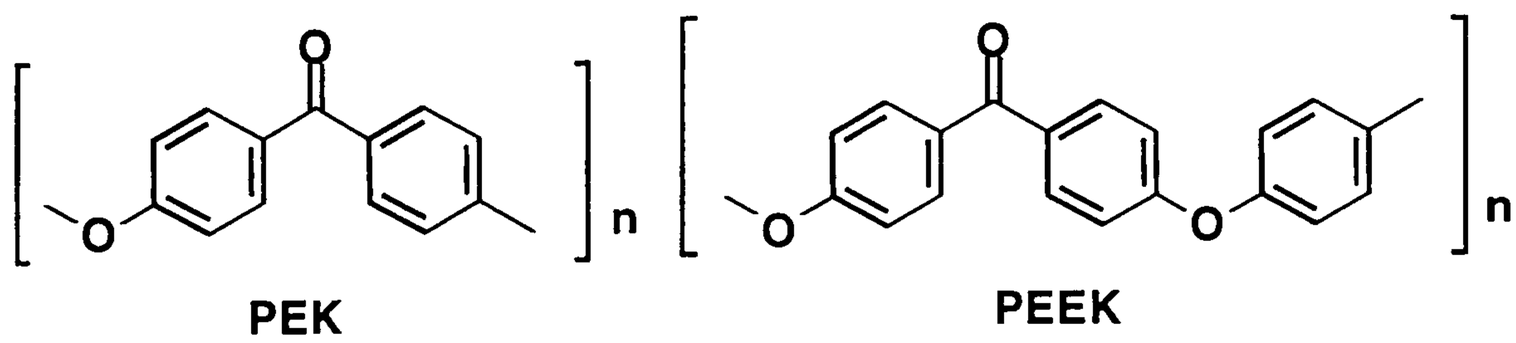
Dexsil 100
crystalline polymer

The elastomeric, mechanical and high-temperature behaviour of this class of polymers has been thoroughly investigated,[74-76] and as a result of the wide range of chemical and physical properties the Dexsils possess, they have found applications in roles such as jet engine components, oils, greases and fire retardants.

A more complete description of the diversity of this field is beyond the scope of this report but can be found in various reviews by Heying,[77] Schroeder[69] and Korshak et al.[78]

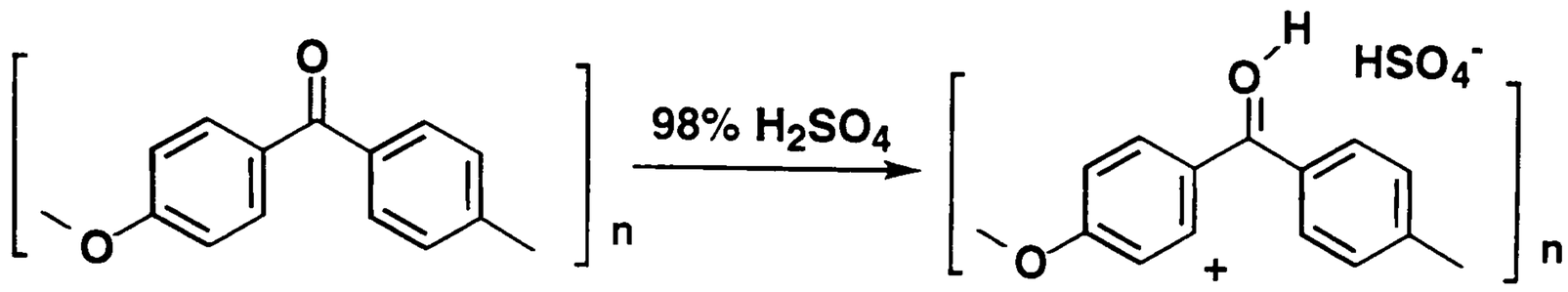
1.6.2. Thermally Stable Organic Polymers:

In recent years there has been a lot of research into the development of organic polymers (not containing carboranes) that are capable of withstanding extremes of temperature and stress. High performance thermoplastics based on aromatic structures have increasing technological importance due to their dimensional stability at high temperatures, and resistance to thermo-oxidative degradation.[79] One such type of polymer class is the type known as the poly(etherketone)s for example PEEK and PEK type polymers.[80-82]



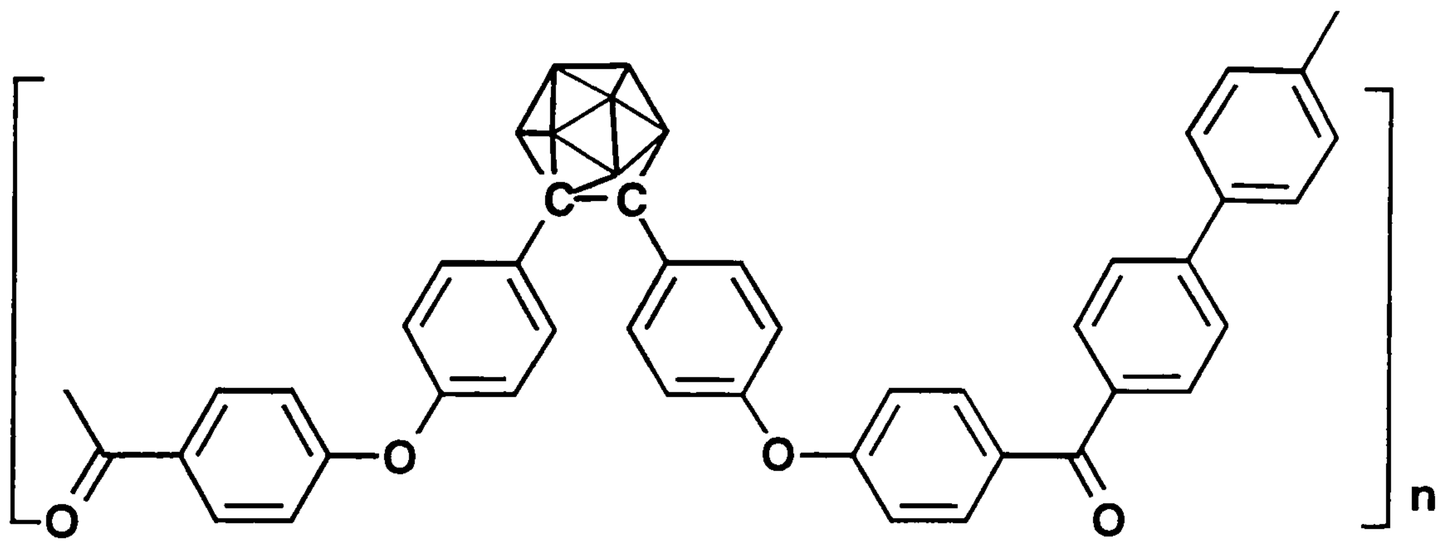
This is a class of semi-crystalline aromatic thermoplastics that display exceptional thermal and hydrolytic stability, resistance to oxidative degradation and have the ability to withstand contact with organic solvents.

They are also soluble, without degradation, in strong acids such as liquid hydrofluoric acid, concentrated sulphuric acid and trifluoromethane sulphonic (triflic) acid, which dissolve the polymer by protonation of the carbonyl group, and/or the ether oxygen.



However, their relatively low glass transition temperatures (T_g) (*ca.* 150°C), in comparison to poly(sulphone)s for example, has led to limitations in their applications.

The incorporation of icosahedral carborane units into the structure of an already thermally resistant group of polymers, the aromatic PEK-type polymers,[83] such as the polymer shown below, has lead to products with enhanced mass retention on pyrolysis and with potential as high char-yield pre-ceramic materials.[84]



This initial work has been extended during the course of this study and is described in detail in Chapter 4.

1.6.3.Ceramics:

Studies have shown that the heating of arylene-carboranes causes spontaneous crosslinking to occur by elimination of hydrogen between CH and BH positions[85] without melting. This results in high yields of insoluble ceramic residues with minimal disruption of the bulk morphology. The study of aryl carboranes as precursors to ceramic materials related to boron carbide has been provisionally studied and a brief background to ceramic materials is given here.

Ceramics are defined as refractory, inorganic materials.[86] Non-oxide ceramics, such as borides, carbides, nitrides and silicides, are known for their high mechanical strength, hardness, corrosion resistance, oxidation resistance, thermal shock stability, wide variation in electronic properties and unfortunately, their brittle character.

Ceramic and ceramic composite materials are at the forefront of advanced material technologies due to the wide range of favourable properties that they possess.

Many ceramic applications require the development of new processable ceramic precursors from which films, coatings, fibres or shaped materials may be formed, before the final ceramic is produced.

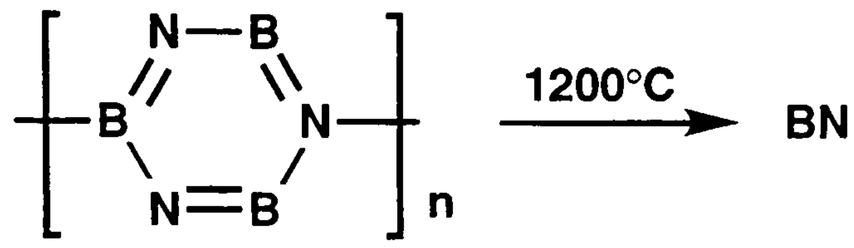
There are a number of boron-containing ceramics for which the development of polymer-based synthetic routes would be an advantage. Because of their unique mechanical and electronic properties, boron carbide and boron nitride are materials of particular interest.

For example boron carbide has been shown to have excellent promise as a high temperature thermoelectric material,[87] while hexagonal-boron nitride (h-BN, with a graphite-like structure) has been proposed as both a dielectric material for semiconductor devices and as a fibre coating which will improve the strength of ceramic composite materials.

As an alternative to conventional high temperature powder techniques, there has recently been much interest in the development of polymer precursors to ceramic materials[88,89] which would allow the precise control of ceramic compositions and the ability to preform objects before firing. The decomposition of a polymer at low temperatures would enable ceramic formation under milder conditions than those used in conventional methods.

Economy and Anderson may be able to lay claim to the first polymer precursor route to h-BN in which a ceramic was clearly identified,[90] as although there was a concerted effort between 1940-65 to prepare a number of inorganic polymers, including polymeric BN compounds, most of the work was not aimed at ceramic products and few pyrolyses were carried out.

Polymer systems such as poly(vinyl borazine) have recently proven to be high yield precursors to boron ceramics such as boron nitrides and boron carbide.[91] Bulk pyroloses of polymers under either argon or ammonia at 1200 °C were reported to afford boron nitride in ceramic yields of over 85%.



The conversion of some of the polymeric products formed during the course of this work into ceramic composites has been provisionally investigated and the results are reported in detail in Chapters 4 and 5.

1.6.4. Membrane Applications:

As the actual separating layer of a membrane may range from 0.1-50mm thick, therefore the quantity of polymer required for a given membrane area may be only grams or milligrams per m^2, so that the polymer cost should not be a dominating factor in the production of carborane based membranes. For this reason the fabrication of carborane-based membranes has been provisionally investigated. Although the target carborane-based membranes were considered unlikely to have novel properties, it was hoped that the thermal stability of the carborane polymers would permit the firing of these membrane systems to form a new range of ceramic membranes and investigations in this area are described in chapter 6. A brief summary of membrane preparation and characterisation is given below, with more specialised literature being referenced if required by the reader.

A membrane may be regarded in simple terms as a selective interface which may select for or against a substance on the basis of size, charge or chemical affinity.

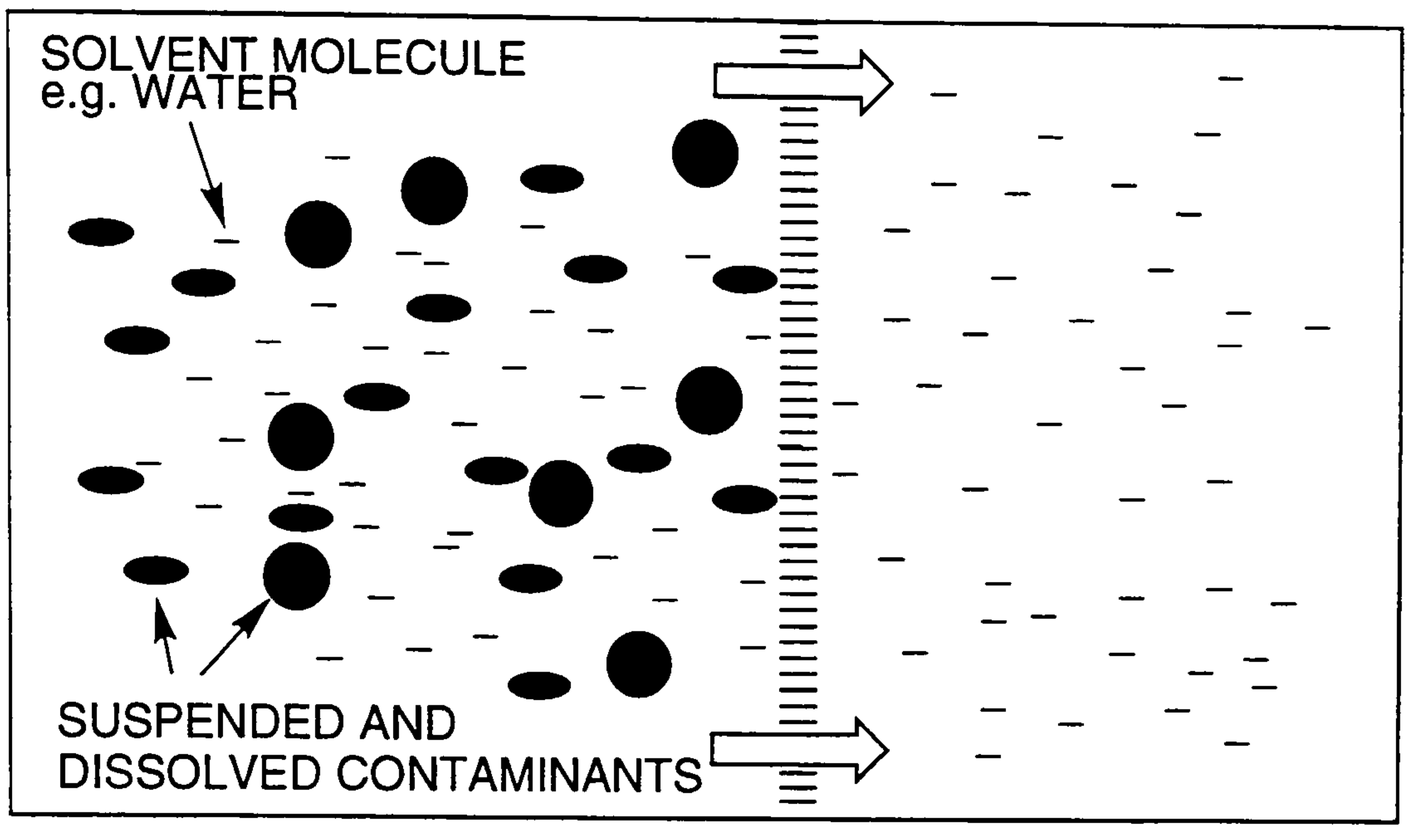


Figure 1.6: *Schematic Representation of a Membrane*

Transport of materials through the membrane interface may occur by different mechanisms. In "porous-flow" membranes, such as those used in micro- and ultra-filtration, the selectivity is controlled by pore-size only, and the permeability by pore-size, porosity (i.e. the number of pores), and the membrane thickness. Both the selectivity and the permeability are essentially independent of the membrane material.

In contrast for "solution-diffusion" systems (such as gas separation membranes, and possibly nano-filtration and reverse osmosis membranes), the selectivity and permeability are *both* controlled by the relative solubility and diffusivity of permeants in the membrane material. In addition the permeability is controlled by the membrane thickness.

Membrane filtration was not considered a technically important separation process until approximately 25 years ago. However today membrane processes are used in a wide range of applications and separations and synthetic membranes have become increasingly important in a variety of industries. Synthetic membranes have been made from a variety of polymers and have been used in processes such as microfiltration (MF), ultrafiltration (UF), reverse osmosis (RO), electrodialysis and gas separation.

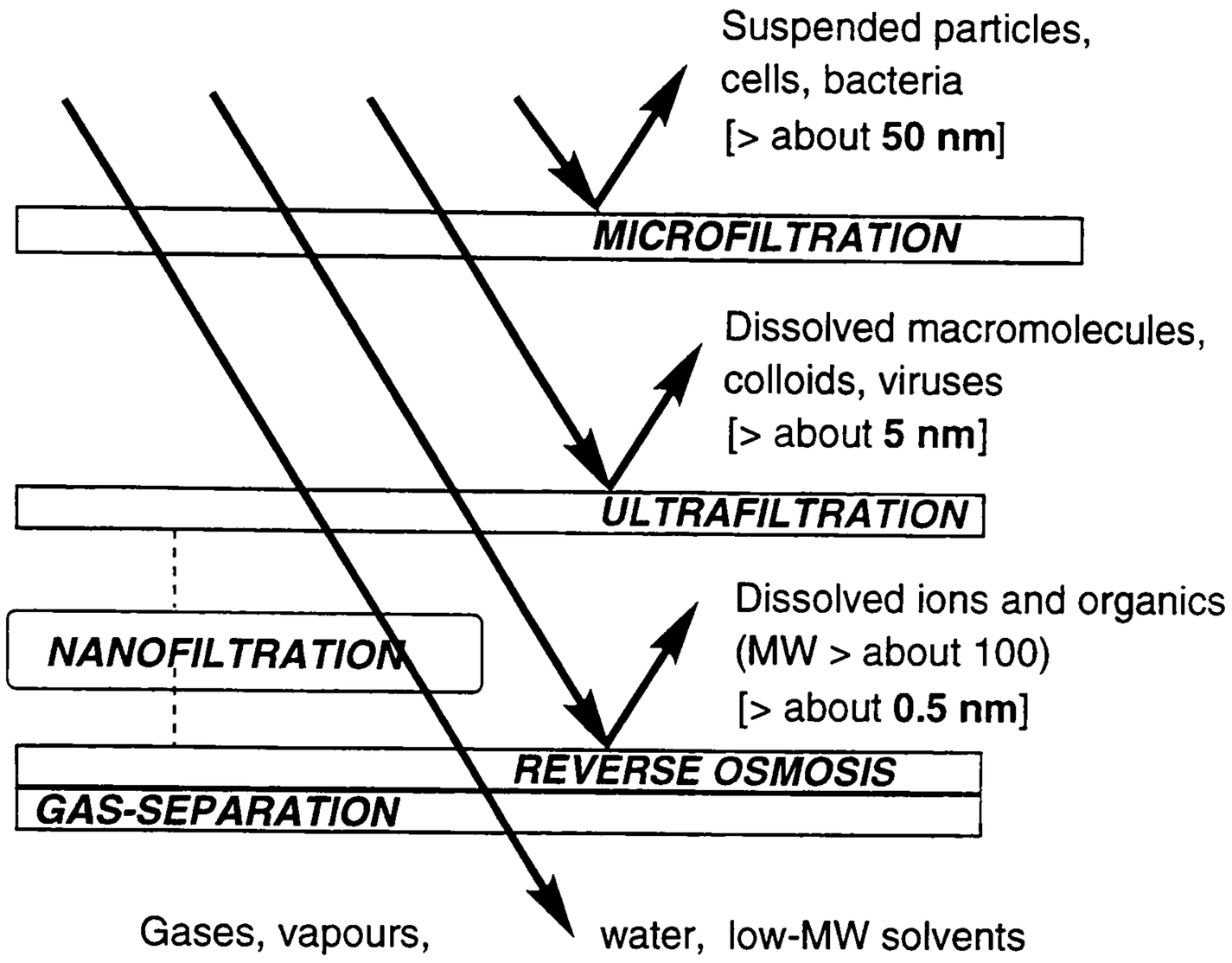


Figure 1.7: *Membrane Porosities and Applications*

Reverse osmosis was first reported in the 1930's[92] when it was discovered that when a dilute solution of salt or non-electrolytes was passed through a cellulose nitrate membrane the permeate was more concentrated than the feed.

This work was extended to cellulose acetate in the fifties in America by Loed and co-workers and various membranes are now used in a variety of applications, such as the desalination of sea water, and in the food industry.

Composite membranes are mainly used for RO applications where the actual selective barrier is deposited onto the surface of a suitable, finely porous substrate. The real breakthrough in this technology came when interfacial polymerisation was used[93] to form the polymer film at the membrane surface. Such systems may be prepared by interfacial polymerisation where a porous support is filled with an aqueous solution of one monomer (for example diamine) and the surface is subsequently contacted with an immiscible organic solution of a second monomer, (for example a diacid chloride). Fig. 1.8 provides a schematic representation of a composite reverse osmosis membrane and this process may be applied to carborane monomers and has been used to prepared composite RO and NF membranes as described in more detail in chapter 6.

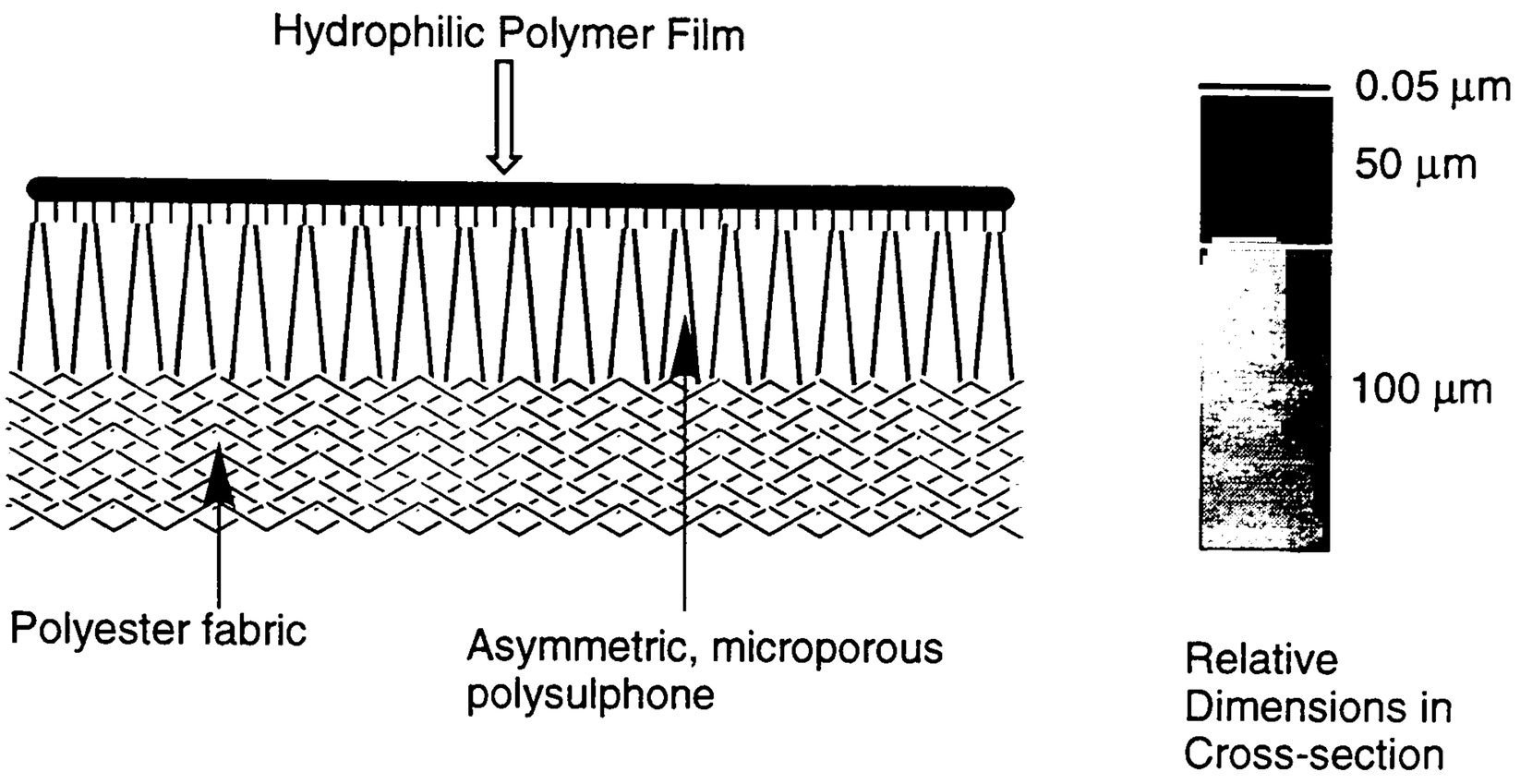


Figure 1.8: *Composite Reverse Osmosis Membrane*

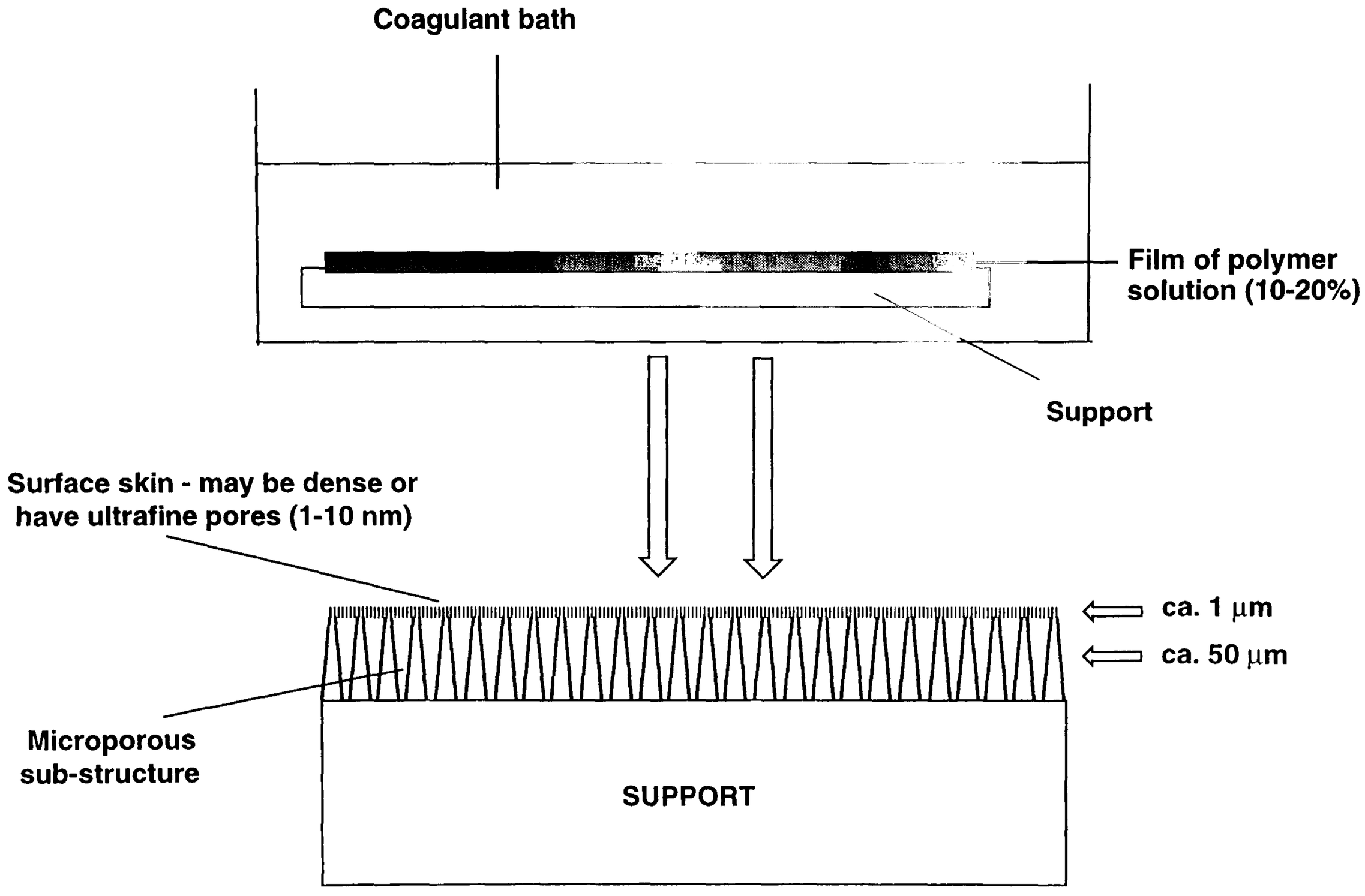
Phase-inversion has been used to prepare a second new type of carborane-containing membrane.

A prepared polymer solution (such as the PECK-type polymers described in chapter 4) was cast onto a support and then contacted with a non-solvent. Polymer precipitation occurs to afford a coherent porous film. (Figure 1.8).

This technique is very powerful and versatile and may be applied to MF, UF, NF, RO and gas separation membranes, and is described in more detail in chapter 6.

There is still considerable scope for the development of new membranes and materials offering increased selectivity, productivity, chemical stability and resistance to mechanical degradation.

Figure 1.8: *Phase Inversion Preparation of Membranes*



1.7.Scope of Work:

The primary aim of this study has been to extend the chemistry of the icosahedral carboranes and to incorporate their derivatives into the backbone of the aromatic poly(etherketone)s. The chemical and physical properties of materials had already been studied briefly, and found to be superior to a few such related organic polymers. The properties of such materials when cast as membranes have been explored and are reported in detail.

This thesis describes how this earlier work[84] has been extended to include incorporation of *meta*-and *para*-carborane derivatives that were previously inaccessible.

The effect of the reduced steric, and possibly reduced electron demand of the icosahedral cluster when going from *ortho*- to *meta*- to *para*-carborane has been studied with regard to producing polymers of higher molecular weight. Their subsequent conversion into ceramic materials has been explored and is described in the subsequent chapters.

Chapter 2 describes the preparation and characterisation of *ortho*-, *meta*- and *para*-carboranyl derivatives, many of which were inaccessible by classical routes. Chapter 3 reports studies conducted to investigate new methods of deboronation to afford the open *nido*-carborane structures. Many previously inaccessible carborane derivatives have been synthesised and are described.

Chapter 4 describes the preparation of aromatic poly (carboranyletherketone)s and their full characterisation and comparison with the properties displayed by their parent poly(etherketone)s. Their subsequent conversion into ceramic materials is discussed.

Chapter 5 describes various attempts to prepare high molecular weight materials based on the aromatic poly (phenylene) polymers. The preparation of oxygen-free oligomers and polymers is discussed along with their subsequent conversion into ceramic materials.

Chapter 6. reports the preparation and characterisation of novel carborane-based membranes prepared either by interfacial polycondensation or phase-transfer.

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Chapter 2

FUNCTIONALLY SUBSTITUTED ARYL AND DIARYL CARBORANES

SYNTHESIS OF ARYL CARBORANES:

2.1. Introduction:

The majority of applications for carboranes require derivatives with reactive sites suitable for coupling reactions, for example polymerisation or attachment to peptides for boron neutron capture therapy (B.N.C.T.). The stability of aromatic groups and the diversity of their synthetic reactions render them particularly suitable for these purposes, but hitherto the available range of functional aryl carboranes has been limited. This chapter describes the synthesis and characterisation of a variety of *ortho*-, *meta*- and *para*-carboranes bearing functionally substituted aryl groups.

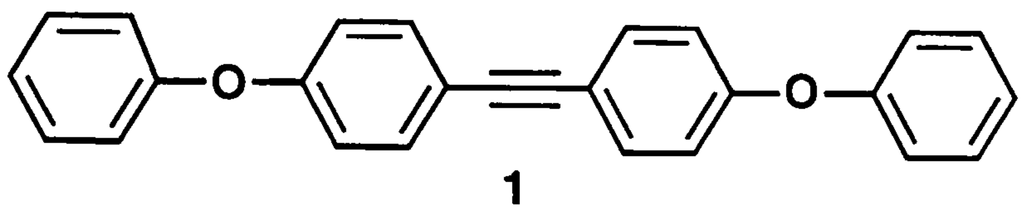
Classically *ortho*-carborane compounds are prepared by the reaction of a preformed alkyne RC≡CR' and decaborane in the presence of a Lewis base, as previously described (Section 1.3). The requirement for compatibility with this reagent system precludes the incorporation of groups bearing substituents which are acidic (e.g. OH, CO_2H), reducible (NO_2) or susceptible to nucleophilic attack (e.g. C_6F_5). Nucleophilic groups which form stable complexes with the decaborane unit may also complicate the reaction. The yields of *ortho*-carborane are variable and are often lowered by side reactions, notably hydroboration of the triple bond. Nevertheless, in general a wide range of *ortho*-carborane derivatives may be prepared in this manner.

$$B_{10}H_{14} + RC \equiv CR' \longrightarrow C_2B_{10}H_{10}RR' + H_2$$

2.2. Results and Discussion:

2.2.1. Preparation of *ortho*-Carborane Derivatives via Aryl Alkynes.

Compounds **1**, and **2** were prepared by coupling 4-iododiphenylether, and 1,3,5-tribromobenzene, respectively, with acetylene in the presence of a palladium/copper catalyst. Compound **4** was prepared in a similar manner using ethynyl(trimethyl)silane and deprotecting the isolated product using a weakly basic solution. (Compounds **3** and **5** were used as supplied by Aldrich)



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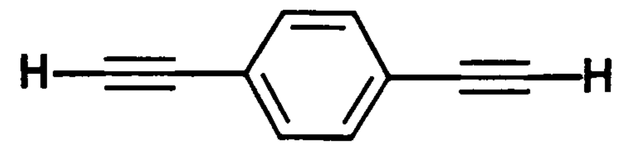

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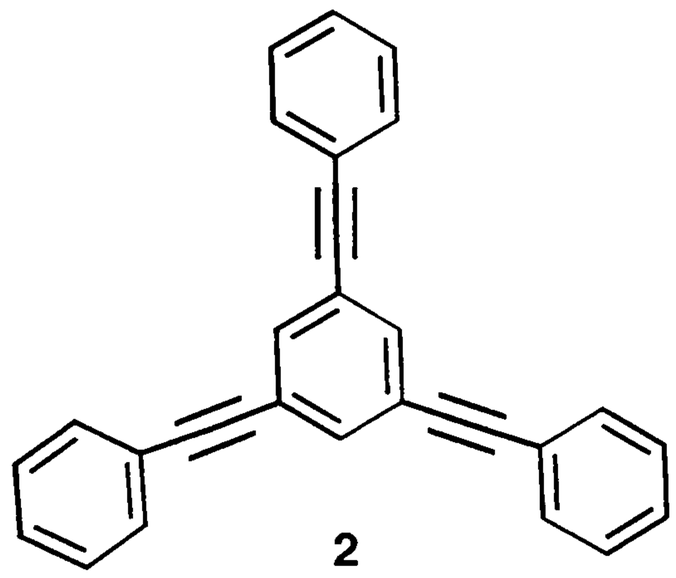

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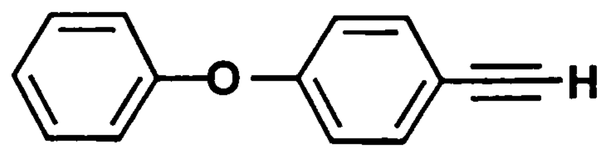

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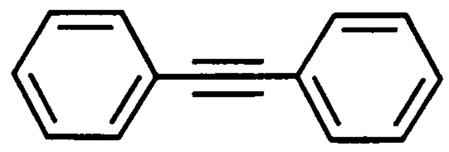

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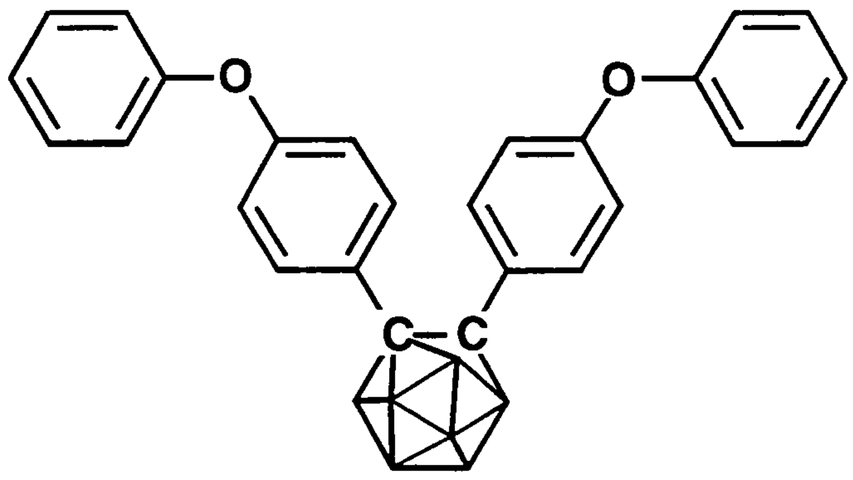
These acetylenic compounds were treated with bis-(dimethylsulphide)-decaborane, in toluene, to afford the *ortho*-carborane products **6-10**, shown below.



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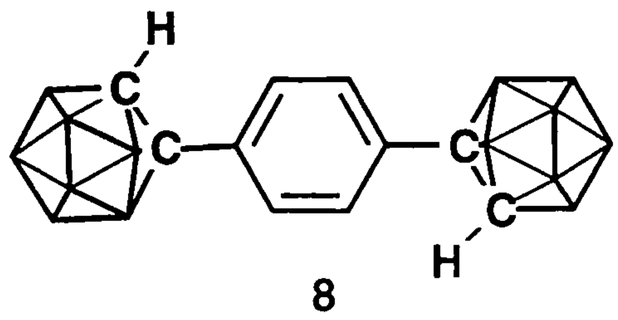

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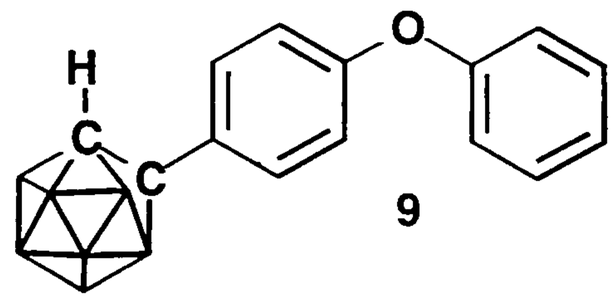

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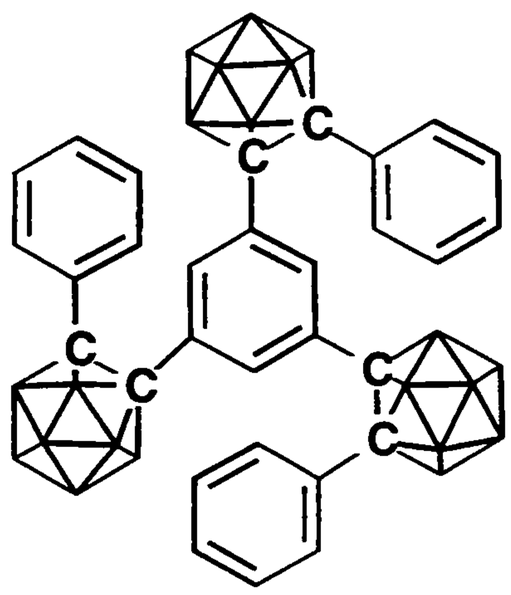

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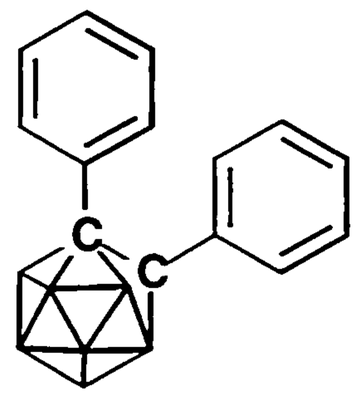
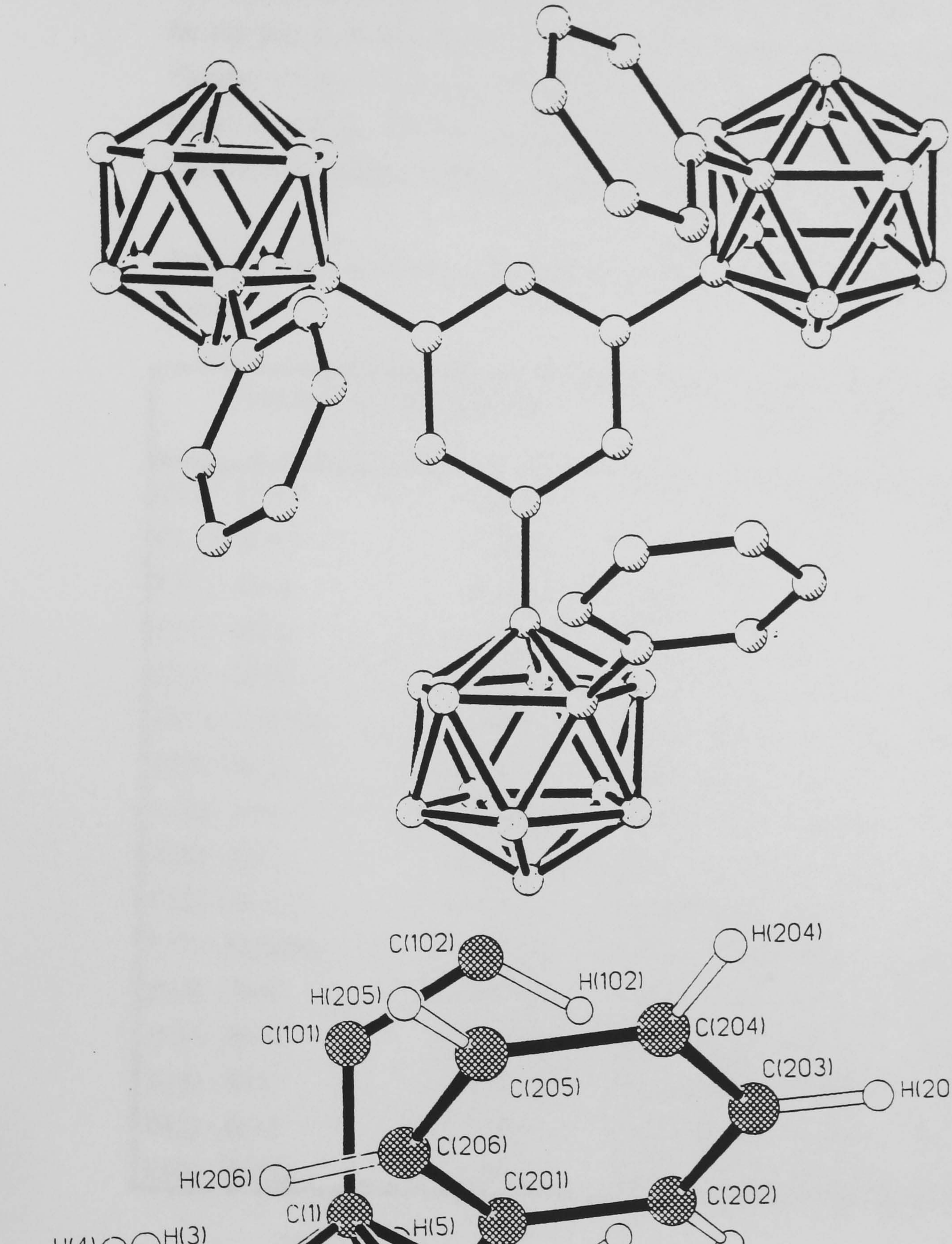


10

X-ray diffraction studies were conducted on compound **7**, by Copley and Howard at Durham, and the structure is shown in Figure 2.1.

Figure 2.1: *Molecular Structure of 1,3,5-tris-1-(2-phenyl-ortho-carboranyl)-benzene (7).*



Unique Atoms Viewed Along c

This represents the first structurally characterised carborane derivative containg three cages. A three-fold symmetry is clearly established in this structure and as in the structure of 1,2-diphenyl-*ortho*-carborane[1] where the two phenyl rings lie roughly perpendicular to through the aromatic sequence C(aryl)-C(cage)-C(cage)-C(aryl), a similar structure seems to be adopted within the limits of steric crowding. Selected distances and bond angles are given in Table 2.1, (full crystallographic details are given in Section 2.3.5).

Table 2.1: *Selected Distances and Bond Angles For 1,3,5-tris-1-(2-phenyl-ortho-carboranyl)-benzene (7)*

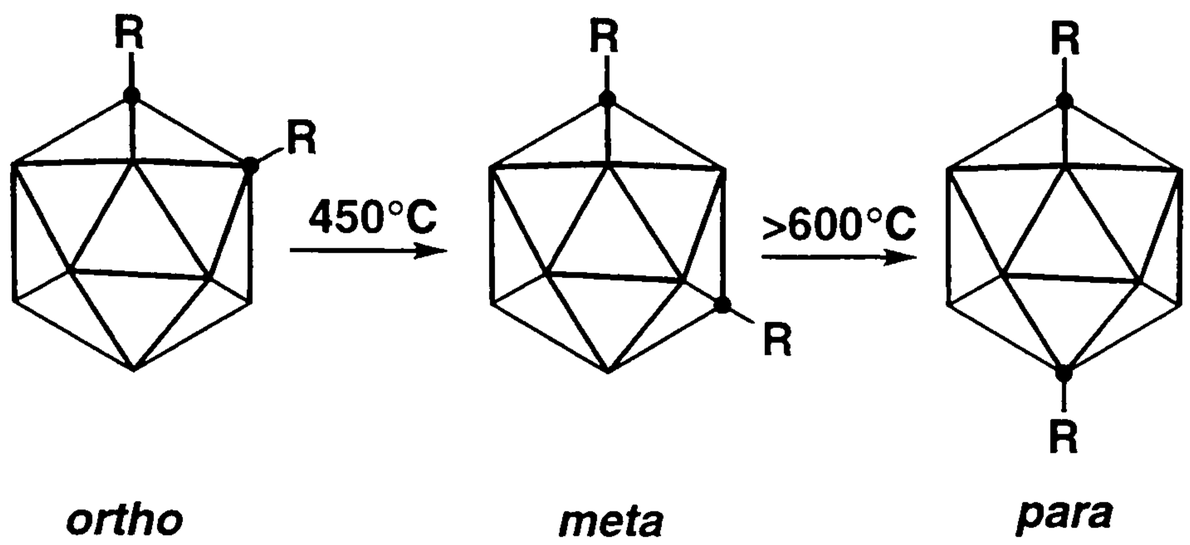
Interatomic Distances (Å)		Bond Angles (°)	
C(1) - C(2)	1.709 (2)	C(2) - C(1) - B(3)	60.50 (9)
C(1) - B(3)	1.726 (2)	C(2) - C(1) - B(4)	109.9 (1)
C(1) - B(4)	1.713 (2)	B(3) - C(1) - B(4)	61.8 (1)
C(1) - B(5)	1.711 (2)	C(2) - C(1) - B(5)	110.6 (1)
C(1) - B(6)	1.727 (2)	C(2) - C(1) - C(101)	118.8 (1)
C(1) - C(101)	1.509 (2)	B(3) - C(1) - C(101)	117.4 (1)
C(2) - B(3)	1.731 (2)	B(4) - C(1) - C(101)	121.0 (1)
C(2) - B(6)	1.740 (2)	B(5) - C(1) - C(101)	121.5 (1)
C(2) - B(7)	1.710 (2)	B(6) - C(1) - C(101)	119.0 (1)
C(2) - B(11)	1.714 (2)	C(1) - C(2) - B(3)	60.24 (9)
C(2) - C(201)	1.503 (2)	C(1) - C(2) - B(6)	60.09 (9)
B(3) - B(4)	1.766 (3)	C(1) - C(2) - B(7)	110.0 (1)
B(3) - B(8)	1.757 (3)	C(1) - C(2) - B(11)	109.6 (1)
B(4) - B(5)	1.773 (3)	C(1) - C(2) - C(201)	118.8 (1)
B(5) - B(6)	1.773 (3)	B(6) - C(2) - C(201)	117.6 (1)
B(6) - B(11)	1.776 (3)	B(11) - C(2) - C(201)	121.2 (1)

2.2.2. Preparation of *meta*- and *para*-Carborane Derivatives:

Incorporation of *meta*-and *para*-carborane cages into polymer chains potentially leads to a more extended chain geometry than is likely for the corresponding *ortho*-carborane isomer.

In addition, such materials should display greater resistance to nucleophilic degradation than their *ortho*-carborane-containing analogues, as a direct result of the higher resistance to nucleophilic degradation displayed by *meta*-and *para*-carborane cages.

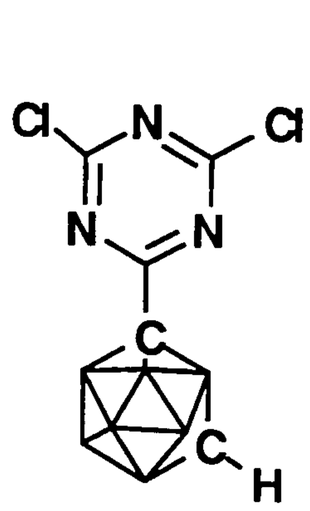
Aryl derivatives of *meta*- and *para*-carborane can in principle be prepared by thermal isomerisation of the corresponding *ortho*-carborane derivatives



The actual temperature at which isomerisation occurs is very much dependent on the substituent bound to the cage, and only the most stable and unreactive substituted aryl groups may be used in this preparation. Indeed some groups completely suppress the isomerisation at temperatures below the onset of cage degradation.

The direct attachment of aryl groups to the carbon atoms of *ortho*-, *meta*- and *para*-carborane has the intrinsic difficulty that in order for the reaction to proceed, the aryl group must be activated in some manner, (e.g. by a nitro substituent). Such functionalities are however normally incompatible with lithiated carboranes.

If the aromatic system is inherently electron withdrawing, as in the case of the heterocyclic triazene compounds, then it is possible to prepare a variety of compounds such as **11**-**13** shown overleaf.



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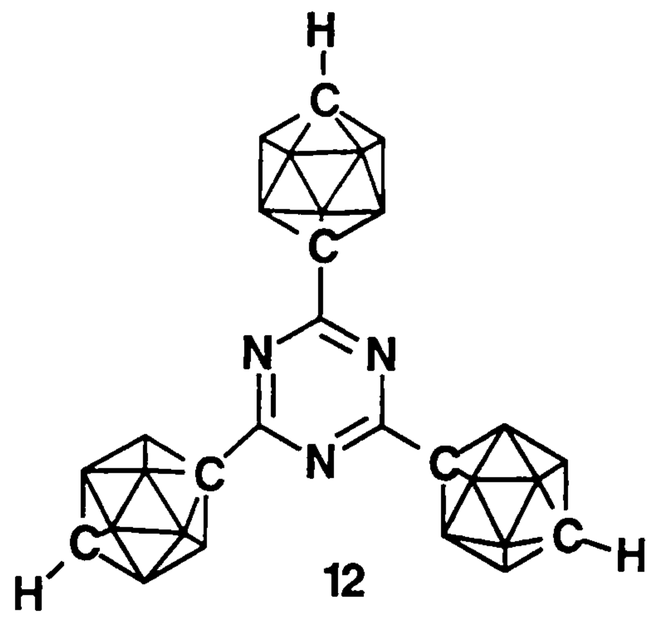

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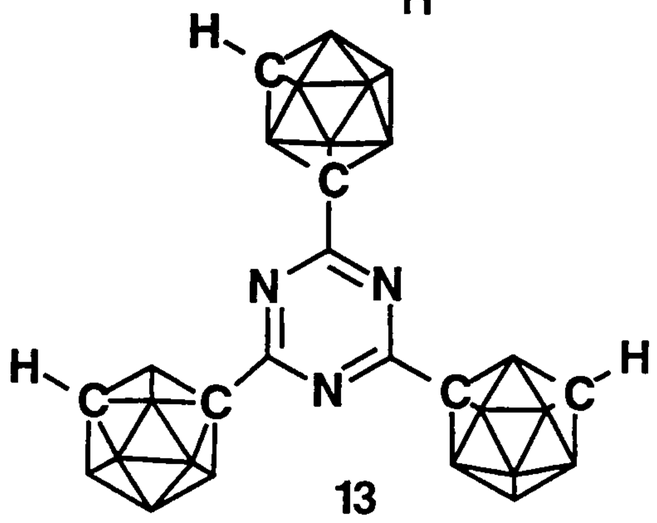


13

Each product was prepared by the addition of cyanuric chloride to a solution of mono-lithiated carborane, in 1,2-dimethoxyethane. This solvent is preferred to diethylether, in which an equilibrium exists between mono- and di-lithiated carborane and the parent carborane.

2.2.3. Preparation of Aryl Carborane Monomers via Copper-Coupling Routes.

Work by MacBride *et al*[2] and the present author has led to the development of a new, one-pot synthetic route to previously unavailable *meta-* and *para-* carborane derivatives utilising coupling reactions between a carboranyl-copper species and an aromatic halide, usually the iodide.

Electron-donor compounds are known to catalyse the related Ullmann coupling reaction and so pyridine was added to the system in an attempt to improve the reaction between the aryl iodide and the copper derivative.[3] An increase in the overall rate of reaction was indeed observed, resulting from the increased solubility of the carboranyl copper (I) species. This may depend on the formation of intermediate copper-pyridine adducts.

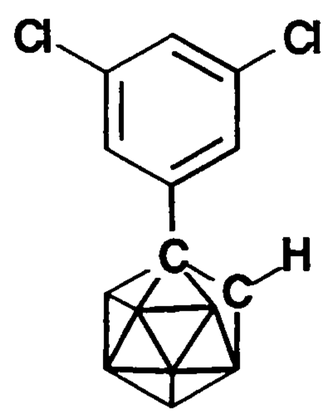
Many of the reactions afforded a crystalline precipitate of a copper (I) iodide/pyridine complex which does not appear to correspond with any of the similar complexes previously described.[4-6] Unfortunately it has not been possible to isolate and characterise any such intermediates or by-products to date.

Suspensions of the mono- or di-copper (I) derivatives of *ortho*-, *meta* - and *para*-carborane in 1,2-dimethoxyethane were prepared by the conventional method of treating the corresponding lithiocarboranes (from the parent carborane and butyllithium) with copper(I) chloride or iodide.[7,8]

Addition of pyridine and an aryl iodide, followed by heating at reflux, gave the aryl carboranes **14-35** shown in Figure 2.2.

Figure 2.2: *C-Aryl Substituted Derivatives of ortho- meta- and para-carborane.*

***ortho*-Carborane Derivatives**



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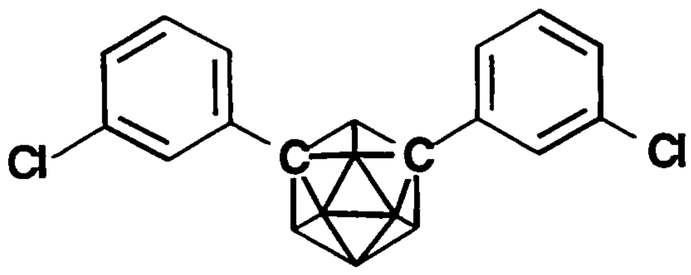
***meta*-Carborane Derivatives**



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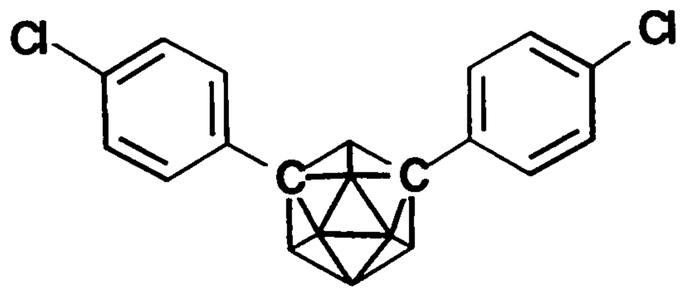

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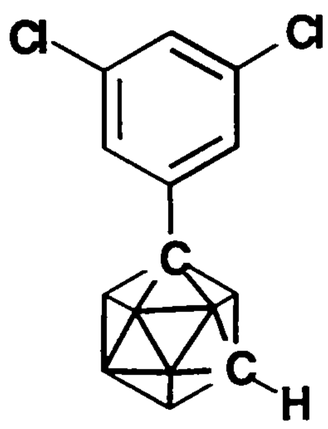

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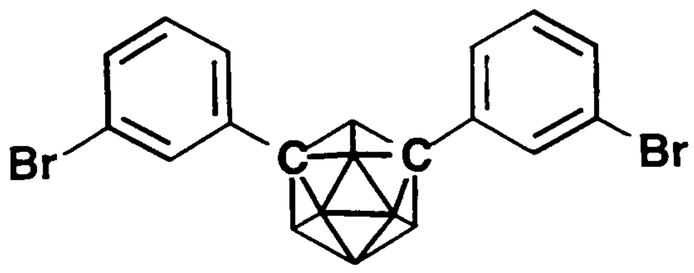

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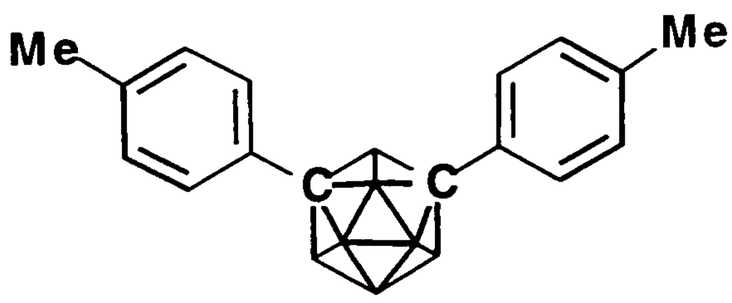

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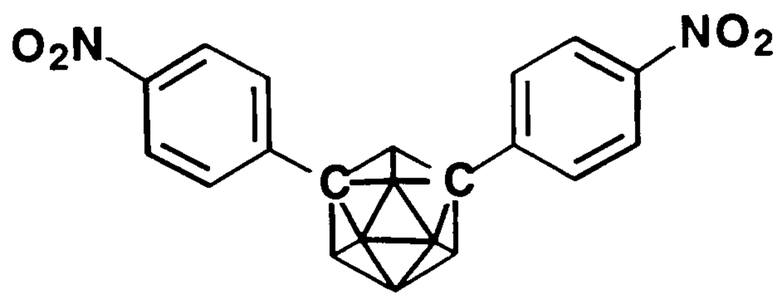

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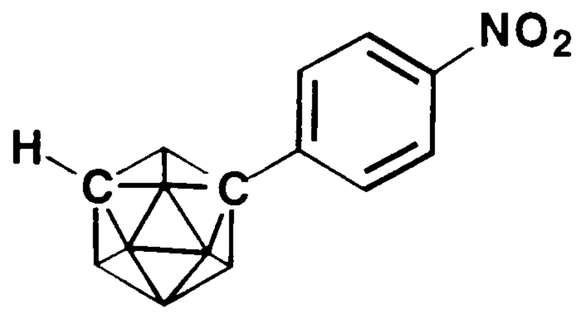

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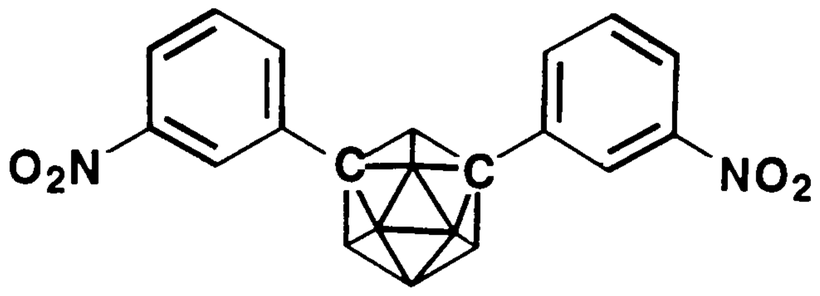

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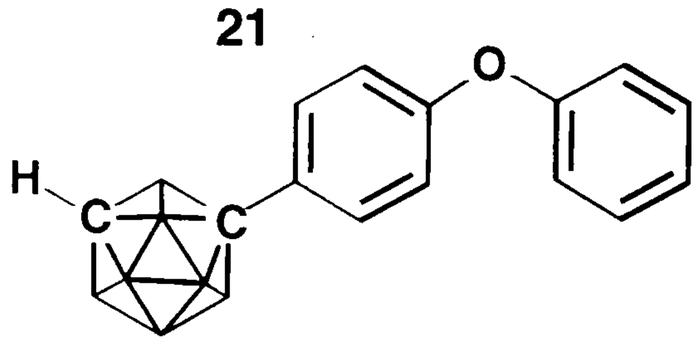

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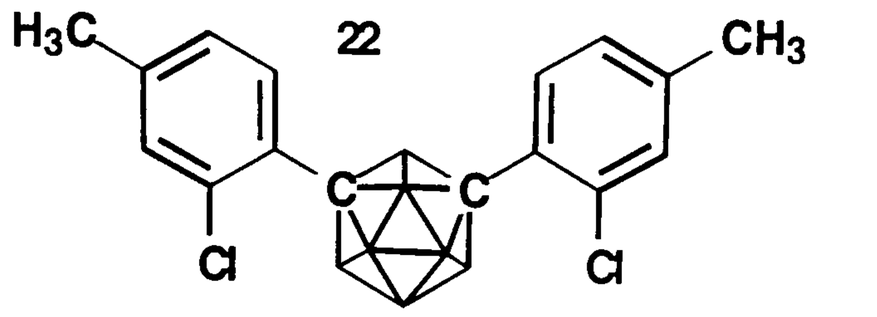

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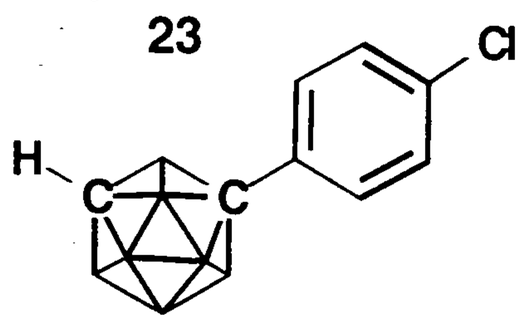

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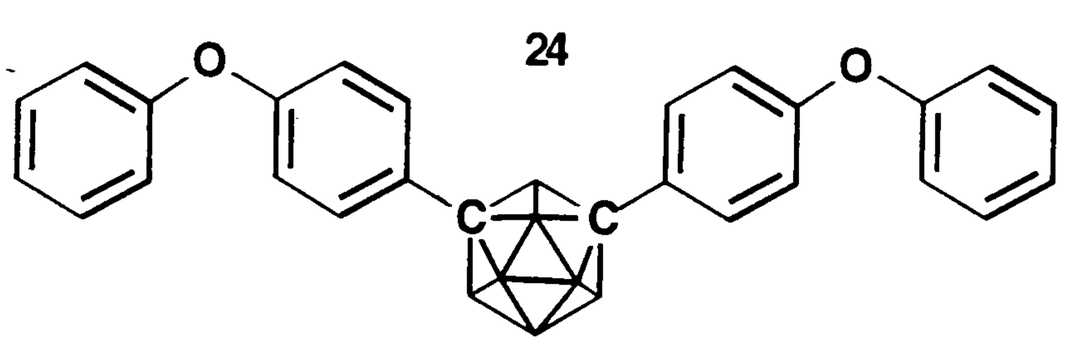

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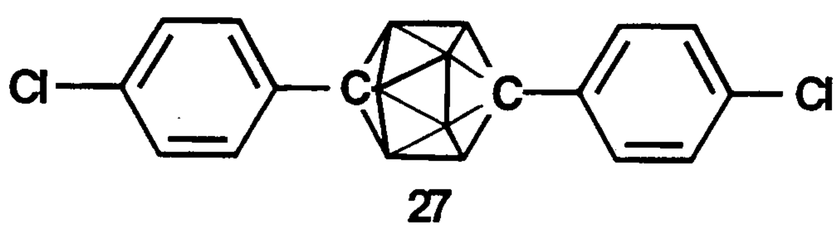
***para*-Carborane Derivatives**



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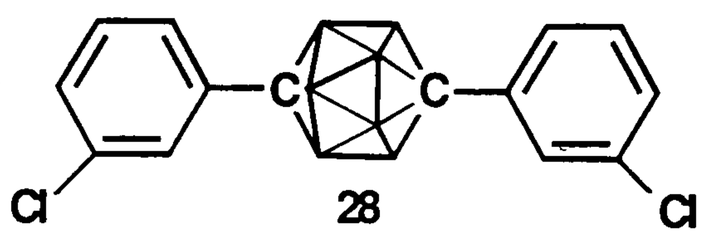

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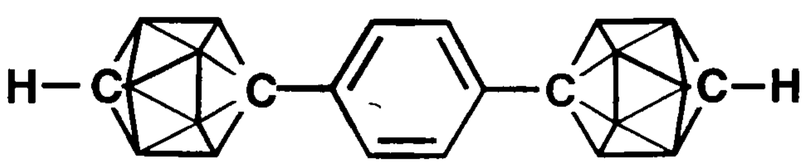

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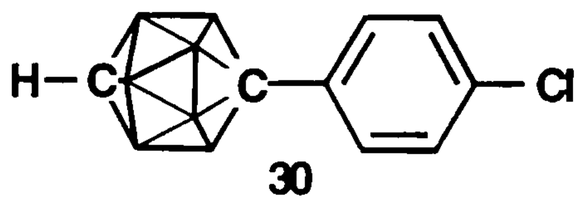

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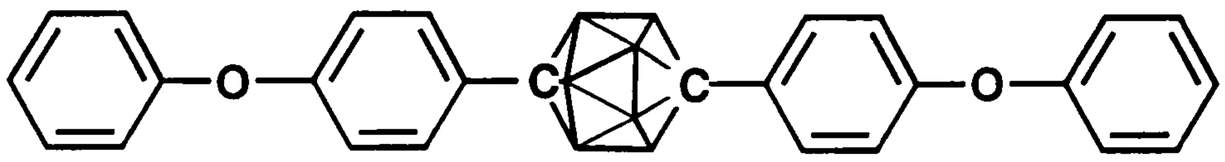

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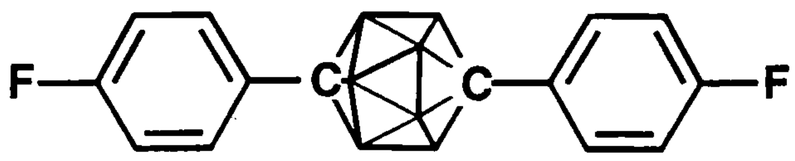

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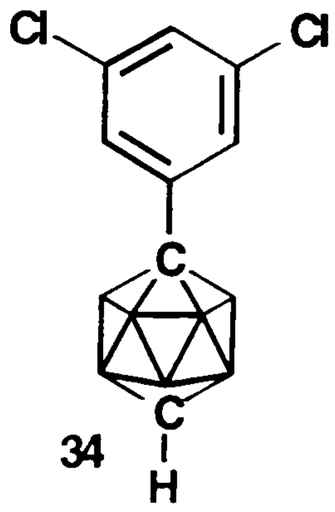

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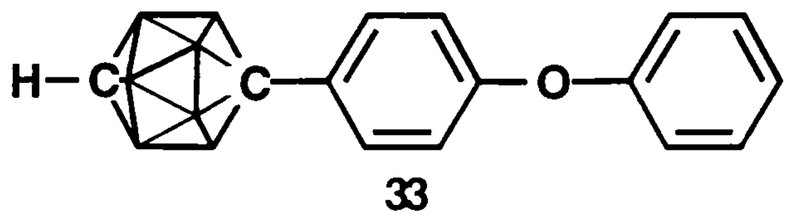

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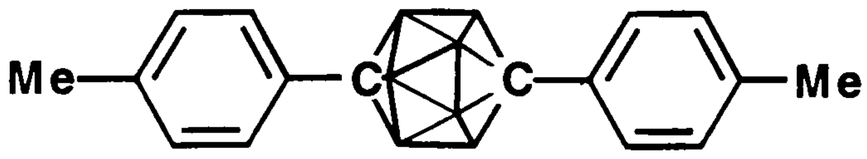


35

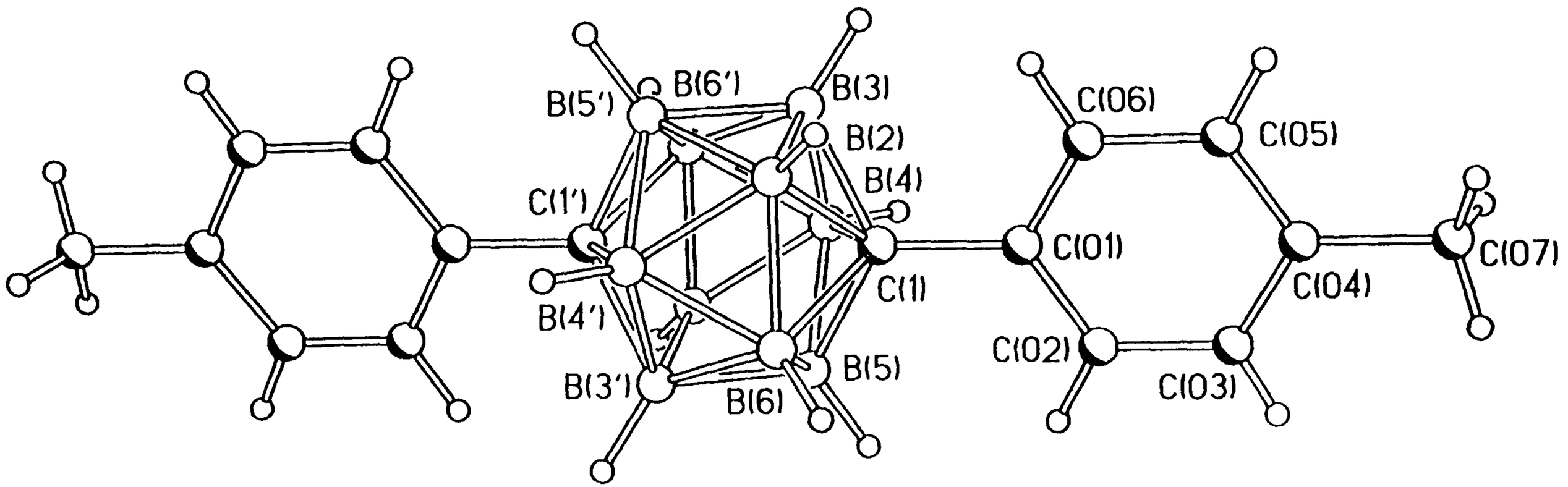
X-ray diffraction studies were conducted on compound **35**, 1,12-bis-(4-methylphenyl)-*para*-carborane, by Batsanov and Howard at Durham, and the structure is shown in Figure 2.3. The phenyl rings are approximately coplanar in the solid state structure and selected interatomic distances and bond angles are given in Table 2.2. These structural parameters where used for molecular modelling calculations as described in Section 5.2.2.3.

Table 2.2: *Selected Distances and Bond Angles for 1,12-bis-(4-methylphenyl)-para-carborane (35).*

Interatomic Distances (Å)		Bond Angles (°)	
C(1) - C(01)	1.517 (2)	C(01) - C(1) - B(3)	118.25 (13)
C(1) - B(2)	1.727 (3)	C(01) - C(1) - B(6)	119.1 (2)
C(1) - B(3)	1.718 (3)	B(3) - C(1) - B(6)	112.82 (13)
C(1) - B(4)	1.731 (3)	C(01) - C(1) - B(2)	118.2 (2)
C(1) - B(5)	1.730 (3)	B(3) - C(1) - C(101)	118.8 (1)
C(1) - B(6)	1.729 (3)	B(3) - C(1) - B(2)	62.08 (12)
B(2) - B(3)	1.776 (3)	C(01) - C(1) - B(5)	120.11 (13)
B(2) - B(6)	1.778 (3)	B(6) - C(1) - B(5)	61.87 (12)
B(3) - B(4)	1.773 (3)	C(1) - C(101) - B(4)	119.17 (14)
B(5) - B(6)	1.778 (3)	B(6) - C(1) - B(4)	112.69 (14)
C(01) - C(01)	1.379 (3)	B(5) - C(1) - B(4)	61.67 (12)
C(01) - C(06)	1.367 (3)	C(02) - C(01) - C(1)	121.5 (2)
C(02) - C(03)	1.386 (3)	C(01) - C(02) - C(03)	120.6 (2)
C(03) - C(04)	1.369 (3)	C(03) - C(04) - C(05)	117.0 (2)
C(05) - C(06)	1.381 (3)	C(05) - C(04) - C(07)	121.6 (2)
C(04) - C(07)	1.512 (3)	C(03) - C(04) - C(07)	121.4 (2)

This reaction may also be used to prepare specifically mono-arylated *ortho*-carborane derivatives in contrast to recent work[9] on alkylation of icosahedral carboranes, in which a t-butyldimethylsilyl (TBDMS) protecting group was found necessary for the efficient formation of the mono-alkyl derivative without accompanying dialkylation.

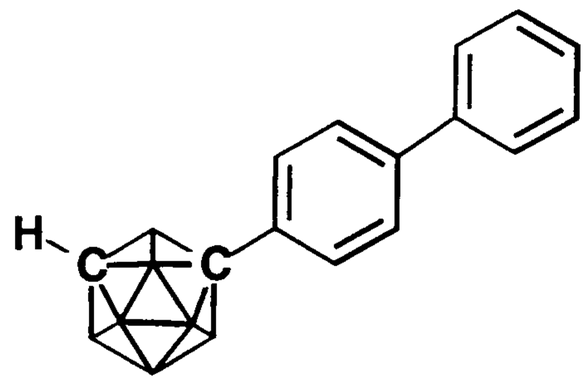
Figure 2.3: *Molecular Structure of 1,12-bis-(4-methylphenyl)-para-carborane (**35**).*



Reactions of *meta*- and *para*- carborane afford either mono- or di-aryl derivatives according to the stoichiometric proportion of reagents used. Highly selective formation of either derivative was possible in many cases, although in some instances mixtures were formed, perhaps as a result of disproportionation of the monometallated intermediates, or because of incomplete reaction. However, separation of the mono- and diarylcarboranes by sublimation. crystallisation or chromotography on silica proved relatively straight forward.

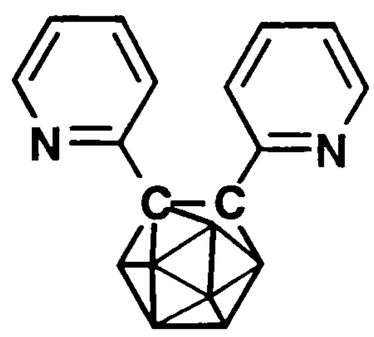
The mechanism of the coupling between the C-carboranyl copper (I) reagents and aryl iodides has not yet been established but is probably related to the proposed mechanisms for the corresponding reactions of arylcopper(I) intermediates.

It is a feature of copper-promoted aryl-aryl coupling that iodine is distinctly the most reactive halogen in otherwise unsubstituted arenes.[10-12] Electron withdrawing groups, (particularly nitro) and heteocyclic ring nitrogen atoms facilitate reaction of bromides and chlorides, as with simple nucleophilic aromatic substitution, and electron donor molecules catalyse the reaction. The same reactivity relationships are found in the palladium-with-copper catalysed coupling of alkynes to aryl halides.[13] Aryl iodides appeared to be more reactive than the corresponding aryl bromides as reaction with 4-bromobiphenyl gave only the monosubstituted product (**36**) in moderate yield.

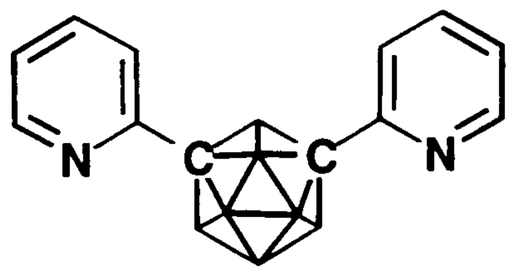


36

This comparison suggested that 2-bromopyridines might couple with copper(I) carboranes and this was indeed found to be the case, affording the products **37** and **38** shown below.



37

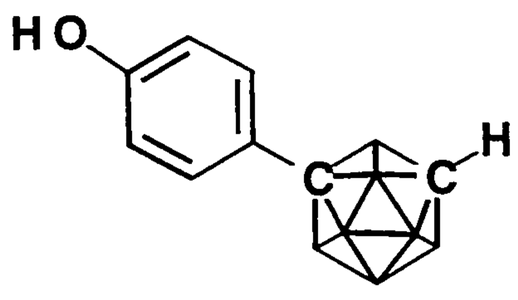


38

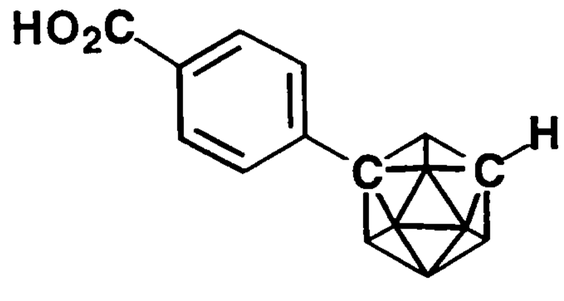
Although rather long reaction times are often required, perhaps because of the low solubility of the intermediate copper(I) carborane derivatives, mono- or di-arylation of *meta*- and *para*-carboranes with various substituted aryl iodides can be effected in the presence of pyridine in excellent yield. The examples shown in Figure 2.2 suggest that a very wide range of previously inaccessible C-aryl carboranes can be prepared by this type of reaction.

