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Studies Directed Towards the
Synthesis and Characterisation
of
Rigid Rod Polymer Networks.

by

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(University of Stirling)

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A thesis submitted in partial fulfilment of
the requirements for the degree of Doctor
of Philosophy at the University of Durham.

September 1992



- 5 JAN 1993

Abstract.

The properties of polymer networks composed of flexible monomer units are well understood, however only limited investigations into the properties of networks composed of rigid rodlike monomer units linked by flexible netpoints have been carried out to date. The aim of this work was to develop a method of synthesising processable difunctional rigid rodlike molecules which could be incorporated into polymer networks; the physical properties of the polymer networks would then be investigated. The following thesis describes the background to both processable rigid rod polymers and to rigid rod polymer networks. The route utilised in an attempt to synthesise processable, difunctional rigid rodlike materials is described and details of the characterisation and properties of those difunctional rods successfully synthesised are given. Attempts to incorporate the difunctional rods into polymer networks are discussed.

A series of rigid rod polymers, in the class of either poly(arylene diynylene)s or poly(arylene ynylene)s, were synthesised. The materials were either unsubstituted linear polymers, linear polymers substituted with alkyl side chains, or polymers containing a bend via an ether or a ketone link. The synthesis and molecular structural characterisation of the polymers is described and investigations of their solubilities, thermal properties and, in some cases, bulk and LB film ordering behaviour are discussed.

Acknowledgements.

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I am grateful to Dr. H. MacBride for sharing his knowledge of acetylene coupling reactions and for providing the initial 1,4-diethynylbenzene.

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I would like to express my appreciation to Stuart, my parents and Elspeth for their continual love and support and finally, to thank Stuart for his help in the writing of this thesis.

MEMORANDUM.

The work described in this thesis was carried out in the Durham Laboratories of the Interdisciplinary Research Centre in Polymer Science and Technology, the University of Durham, between October 1989 and September 1992. This work has not been submitted for any other degree and is the original work of the author, except where acknowledged by reference.

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Chapter One
Origin of the work

1 Origin of the work.

1.1 Introduction.

The aim of the project was to synthesise and characterise networks composed of rigid rod segments joined by flexible netpoints. The initial interest in the area was stimulated by theoretical papers which proposed models on the basis of which the physical behaviour of networks composed of rigid rod segments could be predicted. In this section a qualitative description of the theoretical picture which has evolved is given. In particular, the work of Edwards in this area is elaborated since he was the first to describe a theory for the behaviour of networks made up of rigid rod segments.^[B4,B5,V2]

1.2 Theoretical descriptions of networks composed of rigid rod polymers.

Rubber networks are a long standing area of interest in polymer science, their technical importance being vast, and the physics and chemistry of such networks is well documented and understood. The networks employed in technical applications are formed from flexible macromolecules which are chemically crosslinked and the successful physical theories are based on the assumptions that the chains are flexible and randomly crosslinked. Edwards, Bouè and Vilgis were the first to describe a theory for the rubber elasticity of networks made up of rigid rod segments.^[B4,V2]

The theory is mathematically complex but Ballauff^[B1] has published a useful and readily understandable brief qualitative review of Edwards' work concerned with predicting the stress-strain relationship of a rigid rod polymer network.

In his review Ballauff considers a network as being made up of rigid rods connected by flexible hinges. A plot of stress per unit area (f) as a function of strain (λ), where strain is defined as linear extension divided by length at rest, shows that at low extensions the behaviour of the rigid rod network resembles that of conventional rubber networks, see figure 1.1 part *a*. At larger deformations the rodlike nature of the



chains comes into play and the stress-strain relation crosses over to an exponential increase of stress against strain, see figure 1.1 solid line. This theory was evolved for phantom networks, i.e. ideal networks that have no entanglement constraints. For a non-phantom network, however, theory predicts a maximum deformation at which the stress as a function of strain will diverge from the simpler system, see figure 1.1 dashed line. Entanglement constraints mean that the rods cannot move through one another but exert a mutual steric hindrance, as the extension of the network increases a greater number of rods will intersect resulting in a decrease in the number of degrees of freedom of the system until the critical strain is reached.

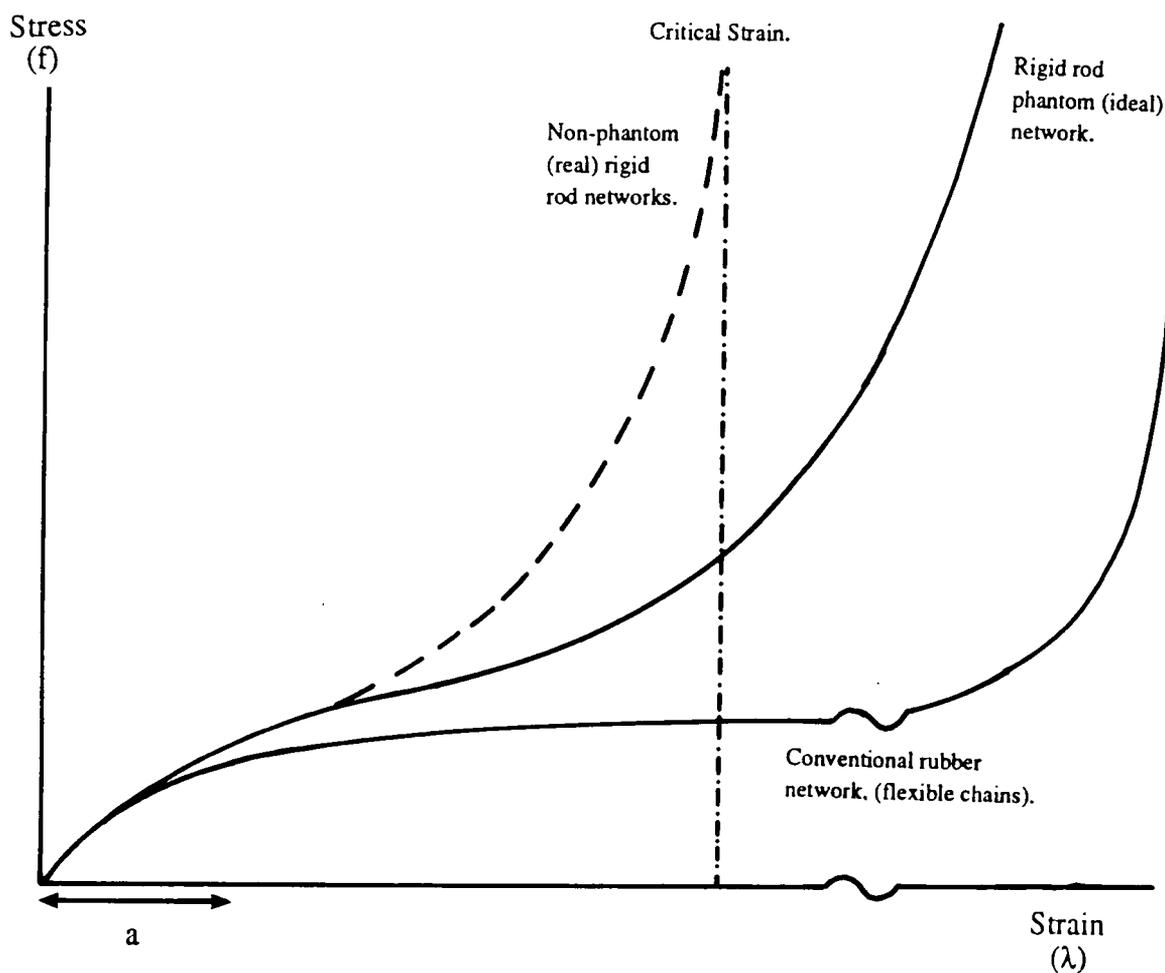


Figure 1.1 Diagrammatic representation of the theoretical stress-strain relation for networks composed of rigid rods.

The theory was the first to describe the behaviour of rigid rod networks and was a mean field approach, treating only isotropic systems. Systems of the type described by the theory would have to be synthesised by simultaneous polymerisation and crosslinking reactions, an entirely different situation would apply if crosslinking took place in a sample of rigid rod polymer in the ordered liquid crystalline state. Since rigid rods display a marked tendency to associate in an ordered way it will clearly be difficult to make real isotropic networks to test the theoretical predictions.

This theoretical study provided the initial interest in the area of rigid rod networks since it suggested opportunities to design a class of new polymeric materials. The theoretical ideas put forward by Edwards et al thus provided the stimulus for a potentially interesting development.

In 1974, Flory discussed the interest of his group in the liquid crystalline state of polymers containing rigid molecules. He described the goal of their studies of such systems as: "Elucidation of the respective roles of molecular asymmetry and anisotropy of intermolecular forces in bringing about the occurrence of the liquid crystalline state". His work developed theoretical models for rigid molecules, those with a degree of flexibility and fully flexible molecules, as well as those with alternating rigid and flexible segments.^[F2-8]

The molecular theory developed by Flory et al describing the isotropic-nematic phase equilibria of rodlike systems, demonstrated the importance of the steric forces or packing entropy of rigid molecules in determining the phase behaviour of such systems.^[F2,F10,Y2]

Farmer, Wierschke and Adams ^[F1] have used semiempirical molecular orbital calculations to investigate the conformational properties of a series of rigid rod polymers. The polymers investigated included poly(2,5-benzimidazole) (ABPBI), poly(2,5-benzoxazole) (ABPBO), poly(2,6-benzothiazole) (ABPBT), poly(p-phenylene benzobisimidazole) (PBI), poly(p-phenylene benzobisoxazole) (PBO) and poly(p-phenylene benzobisthiazole) (PBZT), see figure 1.2.

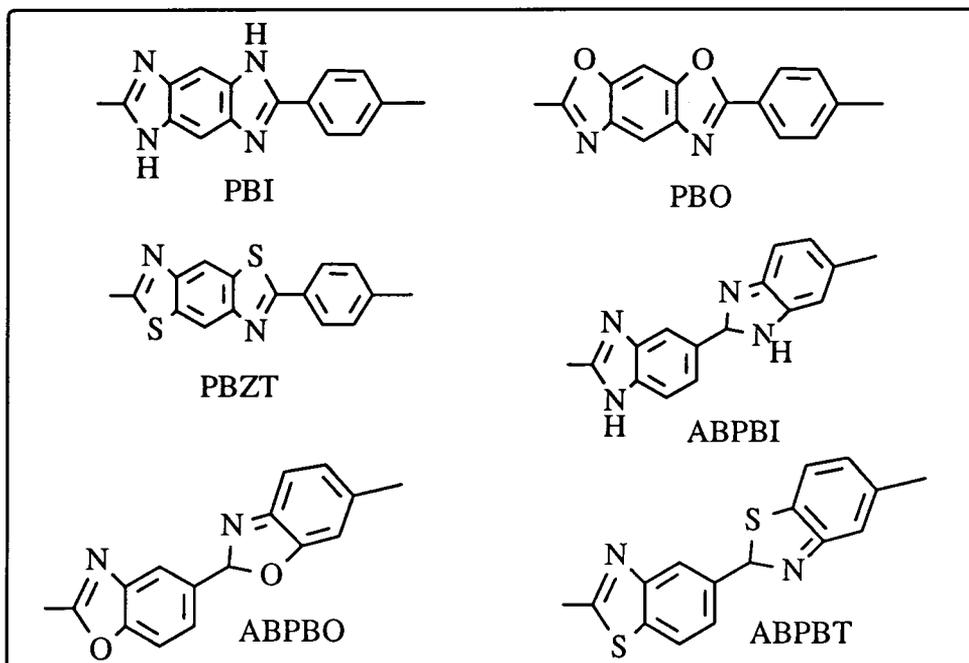


Figure 1.2 Diagrammatic representation of stiff chain rigid rod polymers.

Poly(2,5-benzoxazole) ABPBO and poly(p-phenylene benzobisoxazole) PBO were both found to have a coplanar arrangement of the heterocyclic and phenyl rings in their lowest energy conformations. Calculations for the other polymers indicated that the lowest energy conformation for isolated molecules was non-coplanar. The effect of having substituents on the phenylene ring in syn-poly(p-phenylene benzobisoxazole) and anti- and syn-poly(p-phenylene benzobisthiazole) was also investigated and their results indicated that simple alkyl substituents had very little effect upon the conformations of the molecules. More bulky substituents, such as t-butyl, and those which introduced coulombic or hydrogen bonding interactions played a greater role in making specific conformations energetically favourable.

Since many of the papers published in the area of rigid rod polymers are theoretical it was proposed that the synthesis of difunctional rigid rodlike molecules which could subsequently be incorporated into polymer networks should be undertaken. If this could be achieved the properties of the resulting networks would be

investigated and the experimental results on well defined structures could be compared with theoretical predictions. The work would also be of interest as part of ongoing work into the synthesis of polymeric materials with novel topologies.

1.3 Nomenclature of rigid rodlike polymers.

There is some ambiguity and lack of precision in the use of the term "rigid rod polymer". There are several examples of polymeric materials which are stiff in bulk but where the isolated molecular chains might reasonably be expected to have a measure of flexibility allowing access to a range of conformations. In such cases the bulk stiffness is achieved through the summation of intermolecular interactions in aggregations of molecular chains, this class of materials could be distinguished within the larger group of stiff or rigid polymers by calling them collectively or cooperatively stiff or rigid polymers. Another class of polymers exist which have a fixed rodlike topology and can be described as molecularly stiff or rigid rods, we shall distinguish this class by referring to them as molecularly rigid or stiff rod molecules and/or polymers. It is systems based on this second class with which we are concerned in this thesis. These distinctions will be elaborated in Chapter 2.

1.4 Proposed construction of molecularly rigid rodlike molecules and linear molecularly rigid rod polymers.

In this project our objective was the synthesis of truly molecularly rigid rod monomers, linear polymers and polymer networks.

The rodlike molecules were, therefore, to be synthesised from a combination of 1,4-phenylene and acetylene units since this would produce linear, truly molecularly rigid rodlike molecules. The problem was foreseen that molecules composed simply of such units would become insoluble very rapidly as their length increased. In an attempt to overcome this problem it was decided to incorporate flexible alkyl side chains onto the aromatic units. Attaching side chains to a polymer in order to increase its solubility

had been successfully employed in several cases including the synthesis of soluble poly(p-phenylenes),^[R5,R6] soluble polythiophenes,^[E2-4] polybenzthiazoles,^[A4,F11] and polybenzoxazoles.^[A4]

Linear molecularly rigid rod polymers are of increasing interest and it was proposed that the properties of linear rigid rod polymers which could be produced on route to the difunctional rodlike molecules would also be investigated.

As an introduction to the area of rigid rod polymers a review of their general properties and behaviour is detailed in Chapter two. Examples of recent investigations into the synthesis and characterisation of rigid rod polymers can also be found in Chapter two.

Chapter three describes the synthesis and characterisation of the monomers required for this study and their polymerisation to linear polymers. The synthesis and characterisation of rigid rodlike molecules is also described in Chapter three. Chapter four describes the characterisation of the linear polymeric materials obtained and discusses the progress made and problems encountered in the routes explored. Chapter five outlines possible routes to networks containing molecularly rigid rod segments, some preliminary experiments directed towards this objective and suggestions for future work.

Chapter Two

Molecularly and
Cooperatively Rigid
Rodlike Polymers.

2 Molecularly and cooperatively rigid rodlike polymers.

When considering the range of polymers in production at present, it can be seen that the vast majority consist of flexible macromolecules in which most of the bonds in the polymer backbone are able to rotate about the internuclear axis. Stiff linear polymers are a relatively recent development and their use is far less widespread. The properties of such systems have not been studied in great detail so far and still require investigation.

Stiff linear chain polymers can be considered as being made up from rigid units. Polymers which are generally considered to fit this classification may be divided into two broad classes. The first class is exemplified by

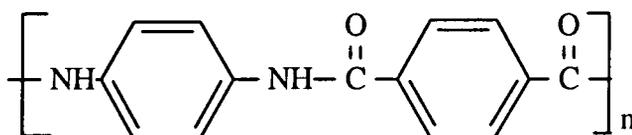


Figure 2.1 Poly(p-phenyleneterephthalamide).

poly(p-phenyleneterephthalamide), figure 2.1. The polymer would be described as being cooperatively rigid due to association between a number of adjacent polymer chains brought about via crystalline ordering and hydrogen bonding even though individual isolated molecules or chains would be able to exhibit rotation around the aryl carbon to nitrogen and carbonyl carbon linkages. Poly(arylene esters) are another example of this class in which the degree of conformational mobility of the isolated chain would be greater but the bulk polymer is never-the-less stiff and displays anisotropic properties due to cooperative interchain ordering and interaction.

Poly(p-phenylenebenzodithiazole), figure 2.2, is an example of the second class, that is, a molecularly stiff rigid rod polymer. That is, the individual polymer chains are rigid in their own right and such flexibility as exists results from bending of, rather than rotation about, backbone bonds.

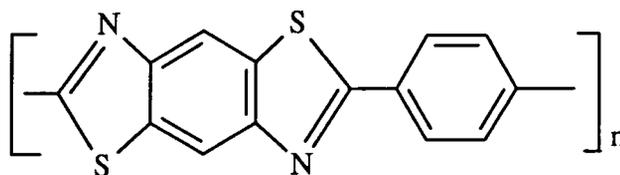


Figure 2.2 Poly(p-phenylenebenzodithiazole).

Technical interest in these types of polymer has become of increasing interest because of the enhanced mechanical properties displayed by high modulus fibres and mouldings produced from certain rigid polymers.^[M1,K4] The initial discovery was made that poly(p-phenyleneterephthalamide) formed liquid crystalline solutions from which it was possible to spin high modulus fibres. These fibres exhibited a higher specific modulus than steel and were thermally stable having a small thermal expansion coefficient.^[K9]

The major holdback to the technological development of rigid chain polymers lies in their inherently low solubility and high melting points. Both of these factors mean that processing of rigid chain polymers is difficult and that investigations of the polymers properties by traditional solution or melt techniques are fraught with great difficulty and virtually impossible by established techniques developed for flexible chain polymers. The cause of these problems lies in the rodlike nature of the polymers. Flexible macromolecules can adopt an infinite number of conformations in solution or in the melt. A substantial increase in entropy is therefore associated with melting or dissolution of a flexible polymer making the process thermodynamically favourable. A molecularly rigid rod polymer does not have any inbuilt flexibility by definition and, thus, it is not possible for it to experience any alteration in shape regardless of its state of aggregation. Thus, the action of dissolution or melting requires the cleavage of intermolecular forces but does not lead to as large an increase in entropy; the processes of melting and dissolution are thus energetically unfavourable for all rigid rod polymers and particularly so for molecularly rigid rod materials.

2.1 Comparison of the phase behaviour of flexible and rigid macromolecules.

The theoretical phase behaviour of flexible and rigid rod macromolecules can be compared in solution or in the melt and the results which can be predicted for both are described below.

Flexible polymers will adopt a coiled conformation in the melt and these coils can overlap and tangle with one another. The dynamics of the melt is then governed by the degree of polymerisation and the extent of overlap of the polymer chains. It can be seen that such a melt will be isotropic, that is there is no preferred direction for the chains. On cooling crystallisation may only occur if the polymer chains are able to untangle and adopt a conformation that allows packing on a crystal lattice to take place. As a result flexible polymers normally only form semicrystalline macromolecules when cooled from the melt.

Molecularly rigid rod polymers are not capable of forming entanglements with one another at the kinds of molecular size likely to be attainable. However, at high concentrations the rods will orientate with respect to one another because of interactions occurring between the rods. This orientation causes a constraint to movement of the polymer chains and the dynamics of such a solution or melt can be described. In the melt or in concentrated solution the rigid rods can be envisaged as having domains displaying parallel alignment with respect to one another and the system will exhibit liquid crystalline behaviour. It follows that cooling a melt of a rigid rod macromolecule will lead to a solid state that possesses a highly ordered structure with domains of the rods arranged in parallel alignment. The solid will be highly crystalline.

2.2 Poly(4-oxybenzoate) and poly (p-phenyleneterephthalamide) as examples of rigid polymers.

The polymerisation reaction of p-hydroxybenzoic acid has been known since the end of the last century and as such is amongst the oldest of polymerisations recognised

in polymer science.^[K5] Fischer and Freudenberg polymerised p-hydroxybenzoic acid and vanillic acid (4-hydroxy-3-methoxybenzoic acid) and found that their solubilities decreased rapidly with increasing degree of polymerisation.^[F9] Economy^[E1] carried out the first systematic study of the polyester and utilised electron and X-ray diffraction to investigate the structure of the polymer. Leiser^[L2] carried out more electron diffraction work after Kricheldorf and Schwarz^[K6-8] had improved the polymerisation reaction to produce higher molecular weight products. In 1983 Leiser reported that poly(4-oxybenzoate) forms two orthorhombic modifications at room temperature and both are transformed into a pseudohexagonal phase at 330°C.^[L2] On cooling back to room temperature a mixture of the orthorhombic forms is again seen along with a number of structural defects. The polymer does not exhibit a melting process making moulding by traditional techniques impossible and moulding has only been achieved by an expensive high energy forging process, somewhat akin to the processes used in powder metallurgy.

In the case of another rigid rod macromolecule, poly (p-phenylene terephthalamide) the polymer is sufficiently soluble in concentrated sulphuric acid to allow processing from solution.^[M1,K9,C2] As would be expected, processing from such an aggressive solvent gives rise to technical problems. The polymer is the aramid upon which the high strength, high modulus fibres of Kevlar are based.

A solution to the processing problems of rigid rod polymers would be to develop ways in which the melting point of the polymers could be reduced and the solubility of the polymers could be increased without loss of the desirable mechanical properties. Such alterations would also allow the physicochemical properties of the polymers to be investigated by traditional solution or melt techniques.

2.3 Techniques for lowering the melting point and improving the solubility of rigid polymers.

Since the low solubility and high melting points of rigid chain polymers are a

result of the stiffness of the polymer backbone it should be possible to bring about the lowering of the melting point and to improve the solubility of rigid chain polymers by making modifications to the structure of the macromolecular main chain. Some ways in which the backbone of the polymer could be modified are discussed in this section.

I) Addition of flexible spacer units along the polymer backbone.

Copolymerisation of the rigid rod monomer with flexible comonomer groups leads to the formation of a rigid polymer containing flexible spacer units.

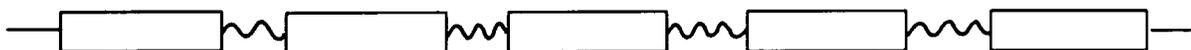


Figure 2.3 A polymer backbone consisting of alternating rodlike (□) and flexible (∩) units.

Whilst this modification brings about the required changes in the melting point and solubility of the polymer the addition of the flexible units greatly reduces the rigidity of the final polymer and the rodlike behaviour of the macromolecule is lost along with its original interesting properties. This method of adapting the rigid polymer chain must be evaluated for the reaction under consideration in order to decide whether the improvements in the solubility properties of the final polymer outweigh the inevitable loss in rigidity; it may be possible to arrange the ratios of the comonomers in such a way as to achieve a reasonable compromise between the two effects.

II) Disruption of the crystal structure via inclusion of bends into the polymer backbone.

The crystal structure of the rigid rod polymer can be disturbed by building bends into the main polymer chain.

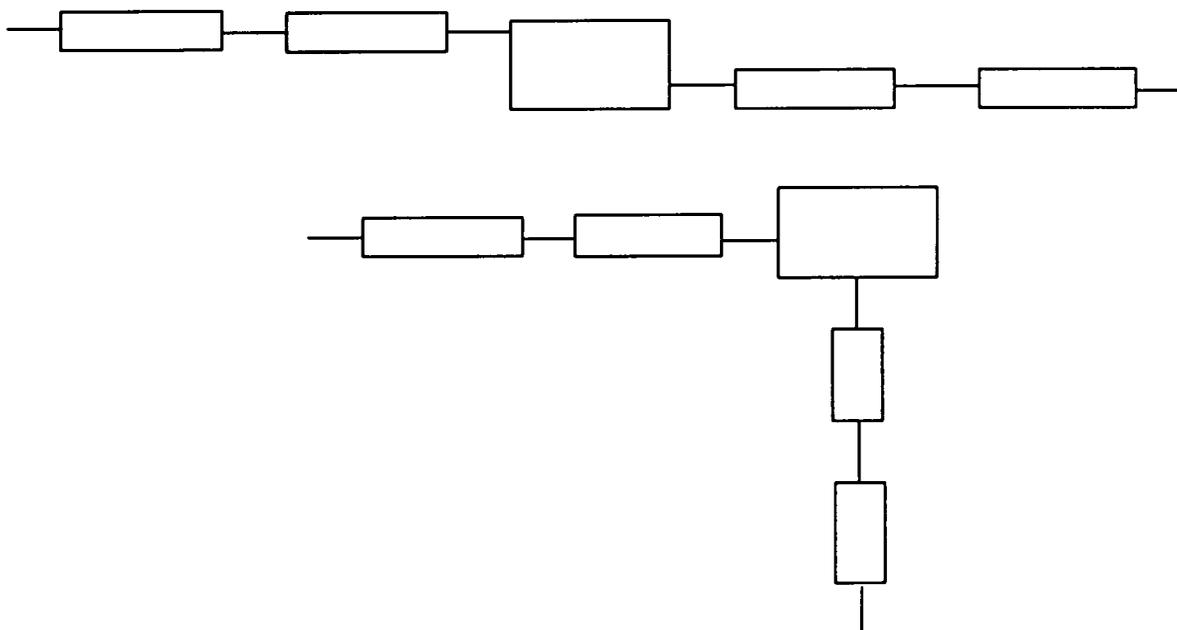


Figure 2.4 Rigid polymer chains containing bends.

This has the effect of lowering the melting point of the polymer. Examples of this technique being put to use are described in section 2.4.

III) Addition of flexible side chains to the polymer backbone.

A third technique for bringing about the required change in properties is to attach flexible side chains to the main polymer backbone.

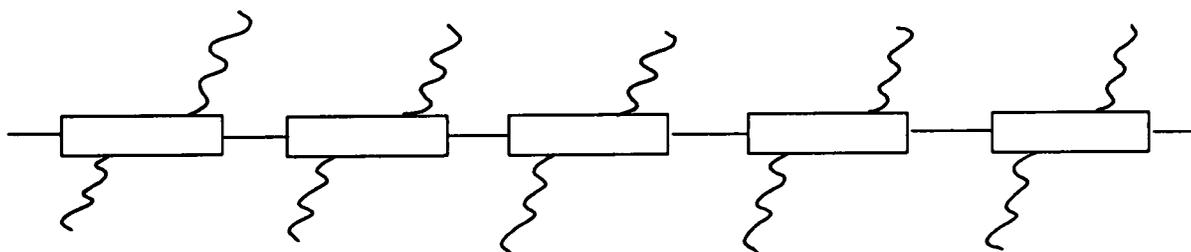


Figure 2.5 A rigid rod polymer main chain with flexible side chains attached.

The flexible side chains can be thought of as a solvent which is permanently bound to the polymer and they have the effect of lowering the interactions between the main polymer chains. The side chains are able to adopt a wide number of

conformations on dissolution or in the melt providing a large increase in entropy and making the processes far more thermodynamically favourable than in the case of the polymer without side chains. This approach has been widely adopted and will be discussed in section 2.5.

2.4 Synthesis of rigid polymers with bends along the polymer backbone.

A large number of polyesters and polyamides have been synthesised using readily accessible fully aromatic hydroxycarboxylic acids, phenols and amines. Hoechst-Celanese utilised 2-oxy-6-napthaloyl and p-oxybenzoyl units to form a copolymer, "Vectra", which shows disturbance of crystallisation via the introduction of bends into the polymer chain.^[C2] The polymer adopts a conformation that can be described as a crankshaft-like structure along the polymer chain, see figure 2.6.

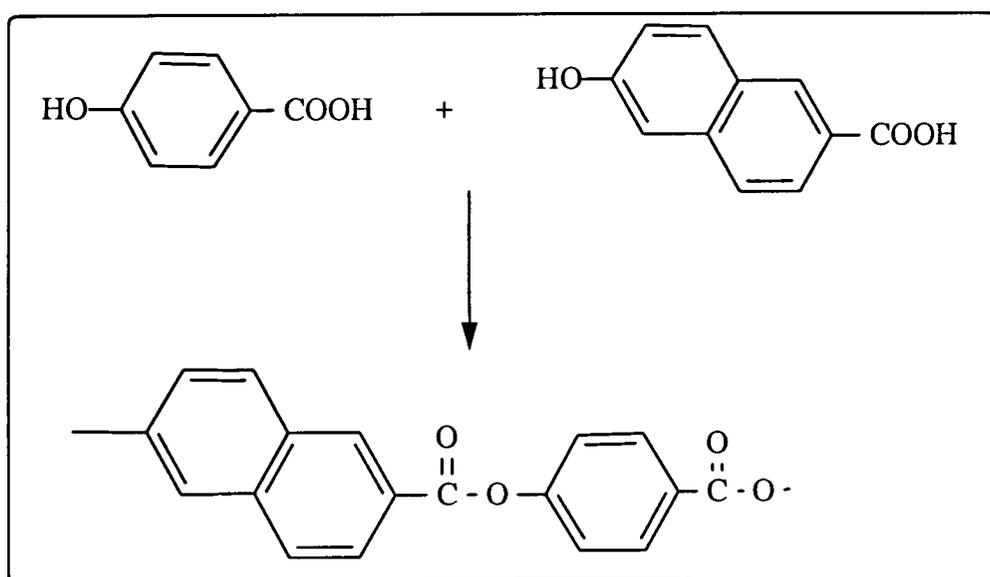


Figure 2.6 Synthesis of Vectra.

The resulting copolyester is processable from N-methylpyrrolidone solution.

The copolyamide which results from reaction of the monomers shown in figure 2.7 is able to adopt either a coiled or an extended conformation due to the 3,4'-linkage

of the diaminodiphenyl ether derived repeat unit. This allows the influence of intermolecular interactions on the chain conformations to be investigated.^[B8,M3]

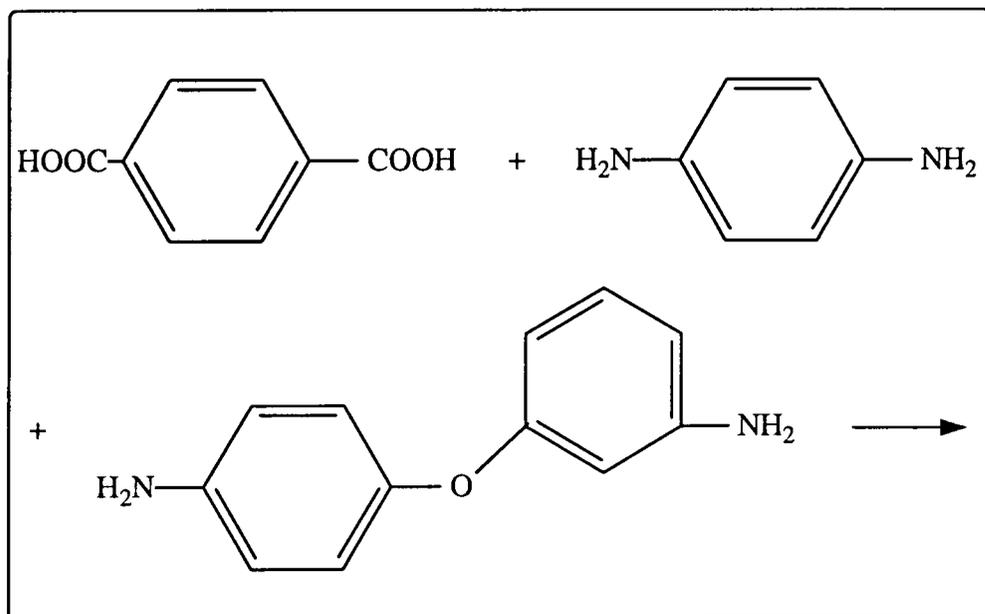


Figure 2.7 Synthesis of a processable copolyamide.

Aromatic polyesters can be processed from the thermotropic mesophase if the amount of disruptive units along the main polymer chain is sufficient. Of technical importance is the copolyester of p-hydroxybenzoic acid, terephthalic acid and 4,4'-biphenyldiol known as "Xydar".^[K9] The polymer is processed by injection moulding and as with other liquid crystalline materials its modulus was found to be greater in the direction of flow rather than transverse to the direction of flow. At 302°C the material shows a tensile strength of 3800psi, (compared with 4500psi for natural rubber and 3000psi for styrene butadiene rubber), and it has a continuous use temperature of 240°C for mechanical, impact and electrical properties.

2.5 Rigid polymers containing flexible side chains.

The appendage of flexible side chains to a rigid rod polymer chain as a method of lowering the melting point and increasing the solubility of the polymer was mentioned

in section 2.3. This procedure has the advantage over other techniques that both the rigidity and the homogeneity of the main chain are retained. When the polymer is melted or dissolved the side chains can adopt a vast number of conformations in the same way that a flexible polymer chain can, thus the flexible side chains can be considered as being present as a bound solvent. It is therefore possible to alter the amount of bound solvent as a consequence of varying the length and/or the frequency of the flexible side chains.^[B6] This concept is exemplified by derivatives of poly(γ -benzylglutamate) and other helical polypeptides where the phenyl ring of the benzyl ester has long n-alkyl substituents attached to it and the polymer is soluble in organic solvents in spite of the conformational stiffness of the main polymer chain resulting from the α -helix adopted by this polyamide.^[U1]

Lenz was first to introduce polymers containing flexible side chains.^[M2,B9] In 1983 he copolymerised terephthalic acid and 2-n-alkylhydroquinone to give a comb-like polymer. Lenz showed that the melting point of the polymer decreased steadily with increasing length of flexible side chain. Since then a variety of polymers with this comb-like structure have been synthesised, some examples of which are described in figure 2.8.^[M2,L3,B7,E6,B9-11]

All the polymers (I-VIII), figure 2.8, show the same pattern of increasing solubility and decreasing melting point with increasing length of flexible side chain. These improvements mean that polymerisation reactions can be carried out in solution to give polymers of much higher molecular weight than is attainable with the unsubstituted systems and that it is possible to purify the polymers by reprecipitation, thus giving access to genuine high polymers of well defined structure. The addition of side chains has enabled some rigid rod polymers to be made sufficiently soluble to allow characterisation by the traditional solution methods used for flexible polymers.

There are several examples of X-ray diffraction studies being used to study rigid rod polymers containing flexible side chains.^[B11,B12,S2,S10] The studies have been carried out in an attempt to investigate the structure and solid state organisation of the

polymers. In particular the conformation adopted by the side chains has been investigated and the morphology of polymers containing different lengths of side chain. The change in morphology of the polymers with increasing temperature has also been discussed.

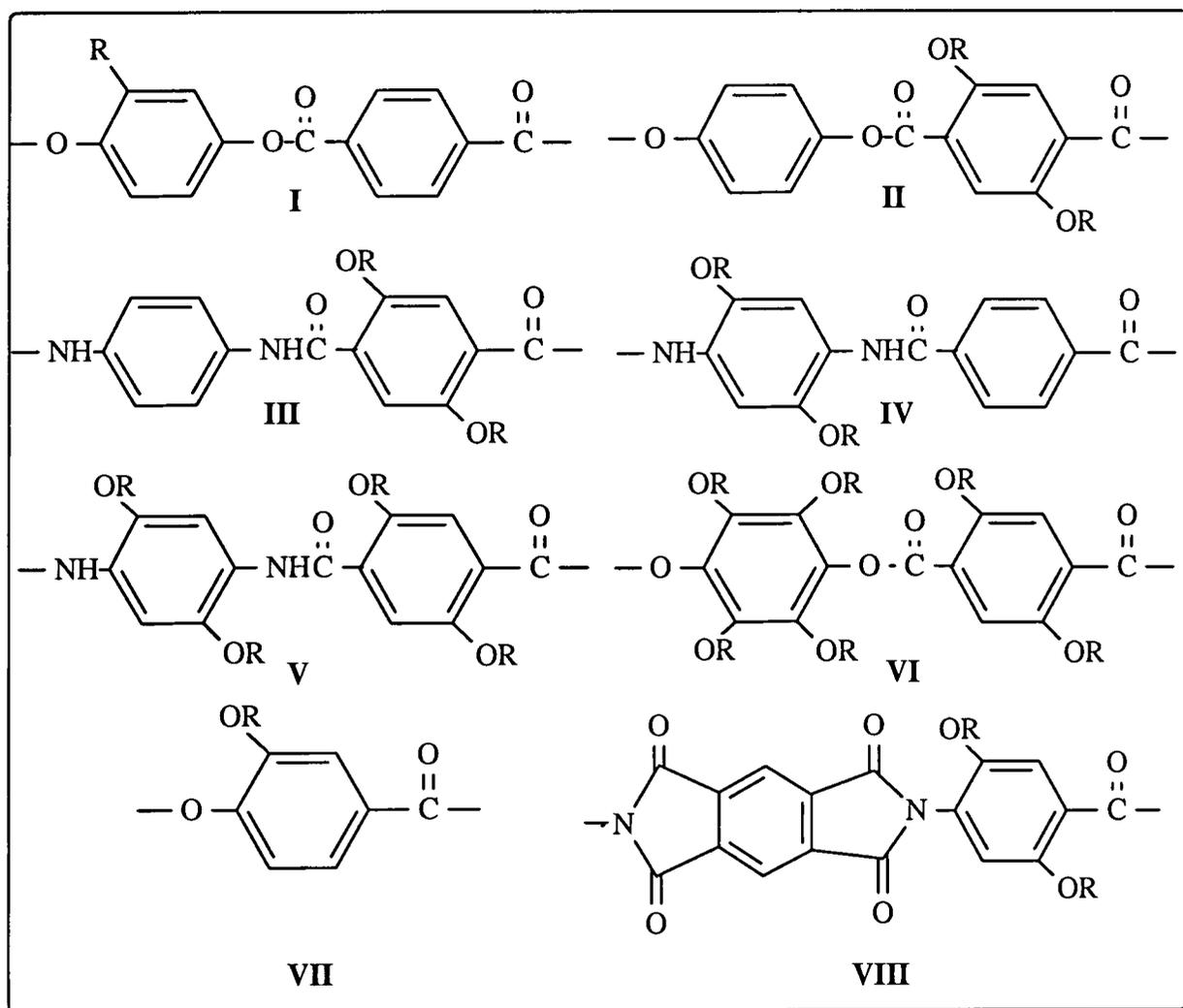


Figure 2.8 Rigid polymers containing flexible side chains.

In their investigation of the morphology of rigid rod polyesters containing flexible alkoxy side chains of different length, Schrauwen et al^[S2] studied solution cast films. Layered structures were observed with the backbone forming layers which were separated by the side chain hydrocarbons. They defined two structural modifications due to different modes of organisation of side chains, modification A, which they

defined as having the side chains normal to the backbone layers and modification B, where the side chains were parallel to the backbone layer, see figure 2.9.^[B2]

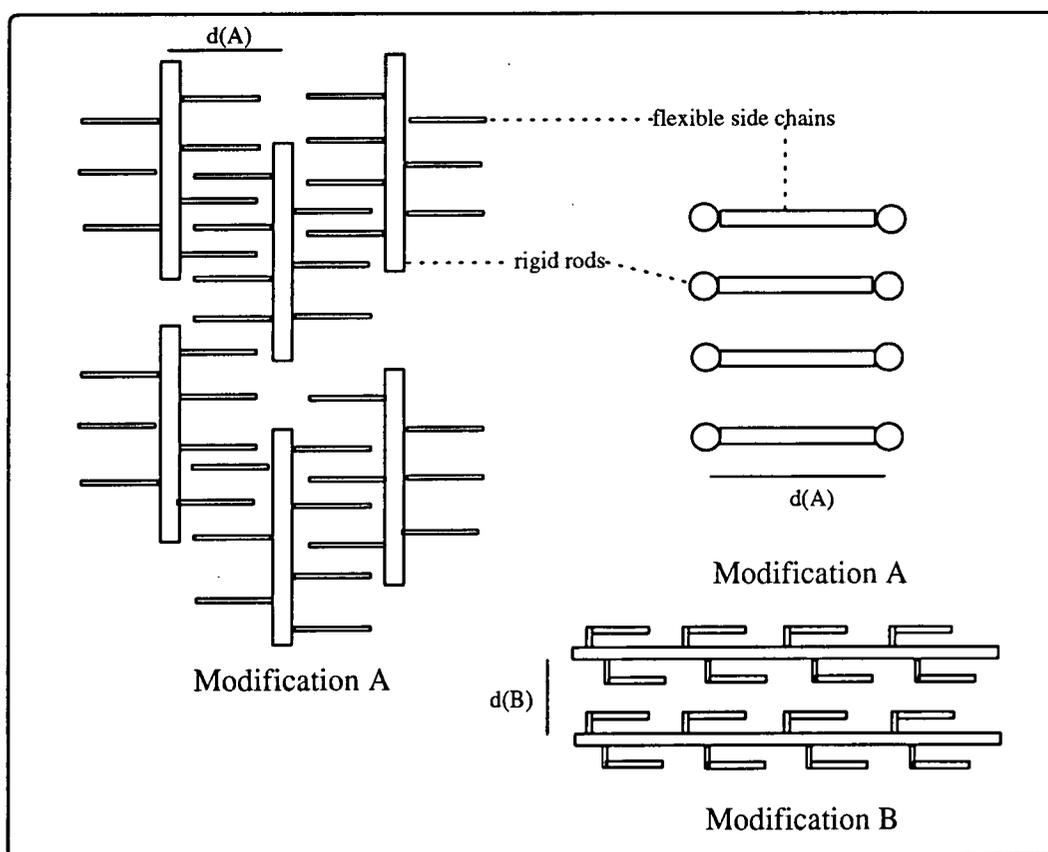


Figure 2.9 Model describing the molecular structure of modifications A and B of polymers containing flexible side chains.

The d-spacings (d) defined in figure 2.9 can be determined from X-ray diffraction patterns of the polymer sample. The model is an idealised one and at high temperatures there are likely to be a number of structural defects.

Stern utilised X-ray diffraction in order to study the phase behaviour of poly(3-n-alkyl-4-oxybenzoate)s (PAOB).^[S6] He found that when $n = 3$ the structure and thermal transitions of the polymer were controlled by the main chain. However, with longer side chains the packing was determined by the most favourable arrangement of the side chains. This was true for both the solid state and the mesophase.

The type of result that can be obtained using this sort of system is exemplified by a consideration of the results published for the polyester II, see figure 2.8.^[B7,B10-11] X-ray diffraction studies showed the polymer to be highly crystalline at room temperature and the Bragg reflections indicated that two layered modifications were present.^[B11] The structural differences were due to the conformations adopted by the side chains and the spacings indicated that the length of the side chains was decisive in the build up of the crystal structure. For this polymer, as for most others of this type, three first order phase transitions are observed. At low temperatures an increase of disorder in the packing of the side chains is observed which is compared to the transition from the crystalline to the liquid phase in n-alkanes. Increasing the temperature leads to the formation of a mesophase and finally to the disappearance of the liquid crystalline order of the polymer as an isotropic melt is formed. Polyester II forms nematic mesophases when the side chains are short (2-6 carbon atoms) and with longer side chains ($n > 8$) the phase modification already present in the solid state remains stable into the liquid crystalline phase. Such phase behaviour is characterised by the observation of strong Bragg reflections.

Polyester I, see figure 2.8, also forms nematic mesophases when the length of side chain is shorter than twelve carbon atoms, above this length layered mesophases are formed.^[B7,B10-11]

2.5.1 The production of soluble poly(p-phenylenes).

Over recent years there has been much interest in poly(p-phenylenes) due to the possibilities that they were expected to exhibit good thermal and oxidative stability and that they would be electrically conducting in the oxidised or reduced states.^[K12,S8] Attempts to synthesise poly(p-phenylenes) encountered a number of problems; direct routes only resulted in low molecular weight materials that were insoluble making it impossible to carry out adequate structure elucidations on them.^[K10,K11,Y1,B12,I1,S7,T2] Synthetic routes from precursors led to higher molecular weight materials but the

resultant polymers had many structural defects.^[M4,B13-14] The problem of the low solubility of poly(p-phenylene) can be exemplified by considering that while paraterphenyl has a solubility of 8.5g l⁻¹ in toluene, sexiparaphenylene is only soluble to the extent of 10mg l⁻¹. Ways in which the solubility of poly(p-phenylenes) could be improved were therefore of great interest.

Kern and Heitz^[K1] and others^[H4,K13] proved that methyl groups attached to oligomeric phenylenes had the effect of increasing their solubility and Kovacic^[J4] had shown that it was possible to make poly(p-phenylenes) soluble by carrying out Friedel-Crafts alkylation reactions on them. In the light of these findings Wegner et al^[R6] decided to employ an adaptation of the Yamamoto synthesis in order to couple 1,4-dibromo-2,5-dialkylbenzenes in an attempt to form soluble poly(p-phenylenes), figure 2.10.

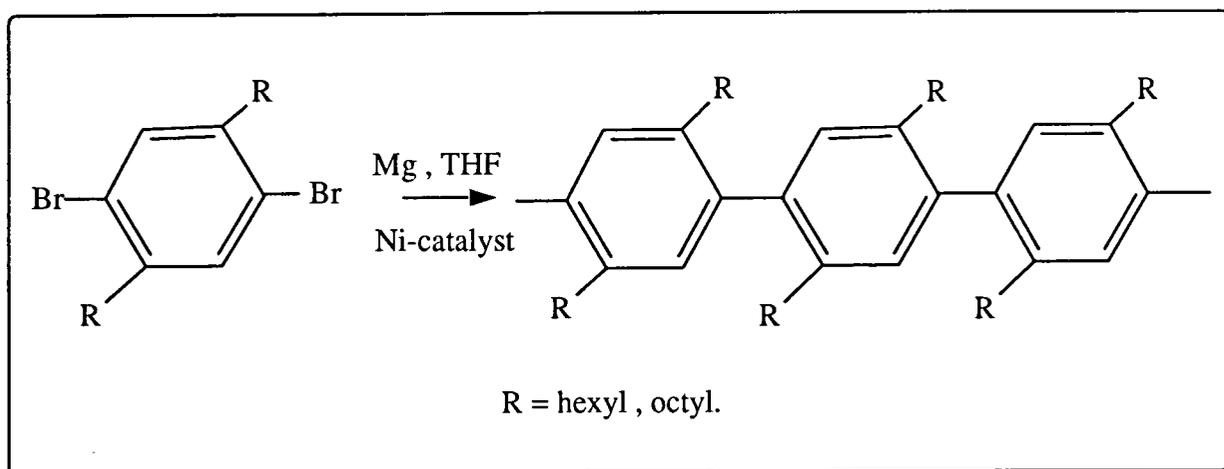


Figure 2.10 Synthesis of soluble poly(p-phenylenes) via the Yamamoto synthesis.

They employed hexyl or octyl side chains following their assumption that these would be long enough to provide sufficient solubility but short enough to suppress side chain crystallisation. The resulting polymers were found to have a degree of polymerisation of around 12 and were soluble in acetone to the extent of 4g l⁻¹.

In an attempt to improve the degree of polymerisation of the polymers the palladium catalysed coupling reaction of 4-bromo-2,5-dihexylbenzeneboronic acid was carried out, figure 2.11.^[R5]

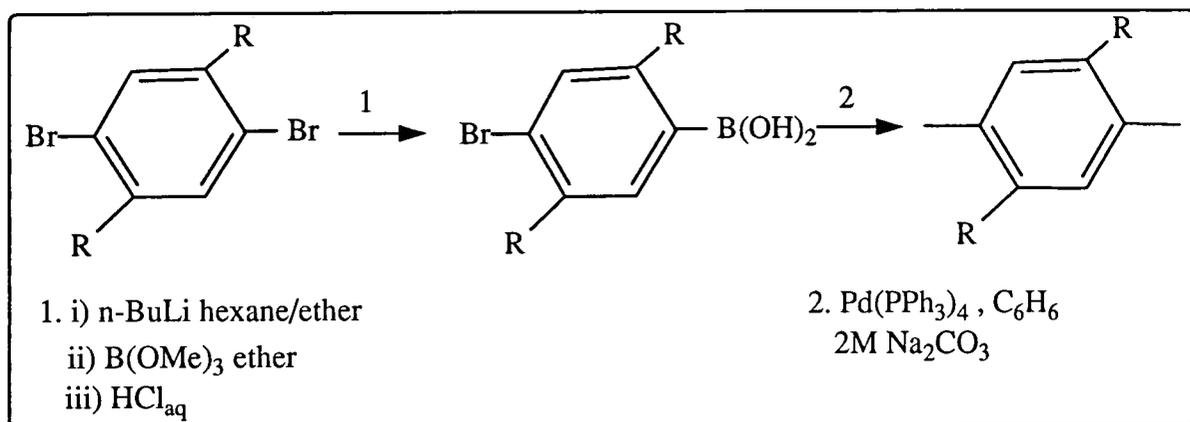


Figure 2.11 Synthesis of soluble poly(p-phenylenes) via the palladium catalysed coupling of 4-bromo-2,5-dihexylbenzeneboronic acid.

In a subsequent paper both the length and the frequency of the side chains along the main polymer chain were altered in order to assess the effect this had upon the properties of the polymers.^[R4]

DSC investigations on polymers containing varying length of side chains showed two transitions. The first transition was around 70°C and did not vary greatly with side chain length; it was proposed that the transition was associated with side chain melting. The second transition varied from 160 to 280°C; it was proposed that this was associated with the transition into the isotropic melt. This was confirmed by X-ray and polarizing microscopy investigations. Copolymers were also synthesised from functionalised telomers, figure 2.12, in order to investigate how the frequency of the side chains effected the properties of the final polymers. As would have been expected, the solubility was found to be greater for materials having longer, or a greater frequency of alkyl side chains. The copolymers were synthesised with degrees of polymerisation of up to 37, using the chemistry shown in figure 2.11.

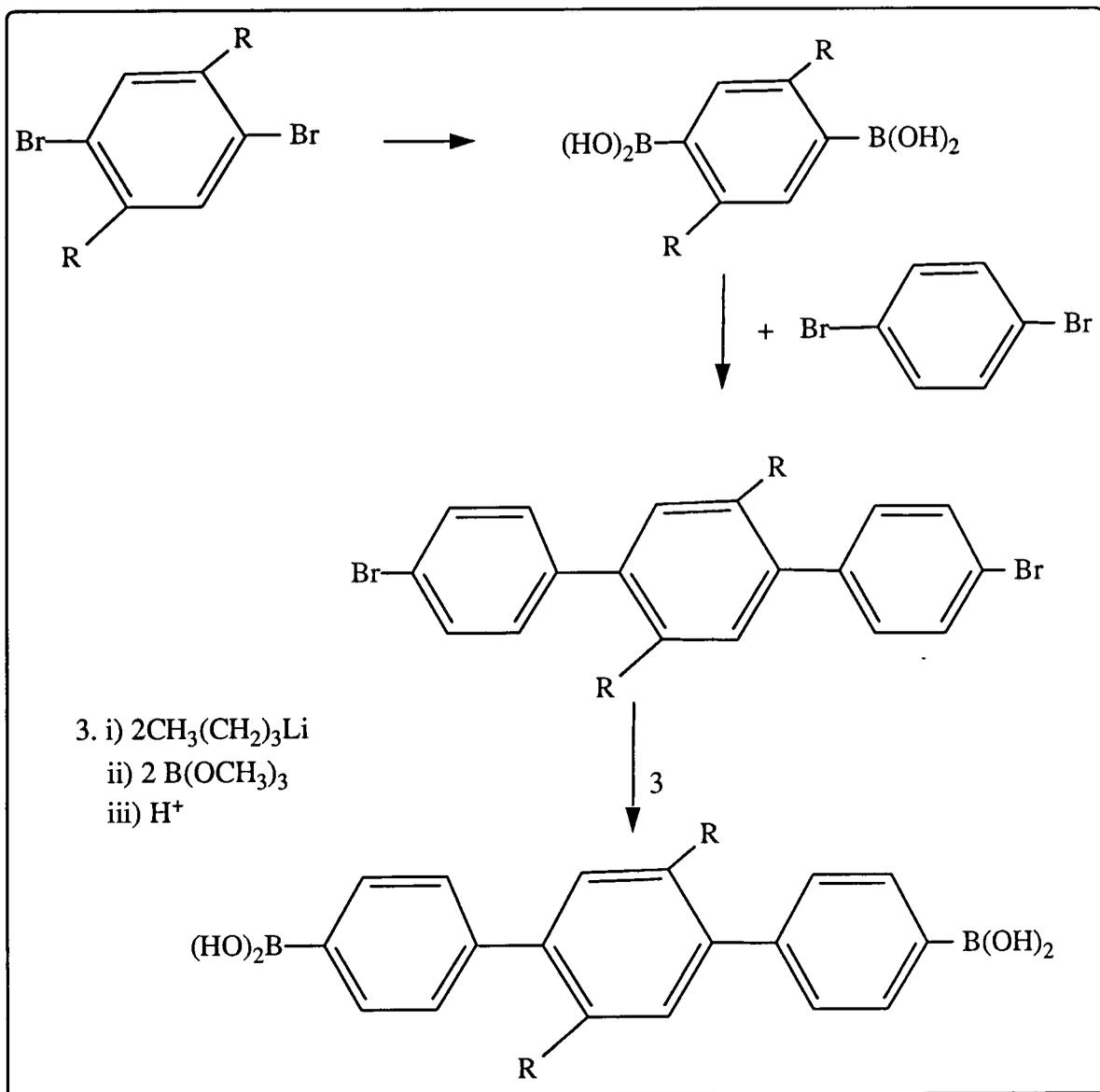


Figure 2.12 Synthesis of copolymers with varying frequency of flexible side chains.

The work was continued by applying the palladium catalysed coupling method to synthesise poly(arylethers), poly(arylketones) and poly(arylbenzils), figures 2.13, 2.14, 2.15.^[R2] The polymers which resulted from the reactions were found to have degrees of polymerisation in the range of 12-27.

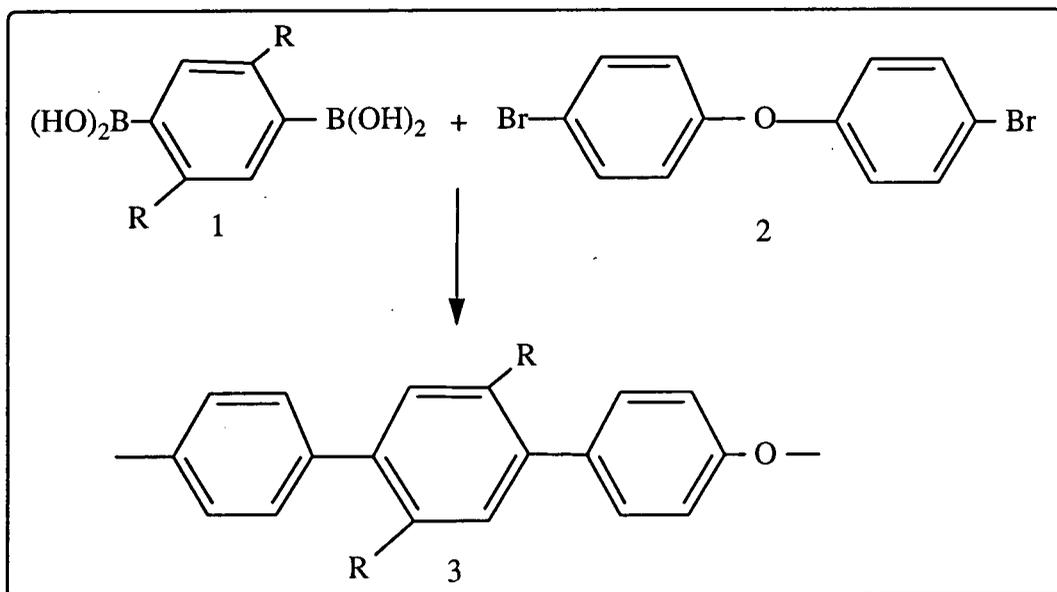


Figure 2.13 Synthesis of poly(arylethers) containing flexible side chains.

These types of polymer are often formed under strongly electrophilic conditions which can result in polymers with ill defined structures. The palladium catalysed coupling reaction has the advantage of being regiospecific and the resulting polymers are connected entirely by para linkages.

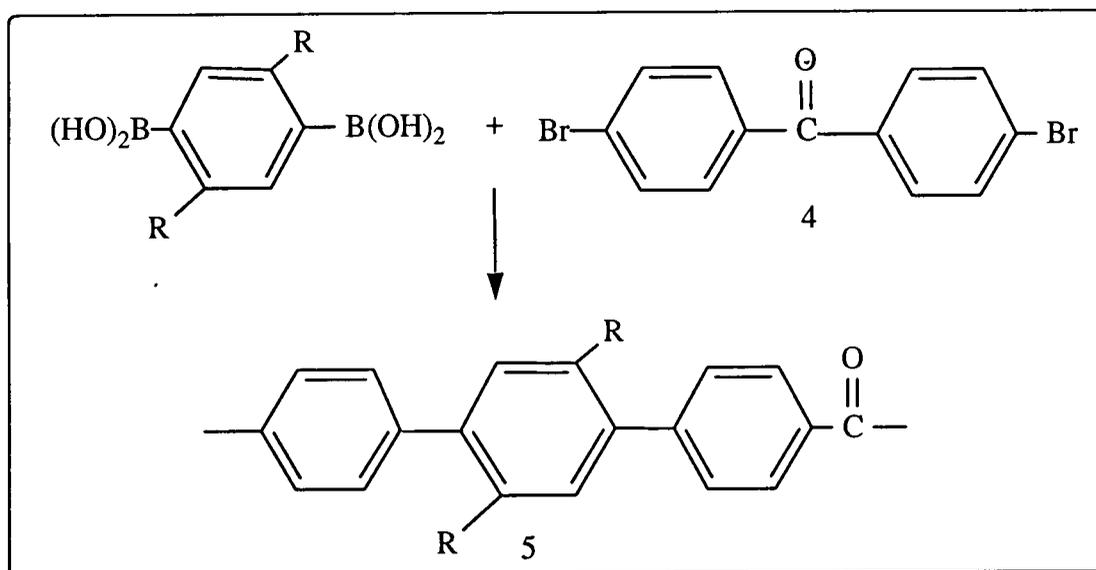


Figure 2.14 Synthesis of poly(arylketones) containing flexible side chains.

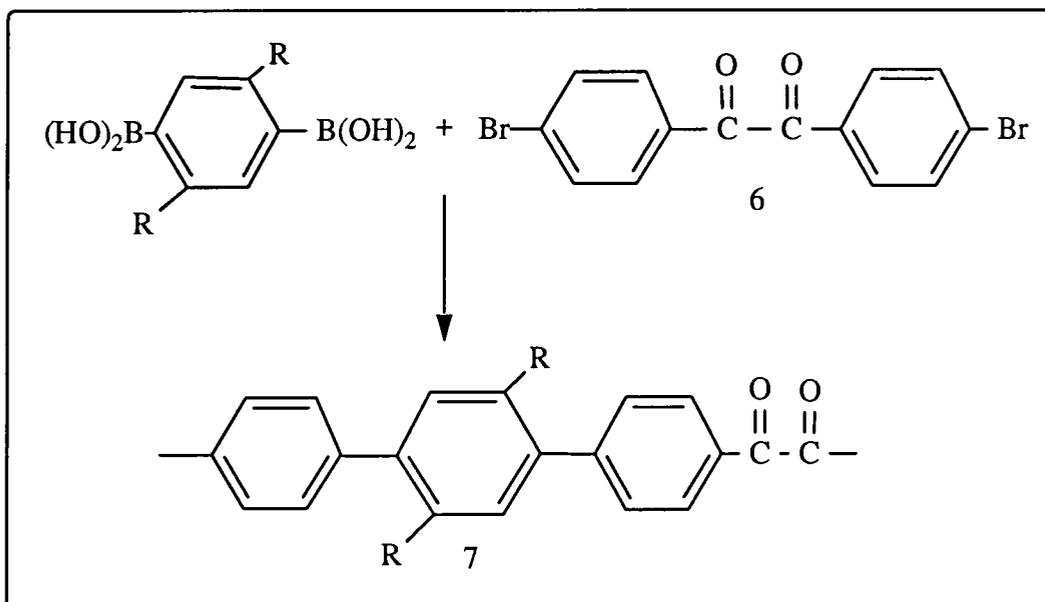


Figure 2.15 Synthesis of poly(arylbenzils) containing flexible side chains.

2.5.2 Processable cooperatively rigid rod polyesters.

Wegner's group have synthesised cooperatively stiff polyesters containing flexible alkyl and alkoxy side chains.^[R5,R6,S2,D2]

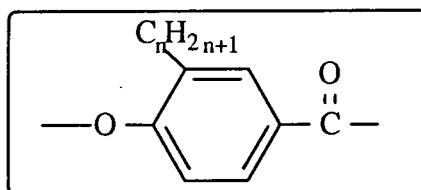


Figure 2.16 Poly(3-n-alkyl-4-oxybenzoates).

Poly(3-n-alkyl-4-oxybenzoates) (PAOB) with $n = 3 - 18$, see figure 2.16, were synthesised and the polymers were found to be sufficiently soluble to allow the Kuhn length, section 2.6 to be measured (it turns out to be $100-200\text{\AA}$).^[S2,S3] The unit cell dimensions for PAOB-n when $n=3$ and $n=5$ were determined. The polymers were all found to form thermotropic mesophases, for $n=3$ a nematic phase was found, for $n=5$ there was a transition from a smectic-like layered mesophase to a nematic mesophase

and when $n \geq 6$ the polymer formed layered mesophases and all polymers, with the exception of $n=3$, showed a transition to the isotropic state. This transition temperature was lowered monotonically with increasing length of flexible side chain.

A series of conformationally stiff, rodlike polyesters containing flexible alkoxy side chains were also synthesised and studies carried out to determine the structure and properties of the polymers in a variety of states; solid, mesophase and melt, figure 2.17.^[S2] The flexible side chains were found to lead to the formation of liquid crystalline phases at temperatures where degradation was not a problem. Also, with side chains of sufficient length the systems were seen to form layered mesophases as shown by characteristic Bragg reflections which varied with the side chain length. Wide angle X-ray scattering (WAXS) provided a method by which it was possible to describe the layering adopted by the systems at a molecular level; studies were carried out on both the as made polymer and on polymer films cast from solution. The effect of temperature on the conformation of the polymer was also investigated. The polymers formed layered structures with the polymer backbones being separated by the flexible side chains. When films of the polymers were cast from solution the side chains adopted one of two orientations; A when the side chains lay normal to the polymer backbone and B when they lay parallel to the polymer backbone.

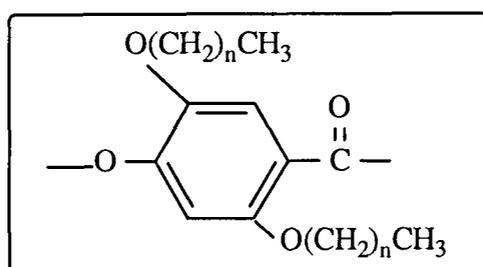


Figure 2.17 Poly(3-n-alkoxy-4-oxybenzoates).

2.5.3 Synthesis of soluble polythiophenes.^[G2]

Soluble derivatives of polythiophene have been synthesised via the reaction scheme outlined in figure 2.18 in an attempt to produce processable, highly conductive

materials. Polythiophene is traditionally synthesised electrochemically which results in uncertainty as to the polymer structure and in over oxidation of the polymer.^[K2]

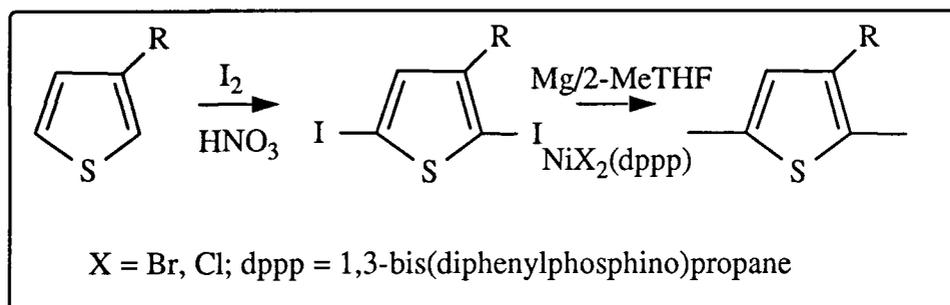


Figure 2.18 Synthesis of soluble polythiophenes.

When R = H an insoluble polymer results. However, polymerisation of a thiophene monomer with a flexible alkyl side chain present at the three position produced a soluble polymer. When alkyl side chains of six or eight carbon atoms are present molecular weights of 48,000 are observed. The side chains are found to render the polymers amorphous and they were not as highly conductive as unsubstituted materials even after stretch alignment.^[E2-4,K15]

The synthetic strategy has been applied to the synthesis of soluble poly(3-octylpyrrole), however, to date there has been little information published on this polymer.^[M6]

2.5.4 Synthesis of soluble ladder polymers.

Flexible alkyl side chains have been attached to ladder polymers in order to solubilise these conformationally rigid species. Schlüter employed the synthetic route outlined in figure 2.19 to produce a series of soluble ladder polymers.^[V2]

The resulting polymers were sufficiently soluble in chloroform to allow nmr spectra to be run and the structural proof of the polymers is based upon these spectra. Thermogravimetric analysis showed the polymer to be stable up to 300°C after which loss of water, oxygen and the side chains occurs. The polymers were found to have a

Mn of 16500 and have a Mw of 29000.