2.2.4. Incorporation of Protic Functionalities.

Protic functionalities usually prevents Ullmann coupling,[14] probably as a result of protolysis of the arylcopper intermediates. However, amino, hydroxy and carboxy groups may be protected as their trimethylsilyl derivatives by treatment with diethylamino(trimethyl)silane and subsequently deprotected by treatment with aqueous methanol.[15] Several attempts during the course of this work have been made to use such procedures for the incorporation of protic functionalities onto aryl carboranes. Unfortunately only mono-substitued products (**39** and **40**) have been isolated from reactions involving TMS- or TBDMS-protected aryl iodides. The reason for this has not yet been established.

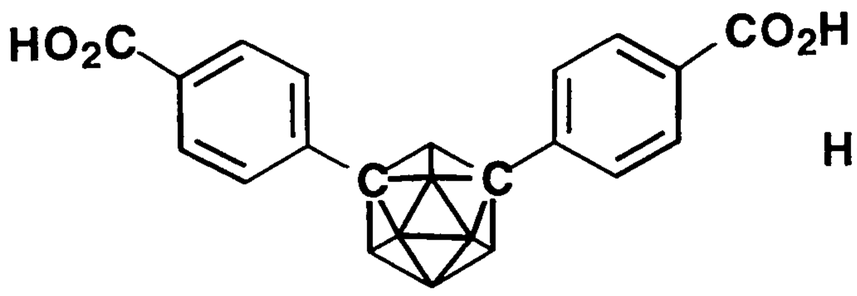


39

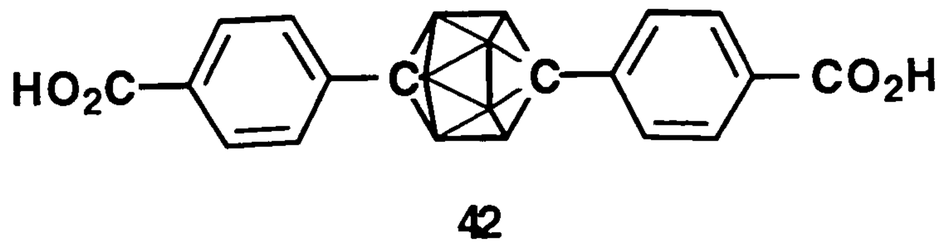


40

Compounds **41** and **42** were therefore prepared by classical methods[16] involving the oxidation of previously prepared tolyl derivatives.



41



42

2.3. Experimental:

2.3.1. Preparation of the decaborane-dimethylsulphide complex.

Decaborane (20.13 g, 0.165 mmol) was placed in a 250 ml round bottomed flask which was flushed with nitrogen. Dimethylsulphide (80 ml) was added to the reaction vessel forming a brown solution. This was stirred for five minutes at room temperature and then filtered into a clean round bottomed flask, via filter aid. The clear yellow filtrate was combined with dimethylsulphide washings from the reaction vessel and stirred at room temperature overnight. The resulting white precipitate was filtered off, dried and identified as the dimethylsulphide complex $(Me_2S)_2B_{10}H_{12}$ (80% yield).

I.R. ν cm^{-1} 3023 w, 2925 w (aliphatic CH), 2517 s (BH), 1473 m, 1433 s, 1418 sh., 1344 m, 1210 m, 1095 m, 1038 m, 1006 s, 998 m, 976 m, 952 m, 767 m, 647 m, 473 m.

2.3.2 Preparation of bis-(4-phenoxyphenyl)-acetylene (1).

Freshly sublimed 4-iododiphenylether (10.23 g, 34.5 mmol) was dissolved in diethylamine (60 ml) with stirring in a saturated atmosphere of acetylene. Bis-(triphenylphosphine)palladium (II) chloride (70 mg, 1 mmol) and copper (I) iodide (20 mg, 1.1 mmol) were dissolved in piperidine (4 ml) by warming to ca. 60 °C, forming a clear orange solution, which was transferred without exposure to air to the reaction vessel. The reaction mixture became turbid and a pink-brown oil formed almost immediately. The reaction mixture was stirred at room temperature under acetylene for 6 hours and a crystalline solid was observed to form after *ca.* 20 minutes. The acetylene flow was then stopped and the reaction solution was stirred under nitrogen overnight. The mixture was filtered and the yellow precipitate was washed with methanol (3 x 25 ml) and dried to afford shiny cream coloured crystals identified as bis-(4-phenoxyphenyl)-acetylene (**1**). Yield 4.82 g, 82%. Melting point 166-169 °C. The product was characterised as follows:

Analysis: Found; C, 86.82; H, 4.41%; M_r (mass spectrum) 361-364; $C_{26}H_{18}O_2$ requires C, 86.17; H, 5.01%; M_r 362-364.

I.R. $\nu_{max}cm^{-1}$: 3088 w, 3039 w (aromatic CH), 2068 w (C≡C), 1938 w, 1592 s, 1512 s, 1491 s, 1455 sh., 1410 w, 1316 w, 1303 w, 1278 s, 1256 m, 1235 sh., 1197 m, 1164 m, 1151 sh., 1104 m, 1071 w, 899 m, 873 sh., 848 s, 837 sh., 774 m, 737 s, 691 s, 614 w, 512 m, 489 m, 469 w.

NMR: δ ^{1}H: 6.96-7.51 (m, 10H, ArH), 7.04-7.39 (d. of d., 8H, ArH).
δ ^{13}C: 88.27 (C≡C), 117.91, 118.356, 119.38, 123.76, 129.80, 133.05, 156.45, 157.45 (ArC)

2.3.3. Preparation of (4-phenoxyphenyl)acetylene. (4)

Freshly sublimed 4-iododiphenylether (7.4 g, 25 mmol) and trimethylsilylacetylene (4.25 ml, 2.95 g, 30 mmol; d = 0.685) were dissolved in diethylamine (50 ml) in a 100 ml round bottomed flask, flushed with nitrogen. Bis(triphenylphosphine)palladium(II) chloride (70 mg, 1 mmol) and copper(I) chloride (20 mg, 1.1 mmol) were dissolved in piperidine (4 ml) with heating to ca 60 °C. The resulting clear, orange solution was transferred without exposure to air to the reaction vessel and the yellow reaction mixture was stirred under acetylene for 6 hours. The acetylene flow was replaced with nitrogen and the reaction mixture stirred overnight. The solvents were removed under vacuum to afford an orange-brown residue which was taken up in diethylether and washed with 2M HCl (2x 50 ml), water (4 x 25 ml) and dried over $MgSO_4$. The solvents were removed under vacuum to afford a brown oil which was dissolved in methanol (10 ml) and 1M KOH solution (5 ml) was added. The solution was stirred for an hour at room temperature and then neutralised with 1M HCl (6 ml). The methanol was removed under vacuum and the resulting brown oil taken up in diethylether (25 ml) and washed in the manner described above. The solvents were removed and the brown-black oil was vacuum-transferred to afford an orange-yellow oil identified as (4-phenoxyphenyl)acetylene (**4**). Yield 4.74 g, 96%. The product was characterised as follows:

Analysis: Found; C, 85.94; H, 5.32%; M_r (mass spectrum) 193-196; $C_{14}H_{10}O$ requires C, 86.57; H, 5.19%; M_r 194-196.

I.R. $\nu_{max}cm^{-1}$: 3289 m (alkyne C-H), 3040 w (aromatic CH), 2108 w (C≡C), 1680 w, 1589 s (C-C), 1501 s, 1490 s, 1241 s (C-O-C asym.), 1199 m, 1165 w, 1103 w, 1071 w, 1023 sh., 871 m, 769 m, 692 w, 669 w, 530 m, 505 m.

NMR: δ ^{13}C: 77.4 (C≡C), 118.8, 120.1, 130.5, 134.4.
δ ^{1}H: 2.99 (s, 1H, C≡C-H), 6.85-7.43 (m, 9H, ArH).

General Reaction For The Preparation of *ortho*-Carborane Derivatives.

2.3.4. Preparation of 1,2-bis(4-phenoxyphenyl)-ortho-carborane (5).

Bis-(4-phenoxyphenyl)-acetylene (4.6 g, 12.7 mmol) was placed in a two-necked round bottomed flask, fitted with a condenser and flushed with nitrogen. Dry toluene (50 ml) was added forming a pale yellow solution, to which bis(dimethylsulphide)decaborane (4.8 g, 19 mmol) was added. The resulting milky white precipitate was heated to reflux forming a clear, yellow solution, which was stirred under nitrogen overnight. The solvent was removed under vacuum to afford a yellow oil, to which methanol (30 ml) was cautiously added affording a yellow solution and a white solid. This was refluxed for 5 hours and gas evolution was observed. The reaction mixture was allowed to cool to room temperature and the yellow precipitate was filtered off and recrystallised (ethanol), to afford 2.66 g (44%) of product identified as 1,2-bis-(4-phenoxyphenyl)-*ortho*-carborane (**5**), melting point 120-121.5 °C. The product was characterised as follows:

Analysis: Found; C, 64.33; H, 6.04%; M_r (mass spectrum) 476-482; $C_{26}B_{10}H_{28}O_2$ requires C, 65.0; H, 5.87%; M_r 472-484.

I.R. $\nu_{max}cm^{-1}$: 3040 w.sh. (aromatic CH), 2570 s (BH), 1605 sh., 1588 s, 1502 m, 1488 s, 1295 sh., 1287 m, 1252 s (C-O-C asym.), 1200 m, 1180 m, 1160 m, 1130 m, 1121 w, 1074 m, 1023 m, 1005 m, 905 m, 892 m, 882 m, 872 sh., 842 sh., 790 m, 753 s, 733 m, 717 m, 693 s, 581 m, 568 m, 525 m, 520 m, 484 m, 440 w.

NMR: δ ^{1}H: 1.0-3.8 (broad m., 10H, BH), 6.96-7.39 (m, 18H, ArH)
δ ^{13}C: 85.26 (carboranyl C), 125.01, 133.0, 119.80, 155.6, 159.30, 117.50, 129.30, 125.40 (Ar C).

δ ^{11}B: -2.87 (2B, B(9), B(12)), -10.67 (8B)

2.3.5. Preparation of 1,3,5-tris-1-(2-phenyl-*ortho*-carboranyl)-benzene (7).

1,3,5-triphenylethnylbenzene (1.5 g, 4.0 mmol) was placed in a two-necked round bottomed flask, fitted with a condenser and flushed with nitrogen. Dry toluene (50 ml) was added forming a pale yellow solution, to which bis(dimethylsulphide) decaborane (4.2 g, 17.0 mmol) was added. The resulting milky white precipitate was heated to reflux forming a yellow clear solution, which was stirred under nitrogen overnight. The solvents were removed under vacuum to afford a yellow-orange oil, to which methanol (30 ml) was cautiously added affording a yellow solution and a white solid. This was refluxed for 5 hours and gas evolution was observed. The reaction mixture was allowed to cool to room temperature and the white chalky precipitate was filtered off and recrystallised (1,2-dichlorobenzene), to afford 1.40 g (47%) of product identified as (**7**), melting point 359-361 °C. The product was characterised as follows:

Analysis: Found; C, 49.6, H, 6.49%; M_r (mass spectrum) 728-736; $C_{30}B_{30}H_{48}$ requires C, 49.2; H, 6.6%; M_r 708-741.

I.R. $\nu_{max}cm^{-1}$: 3061 w (carboranyl CH), 2636 sh., 2592 s, 2568 s (BH), 1598 m, 1495 m, 1447 s, 1118 m, 1068 m, 1001 w, 894 m, 807 w, 777 m, 757 m, 731 m, 689 s, 597 m.

NMR:

δ ^{13}C: 71.68, 73.31 (carboranyl C), 134.20, 134.95, 136.15, 136.57, 136.63, 137.20, 139.50 (ArC).

δ ^{1}H: 1.1-3.8 (broad m., 10H, BH), 3.1 (s, 1H, carboranyl C-H), 6.83-7.38 (multiplet, 9H, Ar-H).

δ ^{11}B: -2.64 (B 9.12), -9.11 (B 7, 11, 4, 5), -10.55 (B 8, 10), -11.30 (B 3,6).

X-ray Analysis (R.C.B. Copley and J.A.K. Howard, Durham University).

Crystallographic data, MoK_α radiation

Formula = $C_{30}H_{48}B_{30}$
Formula weight, M_r = 732.98
System = trigonal
Space group = R -3 (#148)
a = 20.082 (3) Å
b = 20.082 (3) Å
c = 18.049 (4) Å
α = 90.0°
β = 90.0°
γ = 120.0°
Unit cell volume, V = 6303.7 (Å^3)
Calculated density, D_c = 1.159 gcm^{-1}
Number of formulae per unit cell, Z = 6
Absorption coefficient, μ = 0.5 cm^{-1}
F(000) = 2268 electrons

Number of reflections used = 2379
2θ range = 6.0 - 50.0°
Range, *h* = -23 to 20
Range, *k* = 0 to 23
Range, *l* = 0 to 21

Measure of overall precision of data, R_{sigma} = 4.82
Crystal size = 0.25 x 0.25 x 0.30
Crystal colour = colourless
Temperature, T = 293 (K)

Bond Lengths (Å)

C(1) - C(2)	1.709 (2)	B(7) - B(11)	1.780 (3)
C(1) - B(3)	1.726 (2)	B(7) - B(12)	1.785 (3)
C(1) - B(4)	1.713 (2)	B(7) - H(7)	1.08 (2)
C(1) - B(5)	1.711 (2)	B(8) - B(9)	1.775 (3)
C(1) - B(6)	1.727 (2)	B(8) - H(8)	1.11 (2)
C(1) - C(101)	1.509 (2)	B(9) - B(10)	1.775 (3)
C(2) - B(3)	1.731 (2)	B(9) - B(12)	1.768 (3)
C(2) - B(6)	1.740 (2)	B(9) - H(9)	1.12 (2)
C(2) - B(7)	1.710 (2)	B(10) - B(11)	1.773 (3)
C(2) - B(11)	1.714 (2)	B(10) - B(12)	1.10 (2)
C(2) - C(201)	1.503 (2)	B(10) - H(10)	1.776 (3)
B(3) - B(4)	1.766 (2)	B(11) - B(12)	1.10 (2)
B(3) - B(7)	1.772 (2)	B(12) - H(12)	1.12 (2)
B(3) - B(8)	1.757 (3)	C(101) - C(102)	1.387 (2)
B(3) - H(3)	1.07 (2)	C(101) - C(102)	1.393 (2)
B(4) - B(5)	1.773 (3)	C(101) - H(102)	0.99 (2)
B(4) - B(8)	1.769 (3)	C(201) - C(202)	1.384 (2)
B(4) - B(9)	1.764 (3)	C(201) - C(206)	1.384 (2)
B(4) - H(4)	1.10 (2)	C(202) - C(203)	1.382 (3)
B(5) - B(6)	1.773 (3)	C(202) - H(202)	0.97 (2)
B(5) - B(9)	1.775 (3)	C(203) - C(204)	1.359 (3)
B(5) - B(10)	1.782 (3)	C(203) - H(203)	0.97 (2)
B(5) - H(5)	1.09 (2)	C(204) - C(205)	1.369 (3)
B(6) - B(10)	1.757 (3)	C(204) - H(204)	1.04 (2)
B(6) - B(11)	1.776 (3)	C(205) - C(206)	1.388 (3)
B(6) - H(6)	1.08 (2)	C(205) - H(205)	0.98 (2)
B(7) - B(8)	1.777 (3)	C(206) - H(206)	1.02 (2)

Bond angles (°)

C(2) - C(1) - B(3)	60.50 (9)	B(8) - B(4) - H(4)	126.4 (9)
C(2) - C(1) - B(4)	109.9 (1)	B(9) - B(4) - H(4)	128.1 (9)
B(3) - C(1) - B(4)	61.8 (1)	C(1) - B(5) - B(4)	58.9 (1)
C(2) - C(1) - B(5)	110.6 (1)	C(1) - B(5) - B(6)	59.40 (9)
B(3) - C(1) - B(5)	113.0 (1)	B(4) - B(5) - B(6)	107.7 (1)
B(4) - C(1) - B(5)	62.4 (1)	C(1) - B(5) - B(9)	105.2 (1)
C(2) - C(1) - B(6)	60.84 (9)	B(4) - B(5) - B(9)	59.6 (1)
B(3) - C(1) - B(6)	112.0 (1)	B(6) - B(5) - B(9)	107.2 (1)
B(4) - C(1) - B(6)	112.7 (1)	C(1) - B(5) - B(10)	105.3 (1)
B(5) - C(1) - B(6)	62.1 (1)	B(4) - B(5) - B(10)	107.4 (1)
C(2) - C(1) - C(101)	118.8 (1)	B(6) - B(5) - B(10)	59.2 (1)
B(3) - C(1) - C(101)	117.4 (1)	B(9) - B(5) - B(10)	59.9 (1)
B(4) - C(1) - C(101)	121.0 (1)	C(1) - B(5) - H(5)	116.2 (9)
B(5) - C(1) - C(101)	121.5 (1)	B(4) - B(5) - H(5)	120.9 (9)
B(6) - C(1) - C(101)	119.0 (1)	B(6) - B(5) - H(5)	117.5 (9)
C(1) - C(2) - B(3)	60.24 (9)	B(9) - B(5) - H(5)	129.9 (9)
C(1) - C(2) - B(6)	60.09 (9)	B(10) - B(5) - H(5)	127.5 (9)
B(3) - C(2) - B(6)	111.2 (1)	C(1) - B(6) - C(2)	59.07 (8)
C(1) - C(2) - B(7)	110.0 (1)	C(1) - B(6) - B(5)	58.51 (9)
B(3) - C(2) - B(7)	62.00 (9)	C(2) - B(6) - B(5)	106.3 (1)
B(6) - C(2) - B(7)	112.9 (1)	C(2) - B(6) - B(10)	105.7 (1)
C(1) - C(2) - B(11)	109.6 (1)	C(2) - B(6) - B(10)	105.6 (1)
B(3) - C(2) - B(11)	112.7 (1)	B(5) - B(6) - B(10)	60.6 (1)
B(6) - C(2) - B(11)	61.9 (1)	C(1) - B(6) - B(11)	106.0 (1)
B(7) - C(2) - B(11)	62.6 (1)	C(2) - B(6) - B(11)	58.4 (1)
C(1) - C(2) - C(201)	118.8 (1)	B(5) - B(6) - B(11)	108.9 (1)
B(3) - C(2) - C(201)	119.1 (1)	B(10) - B(6) - B(11)	60.3 (1)
B(6) - C(2) - C(201)	117.6 (1)	C(1) - B(6) - H(6)	118.4 (8)
B(7) - C(2) - C(201)	121.9 (1)	C(2) - B(6) - H(6)	118.7 (8)
B(11) - C(2) - C(201)	121.2 (1)	B(5) - B(6) - H(6)	122.9 (8)
C(1) - B(3) - C(2)	59.25 (8)	B(10) - B(6) - H(6)	128.6 (8)
C(1) - B(3) - B(4)	58.74 (9)	B(11) - B(6) - H(6)	123.7 (8)
C(2) - B(3) - B(4)	106.5 (1)	C(2) - B(7) - B(3)	59.58 (9)
C(1) - B(3) - B(7)	106.3 (1)	C(2) - B(7) - B(8)	105.8 (1)
C(2) - B(3) - B(7)	58.41 (9)	B(3) - B(7) - B(8)	59.3 (1)
B(4) - B(3) - B(7)	108.7 (1)	C(2) - B(7) - B(11)	58.8 (1)
C(1) - B(3) - B(8)	105.9 (1)	B(3) - B(7) - B(11)	107.7 (1)
C(2) - B(3) - B(8)	105.8 (1)	B(8) - B(7) - B(11)	107.7 (2)
B(4) - B(3) - B(8)	60.3 (1)	C(2) - B(7) - B(12)	105.3 (1)
B(7) - B(3) - B(8)	60.5 (1)	B(3) - B(7) - B(12)	106.9 (2)
C(1) - B(3) - H(3)	117.6 (8)	B(8) - B(7) - B(12)	59.7 (1)
C(2) - B(3) - H(3)	119.0 (1)	B(11) - B(7) - B(12)	59.8 (1)
B(4) - B(3) - H(3)	122.2 (9)	C(2) - B(7) - H(7)	115.9 (10)
B(7) - B(3) - H(3)	124.5 (9)	B(3) - B(7) - H(7)	116.8 (9)
B(8) - B(3) - H(3)	128.6 (8)	B(8) - B(7) - H(7)	126.7 (9)
C(1) - B(4) - B(3)	59.48 (9)	B(11) - B(7) - H(7)	121.6 (9)
C(1) - B(4) - B(5)	58.76 (9)	B(12) - B(7) - H(7)	130.5 (9)
B(3) - B(4) - B(5)	108.2 (1)	B(3) - B(8) - B(4)	60.1 (1)
C(1) - B(4) - B(8)	105.9 (1)	B(3) - B(8) - B(7)	60.2 (1)
B(3) - B(4) - B(8)	59.6 (1)	B(4) - B(8) - B(7)	108.4 (1)
B(5) - B(4) - B(8)	108.7 (1)	B(3) - B(8) - B(9)	107.7 (1)
C(1) - B(4) - B(9)	105.6 (1)	B(4) - B(8) - B(9)	59.6 (1)
B(3) - B(4) - B(9)	108.0 (1)	B(7) - B(8) - B(9)	108.1 (1)
B(5) - B(4) - B(9)	60.3 (1)	B(3) - B(8) - B(12)	108.1 (1)
B(8) - B(4) - B(9)	60.5 (1)	B(4) - B(8) - B(12)	107.6 (1)
C(1) - B(4) - H(4)	117.2 (9)	B(7) - B(8) - B(12)	60.3 (1)
B(3) - B(4) - H(4)	118.3 (9)	B(9) - B(8) - B(12)	59.7 (1)
B(5) - B(4) - H(4)	120.0 (9)	B(3) - B(8) - H(8)	118.3 (9)

Bond angles (°) continued.

B(4) - B(8) - H(8)	119.2 (9)	C(2) - B(11) - H(11)	117.1 (9)
B(7) - B(8) - H(8)	121.6 (9)	B(6) - B(11) - H(11)	119.5 (9)
B(9) - B(8) - H(8)	123.8 (9)	B(7) - B(11) - H(11)	119.3 (9)
B(12) - B(8) - H(8)	125.5 (9)	B(10) - B(11) - H(11)	127.3 (9)
B(4) - B(9) - B(5)	60.1 (1)	B(12) - B(11) - H(11)	127.7 (9)
B(4) - B(9) - B(8)	59.9 (1)	B(7) - B(12) - B(8)	59.9 (9)
B(5) - B(9) - B(8)	108.2 (1)	B(7) - B(12) - B(9)	108.2 (1)
B(4) - B(9) - B(10)	108.1 (1)	B(8) - B(12) - B(9)	60.3 (1)
B(5) - B(9) - B(10)	60.3 (1)	B(7) - B(12) - B(10)	108.0 (1)
B(8) - B(9) - B(10)	107.9 (2)	B(8) - B(12) - B(10)	108.2 (1)
B(4) - B(9) - B(12)	108.1 (2)	B(9) - B(12) - B(10)	60.2 (1)
B(5) - B(9) - B(12)	108.5 (1)	B(7) - B(12) - B(11)	60.0 (1)
B(8) - B(9) - B(12)	60.0 (1)	B(8) - B(12) - B(11)	107.9 (1)
B(10) - B(9) - B(12)	60.0 (1)	B(9) - B(12) - B(11)	108.2 (1)
B(4) - B(9) - H(9)	120.1 (9)	B(10) - B(12) - B(11)	60.0 (1)
B(5) - B(9) - H(9)	121.0 (10)	B(7) - B(12) - H(12)	119.9 (10)
B(8) - B(9) - H(9)	121.0 (10)	B(8) - B(12) - H(12)	122.0 (9)
B(10) - B(9) - H(9)	123.1 (10)	B(9) - B(12) - H(12)	123.5 (10)
B(12) - B(9) - H(9)	122.7 (9)	B(10) - B(12) - H(12)	1226. (10)
B(5) - B(10) - B(6)	60.1 (1)	B(11) - B(12) - H(12)	120.2 (9)
B(5) - B(10) - B(9)	59.9 (1)	C(1) - C(101) - C(102)	121.6 (1)
B(6) - B(10) - B(9)	107.9 (1)	C(1) - C(101) - C(102)	119.0 (1)
B(5) - B(10) - B(11)	108.6 (1)	C(102) - C(101) - C(102)	119.4 (1)
B(6) - B(10) - B(11)	60.4 (1)	C(101) - C(102) - C(101)	120.6 (1)
B(9) - B(10) - B(11)	108.0 (2)	C(101) - C(102) - H(102)	120.2 (8)
B(5) - B(10) - B(12)	108.0 (1)	C(101) - C(101) - H(102)	119.2 (8)
B(6) - B(10) - B(12)	108.3 (2)	C(2) - C(201) - C(202)	120.8 (1)
B(9) - B(10) - B(12)	59.8 (1)	C(2) - C(201) - C(206)	121.3 (1)
B(11) - B(10) - B(12)	60.1 (1)	C(202) - C(201) - C(206)	118.0 (2)
B(5) - B(10) - H(10)	119.0 (10)	C(201) - C(202) - C(203)	120.9 (2)
B(6) - B(10) - H(10)	118.8 (9)	C(201) - C(202) - H(202)	117.3 (11)
B(9) - B(10) - H(10)	123.0 (10)	C(203) - C(202) - H(202)	121.7 (11)
B(11) - B(10) - H(10)	122.2 (10)	C(202) - C(203) - C(204)	120.8 (2)
B(12) - B(10) - H(10)	125.0 (9)	C(202) - C(203) - H(203)	119.8 (12)
C(2) - B(11) - B(6)	59.77 (9)	C(204) - C(203) - H(203)	119.4 (12)
C(2) - B(11) - B(7)	58.6 (1)	C(203) - C(204) - C(205)	119.2 (2)
B(6) - B(11) - B(7)	107.9 (1)	C(203) - C(204) - H(204)	120.3 (11)
C(2) - B(11) - B(10)	105.9 (1)	C(205) - C(204) - H(204)	120.6 (11)
B(6) - B(11) - B(10)	59.3 (1)	C(204) - C(205) - C(206)	120.9 (2)
B(7) - B(11) - B(10)	108.2 (1)	C(204) - C(205) - H(205)	120.1 (14)
C(2) - B(11) - B(12)	105.5 (1)	C(206) - C(205) - H(205)	118.9 (14)
B(6) - B(11) - B(12)	107.3 (1)	C(201) - C(206) - C(205	120.3 (2)
B(7) - B(11) - B(12)	60.3 (1)	C(201) - C(206) - H(206)	118.9 (11)
B(10) - B(11) - B(12)	59.9 (1)	C(205) - C(206) - H(206)	120.6 (11)

2.3.6 Preparation of 1,4 bis-(*ortho*-carboranyl)benzene (8).

This was prepared and isolated according to the general reaction procedure described above, (Section 2.3.4), by treating bis(dimethylsulphide)-decaborane (5.4 g, 22 mmol) with 1,4 diethynylbenzene (1.02 g, 8.1 mmol). The resulting yellow solid was recrystallised (ethanol) to afford white crystals identified as (**8**). Yield 1.90 g, 65%; melting point 188-190 °C. The product was characterised as follows:

Analysis: Found; C, 33.8, H, 7.05%; M_r (mass spectrum) 351-366; $C_{10}B_{20}H_{26}$ requires C, 33.1; H, 7.2%; M_r 346-367.

I.R. $\nu_{max}cm^{-1}$: 3072 s (Aromatic CH), 2648 m, 2625 s (BH), 2600 s, 2579 s, 2558 s, 1507 m (Ar skel.), 1407 m, 1261 m, 1072 m, 1035 m, 1001 m, 873 w, 847 m, 801 m, 718 m, 645 m (cage vibration), 571 m, 504 m.

2.3.7. Preparation of 1-(4-phenoxyphenyl)-*ortho*-carborane (9).

This was prepared and isolated according to the general reaction procedure above, (Section 2.3.4), by treating bis(dimethylsulphide)-decaborane (3.2 g, 13 mmol) with (4-phenoxyphenyl) acetylene (2.5 g, 13.0 mmol). The resulting white solid was recrystallised (hexane) to afford white crystals identified as 1-(4-phenoxyphenyl)-*ortho*-carborane (**9**). Yield 2.80 g (69%), melting point 92-93 °C. The product was characterised as follows:

Analysis: Found; C, 53.21, H, 6.03%; M_r (mass spectrum) 309-314; $C_{14}B_{10}H_{20}O$ requires C, 53.8; H, 6.50%; M_r 304-315.

I.R. $\nu_{max}cm^{-1}$: 3062 s (Aromatic CH), 2580 s (BH), 2550 m, 1607 w, 1558 m (C-C), 1510 s, 1482 m (Ar skel.), 1467 m, 1409 m, 1375 m, 1312 sh., 1305 w, 1263 s (C-O-C), 1201 s, 1170 m, 1114 m, 1079 m, 1038 m, 1003 m, 910 m, 881 m, 852 m, 841 m, 794 w, 775 s, 693 m, 689 s (cage vibration), 575 m, 507 m, 485 m.

NMR: δ ^{1}H: 1.0-4.5 (broad multiplet, 11H, B<u>H</u>), 3.05 (s, 1H, carboranyl C-<u>H</u>), 6.83-7.38 (multiplet, 9H, aromatic protons)
δ ^{13}C: 58.5 (carboranyl CH), 79.5 (carboranyl C-Ar), 117.50, 119.80, 125.01, 125.40, 129.30, 133.0, 155.6, 159.30, (Ar C).

2.3.8. Preparation of 1,2-diphenyl-*ortho*-carborane (10).

This was prepared and isolated according to the general reaction procedure described above, (Section 2.3.4), by treating bis(dimethylsulphide)-decaborane (1.56 g, 6.3 mmol) with diphenylacetylene (1.15 g, 6.5 mmol). The resulting yellow solid was recrystallised (hexane) to afford white crystals identified as (**10**). Yield 1.87 g, 65%; melting point 146.5-148 °C. The product was characterised as follows:

Analysis: Found; C, 56.03, H, 6.45%; M_r (mass spectrum) 285-299; $C_{14}B_{10}H_{20}$ requires C, 56.7; H, 6.8%; M_r 288-299.

I.R. $\nu_{max}cm^{-1}$: 3055 w (aromatic CH),2634 m, 2564 s (BH), 1575 m (C-C, 1491 sh. (Ar skel.), 1446 m (Ar ip. deformation) , 1075 m, 1001 m, 921 w, 889 w, 869 w, 804 w, 780 m, 755 m, 689 m (cage vibration), 581 m (Ar-H wag), 473 m.

NMR: δ ^{13}C: 86.0 (carboranyl C), 117.8, 128.7, 130.6, 131.1.
δ ^{1}H: 0.9-3.7 (broad mulitplet, 5H, BH), 7.1-7.4 (m., 4H, Ar-H).

2.3.9. Preparation of 1-*meta*-carboranyl-2,4-dichloro-1,3,5-triazine (11).

Freshly sublimed 1,7-dicarba-*closo*-dodecaborane (1.45 g, 10 mmol) was dissolved in dry 1,2-dimethoxymethane (50 ml) in a 100 ml round bottomed flask and flushed with nitrogen. n-Butyllithium (6.6 ml, 1.6 M in hexanes, 11 mmol) was added to the clear, colourless solution. The solution was cooled to -20 °C and 2,4,6-trichloro-1,3,5-triazene (2.21 g, 12 mmol) was added to the reaction flask forming a red-orange colour. The reaction mixture was allowed to warm to room temperature and stirred under nitrogen overnight. The red-brown suspension was diluted with dichloromethane (100 ml) and filtered. The filtrate was washed with 2M HCl (4 x 25 ml), water (4 x 50 ml), dried over $MgSO_4$ and evaporated to afford a white solid. This was purified by column chromatography (cyclohexane/dichloromethane, 1:2) to afford a white solid which was identified as 1-*meta*-carboranyl-2,4-dichloro-1,3,5-triazine (**11**). Yield 2.25 g, 77%. The product was characterised as follows:

Analysis: M_r (mass spectrum) 285-292; $C_5B_{10}H_{11}N_3Cl_2$ requires M_r 283-289.

I.R. $\nu_{max}cm^{-1}$: 3060 w (carborany CH), 2960 w, 2606 s (BH), 1720 w, 1515 s, 1362 s, 1273 s, 1159 w, 1099 m, 1022 m, 907 w, 859 m, 801 m, 722 m, 618 w.

2.3.10. Preparation of 2,4,6-*para*-carboranyl-1,3,5-triazine (12).

The product was prepared and isolated according to the general reaction procedure described above, (Section 2.3.9), by the reaction of *para*-carborane (1.44 g, 10 mmol) with 2,4,6-trichloro-1,3,5-triazene (0.553 g, 3 mmol). The isolated product was identified as 2,4,6-*para*-carboranyl-1,3,5-triazine (**12**), yield 1.03 g, 68%. The product was characterised as follows:

Analysis: M_r (mass spectrum) 503-512; $C_9B_{30}H_{33}N_3$ requires M_r 483-514.

I.R. $\nu_{max}cm^{-1}$: 3059 w (carboranyl CH), 2957 w, 2923 w, 2609 s (BH), 1532 s, 1464 sh., 1367 m, 1261 w, 1163 w, 1089 s, 1063 m, 899 w, 717 s, 627 w, 436 w.

2.3.11. Preparation of 2,4,6-*meta*-carboranyl-1,3,5-triazine (13).

The product was prepared and isolated according to the general reaction procedure described above, (Section 2.3.9), by the reaction of *meta*-carborane (1.44 g, 10 mmol) with 2,4,6-trichloro-1,3,5-triazene (0.553 g, 3 mmol). The isolated product was identified as 2,4,6-*meta*-carboranyl-1,3,5-triazine (**13**), yield 0.853 g, 56%. The product was characterised as follows:

Analysis: M_r (mass spectrum) 502-512; $C_9B_{30}H_{33}N_3$ requires M_r 483-514.

I.R. $\nu_{max}cm^{-1}$: 3062 m (carboranyl CH), 2923 w, 2923 w, 2603 s (BH), 1533 s, 1368 m, 1261 w, 1160 w, 1069 s, 1024 m, 926 w, 859 w, 803 w, 718s , 616 w, 406 w.

General Reaction For The Preparation of *ortho*-, *meta*- and *para*-Carborane Derivatives via Their Copper(I) Derivatives.

2.3.12. Preparation of 1-(3,5-dichlorophenyl)-*ortho*-carborane (14).

Freshly sublimed 1,2-dicarba-*closo*-dodecaborane (1.45 g, 10 mmol) was dissolved in 1,2-dimethoxyethane (50 ml) in a 100 ml round bottomed flask fitted with a condenser and flushed with nitrogen. n-Butyllithium (6.6 ml, 1.6 M in hexanes, 11 mmol) was added to the clear, colourless solution. The solution was allowed to cool to room temperature and pyridine (3 ml) was added forming a yellow solution. to which copper (I) chloride (1.01 g, 10 mmol) was added. The resulting brown-black suspension was stirred at room temperature for 20 minutes. Freshly sublimed 1,3-dichloro-5-iodobenzene (2.74 g, 11 mmol) was added to the reaction flask and the reaction mixture was heated to reflux under nitrogen for 48 hours. The reaction mixture was allowed to cool to room temperature and diluted with diethylether (100 ml) forming a brown precipitate which was stirred at room temperature for 2 hours. The precipitate was filtered off and washed with ether (30 ml). The combined ethereal solutions were washed with 2M HCl (4 x 25 ml), water (4 x 50 ml), dried over $MgSO_4$ and evaporated to afford an orange oil. This was purified by column chromatography (cyclohexane + 5% ethyl acetate) to afford yellow-orange crystals which were recrystallised (propan-2-ol) to afford white crystals, identified as 1-(3,5-dichlorophenyl)-*ortho*-carborane (**14**). Yield 2.25 g, 78%; melting point 137-138.5 °C. The product was characterised as follows:

Analysis: Found; C, 33.34, H, 4.55%; M_r (mass spectrum) 281-292; $C_8B_{10}H_{14}Cl_2$ requires C, 33.13; H, 4.87%; M_r 279-293 .

I.R. $\nu_{max}cm^{-1}$: 3064 w (carboranyl CH), 3013 w (aromatic CH) 2612 s, (BH), 1737 w, 1652 w 1588 m (C–C), 1576 s., 1439 s. (Ar skel.), 1415 m, 1386 m, 1260 m, 1109 sh., 1098 s, 1021 sh., 892 w, 864 m, 822 m (1,3,5 trisub.-aromatic), 807 sh., 717 w, 669 s (cage vibration), 616 w, 433 w.

2.3.13. Preparation of bis 1,7-(3-chlorophenyl)-*meta*-carborane (15).

The product was prepared and isolated according to the general reaction procedure described above, (Section 2.3.11), by the reaction of *meta*-carborane (1.44 g, 10 mmol) with freshly sublimed 1-chloro-3-iodobenzene (5.15 g, 22 mmol), to afford an orange solid. This was recrystallised (propan-2-ol) to afford white crystals, identified as 1,7-bis-(3-chlorophenyl)-*meta*-carborane (**15**). Yield 2.35 g, 64%; melting point 118-120.5 °C. The product was characterised as follows:

Analysis: Found; C, 46.05, H, 5.04%; M_r (mass spectrum) 355-370; $C_{14}B_{10}H_{18}Cl_2$ requires C, 46.09; H, 4.97%; M_r 356-371.

I.R. $\nu_{max}cm^{-1}$: 3013 w (aromatic CH) 2611 s, 2588 s, 2564 sh., (BH), 1676 s 1593 s (C-C), 1570 sh., 1477 s. (Ar skel.), 1417 s, 1170 s, 1105 s, 903 s, 809 s, 762 s, 726 m (cage vibration), 680 m (m-C_6H_4 o.o.p), 423 m.,

NMR: δ ^1H: 1.1-3.0 (broad m., 10H, BH), 7.19-7.46 (m., 8H, Ar-H).
δ ^{13}C: 78.2 (carborane C), 126.6, 128.6, 129.6, 130.1, 132.5 (Ar-C)

2.3.14. Preparation of bis 1,7-(4-chlorophenyl)-*meta*-carborane (16)

The product was prepared and isolated according to the general reaction procedure described above, (Section 2.3.11), by the reaction of *meta*-carborane (1.44 g, 10 mmol) with resublimed 4-chloroiodobenzene (4.801 g, 20 mmol). The isolated product was chromatographed to give the product identified as 1,7-bis-(4-chlorophenyl)-*meta*-carborane (**16**) (2.914 g, cyclohexane, 20% ethyl acetate), yield 2.59 g, 71%, m.p. 135-136.5 °C (ethanol). The product was characterised as follows:

Analysis: Found; C, 46.26, H, 5.03%; M_r (mass spectrum) 361-368; $C_{14}B_{10}H_{18}Cl_2$ requires C, 46.09; H, 4.97%; M_r 356-371.

I.R. $\nu_{max}cm^{-1}$: 3066 m (aromatic CH) 2638 m, 2611 s, 2565 s, (BH), 1651 w, 1595 w, 1494 s. (Ar skel.), 1104 m, 1075 m, 1017 m, 836 s (p-C_6H_4 o.o.p.), 740 m (cage vibration), 514 m, 493 m, 464 m.

NMR: δ ^{1}H: 1.2-3.01 (broad mulitplet, 5H, BH), 7.23-7.4 (multiplet, 4H, Ar-H).
δ ^{13}C: 77.7 (carborane C-Ar), 129.1, 126.6, 134.1, 135.7 (ArC)
δ ^{11}B: -6.02, -11.5, -13.4

2.3.15. Preparation of 1-(3,5-dichlorophenyl)-*meta*-carborane (17).

The product was prepared and isolated according to the general reaction procedure described above, (Section 2.3.11), by the reaction of *meta*-carborane (1.44 g, 10 mmol) with resublimed 1,3-dichloro-5-iodobenzene (2.74 g, 10 mmol), to afford an orange solid. This was purified by column chromatography (cyclohexane + 5% ethyl acetate) to afford yellow-orange crystals which were recrystallised (propan-2-ol) to afford white crystals, identified as 1-(3,5-dichlorophenyl)-*meta*-carborane (**17**). Yield 2.57 g, 89%; melting point 214-217 °C. The product was characterised as follows:

Analysis: Found; C, 33.55, H, 4.65%; $C_8B_{10}H_{14}Cl_2$ requires C, 33.13; H, 4.87%;

I.R. $\nu_{max}cm^{-1}$: 3064 w (carboranyl CH), 3013 w (aromatic CH) 2612 s, (BH), 1737 w, 1652 w 1588 m (C–C), 1576 s., 1439 s. (Ar skel.), 1415 m, 1386 m, 1260 m, 1109 sh., 1098 s, 1021 sh., 892 w, 864 m, 822 m (1,3,5 trisub.-aromatic), 807sh., 717 w, 669 s (cage vibration), 616 w, 433 w.

NMR: δ ^{1}H: 0.5-4.0 (broad m., 10H, BH), 7.30 (s, 1H), 7.33 (s, sH, Cl-C-C<u>H</u>)
δ ^{13}C: 55.70 (carboranyl CH), 78.24 (carboranyl C-Ar), 127.01, 128.5, 129.73, 135.70

2.3.16. Preparation of 1,7-bis-(3-bromophenyl)-*meta*-carborane (18).

The product was prepared and isolated according to the general reaction procedure described above, (Section 2.3.11), by the reaction of *meta*-carborane (1.44 g, 10 mmol) with 1-bromo-3-iodobenzene (6.20 g, 22 mmol), to afford an orange solid.

This was recrystallised (propan-2-ol) to afford white crystals, identified as 1,7-bis-(3-bromophenyl)-*meta*-carborane (**18**). Melting point 118-120.5 °C, yield 3.26 g 72%; The product was characterised as follows:

Analysis: Found; C, 37.33, H, 3.99%; M_r (mass spectrum) 446-458; $C_{14}B_{10}H_{18}Br_2$ requires C, 37.20; H, 4.01%; M_r 452-467

I.R. $\nu_{max}cm^{-1}$: 3062 m, 2599 s, 1593 m, 1558 s, 1474 s, 1452 s, 1415 s, 1408 m, 1120 sh., 1089 m, 1074 s, 997 m, 886 s, 807 m, 770 s, 737 m, 709 s, 679 s, 670 s, 429 m.

NMR: δ ^{11}B: -2.74, -9.93.

2.3.17. Preparation of 1,7-bis(4-methylphenyl)-*meta*-carborane (19).

The product was prepared and isolated according to the general reaction procedure described above, (Section 2.3.11), by the reaction of *meta*-carborane (1.44 g, 10 mmol) with freshly sublimed 4-iodotoluene (2.38 g, 10 mmol) under nitrogen for 48 hours, to afford an orange oil. This was purified by column chromatography (cyclohexane + 5% ethyl acetate) to afford a cream solid which was recrystallised (ethanol) to yield white crystals, identified as 1,7-bis-(4-tolyl)-*meta*-carborane (**19**). Yield 81%; melting point 138-140 °C. The product was characterised as follows:

Analysis: Found; C, 59.55 H, 7.12%; M_r (mass spectrum) 323-327; $C_{16}B_{10}H_{24}$ requires C, 59.08; H, 7.43%; M_r 322-333

I.R. $\nu_{max}cm^{-1}$: 3034 w, 2967 w, 2924 w, 2857 w, 2613 sh., 2604 s (BH), 2576 s, 1510 m, 1409 m, 1188 m, 1127 w, 1078 m, 857 m, 826 s, 783 m, 737 m, 707 m, 553 w, 711 m, 492 m.

NMR: δ ^{1}H: 0.8-4.0 (broad m., 10H, BH), 2.30 (s, 6H, C$\underline{H}_3$), 7.03-7.07 (d, 4H, ArH), 7.32-7.36 (d, 4H, ArH)
δ ^{13}C: 20.88 (C$\underline{H}_3$), 78.10 (carboranyl C), 127.67, 129.03, 132.51, 138.69 (ArC)
δ ^{11}B: -5.72 (2B, B(5,12)), -10.30 (6B, B(4,6,8,11,9,10), -12.74 (2B, B(2,3))

2.3.18. Preparation of 1,7-bis-(4-nitrophenyl)-*meta*-carborane (20).

The product was prepared and isolated according to the general reaction procedure described above, (Section 2.3.11), by the reaction of *meta*-carborane (1.44 g, 10 mmol) with freshly sublimed 1-nitro-4-iodobenzene (5.48 g, 22 mmol), to afford an orange solid. This was recrystallised (propan-2-ol) to afford white crystals, identified as 1,7-bis-(4-nitrophenyl)-*meta*-carborane (**20**). Yield 1.47 g 38%. The product was characterised as follows:

Analysis: Found; C, 43.31, H, 4.99, N, 6.98%; M_r (mass spectrum) 381-388; $C_{14}B_{10}H_{18}N_2O_4$ requires C, 43.54; H, 4.70, N, 7.25 %; M_r 386-397.

I.R. $\nu_{max}cm^{-1}$: 3024 w, 2603 s (BH), 1613 s, 1519 m, 1317 m (NO_2), 1211 m, 1048 m, 737 s, 689 m, 434 w.

NMR: δ ^{11}B: -5.35, -10.10, -13.48.

A second product was isolated and characterised as the monosubstituted product (**21**).

Analysis: Found; C, 35.75, H, 5.58, N, 5.06%; M_r (mass spectrum) 261-268; $C_8B_{10}H_{15}NO_2$ requires C, 36.26; H, 5.70, N, 5.28 %; M_r 265-275.

NMR: δ^1 H: 1.5-3.5 (br.m, 11H, BH), 3.15, (s, 1H, carboranyl CH), 7.6-8.25 (doublet of doublets, 4H, ArH).
δ ^{11}B: -4.24 (1B), -8.19 (1B), -10.45 (4B), -13.31 (2B), -15.37 (2B).

2.3.19. Preparation of 1,7-bis-(3-nitrophenyl)-*meta*-carborane (22).

The product was prepared and isolated according to the general reaction procedure described above, (Section 2.3.11), by the reaction of *meta*-carborane (1.44 g, 10 mmol) with 1-nitro-3-iodobenzene (5.48 g, 22 mmol), to afford an orange solid. This was recrystallised (propan-2-ol) to afford white crystals, identified as 1,7-bis-(4-nitrophenyl)-*meta*-carborane (**22**). Yield 0.98 g 26%. The product was characterised as follows:

Analysis: Found; C, 47.23, H, 5.67, N, 7.64%; M_r (mass spectrum) 382-389 $C_{14}B_{10}H_{18}N_2O_4$ requires C, 47.18; H, 5.65, N, 7.86 %; M_r 386-397.

I.R. $\nu_{max}cm^{-1}$: 3013 w, 2617 s (BH), 1528 s, 1350 s (NO_2) 1286 m, 1103 m, 907 m, 811 m, 734 m (cage vibration), 689 m, 672 m.

NMR: δ ^{13}C: 76.10 (carboranyl C), 122.87, 123.68, 129.55, 133.76, 135.70, 148.05 (ArC)

2.3.20.Preparation of 1-(4-phenoxyphenyl)-*meta*-carborane (23).

The product was prepared and isolated according to the general reaction procedure described above, (Section 2.3.11), by the reaction of *meta*-carborane (1.45 g, 10 mmol) with freshly sublimed 4-iododiphenylether (2.98 g, 11 mmol), to afford an orange oil. This was purified by column chromatography (hexane) to yield white crystals, recrystallised from ethanol and identified as 1-(4-phenoxyphenyl)-*meta*-carborane (**23**). Yield 2.29 g, 73%; melting point 86-88 °C. The product was characterised as follows:

Analysis: Found; C, 54.39, H, 6.40%; M_r (mass spectrum) 306-314; $C_{14}B_{10}H_{20}O$ requires C, 53.83; H, 6.46%; M_r 304-315.

I.R. $\nu_{max}cm^{-1}$: 3057 m (carboranyl CH), 3013 w (aromatic CH) 2648 sh., 2605 s (BH), 1612 m 1590 s (C-C), 1508 m, 1489 m. (Ar skel.), 1411 w, 1264 s, 1247 s (C-O), 1202 m, 1175 m, 1162 w, 1079 w, 898 m, 853 m (p-C_6H_4 o.o.p), 752 m (p-C_6H_5 o.o.p), 729 m (cage vibration), 690 m (p-C_6H_5 o.o.p), 576 m, 423 w.

NMR: δ ^{1}H: 1.1-3.8 (broad multiplet, 10H, BH), 3.1 (singlet, 1H, carborane CH), 6.83-7.38 (multiplet, 9H, Ar-H).

δ ^{13}C: 55.6 (carboranyl CH), 79.5 (carboranyl C-Ar), 118.2, 119.0, 122.3, 129.7, 130.4, 133.1, 155.6, 159.30 (Ar-C)

2.3.21. Preparation of 1,7-bis-(2-chloro-4-methylphenyl)-*meta*-carborane (24).

The product was prepared and isolated according to the general reaction procedure described above, (Section 2.3.11), by the reaction of *meta*-carborane (1.44 g, 10 mmol) with freshly sublimed 2-chloro-4-iodotoluene (5.57 g, 22 mmol), to afford an orange solid. This was purified by chromatography (cyclohexane/5% ethyl acetate) and recrystallised (propan-2-ol) to afford white crystals, identified as 1,7-(2-chlorotolyl)-*meta*-carborane (**24**). Yield 2.21 g, 56%; melting point 109-111 °C. The product was characterised as follows:

Analysis: Found; C, 49.72, H, 5.64 %; M_r (mass spectrum) 388-398; $C_{16}B_{10}H_{22}Cl_2$ requires C, 49.86; H, 5.75%; M_r 385-400

2.3.22. Preparation of 1,-(4-chlorophenyl)-*meta*-carborane (25).

The product was prepared and isolated according to the general reaction procedure described above, (Section 2.3.11), by the reaction of *meta*-carborane (1.44 g, 10 mmol) with freshly sublimed 1-chloro-4-iodobenzene (2.38 g, 10 mmol) under nitrogen for 48 hours, to afford an orange oil. This was purified by column chromatography (cyclohexane + 5% ethyl acetate) to afford a cream solid which was recrystallised (propan-2-ol) to yield white crystals, identified as 1-(4-chlorophenyl)-*meta*-carborane (**25**). Yield 2.27 g, 89%; melting point 82-85 °C. The product was characterised as follows:

Analysis: Found; C, 38.02, H, 5.88%; Mr (mass spectrum) 254; $C_8B_{10}H_{15}Cl$ requires C, 37.72; H, 5.93%; Mr 246-258

I.R. $\nu_{max}cm^{-1}$: 3056 w (carboranyl CH), 3013 w (aromatic CH) 2602 s, (BH), 1590 s (C–C), 1496 s. (Ar skel.), 1401 m, 1261 m, 1189 w, 1122 w, 1101 m (Ar-Cl), 1078 m, 1039 m, 1015 s, 972 w, 875 m, 836 s, 733 m (cage vibration), 572 w, 499 m, 464 m.

2.3.23. Preparation of 1,7-bis-(4-phenoxyphenyl)-*meta*-carborane (26).

The product was prepared and isolated according to the general reaction procedure described above, (Section 2.3.11), by the reaction of *meta*-carborane (1.50 g, 10.6 mmol) with resublimed 4-iododiphenylether (6.30 g, 21 mmol). The isolated product was chromatographed, (cyclohexane/20% ethyl acetate) to give the product identified as 1,7-bis-(4-phenoxyphenyl)-*meta*-carborane (**26**) 3.85 g, (75%), m.p. 111-112 °C from propan-2-ol. The product was characterised as follows:

Analysis: Found; C, 65.63, H, 6.01%; M_r (mass spectrum) 476-484; $C_{26}B_{10}H_{28}O_2$ requires C, 65.0; H, 5.87%; M_r 470-484.

I.R. $\nu_{max}cm^{-1}$: 3013 w (aromatic CH) 2648 s, 2618 s, 2602 s (BH), 1590 s (C-C), 1506 s, 1490 s. (Ar skel.), 1450 m, 1411 m (Ar skel.), 1254 s, 1243 s (C-O), 1233 m, 1204 m, 1175 m, 1162 m, 1079 m, 1072 m, 900 m, 875 m 862 m (p-C_6H_4 o.o.p), 752 m (p-C_6H_5 o.o.p), 690 m (p-C_6H_5 o.o.p), 520 m, 485 m.

NMR: δ ^{1}H: 1.1-3.9 (broad mulitplet, 10H, BH), 6.82-7.42 (multiplet, 9H, Ar-H).
δ ^{13}C: 77.8 (carborane C), 118.3, 120.0, 124.5, 129.8, 129.9, 130.4, 156.2, 158.1,(ArC)
δ ^{11}B: -5.87 (2B, (B5, B12)), -10.20 (8B)

2.3.24. Preparation of 1,12-bis-(4-chlorophenyl)-*para*-carborane (27).

The product was prepared and isolated according to the general reaction procedure described above, (Section 2.3.11), by the reaction of *para*-carborane (1.44 g, 10 mmol) with freshly sublimed 1-chloro-4-iodobenzene (5.24 g, 22 mmol), for 4 days, to afford an orange solid. This was purified by column chromatography (eluting with cyclohexane) and recrystallised (propan-2-ol) to afford white crystals, identified as 1,12-bis-(4-chlorophenyl)-*para*-carborane (**26**). Yield 2.44 g, 67%; melting point 233-234 °C. The product was characterised as follows:

Analysis: Found; C, 45.01, H, 4.82%; M_r (mass spectrum) 360-370; $C_{14}B_{10}H_{18}Cl_2$ requires C 46.03; H 4.97%; M_r 365-380

I.R. $\nu_{max}cm^{-1}$: 3089 w, 3067 w, 2604 vs, 190 1w, 1712 w, 1656 w, 1589 w, 1488 s, 1397 m, 1261 w, 1183 w, 1073 m, 1012 m, 912 m, 832 s, 750 m, 598 w, 491 s.

NMR: δ ^1H: 1.0-4.0 (broad m., 10H, BH), 7.12-7.15 (d. of d., 8H, ArH)

2.3.25. Preparation of 1,12-bis-(3-chlorophenyl)-*para*-carborane (28).

The product was prepared and isolated according to the general reaction procedure described above, (Section 2.3.11), by the reaction of *para*-carborane (1.44 g, 10 mmol) with 1-chloro-3-iodobenzene (5.15 g, 22 mmol), to afford an orange solid. This was purified by column chromatography (eluting with cyclohexane) and recrystallised (propan-2-ol) to afford white crystals, identified as 1,12-bis-(3-chlorophenyl)-para-carborane (**28**). Yield 2.70 g, 74%. The product was characterised as follows:

Analysis: Found; C, 46.05, H, 5.04%; M_r (mass spectrum) 359-369; $C_{14}B_{10}H_{18}Cl_2$ requires C, 46.09; H, 4.97%; M_r 356-371

I.R. $\nu_{max}cm^{-1}$: 3066 w (aromatic CH) 2607 s (BH), 1568 m, 1470 m (Ar Skel.), 1408 m, 1259 m, 1074 s, 936 w, 875 m, 793 s, 713 m (cage vibration), 677 m (m-C_6H_4 o.o.p), 424 w.

2.3.26. Preparation of 1,4-bis-(*para*-carboranyl)-benzene (29).

The product was prepared and isolated according to the general reaction procedure described above, (Section 2.3.11), by the reaction of *para*-carborane (1.44 g, 10 mmol) with 1,4-diiodobenzene (1.65 g, 5 mmol), for 72 hours, to afford an orange solid. This was chromatographed (cyclohexane + 5% ethyl acetate) and purified by recrystallisation (hexane) to afford white crystals, identified as 1,4-bis-(*para*-carboranyl)-benzene (**29**). Yield 0.45 g, 25%. The product was characterised as follows:

Analysis: Found; C, 33.06, H, 6.98%; M_r (mass spectrum) 350-367; $C_{10}B_{20}H_{26}$ requires C, 32.99 H, 7.19%; M_r 346-366

I.R. $\nu_{max}cm^{-1}$: 3062w, 2615s (BH), 1510m, 1403m, 1141m, 1091s, 1010m, 891w, 861m, 802m, 737m, 697w, 585m, 513m.

NMR: δ ^{1}H: 1.0-4.0 (broad m., 22H, BH), 3.54 (s, 1H, carboranyl CH), 6.98 (s, 4H, ArH).
δ ^{11}B: -12.81 (5B), -15.26 (5B).

2.3.27. Preparation of 1,-(4-chlorophenyl)-*para*-carborane (30).

The product was prepared and isolated according to the general reaction procedure described above, (Section 2.3.11), by the reaction of *para*-carborane (1.44 g, 10 mmol) with freshly sublimed 1-chloro-4-iodobenzene (2.38 g, 10 mmol), for 72 hours, to afford an orange solid. This was chromatographed (cyclohexane + 5% ethyl acetate) and purified by sublimation to afford white crystals, identified as 1-(4-chlorophenyl)-*para*-carborane (**30**). Yield 1.84 g, 72%. The product was characterised as follows:

Analysis: Found; C, 37.58, H, 6.01%; M_r (mass spectrum) 249-259; $C_8B_{10}H_{15}Cl$ requires C, 37.83 H, 5.95%; M_r 254-267

I.R. $\nu_{max}cm^{-1}$: 3055 m (carboranyl CH), 3013 w (Aromatic), 2608 s (BH), 1491 m, 1398 m, 1265 w, 1077 m, 1012 m, 913 w, 834 m, 742 m, 742 m, 598 w, 496 m, 463 w.

2.3.28. Preparation of 1,12-bis-(4-phenoxyphenyl)-*para*-carborane (31).

The product was prepared and isolated according to the general reaction procedure described above, (Section 2.3.11), by the reaction of *para*-carborane (1.45 g, 10 mmol) with freshly sublimed 4-iododiphenylether (5.96 g, 23 mmol) for 48 hours, to afford an orange-yellow solution in which shiny crystals were suspended. These were filtered off and recrystallised (hexane) to afford white needle-like crystals identified as 1,12-bis-(4-phenoxyphenyl)-*para*-carborane (**31**), yield 2.48 g, 52%. The remaining oil and mother liquor were combined and purified by chromatography (pentane) to afford 1.24g, 26% of white crystals, also identified as (**31**). Yield 3.72 g, 78%; melting point 232-233 °C. The product was characterised as follows:

Analysis: Found; C, 65.13, H, 6.02%; M_r (mass spectrum) 476-484; $C_{26}B_{10}H_{28}O_2$ requires C, 64.98; H, 5.87%; M_r 472-484.

I.R. $\nu_{max}cm^{-1}$: 3013 w (aromatic CH) 2613 s (BH), 1589 s (C-C), 1504 m, 1489 m. (Ar skel.), 1388 w, 1283 w, 1226 s (C-O), 1171 m (BH i.p. def.), 1100 w, 1071 m, 1024 m, 916 w, 894 m, 867 m, 845 m (p-C_6H_4 o.o.p), 746 m (p-C_6H_5 o.o.p), 690 m (p-C_6H_5 o.o.p), 600 m, 507 m, 484 m, 416 w.

NMR: δ ^{1}H: 1.1-4.0 (broad m, 10H, BH), 6.75-7.34 (m, 18H, ArH)
δ ^{13}C: 82.03 (carboranyl C), 118.01, 119.99, 124.36, 129.05, 130.33, 133.1, 155.6, 159.30

2.3.29. Preparation of 1,12-bis-(4-fluorophenyl)-*para*-carborane (32).

The product was prepared and isolated according to the general reaction procedure described above, (Section 2.3.11), by the reaction of *para*-carborane (1.45 g, 10 mmol) with 4-fluoro-iodobenzene (4.886 g, 22 mmol) for 48 hours, to afford an orange-yellow solution in which shiny crystals were suspended. These were filtered off and recrystallised (hexane) to afford white needle-like crystals identified as 1,12-bis-(4-fluorophenyl)-*para*-carborane (**32**), yield 2.45 g, 85%, melting point 140-145 °C. The product was characterised as follows:

Analysis: M_r (mass spectrum) 289-296; $C_8B_{10}H_5F$ requires M_r 286-298.

I.R. $\nu_{max}cm^{-1}$: 3055 m, 3013 w (Aromatic), 2608 s (BH), 1491 m, 1398 m, 1265 w, 1077 m, 1012 m, 913 w, 834 m, 742 m, 742 m, 598 w, 496 m, 463 w.

NMR δ ^{19}F -114.22 (singlet)

2.3.30. Preparation of 1-(4-phenoxyphenyl)-*para*-carborane (33).

The product was prepared and isolated according to the general reaction procedure described above, (Section 2.3.11), by the reaction of *para*-carborane (0.72 g, 5 mmol) with freshly sublimed 4-iododiphenylether (1.50 g, 5.5 mmol).

The isolated product was purified by column chromatography (pentane) to yield a white oil which was sublimed at 25 °C at 0.01 mmHg to remove the traces of iodo starting material and then at 60-70 °C; 0.01 mmHg to afford white crystals identified as 1-(4-phenoxyphenyl)-*para*-carborane (**33**). Yield 392 mg, 25%; melting point 96-99 °C. The product was characterised as follows:

Analysis: Found; C, 54.21, H, 6.58%; M_r (mass spectrum) 305-315; $C_{14}B_{10}H_{20}O$ requires C, 53.83; H, 6.46%; M_r 304-315.

I.R. $\nu_{max}cm^{-1}$: 3055 m (carboranyl CH), 3013 m (aromatic CH) 2607 s (BH), 1612 m 1589 s (C-C), 1505 m, 1488 m. (Ar skel.), 1287 m, 1252 s, 1242 s (C-O), 1201 m, 1171 m, 1086 m, 872 m, 845 m (p-C_6H_4 o.o.p), 798 m, 754 m (p-C_6H_5 o.o.p), 736 m (cage vibration), 693 m (p-C_6H_5 o.o.p), 578 m, 511 m, 508 m, 480 m.

NMR: δ^1H: 1.8-2.9 (broad mulitplet, 11H, BH), 3.1 (singlet, 1H, carborane CH), 6.73-7.38 (multiplet, 9H, Ar-H).
δ^{13}C: 58.9, (carboranyl CH), 82.03 (carboranyl C-Ar), 117.48, 119.48, 123.85, 128.44, 129.83, 130.4, 156.2, 158.1,(ArC)

2.3.31. Preparation of 1-(3,5-dichlorophenyl)-*para*-carborane (34).

The product was prepared and isolated according to the general reaction procedure described above, (Section 2.3.11), by the reaction of *para*-carborane (1.44 g, 10 mmol) with resublimed 1,3-dichloro-5-iodobenzene (2.74 g, 10 mmol), to afford an orange solid. This was purified by column chromatography (cyclohexane + 5% ethyl acetate) to afford yellow-orange crystals which were recrystallised (propan-2-ol) to afford white crystals, identified as 1-(3,5-dichlorophenyl)-*para*-carborane (**34**). Yield 2.29 g, 79%; melting point 108-110 °C. The product was characterised as follows:

Analysis: Found; C, 32.96, H, 5.01%; M_r (mass spectrum) 280-293; $C_8B_{10}H_{14}Cl_2$ requires C, 33.13; H, 4.87%; M_r 279-293 .

I.R $\nu_{max}cm^{-1}$: 3057 w (carboranyl CH), 2610 s, (BH), 1587 s, 1563 s, 1439 m, 1416 s, 1386 m, 1252 w, 1141 w (Ar skel.), 1104 sh., 1096 s, 1009 w, 886 w, 866 s, 844 m (1,3,5 trisub. aromatic), 800 s, 737 m, 708 s, 669 s (cage vibration), 622 m, 432 w.

NMR: δ ^{1}H: 1.0-4.0 (broad m., 10H, BH), 7.06 (s, 1H), 7.23 (s, 2H)
δ ^{13}C: 60.05 (carboranyl CH), 80.15 (carboranyl C-Ar), 126.13, 126.30, 129.01, 135.20 (ArC)

2.3.32. Preparation of 1,12-bis-(4-methylphenyl)-*para*-carborane (35).

The product was prepared and isolated according to the general reaction procedure described above, (Section 2.3.11), by the reaction of *para*-carborane (1.44 g, 10 mmol) with freshly sublimed 4-iodotoluene (4.36 g, 20 mmol), to afford an orange solid. This was purified by chromatography to afford white crystals, identified as 1,12-bis-(4-methylphenyl)-*para*-carborane (**35**). Yield 84%; melting point 232-233 °C. The product was characterised as follows:

Analysis: Found; C, 59.23, H, 7.46%; M_r (mass spectrum) 319-326; $C_{16}B_{10}H_{24}$ requires C, 59.08; H, 7.43%; M_r 322-335

I.R. $\nu_{max}cm^{-1}$: 3033 w, 2955 w, 2916 w, 2603 s (BH), 1507 m, 1443 w, 1077 m, 1028 w, 821 m, 741 m, 598 w, 492 m.

2.3.33. Preparation of 4-(*meta*-carboranyl)-biphenyl (36).

The product was prepared and isolated according to the general reaction procedure described above, (Section 2.3.11), by the reaction of *meta*-carborane (1.44 g, 10 mmol) with 4-bromobiphenyl (4.66 g, 20 mmol), to afford an orange solid. This was purified by chromatography (dichloromethane/ cyclohexane 1:1), to afford white crystals, identified as 4-(*meta*-carboranyl)-biphenyl (**36**). Yield 0.74 g, 25%. The product was characterised as follows:

Analysis: Found; C, 58.87, H, 7.48%; M_r (mass spectrum) 287-299; $C_{16}B_{10}H_{24}$ requires C, 59.08, H, 7.41%; M_r 288-300.

I.R. $\nu_{max}cm^{-1}$: 3058 s (carboranyl CH), 3013 w, 2606 s (BH), 1516 w, 1484 m, 1401 m, 1259 w, 1078 m, 1006 m, 847 m, 756 s, 723 m, 694 s, 579 w, 548 w, 502 m, 415 w.

2.3.34. Preparation of 1,7-bis-(2-pyridyl)-*meta*-carborane (38).

The product was prepared and isolated according to the general reaction procedure described above, (Section 2.3.11), by the reaction of *meta*-carborane (1.44 g, 10 mmol) with freshly sublimed 2-bromopyridine (3.16 g, 20 mmol), to afford an orange solid. This was purified by column chromatography (eluting with cyclohexane/CH_2Cl_2 (1:1)) and recrystallised (ethanol) to afford off-white crystals, identified as 1,7-bis-(2-pyridyl)-meta-carborane (**38**). Yield 2.38 g, 79%; melting point 114-117 °C. The product was characterised as follows:

Analysis: Found; C, 48.24, H, 6.19, N, 9.11%; M_r (mass spectrum) 285-301; $C_{12}B_{10}H_{18}N_2$ requires C, 48.32, H, 6.08, N, 9.39%; M_r 290-301

I.R. $\nu_{max}cm^{-1}$: 3090 w, 3055 w, 3010 w (CH); 2647 m, 2600 s (BH); 1583 m, 1572 m, 1463 m, 1431 m (py); 1271 m, 1153 w, 1089 m, 1045 w, 995 m, 908 w, 878 w, 855 m, 821 m, 751 m, 741 m (CH. o.o.p. and carborane skel.); 681 m, 613 w, 491 w.

NMR: δ ^{1}H: 1.0-4.5 (br. multiplet, 10H, BH), 7.24 (doublets of doublets, J= 7.4, 4.8, 1.1 Hz, pyridine H5); 8.51 (doublet of doublets J= 4.8, 1.8, 1.0 Hz 1H, pyridine H6).
δ ^{13}C: 78.67 (carborane C), 121.90, 123.47, 136.74, 148.80, 152.64 (pyridine C2)
δ ^{11}B: -13.9 (br. singlet, 1H, B2 and B3), -11.5 (br. singlet, 3H, B4, B6, B8, B9, B10 and B11), -6.6 (br. singlet, 1H, B5 and B12).

2.3.35. Preparation of 1,-(4-hydroxyphenyl)-*meta*-carborane (39).

Freshly sublimed 1,7-dicarba-*closo*-dodecaborane (1.20 g, 8.3 mmol) was dissolved in 1,2-dimethoxyethane (50 ml) in a 100 ml round bottomed flask fitted with a condenser and flushed with nitrogen. n-Butyllithium (11 ml, 1.6 M in hexanes, 17.6 mmol) was added to the clear, colourless solution. The solution was allowed to cool to room temperature and pyridine (6 ml) was added forming a yellow solution. to which copper(I) chloride (2.02 g, 20 mmol) was added. The resulting brown-black suspension was stirred at room temperature for 20 minutes. TMS-protected 4-iodophenol (2.31 g, 7.9 mmol) was added to the reaction flask and the contents were heated to reflux, under nitrogen for 48 hours. The reaction mixture was allowed to cool to room temperature and diluted with diethylether (100 ml) forming a brown precipitate which was stirred at room temperature for 2 hours. The precipitate was filtered off and washed with ether (30 ml). The combined ethereal solution was washed with 2M HCl (4 x 25 ml), water (4 x 50 ml), dried over $MgSO_4$ and evaporated to afford an orange-brown oil. This was taken up in methanol (25 ml) and sodium hydroxide (0.25 g, 6.4 mmol) was added forming a brown solution which was stirred at room temperature for an hour. Water (25 ml) was added and the aqueous layer was extracted with diethylether (4 x 25 ml). The combined ethereal layers were washed in the usual manner and dried over $MgSO_4$. The solvents were removed under vacuum to afford an orange-yellow oil which was chromatographed (dichloromethane) to afford white crystals which were recrystallised from hexane to give the product identified as 1-(4-hydroxyphenyl)-*meta*-carborane (**39**). Yield 1.36 g, 73%; melting point 163-166 °C. The product was characterised as follows:

Analysis: Found; C, 40.76, H, 6.88%; M_r (mass spectrum) 231-239; $C_8B_{10}H_{16}O$ requires C, 40.66; H, 6.77%; M_r 228-239.

I.R. $\nu_{max}cm^{-1}$: 3254 s (OH), 3058 m (carboranyl CH), 3013 w (aromatic CH) 2601 s, (BH), 1616 m, 1599 s (C-C), 1448 m. (Ar skel.), 1373 m, 1297 w, 1250 s (C-O), 1184 m, 1128 m, 1082 m, 1043 m, 1011 m, 977 m, 921 m, 879 m, 843 m (p-C_6H_4 o.o.p), 826 m, 732 m (cage vibration), 710 m, 643 m, 577 m, 561 m, 529 m, 514 m, 471 m.

NMR: δ ^1H: 1.1-3.0 (broad multiplet, 10H; BH), 4.95 (s, broad 1H, OH), 6.6-6.65 (doublet, Aromatic CH), 7.4-7.5 (doublet, Aromatic CH).

δ ^{11}B: -4.67, -8.95, -11.01, -13.40, -15.32

2.3.36. Preparation of 1-(4-carboxyphenyl)-*meta*-carborane (40).

Freshly sublimed 1,7-dicarba-*closo*-dodecaborane (1.44 g, 10 mmol) was dissolved in 1,2-dimethoxyethane (50 ml) in a 100 ml round bottomed flask fitted with a condenser and flushed with nitrogen. n-Butyllithium (13 ml, 1.6 M in hexanes, 20 mmol) was added to the clear, colourless solution. The solution was allowed to cool to room temperature and pyridine (6 ml) was added forming a yellow solution to which copper(I) chloride (2.02 g, 20 mmol) was added. The resulting brown-black suspension was stirred at room temperature for 20 minutes. TMS-protected 4-iodobenzoic acid (6.53 g, 20 mmol) was added to the reaction flask and the contents were heated to reflux, under nitrogen, for 48 hours. The reaction mixture was allowed to cool to room temperature and diluted with diethylether (100 ml) forming a brown precipitate which was stirred at room temperature for 2 hours. The precipitate was filtered off and washed with ether (30 ml). The combined ethereal solution was washed with 2M HCl (4 x 25 ml), water (4 x 50 ml), dried over $MgSO_4$ and evaporated to afford an orange oil. This was purified by column chromatography (cyclohexane + 5% ethyl acetate) to afford a cream solid which was recrystallised (propan-2-ol) to yield white crystals, identified as 1-(4-carboxyphenyl)-*meta*-carborane (**40**). Yield 1.64 g, 62%. The product was characterised as follows:

Analysis: Found; C, 39.29, H, 5.77%; M_r (mass spectrum) 264-272; $C_9B_{10}H_{16}O_2$ requires C, 40.90, H, 6.10 %; M_r 264-274

I.R. $\nu_{max}cm^{-1}$: 3340 br., 3064 w (carboranyl CH), 2608 s, 1698 s, 1563 m, 1432 m, 1300 s, 1261 s, 1234 m, 1085 m, 1056 m, 940 w, 900 w, 801 m, 746 s, 688 m, 546 w.

2.3.37. Preparation of 1,12-bis-(4-carboxyphenyl)-*para*-carborane (41).

Chromium trioxide (0.78 g, 7.8 mmol) was added to a stirred suspension of 1,12-bis(4-tolyl)-*para*-carborane (0.300 g, 0.78 mmol) in glacial acetic acid (13 ml), acetic anhydride (5 ml) and c. H_2SO_4 (0.78 ml). The red/brown mixture was stirred for two hours at room temperature forming a green solution, which was poured into water (80 ml) forming a precipitate. The solid was filtered off and washed with water to remove the green chromium traces. The off-white solid was dissolved in saturated sodium hydrogen carbonate and filtered hot. The resulting white solid was dissolved in water and the solution was acidified by the addition of hydrochloric acid to afford a white precipitate identified as 1,12-bis-(4-carboxyphenyl)-*para*-carborane (**41**). Yield 0.28 g, 94%; melting point >350 °C. The product was characterised as follows:

Analysis: Found; C, 49.35 H, 5.22%; M_r (mass spectrum) 379-387; $C_{16}B_{10}H_{20}O_4$ requires C, 50.85 H, 5.25%; M_r 384-395

I.R. $\nu_{max}cm^{-1}$: 3420 br., 2617 s, 1686 vs, 1606 m, 1423 m, 1308 s, 1280 sh., 1080 w, 949 w, 874 w, 752 m, 695 w, 559 m, 482 m.

2.3.38. Preparation of 1,7-bis-(4-carboxyphenyl)-*meta*-carborane (42).

This was prepared according to the general procedure above (Section 2.3.37), by adding chromium trioxide (1.01 g, 10 mmol) to a stirred suspension of 1,7-bis(4-tolyl)-*para*-carborane (0.387 g, 1.0 mmol) in glacial acetic acid (17 ml), acetic anhydride (6.5 ml) and c. H_2SO_4 (1.0 ml). The product was isolated, recrystallised from water:acetone and identified as 1,7-bis-(4-carboxyphenyl)-*meta*-carborane (**42**). Yield 0.27 g, 75%; melting point 281-283 °C. The product was characterised as follows:

Analysis: Found; C, 50.1 H, 5.34%; M_r (mass spectrum) 383-387; $C_{16}B_{10}H_{20}O_4$ requires C, 50.85 H, 5.25%; M_r 384-395

I.R. $\nu_{max}cm^{-1}$: 3700-2200 m, br., 2603 m, 1700 s, 1614 s, 1576 m, 1423 s, 1418 m, 1311 m, 1295 s, 1283 m, 1253 s, 1227 m, 1220 m, 1191 m, 1124 m, 1079 m, 1021 m, 796 m, 776 m, 483 w.

NMR: δ ^1H: 1.0-4.5 (br. multiplet, 10H, BH), 7.15 (br. s, OH); 7.73-8.05 (doublet of doublets, ArH).

δ ^{13}C: 76.88 (carborane C), 126.51, 127.08, 128.83, 130.5, 164.98 (ArC).