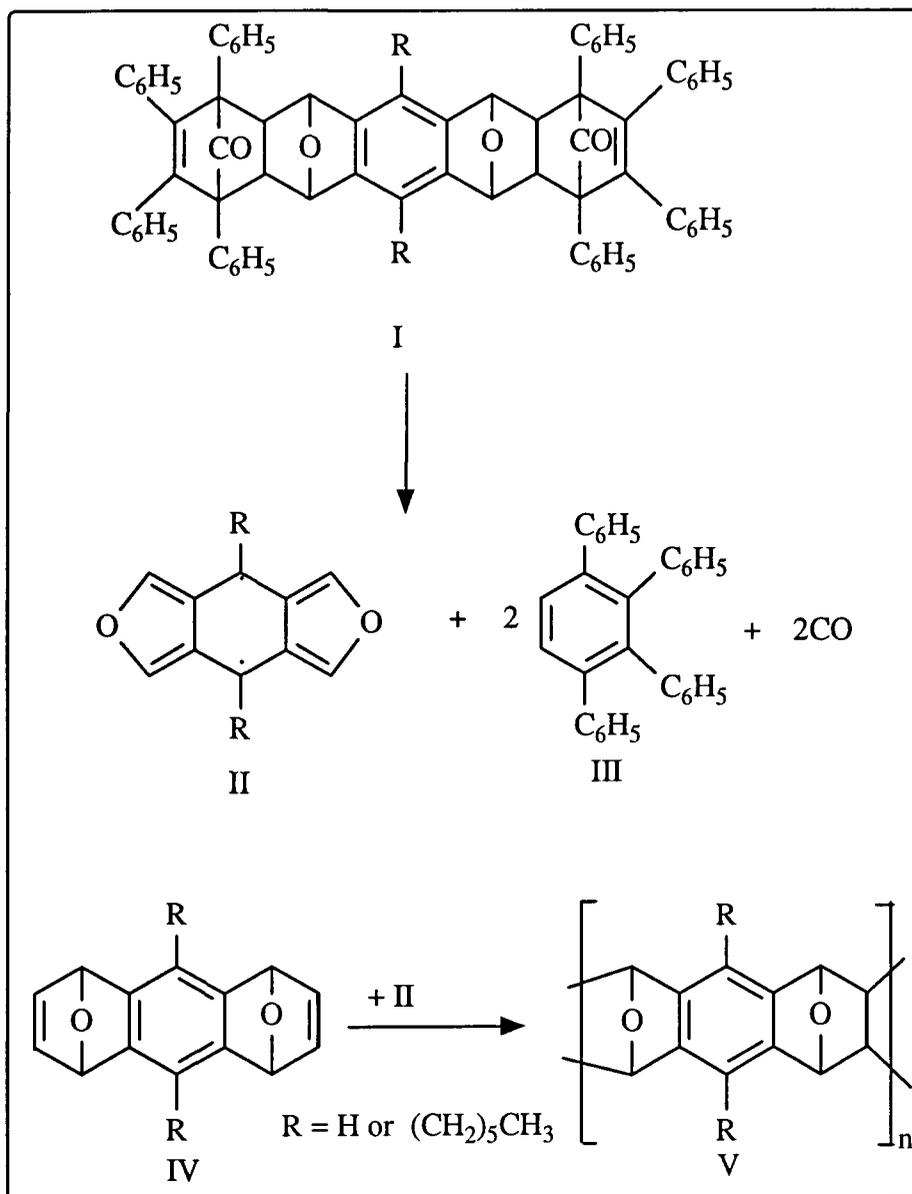


Figure 2.19 Synthesis of soluble ladder polymers, as carried out by Schlüter.^[V2]

As can be seen from the examples described above, the addition of flexible alkyl side chains to a rigid polymer has been found to be an effective method for improving the processability of the polymer. Details of the application of this method to the molecularly rigid rod polymers which are the subject of this project are described in Chapter three.

2.6 Determination of the Rigidity of Polymer Chains.

While there is much information about the shapes and conformation of flexible polymer chains in solution, very little is known about the conformation of rodlike macromolecules. This is mainly due to the insolubility of the materials since techniques for investigating the conformational properties of polymers generally require dissolution of the macromolecule.

Assuming that there are no structural faults along the polymer chain then there are three models which can be used to describe the rigidity of the chain and its conformation: Flory's rotational isomeric state model describes the conformation of the chain and its shape by the use of molecular parameters such as conformational energies and torsion angles;^[F12,F13] the Kuhn model considers the polymer chain as a series of rods possessing the Kuhn length l_k joined together by flexible joints;^[F12] Kratky and Porod consider the rigid rod as a worm-like chain or a continuously bent stick. Whilst overall the chain appears to be flexible, on a smaller scale there is a section over which the chain can be considered as being rigid. This section is of a certain length known as the persistence length (a) and the overall chain rigidity is dependant on the persistence length. Of the above models the determination of the experimental parameters necessary to use the models is more easily accomplished for the later two models. The experimental techniques used to determine the parameters include, scattering methods (light, X-ray and neutron scattering),^[F12] depolarised light scattering,^[F12,Z1] electric and magnetic birefringence^[F12,Z1] and flow induced birefringence.^[T4]

Experiments carried out by Wegner into the conformation of both polydiacetylene^[A7] and poly(phthalocyanatosiloxanes) have shown that these polymers display rodlike behaviour.^[C6]

2.7 Synthesis and characterisation of linear rigid rod polymers.

2.7.1 Introduction.

This section details some of the recent synthetic work that has been carried out to produce rigid rod polymers and considers attempts that have been made to improve their processability.

2.7.2 Literature review.

In the late seventies the US Airforce Materials Laboratory began a research programme involving lyotropic liquid crystalline molecularly rigid rod polymers.^[A4] Their interest was aroused by the promise such materials showed with respect to their strength, modulus, thermal stability and environmental resistance. For these properties to be achieved the polymers must exhibit liquid crystalline behaviour. Their research was aimed towards the production of materials the properties of which were comparable with or better than those obtained from fibres currently in use.

Initially the program concentrated on the ladder polymers poly(6,9-dihydro-6,9-dioxobenzimidazo[2,1-b:1¹,2²-i]benzo[lmn][3,8]phenanthroline-3,12-diyl) (BBB) and poly[(7-oxo-7,10H-benz[de]imidazo[4',5':5,6]benzimidazo[2,1-a]isoquinoline-3,4:10,1]-tetra)-10-carbonyl] (BBL), see figure 2.20, from which it was observed that films could be formed.

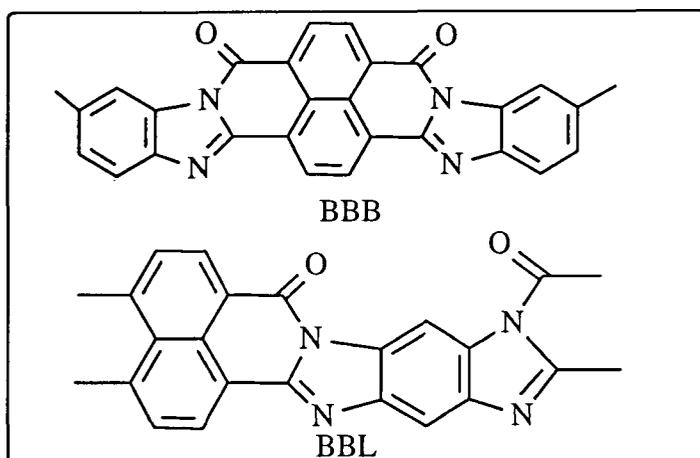


Figure 2.20 The ladder polymers BBB and BBL.

Research subsequently moved onto aromatic heterocyclic systems with a para-ordered geometry. The main class of heterocyclic polymer system investigated which fulfilled the requirements of the aerospace industry was the benzobisazole series; poly(p-phenylene benzobisimidazole) (PBI), poly(p-phenylene benzobisoxazole) (PBO) and poly(p-phenylene benzobisthiazole) (PBT) receiving the most attention, see figure 2.21.

The polymers are prepared by condensation of terephthalic acid with 1,3-diamino-4,6-(p-toluenesulfamido) benzene, 4,6-diamino-1,3-benzenediol dihydrochloride, or 2,5-diamino-1,4-benzenedithiol dihydrochloride in a solution of polyphosphoric acid (PPA).^[A4]

PBO and PBT both form nematic liquid crystalline solutions at low concentrations (5-7%) in methanesulfonic acid and when the polymerisation in PPA is carried out at high concentrations where anisotropic solutions are formed, high modulus fibres can be drawn directly from the reaction mixture. They found that by altering the P_2O_5 content of the PPA during the polymerisation reaction well defined nematic solutions were formed from which processing could take place. When polymerisation took place in the nematic phase the rate of polymerisation was increased and higher molecular weights were achieved than when polymerisation took place in the isotropic phase.

A program of research which encompassed the aspects of theory, synthesis, mechanics, processing and morphology was set up and was aimed at exploiting the potential of ordered polymers as structural materials for aerospace applications. Much of this early work was carried out by Arnold^[A4,A5] who extended his research to cover the structural modification of the rigid rod polymers. He describes the effects of modifying the structure of benzobisazo polymers by adding pendant groups to the main polymer chain without altering the para-ordered geometry of the polymer. The aim of the project was to investigate the solubilising effect of the pendant side groups on the polymer system in new solvents and to look at the concentration effects promoting the

nematic liquid crystalline phase during polymerisation. He was also interested in looking at what length of pendant group could be added before the ability of the polymer to form liquid crystalline solutions was lost.

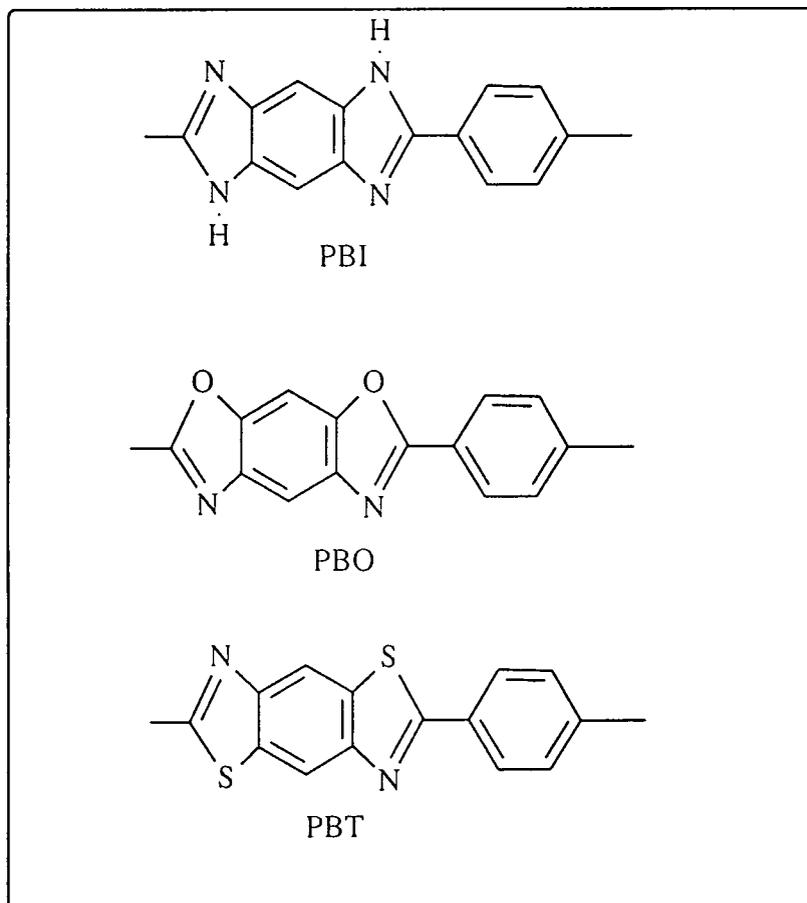


Figure 2.21 The polymers PBI, PBO and PBT.

The preparation of the benzthiazole pendant polymers shown in figure 2.22 was described, the intrinsic viscosities, $[\eta]$, in sulphuric acid were also reported, figure 2.22. The resulting polymers were soluble in sulphuric acid (<1%) unlike the rods without pendant groups but no solubility was found in aprotic solvents. The polymers formed liquid crystalline solutions from which high modulus, high tenacity fibres could be spun.

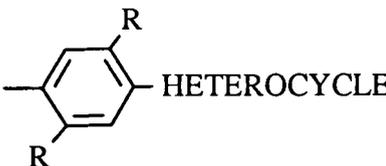
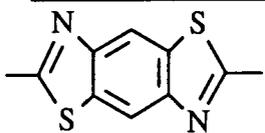
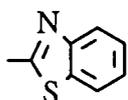
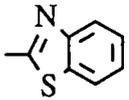
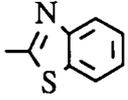
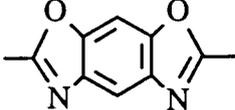
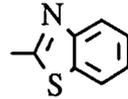
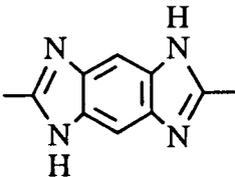
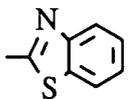
			
HETEROCYCLE STRUCTURE	R	R'	[η]
	H		19.3
"			6.5
	H		4.5
	H		7.5

Figure 2.22 Benzthiazole pendant polymers.

The polymerisation of methyl disubstituted diacids and their derivatives were also detailed, see figure 2.23. The polymers were soluble in sulphuric acid at room temperature and the mono-methyl substituted polymers were more soluble than the disubstituted. Concentrated solutions of the mono-methyl substituted polymer exhibited liquid crystalline behaviour.

Thermal treatment of doped fibres at 450-500°C (N₂) for 30 seconds brought about crosslinking via the pendant methyls and the resulting polymer was insoluble in all acid solutions. The strength of the crosslinked fibres was no better than that of PBT.

In general it was found that structural modification of any polymer system by introducing pendant units always resulted in a sacrifice of some useful mechanical or

physical properties. This had to be balanced with the beneficial aspects of the structural modification on processability.^[C3-5,D5,K17,M7]

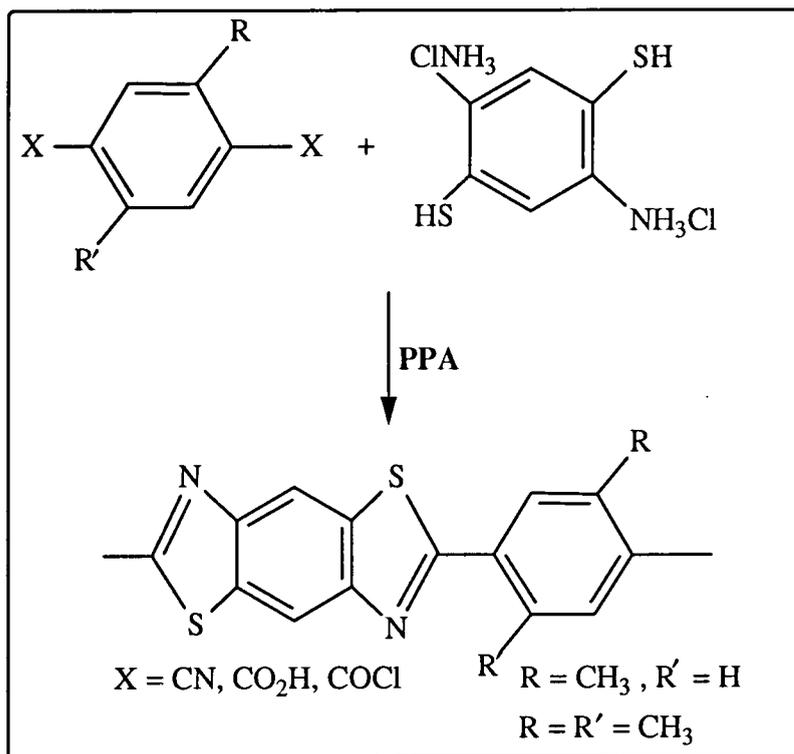


Figure 2.23 Polymerisation reaction of methyl disubstituted diacids and their derivatives.

Another attempt to improve the solubility and modify the properties of PBO and PBT was carried out by Evers and Dotrong.^[E5] Their approach was to incorporate flexible units into the polymer backbone, see figure 2.24. Initial efforts centred on the incorporation of diphenoxybenzene (I) structures into the polymer main chain and later efforts involved the incorporation of 3,3'-biphenyl (II) or 4,4'-(2,2'-bipyridyl) (III) moieties.

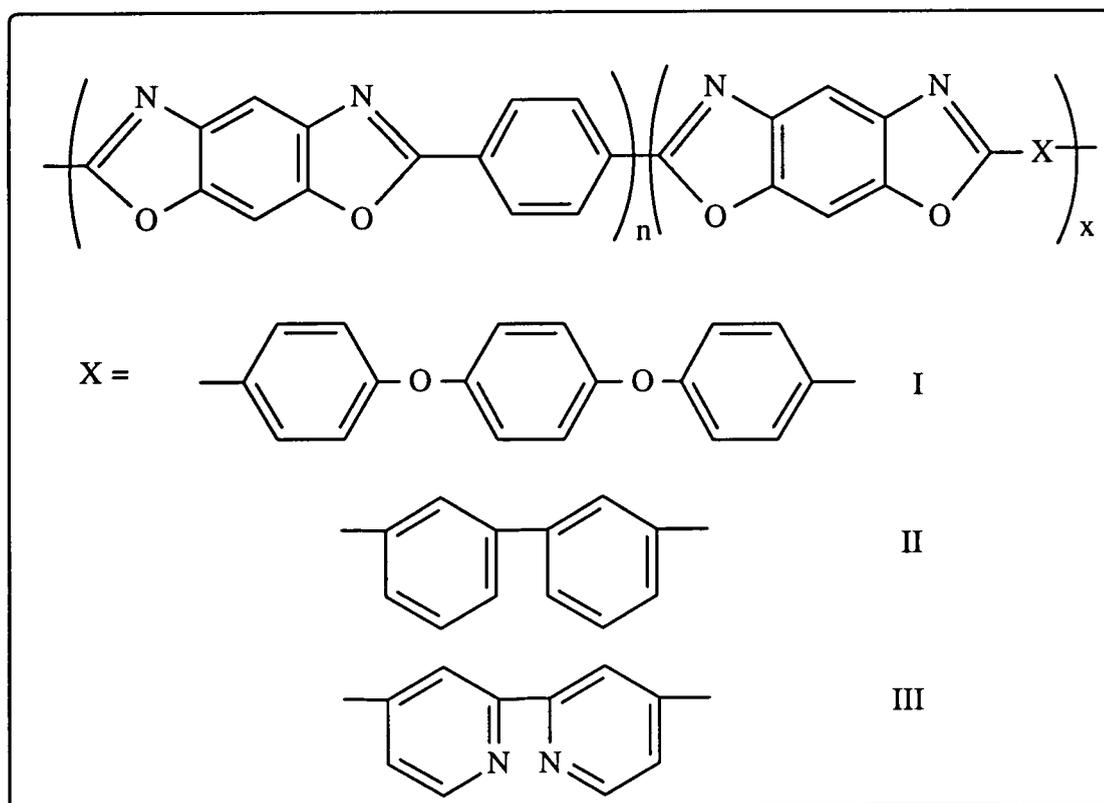


Figure 2.24 Modification of PBO carried out by Evers.

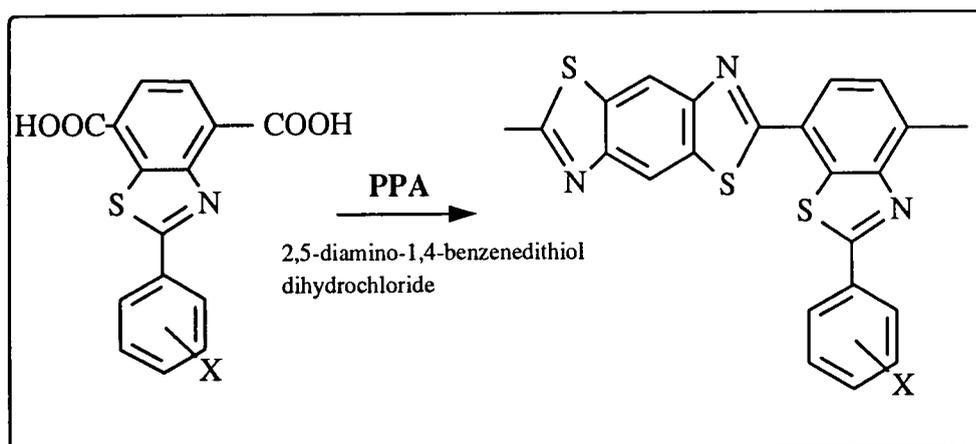


Figure 2.25 Synthesis of benzothiazole polymers with perpendicularly attached phenyl substituents.

Feld et al synthesised benzothiazole polymers with pendant phenyl substituents, see figure 2.25.^[F11] 2-Aryl-4,7-benzothiazole dicarboxylic acids were polymerised with 2,5-diamino-1,4-benzenedithiol dihydrochloride and the properties of the

corresponding poly(benzothiazoles) were investigated. All the polymers were of low molecular weight and no improvement in solubility with respect to the unsubstituted polymers, was observed in common solvents.

Kane^[K16] et al condensed N¹,N⁴-diphenyl-1,2,4,5-tetraaminobenzene with the di-acid chlorides of terephthalic acid, isophthalic acid and 2,5-pyridine-dicarboxylic acid to produce poly(o-phenylamino)amides which were dehydrated to give a series of new N,N'-diphenyl substituted poly(benzimidazoles) (PBI). The resulting polymers are shown in figure 2.26.

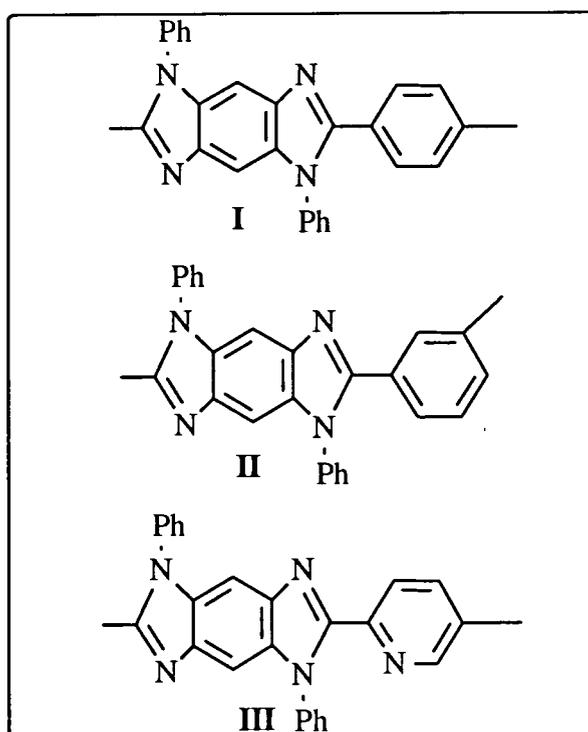


Figure 2.26 N,N'-diphenyl substituted poly(benzimidazoles).

The molecular weights were found to be low and clear brown films were cast from formic acid. The thermal properties of the polymers indicated high thermal stability with III exhibiting very little weight loss before 545°C.

Wolfe and Arnold^[W3] carried out solution polycondensation reactions with 4,6-diamino-1,3-benzenediol dihydrochloride and a variety of para-substituted aromatic dicarboxylic acids using poly(phosphoric acid) as the solvent, figure 2.27. The

resulting rigid rod polymers were soluble in strong acids and thermally stable.

The polymers had 2,6-benzo[1,2-d:5,4-d']-bioxazole units in the main polymer chain. The intrinsic viscosities of the polymers were measured in methanesulfonic acid at 30°C and were in the range of 2.5-9.3 dL/g. All of the polymers showed excellent thermal stability and good thermooxidative stability. The polymers possessing phenyl substituents were sparingly soluble in PPA/sulfolane and in m-cresol/strong acid mixtures, however, for those without phenyl substituents the mixtures were non-solvents.

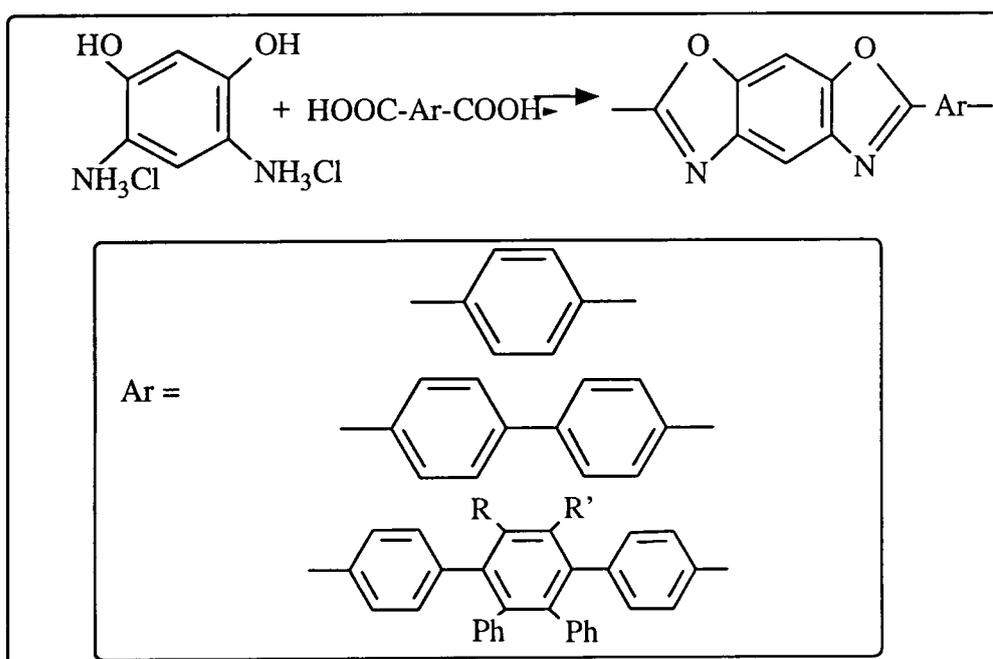


Figure 2.27 Polycondensation reactions of 4,6-diamino-1,3-benzenediol dihydrochloride with a variety of para-substituted aromatic dicarboxylic acids.

Arnold and Wolfe^[W4] also described the synthesis of poly[(benzo[1,2-d-4,5-d'] bithiazole-2,6-diyl-1,4-phenylene)] (PBT) from the polycondensation reaction of 2,5-diamino-1,4-benzenedithiol dihydrochloride and terephthalic acid in poly(phosphoric acid). When the polymer concentration is between 5 and 10 wt % the polymerisation mixture proved to be liquid crystalline in the early stages of conversion and high modulus/strength fibres could be formed.

Isothermal ageing was carried out on the PBT sample. At 316°C, in air, the polymer retained 98% of its weight after 200 hours of testing. Analysis by thermogravimetric techniques showed that thermal decomposition of PBT began near 600°C with the maximum rate being near 700°C. When there were phenyl substituents present on the aromatic ring the decomposition occurred some 70-80°C lower than in PBT. The rigid rod polymers containing varying degrees of phenyl substitution were only soluble at low concentrations in certain mixed solvents and so fibres were not drawn from them.

Aromatic heterocyclic rigid rod polymers such as poly(benzazoles) are known to have excellent tensile strength and modulus properties and to be able to withstand harsh conditions. Their ability to develop molecular ordering, even in relatively low concentrations has allowed a method of processing these polymers into films and fibres to be developed. It has been reported that poly(p-phenylenebenzobisthiazole) (PBZT) is being developed as a non linear optical material owing to the highly delocalized π -electron density along its backbone.^[R7]

A drawback to the usefulness of these polymers is their colour, meaning that they cannot be used in situations when colourlessness or transparency are important factors to be considered. Dang et al therefore set about synthetically modifying the rigid rod polymers in order to disrupt their conjugation systems. A variety of cage-like hydrocarbons such as adamantane, diamantane and cubane were considered as comonomers, see figure 2.28. These authors described the synthesis and properties of diamantane based polybenzazoles.^[D4]

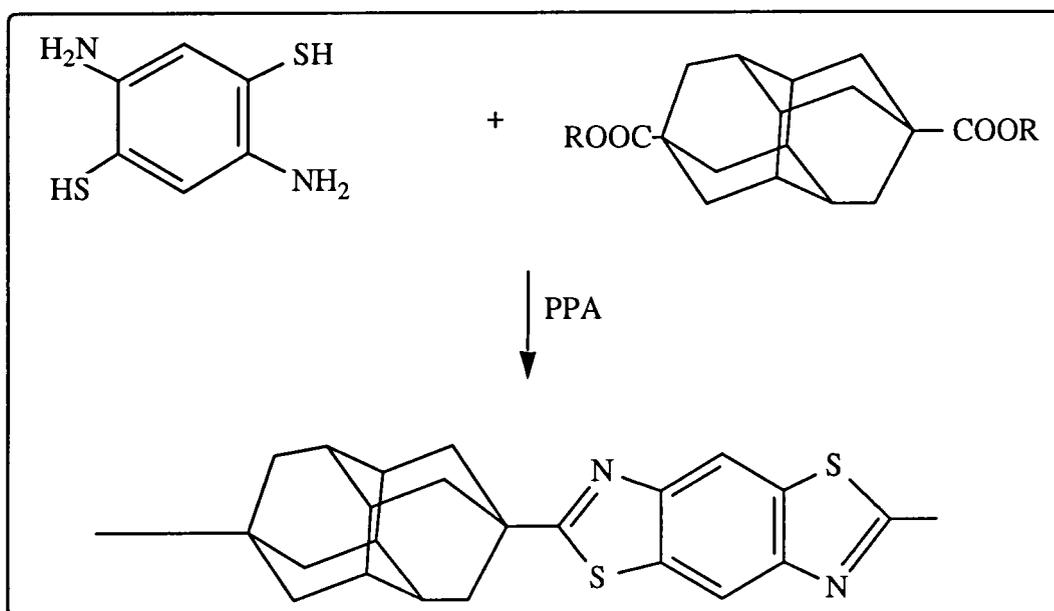


Figure 2.28 Synthesis of diamantane based polybenzazoles.

The resulting polymer was white and translucent, the conjugation of the polymer backbone being effectively destroyed by the substitution of the phenyl units with diamantane. The thermal stability of the polymer was essentially retained; decomposition began at 670°C in Helium, but the thermooxidative stability of the polymer was somewhat lowered by the presence of the diamantane units and decomposition in air began at 432°C.

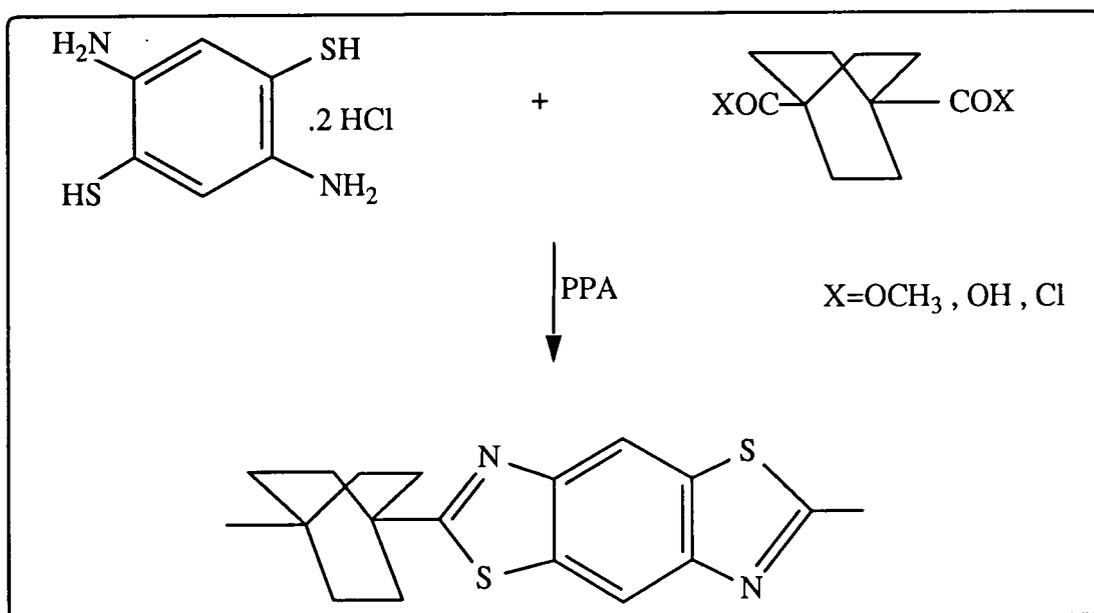


Figure 2.29 Synthesis of bicyclo[2.2.2]octane based polybenzazoles.

Work related to that described above was carried out by Dotrong et al.^[D5] In this case they employed bicyclo[2.2.2]octane moieties in order to disrupt the conjugation along the polymer backbone of the PBT, see figure 2.29. A film cast from methane sulfonic acid was described as "water-white in colour", which presumably means transparent and colourless, and onset of degradation was seen at 423°C.

Wallow and Novak^[W1] synthesised water soluble rigid chain polymers by means of an ionic poly(p-phenylene) analogue. They employed the palladium(0) catalysed coupling reaction between aryl-bromides and aryl-boronates originally developed by Suzuki^[S7] and employed by Rehan et al,^[R4,R5] figure 2.30.

The polymer had good thermal stability, thermogravimetric analysis showing onset of thermal decomposition at 520°C. Differential scanning calorimetry showed no apparent melting point. In both methods the polymer was seen to undergo dehydration at 300-330°C to give the poly(anhydride) structure and they confirmed this by infrared investigations. The polymer had a M_w of 50,000, measured by GPC, relative to single stranded DNA as standard.

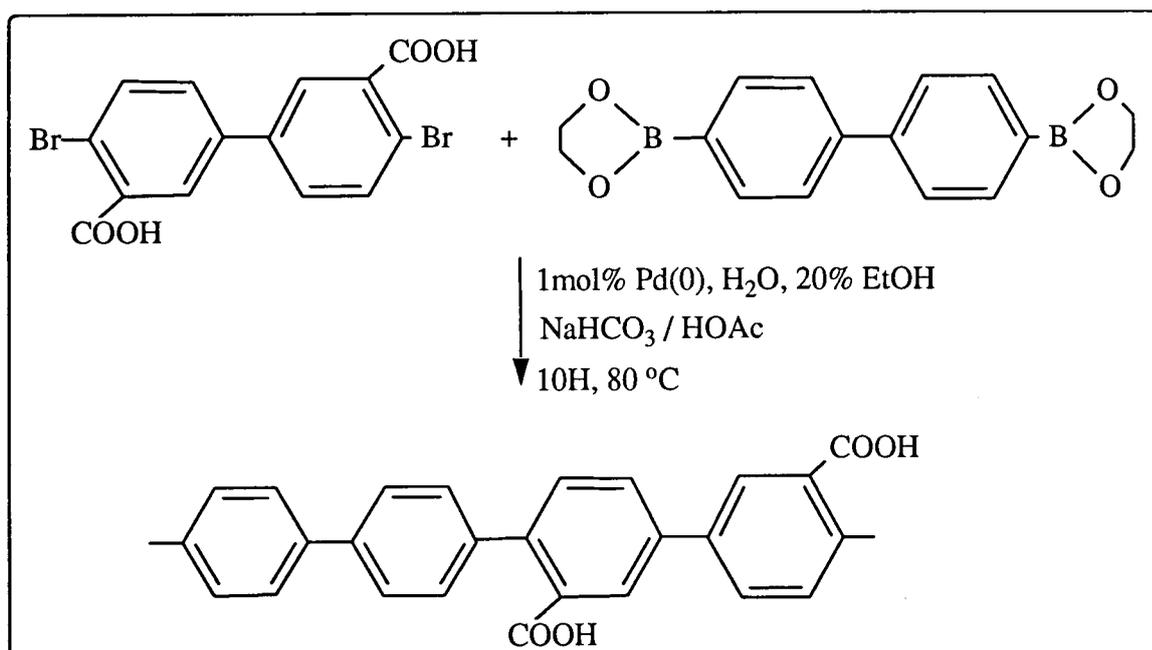


Figure 2.30 Synthesis of water soluble rigid chain polymers by means of an ionic poly(p-phenylene) analogue.

Liepins and Benicewicz^[L4] have synthesised poly(p-phenylene terephthalamide) (PPT) rigid rod polymers containing diphenylthiazolothiazole pendant groups, figure 2.31. Their aim was to improve the tensile strength and compressive properties of PPT.

The resulting polymer exhibited a glass transition temperature of 212°C and showed a melting isotherm at 393°C. This may be compared with commercial PPT which has a glass transition temperature of 345°C and exhibits no endotherms up to 500°C.

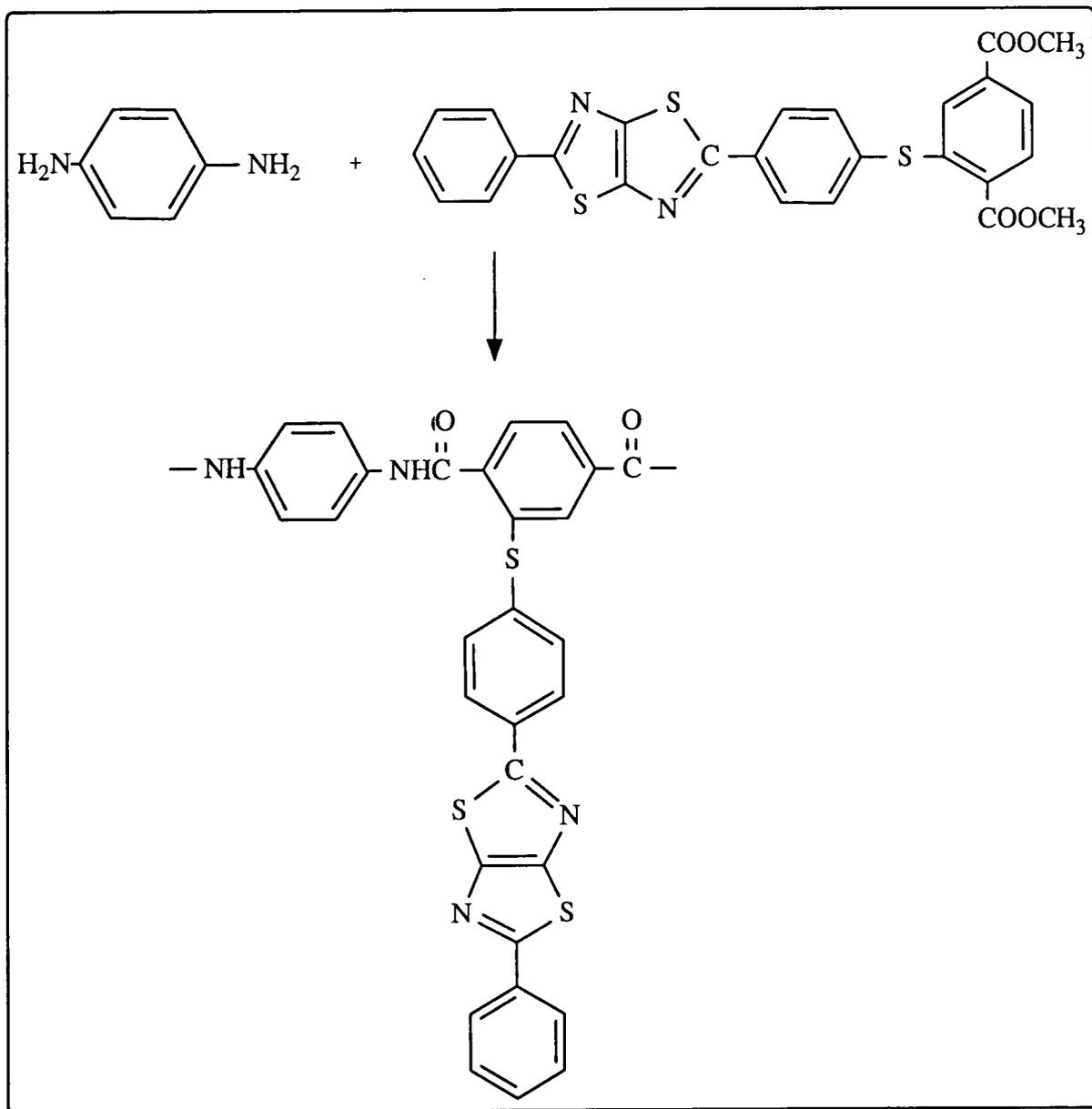


Figure 2.31 Synthesis of PPT rigid rod polymers containing pendant groups.

Arnold and Tan^[T3] prepared rigid rod molecular composites via ionic interactions in order to investigate whether it was possible to overcome the tendency of rigid rod molecular composite systems to phase separate, figure 2.33, page 41. A blend of poly(2-acrylamido-2-methylpropane sulfonic acid) (HAMPS) and poly(p-phenylene benzobisthiazole) (PBZT) was prepared by dissolving the components in methanesulfonic acid. The molecular composite was obtained on precipitation of the resulting solution into cold water and was obtained as an orange fibre which turned red upon drying. This ability to alter colour was also observed when the polymer film was immersed in a variety of solvents. The film showed little shrinkage after it had been vacuum dried overnight at 110°C and no phase separated morphology could be observed by scanning electron microscopy at 500Å resolution.

A second method of minimising the phase separation of rigid rod molecular composites was proposed by Arnold, Wallace and Tan.^[W6] Their approach was to employ a coil like aromatic polyisoimide that was soluble and compatible with an amorphous matrix polymer or a thermosettable oligomer and which could easily undergo transformation to the corresponding rigid rod polyimide resulting in a high strength / high modulus compound, see figure 2.32. They synthesised a variety of polyimides from which films were cast; that derived from pyromellitic dianhydride and 3,3',5,5'-tetra methylbenzidine showed no visible phase separation.

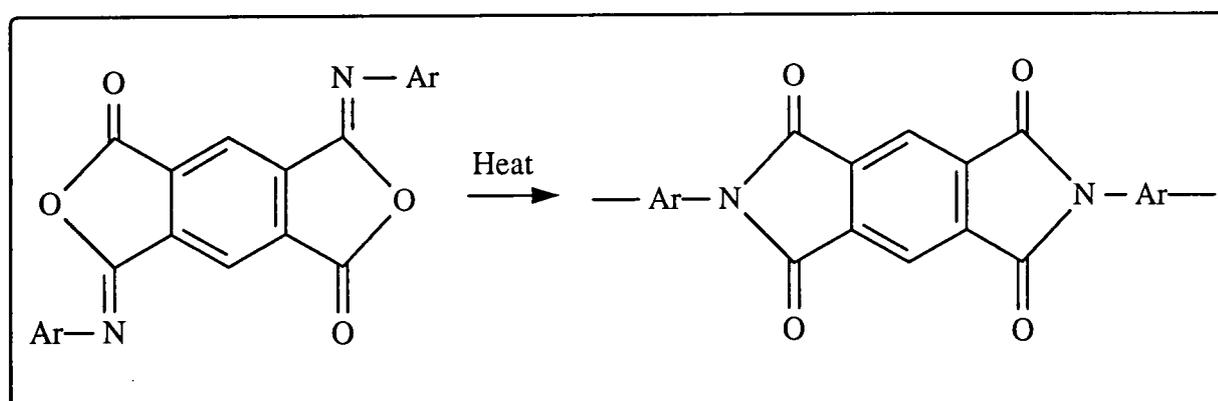


Figure 2.32 Polyisoimide transformation to the corresponding rigid rod polyimide.

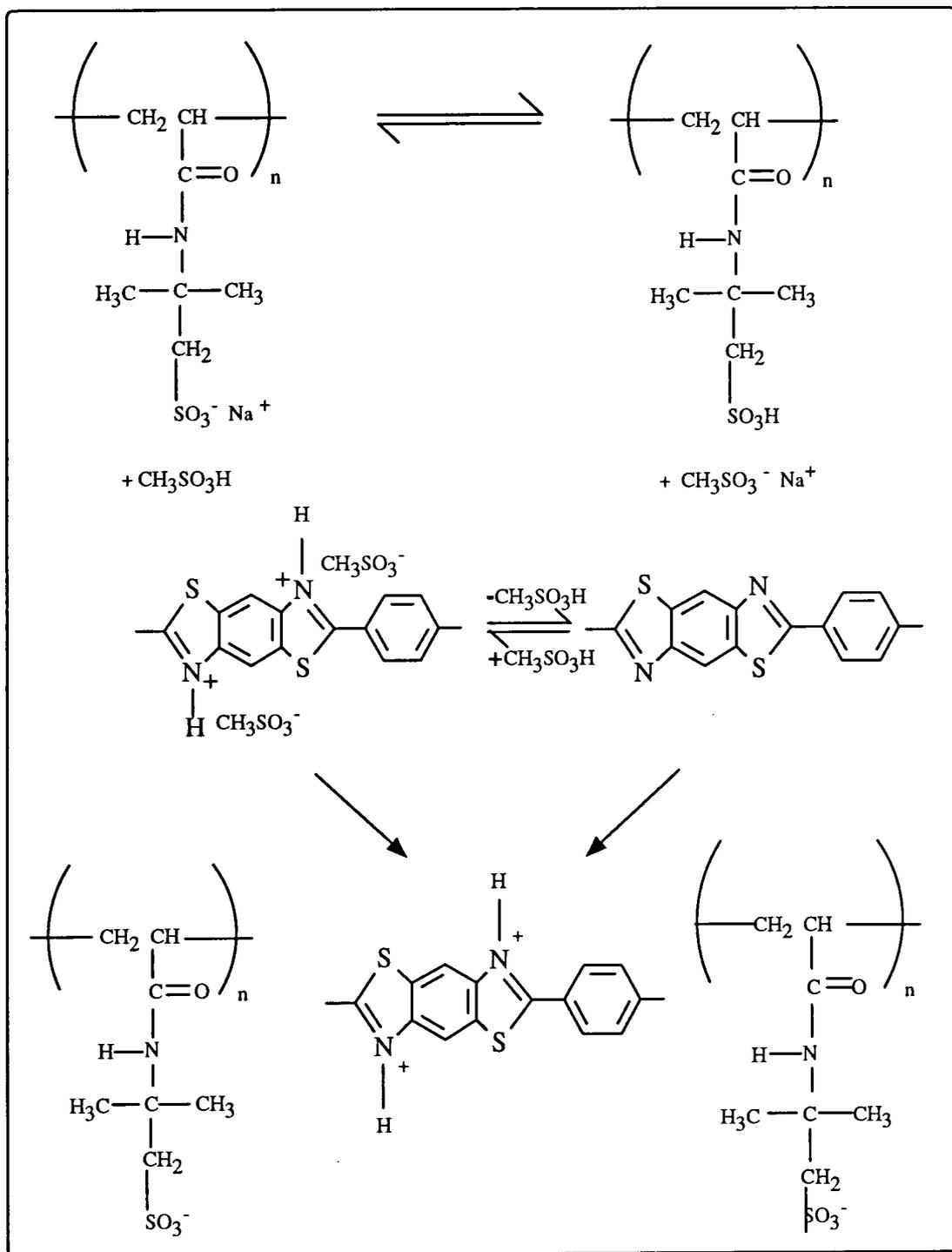


Figure 2.33 Synthesis of rigid rod molecular composites via ionic interactions.

Aharoni in conjunction with Edwards prepared highly branched polymers consisting of stiff trifunctional branchpoints connected by rigid rodlike segments.^[A2] Networks were synthesised from 1,3,5-benzenetricarboxylic acid (BTCA) or

N,N',N'' tris(*p*-carboxyphenyl)-1,3,5-benzenetriamide (TCPBT) as branch points with 4,4'-diaminobenzanilide, see figure 2.34. The corresponding networks contained rigid segments 19.5Å and 32.5Å long. The fractal nature of the networks was then compared with that of systems containing flexible segments.

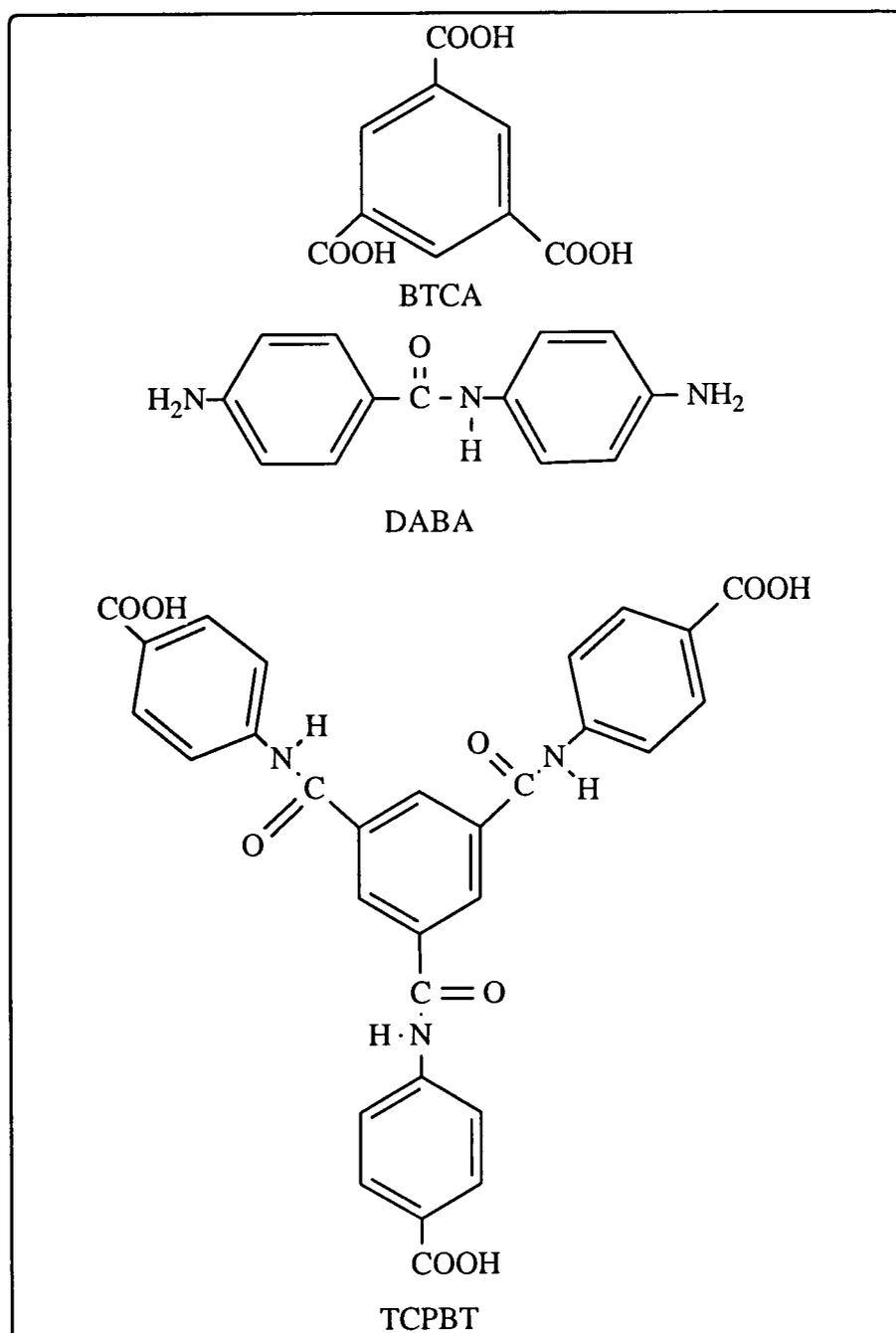


Figure 2.34 1,3,5-Benzenetricarboxylic acid (BTCA), N,N',N'' tris(*p*-carboxyphenyl)-1,3,5-benzenetriamide (TCPBT) and 4,4'-diaminobenzanilide (DABA).

In a second paper gels of the rigid polyamide networks were investigated.^[A1] The networks showed a steep approach to the gel point and large viscosity increases after it. The greater the degree of rigidity of the network the less sol it was possible to extract from it and the lower was its molecular weight. This is believed to be because segmental rigidity means that highly branched macromolecules are unable to diffuse out of the network, although flexible molecules can diffuse out slowly. They found that the modulus of the networks increased with increasing branch point concentration and that the modulus appeared to be unaffected by changes in temperature in the range 23-150°C. This is an unusual phenomenon and should be compared with that of networks containing flexible segments where the modulus was seen to drop with temperature.

From the above it can be seen that there have been recent significant developments in the area of the synthesis of rigid rod polymers. The polymers which have been produced are of interest on the grounds of both their novel syntheses and their properties. As part of the work carried out in this project the synthesis of a series of linear molecularly rigid rod polymers was undertaken, section 3.3 and the properties of the product polymers was investigated, Chapter 4.

Chapter Three

Experimental

3 Experimental.

3.1 Aims of the project and proposed synthetic route.

The long term aim of this project is the synthesis and characterisation of novel rigid rod polymer networks. Investigation of the properties of these new networks would allow a comparison to be made with the properties of traditional polymer networks containing flexible segments between crosslinks.

The intention of this work was to synthesise difunctional rigid rodlike molecules of known composition which could then be incorporated into polymer networks. The rodlike molecules were to be synthesised from a combination of 1,4-phenylene and acetylene units since this would produce unambiguously linear, molecularly rigid rodlike structures.

The problem was foreseen that molecules composed simply of 1,4-phenylene and acetylene units would become insoluble very rapidly as their length increased. This would mean that processing of the rods would be problematic and that it would not be possible to assess the properties of the rod like materials by means of conventional physicochemical techniques. In an attempt to overcome this problem it was decided to incorporate flexible alkyl side chains onto the aromatic units. This method of increasing the solubility of rigid rod polymers had been successfully employed by several workers, a good example being the work of Wegner's group in Mainz in the synthesis of soluble poly(p-phenylenes).^[R5,R6]

The 1,4-dialkyl-2,5-dibromobenzenes were to be synthesised following a procedure developed in Mainz^[R5,R6] and were then to be converted into the 1,4-diethynyl-2,5-dialkylbenzenes via a palladium catalysed coupling reaction with 2-methyl-3-butyn-2-ol followed by a deprotection step using sodium in isopropanol, figure 3.1, step 1. The difunctional rodlike molecules were then to be synthesised via the palladium catalysed coupling reaction between the 1,4-diethynyl-2,5-dialkyl benzenes and 4-bromomethylbenzoate, figure 3.1, step 2. It was proposed that the resulting difunctional rodlike molecules could subsequently be incorporated into

polymer networks in varying amounts via ester exchange reactions with mixtures of conventional di- and polyfunctional monomers to provide information on the effect of the introduction of rigid segments upon the physical properties of polymer network, thus allowing comparison with theoretical predictions.

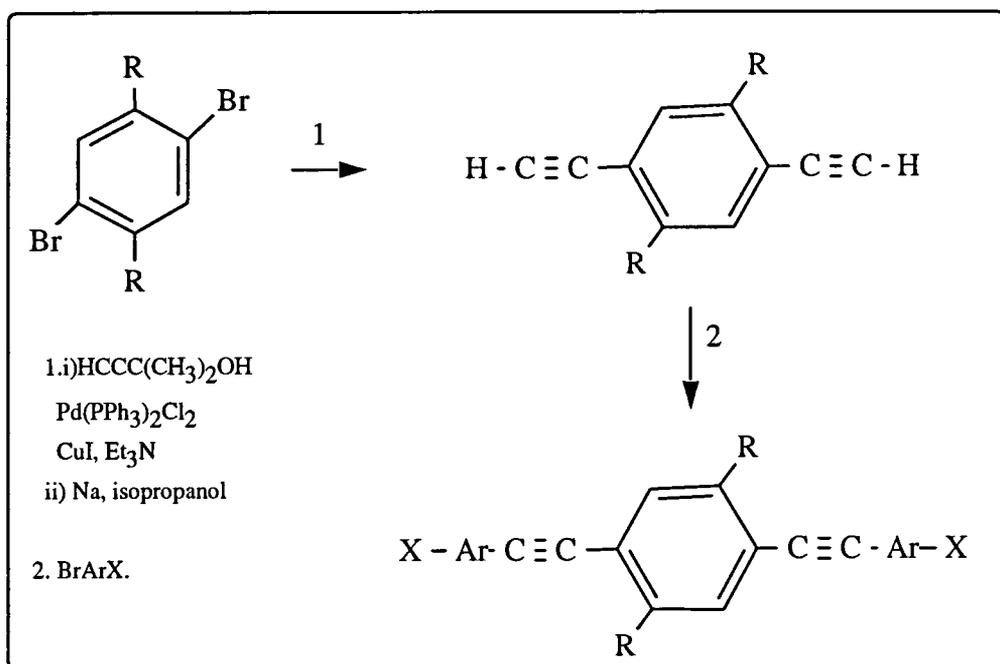


Figure 3.1 The synthetic route to difunctional rigid rod molecules.

This Chapter describes the synthesis of the 1,4-dibromo-2,5-dialkylbenzenes, the 1,4-diethynyl-2,5-dialkylbenzenes and the syntheses of 1,4 -diethynylbenzene and 4,4'-diethynyl biphenyl, which were used both as model compounds and in the formation of rodlike molecules. The production of difunctional rigid rodlike molecules is then described and, finally the synthesis of a series of rigid rodlike polymers is described.

3.1.1 Synthesis of diacetylenes.

The requirement for diacetylene monomers was described above, here the synthesis and characterisation of the monomers is described.

3.1.2 Review of arylhalide-acetylene coupling reactions.

It has been established that the halogen atom in an aromatic halide compound can be replaced by an acetylene containing moiety via reaction with monosubstituted acetylenes in the presence of a basic agent and a copper catalyst.

In 1971, Shvartsberg^[55] employed catalytic replacement of iodine from iodo substituted nitrobenzenes to produce acetylene substituted nitrobenzenes. The nitro group activates the halogen and the rate of reaction was found to decrease in the order of $o \gg p \gg m$ - isomers. Shvartsberg also showed that the reaction could be used to introduce two acetylenic substituents into the benzene ring from diiodobenzenes without nitro group activation.

Ortho, meta, and para-nitrophenylacetylenes and diethynylbenzenes were synthesised from iodonitro- and diiodobenzenes with ethyl (2-methyl-3-butyn-2-yl) acetal followed by acid hydrolysis to give the aromatic alcohol acetals and subsequent alkaline cleavage to the acetylene derivative, figure 3.1.1.

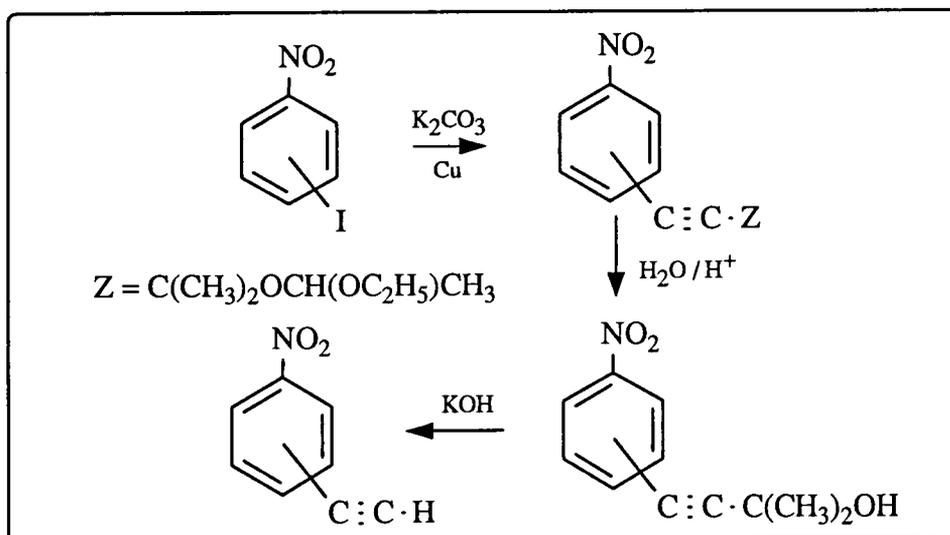


Figure 3.1.1 Synthesis of nitrophenylacetylenes.

In a continuation of their studies^[S4] Shvartsberg and Moroz used the same reaction conditions to replace the halogen in an aromatic halide containing the ortho, meta and para esters of benzoic acid. The isomeric esters followed the reactivity pattern of $o \gg p = m$ ($>$ unsubstituted compound), figure 3.1.2.

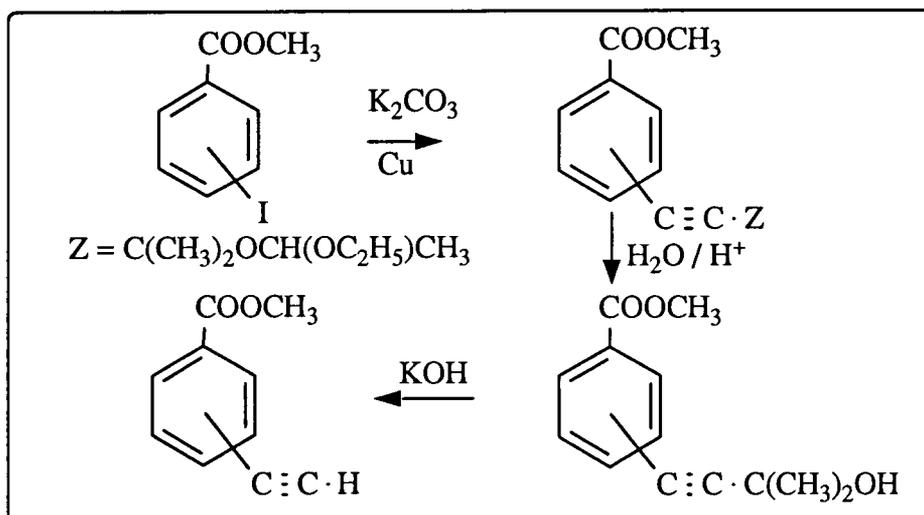


Figure 3.1.2 Synthesis of acetylene substituted phenylesters.

In 1975, Heck^[D1] converted monosubstituted acetylenes into disubstituted acetylenes via their reaction with aryl, heterocyclic or vinylic bromides or iodides at 100°C in the presence of an amine with diacetatobis(triphenylphosphine)palladium (II) as catalyst, figure 3.1.3.

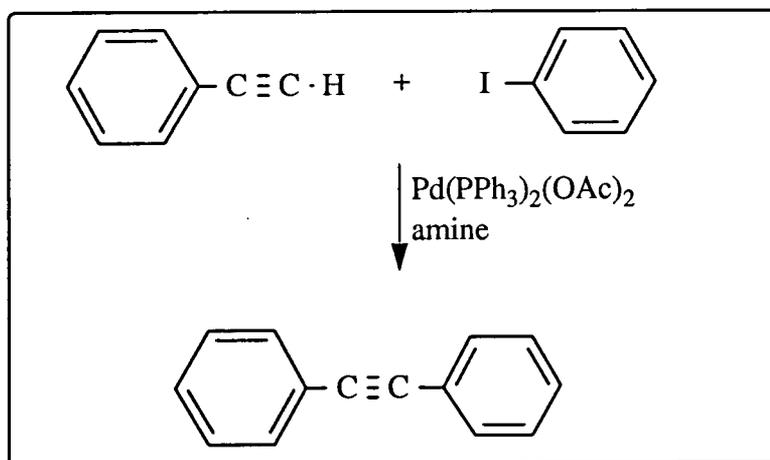


Figure 3.1.3 Conversion of monosubstituted into disubstituted acetylenes.

Increasing the amount of acetylene relative to the halide present led to a higher overall yield of disubstituted product and it was concluded that the reacting acetylenes were consumed to give products other than the desired disubstituted acetylene. It was also found that dilution of the reaction mixture to such an extent that a large excess of amine was present decreased the amount of side reaction. Heck proposed that the major side reaction was due to polymerisation of diacetylenes produced in the first step of the process, figure 3.1.4. The final yield of product was found to be strongly influenced by the structure of the organic halide. When the halide was susceptible to oxidative addition the reaction was seen to proceed more efficiently; iodobenzene thus gave higher yields of product than bromobenzene. Also, when there were electron withdrawing substituents effecting the halide the reaction yields were found to improve. Heck proposed a chain mechanism for the reaction which involved an initial reduction of the catalyst by the acetylene forming a symmetrical by-product and bis(triphenylphosphine)palladium [0], figure 3.1.4, step 1. The bis(triphenylphosphine)palladium [0] then reacts with the arylhalide to give a bis(triphenylphosphine)arylhalopalladium derivative, figure 3.1.4, step 2, which is attacked by acetylide to give the unsymmetrical diacetylene product, via a reductive elimination, and to regenerate bis(triphenylphosphine)palladium [0], figure 3.1.4, step 3. The role of the base is therefore to assist in removing the acetylenic proton. Cassar^[C1] demonstrated that the reductive elimination reaction takes place with analogous arylnickel complexes. If the acetylide intermediate is not formed quickly then acetylene polymerisation can take place. Triethylamine does not reduce the catalyst.

Heck concluded that the major limitation of the method as a route to disubstituted acetylenes was that halides with strongly electron donating substituents or those halides that form stable complexes in the oxidation reaction with the palladium (0) catalyst do not give good yields. Otherwise the reaction was widely applicable and provided a convenient method for synthesising a variety of acetylene derivatives.

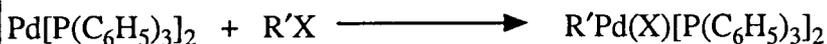
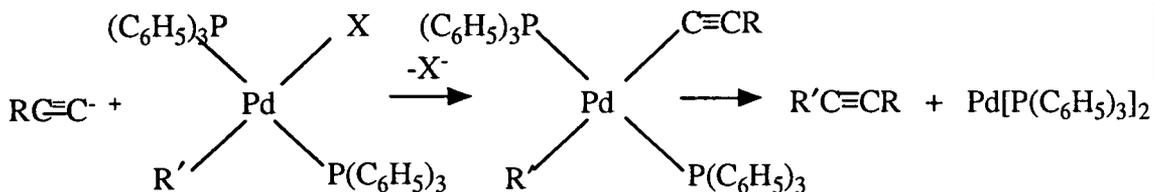
STEP ONE**STEP TWO****STEP THREE**

Figure 3.1.4 Heck's proposed mechanism for the palladium catalysed coupling reaction of arylhalides with acetylenes.

Cassar^[C1] converted acetylene or monosubstituted acetylenes into both aryl and vinyl substituted acetylene derivatives by the reaction of aryl and vinyl halides in the presence of either nickel or palladium triarylphosphine complexes and a base; the palladium triphenylphosphine complexes allowed the conversion to be carried out under mild conditions. The reaction is proposed to be a multi-step process involving the initial oxidative addition between the palladium complex and the aryl halide, figure 3.1.5.

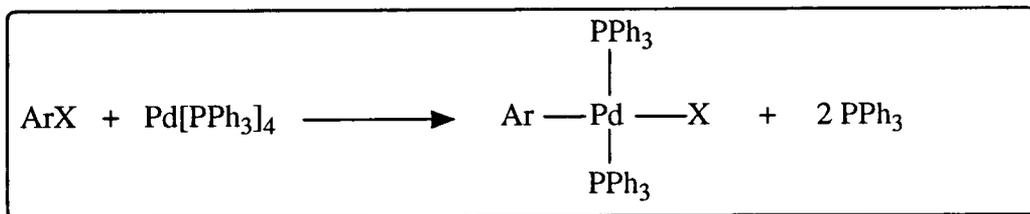


Figure 3.1.5 First step in the coupling of arylhalides with substituted acetylenes in the presence of a palladium triphenylphosphine complex.

form the monosubstituted derivative when reacted in a 1:1 ratio. This efficient method for the condensation of aryl halides with monosubstituted acetylenes in the presence of a palladium complex and a copper (I) salt was also described by Sonogashira.^[S12] Although the above method is an efficient one the high cost of the protected acetylene means that its use is likely to be limited to small scale reactions.

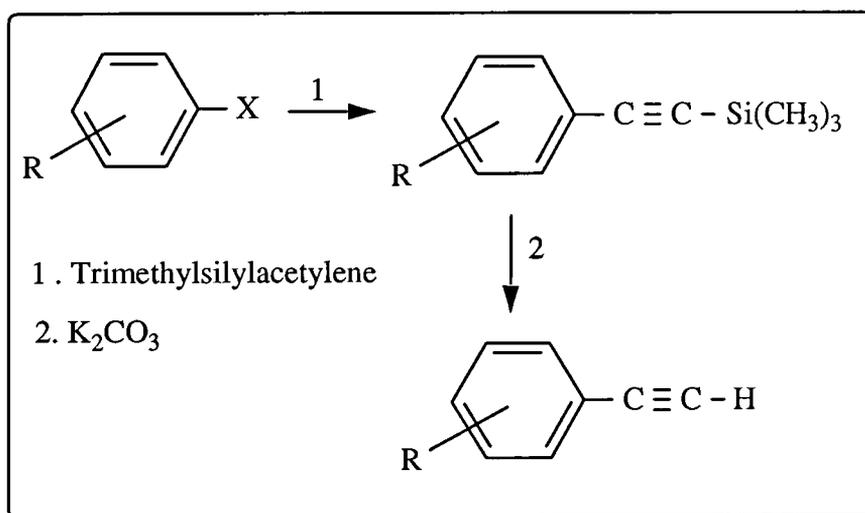


Figure 3.1.7 Synthesis of monosubstituted ethynylarenes and diethynylarenes via a trimethylsilyl protecting group.

A second well documented protecting group is 2-methyl-3-butyn-2-ol which is coupled to an arylhalide in the presence of bis(triphenylphosphine)palladium dichloride and an amine. Reaction yields of up to 95% are quoted in the literature. The protecting group is subsequently removed by the reaction with sodium hydroxide and methanol or toluene. This more vigorous deprotection step means that the reaction is unsuitable for use where the reacting compounds contain base sensitive functionalities. Ames^[A3] used this method to produce a number of ethynyl-N-heterocycles, figure 3.1.8. The reaction proceeds in high yields with a variety of starting materials.

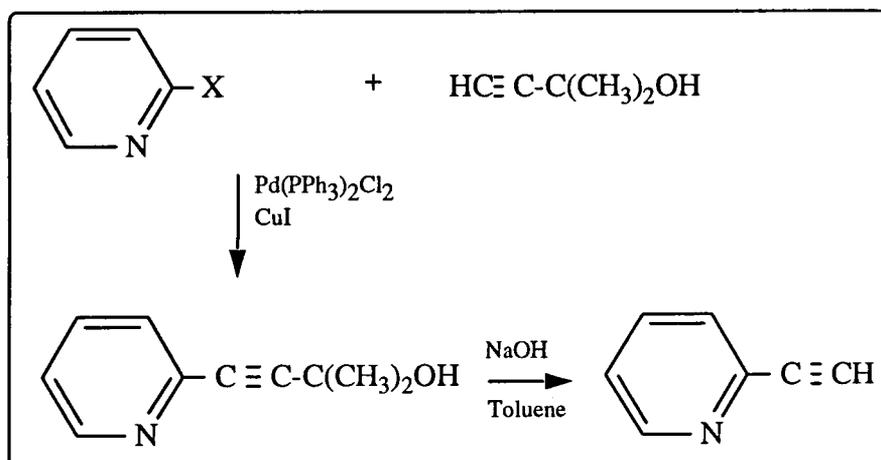


Figure 3.1.8 Synthesis of monosubstituted ethynyl-N-heterocycles.

Sabourin^[S1] describes a convenient synthesis of 4-ethynylphthalic anhydride via 2-methyl-3-butyn-2-ol, figure 3.1.9.

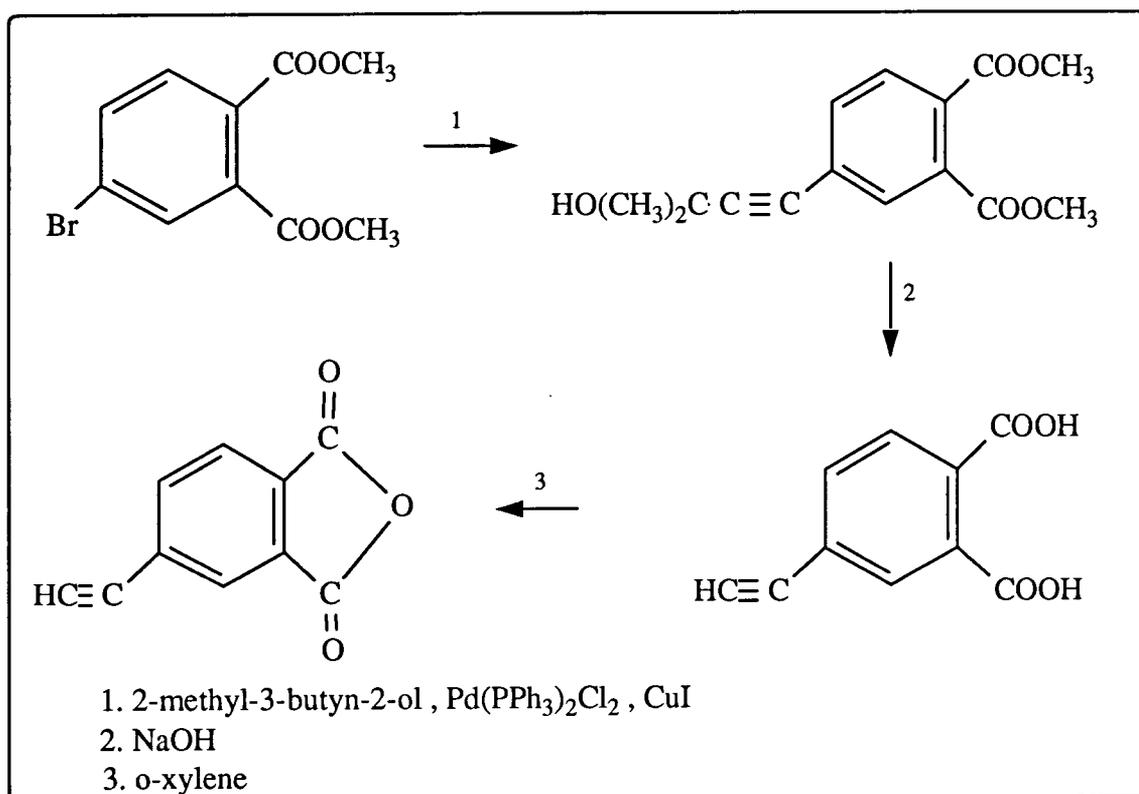


Figure 3.1.9 Synthesis of 4-ethynylphthalic anhydride via 2-methyl-3-butyn-2-ol.

Bis(triphenylphosphine)palladium dichloride proved to be the most active catalyst for the coupling reaction. Copper (I) iodide and triphenylphosphine were both found to greatly increase the rate of the reaction. Sabourin found that the presence of triphenylphosphine was necessary to take the reaction to completion but that if there was too much present the reaction was greatly slowed down leading to a loss in selectivity. The quantities of catalysts were optimised to achieve a balance between the reaction rate, catalytic activity and selectivity. Triethylamine was chosen as the solvent since it provided reasonable reaction rates at the reflux temperature while still being easily separated from the product.

The reaction conditions developed in the above papers were used to optimise the conditions for the palladium catalysed coupling reactions used in this project to form diacetylene containing compounds.

3.1.3 Synthesis and Characterisation of 1,4-dibromo-2,5-dialkylbenzenes.

A series of 1,4-dibromo-2,5-dialkylbenzenes were synthesised as precursors to 1,4-diethynyl-2,5-dialkylbenzenes. The length of the alkyl side chain was varied from butyl to dodecyl in order to establish how varying the length of the side chain influenced the properties of the final rodlike molecules and eventually the properties of the polymer networks.

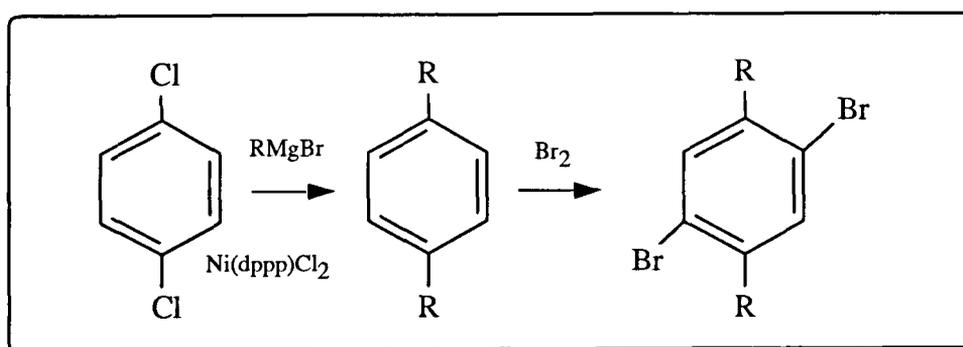


Figure 3.1.10 Reaction scheme to synthesise 1,4-dibromo-2,5-dialkylbenzenes.

Grignard reactions were employed in order to attach the flexible side chains to the aromatic ring and then a bromination reaction was carried out on the

1,4-dialkylbenzene, figure 3.1.10. The reaction scheme employed was developed in Mainz as part of a project to synthesise soluble poly(p-phenylene)s^[R5,R6] and the spectra of the compounds synthesised were identical with those published.^[R1]

3.1.4 Synthesis and characterisation of 1,4-diethynyl-2,5-dialkylbenzenes.

Diethynyldialkylbenzenes were to be synthesised from the dibromodialkylbenzenes in order to provide diacetylenes which could then be coupled to form rodlike materials, figure 3.1.11. In the first instance model coupling reactions on unalkylated compounds, 1,4-dibromobenzene and 4,4'-dibromobiphenyl, were carried out. This allowed the reaction conditions to be investigated and the spectroscopic data from the resulting diacetylenes were used as a reference for the 1,4-diethynyl-2,5-dialkylbenzenes. Polymerisation reactions were carried out on 1,4-diethynylbenzene and 4,4'-diethynylbiphenyl to form linear rigid rod macromolecules, the materials were also coupled with 4-bromomethylbenzoate to provide examples of difunctional rigid rodlike molecules.

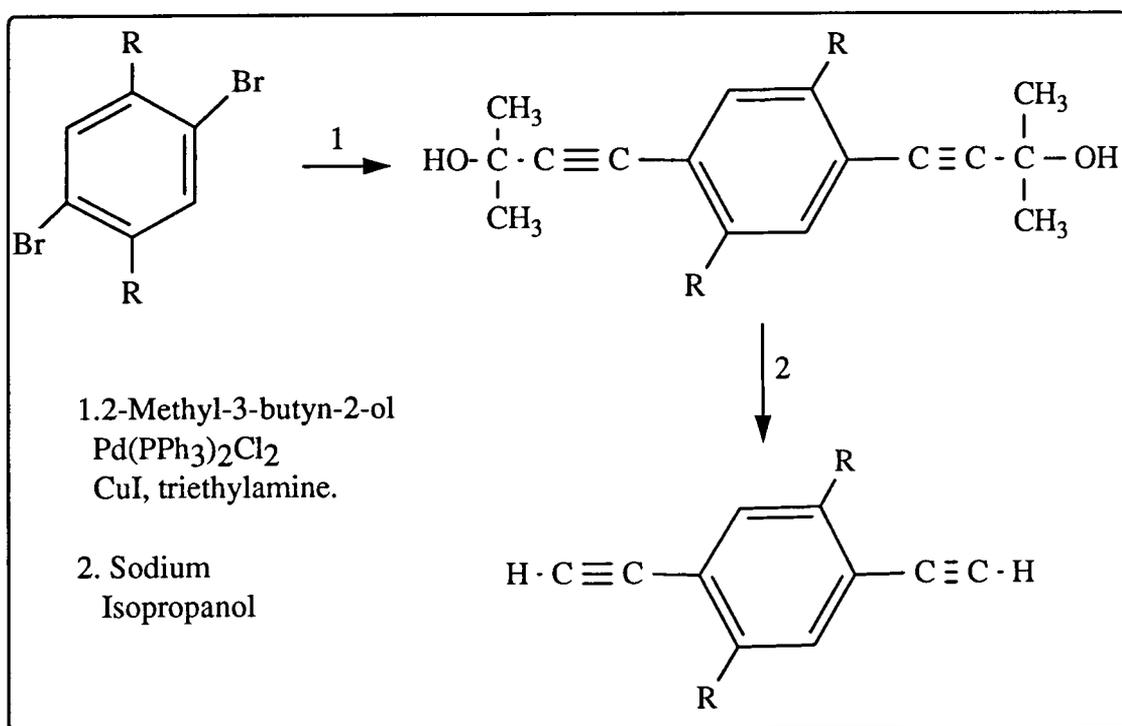


Figure 3.1.11 Reaction scheme to synthesise 1,4-diethynyl-2,5-dialkylbenzenes.

3.1.5 Synthesis and characterisation of 1,4-diethynylbenzene.

1,4-Diethynylbenzene was synthesised in 80% yield via the palladium catalysed coupling reaction between 1,4-dibromobenzene and 2-methyl-3-butyn-2-ol, for details of the experimental procedure see section 3.1.10. The deprotection step was carried out by refluxing in a sodium-isopropanol solution.

1,4-Diethynylbenzene, figure 3.1.12, was prepared as a white crystalline material which melted at 94.5°C and was soluble in chloroform and acetone. It was stable over a period of months; however to avoid oxidation the material was stored under nitrogen. The ^1H and ^{13}C nmr spectra were recorded in chloroform and the resulting spectra were fully assigned, see tables 3.1.1 and 3.1.2, distinct peaks were observed for each proton and carbon environment. There are two singlets in the ^1H nmr spectrum, appendix D1, at 3.18 and 7.44ppm and their integrals are consistent with the product being 1,4-diethynylbenzene. The ^{13}C nmr spectrum consists of four peaks each of which can be unambiguously assigned on the basis of their chemical shifts and intensities, appendix E1. The infrared spectrum shows a distinctive peak at 3272cm^{-1} which is assigned to the terminal acetylenic carbon-hydrogen stretch, appendix C1. The mass spectrum shows a peak for the molecular ion at 126 and a fragmentation pattern which is readily rationalised in terms of the assigned structure, appendix B1.

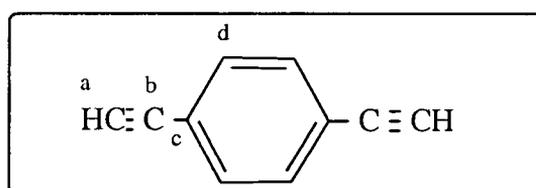


Figure 3.1.12 1,4-Diethynylbenzene.

Hydrogen assignments	Observed Shift (ppm)	Integral
a	3.18	1
d	7.44	2

Table 3.1.1 Assignment of ^1H nmr chemical shifts for 1,4-diethynylbenzene.

Carbon	Observed Shift (ppm)
a, strong CH	79.1
b, weak	83.0
c, weak quaternary	122.6
d, strong CH	132.0

Table 3.1.2 Assignment of ^{13}C nmr chemical shifts for 1,4-diethynylbenzene.

Peak	Assignment
126	Molecular ion
76	C_6H_4^+

Table 3.1.3 Diagnostic peaks in the mass spectrum of 1,4-diethynylbenzene.

The spectroscopic data presented above were consistent with the product being 1,4-diethynylbenzene. The compound was then polymerised to provide an example of a linear polymer comprising of phenylene and diacetylene units. The coupling reaction between 1,4-diethynylbenzene and 4-bromomethylbenzoate was also investigated in an attempt to synthesise a rigid rodlike difunctional monomer for further work.

3.1.6 Synthesis and characterisation of 4,4'-diethynylbiphenyl.

4,4'-Diethynylbiphenyl was synthesised in 80% yield via the palladium catalysed coupling reaction between 4,4'-dibromobiphenyl and 2-methyl-3-butyn-2-ol, section 3.1.10. The deprotection step being carried out by refluxing in a sodium-isopropanol solution.

4,4'-Diethynylbiphenyl, figure 3.1.13, was prepared as a white crystalline material which melted at 165°C and was soluble in chloroform and acetone. It was stable over a period of months, however to avoid oxidation the material was stored under nitrogen. The ^1H and ^{13}C nmr spectra were recorded in chloroform and the resulting spectra were fully assigned, see tables 3.1.4 and 3.1.5, distinct peaks were observed for each proton and carbon environment. The singlet at 3.75ppm in the ^1H nmr spectrum is characteristic of a terminal acetylenic proton and the splitting pattern at 7.5-7.7ppm is characteristic of the type of AB system present in 4,4'-diethynylbiphenyl. The proton integrals are in agreement with product being 4,4'-diethynylbiphenyl, appendix D2. The ^{13}C nmr spectrum shows six carbon environments and can be unambiguously assigned on the basis of their chemical shifts and intensities, see table 3.1.5, appendix E2. A peak due to the acetylenic C-H stretch can be seen in the infrared spectrum at 3272cm^{-1} , appendix C2. The mass spectrum shows a peak for the molecular ion at 202, table 3.1.6, and a fragmentation pattern which is readily rationalised in terms of the assigned structure, appendix B2.

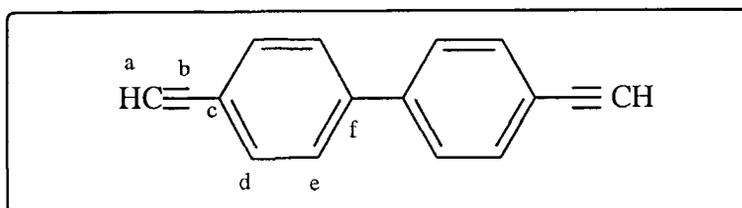


Figure 3.1.13 4,4'-Diethynylbiphenyl.

Hydrogen assignments	Observed Shift (ppm)	Integral
a	3.75	1
d & e	7.5-7.7	4

Table 3.1.4 Assignment of ^1H nmr chemical shifts for 4,4'-diethynylbiphenyl.

Carbon	Observed Shift (ppm)
a, strong CH	80.1
b, weak quaternary	83.9
c, weak quaternary	122.6
d, strong CH	133.3
e, strong CH	127.8
f, weak quaternary	141.0

Table 3.1.5 Assignment of ^{13}C nmr chemical shifts for 4,4'-diethynylbiphenyl.

Peak	Assignment
202	Molecular ion

Table 3.1.6 Diagnostic peaks in the mass spectrum of 4,4'-diethynylbiphenyl.

The spectroscopic data presented above were consistent with the product being 4,4'-diethynylbiphenyl. The compound was then polymerised, section 3.3, to provide an example of a linear polymer comprising phenylene and acetylene units. The coupling reaction between 4,4'-diethynylbiphenyl and 4-bromomethylbenzoate was also investigated in an attempt to synthesise a rigid rodlike material and is discussed in section 3.2.

3.1.7 Synthesis and characterisation of 1,4-diethynyl-2,5-dialkylbenzenes.

The palladium catalysed coupling reaction employed in the synthesis of the model compounds, 1,4-diethynylbenzene and 4,4'-diethynylbiphenyl, was applied to the synthesis of a series of 1,4-diethynyl-2,5-dialkylbenzenes. Attempts to carry out the coupling reactions between 1,4-dibromo-2,5-dialkylbenzenes and 2-methyl-3-butyn-2-ol gave variable results and a frustrating level of irreproducibility. The reaction between the 1,4-dibromo-2,5-dialkylbenzenes and trimethylsilylacetylene was equally unpredictable and due to the cost of the trimethylsilylacetylene was not extensively pursued. The general reaction scheme is detailed and the spectroscopic data of 1,4-diethynyl-2,5-dihexylbenzene which was successfully obtained are tabulated and discussed in this section.

Characterisation of

1,4-di(2'-hydroxy-2'-methylbut-3'-yn-4'-yl)-2,5-dihexylbenzene.

1,4-Di(2'-hydroxy-2'-methylbut-3'-yn-4'-yl)-2,5-dihexylbenzene (Compound 3), figure 3.1.14, was isolated as a cream powder which melted at 130-132°C and was soluble in common solvents such as chloroform and acetone. The ¹H and ¹³C nmr spectra of the compound were recorded in chloroform and were unambiguously assigned on the basis of their chemical shifts and intensities, see tables 3.1.7 and 3.1.8. The splitting pattern and positions seen for the hexyl protons are consistent with that of 1,4-dibromo-2,5-dihexylbenzene, described elsewhere, and the other protons are assigned by comparison with the spectrum of 2-methyl-3-butyn-2-ol. The proton integrations are consistent with the product being 1,4-di(2'-hydroxy-2'-methylbut-3'-yn-4'-yl)-2,5-dihexylbenzene, appendix D3.

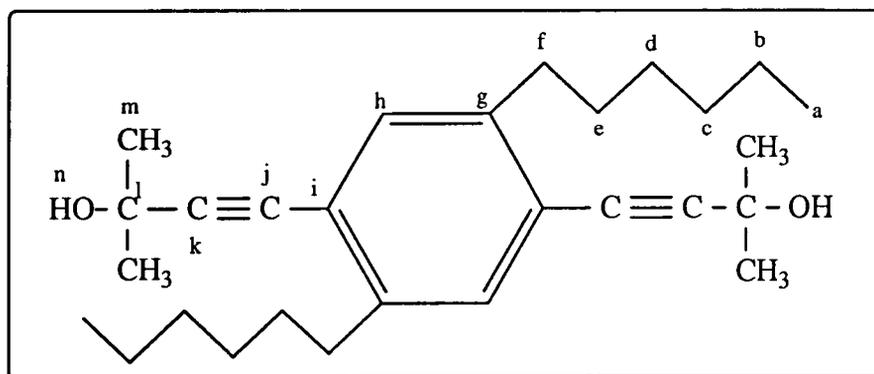


Figure 3.1.14 1,4-(2'-hydroxy-2'-methyl-3'-yn-4'-yl)-2,5-dihexylbenzene.

The carbon assignments are arrived at by comparison of the spectrum with those of 1,4-dibromo-2,5-dihexylbenzene and 2-methyl-3-butyn-2-ol, appendix E3. There are no peaks unaccounted for and the absence of a peak at 3.3ppm in the ^1H nmr spectrum is an indication that there is no unreacted 2-methyl-3-butyn-2-ol in the final product. The mass spectrum shows a peak for the molecular ion at 410, table 3.1.9, and a fragmentation pattern which is readily rationalised in terms of the assigned structure, appendix B3. The infrared spectrum shows a peak at 2144cm^{-1} due to an acetylenic stretch and a peak at 3270cm^{-1} due to the hydroxyl groups, appendix C3.

Hydrogen	Observed Shift (ppm)	Integrated intensities
a	0.88	3
b - d	1.31	6
e	1.57	2
f	2.65	2
h	7.24	1
m	1.61	6
n	1.99	1

Table 3.1.7 Assignment of the ^1H nmr chemical shifts for Compound 3.

Carbon	Observed Shift (ppm)
a	14.11
b - f	22.64-34.07
g	142.2
h	122.0
i	132.34
j	98.14
k	81.00
l	65.79
m	31.54

Table 3.1.8 Assignment of the ^{13}C nmr chemical shifts for Compound 3.

Peak	Assignment
410	Molecular ion M
395	M - 15 (Methyl)
325	M - 85 (Hexyl)

Table 3.1.9 Diagnostic peaks in the mass spectrum of Compound 3.

The spectroscopic data presented above were consistent with the product being 1,4-di(2'-hydroxy-2'-methylbut-3'-yn-4'-yl)-2,5-dihexylbenzene. The compound was then deprotected, via the reaction with sodium in isopropanol, to give 1,4-diethynyl-2,5-dihexylbenzene.

Characterisation of 1,4-diethynyl-2,5-dihexylbenzene.

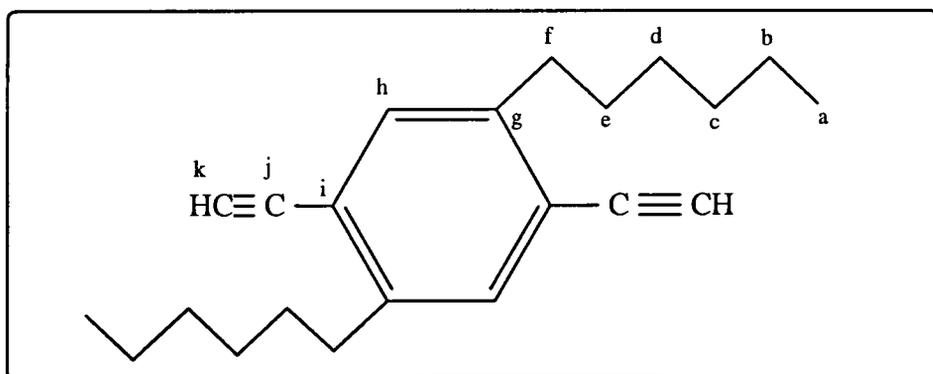


Figure 3.1.15 1,4-Diethynyl-2,5-dihexylbenzene.

1,4-Diethynyl-2,5-dihexylbenzene, figure 3.1.15, was isolated as a cream crystalline material which melted at 65°C and was soluble in chloroform. The ^1H and ^{13}C nmr spectra were recorded in chloroform and assigned on the basis of their chemical shifts and intensities, see tables 3.1.10 and 3.1.11. The ^1H spectrum shows a singlet at 3.26ppm which is characteristic of a terminal acetylenic proton and the absence of both the hydroxyl peak and the peak at 1.61ppm are indicators that there is no protected material remaining in the product. The proton integrations are in agreement with the product being 1,4-diethynyl-2,5-dihexylbenzene, appendix D4.

The ^{13}C nmr spectrum is fully assigned in table 3.1.11 and shows peaks for the hexyl carbons and for the three aromatic carbon environments, as well as peaks at 82.28 and 81.54ppm which can be assigned to the two acetylenic carbons, appendix E4. The mass spectrum, appendix B4, shows a peak for the molecular ion at 294 and a fragmentation pattern which is readily rationalised in terms of the assigned structure, see table 3.1.12. The infrared spectrum shows a peak at 3310 cm^{-1} characteristic of a terminal acetylenic carbon-hydrogen stretch and a peak at 2103 cm^{-1} assigned to the internal carbon-carbon stretch of the acetylene, appendix C4.

Hydrogen	Observed Shift(ppm)	Integrated intensities
a	0.89	3
b-d	1.33	6
e	1.59	2
f	2.71	2
h	7.31	1
k	3.26	1

Table 3.1.10 Assignment of the ^1H nmr chemical shifts for 1,4-diethynyl-2,5-dihexylbenzene.

Carbon	Observed Shift(ppm)
a	14.10
b-f	22.61-33.80
g	142.75
h	121.94
i	132.99
j	82.28
k	81.54

Table 3.1.11 Assignment of the ^{13}C nmr chemical shifts for 1,4-diethynyl-2,5-dihexylbenzene.

Peak	Assignment
294	Molecular ion M
223	M - 71 (C ₅ H ₁₁)
209	M - 85 (C ₆ H ₁₃)

Table 3.1.12 Diagnostic peaks in the mass spectrum of
1,4-diethynyl-2,5-dihexylbenzene.

The spectroscopic data presented above were consistent with the product being 1,4-diethynyl-2,5-dihexylbenzene. The material was then used in the synthesis of the linear rigid rod polymer poly(1,4-diethynyl-2,5-dihexylbenzene).

3.1.8 Synthesis and characterisation of 4,4'-diethynylbenzophenone.

4,4'-Diethynylbenzophenone was synthesised as a precursor to a difunctional, hinged, rigid rodlike molecule, since it was expected that the bend would lead to an increase in the solubility of the rodlike compound. 4,4'-Diethynylbiphenyl was synthesised via the palladium catalysed coupling reaction between 4,4'-dibromobenzophenone and 2-methyl-3-butyn-2-ol, section 3.1.10. The deprotection step being carried out by refluxing in a sodium-isopropanol solution.

Characterisation of

4,4'-di(2''-hydroxy-2''-methylbut-3''-yn-4''-yl)benzophenone.

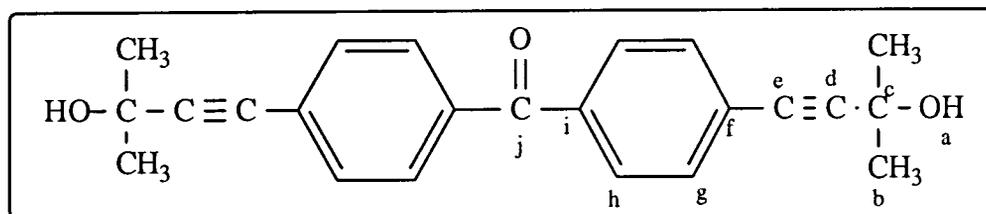


Figure 3.1.16 4,4'-Di(2''-hydroxy-2''-methylbut-3''-yn-4''-yl)benzophenone.

4,4'-Di(2''-hydroxy-2''-methylbut-3''-yn-4''-yl)benzophenone, figure 3.1.16, was isolated as a cream powder which was soluble in common solvents such as chloroform and acetone. The ^1H and ^{13}C nmr spectra of the compound were recorded in chloroform and were assigned on the basis of their chemical shifts and intensities, see tables 3.1.13 and 3.1.14. The splitting pattern and chemical shifts of the aromatic protons, appendix D11, are consistent with those of 4,4'-dibromobenzophenone and the other protons were assigned by comparison with the spectrum of 2-methyl-3-butyn-2-ol.

The carbon assignments, appendix E11, are arrived at by comparison of the spectrum with those of 4,4'-dibromobenzophenone and 2-methyl-3-butyn-2-ol and with the calculated values for the aromatic carbons, calculated via substituent shift effects. There are peaks which suggest the presence of 4,4'-dibromobenzophenone, however, the absence of a peak at 3.3ppm in the ^1H nmr spectrum is an indication that there is no unreacted 2-methyl-3-butyn-2-ol in the final product. The infrared spectrum, appendix C11, shows a peak at 2300cm^{-1} due to an acetylenic stretch, a peak at 3400cm^{-1} due to the hydroxyl groups and a peak at 1644cm^{-1} for the carbonyl group which is a little lower in frequency than that found in benzophenone (1660cm^{-1}), presumably as a result of extended conjugation with the acetylene units.

Hydrogen	Observed Shift(ppm)
a	2.05
b	1.57
g & h	7.44 - 7.66

Table 3.1.13 Assignment of the ^1H nmr chemical shifts for 4,4'-di(2''-hydroxy-2''-methylbut-3''-yn-4''-yl)benzophenone.

Carbon	Observed Shift (ppm)	Calculated Shift (ppm)
b	31.35	
c	65.64	
d	81.33	
e	97.07	
f	127.76	126.6
g	131.56	132.5
h	129.10	129.1
i	136.05	137.6
j	194.85	

Table 3.1.14 Assignment of the ^{13}C nmr chemical shifts for 4,4'-di(2''-hydroxy-2''-methylbut-3''-yn-4''-yl) benzophenone.

The spectroscopic data presented above were consistent with the product being 4,4'-di(2''-hydroxy-2''-methylbut-3''-yn-4''-yl)benzophenone. The compound was then deprotected, via the reaction with sodium in isopropanol, to give 4,4'-diethynylbenzophenone.

Characterisation of 4,4'-diethynylbenzophenone.

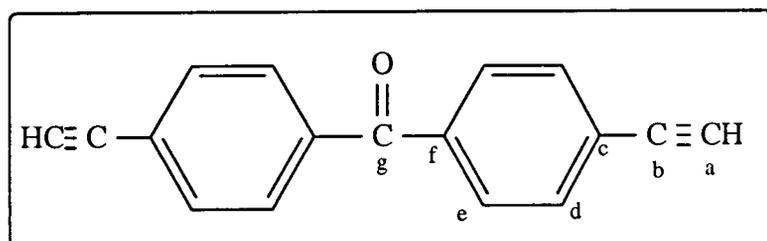


Figure 3.1.17 4,4'-Diethynylbenzophenone.

4,4'-Diethynylbenzophenone, figure 3.1.17, was isolated as a cream crystalline material which melted at 154°C and was soluble in chloroform. The ^1H and ^{13}C nmr spectra were recorded in chloroform and assigned on the basis of their chemical shifts and intensities, see tables 3.1.15 and 3.1.16. The ^1H spectrum, appendix D12, shows a singlet at 3.19ppm which is characteristic of a terminal acetylenic proton and the absence of both the hydroxyl peak and the peak at 1.61ppm are indicators that there is no protected material remaining in the product.

The ^{13}C nmr spectrum, appendix E12, is assigned on the basis of chemical shifts and intensities in table 3.1.16 and by comparison with the spectra of both 4,4'-dibromobenzophenone and 4,4'-di(2''-hydroxy-2''-methylbut-3''-yn-4''-yl)benzophenone. The ^{13}C nmr spectrum indicates that there are traces of starting material present in the sample. However attempts to purify the material further proved unsuccessful and it was decided to use the material as made. The infrared spectrum shows a peak at 3292cm^{-1} characteristic of a terminal acetylenic carbon-hydrogen stretch, a peak at 2112cm^{-1} assigned to the internal carbon-carbon stretch of the acetylene and a peak at 1643cm^{-1} analogous to of the carbonyl group in the precursor, appendix C12.

Hydrogen	Observed Shift(ppm)
a	3.19
d & e	7.5 - 7.6

Table 3.1.15 Assignment of the ^1H nmr chemical shifts for 4,4'-diethynylbenzophenone.

Carbon	Observed Shift(ppm)
a	80.4
b	82.7
c	127.8
d	131.7
e	129.8
f	135.8
g	194.6

Table 3.1.16 Assignment of the ^{13}C nmr chemical shifts for 4,4'-diethynylbenzophenone.

The spectroscopic data presented above were consistent with the product 4,4'-diethynylbenzophenone being present along with a certain amount of starting material. The material was then used in the synthesis of the linear rigid rod polymer poly(4,4'-diethynylbenzophenone), section 3.3.5 and in the synthesis of a difunctional, hinged rigid rodlike molecule, section 3.2.4.

3.1.9 Problems encountered with the coupling reaction.

The arylbromide-acetylene coupling reactions proceeded well for the reactions between 1,4-dibromobenzene and 4,4'-dibromobiphenyl with 2-methyl-3-butyn-2-ol, generally providing an overall yield of diethynyl compound of around 60%. However, when the aromatic ring contained an alkyl side chain the initial coupling reaction proved to be far less reliable. Successful couplings were rare events, unsuccessful

coupling reactions resulted in a black tar like material being produced from which it was neither possible to extract product nor starting materials. The tar like material was insoluble and attempts to analyse it were unsuccessful. Its infrared spectrum showed no evidence for significant concentrations of functional groups, such as OH, CO, or COOH, and did not resemble the spectra of either of the reagents or the solvent. The absence of any hydroxyl functionality may be indicative of side reactions involving the 2-methyl-3-butyn-2-ol becoming dominant when the alkyl side chains are present in the aromatic.

Several variations in the reaction conditions for the coupling reaction were investigated including altering the catalysts, the solvent and the concentrations of reagents and catalysts. However, these changes appeared to make no difference to the final outcome of the reaction and in an extensive series of experiments only the relative amount and rate of formation of the tar changed.

It is known that the presence of electron donating groups on the arylbromide moiety deactivates the molecule in the coupling reaction with acetylenes and also that it is possible that acetylene groups can react with one another if the reaction conditions are suitable. Therefore, it is possible that the minor side reactions which normally occur in arylbromide-acetylene coupling reactions, but can be overcome by dilution,^[D1] become significant in the reaction when alkyl side chains are present on the arylbromide. Even when the reactions were carried out at large dilution the tarlike material still resulted, this is attributed to the fact that since the arylbromide-acetylene coupling reaction is slowed down to a large extent by the electron donating effect, and probably also the steric effect of the alkyl chains, the alternative reactions of the acetylene derivative, initial coupling and/or dehydration become dominant. While this seems a plausible explanation it has to be admitted that on rare occasions (in many attempts to optimise conditions) a reasonable yield (up to 50%) of coupled product was obtained. However, the irreproducibility between superficially identical experiments remained a major frustration to the progress of the work.

3.1.10 Details of experimental procedures.

Reagents

Reagents used in this work were purchased from the Aldrich Chemical Company Ltd, with the exception of bis(triphenylphosphine) palladium(II) chloride ($\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$) which was purchased from Lancaster Synthesis. The reagents were used as purchased with the exception of 2-methyl-3-butyn-2-ol and triethylamine which were distilled prior to use.

Synthesis of 1,4-dibromo-2,5-dialkylbenzenes.

General Procedure.

Magnesium turnings (2.64g, 0.11m) and an iodine crystal were placed into a dry 500ml round bottomed flask to which a condenser with a nitrogen inlet and a dropping funnel were connected. An egg shaped magnetic flea was used to stir the contents of the flask. 1-Bromoalkane (0.1m) and sodium dried diethyl ether (200ml) were measured into dry vessels and 100ml of the diethyl ether was measured into the dropping funnel with 10ml of the 1-bromoalkane. The solution in the dropping funnel was added to the contents of the flask and the ether began to reflux, the stirrer was set in motion. The remaining bromoalkane dissolved in the remaining ether was added dropwise to the flask over a period of thirty minutes. Refluxing and stirring was continued until all of the magnesium had reacted. The flask was cooled in an ice/water bath and a solution of 1,4-dichlorobenzene (5.88g, 0.04m) and $\text{Ni}(\text{dppp})\text{Cl}_2$ (0.033g, $4.5 \times 10^{-5}\text{m}$) in dry diethyl ether (100ml) was added dropwise to the stirred solution of alkylmagnesiumbromide over a period of thirty minutes. The cooling bath was removed and the contents of the flask allowed to come to room temperature. The solution was refluxed for one day, cooled to 0°C and quenched with water (20ml) followed by HCl (2M, 50ml). The layers were separated and the aqueous layer was extracted with ether (2x100ml). The combined organic layers were washed with water, extracted with ether and the ether layer dried over magnesium sulphate. The ether was removed on a Rotavap and the resulting 1,4-dialkylbenzene was purified by distillation,

yields and physical characteristics were identical with those reported previously.

Bromine (10.9g, 0.067m) was added dropwise over a period of thirty minutes to a stirred and ice cooled solution of the 1,4-dialkylbenzene (0.03m) and an iodine crystal under rigorous exclusion of light. After one day at room temperature, 20% potassium hydroxide (50ml) was added and the flask shaken with slight warming until the yellow colour of the bromine had disappeared. The mixture was cooled to room temperature, the aqueous solution decanted and the remaining residue recrystallised twice from ethanol (70ml) to give 1,4-dibromo-2,5-dialkylbenzene as white crystals, yields and physical characteristics were identical with those reported previously.

Synthesis of

dichloro[1,3-bis(diphenylphosphinopropane)]nickel(II), Ni(dppp)Cl₂.^[V1]

A hot solution of the ligand diphenylphosphinopropane (1.51g, 3.66mmols) in 2-propanol (20ml) was added to a solution of NiCl₂.6H₂O (1.0g, 4.19mmol) in a mixture of 2-propanol:methanol (5:2, 15ml). An immediate brown flakey precipitate was formed which, on heating, gave dichloro[1,3-bis(diphenylphosphinopropane)]nickel(II) as a fine red microcrystalline powder (1.8g, 96%).

Synthesis of 1,4-Diethynylbenzene.

1,4-Dibromobenzene (23.6g, 0.1m) and 2-methyl-3-butyn-2-ol (17.0g, 0.2m) were dissolved in triethylamine (200ml) in a two necked round bottomed flask to which a condenser and a nitrogen inlet were attached. Nitrogen was bubbled through the solution for 45 minutes, the solution being stirred with a magnetic flea. A solution of Pd(PPh₃)₂Cl₂ (0.1g, 1x10⁻³m) and CuI (0.02g, 1x10⁻³) dissolved in piperidine (10ml) under nitrogen was added dropwise to the contents of the flask. The resulting solution was refluxed for four hours, cooled to room temperature and the precipitated white triethylamine salt filtered off on a Buchner funnel. The excess triethylamine from the filtrate was removed using a Rotavap, water was added to the residue to remove any remaining triethylamine salt and the organic product was extracted with ether. On removal of the ether a pink solid was formed, which was recrystallised from hexane to

give: 1,4-di(2'-hydroxy-2'-methylbut-3'-yn-4'-yl)benzene as a cream powder, (19.6g, 80%, mp 74°C).

A solution of 1,4-di(2'-hydroxy-2'-methylbut-3'-yn-4'-yl)benzene (12.1g, 0.05m) in methanol (250ml) containing potassium hydroxide (10g, 0.18m) was heated under reflux for 14 hours. A cream precipitate formed as the reaction proceeded. The precipitate was recovered by filtration using a Buchner funnel, washed with water containing a little HCl, and dried under vacuum. The product was then purified by sublimation to give: 1,4-diethynylbenzene as a cream powder, (5.17g, 82%, mp 94.5°C).

Synthesis of 4,4'-diethynylbiphenyl.

Following the procedure described for 1,4-di(2'-hydroxy-2'-methylbut-3'-yn-4'-yl)benzene, 4,4'-dibromobiphenyl (31.2g, 0.1m) was reacted with 2-methyl-3-butyn-2-ol (17.0g, 0.2m) in triethylamine (200ml) to give 4,4'-di(2'-hydroxy-2'-methylbut-3'-yn-4'-yl)biphenyl as a cream powder, (24.8g, 78%, mp 167°C). 4,4'-Di(2'-hydroxy-2'-methylbut-3'-yn-4'-yl)biphenyl (15g, 0.05m) was then reacted in methanol (250ml) containing potassium hydroxide (10g, 0.18m) following the procedure described for 1,4-diethynylbenzene to give 4,4'-diethynylbiphenyl as a cream powder, (8.3g, 82%, mp 165°C).

General reaction scheme for the coupling reactions between 1,4-dibromo-2,5-dialkylbenzenes and 2-methyl-3-butyn-2-ol and deprotection of the products.

1,4-Dibromo-2,5-dialkylbenzene (0.1m) and 2-methyl-3-butyn-2-ol (17.0g, 0.2m) were dissolved in triethylamine (200ml) in a two necked round bottomed flask to which a condenser and a nitrogen inlet were attached. Nitrogen was bubbled through the solution for 45 minutes, the solution being stirred with a magnetic flea. A solution of Pd(PPh₃)₂Cl₂ (0.1g, 1x10⁻³m) and CuI (0.02g, 1x10⁻³) dissolved in piperidine (10ml) under nitrogen was added dropwise to the contents of the flask. The resulting solution was refluxed for four hours, cooled and the white precipitated triethylamine salt filtered off on a Buchner funnel. The excess triethylamine from the filtrate was removed using

a Rotavap, water added to the residue to remove any remaining triethylamine salt and the organic product extracted with ether. On removal of ether a pink solid was formed, which was recrystallised from hexane to give: *1,4-di(2'-hydroxy-2'-methylbut-3'-yn-4'-yl)-2,5-dialkylbenzene* as a cream powder.

A solution of *1,4-di(2'-hydroxy-2'-methylbut-3'-yn-4'-yl)-2,5-dialkylbenzene* (0.05m) in methanol (250ml) containing potassium hydroxide (10g, 0.18m) was heated under reflux for 14 hours. A cream precipitate formed as the reaction proceeded. The precipitate was recovered by filtration using a Buchner funnel, washed with water containing a little HCl and dried under vacuum. The product was then purified by sublimation to give: *1,4-diethynyl-2,5-dialkylbenzene*.

On the occasion that the above procedure was carried out using *1,4-dibromo-2,5-dihexylbenzene* (40.4g, 0.1m) and *2-methyl-3-butyn-2-ol* (17.0g, 0.2m) the yield of coupled product was (20.5g, 50%). The deprotection reaction proceeded as described above to give *1,4-diethynyl-2,5-dihexylbenzene* (8.82g, 60%). This reaction was the most successful achieved when side chains were present. The reaction was carried out with *1,4-dibromo-2,5-dialkylbenzenes*, where the alkyl group ranged from butyl to dodecyl, each reaction being carried out several times over a period of two years. However, it never proved possible to carry out the coupling successfully with any of these starting materials.

Synthesis of 4,4'-diethynylbenzophenone.

Following the procedure described for *1,4-di(2'-hydroxy-2'-methylbut-3'-yn-4'-yl)benzene*, *4,4'-dibromobenzophenone* (50g, 0.15m) was reacted with *2-methyl-3-butyn-2-ol* (25g, 0.3m) in triethylamine (500ml) to give *4,4'-di(2''-hydroxy-2''-methylbut-3''-yn-4''-yl)benzophenone* as a cream powder, (7.25g, 14%). *4,4'-Di(2''-hydroxy-2''-methylbut-3''-yn-4''-yl)benzophenone* (7.25g, 0.02m) was then reacted in methanol (250ml) containing sodium hydroxide (1.6g, 0.04m) following the procedure described for *1,4-diethynylbenzene* to give *4,4'-diethynylbenzophenone* as a cream powder, (4.0g, 87%, mp 154°C).

3.2 Synthesis and characterisation of rigid rodlike diesters.

Rigid rodlike diesters were synthesised from diethynylbenzenes and aromatic bromoesters. The rodlike molecules needed to be difunctional to allow their incorporation into polymer networks. In the first instance model reactions were carried out in order to investigate the feasibility of employing either 4-bromomethylbenzoate or 4-bromobenzoic acid to provide the functionalised end groups. There are two plausible strategies for preparing the diesters required; coupling the bromoarylester to an aryldiacetylene or coupling the ethynylarylester to an aryldibromide. 4-Bromobenzoic acid could not be successfully coupled with 2-methyl-3-butyn-2-ol so it was decided to use the ester, 4-bromomethylbenzoate, in the reactions to synthesise rigid rodlike compounds. The coupling reaction between 4-bromomethylbenzoate and 2-methyl-3-butyn-2-ol is described and assignments of the spectroscopic data are tabulated for reference purposes, section 3.2.1. Rodlike molecules were synthesised from 1,4-diethynylbenzene and 4,4'-diethynylbiphenyl with 4-bromomethylbenzoate via a palladium catalysed coupling reaction. The synthesis and characterisation of the rodlike molecules formed is described in section 3.2.2, and 3.2.5. A hinged rigid rodlike molecule was synthesised via the reaction between 4,4'-diethynylbenzophenone and 4-bromomethylbenzoate, section 3.2.7. It was expected that the bend in the molecule due to the carbonyl group would lead to an example of a more processable rod than the linear rigid rod molecules.

3.2.1 Coupling reaction between 4-bromomethylbenzoate and 2-methyl-3-butyn-2-ol.

The palladium catalysed coupling reaction between 4-bromomethylbenzoate and 2-methyl-3-butyn-2-ol was carried out in order to investigate the feasibility of utilising 4-bromomethylbenzoate in the formation of difunctional rigid rodlike molecules. The reaction proceeded in yields of greater than 80% to give a white crystalline material, see section 3.2.8 for experimental procedure.

Characterisation of

4-(2'-hydroxy-2'-methylbut-3'-yn-4'-yl)methylbenzoate.

The ^1H and ^{13}C nmr spectra, appendices D5 and E5, were recorded in chloroform and were fully assigned, see tables 3.2.1 and 3.2.2, by comparison with both similar spectra and with the values calculated via substituent shift effects, for the aromatic carbons. The splitting patterns and integrations for the proton spectrum are consistent with the product being 4-(2'-hydroxy-2'-methylbut-3'-yn-4'-yl) methylbenzoate, see figure 3.2.1.

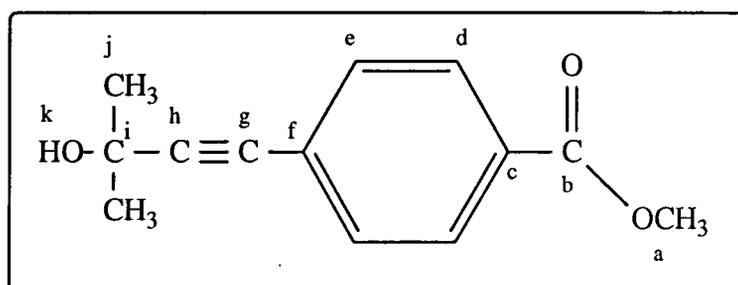


Figure 3.2.1 4-(2'-hydroxy-2'-methylbut-3'-yn-4'-yl)methylbenzoate.

Carbon	Observed Shift (ppm)	Calculated Shift (ppm)
a	65.61	
b	166.58	
c	129.53	130.4
d	129.43	130.1
e	131.57	132.3
f	127.51	126.8
g	96.80	
h	81.44	
i	52.25	
j	31.37	

Table 3.2.1 Assignment of the ^{13}C nmr chemical shifts for 4-(2'-hydroxy-2'-methylbut-3'-yn-4'-yl)methylbenzoate.

Hydrogen	Observed Shift (ppm) & integrated intensities
a	3.90, 3H
d & e	7.45-7.98, 4H
j	1.62, 6H
k	2.27, 1H

Table 3.2.2 Assignment of the ^1H nmr shifts for 4-(2'-hydroxy-2'-methylbut-3'-yn-4'-yl)methylbenzoate.

It was decided in the light of the above evidence that 4-bromomethylbenzoate would be used to provide the functionalised ends for the difunctional rigid rodlike molecules. Attempts to deprotect 4-(2'-hydroxy-2'-methylbut-3'-yn-4'-yl)methyl benzoate always led to the formation of the acid, 4-ethynylbenzoic which was unsuitable for further use in coupling reactions since the acid had a deactivating effect. This potential route to difunctional monomers was abandoned and the alternative strategy, that is the coupling of the bromoarylester to an aryl diacetylene, was employed in preference.

3.2.2 Synthesis and characterisation of 1,4-bis(4'-ethynylmethylbenzoate)benzene.

1,4-Bis(4'-ethynylmethylbenzoate) benzene was synthesised via the palladium catalysed coupling reaction between 1,4-diethynylbenzene and 4-bromomethyl benzoate, see section 3.2.8 for experimental procedure.

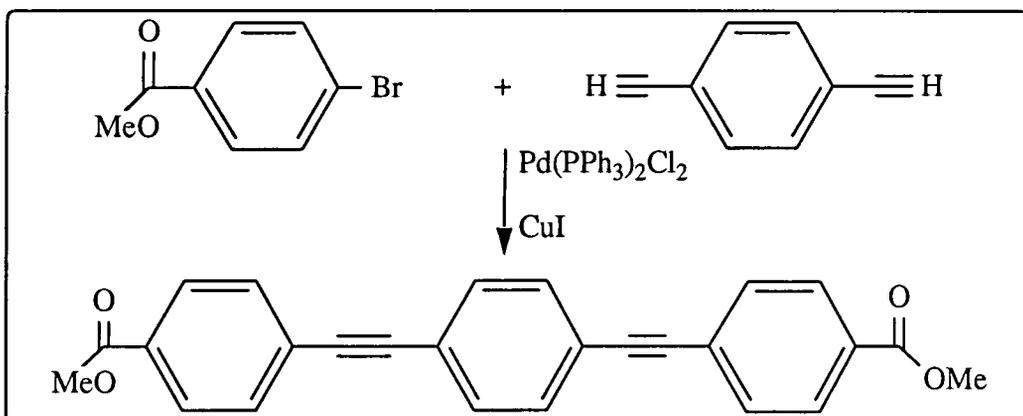


Figure 3.2.2 Reaction between 1,4-diethynylbenzene and 4-bromomethylbenzoate.

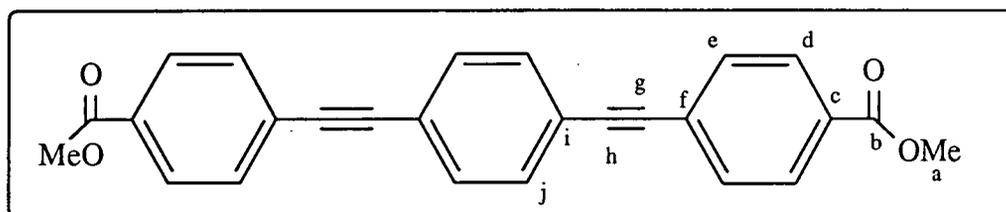


Figure 3.2.3 1,4-Bis(4'-ethynylmethylbenzoate)benzene.

The material exhibited a melting point at 285°C and proved to be insoluble in all common solvents and so a solid state ^{13}C nmr spectrum was recorded in order to confirm the structure as 1,4-bis (4'-ethynylmethylbenzoate) benzene, figure 3.2.3. The ^{13}C nmr spectrum was completely assigned, see table 3.2.3, using the separate spectra recorded for the sets of quaternary carbons and those bearing protons, together with the calculated shifts for the aromatic carbons. Distinct peaks were observed for each carbon environment except the ethyne carbons (*g* and *h*) which were coincident. There were no signals unaccounted for and the S/N is sufficiently good to be confident that the compound is reasonably pure (>95%), appendix E6.

Carbon	Observed Shift (ppm)	Calculated Shift (ppm)
a	54.5	
b	166.0	
c	130.5	130.4
d	129.3	130.1
e	130.6	132.3
f	126.6	126.8
g & h	91.8	
i	123.1	122.2
j	132.5	132.7

Table 3.2.3 Assignment of the ^{13}C nmr chemical shifts for 1,4-bis(4'-ethynylmethylbenzoate)benzene.

Peak	Assignment
394	M+ Ion
363	M+ - OMe
276	M+ - 2 COOMe
76	C ₆ H ₄ +

Table 3.2.4 Diagnostic peaks in the mass spectrum of 1,4-bis(4'-ethynylmethylbenzoate)benzene.

Peak (cm-1)	Assignment
1720	Carbonyl str
2284	Acetylene str

Table 3.2.5 Assignment of characteristic peaks in the infrared spectrum of 1,4-bis(4'-ethynylmethylbenzoate)benzene.

The spectroscopic data presented above were consistent with the product being 1,4-bis(4'-ethynylmethylbenzoate)benzene. The ^{13}C spectra provided strong support (see above), the mass spectrum shows a peak for the molecular ion at 394 and a

fragmentation pattern which is readily rationalised in terms of the assigned structure, appendix B6. The infrared spectrum indicates the presence of a carbonyl group (1720cm^{-1}), in the correct position for an aryl ester, and an internal acetylene (2284cm^{-1}); there is no evidence of a terminal acetylenic hydrogen, appendix C6. This indicates that there is no unreacted 1,4-diethynylbenzene present in the final product.

Consideration of the molecular structure of the rigid rodlike molecule led to the supposition that the material might be expected to exhibit liquid crystalline behaviour. It is probable that this behaviour, should it exist, would be carried over into the properties of polymers containing the rodlike molecules. A description of the factors leading to liquid crystalline behaviour and the techniques that can be used to assess it are detailed in section 3.2.3 as an introduction to the investigation of the liquid crystalline nature of the molecularly rigid rodlike molecule, section 3.2.4.

3.2.3 Liquid crystalline materials.

Friedrich Reintzer is credited with being the first to notice that cholesteryl esters formed opaque liquids when they were melted; these opaque liquids became clear on further heating and formed isotropic melts. Lehman interpreted the observation to mean that there was a new phase which lay between the solid and the isotropic liquid states previously known. Friedel continued the work and this new state became known as a mesophase (Greek; meso = in between or intermediate). The mesophase was found to be quite fluid and to exhibit birefringence. The properties that it possessed were also associated with crystals and with liquids and hence the compounds became known as liquid crystals.

There are two main types of liquid crystalline materials; thermotropic and lyotropic. A thermotropic material is one in which the liquid crystalline phases are formed on heating the pure compound. A lyotropic material is one in which the liquid crystalline phases are formed when the molecules are mixed with a solvent.

Thermotropic types of material are subdivided into enantiotropic types, in which

the liquid crystalline phases can be seen on both the heating and the cooling cycles, and monotropic types in which the mesophase is only stable on supercooling from the isotropic melt. Further work led to three main types of mesophase being discovered; the smectic, the nematic and the cholesteric states.

Flory suggested in 1956 that concentrated solutions of rigid rodlike polymers should also form ordered structures at a critical concentration; these polymeric liquid crystalline materials would be comparable with those formed from small molecules as described earlier. Actual studies of the phenomenon were carried out on concentrated solutions of the polymers poly(γ -methylglutamate) and poly(γ -benzylglutamate). These polymers existed in an extended helical form that was able to pack into ordered bundles, their long axes being aligned in one direction resulting in a pseudo-parallel distribution of the chains throughout the solution; anisotropic liquid crystalline properties are observed. Other lyotropic polymers which exhibit liquid crystalline properties include certain polyamides and some cellulose derivatives. Once again the molecules are relatively rigid.

Liquid crystalline molecules.

Those molecules which form a liquid crystalline phase can be assigned as having a rigid structure in which their aspect ratio (length/breadth ratio) is high or as having a disc shaped structure. Illustrative examples of molecules which exhibit liquid crystalline behaviour are shown in figure 3.2.4 and are known as mesogens.

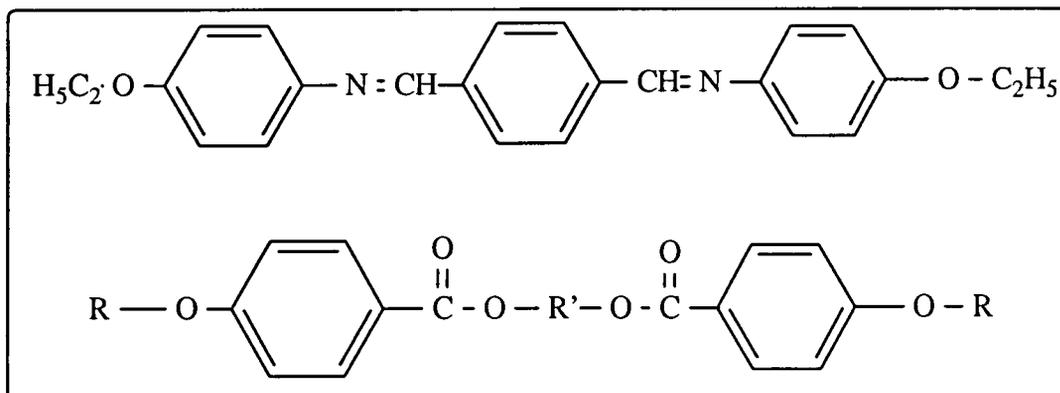


Figure 3.2.4 Molecules which exhibit liquid crystalline behaviour, mesogens.

Liquid crystalline polymers.

Polymers containing mesogens can also exhibit liquid crystalline behaviour, the phase which is formed being dependant upon the alignment of the mesogenic groups within the polymer structure. The ordered structures formed are characterised by long range orientational order, the long axes of the mesogenic groups being preferentially aligned in a certain direction, known as the director. In cases where the ordering is such that the mesogens are arranged in layers with respect to their centres of gravity, they are said to be in a smectic phase.

In the smectic phase the lateral forces between molecules are stronger than the forces between the layers, thus when one layer moves over another the classic fluidity of the system can be exhibited without destruction of the ordering within the layer. Several smectic phases can be defined, the main two being; A)Smectic B - the most ordered phase, having a hexagonally close packed structure of the mesogens in the layers, B)Smectic A - has random lateral distribution of the mesogens in the layers. The tilted modifications of both of the above also exist, the most important being Smectic C, the tilted modification of Smectic A.

The nematic phase has far less ordering associated with it than the smectic phase. Disordering of the long axes of the mesogen is maintained but the centres of gravity are no longer contained in layers, but are randomly distributed in the phase. In general the nematic phase is much more fluid than the smectic phase but birefringence is still seen.

Identification of mesophases.

When attempting to assign the liquid crystalline phases present in polymeric materials there are a number of techniques which can be exploited in order to provide information on the nature of the molecular orientation within the phase. When these techniques are utilised in conjunction with one another fairly reliable deductions about the state of the mesogenic groups can be made. The techniques available for assessing the liquid crystalline properties of a polymer are described below.

Optical microscopy.

It is possible to identify the liquid crystalline phases present in a polymer sample using the technique of polarising microscopy. Thin layers of the polymer are observed on a hot stage through a polarising microscope. Characteristic textures develop that can be used to assign the types of phase that are present in the polymer sample under observation.

The preparation of the glass slides used to hold the polymer sample is important. The slide must be rubbed in one direction with a cotton cloth before use so that the mesogens at the surface will all lie parallel, this leads to uniform birefringence. If this is not done the mesogens lie at right angles to the surface and movement of the cover slip is required before birefringence is observed as the mesogens are tilted under the applied pressure.

When a liquid crystal forming material is cooled from the isotropic melt the first change will be a separation of ordered droplets which in turn coalesce into larger ordered domains, there may be further phase changes within these domains as cooling continues. When this process is viewed through a polarising microscope characteristic patterns (textures) develop in the field of view from which the nature of the liquid crystalline order present at a particular stage can be deduced. When nematic droplets separate multi coloured domains appear with striations running through them. The texture observed is dependant upon the way in which the droplets form larger domains, and one of three possible textures, known as the Schlieren, the threaded or the marbled nematic texture may be seen, illustrations can be found in reference C8. Likewise smectic phases can be detected by analysis of the textures observed through the polarising microscope. A number of textures are indicative of a smectic phase including, the focal conic and fan texture which is attributed to the smectic A phase, the mosaic texture which indicates a smectic B phase and the broken conic structure which results from smectic C phases; details of the nature of the various kinds of smectic phases and illustrations of the associated textures can be found in reference C8.

X-ray diffraction.

X-ray diffraction provides a method by which the extent of crystallinity in a polymer sample can be investigated. Where there are crystallites present in a powdered polymer sample they diffract X-ray beams by angles Θ which may be determined from the Bragg equation;

$$n\lambda = 2d\sin\Theta$$

where;

n = an integer,

d = the distance between parallel planes in the crystallites, and

λ = the wavelength of the radiation.

The reflected waves produce diffraction rings or haloes from a bulk isotropic sample. These haloes are most sharply defined for highly crystalline materials and as the amorphous content of the polymer increases the haloes become more diffuse. Orientation of a polymer sample, for instance brought about by drawing a fibre or by applying tension to a film, causes alignment of the crystallites and the X-ray pattern can be made sharper. The degree of crystallinity present in a polymer sample can be estimated by comparing plots of the density of the scattered beam against the angle of incidence for an amorphous sample and a corresponding highly crystalline sample. This procedure provides reference points for the measurement of the crystallinity of other samples of the same polymer.

Liquid crystalline polymers can be investigated by X-ray diffraction and the powder diagrams produced can be interpreted to provide information about the amount and type of order present in the sample.

When the sample exists in the nematic phase one diffuse halo is seen at large diffraction angles. This is indicative of a disordered arrangement of the mesogens within different domains. On moving to the more ordered smectic phases one or more Bragg reflections are seen. The halo now contains one or more sharp inner rings which are a consequence of the more ordered structure. The most efficient way of obtaining

information is to orient the polymer samples by cooling them from the isotropic liquid phase under the influence of a strong magnetic field or by drawing fibres from the mesophase followed by quenching to achieve the orientated structure.

Differential scanning calorimetry.

Differential scanning calorimetry measures the heat flow into or from a sample as a function of temperature at constant rate of change of temperature, or time at constant temperature. In favourable cases phase changes can be detected and the energy associated with the processes determined quantitatively. In the field of liquid crystalline materials the technique has been used to define the range of stability of the various phases in which a particular liquid crystal can exist.

3.2.4 An investigation of the properties of 1,4-bis(4'-ethynylmethylbenzoate)benzene.

1,4-Bis(4'-ethynylmethylbenzoate)benzene was prepared as described in section 3.2.2. The properties of the material were then investigated with respect to its solubility and thermal behaviour. The details of these investigations are described in sections 3.2.4a & b. It was expected that the rigid rodlike molecule would exhibit liquid crystalline behaviour, hence polarising microscopy, differential scanning calorimetry and X-ray diffraction investigations were carried out. The results of these investigations are described in sections 3.2.4c-e.

3.2.4a Solubility properties of 1,4-bis(4'-ethynylmethylbenzoate)benzene.

The material proved to be insoluble in a wide range of organic solvents and was decomposed by mineral acids.

3.2.4b Thermal properties of 1,4-bis(4'-ethynylmethylbenzoate)benzene.

1,4-Bis(4'-ethynylmethylbenzoate)benzene was found to melt at 285°C.

The TG trace of the material shows no evidence of weight loss below 80°C.

Slow decomposition occurs to the extent of 4.5% up to 250°C, which may be due in part to loss of entrained solvent, then there is an increase in the rate of decomposition up to an inflection at about 415°C when 29% of the weight of the compound has been lost. This corresponds to the loss of the ester groups from the material. The rate of decomposition decreases once again at about 550°C and by 685°C around 50% of the weight of the compound remains.