2.4. References:

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Chapter 3

DEBORONATION OF ARYL AND DIARYL CARBORANES

3.1. Introduction:

Hawthorne and co-workers[1-3] demonstrated that *ortho*- and *meta*-carborane, 1,2- and 1,7- $C_2B_{10}H_{12}$, were partially degraded in the presence of strong bases such as potassium hydroxide in methanol to the corresponding *nido* mono-anions $[7,8\text{-}C_2B_9H_{12}]^-$ and $[7,9\text{-}C_2B_9H_{12}]^-$, according to the equation below:

$$C_2B_{10}H_{12} + 2\,CH_3O^- + 2\,CH_3OH \longrightarrow H_2 + B(OCH_3)_4^- + C_2B_9H_{12}$$

The carbon atoms present in the icosahedral cage bear partial positive charges in the ground state[3,4] and as a consequence activate the two equivalent neighbouring boron atoms B(3,6) to nucleophilic attack. The twelfth hydrogen atom required by the formula $C_2B_9H_{12}^-$ was assumed for many years to be in constant motion about the periphery of the open pentagonal face of the cage as a B-H-B bridge. Recently, however Welch *et al* [5] observed the 'extra' hydrogen via NMR spectroscopy and showed it to exist as an endo-H atom, bound, in the case of $[7,8\text{-}C_2B_9H_{12}]^-$ to B(10), although in solution and the solid state weak bonds between the endo-H and B(9)/B(11) have been observed.

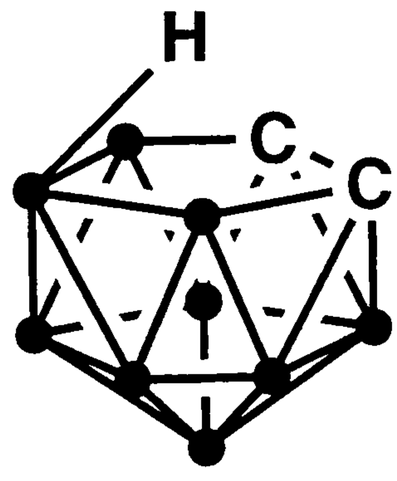


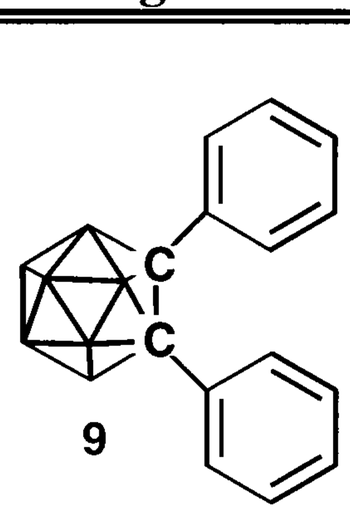
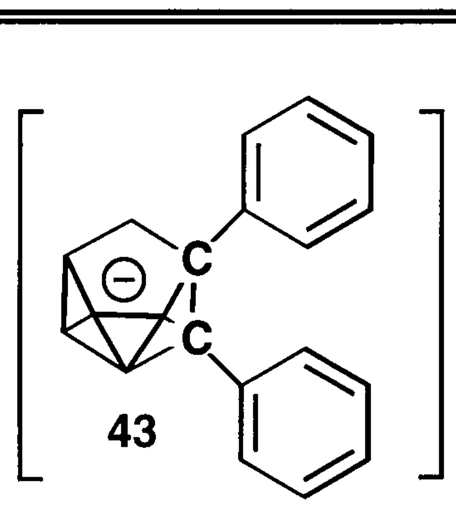
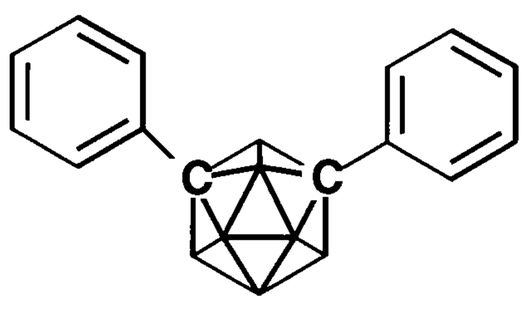
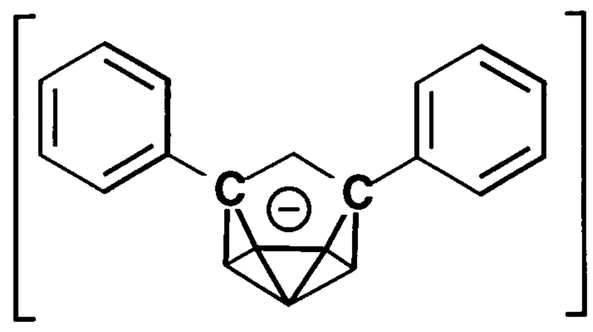
Figure 3.1: *Structure of nido-$C_2B_9H_{12}^-$*

This chapter briefly reviews the literature describing deboronation and goes on to describe developments made using "wet" fluoride ions to prepare previously inaccessible mono-anionic carborane derivatives.

3.1.1. Background.

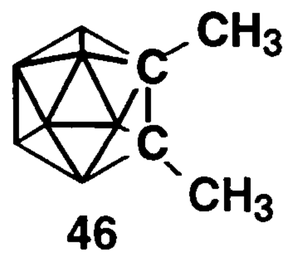
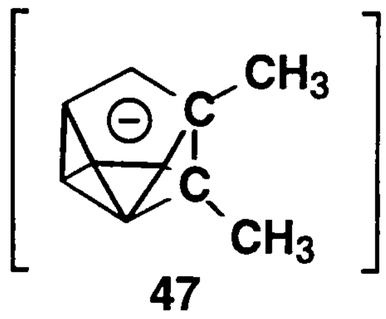
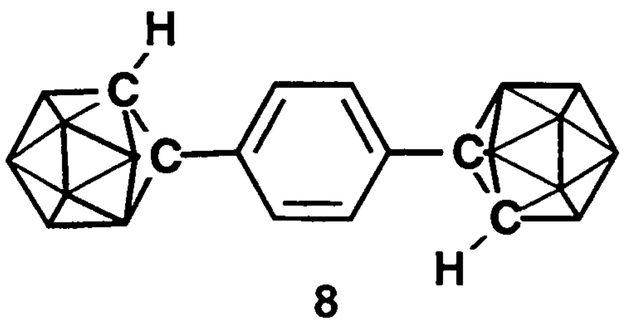
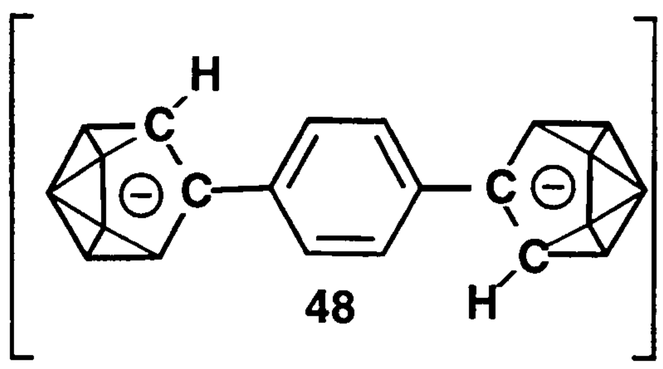
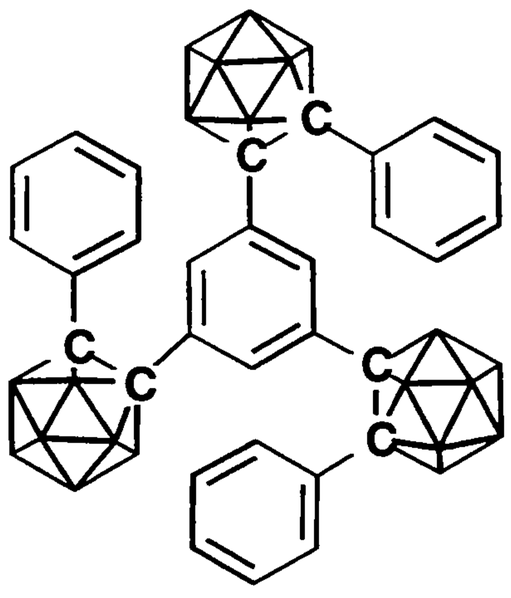
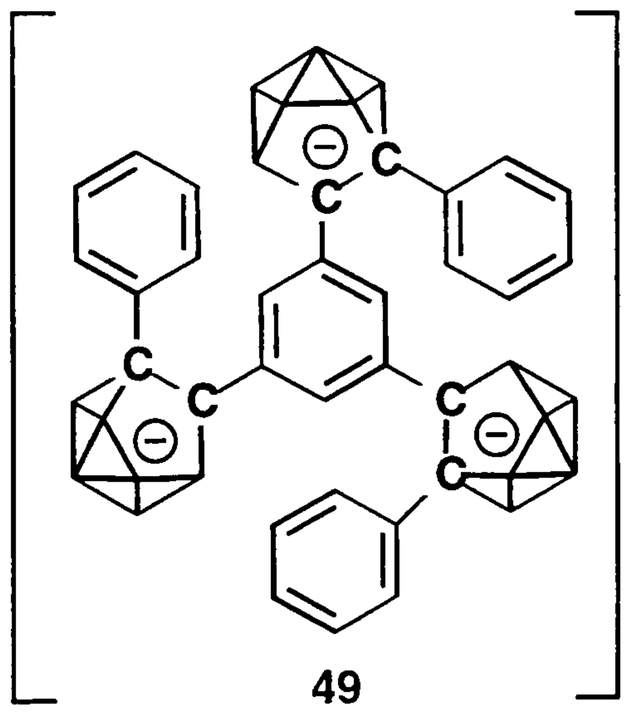
Deboronation of carborane cages using methanoic potassium hydroxide has its limitations. It is unsuitable for derivatives containing functional groups that are susceptible to attack by strong base or nucleophiles, for example nitro derivatives, esters and reactive halogen derivatives. Moreover, *meta*-carborane and its derivatives require forcing conditions to induce the removal of the BH unit, eg. autoclaving at 170 °C for 10 hours.

For example, the deboronation of 1,2-bis-(4-phenyl)-*ortho*-carborane (**9**), with five equivalents of potassium hydroxide, in methanol afforded the mono-anionic product (**43**) in quantitative yield, but the analogous reaction with 1,7-bis-(4-phenyl)-*meta*-carborane (**44**) gave the corresponding *meta*-carborane derivative (**45**) in only 25% yield.

Starting Material	Product	Yield (%)
 **9**	 **43**	96
 **44**	 **45**	25

However, this classical route has been successfully used during the course of this work to deboronate a number of *ortho*-carborane derivatives as shown in Figure 3.2.

Figure 3.2: *Mono-anionic Compounds Produced by "Classical" routes.*

Starting Material	Product	Yield
 **46**	 **47**	93
 **8**	 **48**	85
 **7**	 **49**	85

Studies on compounds **7** and **8** have shown that two or three carborane cages linked through a benzene ring may be deboronated in a one step reaction to afford compounds **48** and **49**. ^{13}C NMR of products **48** and **49** suggested that two and three isomers had been formed respectively, presumably because rotation of the *closo*-carborane cage in the parent compounds is restricted in the deboronated products for steric reasons.

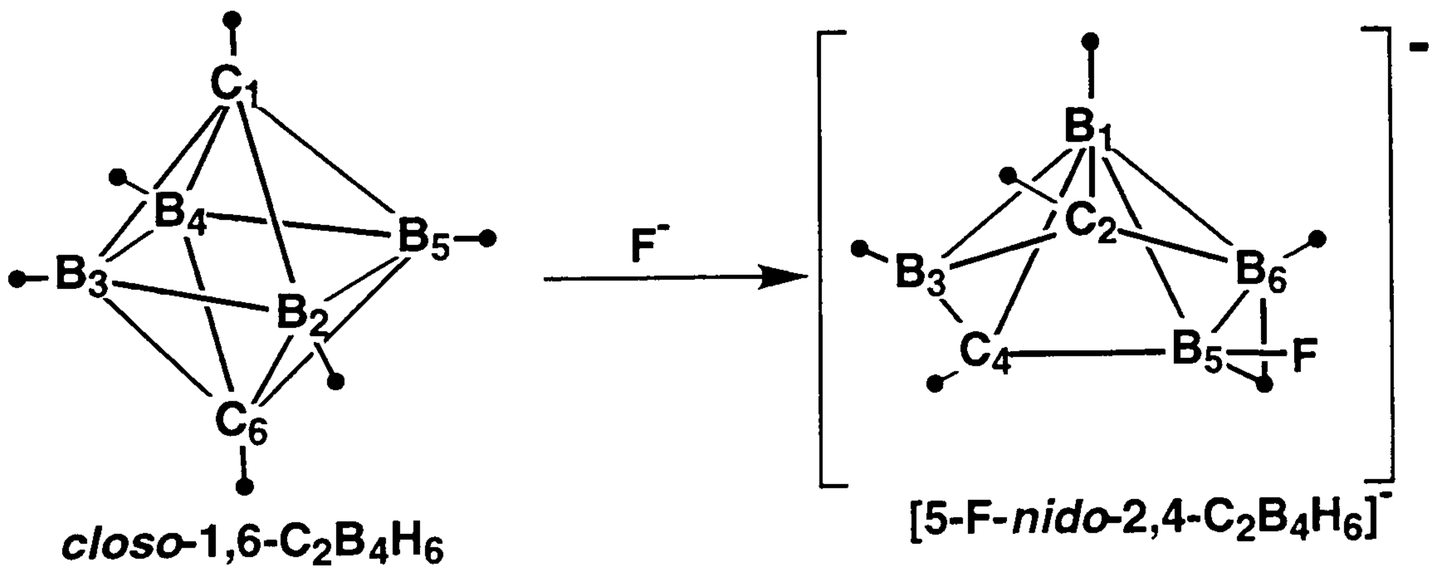
The close proximity of the cages does not appear to hinder further deboronation in the same compound. This is of particular interest with respect to the potential deboronation of carborane-cages incorporated into the backbone of polymers, and is discussed in more detail in Section 4.4.

More recently other reagents have been found to effect this partial cage degradation, for example tertiary amines such as triethylamine,[6] hydrazine,[7-11] ammonia,[12] and piperidine.[13,14] In such reactions *ortho*-carborane and its derivatives usually react more rapidly than *meta*-carborane, and Teixidor and co-workers[15-19] reported that salts of 1,2-dimercapto-*ortho*-carborane can be deboronated by a variety of methods not normally effective with carborane derivatives. For example, the diammonium salt, $(NH_4^+)_2$ $(1,2\text{-}S_2C_2B_{10}H_{10})^{2-}$ may be deboronated by refluxing in ethanol, and the sodium or potassium salts are deboronated by refluxing with dichloromethane or 1,2 dibromoethane.

para-Carborane and its derivatives are resistant to cage degradation by the methods so far described, but Plesek and co-workers[20] demonstrated that the mono-anion may be formed in 15% yield by heating with 20% potassium hydroxide in propanediol for 6 hours. Hawthorne and co-workers[21] showed that refluxing *para*-carborane in benzene, in the presence of potassium hydroxide and 18-crown-6 for 42 hours, increased the yield to 95%.

Few studies of *para*-carborane derivatives have been made as until recently only those compounds that are capable of withstanding the temperatures required for the thermal isomerisation of the *ortho*-carborane derivatives were available. However the development of the copper-based coupling route to mono and diaryl derivatives of carboranes, described in chapter 2, has considerably extended the chemistry of *meta*-and *para*-carborane derivatives.

Onak and co-workers[22] recently reported that "anhydrous" fluoride ion, in aprotic solvents, at room temperature, was effective in the cage opening of *closo*carboranes such as $1,6\text{-}C_2B_4H_6$ and icosahedral *ortho*- and *meta*-carborane.



closo-1,6-$C_2B_4H_6$

The author, in collaboration with others[3] has developed a new deboronation technique using fluoride ions in the presence of water, which allows the deboronation of carbon-substituted *meta*-carboranes which are difficult to degrade by classical routes.

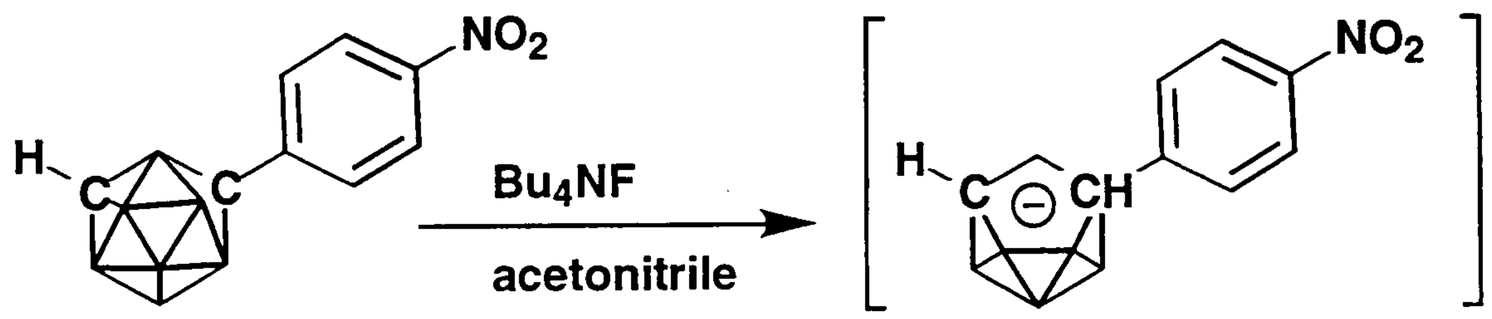
3.2. Results and Discussion:

3.2.1. Use of Tetrabutylammonium fluoride Solutions:

Both *ortho*- and *meta*-carborane are deboronated quantitatively at room temperature by stirring with a solution of hydrated tetrabutylammonium fluoride in THF. Water appears to play a vital role in the deboronation as postulated by Onak *et al.*[22] and several mono-boron species, such as HBF_3^- and BF_3L were thought to be side-products from the reaction.

The progress of the reaction may be conveniently monitored by IR, the reactions being considered complete when the *closo* BH stretching absorption (@ ca. 2600 cm^{-1}) has essentially disappeared and been replaced by the *nido* BH stretching band (@ 2510-2520 cm^{-1}). Attempts were made to monitor the reactions by NMR, but peak overlapping occurs with the *closo*-starting material the *nido* product, so this technique was not conspicuously successful.

The deboronation of 1-(4-nitrophenyl)-*meta*-carborane (**21**), with Bu_4NF in wet THF at ambient temperature was followed using boron and fluorine NMR spectroscopy.



21 **50**

The ^{11}B NMR spectrum after only three minutes of the reaction contained no observable peaks corresponding to the starting carborane, but peaks corresponding to the mono-anionic product and to monoboron species were observed, Figure 3.3.

Figure 3.3: *^{11}B NMR Spectrum for the Reaction of 1-(4-nitrophenyl)-meta-carborane (20) with Bu_4NF.*

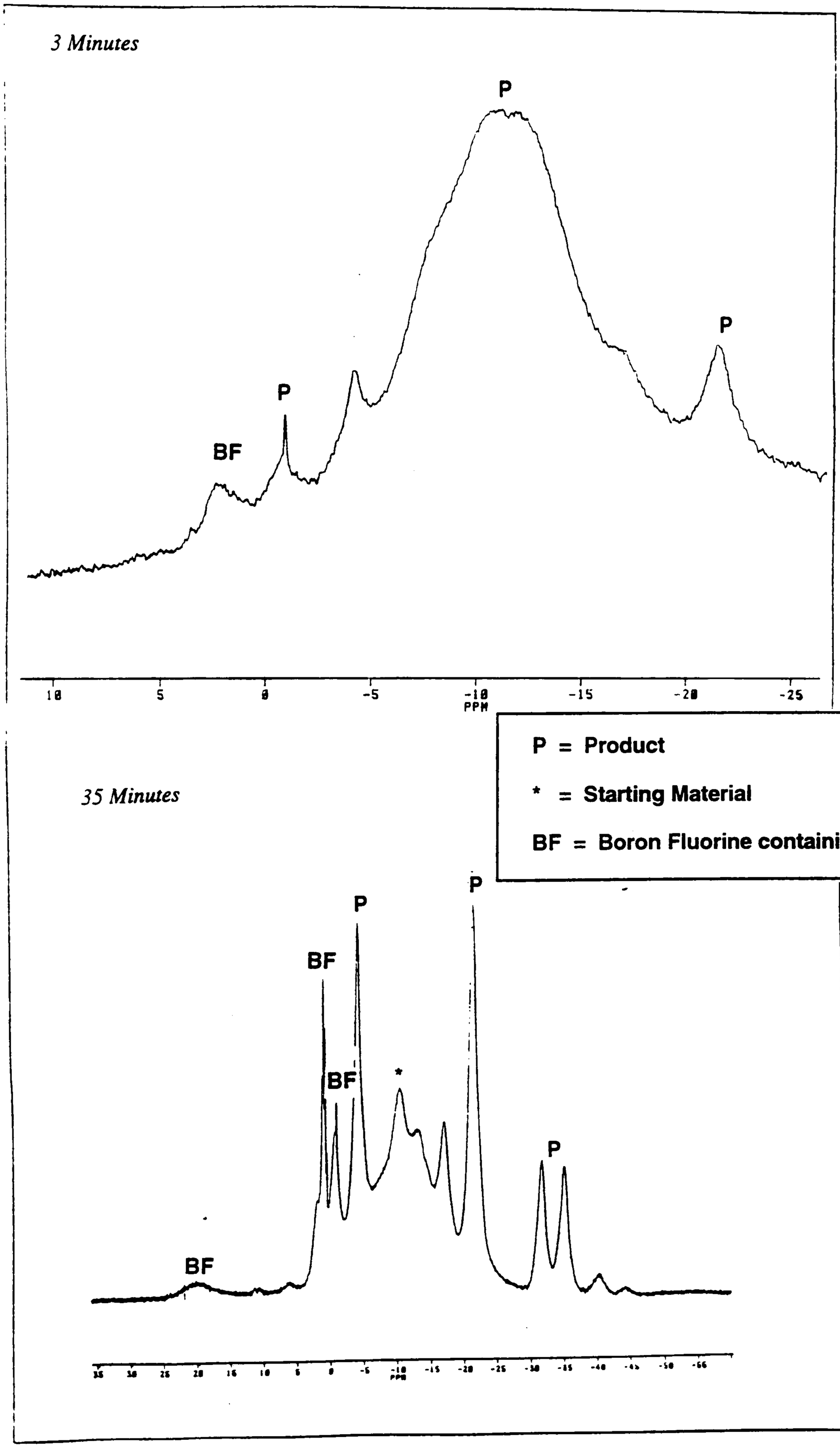
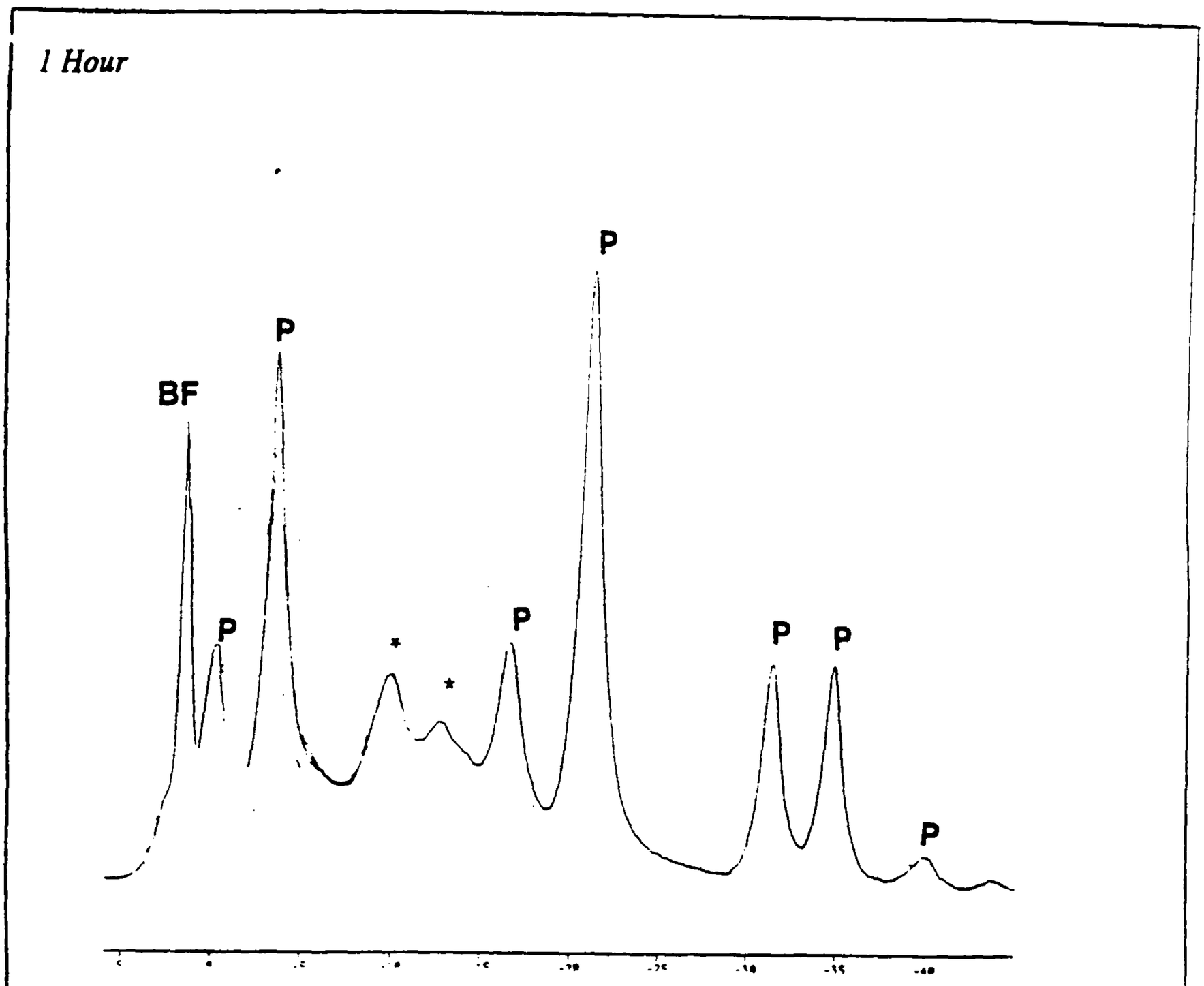


Figure 3.3: *Continued*



P = Product

* = Starting Material

BF = Boron Fluorine containing species

Figure 3.4: *^{19}F NMR Spectrum for the Reaction of 1-(4-nitrophenyl)-meta-carborane (20) with Bu_4NF.*

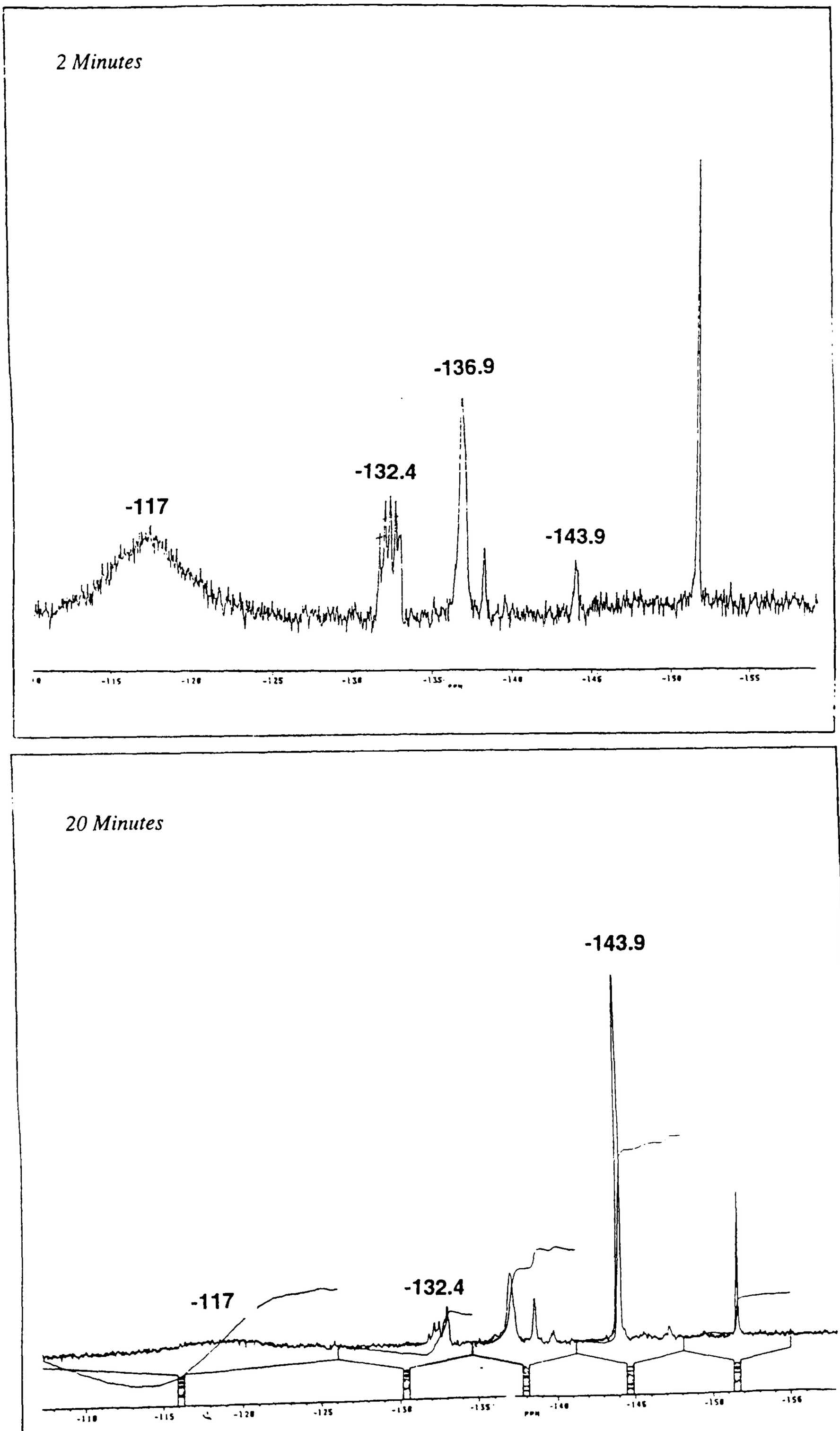
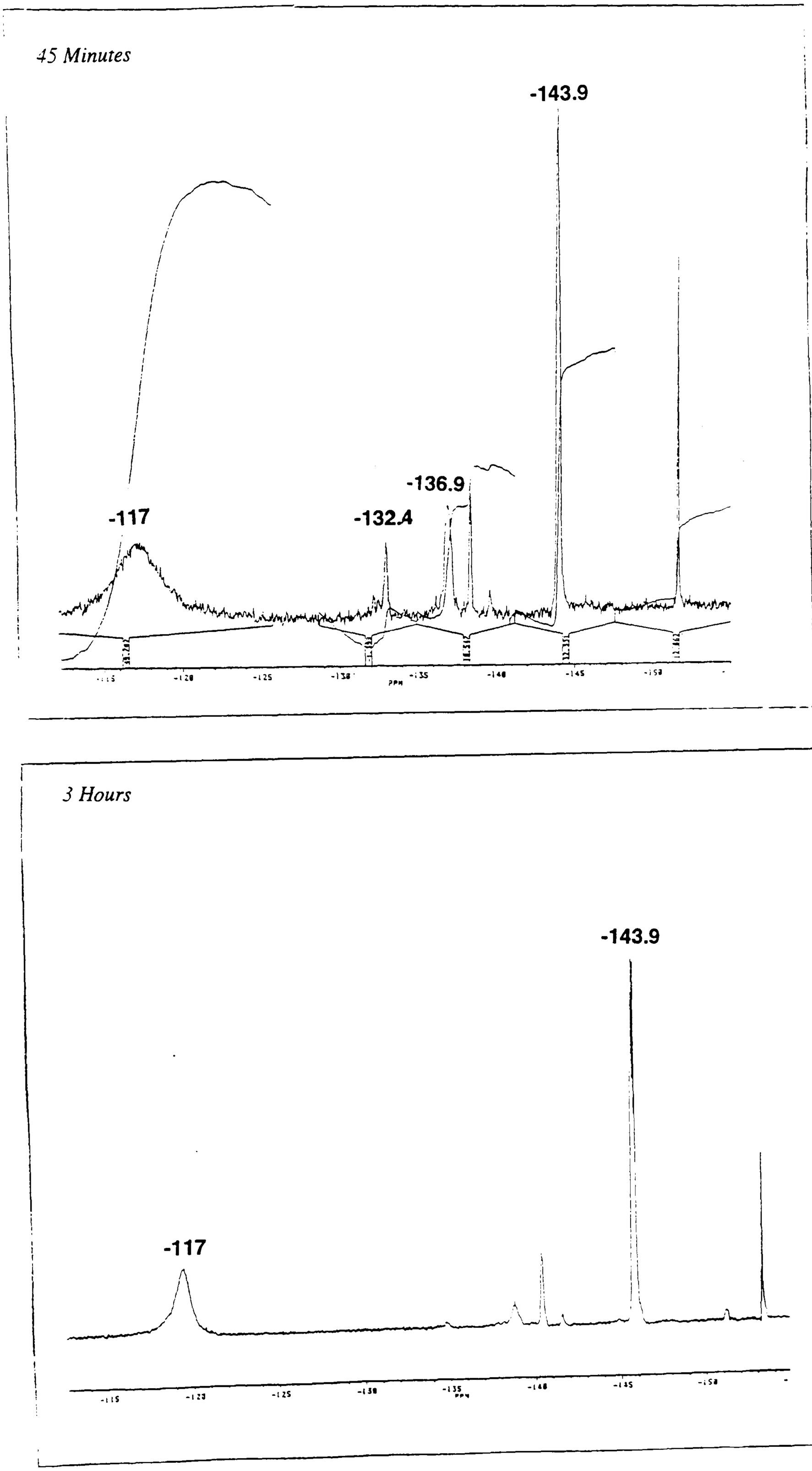


Figure 3.4: *Continued*



During the next hour the peaks of the monoboron compounds varied while the carborane anion peaks remained largely unchanged although changes in the intensity of the *closo* and *nido* BH stretching absorptions were observed by infrared spectroscopy.

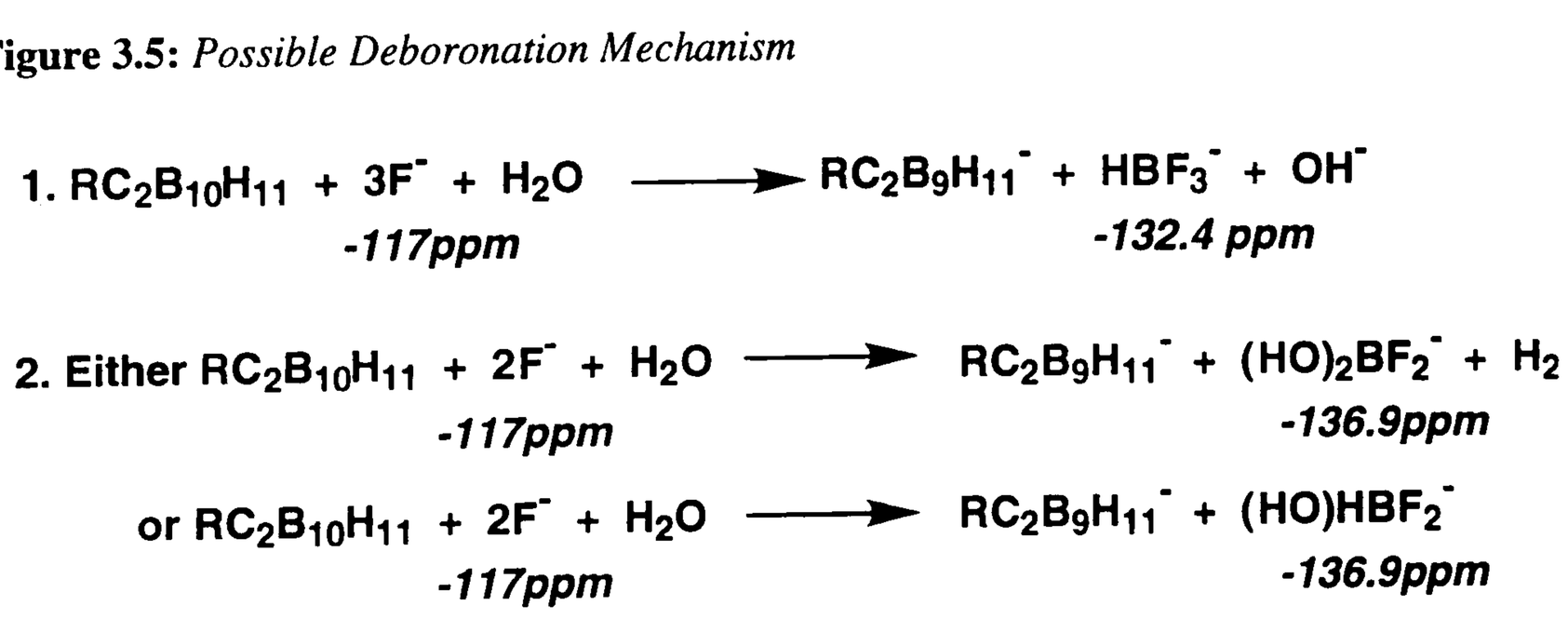
Following the monoboron products by ^{19}F NMR spectroscopy showed only two main changes during the first hour. The initial spectrum at two minutes showed a 1:1:1:1 quartet at -132.4 ppm (J_{HF} ~ 90 Hz, J_{BF} ~ 68 Hz), an unresolved multiplet at -136.9 ppm (base peak line width ~ 160 Hz), a 1:1:1:1 quartet at -143.9 ppm (J_{BF} ~ 16 Hz) and a very broad singlet at -117 ppm.

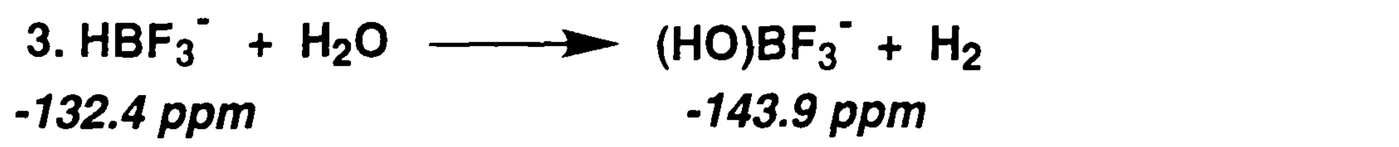
The -132.4 and -117 ppm peak intensities were reduced after 20 minutes while the intensity at -143.9 ppm increased. After 45 minutes the -117 ppm peak intensity increased, whereas the -136.9 ppm peak intensity decreased. At 3 hours the spectrum consisted of mainly the -117 and -143.9 ppm peaks in approximately 1:1 intensity ratio, (Figure 3.4).

The reported[22] deboronation of *ortho*-carborane with Bu_4NF gave a monoboron product at -143.5 ppm (J_{BF} ~ 16 Hz) suggested to be a BF_3 group bound to a solvent molecule or an OH group. For the deboronation of *meta*-carborane, the monoboron product at -136.2 ppm (J_{HF} ~ 91 Hz, J_{BF} ~ 69 Hz) was suggested to be HBF_3^- (or $F_3BHF_3^-$). The peaks observed here at -132.4 and -143.5 ppm are probably $H(HO)BF_2^-$ and $HOBF_3^-$ respectively. The broad singlet at -117 ppm corresponds to the free fluoride ion whereas the resonance at -136.9 ppm may be due to $(HO)_2BF_2^-$. This suggests that the deboronations of *ortho*- and *meta*-carborane proceed in a similar manner.

The series of reactions below could explain the changes of the monoboron products.

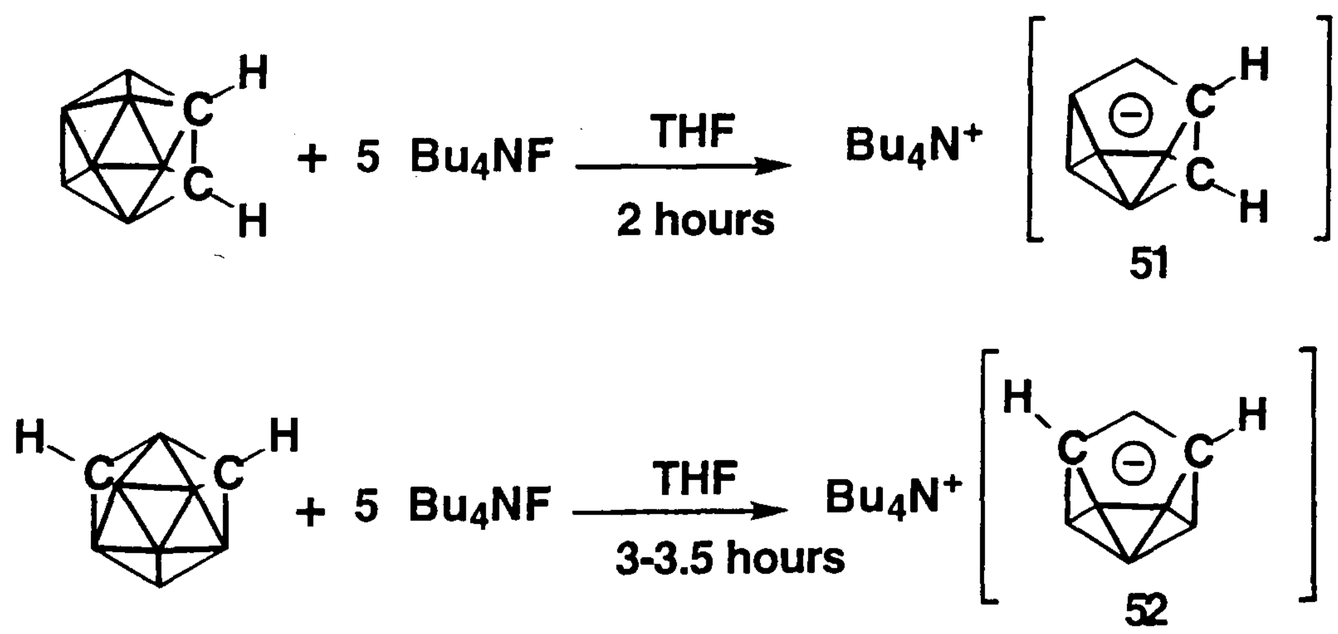
Figure 3.5: *Possible Deboronation Mechanism*





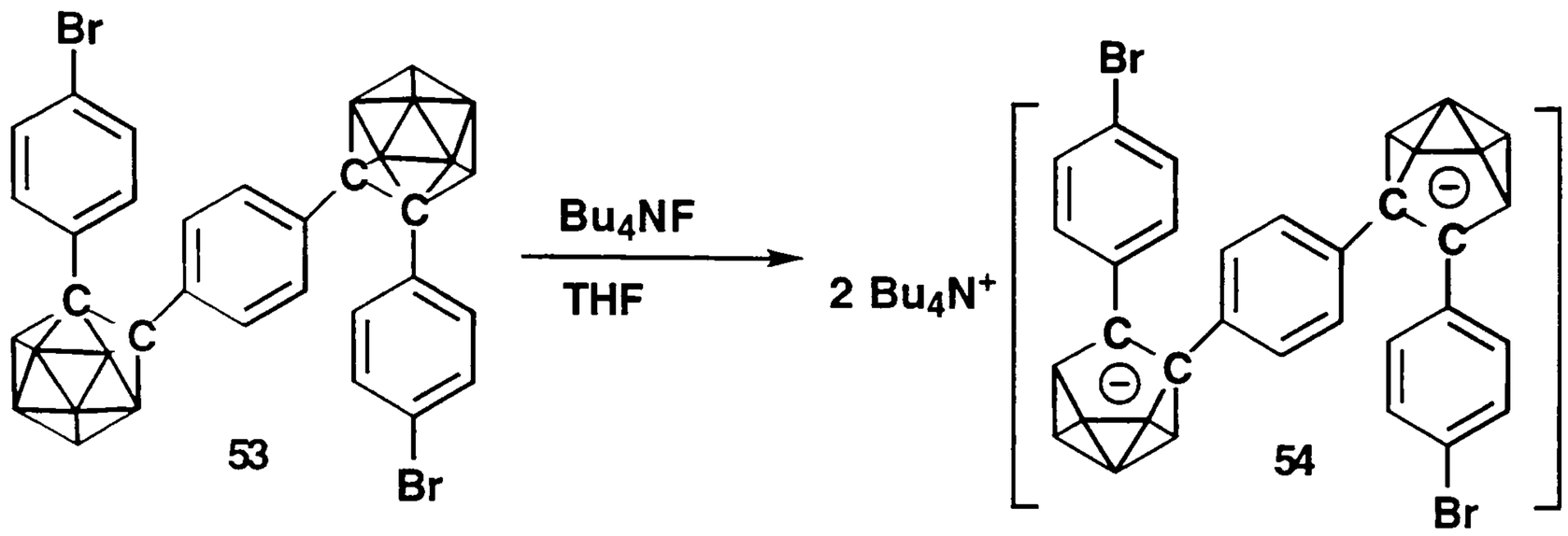
Colour changes corresponding with the appearance in the IR of the *nido* BH stretching absorption and the disappearance of the *closo* ν-BH band were observed, but no coloured intermediates could be isolated.

Using five equivalents of tetrabutylammonium fluoride per carborane cage allowed the complete conversion of the *ortho*-carborane isomer into its mono-anion (**51**) in less than two hours at room temperature, and conversion of the *meta*-carborane cage into the *nido* monoanion (**52**) was complete in 3-3.5 hours under the same conditions.



In contrast when deboronation was attempted using Bu_4NF under the anhydrous conditions described by Onak[22], conversion was still incomplete after stirring overnight at room temperature.

A series of reactions using the multicage system (**53**) shown below were conducted by Gill *et al.*[23] in an attempt to establish the molar ratio of tetrabutylammonium fluoride required to effect complete deboronation of each cage.



The reaction was still observed to occur using only a 1:1 ratio of fluoride ion to cage in contrast to the five equivalents previously used, although the initiation step of the reaction appeared to occur more slowly, at the reduced molar ratios. Two isomers were observed by ^{11}B and ^{13}C NMR as observed with similar species using the classical alkoxide ions.

Prior to the initial report of Bu_4NF as a deboronating agent,[22] forcing conditions were required to effect the conversion of the *closo meta* carborane into the *nido* mono anion.

The method developed in the present work allowed deboronation of a series of substituted *meta*-carborane derivatives, such as those shown in Figure 3.6, a study aimed at relating the rate of reaction to the electronic character of the substituent.

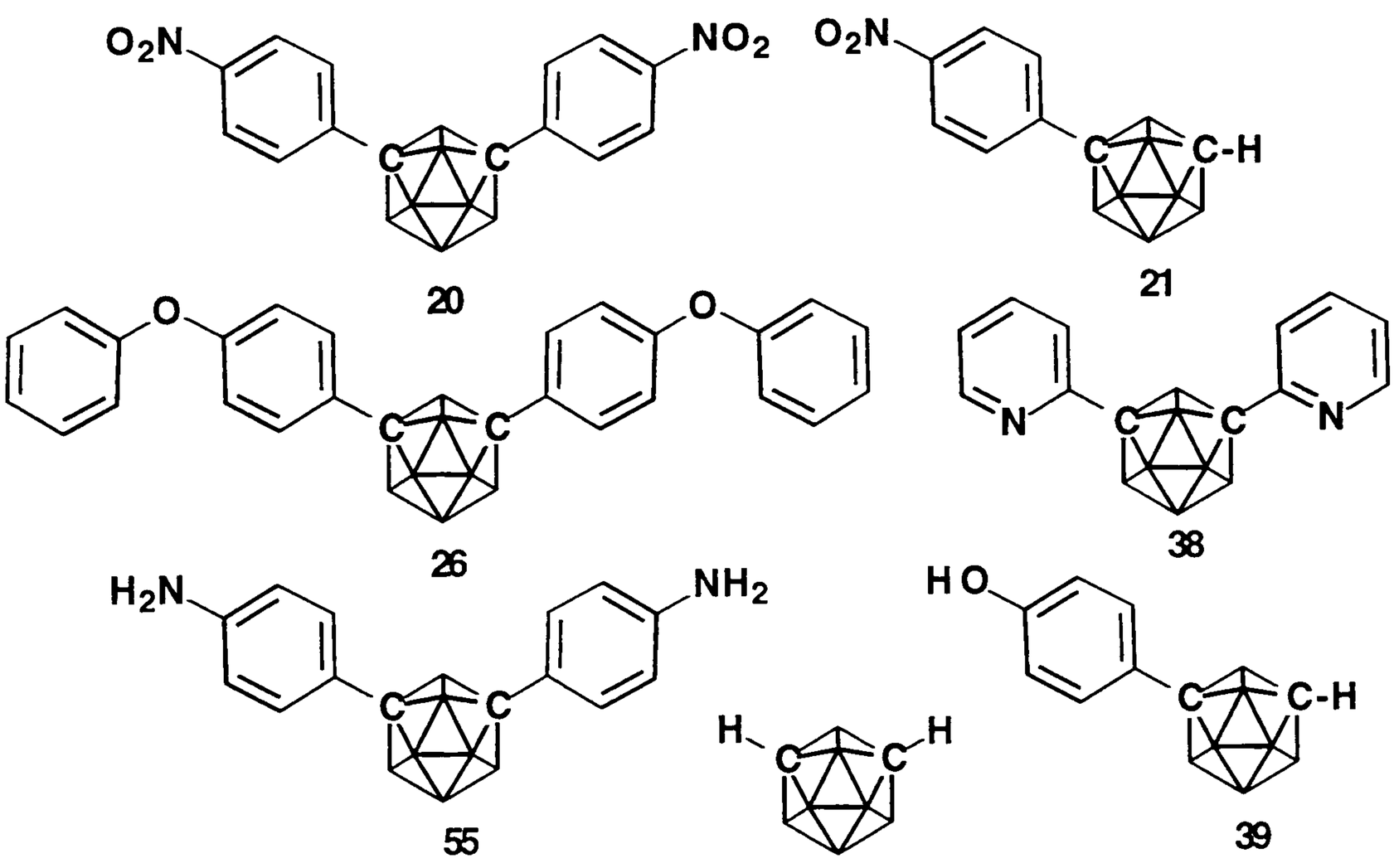


Figure 3.6: *Carborane Derivatives Deboronated using Bu4NF*

Table 3.1: *Times for Complete Conversion to nido-Anion*

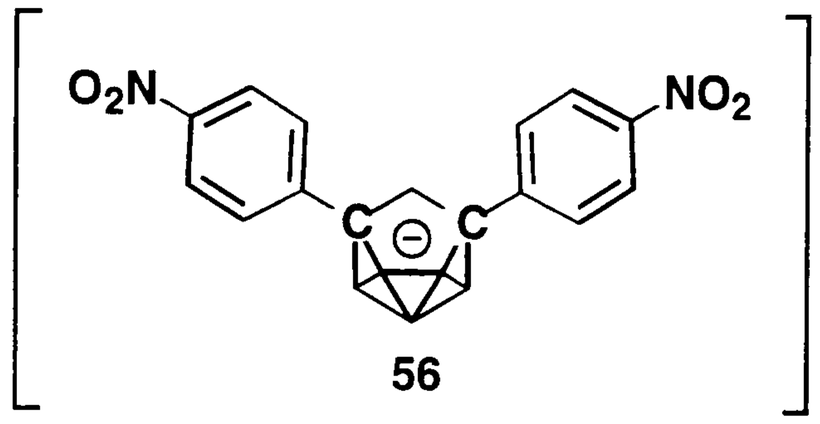
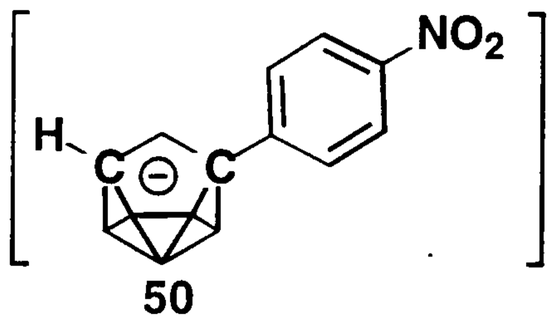
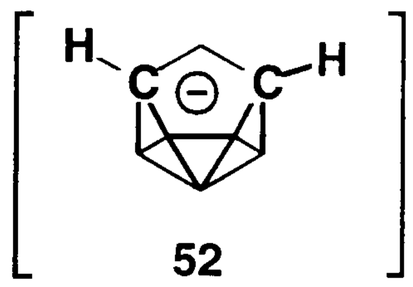
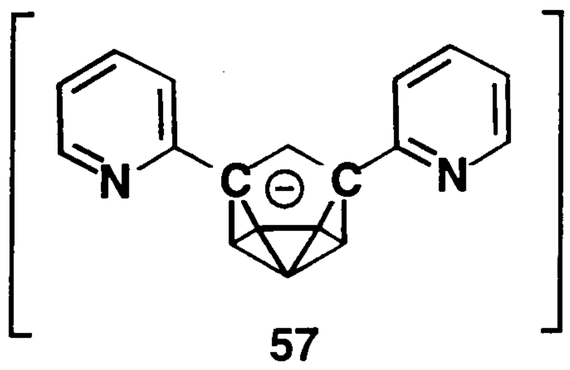
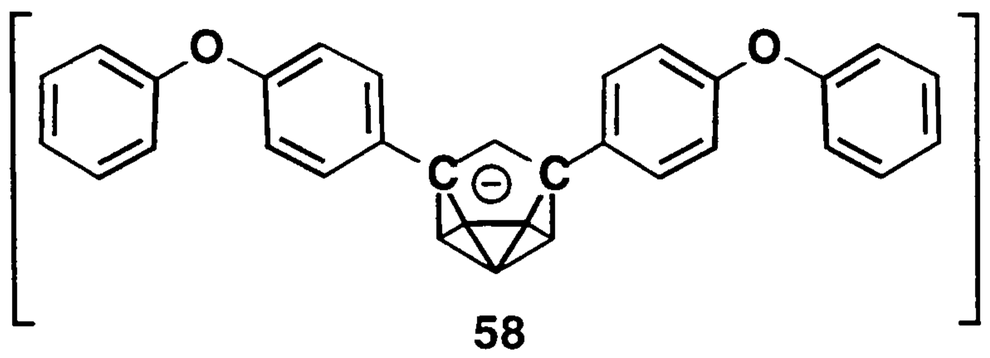
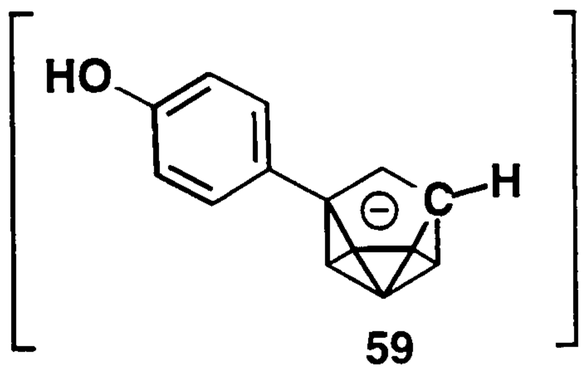
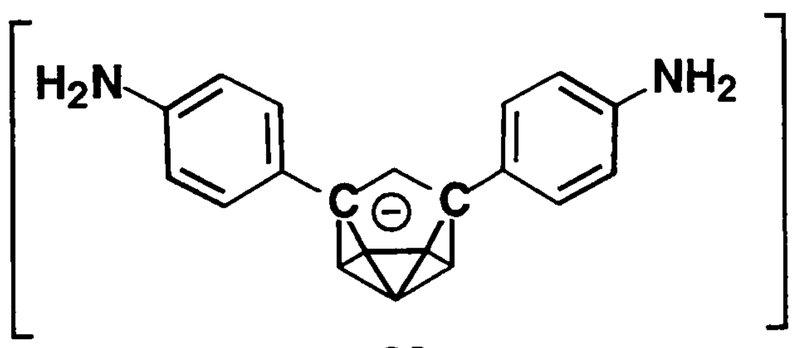
Compound	Time (hours)	σ
 **56**	0.5	-
 **50**	0.75	+0.778
 **52**	3.0	0
 **57**	6.0	-

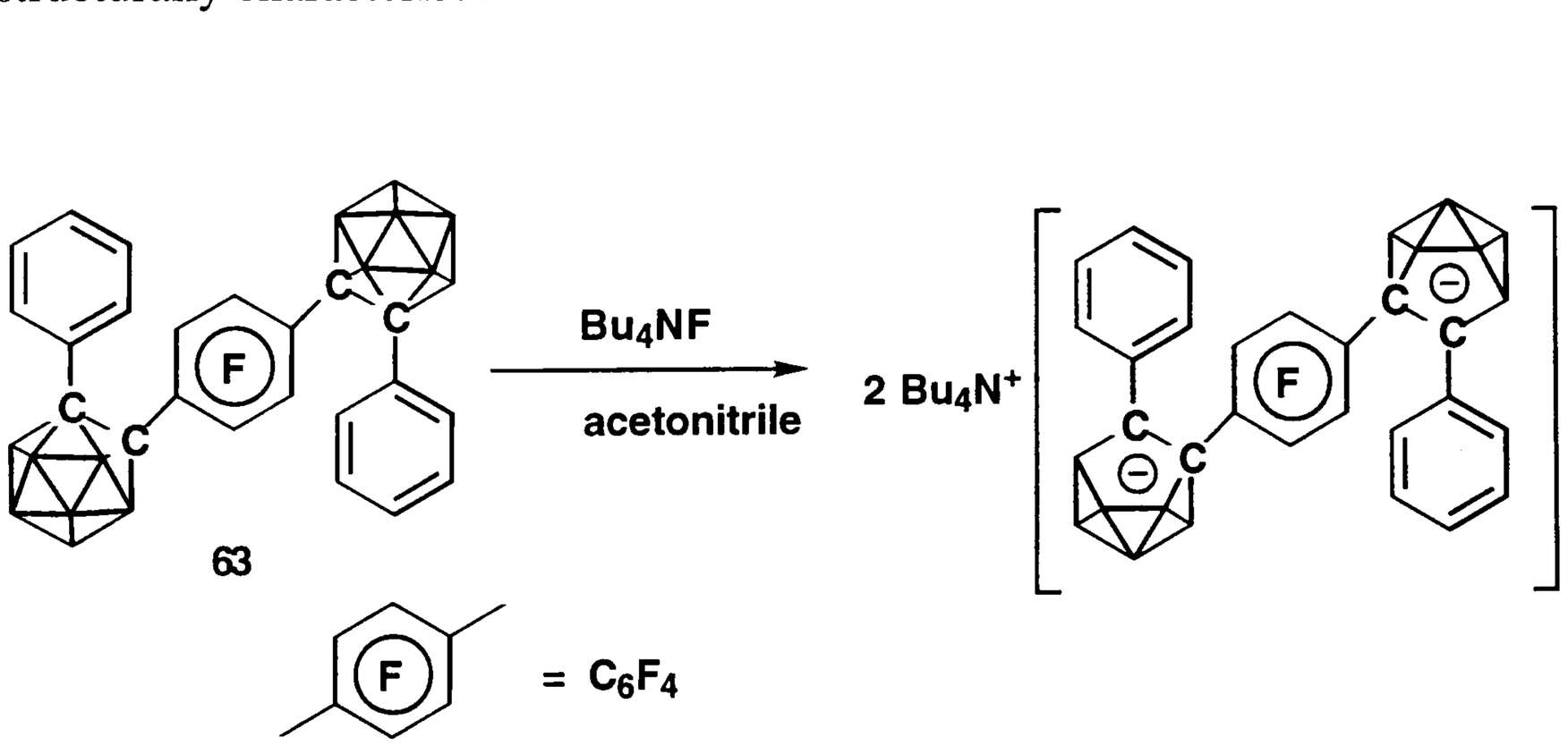
Table 3.1: *Times for Complete Conversion to nido-Anion*

Compound	Time (hours)	σ
 **58**	8.0	-0.320
 **59**	>12	-0.37
 **60**	8	-0.66

The rate of deboronation follows the same order as the Hammett σ function of the substituent,[24] and indicates that compounds bearing more electron-withdrawing substituents have a faster rate of reaction and the results are shown in Table 3.1

The rate of deboronation under anhydrous conditions is considerably slower suggesting that water plays a vital role in the rate of deboronation. Various experiments were performed by Fox *et al*[23] using 1-(4-fluorophenyl)-*ortho*-carborane and the analogous *meta*-carborane isomer, in an attempt to assess the exact role played by water in the reaction. Reactions were monitored by ^{19}F NMR, the spectra obtained for the deboronation of (1-(4-nitrophenyl)-*meta*-carborane) (**21**) being used for reference.

In addition a series of experiments were performed using fluorine substituted carborane derivatives such as (**63**), in an attempt to determine the different proportions of isomers produced in the deboronation reaction. NMR studies again showed that different isomers were produced using Bu_4NF as observed using classical deboronation reagents, although no isomer has yet been structurally characterised.



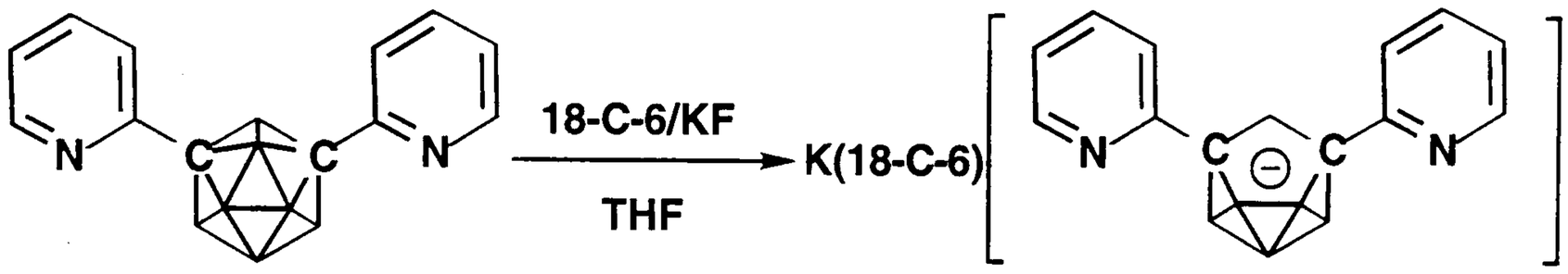
63

3.2.2 *para*-Carborane

Preliminary experiments with *para*-carborane have proved disappointing. *para*-Carborane itself showed no sign of degradation after refluxing with five equivalents of tetrabutylammonium fluoride for 4 days, although approximately 50% conversion of 1,12-bis-(4-nitrophenyl)-*para*-carborane to its monoanion was achieved after 24 hours of reflux.

3.2.3. Use of Other Fluoride Sources.

Studies have shown[23] that other fluoride salts can be used to effect the deboronation reaction. For example 1,7-bis-(2-pyridyl)-meta-carborane may be quantitatively deboronated in the presence of potassium fluoride and 18-crown-6 in approximately 48 hours in refluxing acetonitrile.



X-ray studies of a number of compounds have shown that the cation does not sit on the open face of the *nido*carborane fragment, but adopts different positions depending on the substituents attached to the cage. In the case of unsubstituted *ortho*-carborane, the counter ion was found to be on a triangular site opposite the open face of the carborane cage, (Figure 3.7a). However in the case of the deboronated product of 1,2-(diphenyl)-*ortho*-carborane (Figure 3.7b), the cation was found to sit on the edge of the open vertex, away from the carbon atoms. Further work is currently in progress in this area.

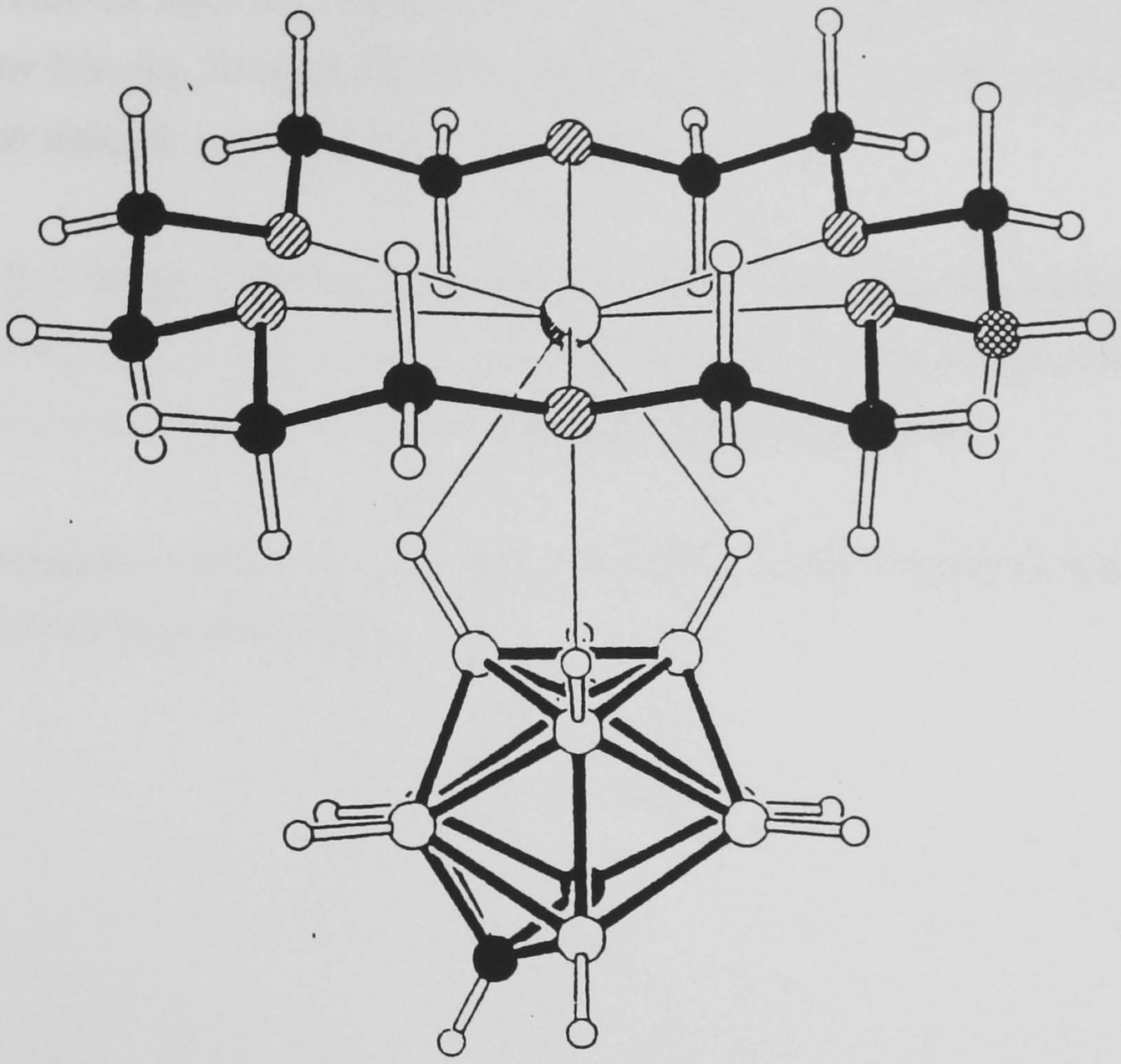
3.2.4. Conversion to the dianion:

Monoanionic *nido*-carborane salts of alkali metals such as potassium and caesium may be readily converted into the dianionic salts by reaction with sodium hydride in THF.

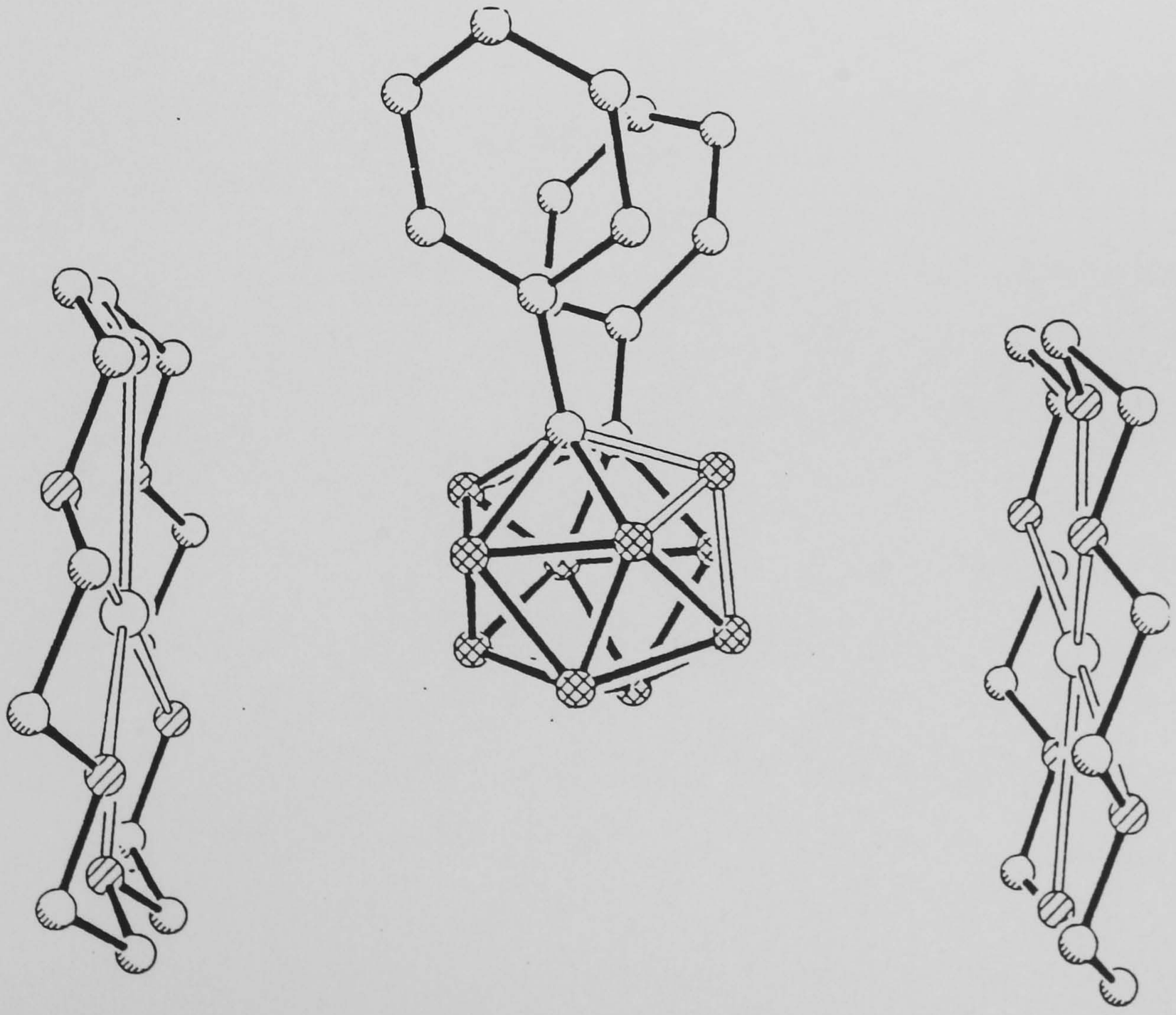
Several attempts were made to remove the tetrabutyl ammonium cation and subsequently convert the mono anionic carboranyl species into dianionic compounds and metallacarboranes. However the cation was stable to reaction with thallium acetate, sodium hydride and butyl lithium and could only be effectively removed from Bu_4N^+ $[1,2\text{-}C_2B_9H_{12}]^-$ by boiling with potassium t-butoxide in toluene, which afforded $K_2C_2B_9H_{10}$ which may be readily converted to metallocene-type species. Further work in this area is currently in progress.

Figure 3.7: *Unusual Geometries Adopted by nido-Carborane Anions*

[*nido*-7,8-$C_2B_9H_{10}$]$^-$ [Kcrown6]$^+$



[*nido*-7,8-diphenyl-7,8-$C_2B_9H_{10}$]$^-$ [Kcrown6]$^+$



3.3. Conclusion:

Preliminary studies have shown that fluoride ion in wet THF solution is a useful reagent for conversion of *ortho*- and *meta*-carboranes and their derivatives into the corresponding *nido*-anions, and that the introduction of water into the reaction mixture significantly decreased the reaction times from those reported by Onak and co-workers.[22]

Studies using fluoride ion in the presence of water as the deboronation agent showed this to be particularly suitable for C-substituted *meta*-carborane derivatives which are difficult to degrade by other means.

Subsequent work by Fox has provided NMR evidence for the reaction sequence shown in Figure 3.5.

3.4. Experimental:

General Procedure for the Deboronation of *ortho*-Carborane Derivatives by Classical Routes.

3.4.1. Preparation of Tetraethylammonium-(3)-7,8-bis-(phenyl)-1,2-dicarbadodecahydroundecaborate (-1) (43).

1,2-diphenyl-*ortho*-carborane (1.08 g, 3.65 mmol) was suspended in methanol (20 ml) in a 50 ml round bottomed flask. Potassium hydroxide (1.02 g, 18.2 mmol) was added. The reaction mixture was heated to 80 °C and refluxed for 18 hours, when an IR spectrum of the solution showed a *nido*-carborane peak (at 2527 cm^{-1}) and no *closo* peak, and the reaction was considered complete. The solution was allowed to cool to room temperature and solid carbon dioxide was then added to the reaction vessel to precipitate any excess potassium hydroxide as K_2CO_3. The precipitate was removed by filtration, and washed with boiling methanol. The filtrate and washings were combined and the solvents were removed under vacuum, to afford a white solid which was dissolved in water (10 ml) and added to a solution of tetraethylammoniumiodide (0.750 g, 7.8 mmol) in water (10 ml). A flocculent white precipitate immediately formed and was isolated by filtration, washed (4 x 20 ml of water), and recrystallised from water to afford white needle-like crystals identified as (**43**) (1.45 g, 96%).

Analysis: M_r (FAB^+) 130, (FAB^-) 281-290 $C_{14}B_9H_{20}$ requires M_r;(FAB^+) 130; (FAB^-) 278-289.

IR ν_{max}: 3076 vw; 3048 w; (Ar-H) 2980 m; 2949 w; (ethyl C-H), 2528 vs; (B-H), 1598 m; (C-N), 1482 s; 1442 s; 1393 m; (phenyl in-plane deformations), 1172 s; 774 s; 703 s; (phenyl out-of-plane deformations), 731 w; (B-H stretch)

NMR:

δ ^1H 1.195 (s, ethyl CH_3), 3.131 (t, ethyl CH_2), 6.862 (m, phenyl ring), 7.124 (m, phenyl ring)

δ ^{13}C 6.16 (m, ethyl group), 57.88 (s, carboranyl carbons), 131.08, 132.37, 137.37 (ArC)

3.4.2. Preparation of Tetramethylammonium-(3)-1,7-(diphenyl)-1,7-dicarbadodecahydroundecaborate (-1) (45).

1,7-(diphenyl)-*meta*-carborane (0.34 g, 1.14 mmol) was treated with refluxing ethanolic potassium hydroxide solution (0.23 g, 6 mmol, in 2.5 ml) according to the general reaction procedure described above, (Section 3.4.1), for 7 days. The reaction mixture was washed with dichloromethane (3 x 25 ml) which was then dried and evaporated to dryness to afford a white solid identified as the starting material 1,7-bis(phenyl)-*meta*-carborane, (0.225 g, 0.76 mmol). The remaining alcoholic solution was saturated with a stream of carbon dioxide and the filtrate and washings were evaporated to dryness to afford the crude potassium salt. This was converted into the tetramethylammonium salt, forming a white precipitate. This was isolated by filtration, washed with water and dried. The solid was recrystallised from ethanol to afford white crystals identified as (**45**), yield 0.08 g, 25%, melting point 315-316 °C. The product was characterised as follows:

Analysis: Found; C, 59.94, H, 9.02, N, 3.69%; $C_{18}B_9H_{32}N$ requires C, 60.10, H, 8.97, N, 3.89%;

IR $\nu_{max}cm^{-1}$: 3028 w (Ar CH), 2526 s (BH), 1598 m, 1481 s, 1444 m, 1260 m, 1171 w, 1069 m, 950 m, 765 m, 698 s, 494 w.

3.4.3. Preparation of Trimethylammonium-(3)-1,2-bis-(methyl)-1,2 dicarbadodecahydroundecaborate) (47)

1,2-Dimethyl-*ortho*-carborane (1.20 g, 6.98 mmol) was treated with refluxing ethanolic potassium hydroxide solution (0.78 g, 20 mmol, in 8 ml) for 2 days, according to the general reaction procedure described above, (Section 3.4.1). The crude potassium salt was converted into the tetramethylammonium analogue by the addition of a solution of trimethylammonium chloride (0.495 g, 4.5 mmol) in water (10 ml) to a solution of the crude potassium salt in water (10 ml), forming a white precipitate. which was isolated by filtration, washed (4 x 20 ml of water), and recrystallised from water to afford white needle-like crystals identified as (**47**) (1.44 g, 93%).

IR ν_{max} : 3439 vs,br; (N-H), 2995 m, 2943 m, 2863 m, 2519 s; (*nido* B-H), 1440 m, 1382 m, 1192 m, 1082 m, 1069 s, 946 m, 918 w, 899 m, 782 s, 660 m, 639 w, 511 w, 451 w.

3.4.4. Preparation of Tetramethylammonium-(3)-1,4-phenylene-bis-(1,2-dicarbadodecahydroundecaborate) (-2) (48).

1,4-bis-(1,2-carboranyl)benzene (1.38 g, 4 mmol) was treated with refluxing ethanolic potassium hydroxide solution (0.78 g, 20 mmol, in 8 ml) for 2 days, according to the general reaction procedure described above, (Section 3.4.1). The crude potassium salt was converted into the tetramethylammonium analogue by the addition of a solution of tetramethylammonium chloride (0.495 g, 4.5 mmol) in water (10 ml) to a solution of the crude potassium salt in water (10 ml), forming a white precipitate. This was isolated by filtration and washed with water. The solid was recrystallised from ethanol to afford white crystals identified as (**48**), yield 1.65 g, 85%, melting point 285-289 °C. The product was characterised as follows:

Analysis: Found; C, 54.94, H, 12.87, N, 7.25%; M_r (FAB^+) 73-75, and M_r (FAB^-) 332-341; $C_{18}B_{18}H_{50}N_2$ requires C, 55.07, H, 12.84, N, 7.13%; M_r (FAB^+) 74, and M_r (FAB^-) 326-345

IR $\nu_{max}cm^{-1}$: 3061 w (carboranyl CH), 3028 w (Ar CH), 2526 s (BH), 1590 m, 1489 s, 1409 m, 1310 w, 1254 s, 1202 m, 1174 s, 1060 m, 1117 m, 1071 m, 1016m, 898 m, 874 m, 860 m, 798 w, 751 s, 690 m, 575 w, 519 m, 483 m, 421 w.

3.4.5. Preparation of Tetramethylammonium-(3)-1,3,5-tris-1-(2-phenyl-1,2 dicarbadodecahydroundecaborate)benzene (3-) (49).

1,3,5-tris-(2-phenyl-1-*ortho*-carboranyl)-benzene (0.60 g, 0.8 mmol) was treated with refluxing ethanolic potassium hydroxide solution (0.156 g, 4 mmol, in 2.5 ml) for 72 hours, according to the general reaction procedure described above, (Section 3.4.1) to afford the crude potassium salt. This was converted into the tetramethylammonium salt and recrystallised from ethanol to afford white crystals, yield 0.54 g, 85%, melting point > 350°C. The product was characterised as follows:

Analysis: Found; C, 53.12, H, 9.05, N, 3.99%; $C_{42}B_{27}H_{84}N_3$ requires C, 54.65, H, 9.17, N, 4.55%;

IR $\nu_{max}cm^{-1}$: 3067 w, 3002 w (Ar CH), 2955 w, 2528 s (BH), 1716 s, 1573 s, 1456 s, 1409 m, 1361 s, 1221 s, 1127 s, 1034 s, 946 m, 902 m, 754 m, 658 s, 530 s.

General Procedure for the Deboronation of *ortho*- and *meta*-Carborane Derivatives by Tetrabutylammonium Fluoride

3.4.6. The preparation of Tetrabutylammonium-(7-(4-nitrophenyl)-1,7-dicarbadodecahydroundecaborate (-1) (50).

1-(4-nitrophenyl) *meta* carborane (0.331 g, 1.25 mmol) was added to a stirred solution of Bu_4NF hydrate (1.63 g, 6.25 mmol) in THF (3 ml), forming a blue-green solution that quickly changed to orange-brown. This was stirred at room temperature for 45 minutes, when its infrared spectrum suggested the reaction to be complete. Dichloromethane (8 ml) was added and the reaction mixture was washed with water (3 x 25 ml) and dried over $MgSO_4$. The solvents were removed under vacuum and the resulting crude product was recrystallised from ethanol to afford a bright yellow crystalline solid (0.610 g, 98%) identified as (**50**). The product was characterised as follows:

Analysis: Found; C, 57.04, H, 10.60, N, 5.25 %; M_r (FAB^+) 242 and (FAB^-) 248-259; $C_{24}B_9H_{51}N_2O_2$ requires C, 58.30, H, 10.06, N, 5.63%; M_r (FAB^+) 242-243 and (FAB^-) 247-258

IR $\nu_{max}cm^{-1}$: 3038 w, 2508 s (BH), 1590 s, 1505 s, 1342 m, 1168 m, 1113 m 1061 m, 1033 m, 976 m, 896 m, 877 m, 866 m, 847 m, 800 w, 756 m, 694 w, 631 w, 520 w, 482 w, 459 w, 437 m.

3.4.7. The preparation of Tetrabutylammonium-(3)-1,7-dicarbado-decahydroundecaborate (-1) Ion (52).

Freshly sublimed *meta* carborane (0.361 g, 2.5 mmol) was treated with a solution of Bu_4NF hydrate (3.265 g, 12.5 mmol) in THF (5 ml), according to the reaction described above (Section 3.4.6). The solution was stirred at room temperature for 3 hours, when its infrared spectrum suggested the reaction to be complete. Dichloromethane (15 ml) was added and the reaction mixture was washed with water (3 x 50 ml) and dried over $MgSO_4$. The solvents were removed under vacuum and the resulting crude product was recrystallised from ethanol to afford a white crystalline solid (0.917 g, 98%) identified as (**52**) The product was characterised as follows:

Analysis: Found; C, 57.05, H, 12.67, N, 3.79 %; M_r $C_{18}B_9H_{48}N$ requires C, 57.78, H, 12.78, N, 3.73%;

IR $_{max}cm^{-1}$: 3228 br, 2964 s, 2876 m, 2521 s (BH), 1460 m, 1364 m, 1300 s, 1188 m, 1195 m, 1144 m, 1069 s, 1031 sh., 911 s, 786 w, 656 w.

3.4.8. The preparation of Tetrabutylammonium-(7,9-bis-(4-nitrophenyl) 1,7-dicarbadodecahydroundecaborate (-1) (56).

1,7-bis-(4-nitrophenyl) *meta* carborane (0.480 g, 1.25 mmol) was treated with a solution of Bu_4NF hydrate (1.63 g, 6.25 mmol) in THF (3 ml), according to the reaction procedure described above, (Section 3.4.6), forming a red-brown solution This was stirred at room temperature for 30 minutes, when infrared suggested the reaction to be complete. Dichloromethane (8 ml) was added and the reaction mixture was washed with water (3 x 25 ml) and dried over $MgSO_4$. The solvents were removed under vacuum and the resulting crude product was recrystallised from propan-2-ol to afford an orange microcrystalline solid (0.741 g, 96%) identified as (**56**). The product was characterised as follows:

Analysis: Found; C, 57.98, H, 7.89, N, 6.60 %; $C_{30}B_9H_{54}N_3O_4$ requires C, 58.33, H, 8.75, N, 6.80%;

IR $\nu_{max}cm^{-1}$: 3024 w, 2522 s (BH), 1613 s, 1517 s 1317 m, 1211 m 1176 m, 1048 m, 828 m, 737 m, 430 w.

3.4.9. The preparation of Tetrabutylammonium-(7,9-bis-(2-pyridyl)-1,7-dicarbadodecahydroundecaborate (-1) (57).

1,7-bis-(2-pyridyl) meta carborane (0.369 g, 1.24 mmol) was treated with a solution of Bu_4NF hydrate (1.63 g, 6.25 mmol) in THF (3 ml), according to the reaction described above (Section 3.4.6), forming a yellow solution This was stirred at room temperature for 6 hours, when infrared suggested the reaction to be complete. Dichloromethane (8 ml) was added and the reaction mixture was washed with water (3 x 25 ml) and dried over $MgSO_4$. The solvents were removed under vacuum and the resulting crude product was recrystallised from propan-2-ol to afford a white crystalline solid (0.625 g, 95%) identified as (**57**). The product was characterised as follows:

Analysis: Found; C, 63.97, H, 10.56, N, 8.01 %; $C_{28}B_9H_{54}N_3$ requires C, 63.49, H, 10.19, N, 7.93%;

IR $\nu_{max}cm^{-1}$: 2544 s (BH str.), 1925 s, 1656 s, 1599 s, 1422 s, 1336 s, 1272 s, 1092 s, 1051 s, 881 s, 803 m, 668 m, 434 m.

3.4.10. The preparation of Tetrabutylammonium-7,9-bis-(4-phenoxy-phenyl) -1,7-dicarbadodecahydroundecaborate (-1) (58)

1,7-Bis-(4-phenoxyphenyl) *meta* carborane (0.500 g, 1.04 mmol) was treated with a solution of Bu_4NF hydrate (1.64 g, 6.4 mmol) in THF (3 ml), according to the reaction described above (Section 3.4.6). The solution was stirred at room temperature for 8 hours, when its infrared spectrum suggested the reaction to be complete. Dichloromethane (10 ml) was added and the reaction mixture was washed with water (3 x 25 ml) and dried over $MgSO_4$. The solvents were removed under vacuum and the resulting crude product was recrystallised from ethanol to afford a white crystalline solid (0.916 g, 91%) identified as (**58**). The product was characterised as follows:

Analysis: Found; C, 71.02, H, 8.69, N, 1.89 %; $C_{42}B_9H_{64}NO_2$ requires C, 70.88, H, 8.99, N, 1.97%;

IR $_{max}cm^{-1}$:3038 w, 2538 s (BH.), 1589 s, 1504 s, 1332 m, 1239s , 1166 m, 1091 m, 1049 m, 875 m, 752 m, 693 m, 576 w, 512 w, 420 w.

3.4.11. The preparation of Tetrabutylammonium-7-(4-hydroxyphenyl)-1,7-dicarbadodecahydroundecaborate (-1) (59).

1-(4-hydroxyphenyl) *meta* carborane (0.102 g, 0.432 mmol) was treated with a solution of Bu_4NF hydrate (0.342 g, 1.31 mmol) in THF (0.5 ml), according to the reaction described above, (Section 3.4.6). No reaction was observed after stirring for 12 hours at room temperature so the reaction mixture was heated to reflux and found to be complete after 5 hours. The reaction mixture was allowed to cool to room temperature and dichloromethane (2 ml) was added and the reaction mixture was washed with water (3 x 10 ml) and dried over $MgSO_4$. The solvents were removed under vacuum and the resulting crude product was recrystallised from ethanol to afford a white crystalline solid (0.195.g, 90%) identified as (**59**). The product was characterised as follows:

Analysis: Found; C, 61.85, H, 11.52, N, 2.89 %; M_r (FAB^+) 242 and (FAB^-) 224-229; $C_{24}B_9H_{52}NO$ requires C, 61.65, H, 11.12, N, 3.00%; M_r (FAB^+) 242-243 and (FAB^-) 218-229.

IR $\nu_{max}cm^{-1}$: 3489 s, 3038 w, 2516 s (BH), 1609 m, 1506 s, 1258 s, 1194 m, 1172 m, 1107 m, 1038 m, 877 m, 850 m, 800 m, 739 m, 534 m.

3.4.12. The preparation of Tetrabutylammonium-(7,9-bis-(4-aminophenyl)-1,7-dicarbadodecahydroundecaborate (-1) (60).

1,7-bis-(4-aminophenyl) *meta* carborane (0.400 g, 1.20 mmol) was treated with a solution of Bu_4NF hydrate (1.60 g, 6.1 mmol) in THF (3 ml), according to the reaction described above (Section 3.4.6). This was stirred at reflux for 8 hours, when its infrared spectrum suggested the reaction to be complete. Dichloromethane (8 ml) was added and the reaction mixture was washed with water (3 x 25 ml) and dried over $MgSO_4$.

The solvents were removed under vacuum and the resulting crude product was recrystallised from ethanol to afford an orange crystalline solid (0.663 g, 99%) identified as (**60**). The product was characterised as follows:

Analysis: Found; C, 64.26, H, 10.07, N, 7.13%; $C_{30}B_9H_{58}N_3$ requires C, 64.56, H, 10.47, N, 7.52%;

IR $\nu_{max}cm^{-1}$: 3200 br., 2961 s, 2874 s, 2537 s, 1625 m, 1512 s, 1464 s, 1380 s, 1361 m, 1065 m, 983 m, 895 s, 739 m, 525 w.

3.5 References:

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Chapter 4

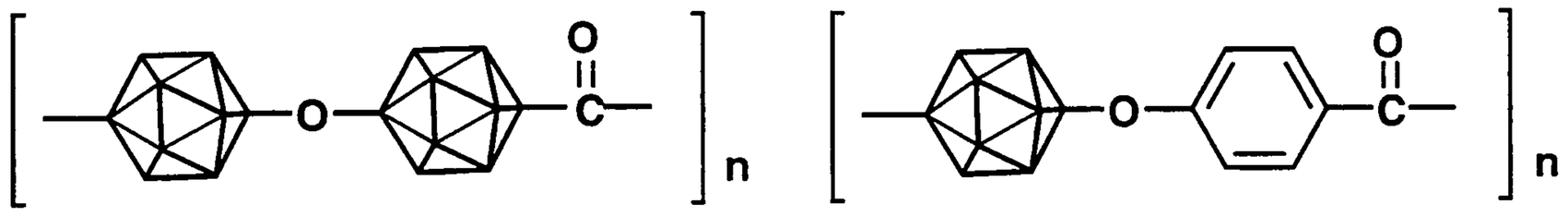
THE PREPARATION OF POLY(ARYLETHERCARBORANYLKETONE)S

4.1 Introduction:

4.1.1 Polymer Synthesis:

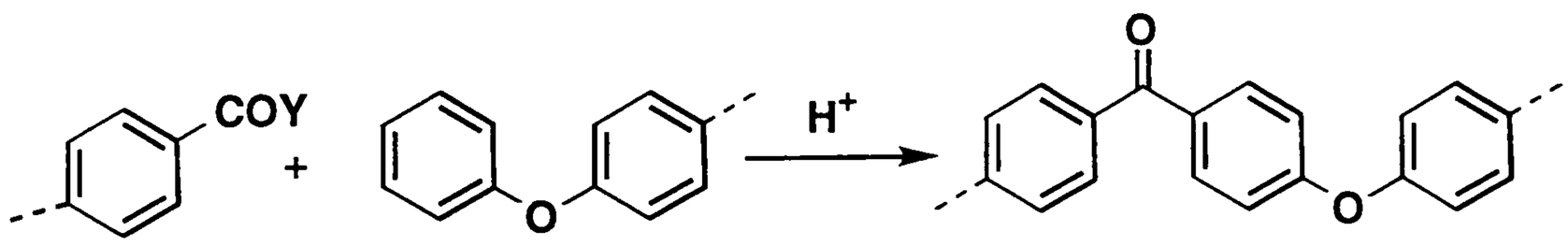
Aromatic poly(etherketone)s are a class of semi-crystalline aromatic thermoplastics that display excellent resistance to high temperatures (up to 300°C) and hydrolytic conditions, and hence are well established as high-performance engineering polymers.[1] However their relatively low glass transition temperatures (T_g's) particularly relative to the non-crystalline poly(sulphone)s and poly(imide)s are a limiting design feature where continuous load is experienced above the T_g.

The aim of the present work was to determine whether the incorporation of the thermally and chemically resistant icosahedral carboranes into the backbones of such polymers would improve the overall thermal and chemical properties of the resulting systems, giving a new class of materials - the poly(ethercarboranylketone)s (PECK's).



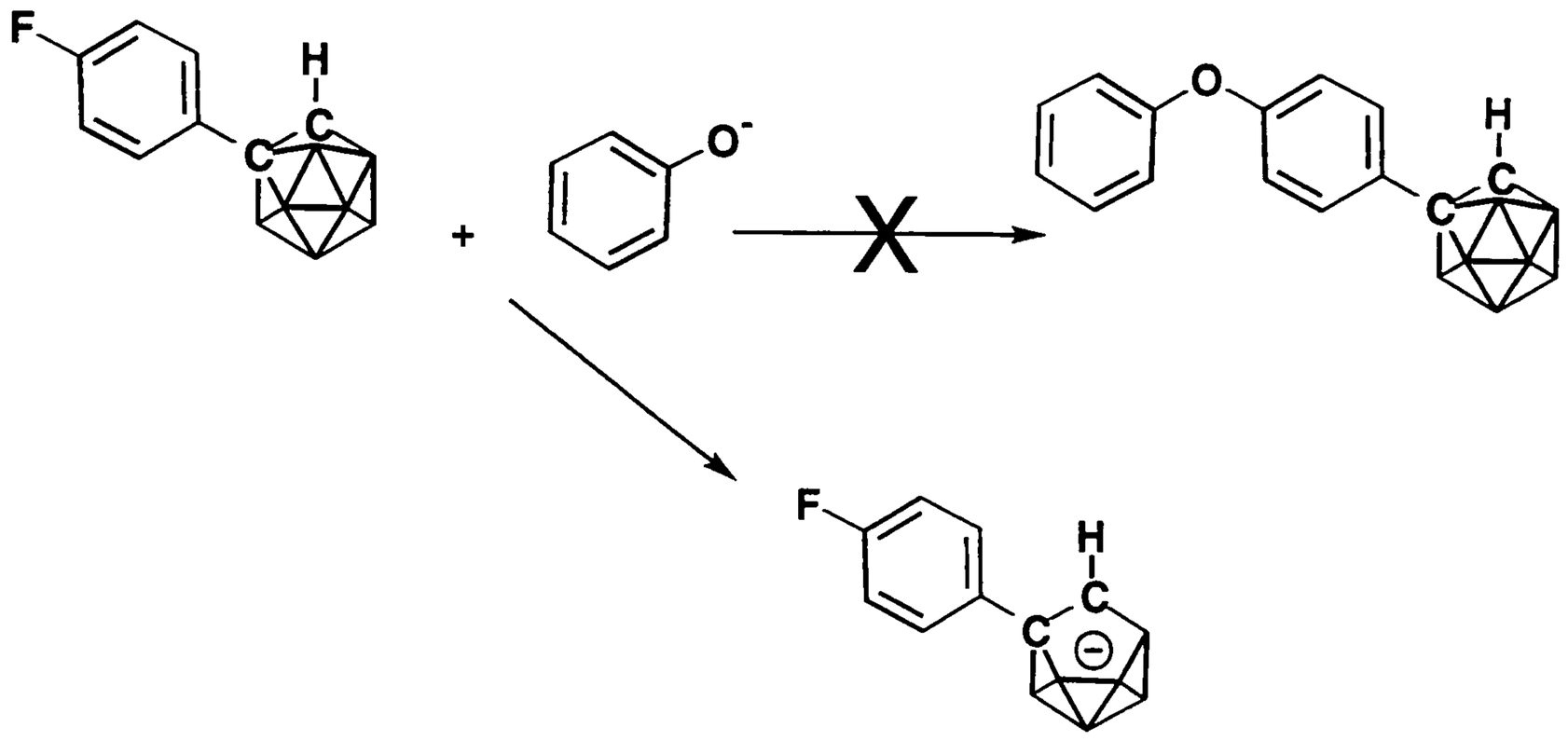
PECK's

Of the two potential routes to poly(ethercarboranylketone)s only acid catalysed electrophilic polycondensation (the polyketone synthesis) of a carborane-diether moiety with a diacid chloride or dicarboxylic acid has so far provided a feasible route to the incorporation of icosahedral carboranes into a poly(etherketone)-type backbone.



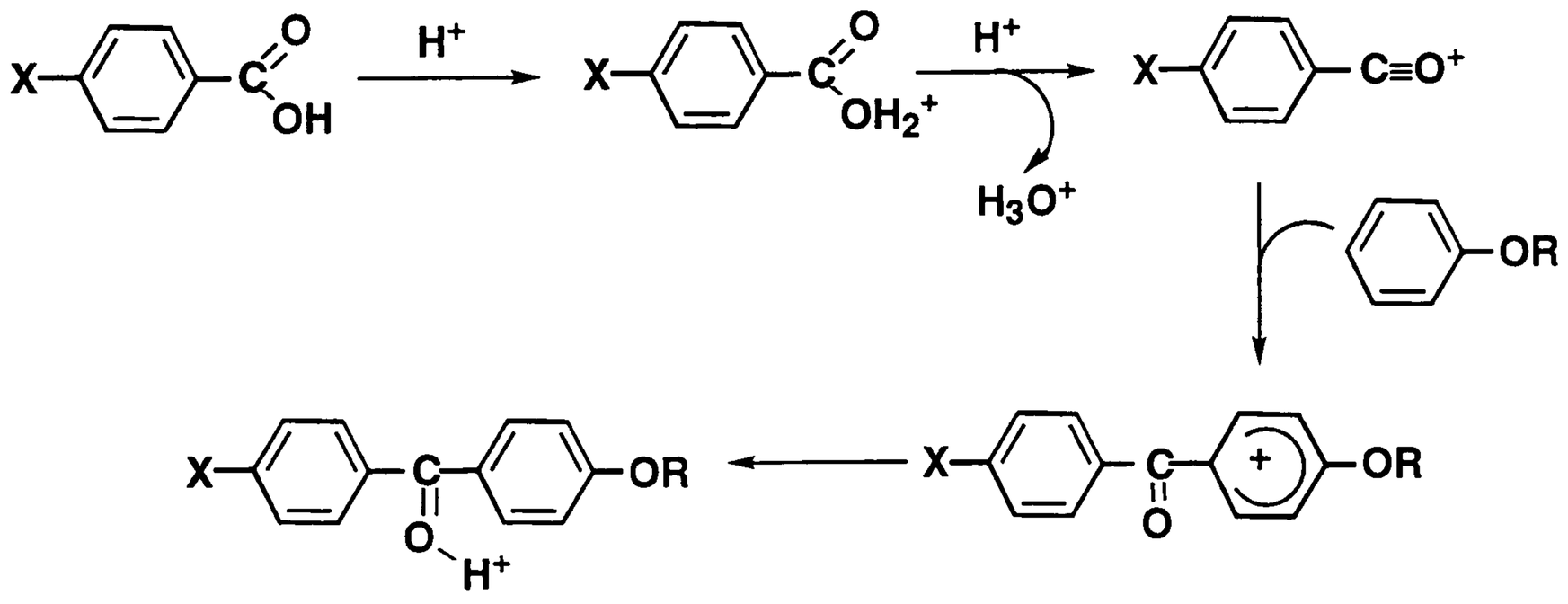
Where Y = halide or -OH

The carborane cage is susceptible to degradation under nucleophilic conditions, and was found to be too reactive to survive under the conditions required for the nucleophilic polyether synthesis,[2] as shown below:



Although there are numerous synthetic methods for electrophilic synthesis of aromatic PEK-type polymers, the most convenient laboratory technique has been found to be the polycondensation of aryl ethers with benzoic acid derivatives in trifluoromethanesulphonic (triflic) acid, (TFSA) although only low molecular weight materials were achieved.[3] Triflic acid acts as both a solvent and a catalyst for the reaction and can be conveniently removed at the end of the polymer synthesis by quenching the reaction mixture in water, simultaneously precipitating the polymer.

The condensation reaction is believed to involve the generation of an acylium ion ($Ar\text{-}CO^+$) through protonation of the carboxylic acid functionality, followed by elimination of water. Electrophilic attack on the aryl ether by the cation affords the ketone linkage. A proposed mechanism[4] is shown below.



Mixed anhydrides of carboxylic acids and TFSA have also been shown to act as powerful acylating agents[5] leading to their being proposed as alternative intermediate species in the acylation of aromatic hydrocarbons by carboxylic acids in TFSA.[6]

4.2. Results and Discussion:

Icosahedral carborane cages were successfully incorporated into the backbone of poly(etherketone)s by electrophilic polycondensation reactions carried out in anhydrous, freshly distilled trifluoromethanesulphonic (triflic) acid, at room temperature (with the exception of the polymerisation of 1,12-bis-(4-phenoxyphenyl)-*para*-carborane and terephthalic acid, which was conducted in TFSA in the presence of triflic anhydride at 80 °C).

To ensure that all of the carboxyl groups present at the start of the polymer synthesis had reacted, end capping of polymers with nonreactive groups was necessary. This was conveniently achieved by using a small excess (ca. 1%) of the diether monomeric species in the reaction mixture.

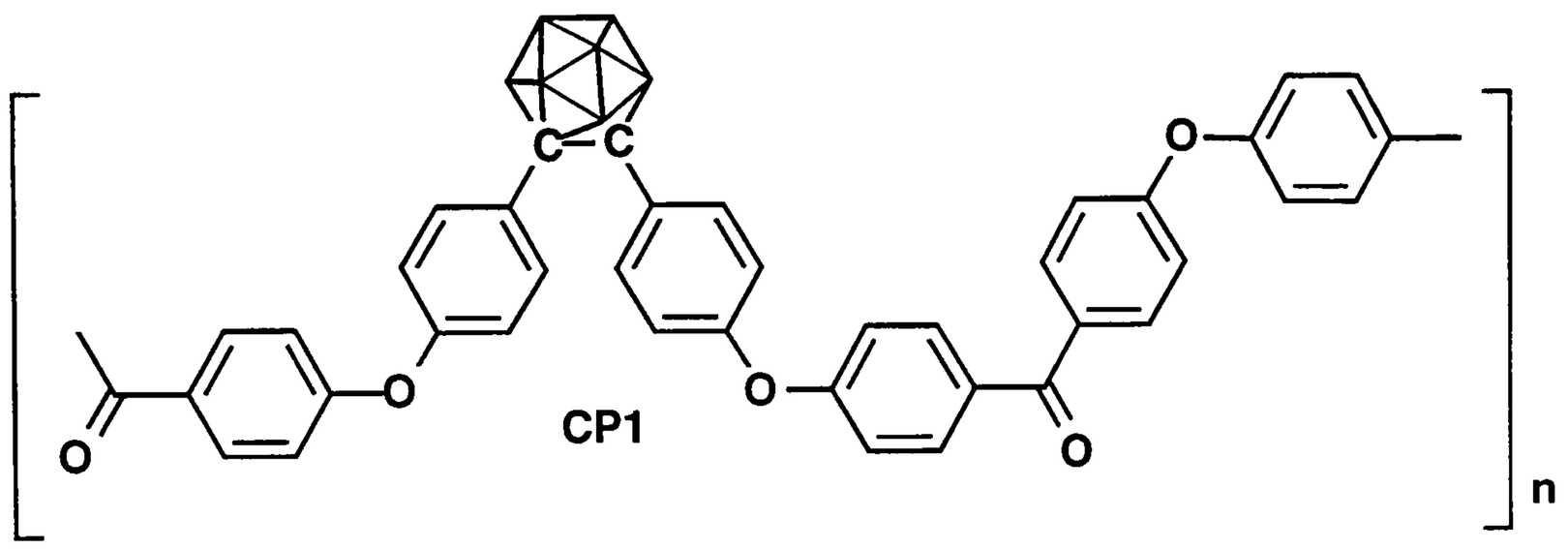
All of the polymers synthesised were isolated as white solids in the form of tough beads, by precipitation in water and were washed to remove the excess acid with 1% sodium hydroxide in refluxing aqueous ethanol. Certain polymers were also isolated as fibres cast by wet-spinning techniques.

Characterisation of these polymers has shown that their physical and chemical properties differ substantially from the all-organic poly(etherketone)s from which they are formally derived. Differential scanning calorimetric (DSC) studies on each of the new polymers made showed that the T_g (onset) increased markedly as a result of the introduction of the carborane residue into the polymer backbone. In addition the crystallinity normally observed in PEK-type polymers was disrupted in the majority of polymers prepared. The characteristics of the polymers prepared in the present work and their variation with type (carborane isomer, presence or absence of alkyl chains) are described below and compared with those of related all-organic polymers.

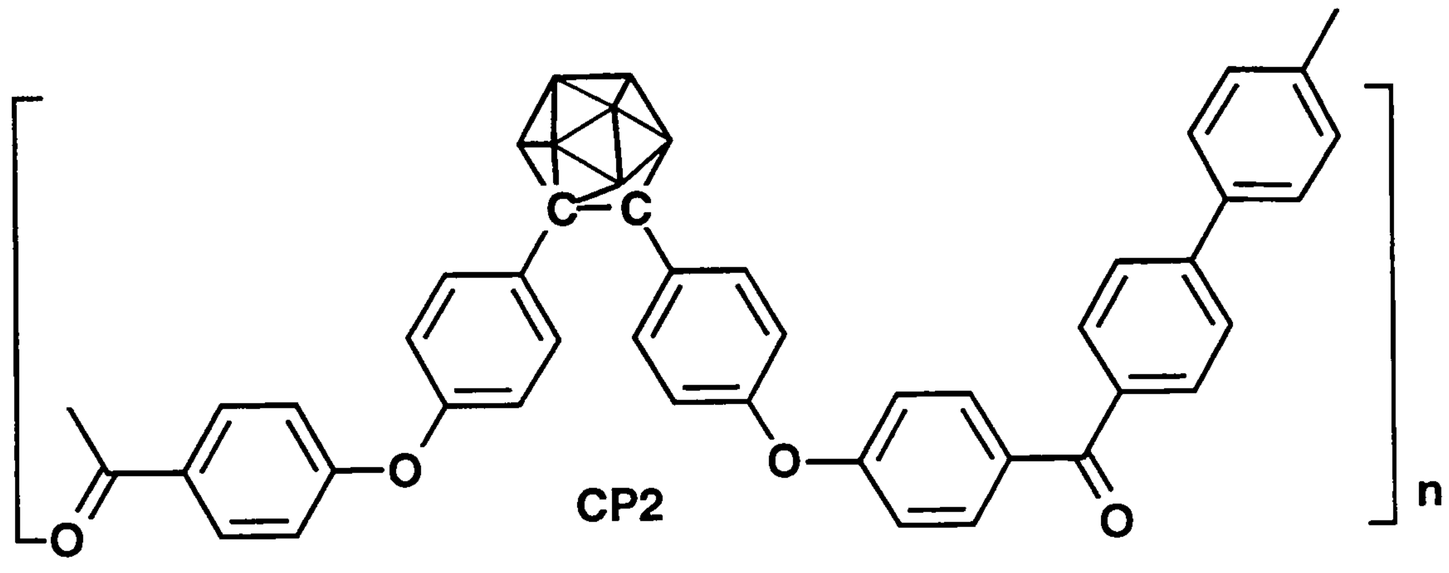
4.2.1. Aromatic Poly(ethercarboranylketone)s

4.2.1.1. *ortho* -Carborane-Based Polymers:

Incorporation of the *ortho*- carborane unit into the backbone of PEK was achieved as described above using freshly distilled triflic acid. The reaction between 1,2-bis-(4-phenoxyphenyl)-*ortho*-carborane and 4,4'-biphenyldicarboxylic acid and 4,4'-oxybis(benzoic acid) afforded the polymers **CP1** and **CP2,** shown below.



CP1

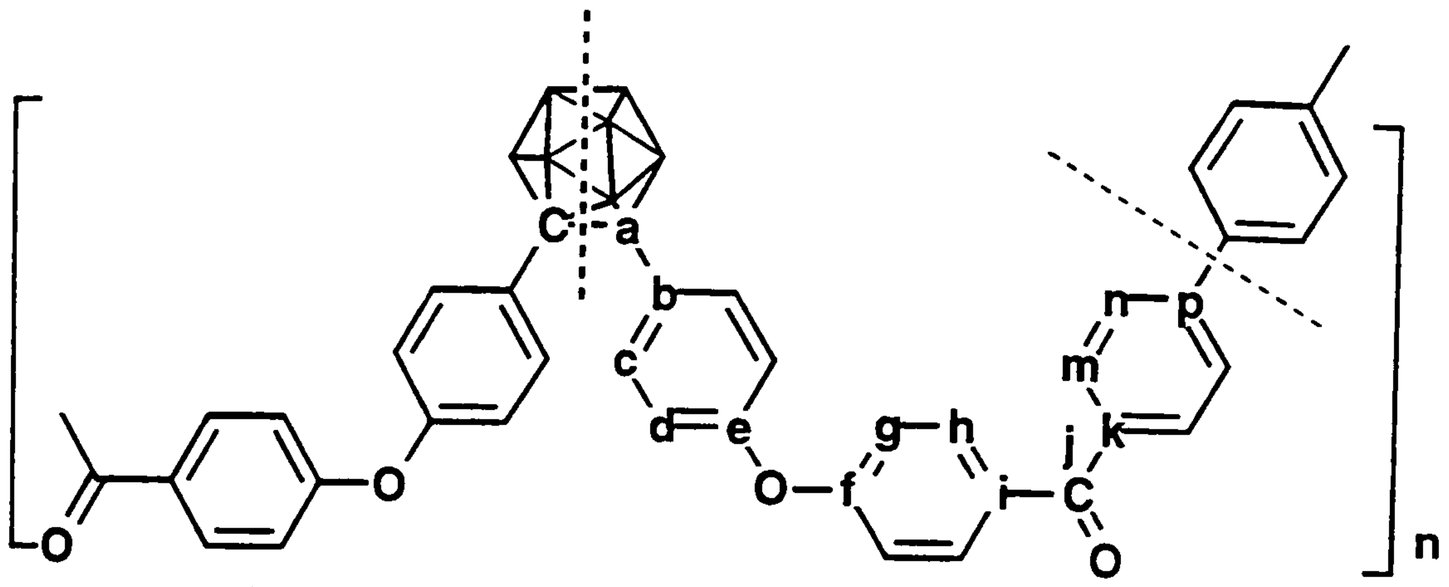


CP2

CP2 was previously prepared in the preliminary work reported by Stephenson *et al.*[7] However, only modest molecular weights were achieved (η inh = 0.24) in this earlier work probably because the triflic acid was used as supplied and has since been found to be wet.

^{1}H and ^{13}C NMR showed that the aromatic substitution patterns of the polymers were as shown above with only 1,4-linked aromatics being observed. This exclusively *para*-linkage of aromatic rings was observed for all of the polymers reported in this chapter and a typical spectrum is shown in Figure 4.1.

Figure 4.1 a): *^{13}C NMR Spectra of polymer CP2*



C atom	δ (^{13}C) ppm
a	85.31
b	126.92
c	132.94
d	119.46
e	158.07
f	160.52
g	118.60
h	133.32
i	133.13
j	195.09
k	137.53
m	131.06
n	147.65
p	195.00

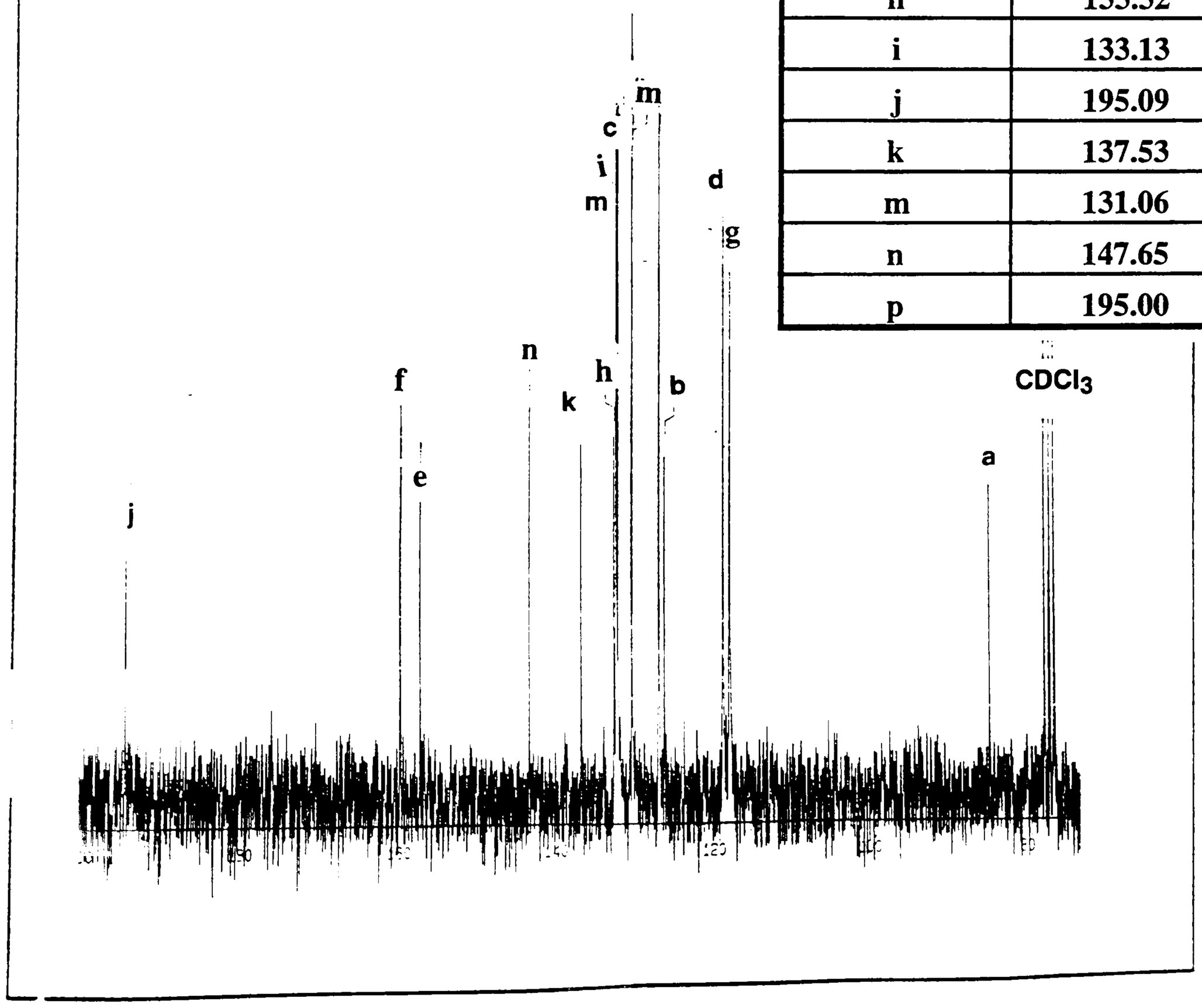
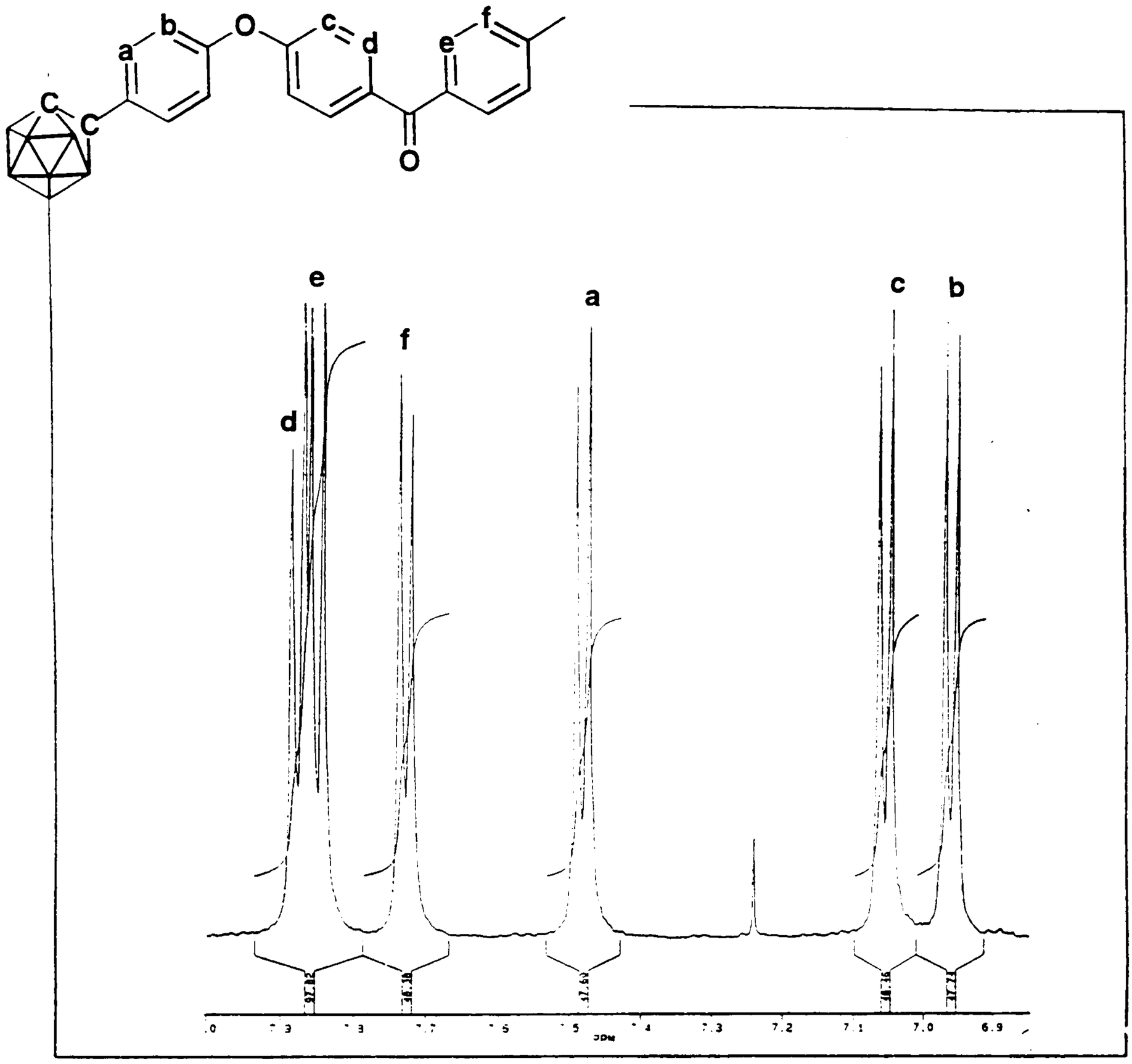


Figure 4.1 b): *^1H Spectra of polymer CP2*



GPC and viscosity measurements indicated that moderate to high molecular weight materials had been formed and the characterisation data for all of the polymers reported in this chapter are shown in Table 4.1.

Differential scanning calorimetry (DSC) showed that the resulting polymers were completely amorphous in contrast to the semi-crystalline PEK's from which they are formally derived.,

In the case of **CP1** and **CP2** DSC showed a marked increase in the T_g of the polycarboranes when compared to all-organic systems such as **OP1** and **OP2** synthesised under the same conditions and a typical scan in shown in Figure 4.2.

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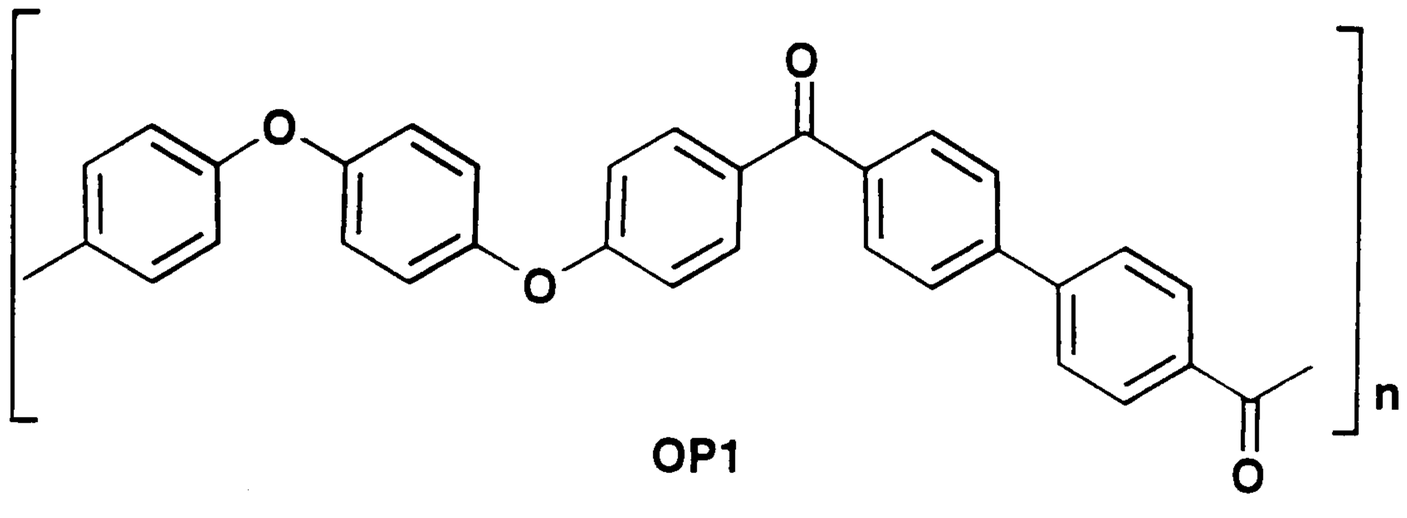
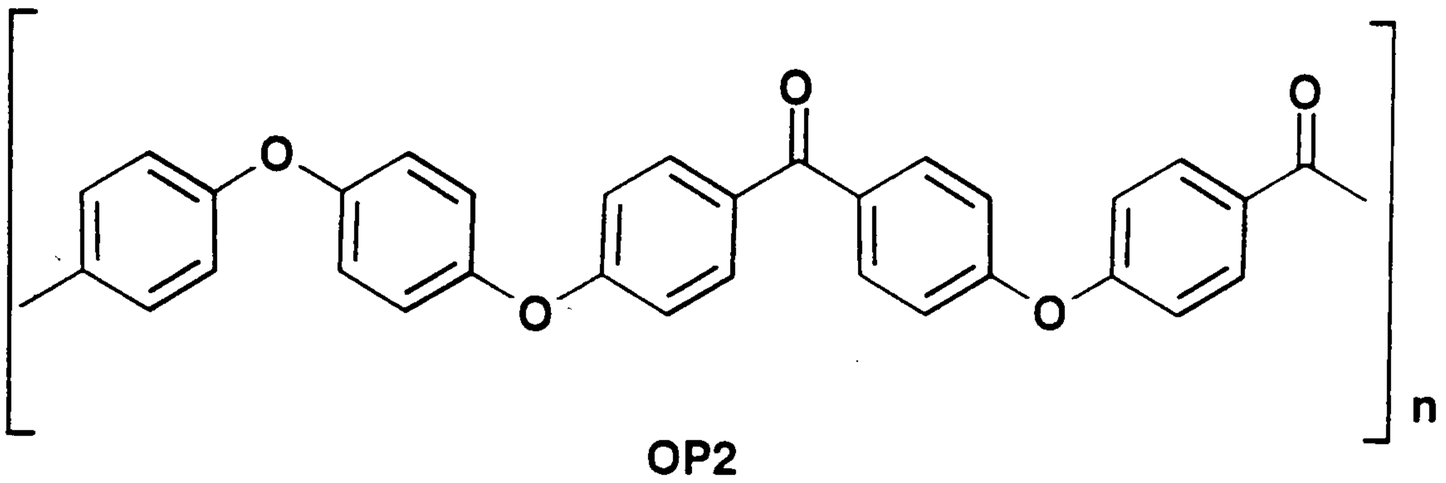


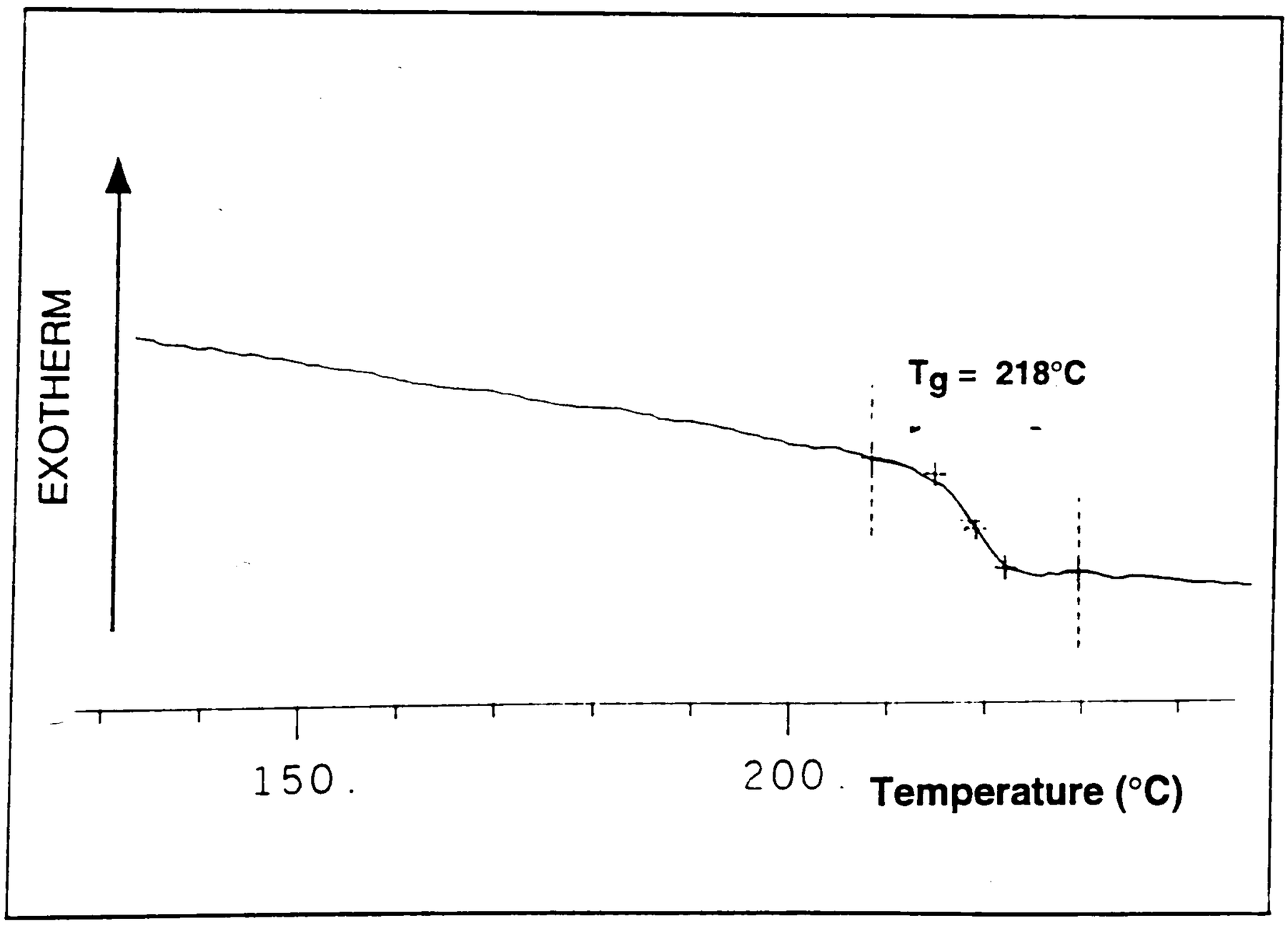
OP1



OP2

This is presumably due to incorporation of the rigid, bulky diphenylcarborane unit into the polymer backbone.

Figure 4.2: *Differential Scanning Calorimetry of Polymer **CP2** as-made.*



The mass retention of the all-organic polymers (**OP1** and **OP2**) were examined by thermogravimetric analysis (TGA) under nitrogen and under static air. It was found that the onset of weight loss of the PECK's was approximately 100 °C lower than that of the all-organic polymers. However, the carborane-containing polymers all retained over 90% of their original weight on heating to 850 °C under N_2, in comparison to approximately 50% weight loss by the all-organic polymers under the same conditions. This can be seen in Figure 4.3.

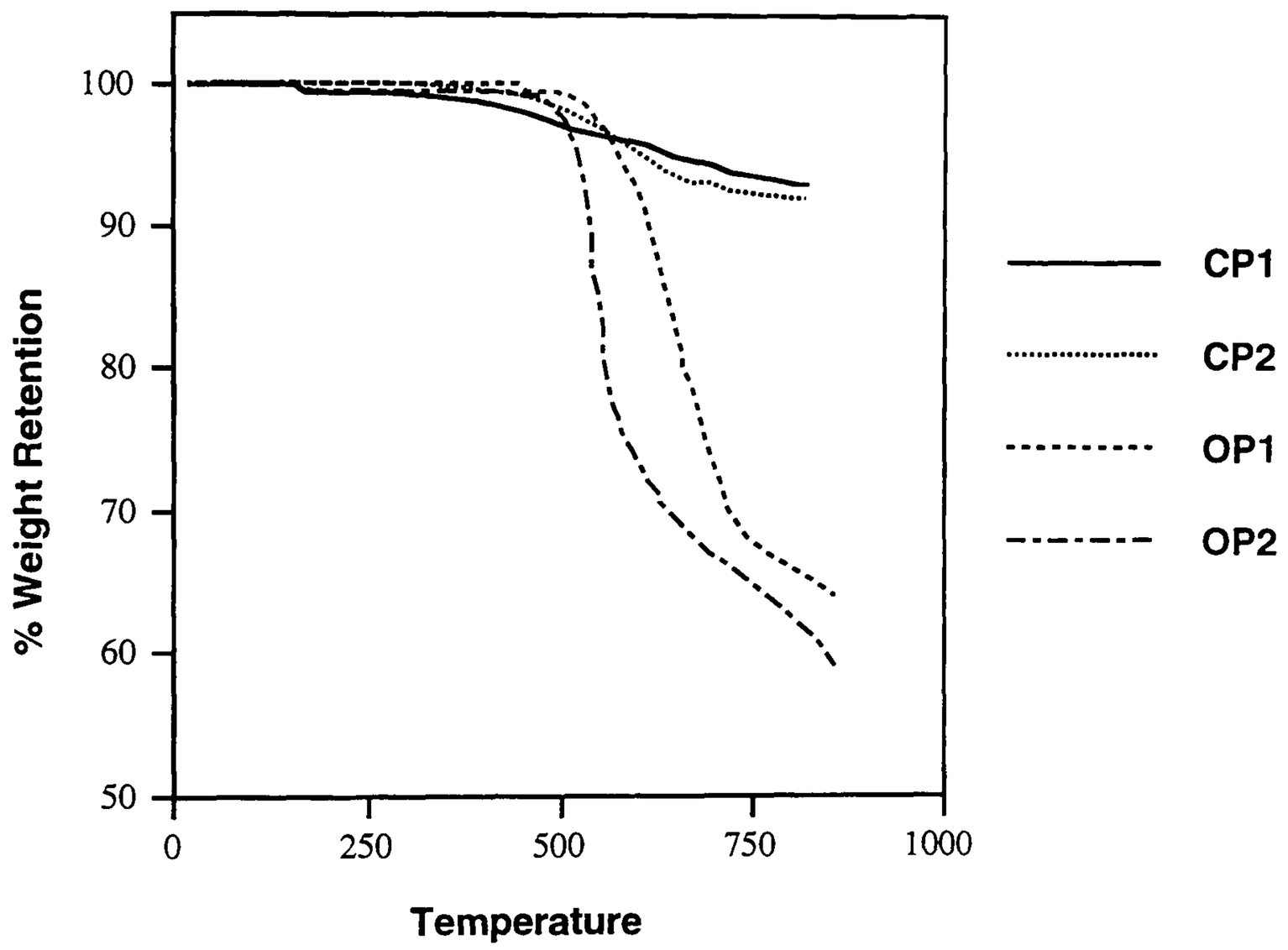


Figure 4.3: Comparison *of the Mass Retention of Polymers **CP1**, **CP2**, **OP1** and **OP2** under Nitrogen (to 850 °C).*

Similar results were observed for the polycarboranes when samples were heated under static air. The carborane-based polymer retained over 95% of its original weight on heating up to 850 °C. In contrast the all-organic system suffer drastic weight loss under these conditions and only approximately 4% of the original weight of sample remained after heating under the same conditions, as shown in Figure 4.4.

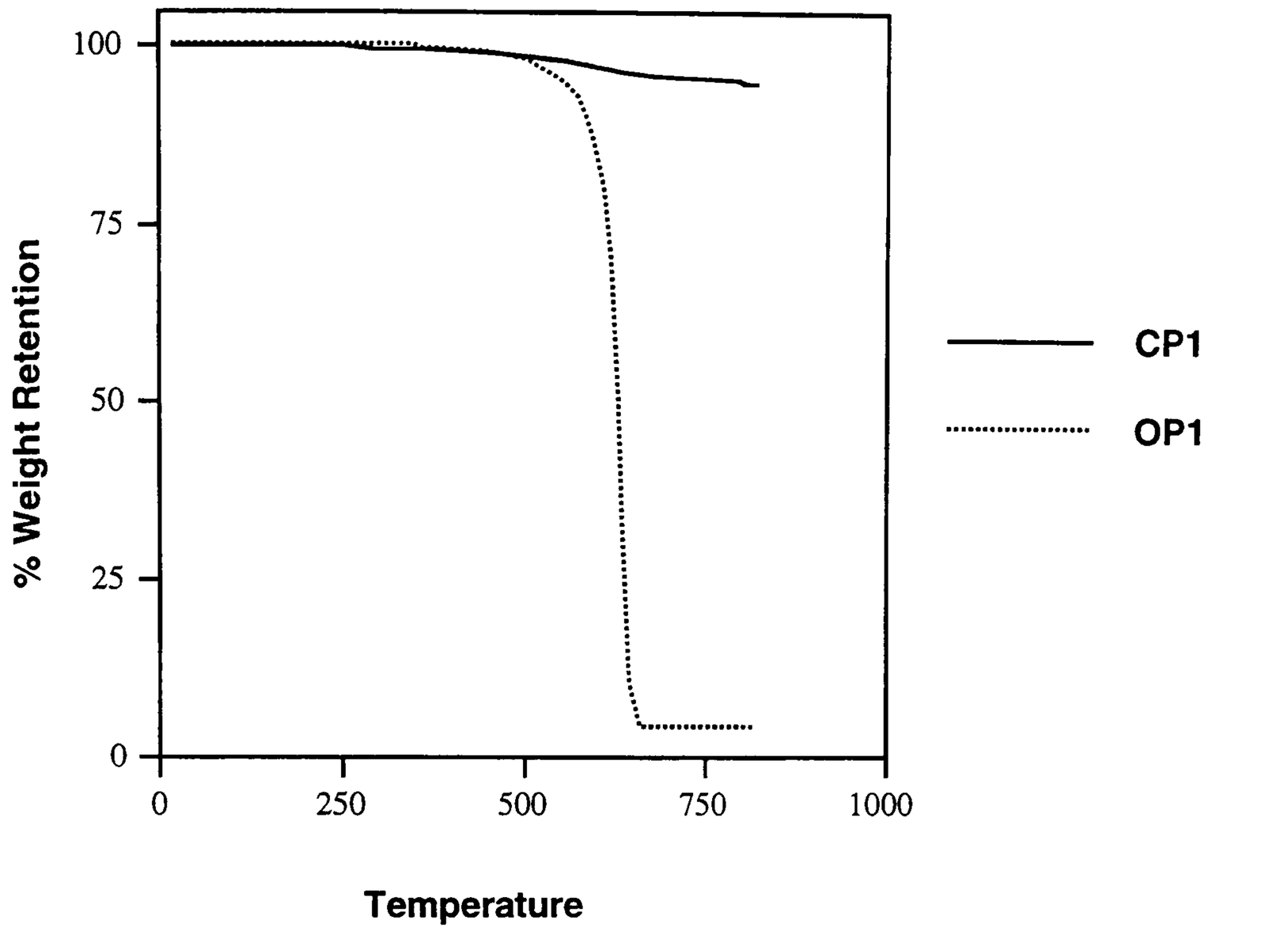
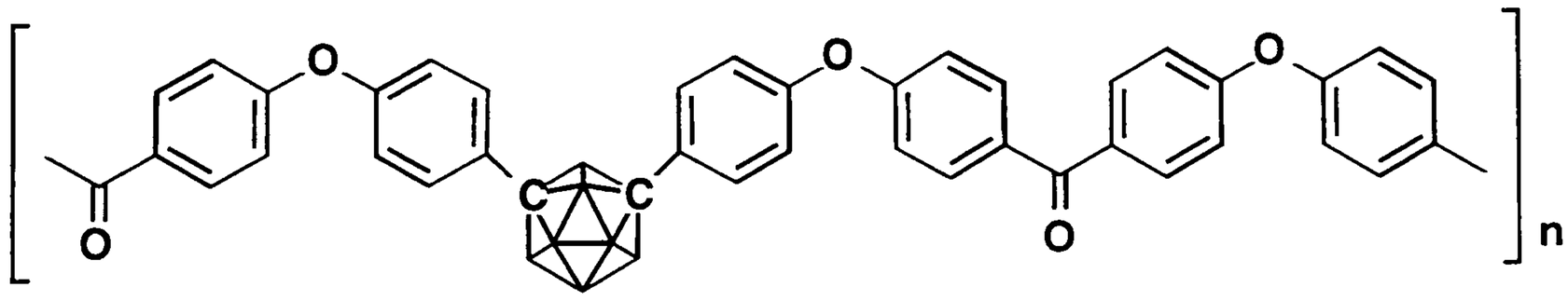


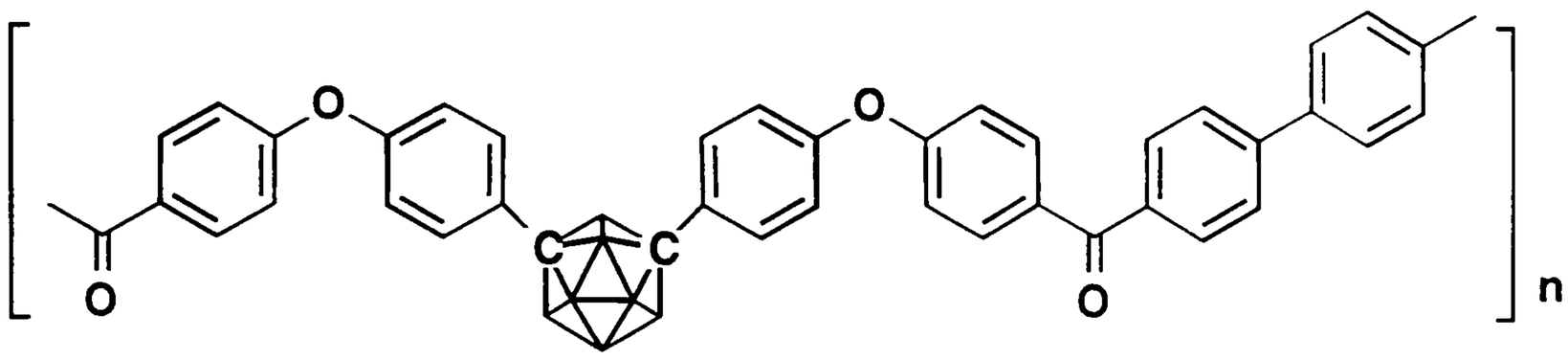
Figure 4.4: Comparison *of the Mass Retention of Polymers* ***CP1*** *and* ***OP1*** *under Static Air (to 850 °C).*

4.2.1.2. *meta* -Carborane-based Polymers:

Incorporation of the *meta*-carborane unit into the backbone of PEK was achieved as described previously (Section 4.2.1) affording a new class of polymers. The reaction between 1,7-bis-(4-phenoxyphenyl)-*meta*-carborane and 4,4'-biphenyldicarboxylic acid and 4,4'-oxybis(benzoic acid) afforded polymers **CP3** and **CP4,** shown below.



CP3



CP4

GPC and viscosity measurements indicated that significantly higher molecular weight materials than those based on *ortho*-carborane had been formed, which may be due to the reduced electron withdrawing effect of the *meta*-carborane isomer and/or the reduced steric hindrance it effects on the system.

Again the incorporation of the now *meta*-substituted icosahedral carborane unit into the backbones of poly(etherketone)s rendered all of the isolated polymers completely amorphous. Products were characterised by DSC and substantial increases in the T_g of the resulting materials compared to those of the all-organic systems were observed.

Thermal Stability:

Thermogravimetric and DSC analysis of polymer **CP4** provided evidence of exothermic decomposition and crosslinking between 420 and 600 °C.

Evolved gas analysis under argon showed that these processes were associated with generation of carbon monoxide, hydrogen, water and benzene, leading to a weight loss of 7% up to 600 °C as shown in Figure 4.5.

At higher temperatures (up to 1000 °C) a further 6% weight loss occurred, associated mainly with the evolution of water, and finally between 1000 and 1600 °C, an additional weight loss of 9% was observed, giving a final ceramic yield of approximately 78%. This corresponds roughly with the expected weight retained (80%) if all of the hydrogen and all the ether and ketone oxygen were driven out as H_2, CO and H_2O.

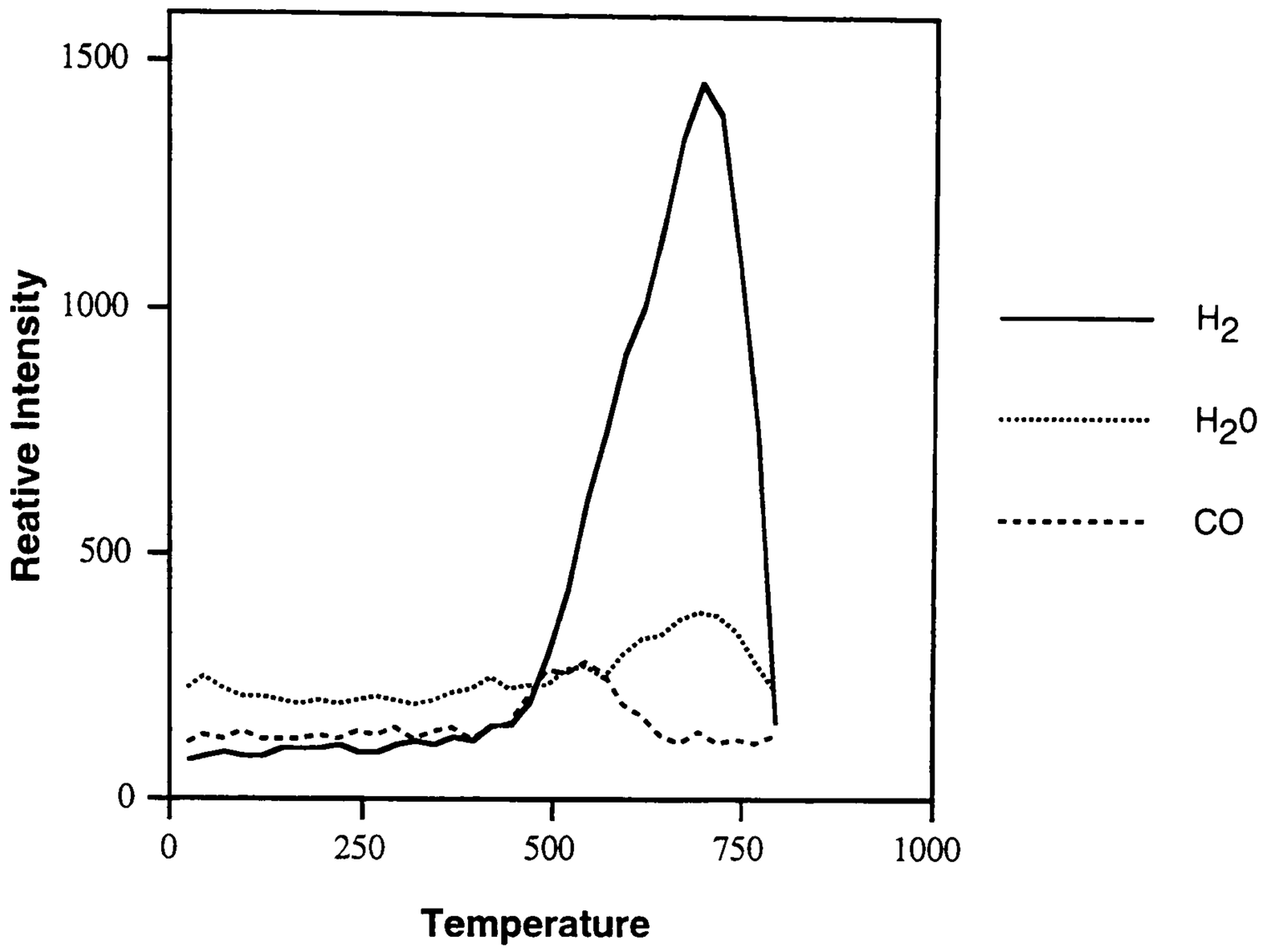


Figure 4.5: Evolved *gas Analysis Data Showing Volatiles Evolved From Carborane-PEK-Type Polymers (Up to 850 °C)*

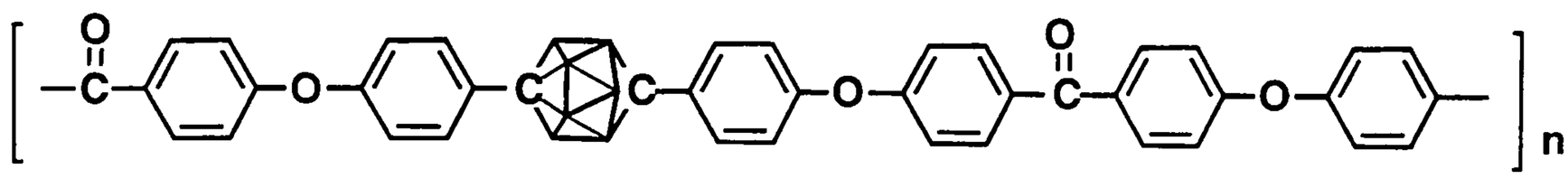
4.2.1.3. *para* -Carborane-based Polymers

The non-crystalline nature of the *ortho*- and *meta*-carborane polymers described so far might be ascribed to the angular 1,2' and 1,7-linkages (*ca.* 60° and 120° respectively) preventing the polymer achieving a linear and therefore readily crystallisable chain-conformation. Incorporation of the linear 1,12-dicarba-*para*-carboranylene isomer linkages into the polymer backbone was thought to be an obvious approach to achieving crystallinity in a PECK.

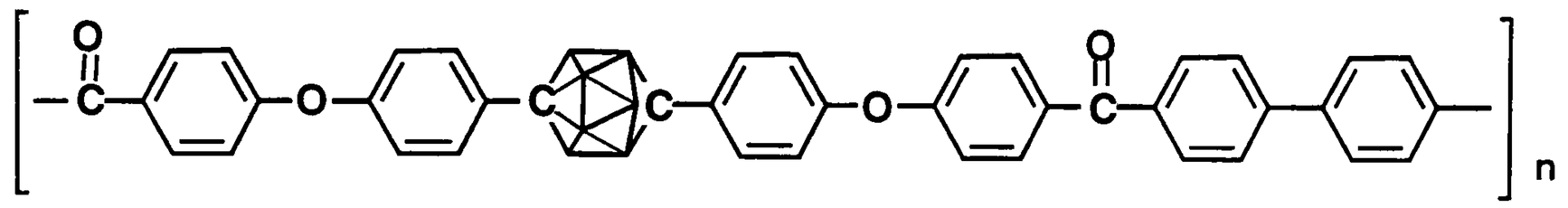
Moreover, it seemed appropriate to investigate whether the reduced electron demand of this isomer would allow more facile electrophilic attack on its phenoxyphenyl substituents and could hence lead to higher molecular weight polymers.

Para-carborane was incorporated into poly(etherketone)s under the same reaction conditions as those previously described for the *ortho*- and *meta*-carborane isomers.

The reaction between 1,12-bis-(4-phenoxyphenyl)-*para*-carborane and 4,4'-biphenyldicarboxylic acid and 4,4'-oxybis(benzoic acid) afforded the polymers **CP5** and **CP6,** shown below.

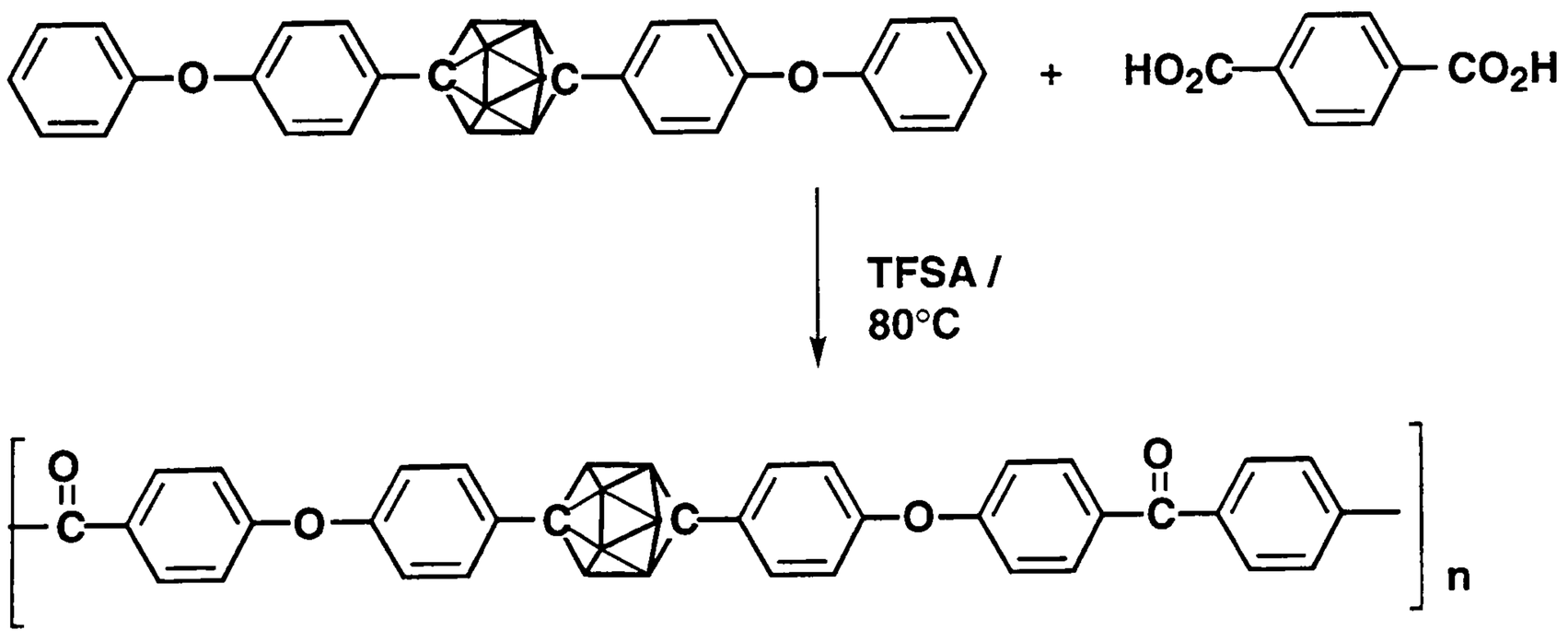


CP5



CP6

Aromatic diacids in which both of the carboxyl functionalities lie on the same aromatic ring are relatively unreactive towards polyketone formation in pure trifluoromethanesulphonic acid.[8] However, it has recently been shown that terephthalic acid can be activated for the synthesis of polyketones by including trifluromethanesulphonic anhydride in the reaction mixture.[9] Using this technique it proved possible to obtain a high molecular weight polyketone **CP7** from terephthalic acid and 1,12-(4-bisphenoxyphenyl)-*para*- carborane, although higher temperatures and longer reaction times were required to promote the reaction, compared to the conditions required for the incorporation of diacids based on diphenyl ether or biphenyl.



CP7

GPC and viscosity measurements indicated that very high molecular weight materials had indeed been formed.

The *para*-carborane analogues showed even higher T_g values than their *ortho*- and *meta*- based counterparts, and were crystalline or amorphous depending on the exact nature of the monomers employed.

In the case of the crystalline polymers, the remarkably low T_m relative to their T_g's suggests that the incorporation of the icosahedral carborane unit into the PEEK-polymer backbone affords crystal structures of unusually low lattice-energy.

Characterisation:

Characterisation of the *para*-carborane based polymers by DSC showed that 4,4'-oxydi(benzoic acid) gave a purely amorphous material, with a T_g (onset) at 236 °C. In contrast, the polymer obtained from terephthalic acid (**CP7**), showed not only a well-defined T_g at 267 °C but also a weak melting endotherm at 317 °C (ΔH = 3 J/g), which was the first indication of crystallinity in a poly(etherketone-carborane).

CP6, derived from 4,4'-biphenyldicarboxylic acid, displayed emphatic evidence of crystallinity. On initial heating, no evidence of a T_g was evident, but a strong cold-crystallisation exotherm (16 J/g) appeared as a double peak centred at 286 °C, followed by a melting endotherm of similar magnitude at 386 °C as shown in Figure 4.6.