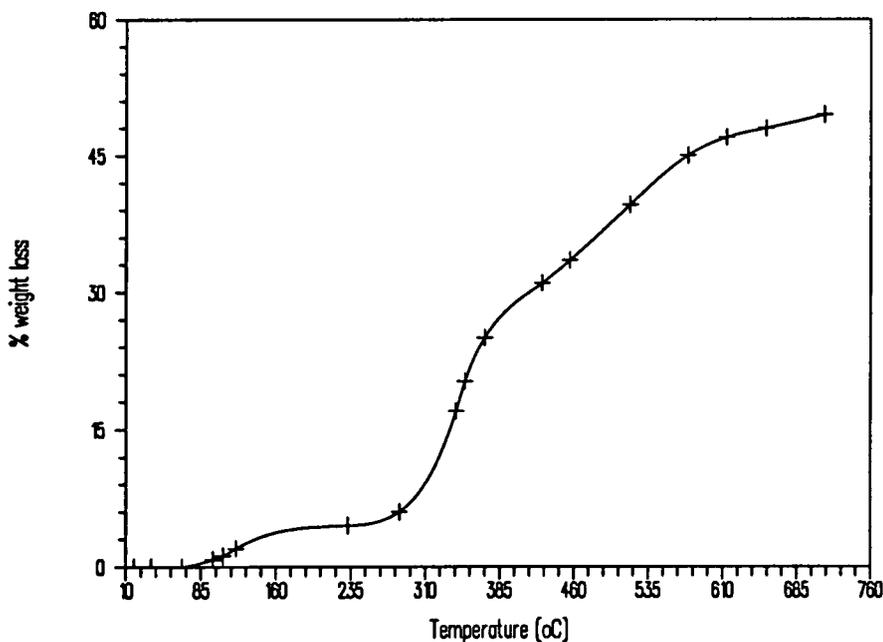
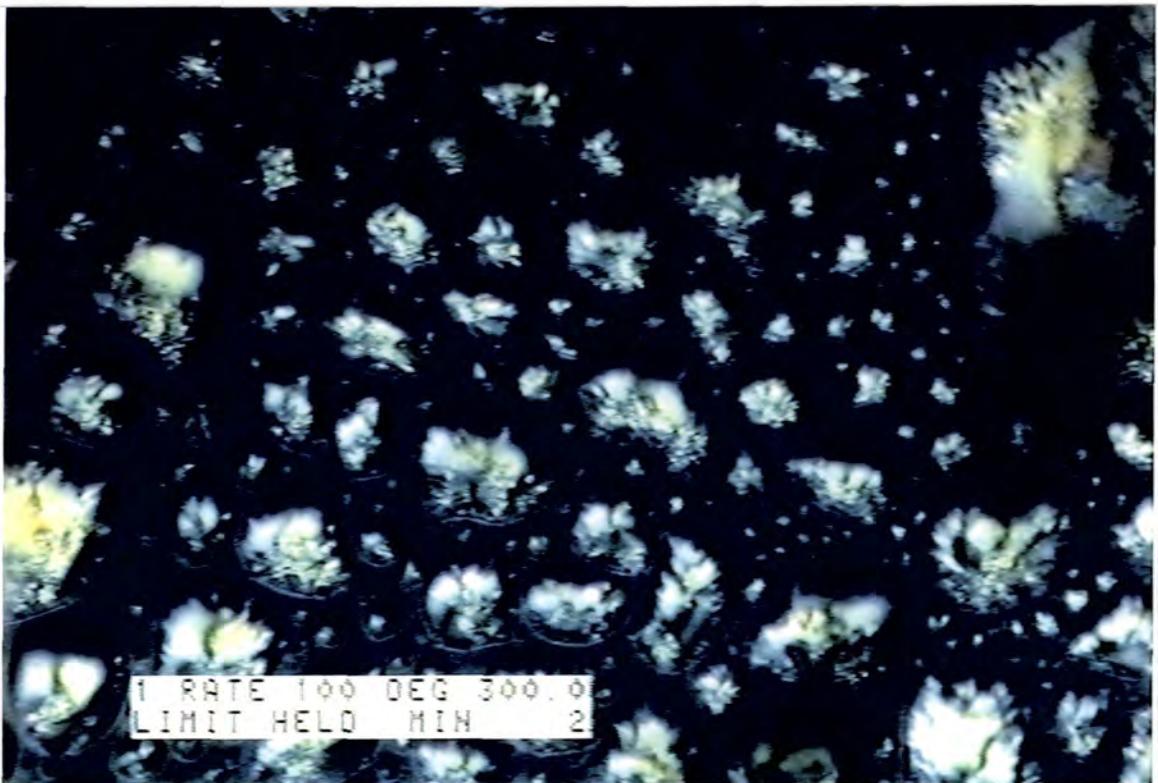


Figure 3.2.5 TG trace for 1,4-bis(4'-ethynylmethylbenzoate)benzene (0.526mg, 10°/min).

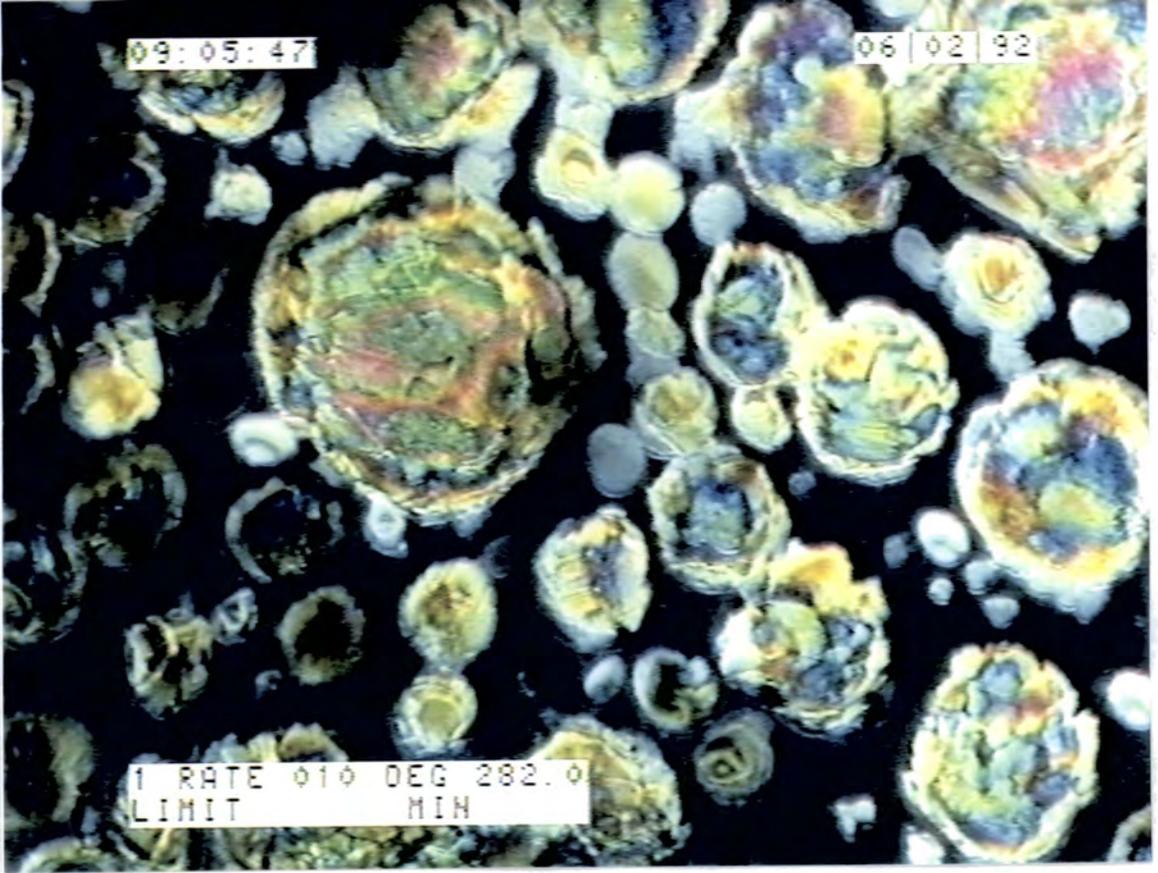
3.2.4c Polarising microscopy studies.

A sample of as made 1,4-bis(4'-ethynylmethylbenzoate)benzene was viewed through the microscope. It was heated from 20-300°C at a rate of 10°/minute and observed to melt at 285°C, the temperature was held at 300°C for 5 minutes. At this stage clear droplets with no structure were observed which is characteristic of an isotropic melt, photograph 1. On cooling the droplets exhibited birefringence below 285°C, photograph 2. The observed texture was maintained down to room temperature with no evidence for further phase changes, photograph three. The phase transition

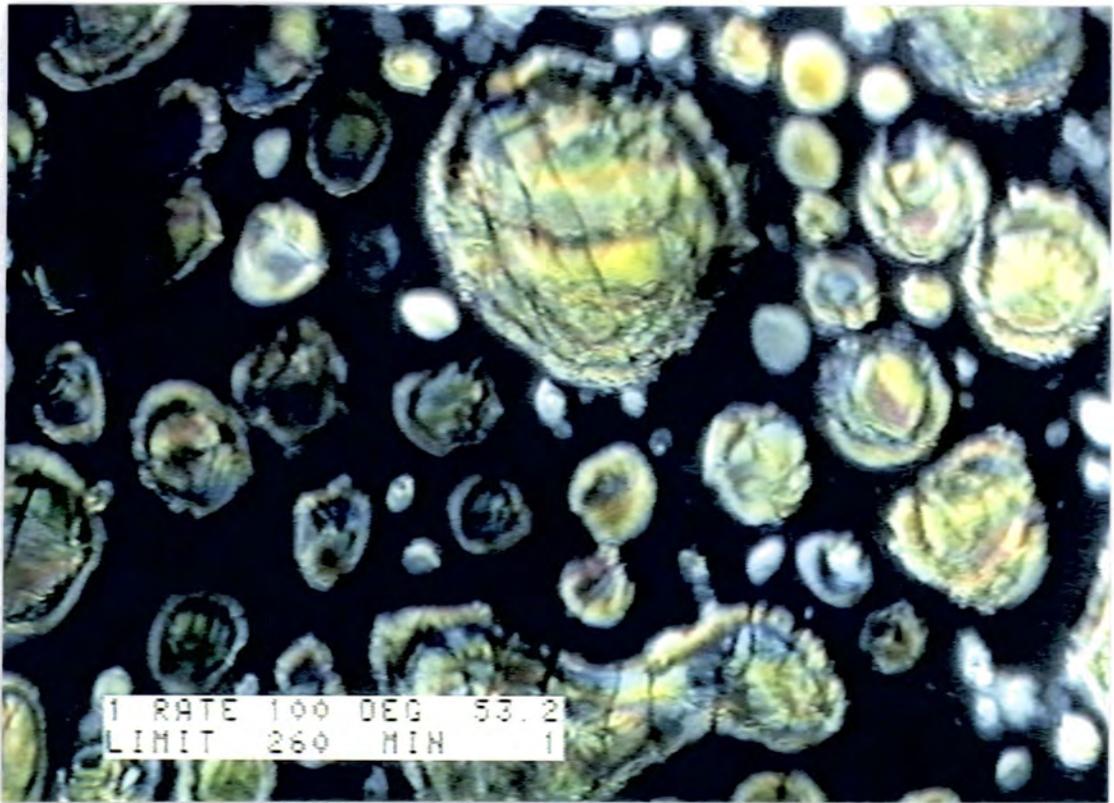
observed on cooling from the isotropic melt was either a simple crystallisation or an isotropic to nematic phase change, the texture is somewhat similar to those described as "marbled" and indicative of a nematic phase but the absence of a detectable transition to the crystalline solid, the inability to shear the coverslip once birefringence is observed and the lack of any induced structure on shearing above 285°C suggests that we are observing, contrary to our expectations, a simple crystallisation.



Photograph 1.



Photograph 2.



Photograph three.

3.2.4d Differential scanning calorimetry investigations.

Only a single melting point transition at 285°C was observed in repeated measurements, figure 3.2.6.

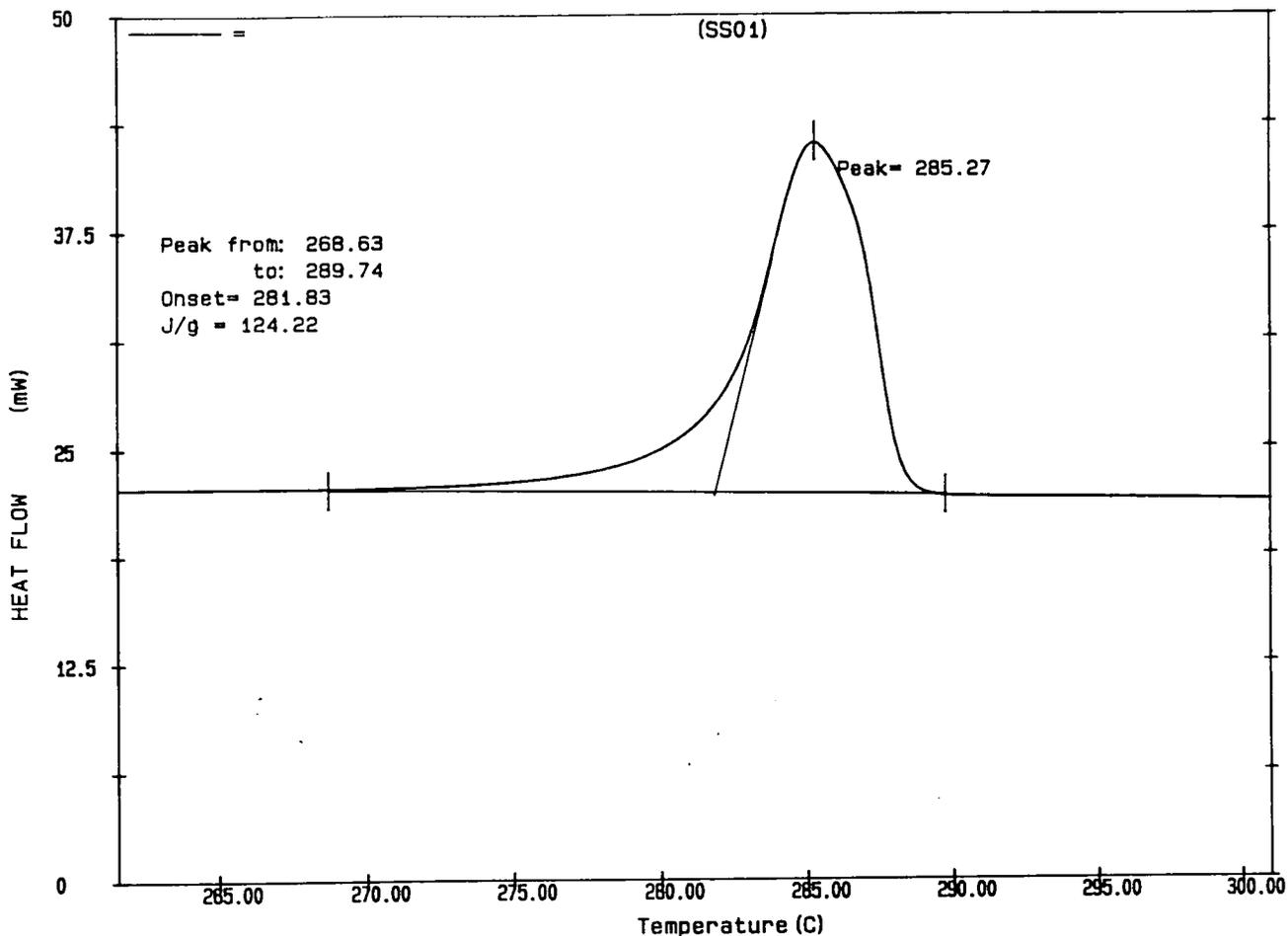


Figure 3.2.6 DSC trace for 1,4-bis(4'-ethynylmethylbenzoate) benzene.

3.2.4e X-ray diffraction studies.

The X-ray diffraction patterns were recorded for both as made 1,4-bis(4'-ethynylmethylbenzoate)benzene and for a sample of the material that had been held at 300°C for fifteen minutes before allowing it to cool to room temperature. The resulting X-ray diffraction patterns are shown in figure 3.2.7 and the calculated d-spacings are tabulated in tables 3.2.6 and 3.2.7.

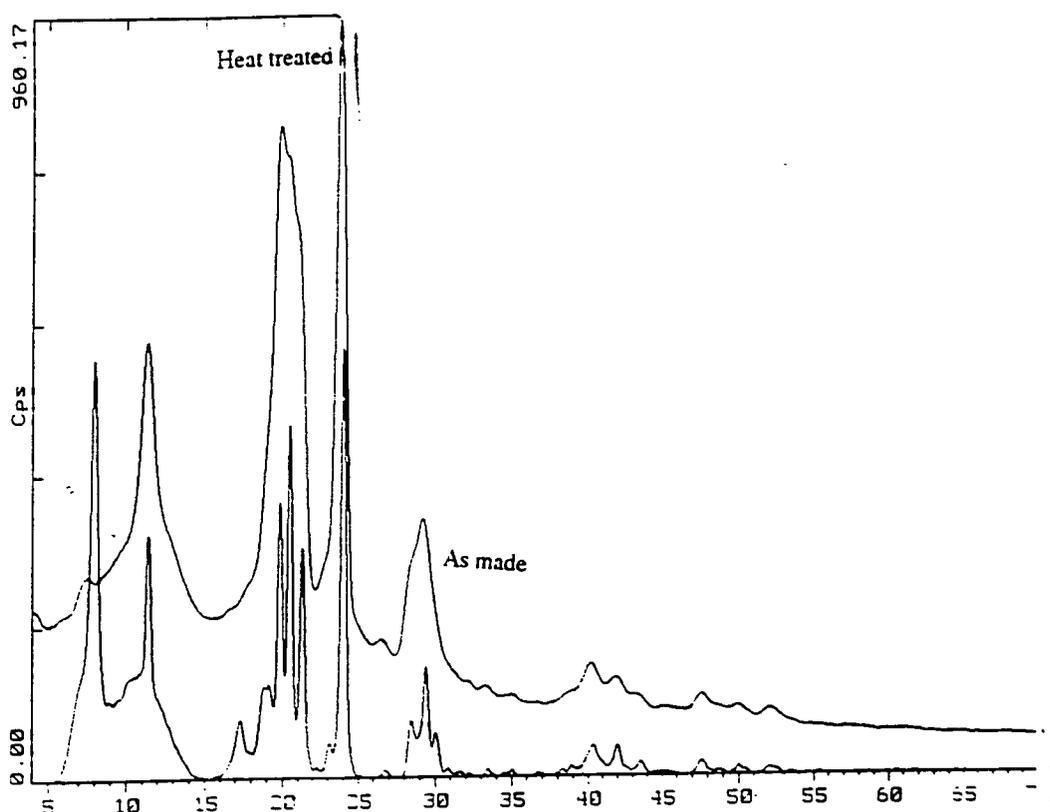


Figure 3.2.7 X-ray diffraction pattern for as made and heat treated 1,4-bis(4'-ethynylmethylbenzoate)benzene.

The increased number of peaks observed for the heat treated sample of 1,4-bis(4'-ethynylmethylbenzoate)benzene and their increased definition is indicative of an increase in the degree of crystallisation within the sample as compared with that of the as made sample of 1,4-bis(4'-ethynylmethylbenzoate)benzene.

Peak	Theta angle	d-spacing
1	7.06	12.51
2	11.35	7.79
3	12.84	6.89
4	19.12	4.64
5	19.82	4.48
6	20.43	4.34
7	21.09	4.21
8	22.84	3.89
9	23.89	3.72
10	28.47	3.13
11	29.04	3.07
12	29.26	3.05
13	29.94	2.98
14	33.21	2.70
15	40.15	2.24

Table 3.2.6 X-ray diffraction data for as made
1,4-bis(4'-ethynylmethylbenzoate)benzene.

Peak	Theta angle	d-spacing
1	6.94	12.72
2	7.94	11.12
3	10.45	8.46
4	11.38	7.77
5	12.32	7.18
6	17.27	5.13
7	18.92	4.69
8	19.85	4.47
9	20.45	4.33
10	21.29	4.17
11	24.00	3.70
12	26.73	3.33
13	28.51	3.13
14	29.36	3.04
15	33.46	2.67
16	34.91	2.57
17	40.31	2.24
18	41.95	2.15

Table 3.2.7 X-ray diffraction data for heat treated
1,4-bis(4'-ethynylmethylbenzoate)benzene.

Conclusions.

Contrary to expectations and to the assertions of other workers the author concludes that 1,4-bis(4'-ethynylmethylbenzoate)benzene is a simple crystalline solid which does not display liquid crystalline behaviour. In a sample of the as made material the rigid rod molecules are randomly ordered throughout the material, when the sample is melted the rods are able to move and preferentially align with respect to one another to some degree to give a more highly crystalline sample. This matter has been dealt with in some detail because it was a question of "lively debate" during the course of the work.

3.2.5 Synthesis and characterisation of 4,4'-bis(4''-ethynylmethylbenzoate)biphenyl.

4,4'-Bis(4''-ethynylmethylbenzoate)biphenyl was synthesised via the palladium catalysed coupling reaction between 4,4'-diethynylbiphenyl and 4-bromomethylbenzoate, figure 3.2.8 and section 3.2.8 for experimental procedure.

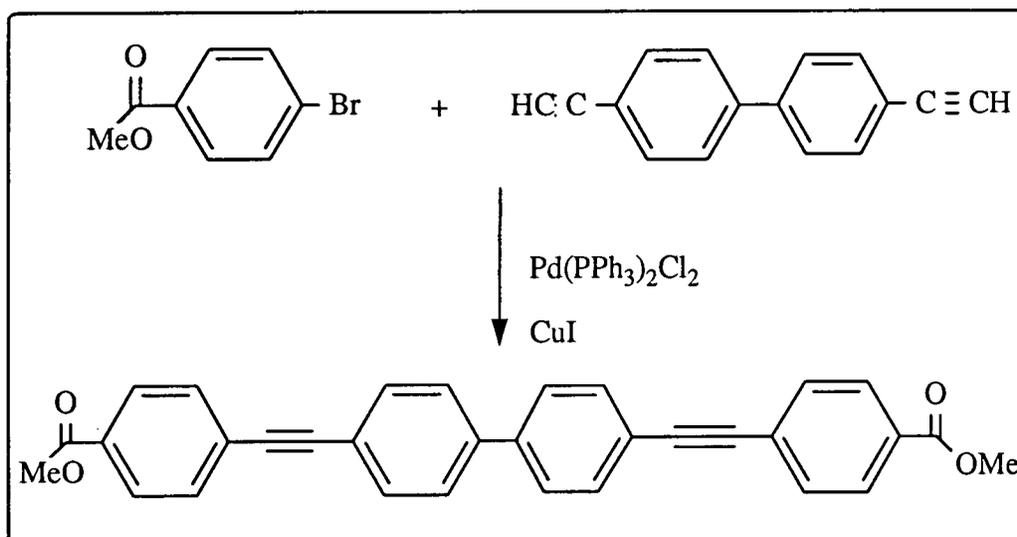


Figure 3.2.8 Reaction scheme for the coupling between 4,4'-diethynylbiphenyl and 4-bromomethylbenzoate.

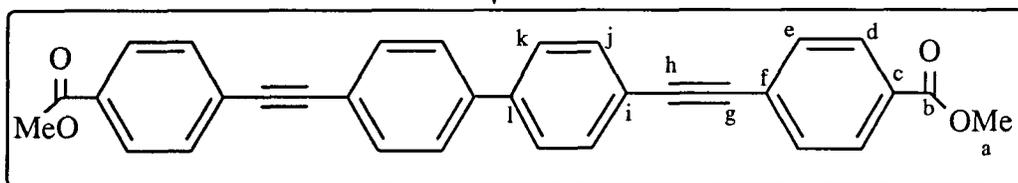


Figure 3.2.9 4,4'-Bis(4''-ethynylmethylbenzoate)biphenyl.

The material proved to be insoluble in all common solvents and so a solid state ^{13}C nmr spectrum was recorded in order to confirm the structure as 4,4'-bis(4''-ethynylmethylbenzoate)biphenyl, figure 3.2.9. No melting point was observed for the material below 500°C and the material proved to be too involatile for the mass spectrum to be recorded. The ^{13}C nmr spectrum was completely assigned, see table 3.2.8, using the separate spectra recorded for the sets of quaternary carbons and those bearing protons, together with the calculated shifts for the aromatic carbons, appendix E7.

Carbon	Observed Shift (ppm)	Calculated Shift (ppm)
a	79.2	
b	165.9	
c	132.6	130.5
d & k	127.6	130.6/127.8
e & j	132.9	132.5/132.8
f	127.0	126.5
g	82.3	
h	91.1	
i	121.1	121.4
l	140.0	141.3

Table 3.2.8 Assignment of the ^{13}C nmr shifts for 4,4'-bis(4''-ethynylmethylbenzoate)biphenyl.

Peak (cm-1)	Assignment
1720	Carbonyl str
2210	Acetylene str

Table 3.2.9 Assignment of characteristic peaks in the infrared spectrum of 4,4'-bis(4''-ethynylmethylbenzoate)biphenyl.

The spectroscopic data presented above were consistent with the product being 4,4'-bis(4''-ethynylmethylbenzoate)biphenyl. The infrared spectrum, appendix C7, indicates the presence of a carbonyl group, in the correct position for an aryl ester (1720cm^{-1}), and an internal acetylene (2285cm^{-1}), see table 3.2.9. There is no evidence of a terminal acetylenic hydrogen indicating that there is no unreacted material present in the final product.

3.2.6 Investigation of the physical properties of 4,4'-bis(4''-ethynyl methylbenzoate)biphenyl.

The physical properties of the rigid rodlike molecule, 4,4'-bis(4''-ethynylmethylbenzoate)biphenyl, figure 3.2.9 was investigated using a variety of techniques. The results from the thermal and XRD investigations are reported in sections 3.2.6a & b.

As described for 1,4-bis(4'-ethynylmethylbenzoate) benzene, section 3.2.2, consideration of the molecular structure of the rigid rodlike molecule led to the supposition that the material should exhibit liquid crystalline behaviour. However, since the material exhibited no melting point below 500°C and was insoluble in a wide range of organic solvents it was not possible to investigate the supposition.

3.2.6a Thermal properties of 4,4'-bis(4''-ethynylmethylbenzoate)biphenyl.

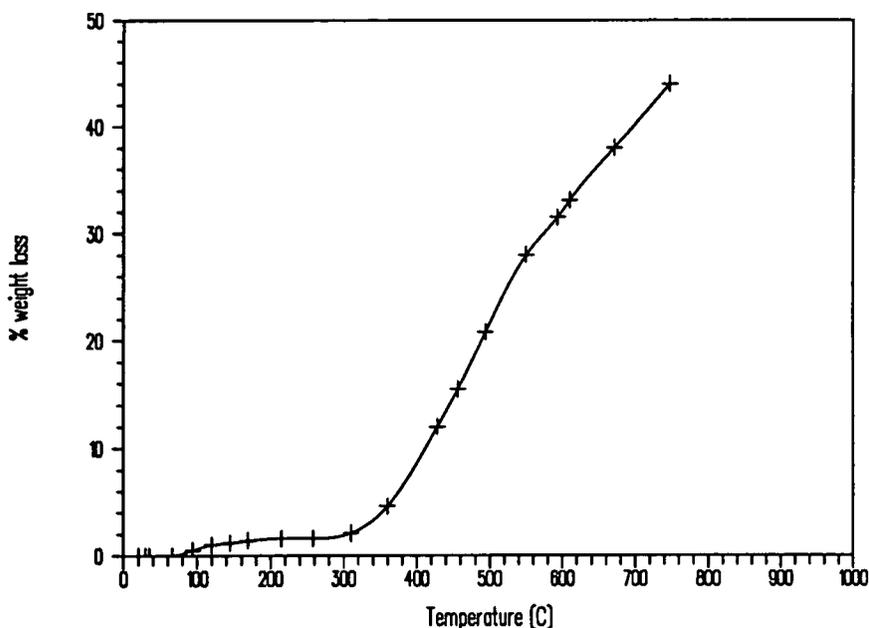


Figure 3.2.10 TG trace for 4,4'-bis(4''-ethynylmethylbenzoate)biphenyl.

The TG trace of the material shows no evidence of weight loss below 80°C, weight loss to the extent of 1.5% up to 250°C, possibly due to loss of entrained solvent, and then there is an increase in the rate of decomposition until by 530°C 25% of the weight of the compound has been lost. This corresponds to the loss of the ester groups from the material. The rate of decomposition then slows somewhat and by 700°C around 60% of the weight of the compound remains.

3.2.6b X-ray diffraction studies.

The X-ray diffraction pattern was recorded for as made 4,4'-bis(4''-ethynylmethylbenzoate)biphenyl. The resulting X-ray diffraction pattern is shown in figure 3.2.11 and the calculated d-spacings are tabulated in table 3.2.10. Comparison of the X-ray diffraction patterns of 4,4'-bis(4''-ethynyl methylbenzoate)biphenyl (1) and 1,4-bis(ethynylmethylbenzoate)benzene (2), figure 3.2.11, indicates that the sample of as made 4,4'-bis(4''-ethynylmethylbenzoate) biphenyl is far less ordered than that of 1,4-bis(ethynylmethylbenzoate)benzene, which is a surprising observation.

Peak	Theta angle	d-spacing
1	5.93	14.89
2	9.70	9.11
3	11.63	7.61
4	20.72	4.28
5	25.71	3.46
6	28.48	3.13
7	42.67	2.12
8	50.45	1.81

Table 3.2.10 X-ray diffraction data for as made 4,4'-bis(4'-ethynylmethylbenzoate)biphenyl.

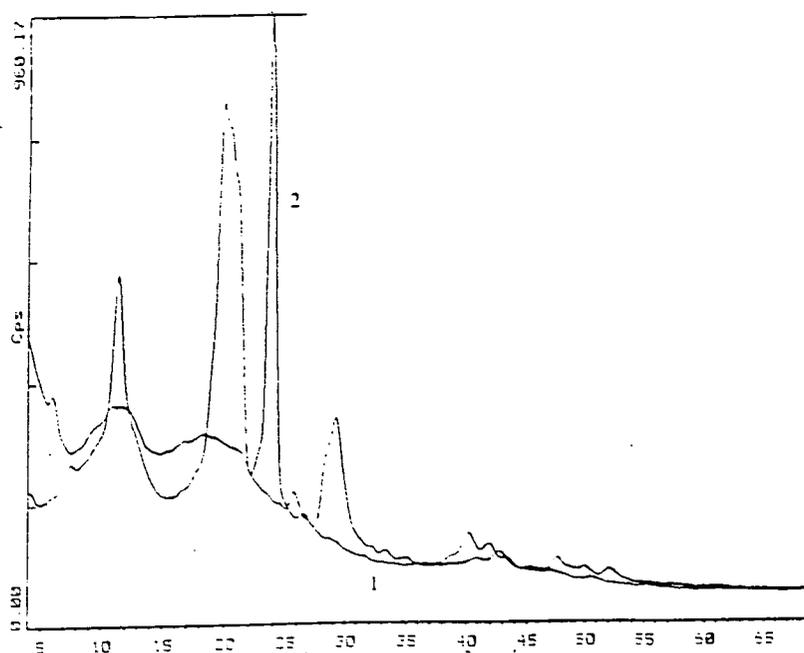


Figure 3.2.11 X-ray diffraction patterns for 4,4'-bis(4''-ethynylmethylbenzoate) biphenyl and 1,4-bis(ethynylmethylbenzoate)benzene.

3.2.7 Synthesis and characterisation of 4,4'-bis(4''-ethynylmethylbenzoate)benzophenone

4,4'-Bis(4''-ethynylmethylbenzoate)benzophenone was synthesised via the palladium catalysed coupling reaction between 4,4'-diethynylbenzophenone and 4-bromomethylbenzoate, figure 3.2.12 and section 3.2.8 for experimental procedure.

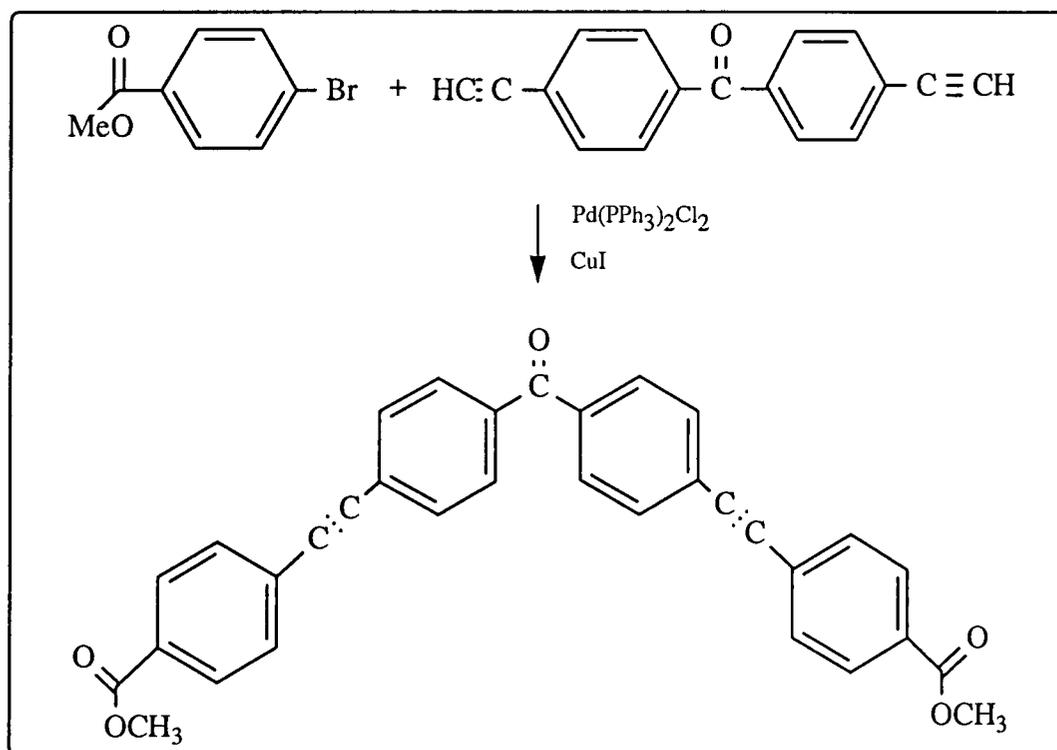


Figure 3.2.12 Reaction scheme for the coupling between 4,4'-diethynylbenzophenone and 4-bromomethylbenzoate.

The material proved to be soluble in hot DMSO but not sufficiently so for solution ¹³C nmr to be carried out, so a solid state nmr spectrum was recorded in order to confirm the structure as 4,4'-bis(4''-ethynylmethylbenzoate)benzophenone, figure 3.2.13. The material melted at 245°C. The ¹³C nmr spectrum, appendix E13, was completely assigned, see table 3.2.11, using the separate spectra recorded for the sets of quaternary carbons and those bearing protons, and the spectra of the starting materials together with the calculated shifts for the aromatic carbons.

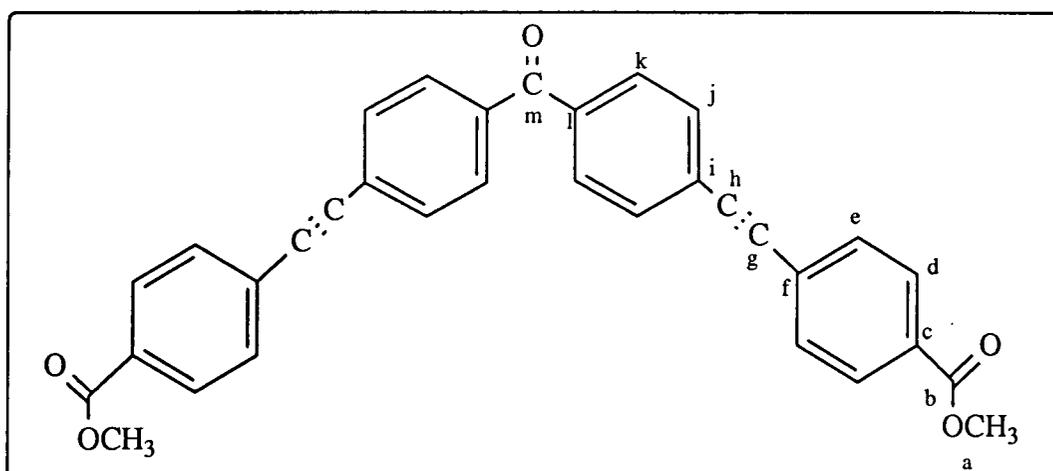


Figure 3.2.13 4,4'-Bis(4''-ethynylmethylbenzoate)benzophenone.

Carbon	Observed Shift (ppm)	Calculated Shift (ppm)
a	79.2	
b	166.0	
c	135.1	130.4
d	P	130.1
e	P	128.7
f	130.7	126.8
g	91.6	
h	91.6	
i	126.6	126.6
j	P	132.5
k	P	129.1
l	160.9	137.6
m	193.4	

P = Protonated aromatic carbons are all under the peak at 131.5, appendix E13.

Table 3.2.11 Assignment of the ^{13}C nmr shifts for 4,4'-bis(4''-ethynylmethylbenzoate)benzophenone.

Peak (cm-1)	Assignment
1721	Carbonyl str
2285	Acetylene str
1648	Carbonyl str

Table 3.2.12 Assignment of characteristic peaks in the infrared spectrum of 4,4'-bis(4''-ethynylmethylbenzoate)benzophenone.

The spectroscopic data presented above were consistent with the product being 4,4'-bis(4''-ethynylmethylbenzoate)benzophenone. The infrared spectrum, appendix C13, indicates the presence of two carbonyl groups, one in the correct position for an aryl ester (1721cm^{-1}) and one in the position for the carbonyl in the ethynyl substituted benzophenone moiety (1648cm^{-1}) as well as an internal acetylene (2285cm^{-1}), see table 3.2.12. There is no evidence of a terminal acetylenic hydrogen indicating that there is no unreacted material present in the final product.

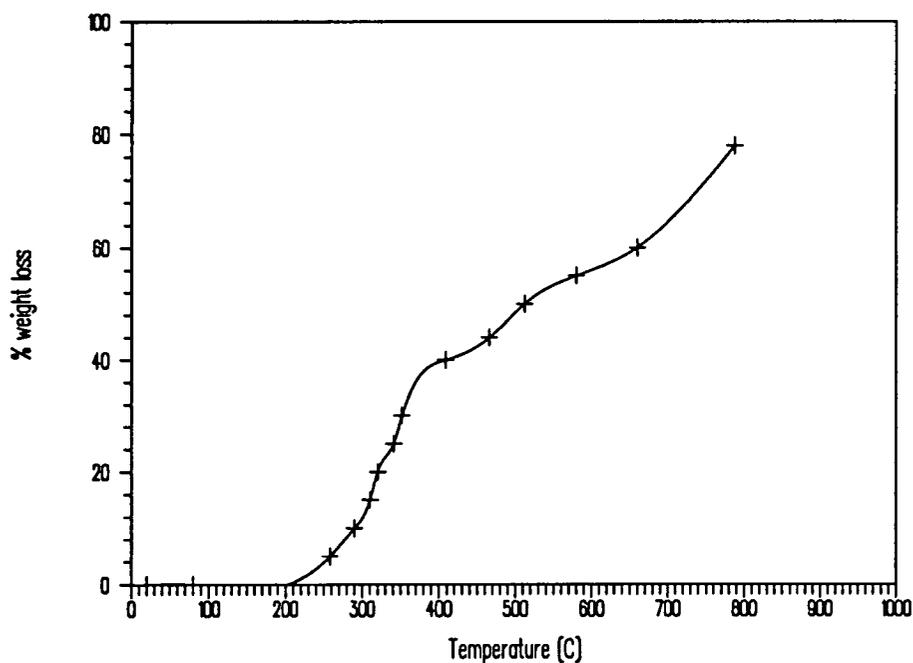


Figure 3.2.14 TG trace for 4,4'-bis(4''-ethynylmethylbenzoate)benzophenone.

The TG trace of the material shows no evidence of weight loss below 200°C. Decomposition then occurs until by 360°C 40% of the weight of the compound has been lost. By 600°C 55% of the compound weight has been lost.

3.2.8 Details of the experimental procedure.

Coupling reaction between 4-bromomethylbenzoate and 2-methyl-3-butyn-2-ol.

4-Bromomethylbenzoate (2.15g, 0.1m) and 2-methyl-3-butyn-2-ol (17.0g, 0.2m) were dissolved in triethylamine (200ml) in a two necked round bottomed flask to which a condenser and a nitrogen inlet were attached. Nitrogen was bubbled through the solution for 45 minutes, the solution being stirred with a magnetic flea. A solution of Pd(PPh₃)₂Cl₂ (0.1g, 1x10⁻³m) and CuI (0.02g, 1x10⁻³) dissolved in piperidine (10ml) under nitrogen was added dropwise to the contents of the flask. The resulting solution was refluxed for four hours, cooled and the precipitated white triethylamine salt filtered off on a Buchner funnel. The excess triethylamine from the filtrate was removed using a Rotavap, water added to the residue to remove any remaining triethylamine salt and the organic product extracted with ether. On removal of ether a pink solid was formed, which was recrystallised from hexane to give: 4-(2'-hydroxy-2'-methylbut-3'-yn-4'-yl) methylbenzoate as a cream powder, (17.44g, 80%).

Synthesis of 1,4-bis(4'-ethynylmethylbenzoate)benzene.

1,4-Diethynylbenzene (1.26g, 0.01m) and 4-bromomethylbenzoate (4.60g, 0.021m) were dissolved in dry triethylamine (80ml) contained in a two necked round bottomed flask connected to a condenser and a nitrogen bubbler. The solution was stirred with a magnetic flea. After nitrogen had been bubbled through the stirred solution for 30 minutes, a solution of Pd(PPh₃)₂Cl₂ (0.05g, 7x10⁻⁵m) and CuI (0.006g, 3x10⁻⁵m) in piperidine (5ml), also under nitrogen, was added dropwise to the stirred triethylamine solution. The resulting mixture was refluxed for 4 hours and as the reaction proceeded a yellow precipitate formed, the precipitate was recovered by filtration using a Buchner funnel, washed with hot water to remove any triethylamine salt, then with acetone and dried *in vacuo* to give:

1,4-bis(4'-ethynylmethylbenzoate)benzene as a yellow powder, (3.15g, 80%, mp 285°C).

Synthesis of 4,4'-bis(4''-ethynylmethylbenzoate)biphenyl.

4,4'-Bis(4''-ethynylmethylbenzoate)biphenyl was synthesised following the method described for *1,4-bis(4'-ethynylmethylbenzoate)benzene* by reacting *4,4'-diethynylbiphenyl* (2.02g, 0.01m) with *4-bromomethylbenzoate* (4.60g, 0.021m) in triethylamine. *4,4'-Bis(4''-ethynylmethylbenzoate)biphenyl* was recovered as a yellow powder, (3.53g, 75%).

Synthesis of 4,4'-bis(4''-ethynylmethylbenzoate)benzophenone.

4,4'-Bis(4''-ethynylmethylbenzoate)benzophenone was synthesised following the method described for *1,4-bis(4'-ethynylmethylbenzoate)benzene* by reacting *4,4'-diethynylbenzophenone* (2.5g, 0.01m) with *4-bromomethylbenzoate* (4.3g, 0.02m) in triethylamine (100ml). *4,4'-Bis(4''-ethynylmethylbenzoate)benzophenone* was recovered as a yellow powder, (3.74g, 75%).

3.3 Polymerisation of diacetylenes to form linear rigid rod macromolecules.

This section details the formation of linear rigid rod macromolecules and hinged macromolecules containing rigid segments. A series of poly(arylene diynylene)s, (poly(1,4-phenylene diynylene), poly (1,4-(2,5-dihexylphenylene) diynylene), poly (4,4'-biphenylene diynylene) and poly(4,4'-biphenyleneketone diynylene)) were synthesised following the method developed by Hay, see section 3.3.4.^[H6] A series of poly(arylene ynylene)s, (poly(1,4-phenylene ynylene-1,4-(2,5-dipentylphenylene ynylene), poly(1,4-phenylene ynylene-1,4-(2,5-diheptylphenylene ynylene) and poly(4,4'-biphenylene ether ynylene-1,4-phenylene ynylene)), were synthesised via the palladium catalysed coupling reaction between 1,4-dibromoarylenes and 1,4-diethynylbenzene, see section 3.3.5.

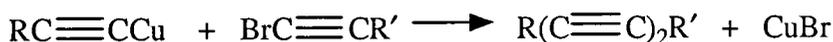
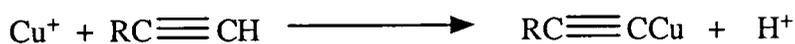
The aim was to produce a series of molecularly rigid polymers, some of which would contain flexible side chains or bends in order that the effect of these structural changes upon the properties of rigid rod poly(arylene diynylene)s and poly(arylene ynylene)s could be investigated, see Chapter 4. As an introduction to the area of acetylene couplings a review of reactions is given in section 3.3.1. The synthesis and characterisation of the polymers is then detailed in sections 3.3.2 and 3.3.3.

3.3.1 Review of acetylene - acetylene coupling reactions.

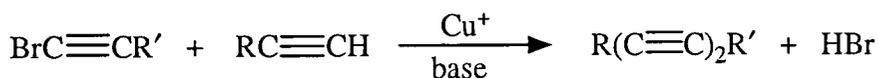
Acetylenes may be oxidatively coupled with the aid of a copper catalyst. Terminal acetylenes are coupled by heating with stoichiometric amounts of cupric salts in pyridine or a similar base. This reaction, which produces symmetrical acetylenes in high yields, is known as the Eglinton reaction;^[E7,C7] it is wide ranging and many functional groups may be present on the alkyne. The cuprous ion which is necessary is normally present in cupric salts at high enough concentration to make the reaction possible. The Glaser reaction employs catalytic amounts of cupric salts in the presence of ammonia or ammonium chloride. An oxidising agent such as atmospheric oxygen, permanganate or hydrogen peroxide is required in both procedures.



Unsymmetrical couplings can be brought about by means of the Cadiot-Chodkiewicz reaction.^[C7] Cuprous salt catalysed elimination of hydrogen bromide takes place between a 1-bromoacetylene and an ethynyl compound in the presence of a base, the unsymmetrical diyne being formed rapidly and in high yield. The fundamental reactions said to be taking place are:-



Low concentrations (ca 1%) of the cuprous ion help to avoid the self coupling reaction of the bromoalkyne. The overall reaction can be considered as:-



The addition of a base to the reaction assists by removing the free acid as it is formed.

Hay^[H1,2,3] has been at the forefront of investigations into the coupling of diacetylenes in order to form polymers. In 1959 he prepared m- and p-diethynyl benzenes from a commercially available divinylbenzene mixture (40% m- and p-divinylbenzenes). The mixture was brominated in a chloroform solution and 1,4-bis(1,2-dibromoethyl)benzene separated on cooling, this was purified by recrystallisation from chloroform. The residue of the bromination was distilled to separate the dibromodiethylbenzenes from the tetrabromodiethylbenzene, the latter fraction yields pure 1,3-bis(1,2-dibromoethyl)benzene on crystallisation from ethanol. Treatment of the tetrabromodiethylbenzenes with potassium t-butoxide in t-butanol yielded the respective diethynylbenzenes.

The diethynyl compounds were readily polymerised to linear polymers by oxidative coupling with oxygen in the presence of an amine complex of a copper salt which acted as a catalyst for the reaction. Hay also incorporated organometallic moieties, such as silicon, arsenic and mercury, into the polymer backbone.

Poly(m- and p-diethynylbenzene) as investigated by Hay.^[H2, H3]

Polymer from meta-Diethynylbenzene.

The pale yellow, solid material was soluble in solvents such as chlorobenzene and nitrobenzene above 100°C. Evaporation of a nitrobenzene solution at 170°C produced a tough, transparent film that had a tensile strength of 5000-8000 psi. As made the polymer is practically amorphous, but may be crystallised from tetrahydrofuran showing excellent spherulite growth. Hay estimated the molecular weight of this type of polymer from the ethynyl carbon-hydrogen stretching band in the infrared at 3310cm^{-1} , for m-diethynylbenzene he estimated molecular weights of 8700 and 12400 for polymerisations carried out at different temperatures. On addition of N,N,N',N'-tetramethylethylenediamine-CuCl catalyst to the polymerisation reaction a polymer with a molecular weight of 30000 was achieved. The last polymer formed the toughest and most flexible film. On heating the polymer above 180°C it rapidly became insoluble.

Polymer from para-Diethynylbenzene.

The polymer that resulted from the oxidative coupling reaction of p-diethynylbenzene was bright yellow and highly crystalline. On heating the polymer it was seen to rapidly decompose at 100°C. Since the polymer was insoluble no further work was carried out on it. However,^[H2] X-ray diffraction patterns showed the polymer to be highly crystalline and the observed d-spacings are quoted. The structure is assigned as being a hexagonal unit cell, $a_0 = 7.74\text{\AA}$, $c_0 = 8.97\text{\AA}$, containing three monomer units.

3.3.2 Synthesis and characterisation of poly(arylene diynylene)s.

1,4-Diacetylenes were oxidatively coupled, following the method described in section 3.3.4, to produce poly(arylene diynylene)s.

3.3.2a Synthesis and characterisation of poly(1,4-phenylene diynylene).

This synthesis has been reported previously^[H2] but was conducted to gain experience of the experimental technique and to record spectroscopic parameters for reference purposes since these had not been reported. The other polymerisations in this section have not been previously reported.

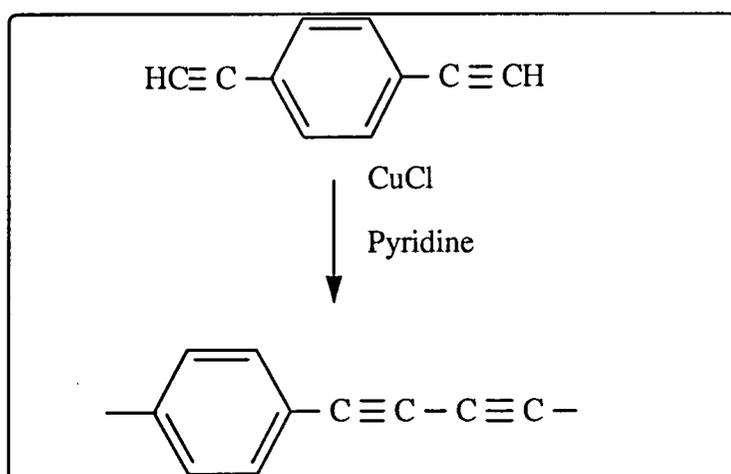


Figure 3.3.1 Polymerisation reaction of 1,4-diethynylbenzene.

1,4-Diethynylbenzene was oxidatively coupled to produce the linear polymer poly(1,4-phenylene diynylene), figure 3.3.1. As expected the polymer was a yellow powder which proved to be stable to air over a period of months. The polymer proved insoluble in all solvents and so it was not possible to determine the degree of polymerisation by GPC. A solid state ¹³C nmr spectrum was recorded in order to characterise the polymer, appendix E8.

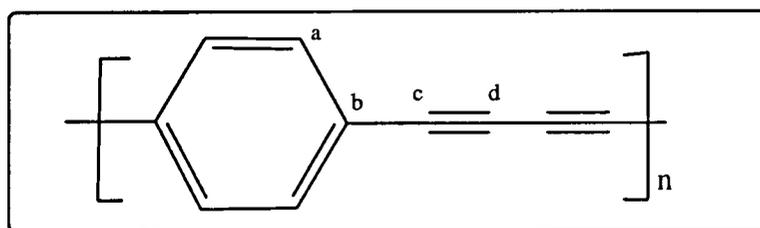


Figure 3.3.2 Poly(1,4-phenylene diynylene).

The ^{13}C nmr spectrum was completely assigned, see table 3.3.1, using the separate spectra recorded for the sets of quaternary carbons, together with the calculated shifts for the aromatic carbons, calculated via substituent shift effects.

Carbon	Observed Shift (ppm)	Calculated Shift (ppm)
a	133.07	132.7
b	121.44	122.2
c	83.37	
d	77.93	

Table 3.3.1 Assignment of the ^{13}C nmr chemical shifts in poly(1,4-phenylene diynylene).

The spectroscopic data presented above were consistent with the product being poly(1,4-phenylene diynylene), figure 3.3.2. The ^{13}C nmr spectrum shows two aromatic carbon environments and distinct peaks are observed for the ethyne carbons (c and d). The peak at 83.37ppm is typical of an ethyne carbon attached to a benzene ring, and the peak at 77.93ppm is at a position comparable with the central carbon atom in other diacetylenic compounds. The infrared spectrum, appendix C8, shows evidence of both terminal acetylenic carbon-hydrogen stretching (3289cm^{-1}) and internal acetylenic carbon-carbon stretching (2201cm^{-1}), both peaks are in different positions to those in the starting material confirming that reaction has taken place. The evidence of terminal acetylene groups indicates that a low molecular weight polymer or telomer has been formed. Analysis of the infrared spectra for this and subsequent materials could provide a rough estimate of the degree of polymerisation, computed on the basis of the relative integrated intensities of the stretching modes for acetylenic and aryl C-Hs in the monomer and polymer. However, the polymer spectra were not of good enough quality to enable this analysis to be quantified accurately.

3.3.2b Synthesis and characterisation of poly(1,4-(2,5-dihexylphenylene) diynylene).

1,4-Diethynyl-2,5-dihexylbenzene was oxidatively coupled in the presence of a copper catalyst to produce the linear polymer poly(1,4-(2,5-dihexylphenylene) diynylene), figure 3.3.3. The polymer was a yellow powder and proved to be stable to air over a period of months. The polymer was slightly soluble in chlorinated solvents, THF and toluene, for example, to the extent of 1g/L in chloroform.

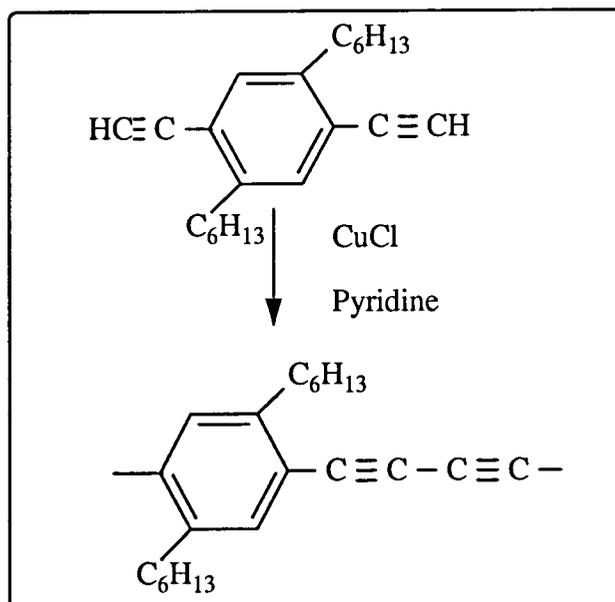


Figure 3.3.3 Polymerisation reaction of 1,4-diethynyl-2,5-dihexylbenzene.

The ¹H and ¹³C nmr spectra were recorded in chloroform, appendices D10 and E10.

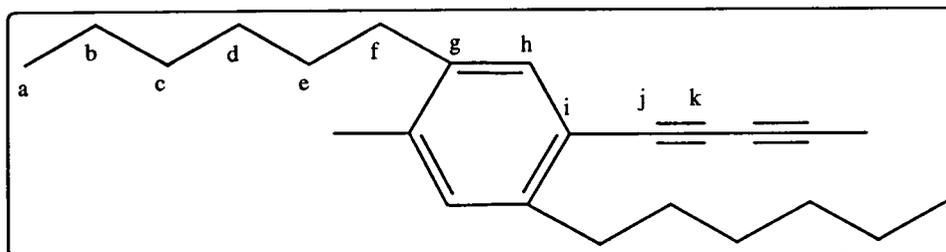


Figure 3.3.4 Poly(1,4-(2,5-dihexylphenylene) diynylene).

The ¹H and ¹³C nmr spectra of poly(1,4-(2,5-dihexylphenylene) diynylene),

figure 3.3.4, were completely assigned, tables 3.3.2 and 3.3.3, by comparison with the spectra for 1,4-diethynyl-2,5-dihexylbenzene, together with the calculated shifts for the aromatic carbons.

Carbon	Observed Shift (ppm)	Calculated Shift (ppm)
a	14.0	
b-f	22-33	
g	143.7	144.1
h	122.2	121.8
i	133.3	132.3
j	81.9	
k	78.9	

Table 3.3.2 Assignment of the ^{13}C nmr chemical shifts in poly(1,4-(2,5-dihexylphenylene) diynylene).

Hydrogen	Observed Shift (ppm)	Integral
a	0.88	3
b-d	1.33	6
e	1.65	2
f	2.73	2
h	7.35	1

Table 3.3.3 Assignment of the proton nmr shifts in poly(1,4-(2,5-dihexylphenylene) diynylene).

The spectroscopic data presented above were consistent with the product being poly(1,4-(2,5-dihexylphenylene) diynylene). A further sign that polymerisation has taken place is the virtual disappearance of the terminal acetylenic hydrogens at 3.26ppm, however the S/N was not very good. The infrared spectrum, appendix C10,

shows evidence of both terminal acetylenic carbon-hydrogen stretching (3354cm^{-1}) and internal acetylenic carbon-carbon stretching (2202cm^{-1}), both peaks were in different positions to those in the starting material confirming that reaction has taken place. The evidence of terminal acetylene groups indicates that a low molecular weight polymer or telomer has been formed. A GPC trace of poly(1,4-(2,5-dihexylphenylene) diynylene) was recorded in chloroform and the resulting data is tabulated in table 3.3.4. The number average degree of polymerisation was found to be 20 which is comparable with that found for other rigid rod polymers containing flexible side chains.^[R5,R6] The values are "polystyrene equivalents" and it is uncertain how good an estimate they represent but it is likely that they are optimistic.

GPC INFORMATION	
Mw	5500
Mn	4000
Polydispersity	1.37
Degree of polyn.	20

Table 3.3.4 GPC analysis on poly(1,4-(2,5-dihexylphenylene) diynylene).

3.3.2c Synthesis and characterisation of poly(4,4'-biphenylene diynylene).

4,4'-Diethynylbiphenyl was oxidatively coupled to produce the linear polymer poly(4,4'-biphenylene diynylene), figure 3.3.5. The resulting polymer was a pale yellow powder which proved to be stable to air over a period of months. The polymer proved insoluble in all solvents and so it was not possible to determine the degree of polymerisation by GPC. A solid state ^{13}C nmr spectrum was recorded in order to characterise the polymer, appendix E9.

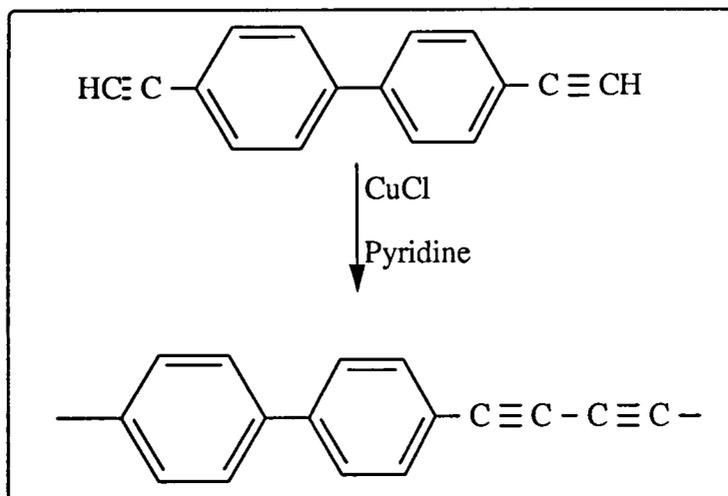


Figure 3.3.5 Polymerisation reaction of 4,4'-diethynylbiphenyl.

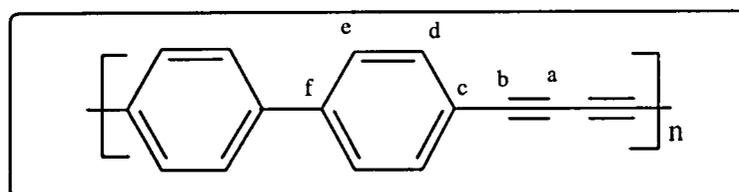


Figure 3.3.6 Poly(4,4'-biphenylene diynylene).

The ^{13}C nmr spectrum was completely assigned, table 3.3.5, using the separate spectra recorded for the sets of quaternary carbons and those bearing protons, together with the calculated shifts for the aromatic carbons.

Carbon	Observed Shift (ppm)	Calculated Shift (ppm)
a	75.7	
b	82.4	
c	120.6	121.4
d	133.3	132.8
e	127.5	127.8
f	140.6	141.3

Table 3.3.5 Assignment of the ^{13}C nmr chemical shifts in poly (4,4'-biphenylene diynylene).

The spectroscopic data presented above were consistent with the product being poly(4,4'-biphenylene diynylene), figure 3.3.6. Comparison of the position of the terminal ethynyl protons in the monomer (81.51ppm) with that of the central carbon (a) in the diacetylene of the polymer (75.7ppm) provides further evidence that polymerisation has taken place. The infrared spectrum, appendix C9, shows evidence of both terminal acetylenic carbon-hydrogen stretching (3315cm^{-1}) and internal acetylenic carbon-carbon stretching (2201cm^{-1}), both peaks are in different positions to those in the starting material confirming that reaction has taken place. The evidence of terminal acetylene groups indicates that a low molecular weight polymer or telomer has been formed.

3.3.2d Synthesis and characterisation of poly(4,4'-biphenyleneketone diynylene).

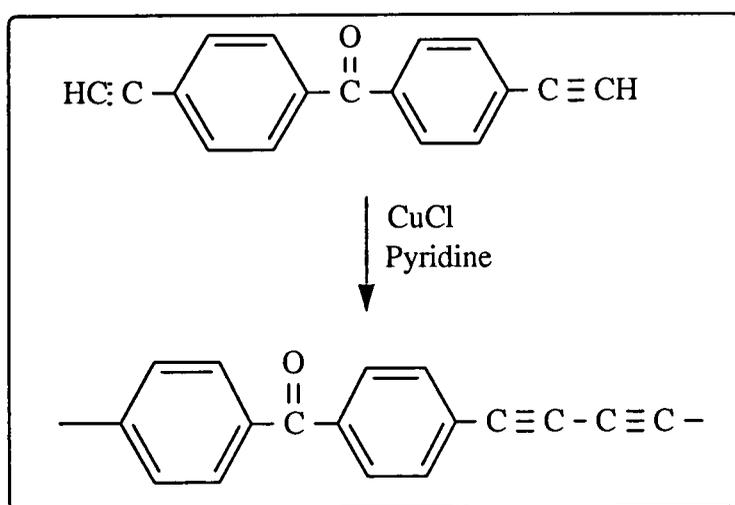


Figure 3.3.7 Polymerisation reaction of 4,4'-diethynylbenzophenone.

4,4'-Diethynylbenzophenone was oxidatively coupled to produce the linear polymer poly(4,4'-biphenyleneketone diynylene), figure 3.3.7. The resulting polymer was a pale cream powder and was slightly soluble in hot DMSO. However, it did not prove possible to achieve a solution nmr and so a solid state ^{13}C nmr spectrum was recorded in order to characterise the polymer, appendix E14.

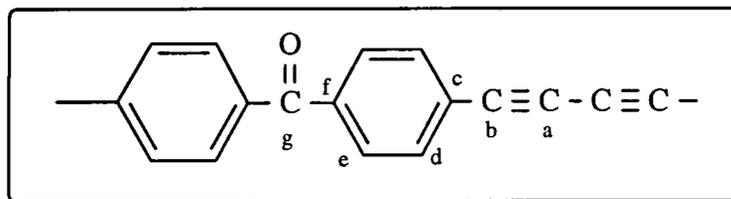


Figure 3.3.8 Poly(4,4'-biphenyleneketone diynylene).

The ^{13}C nmr spectrum of poly(4,4'-biphenyleneketone diynylene) was completely assigned, table 3.3.6, using the separate spectra recorded for the sets of quaternary carbons and those bearing protons, together with comparison with the shifts observed in the starting materials.

Carbon	Observed Shift (ppm)
a	76.8
b	81.4
c	126.6
d	P
e	P
f	134.6
g	193.3

P = Peaks for these protonated carbons are under the peak at 133.3ppm.

Table 3.3.6 Assignment of the ^{13}C nmr chemical shifts in poly(4,4'-biphenyleneketone diynylene).

The spectroscopic data presented above were consistent with the product being poly(4,4'-biphenyleneketone diynylene), figure 3.3.8. Comparison of the position of the terminal ethynyl protons in the monomer (80.4ppm) with that of the central carbon (a) in the diacetylene of the polymer (76.8ppm) provides further evidence that polymerisation has taken place. The infrared spectrum, appendix C14, shows evidence of both terminal acetylenic carbon-hydrogen stretching (3292cm^{-1}) and internal

acetylenic carbon-carbon stretching (2112cm^{-1}), both peaks were in different positions to those in the starting material confirming that reaction has taken place. The evidence of terminal acetylene groups indicates that a low molecular weight polymer or telomer has been formed.

3.3.3 Synthesis and characterisation of poly(arylene ynylene)s.

Poly(arylene ynylene)s were synthesised via the coupling reaction between 1,4-dibromoarylenes and 1,4-diethynylbenzene following the procedure described in section 3.3.5.

3.3.3a Synthesis and characterisation of poly(1,4-phenylene ynylene-1,4-(2,5-dipentylphenylene) ynylene).

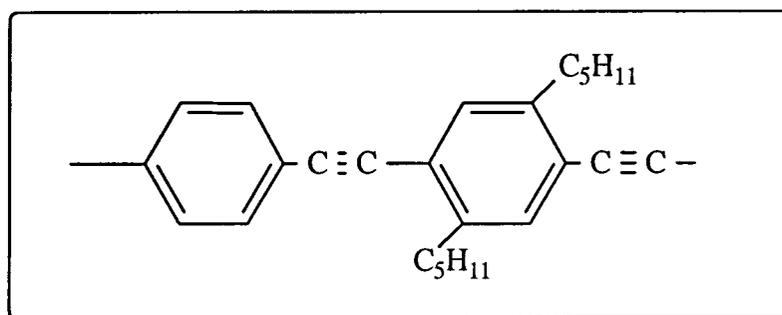


Figure 3.3.9 Poly(1,4-phenylene ynylene-1,4-(2,5-dipentylphenylene) ynylene).

1,4-dibromo-2,5-dipentylbenzene was coupled with 1,4-diethynylbenzene to produce the linear polymer, poly(1,4-phenylene ynylene-1,4-(2,5-dipentylphenylene) ynylene), figure 3.3.9, as a brown powder which was precipitated as the reaction proceeded. The polymer did not melt below 500°C and was insoluble in a wide range of solvents making it impossible to carry out GPC investigations. A solid state ^{13}C nmr spectrum was recorded in an attempt to characterise the polymer, however the resolution was poor and it was only possible to conclude the presence of aromatic and aliphatic carbons, appendix E15. The infrared spectrum, appendix C15, of the material

shows a peak at 3293cm^{-1} due to terminal acetylenes, a peak at 2196cm^{-1} due to internal acetylenic stretching and the presence of both aromatic (3293cm^{-1}) and aliphatic carbons (2926 and 2855cm^{-1}). The infrared spectrum is consistent with telomeric material having been produced.

3.3.3b Synthesis and characterisation of poly(1,4-phenyleneynylene-1,4-(2,5-diheptylphenylene)nylene)

1,4-Dibromo-2,5-diheptylbenzene was coupled with 1,4-diethynylbenzene to produce the linear polymer, poly(1,4-phenylene nylyene-1,4-(2,5-diheptylphenylene)nylene), figure 3.3.10, as a brown powder which was precipitated as the reaction proceeded. The polymer did not melt below 500°C and was insoluble in a wide range of solvents making it impossible to carry out GPC investigations. A solid state ^{13}C nmr spectrum was recorded in an attempt to characterise the polymer, however the resolution was poor and it was only possible to conclude the presence of aromatic and aliphatic carbons, appendix E16. The infrared spectrum, appendix C16, of the material shows a peak at 3290cm^{-1} due to terminal acetylenes, a peak at 2193cm^{-1} due to internal acetylenic stretching and the presence of both aromatic (3029cm^{-1}) and aliphatic carbons (2928 and 2852cm^{-1}). The infrared spectrum is consistent with telomeric material having been produced.