The sample was allowed to cool to room temperature under an inert atmosphere and the subsequent DSC heating trace showed evidence of a T_g at 268 °C, and no crystallisation exotherm, suggesting that the crystallinity of the polymer is solvent rather than melt dependent.

Since the crystallisation exotherm and the melting endotherm are of approximately the same magnitude it follows that the polymer in its "as made" state must be essentially amorphous.

Figure 4.6: *Differential Scanning Calorimetry of Polymer* ***CP6*** *a) as-made, and b) after crystallisation at 300 °C*

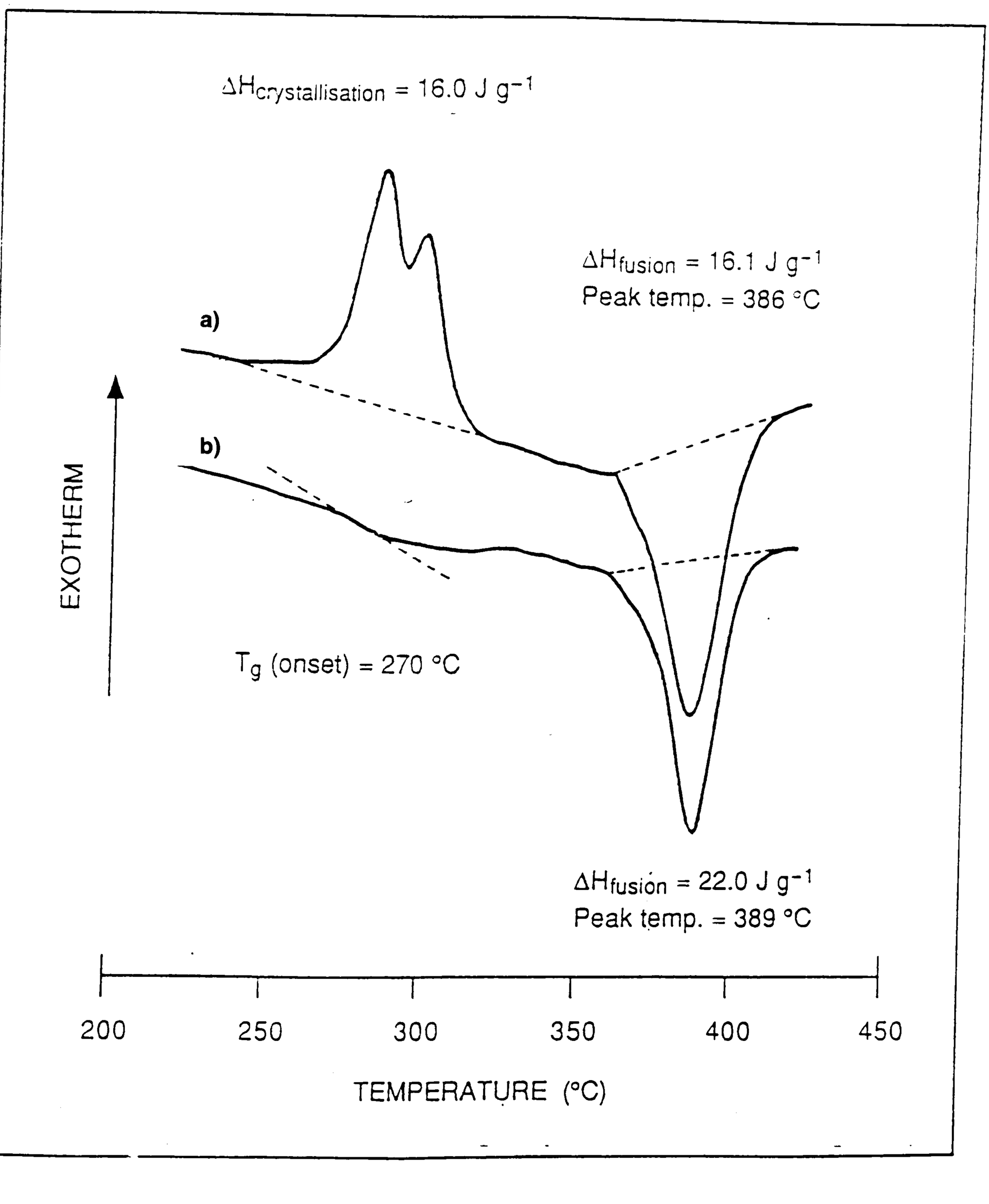
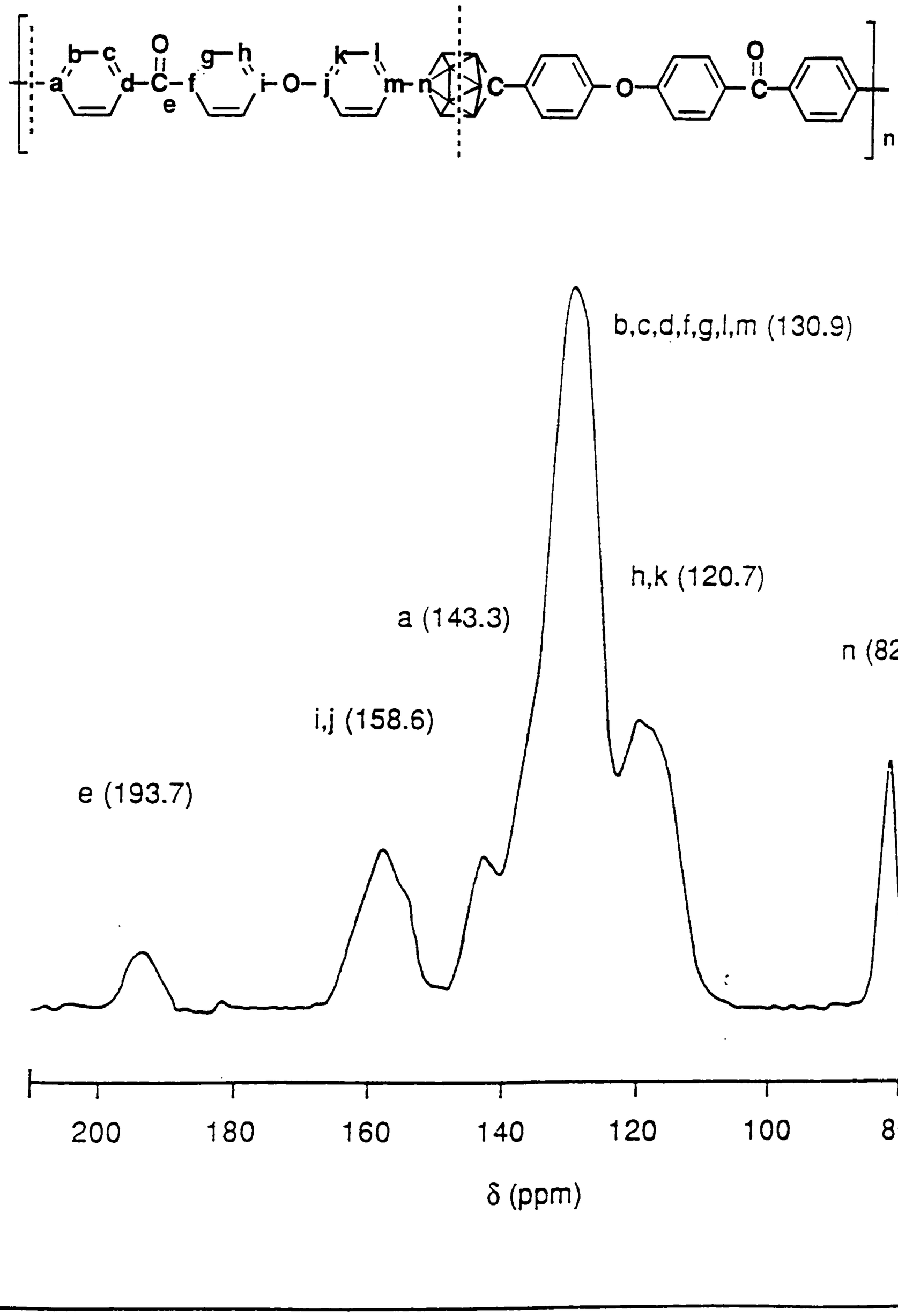


Figure 4.7: *Solid-state ^{13}C NMR Spectrum of Polymer* ***CP6***



Consistent with this, the "as made" sample was soluble in chloroform to give solutions from which strong, transparent films could be cast, suitable for IR characterisation. Solution state and solid-state NMR confirmed exclusively para-substitution of the benzene rings. The solid-state CP/MAS ^{13}C NMR spectrum of polymer **CP6** is shown in Figure 4.7. Assignments are based on published solid-state data for PEEK[10] and on solution data for *ortho*-carborane-based polyetherketones.[7]

Dilute solutions (<1%) of the polymer were noted to be stable for several days, but at higher concentrations (ca. >10%) polymer crystallisation was observed after only a few hours.

Fibres of polymer (**CP6**) were spun into water from a 10% solution in trifluoromethansulphonic acid, and after washing and drying were drawn at around the T_g to five times their original length. The crystalline X-ray diffraction pattern (Cu-K_α radiation) from such a fibre is shown schematically in Figure 4.8. where the meridional arcs apparently represent high order reflections (005, 006, 007) from a d-spacing (ca. 32.7Å) associated with the chemical repeat unit along the polymer chain.

This is unlike the situation observed for conventional poly(etherketone)s which typically have a polymer repeat unit of ca. 10 Å, corresponding to two benzene rings and either two ketone links or one ether and one ketone functionality.[10]

4.2.2. Aliphatic Poly(ethercarboranylketone)s:

All of the PECK's described so far have been formed from the reaction between the carborane-diether and an aromatic dicarboxylic acid. Characterisation of these polymers has shown that their physical and chemical properties differ quite substantially from the all-organic PEK's from which they are formally derived.

In particular the crystallinity that is normally observed in such polymers is disrupted on incorporation of the carborane unit into the polymer backbone, rendering the majority of the PECK's completely amorphous.

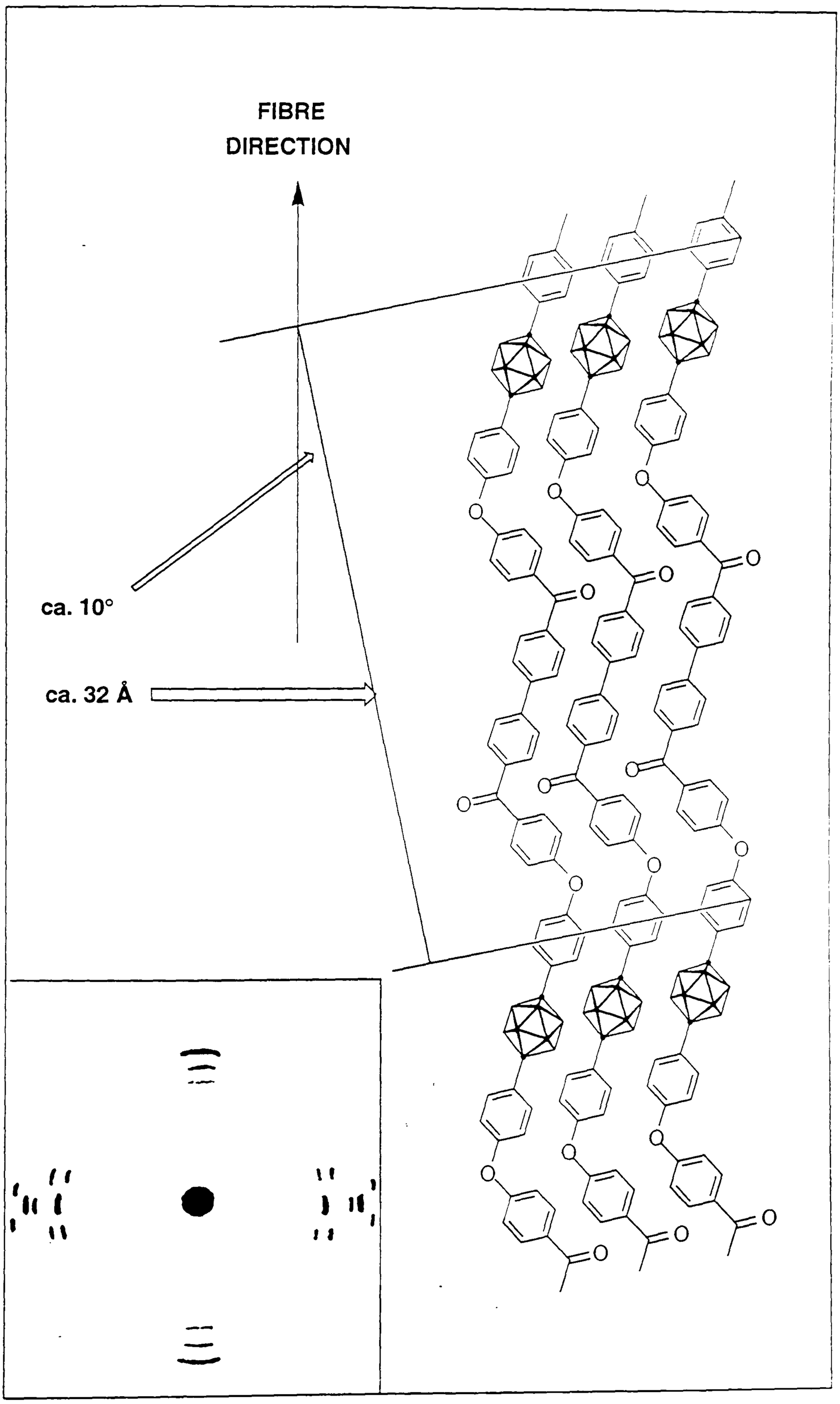
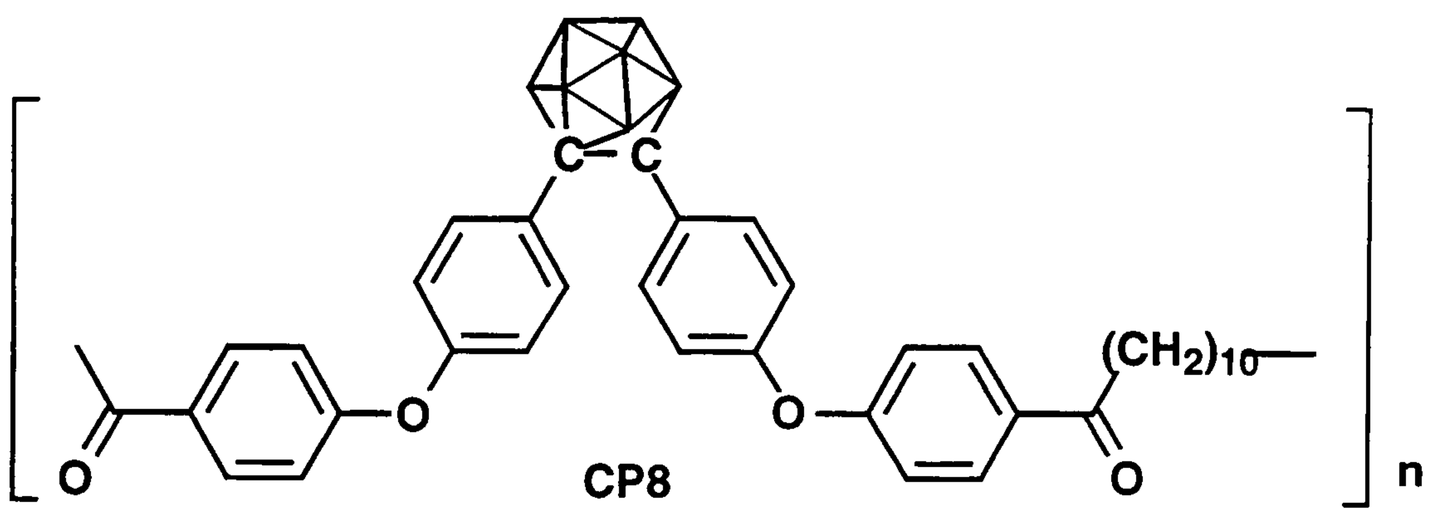


Figure 4.8: *Provisional X-ray Fibre Data for Polymer CP6*

Two questions were posed: could an aliphatic unit be incorporated into the polymer backbone using the electrophilic polycondensation reaction conditions described and, if this were possible, would the incorporation of a long carbon chain impose some regions of crystallinity into the resulting polymer introducing some crystallinity into the carborane-PEK's.

4.2.2.1. *ortho*-Carborane-based Poly(ethercarboranylketone)s:

The reaction between 1,2-bis-(4-phenoxyphenyl)-*ortho*-carborane and dodecanedioic acid afforded polymer **CP8** shown below.



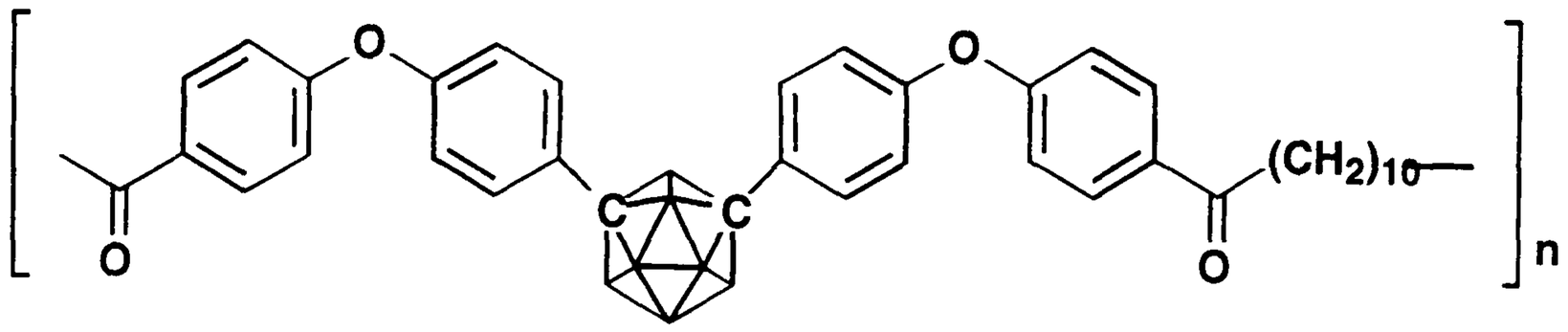
CP8

^{1}H and ^{13}C NMR confirmed that the substitution pattern of the polymer, and those subsequently reported, was as shown above with only 1,4-linked aromatics being observed. GPC and viscosity measurements again indicated that a medium to high molecular weight material had been formed.

The resulting polymer was found to be completely amorphous with a T_g at 98°C and readily soluble in organic solvents such as chloroform and dichloromethane.

4.2.2.2. *meta*-Carborane-based Poly(ethercarboranylketone)s:

The reaction between 1,7-bis-(4-phenoxyphenyl)-*meta*-carborane and dodecanedioic acid afforded polymer **CP9** shown overleaf.



CP9

GPC and viscosity measurements again indicated moderate to high molecular weight materials had been formed.

The resulting polymer was found to be completely amorphous and readily soluble in organic solvents as with the analogous **CP8**. A weak melting endotherm was observed by DSC at *ca.* 105 °C, with ΔH = 1.5 J/g indicating that the overall degree of crystallinity was very low.

TGA indicated that the carborane-containing polymers (**CP8** and **CP9**), lost approximately 45% of their original weight on heating to 850°C under N_2 and over a wider temperature range than the weight loss by the all-organic polymers under the same conditions, Figure 4.9.

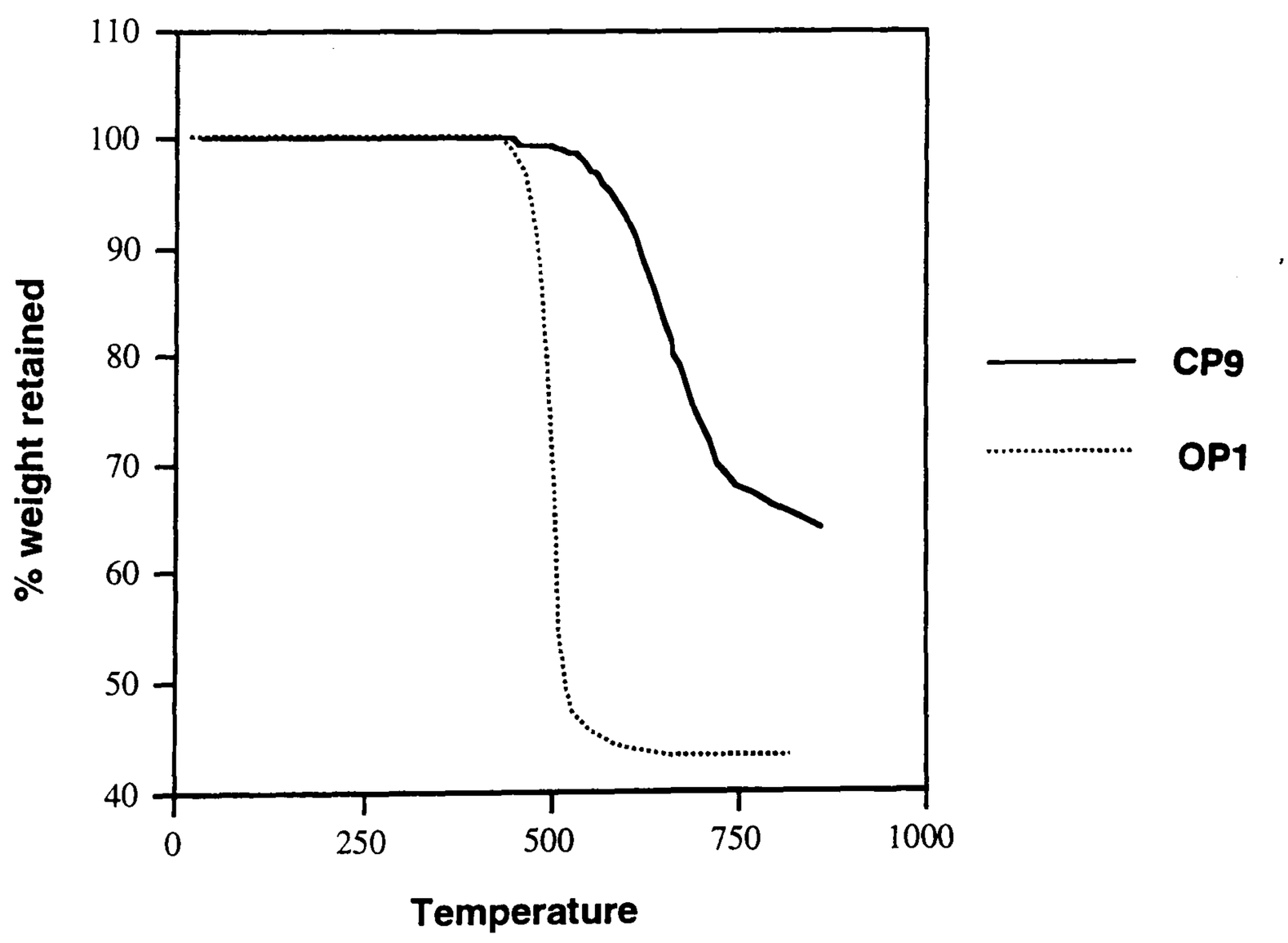
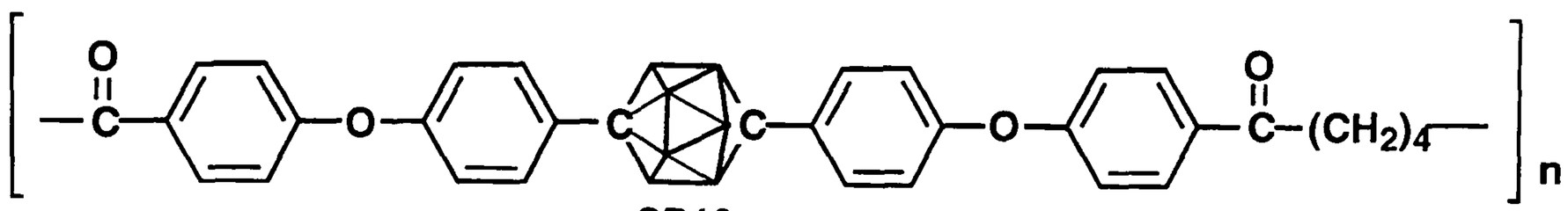


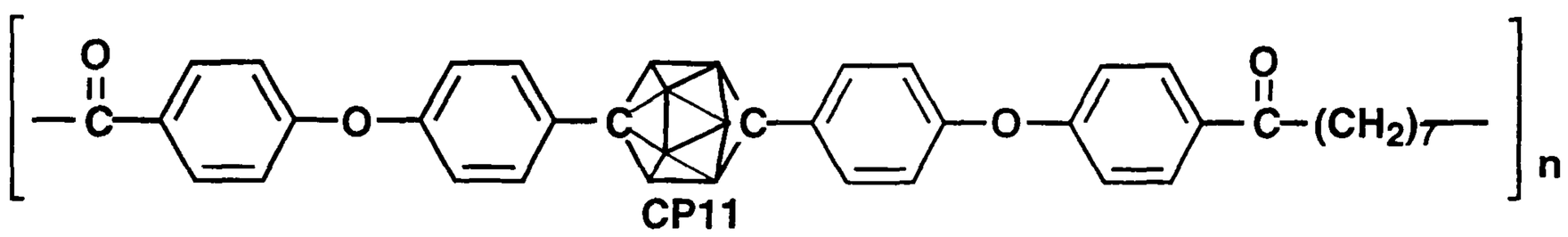
Figure 4.9: *Comparison of the Weight Retention of aliphatic-based meta-Carborane-Containing and all-organic PEK-Type Polymers, CP9 and OP1 (Under Nitrogen)*

4.2.2.3. *para*-Carborane-based Poly(ethercarboranylketone)s:

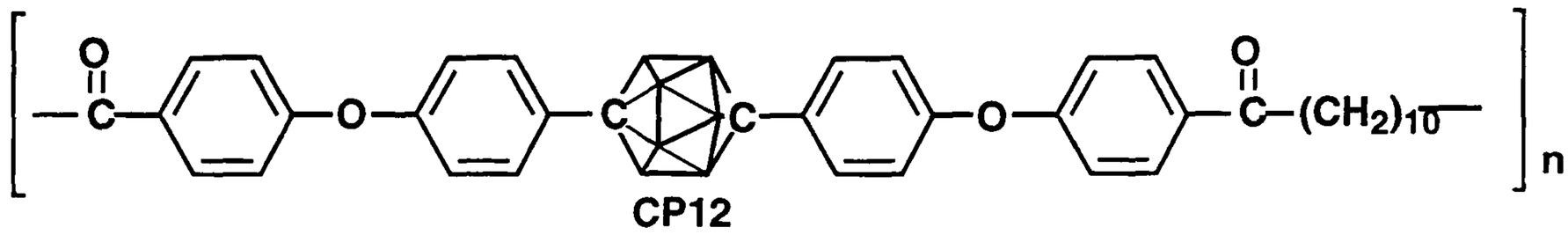
1,12-bis-(4-phenoxyphenyl)-*para*-carborane was found to react with several aliphatic diacids specifically, adipic [$HO_2C(CH_2)_4CO_2H$], azelaic [$HO_2C(CH_2)_7CO_2H$], dodecanedioic [$HO_2C(CH_2)_{10}CO_2H$] and hexadecanedioic acid [$HO_2C(CH_2)_{14}CO_2H$], to afford the polymers **CP10-CP13** shown below.



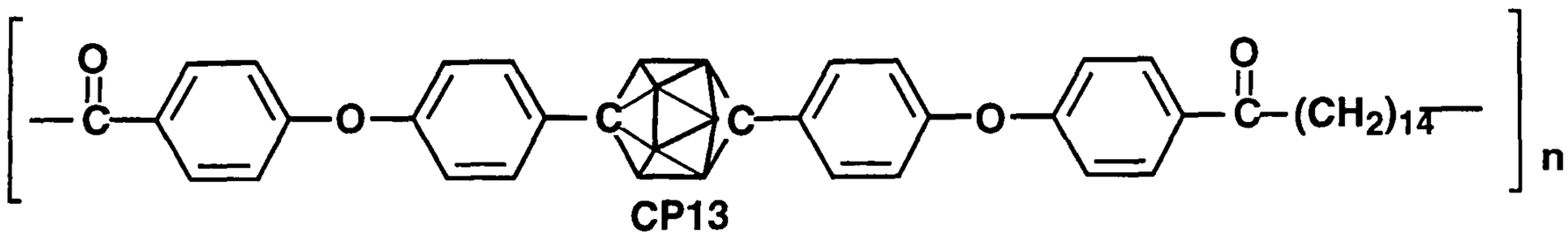
CP10



CP11



CP12



CP13

GPC and viscosity measurements indicated high molecular weight materials had been formed.

The resulting polymers were found to be essentially amorphous and readily soluble in certain organic solvents. However, in the case of polymer **CP12** two weak melting endotherms were observed by DSC at *ca.* 170 °C and *ca.* 197 °C with a total $\Delta H = 1.2$ J/g indicating some slight degree of crystallinity. A second scan showed only the weak endotherm at 197 °C.

Polymer **CP13** proved insoluble in NMP. After soaking in NMP for several hours, the polymer beads were isolated, washed with ethanol and dried under vacuum for several hours. DSC (1st scan) showed a pronounced crystal melting endotherm at 122°C (ΔH = 20.4 J/g) as can be seen in Figure 4.10

DSC of the as made polymer sample, however, showed only a T_g at 91 °C, implying that crystallisation is dependent on plasticisation of the polymer by NMP.

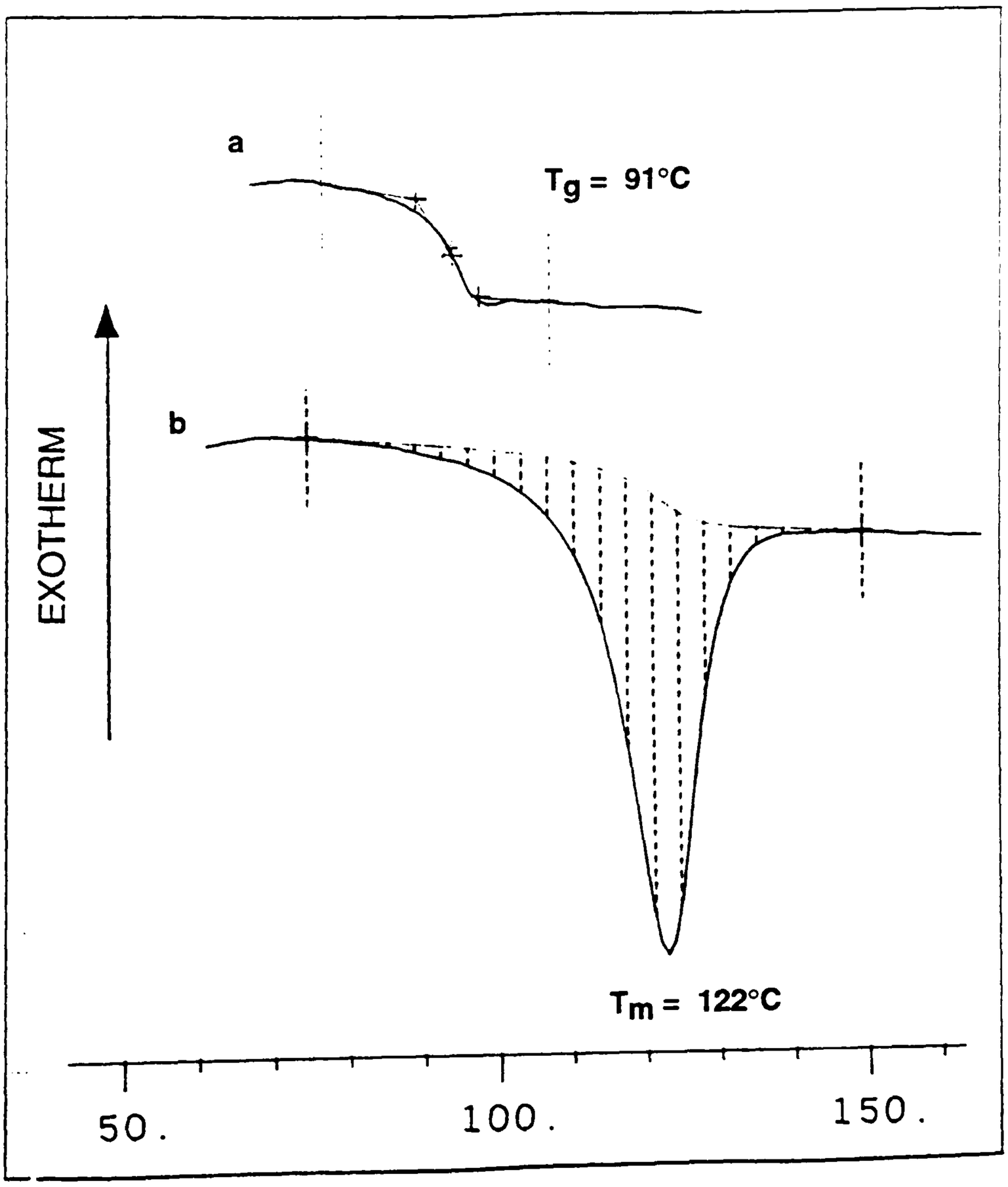


Figure 4.10: *Differential Scanning Calorimetry of Polymer* ***CP13*** ***a)*** *as-made, and* ***b)*** *after crystallisation induced by solvent*

TGA indicated that the carborane-containing polymers lost approximately 50% of their original weight on heating to 850 °C under N_2. A comparison between the weight retentions displayed by analogous polymers of *ortho-*, *meta-* and *para*-carborane can be seen in Figure 4.11:

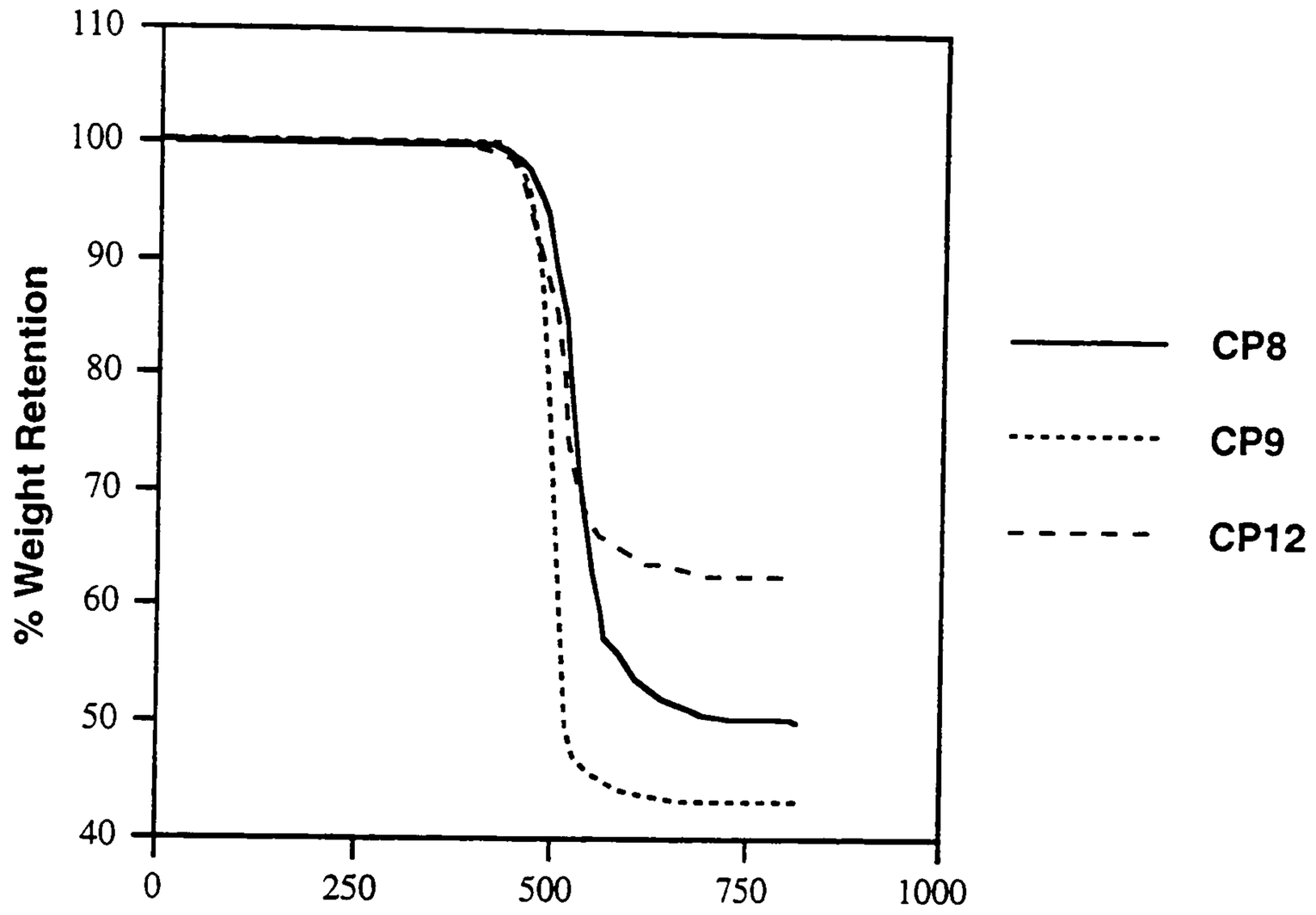


Figure 4.11: *Comparison of Weight Retention of ortho- meta- and para-Carborane-Containing PEK-Type Polymers, (Under Nitrogen).*

The data suggest that there is a difference in the % weight retention of the polymers depending on which carborane isomer is incorporated into the polymer backbone. The *para*-carborane isomer appears to confer the greatest mass-retention characteristics on the resulting system, with the resulting polymer retaining approximately 65% of its original weight on heating to 850 °C under N_2. The *meta-* carborane-containing analogue displays the greatest weight loss (ca. 55%) with the *ortho-* carborane analogue falling somewhere in between retaining approximately 50% of its original weight. The order *p>o>m* suggests that some type of cage-conjugative effect may be responsible for the distinct effect that the carborane cage exerts on the mass-retention behaviour of aromatic-aliphatic PECK-type polymers.

This effect is not displayed in the all-aromatic polymer systems, however, as can be seen below in Figure 4.12, presumably because the overall weight loss is quite small.

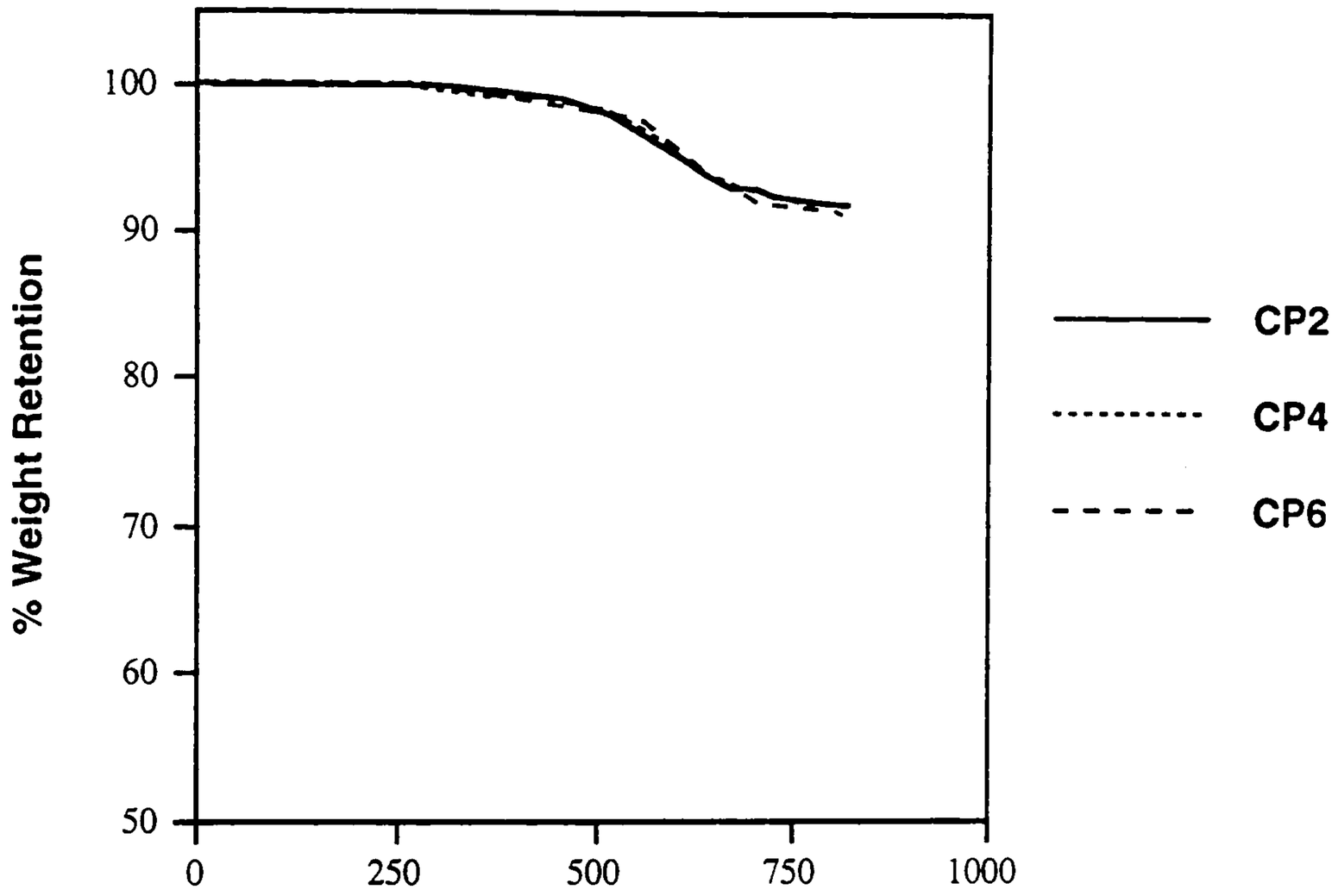


Figure 4.12: *Comparison of the Weight Retention of ortho- meta- and para-Carborane-Containing PEK-Type Polymers, CP2, CP4 and CP6 (Under Nitrogen)*

4.2.3. Molecular Weight Determination.

Viscosity and GPC measurements may be used to give an indication of the molecular weight of the polymer by comparing values obtained with those of a polymer sample of known molecular weight. The GPC technique allows the determination of polymer molecular weight by differentiating between polymer molecules by their size in solution - the higher molecular weights being eluted before lower molecular weight materials and oligomers.

The GPC data are all quoted with reference to commercial samples of polystyrene, the elution-behaviour of which may not be comparable to that of the carborane-containing poly(etherketone)s.

Ideally the GPC instrument should be calibrated using a polymer sample of known molecular weight and of a similar structure to the unknown. Unfortunately such polymer samples are not available.

Absolute molecular weights (M_W) may be determined by laser light scattering, and such experiments were conducted on two polymer samples (**CP1** and **CP5**) to check the reliability of molecular weights as determined by GPC

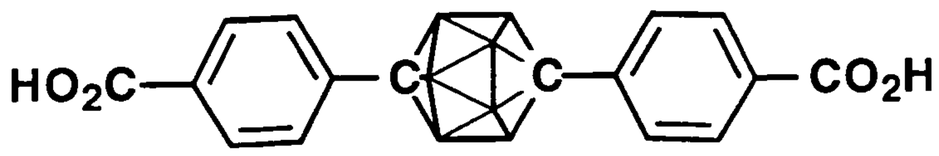
The values for molecular weight as determined by GPC and light-scattering in fact proved remarkably similar suggesting that the polystyrene standards used to calibrate the GPC instrument provide good models for the carborane-containing poly(etherketone)s.

Table 4.2: *Comparison of Molecular Weight Values Obtained by Laser Light Scattering and Gel Permeation Chromatography Experiments.*

Polymer	Mw (10^4) GPC	Mw (10^4) LS
CP1	5.4	5.9
CP5	13.3	13.4

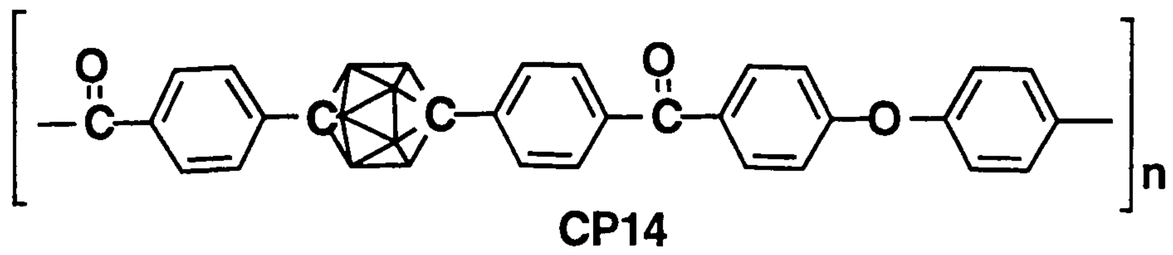
4.3 Polymers From 1,12-bis-(4-carboxyphenyl)-*para*-Carborane

1,12-bis-(4-carboxyphenyl)-*para*carborane (**42**) was synthesised by oxidation of the 1,12-bis(4-methylphenyl)-*para*-carborane as described in Chapter 2.

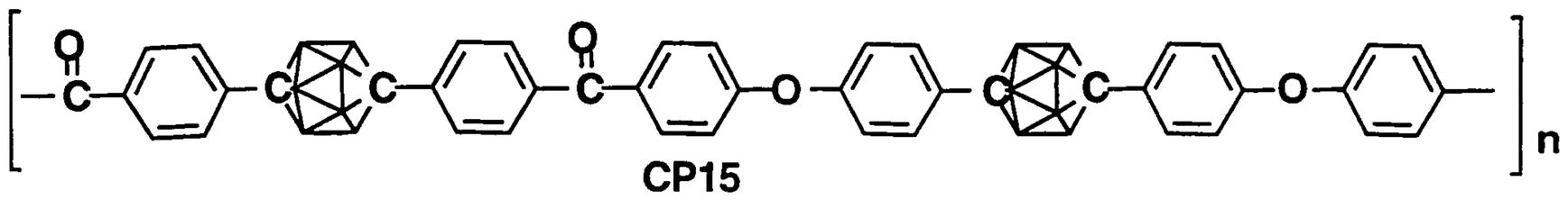


42

This monomer has the potential to provide access to a wide range of new polymers, such as polymers **CP14** and **CP15** prepared from 1,4-diphenoxybenzene and 1,12-bis-(4-phenoxyphenyl)-*para*-carborane respectively.



CP14



CP15

Such polymers could be subsequently sulphonated in an attempt to afford reverse osmosis membranes as described in Chapters 1 and 6.

Polymerisation was attempted under the same reactions conditions as those previously described for the preparation of polymers **CP1-CP13**. After 1-3 hours stirring at room temperature the orange-red polymer solutions were observed to have gelled suggesting that the materials had crosslinked. The isolated yellow-orange polymers were found to be insoluble, precluding characterisation.

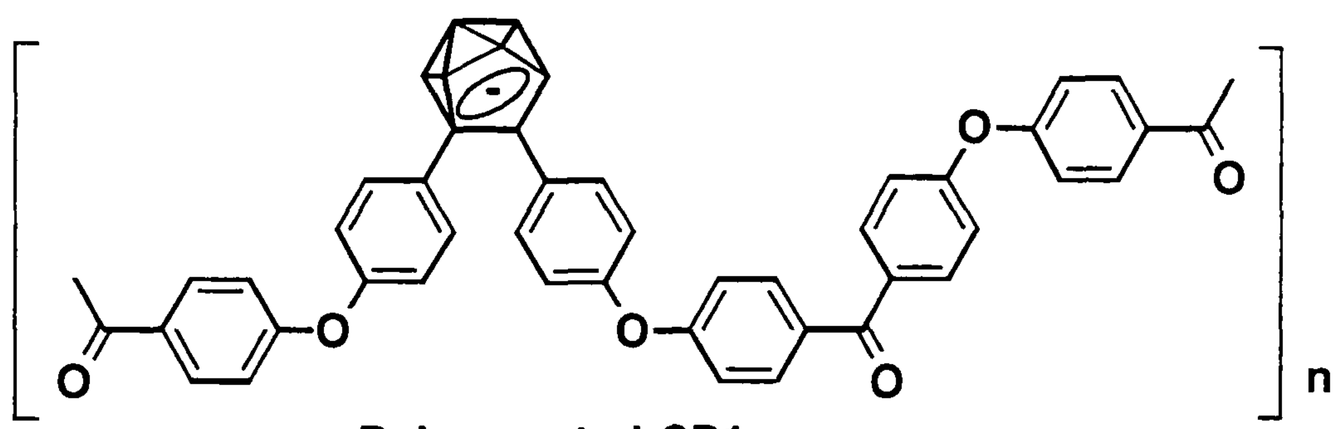
A model reaction between 1,12-bis-(4-carboxyphenyl)-*para*-carborane and 1,4-diphenoxybenzene to afford the oligomer **61**, shown below, in an attempt to establish the position of crosslinking. The ^{11}B NMR spectrum of the product was unchanged from the starting material indicating that if the polymers are indeed cross-linked that the B-H units on the carborane cage are not involved.

61

4.4. Deboronation of Polymers:

Extension of the deboronation reactions described in Chapter 3 to carborane-containing polymers could provide a range of ionomeric materials where the anionic residue would have the ability to act as an ion exchange site, or as a ligand for a range of main group and transition metal elements, potentially providing specific catalytic or transport properties.

Preliminary experiments were conducted using the *ortho*-carborane-containing polymer **CP1** This was successfully deboronated using the classical ethoxide reagents or the fluoride ion route described in Chapter 3, although the reaction took several days to go to completion.

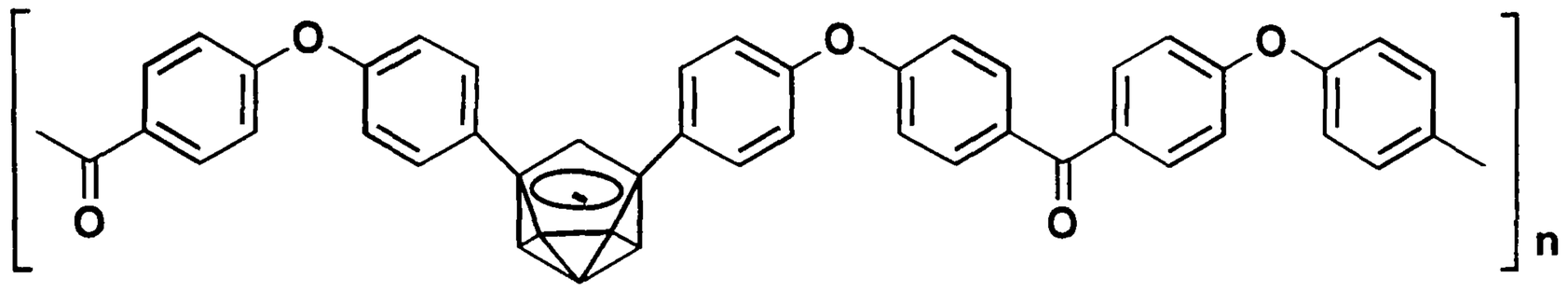


Deboronated CP1

The crude potassium salt was converted to the tetramethylammonium salt in the usual manner, by precipitation from solution. Infrared spectroscopy showed only *nido* -BH stretching absorption suggesting that <u>all</u> of the cages in the polymer chain had been successfully degraded and this was supported by ^{11}B NMR spectroscopy which showed no evidence for residual starting material.

An increase in the solution viscosity measurements of the product compared to the parent polymer, indicated that the polymer chains had not been degraded during the degradation reaction although the viscosity measurements obtained from the fluoride ion reaction were quite significantly lower than those obtained from the polymer deboronated by the classical routes. As all of the carborane cages appeared to have be deboronated in both experiments, the fluoride ion may have affected some chain cleavage.

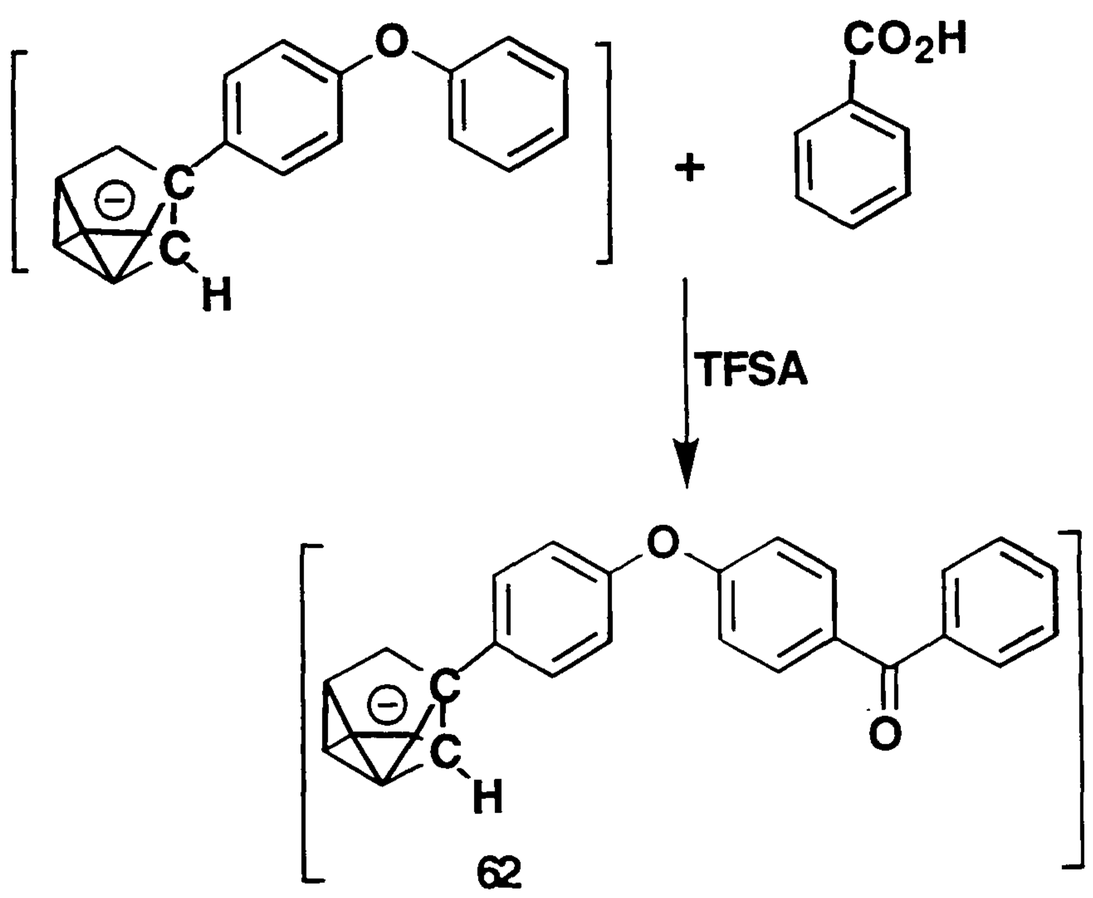
This theory was supported when the fluoride ion route was applied to the analogous *meta*-carborane-containing polymer **CP3**. Solution viscosity measurements indicated that the polymer chain had broken up quite substantially during the course of the degradation reaction, and infra red spectroscopy showed a marked decrease in the intensity of the ether and ketone stretching absorptions.



Deboronated CP3

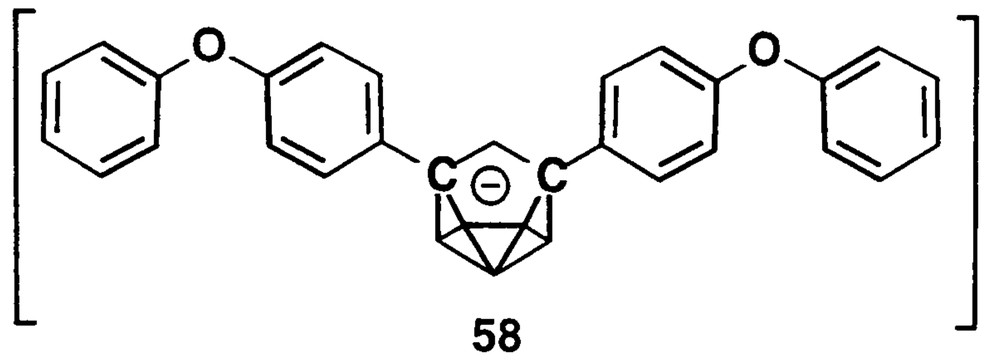
As the classical deboronation reactions are unsuitable for *meta*-carborane and its derivatives, and hence *meta*-carborane-containing polymers, an alternative approach to ionomeric materials was the polymerisation of suitable *nido*-carborane derivatives.

The reaction of the *nido*-derivative of 1-(4-phenoxyphenyl)*meta*-carborane with benzoic acid in the presence of triflic acid afforded **62** in quantitative yield indicating that *nido*-carborane derivatives were both soluble and reactive enough in TFSA to afford high molecular weight ionomers.



62

Compound **58** and the *ortho*-carborane analogue were each reacted with 4,4'-biphenyldicarboxylic acid in triflic acid in the usual manner, but unfortunately the isolated products were found to be gelatinous, and polymer characterisation was not feasible and further work in this area is obviously required.

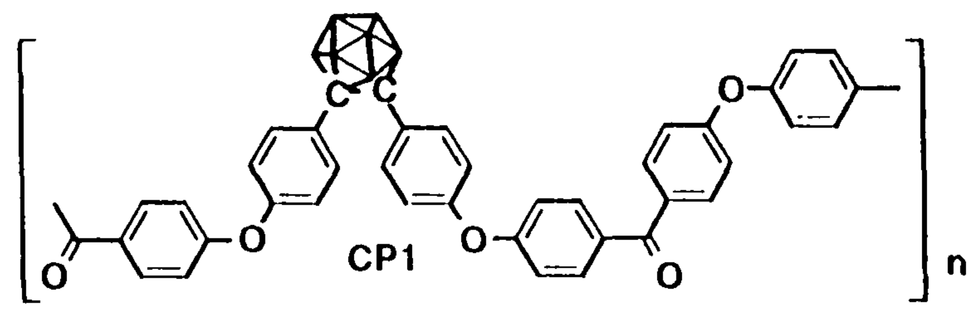


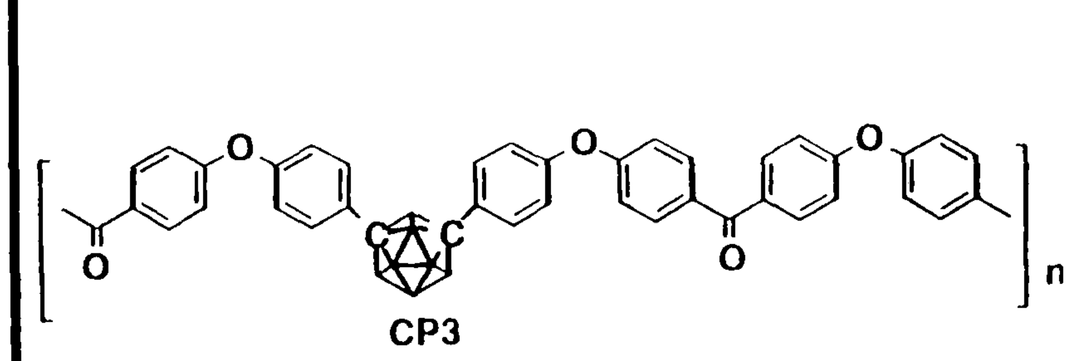
58

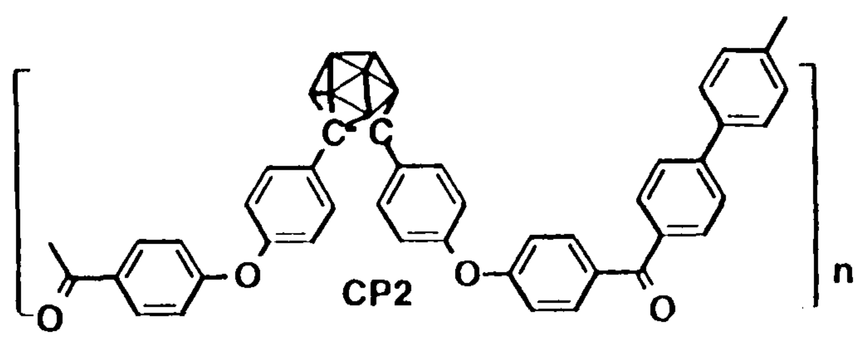
4.5. Summary:

To summarise:- *ortho- meta-* and *para*-carborane have been successfully incorporated into the backbone of the all-organic poly(etherketone)'s to afford and new class of materials displaying excellent resistance to temperatures up to 1000 °C. All of the products have been fully characterised and the results are shown in Table 4.1.

Table 4.1 *Characterisation Data for Polymers* ***CP1-CP13***

 CP1	
T_g (°C)	181
η (dL/g)	0.41
M_n	34,258
M_w	52,969
PD	1.55

 CP3	
T_g (°C)	183
η (dL/g)	0.88
M_n	83,860
M_w	170,035
PD	2.03

 CP2	
T_g (°C)	212
η (dL/g)	0.58
M_n	45,422
M_w	73,864
PD	1.63

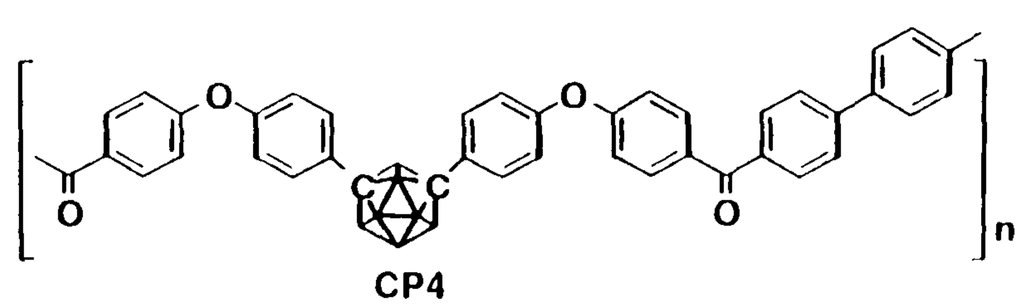
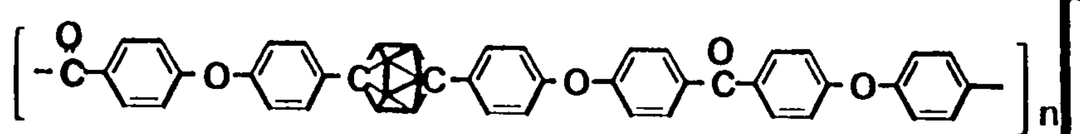
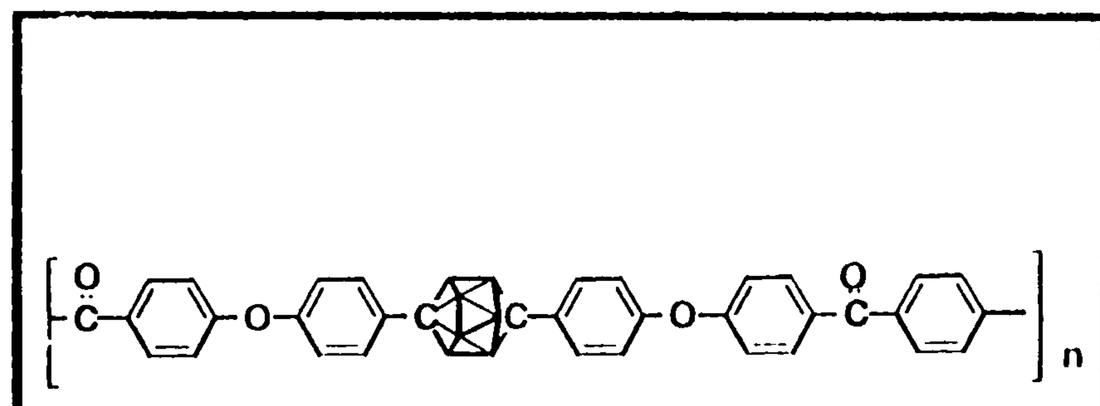
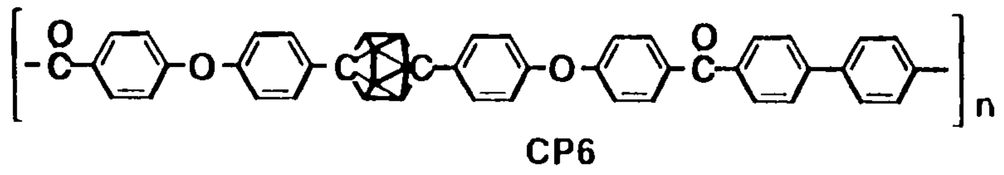
 CP4	
T_g (°C)	210
η (dL/g)	0.66
M_n	45,855
M_w	90,390
PD	1.97

Table 4.1 *Continued*

 CP5	T_g (°C)	236
	η (dL/g)	1.09
	M_n	53,842
	M_w	111,451
	PD	2.08

 CP7	T_g (°C)	267
	T_m (°C)	317
	η (dL/g)	0.86

 CP6	T_g (°C)	286†
	T_m (°C)	386
	η (dL/g)	1.21*
	M_n	155,000
	M_w	254,200
	PD	1.64

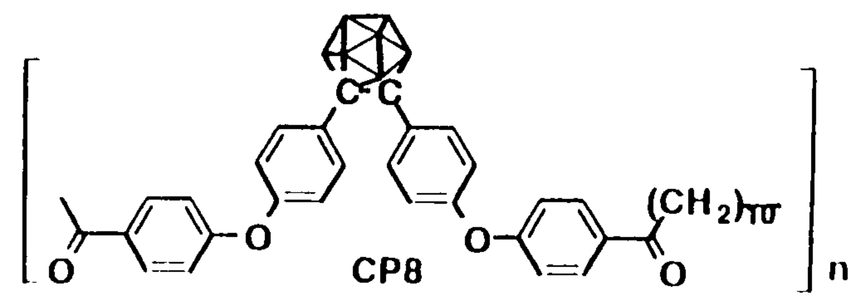
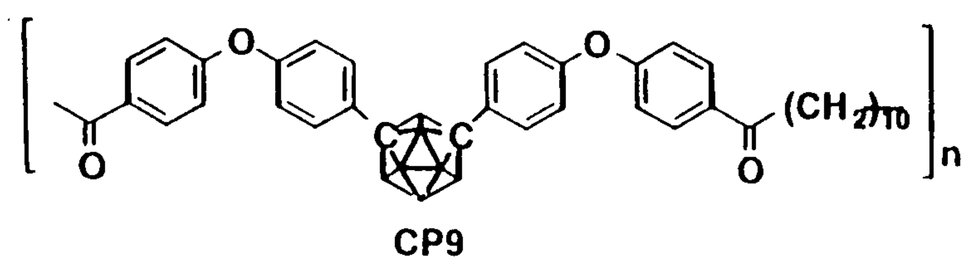
 CP8	T_g (°C)	98
	η (dL/g)	0.43
	M_n	45,855
	M_w	90,390
	PD	1.97

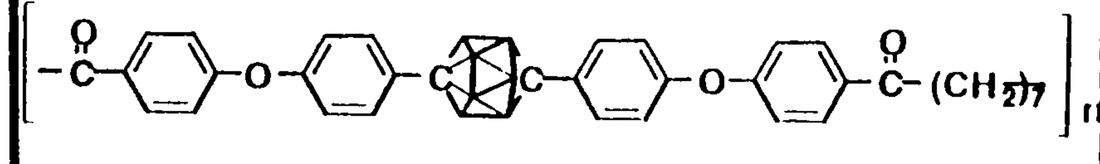
Table 4.1 *Continued*

T_g (°C)	87
T_m (°C)	105
η (dL/g)	0.66
M_n	37,064
M_w	61,526
PD	1.66



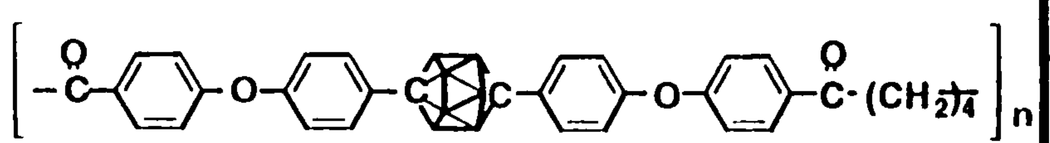
CP9

T_g (°C)	140
η (dL/g)	0.85
M_n	53,731
M_w	81,199
PD	1.60



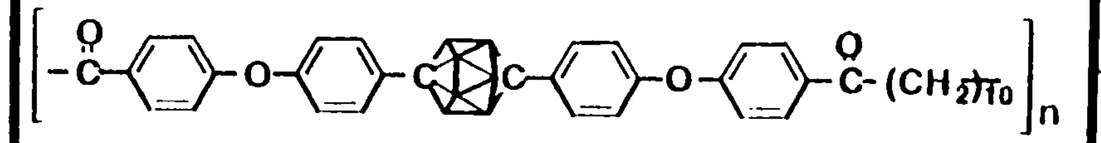
CP11

T_g (°C)	182
η (dL/g)	0.99*
M_n	25,648
M_w	89,768
PD	3.5



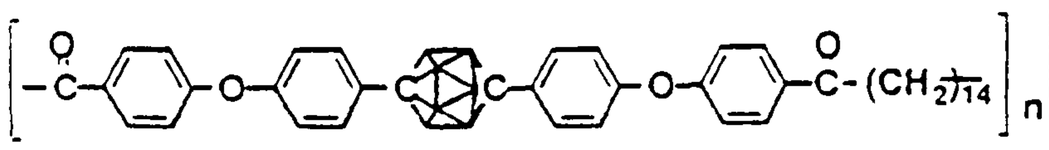
CP10

T_g (°C)	120
T_m (°C)	-
η (dL/g)	1.28



CP12

Table 4.1 *Continued*

 CP13	T_g (°C) 91
	T_m (°C) 122
	η (dL/g) 0.85*
	M_n 20,105
	M_w 66,890
	PD 3.33

† Reheated. First run obscured by cold crystallisation at 286 °C.

* Measured in $CHCl_3$

4.6. Experimental:

4.6.1. The preparation of CP1.

1,2-bis-(4-phenoxyphenyl)-*ortho*-carborane (**6**), (0.5 g, 1.04 mmol) and 4,4'-oxy-bis(benzoic acid) (0.267 g, 1.03 mmol) were placed into a 25 cm^3 conical flask purged with nitrogen. Freshly distilled triflic acid (9 cm^3) was added and the reaction mixture was stirred for 20 hours to afford a clear, viscous, orange solution. The polymer was precipitated as pink beads by adding dropwise to distilled water (250 cm^3) and stirring for half an hour. The beads were filtered off and stirred in 1%w/v sodium hydroxide solution (water/ethanol; 1:1) for an hour and finally refluxed in ethanol (250 cm^3) for 30 minutes. The resulting white beads were filtered off and dried in a vacuum oven (70°C) for 12 hours to give the product identified as **CP1**, yield 0.64 g, 91%. The product was characterised as follows:

IR (polymer film from CH_2Cl_2) ν_{max} cm^{-1}: 3063 w, 3016 sh., 2592 s (BH), 2031 w, 1655 s (ketone C=O), 1592 s, 1499 s, 1416 m, 1307 m, 1278 m, 1243 s (ether C-O), 1175 m, 1161 s, 1015 m, 953 s, 928 m, 895 m, 883 m, 841 m, 763 m, 595 m, 580 w.

NMR: δ ^{13}C: 85.3 (carboranyl C), 118.6, 119.1, 119.4, 126.9, 132.8, 133.1, 133.5, 133.7, 158.1, 160.2 (ArC), 194.4 (C=O).
δ ^{1}H: 1.10-3.9 (broad multiplet; 10H, BH), 6.8-7.8 (ArH).

4.6.2. The preparation of CP2.

CP2 was prepared and isolated according to the general procedure described above, (Section 4.6.1), by treating 1,7-bis(4-phenoxyphenyl)-*ortho*-carborane (0.50 g, 1.04 mmol) with 4,4'-biphenyldicarboxylic acid (0.249 g, 1.03 mmol) in freshly distilled triflic acid (9 cm^3), to afford white polymeric beads identified as **CP2**. Yield 0.6 g, 92%. The product was characterised as follows:

IR (polymer film from CH_2Cl_2) ν_{max} cm^{-1}: 3016 w, 2593 s (BH), 1655 s (ketone C=O), 1592 s, 1500 s, 1416 m, 1395 sh., 1309 m, 1279 m, 1248 s (ether C-O), 1174 m, 1119 m, 1074 m, 1015 m, 1004 m, 955 s, 895 m, 759 s, 684 m, 449 w.

NMR: δ ^{1}H: 1.1-3.6 (broad multiplet; 10H, BH), 6.8-7.9 (ArH).
δ ^{13}C: 84.8 (carboranyl C), 118.1, 118.9, 126.3, 127.1, 130.5, 132.4, 132.6, 136.9, 143.6, 157.5, 159.9 (ArC), 194.6 (C=O).

4.6.3. The preparation of CP3.

CP3 was prepared and isolated according to the general procedure described above, (Section 4.6.1), by treating 1,7-bis-(4-phenoxyphenyl)-*meta*-carborane (0.50 g, 1.04 mmol) with 4,4'- oxydibenzoic acid (0.267 g, 1.03 mmol) in freshly distilled triflic acid (9 cm^3), to afford white polymeric beads identified as **CP3**. Yield 0.6 g, 86%. The product was characterised as follows:

IR (polymer film from CH_2Cl_2) ν_{max} cm^{-1}: 3016 sh., 2604 s (BH), 2031 w, 1656 s (ketone C=O), 1593 s, 1499 s, 1415 m, 1307 m, 1278 m, 1243 s (ether C-O), 1175 m, 1161 s, 1114 w, 1080 m, 1015 m, 953 s, 843 m, 763 m, 598 m.

NMR: δ ^{1}H: 1.1-3.9 (broad multiplet; 10H, BH), 6.85-7.87 (ArH).
δ ^{13}C: 78.2 (carboranyl C), 118.4, 119.1, 119.8, 130.0, 131.6, 132.8, 133.2, 133.8, 156.9, 160.2 (ArC), 194.5 (C=O).

4.6.4. The preparation of CP4.

CP4 was prepared and isolated according to the general procedure described above, (Section 4.6.1), by treating 1,7-bis(4-phenoxyphenyl)-*meta*-carborane (0.50 g, 1.04 mmol) with 4,4'biphenyldicarboxylic acid (0.249 g, 1.03 mmol) in freshly distilled triflic acid (9 cm^3), to afford white polymeric beads identified as **CP4**. Yield 0.61 g, 91%. The product was characterised as follows:

IR (polymer film from CH_2Cl_2) ν_{max} cm^{-1}: 3016 sh., 2603 s (BH), 2081 w, 1654 s (ketone C=O), 1593 s, 1507 s, 1498 m, 1416 sh., 1395 sh., 1309 s, 1278 s, 1244 s (ether C-O), 1174 s, 1117 m, 1080 m, 1055 m, 1016 m, 955 s, 927 m, 847 m, 758 s, 685 m, 617 m, 512 m, 407 w.

NMR: δ ^{1}H: 0.9-3.2 (broad multiplet; 10H, BH), 6.9-7.9 (ArH).
δ ^{13}C: 77.5 (carboranyl C), 118.3, 119.8, 127.6, 130.1, 131.1, 131.6, 132.9, 137.7, 144.2, 161.1(ArC), 195.3 (C=O).

4.6.5. The preparation of CP5.

CP5 was prepared and isolated according to the general procedure described above, (Section 4.6.1), by treating 1,12-bis-(4-phenoxyphenyl)-*para*-carborane (0.49 g, 1.02 mmol) with 4,4'- oxydibenzoic acid (0.258 g, 1.00 mmol) in freshly distilled triflic acid (9 cm^3), to afford white polymeric beads identified as **CP5**. Yield 0.667 g 95% The product was characterised as follows:

IR (polymer film from CH_2Cl_2) ν_{max} cm^{-1}: 3056 sh., 2609 s (BH), 1656 s (ketone C=O), 1594 s, 1499 s, 1415 m, 1307 m, 1278 m, 1244 s (ether C-O), 1174 m, 1161 s, 1117 w, 1083 m, 1013 m, 953 s, 844 m, 764 m, 598 m.

NMR: δ ^{1}H: 1.0-3.5 (broad m, 10H, BH), 6.88-7.85 (m, 24H, ArH).
δ ^{13}C: 82.01 (carboranyl C), 117.80, 118.58, 119.02, 128.87, 132.31, 132.52, 133.36, 156.06, 159.69, 160.58 (ArC), 194.07 (C=O).

4.6.6. The preparation of CP6

CP6 was prepared and isolated according to the general procedure described above, (Section 4.6.1), by treating 1,12-bis-(4-phenoxyphenyl)-*para*-carborane (1.47 g, 3.06 mmol) with 4,4'biphenyldicarboxylic acid (0.726 g, 3.0 mmol) in freshly distilled triflic acid (25 cm^3). Fibres were spun from the reaction solution into deionised water, isolated and washed in refluxing 10% sodium hydroxide in ethanol. The remaining solution was worked up in the usual manner to afford white polymeric beads identified as **CP6** Yield 1.85 g, 90%. The product was characterised as follows:

IR (polymer film from CH_2Cl_2) ν_{max} cm^{-1}: 3070 w, 3034 w, 2607 s, 1655 s, 1593 s, 1500 s, 1413 m, 1307 s, 1242 s, 1241 s, 1169 s, 1115 m, 1083 s, 1011 m, 954 w, 925 s, 870 s, 839 s, 756 s, 680 s, 616 m, 512 m.

NMR: δ ^1H: 1.1-3.9 (broad multiplet; 10H, BH), 6.85-7.87 (ArH).
δ ^{13}C: 81.2 (carboranyl C), 118.4, 119.1, 119.8, 130.0, 131.6, 132.8, 133.2, 133.8, 156.9, 160.2 (ArC), 194.5 (C=O).

d-Spacings (XRD powder pattern data): 5.424 (5.45), 4.752 (4.67) 4.423. (Figures in parenthesis from fibre x-ray pattern)

4.6.7. The preparation of CP7

1,12-bis-(4-phenoxyphenyl)-*para*-carborane (**31**), (0.49 g, 1.02 mmol) and terephthalic acid (0.166 g, 1.00 mmol) were placed into a 25 cm^3 conical flask purged with nitrogen. Freshly distilled triflic acid (9 cm^3) was added forming a yellow solution to which trifluoromethanesulphonic anhydride (1 cm^3, d= 1.677, 6 mmol) was added. The flask was flushed with nitrogen and stoppered. The reaction mixture was stirred for 20 hours and was observed to form an orange solution, although not all of the starting material had dissolved. The reaction vessel was fitted with a condenser and the solution was heated to 80 °C under nitrogen to afford a clear, orange-brown solution. This was stirred under nitrogen overnight. The reaction mixture was allowed to cool to room temperature and worked up in the usual manner to afford creamy-white beads identified as **CP7**, yield 0.64 g, 91%. The product was characterised as follows:

IR (polymer film from CH_2Cl_2) ν_{max} cm^{-1}: 3070 m, 3050 m, 2604 s, 1668 s, 1648 s, 1592 s, 1455 m, 1416 s, 1307 s, 1172 s, 1112 m, 1084 s, 1038 w, 1016 s, 920 s, 871 s, 841 s, 790 m, 731 s, 694 s, 648 m, 610 m, 513 s.

NMR: δ ^1H: 1.0-3.5 (broad m, 10H, BH), 6.8-6.9 (d, 2H, ArH), 7.02-7.04 (d, 2H, ArH), 7.26 (s, 4H, ArH), 7.83-7.85 (d, 2H, ArH).
δ ^{13}C: 81.05 (carboranyl C), 117.76, 119.19, 128.92, 129.49, 131.77, 132.56, 140.75, 161.1(ArC), 195.3 (C=O).

4.6.8. The preparation of CP8

CP8 was prepared and isolated according to the general procedure described above, (Section 4.6.1), by treating 1,2-bis(4-phenoxyphenyl)-*ortho*-carborane (0.49 g, 1.02 mmol) with dodecanedioic acid (0.230 g, 1.00 mmol) in freshly distilled triflic acid (9 cm^3), to afford white polymeric beads identified as **CP8** Yield 0.62 g, 92%. The product was characterised as follows:

IR (polymer film from CH_2Cl_2) ν_{max} cm^{-1}: 3074 w, 3050 w, 2924 s, 2852 s, 2610 s, 1681 s, 1593 s, 1499 s, 1465 m, 1409 m, 1362 m, 1244 s, 1172 s, 1162 s, 1109 m, 1083 m, 1015 m, 918 m, 874 m, 837 m, 755 m, 678 m, 601 w, 566 w, 513 m.

NMR: δ ^1H: 1.0-3.5 (broad m, BH), 1.29-1.33 (m, aliphatic CH), 1.69-1.71 (m, aliphatic CH), 2.89-2.93 (m, aliphatic CH), 6.85-7.95 (m, ArH)
δ ^{13}C: 24.46, 29.42, 38.45 (aliphatic C), 78.2 (carboranyl C), 117.93, 118.95, 128.83, 130.33, 132.15, 132.32, 156.10, 160.75 (ArC), 199.15 (C=O)

4.6.9. The preparation of CP9

CP9 was prepared and isolated according to the general procedure described above, (Section 4.6.1), by treating 1,7-bis-(4-phenoxyphenyl)-*meta*-carborane (0.50 g, 1.04 mmol) with dodecanedioic acid (0.237 g, 1.03 mmol) in freshly distilled triflic acid (9 cm^3), to afford white polymeric beads identified as **CP9**. Yield 0.55 g, 83%. The product was characterised as follows:

IR (polymer film from CH_2Cl_2) ν_{max} cm^{-1}: 3018 w (Ar CH), 2927 m (aliphatic CH), 2605s (BH), 2033 w, 1770 s (ketone C=O), 1594 s, 1500s, 1464 m, 1411 m, 1365 m, 1284 sh., 1244 s (ether C-O), 1174 m, 1163 s, 1056 w, 1015 m, 977 m, 910 w, 880 m, 839 m, 757 m, 619 m, 522 m, 412 w.

NMR: δ ^1H: 1.32, 1.6-1.7, 2.8-2.96, 1.1-3.9 (broad multiplet; BH), 6.85-7.87 (ArH).
δ ^{13}C: 8.3, 24.9, 29.8, 38.9, 77.1 (carboranyl CH), 118.5, 119.7, 130.0, 130.8, 131.4, 132.9, 156.1, 158.9 (ArC), 194.1 (C=O).

4.6.10. The preparation of CP10

CP10 was prepared and isolated according to the general procedure described above, (Section 4.6.1), by treating 1,12-bis-(4-phenoxyphenyl)-*para*-carborane (0.24 g, 0.50 mmol) with adipic acid (0.070 g, 0.48 mmol) in freshly distilled triflic acid (5 cm^3). The solution was worked up in the usual manner to afford white polymeric beads identified as **CP10** Yield 0.27 g, 95%. The product was found to be insoluble in NMP but characterised as follows:

IR (polymer film from CH_2Cl_2) ν_{max} cm^{-1}: 3070 w, 3030 w, 2940 w, 2892 w, 2609 s, 1680 s, 1591 s, 1412 m, 1365 m, 1243 s, 1171 s, 1110 m, 1083 m, 1013 m, 967 m, 918 m, 873 m, 836 m, 754 m, 679 m, 567 w, 513 m.

NMR: δ ^1H: 0.5-3.5 (broad m, 10H, BH), 1.61 (m, 4H, $C\underline{H}_2$-CH_2-C=O), 1.82 (t, 4H, -$C\underline{H}_2$-C=O), 6.84-6.87 (d, ArH), 6.97-6.99 (d, ArH), 7.23-7.26 (t, ArH), 7.93-7.95 (d, ArH)
δ ^{13}C: 23.98, 38.21, 82.02 (carboranyl C), 117.93, 118.98, 128.84, 130.31, 132.16, 156.04, 160.88 (ArC), 198.52(C=O).

4.6.11. The preparation of CP11

CP11 was prepared and isolated according to the general procedure described above, (Section 4.6.1), by treating 1,12-bis-(4-phenoxyphenyl)-*para*-carborane (0.24 g, 0.50 mmol) with azelaic acid (0.90 g, 0.48 mmol) in freshly distilled triflic acid (5 cm^3). The solution was worked up in the usual manner to afford white polymeric beads identified as **CP11** Yield 0.284 g, 94%. The product was characterised as follows:

IR (polymer film from CH_2Cl_2) ν_{max} cm^{-1}: 3070 w, 3026 w, 2930 m, 2854 m, 2610 s, 1681 s, 1593 s, 1499 s, 1436 sh., 1409 m, 1363 m, 1283 s, 1244 s, 1207 m, 1173 s, 1163 s, 1109 w, 1083 m, 1015 m, 797 m, 918 m, 873 m, 838 m, 754 s, 679 m, 601 w, 566 w, 514 m.

NMR: δ ^1H: 0.5-3.5 (broad m, BH), 1.61 (m, 4H, aliphatic CH), 1.74 (m, 4H, $C\underline{H}_2$-CH_2-C=O), 2.91-2.95 (t, 4H, $C\underline{H}_2$-C=O), 6.98-7.96 (m, ArH).

δ ^{13}C: 24.45, 29.38, 29.48, 38.46 (aliphatic C), 81.99 (carboranyl C), 117.92, 118.93, 128.82, 130.31, 132.13, 132.32, 156.09, 160.72 (ArC), 199.14 (C=O)

4.6.12. The preparation of CP12

CP12 was prepared and isolated according to the general procedure described above, (Section 4.6.1), by treating 1,12-bis-(4-phenoxyphenyl)-*para*-carborane (0.24 g, 0.52 mmol) with dodecanedioic acid (0.116 g, 0.50 mmol) in freshly distilled triflic acid (5 cm3), to afford white polymeric beads identified as **CP12**. Yield 0.283 g, 84%. The product was characterised as follows:

IR (polymer film from CH_2Cl_2) ν_{max} cm^{-1}: 3074 w, 3050 w, 2924 s, 2852 s, 2610 s, 1681 s, 1593 s, 1499 s, 1465 m, 1409 m, 1362 m, 1244 s, 1172 s, 1162 s, 1109 m, 1083 m, 1015 m, 918 m, 874 m, 837 m, 755 m, 678 m, 601 w, 566 w, 513 m.

NMR: δ ^{1}H: 1.0-3.5 (broad m, BH), 1.29-1.33 (m, aliphatic CH), 1.69-1.71 (m, aliphatic CH), 2.89-2.93 (m, alpihatic CH), 6.85-7.95 (m, ArH)

δ ^{13}C: 24.46, 29.42, 38.45 (aliphatic C), 82.04 (carboranyl C), 117.93,118.95, 128.83, 130.33, 132.15, 132.32, 156.10, 160.75 (ArC), 199.15 (C=O)

4.6.13. The preparation of CP13

CP13 was prepared and isolated according to the general procedure described above, (Section 4.6.1), by treating 1,12-bis-(4-phenoxyphenyl)-*para*-carborane (0.24 g, 0.50 mmol) with hexadecanedioic acid (0.137 g, 0.48 mmol) in freshly distilled triflic acid (5cm3). The solution was worked up in the usual manner to afford white polymeric beads identified as **CP13** Yield 0.339 g, 97%. The product was characterised as follows:

IR (polymer film from CH_2Cl_2) ν_{max} cm^{-1}: 3054 w, 2922 s, 2851 s, 2609 s, 1681 s, 1593 s, 1499 s, 1465 m, 1409 m, 1365 m, 1243 s, 1173 s, 1109 m, 1083 s, 1015 m, 973 m, 918 m, 873 m, 838 m, 739 m, 566 w, 513 w.

NMR: δ ^1H: 1.0-3.5 (broad m, BH), 1.68-1.73 (m, aliphatic CH), 2.89-2.93 (m, aliphatic CH), 6.84-7.95 (m, ArH).
δ ^{13}C: 24.35, 24.45, 29.18, 29.31, 29.48, 29.62, 38.37 (aliphatic C), 82.30 (carboranyl C), 117.94, 118.95, 128.83, 130.32, 132.16, 132.29, 156.09, 160.77 (ArC), 199.04 (C=O).

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Chapter 5

POLYARYLENE CARBORANES

5.1. Introduction:

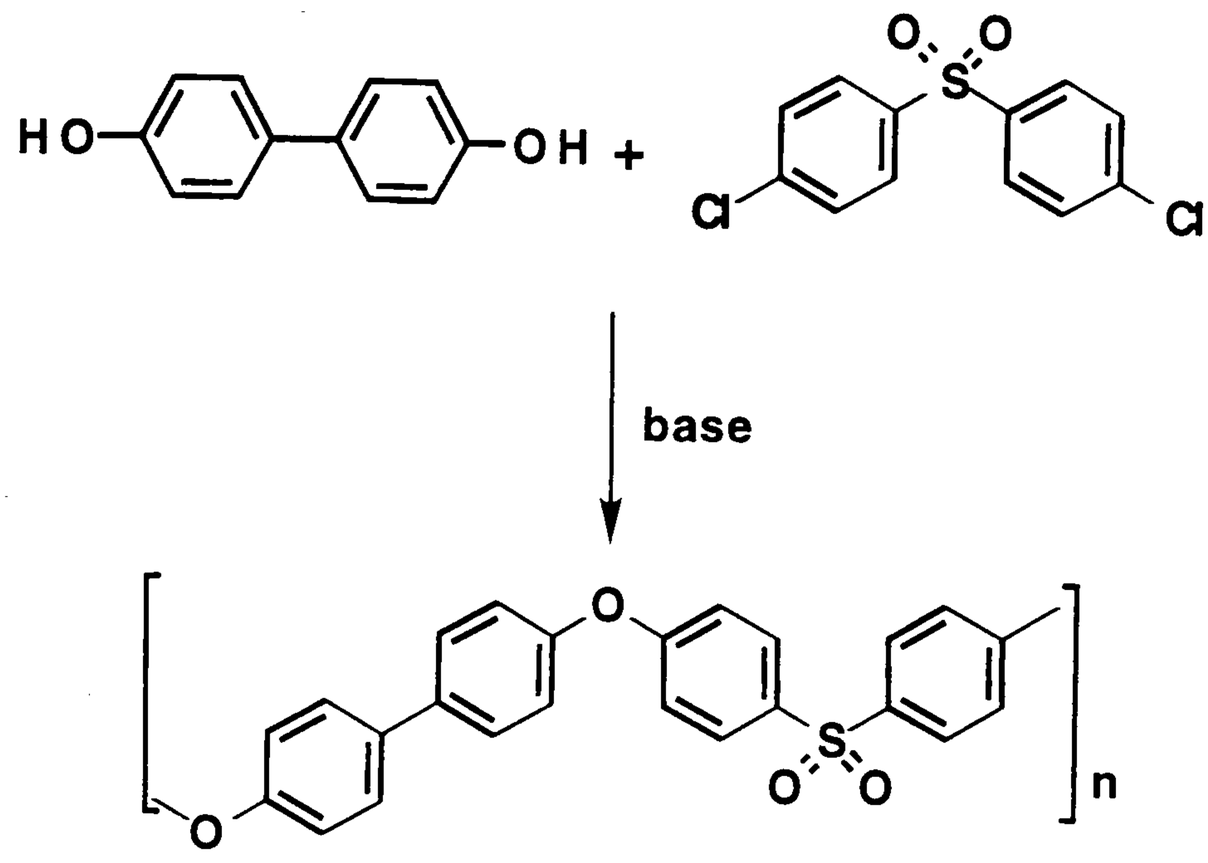
As reported in Chapter 4, polyacylation in triflic acid provides an accessible route to relatively high molecular weight carborane based materials of the form $[\text{-CO-Ar-CO-C}_6\text{H}_4\text{-O-C}_6\text{H}_4\text{-C}_2\text{B}_{10}\text{H}_{10}\text{-C}_6\text{H}_4\text{-O-C}_6\text{H}_4\text{-}]_n$ containing ether and ketone moieties. However, the electronic requirements of this electrophilic aromatic substitution reaction restrict the ratio of carborane cages to aromatic rings that it is possible to obtain in a polymer, as phenoxy groups are required to facilitate Friedel-Crafts acylation. Investigations using transition metal catalysed polymerisation chemistry have now been undertaken in an attempt to achieve a higher proportion of carborane functionality in the resulting polymers. This chapter considers the history behind nickel catalysed aryl coupling reactions and then describes attempts to synthesise oxygen-free polycarboranes having direct aryl-aryl linkages.

$$\text{X-Ar-C}_2\text{B}_{10}\text{H}_{10}\text{-Ar-X} \xrightarrow{\text{M}} [\text{-Ar-C}_2\text{B}_{10}\text{H}_{10}\text{-Ar-}]_n + \text{MX}_2$$

Due to many ambiguities in the literature this target was approached in two stages - the general coupling of simple aromatic units (to optimise the polymerisation conditions) and the subsequent coupling of aromatic species incorporating the icosahedral carborane unit, with the general aim of increasing the carborane : aromatic ratio, and potentially the pyrolytic ceramic yield of such systems.

5.1.1. Transition Metal Coupling Reactions:

Coupled biaryl products have been used as thermal transfer media, liquid crystal intermediates, fluorescent brighteners and polymer additives and there has been much interest in the development of aromatic polymers which contain biphenyl as part of the repeat unit,[1] for example poly(ethersulphone)s such as "RADEL" (Figure 5.1) which may be produced by nucleophilic aromatic substitution.



"RADEL"

Such polymers generally exhibit high toughness and very good thermo-oxidative stability which has been attributed at least in part to the presence of the biaryl linkage.

Direct aryl-aryl bonds have been formed by many routes requiring metals[1], for example direct oxidative dehydrodimerization by palladium(II)[3], vanadium(II)[4], copper(II)[5] and thallium(II)[6], and reductive coupling with the loss of a substituent group as in the classical[7] and modified[8] Ullmann reactions. More recently Kharasch-type cross-couplings of aromatic Grignard reagents with an aryl halide catalysed by nickel(II) and palladium(II)[9,10] have been reported.

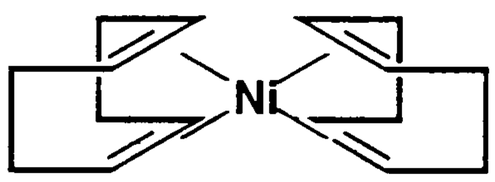
Homo-coupling of aryl and alkenyl halides may be achieved by a variety of methods involving transition metal catalysts and reagents. The use of copper in the classical Ullmann[11] reaction has been reviewed in detail[12,13] and related copper-based coupling reactions have been utilised in the work described in chapter 2, where they provide a new synthetic approach to aryl-substituted carboranes.

Transition metal catalysed polymerisation chemistry based on biaryl formation appeared to be a viable route into materials with higher degrees of carborane functionality, but despite such reactions being well established no general route to highly polymeric materials has been described.

Indeed many amibiguous and apparently conflicting reports regarding the reaction conditions appear in the literature. The following sections attempt to summarise these, and describe approaches made in the present work to develop a general route to high molecular weight, carborane-containing poly(arylene)s.

5.1.2. Nickel Catalysed Coupling Reactions:

The use of nickel(0) complexes to promote formation of C-C bonds was first described by Semmelhack at al [14-16] and has since been widely investigated.[17] These reactions proceed under mild conditions, but require air sensitive nickel complexes such as $Ni(COD)_2$ or $Ni(PPh_3)_4$ in stoichiometric amounts.

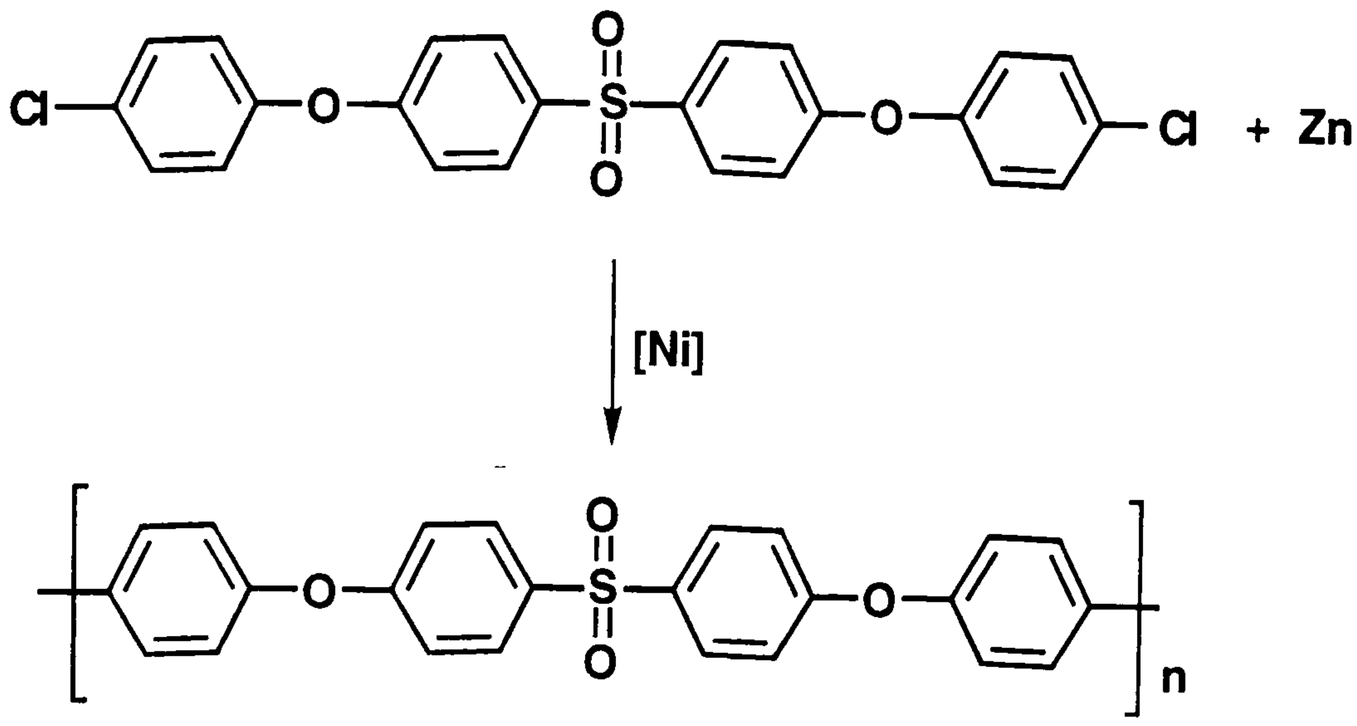


$$+ \ 2ArX \xrightarrow[25\text{-}40^{\circ}C]{DMF} Ar\text{-}Ar + NiX_2 + COD$$

In 1975 Kende *et al.*[18] reported a modification of Semmelhack's method, in which reactive Ni(0) may be generated *in situ* from air-stable $Ni(PPh_3)_2Cl_2$ by reduction with zinc dust, in the presence of triphenylphosphine and used to couple aryl bromides.[19,20] A relatively large excess of triphenylphosphine is required, as the phosphine coordinates to the co-produced zinc salt,[21] but the reaction can tolerate a variety of functional groups such as carbonyls, aldehydes, esters and nitriles which are unsuitable for similar coupling reactions using organomagnesium reagents.[22-24]

$$RMgX + R'X' \xrightarrow{NiL_2Cl_2} R\text{-}R' + MgXX'$$

Due to the essentially quantitative yields of biaryls that can be produced by such reactions this method should be suitable for the preparation of high polymers by reactions with difunctional monomers. Colon *et al.*[25] have in fact demonstrated that this procedure provides a viable synthesis of poly(etherethersulphone)s.

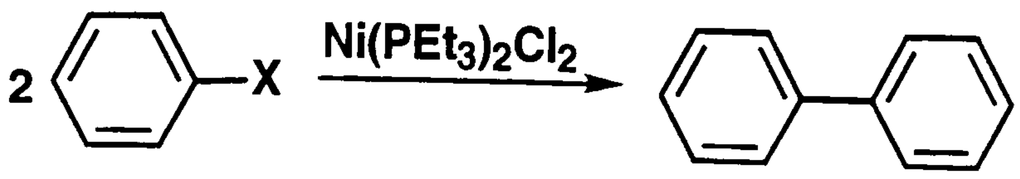


A survey of the literature showed that the specific conditions required for this type of polycondensation are highly monomer-dependent and a general set of reaction parameters did not appear to have been established. The immediate aim of the present work was to establish the reaction conditions that would be generally applicable to the coupling of haloaryl carboranes.

The mechanism of the reaction and indeed the identity of the coupling reagent has still to be established, but is thought to be $Ni(0)L_n$ formed in situ, either in the presence of the aryl chloride or prior to its addition.

The key step in the coupling mechanism is believed to be the regeneration of the active nickel(0) species by zinc from an aryl nickel(II) complex. Reagents should be scrupulously dry to avoid hydrodehalogenation occuring as a side-reaction which could obviously limit molecular weight.

The question of which halogen is the best "leaving group" is not clear-cut. Results from a system utilising tetraethylammonium iodide as promoter, zinc and nickel(II) chloride as reported by Iyoda[26] indicated that chloroarenes coupled in higher yield than the corresponding bromo-compounds although later the same author reported that efficiences for the same reaction actually followed the order ArI >> ArBr > ArCl,[27] as was also observed by Takagi *et al.*[28]



X	Yield (%)
I	88
Br	74
Cl	25

Colon and co-workers[29] reported that the efficiency of coupling of arylhalides via nickel catalysis follows the order ArCl > ArBr > ArI, whereas procedures reported to couple aryl iodides with KI and zinc in the presence of nickel (II) chloride were ineffective with aryl chlorides.[30,31]

In contrast, Semmelhack and co-workers[32] reported that only bromo and iodo arenes give satisfactory yields when coupled in the presence of zero valent nickel.

Colon[29] reported the reaction to be pseudo first-order with respect to aryl halide and to be promoted by bipyridyl and halide salts, the effectiveness of the latter in the order I > Br > Cl > F, achieving high yields in minutes. Iyoda reported that although iodide accelerates the reaction markedly, no acceleration was found with bromide, and Ueda *et al.* reported that the addition of halide ions appeared to exert a negligible effect in the polymerisation of poly(ethersulphone)s,[33] and poly(etherketone)s.[34,35] Powers[36] reported that in the attempted polymerisation of adamatane-based monomers, the addition of KI actually lowered the molecular weight achieved.

There are many variables that may affect the attainable molecular weight of the polymeric material- the relative proportions of nickel, zinc, triphenylphosphine, solvent and promoter, in addition to the reaction time and temperature. Colon[37], however, reported that only three of these have a significant effect on the inherent viscosity and hence on the molecular weight of the resulting polymer. For systems based on nickel/ zinc/triphenylphosphine/NMP/sodium bromide the most significant variable has been found to be the concentration of triphenylphosphine.

Although this reagent does not have a great effect in the coupling of aryl halides, where a difference in yield between 95 and 99% is relatively insignificant, it should be recognised that in polymer chemistry such a difference is extremely important and results in the difference between forming a polymer with a degree of polymerisation (DP) of 20 or one with a DP of 100. Reaction temperature has been shown to have a strong effect on the reaction, with side reactions increasing with increasing temperature, although slightly different optimum reaction temperatures have been reported by different groups.

A significant effect was also observed with respect to the level of nickel used. Results[37] suggested that the concentrations of nickel catalyst should be kept low in order to produce high polymer, as once the majority of aryl chloride had been consumed the residual aryl-nickel species remained in solution and effectively end-capped the polymer, limiting the molecular weight that could be attained.

A real effect was observed relating to the amount of excess zinc used in the reaction, although this was found not to be as statistically important as those variables previously discussed. Large excesses of zinc appear to be generally required to achieve high molecular weight polymeric materials, although the preferred literature value for the actual ratio of zinc to monomer is ambiguous.

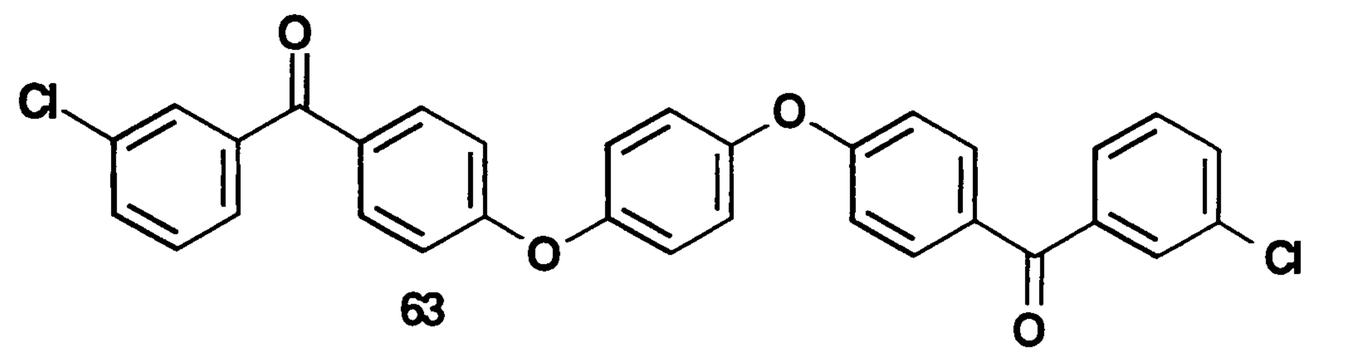
The active catalyst is homogeneous and therefore it is essential that the aryl halide remains in solution if high molecular weight polymers are to be obtained. In addition, the resulting polymer must also be soluble in the reaction solvent, otherwise early precipitation will limit the attainable molecular weight of the final product. To this end many solvent systems have been tried including DMAc[32], NMP[37] THF[25] and acetone.[25]

5.2. Results and Discussion:

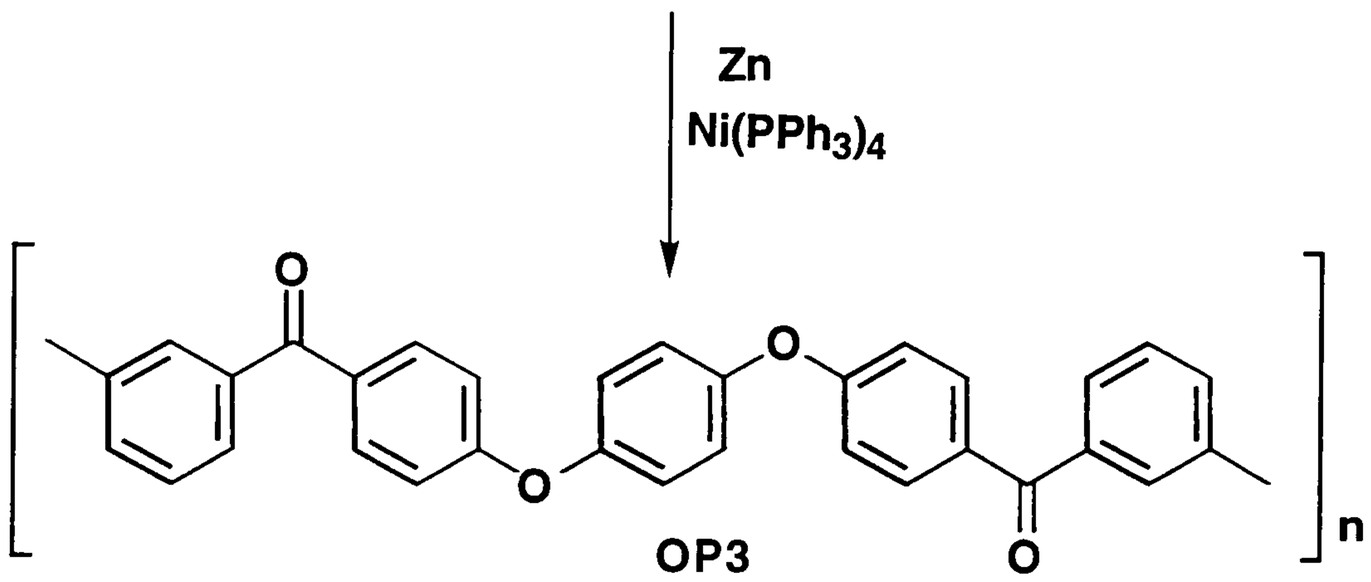
In view of the quantity of ambiguous and apparently conflicting literature regarding the optimum reaction conditions for nickel-catalysed polycondensation of aryl halides, attempts were made to optimise the conditions for the production of a high molecular weight polymer.

As the carborane monomers are extremely costly, it was decided that the most efficient strategy would be to attempt to reproduce the polymerisation described by Ueda for the synthesis of carborane-free poly(etherketone)s.

The all organic monomer chosen for the model polymerisation reaction was 4',4"-bis(3-chlorobenzoyl)-1,4-diphenoxybenzene, (**63**) shown below, which was prepared according to literature methods.[34]



63



OP3

5.2.1. Optimisation of Reaction Conditions:

The initial attempt to repeat the results obtained by Ueda[34] failed because of an error in the reported quantities of triphenylphosphine. Two mole equivalents of PPh_3 to nickel were reported by Ueda whereas at least three molar equivalents are required to generate the active catalytic species. Several attempts were made before the optimum reaction conditions (20 mole equivalents of PPh_3) were established. The results are summarised in Table 5.1. Reactions were all conducted at 80 °C, which was reported[34] to be the optimum temperature required to achieve high molecular weight poly(etherketone)s. This was later confirmed independently by a further series of experiments, (see section 5.2.2.)

In total thirteen polymerisations of **63** were carried out and it was established that it was necessary to purify all of the commercial starting materials before use in order to achieve high molecular weight polymers. The choice of solvent for the polymerisation of **63** did not appear to be crucial with reactions conducted in both DMAc and NMP affording polymers with similar molecular weights. However it was critical that the actual solvent used had been freshly distilled beforehand. The reaction conditions and molecular weights of the products are given in Table 5.1 (section 5.3.1.), and a discussion of the results is given below. The reaction was also carried out using the conditions described by Colon[37] using molar equivalents of zinc:nickel:PPh_3:NaBr of 162:1:20:1 in NMP, but a high molecular weight system could not be achieved.

In each case the product was recovered from the reaction solution by filtering off the excess zinc and inorganic by-products from the reaction and precipitating the polymer into methanol and concentrated HCl (3:1). The suspension was stirred overnight and the polymer was isolated by filtration, washed with methanol and dried. Recovery of the polymer was over 90% in each attempt, and ^{1}H and ^{13}C NMR confirmed that the product had a structure consistent with that of the desired product. Molecular weights were obtained by GPC, using a calibration graph obtained from a polystyrene standard.

5.2.2. Effect of Temperature on the Reaction:

The optimum reaction temperature was established using the reaction conditions established in attempt **OP3**(f) (Table 5.1). The results are shown overleaf in Figure 5.1.

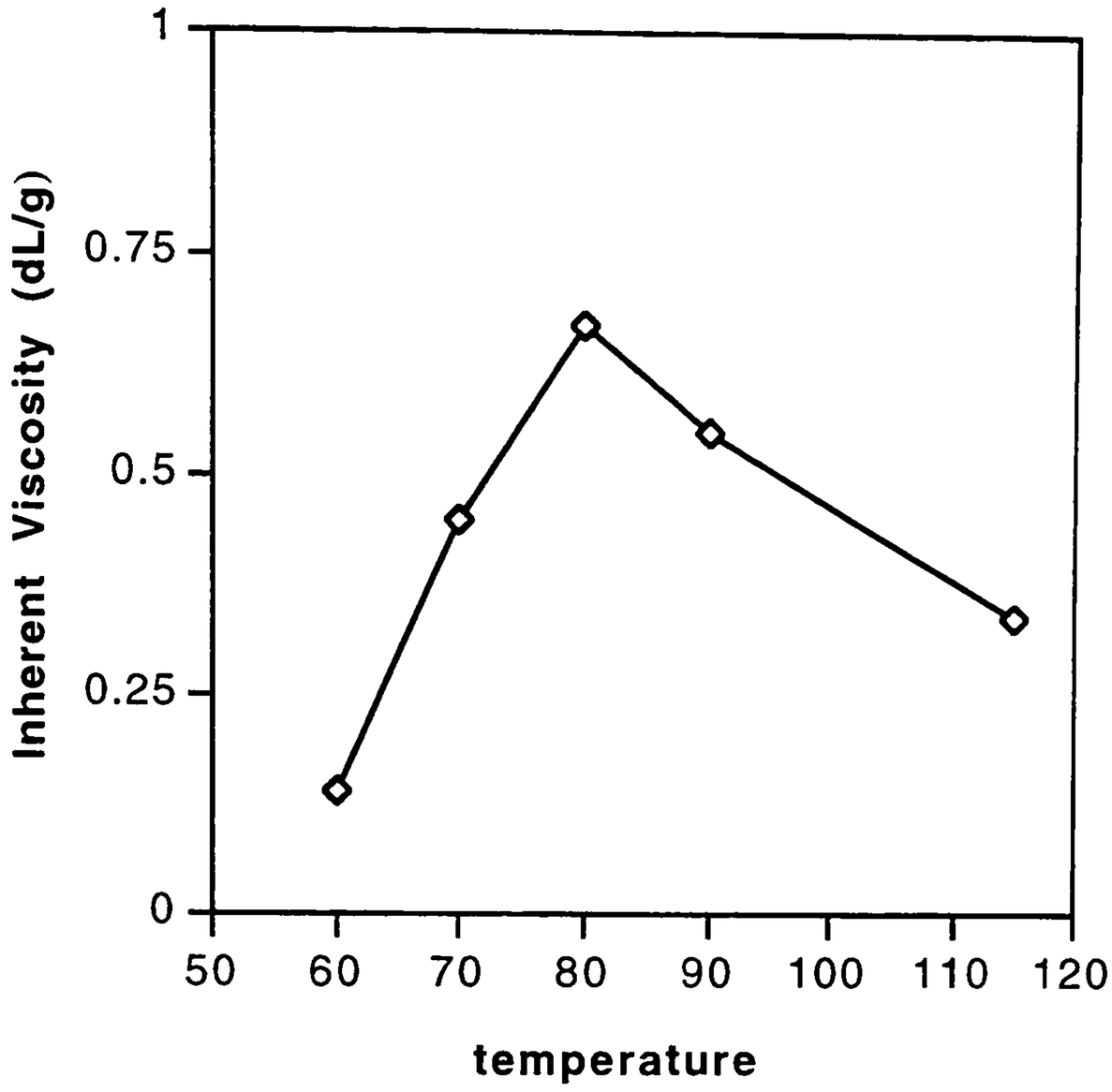


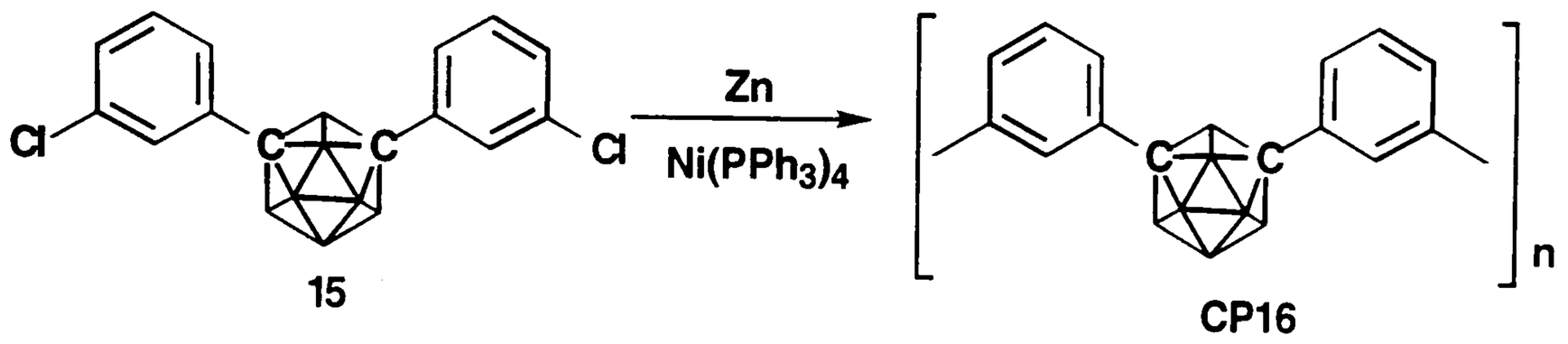
Figure 5.1:. *The Effect of Reaction Temperature on Polymer Viscosity*

The experiments confirmed the optimum temperature reported by Ueda[34] for the preparation of poly(etherketone)s.

5.2.3. Carborane-Containing Polymers:

5.2.3.1. The All *meta* System:

Both NMP and DMAc were clearly suitable solvents for the polymerisation of **63** affording high molecular weight all-organic polymers. All of the poly(etherketone) carborane-containing polymers described in Chapter 4, had been found to be readily soluble in NMP, so this solvent was originally chosen for the polymerisation of 1,7-bis-(3-chlorophenyl)-*meta*-carborane, (**15**), and the remaining reaction conditions were those described for the preparation of **OP3**(f), (Table 5.1).



15 CP16

Analysis of the resulting polymer showed that only a low molecular weight material had been formed suggesting that the reaction conditions were not optimum for this system. The reaction was repeated using sodium bromide as the promoter, to investigate the extent of polymerisation achieved compared to using 2,2'bipyridine (Table 5.2. entry **CP16**(b)). The addition of sodium bromide to the reaction mixture substantially increased the degree of polymerisation achieved compared to Bipy, and the catalyst solution was observed to be a much more distinct orange-red colour under these conditions, perhaps due to less precipitation of the nickel metal.

The reaction was repeated using sodium bromide as promoter to polymerise 1,7-bis-(3-bromophenyl)-*meta*-carborane (**18**), in order to compare the effect of the halogen leaving-group on the reaction. After 3 hours the reaction mixture appeared to be much more viscous than that in the polymerisation attempt with the chloro-monomer but only a slight increase in the molecular weight of the isolated product was observed. After 24 hours, however, the isolated product showed a substantial increase in molecular weight suggesting that coupling occurs more effectively with the bromo- than with the chloro-substituent, in contrast to the results found by Colon.[29] (Table 5.2, entries **CP16** (c) and (d)).

In the polymerisation of **63** both DMAc and NMP had been found to be suitable solvents in order to achieve high molecular weight materials. The polymerisation of 1,7-bis-(3-bromophenyl)-*meta*-carborane was attempted using DMAc, but no increase in the molecular weight of the product was observed after 3 hours. After 24 hours thermal analysis and viscosity measurements showed that the molecular weight of the product was minimal, suggesting that the polymer may be unstable in the catalyst solution under these conditions.

As many groups[32,38-44] have reported that iodide ion causes an acceleration of the nickel-catalysed coupling reaction, the reaction was repeated using sodium iodide as the promoter.

Lower molecular weight products were obtained compared to the reactions carried out using sodium bromide, but the polymer did not break up in the catalyst solution as previously observed.

The polymerisation of 1,7-bis-(3-chlorophenyl)-*meta*-carborane was repeated using the conditions optimised for the polymerisation of the all-organic monomer, but now using DMAc as solvent. This procedure afforded the highest molecular weight material yet, with an inherent viscosity of 0.42 dL/g. The analogous reaction with the bromo- leaving group was planned, but unfortunately there was insufficient time to conduct the experiment and further work is required in this area.

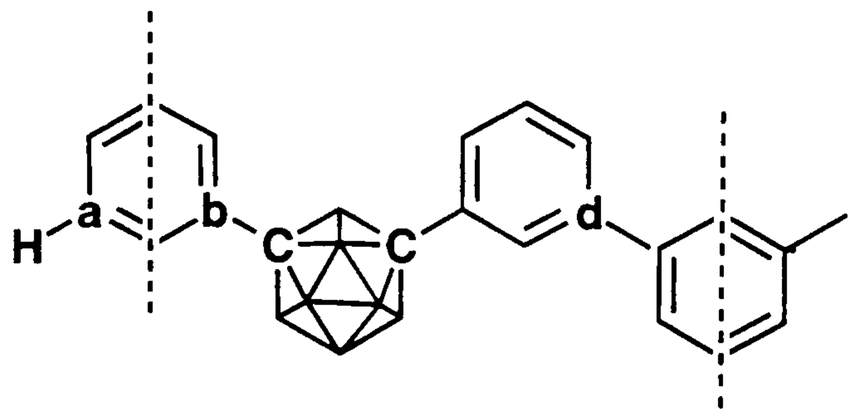
In total nine polymerisations were conducted in an attempt to obtain a high molecular weight polymer, and the results are summarised in Table 5.2, (Section 5.4.).

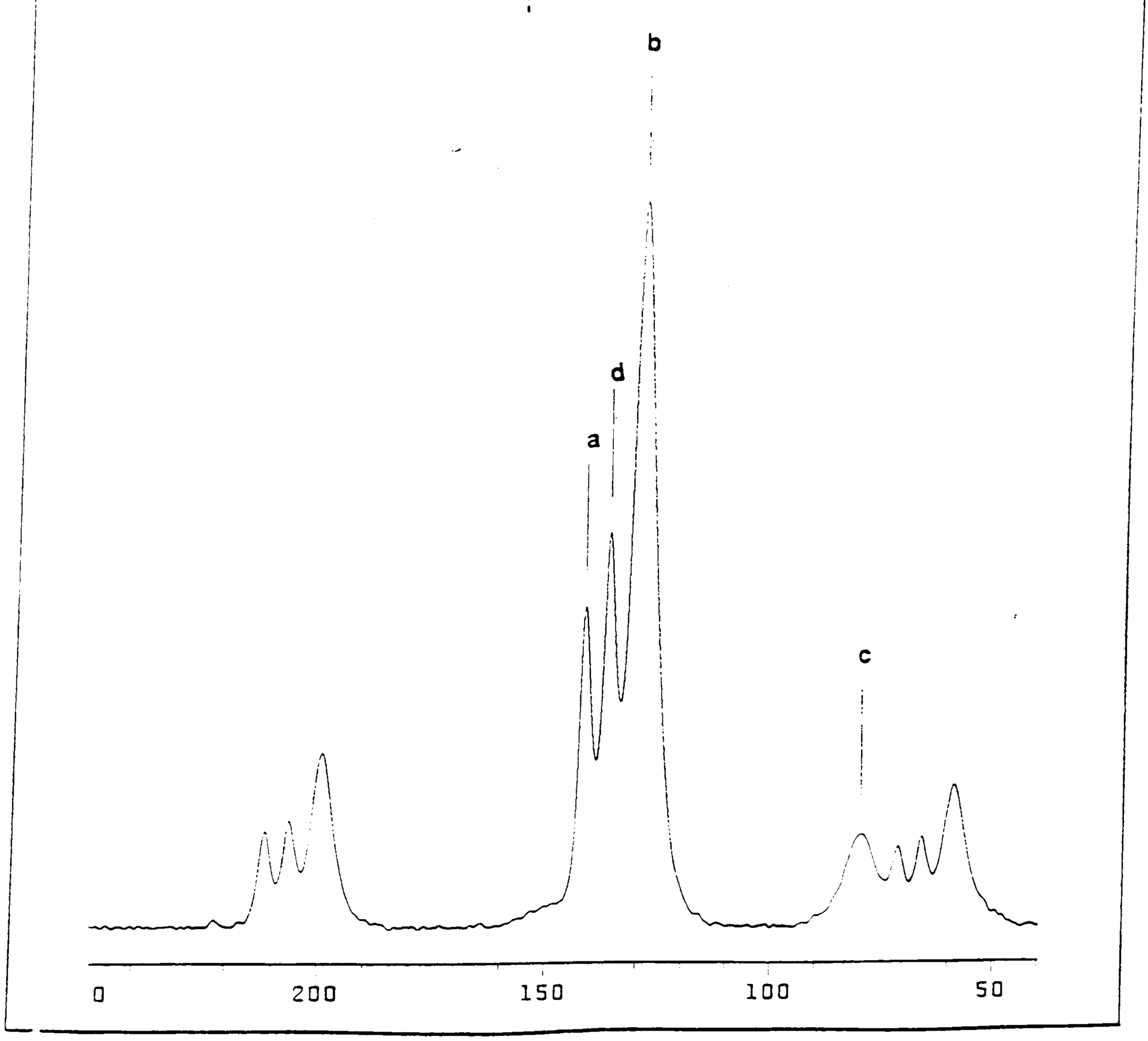
Characterisation

The products formed were found to be only sparingly soluble in most organic solvents and in the case of NMP, for example, only went into solution with heating to approximately 60 °C. This precluded molecular weight determination by GPC and analysis by solution state NMR. Some structural information was however obtained using solid-state NMR and a typical spectrum is shown in Figure 5.2.

Figure 5.2: *Solid-state ^{13}C NMR Spectrum of Polymer CP16*

C atom	δ (^{13}C) ppm
a	141.23
b	128.48
c	79.28
d	135.86



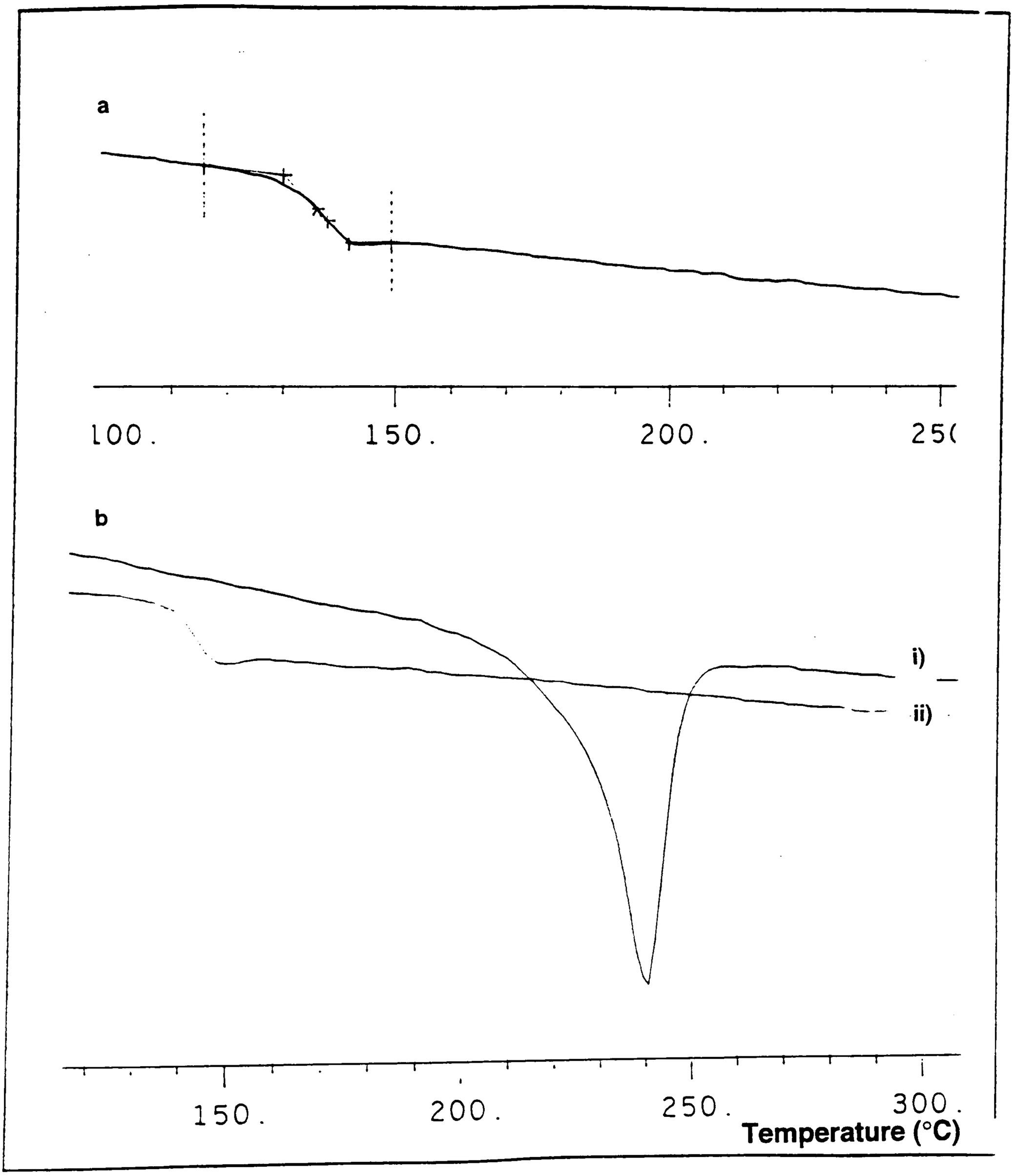


Thermal analysis of the various polymers by DSC showed a glass transition (T_g) temperature between 120 and 170 °C and a typical scan is shown in Figure 5.3. The initial scan of the polymers produced in DMAc showed a possible crystal melting endotherm at approximately 220 °C and no apparent T_g. Subsequent cooling and reanalysis showed only a T_g suggesting that any crystallinity in the polymer was derived from a solvent-dependent process, or alternatively to loss of trapped DMAc from the polymer.

Thermal Analysis

The pyrolytic yields of the polymers were examined by thermogravimetric analysis (TGA) under nitrogen and under static air. (Figures 5.4 and 5.5 respectively). It was found that onset of weight loss occurred at approximately 100 °C and continued at an approximately constant rate up to 850 °C. The carborane-containing polymer retained approximately 95% of its original weight under these conditions, which corresponds to the total mass of hydrogen in the polymer sample, suggesting that the "oxygen-free" polymers degrade in a similar manner to the PECK-type polymers discussed in Chapter 4. In contrast, the all-organic system **OP3** lost almost 40% of its original mass under the same conditions.

Figure 5.3: *Differential Scanning Calorimetry of Polymer* ***CP16****; **a)** from NMP **b)** from DMAc; **i)** first scan and **ii)** second scan.*



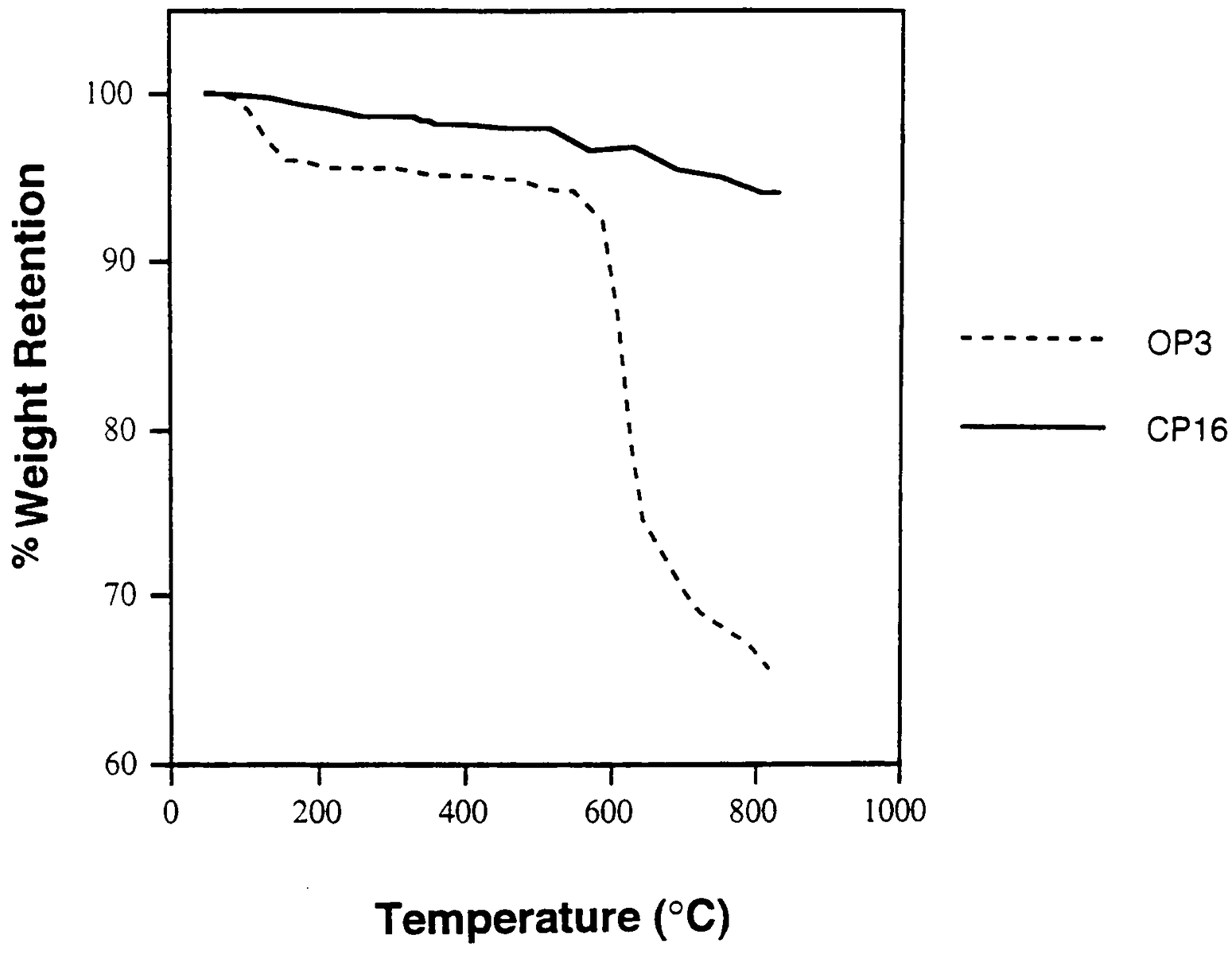


Figure 5.4: *Comparison of Weight Retention of Polymers **CP16** and **OP3**, Under Nitrogen*

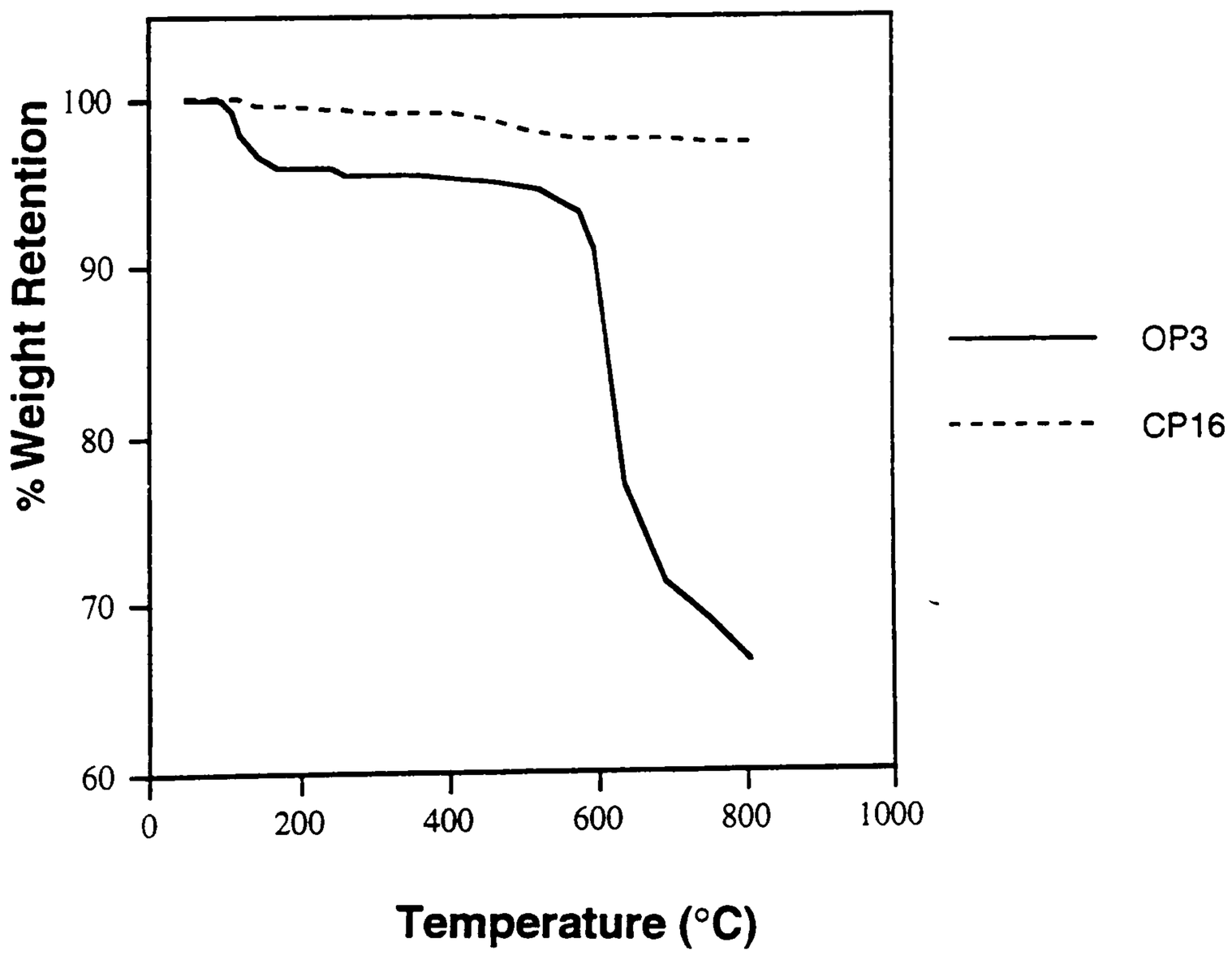
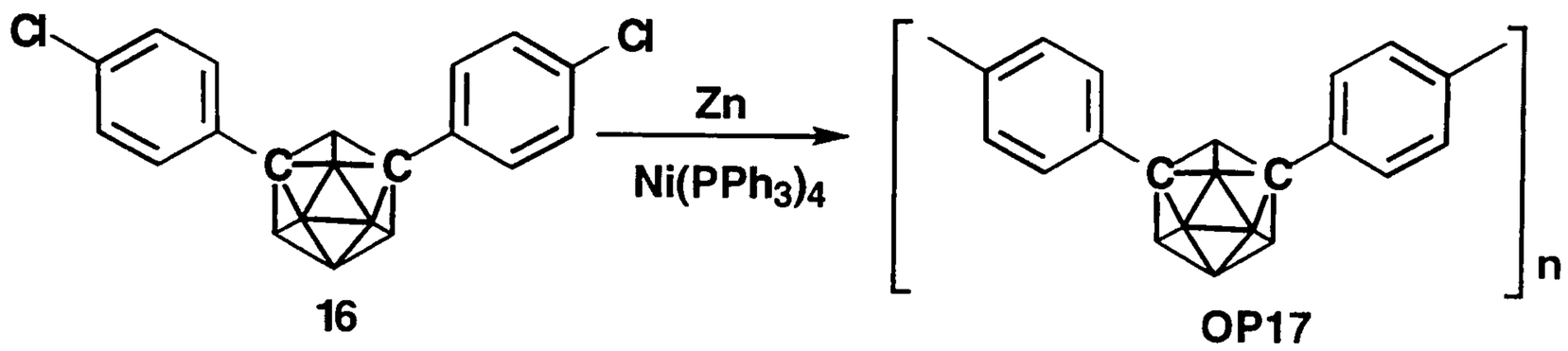


Figure 5.5: *Comparison of Weight Retention of Polymers **CP16** and **OP3**, Under Static Air*

5.2.3.2. The *meta-para* system:

The polymerisation of 1,7-bis-(4-chlorophenyl)-*meta*-carborane (**16**), in a solution of nickel(II)chloride, triphenylphosphine and zinc in DMAc, was carried out to form a poly(arylenecarborane) (**CP17**).

Analysis of the product by DSC showed a complex set of peaks, suggesting that a range of different molecular weight materials had been formed.



16 OP17

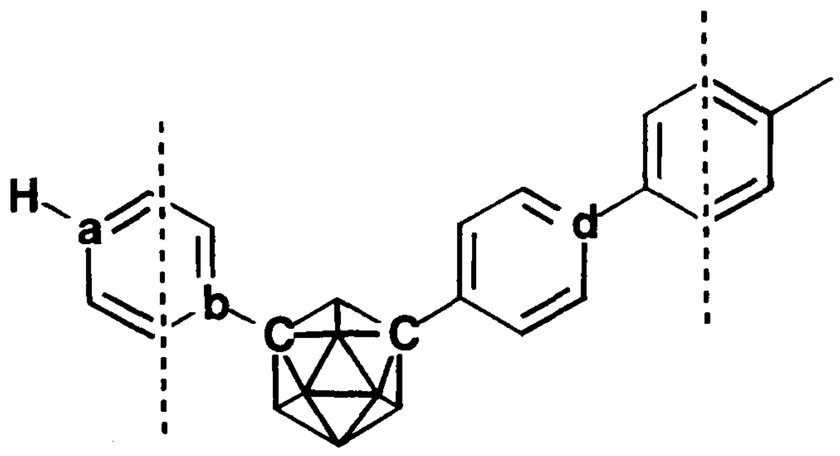
The product was extracted with boiling DMAc in an attempt to remove any soluble lower molecular weight polymeric material, and the insoluble fraction from this extraction showed a strong double melting peak (ca. 60 J/g) between 430 and 470 °C and no apparent Tg.

The insolubility and very high melting point are consistent with the product being crystalline poly(biphenylene-*meta*-carborane), but the molten material appeared to be of low viscosity and therefore probably not of very high molecular weight. Powder x-ray diffraction confirmed that some degree of crystallinity was present in the polymer.

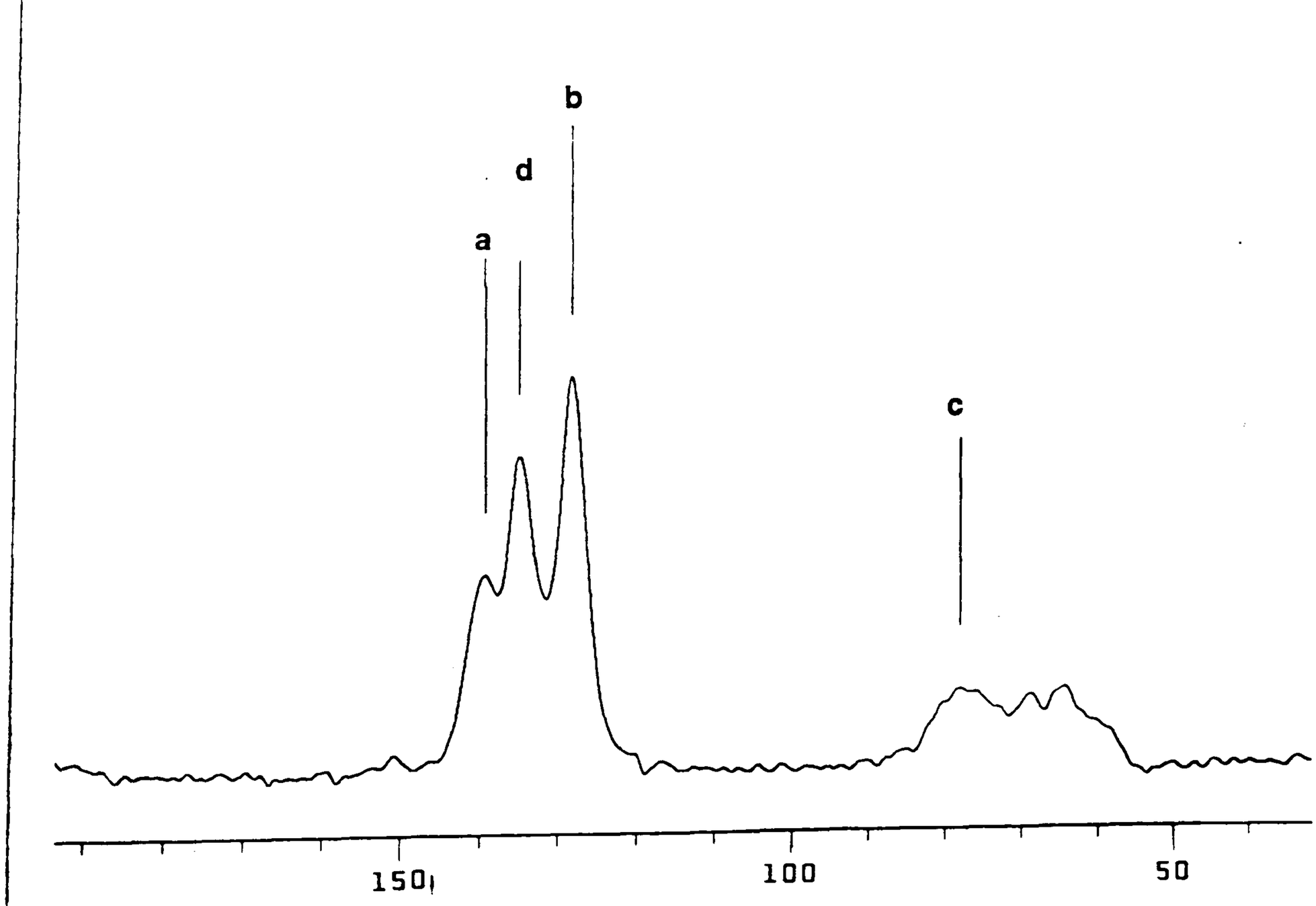
The low molecular weight obtained may be due to the crystallisation of the polymer from the reaction solvent at an early stage of the polymerisation, thus limiting the possible molecular weight that may be achieved.

The reaction was repeated using NMP as the reaction solvent in an attempt to maintain the polymer in solution long enough for a higher molecular weight material to be formed. Unfortunately the product was found to be insoluble and molecular weight determination was not feasible, but analysis of the product by ^{13}C solid state NMR again showed that the desired polymer had been formed and a typical spectrum is shown in Figure 5.6.

Figure 5.6: *Solid-state ^{13}C NMR Spectrum of Polymer* ***CP17***



C atom	δ (^{13}C) ppm
a	139.26
b	128.12
c	78.02
d	134.05

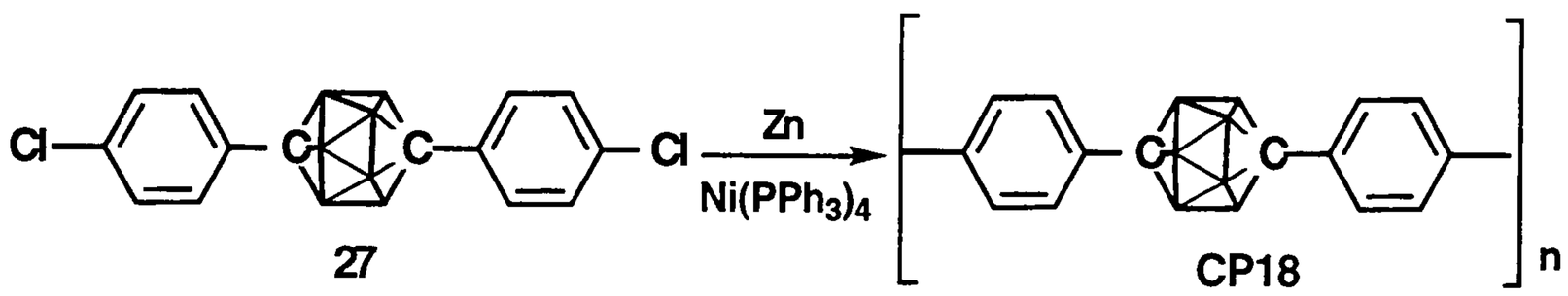


Thermal Analysis

TGA analysis showed that the carborane-containing polymer retained over 98% of its original weight on heating to 850 °C under nitrogen as observed with the all-*meta* polymer system **CP16**.

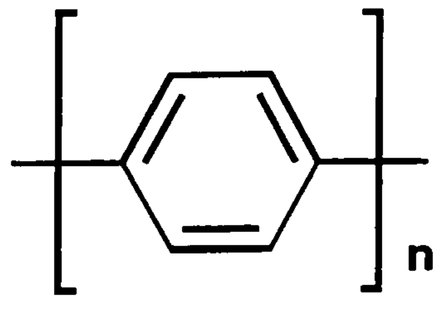
5.2.3.3. The All *para* system:

Utilising the reaction conditions established for the organic system, polymerisation of 1,12-bis-(4-chlorophenyl)-*para*-carborane was attempted.



27 **CP18**

It was observed that the linearity of the monomer unit might promote crystallisation and early precipitation of the resulting polymer particularly in view of its similarity to the poly(*para*phenylene) (PPP) system.



Poly(*para*phenylene) (PPP)

Studies of the incorporation of carboranes into PEEK/PEK type polymers showed that the introduction of the pseudospherical carborane unit rendered the majority of polymers formed completely amorphous, and it was hoped that the icosahedral unit would have a similar effect in this instance, allowing the polymer to remain in solution until at least moderate molecular weights were achieved.

Indeed, the reaction mixture was observed to form a viscous solution during the course of the polymerisation suggesting that moderate to high molecular weight material was being formed. However, further experiments on the carborane system suggested that the apparent increase in viscosity of the reaction mixture may actually be due to precipitation of very finely divided polymer from solution.

Unfortunately once the material had been precipitated from the reaction solution it was found to be completely insoluble in common organic solvents. Hence viscosity measurements and an indication of the molecular weight of the polymer sample could not be obtained.

Powder XRD patterns showed strong, sharp peaks even before the polymer sample was annealed, indicating that the polymer sample had a very high degree of crystallinity.

Molecular modelling and diffraction simulation was carried out using the program "Cerius^2" (Molecular Simulations Inc.) running on a Silicon Graphics Indigo workstation at the CCLRC Daresbury Laboratory.

Using the molecular geometry of 1,12-bis-(4-methylphenyl)-*para*-carborane (**35**), (crystal structure described in Chapter 2), as a starting point, the 1,12-bis-(1,4-phenylene)-*para*-carborane monomer unit was defined with coplanar aromatic rings. A preliminary polymer crystal structure was generated by packing this monomer in an arbitrary unit cell [triclinic, space group P1, a = b = 10, c = 13 Å, (c is the monomer-repeat distance), $\alpha = \beta = \gamma = 90°$]. (Simulation of the X-ray fibre pattern from this initial structure gave a pattern bearing no resemblance to the experimental data.)