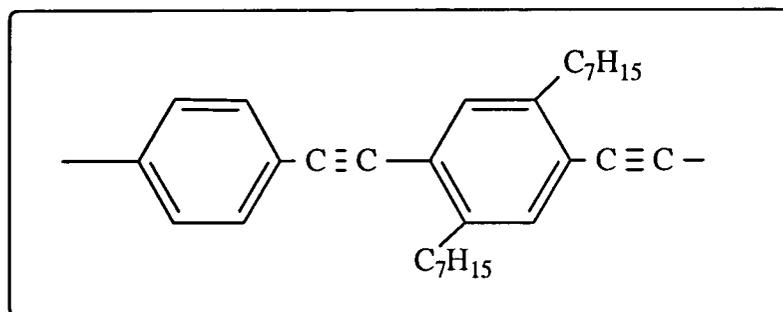


Figure 3.3.10 Poly(1,4-phenylene nylyene-1,4-(2,5-diheptylphenylene)nylene).

3.3.3c Synthesis and characterisation of poly(4,4'-biphenylene etherynylene-1,4-phenylene ynylene).

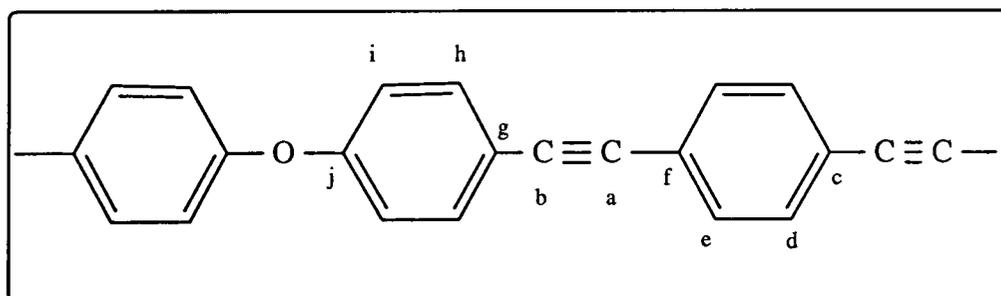


Figure 3.3.11 Poly(4,4'-biphenylene ether ynylene-1,4-phenylene ynylene).

4-Bromophenylether was coupled with 1,4-diethynylbenzene to produce the linear polymer, poly(4,4'-biphenylene ether ynylene-1,4-phenylene ynylene), figure 3.3.11, as a brown powder which was precipitated as the reaction proceeded. The polymer did not melt below 500°C and was insoluble in a wide range of solvents making it impossible to carry out GPC investigations. A solid state ^{13}C nmr spectrum was recorded in an attempt to characterise the polymer, appendix E17. The ^{13}C nmr spectrum was completely assigned, table 3.3.7. using the separate spectra recorded for the sets of quaternary carbons and those bearing protons, together with comparison with the shifts observed in the starting materials and the calculated shifts for the aromatic carbons.

Comparison of the position of the terminal ethynyl protons in the monomer (79.1ppm) with that of the central carbon (a) in the diacetylene of the polymer (90.04ppm) provides further evidence that polymerisation has taken place. The infrared spectrum of the material, appendix C17, shows a peak at 3250cm^{-1} due to terminal acetylenes, a peak at 2150cm^{-1} due to internal acetylenic stretching and a peak at 1579cm^{-1} indicating the presence of an ether link. The spectroscopic data presented above were consistent with the product being poly(4,4'-biphenylene ether ynylene-1,4-phenylene ynylene), figure 3.3.11.

Carbon	Observed Shift (ppm)	Calculated Shift (ppm)
a & b	90.04	
c	122.4	122.2
d & e	128.7	133.2
f	122.4	122.2
g	118.5	114.3
h	131.8	133.2
i	116.6	114.2
j	155.2	158.5

Table 3.3.7 Assignment of the ^{13}C nmr chemical shifts in poly(4,4'-biphenylene ether ynylene-1,4-phenylene ynylene).

3.3.4 General method for polymerising diacetylenes.

CuCl (0.001m), pyridine (2ml per g of diacetylene) and N,N,N',N'-tetramethylethylenediamine (0.001m) were added to a 100ml Erlenmeyer flask. Oxygen was passed through the vigorously stirred solution and the diacetylene (0.1m) added. An exothermic reaction ensued, the temperature of the reaction increasing by 30°C in 15 minutes and a precipitate was seen to form. The reaction was continued for a further 15 minutes, precipitated into methanol and then filtered using a Buchner funnel. The precipitate was washed with methanol containing HCl (5%) and dried in vacuo. The mass balance was $98 \pm 1\%$.

3.3.5 General method for the coupling reaction between 1,4-dibromoarylenes and 1,4-diethynylbenzene.

1,4-Dibromoarylene (0.1m) and 1,4-diethynylbenzene (0.1m) were dissolved in triethylamine (250ml) in a two necked round bottomed flask to which a condenser and a nitrogen inlet were attached. Nitrogen was bubbled through the solution for one hour, the solution being stirred with a magnetic flea. A solution of $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$ (0.1g,

$1 \times 10^{-3} \text{m}$) and CuI (0.02g, 1×10^{-3}) dissolved in piperidine (10ml) under nitrogen was added dropwise to the contents of the flask. The resulting solution was stirred for twelve hours and a brown precipitate was formed. The precipitated material was filtered off and any triethylamine salt washed away with water. The remaining brown powder was washed with ether and dried in a vacuum oven to give poly(arylene ynylene). The mass balance was $97 \pm 1\%$.

Chapter Four

An investigation of the
properties of linear rigid
rod polymers

4 An investigation of the properties of linear rigid rod polymers.

This chapter describes the properties of the linear rigid rod polymers produced in this study. The structures of the repeat units are shown in figure 4.1 along with their systematic names and reference numbers. There is some variation in the nomenclature used in the literature, here the systematic name is given first and where an alternative has been used it is also included. The systematic nomenclature adopted here parallels that used for the arylene vinylene polymers. In this discussion reference to the polymers will be made using their numbers, figure 4.1. The syntheses and molecular structural characterisation of the polymers were reported in Chapter 3, section 3.3. Here the results of investigations into their solubilities, thermal properties (TG and DSC) and, in some cases, bulk and LB film ordering behaviour are described and discussed.

The discussion is divided into the following sections:-

4.1 Introduction.

4.2 Properties of the linear rigid rod polymers.

4.2.1 Solubility properties.

4.2.2 Thermal properties.

4.2.3 X-ray diffraction studies.

4.2.4 Polarising microscopy studies.

4.3 Investigation of Langmuir Blodgett films of PIII.

4.4 Summary and conclusions.

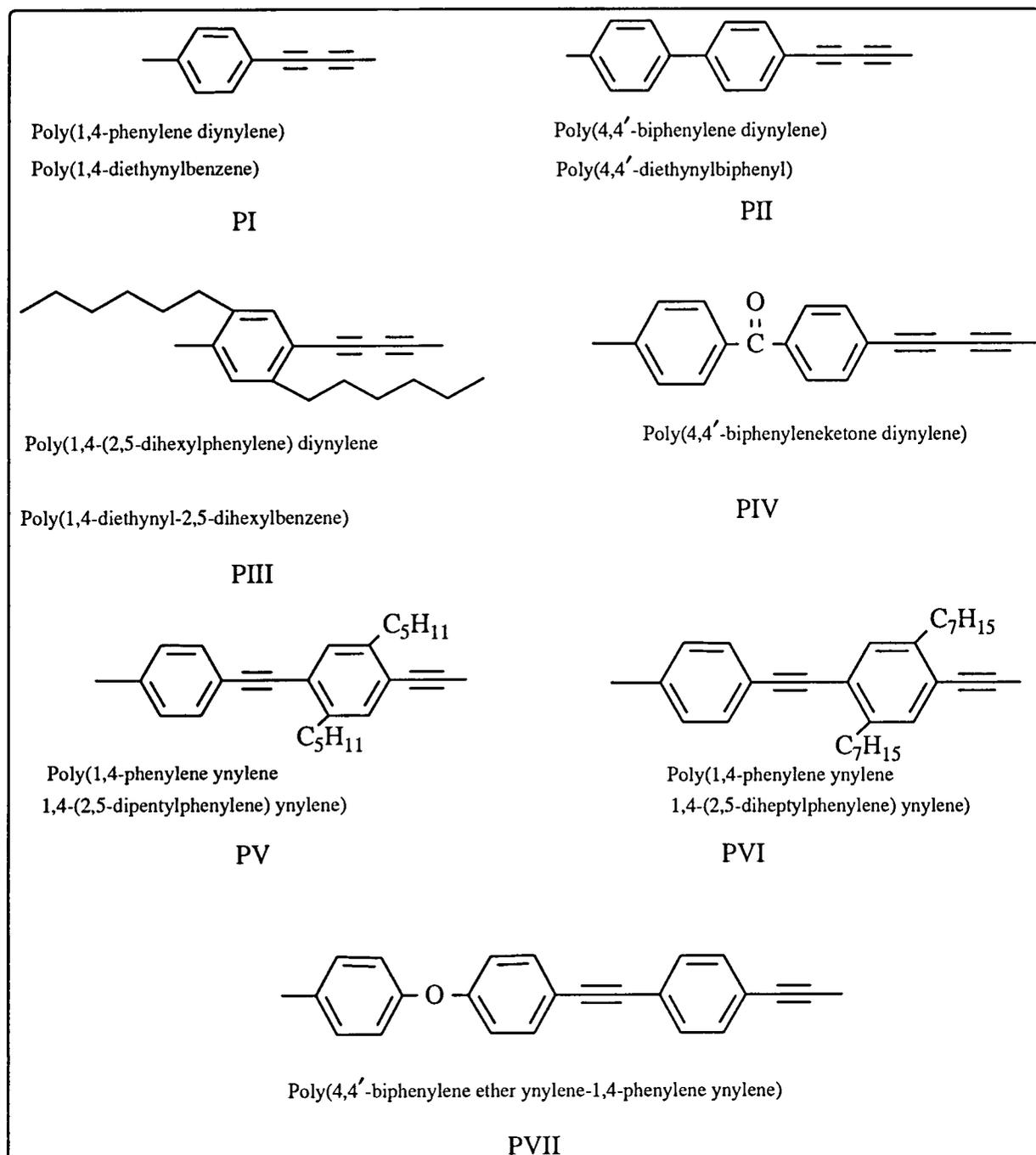


Figure 4.1 Rigid rod polymers studied in this Chapter.

4.1 Introduction.

A variety of structures have been prepared and characterised with a view to establishing how the introduction of structural features such as flexible side chains and bends at ether and ketone links influence the properties and tractability of otherwise intractable rigid rod polymers.

4.2 Investigation of the properties of linear rigid rod polymers.

4.2.1 An investigation of the solubility properties of the linear rigid rod polymers.

The extent of the solubility of the polymers in a range of solvents was assessed and the results are tabulated in table 4.1. Polymer was added to the refluxing solvent until a saturated solution was formed. A measured sample of the liquid phase (1ml) was then taken at room temperature and the solvent evaporated. The remaining polymer was weighed and hence, the solubility of the polymer in the solvent established.

	Hexane	Toluene	Benzene	Diethyl ether	Chloroform	Acetone	DMSO	DMF
PI	X	X	X	X	X	X	X	X
PII	X	X	X	X	X	X	X	-
PIII	X	C	-	X	S 1g/L	X	-	X
PIV	X	X	X	X	X	X	C	C
PV	X	C	C	X	X	X	C	C
PVI	X	C	C	X	X	X	C	C
PVII	X	C	C	X	S 0.5g/l	X	-	X

X = No evidence of the polymer dissolving in this solvent was detected.

C = Solvent became coloured, however upon evaporation no evidence of dissolved polymer was found.

S = Polymer was soluble to the extent shown.

- = Test was not carried out.

Table 4.1 Results from solubility investigations of the polymers.

The levels of insolubility found for the polymers was both surprising and disappointing in view of the work carried out by Wegner^[R4,R5,R6] into the effect of flexible side chains upon the solubility of poly(p-phenylene), where it was established that low frequency of side chains led to useful levels of solubility. Poly(p-phenylene)s substituted with alkyl side chains in the 2,5-positions were found to be completely soluble in hot toluene when the side chain was hexyl or longer. The work then went on to investigate how the frequency of side chains effected the solubility of the polymers. Random copolymers were produced via the bromo - boronic acid coupling reaction between substituted and unsubstituted benzene derivatives, figure 4.2, and the solubility of the polymers in refluxing toluene investigated. It can be seen from the table in figure 4.2 that one substituted ring in six gave a polymer with useful levels of solubility.

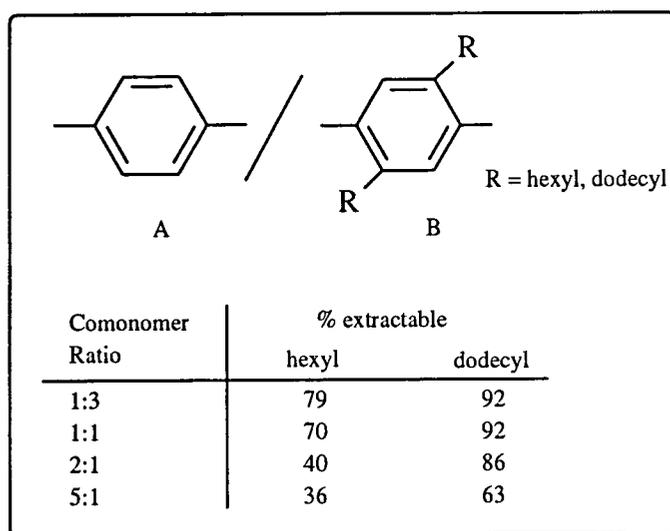


Figure 4.2 Extractability of substituted poly(p-phenylene)s.

In polymer science insolubility can result from two phenomena; the innate insolubility of the polymer, for example, polyethylene in water to take an extreme, or, insolubility of the polymer due to crosslinking. The action of crosslinking of a linear polymer chain means that anchor points are provided for the chains which hinder movement and maintain the position of the chains in the resultant network, hence the

materials dimensional stability is improved. Upon crosslinking a material's creep rate is lowered and it becomes less prone to distortion by heat and its resistance to solvents is increased. The greater the density of crosslinks the greater the effect upon the polymers properties.

In this work the feeling is that innate solubility is possible for the simple rigid rod polymers (PI and PII), but is unlikely in the kinds of substituted or bent structures synthesised, hence possible mechanisms by which crosslinking could be taking place must be considered. Ethynyl capped prepolymers or telomers, such as phenylenes, imides, phenylquinoxalines, sulfones, esters and perfluoroalkyne etherbenzoxazoles have been used as resins for the synthesis of high performance thermosetting composites. Usually this is a high temperature process and the telomers themselves are handleable. Polymers with pendant acetylene groups have also been employed and examples include phenylquinoxalines, imides, sulfones and phenoxy resin, (*Kroschwitz, J.I., Concise encyclopedia of polymer science and engineering, p 5-9, 1990, John Wiley and Sons.*). Jensen described the use of 4-ethynylbenzoylchloride (EBC) as an end capping agent for polysulfones, figure 4.3, where the phenolic hydroxyls at chain ends are connected to 4-ethynylbenzoates.^[J2] He prepared a series of ethynyl terminated polymers with varying number average molecular weights and blended them with various amounts of unspecified ethynyl terminated coreactant. Crosslinking of the ethynyl groups was found to occur in the range 240-245°C and the critical stress intensity factor of the materials was determined; the values determined were inversely proportional to the ethynyl content of the original formulation.

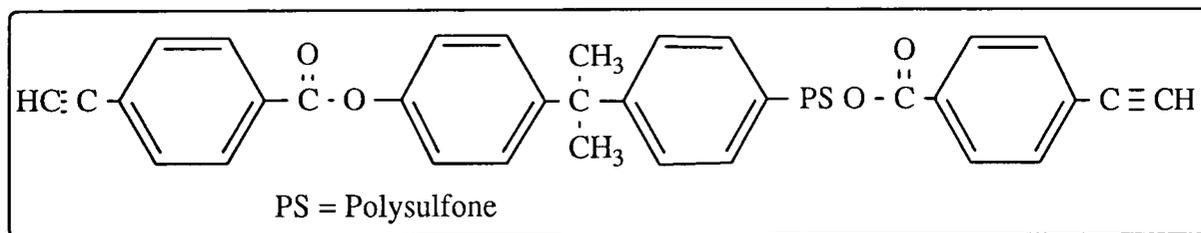


Figure 4.3 EBC endcapped polysulfones.

Núñez prepared a series of hydroxy terminated oligo(etherketones) based on isophthaloyl and oxyphenylene units (Ar'), he then end capped the oligomers with 3- and 4-ethynylbenzoyl chloride, to provide materials of the type shown in figure 4.4.^[N1] All of the materials underwent a crosslinking reaction in the range of 150-300°C, producing insoluble, thermally stable materials.

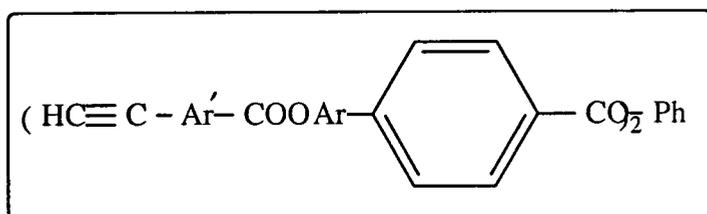


Figure 4.4 Acetylene terminated ether-ketone oligomers.

Douglas investigated the thermal crosslinking of the ethynyl terminated monomer (1,4-(1,3-HCCC₆H₄CH₂O)C₆H₄)₂CMe₂, with a variety of catalysts and found nickelocene to be particularly effective.^[D6] A variety of palladium compounds also catalysed the reaction. Pérez synthesised poly(m,m'-butadiynylenedibenzyltere phthalate), figure 4.5, and found it to be a highly crystalline polymer which was soluble in hot dimethylformamide and hot dimethylsulfoxide.^[P2]

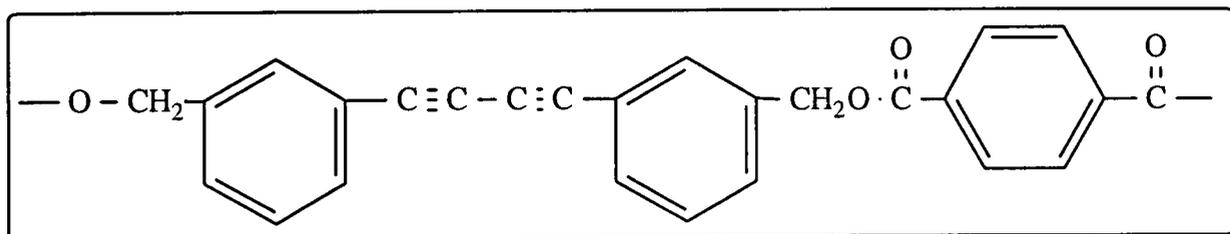


Figure 4.5 Poly(m,m'-butadiynylene dibenzylterephthalate).

The polymer melted at 200°C and further heating produced crosslinked material. Burillo prepared various diacetylene derivatives of benzoic acid and investigated their polymerisation reactions, figure 4.6.^[B15]

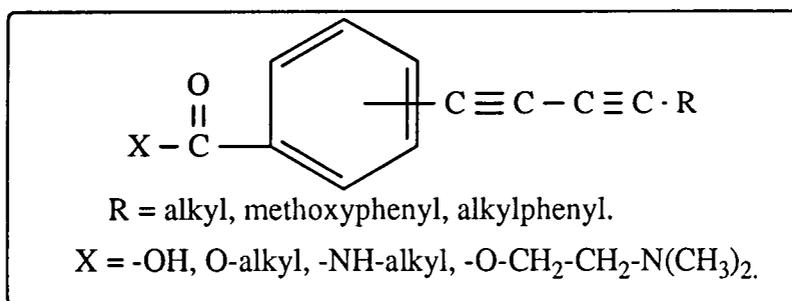


Figure 4.6 Diacetylene containing benzoic acid derivatives.

Crosslinking was brought about by heating to temperatures above 200°C and by Gamma ray irradiation. Vasquez studied polymers formed from the reactions between the diacetylene containing material, m,m'-butadiynylenedibenzylalcohol and a variety of diacid chlorides, once again polymerisation of the diacetylene groups took place at temperatures above 200°C, figure 4.7.^[V3]

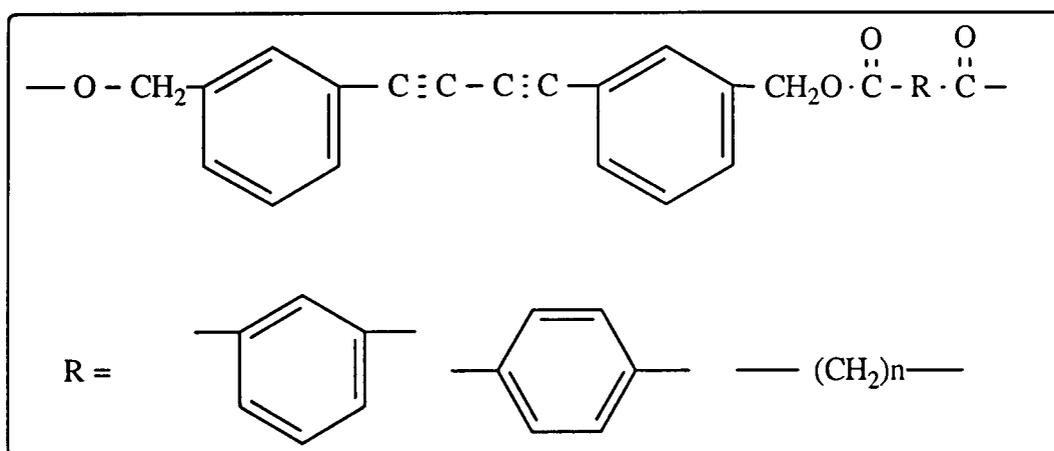


Figure 4.7 Diacetylene containing polyesters.

In this work it was anticipated that the mild conditions of the polymerisation reactions would avoid complications associated with crosslinking. However, it is a possibility that crosslinking due to the terminal ethynes is occurring to a small extent and is, at least in part responsible for the observed low solubility of the polymers. There is evidence of terminal acetylenic protons in the as made polymeric material, (see infrareds of the polymers Appendices C8-10, 14-17), so crosslinking has definitely

not consumed all the functional groups at this stage in the life history when they have not been exposed to high temperatures (see section 4.2.2). However, crosslinking may have happened to a limited extent which is all that is required to remove any inherent solubility. A second problem in these arylene nylene systems which does not affect the arylene polymers of Wegner is the propensity of acetylenes to trimerise to give aromatic rings. On heating of acetylenes with nickel cyanide benzene and cyclooctatetraene are formed,^[R9] with substituted acetylenes substituted benzenes are formed.^[F14] The trimerisation reaction has also been observed to be catalysed by palladium compounds, however when large substituents are present the yield of trimerised product is minimised. If this process was to occur to such a small extent that it was not detectable by our spectroscopic analyses, say less than 2%, during the synthesis of the polymers, section 3.3, it would inevitably lead to branched or network polymers and consequently limited solubility.

4.2.2 An investigation of the thermal properties of the linear rigid rod polymers.

The thermal properties of the linear rigid rod polymers were investigated by thermogravimetry and by differential scanning calorimetry. The effect of heating the polymers was investigated by infrared spectroscopy.

Thermogravimetry investigations of the linear rigid rod polymers.

The TG trace for PI is shown in figure 4.8. By 250°C, 3% of the polymer was lost and this probably represents volatilisation of traces of residual solvent, by 500°C, 12.5% and by 700°C 24.5 % of the polymer had degraded. The TG trace for PII is shown in figure 4.8, no weight loss occurred below 150°C, by 250°C , 3% of the polymer was lost once again probably due to volatilisation of solvents. By 500°C 20% and by 850°C 75% weight loss had taken place.

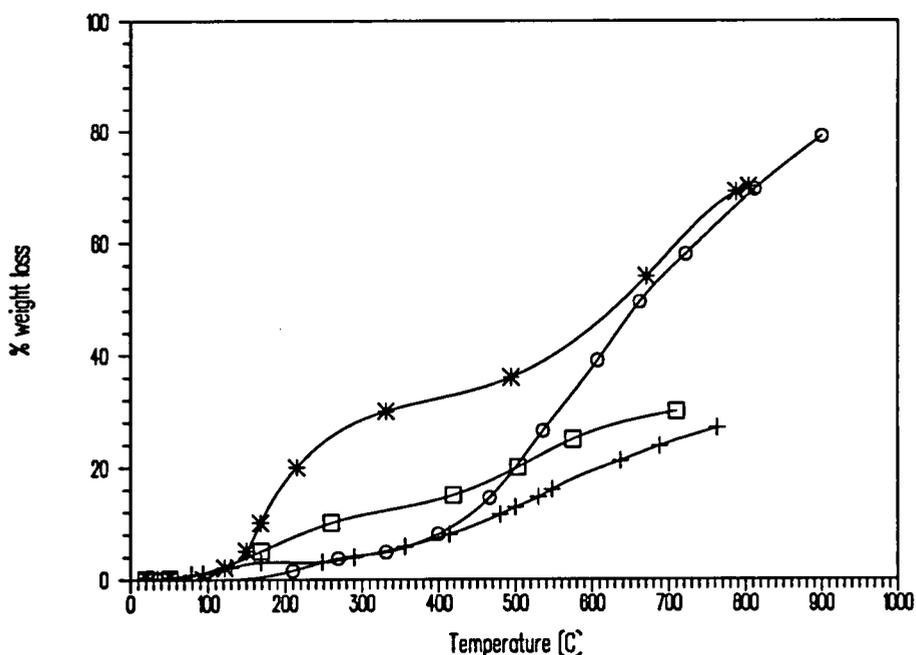


Figure 4.8 TG traces for PI (cross), PII (circle), PIII (square) and PIV (star), material weight, 5.04, 6.03, 1.004 and 6.04mg respectively ($10^{\circ}/\text{min}$ under N_2).

The TG trace for PIII is shown in figure 4.8, again after initial loss of volatile solvent the polymer was thermally stable up to 160°C after which decomposition began. By 330°C , 10% of the polymer weight was lost, by 500°C , 20% and by 900°C 80% of the polymer had degraded. The TG trace for PIV, figure 4.8, indicates no weight loss below 90°C . Rapid weight loss to the extent of 20% occurs by 210°C and the rate then decreases until by 500°C 35% of the polymer has degraded. The rate of weight loss increases once again until by 800°C 75% of the polymer has been lost.

All three polymers, PV-VII, have similar TG traces, figure 4.9. PV (crosses) shows no sign of weight loss below 40°C and then exhibits a steady weight loss until 330° (10% loss). The rate of decomposition then increases and by 700°C 50% of the polymers weight has been lost. PVI (squares) also shows no sign of weight loss below 40°C . This is followed by a steady weight loss up to 270°C by which time a loss of 4% has taken place. The rate of loss then increases until by 700°C 50% of the polymer weight remains. PVII (circles) shows a greater thermal stability than either PV or PVI

with no evidence of weight loss below 220°C. Degradation then begins until by 700°C 60% of the polymer weight has been lost. PVII is the most thermally stable of the three poly(arylene nylene)s since it does not contain flexible alkyl side chains which are mobile and degrade at lower temperatures than the rigid polymer backbone.

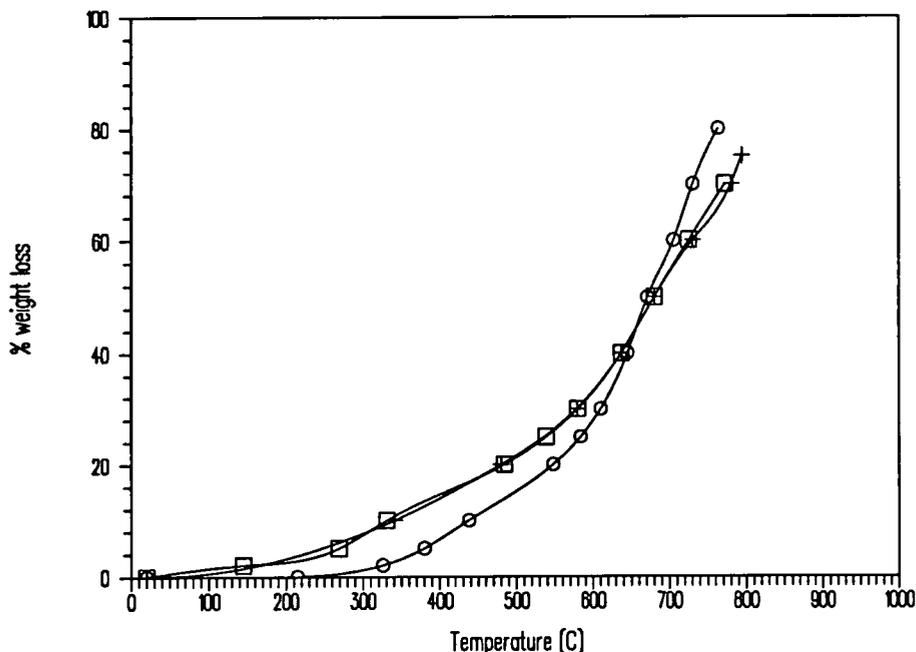


Figure 4.9 TG traces for polymers PV (6.04mg, 10°/min), PVI (0.948mg, 10°/min) and PVII (0.309mg, 10°/min).

The polymers have the resistance to thermal degradation expected for structures of this kind; in general polymers bearing flexible side chains undergo weight loss at lower temperatures than unsubstituted structures which is presumably associated with side chain fragmentation. The degradation of PIV, the ketone containing material appears to be anomalous in that it undergoes major weight loss at ca. 200°C which is lower than expected and the only difference between it and PII is the carbonyl group which is not normally associated with low temperature degradation. The results were reproducible so the anomalous behaviour of PIV is real and its rationalisation may be associated with the physical state of the material rather than its molecular structure.

For example, a more "open structure" may be allowing access to air which initiates the degradation process.

Differential scanning calorimetry investigation of the linear rigid rod polymers.

Samples of the materials were heated under nitrogen from room temperature to 300°C at a rate of 10°/ minute and cooled back to room temperature at a rate of 10°/ minute. The heating and cooling runs were then repeated, no clear trends emerged from examinations of the various materials. PI exhibited a transition on the first heating run centred at 185.4°C, appendix F1. This was the only transition observed and was not detected on second or third heating cycles, neither was there any detectable transition on cooling cycles. The base line shift is in an exothermic direction and the origin of this process is obscure. It may be a consequence of a broad exothermic cure reaction. The cure of yne capped polymers, see above, occurs in a similar temperature range. Similarly, PII exhibited an endothermic transition centred at 215°C on the first heating run only, appendix F2. Why polymer PI should show an exothermic process and PII an endothermic process is uncertain, although the measurements were reproducible. PIII was seen to exhibit two transitions both of which were reproducible on subsequent runs, appendices F3 and F4. The first transition was centred at 67°C and appears to be an exothermic process but cannot be a cure process analogous to PI since it appears to be reproducible, it is possible that a progressive chemical degradation is occurring. The second reproducible transition centred at 113°C resembles a melting point, the material does not, however, show any visible signs of melting at this temperature and it is possible that we are observing a side chain process.

Wegner^[R4] has shown that for polymers containing flexible side chains of varying length a transition due to melting of the side chains was consistently found around 70°C. Wegner's data relate to 2,5-dialkylphenylene polymers where the packing would be expected to be different to the situation in PIII and it seems reasonable to assume that the peak at 113°C is associated with side chain melting. In the

poly(phenylene) polymers there is less space between adjacent side chains than in the poly(arylene diynylene) polymers, therefore it is feasible that while the side chains pack in an interlocked conformation in the former, model A, figure 4.10, they may be able to pack parallel to the polymer backbone in the later, model B, figure 4.10, thus accounting for the different temperature of apparent side chain melting.

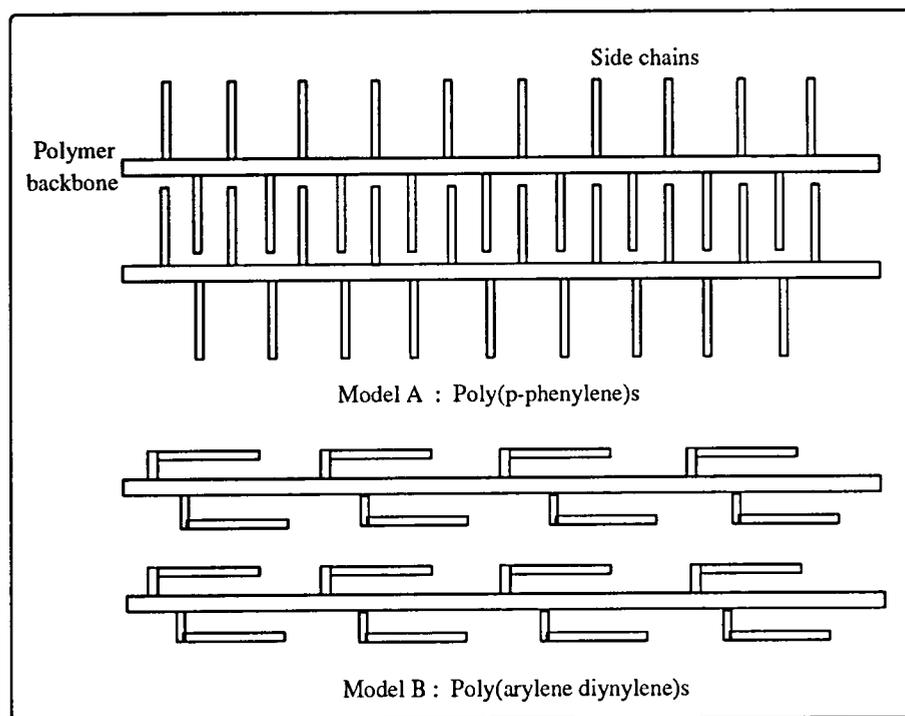


Figure 4.10 Packing of flexible side chains in poly(phenylene)s and poly(arylene diynylene)s.

DSC investigation of the other polymers prepared in this work revealed no transitions below 300°C. Investigations were not conducted above this temperature since earlier TG studies had revealed significant loss of volatiles above 300°C and this was considered to represent a hazard to the life expectancy of the DSC head.

Infrared spectroscopic examination of the consequences of heating polymers PI to PVII.

In appendices C8-10, 14-17 the FTIR spectra of the polymers PI to PVII before

and after heating are compared. In all cases KBr discs of the as made polymers had their spectra recorded before and after heating in a vacuum oven to 220°C. One example, PVI, is reproduced in figure 4.11 to illustrate the main features emerging from this analysis. The first point to note is the presence of a terminal ethyne in the as made polymer (solid line) clearly indicated by the 3290cm⁻¹ absorption which disappears in the heated product (dashed line). The aromatic CH stretch band (3029cm⁻¹) increases in intensity with respect to the aliphatic bands (2928 and 2852cm⁻¹) and there is a small shift and a decrease in intensity of the internal yne band at (2193cm⁻¹). The heated polymer shows broader bands than the as made material. All of these observations are consistent with a thermally promoted cure/crosslinking process involving consumption of terminal and internal alkyne functionalities.

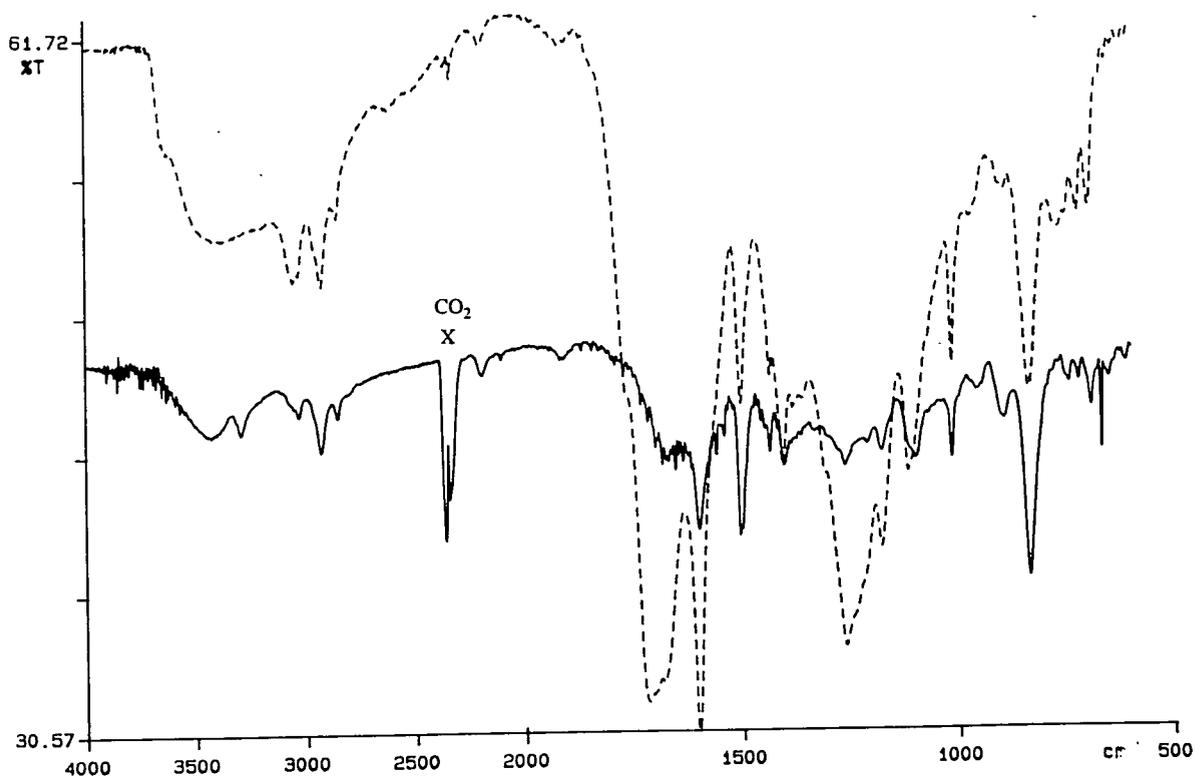


Figure 4.11 Infrared spectra of PVI, before and after heating.

4.2.3 Investigation of the linear rigid rod polymers by X-ray diffraction.

The X-ray diffraction patterns for the linear rigid rod polymers PI, PII and PIII were recorded and the resulting X-ray diffraction patterns are shown in figure 4.12. The d-spacings calculated from the diffraction patterns are tabulated in tables 4.2 to 4.4.

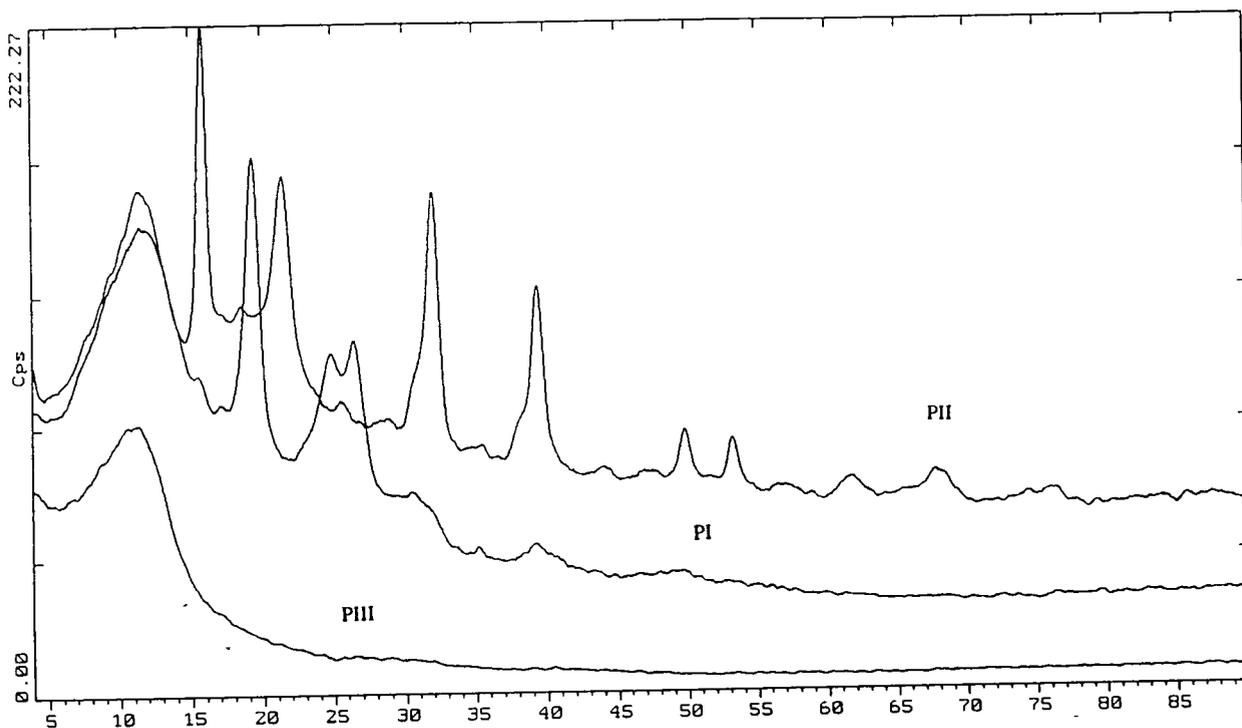


Figure 4.12 X-ray diffraction patterns for PI - PIII.

Peak	Theta angle	d-spacing Å
1	7.540	11.72
2	9.580	9.22
3	11.615	7.61
4	19.375	4.58
5	24.870	3.58
6	26.470	3.36
7	31.520	2.84

Table 4.2 XRD data for PI.

Peak	Theta angle	d-spacing Å
1	11.490	7.70
2	15.886	5.57
3	21.446	4.14
4	30.74	2.91
5	32.040	2.79
6	38.220	2.35
7	39.411	2.28
8	49.808	1.83
9	53.227	1.72
10	61.671	1.50
11	67.719	1.38

Table 4.3 XRD data for PII.

Peak	Theta angle	d-spacing Å
1	11.315	7.81

Table 4.4 XRD data for PIII.

PI and PII both possess some degree of crystallinity with PII appearing to be the more crystalline, however it is difficult to make a direct comparison since the samples histories will have been different. From the X-ray diffraction pattern of PIII it appears that the polymer is amorphous.

4.3 Investigation of Langmuir Blodgett films of PIII.

4.3.1 Introduction.

Certain materials possess the ability to form thin films on the surface of an aqueous subphase, in the case of amphiphilic molecules these films are often one molecule thick. The resultant films can be transferred onto a solid substrate, such as a

glass slide, where they may be studied. The Langmuir Blodgett (LB) technique can be used to transport these films by virtue of controlled movement of the substrate through the air subphase interface, the film deposits on the substrate and it is possible to build up multilayered structures. The deposition method has been described in detail by Roberts.^[R8]

The materials employed in the technique are normally amphiphilic; they consist of a hydrophilic head group and a hydrophobic tail group. Hence, on compression of the surface layer the molecules sit upright and are ordered on the water's surface. They do not dissolve in the water.

In the case of PIII, the rigid backbone causes the polymer chains to preferentially lie like logs along the surface of the water forming a monolayer. The intention of this section is to describe the investigations carried out into the properties of the monolayers that were formed using the LB technique.

Langmuir-Blodgett films were cast from PIII in chloroform. The films were characterised using a variety of techniques in an attempt to understand the molecular structure and properties possessed by thin films of the rigid rod polymer. Films also containing benzophenone were cast in order to investigate the possibility of forming a network via photochemically induced crosslinking of the alkyl side chains.

4.3.2 Results.

On compression of a film on the surface of a trough a plot of constant surface area against time is generally observed, however, in the case of this material the surface area was seen to decrease in small steps as time progressed.

Upon initial compression of the monolayer domains of aligned rods result. It seems reasonable to assume that these domains are randomly oriented with respect to one another, but within each domain the backbones of the rods are aligned parallel to one another. Wegner reported that similar domains of dialkylpolyphenylenes align in the direction of dipping when dipping is performed. A suggestion as to why the plot does not show constant surface area with time is that the individual domains are

reorganising on the aqueous surface and the ordered domains are growing into larger domains, the spaces between the domains being eliminated and so the surface area decreases slowly with time. This process might be regarded as a kind of slow crystallisation or annealing in two dimensions.

The isotherm was extrapolated, see figure 4.13, and the area per telomer rod was calculated as 191.3\AA^2 , taking the average degree of polymerisation as 20, the area per repeat unit indicated from these measurements is 9.34\AA^2 . This seems very small since a typical amphiphilic "soap" has an area per molecule of ca. 30\AA^2 and may indicate an edgewise uniform packing of a monolayer at the water surface or probably, and more likely in the view of the author, overlap and multilayered films. Dipping a glass microscope slide through this floating film resulted in transfer of material to the slide when it moved through from the subphase. Multilayers required immersion through a relaxed "gas like" layer and emergence through the compressed film. When the substrate was immersed through a compressed layer material already accumulated was wiped off the slide. The remainder of this section relates to studies of transferred films on a glass slide.

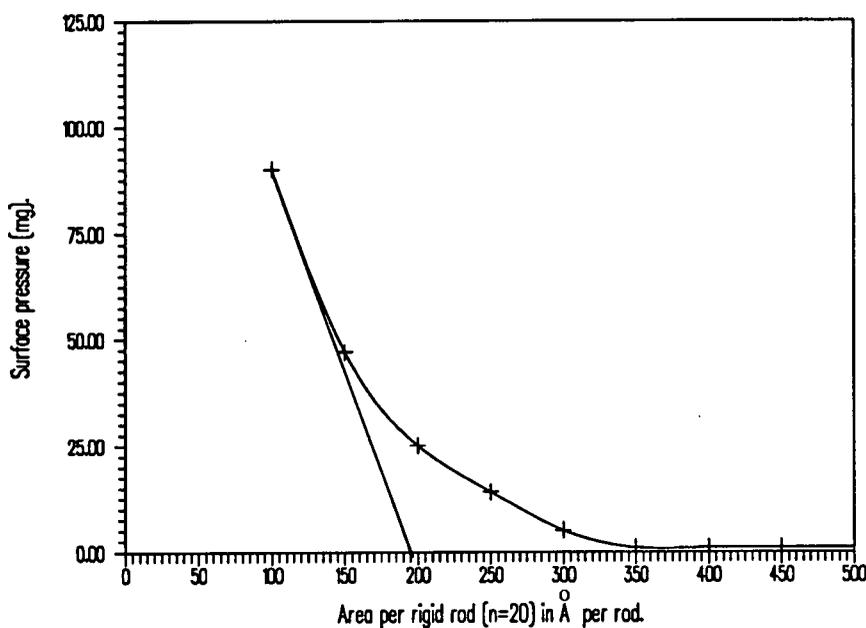


Figure 4.13 Isotherm for the rigid rod molecule.

Crosslinking of the polymer film.

The unirradiated polymer film was reasonably stable, however it was possible to wash it away using chloroform. When benzophenone was present in the film and the film was irradiated with ultra-violet radiation it proved no longer possible to wash the film from the glass substrate. Irradiation had allowed crosslinking presumably via a radical process initiated by abstraction of benzylic hydrogen by triplet benzophenone to form a three-dimensional network.

Spectrophotometry.

The material in film form had an intense yellow colour typical of a diacetylenic material. The absorption spectrum of the material was scanned between 300 and 500nm. Two consistent absorption peaks were observed at 400 ± 1 and 436 ± 1 nm, appendix G1. Samples containing increasing numbers of layers of material were scanned and the absorption of the material was found to increase with the amount of material present. It was found that the absorption bands disappeared after UV irradiation in air for twenty five minutes.

The disappearance of the bands at 400 and 436nm was not accompanied with the appearance of any other band in the absorption spectrum which allows the possibility that the main chain diacetylene units were polymerising to be discounted since this would have led to the formation of a conjugated system of double and triple bonds, which would have been observed within the region of spectrum scanned. This confirms expectations that it would be unlikely that the main chain diacetylene units would be able to get close enough to those on an adjacent chain to be able to polymerise since steric hindrance from the hexyl side chains would prevent it.

The probability is that the polymer underwent photooxidative degradation and was lost from the substrate during irradiation, suggesting the possibility of lithography in such films.

Ellipsometry.

Ellipsometry involves the measurement of the polarised light reflected from

thin-film-coated solids. Information about the reflecting surface can then be obtained by comparison to a reference, normally a clean substrate. A Rudolph research / AutoEl ellipsometer was employed to make the thickness measurements. The average refractive index was also determined from the ellipsometer and was found to be 1.670.

Ellipsometry was carried out at various stages of dipping. The average film thickness per dipping cycle, table 4.5, was calculated to be 8.6Å suggesting that one dipping cycle results in a film four or five monolayers thick, although this will depend on whether the polymer is lying flat on its edge or not.

No. layers	Sample Thickness Å	Refractive index
9	77.4	1.758
9	81.5	1.713
9	92.8	1.642
9	60.3	1.623
9	75.2	1.701
Average	77.4	1.687
Average/layer	8.6	
6	50.6	1.606
6	51.4	1.675
6	46.0	1.623
6	62.1	1.710
6	48.0	1.644
Average	51.6	1.652
Average/layer	8.6	

Table 4.5 Results from ellipsometry investigations.

Wide angle X-ray scattering.

Samples of the polymer dipped onto a glass substrate were investigated via WAXS. The samples investigated were those that had been dipped once and three times and the diffraction patterns of both were collected for two instances; in the first instance the direction of the incident X-rays was parallel to the direction of dipping and in the second instance the incident X-rays were perpendicular to the direction of dipping.

When the incident X-rays were parallel to the direction of dipping the d-spacings obtained were 8.71 and 8.77 Å. If, following Wegner, we assume that the backbone of the polymer aligns with the dipping direction this is possibly indicative of the length of a repeat unit in the polymer, the theoretical value of which is 9 Å which compares reasonably well, figure 4.14.

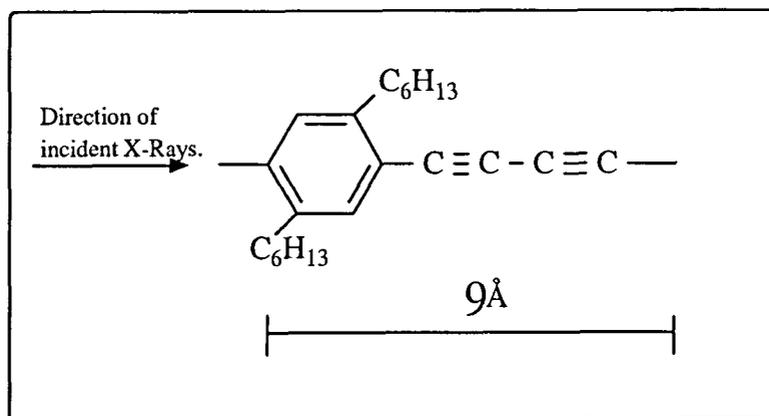


Figure 4.14 A repeat unit in the polymer.

When the incident X-rays were perpendicular to the direction of dipping the d-spacings obtained were 6.88 and 7.19 Å. This provides information about the inter chain spacing and by implication the conformation of the alkyl side chains with respect to the polymer backbone.

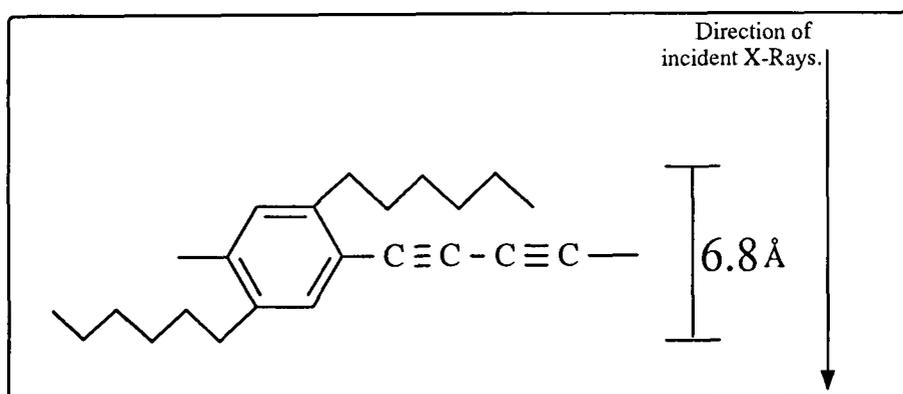


Figure 4.15 Conformation of the alkyl side chains with respect to the polymer backbone.

The results indicate that the side chains are probably arranged parallel to the main chain diacetylene backbone, as shown in figure 4.15, certainly the spacing does not indicate that the chains are "sticking out" from the backbone significantly but their actual conformation cannot be deduced with any certainty. The WAXS records are shown in Appendices G2 and G3.

4.3.3 Conclusions.

The conditions required to produce good, stable, defect free Langmuir-Blodgett multilayers from PIII have been investigated. Although it cannot be proved with certainty it seems that the transferred layers consist of either monolayers with the phenylene units lying perpendicular to the subphase or overlapping multilayers. The analyses are consistent with the hypothesis that the rigid rod units align upon the glass substrate in the direction of dipping.

It has been shown that it is possible to crosslink the transferred layers. The arrangement of the side chains within the main polymer chain has also been investigated and parallel alignment accounts for the limited structural data available.

Spectroscopic investigations have shown that polymerisation of the diacetylene units in the main polymer chain do not occur when the polymer is irradiated with UV radiation.

4.4 Summary and conclusions.

Several rigid rod polymers have been synthesised and their properties investigated. The polymers were either unsubstituted linear rigid rod polymers (PI and PII), or polymers substituted with flexible alkyl side chains (PIII, PV and PVI) or contained bends at diaryl carbonyl or ether units (PIV and PVII). It was expected that the substituted and the bent polymers would have greater solubility and lower melting points than the unsubstituted polymers, however investigations established only minor differences in the polymers' properties. As a rationalisation of these unexpected observations it is proposed that during the course of the polymerisation crosslinking

had taken place and hypotheses for ways in which this could be occurring have been described, section 4.2.1. The polymers all exhibited the thermal stability expected for polymers of this type and their decomposition profiles have been described, section 4.2.2. The curing of alkyne groups in the polymers has been investigated and the materials have been shown to undergo reaction at temperatures above 200°C, section 4.2.2, this is consistent with the results of other workers.^[V3,B15,J2] Only two of the polymers obtained (PIII and PVII) displayed any degree of solubility. PIII has been shown to form thin films at an air/water interface which can be transferred to a glass substrate and photocrosslinked with a triplet sensitizer and photodegraded in air. X-ray studies indicate that while PI and PII display ordered structures PIII was essentially amorphous, this is consistent with the hypothesis of branching and crosslinking during synthesis since PI and PII precipitate at very low dp and cease to react whereas PIII remains in solution long enough to undergo the postulated side reactions leading to a branched structure. Unfortunately the X-ray diffraction equipment has been out of commission since PIV to PVII were synthesised.

The main conclusion from this study is therefore that while the overall methodology adopted for the synthesis of the rigid rod polymers has been demonstrated to work it is of limited usefulness as a consequence of side reactions leading to branching and possible crosslinking and consequently to intractable products. Any continuation of work in this area will need to address these problems.

Chapter Five

Conclusions and suggestions for future work

5 Conclusions and suggestions for future work.

5.1 Difunctional rigid rodlike molecules and their incorporation into polymer networks.

The long term aim of the project was to synthesise and characterise networks composed of rigid rod polymers joined by flexible netpoints. It was proposed, Chapter 1, that the synthesis of difunctional rigid rodlike molecules which could subsequently be incorporated into polymer networks should be undertaken. If this could be achieved the properties of the resulting networks would be investigated and the resultant findings compared with theoretical predictions.

Difunctional rigid rodlike molecules have been successfully synthesised, see section 3.2. Attempts to produce polymers containing the molecules have been made via the reaction between the rodlike molecules and diols or triols, figure 5.1. The polymerisation reaction was catalysed by titanium butoxide, however, due to the insolubility and high melting points of the materials it has not yet proved possible to incorporate them into polymer networks as was originally intended.

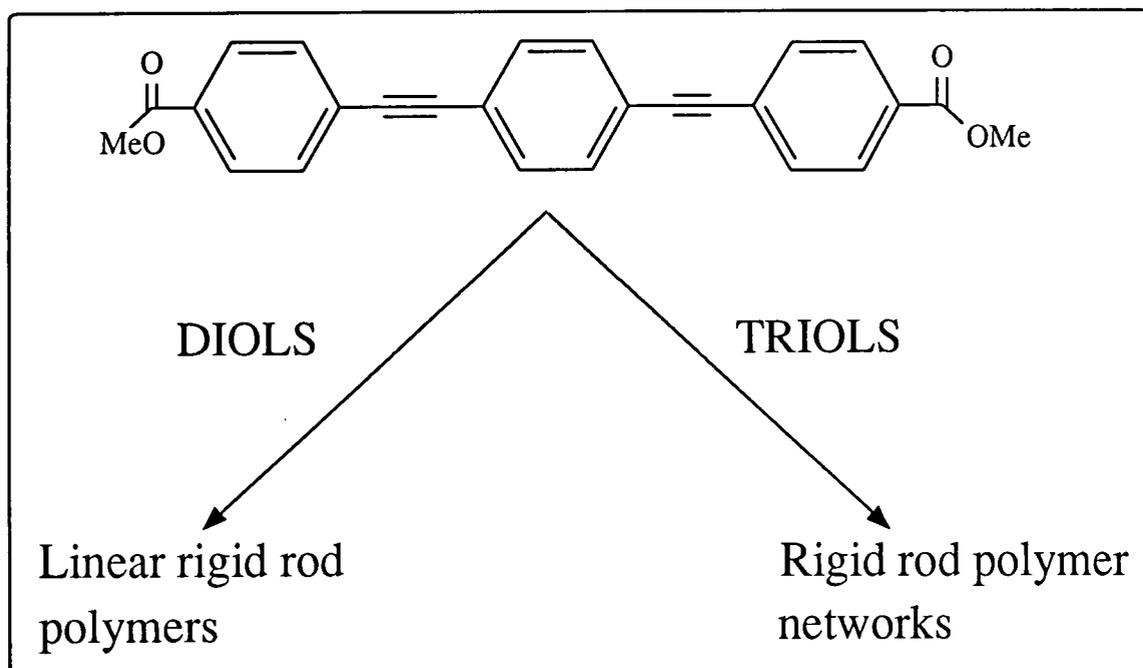


Figure 5.1 Synthesis of linear rigid rod polymers and rigid rod polymer networks.

The difunctional rigid rodlike molecules synthesised were insoluble and it was not possible to synthesise molecules containing flexible alkyl side chains due to the poor results from the coupling reactions between 1,4-dialkyl-2,5-dibromobenzenes and acetylenes. Attempts to incorporate bends into the molecules in an attempt to increase their solubility were undertaken towards the end of the work and 4,4'-bis(4''-ethynylmethylbenzoate)benzophenone was successfully synthesised, section 3.3.7. Attempts have not yet been made to incorporate this rod into polymer networks and this is an area which could be developed.

5.2 Synthesis of linear rigid rod polymers.

It was proposed that the properties of those rigid rod polymers which could be synthesised on route to the rodlike molecules would be investigated, Chapter 1. The properties of a series of linear rigid rod polymers have been investigated, Chapter 4 and the effect of adding flexible alkyl side chains or bends to a rigid polymer backbone has been described.

The polymerisation reactions between 1,4-diethynylaryl compounds and 1,4-dibromo-2,5-dialkylbenzenes undertaken towards the end of the work appears to be the most effective strategy for the synthesis of rigid rod polymers containing phenylene and ethynyl sub units and could be further investigated. To date 1,4-dibromo-2,5-dipentylbenzene, 1,4-dibromo-2,5-diheptylbenzene and 4-bromophenylether have been polymerised with 1,4-diethynylbenzene via a palladium catalysed coupling reaction, section 3.3.3. The resulting polymers have been characterised and certain of their physical properties investigated, Chapter 4. The monomers are more easily prepared than those used in other strategies and it would be possible to produce a series of polymers with the generalised structure shown in figure 5.2.

The alkyl (R) group could be altered to provide polymers with a range of side chain lengths and their properties investigated. There has been work carried out investigating the effect the length of flexible side chain has upon the properties of

polymers, such investigations have considered, for example, solubility^[R4,R5,R6], thermal properties^[R4] and structural modifications.^[S6,S2] It would be possible to investigate changes in morphology brought about by heating via X-ray investigations.

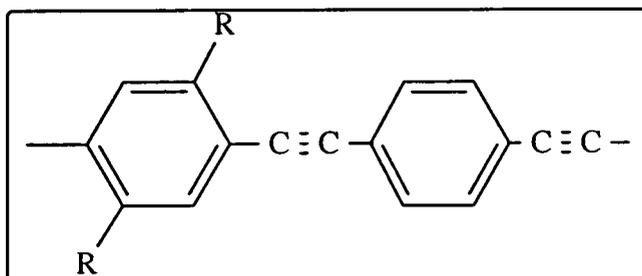


Figure 5.2 Linear rigid rod polymers containing flexible alkyl side chains (R).

The range of polymers could be extended by using different 1,4-diethynylaryl compounds, for example, 4,4'-diethynylbiphenyl or 4,4'-diethynylbenzophenone, which have been synthesised in this work, section 3.1, or 4-ethynylphenylether. The polymers could be synthesised to contain either bends or flexible side chains, or a combination of the two, figure 5.3.

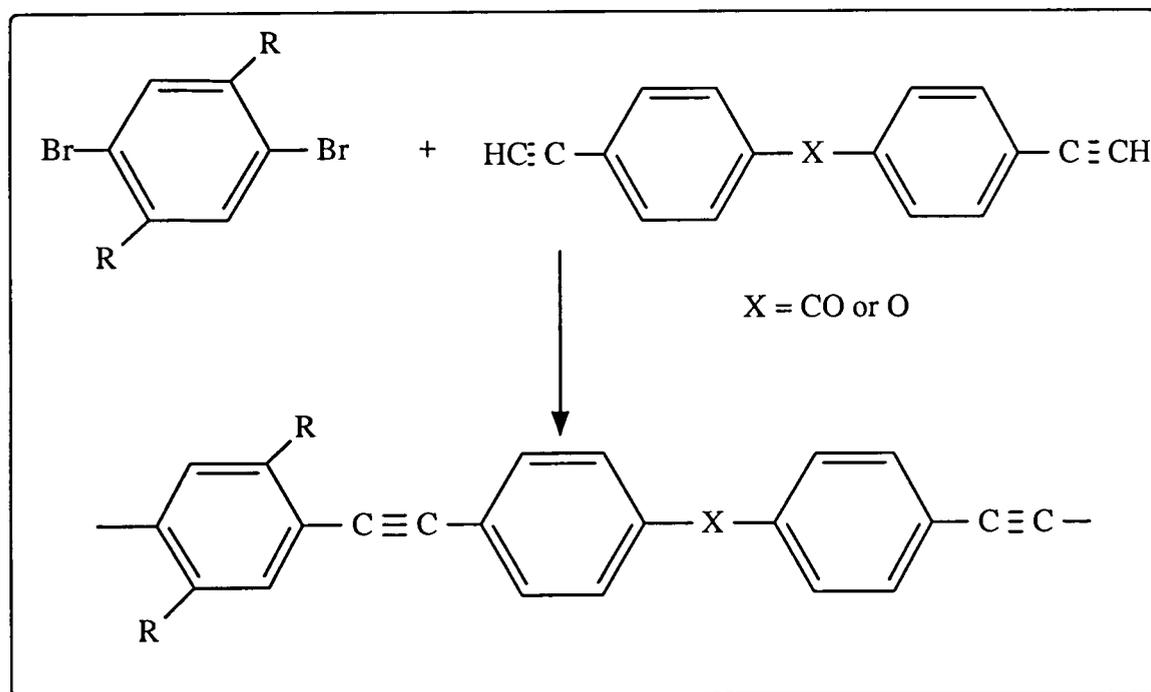


Figure 5.3 Linear polymers containing bends and flexible side chains.

The polymer containing an ether link, where R = H has been synthesised in this work, section 3.3.3c (PVII) and its solubility and thermal properties discussed, Chapter 4. Once again, investigation of the morphology of such polymers would allow the organisation of the side chains to be assessed and changes in conformation with altering length of side chain could be investigated.

An analogous series of polymers have been synthesised by Wegner's group.^[R2] The poly(arylether)s and poly(arylketone)s were prepared via the palladium catalysed coupling reaction between the boronic acid derivatives of alkyl substituted benzenes and dibromo compounds containing keto or ether functions. The number average degree of polymerisation of the materials was found to be between 13 and 27 all polymers were soluble in a range of organic solvents at room temperature.

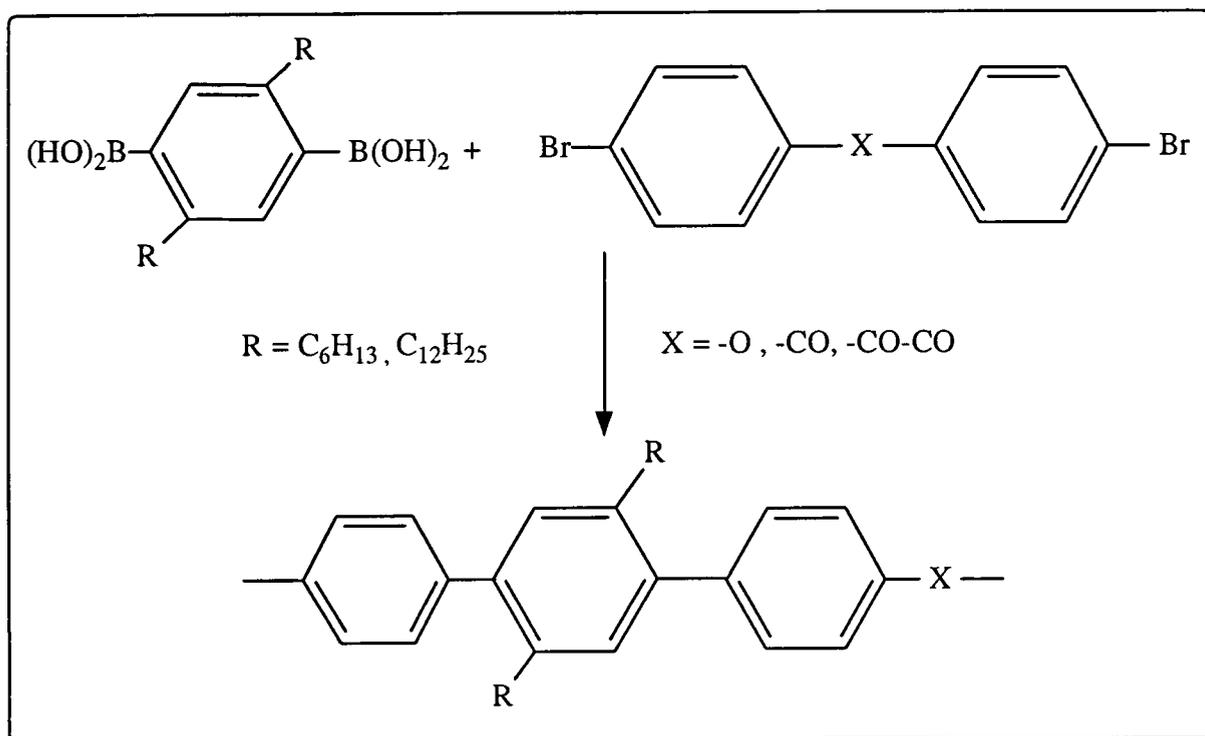


Figure 5.4 Palladium catalysed polycondensation of aromatic monomers with functional groups.

As detailed in Chapter 4, a problem associated with the polymerisation of the acetylene containing monomers is the possibility of crosslinking occurring during the

reaction. In order for the routes proposed above to successfully produce linear polymers attempts must be made to exclude branching and crosslinking. Palladium compounds, as well as certain other transition metal compounds, have been reported to catalyse the trimerisation of acetylenes in certain reactions, (Heck, R.F., *Palladium reagents in organic synthesis*. p. 337-338, 1985, Academic Press), although relatively few examples are known. Investigation of other catalysts and of the conditions by which trimerisation is encouraged need to be carried out.

APPENDIX A
INSTRUMENTATION

Instrumentation.

- 1: Mass spectra** were recorded on a VG Analytical Model 7070E Mass Spectrometer.
- 2: Infrared spectra** were recorded on a Perkin Elmer 1600 series Fourier Transform Infrared Spectrometer.
- 3: ^1H and ^{13}C solution nmr spectra** were recorded on a Varian VXR 400 nmr Spectrometer. ^1H nmr spectra were recorded at 399.952MHz and ^{13}C nmr spectra were recorded at 100.577MHz.
- 4: ^1H and ^{13}C solid state nmr spectra** were recorded on a Varian VXR 300 nmr Spectrometer. The ^{13}C spectra were recorded at 75.431MHz.
- 5: Thermogravimetric analysis** was performed using a Stanton Redcroft TG760 thermobalance.
- 6: Differential Scanning Calorimetry** was performed using a Perkin Elmer DSC7.
- 7: Polarising Microscopy** was performed using an Olympus BH2 microscope, equipped with a Linkam TMS91 temperature controller and a linkam THM600 hot stage. A Sony KX-14EPI display with screen magnification x100 and a Linkam VTO232 video text overlay for recording of temperatures and holding times of the hotstage was used. A JVC video recorder was used to tape the experiments and a Sony colour video printer UP-5000P produced the photographs.
- 8: Gel Permeation Chromatography** was performed using a Waters Differential Refractometer R401 fitted with a Waters 590 pump. The machine was fitted with four columns, $5\mu\text{m}$ Guard column, $5\mu\text{m}$ 100\AA column, $5\mu\text{m}$ 10^3\AA column and a $5\mu\text{m}$ 10^5\AA column. The samples were dissolved in chloroform and the flow rate was 1ml/min. Analysis of the results was carried out using Polymer Labs software version 4.
- 9: Wide Angle X-ray Scattering** was performed using a Siemens D5000 Diffractometer, the diffraction patterns were analysed using a Siemens software package Diffrac AT.V3.1.

APPENDIX B
MASS SPECTRA

Notes on the appendices.

Throughout the appendices B to E a given compound retains the same reference number, for information the compounds and their numbers are detailed below.

1 1,4-Diethynylbenzene

2 4,4'-Diethynylbiphenyl

3 1,4-(2'-hydroxy-2'-methyl-3'-yn-4'-yl)-2,5-dihexylbenzene

4 1,4-Diethynyl-2,5-dihexylbenzene

5 4-(2'-hydroxy-2'-methylbut-3'-yn-4'-yl)methylbenzoate

6 1,4-bis(4'-ethynylmethylbenzoate)benzene

7 4,4'-bis(4''-ethynylmethylbenzoate)biphenyl

8 PI

9 PII

10 PIII

11 4,4'-Di(2''-hydroxy-2''-methylbut-3''-yn-4''-yl)benzophenone

12 4,4'-Diethynylbenzophenone

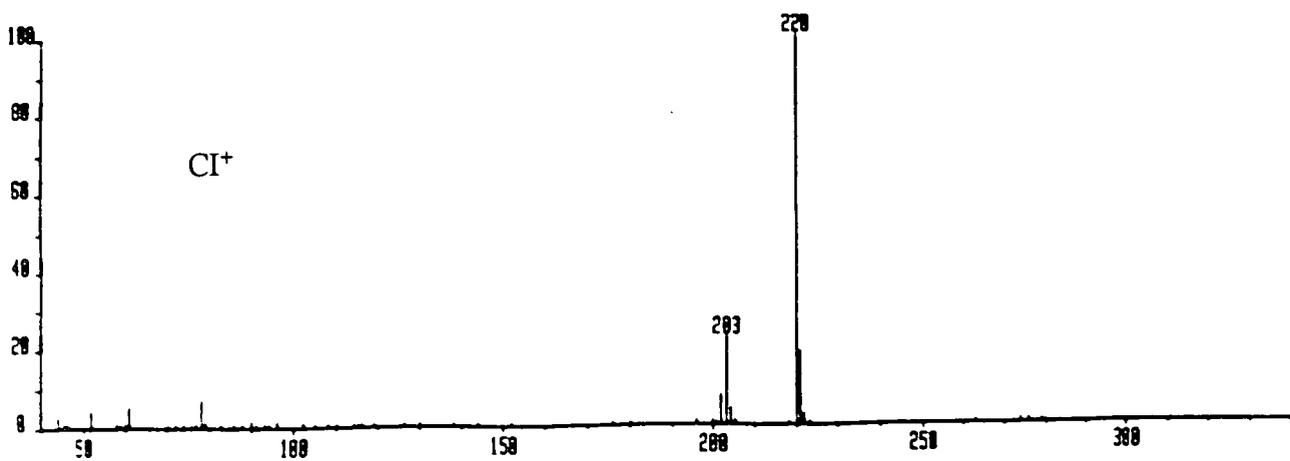
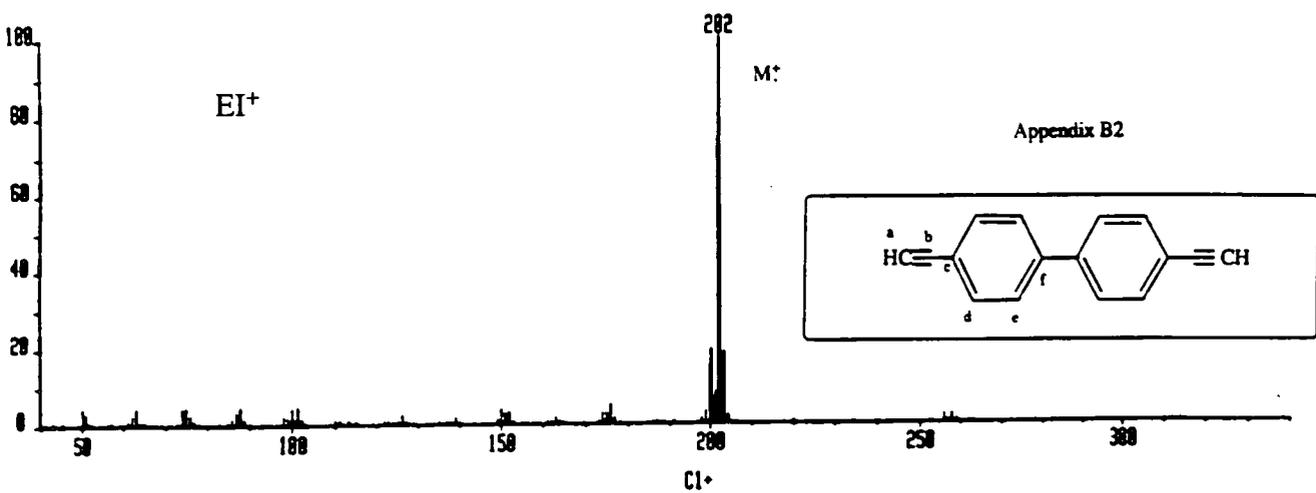
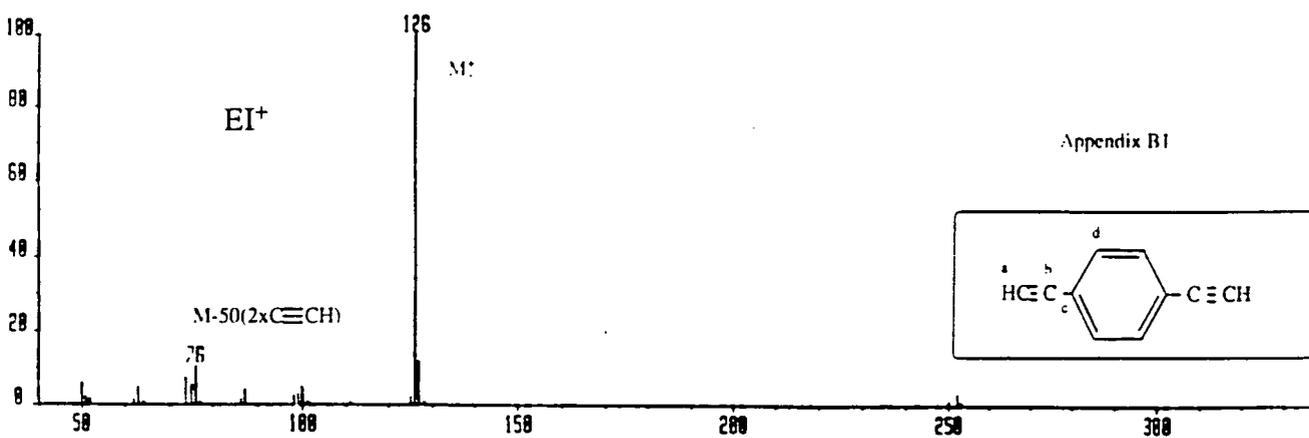
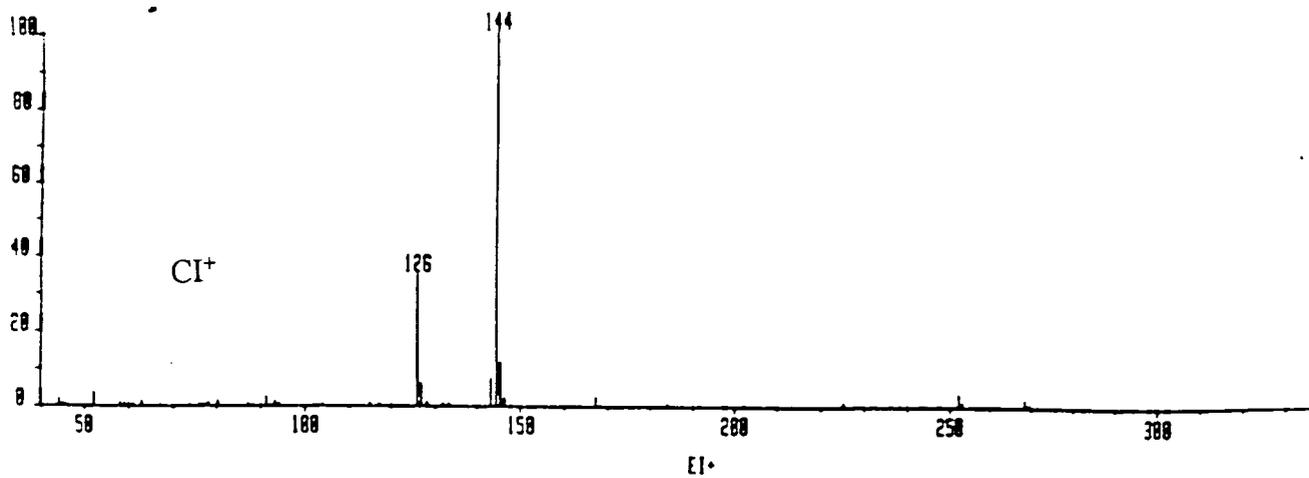
13 4,4'-bis(4''-ethynylmethylbenzoate)benzophenone

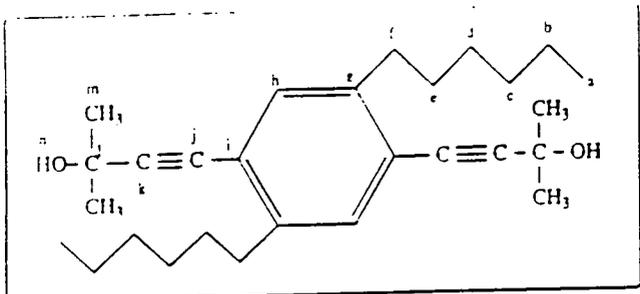
14 PIV

15 PV

16 PVI

17 PVII





EI⁺

M - 15(CH₃)

395.3

M-73(CH₃(CH₂)₄)

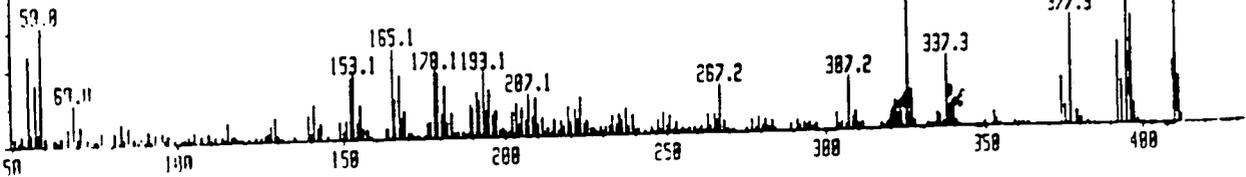
M⁺

M-85(C₆H₁₃)

325.2

377.3

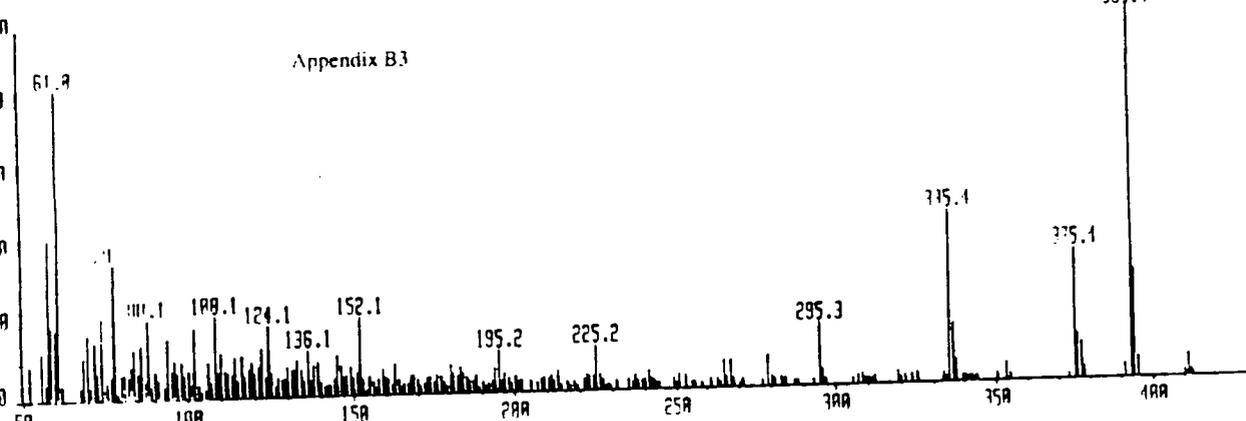
418.3



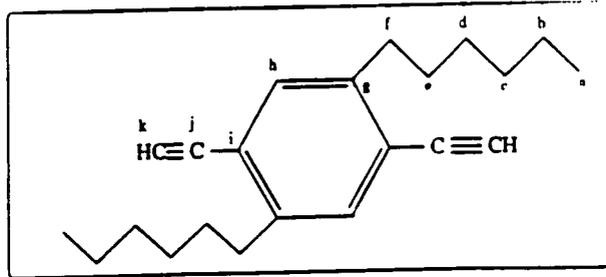
CI⁺

Appendix B3

393.4



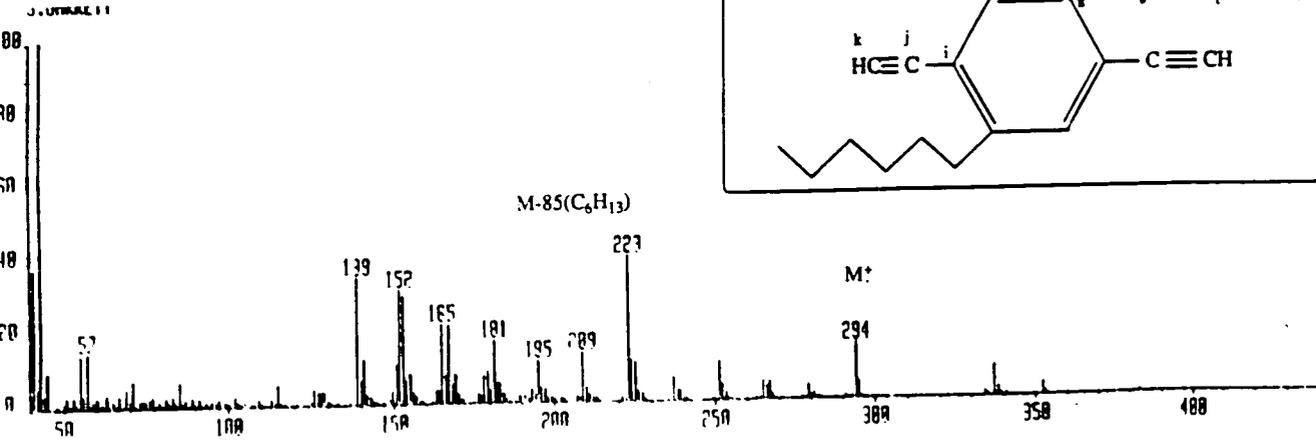
EI⁺



M-85(C₆H₁₃)

M⁺

294

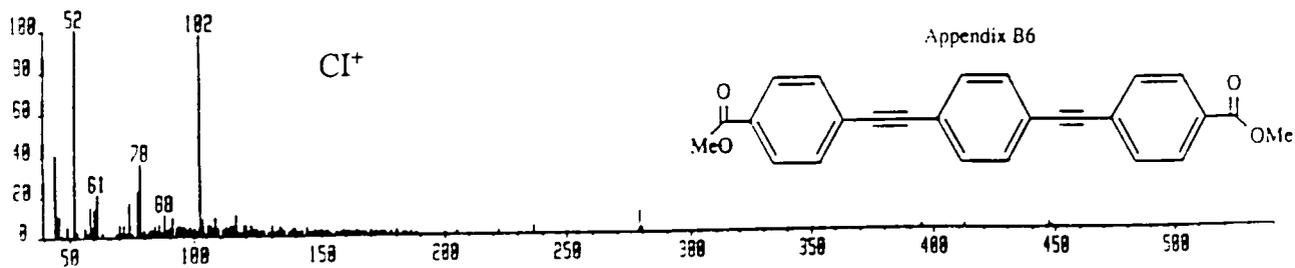
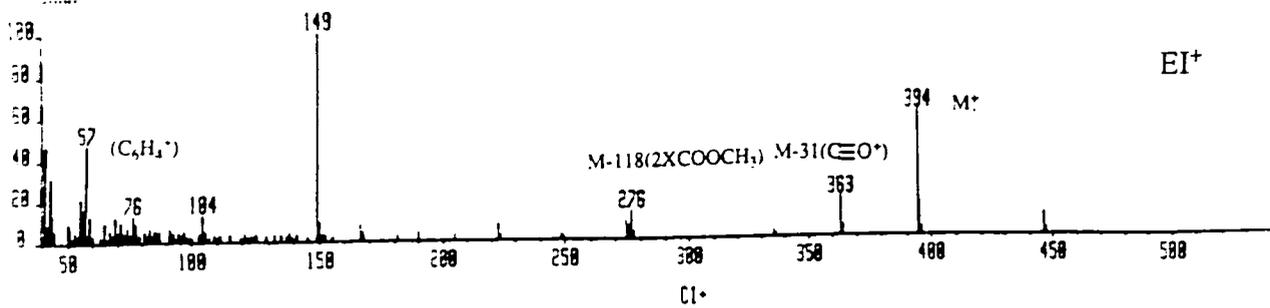


CI⁺

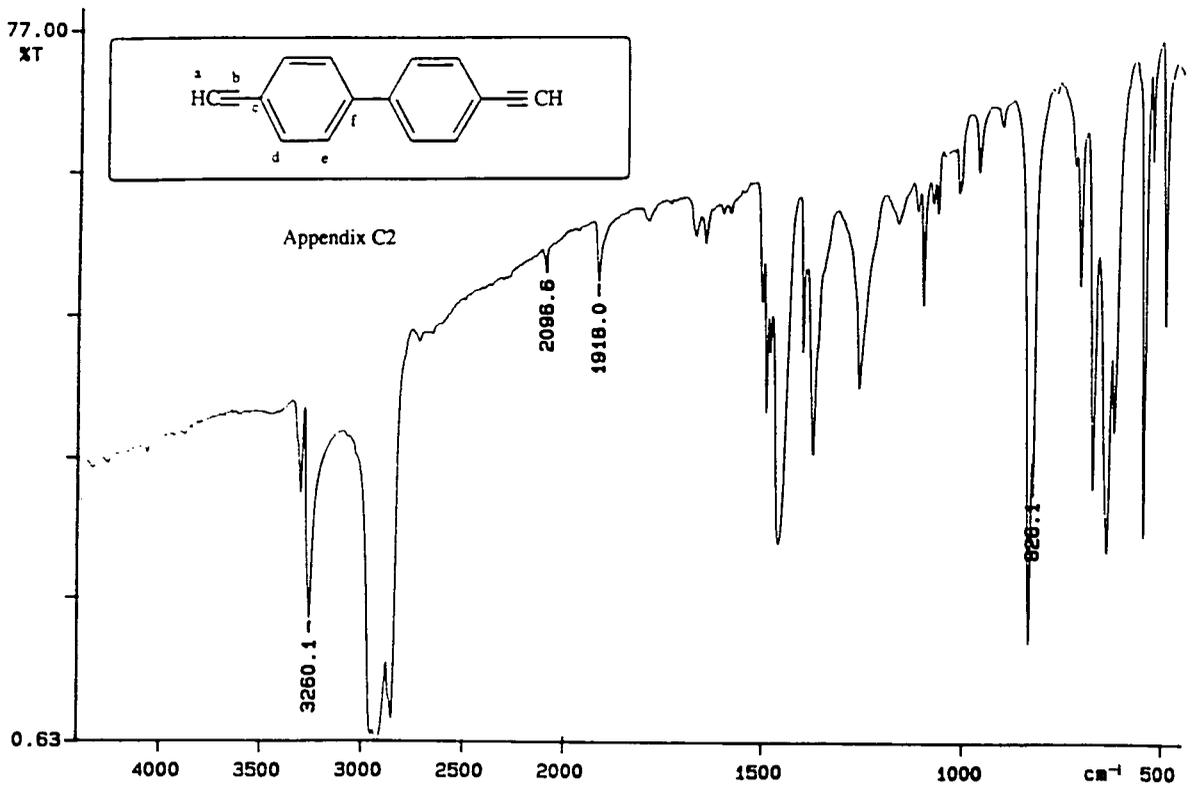
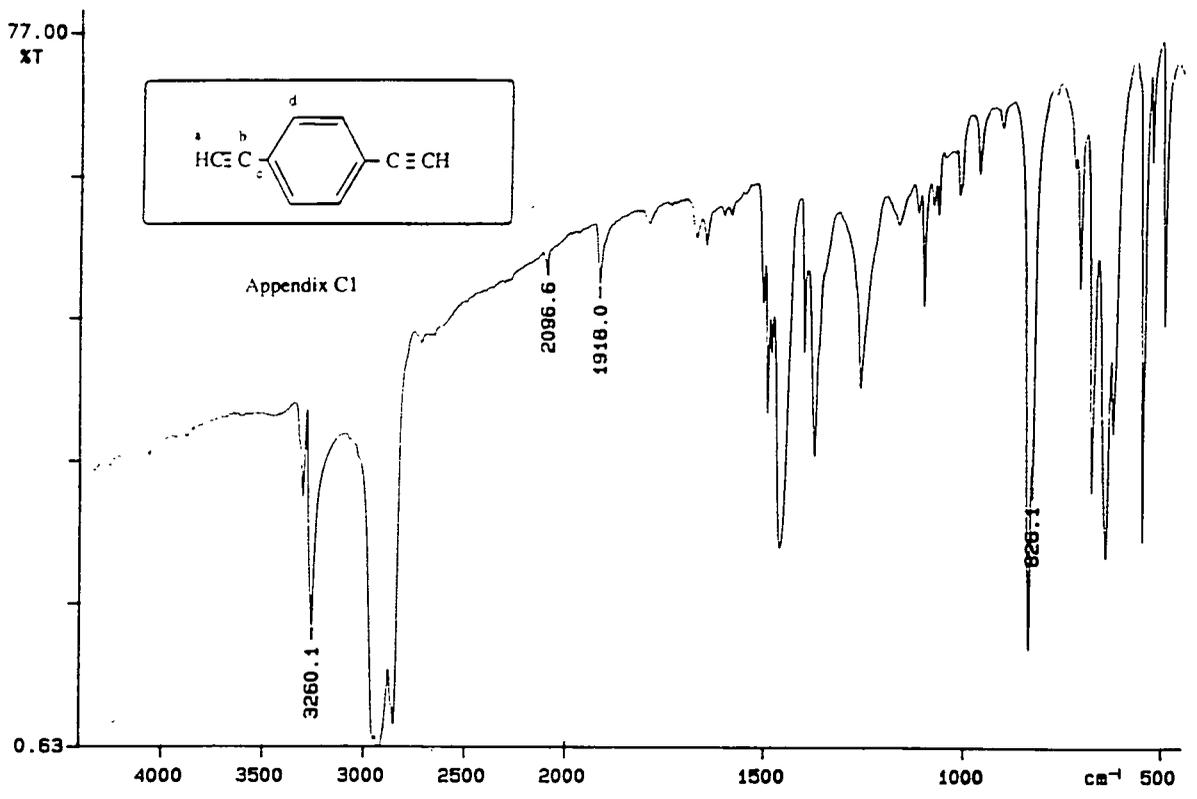
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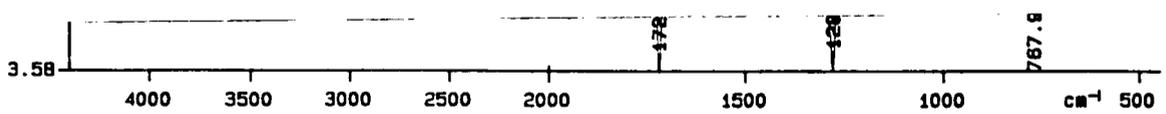
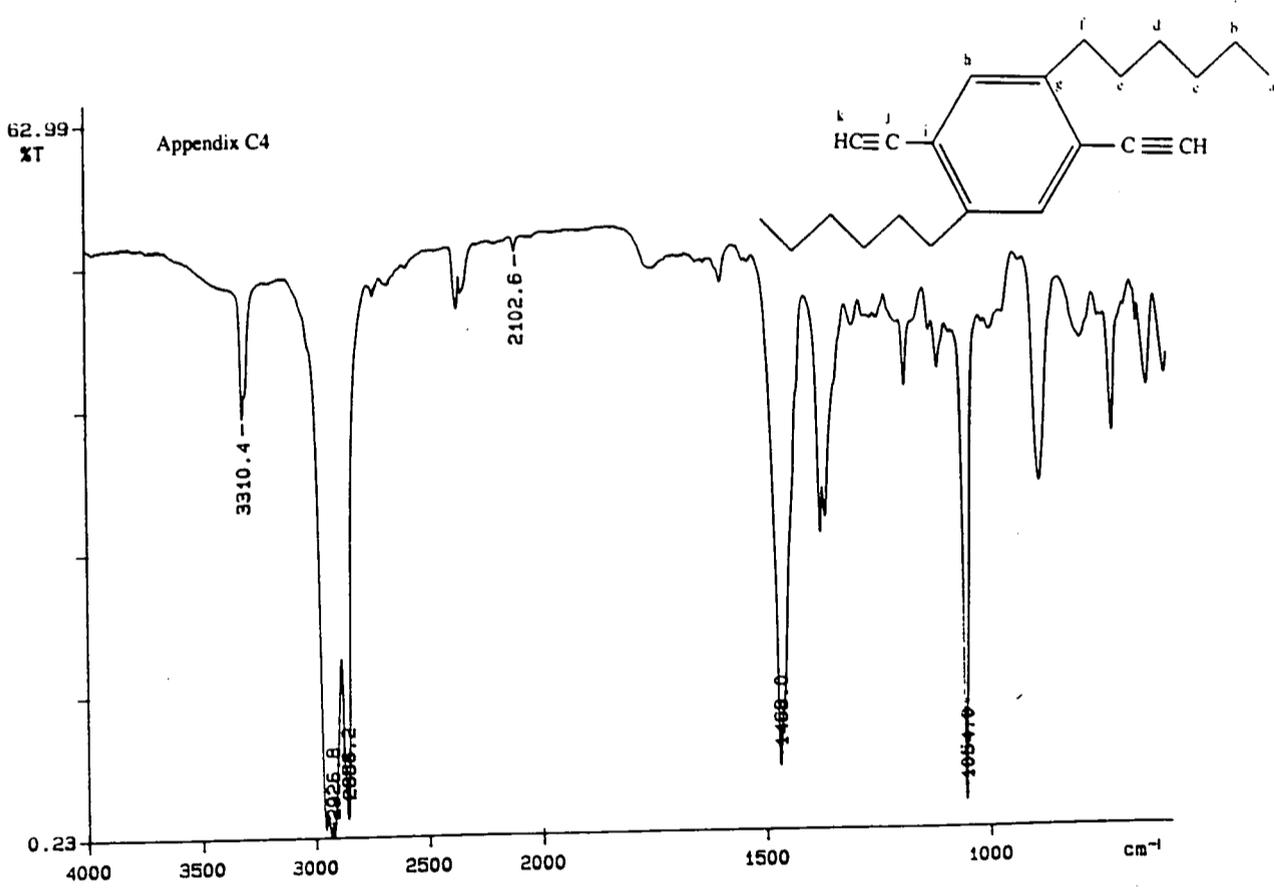
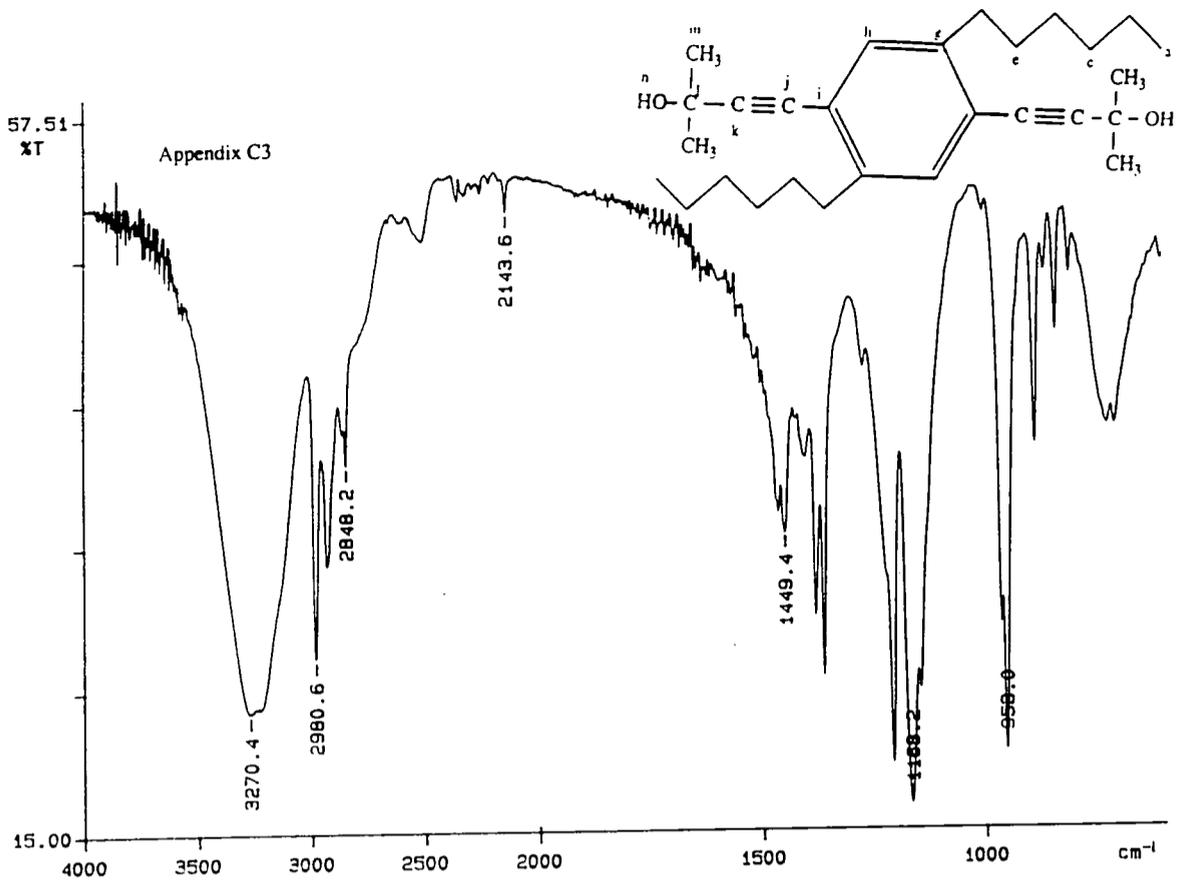
Appendix B4



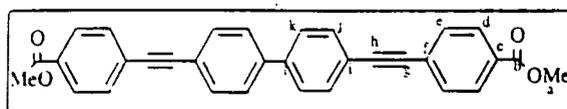


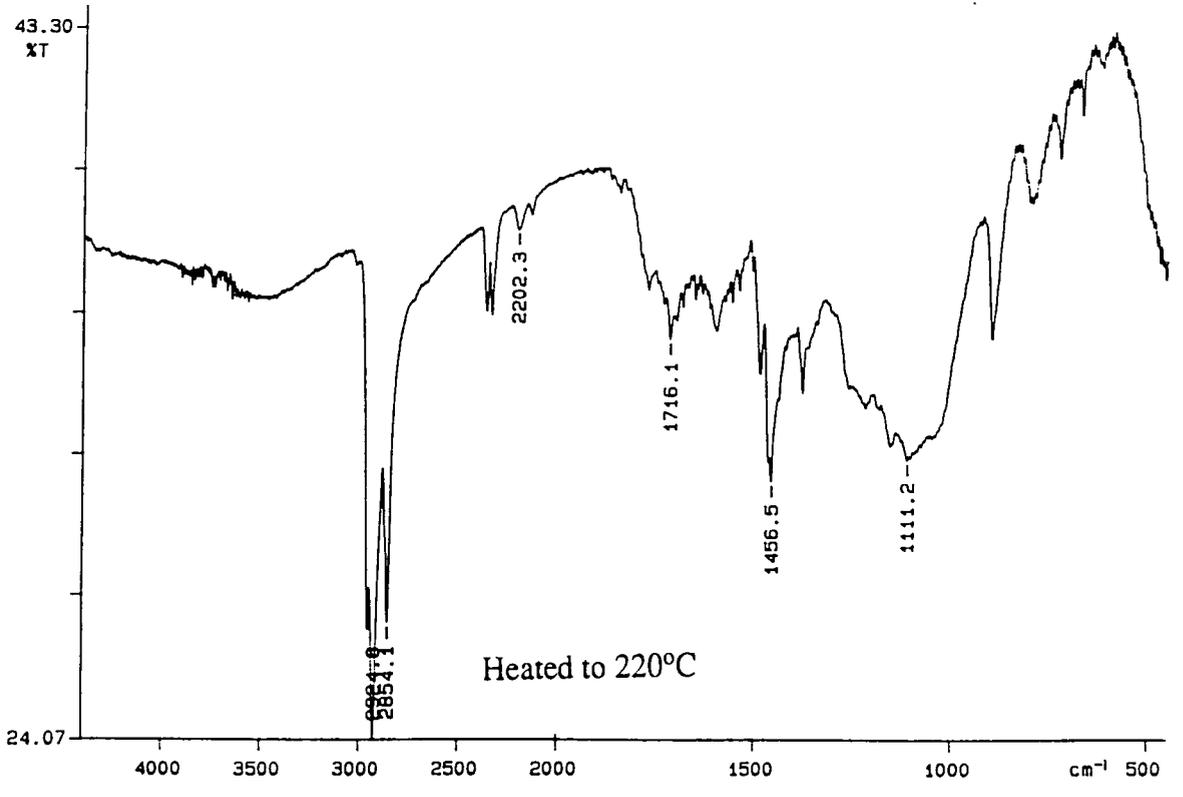
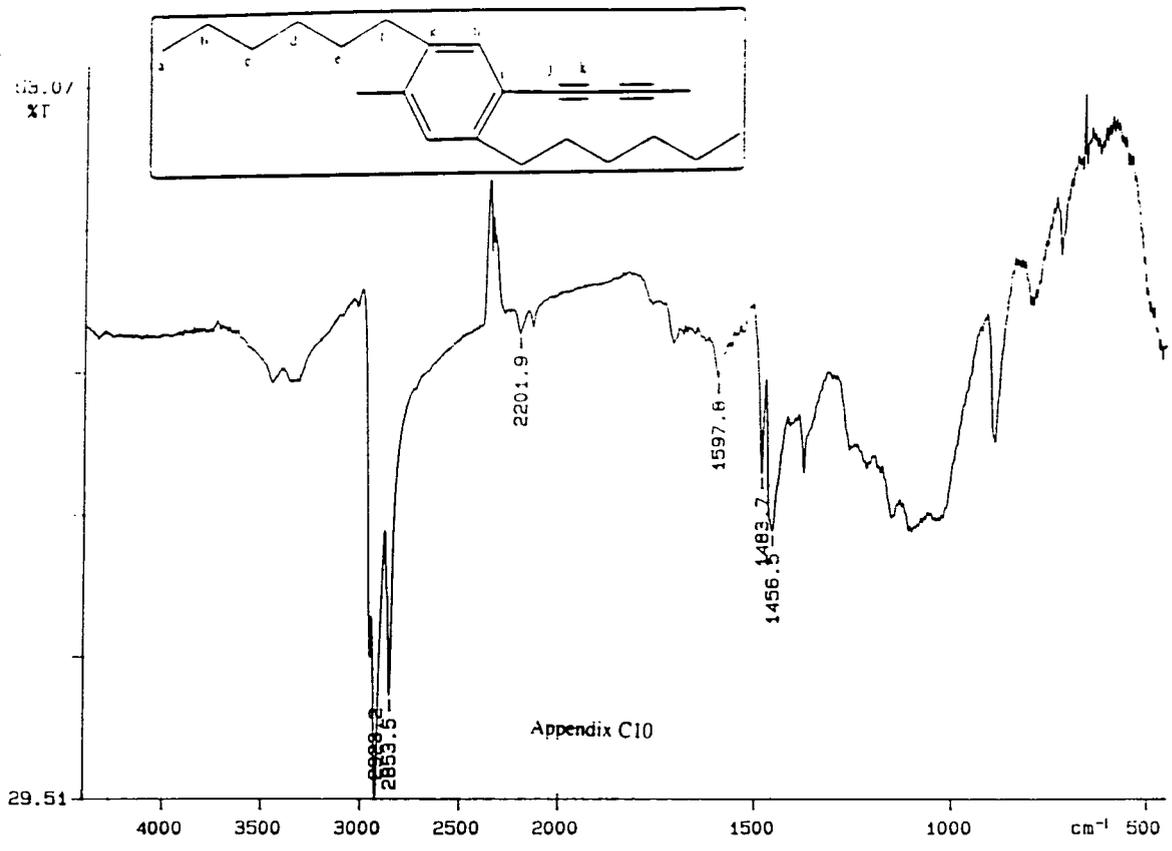
APPENDIX C
INFRARED SPECTRA

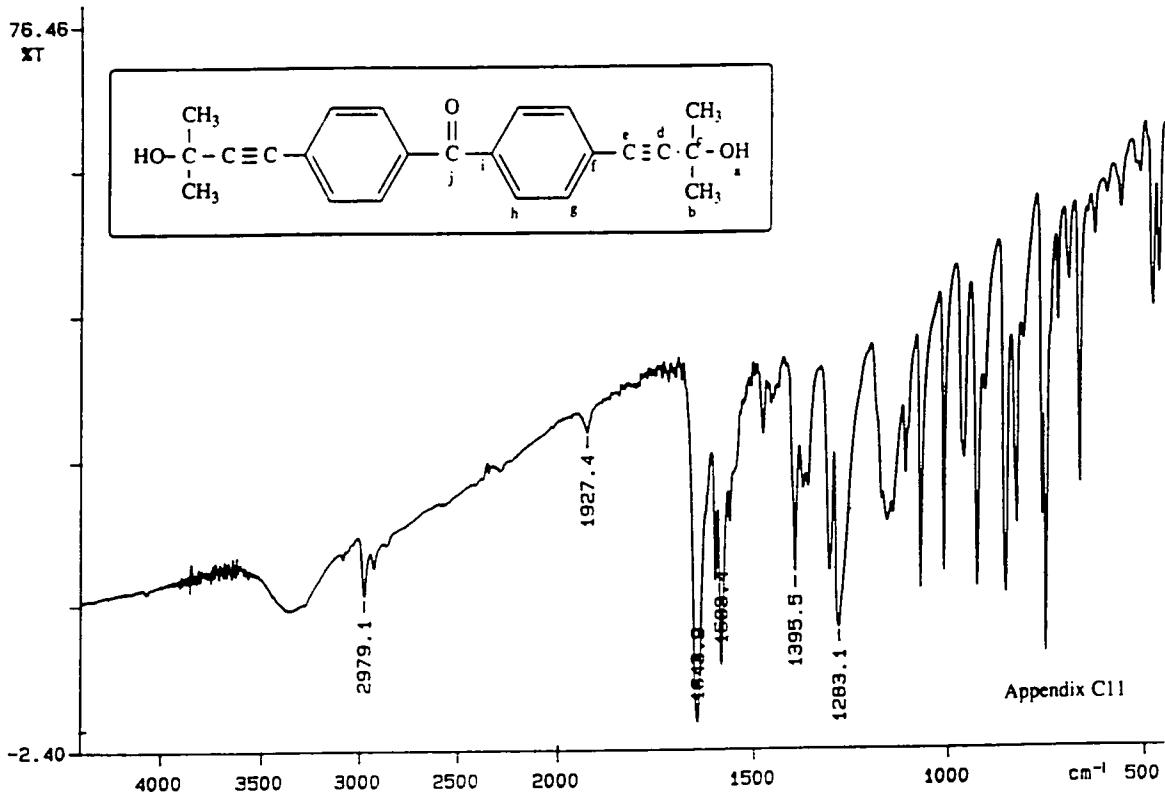


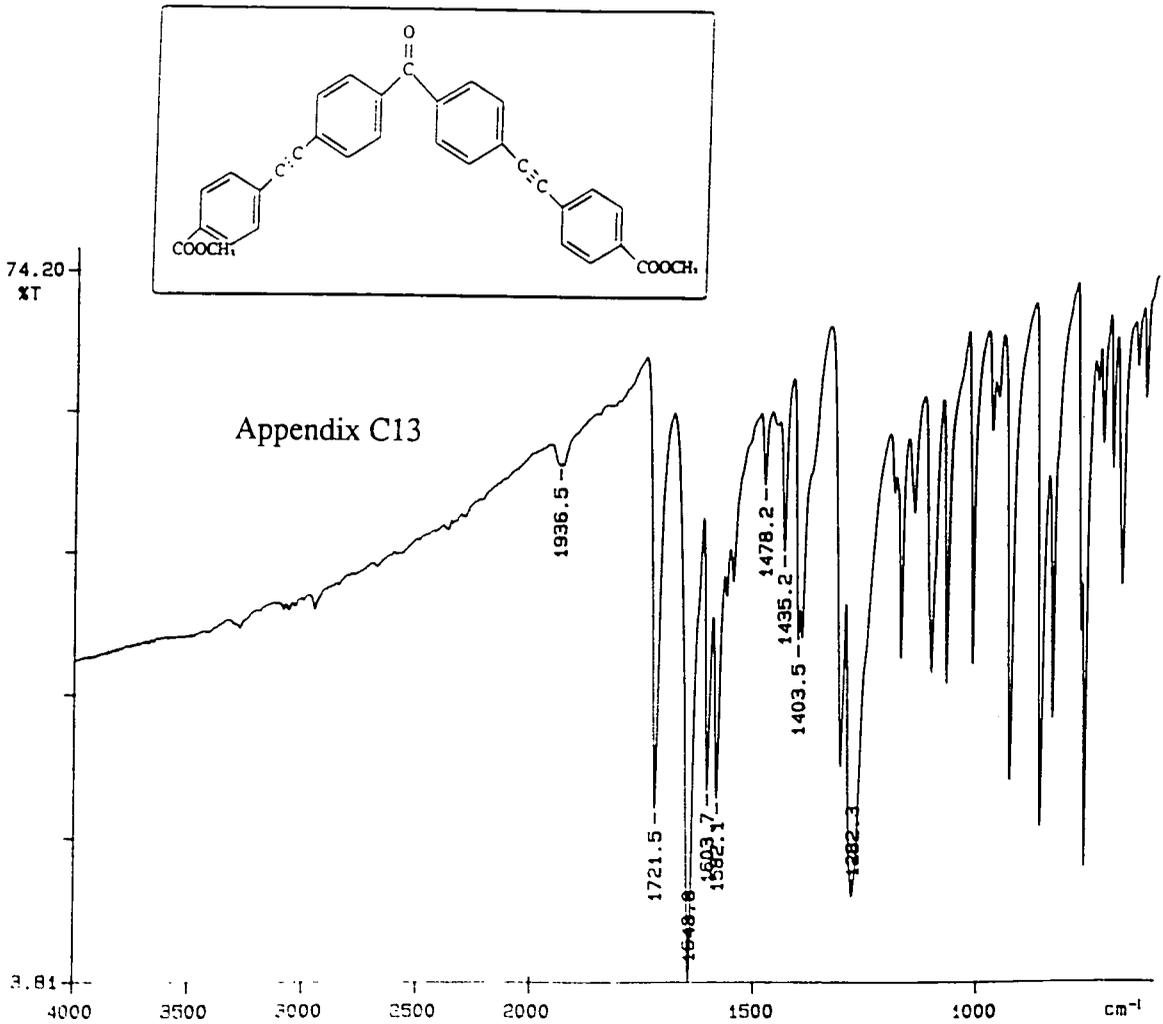
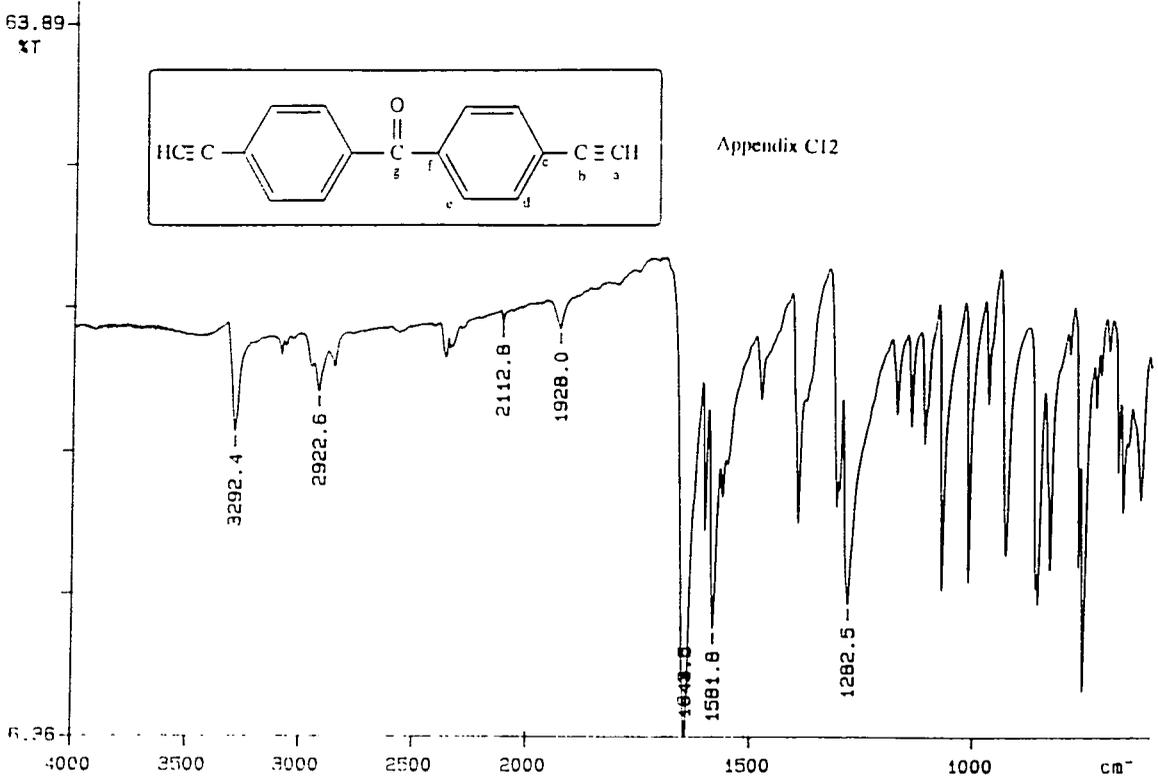


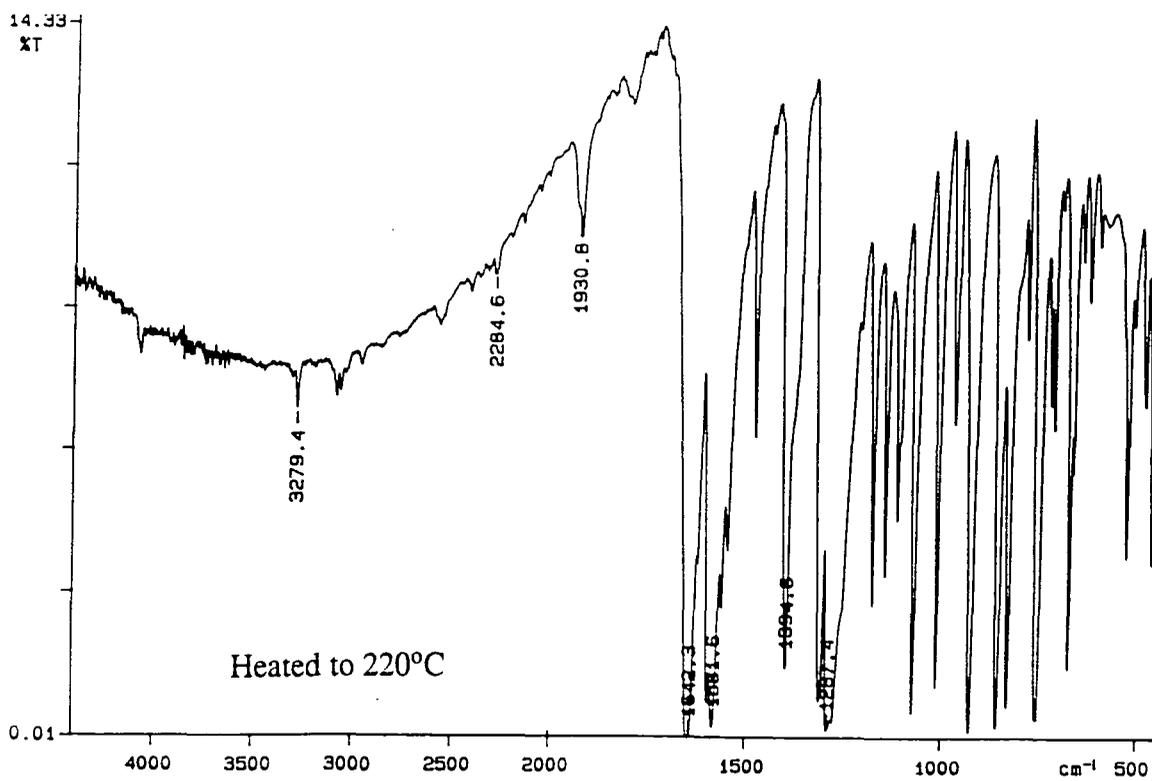
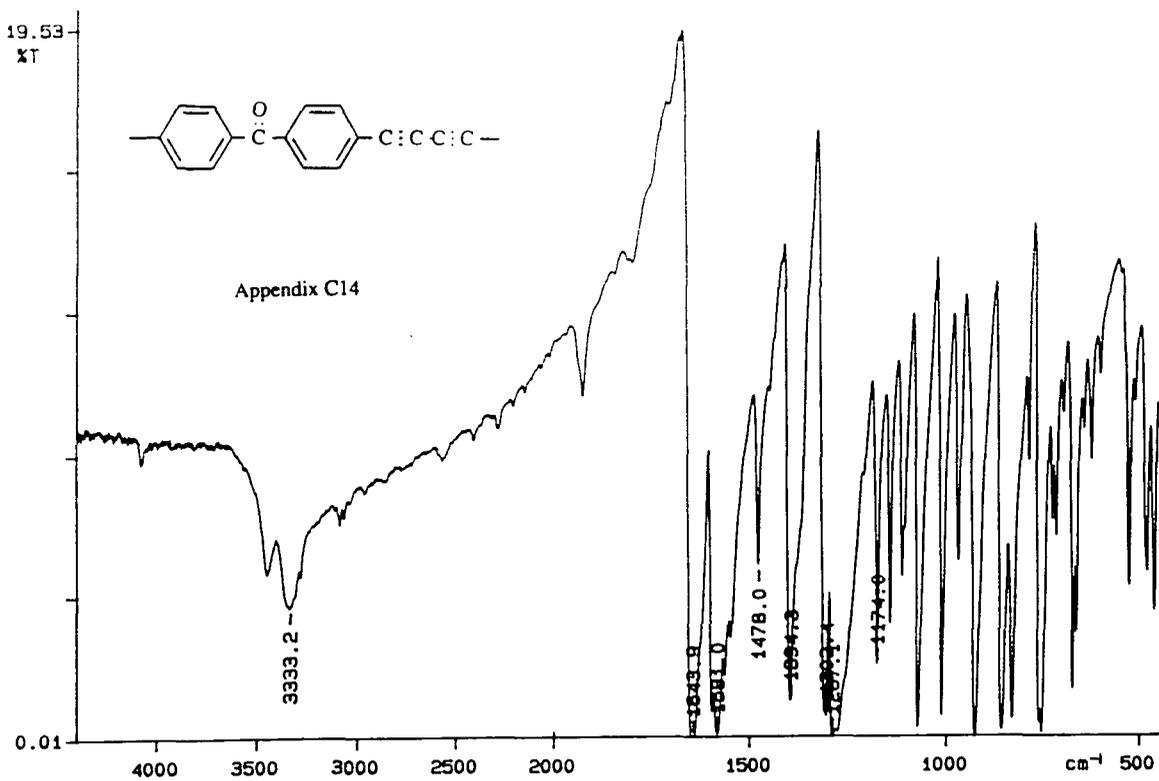
Appendix C7

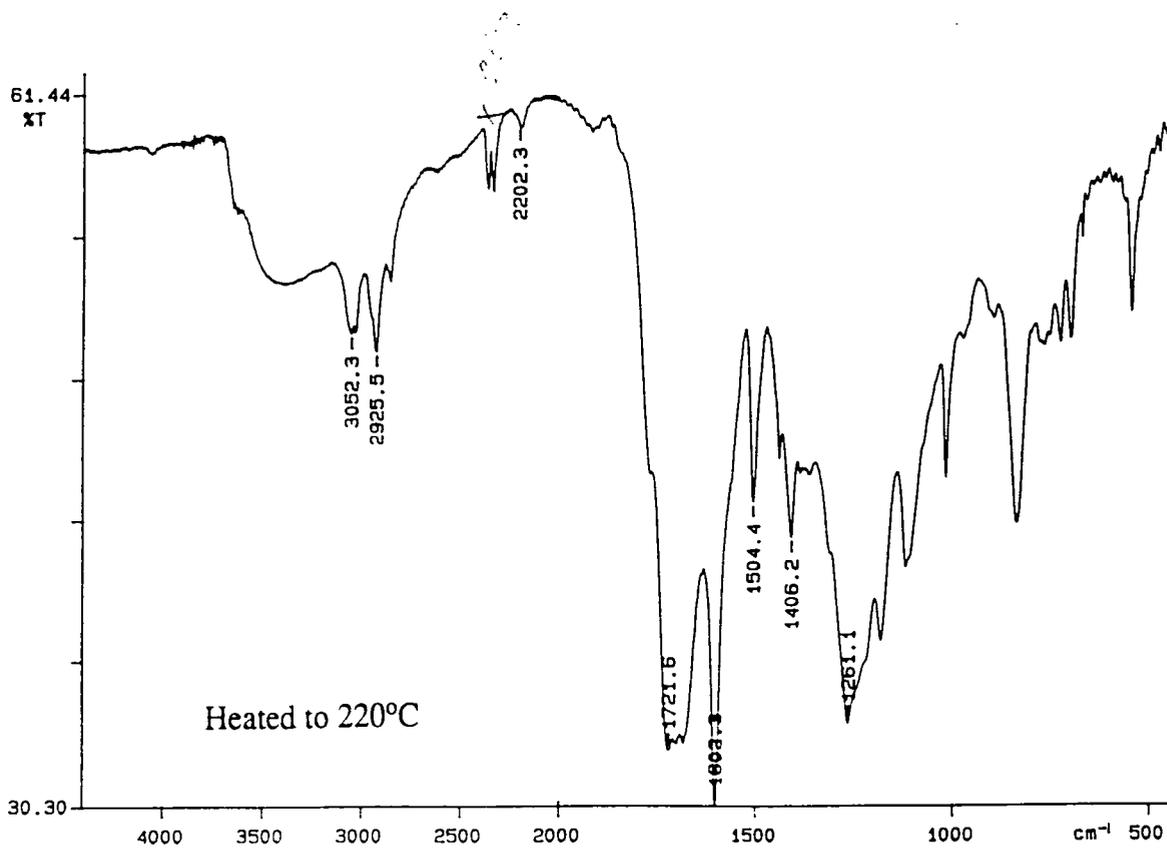
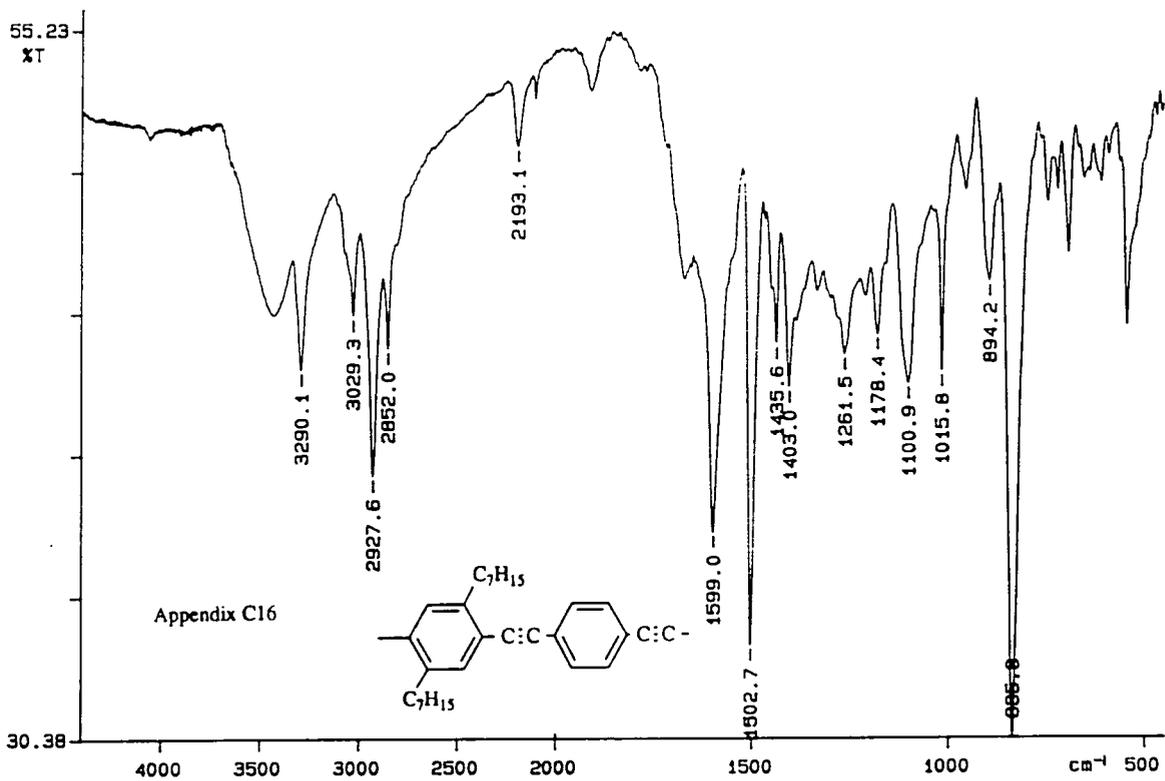


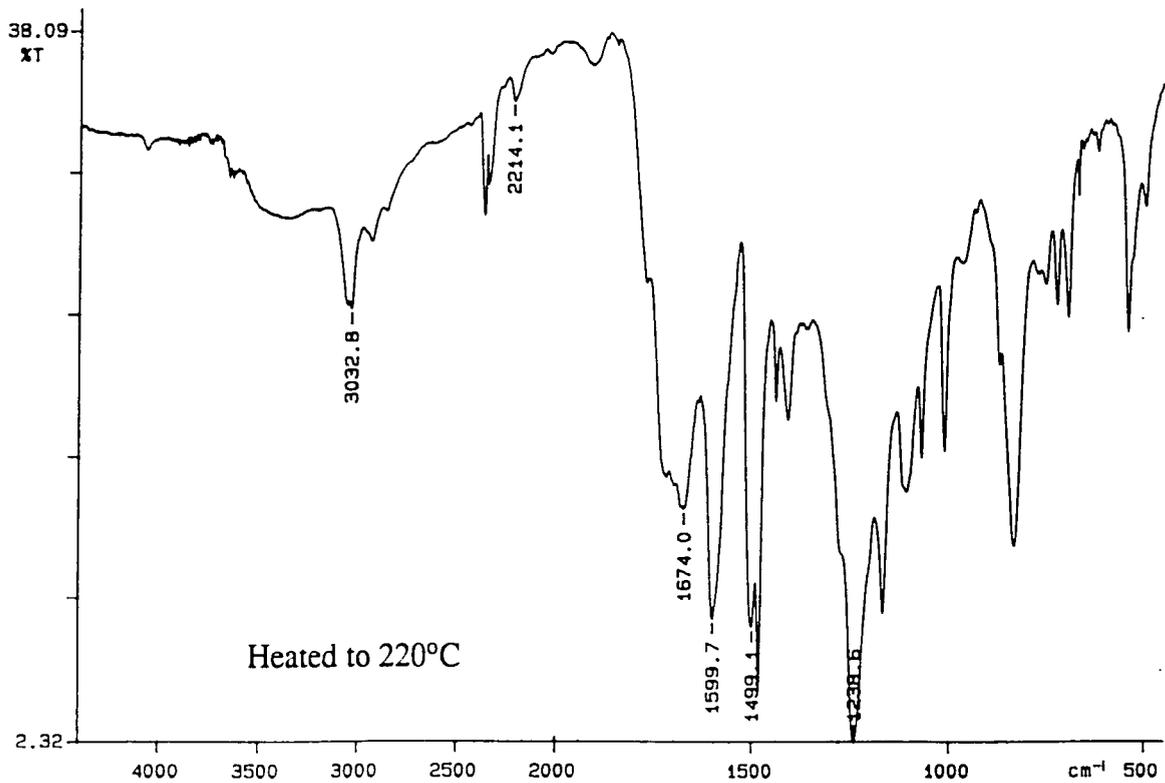
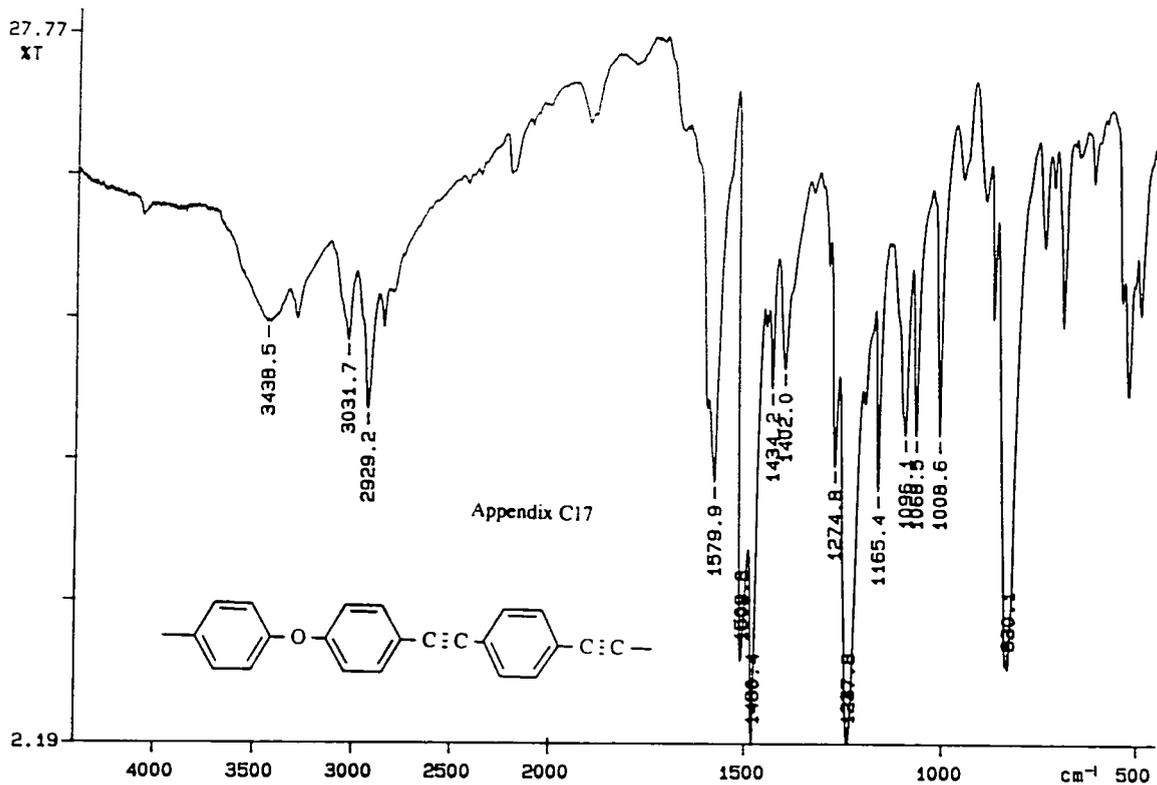