With the molecular conformation fixed (all phenylene rings remaining co-planar) the crystal structure was minimised using the Dreiding II force field, leading to a structure (Figure 5.7) with the unit cell parameters shown below:

a = 6.99 Å	α = 136 °
b = 7.30 Å	β = 113 °
c = 13.04 Å	γ = 89 °

The triclinic space group P1 was retained

Figure 5.7: *Simulated Structure of Polymer CP18 using the Modelling Program Cerius*^{2} *- Energy of the system was minimised with the molecular conformation fixed.*

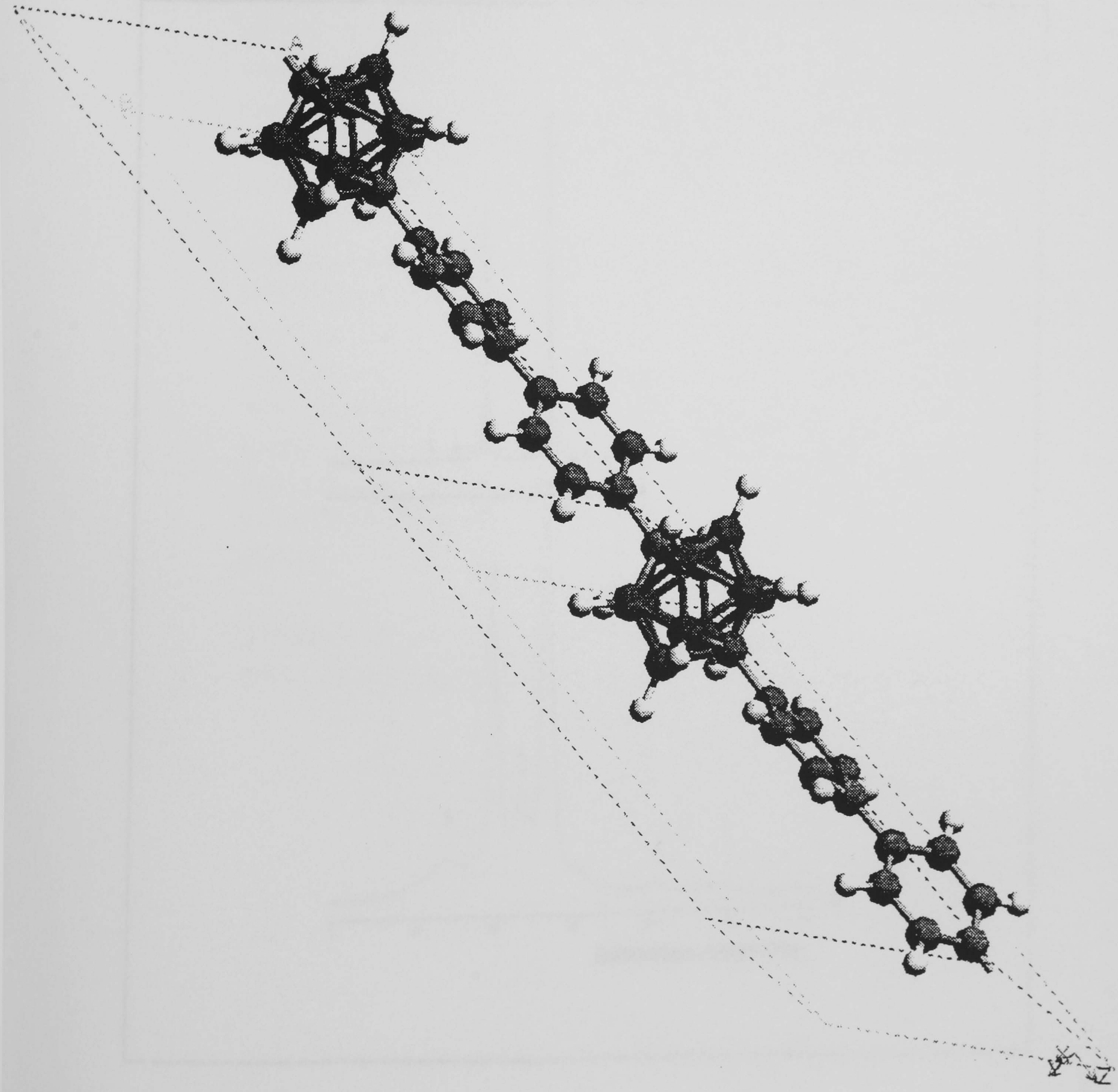
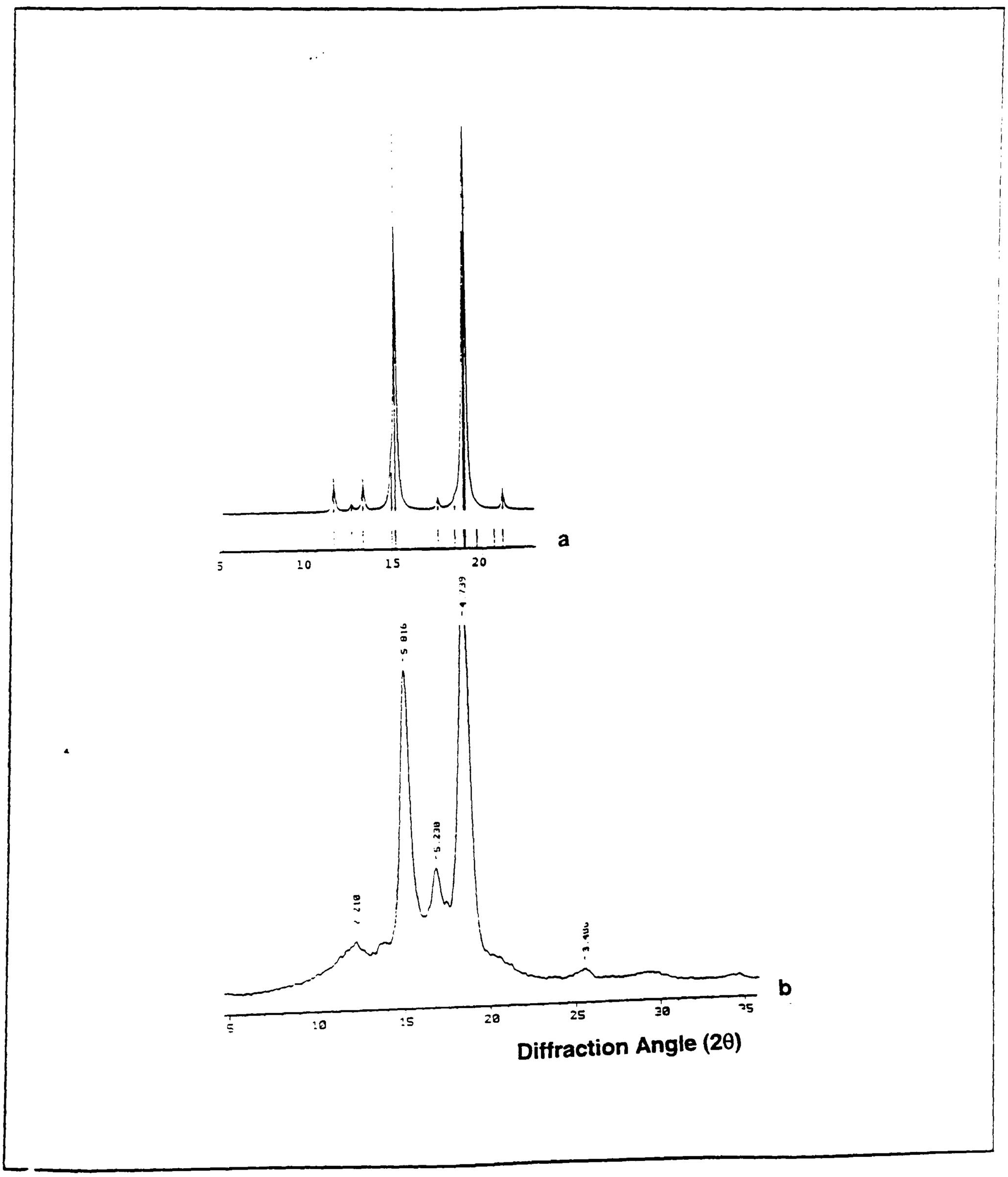


Figure 5.8: *The simulated a) and experimental b) powder X-ray diffraction patterns for Polymer* ***CP18*** *- Energy of the system was minimised with the molecular conformation fixed.*



Simulation of an X-ray powder pattern for this structure gave remarkably good (qualitative) agreement, both in peak positions and relative intensities with the experimental pattern. The comparative simulated and experimental powder X-ray diffraction patterns are shown in Figure 5.8.

The molecular conformation of the structure was minimised within the new unit cell, resulting in loss of coplanarity of the biphenyl units, Figure 5.9. The simulated diffraction pattern was however virtually unchanged, indicating that, although strongly affected by changes in the crystal packing, the diffraction pattern of this particular polymer is relatively insensitive to conformational effects.

Undoped poly(*para*phenylene) is an insulator with resistivity in the range of $10^{10\text{-}12}$ Ωcm^{-1}. On doping, for example with SbF_5, poly(*para*phenylene) becomes a semi-conductor[45] with conductivity in the range of 10^{-2} Ωcm^{-1}. Conductivity measurements were made on the analogous poly(*para*-carboranyl-phenylene) system. Measurements up to 10^{12} Ωcm^{-1} were not feasible due to the limitations of the instruments used, but results indicated that the resistivity of the sample was at least of the same general order as the all organic analogue and that the undoped carborane analogue was an insulator.

Quaternary ^{13}C solid state NMR showed evidence of four peaks confirming that a regular polymer structure had been formed as shown in Figure 5.10.

Figure 5.9: *Simulated Structure of Polymer* ***CP18*** *using the Modelling Program Cerius*^{2} *- Second Energy Minimisation.*

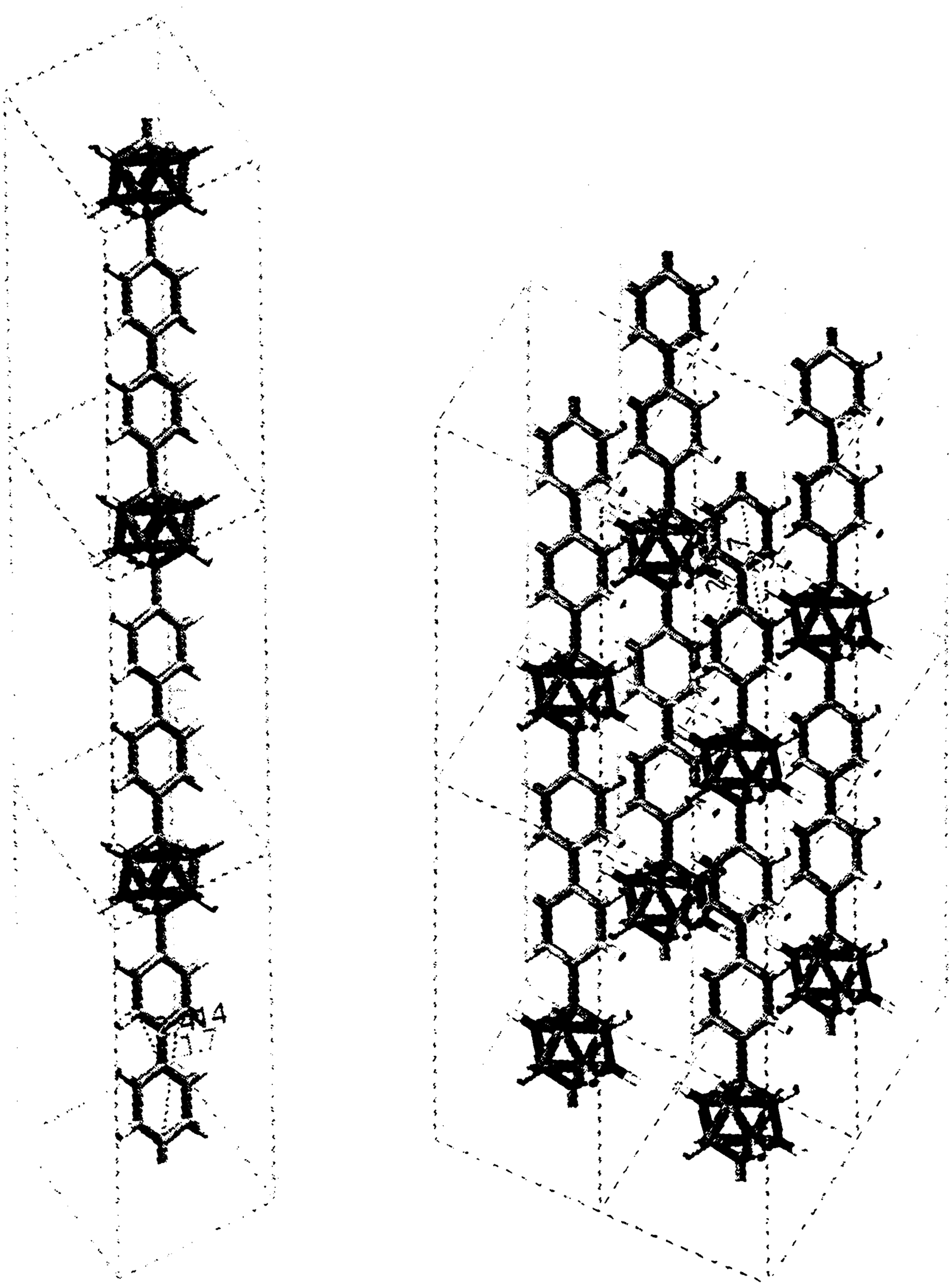
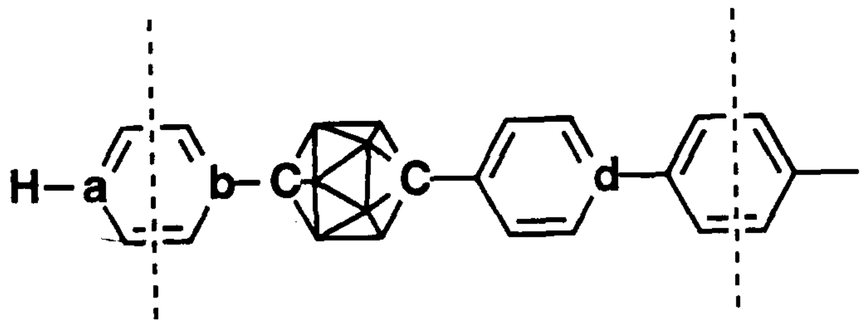
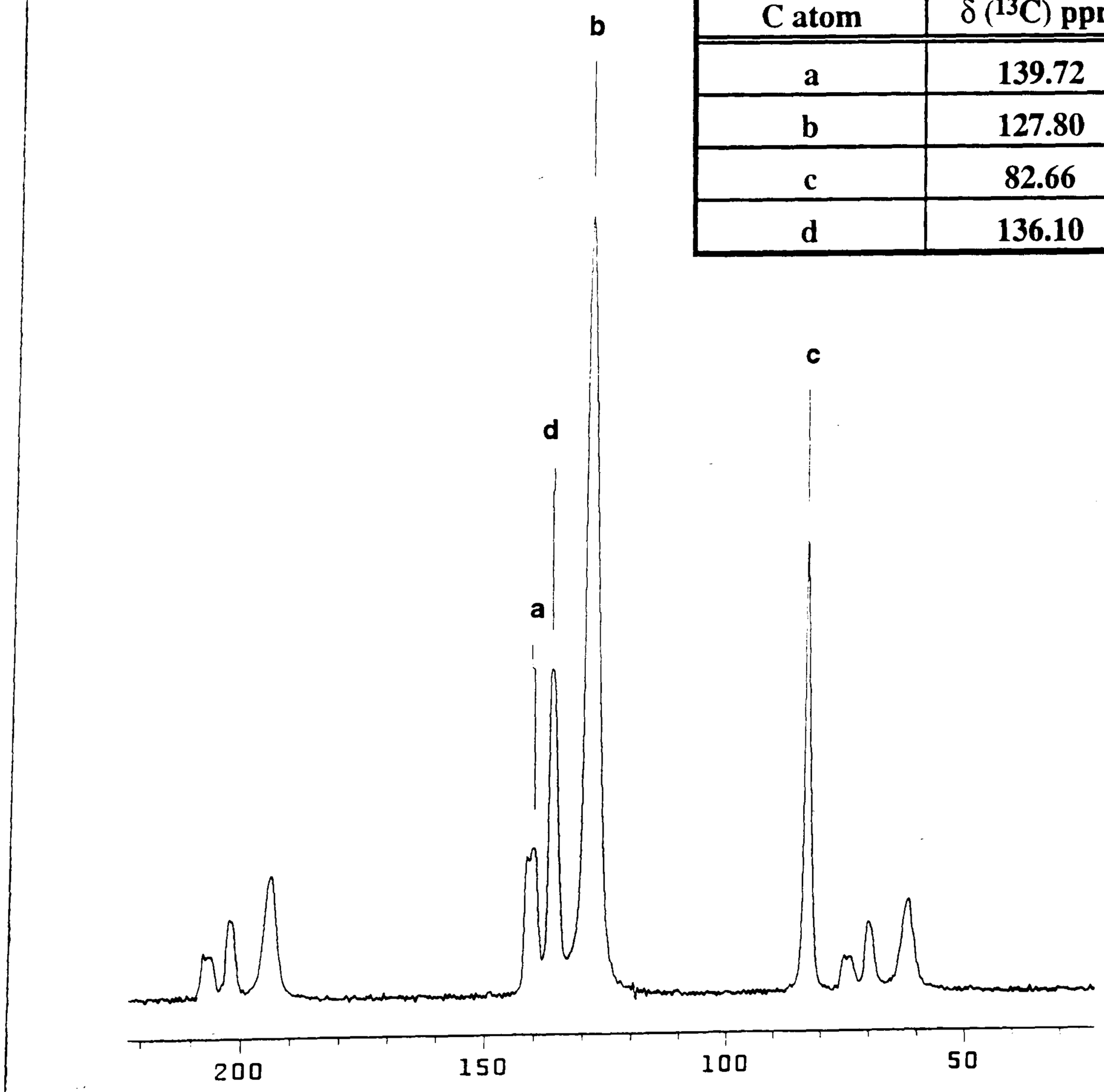


Figure 5.10: *Solid-state ^{13}C NMR Spectrum of Polymer* ***CP18***



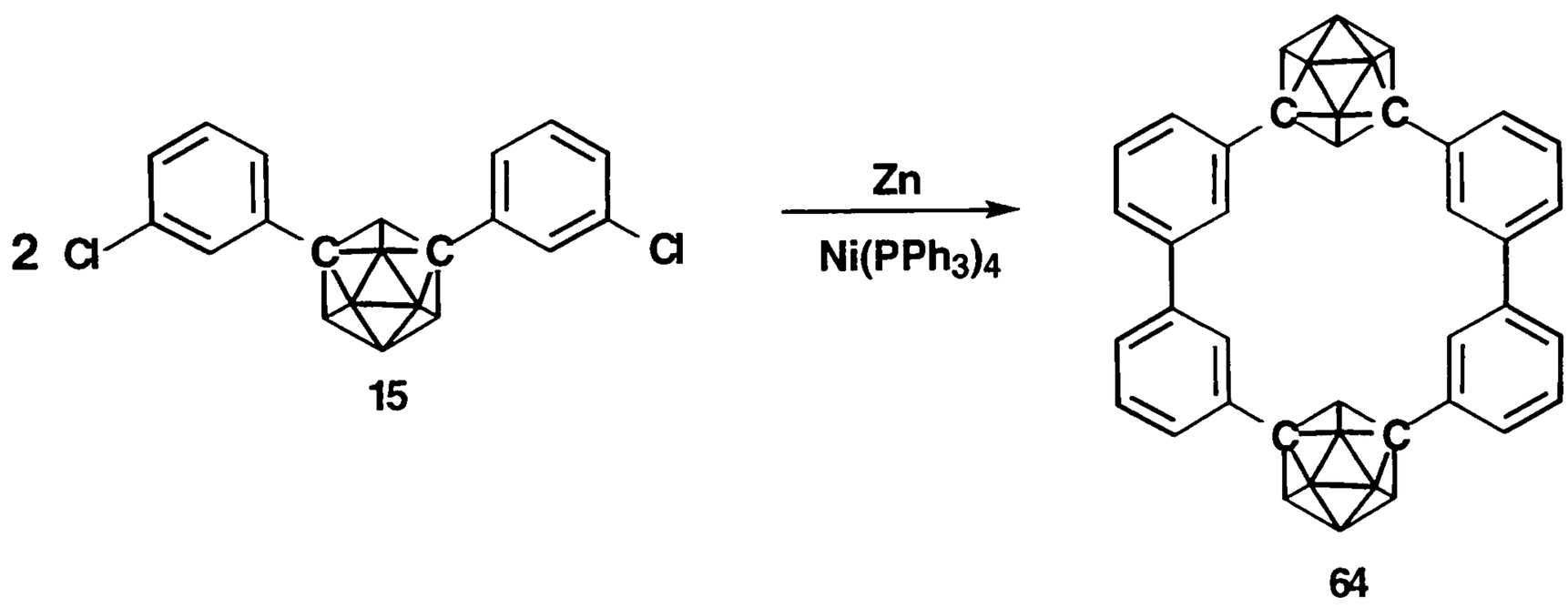
C atom	δ (^{13}C) ppm
a	139.72
b	127.80
c	82.66
d	136.10



5.2.4. Oligomers and Macrocycles:

Preliminary studies were conducted using the optimised coupling reaction conditions, under high dilution, in an attempt to prepare macrocycles incorporating the carboranyl cage. The reactions were conducted in the same manner as the polymerisations previously reported, but the monomer was dissolved in freshly distilled solvent and added dropwise to the catalyst solution over a period of an hour. The products were isolated by column chromatography and identified by mass spectroscopy. Unfortunately there was insufficient time to maximise yields.

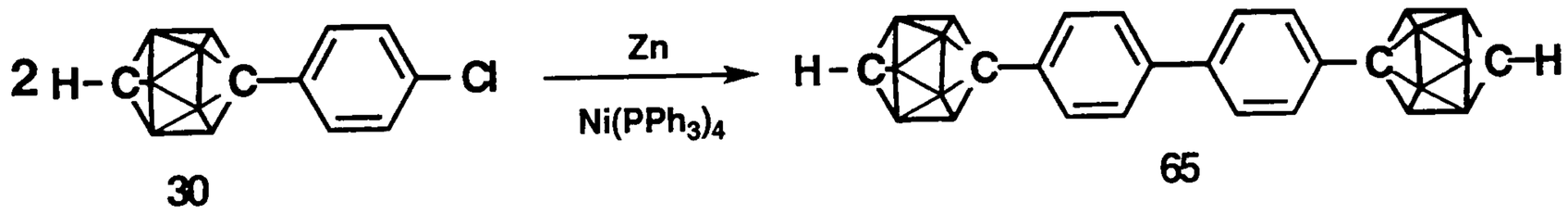
1,7-bis-(3-chlorophenyl)-*meta* -carborane (**15**) was coupled to afford the cyclic product **64** shown below in 40% yield.



15

64

Coupling was also achieved between 1-(4-chlorophenyl)-*para* -carborane (**30**) to afford the linear oligomer (**65**) shown below in approximately 30% yield.



30

65

5.3. Conclusions:

Nickel(0)-catalysed coupling reactions with aryl carboranes have produced a novel class of polymers from the monomers (**15,16,18** and **27**), although only limited molecular weights were achieved.

Dehalogenation reactions have, in the past, generally required high temperature and the polymers formed hence have structural irregularity and/or branching, possibly due to radical formation during conventional dehalogenation reaction by metals.

However, in this work, aryl C-C bond formation has been achieved at low temperatures using a nickel(0) catalysed system, to afford a series of carborane-containing polymers with essentially regular structures.

The inability to achieve high degrees of polymerisation may be attributed to a number of factors associated with the reaction conditions employed. It appears that the most likely cause of the limited molecular weights achieved was premature crystallisation of polymer from solution, despite numerous attempts to optimise the reaction conditions.

Higher molecular weight polymers were formed in DMAc compared to NMP, despite the resulting polymers (in the case of the all *meta* system) being soluble in hot NMP and insoluble in DMAc. In addition, the bromine "leaving group" was observed to couple much more efficently than chlorine, in contrast to the results found by Colon and co-workers.[29] This effect maybe related to the presence of the carborane cage in the system, and the polymerisation of 1,7-bis-(3-iodophenyl)-*meta*-carborane may afford a polymer with even higher molecular weight than achieved during the course of these investigations.

It is probably worth noting that the polymerisation conditions were originally optimised using a monomer which yields a non-crystalline polymer with a high degree of solubility in the chosen solvents. Therefore in order to achieve high molecular weights in the polycarboranyl system it may be necessary to use co-monomers which increase the overall solubility of the resulting material. Indeed the use of a nickel system to produce copolymers has been reported and high molecular weight materials were obtained.[46]

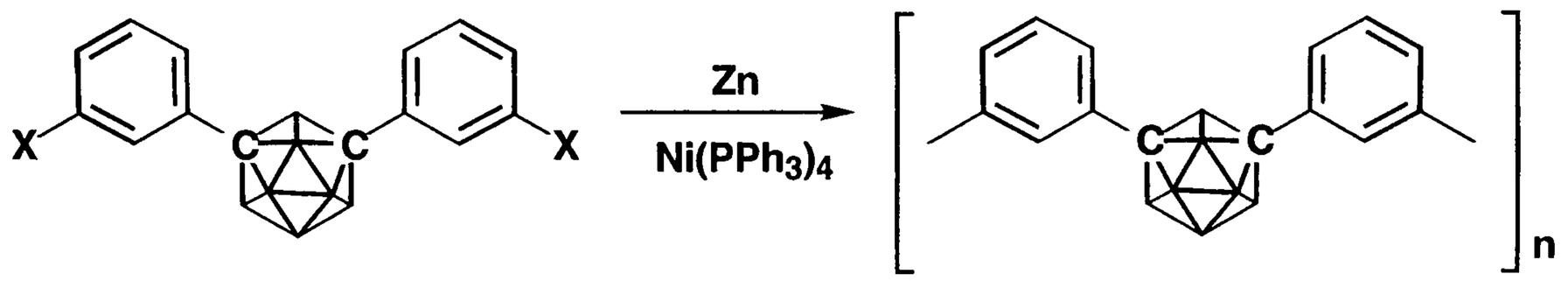
Modification of the polymerisation conditions permitted preliminary studies of the synthesis of novel carborane-containing macrocycles and oligomers in good yields and further work should be carried out in this and related areas.

Table 5.1: *Experimental Results For the Polymerisation of 4',4''-bis-(3-chlorobenzoyl)-1,4-diphenoxybenzene.*

Polymer	Molar Ratios: 20 mol monomer			Promoter	Solvent	Time (hours)	Temp. (°C)	% Yield	η_{inh} (dL/g)
	$Ni(PPh_3)_2Cl_2$	Zinc	PPh_3						
a	1	62	2	Bpy	DMAc†	3	80	0	-
b	1	62	7	Bpy	DMAc†	3	80	75	0.21
c	1	62	12	Bpy	DMAc†	3	80	91	0.20
d	1	62	20	Bpy	DMAc†	3	80	92	0.26
e	1	62	20	Bpy	DMAc	3	80	94	0.61
f	1	62	20	Bpy	NMP	3	80	98	0.67
g	1	62	20	Bpy	THF	3	65	0	-
h	1	62	20	Bpy	NMP	1.5	80	95	0.31
i	1	62	20	Bpy	NMP	3	60	95	0.14
j	1	62	20	Bpy	NMP	3	70	91	0.45
k	1	62	20	Bpy	NMP	3	90	96	0.55
l	1	62	20	Bpy	NMP	3	115	98	0.34

† Solvent used as received.

Table 5.2: *Experimental Results For the Polymerisation of 1,7-bis-(3-chlorophenyl)-meta-carborane*†(**CP16**).



Polymer	X	Promoter	Solvent	Time (hours)	% Yield	T_g (°C)	η_{inh} (dL/g)
a	Cl	Bpy	NMP	3	90	130	0.13
b	Cl	NaBr	NMP	3	95	135	0.22
c	Br	NaBr	NMP	3	94	137	0.24
d	Br	NaBr	NMP	24	97	142	0.38
e	Cl	Bpy	DMAc	3	97	169	0.42
f	Br	NaBr	DMAc	3	95	137	0.23
g	Br	NaBr	DMAc	24	94	120	0.05
h	Br	NaI	DMAc	3	98	128	0.19
i	Br	NaI	DMAc	24	89	129	0.19

† All reactions carried out at 80°C.

5.4. Experimental:

5.4.1. Purification of starting materials:

Triphenylphosphine was purified by recrystallisation from hexane, and then dried under vacuum at 50 °C for 5 hours and stored under an inert atmosphere. NMP and DMAc were dried over calcium hydide for two days and then freshly distilled, under nitrogen, before each polymerisation attempt. Zinc (99.99% grade) was activated by washing with molar hydrochloric acid, ethanol and ether before being dried at 100 °C, for 5 hours, and stored under an inert atmosphere. Bis(triphenylphosphine)nickel(II) chloride (ALDRICH) was stored under an inert atmosphere, and used as received.

5.4.2. The Preparation of 4',4''-bis-(3-chlorobenzoyl)-1,4- diphenoxy-benzene. (63)

4-diphenoxybenzene (2.62 g, 10 mmol) and 3-chlorobenzoic acid (3.34 g, 22 mmol) were placed in a 100 cm^3 conical flask purged with nitrogen. Trifluoromethanesulphonic acid (40 cm^3) was added and the reaction mixture was purged with nitrogen and stoppered. The resulting red/orange solution was stirred at room temperature for 3 hours then poured with stirring into distilled water (250 cm^3) causing a pink solid to precipitate from solution. The suspension was stirred at room temperature for an hour and the solid was isolated by filtration and refluxed in abs. ethanol for an hour. The resulting white solid was isolated again by filtration, dried and recrystallised from toluene to afford white needle-like crystals (mp. 197-199 °C), yield 85%.

Elemental analysis: Found; C, 71.45, H, 3.63% M_r (mass spectrum) 538-545 $C_{32}H_{20}O_4Cl_2$ requires C, 71.19, H, 3.70% M_r .

IR (KBr disc) ν_{max} cm^{-1}:3063 w, 1654 vs (C=O), 1599 s, 1567 s, 1502 s, 1463 sh., 1419 m, 1308 m, 1286 s, 1252 s (C-O-C), 1192 m, 1166 m, 756 s, 701 m, 508 m.

NMR: δ ^{13}C 117.6, 122.3, 128.8, 129.4, 129.6, 131.3, 132.4, 133.0, 139.2, 140.6, 152.5, 163.0 (ArC), 194.8 (C=O).
δ ^{1}H 7.1-8.01 (m, ArH).

5.4.3. General Polymerisation of 4',4''-bis-(3-chlorobenzoyl)-1,4-diphenoxybenzene (OP3):

Bis(triphenylphosphine)nickel(II) chloride (81.8 mg, 0.125 mmol), zinc (506 mg, 7.75 mmol), triphenylphosphine (590 mg, 2.25 mmol), and bpy (19.5 mg, 0.125 mmol) were weighed into a 50 cm^3 round bottom flask in an inert atmosphere glove-box. The reaction vessel was removed from the box and evacuated and purged with nitrogen three times. Freshly distilled solvent (3 cm^3) was added and the catalyst solution was heated at the reaction temperature for 30 minutes, usually forming the characterisatic red-orange catalyst colour The reaction mixture was allowed to cool to room temperature and 4',4'-bis-(3-chlorobenzoyl)-1,4-diphenoxybenzene (1.35 g, 2.5 mmol) was added. The resulting mixture was heated under nitrogen and left for several hours. The resulting solution was diluted with the solvent used to prepare the catalyst and the polymer was precipitated from solution by pouring into methanol/c. HCl (3:1) (150 cm^3) and left stirring at room temperature overnight. The solid was isolated by filtration, washed with methanol and dried in a vacuum oven at 70 °C for several hours, before being characterised. The reaction conditions and results for all of the reactions are shown in Table 5.1.

NMR: $\delta^{13}C$ 194.8, 163.0, 152.5, 140.6, 139.0, 133.0, 132.4, 131.3, 129.6, 129.4, 128.8, 122.3, 117.5
$\delta^{1}H$ 7.57, 7.1, 7.8, 7.7, 7.89, 7.84, 8.01

IR $\nu_{max}cm^{-1}$ 3057 w, 1654 s, 1595 s, 1491 s, 1412 m, 1307 m, 1276 m, 1228 s, 1187 s, 1163 s, 1009 m, 971 w, 935 m, 864 m, 844 m, 808 sh., 754 m, 704 m, 616 w, 503 w.

5.3.4. The Preparation of CP16

The polymer was prepared according to the general procedure described above (Section 5.3.3.), by dissolving bis(triphenylphosphine)nickel(II) chloride (81.8 mg, 0.125 mmol), zinc (506 mg, 7.75 mmol), triphenylphosphine (590 mg, 2.25 mmol), and bpy (19.5 mg, 0.125 mmol) in freshly distilled solvent (3 cm^3). After stirring the catalyst solution for 30 minutes at 80 °C the reaction mixture was allowed to cool to room temperature and 1,7-bis-(3-chlorophenyl)-*meta*-carborane (0.912 g, 2.5 mmol) was added. The reaction mixture was stirred at 80 °C for 3 hours forming a viscous, red-orange solution. This was worked up as described to afford 0.70 g, 2.38 mmol, (> 90%) of product identified as **CP16**. The results are shown in Table 5.2. The product was characterised as follows and as described in section 5.2.2.1.

IR $\nu_{max}cm^{-1}$: 3038 w, 2599 s (BH), 1689 m, 1597 m, 1575 sh., 1474 m, 1396 m, 1262 w, 1089 m, 1000 w, 913 w, 809 m, 779 m, 740 m, 695 s, 670 m, 607 m, 540 w, 463 w.

5.3.5. The Preparation of CP17

The polymer was prepared according to the general procedure described above (Section 5.3.3.), by dissolving bis(triphenylphosphine)nickel(II) chloride (40.9 mg, 0.063 mmol), zinc (253 mg, 3.88 mmol), triphenylphosphine (295 mg, 1.125 mmol), and bpy (9.75 mg, 0.063 mmol) in freshly distilled 2-methyl-pyrrolidinone (NMP) (1.5 cm^3). After stirring the catalyst solution for 30 minutes at 80 °C the reaction mixture was allowed to cool to room temperature and 1,7-bis-(4-bromophenyl)-*meta*-carborane (567 g, 1.25 mmol) was added. The reaction mixture was stirred at 80 °C for 3 hours forming a viscous, red-orange solution. This was worked up as described for **CP16** to afford 335 g, 1.15 mmol, (92%) of product identified as **CP17**. The product was characterised was found to be insoluble and was characterised as described in Section 5.2.2.2. and as shown below:

IR $\nu_{max}cm^{-1}$: 3037 w, 2600 s (BH), 1495 s, 1396 m, 1192 w, 1083 m, 1003 m, 877 w, 853 m, 831 s, 740 m, 691 m, 508m.

5.3.6. The Preparation of CP18

The polymer was prepared according to the general procedure described above by dissolving bis(triphenylphosphine)nickel(II) chloride (81.8 mg, 0.125 mmol), zinc (506 mg, 7.75 mmol), triphenylphosphine (590 mg, 2.25 mmol), and bpy (19.5 mg, 0.125 mmol) in freshly distilled 2-methyl-pyrrolidinone (NMP) (3 cm^3). After stirring the catalyst solution for 30 minutes at 80 °C the reaction mixture was allowed to cool to room temperature and 1,12-bis-(4-chlorophenyl)*para*-carborane (0.91 g, 2.5 mmol) was added. The reaction mixture was stirred at 80 °C for 3 hours forming a viscous, red-orange solution. This was worked up as described to afford 0.78 g, mmol, (92%) of product identified as **CP18**. The isolated product was insoluble in common organic solvent precluding full characterisation but the product was characterised as described in Section 5.2.2.3. and as shown below.

IR $\nu_{max}cm^{-1}$: 3038 w, 2610 s (BH), 1689 w, 1494 s, 1396 m, 1252 w, 1189 w, 1082 s, 1004 m, 912 m, 824 s, 749 m, 690 m, 643 w, 600 m, 550 w, 499 m, 437 sh.

5.3.7. The coupling of 1,7-bis-(3-chlorophenyl)-*meta*-carborane (64)

Bis(triphenylphosphine)nickel(II) chloride (81.8 mg, 0.125 mmol), zinc (506 mg, 7.75 mmol), triphenylphosphine (590 mg, 2.25 mmol), and bpy (19.5 mg, 0.125 mmol) were weighed into a 50 cm^3 round bottom flask in an inert atmosphere glove-box. The reaction vessel was removed from the box and evacuated and purged with nitrogen three times. Freshly DMAc (30 cm^3) was added and the catalyst solution was heated at 80 °C for 30 minutes, forming the characterisatic red-orange catalyst colour. 1,7-bis-(3-chlorophenyl)-*meta*-carborane (0.912 g, 2.5 mmol) dissolved in dry DMAc (20 cm^3) was added dropwise over a period of three hours. After the addition of all of the monomer, the reaction mixture was stirred for a further two hours and then allowed to cool to room temperature. The product was precipitated from solution by pouring into methanol/c. HCl (3:1) (150ml) and left stirring at room temperature overnight. The solid was isolated by filtration and purified by column chromatography (cylcohexane:5% ethylacetate). The product was identified as (**64**) and characterised as follows:

Analysis: Found; M_r (mass spectrum) 576-589; $C_{28}B_{20}H_{36}$ requires M_r 572-595.

I.R. $\nu_{max}cm^{-1}$: 2634 m, 2564 s (BH), 1575 m (C-C, 1491 sh. (Ar skel.), 1446 m (Ar ip. deformation), 1261 s, 1094 s, 1075 m, 1022 s, 1001 m, 921 w, 889 w, 869 w, 804 w, 688 m, 755 m, 689 m (cage vibration), 581 m (Ar-H wag), 542 w, 479 w.

5.3.8. The coupling of 1,(4-chlorophenyl)-*para*-carborane (65)

The product was prepared exactly as described above (Section 5.3.8.) by treating 1-(4-chlorophenyl)-*para*-carborane (0.636 g, 2.25 mmol), with the nickel catalyst, except that NMP was used in place of DMAc. The product was isolated by filtration and purified by column chromatography, to afford white crystals identified as **65**. Yield 0.470 g (48%) The product was characterised as follows:

Analysis: Found; M_r (mass spectrum) 401-418; $C_{14}B_{20}H_{30}$ requires M_r 398-419.

I.R. $\nu_{max}cm^{-1}$: 3058 w, 2607 s, 1493 m, 1444 m, 1141 w, 1083 m, 1008 m, 893 w, 739 m, 463 w.

NMR: δ ^{11}B -42.42 and -45.00
δ ^{1}H 1.0-4.0 (br. BH), 3.15 (carboranyl CH), 7.13- 7.21 (m, ArH).

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Chapter 6

CARBORANE-CONTAINING MEMBRANES

6.1. Introduction.

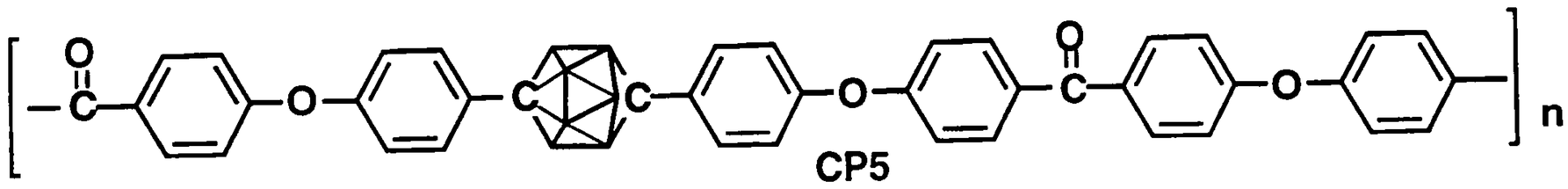
There is considerable scope for the development of new membranes by use of new materials offering increased selectivity, productivity, chemical stability and resistance to mechanical degradation. Work described earlier in this thesis has shown that icosahedral carboranes inhibit close-packing and render the majority of carborane-containing polymers completely amorphous. This phenomenon could give rise to novel membrane properties such as enhanced permeability or selectivity.

This chapter describes work conducted to prepare and characterise new types of membrane derived from polymeric carboranes. The work is reported under three subject headings related to the process used to generate the resulting membrane. Ultra-filtration (UF) membranes were prepared by a phase inversion process (see Chapter 1) while reverse osmosis (RO) and nanofiltration (NF) membranes were prepared by interfacial synthesis and solution coating techniques.

A series of UF-type membranes was cast from some of the carborane-containing poly(etherketone)s prepared in the course of the work described in chapter 4, and are described below.

6.2. Casting of Ultrafiltration Membranes from Polycarboranes by Phase Inversion. (Membrane A).

Three casting solutions were made up by dissolving different weights of **CP5** in NMP, to afford 7%, 10% and 13% w/v solutions of polymer.



CP5

The 7% solution was cast using a 250 μm blade-gap onto a sheet of "Awa 10" non-woven polyester cloth (100 μ thick) taped to a glass plate, and the membrane was precipitated by sliding the plate into a bath of deionised water. The resulting membrane was thoroughly washed with water, then soaked in glycerol for an hour and allowed to dry at room temperature overnight. This procedure was repeated for each of the polymer solutions in turn.

Membrane Characterisation:

The membranes were characterised in terms of their permeability to water and their selectivity. Permeability is the quantity of gas or liquid that permeates through a given area of membrane in a given time under a known driving force. Selectivity is quoted in terms of molecular weight cut-off (MWCO) which is the lowest molecular weight of a polymer for which 90% rejection is observed.

6.2.1. Results and Discussion:

Each test was performed in duplicate to determine the flux and approximate molecular weight cut-off of the membranes. The results are shown in Table 6.1.

The molecular weight cut-off data were obtained by passing a solution containing 0.1% each of three polyethylene glycol fractions (1K, 10K and 100K) through the membranes and measuring, by GPC, how much of each fraction appeared in the permeate. A typical GPC trace is shown in Figure 6.1. Essentially all of the 100K fraction and most of the 10K, was rejected by all three membranes. The 1K fraction, however, showed very low rejection.

The MWCO can be directly obtained by plotting the rejection data against MW for each membrane as shown in Figure 6.2.

Figure 6.1: GPC Trace of Permeate From 7% Membrane Cast from **CP5**.

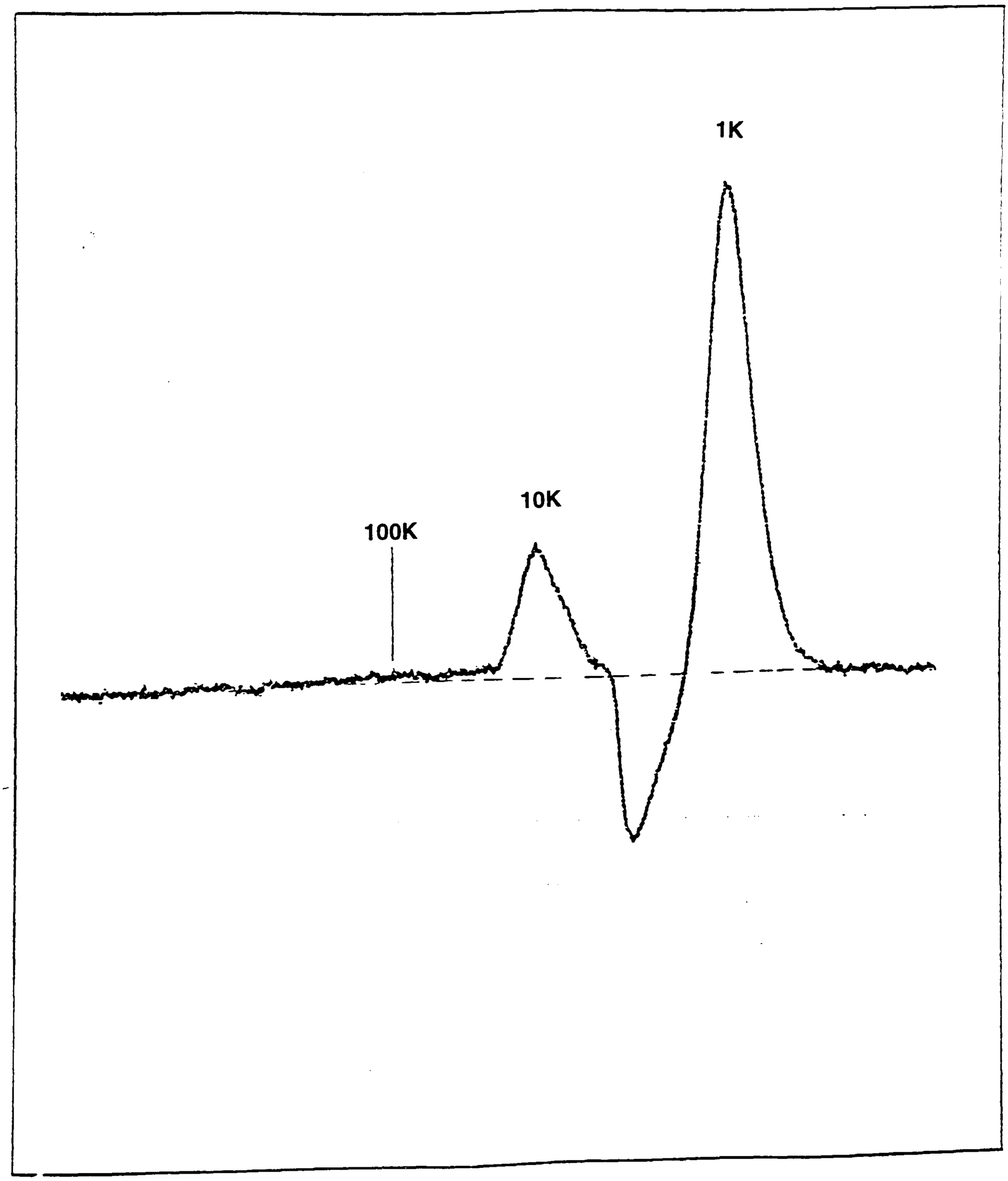


Figure 6.2: Molecular Weight Cut Off Data for PEG Solutions.

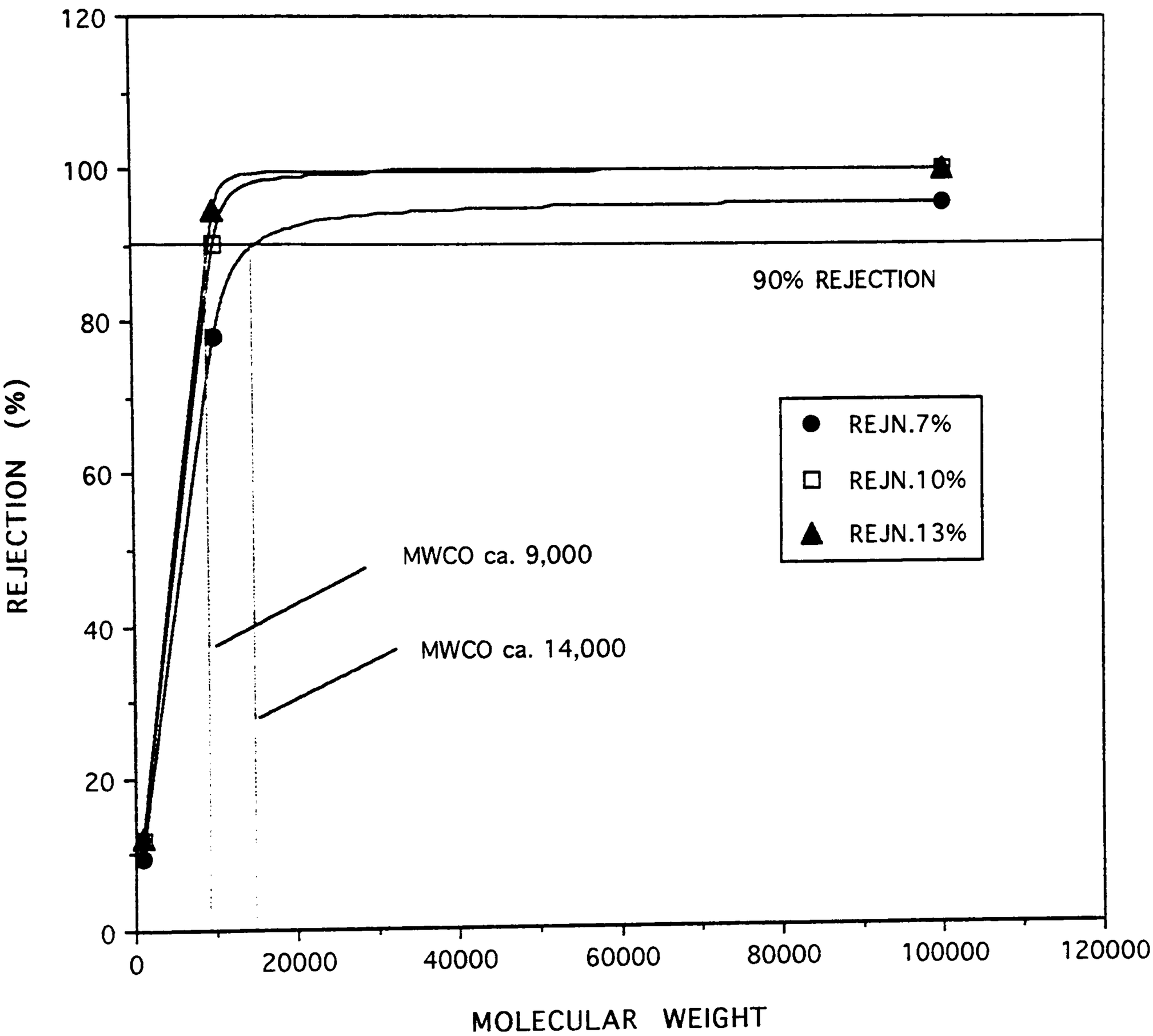


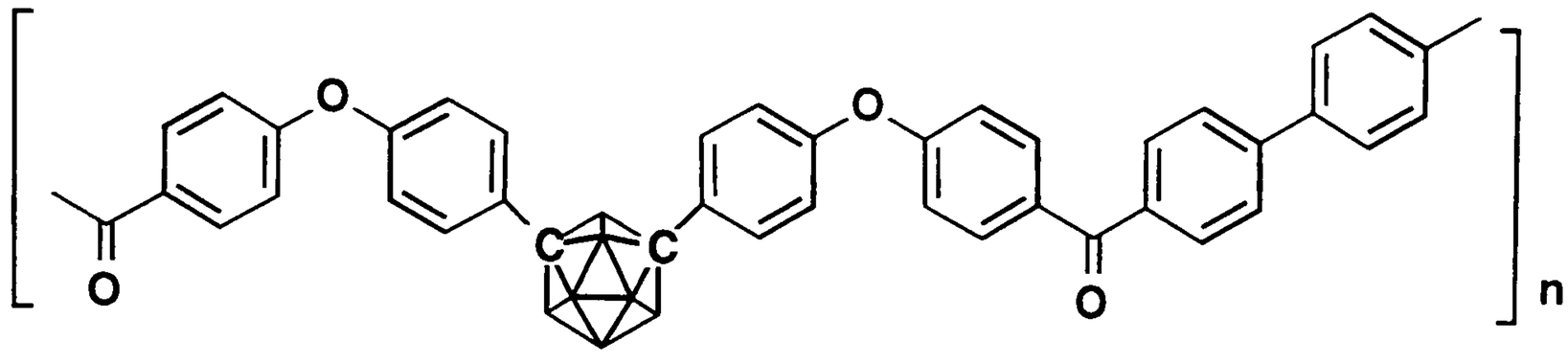
Table 6.1: *Performance Results For* ***Membrane A*** *Cast From Solutions of* ***CP6****.*

Polymer Conc.	Water Flux (l/m²/h, 2 bar)	PEG Solution Flux (l/m²/h,, 2 bar)	Rejection for PEG's 1K (%)	10K (%)	100K (%)	MWCO
CP5 7%	674	75	9.5	78.2	95.7	14,000
CP5 10%	491	61	11.9	90.4	100	10,000
CP5 13%	206	68	12.1	94.7	100	9,000

The MWCO can be seen to fall as the polymer concentration increases. This indicates that the average surface pore size becomes smaller as the polymer concentration in the polymer casting solution is increased. This trend is quite normal and a MW of 10,000 typically corresponds to a molecular diameter of no more than about 50 Å, indicating that the maximum pore size of the 10% and 13% membranes must be close to this value.

The pure water flux also follows the same trend, falling dramatically as the concentration of polymer in the casting solution is increased. The permeate fluxes obtained for during the ultrafiltration of the PEG solutions are very much lower than those for the pure water, but this is a commonly observed phenomenon, and occurs due to a build up on the membrane surface of the material which is being filtered, despite the ultrafiltration being performed under cross-flow conditions.

6.2.2. Casting of Phase Inversion Membranes from CP4 onto a Metal Mesh Support, ("Inconel"). (Membrane B).



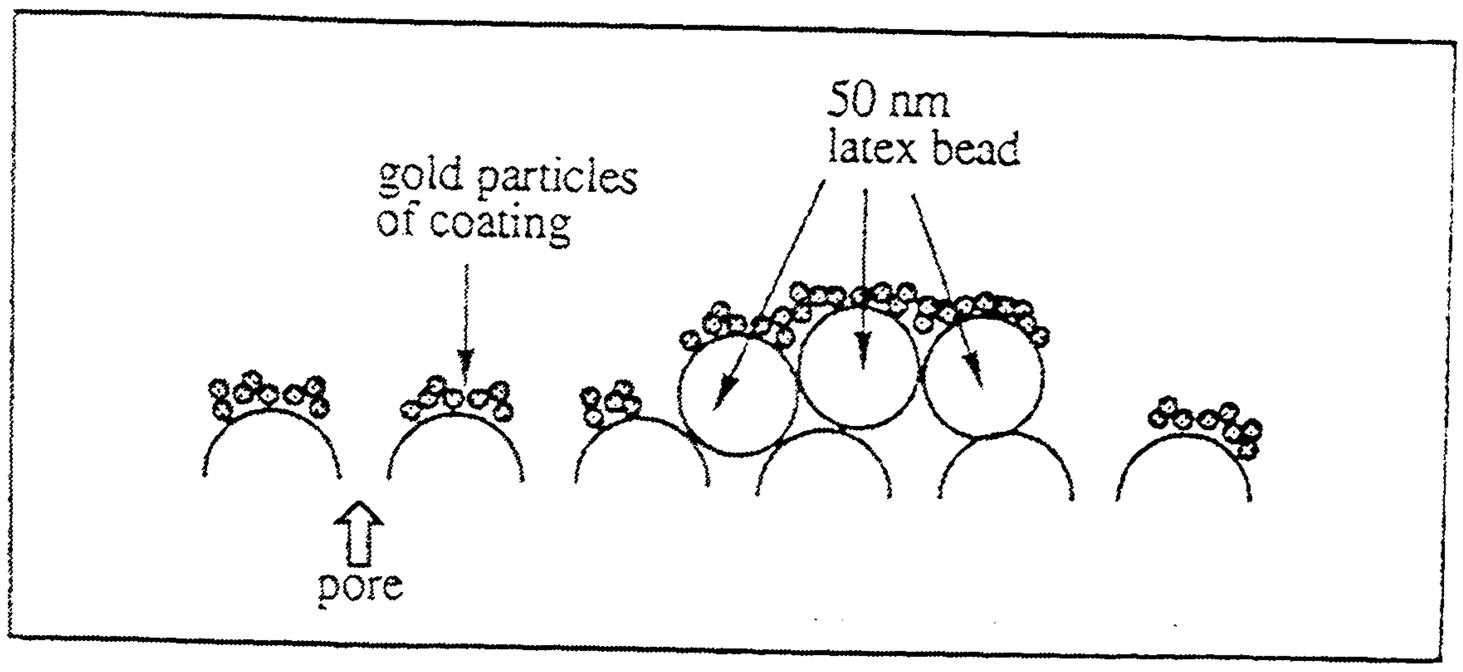
CP4

A 10% solution of polymer **CP4** in NMP was cast onto a sheet of "Inconel" mesh (as supplied by Ceramesh Ltd.) as described in Section 6.2 Dead-end filtration experiments with a latex of polystyrene particles, of known particle size, indicated that the membrane had a flux of > 1300 l/m^2/h (at 2 bar), much higher than that found for the membranes cast from **CP5**, and an estimated pore size of < 50 nm.

6.2.3. Electron Microscopy:

Examination of the surface of **Membrane B** using high-resolution scanning electron microscopy (SEM) showed a nodular morphology with an average nodule size of approximately 100 nm. Figure 6.3a shows the UF membrane from **CP4** after absorbing a very dilute latex of polystyrene particles onto the surface. The particles can be clearly seen and appear to be held entirely on the surface of the membrane confirming that the surface pore size is appreciably less than 50 nm.

Unfortunately the gold coating of the membrane surface as required for SEM can disguise the real surface structure of the material. The cluster of latex particles in the lower right hand corner of the photograph appear to be sitting on a cluster-sized pore. However, the gold coating has formed *around* the cluster of latex particles, leaving a slight gap, and the pore-structure that can be seen is actually a modified surface rather than the real one.



The membrane was coated with chromium rather than gold to check the interpretation of the membrane as chromium gives a much finer-texture coating, (Figure 6.3b). Although the contrast is poorer with chromium than with gold, the membrane surface can be seen to indeed by nodular, with the pores being formed at nodule junctions.

Figure 6.3: *Scanning Electron Micrograph of* ***Membrane B*** *Cast from a 10% solution of* ***CP4***

a) The gold coated surface with the 50 nm latex particles (x 100K) taken perpendicular to the surface.

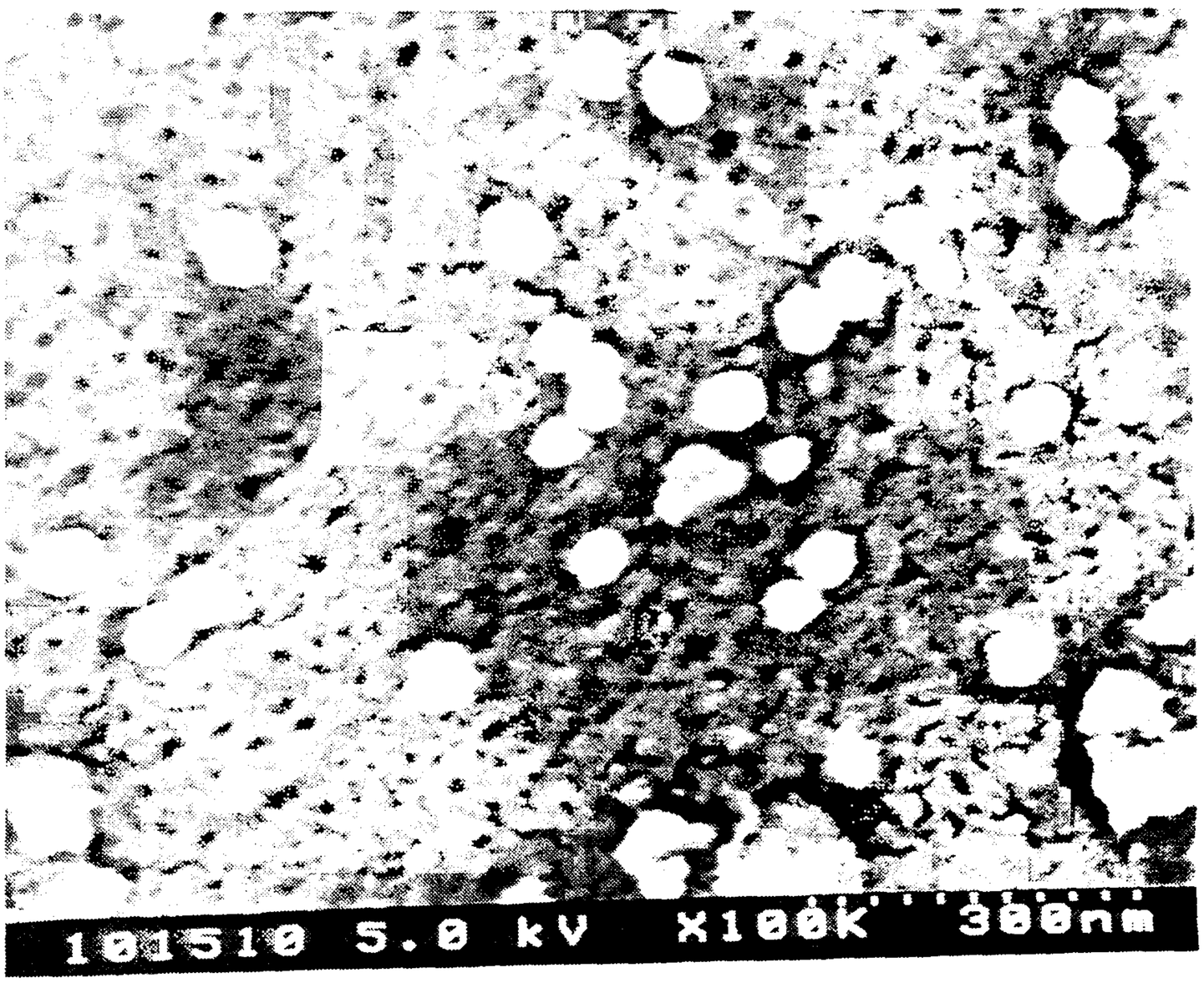
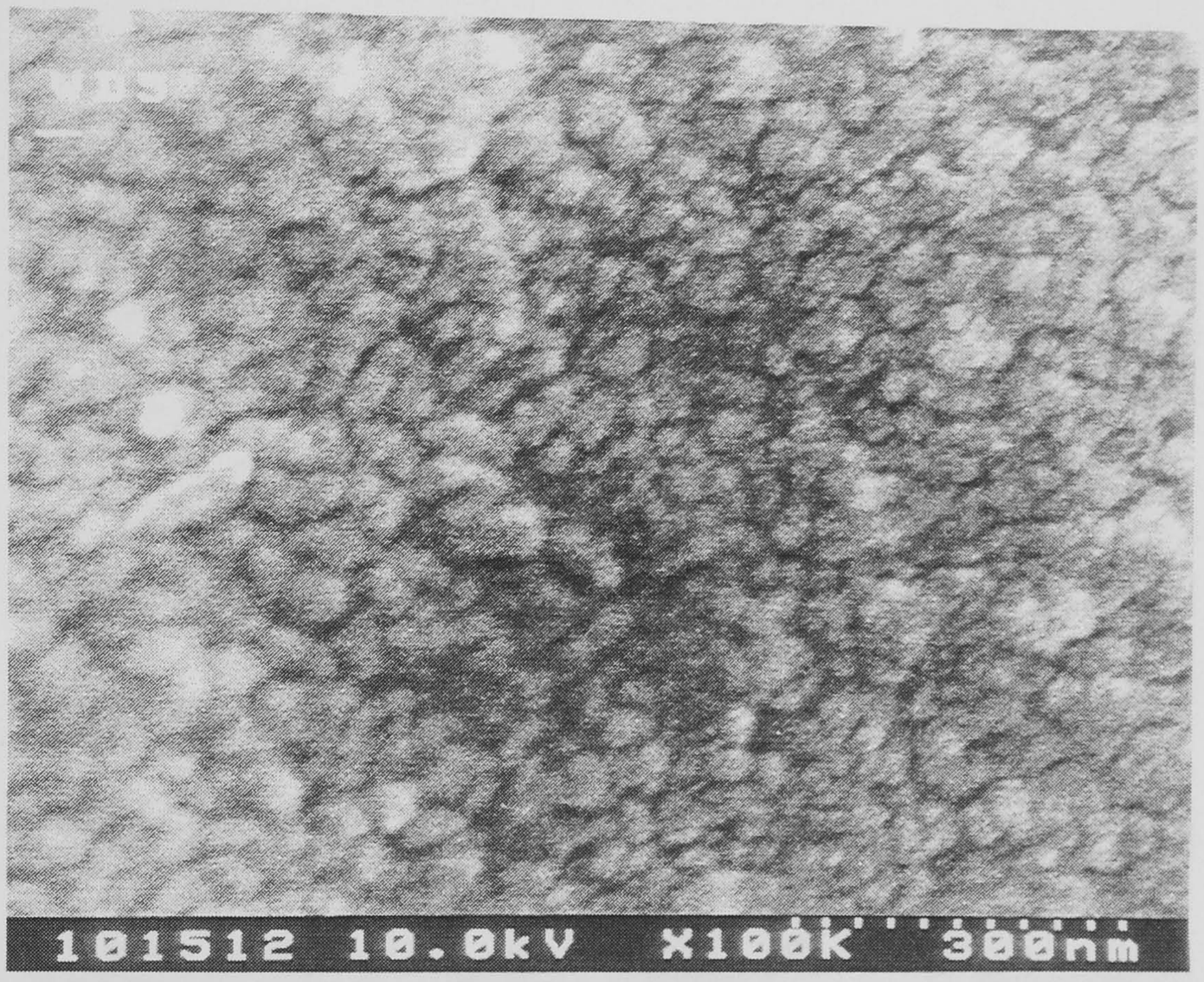


Figure 6.3: *Continued*

b) The chromium coated surface (x 100K)



c) The chromium coated surface (x 60K)

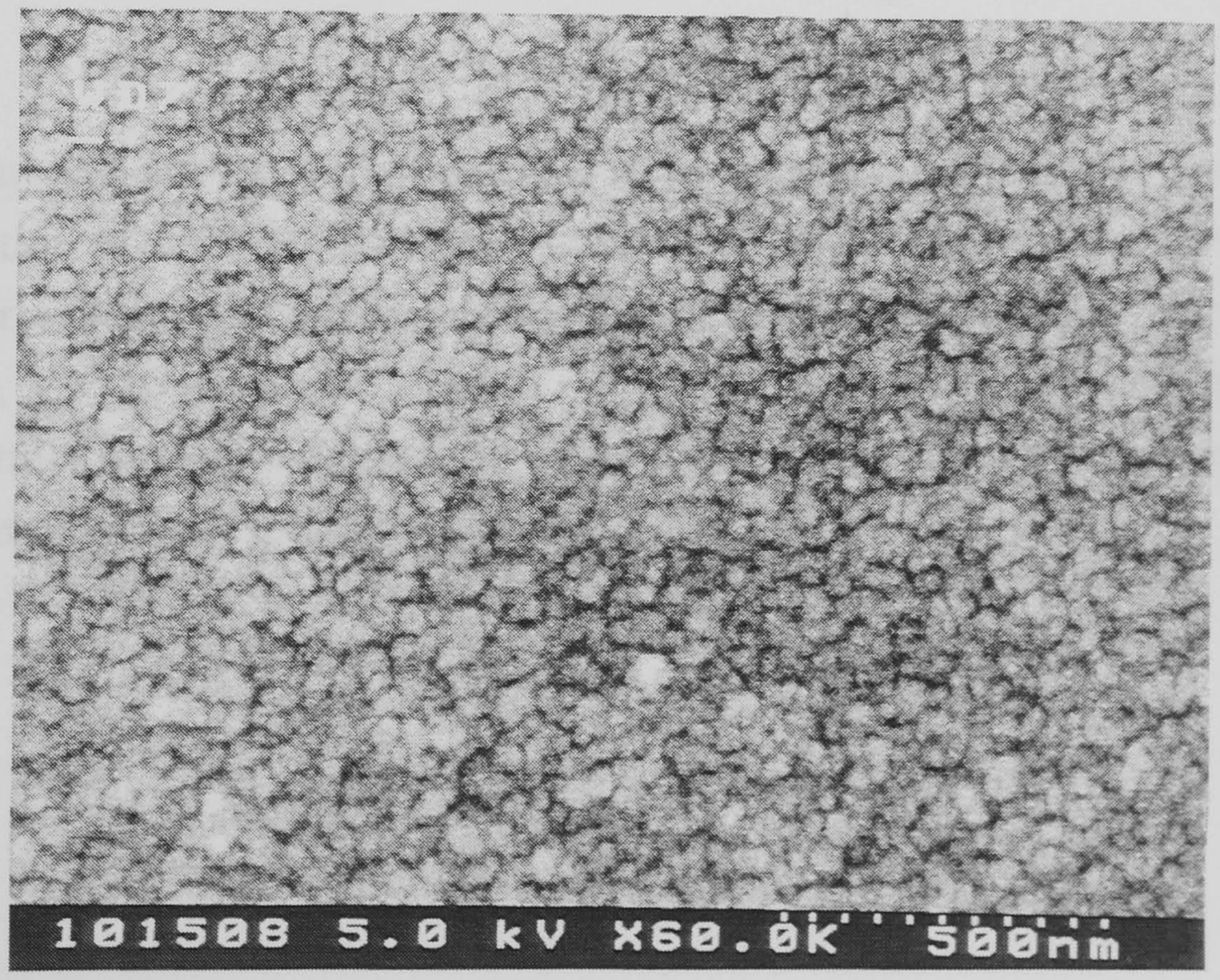


Figure 6.3: *Continued*

d) The chromium coated surface taken at an angle of 45° (x 60K)

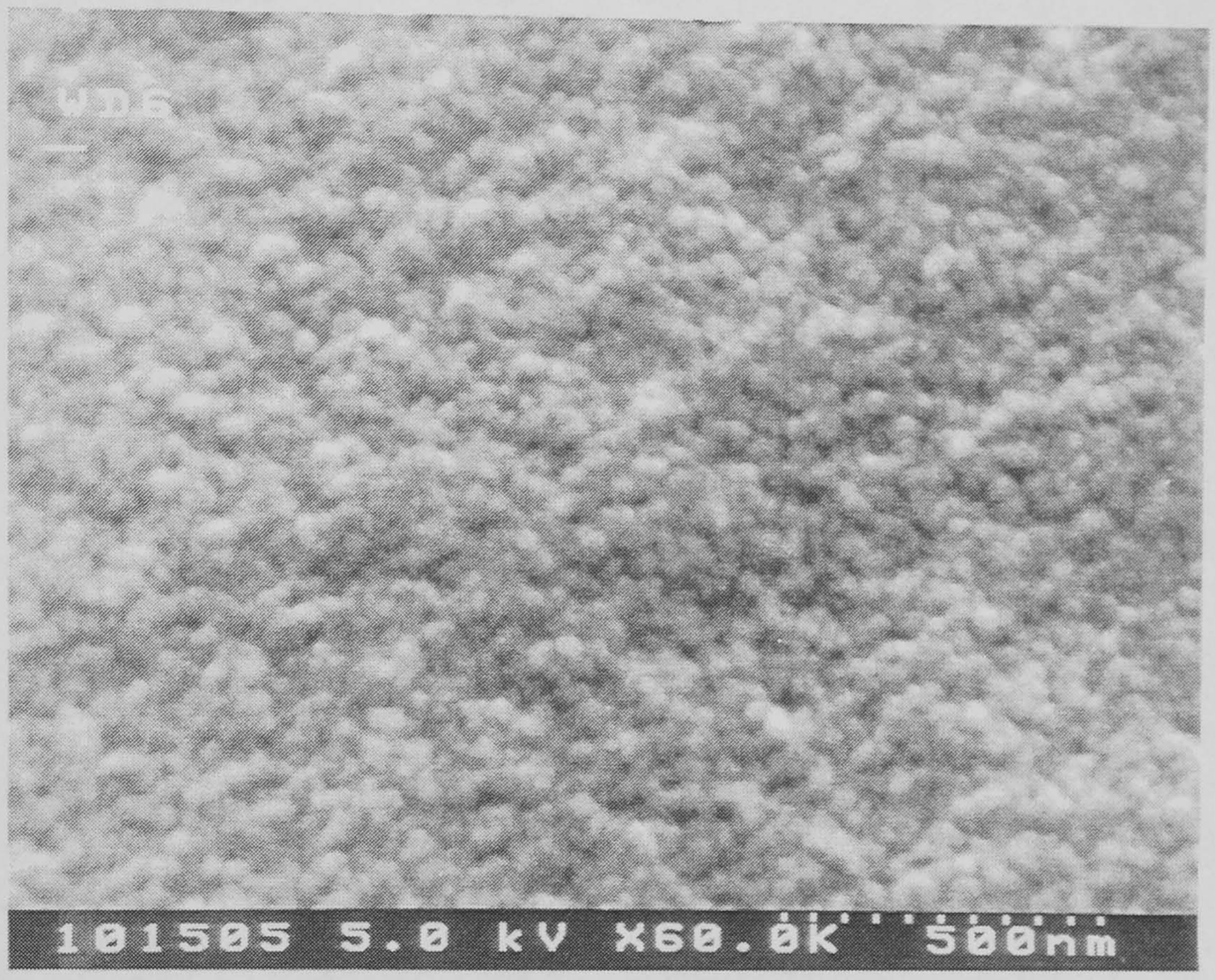
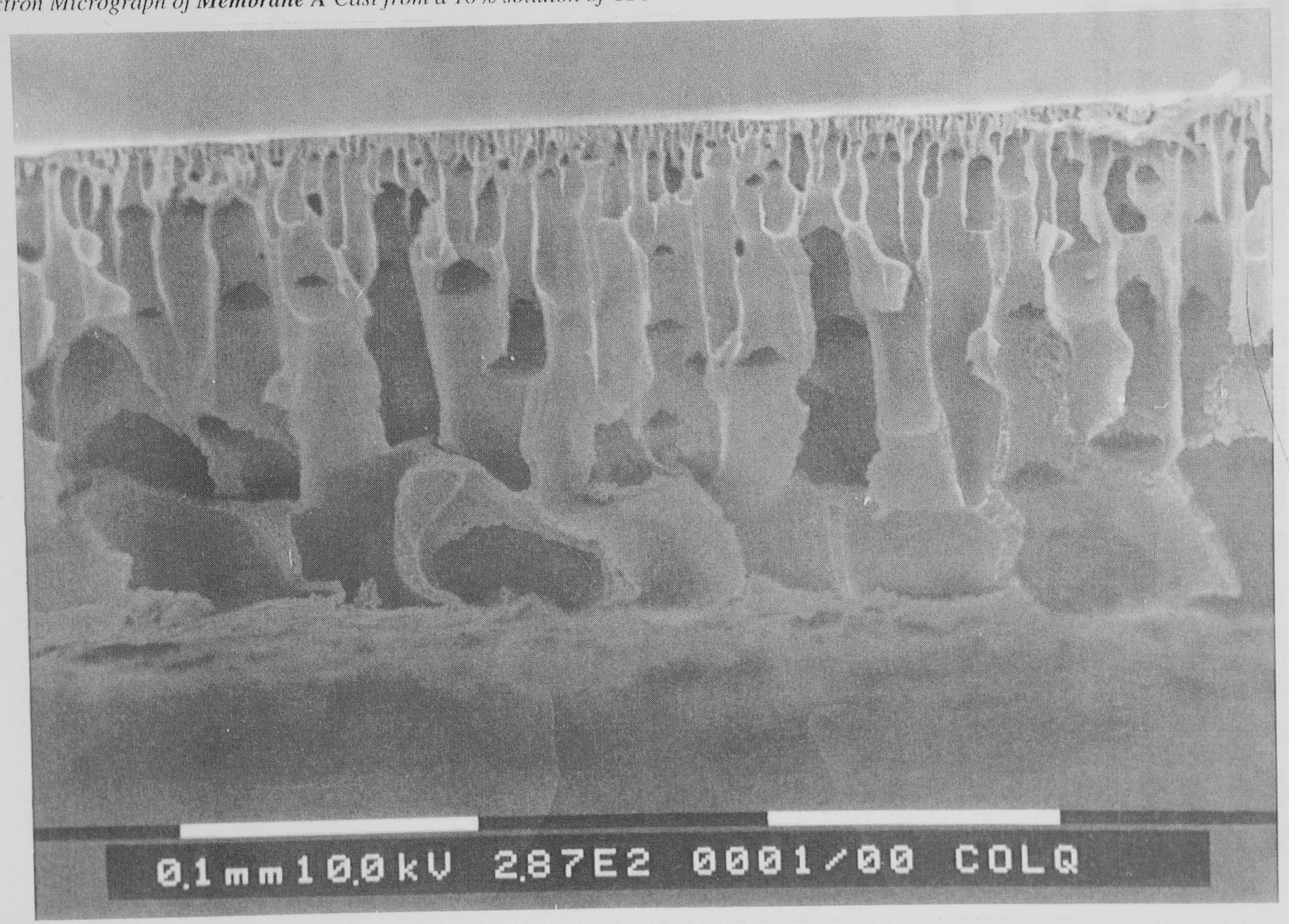


Figure 6.4 shows a cross-section of the membrane obtained from the 10% solution of **CP5** as observed by scanning electron microscopy. A strongly macrovoided structure, beneath a finely porous surface can be clearly seen. This type of asymmetric structure is typical of ultrafiltration membranes, and provides a thin selective surface supported on a more open and highly permeable substructure.