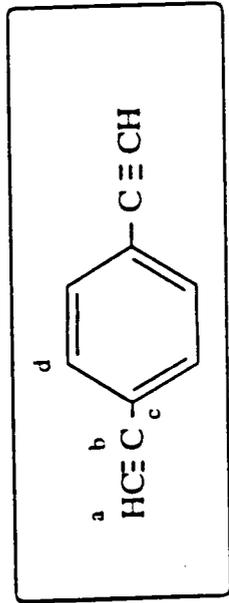




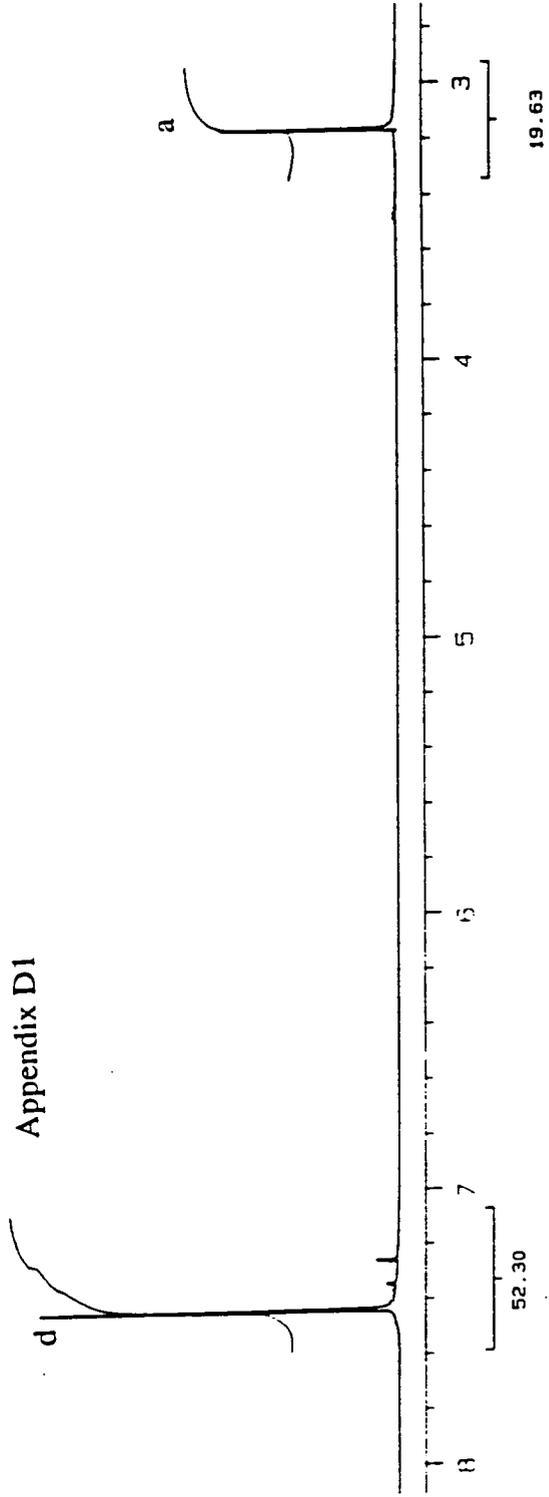


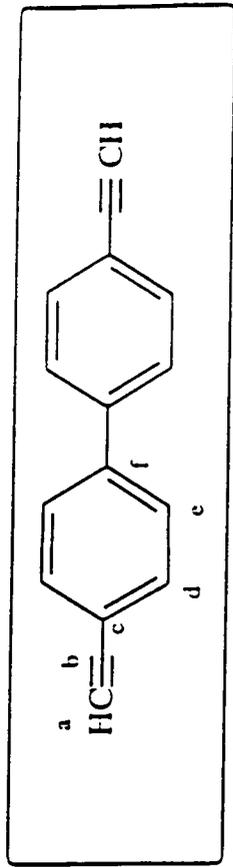
APPENDIX D

¹H NMR SPECTRA



Appendix D1





Appendix D2

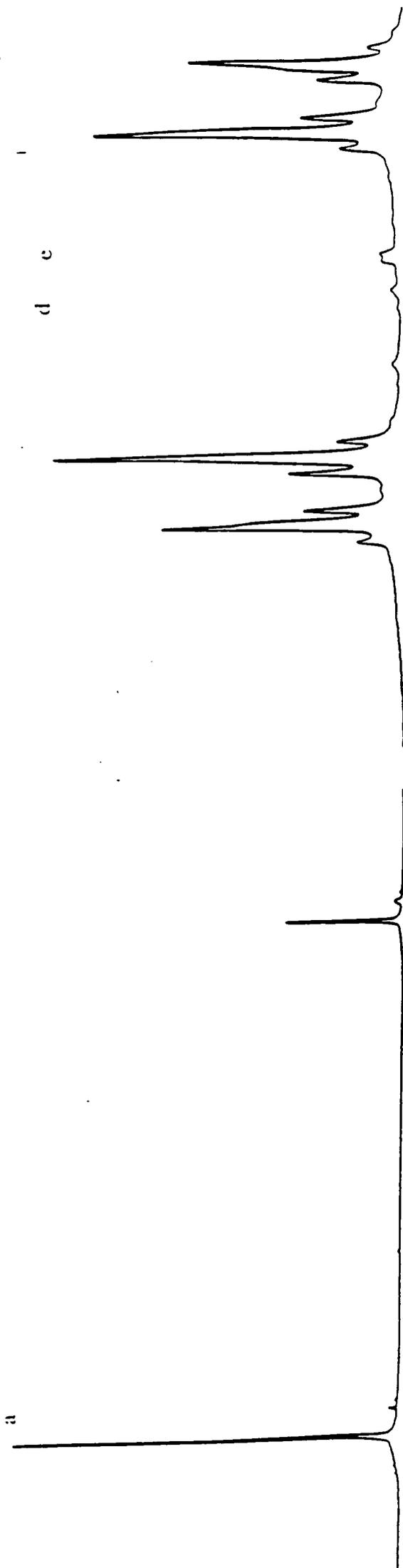
3.75

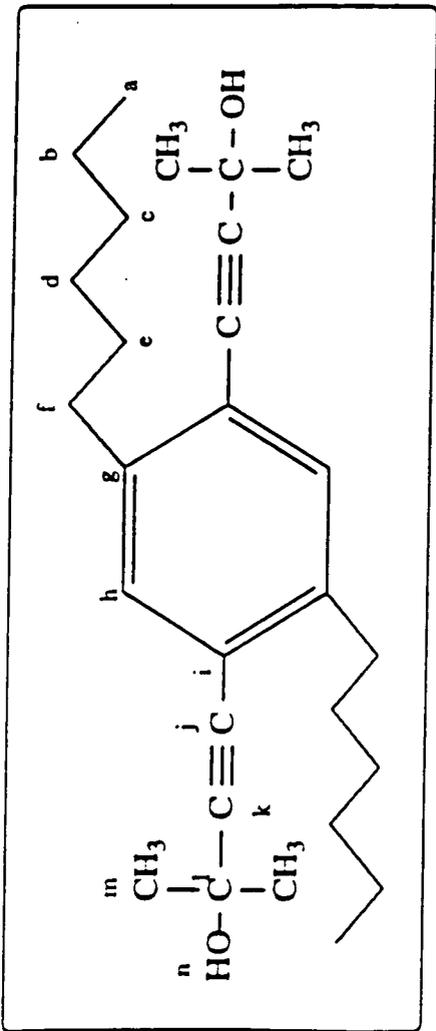
Observed
Shift (ppm)

7.5-7.7

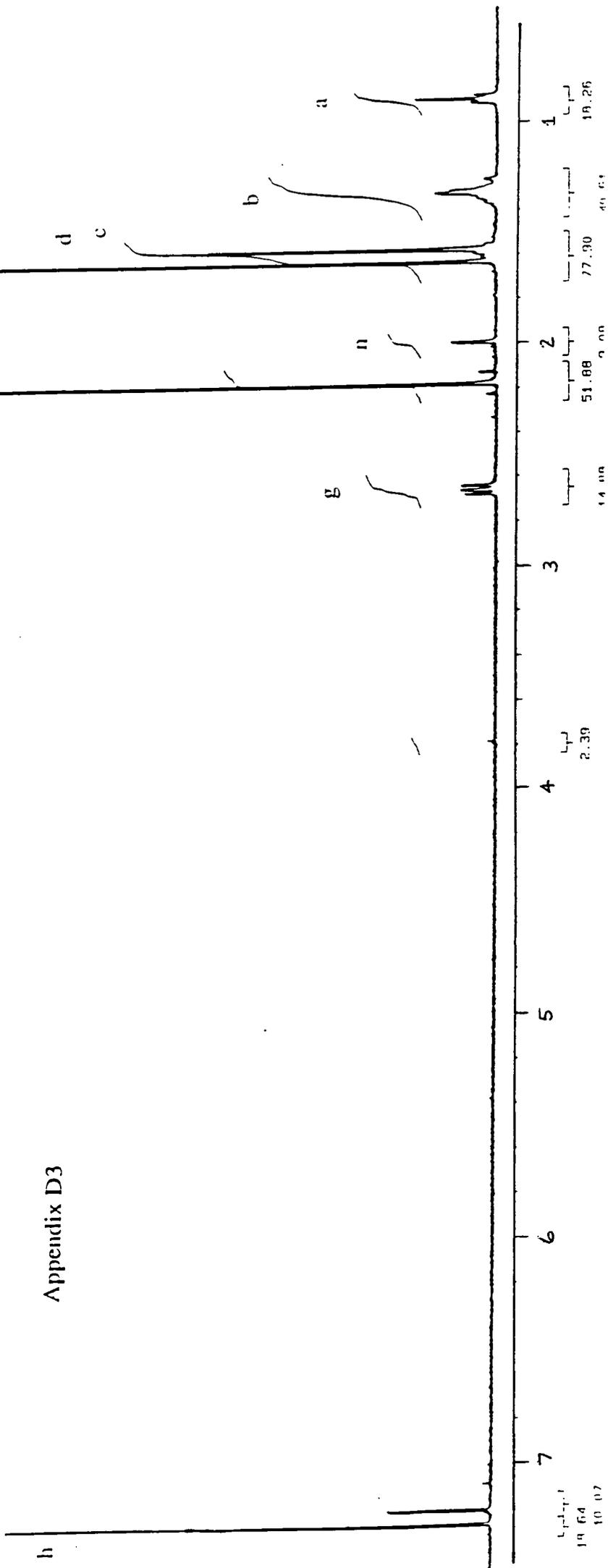
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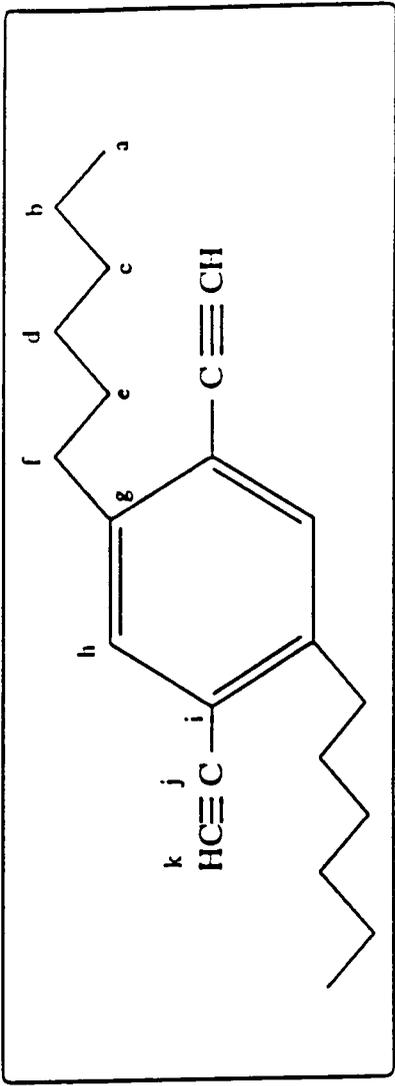
d e



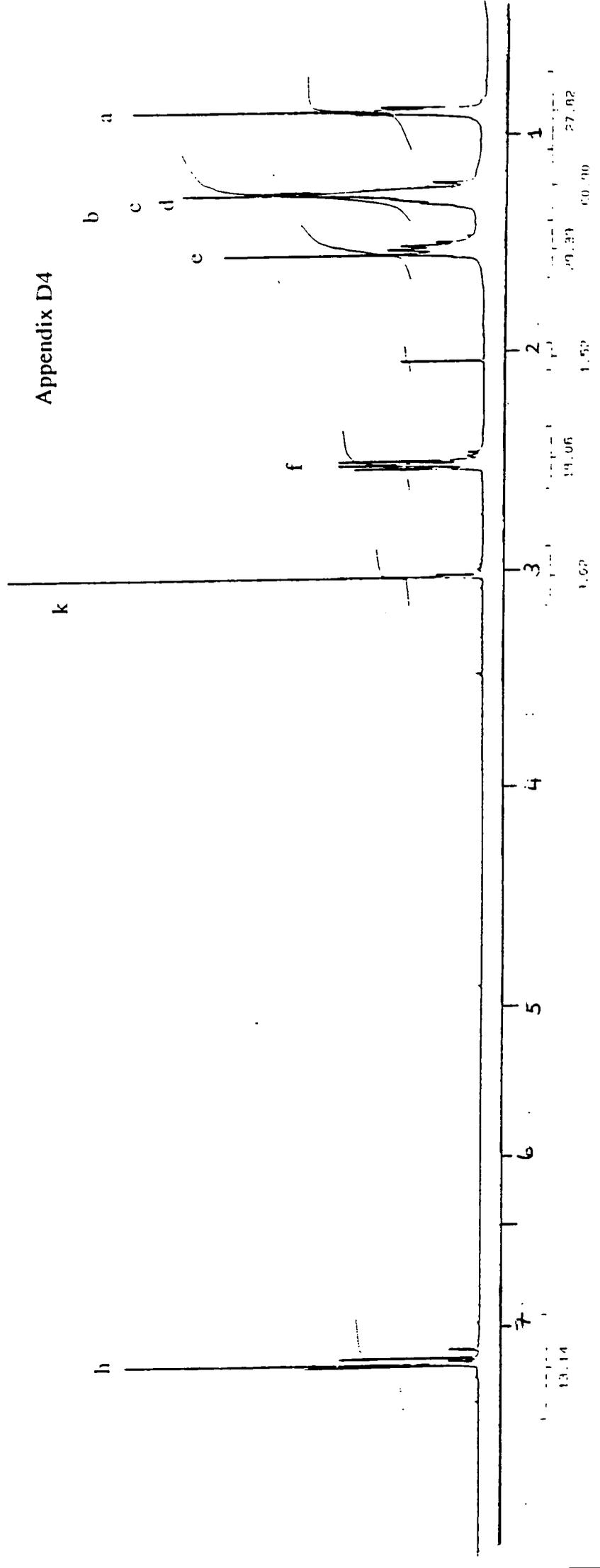


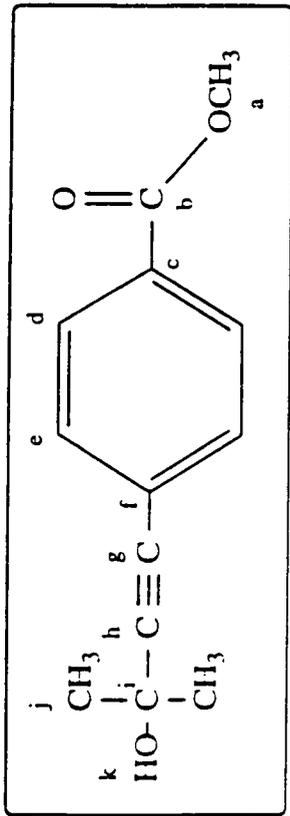
Appendix D3



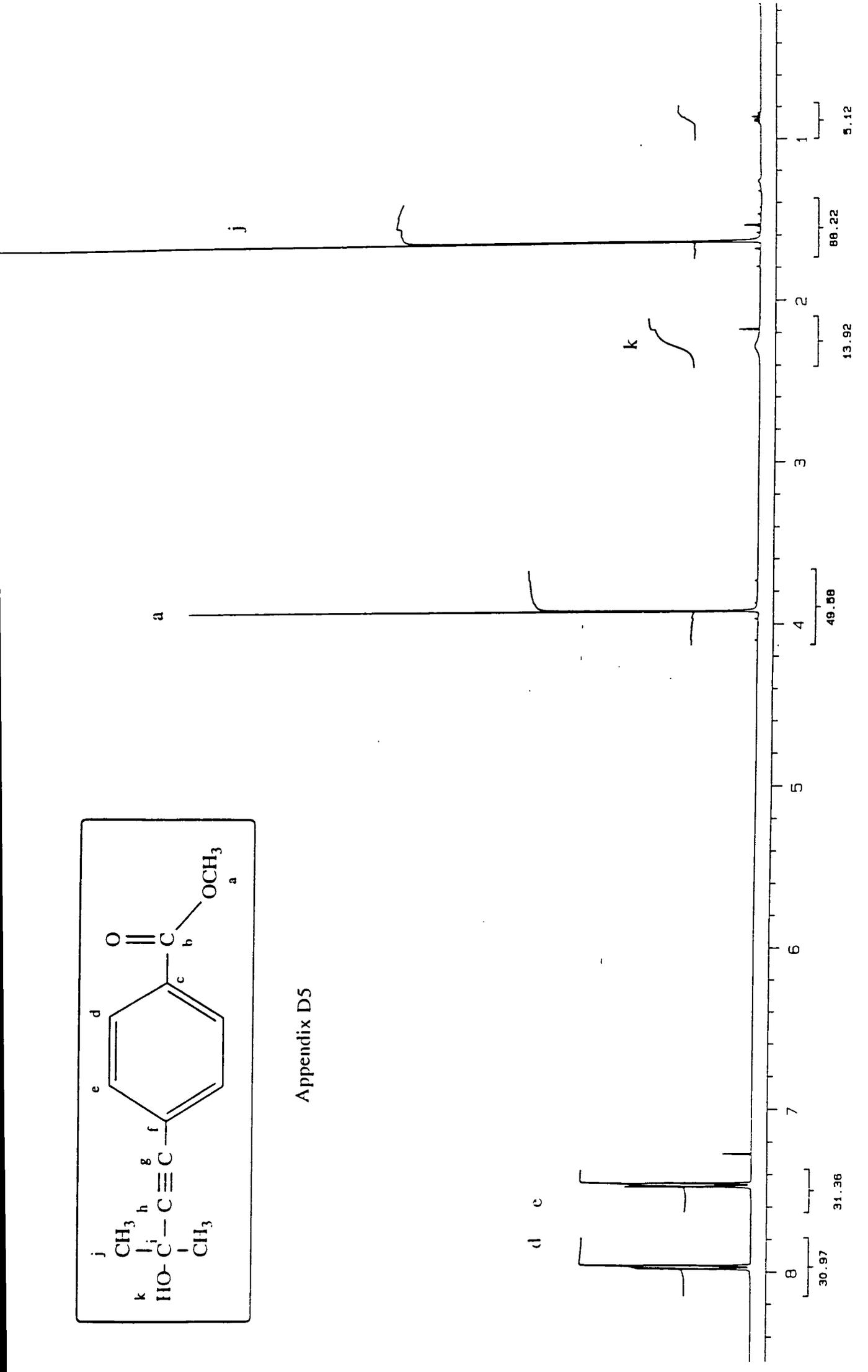


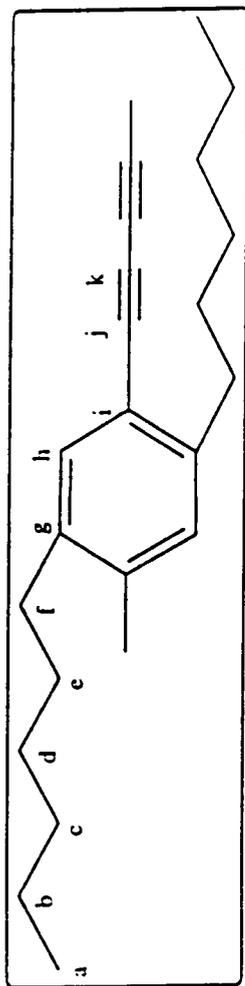
Appendix D4



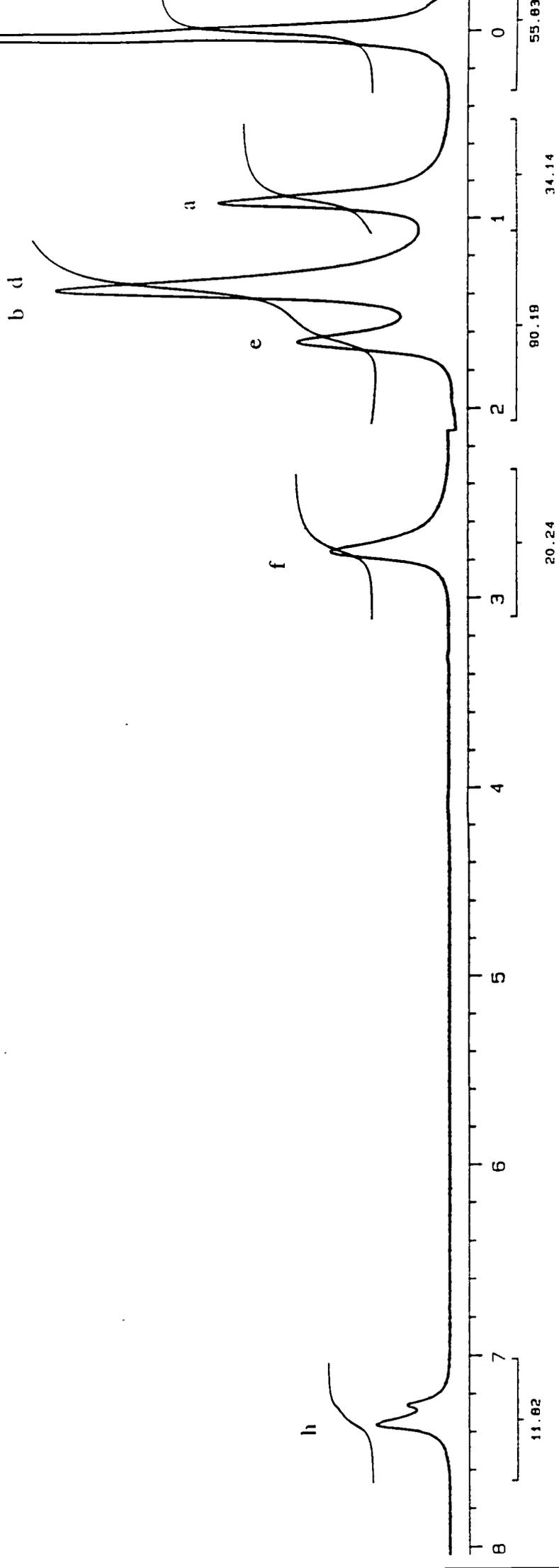


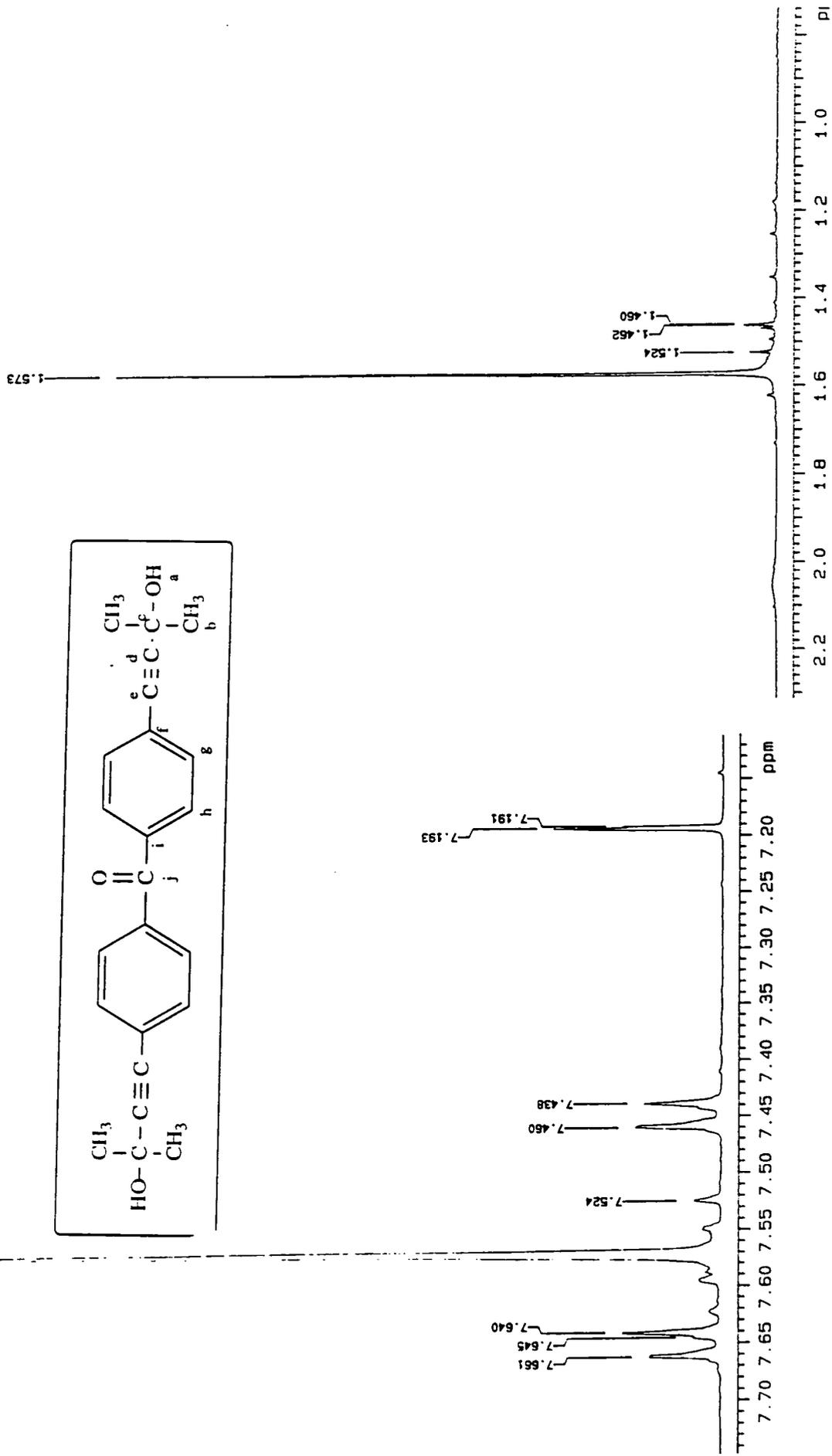
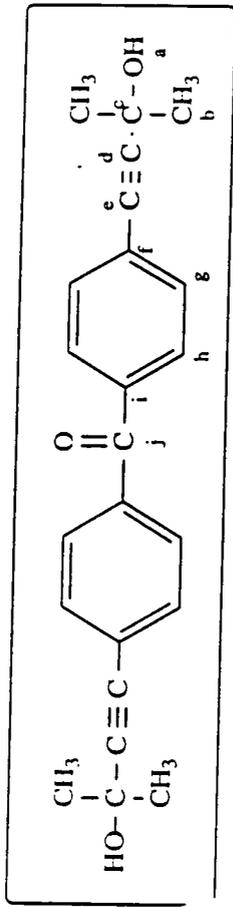
Appendix D5

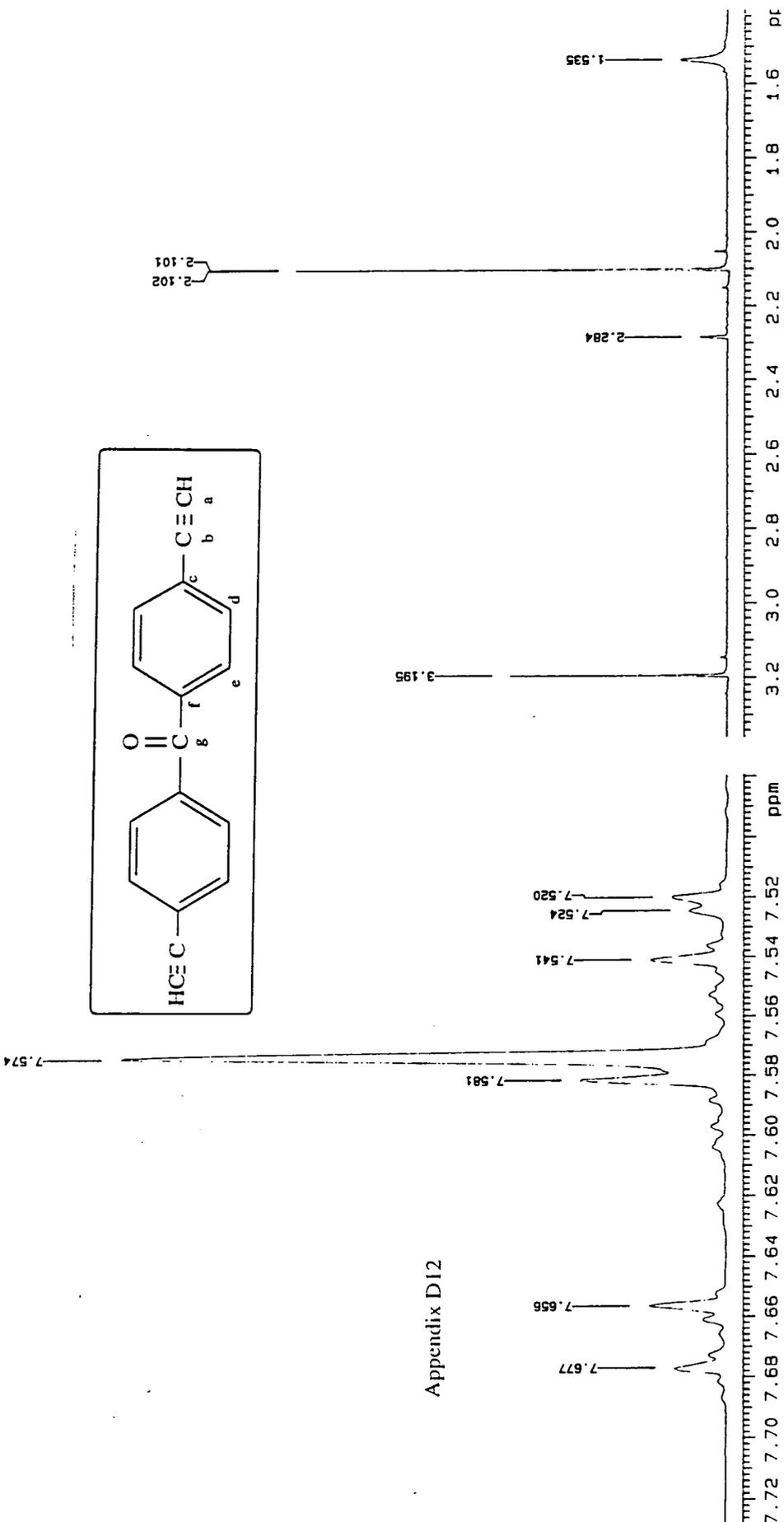




Appendix D10



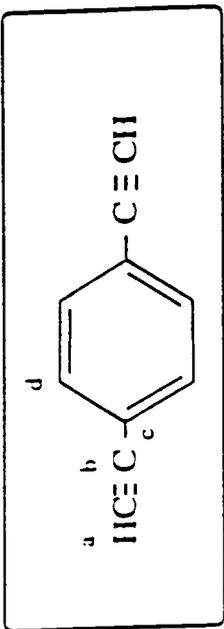
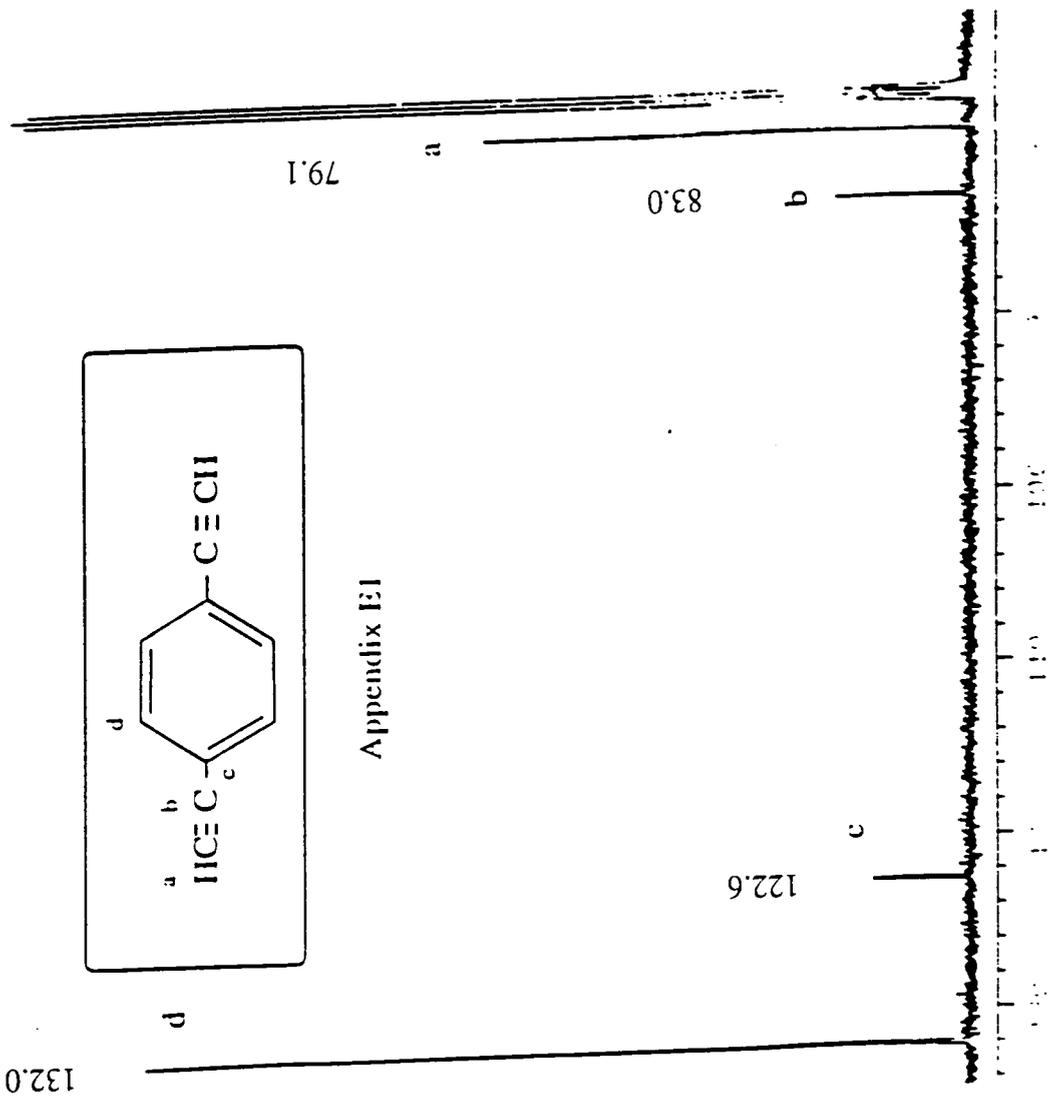




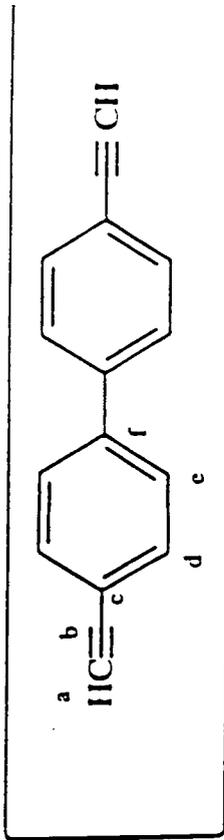
Appendix D12

APPENDIX E

^{13}C NMR SPECTRA

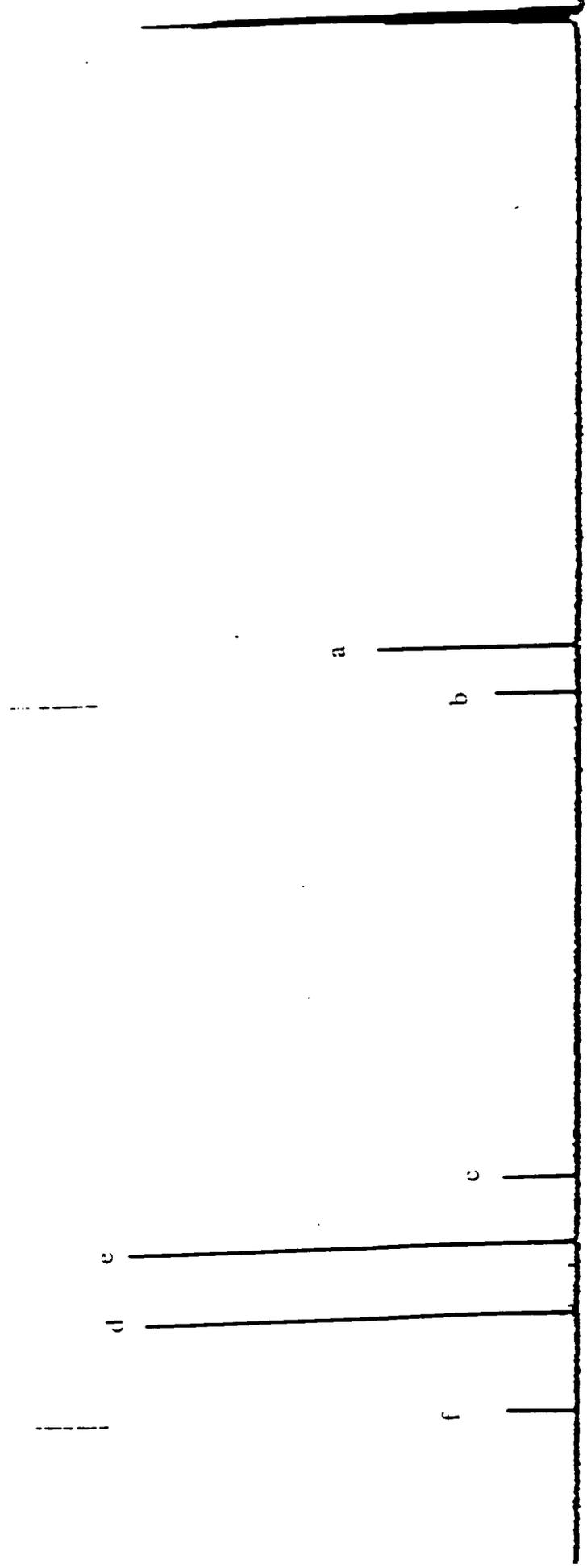


Appendix B1

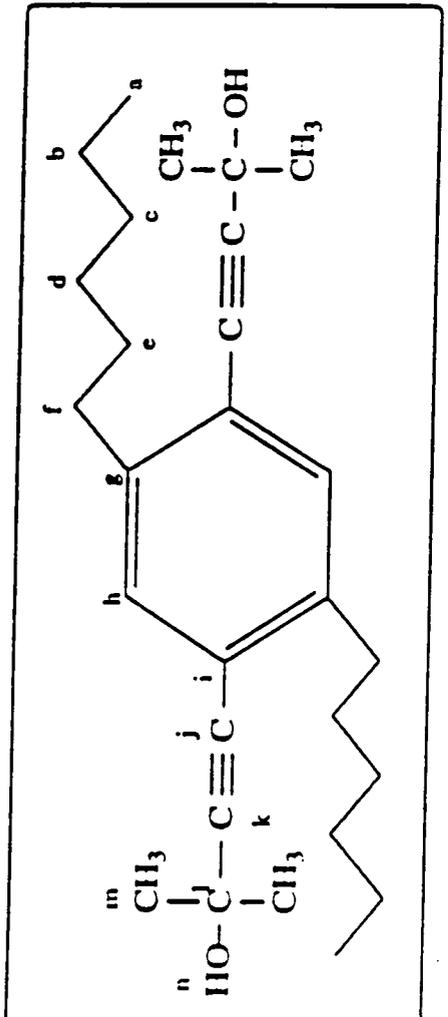


Appendix E2

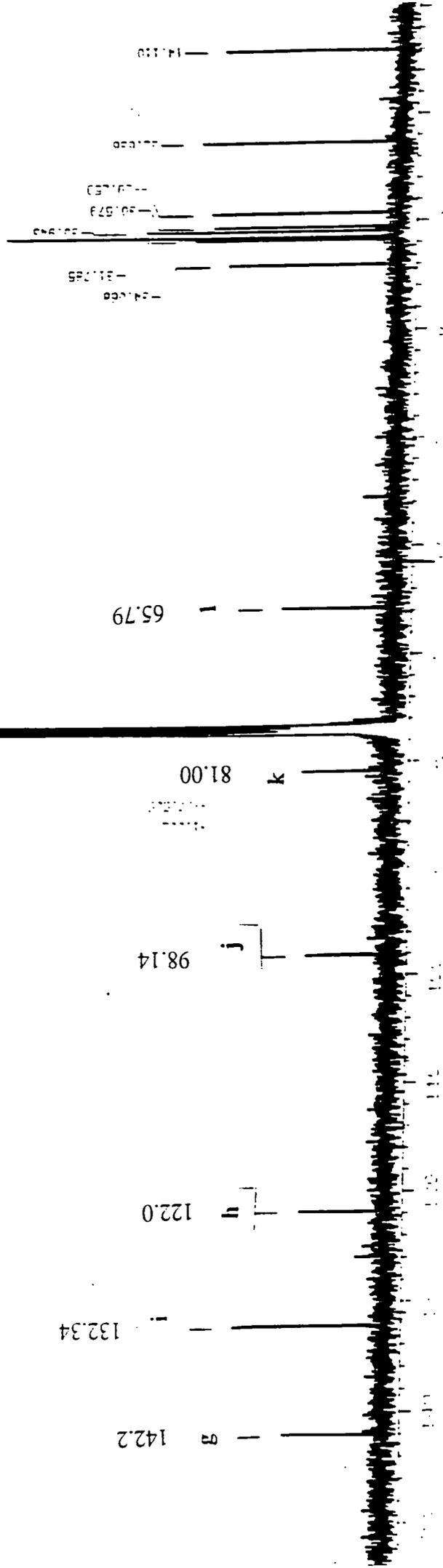
80.1
83.9
122.6
127.8
133.3
141.0

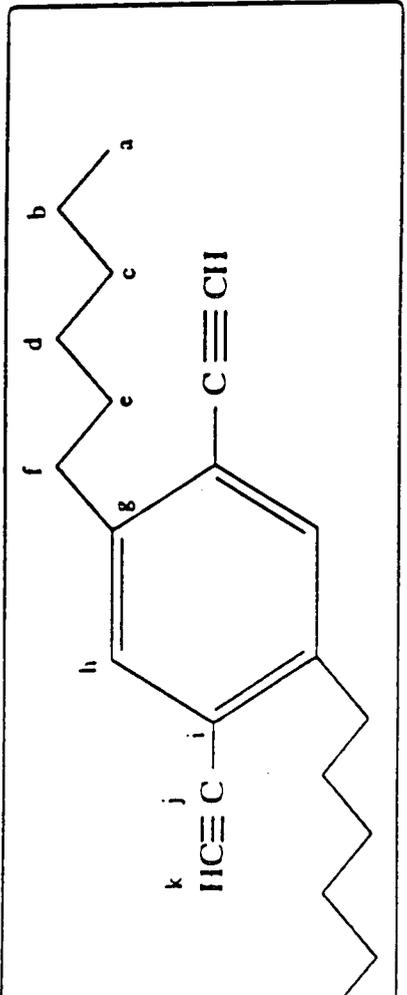


14.110
 22.000
 29.153
 31.573
 31.785
 31.54
 65.79
 81.00
 98.14
 122.0
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 76.723
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 77.243
 77.442

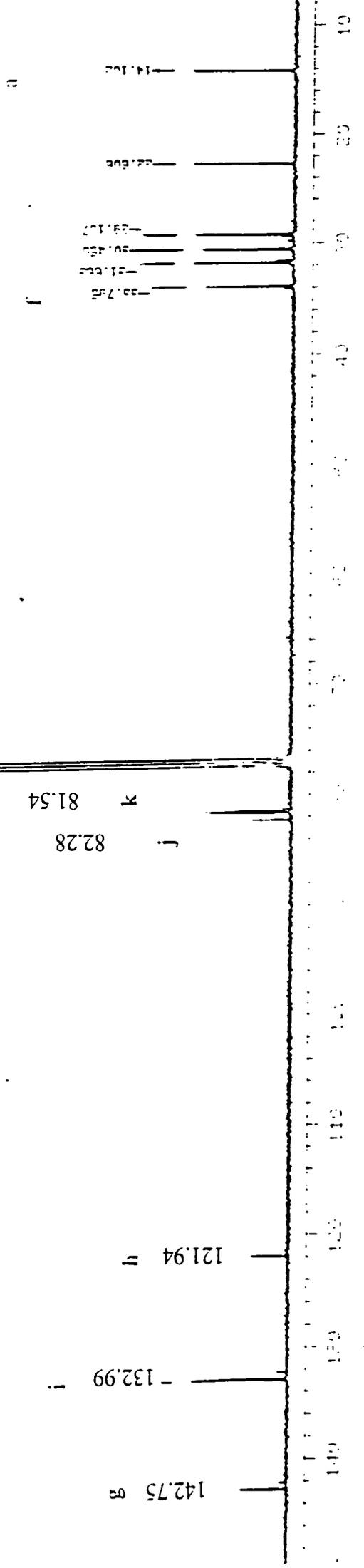


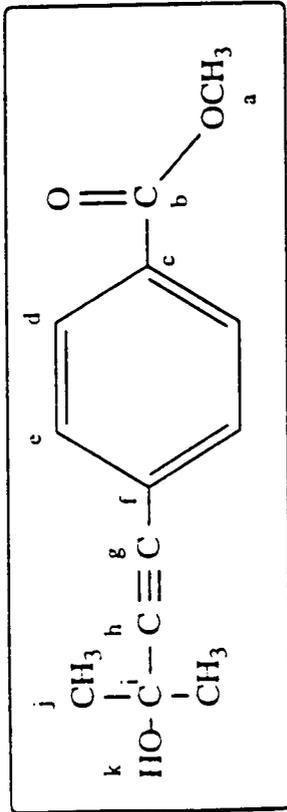
Appendix E3



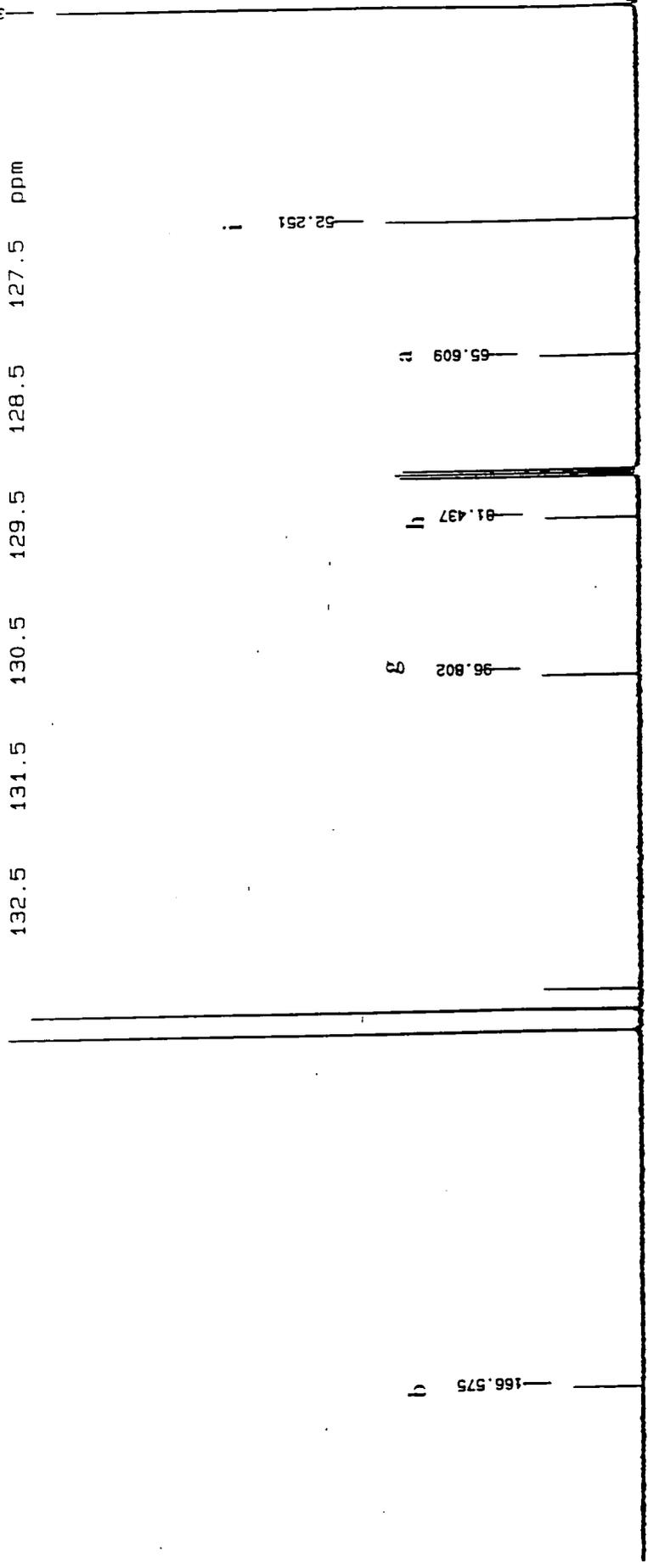
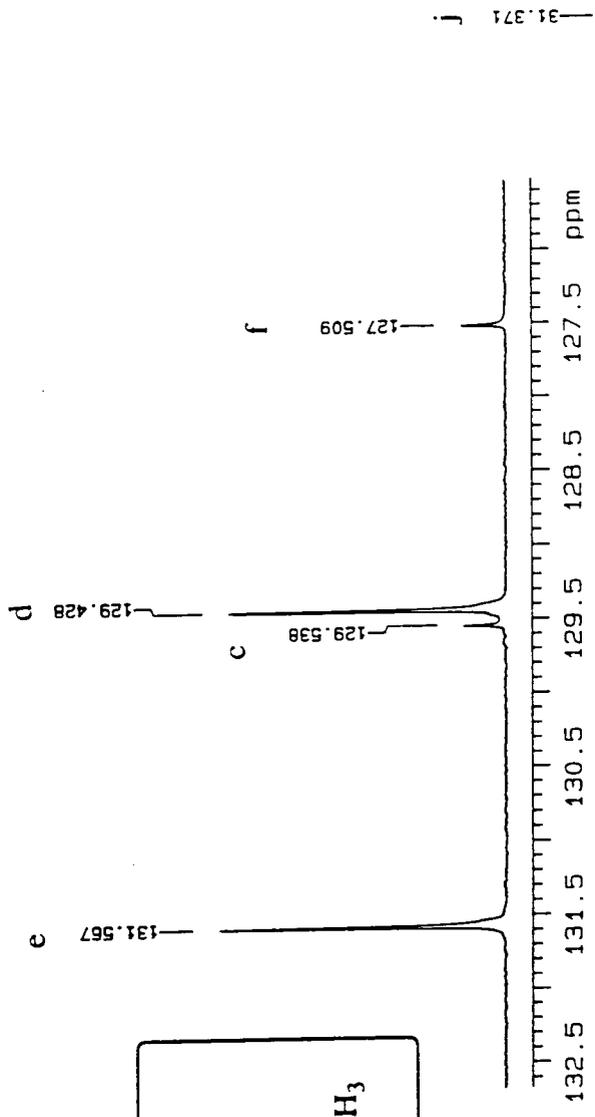


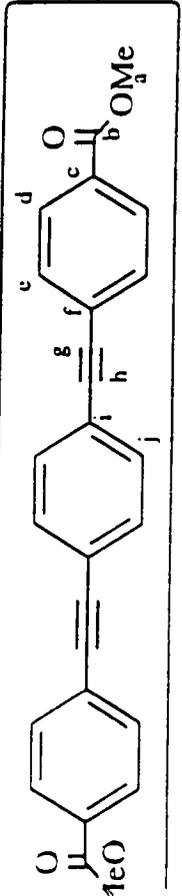
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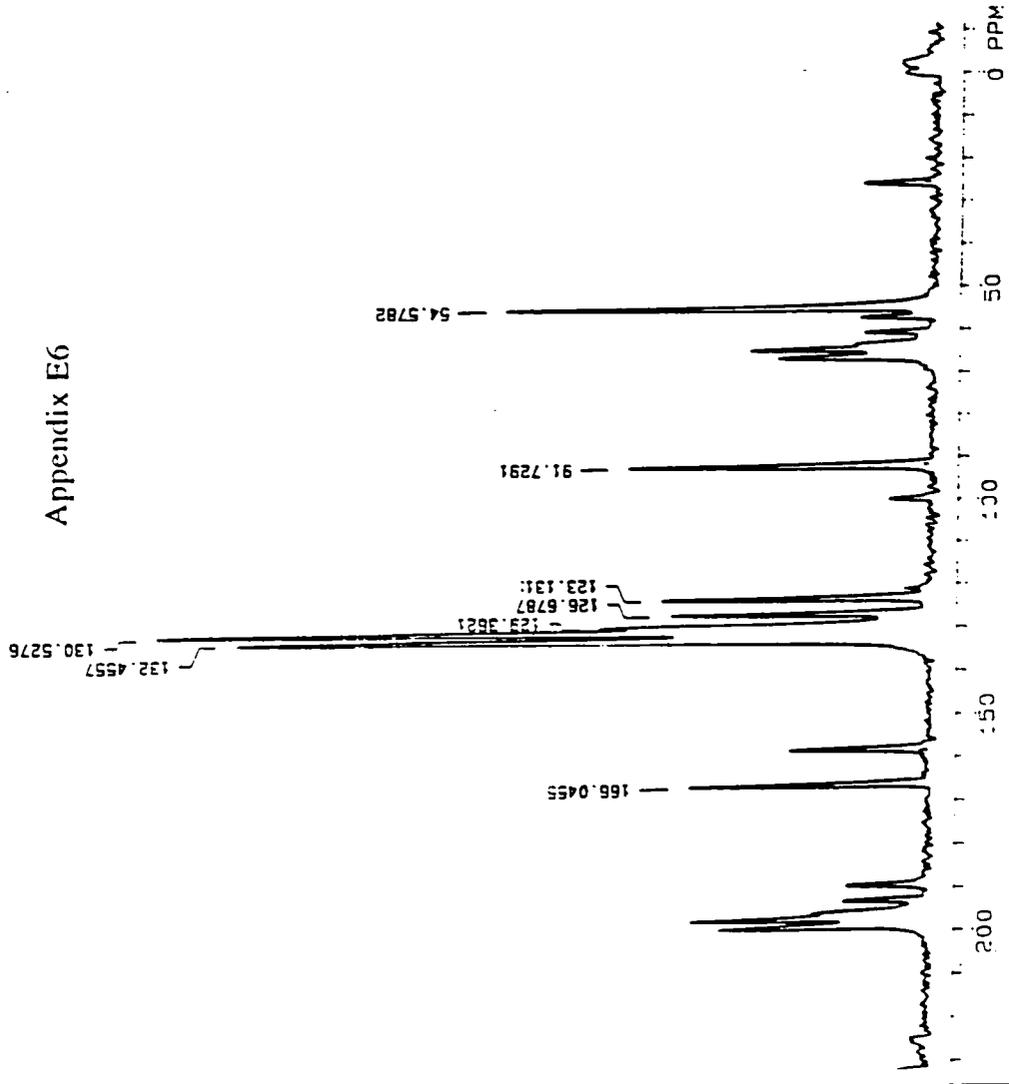


Appendix E5

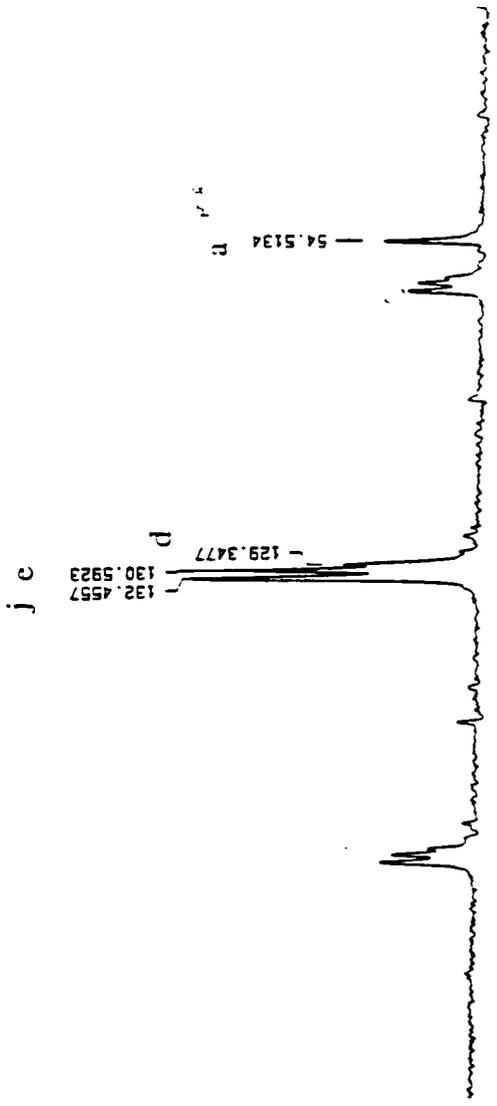




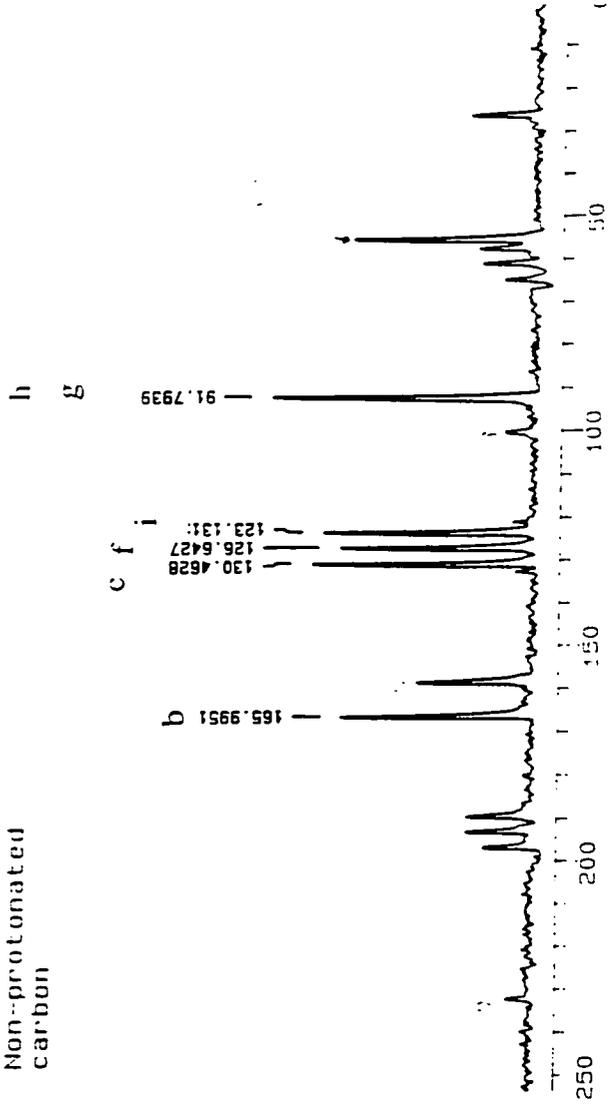
Appendix E6

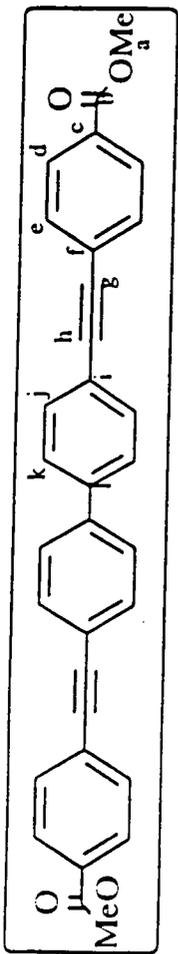


Protonated carbon



Non-protonated carbon





Appendix E7

Protonated carbon

e d

j k

127.5852
132.8945

79.2472

Non-protonated carbon

f i

121.1391
126.9665

132.5708

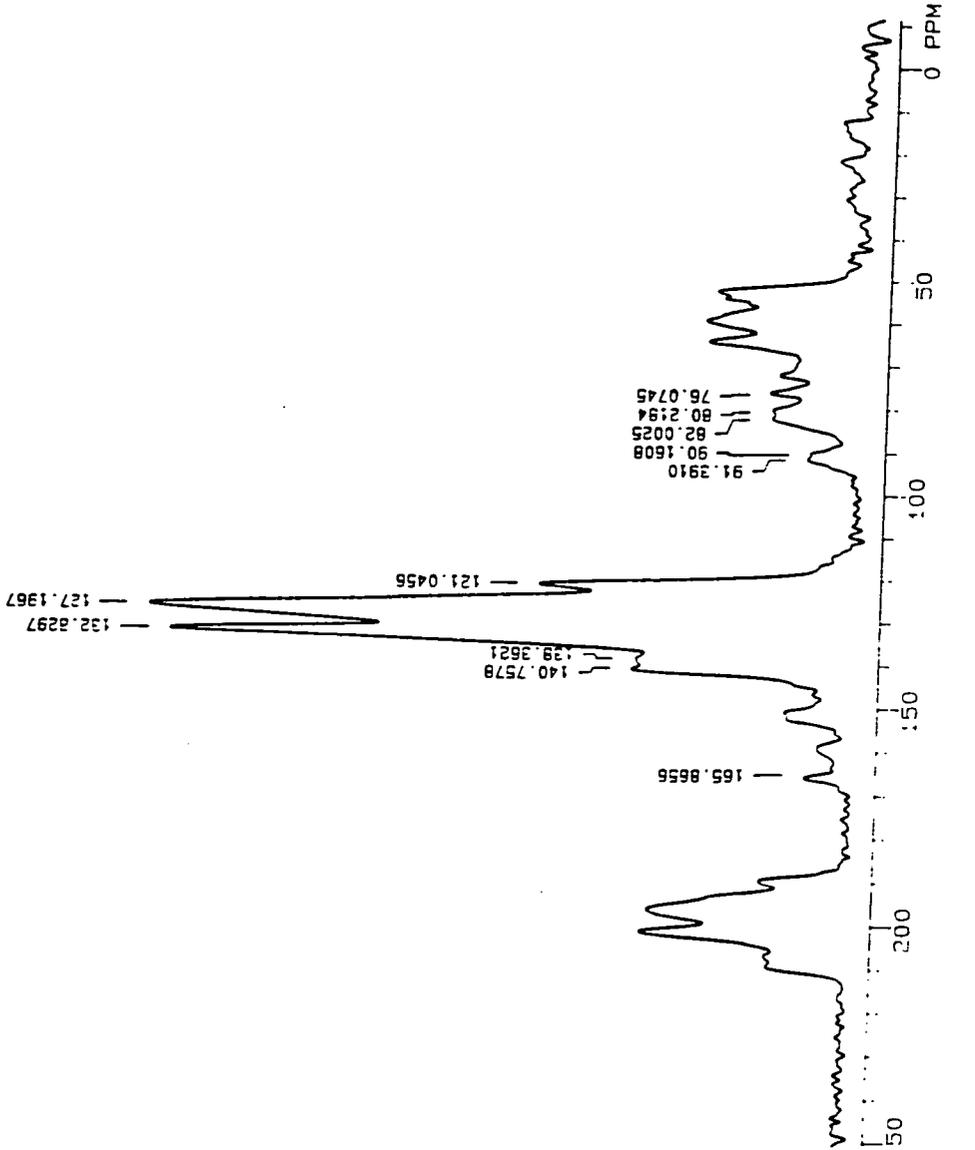
140.0168

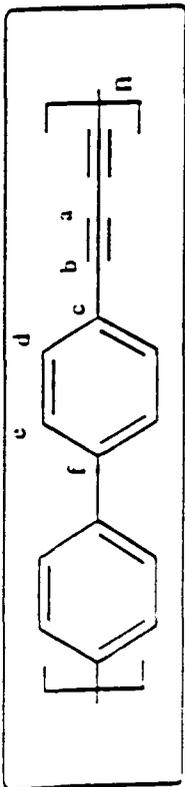
165.915

91.1320

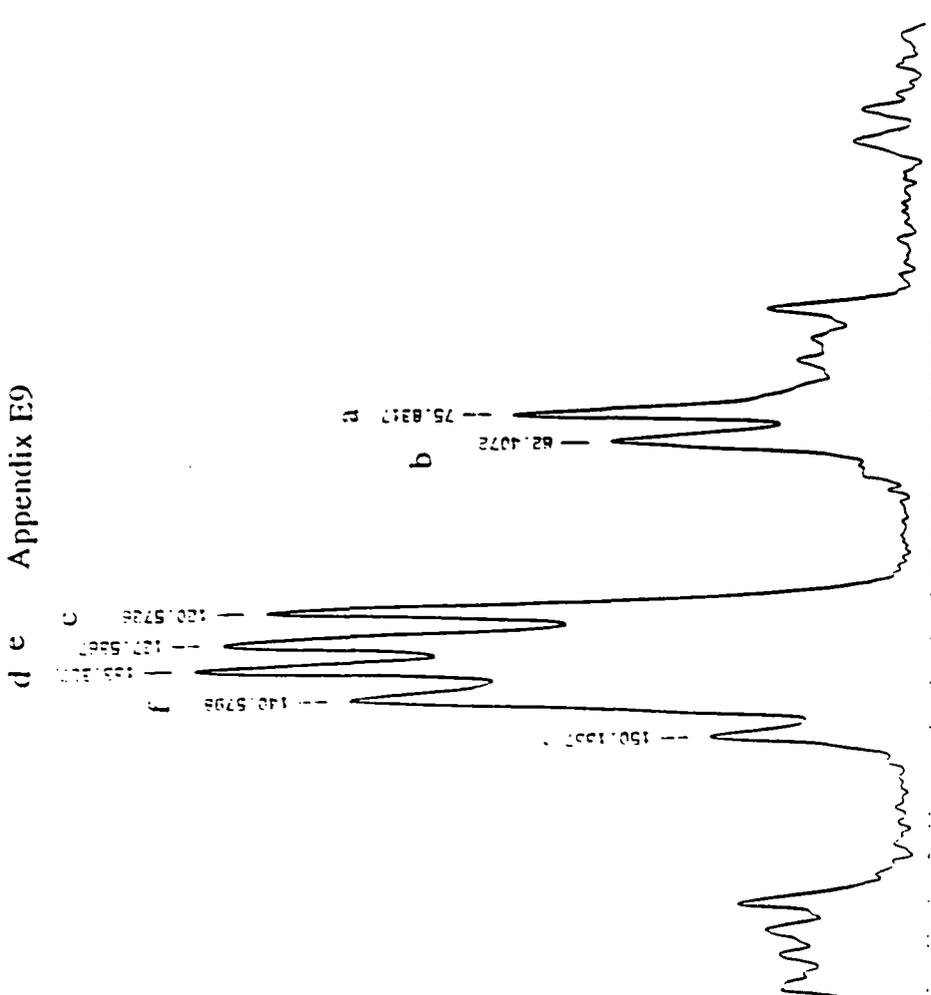
82.2903

75.8155





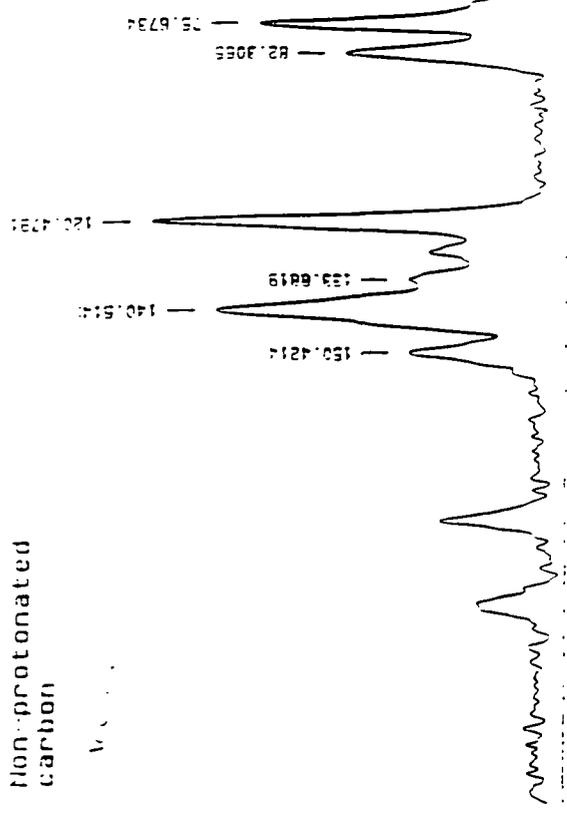
Appendix E9

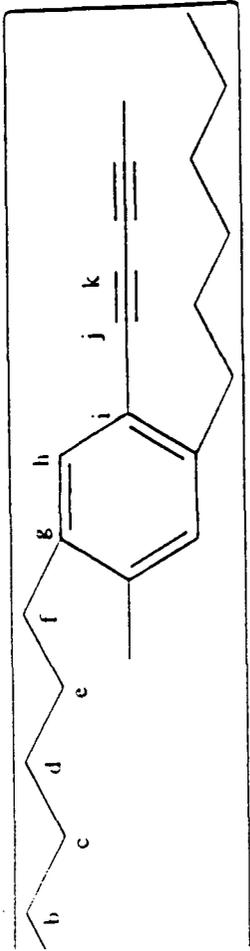


Protonated carbon

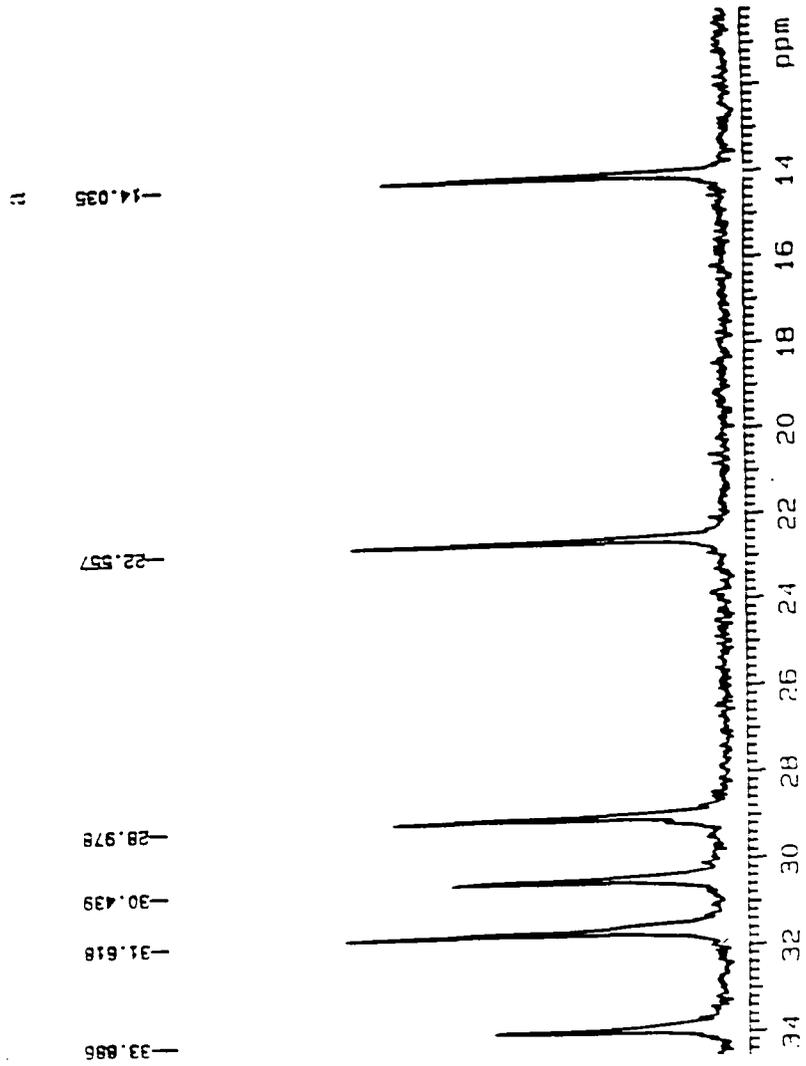
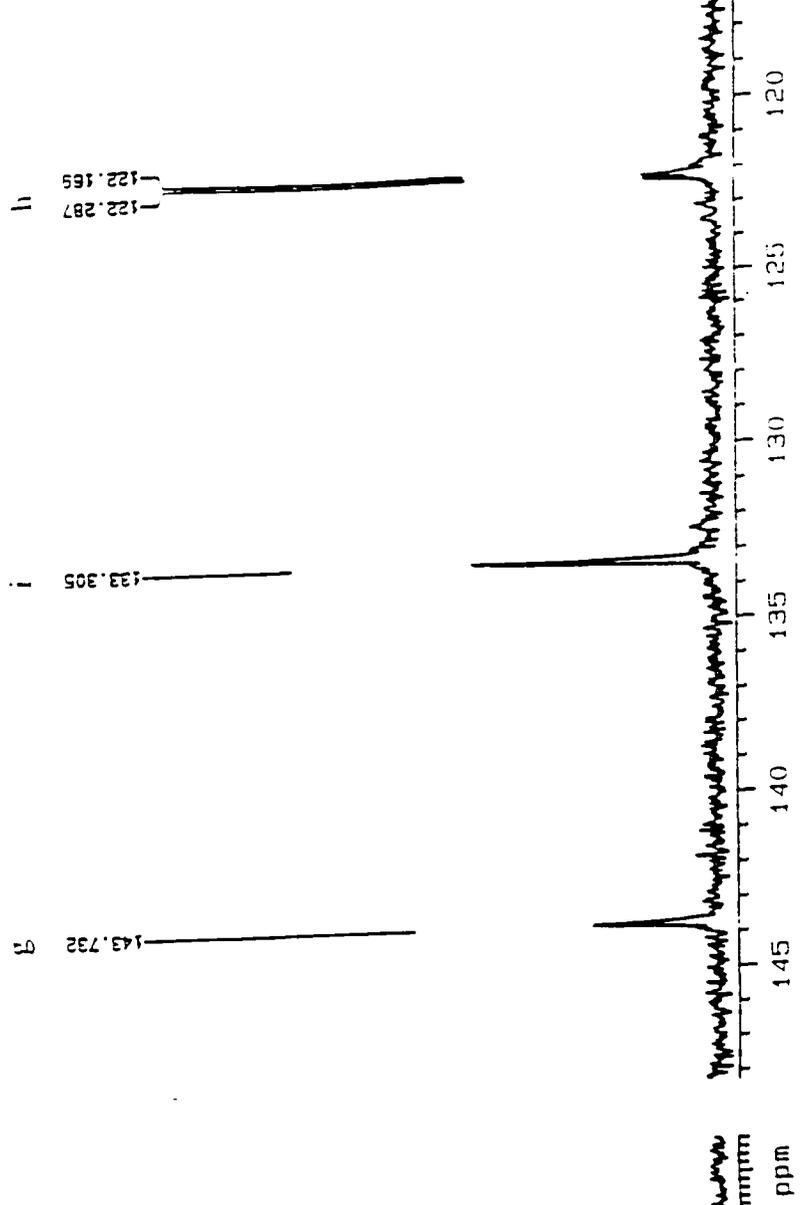
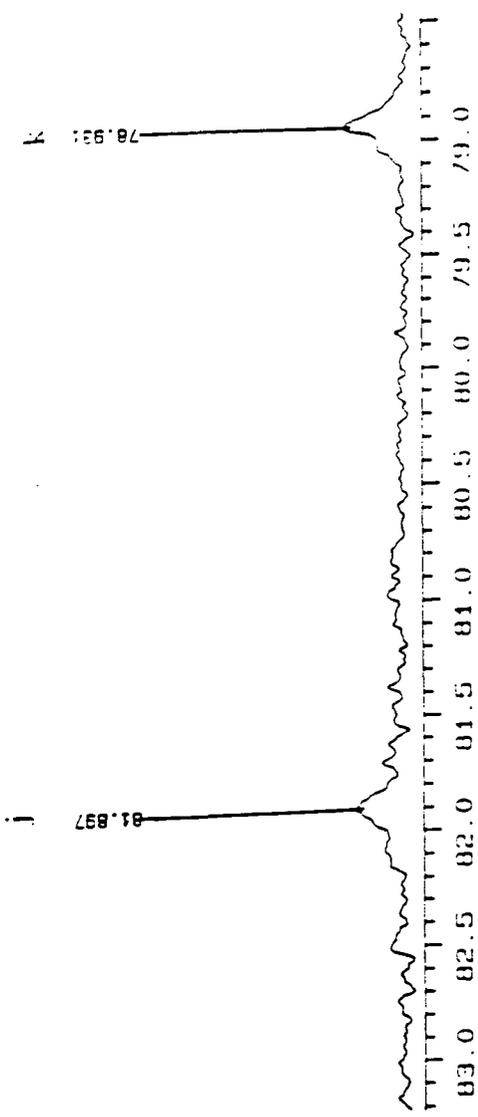


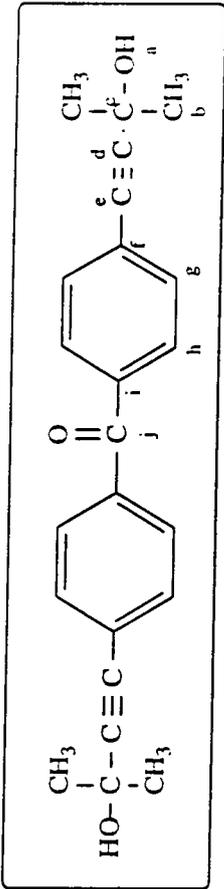
Non-protonated carbon



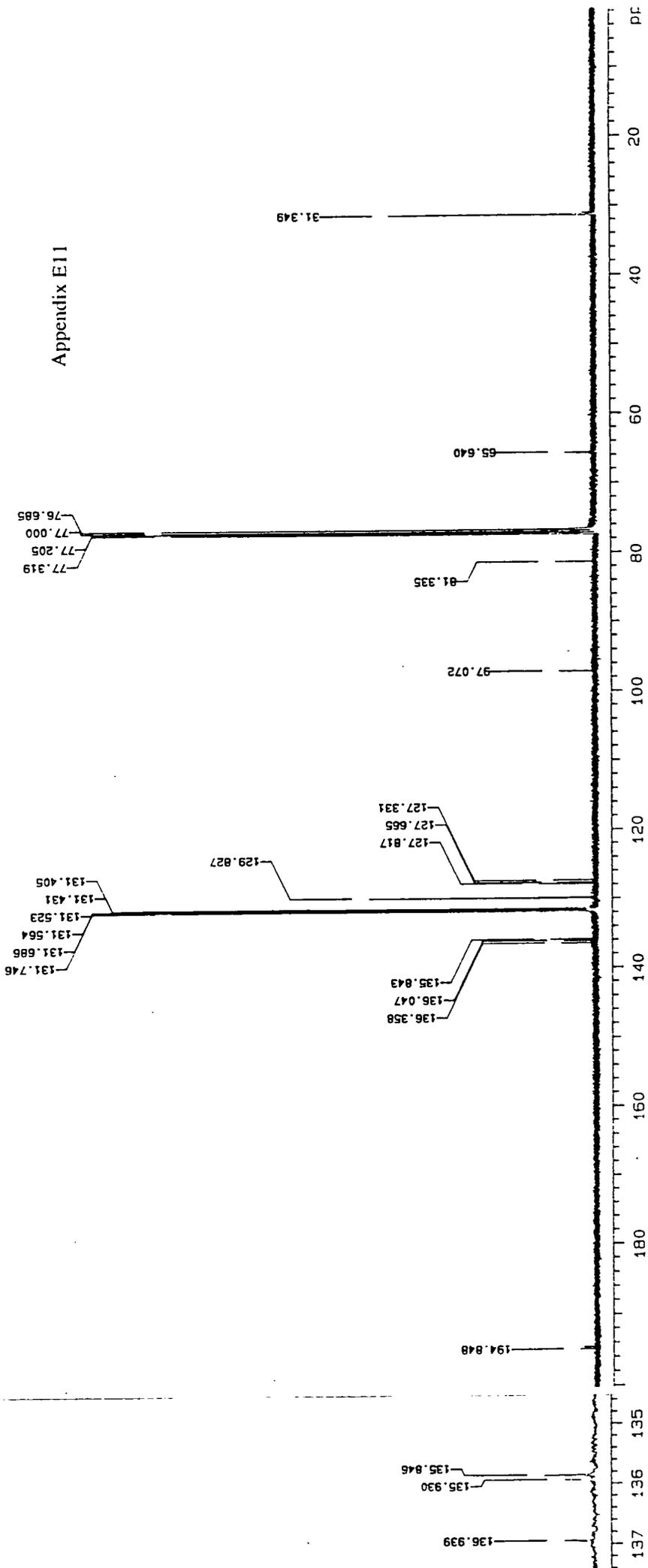


Appendix E10





Appendix E11

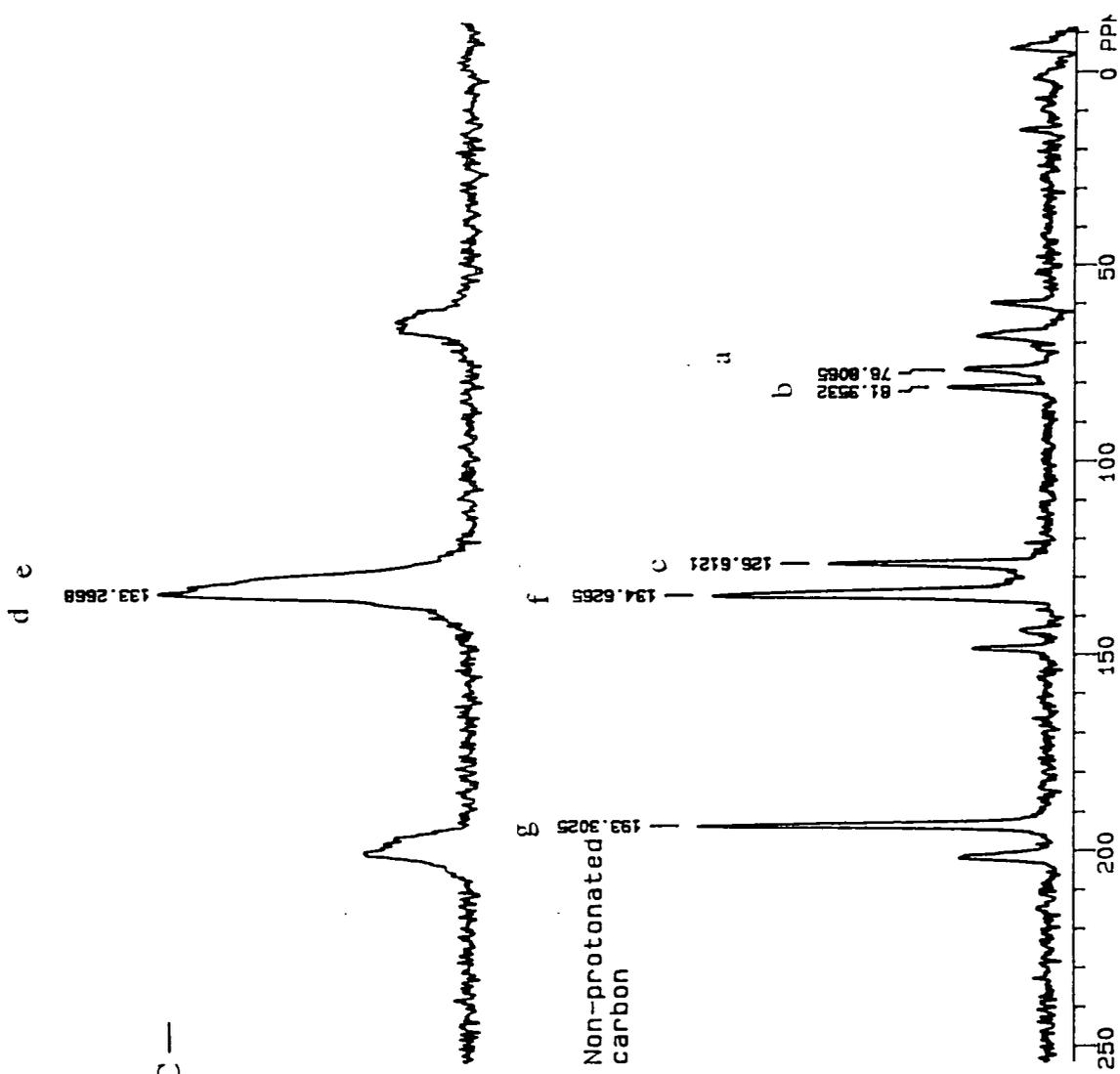


C18
 PMA9
 SKH
 PULSE SEQUENCE: SK9EQ
 DATE 28-08-82
 DIRECT IRC2
 FILE LC19C1

OBSERVE CARBON
 FREQUENCY 75.431 MHZ
 SPECTRAL WIDTH 20000 HZ
 CO. TIME 40.0 MSEC
 RELAXATION DELAY 5.0 SEC
 NO. REPETITIONS 300
 CROSS POLARIZATION
 CONTACT TIME 3.0 MSEC
 SPIN RATE 5020 HZ
 T F TIME CONSTANT 0.02 9
 T SIZE 8K

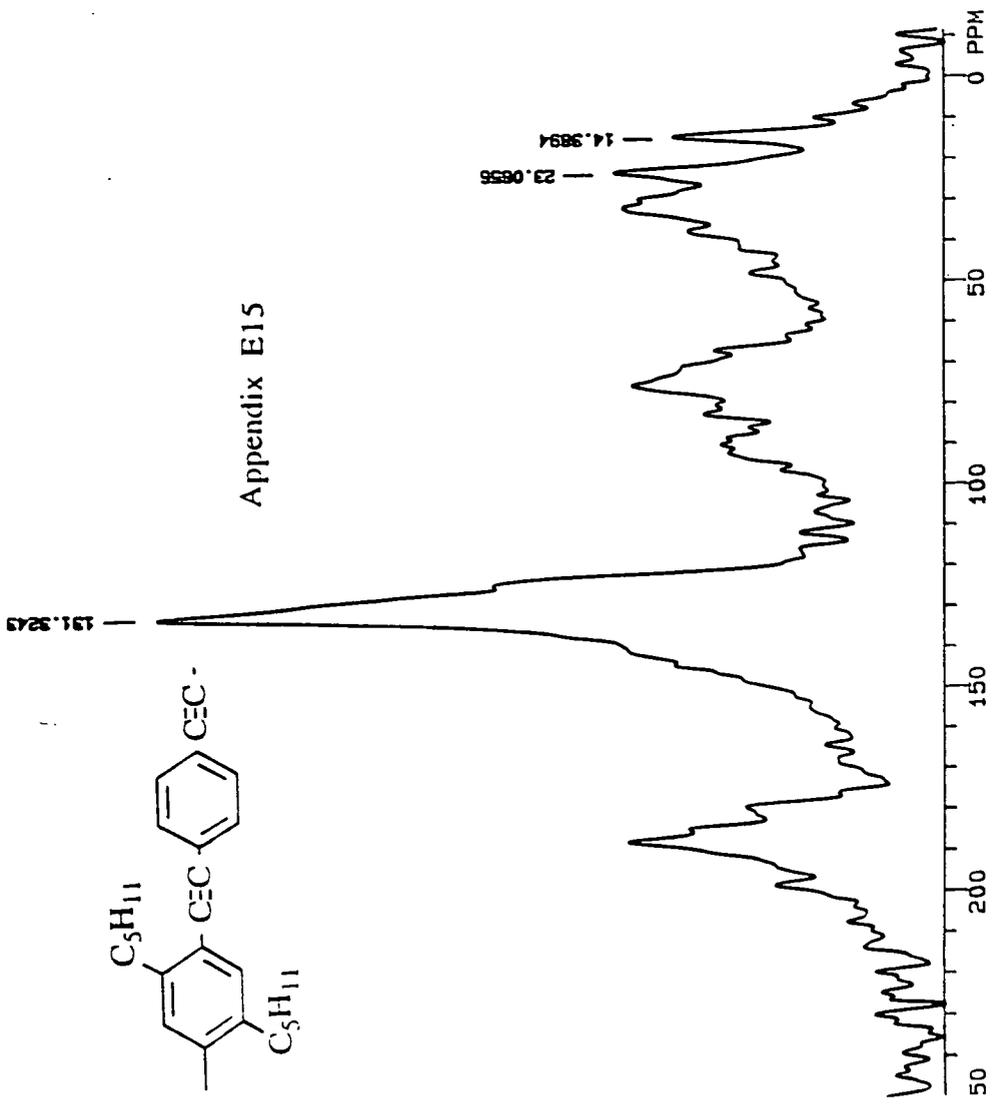


Appendix E14

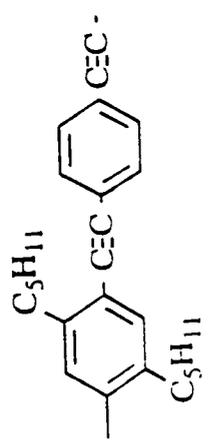


Protonated carbon

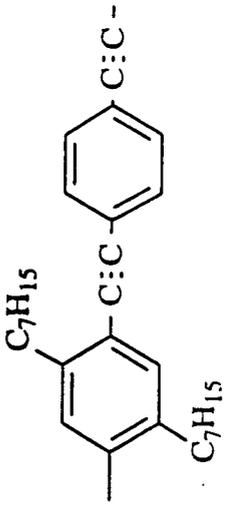
Non-protonated carbon



Appendix E15

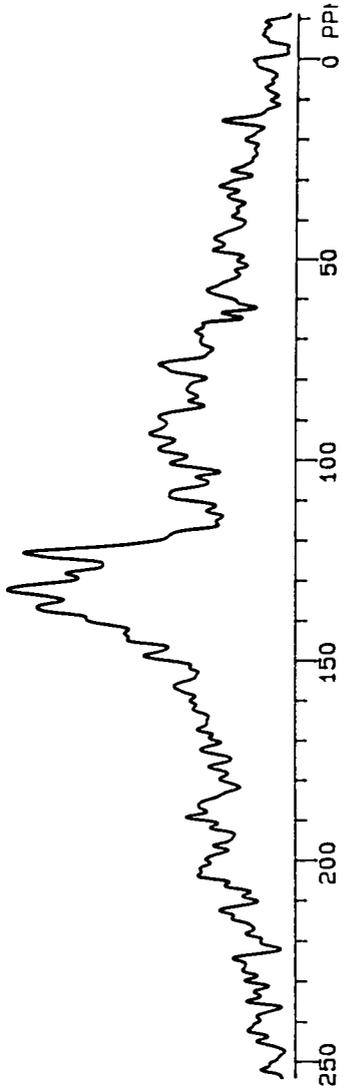
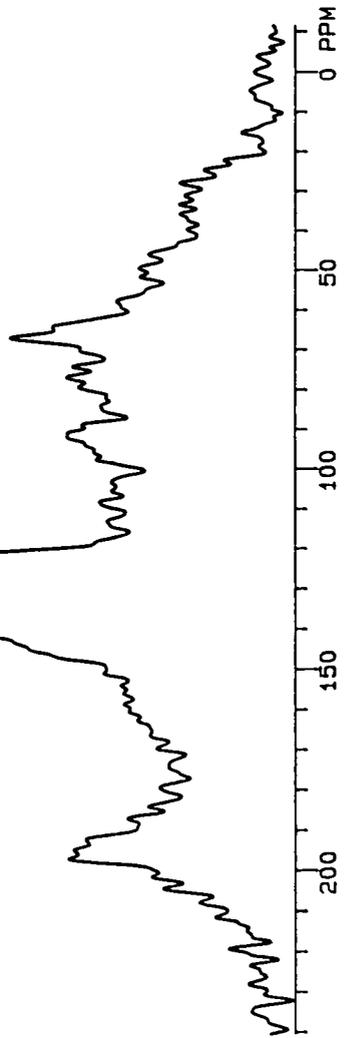


131.2884



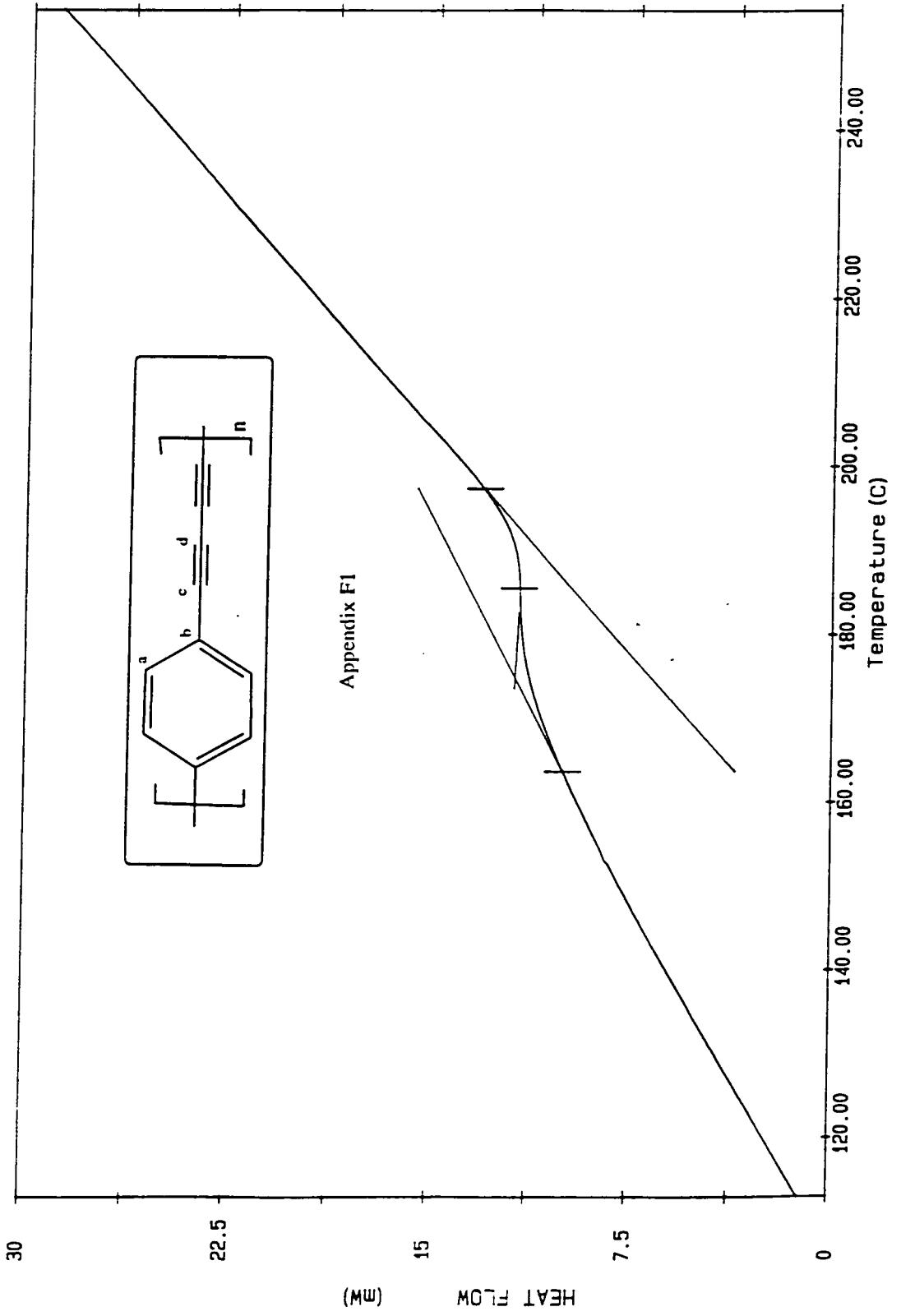
Appendix E16

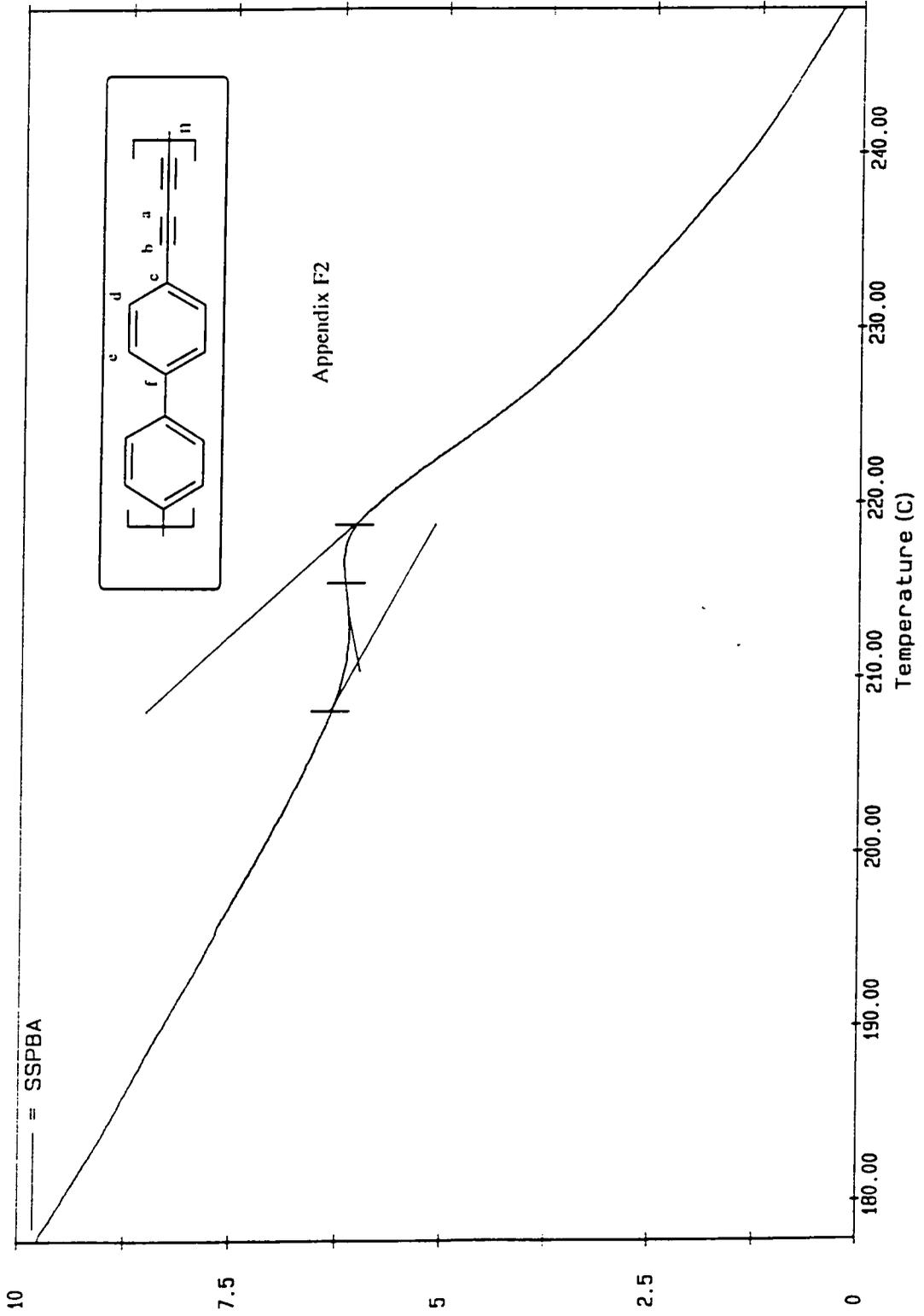
Non-protonated
carbon

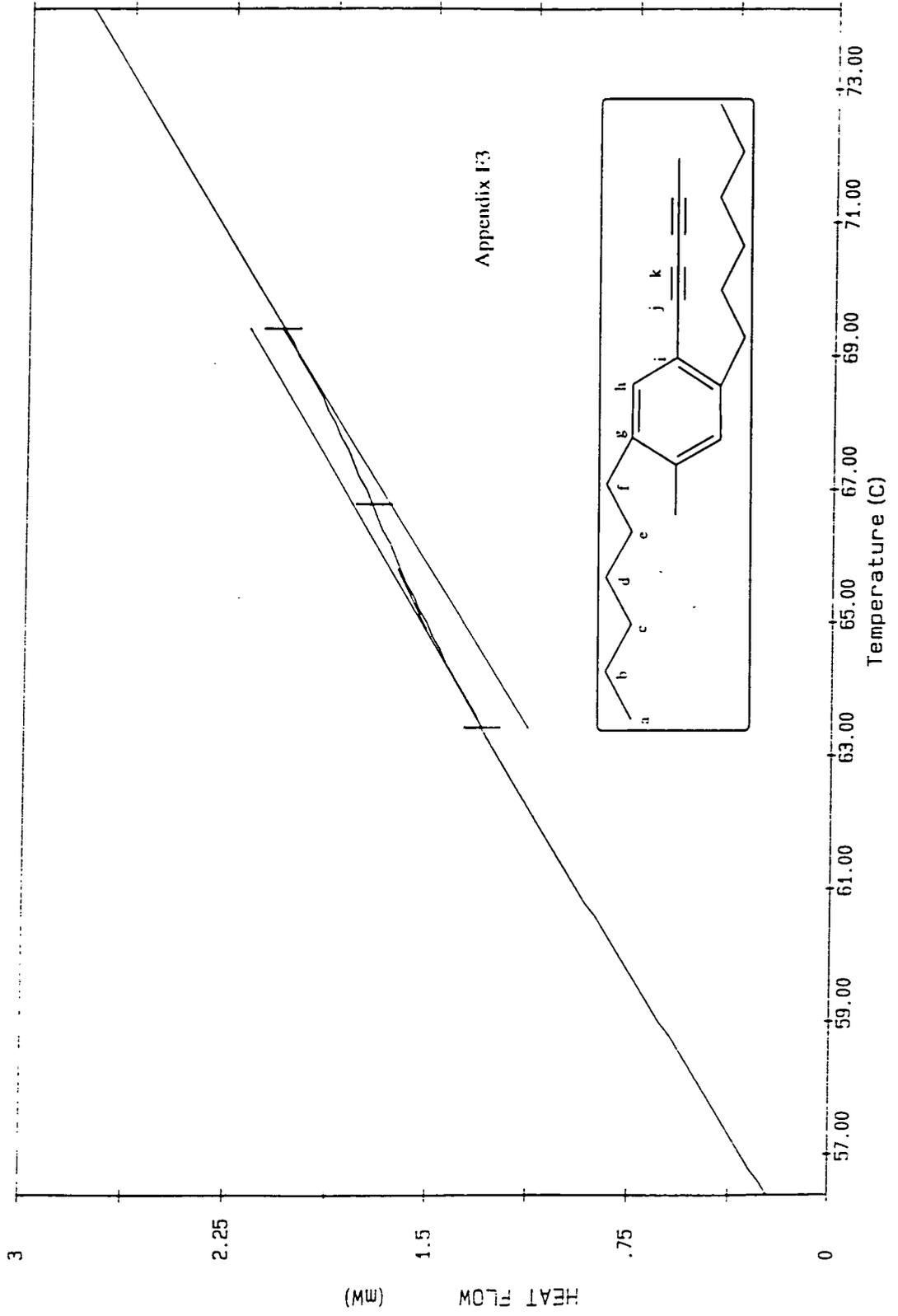


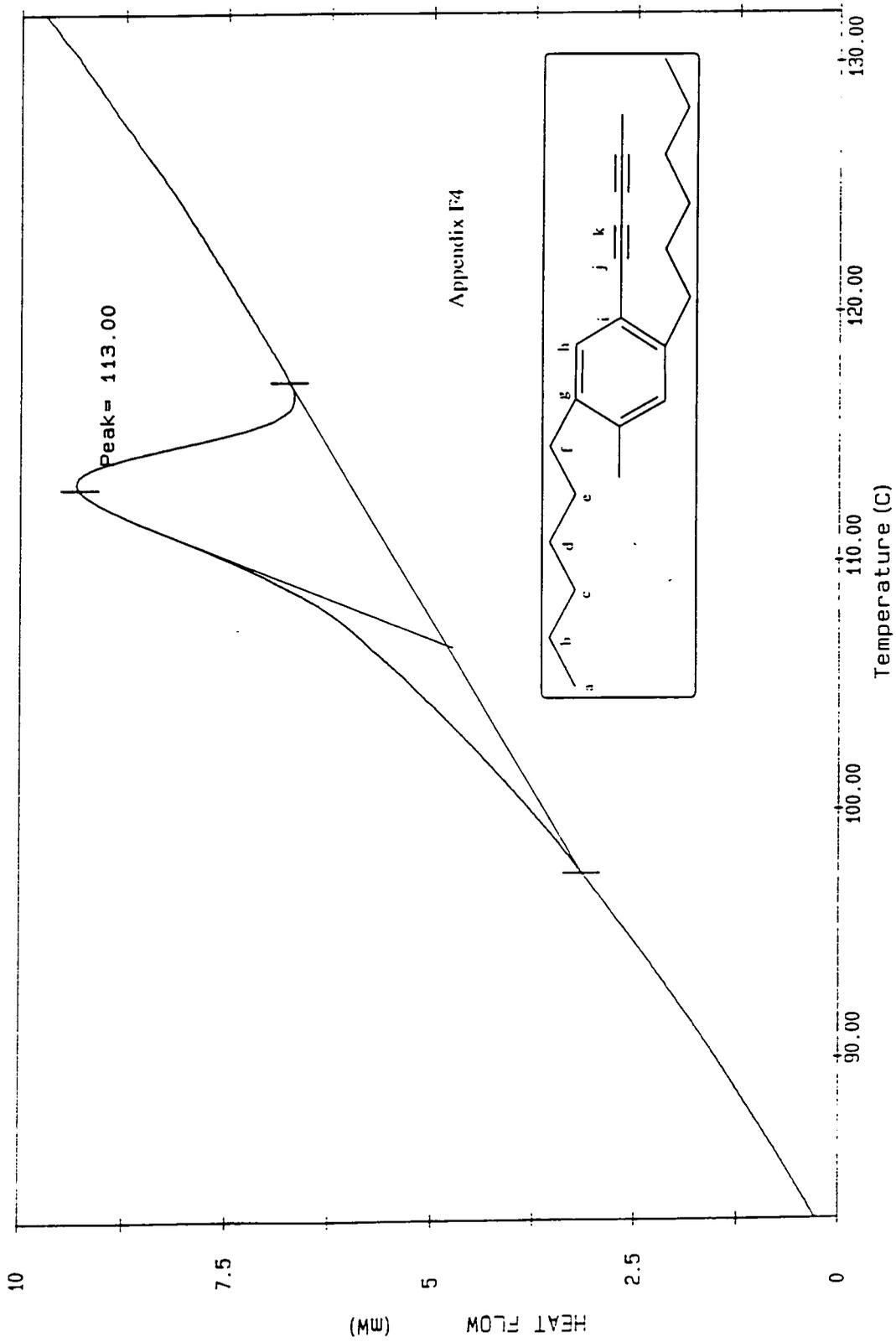
APPENDIX F

DSC TRACES



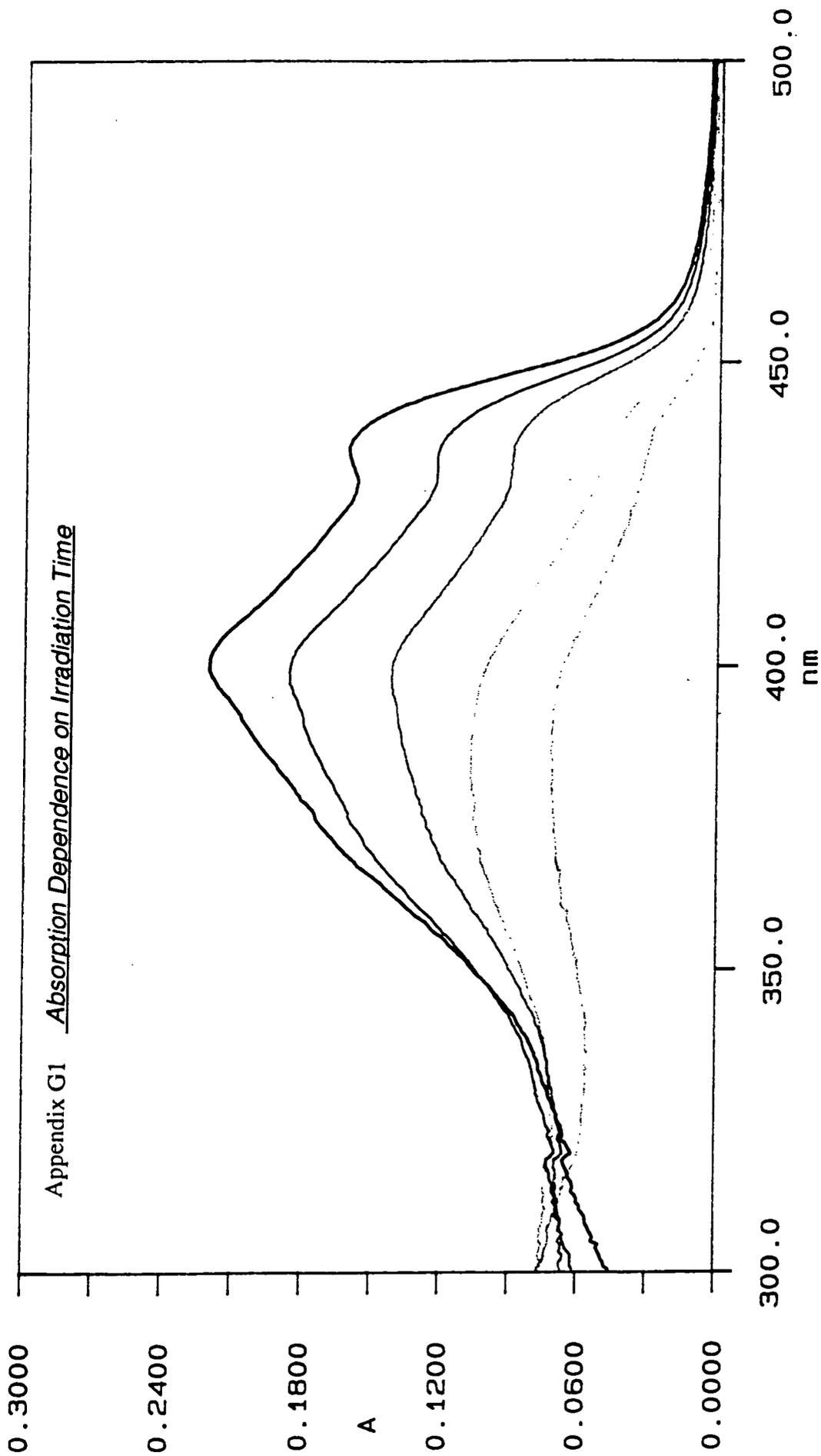


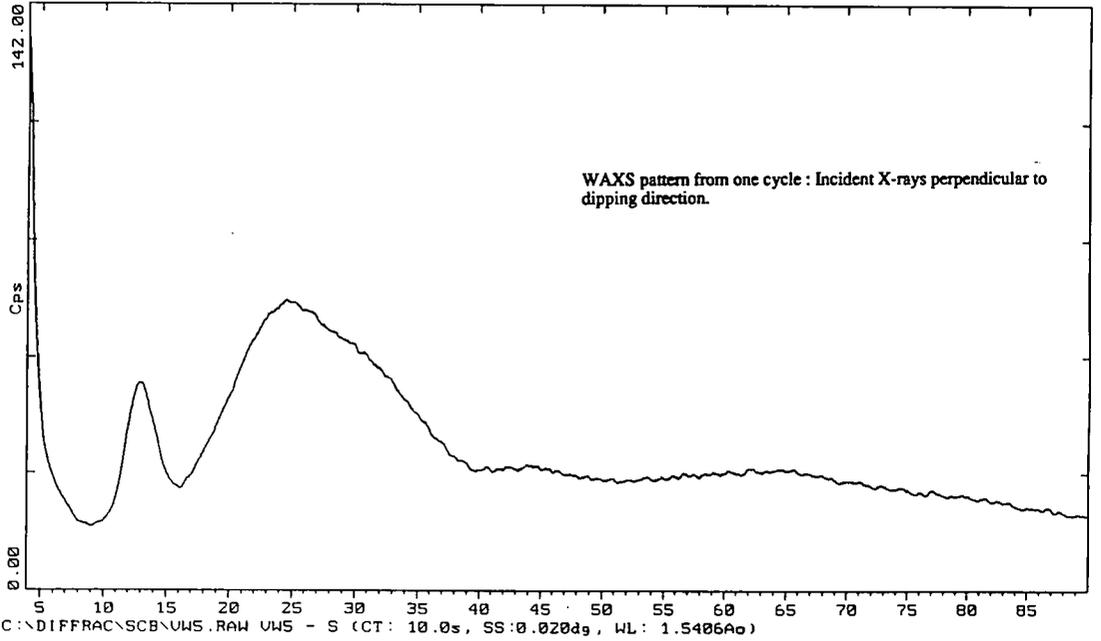
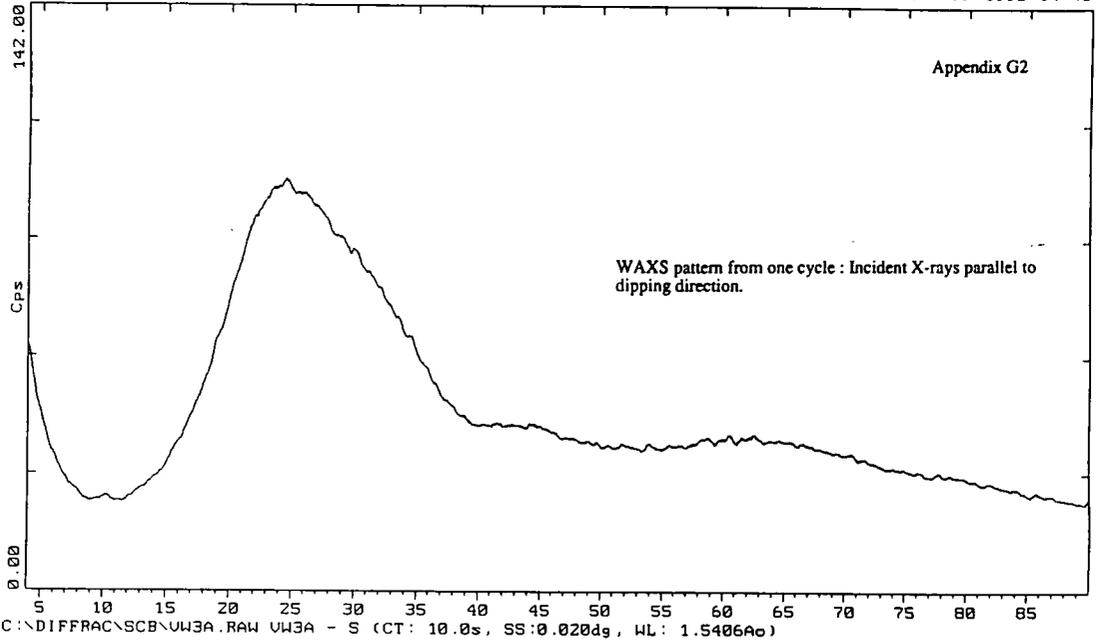


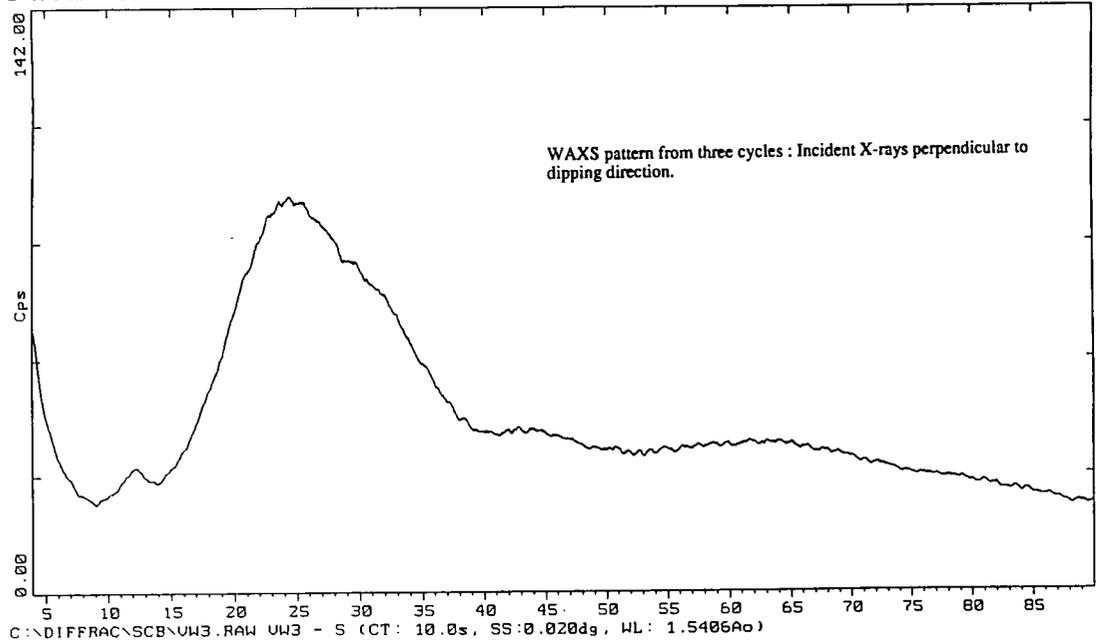
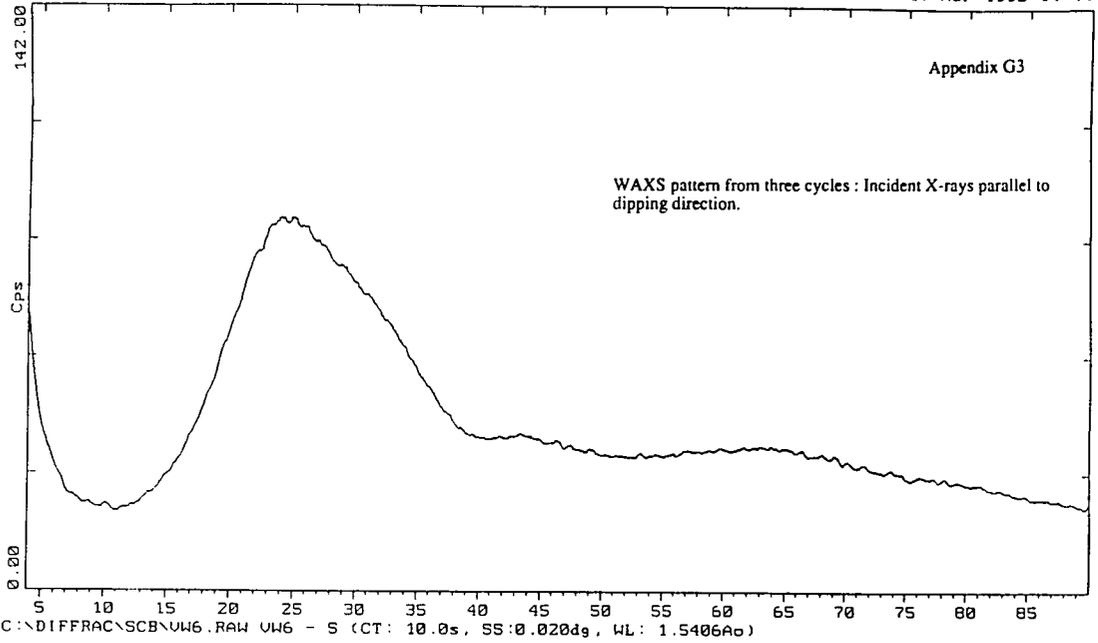


Appendix G

Appendix G1 Absorption Dependence on Irradiation Time







Research Colloquia, Seminars,
Lectures and Conferences.

RESEARCH COLLOQUIA, SEMINARS, LECTURES AND
CONFERENCES

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

(a) all research colloquia, seminars and lectures arranged by the Department of Chemistry during the period of the author's residence as a postgraduate student

(b) all research conferences attended by the author during the period of study.

UNIVERSITY OF DURHAM

Board of Studies in Chemistry

COLLOQUIA, LECTURES AND SEMINARS GIVEN BY INVITED SPEAKERS
1ST AUGUST 1989 TO 31ST JULY 1990

- BADYAL, Dr. J.P.S. (Durham University) 1st November, 1989
Breakthroughs in Heterogeneous Catalysis
- * BECHER, Dr. J. (Odense University) 13th November, 1989
Synthesis of New Macrocyclic Systems using
Heterocyclic Building Blocks
- * BERCAW, Prof. J.E. (California Institute of Technology) 10th November, 1989
Synthetic and Mechanistic Approaches to
Ziegler-natta Polymerization of Olefins
- * BLEASDALE, Dr. C. (Newcastle University) 21st February, 1990
The Mode of Action of some Anti-tumour Agents
- BOWMAN, Prof. J.M. (Emory University) 23rd March, 1990
Fitting Experiment with Theory in Ar-OH
- BUTLER, Dr. A. (St. Andrews University) 7th December, 1989
The Discovery of Penicillin: Facts and Fancies
- * CHEETHAM, Dr. A.K. (Oxford University) 8th March, 1990
Chemistry of Zeolite Cages
- CLARK, Prof. D.T. (ICI Wilton) 22nd February, 1990
Spatially Resolved Chemistry (using Nature's
Paradigm in the Advanced Materials Arena)
- * COLE-HAMILTON, Prof. D.J. (St. Andrews University) 29th November, 1989
New Polymers from Homogeneous Catalysis
- * CROMBIE, Prof. L. (Nottingham University) 15th February, 1990
The Chemistry of Cannabis and Khat
- DYER, Dr. U. (Glaxo) 31st January, 1990
Synthesis and Conformation of C-Glycosides
- * FLORIANI, Prof. C. (University of Lausanne,
Switzerland) 25th October, 1989
Molecular Aggregates - A Bridge between
homogeneous and Heterogeneous Systems
- GERMAN, Prof. L.S. (USSR Academy of Sciences -
Moscow) 9th July, 1990
New Syntheses in Fluoroaliphatic Chemistry:
Recent Advances in the Chemistry of Fluorinated
Oxiranes
- GRAHAM, Dr. D. (B.P. Reserch Centre) 4th December, 1989
How Proteins Absorb to Interfaces
- * GREENWOOD, Prof. N.N. (University of Leeds) 9th November, 1989
Novel Cluster Geometries in Metalloborane
Chemistry

- * HOLLOWAY, Prof. J.H. (University of Leicester)
Noble Gas Chemistry 1st February, 1990
- HUGHES, Dr. M.N. (King's College, London)
A Bug's Eye View of the Periodic Table 30th November, 1989
- * HUISGEN, Prof. R. (Universität München)
Recent Mechanistic Studies of [2+2] Additions 15th December, 1989
- * KLINOWSKI, Dr. J. (Cambridge University)
Solid State NMR Studies of Zeolite Catalysts 13th December 1989
- * LANCASTER, Rev. R. (Kimbolton Fireworks)
Fireworks – Principles and Practice 8th February, 1990
- LUNAZZI, Prof. L. (University of Bologna)
Application of Dynamic NMR to the Study of
Conformational Enantiomerism 12th February, 1990
- * PALMER, Dr. F. (Nottingham University)
Thunder and Lightning 17th October, 1989
- * PARKER, Dr. D. (Durham University)
Macrocycles, Drugs and Rock 'n' roll 16th November, 1989
- PERUTZ, Dr. R.N. (York University)
Plotting the Course of C–H Activations with
Organometallics 24th January, 1990
- PLATONOV, Prof. V.E. (USSR Academy of Sciences –
Novosibirsk) 9th July, 1990
Polyfluoroindanes: Synthesis and Transformation
- POWELL, Dr. R.L. (ICI) 6th December, 1989
The Development of CFC Replacements
- * POWIS, Dr. I. (Nottingham University) 21st March, 1990
Spinning off in a huff: Photodissociation of
Methyl Iodide
- ROZHKOVA, Prof. I.N. (USSR Academy of Sciences –
Moscow) 9th July, 1990
Reactivity of Perfluoroalkyl Bromides
- * STODDART, Dr. J.F. (Sheffield University) 1st March, 1990
Molecular Lego
- SUTTON, Prof. D. (Simon Fraser University,
Vancouver B.C.) 14th February, 1990
Synthesis and Applications of Dinitrogen and Diazo
Compounds of Rhenium and Iridium
- * THOMAS, Dr. R.K. (Oxford University) 28th February, 1990
Neutron Reflectometry from Surfaces
- THOMPSON, Dr. D.P. (Newcastle University) 7th February, 1990
The role of Nitrogen in Extending Silicate
Crystal Chemistry

COLLOQUIA, LECTURES AND SEMINARS GIVEN BY INVITED SPEAKERS
1ST AUGUST 1990 TO 31ST JULY 1991

- ALDER, Dr. B.J. (Lawrence Livermore Labs., California) 15th January, 1991
Hydrogen in all its Glory
- * BELL[†], Prof. T. (SUNY, Stony Brook, U.S.A.) 14th November, 1990
Functional Molecular Architecture and Molecular Recognition
- * BOCHMANN[†], Dr. M. (University of East Anglia) 24th October, 1990
Synthesis, Reactions and Catalytic Activity of Cationic Titanium Alkyls
- BRIMBLE, Dr. M.A. (Massey University, New Zealand) 29th July, 1991
Synthetic Studies Towards the Antibiotic Griseusin-A
- BROOKHART, Prof. M.S. (University of N. Carolina) 20th June, 1991
Olefin Polymerizations, Oligomerizations and Dimerizations Using Electrophilic Late Transition Metal Catalysts
- BROWN, Dr. J. (Oxford University) 28th February, 1991
Can Chemistry Provide Catalysts Superior to Enzymes?
- * BUSHBY[†], Dr. R. (Leeds University) 6th February, 1991
Biradicals and Organic Magnets
- * COWLEY, Prof. A.H. (University of Texas) 13th December, 1990
New Organometallic Routes to Electronic Materials
- CROUT, Prof. D. (Warwick University) 29th November, 1990
Enzymes in Organic Synthesis
- DOBSON[†], Dr. C.M. (Oxford University) 6th March, 1991
NMR Studies of Dynamics in Molecular Crystals
- GERRARD[†], Dr. D. (British Petroleum) 7th November, 1990
Raman Spectroscopy for Industrial Analysis
- HUDLICKY, Prof. T. (Virginia Polytechnic Institute) 25th April, 1991
Biocatalysis and Symmetry Based Approaches to the Efficient Synthesis of Complex Natural Products
- JACKSON[†], Dr. R. (Newcastle University) 31st October, 1990
New Synthetic Methods: α -Amino Acids and Small Rings
- KOCOVSKY[†], Dr. P. (Uppsala University) 6th November, 1990
Stereo-Controlled Reactions Mediated by Transition and Non-Transition Metals

- * LACEY, Dr. D. (Hull University)
Liquid Crystals 31st January, 1991
- LOGAN, Dr. N. (Nottingham University)
Rocket Propellants 1st November, 1990
- * MACDONALD, Dr. W.A. (ICI Wilton)
Materials for the Space Age 11th October, 1990
- MARKAM, Dr. J. (ICI Pharmaceuticals)
DNA Fingerprinting 7th March, 1991
- * PETTY, Dr. M.C. (Durham University)
Molecular Electronics 14th February, 1991
- * PRINGLE[†], Dr. P.G. (Bristol University)
Metal Complexes with Functionalised Phosphines 5th December, 1990
- PRITCHARD, Prof. J. (Queen Mary & Westfield College,
London University)
Copper Surfaces and Catalysts 21st November, 1990
- SADLER, Dr. P.J. (Birkbeck College London)
Design of Inorganic Drugs: Precious Metals,
Hypertension + HIV 24th January, 1991
- SARRE, Dr. P. (Nottingham University)
Comet Chemistry 17th January, 1991
- * SCHROCK, Prof. R.R. (Massachusetts Institute of Technology)
Metal-ligand Multiple Bonds and Metathesis Initiators 24th April, 1991
- SCOTT, Dr. S.K. (Leeds University)
Clocks, Oscillations and Chaos 8th November, 1990
- * SHAW[†], Prof. B.L. (Leeds University)
Syntheses with Coordinated, Unsaturated Phosphine
Ligands 20th February, 1991
- SINN[†], Prof. E. (Hull University)
Coupling of Little Electrons in Big Molecules.
Implications for the Active Sites of (Metalloproteins
and other) Macromolecules 30th January, 1991
- * SOULEN[†], Prof. R. (South Western University, Texas)
Preparation and Reactions of Bicycloalkenes 26th October, 1990
- * WHITAKER[†], Dr. B.J. (Leeds University)
Two-Dimensional Velocity Imaging of State-Selected
Reaction Products 28th November, 1990

[†] Invited specifically for the postgraduate training programme.

UNIVERSITY OF DURHAM

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COLLOQUIA, LECTURES AND SEMINARS FROM INVITED SPEAKERS

1991 - 1992 (August 1 - July 31)

1991

- * October 17 Dr. J.A. Salthouse, University of Manchester
Son et Lumiere - a demonstration lecture
- * October 31 Dr. R. Keeley, Metropolitan Police Forensic Science
Modern forensic science
- November 6 Prof. B.F.G. Johnson[†], Edinburgh University
Cluster-surface analogies
- * November 7 Dr. A.R. Butler, St. Andrews University
Traditional Chinese herbal drugs: a different way of treating disease
- November 13 Prof. D. Gani[†], St. Andrews University
The chemistry of PLP-dependent enzymes
- * November 20 Dr. R. More O'Ferrall[†], University College, Dublin
Some acid-catalysed rearrangements in organic chemistry
- * November 28 Prof. I.M. Ward, IRC in Polymer Science, University of Leeds
The SCI lecture: the science and technology of orientated polymers
- * December 4 Prof. R. Grigg[†], Leeds University
Palladium-catalysed cyclisation and ion-capture processes
- December 5 Prof. A.L. Smith, ex Unilever
Soap, detergents and black puddings
- December 11 Dr. W.D. Cooper[†], Shell Research
Colloid science: theory and practice

1992

- January 22 Dr. K.D.M. Harris[†], St. Andrews University
Understanding the properties of solid inclusion compounds
- * January 29 Dr. A. Holmes[†], Cambridge University
Cycloaddition reactions in the service of the synthesis of piperidine and indolizidine natural products

January	30	Dr. M. Anderson, Sittingbourne Research Centre, Shell Research Recent Advances in the Safe and Selective Chemical Control of Insect Pests
February	12	Prof. D.E. Fenton [†] , Sheffield University Polynuclear complexes of molecular clefts as models for copper biosites
February	13	Dr. J. Saunders, Glaxo Group Research Limited Molecular Modelling in Drug Discovery
* February	19	Prof. E.J. Thomas [†] , Manchester University Applications of organostannanes to organic synthesis
* February	20	Prof. E. Vogel, University of Cologne <i>The Musgrave Lecture</i> Porphyrins: Molecules of Interdisciplinary Interest
* February	25	Prof. J.F. Nixon, University of Sussex <i>The Tilden Lecture</i> Phosphaalkynes: new building blocks in inorganic and organometallic chemistry
February	26	Prof. M.L. Hitchman [†] , Strathclyde University Chemical vapour deposition
* March	5	Dr. N.C. Billingham, University of Sussex Degradable Plastics – Myth or Magic?
March	11	Dr. S.E. Thomas [†] , Imperial College Recent advances in organoiron chemistry
March	12	Dr. R.A. Hann, ICI Imagedata Electronic Photography – An Image of the Future
* March	18	Dr. H. Maskill [†] , Newcastle University Concerted or stepwise fragmentation in a deamination-type reaction
April	7	Prof. D.M. Knight, Philosophy Department, University of Durham Interpreting experiments: the beginning of electrochemistry
May	13	Dr. J-C Gehret, Ciba Geigy, Basel Some aspects of industrial agrochemical research

[†] Invited specially for the postgraduate training programme.

Conferences.

The following conferences were attended by the author;

- | | |
|----------------------|---|
| 21 March 1990 | University of Lancaster, Macro Group UK,
Polymer Conference. |
| 10-12 September 1990 | University of Durham, RSC Macro Group,
International Symposium, New Organic Materials. |
| 26-28 March 1991 | University of Lancaster, Macro Group UK,
Polymer Conference. |
| 6-8 April 1992 | University of Durham, Macro Group UK, Aspects
of Contemporary Polymer Science. |

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- B1:** Ballauff, M. *Adv. Mater.*, **1989**, 8, 302.
- B2:** Ballauff, M. *Angewandte Chemie*, **1989**, 28, 3, 253.
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