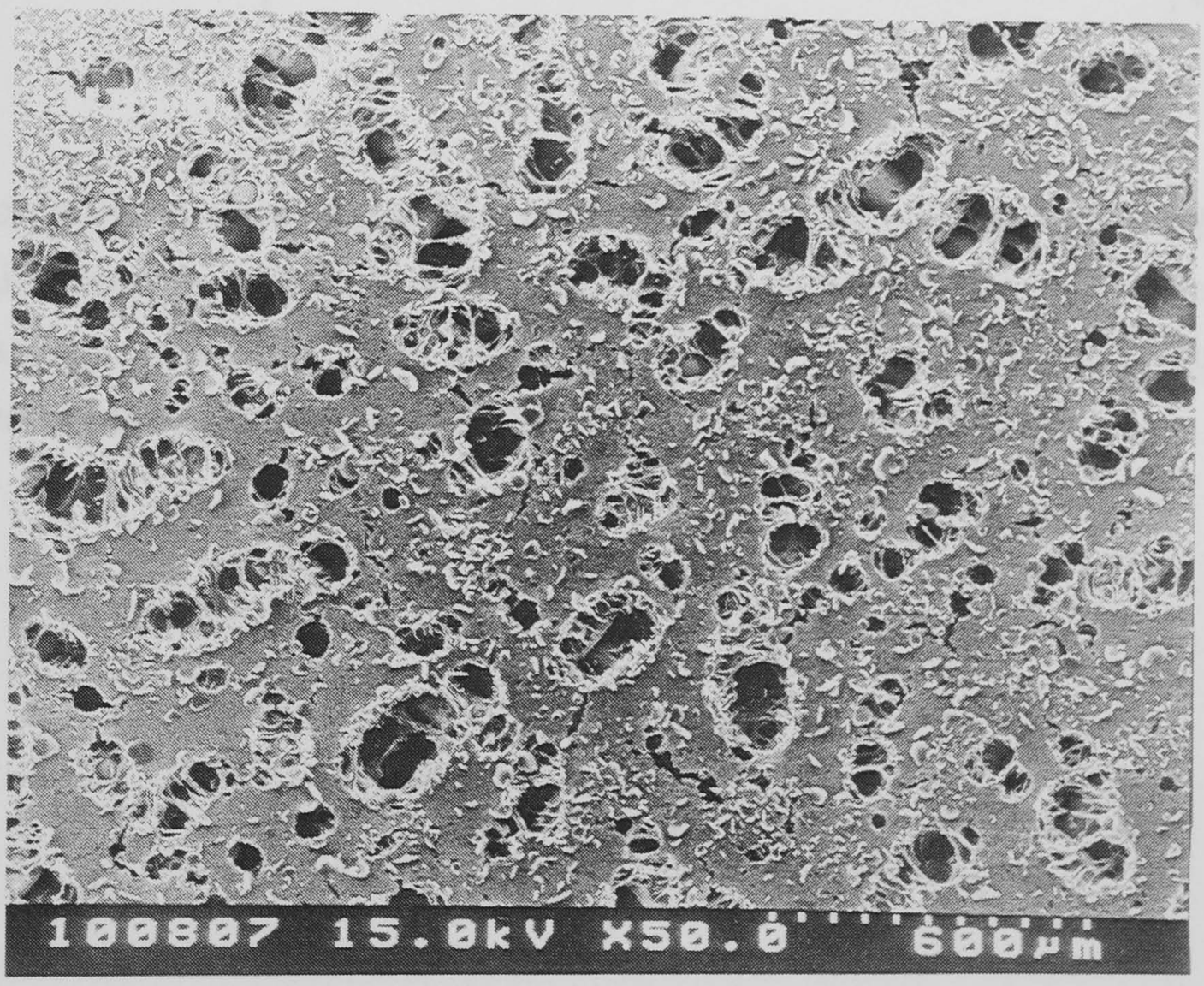
Figure 6.4: *Scanning Electron Micrograph of* ***Membrane A*** *Cast from a 10% solution of* ***CP5***



6.2.4. Pyrolytic Conversion of Carborane Polyketone Membranes

Membrane B was heated to 600 °C (at 20 °C/min), under nitrogen, to investigate the effect of high temperatures on the membrane structure. Although areas of microporosity appeared to be retained after heating the sample, large voids were formed in the surface. The membrane also appeared to have shrunk away from the edge of the support, and the voids themselves appear to have been caused by a shrinkage effect. (Figure 6.5)

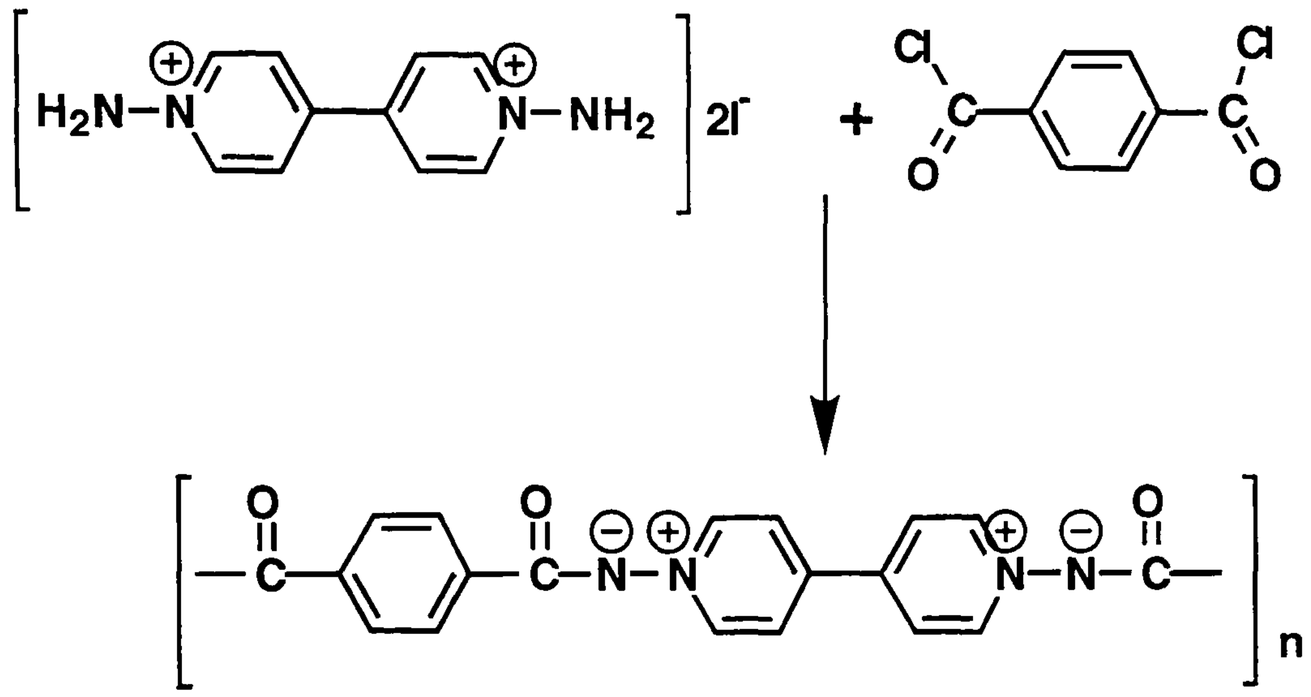
Figure 6.5: *Scanning Electron Micrograph of* ***Membrane B*** *after heating to 600 °C.*



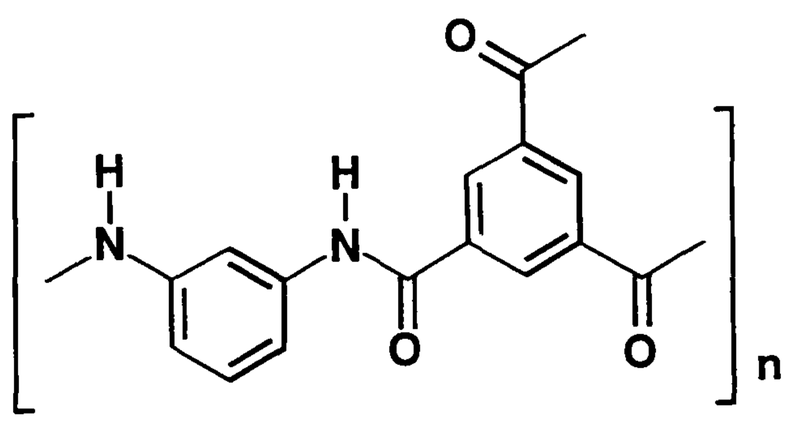
It may be possible that the mesh support is actually *causing* the voids by preventing the membrane from shrinking uniformly as the polymer cross-links. Unfortunately unsupported membranes would probably be difficult to handle after pyrolysis.

6.3. Preparation of Nanofiltration Membranes by Interfacial Polycondensation.

Previous work[1] has shown that condensation of 1,1' diamino 4,4' bipyridinium di-iodide with isophthaloyl chloride yielded a condensation polymer with an ylid-type structural linkage.



Such polymers are of potential interest for RO and NF membrane applications, which seem to require that the membrane polymer chains be relatively rigid, possibly cross-linked and strongly hydrated, as in the aromatic polyamides used in many high-performance RO and NF membranes.[2]

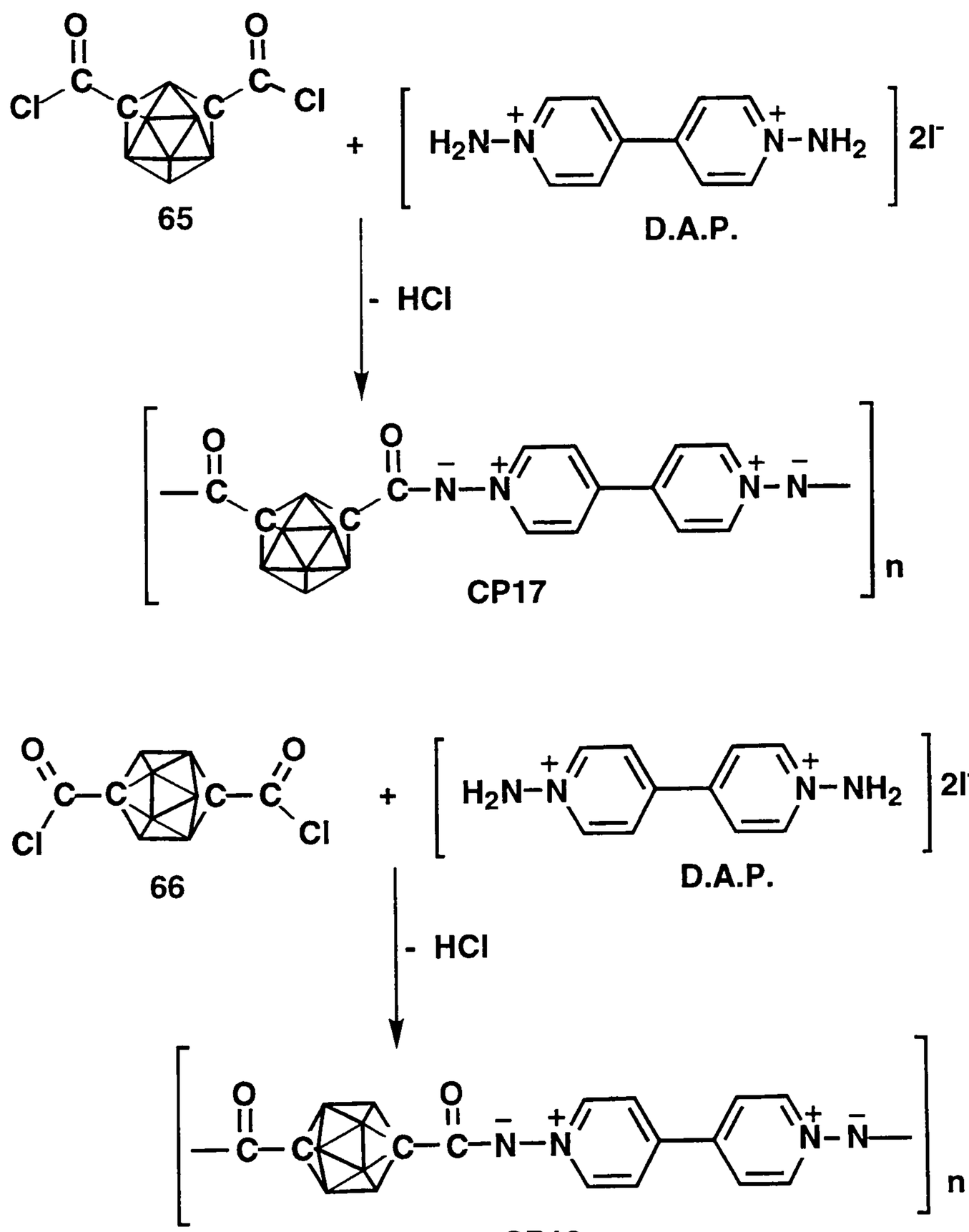


Carborane-containing poly-ylids were prepared by interfacial polycondensation in order to investigate the properties of this new class of materials.

6.3.1. Results and Discussion:

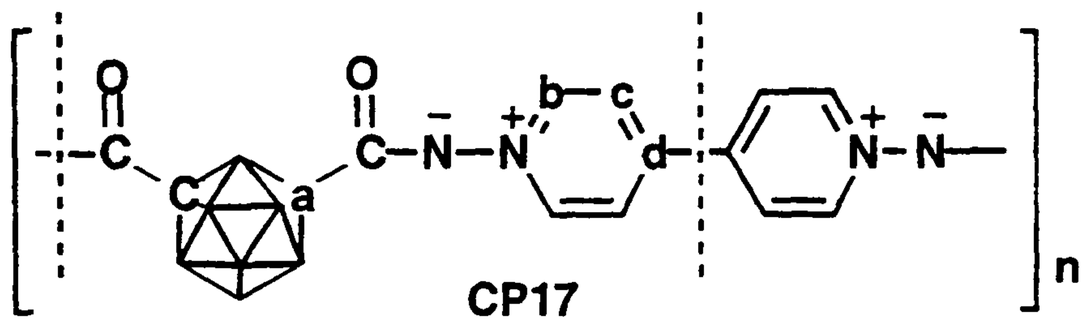
Poly-ylid-Type Membranes

Polymer **CP17** was prepared by stirred interfacial reaction of a basic, aqueous solution of 1,1'-diamino-4,4-bipyridinium di-iodide (D.A.P.) (1% w/v) with 1,7-bis-(chlorocarbonyl)-*meta*-carborane[3] (**65**) (1%) in dichloromethane affording a bright yellow fibrous polymer. Poly-ylid **CP18** was prepared in an analogous manner from 1,12-bis-(chlorocarbonyl)-*para*-carborane[3] (**66**).



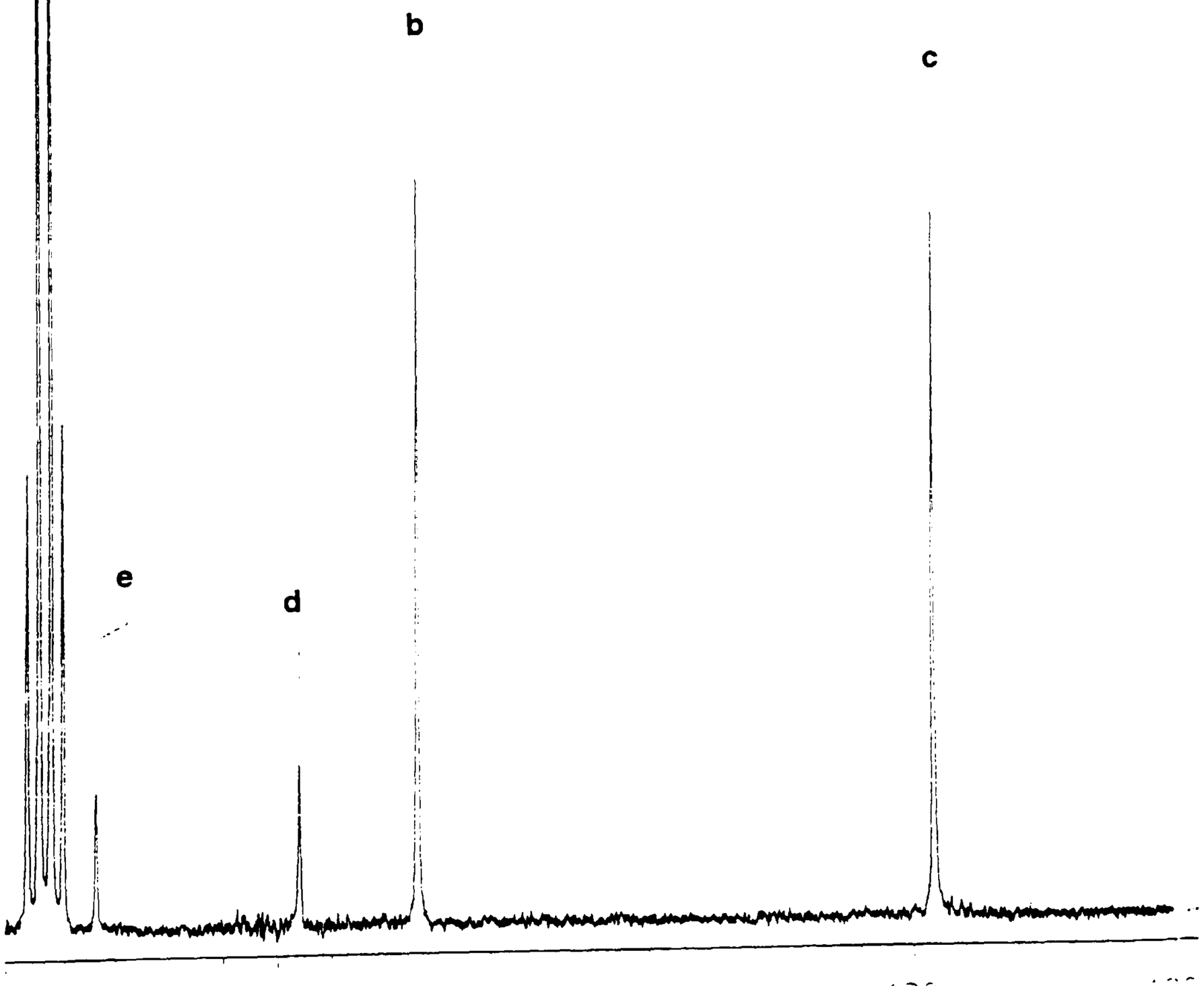
The resulting polymers are soluble in strong proton-donor solvents such as formic and trifluoroacetic acids. Inherent viscosity measurements suggested that high molecular weight materials had been formed.

Figure 6.6: *^{13}C NMR Spectrum of* ***CP17***



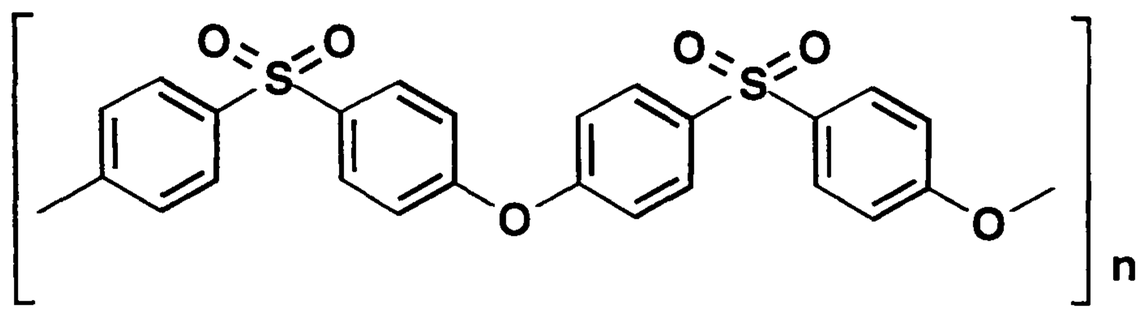
CP17

C atom	δ (^{13}C) ppm
a	71.69
b	148.73
c	129.19
d	153.17
e	160.68



The polymers were also characterised by ^{1}H and ^{13}C NMR (for example Figure 6.6) and IR spectroscopy confirming that the desired products had been formed. DSC suggested that the ylid-linkage was unstable at high temperatures, probably rearranging and leading to polymer degradation.

Supported ('"composite") poly-ylid membranes were fabricated by interfacial polycondensation at the surface of an ultrafiltration membrane. The support used was a commercially available poly(sulphone) ("UDEL") UF membrane which was soaked in a 1% (w/v) solution of D.A.P. in 0.08 M aqueous sodium hydroxide.

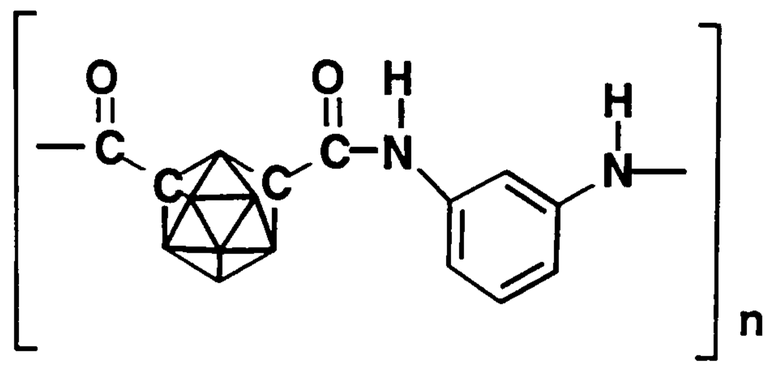


Polysulphone = "UDEL"

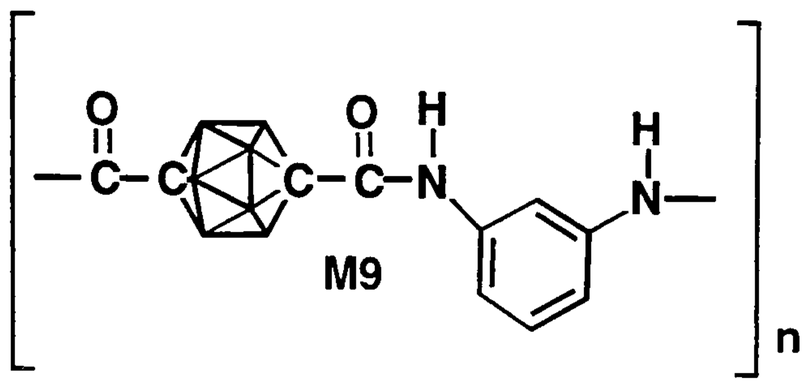
The base-membrane was drained and the surface was contacted with a 0.1% (w/v) solution of 1,7-bis-(chlorocarbonyl)-*meta*-carborane in hexane for a known time. The resulting pale yellow composite membrane (**M4**) was rinsed in deionised water and characterised in terms of its rejection properties for salt and permeability to water. Membranes **M5-M7** were prepared in an analogous manner.

Poly-amide Membranes

For comparison with conventional aromatic polyamide membranes solutions of 1,7-bis-(chlorocarbonyl)-*meta*-carborane and 1,12-bis-(chlorocarbonyl)-*meta*-carborane were contacted for five minutes with UF membrane base that had been previously soaked in a solution of 3,3'-phenylene diamine to afford the polyamide membranes **M8** and **M9** as shown below.



M8



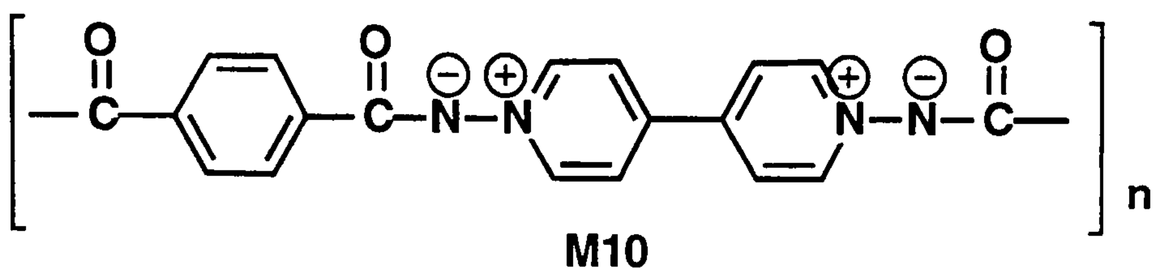
M9

Table 6.2: *Conditions Used For The Preparation of Membranes **M4-M7**.*

Membrane	Monomer	Contact Time (min)
M4	**65**	1
M5	**65**	5
M6	**66**	1
M7	**66**	5

The interfacial NF membranes were characterised in terms of their permeability and their salt rejection - which is the % salt in the feed solution which is <u>not</u> transmitted by the membrane.

The characterisation data indicated that the carborane-membranes behaved in a similar manner to the analogous all-organic membranes formed under the same reaction conditions, for example membrane **M10**. The results are shown in Table 6.3. Tests were carried out in duplicate and average values are given.



M10

6.3.2. Electron Microscopy

Scanning electron microscopy showed the surfaces of the carborane-based poly-ylid membranes to be flat and featureless as observed in polyamide-type membranes.[4] In contrast, the analogous poly-ylid membranes such as **M10** have been shown to possess a unique nodular morphology.

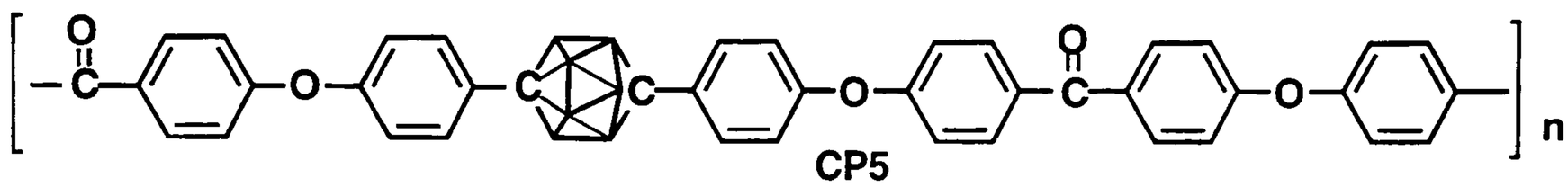
Table 6.3 *Characterisation Data for Poly-ylid Membranes (**M4-M7**) and Poly-amide Membranes (**M8 and M9**) formed By Interfacial Polycondensation.*

Membrane	Rejection for		Water Flux ($l/m^2/h$, 5 bar)
	$MgSO_4$ (%)	NaCl (%)	
Backing membrane	0	0	500
M4	55	12	35
M5	78	52	27
M6	38	12	18
M7	33	27	12
M8	1.5	7	245
M9	11	0.5	268

6.4. Nanofiltration and Reverse Osmosis Membranes from Sulphonated Poly(ethercarborarylketone)s.

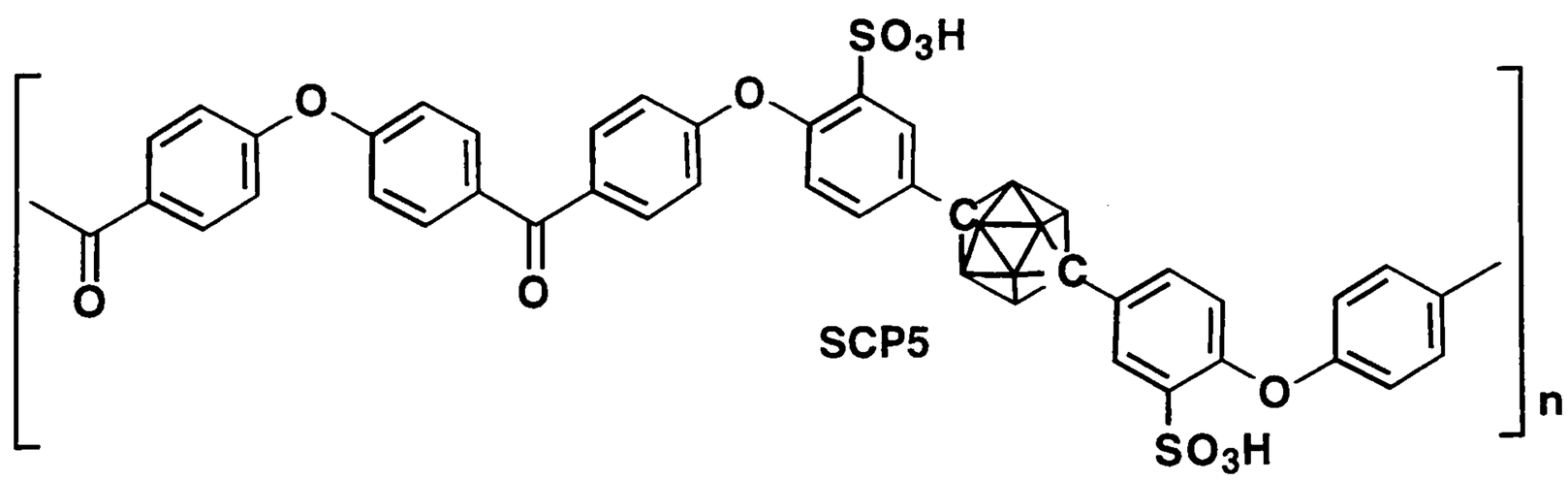
Previous work[5] has shown that sulphonated poly(etherketone)s are suitable for RO membrane applications.

In experiments to establish the stability of the icosahedral carborane cage to concentrated sulphuric acid **CP5** was dissolved in concentrated sulphuric acid for 10 days.



CP5

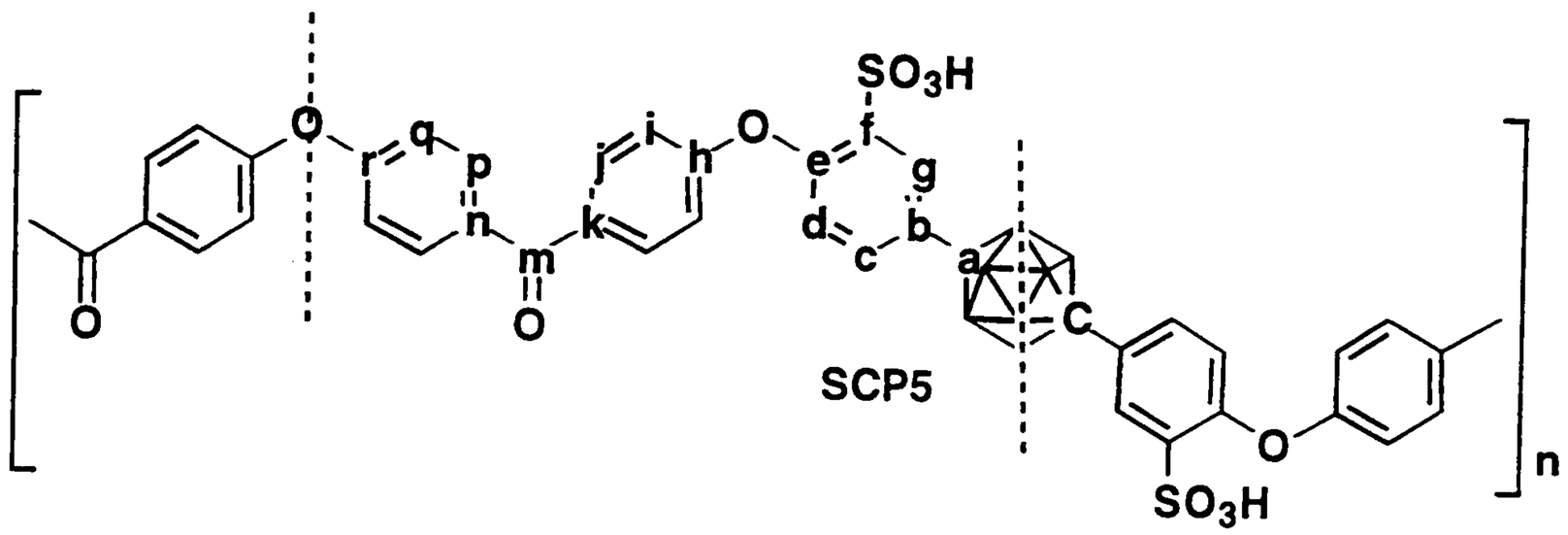
The polymer was isolated in the form of orange-pink beads by precipitation into deionised water. The product was found to be soluble in methanol unlike the parent **CP5**, suggesting that sulphonation of aromatic rings had occurred. ^{13}C NMR experiments showed that the polymer had sulphonated in the position shown below. (Figure 6.7) Solution viscosity measurements gave an inherent viscosity of 4.54 dL/g.

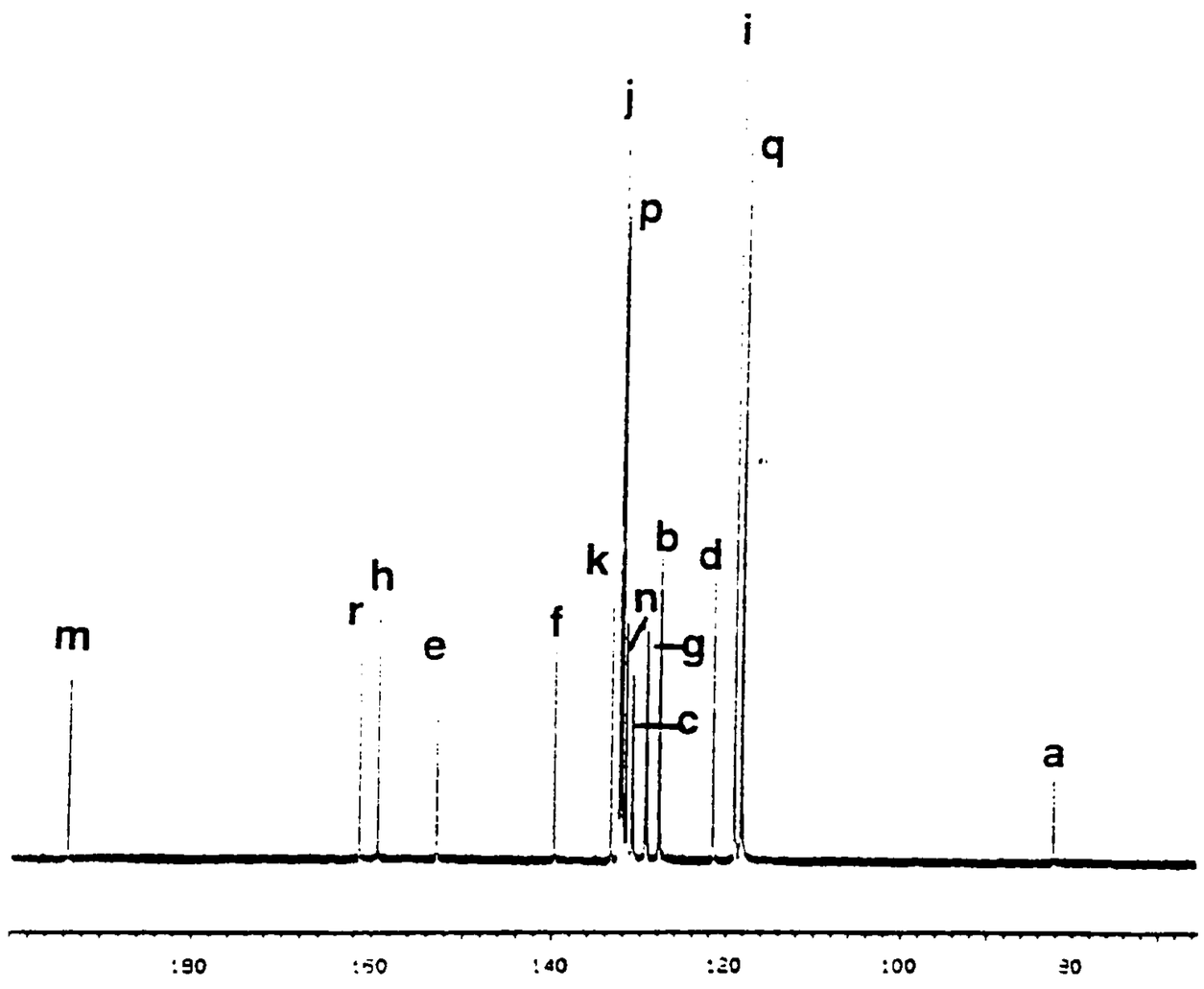


SCP5

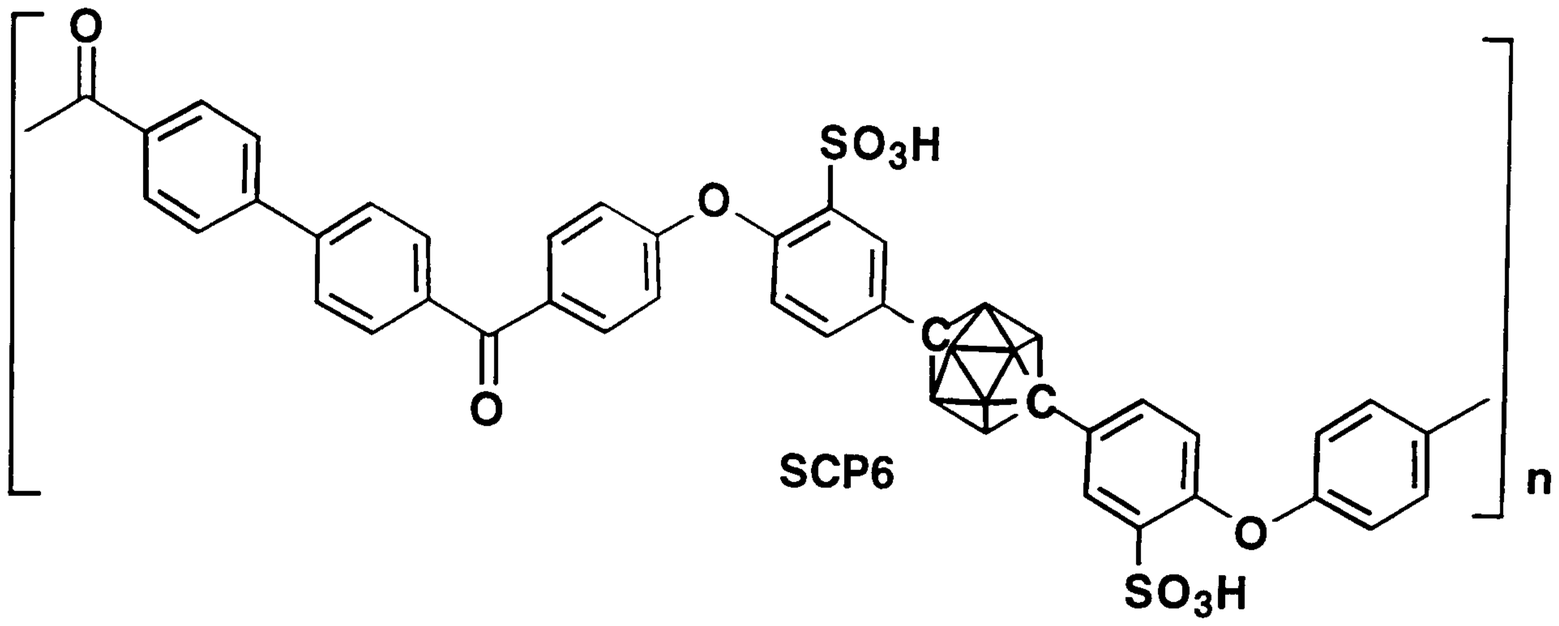
This procedure was repeated with polymer **CP6** which was again found to be soluble in methanol after precipitation into water. ^{13}C NMR again showed that the polymer had been sulphonated in the positions shown overleaf.

Figure 6.7: *^{13}C NMR Spectrum of* ***SCP5***





C atom	δ (^{13}C) ppm
a	82.34
b	118.24
c	119.08
d	121.60
e	127.93
f	129.45
g	130.99
h	131.76
i	132.23
j	133.49
k	139.81
m	152.97
n	152.97
p	159.49
q	161.54
r	193.69



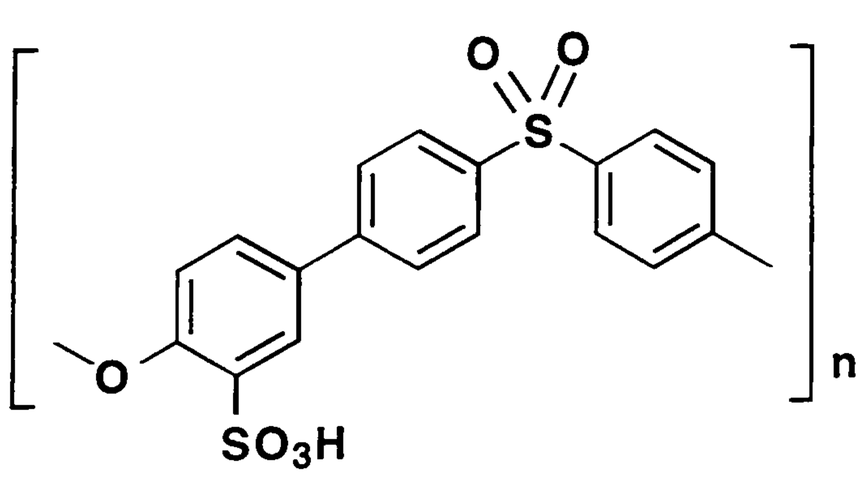
SCP6

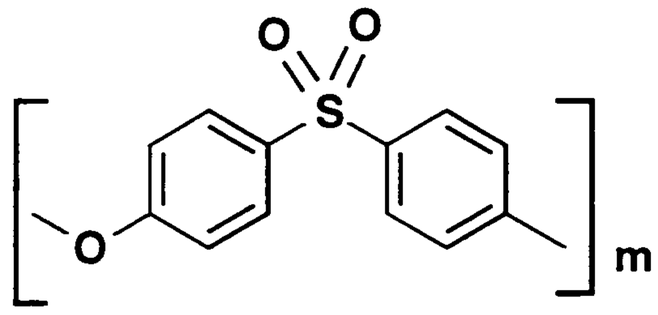
All of the resulting polymers were readily soluble in alcohols such as ethanol and methanol facilitating composite membrane fabrication.

Preparation of NF/RO membranes:

A small scale bead-coating unit, at NWW Acumem Ltd., was used for the fabrication of thin film composite membranes from a 1% solution of **SCP5** in methanol. This allows coating of base membrane and air drying at various temperatures. A schematic representation of the bead-coater is shown in Figure 6.8

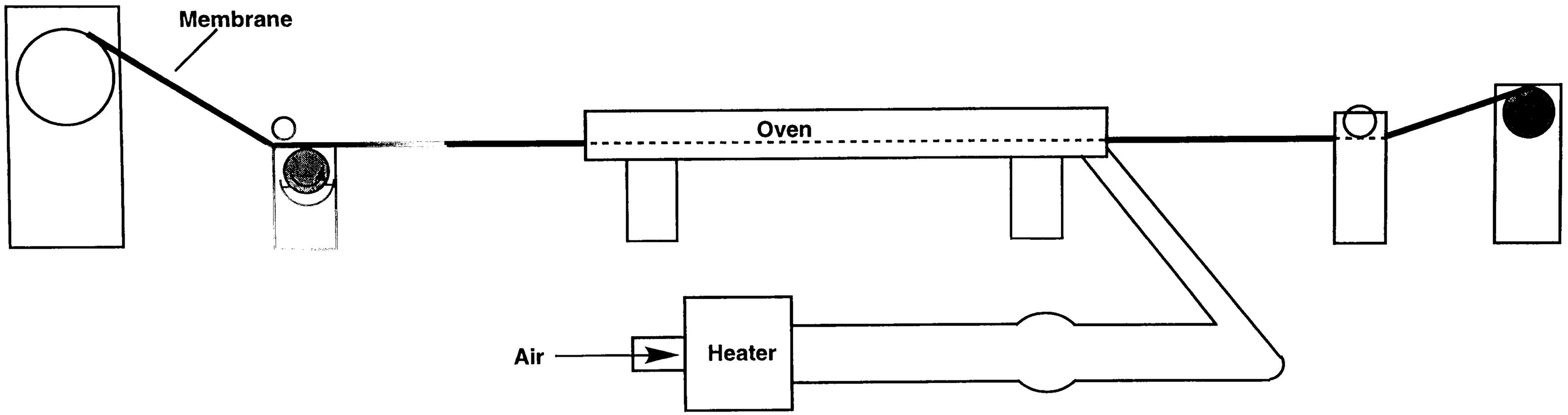
An ultrafiltration membrane is attached to the spools, passed over the coating roller and through the drying oven to the rewind spool. The rotating roller picks up a film of coating solution which forms a bead at the point of contact between the roller and membrane sample. The dry, coated membrane may be unwound from the rewind spool and its membrane properties evaluated. The procedure was repeated with **SCP6** and with the organic copolymer **OP4**, shown below, for comparison.





OP4

Figure 6.8: *Schematic Representation of the Laboratory Bead-Coater*



Characterisation:

The membranes were characterised in terms of their permeability and their water-permeability and salt rejection.

6.4.1. Results and Discussion:

The membranes were soaked in 10% aqueous ethanol for 15 minutes before testing, to ensure that all of the pores were fully wetted. The performance results for the membranes cast from **SCP5** using 500 ppm salt solution at 5 bar pressure and a cross-flow velocity over the membrane surface of 1m/sec are given in Table 6.4 . All tests were carried out in duplicate and average values are given.

Table 6.4: *Test Results For Membrane SCP5 and OP4.*

Polymer	**Oven Temp.**	**Rejection for NaCl (%)**	**Water Flux at 5 bar ($l/m^2/h$)**
UF support membrane	-	0.8	502
OP4	60	90	20
SCP5	60	67	44
SCP5	80	92	6
SCP5	100	90	1.5

The membrane dried at 60°C shows salt rejection and permeability comparable with values observed for a number of commercial NF membranes.[6] Drying at higher temperatures moves the membrane rejection into the reverse osmosis region, but the flux values fall dramatically to give an overall performance very much lower than that of most RO membranes including **OP4**.

The performance results for the membrane fabricated from **SCP6**, dried at 60°C are shown in Table 6.5. The tests were conducted under the same conditions as those described for the membranes from **SCP5**.

Table 6.5. *Test Results For Membrane **SCP6.***

	$CaCl_2$	$MgSO_4$	NaCl	Na_2SO_4
Water Flux $l/m^2/d$	50	46	54	46
Rejection (%)	9.5	26	64	96

Table 6.5 shows that sulphate ions (SO_4^{2-}) are rejected much more strongly than chloride ions (Cl^-), which is consistent with the membrane surface possessing a high negative charge. Very high rejection of sodium sulphate was observed, due to the singly charged cation binding only weakly to the membrane surface. Hence the electrostatic repulsion between the membrane and the approaching anion is very strong, and the salt is strongly rejected. In contrast when a cation is doubly charged, (e.g. Mg^{2+}), it binds more strongly to the membrane and effectively shields the negative charge at the surface. As a consequence the salts of divalent cations are rejected poorly as observed. This type of electrostatic repulsion is known as the "Donnan exclusion".

Polymers (**CP14** and **CP15**) from the benzoic acid derivatives of *para*-carborane were prepared with the intention of sulphonation and subsequent membrane fabrication. Unfortunately as described in chapter 4. the resulting polymers were shown to have cross-linked, forming an insoluble gel and were unsuitable for sulphonation studies.

6.5. Conclusions:

The solubility of the poly(ethercarboranylketone)s produced during the work described in chapter 4. readily permits the casting of membranes by phase-inversion, affording a new class of membranes suitable for NF applications. Preliminary results reported here have shown that the carborane-based membranes do not show vastly different properties to those of conventional all-organic materials. Good performance results for NF/UF membranes were readily obtained, but further work is required to see if superior properties can be derived from the new classes of carborane-based polymers described.

6.6. Experimental:

6.6.1. Casting of Ultrafiltration Membranes From Polycarborane

Casting solutions were made up by dissolving:

a) 1.4 g of polymer in 18.6 g of NMP (7% w/w)

b) 1.0 g of polymer in 9.0 g of NMP (10% w/w)

c) 2.6 g of polymer in 17.4 g of NMP (13% w/w)

5 cm^3 of solution were pipetted onto a sheet of "Awa 10" non-woven polyester cloth (100 μm thick, and 15 x 22 cm in area) taped to a glass plate. The solution was then drawn down with a casting blade set to give a solution coating thickness of 150 μm. After 10 seconds to allow the solution to sink slightly into the support cloth, the plate was immersed in water, precipitating the polymer in the form of a smooth, shiny white film adhering to the support cloth. After soaking for 15 minutes, the membrane (i.e. the combined support and polymer film) was removed from the glass plate rinsed in running water for 15 minutes and finally soaked in water at 60 °C for 5 minutes to remove the last traces of solvent. the membrane was then immersed in 15% aqueous glycerol for an hour and allowed to dry in air overnight.

6.6.2. Testing of Ultrafiltration Membranes From Polycarborane

Duplicate discs were soaked in 10% aqueous ethanol for 10 minutes to remove glycerol and to ensure that the membrane pores were fully wetted. The discs were then soaked in distilled water for an hour, rinsed with distilled water and placed in two stainless steel pressure cells for testing. A feed solution containing 0.1% each of 1K, 10K and 100K polyethylene glycols was circulated across the membrane surface at a cross-flow velocity of 1 m/sec and a pressure of 2 bar. After collecting 10 cm^3 of initial permeate, which was discarded, the system was run with total recirculation of feed and permeate to a reservoir for 30 minutes, and permeate samples (15 - 20 cm^3) were then collected over a measured time interval and weighed. A sample of the feed solution was also taken half way through the run and feed and permeates were analysed by GPC.

6.6.3. Preparation of CP17 by Interfacial Polymerisation.

A solution of 1,1'-diamino-4,4'-pyridinium diiodide (250 mg) in 0.1 M sodium hydroxide solution (25 cm^3), was shaken with a 1% w/v solution of 1,7-bis-(chlorocarbonyl)-*meta*-carborane (200 mg, 0.74 mmol) in dichloromethane (20 cm^3) in a 50 cm^3 beaker, forming a dark orange solution. The polymer was precipitated into water (200 cm^3) to afford a bright yellow, fibrous product. The polymer was isolated by filtration and stirred in ethanol (200 cm^3) overnight. The product was dried for several hours under vacuum to afford 0.127 g, 46% of material identified as **CP17**. The polymer was characterised as follows:

Inherent viscosity 2.24 dL/g (in formic acid)

IR ν max cm^{-1}: 3425 br, 3115 w, 3046 w, 2607 s, 1627 m, 1590 s, 1447 m, 1426 m, 1303 s, 1242 sh., 1166 w, 1114 m, 929 w, 821 m, 734 w.

NMR: $\delta\ ^{13}C$: 71.69 (carboranyl C), 129.19, 148.72, 153.17, 160.68.

6.6.4. Preparation of CP18 by Interfacial Polymerisation.

A solution of 1,1'-diamino-4,4'-pyridinium diiodide (250 mg) in 0.1 M sodium hydroxide solution (25 cm^3), was shaken with a 1% w/v solution of 1,12-bis-(chlorocarbonyl)-*para*-carborane (200 mg, 0.74 mmol) in dichloromethane (20 cm^3) in a 50 cm^3 beaker, forming a dark orange solution. The polymer was precipitated into water (200 cm^3) to afford a bright yellow, fibrous product. The polymer was isolated by filtration and stirred in ethanol (200 cm^3) overnight. The product was dried for several hours under vacuum to afford 0.195 g, 71% of material identified as **CP18**. The polymer was characterised as follows:

Inherent viscosity 4.49 dL/g (in formic acid)

IR ν max cm^{-1}: 3124 w, 3046 w, 2617 s, 1754 s, 1566 m, 1304 m, 1208 m, 1110 s, 882 m, 832 m, 657 s.

6.7. References:

1. H.M. Colquhoun, A.L.Lewis, C.A. O'Mahoney and D.J. Williams, *Polymer*, 1995, **36**, 443.

2. J.E. Caddotte in "*Materials Science of Synthetic Membranes*", Ed. D.R. Lloyd, ACS Symposium Series 269, American Chemical Society, Washington DC, 1985, p273.

3. D. Grafstein and J. Dvorak, *Inorg. Chem.* 1963, **2**, 1128.

4. R.J. Petersen and J.E. Caddotte in "*Industrial Handbook of Membrane Technology*", Ed. M.C. Porter, Noyes Publications, New Jersey, 1990, p328.

5. J.E. Tomaschke, A.J. Testa and J.G. Vouros, *U.S. Pat. No.* 4, 990 252 (1991).

6. L.P. Raman M. Cheryan and N. Rajagopalan, *Chem. Eng. Prog.*, 1994, 68.

Chapter 7

CONCLUSIONS

CONCLUSIONS:

The initial stages of this work were concerned with extending the aryl derivative chemistry of *meta*- and *para*-carborane. This was conveniently achieved by copper mediated reactions based on the classical Ullmann-type coupling, with reactions between C-mono- or C,C'-di-copper(I) derivatives of 1,7- or 1,12-dicarba-*closo*-dodecaborane and aryl iodides in the presence of pyridine to afford the corresponding C-mono- or C,C'-diaryl derivatives. Many new and previously inaccessible carborane derivatives of *meta*- and *para*-carborane were prepared in high yield and characterised.

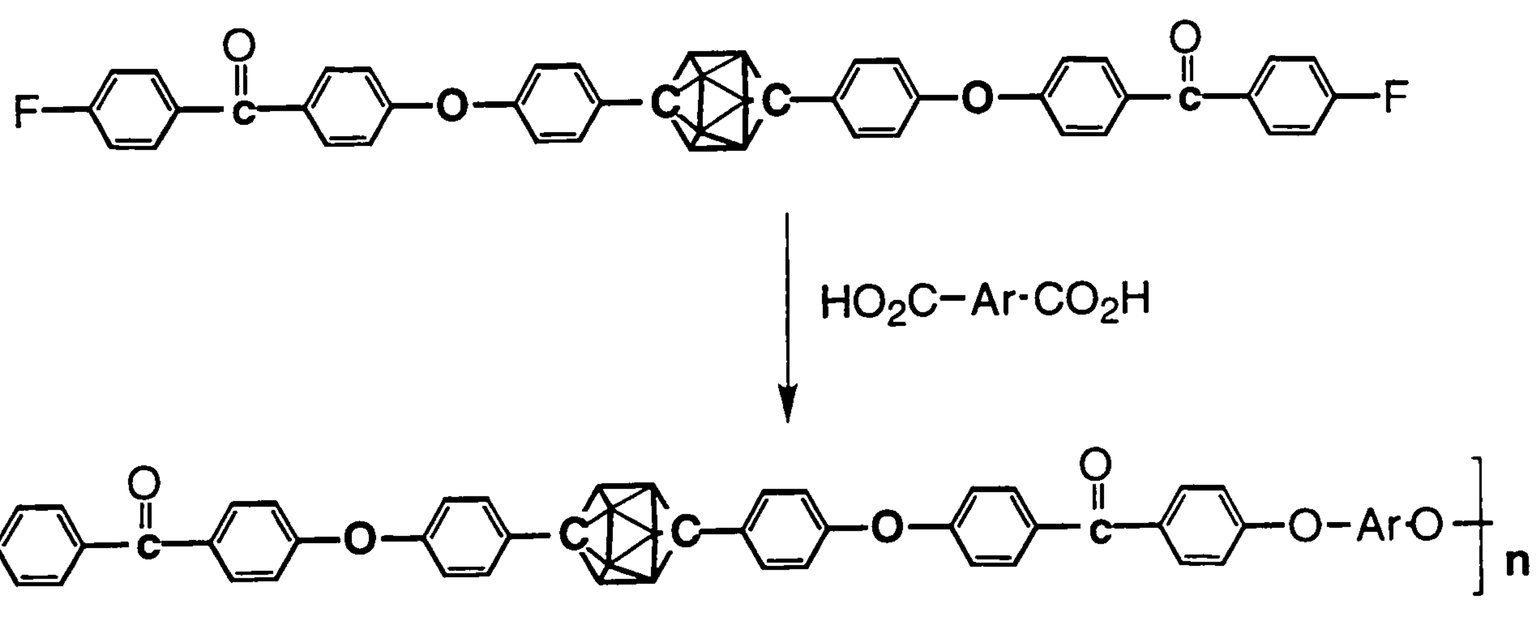
During the course of this work a new deboronation technique was developed for the conversion of neutral *closo* carboranes $RR'C_2B_{10}H_{10}$ into *nido* anions $[RR'C_2B_9H_{10}]^-$ using wet fluoride solutions. This allows the deboronation of carbon-substituted *meta*-carborane derivatives which are difficult to degrade by classical routes. The use of fluoride ions in wet solutions of THF or acetonitrile is a useful reagent for the deboronation of *ortho*- and *meta*-carboranes and their derivatives (though not *para*-carborane) and various NMR studies have identified side products, giving insight into the possible deboronation mechanism.

1,7-bis-(4-phenoxyphenyl)-*meta*-carborane and 1,12-(4-phenoxyphenyl)-*para*-carborane were prepared and incorporated into a series of PEEK-type polymers by reaction with suitable dicarboxylic acids in triflic acid. In addition the range of *ortho*-carborane-containing PEEK-type polymers was extended and higher molecular weights than those previously reported by Stephenson[1] were obtained by using freshly distilled triflic acid. DSC studies on the carborane-containing PEEK-type polymers showed that the introduction of the carborane moiety renders the majority of the polymers completely amorphous in contrast to the all-organic systems from which they are formally derived.

Higher molecular weight materials were obtained with the *meta*- and *para*-carborane isomers than with the polymers containing *ortho*-carborane. This may be a result of the reduced electron demand of the *meta*- and *para*-carborane isomers leading to a higher degree of polymerisation and/or a result of the reduced steric demand of the system when going from *ortho*- to *meta*- to *para*-carborane.

Studies of the thermal decomposition of the PECK polymers produced here have been carried out. Evolved gas analysis showed that the main volatiles were carbon monoxide, hydrogen and water, and the final ceramic yields obtained were very close to those calculated for the loss of all of the hydrogen and ether and ketone oxygen from the polymer. Provisional solid state NMR studies of residues after heating to different temperatures have been attempted to gain an insight into the chemical form of the residues, but insufficient time was available to complete this study.

The inherent stability of the *para*-carborane cage to nucleophilic conditions may permit the incorporation of *para*-carborane into the backbone of PEEK-type polymers via nucleophilic polycondensation, which is unsuitable for the *ortho*- and *meta*-carborane derivatives. Success in nucleophilic polycondensation reactions[2] is dependent on the halogen being sufficiently activated to promote nucleophilic attack at the carbon atom. Fluorine is by far the best halogen for this purpose - not only is it the most electronegative halogen, thereby making its attached carbon more susceptible to nucleophilic attack, but it also helps to stabilise the anionic intermediate from the positions *ortho* and *meta* to the reacting carborane. The polymerisation of fluorine-substituted aryl carboranes, which can be conveniently synthesised using the copper(I)-mediated reactions developed during the course of this work could provide a wide range of new carborane-containing polymers which could display interesting properties.



The solubility of poly(ethercarboranylketone)s which may be contrasted to the insolubility of their organic counterparts readily permits the casting of membranes by phase-inversion, affording a new class of membranes suitable for nano- and ultra-filtration applications. Preliminary results reported here have shown that the carborane-based membranes do not, however, show vastly different properties to those of conventional all-organic materials. Good performance results for nano-/ultra filtration membranes were readily obtained, but further work is required to see if superior properties can be derived from the new classes of carborane-based polymers described. In the long term, the exploitation of new fabrication methods for ceramic filtration membranes could lead to the formation of high porosity materials with the minimum disruption of the bulk morphology.

7.1. References:

1. I.R. Stephenson, Ph.D. Thesis, Univesity of Durham, 1988.

2. M.J. Mullins and E.P. Woo, *J. Macromol. Sci., Rev. Macromol. Chem.* 1987, **C27**, 313

Appendix A

General Techniques

Reactions where stated were conducted under a dry, oxygen-free dinitrogen atmosphere, after passing the gas through columns packed with phosphorous pentoxide and A4 molecular sieves. The glasswear was dried proir to use by heating to *ca.* 120 °C, and cooled under a nitrogen purge using normal Schlenk techniques. Reaction workups were conducted under normal atmospheric conditions unless otherwise stated.

Solvents

1,2-dimethoxyethane was dried by refluxing and distillation over potassium and stored over sodium wire. Pyridine was obtained from Aldrich and dried by distillation from potassium hydroxide. Trifluoromethanesulphonic acid was obtained from Lancaster and distilled under nitrogen before use. THF was dried by refluxing with potassium (with benzophenone added as an indicator).

Reagents

Triphenylphosphine was obtained from Aldrich and recrystallised from hexane. All other chemicals were used as received unless otherwise stated. Zinc (99.99% pure) was obtained from Aldrich and activated by washing with molar hydrochloric acid, ethanol and diethylether, then dried under vacuum at 100 °C for 3 hours prior to use. Butyllithium in hexane solution, was standardised by titration with ^{t}butanol in toluene, using 4,5-diazaphenanthrene as the indicator. Carboranes were obtained commercially and purified by sublimation (ca. 70 °C, 0.01 mmHg) prior to use.

Melting Points

Melting points were measured using capillary tubes and an electrically heated block and are uncorrected.

TLC

Thin layer chromatography (TLC) was conducted on Merck DC-Plastifolien Kieselgel 60 F_{254} (Art 5735), with u.v. detection.

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Infra Red Spectroscopy

Infra Red spectra were obtained as KBr discs, unless otherwise stated, using a Perkin-Elmer 1600 FTIR spectrometer, in the range 4000-400 cm^{-1}. IR spectroscopy is a useful tool as it shows characteristic bands of the carboranes cage along with bands of organic functional groups if appropriate. The BH stretching vibrations are usually very strong and broad at approximately 2600 - 2500 cm^{-1} in icosahedral carboranes.

NMR Spectroscopy

Solution state NMR spectra were recorded on a Varian VXR 200 MHz (^{1}H), Gemini 200 MHz (^{1}H, ^{13}C), VXR/S 400 MHz (^{13}C) and AMX 500 MHz (^{11}B) machines as $CDCl_3$ solutions, unless otherwise stated, and referenced internally to tetramethylsilane. Solid-state NMR spectra were recorded on a Varian VXR-300 solid-state nuclear magnetic ressonance spectrometer and used for compounds that were either insoluble or only sparlingly soluble in deuterated solvents giving no or poor quality solution state ^{13}C spectra.

Mass Spectroscopy

Mass spectra were obtained using a VG Micromass Analytical 7070E instrument operating in the E.I. mode at 70 eV. Calculated values of M_r show the full isotope range $^{10}B_n$ to $^{11}B_n$, including a ^{13}C combination where this is likely to have the observable intensity.

Elemental Analysis

Carbon, hydrogen and nitrogen were determined on a Carlo Erba Strumentazione Elemental Analyser 1106 instrument. Halogen analysis was determined by oxygen flask combustion followed by potentiometric titration.

DSC

Differential Scanning Calorimetry was obtained using a Mettler TA400 . The determination of the T_g and T_m of a polymer sample is an essential part of the characterisation of a thermoplastic material.

At its T_g a polymer undergoes a number of physical changes as a result of the increased molecular motion within it allowing the T_g to be observed. In particular there is an increase in the number of degrees of freedom of the polymer molecules and as a consequence the heat capacity (C_p) rises markedly and it is the change in C_p that is monitored in the DSC experiment.

The DSC technique involves supplying a heat source to the sample and a reference simultaneously so that the temperatures of the two increase but remain equal. As the temperature of the sample passes through its T_g, its C_p increases, and more energy is required to keep it at the same temperature as the reference. This difference in energy enables the T_g to be measured. In contrast the T_m is registered as an endothermic peak produced by the temporary increase in C_p of the sample as a result of the latent heat required to break down the crystallinity of the polymer.

TGA

Thermogravimetric analysis was obtained using a Mettler TG 760 series DSC. The TGA technique involves measuring the fractional weight change of a polymer sample whilst it is heated at a known rate to a given temperature. As such it gives an indication of the thermal stability of the polymer, with weight changes at particular temperatures highlighting chemical changes in the material, (for example decomposition or oxidation). Runs were carried out at a heating rate of 10 °C/min from 40°C to 820 °C.

GPC

The GPC technique allows the determination of molecular weight through differentiating between polymer molecules by their size in solution. This occurs through absorption of the polymer molecules into the porous stationary phase used in the chromatograph columns. Small molecules are readily absorbed into, and retained in the pores of the stationary phase, with the higher molecular weight materials being eluted first. Gel Permeation Chromatography was performed using a Waters Model 590 Detector equipped with a differential refractometer R401 with three 30 cm column PL gel columns of pore size 10^5, 10^3 and 10^2 Å. The chromatograph was operated using THF as the solvent at a flow rate of 1 cm^3/min. The sample concentrations were 0.5% by weight, injected in 10 µl aliquots.

Laser Light Scattering

Laser Light Scattering Measurements were conducted using a Otsuka DLS-700 Dynamic Light Scattering Spectrophotometer at Manchester University.

X-ray Diffraction

Powder X-ray diffraction patterns were obtained using a Phillips x-ray generator PW 1009/80 CuK_α tube with λ = -1.5443 Å. Beams were controlled using a Hilton Brocks DG 2-2 window shutter control. An Errat Nanus Guiner de Waff camera (No. 2) was used.

Solution Viscosities

The solution viscosities (η_{inh}) (equation 1) of 0.1% polymer solutions were measured using an Ubbelhode 660 viscometer at 25 °C. The η_{inh} measurements were determined in NMP unless otherwise stated.

$$\eta_{inh} = \frac{\ln\left(\frac{\eta}{\eta_0}\right)}{c}, \quad \frac{\eta}{\eta_0} \approx \frac{t}{t_0} \qquad (1)$$

c = Polymer solution concentration (%)
t = Time for fixed volume of polymer solution to pass down a capillary
t_0 = Time for a fixed volume of solvent to pass down the same capillary

Appendix B

Colloquia

The Board of Studies in Chemistry requires that each postgraduate research thesis contains an appendix listing all research colloquia, research seminars and lectures arranged by the Department of Chemistry and all research conferences attended and papers presented during the period when research for the thesis was carried out.

UNIVERSITY OF DURHAM

Board of Studies in Chemistry

COLLOQUIA, LECTURES AND SEMINARS FROM INVITED SPEAKERS

1992- 1995

October 14	**Dr. S. C. Rawle, University of Warwick** ***Flourescent Sensors for Metal Ions.***
October 15	Dr M. Glazer & Dr. S. Tarling, Oxford University & Birbeck College, London *It Pays to be British! - The Chemist's Role as an Expert Witness in Patent Litigation.*
October 20	**Dr. H. E. Bryndza, Du Pont Central Research** ***Synthesis, Reactions and Thermochemistry of Metal(Alkyl) Cyanide Complexes and Their Impact on Olefin Hydrocyanation Catalysis.***
October 22	**Prof. A. Davies, University College London** ***The Ingold-Albert Lecture The Behaviour of Hydrogen as a Pseudometal.***
October 28	Dr. J. K . Cockcroft, University of Durham *Recent Developments in Powder Diffraction.*
October 29	Dr. J. Emsley, Imperial College, London *The Shocking History of Phosphorus.*
November 4	**Dr. T. P. Kee, University of Leeds** ***Synthesis and Co-ordination Chemistry of Silylated Phosphites.***
November 5	**Dr. C. J. Ludman, University of Durham** ***Explosions, A Demonstration Lecture.***

November 11	Prof. D. Robins, Glasgow University *Pyrrolizidine Alkaloids : Biological Activity, Biosynthesis and Benefits.*
November 12	Prof. M. R. Truter, University College, London *Luck and Logic in Host - Guest Chemistry.*
November 18	**Dr. R. Nix, Queen Mary College, London** ***Characterisation of Heterogeneous Catalysts.***
November 25	Prof. Y. Vallee. University of Caen *Reactive Thiocarbonyl Compounds.*
November 25	Prof. L. D. Quin, University of Massachusetts, Amherst *Fragmentation of Phosphorous Heterocycles as a Route to Phosphoryl Species with Uncommon Bonding.*
November 26	Dr. D. Humber, Glaxo, Greenford *AIDS - The Development of a Novel Series of Inhibitors of HIV.*
December 2	Prof. A. F. Hegarty, University College, Dublin *Highly Reactive Enols Stabilised by Steric Protection.*
December 2	Dr. R. A. Aitken, University of St. Andrews *The Versatile Cycloaddition Chemistry of* $Bu_3P.CS_2$.
December 3	**Prof. P. Edwards, Birmingham University** ***The SCI Lecture - What is Metal?***
December 9	Dr. A. N. Burgess, ICI Runcorn *The Structure of Perfluorinated Ionomer Membranes.*
<u>1993</u>	
January 20	Dr. D. C. Clary, University of Cambridge *Energy Flow in Chemical Reactions.*

January 21	Prof. L. Hall, Cambridge *NMR - Window to the Human Body.*
January 27	Dr. W. Kerr, University of Strathclyde *Development of the Pauson-Khand Annulation Reaction : Organocobalt Mediated Synthesis of Natural and Unnatural Products.*
January 28	**Prof. J. Mann, University of Reading** ***Murder, Magic and Medicine.***
February 3	Prof. S. M. Roberts, University of Exeter *Enzymes in Organic Synthesis.*
February 10	Dr. D. Gillies, University of Surrey *NMR and Molecular Motion in Solution.*
February 11	**Prof. S. Knox, Bristol University** ***The Tilden Lecture: Organic Chemistry at Polynuclear Metal Centres.***
February 17	**Dr. R. W. Kemmitt, University of Leicester** ***Oxatrimethylenemethane Metal Complexes.***
February 18	Dr. I. Fraser, ICI Wilton *Reactive Processing of Composite Materials.*
February 22	Prof. D. M. Grant, University of Utah *Single Crystals, Molecular Structure, and Chemical-Shift Anisotropy.*
February 24	**Prof. C. J. M. Stirling, University of Sheffield** ***Chemistry on the Flat-Reactivity of Ordered Systems.***
March 3	**Dr. P. Fagan, DuPont** ***Advances in Chemistry of C_{60}***

March 10	**Dr. P. K. Baker, University College of North Wales, Bangor** ***'Chemistry of Highly Versatile 7-Coordinate Complexes'.***
March 11	Dr. R. A. Y. Jones, University of East Anglia *The Chemistry of Wine Making.*
March 17	Dr. R. J. K. Taylor, University of East Anglia *Adventures in Natural Product Synthesis.*
March 24	**Prof. I. O. Sutherland, University of Liverpool** ***Chromogenic Reagents for Cations.***
May 13	Prof. J. A. Pople, Carnegie-Mellon University, Pittsburgh, USA *The Boys-Rahman Lecture: Applications of Molecular Orbital Theory*
May 21	Prof. L. Weber, University of Bielefeld *Metallo-phospha Alkenes as Synthons in Organometallic Chemistry*
June 1	Prof. J. P. Konopelski, University of California, Santa Cruz *Synthetic Adventures with Enantiomerically Pure Acetals*
June 2	Prof. F. Ciardelli, University of Pisa *Chiral Discrimination in the Stereospecific Polymerisation of Alpha Olefins*
June 7	**Prof. R. S. Stein, University of Massachusetts** ***Scattering Studies of Crystalline and Liquid Crystalline Polymers***

June 16 — Prof. A. K. Covington, University of Newcastle
Use of Ion Selective Electrodes as Detectors in Ion Chromatography.

June 17 — Prof. O. F. Nielsen, H. C. Arsted Institute, University of Copenhagen
Low-Frequency IR - and Raman Studies of Hydrogen Bonded Liquids.

June 24 — **Dr. L.S. Field, University of Sydney**
Activation of C-H Bonds at Metal Centre.

July 23 — **Dr. F Wudl, University of California, Santa Barbara**
Recent Advances in the Chemistry of Buckminsterfullerene., C60

September 13 — Prof. Dr. A. D. Schlüter, Freie Universität Berlin, Germany
Synthesis and Characterisation of Molecular Rods and Ribbons.

September 13 — Prof. K. J. Wynne, Office of Naval Research, Washington, U.S.A.
Polymer Surface Design for Minimal Adhesion

September 14 — Prof. J. M. DeSimone, University of North Carolina, Chapel Hill, U.S.A.
Homogeneous and Heterogeneous Polymerisations in Environmentally Responsible Carbon Dioxide.

September 28 — Prof. H. Ila., North Eastern University, India
Synthetic Strategies for Cyclopentanoids via OxoKetene Dithiacetals.

October 4 — **Prof. F. J. Feher, University of California at Irvine**
Bridging the Gap between Surfaces and Solution with Sessilquioxanes.

October 14	**Dr. P. Hubberstey, University of Nottingham** ***Alkali Metals: Alchemist's Nightmare, Biochemist's Puzzle and Technologist's Dream.***
October 20	**Dr. P. Qualye, University of Manchester** ***Aspects of Aqueous Romp Chemistry.***
October 21	**Prof. R. Adams, University of S. Carolina** ***The Chemistry of Metal Carbonyl Cluster Complexes Containing Platinum and Iron, Ruthenium or Osmium and the Development of a Cluster Based Alkyne Hydrogenating Catalyst.***
October 27	**Dr. R. A. L. Jones, Cavendish Laboratory** ***'Perambulating Polymers'.***
November 10	Prof. M. N. R. Ashfold, University of Bristol *High-Resolution Photofragment Translational Spectroscopy: A New Way to Watch Photodissociation.*
November 17	Dr. A. Parker, Laser Support Facility *Applications of Time Resolved Resonance Raman Spectroscopy to Chemical and Biochemical Problems.*
November 24	**Dr. P. G. Bruce, University of St. Andrews** ***Synthesis and Applications of Inorganic Materials.***
November 25	Dr. R.P. Wayne, University of Oxford *The Origin and Evolution of the Atmosphere*
December 1	**Prof. M. A. McKervey, Queens University, Belfast** ***Functionalised Calixerenes.***
December 8	Prof. O. Meth-Cohen, Sunderland University *Friedel's Folly Revisited.*
December 16	Prof. R. F. Hudson, University of Kent *Close Encounters of the Second Kind.*

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January 26	**Prof. J. Evans, University of Southhampton** ***Shining Light on Catalysts.***
February 2	Dr. A. Masters, University of Manchester *Modelling Water Without Using Pair Potentials.*
February 9	Prof. D. Young, University of Sussex *Chemical and Biological Studies on the Coenzyme Tetrahydrofolic Acid.*
February 16	Prof. K. H. Theopold, University of Delaware, U.S.A *Paramagnetic Chromium Alkyls: Synthesis and Reactivity.*
February 23	**Prof. P. M. Maitlis, University of Sheffield** ***Why Rhodium in Homogenous Catalysis.***
March 2	**Dr. C. Hunter, University of Sheffield** ***Non Covalent Interactions between Aromatic Molecules.***
March 9	Prof. F. Wilkinson, Loughborough University of Technology *Nanosecond and Picosecond Laser Flash Photolysis.*
March 10	Prof. S.V. Ley, University of Cambridge *New Methods for Organic Synthesis.*
March 25	Prof. J. Dilworth, University of Essex *Technetium and Rhenium Compounds with Applications as Imaging Agents.*
April 28	**Prof. R. J. Gillespie, McMaster University, Canada** ***The Molecular Structure of some Metal Fluorides and OxoFluorides: Apparent Exceptions to the VSEPR Model.***

May 12	**Prof. D. A. Humphreys, McMaster University, Canada** ***Bringing Knowledge to Life***
October 5	Prof. N. L. Owens, Bringham Young University, Utah, USA *Determining Molecular Structure - The INADEQUATE NMR Way*
October 19	**Prof. N. Bartlett, University of California,** ***Some Aspects of Ag(II) and Ag(III) Chemistry***
November 2	**Dr. P.G. Edwards, University of Wales, Cardiff,** ***The Manipulation of Electronic and Structural Diversity in Metal Complexes - New Ligands***
November 3	**Prof. B.F.G. Johnson, Edinburgh University,** ***Arene-Metal Clusters***
November 9	**Dr. G. Hogarth, University College, London,** ***New Vistas in Metal-imido Chemistry***
November 10	**Dr. M. Block, Zenneca Pharmaceuticals, Macclesfield,** ***Large-scale Manufacture of ZD 1542, a Thromboxane Antagonist Synthase Inhibitor***
November 16	**Prof. M. Page, University of Huddersfield** ***Four-membered Rings and bLactamase***
November 23	Dr. J.M.J. Williams, University of Loughborough, *New Approaches to Asymmetric Catalysis*
December 7	Prof. D. Briggs, ICI and University of Durham. *Surface Mass Spectroscopy*

1995

January 11 — Prof. P. Parsons, University of Reading,
Applications of Tandem Reactions in Organic Synthesis

January 18 — Dr. G. Rumbles, Imperial College, London,
Real or Imaginary Third Order Non-Linear Optical Materials

January 19 — **Prof. R. Bonnett, University of London, Queen Mary and Westfield College,**
Chemical Aspects of Photodynamic Therapy

January 25 — Dr. D.A. Roberts, Zeneca Pharmaceuticals
The Design and Synthesis of Inhibitors of the Rennin-angiotensin System

January 26 — **Mrs S. Owen, Northumbria Water,**
Aspects of Trace Organic Species in The Environment

February 1 — **Dr. T. Crosgrove, Bristol University**
Polymers do it at Interfaces

February 8 — **Dr. D. O'Hare, Oxford University,**
Synthesis and Solid-state Properties of Poly, Oligo- and Multidecker Metallocenes

February 22 — Prof. E. Schaumann, University of Clausthal,
Silicon- and Sulphur-mediated Ring-opening Reactions of Epoxide

March 1 — Dr. M. Rosseinsky, Oxford University,
Fullerene Intercalation Chemistry

March 22 — Dr. M. Taylor, University of Auckland, New Zealand,
Structural Methods in Main Group Chemistry

April 26	**Dr. M. Schroder, University of Edinburgh,** ***Redox-active Macrocyclic Complexes : Rings, Stacks and Liquid Crystals***
May 3	Prof. E.W. Randell, Queen Mary and Westfield College, *New Perspectives in NMR Imaging*
May 4	**Prof. A.J. Kresge, University of Toronto,** ***The Ingold Lecture ; Reactive Intermediates : Carboxylic-acid Enols and Other Unstable Species***
June 6	**Dr. R. Snaith, Cambridge University,** ***The S-block Metals: Synthesis, Characterisation and Uses***
June 8	**Dr. N.G. Connelly, University of Bristol,** ***Organometallic Electrochemistry - Synthesis and Structural Consequences***
June 14	**Dr. M. McGlinchy, MacMaster University,** ***Metal Stabilised Cations ; Synthesis and Characterisation***
July 7	**Dr. M. G. Davidson, Cambridge University,** ***Phosphorous Ylids - Interaction With Alkali Metals and Organic Acids***

Colloquia attended in **bold**.

Research Conferences attended and papers† and posters* presented.

September 1992	Intraboron 12, University of Wales Bangor.
August 1993*	2nd Anglo-German Inorganic Conference, Universität Stuttgart, Germany
September 1993†	Intraboron 13, Manchester Metropolitan University
July 1994	16th Organometallic Conference, University of Sussex
September 1994*	RSC Autumn Meeting, University of Glasgow,
September 1994†	Intraboron 14, Strathclyde University
April 1995*	RSC Annual Meeting, Herriot-Watt University
June 1995†	North East Graduate Symposium, University of Durham
July 1995	ISOM 11, University of Durham
September 1995†	Intraboron 15, Leeds University